phite, but the yield of the reaction decreased to 33%.

In conclusion, we have found that nickel catalysts promote the cycloaddition of norbornadienes bearing electron-withdrawing and -donating substituents and that ligands can affect the regioselectivity. Importantly, the substituents exhibited complementary behavior in that *an electron-deficient diene favored the adduct with the diene substituent attached to the cyclopropane, while an electron-donating substituent was strongly disfavored on the cyclopropane carbon.* The overall tendency follows the Diels-Alder reaction in that ortho and para orientations are greatly preferred. The homo-Diels-Alder reaction is complicated by the possibility that both ortho and para isomers can arise from the *same* substrates depending on the direction of approach of the dienophile. The absence of the meta isomer in any of the cycloaddition reactions we have carried out is noteworthy. A mechanistic interpretation of these results is difficult in light of the complex multistep mechanism that is undoubtedly involved, and we will resist speculation prior to the results of further experimentation which is now in progress.

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Supplementary Material Available: General and specific procedures and characterization for the compounds reported (6 pages). Ordering information is given on any current masthead page.

Articles

Sequential Directed Ortho Metalation-Boronic Acid Cross-Coupling Reactions. A General Regiospecific Route to Oxygenated Dibenzo[*b*,*d*]pyran-6-ones Related to Ellagic Acid

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A general regiospecific synthesis of dibenzo[*b*,*d*]pyran-6-one derivatives **1a**,**c** and **8a-i** related to ellagic acid is described (Scheme I, Table I). The sequence involves directed ortho metalation-boronation of benzamides **4** to give the arylboronic acids **5**, which, upon palladium-catalyzed cross-coupling with alkoxybromobenzenes **6** leads to the biphenylamides **7**. BBr_3 demethylation followed by acid-catalyzed cyclization affords pyranone **8**. In this manner, the naturally occurring dibenzopyranones **1a**, autumnariol (**1c**), and the heterocyclic analogue **13** (Scheme III) were efficiently prepared.

The dibenzo[*b*,*d*]pyran-6-one skeleton **1** is a somewhat neglected condensed heterocycle, which, nevertheless, is embodied in a small group of oxygenated natural products consisting of **1a** (from castoreum, the secretion of the scent gland of the Canadian beaver *Castor fiber*),[1] alternariol **1b** (*Dematiaceae* moulds),[2] autumnariol **1c**,[3] autumnariniol **1d**,[3] **1e**[4] (*Tamarix nilotica*), and altenuisol **1f** (*Alternaria tenius*).[5] Recently, the benzo[*d*]naphthopyran-6-one nucleus **2**, a benzannelated analogue of **1**, has surfaced as common ring system of a group of antibiotics isolated from various strains of *Streptomyces*,[6-9] which, mainly as a result of promising antitumor activity, has stimulated noteworthy synthetic efforts.[10] Structurally related to **1**

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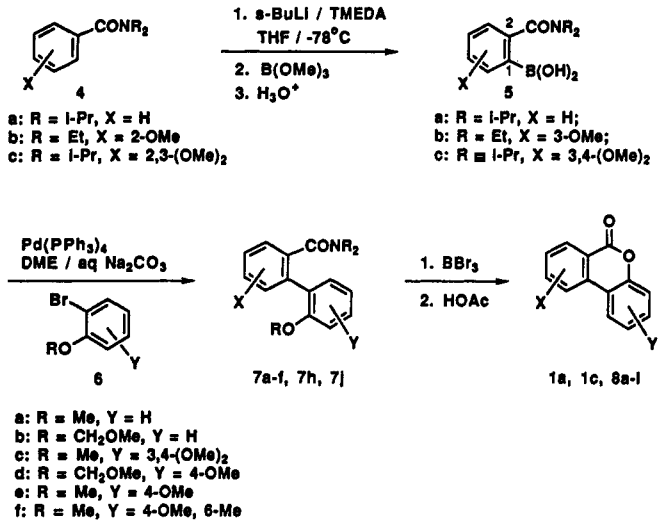
Scheme I



4: a: R = i-Pr, X = H; b: R = Et, X = 2-OMe; c: R = i-Pr, X = 2,3-(OMe)2

5: a: R = i-Pr, X = H; b: R = Et, X = 3-OMe; c: R = i-Pr, X = 3,4-(OMe)2

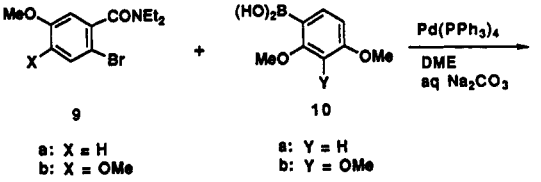
6

7a-f, 7h, 7j

1a, 1c, 8a-f

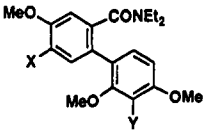
a: R = Me, Y = H
b: R = CH_2OMe, Y = H
c: R = Me, Y = 3,4-$(OMe)_2$
d: R = CH_2OMe, Y = 4-OMe
e: R = Me, Y = 4-OMe
f: R = Me, Y = 4-OMe, 6-Me

Scheme II



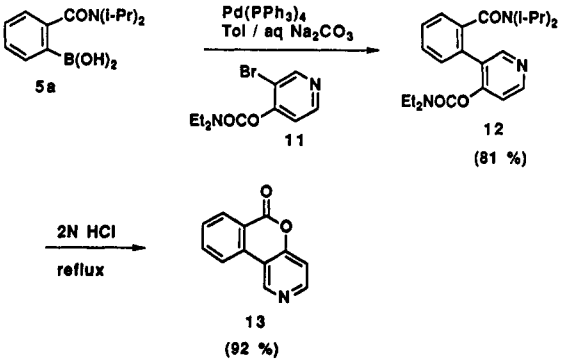
9: a: X = H; b: X = OMe

10: a: Y = H; b: Y = OMe



7g: X = Y = H
7i: X = Y = OMe

Scheme III



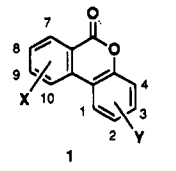
5a

11

12 (81 %)

