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Rhodium-Catalyzed Cascade Reaction of 1,6-Enynes Involving Addition, Cyclization, and β-Oxygen Elimination

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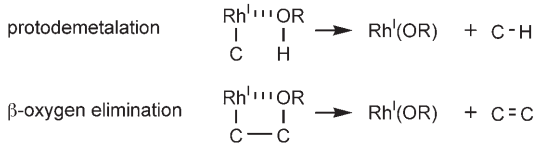
Abstract: The reaction of arylboronic acids with 1,6-enynes that contain an allylic ether moiety is catalyzed by a rhodium(I) complex to produce cyclopentanes with a tetrasubstituted *exo* olefin and a pendant vinyl group. The reaction is initiated by the regioselective addition of an arylrhodium(I) species to the carbon–carbon triple bond of the 1,6-enyne. The resulting alkenylrhodium(I) compound subsequently undergoes intramolecular carborhodation of the allylic double bond in a 5-*exo*-trig mode. β Elimination of the methoxy group affords the cyclization product and the catalytically active methoxorhodium(I) species. The use of alkyl Grignard reagents instead of arylboronic acids as organometallic nucleophiles was also examined.

Keywords: addition · boron · cyclization · elimination · rhodium

Introduction

The transition-metal-catalyzed addition of organometallic reagents to unsaturated functionalities is currently an active research area in synthetic organic chemistry. An organorhodium(I) intermediate[1] generated by transmetalation of a rhodium catalyst with a main-group organometallic reagent adds intermolecularly to alkynes,[2] alkenes,[3] aldehydes,[4] ketones,[5] imines,[6] and even nitriles.[7] Arylboronic acids and esters are relatively stable toward air and water, hence they are often the main-group organometal of choice in rhodium(I)-catalyzed addition reactions. In these reactions, hydroxorhodium(I) and alkoxorhodium(I) exhibit superior activity as the rhodium(I) catalyst.[2f] This is presumably because the hydroxo and alkoxo ligands on rhodium are nucleophilic enough to coordinate to the boronic compound, facilitating transmetalation between rhodium and boron.[8] The resulting arylrhodium(I) species then adds to an unsaturated organic compound. The concomitant formation of a thermodynamically stable boronic acid derivative contributes to the driving force of the entire reaction.

Efficient turnover of such a catalytic cycle requires the regeneration of a catalytically active Rh^I–OR species at the termination step. There are two elementary steps available for straightforward generation of the requisite Rh^I–OR species from an intermediate organorhodium(I) complex. One is protodemetalation by a proton source such as water, the other is β-oxygen elimination from β-oxy-substituted organorhodium(I).[9,10] In the latter case, a proton source is not required for catalytic-cycle turnover (Scheme 1).



Scheme 1. Generation of a catalytically active Rh^I–OR species.

Cascade reactions that consist of a sequence of multiple carbon–carbon bond-forming steps present a powerful method to construct structurally complex molecules in an atom-economical manner.[11] Although numerous excellent cascade reactions have been developed in organopalladium chemistry,[12] the potential of rhodium(I)-catalyzed cascade reactions is yet to be explored. Several reports recently appeared on rhodium-catalyzed cascade reactions triggered by addition of organoborons, during which the Rh^I–OR species is regenerated by protodemetalation under aqueous conditions.[13] For the termination step of cascade processes, however, β-oxygen elimination has an advantage over protodemetalation, which could intercept the propagation of multiple carbon–carbon bond formation at any intermediate

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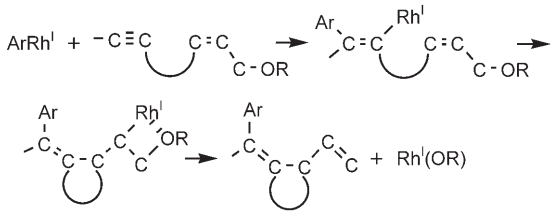
stage. Thus, we designed a cascade reaction that regenerates methoxorhodium(I) by β elimination of rhodium with the methoxy group at the allylic position (Scheme 2).[14] We report herein a full account of our study on the rhodium-



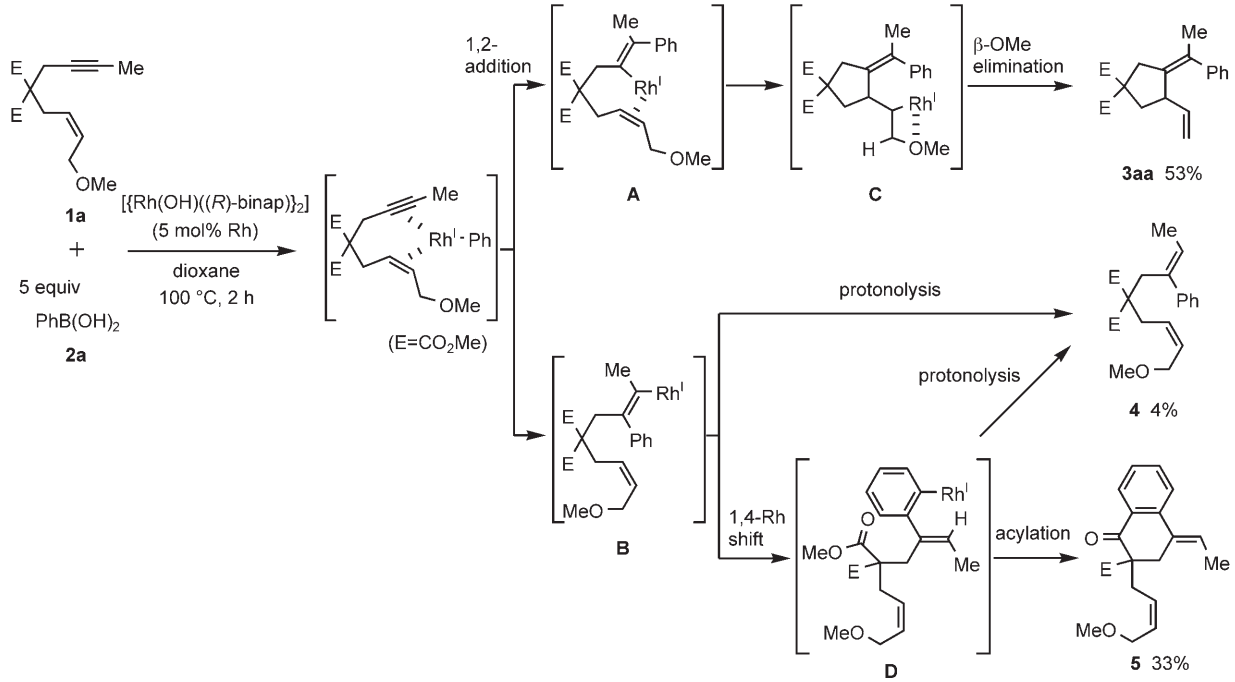
Scheme 2. Cascade reaction involving addition, cyclization, and β-oxygen elimination.

catalyzed cascade reaction of 1,6-enynes with arylboronic acids.[15] The use of alkyl Grignard reagents instead of arylboronic acids as a nucleophilic main-group organometal was also examined.

Results and Discussion

We designed 1,6-enyne **1a** with an allylic ether moiety as the model substrate for the reaction in Scheme 2 and examined the reaction of **1a** with phenylboronic acid (**2a**). A mixture of **1a** and **2a** (5 equiv) in 1,4-dioxane was heated at 100 °C in the presence of [{Rh(OH)((*R*)-binap)}$_2$] (5 mol % Rh) (Scheme 3). The 1,6-enyne **1a** was consumed in 2 h, and after chromatographic isolation, three phenylated products **3aa**, **4**, and **5** were obtained in 53 %, 4 %, and 33 % yield, respectively (see below for asymmetric induction).

In this model reaction, the catalytic cycle is initiated by transmetalation of hydoxorhodium(I) with phenylboronic acid (**2a**) to generate phenylrhodium(I) and boronic acid. The phenylrhodium(I) species undergoes 1,2-addition across the carbon–carbon triple bond of **1a** in a *syn* fashion to give the regioisomeric alkenylrhodium(I) intermediates **A** and **B**, depending on the direction of 1,2-addition. With the major regioisomer **A**, intramolecular carborhodation to the neighboring allylic double bond occurs in a 5-*exo*-trig mode, furnishing the (cyclopentylmethyl)rhodium(I) intermediate **C**. Subsequent β elimination of the methoxy group generates the cyclization product **3aa** with release of methoxorhodium(I), which promotes the next catalytic cycle, just as hydroxorhodium(I) has done in the initial cycle. Notably, with the organorhodium(I) intermediate **C**, β-oxygen elimination predominates over β-hydrogen elimination. This preference for the former sharply contrasts with the palladium-catalyzed Heck-type carbopalladation/cyclization reaction of a similar 1,6-enyne substrate, in which an organopalladium(II)



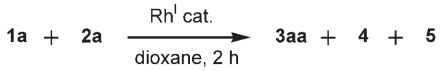
Scheme 3. Reaction of 1,6-enyne **1a** with phenylboronic acid (**2a**) catalyzed by [{Rh(OH)((*R*)-binap)}$_2$]. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

Abstract in Japanese:
ロジウム触媒存在下、アリル位にエーテル結合を持つ１，６－エンインにアリールボロン酸を作用させると、連続的に炭素－炭素結合生成が起こりシクロペンタン誘導体が得られた。これは、ロジウムがアリールホウ酸と金属交換した後にアルキンに付加してアルケニルロジウム中間体を与え、さらに分子内のアリルエーテル部位との5-*exo*型環化反応、続いてβ－酸素脱離が起こった結果生成したものと考えられる。

intermediate undergoes β-hydride rather than β-oxygen elimination.[14c] On the other hand, the minor regioisomer **B** is subject to either protonolysis to give the product **4** or 1,4-shift of rhodium onto the phenyl ring.[16] In the latter case, the resultant arylrhodium(I) compound **D** is subsequently acylated by the neighboring ester group to afford α-tetralone **5**[17] or hydrolyzed to afford **4**.

The reaction of **1a** with **2a** was examined under various conditions (Table 1). For the initial 1,2-addition of the phenylrhodium(I) species across the carbon–carbon triple bond, a better regioselectivity was observed at room temperature than at 100 °C (Table 1, entries 1 and 2). The ligand of rhodium also influenced the regioselectivity. The use of cycloocta-1,5-diene (cod) as the ligand led to the selective formation of **3aa** (**3aa**/(**4**+**5**) ≥ 95:5; Table 1, entries 3–6). In particular, the reaction at room temperature with the cod ligand proceeded efficiently to afford **3aa** in 72% yield, even with the use of two equivalents of **2a** and a lower catalyst loading (Table 1, entry 6). It is conceivable that the stronger π-acidic and less sterically demanding character of the cod ligand led to the highly regioselective addition of the phenylrhodium(I) species.

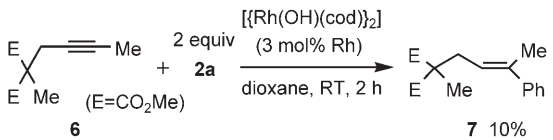
Table 1. Reaction of 1,6-enyne **1a** with phenylboronic acid (**2a**) in the presence of a Rh^I complex.



Entry	**2a** [equiv]	Rh^I complex ([mol% Rh])	*T* [°C]	**3aa**/(**4**+**5**)[a]	**3aa** [%][b]
1	5	[{Rh(OH)((*R*)-binap)}$_2$] (5)	100	59:41	53
2	5	[{Rh(OH)((*R*)-binap)}$_2$] (5)	RT	73:27	66
3	5	[{Rh(OH)(cod)}$_2$] (5)	100	>95:5	60
4	5	[{Rh(OH)(cod)}$_2$] (3)	100	>95:5	69
5	2	[{Rh(OH)(cod)}$_2$] (3)	100	>95:5	60
6	2	[{Rh(OH)(cod)}$_2$] (3)	RT	>95:5	72

[a] Ratio determined by ^{1}H NMR spectroscopy. [b] Yield of isolated product.

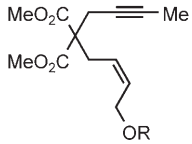
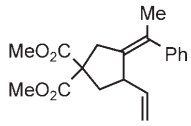
For comparison, an analogous reaction was carried out with substrate **6**, which lacks an olefin moiety.[13c] Almost no reaction occurred at room temperature when (*R*)-binap was used as the ligand. The addition reaction with the cod ligand proceeded only sluggishly at room temperature, and after 2 h, the 1,2-adduct **7** was formed in 10% yield (Scheme 4). These contrasting results indicate that the olefin moiety of **1a** coordinates intramolecularly to rhodium to facilitate the initial 1,2-addition.



