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Ru(0)-Catalyzed Direct Coupling of Internal Alkynes with Conjugated Dienes: An Efficient Access to Conjugated Trienes

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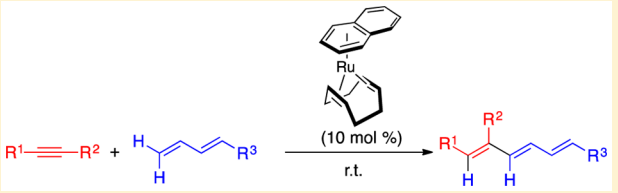
Supporting Information

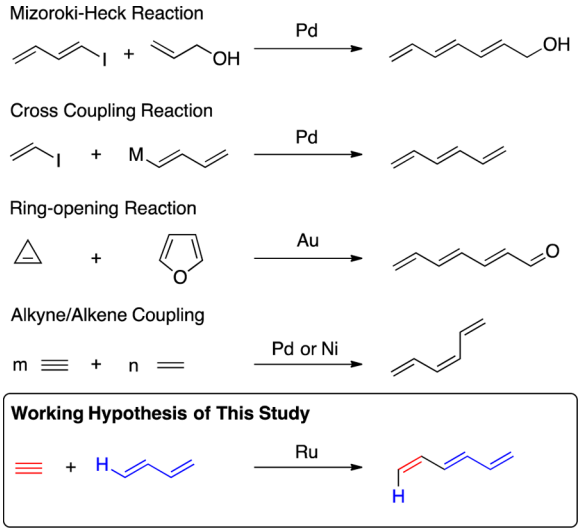
ABSTRACT: Ru(0)-catalyzed direct coupling of internal alkynes with conjugated dienes enables a direct access to conjugated trienes, where the reaction is formally regarded as a stereoselective syn alkyne insertion into the terminal C−H bond in the conjugated diene. The reaction is catalyzed by Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**; 3−10 mol %) with high regio- and stereoselectivities.



INTRODUCTION

Conjugated trienes are important motifs in many natural products, biologically active compounds, and electronic materials.[1] They are conventionally prepared by stoichiometric reactions such as Wittig and Horner−Wadsworth−Emmons reactions[2] and alkyne/zirconacyclopentadiene coupling.[3] Scheme 1 gives an overview of the current transition-metal-catalyzed approaches. Namely, these strategies involve Mizoroki−Heck reactions,[4] cross-coupling reactions,[5] intermolecular ring-opening reactions,[6] and alkyne/alkene coupling reactions.[7] However, these processes have somewhat limited scopes with respect to both coupling partners, and those using organic halides are problematic from an atom-economical point of view. A more straightforward and greener strategy to prepare conjugated trienes could be a catalytic conjugate expansion by alkyne insertion into the C−H bond in a conjugated diene. However, this attractive approach has not yet been reported to the best of our knowledge. Note that Mitsudo,[8] Suginome,[9] and co-workers have reported coupling reactions of terminal alkynes with conjugated dienes catalyzed by Ru(II) and Ni(0) complexes but these protocols do not produce conjugated trienes but enynes.

Scheme 1. Simplified Concepts for Catalytic Production of Conjugated Trienes



We have reported cross-dimerization of alkenes with conjugated dienes catalyzed by a Ru(0) complex that proceeds by an oxidative coupling mechanism.[10] We now report a straightforward access to conjugated trienes by cross-dimerization between internal alkynes and conjugated dienes.

RESULTS AND DISCUSSION

Treatment of diphenylacetylene (**2a**) with methyl (2*E*,4*E*)-penta-2,4-dienoate (**3a**) catalyzed by Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**; 10 mol %) at room temperature resulted in the formation of methyl (2*E*,4*E*,6*Z*)-6,7-diphenylhepta-2,4,6-trienoate (**4aa**) in 84% NMR yield within 10 min without formation of any isomers. The stereochemistry of **4aa** was determined by NMR experiments involving pNOESY. Adopting the above as a standard set of conditions, we evaluated the scope of alkynes with **3a**. With 1,2-bis(4-methylphenyl)acetylene (**2b**), 1,2-bis(4-trifluoromethylphenyl)acetylene (**2c**), and 1,2-bis(4-nitrophenyl)acetylene (**2d**), the corresponding conjugated trienes (2*E*,4*E*,6*Z*)-**4ba**, -**4ca**,[11] and -**4da** were obtained in moderate to high NMR yields, suggesting no significant electronic effect among diarylacetylenes on the reactivity (Table 1). Unlike the case for **4aa**, (2*E*,4*E*,6*Z*)-**4ba** and (2*E*,4*E*,6*Z*)-**4ca** were produced along with the isomers in 4% and ∼10% yields, respectively, although their detailed structures wereare not clear at present. Isolated yields were lower, ranging from 9% to 60% for **4aa**−**4ed**.

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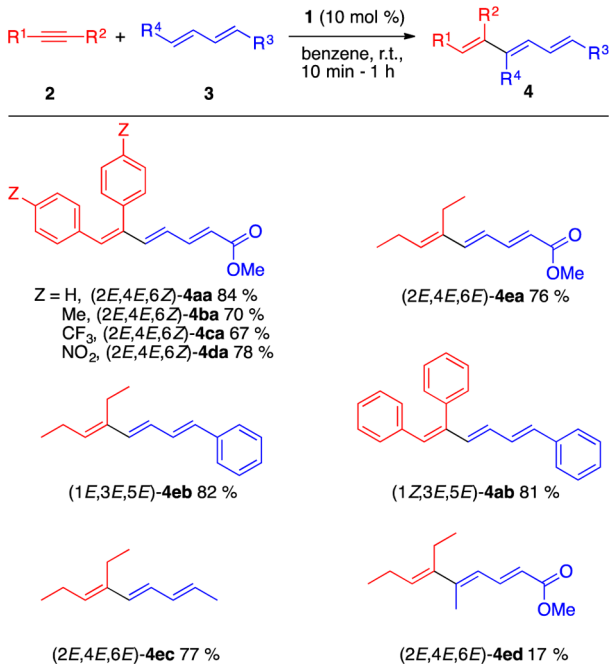
Table 1. Direct Coupling of Alkynes with Conjugated Dienes[a]



[a]Typical conditions: **1** (10 mol %), **2** (0.2 mmol), **3** (0.2 mmol), room temperature, time 10 min to 1 h, solvent benzene. Yields were estimated by ^{1}H NMR using triphenylmethane as an internal standard.

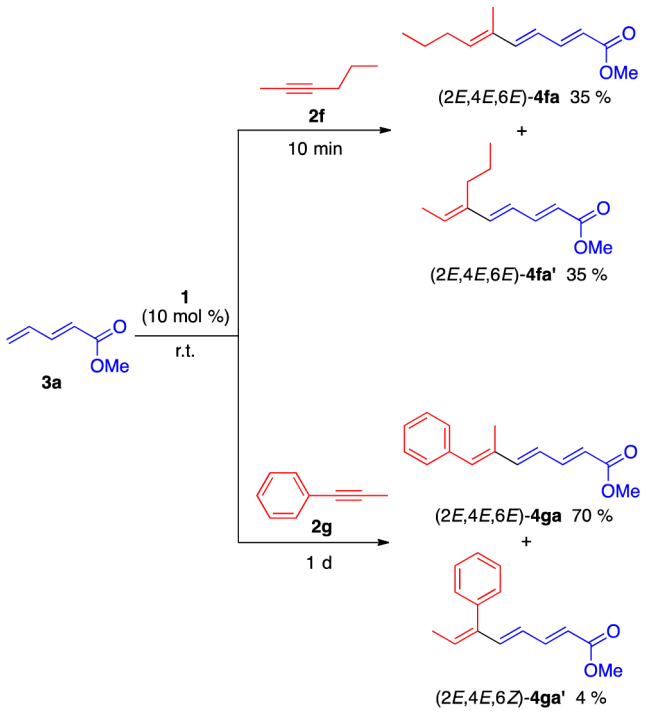
Electron-rich 3-hexyne (**2e**) also reacted with **3a** to give (2*E*,4*E*,6*E*)-**4ea** in 76% NMR yield. With an extremely electron-deficient alkyne, such as dimethyl acetylenedicarboxylate or ethyl 1-pentynoate, and terminal alkynes such as phenylacetylene and 1-hexyne complex mixtures were obtained. The reaction did not occur with 2,4-hexadiyne even at 50 °C.

The scope of the conjugated dienes was evaluated with 3-hexyne (**2e**). In addition to the electron-deficient **3a**, 1-phenyl-1,3-butadiene (**3b**) and electron-rich 1,3-pentadiene (**3c**) are also excellent coupling partners in this reaction. An internal diene, methyl (2*E*,4*E*)-hexa-2,4-dienoate (**3d**), also reacted with **2e** to give **4ed**, although the product yield was not high. Notably, this reaction requires a formal C═C bond rotation in **3d** (vide infra). Danishefski–Kitahara diene[12] remained unreacted even at 50 °C. By a similar token, 1,3-dienes bearing a substituent at the C(2) position, such as isoprene, 2,3-dimethylbutadiene (**3e**) and *β*-myrcene, did not undergo direct coupling.