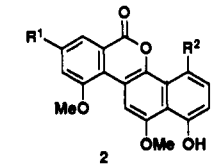
13 (92 %)

are also the lactonic analogues, ellagic acid **3a**,[11] coruleoellagic acid **3b**,[12] and several alkylated and more highly oxygenated derivatives isolated from *Shorea worthingtonii* and *Vatica obscura*. Interest in ellagic acid, a well-known and readily available product, has been rekindled recently by the demonstration that it inhibits the mutagenicity of polycyclic aromatic hydrocarbons (PAH) in vivo.[11b,13]



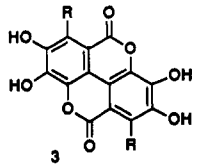
1

	X	Y	
a:	8-OH	3-OH	
b:	7,9-$(OH)_2$	1-Me, 3-OH	(alternariol)
c:	7-OH	1-Me, 3-OH	(autumnariol)
d:	7-OH	1-Me, 3-OH, 4-OMe	(autumnariniol)
e:	8,9,10-$(OH)_3$	3,4-$(OH)_2$	
f:	7,9-$(OH)_2$	2-OH, 3-OMe	(altenuisol)



2

R^1 = Me, $CH=CH_2$, Et
R^2 = glycoside



3

a: R = H (Ellagic acid)
b: R = OH (Coruleoellagic acid)

The most travelled synthetic route to dibenzopyranones 1 involves the condensation of resorcinol with *o*-bromobenzoic acid in alkaline medium in the presence of copper sulfate catalyst (Hurtley reaction).[14] This reaction has been applied to the total synthesis of **1a**,[15] alternariol **1b**,[16] alternariol 9-methyl ether,[16] alternariol trimethyl ether,[2] autumnariol **1c**,[17] and autumnariniol **1d**.[17] The Hurtley reaction has reasonable scope for the preparation of oxygenated dibenzopyranones[14b] but is restricted by the requirement of highly activated phenols (resorcinols and orcinols) and by low yields (typically 10–25%). Alternative routes to compounds 1 are generally limited in scope and inefficient.[18,19]

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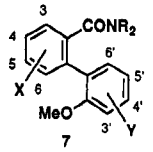
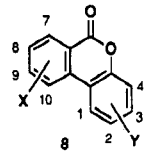
Table I. Synthesis of Biphenyl-2-carboxamides and Dibenzo[*b*,*d*]pyran-6-ones



7



8

compd	R	X	Y	yield, %
7a	*i*-Pr	H	H	85
7b	Et	3-OMe	H	64
7c[a]	*i*-Pr	3,4-$(OMe)_2$	H	71
7d	*i*-Pr	H	3′,4′-$(OMe)_2$	73
7e[a]	Et	3-OMe	4′-OMe	85
7f	Et	3-OMe	4′-OMe	88
7g	Et	4-OMe	4′-OMe	76
7h	*i*-Pr	3,4-$(OMe)_2$	3′,4′-$(OMe)_2$	74
7i	Et	4,5-$(OMe)_2$	3′,4′-$(OMe)_2$	77
7j	Et	3-OMe	4′-OMe, 6′-Me	45

compd	X	Y	yield, %
8a	H	H	89
8b	7-OH	H	79
8c[b]	7,8-$(OMe)_2$	H	85
8d	7,8-$(OH)_2$	H	82
8e	H	3,4-$(OH)_2$	71
8f[b]	7-OMe	3-OMe	73
8g	7-OH	3-OH	62
1a	8-OH	3-OH	47
8h	7,8-$(OH)_2$	3,4-$(OH)_2$	55
8i	8,9-$(OH)_2$	3,4-$(OH)_2$	75
1c	7-OH	1-Me, 3-OH	88

[a] The corresponding 2′-OMOM derivative. [b] The BBr_3 step (Scheme I) was omitted.

In 1985, we reported[20] a new approach to the dibenzo[*b*,*d*]pyran-6-one skeleton by a strategy that linked the regiospecific directed ortho metalation reaction[21] and the Pd(0)-catalyzed arylboronic acid cross-coupling process.[22] As part of programs aimed to derive broad synthetic utility from the metalation–cross-coupling connection[23] and to provide ellagic acid congeners for comprehensive structure–activity studies in inhibition of PAH mutagenicity,[24-25] we have developed and report herein a general, regiospecific, and efficient synthesis of dibenzopyranones (Scheme I) including natural products **1a** and autumnariol **1c**.

Standard metalation (*s*-BuLi/TMEDA/THF/−78 °C) of benzamides **4** (Scheme I) followed by trimethyl borate quench and acidic workup gave the crude arylboronic acid **5**. For characterization purposes, arylboronic acids **5a** and **5b** were converted into stable, high-melting diethanolamine adducts (see Experimental Section). In practice, however, the boronic acids were directly subjected to modified Suzuki cross-coupling conditions (DME/aqueous Na_2CO_3/$Pd(PPh_3)_4$/reflux) with aryl bromides **6** to give the biaryl derivatives **7**. In two cases **7g**, **7i**, convenience dictated inversion of the boronic acid–bromide functional groups in the cross-coupling partners (Scheme II). Thus coupling of **9a** and **9b** with the boronic acids **10a** and **10b** under the standard Pd(0)-catalyzed conditions led to **7g** and **7i**, respectively. Demethylation of biaryls **7** with excess BBr_3 led to the polyphenol, which, without purification, was subjected to acetic acid mediated cyclization to afford the dibenzopyranones **8**. The results of this sequence for the preparation of a variety of oxygenated derivatives **8** are summarized in Table I. The dibenzopyranones are high-melting, somewhat insoluble materials obtained in good to excellent yields. Methoxy derivatives **8c** and **8f** were obtained by direct HOAc treatment of **7c** and **7e**, respectively, under which conditions selective OMOM deprotection and cyclization occurred.

The metalation–cross-coupling sequence was readily applied to the total synthesis of **1a**, the natural product of castoreum,[1] and an ellagic acid metabolite.[11a] Furthermore, autumnariol **1c**, previously obtained in 10% overall yield by employing the Hurtley reaction,[17] was similarly synthesized from **7j** in 40% overall yield based on **6f**.

To demonstrate further generalization, the (*o*-carbamoylaryl)boronic acid **5a** (Scheme III) was cross-coupled with the *o*-pyridyl carbamate **11**, available by directed ortho metalation,[26] to afford the heterobiaryl **12**. Mild acid treatment gave, in high yield, the previously unknown benzopyranopyridone **13**.

