[2+2+2] Annulation of N-(1-Naphthyl)acetamide with Two Alkynoates via Cleavage of Adjacent C–H and C–N Bonds Catalyzed by an Electron-Deficient Rhodium(III) Complex

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Abstract: It has been established that an electron-deficient cationic CpE-rhodium(III) complex catalyzes the non-oxidative [2+2+2] annulation of N-(1-naphthyl)acetamide with two alkynoates via cleavage of the adjacent C–H and C–N bonds to give densely substituted phenanthrenes under mild conditions (at 40 °C under air). In this reaction, a dearomatized spiro compound was isolated, which may support the formation of a cationic spiro rhodacycle intermediate in the catalytic cycle. The use of N-(1-naphthyl)acetamide in place of acetanilide switched the reaction pathway from the oxidative [2+2+2] annulation-lactamization via C–H/C–H cleavage to the non-oxidative [2+2+2] annulation via C–H/C–N cleavage. This chemoselectivity switch may arise from stabilization of the carbocation in the above cationic spiro rhodacycle by the neighboring phenyl and acetylamino groups, resulting in the nucleophilic C–C bond formation followed by β-nitrogen elimination.

Keywords: alkynes; C–H bond cleavage; C–N bond cleavage; cyclopentadienyl complexes; N-(1-naphthyl)acetamide; rhodium; [2+2+2] annulation

1. Introduction

The transition-metal-catalyzed [2+2+2] annulation of three unsaturated compounds is a useful method for the synthesis of six-membered carbocycles and heterocycles [1–9]. For example, the transition-metal-catalyzed [2+2+2] annulation of three alkynes is able to afford densely substituted benzenes with an atom- and step-economical manner [10–14]. For the synthesis of naphthalene derivatives, benzenes have been employed as one of the three alkynes but the use of the benzenes suffers from the redundant precursor synthesis and harsh reaction conditions [15–17]. Alternatively, several examples of the transition-metal-catalyzed oxidative [2+2+2] annulation via cleavage of adjacent two C–H bonds of benzenes, in which formally dehydrogenated benzenes are employed as benzyne equivalents, have been reported [18–22]. As such, our research group reported that an electron-deficient cationic CpE-rhodium(III) complex, derived from 1, catalyzes the oxidative tandem [2+2+2] annulation-lactamization of acetanilide (2a) with two alkynoates 3 via cleavage of adjacent two C–H bonds at room temperature under air to give densely substituted banzo[cd]indolones 4a (Scheme 1, top) [23]. In this catalysis, not only acetanilide (2a) but also ortho-substituted acetanilide 2b was able to react with two alkynoates 3 to give the corresponding banzo[cd]indolones 4b after treatment with KOH in ethanol (Scheme 1, top) [23]. In this paper, we have established that the electron-deficient cationic CpE-rhodium(III) complex is able to catalyze the non-oxidative [2+2+2] annulation of N-(1-naphthyl)acetamide (2c) with two alkynoates 3 via cleavage of...
the adjacent C–H and C–N bonds, leading to densely substituted phenanthrenes 5, under mild conditions (at 40 °C under air) (Scheme 1, middle). Although several examples of the transition-metal-catalyzed decarboxylative and oxidative [2+2+2] annulation of benzoic acids with two alkynoates via cleavage of the adjacent C–H and C–C bonds, leading to densely substituted naphthalenes, have been reported [24–27], only a single example of the non-oxidative [2+2+2] annulation via cleavage of the adjacent C–H and C–N bonds, in which the acylamino moiety is employed as a traceless directing group, has been reported in the neutral Cp*-rhodium(III) complex-catalyzed synthesis of tetraarylnaphthalenes from N-acylanilines and two diarylacetylenes at elevated temperature (110 °C) (Scheme 1, bottom) [28].

**Scheme 1.** Cationic CpE-rhodium(III) complex-catalyzed [2+2+2] annulations of acetanilides 2a/2b and N-(1-naphthyl)acetamide (2c) with two alkynoates 3 via cleavage of adjacent C–H/C–H and C–H/C–N bonds, respectively.
2. Results

In the course of our study of the cationic CpE-rhodium(III) complex-catalyzed oxidative tandem [2+2+2] annulation-lactamization of acetanilides with two alkynoatoles, leading to banzo[cd]indolones, the reaction of 2-methyl acetanilide 2b and ethyl 2-butynoatoles (3a) was examined. As already shown in Scheme 1, the expected banzo[cd]indolones 4b were generated after treatment with KOH in ethanol [23]. Surprisingly, the use of N-(1-naphthyl)acetamide (2c) in place of 2b failed to afford the expected naphtho[cd]indolone 4ca. Instead, densely substituted phenanthrene 5ca was generated as a major product along with a mixture of the corresponding regioisomeric [3+2] annulation products 6ca/6ca′ (Scheme 2). In addition to the above products, unidentified oligomerization products derived from 2c and 3a were generated as by-products.