Scheme 4. Arylation of substrate **6** with phenylboronic acid (**2a**).

Next, we examined the effect of the leaving group at the allylic position (Table 2). The addition/cyclization reaction successfully occurred with substrates **1b** and **1c**, which have a free hydroxy group and a silyl ether at the allylic position, respectively (Table 2, entries 1 and 2). The reaction of the allylic acetate **1d**, however, was considerably slower, and the starting material remained after 2 h (Table 2, entry 3). The lower reactivity of the acetate **1d** can be ascribed to the lower nucleophilicity of the acetoxy ligand that resulted from β elimination. The transmetalation step between rhodium and boron would be slower with the less-nucleophilic acetoxy ligand. Furthermore, the lower reactivity of **1d** suggests that an oxidative-addition mechanism involving a π-allylrhodium intermediate is unlikely.

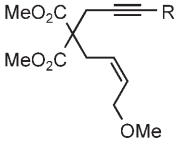
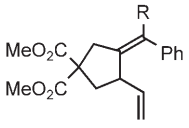
Table 2. Rhodium-catalyzed arylative cyclization: effect of the leaving group at the allylic position.[a]

Entry	Substrate	Product	Yield [%][b]
			
1	**1b** R = H	**3aa**	63
2	**1c** R = TBS		78
3	**1d** R = Ac		37[c]

[a] **1** (0.2 mmol) was treated with **2a** (0.4 mmol) in dioxane (2.0 mL) in the presence of [{Rh(OH)(cod)}$_2$] (3 mol% Rh) at RT for 2 h. [b] Yield of isolated product. [c] The starting material remained. TBS = *tert*-butyldimethylsilyl.

The regiochemistry of the initial 1,2-addition of phenylrhodium(I) to the carbon–carbon triple bond is influenced by the alkyne substituent (Table 3). A good regioselectivity was observed with the ethyl-substituted **1e**, which gave a slightly better yield of **3** than methyl-substituted **1a** (Table 3, entries 1 and 2). The reaction of phenyl- and trimethylsilyl-substituted alkynes **1f** and **1g** gave the corre-

Table 3. Rhodium-catalyzed arylative cyclization: effect of the alkyne substituent.[a]

Entry	Substrate	Product	*t* [h]	Yield [%][b]
				
1	**1a** R = Me	**3aa**	2	72
2	**1e** R = Et	**3ea**	2	80
3	**1f** R = Ph	**3fa**	9	15[c,d]
4	**1g** R = TMS	**3ga**	5	20[c,d]

[a] **1** (0.2 mmol) was treated with **2a** (0.4 mmol) in dioxane (2.0 mL) in the presence of [{Rh(OH)(cod)}$_2$] (3 mol% Rh) at RT. [b] Yield of isolated product. [c] Compounds corresponding to **4** and **5** were formed. [d] The starting material remained. TMS = trimethylsilyl.

sponding products **3fa** and **3ga** in low yield, owing to the lower regioselectivity of the initial 1,2-addition of the phenylrhodium(I) species (Table 3, entries 3 and 4).

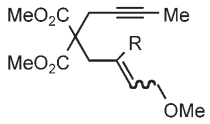
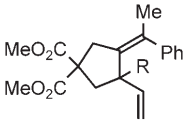
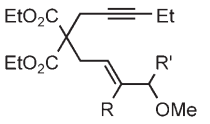
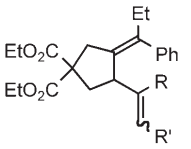
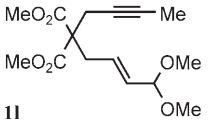
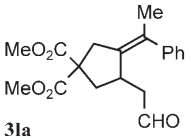
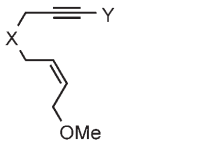
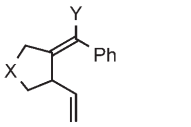
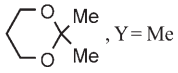
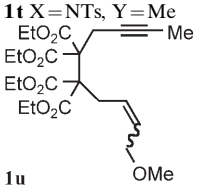
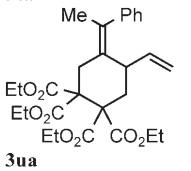
Other examples of rhodium-catalyzed cascade reactions of 1,6-enynes are listed in Table 4. 1,6-Enyne **1h** with an *E* olefin was also converted into the product **3aa** in good yield (Table 4, entry 1). Even substrates **1i** and **1j** equipped with trisubstituted olefins reacted well (Table 4, entries 2 and 3). The reaction of substrate **1k** afforded the product **3ka** as a mixture of *cis* and *trans* isomers (Table 4, entry 4). Substrate **1l** with a dimethyl acetal moiety at the allylic position gave the aldehyde **3la** in 70% yield after acidic hydrolysis of the resulting enol ether (Table 4, entry 5). A variety of functionalized linkers, including ether and sulfone, were tolerated (Table 4, entries 6–12). The reaction of aza-1,6-enyne **1t**, which bears a sulfonamide group in the linker, gave the product **3ta** in only 27% yield owing to the lower regioselectivity of the initial 1,2-addition (Table 4, entry 13). The reaction of 1,7-enyne **1u**, which has a tether one carbon atom longer, proceeded far less efficiently to give the six-membered-ring product **3ua** in only 32% yield (Table 4, entry 14).

A variety of arylboronic acids **2** were subjected to the cascade reaction of **1a** with a rhodium/diene catalyst (Table 5). Both electron-donating and -withdrawing arylboronic acids **2b**–**2f** were suitably reactive (Table 5, entries 1–5). In the case of sterically bulkier *o*-tolylboronic acid (**2g**) and 1-naphthylboronic acid (**2h**), the corresponding products **3ag** and **3ah** were obtained in good yield as a mixture of atropisomers (Table 5, entries 6 and 7). However, no reaction occurred when methylboronic acid was used instead of the arylboronic acids under the same conditions.

Thus, the cascade reaction is prompted by the carborhodation of a carbon–carbon triple bond, and the intermediate alkenylrhodium(I) species successively participates in the second carbon–carbon bond formation. We then examined a cascade addition/cyclization process by using enediyne **8**. When **8** was treated with phenylboronic acid (**2a**) in the presence of [{Rh(OH)(cod)}$_2$] (6 mol% Rh) for 18 h, bicyclic triene derivative **9** was obtained in 53% yield through three successive carborhodation processes followed by β-oxygen elimination (Scheme 5).

Next, the asymmetric version was examined by using chiral ligands (Table 6). The (*R*)-binap ligand brought forth an excellent level of asymmetric induction on the product **3aa** (94% *ee*; Table 6, entry 1). However, the product selectivity was moderate owing to low regioselectivity associated with the use of phosphine ligands (see above). The use of [{Rh(OH)((*R*)-binap)}$_2$] at room temperature slightly increased both chemical yield and enantioselectivity (66%

Table 4. Rhodium-catalyzed arylative cyclization: scope of the substrate.[a]

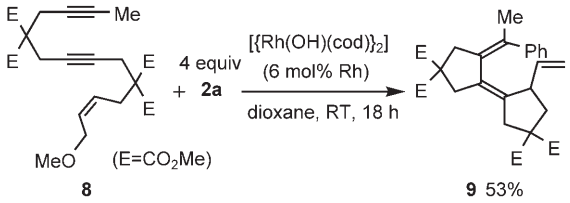
Entry	Substrate	Product	*t* [h]	Yield [%][b]
				
1	**1h** R = H	**3aa**	2	75
2	**1i** R = Me[c]	**3ia**	23	61
				
3	**1j** R = Me, R′ = H	**3ja**	17	71[d]
4	**1k** R = H, R′ = Me	**3ka**	6	79[e]
5	 **1l**	 **3la**	2	70
				
6	**1m** X = C(CO$_2$*t*Bu)$_2$, Y = Me	**3ma**	2	69
7	**1n** X = C(CH$_2$OMe)$_2$, Y = Me	**3na**	2	81
8	**1o** X = C(CH$_2$OAc)$_2$, Y = Me	**3oa**	5	69
9	**1p** X = C(CH$_2$OBn)$_2$, Y = Me	**3pa**	5	72
10	**1q** X = C(CH$_2$OBn)$_2$, Y = Et	**3qa**	16	79
11	**1r** X =  , Y = Me	**3ra**	4	72
12	**1s** X = C(SO$_2$Ph)$_2$, Y = Me	**3sa**	16	70[d]
13	**1t** X = NTs, Y = Me	**3ta**	12	27[d,f]
14	 **1u**	 **3ua**	4	32

[a] **1** (0.2 mmol) was treated with **2a** (0.4 mmol) in dioxane (2.0 mL) in the presence of [{Rh(OH)(cod)}$_2$] (3 mol% Rh) at RT, unless otherwise noted. [b] Yield of isolated product. [c] *E*/*Z* = 9:1. [d] **2a** (4 equiv) and [{Rh(OH)(cod)}$_2$] (6 mol% Rh) were used. [e] A 59:41 mixture of geometrical isomers was obtained. [f] Compounds corresponding to **4** and **5** were formed. [g] *E*/*Z* = 1:4.

Table 5. Rhodium-catalyzed arylative cyclization: scope of the arylboronic acid.[a]

Entry	ArB(OH)$_2$	Product	*t* [h]	Yield [%][b]
1	**2b** Ar = 4-F-C$_6$H$_4$	**3ab**	2	77
2	**2c** Ar = 4-NO$_2$-C$_6$H$_4$	**3ac**	6	82
3	**2d** Ar = 4-Me-C$_6$H$_4$	**3ad**	10	68
4	**2e** Ar = 3-MeO-C$_6$H$_4$	**3ae**	2	77
5	**2f** Ar = 3-Cl-C$_6$H$_4$	**3af**	2	77
6	**2g** Ar = 2-Me-C$_6$H$_4$	**3ag**	8	80[c]
7	**2h** Ar = 1-naphthyl	**3ah**	13	81[c]

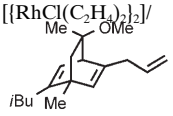
[a] **1a** (0.2 mmol) was treated with **2** (0.4 mmol) in dioxane (2.0 mL) in the presence of [{Rh(OH)(cod)}$_2$] (3 mol% Rh) at RT. [b] Yield of isolated product. [c] Mixture of atropisomers (52:48 for **3ag**, 62:38 for **3ah**).



8 9 53%

Scheme 5. Rhodium-catalyzed arylative cyclization of enediyne **8**.

Table 6. Asymmetric arylative cyclization catalyzed by rhodium.[a]

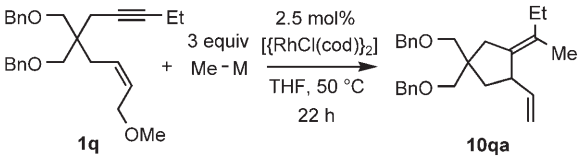
Entry	1	Rh^I complex (Rh/ligand = 1:1)	T [°C]	t [h]	3/(4+5)[b]	3a [%][c]	ee [%][d]
1	**1a**	$[\{RhCl(C_2H_4)_2\}_2]$/(*R*)-binap	100	2	64:36	49	94
2	**1a**	$[\{RhCl((R)\text{-binap})\}_2]$	100	2	64:36	56	89
3	**1a**	$[\{Rh(OH)((R)\text{-binap})\}_2]$	100	2	59:41	53	92
4	**1a**	$[\{Rh(OH)((R)\text{-binap})\}_2]$	RT	2	73:27	66	97
5	**1a**	$[\{RhCl(C_2H_4)_2\}_2]$/ 	90	5	85:15	54	61
6	**1q**	$[\{Rh(OH)((R)\text{-binap})\}_2]$	RT	35	–	61	87

[a] **1** (0.2 mmol) was treated with **2a** (1.0 mmol) in dioxane (2.0 mL) in the presence of the rhodium(I) complex (5 mol% Rh). [b] Ratio determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product. [d] Determined by chiral HPLC.

yield, 97% *ee*; Table 6, entry 4). On the other hand, a better product ratio was observed with a moderate enantioselectivity of 61% *ee* when the chiral diene ligand developed by Carreira and co-workers was used (Table 6, entry 5).[18]

As mentioned above, methylboronic acid failed to undergo the cascade reaction with 1,6-enynes (Table 7, entry 1). As there have been limited examples in which a $C(sp^3)$–rhodium linkage adds intermolecularly to unsaturated functionalities,[19,20] we next examined the use of other organometallic reagents for the installation of a methyl group. The model substrate **1q**, which lacks ester groups, was treated with a methyl–metal reagent in the presence of $[\{RhCl(cod)\}_2]$ (5 mol% Rh) at 50°C for 22 h. Methyllithium and dimethylzinc failed to participate in the catalytic cyclization (Table 7, entries 2 and 3), although the reason was unclear. On the other hand, methylzinc chloride and trimethylaluminum afforded the cyclized product **10qa** in 25% and 29% yield, respectively (Table 7, entries 4 and 5). Notably, the use of MeMgCl efficiently promoted the reaction to give the methylated cyclization product **10qa** in 72% yield (Table 7, entry 6).

