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Ru(0)-Catalyzed Straightforward Synthesis of Conjugated Tetraenes: An Approach using Two Internal Alkynes with 1,3-Butadiene

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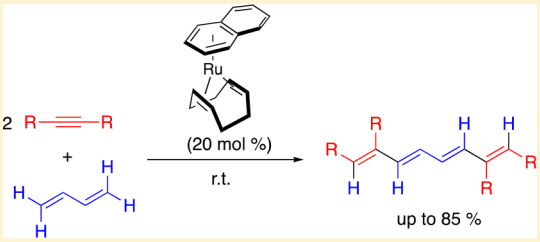
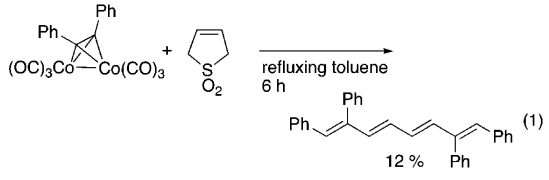
Supporting Information

ABSTRACT: The Ru(0)-catalyzed straightforward synthesis of conjugated tetraenes has been achieved in up to 85% yield by coupling of 2 equiv of internal alkynes with 1,3-butadiene at room temperature. The stoichiometric reaction of [Ru(η^4-*cisoid*-1,3-butadiene)(η^4-1,5-COD)(NCMe)] with 2 equiv of 3-hexyne produces a tetraene complex of Ru(0), [Ru{3−6-η^4-(3*E*,5*E*,7*E*,9*E*)-4,9-diethyldodeca-3,5,7,9-tetraene}(η^4-1,5-COD)(NCMe)], in 98% yield, which releases the conjugated tetraene ligand in 92% yield by exposure to 1,3-butadiene.

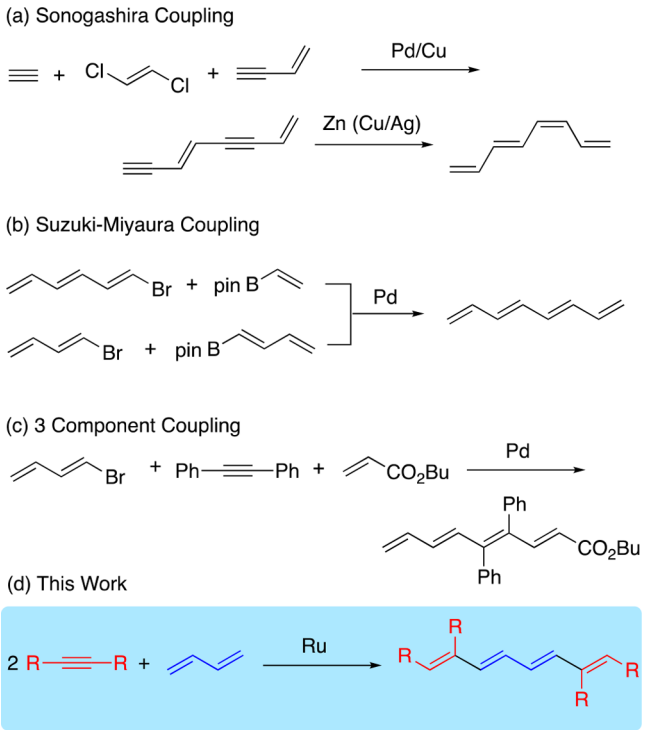


INTRODUCTION

Conjugated tetraenes are important substructures of many biologically active and natural products.[1] Wittig and Horner−Wadsworth−Emmons reactions[2] are conventional methods of choice for their preparation. However, these reactions require repetition of the subsequent reduction of the resulting ester to a primary alcohol and partial oxidation to the corresponding aldehyde to expand further C=C bonds. Takahashi and co-workers reported stoichiometric synthesis of conjugated tetraenes from zirconacyclopentadiene.[3] The catalytic approaches involve combination of Sonogashira coupling and subsequent reduction of the alkynyl fragment (Scheme 1a).[4] This method contains the (*Z*)-C=C substructure resulting from the partial hydrogenation of the C≡C bond. The most used catalytic approach is presumably Suzuki−Miyaura coupling (Scheme 1b).[5] This method employs trienyl halide, which is normally prepared by a stoichiometric Wittig reaction, or dienyl halide, with an alkenyl- or dienylborane. Therefore, the overall step and atom efficiency are limited. Satoh, Miura, and co-worker documented an interesting three-component coupling among dienyl bromide, diphenylacetylene, and an acrylate (Scheme 1c).[6] Because they showed only one synthetic example, the scope and limitation of this reaction are not clear. In 1977, Pauson and Khand reported the stoichiometric reaction of [Co_2(μ-PhC≡CPh)$(CO)_6$] with 3-sulfolene to produce 1,2,7,8-tetraphenyloctateteraene in 12% yield (eq 1).[7] In this paper, we report the catalytic approach to conjugated tetraenes from two internal alkynes with 1,3-butadiene catalyzed by a Ru(0) complex (Scheme 1d).



Scheme 1. Catalytic Approaches to Conjugated Tetraenes



RESULTS AND DISCUSSION

We recently reported the direct coupling of internal alkenes with 1-substituted 1,3-dienes to give conjugated trienes catalyzed by [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1**).[8] When this strategy was extended to 1,3-butadiene, the terminal C1

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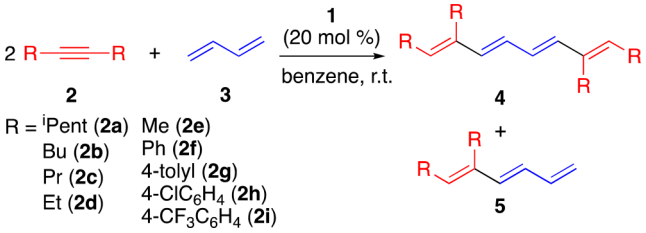
and C4 carbons in 1,3-butadiene both reacted with internal alkynes to give conjugated tetraenes with perfect regio- and stereoselectivity (Table 1).[9]

Table 1. Reactions of Internal Alkyes 2 with 1,3-Butadiene (3) Catalyzed by 1[a]



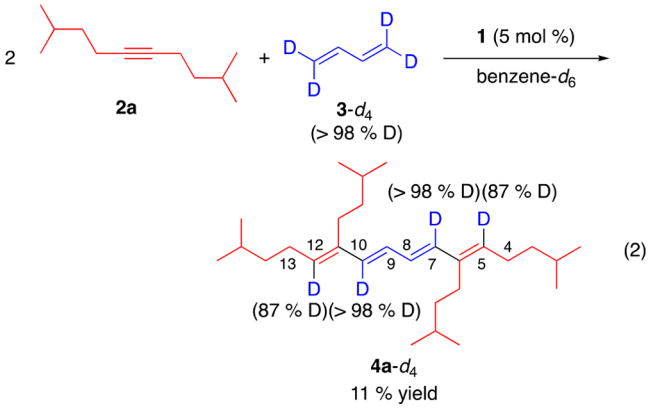
entry	R	yield/% 4a–i	5a–i
1	isopentyl	85 (4a)	13 (5a)
2[b,c]	isopentyl	65 (4a)	7 (5a)
3[c,d]	isopentyl	50 (4a)	21 (5a)
4[c,e]	isopentyl	71 (4a)	4 (5a)
5[f,g]	isopentyl	19 (4a)	53 (5a)
6[f,h]	isopentyl	23 (4a)	59 (5a)
7	butyl	60 (4b)	13 (5b)
8	propyl	57 (4c)	11 (5c)
9[i]	ethyl	64 (4d)	13 (5d)
10[j]	methyl	11 (4e)	13 (5e)
11[k]	phenyl	41 (4f)	8 (5f)
12[l]	4-tolyl	41 (4g)	0 (5g)
13[m]	4-chlorophenyl	23 (4h)	8 (5h)[n]
14[m]	4-trifluoromethylphenyl	2 (4i)	0 (5i)

