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Electrochemically-mediated oxidative transformations of substituted 4-methoxystilbenes – the effect of *ortho*-substituted nucleophilic groups

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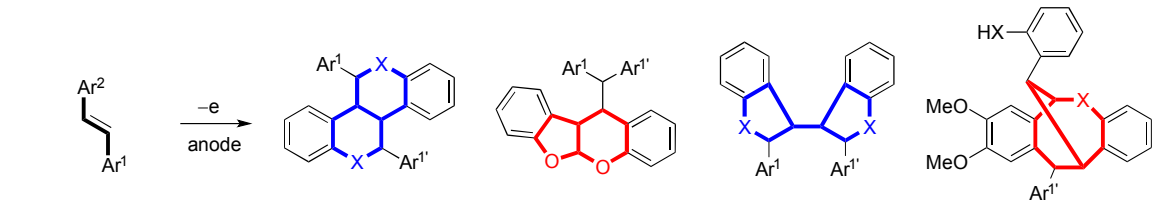


Ar^1 = 4-MeO–C_6H_4– or 3,4-$(MeO)_2$–C_6H_3–;
Ar^2 = 2-X–C_6H_4–;
X = OH or NHR

Ar^1 = 4-MeO–C_6H_4– or 3,4-$(MeO)_2$–C_6H_3–; Ar^2 = 2-X–C_6H_4–; X = O or NR

Abstract

A systematic study was undertaken to determine the influence of *ortho'*-substituted nucleophilic groups (OH, NH_2 or NHR) on the reactivity of anodically-generated 4-methoxy- and 3,4-dimethoxystilbene cation radicals. The results showed that when *ortho*-substituted nucleophilic groups such as OH or NHR are present in the other ring, both direct and crossover intramolecular cation-nucleophile reactions occur to give bisbenzofurans/bisindoles or fused bisbenzopyrans/bisquinolines, respectively. Where an additional 3-methoxy substituent is present, bridged oxocine/azocine products are formed in addition to the bisbenzopyrans/bisquinolines and bisbenzofurans/bisindoles. Mechanistic rationalization of the observed behavior is presented based on a generalized pathway involving fast cation radical dimerization following electron transfer, followed by direct and crossover trapping of the benzylic cations by the *ortho*-substituted oxygen and nitrogen nucleophilic groups. In the instances where an additional 3-methoxy group is present, the bridged oxocine/azocine products are also formed as a result of competing aromatic substitution (Friedel Crafts reaction). The results have shed further light and provided additional clarification on the reactivity of anodically-generated stilbene cation radicals.

Introduction

Although relatively underexploited as a tool in organic synthesis, electrochemically-mediated processes nevertheless remain an attractive and complimentary alternative in the organic chemists' armory of methods for functional group manipulation and C-C bond formation.[1-5] This is in large part due to certain inherent advantages associated with the electrochemical technique which includes *inter alia*, high chemoselectivity, umpolung reactivity, the use of comparatively mild reaction conditions and environmentally friendly procedures, and in some instances the amenability to scale up.[1-5] As part of our interest in electrochemically-mediated transformations in organic chemistry,[6] we recently carried out a reinvestigation of the anodic oxidation of 4,4'-dimethoxystilbene followed by a systematic study of the effect of aromatic substitution on the nature and distribution of the products as well as the reaction pathways, in the oxidation of substituted stilbenes.[7] The motivation for these studies was to explore access to natural polyphenol skeletons via anodic oxidation, as well as to gain a better understanding of the behavior of the first-formed intermediate, viz., the cation radical, a species endowed with high reactivity and an inherent ambident or dualistic character.[8] The results showed that the aromatic substituents fall into three categories: those that resulted in the formation of tetrahydrofurans and dehydrotetralins, those that gave rise to a mixture of indanyl (or tetralinyl) acetamides and dehydrotetralins (or pallidols), and those where strategic placement of donor groups resulted in products incorporating pallidol and ampelopsin F carbon skeletons (Figure 1). The results from this study have provided valuable insight into how subtle changes in the nature and position of the aromatic substituents can affect the course of the electrochemical oxidation of substituted stilbenes, in addition to

clarifying the reactivity and fate of the cation radical intermediate, subsequent to the initial electron transfer step.[7]

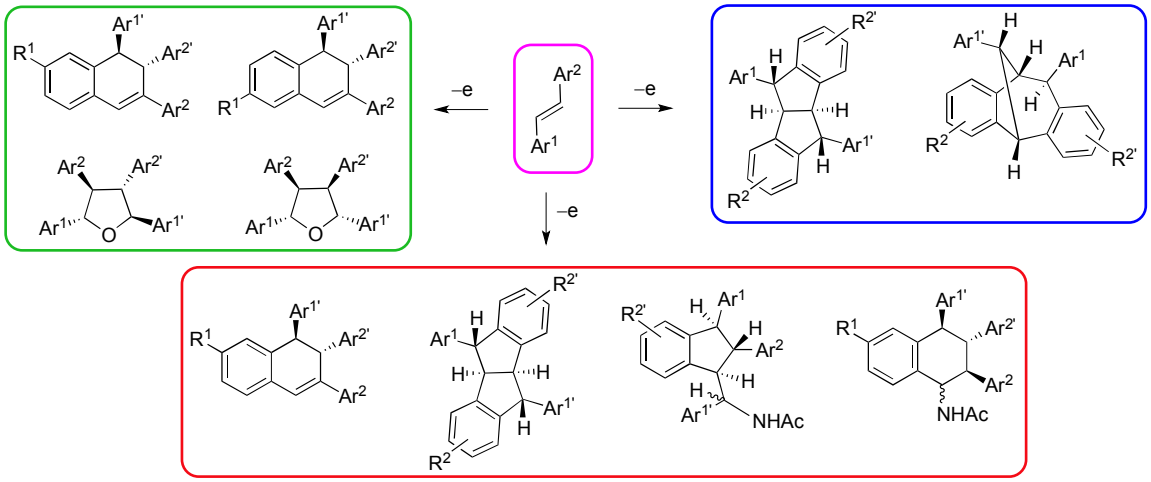


Figure 1. Reactivity of anodically generated stilbene cation radicals: effect of aromatic substitution.

In continuation of our studies of stilbene cation radicals generated by anodic oxidation, we next investigated what would be the effect of placing nucleophilic groups (such as OH and NH_2) at the *ortho* position of one ring in 4-methoxy and 3,4-dimethoxy substituted stilbenes, and herein report the results.

RESULTS AND DISCUSSION

The required stilbenes were synthesized by Heck coupling of the appropriate styrene and aryl halide precursors.[7,9] It has been previously noted that anodic oxidation of 4-methoxystilbene substituted by an *ortho*-methoxy group in the other ring gave a mixture comprising the stereoisomeric tetraaryltetrahydrofurans accompanied by the

methoxy-migrated dehydrotetralin.[7] In the present study, similar results were also obtained on oxidation of 4-methoxy-2'-acetoxystilbene, which gave the corresponding tetraaryltetrahydrofurans and the unrearranged dehydrotetralin (Figure 2).

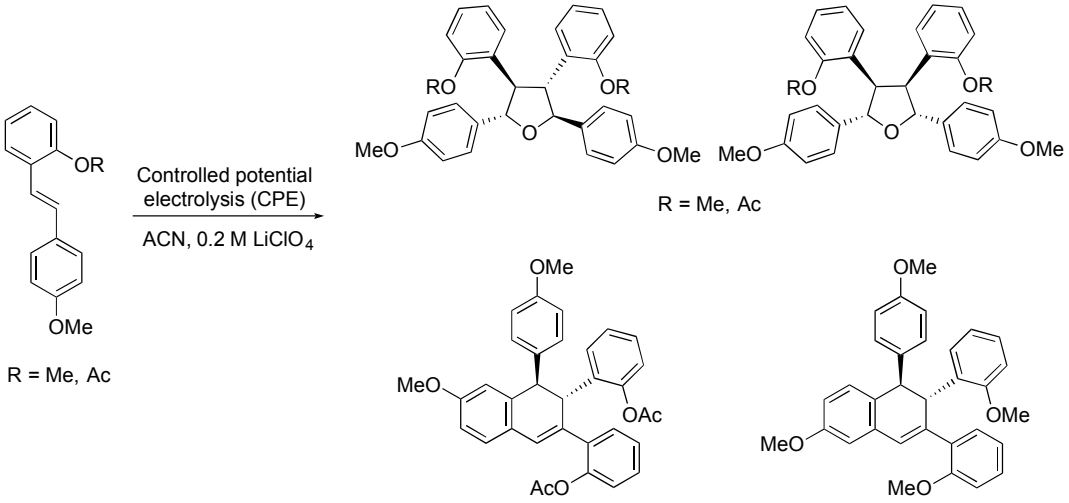
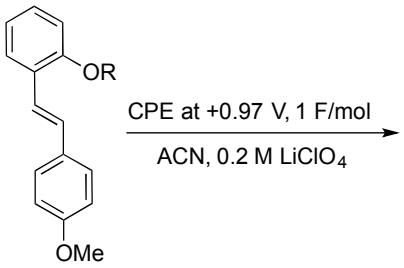
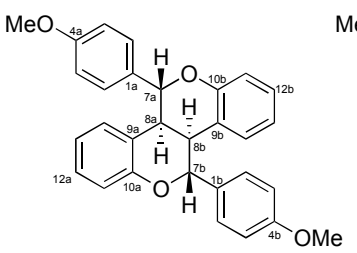


Figure 2. Products from the anodic oxidation of 4,2'-dimethoxystilbene and 4-methoxy-2'-acetoxystilbene

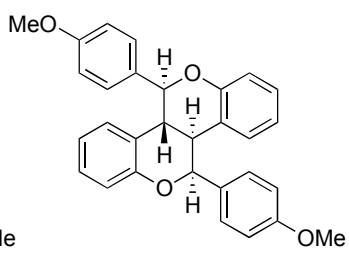
Arising from these observations, the next stilbene chosen for investigation was 4-methoxy-2'-hydroxystilbene **1**, which has an *ortho*-hydroxy group present in one ring and a *para*-methoxy group in the other ring. Anodic oxidation of **1** (Pt anode, MeCN/0.2 M $LiClO_4$) showed the presence of one irreversible wave at +0.87 V versus $Ag/AgNO_3$ in the potential range investigated as revealed by cyclic voltammetry. Controlled potential electrolysis (Pt gauze anode, Pt cathode; MeCN/0.2 M $LiClO_4$) at the anodic wave (+0.97 V) was allowed to proceed until about 1 F of charge had been transferred. A mixture of dimeric products (as indicated by their MS data) was obtained in total yield of about 80%, comprising the stereoisomeric fused bisbenzopyrans (as the major products in

Scheme 1. Products from the anodic oxidation of stilbenes **1** and **2**

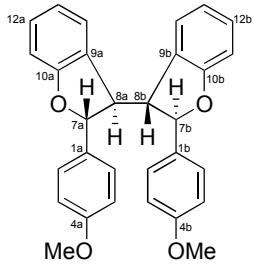




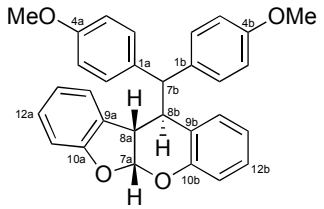
1a



1b



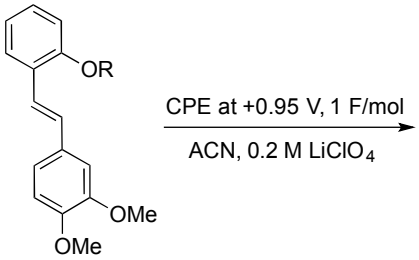
1c

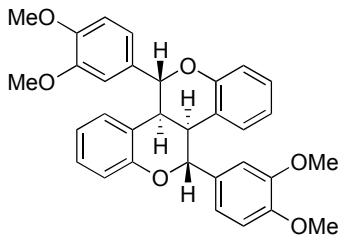


1e

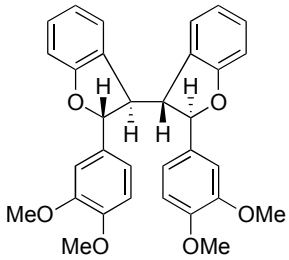
1 R = H	R = H, Total = 80%	25%	14%	19%	22%
2 R = $SiMe_3$	R = $SiMe_3$, Total = 82%	27%	15%	20%	20%

Scheme 2. Products from the anodic oxidation of stilbenes **3** and **4**

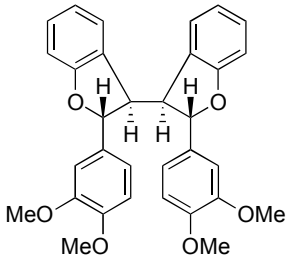




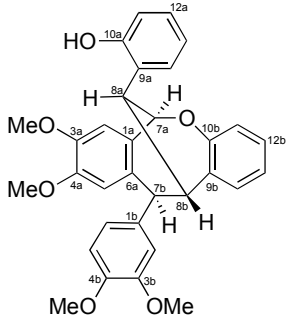
3a



3c



3d



3f

3 R = H	R = H, Total = 88%	21%	17%	18%	32%
4 R = $SiMe_3$	R = $SiMe_3$, Total = 85%	19%	18%	18%	30%

combined yield of ca. 40% (**1a**, 25%; **1b**, 14%), the bisbenzofuran **1c (**19%), and the fused benzofurano-benzopyran **1e** (22%) (Scheme 1). The product mixture was separated by a combination of preparative radial chromatography on SiO_2 (Chromatotron), RP-HPLC, and Sephadex LH20, and the products were characterized by their spectroscopic data (HRESIMS, ^{1}H and ^{13}C{^{1}H} NMR), as well as X-ray analysis.

Compound **1a** had molecular formula $C_{30}H_{26}O_4$ from HRESIMS measurements. However, the ^{1}H and ^{13}C{^{1}H} NMR data showed only resonances due to one half of the molecule, indicating the presence of an element of symmetry. Aside from the readily recognizable aromatic and methoxy resonances, the ^{1}H NMR spectrum showed two mutually coupled methine hydrogens at δ 5.28 (H-7a) and 3.33 (H-8a) with a coupling constant of *ca.* 10 Hz. The former resonance corresponds to an oxymethine while the latter is likely a benzylic methine. Analysis of the 2-D NMR data (COSY, HSQC, HMBC) led to two possible structures, one a fused bisbenzopyran and the other a bisbenzofuran (Figure 3). Differentiation between the two structures was made possible by comparison of the ^{13}C{^{1}H} shifts of the α and β methine carbons with model benzopyran[10] and benzofuran[11] compounds from the literature (Figure 3) which allowed **1a** to be assigned the fused bisbenzopyran structure (and compound **1c**, the bisbenzofuran structure, vide infra). Assignment of the stereochemistry was based on the observed H-7a/H-8a coupling of *ca.* 10 Hz in the ^{1}H NMR spectrum of **1a**, indicating that these hydrogens are *trans*-diaxially oriented in the six-membered pyran ring, leading to a fused bisbenzopyran with a C_2 axis. In the event these conclusions were confirmed by X-ray analysis, which also revealed the *cis*-fusion of the pyran rings (Figure 3).

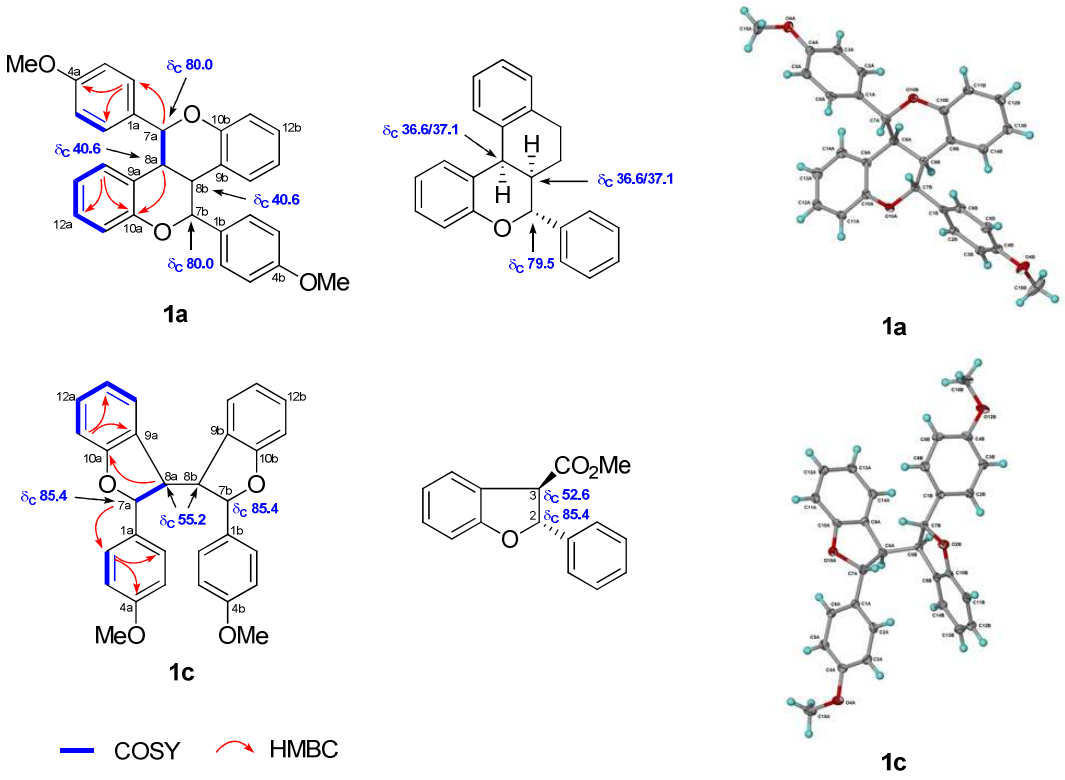


Figure 3. COSY and selected HMBCs of **1a** and **1c**, $^{13}C\{^{1}H\}$ shifts of the α and β methine carbons of model benzopyran[10] and benzofuran,[11] and X-ray structures of **1a** and **1c**.

Unlike the previous compound (**1a**), the ^{1}H and $^{13}C\{^{1}H\}$ NMR data of compound **1b** ($C_{30}H_{26}O_4$, isomeric with **1a**) indicated a dimerization product devoid of any symmetry, and, based on comparison of the observed $^{13}C\{^{1}H\}$ shifts of the α and β carbons as before, indicated that **1b** possesses a similar fused bisbenzopyran structure. In the ^{1}H NMR spectrum, H-8a was observed as a triplet with a coupling constant of 10.8 Hz, indicating that both the adjacent hydrogens (H-7a and H-8b) were in a *trans* relationship with H-8a (a *trans*-fused bisbenzopyran). H-8b on the other hand was observed as a doublet of doublets with coupling constants of 10.8 and 3.9 Hz, indicating

that H-7b and H-8b were *cis* to each other. These conclusions were also confirmed by X-ray analysis (Figure 4).

