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Mechanistic Investigation of Rh^{I}–Catalyzed Cycloisomerization of Benzylallene-Internal Alkynes via C–H Activation

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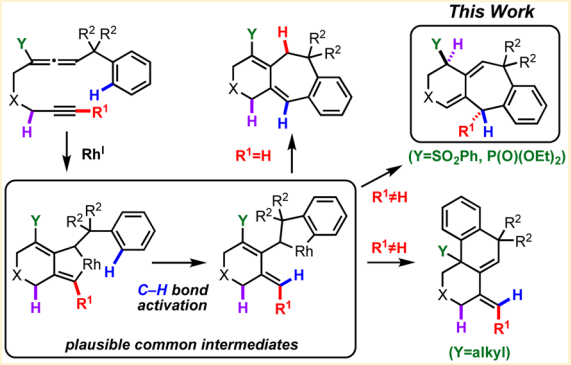
Supporting Information

ABSTRACT: Treatment of the benzylallene-internal alkynes with $[RhCl(CO)_2]_2$ effected a cycloisomerization via a C_{sp2}–H bond activation to produce the tricyclo[9.4.0.0^{3,8}]pentadecapentaene skeleton. The reaction mechanism via formation of the rhodabicyclo[4.3.0] intermediates and σ-bond metathesis between the C_{sp2}–H bond on the benzene ring and the C_{sp2}–Rh^{III} bond was proposed. In addition, a plausible alternative mechanism for the previously reported cycloisomerization of the benzylallene-terminal alkynes could also be proposed.



Cyclization reactions utilizing the transition-metal-catalyzed C–H[1] and/or C–C[2] 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 = SO_2Ph, 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** ($R^1 \neq H$, 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]

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, such as **8**, 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.[8a,c,d] Thus, our next efforts directed toward 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).

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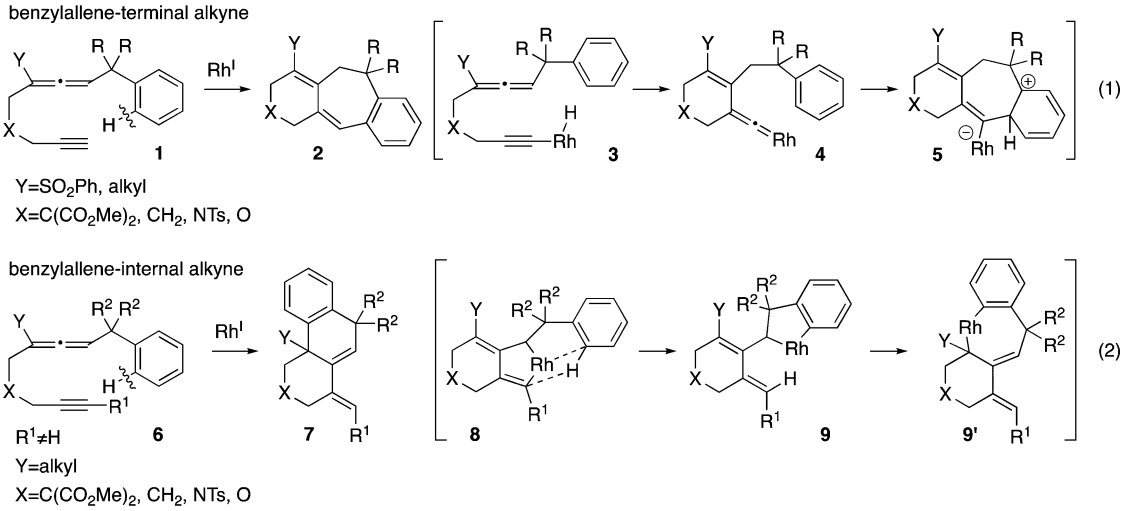
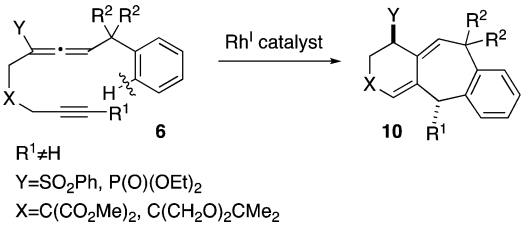
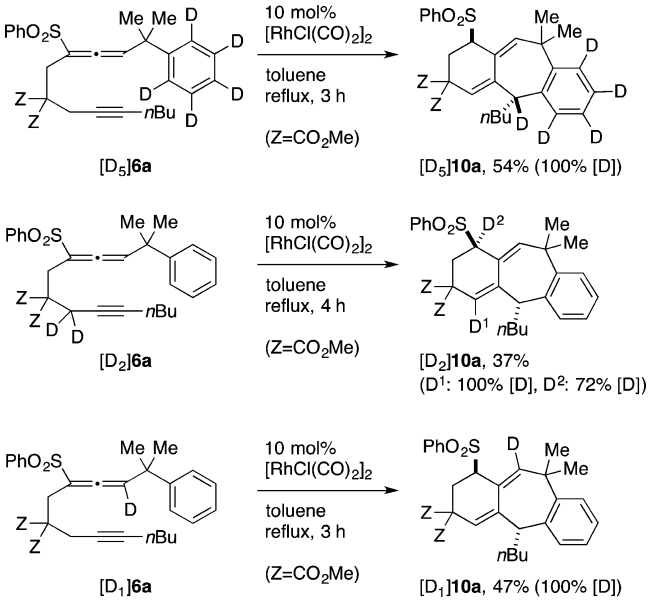
Scheme 1. Our Previous Study: Rh^I−Catalyzed Cycloisomerization of Benzylallene-Alkynes via C−H Bond Activation