![Scheme 2](image)

**Scheme 2.** Cationic CpE-rhodium(III) complex-catalyzed non-oxidative [2+2+2] annulation of N-(1-naphthyl)acetamide (2c) with two ethyl 2-butynoatoles (3a).

Then the screening of the reaction conditions and the acyl groups on the nitrogen of 1-aminonaphthalene was conducted as shown in Table 1. Elevating the reaction temperature (40 °C) slightly increased the yields of 5ca and 6ca/6ca′ (entry 2). Increasing the amount of 3a increased the yield of 5ca and decreased that of 6ca/6ca′ (entry 3). However, this increase was very small, therefore, the conditions of entry 2 were selected as the best conditions. With respect to the acyl groups on the nitrogen of the 1-aminonaphthalene moiety, electron-poor N-(1-naphthyl)amide 2d, possessing the highly acidic amide proton, was tested in place of 2c, while no reaction was observed even at 80 °C (entry 4). Sterically demanding N-(1-naphthyl)amide 2e was also tested with expectation for acceleration of reductive elimination. Unfortunately, the use of 2e significantly increased the yield of not the [2+2+2] annulation product 5ea but the [3+2] annulation products 6ea/6ea′ (entry 5). Finally, the reaction was conducted using the Cp*-rhodium(III) complex instead of the CpE-rhodium(III) complex 1, which resulted in significant decrease of the yields of 5ca and 6ca/6ca′ (entry 6).
Table 1. Optimization of reaction conditions for rhodium (III)-catalyzed [2+2+2] annulation of N-(1-naphthyl)acetonitriles 2 with two ethyl 2-butenoylates (3a)\(^a\).

| Entry | L   | 2 (R)       | Conditions   | 3a (Equiv.) | Yield (%)\(^b\) |
|-------|-----|-------------|--------------|-------------|-----------------|
| 1     | Cp\(^E\) | 2c (Ac)   | rt, 72 h     | 3            | 5ca/26 6ca (6ca')/18 (7) |
| 2     | Cp\(^E\) | 2c (Ac)   | 40 °C, 16 h   | 3            | 5ca/31 6ca (6ca')/24 (13) |
| 3     | Cp\(^E\) | 2c (Ac)   | 40 °C, 16 h   | 3            | 5ca/33 6ca (6ca')/22 (10) |
| 4\(^c\) | Cp\(^E\) | 2d (CO\(_2\)F\(_2\)) | 80 °C, 16 h | 3  | 5da/0 6da (6da')/0 (0) |
| 5     | Cp\(^E\) | 2e (CO\(_2\)-Bu) | 40 °C, 16 h | 3  | 5ea/0 6ea (6ea')/55 (3) |
| 6     | Cp\(^a\) | 2c (Ac)   | 40 °C, 16 h   | 3            | 5ca/13 6ca (6ca')/3 (<1) |

\(^a\) [Rh\(_3\)] (0.020 mmol), AgNTf\(_2\) (0.080 mmol), Cu(O\(_2\)Ac\(_2\))–H\(_2\)O (0.040 mmol), 2 (0.200 mmol), 3a (0.60–2.00 mmol), CH\(_2\)Cl\(_2\) (1.0 mL) and acetone (1.0 mL) were used. \(^b\) Determined by \(^1\)H NMR yield using C\(_6\)H\(_6\) as an internal standard. \(^c\) (CH\(_2\)Cl\(_2\)) (2.0 mL) was used.

