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Synthesis of the Phenanthrene and Cyclohepta[*a*]naphthalene Skeletons via Gold(I)-Catalyzed Intramolecular Cyclization of Unactivated Cyclic 5-(2-Arylethyl)-1,3-dienes

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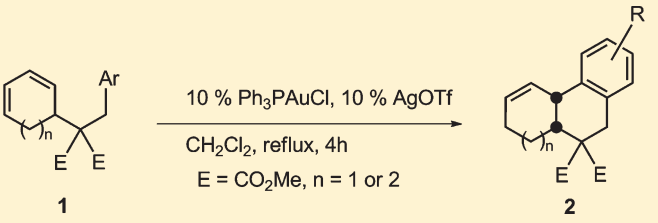
Supporting Information

ABSTRACT: The gold(I)-catalyzed hydroarylation of cyclohexa-1,3-dienes bearing an aryl group and a *gem*-diester in the tether proceeds in a 1,4-addition manner and in a diastereoselective fashion to afford perhydrophenanthrene rings. The reaction proceeded via attack of the aryl group onto the gold-activated cyclic dienes followed by rearomatization and protodeauration to generate perhydrophenanthrenes in good yields. This hydroarylation can be applied to the synthesis of perhydrocyclohepta[*a*]naphthalenes from aryl-tethered cycloheptadienes and the gold(I) catalyst.



INTRODUCTION

The construction of perhydrophenanthrene building blocks is an important synthetic goal because such ring skeletons are present in numerous natural products of biological interest.[1] Because the availability of functionalized perhydrophenanthrene building blocks could greatly facilitate the elaboration of more complex target molecules, the design of expedient and efficient synthetic routes to such intermediates has been actively pursued.[2] Many synthetic methods, as the key step, have been developed in pursuit of perhydrophenanthrenes, including the Robinson annulation of perhydronaphthalenone derivatives bearing a tethered methyl ketone[3] and the Diels−Alder reaction of perhydronaphthalene derivatives with dienes.[4] Among them, the Diels−Alder cycloaddition is generally regarded as a high-performance method for construction of phenanthrene skeletons. Recently, cationic phosphine gold(I) complexes have emerged as versatile catalysts for electronic activation of unsaturated carbon−carbon bonds toward a variety of nucleophiles under mild reaction conditions, allowing numerous synthetic formations of unsaturated systems into useful structural motifs.[5] Although gold(III)- and Ag(I)-catalyzed intermolecular Friedel−Crafts-type reaction of electron-rich phenols with cyclohexa-1,3-diene followed by intramolecular hydroalkoxylation have been reported to give benzofurans,[6] the cationic gold(I) triphenylphosphine complex (5 mol % of $AuPPh_3Cl/AgOTf$) failed to catalyze the annulation of phenols with dienes.[6a] We have now demonstrated that the phosphine gold(I) can be applied toward the synthesis of perhydrophenanthrenes by treatment of 5-(2-arylethyl)cyclohexa-1,3-dienes with a catalytic amount of $AuPPh_3Cl/AgOTf$. In this transformation, an intramolecular electrophilic addition of the tethered aryl group onto the gold(I)-activated cyclohexa-1,3-diene followed by rearomatization and protodeauration produced perhydrophenanthrenes. Moreover, the gold(I)-catalyzed hydroarylation of 5-(2-arylethyl)cyclohepta-1,3-dienes afforded perhydrocyclohepta[*a*]naphthalene under the same reaction conditions.

RESULTS AND DISCUSSION

The requisite 5-(2-arylethyl)cyclohexa-1,3-dienes **1a**−**k** were prepared starting from addition of sodium dimethylmalonate to the (η^5-cyclohexadienyl)tricarbonyliron cation salt in THF according to literature procedures.[7] Decomplexation of the resulting complex with cerium ammonium nitrate (CAN) in acetone at 0 °C afforded dimethyl 2-cyclohexa-2,4-dienylmalonate. Treatment of the malonate with sodium hydride in THF followed by addition of the corresponding benzylic bromide furnished **1a**−**k** in 60−70% overall yields. Seven-membered ring substrates **12a**−**c** were prepared starting from addition of sodium dimethylmalonate to the (η^5-cycloheptadienyl)tricarbonyliron cation salt following the same procedure as described above for synthesis of **1**. Our study of intramolecular gold(I)-catalyzed cyclization of cyclic aryldienes began with the parent compound **1a** (Scheme 1). Treatment of **1a** with 10 mol % of $Ph_3PAuCl/AgOTf$ in refluxing CH_2Cl_2 for 4 h produced dimethyl 7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (**2a**) as the sole diastereoisomer isolated in 65% yield (Scheme 1). Treating **1a** with 10 mol % of AgOTf or 20 mol % of TfOH or $BF_3 \cdot OEt_2$ in refluxing CH_2Cl_2 for 4 h failed to give any tetrahydrophenanthrene ring, and **1a** was recovered quantitatively in each case. However, compound **2d** was isolated in 30% after stirring **1d** with TfOH in refluxing toluene for 20 h. In general, perhydrophenanthrene ring skeletons require lengthy synthetic procedures and are constructed via intramolecular

