Facile Synthesis of Carbotetracycles via Gold(I)-Catalyzed Cyclization of Unactivated Cyclic 1-Aryl-6,8-dien-1-ynes

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The gold(I)-catalyzed cyclization of the cyclohexa-1,3-diene bearing a terminal alkyne and a *gem*-diester in the tether proceeds via a cationic gold intermediate to give a tetrahydromethyleneindene derivative. Changing the *gem*-diester to a *gem*-diketone in the tether, the transient gold-stabilized carbocation is trapped intramolecularly by a methyl ketone to afford a tricyclo[5.4.0.0^{4,8}]undecane ring skeleton. Under the same reaction conditions, aryl-substituted cyclohexadienynes afford hexahydroacephenanthrylene rings in a diastereoselective fashion and in good yields. The reaction proceeded via attack of the aryl group onto the gold-stabilized carbocations followed by aromatization and protodemetalation to generate the tetracarbocycles. This cycloaddition can be applied to the synthesis of pentahydronapthoazulenes from aryl-substituted cycloheptadienynes and the gold(I) catalyst.

Introduction

Transition-metal-catalyzed cycloadditions of enynes provide convenient and efficient methods for the synthesis of a variety of carbocycles. The intramolecular versions are of special interests due to their high regio- and stereoselectivity. Development of the electrophilic activation of unsaturated carbon−carbon bonds using copper,[1] platinum,[2] and nickel complexes[3] or salts[4] to produce carbocycles has been reported. Recently, gold(I) complexes have emerged as efficient catalysts for intramolecular cycloaddition of unactivated enynes.[5] It has been shown that coordination of electrophilic phosphine gold(I) complexes to the alkyne group of enynes generates an (η^2-alkyne)gold complex, which evolves to form a cationic gold intermediate. Attack of nucleophiles (water or alcohols) at the transient reactive intermediate produced five- or six-membered carbo- or heterocyclic rings. For aryl-substituted enynes, attack of the aryl group onto the cationic intermediate provides tricyclic compounds in good yields.[1,6] However, gold(I)-catalyzed cycloadditions of acyclic aryl-substituted dienynes required long reaction times and the reactions proceeded via both aromatic electrophilic addition and "metallo-Cope" rearrangement of the proposed aryl-substituted cationic gold intermediates to give carbotricycles and 1,4-cyclohexadienes, respectively. We have now demonstrated that hexahydroacephenanthrylenes are produced exclusively in a highly diastereoselective fashion by treatment of aryl-substituted cyclohexadienynes with 2 mol % of $Ph_3PAuCl/AgOTf$ in CH_2Cl_2 for 5 min, whereas pentahydronaphthoazulene derivatives can be obtained using aryl-substituted cycloheptadienynes under the same reaction conditions.

Results and Discussion

The requisite cyclohexadienynes **1a** and **1b** were prepared according to literature procedures.[7] Our study of intramolecular gold(I)-catalyzed cyclization of cyclic dienynes began with the parent compound **1a** (Scheme 1). Treatment of **1a** with 2 mol % of $Ph_3PAuCl/AgOTf$ in dichloromethane at 30 °C for 5 min produced the 2,3,3a,7a-tetrahydro-1-methylene-1*H*-indene derivative **2** in 65% isolated yield. In general, *cis*-fused hexahydroindene skeletons are constructed via intramolecular Diels−Alder reaction. However, the Diels−Alder reaction required heating substrates at elevated temperature in toluene in a sealed tube.[8] The current approach to the synthesis of the *cis*-fused hexahydroindene derivative **2** is achieved without the use of complex catalysts or critical reaction conditions, only requiring 2 mol % of $Ph_3PAuCl/AgOTf$ in dichloromethane at 30 °C for 5 min.

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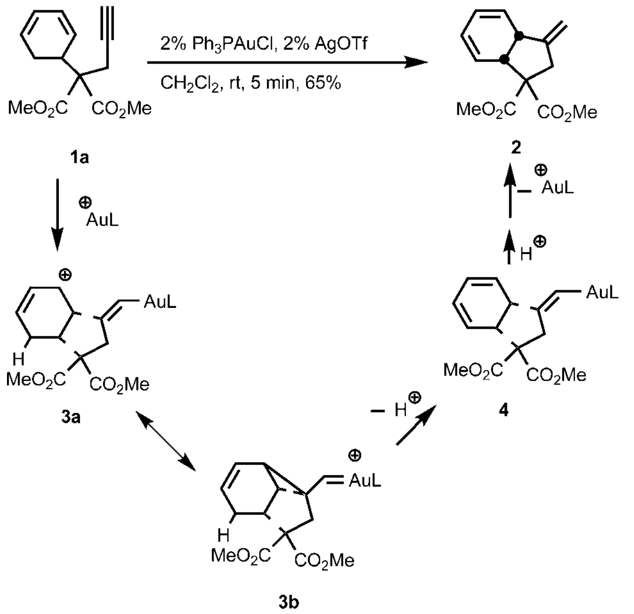
10.1021/om8005917 CCC: $40.75