The scope of the present cationic Cp\(^E\)-rhodium(III) complex-catalyzed [2+2+2] annulation is shown in Table 2. As with our previously reported cationic Cp\(^E\)-rhodium(III) complex-catalyzed oxidative tandem [2+2+2] annulation-lactamization of acetanilides with two alkynoates, leading to benzol[cf]indolones, a wide variety of primary alkyl-substituted alkynoates 3a–e reacted with N-(1-naphthyl)acetamide (2c) to give the corresponding [2+2+2] annulation products 5ca–ce (entries 1–5). However, phenyl-substituted alkynoate 3f failed to afford the corresponding [2+2+2] annulation product 5cf and gave the corresponding [3+2] annulation product 6cf in good yield with perfect regioselectivity (entry 6). This product switch is also the same as our previously reported tandem [2+2+2] annulation-lactamization of acetanilide (2a) with 3f [23]. Unfortunately, the use of electron-deficient alkynes did not afford the corresponding annulation products at all. For example, the use of ethyl propiolate afforded a complex mixture of products and no reaction was observed when using ethyl 2-butyroate. The structure and regiochemistry of the [2+2+2] annulation product 5ce were unambiguously determined by the X-ray crystallographic analysis as shown in Figure 1.

Table 2. Scope of alkynoates 3 on rhodium(III)-catalyzed [2+2+2] annulation with N-(1-naphthyl)acetamide (2c)\(^a\).

| Entry | 3 (equiv) | R\(^1\) | R\(^2\) | Yield (%)\(^b\) |
|-------|-----------|---------|---------|-----------------|
| 1     | 3a        | Me      | Et      | 5ca/33 6ca (6ca')/22 (10) |
| 2     | 3b        | Me      | Me      | 5cb/30 6cb (6cb')/22 (8) |
| 3     | 3c        | n-Bu    | Et      | 5ce/32 6cc (6cc')/37 (7) |
| 4     | 3d        | Ph(CH\(_2\))\(_3\) | Me      | 5cd/35 6cd (6cd')/38 (5) |
| 5     | 3e        | Cl(CH\(_2\))\(_3\) | Me      | 5ce/36 6ce (6ce')/31 (5) |
| 6     | 3f        | Ph      | Et      | 5cf/0 6cf (6cf')/0 (69) |

\(^a\) 1 (0.020 mmol), AgNTf\(_2\) (0.080 mmol), Cu(O\(_2\)Ac\(_2\))–H\(_2\)O (0.040 mmol), 2c (0.200 mmol), 3 (0.600 mmol), CH\(_2\)Cl\(_2\) (1.0 mL) and acetone (1.0 mL) were used. \(^b\) Determined by \(^1\)H NMR yield using C\(_6\)H\(_6\) as an internal standard.
1-aminonaphthalene ring gives quinodimethane structures in 5ca (entry 6). Electrophilic metalation of the electron-rich 1-aminonaphthalene ring produces cationic spiro demanding phenyl-substituted alkynoate.

Importantly, an interesting by-product was generated in the reaction of 2c and 3a as shown in Scheme 3. When using 3 equiv of 3a, a very small amount of dearomatized spiro compound 7ca was detected in the crude reaction mixture (3% yield). An isolable amount (13% yield) of 7ca was generated when using an excess amount of 3a.

Plausible mechanisms for the formation of 5ca, 6ca and 7ca from 2c and 3a are shown in Scheme 4. First, C–H bond cleavage of 2c by CpF-rhodium(III) species A affords naphthylrhodium B. Next, insertion of 3a into B gives alkenylrhodium C. The subsequent insertion of 3a into C gives dienylrhodium D. The second alkyne insertion may not proceed in the case of sterically demanding phenyl-substituted alkynoate 3f, thus generating [3+2] annulation product 6cf' (Table 2, entry 6). Electrophilic metalation of the electron-rich 1-aminonaphthalene ring produces cationic spiro rhodacycle E, in which the carboxation is stabilized by the neighboring phenyl and acetylamino groups. Nucleophilic attack of the dienylrhodium moiety to the electrophilic 1-position of the 1-aminonaphthalene ring gives π-pentadienyl complex F [29]. Importantly, nucleophilic attack of the dienylrhodium moiety to the 3-position of the 1-aminonaphthalene ring in spiro rhodacycle E', leading to π-pentadienyl complex F', would be unfavorable due to the unstable dearomatized quinodimethane structures in E' and F'. β-Nitrogen elimination [30,31] from intermediate F affords 5ca and the catalytically active rhodium(III) species A. However, the copper(II) co-catalyst was necessary in order to reoxidize rhodium(I) species generated through the competing oxidative [3+2] annulation giving 6ca. In this reaction, dearomatized spiro compound 7ca was isolated as a
by-product. This compound may be generated by reductive elimination and deprotonation from spiro rhodacycle E. Increasing the amount of 3a may facilitate the reductive elimination, which increased the yield of 7ca. This result may support the intermediacy of spiro rhodacycle E in the catalytic cycle. Interestingly, the regioselectivity of both the present CpE-rhodium(III)-catalyzed [2+2+2] and [3+2] annulations of N-(1-naphthyl)acetamide (2c) is opposite to that of our previously reported CpE-rhodium(III)-catalyzed [2+2+2] and [3+2] annulations of acetanilides that proceed presumably via alkenylrhodium G [23], although the reason is not clear at the present stage.

