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Tris(polymethoxyphenyl)bismuth derivatives: Synthesis and reactivity

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Abstract

Tris-(polymethoxyphenyl)bismuth diacetate and dichloride derivatives react with C-nucleophiles in basic medium, as well as with N- and O-nucleophiles under copper catalysis to give good to high yields of the corresponding C-, N- and O-arylation products.
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1. Introduction

Bismuth compounds are low-costing, easily handled reagents that present the lowest toxicity of the heavy non-radioactive main group elements [1,2]. The use of inorganic and organic derivatives of bismuth in organic synthesis has considerably increased in the last 20 years [3]. Among the organobismuth derivatives, arylbismuth (III) and (V) compounds are selective reagents that can perform oxidation as well as arylation of different types of organic substrates [4–8]. Pentavalent triarylbismuth derivatives are highly reactive reagents for nucleophilic aromatic substitutions taking place by the ligand coupling mechanism [4,5]. These reactions occur regioselectively at the *ipso* position leading to C-arylation with soft carbon nucleophiles under basic conditions [5,6] (Scheme 1). In the presence of a copper catalyst, N-arylation of amines and O-arylation of alcohols and phenols are performed under mild conditions [5–8] (Scheme 2).

A relatively broad range of aryl groups containing electron-withdrawing as well as electron-neutral substituents is compatible with these reactions. The high regioselectivity of these processes and mild reaction conditions made these reagents attractive for a number of transformations of pharmacologically active products [9]. However, in the case of methoxy-substituted aryl groups, relatively few examples of arylation reactions were reported. Barton et al. observed a lower reactivity for tri(*p*-methoxyphenyl)bismuth carbonate toward C-arylation of enolic and phenolic substrates [10]. On the other hand, Suzuki et al. reported the strong influence of an *ortho*-methoxy group on the basicity and reactivity of triarylbismuth derivatives [11]. However, the presence of an *ortho*-alkoxy group is not detrimental to the reactivity of these compounds in ligand coupling reactions [12,13]. In view of the interest of C-, N- and O-arylation reactions with electron-rich aryl groups for the synthesis of natural and/or biologically active compounds [14], we have investigated the synthesis of tris(polymethoxyphenyl)bismuth derivatives and we have studied their reactivity in typical examples of C-, N- and O-arylation reactions.

## 2. Results and discussion

The bromine–lithium exchange on compounds **1**–**5**, followed by a transmetallation reaction with BiCl₃ (Scheme 3), afforded the corresponding triarylbismuthanes **6**–**10** in poor to good yields (Table 1). Triarylbismuth diacetates

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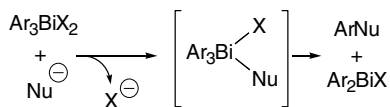
Scheme 1. Base-catalyzed C-arylation with pentavalent triarylbismuth derivatives.
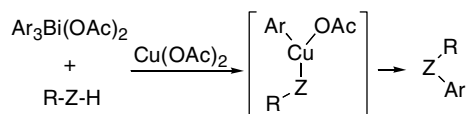
Scheme 2. Copper-catalyzed N- or O-arylation with triarylbismuth diacetate.

11–14 were prepared in modest to relatively good yields by treatment of the bismuthane derivative with sodium perborate in acetic acid [15] (Method A, Table 1) or by using iodobenzene diacetate as the oxidizing agent [12] (Method B, Table 1). The latter reagent was not efficient for the oxidation of *ortho*-methoxy-substituted arylbismuth derivatives **7** and **8**. Moreover, application of these two methodologies, as well as oxidation with the *tert*-butylhydroperoxide-acetic acid [16] or with the benzoyl peroxide-boron trifluoride diethyl etherate [17] systems, did not yield the diacylates of tris(2,4-dimethoxyphenyl)bismuth **7**. On the other hand, the triarylbismuth dichlorides **15–19** were prepared by reaction of the corresponding triarylbismuthanes

with sulfuryl chloride in dichloromethane at −78 °C (Scheme 3). However, the tris(3,4,5-trimethoxyphenyl)bismuth dichloride **18** could not be isolated as a pure compound (Table 1).