In summary, the establishment of a link between the benzamide-directed ortho metalation[21] and the arylboronic acid–aryl bromide cross-coupling[22] regimens provides a general and rapid route for the synthesis of dibenzo[*b*,*d*]pyran-6-ones **8** and heterocyclic analogues, e.g., **13**. The demonstration of this synthetic connection[23] for the preparation of condensed aromatic and heteroaromatic systems, including natural products **1a** and **1c**, suggests that its broader application may be anticipated.

Experimental Section

General Procedures. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN, or M-H-W Laboratories, Phoenix, AZ. Melting points were determined on a Buchi SMP-20 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. ^1H NMR spectra were recorded on a Bruker AM-250 instrument with tetramethylsilane as an internal standard unless otherwise stated. Mass spectra (MS) were determined on a high-resolution Varian MAT-CH7 instrument at 70 eV unless otherwise indicated.

n-BuLi, *s*-BuLi, *t*-BuLi, diisopropylamine (DIA), *N,N,N′,N′*-tetramethylethylenediamine, trimethyl borate, and boron tribromide were purchased from Aldrich Chemical Co. Ltd. DIA and TMEDA were dried and distilled from CaH_2 and stored under argon. The titer of all alkyllithium reagents were determined with 2,5-dimethoxybenzyl alcohol as standard.[27] THF, Et_2O, and 1,2-dimethoxyethane were freshly distilled from sodium benzophenone ketyl prior to use. The $Pd(PPh_3)_4$ catalyst were prepared

(19) The recently described variation of the von Pechmann reaction between resorcinol and 2-oxycyclohexanecarboxylate [see refs 10e and 10i] and Pd(II)-mediated intramolecular cyclization of *o*-bromobenzoyl naphthalenes [see refs 10j and 10h] appear to have general synthetic potential.

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(24) Several of the compounds (e.g., **8e**, **8h**) have shown inhibitory activity of benzo[*a*]pyrenedihydrodiol epoxide (BPDE) mutagenicity in the Ames test (*Salmonella typhimurium* strain TA 100) comparable to ellagic acid. See: Josephy, P. D.; Lord, H. L.; Snieckus, V. *Mutagenesis* **1989**, *4*, 453. (b) Josephy, P. D.; Snieckus, V. U.S. Patent 7 165 471, 1991.

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according to a literature procedure[28] and stored in a refrigerator; its stability varied but activity was normally retained for 3 months. Metalation reactions were performed in oven- or flame-dried glassware under argon, using syringe–septum cap techniques. The phrase standard workup is the equivalent of addition of water or saturated NH_4Cl solution, extraction with CH_2Cl_2, washing the organic extract with saturated brine solution, drying (Na_2SO_4), filtration, and evaporation to dryness in vacuo. TLC was performed on E-Merck silica gel 60 strips and medium pressure column chromatography was carried out on BDH silica gel 60 (0.04–0.063 mm and 0.063–0.20 mm) with hexane/EtOAc (1:1 to 9:1) eluent unless otherwise indicated.

Benzamides. The following benzamides were prepared according to standard procedures and purified by Kugelrohr distillation or by recrystallization.

***N,N*-Diisopropylbenzamide (4a)**: mp 69–72 °C (ether–hexane) (lit.[29] mp 69–71 °C).

***N,N*-Diethyl-2-methoxybenzamide (4b)**: bp 105–106 °C (0.25 Torr) [lit.[30] bp 100–104 °C (1 Torr)].

***N,N*-Diisopropyl-2,3-dimethoxybenzamide (4c)**: mp 107–108 °C (ether–hexane) (lit.[31] mp not given).

Aryl Bromides. 2-Methoxybromobenzene **6a** and 2,4-dimethoxybromobenzene **6e** were purchased from Aldrich Chemical Co. All other aryl bromides were prepared by literature methods.

2-(Methoxymethoxy)bromobenzene (6b):[32] bp 82-84 °C (4.5 Torr).

2,3,4-Trimethoxybromobenzene (6c): bp 74–75 °C (0.2 Torr) [lit.[33] bp 97 °C (0.5 Torr)].

2-(Methoxymethoxy)-4-methoxybromobenzene (6d). In a modification of the literature procedure,[34] the sodium salt of 2-hydroxy-4-methoxybromobenzene (4.8 g, 24.0 mmol) generated with NaH (1.2 g, 25.0 mmol) in DME (100 mL) was treated with chloromethyl methyl ether (3.8 mL, 50 mmol). Standard workup followed by distillation gave 5.4 g (90%) of product: bp 83–85 °C (0.1 Torr); IR ($CHCl_3$) ν(max) 1590, 1483, 1156 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.51 (s, 3 H), 3.77 (s, 3 H), 5.22 (s, 2 H), 6.39 (dd, 1 H, J = 2.6 and 8.8 Hz, C_5-H), 6.75 (d, 1 H, J = 2.6 Hz, C_3-H), 7.40 (d, 1 H, J = 8.8 Hz, C_6-H); MS m/e (rel intensity) 248 (M^+, 95), 246 (M^+, 100), 218 (60), 216 (59).

Anal. Calcd for $C_9H_{11}O_3Br$: C, 43.75; H, 4.49. Found: C, 43.92; H, 4.61.

2,4-Dimethoxy-6-methylbromobenzene (6f): mp 54–55 °C (EtOAc–hexane) (lit.[35] mp 55–56 °C).

***N,N*-Diethyl-2-bromo-5-methoxybenzamide (9a).** *N,N*-Diethyl-3-methoxybenzamide was treated with Br_2 (1.1 equiv) in glacial HOAc at 10 °C. Standard workup followed by distillation gave **9a** in 80% yield: bp 158–160 °C (1.5 Torr); IR (neat) ν(max) 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, 3 H, J = 7.1 Hz), 1.26 (t, 3 H, J = 7.1 Hz), 2.21 (q, 2 H, J = 7.1 Hz), 3.20–3.35 (m, 1 H), 3.78 (s, 3 H), 3.80–3.88 (m, 1 H), 6.74–6.79 (m, 2 H), 7.41 (d, 1 H, J = 9.3 Hz).

Anal. Calcd for $C_{12}H_{16}NO_2Br$: C, 50.35; H, 5.59; N, 4.90. Found: C, 50.01; H, 5.35; N, 4.53.

