Lewis Acid-Controlled Regioselectivity in Reactions of Styrenyl Systems with Benzoquinone Monoimides: New Regioselective Syntheses of Substituted 2-Aryl-2,3-dihydrobenzofurans, 2-Aryl-2,3-dihydroindoles, and 2-Arylindoles

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Reactions of 4-(*N*-phenylsulfonyl)-2-alkoxy-1,4-benzoquinone monoimines **2**−**4** with electron-rich propenylbenzenes promoted by BF_3 yield 7-alkoxy-2-aryl-3-methyl-5-[(*N*-phenylsulfonyl)amino]-2,3-dihydrobenzofurans **5**−**7** nearly exclusively, whereas promotion of the reactions by Ti^{4+} gives mixtures of the dihydrobenzofurans and their *N*-(phenylsulfonyl)-6-alkoxy-2-aryl-5-hydroxy-3-methyl-2,3-dihydroindole isomers **8**−**10**, depending upon substituents present on the propenylbenzene. However, reactions promoted with excess Ti^{4+}, as mixtures of $TiCl_4$:$Ti(OiPr)_4$, give the dihydroindoles as nearly the exclusive products. Evidence for a mechanism involving initial 5 + 2 cycloaddition of the Lewis acid-bound quinone monoimide with the propenylbenzene is found in reactions of styrenes **1f/g** with monoimide **3** in which 7-aryl-3-hydroxy-6-methylbicyclo[3.2.1]oct-3-ene-2,8-diones **33** (5 + 2 adducts) are isolated. These reactions have been applied to stereoselective syntheses of pterocarpans bearing *N*-phenylsulfonyl groups, azapterocarpans and diazapterocarpans. In addition, DDQ oxidation of derivatives of several of the 2-aryl-2,3-dihydroindoles afford the corresponding 2-arylindoles in good yield. Finally, the experimental details of a general synthetic approach to 7-alkoxy-benzofuranoid neolignans, including (±)-licarin B and eupomatenoids-1 and −12 are reported.

Introduction

Substituted benzoquinones are remarkably versatile starting materials and reagents for synthesis.[1] Their cycloaddition reactions, for example, have been used in an impressive array of stereo- and regioselective syntheses of complex natural and non-natural products. We have recently developed Lewis acid-promoted cycloaddition reactions of quinones with styrenyl systems as efficient routes to 2-aryl-2,3-dihydrobenzofuran and bicyclo[3.2.1]octendione neolignans, and pterocarpan natural products and analogs.[2]

By comparison, reactions of quinone monoimides have received relatively little attention,[3] although their potential in synthetic applications is arguably as high or greater than that of the quinones. Herein, we report the details of an initial study to explore the scope, limitations, and potential for synthetic applications of Lewis acid-promoted reactions of styrenes with 2-alkoxy-4-(*N*-phenylsulfonyl)benzoquinone monimines.[4] Of particular note is that the regioselectivity of these reactions is determined by the nature of the Lewis acid promoter providing convenient access to either highly substituted 2-aryl-2,3-dihydrobenzofurans or 2-aryl-2,3-dihydroindoles from the same starting materials. Our interest in developing these reactions stems from the presence of 2-aryl-2,3-dihydrobenzofuran, -benzofuran, and 2-arylindole substructures in a wide variety of biologically active molecules.

Results and Discussion

BF_3-Promoted Reactions. Addition of styrenes **1a**−**c** bearing strong electron-donating substituents to solutions of imides **2**−**4** and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at low temperature resulted in the formation of dihydrobenzofurans **5**−**7** as the major, if not exclusive, products (eq 1 and Table 1). Small amounts of dihydroindoles **8**−**10** were found in some cases. Reactions of non-nucleophilic styrene **1d** required warming to room temperature, and even then only a low yield of **5d** was obtained. Attempted reactions of styrenes **1f/g**, without good electron-donating groups, failed to provide a product; only starting materials were evident by TLC. Reactions of acetoxystyrene **1e** also failed, perhaps due to competing complexation of the ester moiety with the Lewis acid.

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(1) (a) *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1988; Vol. II, Parts 1 and 2. (b) Bruce, J. M. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1974; Vol. III (Aromatic Compounds), Part B, Chapter 8. (c) See references cited in Engler, T. A.; Letavic, M. A.; Lynch, K. O., Jr.; Takusagawa, F. *J. Org. Chem.* **1994**, *59*, 1179−1183.

(2) (a) Engler, T. A.; Combrink, K. D.; Letavic, M. A.; Lynch, K. O., Jr.; Ray, J. E. *J. Org. Chem.* **1994**, *59*, 6567−6587. (b) Engler, T. A.; Wei, D.; Letavic, M. A.; Combrink, K. D.; Reddy, J. P. *J. Org. Chem.* **1994**, *59*, 6588−6599. (c) Engler, T. A.; Reddy, J. P.; Combrink, K. D.; Vander Velde, D. *J. Org. Chem.* **1990**, *55*, 1248−1254. (d) Engler, T. A.; Lynch, K. O., Jr.; Reddy, J. P.; Gregory, G. S. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 1229−1232. (e) Engler, T. A.; LaTessa, K. O.; Iyengar, R.; Chai, W.; Agrios, K. *Bioorg. Med. Chem.* **1996**, *7*, in press.

(3) (a) Brown, E. R. In *The Chemistry of Quinonoid Compounds*; Patai, S.; Rappoport, Z., Eds.; John Wiley and Sons: New York, 1988; Vol. II, Part 2, Chapter 21. (b) Adams, R.; Reifschneider, W. *Bull. Chim. Soc. Fr.* **1958**, 23−65.

(4) For preliminary reports, see (a) Engler, T. A.; Lynch, K. O., Jr.; Chai, W.; Meduna, S. P. *Tetrahedron Lett.* **1995**, *36*, 2713−2716. (b) Engler, T. A.; Chai, W.; Lynch, K. O., Jr. *Tetrahedron Lett.* **1995**, *36*, 7003−7006.

(5) Dihydroquinoline **12** was actually prepared and used as a 2−3:1 mixture of **12** and its 5-methoxy isomer. The minor component did not react in the Lewis acid-promoted reactions with the quinone monoimides and could be recovered cleanly; see references 2e and 4a.

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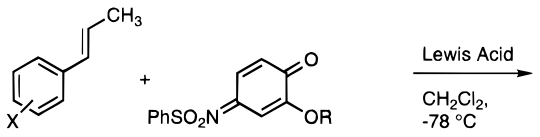
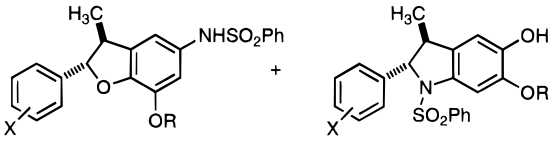


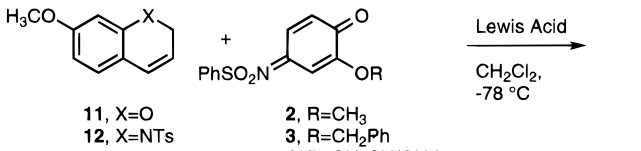
1a, X=4-OCH_3 **2**, R=CH_3
1b, X=3,4-$(OCH_3)_2$ **3**, R=CH_2Ph
1c, X=3,4-OCH_2O- **4**, R=$CH_2CH(CH_3)_2$
1d, X=4-CH_3
1e, X=4-OAc
1f, X=H
1g, X=3-OCH_3

(1)



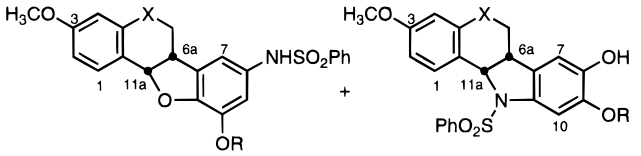
5, R=CH_3 **8**, R=CH_3
6, R=CH_2Ph **9**, R=CH_2Ph
7, R=$CH_2CH(CH_3)_2$ **10**, R=$CH_2CH(CH_3)_2$

In a similar manner, reactions of 2*H*-chromene **11** and dihydroquinoline **12**[5] were also examined (eq 2). These electron-rich styrenyl systems also gave dihydrobenzofuran-type products nearly exclusively and in generally good yield (Table 1).



11, X=O **2**, R=CH_3
12, X=NTs **3**, R=CH_2Ph
4, R=$CH_2CH(CH_3)_2$

(2)



13, X=O, R=CH_3 **19**, X=O, R=CH_3
14, X=O, R=CH_2Ph **20**, X=O, R=CH_2Ph
15, X=O, R=$CH_2CH(CH_3)_2$ **21**, X=O, R=$CH_2CH(CH_3)_2$
16, X=NTs, R=CH_3 **22**, X=NTs, R=CH_3
17, X=NTs, R=CH_2Ph **23**, X=NTs, R=CH_2Ph
18, X=NTs, R=$CH_2CH(CH_3)_2$ **24**, X=NTs, R=$CH_2CH(CH_3)_2$

The structures of dihydrobenzofurans **5**−**7** and **13**−**18** are assigned by mass spectra, the presence of a sulfonamide N−H stretch at ∼3360 cm^{-1} in their IR spectra, and by NMR studies, including NOE and 2D experiments. The signals for H-4 and H-6 in **5**−**7**, and H-7 and H-9 in **13**−**18**, appear as doublets (J = 1−2 Hz) or broadened singlets at ∼6.38−6.52 and 6.48−6.54 ppm, respectivley. $^1H-^1H$ Decoupling or COSY experiments confirmed that these signals were coupled. The position of the alkoxy group on the benzofuran ring was further established by HETCOR and HMBC experiments on **5b** (Figure 1). In their ^1H-NMR spectra, the H-2 and C-3 CH_3 signals appear at 5.03−5.12 and 1.24−1.27 ppm, respectively, with $J_{H-2/H-3} \sim 9$ Hz. Similarly, signals for H-11a in **13**−**15** are observed at ∼5.5 ppm, and those for **16**−**18** at ∼5.1 ppm; $J_{H-11a/H-6a}$ are ∼7−8 Hz. In **5b/6b**, strong $^1H-^1H$ NOE's are observed between the C-3 methyl and both H-2 and H-4 (Figure 2), and also between H-6a and H-11a in **15** and **17**, confirming the stereochemistry. The spectra of the other dihydrobenzofurans are very similar to those of **5b/6b** and **15/17**, and their structures are assigned by analogy.

The formation of the major products in the BF_3-promoted reactions can be explained by regioselective activation[7] of the quinone monoimides by coordination of the BF_3 to the basic sulfonyl nitrogen to afford complex **25** (Scheme 1). Cycloaddition[2] with the styrenyl C=C bond of **1** gives intermediate **26** which proceeds on to the observed products by fragmentation to **27** followed by C−O bond formation and loss of H^+. Alternatively, simple alkylation of **25** by the styrene may afford **27** directly which then proceeds on to **5**−**7**.[8] Formation of **13**−**18** likely occur in an analogous manner. The cycloaddition route is suggested by similar processes postulated in Lewis acid-promoted reactions of 1,4-benzoquinones with styrenes.[2]

Ti(IV)/Sn(IV)-Promoted Reactions. The results of reactions of the styrenes with the quinone monoimides promoted by Ti(IV) or Sn(IV) were influenced by the substituents on the styrenes and, to a lesser extent, on the monoimide (Table 2). More significantly, the number of equiv of Lewis acid used had a dramatic impact. Initial experiments focused on electron-rich styrenyl systems **1b/c**, **11**, and **12**. Reactions with 1 equiv of Lewis acid produced either or both of the dihydrobenzofuran- or the dihydroindole-type products as major products. Different combinations of $TiCl_4$ and $Ti(OiPr)_4$ were surveyed because of the varying sensitivity of the styrenes to strongly acidic conditions.

The different $TiCl_4$:$Ti(OiPr)_4$ mixtures vary significantly in acidity, and this is but one of a number of issues that confound a simple analysis of the data and prevent a clear pattern from emerging. As a bidentate Lewis acid, Ti^{4+} might be expected to complex with the C-1 carbonyl and C-alkoxy oxygens of the monoimide and activate C-3 and C-5 to cycloaddition with, or alkylation

(6) The styrenes were purchased, or made,[15] and used as is; **1a/f** were ∼100% *(E)*, whereas the others were 3.5−15:1 mixtures of *(E)*:*(Z)*-isomers. The *(Z)*-isomer did not react competitively with the *(E)*-isomer; see reference 2a for a discussion of the relative rates of reactions of *(E)* vs *(Z)* styrenes with quinones.

(7) Regioselective Lewis acid-activation of quinone bisimides has been described in some detail by Boger and others. See reference 3 and (a) Boger, D. L.; Zarrinmayeh, H. *J. Org. Chem.* **1990**, *55*, 1379−1390. (b) Boger, D. L.; Coleman, R. S. *J. Am. Chem Soc.* **1988**, *110*, 4796−4807. (c) Holmes, T. J., Jr.; Lawton, R. G. *J. Org. Chem.* **1983**, *48*, 3146−3150. Similarly, regioselective activation of substituted quinones has been reported. (d) Tou, J. S.; Reusch, W. *J. Org. Chem.* **1980**, *45*, 5012−5014. (e) Dickinson, R. A.; Kubela, R.; MacAlpine, G. A.; Stojanac, Z.; Valenta, Z. *Can. J. Chem.* **1972**, *50*, 2377−2380. (f) Stojanac, Z.; Dickinson, R. A.; Stojanac, N.; Woznow, R. J.; Valenta, Z. *Can. J. Chem.* **1975**, *53*, 616−618. (g) Das, J.; Kubela, R.; MacAlpine, G. A.; Stojanac, Z.; Valenta, Z. *Can J. Chem.* **1979**, *57*, 3308−3319. For reasons that are not clear, results of some Ti(IV)-promoted quinone Diels−Alder reactions do not always fit this generalization; see, for examples, (h) Hendrickson, J. B.; Singh, V. *J. Chem. Soc., Chem. Commum.* **1983**, 837−838. (i) Hendrickson, J. B.; Haestier, A. M.; Stieglitz, S. G.; Foxman, B. M. *New J. Chem.* **1990**, *14*, 689−693. (j) Engler, T. A.; Letavic, M. A.; Lynch, K. O., Jr.; Takusagawa, F. *J. Org. Chem.* **1994**, *59*, 1179−1183.

(8) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, S.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 2135−2143.