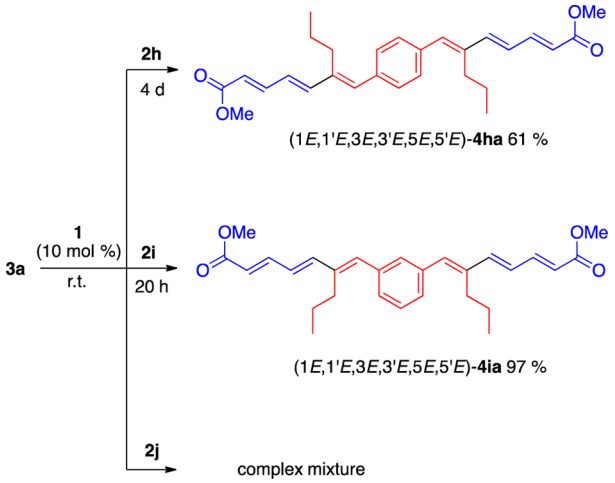
Unsymmetrical internal alkynes are interesting coupling partners from a regioselectivity point of view. Although it was difficult to control the regioselectivity of 2-hexyne (**2f**) in the formation of **4fa** (**4fa**/**4fa′** = 50/50), a highly regioselective coupling of 1-phenyl-1-propyne (**2g**) with **3a** was achieved to give (2*E*,4*E*,6*E*)-**4ga** in 70% yield and the regioisomer (2*E*,4*E*,6*Z*)-**4ga′** in 4% yield (Scheme 2) along with unidentified isomers.

With this promising regioselectivity in hand, our next challenge was coupling reactions using dialkynylbenzenes. Treatment of 1,4-bis(1-pentynyl)benzene (**2h**) with 2.6 equiv of **3a** in the presence of **1** (10 mol %) deposited a yellow-brown precipitate of (1*E*,1′*E*,3*E*,3′*E*,5*E*,5′*E*)-**4ha**, whose regio- and stereochemistries were fully characterized by NMR experiments (Scheme 3).[13] Similar treatment of 1,3-bis(1-pentynyl)benzene (**2i**) also produced (1*E*,1′*E*,3*E*,3′*E*,5*E*,5′*E*)-**4ia** in 97% yield. With 1,2-bis(1-pentynyl)benzene (**2j**), NMR experiments suggested that the reaction produced an initial product having a new propyl group, putatively assigned as 1-alkynyl-2-trienylbenzene, which gradually converted into a complex mixture.

Scheme 2. Reactions using Unsymmetrical Internal Alkynes



Scheme 3. Reactions using 1,4-, 1,3-, and 1,2-Bis(1-pentynyl)benzenes



In order to understand the reaction mechanism for this process, we performed the reaction of **2a** with 1-phenyl-[4,4′-$^2H_2$]-1,3-butadiene (**3b**-d_2) (eq 1). This reaction produced (1*Z*,3*E*,5*E*)-[1,3-$^2H_2$]-**4ab**-d_2 in 82% yield, and the deuterium atoms were observed at the C(1) and C(3) positions, which were shown by ^{1}H and ^{2}H NMR. This result clearly demonstrates the formal syn addition of the C–D bond in **3b**-d_2 to **2a**.

Bennett's group and our group documented the facile formation of the cisoid-conjugated diene complexes of Ru(0) by reaction of **1** with a series of conjugated dienes,[14,15] and

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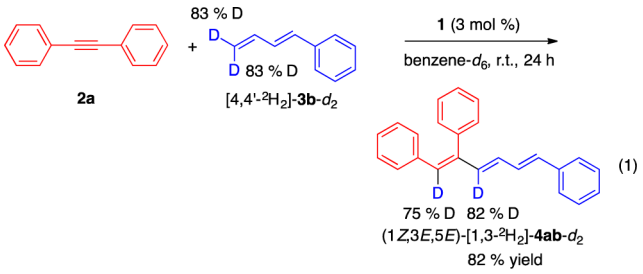
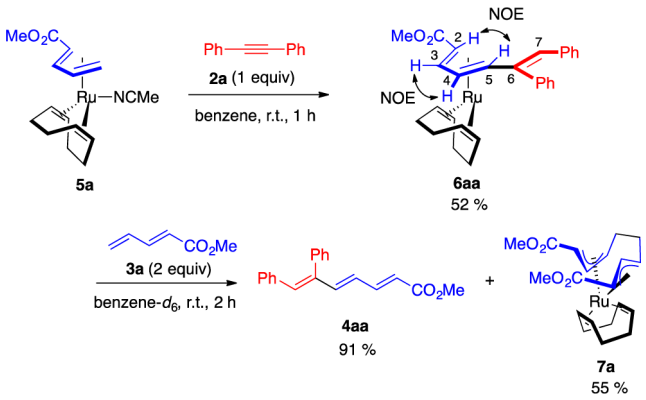


Ru(η^4-methyl penta-2,4-dienoate)(η^4-1,5-COD)(NCMe) (**5a**) was also prepared accordingly. Treatment of **5a** with **2a** instantly gave Ru[η^4-methyl (2*E*,4*E*,6*E*)-6,7-diphenylpenta-2,4,6-trienoate](η^4-1,5-COD) (**6aa**) in 52% yield at room temperature (Scheme 4). The pNOESY measurements suggest

Scheme 4. Stoichiometric Reaction of Conjugated Diene Complex 5a with Diphenylacetylene (2a)



a cisoid conformation of the C(2)−C(5) fragment. The ^{1}H NMR resonances for C(2)−H (δ 4.24(d)), C(5)−H (δ 2.93(d)), and C(7)−H (δ 5.16(s)), and the ^{13}C{^{1}H} NMR resonances at C(2) (δ 39.19), C(5) (δ 85.30), C(6) (δ 112.83), and C(7) (δ 51.38) are basically consistent with the proposed structure with some contribution of the interaction between the C(6)═C(7) fragment and the Ru(0) center.

Further treatment of **6aa** with 2 equiv of **3a** gave (2*E*,4*E*,6*Z*)-**4aa** in 91% yield with formation of **7a** in 55% yield, which was independently obtained by treatment of **5a** with **3a**. The molecular structure of **7a** is shown in Figure 1, which is well described as a *supine,prone*-η^3:η^3-bis(allylic)ruthenium(II), suggesting that the oxidative coupling reaction occurred between *cisoid*-η^4-(methyl penta-2,4-dienoate) and *transoid*-η^2-(methyl penta-2,4-dienoate) fragments at the Ru(0) center.[15b,16]

A similar stoichiometric reaction of **5a** with 3-hexyne (**2e**) completely consumed the starting compounds and gave a complex mixture involving (2*E*,4*E*,6*E*)-**4ea** in 36% yield, and further treatment of the mixture with 1 equiv of **3a** gave (2*E*,4*E*,6*E*)-**4ea** in 80% yield with recovery of **5a** in 63% yield.

These two stoichiometric reactions are regarded as stepwise reactions of a part of the catalytic process. On the other hand, a similar reaction using 2,3-dimethylbutadiene (**3e**) is worth noting from a mechanistic point of view. Treatment of Ru(η^4-2,3-dimethylbutadiene)(η^4-1,5-COD)(NCMe) (**5e**) with **2a** also produced Ru[η^4-1,2-diphenyl-4,5-dimethylhexa-1,3,5-triene](η^4-1,5-COD) (**6ae**) in 51% yield (Scheme 5).

Unlike **6aa**, however, **6ae** never reacted with **3e**. Note that no reaction occurred between **2a** and **3e** under the catalytic

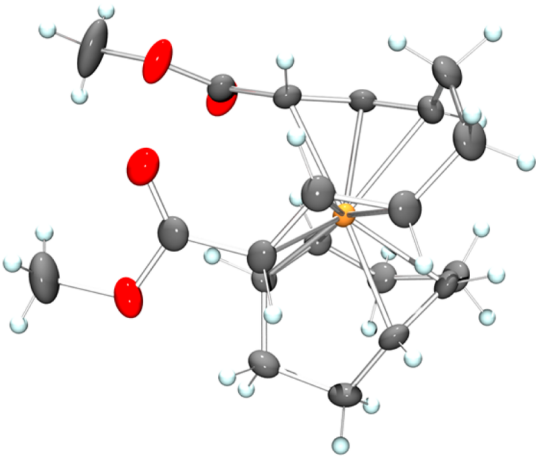
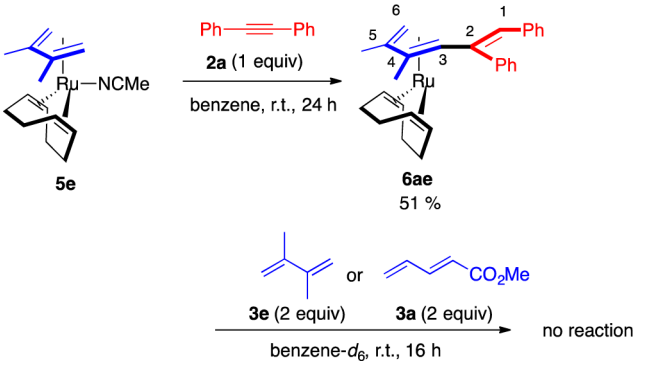


Figure 1. Molecular structure of *supine,prone*-**7a**. Ellipsoids represent 50% probability.

Scheme 5. Stoichiometric Reaction of Conjugated Diene Complex 5e with Diphenylacetylene (2a)



conditions. This means that the coordinated **3e** does react with **2a** at the Ru(0) center but the resulting triene ligand in **6ae** cannot be replaced with **3e**. This is one of the reasons some conjugated dienes are inactive in the present catalysis. Because **6ae** does not react with **3a** as well, the failure of the reaction of **6ae** with a diene does not arise from the employed diene but from the inert nature of **6ae** toward dienes.