Organobismuth reagents allow two major types of arylation reactions: (i) C-arylation under basic conditions via a covalent intermediate and (ii) N- or O-arylation under copper catalysis. Although all the reagents were not obtained as diacetates and dichlorides, the study of their reactivity in C-arylation reactions was possible, as they can be performed with the diacetates as well as with the dichlorides. Indeed, the first step of the sequence involves a SN2 type reaction taking place on the bismuth atom (Scheme 1). A covalent bismuth-substrate intermediate species is formed and subsequently undergoes a reductive ligand coupling reaction affording the final C-arylation products. Thus, the pentavalent derivatives of bismuthanes **6–9** were tested as C-arylating agents (Table 2). The dichloride **16** was used as a substitute for the diacetate **12**, that could not be prepared from bismuthane **2**. Three substrates (2-naphthol **20**, β-ketoester **25** and the substituted 4-hydroxycoumarin **30** [18], 4-hydroxy-5,7-dimethoxy-2*H*-1-benzopyrane-2-one) were selected to evaluate the reactivity of the bismuth (V) derivatives **11**, **13**, **14** and **16**, containing polymethoxyaryl fragments as C-arylating agents.

The reactions of 2-naphthol **20** and of the β-ketoester **25** with organobismuth derivatives **11**, **13**, **14** and **16** were realized in THF (tetrahydrofurane) in the presence of 1.2
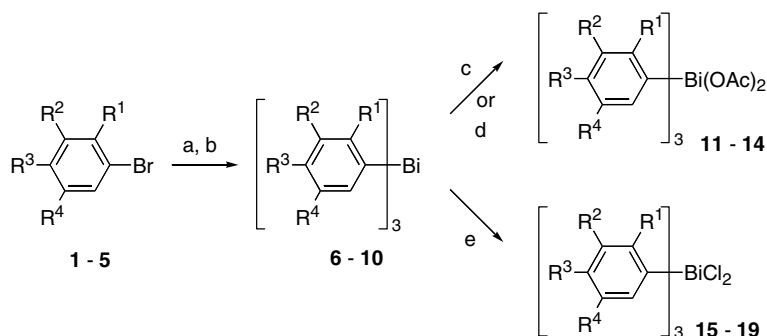
Scheme 3. Synthesis of triarylbismuth diacetates **11**–**14** and triarylbismuth dichlorides **15**–**19**. *Reagents and conditions*: (a) BuLi, THF, −78 °C; (b) BiCl₃, −78 °C to room temperature, overnight; (c) NaBO₃, AcOH, room temperature, 1 h; (d) PhI(OAc)₂, CH₂Cl₂, 25 °C, 48 h; (e) SO₂Cl₂, CH₂Cl₂, −78 °C to room temperature.

Table 1
Structure and yields of the triarylbismuthanes, triarylbismuth diacetates and triarylbismuth dichlorides

R¹	R²	R³	R⁴	ArBr	Ar₃Bi (%)	Ar₃Bi(OAc)₂ (%)	Ar₃BiCl₂ (%)
H	MeO	MeO	H	**1**	**6** (34)	**11** (29[a], 50[b])	**15** (58)
MeO	H	MeO	H	**2**	**7** (64)	**12** (0)	**16** (65)
MeO	H	H	MeO	**3**	**8** (60)	**13** (61[a])	**17** (93)
H	MeO	MeO	MeO	**4**	**9** (26)	**14** (18[a], 69[b])	**18**[c]
MeO	MeO	MeO	H	**5**	**10** (5)	–	**19** (81)

[a] Method A: oxidation by NaBO₃/AcOH system.
[b] Method B: oxidation with PhI(OAc)₂.
[c] Not isolated as a pure compound.

Table 2
Arylation reactions under basic conditions

$$Ar_3BiX_2 + NuH + Base \longrightarrow ArNu + Ar_2BiX + Base,H^{\oplus} X^{\ominus}$$
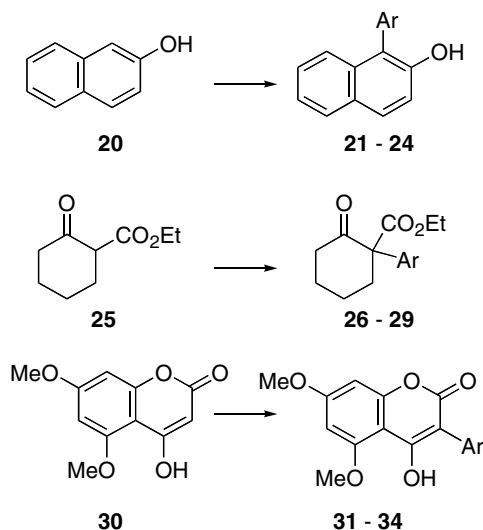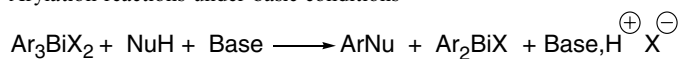
Substrate	Reagent	Reaction conditions[a]	Products (%)
20	11	RT, 5 h	21 (74)
	16	RT, 15 h	22 (69)
	13	RT, 3 h	23 (94)
	14	RT, 2 h	24 (83)
25	11	RT, 20 h	26 (83)
	16	RT, 16 h	27 (43)
	13	40 °C, 24 h	28 (71)
	14	RT, 4 h	29 (82)
30	11	40 °C, 70 h, CH$_2$Cl$_2$	31 (31)
	16	35 °C, 20 h, CH$_2$Cl$_2$	32 (29)
	13	40 °C, 24 h, CH$_2$Cl$_2$	33 (58)
	14	40 °C, 24 h, CH$_2$Cl$_2$	34 (25)

