JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00939 • Publication Date (Web): 06 May 2019

Just Accepted

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Reactions of Anodically Generated Methoxystilbene Cation Radicals: The Influence of Ortho-Substituted Vinyl and Formyl Groups

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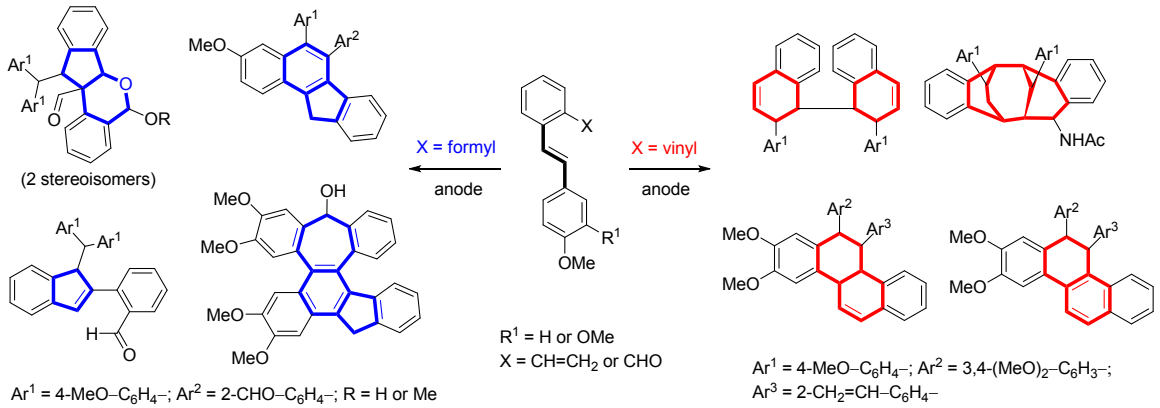


Abstract

The present investigation represents a continuation of studies on the effect of ortho'-substitution on the reactivity of anodically generated methoxystilbene cation radicals. Whereas previous studies have focused on the effect of ortho'-substituted nucleophilic groups such as OH, NH_2, CH_2OH, CH_2NH_2 and COOH, the present study extends the investigation to ortho'-substituted vinyl and formyl groups. The results show that when the ortho'-substituent is a vinyl group, the products include a bisdihydronaphthalene derivative and a doubly-bridged, dibenzofused cyclononane from direct trapping of a bis carbocation intermediate. In the presence of an additional 3-methoxy substituent, the products are the tetracyclic chrysene derivatives. When the ortho'-substituent is a non-nucleophilic formyl group, the products include fused indanylnaphthalenes and indanylbenzopyran aldehydes. When an additional 3-methoxy group is present, an unusual fused benzofluorene-dibenzoannulene product is obtained. Mechanistic rationalization for the formation of the various products is presented. The results have contributed to a deeper understanding of how the reactivity of the methoxystilbene cation radicals is affected by the nature of the ortho'-substituents.

Introduction

While less frequently employed compared to conventional reactions, electrochemically-mediated transformations has always retained its place as a useful option in organic synthetic methodology for the formation of C-C bonds and for functional group transformations.[1-4] This is in large part due to several inherent advantages associated with the approach such as the use of mild conditions, the high chemoselectivity, umpolung reactivity, and the use of green methodology.[4-7] It is therefore hardly surprising that there has been a recent revival of interest in the application of electrochemically-mediated transformations in organic synthesis.[8-17] The electrochemical method involves in essence the removal or addition of an electron from a substrate through the application of an electric potential. As such for organic substrates the first formed species is either the cation radical (anodic oxidation) or the anion radical (cathodic reduction). An understanding of the properties and reactivity of these species would be useful in applying electrochemical methodology to synthesis.[18,19] In our systematic studies of the reactions of anodically-generated stilbene cation radicals, we first investigated the effect of aromatic substitution (*para* and *meta* substituents) on the nature and distribution of the products in the oxidation of substituted stilbenes. The aromatic substituents were found to fall into three groups based on the type of products formed (Figure 1).[20] This was then followed by a study of the influence of *ortho'*-substituted nucleophilic groups (OH, NH_2, CH_2OH, CH_2NH_2, CO_2H) on the reactivity of anodically-generated 4-methoxy- and 3,4-dimethoxystilbene cation radicals (Figure 2).[21,22] The results showed that when *ortho'*-substituted OH or NHR groups are present in the other ring, the products are the bisbenzofurans/bisindoles or fused bisbenzopyrans/bisquinolines, formed respectively as

a result of both direct and crossover intramolecular cation-nucleophile reactions. Bridged oxocine/azocine products are also formed in the presence of an additional 3-methoxy substituent.[21] When the *ortho'* substituents are hydroxymethyl, aminomethyl, and carboxylic acid groups, the products are bisbenzopyrans, or bisisoquinolines, or bis-δ-lactones, respectively, a result of direct intramolecular cation-nucleophile reactions. Crossover products (e.g., fused benzoxepanes or fused benzoazepanes) were not formed. In the presence of an additional 3-methoxy substituent, competing Friedel-Crafts reactions occur to give other fused polycyclic products.[22]

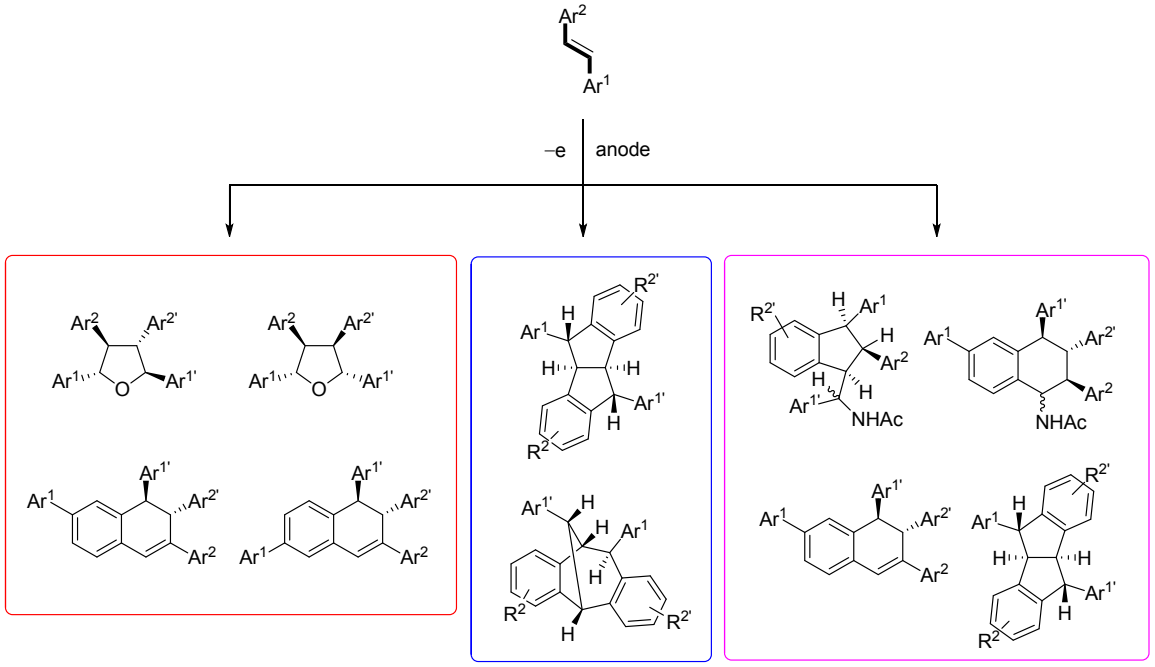


Figure 1. Effect of aromatic substitution (*p*- and *m*-substituents) on the distribution of products in the anodic oxidation of stilbenes.

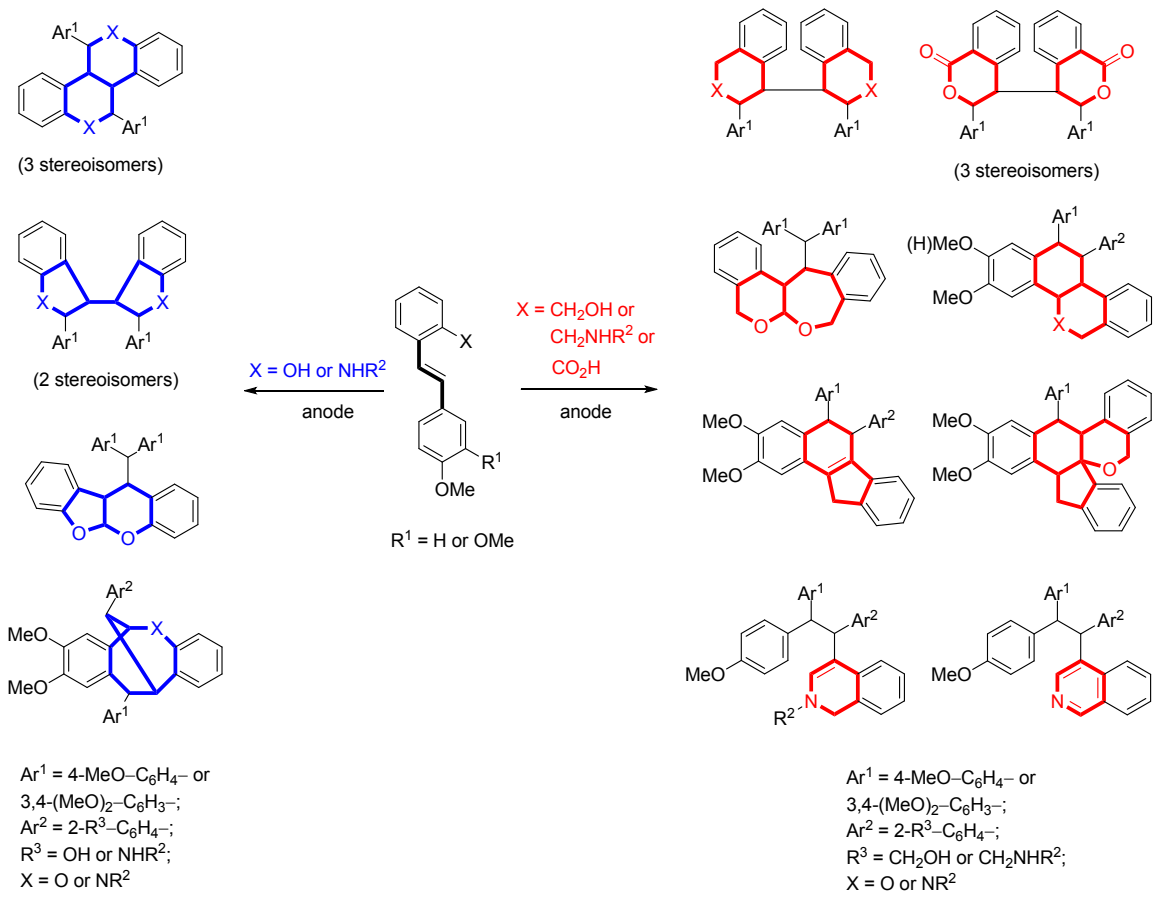


Figure 2. Effect of *ortho'*-substituted nucleophilic groups on the distribution of products in the anodic oxidation of methoxystilbenes.