Compound **1c** ($C_{30}H_{26}O_4$) was deduced to be a bisbenzofuran possessing an element of symmetry, based on the ^{1}H and $^{13}C\{^{1}H\}$ NMR data (vide supra). In this instance (five-membered furan rings), the observed H-7a/H-8a coupling of 3.6 Hz was insufficient for definitive assignment of the relative configurations at C-7a and C-8a. Fortunately suitable crystals were obtained, and X-ray analysis revealed a *trans* arrangement between H-7a and H-8a, resulting in the presence of a C_2 axis (Figure 3).

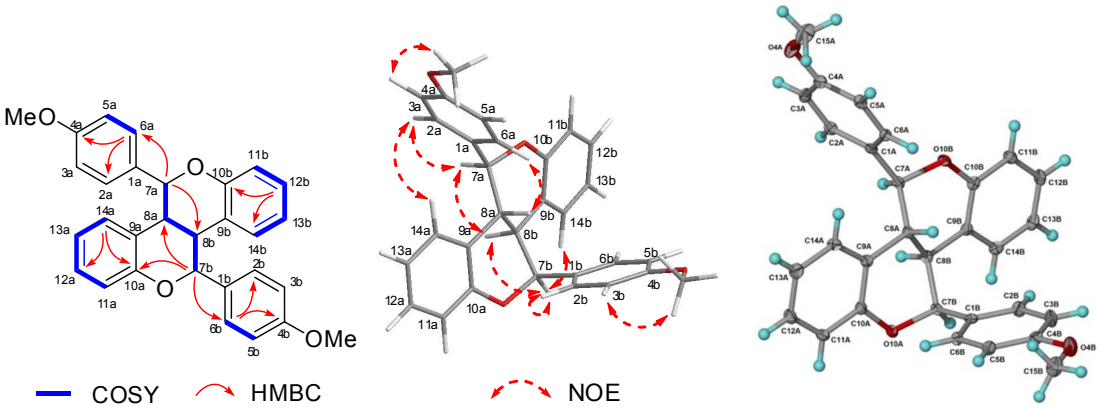


Figure 4. COSY, selected HMBCs, selected NOEs and X-ray crystal structure of **1b**

The ^{1}H NMR data of compound **1e** ($C_{30}H_{26}O_4$) showed the presence of 16 aromatic resonances, four methine protons and two methoxy groups. The resonance at δ_H 6.36 (δ_C 104.2) was assigned to a methine (H-7a) linked to two oxygen atoms while the resonance at δ_H 4.04 (δ_C 44.8) which was coupled to H-7a, was attributed to the adjacent benzylic methine (H-8a). The COSY spectrum revealed in addition to the OCH(O)–CH partial structure, the presence of another fragment, CH–CH, which was assigned to H-8b

(δ_H 3.74, δ_C 45.7) and H-7b (δ_H 4.23, δ_C 53.6). The observed H-8a to C-7b three-bond correlation in the HMBC spectrum (Figure 5) indicated that H-8b was linked to H-8a resulting in the partial structure, C-7a–C-8a–C-8b–C-7b. The rest of the molecule can be assembled based on the HMBC data (Figure 5), which revealed a fused benzofurano-benzopyran as shown in **1e**. *Cis*-fusion of the furan and pyran rings was based on the observed $J_{7a\text{-}8a}$ vicinal coupling of 7.8 Hz, as well as the reciprocal NOEs observed between H-7a and H-8a (Figure 5). The resonance for H-8b was observed as a doublet with J = 11.8 Hz, as a result of H-8a and H-8b being orthogonal to each other, which was also consistent with the *cis*-fused geometry. The α-orientation of H-8b was also consistent with the NOEs observed for H-8b/H-14a, H-8b/H-14b, and H-8b/H-2a, H-6a. The structure and relative configuration were also confirmed by X-ray diffraction (Figure 5).

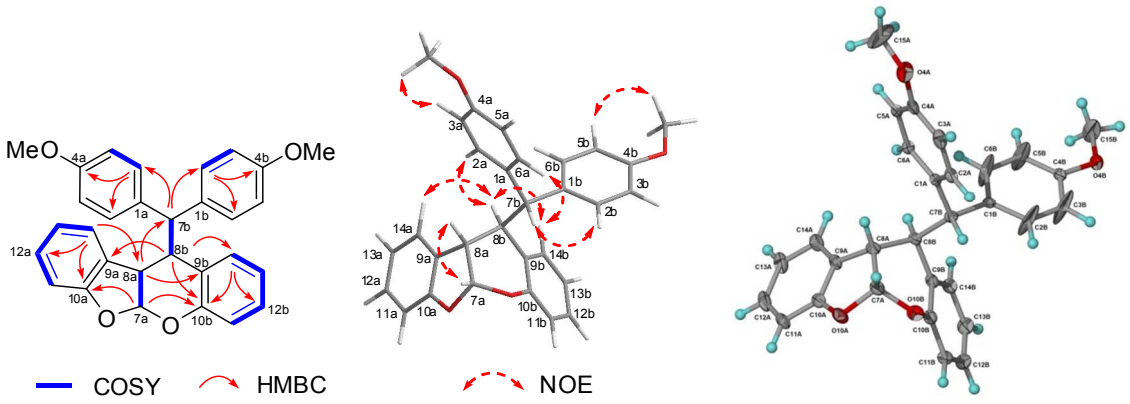


Figure 5. COSY, selected HMBCs, selected NOEs, and X-ray crystal structure of **1e**

We next investigated the anodic oxidation of the TMS protected 4-methoxy-2'-hydroxystilbene **2**. The results showed that the same four products (**1a**, **1b**, **1c**, **1d**) were

obtained and although there were minor variations in the product distribution, the overall yield was essentially unchanged (Scheme 1).

The next compound investigated was 3,4-dimethoxy-2'-hydroxystilbene **3**, which has an additional methoxy substituent at the *meta* position in the *p*-methoxysubstituted ring. In this case, anodic oxidation gave 4 isomeric products, the C_2 symmetric fused bisbenzopyran **3a** (analogous to **1a**), the C_2 symmetric bisbenzofuran **3c** (analogous to **1c**), another symmetric bisbenzofuran **3d**, and the bridged oxocine **3f** (Scheme 2). The structures of **3a** and **3c** were readily assigned based on their ^{1}H and $^{13}C\{^{1}H\}$ NMR data and by analogy to **1a** and **1c**, respectively (which have been thoroughly characterized by MS, NMR, and X-ray diffraction analysis, vide supra; structure of **3a** was also confirmed by X-ray analysis).

Compound **3d** ($C_{32}H_{30}O_6$) was a symmetric bisbenzofuran as indicated by the MS and NMR data. For the bisbenzofurans, there are a total of eight possible diastereomers (after discounting enantiomeric partners). Of these, there are four symmetric and four non-symmetric stereoisomers. Of the symmetric arrangements, two have C_2 axis and two are *meso* structures characterized by the presence of a mirror plane σ. Compound **3c** (C_2) showed the presence of two enantiomers on chiral phase HPLC analysis. Compound **3d** on the other hand showed only one peak on chiral phase HPLC analysis (tested on two different chiral stationary phases). Compound **3d** must therefore correspond to either one of two *meso* bisbenzofurans (**3d** and **3d'**, Figure 6). Examination of models showed that **3d'** with an all *cis* configuration of the methine hydrogens should suffer from appreciable steric congestion (hence less stable) compared to **3d** (**3d** is estimated to be more stable than **3d'** by *ca.* 14.74 kcal mol^{-1}, see supporting information). The structure of this

compound is probably **3d**, which received further confirmation by analogy to the corresponding nitrogen analogue (**6d**, *vide infra*) whose structure was verified by X-ray analysis (Figure 6).[12]

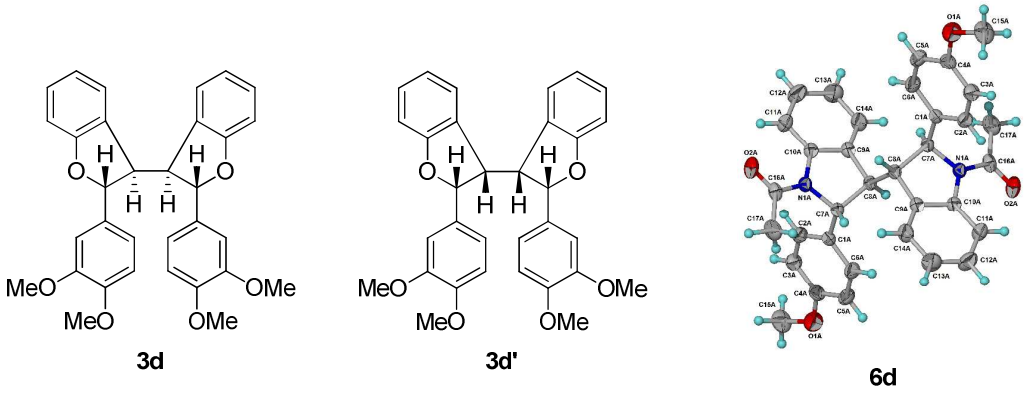


Figure 6. Structures of **3d, 3d′**, and X-ray crystal structure of **6d**

HRMS measurements of compound **3f** established the molecular formula as $C_{32}H_{30}O_6$, indicating that it is isomeric with compounds **3a**, **3c** and **3d**. The ^{1}H NMR spectrum showed the presence of 13 aromatic resonances, four methoxy groups, four methine protons (δ 5.60, 4.48, 3.81, 3.35) and an OH group (δ 5.40, exchanged with D_2O). The low field resonance at δ 5.60 (δ_C 73.5) was due to an oxymethine (H-7a), while the resonance at δ 4.48 (δ_C 56.1) can be attributed the doubly benzylic H-7b by analogy to H-7b in compound **1e**. The COSY spectrum (Figure 7) showed the presence of an OCH–CH–CH–CH fragment, corresponding to C-7a–C-8a–C-8b–C-7b, based on the observed three bond correlations from H-7b to C-8a and from H-8b to C-7a in the HMBC spectrum (Figure 7). In addition, the ^{1}H NMR spectrum of **3f** showed two of the aromatic hydrogens of one ring as singlets (H-2a, δ 6.99; H-5a, δ 6.43), indicating that one aromatic moiety was 1,2,4,5-tetrasubstituted. The observed three-bond correlations (^3J)

for H-7a/C-2a, C-6a and H-7b/C-1a, C-5a, in the HMBC spectrum indicated the attachment of C-7a to the aromatic C-1a, and C-7b to C-6a. This accounted for the 1,2-substitution of a 4,5-dimethoxyaryl moiety by the four-carbon CHCHCHCH unit. The HMBC data (Figure 7) also showed that the oxygen linked to C-7a is attached to the aromatic C-10b (^3J for H-7a/ C-10b), while the adjacent aromatic C-9b is linked to the methine C-8b (^3J for H-8b/C-10b, H-14b/ C-8b), thus forging the bridged oxocine core. Attachment of the remaining aryl units at C-7b (^3J for H-7b/C-6b, H-2b/C-7b) and C-8a (^3J for H-14a/C-8a) completed the assembly of the structure of **3f**, which was also consistent with the NOE data. In addition, the IR spectrum of **3f** showed a sharp band due to an OH function at 3441 cm^{-1} indicating the presence of a free OH that remained intact throughout the reaction.

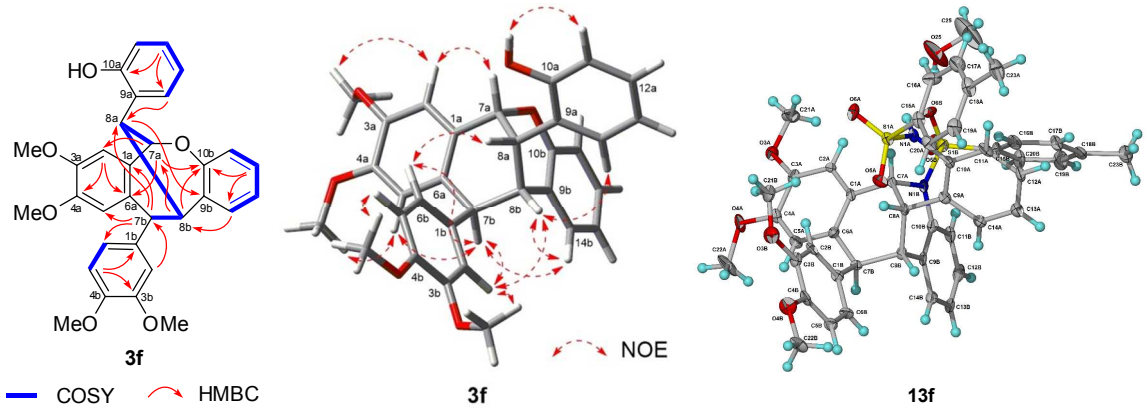


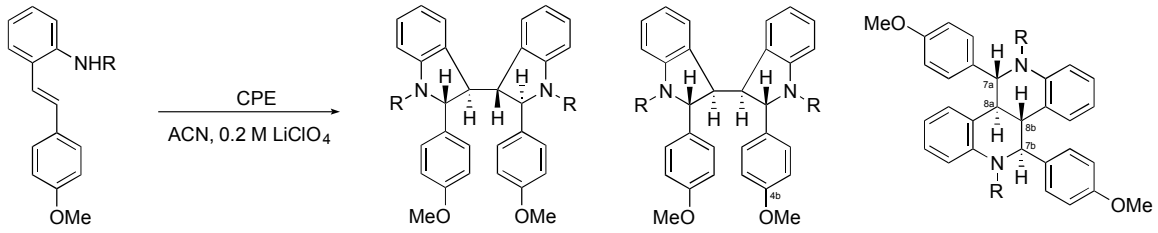
Figure 7. COSY, selected HMBCs, and selected NOEs of **3f**, and X-ray crystal structure of **13f**

Of the four stereogenic centers in **3f**, the relative configurations of two, C-7a and C-8b, are fixed by the geometry of their attachment to the methine bridge (C-8a). The NOEs observed for H-6b/H-8a required H-8a to be directed towards ring A, while the substitution of ring A' at C-7b is deduced to be β from the observed H-6b/H-8a and H-

7b/H-14b NOEs. Attempts to obtain suitable crystals of **3f** and its derivatives (tosylate, acetate, *p*-bromobenzoate; see Supporting Information) were singularly unsuccessful. However, the nitrogen analogue of **3f** (**13f**) furnished suitable crystals, which allowed X-ray analysis to be carried out (Figure 7), providing verification of the structure of **13f** and support for the structure proposed for **3f**.

We next investigated the effect of an *ortho*-substituted amino group. Anodic oxidation of 4-methoxy-2'-aminostilbene **5** was unsuccessful due to significant electrode fouling which was not unanticipated in the light of our previous experience.[6,7] Anodic oxidation of the *N*-acetylated derivative **6** gave two dimeric products in total yield of *ca*. 40%: the C_2 symmetric bisindole **6c** (35%) and the *meso* bisindole **6d** (6%) (Scheme 3). The structure of **6c** can be assigned based on their MS and NMR data and by analogy to **1c** and **9c** (X-ray structures available for both), while the structure of **6d** was confirmed by X-ray analysis (Figure 6).[12] A bisindole was previously reported in an $FeCl_3$ mediated oxidation of the *o*-acetamidostilbene **6**, which was assigned the structure **6d**.[13a] Based on the present results however, the previous assignment requires amendment as the bisindole reported does not correspond to **6d** but to **6c**.

Scheme 3. Products from the anodic oxidation of stilbenes **6**–**8**



6 R = Ac	R = Ac Total = 41%	**6c** 35%	**6d** 6%	
7 R = Boc	R = H Total = 35%	**7c** 23%		**7g** 12%
8 R = CO_2Me	R = CO_2Me Total = 79%	**8c** 57%		**8g** 22%

Since only a moderate yield was obtained for the acetylated derivative, it was of interest to investigate the dependence of both the product distribution and the yields on the nature of the protecting group. Anodic oxidation of the *N*-Boc derivative **7** gave two products in combined yield of only 35%, viz., the C_2 symmetric bisindole **7c** (23%) and the symmetric fused bisquinoline **7g** (12%) (Scheme 3). In this instance both products have lost their respective protecting groups during electrolysis and a substantial quantity (*ca*. 40%) of deprotected starting material was also recovered. The fused bisquinoline structure of **7g** was indicated by the characteristic carbon shifts of the non-aromatic carbons (C-7a, C-8a), which were different from those of the bisindoles, corresponding to quinoline as opposed to indoline units (Figure 8). The ^{1}H NMR spectrum showed resonances due to only one half of the molecule, including a pair of doublet of doublets at δ 4.60 (H-7a) and 3.39 (H-8a) with J = 6.9, 2.8 Hz (attributed to a pair of mutually coupled methine hydrogens), in addition to the aromatic and methoxy resonances. The NMR data other than indicating the presence of an element of symmetry was insufficient for complete stereochemical assignment of the structure of this bisquinolinic compound.

In view of this finding, as well as the poor yields obtained for the *N*-Boc derivative, we next investigated the oxidation of the carbamate **8**. Anodic oxidation proceeded smoothly in this case and gave a mixture of products comprising the bisindole **8c** (57%) and the fused bisquinoline **8g** (22%) in combined yield of ca. 80% (Scheme 3). In this case, the bisquinoline **8g** provided suitable crystals for X-ray analysis (Figure 8), which confirmed its structure as well as that for the previous amide analog **7g**. The X-ray structure also showed that the element of symmetry present in **7g** and **8g** was a center of inversion (*i*).