[a] All reactions were performed in THF (tetrahydrofurane) unless otherwise indicated. TMG (*N,N,N′,N′*-tetramethylguanidine) was used as the base (1.2 equiv.).

equivalent of TMG (*N,N,N′,N′*-tetramethylguanidine) used as the base. The expected arylation products **21–24** and **26–29**, respectively, were obtained in good to high yields (Table 2). In these C-arylation reactions, the triaryl-bismuth diacetates **11**, **13** and **14** appeared as relatively more efficient than the triarylbismuth dichloride **16**. The reactions of the conjugated cyclic enolate **30** with organo-bismuth reagents **11**, **13**, **14** and **16** afforded only the mono-α-arylation products **31–34** in moderate yields (Table 2) in contrast with the corresponding reactions with the related organolead derivatives [19]. Mono- *ortho*-sub-stitution of the aryl moiety of the organobismuth reagents did not seriously influence the yields of the arylation products, that are comparable to the yields obtained with the analogs having a free *ortho*-site (Table 2) [20]. Relatively low yields of α-arylated products were observed when the triarylbismuth dichloride **16** was employed in comparison with the reaction involving the diacetate derivatives. Tak-ing into account this fact, no considerable influence of

the position of the methoxy substituents in the aromatic moiety of organometallic reagent was observed on the ary-lation reaction. Thus, organobismuth reagents containing electron-rich aromatic fragments present a general pattern of reactivity similar to those of the analogs bearing elec-tron-neutral substituents (for example, triphenylbismuth diacetate [21] or other pentavalent bismuth derivatives containing dimethyl-substituted phenyl groups [20]). It is worth noting that these facts do not fully correlate with the relative migratory aptitudes of the aryl groups (p-NO$_2$C$_6$H$_4 \gg$ C$_6$H$_5 > p$-MeC$_6$H$_4 > p$-MeOC$_6$H$_4$), previ-ously reported for the C-arylation reactions with non-sym-metrical triarylbismuth carbonates [10], Ph$_n$Ar$_{3-n}$BiCO$_3$ ($n = 1, 2$; Ar $= p$-NO$_2$C$_6$H$_4$, p-MeC$_6$H$_4$ and p-MeO C$_6$H$_4$), or with unsymmetrical tetraarylbismuthonium salts [22], Ph$_3$ArBiX (Ar $= p$-MeC$_6$H$_4$ and p-MeOC$_6$H$_4$). Thus, our observations show that organobismuth derivatives can be used in arylation reactions as a useful source of electron-rich aryl groups as well as of electron-neutral and electron-acceptor aryl fragments. However, it must be recognized that the yields observed in these C-arylation reactions do not compete with those obtained with the related organo-lead triacetates which accommodate a wider range of methoxy substitutions on the aryl rings. For example, 2,4,6-trimethoxyphenyllead triacetate affords sometimes near quantitative yields of C-arylation products [23].

To study the reactivity of the organobismuth diacetates **11**, **13** and **14** in the arylation of N- and O-nucleophiles under copper catalysis, two typical substrates, 3,4-dimethy-laniline **35** and the 1,3-diol **39**, were selected. The reactions

Table 3
Copper-catalyzed arylation reactions

$$Ar_3Bi(OAc)_2 + R\text{-}Z\text{-}H \xrightarrow[Z = O \text{ or } NH]{Cat. Cu(OAc)_2} R\text{-}Z\text{-}Ar$$
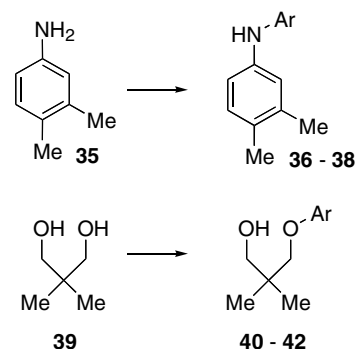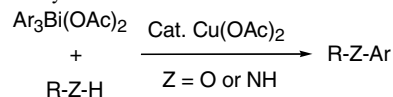
Substrate	Bismuth reagent	Reaction conditions[a]	Products (%)
35	11	RT, 10 h	36 (83)
35	13	RT, 15 h	37 (78)
35	14	RT, 1 h	38 (86)
39	11	RT, 15 h	40 (67)
39	13	40 °C, 15 h	41 (68)
39	14	40 °C, 24 h	42 (78)