In this final part of the study, we propose to investigate the effect of *ortho'*-substituted vinyl and formyl groups and herein report our results.

RESULTS AND DISCUSSION

Stilbenes were synthesized by coupling (Heck) of the appropriate aryl halide and styrene precursors. The choice of the appropriate potential for carrying out controlled potential electrolysis (CPE) was based on a preliminary cyclic voltammogram.

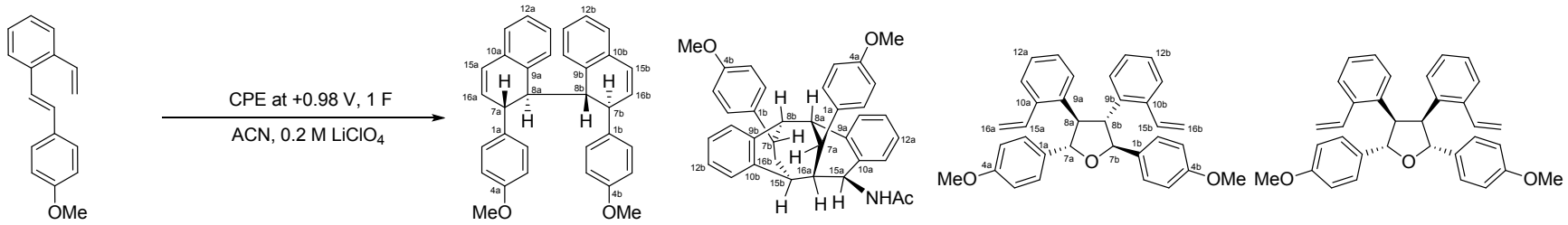
Preparative electrolyses were carried out at the first anodic wave until consumption of *ca*. 0.9–1 F, after which the products were separated by preparative radial chromatography and/or HPLC.

We first investigated the anodic oxidation (0.98 V, Pt gauze anode, Pt cathode, MeCN/0.2 M $LiClO_4$) of methoxystilbene **1** in which the *ortho'*-substituent is a vinyl group, in order to determine whether and how efficiently the π-electrons of the vinyl moiety can engage the benzylic cation in an cation-olefin cyclization process. A preliminary cyclic voltammogram of **1** (Pt anode, MeCN/0.2 M $LiClO_4$) showed the presence of two irreversible waves at +0.89 V and +1.13 V versus $Ag/AgNO_3$. Controlled potential electrolysis at the first anodic wave (+0.98 V, Pt-gauze anode, Pt cathode; MeCN/0.2 M $LiClO_4$) gave a product mixture comprising the C_2 symmetric bisdihydronaphthalene **1a** (27%), the unusual, doubly-bridged, dibenzofused cyclononane **1b** (6%), and the stereoisomeric tetraaryltetrahydrofurans **1c** (15%) and **1d** (12%) (Scheme 1).[20] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1a** ($C_{34}H_{30}O_2$) can be assigned by analogy to the related C_2 symmetric compounds such as the bisbenzopyran, bisisoquinolines, and bis-δ-lactones obtained in the previous study.[22] The presence of the C-15–C-16 double bond is indicated by the olefinic resonances at δ_H 6.01 (δ_C 130.1) and δ_H 6.68 (δ_C 130.0).

The ^1H NMR data of the cyclononane derivative **1b** ($C_{36}H_{35}NO_3$) showed resonances due to 16 aromatic hydrogens, 2 methoxy groups, 7 methines, one methylene, and one methyl of an acetamide group. A distinctly deshielded doublet at δ_H 5.31 (δ_C 48.1) is assigned to an aminomethine (H-15a), while the NH resonance is observed at δ_H 4.52. The presence of an amide group is also indicated by the IR bands at 1655 (C=O)

and 3305 (NH) cm^{-1} in addition to the amide carbonyl resonance at δ_C 168.5. The aromatic resonances are attributed to two 1,4-disubstituted (two *p*-methoxyphenyl) and two 1,2-disubstituted aromatic moieties, corresponding to rings A, A′, B and B′. The COSY data (Figure 3) showed the presence of a −NHCHCHCHCHCHCHCH− partial structure, corresponding to NH−C-15a−C-16a−C-7a−C-8a−C-8b−C-7b−C-16b−C-15b, with C-15b linked to C-16a to forge a substituted seven-membered ring. Examination of the HMBC data permitted assembly of the complete structure of **1b**, revealing a doubly-bridged, dibenzofused cyclononane derivative. The acetamido side chain is linked to the cyclononane core at C-15a from the H-15a/C-17 three bond correlation in the HMBC spectrum. The strong NOE interaction between H-15a and H-16-b (Figure 3) requires the methano (C-7a) and ethano (C-7b–C16-b) bridges to be oriented anti to each other resulting in these hydrogens being proximate and pointing towards each other (the same NOE would be impossible for the alternative structure with a syn disposition of the methano and ethano bridges). With the geometry of the methano (C-7a) and ethano (C-7b–C16b) bridges fixed, the orientation of H-8a, H-8b, H-15b, and H-16a can be accordingly assigned, while the orientations of H-7a and H-7b are assigned from the H-2a (H-6a)/H-16a and H-2b (H-6b)/H-16b NOEs. The resulting relative configuration of **1b** is in perfect agreement with the NOESY data (Figure 3). Other observations which are consistent with the structure include the observation that H-15a and H-16a are orthogonal ($J_{15a\text{-}16a} = 0$) consistent with the α-orientation of H-15a, and the observation of long-range *W*-coupling (3.2 Hz) between H-8a and H-16a.

Scheme 1. Products from the Anodic Oxidation of Stilbene **1**



1

Total yield = 60%

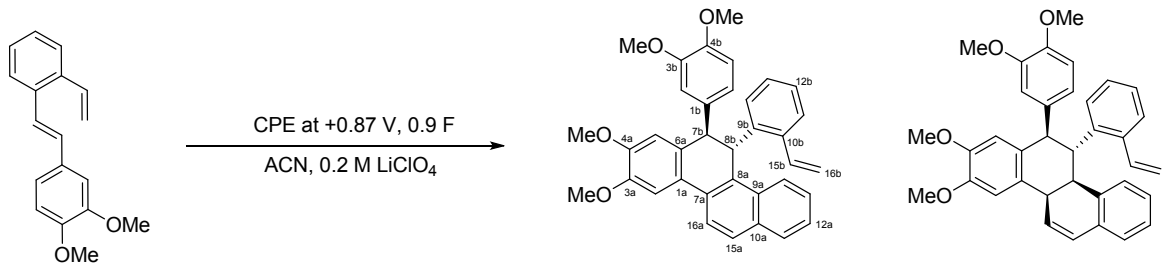
1a
27%

1b
6%

1c
15%

1d
12%

Scheme 2. Products from the Anodic Oxidation of Stilbene **2**



2

Total yield = 42%

2a
28%

2b
14%

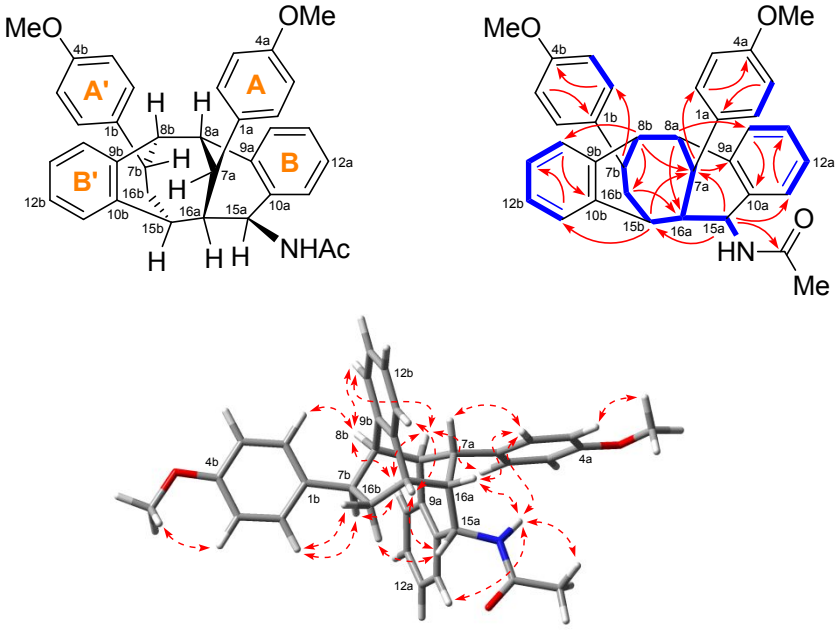


Figure 3. COSY, selected HMBCs, and selected NOEs of **1b**

Anodic oxidation of the dimethoxystilbene **2** gave two products which are derivatives of the polyaromatic hydrocarbon, chrysene, viz., the dihydrochrysene **2a** (28%) and the tertrahydrochrysene **2b** (14%) (Scheme 2). The ^{1}H and $^{13}C\{^{1}H\}$ NMR data of **2a** ($C_{36}H_{32}O_4$) can be readily assigned with the aid of the 2-D data. The resonances of H-7b and H-8b (constituting the CHCH fragment linked to C-6a) are singlets indicating that they are orthogonal, which has been noted previously in related dehydrotetralin derivatives.[20] The benzylic C-7b is linked to a 1,2-dimethoxyphenyl group while the adjacent C-8b is linked to a vinyl substituted aromatic moiety (Figure 4). The hydrogens of the vinyl group are seen at δ 5.65, 5.92, and 7.69. Compound **2b** is readily identified as the dihydro derivative of **2a** from the HRMS ($C_{36}H_{34}O_4$) and the ^{1}H and $^{13}C\{^{1}H\}$ NMR data. The ^{1}H spectrum of **2b** is generally similar to that of **2a** except for the observation

of a CHCHCHCHCH=CH fragment (in place of a CHCH and CH=CH fragment in **2a**) corresponding to C-7b–C-8b–C-8a–C-7a–C-16a–C-15a, as a consequence of C-8a and C-7a (quarternary sp^2 carbons in **2a**) being methines in **2b** (Figure 5). This change is also shown in the $^{13}C\{^1H\}$ NMR spectrum of **2b** in which C-8a and C-7a appear as methines (δ 44.3, 41.0) instead of as olefinic carbons in **2a** (δ 130.9, 132.5).