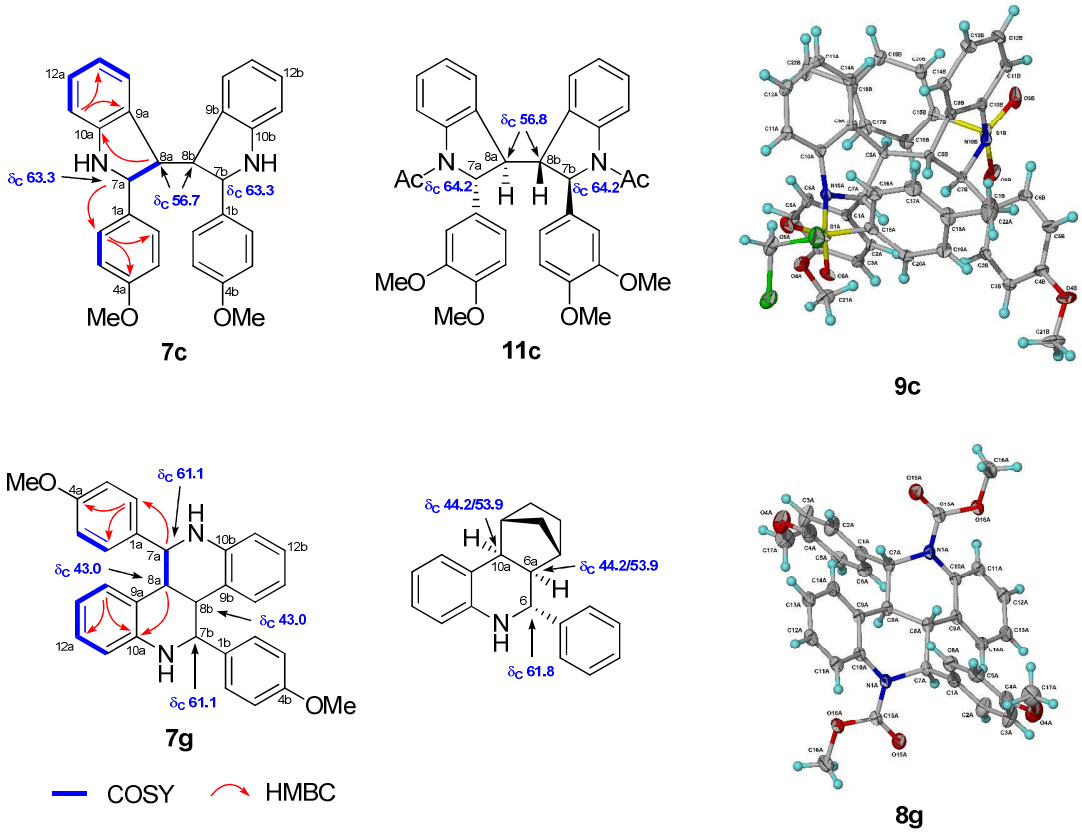
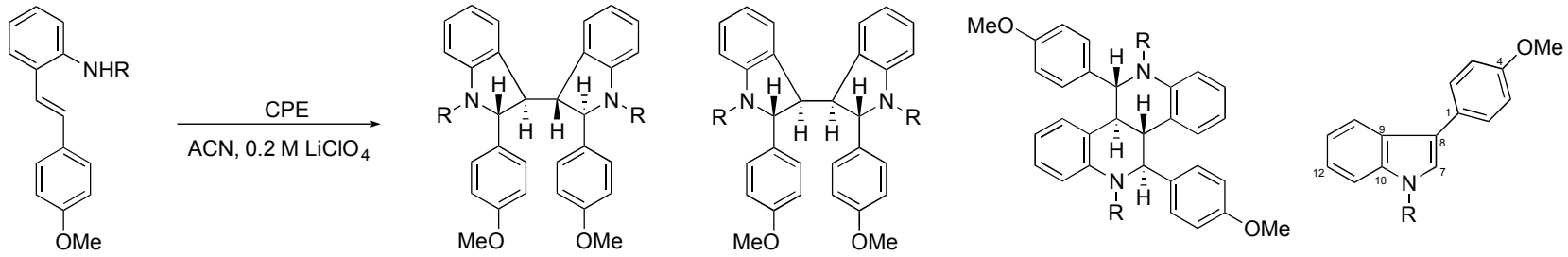


Figure 8. COSY, selected HMBCs of **7c** and **7g**, comparison of the $^{13}C\{^{1}H\}$ shifts of the α and β methine carbons with model bisindole[13b] and quinoline[14] and X-ray crystal structures of **9c** and **8g**

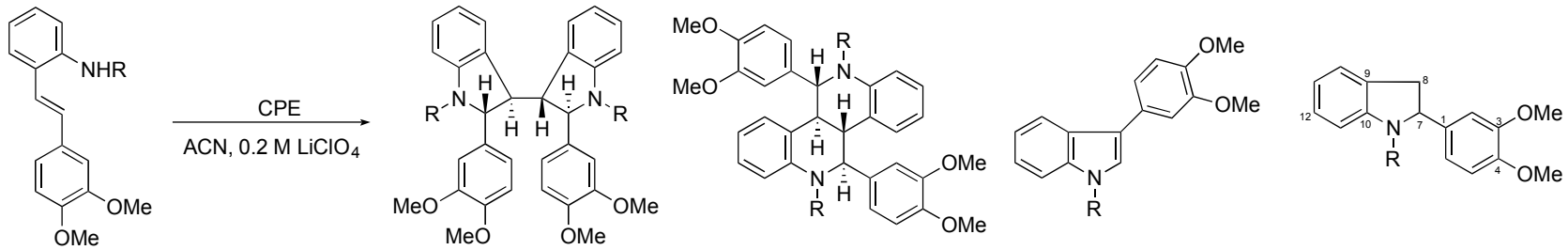
Anodic oxidation of the *N*-tosyl aminostilbene **9** gave a mixture comprising the bisindole **9c** (52%) and the fused bisquinoline **9g** (25%). In addition, the rearranged monomeric indole **9h** was also isolated as a minor product (6%) (Scheme 4). X-ray structures were available for both **9c** (Figure 8) and **9g**. In the case of the *N*-nosyl protected stilbene, anodic oxidation gave the symmetric bisindoles **10c** (C_2, 49%) and **10d** (σ, 21%), the symmetric fused bisquinoline **10g** (*i*, 13%), and a trace of the monomer, **10h** (Scheme 4). X-ray structure was available for **10g**.

Scheme 4. Products from the anodic oxidation of stilbenes **9** and **10**



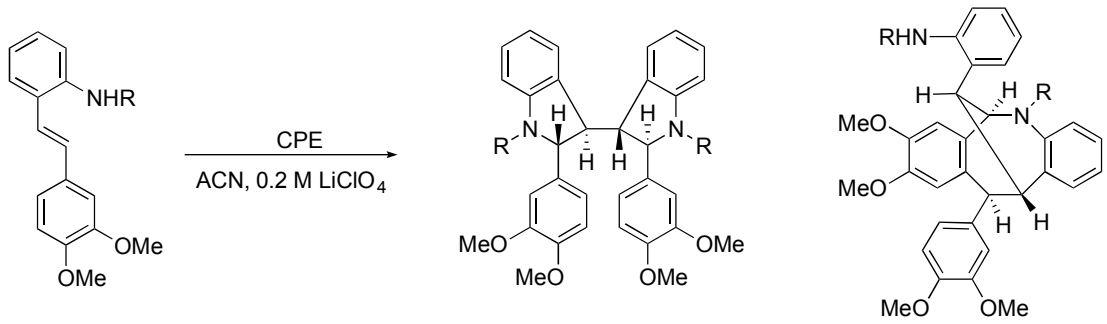
9 R = Ts	R = Ts Total = 83%	**9c** 52%	**9d** trace	**9g** 25%	**9h** 6%
10 R = Ns	R = Ns Total = 83%	**10c** 49%	**10d** 21%	**10g** 13%	**10h** trace

Scheme 5. Products from the anodic oxidation of stilbenes **11** and **12**



11 R = Ac	R = Ac Total = 39%	**11c** 27%			**11i** 12%
12 R = CO_2Me	R = CO_2Me Total = 73%	**12c** 67%	**12g** 5%	**12h** 1%	

Scheme 6. Products from the anodic oxidation of stilbenes **13** and **14**



13 R = Ts	R = Ts Total = 70%	**13c** 54%	**13f** 16%
14 R = Ns	R = Ns Total = 70%	**14c** 61%	**14f** 9%

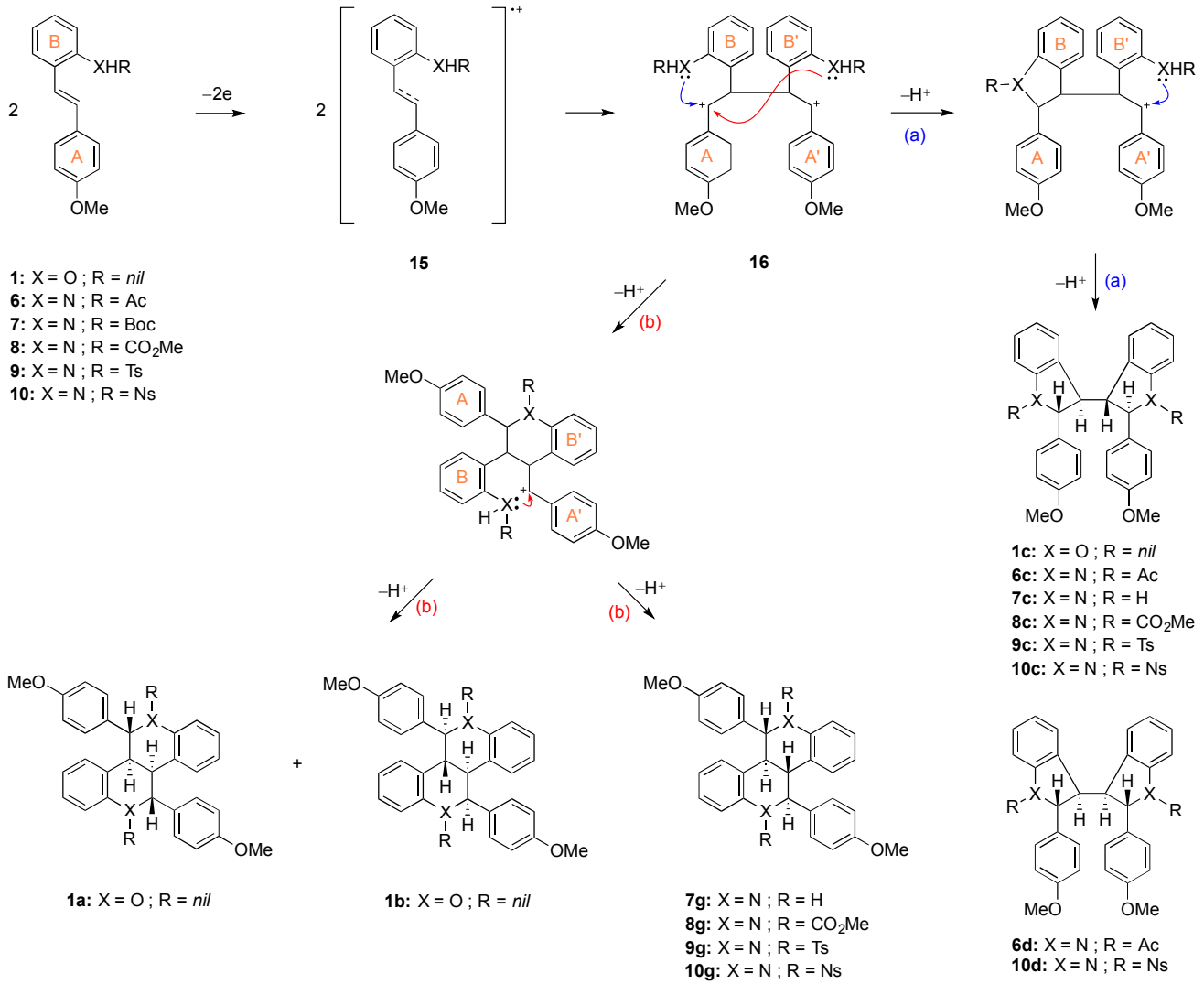
In the case of the 3,4-dimethoxsubstituted aminostilbenes, some variation in the product type and distribution were noted. The acetylated derivative **11** gave only the bisindole **11c** and the monomeric indole **11i** in a total yield of only 39% (Scheme 5). In an earlier study of $FeCl_3$-promoted oxidation of *o*-amidostilbenes, bisindole **11c** and dihydroindole **11i** were also obtained for the reaction of the *o*-acetamidostilbene **11**.[13b,c] As before, in view of the poor yields for the acetylated derivative, anodic oxidation of the carbamate derivative **12** was next attempted which gave the bisindole **12c** as the major product in 67% yield, the bisquinoline **12g** (5%), and the rearranged monomeric indole **12h** as a very minor product (1%) (Scheme 5). The tosyl and nosyl derivatives **13** and **14,** respectively, gave only two products, the bisindoles **13c** and **14c**, and the bridged azocines **13f** and **14f** (Scheme 6). The structures of **12c**, **12g** (Figure 8), **13c**, and **13f** (Figure 7) were also confirmed by X-ray analysis. The X-ray structure of the azocine **13f** provides additional support for the structure proposed for the oxocine analogue, **3f** (vide supra). The products for the oxidation of stilbenes **1**-**14** are summarized in Table 1.

Table 1. Products from the anodic oxidation of stilbenes (**1**–**14**)[a]

Entry	Stilbene	% Yield									
		a (*threo*)	**b** (*meso*)	**g** (*meso*)	**c** (*threo*)	**d** (*meso*)	**e** (*meso*)	**f** (*meso*)	**h**	**i**	Total
1	**1**	**1a** 25	**1b** 14		**1c** 19		**1e** 22				80
2	**2**	**1a** 27	**1b** 15		**1c** 20		**1e** 20				82
3	**3**	**3a** 21			**3c** 17	**3d** 18		**3f** 32			88
4	**4**	**3a** 19			**3c** 18	**3d** 18		**3f** 30			85
5	**6**[b]				**6c** 35	**6d** 6					41
6	**7**[c]			**7g** 12	**7c** 23						35
7	**8**			**8g** 22	**8c** 57						79
8	**9**[d]			**9g** 25	**9c** 52				**9h** 6		83
9	**10**[b]			**10g** 13	**10c** 49	**10d** 21					83
10	**11**				**11c** 27					**11i** 12	39
11	**12**			**12g** 5	**12c** 67				**12h** 1		73
12	**13**				**13c** 54			**13f** 16			70
13	**14**				**14c** 61			**14f** 9			70

[a]Pt anode, Pt cathode, versus $Ag/AgNO_3$ in MeCN/0.2 M $LiClO_4$, [b]Traces of monomer (**6i** and **10h**) observed in NMR spectra of product mixtures. [c]Yield based on stilbene reacted, reaction accompanied by recovery of ca. 35% of the deprotected stilbene **7**. [d]Traces of *meso* bisindole **9d** observed in NMR spectra of product mixtures.

Scheme 7. Proposed mechanism for the formation of products in the anodic oxidation of stilbenes (**1**, **6**–**10**) in MeCN/$LiClO_4$



The current investigation was carried out to address several questions regarding stilbene cation radical reactivity. First, will the proximate *ortho*-substituted nucleophilic groups (OH, NH_2) engage the cation radical in an intramolecular reaction? Second, if intramolecular cation trapping occurs, does it precede bimolecular dimerization of the first formed cation radical, or does trapping by the internal nucleophile take place subsequent to cation radical dimerization? Additionally, can 'crossover trapping' occur to provide six-membered ring products (pyrans/quinolines) in addition to five-membered ring products (furans/indoles) from direct trapping? The formation of the fused bisbenzopyrans/ bisquinolines (a result of crossover trapping), in addition to the bisbenzofurans/bisindoles clearly showed that the *ortho*-substituted OH (and NHR) groups do react with cationic groups, and that such engagements occur subsequent to cation radical dimerization. We propose the following mechanism to rationalize the formation of the products in the oxidation of the 4-methoxy-2'-hydroxy(or 2'-amino)stilbenes, **1**, **2**, **6–10**.

One-electron oxidation of the starting stilbene gave the cation radical **15**, which under the conditions of preparative electrolysis undergoes facile cation radical dimerization to give the dicationic intermediate **16** as the dominant step, as demonstrated by previous studies.[7] Formation of the fused bisbenzopyrans (**1a**, **1b**) or bisquinolines (**7g**–**10g**) is a result of "crossover trapping" by the *ortho*-substituted nucleophiles, i.e., *o*-OH (or *o*-NHR) in ring B of one stilbene half attacks the benzylic cation associated with ring A' of the other stilbene half, while, *o*-OH (or *o*-NHR) in ring B' attacks the benzylic cation of ring A (Scheme 7, path b). On the other hand, the formation of the bisbenzofuran (**1c**) or bisindoles (**6c**–**10c**, **6d**, **10d**) is a consequence of the respective

direct trapping of the cation by the *ortho*-substituted nucleophiles belonging to the same stilbene half, i.e., *o*-OH (or *o*-NHR) belonging to ring B of one stilbene half reacts with the benzylic cation of ring A of the same stilbene half, while, *o*-OH (or *o*-NHR) in ring B' reacts with the benzylic cation of ring A', as shown in Scheme 7, path a. The occurrence of crossover trapping represents firm evidence for intramolecular cation trapping by the internal nucleophile taking place subsequent to cation radical dimerization.

