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To be cited as: *Chem. Asian J.* 10.1002/asia.201801670

Link to VoR: http://dx.doi.org/10.1002/asia.201801670

A Journal of
ACES Asian Chemical Editorial Society

A sister journal of Angewandte Chemie and Chemistry – A European Journal

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10.1002/asia.201801670

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Facile Synthesis of Dibenzotetracenedione Derivatives by Rhodium-Catalyzed [2+2+2] Cycloaddition/Spontaneous Aromatization

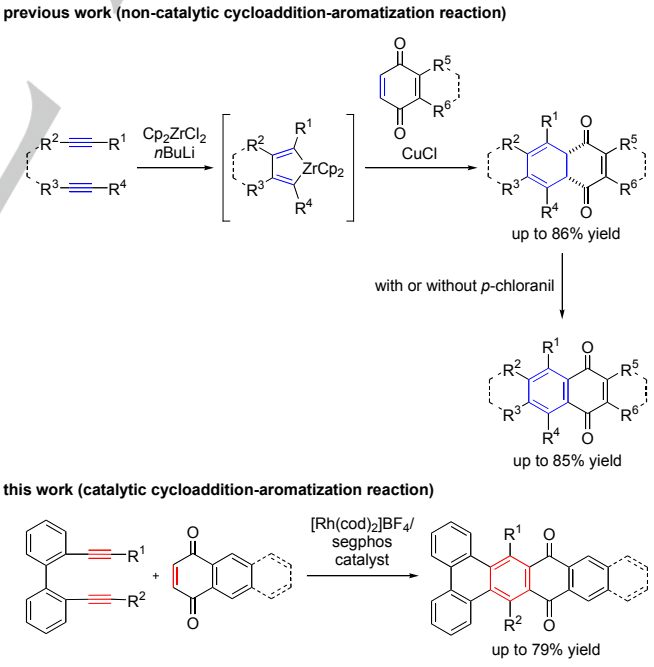
Yukimasa Aida,[a] Yu Shibata,[a] and Ken Tanaka*[a]

Abstract: It has been established that a cationic rhodium(I)/segphos complex catalyzes the [2+2+2] cycloaddition of biphenyl-linked 1,7-diynes with 1,4-naphthoquinone and anthracene-1,4-dione. Conveniently, spontaneous aromatization proceeded upon removal of the rhodium complex by passing the reaction mixture through an alumina column to give the corresponding dibenzotetracenediones and dibenzopentacenediones, respectively, in good yields. The thus obtained dibenzotetracenedione could be readily transformed into the corresponding dibenzotetracene in good yield. This dibenzotetracene showed blue fluorescence with a good quantum yield, which is significantly higher than those of tetracene, tetrabenzotetracene, and hexabenzotetracene.

Introduction

The transition-metal-catalyzed [2+2+2] cycloaddition of three alkynes is one of the most convenient methods for the synthesis of substituted benzenes.[1] Instead, that of two alkynes with an alkene giving 1,3-cyclohexadienes[2] followed by dehydrogenation is sometimes advantageous for this purpose. For example, the use of cyclohexene and dihydronaphthalene derivatives[3] allows the synthesis of naphthalene and anthracene derivatives without using benzynes and naphthynes,[4] the preparation of which is troublesome due to employing not readily available substrates and harsh reaction conditions. As readily available dihydronaphthalene derivatives, commercially available 1,4-naphthoquinone has been employed for the convenient synthesis of anthraquinones. In 2006, the Xi research group reported the [2+2+2] cycloaddition of two alkynes with 1,4-naphthoquinone and anthracene-1,4-dione giving multicyclic cyclohexadiene derivatives by using stoichiometric amounts of zirconium and copper complexes.[5–7] Subsequently, the thus obtained cyclohexadienes could be transformed into the corresponding anthraquinones and dibenzopentacenediones in good yields by spontaneous aromatization or treatment with a stoichiometric amount of an external oxidant (*p*-chloranil) (Scheme 1, top). However, a catalytic variant of this [2+2+2] cycloaddition has not been reported to date.

On the other hand, cationic rhodium(I)/biaryl bisphosphine complexes are highly active and selective catalysts for the [2+2+2] cycloaddition[8] of α,ω-diynes with cyclic alkenes,[9] such as norbornene,[9a] benzothiophene dioxides,[9b] 2,3-dihydrofuran,[9c] cyclopentene,[9c] indene,[9c] and acenaphthylene.[9d] In this paper, we found that a cationic rhodium(I)/segphos complex is able to catalyze the [2+2+2] cycloaddition of biphenyl-linked diynes with 1,4-naphthoquinone and anthracene-1,4-dione (Scheme 1, bottom).[10] Interestingly, in the presence of this rhodium complex, aromatization of the cyclohexadiene products did not proceed, while spontaneous aromatization proceeded to give dibenzotetracenediones and dibenzopentacenediones upon removal of the rhodium complex by passing the reaction mixture through an alumina column even under an argon atmosphere. It is well known that acene-m,n-diones are good precursors for the synthesis of acenes.[11] Therefore, the present method is useful for the facile synthesis of dibenzo-fused acene derivatives.



Scheme 1. Transition-metal-mediated [2+2+2] cycloaddition/aromatization of two alkynes with 1,4-naphthoquinone (cod = 1,5-cyclooctadiene).