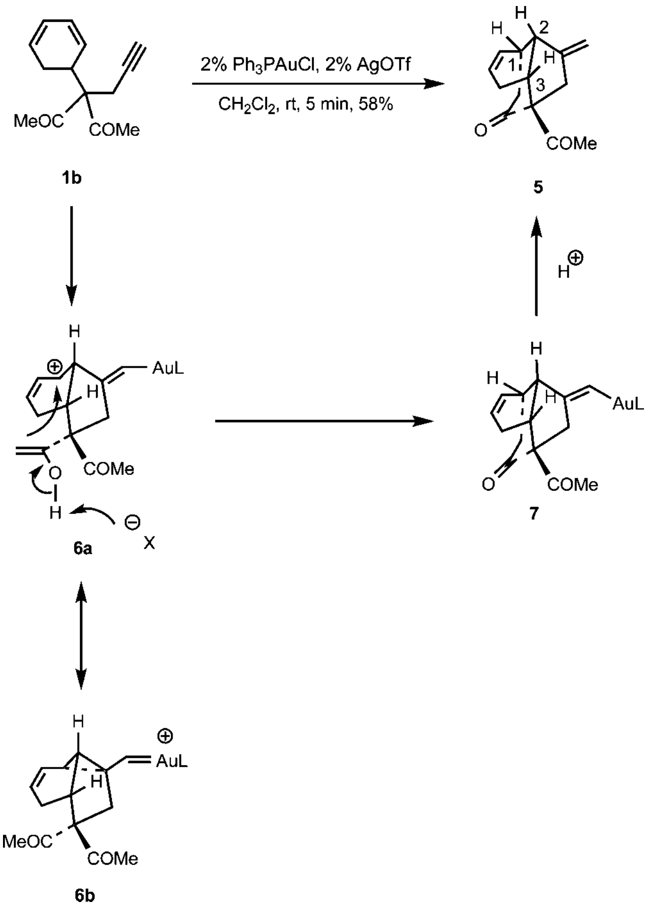
Scheme 1



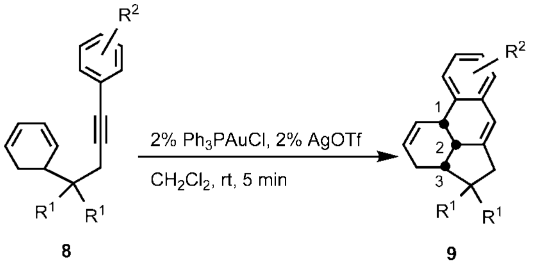
The reaction pathway leading to **2** was suggested as follows. Addition of the proximal double bond of the conjugated diene to the gold-activated alkyne of **1a** would generate the cationic gold **3a** with the newly formed carbon−carbon bond. The *cis* relative stereochemistry of the ring juncture of **3a** was fixed by the alkyne−gold moiety aligned with the face of the cyclic diene in which the tethering chain resides. Intermediate **3a** led to the gold cyclopropyl carbene intermediate **3b**, as suggested in the literature.[1,6] Deprotonation of the allylic proton of the postulated intermediate **3a** or **3b** gave **4**. Protonation of **4** at the metal center followed by reductive elimination led to **2** and regenerated the gold(I) catalyst in the catalytic cycle.

Interestingly, using the same reaction conditions, we were able to construct the tricyclo[5.4.0.$0^{4,8}$]undecane ring skeleton **5** by intramolecular C-alkylation of a methyl ketone to the postulated reactive cationic gold intermediate. Thus, treatment of cyclohexadienyndione **1b** with 2 mol % of Ph_3PAuCl/AgOTf in CH_2Cl_2 at room temperature for 5 min furnished the tricyclic compound **5** in 58% isolated yield (Scheme 2). The product of the relative stereochemistry as depicted was obtained as a single diastereomer, which is derived from a *syn* addition of the alkyne and the methyl ketone across the proximal double bond of the conjugated diene. NOESY (nuclear Overhauser enhancement spectroscopy) experiments provided the initial evidence for support of all *syn* relationships among hydrogen atoms at C-1, C-2, and C-3 of **5**. The formation of **5** was suggested in Scheme 2. Coordination of the alkyne of **1b** to the Au metal center followed by intramolecular nucleophilic addition of the diene to the Au-alkyne moiety generated the gold cationic intermediates **6a** and **6b**. Due to two fused protons present on the convex face, the enol would attack at the gold-stabilized allylic cation of **6a** from the concave face to give the vinyl gold species **7**, which underwent protodemetalation to afford the carbotricycle **5**.

Scheme 2



Scheme 3



R^1 = CO_2Me or COMe

- **a**: R^1 = CO_2Me, R^2 = H 93%
- **b**: R^1 = CO_2Me, R^2 = 3-Me 92%
- **c**: R^1 = CO_2Me, R^2 = 3-OMe 94%
- **d**: R^1 = CO_2Me, R^2 = 3-Br 90%
- **e**: R^1 = CO_2Me, R^2 = 5-Br 86%
- **f**: R^1 = CO_2Me, R^2 = 3-OH 50%
- **g**: R^1 = COMe, R^2 = H 83%
- **h**: R^1 = COMe, R^2 = 3-Me 72%
- **i**: R^1 = COMe, R^2 = 3-Ph 54%
- **j**: R^1 = COMe, R^2 = 5-OMe 63%

With aryl end groups on the alkyne of cyclic dienynes, the intramolecular gold(I)-catalyzed cyclization reactions of cyclic dienynes proceeded by a different reaction path. Thus, substrate **8a**, bearing an aryl group at the alkyne, reacted smoothly with 2 mol % of Ph_3PAuCl/AgOTf in CH_2Cl_2 at 30 °C for 5 min to generate dimethyl 3,3a-dihydroacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (**9a**) as the only diastereomer in 93% yield (Scheme 3). In general, the reactive gold(I) cationic complex $Ph_3PAuSbF_6$ generated in situ from $Ph_3PAuCl/AgSbF_6$ required longer reaction times (ca. 12 h) to catalyzed the intramolecular cyclizations of acyclic 1-aryl-1,6-enynes in CH_2Cl_2 at room temperature, whereas bulkier phosphines ligands for Au(I) were more efficient under these conditions.[6,9] Thus, it is reasonable to state that 1-arylcyclohexa-6,8-dien-1-ynes are extremely reactive substrates toward the simple cationic $Ph_3PAuOTf$ complex generated in situ from Ph_3PAuCl and AgOTf. The product of the relative stereochemistry as depicted was obtained

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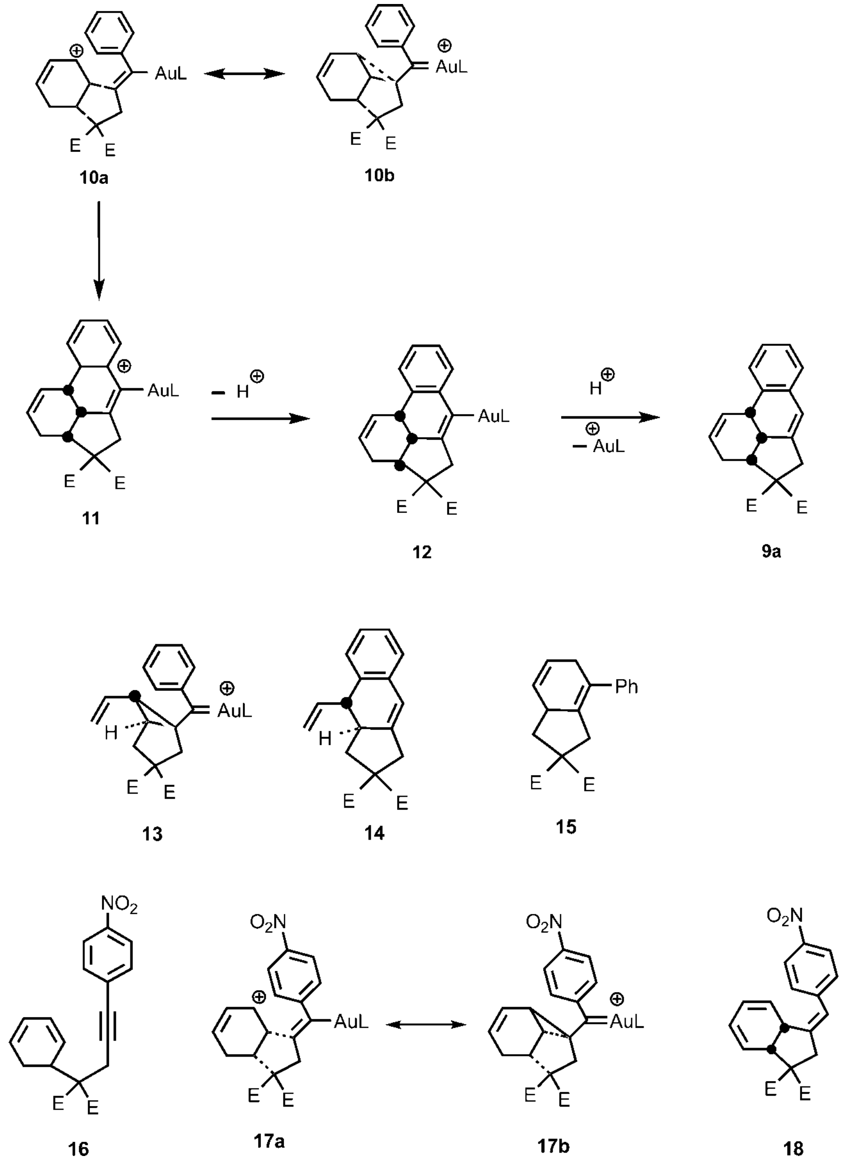
Scheme 4