***N,N*-Diethyl-2-bromo-4,5-dimethoxybenzamide (9b)**: mp 104–105 °C (EtOAc–hexane) (lit.[36] mp not given).

Preparation of (2-Carbamoylphenyl)boronic Acids (General Procedure). Boronic acid derivatives were obtained as colorless fluffy powders, which were generally used directly without purification in cross-coupling reactions. Absence of starting material by TLC (hexane–EtOAc, 1:1) was used as a criterion of complete conversion. For characterization purposes, boronic acids may be converted into their diethanolamine adducts as carried out for two cases (see below).

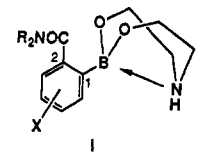
(2-(Diisopropylcarbamoyl)phenyl)boronic Acid (5a). To a solution of *s*-BuLi (39.2 mL, 39.2 mmol of a 1.0 M solution) and TMEDA (5.9 mL, 39.2 mmol) in anhydrous THF (200 mL) at −78 °C under argon was added dropwise a solution of *N,N*-diisopropylbenzamide **4a** (7.3 g, 35.7 mmol) in anhydrous THF (20 mL). The mixture was stirred for 45 min and treated with $B(OMe)_3$ (11.7 mL, 107.1 mmol). The solution was allowed to warm to ambient temperature over 12 h, cooled to 0 °C, and acidified to pH 6.5 with 5% aqueous HCl. Removal of THF in vacuo followed by standard workup afforded 8.5 g (95%) of crude boronic acid **5a**, which was used directly in the cross-coupling reaction.

The following arylboronic acids were similarly prepared.

(3-Methoxy-2-(diethylcarbamoyl)phenyl)boronic Acid (5b). From *N,N*-diethyl-2-methoxybenzamide **4b** (3.2 g, 15.4 mmol) and *s*-BuLi–TMEDA (1.1 equiv, 40 mmol) in THF (100 mL) and $B(OMe)_3$ (5.3 mL, 46.2 mmol), there was obtained 3.0 g (80%) of **5b** as a colorless powder.

(3,4-Dimethoxy-2-(diisopropylcarbamoyl)phenyl)boronic Acid (5c). From *N,N*-diisopropyl-2,3-dimethoxybenzamide **4c** (5.3 g, 20.0 mmol) and *s*-BuLi–TMEDA (1.1 equiv, 22 mmol) in THF (140 mL) and $B(OMe)_3$ (6.8 mL, 60.0 mmol), there was obtained 6.0 g (97%) of **5c** as a colorless fluffy solid.

Diethanolamine Esters of Arylboronic Acids. The procedure of Letsinger and Skoog[37] was adopted.



I

***(N–B)*-Perhydro-2-(2-(diisopropylcarbamoyl)phenyl)-1,3-dioxa-6-aza-2-borocine (i, R = *i*-Pr, X = H).** From crude boronic acid **5a** (0.50 g, 2.0 mmol) and diethanolamine (0.2 g, 2.0 mmol), there was obtained 0.52 g (81%) of product as colorless crystals: mp 203–204 °C (toluene); IR ($CHCl_3$) ν(max) 1597 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, 6 H, J = 7.7 Hz), 1.51 (d, 3 H, J = 6.8 Hz), 1.56 (d, 3 H, J = 6.8 Hz), 2.6–2.9 (m, 2 H), 3.1–3.3 (m, 1 H), 3.4–3.6 (m, 2 H), 3.7–4.2 (m, 5 H), 6.26 (br s, 1 H, NH), 7.01 (dd, 1 H, J = 7.0 and 1.6 Hz), 7.25 (dq, 2 H, J = 7.6 and 1.9 Hz), 7.82 (dd, 1 H, J = 7.5 and 1.7 Hz),; MS (CI, isobutane) m/e (rel intensity) 319 [$(M + 1)^+$, 100].

Anal. Calcd for $C_{17}H_{27}N_2O_3B$: C, 64.16; H, 8.55; N, 8.80. Found: C, 64.05; H, 8.66; N, 8.82.

***(N–B)*-Perhydro-2-(3-methoxy-2-(diethylcarbamoyl)-phenyl)-1,3-dioxa-6-aza-2-borocine (i, R = Et, X = 3-OMe).** From crude boronic acid **5b** (0.42 g, 1.7 mmol) and diethanolamine (0.18 g; 1.7 mmol), there was obtained 0.43 g (82%) of product, mp 185–190 °C (toluene); IR ($CHCl_3$) ν(max) 3202, 1587 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3 H, J = 7.1 Hz), 1.24 (t, 3 H, J = 7.2 Hz), 3.1–3.7 (m, 9 H), 3.77 (s, 3 H), 3.8–4.1 (m, 3 H), 6.24 (br s, 1 H, NH), 6.79 (dd, 1 H, J = 8.1 and 0.9 Hz), 7.26 (t, 1 H, J = 8.1 Hz), 7.40 (dd, 1 H, J = 7.3 and 0.9 Hz); MS (CI isobutane) m/e (rel intensity) 321 (M^+ + 1, 23), 106 (100).

Anal. Calcd for $C_{16}H_{25}N_2O_4B$: C, 60.02; H, 7.87; N, 8.75. Found: C, 59.58; H, 7.40; N, 9.05.

Preparation of Arylboronic Acids by Metal–Halogen Exchange. To a 1 M THF solution of the aryl bromide under argon at −78 °C was added dropwise a hexane solution of *n*-BuLi (1.1 equiv) over 15–30 min. The reaction mixture was stirred for an additional 15 min at −78 °C, treated with $B(OMe)_3$ (3 equiv), and allowed to warm to room temperature over 12 h. It was cooled to 0 °C and acidified to pH 6.5 with 5% aqueous HCl, and the whole was extracted with CH_2Cl_2. The organic layer was washed with saturated brine solution, dried (Na_2SO_4), and evaporated to dryness to yield a foamy material, which was used immediately in the cross-coupling reaction.

In the above manner, 2,4-dimethoxybromobenzene **6e** and 2,3,4-trimethoxybromobenzene **6c** were converted into (2,4-dimethoxyphenyl)boronic acid **10a** and (2,3,4-trimethoxyphenyl)-boronic acid **10b** in 88% and 89% yields, respectively.