All of these experimental results are consistent with the catalytic cycle shown in Scheme 6. The naphthalene ligand (6π) is readily displaced by a conjugated diene (4π) and alkyne (2π) to satisfy the 18e rule to give **A**, which determines the substrate selectivity in this reaction. We tentatively denote the terminal methylene protons of the *cisoid*-diene ligand in **A** as H_{endo} and H_{exo}. Then the oxidative coupling reaction produces a ruthenacycle (**B**). Without exception, we obtain the *E* products with respect to the central C═C bond in conjugated trienes. This fact means that the subsequent β-hydride elimination selectively occurs at H_{endo} to give **C**. Thus, unlike the working hypothesis shown in Scheme 1, a terminal C−H_{endo} bond in a conjugated diene has been cleaved (Scheme 6). This probably enables the reaction using an internal diene (2*E*,4*E*)-**3d** to give **4ed**. The reductive elimination from **C** produces the *transoid*-triene complex **D**, which eventually isomerizes to the *cisoid*-triene complex **E**.[17] This is precisely same as **6aa** obtained by the stoichiometric reaction.

Finally, replacement of the conjugated triene ligand by incoming **2** and **3** releases the conjugated triene product **4** with regeneration of **A**.

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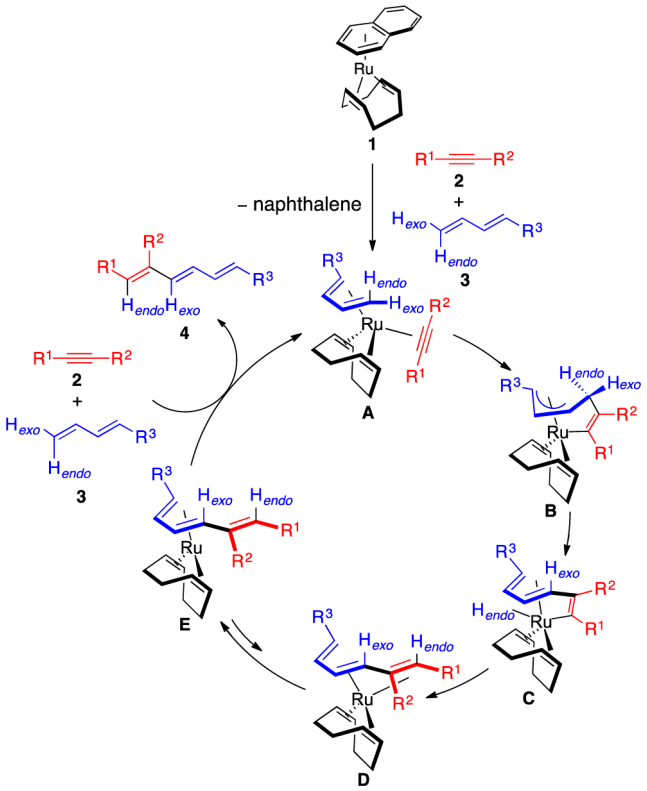
Scheme 6. Proposed Mechanism



The DFT calculations using 2-butyne and 1,3-butadiene are also consistent with this mechanism, and the energy diagram suggests that this reaction can proceed at room temperature (Figure 2).

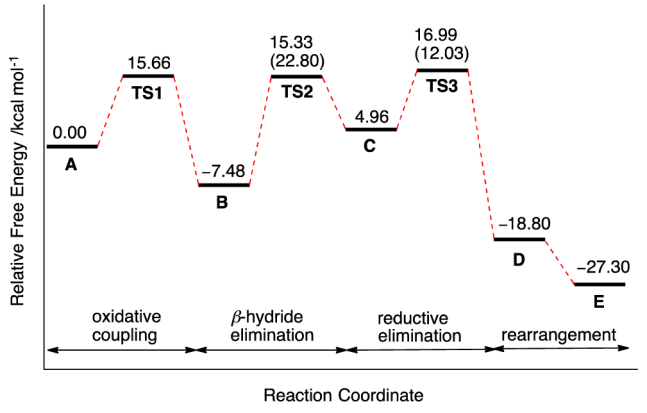


Figure 2. Energy diagram by DFT calculations for the coupling reaction of 2-butyne with 1,3-butadiene. The free energies of activation on the basis of each step are shown in parentheses in kcal mol^{-1}. Basis sets: B3LYP/LANL2DZ for Ru and 6-31G(d) for C and H, benzene (PCM).

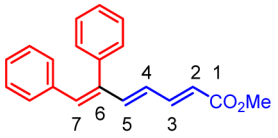
CONCLUDING REMARKS

In summary, we have developed a new protocol for the conjugated triene synthesis by the direct coupling reaction between internal alkynes and conjugated dienes. The reaction proceeds well with a wide range of internal alkynes and conjugated dienes. This new catalysis is also regarded as a direct conjugate expansion of conjugated dienes using alkynes. One of the features of the present reaction is the high regio- and stereoselectivity. Because alkynylarenes are readily available by the Sonogashira coupling reaction, this catalysis also provides a wide range of conjugated trienylarenes.

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, toluene, hexane, THF, and Et_2O were dried and purified using an Ultimate Solvent System. Acetone was dried over Drierite and distilled under nitrogen. Benzene-d_6 was dried over sodium wire and stored under vacuum, and it was transferred into an NMR tube or a 25 mL Schlenk tube by vacuum distillation prior to use. Chloroform-*d* was dried over P_2O_5 or its equivalent and stored under vacuum. Phenylacetylene (**2a**), methyl (2*E*,4*E*)-penta-2,4-dienoate (**3a**) (containing 8% of the stereoisomer), *trans*-1-phenyl-1,3-butadiene (**3b**), *trans*-1,3-pentadiene (**3c**), and methyl sorbate (**3d**) were purchased from commercial suppliers and stored under a nitrogen atmosphere after three freeze–pump–thaw cycles. Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**), 1,2-diarylacetylenes **2b–d**, and diynes **2h,i** were prepared according to the literature procedures.[18−22] 1-Phenyl-[4,4′-$^2H_2$]-1,3-butadiene (**3b**-d_2) was prepared according to a related literature procedure.[23]

Typical Reaction of Diphenylacetylene (2a) with Methyl Penta-2,4-dienoate (3a) To Give (2*E*,4*E*,6*Z*)-4aa.



(2*E*,4*E*,6*Z*)-**4aa**

Method A. In a 25 mL Schlenk tube was placed diphenylacetylene (**2a**; 99.8 mg, 0.600 mmol). After addition of benzene (1.0 mL), methyl penta-2,4-dienoate (**3a**; 65.0 μL, 0.559 mmol), and Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**; 19.4 mg, 0.0576 mmol) under a nitrogen atmosphere, the reaction mixture was stirred at room temperature for 1 h. All volatile materials were removed under reduced pressure. Recrystallization of the resulting solid from cold Et_2O gave colorless needles of **4aa** (36.5 mg, 0.126 mmol) in 22% yield. The other compounds obtained by method A were also prepared in a similar way.

Method B. Complex **1** (6.01 mg, 0.0178 mmol) was placed in an NMR tube under a nitrogen atmosphere, and **2a** (31.9 mg, 0.179 mmol) and benzene-d_6 (550 μL) were added. To the solution was added **3a** (21.0 μL, 0.181 mmol) by a hypodermic syringe at room temperature. The mixture was allowed to react at room temperature for 10 min, during which time the reaction was monitored by ^{1}H NMR spectroscopy. In order to determine the yield of the product, triphenylmethane (12.4 mg, 0.0508 mmol) was added to the reaction mixture as an internal standard. The yield of (2*E*,4*E*,6*Z*)-**4aa** was estimated as 84% along with a tiny amount of the minor isomer. The other compounds obtained by method B were also prepared in a similar way. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 3.40 (s, 3H, $-CO_2Me$), 5.57 (d, $^3J_{H-H}$ = 15.4 Hz, 1H, 2-C*H*), 5.96 (dd, $^3J_{H-H}$ = 14.9, 11.5 Hz, 1H, 4-C*H*), 6.46 (s, 1 H, 7-C*H*), 6.53 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 5-C*H*), 6.85–6.91 (m, 5H, C_6H_4), 7.00–7.03 (m, 2H, C_6H_4), 7.07–7.12 (m, 3H, C_6H_4), 7.60 (dd, $^3J_{H-H}$ = 15.4, 11.5 Hz, 1H, 3-C*H*). ^{13}C{^{1}H} NMR

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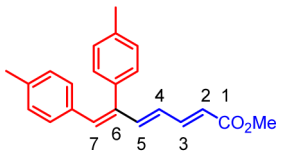
(100.5 MHz, C_6D_6, room temperature): δ 51.0, 121.2, 129.1, 129.3, 129.6, 130.1, 135.7, 136.7, 138.0, 141.3, 144.7, 145.9, 167.1. MS (EI): m/z 290 (M^+). Anal. Calcd for $C_{20}H_{18}O_2$ (290.36): C, 82.73; H, 6.25. Found: C, 82.54; H, 6.47.

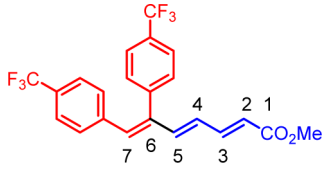
Reaction of 1,2-Bis(4-methylphenyl)acetylene (2b) with Methyl Penta-2,4-dienoate (3a) To Give (2*E*,4*E*,6*Z*)-4ba.