We considered that it is possible to regenerate spiro rhodacycle E by oxidative addition with a neutral rhodium(I) complex and protonation of 7ca. Therefore, 7ca was treated with acetic acid and an in situ generated neutral CpE-rhodium(I) complex, prepared by the reaction of 1, AgNTf2, NaOAc, 2a and 3a. However, no reaction was observed, thus excluding the intermediacy of 7ca in the catalytic cycle (Scheme 5).

Scheme 4. Plausible mechanisms for formation of 5ca, 6ca and 7ca from 2c and 3a.
Materials and Methods

3.1. General Information

Anhydrous acetone (No. 27,072-5) and CH2Cl2 (No. 130-02457) were obtained from Aldrich (St. Louis, MO, USA) and Wako (Osaka, Japan) and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4Å (Wako) prior to use. Anilides 2d [32] and 2e [33] were prepared according to the literature. Internal alkynes 3d [34] and 3e [35] were prepared according to the literature. All other reagents were obtained from commercial sources and used as received. 1H and 13C data were collected on a Bruker AVANCE III (Billerica, MA, USA) HD 400 (400 MHz) at ambient temperature. HRMS data were obtained on a Bruker micro TOF Focus II (Billerica, MA, USA). A single crystal X-ray diffraction measurement was made on Rigaku XtaLAB mini II diffractometer (Akishima, Japan) using graphite monochromated Mo-Kα radiation. All reactions were carried out in oven-dried glassware with magnetic stirring.

3.2. General Procedure for the Rhodium-Catalyzed Annulation of N-(1-Naphthyl)amides with Two Alkynoates (5ca, 6ca and 6ca’; Table 1, entry 2)

To a Schlenk tube was added AgNTf2 (15.5 mg, 0.040 mmol), [CpEBrh]2 1 (8.5 mg, 0.010 mmol), Cu(OAc)2·H2O (4.0 mg, 0.020 mmol), N-(naphthalen-1-yl)acetamide (2c, 18.5 mg, 0.100 mmol), ethyl 2-butynoate (3a, 33.6 mg, 0.300 mmol), acetone (0.5 mL) and CH2Cl2 (0.5 mL) under air in this order. The mixture was sealed and stirred at 40 °C under air for 16 hours. The resulting mixture was diluted with ether, filtered through a silica gel pad and washed with ether. The solvent was removed under reduced pressure and the residue was purified by a preparative thin layer chromatography (TLC, hexane/AcOEt = 2:1), to give a mixture of 5ca, 6ca and 6ca’. The yields of 5ca (31%), 6ca (22%) and 6ca’ (10%) were determined by 1H NMR with hexamethylbenzene as an internal standard.

3.3. Product Characterization

Ethyl 1,3-dimethylbenzanthrene-2,4-dicarboxylate (5ca). Analytically pure 5ca was isolated from a mixture of 5ca, 6ca and 6ca’ (21.8 mg, 5ca/6ca/6ca’ = 45:41:14) by a gel permeation chromatography (GPC). The regiochemistry of the title compound was determined by the NOESY experiment as well as analogy to the 1H NMR chemical shifts of 5ce. Colorless solid, 7.2 mg, 0.0205 mmol, 21% isolated yield, mp 83.8–85.0 °C; 1H NMR (CDCl3, 400 MHz) δ 8.44 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.92–7.87 (m, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.63–7.51 (m, 2H), 4.57–7.44 (m, 4H), 2.70 (s, 3H), 2.47 (s, 3H), 1.95 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H); 13C NMR (CDCl3, 100 MHz) δ 172.0, 170.0, 134.1, 133.0, 132.3, 129.8, 129.6, 129.5, 129.1, 128.7, 127.8, 127.5, 127.0, 126.3, 125.6, 122.4, 61.8, 61.4, 17.4, 17.2, 14.3, 13.9; HRMS (ESI) calcd for C22H22O4Na [M + Na]+ 373.1414, found 373.1410.