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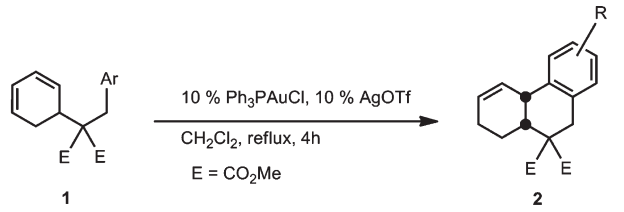
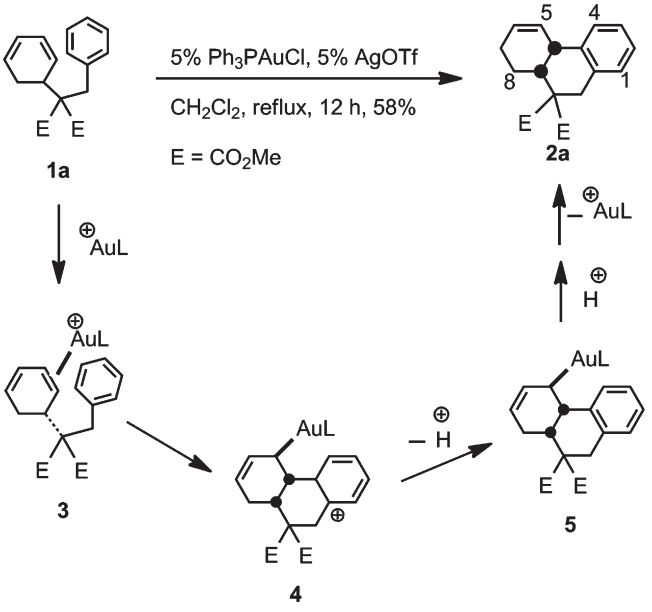
Scheme 1



a: Ar = Ph 57%
b: Ar = 2-naphthyl 91%
c: Ar = 4-methoxyphenyl 63%
d: Ar = 4-phenylphenyl 92%
e: Ar = 3-methoxyphenyl 60%
f: Ar = 2-methoxyphenyl 62%
g: Ar = 3,4-dimethoxyphenyl, 68%
h: Ar = 4-bromophenyl 0%
i: Ar = 4-carbethoxyphenyl 0%
j: Ar = 4-CN 0%
k: Ar = 2-pyridinyl 0%

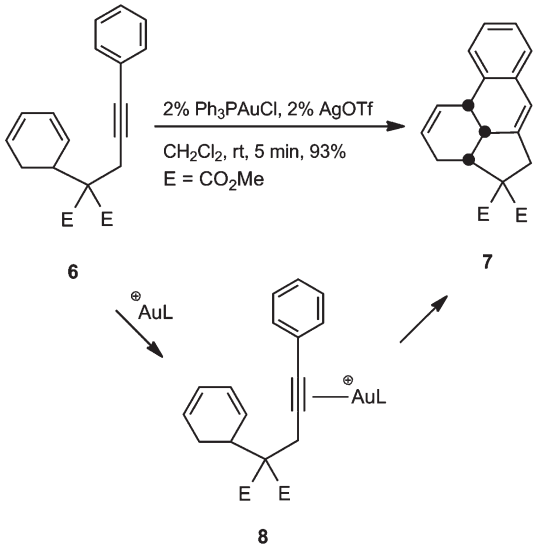
Scheme 2



Diels–Alder reaction at elevated temperature in a sealed tube.[4a,c] Moreover, in most cases the Diels–Alder reaction of the trienes leading to perhydrophenanthrenes proceeded in both exo and endo cycloaddition manners to give a mixture of diastereomeric isomers.[4a,c,f] The current approach to the synthesis of the *cis*-fused perhydrophenanthrene derivative **2** is achieved without the use of complex catalysts or critical reaction conditions, only requiring 10 mol % of $Ph_3PAuCl/AgOTf$ in dichloromethane at reflux for 4 h. The product of the relative stereochemistry as depicted was obtained as a single diastereomer, which is derived from 1,4-addition of the phenyl group and a hydrogen atom across the conjugated diene.

The reaction pathway leading to **2a** was suggested in Scheme 2. Coordination of the π-bond (C_3-C_4) of **1a** to the Au metal center from the opposite face of the tethering chain gave the η^2-alkene–gold complex **3**. Anti addition of the aryl group to the Au-alkene moiety generated the σ-allyl gold intermediate **4** with

Scheme 3



the newly formed carbon–carbon bond. The *cis* relative stereochemistry of the ring juncture of **4** was fixed by the aryl moiety aligned with the face of the cyclic diene in which the tethering chain resides. Allyl gold complex **4** underwent rearomatization (by deprotonation) to give **5**. Isomerization of the η^1-allyl gold followed by protodeauration led to **2a** and regenerated the gold(I) catalyst in the catalytic cycle. The postulated reaction path is consistent with the reports of nucleophilic addition to gold activated unsaturated carbon–carbon bonds followed by deprotonation/protodeauration to generate cyclized products.[8a] Moreover, the proposed deprotonation/protodeauration process involving a proton shuttle of gold species has been well documented by Hashmi et al.[8b] In the current study, the diene was activated by the cationic gold(I) complex and was then attacked by the pendant aryl group. However, cyclohexa-1,3-diene with an arylalkyne moiety in the tethered, for example, **6**, where the diene reacted as a nucleophile and added to the gold-activated alkyne of **8** followed by attack of the adjacent phenyl group at the allyl cation, afforded the perhydroacephenanthrylene derivative **7** (Scheme 3).[5i] Related gold-catalyzed cyclizations of enyne-like substrates with phenyl groups attached to the alkyne moiety, producing polycyclic systems, have been reported.[9] ^1H NMR studies provided the initial evidence for support of the structural assignments of **2a**. The proton at δ 2.89 as a dd, J = 12.6, 5.2 Hz, was assigned to the proton at C-8a. The coupling constant of $H_{4b}-H_{8a}$ (J_{4b8a}) of 5.2 Hz agrees with the 4.4–6.0 Hz coupling constant for similarly fused *cis*-hydrogens compared to the 10–11 Hz observed when these protons are *trans*.[10] The results of the gold(I)-catalyzed cyclization of 5-(2-arylethyl)cyclohexa-1,3-dienes **1a**–**g** to produce perhydrophenanthrenes **2a**–**g** are listed in Scheme 1. The relative stereochemistry of products **2a**–**g** was assigned as the same *cis* relationship between hydrogen atoms at two adjacent stereogenic centers on the basis of their close chemical shift values and similar coupling patterns of the fused protons in their ^1H NMR spectra. Electron-neutral and -rich arenes were proven to be good substrates, as the yields of desired perhydrophenanthrenes **2a**–**g** ranged from 57% to 92% (Scheme 1). Substrates **1b** bearing a naphthyl group at the tether reacted smoothly with the catalysts to afford the perhydrobenzo[*c*]phenanthrene derivative **2b** in