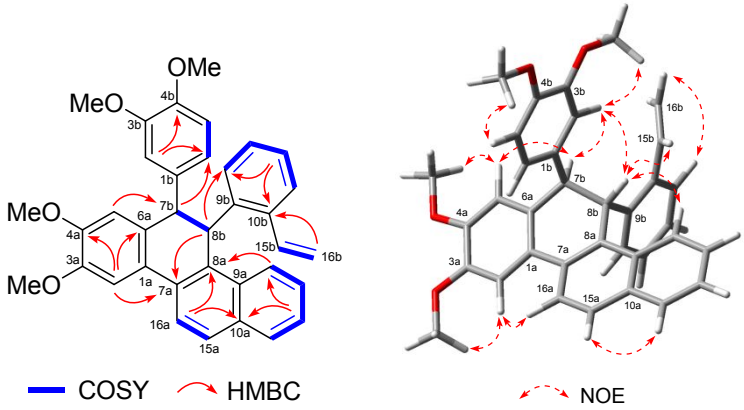


Figure 4. COSY, selected HMBCs, and selected NOEs of **2a**

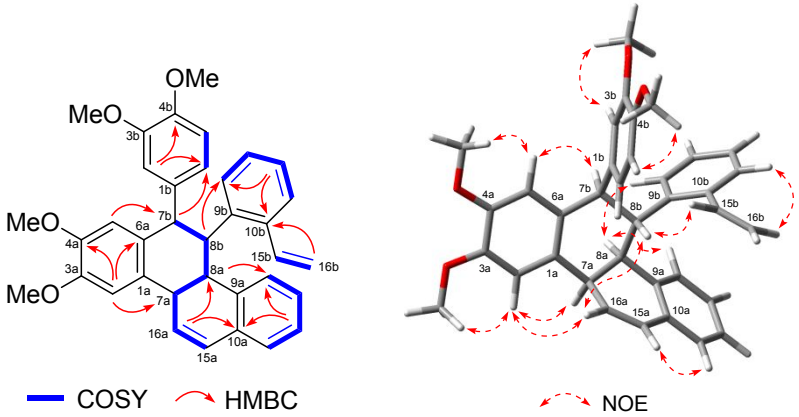
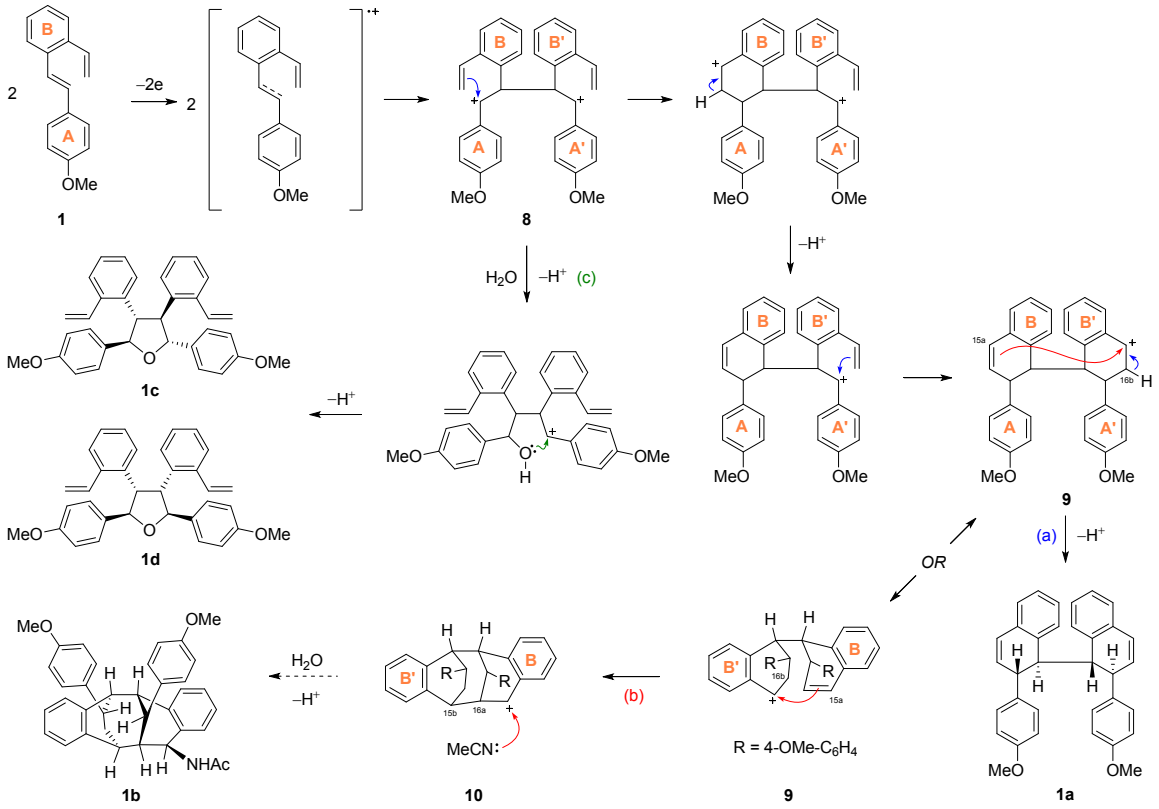


Figure 5. COSY, selected HMBCs, and selected NOEs of **2b**

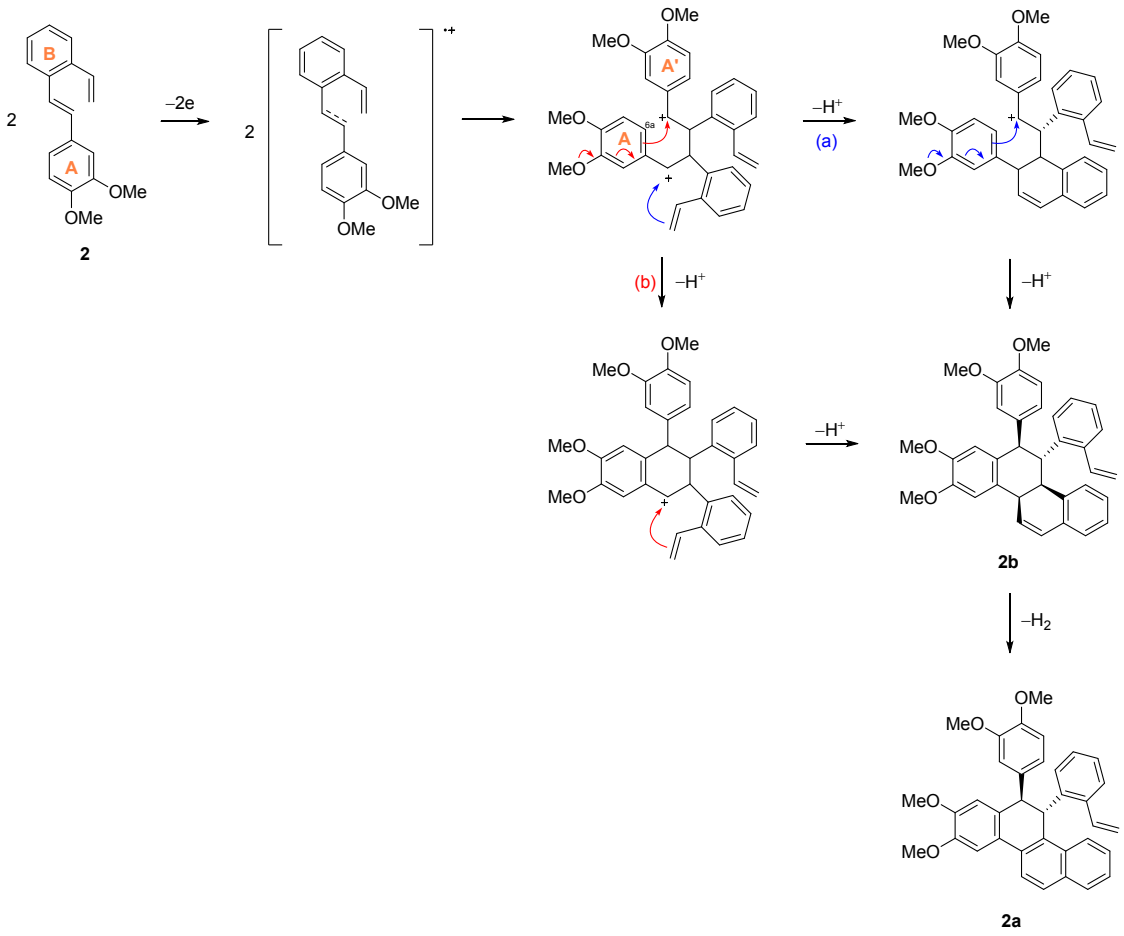
The choice of a vinyl group as the ortho′-substituent is to test whether, and to what extent, the π-electrons of a vinyl group can efficiently trap the benzylic cations. The

results showed that although intramolecular cation trapping products are formed (**1a**, **1b**; 33%), the products of competing intermolecular cation trapping are also obtained (**1c**, **1d**; 27%).[20] The proposed mechanism leading to the formation of the products is shown in Scheme 3. The bisdihydronaphthalene **1a** is a result of direct trapping of the dication **8** from cation radical dimerization, followed by deprotonation (path a). The doubly-bridged, dibenzofused cyclononane **1b** is a result of further reaction of the cationic intermediate **9**, formed after the second direct cation trapping step. Instead of deprotonation to **1a**, the benzylic cation in **9** is trapped in a 'crossover' manner by the π-electrons of the conjugated double bond associated with the first formed dihydronaphthalene moiety (path b). Subsequent capture of the resulting cation intermediate **10** by acetonitrile, followed by hydrolysis (Ritter reaction) gave **1b**.

Scheme 3. Proposed Mechanism for the Formation of Products in the Anodic Oxidation of Stilbene 1 in MeCN/$LiClO_4$



Scheme 4. Proposed Mechanism for the Formation of Products in the Anodic Oxidation of Stilbene 2 in MeCN/$LiClO_4$



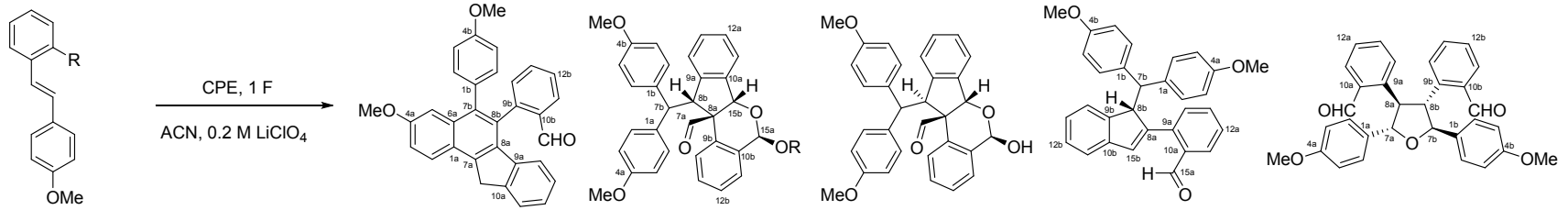
The formation of the chrysene derivatives in the oxidation of the dimethoxystilbene **2** is a consequence of additional methoxy substitution in the *meta*-position, resulting in enhanced nucleophilicity of the aromatic carbon *para* to the *m*-methoxy substituent (e.g., C-6a, ring A), and the consequent activation of the dimethoxy-substituted ring towards electrophilic substitution (Friedel-Crafts reaction). As shown in Scheme 4, two different order of the events can be envisaged viz., cation trapping by the vinyl group followed by Friedel-Crafts reaction (path a), or, cyclization followed by cation trapping (path b). Both lead to the same chrysene products, **2b**, and then **2a**.

A notable departure was observed in the oxidation of methoxystilbenes where the ortho′-substituent is a formyl group (**3**–**7**). The product mixture obtained in the case of **3** comprises the tetracylic fused indanylnaphthalene **3a** (7%), the epimeric indanylbenzopyran aldehydes (**3b** 23%, **3c** 10%), in addition to the tetraaryltetrahydrofuran **3d** (24%) (Scheme 5). The products obtained for the oxidation of **4** include **3a**, **3b**, **3c**, **3d**, and **4a**, while oxidation of **5** gave in addition to **3a**, **3b**, **3c**, and **3d**, the indene aldehyde **5a** (Scheme 5). The acetal protected stilbene aldehyde **4** gave the best overall yield (87%).