Results and Discussion

We first investigated the reaction of biphenyl-linked diyne **1a**, possessing the *n*-butoxycarbonyl and methyl groups at the alkyne termini, and 1,4-naphthoquinone (**2a**) (1.1 equiv) in the

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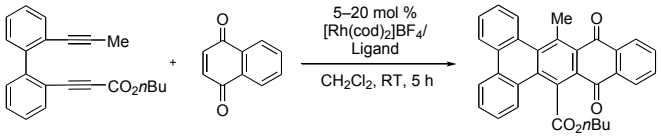
presence of a cationic rhodium(I)/H_8-binap complex (20 mol %). Pleasingly, spontaneous aromatization, as well as the desired [2+2+2] cycloaddition, proceeded to give the corresponding dibenzotetracenedione product **3aa** in good yield (Table 1, entry 1). In order to improve the product yield, various biaryl bisphosphine ligands (Figure 1) were screened (entries 1–5), which revealed that the use of segphos afforded **3aa** in the highest yield (entry 3). In sharp contrast to our previously reported [2+2+2] cycloadditions using cyclic alkenes, the use of non-biaryl bisphosphine ligand (dppf, Figure 1) and PPh_3 also afforded **3aa**, although the yields were moderate (entries 6 and 7). Increasing the steric bulk of the aryl groups on the phosphorus atom of segphos was also tested, while the yields of **3aa** decreased (entries 8–10). Thus, segphos was selected as the best ligand. Finally, the catalyst loading could be reduced to 5 mol % without erosion of the product yield (entry 11).

Table 1. Optimization of reaction conditions for rhodium-catalyzed [2+2+2] cycloaddition-spontaneous aromatization of **1a** with **2a**[a]



1a **2a** (1.1 equiv) **3aa**

Entry	Catalyst [mol %]	Ligand	Conv [%][b]	Yield [%][b]
1	20	H_8-binap	100	61
2	20	binap	100	55
3	20	segphos	100	66
4	20	difluorphos	100	45
5	20	biphep	100	32
6	20	dppf	100	44
7	20	$2PPh_3$	77	46
8	20	tol-segphos	100	29
9	20	xyl-segphos	100	50
10	20	dtbm-segphos	100	38
11	5	segphos	100	63

[a] $[Rh(cod)_2]BF_4$ (0.0050–0.020 mmol), ligand (0.0050–0.020 mmol), **1a** (0.100 mmol), **2a** (0.110 mmol), and CH_2Cl_2 (2.0 mL) were used. [b] Isolated yield.

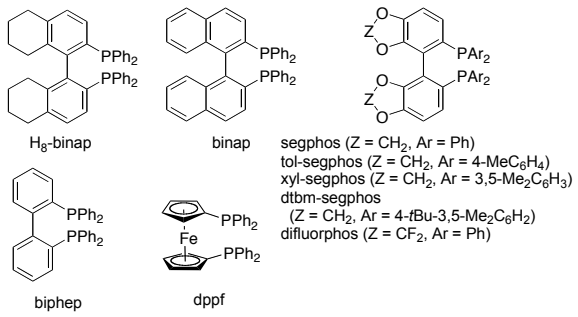
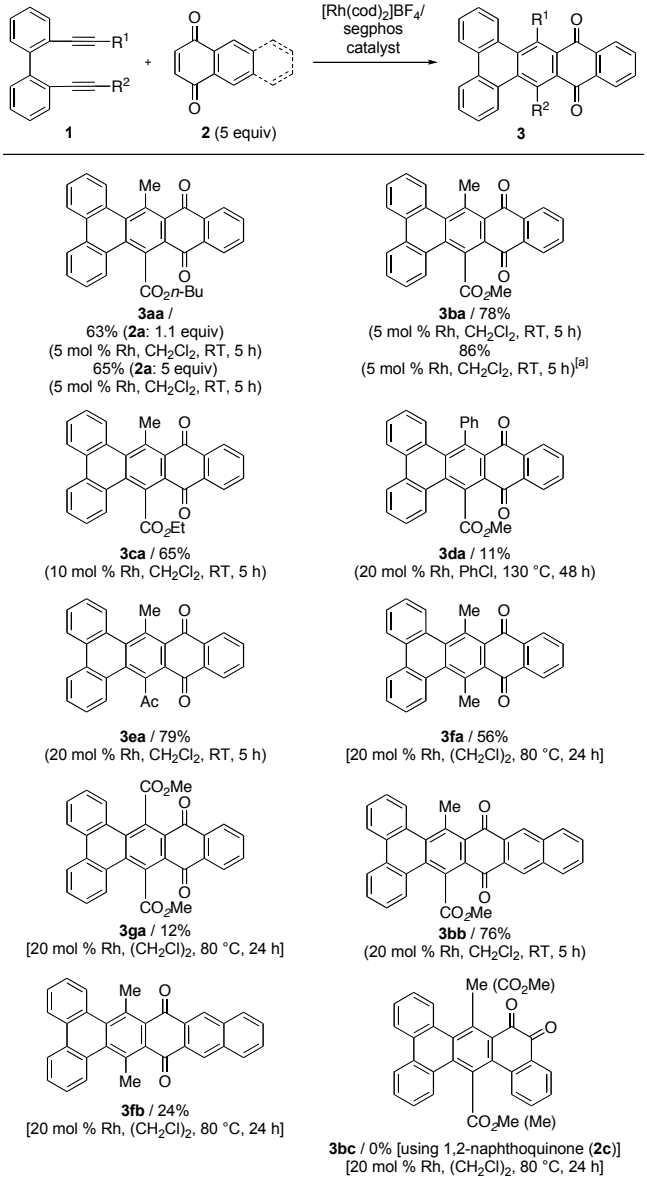


Figure 1. Structures of bisphosphine ligands.