[a]Typical conditions: **1** (20 mol %), **2** (0.24 mmol), **3** (0.11 mmol), room temperature, time 1 day. Yields were estimated by ^{1}H NMR using triphenylmethane or dibenzyl as an internal standard. [b]Solvent toluene-d_8. [c]Temperature 30 °C. [d]Solvent dichloromethane-d_2. [e]Solvent acetone-d_6. [f]**1** (5 mol %). [g]Temperature 18 °C. [h]Temperature 50 °C. [i]Time 5 days. [j]Time 3 days. [k]**1** (10 mol %), time 14 h. [l]**1** (10 mol %), **2** (0.13 mmol), **3** (0.055 mmol). [m]**2** (0.13 mmol), **3** (0.055 mmol), time 3 days. [n]NMR resonances for **5h** were obscured by overlapping with unidentified resonances. **5h** was tentatively identified by the characteristic terminal dienyl resonances.

Treatment of 2 equiv of 2,9-dimethyldeca-5-yne (**2a**) with 1,3-butadiene (**3**) in the presence of a catalytic amount of **1** (20 mol % based on **3**) at room temperature in benzene produced (5*E*,7*E*,9*E*,11*E*)-2,15-dimethyl-6,11-isopentylhexadeca-5,7,9,11-tetraene (**4a**) in 85% yield along with (3*E*,5*E*)-9-methyl-5-isopentyldeca-1,3,5-triene (**5a**) in 13% yield (Table 1, entry 1). Compounds **4a** and **5a** can be separated by recycling HPLC (GPC) using chloroform as the eluent. Conjugated tetraene **4a** was fully characterized by ^{1}H and ^{13}C{^{1}H} NMR and HRMS (APCI), and the stereochemistry was confirmed by a pNOESY experiment. This reaction also proceeded in toluene, dichloromethane, and acetone, but benzene was the most promising solvent among them (entries 2–4). With low catalyst loading (5 mol %), the formation of **5a** was promoted and no significant improvement was observed at 50 °C (entries 5 and 6). Although the reason for the catalysis with low catalyst loading to encourage the formation of conjugated triene **5a** is not clear, one of the possible explanations is that the conjugated triene ligand is liberated from an intermediate but the low catalyst concentration discourages the subsequent reaction to give a tetraene. Although similar reactions using alkylacetylenes dominantly produced tetraenes (entries 7–9), the reaction using 2-butyne (**2e**) gave the coupling products in modest yield and the concomitant [2 + 2 + 2] cyclotrimerization product was observed (entry 10). This fact shows the cyclotrimerization of alkynes to be a potential side reaction in this process. With diphenylacetylene (**2f**), the tetraene product (1*Z*,3*E*,5*E*,7*Z*)-1,2,7,8-tetraphenylocta-1,3,5,7-tetraene (**4f**) exclusively deposited from the reaction mixture (entry 11). Electron-deficient diarylacetylene gave the coupling product in low yield (entries 13 and 14). Note that reactions using 1-substituted butadiene such as 1,3-pentadiene produced conjugated trienes and those using 2-substituted butadiene such as isoprene and 2,3-dimethylbutadiene shut down the catalysis.[8] Reactions using terminal alkynes gave complex mixtures. These are limitations of the present catalysis.

Treatment of 3-hexyne (**2d**) with **3** in a 1/1 ratio in the presence of a catalytic amount of **1** (10 mol %) produced a mixture of tetraene **4d** (17%) and triene **5d** (43%). Further addition of 1 equiv of **2d** to this mixture increased **4d** (50%) with a decrease in **5d** (5%). This experiment suggests that the conjugated triene does react with an added alkyne to produce tetraene.

When [1,1,4,4-^{2}H$_4$]-1,3-butadiene (**3**-d_4) was employed in the reaction with **2a**, [5,7,10,12-^{2}H$_4$]-**4a**-d_4 was observed by ^{1}H



and ^{2}H{^{1}H} NMR along with the triene (eq 2 and Figure 1). In ^{1}H NMR spectrum of **4a**-d_4, the AA′BB′ pattern assignable to 7- and 10-C*H* almost completely disappeared, and the 8- and 9-C*H* resonances appeared as a singlet. Consistently, the 4- and 13-CH_2 protons, which were observed as a doublet of triplets for **4a**, changed to a triplet. The deuterium contents were estimated to be up to 98 atom % D for 7- and 10-C*H* and 87 atom % D for 5- and 12-C*H* in **4a**-d_4.

This result is regarded as a formal syn addition of the C–H bond in butadiene to internal alkynes.

A stoichiometric reaction of [Ru(η^4-*cisoid*-1,3-butadiene)(η^4-1,5-COD)(NCMe)] (**6**)[10] with **2d** in benzene-d_6 quickly gave a transient intermediate at room temperature, which was supposed to be a conjugated triene complex along with the tetraene complex [Ru{3–6-η^4-(3*E*,5*E*,7*E*,9*E*)-4,9-diethyldodeca-3,5,7,9-tetraene}(η^4-1,5-COD)(NCMe)] (**7**), and all species were eventually converted into **7** in 98% yield within 5 min (Scheme 2). Complex **7** has a conjugated tetraene ligand, whose stereochemistry was unequivocally determined by a pNOESY experiment. The methine resonances in the tetraene ligand are observed in benzene-d_6 at δ 0.78 (dd, J = 7.4, 4.6 Hz, 3-C*H*), 1.78 (dd, J = 9.7, 8.0 Hz, 6-C*H*), 5.06 (d, J = 8.0 Hz, 5-