The molecular formula of **3a** ($C_{32}H_{24}O_3$) established from HRMS indicated loss of H_2O from the dimerization of the two starting stilbenes (**3**). The ^1H NMR spectrum showed the presence of 15 aromatic resonances, 2 aromatic methoxy groups, an isolated benzylic methylene (δ_H 4.28, δ_C 35.8), and an aldehyde-H (δ_H 9.81, δ_C 191.8). The aromatic resonances correspond to a 1,3,4-trisubstituted aryl, a 1,2-disubstituted aryl, a 4-methoxyaryl, and a 2-formylaryl moiety. These partial structures can be linked by the COSY and HMBC data (Figure 6) to give the structure shown in **3a**, which received further confirmation by X-ray analysis (Figure 6).

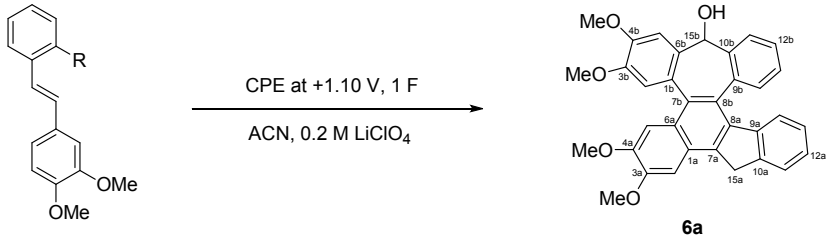
The HRMS of **3b** ($C_{32}H_{28}O_5$) showed that it is derived from dimerization of two starting stilbenes with addition of H_2O. The ^1H NMR data showed the presence of 16 aromatic resonances, 2 aromatic methoxy groups, 4 methine hydrogens, an aldehyde-H (δ_H 9.31, δ_C 197.6), and a hemiacetal OH (δ_H 3.51, exchanged with D_2O). The aromatic resonances are due to two 4-methoxyaryl and two 1,2-disubstituted aryl moieties.

Scheme 5. Products from the Anodic Oxidation of Stilbenes **3**–**5**



3 R = CHO	Total yield = 64%	**3a** 7%	**3b** R = H 23%	**3c** 10%		**3d** 24%
4 R = $CH(OMe)_2$	Total yield = 87%	**3a** 8%	**3b** R = H 25% **4a** R = Me 17%	**3c** 14%		**3d** 23%
5 R = $CH(OCH_2CH_2O)$	Total yield = 68%	**3a** 6%	**3b** R = H 24%	**3c** 13%	**5a** 5%	**3d** 20%

Scheme 6. Product from the Anodic Oxidation of Stilbenes **6** and **7**



6a

6 R = CHO	Total yield = 20%	20%
7 R = $CH(OMe)_2$	Total yield = 30%	30%

The two 4-methoxyaryl groups are linked to the same carbon (δ 52.9, C-7b) from the HMBC data (Figure 7), while the hemiacetal H and C resonances, are observed at δ_H 5.93 (H-15a) and δ_C 91.9 (C-15a), respectively. Examination of the 2-D NMR data (Figure 7), leads to the structure shown in **3b**, which also received confirmation from X-ray analysis (Figure 7).

Compound **3c** is an isomer of **3b** from the MS data. The ^{1}H and ^{13}C{^{1}H} NMR data of the two compounds are very similar, except for small differences in chemical shifts, suggesting a stereoisomeric relationship. In particular, noticeable differences are seen for the resonances of H-13a, 14a, and 15b in the ^{1}H NMR spectra and C-8b in the ^{13}C{^{1}H} NMR spectra. The large carbon chemical shift difference (10 ppm) for C-8b suggests that C-8b could be the epimeric center, which was confirmed by the NOESY data (Figure 8). Comparison of the NOESY data for **3c** (Figure 8) with that of **3b** (Figure 7), readily establish **3c** as the C-8b epimer of **3b** (H-7a/H-7b and H-15a/H-14b NOEs observed for **3c** but not **3b**, whereas, H-7a/H-8b and H-15a/H-8b NOEs observed for **3b** but not **3c**). The acetal **4a** is readily identified from comparison of the spectroscopic data (NMR and MS) with that of the precursor hemiacetal **3b**. The molecular formula of **4a** differs from that of **3b** (and **3c**) by 14 mass units or replacement of H with CH_3. In addition, the hemiacetal OH (δ_H 3.51), H-15a (δ_H 5.93), and C-15a (δ_C 91.9) resonances in **3b** have been replaced by the acetal OMe (δ_H 3.71, δ_C 55.9), H-15a (δ_H 5.50), and C-15a (δ_C 98.5) resonances, respectively, in **4a**.

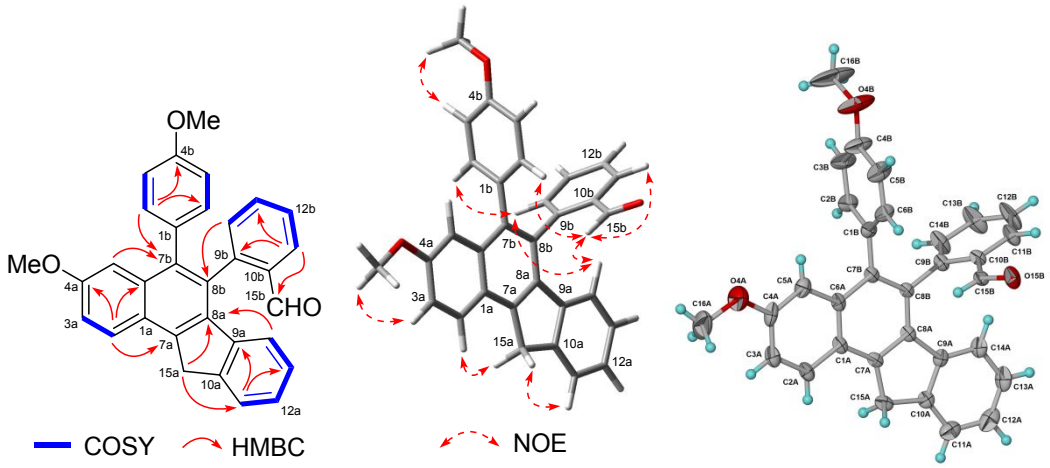


Figure 6. COSY, selected HMBCs, selected NOEs, and X-ray structure of **3a**

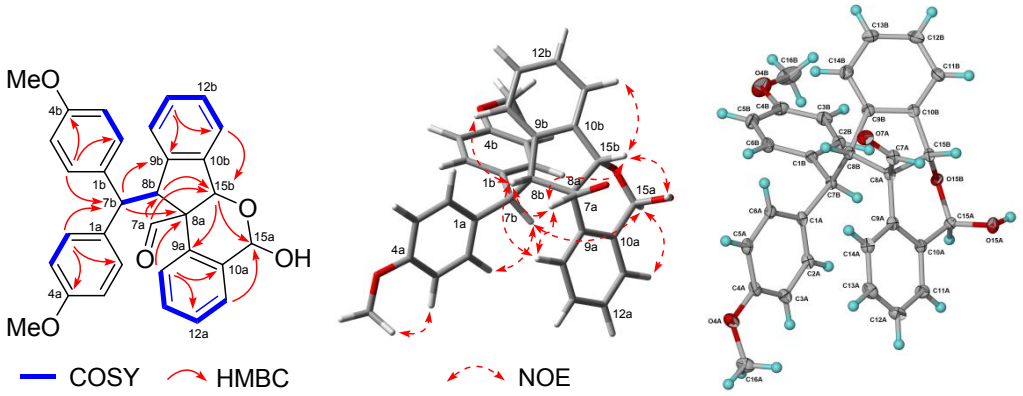


Figure 7. COSY, selected HMBCs, selected NOEs, and X-ray structure of **3b**

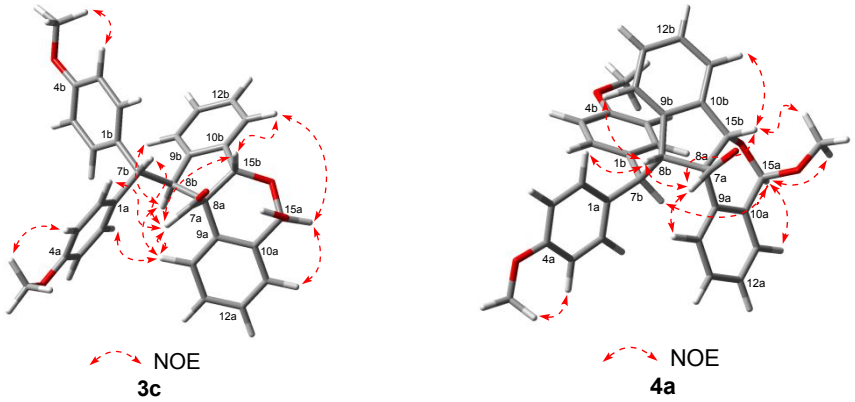


Figure 8. Selected NOEs of **3c** and **4a**

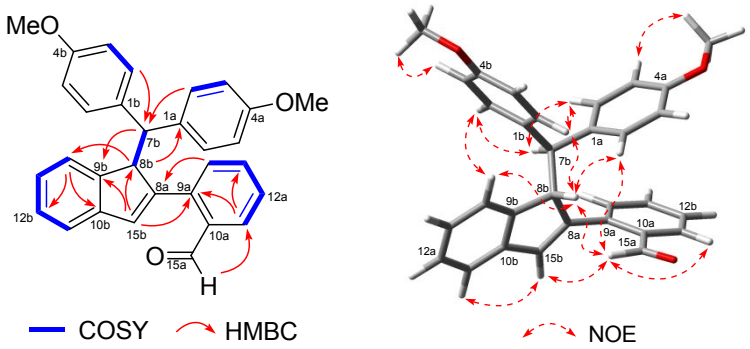


Figure 9. COSY, selected HMBCs, and selected NOEs of **5a**

The HRMS data of **5a** ($C_{31}H_{26}O_3$) indicated loss of a formic acid moiety when compared to **3b** and **3c**. The NMR data showed the presence of two 1,2-disubstituted aromatic moieties, and two 4-methoxyaryl groups which are linked to the same carbon (δ 50.0, C-7b, HMBC, Figure 9). This carbon (C-7b) is in turned linked to the benzylic methine (C-8b) of an indene moiety from the observed vicinal ($J_{7b\text{-}8b}$) coupling of 6 Hz. The presence of the trisubstituted indene double bond was consistent with the observed NMR resonances at $\delta_{\square}$ 6.56, H-15b; δ_C 135.8, C-15b; δ_C 146.1, C-8a. The NMR and IR data also indicated that in **5a**, an aromatic aldehyde group (δ_H 8.90, δ_C 192.6; IR 1686 cm^{-1}) has replaced the formyl group present in **3b** (δ_H 9.31, δ_C 197.6; IR 1720 cm^{-1}). This aromatic aldehyde is part of the other 1,2-disubstituted aryl group, and linking the partial structures by reference to the HMBC data (Figure 9) gave the structure shown in **5a**.