Scheme 2. Substrate Scope. $[Rh(cod)_2]BF_4$ (0.0050–0.020 mmol), segphos (0.0050–0.020 mmol), **1** (0.100 mmol), **2** (0.110–0.500 mmol), and solvents (2.0 mL) were used. The cited yields were of isolated products. [a] $[Rh(cod)_2]BF_4$ (0.025 mmol), segphos (0.025 mmol), **1b** (0.500 mmol), **2a** (2.50 mmol), and CH_2Cl_2 (2.0 mL) were used.

The scope of biphenyl-linked diynes **1** was then examined under the above-optimized reaction conditions as shown in Scheme 2.[12] With respect to the substituents at the alkyne termini, biphenyl-linked 1,7-diynes, possessing not only the *n*-butoxycarbonyl group (**1a**) but also the methoxy- and ethoxycarbonyl groups (**1b** and **1c**), reacted with **2a** to give the corresponding dibenzotetracenediones **3aa**–**3ca** with good yields. Diyne **1d** possessing the phenyl group also reacted with **2a** to afford the desired product **3da** in low yield, although elevation of the reaction temperature (130 °C), high catalyst loading (20 mol% Rh), and longer reaction time (48 h) were required. Acetyl-substituted diyne **1e** was also capable of reacting with **2a** to give the corresponding

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dibenzotetracenedione **3ea** with good yield. In addition to unsymmetrical diynes, symmetrical one **1f** could participate in this reaction to give **3fa** in good yield, but diyne **1g**, possessing two methoxycarbonyl groups at the alkyne termini, reacted with **2a** to give **3ga** in low yield. With respect to alkenes, not only 1,4-naphthoquinone (**2a**) but also anthracene-1,4-dione (**2b**) could participate in this cycloaddition-aromatization to give the corresponding dibenzopentacenediones **3bb** and **3fb** in 76% and 24% yields, respectively. However, unfortunately, no substrate conversion was observed in the reaction of **1b** and 1,2-naphthoquinone (**2c**) even at the elevated reaction temperature of 80 °C.[13] Similarly, we previously reported that a six-membered 1,2-dicarbonyl compound (phenanthrene-9,10-dione) cannot be employed in the cationic rhodium(I) complex-catalyzed [2+2+2] cycloaddition of 1,6- and 1,7-diynes with carbonyl compounds.[14] The formation of stable and unreactive cationic rhodium(I)/(**2c**)$_2$ complex **A** from **2c** and the cationic rhodium(I)/bisphosphine complex may account for no substrate conversion when using **2c** (Figure 2).[15] 1,4-Benzoquinone was also tested, but the corresponding cycloadducts were unstable and decomposed upon isolation.

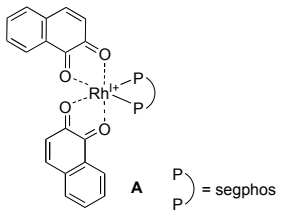
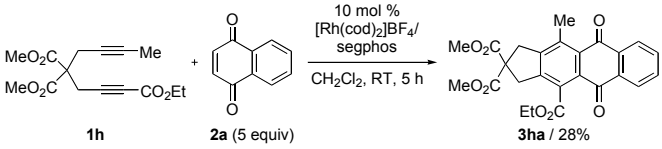


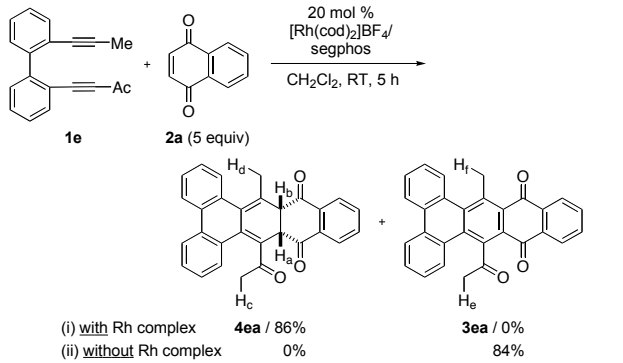
Figure 2. Structure of cationic rhodium(I)/(**2c**)$_2$ complex **A**.

The reaction of **2a** with malonate-linked 1,6-diyne **1h**, instead of the biphenyl-linked 1,7-diyne, was also investigated. However, the yield of the corresponding anthraquinone **3ha** was low (Scheme 3).

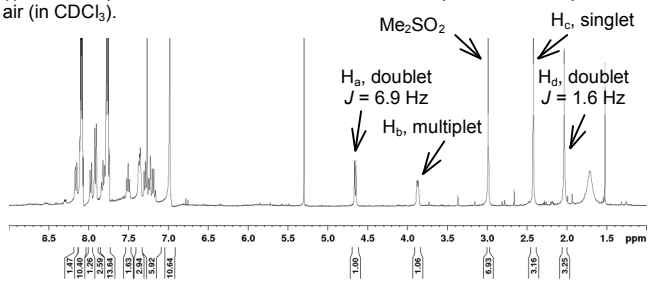


Scheme 3. Rhodium-catalyzed [2+2+2] cycloaddition-spontaneous aromatization of 1,6-diyne **1h** with 1,4-naphthoquinone (**2a**).