(2*E*,4*E*,6*Z*)-**4ba**

Using method A, the reaction of 1,2-bis(4-methylphenyl)-acetylene (**2b**; 130.0 mg (18% diyne included), 0.5168 mmol) and **3a** (65.0 μL, 0.559 mmol) in the presence of **1** (19.9 mg, 0.0591 mmol) proceeded at room temperature for 1 h. Recrystallization of the resulting crude product from cold Et_2O gave pale yellow needles of **4ba** (46.9 mg, 0.147 mmol) in 29% yield. Using method B, the reaction of **2b** (34.2 mg, 0.166 mmol) with **3a** (18.5 μL, 0.159 mmol) catalyzed by **1** (5.41 mg, 0.0160 mmol) in an NMR tube proceeded at room temperature for 22.5 h. On the basis of triphenylmethane (6.81 mg, 0.0279 mmol) as an internal standard, (2*E*,4*E*,6*Z*)-**4ba** was obtained in 70% yield along with a tiny amount of the minor isomer (4%). ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 1.94 (s, 3H, −*Me*), 2.10 (s, 3H, −*Me*), 3.40 (s, 3H, $-CO_2Me$), 5.62 (d, $^3J_{H-H}$ = 15.0 Hz, 1H, 2-C*H*), 6.04 (dd, $^3J_{H-H}$ = 14.9, 11.2 Hz, 1H, 4-C*H*), 6.52 (s, 1H, 7-C*H*), 6.60 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 5-C*H*), 6.73 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, C_6H_4), 6.92 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, C_6H_4), 6.99 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, C_6H_4), 7.01 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, C_6H_4), 7.64 (dd, $^3J_{H-H}$ = 15.0, 11.2 Hz, 1H, 3-C*H*). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, room temperature): δ 21.0, 21.2, 51.0, 120.8, 128.6, 129.2, 129.7, 130.09, 130.11, 134.2, 135.3, 135.8, 137.3, 137.7, 140.6, 144.9, 146.4, 167.3. MS (EI): m/z 318 (M^+). HRMS (APCI): $C_{22}H_{22}O_2$ (318.42) m/z 319.1694 $[M + 1H]^+$, calcd for $C_{22}H_{23}O_2$ 319.1693.

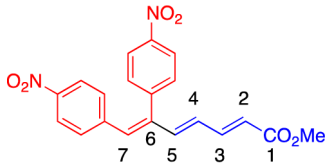
Reaction of 1,2-Bis(4-trifluoromethylphenyl)-acetyelene (2c) with Methyl Penta-2,4-dienoate (3a) To Give (2*E*,4*E*,6*Z*)-4ca.



(2*E*,4*E*,6*Z*)-**4ca**

Using method A, the reaction of 1,2-bis(4-trifluoromethylphenyl)acetylene (**2c**; 120 mg, 0.382 mmol) with **3a** (50.0 μL, 0.430 mmol) catalyzed by **1** (10.1 mg, 0.0299 mmol) proceeded at room temperature for 14 h. A yellow precipitate deposited from the solution, which was separated by a cannula tube. After the precipitate was washed three times with benzene (1 mL), the dried precipitate under vacuum was recrystallized from cold Et_2O to give **4ca** as analytically pure colorless needles (30.8 mg, 0.0722 mmol) in 19% yield. Using method B, the reaction of **2c** (49.7 mg, 0.158 mmol) with **3a** (18.5 μL, 0.159 mmol) catalyzed by **1** (5.41 mg, 0.0160 mmol) proceeded at room temperature for 12 h. On the basis of triphenylmethane (8.67 mg, 0.0355 mmol) as an internal standard, the yield of (2*E*,4*E*,6*Z*)-**4ca** was estimated as 67% along with an unidentified minor isomer (~10%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 3.72 (s, 3H, $-CO_2Me$), 5.79 (d, $^3J_{H-H}$ = 15.4 Hz, 1H, 2-C*H*), 5.88 (dd, $^3J_{H-H}$ = 15.5, 11.4 Hz, 1H, 4-C*H*), 6.81 (s, 1 H, 7-C*H*), 6.91 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 5-C*H*), 6.94 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, C_6H_4), 7.28 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, C_6H_4), 7.36 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, C_6H_4), 7.37 (1H, 3-C*H*, overlapped with resonances for C_6H_4), 7.69 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, C_6H_4). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ −62.7 (s, 3F, CF_3), −62.4 (s, 3F, CF_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, room temperature): δ 51.6, 122.0, 125.2, 126.2, 129.6, 129.8, 130.2, 134.0, 139.0, 140.7, 141.5, 143.8, 144.0, 167.3. MS (EI): m/z 426 (M^+). HRMS (APCI): $C_{22}H_{16}F_6O_2$ (426.36) m/z 427.1138 $[M + 1H]^+$, calcd for $C_{22}H_{17}F_6O_2$ 427.1127.

Reaction of 1,2-Bis(4-nitrophenyl)acetylene (2d) with Methyl Penta-2,4-Dienoate (3a) To Give (2*E*,4*E*,6*Z*)-4da.



(2*E*,4*E*,6*Z*)-**4da**

Using method A, the reaction of 1,2-bis(4-nitrophenyl)-acetylene (**2d**; 119.1 mg, 0.444 mmol) with **3a** (53.0 μL, 0.456 mmol) was catalyzed by **1** (15.8 mg, 0.0469 mmol) at room temperature for 40.5 h. All volatile materials were removed under reduced pressure. After recrystallization from cold chloroform and recycle HPLC using a GPC column, the resulting solid gave a yellow powder of **4da** (15.0 mg, 0.0394 mmol) in 9% yield. Using method B, the reaction of **2d** (39.9 mg, 0.149 mmol) with **3a** (18.0 μL, 0.155 mmol) was catalyzed by **1** (5.14 mg, 0.0152 mmol) in benzene-d_6 (600 μL) at room temperature for 22 h. On the basis of triphenylmethane (8.22 mg, 0.0336 mmol) as an internal standard, the yield of (2*E*,4*E*,6*Z*)-**4da** was estimated as 78% along with a tiny amount of the minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 3.73 (s, 3H, $-CO_2Me$), 5.81 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 2-C*H*), 5.90 (dd, $^3J_{H-H}$ = 15.2, 11.5 Hz, 1H, 4-C*H*), 6.88 (s, 1H, 7-C*H*), 6.92 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 5-C*H*), 6.99 (AA′BB′, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = −0.5 Hz, $^5J_{H-H}$ = 0.5 Hz, 2H, C_6H_4), 7.35 (AA′BB′, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = −0.5 Hz, $^5J_{H-H}$ = 0.5 Hz, 2H, C_6H_4), 7.60 (1 H, 3-C*H*, overlapped with resonances for C_6H_4), 7.97 (AA′BB′, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, C_6H_4), 8.31 (d, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = −1.0 Hz, $^5J_{H-H}$ = 0.1 Hz, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, room temperature): δ 51.6, 123.0, 123.6, 124.6, 130.0, 130.4, 131.3, 133.3, 141.7, 142.3, 142.9, 143.3, 143.5, 146.7, 147.8, 167.1. MS (EI): m/z 380 (M^+). HRMS (APCI): $C_{20}H_{16}N_2O_6$ (380.36) m/z 381.1076 $[M + 1H]^+$, calcd for $C_{20}H_{17}N_2O_6$ 381.1081.

Reaction of 3-Hexyne (2e) with Methyl Penta-2,4-Dienoate (3a) To Give (2*E*,4*E*,6*E*)-4ea.

(2*E*,4*E*,6*E*)-**4ea**

Using method A, the reaction of 3-hexyne (**2e**; 100.0 μL, 0.860 mmol) with **3a** (100.0 μL, 0.880 mmol) was catalyzed by **1** (11.3 mg, 0.0333 mmol) at room temperature for 1 h. After the

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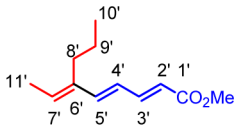
reaction mixture was evaporated, the crude product was directly purified by flash chromatography using silica gel (hexane/Et_2O = 9/1) to give a yellow oil of (2*E*,4*E*,6*E*)-**4ea** (99.4 mg, 0.512 mmol) in 60% yield. Using method B, the reaction of 3-hexyne (**2e**; 26.0 μL, 0.229 mmol) with **3a** (27.0 μL, 0.232 mmol) was catalyzed by **1** (7.8 mg, 0.023 mmol) in C_6D_6 (600 μL) at room temperature for 10 min. On the basis of triphenylmethane (18.0 mg, 0.0737 mmol) as an internal standard, the product was determined by NMR and GLC/GC-MS to be (2*E*,4*E*,6*E*)-**4ea** (76% yield) and isomer (15% yield). ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.82 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 9-C*H*$_3$), 0.86 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 11-C*H*$_3$), 1.90 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 8-C*H*$_2$), 2.03 (q, $^3J_{H-H}$ = 7.4 Hz, 2H, 10-C*H*$_2$), 3.48 (s, 3H, 1-CO_2C*H*$_3$), 5.34 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 7-C*H*), 5.91 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 2-C*H*), 6.12 (dd, $^3J_{H-H}$ = 15.2, 10.9 Hz, 1H, 4-C*H*), 6.22 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 5-C*H*), 7.52 (dd, $^3J_{H-H}$ = 15.2, 10.9 Hz, 1H, 3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, room temperature): δ 13.74, 13.99, 19.77, 21.77, 50.97, 119.80, 123.72, 139.26, 139.66, 144.82, 145.85, 167.20. MS (EI): *m*/*z* 194 (M^+). HRMS (APCI): $C_{12}H_{18}O_2$ (194.27) *m*/*z* 195.1377 $[M + 1H]^+$, calcd for $C_{12}H_{19}O_2$ 195.1380.