Synthesis of Biaryls (General Procedure). To a suspension of $Pd(PPh_3)_4$ (0.03 equiv) in anhydrous DME was added the aryl

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bromide and the mixture was stirred for 10 min at rt. To this solution were added sequentially the arylboronic acid (1.5 equiv) in a minimum of EtOH and aqueous Na_2CO_3 (2 M solution, 2.0 equiv), and the mixture was refluxed for 18 h, cooled, and subjected to filtration. The filtrate was evaporated to dryness and the residue was treated with saturated NaCl solution. Standard workup followed by column chromatography gave the biaryl product.

The following biaryls were prepared according to the above procedure.

N,N-Diisopropyl-2'-methoxy-2-biphenylcarboxamide (7a). From (2-(diisopropylcarbamoyl)phenyl)boronic acid **5a** (0.5 g, 2.2 mmol), 2-methoxybromobenzene **6a** (0.37 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol), and Na_2CO_3 solution (2 M, 2 mL), there was obtained, after standard workup and chromatography, 0.53 g (85%) of product **7a**: mp 95–96 °C; (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (d, 3 H, J = 6.7 Hz), 0.92 (d, 3 H, J = 6.7 Hz), 1.11 (d, 3 H, J = 6.7 Hz), 1.48 (d, 3 H, J = 6.7 Hz), 3.20 (septet, 1 H, J = 6.7 Hz), 3.6 (septet, 1 H, J = 6.7 Hz), 3.8 (s, 3 H), 7.5–7.7 (m, 8 H): MS m/e (rel intensity) 311 (M^+, 21), 211 (100), 196 (22).

Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.96; H, 8.07; N, 4.52.

N,N-Diethyl-3,2'-dimethoxy-2-biphenylcarboxamide (7b). From (3-methoxy-2-(diethylcarbamoyl)phenyl)boronic acid **5b** (1.0 g, 4.0 mmol), 2-methoxybromobenzene **6a** (0.75 g, 4.0 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.12 mmol), and Na_2CO_3 (2 M solution, 4 mL), there was obtained, after standard workup and chromatography, 0.80 g (64%) of product **7b**: mp 111–112 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65 (t, 3 H, J = 7.1 Hz), 0.89 (t, 3 H, J = 7.1 Hz), 2.80 (m, 2 H), 3.19 (m, 2 H), 3.74 (s, 3 H), 3.85 (s, 3 H), 6.80–7.00 (m, 4 H), 7.20–7.40 (m, 3 H); MS m/e (rel intensity) 313 (M^+, 10), 241 (100).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.62; H, 7.24; N, 4.36.

N,N-Diisopropyl-2'-(methoxymethoxy)-3,4-dimethoxy-2-biphenylcarboxamide (7c). From (3,4-dimethoxy-2-(diisopropylcarbamoyl)phenyl)boronic acid **5c** (4.4 g, 14.3 mmol), 2-(methoxymethoxy)bromobenzene **6b** (2.8 g, 12.9 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol), and Na_2CO_3 (2 M solution, 13 mL), there was obtained, after standard workup and chromatography, 3.7 g (71%) of **7c**: mp 92–95 °C (EtOAc–hexane); IR ($CHCl_3$) ν(max) 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.49 (m, 3 H), 0.95–1.28 (m, 6 H), 1.45–1.66 (m, 3 H), 3.45 (s, 3 H), 3.18–3.64 (m, 2 H), 3.93 (s, 3 H), 3.94 (s, 3 H), 5.04–5.22 (m, 2 H), 6.91–7.31 (m, 5 H), 7.54 (dd, 1 H, J = 7.6 and 1.7 Hz); MS m/e (rel intensity) 401 (M^+, 5), 165 (100); HRMS calcd for $C_{23}H_{31}NO_5$ 401.2203, found 401.2211.

N,N-Diisopropyl-2',3',4'-trimethoxy-2-biphenylcarboxamide (7d). From **5a** (1.05 g, 4.2 mmol), 2,3,4-trimethoxybromobenzene **6c** (1.0 g, 3.8 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), and Na_2CO_3 (2 M solution, 3.8 mL), there was obtained, after standard workup and chromatography, 1.0 g (73%) of **7d**: mp 166–168 °C (petroleum ether); IR ($CHCl_3$) ν(max) 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71 (d, 3 H, J = 6.7 Hz), 0.99 (d, 3 H, J = 6.7 Hz), 1.23 (d, 3 H, J = 6.7 Hz), 1.50 (d, 3 H, J = 6.7 Hz), 3.28 (m, 1 H), 3.67 (m, 1 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 6.66 (d, 1 H, J = 8.7 Hz), 7.17 (d, 1 H, J = 8.7 Hz), 7.26–7.39 (m, 4 H); MS m/e (rel intensity) 371 (M^+, 20), 271 (100), 256 (30).

Anal. Calcd for $C_{22}H_{29}NO_4$: C, 71.13; H, 7.87; N, 3.77. Found: C, 71.07; H, 7.45; N, 3.31.

N,N-Diethyl-2'-(methoxymethoxy)-3,4'-dimethoxy-2-biphenylcarboxamide (7e). From **5b** (4.0 g, 16.0 mmol), 2-(methoxymethoxy)-4-methoxybromobenzene **6d** (2.9 g, 12.0 mmol), $Pd(PPh_3)_4$ (0.55 g, 0.48 mmol), and Na_2CO_3 (2 M solution, 16 mL), there was obtained, after standard workup and chromatography, 3.8 g (85%) of **7e**: bp 170–175 °C (0.05 Torr); IR ($CHCl_3$) ν(max) 1614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (t, 2 H, J = 7.1 Hz), 0.89 (t, 2 H, J = 7.1 Hz), 1.03 (t, 1 H, J = 7.1 Hz), 1.24 (t, 1 H, J = 7.1 Hz), 2.88 (m, 2 H), 3.16 (m, 2 H), 3.39 (s, 3 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.09 (s, 2 H), 6.53 (dd, 1 H, J = 8.5 and 2.4 Hz), 6.75 (d, 1 H, J = 2.4 Hz), 6.9 (m, 2 H), 7.2–7.3 (m, 2 H); MS m/e (rel intensity) 373 (M^+, 24), 358 (29), 301 (58), 271 (100).