as a single diastereomer, which is derived from *syn* addition of the alkyne and the aryl group across the proximal double bond of the conjugated diene. The relative stereochemistry of **9a** was determined as a 1,2-*cis*, 2,3-*cis* relationship on the basis of NOESY measurements. In general, acephenanthrylene skeletons require lengthy synthetic procedures[10] and are constructed via elevated temperature cyclization using flash vacuum pyrolysis (FVP).[11] The current approach to the synthesis of all-*syn* relative stereochemistry of acephenanthrylenes is achieved without the use of complex catalysts or critical reaction conditions, only requiring a catalytic amount of $Ph_3PAuCl/AgOTf$. The initial cationic gold intermediate **10a** was attacked by the aryl group at the gold-stabilized allylic carbocation from the concave face to give the tetracyclic skeleton **11**, containing an η^1-alkenylgold bond (Scheme 4). Aromatization (to give **12**) followed by protodemetalation afforded **9a** and release of the gold(I) catalyst into the catalytic cycle. It must be mentioned that an acyclic analogue of intermediate **10b**, for example **13**, underwent both intramolecular cycloaddition and "metallo-Cope" rearrangement to give tricyclic compound **14** and 1,4-cyclohexadiene derivative **15**, respectively, in a ratio of 4:3.[1] However, the tricyclic gold cyclopropyl carbene **10b** did not undergo "metallo-Cope" rearrangement, and attack of the phenyl ring onto the gold-stabilized allylic carbocation of **10a** predominately produced hexahydroacephenanthrylene derivative **9a**. Results of cyclization of aryl-substituted cyclohexadienynes **8a**–**j** are listed in Scheme 3. The relative stereochemistry of products **9a**–**j** was assigned as the same all-*syn* relationship among hydrogen atoms at three contiguous stereogenic centers on the basis of their close chemical shift values and similar coupling patterns of the fused protons in their ^{1}H NMR spectra. Electron-neutral and -rich arenes were proven to be good substrates, as the yields of desired tetracyclic products **9b**,**c** ranged from 92% to 94% (Scheme 3). In addition, substrates with a bromine atom, for example, **8d**,**e**, did not inhibit the catalytic activity of the gold species, as evidenced by good yields of products **9d**,**e** (90% and 86%, respectively). However, substrate **8f**, possessing a *para* hydroxyl group at the phenyl ring, was less effective and provided **9f** in 50% yield. Cyclohexadienynes bearing an aryl group at the alkyne and a *gem*-diketone in the tether, for example, **8g**–**j**, also generated cyclization products (**9g**–**j**), albeit with lower yields (54–83%). The structure elucidations of tetracyclic

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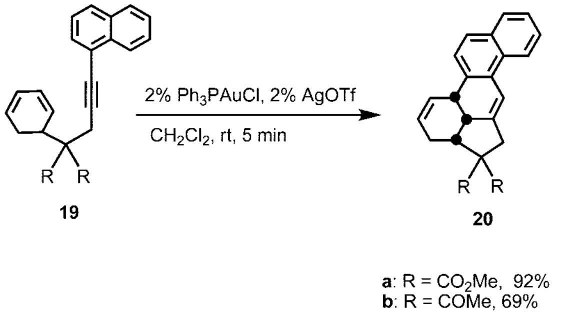
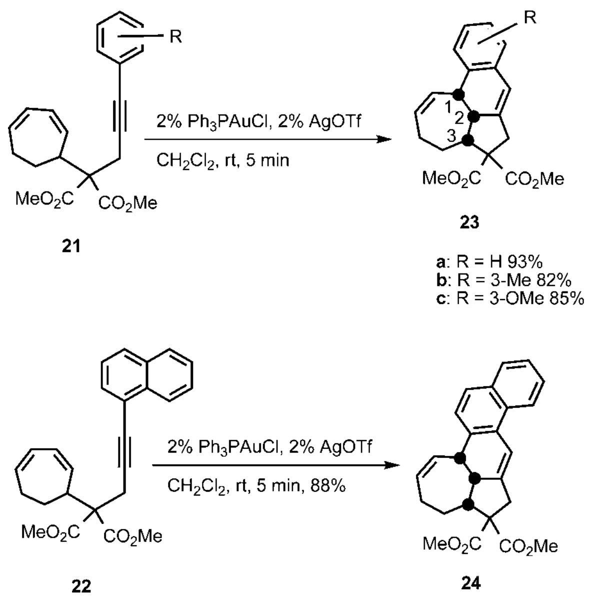
Scheme 5



Scheme 6



compound **9g**,**h** were accomplished by X-ray diffraction analysis. The all-*syn* relative stereochemistry among hydrogen atoms at three contiguous stereogenic centers further supports the proposed reaction path suggested for the formation of carbotetracycles (Scheme 4). However, with an electron-withdrawing group at the *para*-position of the arene, for example, the nitroaryl-substituted cyclohexadienyne **16**, the cycloaddition led to the tetrahydroindene derivative **18** in 65% yield under the same reaction conditions. Thus, attack of the nitroaryl group to the gold-stabilized carbocation of the transient cationic gold intermediate **17a** failed, and the reaction proceeded in a manner similar to that found for the parent compound **1a** to afford **18**. Results of the Friedel−Crafts reaction of the electron-neutral and -rich arenes (Scheme 3) and the reaction of nitroaryl-substituted cyclohexadienyne **16** clearly show an exact pattern of electrophilic addition of arenes. Moreover, the trapping of the allylic cation by the enol of **1b** (Scheme 2) provides strong evidence for the proposed ionic pathway. Although gold-catalyzed cyclization of aryl-substituted enynes was suggested to proceed via metal cyclopropyl carbenoids,[6] the formation of **5** (Scheme 2) and **9a**−**j** (Scheme 3) may indicate that the reactive gold intermediates may have significant cationic character in the gold-catalyzed cyclization of cyclic dienynes. Moreover, the striking experimental evidence recently reported by the Fürstner group strongly supports that the reactive gold species involved in gold-catalyzed cycloisomerization of methyl-substituted enynes with a pendant carboxylic acid or an alcohol group are more appropriately described as gold-stabilized carbocations rather than "gold carbenes".[12]

Substrates **19a**,**b**, bearing a napthyl group at the alkyne, reacted smoothly with the catalysts to afford pentacarbocycles **20a** (88%) and **20b** (69%), respectively (Scheme 5). The structure elucidation of **20b** was accomplished by X-ray diffraction analysis.