Table 7. Rhodium-catalyzed methylative cyclization with methyl–metal reagents.



1q 10qa

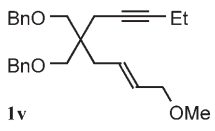
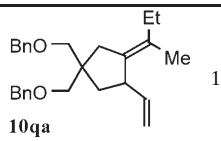
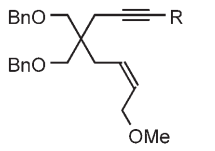
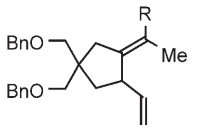
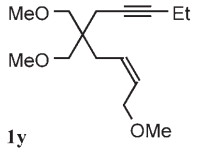
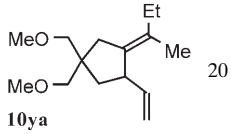
Entry	Me–M	Yield [%][a]	Entry	Me–M	Yield [%][a]
1	$MeB(OH)_2$	0	4	MeZnCl	25
2	MeLi	0	5	Me_3Al	29
3	Me_2Zn	0	6	MeMgCl	72

[a] Yield of isolated product.

Mechanistically, the reaction may proceed via a methylrhodium(I) species, which is generated by transmetalation of $[\{RhCl(cod)\}_2]$ with MeMgCl.[21] Then, the rhodium-catalyzed cascade of addition/cyclization/β-oxygen elimination follows as with the case of arylboronic acids. However, no 1,2-addition across the carbon–carbon triple bond took place when 4-octyne was reacted with MeMgCl in the presence of the rhodium catalyst. At this stage, an oxidative-cyclization mechanism involving a rhoda(III)cycle with a five-membered ring can hardly be ruled out.[22]

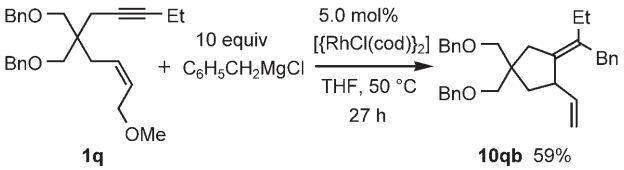
We examined the reaction of other enyne substrates with MeMgCl (Table 8). The cascade reaction successfully occurred with substrate **1v**, which has an *E* olefin (Table 8, entry 1). The reaction tolerated various substituents on the alkyne terminus, including phenyl (**1w**) and trimethylsilyl (**1x**) (Table 8, entries 3 and 4).

Table 8. Rhodium-catalyzed methylative cyclization of 1,6-enynes **1** with methyl Grignard reagents.[a]

Entry	Substrate	Product	t [h]	Yield [%][b]
1	 **1v**	 **10qa**	12	71
2	 **1p** R = Me	 **10pa**	20	70
3	**1w** R = Ph[c]	**10wa**	9	72
4	**1x** R = TMS	**10xa**	48	50[d]
5	 **1y**	 **10ya**	20	61

[a] **1** (0.12 mmol) was treated with MeMgCl (0.36 mmol) in the presence of $[\{RhCl(cod)\}_2]$ (5 mol% Rh) at 50°C in THF (1.2 mL), unless otherwise noted. [b] Yield of isolated product. [c] A 62:38 mixture of geometrical isomers was obtained. [d] $[\{RhCl(cod)\}_2]$ (10 mol% Rh) was used.

The reaction of $C_6H_5CH_2MgCl$ with **1q** gave the cyclized product **10qb** in 59% yield (Scheme 6). Aliphatic Grignard



1q **10qb** 59%

Scheme 6. Rhodium-catalyzed cyclization of 1,6-enyne **1q** with $C_6H_5CH_2MgCl$.

reagents that contain a β-hydrogen atom, such as *n*BuMgCl and *i*PrMgCl, failed to participate in the cascade reaction and afforded a mixture of unidentified products.

Conclusions

We have developed new cyclization reactions of 1,6-enynes with arylboronic acids catalyzed by rhodium, in which the methoxorhodium(I) species is regenerated by β elimination of the methoxy group at the allylic position. The cod ligand showed good regioselectivity in the addition of the organorhodium(I) species to the carbon–carbon triple bond. These findings could lead to the rational design of rhodium-catalyzed cascade processes that involve multiple carbon–carbon bond formation. Furthermore, the potential of MeMgCl as the source of a methyl group in the rhodium-catalyzed cascade reaction is revealed.

Experimental Section

General

All reactions were carried out under nitrogen atmosphere. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300 MHz and ^{13}C at 75 MHz) spectrometer with $CHCl_3$ (^{1}H: $\delta=7.26$ ppm) or $CDCl_3$ (^{13}C: $\delta=77.0$ ppm) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102 A spectrometer. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). 1,4-Dioxane was distilled from sodium. THF was dried and deoxygenized by using an alumina/catalyst column system (Glass Contour Co.).

Syntheses

1a: IR (neat): $\tilde{\nu}=2956$, 1738, 1437, 1293, 1211, 1115 cm^{-1}; ^{1}H NMR: $\delta=$ 1.75 (t, $J=2.7$ Hz, 3H), 2.72 (q, $J=2.5$ Hz, 2H), 2.82 (d, $J=8.1$ Hz, 2H), 3.32 (s, 3H), 3.72 (s, 6H), 4.01 (d, $J=6.6$ Hz, 2H), 5.30–5.41 (m, 1H), 5.64–5.75 ppm (m, 1H); ^{13}C NMR: $\delta=3.5$, 23.0, 30.3, 52.7, 57.0, 58.0, 68.0, 73.3, 79.0, 125.7, 131.0, 170.4 ppm; elemental analysis: calcd (%) for $C_{14}H_{20}O_5$: C 62.67, H 7.51; found: C 62.82, H 7.56.

1b: IR (neat): $\tilde{\nu}=3409$, 2955, 1737, 1439, 1294, 1210 cm^{-1}; ^{1}H NMR: $\delta=$ 1.77 (t, $J=2.6$ Hz, 3H), 2.74 (q, $J=2.5$ Hz, 2H), 2.85 (dd, $J=7.8$, 1.2 Hz, 2H), 3.74 (s, 6H), 4.20 (dd, $J=7.2$, 1.2 Hz, 2H), 5.29–5.41 (m, 1H), 5.76–5.87 ppm (m, 1H); ^{13}C NMR: $\delta=3.5$, 23.1, 30.1, 52.8, 57.0, 58.1, 73.3, 79.3, 125.4, 133.1, 170.4 ppm; HRMS (CI): calcd for $C_{13}H_{19}O_5$: 255.1233 $[M+H]^+$; found: 255.1229.

1c: IR (neat): $\tilde{\nu}=2955$, 1740, 1437, 1293, 1254, 1210 cm^{-1}; ^{1}H NMR: $\delta=$ 0.07 (s, 6H), 0.89 (s, 9H), 1.75 (t, $J=2.6$ Hz, 3H), 2.72 (q, $J=2.6$ Hz, 2H), 2.79 (d, $J=7.8$ Hz, 2H), 3.72 (s, 6H), 4.72 (dd, $J=6.3$, 1.5 Hz, 2H), 5.14–5.26 (m, 1H), 5.63–5.73 ppm (m, 1H); ^{13}C NMR: $\delta=-5.2$, 3.5, 18.4, 22.9, 25.9, 30.3, 52.7, 57.0, 59.4, 73.3, 78.9, 122.8, 134.7, 170.4 ppm; HRMS (CI): calcd for $C_{19}H_{33}O_5Si$: 369.2097 $[M+H]^+$; found: 369.2096.

1d: IR (neat): $\tilde{\nu}=2957$, 1738, 1437, 1375, 1293, 1216 cm^{-1}; ^{1}H NMR: $\delta=$ 1.74 (t, $J=2.4$ Hz, 3H), 2.04 (s, 3H), 2.71 (q, $J=2.6$ Hz, 2H), 2.84 (dd, $J=8.0$, 0.8 Hz, 2H), 3.72 (s, 6H), 4.65 (dd, $J=6.6$, 1.2 Hz, 2H), 5.36–5.49 (m, 1H), 5.64–5.76 ppm (m, 1H); ^{13}C NMR: $\delta=3.4$, 20.9, 23.0, 30.2, 52.8, 56.9, 60.2, 73.0, 79.3, 127.5, 128.1, 170.2, 170.8 ppm; HRMS (CI): calcd for $C_{15}H_{21}O_6$: 297.1338 $[M+H]^+$; found: 297.1332.

1e: IR (neat): $\tilde{\nu}=2995$, 1735, 1437, 1293, 1211, 1115 cm^{-1}; ^{1}H NMR: $\delta=$ 1.09 (t, $J=7.7$ Hz, 3H), 2.13 (qt, $J=7.7$, 2.4 Hz, 2H), 2.74 (t, $J=2.4$ Hz, 2H), 2.80–2.86 (m, 2H), 3.33 (s, 3H), 3.73 (s, 6H), 4.00–4.06 (m, 2H), 5.31–5.42 (m, 1H), 5.65–5.76 ppm (m, 1H); ^{13}C NMR: $\delta=12.4$, 14.1, 22.9, 30.3, 52.7, 57.1, 58.0, 68.0, 73.6, 85.1, 125.7, 131.0, 170.3 ppm; HRMS (CI): calcd for $C_{15}H_{23}O_5$: 283.1545 $[M+H]^+$; found: 283.1543.

1f: IR (neat): $\tilde{\nu}=2953$, 1738, 1437, 1294, 1211, 1113 cm^{-1}; ^{1}H NMR: $\delta=$ 2.88 (d, $J=8.1$ Hz, 2H), 2.98 (s, 2H), 3.25 (s, 3H), 3.74 (s, 6H), 4.01 (dd, $J=6.6$, 1.5 Hz, 2H), 5.32–5.43 (m, 1H), 5.66–5.76 (m, 1H), 7.22–7.28 (m, 3H), 7.30–7.36 ppm (m, 2H); ^{13}C NMR: $\delta=23.6$, 30.5, 52.9, 57.1, 58.0, 68.0, 83.6, 84.2, 123.0, 125.5, 128.0, 128.2, 131.3, 131.6, 170.2 ppm; HRMS (CI): calcd for $C_{19}H_{23}O_5$: 331.1545 $[M+H]^+$; found: 331.1544.

1g: IR (neat): $\tilde{\nu}=2957$, 1740, 1437, 1211, 1115, 1028 cm^{-1}; ^{1}H NMR: $\delta=$ 0.14 (s, 9H), 2.80 (s, 2H), 2.84 (d, $J=7.8$ Hz, 2H), 3.33 (s, 3H), 3.73 (s, 6H), 4.03 (dd, $J=6.5$, 1.4 Hz, 2H), 5.28–5.41 (m, 1H), 5.66–5.77 ppm (m, 1H); ^{13}C NMR: $\delta=0.0$, 24.0, 30.3, 52.8, 57.0, 58.1, 68.0, 88.3, 101.2, 125.5, 131.3, 170.0 ppm; HRMS (CI): calcd for $C_{16}H_{27}O_5Si$: 327.1628 $[M+H]$; found: 327.1624.

1h: IR (neat): $\tilde{\nu}=2950$, 1738, 1439, 1283, 1210, 1114 cm^{-1}; ^{1}H NMR: $\delta=$ 1.76 (t, $J=2.7$ Hz, 3H), 2.73 (q, $J=2.5$ Hz, 2H), 2.79 (d, $J=7.2$ Hz, 2H), 3.29 (s, 3H), 3.73 (s, 6H), 3.86 (d, $J=5.7$ Hz, 2H), 5.45–5.58 (m, 1H), 5.62–5.74 ppm (m, 1H); ^{13}C NMR: $\delta=3.7$, 23.3, 35.3, 52.9, 57.5, 57.9, 72.9, 73.4, 79.3, 127.2, 131.7, 170.6 ppm; HRMS (CI): calcd for $C_{14}H_{21}O_5$: 268.1389 $[M+H]$; found: 268.1389.