Anal. Calcd for $C_{21}H_{27}NO_5$: C, 67.54; H, 7.29; N, 3.75. Found: C, 67.47; H, 7.29; N, 4.09.

N,N-Diethyl-2',3,4'-trimethoxy-2-biphenylcarboxamide (7f). From **5b** (1.4 g, 6.1 mmol), 2,4-dimethoxybromobenzene **6e** (1.2 g, 5.5 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), and Na_2CO_3 (2 M solution, 5.5 mL), there was obtained, after standard workup and chromatography (Et_2O eluent), 1.8 g (88%) of **7f**: mp 110–112 °C (Et_2O–hexane); IR (KBr) ν(max) 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69–1.42 (m, 6 H), 2.65–3.72 (m, 4 H), 3.85 (s, 3 H), 3.95 (s, 3 H), 4.00 (s, 3 H), 6.42–7.55 (m, 6 H); MS m/e (rel intensity) 343 (M^+, 24), 271 (100); HRMS calcd for $C_{20}H_{25}NO_4$ 343.1784, found 343.1775.

N,N-Diethyl-2',4,4'-trimethoxy-2-biphenylcarboxamide (7g). From (2,4-dimethoxyphenyl)boronic acid **10a** (1.6 g, 8.5 mmol), N,N-diethyl-2-bromo-5-methoxybenzamide **9a** (2.2 g, 7.7 mmol), $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol), and Na_2CO_3 (2 M solution, 7.7 mL), there was obtained 2.0 g (76%) of **7g**: mp 90–92 °C (Et_2O–hexane); IR (KBr) ν(max) 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7.0 Hz), 1.21 (t, 3 H, J = 7.0 Hz), 2.68–3.62 (m, 4 H), 3.75 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 6.31–7.41 (m, 6 H); MS m/e (rel intensity) 343 (M^+, 73), 312 (45), 271 (100), 256 (86), 241 (35), 220 (46); HRMS calcd for $C_{20}H_{25}NO_4$ 343.1784, found 343.1782.

N,N-Diisopropyl-2',3,4,3',4'-pentamethoxy-2-biphenylcarboxamide (7h). From **5c** (6.0 g, 19.0 mmol), 2,3,4-trimethoxybromobenzene **6c** (4.3 g, 17.0 mmol), $Pd(PPh_3)_4$ (0.69 mg, 0.6 mmol), and Na_2CO_3 (2 M solution, 19.0 mL), there was obtained, after standard workup and chromatography, 5.5 g (74%) of **7h**: mp 170–172 °C (hexane–EtOAc); IR (KBr) ν(max) 1626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63 (d, 3 H, J = 6.6 Hz), 1.02 (d, 3 H, J = 6.6), 1.15 (d, 3 H, J = 6.6 Hz), 1.51 (d, 3 H, J = 6.6 Hz), 3.25 (q, 1 H, J = 6.7 Hz), 3.62 (q, 1 H, J = 6.7 Hz), 3.83, 3.84, 3.86, 3.88, 3.91 (5 × s, 15H), 6.62, (d, 1 H, J = 8.7 Hz), 6.90 (d, 1 H, J = 8.6 Hz), 7.09 (d, 1 H, J = 8.5 Hz), 7.25 (d, 1 H, J = 8.6 Hz); MS m/e (rel intensity) 431 (M^+, 4), 265 (19), 165 (100); HRMS calcd for $C_{24}H_{33}NO_6$ 431.2308, found 431.2306.

N,N-Diethyl-2',3',4',4,5-pentamethoxy-2-biphenylcarboxamide (7i). From (2,3,4-trimethoxyphenyl)boronic acid **10b** (2.3 g, 10.8 mmol), N,N-diethyl-2-bromo-4,5-dimethoxybenzamide **9b** (2.3 g, 7.2 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), and Na_2CO_3 (2 M solution, 7.1 mL), there was obtained, following standard workup and chromatography, 2.2g (77%) of **7i**: mp 88–90 °C (Et_2O–hexane); IR (KBr) ν(max) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–0.94 (m, 6 H), 2.62–3.45 (m, 4 H), 3.80, 3.86, 3.88, 3.90, 3.91 (5 × s, 15 H), 6.64 (d, 1 H, J = 8.6 Hz), 6.86 (s, 1 H), 6.88 (s, 1 H), 7.00 (d, 1 H, J = 8.6 Hz); MS m/e (rel intensity) 402 (M^+ – 1, 20), 371 (33), 330 (29), 165 (100); HRMS calcd for $C_{22}H_{29}NO_6$ (M^+ – 1) 402.1917, found 402.1912.

N,N-Diethyl-2',3,4'-trimethoxy-6'-methyl-2-biphenylcarboxamide (7j). From **5b** (1.83 g, 7.27 mmol), 2,4-dimethoxy-6-methylbromobenzene **6f** (0.84 g, 3.64 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol), and Na_2CO_3 (2 M solution, 7.5 mL), there was obtained, after standard workup and chromatography, 0.58 g (45%) of **7j**: mp 145–146 °C (EtOAc–hexane); IR (Nujol) ν(max) 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (t, J = 7.1 Hz, 3 H), 1.0 (t, J = 7.1 Hz, 3 H), 2.11 (s, 3 H), 2.75–2.94 (m, 2 H), 3.3–3.5 (m, 1 H), 3.62 (s, 3 H), 3.80, 3.84 (2 × s, 7 H), 6.26 (d, 1 H, J = 2.2 Hz), 6.37 (d, 1 H, J = 2.2 Hz), 6.75 (d, 1 H, J = 7.6 Hz), 6.88 (d, 1 H, J = 7.6 Hz), 7.3 (t, 1 H, J = 7.6 Hz); MS m/e (rel intensity) 357 (M^+, 17), 285 (100), 284 (30), 149 (70); HRMS calcd for $C_{21}H_{27}NO_4$ 357.1946, found 357.1943.