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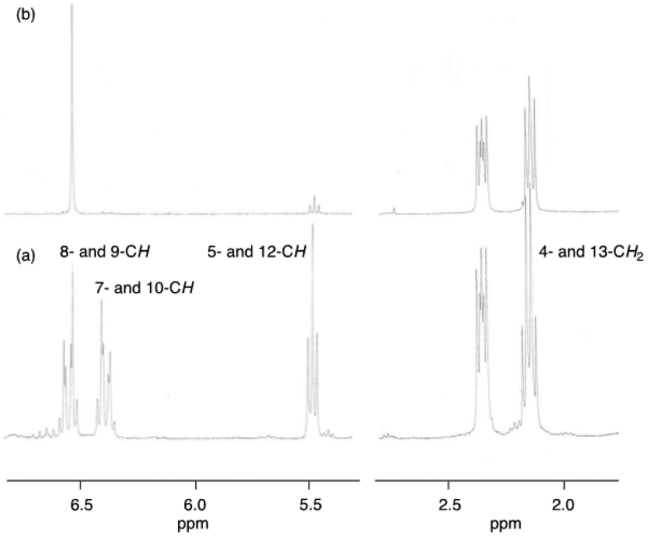
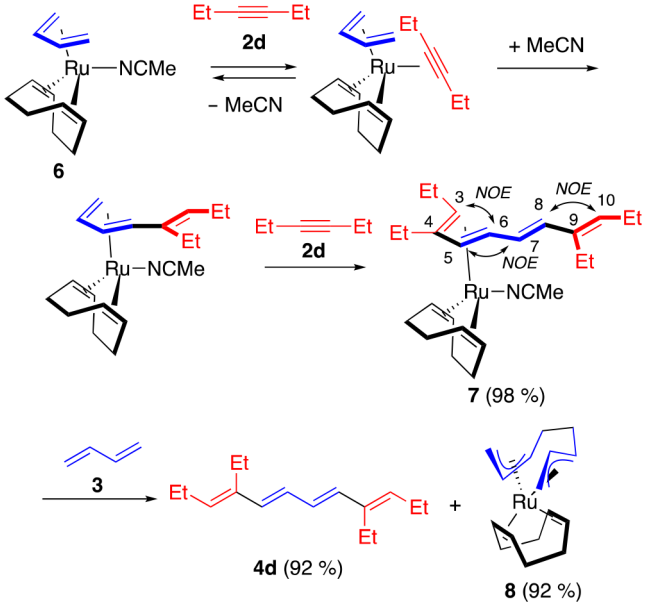


Figure 1. ^{1}H NMR spectra in the region of alkenyl and methylene protons for **4a** (a) and **4a**-d_4 (b) in C_6D_6.

Scheme 2. Stoichiometric Reaction of Butadiene Complex 6 with 2-Hexyne (2d)

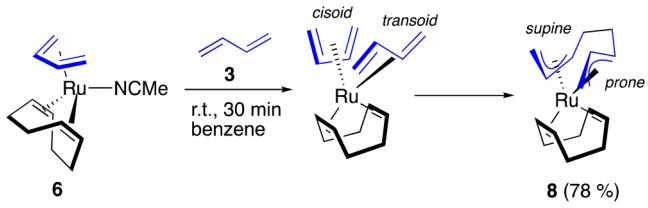


CH), 5.38 (t, J = 7.4 Hz, 10-CH), 5.94 (dd, J = 15.5, 9.7 Hz, 7-CH), and 6.18 (d, J = 15.5 Hz, 8-CH). The methylene protons in the 2-position and in the 4-ethyl group were observed as diastereotopic protons, consistent with the coordination of the tetraene fragment to Ru.

A 3H broad resonance at δ 0.83−0.88 suggests coordination of an acetonitrile ligand. Further treatment of **7** with 2.5 equiv of 1,3-butadiene (**3**) released conjugated tetraene **4d** in 92% yield along with *supine,prone*-bis(η^3-allylic)ruthenium(II) complex **8**. Because **8** is formed by the independent reaction of **6** with **3** (Scheme 3),[11] the observation of **8** suggests regeneration of **6** from **7**.

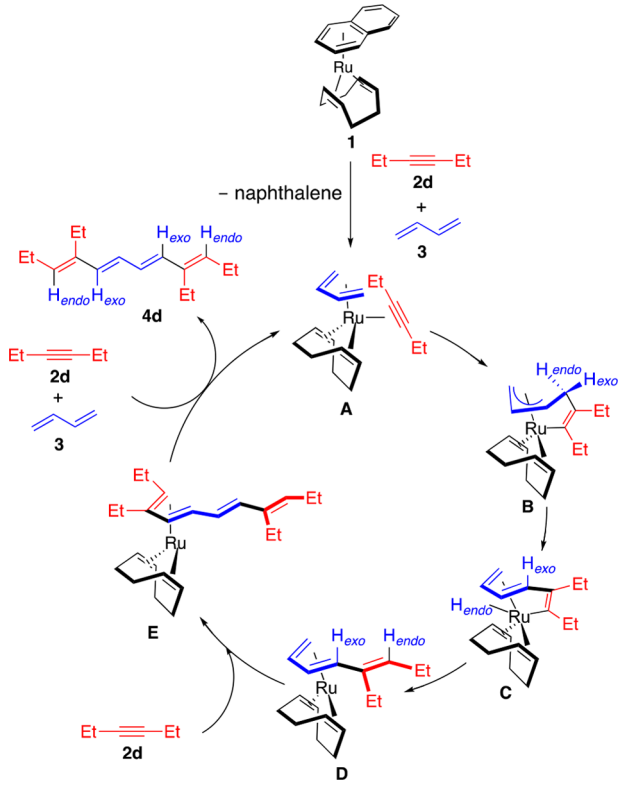
On the other hand, the tetraene complex **7** did not release **4d** even when 5 equiv of 3-hexyne (**2d**) was added. **7** gradually decomposed at room temperature; after 10 h it became an unidentified complex mixture, in which conjugated tetraene **4d** was not observed.

Scheme 3. Formation of *supine,prone*-8 by the Oxidative Coupling between *cisoid*- and *transoid*-Butadiene Ligands on Ru(0)



All of these catalytic and stoichiometric reactions and isotopic labeling experiments are consistent with the mechanism shown in Scheme 4, for the reaction of 3-hexyne (**2d**) with **3** as a typical example.[8,12]

Scheme 4. Possible Mechanism for Conjugated Tetraene Synthesis Catalyzed by a Ru(0) Complex



First of all, the 6π naphthalene ligand in **1** was readily displaced by 4π butadiene (**3**) and 2π 3-hexyne (**2d**), giving **A** to satisfy the 18e rule. The excellent substrate selectivity in this reaction comes from this identification on the basis of coordination numbers. Then, the oxidative coupling reaction occurs to give **B**.[13] The subsequent β-hydride elimination selectively occurs from the H_{endo} methylene protons by rotation of the resulting C−C single bonds. This diastereotopic selectivity determines the stereoselectivity to give the (*E*)-C=C bond. After the reductive elimination giving **D**, the second **2d** comes to the Ru center to produce **E** probably by the same mechanism noted in the processes from **A** to **D**. Because Fukumoto and Mashima have documented facile migration of the RuClCp fragment on the conjugated polyenes,[14] migration of the coordinated Ru(η^4-1,5-COD) fragment on the conjugated tetraene ligand is probably facile

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and it finally settles into the most stable position. Note that we observed **7**, which strongly supports **E**. Finally, reaction of **2d** and **3** with **E** liberates the conjugated tetraene **4d** with regeneration of **A**.

Conjugated triene, a side product in this reaction, is probably liberated from **D**. According to the stoichiometric reaction shown in Scheme 2, there is presumably no need to liberate the conjugated triene ligand from **D**, although a coupling reaction using a bulky alkyne such as 2,9-dimethyldeca-5-yne (**2a**) may be prone to liberate the conjugated triene ligand. In either event, the present study shows that the conjugated triene can get back in the catalytic cycle again.