1i: A mixture of geometrical isomers ($E/Z=9:1$) was obtained. IR (neat, mixture): $\tilde{\nu}=2955$, 1738, 1437, 1289, 1203, 1088 cm^{-1}; ^{1}H NMR (*E* isomer): $\delta=1.59$ (brs, 3H), 1.76 (t, $J=2.6$ Hz, 3H), 2.74 (q, $J=2.5$ Hz, 2H), 2.83 (brs, 2H), 3.31 (s, 3H), 3.73 (s, 6H), 3.92 (dd, $J=6.3$, 0.6 Hz, 2H), 5.43–5.53 ppm (m, 1H); ^{13}C NMR (*E* isomer): $\delta=3.5$, 17.3, 23.0, 41.4, 52.6, 57.0, 57.8, 68.8, 73.5, 79.3, 127.2, 133.9, 170.8 ppm; HRMS (CI): calcd for $C_{14}H_{19}O_4$: 251.1283 $[M-OMe]$; found: 251.1289.

1j: IR (neat): $\tilde{\nu}=2980$, 1736, 1449, 1289, 1198, 1096 cm^{-1}; ^{1}H NMR: $\delta=$ 1.08 (t, $J=7.5$ Hz, 3H), 1.25 (t, $J=7.1$ Hz, 6H), 1.69 (brs, 3H), 2.12 (qt, $J=7.4$, 2.4 Hz, 2H), 2.73 (t, $J=2.3$ Hz, 2H), 2.83 (d, $J=7.8$ Hz, 2H), 3.24 (s, 3H), 3.78 (s, 2H), 4.10–4.28 (m, 4H), 5.18–5.26 ppm (m, 1H); ^{13}C NMR: $\delta=12.4$, 13.9, 14.07, 14.12, 22.9, 30.2, 57.1, 57.3, 61.4, 73.9, 78.3, 84.8, 120.9, 136.6, 170.1 ppm; HRMS (CI): calcd for $C_{18}H_{29}O_5$: 325.2015 $[M+H]$; found: 325.2014.

1k: IR (neat): $\tilde{\nu}=2980$, 1738, 1289, 1198, 1098, 1071 cm^{-1}; ^{1}H NMR: $\delta=$ 1.09 (t, $J=7.5$ Hz, 3H), 1.20 (d, $J=6.3$ Hz, 3H), 1.25 (t, $J=7.1$ Hz, 6H), 2.13 (qt, $J=7.4$, 2.4 Hz, 2H), 2.74 (t, $J=2.4$ Hz, 2H), 2.75–2.81 (m, 2H), 3.23 (s, 3H), 3.58–3.73 (m, 1H), 4.10–4.28 (m, 4H), 5.38–5.52 ppm (m, 2H); ^{13}C NMR: $\delta=12.4$, 14.1, 14.2, 21.5, 22.9, 34.9, 55.8, 57.2, 61.4, 73.6, 77.7, 85.0, 125.8, 136.9, 169.9 ppm; HRMS (CI): calcd for $C_{18}H_{29}O_5$: 325.2015 $[M+H]$; found: 325.2017.

1l: IR (neat): $\tilde{\nu}=2955$, 1738, 1437, 1202, 1130, 1053 cm^{-1}; ^{1}H NMR: $\delta=$ 1.75 (t, $J=2.4$ Hz, 3H), 2.74 (q, $J=2.6$ Hz, 2H), 2.82 (d, $J=7.2$ Hz, 2H), 3.28 (s, 6H), 3.73 (s, 6H), 4.71 (d, $J=4.2$ Hz, 1H), 5.52–5.73 ppm (m, 2H); ^{13}C NMR: $\delta=3.5$, 23.1, 35.0, 52.6, 52.7, 57.1, 73.0, 79.1, 102.4, 128.4, 131.6, 170.3 ppm; HRMS (CI): calcd for $C_{15}H_{23}O_6$: 299.1495 $[M+H]$; found: 299.1493.

1m: IR (neat): $\tilde{\nu}=2975$, 1728, 1368, 1300, 1143, 1115 cm^{-1}; ^{1}H NMR: $\delta=$ 1.45 (s, 18H), 1.75 (t, $J=2.7$ Hz, 3H), 2.61 (q, $J=2.5$ Hz, 2H), 2.73 (d, $J=7.5$ Hz, 2H), 3.34 (s, 3H), 4.06 (dd, $J=6.3$, 1.5 Hz, 2H), 5.31–5.43 (m, 1H), 5.64–5.75 ppm (m, 1H); ^{13}C NMR: $\delta=3.4$, 22.7, 27.8, 30.0, 57.5, 57.9, 68.2, 74.0, 78.4, 81.5, 126.3, 130.5, 169.2 ppm; HRMS (CI): calcd for $C_{20}H_{33}O_5$: 353.2328 $[M+H]$; found: 353.2332.

1n: IR (neat): $\tilde{\nu}=2921$, 2361, 1459, 1198, 1109 cm^{-1}; ^{1}H NMR: $\delta=1.79$ (t, $J=2.4$ Hz, 3H), 2.11 (q, $J=2.7$ Hz, 2H), 2.15 (d, $J=7.2$ Hz, 2H), 3.19 (d, $J=9.0$ Hz, 2H), 3.23 (d, $J=9.3$ Hz, 2H), 3.32 (s, 6H), 3.33 (s, 3H), 4.02 (d, $J=5.7$ Hz, 2H), 5.53–5.70 ppm (m, 2H); ^{13}C NMR: $\delta=3.6$, 22.2, 29.7, 42.3, 57.9, 59.2, 68.2, 74.2, 75.5, 77.3, 128.0, 129.1 ppm; HRMS (CI): calcd for $C_{13}H_{21}O_2$: 209.1542 $[M-OMe]$; found: 209.1542.

1o: IR (neat): $\tilde{\nu}=2922$, 1747, 1368, 1231, 1105, 1042 cm^{-1}; ^{1}H NMR: $\delta=$ 1.78 (t, $J=2.6$ Hz, 3H), 2.06 (s, 6H), 2.19 (q, $J=2.5$ Hz, 2H), 2.24 (d, $J=8.1$ Hz, 2H), 3.33 (s, 3H), 3.94–4.04 (m, 6H), 5.47–5.63 (m, 1H), 5.65–5.80 ppm (m, 1H); ^{13}C NMR: $\delta=3.5$, 20.9, 22.3, 29.5, 40.5, 58.0, 65.4, 68.0, 73.8, 78.7, 126.4, 130.2, 170.7 ppm; HRMS (CI): calcd for $C_{16}H_{25}O_5$: 297.1702 $[M+H]$; found: 297.1702.

1p: IR (neat): $\tilde{\nu}$ = 2859, 1497, 1455, 1366, 1102, 1028 cm^{-1}; ^1H NMR: δ = 1.76 (t, J = 2.6 Hz, 3H), 2.16–2.25 (m, 4H), 3.27 (s, 3H), 3.35 (d, J = 9.0 Hz, 2H), 3.39 (d, J = 8.7 Hz, 2H), 3.99 (d, J = 5.1 Hz, 2H), 4.50 (s, 4H), 5.52–5.69 (m, 2H), 7.21–7.36 ppm (m, 10H); ^{13}C NMR: δ = 3.6, 22.4, 29.8, 42.6, 57.9, 68.3, 71.7, 73.2, 75.6, 77.4, 127.3, 128.1, 128.2, 129.1, 138.7 ppm; HRMS (CI): calcd for $C_{26}H_{33}O_3$: 393.2430 [M+H]; found: 393.2436.

1q: IR (neat): $\tilde{\nu}$ = 2861, 1497, 1455, 1366, 1102, 1028 cm^{-1}; ^1H NMR: δ = 1.10 (t, J = 7.4 Hz, 3H), 2.14 (qt, J = 7.6, 2.3 Hz, 2H), 2.18–2.26 (m, 4H), 3.28 (s, 3H), 3.35 (d, J = 9.0 Hz, 2H), 3.40 (d, J = 8.7 Hz, 2H), 4.00 (d, J = 4.8 Hz, 2H), 4.50 (s, 4H), 5.53–5.70 (m, 2H), 7,21–7.39 ppm (m, 10H); ^{13}C NMR: δ = 12.5, 14.4, 22.3, 29.7, 42.6, 57.9, 68.2, 71.7, 73.2, 75.8, 83.6, 127.3, 128.1, 128.2, 129.1, 138.7 ppm; HRMS (CI): calcd for $C_{27}H_{35}O_3$: 407.2586 [M+H]; found: 407.2590.

1r: IR (neat): $\tilde{\nu}$ = 2992, 1452, 1372, 1258, 1198, cm^{-1}; ^1H NMR: δ = 1.40 (s, 3H), 1.41 (s, 3H), 1.79 (t, J = 2.3 Hz, 3H), 2.18–2.28 (m, 4H), 3.34 (s, 3H), 3.61 (d, J = 11.7 Hz, 2H), 3.67 (d, J = 11.7 Hz, 2H), 4.03 (d, J = 6.3 Hz, 2H), 5.48–5.78 ppm (m, 2H); ^{13}C NMR: δ = 3.5, 22.6, 23.0, 24.6, 30.4, 36.0, 58.0, 66.7, 68.0, 74.9, 78.2, 98.0, 126.9, 129.9 ppm; HRMS (CI): calcd for $C_{15}H_{25}O_3$: 253.1804 [M+H]; found: 253.1806.

1s: IR (nujol): $\tilde{\nu}$ = 1333, 1308, 1146, 1076 cm^{-1}; ^1H NMR: δ = 1.64 (t, J = 2.7 Hz, 3H), 3.10 (d, J = 6.0 Hz, 2H), 3.16 (q, J = 2.5 Hz, 2H), 3.33 (s, 3H), 3.97 (d, J = 6.0 Hz, 2H), 5.75–5.94 (m, 2H), 7.54–7.61 (m, 4H), 7.67–7.74 (m, 2H), 8.06–8.13 ppm (m, 4H); ^{13}C NMR: δ = 3.7, 20.9, 27.7, 58.3, 68.3, 70.6, 81.9, 88.9, 123.5, 128.5, 130.7, 131.5, 134.6, 136.7 ppm; HRMS (CI): calcd for $C_{22}H_{25}O_5S_2$: 433.1143 [M+H]; found: 433.1143.

1t: IR (nujol): $\tilde{\nu}$ = 1597, 1340, 1161, 1094 cm^{-1}; ^1H NMR: δ = 1.55 (t, J = 2.4 Hz, 3H), 2.43 (s, 3H), 3.31 (s, 3H), 3.85 (d, J = 7.2 Hz, 2H), 3.97–4.04 (m, 4H), 5.46–5.58 (m, 1H), 5.72–5.83 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.73 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR: δ = 3.3, 21.5, 36.4, 43.1, 58.1, 67.7, 71.8, 81.6, 126.6, 127.9, 129.3, 131.8, 136.0, 143.3 ppm; HRMS (CI): calcd for $C_{16}H_{22}NO_3S$: 308.1320 [M+H]; found: 308.1321.

1u: A mixture of geometrical isomers (E/Z = 1:4) was obtained. IR (neat, mixture): $\tilde{\nu}$ = 2984, 1732, 1368, 1206, 1097, 1036 cm^{-1}; ^1H NMR (mixture): δ = 1.19–1.33 (m, 12H), 1.69–1.77 (m, 3H), 2.86 (d, J = 6.9 Hz, 0.4H), 2.98 (d, J = 6.9 Hz, 1.6H), 3.00–3.09 (m, 2H), 3.27 (s, 0.6H), 3.33 (s, 2.4H), 3.82 (d, J = 5.7 Hz, 0.4H), 4.00 (d, J = 6.3 Hz, 1.6H), 4.06–4.32 (m, 8H), 5.53–5.93 ppm (m, 2H); ^{13}C NMR (mixture): δ = 3.6, 13.8, 13.8, 22.6, 22.8, 29.6, 34.6, 57.6, 58.0, 61.6, 61.6, 61.7, 61.7, 62.0, 62.1, 62.1, 62.4, 68.2, 72.7, 74.6, 74.6, 77.9, 78.1, 127.7, 129.0, 129.7, 130.9, 168.8, 168.8, 168.9, 169.0 ppm; HRMS (CI, mixture): calcd for $C_{23}H_{35}O_9$: 455.2281 [M+H]; found: 455.2269 (major isomer), 455.2271 (minor isomer).

1v: IR (neat): $\tilde{\nu}$ = 2857, 1455, 1364, 1102, 1028 cm^{-1}; ^1H NMR: δ = 1.09 (t, J = 7.4 Hz, 3H), 2.13 (qt, J = 7.4, 2.4 Hz, 2H), 2.18–2.24 (m, 4H), 3.28 (s, 3H), 3.35 (d, J = 9.0 Hz, 2H), 3.39 (d, J = 8.7 Hz, 2H), 3.84 (d, J = 5.4 Hz, 2H), 4.50 (s, 4H), 5.53–5.73 (m, 2H), 7.22–7.36 ppm (m, 10H); ^{13}C NMR: δ = 12.5, 14.4, 22.4, 34.7, 42.3, 57.6, 71.9, 73.1, 73.2, 75.8, 83.7, 127.3, 127.3, 128.2, 129.5, 129.7, 138.8 ppm; HRMS (CI): calcd for $C_{27}H_{35}O_3$: 407.2586 [M+H]; found: 407.2591.