Ethyl 1-acetyl-3-methyl-1H-benzol[gl]indole-2-carboxylate (6ca) and ethyl 1-acetyl-2-methyl-1H-benzol[gl]indole-3-carboxylate (6ca’)[36]. An analytically pure mixture of 6ca and 6ca’ was isolated from a mixture of 5ca, 6ca and 6ca’ (21.8 mg, 5ca/6ca/6ca’ = 45:41:14) by GPC. The regiochemistry of the title compounds was determined by comparison with the 1H NMR chemical shifts of the literature.
Colorless solid, 7.6 mg, 0.0257 mmol, 26% isolated yield, 6ca/6ca’ = 75:25, mp 86.1-87.2 °C; 1H NMR (CDCl3, 400 MHz) δ 6ca: 8.17–8.11 (1H), 7.96–7.90 (1H), 7.67 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.55–7.48 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 2.76 (s, 3H), 2.65 (s, 3H), 2.04 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); 6ca’: 8.28 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.74 (t, J = 7.9 Hz, 1H), 7.57–7.44 (m, 3H), 4.50–4.40 (m, 2H), 2.85 (s, 3H), 2.62 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); 13C NMR (CDCl3, 100 MHz) δ 177.6, 162.3, 133.5, 129.41, 129.36, 126.3, 126.2, 125.8, 125.2, 124.7, 124.4, 124.0, 123.7, 123.2, 121.8, 121.7, 121.3, 120.8, 119.0, 61.2, 30.0, 14.3, 10.4; HRMS (ESI) calcd for C17H15NONa [M + Na]+ 318.1101, found 318.1115.

Dimethyl 1,3-dimethylphenanthrene-2,4-dicarboxylate (5cb). The yield of 5cb (30%) was determined by 1H NMR with hexamethylbenzene as an internal standard. Analytically pure 5cb was isolated from a mixture of 5cb, 6cb and 6cb’ (19.2 mg, 5cb/6cb/6cb’ = 51.37:12) by GPC. The regiochemistry of the title compound was determined by analogy to the 1H NMR chemical shifts of 5ce. Colorless solid, 8.8 mg, 0.0273 mmol, 27% isolated yield, mp 62.8–64.5 °C; 1H NMR (CDCl3, 400 MHz); 13C NMR (CDCl3, 400 MHz) δ 8.35 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 9.1 Hz, 1H), 7.93–7.87 (m, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.64–7.53 (m, 2H), 4.00 (s, 3H), 3.99 (s, 3H), 2.68 (s, 3H), 2.44 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 172.4, 170.5, 133.9, 133.1, 132.6, 129.83, 129.79, 129.1, 129.0, 128.8, 127.9, 127.7, 127.1, 126.4, 125.3, 122.3, 52.7, 52.3 17.5, 17.4; HRMS (ESI) calcd for C20H18O2Na [M + Na]+ 345.1097, found 345.1101.

Methyl 1-acetyl-3-methyl-1H-benzol[glindole-2-carboxylate (6cb) and methyl 1-acetyl-2-methyl-1H-benzol[glindole-3-carboxylate (6cb’). The yields of 6cb (22%) and 6cb’ (8%) was determined by 1H NMR with hexamethylbenzene as an internal standard. An analytically pure mixture of 6cb and 6cb’ was isolated from a mixture of 5cb, 6cb and 6cb’ (19.2 mg, 5cb/6cb/6cb’ = 51.37:12) by GPC. The regiochemistry of the title compounds was determined by analogy to the 1H NMR chemical shifts of 6ca and 6ca’. Colorless solid, 6.0 mg, 0.0213 mmol, 21% isolated yield, 6cb/6cb’ = 75:25, mp 93.7–95.0 °C; 1H NMR (CDCl3, 400 MHz) 6cb: δ 8.17–8.10 (m, 1H), 7.95–7.89 (m, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.57–7.44 (m, 2H), 3.97 (s, 3H), 2.76 (s, 3H), 2.64 (s, 3H); 6cb’: δ 8.26 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.93–7.87 (m, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.64–7.55 (m, 2H), 4.00 (s, 3H), 3.99 (s, 3H), 2.68 (s, 3H), 2.44 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 171.0, 136.8, 134.9, 133.6, 130.3, 130.2, 128.7, 128.5, 125.3, 123.4, 118.6, 118.1, 116.3, 27.6, 9.2; HRMS (ESI) calcd for C17H15NONa [M + Na]+ 304.0944, found 304.0952.