CONCLUDING REMARKS

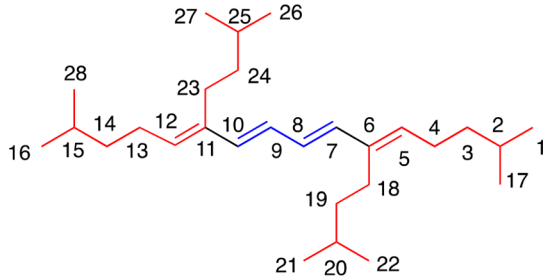
In summary, we have developed a new protocol for conjugated tetraene synthesis by the Ru(0)-catalyzed direct coupling of internal alkynes with 1,3-butadiene. This is the most direct approach to conjugated tetraene ever reported, which can start from commercially available reagents.

EXPERIMENTAL SECTION

General Procedures. All procedures described in this paper were carried out under a nitrogen or argon atmosphere by use of Schlenk and vacuum line techniques. Benzene was dried and purified using a Glass Contour Ultimate Solvent System. Benzene-d_6 and toluene-d_8 were dried over sodium wire and stored under vacuum, and they were transferred into an NMR tube or a 25 mL Schlenk tube by vacuum distillation prior to use. Chloroform-*d* was used as received. Dichloromethane-d_2 and acetone-d_6 were deried over Drierite and P_2O_{10}, respectively, and were distilled under reduced pressure. 2,9-Dimethyldeca-5-yne (**2a**), 5-decyne (**2b**), 4-octyne (**2c**), 3-hexyne (**2d**), 2-butyne (**2e**), and diphenylacetylene (**2f**) were purchased from the commercial suppliers and stored under a nitrogen atmosphere after three freeze−pump−thaw cycles. 1,3-Butadiene (**3**) was purchased from commercial suppliers and was used as received. [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1**) and diarylacetylenes **2g−i** were prepared according to literature procedures.[15−19] ^{1}H, ^{2}H{^{1}H}, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were measured on a JEOL ECX-400P spectrometer (400 MHz for ^{1}H). Some coupling constants for multiplet resonances were estimated by gNMR.[20] GC and GC-MS were performed on Shimadzu GC-2014 (FID) and Shimadzu GCMS-2010 (EI) instruments, respectively, equipped with a TC-1 column (0.25 mm i.d. × 30 m). HRMS(APCI) analysis was performed on a Bruker Daltonics micrOTOF-QII instrument. Preparative scale HPLC was performed with a Japan Analytical Industry LaboACE LC-5060 instrument equipped with JAIGEL-1H and JAIGEL-2HR tandem columns using chloroform as the eluent.

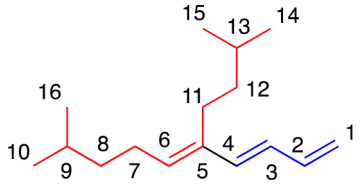
Typical Reaction of 2,9-Dimethyldeca-5-yne (2a) with 1,3-Butadiene (3). Complex **1** (7.43 mg, 0.0220 mmol) was placed in an NMR tube under a nitrogen atmosphere, and 2,9-dimethyldeca-5-yne (**2a**; 52.0 μL, 0.242 mmol) and C_6D_6 (600 μL) were added. To the solution was added 1,3-butadiene (**3**; 2.44 mL, 0.109 mmol) by a hypodermic syringe at room temperature. The mixture was allowed to react at room temperature for 1 day, during which time the reaction was monitored by ^{1}H NMR spectroscopy. In order to determine the yield of the product, dibenzyl (6.35 mg, 0.0348 mmol) was added to the reaction mixture as an internal standard. The yield of (5*E*,7*E*,9*E*,11*E*)-2,15-dimethyl-6,11-isopentylhexadeca-5,7,9,11-tetraene (**4a**) was estimated as 85% along with (3*E*,5*E*)-9-methyl-5-isopentyldeca-1,3,5-triene (**5a**) in 13% yield. The reaction mixture was purified by a recycle HPLC to obtain a pale brown oil of **4a** (18.5 mg, 0.0478 mmol) in 44% yield.

Similar treatments using 5 mol % of **1** in benzene-d_6 at 18 and 50 °C and treatments using 20 mol % of **1** in toluene-d_8, dichloromethane-d_2, acetone-d_6 at 30 °C produced **4a** and **5a**, as shown in Table 1.



(5*E*,7*E*,9*E*,11*E*)-**4a**

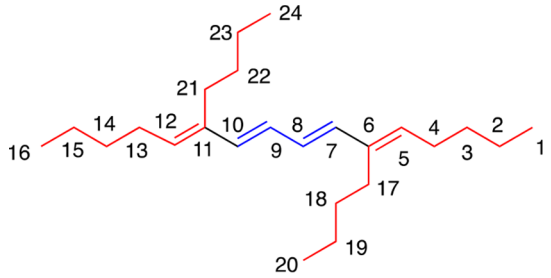
^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.88 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, 1-, 16-, 17- and 28-C*H*$_3$), 0.93 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, 21-, 22-, 26- and 27-C*H*$_3$), 1.27 (dt, $^3J_{H-H}$ = 8.8, 6.8 Hz, 4H, 3- and 14-C*H*$_2$), 1.48 (AA′XX′Y, $^2J_{H-H}$ = −10 Hz, $^3J_{H-H}$ = 8.7, 6.5 Hz, 4H, 19- and 24-C*H*$_2$), 1.53 (n, $^3J_{H-H}$ = 6.8 Hz, 2H, 20- and 25-C*H*) 1.58 (n, $^3J_{H-H}$ = 6.8 Hz, 2H, 2- and 15-C*H*), 2.16 (dt, $^3J_{H-H}$ = 8.4, 7.2 Hz, 4H, 4- and 13-C*H*$_2$), 2.36 (AA′XX′, $^2J_{H-H}$ = −10 Hz, $^3J_{H-H}$ = 8.7, 6.5 Hz, 4H, 18- and 23-C*H*$_2$), 5.50 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, 5- and 12-C*H*), 6.37 (AA′BB′, $^3J_{H-H}$ = 17.5, $^4J_{H-H}$ = 0.5 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, 7- and 10-C*H*), 6.53 (AA′BB′, $^3J_{H-H}$ = 17.5, 10.5 Hz, $^4J_{H-H}$ = 0.1 Hz, 2H, 8- and 9-C*H*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 22.67, 22.69, 25.2, 26.6, 28.0, 28.8, 38.8, 39.3, 127.4, 133.1, 136.3, 139.4. HRMS(APCI): $C_{28}H_{50}$ (386.39) *m*/*z* 387.3972 (M + 1H)$^+$, calcd for $C_{28}H_{51}$ 387.3951.