Anodic oxidation of the ortho′-formyl substituted 3,4-dimethoxystilbenes (**6,7**) gave only one product, viz., the fused benzofluorene-dibenzoannulene alcohol **6a** (Scheme 6). The acetal protected stilbene **7** gave the better yield (30% vs 20%), although in both cases the reactions were accompanied by formation of a significant quantity of polymeric products. The ^1H NMR data of **6a** ($C_{34}H_{28}O_5$ from HRMS) showed the

presence of 12 aromatic resonances, 4 methoxy groups, two hydrogens of a benzylic methylene which is part of an indene moiety (δ 4.14, 4.34), an oxymethine H (δ 5.71), and an OH group (δ 2.51, exchanged with D_2O). The aromatic resonances are due to two 1,2-disubstituted and two 1,2,4-5-tetrasubstituted aromatic moieties (each substituted by 2 aromatic OMe groups). In addition to the two quaternary olefinic carbons of the indene unit at δ_C134.7 and 139.7, two additional quaternary carbons are seen at δ_C130.1 and 133.3. In view of the many quaternary centers, further elucidation of the structure requires HMBC data (Figure 10), which led to the structure shown in **6a**. The structure of **6a** was also confirmed by X-ray analysis (Figure 10).

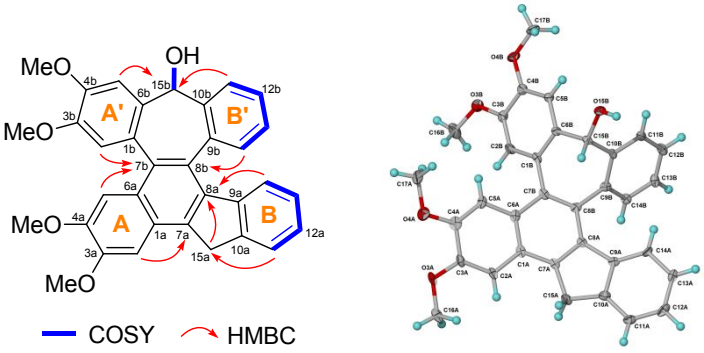
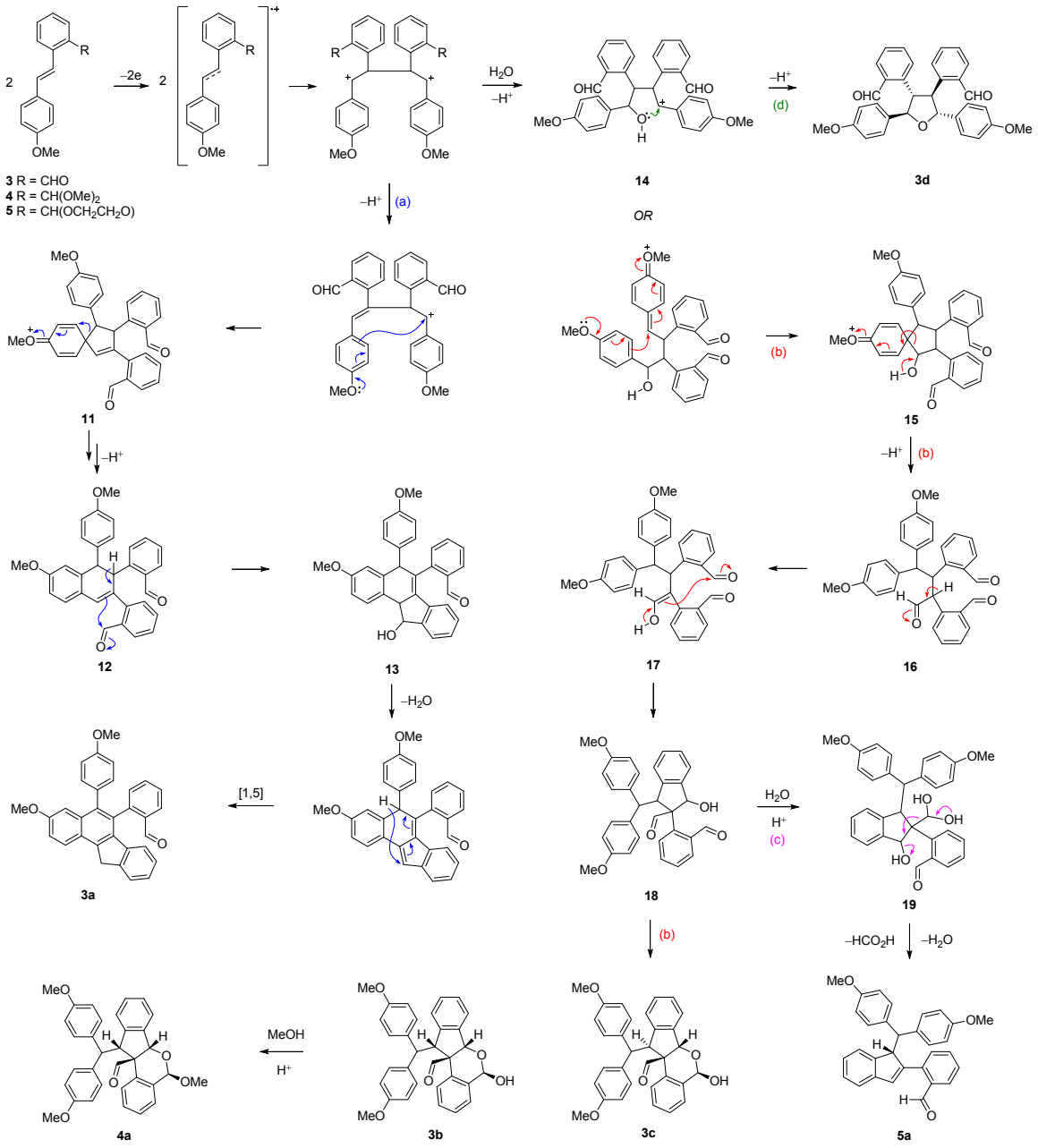


Figure 10. COSY, selected HMBCs, and X-ray structure of **6a**

An overall mechanism which accounts for the formation of the products from the anodic oxidation of the formyl substituted stilbenes **3**–**5** is shown in Scheme 7. Formation of the spirocyclic cation **11** via a Friedel-Crafts reaction, followed by ring-expansion and deprotonation as described previously[20,22] leads to the dehydrotetralin **12**. A concerted deprotonation-Prins-type cyclization leads to the tetracyclic carbinol **13**, which on

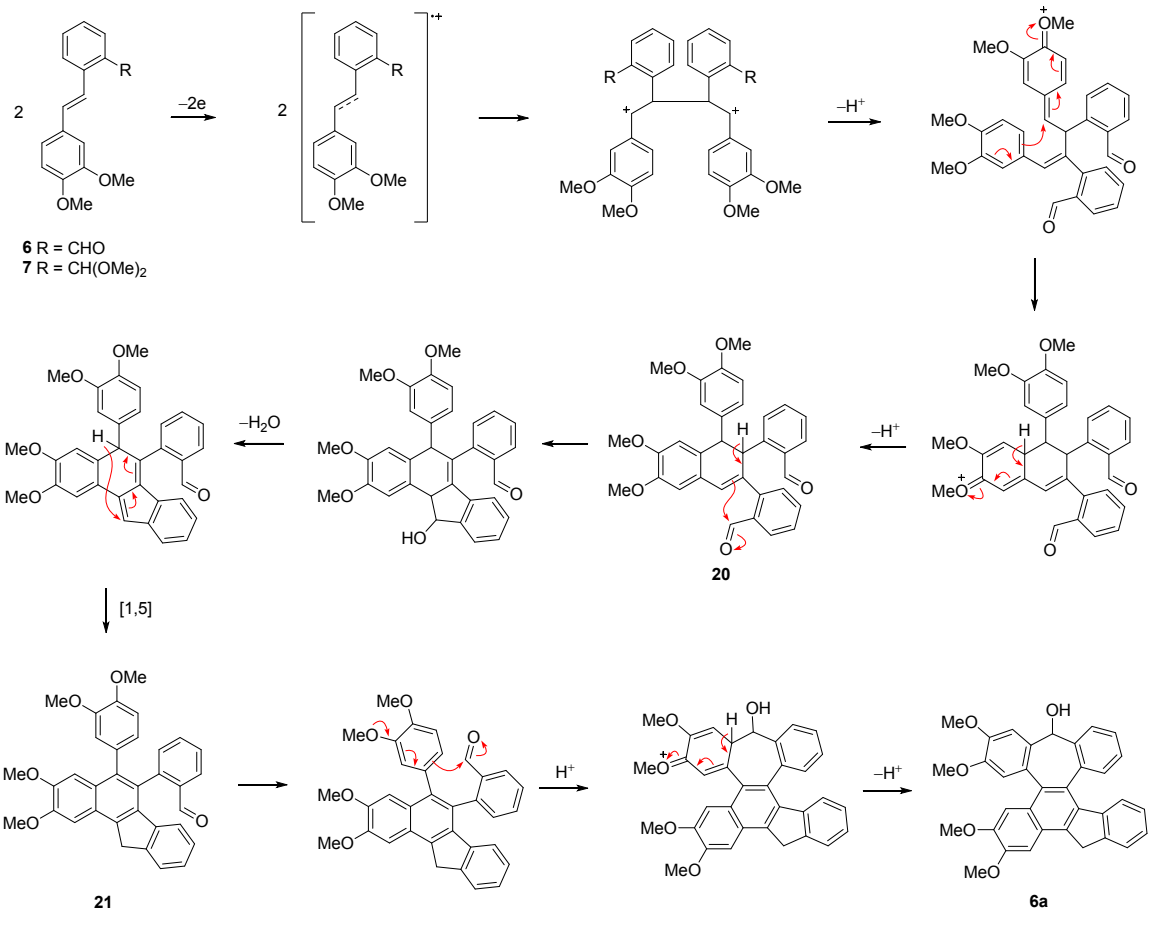
Scheme 7. Proposed Mechanism for the Formation of Products in the Anodic Oxidation of Stilbenes 3–5 in MeCN/$LiClO_4$



dehydration, followed by a [1,5] hydrogen shift, gives the indanylnaphthalene **3a**. Friedel-Crafts cyclization of the cationic intermediate **14** on the other hand, leads to the spirocyclic alcohol **15**, which on ring opening as described before[20,22] gives the aldehyde

16. Formation of the enol **17** followed by an aldol addition gives the hydroxyaldehyde **18**. A Grob-like fragmentation from the aldehyde hydrate **19** with elimination of formic acid and water, gives the indene aldehyde **5a**. Alternatively, cyclization of the hydroxyaldehyde **18** leads to the epimeric hemiacetals **3b** and **3c**, and thence to the acetal **4a**.