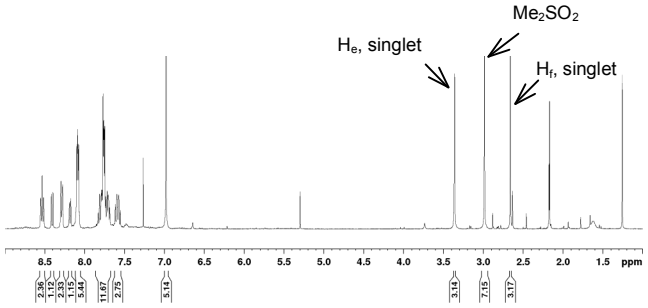
In order to ascertain at what stage aromatization proceeds, we conducted ^{1}H NMR analyses of the reaction mixtures before and after removal of the rhodium complex (Scheme 4). The ^{1}H NMR spectrum of the reaction mixture after evaporation and exposure to air in the presence of the rhodium complex revealed that non-aromatized product **4ea** is generated [Scheme 4, (i)]. However, the ^{1}H NMR spectrum of the reaction mixture after removal of the rhodium complex by passing through an alumina column under argon followed by evaporation revealed that aromatized product **3ea** is solely generated [Scheme 4, (ii)]. Additionally, we conducted the ^{1}H NMR analysis of the reaction mixture being stirred for 16 h under argon after the addition of an excess amount of PPh_3 (10 equiv relative to rhodium) followed by evaporation, which revealed that aromatized product **3ea** is generated as a major product (Supporting Information, Scheme S1). Therefore the alumina is not responsible for the aromatization and the presence of a catalytic amount of the rhodium complex with free coordination sites indeed inhibits spontaneous aromatization even under air, although the mechanism of this stabilization effect by the rhodium complex is not clear at the present stage.



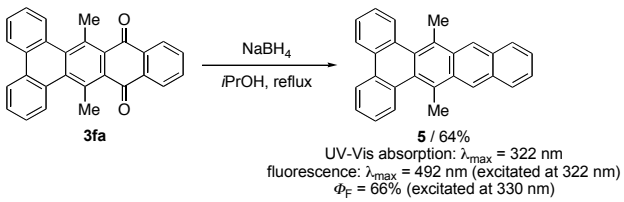
(i) ^{1}H NMR spectrum of the reaction mixture after evaporation and exposure to air (in $CDCl_3$).



(ii) ^{1}H NMR spectrum of the reaction mixture after passing through an alumina column under argon followed by evaporation (in $CDCl_3$).



Scheme 4. ^{1}H NMR analyses of the reaction of **1e** with **2a**. The reaction was conducted using $[Rh(cod)_2]BF_4$ (0.020 mmol), segphos (0.020 mmol), **1e** (0.100 mmol), **2a** (0.500 mmol), and CH_2Cl_2 (2.0 mL). The cited yields were determined by ^{1}H NMR using dimethyl sulfone (0.100 mmol) as an internal standard. (i) The doublet peak at 4.66 ppm, the multiplet peak at 3.92–3.83 ppm, the singlet peak at 2.42 ppm, and the doublet peak at 2.03 ppm are assigned to the protons H_a, H_b, H_c, and H_d of **4ea**. (ii) The singlet peaks at 3.36 ppm and 2.66 ppm are assigned to the protons H_e and H_f of **3ea**.



Scheme 5. Synthesis of dibenzotetracene derivative **5**.

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As mentioned in the introduction, acene-m,n-dione is a good precursor for the synthesis of acene.[11] Indeed, reductive aromatization of **3fa** with $NaBH_4$[11e] proceeded to give dimethyl-substituted dibenzotetracene **5** as an air-stable solid in good yield (Scheme 5).[16]

Although several examples of the synthesis of dibenzo[*a*,*c*]-fused tetracenes have been reported, their photophysical properties including fluorescence quantum yields have not been examined. Thus we briefly examined the photophysical properties of the thus obtained dibenzotetracene **5**. Absorption and fluorescence spectra of **5** are shown in Figure 3. Pleasingly, dibenzotetracene **5** showed blue fluorescence with a good quantum yield of 66%. This value is significantly higher than fluorescence quantum yields of tetracene (**6**),[17] tetrabenzotetracene (**7**),[18] and hexabenzotetracene (**8**)[19] (Figure 4).

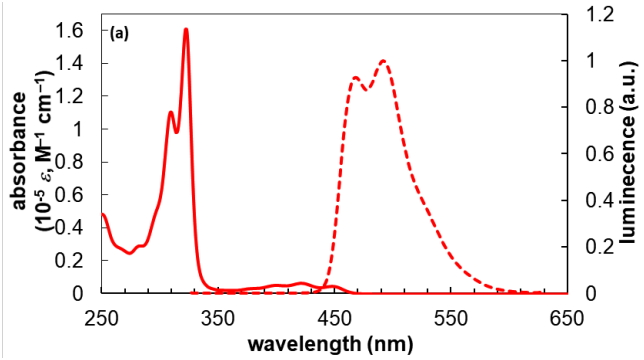
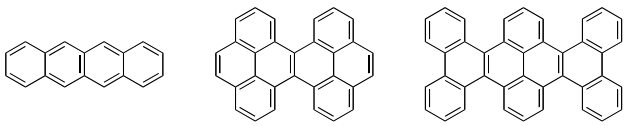


Figure 3. Absorption (solid line) and fluorescence (dashed line) spectra of **5**.



6 Φ_F = 16% (ref 16) **7** Φ_F = 28% (ref 17) **8** Φ_F = 31% (ref 18)

Figure 4. Structures and fluorescence quantum yields of tetracene (**6**), tetrabenzotetracene (**7**), and hexabenzotetracene (**8**).

