Mechanistic Investigation of RhI-Catalyzed Cycloisomerization of Benzylallene-Internal Alkynes via C-H Activation

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journal or publication title	Journal of Organic Chemistry
volume	82
number	14
page range	7666-7674
year	2017-07-21
URL	http://hdl.handle.net/2297/48552

doi: 10.1021/acs.joc.7b01048

The Journal of Organic Chemistry

Note

**Rh^I-Catalyzed Cycloisomerization of Benzylallene-Internal Alkynes via C–H
Activation**

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Abstract

Treatment of the benzylallene-internal alkynes with $[\text{RhCl}(\text{CO})_2]_2$ effected a novel cycloisomerization via a $\text{C}_{\text{sp}^2}\text{-H}$ bond activation to produce the tricyclo[9.4.0.0^{3,8}]pentadecapentaene skeleton. The plausible reaction mechanism via consecutive formation of the rhodabicyclo[4.3.0] intermediates and σ -bond metathesis between the $\text{C}_{\text{sp}^2}\text{-H}$ bond on the benzene ring and the $\text{C}_{\text{sp}^2}\text{-Rh}^{\text{III}}$ bond ($\text{C}_{\text{sp}^2}\text{-H}$ bond activation step) was proposed based on the experiments using deuterated substrates. In addition, a plausible alternative mechanism for the previously reported cycloisomerization of the benzylallene-terminal alkynes could also be proposed based on the current mechanistic study.

Cyclization reactions utilizing the transition-metal-catalyzed C–H¹ and/or C–C² bond activation provide a powerful step- and atom-economical methodology for the straightforward construction of complex polycyclic skeletons inaccessible by other conventional methods. Recent efforts from this laboratory disclosed that the [RhCl(CO)₂]₂-catalyzed cycloisomerization of the benzylallene-terminal alkynes **1** (Y=SO₂Ph, alkyl) took place via the C_{sp2}–H bond activation on the benzene ring to produce the tricyclo[9.4.0.0^{3,8}]pentadecapentaene derivatives **2** [Scheme 1, Eq. (1)].³ Based on preliminary investigations using deuterated substrates,³ we tentatively interpreted this ring-closing reaction as follows: (i) oxidative addition of the acetylenic C–H bond to Rh^I would form the intermediate **3** as the first step, (ii) ene-type cyclization of **3** would lead to the unique vinylidenecarbene-Rh intermediate **4**,⁴ which is electrophilically captured by benzene to form **5**, and (iii) migration of the proton of benzene of **5** to Rh (C_{sp2}–H bond activation) would finally be followed by reductive elimination.⁵ We subsequently focused on the ring-closing reaction using the internal alkyne instead of the terminal acetylene species. As a result, treatment of the benzylallene-internal alkyne species **6** (R¹≠H, Y=alkyl) with [RhCl(CO)₂]₂ dramatically

changed the ring-closing mode to furnish the hexahydrophenanthrene skeleton **7** in high yields [Scheme 1, Eq. (2)].⁶ The reaction likely proceeds by consecutive formation of a rhodabicyclo[4.3.0] intermediate **8**, σ -bond metathesis between the C_{sp2}-H bond on the benzene ring and the C_{sp2}-Rh bond (C_{sp2}-H bond activation step), and isomerization between three σ -, π -, and σ -allylrhodium species (**9** and **9'**: σ -allylrhodium). This plausible mechanism was proposed on the basis of several experiments using deuterated substrates.⁶

Scheme 1. Our Previous Study: Rh^I-Catalyzed Cycloisomerization of Benzylallene-Alkynes via C-H Bond Activation

During the course of our investigation of the Rh^I-catalyzed cyclization of

allenes possessing an additional π -component,^{7,8} we generally assumed the formation of the rhodabicyclic intermediate, such as **8**, as the first step in order to understand the experimental results. However, the proposed mechanism for the construction of **2** from **1** is quite different from our precedents, whereas the mechanism for the formation of **7** from **6** is in line with our previously proposed one involving the rhodabicyclic intermediate. Therefore, at this stage we wondered if the rhodabicyclo[4.3.0]nonadiene intermediate might be involved in the transformation of **1** into **2**. On the other hand, we had already observed that the substituent on the allenyl moiety significantly affected the reactivity and chemoselectivity of several reactions.^{8c,g,h} Thus, our next efforts directed towards making the reaction mechanism for the transformation of **1** into **2** clearer using benzylallene-alkyne substrates **6**⁹ with varying substituents on the allenyl moiety and at the alkyne terminus. Herein we describe the preparation of other type of tricyclo[9.4.0.0^{3,8}]derivative **10**, a double bond isomer of **2**, from the benzylallene-internal alkynes **6** with an electron-withdrawing group (EWG) on the allenyl moiety ($R^1 \neq H$, $Y = SO_2Ph$, $P(O)(OEt)_2$). With three transformations (the newly obtained results with the previous ones) considered, we now propose the reaction

mechanism that can rationalize the formation of all tricyclic compounds **2**, **7**, and **10** from benzylallene-alkyne substrates **1** and **6** via the common rhodabicyclo[4.3.0] intermediate (Scheme 2).

Scheme 2. This Study: Rh^I-Catalyzed Cycloisomerization of Benzylallene-Internal Alkynes via C–H Bond Activation

The benzylallene-internal alkyne **6a** having a dimethyl group at the benzylic position¹⁰ was exposed to the optimized conditions ($[\text{RhCl}(\text{CO})_2]_2$ in 1,2-dichloroethane (DCE) heated at 110 °C by microwave (MW) irradiation) to provide the tricyclo[9.4.0.0^{3,8}]pentadecapentaene derivative **10a** with a *trans* stereochemistry between the *n*-butyl residue and the phenylsulfonyl group (64%, entry 1).^{11,12} Compound **10a** has the benzene-fused seven-six membered structure similar to that of **2**, but different regarding the position of the two double bonds. The allene-alkyne **6b** also

gave the tricyclic product **10b** in 66% yield (entry 2). In the cases of the benzylallenes possessing a phosphonate group on the allenyl moiety **6c** and **6d**, the reaction occurred in refluxing toluene to afford **10c** (64% yield) and **10d** (73% yield), respectively (entries 3 and 4). The substrate having a benzyloxymethyl group at the alkyne terminus **6e** provided the corresponding cycloadduct **10e** in 52% yield (entry 5). The cyclic ketal derivative **6f**¹³ was exposed to the standard conditions to furnish **10f** in 41% yield (entry 6). Both compounds **6g** (R³=Me) and **6h** (R³=Cl) with substituents at the *para*-position on the benzene ring produced **10g** in 56% yield (entry 7) and **10h** in 62% yield (entry 8), although a longer reaction time was needed in the latter case. Thus, it became clear that the benzylallene-internal alkynes **6** with an EWG on the allenyl moiety consistently produced the third type of compound **10** being obviously different from compounds **2** and **7**.

Table 1. [RhCl(CO)₂]₂-Catalyzed Cycloisomerization of Benzylallene-Alkynes **6^a**

entry	substrate	R ¹	R ²	R ³	X	time (h)	product and yield (%) ^b
1	6a	<i>n</i> Bu	SO ₂ Ph	H	C(CO ₂ Me) ₂	12	10a : 64
2	6b	Me	SO ₂ Ph	H	C(CO ₂ Me) ₂	10	10b : 66
3 ^c	6c	<i>n</i> Bu	P(O)(OEt) ₂	H	C(CO ₂ Me) ₂	3	10c : 64
4 ^c	6d	Me	P(O)(OEt) ₂	H	C(CO ₂ Me) ₂	3	10d : 73
5	6e	CH ₂ OBn	SO ₂ Ph	H	C(CO ₂ Me) ₂	7	10e : 52
6	6f	<i>n</i> Bu	SO ₂ Ph	H	C(CH ₂ O) ₂ CMe ₂	20	10f : 41
7	6g	<i>n</i> Bu	SO ₂ Ph	Me	C(CO ₂ Me) ₂	4	10g : 56
8	6h	<i>n</i> Bu	SO ₂ Ph	Cl	C(CO ₂ Me) ₂	20	10h : 62

^aReaction conditions: A solution of **6** in DCE was heated in a microwave reactor at 110 °C. ^bIsolated yield.