1w: A mixture of geometrical isomers (62:38) was obtained. IR (neat, mixture): $\tilde{\nu}$ = 2861, 1491, 1455, 1364, 1102, 1028 cm^{-1}; ^1H NMR (major isomer): δ = 2.32 (d, J = 6.6 Hz, 2H), 2.50 (s, 2H), 3.26 (s, 3H), 3.43 (d, J = 9.0 Hz, 2H), 3.47 (d, J = 9.0 Hz, 2H), 4.02 (d, J = 5.1 Hz, 2H), 4.53 (s, 4H), 5.57–5.74 (m, 2H), 7.21–7.40 ppm (m, 15H); ^1H NMR (minor isomer): δ = 2.30 (d, J = 6.6 Hz, 2H), 2.49 (s, 2H), 3.28 (s, 3H), 3.43 (d, J = 9.0 Hz, 2H), 3.47 (d, J = 9.0 Hz, 2H), 3.85 (d, J = 5.1 Hz, 2H), 4.52 (s, 4H), 5.57–5.77 (m, 2H), 7.21–7.40 ppm (m, 15H); ^{13}C NMR (major isomer): δ = 23.1, 30.0, 43.0, 58.0, 68.3, 71.8, 73.3, 82.5, 87.0, 123.9, 127.3, 127.6, 127.9, 128.1, 128.2, 129.4, 131.5, 138.6 ppm; ^{13}C NMR (minor isomer): δ = 23.2, 35.0, 42.7, 57.6, 72.0, 73.1, 73.3, 82.6, 87.0, 124.0, 127.3, 127.4, 127.5, 128.1, 128.2, 129.4, 129.9, 131.5, 138.7 ppm; HRMS (CI, mixture): calcd for $C_{31}H_{35}O_3$: 455.2586 [M+H]; found: 455.2588.

1x: IR (neat): $\tilde{\nu}$ = 2859, 2174, 1455, 1364, 1250, 1102 cm^{-1}; ^1H NMR: δ = 0.13 (s, 9H), 2.24 (d, J = 6.6 Hz, 2H), 2.30 (s, 2H), 3.28 (s, 3H), 3.36 (d, J = 9.0 Hz, 2H), 3.40 (d, J = 8.7 Hz, 2H), 4.00 (d, J = 5.4 Hz, 2H), 4.49 (s, 4H), 5.52–5.70 (m, 2H), 7.22–7.36 ppm (m, 10H); ^{13}C NMR: δ = 0.2, 23.5, 29.8, 42.6, 58.0, 68.2, 71.7, 73.3, 86.7, 104.2, 127.3, 127.4, 127.9, 128.2, 129.3, 138.7 ppm; HRMS (CI): calcd for $C_{28}H_{39}O_3Si$: 451.2668 [M+H]; found: 451.2662.

1y: IR (neat): $\tilde{\nu}$ = 2887, 1459, 1320, 1198, 1109 cm^{-1}; ^1H NMR: δ = 1.13 (t, J = 7.2 Hz, 3H), 2.10–2.23 (m, 6H), 3.20 (d, J = 8.7 Hz, 2H), 3.24 (d, J = 9.0 Hz, 2H), 3.32 (s, 6H), 3.34 (s, 3H), 4.03 (d, J = 5.4 Hz, 2H), 5.53–5.72 ppm (m, 2H); ^{13}C NMR: δ = 12.5, 14.4, 22.2, 29.7, 42.3, 57.9, 59.2, 68.2, 74.2, 75.7, 83.6, 128.1, 129.1 ppm; HRMS (CI): calcd for $C_{15}H_{27}O_3$: 255.1960 [M+H]; found: 255.1961.

6: IR (neat): $\tilde{\nu}$ = 2955, 1736, 1437, 1252, 1206, 1115 cm^{-1}; ^1H NMR: δ = 1.52 (s, 3H), 1.75 (t, J = 3.0 Hz, 3H), 2.73 (q, J = 2.7 Hz, 2H), 3.73 ppm (s, 6H); ^{13}C NMR: δ = 3.5, 19.9, 26.2, 52.7, 53.5, 73.6, 78.8, 171.6 ppm; HRMS (CI): calcd for $C_{10}H_{15}O_4$: 199.0970 [M+H]; found: 199.0974.

8: IR (neat): $\tilde{\nu}$ = 2957, 1739, 1437, 1329, 1294, 1239 cm^{-1}; ^1H NMR: δ = 1.74 (t, J = 2.6 Hz, 3H), 2.75 (t, J = 2.4 Hz, 2H), 2.78 (d, J = 7.8 Hz, 2H), 2.87 (q, J = 2.5 Hz, 2H), 2.93 (t, J = 2.3 Hz, 2H), 3.34 (s, 3H), 3.73 (s, 6H), 3.74 (s, 6H), 4.01 (dd, J = 6.6, 1.5 Hz, 2H), 5.28–5.40 (m, 1H), 5.64–5.75 ppm (m, 1H); ^{13}C NMR: δ = 3.5, 22.9, 22.9, 30.2, 52.8, 52.9, 56.7, 56.9, 58.0, 67.9, 72.9, 77.7, 77.8, 79.1, 125.5, 128.3, 131.1, 169.3, 170.1 ppm; HRMS (CI): calcd for $C_{23}H_{31}O_9$: 451.1968 [M+H]; found: 451.1979.

Typical procedure for rhodium-catalyzed cyclization of 1,6-enynes with arylboronic acids: [{Rh(OH)(cod)}$_2$] (1.37 mg, 0.3 μmol, 0.03 equiv Rh) and arylboronic acid (0.4 mmol, 2.0 equiv) were added to an oven-dried, N_2-purged flask, followed by 1,4-dioxane (1 mL). A solution of substrate (0.2 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was added to the reaction mixture at room temperature. After complete consumption of substrate, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate) to give the purified product.

3aa: The Z configuration of the *exo* double bond was assigned on the basis of the observed NOE. $[\alpha]_D^{23}$ = +58.6 (c = 0.95, $CHCl_3$) (97% *ee*); IR (neat): $\tilde{\nu}$ = 2953, 1732, 1435, 1254, 1204, 1069 cm^{-1}; ^1H NMR: δ = 1.98–2.02 (m, 3H), 2.14 (dd, J = 13.2, 6.3 Hz, 1H), 2.52 (ddd, J = 13.1, 7.9, 1.0 Hz, 1H), 3.04 (d, J = 16.8 Hz, 1H), 3.15 (dt, J = 16.5, 1.8 Hz, 1H), 3.33–3.45 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.56 (dt, J = 17.1, 1.5 Hz, 1H), 4.63 (dt, J = 10.2, 1.5 Hz, 1H), 5.37 (ddd, J = 17.1, 10.2, 6.9 Hz, 1H), 7.09–7.28 ppm (m, 5H); ^{13}C NMR: δ = 22.2, 38.9, 40.5, 45.4, 52.7, 52.9, 58.8, 113.9, 126.2, 127.8, 131.4, 136.1, 139.6, 143.5, 172.2, 172.4 ppm; elemental analysis: calcd (%) for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found: C 72.78, H 7.07; HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 93:7, flow rate = 0.6 mL min^{-1}): t = 8.04 min (major), t = 9.47 min (minor).

5: IR (neat): $\tilde{\nu}$ = 2923, 1738, 1688, 1437, 1210, 1113 cm^{-1}; ^1H NMR: δ = 1.90 (d, J = 6.9 Hz, 3H), 2.69–2.80 (m, 3H), 3.26–3.33 (m, 1H), 3.31 (s, 3H), 3.65 (s, 3H), 3.98 (d, J = 5.9 Hz, 2H), 5.54–5.74 (m, 2H), 6.36 (q, J = 7.0 Hz, 1H), 7.33 (td, J = 7.4, 1.4 Hz, 1H), 7.50 (td, J = 7.4, 1.4 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 8.32 ppm (dd, J = 7.7, 1.1 Hz, 1H); ^{13}C NMR: δ = 14.2, 31.9, 33.3, 52.5, 58.0, 58.7, 68.1, 123.7, 124.8, 127.0, 127.5, 127.9, 129.6, 129.9, 130.4, 133.8, 141.7, 171.7, 194.8 ppm; HRMS (CI): calcd for $C_{19}H_{23}O_4$: 315.1596 $[M+H]^+$; found: 315.1584.

3ea: IR (neat): $\tilde{\nu}$ = 2957, 1738, 1435, 1262, 1204, 1171 cm^{-1}; ^1H NMR: δ = 0.91 (t, J = 7.5 Hz, 3H), 2.08 (dd, J = 12.9, 6.0 Hz, 1H), 2.20–2.48 (m, 2H), 2.53 (dd, J = 13.2, 8.1 Hz, 1H), 3.09 (s, 2H), 3.25–3.36 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.48 (dt, J = 16.8, 1.5 Hz, 1H), 4.59 (dt, J = 9.9, 1.8 Hz, 1H), 5.35 (ddd, J = 17.1, 10.5, 6.9 Hz, 1H), 7.03–7.08 (m, 2H), 7.16–7.27 ppm (m, 3H); ^{13}C NMR: δ = 12.5, 29.2, 38.1, 40.0, 45.0, 52.7, 52.8, 58.9, 113.6, 126.2, 127.7, 128.5, 135.3, 138.4, 139.5, 142.0, 172.1, 172.3 ppm; HRMS (EI): calcd for $C_{20}H_{24}O_4$: 328.1675 $[M]^+$; found: 328.1674.

3fa: IR (neat): $\tilde{\nu}$ = 2953, 1734, 1267, 1206, 1167, 1075 cm^{-1}; ^1H NMR: δ = 2.08 (dd, J = 13.2, 7.2 Hz, 1H), 2.66 (ddd, J = 12.9, 8.1, 1.8 Hz, 1H), 2.94 (dd, J = 16.5, 1.8 Hz, 1H), 3.24 (dd, J = 16.5, 2.4 Hz, 1H), 3.68–3.75 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 4.57 (dt, J = 17.1, 1.2 Hz, 1H), 4.66 (dt, J = 10.2, 1.2 Hz, 1H), 5.48 (ddd, J = 17.1, 10.2, 6.9 Hz, 1H), 7.08–7.32 ppm (m, 10H); ^{13}C NMR: δ = 39.7, 40.3, 45.4, 52.8, 59.2, 114.0, 126.6, 126.6, 128.0, 129.0, 129.3, 138.1, 138.9, 139.3, 141.8, 142.6, 171.9, 172.0 ppm; HRMS (EI): calcd for $C_{24}H_{24}O_4$: 376.1675 $[M]^+$; found: 376.1674.

3ga: IR (neat): $\tilde{\nu}$ = 2955, 1737, 1435, 1252, 1206, 1073 cm^{-1}; ^1H NMR: δ = 0.06 (s, 9H), 1.98 (dd, J = 13.5, 6.0 Hz, 1H), 2.55 (dd, J = 13.4, 8.6 Hz, 1H), 3.12 (s, 2H), 3.21–3.32 (m, 1H), 3.74 (s, 3H), 3.77 (s, 3H), 4.45 (d, J = 17.1 Hz, 1H), 4.60 (d, J = 10.3 Hz, 1H), 5.41 (ddd, J = 17.1, 10.2, 7.1 Hz, 1H), 6.81 (d, J = 7.2 Hz, 2H), 7.05–7.14 (m, 1H), 7.15–7.25 ppm (m, 2H); ^{13}C NMR: δ = −0.1, 38.8, 40.5, 46.2, 52.8, 59.2, 113.5, 125.1, 127.6, 139.4, 139.5, 143.6, 151.7, 171.96, 172.01 ppm; HRMS (EI): calcd for $C_{21}H_{28}O_4Si$: 372.1757 $[M]^+$; found: 372.1757.

3ia: IR (neat): $\tilde{\nu}$ = 2953, 1740, 1435, 1256, 1204, 1171 cm^{-1}; ^1H NMR: δ = 0.79 (s, 3H), 1.92–1.98 (m, 3H), 2.25 (d, J = 13.5 Hz, 1H), 2.47 (dd, J = 13.4, 1.1 Hz, 1H), 3.16 (dd, J = 17.4, 1.2 Hz, 1H), 3.31 (dt, J = 17.6, 1.3 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.69 (dd, J = 10.5, 1.2 Hz, 1H), 4.76 (dd, J = 17.4, 1.2 Hz, 1H), 5.58 (dd, J = 17.4, 10.8 Hz, 1H), 7.02–7.09 (m, 2H), 7.12–7.25 ppm (m, 3H); ^{13}C NMR: δ = 24.4, 25.3, 40.3, 49.1, 49.3, 52.7, 52.9, 57.1, 111.1, 126.1, 127.4, 128.5, 131.1, 138.7, 143.6, 145.5, 172.3, 172.9 ppm; HRMS (EI): calcd for $C_{20}H_{24}O_4$: 328.1675 $[M]^+$; found: 328.1667.