Conclusions

In conclusion, we have established that a cationic rhodium(I)/segphos complex is able to catalyze the [2+2+2] cycloaddition of biphenyl-linked 1,7-diynes with 1,4-naphthoquinone and anthracene-1,4-dione. Interestingly, in the presence of this rhodium complex, aromatization of the cyclohexadiene products did not proceed, while spontaneous aromatization proceeded to give dibenzotetracenediones and dibenzopentacenediones in good yields upon removal of the rhodium complex by passing the reaction mixture through an alumina column even under an argon atmosphere. The thus obtained dibenzotetracenedione could be readily transformed into the corresponding dibenzotetracene in good yield. This dibenzotetracene showed blue fluorescence with a good quantum yield, which is significantly higher than fluorescence quantum yields of tetracene, tetrabenzotetracene, and hexabenzotetracene.

Experimental Section

General

Anhydrous 1,4-dioxane (No. 042-31655), PhCl (No. 28,451-3), $(CH_2Cl)_2$ (No. 28,450-5), and *i*PrOH (No. 27,847-5) were obtained from Aldrich and Wako, and used as received. Anhydrous and degassed CH_2Cl_2 (No. 041-32345), and THF (No. 209-18705) were obtained from Aldrich and Wako, and used as received. *i*Pr_2NH was dried over KOH. Et_3N was dried over KOH and bubbling with nitrogen, and the other solvents except for MeOH and 1,4-dioxane for the synthesis of substrates were dried over Molecular Sieves 4Å (Wako) prior to use. H_8-binap, segphos, tol-segphos, xyl-segphos, and DTBM-segphos were obtained from Takasago International Corporation. α,ω-Diynes **1b**,[9d] **1c**,[9d] **1e**,[9d] **1f**,[20] **1g**,[9c] and **1h**,[9d] and anthracene-1,4-dione (**2b**)[21] were prepared according to the literatures. All other reagents were obtained from commercial sources and used as received. ^1H (400 MHz) and ^{13}C (100 MHz) NMR data were collected on a Bruker AVANCE III HD 400 at ambient temperature unless otherwise specified. HRMS data were obtained on a Bruker micrOTOF Focus II. All reactions were carried out under nitrogen or argon in oven-dried glassware with magnetic stirring unless otherwise noted. The UV/Vis absorption of **5** in $CHCl_3$ (0.5×10^{-5} M) was recorded on a JASCO V-630 spectrometer with a resolution of 1.0 nm. The emission spectra of **5** in $CHCl_3$ (0.5×10^{-5} M) was recorded on a JASCO FP-6200 spectrometer with a resolution of 1.0 nm upon excitation at 322 nm. The fluorescence quantum yield was measured on a Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System, C11347-01.

Synthesis of Diynes

Butyl 3-(2'-(prop-1-yn-1-yl)-[1,1'-biphenyl]-2-yl)propiolate (1a)

The title compound was prepared according to the conditions of the literature used in the synthesis of structurally related compounds.[9d] To a stirred solution of ((2-bromophenyl)ethynyl)trimethylsilane[22] (1.75 g, 6.91 mmol) in MeOH/THF (5:1, 24 mL) was added K_2CO_3 (1.91 g, 13.8 mmol) at room temperature under air. After being stirred at the same temperature for 30 min, the reaction mixture was poured into H_2O/*n*-hexane. The aqueous phase was extracted with two portions of *n*-hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was used for the next reaction without further purification. To a stirred solution of *i*Pr_2NH (1.90 mL, 13.8 mmol) in THF (14 mL) was added *n*BuLi (8.80 mL, 13.8 mmol, 1.57 mol/L in *n*-hexane) at −78 °C and the resulting mixture was stirred at the same temperature for 10 min. To this mixture was added a solution of the above residue in THF (10 mL) at −78 °C and the resulting mixture was stirred at the same temperature for 30 min. To the mixture was added $ClCO_2$*n*Bu (3.60 mL, 27.6 mmol) at −78 °C. After being stirred at room temperature for 1 h, the reaction mixture was quenched with water and poured into saturated aqueous NH_4Cl/EtOAc. The aqueous phase was extracted with two portions of EtOAc. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 85:15) to give crude butyl 3-(2-bromophenyl)propiolate (1.60 g). To a stirred solution of this crude butyl 3-(2-bromophenyl)propiolate (1.60 g), (2-(prop-1-yn-1-yl)phenyl)boronic acid[23] (1.00 g, 6.27 mmol), and Cs_2CO_3 (2.41 g, 7.41 mmol) in 1,4-dioxane (11 mL) was added Pd_2dba_3 (78.3 mg, 0.0855 mmol) and [(*t*Bu_3P)H]BF_4 (59.5 mg, 0.205 mmol) at room temperature. After being stirred at 80 °C for 13 h, the reaction mixture was filtered

through a pad of Celite and concentrated. The residue was purified by a silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 85:15) to give crude **1a**. This crude **1a** was purified by a gel permeation chromatography (GPC) to give **1a** (0.612 g, 1.94 mmol, 34% yield in 3 steps from ((2-bromophenyl)ethynyl)trimethylsilane) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70–7.66 (m, 1H), 7.52–7.44 (m, 3H), 7.40–7.27 (m, 4H), 4.10 (t, *J* = 6.6 Hz, 2H), 1.85 (s, 3H), 1.64–1.55 (m, 2H), 1.41–1.30 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.1, 144.9, 141.4, 133.6, 132.5, 130.6, 130.0, 129.7, 127.7, 127.3, 127.1, 123.3, 119.3, 89.3, 85.8, 83.2, 78.7, 65.7, 30.4, 19.0, 13.6, 4.3; HRMS (ESI) calcd for $C_{22}H_{20}O_2Na$ $[M+Na]^+$ 339.1356 found 339.1345.