The chemistry can be applied to synthesis of pentahydronaphthoazulenes from seven-membered-ring substrates. Thus, cycloheptadienynes **21a**−**c** and **22**, possessing an aryl or napthyl group at the alkyne (Scheme 6), underwent cyclization using the same reaction protocols to provide pentahydronaphthoazulene derivatives **23a**−**c** and **24**, respectively, as the only stereoisomer in each case and in good yield. NOESY experiments provided the initial evidence for support of an all-*syn* relationship among hydrogen atoms at C-1, C-2, and C-3 of **23a**. The relative stereochemistries of **23b**,**c** and **24** were assigned as the same all-*syn* relationship on the basis of their close chemical shift values and similar coupling patterns of the protons at the C-2 position in their ^{1}H NMR spectra. The structure **24** was further confirmed by X-ray diffraction analysis.

In conclusion, a gold(I)-catalyzed cyclization of cyclic dienynes has been successfully developed. The conjugated diene added to the terminal alkyne in the presence of a catalytic amount of $Ph_3PAuCl/AgOTf$ to afford an exomethylenetetrahydroindene derivative, whereas treatment of aryl-substituted cyclic dienynes under the same reaction conditions furnished in high diastereoselective fashion hexahydroacephenanthrylene and pentahydronaphthoazulene derivatives in good yields. Key steps in the synthesis of the tetracarbocycles involve an intramolecular addition of the conjugated diene of aryl-substituted cyclic dienynes to the electrophilic (η^2-alkyne)gold moiety to form reactive gold intermediates. Attack of the aryl group onto the gold-stabilized carbocation followed by aromatization followed by protodemetalation produced the carbotetracycles.

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Methylene chloride was predried by molecular sieves and then by passing through an Al_2O_3 column.[13] Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230−400 mesh) using the indicated solvents.[14] ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with Bruker-AC 400 (400 MHz) and 500 (500 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with Bruker-AC 400 (100 MHz) and 500 (125 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and were reported as mass/charge (*m/e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure for Gold(I)-Catalyzed Cyclization of Cyclic 6,8-Dien-1-ynes. To an oven-dried 100 mL round-bottom flask equipped with a stirrer bar and capped with a rubber septa was added AgOTf (5.14 mg, 0.02 mmol). The apparatus was

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evacuated (oil pump) and filled with nitrogen three times. To the reaction mixture were then added via syringe dimethyl 2-(cyclohexa-2,4-dienyl)-2-(prop-2-ynyl)malonate (**1a**) (0.25 g, 1.0 mmol) and PPh_3AuCl (0.01 g, 0.02 mmol) in 30 mL of CH_2Cl_2. The resulting mixture was stirred at room temperature for 5 min. The reaction mixture was filtered through a bed of Celite. The filtrate was concentrated in vacuo to give the crude mixture.

(±)-(3a*S*,7a*R*)-Dimethyl 3,3a-Dihydro-3-methylene-2*H*-indene-1,1(7a*H*)-dicarboxylate (2). The crude mixture obtained from intramolecular cyclization of **1a** (0.26 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate/hexanes) to give **2** (0.16 g, 0.65 mmol, 65%) as a pale yellow liquid: IR (CH_2Cl_2) 2918, 2750, 1680, 1515, 1443, 1372, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.91 (m, 1 H), 5.76 (m, 2 H), 5.44 (dd, *J* = 9.8, 3.8 Hz, 1 H), 5.01 (dd, *J* = 4.0, 2.0 Hz, 1 H), 4.92 (dd, *J* = 4.3, 2.1 Hz, 1 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 3.51 (m, 1 H), 3.51 (m, 1 H), 3.11 (ddd, *J* = 16.5, 4.4, 2.1 Hz, 1 H), 2.73 (d, *J* = 16.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.80, 170.47, 152.92, 128.23, 124.73, 123.71, 120.94, 107.03, 65.37, 52.80, 52.31, 43.83, 41.15, 39.85; MS (EI) *m*/*e* (rel intensity) 248.3 (M^+, 22), 188.2 (64), 186.2 (53), 149.1 (34), 129.2 (100), 128.2 (84); HRMS (EI) *m*/*e* calcd for $C_{14}H_{16}O_4$ 248.1049, found 248.1047.