(9) Several studies indicate that with some carbonyl compounds $TiCl_4$ forms either 2:1 or 1:1 C=O:$TiCl_4$ complexes depending upon stoichiometry. In addition, the stereochemistry of Lewis acid-promoted allylmetal−aldehyde reactions is dependent upon stoichiometry. Thus, the complexes formed from the quinone monoimides with 1 equiv of Ti^{4+} may not be 1:1 complexes as represented herein; i.e. with 1 equiv of Ti(IV), 2:1 monoimide:Ti(IV) complexes may be present, whereas excess Ti(IV) may shift an equilibrium to 1:1, and therefore bidentate, complexes. Furthermore, concerns regarding the Curtin−Hammett principle may be relevant to the results presently described. For leading references and pertinent discussions, see, (a) Turin, E.; Nielson, R.M.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *134*, 79−85, 67−78. (b) Bachand, B.; Wuest, J. D.; *Organometallics* **1991**, *10*, 2015−2025. (c) Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565−5578. (d) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133−3139. (e) Springer, J. B.; DeBoard, J.; Corcoran, R. C. *Tetrahedron Lett.* **1995**, *36*, 8733−8736. For other discussions of carbonyl−(Lewis acid)$_2$ complexes as potential intermediates, see reference 2b and references cited therein.

Table 1. BF_3·OEt_2-Promoted Reactions of Styrenyl Systems 1 and 11/12 with Quinone Monoimides 2−4[a]

entry	styrene: X[b]	monoimide: R	temp (°C)	time (h)	product(s)[c]	(% yields)[d]
1	**1a**: 4-OCH_3	**2**: CH_3	−78	<1	**5a** (91)	**8a** (8)
2	**1b**: 3,4-$(OCH_3)_2$	**2**: CH_3	−78	<1	**5b** (81)	**8b** (1)
3	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	−78	<1	**6b** (86)	*e*
4	**1b**: 3,4-$(OCH_3)_2$	**4**: $CH_2CH(CH_3)_2$	−78	<1	**7b** (89)	**10b** (10)
5	**1c**: 3,4-OCH_2O	**2**: CH_3	−78	<1	**5c** (82)	**8c** (13)
6	**1c**: 3,4-OCH_2O	**3**: CH_2Ph	−78	<1	**6c** (73)	**9c** (8)
7	**1c**: 3,4-OCH_2O	**4**: $CH_2CH(CH_3)_2$	−78	<1	**7c** (48)	−
8	**1d**: 4-CH_3	**2**: CH_3	−78 to rt	16	**5d** (14)	−
9	**1e**: 4-OAc	**2**: CH_3	−78 to rt	16	−	−
10	**1f**: H	**2**: CH_3	−78 to rt	16	−	−
11	**1g**: 3-OCH_3	**3**: CH_2Ph	−78	<1	−	−
12	**11**: O	**2**: CH_3	−78	<1	**13** (87)	−
13	**11**: O	**3**: CH_2Ph	−78	<1	**14** (91)	−
14	**11**: O	**4**: $CH_2CH(CH_3)_2$	−78	<1	**15** (81)	**21** (2)
15	**12**: NTs	**2**: CH_3	−78	<1	**16** (70)	−
16	**12**: NTs	**3**: CH_2Ph	−78	<1	**17** (53)	−
17	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	−78	<1	**18** (29)	−

[a] All reactions were done in CH_2Cl_2 with 1−1.3 equiv of BF_3·OEt_2 (with respect to the monoimide) as promoter. [b] Used as (*E*):(*Z*) mixtures as purchased or prepared (see reference 6). [c] Substituents X and R same as starting **1**/**2**−**4**. [d] Isolated yields. [e] Indicates that this product was not isolated.

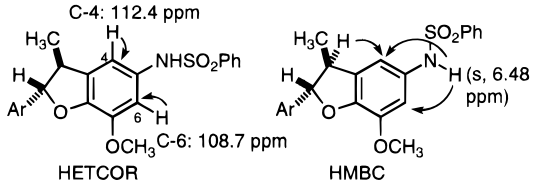


Figure 1. Selected data from HETCOR and HMBC experiments on **5b**.

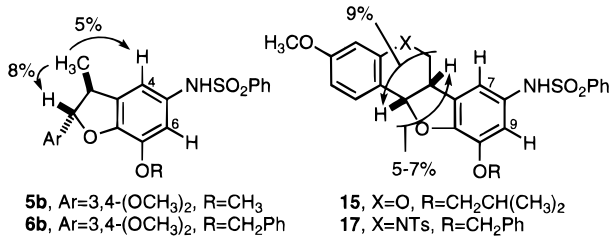
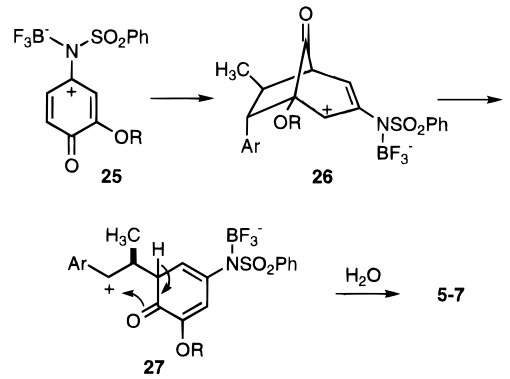


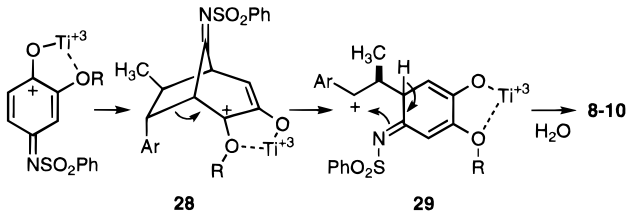
Figure 2. Summary of selected NOE data on **5b**/**6b** and **15**/**17**.

Scheme 1

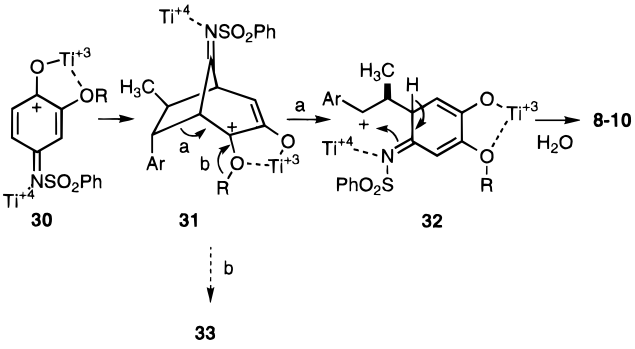


by, the styrene ultimately resulting in dihydroindole products **8**−**10**/**19**−**24** (Scheme 2). On the other hand, monodentate binding to the sulfonyl nitrogen moiety would lead to the dihydobenzofuran products **5**−**7**/**13**−**18** (vide supra). It is not clear which mode of complexation should prevail.[9] Indeed, an equilibrium between the two is possible, and the different steric bulk and electronics of the alkoxy R groups may influence the complexation and/or the cycloaddition step. In addition, most of the styrenes also possess basic groups which may

Scheme 2



Scheme 3



compete with the monoimides for complexation with the Lewis acid and alter the electronics of the styrene C=C, or act as ligands in addition to the monoimide. This is perhaps particularly important in reactions of styrenes **1b** and **11** and quinoline **12**. Finally, different styrenes may react via different mechanisms, i.e. nucleophilic styrenes via an alkylation process directly accessing the benzylic carbocations **27** or **29**, and non-nucleophilic styrenes via cycloaddition processes in which intermediate bicyclo[3.2.1] adducts are formed. In the latter process, bicyclic-cationic intermediate **28** should be preferred over **26** due to stabilization of the positive charge by oxygen.

To avoid the complications due to these mechanistic issues, and others,[9] reactions with greater than 2−3 equiv of the Lewis acid were studied anticipating that monoimide-$[Ti^{4+}]_2$ complexes **30** might be formed as reactive species (Scheme 3). In such complexes, it is not unreasonable to suspect that C-5 or C-3/C-5 would be the more reactive site(s) if, as suggested by the reactions promoted by 1 equiv of BF_3, the C-4 imide nitrogen is the most basic site; i.e. attachment of a second equivalent of the Lewis acid to the C-1 carbonyl and C-2 alkoxy

Table 2. Ti(IV)/Sn(IV)-Promoted Reactions of Styrenyl Systems 1 and 11/12 with Quinone Monoimides 2−4[a]

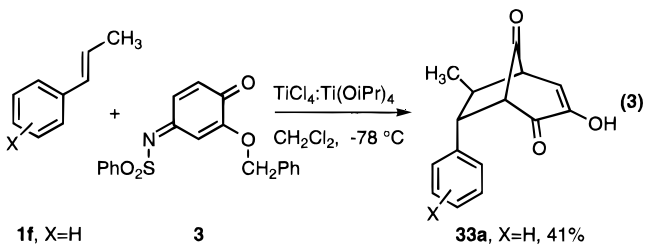
entry	styrene: X[b]	monoimide: R	Lewis acid	temp (°C)	time (h)	product(s)[c]	(% yields)[d]
1	**1a**: OCH_3	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)[e]	−78	<1	**5a** (8)	**8a** (82)
2	**1a**: OCH_3	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78 to rt	16	**5a** (13)	**8a** (76)
3	**1a**: OCH_3	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (6)	−78	<1	**5a** (3)	**8a** (81)
4	**1b**: 3,4-$(OCH_3)_2$	**2**: CH_3	$TiCl_4$ (1)	−78	<1	**5b** (80)	*f*
5	**1b**: 3,4-$(OCH_3)_2$	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**5b** (23)	**8b** (57)
6	**1b**: 3,4-$(OCH_3)_2$	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (6)	−78	<1	**5b** (11)	**8b** (60)
7	**1b**: 3,4-$(OCH_3)_2$	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (10)	−78	<1	−	**8b** (89)
8	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**6b** (76)	**9b** (21)
9	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	**6b** (63)	**9b** (9)
10	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	2:1 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	**6b** (65)	−
11	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (5)	−78	<1	**6b** (31)	**9b** (40)
12	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	1:2 $TiCl_4$:$Ti(OiPr)_4$ (7.5)	−78	<1	−	**9b** (100)
13	**1b**: 3,4-$(OCH_3)_2$	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (10)	−78	<1	**6b** (4)	**9b** (79)
14	**1b**: 3,4-$(OCH_3)_2$	**4**: $CH_2CH(CH_3)_2$	$TiCl_4$ (1)	−78	<1	**7b** (44)	**10b** (19)
15	**1b**: 3,4-$(OCH_3)_2$	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78	<1	**7b** (77)	**10b** (7)
16	**1b**: 3,4-$(OCH_3)_2$	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78	<1	**7b** (35)	**10b** (64)
17	**1b**: 3,4-$(OCH_3)_2$	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (10)	−78	<1	**7b** (3)	**10b** (64)
18	**1c**: 3,4-OCH_2O	**2**: CH_3	$TiCl_4$ (1)	−78	<1	−	**8c** (25)
19	**1c**: 3,4-OCH_2O	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78	<1	−	**8c** (52)
20	**1c**: 3,4-OCH_2O	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	−	**8c** (67)
21	**1c**: 3,4-OCH_2O	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (7.5)	−78	<1	−	**8c** (73)
22	**1c**: 3,4-OCH_2O	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**6c** (29)	**9c** (59)
23	**1c**: 3,4-OCH_2O	**3**: CH_2Ph	1:2 $TiCl_4$:$Ti(OiPr)_4$ (7.5)	−78	<1	−	**9c** (59)
24	**1c**: 3,4-OCH_2O	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (10)	−78	<1	−	**9c** (67)
25	**1c**: 3,4-OCH_2O	**4**: $CH_2CH(CH_3)_2$	$TiCl_4$ (1)	−78	<1	−	**10c** (13)
26	**1c**: 3,4-OCH_2O	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78	<1	**7c** (9)	**10c** (60)
27	**1c**: 3,4-OCH_2O	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	−	**10c** (87)
28	**1c**: 3,4-OCH_2O	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (10)	−78	<1	−	**10c** (93)
29	**1d**: 4-CH_3	**2**: CH_3	$TiCl_4$ (2)	−78	<1	−	**8d** (61)
30	**1d**: 4-CH_3	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78 to rt	16	NR	NR
31	**1d**: 4-CH_3	**2**: CH_3	$TiCl_4$ (4)	−78	<1	−	**8d** (45)
32	**1d**: 4-CH_3	**2**: CH_3	2:1 $TiCl_4$:$Ti(OiPr)_4$ (14)	−78	<1	−	**8d** (74)
33	**1e**: 4-OAc	**2**: CH_3	$TiCl_4$ (4)	−78	<1	−	**8e** (18)
34	**1f**: H	**2**: CH_3	$TiCl_4$ (1)	−78	<1	−	**8f** (75)
35	**1f**: H	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	16	−	**8f** (6)
36	**11:** O	**2**: CH_3	$SnCl_4$ (1)	−78	<1	**13** (85)	−
37	**11:** O	**2**: CH_3	$TiCl_4$ (1)	−78	<1	**13** (90)	−
38	**11:** O	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**13** (15)	**19** (34)
39	**11:** O	**2**: CH_3	1:2 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	−	**19** (48)
40	**11:** O	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1.3)	−78	<1	**14** (9)	**20** (38)
41	**11:** O	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	−	**20** (41)
42	**11:** O	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (4)	−78	<1	−	**20** (51)
43	**11:** O	**4**: $CH_2CH(CH_3)_2$	$TiCl_4$ (1)	−78	<1	**15** (15)	**21** (15)
44	**11:** O	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**15** (2)	**21** (55)
45	**11:** O	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	−	**21** (57)
46	**12**: NTs	**2**: CH_3	$TiCl_4$ (1)	−78	<1	**16** (10)	−
47	**12**: NTs	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78 to rt	16	NR	NR
48	**12**: NTs	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78 to rt	16	NR	NR
49	**12**: NTs	**2**: CH_3	1:1 $TiCl_4$:$Ti(OiPr)_4$ (4)[g]	−78 to rt	16	NR	NR
50	**12**: NTs	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**17** (60)	**23** (24)
51	**12**: NTs	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**17** (41)	**23** (27)
52	**12**: NTs	**3**: CH_2Ph	2:1 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	**17** (51)	**23** (19)
53	**12**: NTs	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (3.4)	−78	<2	**17** (26)	**23** (48)
54	**12**: NTs	**3**: CH_2Ph	1:1 $TiCl_4$:$Ti(OiPr)_4$ (4)[g]	−78	<1	**17** (32)	**23** (44)
55	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (1)	−78	<1	**18** (12)	−
56	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**18** (46)	**24** (31)
57	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (2)	−78	<1	**18** (41)	**24** (28)
58	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	2:1 $TiCl_4$:$Ti(OiPr)_4$ (3)	−78	<1	**18** (47)	**24** (15)
59	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (3.4)	−78	<1	**18** (37)	**24** (55)
60	**12**: NTs	**4**: $CH_2CH(CH_3)_2$	1:1 $TiCl_4$:$Ti(OiPr)_4$ (4)[g]	−78	<1	**18** (10)	**24** (50)

[a] All reactions were done in CH_2Cl_2. [b] Used as (*E*):(*Z*) mixtures as purchased or prepared (see reference 6). [c] Substituents X and R same as starting **1** and **2**−**4**. [d] Isolated yields. [e] Total equivalents of Ti(IV)/Sn(IV) with respect to the monoimide. [f] Indicates that this product was not isolated. [g] Larger amounts of Ti(IV) led to much decomposition.

oxygens would perhaps be more activating than complexation of the first Ti^{4+}. In these reactions, the dihydroindoles were uniformly formed as the major products in good yield, accompanied by lesser amounts of the dihydrobenzofurans. Reactions promoted by large amounts of Ti(IV) were best conducted with mixtures of $TiCl_4$:$Ti(OiPr)_4$ to minimize degradation of the styrene or monoimide. In general, for any one styrene-monoimide combination, the more Ti(IV) used as promoter, the higher the dihydroindole:dihydrobenzofuran product ratio. Unfortunately, some of the styrenes did not stand up to large amounts of Ti(IV), particularly **11** and **12**, preventing high yields or optimization of the dihydroindole:dihydrobenzofuran product ratio in these cases. Although the intermediacy of monoimide−$[Ti^{4+}]_2$ complexes is not unequivocally established, the data convincingly demonstrate that reversal of regioselectivity can be achieved by use of large amounts of Ti(IV) Lewis acids as promoters. We are continuing to examine these phenomena.