[a] All reactions performed in THF with 1.1 equiv. of the Ar$_3$Bi(OAc)$_2$ reagent in the presence of Cu(OAc)$_2$ (0.1 equiv.).

were performed in THF using copper(II) diacetate as a catalyst under mild reaction conditions (room temperature or 40 °C). With both substrates, the arylation reactions led only to the formation of the mono-arylation products, **36**–**38** and **40**–**42**, respectively, in good yields (Table 3). No products of N- or O,O′-diarylation were observed under the conditions used with a stoichiometric substrate-reagent ratio (1:1.1).

The reactivity of the available organobismuth diacetates **11**, **13** and **14**, that were tested in these N- and O-arylation reactions, was comparable to the case of previously reported triarylbismuth diacetates containing electron-neutral substituents in the aryl moiety [24]. Thus, tris(poly-methoxyphenyl)bismuth diacetates, provided they can be prepared, constitute efficient non-toxic reagents for the selective O- or N-arylation under mild neutral reaction conditions. In contrast, the palladium-catalyzed N- and O-arylation reactions [25,26], now the most frequently used methods, require rather toxic [1,27] and expensive palladium salts, and a scrupulous but empiric search of the appropriate combination of phosphane or other sophisticated ligands for optimization of the yields. An attractive alternative to the pathway reported above is the renaissance Ullmann reactions, developed in the past recent years [6,28]. Although these methodologies largely simplify the coupling reaction with donor aryl species, they are suffering from the same drawbacks as the classical Ullmann transformations [7,29], the reaction conditions remaining relatively harsh.

3. Conclusion

In conclusion, pentavalent organobismuth compounds can be considered as valuable and attractive reagents for the transfer of aryl fragments with electron-donating substituents in C-arylation reaction under basic conditions, as well as for the copper-catalyzed N- and O-arylation reactions. The present observations demonstrate that electronic factors are not the major limiting feature for the usefulness of the bismuth-mediated arylation reactions. Moreover, they break the commonly accepted stereotype that organobismuth arylation agents are effective only for the transfer of aryl groups with electron-poor and electron-neutral substituents.

4. Experimental

4.1. General remarks

Melting points were taken on a Büchi capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer. Chemical shifts (δ) are reported in ppm for a solution of the compound in CDCl$_3$ with internal reference Me$_4$Si. Combustion analyses were performed at the ''Laboratoire de Microanalyse du Centre National de la Recherche Scientifique'', Vernaison (France). Separations by column chromatography were performed using Merck Kieselgel 60 (70–230 mesh). CC refers to column chromatography on silicagel and PLC refers to preparative layer chromatography on silicagel. Ether refers to diethyl ether. THF was distilled from sodium-benzophenone and CH$_2$Cl$_2$ was distilled over P$_2$O$_5$.

4.2. General procedure for the preparation of triarylbismuthanes

A solution of *n*-butyllithium (10.05–10.10 mmol, 2.5 M or 1.6 M in hexane) was added dropwise to a solution of the aryl bromide (10 mmol) in anhydrous THF (30–40 mL) at −78 °C over 15 min. The mixture was stirred for 15 min, and then BiCl$_3$ was added by little portions over 30 min. The mixture was stirred for 1 h at −78 °C, and then it was allowed to reach room temperature and stirred overnight. The reaction mixture was quenched with a 10% aqueous solution of NH$_4$Cl, extracted with ethyl acetate or with CH$_2$Cl$_2$ (3 × 30 mL) and the combined organic layers were washed with brine and dried over Na$_2$SO$_4$ or MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography or by recrystallization as indicated below to afford the bismuthane derivatives.

Tris(3,4-dimethoxyphenyl)bismuthane (**6**): CC (pentane/ether, 1:1), colourless plates; m.p. 129 °C; 34%. ^{1}H NMR: $\delta = 3.72$ (s, 9H, OCH$_3$), 3.84 (s, 9H, OCH$_3$), 6.90 (d, 3H, $J = 8.1$ Hz, 5-H) and 7.25 (m, 6H, 2-H and 6-H) ppm. ^{13}C NMR: $\delta = 55.7$ (OMe at C-3 and OMe at C-4), 113.5 (C-2), 120.2 (C-5), 130.2 (C-6), 146.1 and 148.8 (C-3 and C-4) and 151.1 (C-1) ppm. C$_{24}$H$_{27}$BiO$_6$ (620.45): calc. C 46.46, H 4.39; found C 46.38, H 4.23%.