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



Scheme 3. $[RhCl(CO)_2]_2$-Catalyzed Cycloisomerization of $[D_5]$6a, $[D_2]$6a, $[D_1]$6a



The benzylallene-internal alkyne **6a** having a dimethyl group at the benzylic position[10] was exposed to the optimized conditions ($[RhCl(CO)_2]_2$ 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** (R^3=Me) and **6h** (R^3=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**.[14]

To obtain information about the mechanism for the stereoselective production of **10**, we performed three experiments with the deuterated substrates, $[D_5]$**6a**, $[D_2]$**6a**, and $[D_1]$**6a** (Scheme 3). Treatment of the pentadeuterated substrate $[D_5]$**6a** with $[RhCl(CO)_2]_2$ in refluxing toluene[15] produced the deuterated product $[D_5]$**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 $[D_5]$**10a** in a highly stereoselective manner. In the case of the dideuterated substrate $[D_2]$**6a**, one of the deuterium atoms at the propargylic position was stereoselectively transferred into the allylic position of the six-membered ring of $[D_2]$**10a**. For the monodeuterated substrate $[D_1]$**6a**, the deuterium atom at the allenic position was completely incorporated into the olefinic position of the seven-membered ring in $[D_1]$**10a**. In other words, migration of the deuterium atom could not be observed.

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**.

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

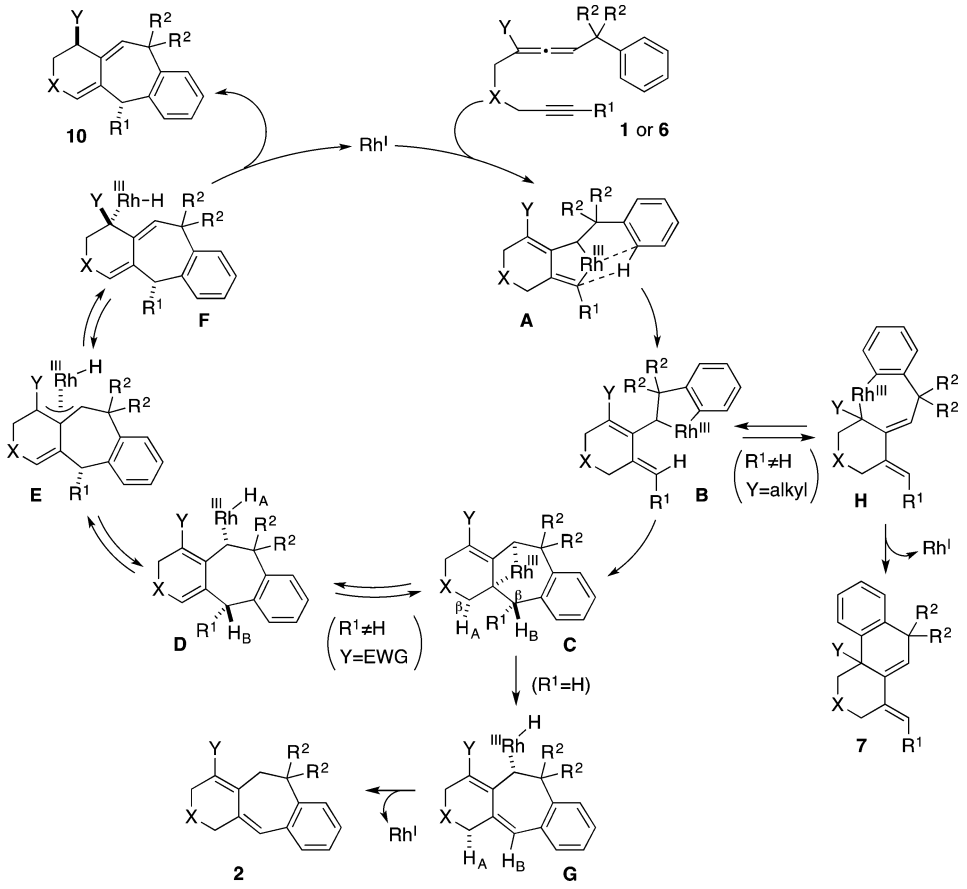
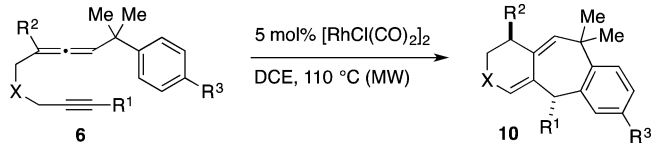


