Reductive coupling of polyfunctionalized organobismuth and organolead arylating reagents in the synthesis of benzopyran derivatives

A. Yu. Fedorov,[a] J.-P. Finet,[b] O. G. Ganina,[a,c] M. I. Naumov,[a] and A. S. Shavyrin[d]*

[a]Nizhny Novgorod N. I. Lobachevsky State University,
23 prosp. Gagarina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8592. E-mail: afnn@rambler.ru
[b]Faculty of Science of St. Jerome,
*University of Aix-Marseille I and III, 13397 Marseille, France.**
Fax: +33 (0) 4 9128 8758. E-mail: jean-pierre.finet@up.univ-mrs.fr
[c]Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: gognn@rambler.ru
[d]G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 12 7497. E-mail: andrew@imoc.sinn.ru

Benzopyran derivatives were synthesized in good yields by the reactions of tris[2-(chloromethyl)phenyl]bismuth diacetate and 2-(halomethyl)aryllead triacetates with phenols and naturally occurring 4-hydroxycoumarins in the presence of bases according to a three-step one-pot procedure.

Key words: reductive coupling, α-arylation, benzopyran derivatives, tris[2-(chloromethyl)phenyl]bismuth diacetate, 2-(halomethyl)arylboronic acids, 2-(halomethyl)aryllead triacetates.

Benzopyran fragments are present in many natural compounds exhibiting a wide spectrum of biological activities.[1] The aim of the present study was to synthesize oxaphenanthrene derivatives **1** with the use of electron-donating phenols and to prepare benzopyran derivatives **2** based on polymethoxy-substituted 4-hydroxycoumarins. Being isostructural analogs of polymethoxy- and/or polyhydroxy-substituted *cis*-stilbenes **3**, which are inhibitors of tumor growth,[2] derivatives **1** potentially can have high therapeutic activity. At the same time, benzazepine analogs **4** of derivatives **2** are efficient antitumor agents against 60 types of human cancer cells.[3] Structurally similar alloxanthoxyletin-type pyranocoumarins **5** possess a number of unique pharmacological properties, including antitumor[4] and anti-HIV[5] activities. Dihydropyranocoumarins belonging to the same family of organic compounds can be used for the treatment of neurodegenerative diseases, for example, of Alzheimer's disease.[6] Wedelolactone **6**, which is a tetracyclic natural compound constructed by combining polyhydroxy-substituted coumarin and benzofuran fragments, is used as an antidote for rattlesnake bites.[7]

Unlike various known approaches to the synthesis of benzopyran derivatives,[7—12] our procedure is based on arylation involving polyfunctionalized organobismuth and organolead reagents.

Organobismuth reagents have attracted interest because they are mild regioselective O-, N-, and C-arylating reagents stable to atmospheric oxygen and moisture.[13—15] In addition, although bismuth is the heaviest of nonradioactive elements, its aryl derivatives have a low toxicity[16] due to which this class of arylating reagents holds promise for the functionalization of a broad range of physiologically active molecules.[17]

We chose tris[2-(chloromethyl)phenyl]bismuth as a model reagent for the synthesis of benzopyran compounds with the use of organobismuth derivatives. This compound was prepared in 27% yield by the reaction of a functionalized aryl Grignard reagent[18,19] with bismuth trichloride (Scheme 1). The next three steps of the synthesis of benzopyran compounds were carried out without isolation of intermediates. Oxidation of tris[2-(chloromethyl)phenyl]bismuth (**9**) with iodobenzene diacetate[20] affords

* UMR-CNRS 6517, Universités d'Aix-Marseille 1 et 3, Faculté des Sciences Saint-Jérôme, 13397 Marseille Cedex 20, France.

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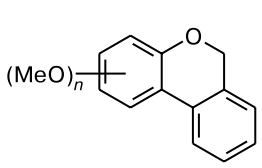

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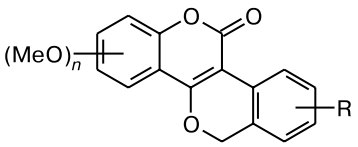

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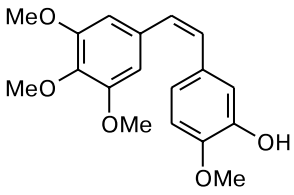

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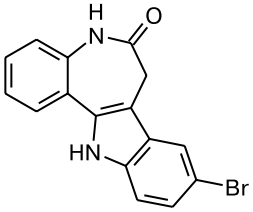

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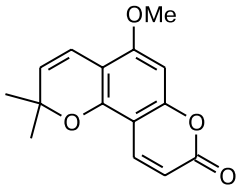

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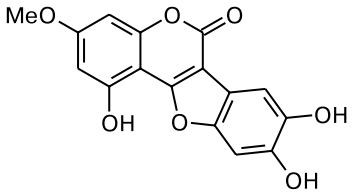

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triarylbismuth diacetate **10** (see Scheme 1). In the following step, the latter reacts with various enolizable substrates in the presence of triethylamine. This step is called reductive coupling and is typical not only of bismuth derivatives[13—15] but also of aryl compounds of lead,[13,14,21] iodine,[13,22] and some other main-group elements.[13] Presumably, reductive coupling proceeds through the formation of intermediate **11**,[23] which is subject to reductive elimination giving rise to α-arylation product **12**. In the final step, the intramolecular nucleophilic substitution affords benzopyran product **13**. Therefore, this procedure provides an approach to the three-step one-pot synthesis of benzopyran derivatives.

We chose β-naphthol **14**, substituted phenols **16**—**20**, natural β-keto lactone **30b**, and β-diketone **33** as substrates for the synthesis of benzopyran derivatives.

The reactions with the use of β-naphthol **14** and phenols **16** and **17** as the starting compounds produced oxaphenanthrene derivatives **15**, **23**, and **24** in good overall yields after three steps (55, 48, and 49%, respectively, see Table 1). The reaction with weaker electron-donating 4-*tert*-butylphenol **19** gave a benzopyran derivative in low yield (27%), whereas the reaction with its 4-methoxy-substituted analog **18** afforded cyclization product **25** in trace amounts (see Table 1). It should be noted that phenols containing electron-withdrawing groups, for example, 4-bromo-2-methylphenol **20**, do not react with organobismuth compound **10**. These results are consistent with the traditional reactivity of aryl derivatives of pentavalent bismuth in reactions with phenols.[24]

Triarylbismuth diacetate **10** reacts not only with phenols but also with β-keto esters and β-dicarbonyl compounds. For example, the reactions with cyclic β-keto ester **30b** and pentane-2,4-dione **33** produced tetracyclic and bicyclic derivatives **31b** and **34**, respectively, in good yields (see Table 1).