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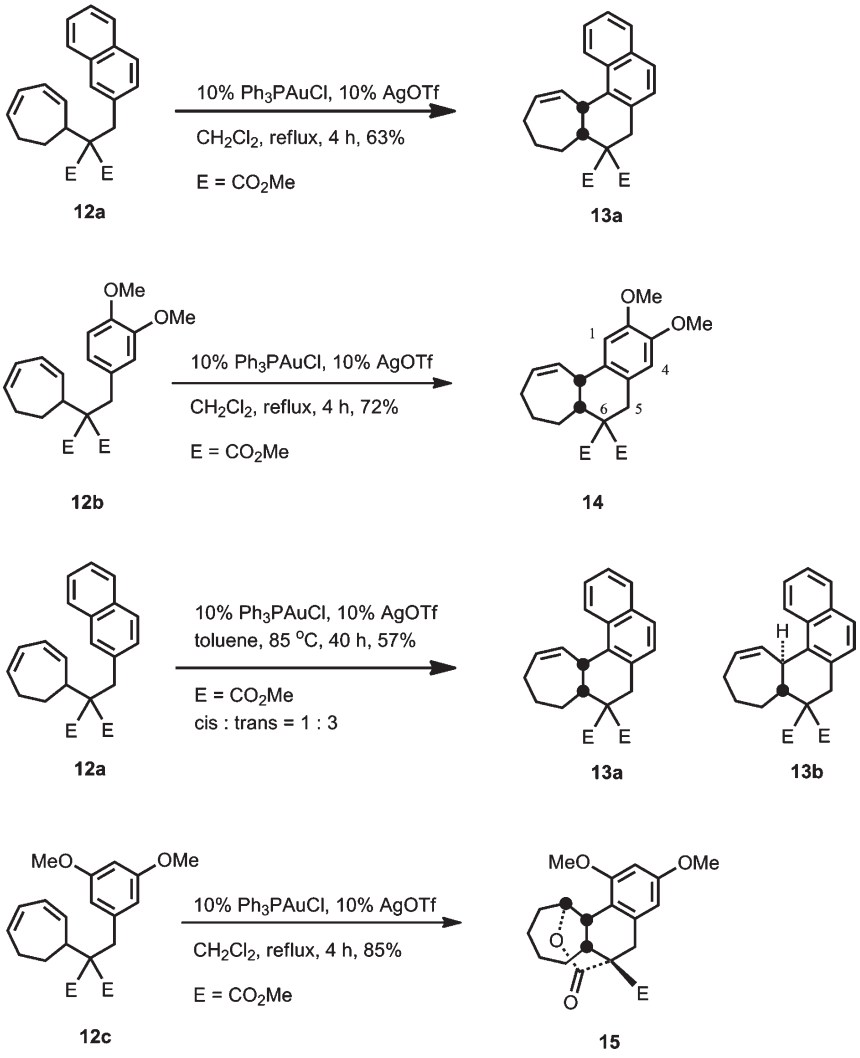
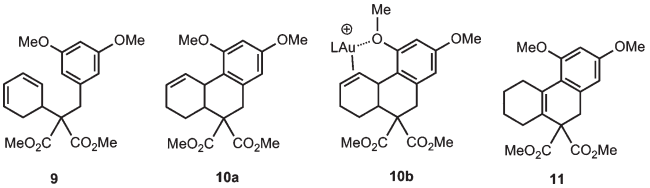
Scheme 4



92% isolated yield (Scheme 1). However, substrates with a bromine atom at the phenyl ring, for example, **2h**, or an electron-withdrawing group, such as an ester or nitrile group, for example, **2i,j**, or a pyridinyl group in the tether, for example, **2k**, inhibited the catalytic activity of the gold species, and the reactions failed to give any cyclized product. An unidentified mixture of crude oil was formed in each case. It is worthy to mention that treatment of cyclohexa-1,3-diene and phenol with 5 mol % of $Ph_3PAuCl/AgOTf$ in refluxing CH_2Cl_2 for 16 h failed to give any benzofuran derivatives.[6a] In addition, treatment of **1a** with a catalytic amount of AgOTf (5 mol %) in refluxing dichloroethane (DCE) according to Youn's protocols gave **2a** in only 28% yield.[6b] Structure elucidation of the perhydrophenanthrene derivatives **2a**−**c** was achieved by X-ray crystallography. The *cis* relative stereochemistry between the fused hydrogen atoms at the adjacent stereogenic centers further supports the proposed reaction path suggested for the formation of the perhydrophenanthrenes (Scheme 2).