Reaction of 2-Hexyne (2f) with Methyl Penta-2,4-Dienoate (3a) To Give (2*E*,4*E*,6*E*)-4fa and (2*E*,4*E*,6*E*)-4fa′.

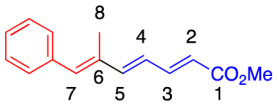
(2*E*,4*E*,6*E*)-**4fa**



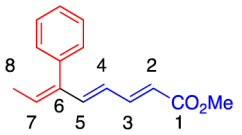
(2*E*,4*E*,6*E*)-**4fa'**

In an NMR tube was placed **1** (7.24 mg, 0.0215 mmol), and benzene-d_6 (600 μL) was introduced into the tube by vacuum distillation. Then 2-hexyne (24.0 μL, 0.214 mmol) and **3a** (25.0 μL, 0.215 mmol) were added by a hypodermic syringe at room temperature. After 10 min, dibenzyl (6.60 mg, 0.0362 mmol, internal standard) was added to the reaction mixture as an internal standard. The yield of the product was determined by ^{1}H NMR and by GLC and GC-MS. The total yields of (2*E*,4*E*,6*E*)-**4fa** and -**4fa**′ were estimated as 70% (**4fa**/**4fa**′ = 50/50) along with a minor isomer. Data for **4fa** are as follows. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.78 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 10-*Me*, overlapped with resonances for 10′−*Me*), 1.18−1.28 (m, 1H, 9-C*H*$_2$, overlapped with resonances for 9′-C*H*$_2$), 1.50 (s, 3H, 11−*Me*), 1.90 (q, $^3J_{H-H}$ = 7.5 Hz, 2H, 8-C*H*$_2$), 2.73 (s, 3H, 1-CO_2*Me*, overlapped with resonances for 1′-CO_2*Me*), 5.39−5.43 (br, 1H, 7-C*H*, overlapped with resonances for 7′-C*H*), 5.95 (d, $^3J_{H-H}$ = 15.4 Hz, 1H, 2-C*H*), 6.05 (dd, $^3J_{H-H}$ = 15.2, 10.9 Hz, 1H, 4-C*H*), 6.29 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 5-C*H*), 7.56 (dd, $^3J_{H-H}$ = 15.4, 10.9 Hz, 1H, 3-C*H*). Data for **4fa**′ are as follows. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.78 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 10′-*Me*, overlapped with resonances for 10-CH_3), 1.18−1.28 (m, 1H, 9′-C*H*$_2$, overlapped with resonances for 9-C*H*$_2$), 1.47 (d, $^3J_{H-H}$ = 7.8 Hz, 3H, 11′-*Me*), 2.03 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, 8′-C*H*$_2$), 2.73 (s, 3H, 1′-CO_2*Me*, overlapped with resonances for 1-CO_2*Me*), 5.39−5.43 (br, 1H, 7′-C*H*, overlapped with resonances for 7-C*H*), 5.92 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 2′-C*H*), 6.12 (dd, $^3J_{H-H}$ = 15.5, 10.3 Hz, 1H, 4′-C*H*), 6.20 (d, $^3J_{H-H}$ *J* = 15.5 Hz, 1H, 5′-C*H*), 7.53 (dd, $^3J_{H-H}$ = 14.9, 10.6 Hz, 1H, 3′-C*H*). MS (EI): *m*/*z* 194 (M^+). These compounds were characterized by spectroscopic methods.

Reaction of 1-Phenyl-1-Propyne (2g) with Methyl Penta-2,4-dienoate (3a) To Give (2*E*,4*E*,6*E*)-4ga and (2*E*,4*E*,6*Z*)-4ga′.



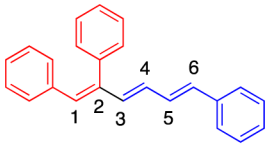
(2*E*,4*E*,6*E*)-**4ga**



(2*E*,4*E*,6*Z*)-**4ga'**

Using method A, the reaction of 1-phenyl-1-propyne (**2g**; 170 μL, 1.38 mmol) with **3a** (170 μL, 1.46 mmol) was catalyzed by **1** (51.2 mg, 0.152 mmol) at room temperature for 1 day, during which time a white precipitate deposited from the solution. The precipitate was separated by a cannula tube. After the precipitate was washed with hexane, the precipitate was dried under reduced pressure to give **4ga** as an analytically pure white powder (125.1 mg, 0.548 mmol) in 40% yield. In addition to the precipitate, **4ga** was also obtained from the mother liquor and the crude product was purified by flash chromatography using silica gel (hexane/ethyl acetate 1/0 to 30/1) to give a yellow oil of methyl (2*E*,4*E*,6*E*)-6-methyl-7-phenylhepta-2,4,6-triene ((2*E*,4*E*,6*E*)-**4ga**; 111.4 mg, 0.488 mmol). The total yield of (2*E*,4*E*,6*E*)-**4ga** was 75%. The regioisomer, methyl (2*E*,4*E*,6*Z*)-6-phenylocta-2,4,6-triene ((2*E*,4*E*,6*Z*)-**4ga**′), was also obtained in 4% yield. Using method B, the reaction of 1-phenyl-1-propyne (**2g**; 25.0 μL, 0.203 mmol) with methyl 2,4-pentadienoate (**3a**; 24.0 μL, 0.206 mmol) was catalyzed by **1** (6.8 mg, 0.020 mmol) at room temperature for 5 min. The reaction was monitored by ^{1}H NMR spectroscopy. Yields: (2*E*,4*E*,6*E*)-**4ga**, 70%; (2*E*,4*E*,6*Z*)-**4ga**′, 4%. Along with these products, unidentified isomers (*m*/*z* 228) were also formed in 28% yield. Data for (2*E*,4*E*,6*E*)-**4ga** are as follows. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 1.70 (s, 3H, 8-*Me*), 3.49 (s, 3H, 1-CO_2*Me*), 5.96 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 2-C*H*), 6.13 (dd, $^3J_{H-H}$ = 15.2, 11.4 Hz, 1H, 4-C*H*), 6.35 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 5-C*H*), 6.39 (s, 1H, 7-CH), 7.3−7.0 (m, 5 H, *Ph*), 7.57 (dd, $^3J_{H-H}$ = 15.1, 11.4 Hz, 1H, 3-C*H*). MS (EI): *m*/*z* 228 (M^+). Anal. Calcd for $C_{15}H_{16}O_2$ (228.29): C, 78.92; H, 7.06. Found: C, 78.67; H, 6.62. Data for (2*E*,4*E*,6*Z*)-**4ga**′ are as follows. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 1.39 (d, $^3J_{H-H}$ = 7.4 Hz, 3H, *Me*), 3.39 (s, 3H, 1-CO_2*Me*), 5.57 (d, $^3J_{H-H}$ = 15.8 Hz, 1H, 2-C*H*), 5.58 (q, $^3J_{H-H}$ = 7.2 Hz, 1H, 7-C*H*), 5.88 (dd, $^3J_{H-H}$ = 15.2, 11.4 Hz, 1H, 4-C*H*), 6.42 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 5-C*H*), 7.3−7.0 (m, 5H, *Ph*), 7.56 (dd, $^3J_{H-H}$ = 16.3, 11.4 Hz, 1H, 3-C*H*). MS (EI): *m*/*z* 228 (M^+). This minor compound was only characterized by spectroscopic methods.

Reaction of Diphenylacetylene (2a) with 1-Phenyl-1,3-Butadiene (3b) To Give (1*Z*,3*E*,5*E*)-4ab.