Table 1. Synthesis of benzopyran derivatives according to a cascade procedure with the use of tris[2-(chloromethyl)phenyl]bismuth **9**

Substrate	Conditions[a]		Product	Yield[b] (%)
	τ/h	*T*/°C		
14	30	25	**15**	55
16	3	Δ	**23**	48
	30	25		
17	3	Δ	**24**	49
	30	25		
18	4	Δ	**25**	5
	30	25		
19	4	Δ	**26**	27
	30	25		
30b	4	Δ	**31b**	46
	30	25		
33[c]	4	Δ	**34**	35
	30	25		

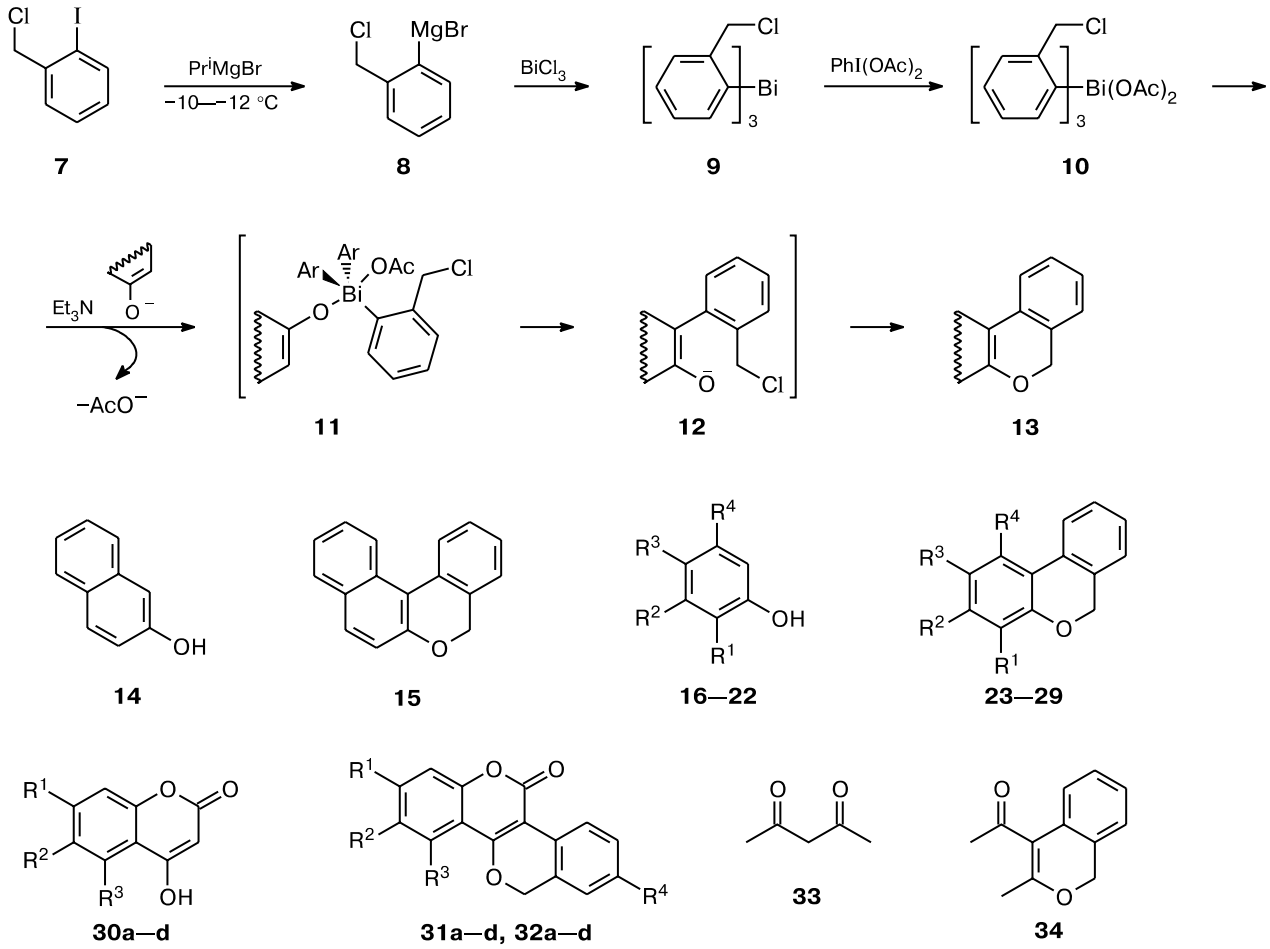
[a] All reactions involved three steps without isolation of intermediates: I, a mixture of Bi^{III} derivative **9** (1.0 equiv.) and $PhI(OAc)_2$ (1.1 equiv.) in CH_2Cl_2 was stirred at room temperature under argon for 6—8 h; II, the substrate (1.0 equiv.) and triethylamine (3.0 equiv.) were added to the reaction mixture and the reaction was performed as described in the table; III, annelation.

[b] The overall yields after three steps without isolation of intermediates.

[c] Sodium hydride was used instead of triethylamine; freshly distilled acetylacetone was used.

Therefore, the proposed strategy is efficient in the synthesis of benzopyran derivatives based on electron-donating phenols and β-dicarbonyl compounds. However, an essential drawback of tris[2-(chloromethyl)phenyl]bismuth diacetate **10** as the reagent is that it does not satisfy the principle of "ligand saving" because only one 2-(chloromethyl)phenyl fragment of the three aryl groups,

Scheme 1

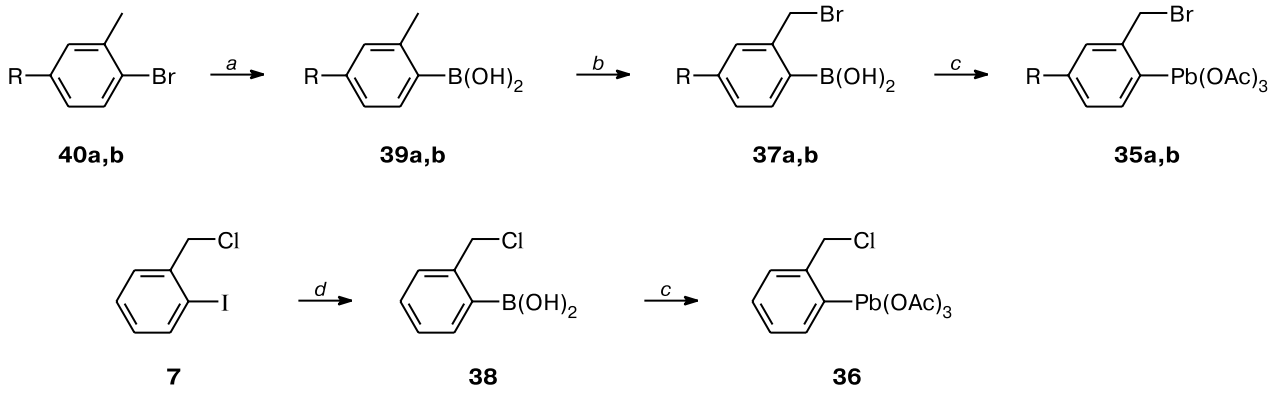


Compound	R^1	R^2	R^3	R^4
16, 23	H	MeO	H	MeO
17, 24	H	MeO	MeO	MeO
18, 25	H	H	MeO	H
19, 26	H	H	Bu^t	H
20, 27	Me	H	Br	H
21, 28	H	MeO	H	H
22, 29	H	Bu^t	H	Bu^t
30a	H	H	H	—
30b	MeO	H	MeO	—