Diethyl 1,3-dibutylphenanthrene-2,4-dicarboxylate (5cc). The yield of 5cc (32%) was determined by 1H NMR with hexamethylbenzene as an internal standard. Analytically pure 5cc was isolated from a mixture of 5ce, 6cc and 6cc’ (40.0 mg, 5cc/6cc/6cc’ = 42:9:49) by GPC. The regiochemistry of the title compound was determined by analogy to the 1H NMR chemical shifts of 5ce. Pale yellow oil, 11.7 mg, 0.0269 mmol, 27% isolated yield; 1H NMR (CDCl3, 400 MHz) δ 8.42 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.90–7.86 (m, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.61–7.56 (m, 1H), 7.55–7.50 (m, 1H), 4.51–4.43 (m, 4H), 3.04–2.97 (m, 2H), 2.80–2.68 (m, 2H), 1.78–1.64 (m, 4H), 1.55–1.29 (m, 4H), 1.44 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.02–0.92 (m, 6H); 13C NMR (CDCl3, 100 MHz) δ 171.9, 170.0, 137.5, 135.0, 133.7, 132.9, 129.4, 129.2, 129.1, 128.5, 128.1, 127.7, 127.0, 126.1, 125.7, 122.3, 61.7, 61.3, 33.9, 33.5, 32.1, 31.3, 23.4, 23.3, 14.2, 13.9, 13.83, 13.79; HRMS (ESI) calcd for C25H34O4Na [M + Na]+ 457.2349, found 457.2359.

Ethyl 1-acetyl-3-buty1-1H-benzol[glindole-2-carboxylate (6cc) and ethyl 1-acetyl-2-buty1-1H-benzol[glindole-3-carboxylate (6cc’). The yields of 6cc (37%) and 6cc’ (7%) were determined by 1H NMR with hexamethylbenzene as an internal standard. An analytically pure mixture of 6cc and 6cc’ was isolated from a mixture of 5cc, 6cc and 6cc’ (40.0 mg, 5cc/6cc/6cc’ = 42:9:49) by GPC. The regiochemistry of the title compounds was determined by analogy to the 1H NMR chemical shifts of 6ca and 6ca’. Colorless solid, 13.2 mg, 0.0391 mmol, 39% isolated yield, 6cc/6cc’ = 86:14, mp 61.0–62.4 °C; 1H NMR (CDCl3, 400 MHz) δ 6cc: 8.16–8.09 (m, 1H), 7.95–7.88 (m, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.56–7.43 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.11 (t, J = 7.7 Hz,
2H), 2.77 (s, 3H), 1.75–1.63 (m, 2H), 1.52–1.40 (m, 5H), 1.00–0.93 (m, 3H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \(\delta\) 177.7, 162.2, 133.4, 131.0, 129.4, 129.0, 126.3, 125.7, 124.8, 123.4, 123.1, 121.9, 121.6, 119.1, 61.2, 33.4, 30.0, 24.7, 22.9, 14.2, 14.0; HRMS (ESI) calcld for C\(_{21}\)H\(_{23}\)NO\(_3\)Na [M + Na\(^+\)] \(\delta\) 360.1570, found 360.1575.

**Dimethyl 1,3-bis(3-phenylpropyl)phenanthrene-2,4-dicarboxylate (5cd)**. The yield of 5cd (35%) was determined by \(^1H\) NMR with hexamethylbenzene as an internal standard. Analytically pure 5cd was isolated from a mixture of 5cd, 6cd and 6cd\(^{'}\) (42.3 mg, 5cd/6cd/6cd\(^{'}\) = 46.7:4:1) by GPC. The regiochemistry of the title compound was determined by analogy to the \(^1H\) NMR chemical shifts of 5ce. Pale yellow solid, 16.4 mg, 0.0294 mmol, 29% isolated yield, mp 108.1–109.2 \(^\circ\)C; \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.30 (d, \(J = 8.4\) Hz, 1H), 7.89–7.83 (m, 1H), 7.78–7.68 (m, 2H), 7.61–7.44 (m, 2H), 7.36–7.14 (m, 10H), 3.84 (s, 3H), 3.65 (s, 3H), 3.00–2.90 (m, 2H), 2.78 (t, \(J = 7.2\) Hz, 2H), 2.70–2.62 (m, 2H), 2.10–1.94 (m, 4H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \(\delta\) 172.2, 170.1, 141.8, 141.6, 137.3, 134.6, 133.5, 132.9, 129.3, 129.2, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.1 126.3, 126.0, 125.8, 125.3, 122.1, 52.5, 52.0, 36.4, 36.2, 33.2, 32.6, 32.0, 30.9; HRMS (ESI) calcld for C\(_{134}\)H\(_{132}\)O\(_2\)Na [M + Na\(^+\)]\(^{+}\) 553.2349, found 553.2354.