(±)-(3a*R*,4*R*,7a*R*)-1-Acetyl-3-methylene-2,3,3a,4,7,7a-hexahydro-1*H*-1,4-ethanoinden-9-one (5). The crude mixture obtained from intramolecular cyclization of **1b** (0.22 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **5** (0.13 g, 0.58 mmol, 58%) as a pale yellow liquid: IR (CH_2Cl_2) 2918, 2750, 1680, 1515, 1443, 1372, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 9.9 Hz, 6.4 Hz, 2.3 Hz, 1H), 5.60 (dt, *J* = 9.9, 3.4 Hz, 1 H), 5.19 (s, 1 H), 5.08 (s, 1 H), 2.82 (m, 4 H), 2.60 (m, 2 H), 2.41 (ddt, *J* = 20.3, 8.2, 2.4 Hz, 1 H), 2.28, (dt, *J* = 20.3, 2.4 Hz, 1 H), 2.17 (s, 3 H), 2.12 (d, *J* = 14.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.97, 206.84, 149.22, 128.19, 126.22, 108.31, 71.40, 44.72, 43.43, 42.94, 40.34, 37.95, 28.84, 24.58; MS (EI) *m*/*e* (rel intensity) 216.2 (M^+, 100), 174.1 (55), 173.1 (35), 131.1 (34), 122.1 (55), 91.1 (43); HRMS (EI) *m*/*e* calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1155.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 3,3a-Dihydroacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9a). The crude mixture obtained from intramolecular cyclization of **8a** (0.32 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9a** (0.30 g, 0.93 mmol, 93%) as a yellow solid: mp 66−67 °C; IR (CH_2Cl_2) 2918, 2744, 1680, 1505, 1443, 1382, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (m, 3 H), 6.94 (m, 1 H), 6.23 (d, *J* = 2.2 Hz, 1 H), 5.62 (ddd, *J* = 9.9, 5.5, 2.7 Hz, 1 H), 5.40 (dd, *J* = 10.1, 1.3 Hz, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.69 (m, 1 H), 3.38 (dt, *J* = 19.2, 2.5 Hz, 1 H), 3.31 (m, 1 H), 3.11 (m, 2 H), 1.96 (m, 1 H), 1.66 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.81, 170.12, 140.98, 136.07, 133.28, 129.05, 128.45, 126.85, 126.82, 126.24, 123.76, 119.45, 63.20, 52.87, 52.68, 40.40, 39.62, 36.79, 34.72, 22.10; MS (EI) *m*/*e* (rel intensity) 324.4 (M^+, 49), 264.3 (87), 205.3 (100), 179.2 (72), 178.2 (54), 165.2 (39); HRMS (EI) *m*/*e* calcd for $C_{20}H_{20}O_4$ 324.1362, found 324.1366.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 3,3a-Dihydro-9-methylacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9b). The crude mixture obtained from intramolecular cyclization of **8b** (0.34 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9b** (0.31 g, 0.92 mmol, 92%) as a yellow liquid: IR (CH_2Cl_2) 2740, 2430, 1686, 1506, 1255, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 1 H), 6.93 (d, *J* = 7.7 Hz, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.20 (d, *J* = 2.1 Hz, 1 H), 5.61 (m, 1 H), 5.40 (dd, *J* = 10.0, 1.2 Hz, 1 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.64 (m, 1 H), 3.36 (d, *J* = 19.5 Hz, 1 H), 3.29 (m, 1 H), 3.09 (m, 2 H), 2.99 (s, 3 H), 1.95 (dt, *J* = 17.7, 6.1 Hz, 1 H), 1.66 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.84, 170.16, 139.70, 136.43, 135.97, 130.55, 129.27, 129.13, 127.41, 126.09, 123.67, 119.22, 63.17, 52.85, 52.67, 40.36, 39.60, 36.81, 34.61, 22.08, 21.17; MS (EI) *m*/*e* (rel intensity) 338.2 (M^+, 100), 278.2 (91), 219.1 (95), 203.1 (69), 178.1 (45), 84.0 (78); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}O_4$ 338.1518, found 338.1513.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 3,3a-Dihydro-9-methoxyacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9c). The crude mixture obtained from intramolecular cyclization of **8c** (0.35 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9c** (0.33 g, 0.94 mmol, 94%) as a yellow solid: mp 88−89 °C; IR (CH_2Cl_2) 2738, 2430, 1686, 1506, 1255, 1208, 1003 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ6.90 (d, *J* = 8.3 Hz, 1 H), 6.74 (d, *J* = 2.4 Hz, 1 H), 6.66 (dd, *J* = 8.3, 2.5 Hz, 1 H), 6.19 (d, *J* = 2.1 Hz, 1 H), 5.64 (m, 1 H), 5.41 (dd, *J* = 10.0, 1.2 Hz, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.66 (m, 1 H), 3.56 (dt, *J* = 19.0, 2.4 Hz, 1 H), 3.28 (m, 1 H), 3.09 (m, 2 H), 1.95 (dt, *J* = 17.6, 6.1 Hz, 1 H), 1.65 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.88, 170.19, 158.49, 138.19, 137.77, 128.79, 127.07, 126.48, 124.01, 118.77, 114.81, 111.31, 63.23, 55.27, 52.89, 52.71, 40.10, 39.56, 37.27, 34.54, 22.11; MS (EI) *m*/*e* (rel intensity) 354.2 (M^+, 100), 294.2 (70), 290.1 (34), 235.1 (61), 209.1 (95), 178.1 (21), 117.1 (11), 59.0 (14); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}O_5$ 354.1467, found 354.1458.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 9-Bromo-3,3a-dihydroacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9d). The crude mixture obtained from intramolecular cyclization of **8d** (0.40 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9d** (0.36 g, 0.90 mmol, 90%) as a yellow solid: mp 82−83 °C; IR (CH_2Cl_2) 2738, 2430, 1680, 1506, 1255, 1199, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.7 Hz, 1 H), 7.22 (dd, *J* = 8.0, 1.9 Hz, 1 H), 6.17 (d, *J* = 2.2 Hz, 1 H), 6.79 (d, *J* = 8.1 Hz, 1 H), 5.63 (m, 1 H), 5.35 (dd, *J* = 10.1, 1.2 Hz, 1 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.65 (m, 1 H), 3.35 (dt, *J* = 19.3, 2.3 Hz, 1 H), 3.27 (m, 1 H), 3.09 (m, 2 H), 1.96 (dt, *J* = 17.8, 6.0 Hz, 1 H), 1.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.60, 169.87, 141.75, 138.22, 132.23, 131.24, 129.71, 128.24, 127.50, 124.26, 119.65, 118.56, 63.04, 52.85, 52.65, 40.13, 39.37, 36.36, 34.70, 21.96; MS (EI) *m*/*e* (rel intensity) 402.1 (M^+, 31), 344.1 (54), 342.1 (57), 283.1 (19), 203.1 (100), 178.1 (57), 87.0 (93); HRMS (EI) *m*/*e* calcd for $C_{20}H_{19}BrO_4$ 402.0467, found 402.0465.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 7-Bromo-3,3a-dihydroacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9e). The crude mixture obtained from intramolecular cyclization of **8e** (0.40 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9e** (0.35 g, 0.86 mmol, 86%) as a yellow liquid: IR (CH_2Cl_2) 2738, 2430, 1680, 1506, 1255, 1199, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 1 H), 7.09 (d, *J* = 7.4 Hz, 1 H), 6.95 (t, *J* = 7.7 Hz, 1 H), 6.66 (d, *J* = 2.1 Hz, 1 H), 5.64 (m, 1 H), 5.35 (dd, *J* = 10.0, 1.2 Hz, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.69 (m, 1 H), 3.42 (dt, *J* = 19.5, 2.3 Hz, 1 H), 3.31 (m, 1 H), 3.21 (m, 2 H), 1.98 (dt, *J* = 17.8, 6.2 Hz, 1 H), 1.65 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.63, 169.91, 143.92, 138.74, 132.30, 131.12, 128.24, 127.69, 124.35, 122.01, 118.02, 63.11, 52.90, 52.72, 40.20, 39.35, 37.34, 35.09, 21.99; MS (EI) *m*/*e* (rel intensity) 402.1 (M^+, 32), 344.1 (58), 342.1 (66), 283.1 (21), 203.1 (100), 178.1 (51); HRMS (EI) *m*/*e* calcd for $C_{20}H_{19}BrO_4$ 402.0467, found 402.0465.

(±)-(3a*R*,4*R*,10b*S*)-Dimethyl 3,3a-Dihydro-9-hydroxyacephenanthrylene-4,4(5*H*,10b*H*)-dicarboxylate (9f). The crude mixture obtained from intramolecular cyclization of **8f** (0.34 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9f** (0.24 g, 0.50 mmol, 50%) as a yellow liquid: IR (CH_2Cl_2) 2954, 1731, 1512, 1435, 1259 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.0 Hz, 1 H), 6.67 (s, 1 H), 6.60 (d, *J* = 7.9 Hz, 1 H), 6.16 (s, 1 H), 5.63−5.60 (m, 1 H), 5.37 (d, *J* = 10.0 Hz, 1 H), 3.76 (s, 3 H), 3.73 (s, 3 H), 3.59−3.57 (m, 1 H), 3.37−3.32 (m, 1 H), 3.26 (s, 1 H), 3.11−3.02 (m, 2 H), 1.97−1.92

(m, 1 H), 1.68−1.64 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 172.09, 170.27, 154.77, 137.87, 137.69, 128.72, 127.23, 126.17, 123.89, 118.85, 115.70, 113.40, 63.27, 52.95, 52.74, 40.02, 39.56, 37.08, 34.47, 22.07; MS (EI) *m*/*e* (rel intensity) 340.2 (M$^+$, 12), 294.1 (42), 276.1 (79), 235.1 (55), 218.1 (100), 189.1 (99), 165.1 (51), 121.0 (48), 91.1 (47), 77.0 (67); HRMS (EI) *m*/*e* calcd for C$_{20}$H$_{20}$O$_5$ 340.1310, found 340.1319.