Tris(2,4-dimethoxyphenyl)bismuthane (**7**): crystallization from CH$_2$Cl$_2$/ether/hexane mixture, pale grey needles; m.p. 178–179 °C; 64%. ^{1}H NMR: $\delta = 3.71$ (s, 9H, OMe), 3.77 (s, 9H, OMe), 6.40 (dd, 3H, $J = 7.9$ and $J = 2.2$ Hz, 5-H), 6.53 (d, 3H, $J = 2.2$ Hz, 3-H) and 7.28 (d, 3H, $J = 7.9$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 55.2$ and 55.4 (OCH$_3$), 98.2 (C-3), 108.2 (C-5), 139.7 (C-6), 161.2 (C-4), 163.5 (C-2) and 172.0 (C-1) ppm. C$_{24}$H$_{27}$BiO$_6$ (620.45): calc. C 46.46, H 4.39; found C 46.52, H 4.49.

Tris(2,5-dimethoxyphenyl)bismuthane (**8**): crystallization from CH$_2$Cl$_2$/ether/hexane mixture; pale grey plates; m.p. 127 °C; 60%. ^{1}H NMR: $\delta = 3.55$ (s, 9H, OMe), 3.72 (s, 9H, OMe), 6.80 (dd, 3H, $J = 8.7$ and $J = 3.0$ Hz, 4-H), 6.93 (d, 3H, $J = 8.7$ Hz, 3-H) and 7.09 (d, 3H, $J = 3.0$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 55.5$ and 56.2 (OMe), 110.4 and 113.9 (C-3 and C-4), 124.6 (C-6), 144.7 (C-5), 156.4 (C-2) and 157.0 (C-1) ppm. C$_{24}$H$_{27}$BiO$_6$ (620.45): calc. C 46.46, H 4.39; found C 46.32, H 4.32%.

Tris(3,4,5-trimethoxyphenyl)bismuthane (**9**): CC (pentane/ether, 2:3), colourless needles, m.p. 104–105 °C; 26%. ^{1}H NMR: $\delta = 3.71$ (s, 18H, OMe), 3.79 (s, 9H, OMe) and 6.98 (s, 6H, 2-H and 6-H) ppm. ^{13}C NMR: $\delta = 56.1$ (OMe), 60.7 (OMe), 114.2 (C-2 and C-6), 137.9 (C-4), 150.9 (C-1) and 155.6 (C-3 and C-5) ppm. C$_{27}$H$_{33}$BiO$_9$ (710.53): calc. C 45.64, H 4.68; found C 45.52, H 4.60.

Tris(2,3,4-trimethoxyphenyl)bismuthane (**10**): crystallization from CH_2Cl_2/ether/hexane mixture; colourless plates; m.p. 196 °C; 5%. ^1H NMR: $\delta = 3.82$ (s, 18H, OMe), 3.87 (s, 9H, OMe), 6.65 (d, 3H, $J = 8.1$ Hz, 5-H) and 7.12 (d, 3H, $J = 8.1$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 55.9$, 60.6 and 60.8 (OMe), 111.4 (C-5), 132.9 (C-6), 138.5 (C-1), 142.0 (C-3), 154.0 (C-4) and 156.0 (C-2) ppm. $C_{27}H_{33}BiO_9$ (710.53): calc. C 45.64, H 4.68; found C 45.37, H 4.61%.

4.3. Synthesis of triarylbismuth diacetates 11, 13 and 14: general procedure

Method A: A mixture of sodium perborate, monohydrate (4.2 mmol) and triarylbismuthane (1.4 mmol) in acetic acid (15 mL) was stirred at room temperature for 30 min. The resulting mixture was poured into water (40 mL) and was extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined, washed with water, dried over $MgSO_4$ and the solvent was distilled off under reduced pressure. The crude product was recrystallized from a mixture CH_2Cl_2/pentane at −15 °C.

Method B: A mixture of iodobenzene diacetate (2.1 mmol) and triarylbismuthane (1.8 mmol) in CH_2Cl_2 was stirred under argon atmosphere for 48 h at 25 °C. The solvent was distilled off and the crude product was recrystallized from a mixture CH_2Cl_2/ether/pentane to afford the corresponding triarylbismuth diacetate.