3ja: IR (neat): $\tilde{\nu}$ = 2965, 1732, 1445, 1254, 1181, 1071 cm^{-1}; ^1H NMR: δ = 0.92 (t, J = 7.5 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.45 (s, 3H), 2.10 (dd, J = 13.1, 7.1 Hz, 1H), 2.23–2.49 (m, 2H), 2.47 (ddd, J = 13.3, 8.3, 1.4 Hz, 1H), 3.04 (d, J = 16.2 Hz, 1H), 3.17 (dd, J = 16.1, 1.4 Hz, 1H), 3.24–3.33 (m, 1H), 4.11–4.29 (m, 4H), 4.31–4.36 (m, 1H), 4.37–4.42 (m, 1H), 7.01–7.09 (m, 2H), 7.10–7.26 ppm (m, 3H); ^{13}C NMR: δ = 12.6, 14.0, 14.2, 19.4, 29.1, 38.7, 38.9, 48.7, 59.2, 61.4, 61.5, 111.6, 126.0, 127.6, 128.2, 135.5, 138.1, 142.2 , 145.7, 171.6, 171.8 ppm; HRMS (EI): calcd for $C_{23}H_{30}O_4$: 370.2144 $[M]^+$; found: 370.2143.

3ka: A mixture of geometrical isomers (59:41) was obtained. IR (neat, mixture:): $\tilde{\nu}$ = 2979, 1732, 1445, 1256, 1179, 1094 cm^{-1}. Major isomer: ^1H NMR: δ = 0.90 (t, J = 7.5 Hz, 3H), 1.21–1.32 (m, 9H) 1.97 (dd, J = 13.1, 7.1 Hz, 1H), 2.17–2.32 (m, 1H), 2.32–2.44 (m, 1H), 2.49 (dd, J = 13.1, 8.3 Hz, 1H), 3.05 (s, 2H), 3.13–3.25 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 4.72 (dq, J = 15.0, 6.4 Hz, 1H), 4.84–4.94 (m, 1H), 6.99–7.05 (m, 2H), 7.11–7.17 ppm (m, 3H); ^{13}C NMR: δ = 12.5, 14.1, 14.1, 17.7, 29.2, 38.1, 40.5, 44.4, 59.0, 61.4, 61.5, 124.5, 126.0, 127.6, 128.6, 132.4, 136.3, 137.8, 142.0, 171.8, 171.9 ppm; HRMS (EI): calcd for $C_{23}H_{30}O_4$: 370.2144 $[M]$; found: 370.2153. Minor isomer: ^1H NMR: δ = 0.89 (t, J = 7.4 Hz, 3H), 1.04 (d, J = 5.1 Hz, 3H), 1.26 (t, J = 7.3 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.80 (dd, J = 13.1, 8.0 Hz, 1H), 2.15–2.30 (m, 1H), 2.31–2.46 (m, 1H), 2.58 (ddd, J = 13.1, 8.3, 1.2 Hz, 1H), 3.05 (d, J = 16.2 Hz, 1H), 3.12 (d, J = 16.2 Hz, 1H), 3.54–3.65 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 4.85–4.98 (m, 2H), 6.99–7.05 (m, 2H), 7.10–7.16 (m, 1H), 7.18–7.26 (m, 2H) ppm; ^{13}C NMR: δ = 12.1, 12.5, 14.1, 14.2, 29.3, 38.3, 38.9, 40.7, 59.1, 61.4, 61.5, 122.1, 125.9, 127.7, 128.6, 132.8, 136.8, 137.7, 142.1, 171.78, 171.81 ppm; HRMS (EI): calcd for $C_{23}H_{30}O_4$: 370.2144 $[M]^+$; found: 370.2153.

3la: IR (neat): $\tilde{\nu}$ = 2955, 2726, 1722, 1435, 1261, 1203 cm^{-1}; ^1H NMR: δ = 1.91 (dd, J = 13.5, 7.7 Hz, 1H), 1.97 (brs, 3H), 2.04 (ddd, J = 17.7, 9.3, 2.1 Hz, 1H), 2.11 (ddd, J = 17.4, 4.2, 1.2 Hz, 1H), 2.68 (ddd, J = 13.4, 8.3, 1.6 Hz, 1H), 3.01 (dt, J = 16.7, 1.9 Hz, 1H), 3.13 (d, J = 16.5 Hz, 1H), 3.29–3.43 (m, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 7.09–7.14 (m, 2H), 7.17–7.25 (m, 1H), 7.26–7.34 (m, 2H), 9.32–9.34 ppm (m, 1H); ^{13}C NMR: δ = 22.6, 35.0, 39.3, 40.0, 47.8, 52.85, 52.91, 58.8, 126.8, 127.5, 128.5, 131.0, 136.5, 143.2, 172.0, 172.1, 201.3 ppm; HRMS (CI): calcd for $C_{19}H_{23}O_5$: 331.1545 $[M+H]^+$; found: 331.1547.

3ma: IR (neat): $\tilde{\nu}$ = 2979, 1728, 1370, 1258, 1165, 1144 cm^{-1}; ^1H NMR: δ = 1.46 (s, 9H), 1.48 (s, 9H), 1.97 (dd, J = 12.9, 6.0 Hz, 1H), 2.00 (d, J = 1.5 Hz, 3H), 2.46 (dd, J = 12.9, 8.4 Hz, 1H), 2.90–3.06 (m, 2H), 3.30–3.42 (m, 1H), 4.52 (dt, J = 17.1, 1.6 Hz, 1H), 4.59 (ddd, J = 10.0, 1.7, 1.1 Hz, 1H), 5.40 (ddd, J = 17.2, 10.0, 7.3 Hz, 1H), 7.08–7.19 (m, 3H), 7.20–7.30 ppm (m, 2H); ^{13}C NMR: δ = 22.2, 27.9, 38.6, 40.2, 45.4, 60.2, 81.1, 81.2, 113.5, 126.1, 127.8, 127.9, 130.9, 136.9, 140.1, 143.7, 170.9, 171.1 ppm; HRMS (FAB): calcd for $C_{25}H_{35}O_4$: 399.2535 $[M+H]^+$; found: 399.2536.

3na: IR (neat): $\tilde{\nu}$ = 2975, 1458, 1447, 1198, 1109 cm^{-1}; ^1H NMR: δ = 1.45 (dd, J = 13.2, 6.3 Hz, 1H), 1.80 (ddd, J = 13.2, 8.7, 0.9 Hz, 1H), 1.98 (brs, 3H), 2.26 (dt, J = 16.2, 1.8 Hz, 1H), 2.43 (d, J = 16.5 Hz, 1H), 3,24 (d, J = 9.3 Hz, 1H), 3.28 (d, J = 9.0 Hz, 1H), 3.32–3.36 (m, 3H), 3.36 (s, 3H), 3.38 (s, 3H), 4.47–4.59 (m, 2H), 5.43 (ddd, J = 17.4, 10.2, 7.2 Hz, 1H), 7.11–7.29 ppm (m, 5H); ^{13}C NMR: δ = 22.3, 37.7, 38.4, 44.9, 46.4, 59.3, 59.4, 75.5, 77.0, 112.4, 125.9, 127.7, 128.0, 130.6, 139.0, 141.6, 144.1 ppm; HRMS (CI): calcd for $C_{19}H_{26}O_2$: 286.1933 $[M]^+$; found: 286.1928.

3oa: IR (neat): $\tilde{\nu}$ = 2953, 1744, 1379, 1364, 1229, 1038 cm^{-1}; ^1H NMR: δ = 1.49 (dd, J = 13.4, 6.8 Hz, 1H), 1.84 (ddd, J = 13.6, 8.6, 1.0 Hz, 1H), 1.98 (brs, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.31 (d, J = 16.1 Hz, 1H), 2.47 (d, J = 16.2 Hz, 1H), 3.30–3.43 (m, 1H), 3.98 (d, J = 10.8 Hz, 1H), 4.03 (d, J = 11.1 Hz, 1H), 4.08 (s, 2H), 4.52 (dt, J = 16.9, 1.6 Hz, 1H), 4.60 (dt, J = 10.1, 1.4 Hz, 1H), 5.41 (ddd, J = 17.1, 10.1, 7.1 Hz, 1H), 7.09–7.21 (m, 3H), 7.22–7.30 ppm (m, 2H); ^{13}C NMR: δ = 20.9, 22.4, 37.4, 38.3, 44.4, 44.6, 66.2, 67.8, 113.1, 126.2, 127.8, 131.8, 137.2, 140.8, 143.6, 171.0, 171.1 ppm; HRMS (CI): calcd for $C_{21}H_{26}O_4$: 342.1831 $[M]^+$; found: 342.1824.

3pa: IR (neat): $\tilde{\nu}$ = 2855, 1495, 1455, 1364, 1100, 1028 cm^{-1}; ^1H NMR: δ = 1.48 (dd, J = 13.2, 6.9 Hz, 1H), 1.85 (dd, J = 13.2, 8.7 Hz, 1H), 1.95 (brs, 3H), 2.27 (dt, J = 16.2, 1.8 Hz, 1H), 2.49 (d, J = 16.2 Hz, 1H), 3.19–3.32 (m, 1H), 3.36 (d, J = 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 3.49 (s, 2H), 4.44 (dd, J = 17.1, 1.2 Hz, 1H), 4.51 (dd, J = 10.2, 0.9 Hz, 1H), 4.53 (s, 2H), 4.55 (s, 2H), 5.38 (ddd, J = 17.2, 10.1, 7.1 Hz, 1H), 7.02–7.08 (m, 2H), 7.11–7.18 (m, 1H), 7.19–7.38 ppm (m, 12H); ^{13}C NMR: δ = 22.4, 37.8, 38.6, 44.9, 46.6, 72.6, 73.1, 73.2, 74.5, 112.4, 125.9, 127.3, 127.4, 127.5, 127.7, 128.0, 128.2, 130.5, 138.9, 139.1, 141.6, 144.2 ppm; HRMS (CI): calcd for $C_{31}H_{35}O_2$: 439.2637 $[M+H]^+$; found: 439.2642.

3qa: $[\alpha]_D^{27}$ = +50.7 (c = 1.33, $CHCl_3$) (87% *ee*); IR (neat): $\tilde{\nu}$ = 2857, 1455, 1364, 1100, 1028 cm^{-1}; ^1H NMR: δ = 0.87 (t, J = 7.5 Hz, 3H), 1.45 (dd, J = 13.4, 6.8 Hz, 1H), 1.83 (dd, J = 13.2, 8.7 Hz, 1H), 2.16–2.44 (m, 3H), 2.51 (d, J = 15.9 Hz, 1H), 3.10–3.23 (m, 1H), 3.36 (d, J = 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 3.49 (s, 2H), 4.39 (dt, J = 17.1, 1.5 Hz, 1H), 4.49 (d, J = 10.2 Hz, 1H), 4.53 (s, 2H), 4.54 (s, 2H), 5.37 (ddd, J = 17.2, 10.1, 7.3 Hz, 1H), 6.97–7.03 (m, 2H), 7.11–7.39 ppm (m, 13H); ^{13}C NMR: δ = 12.8, 29.2, 36.8, 38.2, 44.7, 46.7, 72.6, 73.2, 74.6, 112.1, 125.9, 127.3, 127.37, 127.42, 127.5, 127.6, 128.2, 128.7, 137.4, 138.4, 138.8, 138.9, 141.5, 142.7 ppm; HRMS (CI): calcd for $C_{32}H_{37}O_2$: 453.2794 $[M+H]^+$; found: 453.2793; HPLC (Daicel Chiralcel OD-H, hexane/*i*PrOH = 99.8:0.2, flow rate = 0.6 mL min^{-1}): t = 15.98 min (major), t = 17.99 min (minor).