^cReaction was performed in refluxing toluene. DCE=1,2-dichloroethane, MW=microwave.

To obtain information about the mechanism for the stereoselective production of **10**, we performed three experiments with the deuterated substrates, [D₅]**6a**, [D₂]**6a**, and [D₁]**6a** (Scheme 3). Treatment of the pentadeuterated substrate [D₅]**6a** with [RhCl(CO)₂]₂ in refluxing toluene¹⁴ produced the deuterated product [D₅]**10a** in 54% yield. It became apparent that one deuterium atom on the benzene ring was exclusively incorporated at the benzylic position of the seven-membered ring of [D₅]**10a** in a highly stereoselective manner. In the case of the dideuterated substrate [D₂]**6a**, one of the deuterium atoms at the propargylic position was stereoselectively transferred into the allylic position of the six-membered ring of [D₂]**10a**. For the monodeuterated substrate [D₁]**6a**, the deuterium atom at the allenic position was completely incorporated into the

olefinic position of the seven-membered ring in **[D₁]**10a****. In other words, migration of the deuterium atom could not be observed.

Scheme 3. [RhCl(CO)₂]₂-Catalyzed Cycloisomerization of **[D₅]6a****, **[D₂]**6a****, **[D₁]**6a******

These deuteration experiments provided a fairly informative insight into the mechanistic consideration for the cycloisomerization of **6** into **10** (Scheme 4). The first two steps should be in accordance with those described for the mechanism involving the production of **7** from **6** [Scheme 1, Eq. (2)]. Namely, the oxidative cyclization of an allenic distal double bond and an alkyne in **6** with Rh^I would initially occur as usual to

form the bicyclic rhodacyclopentene intermediate **A**. The σ -bond metathesis¹⁵ between the C_{sp^2} -H bond on the benzene ring and the C_{sp^2} -Rh^{III} bond of **A** would form the arylrhodium intermediate **B**. The insertion of the exocyclic olefin of **B** into the C_{sp^2} -Rh^{III} bond would result in the formation of the intermediate **C**, which collapsed to the σ -allylrhodium intermediate **D** via β -hydride elimination with H_A . The intermediate **D** can be considered being in equilibrium with another σ -allylrhodium intermediate **F** through the π -allylrhodium intermediate **E**. The reductive elimination of Rh^{III} from **F** would produce the final product **10**.

Scheme 4. Plausible Mechanisms for the Formations of 2, 7, and 10

As already mentioned, we previously presumed that the cycloisomerization of benzylallene-terminal alkynes **1**³ proceeded via the mechanism involving the vinylidenecarbene-Rh intermediate **4** [Scheme 1, Eq. (1)].⁴ By taking into consideration the mechanism for the formation of **10** into account, we reconsidered the mechanism for the cycloisomerization of **1** into **2** and the following plausible alternative is now proposed (Scheme 4). Benzylallene-terminal alkynes **1** must undergo the consecutive

oxidative cyclization and the σ -bond metathesis to form the intermediate **C** ($R^1=H$) in a way similar to the formation of **C** ($R^1\neq H$) (Scheme 4). This intermediate **C** ($R^1=H$) now has two β -protons. The molecular model analysis of **C** ($R^1=H$) indicated that the down side hydrogen atom on the seven-membered ring became closely oriented to the Rh center. Thus, β -hydride elimination with H resulting from the acetylenic proton might exclusively occur to produce the σ -allylrhodium intermediate **G**. The reductive elimination of Rh^{III} from **G** finally leads to **2**. The newly proposed mechanism for the production of **2** from **1** does not contradict the experimental results using deuterated substrates shown in a previous paper.³

On the other hand, we already proposed the mechanism for the formation of **7** from **6** ($R^1\neq H$, $Y=alkyl$), which involved intermediates **A** and **B**.⁶ The intermediate **B** would be in equilibrium with another σ -allylrhodium intermediate **H**, which should collapse into **7**.

In summary, treatment of the benzylallene-internal alkynes possessing an EWG (SO_2Ph , $P(O)(OEt)_2$) on the allenyl moiety with $[RhCl(CO)_2]_2$ produced tricyclo[9.4.0.0^{3,8}]pentadecapentaene derivatives. With the aid of deuteration

experiments, we proposed the reaction mechanism that gave us other possibilities about the reaction mechanism for the transformation of benzylallene-terminal alkynes **1** into the tricyclic compounds **2**. The three types of products **2**, **7**, and **10** can be now rationalized in terms of the initial formation of rhodabicyclo[4.3.0]nonadienes as a key and common intermediate in the $[\text{RhCl}(\text{CO})_2]_2$ -catalyzed cycloisomerization of allene-alkyne species (Scheme 4).

Experimental Section

General. Melting points were measured with YANAGIMOTO micro melting point apparatus, and are uncorrected. Infrared spectra were measured with a SHIMADZU FTIR-8700 spectrometer for samples in CHCl_3 . ^1H NMR spectra were measured with JNM-ECS400 or JNM-ECA600 spectrometers for samples in chloroform-*d* (CDCl_3), using either tetramethylsilane (for compound with a phenyl group, 0.00 ppm), CHCl_3 (7.26 ppm) as an internal reference. ^{13}C NMR spectra were measured with JNM-ECS400 or JNM-ECA600 spectrometers for samples in CDCl_3 (77.0 ppm) as an internal reference. High-resolution mass spectra were measured with JMS-T100TD

(DART) mass spectrometers, and mass spectra were measured with JMS-T100TD (DART) mass spectrometers. Microwave reactions were performed in sealed reaction vessels under N₂ atmosphere with a low-power, focused microwave (Biotage initiatorTM 2.5) and the reaction temperatures were monitored by an external surface sensor. Single-crystal X-ray diffraction was measured with R-Axis RAPID II. Commercially available anhydrous Et₂O, CH₂Cl₂, THF, toluene and 1,2-dichloroethane were employed for reactions. Et₃N was distilled from CaH₂. Commercially available [RhCl(CO)₂]₂ (Kanto Chemical Co.) were employed for reactions. Commercially available hept-2-ynoic acid (Tokyo Chemical Industry), dimethyl 2-(prop-2-ynyl)malonate (Sigma-Aldrich) were employed for reactions. 4-(benzyloxy)but-2-ynol (**S1e**),¹⁶ 5-(hept-2-ynyl)-2,2-dimethyl-5-(prop-2-ynyl)-1,3-dioxane (**S2f**),⁸ⁱ dimethyl 2-(hept-2-ynyl)-2-(prop-2-ynyl)malonate (**S2a**),⁶ 2-methyl-2-phenylpropanal,¹⁷ 2-methyl-2-(*p*-tolyl)propanal,¹⁷ 2-(4-chlorophenyl)-2-methylpropanal,¹⁸ dimethyl 2-(but-2-ynyl)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)malonate (**S3b**),⁶ dimethyl 2-(hept-2-ynyl)-2-[4-hydroxy-5-methyl-5-(phenyl-*d*₅)hex-2-ynyl]malonate ([D₅]**S3a**),⁶ dimethyl 2-(hept-2-ynyl)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl-4-*d*)malonate

([D₁]S3a),⁶ dimethyl

2-(hept-2-ynyl)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)malonate (S3a),⁶ dimethyl

2-(hept-2-ynyl)-2-[5,5-dimethyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate

(6a)³ were known compounds and prepared according to literature procedures. Silica

gel (Silica gel 60 N, 40-50 μm, Kanto Chemical Co.) was used for chromatography. All

reactions were carried out under N₂ atmosphere. Organic extracts were dried over

Na₂SO₄. All other reagents were obtained from commercial sources and used as

received.

Preparation of Hept-2-yn-1,1-*d*₂-1-ol ([D₂]S1a).