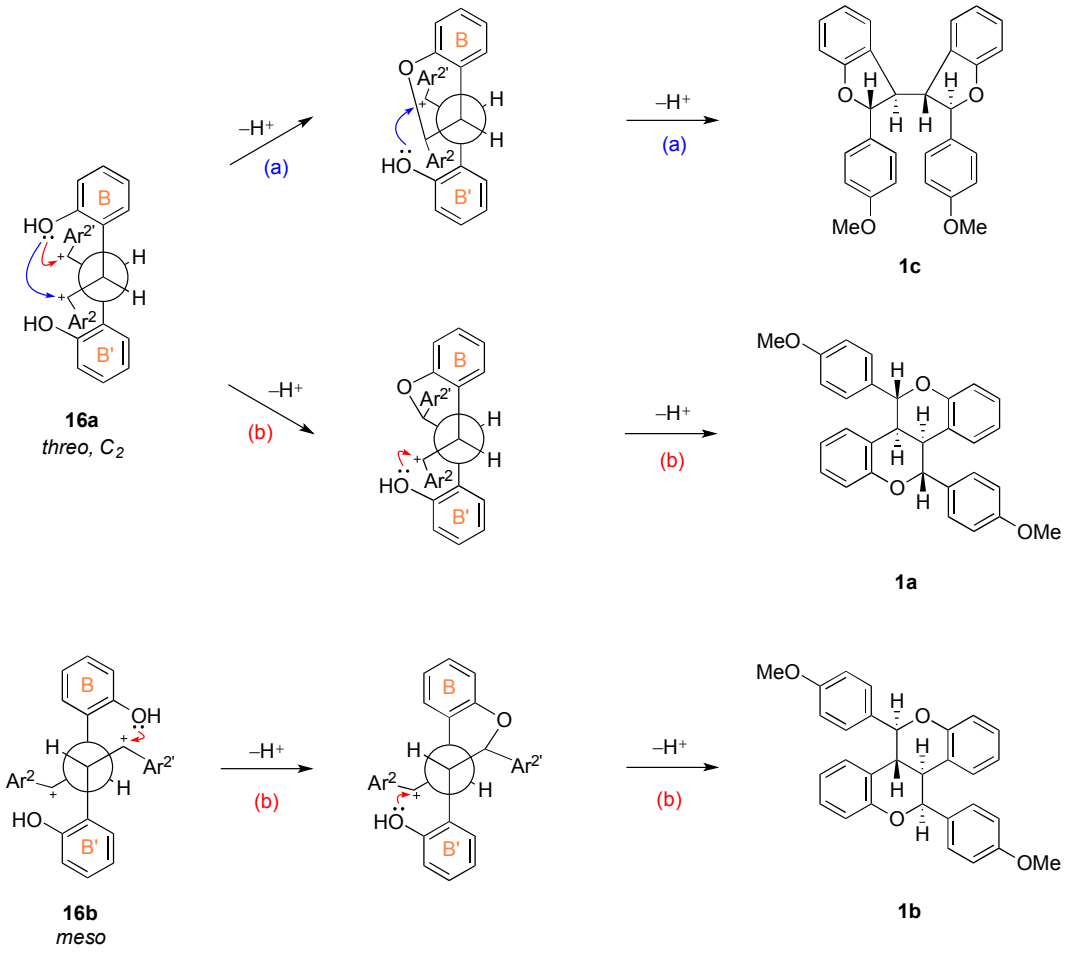
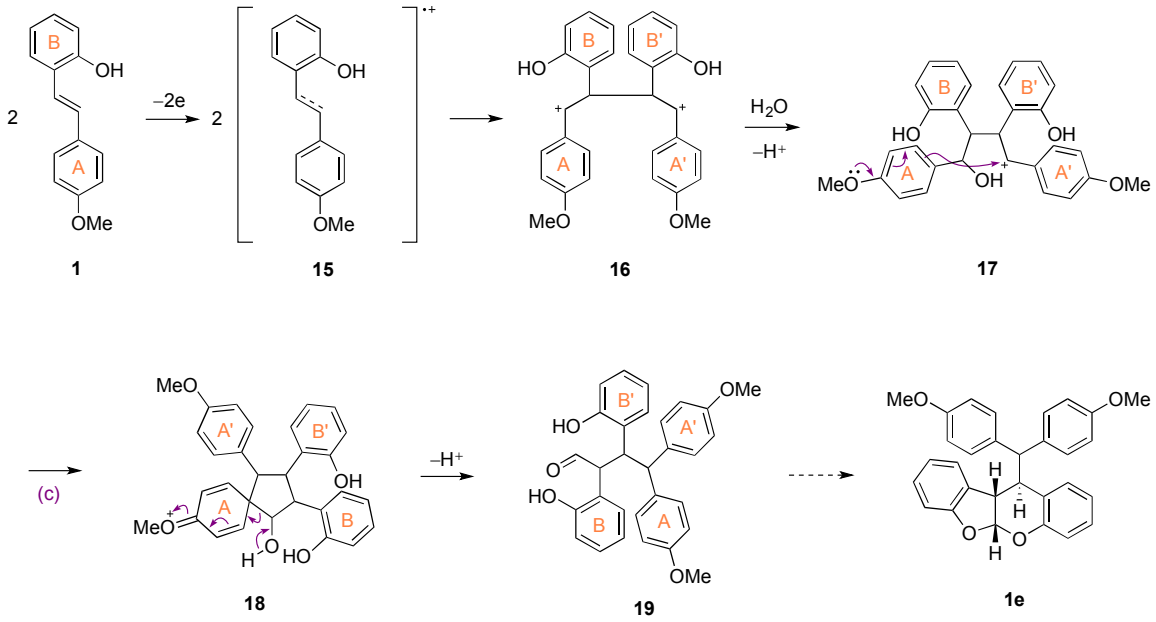


Figure 9. Origin of the fused benzopyrans **1a**, **1b**, and bisbenzofuran **1c** from the *threo* and *meso* dications

There are two possible modes for the initial cation radical coupling to give the dication **16**, from which all the products are derived.[7] The two regioisomers **1a** and **1c** formed in the oxidation of **1** originate from the *threo*-dication **16a**, which is characterized by the presence of a C_2 axis. On the other hand, the fused benzopyran **1b** originates from the *meso*-dication **16b**, as shown in Figure 9. The origin of the various products from the corresponding *threo*- or *meso*-dications is also given in Table 1.

The fused benzofurano-benzopyran **1e** formed in the anodic oxidation of stilbene **1**, appeared at first sight to be an unusual product. It possesses an acetal function shared between two rings and in addition showed evidence of aryl migration, features which had been noted previously.[7] Interception of the dicationic intermediate **16** by water gives cation **17** which then forms the spirocyclic carbocation intermediate **18**, as shown in Scheme 8, path c. The formation of such spirocationic intermediates has been postulated previously by Hong in the anodic oxidation of substituted stilbenes,[7] and is assisted by the *p*-OMe substituent in ring A. Subsequent ring opening, leads to the aldehyde **19** which upon intramolecular acetalization via attack by the *ortho*-OH groups in rings B and B' furnishes the cyclic acetal **1e**, as shown in Scheme 8. The formation of this acetal product (**1e**) and its purported origin suggest that not all of the dicationic intermediate in this case is trapped by the internal nucleophile. A portion is diverted by intermolecular capture leading eventually to the acetal product **1e**.

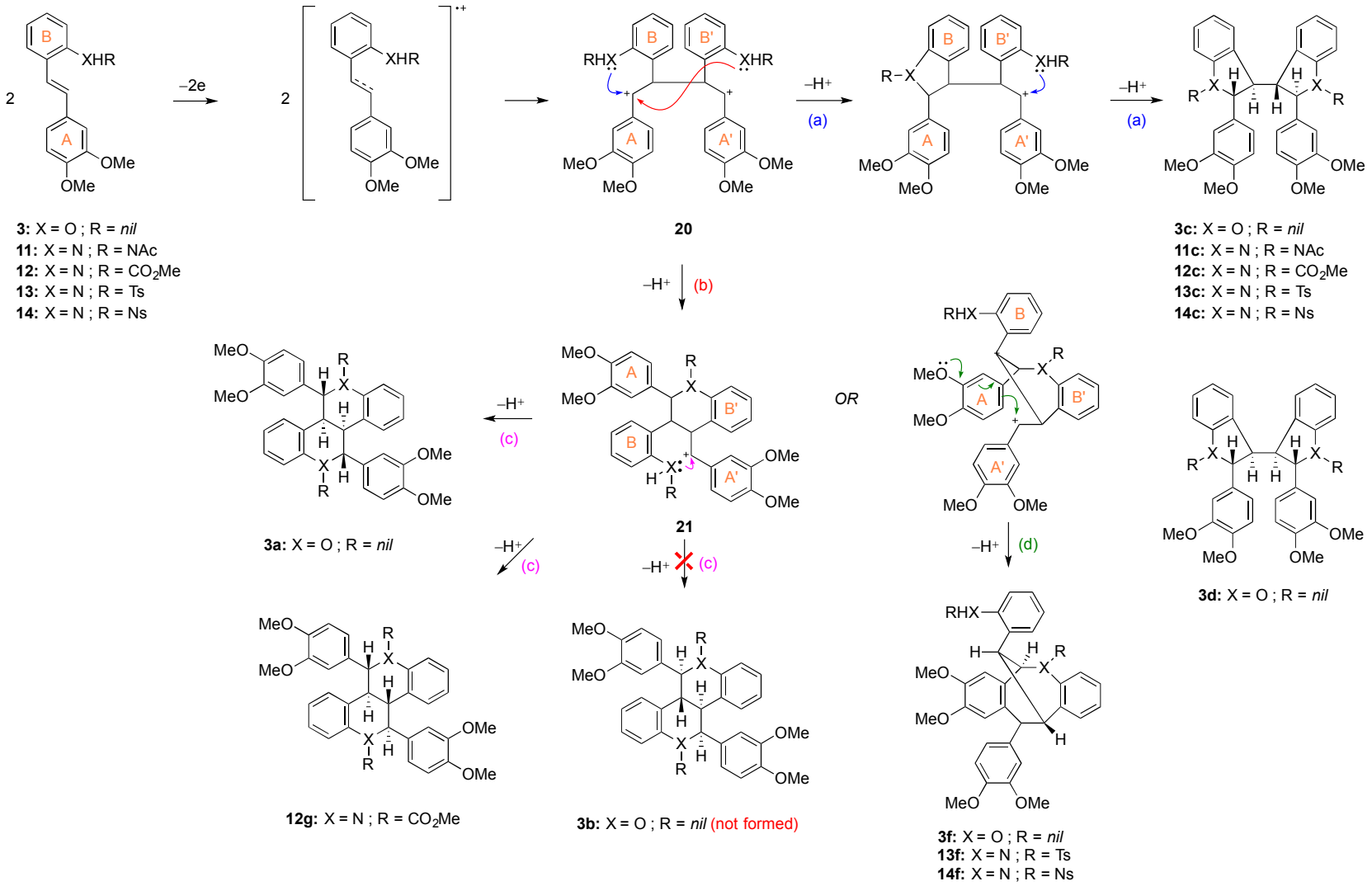
Scheme 8. Proposed mechanism for the formation of **1e** in the anodic oxidation of **1** in $MeCN/LiClO_4$



Anodic oxidation of the 3,4-dimethoxysubstituted 2'-hydroxystilbene **3** (and the corresponding aminostilbenes **11**–**14**) were also investigated, since it has been shown in the previous study that the presence of a *m*-methoxy group in addition to a *p*-methoxy substituent, enhances the nucleophilicity of the aromatic carbon *para* to the *m*-OMe group (C-6), and this had an effect on the product distribution.[7] Indeed, oxidation of **3** (as a representative example) gave in addition to the expected bisbenzopyran **3a**, bisbenzofurans **3c** and **3d**, the unexpected bridged oxocine **3f**. The latter product was formed as a result of 3,4-dimethoxy substitution in the starting 2'-hydroxystilbene and was also obtained in the oxidation of the corresponding 3,4-dimethoxy-, tosyl- and nosyl-protected 2'-amino analogues, **13** and **14**, respectively. We propose the following mechanism (Scheme 9) to rationalize the formation of these products. Direct trapping of

the dication **20** from the initial cation radical dimerization leads to the isomeric fused bisbenzofurans **3c** and **3d**. Two successive crossover trapping reactions lead to the formation of one of the expected bisbenzopyrans, **3a**. The other bisbenzopyran **3b** however was not formed, instead the bridged oxocine was isolated in 32% yield. The cationic intermediate **21** formed after the first crossover trapping instead of undergoing a second crossover trapping to **3b**, undergoes electrophilic substitution (Friedel-Crafts alkylation) via attack of the benzylic cation (associated with ring A') on the activated C-6 of ring A.[7,15] This aromatic substitution is facilitated by the activation of ring A due to the appropriately placed *m*-OMe group, and as a result is able to compete favorably with the second crossover trapping by *o*-OH.

Scheme 9. Proposed mechanism for the formation of products in the anodic oxidation of stilbenes (**3**, **11**–**14**) in MeCN/$LiClO_4$

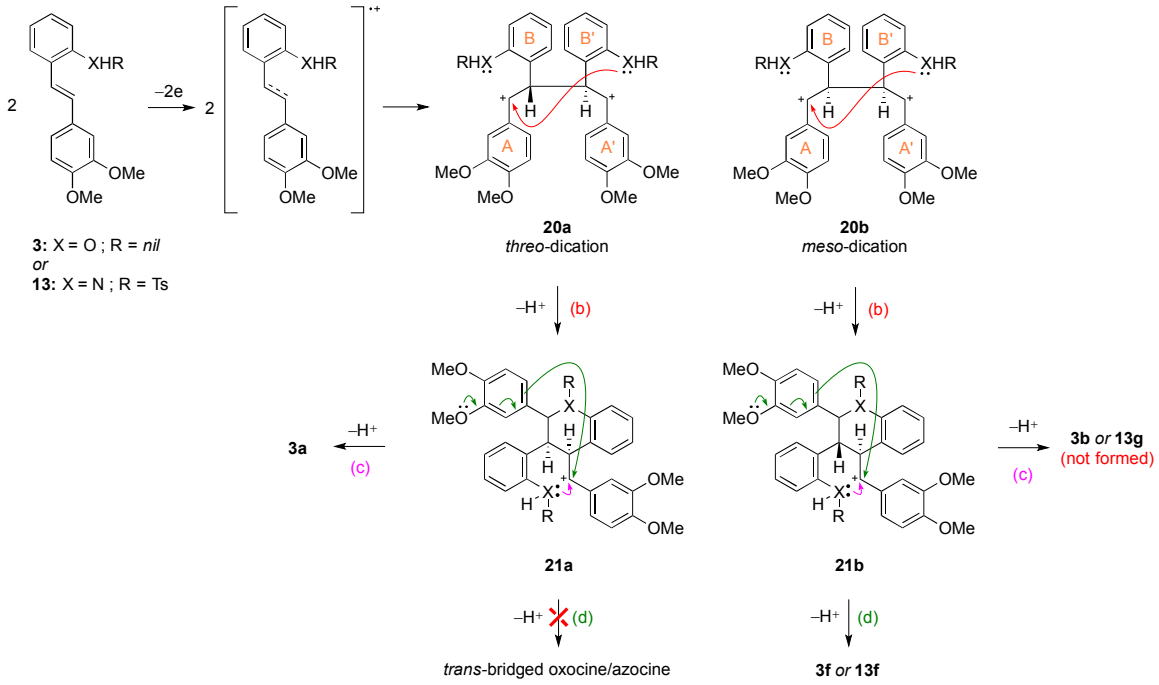


Arising from the above, a pertinent question is why **3a** was formed while **3b** was not, instead the oxocine **3f** was formed in its place, and not *vice versa* (i.e., formation of **3b** and the corresponding oxocine in place of **3a**). The bisbenzopyrans **3a** and **3b** originate from different dications arising from the initial cation radical coupling. Bisbenzopyran **3a** results from two successive crossover trapping reactions from the *threo*-dication. Bisbenzopyran **3b** on the other hand is a result of two successive crossover trapping reactions from the *meso*-dication (Scheme 10). Examination of models showed that while the second crossover reaction from the cationic intermediate **21b** (from the *meso*-dication) to give **3b** is feasible, the alternative electrophilic substitution reaction was able to compete effectively, resulting instead in the formation of the bridged oxocine product at the expense of **3b**. In the case of the cation **21a** (from the *threo*-dication), examination of models showed that while a second cyclization from **21a** to **3a** is feasible, the alternative aromatic substitution to the bridged oxocine product is highly unlikely for geometric reasons, as it will result in formation of a *trans*-bridged oxocine. A similar explanation applies in the case of the *ortho*-NHR-substituted dimethoxystilbenes (e.g., **13** and **14** in Scheme 10).[16]

Another difference in the oxidation of **1** versus **3** was the absence of the acetal product (analogous to **1e**) in the reaction of the 3,4-dimethoxy-substituted stilbene **3**. A possible explanation for this is that activation of the aromatic ring A (at C-6) towards aromatic substitution by the 3-OMe group has resulted in intramolecular pathways being overwhelmingly favored over competing intermolecular reactions. The same difference was noted when comparing the results for the reactions of the *o*-aminostilbenes (**6**–**10**) *versus* the reaction of the *o*-hydroxystilbene **1**, where the amino acetal (or aminal)

analogue of **1e** was not detected among the products in the reactions of **6**–**10**, which may be attributed to the greater nucleophilicity of nitrogen versus oxygen, resulting in the predominance of the more facile intramolecular reactions over competing intermolecular pathways.

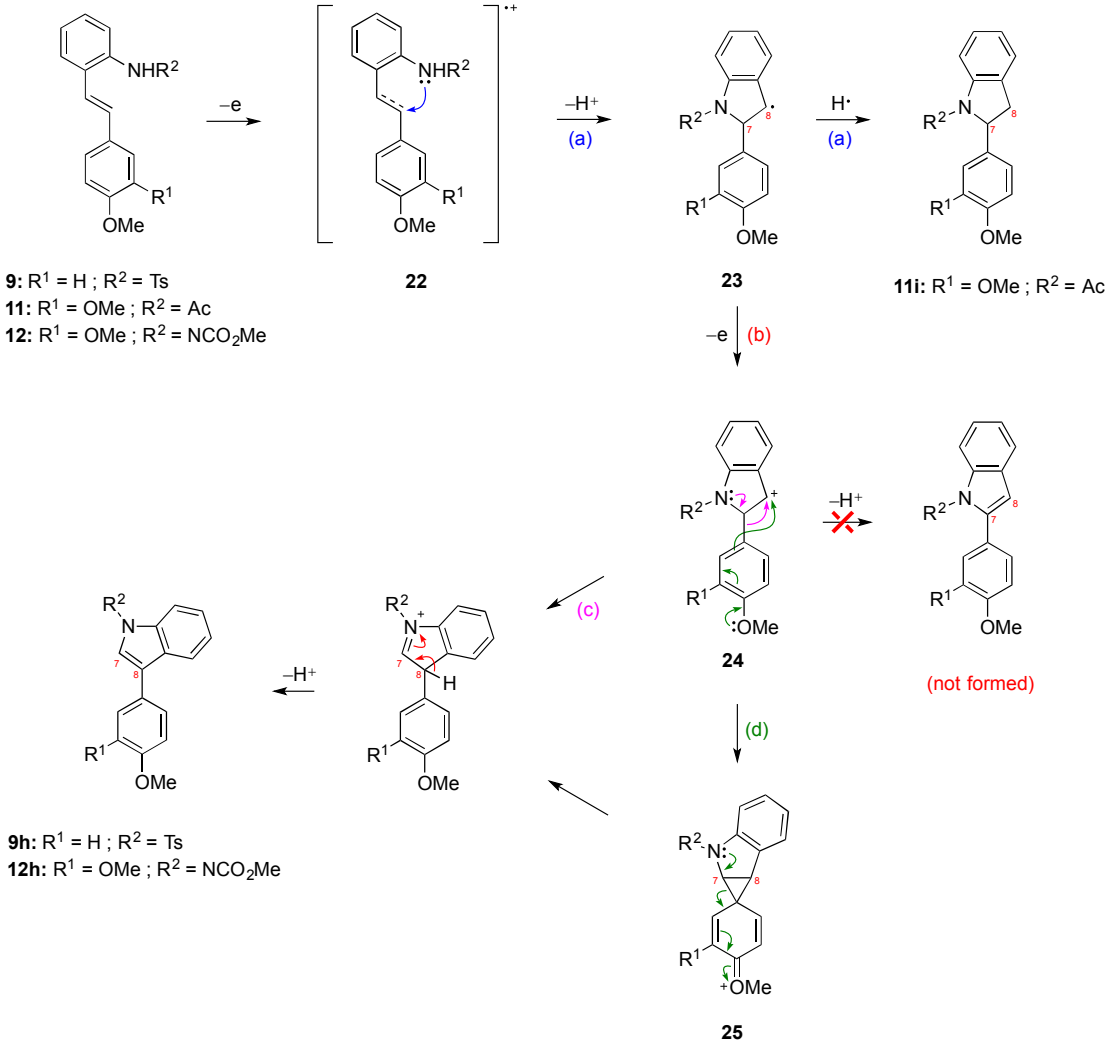
Scheme 10. Pathway showing the formation of **3a** and **3f** (or **13f**) instead of **3b** (or **13g**) and the *trans*-bridged oxocine/azocine



Another difference when comparing the products of the *ortho'*-OH- *versus* those of the *ortho'*-NHR-substituted 4-methoxystilbenes (for which we were unable to formulate a convincing explanation), was the formation of the crossover trapping derived bisquinolines of the **g** series (from the *meso*-dication, and characterized by presence of a center of inversion, *i*) for the *ortho'*-NHR-substituted stilbenes, whereas this type of

product was absent for the reaction of the *ortho'*-OH-substituted stilbenes, where *meso*-dication derived crossover bisbenzopyran products of the **b** type were formed instead.[17]

Scheme 11. Proposed mechanism for the formation of the rearranged monomeric indoles **9h**, **12h** and dihydroindole **11i**



The monomeric indoles (**9h**, **12h**) and dihydroindole (**11i**) were minor products and were detected only in the oxidation of the *ortho*-amino substrates (**9**, **11**, **12**). Their

formation is shown in Scheme 11. The rearranged structure of the indoles **9h** and **12h** *versus* the non-rearranged structure for the dihydroindole **11i** was not immediately apparent on a cursory inspection of the NMR data. Examination of the HMBC data however showed that the correct structure of the indoles correspond to **9h** and **12h**, while that of the dihydroindole to **11i**. The dihydroindole (**11i**) derives from hydrogen abstraction by the radical **23** formed after direct trapping of the cation radical **22**, and subsequent deprotonation (path a). The rearranged indoles (**9h** and **12h**) can be rationalized by two alternative pathways, either via a lone-pair assisted 1,2-aryl shift of the cation **24**, followed by deprotonation (Scheme 11, path c), or via involvement of the phenonium ion intermediate **25** (Scheme 11, path d).