3ra: IR (neat): $\tilde{\nu}$ = 2992, 2857, 1383, 1370, 1200, 1069 cm^{-1}; ^1H NMR: δ = 1.41 (dd, J = 13.2, 6.0 Hz, 1H), 1.443 (s, 3H), 1.447 (s, 3H), 1.77 (ddd, J = 13.2, 8.4, 0.6 Hz, 1H), 2.00 (brs, 3H), 2.32 (d, J = 16.8 Hz, 1H), 2.65 (d, J = 16.8 Hz, 1H), 3.25–3.38 (m, 1H), 3.59 (dd, J = 11.4, 1.2 Hz, 1H), 3.67 (d, J = 11.7 Hz, 1H), 3.69 (dd, J = 11.1, 1.2 Hz, 1H), 3.76 (d, J = 11.4 Hz, 1H), 4.56 (dt, J = 17.1, 1.7 Hz, 1H), 4.62 (dt, J = 10.2, 1.3 Hz, 1H), 5.44 (ddd, J = 17.0, 10.1, 6.8 Hz, 1H), 7.10–7.20 (m, 3H), 7.21–7.30 ppm (m, 2H); ^{13}C NMR: δ = 22.3, 22.4, 25.3, 38.7, 39.5, 40.6, 44.7, 68.6, 69.7, 97.8, 113.0, 126.0, 127.8, 127.8, 131.3, 137.9, 141.3, 143.9 ppm; HRMS (CI): calcd for $C_{20}H_{26}O_2$: 298.1933 $[M]^+$; found: 298.1933.

3sa: IR (nujol): $\tilde{\nu}$ = 1330, 1314, 1148, 1080 cm^{-1}; ^1H NMR: δ = 1.89 (s, 3H), 2.53 (dd, J = 15.3, 7.2 Hz, 1H), 2.77 (ddd, J = 15.2, 8.5, 1.6 Hz, 1H), 3.09 (d, J = 18.3 Hz, 1H), 3.57 (dt, J = 18.0, 2.2 Hz, 1H), 3.58–3.70 (m, 1H), 4.33 (d, J = 16.8 Hz, 1H), 4.53 (d, J = 10.2 Hz, 1H), 5.33 (ddd, J = 17.0, 10.1, 8.3 Hz, 1H), 7.01–7.05 (m, 2H), 7.15–7.29 (m, 3H), 7.58–7.66 (m, 4H), 7.70–7.79 (m, 2H), 8.06–8.13 ppm (m, 4H); ^{13}C NMR: δ = 22.7, 36.3, 37.6, 45.9, 92.5, 114.2, 126.6, 127.8, 128.0, 128.7, 128.8, 131.0, 131.1, 132.5, 134.3, 134.5, 134.7, 136.1, 137.2, 138.7, 142.6 ppm; HRMS (CI): calcd for $C_{27}H_{27}O_4S_2$: 479.1351 $[M+H]^+$; found: 479.1354.

3ta: IR (neat): $\tilde{\nu}$ = 2984, 1599, 1495, 1338, 1163, 1096 cm^{-1}; ^1H NMR: δ = 1.91 (brs, 3H), 2.46 (s, 3H), 3.17 (dd, J = 9.3, 6.6 Hz, 1H), 3.23–3.33 (m, 1H), 3.26 (dd, J = 9.2, 2.3 Hz, 1H), 3.85 (d, J = 14.1 Hz, 1H), 4.01 (dt, J = 14.0, 1.4 Hz, 1H), 4.63 (dt, J = 17.1, 1.4 Hz, 1H), 4.76 (dt, J = 10.1, 1.1 Hz, 1H), 5.53 (ddd, J = 17.0, 10.0, 7.0 Hz, 1H), 7.04–7.11 (m, 2H), 7.16–7.29 (m, 3H), 7.36 (d, J = 8.1 Hz, 2H), 7.71–7.78 ppm (m, 2H); ^{13}C NMR: δ = 21.6, 21.8, 45.2, 50.5, 53.8, 115.0, 126.8, 127.4, 127.9, 128.0, 129.6, 131.7, 132.8, 132.9, 137.5, 142.3, 143.6 ppm; HRMS (CI): calcd for $C_{21}H_{24}O_2NS$: 354.1528 $[M+H]^+$; found: 354.1525.

3ua: IR (neat): $\tilde{\nu}$ = 2982, 1733, 1445, 1267, 1200, 1040 cm^{-1}; ^1H NMR: δ = 1.24 (t, J = 7.5 Hz, 3H), 1.260 (t, J = 7.2 Hz, 3H), 1.264 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.98 (brs, 3H), 2.40 (dd, J = 13.8, 2.1 Hz, 1H), 2.82–2.90 (m, 2H), 3.14–3.23 (m, 1H), 3.24 (d, J = 15.6 Hz, 1H), 3.96–4.28 (m, 8H), 4.84 (dt, J = 17.4, 1.8 Hz, 1H), 4.91 (dt, J = 10.7,

2.0 Hz, 1H), 5.61 (ddd, J=17.4, 10.4, 4.4 Hz, 1H), 7.10–7.16 (m, 2H), 7.17–7.31 (m, 3H) ppm; ^{13}C NMR: δ=13.7, 13.8, 14.1, 20.7, 29.8, 34.8, 40.2, 58.5, 59.0, 61.2, 61.35, 61.45, 61.8, 114.0, 126.2, 127.2, 127.6, 128.0, 134.6, 140.4, 144.4, 168.6, 169.3, 170.5, 170.7 ppm; HRMS (CI): calcd for $C_{28}H_{37}O_8$: 501.2488 $[M+H]^+$; found: 501.2485.

3ab: IR (neat): $\tilde{\nu}$=2955, 1733, 1603, 1509, 1435, 1260 cm^{-1}; ^{1}H NMR: δ= 1.97 (brs, 3H), 2.11 (dd, J=13.2, 6.3 Hz, 1H), 2.52 (dd, J=13.1, 8.0 Hz, 1H), 3.03 (d, J=16.8 Hz, 1H), 3.13 (dt, J=17.0, 1.7 Hz, 1H), 3.27–3.41 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 4.55 (dt, J=17.1, 1.4 Hz, 1H), 4.62 (d, J=10.2 Hz, 1H), 5.34 (ddd, J=17.1, 10.1, 7.1 Hz, 1H), 6.85–6.98 (m, 2H), 7.00–7.14 ppm (m, 2H); ^{13}C NMR: δ=22.3, 39.0, 40.6, 45.5, 52.7, 52.9, 58.7, 114.1, 114.6 (d, J=20.7 Hz), 129.4 (d, J=8.1 Hz), 130.5, 136.6, 139.3, 139.5, 161.3 (d, J=243.2 Hz), 172.1, 172.3 ppm; HRMS (EI): calcd for $C_{19}H_{21}FO_4$: 332.1424 $[M]^+$; found: 332.1423

3ac: IR (neat): $\tilde{\nu}$=2953, 1734, 1541, 1509, 1456, 1340 cm^{-1}; ^{1}H NMR: δ= 2.02 (brs, 3H), 2.13 (dd, J=13.2, 6.6 Hz, 1H), 2.54 (ddd, J=13.2, 6.6, 1.1 Hz, 1H), 3.07 (d, J=17.1 Hz, 1H), 3.16 (dt, J=17.1, 1.8 Hz, 1H), 3.30–3.42 (m, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 4.54 (dt, J=17.1, 1.4 Hz, 1H), 4.62 (dt, J=10.3, 1.2 Hz, 1H), 5.31 (ddd, J=17.2, 10.0, 7.3 Hz, 1H), 7.25–7.31 (m, 2H), 8.08–8.14 ppm (m, 2H); ^{13}C NMR: δ=21.8, 39.3, 40.8, 45.8, 52.8, 52.9, 58.5, 114.9, 123.2, 128.8, 129.7, 139.0, 146.2, 150.4, 171.8, 172.1 ppm; HRMS (EI): calcd for $C_{19}H_{21}NO_6$: 359.1369 $[M]^+$; found: 359.1374.

3ad: IR (neat): $\tilde{\nu}$=2954, 1734, 1435, 1256, 1204, 1171 cm^{-1}; ^{1}H NMR: δ= 1.98 (brs, 3H), 2.16 (dd, J=13.2, 5.7 Hz, 1H), 2.31 (s, 3H), 2.51 (ddd, J= 13.1, 8.0, 0.9 Hz, 1H), 3.03 (d, J=17.1 Hz, 1H), 3.15 (dt, J=16.8, 1.8 Hz, 1H), 3.35–3.44 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 4.57–4.72 (m, 2H), 5.41 (ddd, J=17.0, 10.4, 6.5 Hz, 1H), 6.99–7.10 ppm (m, 4H); ^{13}C NMR: δ=21.1, 22.2, 38.9, 40.4, 45.3, 52.7, 52.9, 58.8, 114.0, 127.6, 128.5, 131.2, 135.7, 135.8, 139.7, 140.6, 172.2, 172.4 ppm; HRMS (EI): calcd for $C_{20}H_{24}O_4$: 328.1675 $[M]^+$; found: 328.1670.

3ae: IR (neat): $\tilde{\nu}$=2953, 1734, 1489, 1435, 1260, 1205 cm^{-1}; ^{1}H NMR: δ= 1.99 (brs, 3H), 2.16 (dd, J=13.2, 5.7 Hz, 1H), 2.51 (ddd, J=13.1, 8.0, 0.9 Hz, 1H), 3.03 (d, J=16.8 Hz, 1H), 3.15 (dt, J=16.9, 1.8 Hz, 1H), 3.33–3.46 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 3.77 (s, 3H), 4.58–4.71 (m, 2H), 5.42 (ddd, J=17.1, 10.5, 6.6 Hz, 1H), 6.65–6.78 (m, 3H), 7.16 ppm (t, J=8.0 Hz, 1H); ^{13}C NMR: δ=22.1, 38.9, 40.4, 45.5, 52,7, 52.9, 55.2, 58.7, 111.6, 113.6, 114.0, 120.3, 128.8, 131.2, 136.2, 139.7, 144.9, 159.1, 172.2, 172.4 ppm; HRMS (EI): calcd for $C_{20}H_{24}O_5$: 344.1624 $[M]^+$; found: 344.1624.

3af: IR (neat): $\tilde{\nu}$=2953, 1733, 1435, 1259, 1205, 1173 cm^{-1}; ^{1}H NMR: δ= 1.97 (brs, 3H), 2.12 (dd, J=13.2, 6.5 Hz, 1H), 2.52 (dd, J=13.2, 7.8 Hz, 1H), 3.04 (d, J=17.1 Hz, 1H), 3.13 (dt, J=17.1, 1.5 Hz, 1H), 3.30–3.43 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.57 (dt, J=17.0, 1.4 Hz, 1H), 4.64 (dt, J=9.9, 1.4 Hz, 1H), 5.34 (ddd, J=17.2, 10.1, 7.1 Hz, 1H), 6.96–7.02 (m, 1H), 7.08–7.21 ppm (m, 3H); ^{13}C NMR: δ=22.0, 39.0, 40.7, 45.6, 52.8, 52.9, 58.6, 114.4, 126.1, 126.3, 128.1, 129.1, 130.2, 133.5, 137.3, 139.3, 145.2, 172.0, 172.2 ppm; HRMS (EI): calcd for $C_{19}H_{21}ClO_4$: 348.1128 $[M]^+$; found: 348.1127.

3ag: A mixture of atropisomers (52:48) was obtained. IR (neat, mixture): $\tilde{\nu}$=2953, 1736, 1435, 1256, 1204, 1171 cm^{-1}; ^{1}H NMR (mixture): δ=1.89 (brs, 1.5H), 1.91 (brs, 1.5H), 2.02 (dd, J=13.5, 8.1 Hz, 0.5H), 2.10 (dd, J=13.2, 6.6 Hz, 0.5H), 2.13 (s, 1.5H), 2.14 (s, 1.5H), 2.48–2.60 (m, 1H), 2.83–2.94 (m, 0.5H), 2.98–3.17 (m, 2H), 3.17–3.29 (m, 0.5H), 3.74 (s, 1.5H), 3.746 (s, 1.5H), 3.754 (s, 1.5H), 3.79 (s, 1.5H), 4.20 (d, J=17.1 Hz, 0.5H), 4.37–4.48 (m, 1H), 4.54 (dt, J=10.1, 1.3 Hz, 0.5H), 5.23 (ddd, J= 18.3, 10.2, 8.4 Hz, 0.5H), 5.36 (ddd, J=17.1, 10.2, 7.2 Hz, 0.5H), 6.87–6.96 (m, 1H), 7.01–7.15 ppm (m, 3H); ^{13}C NMR (mixture): δ=18.8, 19.6, 21.5, 22.1, 38.4, 38.6, 40.1, 40.4, 45.5, 45.8, 52.7, 52.8, 58.9, 113.2, 113.5, 125.1, 125.5, 126.4, 126.5, 128.0, 129.0, 129.6, 129.8, 131.0, 132.2, 134.0, 135.4, 135.9, 136.2, 138.2, 139.5, 142.5, 143.0, 172.1, 172.2, 172.3 ppm; HRMS (EI, mixture): calcd for $C_{20}H_{24}O_4$: 328.1675 $[M]^+$; found: 328.1671.