Interestingly, with two methoxy groups at C-3 and C-5 positions of the arene, for example, **9**, the cyclization led to the conjugated perhydrophenanthrene derivative **11** in 63% yield under the same reaction conditions. Chelation of both the proximal methoxy group and the olefin to the gold center of the proposed initial product **10a** would give the chelating intermediate **10b**. The similar chelating intermediates are known in the literature.[11] The postulated intermediate **10b** may undergo a sequential double bond migration by deprotonation of allylic protons followed by a protodeauration process involving a proton shuttle as stated previously to form **11**.[8b]



The chemistry can be applied to synthesis of cyclohepta[*c*]phenanthrenes and cyclohepta[*a*]naphthalenes from seven-membered ring substrates. Thus, arylcycloheptadienes **12a** and **12b**, possessing a 2-naphthyl or a 3,4-dimethoxyphenyl group in the tether (Scheme 4), underwent cyclization smoothly using the same reaction conditions (10 mol % of $Ph_3PAuCl/AgOTf$ in

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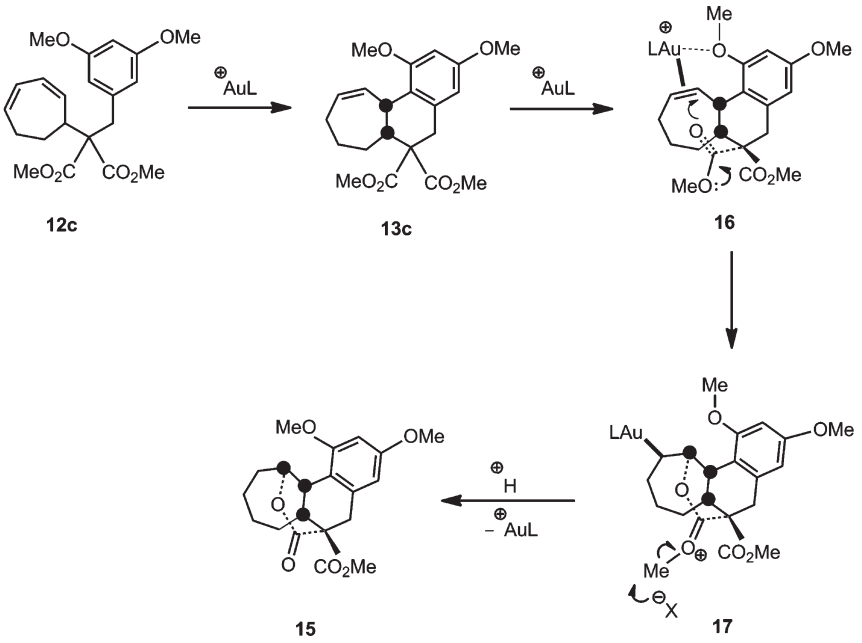
Scheme 5



CH_2Cl_2 at reflux for 4 h) to provide the cyclohepta[*c*]phenanthrene derivative **13a** and the cyclohepta[*a*]naphthalene derivative **14**, respectively, as the only stereoisomer in each case and in good yield. NOESY experiments provided the initial evidence for support of a *cis* relationship between the fused hydrogen atoms of **13a**. The structure **13a** was further confirmed by X-ray diffraction analysis. Interestingly, when treated with 10 mol % of $Ph_3PAuCl/AgOTf$ in toluene at 85 °C for 40 h, compound **12a** was transformed to both the *cis* isomer **13a** and the *trans* isomer **13b** in a ratio of 1:3 and in a 57% total yield (Scheme 4). In this case, the intramolecular Friedel−Crafts-type reaction occurred on both faces of the cycloheptadienyl ring at higher temperature (ca. 85 °C) and led to both *cis* and *trans* isomers. However, treating **1a** with the gold(I) catalyst in toluene at 85 °C for 40 h gave only *cis* isomer **2a** in 50% yield and none of the *trans* isomer was detected. The structure elucidation of the *trans* cyclohepta[*c*]phenanthrene derivative **13b** was accomplished by X-ray diffraction analysis. As expected, the electron-rich substrate **12b** underwent the intramolecular Friedel−Crafts-type reaction in refluxing methylene chloride to afford the cyclohepta[*a*]naphthalene derivative **14** in 72% isolated yield. The relative stereochemistry of **14** was assigned as the same *cis* relationship as that of **13a** on the basis of their close chemical shift values and the similar coupling patterns of the proton at the C-6a position in the ^1H NMR spectra.

Interestingly, using the same reaction conditions, we were able to construct the tetracyclic ring skeleton, such as **15**, via the initial hydroarylation followed by intramolecular hydroalkoxylation of a tethered methyl ester and a hydrogen atom to the double bond of the cycloheptene ring. Thus, treatment of **12c** with 10 mol % of $Ph_3PAuCl/AgOTf$ in CH_2Cl_2 at reflux for 4 h furnished the carbotetracycle **15** in 85% isolated yield (Scheme 4). The product of the relative stereochemistry as depicted was obtained as a single diastereomer. NOESY (nuclear Overhauser enhancement spectroscopy) experiments and X-ray diffraction analysis provided the initial evidence for support of all *syn* relationships among hydrogen atoms at three contiguous stereogenic centers of **15**. The formation of **15** was suggested in Scheme 5. Coordination of the alkene of the initial formed **13c** to the Au metal center from the exo face produced the η^2-gold-alkene **16**. As stated for compound **10a**, chelation of both the olefin and the proximal methoxy group to the gold center of **13c** would form the postulated intermediate **16**. The ester group would attack at the Au-alkene moiety from the endo face to give the tetracyclic ring skeleton **17**, containing an η^1-alkylgold bond at the benzylic position. The stereoselectivity outcome is consistent with *anti* addition of nucleophiles to gold(I)−alkene complexes known in the literature.[5h] The postulated intermediate **17** underwent protodeauration and demethylation to afford **15**.