(±)-1,1′-((3a*R*,3a′*R*,10b*S*)-3,3a,3a′,4,5,10b-Hexahydroacephenanthrylene-4,4-diyl)diethanone (9g). The crude mixture obtained from intramolecular cyclization of **8g** (0.29 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9g** (0.24 g, 0.83 mmol, 83%) as a yellow solid: mp 157−158 °C; IR (CH$_2$Cl$_2$) 2851, 1697, 1508, 1438, 1266 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15−7.10 (m, 3 H), 6.96−6.94 (m,1 H), 6.25 (s, 1 H), 5.63−5.59 (m, 1 H), 5.39−5.37 (m,1 H), 3.64−3.61 (m, 1 H), 3.32−3.24 (m, 2 H), 3.03 (d, J = 19.6 Hz, 1 H), 3.00−3.29 (m, 1 H), 2.16 (s, 3 H), 2.15 (s, 3 H), 2.05−2.00 (m, 1 H), 1.53−1.46 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 205.35, 203.55, 140.73, 136.02, 133.17, 128.72, 128.37, 126.83, 126.83, 126.16, 123.82, 119.76, 79.46, 40.00, 38.31, 36.63, 31.48, 27.87, 26.27, 22.16; MS (EI) *m*/*e* (rel intensity) 292.2 (M$^+$, 17), 249.2 (86), 231.2 (13), 203.1 (10), 179.1 (33), 165.1 (16); HRMS (EI) *m*/*e* calcd for C$_{20}$H$_{20}$O$_2$ 292.1463, found 292.1465. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

(±)-1,1′-((3a*R*,3a′*R*,10b*S*)-9-Methyl-3,3a,3a′,4,5,10b-hexahydroacephenanthrylene-4,4-diyl)diethanone (9h). The crude mixture obtained from intramolecular cyclization of **8h** (0.29 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9h** (0.22 g, 0.72 mmol, 72%) as a yellow solid: mp 151−154 °C; IR (CH$_2$Cl$_2$) 2732, 1694, 1490, 1441, 1266 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.96 (s, 1 H), 6.93 (d, J = 7.8 Hz, 1 H), 6.85 (d, J = 7.5 Hz, 1 H), 6.22 (s, 1 H), 5.60−5.59 (m, 1 H), 5.38 (d, J = 9.9 Hz, 1 H), 3.58−3.56 (m, 1 H), 3.28 (d, J = 19.1 Hz, 1 H), 3.25−3.23 (m, 1 H), 3.15 (d, J = 19.8 Hz, 1 H), 3.00−2.97 (m, 1 H), 2.30 (s, 3 H), 2.15 (s, 6 H), 2.04−1.99 (m, 1 H), 1.53−1.46 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 205.32, 203.51, 139.43, 136.36, 135.92, 130.46, 129.15, 128.77, 127.35, 125.98, 123.70, 119.50, 79.44, 39.95, 38.30, 36.65, 31.37, 27.79, 26.20, 22.14, 21.06; MS (EI) *m*/*e* (rel intensity) 306.2 (M$^+$, 17), 263.2 (100), 245.2 (16), 202.1 (17), 193.1 (33), 178.1 (22), 165.1 (14); HRMS (EI) *m*/*e* calcd for C$_{21}$H$_{22}$O$_2$ 306.1619, found 306.1621. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

(±)-1,1′-((3a*R*,3a′*R*,10b*S*)-9-Phenyl-3,3a,3a′,4,5,10b-hexahydroacephenanthrylene-4,4-diyl)diethanone (9i). The crude mixture from intramolecular cyclization of **8i** (0.37 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9i** (0.20 g, 0.54 mmol, 54%) as a white solid: mp 105−107 °C; IR (CH$_2$Cl$_2$) 2862, 1697, 1482, 1440, 1265 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 7.3 Hz, 2 H), 7.45−7.37 (m, 4 H), 7.35−7.33 (m,1 H), 7.03 (d, J = 7.6 Hz, 1 H), 6.31 (d, J = 1.6 Hz, 1 H), 5.64−5.46 (m, 1 H), 5.44 (dd, J = 10.1 Hz, J = 1.0 Hz, 1 H), 3.72−3.71 (m, 1 H), 3.36−3.28 (m, 2 H), 3.06 (d, J = 18.7 Hz, 1 H), 3.08−3.04 (m, 1 H), 2.18 (s, 3 H), 2.17 (s, 3 H), 2.08−2.01 (m, 1 H), 1.56−1.49 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 205.37, 203.56, 141.08, 140.90, 139.67, 136.59, 132.43, 128.69, 127.21, 127.06, 127.00, 126.78, 126.58, 125.58, 124.05, 119.46, 79.53, 40.17, 38.37, 36.90, 31.61, 27.91, 26.32, 22.24; MS (EI) *m*/*e* (rel intensity) 368.3 (M$^+$, 5), 325.2 (13), 290.2 (19), 275.2 (16), 247.2 (100), 202.1 (20), 191.1 (26), 178.1 (24), 152.1 (12), 91.1 (14), 77.0 (19); HRMS (EI) *m*/*e* calcd for C$_{26}$H$_{24}$O$_2$ 368.1777, found 368.1772.

(±)-1,1′-((3a*R*,3a′*R*,10b*S*)-7-Methoxy-3,3a,3a′,4,5,10b-hexahydroacephenanthrylene-4,4-diyl)diethanone (9j). The crude mixture obtained from intramolecular cyclization of **8j** (0.32 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **9j** (0.20 g, 0.63 mmol, 63%) as a yellow liquid; IR (CH$_2$Cl$_2$) 2845, 1731, 1635, 1436, 1239 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (t, J = 7.9 Hz, 1 H), 6.77 (d, J = 7.5 Hz, 1 H), 6.73 (d, J = 8.2 Hz, 1 H), 6.67 (d, J = 2.0 Hz, 1 H), 5.62−5.58 (m, 1 H), 5.38 (dd, J = 10.0 Hz, J = 1.1 Hz, 1 H), 3.79 (s, 3 H), 3.61−3.59 (m, 1 H), 3.32−3.24 (m, 2 H), 3.05 (d, J = 19.2 Hz, 1 H), 2.98−2.96 (m, 1 H), 2.17−2.15 (m, 6 H), 2.04−2.00 (m, 1 H), 1.53−1.45 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 205.49, 203.66, 154.51, 139.78, 137.36, 128.35, 127.25, 123.96, 122.09, 120.94, 113.33, 109.10, 79.58, 55.47, 39.54, 38.28, 36.75, 31.82, 27.84, 26.34, 22.20; MS (EI) *m*/*e* (rel intensity) 322.2 (M$^+$, 4), 277.2 (55), 243.2 (25), 201.1 (100), 198.1 (15), 165.1 (13), 131 (34), 91.1 (62), 77 (57); HRMS (EI) *m*/*e* calcd for C$_{21}$H$_{22}$O$_3$ 322.1568, found 322.1566.