(1*Z*,3*E*,5*E*)-**4ab**

Using method A, the reaction of diphenylacetylene (**2a**; 109.12 mg, 0.6122 mmol) with 1-phenyl-1,3-butadiene (**3b**; 90.0 μL, 0.642 mmol) was catalyzed by **1** (20.43 mg, 0.0605 mmol) at room temperature for 1 h. After workup procedures, the crude product was obtained as a brown solid (179.4 mg). A part of the product (54.3 mg) purified by recycle HPLC gave a pale yellow powder of (1*Z*,3*E*,5*Z*)-**4ab** (16.7 mg, 0.0541 mmol) in

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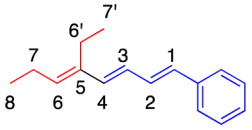
Organometallics XXXX, XXX, XXX−XXX

9% yield. Using method B, the reaction of **2a** (32.1 mg, 0.180 mmol) with **3b** (25.0 μL, 0.177 mmol) was catalyzed by **1** (5.94 mg, 0.0176 mmol) in benzene (600 μL) at room temperature for 1 h to give (1*Z*,3*E*,5*E*)-**4ab** in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 5.94 (dd, $^3J_{H-H}$ = 14.9, 12.9 Hz, 1H, 4-C*H*), 6.37 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 6-C*H*), 6.57 (s, 1H, 1-C*H*), 6.69 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 3-C*H*), 6.81−6.83 (m, 2H, *Ph*), 6.85 (dd, $^3J_{H-H}$ = 15.5, 10.9 Hz, 1H, 5-C*H*), 7.00−7.05 (m, 3H, *Ph*), 7.12−7.16 (m, 3H, *Ph*), 7.23 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *Ph*), 7.30−7.39 (m, 5H, *Ph*). ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 6.07 (d, $^3J_{H-H}$ = 15.4 Hz, 1 H, 6-C*H*), 6.19 (dd, $^3J_{H-H}$ = 15.4, 10.6 Hz, 1 H, 4-C*H*), 6.63 (s, 1 H, 1-C*H*), 6.63 (d, $^3J_{H-H}$ = 15.4 Hz, 1 H, 3-C*H*), 6.86 (dd, $^3J_{H-H}$ = 15.5, 10.9 Hz, 1 H, 5-C*H*), 6.86−7.24 (m, 15 H, *Ph*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 126.3, 126.9, 127.4, 128.0, 128.6 128.9, 129.1, 129.3, 129.4, 131.7, 132.0, 132.8, 136.8, 137.4, 138.3, 138.6, 141.9. MS (EI): *m*/*z* 308 (M^+). HRMS (APCI): $C_{24}H_{12}$ (308.42) *m*/*z* 308.1552 (M^+), calcd for $C_{24}H_{20}$ 308.1560.

Reaction of 3-Hexyne (3e) with 1-Phenyl-1,3-butadiene (3b) To Give (1*E*,3*E*,6*E*)-4eb.



(1*E*,3*E*,6*E*)-**4eb**

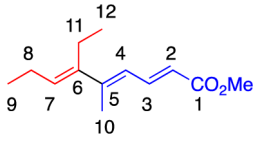
Using method A, the reaction of 3-hexyne (**2e**; 80.0 μL, 0.704 mmol) with 1-phenyl-1,3-butadiene (**3b**; 100.0 μL, 0.713 mmol) was catalyzed by **1** (23.3 mg, 0.0691 mmol) at room temperature for 1 h. The crude product was directly purified by flash chromatography using silica gel (hexane) to give a colorless oil of (1*E*,3*E*,6*E*)-**4eb** (35.6 mg, 0.168 mmol). The yield of **4eb** was 24%. Using method B, the reaction of 3-hexyne (**2e**; 24.0 μL, 0.211 mmol) with (*E*)-1-phenyl-1,3-butadiene (30.0 μL, 0.214 mmol) was catalyzed by **1** at room temperature for 30 min. On the basis of dibenzyl (11.3 mg, 0.0620 mmol) as an internal standard, (1*E*,3*E*,5*E*)-**4eb** was obtained in 82% yield along with the isomer in 10% yield. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.92 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 8-CH_3), 1.05 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 7′-CH_3), 2.03 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 7-CH_2), 2.24 (q, $^3J_{H-H}$ = 7.5 Hz, 2H, 6′-CH_2), 5.44 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 6-C*H*), 6.27 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 4-C*H*), 6.39 (dd, $^3J_{H-H}$ = 15.5, 10.3 Hz, 1H, 3-C*H*), 6.44 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 1-C*H*), 6.84 (dd, $^3J_{H-H}$ = 15.5, 10.3 Hz, 1H, 2-C*H*), 7.04 (t, $^3J_{H-H}$ = 7.44 Hz, 1H, *p*-*Ph*), 7.12−7.16 (2H, *m*-*Ph*, overlapped with resonances for C_6D_5H), 7.30 (d, $^3J_{H-H}$ = 7.48 Hz, 2H, *o*-*Ph*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 14.1, 14.4, 20.2, 21.8, 126.6, 126.8, 127.4, 128.9, 130.4, 131.6, 135.2, 137.4, 138.2, 140.2. MS (EI): *m*/*z* 212 (M^+) HRMS (APCI): $C_{16}H_{20}$ (212.34) *m*/*z* 213.1642 $[M + 1H]^+$, calcd for $C_{16}H_{21}$ 213.1638.

Reaction of 3-Hexyne (2e) with *trans*-1,3-Pentadiene (3c) To Give (2*E*,4*E*,6*E*)-4ec.

(2*E*,4*E*,6*E*)-**4ec**

Using method A, the reaction of 3-hexyne (**2e**; 80.0 μL, 0.704 mmol) with *trans*-1,3-pentadiene (**3c**; 80.0 μL, 0.793 mmol) was catalyzed by **1** (26.6 mg, 0.0790 mmol) at room temperature for 1 h. After the reaction mixture was evaporated, the crude product was directly purified by flash chromatography using silica gel (hexane) to give a colorless liquid of (2*E*,4*E*,6*E*)-**4ec** (26.4 mg, 0.176 mmol) in 21% yield. Using method B, the reaction of 3-hexyne (**2e**; 30.0 μL, 0.264 mmol) with **3c** (30.0 μL, 0.301 mmol) was catalyzed by **1** (9.8 mg, 0.029 mmol) in benzene-d_6 (600 μL) at room temperature for 5 min. On the basis of dibenzyl (13.5 mg, 0.0741 mmol) as an internal standard, the product was determined by NMR and GLC/GC-MS. Yields: (2*E*,4*E*,6*E*)-**4ec**, 77%; isomer, 5%. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.90 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 9-*Me*), 1.01 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 11-*Me*), 1.63 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, 1−*Me*), 2.01 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 8-CH_2), 2.19 (q, $^3J_{H-H}$ = 7.4 Hz, 2H, 10-CH_2), 5.37 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, 7-C*H*), 5.57 (dq, $^3J_{H-H}$ = 15.0, 7.5 Hz, 1H, 2-C*H*), 6.12 (d, $^3J_{H-H}$ = 15.5 Hz, 1H, 5-C*H*), 6.14 (m, 1H, 3-C*H*), 6.27 (dd, $^3J_{H-H}$ = 15.4, 10.3 Hz, 1H, 4-C*H*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 14.1, 14.5, 18.3, 20.1, 21.6, 126.6, 128.6, 133.1, 133.8, 134.5, 140.0. MS (EI): *m*/*z* 150 (M^+). HRMS (APCI): $C_{11}H_{18}$ (150.14) *m*/*z* 151.1485 $[M + 1H]^+$, calcd for $C_{11}H_{18}$ 151.1481.

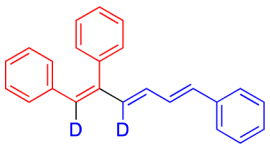
Reaction of 3-Hexyne (2e) with Methyl 2,4-Hexadienoate (3d) To Give (2*E*,4*E*,6*E*)-4ed.



(2*E*,4*E*,6*E*)-**4ed**

Reaction of 3-hexyne (**2e**; 32.0 μL, 0.282 mmol) with methyl hexa-2,4-dienoate (**3d**) in benzene-d_6 (0.255 mmol/100 μL, 110 μL, 0.281 mmol) was catalyzed by **1** (9.6 mg, 0.029 mmol) in C_6D_6 (710 μL) at 50 °C for 27 h. On the basis of dibenzyl (13.7 mg, 0.0752 mmol) as an internal standard, the product was determined by NMR and GLC/GC-MS. Yields: (2*E*,4*E*,6*E*)-**4ed**, 17%; isomer, 1%. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.85 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 8-*Me*), 0.87 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, 10-*Me*), 1.67 (s, 3H, 5-*Me*), 1.94 (quint, $^3J_{H-H}$ = 7.4 Hz, 2H, 7-CH_2), 2.12 (q, $^3J_{H-H}$ = 7.4 Hz, 2H, 9-CH_2), 3.48 (s, 3 H, 1-CO_2*Me*), 5.51 (t, $^3J_{H-H}$ = 7.48 Hz, 1H, 6-C*H*), 5.98 (d, $^3J_{H-H}$ = 14.9 Hz, 1H, 2-C*H*), 6.24 (d, $^3J_{H-H}$ = 11.4 Hz, 1H, 4-C*H*), 7.96 (dd, $^3J_{H-H}$ = 15.2, 12.0 Hz, 1H, 3-C*H*). MS (EI): *m*/*z* 208 (M^+). This compound was only characterized by spectroscopic methods.

Reaction of Diphenylacetylene (2a) with 1-Phenyl-[4,4-$^2H_2$]-1,3-butadiene (3b-d_2) To Give (1*E*,3*E*,5*E*)-[1,3-$^2H_2$]-4ab-d_2.



(1*Z*,3*E*,5*E*)-[1,3-$^2H_2$]-**4ab**-d_2

Reaction of **2a** (44.5 mg, 0.250 mmol) with **3b**-d_2 (33.3 mg, 0.247 mmol; 83 atom % D) was catalyzed by **1** (2.45 mg, 0.00726 mmol) in benzene-d_6 (600 μL) at room temperature for 24 h to give (1*Z*,3*E*,5*E*)-**4ab**-d_2. On the basis of triphenylmethane (7.74 mg, 0.0317 mmol) as an internal standard, the yield of (1*Z*,3*E*,5*E*)-**4ab**-d_2 was estimated as 82%, and the deuterium contents at C(1) and C(3) positions were 75 atom % D and 82 atom % D, respectively. ^{1}H NMR (400

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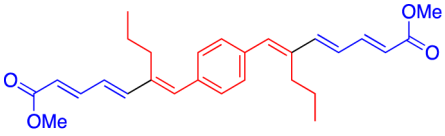
MHz, C_6D_6, room temperature): δ 6.07 (d, $^3J_{H-H}$ = 15.6 Hz, 1 H, 6-C*H*), 6.17 (d, $^3J_{H-H}$ = 10.9 Hz, 1 H, 4-C*H*), 6.86 (dd, $^3J_{H-H}$ = 15.6, 10.9 Hz, 1 H, 5-C*H*), 6.83−7.24 (m, 15 H, *Ph*). ^{2}H NMR (61.4 MHz, C_6H_6, room temperature): δ 6.6 (br, 1-C*D*═ and 3-C*D*═).