Compound	R^1	R^2	R^3	R^4
30c	MeO	MeO	H	—
30d	MeO	MeO	MeO	—
31a	H	H	H	H
31b	MeO	H	MeO	H
31c	MeO	MeO	H	H
31d	MeO	MeO	MeO	H
32a	H	H	H	MeO
32b	MeO	H	MeO	MeO
32c	MeO	MeO	H	MeO
32d	MeO	MeO	MeO	MeO

which are present in the coordination polyhedron of bismuth, is involved in α-arylation. To resolve this problem, we used organolead reagents **35a**,**b** and **36** containing the 2-(bromomethyl)aryl or 2-(chloromethyl)phenyl fragments (Scheme 2). These compounds can easily be synthesized from the corresponding arylboronic acids **37a**,**b** and **38**. Derivatives **37a** and **37b** were synthesized in 60 and 48% yields, respectively, as colorless crystals by radical bromination of 2-methylphenylboronic acid[25] (**39a**) and 4-methoxy-2-methylphenylboronic acid[26] (**39b**) with *N*-bromosuccinimide in CCl_4 in the presence of benzoyl peroxide. It should be noted that 2-bromomethyl-4-methoxyphenylboronic acid **37b** is unstable in air at room temperature (it turns black within 24 h). Under analogous conditions, the reaction with *N*-chlorosuccinimide does not give 2-(chloromethyl)phenylboronic acid **38**. However, the reaction of 2-(chloromethyl)phenylmagnesium bromide[19] with triisopropyl borate allowed us to prepare arylboronic acid **38** in 52% yield. Aryllead triacetates **35a**,**b** and **36** were synthesized according to a procedure,[27] which involves transmetallation between arylboronic acids and lead tetraacetate in the presence of catalytic amounts of mercury diacetate. This approach enabled us to synthesize air-stable 2-(bromomethyl)phenyl derivative of lead

Scheme 2



R = H (**a**), OMe (**b**)

Reagents: (*a*) BuLi/$B(OPr^i)_3$; (*b*) benzoyl peroxide/N-bromosuccinimide/CCl_4; (*c*) $Pb(OAc)_4/Hg(OAc)_2$; (*d*) $Pr^iMgBr/B(OPr^i)_3$.

35a in 48% yield and its chlorine-containing analog **36** in 78% yield. The latter analog is sensitive to atmospheric oxygen and moisture. We failed to prepare aryllead triacetate **35b** in pure form, and we used it in the synthesis of benzopyran derivatives without isolation.

The reactions of organolead derivatives **35a**,**b** and **36** with phenols and enolizable substrates proceed by a mechanism analogous to that presented in Scheme 1. It should be noted that aryllead triacetates have found wide application in C-arylation,[13,14,21] both in racemic and enantioselective[28] modifications, and are particularly efficient for the insertion of electron-donating aromatic fragments, which are often present in natural compounds, into organic substrates. A drawback of this method is that organolead reagents do not always provide high regioselectivity of arylation of phenols and β-keto esters. For example, the reactions with phenols almost always afford, along with mono-*ortho*-arylation products, 2,6-diaryl-substituted compounds.[29] Arylation of enolizable carbonyl derivatives also gives mixtures of mono- and di-α-arylation products[30] regardless of the stoichiometric reagent-to-substrate ratio. Hence, in the presence of the second electrophilic center in an appropriate position of an organolead reagent (for example, in derivatives **35a**,**b** and **36**), the first α-arylation event is followed by cyclization, which renders the formation of a diarylation product impossible. However, for this sequence of reactions to occur, the center bound to the lead atom must be more reactive than the other electrophilic center in the organolead reagent.

Arylation of phenols according to a classical procedure[14,21] with the use of aryllead triacetates (β-naphthol **14** (1.0 equiv.), organolead reagent **35a** (1.1 equiv.), and pyridine (3.0 equiv.) in $CHCl_3$ at 45 °C) afforded oxaphenanthrene derivative **15** in 25% yield (Table 2, entry 1). This reaction did not yield the diarylation product. An analogous result was obtained in the successive three-step one-pot synthesis with the use of aryllead triacetate prepared *in situ* (see Table 2, entry 2). An increase in the amount of the base to 6 equivalents with the aim of achieving more efficient neutralization of HBr that was liberated in the course of the reaction did not lead to an increase in the yield of annelation product **15** (see Table 2, entry 3). However, pyridine evidently not only can serve as a base but also can be involved as a ligand in the coordination environment of the lead atom.[31] Moreover, the kinetics of reductive coupling and the yields of the main products of these reactions were demonstrated[32,33] to depend substantially on the nature of the base or the complex-forming agent. To optimize the conditions of the synthesis of benzopyran derivatives and elucidate the role of bases in these processes, we studied the reactions of organolead reagents **35a**,**b** and **36** with phenols and cyclic β-keto esters **30a**—**d** in the presence of bases, such as triethylamine (TEA), *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG), and *ortho*-phenanthroline (*o*-phen), and systems of bases, such as pyridine—triethylamine, 4-dimethylaminopyridine (DMAP)—triethylamine, and *ortho*-phenanthroline—potassium *tert*-butoxide.

The use of TEA and TMG, which are the most efficient bases in reductive coupling with organobismuth derivatives,[13—15] led only to the formation of benzopyran derivative **15** in trace amounts (see Table 2, entries 4 and 5). However, the addition of a stronger base (TEA) to pyridine resulted in a substantial increase in the yields of annelation products (see Table 2, entries 6 and 9). Cyclization products were prepared in satisfactory yields with a combined use of pyridine and TMG (see Table 2, entry 7), as well as with the use of the DMAP—TEA system (see Table 2, entries 8 and 10), as bases. It is worthy of note that the reaction of **35a** with 3-methoxyphenol afforded oxaphenanthrene derivative **28** as the only product in moderate yield as a result of *ortho*-arylation at the most

Table 2. Synthesis of oxaphenanthrene derivatives with the use of organolead reagent **35a**[a]

Entry	Substrate	**35a** (equiv.)	Reaction conditions			Product	Yield (%)
			Reagents (3 equiv. each)	*T*/°C	τ/h		
1	**14**	1.1[b]	Pyridine	45	10	**15**	25
2	**14**	1.1[c]	Pyridine	45	10	**15**	20
3	**14**	1.1[b]	Pyridine[d]	45	10	**15**	19
4	**14**	1.1[b]	Et_3N	45	10	**15**	2
5	**14**	1.1[b]	TMG	45	10	**15**	—
6	**14**	1.4[c]	Pyridine, Et_3N	25	1	**15**	55
7	**14**	1.4[c]	Pyridine, TMG	25	1	**15**	45
8	**14**	1.4[c]	DMAP, Et_3N	25	1	**15**	65
9	**16**	1.4[c]	Pyridine, Et_3N	25	1	**23**	65
10	**16**	1.4[c]	DMAP, Et_3N	25	1	**23**	60
11	**17**	1.4[c]	DMAP, Et_3N	25	10	**24**	25
12	**17**	1.4[c]	Pyridine, Et_3N	25	10	**24**	38
13	**21**	1.4[c]	DMAP, Et_3N	25	1	**28**	37
14	**22**	1.4[c]	Pyridine, Et_3N	25	10	**29**	13

[a] All reactions were carried out in $CHCl_3$ (5 mL per mmole of the substrate).
[b] Compound **35a**, which was isolated in individual form, was used.
[c] Compound **35a**, which was prepared *in situ*, was used.
[d] 6 equiv.

sterically accessible position 6 of the substrate (see Table 2, entry 13). It is also of interest that tricyclic derivative **29** can be constructed based on sterically hindered 3,5-di-*tert*-butylphenol **22** (see Table 2, entry 14).

All analogous reactions (phenol, aryllead triacetate, and two bases) with 2-(chloromethyl)phenyl derivative of lead **36** produced the corresponding oxaphenanthrene derivatives in lower yields and under more drastic conditions compared to the reactions with the use of 2-(bromomethyl)phenyl analog **35a** (Table 3).