In conclusion, the above study has provided further clarification on the reactivity of anodically-generated 4-methoxy and 3,4-dimethoxy stilbene cation radicals. Where *ortho*-substituted nucleophilic groups such as OH or NHR are present in the other ring, both direct and crossover intramolecular cation-nucleophile reactions occur to give bisbenzofurans/bisindoles or bisbenzopyrans/bisquinolines, respectively. Where an additional 3-methoxy substituent is present, the bridged oxocine/azocine products are formed in addition to the bisbenzopyrans and bisbenzofurans/bisindoles. Compounds possessing these structural motifs are of relevance in natural products as well as organic synthesis.[18] The observed behavior is consistent with a generalized pathway involving fast cation radical dimerization following electron transfer, followed by direct and crossover trapping of the benzylic cations by the *ortho*-substituted oxygen and nitrogen nucleophilic groups. In the instances where an additional 3-methoxy group is present, the

bridged oxocine/azocine products were also formed as a result of competing aromatic substitution (Friedel-Crafts alkylation).

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, 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). All reactions were carried out under Ar or N_2, in oven-dried glasswares. 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 Stilbenes 1, 3, 5, 7, and (*E*)-3,4-dimethoxy-2'-aminostilbene (Heck Coupling).[7,9] Aryl halide (0.22 mmol) was added to a flask containing a mixture of $Pd_2(dba)_3$ (2.7 mg, 0.003 mmol) and $Pd(t\text{-}Bu_3P)_2$ (3.1 mg, 0.006 mmol). The corresponding styrene (0.2 mmol), triethylamine (42 μL, 0.3 mmol), and dioxane (4 mL)

were then added to the mixture. The reaction mixture was microwave irradiated (with the heating program starting at 120 W) at 120 °C for 30–60 min. The mixture was then filtered through a pad of silica gel, washed with 5% HCl (3 × 20 mL), extracted with CH_2Cl_2 (3 × 20 mL), washed with H_2O (3 × 20 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The resulting residue was purified by preparative radial chromatography over SiO_2 to yield the corresponding stilbenes.

Microwave Irradiation Experiments. All microwave irradiation experiments were carried out in a Discover SP microwave synthesizer (CEM Corporation). The reactions were carried out in heavy-walled Pyrex tubes (10 or 35 mL) equipped with a small magnetic stir bar and sealed with silicon caps fitted with a Teflon septum. The Pyrex tubes, magnetic stir bar, and silicon caps were obtained from CEM Corporation. Initially, microwave irradiation of required watts was used (120 W), and the temperature was ramped from room temperature to the desired temperature (120 ^{o}C, measured using a built in vertically focused IR sensor, on the outer surface of the tubes). Once this temperature was reached, the reaction mixture was held at this temperature for the required time (30-60 min). After the irradiation period, gas jet cooling rapidly cooled the reaction vessel to ambient temperature.

Synthesis of Stilbenes 2 and 4 from 1 and 3, respectively.

Hexamethyldisilazane (29 μL, 0.14 mmol) was added dropwise to a solution of the corresponding 2-hydroxystilbene (**1** and **3**, 0.2 mmol) and $LiClO_4$ (10.6 mg, 0.1 mmol) in MeCN (5 ml). The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, the reaction mixture was 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 (Chromatotron) to yield the corresponding stilbene.

Synthesis of Stilbenes 6 and 11 from 5 and 3,4-dimethoxy-2'-aminostilbene, respectively. Triethylamine (67 μL, 0.5 mmol) and acetic anhydride (47 μL, 0.5 mmol) were added dropwise to a solution of the corresponding 2-aminostilbene (**5** and 3,4-dimethoxy-2'-aminostilbene, 0.2 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the corresponding stilbene.

Synthesis of Stilbenes 8 and 12 from 5 and 3,4-dimethoxy-2'-aminostilbene, respectively. K_2CO_3 (0.28g, 2.0 mmol) in THF:H_2O: 3:1 and methyl chloroformate (23 μL, 0.3 mmol) were added dropwise to a solution of the corresponding 2-aminostilbene (**5** and 3,4-dimethoxy-2'-aminostilbene, 0.2 mmol) in CH_2Cl_2 (5 ml). The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the corresponding stilbene.

Synthesis of Stilbenes 9 and 13 from 5 and 3,4-dimethoxy-2'-aminostilbene, respectively. Pyridine (24 μL, 0.3 mmol) and a solution of 4-toluenesulfonyl chloride (57.2 mg, 0.3 mmol) in CH_2Cl_2 (5 ml) were added dropwise to a solution of the

corresponding 2-aminostilbene (**5** and 3,4-dimethoxy-2'-aminostilbene, 0.2 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the corresponding stilbene.

Synthesis of Stilbenes 10 and 14 from 5 and 3,4-dimethoxy-2'-aminostilbene, respectively. Pyridine (24 μL, 0.3 mmol) and a solution of 2-nitrobenzenesulfonyl chloride (66.5mg, 0.3 mmol) in CH_2Cl_2 (5 ml) were added dropwise to a solution of the corresponding 2-aminostilbene (**5** and 3,4-dimethoxy-2'-aminostilbene, 0.2 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the corresponding stilbene.

Synthesis of (*E*)-4-methoxy-2′-acetoxystilbene from 1. Triethylamine (84 μL, 0.6 mmol) and acetic anhydride (57 μL, 0.6 mmol) were added dropwise to a solution of **1** (45.3 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, the reaction was quenched with 5% HCl. The reaction mixture was 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 (Chromatotron) to yield the corresponding stilbene.

*(E)-4-methoxy-2'-hydroxystilbene (**1**)*.[19] Brown solid (38.5 mg, 85%); mp 120–122 ˚C (lit. 117–118 ˚C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83 (3H, s), 5.21 (1H, br s), 6.80 (1H, d, J = 7.6 Hz), 6.89 (2H, d, J = 8.8 Hz), 6.94 (1H, t, J = 7.6 Hz), 7.06 (1H, d, J = 16.4 Hz), 7.12 (1H, td, J = 7.6, 1.5 Hz), 7.22 (1H, d, J = 16.4 Hz), 7.46 (2H, d, J = 8.8 Hz), 7.50 (1H, dd, J = 7.6, 1.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 55.4, 114.2, 116.0, 121.0, 121.1, 125.1, 127.1, 127.8, 128.4, 129.8, 130.5, 153.0, 159.4; ESIMS *m/z* 227 $[M + H]^+$ ($C_{15}H_{14}O_2 + H$).

*(E)-4-methoxy-2'-trimethylsilyloxystilbene (**2**)*. Light yellowish solid (53.1 mg, 89%); mp 68–70 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.33 (9H, s), 3.84 (3H, s), 6.86 (1H, d, J = 8.0 Hz), 6.93 (2H, d, J = 8.8 Hz), 7.00 (1H, t, J = 7.6 Hz), 7.08 (1H, d, J = 16.6 Hz), 7.14 (1H, t, J = 7.6 Hz), 7.30 (1H, d, J = 16.6 Hz), 7.48 (2H, d, J = 8.8 Hz), 7.61 (1H, d, J = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 0.39, 55.2, 114.1, 119.9, 121.7, 121.9, 126.2, 127.5, 128.0, 128.2, 129.1, 130.7, 152.7, 159.1; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_2Si$ 299.1467; Found 299.1469.

*(E)-3,4-dimethoxy-2'-hydroxystilbene (**3**)*.[20] Yellowish oil (46.1 mg, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (3H, s), 3.87 (3H, s), 5.26 (1H, br s), 6.80 (1H, d, J = 7.8 Hz), 6.81 (1H, d, J = 8.2 Hz), 6.91 (1H, t, J = 7.8 Hz), 7.03 (1H, d, J = 8.2 Hz), 7.05 (1H, d, J = 16.5 Hz), 7.08 (1H, s), 7.09 (1H, t, J = 7.8 Hz), 7.28 (1H, d, J = 16.5 Hz), 7.51 (1H, d, J = 7.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 55.9, 56.0, 108.9, 111.3, 116.1, 120.1, 121.0, 121.4, 125.0, 126.9, 128.5, 129.6, 131.1, 148.8, 149.1, 153.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O_3$, 257.1178; Found 257.1173.

*(E)-3,4-dimethoxy-2'-trimethylsilyloxystilbene (**4**)*. Colorless oil (57.2 mg, 87%); mp 73–75 ˚C ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.34 (9H, s), 3.94 (3H, s), 3.97 (3H, s), 6.86 (1H, d, J = 8.0 Hz), 6.90 (1H, d, J = 8.4 Hz), 7.01 (1H, t, J = 8.0 Hz), 7.07 (1H, dd, J = 8.4, 2.0 Hz), 7.08 (1H, d, J = 16.4 Hz), 7.12 (1H, d, J = 2.0 Hz), 7.16 (1H, t, J = 8.0 Hz), 7.31 (1H, d, J = 16.4 Hz), 7.62 (1H, t, J = 8.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 0.4, 55.7, 55.9, 108.6, 111.2, 119.7, 120.0, 121.7, 122.1, 126.1, 128.1, 128.3, 128.9, 131.1, 148.7, 149.1, 152.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}O_3Si$, 329.1573; Found 329.1577.

*(E)-4-methoxy-2'-aminostilbene (**5**)*.[21] Yellowish solid (31.5 mg, 70%); mp 108–110 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83 (3H, s), 6.71 (1H, d, J = 7.8 Hz), 6.81 (1H, t, J = 7.8 Hz), 6.90 (2H, d, J = 8.7 Hz), 6.94 (1H, d, J = 16.0 Hz), 7.03 (1H, d, J = 16.0 Hz), 7.09 (1H, t, J = 7.8 Hz), 7.39 (1H, d, J = 7.8 Hz), 7.45 (2H, d, J = 8.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 55.5, 114.2, 116.3, 119.3, 122.2, 124.3, 127.2, 127.8, 128.4, 130.0, 130.5, 143.9, 159.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO$, 226.1232; Found 226.1235.

*(E)-4-methoxy-2'-acetamidostilbene (**6**)*.[13a] White solid, and subsequently, colorless block crystals from CH_2Cl_2; (37.4 mg, 70%); mp 123–125 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.19 (3H, s), 3.82 (3H, s), 6.89 (2H, d, J = 8.4 Hz), 6.93 (1H, m), 6.98 (1H, d, J = 16.8 Hz), 7.15 (1H, t, J = 8.0 Hz), 7.24 (1H, t, J = 8.0 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.49 (1H, d, J = 8.0 Hz), 7.76 (1H, d, J = 8.0 Hz),; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 24.4, 55.5, 114.3, 121.3, 124,3, 125,7, 126.8, 128.1, 129.9, 130.7, 132.1, 134.5, 159.7, 168.7; ESIMS *m/z* 268 $[M + H]^+$.

*(E)-tert-butyl (2-(4-methoxystyryl)phenyl)carbamate (**7**)*. Yellowish oil, and subsequently, colorless needle crystals from *n*-hexane/CH_2Cl_2; (53.4 mg, 82%); mp 109–111 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.52 (9H, s), 3.83 (3H, s), 6.42 (1H, br s), 6.91 (2H, d, J = 9.1 Hz), 6.92 (1H, d, J = 16.5 Hz), 7.01 (1H, d, J = 16.5 Hz), 7.09 (1H, t, J = 7.8 Hz), 7.25 (1H, t, J = 7.8 Hz), 7.46 (2H, d, J = 9.1 Hz), 7.47 (1H, m), 7.78 (1H, br d, J = 5.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 28.4, 55.5, 80.0, 114.3, 121.5, 124.3, 126.8, 128.0, 128.1, 130.0, 132.0, 135.3, 153.2, 159.7, 178.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}NO_3$, 326.1756; Found 326.1759.

*(E)-methyl (2-(4-methoxystyryl)phenyl)carbamate (**8**)*. Yellowish solid; (48.7 mg, 86%); mp 118–120 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.76 (3H, s), 3.80 (3H, s), 6.71 (1H, br s), 6.88 (2H, d, J = 8.8 Hz), 6.91 (1H, d, J = 15.6 Hz), 7.00 (1H, d, J = 15.6 Hz), 7.11 (1H, t, J = 7.2 Hz), 7.24 (1H, t, J = 7.2 Hz), 7.42 (2H, d, J = 8.8 Hz), 7.48 (1H, d, J = 7.2 Hz), 7.74 (1H, br s); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 52.4, 55.2, 114.1, 120.9, 122.4, 124.6, 126.5, 127.8, 127.9, 129.7, 131.9, 134.5, 154.5, 159.5; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO_3$, 284.1287; Found 284.1285.

*(E)-N-(2-(4-methoxystyryl)phenyl)-4-methylbenzenesulfonamide (**9**)*.[22] Yellowish oil (56.9 mg, 75%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (3H, s), 3.83 (3H, s), 6.63 (1H, br s), 6.65 (1H, d, J = 16.0 Hz), 6.72 (1H, d, J = 16.0 Hz), 6.86 (2H, d, J = 9.2 Hz), 7.15 (2H, d, J = 8.2 Hz), 7.20 (2H, m), 7.24 (2H, d, J = 9.2 Hz), 7.35 (1H, m), 7.44 (1H, m), 7.60 (2H, d, J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.6, 55.4. 126.5, 126.6, 127.1, 127.3, 128.0, 128.1, 129.6, 129.7, 131.9, 133.1, 133.5, 136.7, 144.0, 159.7; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_3S$, 380.1320; Found 380.1310.

*(E)-N-(2-(4-methoxystyryl)phenyl)-2-nitrobenzenesulfonamide (**10**)*. Yellowish oil (73.9 mg, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (3H, s), 6.66 (1H, d, J = 16.5 Hz), 6.83 (2H, d, J = 9.2 Hz), 7.04 (1H, d, J = 16.5 Hz), 7.21 (2H, d, J = 9.2 Hz), 7.25 (1H, m), 7.34 (2H, m), 7.47 (3H, m), 7.54 (1H, m), 7.64 (1H, m); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 55.5, 128.0, 128.1, 128.2, 128.4, 129.5, 131.1, 131.7, 132.3, 132.6, 133.1, 133.8, 134.1, 134.9, 147.9, 159.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O_5S$, 411.1015; Found 411.1011.

(E)-3,4-dimethoxy-2'-aminostilbene.[13b] Yellowish solid (34.1 mg, 89%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.89 (3H, s), 3.93 (3H, s), 6.71 (1H, d, J = 7.8 Hz), 6.80 (1H, t, J = 7.8 Hz), 6.85 (1H, d, J = 7.8 Hz), 6.92 (1H, d, J = 16.0 Hz), 7.02 (1H, d, J = 16.0 Hz), 7.05 (2H, m), 7.09 (1H, d, J = 7.8 Hz), and 7.38 (1H, d, J = 7.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 56.0, 56.1, 108.9, 111.3, 116.4, 119.3, 119.8, 122.5, 124.2, 127.2, 128.5, 130.3, 130.9, 143.9, 149.0, and 149.2; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2$, 256.1338; Found 256.1345.

*(E)-3,4-dimethoxy-2'-acetamidostilbene (**11**)*.[13b] White solid; (53.5 mg, 90%); mp 108−110 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (3H, s), 3.86 (3H, s), 3.88 (3H, s), 6.82 (1H, d, J = 8.7 Hz), 6.87 (1H, d, J = 16.5 Hz), 6.97 (1H, d, J = 16.5 Hz), 6.99 (1H, s), 7.01 (1H, d, J = 8.7 Hz), 7.14 (1H, d, J = 7.8 Hz), 7.21 (1H, d, J = 7.8 Hz), 7.47 (1H, d, J = 7.8 Hz), 7.70 (1H, d, J = 7.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 24.3, 56.0, 109.4, 111.3, 120.0, 121.8, 124.6, 125.7, 126.7, 128.1, 130.3, 130.9, 132.0, 134.6, 149.2, 149.3, 169.0; ESIMS *m/z* 298 $[M + H]^+$.

*(E)-methyl (2-(3,4-dimethoxystyryl)phenyl)carbamate (**12**)*. Yellowish oil; (43.9 mg, 70%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.78 (3H, s), 3.88 (3H, s), 3.93 (3H, s), 6.71

(1H, br s), 6.85 (1H, d, J = 8.7 Hz), 6.91 (1H, d, J = 16.0 Hz), 7.01 (1H, d, J = 16.0 Hz), 7.03 (1H, m), 7.04 (1H, m), 7.13 (1H, t, J = 7.5 Hz), 7.27 (1H, t, J = 7.5 Hz), 7.49 (1H, d, J = 7.5 Hz), 7.76 (1H, br d, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 52.5, 56.0, 109.1, 111.3, 120.1, 121.3, 124.7, 126.9, 128.1, 129.3, 130.1, 132.6, 134.7, 149.2, 149.4, 154.5; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}NO_4$, 314.1392; Found 314.1397.

*(E)-N-(2-(3,4-dimethoxystyryl)phenyl)-4-methylbenzenesulfonamide (**13**)*.