3-(2-(Diisopropylcarbamoyl)phenyl)-4-pyridyl Diethylcarbamate (12). From **5a** (0.76 g, 3.0 mmol) and 3-bromo-4-pyridyl diethylcarbamate **11**[26] (0.55 g, 2.0 mmol), $Pd(PPh_3)_4$ (0.069 g, 0.06 mmol), and Na_2CO_3 (2 M solution, 3.0 mL), there was obtained, after standard workup and chromatography, 0.64 g (81%) of **12**: bp 189–195 °C (0.1 Torr); IR ($CHCl_3$) ν(max) 1722, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (d, 3 H, J = 6.6 Hz), 0.81 (t, 3 H, J = 7.1 Hz), 0.99 (d, 3 H, J = 6.6 Hz), 1.13 (d, 3 H, J = 6.8 Hz), 1.15 (t, 3 H, J = 7.2 Hz), 1.48 (d, 3 H, J = 6.8 Hz), 3.13 (q, 2 H, J = 7.1 Hz), 3.2–3.3 (m, 3 H), 3.62 (septet, 1 H, J = 6.6 Hz), 7.3–7.5 (m, 5 H), 8.55 (d, 1 H, J = 5.7 Hz), 8.67 (s, 1 H); MS m/e (rel intensity) 397 (M^+, 1), 100 (100).

Anal. Calcd for $C_{23}H_{31}N_3O_3$: C, 69.49; H, 7.86; N, 10.57. Found: C, 69.24; H, 7.61; N, 10.32.

Synthesis of Dibenzo[b,d]pyran-6-ones (General Procedure). To a solution of the biphenylamide **7** (1.0 equiv) in CH_2Cl_2 (10–25 mL) at –78 °C was added BBr_3 (1.5 equiv per OMe), and the mixture was stirred under nitrogen overnight. The reaction mixture was cooled to –78 °C, treated with dry methanol, and

allowed to warm to ambient temperature over 2 h. Addition of 5% HCl followed by filtration or extraction (CH_2Cl_2) and normal workup gave the crude phenol, which was refluxed in glacial HOAc (10–25 mL) for 4–24 h. Normal workup or simple filtration followed by column chromatography afforded the dibenzopyranone derivative.

Using above procedure, the following compounds were obtained.

6*H*-Dibenzo[*b*,*d*]pyran-6-one (8a). Treatment of a CH_2Cl_2 solution of **7a** (0.13 g, 0.42 mmol) with BBr_3 (0.08 mL, 0.85 mmol) followed by refluxing the crude product in HOAc (10 mL) for 6 h, normal workup, and column chromatography gave 0.073 g (89%) of product **8a**: mp 92–93 °C (lit.[38] mp 92.5 °C); IR ($CHCl_3$) ν(max) 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.5 (m, 3 H), 7.58 (td, 1 H, J = 8.2 and 1.1 Hz), 7.83 (td, 1 H, J = 7.3 and 1.4 Hz), 8.07 (dd, 1 H, J = 7.9 and 1.4 Hz), 8.13 (d, 1 H, J = 8.1 Hz), 8.41 (dd, 1 H, J = 8.1 and 1.2 Hz).

7-Hydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8b). Treatment of a CH_2Cl_2 solution of **7b** (2.0 g, 6.4 mmol) with BBr_3 (1.5 mL, 16.0 mmol) followed by refluxing the crude product in HOAc (20 mL) for 6 h, normal workup, and column chromatography afforded 1.72 g (79%) of **8b**: mp 122–123 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06 (d, 1 H, J = 8.2 Hz), 7.3–7.4 (m, 2 H), 7.49 (td, 1 H, J = 7.6 and 2.2 Hz), 7.56 (d, 1 H, J = 7.8 Hz), 7.7 (t, 1 H, J = 8.0 Hz), 8.01 (dd, 1 H, J = 8.8 and 1.7 Hz), 11.36 (s, 1 H, D_2O exchangeable); MS m/e (rel intensity) 212 (M^+, 100).

Anal. Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.37; H, 3.92.

7,8-Dimethoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8c). Compound **7c** (0.4 g, 1.1 mmol) was refluxed in HOAc (25 mL) for 20 h and subjected to normal workup to give 0.24 g (85%) of **8c**: mp 120–121 °C (hexane–EtOAc); IR (KBr) ν(max) 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.96 (s, 3 H), 3.99 (s, 3 H), 7.21–7.34 (m, 3 H), 7.39 (d, 1 H, J = 8.8 Hz), 7.79 (d, 1 H, J = 8.8 Hz), 7.91 (m, 1 H); MS m/e (rel intensity) 256 (M^+, 100), 241 (45), 227 (54), 165 (55).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 70.31; H, 4.72. Found: C, 70.34; H, 4.95.

7,8-Dihydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8d). From **7c** (1.0 g, 2.6 mmol) and BBr_3 (1.5 mL, 15.5 mmol), there was obtained, after refluxing (8 h) in HOAc and standard workup, 0.5 g (82%) of **8d**: mp 243–244 °C (Et_2O–CH_2Cl_2); IR (KBr) ν(max) 3423, 1578 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.76–7.93 (m, 4 H), 8.08 (d, 1 H, J = 8.6 Hz), 8.53 (d, 1 H, J = 7.0 Hz), 11.0 (br s, 2 H, D_2O exchangeable); MS m/e (rel intensity) 228 (M^+, 100); HRMS calcd for $C_{13}H_8O_4$ 228.0422, found 228.0425.

3,4-Dihydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8e). From **7d** (0.6 g, 1.5 mmol) and BBr_3 (0.5 mL, 5.6 mmol), there was obtained, after refluxing (18 h) in HOAc and standard workup, 0.25 g (71%) of **8e**: mp 252–254 °C (MeOH–H_2O); IR (KBr) ν(max) 3453, 3286, 1689 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.84 (d, 1 H, J = 8.7 Hz), 7.51–7.57 (m, 1 H), 7.63 (d, 1 H, J = 8.7 Hz), 7.82–7.89 (m, 1 H), 8.17–8.24 (m, 2 H), 9.27 (br s, 1 H, D_2O exchangeable), 9.86 (br s, 1 H, D_2O exchangeable); MS m/e (rel intensity) 228 (M^+, 100), 200 (16), 126 (29), 115 (51).

Anal. Calcd for $C_{13}H_8O_4$; C, 68.42; H, 3.53. Found: C, 68.01; H, 3.50.