(±)-(3*Z*,3a*S*,7a*R*)-Dimethyl 3-(4-nitrobenzylidene)-3,3a-dihydro-2*H*-indene-1,1(7a*H*)-dicarboxylate (18). The crude mixture obtained from intramolecular cyclization of **16** (0.37 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **18** (0.24 g, 0.72 mmol, 65%) as a yellow liquid: IR (CH$_2$Cl$_2$) 2740, 2430, 1688, 1506, 1257, 1209, 1007 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 (s, 1 H), 8.05 (dd, J = 8.2, 1.2 Hz, 1 H), 7.60 (d, J = 7.8 Hz, 1 H), 7.48 (t, J = 7.9 Hz, 1 H), 6.47 (d, J = 1.5 Hz, 1 H), 5.93 (dd, J = 9.3, 5.5 Hz, 1 H), 5.75 (m, 1 H), 5.65 (dd, J = 9.7, 5.0 Hz, 1 H), 5.40 (dd, J = 9.7, 3.4 Hz, 1 H), 4.21 (d, J = 11.9 Hz, 1 H), 3.77 (s, 3 H), 3.73 (m, 1 H), 3.68 (s, 3 H), 3.40 (d, J = 16.5 Hz, 1 H), 2.83 (dd, J = 16.5, 1.4 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.54, 170.31, 148.56, 148.42, 138.95, 133.91, 129.29, 124.48, 124.39, 124.13, 122.85, 122.75, 121.28, 120.80, 64.14, 52.90, 52.34, 43.62, 42.34, 39.41; MS (EI) *m*/*e* (rel intensity) 369.2 (M$^+$, 12), 307.1 (82), 260.1 (37), 202.1 (100), 152.1 (16), 59.0 (31); HRMS (EI) *m*/*e* calcd for C$_{20}$H$_{19}$NO$_6$ 369.1212, found 369.1210.

(±)-(3a*R*,4*R*,12b*S*)-Dimethyl 3,3a-Dihydrocyclopenta[*hi*]chrysene-4,4(5*H*,12b*H*)-dicarboxylate (20a). The crude mixture obtained from intramolecular cyclization of **19a** (0.38 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **20a** (0.33 g, 0.88 mmol, 88%) as a yellow solid: mp 83−84 °C; IR (CH$_2$Cl$_2$) 2738, 2430, 1680, 1506, 1255, 1199, 1007 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 7.9 Hz, 1 H), 7.64 (d, J = 8.3 Hz, 1 H), 7.45 (td, J = 6.9, 1.1 Hz, 1 H), 7.38 (td, J = 7.8, 0.8 Hz, 1 H), 7.31 (d, J = 8.3, 1 H), 7.06 (s, 1 H), 5.65 (m, 1 H), 5.49 (dd, J = 10.0, 1.2 Hz, 1 H), 3.81 (m, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.50 (d, J = 19.2 Hz, 1 H), 3.43 (m, 1 H), 3.19 (m, 2 H), 2.03 (dt, J = 18.0, 5.9 Hz, 1 H), 1.73 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.75, 170.10, 141.99, 132.99, 132.96, 129.43, 128.33, 128.12, 128.02, 127.17, 126.87, 125.76, 124.98, 123.83, 122.58, 114.51, 63.36, 52.88, 52.69, 40.06, 39.47, 37.38, 35.23, 22.23; MS (EI) *m*/*e* (rel intensity) 374.2 (M$^+$, 83), 314.2 (27), 255.1 (51), 229.1 (100), 215.1 (28), 91.1 (32); HRMS (EI) *m*/*e* calcd for C$_{24}$H$_{22}$O$_4$ 374.1518, found 374.1515. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

(±)-1,1′-((3a*R*,3a′*R*,12b*S*)-3,3a,3a′,4,5,12b-Hexahydrocyclopenta[*hi*]chrysene-4,4-diyl)diethanone (20b). The crude mixture obtained from intramolecular cyclization of **19b** (0.34 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **20b** (0.24 g, 0.69 mmol, 69%) as a yellow solid: mp 194−196 °C; IR (CH$_2$Cl$_2$) 2851, 1695, 1508, 1438, 1264 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 7.9 Hz, 1 H), 7.66 (d, J = 8.3 Hz, 1 H), 7.48 (td, J = 7.9 Hz, J = 0.8 Hz, 1 H), 7.42 (td, J = 7.8 Hz, J = 0.8 Hz, 1 H), 7.31 (d, J = 8.3 Hz, 1 H), 7.09 (s, 1 H), 5.65−5.63 (m, 1 H), 5.48 (dd, J = 10.1 Hz, J = 1.1 Hz, 1 H), 3.76−3.73 (m, 1 H), 3.43−3.31 (m, 2 H), 3.18 (d, J = 19.2 Hz, 1 H), 3.15−3.11 (m, 1 H), 2.21 (s, 3 H), 2.21 (s, 3 H), 2.14−2.05 (m, 1 H), 1.60−1.52 (m, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$) δ

205.42, 203.68, 141.79, 133.02, 133.02, 129.42, 128.37, 128.13, 127.70, 127.14, 126.98, 125.84, 125.04, 123.97, 122.57, 114.90, 79.72, 39.75, 38.24, 37.29. 32.15, 27.95, 26.37, 22.39; MS (EI) *m*/*e* (rel intensity) 342.2 (M^+, 23), 299.2 (100), 253.2 (9), 229.1 (45), 215.1 (17); HRMS (EI) *m*/*e* calcd for $C_{24}H_{22}O_2$ 342.1619, found 342.1620. Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate and hexanes.