Tris(3,4-dimethoxyphenyl)bismuth diacetate (**11**): colourless plates; m.p. 160 °C; 29% (method A), 50% (method B); ^1H NMR: $\delta = 1.81$ (s, 6H, CH_3CO), 3.88 (s, 18H, OMe), 6.99 (d, 3H, $J = 8.5$ Hz, 5-H), 7.59 (dd, 3H, $J = 8.5$ and $J = 1.5$ Hz, 6-H) and 7.82 (d, 3H, $J = 1.5$ Hz, 2-H) ppm. ^{13}C NMR: $\delta = 22.0$ (CH_3CO), 55.9 and 56.1 (OMe), 112.4 (C-2), 117.0 (C-5), 126.4 (C6), 133.9 (C-1), 150.7 and 152.3 (C3 and C4) and 177.8 ($C(O)CH_3$) ppm. $C_{28}H_{33}BiO_{10}$ (738.54): calc. C 45.54, H 4.50; found C 45.18, H 4.44.

Tris(2,5-dimethoxyphenyl)bismuth diacetate (**13**): pale yellow powder; m.p. 152–153 °C; 61% (method A); ^1H NMR: $\delta = 1.72$ (s, 6H, C(O)CH$_3$), 3.81 and 3.85 (s, 18H, OMe), 6.94 (dd, 3H, $J = 6.1$ and $J = 3.1$ Hz, 4-H), 7.13 (d, 3H, $J = 6.1$ Hz, 3-H) and 7.88 (d, 3H, $J = 3.1$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 22.4$ (C(O)CH_3), 56.0 and 56.9 (OMe), 113.4, 117.1 and 119.3 (C-3, C-4 and C-6), 151.4 (C-1), 152.6 (C-5), 155.5 (C-2) and 176.0 (CO–CH$_3$) ppm. $C_{28}H_{33}BiO_{10}$ (738.54): calc. C 45.54, H 4.50; found C 45.38, H 4.41%.

Tris(3,4,5-trimethoxyphenyl)bismuth diacetate (**14**): pale yellow crystals; m.p. 138 °C; 18% (method A) and 69% (method B); ^1H NMR: $\delta = 1.85$ (s, 6H, CO–CH$_3$), 3.82 (s, 18H, OMe), 3.85 (s, 9H, OMe) and 7.41 (s, 6H, 2-H and 6-H) ppm. ^{13}C NMR: $\delta = 20.1$ (CO–CH_3), 56.4 (OMe), 58.8 (OMe), 110.9 (C-2 and C-6), 154.9 (C-3 and C-5), 155.7 (C-4), 159.9 (C-1) and 178.1 (CO–CH$_3$) ppm. $C_{31}H_{39}BiO_{13}$ (828.61): calc. C 44.93; H 4.74; found C 44.63, H 4.91.

4.4. Synthesis of triarylbismuth dichlorides 15–19: general procedure

A cold solution (−78 °C) of SO_2Cl_2 (0.22 mmol) in 3 mL of CH_2Cl_2 was added to a magnetically stirred solution of the triarylbismuthane (0.11 mmol) in 4 mL of CH_2Cl_2 at −78 °C under argon atmosphere. The mixture was allowed to warm to ambient temperature. The volatile products were distilled under reduced pressure. The crude product was recrystallized from the mixture CH_2Cl_2/ether to afford the corresponding triarylbismuth dichlorides.

Tris(2,4-dimethoxyphenyl)bismuth dichloride (**16**): pale yellow crystals; m.p. 135 °C (decomposition); 65%. ^1H NMR: $\delta = 3.82$ and 3.83 (2s, 18H, OMe), 6.69 (m, 6H, 3-H and 5-H) and 7.97 (d, 3H, $J = 9.3$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 55.7$ and 56.2 (OMe), 100.0 (C-3), 107.7 (C-5), 134.4 (C-6), 143.2 (C-1) and 159.4 and 163.2 (C-2 and C-4) ppm. $C_{24}H_{27}BiCl_2O_6$ (691.35): calc. C 41.69, H 3.94; found C 41.57, H 3.75%.

Tris(2,5-dimethoxyphenyl)bismuth dichloride (**17**): pale yellow powder; m.p. 180 °C; 93%. ^1H NMR: $\delta = 3.81$ and 3.85 (2s, 18H, OMe), 7.02 (dd, 3H, $J = 8.9$ and $J = 2.8$ Hz, 4-H), 7.19 (d, 3H, $J = 9.0$ Hz, 3-H) and 7.74 (d, 3H, $J = 2.8$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 56.3$ and 57.1 (OMe), 114.0, 118.4 and 118.6 (C-3, C-4 and C-6) and 151.8, 152.2 and 155.7 (C-1, C-2 and C-5) ppm. $C_{24}H_{27}BiCl_2O_6$ (691.35): calc. C 41.69, H 3.94; found C 41.47, H 3.95%.