Finally, Ti(IV)-promoted reactions of styrenes **1f/g** (X = H/3-OCH_3) with quinone monoimide **3** gave bicyclo-

[3.2.1] adducts **33** (eq 3). Large amounts of Ti(IV)-



1f, X=H **1g**, X=3-OCH_3 **3** **33a**, X=H, 41% **33b**, X=OCH_3, 49%

promoter were required to sufficiently activate the monimides to reaction, presumably because of the lower nucleophilicity of these styrenes. These products, which were also obtained in reactions of quinones with styrenes, support a cycloaddition mechanism (Scheme 3).[2] We reason that cycloaddition of **30** with the styrene gives intermediate **31** which proceeds on to the observed products by fragmentation to **32** followed by C−N bond formation and loss of H^+ (path a) or by dealkylation and hydrolysis of the bridging sulfonylimine (path b).[10] With electron-rich styrenes **1a**−**c**, the dihydroindoles **8**−**10** are formed because the fragmentation is faster than dealkylation due to stabilization of the benzylic carbocation in **32** by the aryl ring. With more neutral styrenyl systems **1f/g**, and with an R group that is easily displaced (e.g. CH_2Ph) presumably by Cl^- in either an S_N1 or S_N2 fashion, dealkylation competes.[2a,b] Nevertheless, the data do not exclude the alkylation/cyclization alternative since **32** may also cyclize to **31** and then undergo dealkylation/hydrolysis to **33**.

Structural assignments for dihydroindoles **8**−**10** and **19**−**24** are supported by the observance of molecular ions in their mass spectra and an O−H stretch at 3540 cm^{-1} in the their IR spectra. Signals for H-4 in **8**−**10** appear as singlets at ∼6.56−6.58 ppm in their ^1H NMR spectra (signals for H-7 are buried at ∼7.4 ppm). The H-2 and C-3 CH_3 resonances are found at 4.48−4.60 and 0.63−0.68 ppm, respectively. Again, strong $^1H-^1H$ NOE's are observed between the C-3 methyl and both H-2 and H-4 in **8b/9c** (Figure 3), supporting a cis stereochemistry between the CH_3 and H-2. Although the C-3 CH_3 chemical shifts are upfield, H-2/H-3 coupling constants of ∼3 Hz are also considerably different than those found in the dihydrobenzofurans **5-7** (vide supra). A possible explanation is some type of $\pi-\pi$ interaction between the *N*-phenylsulfonyl moiety and the C-2 aryl groups significantly altering the H-2/H-3 dihedral angle.[11] The spectra of the other dihydroindoles are very similar to those of **8b/9c**, and the structures are assigned by analogy.

For azapterocarpans **19**−**21**, signals for H-11a appear at 5.35−5.53 ppm and $J_{H-11a/H-6a}$ are ∼8 Hz; in diazapterocarpans **22**−**24**, the H-11a signals are found at ∼4.4 ppm with $J_{H-11a/H-6a}$ ∼9.5 Hz. In the former series, H-7 are observed as singlets at ∼6.7 ppm and in the latter series, these signals are found at ∼6.5 ppm. Finally, $^1H-^1H$ NOE experiments on **21**/**24** confirm the ring fusion stereochemistry.

Synthetic Applications. 2-Arylindoles possessing C-1/3 alkyl substituents and oxygen substitution on both

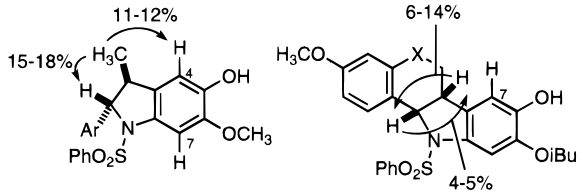


Figure 3. Summary of selected NOE data on **8b**/**9c** and **21**/**24**.

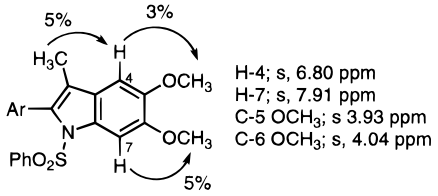
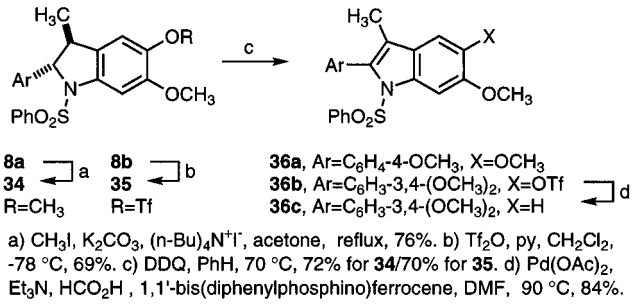


Figure 4. Summary of selected NOE data on **36a**.

Scheme 4



a) CH_3I, K_2CO_3, $(n\text{-}Bu)_4N^+I^-$, acetone, reflux, 76%. b) Tf_2O, py, CH_2Cl_2, -78 °C, 69%. c) DDQ, PhH, 70 °C, 72% for **34**/70% for **35**. d) $Pd(OAc)_2$, Et_3N, HCO_2H , 1,1'-bis(diphenylphosphino)ferrocene, DMF, 90 °C, 84%.

the indole nucleus and the C-2 aryl group display significant antiestrogenic activity.[12] Since Ti(IV)-promoted reactions of styrenes **1a**−**c** with the monoimides provide dihydroindoles **8**−**10** in good yield, their direct oxidation to the corresponding indoles were examined. Attempted reactions of the free phenols with DDQ produced extensive decomposition, perhaps due to oxidation of the phenolic moiety. However, conversion of the phenol moiety in **8a** and **8b** to methyl ether **34** and triflate **35**, respectively, followed by DDQ oxidation afforded indoles **36a/b** in good yields (Scheme 4). To further demonstrate the potential of this approach for synthesis of other indoles, a Pd(0)-catalyzed reduction of triflate **36b** was carried out producing **36c** in good yield. The latter reaction suggests that similar Pd(0)-promoted alkenyl-/alkynyl-/arylations or carbonylations could be used to access a wide variety of 2-arylindoles for SAR studies. In addition to the NMR/NOE studies carried out on dihydroindoles **8**−**10**, similar experiments on indole **36a** further confirm the position of the C-6 alkoxy group (Figure 4).

Pterocarpans are naturally occurring plant products possessing the fused benzofuranyl-benzopyran ring system. Many are phytoalexins displaying potent antifungal and antibacterial activity.[2c] In addition, several pterocarpans have been reported to inhibit HIV-1 reverse transcriptase and the cytopathic effect of HIV-1 in cell culture.[2] These novel anti-HIV agents represent new lead structures for potential drug development. The SAR

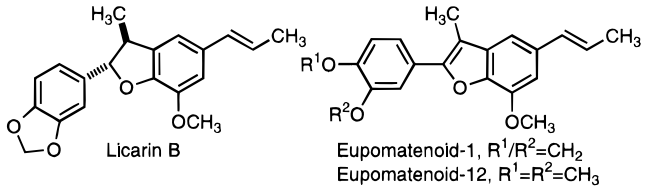
(10) The hydrolysis of the bridging *N*-(phenylsulfonyl)imine, either on workup or silica gel chromatography, is remarkably facile. Even though a basic workup was used, we were unable to find, or detect, a product with this group intact.

(11) Eto, M.; Ito, F.; Kitamura, T.; Harano, K. *Heterocycles* **1996** *43*, 1159−1163.

(12) (a) von Angerer, E.; Knebel, N.; Kager, M.; Ganss, B. *J. Med. Chem.* **1990**, *33*, 2635−2640. (b) von Angerer, E.; Prekajac, J.; Berger, M. *Eur. J. Cancer Clin. Oncol.* **1985**, *21*, 531−537. (c) von Angerer, E.; Strohmeier, J. *J. Med. Chem.* **1987**, *30*, 131−136. (d) von Angerer, E.; Prekajac, J.; Strohmeier, J. *J. Med. Chem.* **1984**, *27*, 1439−1447. (e) von Angerer, E.; Prekajac, J. *J. Med. Chem.* **1983**, *26*, 113−116.

profiles of the pterocarpans have not been comprehensively examined, particularly regarding potential nitrogen bioisosteres, and there has been recent interest in synthesis of azapterocarpans.[4,13] The development of the reactions employing 2*H*-chromene **11** and dihydroquinoline **12** as the styrenyl components described above were in fact explored with the intent of developing an efficient route to amino-substituted pterocarpans, and aza- and diazapterocarpan isosteres. As described, all of the desired products can be obtained in reasonably good to excellent yields.

Finally, we have recently reported a route to 7-alkoxy-2-arylbenzofuranoid neolignans licarin B and eupomatenoids-1 and −12 starting from **5b/c**.[14] Full experimental details for these syntheses are presented in the supporting information. We are presently exploring further applications of this new methodology.



Experimental Section[15]

***N*-(3-Methoxy-4-oxo-2,5-cyclohexadien-1-ylidene)benzenesulfonamide (2).** A solution of ceric ammonium nitrate (14.67 g, 26.76 mmol) in H_2O (40 mL) was added dropwise rapidly to a solution of *N*-(3,4-dimethoxyphenyl)benzenesulfonamide[16] (2.63 g, 8.96 mmol) in acetonitrile (35 mL). The reaction mixture was stirred for 10 min and then diluted with CH_2Cl_2 (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 40 mL). The combined extracts were washed with water (2 × 100 mL) and brine (150 mL), dried (Na_2SO_4), decanted, and concentrated to a dark orange oil. Chromatography (2:2:6 CH_2Cl_2:Et_2O:hexanes) afforded monoimide **2** (1.60 g, 64%) as a bright yellow powder, mp 135−136 °C (EtOAc/hexanes); R_f 0.32 (2:2:6 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (300 MHz) 8.03 (d, J = 7.4, 2H), 7.71−7.50 (m, 3H), 7.27 (d, J = 2.4, 1H), 6.92 (dd, J = 2.4, 10, 1H), 6.67 (d, J = 10, 1H), 3.97 (s, 3H); ^{13}C NMR (75 MHz) 180.1, 165.2, 157.3, 141.4, 133.9, 133.5, 130.5, 129.1, 127.4, 102.0, 56.8. Anal. Calcd for $C_{13}H_{11}NO_4S$: C, 56.30; H, 4.01; N, 5.05. Found: C, 56.60; H, 3.76; N, 4.80.

***N*-[3-(Benzyloxy)-4-oxo-2,5-cyclohexadien-1-ylidene]benzenesulfonamide (3). A) *N*-[3-(Benzyloxy)-4-methoxyphenyl]benzenesulfonamide.** 2-(Benzyloxy)-1-methoxy-4-nitrobenzene[17] (1.60 g, 6.17 mmol) was dissolved in 1:1 EtOH:EtOAc (32 mL). The solution was heated to 70 °C, and $SnCl_2$·$2H_2O$ (6.16 g, 27.3 mmol) was added. The reaction mixture was stirred for 7 h, cooled to rt, diluted with water (50 mL), and neutralized by the careful addition of solid $NaHCO_3$. The aqueous layer was separated and extracted with EtOAc (3 × 20 mL). The combined extracts were washed with H_2O (50 mL) and brine (65 mL), dried (Na_2SO_4), filtered, and concentrated to give the corresponding amine as a red solid (1.21 g, 86%). The amine was used routinely without further purification.

Pyridine (0.67 mL, 8.3 mmol) and benzenesulfonyl chloride (1.0 mL, 7.84 mmol) were added to a solution of the amine prepared above (1.72 g, 7.5 mmol) in THF (250 mL). The reaction mixture was stirred for 22 h at rt, diluted with H_2O (100 mL), and acidified with concentrated aqueous HCl (100 mL, pH ∼ 1−2). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 75 mL). The combined extracts were washed with 10% aqueous HCl (150 mL), H_2O (2 × 150 mL), and brine (200 mL) and dried ($MgSO_4$). The solution was treated with charcoal, filtered through Celite, and concentrated to a purple oil. Addition of hexanes gave a light purple solid. Recrystallization from EtOH gave the title compound (2.45 g, 88%) as a light tan solid, mp 144−145 °C; R_f 0.20 (2:5 EtOAc:hexanes); ^{1}H NMR (300 MHz) 7.61 (d, J = 8.5, 2H), 7.54−7.30 (m, 8H), 6.76 (d, J = 2.4, 1H), 6.69 (d, J = 8.6, 1H), 6.56 (bs, 1H), 6.49 (dd, J = 2.4, 8.6, 1H), 5.05 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz) 148.2, 148.1, 138.7, 136.6, 132.8, 129.0, 128.9, 128.6, 128.0, 127.4, 127.3, 116.1, 111.8, 110.1, 70.9, 56.1; HRMS m/z 369.1045 (M^+) (calcd for $C_{20}H_{19}NO_4S$ 369.1035).