3ah: A mixture of atropisomers (62:38) was obtained. IR (neat, mixture): $\tilde{\nu}$=2953, 1733, 1435, 1266, 1200, 1169 cm^{-1}; ^{1}H NMR (mixture): δ=2.00–2.16 (m, 4H), 2.45 (ddd, J=13.2, 8.0, 1.4 Hz, 0.625H), 2.56 (dd, J=13.2, 7.8 Hz, 0.375H), 2.75–2.88 (m, 0.625H), 3.06–3.41 (m, 2.375H), 3.75 (s, 1.875H), 3.76 (s, 1.125H), 3.82 (s, 1.125H), 3.84 (s, 1.875H), 3.97–4.11 (m, 1.375H), 4.37 (ddd, J=10.2, 1.5, 0.9 Hz, 0.625H), 5.00 (ddd, J=17.1, 10.1, 8.0 Hz, 0.375H), 5.27 (ddd, J=17.2, 10.0, 7.4 Hz, 0.625H), 7.12 (dd, J=7.2, 1.2 Hz, 0.375H), 7.18 (dd, J=7.2, 1.2 Hz, 0.625H), 7.32–7.49 (m, 3H), 7.67–7.87 ppm (m, 3H); ^{13}C NMR (mixture): δ=22.5, 22.9, 38.8, 38.9, 40.3, 40.5, 45.8, 45.9, 52.8, 52.9, 52.9, 58.9, 58.9, 113.1, 113.4, 124.9, 125.1, 125.2, 125.3, 125.3, 125.4, 125.8, 125.9, 126.0, 126.6, 126.8, 128.0, 128.4, 129.5, 130.2, 130.9, 131.8, 133.5, 133.6, 137.6, 138.1, 138.5, 139.4, 140.9, 141.5, 172.11, 172.14, 172.2, 172.4 ppm; HRMS (EI, mixture): calcd for $C_{23}H_{24}O_4$: 364.1675 $[M]^+$; found: 364.1678.

7: IR (neat): $\tilde{\nu}$=2953, 1736, 1435, 1244, 1204, 1111 cm^{-1}; ^{1}H NMR: δ= 1.47 (s, 3H), 2.05 (brs, 3H), 2.80 (d, J=7.5 Hz, 2H), 3.74 (s, 6H), 5.61 (tq, J=7.8, 1.5 Hz, 1H), 7.19–7.37 ppm (m, 5H); ^{13}C NMR: δ=16.2, 20.0, 34.8, 52.6, 53.9, 121.7, 125.8, 126.9, 128.1, 138.7, 143.6, 172.5 ppm; HRMS (EI): calcd for $C_{16}H_{20}O_4$: 276.1362 $[M]^+$; found: 276.1362.

9: The Z configuration of both double bonds was assigned on the basis of the observed NOE. IR (neat): $\tilde{\nu}$=2955, 1732, 1435, 1270, 1204, 1063 cm^{-1}; ^{1}H NMR: δ=1.39–1.52 (m, 1H), 1.82 (dd, J=12.9, 9.3 Hz, 1H), 1.97 (brs, 3H), 2.14 (ddd, J=12.7, 8.3, 1.7 Hz, 1H), 2.72–2.82 (m, 1H), 2.82–2.98 (m, 3H), 3.01–3.11 (m, 2H), 3.64 (s, 3H), 3.65 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 4.61 (dt, J=17.3, 1.7 Hz, 1H), 4.79 (dt, J=10.5, 1.5 Hz, 1H), 5.35 (ddd, J=17.2, 10.6, 6.5 Hz, 1H), 7.08–7.16 (m, 3H), 7.18–7.25 ppm (m, 2H); ^{13}C NMR: δ=21.3, 39.1, 39.4, 40.9, 41.2, 44.0, 52.6, 52.6, 52.8, 52.9, 56.6, 58.4, 113.4, 126.2, 127.9, 128.0, 130.6, 131.7, 132.5, 135.6, 139.3, 143.8, 171.1, 171.8, 172.1, 172.3 ppm; HRMS (CI): calcd for $C_{28}H_{32}O_8$: 496.2097 $[M]^+$; found: 496.2095.

Typical procedure for rhodium-catalyzed cyclization of 1,6-enynes with Grignard reagents: [{RhCl(cod)}$_2$] (1.5 mg, 3.0 μmol, 0.05 equiv Rh) and a solution of substrate (0.12 mmol, 1.0 equiv) in THF (1.2 mL) were added to an oven-dried, N_2-purged flask, and the reaction mixture was stirred for 5 min at room temperature. The Grignard reagent (in THF, 0.36 mmol, 3.0 equiv) was added to the resulting solution, which was then heated to 50 °C. After complete consumption of substrate, the reaction was quenched with HCl (1 M). The aqueous layer was extracted three times with ethyl acetate, and the combined extracts were washed with saturated $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate) to give the purified product.

10pa: IR (neat): $\tilde{\nu}$=2855, 1455, 1364, 1100, 1028 cm^{-1}; ^{1}H NMR: δ=1.49 (dd, J=13.1, 6.8 Hz, 1H), 1.58 (s, 3H), 1.63 (s, 3H), 1.94 (ddd, J=13.4, 8.8, 1.3 Hz, 1H), 2.11 (d, J=15.9 Hz, 1H), 2.35 (d, J=15.6 Hz, 1H), 3.14–3.28 (m, 1H), 3.29 (d, J=9.0 Hz, 1H), 3.33 (d, J=8.7 Hz, 1H), 3.44 (s, 2H), 4.50 (s, 2H), 4.51 (s, 2H), 4.82–4.95 (m, 2H), 5.68 (ddd, J=17.2, 10.0, 7.3 Hz, 1H), 7.22–7.36 ppm (m, 10H); ^{13}C NMR: δ=20.7, 21.8, 37.5, 39.0, 44.9, 47.0, 72.7, 73.1, 73.2, 74.4, 112.3, 125.2, 127.2, 127.3, 127.4, 128.2, 135.4, 138.9, 139.0, 142.5 ppm; HRMS (CI): calcd for $C_{26}H_{33}O_2$: 377.2481 $[M+H]$; found: 377.2481.

10qa: The E configuration of the *exo* double bond was assigned on the basis of the observed NOE. IR (neat): $\tilde{\nu}$=2857, 1455, 1364, 1098, 1028 cm^{-1}; ^{1}H NMR: δ=0.94 (t, J=7.5 Hz, 3H), 1.49 (dd, J=13.4, 6.8 Hz, 1H), 1.57 (brs, 3H), 1.88–2.06 (m, 3H), 2.10 (d, J=16.2 Hz, 1H), 2.39 (d, J=15.9 Hz, 1H), 3.13–3.26 (m, 1H), 3.31 (s, 2H), 3.45 (s, 2H), 4.50 (s, 2H), 4.51 (s, 2H), 4.81–4.98 (m, 2H), 5.68 (ddd, J=17.2, 10.0, 7.3 Hz, 1H), 7.20–7.41 ppm (m, 10H); ^{13}C NMR: δ=12.6, 17.9, 28.9, 36.7, 38.8, 44.7, 47.0, 72.7, 73.1, 73.2, 74.4, 112.2, 127.2, 127.3, 127.4, 128.2, 131.3, 134.8, 138.9, 142.4 ppm; HRMS (CI): calcd for $C_{27}H_{35}O_2$: 391.2637 $[M+H]$; found: 391.2638.

10wa: IR (neat): $\tilde{\nu}$=2857, 1495, 1455, 1364, 1100, 1028 cm^{-1}; ^{1}H NMR: δ=1.55 (dd, J=13.4, 7.1 Hz, 1H), 1.95 (brs, 3H), 2.05 (dd, J=13.5, 9.0 Hz, 1H), 2.26 (s, 2H), 3.25 (s, 2H), 3.32–3.44 (m, 1H), 3.40 (d, J= 8.7 Hz, 1H), 3.43 (d, J=9.0 Hz, 1H), 4.40 (d, J=12.0 Hz, 1H), 4.45 (d, J=12.3 Hz, 1H), 4.48 (s, 2H), 4.98 (d, J=10.2 Hz, 1H), 5.04 (d, J= 17.1 Hz, 1H), 5.81 (ddd, J=17.2, 9.8, 7.4 Hz, 1H), 7.18–7.39 ppm (m, 15H); ^{13}C NMR: δ=20.3, 38.5, 38.6, 45.2, 47.3, 72.3, 73.2, 73.2, 74.5, 112.7, 126.0, 127.2, 127.3, 127.4, 127.9, 128.2, 128.2, 130.8, 138.8, 139.3, 141.5, 144.8 ppm; HRMS (CI): calcd for $C_{31}H_{35}O_2$: 439.2637 $[M+H]$; found: 439.2641.

10xa: IR (neat): $\tilde{\nu}$=2857, 1455, 1364, 1248, 1098, 1028 cm^{-1}; ^{1}H NMR: δ=0.10 (s, 9H), 1.49 (dd, J=13.4, 9.2 Hz, 1H), 1.62 (brs, 3H), 1.91 (dd,

J=13.4, 9.2 Hz, 1H), 2.17 (d, J=15.3 Hz, 1H), 2.44 (d, J=15.6 Hz, 1H), 3.21–3.52 (m, 1H), 3.25 (d, J=9.0 Hz, 1H), 3.30 (d, J=9.0 Hz, 1H), 3.40 (d, J=8.7 Hz, 1H), 3.49 (d, J=9.0 Hz, 1H), 4.43 (d, J=12.3 Hz, 1H), 4.508 (s, 2H), 4.510 (d, J=12.0 Hz, 1H), 4.85–4.95 (m, 2H), 5.61–5.75 (m, 1H), 7.21–7.36 ppm (m, 10H); ^{13}C NMR: δ=−0.3, 18.3, 38.0, 39.8, 45.5, 47.2, 72.3, 73.2, 74.5, 112.4, 127.2, 127.3, 128.2, 128.5, 138.9, 138.9, 141.4, 152.6 ppm; HRMS (CI): calcd for $C_{28}H_{38}O_2Si$: 434.2641 $[M]^+$; found: 434.2639.

10ya: IR (neat): $\tilde{\nu}$=2874, 1636, 1458, 1198, 1115 cm^{-1}; ^{1}H NMR: δ=0.93 (t, J=7.5 Hz, 3H), 1.42 (dd, J=13.4, 6.8 Hz, 1H), 1.57 (brs, 3H), 1.88 (ddd, J=13.4, 8.9, 1.2 Hz, 1H), 1.92–2.06 (m, 2H), 2.05 (d, J=15.6 Hz, 1H), 2.30 (d, J=15.9 Hz, 1H), 3.14 (s, 2H), 3.16–3.28 (m, 1H), 3.29 (s, 2H), 3.32 (s, 3H), 3.33 (s, 3H), 4.86–4.96 (m, 2H), 5.70 ppm (ddd, J=17.0, 10.0, 7.1 Hz, 1H); ^{13}C NMR: δ=12.5, 17.9, 28.8, 36.5, 38.5, 44.6, 46.8, 59.3, 75.2, 77.0, 112.2, 131.4, 134.8, 142.3; HRMS (EI): calcd for $C_{15}H_{26}O_2$: 238.1933 $[M]^+$; found: 238.1924.

10qb: IR (neat): $\tilde{\nu}$=2857, 1495, 1453, 1364, 1100, 1028 cm^{-1}; ^{1}H NMR: δ=0.86 (t, J=7.5 Hz, 3H), 1.52 (dd, J=13.5, 6.6 Hz, 1H), 1.77–2.05 (m, 3H), 2.20 (d, J=15.6 Hz, 1H), 2.47 (d, J=16.2 Hz, 1H), 3.21–3.40 (m, 4H), 3.44–3.57 (m, 3H), 4.52 (s, 2H), 4.53 (s, 2H), 4.83–4.98 (m, 2H), 5.76 (ddd, J=17.2, 9.8, 7.4 Hz, 1H), 7.08 (d, J=6.9 Hz, 2H), 7.11–7.37 ppm (m, 13H); ^{13}C NMR: δ=12.8, 25.9, 36.8, 37.1, 38.9, 44.9, 46.9, 72.7, 73.2, 74.4, 112.6, 125.5, 127.3, 127.4, 128.1, 128.22, 128.25, 128.7, 134.3, 137.5, 138.8, 138.9, 140.7, 142.7 ppm; HRMS (CI): calcd for $C_{33}H_{39}O_2$: 467.2950 $[M+H]^+$; found: 467.2952.

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