In conclusion, a gold-catalyzed 1,4-hydroarylation of unactivated cyclic 5-(2-arylethyl)-1,3-dienes has been successfully developed. The aryl group added to the terminal position of the diene in the presence of a catalytic amount of $Ph_3PAuCl/AgOTf$ followed by protodemetalation to afford perhydrophenanthrenes and perhydrocyclohepta[*a*]naphthalenes. The transformation is characterized by its efficiency, the mild conditions employed, and the easy formation of the desired carbotricycles in good yields with *cis* diastereoselectivity at the fused carbons from readily available starting substrates. The *trans* isomer of the perhydrocyclohepta[*c*]phenanthrene derivative can be obtained when treated with a naphthyl-tethered cycloheptadienyl substrate at elevated temperature.

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.[12] Flash column chromatography followed the method of Still,[13] using the indicated solvents. ^1H nuclear magnetic resonance (NMR) spectra were obtained with 400 and 500 MHz spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$

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(7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with a 100 MHz spectrometer with $CDCl_3$ (77.0 ppm) as the internal standard. Mass spectra were acquired on a 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 a double-focusing mass spectrometer.

General Procedure for Gold(I)-Catalyzed Intramolecular Hydroarylation of Cyclic 5-(2-Arylethyl)-1,3-dienes. To an oven-dried 50 mL round-bottom flask equipped with a stirrer bar and capped with a rubber septum was added AgOTf (41.6 mg, 0.16 mmol). The apparatus was evacuated (oil pump) and filled with nitrogen three times. To the reaction mixture were then added via syringe compound **1a** (0.49 g, 1.63 mmol) and PPh_3AuCl (0.08 g, 0.16 mmol) in 30 mL of CH_2Cl_2. The resulting mixture was stirred at reflux for 4 h. The resulting reaction mixture was filtered through a bed of Celite. The filtrate was concentrated in vacuo to give the crude mixture.

(±)-(4b*S*,8a*R*)-Dimethyl 7,8,8a,10-Tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2a). The crude mixture obtained from intramolecular hydroarylation of **1a** (0.49 g, 1.63 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2a** (0.28 g, 0.93 mmol, 57%) as a white solid: mp 82−83 °C; IR (CH_2Cl_2) 2952, 1732, 1647, 1493, 1432, 1308, 1176, 1135, 1043 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 10.6 Hz, 1 H), 7.16−7.07 (m, 3 H), 6.23 (m, 1 H), 5.81 (m, 1 H), 3.78 (s, 3 H), 3.70 (m, 1 H), 3.63 (s, 3 H), 3.41 (d, J = 17.2 Hz, 1 H), 3.29 (d, J = 17.2 Hz, 1 H), 2.89 (dd, J = 12.6, 5.2 Hz, 1 H), 2.16 (m, 1 H), 2.05 (dt, J = 17.8, 5.2 Hz, 1 H), 1.51 (m, 1 H), 1.34 (qd, J = 12.5, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.8, 137.5, 131.7, 129.1, 128.8, 127.8, 127.3, 126.5, 125.6, 52.8, 52.7, 57.8, 37.1, 35.6, 30.4, 25.6, 21.5; MS (EI) m/e (%) 300.2 (M^+, 16), 240.2 (62), 181.1 (100), 178.1 (12), 167.1 (10), 166.1 (21), 165.1 (28), 153.1 (10), 141.1 (11); HRMS (EI) m/e calcd for $C_{18}H_{20}O_4$ 300.1370, found 300.1362. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(4a*R*,12c*S*)-Dimethyl 4,4a,6,12c-Tetrahydrobenzo[*c*]-phenanthrene-5,5(3*H*)-dicarboxylate (2b). The crude mixture obtained from intramolecular hydroarylation of **1b** (0.42 g, 1.19 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2b** (0.38 g, 1.09 mmol, 91%) as a white solid: mp 146−147 °C; IR (CH_2Cl_2) 3429, 1734, 1638, 1432, 1241 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1 H), 7.76 (d, J = 7.9 Hz, 1 H), 7.57 (d, J = 8.3 Hz, 1 H), 7.45 (m, 1 H), 7.39 (m, 1 H), 7.18 (d, J = 8.4 Hz, 1 H), 6.15 (br d, J = 7.6 Hz, 1 H), 5.79 (m, 1 H), 4.61 (m, 1 H), 3.77 (s, 3 H), 3.57 (d, J = 16.4 Hz, 1 H), 3.42 (s, 3 H), 3.34 (d, J = 16.4 Hz, 1 H), 3.24 (m, 1 H), 2.11−2.05 (m, 2 H), 1.47−1.59 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.5, 133.4, 133.3, 131.2, 130.2, 129.5, 128.7, 1278.0, 127.5, 126.4,125.5, 124.5, 124.3, 58.8, 52.7, 52.5, 37.2, 34.6, 32.2, 23.8, 23.2; MS (EI) m/e (%) 350.2 (M^+, 49), 351.3 (10), 291.2 (12), 290.2 (33), 259.2 (14), 231.2 (100), 230.2 (23), 229.2 (14), 216.1 (17), 215.1 (21), 205.1 (11), 203.1 (14), 202.1 (17), 178.1 (10), 141.1 (15); HRMS (EI) m/e calcd for $C_{22}H_{22}O_4$ 350.1520, found 350.1518. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(4b*S*,8a*R*)-Dimethyl 3-Methoxy-7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2c). The crude mixture obtained from intramolecular hydroarylation of **1c** (0.50 g, 1.51 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2c** (0.32 g, 0.94 mmol, 63%) as a white solid: mp 102−103 °C; IR (CH_2Cl_2) 3439, 1731, 1645, 1500, 1435, 1233, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 8.4 Hz, 1 H), 6.79 (s, 1 H), 6.67 (dd, J = 8.2 Hz, 8.4 Hz, 1 H), 6.20 (m, 1 H), 5.81 (m, 1 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 3.67 (m, 1 H), 3.63 (s, 3 H), 3.34 (d, J = 16.9 Hz, 1 H), 3.21 (d, J = 16.9 Hz, 1 H), 2.89−2.85 (dd, J = 12.4, 5.2 Hz, 1 H), 2.13 (m, 1 H), 2.05 (m, 1 H), 1.50 (m, 1 H), 1.33 (qd, J = 12.4, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.8, 158.2, 138.7, 130.0, 128.6, 127.5, 123.8, 112.8, 111.9, 57.9, 55.1, 52.7, 52.7, 37.0, 35.8, 29.7, 25.6, 21.5; MS (EI) m/e (%) 330.2 (M^+, 17), 271.2 (17), 270.2 (42), 239.2 (15), 225.1 (12), 211.2 (100), 210.1 (30), 209.1 (14), 197.1 (10), 196.1 (10), 185.1 (11), 184.1 (11), 179.1 (16), 165.1 (14), 121.1 (35); HRMS (EI) m/e calcd for $C_{19}H_{22}O_5$ 330.1469, found 330.1467.