**Diethyl 1,3-dibutylphenanthrene-2,4-dicarboxylate (5ce)**. The yield of 5ce (36%) was determined by \(^1H\) NMR with hexamethylbenzene as an internal standard. Analytically pure 5ce was isolated from a mixture of 5ce, 6ce and 6ce\(^{'}\) (42.6 mg, 5ce/6ce/6ce\(^{'}\) = 50:7:43) by GPC. The regiochemistry of the title compound was determined by the X-ray crystallographic analysis as shown in Figure 1. Colorless solid, 13.5 mg, 0.0284 mmol, 28% isolated yield, mp 108.1–109.2 \(^\circ\)C; \(^1H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.34 (d, \(J = 8.4\) Hz, 1H), 7.97 (d, \(J = 9.2\) Hz, 1H), 7.93–7.88 (m, 1H), 7.82 (d, \(J = 9.2\) Hz, 1H), 7.65–7.53 (m, 2H), 4.02 (s, 3H), 3.98 (s, 3H), 3.68 (t, \(J = 6.1\) Hz, 2H), 3.63 (t, \(J = 6.1\) Hz, 2H), 3.24–3.16 (m, 2H), 2.93–2.84 (m, 2H), 2.26–2.13 (m, 4H); \(^{13}C\) NMR (CDCl\(_3\), 100 MHz) \(\delta\) 172.0, 170.0, 152.2, 141.8, 141.6, 137.3, 134.6, 133.5, 132.9, 129.3, 129.2, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.1 126.3, 126.0, 125.8, 125.3, 125.8, 124.7, 123.3, 123.2, 121.8, 121.6, 119.0, 51.9, 53.9, 32.5, 29.9, 24.5; HRMS (ESI) calcld for C\(_{38}\)H\(_{34}\)O\(_2\)Na [M + Na\(^+\)]\(^{+}\) 408.1570, found 408.1574.
123.3, 121.7, 121.60, 120.8, 118.8, 52.1, 44.7, 33.7, 29.9, 22.1; HRMS (ESI) calcd for C₁₉H₁₈O₃NaClNa [M + Na]^+ 366.0867, found 366.0871.

Ethyl 2-phenyl-1-pivaloyl-1H-benzol[g]indole-3-carboxylate (6cf'). The yield of 6cf' (69%) was determined by 1H NMR with hexamethylbenzene as an internal standard. Analytically pure 6cf' was isolated by repeated preparative TLCs. Pale yellow oil, 21.9 mg, 0.0612 mmol, 61% isolated yield; 1H NMR (CDCl₃, 400 MHz) δ 8.43 (d, J = 8.8 Hz, 1H), 8.00–7.95 (m, 1H), 7.91–7.86 (m, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.55–7.44 (m, 7H), 4.22 (q, J = 7.1 Hz, 2H), 2.27 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.17 (s, 9H); 13C NMR (CDCl₃, 100 MHz) δ 176.0, 164.5, 142.4, 132.0, 131.2, 130.8, 129.43, 129.41, 129.1, 129.3, 128.0, 126.1, 125.2, 125.0, 124.7, 121.7, 121.3, 120.6, 110.1, 59.9, 29.3, 14.0; HRMS (ESI) calcd for C₂₅H₂₂NO₃Na [M + Na]^+ 380.1570, found 380.1570.

Ethyl 3-methyl-1-pivaloyl-1H-benzol[g]indole-2-carboxylate (6ea) and ethyl 2-methyl-1-pivaloyl-1H-benzol[g]indole-3-carboxylate (6ea'). The yields of 6ea (55%) and 6ea' (3%) were determined by 1H NMR with hexamethylbenzene as an internal standard. An analytically pure mixture of 6ea and 6ea' was isolated by repeated preparative TLCs. Colorless solid; 15.5 g, 0.0459 mmol, 46% isolated yield, 6ea. mp 128.4–129.5 °C; 1H NMR (CDCl₃, 400 MHz) δ 8.24–8.17 (m, 1H), 7.91–7.86 (m, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.52–7.42 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 2.66 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H), 1.17 (s, 9H); 13C NMR (CDCl₃, 100 MHz) δ 187.5, 162.9, 133.4, 131.3, 129.1, 125.8, 125.7, 125.1, 124.7, 122.9, 122.8, 122.4, 122.3, 119.0, 61.2, 46.8, 28.2, 14.3, 10.4; HRMS (ESI) calcd for C₂₁H₂₁NO₃Na [M + Na]^+ 360.1570, found 360.1570.