Tris(2,3,4-trimethoxyphenyl)bismuth dichloride (**19**): pale yellow powder; m.p. 197–198 °C; 81%. ^1H NMR: $\delta = 3.92$, 3.93 and 4.06 (3s, 27H, OMe), 6.87 (d, 3H, $J = 8.9$ Hz, 5-H) and 7.87 (d, 3H, $J = 8.9$ Hz, 6-H) ppm. ^{13}C NMR: $\delta = 56.3$, 60.9 and 61.8 (OMe), 108.6 (C-5), 128.1 (C-6), 141.9 (C-3), 148.7 (C-1), 152.5 (C-4) and 156.4 (C-2) ppm. $C_{27}H_{33}BiCl_2O_9$ (781.43): calc. C 41.50, H 4.26; found C 40.27, H 4.03%.

4.5. Arylation reactions with triarylbismuth derivatives in the presence of N,N,N′,N′-tetramethylguanidine (TMG): general procedure

A mixture of the substrate (0.25–0.5 mmol, 1.0 equiv.) and TMG (1.2 equiv.) in distilled THF or dichloromethane (5 mL/mmol of substrate) was stirred for 10 min at room temperature. The triarylbismuth diacetate or dichloride (1.2 equiv.) was added and the mixture stirred as indicated in Table 2. The solvent was distilled off and the residue was purified by chromatography as described below to afford the reaction products.

4.5.1. With 2-Naphthol (20)

1-(3′,4′-Dimethoxyphenyl)-2-naphthol (**21**): CC (pentane/ether/CH_2Cl_2, 32:9:9), followed by PLC (pentane/ether, 4:1, followed by pentane/1,4-dioxane, 4:1); colourless plates; m.p. 186 °C (decomposition); 74%. ^1H NMR: $\delta = 3.86$ (s, 3H, OMe), 3.97 (s, 3H, OMe), 5.23 (s, 1H, OH), 6.84–7.06 (m, 3H, ArH), 7.22–7.42 (m, 4H, ArH)

and 7.73–7.83 (m, 2H, Ar-H) ppm. ^{13}C NMR: $\delta = 55.9$ (OMe), 112.1 and 113.9 (C-2$'$ and C-5$'$), 117.2 (C-3), 120.7 (C-1), 123.2, 124.6, 126.2, 126.4, 128.0, 129.3 (C-4, C-5, C-6, C-7, C-8 and C-6$'$), 128.8 (C-1$'$), 133.5 and 134.2 (C-9 and C-10) and 149.1, 149.8 and 150.4 (C-2, C-3$'$ and C-4$'$) ppm. $C_{18}H_{16}O_3$ (280.32): calc. C 77.12, H 5.75; found C 77.30, H 6.05%.

1-(2$'$,4$'$-Dimethoxyphenyl)-2-naphthol (**22**): CC (pentane/ether/CH_2Cl_2, 7:2:1); colourless plates; m.p. 144 °C; 69%. ^{1}H NMR: $\delta = 3.71$ (s, 3H, OMe), 3.90 (s, 3H, OMe), 5.28 (s, 1H, OH), 6.64–6.70 (m, 2H, ArH), 7.16–7.34 (m, 5H, ArH) and 7.74–7.81 (m, 2H, ArH) ppm. ^{13}C NMR: $\delta = 55.5$ and 55.8 (OMe), 99.6 (C-3$'$), 105.6 (C-5$'$), 114.5 (C-1$'$), 117.5 (C-3), 123.1, 124.8, 126.1, 128.0, 129.3 and 133.8 (C-4, C-5, C-6, C-7, C-8 and C-6$'$), 129.1 (C-1), 133.7 (C-9 and C-10), 150.8 (C-2) and 161.5 (C-2$'$ and C-4$'$) ppm. $C_{18}H_{16}O_3$ (280.32): calc. C 77.12, H 5.75; found C 76.87, H 6.15%.