The reactions of 2-(bromomethyl)aryllead triacetates **35a**,**b** with natural keto lactones **30a—d** in the presence of binary pyridine—TEA and DMAP—TEA systems as bases gave tetracyclic products **31** and **32a—d** in low yields

Table 3. Synthesis of oxaphenanthrene derivatives with the use of organolead reagent **36**[a]

Substrate	Conditions		Products	Yield (%)
	T/°C	τ/h		
14	25	10[b]	**15**	55
16	50	10[b]	**23**	42
17	50	6[b]	**24**	33
19	50	6[c]	**26**	26
22	50	6[c]	**29**	6

[a] All reactions were carried out with organolead derivative **36**, which was prepared without isolation in the presence of pyridine or DMAP (3 equiv.) and Et_3N (3 equiv.) in $CHCl_3$ (5 mL per mmole of the substrate).
[b] DMAP was used as the ligand.
[c] Pyridine was used as the ligand.

(Table 4, entries 4 and 5). The results of optimization of the conditions for the synthesis of benzopyran derivatives based on phenols (see Table 2) confirm the earlier suggestion that pyridine or related DMAP serve as ligands in the coordination environment of the lead atom.[31—33] In this connection, we decided to use *ortho*-phenanthroline, which is often used as a bidentate ligand in Ullmann reactions,[34] as a complex-forming agent. Actually, the use of this ligand resulted in a substantial increase in the yields of annelation products to 33—41% in the reactions with polymethoxy-substituted 4-hydroxycoumarins **30b—d** and to 58% in the reactions with the use of unsubstituted coumarin **30a** as the substrate (see Table 4,

Table 4. Influence of coordinating additives on the cascade synthesis of tetracyclic products **31a—d** based on 4-hydroxycoumarins **30a—d** with the use of 2-(bromomethyl)phenyllead triacetate **35a** prepared without isolation*

Entry	Coordinating additive (equiv.)	Total yield after three-step synthesis (%)			
		31a	**31b**	**31c**	**31d**
1	Py (3)	15	11		
2	Et_3N (3)	Traces	Traces	—	—
3	TMG (3)	Traces	Traces	—	—
4	Py + Et_3N (3 : 3)	24	25	18	11
5	Py + DMAP (3 : 3)	20	25	—	—
6	*o*-Phen (3)	58	34	41	33
7	*o*-Phen + Bu^tOK (3 : 1)	76	45	47	47

* The substrate **30a—d** : arylboronic acid **37a** reagent ratio was 1 equiv. : 1.2 equiv.

entry 6). The binary 3 : 1 *ortho*-phenanthroline—potassium *tert*-butoxide system appeared to be even more efficient. This pair of bases allowed us to prepare tetracyclic derivative **31a** from unsubstituted 4-hydroxycoumarin in an overall yield of 76% after three steps and to synthesize derivatives **31b—d** in 45, 47, and 47% yields, respectively (see Table 4, entry 7). The reactions with the use of this system of coordinating additives and organolead reagent **35b** produced also benzopyran derivatives **32a—d** in 51, 39, 44, and 31% yields, respectively.

Presumably, the introduction of the bidentate ligand into the coordination polyhedron of the lead atom results in a substantial increase in the solubility of polar organolead intermediate **11** in chloroform, which can influence the kinetics of reductive coupling. In addition, bidentate *ortho*-phenanthroline saturates the coordination polyhedron of the lead atom, resulting in the shift of the equilibrium between the monomeric and oligomeric forms of organolead reagents **35a**,**b** to the more reactive monomeric form. These effects can be observed in enantioselective arylation involving aryllead triacetates in the presence of sterically hindered chiral bases.[28] The function of the second component of this binary system *viz.*, potassium *tert*-butoxide, is to efficiently neutralize HBr, which is liberated in the annelation step (Fig. 1) and which can cause not only decomposition of the organolead reagent but also cleavage of the lactone bond in 4-hydroxycoumarin.

Noteworthy is the decrease in the yields of cyclization products **31b—d** (45—47%, see Table 4) prepared from polymethoxy-substituted 4-hydroxycoumarins **30b—d** compared to the yield of unsubstituted analog **31a** (76%). Moreover, the yields of 4′-methoxy-substituted products **32a—d** were lower than those of unsubstituted tetracyclic analogs **31a—d**. The results of the present study were unexpected taking into account that aryllead triacetates are most efficient in C- and N-arylation for the transfer of electron-donating aryl fragments to the substrate.

The observed differences in the yields of cyclization products can be attributed to complexation of the potassium cation at the enol oxygen atom to the oxygen atoms of the methoxy substituents at the C(5), C(6), and C(7) atoms of the fragment **A** (see Fig. 1) of the coumarin skeleton and to the methoxy group at the C(4′) atom of the aryl fragment **C**. This coordination of the potassium cation, on the one hand, can decrease the nucleophilicity of the enolate anion and, on the other hand, results in less efficient neutralization of HBr that is eliminated. An increase in the amount of potassium *tert*-butoxide results in the formation of by-products. The use of solvents other than chloroform, which are more tolerant to Bu^tOK (THF, toluene, benzene, or diethyl ether), does not lead to an increase in the yields of tetracyclic derivatives **31a—d** and **32a—d**.

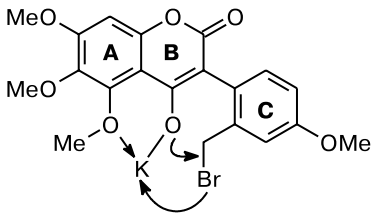
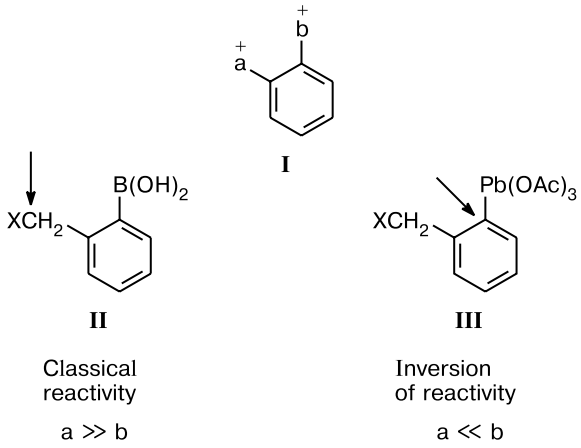


Fig. 1. Influence of complexation of the potassium cation on cyclization.

In conclusion, let us note that interconversions of the functional groups are accompanied by inversion of the reactivities of the electrophilic centers in the dicationic equivalent **I** (Scheme 3). Thus, the benzyl electrophilic center in arylboronic acids **37a**,**b** and **38** (see Scheme 3, compound **II**) is more reactive with respect to nucleophilic reagents than the reaction center at the aromatic fragment.[35] Transmetallation is accompanied by the transfer of the aryl group from the boron atom to the lead atom giving rise to aryllead triacetates **35a**,**b** and **36**, in which the aromatic electrophilic center is more reactive than the benzyl reaction center (see Scheme 3, compound **III**).

Scheme 3



Note. The electrophilic center is indicated by an arrow.

The presence of the halogen atom in compounds **35a**,**b** and **36** or in bismuth(v) derivative **10** has virtually no effect on the reactivity of aryllead triacetates or organobismuth compounds with respect to mild nucleophilic reagents.

To summarize, we found new polyfunctionalized organobismuth and organolead reagents containing 2-(halomethyl)aryl fragments, which allow one to synthesize benzopyran derivatives by cascade reactions according to a three-step one-pot procedure.