(B) Monoimide 3. A solution of ceric ammonium nitrate (8.90 g, 16.2 mmol) in H_2O (15 mL) was added quickly dropwise to a solution of *N*-[3-(benzyloxy)-4-methoxyphenyl]benzenesulfonamide (2.00 g, 5.41 mmol) in CH_3CN (8 mL) at 0 °C. The ice bath was removed, and the reaction mixture was stirred at rt for 15 min and then diluted with CH_2Cl_2 (50 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (60 mL), dried (Na_2SO_4), decanted, and concentrated to an orange oil. Chromatography (2:2:6 CH_2Cl_2:Et_2O:hexanes) afforded monoimide **3** (1.24 g, 65%) as a bright yellow solid, mp 162−163 °C; R_f 0.45 (2:2:6 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.99 (d, J = 8.5, 2H), 7.65 (apparent t, J = 7.4, 1H), 7.56 (apparent t, J = 8.0, 7.4, 2H), 7.48−7.35 [H-2 and benzyl-ring protons, m], 6.89 (dd, J = 2.4, 10, 1H), 6.65 (d, J = 10, 1H), 5.19 (s, 2H); ^{13}C NMR (75 MHz) 180.0, 165.3, 156.2, 141.1, 134.1, 133.6, 133.5, 129.1, 129.0, 128.9, 128.3, 127.6, 127.4, 103.1, 71.6. Anal. Calcd for $C_{19}H_{15}NO_4S$: C, 64.57; H, 4.29; N, 3.96. Found: C, 64.39; H, 3.89; N, 3.78.

***N*-(3-Isobutoxy-4-oxo-2,5-cyclohexadien-1-ylidene)benzenesulfonamide (4). (A) 2-Isobutoxy-4-nitroanisole.** A slurry of 2-methoxy-5-nitrophenol (3.00 g, 17.7 mmol) and K_2CO_3 (2.94 g, 21.3 mmol) in acetone (60 mL) at rt was treated with isobutyl bromide (6.08 mL, 55.9 mmol) and (nBu)$_4$N$^+$ I$^-$ (328 mg, 0.887 mmol). The reaction mixture was refluxed under nitrogen for 48 h, cooled to rt, and then poured into water (150 mL). CH_2Cl_2 (100 mL) was added, and the aqueous layer was separated and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with H_2O (150 mL), brine (150 mL), dried (Na_2SO_4), and concentrated to afford the title compound (3.97 g, 99.5%) as a dark yellow solid, mp 74−75 °C (EtOAc/hexanes); R_f 0.15 (1:5 EtOAc:hexanes); ^{1}H NMR (300 MHz) 7.81 (dd, 1H, J = 2.0, 9.0), 7.64 (d, 1H, J = 2.0), 6.83 (d, 1H, J = 9.0), 3.89 (s, 3H), 3.76 (d, 2H, J = 7.0), 2.12 (m, 1H), 0.99 (d, 6H, J = 7.0); ^{13}C NMR (75 MHz) 155.3, 148.9, 141.7, 117.9, 110.4, 108.0, 76.0, 56.8, 28.5, 19.6. Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.65; H, 6.77; N, 6.22. Found: C, 59.00; H, 6.90; N, 6.18.

(B) *N*-(3-Isobutoxy-4-methoxyphenyl)benzenesulfonamide. 2-Isobutoxy-4-nitroanisole (3.97 g, 17.6 mmol) was dissolved in 1:1 EtOH/EtOAc (80 mL). The solution was heated to 70 °C and $SnCl_2$·$2H_2O$ (19.9 g, 88.2 mmol) added. The reaction mixture was stirred for 12 h, cooled to rt, diluted with ice−water (80 mL), and neutralized by the careful addition of solid $NaHCO_3$. The resulting mixture was filtered through Celite, the Celite was rinsed with CH_2Cl_2, and the

(13) Tökés, A. L.; Antus, S. *Liebigs Ann. Chem.* **1994**, 911−915.
(14) Engler, T. A.; Chai, W. *Tetrahedron Lett.* **1996**, *37*, 6969−6970.
(15) All compounds were prepared as racemic mixtures. All reactions were done in oven- or flame-dried glassware under a nitrogen atmosphere with magnetic stirring. CH_2Cl_2, BF_3·OEt_2, and $TiCl_4$ were distilled under nitrogen from CaH_2 immediately before use. Brine refers to saturated aqueous sodium chloride. NMR spectra were recorded on samples dissolved in $CDCl_3$, unless otherwise noted, and chemical shifts are reported in δ (ppm) relative to internal Me_4Si or residual $CHCl_3$. Coupling constants (J) are reported in Hz. Reactions were monitored by thin-layer chromatography (TLC) on precoated 0.25 mm silica gel plates with a fluorescent indicator (Merck Kieselgel 60_{F254}); visualization was effected with a UV lamp or by staining with solutions of *p*-anisaldehyde/H_2SO_4 or phosphomolybdic acid. R_f's reported are from TLC. Chromatography refers to flash chromatography on silica gel [EM-Kieselgel 60 (0.04−0.063 mm mesh) or Selectro Scientific (0.032−0.063 mm mesh)] with the eluent indicated. Melting points are uncorrected. Styrenes **1a**−**c,f** were commercially available; **1d** and chromene **11** and quinoline **12** were prepared as described previously; and the preparations of **1e** and **1g** are described in the supporting information.[2]
(16) Adachi, T.; Otsuki, K. *Chem. Pharm. Bull.* **1976**, *24*, 2803−2809.
(17) White, R. L., Jr.; Schwan, T. J.; Alaino, R. J. *J. Heterocycl. Chem.* **1980**, *17*, 817−18.

filtrate was extracted with CH_2Cl_2 (3 × 80 mL). The extracts were washed with brine (100 mL), dried (Na_2SO_4), and concentrated to give 3-isobutoxy-4-methoxyaniline as a red solid (2.77 g, 81%) which was used without futher purification.

Pyridine (2.85 mL, 35.3 mmol) and benzenesulfonyl chloride (2.70 mL, 21.2 mmol) were added to a solution of the aniline prepared as described above (2.77 g, 14.2 mmol) in THF (200 mL). The reaction mixture was stirred for 24 h at rt, diluted with water (150 mL), and acidified with concentrated aqueous HCl (pH = 1−2). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 70 mL). The combined organic extracts were washed with brine (150 mL), dried (Na_2SO_4), and concentrated. The residue was passed through neutral alumina with 1:5 EtOAc:hexanes as eluent. Concentration gave the title benzenesulfonamide (3.94 g, 83%) as a white solid, mp 103−104 °C (EtOAc/hexanes); R_f 0.10 (2:2:6 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (300 MHz) 7.71 (m, 2H), 7.49 (t, 1H, J = 7.5), 7.40 (apparent t, 2H), 7.11 (s, 1H, NH), 6.65 (m, 2H), 6.52 (dd, 1H, J = 2.4, 8.4), 3.75 (s, 3H), 3.59 (d, 2H, J = 7.0), 2.02 (m, 1H), 0.94 (d, 6H, J = 7.0); ^{13}C NMR (75 MHz) 149.5, 148.4, 139.3, 139.2, 129.6, 129.3, 127.8, 116.2, 112.6, 110.1, 75.8, 56.7, 28.4, 19.6. Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.60; H, 6.68; N, 4.10.

(C) Monoimide 4. A solution of ceric ammonium nitrate (3.55 g, 6.45 mmol) in water (12 mL) was added dropwise to a solution of *N*-(3-isobutoxy-4-methoxyphenyl)benzenesulfonamide (720 mg, 2.15 mmol) in CH_3CN (12 mL) at 0 °C. The mixture was stirred for 0.5 h and diluted with CH_2Cl_2 (50 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 30 mL). The extracts were dried (Na_2SO_4), decanted, and concentrated. Chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the red residue afforded **4** as a 4:1 (*E*):(*Z*) mixture of isomers (400 mg, 58.3%) as a yellow oil; R_f 0.28 (2:2:6 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) (*E*)-isomer: 7.95 (d, 2H, J = 7.5), 7.58 (t, 1H, J = 7.5), 7.51 (apparent t, 2H, J = 7.5), 7.14 (d, 1H, J = 2.4), 6.82 (dd, 1H, J = 2.4, 10.0), 6.57 (d, 1H, J = 10.0), 3.76 (d, 2H, J = 6.6), 2.14 (m, 1H), 0.98 (d, 6H, J = 6.6); ^{13}C NMR (125 MHz) (*E*)-isomer: 179.7, 165.3, 156.6, 140.8, 140.2, 133.7, 133.2, 128.9, 127.0, 101.9, 75.6, 27.4, 18.8; HRMS m/z 319.0856 (M^+) (Calcd for $C_{16}H_{17}NO_4S$ 319.0878).

General Method A: General Procedure for the BF_3·Et_2O-Promoted Reactions of Styrenes with 1,4-Benzoquinone Monoimides. BF_3·Et_2O was added to a solution of the imide in CH_2Cl_2 maintained at −78 °C followed, after 5−15 min, by the styrene, either neat or as a solution in CH_2Cl_2. The reaction mixture was stirred until no imide was present by TLC, generally 15−60 min, and then quenched by the addition of saturated aqueous sodium bicarbonate. The resulting mixture was extracted with CH_2Cl_2, and the extracts were washed with water and brine, dried (Na_2SO_4), and concentrated. Purification was effected by chromatography, and/or recrystallization.

General Method B: General Procedure for the Ti(IV)-Promoted Reactions of Styrenes with 1,4-Benzoquinone Monoimides. $TiCl_4$ was added to a solution of $Ti(OiPr)_4$ in CH_2Cl_2 at 0 °C to rt. After stirring for 5−15 min, this mixture, or neat $TiCl_4$, was added to a solution of the imide in CH_2Cl_2 maintained at −78 °C followed, after 5−15 min, by the styrene, either neat or as a solution in CH_2Cl_2. The reaction mixture was stirred at −78 °C until no imide was present by TLC, generally 15−60 min unless otherwise stated and then quenched by the addition of saturated aqueous sodium bicarbonate. The resulting mixture was filtered through Celite, the Celite was rinsed with CH_2Cl_2, and the filtrate was extracted with CH_2Cl_2. The extracts were washed with water and brine, dried (Na_2SO_4), and concentrated. Purification was effected by chromatography, and/or recrystallization.

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-methoxy-2-(4-methoxyphenyl)-3-methylbenzofuran-5-yl]benzenesulfonamide (5a).** According to general method A, (*E*)-4-propenylanisole (30 μL, 0.20 mmol) was added to a solution of BF_3·Et_2O (29 μL, 0.23 mmol) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8a** (6 mg, 8%) and **5a** (70 mg, 91%). Physical and spectral properties of **5a**, a white solid, mp 160−161 °C (Et_2O/CH_2Cl_2/hexanes); R_f 0.20 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.73 (d, 2H, J = 6.5), 7.56 (t, 1H, J = 7.4), 7.47 (apparent t, 2H), 7.31 (d, 2H, J = 8.5), 6.68 (d, 2H, J = 8.5), 6.49 (s, 1H), 6.40 (s, 1H), 5.10 (d, 1H, J = 9.2), 3.80 (s, 3H), 3.74 (s, 3H), 3.37 (apparent quintet, 1H), 1.26 (d, 3H, J = 6.8); ^{13}C NMR (125 MHz) 159.7, 146.1, 144.1, 138.8, 133.4, 132.9,131.8, 129.2, 128.9, 127.9, 127.4, 113.9, 112.6, 108.8, 93.5, 56.0, 55.3, 45.4, 17.6. Anal. Calcd for $C_{23}H_{23}NO_5S$: C, 64.92; H, 5.45; N, 3.29. Found: C, 64.60; H, 5.18; N, 3.00.

Compound **8a** was identified by spectral comparison to the product isolated from the Ti(IV)-promoted reaction, see below.

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-methoxy-2-(3,4-dimethoxyphenyl)-3-methylbenzofuran-5-yl]benzenesulfonamide (5b).** According to general method A, (*E*)-1,2-dimethoxy-4-propenylbenzene (50 μL, 0.30 mmol) was added to a solution of BF_3·OEt_2 (40 μL, 0.32 mmol) and monoimide **2** (72 mg, 0.26 mmol) in CH_2Cl_2 (2 mL). Workup and chromatography (2:5 EtOAc:hexanes) afforded **5b** (97 mg, 82%) as a white solid, mp 179−180 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.18 (2:4:4 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.75 (d, J = 7.5, 2H), 7.57 (apparent t, J = 7.4, 1H), 7.46 (apparent t, J = 7.5, 2H), 6.93 (s, 1H), 6.92 (d, J = 8.0, 1H), 6.84 (d, J = 8.0, 1H), 6.50 [H-6 (s)], 6.48 [N-H (s)], 6.42 [H-4 (s)], 5.09 (d, J = 9.5, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 3.39 (dq, J = 6.7, 9.5, 1H), 1.27 (d, J = 6.8, 3H); ^{13}C NMR (75 MHz) 149.2, 149.1, 146.0, 144.1, 138.9, 133.4, 132.9, 132.1, 129.4, 128.9, 127.5, 119.2, 112.4, 110.8, 109.5, 108.7, 93.8, 56.0, 55.9 (2C), 45.4, 17.5; HRMS m/z 456.1487 (M^+ + 1) (calcd for $C_{24}H_{25}NO_6S$ 456.1481).