To a suspension of LiAlD₄ (130 mg, 3.0 mmol) in Et₂O (5.0 mL) was

added hept-2-ynoic acid (250 mg, 2.0 mmol) at 0 °C. After being stirred

for 1 h at room temperature, the reaction was quenched by addition of water at 0 °C,

dried, and passed through a pad of Celite. The filtrate was concentrated to dryness, and

the residue was chromatographed with CH₂Cl₂ to afford [D₂]S1a (120 mg, 52% yield)

as a colorless oil: IR 3325 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 2.19 (t, 2H, *J* = 7.2 Hz),

1.99 (s, 1H), 1.49–1.45 (m, 2H), 1.41–1.35 (m, 2H), 0.89 (t, 3H, *J* = 7.2 Hz); ¹³C NMR

(151 MHz, CDCl₃) δ 86.4, 78.2, 50.7 (quin, $J = 23.1$ Hz), 30.6, 21.8, 18.3, 13.5; DART MS m/z 115 ($M^{+}+1$, 22.9); DART HRMS calcd for C₇H₁₁D₂O 115.1092, found 115.1091.

General Procedure for Preparation of Diynes S2e, [D₂]S2a from S1e, [D₂]S1a. To a solution of alcohol **S1** (7.5 mmol), PPh₃ (2.4 g, 9.0 mmol) and imidazole (610 mg, 9.0 mmol) in CH₂Cl₂ (15 mL) was added I₂ (2.3 g, 9.0 mmol) at 0 °C. After being stirred for 1 h at the same temperature, the reaction was quenched by addition of saturated aqueous NaHCO₃ and Na₂S₂O₃, and the mixture was extracted with CH₂Cl₂. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane to afford the crude propargylic iodide. To a suspension of NaH (220 mg, 5.5 mmol, 60% in mineral oil) in THF (25 mL) was added dimethyl 2-(prop-2-ynyl)malonate (850 mg, 5.0 mmol) at 0 °C. After being stirred for 30 min at room temperature, the crude propargylic iodide was added at 0 °C and the reaction mixture was further stirred for additional 30 min at room temperature. The reaction was quenched by addition of saturated aqueous NH₄Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine,

dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding diyne **S2**.

Dimethyl 2-[4-(Benzyloxy)but-2-ynyl]-2-(prop-2-ynyl)malonate (S2e**).**

Compound **S2e** was prepared from **S1e** and was obtained in 78%

yield as a pale yellow oil: IR 3287, 1736 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.36–7.35

(m, 4H), 7.32–7.28 (m, 1H), 4.55 (s, 2H), 4.13 (t, 2H, $J = 2.1$ Hz), 3.765 (s, 3H), 3.764

(s, 3H), 3.07 (t, 2H, $J = 2.1$ Hz), 3.01 (d, 2H, $J = 2.7$ Hz), 2.05 (t, 1H, $J = 2.7$ Hz); ^{13}C

NMR (151 MHz, CDCl_3) δ 169.1, 137.4, 128.4, 128.1, 127.8, 80.8, 79.5, 78.3, 71.8,

71.2, 57.3, 56.5, 53.1, 23.0, 22.8; DART MS m/z 329 ($M^+ + 1$, 100); DART HRMS calcd

for $\text{C}_{19}\text{H}_{21}\text{O}_5$ 329.1389, found 329.1375.

Dimethyl 2-(Hept-2-ynyl-1,1- d_2)-2-(prop-2-ynyl)malonate ([D_2]S2a**).**

Compound [D_2]**S2a** was prepared from [D_2]**S1a** and was obtained

in 83% yield as a colorless oil: IR 3286, 1740 cm^{-1} ; ^1H NMR (600

MHz, CDCl_3) δ 3.73 (s, 6H), 2.94 (d, 2H, $J = 2.7$ Hz), 2.09 (t, 2H, $J = 6.9$ Hz), 2.00 (t,

1H, $J = 2.7$ Hz), 1.43–1.31 (m, 4H), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz,

CDCl_3) δ 169.3, 83.9, 78.6, 73.6, 71.4, 56.7, 52.9, 30.8, 22.8–22.2 (m), 21.7, 18.2, 13.5;

DART MS m/z 267 ($M^+ + 1$, 100); DART HRMS calcd for $C_{15}H_{19}D_2O_4$ 267.1565, found 267.1572.

General Procedure for Preparation of Propargylic Alcohols S3e–h, [D₂]S3a from

S2e–h, [D₂]S2a. To a solution of diyne **S2** (1.0 mmol) in THF (10 mL) was added LHMDS (1.2 mL, 1.2 mmol, 1.0 M solution in THF) at $-78\text{ }^{\circ}\text{C}$. After being stirred for 30 min, aldehyde (1.3 mmol) was added to the mixture, and the reaction mixture was further stirred for additional 5 min at the same temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl , and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding propargylic alcohol **S3**.

Dimethyl 2-[4-(Benzyloxy)but-2-ynyl]-

2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)malonate (S3e).

Compound **S3e** was prepared from **S2e** and 2-methyl-2-phenylpropanal and was obtained in 87% yield as

a colorless oil: IR $3533, 1739\text{ cm}^{-1}$; 1H NMR (600 MHz, $CDCl_3$) δ 7.42–7.40 (m, 2H),

7.35–7.28 (m, 7H), 7.24–7.22 (m, 1H), 4.55 (s, 2H), 4.40–4.38 (m, 1H), 4.13 (t, 2H, $J = 2.1$ Hz), 3.74 (s, 3H), 3.73 (s, 3H), 3.05–2.93 (m, 4H), 1.62 (d, 1H, $J = 5.8$ Hz), 1.42 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.2, 144.9, 137.4, 128.4, 128.2, 128.1, 127.8, 126.7, 126.5, 82.7, 80.9, 80.7, 79.4, 71.23, 71.18, 57.3, 56.5, 53.1, 42.9, 25.1, 23.2, 23.13, 23.06; DART MS m/z 477 ($\text{M}^+ + 1$, 22.6); DART HRMS calcd for $\text{C}_{29}\text{H}_{33}\text{O}_6$ 477.2277, found 477.2275.

6-[5-(Hept-2-ynyl)-2,2-dimethyl-1,3-dioxan-5-yl]-2-methyl-2-phenylhex-4-yn-3-ol

(S3f).

Compound **S3f** was prepared from **S2f** and 2-methyl-2-phenylpropanal and was obtained in 52% yield as

a colorless oil: IR 3449 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.44–7.42 (m, 2H), 7.35–7.33 (m, 2H), 7.25–7.22 (m, 1H), 4.45–4.44 (m, 1H), 3.73–3.70 (m, 2H), 3.63 (d, 1H, $J = 11.7$ Hz), 3.60 (d, 1H, $J = 11.7$ Hz), 2.42 (d, 2H, $J = 2.1$ Hz), 2.21 (t, 2H, $J = 2.4$ Hz), 2.17 (tt, 2H, $J = 6.9, 2.4$ Hz), 1.64 (d, 1H, $J = 5.8$ Hz), 1.50–1.39 (m, 16H), 0.91 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 145.2, 128.2, 126.7, 126.5, 98.0, 83.4, 82.6, 82.0, 75.0, 71.4, 66.09, 66.07, 43.1, 35.5, 31.1, 24.9, 24.4, 23.5, 23.1, 23.0,

21.9, 18.4, 13.6; DART MS m/z 397 ($M^+ + 1$, 58.6); DART HRMS calcd for $C_{26}H_{37}O_3$ 397.2743, found 397.2735.

Dimethyl 2-(Hept-2-ynyl)-2-[4-hydroxy-5-methyl-5-(*p*-tolyl)hex-2-ynyl]malonate (S3g).

Compound **S3g** was prepared from **S2g** and 2-methyl-2-(*p*-tolyl)propanal and was obtained in 73%

yield as a colorless oil: IR 3536, 1738 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, 2H, $J = 8.2$ Hz), 7.15 (d, 2H, $J = 7.9$ Hz), 4.36–4.35 (m, 1H), 3.733 (s, 3H), 3.726 (s, 3H), 2.99 (d, 2H, $J = 1.4$ Hz), 2.90–2.84 (m, 2H), 2.33 (s, 3H), 2.12 (tt, 2H, $J = 7.2, 2.4$ Hz), 1.59 (d, 1H, $J = 5.8$ Hz), 1.47–1.34 (m, 10H), 0.90 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 141.9, 136.0, 128.9, 126.7, 83.9, 82.5, 80.9, 73.8, 71.3, 56.9, 52.9, 42.6, 30.9, 25.4, 23.2, 23.0, 22.9, 21.8, 20.9, 18.3, 13.5; DART MS m/z 427 ($M^+ + 1$, 2.14); DART HRMS calcd for $C_{26}H_{35}O_5$ 427.2485, found 427.2482.