(±)-(4b*S*,8a*R*)-Dimethyl 3-Phenyl-7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2d). The crude mixture obtained from intramolecular hydroarylation of **1d** (0.68 g, 1.80 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2d** (0.62 g, 1.65 mmol, 92%) as a yellow liquid: IR (CH_2Cl_2) 3031, 2953, 1734, 1647, 1601, 1485, 1435, 1261, 1177, 1046, 970 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2 H), 7.52 (s, 1 H), 7.43 (t, J = 6.1 Hz, 2 H), 7.37−7.31 (m, 2 H), 7.23 (d, J = 6.4 Hz, 1 H), 6.34 (m, 1 H), 5.86 (m, 1 H), 3.82 (s, 3 H), 3.80 (m, 1 H), 3.68 (s, 3 H), 3.50 (d, J = 13.8 Hz, 1 H), 3.36 (d, J = 13.8 Hz, 1 H), 2.98 (dd, J = 10.0, 4.4 Hz, 1 H), 2.20 (m, 1 H), 2.10 (td, J = 14.2, 4.0 Hz, 1 H), 1.58 (m, 1 H), 1.42 (qd, J = 9.9, 4.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 141.2, 139.4, 137.8, 130.8, 129.4, 128.6, 128.5, 127.4, 126.9, 126.55, 124.5, 57.7, 52.7, 52.7, 37.1, 35.6, 30.2, 25.6, 21.4; MS (EI) m/e (%) 376.3 (M^+, 0.8), 317.2 (15), 316.2 (37), 298.2 (14), 285.2 (11), 258.2 (22), 257.2 (100), 255.2 (10), 241.2 (14), 239.2 (12), 238.2 (26), 215.1 (15), 207.1 (12), 202.1 (11), 179.1 (13), 178.1 (16), 167.1 (44), 165.1 (22), 152.1 (12); HRMS (EI) m/e calcd for $C_{24}H_{24}O_4$ 376.1666, found 376.1674.

(±)-(4b*S*,8a*R*)-Dimethyl 2-Methoxy-7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2e). The crude mixture obtained from intramolecular hydroarylation of **1e** (0.62 g, 1.87 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2e** (0.37 g, 1.10 mmol, 60%) as a yellow liquid: IR (CH_2Cl_2) 3435, 2954, 1731, 1638, 1502, 1434, 1257, 1036, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.6 Hz, 1 H), 6.72 (d, J = 7.6 Hz, 1 H), 6.65 (s, 1 H), 6.20 (m, 1 H), 5.79 (m, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.64 (s, 3 H), 3.60 (s, 1 H), 3.38 (d, J = 17.2 Hz, 1 H), 3.25 (d, J = 17.2 Hz, 1 H), 2.84 (dd, J = 12.3, 4.7 Hz, 1 H), 2.15 (m, 1 H), 2.03 (m, 1 H), 1.50 (m, 1 H), 1.33 (qd, J = 12.3, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 157.3, 133.0, 129.7, 129.0, 128.7, 127.05, 113.4, 113.0, 57.8, 55.0, 52.8, 52.7, 37.2, 34.9, 30.7, 25.6, 21.3; MS (EI) m/e (%) 330.3 (M^+, 35), 285.2 (10), 271.2 (15), 270.2 (26), 253.2 (13), 239.2 (18), 233.1 (11), 225.1 (13), 212.2 (19), 211.2 (100), 210.1 (14), 209.1 (14), 201.1 (10), 197.1 (10), 196.1 (10), 185.1 (11), 179.1 (11), 171.1 (10), 165.1 (15), 121.1 (13); HRMS (EI) m/e calcd for $C_{19}H_{22}O_5$ 330.1470, found 330.1467.