Experimental

The NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13 (^{1}H) and 50.32 MHz (^{13}C). The chemical shifts are given on the δ scale relative to Me_4Si. The IR spectra were measured on a Specord IR-75 spectrometer. 4-Hydroxycoumarin derivatives **30a—d** were prepared according to known procedures.[30,36] Commercial (Lancaster) $Pb(OAc)_4$, $Hg(OAc)_2$, and *ortho*-phenanthroline were used without prepurification. Acetylacetone **33** was distilled immediately before use.

Tris[2-(chloromethyl)phenyl]bismuth (9). The reaction was carried out under an inert atmosphere. A solution of isopropyl bromide (1.9 mL) in anhydrous THF (20 mL) was added dropwise with continuous stirring and cooling (an ice bath) to magnesium chips (2.26 g 0.094 mol) (we failed to synthesize derivative **9** with the use of an activated magnesium powder) in anhydrous THF (3 mL). Then the reaction mixture was kept at room temperature for 16 h. The resulting solution of isopropylmagnesium bromide was filtered through a porous filter under an inert atmosphere. A solution of 2-iodobenzyl chloride **7** (4 g, 0.016 mol) in anhydrous THF (20 mL) was placed into a three-neck flask. Then isopropylmagnesium bromide was added dropwise with continuous stirring and cooling (−18 °C). The reaction mixture was kept at −10 °C for 3 h, and bismuth trichloride (1.58 g, 0.005 mol) was added portionwise with cooling (−10 °C). The reaction mixture was kept at −10 °C with continuous stirring for 1.5 h and kept at room temperature for 16 h. A saturated NH_4Cl solution (20 mL) was added. The organic layer was separated in a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The organic extract was dried over anhydrous Na_2SO_4. After removal of volatile products under reduced pressure and recrystallization of the solid residue from a CH_2Cl_2—hexane mixture, tris[2-(chloromethyl)phenyl]bismuth was isolated as gray crystals in a yield of 0.6 g (27%), m.p. (dichloromethane—hexane) 143 °C. Found (%): C, 43.34; H, 3.31; Bi, 35.35. $C_{21}H_{18}Cl_3Bi$. Calculated (%): C, 43.04; H, 3.07; Bi, 35.70. ^{1}H NMR ($CDCl_3$), δ: 4.69 (s, 2 H, CH_2); 7.25 (dt, 1 H, H(4), J = 7.4 Hz, J = 1.6 Hz); 7.36 (dt, 1 H, H(5), J = 7.4 Hz, J = 1.6 Hz); 7.52 (dd, 1 H, H(3), J = 7.6 Hz, J = 1.4 Hz); 7.77 (dd, 1 H, H(6), J = 7.4 Hz, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 51.2 (CH_2); 129.1 (C(3)); 130.7 (C(4)); 131.8 (C(5)); 140.5 (C(6)); 142.2 (C(2)).

Synthesis of benzopyran derivatives 15, 23—26, 31b, and 34 with the use of organobismuth reagent 9 (general method). Iodobenzene diacetate (1.2 equiv.) was added to tris[2-(chloromethyl)phenyl]bismuth **9** (1 equiv.) in CH_2Cl_2 (1 mL per 4 mmol of compound **9**). The reaction mixture was stirred at room temperature under an inert atmosphere for 6—8 h until the starting product **9** completely disappeared (TLC, diethyl ether—hexane, 1 : 4, as the eluent). Then a solution of triethylamine (3 equiv.) and the substrate (0.9 equiv.) in CH_2Cl_2 (1 mL per 6 mmol of the substrate) was added dropwise to the reaction mixture, and the mixture was worked up as described in Table 1. After completion of the reaction, the solvent was removed under reduced pressure. Nonvolatile products were filtered through a layer of silica gel on a porous filter. Benzopyran derivatives were isolated by preparative TLC. To remove traces of finely dispersed silica gel from the reaction products, the latter were filtered through a layer of Celite.

5*H*-Benzo[*d*]naphtho[2,1-b]pyran (15) was isolated by PTLC (diethyl ether—hexane, 1 : 9, as the eluent) as a colorless viscous oil in 55% yield. Found (%): C, 87.64; H, 5.34. $C_{17}H_{12}O$ (232.09). Calculated (%): C, 87.90; H, 5.21. ^{1}H NMR ($CDCl_3$), δ: 5.04 (s, 2 H, OCH_2); 7.23 (d, 1 H, H(3), J = 8.9 Hz); 7.29—7.56 (m, 5 H); 7.73 (d, 1 H, J = 8.7 Hz); 7.83 (d, 1 H, J = 8.2 Hz); 8.01 (d, 1 H, J = 7.8 Hz), 8.53 (d, 1 H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 69.3 (OCH_2); 117.7 (C(1)); 118.2 (C(3)); 123.9, 124.7, 125.2, 126.2, 126.8, 127.0, 128.1, 128.8, 130.1, 130.2, 130.3, 130.6, 132.9, 154.2.

1,3-Dimethoxy-6*H*-benzo[*c*]chromene (23) was isolated by PTLC (diethyl ether—hexane, 3 : 17, as the eluent) as a colorless viscous oil in 48% yield. Found (%): C, 74.61; H, 5.74. $C_{15}H_{14}O_3$ (242.09). Calculated (%): C, 74.36; H, 5.82. ^{1}H NMR ($CDCl_3$), δ: 3.81 and 3.92 (s, 6 H, OMe); 4.98 (s, 2 H, CH_2); 6.24 (m, 2 H, H(4) and H(6)); 7.13 (d, 1 H, H(3′), J = 7.4 Hz); 7.19 (t, 1 H, H(4′), J = 7.1 Hz); 7.32 (dt, 1 H, H(5′), J = 7.5 Hz, J = 1.0 Hz); 8.25 (d, 1 H, H(6′), J = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4 and 55.6 (OMe); 69.1 (CH_2); 93.6 and 94.3 (C(4) and C(6)); 124.2, 125.6, 126.0, and 128.0 (C(3′), C(4′), C(5′), and C(6′)); 129.4 and 130.6 (C(2) and C(1′)); 157.7 (C(2′)); 158.9 and 160.7 (C(3) and C(5)).

1,2,3-Trimethoxy-6*H*-benzo[*c*]chromene (24) was isolated by PTLC (diethyl ether—hexane, 1 : 4, as the eluent) as colorless crystals, m.p. 70 °C (diethyl ether—hexane); the yield was 49%. Found (%): C, 70.86; H, 5.71. $C_{16}H_{16}O_4$ (272.10). Calculated (%): C, 70.57; H, 5.92. ^{1}H NMR ($CDCl_3$), δ: 3.86, 3.88, and 3.42 (s, 9 H, OMe); 4.98 (s, 2 H, CH_2); 6.41 (s, 1 H, H(6)); 7.15—7.41 (m, 3 H, H(3′), H(4′) and H(5′)); 8.26 (d, 1 H, H(6′), J = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.9, 60.8, and 61.2 (OMe); 69.1 (CH_2); 97.0 (C(6)); 109.8 (C(2)); 124.4, 125.2, 126.6.5 (C(3′), C(4′), C(5′) and C(6′)); 129.1 (C(1′)); 130.9 (C(2, 128′)); 137.8 (C(1′)); 152.2, 152.3, and 153.8 (C(3), C(4), and C(5)).