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-methoxy-3-methyl-2-[(3,4-methylenedioxy)phenyl]benzofuran-5-yl]benzenesulfonamide (5c).** According to general method A, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (115 μL, 0.794 mmol), was added to a solution of BF_3·Et_2O (57 μL, 0.45 mmol) and monoimide **2** (100 mg, 0.361 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8c** (20 mg, 13%) and **5c** (130 mg, 82%). Physical and spectral properties of **5c**, a white solid, mp 145−146 °C (EtOAc/hexanes); R_f 0.22 (3:3:4 Et_2O:CH_2Cl_2:hexane); ^{1}H NMR (500 MHz) 7.76 (d, 2H, J = 7.0), 7.54 (apparent t, 1H, J = 7.4), 7.43 (apparent t, 2H), 7.09 (s, 1H, NH), 6.84 (d, 1H, J = 1.5), 6.81 (dd, 1H, J = 1.5, 8.0), 6.75 (d, 1H, J = 8.0), 6.52 (d, 1H, J = 1.0), 6.44 (d, 1H, J = 1.0), 5.93 (s, 2H), 5.03 (d, 1H, J = 9.0), 3.72 (s, 3H), 3.30 (apparent quintet, 1H), 1.24 (d, 3H, J = 6.9), ^{13}C NMR (125 MHz) 147.9, 147.7, 145.7, 144.0, 138.7, 133.8, 133.2, 132.9, 129.6, 128.9, 127.4, 120.2, 112.1, 108.5, 108.0, 106.6, 101.1, 93.4, 56.0, 45.6, 17.7. Anal. Calcd for $C_{23}H_{21}NO_6S$: C, 62.86; H, 4.82; N, 3.19. Found: C, 63.12; H, 4.96; N, 3.18.

Compound **8c** was identified by spectral comparison to the product isolated from the Ti(IV)-promoted reaction, see below.

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-methoxy-3-methyl-2-(4-methylphenyl)benzofuran-5-yl]benzenesulfonamide (5d).** According to general method A, (*E*)-1-methyl-4-propenylbenzene (79 mg, 0.60 mmol) in CH_2Cl_2 (2 mL) was added to a solution of BF_3·Et_2O (87 μL, 0.69 mmol) and monoimide **2** (150 mg, 0.542 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **5d** (30 mg, 14%) as a white solid, mp 132−133 °C (Et_2O/hexanes); R_f 0.13 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.74 (d, 2H, J = 8.1), 7.57 (t, 1H, J = 7.4), 7.45 (apparent t, 2H), 7.27 (d, 2H, J = 8.0), 7.16 (d, 2H, J = 8.0), 6.58 (s, 1H, NH), 6.51 (d, 1H, J = 1.6), 6.40 (apparent s, 1H), 5.12 (d, 1H, J = 9.0), 3.75 (s, 3H), 3.37 (apparent quintet, 1H), 2.34 (s, 3H), 1.27 (d, 1H, J = 6.8); ^{13}C NMR (125 MHz) 146.1, 144.1, 138.8, 138.1, 137.3, 133.4, 132.8, 129.3, 129.2, 128.9, 127.4, 126.2, 112.5, 108.8, 93.5, 56.0, 45.6, 21.2, 17.8; HRMS m/z 409.1332 (M^+) (Calcd for $C_{23}H_{23}NO_4S$ 409.1348).

***N*-[(2*R**,3*R**)-7-(Benzyloxy)-2,3-dihydro-2-(3,4-dimethoxyphenyl)-3-methylbenzofuran-5-yl]benzenesulfonamide (6b).** According to general method A, (*E*)-1,2-dimethoxy-4-propenylbenzene (50 μL, 0.30 mmol) was added to a solution of BF_3·OEt_2 (40 μL, 0.32 mmol) and monoimide **3** (91 mg, 0.26 mmol) in CH_2Cl_2 (2 mL). Workup and chromatography (2:5 EtOAc:hexanes) furnished **6b** (118 mg, 86%) as a white solid, mp 136−137 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.25 (3:3:4 CH_2Cl_2/Et_2O/hexanes); ^{1}H NMR (500 MHz) 7.66

(d, J = 8.5 Hz, 2H), 7.54 (apparent t, J = 7.5, 1H), 7.41 (apparent t, J = 7.9, 2H), 7.36−7.29 (m, 6H), 6.94 (bs, 1H), 6.93 (dd, J = 1.9, 8.6, 1H), 6.85 (d, J = 8.6, 1H), 6.57 [H-6 (bs)], 6.42 [H-4 (bs)], 6.38 [N-H (s)], 5.09 (d, J = 9.3, 1H), 5.05 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.37 (dq, J = 6.8, 9.3, 1H), 1.27 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz) 149.2, 149.1, 146.5, 143.0, 138.9, 136.6, 133.9, 132.8, 132.3, 129.3, 128.9, 128.5, 128.0, 127.5, 127.4, 119.2, 112.6, 110.9 (2C), 109.5, 93.6, 71.1, 56.0 (2C), 45.4, 17.5; HRMS m/z 532.1790 ($M^+ + 1$) (calcd for $C_{30}H_{29}NO_6S$ − 532.1794).

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-benzyloxy-3-methyl-2-(3,4-methylenedioxyphenyl)benzofuran-5-yl]benzenesulfonamide (6c).** According to general method A, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (45 μL, 0.31 mmol) was added to a solution of BF_3·Et_2O (21 μL, 0.17 mmol) and monoimide **3** (50 mg, 0.14 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **9c** (6 mg, 8.2%) and **6c** (53 mg, 73%). Physical and spectral properties of **6c**, a white solid, mp 119−120 °C (Et_2O/hexanes); R_f 0.25 (3:3:4 Et_2O:CH_2Cl_2:hexane); ^{1}H NMR (500 MHz) 7.66 (d, 2H, J = 8.0), 7.53 (apparent t, 1H, J = 7.4), 7.42- 7.26 (m, 7H), 6.86 (d, 1H, J = 1.5), 6.83 (dd, 1H, J = 1.5, 8.0), 6.77 (d, 1H, J = 8.0), 6.73 (s, 1H, NH), 6.59 (d, 1H, J = 1.5), 6.41 (d, 1H, J = 1.5), 5.95 (s, 2H), 5.06 (d, 1H, J = 9.5), 5.05 (s, 2H), 3.29 (apparent quintet, 1H), 2.18 (s, 3H), 1.25 (d, 3H, J = 6.5 Hz); ^{13}C NMR (125 MHz) 147.9, 147.6, 146.3, 142.8, 138.7, 136.6, 133.9, 133.7, 132.8, 129.4, 128.8, 128.5, 127.9, 127.5, 127.3, 120.0, 112.5, 110.8, 108.0, 106.6, 101.1, 93.3, 71.0, 45.6, 17.7; HRMS m/z 515.1375 (M^+) (Calcd for $C_{29}H_{25}NO_6S$ 515.1403).

Compound **9c** was identified by spectral comparison to that isolated from the Ti(IV)-promoted reaction, see below.

***N*-[(2*R**,3*R**)-2,3-Dihydro-2-(3,4-dimethoxyphenyl)-7-isobutoxy-3-methylbenzofuran-5-yl]benzenesulfonamide (7b).** According to general method A, (*E*)-1,2-dimethoxy-4-propenylbenzene (59 μL, 0.35 mmol) was added to a solution of BF_3·Et_2O (25 μL, 0.20 mmol) and monoimide **4** (50 mg, 0.19 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **10b** (8 mg, 10%) and **7b** (70 mg, 89%). Physical and spectral properties of **7b**, a white solid, mp 138−139 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.25 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.76 (d, 2H, J = 7.5), 7.55 (t, 1H, J = 7.4), 7.45 (t, 2H, J = 7.5), 6.93 (d, 1H, J = 1.7), 6.91 (dd, 1H, J = 8.2, 1.7), 6.83 (d, 1H, J = 8.2), 6.75 (s, 1H, NH), 6.50 (d, 1H, J = 1.0), 6.41 (d, 1H, J = 1.0), 5.08 (d, 1H, J = 9.2), 3.87 (s, 3H), 3.85 (s, 3H), 3.66 (m, 2H), 3.33 (apparent quintet, 1H), 2.00 (septet, 1H, J = 6.7), 1.26 (d, 3H, J = 6.8), 0.95 (d, 3H, J = 6.7); 0.94 (d, 3H, J = 6.7); ^{13}C NMR (125 MHz) 149.1, 146.4, 143.6, 138.9, 133.6 132.8, 132.6, 129.3, 128.9, 127.4, 119.0, 112.3, 110.9, 110.4, 109.3, 93.3, 75.6, 55.9 (2C), 45.6, 28.0, 19.2, 19.2, 17.6 (one quaternary sp^2-C signal is not apparent). Anal. Calcd for $C_{27}H_{31}NO_6S$: C, 65.17; H, 6.28; N, 2.81. Found: C, 65.00; H, 6.40; N, 2.50.

Compound **10b** was identified by spectral comparison to the product isolated from the Ti(IV)-promoted reaction, see below.

***N*-[(2*R**,3*R**)-2,3-Dihydro-7-isobutoxy-3-methyl-2-(3,4-methylenedioxyphenyl)benzofuran-5-yl]benzenesulfonamide (7c).** According to general method A, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (33 μL, 0.23 mmol) was added to a solution of BF_3·Et_2O (15 μL, 0.12 mmol) and monoimide **4** (33 mg, 0.10 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **7c** (24 mg, 48%) as a white solid, mp 104−106 °C (Et_2O/hexanes); R_f 0.30 (3:3:4 Et_2O/CH_2Cl_2/hexanes); ^{1}H NMR (500 MHz) 7.74 (d, 2H, J = 7.4), 7.55 (apparent t, 1H, J = 7.4), 7.45 (apparent t, 2H, J = 7.4), 6.87 (d, 1H, J = 1.0), 6.83 (dd, 1H, J = 1.0, 8.0), 6.77 (d, 1H, J = 8.0), 6.54 (s, 1H, NH), 6.48 (d, 1H, J = 1.7), 6.38 (b s, 1H) [a COSY spectrum revealed that the 6.48 and 6.38 signals were coupled], 5.92 (s, 2H), 5.06 (d, 1H, J = 8.9), 3.66 (m, 2H), 3.29 (apparent quintet, 1H), 2.01 (septet, 1H, J = 6.7), 1.26 (d, 3H, J = 6.7), 0.96 (d, 3H, J = 6.7); 0.95 (d, 3H, J = 6.7); ^{13}C NMR (125 MHz) 147.9, 147.6, 146.3, 143.6, 138.9, 134.2, 133.4, 132.8, 129.2, 128.9, 127.4, 120.0, 112.4, 110.6, 108.1, 106.6, 101.1, 93.1, 75.6, 45.7, 28.0, 19.21, 19.17, 17.8. Anal. Calcd for $C_{26}H_{27}NO_6S$: C, 64.84; H, 5.65; N, 2.91. Found: C, 64.78; H, 5.80; N, 2.80.

***(2R*,3R*)*-1-(Benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-methoxy-2-(4-methoxyphenyl)-3-methylindole (8a).** According to general method B, (*E*)-4-propenylanisole (30 μL, 0.20 mmol) was added to a solution of a mixture of $TiCl_4$ (20 μL, 0.18 mmol) and $Ti(OiPr)_4$ (108 μL, 0.365 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8a** (58 mg, 76%) and **5a** (10 mg, 13%). Physical and spectral properties of **8a**, a white solid, mp 67−68 °C (Et_2O/hexanes); R_f 0.30 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.71 (d, 2H, J = 7.5), 7.54 (t, 1H, J = 7.5), 7.42 (apparent t, 3H), 7.22 (d, 1H, J = 8.7), 6.83 (d, 1H, J = 8.7), 6.58 (s, 1H), 5.56 (s, 1H), 4.56 (d, 1H, J = 3.0), 3.98 (s, 3H), 3.78 (s, 3H), 2.95 (dq, 1H, J = 3, 7), 0.65 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 159.0, 146.4, 143.3, 137.4, 134.9, 133.6, 133.0, 128.9, 128.4, 127.3, 126.9, 114.0, 110.0, 100.4, 72.7, 56.4, 55.3, 45.8, 21.8. Anal. Calcd for $C_{23}H_{23}NO_5S$: C, 64.92; H, 5.45; N, 3.29. Found: C, 65.17; H, 5.48; N, 2.98.

***(2R*,3R*)*-1-(Benzenesulfonyl)-2,3-dihydro-2-(3,4-dimethoxyphenyl)-5-hydroxy-6-methoxy-3-methylindole (8b).** According to general method B, (*E*)-1,2-dimethoxy-4-propenylbenzene (134 μL, 0.794 mmol) was added to a solution of a mixture of $TiCl_4$ (200 μL, 1.81 mmol) and $Ti(OiPr)_4$ (537 μL, 1.81 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **2** (100 mg, 0.361 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8b** (146 mg, 89%) as a white solid, mp 178−179 °C (Et_2O/hexanes); R_f 0.22 (3:3:4 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 2H, J = 7.9), 7.53 (t, 1H, J = 7.5), 7.42 (m, 3H), 6.86 (dd, 1H, J = 2.0, 8.3), 6.78 (m, 2H), 6.58 (s, 1H), 5.50 (s, 1H, OH), 4.55 (d, 1H, J = 3.2), 3.99 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 2.98 (dq, 1H, J = 7.0, 3.2), 0.68 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 149.1, 148.6, 146.4, 143.3, 137.4, 135.2, 133.6, 133.1, 128.9, 128.3, 127.3, 118.0, 111.1, 109.9, 109.0, 100.3, 72.9, 56.4, 55.9, 55.89, 45.7, 21.8. Anal. Calcd for $C_{24}H_{25}NO_6S$: C, 63.28; H, 5.53; N, 3.08. Found: C, 62.90; H, 5.60; N, 2.90.

***(2R*,3R*)*-1-(Benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-methoxy-3-methyl-2-[3,4-(methylenedioxy)phenyl]indole (8c).** According to general method B, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (52 μL, 0.36 mmol) was added to a solution of a mixture of $TiCl_4$ (50 μL, 0.46 mmol) and $Ti(OiPr)_4$ (269 μL, 0.908 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8c** (58 mg, 73%) as a white solid, mp 166−167 °C (MeOH/hexanes); R_f 0.30 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.71 (d, 2H, J = 7.9), 7.54 (t, 1H, J = 7.4), 7.42 (m, 3H), 6.80−6.72 (m, 3H), 6.57 (s, 1H), 5.91 (s, 2H), 5.57 (s, 1H), 4.50 (d, 1H, J = 3.0), 3.98 (s, 3H), 2.92 (dq, 1H, J = 7, 3), 0.64 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 147.8, 147.0, 146.4, 143.3, 137.2, 136.7, 133.5, 133.1, 128.9, 128.2, 127.2, 119.1, 109.9, 108.1, 106.2, 101.0, 100.4, 72.9, 56.4, 45.9, 21.8. Anal. Calcd for $C_{23}H_{21}NO_6S$: C, 62.86; H, 4.82; N, 3.19. Found: C, 62.52; H, 5.00; N, 3.00.