Yellowish solid, and subsequently, colorless block crystals from hexane/CH_2Cl_2 (68.0 mg, 83%); mp 153−155 ˚C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.26 (3H, s), 3.89 (3H, s), 3.91 (3H, s), 6.67 (1H, d, J = 16.0 Hz), 6.76 (1H, d, J = 16.0 Hz), 6.80 (1H, d, J = 8.2 Hz), 6.88 (1H, dd, J = 8.2, 1.8 Hz), 6.90 (1H, d, J = 1.8 Hz), 7.04 (1H, br s), 7.12 (2H, d, J = 8.2 Hz), 7.20 (1H, t, J = 7.4 Hz), 7.22 (1H, t, J = 7.4 Hz), 7.37 (1H, m), 7.45 (1H, m), 7.60 (2H, d, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.9, 108.9, 111.1, 120.2, 120.6, 126.4, 126.5, 126.9, 127.1, 128.0, 129.6, 129.9, 132.1, 133.1, 133.3, 136.5, 145.7, 149.0, 149.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_4S$, 410.1426; Found 410.1422.

*(E)-N-(2-(3,4-dimethoxystyryl)phenyl)-2-nitrobenzenesulfonamide (**14**)*.

Yellowish oil (62.5 mg, 71%); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.89 (3H, s), 3.90 (3H, s), 6.66 (1H, d, 16.4 Hz), 6.80 (2H, m), 6.92 (1H, s), 7.08 (1H, d, 16.4 Hz), 7.26 (2H, m), 7.37 (1H, br s), 7.43 (1H, m), 7.49 (3H, m), 7.55 (1H, m), 7.66 (1H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.9, 56.0, 108.2, 111.1, 120.4. 120.6, 125.2, 126.2, 128.1, 128.2, 131.2, 132.0, 132.3, 132.6, 133.8, 147.9, 149.3, 149.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O_6S$, 441.1120; Found 441.1103.

(E)-4-Methoxy-2'-acetoxystilbene.[20] White solid (32.7 mg, 61%); mp 70–71 ˚C [lit 75.8 ˚C]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (3H, s), 3.84 (3H, s), 6.89 (2H, d, J = 8.8 Hz), 6.97 (1H, d, J = 16.3 Hz), 7.06 (1H, d, J = 16.3 Hz), 7.07 (1H, dd, J = 7.7, 2.0 Hz), 7.24 (2H, m), 7.42 (2H, d, J = 8.8 Hz), 7.66, (1H, dd, J = 7.0, 2.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.1, 55.4, 114.3, 119.8, 122.8, 126.3, 126.4, 128.0, 128.1, 130.1, 130.4, 130.7, 148.1, 159.7, 169.5; ESIMS *m/z* 269 $[M + H]^+$ ($C_{17}H_{16}O_3 + H$).

Cyclic Voltammetry. All cyclic voltammetry experiments were carried out in a divided cell fitted with a Teflon cell top and a nitrogen inlet. The electrodes used were a Pt electrode (1.6 mm diameter) as the working electrode, Pt as the counter electrode and $Ag/AgNO_3$ (0.01 M)/TEAP (0.1 M in MeCN) as the reference electrode.

General Procedure for Electrochemical Oxidation (Controlled Potential Electrolysis). To the electrochemical cell containing 0.2 M $LiClO_4$ in 25 mL of MeCN was added the corresponding stilbene (ca. 0.2 mmol) under nitrogen or argon. Bulk electrolysis was carried out using a Pt gauze electrode (working electrode), Pt (counter electrode), and $Ag/AgNO_3$ (0.01 M)/TEAP (0.1 M in MeCN) (reference electrode), with stirring, and the electrolysis was allowed to proceed until 1 F of charge had been transferred at the first anodic wave. The reaction mixture was then concentrated by evaporation under reduced pressure, and CH_2Cl_2 (10 mL) was then added. The mixture was then poured into H_2O and 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, and the resulting residue was then fractionated by various chromatographic methods (preparative radial chromatography; HPLC; LH20) until pure compounds were obtained.

Anodic oxidation of 1 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **1** (+0.97 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 1:1 to 100% CH_2Cl_2), followed by HPLC (X-Bridge Prep OBD^{TM}, C_{18} column, 20% H_2O:MeCN to 100% MeCN in 7 min, 5 ml/min), and Sephadex LH20 (MeOH as mobile phase), gave **1a (**12.4 mg, 25%), **1b** (7.0 mg, 14%), **1c** (9.5 mg, 19%), and **1e** (11.0 mg, 22%).

*Bisbenzopyran (**1a**)*. Light yellowish oil, and subsequently, colorless block crystals from *n*-hexane/CH_2Cl_2; mp 237–240 ˚C; UV (EtOH) λ_{max} (log ε) 205 (4.75), 227 (4.40), and 281 (3.75) nm; IR (dry film) ν_{max} 2054, 2020, 1943, 1889, 1786, 1611, 1514, 831, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.33 (2H, d, J = 9.8 Hz), 3.85 (6H, s), 5.28 (2H, d, J = 9.8 Hz), 5.99 (2H, dd, J = 7.6, 1.2 Hz), 6.52 (2H, td, J = 7.6, 1.2 Hz), 6.90 (6H, m), 7.09 (2H, td, J = 7.6, 1.2 Hz), and 7.19 (4H, d, J = 8.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 40.6, 55.4, 80.0, 113.7, 116.6, 119.0, 119.6, 128.5, 129.3, 131.5, 131.8, 155.0, and 159.8; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{30}H_{26}O_4K$, 489.1463; Found 489.1443.

*Bisbenzopyran (**1b**)*. Light yellowish oil, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 189–190 ˚C; UV (EtOH) λ_{max} (log ε) 232 (3.54), 256 (3.11), and 280 (2.84) nm; IR (dry film) ν_{max} 2055, 2020, 1943, 1891, 1791, 1611, 1514, 834, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.49 (1H, t, J = 10.8 Hz), 3.71 (3H, s), 3.86 (3H, s), 3.90 (1H, dd, J = 10.8, 3.6 Hz), 4.99 (1H, d, J = 10.8 Hz), 6.19 (1H, d, J = 3.6 Hz), 6.26 (1H, dd, J = 7.2, 1.1 Hz), 6.51 (1H, td, J = 7.2, 1.1 Hz), 6.68 (2H, d, J = 8.9 Hz), 6.83 (1H, d, J = 8.2 Hz), 6.97 (2H, d, J = 8.6 Hz), 7.02 (2H, d, J = 8.9 Hz), 7.00 (2H, m), 7.11 (1H, td, J = 7.2, 1.1 Hz), 7.14 (1H, t, J = 8.2 Hz), 7.35 (2H, d, J = 8.6 Hz), and

7.52 (1H, d, J = 8.2 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 34.1, 41.7, 55.2, 55.5, 77.2, 80.9, 113.6, 114.6, 117.2, 117.6, 119.7, 120.5, 120.8, 122.4, 127.3, 127.7, 128.1, 128.2, 128.5, 129.7, 131.0, 132.8, 154.7, 155.5, 159.0, and 160.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{27}O_4$, 451.1904; Found 451.1894.

*Bisbenzofuran (**1c**)*. Light yellowish oil, and subsequently, colorless block crystals from *n*-hexane/CH_2Cl_2; mp 132–134 ˚C; UV (EtOH) λ_{max} (log ε) 208 (4.65), 227 (4.54), and 283 (3.98) nm; IR (dry film) ν_{max} 2059, 2020, 1942, 1892, 1782, 1612, 1513, 828, and 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (6H, s), 3.90 (2H, d, J = 3.6 Hz), 5.44 (2H, d, J = 3.6 Hz), 6.70 (4H, d, J = 8.8 Hz), 6.75 (4H, d, J = 8.8 Hz), 6.88 (2H, m), 7.00 (2H, d, J = 8.2 Hz), 7.06 (2H, d, J = 8.2 Hz), and 7.26 (2H, m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.2, 55.4, 85.4, 109.9, 113.9, 121.0, 125.3, 126.5, 126.7, 129.4, 134.6, 159.2, and 160.5; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{30}H_{26}O_4K$, 489.1463; Found 489.1477.

*Benzofurano-benzopyran (**1e**)*. Light yellowish oil, and subsequently, colorless needle crystals from MeOH/CH_2Cl_2; mp 154–156 ˚C; UV (EtOH) λ_{max} (log ε) 202 (4.01), 225 (3.21), 240 (3.04), 255 (2.83), and 280 (2.52) nm; IR (dry film) ν_{max} 2058, 2021, 1941, 1890, 1779, 1610, 1511, 827, and 751 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.69 (3H, s), 3.74 (1H, dd, J = 11.8 Hz), 3.79 (3H, s), 4.04 (1H, dd, J = 7.8 Hz), 4.23 (1H, d, J = 11.8 Hz), 6.29 (1H, dd, J = 7.2, 1.3 Hz), 6.36 (1H, d, J = 7.8 Hz), 6.52 (1H, dd, J = 7.2, 1.3 Hz), 6.63 (3H, m), 6.78 (1H, t, J = 7.5 Hz), 6.93 (7H, m), 7.12 (1H, d, J = 7.5 Hz), and 7.45 (2H, d, J = 8.6 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 44.8, 45.7, 53.6, 55.2, 55.4, 104.2, 109.2, 113.6, 114.7, 118.1, 121.2, 122.5, 123.3, 127.1, 127.6, 127.8, 128.3,

128.9, 128.9, 130.6, 134.9, 135.5, 152.0, 158.0, 158.6, and 158.8; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{30}H_{26}O_4K$, 489.1463; Found 489.1452.

Anodic oxidation of 2 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **2** (+0.97 V, 1 F) yielded essentially the same compounds from the anodic oxidation of **1**, namely, **1a** (12.2 mg, 27%), **1b** (6.8 mg, 15%), **1c** (9.0 mg, 20%), and **1e** (9.0 mg, 20%).

Anodic oxidation of 3 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **3** (+0.95 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, hexanes:CH_2Cl_2, 2:1 to 3% MeOH:CH_2Cl_2), followed by Sephadex LH20 (20% MeCN:MeOH as mobile phase), gave **3a** (10.7 mg, 21%), **3c** (9.2 mg, 18%), **3d** (8.7 mg, 17%), and **3f** (16.3 mg, 32%).

*Bisbenzopyran (**3a**)*. Colorless oil, and subsequently, colorless block crystals from *n*-hexane/CH_2Cl_2; mp 250–252 ˚C; UV (EtOH) λ_{max} (log ε) 212 (4.49), 229 (4.18), 279 (3.80), and 284 (3.81) nm; IR (dry film) ν_{max} 1608, 1516, 1237, 1026, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.35 (2H, d, J = 9.2 Hz), 3.81 (6H, s), 3.92 (6H, s), 5.27 (2H, d, J = 9.2 Hz), 6.02 (2H, d, J = 7.6 Hz), 6.54 (2H, t, J = 7.6 Hz), 6.82 (6H, m), 6.93 (H-11a, H-11b, 2H, d, J = 7.6 Hz), and 7.11 (2H, t, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 40.5, 55.9, 56.0, 80.1, 110.7, 110.8, 116.5, 118.9, 119.6, 120.6, 128.5, 131.6, 131.7, 148.8, 149.1, and 154.7; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{31}O_6$, 511.2121; Found 511.2101.

*Bisbenzofuran (**3c**)*. Colorless oil; UV (EtOH) λ_{max} (log ε) 212 (4.68), 232 (4.33), 283 (4.09), and 292 (3.91) nm; IR (dry film) ν_{max} 1608, 1517, 1235, 1027, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.68 (6H, s), 3.81 (6H, s), 3.91 (2H, d, J = 3.4 Hz), 5.44

(2H, d, J = 3.4 Hz), 6.20 (2H, d, J = 1.7 Hz), 6.48 (2H, dd, J = 8.3, 1.7 Hz), 6.68 (2H, d, J = 8.3 Hz), 6.90 (2H, t, J = 7.8 Hz), 7.02 (2H, d, J = 7.8 Hz), 7.12 (2H, d, J = 7.8 Hz), and 7.27 (2H, t, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 55.5, 55.7, 55.9, 85.2, 108.1, 109.8, 111.1, 116.9, 121.0, 125.3, 126.7, 129.3, 134.9, 148.4, 148.8, and 160.5; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{31}O_6$, 511.2121; Found 511.2115.

*Bisbenzofuran (**3d**)*. Colorless oil; UV (EtOH) λ_{max} (log ε) 212 (4.74), 230 (4.45), 282 (4.18), and 289 (4.11) nm; IR (dry film) ν_{max} 1594, 1517, 1233, 1026, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.68 (6H, s), 3.81 (6H, s), 3.99 (2H, d, J = 6.9 Hz), 5.36 (2H, d, J = 6.9 Hz), 6.76 (2H, d, J = 7.8 Hz), 6.78 (2H, s), 6.82 (4H, m), 6.84 (2H, t, J = 7.8 Hz), 6.88 (2H, d, J = 7.8 Hz), and 7.22 (2H, t, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 53.1, 56.0, 56.0, 86.6, 109.2, 109.8, 111.2, 119.0, 121.1, 124.9, 127.1, 129.3, 133.8, 149.3, 149.4, and 160.2; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{31}O_6$, 511.2121; Found 511.2115.

*Bridged oxocine (**3f**)*. Colourless oil; UV (EtOH) λ_{max} (log ε) 215 (4.88), 237 (4.50), 281 (4.31), and 288 (4.23) nm; IR (dry film) ν_{max} 3441, 1608, 1513, 1354, 1238, 1217, 1026, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.35 (1H, br s), 3.68 (3H, s), 3.81 (4H, s), 3.82 (3H, s), 3.89 (3H, s), 4.48 (1H, d, J = 1.4 Hz), 5.40 (1H, br s), 5.60 (1H, br t, J = 1.4 Hz), 6.43 (1H, s), 6.60 (1H, dd, J = 7.8, 1.0 Hz), 6.63 (1H, dd, J = 8.3, 1.8 Hz), 6.64 (1H, td, J = 7.8, 1.0 Hz), 6.68 (1H, dd, J = 7.8, 1.1 Hz), 6.74 (1H, d, J = 1.8 Hz), 6.79 (1H, d, J = 8.3 Hz), 6.92 (1H, dd, J = 7.8, 1.0 Hz), 6.95 (1H, td, J = 7.8, 1.1 Hz), 6.96 (1H, td, J = 7.8, 1.0 Hz), 6.99 (1H, s), 7.08 (1H, td, J = 7.8, 1.1 Hz), and 7.43 (1H, dd, J = 7.8, 1.1 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 30.1, 42.4, 55.8, 55.9, 55.9, 56.0, 56.1, 73.5, 111.1, 112.3, 112.5, 112.7, 115.0, 117.0, 120.6, 120.9, 121.5,

125.8, 127.4, 127.6, 127.9, 128.2, 128.8, 129.3, 129.3, 136.8, 147.7, 148.1, 148.9, 149.5, 152.2, and 153.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{31}O_6$, 511.2121; Found 511.2119.

Anodic oxidation of 4 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **4** (+0.95 V, 1 F) yielded essentially the same compounds from the anodic oxidation of **3**, namely, **3a** (9.7 mg, 19%), **3c** (9.2 mg, 18%), **3d** (9.2 mg, 18%), and **3f** (15.3 mg, 30%).

Anodic oxidation of 6 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **6** (+1.05 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, 100% CH_2Cl_2 to 8% MeOH:CH_2Cl_2), gave **6c** (18.6 mg, 35%) and **6d** (3.2 mg, 6%).

*Bisindole (**6c**).*[13a] Light yellowish oil; UV (EtOH) λ_{max} (log ε) 212 (5.00), 228 (4.89), 251 (4.69), 279 (4.29), and 292 (4.13) nm; IR (dry film) ν_{max} 1666, 1611, 1512, 1394, 1282, 1250, 1032, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.86 (6H, s), 3.48 (2H, s), 3.69 (6H, s), 4.66 (2H, s), 6.44 (4H, d, J = 8.7 Hz), 6.66 (4H, d, J = 8.4 Hz), 7.24 (2H, m), 7.25 (2H, m), 7.47 (2H, t, J = 8.0 Hz), and 8.45 (2H, d, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 23.7, 55.3, 56.7, 64.1, 114.5, 117.7, 124.9, 125.3, 125.7, 129.4, 130.1, 133.9, 143.9, 159.1, and 169.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{33}N_2O_4$, 533.2440; Found 533.2450.

*Bisindole (**6d**).* Light yellowish oil, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 259–261 ˚C; UV (EtOH) λ_{max} (log ε) 211 (4.25), 227 (4.13), 256 (3.95), 285 (3.54), and 293 (3.39) nm; IR (dry film) ν_{max} 1665, 1611, 1512, 1392, 1281, 1250, 1031, and 754 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.85 (6H, s), 3.47 (2H,

s), 3.76 (6H, s), 4.94 (2H, s), 6.63 (2H, br s), 6.82 (4H, d, J = 8.4 Hz), 6.98 (2H, m), 6.99 (4H, d, J = 8.4 Hz), 7.31(2H, t, J = 8.0 Hz), and 8.26 (2H, br d, J = 6.4 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 23.9, 55.4, 56.8, 67.0, 114.8, 117.2, 124.4, 125.0, 126.2, 129.2, 129.5, 134.2, 143.9, 159.5, and 169.0; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{33}N_2O_4$, 533.2440; Found 533.2430.

Anodic oxidation of 7 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **7** (+1.04 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 4:1 to 100% CH_2Cl_2), followed by HPLC (Luna Phenyl-Hexyl column, 15% H_2O:MeCN, 10 ml/min), gave **7c** (10.3 mg, 23%) and **7g** (5.4 mg, 12%).

*Bisindole (**7c**).* Light yellowish solid; UV (EtOH) λ_{max} (log ε) 212 (4.46), 227 (4.18), 253 (3.96), and 307 (3.58) nm; IR (dry film) ν_{max} 3382, 1603, 1510, 1243, 1030, and 741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.69 (2H, d, J = 2.3 Hz), 3.73 (6H, s), 4.64 (2H, d, J = 2.3 Hz), 6.66 (4H, d, J = 8.2 Hz), 6.67 (2H, t, J = 7.8 Hz), 6.72 (2H, d, J = 7.8 Hz), 6.76 (4H, d, J = 8.2 Hz), 6.91 (2H, d, J = 7.8 Hz), and 7.12 (2H, t, J = 7.8 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 56.7, 55.3, 63.3, 108.6, 113.9, 118.6, 125.5, 126.8, 128.3, 138.4, 151.6, and 158.6; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{29}N_2O_2$, 449.2229; Found 449.2236.

*Bisquinoline (**7g**).* Light yellowish solid; UV (EtOH) λ_{max} (log ε) 211 (4.22), 227 (3.97), 249 (3.87), and 307 (3.50) nm; IR (dry film) ν_{max} 3378, 1606, 1511, 1244, 1034, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (2H, dd, J = 6.9, 2.8 Hz), 3.82 (6H, s), 4.60 (2H, dd, J = 6.9, 2.8 Hz), 6.46 (2H, t, J = 7.8 Hz), 6.49 (2H, d, J = 7.8 Hz), 6.63 (2H, d, J = 7.8 Hz), 6.92 (4H, d, J = 8.7 Hz), 6.95 (2H, t, J = 7.8 Hz), and 7.33 (4H, d, J = 8.7

Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 43.0, 55.4, 61.1, 144.3, 114.6, 117.8, 125.0, 126.7, 127.1, 129.0, 136.4, 144.3, and 159.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{29}N_2O_2$, 449.2229; Found 449.2234.