Table 1. $[RhCl(CO)_2]_2$-Catalyzed Cycloisomerization of Benzylallene-Alkynes 6[a]



entry	substrate	R^1	R^2	R^3	X	time (h)	product and yield (%)[b]
1	**6a**	*n*Bu	SO_2Ph	H	$C(CO_2Me)_2$	12	**10a**:64
2	**6b**	Me	SO_2Ph	H	$C(CO_2Me)_2$	10	**10b**:66
3[c]	**6c**	*n*Bu	$P(O)(OEt)_2$	H	$C(CO_2Me)_2$	3	**10c**:64
4[c]	**6d**	Me	$P(O)(OEt)_2$	H	$C(CO_2Me)_2$	3	**10d**:73
5	**6e**	CH_2OBn	SO_2Ph	H	$C(CO_2Me)_2$	7	**10e**:52
6	**6f**	*n*Bu	SO_2Ph	H	$C(CH_2O)_2CMe_2$	20	**10f**:41
7	**6g**	*n*Bu	SO_2Ph	Me	$C(CO_2Me)_2$	4	**10g**:56
8	**6h**	*n*Bu	SO_2Ph	Cl	$C(CO_2Me)_2$	20	**10h**:62

[a]Reaction conditions: A solution of **6** in DCE was heated in a microwave reactor at 110 °C. [b]Isolated yield. [c]Reaction was performed in refluxing toluene. DCE = 1,2-dichloroethane, MW = microwave.

The σ-bond metathesis[16] between the C_{sp2}–H bond on the benzene ring and the C_{sp2}–Rh^{III} bond of **A** would form the arylrhodium intermediate **B**. The insertion of the exocyclic olefin of **B** into the C_{sp2}–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** should have the *cis*-stereochemistry between the Rh center and the substituent R^1. 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**, which also possesses the *cis*-stereochemistry between the Rh center and the substituent R^1, would stereoselectively produce the final product **10**. As a result, highly *trans*-stereoselective transformation of **6** into **10** in Table 1 would be explained (two substituents R^1 and Y in Scheme 4 were depicted as R^1 and R^2 in Table 1).

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

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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]

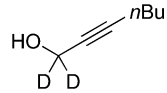
On the other hand, we already proposed the mechanism for the formation of **7** from **6** ($R^1 \neq$ H, Y = alkyl), which involved intermediates **A** and **B**.[6] The intermediate **B** would be in equilibrium with another σ-allylrhodium intermediate **H**, which should collapse into **7**.