Methyl 3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)propiolate (1d)

The title compound was prepared according to the conditions of the literature used in the synthesis of structurally related compounds.[9d] To a stirred solution of 2,2'-diethynyl-1,1'-biphenyl[20] (0.809 g, 4.00 mmol) in THF (80 mL) was added *n*BuLi (2.40 mL, 4.00 mmol; 1.64 mol/L in *n*-hexane) at −78 °C and the resulting mixture was stirred at −78 °C for 30 min. To the resulting mixture was added $ClCO_2Me$ (0.37 mL, 4.80 mmol) at −78 °C. After being stirred at room temperature for 1 h, the reaction mixture was quenched with water and poured into saturated aqueous NH_4Cl/EtOAc. The aqueous phase was extracted with two portions of EtOAc. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was used for the next reaction without further purification. To a solution of the residue in Et_3N/THF (3.2:1, 21 mL) was added iodobenzene (0.89 mL, 8.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.169 g, 0.240 mmol), and CuI (91.4 mg, 0.480 mmol) at room temperature. After being stirred at the same temperature for 17 h, the reaction mixture was poured into saturated aqueous NH_4Cl/CH_2Cl_2. The aqueous phase was extracted with two portions of CH_2Cl_2. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 50:50) to give **1d** (0.420 g, 1.32 mmol, 31% yield in 2 steps from 2,2'-diethynyl-1,1'-biphenyl) as a sticky brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75–7.68 (m, 1H), 7.68–7.61 (m, 1H), 7.59–7.48 (m, 2H), 7.47–7.33 (m, 5H), 7.28–7.17 (m, 4H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.4, 144.7, 141.8, 133.8, 132.3, 131.4, 130.8, 130.0, 129.9, 128.2, 128.1, 127.98, 127.96, 127.6, 123.3, 122.6, 119.3, 92.8, 88.7, 86.0, 82.9, 52.6; HRMS (ESI) calcd for $C_{24}H_{16}O_2Na$ $[M+Na]^+$ 359.1043, found 359.1044.

Rhodium-Catalyzed [2+2+2] Cycloaddition/Spontaneous Aromatizaion

Representative Procedure for the Rhodium-Catalyzed [2+2+2] Cycloaddition-Aromatizaion of α,ω-Diynes 1 with 1,4-Naphthoquinone (2a) (Scheme 2, 3aa): Segphos (3.1 mg, 0.0050 mmol) and $[Rh(cod)_2]BF_4$ (2.0 mg, 0.0050 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After being stirred at room temperature for 30 min, the resulting mixture was concentrated to dryness and dissolved in CH_2Cl_2 (0.5 mL). To the residue was added a CH_2Cl_2 (1.0 mL) solution of **2a** (79.1 mg, 0.500 mmol) and a CH_2Cl_2 (0.5 mL) solution of **1a** (31.6 mg, 0.100 mmol) in this order at room temperature. The mixture was stirred at room temperature for 5 h. The resulting solution was concentrated and purified by a preparative TLC (*n*-hexane/CH_2Cl_2 = 1:2) twice to give **3aa** (30.6 mg, 0.0648 mmol, 65% yield) as a yellow solid.

Butyl 16-methyl-10,15-dioxo-10,15-dihydrodibenzo[*a*,*c*]tetracene-9-carboxylate (3aa, Scheme 2)

Mp 182−184 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54–8.42 (m, 3H), 8.31–8.26 (m, 1H), 8.26–8.20 (m, 2H), 7.84–7.73 (m, 2H), 7.72–7.62 (m, 2H), 7.58–7.50 (m, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.35 (s, 3H), 1.81–1.72 (m, 2H), 1.38 (sext, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz); HRMS (ESI) calcd for $C_{32}H_{24}O_4Na$ $[M+Na]^+$ 495.1567, found 495.1556.

Lage-scale Procedure for the Rhodium-Catalyzed [2+2+2] Cycloaddition-Aromatizaion of α,ω-dDyne 1b with 1,4-Naphthoquinone (2a) (Scheme 2, 3ba): Segphos (15.3 mg, 0.025 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.025 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After being stirred at room temperature for 30 min, the resulting mixture was concentrated to dryness and dissolved in CH_2Cl_2 (0.5 mL). To the residue was added a CH_2Cl_2 (1.0 mL) solution of **2a** (0.395 g, 2.50 mmol) and a CH_2Cl_2 (0.5 mL) solution of **1b** (0.137 g, 0.500 mmol) in this order at room temperature. The mixture was stirred at room temperature for 5 h. The resulting solution was concentrated and purified by a preparative TLC (*n*-hexane/CH_2Cl_2 = 1:2) twice to give **3ba** (0.186 g, 0.431 mmol, 86% yield) as a yellow solid.

Methyl 16-methyl-10,15-dioxo-10,15-dihydrodibenzo[*a*,*c*]tetracene-9-carboxylate (3ba, Scheme 2)

Mp 246−248 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54–8.44 (m, 2H), 8.44–8.37 (m, 1H), 8.31–8.26 (m, 1H), 8.26–8.20 (m, 2H), 7.83–7.73 (m, 2H), 7.72–7.62 (m, 2H), 7.60–7.50 (m, 2H), 4.09 (s, 3H), 3.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.8, 183.9, 171.5, 140.0, 139.9, 135.2, 134.2, 133.7, 133.3, 132.9, 132.1, 131.9, 130.1, 130.0, 129.6, 129.3, 129.1, 128.5, 127.7, 127.2, 126.9, 126.8, 126.6, 123.81, 123.80, 53.3, 25.1; HRMS (ESI) calcd for $C_{29}H_{18}O_4Na$ $[M+Na]^+$ 453.1097, found 453.1084.