Anodic oxidation of 8 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **8** (+0.96 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 4:1 to 100% CH_2Cl_2), gave **8c** (32.2 mg, 57%) bisquinoline **8g** (12.4 mg, 22%).

*Bisindole (**8c**).* Light yellowish solid; UV (EtOH) λ_{max} (log ε) 228 (4.47), 249 (4.24), and 285 (3.79) nm; IR (dry film) ν_{max} 2955, 1707, 1511, 1440, 1384, 1247, 1033, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.46 (2H, s), 3.62 (6H, br s), 3.70 (6H, s), 4.90 (2H, br s), 6.52 (4H, br s), 6.65 (4H, d, J = 8.5 Hz), 7.12 (4H, m), 7.41 (2H, br t, J = 7.5 Hz), and 8.10 (2H, br s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 52.8, 52.7, 55.8, 63.3, 113.9, 115.4, 123.5, 125.3, 125.8, 129.1, 130.0, 135.1, 143.5, 153.5, and 158.7; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{33}N_2O_6$, 565.2339; Found 565.2348.

*Bisquinoline (**8g**).* Light yellowish solid, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 264–266 ˚C; UV (EtOH) λ_{max} (log ε) 230 (4.30) and 274 (3.46) nm; IR (dry film) ν_{max} 2949, 1693, 1439, 1328, 1249, 1022, and 751 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.13 (2H, dd, J = 4.5, 2.4 Hz), 3.82 (6H, s), 3.74 (6H, s), 6.26 (2H, dd, J = 4.5, 2.4 Hz), 6.78 (4H, d, J = 8.7 Hz), 7.19 (4H, d, J = 8.7 Hz). 7.29 (6H, m), and 7.71 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.5, 55.4, 55.2, 57.1, 113.9, 124.2, 125.7, 126.6, 127.1, 128.6, 134.4, 134.6, 137.3, 155.3, and 158.9; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{33}N_2O_6$, 565.2339; Found 565.2349.

Anodic oxidation of 9 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **9** (+1.04 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 2:1 to 2% MeOH:CH_2Cl_2), gave **9c** (39.4 mg, 52%), **9g** (18.9 mg, 25%), and **9h** (4.5 mg, 6%).

*Bisindole (**9c**).* Light yellowish oil and subsequent as colorless needle crystals from MeOH/CH_2Cl_2; ; mp 182−184 ˚C; UV (EtOH) λ_{max} (log ε) 212 (4.58), 226 (4.52), and 275 (3.99) nm; IR (dry film) ν_{max} 1611, 1513, 1357, 1248, 1168, 1032, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.86 (2H, s), 2.11 (6H, s), 3.85 (6H, s), 4.95 (2H, s), 5.96 (2H, dd, J = 7.4, 0.8 Hz), 6.71 (4H, d, J = 8.3 Hz), 6.84 (2H, td, J = 7.4, 0.8 Hz), 6.84 (4H, d, J = 8.7 Hz), 6.99 (4H, d, J = 8.7 Hz), 7.27 (2H, td, J = 7.4, 0.8 Hz), 7.33 (4H, d, J = 8.3 Hz), and 7.71 (2H, dd, J = 7.4, 0.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.4, 54.9, 55.4, 70.7, 114.2, 115.8, 122.9, 126.6, 127.0, 128.2, 129.1, 129.4, 130.1, 134.0, 135.3, 142.4, 143.7, and 159.6; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{41}N_2O_6S_2$, 757.2406; Found 757.2433.

*Bisquinoline (**9g**).* White solid, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 342−344 ˚C; UV (EtOH) λ_{max} (log ε) 210 (3.86) and 230 (3.50) nm; IR (dry film) ν_{max} 1610, 1512, 1346, 1251, 1162, 1031, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.96 (2H, dd, J = 4.8, 2.8 Hz), 2.17 (6H, s), 3.77 (6H, s), 5.88 (2H, dd, J = 4.8, 2.8 Hz), 6.69 (4H, d, J = 8.7 Hz), 6.78 (4H, d, J = 8.7 Hz), 6.85 (4H, d, J = 8.7 Hz), 7.16 (4H, d, J = 8.7 Hz), 7.34 (4H, m), 7.44 (2H, m), and 7.59 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.6, 47.7, 55.3, 59.1, 113.8, 124.5, 126.7, 127.5, 128.0, 128.1, 129.4, 129.6, 133.9, 135.3, 136.7, 136.9, 143.5, and 158.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{41}N_2O_6S_2$, 757.2406; Found 757.2397.

*Indole (**9h**).*[22] Light yellowish oil; UV (EtOH) λ_{max} (log ε) 211 (4.35), 224 (4.25), 245 (4.18), and 296 (3.82) nm; IR (dry film) ν_{max} 1612, 1506, 1370, 1249, 1174, 1035, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.33 (3H, s), 3.85 (3H, s), 6.99 (2H, d, J = 8.7 Hz), 7.21 (2H, d, J = 8.2 Hz), 7.26 (1H, t, J = 8.2 Hz), 7.34 (1H, t, J = 8.2 Hz), 7.51 (2H, d, J = 8.7 Hz), 7.62 (1H, s), 7.73 (1H, d, J = 8.2 Hz), 7.79 (2H, d, J = 8.2 Hz), and 8.04 (1H, d, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.7, 55.5, 113.9, 114.4, 120.5, 122.4, 123.5, 124.9, 125.6, 125.8, 127.0, 129.1, 129.6, 130.0, 135.3, 135.6, 145.0, and 159.2; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_3S$, 378.1164; Found 378.1163.

Anodic oxidation of 10 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **10** (+1.06 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 2:1 to 2% MeOH:CH_2Cl_2), gave **10c** (40.1 mg, 49%), **10d** (17.2 mg, 21%), and **10g** (10.6 mg, 13%).

*Bisindole (**10c**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 212 (4.69), 228 (4.55), and 284 (3.97) nm; IR (dry film) ν_{max} 1611, 1538, 1513, 1371, 1249, 1175, 1030, 756, and 586 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.79 (2H, s), 3.75 (6H, s), 5.15 (2H, s), 6.38 (2H, d, J = 7.8 Hz), 6.63 (4H, d, J = 8.7 Hz), 6.83 (4H, d, J = 8.7 Hz), 6.91 (2H, t, J = 7.8 Hz), 7.24 (2H, m), 7.25 (2H, m), 7.31 (2H, m), 7.38 (2H, t, J = 7.8 Hz), 7.57 (2H, d, J = 7.8 Hz), and 7.59 (2H, d, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 54.5, 55.4, 69.4, 114.1, 115.8, 123.6, 124.2, 127.5, 127.8, 129.4, 130.0, 131.3, 132.2, 132.8, 133.8, 142.2, 147.7, and 159.5; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{35}N_4O_{10}S_2$, 819.1795; Found 819.1806.

*Bisindole (**10d**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 212 (4.74), 230 (4.59), and 284 (4.12) nm; IR (dry film) ν_{max} 1611, 1543, 1513, 1371, 1250, 1176, 1030, 753, and 586 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.45 (2H, s), 3.71 (6H, s), 5.34 (2H, s), 6.62 (4H, d, J = 8.7 Hz), 6.85 (2H, d, J = 8.2 Hz), 6.92 (4H, d, J = 8.7 Hz), 6.94 (2H, t, J = 8.2 Hz), 7.23 (2H, t, J = 8.2 Hz), 7.32 (2H, m), 7.48 (4H, m), 7.50 (2H, d, J = 8.2 Hz), and 7.58 (2H, d, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 54.7, 55.3, 67.6, 114.2, 115.1, 124.2, 125.6, 127.6, 129.3, 129.5, 130.4, 131.7, 132.9, 133.2, 133.5, 142.7, 147.6, and 159.4; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{35}N_4O_{10}S_2$, 819.1795; Found 819.1815.

*Bisquinoline (**10g**).* White solid, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 306–308 ˚C; UV (EtOH) λ_{max} (log ε) 210 (4.54) and 228 (4.23) nm; IR (dry film) ν_{max} 1608, 1531, 1513, 1365, 1349, 1261, 1174, 1024, 743, and 590 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 2.56 (2H, dd, J = 4.6, 2.8 Hz), 3.74 (6H, s), 6.06 (2H, dd, J = 4.6, 2.8 Hz), 6.68 (4H, d, J = 8.7 Hz), 6.84 (4H, d, J = 8.7 Hz), 7.14 (4H, m), 7.28 (2H, d, J = 7.3 Hz), 7.38 (2H, m), 7.40 (2H, m), 7.44 (2H, td, J = 7.8, 1.4 Hz), 7.56 (2H, dd, J = 7.8, 1.4 Hz), and 7.60 (2H, d, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz) δ 47.8, 55.3, 59.6, 114.0, 123.5, 125.8, 127.8, 128.0, 128.3, 130.6, 131.0, 131.3, 133.5, 133.9, 134.4, 136.5, 147.3, and 159.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{35}N_4O_{10}S_2$, 819.1795; Found 819.1799.

Anodic oxidation of 11 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **11** (+1.14 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:$CHCl_3$, 1:2 to 2% MeOH:$CHCl_3$), gave **11c** (16.0 mg, 27%) and **11i** (7.1 mg, 12%).

*Bisindole (**11c**).*[13b] Light yellowish oil; UV (EtOH) λ_{max} (log ε) 212 (4.85), 238 (4.49), 282 (4.17), and 290 (4.09) nm; IR (dry film) ν_{max} 1667, 1597, 1515, 1392, 1256, 1026, and 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.88 (6H, s), 3.51 (2H, s), 3.59 (6H, s), 3.74 (6H, s), 4.66 (2H, s), 5.80 (2H, s), 6.22 (2H, d, J = 8.7 Hz), 6.60 (2H, d, J = 8.7 Hz), 7.21 (2H, t, J = 8.2 Hz), 7.31 (2H, d, J = 8.2 Hz), 7.45 (2H, t, J = 8.2 Hz), and 8.47 (2H, d, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 23.7, 55.8, 55.9, 56.8, 64.2, 107.6, 111.4, 115.9, 117.8, 124.8, 125.3, 129.4, 130.2, 134.2, 144.0, 148.5, 149.5, and 169.9; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{37}N_2O_6$, 593.2652; Found 593.2656.

*Dihydroindole (**11i**).*[13a] Light yellowish oil; UV (EtOH) λ_{max} (log ε) 211 (4.16), 238 (3.71), 254 (3.69), 282 (3.43), and 290 (3.35) nm; IR (dry film) ν_{max} 1660, 1596, 1516, 1395, 1257, 1026, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.04 (3H, s), 2.95 (1H, d, J = 16.0 Hz), 3.77 (1H, m), 3.77 (3, 3H, s), 3.82 (4, 3H, s), 5.31 (1H, d, J = 9.6 Hz), 6.63 (1H, s), 6.69 (1H, d, J = 8.2 Hz), 6.76 (1H, d, J = 8.2 Hz), 7.03 (1H, t, J = 8.2 Hz), 7.12 (1H, d, J = 8.2 Hz), 7.24 (1H, t, J = 8.2 Hz), and 8.29 (1H, d, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 24.2, 39.2, 55.9, 56.0, 63.4, 108.0, 111.5, 117.0, 117.2, 124.1, 124.9, 127.8, 129.3, 135.8, 143.4, 148.6, 149.6, and 169.7; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}NO_3$, 298.1443; Found 298.1452.

Anodic oxidation of 12 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **12** (+0.96 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 4:1 to 100% CH_2Cl_2), gave **12c** (41.9 mg, 67%), **12g** (3.1 mg, 5%), and **12h** (0.6 mg, 1%).

*Bisindole (**12c**).* Light yellowish solid, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 210–212 ˚C; UV (EtOH) λ_{max} (log ε) 234 (4.06) and 285 (3.57) nm; IR (dry film) ν_{max} 2935, 1709, 1516, 1441, 1385, 1256, 1025, and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.49 (2H, s), 3.62 (16a, 16b, 12H, br s), 3.77 (6H, s), 4.90 (2H, br s), 5.87 (2H, br s), 6.29 (2H, br d, J = 5.2 Hz), 6.61 (2H, d, J = 8.3 Hz), 7.11 (2H, br t, J = 6.9 Hz), 7.22 (2H, br d, J = 5.7 Hz), 7.42 (2H, br t, J = 6.7 Hz), and 8.15 (2H, br s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 52.8, 55.7, 55.8, 56.4, 63.3, 107.9, 111.1, 115.5, 115.7, 123.5, 125.3, 129.1, 130.1, 135.5, 143.6, 148.0, 148.9, and 153.5; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{37}N_2O_8$, 625.2550; Found 625.2558.

*Bisquinoline (**12g**).* Light yellowish solid, and subsequently, colorless block crystals from MeOH/CH_2Cl_2; mp 251–253 ˚C; UV (EtOH) λ_{max} (log ε) 233 (4.16), 273 (3.78), and 334 (3.19) nm; IR (dry film) ν_{max} 2949, 1703, 1515, 1440, 1320, 1259, 1026, and 758 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.12 (2H, dd, J = 4.8, 2.4 Hz), 3.70 (6H, s), 3.72 (12H, br s), 3.82 (6H, s), 6.28 (2H, dd, J = 4.8, 2.4 Hz), 6.64 (2H, d, J = 1.6 Hz), 6.75 (2H, d, J = 8.4 Hz), 6.89 (2H, dd, J = 8.4, 1.6 Hz), 7.31 (6H, m), and 7.76 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.8, 53.2, 55.89, 55.93, 57.4, 110.5, 111.0, 120.0, 124.2, 125.8, 126.7, 127.2, 134.6, 134.9, 137.6, 148.5, 149.0, and 155.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{37}N_2O_8$, 625.2550; Found 625.2550.

*Indole (**12h**).* Light yellowish solid; UV (EtOH) λ_{max} (log ε) 223 (4.14) and 298 (3.81) nm; IR (dry film) ν_{max} 2955, 1736, 1511, 1453, 1375, 1241 and 761 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.95 (3H, s), 3.96 (3H, s), 4.08 (3H, s), 6.99 (1H, d, J = 8.4 Hz), 7.14 (1H, d, J = 2.0 Hz), 7.21 (1H, dd, J = 8.4, 2.0 Hz), 7.32 (1H, t, J = 7.6 Hz), 7.40 (1H, t, J = 7.6 Hz), 7.69 (1H, s), 7.81 (1H, d, J = 7.6 Hz), and 8.25 (1H, d, J = 7.6 Hz);

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 54.0, 56.1, 111.3, 111.6, 115.5, 120.1, 120.4, 121.9, 123.0, 123.4, 125.0, 126.4, 129.2, 135.0, 148.6, 149.3, and 152.0; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_4$, 312.1236; Found 312.1230.

Anodic oxidation of 13 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **13** (+0.96 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:EtOAc, 4:1 to 100% EtOAc), gave **13c** (44.1 mg, 54%) and **13f** (13.1 mg, 16%).

*Bisindole (**13c**).* Light yellowish oil, and subsequently, colorless block crystals from MeOH/MeCN; mp 154–156 ˚C; UV (EtOH) λ_{max} (log ε) 222 (4.70) and 278 (4.26) nm; IR (dry film) ν_{max} 2936, 1514, 1460, 1353, 1260, 1162, 1025, 676, and 569 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.14 (6H, s), 2.20 (2H, s), 3.65 (6H, s), 3.91 (6H, s), 5.09 (2H, s), 6.09 (2H, d, J = 7.8 Hz), 6.40 (2H, d, J = 1.2 Hz), 6.74 (2H, dd, J = 8.3, 1.2 Hz), 6.78 (4H, d, J = 8.1 Hz), 6.81 (2H, d, J = 8.3 Hz), 6.86 (2H, t, J = 7.8 Hz), 7.27 (2H, t, J = 7.8 Hz), 7.36 (4H, d, J = 8.1 Hz), and 7.69 (2H, d, J = 7.8 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.2, 54.7, 55.6, 56.1, 70.5, 108.6, 111.1, 115.3, 118.3, 122.9, 126.8, 127.9, 129.1, 129.2, 130.1, 134.0, 135.5, 142.3, 143.7, 149.0, and 149.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{46}H_{45}N_2O_8S_2$, 817.2617; Found 817.2646.

*Bridged azocine (**13f**).* Light yellowish oil and subsequent as colorless block crystals from MeOH/CH_2Cl_2; mp 188–190 ˚C; UV (EtOH) λ_{max} (log ε) 224 (3.90) and 279 (3.25) nm; IR (dry film) ν_{max} 2938, 1511, 1327, 1261, 1156, 1026, 759, and 553 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (3H, s), 2.40 (3H, s), 3.40 (1H, br s), 3.70 (4a, 3H, s), 3.87 (6H, s), 3.88 (3H, s), 4.30 (1H, d, J = 2.5 Hz), 4.45 (1H, d, J = 1.4 Hz), 6.29 (1H, br s), 6.31 (1H, d, J = 2.5 Hz), 6.39 (1H, s), 6.69 (1H, d, J = 7.9 Hz), 6.70 (1H, d, J

= 1.9 Hz), 6.72 (1H, d, *J* = 7.9 Hz), 6.78 (1H, dd, *J* = 8.3, 1.9 Hz), 6.84 (1H, t, *J* = 7.9 Hz), 6.90 (1H, d, *J* = 8.3 Hz), 6.98 (2H, d, *J* = 8.2 Hz), 7.00 (1H, m), 7.01 (1H, m), 7.07 (1H, m), 7.08 (2H, d, *J* = 8.2 Hz), 7.09 (1H, s), 7.17 (1H, d, *J* = 8.1 Hz), 7.20 (2H, d, *J* = 8.1 Hz), and 7.56 (3H, d, *J* = 8.1 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.4 (Me, 4b′), 21.6, 31.2, 44.8, 55.7, 55.8, 55.9, 55.9, 56.8, 111.3, 111.6, 112.3, 112.4, 119.0, 121.4, 123.3, 127.1, 127.2, 127.3, 127.7, 127.9, 128.2, 128.7, 129.3, 129.5, 129.8, 129.9, 134.7, 135.3, 136.3, 136.4, 137.9, 138.4, 143.4, 143.8, 147.8, 148.2, 149.0, and 149.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{46}H_{45}N_2O_8S_2$, 817.2617; Found 817.2598.

Anodic oxidation of 14 in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of **14** (+1.02 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 1:2 to 3% MeOH:CH_2Cl_2), gave **14c** (53.6 mg, 61%) and **14f** (7.9 mg, 9%).