Dimethyl 2-[5-(4-Chlorophenyl)-4-hydroxy-5-methylhex-2-ynyl]-2-(hept-2-ynyl)malonate (S3h).

Compound **S3h** was prepared from **S2h** and

2-(4-chlorophenyl)-2-methylpropanal and was obtained in 55% yield as a colorless oil:
 IR 3519, 1738 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.33 (m, 2H), 7.31–7.28 (m, 2H), 4.34–4.33 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.97 (d, 2H, $J = 1.8$ Hz), 2.84 (t, 2H, $J = 2.3$ Hz), 2.12 (tt, 2H, $J = 6.9, 2.3$ Hz), 1.66 (d, 1H, $J = 5.5$ Hz), 1.47–1.32 (m, 10H), 0.90 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 143.6, 132.3, 128.3, 128.1, 84.0, 82.3, 81.4, 73.6, 71.0, 56.8, 52.9, 42.7, 30.9, 24.9, 23.4, 23.2, 22.9, 21.8, 18.3, 13.5; DART MS m/z 447 ($\text{M}^+ + 1$, 9.27); DART HRMS calcd for $\text{C}_{25}\text{H}_{32}\text{ClO}_5$ 447.1938, found 447.1933.

Dimethyl 2-(Hept-2-ynyl-1,1- d_2)-

2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)malonate ([D₂]S3a).

Compound [D₂]S3a was prepared from [D₂]S2a and 2-methyl-2-phenylpropanal and was obtained in 98% yield as

a colorless oil: IR 3538, 1739 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.42–7.40 (m, 2H), 7.34–7.32 (m, 2H), 7.24–7.21 (m, 1H), 4.38 (brs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.98 (d, 2H, $J = 1.0$ Hz), 2.11 (t, 2H, $J = 6.9$ Hz), 1.82 (d, 1H, $J = 5.2$ Hz), 1.45–1.33 (m, 10H), 0.89 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 145.0, 128.1, 126.7,

126.3, 83.9, 82.4, 80.8, 73.7, 71.1, 56.7, 52.8, 42.9, 30.8, 25.0, 23.0, 22.9–22.3 (m), 21.7, 18.2, 13.5; DART MS m/z 415 ($M^+ + 1$, 9.95); DART HRMS calcd for $C_{25}H_{31}D_2O_5$ 415.2454, found 415.2454.

General Procedure for Preparation of Benzylallene-Alkynes 6b,e–h, [D₅]6a, [D₂]6a, [D₁]6a from S3b,e–h, [D₅]S3a, [D₂]S3a, [D₁]S3a. To a solution of propargylic alcohol **S3** (1.0 mmol) and Et₃N (0.56 mL, 4.0 mmol) in THF (10 mL) was added a solution of PhSCl (0.39 mL, 3.5 mmol) in THF (3.5 mL) slowly at –78 °C. After being stirred for 1 h at the same temperature, the reaction was quenched by addition of saturated aqueous NaHCO₃, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane-AcOEt to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH₂Cl₂ (10 mL) was added *m*CPBA (260 mg, 1.5 mmol) at 0 °C. After being stirred for 1 h at the same temperature, the reaction was quenched by addition of saturated aqueous NaHCO₃ and Na₂S₂O₃, and the mixture was extracted with CH₂Cl₂. The extract was washed with water, brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the

corresponding benzylallene-alkyne **6**.

**Dimethyl 2-(But-2-ynyl)-2-[5-methyl-5-phenyl-
2-(phenylsulfonyl)hexa-2,3-dienyl]malonate (6b).**

Compound **6b** was prepared from **S3b** and was obtained in 96% yield as a colorless crystal: m.p. 86–88 °C (hexane-AcOEt); IR 1956, 1736, 1317, 1148 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.85–7.83 (m, 2H), 7.61–7.59 (m, 1H), 7.51–7.49 (m, 2H), 7.42–7.41 (m, 2H), 7.34–7.31 (m, 2H), 7.24–7.21 (m, 1H), 5.98 (t, 1H, $J = 2.7$ Hz), 3.67 (s, 3H), 3.65 (s, 3H), 3.14 (dd, 1H, $J = 16.2, 2.7$ Hz), 3.07 (dd, 1H, $J = 16.2, 2.7$ Hz), 2.88–2.81 (m, 2H), 1.67 (t, 3H, $J = 2.4$ Hz), 1.46 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 203.3, 169.6, 169.4, 147.1, 140.1, 133.3, 129.0, 128.4, 128.3, 126.5, 126.0, 112.8, 110.5, 79.5, 72.9, 56.6, 52.92, 52.89, 40.9, 29.1, 28.9, 28.0, 23.1, 3.5; DART MS m/z 495 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6\text{S}$ 495.1841, found 495.1847.

**Dimethyl 2-[4-(Benzyloxy)but-2-ynyl]-
2-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate (6e).**

Compound **6e** was prepared from **S3e** and was obtained in 88% yield as a yellow oil: IR

1955, 1737, 1305, 1149 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.84–7.82 (m, 2H), 7.58–7.55 (m, 1H), 7.48–7.45 (m, 2H), 7.41–7.39 (m, 2H), 7.36–7.27 (m, 7H), 7.23–7.20 (m, 1H), 5.99 (dd, 1H, $J = 3.1, 2.4$ Hz), 4.51 (s, 2H), 4.05 (t, 2H, $J = 2.1$ Hz), 3.67 (s, 6H), 3.15 (dd, 1H, $J = 15.8, 3.1$ Hz), 3.10 (dd, 1H, $J = 15.8, 2.4$ Hz), 2.970–2.968 (m, 2H), 1.46 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 203.2, 169.3, 169.2, 146.9, 139.9, 137.4, 133.4, 129.0, 128.4, 128.3, 128.1, 127.8, 126.5, 125.9, 113.0, 110.4, 80.8, 79.7, 71.1, 57.2, 56.4, 53.0, 40.8, 29.2, 29.0, 28.0, 23.1; DART MS m/z 601 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{35}\text{H}_{37}\text{O}_7\text{S}$ 601.2260, found 601.2271.

5-(Hept-2-ynyl)-2,2-dimethyl-5-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]-1,3-dioxane (6f).

Compound **6f** was prepared from **S3f** and was obtained in 76% yield as a colorless oil:

IR 1953, 1306, 1149 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.84–7.83 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.40–7.38 (m, 2H), 7.33–7.31 (m, 2H), 7.24–7.21 (m, 1H), 5.95 (dd, 1H, $J = 3.4, 2.1$ Hz), 3.72 (d, 1H, $J = 11.7$ Hz), 3.67 (s, 2H), 3.63 (d, 1H, $J = 11.7$ Hz), 2.57 (dd, 1H, $J = 15.5, 3.4$ Hz), 2.44–2.40 (m, 2H), 2.36 (dt, 1H, $J = 16.8, 2.4$ Hz), 2.10 (tt, 2H, $J = 7.2, 2.4$ Hz), 1.46–1.32 (m, 16H), 0.88 (t, 3H, $J = 7.2$ Hz); ^{13}C

NMR (151 MHz, CDCl₃) δ 203.7, 147.0, 140.1, 133.3, 129.0, 128.4, 128.3, 126.5, 126.0, 111.9, 111.1, 98.1, 83.5, 75.3, 66.41, 66.37, 40.9, 36.4, 31.1, 29.6, 29.1, 28.5, 24.5, 23.0, 22.6, 22.0, 18.4, 13.6; DART MS m/z 521 ($M^+ + 1$, 100); DART HRMS calcd for C₃₂H₄₁O₄S 521.2726, found 521.2729.