Scheme 8. Proposed Mechanism for the Formation of 6a in the Anodic Oxidation of Stilbenes 6 and 7 in MeCN/$LiClO_4$



A mechanism which accounts for the formation of the fused benzofluorene-dibenzoannulene **6a** in the oxidation of the dimethoxystilbenes **6** and **7** is shown in Scheme 8. The pathway follows essentially the same route as in path a Scheme 7 via the dication to the dehydrotetralin **20**, and thence to the indanylnaphthalene **21**, except that in the case of the dimethoxystilbenes **6** and **7**, a further aromatic substitution (Friedel-Crafts) reaction is possible due to the presence of the 3-methoxy substituent, which leads to the fused benzofluorene-dibenzoannulene **6a** as the final product. It is noteworthy that in the case of the dimethoxystilbene **2** where the ortho′-substituent is vinyl, a similar reaction from the chrysene derivatives (**2a** or **2b**, Scheme 4) is not possible, since unlike the carbonyl of the formyl group, the corresponding sp^2 carbon of the vinyl group is not electrophilic.

The primary objective of the current study was to evaluate the effect of two different types of ortho′-substituents of the reactivity of methoxystilbene cation radicals generated by anodic oxidation. In the first instance, the choice of an ortho′-vinyl substituent was to assess how efficiently the π-electrons of the vinyl group can effectively trap the benzylic cations. The results showed that although intramolecular cation trapping products are formed (33%), the products of competing intermolecular cation trapping are also obtained (27%). The doubly-bridged, dibenzofused cyclononane **1b** is an unusual and unexpected product formed as a result of a further reaction of the cationic intermediate (**9**, Scheme 3) formed after the second direct cation trapping step (crossover-type cation trapping by the π-electrons of the first formed conjugated double bond). In contrast to ortho′-substituted nucleophilic groups, the choice of a formyl group as the ortho′-substituent was to test whether the electrophilic carbonyl carbon of the formyl

group can interact with aromatic carbons in the other ring, rendered nucleophilic by 4-methoxy or 3-methoxy substituents. The results showed that this was indeed the case with the reactions producing a variety of surprising and unexpected products reflecting the varied and rich chemistry of stilbene cation radicals.

Experimental Section

General Experimental Procedures. Melting points were measured on a Mel-Temp melting point apparatus and an Electrothermal IA9100 digital melting point apparatus and are uncorrected. UV spectra were obtained on a Shimadzu UV-3101PC and UV-2600 spectrophotometers. IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrophotometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ using TMS as internal standard on JEOL JNM-ECA 400 or Bruker Avance III 400 and 600 spectrometers. ESIMS and HRESIMS were obtained on an Agilent 6530 Q-TOF spectrometer and HRDARTMS were recorded on a JEOL Accu TOF-DART mass spectrometer. X-ray diffraction analysis was carried out on a Bruker APEX II CCD area detector system equipped with a graphite monochromator and using Mo Kα radiation (λ = 0.71073 Å) or a Rigaku Oxford (formerly Agilent Technologies) SuperNova Dual diffractometer with Cu Kα radiation (λ = 1.54184 Å). Electrochemical experiments (cyclic voltammetry and controlled potential electrolysis) were performed on a Metrohm-Autolab electrochemical workstation PGSTAT100. All reactions were carried out under Ar or N_2, in oven-dried glassware. THF was distilled from Na/benzophenone under N_2. CH_2Cl_2 and MeCN were distilled from CaH_2, while MeOH was distilled from Mg under N_2.

Synthesis of 3 and 6 (Heck Coupling). Stilbenes **3** and **6** were synthesized following procedures which have been described previously.[20-23]

Microwave Irradiation Experiments. General procedure for microwave irradiation experiments have been described previously.[20-22]

Synthesis of Stilbenes 1 and 2 from 3 and 6, respectively. A solution of the corresponding stilbene (**3** and **6**, 0.2 mmol) in THF was added to a suspension of methyltriphenylphosphonium bromide (85.7 mg, 0.24 mmol) and NaH (21.6 mg, 0.9 mmol) in THF (10 mL) at 0 °C under Ar. The reaction mixture was refluxed with TLC monitoring. The reaction was cooled in an ice bath and cold distilled water was slowly added. The mixture was then extracted with CH_2Cl_2 (3 × 20 ml), and the combined organic layer was then washed with H_2O, dried (Na_2SO_4) and concentrated under reduced pressure. The resulting residue was then fractionated by preparative radial chromatography to yield the corresponding stilbene.

Synthesis of Stilbenes 4 and 7 from 3 and 6, respectively. A mixture of the corresponding stilbene (**3** and **6**, 0.2 mmol), trimethylorthoformate (66 μL, 0.6 mmol), and PTSA (1.9 mg, 0.01 mmol) in MeOH was microwave irradiated (with the heating program starting at 100 W) at 60 °C for 25 min. Triethylamine (1.4 μL, 0.01 mmol) was added to neutralize the reaction mixture. The mixture was then extracted with CH_2Cl_2 (3 × 20 ml), and the combined organic layer was then washed with H_2O, dried (Na_2SO_4) and concentrated under reduced pressure. The

resulting residue was then fractionated by preparative radial chromatography to yield the corresponding stilbene.

Synthesis of Stilbene 5 from 3. Ethylene glycol (22 μL, 0.4 mmol) and PTSA (1.9 mg, 0.01 mmol) were added separately to a solution of the corresponding stilbene (**3**, 0.2 mmol) in toluene (5 ml) at room temperature. The reaction mixture was microwave irradiated (with the heating program starting at 120 W) at 100 °C for 45 min. NaOH (5%) was added and the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was then washed with H_2O, dried (Na_2SO_4) and concentrated under reduced pressure. The resulting residue was then fractionated by preparative radial chromatography to yield the corresponding stilbene.

*(E)-1-(4-methoxystyryl)-2-vinylbenzene (**1**)*. Colorless oil; (26.9 mg, 57%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (3H, s), 5.34 (1H, d, J = 10.8 Hz), 5.63 (1H, d, J = 17.2 Hz), 6.88 (2H, d, J = 8.4 Hz), 6.91 (1H, d, J = 15.6 Hz), 7.09 (1H, dd, J = 17.2, 10.8 Hz), 7.23 (3H, m), 7.43 (2H, d, J = 8.4 Hz), 7.44 (1H, d, J = 15.6 Hz), 7.53 (1H, d, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100MHz) δ 55.5, 114.3, 116.5, 124.5, 126.2, 126.7, 127.5, 127.97, 128.00, 130.5, 130.7, 135.2, 136.0, 136.4, 159.5; HRMS (DART-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{17}H_{17}O$, 237.1279; Found 237.1282.

*(E)-1,2-dimethoxy-4-(2-vinylstyryl)benzene (**2**).* Colorless oil; (33.0 mg, 62%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.90 (3H, s), 3.94 (3H, s), 5.37 (1H, dd, J = 11.2, 1.6 Hz), 5.66 (1H, dd, J = 17.6, 1.6 Hz), 6.86 (1H, d, J = 9.2 Hz), 6.91 (1H, d, J = 16.0 Hz), 7.05

(1H, s), 7.06 (1H, m), 7.10 (1H, dd, J = 18.0, 11.6 Hz), 7.25 (3H, m), 7.47 (1H, d, J = 7.2 Hz), 7.54 (1H, d, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 56.0, 56.1, 109.1, 111.4, 116.5, 120.0, 124.7, 126.3, 126.7, 127.5, 128.0, 130.8, 131.0, 135.2, 135.9, 136.3, 149.1, 149.2; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_2$, 267.1385; Found 267.1382.

*(E)-2-(4-methoxystyryl)benzaldehyde (**3**)*.[24] Yellow solid (42.9 mg, 90%); mp 116–118 ˚C; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.84 (3H, s), 6.92 (2H, d, J = 8.8 Hz), 7.01 (1H, d, J = 16.2 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.51 (2H, d, J = 8.8 Hz), 7.56 (1H, t, J = 7.8 Hz), 7.70 (1H, d, J = 7.8 Hz), 7.83 (1H, d, J = 7.8 Hz), 7.91 (1H, d, J = 16.2 Hz), 10.33 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.4, 114.2, 122.5, 127.0, 127.2, 128.3, 129.8, 132.2, 132.8, 133.7, 140.4, 159.9, 192.7; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}O_2$, 239.1072; Found 239.1069.

*(E)-1-(dimethoxymethyl)-2-(4-methoxystyryl)benzene (**4**)*. Yellowish oil (54.6 mg, 96%); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.33 (6H, s), 3.80 (3H, s), 5.59 (1H, s), 6.89 (2H, d, J = 8.8 Hz), 6.94 (1H, d, J = 16.2 Hz), 7.25 (1H, t, J = 7.7 Hz), 7.31 (1H, t, J = 7.7 Hz), 7.46 (2H, d, J = 8.8 Hz), 7.58 (1H, d, J = 7.7 Hz), 7.61 (1H, d, J = 7.7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 53.0, 55.3, 101.7, 114.2, 123.7, 125.8, 126.8, 127.0, 128.0, 128.7, 130.4, 130.4, 134.6, 136.6, 159.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}O_3$, 285.1491; Found 285.1496.

*(E)-2-(2-(4-methoxystyryl)phenyl)-1,3-dioxolane (**5**)*. Yellowish oil (45.2 mg, 80%); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.80 (3H, s), 4.04 (2H, m), 4.15 (2H, m), 6.09 (1H, s), 6.88 (2H, d, J = 8.8 Hz), 6.96 (1H, d, J = 16.0 Hz), 7.26 (1H, t, J = 7.6 Hz), 7.34 (1H,

t, J = 7.6 Hz), 7.40 (1H, d, J = 16.0 Hz), 7.45 (2H, d, J = 8.8 Hz), 7.59 (1H, d, J = 7.6 Hz), 7.60 (1H, d, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.4, 65.4, 101.9, 114.1, 123.5, 126.0, 126.1, 127.1, 128.0, 129.2, 130.4, 130.9, 134.4, 137.0, 159.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_3$, 283.1334; Found 283.1340.

*(E)-2-(3,4-dimethoxystyryl)benzaldehyde (**6**)*. Yellow solid (51.0 mg, 95%); mp 125–127 ˚C; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.90 (3H, s), 3.95 (3H, s), 6.86 (1H, d, J = 8.0 Hz), 6.99 (1H, d, J = 16.0 Hz), 7.10 (1H, dd, J = 8.0, 2.4 Hz), 7.11 (1H, s), 7.40 (1H, t, J = 7.6 Hz), 7.55 (1H, t, J = 7.6 Hz), 7.69 (1H, d, J = 7.6 Hz), 7.81 (1H, d, J = 7.6 Hz), 7.91 (1H, d, J = 16.0 Hz), 10.31 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.99, 56.04, 109.2, 111.3, 120.7, 122.8, 127.1, 127.4, 130.1, 132.4, 132.8, 133.8, 134.0, 140.3, 149.3, 149.6, 192.9; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_3$, 269.1178; Found 269.1170.