(3*E*,5*E*)-**5a**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.85 (12H, 10-, 14-, 15- and 16-C*H*$_3$, overlapped with signals for **4a**), 1.2−1.3 (m, 4H, 8- and 12-C*H*$_2$, overlapped with signals for **4a**), 1.5−1.7 (2H, 9- and 13-C*H*$_2$, overlapped with signals for **4a**), 2.1 (2H, 7-C*H*$_2$, overlapped with signals for **4a**), 2.25 (m, 2H, 11-C*H*$_2$), 5.01 (dd, $^3J_{H-H}$ = 9.8 Hz, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-C*H*), 5.18 (dd, $^3J_{H-H}$ = 16.0, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-C*H*), 5.44 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 6-C*H*), 6.21 (d, $^3J_{H-H}$ = 15.0 Hz, 1H, 4-C*H*), 6.3−6.5 (2H, 3- and 2-C*H*, overlapped with signals for **4a**).

Reaction of 5-Decyne (2b) with 1,3-Butadiene (3). (5*E*,7*E*,9*E*,11*E*)-6,11-Dibutylhexadeca-5,7,9,11-tetraene (**4b**): pale brown oil, 60% yield.



(5*E*,7*E*,9*E*,11*E*)-**4b**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.88 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, 1- and 16-C*H*$_3$), 0.90 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, 20- and 24-C*H*$_3$), 1.24−1.40 (m, 12H, 2-, 3-, 14-, 15-, 19- and 23-C*H*$_2$), 1.52 (pseudo quint, 4H, 18- and 22-C*H*$_2$), 2.13 (q, $^3J_{H-H}$ = 7.4 Hz, 4H, 4- and 13-C*H*$_2$), 2.33 (pseudo t, 4H, 17- and 21-C*H*$_2$), 5.50 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, 5- and 12-C*H*), 6.33 (AA′BB′, $^3J_{H-H}$ = 16.5 Hz, $^4J_{H-H}$ = 0.1 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, 7- and 10-C*H*), 6.49 (AA′BB′, $^3J_{H-H}$ = 16.5, 11.0 Hz, $^4J_{H-H}$ = 0.1 Hz, 2H, 8- and 9-C*H*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 14.21, 14.24, 22.8, 23.3,

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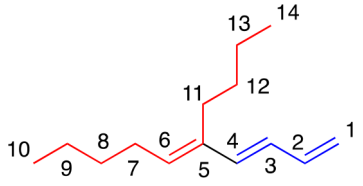
27.0, 28.4, 31.8, 32.3, 127.5, 133.2, 136.4, 139.2. HRMS(APCI): $C_{24}H_{42}$ (330.33) m/z 331.3351 $(M + H)^+$, calcd for $C_{24}H_{43}$ 331.3365.

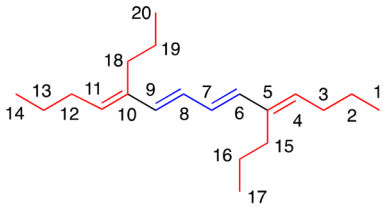
(3*E*,5*E*)-5-butyldeca-1,3,5-triene (**5b**): 13% yield.



(3*E*,5*E*)-**5b**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.86 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, 10-CH_3), 0.86 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, 14-CH_3), 1.20−1.38 (m, 6H, 8-, 9- and 13-CH_2), 1.44 (quint, $^3J_{H-H}$ = 7.6 Hz, 2H, 12-CH_2), 2.07 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, 7-CH_2), 2.19 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, 11-CH_2), 5.02 (dd, $^3J_{H-H}$ = 10.0 Hz, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-CH), 5.18 (dd, $^3J_{H-H}$ = 16.4, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-CH), 5.45 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, 6-CH), 6.21 (d, $^3J_{H-H}$ = 15.6 Hz, 1H, 4-CH), 6.33 (dd, $^3J_{H-H}$ = 15.6, 10.4 Hz, 1H, 3-CH), 6.43 (dt, $^3J_{H-H}$ = 16.4, 10.4 Hz, 1H, 2-CH).

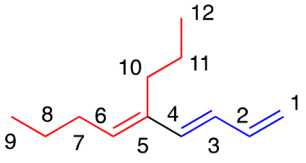
Reaction of 4-Octyne (2c) with 1,3-Butadiene (3). (4*E*,6*E*,8*E*,10*E*)-5,10-Dipropyltetradeca-4,6,8,10-tetraene (**4c**): pale brown oil, 57% yield.



(4*E*,6*E*,8*E*,10*E*)-**4c**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.88 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, 1- and 14-CH_3), 0.92 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, 17- and 20-CH_3), 1.35 (sext, $^3J_{H-H}$ = 7.5 Hz, 4H, 2- and 13-CH_2), 1.53 (sext, $^3J_{H-H}$ = 7.5 Hz, 4H, 16- and 19-CH_2), 2.07 (q, $^3J_{H-H}$ = 7.4 Hz, 4H, 3- and 12-CH_2), 2.28 (t, $^3J_{H-H}$ = 7.5 Hz, 4H, 15- and 18-CH_2), 5.50 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, 4- and 11-CH), 6.27 (AA′BB′, $^3J_{H-H}$ = 15.8 Hz, $^4J_{H-H}$ = 0.5 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, 6- and 9-CH), 6.43 (AA′BB′, $^3J_{H-H}$ = 15.8, 10.5 Hz, $^4J_{H-H}$ = 0.1 Hz, 2H, 7- and 8- CH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 14.1, 14.4, 22.7, 23.3, 29.2, 30.8, 127.5, 133.2, 136.3, 139.1. HRMS(APCI): $C_{20}H_{34}$ (274.27) m/z 275.2737 $(M + H)^+$, calcd for $C_{20}H_{35}$ 275.2739.

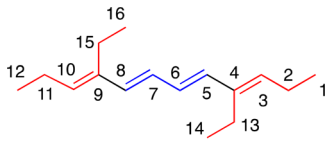
(3*E*,5*E*)-5-Propylnona-1,3,5-triene (**5c**): 11% yield.



(3*E*,5*E*)-**5c**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.85 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, 9-CH_3), 0.86 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, 12-CH_3), 1.31 (sext, $^3J_{H-H}$ = 7.6 Hz, 2H, 8-CH_2), 1.44 (sext, $^3J_{H-H}$ = 7.6 Hz, 2H, 11-CH_2), 2.00 (q, $^3J_{H-H}$ = 7.6 Hz, 2H, 7-CH_2), 2.19 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, 10-CH_2), 5.01 (dd, $^3J_{H-H}$ = 10.0 Hz, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-CH), 5.17 (dd, $^3J_{H-H}$ = 16.6, $^2J_{H-H}$ = 1.6 Hz, 1H, 1-CH), 5.43 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, 6-CH), 6.18 (d, $^3J_{H-H}$ = 16.0 Hz, 1H, 4-CH), 6.29 (dd, $^3J_{H-H}$ = 16.0, 10.0 Hz, 1H, 3-CH), 6.42 (dt, $^3J_{H-H}$ = 16.6, 10.0 Hz, 1H, 2-CH). HRMS(APCI): $C_{12}H_{20}$ (164.16) m/z 165.1647 $(M + H)^+$, calcd for $C_{12}H_{21}$ 165.1643.

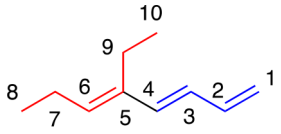
Reaction of 3-Hexyne (2d) with 1,3-Butadiene (3). (3*E*,5*E*,7*E*,9*E*)-4,9-Diethyldodeca-3,5,7,9-tetraene (**4d**): pale gray solid, 64% yield.