***(2R*,3R*)*-1-(Benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-methoxy-3-methyl-2-(4-methylphenyl)indole (8d).** According to general method B, (*E*)-1-methyl-4-propenylbenzene (26 mg, 0.20 mmol) was added to a solution of $TiCl_4$ (179 μL, 1.62 mmol) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **8d** (55 mg, 74%) as a white solid, mp 139−140 °C (Et_2O/hexanes); R_f 0.40 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.22 (d, 2H, J = 7.4), 7.54 (t, 1H, J = 7.4), 7.43 (m, 3H), 7.20 (d, 2H, J = 8.0), 7.10 (d, 2H, J = 8.0), 6.57 (s, 1H), 5.51 (s, 1H, NH), 4.56 (d, 1H, J = 3.0), 3.99 (s, 3H), 2.96 (dq, 1H, J = 7.0, 3.0), 2.28 (s, 3H), 0.66 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 146.3, 143.3, 139.7, 137.3, 137.2, 133.6, 133.0, 129.3, 128.9, 128.3, 127.3, 125.6, 109.9, 100.4, 72.9, 56.4, 45.9, 21.9, 21.1. Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.66; N, 3.42. Found: C, 67.10; H, 6.00; N, 3.02.

(2*R,3*R**)-2-(4-Acetoxyphenyl)-1-(benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-methoxy-3-methylindole (8e).** According to general method B, (*E*)-1-acetoxy-4-propenylbenzene (32 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $TiCl_4$ (79 μL, 0.72 mmol) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **8e** (15 mg, 18%) as a white solid, mp 136−137 °C (Et_2O/hexanes); R_f 0.11 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 2H, J = 7.5), 7.54 (t, 1H, J = 7.4), 7.43 (apparent t, 3H), 7.31 (d, 2H, J = 8.6), 7.01 (d, 2H, J = 8.5), 6.56 (s, 1H), 5.51 (s, 1H, OH), 4.60 (d, 1H, J = 3), 3.99 (s, 3H), 2.97 (dq, 1H, J = 3, 7), 2.28 (s, 3H), 0.64 (d, 3H, J = 7); ^{13}C NMR (125 MHz) 169.4, 150.0, 146.4, 143.4, 140.1, 137.2, 133.4, 133.2, 129.0, 128.2, 127.3, 126.8, 121.7, 110.0, 100.4, 72.4, 56.5, 45.8, 22.0, 21.1; HRMS m/z 453.1251 (M^+) (Calcd for $C_{24}H_{23}NO_6S$ 453.1246)

(2*R,3*R**)-1-(Benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-methoxy-3-methyl-2-phenylindole (8f).** According to general method B, *trans*-β-methylstyrene (39 μL, 0.30 mmol) was added to a solution of $TiCl_4$ (33 μL, 0.30 mmol) and monoimide **2** (75 mg, 0.27 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **8f** (80 mg, 75%) as a white solid, mp 169−171°C (Et_2O/hexanes); R_f 0.15 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.72 (d, 2H, J = 7.9), 7.55 (t, 1H, J = 7.4), 7.44 (apparent t, 3H), 7.30 −7.23 (m, 5H), 6.57 (s, 1H), 5.52 (s, 1H, OH), 4.60 (d, 1H, J = 3.0), 4.00 (s, 3H), 2.97 (dq, 1H, J = 7.0, 3.0), 0.66 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 145.4, 143.4,142.6, 137.2, 133.6, 133.1, 128.9, 128.6, 128.3, 127.6, 127.3, 125.6, 110.0, 100.0, 73.0, 56.4, 45.9, 22.0. Anal. Calcd for $C_{22}H_{21}NO_4S$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.43; H, 5.68; N, 3.20.

(2*R,3*R**)-1-(Benzenesulfonyl)-6-benzyloxy-2,3-dihydro-5-hydroxy-2-(3,4-dimethoxyphenyl)-3-methylindole (9b).** According to general method B, (*E*)-1,2-dimethoxy-4-propenylbenzene (31 μL, 0.19 mmol) was added to a solution of a mixture of $TiCl_4$ (23 μL, 0.21 mmol) and $Ti(OiPr)_4$ (126 μL, 0.425 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **3** (30 mg, 0.085 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **9b** (45 mg, 100%) as a white solid, mp 76−77 °C (Et_2O/hexanes); R_f 0.18 (2:2:6 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.52−7.33 (m, 11H), 6.86 (dd, 1H, J = 1.9, 8.2), 6.78 (m, 2H), 6.59 (s, 1H), 5.61 (s, 1H, OH), 5.26 (s, 2H), 4.53 (d, 1H, J = 3.4), 3.85 (s, 3H), 3.81 (s, 3H), 2.97 (dq, 1H, J = 3.4, 7.0), 0.67 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 149.1, 148.6, 145.0, 143.5, 137.2, 136.1, 135.2, 133.5, 132.9, 128.8 (2C), 128.6, 128.4, 127.9, 127.2, 118.0, 111.1, 110.2, 109.0, 101.8, 73.0, 71.2, 55.9 (2C), 45.7, 21.8; HRMS m/z 531.1707 (M^+) (Calcd for $C_{30}H_{29}NO_6S$ − 531.1716).

(2*R,3*R**)-1-(Benzenesulfonyl)-6-(benzyloxy)-2,3-dihydro-5-hydroxy-3-methyl-2-[3,4-(methylenedioxy)phenyl]-indole (9c).** According to general method B, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (45 μL, 0.31 mmol) was added to a solution of a mixture of $TiCl_4$ (78 μL, 0.71 mmol) and $Ti(OiPr)_4$ (211 μL, 0.712 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **3** (50 mg, 0.14 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 Et_2O:CH_2Cl_2:hexanes) of the crude yellow oil afforded **9c** (49 mg, 67%) as a white solid, mp 177−178 °C (Et_2O/hexanes); R_f 0.30 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.54−7.33 (m, 11H), 6.80−6.73 (m, 3H), 6.58 (s, 1H), 5.91 (s, 2H), 5.63 (s, 1H), 5.25 (s, 2H), 4.48 (d, 1H, J = 3.2), 2.92 (dq, 1H, J = 3.2, 7.0), 0.64 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 147.8, 147.0, 145.1, 143.5, 137.0, 136.7, 136.1, 133.4, 133.0, 128.82, 128.80, 128.45, 128.44, 128.0, 127.2, 119.1, 110.2, 108.1, 106.2, 101.8, 101.0, 72.9, 71.1, 45.9, 21.8; HRMS m/z 515.1421 (M^+) (Calcd for $C_{29}H_{25}NO_6S$ 515.1403).

(2*R,3*R**)-1-(Benzenesulfonyl)-2,3-dihydro-2-(3,4-dimethoxyphenyl)-5-hydroxy-6-isobutoxy-3-methylindole (10b).** According to general method B, (*E*)-1,2-dimethoxy-4-propenylbenzene (93 μL, 0.64 mmol) was added to a solution of a mixture of $TiCl_4$ (138 μL, 1.26 mmol) and $Ti(OiPr)_4$ (373 μL, 1.26 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **4** (80 mg, 0.25 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **10b** (80 mg, 64%) and **7b** (4 mg, 3%). Physical and spectral properties of **10b**, a white solid, mp 142−143 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.34 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 2H, J = 7.5), 7.53 (t, 1H, J = 7.4), 7.42 (apparent t, 3H), 6.86 (dd, 1H, J = 8.5, 1.7), 6.78 (m, 2H), 6.59 (s, 1H), 5.56 (s, 1H, OH), 4.54 (d, 1H, J = 3.1), 3.90 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 2.97 (dq, 1H, J = 3.1, 7.0), 2.16 (m, 1H), 1.08 (d, 3H, J = 6.7), 1.07 (d, 3H, J = 6.7), 0.67 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 149.1, 148.5, 145.8, 143.4, 137.3, 135.2, 133.5, 133.1, 128.9, 128.2, 127.3, 118.0, 110.1, 109.8, 109.0, 101.1, 75.6, 72.9, 55.9 (2C), 45.8, 28.3, 21.9, 19.3 (2C). Anal. Calcd for $C_{27}H_{31}NO_6S$: C, 65.17; H, 6.28; N, 2.81. Found: C, 64.80; H, 6.40; N, 2.70.

Compound **7b** was identified by spectral comparison to the product isolated from the BF_3·Et_2O-promoted reaction, see above.

(2*R,3*R**)-1-(Benzenesulfonyl)-2,3-dihydro-5-hydroxy-6-isobutoxy-3-methyl-2-[3,4-(methylenedioxy)phenyl]indole (10c).** According to general method B, (*E*)-1,2-(methylenedioxy)-4-propenylbenzene (15 μL, 0.10 mmol) was added to a solution of a mixture of $TiCl_4$ (26 μL, 0.24 mmol) and $Ti(OiPr)_4$ (70 μL, 0.24 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **4** (15 mg, 0.047 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **10c** (21 mg, 93%) as a white solid, mp 132−133 °C (Et_2O/hexanes); R_f 0.5 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.71 (d, 2H, J = 7.5), 7.54 (apparent t, 1H), 7.45−7.40 (m, 3H), 6.79−6.72 (m, 3H), 6.58 (s, 1H), 5.91 (s, 2H), 5.56 (s, 1H, OH), 4.49 (s, 1H, J = 2.8), 3.93 (m, 2H), 2.91 (dq, 1H, J = 2.8, 7.0), 2.18 (septet, 1H, J = 7.0), 1.09 (d, 3H, J = 7.0), 1.08 (d, 3H, J = 7.0), 0.63 (d, 3H, J = 7.0); ^{13}C NMR (75 MHz) 148.3, 147.5, 146.3, 143.9, 137.8, 137.2, 133.9, 133.5, 129.3, 128.5, 127.7, 119.5, 110.3, 108.6, 106.7, 101.7, 101.4, 76.2, 73.4, 46.4, 28.7, 22.3, 19.7 (2C). Anal. Calcd for $C_{26}H_{27}NO_6S$: C, 64.84; H, 5.65; N, 2.91. Found: C, 65.20; H, 5.50; N, 2.80.

***N*-[(6a*S**,11a*S**)-6,6a,11a-Trihydro-3,10-dimethoxy-6*H*-benzofuro[3,2-*c*][1]benzopyran-8-yl]benzenesulfonamide (13).** According to general method A, 7-methoxy-2*H*-chromene (**11**, 170 mg, 1.05 mmol) was added to a solution of BF_3·OEt_2 (140 μL, 1.14 mmol) and monoimide **2** (278 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). Workup and chromatography (2:3:5 to 2:4:4 CH_2Cl_2:Et_2O:hexanes) furnished **13** (384 mg, 87%) as a white solid, mp 112−114 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.28 (2:3:5 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.72 (d, J = 7.3 Hz, 2H), 7.55 (apparent t, J = 7.5, 1H), 7.44 [overlapping d (J = 8.5, 1H) and apparent t (J = 7.5, 2H)], 6.82 (s, 1H), 6.60 (dd, J = 2.5, 8.5, 1H), 6.54 (d, J = 1.8, 1H), 6.52 (d, J = 1.8, 1H), 6.43 (d, J = 2.5, 1H), 5.53 (d, J = 6.9, 1H), 4.12 (dd, J = 4.7, 11, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.58 (apparent t, J = 11, 1H), 3.53−3.48 (m, 1H); ^{13}C NMR (125 MHz) 161.1, 156.5, 146.5, 144.6, 138.7, 133.0, 132.2, 129.5, 128.9, 128.5, 127.4, 113.2, 111.7, 109.5, 109.2, 101.5, 78.8, 66.0, 56.0, 55.3, 40.4. Anal. Calcd for $C_{23}H_{21}NO_6S$: C, 62.85; H, 5.10; N, 3.18. Found: C, 63.10; H, 5.10; N, 3.28.

***N*-[(6a*S**,11a*S**)-10-(Benzyloxy)-6,6a,11a-trihydro-3-methoxy-6*H*-benzofuro[3,2-*c*][1]benzopyran-8-yl]benzenesulfonamide (14).** According to general method A, 7-methoxy-2*H*-chromene (**11**, 50 mg, 0.31 mmol) in CH_2Cl_2 (1 mL) was added to a solution of BF_3·OEt_2 (30 μL, 0.24 mmol) and monoimide **3** (68 mg, 0.19 mmol) in CH_2Cl_2 (4 mL). Workup and chromatography (2:3:5 to 3:2:5 CH_2Cl_2:Et_2O:hexanes) gave **14** (89 mg, 91%) as a white foam, mp 93−95 °C; R_f 0.26 (3:2:5 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.60 (d, J = 7.8, 2H), 7.54 (apparent t, J = 7.3, 7.6, 1H), 7.47 (d, J = 8.6, 1H), 7.40 (apparent t, J = 7.8, 2H), 7.34−7.29 (m, 5H), 6.62 (dd, J = 2.4, 8.6, 1H), 6.54 (d, J = 1.9, 1H), 6.52 (d, J = 1.9, 1H), 6.44 (d, J = 2.4, 1H), 6.30 (bs, 1H), 5.54 (d, J = 7.0, 1H), 5.03 (ABq, J = 12, $\Delta\nu$=15 Hz, 2H), 4.13 (dd, J = 5.0, 11, 1H), 3.78 (s, 3H), 3.59 (apparent t, J = 11, 1H), 3.53−3.48 (m, 1H); ^{13}C NMR (125 MHz) 161.1, 156.5, 147.0, 143.5, 138.6, 136.4, 133.0, 132.2, 129.3, 129.0, 128.9, 128.5, 128.0, 127.5, 127.3, 113.6, 112.0, 111.8, 109.2, 101.5, 78.7, 71.2, 65.9, 55.4, 40.4; HRMS m/z 515.1402 (calcd for $C_{29}H_{25}NO_6S$ 515.1403).