3,7-Dimethoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8f). Compound **7e** (4.0 g, 10.7 mmol) was refluxed in HOAc (20 mL) for 8 h. Workup in the usual manner followed by column chromatography gave 2.0 g (73%) of **8f**: mp 159–160 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 4.03 (s, 3 H), 6.7–6.8 (m, 2 H), 6.98 (d, 1 H, J = 8.2 Hz), 7.57 (d, 1 H, 8.0 Hz), 7.69 (t, 1 H, J = 8.1 Hz), 7.89 (d, 1 H, J = 8.8 Hz); MS m/e (rel intensity) 256 (M^+, 100), 227 (73).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.09; H, 4.56.

(38) Graeb, C.; Schestabow, P. *Liebigs Ann. Chem.* **1985**, *284*, 306.

3,7-Dihydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8g). From **7f** (1.6 g, 4.7 mmol) and BBr_3 (1.6 mL, 17.0 mmol), there was obtained, after refluxing (18 h) in HOAc, filtration, and washing with HOAc, 1.1 g (62%) of **8g**: mp 239–241 °C (Me_2CO–H_2O); IR (KBr) ν(max) 3362, 1684 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.85 (d, 1 H, J = 2.4 Hz), 6.94–7.00 (m, 2 H), 7.65–7.82 (m, 2 H), 8.11 (d, 1 H, J = 8.8 Hz); MS m/e (rel intensity) 228 (M^+, 100), 200 (36), 171 (26), 149 (35), 115 (85); HRMS calcd for $C_{13}H_8O_4$ 228.0422, found 228.0425.

3,8-Dihydroxy-6*H*-benzo[*b*,*d*]pyran-6-one (1a). From **7g** (1.8 g, 5.2 mmol) and BBr_3 (1.8 mL, 18.6 mmol), there was obtained, after refluxing (24 h) in HOAc, filtration, and washing with HOAc, 0.6 g (47%) of **1a**: mp >260 °C [lit.[1] mp >360 °C dec]; IR (KBr) 3337, 1699 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.71 (d, 1 H, J = 2.2 Hz), 6.79 (dd, 1 H, J = 8.7, 2.0 Hz), 7.31 (dd, 1 H, J = 8.7, 2.6 Hz), 7.50 (d, 1 H, J = 2.6 Hz), 7.99–8.11 (m, 2 H), 10.11, 10.18 (2 × br s, 2 H, D_2O exchangeable); MS m/e (rel intensity) 228 (M^+, 95), 200 (37), 171 (30), 144 (31), 115 (100); HRMS calcd for $C_{13}H_8O_4$ 228.0422, found 228.0423.

3,4,7,8-Tetrahydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8h). From **7h** (0.3 g, 0.7 mmol) and BBr_3 (0.68 mL, 7.2 mmol), followed by refluxing (22 h) in HOAc, filtration, and washing with H_2O, there was obtained 0.1 g (55%) of **8h**: mp 337–340 °C dec (Me_2CO–MeOH); IR (KBr) ν(max) 3472, 3236, 1659 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.84 (d, 1 H, J = 8.7 Hz), 7.33 (d, 1 H, J = 8.5 Hz), 7.47 (d, 1 H, J = 8.8 Hz), 7.53 (d, 1 H, J = 8.6 Hz), 9.28, 9.67, 9.77, 11.18 (4 × s, D_2O exchangeable); MS m/e (rel intensity) 260 (M^+, 100).

Anal. Calcd for $C_{13}H_8O_6$: C, 60.01; H, 3.10. Found: C, 60.18; H, 3.58.

3,4,8,9-Tetrahydroxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (8i). From **7i** (0.2 g, 0.53 mmol) and BBr_3 (3.2 mL, 3.2 mmol), there was obtained, after refluxing (18 h) in HOAc, dilution with H_2O, collection by filtration, washing (H_2O), and drying in vacuo, 0.10 g (75%) of **8i**: mp >220 °C, IR (KBr) ν(max) 1700 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.77 (d, 1 H, J = 8.6 Hz), 7.29 (d, 1 H, J = 8.6 Hz), 7.39 (s, 1 H), 7.48 (s, 1 H), 9.10, 9.59, 9.96, 10.32 (4 × s, 4 H, D_2O exchangeable).

Anal. Calcd for $C_{13}H_8O_6$: C, 60.01; H, 3.10. Found: C, 60.31; H, 3.39.

Autumnariol (1c). From **7j** (0.47 g, 1.3 mmol) and BBr_3 (0.6 mL, 5.9 mmol), there was obtained, after refluxing (4 h) in HOAc, filtration, and sequential washing with HOAc and H_2O, 0.28 g (88%) of **1c**: mp 301–303 °C (EtOH) (lit.[17] mp 304–308 °C); IR (Nujol) 3353, 1653 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.74 (s, 3 H), 6.67 (d, 1 H, J = 2.4 Hz), 6.75 (d, 1 H, J = 2.4 Hz), 7.0 (m, 1 H), 7.8 (m, 2 H), 10.4 (br s, 1 H, D_2O exchangeable), 10.58 (br s, 1 H, D_2O exchangeable), in agreement with that reported in the literature.[17]

6*H*-[2]Benzopyrano[4,5-*c*]pyridin-6-one (13). A solution of compound **12** (0.30 g, 0.75 mmol) was refluxed in 2 M HCl (10 mL) for 24 h. Normal workup followed by chromatography (EtOAc eluent) afforded 0.14 g (92%) of **13**: mp 185–186 °C (CH_2Cl_2–hexane); IR ($CHCl_3$) ν (max) 1745 cm^{-1}; ^1H NMR δ 7.29 (d, 1 H, J = 5.6 Hz), 7.67 (td, 1 H, J = 8.0 and 1.1 Hz), 7.91 (td, 1 H, J = 7.4 and 1.4 Hz), 8.24 (d, 1 H, J = 8.1 Hz), 8.43 (dd, 1 H, J = 8.7 and 0.8 Hz), 8.64 (d, 1 H, J = 5.6 Hz), 9.37 (s, 1 H); MS m/e (rel intensity) 197 (M^+, 100), 169 (26).

Anal. Calcd for $C_{12}H_7NO_2$: C, 73.09; H, 3.58; N, 7.10. Found: C, 73.20; H, 3.77; N, 6.92.

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Supplementary Material Available: ^1H NMR spectra for compounds **7c,f–j** and **9a** (7 pages). Ordering information is given on any current masthead page.