2-Methoxy-6*H*-benzo[*c*]chromene (25) was isolated by PTLC (diethyl ether—hexane, 1 : 3, as the eluent) as a viscous pale-green oil in 5% yield. Found (%): C, 78.97; H, 5.87. $C_{14}H_{12}O_2$ (212.08). Calculated (%): C, 79.22; H, 5.70. ^{1}H NMR ($CDCl_3$), δ: 3.87 (s, 3 H, OMe); 4.99 (s, 2 H, CH_2); 7.34—7.57 (m, 7 H, Ar—H).

2-*tert*-Butyl-6*H*-benzo[*c*]chromene (26) was isolated by PTLC (diethyl ether—hexane, 1 : 9, as the eluent) as a viscous colorless oil in 27% yield. Found (%): C, 85.77; H, 7.42. $C_{17}H_{18}O$ (238.14). Calculated (%): C, 85.67; H, 7.61. ^{1}H NMR ($CDCl_3$), δ: 1,37 (s, 9 H, Me); 5.10 (s, 2 H, CH_2); 6.93 (d, 1 H, H(6), J = 8.1 Hz); 7.17 (d, 1 H, H(3′), J = 7.4 Hz); 7.23—7.41 (m, 3 H, H(3), H(5) and H(6′)); 7.65—7.74 (m, 2 H, H(4′) and H(5′)). ^{13}C NMR ($CDCl_3$), δ: 29.7 ($\underline{C}(CH_3)_3$); 30.9 (Me); 68.5 (CH_2); 116.8 (C(6)); 119.9 (C(3′)); 121.9, 124.7, 126.6, 127.5, 128.3 (C(3), C(5), C(4′), C(5′), and C(6′)); 122.1 (C(4)); 125.9 (C(2′)); 131.6 (C(1′)); 144.8 (C(2)); 152.5 (C(1)).

2,4-Dimethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (31b) was isolated by PTLC (diethyl ether—hexane—chloroform, 2 : 1 : 2, as the eluent) and recrystallized from a chloroform—hexane mixture. Colorless crystals with m.p. 202 °C were obtained in 46% yield. Found (%): C, 69.48; H, 4.39. $C_{18}H_{14}O_5$ (310.31). Calculated (%): C, 69.67; H, 4.55. ^{1}H NMR ($CDCl_3$), δ: 3.84 and 3.87 (both s, 3 H each, OMe); 5.28 (s, 2 H, CH_2); 6.29 (d, 1 H, H(6), J = 2.3 Hz); 6.43 (d, 1 H, H(8), J = 2.3 Hz); 7.09 (d, 1 H, H(3′), J = 7.3 Hz); 7.27 (dt, 1 H, H(4′), J = 7.3 Hz, J = 1.1 Hz); 7.38 (dt, 1 H, H(5′), J = 7.9 Hz, J = 1.3 Hz); 8.46 (d, 1 H, H(6′), J = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.7 and 56.3 (OMe); 69.6 (CH_2); 93.0 (C(6)); 96.0 (C(8)); 99.7

and 99.8 (C(10) and C(2′)); 123.6, 124.4, 127.0, 127.3, and 128.8 (C(3′), C(4′), C(5′), C(1′), and C(6′)); 156.4 and 158.8 (C(5) and C(7)); 160.2 (C(9)); 163.5 (C(3)); 164.1 (C(4)); 171.0 (C(2)).

1-(3-Methyl-1*H*-isochromen-4-yl)ethanone (34). Iodobenzene diacetate (0.12 g, 0.38 mmol) was added to a solution of tris[2-(chloromethyl)phenyl]bismuth **9** (0.20 g, 0.34 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at room temperature for 10 h, and the solvent was removed under reduced pressure. A solution of pentane-2,4-dione (0.03 g, 0.31 mmol) and sodium hydride (0.03 g, 0.70 mmol) in dry freshly distilled THF (4 mL) was added to the reaction mixture (before the reaction, the solution of pentane-2,4-dione and sodium hydride in THF has been kept at room temperature for 10 min). The reaction mixture was refluxed under argon for 4 h and then kept at room temperature for 16 h. The solution was filtered through a layer of silica gel on a porous filter (diethyl ether—hexane, 3 : 7, as the eluent). After PTLC (chloroform—diethyl ether—hexane, 1 : 2 : 7, as the eluent), product **34** was isolated as a viscous oil in a yield of 0.02 g (0.11 mmol, 35%). Found (%): C, 76.81; H, 6.28. $C_{12}H_{12}O_2$ (188.08). Calculated (%): C, 76.57; H, 6.43. ^{1}H NMR ($CDCl_3$), δ: 2.17 (s, 3 H, Me); 2.46 (s, 3 H, C(O)Me), 5,01 (s, 2 H, CH_2); 7.05—7.35 (m, 4 H, Ar—H). ^{13}C NMR ($CDCl_3$), δ: 29.7 (Me); 31.6 (C(O)Me); 69.0 (CH_2); 115.3 (C(10)); 127.4 (C(3)); 129.7 (C(5)); 122.4, 124.1, 126.4, and 128.4 (C(5), C(6), C(7), and C(8)); 160.4 (C(9)); 200.8 (C=O).

2-(Bromomethyl)phenyllead triacetate (35a). A solution of 2-(bromomethyl)phenylboronic acid **37a** (0.96 g, 4.5 mmol) in $CHCl_3$ (12 mL) was added dropwise to a solution containing lead tetracetate (1.98 g, 4.5 mmol) and mercury diacetate (0.14 g, 0.45 mmol) in anhydrous $CHCl_3$ (6 mL) at 40 °C under argon. The reaction mixture was stirred at 40 °C for 1 h, kept at room temperature for 16 h, and twice filtered through a layer of Celite. The solvent was removed under reduced pressure. The solid product was recrystallized from a $CHCl_3$—diethyl ether—pentane mixture. Compound **35a** was isolated as colorless needle-like crystals in a yield of 1.1 g (48%), m.p. 142 °C. Found (%): C, 28.01; H, 2.86. $C_{13}H_{15}BrO_6Pb$ (553.98). Calculated (%): C, 28.17; H, 2.73. ^{1}H NMR ($CDCl_3$), δ: 2.12 (s, 9 H, OC(O)C$\underline{H}_3$); 4.65 (s, 2 H, CH_2Br); 7.46—7.54 (m, 2 H, H(4) and H(5)); 7.61 (dd, 1 H, H(3), J = 2.5 Hz, J = 6.8 Hz); 7.76 (dd, 1 H, H(6), J = 1.7 Hz, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.3 (CH_3); 31.7 (CH_2Br); 131.1, 131.6, and 132.2 (C(3), C(4), and C(5)); 133.2 (C(6)); 140.6 (C(2)); 162.5 (C(1)); 180.6 (C=O).

2-(Chloromethyl)phenylboronic acid (38). A solution of isopropylmagnesium bromide (2.58 g, 0.0176 mol) in THF (10 mL) was added dropwise with continuous stirring and cooling (−18 °C) to a solution of 2-iodobenzyl chloride **7** (4 g, 0.016 mol) in anhydrous THF (20 mL). The reaction mixture was kept at −10 °C for 3 h and cooled to −78 °C. Then triisopropyl borate (3.3 mL, 0.014 mol) was added dropwise into the flask using a syringe. The reaction mixture was kept at −78 °C for 1.5 h, slowly warmed to room temperature, and stirred for 16 h. The solvent was removed under reduced pressure. The solid product was dissolved in diethyl ether (200 mL), 10% HCl (40 mL) was added, and the reaction mixture was vigorously shaken in a separatory funnel for 15 min. The organic layer was separated and washed with 10% HCl (2×30 mL) and water (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$, and the volatile products were removed under reduced pressure. The solid residue was recrystallized from a CH_2Cl_2—diethyl ether—pentane mixture. Compound **38** was isolated as a pale-yellow polycrystalline powder in a yield of 1.28 g (52%), m.p. 147 °C. Found (%): C, 49.38; H, 4.95. $C_7H_8BClO_2$ (170.03). Calculated (%): C, 49.34; H, 4.73. ^{1}H NMR ($CDCl_3$), δ: 5.16 (s, 2 H, CH_2Cl); 7.45—7.57 (m, 3 H, H(3), H(4), and H(5)); 8.30—8.34 (m, 1 H, H(6)). ^{13}C NMR ($CDCl_3$), δ: 45.9 (CH_2Cl); 128.3, 130.5, 132.9, and 137.8 (C(3), C(4), C(5), and C(6)); 144.8 (C(2)).