***N*-[(6a*S**,11a*S**)-10-Isobutoxy-3-methoxy-6,6a,11a-trihydrobenzofuro[3,2-*c*][1]benzopyran-8-yl]benzenesulfonamide (15).** According to general method A, 7-methoxy-2*H*-chromene (**11**, 29 mg, 0.18 mmol) was added to a solution of $BF_3{\cdot}Et_2O$ (26 μL, 0.21 mmol) and monoimide **4** (53 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **15** (66 mg, 81%) and **21** (2 mg, 2%). Physical and spectral properties of **15**, a white solid, mp 171−173 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.10 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 2H, J = 7.5), 7.50 (t, 1H, J = 7.5), 7.47−7.43 (m, 3H), 6.62 (dd, 1H, J = 8.5, 2.5), 6.52 (d, 1H, J = 2.0), 6.48 (d, 1H, J = 2.0), 6.46 (s, 1H, NH), 6.43 (d, 1H, J = 2.5), 5.52 (d, 1H, J = 7.0), 4.13 (dd, 1H, J = 11.0, 5.0), 3.78 (s, 3H), 3.64 (d, 2H, J = 6.7), 3.59 (dd, 1H, J = 11.0, 11.0), 3.49 (m, 1H), 2.00 (m, 1H), 0.95 (d, 6H, J = 6.7); ^{13}C NMR (125 MHz) 161.1, 156.5, 146.9, 144.2, 138.7, 132.9, 132.2, 129.2, 128.9, 128.7, 127.4, 113.3, 111.9, 111.3, 109.1, 101.5, 78.5, 75.6, 65.9, 55.3, 40.4, 28.0, 19.2. Anal. Calcd for $C_{26}H_{27}NO_6S$: C, 64.84; H, 5.65; N, 2.91. Found: C, 64.85; H, 5.90; N, 2.99.

Compound **21** was identified by spectral comparison to the product isolated from the Ti(IV)-promoted reaction, see below.

***N*-[(6a*S**,11a*S**)-3,10-Dimethoxy-5-(4-toluenesulfonyl)-6,6a,11,11a-tetrahydrobenzofuro[3,2-*c*][1]quinoline-8-yl]-benzenesulfonamide (16).** According to general method A, a 3.4:1 mixture of dihydroquinoline **12** and its 5-methoxy isomer (70 mg, 0.22 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $BF_3{\cdot}Et_2O$ (27 μL, 0.21 mmol) and monoimide **2** (45 mg, 0.162 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (5:95 to 10:90 EtOH:CH_2Cl_2) of the crude yellow oil afforded **16** (67 mg, 70%) as a white solid, mp 166−168 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.07 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 2H, J = 7.5), 7.57 (t, 1H, J = 7.5), 7.48 (m, 5H), 7.27 (d, 1H, J = 3.0), 7.19 (d, 2H, J = 7.5), 6.82 (dd, 1H, J = 2.5, 8.5), 6.47 (d, 1H , J = 2.0), 6.43 (d, 1H, J = 2.0), 6.27 (s, 1H, NH), 5.16 (d, 1H, J = 8.1), 4.18 (dd, 1H, J = 5.5, 14.0), 3.82 (s, 3H), 3.70 (s, 3H), 3.20 (m, 1H), 3.02 (dd, 1H, J = 11.5, 14.0), 2.38 (s, 3H); ^{13}C NMR (125 MHz) 159.9, 146.0, 144.3, 144.1, 138.7, 137.6, 136.7, 133.0, 131.4, 129.8, 129.7, 129.1, 129.0, 127.4, 127.0, 119.3, 113.2, 113.0, 109.2, 109.1, 79.4, 56.0, 55.5, 47.6, 40.3, 21.5. Anal. Calcd for $C_{30}H_{28}N_2O_7S_2$: C, 60.79; H, 4.76; N, 4.73. Found: C, 60.80; H, 4.68; N, 4.50.

***N*-[(6a*S**,11a*S**)-10-(Benzyloxy)-3-methoxy-5-(4-toluenesulfonyl)-6,6a,11,11a-tetrahydrobenzofuro[3,2-*c*][1]-quinoline-8-yl]benzenesulfonamide (17).** According to general method A, a 3.4:1 mixture of dihydroquinoline **12** and its 5-methoxy isomer (110 mg, 0.35 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $BF_3{\cdot}Et_2O$ (40 μL, 0.33 mmol) and monoimide **3** (86 mg, 0.24 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **17** (86 mg, 53%) as a white solid, mp 88−90 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.14 (1:4 EtOAc:hexanes); ^{1}H NMR (300 MHz) 7.60−7.16 (m, 16H), 6.81 (dd, 1H, J = 8.4, 2.4), 6.56 (s, 1H, NH), 6.53 (d, 1H, J = 1.8), 6.45 (d, 1H, J = 1.8), 5.10 (d, 1H, J = 8.1), 4.96 (s, 2H), 4.18 (dd, 1H, J = 5.4, 13.8), 3.81 (s, 3H), 3.16 (m, 1H), 2.96 (dd, 1H, J = 13.8, 11.7), 2.36 (s, 3H); ^{13}C NMR (75 MHz) 159.7, 146.3, 144.0, 143.0, 138.5, 137.4, 136.6, 136.2, 132.8, 131.2, 129.7, 129.4, 128.8, 128.3, 127.9, 127.3, 127.1, 126.9, 119.3, 113.1, 113.05, 111.4, 109.0, 79.0, 70.9, 55.4, 47.4, 40.1, 21.4 (one sp^2-C signal is not visible). Anal. Calcd for $C_{36}H_{32}N_2O_7S_2$: C, 64.65; H, 4.82; N, 4.19. Found: C, 64.55; H, 5.00; N, 4.10.

***N*-[(6a*S**,11a*S**)-10-Isobutoxy-3-methoxy-5-(4-toluenesulfonyl)-6,6a,11,11a-tetrahydrobenzofuro[3,2-*c*][1]-quinoline-8-yl]benzenesulfonamide (18).** According to general method A, a 2.5:1 mixture of dihydoquinoline **12** and its 5-methoxy isomer (122 mg, 0.386 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $BF_3{\cdot}Et_2O$ (37 μL, 0.29 mmol) and monoimide **4** (80 mg, 0.25 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **18** (46 mg, 29%) as a white solid, mp 108−109 °C (Et_2O/hexanes); R_f 0.08 (2:2:6 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.71 (dd, 2H, J = 1.2, 8.4), 7.55 (t, 1H, J = 7.3), 7.48−7.39 (m, 6H), 7.26 (d, 1H, J = 2.3) 7.19 (d, 1H, J = 8.2), 6.83 (dd, 1H, J = 2.6, 8.6), 6.75 (broad s, 1H, NH), 6.47 (s, 2H), 5.09 (d, 1H, J = 8.2), 4.21 (dd, 1H, J = 5.6, 14.0), 3.82 (s, 3H), 3.58 (d, 2H, J = 6.6), 3.19 (m, 1H), 2.98 (dd, 1H, J = 14.0, 11.7), 2.40 (s, 3H), 1.97 (m, 1H), 0.92 (d, 6H, J = 6.7); ^{13}C NMR (125 MHz) 159.8, 146.4, 144.1, 143.8, 138.7, 137.5, 136.7, 132.9, 131.2, 129.8, 129.5, 129.2, 128.9, 127.4, 127.0, 120.0, 113.3, 112.9, 111.0, 109.2, 78.9, 75.5, 55.5, 47.6, 40.3, 28.0, 21.5, 19.1; HRMS m/z 635.1876 (M + 1) (Calcd $C_{33}H_{35}N_2S_2O_7$ 635.1886).

(6a*S,11a*S**)-11-(Benzenesulfonyl)-3,9-dimethoxy-8-hydroxy-6,6a,11,11a-tetrahydro[1]benzopyrano[4,3-*b*]indole (19).** According to general method B, 7-methoxy-2*H*-chromene (**11**, 32 mg, 0.20 mmol) was added to a solution of a mixture of $TiCl_4$ (20 μL, 0.18 mmol) and $Ti(OiPr)_4$ (107 μL, 0.361 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **2** (50 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **19** (38 mg, 48%) as a white solid, mp > 250 °C (dec) (Et_2O); R_f 0.38 (2:2:6 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (DMSO-d_6, 500 MHz) 8.95 (s, 1H), 7.70−7.62 (m, 3H), 7.54−7.48 (m, 3H), 6.94 (s, 1H), 6.68 (s, 1H), 6.62−6.60 (dd, 1H, J = 8.5, 2.5), 6.18 (d, 1H, J = 2.5), 5.53 (d, 1H, J = 8.5 Hz), 4.41 (dd, 1H, J = 1.5, 12), 3.98 (dd, 1H, J = 12, 2.4), 3.75 (s, 3H), 3.65 (s, 3H), 2.86 (bd, 1H, J = 8.5); ^{13}C NMR (DMSO-d_6, 125 MHz) 159.6, 156.5, 147.5, 145.1, 137.5, 133.5, 132.4, 131.4, 129.3, 127.0, 125.6, 114.0, 110.7, 109.0, 103.8, 100.9, 63.9, 59.8, 55.8, 55.1 (one signal is buried under residual solvent signals). Anal. Calcd for $C_{23}H_{21}NO_6S$: C, 62.86; H, 4.82; N, 3.19. Found: C, 62.64; H, 4.80; N, 3.16.

***N*-[(6a*S**,11a*S**)-9-(Benzyloxy)-6,6a,11,11a-tetrahydro-3-methoxy-11-(benzenesulfonyl)[1]benzopyrano[4,3-*b*]indole-8-ol (20).** According to general method B, 7-methoxy-2*H*-chromene (**11**, 28 mg, 0.17 mmol) was added to a solution of a mixture of $TiCl_4$ (39 μL, 0.35 mmol) and $Ti(OiPr)_4$ (101 μL, 0.34 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **3** (50 mg, 0.14 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (2:2:6 to 2:3:5 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **20** (37 mg, 51%) as a white solid, mp 196−197 °C (EtOAc/hexanes); R_f 0.39 (2:4:4 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.71 (d, J = 8.7, 2H), 7.55−7.32 (m, 10H), 7.27 (s, 1H), 6.71 (s, 1H), 6.61 (dd, J = 2.6, 8.7, 1H), 6.20 (d, J = 2.5, 1H), 5.62 (s, 1H), 5.37 (d, J = 8.4, 1H), 5.12 (ABq, J = 11, $\Delta\nu$=43 Hz, 2H), 4.33 (dd, J = 1.9, 12, 1H), 4.03 (dd, J = 2.4, 12, 1H), 3.70 (s, 3H), 2.81 (bd, J = 8.3, 1H); ^{13}C NMR (125 MHz) 160.2, 156.6, 145.5, 144.6, 137.9, 135.8, 133.9, 133.0, 132.0, 129.0, 128.8, 128.5, 128.2, 127.0, 126.0, 113.3, 109.5, 109.2, 105.3, 101.2, 71.3, 64.2, 60.1, 55.2, 40.1. Anal. Calcd for $C_{29}H_{25}NO_6S$: C, 67.56; H, 4.90; N, 2.72. Found: C, 67.50; H, 5.10; N, 2.60.

(6a*S,11a*S**)-11-(Benzenesulfonyl)-8-hydroxy-9-isobutoxy-3-methoxy-6,6a,11,11a-tetrahydro[1]benzopyrano-[4,3-*b*]indole (21).** According to general method B, 7-methoxy-2*H*-chromene (**11**, 50 mg, 0.31 mmol) was added to a solution of a mixture of $TiCl_4$ (36 μL, 0.33 mmol) and $Ti(OiPr)_4$ (101 μL, 0.340 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **4** (70 mg, 0.22 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **21** (60 mg, 57%) as a white solid, mp 194−196 °C (CH_2Cl_2/Et_2O/hexanes); R_f 0.15 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz) 7.70 (d, 1H, J = 8.5), 7.61 (d, 2H, J = 8.0), 7.55 (t, 1H, J = 8), 7.40 (t, 2H, J = 8), 7.14 (s, 1H), 6.70 (s, 1H), 6.60 (dd, 1H, J = 8.5, 2.5), 6.19 (d, 1H, J = 2.5), 5.60 (s, 1H, OH), 5.35 (d, 1H, J = 8.2), 4.31 (dd, 1H, J = 12, 1.5), 4.02 (dd, 1H, J = 12, 2.4), 3.88 (dd, 1H, J = 8.9, 6.6), 3.74 (dd, 1H, J = 8.9, 6.6), 3.70 (s, 3H), 2.79 (b d, 1H, J = 8.2), 2.11 (m, 1H), 1.04 (d, 3H, J = 6.8), 1.02 (d, 3H, J = 6.8); ^{13}C NMR (125 MHz) 160.2, 156.5, 146.1, 144.5, 138.0, 133.9, 133.1, 132.0, 129.1, 127.1, 125.5, 113.3, 109.5, 108.8, 104.8, 101.1, 75.5, 64.2, 60.1, 55.2, 40.1, 28.2, 19.2. Anal. Calcd for $C_{26}H_{27}NO_6S$: C, 64.84; H, 5.65; N, 2.91. Found: C, 64.50; H, 5.80; N, 2.68.

(6a*S,11a*S**)-11-(Benzenesulfonyl)-9-(benzyloxy)-8-hydroxy-3-methoxy-5-(4-toluenesulfonyl)-6,6a,11,11a-tetrahydroindolo[3.2-*c*][1]quinoline (23).** According to general method B, a 3:1 mixture of dihydroquinoline **12** and its 5-methoxy isomer (63 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was added to a solution of a mixture of $TiCl_4$ (28 μL, 0.26 mmol) and $Ti(OiPr)_4$ (77 μL, 0.26 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **3** (55 mg, 0.16 mmol) in CH_2Cl_2 (10 mL). Workup

and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **23** (50 mg, 48%) and **17** (27 mg, 26%). Physical and spectral properties of **23**, a white solid, mp 143−144 °C (MeOH); R_f 0.21 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.77 (d, 1H, J = 8.7), 7.51 (t, 1H, J = 7.3), 7.46−7.36 (m, 6H), 7.29−7.25 (m, 4H), 7.21 (d, 2H, J = 8.0), 7.14 (d, 2H, J = 7.8), 7.05 (d, 1H, J = 2.3), 6.82 (dd, 1H, J = 2.3, 8.7), 6.52 (s, 1H), 5.61 (s, 1H, OH), 5.16 (ABq, 2H, J = 11.5, $\Delta\upsilon$ = 18 Hz), 4.41 (d, 1H, J = 9.6), 4.21 (dd, 1H, J = 7.0, 14.1), 3.77 (s, 3H), 3.44 (dd, 1H, J = 8.0, 14.1), 3.18 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz) 159.3, 145.3, 144.8, 143.7, 138.0, 137.0, 136.8, 135.7, 133.4, 133.2, 130.1, 129.7, 128.8, 128.7, 128.6, 128.0, 127.6, 127.1, 121.8, 113.1, 109.9, 109.2, 104.6, 71.2, 60.7, 55.5, 47.4, 41.8, 21.6. Anal. Calcd for $C_{36}H_{32}N_2O_7S_2$: C, 64.65; H, 4.82; N, 4.41. Found: C, 62.39; H, 5.10; N, 4.08.