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 $[RhCl(CO)_2]_2$-catalyzed cycloisomerzation 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 $CHCl_3$. ^{1}H 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 N_2 atmosphere with a low-power, focused microwave (Biotage initiator 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 Et_2O, CH_2Cl_2, THF, toluene, and 1,2-dichloroethane were employed for reactions. Et_3N was distilled from CaH_2. 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**),[17] 5-(hept-2-ynyl)-2,2-dimethyl-5-(prop-2-ynyl)-1,3-dioxane (**S2f**),[8e] dimethyl 2-(hept-2-ynyl)-2-(prop-2-ynyl)malonate (**S2a**),[6] 2-methyl-2-phenylpropanal,[18] 2-methyl-2-(*p*-tolyl)propanal,[18] 2-(4-chlorophenyl)-2-methylpropanal,[19] 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 ([D_5]**S3a**),[6] dimethyl 2-(hept-2-ynyl)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl-4-*d*)malonate ([D_1]**S3a**),[6] dimethyl 2-(hept-2-ynyl)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)-malonate (**S3a**),[6] and 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 N_2 atmosphere. Organic extracts were dried over Na_2SO_4. All other reagents were obtained from commercial sources and used as received.

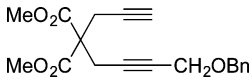
Preparation of Hept-2-yn-1,1-d_2-1-ol ([D_2]S1a).



To a suspension of $LiAlD_4$ (130 mg, 3.0 mmol) in Et_2O (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 CH_2Cl_2 to afford [D_2]**S1a** (120 mg, 52% yield) as a colorless oil: IR 3325 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) δ 86.4, 78.2, 50.7 (quin, J = 23.1 Hz), 30.6, 21.8, 18.3, 13.5; DART MS (ESI$^+$) m/z 115 (M^++1, 22.9); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_7H_{11}D_2O$ 115.1092, found 115.1091.

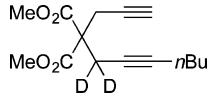
General Procedure for Preparation of Diynes S2e, [D_2]S2a from S1e, [D_2]S1a. *General Procedure 1.* To a solution of alcohol **S1** (7.5 mmol), PPh_3 (2.4 g, 9.0 mmol) and imidazole (610 mg, 9.0 mmol) in CH_2Cl_2 (15 mL) was added I_2 (2.3 g, 9.0 mmol) at 0 °C. After being stirred for 1 h at the same temperature, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. 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 or 5% AcOEt/hexane as the eluent 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 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 9% AcOEt/hexane as the eluent to afford the corresponding diyne **S2**.

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



The title compound **S2e** was prepared from **S1e** (260 mg, 1.5 mmol) according to General Procedure 1 and was obtained in 78% yield (260 mg) as a pale yellow oil: IR 3287, 1736 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 329 (M^++1, 100); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}O_5$ 329.1389, found 329.1375.

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



The title compound [D_2]**S2a** was prepared from [D_2]**S1a** (330 mg, 2.9 mmol) according to General Procedure 1 and was obtained in 83% yield (430 mg) as a colorless oil: IR 3286, 1740 cm^{-1}; ^{1}H 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 =

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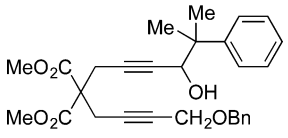
7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 83.9, 78.6, 73.6, 71.4, 56.7, 52.9, 30.8, 22.8−22.2 (m), 21.7, 18.2, 13.5; DART MS (ESI$^+$) m/z 267 (M^++1, 100); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}D_2O_4$ 267.1565, found 267.1572.

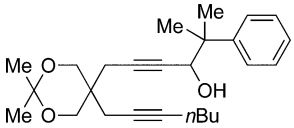
General Procedure for Preparation of Propargylic Alcohols S3e−h, [D$_2$]S3a from S2e−h, [D$_2$]S2a. *General Procedure 2.* To a solution of diyne **S2** (1.0 mmol) in THF (10 mL) was added LHMDS (1.2 mL, 1.2 mmol, 1.0 M solution in THF) at −78 °C. After being stirred for 30 min, aldehyde (1.3 mmol) was 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 9−25% AcOEt/hexane as the eluent 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).



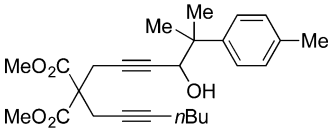
The title compound **S3e** was prepared from **S2e** (260 mg, 0.78 mmol) and 2-methyl-2-phenylpropanal (150 mg, 1.0 mmol) according to General Procedure 2 and was obtained in 87% yield (320 mg) as a colorless oil: IR 3533, 1739 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42−7.40 (m, 2H), 7.35−7.28 (m, 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 (ESI$^+$) m/z 477 (M^++1, 22.6); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{29}H_{33}O_6$ 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).