2-(Chloromethyl)phenyllead triacetate (36). A solution of 2-(chloromethyl)phenylboronic acid **39** (0.76 g, 0.45 mmol) in $CHCl_3$ (12 mL) was added dropwise to a solution of lead tetraacetate (1.98 g, 4.5 mmol) and mercury diacetate (0.14 g, 0.45 mmol) in anhydrous $CHCl_3$ (6 mL) at 40 °C under argon. The reaction mixture was stirred at 40 °C for 1 h, kept at room temperature for 16 h, and twice filtered through a layer of Celite. The solvent was removed under reduced pressure. The solid product was recrystallized from a $CHCl_3$—diethyl ether—pentane mixture at −10 °C. Compound **36** was isolated as pale-yellow prismatic crystals in a yield of 1.7 g (74%), m.p. 118 °C. Found (%): C, 30.45; H, 3.16. $C_{13}H_{15}ClO_6Pb$ (510.03). Calculated (%): C, 30.62; H, 2.97. ^{1}H NMR ($CDCl_3$), δ: 2.12 (s, 9 H, $OC(O)CH_3$); 4.77 (s, 2 H, CH_2Cl); 7.52 (td, 1 H, H(4), J = 7.6 Hz, J = 1.3 Hz); 7.58 (td,1 H, H(5), J = 7.6 Hz, J = 1.8 Hz); 7.64 (dd, 1 H, H(3), J = 7.6 Hz, J = 8.0 Hz); 7.78 (dd, 1 H, H(6), J = 7.6 Hz, J = 1.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.2 (OC(O)$\underline{C}H_3$); 45.1 (CH_2Cl); 131.2, 131.6, 132.2, 132.6 (C(3), C(4), C(5), and C(6)); 140.0 (C(2)); 162.5 (C(1)) and 180.5 (O$\underline{C}$(O)CH_3).

Reactions of aryllead triacetates 35a and 36 with phenols and enolizable substrates (general procedure). A solution of aryllead triacetate **35a** or **36** (1.1 equiv.) in anhydrous $CHCl_3$ (5 mL per mmole of **35a** or **36**) was added dropwise to a solution of the substrate (1 equiv.) and a base (the ratios are given in Tables 2 and 3) in anhydrous $CHCl_3$ (5 mL per mmole of substrate). The reaction was carried out under an inert atmosphere. The reaction mixture was worked up as described in Tables 2 and 3. Volatile products were removed under reduced pressure. Benzopyran products were isolated by silica gel column chromatography.

Synthesis of benzopyran derivatives with the use of a three-step one-pot procedure (general procedure). A mixture of $Pb(OAc)_4$ (1.2 equiv.), $Hg(OAc)_2$ (0.12 equiv.), and arylboronic acid **35a**,**b** or **36** (1.2 equiv.) in anhydrous $CHCl_3$ (5 mL per mmole of $Pb(OAc)_4$) was heated at 40 °C under an inert atmosphere for 1—1.5 h. Then the reaction mixture was kept at room temperature for 10—12 h. The substrate (1.0 equiv.) and a base (the ratios are given in Tables 2—4) were added to the resulting solution, and the reaction mixture was stirred (see Tables 2—4). The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography.

3-Methoxy-6*H*-benzo[*c*]chromene (28) was isolated by column chromatography (Et_2O—petroleum ether, 1 : 19, as the eluent) as a colorless oil. The yield was 37%. Found (%): C, 78.96; H, 5.87. $C_{14}H_{12}O_2$ (212.08). Calculated (%): C, 79.22; H, 5.70. ^{1}H NMR ($CDCl_3$), δ: 3.81 (s, 3 H, OMe); 5.10 (s, 2 H, OCH_2); 6.54 (d, 1 H, H(3), J = 2.5 Hz); 6.63 (dd, 1 H, H(5), J = 8.5 Hz, J = 2.5 Hz); 7.12 (d, 1 H, H(3′), J = 7.5 Hz); 7.22 (t, 1 H, H(4′), J = 7.5 Hz); 7.34 (t, 1 H, H(5′), J = 7.5 Hz); 7.60 (d, 1 H, H(6′), J = 7.5 Hz); 7.64 (d, 1 H, H(6), J = 8.5 Hz).

^{13}C NMR ($CDCl_3$), δ: 55.4 (OMe); 68.7 (OCH_2); 102.3 (C(3)); 108.8 (C(5)); 115.9 (C(1)); 121.2, 124.2, 124.6, 126.7, and 128.4 (C(6), C(3′), C(4′), C(5′), and C(6′)); 130.2 and 130.3 (C(1′) and C(2′)); 156.0 and 160.9 (C(2) and C(4)).

1,3-Di-*tert*-butyl-6*H*-benzo[*c*]chromene (29) was isolated by column chromatography (Et_2O—petroleum ether, 1 : 19, as the eluent) as a colorless oil. The yield was 13%. Found (%): C, 85.40; H, 8.96. $C_{21}H_{26}O$ (294.43). Calculated (%): C, 85.67; H, 8.90. ^{1}H NMR ($CDCl_3$), δ: 1.33 and 1.48 (both s, 9 H each, Bu^t); 6.90 (d, 1 H, H(3), J = 2.6 Hz); 7.22—7.32 (m, 3 H, H(4′), H(5′) and H(6′)); 7.34 (d, 1 H, H(5), J = 2.6 Hz); 7.56 (d, 1 H, H(3′), J = 7.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 31.2 and 33.8 (both Bu^t); 34.8 and 37.2 (C(4) and C(6)); 69.3 (OCH_2); 110.7 (C(3)); 120.6 (C(5)); 121.3 (C(1)); 124.4, 126.2, 126.8, and 129.9 (C(3′), C(4′), C(5′), and C(6′)); 132.7 and 132.9 (C(1′) and C(2′)); 149.0 and 151.5 (C(4) and C(6)); 156.6 (C(2)).

6*H*,11*H*-[2]Benzopyrano[4,3-*c*][1]benzopyran-11-one (31a) was isolated by column chromatography (diethyl ether—petroleum ether, 1 : 1, as the eluent) as a pale-yellow powder, m.p. 154 °C. The yield was 76%. Found (%): C, 76.85; H, 4.09. $C_{16}H_{10}O_3$ (250.25). Calculated (%): C, 76.79; H, 4.03. ^{1}H NMR ($CDCl_3$), δ: 5.41 (s, 2 H, CH_2), 7.13 (d, 1 H, Ar—H, J = 7.2 Hz); 7.27—7.48 (m, 4 H, Ar—H); 7.57 (t, 1 H, Ar—H, J = 7.6 Hz); 7.87 (d, 1 H, Ar—H, J = 7.8 Hz); 8.55 (d, 1 H, H(6′), J = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 69.7 (CH_2); 116.5, 123.1, 123.9, 124.0, 124.9, 128.2, 129.0, and 132.5 (C—H arom.); 102.6, 115.2, 126.6, 127.4, 152.9, 160.1, and 161.2 (quaternary C atoms).