Diethyl (Z)-1'-(acetylmino)-3,5-dimethyl-1'H-spiro[cyclopentane-1,2'-naphthalene]-2,4-diene-2,4-dicarboxylate (7ca). The yield of 7ca (13%) was determined by 1H NMR with hexamethylbenzene as an internal standard. Analytically pure 7ca was isolated by repeated preparative TLCs. The structure was determined by the HSQC and HMBC analyses. Pale yellow oil, 9.7 mg, 0.214 mmol, 11% isolated yield; 1H NMR (CDCl₃, 400 MHz) δ 8.08 (d, J = 8.0 Hz, 1H, H²), 7.48 (td, J = 7.5, 1.3 Hz, 1H, H⁸), 7.31 (td, J = 7.7, 1.3 Hz, 1H, H⁸), 7.28–7.22 (m, 1H, H⁶), 6.79 (d, J = 9.4 Hz, 1H, H⁴), 5.05 (d, J = 9.4 Hz, 1H, H⁴), 4.31 (q, J = 7.1 Hz, 2H, CO₂CH₂CH₃ on C²), 4.04 (q, J = 7.1 Hz, 2H, CO₂CH₂CH₃ on C⁴), 2.50 (s, 3H, CH₃ on C⁴), 2.10 (s, 3H, CH₃ on C¹), 2.01 (s, 3H, NCOCH₃), 1.36 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃ on C³), 0.89 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃ on C⁴); 13C NMR (CDCl₃, 100 MHz) δ 180.6 (NCOCH₃), 164.1 (C⁴), 164.0 (CO₂Et), 163.0 (CO₂Et), 158.7, 154.0 (C'), 136.0 (C'), 135.1, 132.6 (C'), 132.2, 129.9, 129.0 (C'), 127.9 (C'), 127.8 (C'), 127.5 (C'), 127.1 (C'), 67.7 (C'), 60.8 (CO₂CH₂CH₃ on C³), 60.1 (CO₂CH₂CH₃ on C⁴), 24.5 (NCOCH₃), 15.1 (CH₃ on C³), 14.2 (CO₂CH₂CH₃ on C³), 13.9 (CH₃ on C¹), 13.5 (CO₂CH₂CH₃ on C⁴); HRMS (ESI) calcd for C₂₃H₂₃NO₃Na [M + Na]^+ 430.1625, found 430.1623.

The 1H and 13C-NMR spectra of 5ca–5ce, 6ca–6ce, 6ca′–6cf' and 7ca, and crystal data and data collection parameters of 5ce are available in Supplementary Materials.

4. Conclusions

In summary, we have established that an electron-deficient cationic Cp^E^-rhodium(III) complex catalyzes the non-oxidative [2+2+2] annulation of N-(1-naphthyl)acetamide with two alkynoyates via cleavage of the adjacent C–H and C–N bonds to give densely substituted phenanthenes under mild conditions (at 40 °C under air). Importantly, a dearomatized spiro compound was isolated in this reaction, which may support the formation of a spiro rhodacycle intermediate in the catalytic cycle. The use of N-(1-naphthyl)acetamide in place of acetalanilde switched the reaction pathway from the oxidative tandem [2+2+2] annulation-lactamization involving cleavage of adjacent two C–H bonds to the non-oxidative [2+2+2] annulation involving cleavage of the adjacent C–H and C–N bonds. This chemoselectivity switch may arise from stabilization of the carbocation in the above cationic spiro rhodacycle by the neighboring phenyl and acetylamino groups, resulting in nucleophilic attack of the dienylrhodium moiety to this carbocation followed by β-nitrogen elimination.
Supplementary Materials: The following are available online: $^1$H and $^{13}$C NMR spectra of 5ca–5ce, 6ca–6ce, 6ca′–6cf′ and 7ca and crystal data and data collection parameters of 5ce.

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Sample Availability: Samples of the compounds not are available from the authors.

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