Ethyl 16-methyl-10,15-dioxo-10,15-dihydrodibenzo[*a*,*c*]tetracene-9-carboxylate (3ca, Scheme 2)

29.0 mg, 65% yield, Yellow solid; Mp 233−235 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56–8.45 (m, 3H), 8.34–8.28 (m, 1H), 8.28–8.21 (m, 2H), 7.85–7.74 (m, 2H), 7.73–7.64 (m, 2H), 7.61–7.52 (m, 2H), 4.60 (q, *J* = 7.1 Hz, 2H), 3.37 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.9, 184.0, 171.0, 139.88, 139.86, 135.2, 134.2, 133.6, 133.4, 132.9, 132.1, 131.9, 130.13, 130.07, 130.0, 129.3, 129.2, 129.1, 129.0, 128.5, 127.5, 127.19, 127.17, 126.7, 126.6, 123.8, 123.7, 62.4, 25.1, 13.8; HRMS (ESI) calcd for $C_{30}H_{20}O_4Na$ $[M+Na]^+$ 467.1254, found 467.1237.

Methyl 10,15-dioxo-16-phenyl-10,15-dihydrodibenzo[*a*,*c*]tetracene-9-carboxylate (3da, Scheme 2)

5.3 mg, 11% yield, Yellow amorphous; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, *J* = 7.7 Hz, 1H), 8.48–8.44 (m, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.30–8.25 (m, 1H), 8.11–8.06 (m, 1H), 7.83–7.67 (m, 3H), 7.63–7.56 (m, 1H), 7.52–7.39 (m, 5H), 7.35–7.27 (m, 2H), 7.05–6.96 (m, 1H), 4.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.4, 183.3, 171.0, 141.6, 141.5, 137.1, 135.3, 134.9, 134.5, 133.8, 133.3, 132.5, 132.1, 131.4, 130.9, 130.6, 130.5, 130.1, 129.6, 129.5, 129.2, 128.6, 128.5, 128.0, 127.6, 127.22, 127.18, 127.1, 126.0, 123.8, 123.6, 53.4; HRMS (ESI) calcd for $C_{34}H_{20}O_4Na$ $[M+Na]^+$ 515.1254, found 515.1231.

9-Acetyl-16-methyldibenzo[*a*,*c*]tetracene-10,15-dione (3ea, Scheme 2)

32.6 mg, 79% yield, Yellow solid; Mp 250 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52 (t, *J* = 7.8 Hz, 2H), 8.43–8.37 (m, 1H), 8.31–8.24 (m, 2H),

8.21–8.15 (m, 1H), 7.84–7.65 (m, 4H), 7.62–7.52 (m, 2H), 3.34 (s, 3H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.3, 185.2, 184.9, 139.9, 139.7, 139.2, 135.2, 134.3, 133.7, 133.3, 132.0, 131.9, 131.4, 130.6, 130.0, 129.53, 129.46, 129.3, 129.1, 128.3, 128.2, 127.9, 127.2, 126.74, 126.72, 123.9, 123.8, 32.7, 25.0; HRMS (ESI) calcd for $C_{29}H_{18}O_3Na$ $[M+Na]^+$ 437.1148, found 437.1167.

9,16-Dimethyldibenzo[*a,c*]tetracene-10,15-dione (3fa, Scheme 2)

21.5 mg, 56% yield, Yellow solid; Mp 258 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, J = 8.0 Hz, 2H), 8.28–8.21 (m, 4H), 7.79–7.73 (m, 2H), 7.69–7.63 (m, 2H), 7.60–7.53 (m, 2H), 3.30 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.6, 138.9, 136.4, 135.1, 133.3, 132.0, 130.5, 129.84, 129.82, 128.4, 126.50, 126.46, 123.7, 24.4; HRMS (ESI) calcd for $C_{28}H_{18}O_2Na$ $[M+Na]^+$ 409.1199, found 409.1199.

Dimethyl 10,15-dioxo-10,15-dihydrodibenzo[*a,c*]tetracene-9,16-dicarboxylate (3ga, Scheme 2)

5.9 mg, 12% yield, Yellow solid; Mp >300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (d, J = 8.1 Hz, 2H), 8.47 (d, J = 8.2 Hz, 2H), 8.30 (dd, J = 5.6, 3.3 Hz, 2H), 7.84 (dd, J = 5.7, 3.4 Hz, 2H), 7.77–7.70 (m, 2H), 7.62–7.56 (m, 2H), 4.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.6, 170.5, 134.8, 134.6, 133.6, 132.1, 132.0, 130.0, 129.8, 128.4, 127.8, 127.5, 127.1, 123.9, 53.5; HRMS (ESI) calcd for $C_{30}H_{18}O_6Na$ $[M+Na]^+$ 497.0996, found 497.0991.