Dimethyl 2-(Hept-2-ynyl)-2-[5-methyl-2-(phenylsulfonyl)-

5-(*p*-tolyl)hexa-2,3-dienyl]malonate (6g).

Compound **6g** was prepared from **S3g** and was obtained in 23% yield as a colorless oil:

IR 1954, 1738, 1305, 1150 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.84–7.83 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.29 (d, 2H, J = 8.2 Hz), 7.13 (d, 2H, J = 7.9 Hz), 5.96 (dd, 1H, J = 3.4, 2.4 Hz), 3.67 (s, 3H), 3.65 (s, 3H), 3.13 (dd, 1H, J = 16.2, 3.4 Hz), 3.07 (dd, 1H, J = 16.2, 2.4 Hz), 2.90–2.83 (m, 2H), 2.33 (s, 3H), 2.05 (tt, 2H, J = 6.9, 2.4 Hz), 1.45 (s, 3H), 1.40–1.30 (m, 7H), 0.87 (t, 3H, J = 7.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 203.3, 169.6, 169.4, 144.1, 140.2, 136.0, 133.3, 129.01, 128.97, 128.3, 125.9, 112.9, 110.4, 84.2, 73.7, 56.7, 52.9, 52.8, 40.6, 30.8, 29.2, 28.8, 28.1, 23.1, 21.8, 20.9, 18.3, 13.5; DART MS m/z 551 ($M^+ + 1$, 100); DART HRMS calcd for C₃₂H₃₉O₆S 551.2467, found 551.2474.

Dimethyl 2-[5-(4-Chlorophenyl)-5-methyl-2-(phenylsulfonyl)hexa-2,3-dienyl]-2-(hept-2-ynyl)malonate (6h).

Compound **6h** was prepared from **S3h** and was obtained in 61% yield as a colorless oil:

IR 1954, 1738, 1305, 1150 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.82–7.81 (m, 2H), 7.63–7.60 (m, 1H), 7.53–7.50 (m, 2H), 7.37–7.35 (m, 2H), 7.30–7.28 (m, 2H), 5.93 (dd, 1H, $J = 3.1, 2.4$ Hz), 3.68 (s, 3H), 3.64 (s, 3H), 3.11 (dd, 1H, $J = 15.8, 3.1$ Hz), 3.04 (dd, 1H, $J = 15.8, 2.4$ Hz), 2.85 (brs, 2H), 2.04 (tt, 2H, $J = 6.9, 2.4$ Hz), 1.46 (s, 3H), 1.41–1.29 (m, 7H), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 203.2, 169.5, 169.3, 145.6, 140.0, 133.4, 132.3, 129.0, 128.4, 128.2, 127.5, 112.4, 110.7, 84.3, 73.6, 56.7, 52.91, 52.87, 40.6, 30.8, 29.1, 28.8, 28.0, 23.1, 21.8, 18.2, 13.5; DART MS m/z 571 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{31}\text{H}_{36}\text{ClO}_6\text{S}$ 571.1921, found 571.1921.

Dimethyl 2-(Hept-2-ynyl)-

2-[5-methyl-5-(phenyl- d_5)-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate ([D₅]6a).

Compound [D₅]**6a** was prepared from [D₅]**S3a** and was obtained in 84% yield as a colorless oil: IR 1955, 1737, 1305, 1148 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.84–7.83 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 5.97 (dd, 1H, $J = 3.1, 2.4$ Hz), 3.66 (s,

3H), 3.64 (s, 3H), 3.14 (dd, 1H, $J = 16.2, 3.1$ Hz), 3.08 (dd, 1H, $J = 16.2, 2.4$ Hz), 2.90–2.83 (m, 2H), 2.05 (tt, 2H, $J = 6.9, 2.4$ Hz), 1.47 (s, 3H), 1.40–1.30 (m, 7H), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 203.2, 169.5, 169.3, 146.8, 140.1, 133.3, 129.0, 128.2, 127.8 (t, $J = 24.6$ Hz), 125.9 (t, $J = 24.6$ Hz), 125.5 (t, $J = 24.6$ Hz), 112.7, 110.5, 84.2, 73.7, 56.7, 52.80, 52.78, 40.7, 30.8, 29.1, 28.8, 27.9, 23.1, 21.7, 18.2, 13.5; DART MS m/z 542 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{31}\text{H}_{32}\text{D}_5\text{O}_6\text{S}$ 542.2625, found 542.2638.

Dimethyl 2-(Hept-2-ynyl-1,1- d_2)-

2-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate ([D₂]6a).

Compound [D₂]6a was prepared from [D₂]S3a and was obtained in 84% yield as a colorless oil: IR 1954, 1737, 1306, 1148 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.84–7.83 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.41–7.40 (m, 2H), 7.34–7.31 (m, 2H), 7.23–7.21 (m, 1H), 5.97 (dd, 1H, $J = 3.1, 2.4$ Hz), 3.66 (s, 3H), 3.64 (s, 3H), 3.14 (dd, 1H, $J = 16.2, 3.1$ Hz), 3.08 (dd, 1H, $J = 16.2, 2.4$ Hz), 2.04 (t, 2H, $J = 6.9$ Hz), 1.46 (s, 3H), 1.40–1.30 (m, 7H), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 203.2, 169.5, 169.3, 147.0, 140.1, 133.3, 128.9, 128.3, 128.2, 126.4, 125.9, 112.7, 110.5, 84.2,

73.6, 56.6, 52.79, 52.77, 40.8, 30.8, 29.1, 28.7, 27.9, 22.6 (quin, $J = 20.0$ Hz), 21.7, 18.2, 13.5; DART MS m/z 539 ($M^+ + 1$, 100); DART HRMS calcd for $C_{31}H_{35}D_2O_6S$ 539.2436, found 539.2432.

Dimethyl 2-(Hept-2-ynyl)-2-[5-methyl-5-phenyl-2-(phenylsulfonyl)-4- d]malonate ([D₁]6a).

Compound [D₁]6a was prepared from [D₁]S3a and was obtained in 84% yield as a colorless oil: IR 1948, 1737, 1305, 1149 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.61–7.59 (m, 1H), 7.51–7.48 (m, 2H), 7.42–7.40 (m, 2H), 7.34–7.31 (m, 2H), 7.24–7.21 (m, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.14 (d, 1H, $J = 16.2$ Hz), 3.08 (d, 1H, $J = 16.2$ Hz), 2.90–2.83 (m, 2H), 2.04 (tt, 2H, $J = 6.9, 2.4$ Hz), 1.46 (s, 3H), 1.41–1.29 (m, 7H), 0.87 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.3, 169.6, 169.4, 147.1, 140.1, 133.3, 129.0, 128.4, 128.3, 126.5, 126.0, 112.5 (t, $J = 24.6$ Hz), 110.6, 84.3, 73.7, 56.7, 52.87, 52.85, 40.8, 30.8, 29.1, 28.8, 28.0, 23.1, 21.8, 18.3, 14.2, 13.5; DART MS m/z 538 ($M^+ + 1$, 100); DART HRMS calcd for $C_{31}H_{36}DO_6S$ 538.2374, found 538.2384.

General Procedure for Preparation of Benzylallene-Alkynes 6c,d from S3a,b. To a solution of propargylic alcohol S3 (1.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) in THF

(10 mL) was added (EtO)₂PCl (0.43 mL, 3.0 mmol) at -78 °C. After being stirred for 1.5 h at the same temperature, the reaction mixture was refluxed, and further stirred for additional 1.5 h. Then, the reaction was quenched by addition of saturated aqueous NaHCO₃, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding benzylallene-alkyne **6**.

Dimethyl 2-[2-(Diethoxyphosphoryl)-5-methyl-5-phenylhexa-2,3-dienyl]-2-(hept-2-ynyl)malonate (6c).