(3*E*,5*E*,7*E*,9*E*)-**4d**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.92 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, 1- and 12-CH_3), 1.04 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, 14- and 16-CH_3), 2.03 (quint, $^3J_{H-H}$ = 7.6 Hz, 4H, 2- and 11-CH_2), 2.23 (q, $^3J_{H-H}$ = 7.6 Hz, 4H, 13- and 15-CH_2), 5.43 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, 3- and 10-CH), 6.25 (AA′BB′, $^3J_{H-H}$ = 16.5 Hz, $^4J_{H-H}$ = 0.5 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, 5- and 8-CH), 6.40 (AA′BB′, $^3J_{H-H}$ = 16.5, 11.0 Hz, $^4J_{H-H}$ = 0.1 Hz, 2H, 7- and 6-CH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 14.1, 14.5, 20.2, 21.7, 127.4, 134.0, 135.8, 140.3. HRMS(APCI): $C_{16}H_{26}$ (218.20) m/z 219.2103 $(M + H)^+$, calcd for $C_{16}H_{27}$ 219.2107.

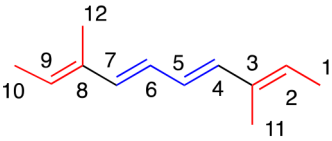
(3*E*,5*E*)-5-Ethylocta-1,3,5-triene (**5d**): 13% yield.



(3*E*,5*E*)-**5d**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.88 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 8-CH_3), 0.99 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 10-CH_3), 2.03 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 7-CH_2), 2.18 (q, $^3J_{H-H}$ = 7.4 Hz, 2H, 9-CH_2), 5.01 (dd, $^3J_{H-H}$ = 10.9 Hz, $^2J_{H-H}$ = 1.4 Hz, 1H, 1-CH), 5.16 (dd, $^3J_{H-H}$ = 16.6, $^2J_{H-H}$ = 1.4 Hz, 1H, 1-CH), 5.35 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 6-CH), 6.14 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 4-CH), 6.2−6.4 (2H, 2- and 3-CH, overlapped with signals for **4d**).

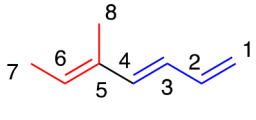
Reaction of 2-Butyne (2e) with 1,3-Butadiene (3). (2*E*,4*E*,6*E*,8*E*)-3,8-Dimethyldeca-2,4,6,8-tetraene (**4e**): pale gray sticky solid, 11% yield.



(2*E*,4*E*,6*E*,8*E*)-**4e**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 1.59 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, 1- and 10-CH_3), 1.69 (s, 6H, 11- and 12-CH_3), 5.52 (qq, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 0.8 Hz, 2H, 2- and 9-CH), 6.33 (AA′BB′, $^3J_{H-H}$ = 15.5, 10.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 3 Hz, 2H, 4- and 7-CH), 6.36 (AA′BB′, $^3J_{H-H}$ = 15.5, 10.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 3 Hz, 2H, 5- and 6-CH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 12.1, 14.0, 126.7, 127.4, 135.4, 137.1.

(3*E*,5*E*)-5-Methylhepta-1,3,5-triene (**5e**): 13% yield.

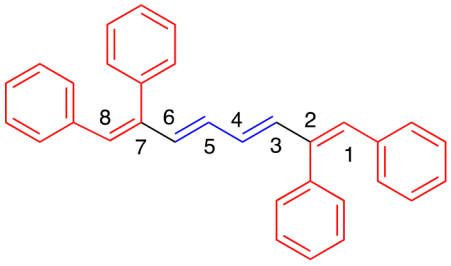


(3*E*,5*E*)-**5e**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 1.59 (d, $^3J_{H-H}$ = 7.4 Hz, 3H, 7-CH_3), 1.68 (s, 3H, 8-CH_3, overlapped with signals for **4e**), 5.01 (d, $^3J_{H-H}$ = 9.7 Hz, 1H, 1-CH), 5.16 (d, $^3J_{H-H}$ = 16.6, 1H, 1-CH), 5.45 (q, $^3J_{H-H}$ = 7.4 Hz, 1H, 6-CH), 6.18 (d, $^3J_{H-H}$ = 16.6 Hz, 1H, 4-CH), 6.2−6.3 (1H, 3-CH, overlapped with signals for **4e**), 6.39 (dt, $^3J_{H-H}$ = 16.6, 9.7 Hz, 1H, 2-CH).

Reaction of Diphenylacetylene (2f) with 1,3-Butadiene (3). (1*Z*,3*E*,5*E*,7*Z*)-1,2,7,8-Tetraphenylocta-1,3,5,7-tetraene (**4f**): yellow powder, 41% yield.

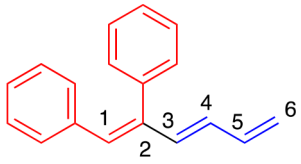
DOI: 10.1021/acs.organomet.7b00801
Organometallics XXXX, XXX, XXX−XXX



(1*Z*,3*E*,5*E*,7*Z*)-**4f**

^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 5.93 (AA′XX′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 3- and 6-C*H*), 6.48 (AA′XX′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 4- and 5-C*H*), 6.50 (s, 2H, 1- and 8-C*H*), 6.81 (dd, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 2.0 Hz, 4H, *o*-C_6H_5), 7.01−7.06 (m, 6H, *m*- and *p*-C_6H_5), 7.14 (dd, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.6 Hz, 4H, *o*-C_6H_5), 7.36−7.43 (m, 6H, *m*- and *p*-C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, room temperature): δ 126.8, 127.4, 127.9, 128.9, 129.3, 129.4, 131.5, 131.9, 136.8, 138.3, 138.7, 142.0. HRMS(APCI): $C_{32}H_{36}$ (410.20) *m*/*z* 411.2113 $(M + H)^+$, calcd for $C_{32}H_{27}$ 411.2113. (1*Z*,3*E*,5*E*,7*Z*)-**4f** was reported in the literature, but it was characterized only by melting point and elemental analysis.[7]

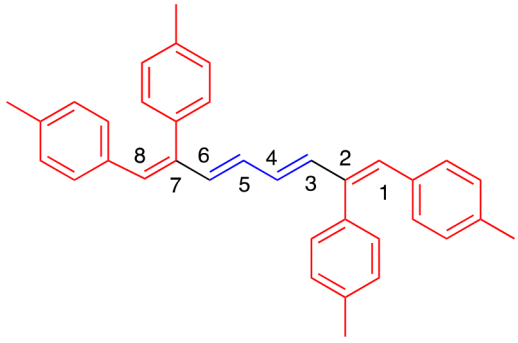
(1*Z*,3*E*)-1,2-Diphenylhexa-1,3,5-triene (**5f**): 8% yield.