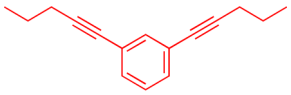
Reaction of 1,4-Bis(1-pentynyl)benzene (2h) with Methyl Penta-2,4-dienoate (3a) To Give (1*E*,1′*E*,3*E*,3′*E*,5*E*,5′*E*)-4ha.



(1*E*,1'*E*,3*E*,3'*E*,5*E*,5'*E*)-**4ha**

Reaction of **2h** (105.7 mg, 0.503 mmol) with **3a** (150 μL, 1.30 mmol) catalyzed by **1** (17.0 mg, 0.0504 mmol) gave a light yellow-brown precipitate within 4 days at room temperature, which was separated by a cannula tube and washed with hexane to give analytically pure **4ha** (133.1 mg, 0.307 mmol) in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.02 (t, $^3J_{H-H}$ = 7.5 Hz, 6H, −CH_2CH_2*Me*), 1.61 (sext, $^3J_{H-H}$ = 7.4 Hz, 4H, −CH_2CH_2Me), 2.48 (m, 4H, -CH_2CH_2Me), 3.74 (s, 6H, CO_2*Me*), 5.92 (d, $^3J_{H-H}$ = 15.5 Hz, 2H, ═C*H*−), 6.42 (dd, $^3J_{H-H}$ = 15.2, 11.2 Hz, 2H, ═C*H*−), 6.59 (s, 2H, ArC*H*═), 6.64 (d, $^3J_{H-H}$ = 15.5 Hz, 2H, ═C*H*−), 7.30 (s, 4H, aromatic), 7.39 (dd, $^3J_{H-H}$ = 10.9, 15.5 Hz, 2H, ═C*H*−). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, room temperature): δ 14.39, 22.37, 29.49, 51.53, 119.93, 125.62, 129.10, 135.10, 136.10, 140.61, 145.32, 145.68, 167.63. Mp (air): 156.1−157.5 °C. λ_{max} (CH_2Cl_2, 1.10 × 10^{-5} M): 384 nm; ε (384 nm) 6.62 × 10^4 L mol^{-1} cm^{-1}. Anal. Calcd for $C_{20}H_{34}O_4$ (424.58): C, 77.39; H, 7.89. Found: C, 77.73; H, 8.31.

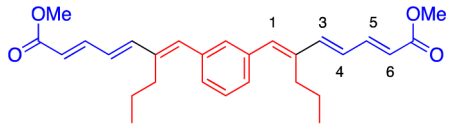
Preparation of 1,3-Bis(1-pentynyl)benzene (2i).



2i

Similar to the case for 1,4-bis(1-pentynyl)benzene (**2h**),[22] **2i** was prepared as follows. Reaction of 1,3-diiodobenzene (996.9 mg, 3.022 mmol) with 1-pentyne (720 μL, 7.30 mmol) in the presence of CuI (120.8 mg, 0.6341 mmol) and $PdCl_2(PPh_3)_2$ (90.6 mg, 0.129 mmol) in THF (31 mL) and NEt_3 (31 mL) at room tempearture in the dark for 13 h resulted in deposition of a white powder. After addition of saturated NH_4Cl/H_2O, the organic layer was separated and dried over $MgSO_4$ and evaporated to give an umber oil. After silica gel column chromatography using hexane, **2i** was obtained as an umber oil (449.2 mg, 2.136 mmol) in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 1.02 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, *Me*), 1.60 (sext, $^3J_{H-H}$ = 7.2 Hz, 4H, CH_2), 2.35 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, CH_2), 7.16 (AMM′N, $^3J_{H-H}$ = 5.75 Hz, $^5J_{H-H}$ = 0.30 Hz, 1H, C_6H_4), 7.26 (AMM′N, $^3J_{H-H}$ = 5.75 Hz, $^4J_{H-H}$ = −0.86 Hz, 2H, C_6H_4), 7.42 (AMM′N, $^4J_{H-H}$ = −0.86 Hz, $^5J_{H-H}$ = 0.30 Hz, 1H, C_6H_4). This compound was used for further reaction without elemental analysis.

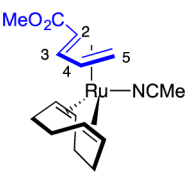
Reaction of 1,3-Bis(1-pentynyl)benzene (2i) with Methyl Penta-2,4-dienoate (3a) To Give (1*E*,1′*E*,3*E*,3′*E*,5*E*,5′*E*)-4ia.



(1*E*,1'*E*,3*E*,3'*E*,5*E*,5'*E*)-**4ia**

Reaction of **2i** (98.5 mg, 0.468 mmol) with **3a** (135 μL, 1.17 mmol) catalyzed by **1** (15.89 mg, 0.04710 mmol) at room temperature for 20 h gave a reddish brown solution. The reaction system was quenched by bubbling of air. After removal of solvent, the resulting black oil was purified by silica gel chromatography (AcOEt/hexane 1/5). Removal of the solvent of a fraction gave a lemon-yellow oil of **4ia** as a yellow oil (198.0 mg, 0.456 mmol) in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 0.97 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, −CH_2CH_2*Me*), 1.54 (m, partly overlapped with water in C_6D_6, −CH_2CH_2Me), 2.44 (m, 4H, -CH_2CH_2Me), 3.74 (s, 6H, CO_2*Me*), 5.92 (d, $^3J_{H-H}$ = 15.4 Hz, 2H, 6-C*H*), 6.42 (dd, $^3J_{H-H}$ = 15.2, 11.2 Hz, 2H, 4-C*H*), 6.61 (s, 2H, 1-C*H*), 6.64 (d, $^3J_{H-H}$ = 15.5 Hz, 2H, 3-C*H*), 7.19 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, aromatic), 7.20 (s, 1H, aromatic), 7.38 (t, $^3J_{H-H}$ = 6,3 Hz, 1H, aromatic), 7.40 (dd, $^3J_{H-H}$ = 15.5, 11.2 Hz, 2H, 5-C*H*). This compound was only characterized by spectroscopic methods.

Synthesis of Ru(η^4-methyl penta-2,4-dienoate)(η^4-1,5-COD)(NCMe) (5a).



5a

According to a previous report,[15] complex **5a** was prepared as follows. Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**; 146.4 mg, 0.4339 mmol) was dissolved in acetonitrile (5 mL), and then (*E*)-methyl penta-2,4-dienoate (**3a**; 50.0 μL, 0.430 mmol) was added by a hypodermic syringe. After 5 h of reaction at room temperature, all volatile materials were removed under reduced pressure and the resulting yellow oil was crystallized from cold hexane/Et_2O to give yellow crystals of **5a** (110.9 mg, 0.3060 mmol) in 71% yield. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.65−0.67 (d, $^3J_{H-H}$ = 8.6 Hz, 1H, 5-*endo*-C*H*), 0.74 (s, 3H, NC*Me*), 1.60−1.62 (d, $^3J_{H-H}$ = 7.4 Hz, 1H, 2-*endo*-C*H*), 1.69−1.70 (d, $^3J_{H-H}$ = 6.3 Hz, 1H, 5-*exo*-C*H*), 1.91−2.03 (m, 3H, CH_2 in COD), 2.14−2.21 (m, 1H, CH_2 in COD), 2.29−2.32 (m, 1H, CH_2 in COD), 2.39−2.43 (m, 1H, CH_2 in COD), 2.50−2.54 (m, 1H, CH_2 in COD), 2.61−2.66 (m, 1H, CH_2 in COD), 2.86−2.89 (m, 1H, C*H* in COD), 3.36−3.40 (m, 1H, C*H* in COD), 3.46 (s, 3H, CO_2*Me*), 4.54−4.56 (m, 1H, C*H* in COD), 4.87−4.92 (br q, ^3J = 7.4 Hz, 1H, 4-C*H*), 6.18−6.21 (dd, $^3J_{H-H}$ = 7.4, 5.2 Hz, 1H, 3-C*H*). This compound was only characterized by spectroscopic methods.

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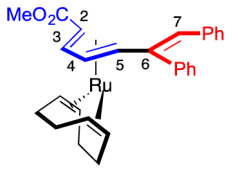
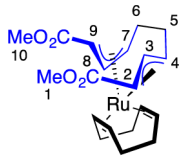
Reaction of Ru(η^4-methyl penta-2,4-dienoate)(η^4-1,5-COD)(NCMe) (5a) with Diphenylacetylene (2a) To Give 6aa.