Compound **6c** was prepared from **S3a** and was obtained in 33% yield as a colorless oil:

IR 1950, 1737 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.47–7.46 (m, 2H), 7.33–7.30 (m, 2H), 7.21–7.18 (m, 1H), 5.60 (dt, 1H, *J* = 13.1, 2.7 Hz), 4.13–3.98 (m, 4H), 3.71 (s, 3H), 3.68 (s, 3H), 3.05–2.93 (m, 2H), 2.92 (t, 2H, *J* = 2.1 Hz), 2.12–2.09 (m, 2H), 1.50 (s, 3H), 1.45 (s, 3H), 1.44–1.35 (m, 4H), 1.32 (td, 6H, *J* = 7.2, 3.8 Hz), 0.88 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 208.3 (d, *J* = 4.3 Hz), 170.0, 169.8, 147.9 (d, *J* = 2.9 Hz), 128.1, 126.2, 126.0, 105.0 (d, *J* = 17.3 Hz), 91.5 (d, *J* = 189.3 Hz), 83.8, 74.3, 62.2 (d, *J* = 5.8 Hz), 62.1 (d, *J* = 5.8 Hz), 57.1 (d, *J* = 7.2 Hz), 52.68, 52.65, 39.9 (d, *J* =

4.3 Hz), 30.9, 29.6 (d, $J = 10.1$ Hz), 29.4 (d, $J = 2.9$ Hz), 28.4 (d, $J = 2.9$ Hz), 22.9, 21.7, 18.3, 16.3 (d, $J = 2.9$ Hz), 16.2 (d, $J = 2.9$ Hz), 13.5; ^{31}P NMR (243 MHz, CDCl_3) δ 17.9; DART MS m/z 533 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{29}\text{H}_{42}\text{O}_7\text{P}$ 533.2668, found 533.2683.

Dimethyl 2-(But-2-ynyl)-

2-[2-(diethoxyphosphoryl)-5-methyl-5-phenylhexa-2,3-dienyl]malonate (6d).

Compound **6d** was prepared from **S3b** and was obtained in 54% yield as a colorless oil:

IR 1949, 1736 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.47–7.46 (m, 2H), 7.33–7.30 (m, 2H), 7.21–7.19 (m, 1H), 5.60 (dt, 1H, $J = 13.1, 2.4$ Hz), 4.13–3.99 (m, 4H), 3.72 (s, 3H), 3.69 (s, 3H), 3.05–2.94 (m, 2H), 2.90 (q, 2H, $J = 2.4$ Hz), 1.74 (t, 3H, $J = 2.4$ Hz), 1.50 (s, 3H), 1.45 (s, 3H), 1.32 (td, 6H, $J = 6.9, 3.1$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 208.3 (d, $J = 2.9$ Hz), 170.0, 169.9, 148.0 (d, $J = 2.9$ Hz), 128.2, 126.2, 126.0, 105.0 (d, $J = 15.9$ Hz), 91.5 (d, $J = 189.3$ Hz), 79.0, 73.5, 62.2 (d, $J = 5.8$ Hz), 62.1 (d, $J = 5.8$ Hz), 57.0 (d, $J = 7.2$ Hz), 52.8, 52.7, 39.9 (d, $J = 5.8$ Hz), 29.7 (d, $J = 10.1$ Hz), 29.4 (d, $J = 2.9$ Hz), 28.4 (d, $J = 2.9$ Hz), 22.9, 16.31 (d, $J = 4.3$ Hz), 16.28 (d, $J = 5.8$ Hz), 3.5; ^{31}P NMR (243 MHz, CDCl_3) δ 17.8; DART MS m/z 491 ($\text{M}^+ + 1$, 100); DART HRMS

calcd for C₂₆H₃₆O₇P 491.2199, found 491.2189.

General Procedure for [RhCl(CO)₂]₂-Catalyzed Cycloisomerization of **6 with Microwave Reactor (Table 1).** A solution of the benzylallene-alkyne **6** (0.10 mmol) and [RhCl(CO)₂]₂ (1.9 mg, 0.0050 mmol) in DCE (1.0 mL) was heated at 110 °C under microwave irradiation until the starting material was completely consumed (monitored by TLC analysis). The reaction mixture was subsequently cooled to 50 °C with compressed air, the vessel was opened, and DCE was evaporated off. The residue was chromatographed with hexane-AcOEt to afford the corresponding cyclized product **10**. The chemical yields are summarized in Table 1.

(2*S,12*R**)-2-Butyl-14,14-Bis(methoxycarbonyl)-9,9-dimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10a**).**

Compound **10a** was a colorless plate: m.p. 129–132 °C (chloroform-hexane); IR 1734, 1308, 1146 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.89–7.88 (m, 2H), 7.68–7.65 (m, 1H), 7.58–7.56 (m, 2H), 7.23–7.17 (m, 3H), 7.12–7.09 (m, 1H), 5.88 (s, 1H), 5.20 (s, 1H), 3.99 (dd, 1H, *J* = 7.2, 4.7 Hz), 3.82 (s, 3H), 3.80 (t, 1H, *J* = 7.6 Hz), 3.43 (s, 3H), 2.92 (dd, 1H, *J* = 14.8, 4.7 Hz), 2.79 (dd, 1H, *J* = 14.8, 7.2 Hz), 2.08–2.02 (m, 1H),

1.98–1.92 (m, 1H), 1.49–1.36 (m, 7H), 1.28 (s, 3H), 0.98 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 169.4, 144.4, 144.1, 141.3, 138.1, 137.5, 133.5, 129.5, 128.9, 127.0, 126.1, 126.0, 125.2, 124.3, 118.9, 66.7, 54.0, 53.1, 53.0, 45.6, 41.2, 33.3, 30.3, 29.5, 28.9, 27.0, 23.0, 14.1; DART MS m/z 537 ($\text{M}^+ + 1$, 31); DART HRMS calcd for $\text{C}_{31}\text{H}_{37}\text{O}_6\text{S}$ 537.2311, found 537.2311. The structure of **10a** was unambiguously determined by an X-ray crystallography (See the Supporting Information for details).

(2*S,12*R**)-14,14-Bis(methoxycarbonyl)-2,9,9-trimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10b).

Compound **10b** was a colorless crystal: m.p. 166–169 °C (hexane-AcOEt); IR 1732, 1306, 1144 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.88–7.87 (m, 2H), 7.67–7.64 (m, 1H), 7.57–7.54 (m, 2H), 7.24–7.23 (m, 2H), 7.20–7.17 (m, 1H), 7.13–7.11 (m, 1H), 5.94 (s, 1H), 5.30 (s, 1H), 4.05 (t, 1H, $J = 6.2$ Hz), 3.96 (q, 1H, $J = 6.9$ Hz), 3.81 (s, 3H), 3.42 (s, 3H), 2.83 (d, 2H, $J = 6.2$ Hz), 1.49 (d, 3H, $J = 6.9$ Hz), 1.45 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 169.3, 144.6, 143.9, 141.7, 139.2, 137.4, 133.5, 129.6, 128.8, 127.0, 126.2, 125.7, 125.2, 124.1, 118.9, 67.0, 53.9, 53.1, 52.9, 41.2, 39.8, 33.1,

30.4, 27.2, 15.7; DART MS m/z 495 ($M^+ + 1$, 100); DART HRMS calcd for $C_{28}H_{31}O_6S$ 495.1841, found 495.1840.

(2*S,12*R**)-2-Butyl-12-(diethoxyphosphoryl)-14,14-bis(methoxycarbonyl)-**

9,9-dimethyltricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10c).