2,3-Dimethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (31c) was isolated by column chromatography (ethyl acetate—petroleum ether, 3 : 7, as the eluent) as a pale-yellow powder, m.p. 158 °C. The yield was 47%. Found (%): C, 69.81; H, 4.67. $C_{18}H_{14}O_5$ (310.31). Calculated (%): C, 69.67; H, 4.55. ^{1}H NMR ($CDCl_3$), δ: 3.96 (s, 6 H, OMe); 5.38 (s, 2 H, CH_2); 6.84 (s, 1 H, H(5)); 7.21 (s, 1 H, H(8)); 7.26—7.41 (m, 3 H, Ar—H); 8.56 (d, 1 H, H(6′), J = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 56.3 and 56.4 (both OMe); 69.7 (CH_2); 99.5 and 103.1 (C(5) and C(8)); 123.8, 127.0, 127.7, and 129.0 (C(3′), C(4′), C(5′), and C(6′)); 100.4, 107.2, 124.5, 146.4, 149.0, 153.6, 159.6, 160.6, and 161.4 (quaternary C atoms).

2,3,4-Trimethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (31d) was isolated by column chromatography (diethyl ether as the eluent) as a pale-yellow powder, m.p. 152 °C. The yield was 47%. Found (%): C, 67.26; H, 4.51. $C_{19}H_{16}O_6$ (340.33). Calculated (%): C, 67.06; H, 4.74. ^{1}H NMR ($CDCl_3$), δ: 3.88, 3.92, and 3.93 (all s, 3 H each, OMe); 5.69 (s, 2 H, CH_2); 6.69 (s, 1 H, H(8)); 7.12 (d, 1 H, H(3′), J = 7.2 Hz); 7.29—7.44 (m, 3 H, Ar—H); 8.46 (d, 1 H, H(6′), J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 56.3, 61.4, and 62.3 (all OMe); 69.8 (CH_2); 96.3 (C(8)); 123.7, 124.6, 127.7, 128.9 (C(3′), C(4′), C(5′), and C(6′)); 100.9, 103.4, 127.0, 127.1, 140.2, 150.8, 150.9, 157.2, 160.1, and 162.9 (quaternary C atoms).

8-Methoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (32a) was isolated by column chromatography (diethyl ether—petroleum ether, 1 : 1, as the eluent) as colorless crystals, m.p. 137 °C. The yield was 51%. Found (%): C, 72.61; H, 4.72. $C_{17}H_{12}O_4$ (280.27). Calculated (%): C, 72.85; H, 4.32. ^{1}H NMR ($CDCl_3$), δ: 3.85 (s, 3 H, OMe); 5.37 (s, 2 H, CH_2); 6.67 (d, 1 H, Ar—H, J = 2.4 Hz); 6.94 (dd, 1 H, Ar—H, J = 8.9 Hz, J = 2.4 Hz); 7.27—2.38 (m, 2 H, Ar—H); 7.54 (dt, 1 H, Ar—H, J = 7.9 Hz, J = 1.4 Hz); 7.84 (d, 1 H, Ar—H, J = 7.8 Hz); 8.50 (d, 1 H, H(6′), J = 8.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4 (OMe); 69.6 (CH_2); 110.2 (C(3′)); 113.5, 116.5, 122.9, 124.0, 124.7, and 132.0 (C(5), C(6), C(7), C(8), C(5′), and C(6′)); 102.8, 123.6, 126.6, 129.3, 152.5, 159.6, 159.7, and 161.4 (quaternary C atoms).

2,4,8-Trimethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (32b) was isolated by column chromatography (ethyl acetate—petroleum ether, 1 : 1, as the eluent) as colorless crystals, m.p. 183 °C. The yield was 39%. Found (%): C, 66.94; H, 4.96. $C_{19}H_{16}O_6$ (340.33). Calculated (%): C, 67.06; H, 4.74. ^{1}H NMR ($CDCl_3$), δ: 3.83 (s, 3 H, OMe); 3.94 (s, 6 H, OMe); 5.33 (s, 2 H, CH_2); 6.64 (d, 1 H, H(6), J = 2.6 Hz); 6.82 (s, 1 H, H(8)); 6.91 (dd, 1 H, Ar—H, J = 8.8 Hz, J = 2.8 Hz); 7.18 (s, 1 H, Ar—H); 8.47 (d, 1 H, H(6′), J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4, 56.3, and 56.4 (all OMe); 69.6 (CH_2); 99.5, 102.9 (C(6) and C(8)); 110.1 (C(3′)); 113.4 (C(5′)); 126.2 (C(6′)); 100.4, 107.4 119.5, 128.9, 146.3, 148.6, 153.2, 159.3, 159.9, and 160.8 (quaternary C atoms).

2,3,8-Trimethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (32c) was isolated by column chromatography (ethyl acetate—petroleum ether, 1 : 1, as the eluent) as colorless crystals, m.p. 207 °C. The yield was 44%. Found (%): C, 67.31; H, 4.62. $C_{19}H_{16}O_6$ (340.33). Calculated (%): C, 67.06; H, 4.74. ^{1}H NMR ($CDCl_3$), δ: 3.83 (s, 3 H, OMe); 3.94 (s, 6 H, OMe); 5.33 (s, 2 H, CH_2); 6.64 (d, 1 H, H(3′), J = 2.6 Hz); 6.82 (s, 1 H, H(5)); 6.91 (dd, 1 H, H(5′), J = 8.8 Hz, J = 2.8 Hz); 7.18 (s, 1 H, H(8)); 8.47 (d, 1 H, H(6′), J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4, 56.3, and 56.4 (all OMe); 69.6 (CH_2); 99.5 and 102.9 (C(5) and C(8)); 110.1 (C(3′)); 113.4 (C(5′)); 126.2 (C(6′)); 100.4, 107.4, 119.5, 128.9, 146.3, 148.6, 153.2, 159.3, 159.9, and 160.8 (quaternary C atoms).

2,3,4,8-Tetramethoxy-6*H*,11*H*-[2]benzopyrano[4,3-*c*][1]benzopyran-11-one (32d) was isolated by column chromatography (ethyl acetate—petroleum ether, 1 : 1, as the eluent) as colorless crystals, m.p. 137 °C. The yield was 31%. Found (%): C, 64.57; H, 5.11. $C_{20}H_{18}O_7$ (370.35). Calculated (%): C, 64.86; H, 4.90. ^{1}H NMR ($CDCl_3$), δ: 3.84 and 3.88 (both s, 3 H each, OMe); 3.91 (s, 6 H, OMe); 5.32 (s, 2 H, CH_2); 6.65—6.68 (m, 2 H, Ar—H); 6.91 (dd, 1 H, H(5′), J = 8.8 Hz, J = 2.6 Hz); 8.43 (d, 1 H, H(6′), J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4, 56.3, 61.4, and 62.3 (all OMe); 69.7 (CH_2); 96.3 (C(8)); 109.9 (C(3′)); 113.6 (C(5′)); 129.2 (C(6′)); 96.6, 111.4, 119.6, 126.4, 148.7, 150.4, 150.7, 156.8, 159.5, 160.3, and 161.3 (quaternary C atoms).

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