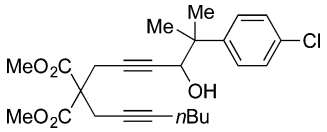
The title compound **S3f** was prepared from **S2f** (230 mg, 0.92 mmol) and 2-methyl-2-phenylpropanal (180 mg, 1.2 mmol) according to General Procedure 2 and was obtained in 52% yield (190 mg) as a colorless oil: IR 3449 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.42 (m, 2H), 7.35−7.33 (m, 2H), 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 (ESI$^+$) m/z 397 (M^++1, 58.6); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ 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).



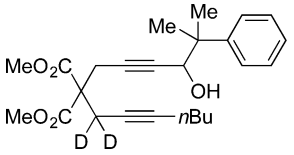
The title compound **S3g** was prepared from **S2a** (260 mg, 1.0 mmol) and 2-methyl-2-(*p*-tolyl)propanal (220 mg, 1.3 mmol) according to General Procedure 2 and was obtained in 73% yield (310 mg) as a colorless oil: IR 3536, 1738 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, 2H, J = 8.2 Hz), 7.15 (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 (ESI$^+$) m/z 427 (M^++1, 2.14); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ 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).



The title compound **S3h** was prepared from **S2a** (260 mg, 1.0 mmol) and 2-(4-chlorophenyl)-2-methylpropanal (250 mg, 1.3 mmol) according to General Procedure 2 and was obtained in 55% yield (250 mg) as a colorless oil: IR 3519, 1738 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 447 (M^++1, 9.27); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{25}H_{32}ClO_5$ 447.1938, found 447.1933.

Dimethyl 2-(Hept-2-ynyl-1,1-*d*$_2$)-2-(4-hydroxy-5-methyl-5-phenylhex-2-ynyl)malonate ([D$_2$]S3a).



The title compound [D$_2$]**S3a** was prepared from [D$_2$]**S2a** (270 mg, 1.0 mmol) and 2-methyl-2-phenylpropanal (190 mg, 1.3 mmol) according to General Procedure 2 and was obtained in 98% yield (410 mg) as a colorless oil: IR 3538, 1739 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 415 (M^++1, 9.95); DART HRMS (ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}D_2O_5$ 415.2454, found 415.2454.

General Procedure for Preparation of Benzylallene-Alkynes 6b,e−h, [D$_5$]6a, [D$_2$]6a, [D$_1$]6a from S3b,e−h, [D$_5$]S3a, [D$_2$]S3a, [D$_1$]S3a. *General Procedure 3.* To a solution of propargylic alcohol **S3** (1.0 mmol) and Et_3N (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 $NaHCO_3$, 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 20−25% AcOEt/hexane as the eluent to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH_2Cl_2 (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 $NaHCO_3$ and $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with 13−20% AcOEt/hexane as the eluent unless otherwise noted 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). The title compound **6b** was prepared from **S3b** (81 mg, 0.22 mmol) according to General Procedure 3 and was obtained in 96% yield (100 mg) as a colorless crystal: mp 86−88 °C (hexane-AcOEt); IR 1956, 1736, 1317, 1148 cm^{-1}; ^{1}H 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),

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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 (ESI$^+$) m/z 495 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{28}H_{31}O_6S$ 495.1841, found 495.1847. Note: This compound was purified by flash chromatography on silica gel using CH_2Cl_2 instead of AcOEt/hexane as the eluent.

Dimethyl 2-[4-(Benzyloxy)but-2-ynyl]-2-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate (6e). The title compound **6e** was prepared from **S3e** (320 mg, 0.68 mmol) according to General Procedure 3 and was obtained in 88% yield (360 mg) as a yellow oil: IR 1955, 1737, 1305, 1149 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 601 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{35}H_{37}O_7S$ 601.2260, found 601.2271. Note: This compound was purified by flash chromatography on silica gel using 5% AcOEt/CH_2Cl_2 instead of AcOEt/hexane as the eluent.

5-(Hept-2-ynyl)-2,2-dimethyl-5-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]-1,3-dioxane (6f). The title compound **6f** was prepared from **S3f** (190 mg, 0.48 mmol) according to General Procedure 3 and was obtained in 76% yield (190 mg) as a colorless oil: IR 1953, 1306, 1149 cm^{-1}; ^{1}H 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, $CDCl_3$) 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 (ESI$^+$) m/z 521 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{32}H_{41}O_4S$ 521.2726, found 521.2729.