Compound **10c** was a colorless oil: IR 1735 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$, 55 °C) δ 7.35–7.33 (m, 1H), 7.18–7.11 (m, 3H), 5.91 (d, 1H, $J = 2.4$ Hz), 5.85 (s, 1H), 4.14–4.10 (m, 4H), 3.84 (t, 1H, $J = 7.2$ Hz), 3.72 (s, 3H), 3.52 (s, 3H), 2.97 (ddd, 1H, $J = 22.0$, 8.9, 5.8 Hz), 2.65 (ddd, 1H, $J = 17.9$, 13.7, 5.8 Hz), 2.32 (ddd, 1H, $J = 13.7$, 11.3, 8.9 Hz), 2.05–1.93 (m, 2H), 1.56 (s, 6H), 1.38–1.26 (m, 10H), 0.91 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (151 MHz, $CDCl_3$, 55 °C) δ 170.8, 170.1, 145.0, 141.7, 140.5 (d, $J = 5.8$ Hz), 139.7 (d, $J = 8.7$ Hz), 126.7, 126.4, 126.1, 119.3, 62.0 (d, $J = 5.8$ Hz), 61.9 (d, $J = 7.2$ Hz), 55.1 (d, $J = 10.1$ Hz), 52.7, 52.5, 50.0, 42.1, 38.4 (d, $J = 143.1$ Hz), 33.6, 32.0, 31.5, 30.0, 29.5, 22.7, 16.50 (d, $J = 5.8$ Hz), 16.46 (d, $J = 5.8$ Hz), 13.9; ^{31}P NMR (243 MHz, $CDCl_3$) δ 28.4; DART MS m/z 533 ($M^+ + 1$, 100); DART HRMS calcd for $C_{29}H_{42}O_7P$ 533.2668, found 533.2667.

(2*S,12*R**)-12-(Diethoxyphosphoryl)-14,14-bis(methoxycarbonyl)-**

2,9,9-trimethyltricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10d).

Compound **10d** was a pale yellow crystal: m.p. 134–136 °C (hexane-AcOEt); IR 1733 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.34–7.33 (m, 1H), 7.29–7.28 (m, 1H), 7.22–7.19 (m, 1H), 7.17–7.14 (m, 1H), 5.94 (s, 1H), 5.83–5.82 (m, 1H), 4.22 (q, 1H, *J* = 7.2 Hz), 4.12–4.05 (m, 4H), 3.75 (s, 3H), 3.49 (s, 3H), 3.03–2.97 (m, 1H), 2.58 (ddd, 1H, *J* = 24.7, 14.1, 6.9 Hz), 2.47 (td, 1H, *J* = 14.1, 6.2 Hz), 1.61 (s, 3H), 1.60 (d, 3H, *J* = 7.2 Hz), 1.54 (s, 3H), 1.33 (td, 6H, *J* = 6.9, 3.8 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 170.7, 169.9, 144.8, 142.1, 140.2 (d, *J* = 10.1 Hz), 140.1 (d, *J* = 4.3 Hz), 127.0 (d, *J* = 7.2 Hz), 126.7, 126.1, 125.4, 124.5, 118.4, 62.0 (d, *J* = 7.2 Hz), 54.4 (d, *J* = 7.2 Hz), 52.84, 52.76, 41.4 (d, *J* = 2.9 Hz), 40.7, 38.4 (d, *J* = 140.2 Hz), 33.5, 30.9 (d, *J* = 4.3 Hz), 28.4 (d, *J* = 4.3 Hz), 16.6, 16.51 (d, *J* = 5.8 Hz), 16.48 (d, *J* = 2.9 Hz); ³¹P NMR (243 MHz, CDCl₃) δ 28.5; DART MS *m/z* 491 (M⁺+1, 100); DART HRMS calcd for C₂₆H₃₆O₇P 491.2199, found 491. 2198.

(2*S,12*R**)-2-[(Benzyloxy)methyl]-14,14-bis(methoxycarbonyl)-9,9-dimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10e).

Compound **10e** was a yellow amorphous solid: IR 1735, 1307, 1146 cm⁻¹; ¹H NMR

(600 MHz, CDCl₃) δ 7.87–7.86 (m, 2H), 7.59–7.56 (m, 1H), 7.51–7.49 (m, 2H), 7.41–7.36 (m, 4H), 7.33–7.30 (m, 1H), 7.25–7.24 (m, 1H), 7.18–7.16 (m, 1H), 7.14–7.10 (m, 2H), 5.79 (s, 1H), 5.27 (s, 1H), 4.68 (d, 1H, J = 12.0 Hz), 4.61 (d, 1H, J = 12.0 Hz), 4.21 (dd, 1H, J = 9.3, 8.6 Hz), 4.12 (dd, 1H, J = 8.6, 5.5 Hz), 4.03 (dd, 1H, J = 6.9, 5.5 Hz), 3.87 (dd, 1H, J = 9.3, 5.5 Hz), 3.78 (s, 3H), 3.41 (s, 3H), 2.87–2.80 (m, 2H), 1.43 (s, 3H), 1.27 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 170.2, 169.2, 144.6, 144.1, 138.7, 138.2, 137.3, 136.4, 133.5, 129.6, 128.9, 128.3, 127.9, 127.6, 127.0, 126.3, 125.5, 124.8, 119.4, 73.4, 68.5, 66.6, 54.0, 53.2, 53.0, 45.9, 41.3, 33.1, 30.4, 27.1; DART MS m/z 601 (M^+ +1, 12.1); DART HRMS calcd for C₃₅H₃₇O₇S 601.2260, found 601.2271.

(2*S,12*R**)-2-Butyl-2',2',9,9-tetramethyl-12-(phenylsulfonyl)**

spiro{tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene-14,5'-[1,3]dioxane}

(10f).

Compound **10f** was a pale yellow oil: IR 1306, 1149 cm⁻¹; ¹H NMR (600 MHz, CDCl₃)

δ 7.91–7.89 (m, 2H), 7.68–7.65 (m, 1H), 7.59–7.56 (m, 2H), 7.24–7.19 (m, 3H), 7.13–7.11 (m, 1H), 5.43 (s, 1H), 4.89 (s, 1H), 3.98 (dd, 1H, J = 11.7, 1.4 Hz), 3.93 (s,

1H, $J = 11.7$ Hz), 3.89 (t, 1H, $J = 7.6$ Hz), 3.80 (dd, 1H, $J = 7.6, 3.1$ Hz), 3.42 (d, 1H, $J = 11.3$ Hz), 3.22 (dd, 1H, $J = 11.3, 1.4$ Hz), 2.73 (dd, 1H, $J = 15.5, 3.1$ Hz), 2.08–1.93 (m, 3H), 1.47–1.42 (m, 7H), 1.40 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H), 0.97 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 144.2, 142.8, 142.2, 137.9, 137.6, 133.4, 129.4, 128.8, 127.9, 127.0, 125.9, 125.2, 124.3, 123.1, 97.7, 69.2, 68.0, 67.9, 45.3, 41.1, 34.5, 33.3, 30.5, 29.5, 28.9, 27.8, 25.9, 23.0, 21.4, 14.1; DART MS m/z 521 ($\text{M}^+ + 1$, 100); DART HRMS calcd for $\text{C}_{32}\text{H}_{41}\text{O}_4\text{S}$ 521.2726, found 521.2735.

(2*S,12*R**)-2-Butyl-14,14-bis(methoxycarbonyl)-5,9,9-trimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10g).

Compound **10g** was a pale yellow oil: IR 1736, 1307, 1146 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.88–7.87 (m, 2H), 7.67–7.65 (m, 1H), 7.58–7.55 (m, 2H), 7.10 (d, 1H, $J = 8.2$ Hz), 6.99 (s, 1H), 6.91 (d, 1H, $J = 7.9$ Hz), 5.88 (s, 1H), 5.16 (s, 1H), 3.97 (dd, 1H, $J = 7.2, 4.5$ Hz), 3.82 (s, 3H), 3.77 (t, 1H, $J = 7.6$ Hz), 3.46 (s, 3H), 2.95 (dd, 1H, $J = 15.1, 4.5$ Hz), 2.78 (dd, 1H, $J = 15.1, 7.2$ Hz), 2.29 (s, 3H), 2.05–1.94 (m, 2H), 1.51–1.35 (m, 7H), 1.24 (s, 3H), 0.99 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 169.5, 144.7, 141.2, 138.0, 137.6, 136.4, 133.5, 129.5, 128.9, 126.6, 126.0, 125.2, 125.1, 118.9,

66.8, 54.0, 53.1, 53.0, 45.5, 40.9, 33.3, 30.4, 29.5, 28.9, 26.9, 23.0, 21.0, 14.1; DART MS m/z 551 ($M^{+}+1$, 66.6); DART HRMS calcd for $C_{32}H_{39}O_6S$ 551.2467, found 551.2458.