(±)-(1*R*,1*Z*,4a*R*,11b*S*)-Dimethyl 4,4a-Dihydro-1*H*-naphtho[3,2,1-*cd*]azulene-5,5(3*H*,6*H*,11b*H*)-dicarboxylate (23a). The crude mixture from intramolecular cyclization of **21a** (0.34 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **23a** (0.32 g, 0.93 mmol, 93%) as a yellow liquid: IR (CH_2Cl_2) 3450, 2348, 2244, 1735, 1439, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.11 (m, 3 H), 7.04 (d, $J = 7.08$ Hz, 1 H), 6.35 (s, 1 H), 5.78−5.72 (m, 1 H), 5.08 (dd, $J = 10.8, 1.6$ Hz, 1 H), 3.86 (m, 1 H), 3.75 (s, 3 H), 3.66 (s, 3 H), 3.48−3.31 (m, 2 H), 3.15 (m, 1 H), 3.08 (d, $J = 18.4$ Hz, 1 H), 2.18 (q, $J = 4.8$ Hz, 2 H), 1.71−1.64 (m, 1 H), 1.32−1.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.66, 169.92, 143.34, 139.98, 134.13, 132.71, 132.62, 127.02, 126.72, 126.54, 125.95, 119.10, 64.19, 52.86, 52.58, 48.03, 44.10, 40.63, 37.14, 26.70, 25.31; MS (EI) *m*/*e* (rel intensity) 338.1 (M^+, 30), 279.1 (24), 278.1 (100), 219.1 (94), 219.1 (22), 218.0 (62), 203.0 (33), 191.0 (37), 178.0 (36), 165.0 (39); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}O_4$ 338.1516, found 338.1518.

(±)-(1*R*,1*Z*,4a*R*,11b*S*)-Dimethyl 4,4a-Dihydro-10-methyl-1*H*-naphtho[3,2,1-*cd*]azulene-5,5(3*H*,6*H*,11bH)-dicarboxylate (23b). The crude mixture from intramolecular cyclization of **21b** (0.35 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **23b** (0.29 g, 0.82 mmol, 82%) as a yellow liquid: IR (CH_2Cl_2) 3448, 2953, 2347, 2092, 1733, 1637, 1261 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.98−6.93 (m, 3 H), 6.32 (s, 1 H), 5.78−5.71 (m, 1 H), 5.07 (dd, $J = 10.8, 2.6$ Hz, 1 H), 3.81 (m, 1 H), 3.75 (s, 3 H,), 3.68 (s, 3 H), 3.43−3.33 (m, 2 H), 3.14−3.04 (m, 2 H), 2.31 (s, 3 H), 2.19−2.15 (m, 2 H), 1.70−1.63 (m, 1 H), 1.32−1.23 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.71, 170.01, 142.11, 140.02, 136.25, 132.89, 132.58, 131.52, 127.91, 127.30, 125.86, 118.91, 64.28, 52.87, 52.59, 48.08, 44.17, 40.75, 37.10, 26.73, 25.35; MS (EI) *m*/*e* (rel intensity) 352.1 (M^+, 11), 292.1 (30), 85.9 (46), 84.9 (38), 83.9 (80), 82.9 (46), 71.0 (30), 69.0 (39), 57.0 (52), 55.0 (38), 48.9 (100); HRMS (EI) *m*/*e* calcd for $C_{22}H_{24}O_4$ 352.1680, found 352.1675.

(±)-(1*R*,1*Z*,4a*R*,11b*S*)-Dimethyl 4,4a-Dihydro-10-methoxy-1 *H*-naphtho[3,2,1-cd]azulene-5,5(3*H*,6*H*,11b*H*)-dicarboxylate (23c). The crude mixture from intramolecular cyclization of **21c** (0.37 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **23c** (0.31 g, 0.85 mmol, 85%) as a yellow liquid: IR (CH_2Cl_2) 3424, 2092, 1774, 1654, 1560, 1498 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, $J = 9.0$ Hz, 1 H), 6.72−6.67 (m, 2 H), 6.30 (s, 1 H), 5.79−5.72 (m, 1 H), 5.07 (dd, $J = 10.8, 2.8$ Hz, 1 H), 3.81−3.80 (m, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.67 (s, 3 H), 3.43−3.32 (m, 2 H), 3.14−3.08 (m, 1 H), 3.02 (d, $J = 6.5$ Hz, 1 H), 2.17 (q, $J = 5.8$ Hz, 2 H), 1.71−1.61 (m, 1 H), 1.32−1.22 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.76, 170.02, 158.33, 141.66, 140.45, 132.73, 132.56, 127.44, 126.90, 118.45, 113.22, 111.54, 64.30, 55.30, 52.87, 52.59, 47.99, 43.94, 41.16, 37.03, 26.70, 25.35; MS (EI) *m*/*e* (rel intensity) 368.1 (M^+, 61), 366.1 (32), 309.1 (32), 308.1 (89), 249.1 (100), 202.0 (32), 135.0 (47), 120.1 (34), 105.0 (91), 58.0 (38); HRMS (EI) *m*/*e* calcd for $C_{22}H_{24}O_5$ 368.1620, found 368.1624.

(±)-(1*R*,6b*S*,7*Z*,10a*R*)-Dimethyl 10,10a-dihydro-1*H*-azuleno[8,1-ab]phenanthrene-11,11(6b*H*,9*H*,12*H*)-dicarboxylate (24). The crude mixture obtained from intramolecular cyclization of **22** (0.37 g, 1.0 mmol) was purified by flash column chromatography (silica gel, gradient elution: 10 to 20% ethyl acetate/hexanes) to give **24** (0.32 g, 0.88 mmol, 88%) as a yellow solid: mp 182−183 °C; IR (CH_2Cl_2) 3437, 2347, 2091, 1846, 1640, 1458, 1266 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, $J = 8.3$ Hz, 1 H), 7.79 (d, $J = 7.8$ Hz, 1 H), 7.66 (d, $J = 8.2$ Hz, 1 H), 7.47 (td, $J = 6.8, 1.3$ Hz, 1 H), 7.41 (t, $J = 7.1$ Hz, 1 H), 7.29 (d, $J = 8.2$ Hz, 1 H), 7.17(s, 1 H), 5.79−5.72 (m, 1 H), 5.12 (dd, $J = 10.7, 2.6$ Hz, 1 H), 3.99 (m, 1 H), 3.78 (s, 3 H), 3.67 (s, 3 H), 3.56 (dt, $J = 18.4, 3.4$ Hz, 1 H), 3.48−3.43 (m, 1 H), 3.25−3.20 (m, 2 H), 2.22−2.21 (m, 2 H), 1.80−1.72 (m, 1 H), 1.41−1.32 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.70, 169.99, 144.53, 137.17, 132.94, 132.68, 131.77, 129.44, 129.23, 128.41, 126.74, 126.34, 125.83, 124.98, 122.84, 114.44, 64.27, 52.91, 52.62, 47.93, 44.14, 41.31, 37.84, 26.88, 25.42; MS (EI) *m*/*e* (rel intensity) 388.1 (M^+, 100), 386.1 (46), 328.1 (87), 326.1 (35), 269.1 (100), 267.1 (62), 265.1 (35), 253.1 (47), 252.1 (50), 228.1 (43), 58.0 (55); HRMS (EI) *m*/*e* calcd for $C_{25}H_{24}O_4$ 388.1671, found 388.1674. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds **2**, **9a**−**c**, **9f**−**j**, **20a**,**b**, **23a**−**c**, and **24** and X-ray crystallographic information files for compounds **9g**, **9h**, **20b**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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