Dimethyl 2-(Hept-2-ynyl)-2-[5-methyl-2-(phenylsulfonyl)-5-(*p*-tolyl)hexa-2,3-dienyl]malonate (6g). The title compound **6g** was prepared from **S3g** (310 mg, 0.73 mmol) according to General Procedure 3 and was obtained in 23% yield (93 mg) as a colorless oil: IR 1954, 1738, 1305, 1150 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84−7.83 (m, 2H), 7.61−7.58 (m, 1H), 7.51−7.48 (m, 2H), 7.29 (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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI$^+$) m/z 551 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{32}H_{39}O_6S$ 551.2467, found 551.2474.

Dimethyl 2-[5-(4-Chlorophenyl)-5-methyl-2-(phenylsulfonyl)hexa-2,3-dienyl]-2-(hept-2-ynyl)malonate (6h). The title compound **6h** was prepared from **S3h** (330 mg, 0.74 mmol) according to General Procedure 3 and was obtained in 61% yield (250 mg) as a colorless oil: IR 1954, 1738, 1305, 1150 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 571 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{31}H_{36}ClO_6S$ 571.1921, found 571.1921.

Dimethyl 2-(Hept-2-ynyl)-2-[5-methyl-5-(phenyl-d_5)-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate ([D$_5$]6a). The title compound [D$_5$]**6a** was prepared from [D$_5$]**S3a** (120 mg, 0.29 mmol) according to General Procedure 3 and was obtained in 84% yield (130 mg) as a colorless oil: IR 1955, 1737, 1305, 1148 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 542 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{31}H_{32}D_5O_6S$ 542.2625, found 542.2638. Note: This compound was purified by flash chromatography on silica gel using CH_2Cl_2 instead of AcOEt/hexane as the eluent.

Dimethyl 2-(Hept-2-ynyl-1,1-d_2)-2-[5-methyl-5-phenyl-2-(phenylsulfonyl)hexa-2,3-dienyl]malonate ([D$_2$]6a). The title compound [D$_2$]**6a** was prepared from [D$_2$]**S3a** (120 mg, 0.30 mmol) according to General Procedure 3 and was obtained in 84% yield (130 mg) as a colorless oil: IR 1954, 1737, 1306, 1148 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 539 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{31}H_{35}D_2O_6S$ 539.2436, found 539.2432. Note: This compound was purified by flash chromatography on silica gel using CH_2Cl_2 instead of AcOEt/hexane as the eluent.

Dimethyl 2-(Hept-2-ynyl)-2-[5-methyl-5-phenyl-2-(phenylsulfonyl)-4-*d*]malonate ([D$_1$]6a). The title compound [D$_1$]**6a** was prepared from [D$_1$]**S3a** (140 mg, 0.35 mmol) according to General Procedure 3 and was obtained in 84% yield (160 mg) as a colorless oil: IR 1948, 1737, 1305, 1149 cm^{-1}; ^{1}H 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 (ESI$^+$) m/z 538 (M$^+$+1, 100); DART HRMS (ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{31}H_{36}DO_6S$ 538.2374, found 538.2384. Note: This compound was purified by flash chromatography on silica gel using CH_2Cl_2 instead of AcOEt/hexane as the eluent.

General Procedure for Preparation of Benzylallene-Alkynes 6c,d from S3a,b. *General Procedure 4.* 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 $NaHCO_3$, 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 33−40% AcOEt/hexane as the eluent to afford the corresponding benzylallene-alkyne **6**.

Dimethyl 2-[2-(Diethoxyphosphoryl)-5-methyl-5-phenylhexa-2,3-dienyl]-2-(hept-2-ynyl)malonate (6c). The title compound **6c** was prepared from **S3a** (110 mg, 0.26 mmol) according to General Procedure 4 and was obtained in 33% yield (46 mg) as a

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colorless oil: IR 1950, 1737 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI^+) m/z 533 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{29}H_{42}O_7P$ 533.2668, found 533.2683.

Dimethyl 2-(But-2-ynyl)-2-[2-(diethoxyphosphoryl)-5-methyl-5-phenylhexa-2,3-dienyl]malonate (6d). The title compound **6d** was prepared from **S3b** (140 mg, 0.38 mmol) according to General Procedure 4 and was obtained in 54% yield (100 mg) 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 (ESI^+) m/z 491 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{26}H_{36}O_7P$ 491.2199, found 491.2189.