(2*S,12*R**)-2-Butyl-5-chloro-14,14-bis(methoxycarbonyl)-9,9-dimethyl-12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene (10h).**

Compound **10h** was a pale yellow oil: IR 1736, 1308, 1146 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 7.88–7.87 (m, 2H), 7.68–7.65 (m, 1H), 7.58–7.56 (m, 2H), 7.15–7.14 (m, 2H), 7.08–7.06 (m, 1H), 5.90 (s, 1H), 5.17 (s, 1H), 3.98 (dd, 1H, $J = 7.6, 4.5$ Hz), 3.82 (s, 3H), 3.79 (t, 1H, $J = 7.5$ Hz), 3.49 (s, 3H), 2.92 (dd, 1H, $J = 15.1, 4.5$ Hz), 2.80 (dd, 1H, $J = 15.1, 7.6$ Hz), 2.01–1.93 (m, 2H), 1.52–1.35 (m, 7H), 1.26 (s, 3H), 1.00 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 169.4, 143.9, 143.5, 142.7, 137.5, 137.2, 133.6, 132.7, 129.5, 128.9, 126.8, 126.2, 125.9, 124.5, 119.7, 66.6, 54.0, 53.13, 53.11, 45.4, 41.0, 33.3, 30.2, 29.3, 28.8, 26.9, 22.9, 14.1; DART MS m/z 571 ($M^{+}+1$, 100); DART HRMS calcd for $C_{31}H_{36}ClO_6S$ 571.1921, found 571.1926.

General Procedure for $[RhCl(CO)_2]_2$ -Catalyzed Cycloisomerization of Deuterated

Substrates $[D_5]6a$, $[D_2]6a$, $[D_1]6a$ (Scheme 3). To a solution of the

benzylallene-alkyne ([D₅]**6a**, [D₂]**6a**, [D₁]**6a**, 0.10 mmol) in toluene (1.0 mL) was added [RhCl(CO)₂]₂ (1.9 mg, 0.0050 mmol) under N₂ atmosphere. Then the reaction mixture was heated to reflux until the starting material was completely consumed (monitored by TLC analysis). Toluene was evaporated off, and the residue was chromatographed with hexane-AcOEt to afford the corresponding cyclized product ([D₅]**10a**, [D₂]**10a**, [D₁]**10a**). Chemical yields are summarized in Scheme 3.

(2*S,12*R**)-2-Butyl-14,14-bis(methoxycarbonyl)-9,9-dimethyl-12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene-2,4,5,6,7-*d*₅ ([D₅]**10a**).**

Compound [D₅]**10a** was a colorless crystal: m.p. 155–157 °C (hexane-AcOEt); IR 1734, 1307, 1145 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.89–7.87 (m, 2H), 7.67–7.65 (m, 1H), 7.58–7.55 (m, 2H), 5.88 (d, 1H, *J* = 0.7 Hz), 5.20 (s, 1H), 4.00 (dd, 1H, *J* = 7.2, 4.5 Hz), 3.81 (s, 3H), 3.42 (s, 3H), 2.92 (dd, 1H, *J* = 15.1, 4.5 Hz), 2.79 (dd, 1H, *J* = 15.1, 7.2 Hz), 2.06–2.02 (m, 1H), 1.97–1.93 (m, 1H), 1.49–1.38 (m, 7H), 1.28 (s, 3H), 0.98 (t, 3H, *J* = 6.9 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 170.3, 169.4, 144.4, 144.0, 141.2, 138.0, 137.5, 133.5, 129.5, 128.8, 126.5 (t, *J* = 23.1 Hz), 126.0, 125.4 (t, *J* = 23.1 Hz), 124.7 (t, *J* = 23.1 Hz), 123.9 (t, *J* = 23.1 Hz), 118.9, 66.7, 53.9, 53.0, 52.9, 45.1 (t, *J* = 18.8 Hz),

41.2, 33.2, 30.3, 29.4, 28.7, 27.0, 22.9, 14.0; DART MS m/z 542 ($M^+ + 1$, 100); DART

HRMS calcd for $C_{31}H_{32}D_5O_6S$ 542.2625, found 542.2635.

(2*S,12*R**)-2-Butyl-14,14-bis(methoxycarbonyl)-9,9-dimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene-12,15-*d*₂

([D₂]10a).

Compound [D₂]10a was a colorless crystal: m.p. 153–156 °C (hexane-AcOEt); IR 1733,

1305, 1146 cm^{-1} ; ¹H NMR (600 MHz, CDCl₃) δ 7.89–7.87 (m, 2H), 7.67–7.64 (m, 1H),

7.58–7.55 (m, 2H), 7.23–7.17 (m, 3H), 7.12–7.09 (m, 1H), 5.19–5.18 (m, 1H), 3.99 (q,

28/100 x 1H, $J = 7.2, 4.8$ Hz), 3.81–3.79 (m, 4H), 3.43 (s, 3H), 2.96–2.92 (m, 1H),

2.81–2.77 (m, 1H), 2.08–2.02 (m, 1H), 1.99–1.94 (m, 1H), 1.49–1.38 (m, 7H), 1.28 (s,

3H), 0.98 (t, 3H, $J = 7.2$ Hz); ¹³C NMR (151 MHz, CDCl₃) δ 170.3, 169.4, 144.43,

144.39, 144.1, 141.3, 137.9, 137.5, 133.5, 129.5, 128.8, 127.0, 126.1, 126.03, 125.98,

125.2, 124.3, 118.6 (t, $J = 24.6$ Hz), 66.7, 66.3 (t, $J = 21.7$ Hz), 53.8, 53.0, 52.9, 45.5,

41.2, 33.3, 30.3, 29.4, 28.8, 26.9, 26.8, 22.9, 14.1; DART MS m/z 539 ($M^+ + 1$, 100);

DART HRMS calcd for $C_{31}H_{35}D_2O_6S$ 539.2436, found 539.2425.

(2*S,12*R**)-2-Butyl-14,14-bis(methoxycarbonyl)-9,9-dimethyl-**

12-(phenylsulfonyl)tricyclo[9.4.0.0^{3,8}]pentadeca-1(15),3(8),4,6,10-pentaene-10-*d*

([D₁]10a).

Compound [D₁]10a was a colorless crystal: m.p. 154–156 °C (hexane-AcOEt); IR 1735, 1307, 1146 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.89–7.88 (m, 2H), 7.67–7.65 (m, 1H), 7.58–7.56 (m, 2H), 7.23–7.17 (m, 3H), 7.12–7.09 (m, 1H), 5.88 (s, 1H), 4.00 (dd, 1H, *J* = 7.2, 4.5 Hz), 3.81–3.79 (m, 4H), 3.43 (s, 3H), 2.92 (dd, 1H, *J* = 15.1, 4.5 Hz), 2.79 (dd, 1H, *J* = 15.1, 7.2 Hz), 2.08–2.02 (m, 1H), 1.98–1.92 (m, 1H), 1.49–1.37 (m, 7H), 1.28 (s, 3H), 0.98 (t, 3H, *J* = 6.9 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 170.4, 169.4, 144.1–143.9 (m), 141.3, 138.0, 137.5, 133.5, 129.5, 128.9, 127.0, 126.00, 125.98, 125.2, 124.3, 118.9, 66.6, 53.9, 53.1, 53.0, 45.6, 41.1, 33.2, 30.3, 29.5, 28.9, 27.0, 23.0, 14.1; DART MS *m/z* 538 (M⁺+1, 100); DART HRMS calcd for C₃₁H₃₆DO₆S 538.2374, found 538.2374.

Acknowledgment

This work was financially supported by JSPS KAKENHI Grant Numbers 15H02490 (C. M.) and 15K18826 (S. Y.), for which we are thankful.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copies of ^1H , ^{13}C , and ^{31}P NMR spectra for new compounds (PDF)

X-ray crystallographic data for **10a** (CIF)

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(12) X-ray analysis of **10a** unambiguously established its tricyclo[9.4.0.0^{3,8}]pentadecapentaene structure (see the Supporting Information for details). CCDC999277 (**10a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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