(±)-(4b*S*,8a*R*)-Dimethyl 1-Methoxy-7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2f). The crude mixture obtained from intramolecular hydroarylation of **1f** (0.60 g, 1.81 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **2f** (0.38 g, 1.14 mmol, 63%) as a yellow liquid: IR (CH_2Cl_2) 2951, 1734, 1583, 1467, 1436, 1259, 1235, 1197, 1104, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, J = 8.0 Hz, 1 H), 6.87 (d, J = 7.9 Hz, 1 H), 6.63 (d, J = 8.1 Hz, 1 H), 6.21 (m, 1 H), 5.79 (m, 1 H), 3.81 (m, 3 H), 3.77 (m, 3 H), 3.67 (m, 1 H), 3.62 (s, 3 H), 3.59 (d, J = 18.1 Hz, 1 H), 2.91 (d, J = 18.1 Hz, 1 H), 2.84 (m, 1 H), 2.15 (m, 1 H), 2.01 (m, 1 H), 1.53 (m, 1 H), 1.31 (qd, J = 12.5, 5.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.22, 171.08, 157.04, 138.79, 129.0, 127.4, 126.8, 121.0, 119.8, 106.8, 57.2, 55.3, 52.8, 36.7, 36.4, 35.5, 25.7, 24.5, 21.28; MS (EI) m/e (%) 330.1 (M^+, 0.1), 271.2 (10), 270.2 (35), 211.1 (100), 210.1 (33), 179.1 (15), 165.1 (14); HRMS (EI) m/e calcd for $C_{19}H_{22}O_5$ 330.1460, found 330.1468.

(±)-(4b*S*,8a*R*)-Dimethyl 2,3-Dimethoxy-7,8,8a,10-tetrahydrophenanthrene-9,9(4b*H*)-dicarboxylate (2g). The crude mixture obtained from intramolecular hydroarylation of **1g** (0.18 g, 0.5 mmol) was purified by flash column chromatography (silica gel,

gradient elution: 5%−10% ethyl acetate/hexanes) to give **2g** (0.12 g, 0.34 mmol, 68%) as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1 H), 6.60 (s, 1 H), 6.19 (m, 1 H), 5.83 (m, 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.78 (s, 3 H), 3.65 (s, 3 H), 3.63 (s, 1 H), 3.27 (m, 2 H), 2.87 (m, 1 H), 2.15 (m, 1 H), 2.07 (m, 1 H), 1.50 (m, 1 H), 1.25 (m, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 171.0, 170.8, 147.9, 147.2, 129.4, 128.8, 127.5, 123.8, 111.6, 110.5, 58.0, 55.8, 52.8, 37.0, 35.3, 30.9, 30.0, 25.6, 21.4; IR (CH_2Cl_2) 1731, 1660, 1505, 1455, 1242, 1216 cm^{-1}; MS (EI) *m*/*e* (%) 360.3 (M^+, 70), 300.3 (26), 269.2 (21), 242.2 (17), 241.2 (100), 59.1 (13); HRMS (EI) *m*/*e* calcd for $C_{20}H_{24}O_6$ 360.1579, found 360.1573.