*(E)-4-(2-(dimethoxymethyl)styryl)-1,2-dimethoxybenzene (**7**)*. Yellowish oil (59.1 mg, 94%); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.34 (6H, s), 3.88 (3H, s), 3.93 (3H, s), 5.60 (1H, s), 6.85 (1H, d, J = 8.4 Hz), 6.93 (1H, d, J = 16.0 Hz), 7.06 (1H, d, J = 2.0 Hz), 7.08 (1H, dd, J = 8.4, 2.0 Hz), 7.26 (1H, t, J = 7.6 Hz), 7.32 (1H, t, J = 7.6 Hz), 7.42 (1H, d, J = 16.0 Hz), 7.59 (1H, d, J = 7.6 Hz), 7.60 (1H, d, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 53.2, 55.95, 55.99, 101.7, 109.4, 111.3, 119.9, 124.1, 125.9, 126.8, 127.0, 128.7, 130.7, 130.8, 134.6, 136.5, 149.0, 149.1; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}O_4$, 315.1596; Found 315.1591.

Cyclic Voltammetry. Cyclic voltammetry experiments were carried out as described previously.[20-22]

General Procedure for Electrochemical Oxidation (Controlled Potential Electrolysis). General procedure for controlled potential electrolysis has been described previously.[20-22]

Anodic oxidation of 1 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **1** (+0.99 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 5% MeOH/CH_2Cl_2), followed by HPLC (Luna Phenyl-Hexyl column, 10% H_2O/MeCN, 10 mL/min), gave **1a** (12.7 mg, 27%), **1b** (3.2 mg, 6%), **1c** (7.3 mg, 15%), and **1d** (5.9 mg, 12%).

*Bisdihydronaphthalene (**1a**)*. Colorless oil. UV (EtOH) λ_{max} (log ε) 227 (4.54), 271 (4.08), and 285 (3.91) nm; IR (dry film) ν_{max} 1607, 1507, 1244, 1175, 1033, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.16 (2H, s), 3.60 (2H, d, J = 6.0 Hz), 3.67 (6H, s), 6.01 (2H, dd, J = 9.5, 6.0 Hz), 6.62 (4H, d, J = 8.8 Hz), 6.67 (4H, d, J = 8.8 Hz), 6.68 (4H, m), 6.99 (2H, m), and 7.16 (4H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 39.7, 52.2, 55.1, 113.8, 125.7, 126.7, 126.9, 127.5, 128.2, 130.0, 130.1, 133.8, 134.0, 135.9, and 158.0; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{31}O_2$, 471.2324; Found 471.2322.

*Doubly-bridged-dibenzofused-cyclononane (**1b**)*. Colorless oil. UV (EtOH) λ_{max} (log ε) 226 (4.26), 267 (3.72), 286 (3.54), and 311 (3.12) nm; IR (dry film) ν_{max} 3305, 1655, 1609, 1248, 1179, 1034, and 754 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49 (3H, s), 1.62 (1H, m), 2.18 (1H, dd, J = 15.6, 10.4 Hz), 2.52 (1H, ddd, J = 10.4, 4.0, 1.6 Hz), 2.75 (1H, br t, J = 3.2 Hz), 2.81 (1H, dt, J = 8.4, 3.2 Hz), 3.30 (1H, dd, J = 9.6, 1.6 Hz), 3.66 (4H, m), 3.68 (4H, m), 4.52 (1H, d, J = 9.2 Hz), 5.31 (1H, d, J = 9.2 Hz), 6.19 (2H, d, J = 8.8 Hz), 6.50 (2H, d, J = 8.8 Hz), 6.64 (2H, d, J = 8.4 Hz), 6.80 (1H, d, J = 7.6 Hz), 6.86

(2H, d, J = 8.4 Hz), 7.08 (1H, br s), 7.15 (1H, t, J = 7.6 Hz), 7.31 (3H, m), and 7.45 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 23.3, 30.9, 39.2, 40.5, 41.6, 42.0, 45.1, 48.1, 52.6, 55.1, 55.3, 113.0, 113.6, 125.9, 126.9, 127.3, 127.6, 128.5, 128.6, 128.7, 129.4, 129.9, 130.6, 135.6, 135.8, 139.4, 140.0, 140.3, 141.3, 157.5, and 168.5; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{36}NO_3$, 530.2695; Found 530.2699.

*Tetraaryltetrahydrofuran (**1c**)*. Colorless oil. UV (EtOH) λ_{max} (log ε) 229 (4.58), 254 (3.99), 276 (3.42), and 284 (3.31) nm; IR (dry film) ν_{max} 1612, 1511, 1247, 1172, 1032, and 771 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.78 (6H, s), 4.08 (2H, dd, J = 6.0, 2.8 Hz), 4.93 (2H, dd, J = 11.2, 1.6 Hz), 5.08 (2H, dd, J = 17.6, 1.6 Hz), 5.38 (2H, dd, J = 6.0, 2.8 Hz), 6.33 (2H, dd, J = 17.6, 11.2 Hz), 6.82 (4H, d, J = 8.8 Hz), 7.10 (2H, t, J = 7.6 Hz), 7.17 (2H, d, J = 7.6 Hz), 7.21 (4H, d, J = 8.8 Hz), 7.22 (2H, t, J = 7.6 Hz), and 7.49 (2H, d, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.3, 58.5, 87.8, 113.8, 116.7, 126.5, 126.7, 126.8, 127.0, 127.9, 133.6, 134.8, 135.3, 138.8, and 159.1; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{33}O_3$, 489.2430; Found 489.2437.

*Tetraaryltetrahydrofuran (**1d**)*. Colorless oil. UV (EtOH) λ_{max} (log ε) 228 (4.71), 254 (4.11), 276 (3.59), and 283 (3.47) nm; IR (dry film) ν_{max} 1612, 1512, 1248, 1175, 1033, and 772 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.79 (6H, s), 4.16 (2H, dd, J = 4.8, 1.6 Hz), 5.04 (2H, dd, J = 10.8, 1.2 Hz), 5.25 (2H, dd, J = 17.6, 1.2 Hz), 5.59 (2H, dd, J = 4.8, 1.6 Hz), 6.58 (2H, dd, J = 17.6, 10.8 Hz), 6.86 (4H, d, J = 8.8 Hz), 7.08 (6H, m), 7.17 (2H, m), and 7.35 (4H, d, J = 8.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 51.9, 55.2, 84.9, 113.8, 116.5, 126.3, 126.6, 127.1, 127.5, 128.0, 133.9, 134.6, 135.5, 138.6, and 159.0; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{33}O_3$, 489.2430; Found 489.2438.

Anodic oxidation of 2 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **2** (+0.87 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane/CH_2Cl_2, 1/1 to 5% MeOH/CH_2Cl_2), gave **2a** (7.4 mg, 14%) and **2b** (14.9 mg, 28%).

*Dihydrochrysene (**2a**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 227 (4.68), 235 (4.70), 265 (4.55), 273 (4.55), 290 (4.06), and 328 (4.15) nm; IR (dry film) ν_{max} 1605, 1513, 1504, 1246, 1140, 1027, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.54 (3H, s), 3.72 (3H, s), 3.77 (3H, s), 4.05 (3H, s), 4.15 (1H, s), 5.30 (1H, s), 5.65 (1H, dd, *J* = 11.2, 1.6 Hz), 5.92 (1H, dd, *J* = 17.6, 1.6 Hz), 6.49 (1H, d, *J* = 7.6 Hz), 6.54 (1H, s), 6.61 (1H, d, *J* = 8.4 Hz), 6.64 (1H, d, *J* = 2.0), 6.67 (1H, dd, *J* = 8.4, 2.0 Hz), 6.82 (1H, t, *J* = 7.6 Hz), 7.10 (1H, t, *J* = 7.6 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 7.33 (1H, t, *J* = 7.6 Hz), 7.50 (1H, s), 7.57 (1H, d, *J* = 7.6 Hz), 7.64 (1H, d, *J* = 7.6), 7.69 (1H, dd, *J* = 17.6, 11.2 Hz), 7.78 (1H, d, *J* = 7.6 Hz), 7.89 (1H, d, *J* = 8.8 Hz), and 8.05 (1H, d, *J* = 8.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 44.4, 51.0, 55.5, 55.8, 56.2, 107.5, 110.8, 111.2, 113.0, 117.2, 119.3, 121.4, 123.8, 125.4, 126.7, 126.8, 126.9, 127.2, 128.0, 128.1, 128.3, 128.5, 129.1, 130.9, 132.5, 132.9, 133.2, 135.4, 135.9, 137.6, 140.1, 147.5, 148.58, 148.64, and 149.2; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{33}O_4$, 529.2379; Found 529.2370.

*Tetrahydrochrysene (**2b**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 225 (4.62), 241 (4.34) and 284 (4.06) nm; IR (dry film) ν_{max} 1607, 1510, 1250, 1233, 1139, 1027, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.31 (1H, dd, *J* = 11.2, 6.0 Hz), 3.56 (3H, s), 3.64 (3H, s), 3.75 (3H, s), 3.90 (1H, t, *J* = 11.2 Hz), 3.94 (3H, s), 4.06 (1H, dt, *J* = 6.0, 2.8 Hz), 4.31 (1H, d, *J* = 11.2 Hz), 4.61 (1H, dd, *J* = 17.2, 2.0 Hz), 4.63 (1H, dd, *J* = 10.8, 2.0

Hz), 5.91 (1H, dd, J = 17.2, 10.8 Hz), 5.96 (1H, d, J = 9.6 Hz), 6.24 (1H, d, J = 2.4), 6.30 (1H, d, J = 7.6 Hz), 6.36 (1H, s), 6.38 (1H, dd, J = 8.4, 2.4 Hz), 6.51 (1H, dd, J = 9.6, 3.2 Hz), 6.56 (1H, d, J = 8.4 Hz), 6.66 (1H, t, J = 7.6 Hz), 6.76 (1H, s), 6.83 (1H, d, J = 7.6 Hz), 6.91 (1H, d, J = 7.6 Hz), 6.96 (1H, t, J = 7.6 Hz), 6.99 (1H, t, J = 7.6 Hz), 7.28 (1H, t, J = 7.6 Hz), and 7.52 (1H, d, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 41.0, 42.0, 44.3, 52.2, 55.7, 55.8, 56.0, 56.1, 110.66, 110.75, 112.4, 115.7, 121.1, 125.80, 125.83, 126.2, 126.3, 126.4, 126.6, 126.9, 129.5, 130.8, 131.6, 132.9, 133.5, 134.9, 136.0, 137.9, 140.0, 140.9, 147.2, 147.7, 148.2; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{35}O_4$, 531.2535; Found 531.2540.

Anodic oxidation of 3 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **3** (+1.10 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 10% MeOH/CH_2Cl_2) gave **3a** (3.2 mg, 7%), **3b** (11.3 mg, 23%), **3c** (4.9 mg, 10%), and **3d** (11.8 mg, 24%).