6aa

Ru(η^4-methyl penta-2,4-dienoate)(η^4-1,5-COD)(NCMe) (**5a**; 19.1 mg, 0.0527 mmol) was treated with **2a** (11.6 mg, 0.0651 mmol) in benzene at room temperature for 1 h. After removal of volatile materials, the residue was recrystallized from cold benzene/hexane to give pale yellow microcrystals of **6aa** (14.7 mg, 0.0272 mmol) in 52% yield. ^{1}H NMR (400 MHz, C_6D_6, room temperature) δ 1.10−1.35 (m, 2H, COD), 1.57−1.70 (m, 1H, COD), 2.01−2.10 (m, 2H, COD), 1.95−2.05 (m, 1H, COD), 2.20−2.30 (m, 1H, COD), 2.55−2.60 (m, 1H, COD), 2.60−2.70 (m, 1H, COD), 2.74 (t, $^3J_{H-H}$ = 4.6 Hz, 1H, 4-C*H*), 2.93 (d, $^3J_{H-H}$ = 4.6 Hz, 1H, 5-C*H*), 2.98−3.12 (m, 1H, COD), 3.59 (s, 3H, −CO_2*Me*), 3.78−3.90 (m, 2H, COD), 4.24 (d, $^3J_{H-H}$ = 8.6 Hz, 1H, 2-C*H*), 4.35−4.55 (m, 1H, COD), 5.16 (s, 1H, 7-C*H*), 5.24 (dd, $^3J_{H-H}$ = 8.6, 5.2 Hz, 1H, 3-C*H*), 7.4−6.9 (m, Ph, 10H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, room temperature): δ 25.69 (*C*H_2 in COD), 26.69 (*C*H_2 in COD), 34.24 (*C*H_2 in COD), 38.89 (*C*H_2 in COD), 39.19 (2-*C*H), 50.86 (−CO_2*Me*), 51.31 (7-*C*H), 73.55 (*C*H in COD), 78.12 (*C*H in COD), 80.99 (*C*H in COD), 81.56 (4-CH), 85.30 (5-*C*H), 88.76 (*C*H in COD), 106.83 (3-CH), 112.83 (6-*C*), 124.94 (CH in Ph), 126.45 (CH in Ph), 127.80 (CH in Ph), 128.29 (CH in Ph), 128.73 (CH in Ph), 128.90 (CH in Ph), 138.23 (8-*C*), 146.08 (9-*C*), 174.83 (1-*C*). This compound was only characterized by spectroscopic methods.

Reaction of 6aa with Methyl Penta-2,4-Dienoate (3a) To Give 7a.

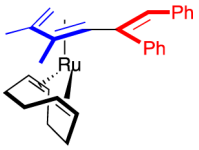


7a

Treatment of **6aa** (15.7 mg, 0.0272 mmol) with 2 equiv of **3a** and triphenylmethane as an internal standard at room temperature for 2 h gave liberation of **4aa** in 91% yield with concomitant formation of the bis(η^3-allylic)ruthenium(II) complex **7a** in 55% yield. Alternatively, **7aa** was directly prepared by the reaction of **6aa** with **3a**. Treatment of **6aa** (7.1 mg, 0.020 mmol) with **3a** (2.4 μL, 0.021 mmol) in the presence of triphenylmethane as an internal standard (7.8 mg, 0.0319 mmol) at room tempearture for 3 days gave *supine,prone*-**7a** in 77% yield. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.58−0.64 (m, 2H, 5-C*H*), 1.44−1.59 (m, 2H, CH_2 in COD), 1.67−1.72 (m, 2H, CH_2 in COD), 1.82−1.88 (m, 2H, CH_2 in COD), 1.83−1.85 (m, 1H, 4-C*H*), 2.07−2.14 (m, 1H, CH_2 in COD), 2.52−2.59 (m, 1H, CH_2 in COD), 2.97−2.99 (d, $^3J_{H-H}$ = 9.7 Hz, 1H, 9-C*H*), 3.36 (s, 3H, 1 or 10−*Me*), 3.38−3.49 (m, 1H, C*H* in COD), 3.50−3.52 (d, $^3J_{H-H}$ = 9.8 Hz, 1H, 2-C*H*), 3.57−3.62 (m, 1H, C*H* in COD), 3.65 (s, 3H, 10- or 1−*Me*), 3.78−3.82 (m, 1H, C*H* in COD), 4.21−4.26 (m, 1H, C*H* in COD), 4.77−4.82 (t, $^3J_{H-H}$ = 9.7 Hz, 1H, 3-C*H*), 4.82−4.86 (m, 1H, 7-C*H*), 5.32−5.35 (t, $^3J_{H-H}$ = 9.7 Hz, 1H, 8-C*H*). By an independent reaction, we have confirmed the molecular structure of **7a** by an X-ray structure analysis.

Reaction of Ru(η^4-methyl penta-2,4-dienoate)(η^4-1,5-COD)(NCMe) (5a) with 3-Hexyne (2e) and Methyl Penta-2,4-dienoate (3a). In an NMR tube was placed **5a** (6.8 mg, 0.019 mmol), and benzene-d_6 was introduced into the tube by vacuum distillation. **2e** (2.2 μL, 0.019 mmol) was added to the solution by a hypodermic syringe. After addition of mesitylene (2.6 μL, 0.019 mmol) as an internal standard at room temperature, ^{1}H NMR was measured. The ^{1}H NMR spectrum suggested formation of a mixture involving the triene complex (48%) and **4ea** (36%), and subsequent addition of **3a** (2.4 μL, 0.020 mmol) produced (2*E*,4*E*,6*E*)-**4ea** in 80% yield with recovery of **5a** in 63% yield.

Reaction of Ru(η^4-2,3-dimethylbutadiene)(η^4-1,5-COD)(NCMe) (5e) with Diphenylacetylene (2a) To Give 6ae.



6ae

Ru(η^4-2,3-dimethylbutadiene)(η^4-1,5-COD)(NCMe) (**5e**;[15] 101.1 mg, 0.3041 mmol) was treated with **2a** (54.4 mg, 0.305 mmol) in benzene at room temperature for 22 h. After removal of volatile materials, the residue was recrystallized from cold Et_2O/hexane to give yellow microcrystals of **6ae** (79.1 mg, 0.155 mmol) in 51% yield. ^{1}H NMR (400 MHz, C_6D_6, room temperature) δ 0.91−0.98 (m, 1H, COD), 1.02 (s, 3H, 3−*Me*), 1.18−1.32 (m, 2H, COD), 1.44 (s, 3H, 2−*Me*), 1.47−1.54 (m, 1H, COD), 1.84−1.92 (m, 2H, COD), 2.45−2.50 (m, 2H, COD), 2.52 (s, 1H, 1-C*H*), 2.54−2.60 (m, 1H, COD), 2.67 (s, 1H, 6-C*H*), 2.68−2.75 (m, 1H, COD), 2.86−2.92 (m, 1H, COD), 3.51 (s, 1H, 4-C*H*), 3.73−3.77 (m, 1H, COD), 4.06−4.09 (m, 1H, COD), 4.79 (s, 1H, 1-C*H*), 7.00−7.19 (m, 10H, *Ph*). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, room temperature): δ 12.6, 18.8, 25.2, 26.4, 32.7, 38.1, 40.0, 53.0, 68.0, 68.8, 75.7, 79.6, 82.6, 85.0, 114.5, 115.9, 123.9, 127−130 (multiple signals), 138.5, 143.6. Anal. Calcd for $C_{28}H_{32}$Ru (469.18): C, 71.61; H, 6.87. Found: C, 71.28; H, 7.43.

Reaction of 6ae with 2,3-Dimethylbutadiene (3). Complex **6ea** (5.83 mg, 0.0124 mmol) and triphenylmethane (4.90 mg, 0.0220 mmol) as an internal standard were placed in an NMR tube. Then, benzene-d_6 (0.6 mL) was transferred into the NMR tube by vacuum distillation. Compound **3e** (3.4 μL, 0.0301 mmol) was added to the solution. However, no reaction was observed after 16 h of reaction at room temperature. Then, **3a** (3.4 μL, 0.0292 mmol) was added but no reaction occurred after 8 h at room temperature.

X-ray Analysis. Single crystals of **7a** suitable for X-ray analysis were obtained from a benzene solution. A single crystal was selected using a polarized microscope was mounted on a glass capillary by use of Paratone-N oil. A Rigaku AFC-7R-Mercury II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used for data collection at 200 K. The collected data were solved by direct methods and refined by a full-matrix least-squares procedure using the CrystalStructure program (version 4.2).[24,25] All hydrogen atoms were treated as a riding model. The optimized structure is depicted in Figure 1 using the POV-Ray program (version 3.6.2).[26]

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DFT Calculations. The intermediates **A**−**E** and transition state structures **TS1**−**TS3** were optimized by density functional theory (DFT) calculations using the B3LYP method with the LANL2DZ basis set for Ru and the 6-31G(d) basis sets on all other atoms.[27] The effect of benzene as a solvent was included in the calculations by using the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM).[28] The optimized molecular structures were verified by vibrational analysis. Intrinsic reaction coordinate (IRC) calculations[29,30] were carried out to check whether or not the transition state leads to the reactant and the product. Relative energies were corrected by adding the unscaled zero-point vibrational energy. All calculations were carried out using the Gaussian 09 program.[31]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00668.

NMR and physical data of new compounds and X-ray data for **7a** and preliminary X-ray structures of **4ca**,**ha** (PDF)

DFT calculations for **A**−**E** and **TS1**−**TS3** (PDF)

Crystallographic data for **7a** (CIF)

Cartesian coordinates for **A**−**E** and **TS1**−**TS3** (XYZ)

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Notes

The authors declare no competing financial interest.

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