Dimethyl 2,4-Dimethoxy-5,6,7,8-tetrahydrophenanthrene-9,9(10*H*)-dicarboxylate (11). The crude mixture obtained from intramolecular hydroarylation of **9** (0.18 g, 0.5 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **11** (0.12 g, 0.34 mmol, 68%) as a white solid: mp 148−150 °C; IR (CH_2Cl_2) 3372, 2100, 1732, 1644, 1434, 1230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1 H), 6.31 (s, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.68 (s, 6 H), 3.27 (s, 2 H), 2.64 (m, 2 H), 2.24 (m, 2 H), 1.7 (m, 2 H), 1.63 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 171.8, 159.0, 157.5, 136.0, 131.4, 127.9, 117.9, 104.8, 98.2, 59.5, 55.3, 55.1, 52.8, 37.6, 29.9, 27.5, 23.2, 22.7; MS (EI) *m*/*e* (%) 360.3 (M^+, 58), 301.2 (100), 269.2 (70), 242.2 (62), 241.2 (33), 227.2 (11), 226.2 (12); HRMS (EI) *m*/*e* calcd for $C_{20}H_{24}O_6$ 360.1564, found 360.1573. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(8a*R*,13a*S*)-Dimethyl 8a,9,10,11-Tetrahydro-7*H*-cyclohepta[*c*]phenanthrene-8,8(13a*H*)-dicarboxylate (13a). The crude mixture obtained from intramolecular hydroarylation of **12a** (0.45 g, 1.25 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **13a** (0.28 g, 0.77 mmol, 63%) as a white solid: mp 136−137 °C; IR (CH_2Cl_2) 3433, 1729, 1638, 1433, 1243, 1066 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 7.9 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.46 (d, *J* = 7.1 Hz, 1 H), 7.44 (d, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 5.52 (m, 1 H), 5.09 (m, 1 H), 4.80 (m, 1 H), 3.74 (s, 3 H), 3.60 (s, 3 H), 3.57 (d, *J* = 16.3 Hz, 1 H), 3.15 (d, *J* = 16.3 Hz, 1 H), 2.98 (dd, *J* = 15.3, 8.4 Hz, 1 H), 2.60 (d, *J* = 15.3 Hz, 1 H), 2.27 (m, 3 H), 2.00 (m, 1 H), 1.79 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.3, 133.5, 132.0, 131.7, 130.9, 128.6, 128.1, 127.0, 126.8, 125.9, 124.8, 124.1, 56.6, 52.5, 51.9, 43.3, 38.7, 35.0, 29.6, 25.6, 21.5; MS (EI) *m*/*e* (%) 364.3 (M^+, 99), 305.2 (21), 304.2 (63), 273.2 (21), 245.2 (100), 244.2 (23), 217.1 (31), 216.1 (20), 215.1 (26), 205.1 (21), 203.1 (28), 202.1 (29), 191.1 (28), 178.1 (28) ; HRMS (EI) *m*/*e* calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1674. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(8a*S*,13a*S*)-Dimethyl 8a,9,10,11-Tetrahydro-7*H*-cyclohepta[*c*]phenanthrene-8,8(13a*H*)-dicarboxylate (13b). The crude mixture obtained from intramolecular hydroarylation of **12a** (0.45 g, 1.25 mmol) at 85 °C in toluene for 4 h was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **13a** (0.065 g, 0.18 mmol, 14%) and **13b** (0.20 g, 0.53 mmol, 42%) both as white solids. **13b**: mp 137−139 °C; IR (CH_2Cl_2) 3433, 1729, 1638, 1433, 1243, 1066 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1 H), 7.77 (m, 1 H), 7.61 (d, *J* = 8.3 Hz, 1 H), 7.48−7.38 (m, 2 H), 7.15 (d, *J* = 8.4 Hz, 1 H), 5.89 (m, 1 H), 5.57 (m, 1 H), 4.55 (m, 1 H), 3.81 (s, 3 H), 3.47 (d, *J* = 15.4 Hz, 1 H), 3.39 (d, *J* = 17.9 Hz, 1 H), 3.36 (s, 3 H), 2.65−2.46 (m, 2 H), 2.41 (m, 1 H), 2.28 (m, 1 H), 2.05−1.93 (m, 2 H), 1.51 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 170.2, 140.1, 134.9, 133.4, 131.3, 131.1, 130.9, 128.5, 127.2, 126.8, 125.8, 125.0, 124.9, 59.6, 52.6, 51.8, 47.4, 40.4, 40.0, 34.4, 28.1, 26.8; MS (EI) *m*/*e* (%) 364.3 (M^+, 99), 305.2 (21), 304.2 (63), 273.2 (21), 245.2 (100), 244.2 (23), 217.1 (31), 216.1 (20), 215.1 (26), 205.1 (21), 203.1 (28), 202.1 (29), 191.1 (28), 178.1 (28); HRMS (EI) *m*/*e* calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1674. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(6a*R*,11a*S*)-Dimethyl 2,3-Dimethoxy-6a,7,8,9-tetrahydro-5*H*-cyclohepta[*a*]naphthalene-6,6(11a*H*)-dicarboxylate (14). The crude mixture obtained from intramolecular hydroarylation of **12b** (0.19 g, 0.5 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **14** (0.13 g, 0.36 mmol, 72%) as a yellow liquid: IR (CH_2Cl_2) 3011, 1731, 1608, 1505, 1434, 1212, 1142 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1 H), 6.65 (s, 1 H), 5.96 (m, 2 H), 3.85 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.65 (m, 1 H), 3.38 (d, *J* = 17.2 Hz, 1 H), 3.22 (d, *J* = 17.3 Hz, 1 H), 2.89 (m, 1 H), 2.22 (m, 1 H), 1.85 (m, 1 H), 1.72−1.65 (m, 2 H), 1.51−1.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.1, 147.5, 147.3, 133.3, 131.2, 129.2, 125.4, 111.2, 110.5, 59.2, 55.9, 55.8, 52.9, 52.6, 41.2, 40.2, 31.4, 28.8, 28.0, 26.0; MS (EI) *m*/*e* (%) 374.2 (M^+, 52), 314.1 (46), 283.1 (41), 256.1 (20), 255.1 (100), 227.1 (16), 84 (15.5); HRMS (EI) *m*/*e* calcd for $C_{21}H_{26}O_6$ 374.1740, found 374.1739.

(±)-(6*S*,6a*R*,11*S*,11a*S*)-Methyl 1,3-Dimethoxy-13-oxo-6,6a,7,8,9,10,11,11a-octahydro-5*H*-11,6-(epoxymethano)cyclohepta-[*c*]naphthalene-6-carboxylate (15). The crude mixture obtained from intramolecular hydroarylation of **12c** (0.19 g, 0.5 mmol) was purified by flash column chromatography (silica gel, gradient elution: 5%−10% ethyl acetate/hexanes) to give **15** (0.15 g, 0.42 mmol, 85%) as a white solid: mp 187−188 °C; IR (CH_2Cl_2) 3402, 1727, 1643, 1462, 1250, 1147 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (d, *J* = 2.0 Hz, 1 H), 6.21 (d, *J* = 2.0 Hz, 1 H), 4.55 (s, 1 H), 3.81(s, 3 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 3.72 (d, *J* = 17.2 Hz, 1 H), 3.55 (d, *J* = 3.2 Hz, 1 H), 3.21 (d, *J* = 17.2 Hz, 1 H), 2.48 (m, 1 H, H-6), 2.22 (m, 1 H), 1.97−1.62 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.6, 159.6, 156.8, 134.2, 120.5, 103.4, 97.1, 88.5, 55.5, 55.4, 54.4, 52.4, 40.4, 28.8, 33.0, 32.7, 32.6, 26.5, 22.6; MS (EI) *m*/*e* (%) 360.2 (M^+, 84), 301.2 (70), 273.2 (39), 257.2 (57), 255.2 (21), 248.2 (25), 247.1 (100), 245.1 (25), 215.1 (41), 203.1 (19), 201.1 (40), 189.1 (34), 188.1 (54), 59 (24); HRMS (EI) *m*/*e* calcd for $C_{20}H_{24}O_6$ 360.1581, found 360.1573. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR and ^{13}C NMR spectra of compounds **2a**−**g**, **11**, **13a**,**b**, **14**, and **15** and X-ray crystallographic information files for compounds **2a**,**b**, **11**, **13a**, **b**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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