Methyl 18-methyl-10,17-dioxo-10,17-dihydrodibenzo[*a,c*]pentacene-9-carboxylate (3bb, Scheme 2)

36.7 mg, 76% yield, Orange solid; Mp 292−292 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (d, J = 11.5 Hz, 2H), 8.54–8.46 (m, 2H), 8.42 (d, J = 7.8 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.12–8.03 (m, 2H), 7.73–7.63 (m, 4H), 7.61–7.52 (m, 2H), 4.12 (s, 3H), 3.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.8, 183.9, 171.7, 140.1, 140.0, 135.5, 135.0, 133.1, 132.1, 132.0, 131.4, 131.1, 130.1, 130.0, 129.8, 129.7, 129.4, 129.34, 129.30, 129.28, 129.1, 129.0, 128.5, 127.7, 127.0, 126.6, 123.82, 123.80, 53.3, 25.3; HRMS (ESI) calcd for $C_{33}H_{20}O_4Na$ $[M+Na]^+$ 503.1254, found 503.1260.

9,18-Dimethyldibenzo[*a,c*]pentacene-10,17-dione (3fb, Scheme 2)

10.3 mg, 24% yield, Red solid; Mp 276 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (s, 2H), 8.46 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.1 Hz, 2H), 8.06 (dd, J = 6.2, 3.4 Hz, 2H), 7.68–7.59 (m, 4H), 7.55 (t, J = 7.6 Hz, 2H), 3.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.6, 138.9, 136.3, 135.1, 132.0, 131.7, 131.4, 129.9, 129.8, 128.9, 128.4, 128.2, 126.5, 123.7, 24.5; HRMS (ESI) calcd for $C_{64}H_{40}O_4Na$ $[2M+Na]^+$ 895.2819, found 895.2776.

4-Ethyl 2,2-dimethyl 11-methyl-5,10-dioxo-1,3,5,10-tetrahydro-2*H*-cyclopenta[*b*]anthracene-2,2,4-tricarboxylate (3ha, Scheme 3)

12.8 mg, 28% yield, White solid; Mp 204−206 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24–8.15 (m, 2H), 7.81–7.70 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 3.78 (s, 6H), 3.75 (s, 2H), 3.73 (s, 2H), 2.78 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.9, 182.9, 171.2, 168.9, 147.8, 142.9, 139.0, 134.5, 134.3, 133.6, 132.5, 131.9, 131.1, 129.6, 127.2, 126.8, 61.8, 58.9, 53.3, 40.6, 39.4, 19.1, 14.1; HRMS (ESI) calcd for $C_{25}H_{22}O_8Na$ $[M+Na]^+$ 473.1207, found 437.1215.

9,16-Dimethyldibenzo[*a,c*]tetracene (5, Scheme 5)

The title compound was prepared according to the conditions of the literature used in the synthesis of structurally related compounds.[11e] To a solution of **3fa** (52.8 mg, 0.137 mmol) in *i*PrOH (4 mL) was added $NaBH_4$ (103.4 mg, 2.73 mmol) at 0 °C and the resulting mixture was stirred at reflux for 9 h. The mixture was cooled to room temperature and stirred at the same temperature for 13 h. The mixture was heated to the reflux point and stirred at the same temperature for 10 h. To the mixture was added 2M aqueous HCl (4 mL) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into 2M aqueous HCl/CH_2Cl_2. The aqueous phase was extracted with two portions of CH_2Cl_2. The combined extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was purified by a preparative TLC (*n*-hexane/toluene = 3:1) to give crude **5**. This crude **5** was purified by a gel permeation chromatography (GPC) to give **5** (31.4 mg, 0.0881 mmol, 64% yield) as a yellow solid. Mp 195 °C (dec.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.72 (s, 2H), 8.25 (dd, J = 7.9, 1.1 Hz, 2H), 8.08 (dd, J = 6.4, 3.2 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.53–7.37 (m, 6H), 3.28 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.2, 132.1, 131.5, 131.1, 130.9, 129.7, 128.4 ,127.3, 126.9, 126.5, 125.5, 123.7, 123.6, 19.8; HRMS (APCI) calcd for $C_{28}H_{20}$ $[M]^+$ 356.1560, found 356.1552.

Acknowledgements

This work was supported by ACT-C (No. JPMJCR1122YR) from Japan Science and Technology Agency (JST), Japan and a Grant-in-Aid for Scientific Research (No. 26102004) from Japan Society for the Promotion of Science (JSPS), Japan. Y.A. thanks JSPS research fellowship for young scientists (No. 17J08763). We thank Takasago International Corp. for the gift of H_8-BINAP, Segphos, tol-Segphos, xyl-Segphos, and DTBM-Segphos, and Umicore for generous support in supplying the rhodium and palladium complexes.

Keywords: alkynes • dibenzotetracenediones • quinones • rhodium • [2+2+2] cycloaddition

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10.1002/asia.201801670

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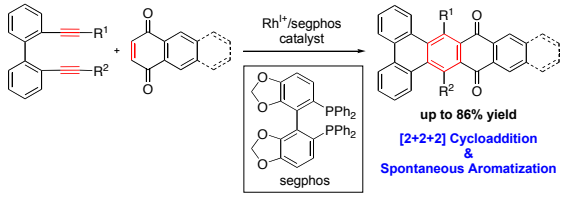

It has been established that a cationic rhodium(I)/Segphos complex catalyzes the [2+2+2] cycloaddition of biphenyl-linked 1,7-diynes with 1,4-naphthoquinone and anthracene-1,4-dione. Conveniently, spontaneous aromatization proceeded upon removal of the rhodium complex by passing the reaction mixture through an alumina column to give the corresponding dibenzotetracenediones and dibenzopentacenediones, respectively, in good yields.

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Facile Synthesis of Dibenzotetracenedione Derivatives by Rhodium-Catalyzed [2+2+2] Cycloaddition/Spontaneous Aromatization