(1*Z*,3*E*)-**5f**

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 5.05 (d, $^3J_{H-H}$ = 10.0 Hz, 1H, 1-C*H*), 5.08 (d, $^3J_{H-H}$ = 17.0, 1H, 1-C*H*), 5.83 (dd, $^3J_{H-H}$ = 15.2, 10.8 Hz, 1H, 4-C*H*), 6.4−6.5 (3H, 1-, 3- and 5-C*H*, overlapped with signals for **4f**), 6.8−6.9 (m, 2H, *o*-C_6H_5), 7.0−7.1 (m, 3H, *m*- and *p*-C_6H_5), 7.1−7.2 (m, 2H, *o*-C_6H_5), 7.3−7.5 (m, 3H, *m*- and *p*-C_6H_5).

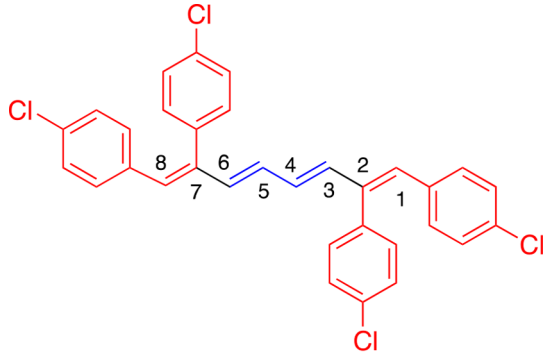
Reaction of 1,2-Bis(4-methylphenyl)acetylene (2g) with 1,3-Butadiene (3). (1*Z*,3*E*,5*E*,7*Z*)-1,2,7,8-Tetrakis(4-methylphenyl)octa-1,3,5,7-tetraene (**4g**): yellow powder, 41% yield.



(1*Z*,3*E*,5*E*,7*Z*)-**4g**

^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 2.20 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 5.92 (AA′BB′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 3- and 6-C*H*), 6.43 (s, 2H, 1- and 8-C*H*), 6.45 (AA′XX′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 4- and 5-C*H*), 6.73 (d, $^3J_{H-H}$ = 8.2 Hz, 4H, *o*-C_6H_4), 6.86 (d, $^3J_{H-H}$ = 8.2 Hz, 4H, *m*-C_6H_4), 7.01 (d, $^3J_{H-H}$ = 8.2 Hz, 4H, *o*-C_6H_4), 7.20 (d, $^3J_{H-H}$ = 8.2 Hz, 4H, *m*-C_6H_4). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, room temperature): δ 21.1, 21.4, 128.7, 129.2, 129.3, 129.6, 131.2, 131.5, 134.2, 135.4, 136.6, 136.8, 138.7, 141.2. HRMS(APCI): $C_{36}H_{34}$ (466.27) *m*/*z* 467.2718 $(M + H)^+$, calcd for $C_{36}H_{35}$ 467.2739.

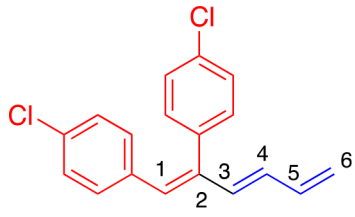
Reaction of 1,2-Bis(4-chlorophenyl)acetylene (2h) with 1,3-Butadiene (3). (1*Z*,3*E*,5*E*,7*Z*)-1,2,7,8-Tetrakis(4-chlorophenyl)octa-1,3,5,7-tetraene (**4h**): yellow powder, 23% yield.



(1*Z*,3*E*,5*E*,7*Z*)-**4h**

^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 5.89 (AA′BB′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 3- and 6-C*H*), 6.45 (AA′XX′, $^3J_{H-H}$ = 15.0, 6.0 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.0 Hz, 2H, 4- and 5-C*H*), 6.46 (s, 2H, 1- and 8-C*H*), 6.74 (d, $^3J_{H-H}$ = 8.6 Hz, 4H, *o*-C_6H_4), 7.04 (d, $^3J_{H-H}$ = 8.6 Hz, 4H, *m*-C_6H_4), 7.06 (d, $^3J_{H-H}$ = 8.6 Hz, 4H, *o*-C_6H_4), 7.39 (d, $^3J_{H-H}$ = 8.6 Hz, 4H, *m*-C_6H_4). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, room temperature): δ 128.3, 129.4, 130.4, 130.8, 130.8, 132.1, 133.0, 133.6, 134.9, 136.2, 138.3, 141.0. HRMS(APCI): $C_{32}H_{22}Cl_4$ (546.05) *m*/*z* 547.0527 $(M + H)^+$, calcd for $C_{32}H_{23}Cl_4$ 547.0554.

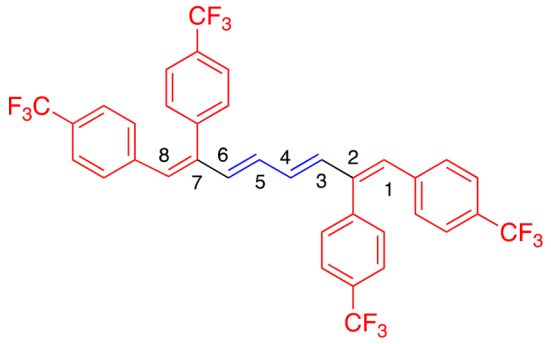
(1*Z*,3*E*)-1,2-Bis(4-chlorophenyl)hexa-1,3,5-triene (**5h**): 8% yield.



(1*Z*,3*E*)-**5h**

^{1}H NMR (400 MHz, acetone-d_6, room temperature): δ 5.08 (d, $^3J_{H-H}$ = 10.4 Hz, 1H, 1-C*H*), 5.14 (d, $^3J_{H-H}$ = 16.0, 1H, 1-C*H*), 6.51(s, 1H, 1-C*H*), 6.9−7.6 (8H, C_6H_4, overlapped with signals for **4h**).

Reaction of 1,2-Bis(4-trifluoromethylphenyl)acetylene (2i). (1*Z*,3*E*,5*E*,7*Z*)-1,2,7,8-Tetrakis(4-trifluoromethylphenyl)octa-1,3,5,7-tetraene (**4i**): 2% yield.



(1*Z*,3*E*,5*E*,7*Z*)-**4i**

^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 5.80 (m, 2H, 3- and 6-C*H*), 6.46 (m, 2H, 4- and 5-C*H*), 6.53 (s, 2H, 1- and 8-C*H*), 6.80 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, *o*-C_6H_4), 7.20 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, *m*-C_6H_4), 7.22 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, *o*-C_6H_4), 7.61 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, *m*-C_6H_4). $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, room temperature): δ −62.6 (s, 3F, CF_3), −62.4 (s, 3F, CF_3).