*Fused indanylnaphthalene (**3a**)*. Light yellowish oil and subsequently, colorless needle crystals from MeOH/CH_2Cl_2; mp 181–183 ˚C; UV (EtOH) λ_{max} (log ε) 216 (4.49), 261 (4.50), 270 (4.48), and 319 (3.88) nm; IR (dry film) ν_{max} 2836, 1693, 1620, 1513, 1463, 1245, 1231, 1173, 1031, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.71 (3H, s), 3.76 (3H, s), 4.28 (1H, s), 6.07 (1H, d, J = 7.8 Hz), 6.76 (2H, m), 6.88 (1H, d, J = 2.5 Hz), 6.95 (1H, t, J = 7.8 Hz), 6.99 (1H, m), 7.02 (1H, m), 7.17 (1H, t, J = 7.8 Hz), 7.27 (1H, dd, J = 9.0, 2.5 Hz), 7.31 (1H, d, J = 7.6 Hz), 7.44 (1H, t, J = 7.6 Hz), 7.54 (1H, t, J = 7.6 Hz), 7.58 (1H, d, J = 7.8 Hz), 7.91 (1H, d, J = 7.6 Hz), 8.05 (1H, d, J = 9.0 Hz), and 9.81 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 35.8, 55.1, 55.2, 106.6, 113.2, 113.7, 119.1, 121.7, 124.7, 125.8, 125.9, 126.6, 127.1, 128.0, 130.7, 130.9, 131.3, 131.9, 132.1,

133.3, 133.7, 133.9, 135.3, 138.0, 140.1, 142.5, 143.4, 144.2, 157.9, 158.2, and 191.8; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{25}O_3$, 457.1804; Found 457.1793.

*Fused indanylbenzopyran aldehyde (**3b**)*. Light yellowish oil and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 202–204 ˚C; V (EtOH) λ_{max} (log ε) 234 (4.12) and 275 (3.36) nm; IR (dry film) ν_{max} 3415, 2836, 1720, 1607, 1509, 1247, 1177, 1026, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.51 (1H, br d, J = 3.2 Hz), 3.67 (3H, s), 3.74 (3H, s), 3.99 (1H, d, J = 8.8 Hz), 4.85 (1H, d, J = 8.8 Hz), 5.65 (1H, s), 5.93 (1H, br d, J = 3.2 Hz), 6.39 (1H, d, J = 7.5 Hz), 6.51 (4H, m), 6.58 (1H, d, J = 7.6 Hz), 6.62 (2H, d, J = 8.7 Hz), 6.89 (1H, t, J = 7.6 Hz), 6.93 (2H, d, J = 8.7 Hz), 6.98 (1H, t, J = 7.5 Hz), 7.17 (1H, t, J = 7.6 Hz), 7.20 (1H, t, J = 7.5 Hz), 7.27 (1H, d, J = 7.6 Hz), 7.44 (1H, d, J = 7.5 Hz), and 9.31 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 51.9, 52.9, 55.1, 55.3, 63.5, 72.6, 91.9, 112.9, 113.7, 125.3, 127.1, 127.2, 127.4, 127.9, 128.0, 128.6, 129.1, 130.45, 130.52, 134.4, 134.9, 135.9, 138.4, 147.3, 157.7, 157.9, and 197.6; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{29}O_5$, 493.2015; Found 493.2013.

*Fused indanylbenzopyran aldehyde (**3c**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 232 (4.23) and 275 (3.60) nm; IR (dry film) ν_{max} 3393, 2836, 1714, 1607, 1511, 1249, 1031, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.96 (1H, br d, J = 9.8 Hz), 3.73 (3H, s), 3.82 (3H, s), 4.15 (1H, d, J = 9.8 Hz), 4.44 (1H, d, J = 9.8 Hz), 5.75 (1H, br d, J = 9.8 Hz), 6.01 (1H, d, J = 7.6 Hz), 6.27 (1H, s), 6.66 (2H, d, J = 8.8 Hz), 6.75 (2H, d, J = 8.8 Hz), 6.84 (1H, t, J = 7.6 Hz), 6.95 (2H, d, J = 8.7 Hz), 7.19 (1H, t, J = 7.6 Hz), 7.25 (1H, t, J = 7.7 Hz), 7.33 (1H, d, J = 7.7 Hz), 7.38 (2H, d, J = 8.7 Hz), 7.44 (1H, t, J = 7.7 Hz), 7.51 (1H, d, J = 7.6 Hz), 7.67 (1H, d, J = 7.7 Hz), and 9.22 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 52.2, 55.2, 55.3, 62.0, 63.1, 78.2, 89.1, 113.6, 114.3, 124.0,

125.6, 127.3, 127.5, 127.6, 128.3, 129.2, 129.9, 130.1, 133.8, 134.4, 137.6, 138.4, 140.8, 158.4, 158.6, and 199.1; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{29}O_5$, 493.2015; Found 493.2014.

*Tetraaryltetrahydrofuran (**3d**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 229 (4.44), 255 (4.05), and 301 (3.48) nm; IR (dry film) ν_{max} 2836, 1689, 1511, 1246, 1175, 1029, 828, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.77 (6H, s), 5.23 (2H, dd, J = 6.2, 2.6 Hz), 5.41 (2H, dd, J = 6.2, 2.6 Hz), 6.82 (4H, d, J = 8.7 Hz), 7.21 (4H, d, J = 8.7 Hz), 7.32 (2H, t, J = 7.8 Hz), 7.58 (2H, d, J = 7.8 Hz), 7.59 (2H, t, J = 7.8 Hz), 7.82 (2H, d, J = 7.8 Hz), and 9.66 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 54.6, 55.2, 88.5, 113.9, 127.2, 127.4, 128.0, 132.1, 132.4, 134.2, 134.7, 139.7, 159.4, and 191.5; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{29}O_5$, 493.2015; Found 493.2019.

Anodic oxidation of 4 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **4** (+1.07 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 10% MeOH/CH_2Cl_2) gave **3a** (3.7 mg, 8%), **3b** (12.3 mg, 25%), **3c** (6.9 mg, 14%), **3d** (11.3 mg, 23%), and **4a** (8.6 mg, 17%).

*Fused indanylbenzopyran aldehyde (**4a**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 231 (4.24) and 275 (3.62) nm; IR (dry film) ν_{max} 2834, 1720, 1608, 1509, 1248, 1177, 1033, and 754 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.69 (3H, s), 3.71 (3H, s), 3.74 (3H, s), 3.99 (1H, d, J = 9.6 Hz), 4.85 (1H, d, J = 9.6 Hz), 5.48 (1H, s), 5.50 (1H, s), 6.36 (1H, d, J = 7.8 Hz), 6.47 (1H, d, J = 7.7 Hz), 6.55 (2H, d, J = 8.8 Hz), 6.59 (2H, d, J = 8.8 Hz), 6.61 (2H, d, J = 8.8 Hz), 6.81 (1H, t, J = 7.7 Hz), 6.90 (2H, d, J = 8.8 Hz), 6.96 (1H, t, J = 7.8 Hz), 7.13 (1H, t, J = 7.7 Hz), 7.19 (1H, t, J = 7.8 Hz), 7.21 (1H, d, J = 7.7 Hz), 7.45 (1H, d, J = 7.8 Hz), and 9.29 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 51.6,

53.3, 55.2, 55.3, 55.9, 63.6, 72.7, 98.5, 113.0, 113.6, 125.2, 127.0, 127.1, 127.3, 127.75, 127.81, 128.5, 129.0, 130.2, 130.6, 134.2, 135.0, 136.0, 138.2, 147.5, 157.6, 157.8, and 197.5; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{33}H_{31}O_5$, 507.2172; Found 507.2175.

Anodic oxidation of 5 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **5** (+1.08 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 10% MeOH/CH_2Cl_2) gave **3a** (2.7 mg, 6%), **3b** (11.8 mg, 24%), **3c** (6.4 mg, 13%), **3d** (9.9 mg, 20%), and **5a** (2.2 mg, 5%).

*Indenyl benzaldehyde (**5a**)*. Light yellowish oil. UV (EtOH) λ_{max} (log ε) 231 (4.19) and 286 (3.80) nm; IR (dry film) ν_{max} 2836, 1686, 1608, 1510, 1248, 1178, 1034, and 758 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.69 (3H, s), 3.83 (3H, s), 4.51 (1H, d, J = 5.8 Hz), 4.80 (1H, d, J = 5.8 Hz), 6.28 (2H, d, J = 8.7 Hz), 6.51 (2H, d, J = 8.7 Hz), 6.56 (1H, s), 6.59 (1H, d, J = 7.4 Hz), 6.87 (2H, d, J = 8.7 Hz), 7.05 (1H, t, J = 7.4 Hz), 7.21 (2H, d, J = 8.7 Hz), 7.31 (1H, t, J = 7.4 Hz), 7.37 (1H, d, J = 7.4 Hz), 7.43 (1H, t, J = 7.5 Hz), 7.52 (1H, d, J = 7.5 Hz), 7.66 (1H, t, J = 7.5 Hz), 7.89 (1H, d, J = 7.5 Hz), and 8.90 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 50.0, 55.2, 55.3, 56.4, 113.5, 113.7, 121.7, 124.8, 125.3, 127.4, 128.0, 129.47, 129.52, 130.6, 133.1, 134.8, 135.0, 135.8, 140.0, 144.3, 145.2, 146.1, 158.1, 158.7, and 192.6; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{31}H_{27}O_3$, 447.1960; Found 447.1968.

Anodic oxidation of 6 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **6** (+1.10 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 10% MeOH/CH_2Cl_2) gave **6a** (10.3 mg, 20%).

*Fused benzofluorene-dibenzoannulene (**6a**)*. Light yellowish oil and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 195–197 ˚C; UV (EtOH) λ_{max} (log ε) 210 (4.43), 233 (4.27), 281 (4.40), 290 (4.42), 301 (4.24), and 335 (3.59) nm; IR (dry film) ν_{max} 3508, 2834, 1505, 1487, 1257, 1240, 1202, 1159, 1133, 1027, and 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.51 (1H, d, J = 2.8 Hz), 3.77 (3H, s), 3.85 (3H, s), 3.99 (3H, s), 4.11 (3H, s), 4.14 (1H, d, J = 21.9 Hz), 4.34 (1H, d, J = 21.9 Hz), 5.71 (1H, d, J = 2.8 Hz), 6.97 (1H, d, J = 7.8 Hz), 7.06 (1H, t, J = 7.8 Hz), 7.15 (1H, s), 7.18 (1H, t, J = 7.8 Hz), 7.21 (1H, t, J = 7.8 Hz), 7.32 (1H, s), 7.34 (1H, s), 7.43 (1H, t, J = 7.8 Hz), 7.58 (1H, s), 7.59 (2H, m), 7.74 (1H, d, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 36.2, 55.8, 55.9, 55.96, 56.01, 70.1, 103.1, 103.3, 107.7, 115.2, 119.5, 123.36, 123.43, 124.5, 125.3, 125.7, 125.8, 126.0, 126.6, 128.1, 130.1, 131.7, 131.9, 133.3, 134.7, 139.7, 140.3, 143.2, 143.6, 146.0, 146.4, 149.0, 149.2, and 149.8; HRMS (DART-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{29}O_5$, 517.2015; Found 517.2005.

Anodic oxidation of 7 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **7** (+1.10 V, 1.0 F) yielded a mixture, which on preparative radial chromatography (SiO_2, *n*-hexane/CH_2Cl_2, 2/1 to 10% MeOH/CH_2Cl_2) gave **6a** (15.5 mg, 30%).

Supporting Information

^1H and $^{13}C\{^1H\}$ NMR spectra for stilbenes and electrochemical oxidation products. Cyclic voltammograms of stilbenes **1** and **3**. X-ray structures and crystallographic data in CIF format for compounds **3a**, **3b**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

We thank the MOE, Malaysia (FRGS-FP073-2018A) for financial support.

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