General Procedure for $[RhCl(CO)_2]_2$-Catalyzed Cycloisomerization of 6 with Microwave Reactor (Table 1). *General Procedure 6.* 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 13−50% AcOEt/hexane as the eluent unless otherwise noted 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).** The title compound **10a** was prepared from **6a** (54 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 64% yield (34 mg) as a colorless plate: mp 129−132 °C (chloroform-hexane); IR 1734, 1308, 1146 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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 (ESI^+) m/z 537 (M^++1, 31); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{31}H_{37}O_6S$ 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).** The title compound **10b** was prepared from **6b** (50 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 66% yield (33 mg) as a colorless crystal: mp 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 (ESI^+) m/z 495 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{28}H_{31}O_6S$ 495.1841, found 495.1840. Note: This compound was purified by flash chromatography on silica gel using 3% AcOEt/toluene instead of AcOEt/hexane as the eluent.

(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).** The title compound **10c** was prepared from **6c** (53 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 64% yield (34 mg) as 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 (ESI^+) m/z 533 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ 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).** The title compound **10d** was prepared from **6d** (49 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 73% yield (36 mg) as a pale yellow crystal: mp 134−136 °C (hexane-AcOEt); IR 1733 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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); ^{31}P NMR (243 MHz, $CDCl_3$) δ 28.5; DART MS (ESI^+) m/z 491 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{26}H_{36}O_7P$ 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).** The title compound **10e** was prepared from **6e** (60 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 52% yield (31 mg) as a yellow amorphous solid: IR 1735, 1307, 1146 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI^+) m/z 601 (M^++1, 12.1); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{35}H_{37}O_7S$ 601.2260, found 601.2271. Note: This compound was purified by flash chromatography on silica gel using 5% AcOEt/toluene instead of AcOEt/hexane as the eluent.

(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).** The title compound **10f** was prepared from **6f** (52 mg, 0.10 mmol) according to General Procedure 6 and

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was obtained in 41% yield (21 mg) as a pale yellow oil: IR 1306, 1149 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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 (ESI^+) m/z 521 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{32}H_{41}O_4S$ 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).** The title compound **10g** was prepared from **6g** (59 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 56% yield (31 mg) as 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 (ESI^+) m/z 551 (M^++1, 66.6); DART HRMS (ESI^+) m/z: $[M+H]^+$ 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).** The title compound **10h** was prepared from **6h** (57 mg, 0.10 mmol) according to General Procedure 6 and was obtained in 62% yield (35 mg) as 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 (ESI^+) m/z 571 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ 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]$6a (Scheme 3). *General Procedure 7.* To a solution of the benzylallene-alkyne ($[D_5]$**6a**, $[D_2]$**6a**, $[D_1]$**6a**, 0.10 mmol) in toluene (1.0 mL) was added $[RhCl(CO)_2]_2$ (1.9 mg, 0.0050 mmol) under N_2 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 17% AcOEt/hexane as the eluent to afford the corresponding cyclized product ($[D_5]$**10a**, $[D_2]$**10a**, $[D_1]$**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 ($[D_5]$10a).** The title compound $[D_5]$**10a** was prepared from $[D_5]$**6a** (54 mg, 0.10 mmol) according to General Procedure 7 and was obtained in 54% yield (29 mg) as a colorless crystal: mp 155−157 °C (hexane-AcOEt); IR 1734, 1307, 1145 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI^+) m/z 542 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ 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 ($[D_2]$10a).** The title compound $[D_2]$**10a** was prepared from $[D_2]$**6a** (54 mg, 0.10 mmol) according to General Procedure 7 and was obtained in 37% yield (20 mg) as a colorless crystal: mp 153−156 °C (hexane-AcOEt); IR 1733, 1305, 1146 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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 × 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI^+) m/z 539 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ 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* ($[D_1]$10a).** The title compound $[D_1]$**10a** was prepared from $[D_1]$**6a** (54 mg, 0.10 mmol) according to General Procedure 7 and was obtained in 47% yield (25 mg) as a colorless crystal: mp 154−156 °C (hexane-AcOEt); IR 1735, 1307, 1146 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 (ESI^+) m/z 538 (M^++1, 100); DART HRMS (ESI^+) m/z: $[M+H]^+$ calcd for $C_{31}H_{36}DO_6S$ 538.2374, found 538.2374.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01048.

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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Notes

The authors declare no competing financial interest.

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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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