Reaction of 2a with [1,1,4,4-$^2H_4$]-1,3-Butadiene (3-*d*$_4$). [1,1,4,4-$^2H_4$]-1,3-Butadiene (**3-*d*$_4$**, >98 atom % D) was prepared by pyrolysis of 3-sulfolene-d_4 according to the literature method.[21] Into a frozen mixture of **2a** (57.0 μL, 0.265 mmol) and **1** (2.19 mg, 0.00649 mmol) in C_6D_6 (600 μL) was introduced **3-*d*$_4$** (2.9 mL, 0.13 mmol) by vacuum line/mercury manometer techniques. The mixture was reacted

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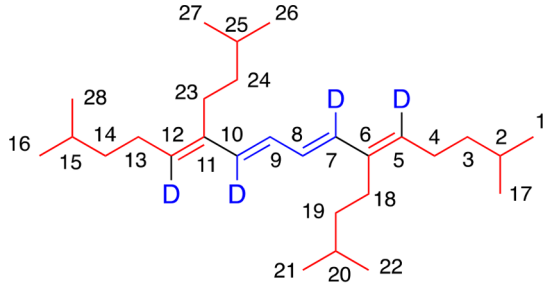
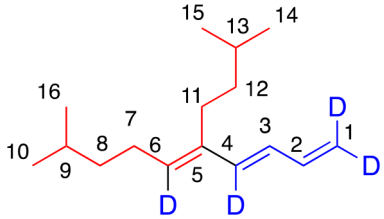
Organometallics XXXX, XXX, XXX−XXX

at room temperature for 4 days to give [5,7,10,12-$^2H_4$]-**4a**-d_4 in 11% yield and [1,1,4,6-$^2H_4$]-**5a**-d_4 in 26% yield (96 atom % D for 4-CD, 81 atom % D for 6-CD, 94 atom % D for 1-CD). This compound was purified by recycle HPLC.



(5*E*,7*E*,9*E*,11*E*)-[5,7,10,12-$^2H_4$]-**4a**-d_4

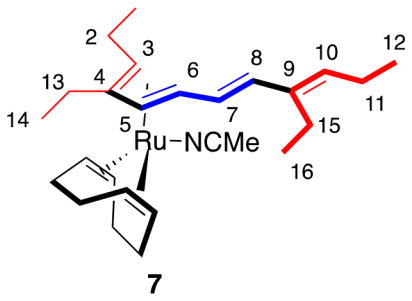
^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.88 (d, $^3J_{H-H}$ = 6.4 Hz, 12H, 1-, 16-, 17- and 28-CH_3), 0.93 (d, $^3J_{H-H}$ = 6.4 Hz, 12H, 21-, 22-, 26- and 27-CH_3), 1.27 (q, $^3J_{H-H}$ = 6.8 Hz, 4H, 3- and 14-CH_2), 1.48 (m, 4H, 19- and 24-CH_2), 1.53 (n, $^3J_{H-H}$ = 6.8 Hz, 2H, 20- and 25-C*H*) 1.58 (n, $^3J_{H-H}$ = 6.8 Hz, 2H, 2- and 15-C*H*), 2.15 (t, $^3J_{H-H}$ = 7.6 Hz, 4H, 4- and 13-CH_2), 2.36 (AA′XX′, $^3J_{H-H}$ = 8.7, 6.5, $^2J_{H-H}$ = −10 Hz, 4H, 18- and 23-CH_2), 6.52 (s, 2H, 8- and 9-C*H*). ^{2}H NMR (61.4 MHz, C_6H_6, room temperature): δ 5.5 (br s, 5- and 12-C*D*), 6.3 (br s, 7- and 10-C*D*).



(3*E*,5*E*)-[1,1,4,6-$^2H_4$]-**5a**-d_4

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.91 (d, $^3J_{H-H}$ = 6.3 Hz, 6H, 10- and 16-CH_3), 0.93 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, 14- and 15-CH_3), 1.27 (q, $^3J_{H-H}$ = 7.7 Hz, 2H, 8-CH_2), 1.36−1.46 (m, 2H, 12-CH_2), 1.46−1.64 (m, 2H, 9- and 13-C*H*), 2.14 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, 7-CH_2), 2.31 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, 11-CH_2), 6.39 (d, $^3J_{H-H}$ = 10.6 Hz, 1H, 3-C*H*), 6.48 (d, $^3J_{H-H}$ = 10.6 Hz, 1H, 2-C*H*).

Reaction of Ru(η^4-butadiene)(η^4-1,5-COD)(NCMe) (6) with 3-Hexyne (2d) To Give 7. [Ru(η^4-butadiene)(η^4-1,5-COD)(NCMe)] (**6**; 13.0 mg, 0.0428 mmol) was treated with **2d** (9.8 μL, 0.086 mmol) in C_6D_6 at room temperature for 5 min. On the basis of *p*-xylene (3.0 μL, 0.024 mmol) as an internal standard, [Ru{3−6-η^4-(3*E*,5*E*,7*E*,9*E*)-4,9-diethyldodeca-3,5,7,9-tetraene}(η^4-1,5-COD)(NCMe)] (**7**) was obtained in 98% yield. After 2 h, to the reaction mixture was added **3** (2.44 mL, 0.109 mmol) to give (3*E*,5*E*,7*E*,9*E*)-**4d** in 92% yield and the bis(η^3-allylic)ruthenium(II) complex *supine*,*prone*-[Ru(1−3-η^3:6−8-η^3-C_8H_{12})(η^4-1,5-COD)] (**8**)[11] in 92% yield.



7

^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.78 (dd, $^3J_{H-H}$ = 7.4, 4.6 Hz, 1H, 3-C*H*), 0.83−0.88 (br, 3H, CH_3CN), 0.94 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 12-CH_3), 1.05 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 1-CH_3), 1.12 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 16-CH_3), 1.27 (dquint, $^2J_{H-H}$ = 14.4 Hz, $^3J_{H-H}$ = 7.4 Hz, 1H, 2-CH_2), 1.41 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 14-CH_3), 1.70 (dqd, $^2J_{H-H}$ = 14.4 Hz, $^3J_{H-H}$ = 7.4, 4.6 Hz, 1H, 2-CH_2), 1.78 (dd, $^3J_{H-H}$ = 9.7, 8.0 Hz, 1H, 6-C*H*), 2.03 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 11-CH_2), 2.1−2.2 (m, 5H, 1H for 13-CH_2 and 4H for COD), 2.29 (q, $^3J_{H-H}$ = 7.4 Hz, 2H, 15-CH_2), 2.3−2.4 (m, 3H, 1H for 13-CH_2 and 2H for COD), 2.56−2.69 (m, 2H, COD), 2.8−2.85 (m, 1H, COD), 3.10−3.14 (m, 1H, COD), 3.18−3.22 (m, 1H, COD), 3.82−3.97 (m, 1H, COD), 5.06 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, 5-C*H*), 5.38 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 10-C*H*), 5.94 (dd, $^3J_{H-H}$ = 15.5, 9.7 Hz, 1H, 7-C*H*), 6.18 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 8-C*H*). This compound was characterized by spectroscopic methods.

Reaction of Complex 7 with 3-Hexyne (3d). Treatment of **6** (6.37 mg, 0.0221 mmol) with 2 equiv of **3d** (5.0 μL, 0.044 mmol) in the presence of *p*-xylene (2.0 μL, 0.016 mmol) as an internal standard in C_6D_6 (0.6 mL) at 18 °C generated **7** in 99% yield. Further addition of 5 equiv of **3d** (12.5 μL, 0.110 mmol) to the reaction mixture gave no additional reaction. However, **7** gradually decomposed at room temperature and a complex mixture was obtained after 10 h. Compound (3*E*,5*E*,7*E*,9*E*)-**4d** was not observed in the complex mixture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00801.

Spectroscopic and physical data (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

COD, cyclooctadiene (C_8H_{12})

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