Compound **17** was identified by spectral comparison to the product isolated from the BF_3·Et_2O-promoted reaction, see above.

(6a*S,11a*S**)-11-(Benzenesulfonyl)-8-hydroxy-9-isobutoxy-3-methoxy-5-(4-toluenesulfonyl)-6,6a,11,11a-tetrahydroindolo[3.2-*c*][1]quinoline (24).** According to general method B, a 3:1 mixture of dihydroquinoline **12** and its 5-methoxy isomer (29 mg, 0.092 mmol) in CH_2Cl_2 (2 mL) was added to a solution of a mixture of $TiCl_4$ (13 μL, 0.12 mmol) and Ti(OiPr)$_4$ (34 μL, 0.12 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **4** (22 mg, 0.069 mmol) in CH_2Cl_2 (10 mL). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **24** (24 mg, 55%) and **18** (16 mg, 37%). Physical and spectral properties of **24**, a white solid, mp 204−205 °C (MeOH); R_f 0.12 (2:2:6 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.77 (d, 1H, J = 8.7), 7.55 (apparent t, 1H, J = 7.2), 7.38 (d, 2H, J = 8.3), 7.35−7.30 (m, 4H), 7.20 (d, 2H, J = 8.2), 7.15 (s, 1H), 7.04 (d, 1H, J = 2.6), 6.81 (dd, 1H, J = 2.6, 8.7), 6.53 (s, 1H), 5.57 (s, 1H, OH), 4.44 (d, 1H, J = 9.6), 4.20 (dd, 1H, J = 6.9, 14.1), 3.88 (dd, 1H, J = 6.6, 9.0), 3.75 (m, 4H), 3.47 (dd, 1H, J = 7.8, 14.1), 3.17 (m, 1H), 2.46 (s, 3H), 2.13 (m, 1H), 1.05 (d, 3H, J = 6.2), 1.04 (d, 3H, J = 6.2); ^{13}C NMR (125 MHz) 159.3, 146.0, 144.6, 143.7, 138.0, 137.0, 136.9, 133.4, 133.2, 130.1, 129.7, 128.8, 127.2 (2C), 121.7, 113.0, 109.6, 109.0, 104.0, 75.6, 60.7, 55.4, 47.3, 41.8, 28.2, 21.6, 19.2 (2C), (one sp^2-C signal is not visible). Anal. Calcd for $C_{33}H_{34}N_2O_7S_2$: C, 62.44; H, 5.40; N, 4.41. Found: C, 62.39; H, 5.10; N, 4.08.

Compound **18** was identified by spectral comparison to the product isolated from the BF_3·Et_2O-promoted reaction, see above.

(1*R,5*R**,6*R**,7*R**)-3-Hydroxy-6-methyl-7-phenylbicyclo[3.2.1]oct-3-ene-2,8-dione (33a).** According to general method B, *trans*-β-methylstyrene (26 μL, 0.20 mmol) was added to a solution of a mixture of $TiCl_4$ (20 μL, 0.181 mmol) and Ti(OiPr)$_4$ (161 μL, 0.542 mmol) in CH_2Cl_2 (0.5 mL) and **3** (63.7 mg, 0.181 mmol) in CH_2Cl_2 (10 mL). The reaction was warmed gradually to rt until finished (16 h). Workup and chromatography (1:1:8 CH_2Cl_2:Et_2O:hexanes) of the crude yellow oil afforded **33a** (18 mg, 41%) as a pale yellow oil which was identified by comparison of spectral data to that reported.[2a]

(1*R,5*R**,6*R**,7*R**)-3-Hydroxy-6-methyl-7-(3-methoxyphenyl)-bicyclo[3.2.1]oct-3-ene-2,8-dione (33b).** According to general method B, (*E*)-3-propenylanisole (15 mg, 0.100 mmol) was added to a solution of a mixture of $TiCl_4$ (33 μL, 0.30 mmol) and Ti(OiPr)$_4$ (89 μL, 0.30 mmol) in CH_2Cl_2 (0.5 mL) and monoimide **3** (35 mg, 0.10 mmol) in CH_2Cl_2 (10 mL). The reaction was warmed gradually to rt until finished (16 h). Workup and chromatography (1:1:8 to 2:2:6 CH_2Cl_2/Et_2O/hexanes) of the crude yellow oil afforded **33b** (13 mg, 48%) as a light yellow oil; R_f 0.16 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.20 (t, 1H, J = 8.0), 6.78 (dd, 1H, J = 2.4, 8.0), 6.75 (d, 1H, J = 8.5), 6.64 (bd, 1H, J = 8.0), 6.60 (bs, 1H), 5.91 (s, 1H, OH), 3.86 (dd, 1H, J = 1.8, 7.0), 3.77 (s, 3H), 3.21 (t, 1H, J = 7), 3.06 (dd, 1H, J = 1.8, 8.5), 2.56 (apparent quintet, 1H), 1.26 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 199.1, 191.5, 159.8, 149.9, 139.4, 129.8, 120.5, 119.6, 114.4, 112.8, 55.1, 54.2, 49.3, 42.3, 21.4, 12.0; HRMS m/z 272.1049 (M$^+$) (Calcd for $C_{16}H_{16}O_4$ 272.1049).

(2*R,3*R**)-1-(Benzenesulfonyl)-2,3-dihydro-5,6-dimethoxy-2-(4-methoxyphenyl)-3-methylindole (34).** A slurry of phenol **8a** (80 mg, 0.19 mmol) and K_2CO_3 (31 mg, 0.23 mmol) in acetone (2 mL) at rt was treated with methyl iodide (12 μL, 0.20 mmol) and (nBu)$_4$N$^+$ I$^-$ (3 mg, 0.009 mmol). The reaction mixture was refluxed under nitrogen for 24 h, cooled to rt, and then poured into water (5 mL). CH_2Cl_2 (5 mL) was added, and the aqueous layer was separated and extracted with CH_2Cl_2 (3 × 5 mL). The combined extracts were washed with H_2O (20 mL), brine (20 mL), dried (Na_2SO_4), and concentrated. Chromatography of the resultant pale yellow solid (2:2:6 Et_2O:CH_2Cl_2:hexanes) afforded **34** (63 mg, 76%) as a white crystalline solid, mp 133−134 °C (Et_2O/CH_2Cl_2/hexanes); R_f 0.16 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.71 (d, 2H, J = 7.6), 7.53 (t, 1H, J = 7.4), 7.43 (m, 3H), 7.20 (d, 2H, J = 8.7), 6.83 (d, 2H, J = 8.7), 6.52 (s, 1H), 4.57 (d, 1H, J = 3), 3.98 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 2.97 (dq, 1H, J = 3, 7), 0.68 (d, 3H, J = 7); ^{13}C NMR (125 MHz) 159.0, 149.1, 146.8, 137.3, 134.9, 134.2, 133.0, 128.9, 127.3, 126.9, 114.0, 107.2, 100.9, 72.8, 56.3, 56.2, 55.3, 46.0, 21.9 (one quaternary sp^2-C signal is not apparent). Anal. Calcd for $C_{24}H_{25}NO_5S$: C, 65.58; H, 5.73; N, 3.19. Found: C, 65.40; H, 5.40; N, 2.90.

(2*R,3*R**)-1-(Benzenesulfonyl)-2,3-dihydro-2-(3,4-dimethoxyphenyl)-6-methoxy-3-methylindol-5-yl Trifluoromethanesulfonate (35).** To a solution of phenol **8b** (90 mg, 0.20 mmol) and pyridine (0.16 mL, 2.0 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added trifluoromethanesulfonic anhydride (0.13 mL, 0.79 mmol). The reaction mixture was stirred for 15 min at −78 °C and poured into water (10 mL), and CH_2Cl_2 (10 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 5 mL). The combined CH_2Cl_2 extracts were washed with saturated aqueous sodium bicarbonate (20 mL), 10% aqueous hydrochloric acid (20 mL), brine (20 mL), dried (Na_2SO_4), and concentrated. Chromotagraphy (1:1:8 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **35** (80 mg, 69%) as a white solid, mp 64−65 °C (Et_2O/hexanes); R_f 0.35 (3:3:4 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 7.68 (d, 2H, J = 7.5), 7.56 (t, 1H, J = 7.5), 7.53 (s, 1H), 7.44 (t, 2H, J = 7.5), 6.88 (s, 1H), 6.83 (dd, 1H, J = 1.8, 8.3), 6.78 (d, 1H, J = 8.3), 6.69 (d, 1H, J = 1.8), 4.67 (d, 1H, J = 3.9), 3.99 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H), 3.07 (dq, 1H, J = 3.9, 7.0), 0.88 (d, 3H, J = 7.0); ^{13}C NMR (125 MHz) 151.5, 149.1, 148.8, 141.7, 137.6, 135.2, 133.9, 133.5, 129.0, 127.4, 127.1, 119.3 (q, J_{C-F} = 320) 118.4, 118.2, 111.0, 108.9, 100.8, 73.7, 56.6, 55.9, 55.8, 45.1, 21.4; HRMS m/z 587.0920 (M$^+$) (Calcd for $C_{25}H_{24}NO_8S_2F_3$ 587.0895).

1-(Benzenesulfonyl)-5,6-dimethoxy-2-(4-methoxyphenyl)-3-methylindole (36a). To a solution of **34** (35 mg, 0.080 mmol) in dry benzene (3 mL) was added DDQ (23.5 mg, 0.104 mmol), and the mixture was stirred for 20 h at rt. The mixture was filtered, concentrated, and the residue was dissolved in ether (20 mL), washed with 10% aqueous NaOH solution (15 mL), dried (Na_2SO_4), and concentrated. Chromatography (1:1:8 Et_2O:CH_2Cl_2:hexanes) afforded **36a** (25 mg, 72%) as a white solid, mp >190 °C dec (Et_2O/hexanes); R_f 0.17 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.91 (s, 1H), 7.44 (t, 1H, J = 7.4), 7.34 (d, 2H, J = 7.5), 7.26−7.21 (m, 4H), 6.95 (d, 2H, J = 8.5), 6.80 (s, 1H), 4.04 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz) 159.4, 147.9, 147.4, 137.7, 135.4, 133.2, 132.5, 131.2, 128.5, 126.6, 125.0, 123.8, 119.6, 112.8, 100.3 (2C), 56.4, 56.1, 55.2, 9.6; HRMS m/z 437.1326 (M$^+$) (Calcd for $C_{24}H_{23}NO_5S$ 437.1297).

1-(Benzenesulfonyl)-2-(3,4-dimethoxyphenyl)-6-methoxy-3-methylindol-5-yl Trifluoromethanesulfonate (36b). To a solution of **35** (65 mg, 0.11 mmol) in dry benzene (6 mL) was added DDQ (65 mg, 0.29 mmol), and the mixture was stirred for 24 h at 70 °C. The mixture was worked up as described for **36a**. Chromatography (1:1:8 Et_2O:CH_2Cl_2:hexanes) afforded **36b** (47 mg, 70%) as a white solid, mp 186−187 °C (Et_2O); R_f 0.39 (3:3:4 CH_2Cl_2:Et_2O:hexanes); ^{1}H NMR (500 MHz) 8.08 (s, 1H), 7.50 (t, 1H, J = 7.3), 7.35 (m, 4H), 7.26 (s, 1H), 6.87 (d, 1H, J = 8.2), 6.73 (dd, 1H, J = 1.9, 8.2), 6.70 (d, 1H, J = 1.9), 4.06 (s, 3H), 3.96 (s, 3H), 3.82 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (125 MHz) 149.4, 149.3, 147.9, 138.2, 136.8, 136.7, 136.4, 133.7, 128.8, 126.8, 124.4, 124.2, 122.8,

118.8 (q, J_{C-F} = 315), 118.5, 115.0, 112.3, 110.0, 101.0, 56.8, 55.9 (2C), 9.4. Anal. Calcd for $C_{25}H_{22}NO_8S_2F_3$: C, 51.28; H, 3.79; N, 2.39. Found: C, 51.33; H, 3.53; N, 2.18.

1-(Benzenesulfonyl)-2-(3,4-dimethoxyphenyl)-6-methoxy-3-methylindole (36c). To triflate **36b** (40 mg, 0.068 mmol) in DMF (0.35 mL) at rt was added palladium(II) acetate trimer (9.7 mg, 0.14 mmol) followed by 1,1′-bis(diphenylphosphino)ferrocene (20 mg, 0.036 mmol), triethylamine (194 μL, 1.40 mmol), and a 90% aqueous formic acid solution (0.05 mL). The mixture was heated at 90 °C for 24 h and then cooled, and water (0.6 mL) was added followed by EtOAc (4 mL). The aqueous layer was separated and extracted with EtOAc (3 × 4 mL). The combined extracts were washed with saturated aqueous ammonium chloride, saturated aqueous sodium bicarbonate, and water (5 mL each), dried (Na_2SO_4), and concentrated. Chromatography (1:1:8 CH_2Cl_2:Et_2O:hexanes) of the crude brown oil afforded **36c** (25 mg, 84%) as a white solid, mp 149−150 °C (Et_2O/hexanes); R_f 0.38 (3:3:4 Et_2O:CH_2Cl_2:hexanes); ^{1}H NMR (500 MHz) 7.91 (d, 1H, J = 2.2), 7.45 (t, 1H J = 7.4), 7.40 (d, 2H, J = 7.5), 7.29 (m, 3H), 6.93 (dd, 1H, J = 2.2, 8.5), 6.89 (d, 1H, J = 8.1), 6.81 (m, 2H), 3.96 (s, 3H), 3.94 (s, 3H), 3.85 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz) 158.1, 149.1, 147.8, 138.2, 135.2, 133.3, 128.5, 126.8, 125.5, 124.0, 123.9, 119.4, 119.3, 115.0, 112.9, 109.9, 100.7, 55.9 (2C), 55.8, 9.5 (one sp^2-C signal is not apparent); HRMS m/z 437.1307 (M^+) (Calcd for $C_{24}H_{23}NO_5S$ 437.1297).

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Supporting Information Available: Full experimental procedures for preparation of styrenes **1e**/**g**, licarin B, and eupomatenoids-1 and -12; IR and mass spectral data for all new products; copies of ^{1}H and ^{13}C NMR spectra of new compounds lacking combustion analytical data (49 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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