*Bisindole (**14c**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 214 (4.83), 237 (4.55), and 281 (4.21) nm; IR (dry film) ν_{max} 1594, 1544, 1517, 1370, 1261, 1173, 1026, 753, and 592 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.22 (2H, s), 3.63 (6H, s), 3.79 (6H, s), 5.24 (2H, s), 6.35 (2H, d, *J* = 1.5 Hz), 6.45 (2H, dd, *J* = 8.2, 1.5 Hz), 6.53 (2H, d, *J* = 7.8 Hz), 6.55 (2H, d, *J* = 8.2 Hz), 6.91 (2H, t, *J* = 7.8 Hz), 7.25 (2H, t, *J* = 7.8 Hz), 7.29 (2H, t, *J* = 7.8 Hz), 7.35 (2H, d, *J* = 7.8 Hz), 7.42 (2H, t, *J* = 7.8 Hz), 7.55 (2H, d, *J* = 7.8 Hz), and 7.60 (2H, d, *J* = 7.8 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 54.2, 55.7, 55.9, 69.1, 109.5, 110.9, 115.4, 118.9, 123.5, 124.1, 126.8, 129.1, 129.2, 130.0, 131.2, 132.4, 132.9, 133.7, 142.4, 147.5, 148.7, and 148.8; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{39}N_4O_{12}S_2$, 879.2006; Found 879.2042.

*Bridged azocine (**14f**).* Light yellowish oil. UV (EtOH) λ_{max} (log ε) 216 (4.97), 238 (4.65) and 281 (4.24) nm; IR (dry film) ν_{max} 3339, 1606, 1538, 1514, 1360, 1264, 1245, 1166, 1027, 753, and 581 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.50 (1H, s), 3.72 (6H, s), 3.83 (3H, s), 3.86 (3H, s), 4.52 (1H, s), 4.59 (1H, d, J = 2.0 Hz), 6.40 (1H, d, J = 2.0 Hz), 6.45 (1H, s), 6.61 (1H, d, J = 7.8 Hz), 6.64 (1H, s), 6.81 (1H, d, J = 8.7 Hz), 6.82 (1H, s), 6.88 (1H, d, J = 8.7 Hz), 6.88 (1H, d, J = 8.0 Hz), 6.89 (1H, t, J = 7.8 Hz), 6.92 (1H, d, J = 7.8 Hz), 6.98 (1H, t, J = 7.8 Hz), 7.05 (1H, t, J = 8.0 Hz), 7.13 (1H, s), 7.19 (1H, t, J = 8.0 Hz), 7.37 (1H, d, J = 7.8 Hz), 7.38 (1H, t, J = 7.8 Hz), 7.57 (1H, t, J = 7.8 Hz), 7.63 (1H, t, J = 7.8 Hz), 7.67 (1H, d, J = 8.0 Hz), 7.70 (1H, d, J = 7.8 Hz), 7.72 (1H, t, J = 7.8 Hz), 7.78 (1H, d, J = 7.8 Hz), and 7.89 (1H, d, J = 7.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 31.3, 44.6, 55.8, 55.9, 56.0, 56.9, 57.1, 111.4, 112.1, 112.3, 112.8, 120.5, 121.5, 124.4, 125.2, 125.3, 127.4, 127.7, 127.9, 128.9, 128.9, 129.0, 129.1, 130.0, 130.2, 132.1, 132.3, 132.6, 133.4, 133.9, 134.2, 135.2, 135.3, 136.2, 139.2, 147.8, 147.8, 148.1, 148.1, 149.0, and 149.6; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{39}N_4O_{12}S_2$, 879.2006; Found 879.2030.

Anodic oxidation of (*E*)-4-methoxy-2′-acetoxystilbene in MeCN/ 0.2 M $LiClO_4$. Controlled potential electrolysis of (*E*)-4-methoxy-2′-acetoxystilbene at the potential peak (+0.94 V, 1 F) yielded a mixture, which on preparative radial chromatography (Chromatotron) (SiO_2, *n*-hexane:CH_2Cl_2, 2:1 to 100% CH_2Cl_2) resulted in the isolation of the stereoisomeric tetraaryltetrahydrofuran **26 (**15.4 mg, 30%), **27** (12.9 mg, 25%), and dehydrotetralin **28** (5.0 mg, 10%).

*Tetraaryltetrahydrofuran (**26**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 228 (4.84), 255 (3.97), and 277 (3.95) nm; IR (dry film) ν_{max} 2054, 2019, 1922, 1887, 1764,

1612, 1513, 829, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.97 (6H, s), 3.77 (6H, s), 3.98 (2H, dd, J = 5.9, 2.8 Hz), 5.36 (2H, dd, J = 5.9, 2.8 Hz), 6.83 (4H, d, J = 8.6 Hz), 6.94 (2H, dd, J = 7.4, 1.7 Hz), 7.16 (4H, m), 7.23 (4H, d, J = 8.6 Hz), and 7.36 (2H, dd, J = 7.4, 1.7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 20.7, 55.3, 56.6, 86.0, 113.9, 123.1, 126.2, 126.8, 127.8, 128.6, 129.9, 133.6, 149.0, 159.1, and 168.7; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{34}H_{32}O_7K$, 591.1780; Found 591.1796.

*Tetraaryltetrahydrofuran (**27**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 228 (4.52), 253 (3.80), and 277 (3.66) nm; IR (dry film) ν_{max} 2318, 2037, 1888, 1758, 1612, 1513, 830, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.04 (6H, s), 3.78 (6H, s), 3.94 (2H, br d, J = 4.6 Hz), 5.51 (2H, br d, J = 4.6 Hz), 6.86 (4H, d, J = 8.6 Hz), 6.88 (2H, d, J = 7.3 Hz), 7.05 (t, J = 7.3 Hz) 7.15 (2H, d, J = 7.3, 1.7 Hz), 7.16 (2H, t, J = 7.3 Hz), and 7.31 (4H, d, J = 8.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 20.6, 55.3, 48.6, 83.5, 113.8, 121.9, 125.8, 127.7, 127.8, 128.8, 130.1, 133.3, 149.3, 159.1, and 169.0; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{34}H_{32}O_7K$, 591.1780; Found 591.1796.

*Dehydrotetralin (**28**).* Light yellowish oil; UV (EtOH) λ_{max} (log ε) 230 (4.04), 285 (3.45), 298 (3.43) nm; IR (dry film) ν_{max} 2413, 2288, 2047, 1920, 1886, 1761, 1609, 1510, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.76 (3H, s), 2.30 (3H, s), 3.70 (3H, s), 3.75 (3H, s), 4.07 (1H, s), 4.30 (1H, s), 6.48 (1H, d, J = 2.3 Hz), 6.78 (1H, dd, J = 8.8, 2.3 Hz), 6.79 (2H, d, J = 8.8 Hz), 6.90 (1H, d, J = 8.0 Hz), 6.92 (1H, s), 7.00 (4H, m), 7.12 (2H, d, J = 8.8 Hz), 7.16 (3H, m), and 7.22 (1H, d, J = 8.8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.8, 44.6, 50.7, 54.9, 55.0, 112.5, 113.7, 114.8, 122.4, 122.6, 125.7, 125.9, 126.5, 127.4, 127.8, 128.2, 128.3, 129.0, 129.8, 132.0, 133.89, 133.94, 136.3,

137.3, 147.6, 158.0, 159.5, 169.1, and 169.3; HRMS (ESI-TOF) m/z: $[M + K]^+$ Calcd for $C_{34}H_{30}O_6K$, 573.1674; Found 573.1687.

Conversion of 3f to the tosylate derivative (29). Triethylamine (21 μL, 0.15 mmol) and a solution of 4-toluenesulfonyl chloride (28.6 mg, 0.15 mmol) in CH_2Cl_2 (5 ml) were added dropwise to a solution of **3f** (51.1 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the tosylate derivative.

*Bridged oxocine (**29**).* Light yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (3H, s), 3.28 (1H, s), 3.71 (3H, s), 3.83 (3H, s), 3.89 (3H, s), 3.96 (3H, s), 4.01 (1H, s), 4.46 (1H, s), 5.41 (1H, s), 6.56 (1H, d, J = 7.8 Hz), 6.67 (1H, s), 6.68 (1H, d, J = 7.9 Hz), 6.83 (1H, d, J = 7.9 Hz), 6.87 (1H, d, J = 7.9 Hz), 6.97 (1H, d, J = 7.9 Hz), 6.91 (1H, d, J = 7.9 Hz), 6.92 (1H, t, J = 7.9 Hz), 6.95 (1H, s), 6.97 (1H, t, J = 7.8 Hz), 7.02 (1H, t, J = 7.9 Hz), 7.10 (1H, t, J = 7.9 Hz), 7.23 (2H, d, J = 8.0 Hz), 7.43 (1H, d, J = 7.8 Hz), and 7.62 (2H, d, J = 8.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.7, 30.2, 42.3, 55.8, 55.9, 55.9, 56.0, 56.4, 73.9, 111.3, 112.2, 112.5, 112.4, 117.1, 121.0, 121.1, 121.4, 125.7, 126.9, 127.6, 128.3, 128.3, 128.6, 128.9, 129.0, 129.1, 129.8, 133.1, 134.3, 136.4, 145.3, 147.8, 148.1, 148.4, 149.0, 149.6, and 152.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{37}O_8S$, 665.2209; Found 665.2208.

Conversion of 3f to the acetate derivative (30). Triethylamine (42 μL, 0.3 mmol) and a solution of acetic anhydride (28 μL, 0.3 mmol) in CH_2Cl_2 (5 ml) were added

dropwise to a solution of **3f** (51.1 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the acetate derivative.

*Bridged oxocine (**30**).* Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (3H, s), 3.33 (1H, br s), 3.64 (1H, br s), 3.69 (3H, s), 3.85 (3H, s), 3.86 (3H, s), 3.95 (3H, s), 4.43 (1H, d, J = 1.7 Hz), 5.40 (1H, t, J = 1.7 Hz), 6.38 (1H, s), 6.56 (1H, dd, J = 8.3, 2.0 Hz), 6.70 (1H, d, J = 2.0 Hz), 6.74 (1H, dd, J = 7.8, 1.6 Hz), 6.80 (1H, d, J = 8.3 Hz), 6.90 (1H, dd, J = 7.8, 1.6 Hz), 6.92 (1H, td, J = 7.8, 1.6 Hz), 6.97 (1H, s), 7.02 (1H, td, J = 7.8, 1.6 Hz), 7.10 (1H, td, J = 7.8, 1.6 Hz), 7.15 (1H, td, J = 7.8, 1.6 Hz), 7.33 (1H, dd, J = 7.8, 1.6 Hz), and 7.37 (1H, dd, J = 7.8, 1.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 20.4, 30.0, 43.1, 55.8, 55.9, 56.0, 56.2, 73.8, 111.2, 111.8, 112.6, 112.7, 117.0, 120.9, 121.4, 122.2, 125.2, 126.3, 127.7, 128.3, 128.4, 128.5, 129.1, 129.5, 133.1, 137.0, 148.0, 148.2, 148.9, 149.1, 149.6, 151.8, and 169.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{33}O_7$, 553.2226; Found 553.2219.

Conversion of 3f to the *p*-bromobenzoate derivative (31). Triethylamine (21 μL, 0.15 mmol) and a solution of *p*-bromobenzoate chloride (32.9 mg, 0.15 mmol) in CH_2Cl_2 (5 ml) were added dropwise to a solution of **3f** (51.1 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) at 0 ˚C. The reaction mixture was stirred at room temperature with TLC monitoring. Upon completion, hydrochloric acid (5%) was added and the mixture 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 (Chromatotron) to yield the acetate derivative.

*Bridged oxocine (**31**).* Light yellowish oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.37 (1H, br s), 3.62 (3H, s), 3.63 (3H, s), 3.71 (3H, s), 3.74 (1H, br s), 3.91 (3H, s), 4.38 (1H, d, J = 2.0 Hz), 5.43 (1H, t, J = 2.0 Hz), 6.30 (1H, s), 6.34 (1H, dd, J = 8.4, 1.6 Hz), 6.37 (1H, d, J = 8.4 Hz), 6.48 (1H, d, J = 1.6 Hz), 6.73 (1H, dd, J = 7.6, 1.6 Hz), 6.91 (1H, s), 6.94 (1H, td, J = 7.6, 1.6 Hz), 7.01 (1H, dd, J = 7.6, 1.6 Hz), 7.04 (1H, td, J = 7.6, 1.6 Hz), 7.11 (1H, td, J = 7.6, 1.6 Hz), 7.20 (1H, td, J = 7.6, 1.6 Hz), 7.29 (1H, dd, J = 7.6, 1.6 Hz), 7.37 (1H, dd, J = 7.6, 1.6 Hz), 7.58 (2H, d, J = 8.8 Hz), and 7.79 (2H, d, J = 8.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 30.2, 42.9, 55.6, 55.76, 55.82, 56.0, 56.2, 74.1, 110.6, 111.8, 112.0, 112.6, 117.1, 121.1, 122.1, 125.4, 126.6, 127.87, 127.95, 128.4, 128.59, 128.64, 128.9, 129.0, 129.5, 131.4, 131.9, 133.5, 136.4, 147.5, 148.2, 148.8, 149.2, 149.6, 152.0, and 164.3; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{34}BrO_7$, 693.1488; Found 693.1463.

Removal of *N*-acetyl protecting group. A solution of the *N*-acetyl derivative (0.01 mmol) in a mixture of MeOH (1.6 mL), H_2O (0.2 mL), and conc. HCl (0.1 mL) was refluxed with TLC monitoring. Upon completion, the reaction mixture was diluted with water and K_2CO_3 was added to neutralize the solution. The reaction mixture was then extracted with EtOAc 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 deprotected compound.

Removal of *N*-CO_2Me protecting group. To a solution of the carbamate derivative (0.01 mmol) in a mixture MeOH (2 mL) and THF (1 mL) was added 5N NaOH (0.5 mmol, 50 equivs) at room temperature. The reaction mixture was refluxed with TLC monitoring. Upon completion, the reaction mixture was extracted with CH_2Cl_2 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 deprotected compound.

Removal of *N*-tosyl protecting group. To a solution of the *N*-tosyl derivative (0.01 mmol) in toluene (2 mL) was added sodium bis(2-methoxyethoxy)aluminium dihydride (8 μL, 0.04 mmol) in toluene (1 mL) at room temperature. The reaction mixture was refluxed with TLC monitoring. Upon completion, the reaction mixture was quenched with 5% HCl (1mL) and stirred for 1 h at room temperature. After filtration through Celite, the filtrate was extracted three times with 5% HCl. The combined aqueous layer was basified with Na_2CO_3 and was extracted with EtOAc, dried (Na_2SO_4) and concentrated under reduced pressure. The resulting residue was then fractionated by preparative radial chromatography to yield the corresponding deprotected compound.

Removal of *N*-nosyl protecting group. To a suspension of the *N*-nosyl derivative (0.01 mmol) and K_2CO_3 (4.1 mg, 0.03 mmol) in DMF, was added PhSH (2 μL, 0.02 mmol) at room temperature. The mixture was stirred at room temperature with TLC monitoring. Upon completion, the reaction mixture was extracted with EtOAc 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 deprotected compound. (Removal of the *N*-

nosyl groups from the bridged azocine **14f** was partially successful with removal of one of the nosyl groups, giving azocine **33**. Attempted removal of the remaining nosyl group in **33** led to decomposition of the compound.)

*Bisindole (**32**).* Light yellowish solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.74 (2H, d, J = 6.8 Hz), 3.80 (6H, s), 4.67 (2H, d, J = 6.8 Hz), 6.65 (4H, m), 6.70 (2H, d, J = 7.6 Hz), 6.83 (4H, d, J = 8.8 Hz), 7.08 (2H, t, J = 7.6 Hz), and 7.17 (4H, d, J = 8.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 54.1, 55.3, 65.1, 108.7, 113.9, 118.7, 124.8, 127.4, 128.0, 129.0, 136.9, 151.1, and 159.0; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{29}N_2O_2$, 449.2229; Found 449.2233 $[M + H]^+$.

*Bridged azocine (**33**).* Light yellowish solid; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.24 (1H, br s), 3.69 (3H, s), 3.85 (3H, s), 3.87 (3H, s), 3.96 (3H, s), 4.20 (1H, br d, J = 1.6 Hz), 4.47 (1H, br s), 4.64 (1H, br s), 6.42 (1H, s), 6.46 (1H, d, J = 7.6 Hz), 6.70 (1H, d, J = 1.9 Hz), 6.73 (1H, dd, J = 8.2, 1.9 Hz), 6.74 (1H, d, J = 7.4 Hz), 6.78 (1H, s), 6.83 (1H, t, J = 7.4 Hz), 6.86 (1H, d J = 8.2 Hz), 6.95 (1H, t, J = 7.6 Hz), 7.02 (3H, m), 7.15 (1H, br s), 7.41 (1H, d, J = 7.6 Hz), 7.62 (1H, td, J = 7.8, 1.0 Hz), 7.73 (1H, td, J = 7.8, 1.0 Hz), 7.83 (1H, dd, J = 7.8, 1.0 Hz), and 7.89 (1H, dd, J = 7.8, 1.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ 30.9, 44.8, 52.8, 55.8, 55.9, 56.0, 57.8, 110.6, 111.3, 112.4, 113.1, 115.6, 118.7, 121.5, 125.4, 125.67, 125.70, 127.0, 127.48, 127.54, 128.1, 129.1, 129.4, 131.8, 132.7, 133.1, 133.4, 133.6, 133.8, 137.5, 140.4, 142.3, 147.6, 148.1, 148.2, 148.6, and 148.9; HRMS (DART-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{36}N_3O_8S$, 694.2223; Found 694.2233.

Computational Methods. Structures corresponding to compounds **3d**, **3d′**, **8b**, **8g**, **12b**, and **12g** were initially built using GaussView 5 and then optimized at the

semiempirical level of theory (AM1). These structures were imported into the Gaussian 09 software[23] for DFT-level geometry optimization using the B3LYP functional with basis set 6−31G(d) or 6−31G+(d,p) to obtain the energy minimized conformations.

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Supporting Information

^{1}H and ^{13}C{^{1}H} NMR spectra for stilbenes and electrochemical oxidation products. Cyclic voltammograms of all starting stilbenes including traces showing effect of potential scan rates. X-ray structures and crystallographic data in CIF format for compounds **1a**, **1b**, **1c**, **1e**, **3a**, **6d**, **8g**, **9c**, **9g**, **10g**, **12c**, **12g**, **13c**, and **13f**. Calculated free energies, and Cartesian coordinates for **3d**, **3d′**, **8b**, **8g**, **12b**, and **12g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) In the case of stilbene **12** (carbamate), the corresponding bridged azocine product was not detected, instead the *meso*-dication derived bisquinoline **12g** was obtained in 5% yield.

(17) Such a comparison may not be entirely valid since it is not between a free -OH *versus* a free -NH_2, but against a protected NH_2 instead. In addition, based on the DFT-calculated energies, **8g** is more stable than **8b** by only 1.66 kcal mol^{-1}, while **12g** is more stable than **12b** by only 1.71 kcal mol^{-1} (see supporting information).

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