1-(2$'$,5$'$-Dimethoxyphenyl)-2-naphthol (**23**): Before purification of the product by CC, the reaction mixture was treated with several drops of HCl; CC (ether/pentane, 3:7); colourless plates; m.p. 125–126 °C; 94%. ^{1}H NMR: $\delta = 3.64$ and 3.73 (2s, 6H, OMe), 5.48 (s, 1H, OH), 6.85 (d, 1H, $J = 2.6$ Hz, 6$'$-H), 6.93–7.05 (m, 2H, ArH), 7.20–7.45 (m, 4H, Ar–H) and 7.73–7.81 (m, 2H, ArH) ppm. ^{13}C NMR: $\delta = 55.7$ and 56.5 (OMe), 113.5 and 115.2 (C-3$'$ and C-4$'$), 117.7 (C-1$'$), 117.8 and 118.3 (C-3 and C-6$'$), 123.2, 124.7, 126.3, 128.0 and 129.5 (C-4, C-5, C-6, C-7 and C-8), 123.5 (C-1), 129.0 and 133.3 (C-9 and C-10), 150.6 and 151.8 (C-2$'$ and C-5$'$) and 154.1 (C-2) ppm. $C_{18}H_{16}O_3$ (280.32): calc. C 77.12, H 5.75; found C 76.93, H 5.69%.

1-(3$'$,4$'$,5$'$-Trimethoxyphenyl)-2-naphthol (**24**): CC (pentane/ether, 11:9); colourless plates; m.p. 153 °C; 83%. ^{1}H NMR: $\delta = 3.84$ (s, 6H, OMe), 3.95 (s, 3H, OMe), 5.33 (s, 1H, OH), 6.61 (s, 2H, 2$'$-H and 6$'$-H), 7.20–7.51 (m, 4H, Ar–H) and 7.72–7.83 (m, 2H, ArH) ppm. ^{13}C NMR: $\delta = 56.2$ (OMe), 60.9 (OMe), 107.8 (C-2$'$ and C-6$'$), 117.3, 123.3, 124.6, 126.6, 128.8 and 129.5 (C-3, C-4, C-5, C-6, C-7 and C-8), 121.0 (C-1), 128.8 (C-1$'$), 129.4 and 133.2 (C-9 and C-10), 137.9 (C-2) and 152.2 and 154.2 (C-3$'$, C-5$'$ and C-4$'$) ppm. $C_{19}H_{18}O_4$ (310.34): calc. C 73.53, H 5.85; found C 73.80, H 5.53%.

4.5.2. With ethyl 2-oxocyclohexanecarboxylate (25)

Ethyl 1-(3$'$,4$'$-dimethoxyphenyl)-2-oxocyclohexanecarboxylate (**26**): CC (pentane/ether, 3:2); colourless oil; 83%. ^{1}H NMR: $\delta = 1.24$ (t, 3H, $J = 7.1$ Hz, CH_3CH_2O), 1.75–1.97 (m, 4H, 4-H and 5-H), 2.23–2.70 (m, 4H, 3-H and 6-H), 3.82 and 3.84 (s, 6H, OMe), 4.18 (q, 2H, $J = 7.1$ Hz, OCH_2CH_3) and 6.72–6.85 (m, 3H, ArH) ppm. ^{13}C NMR: $\delta = 14.0$ (OCH_2CH_3), 22.2 (C-4), 27.6 (C-5), 35.1 (C-3), 40.7 (C-6), 55.7 and 55.8 (OMe), 61.5 (OCH_2CH_3), 65.8 (C-2), 110.8 and 111.6 (C-2$'$ and C-5$'$), 119.8 (C-6$'$), 128.9 (C-1$'$), 148.5 and 148.6 (C-3$'$ and C-4$'$), 171.3 (C-1$'$) and 206.8 (CO_2CH_2) ppm. $C_{17}H_{22}O_5$ (306.35): calc. C 66.65, H 7.24; found C 66.43, H 7.36%.

Ethyl 1-(2$'$,4$'$-dimethoxyphenyl)-2-oxocyclohexanecarboxylate (**27**): CC (pentane/ether, 7:3); colourless oil; 43%. ^{1}H NMR: $\delta = 1.19$ (t, 3H, $J = 7.1$ Hz, OCH_2CH_3), 1.58–1.86 (m, 4H, 4-H and 5-H), 2.43–2.64 (m, 4H, 3-H and 6-H), 3.72 and 3.94 (s, 6H, OMe), 4.10–4.20 (m, 2H, OCH_2CH_3), 6.41–6.50 (m, 2H, 5$'$-H and 3$'$-H) and 6.98 (d, 1H, $J = 9.2$ Hz, 6$'$-H) ppm. ^{13}C NMR: $\delta = 14.0$ (OCH_2CH_3), 21.9 (C-4), 27.5 (C-5), 35.3 (C-3), 40.5 (C-6), 55.3 and 55.6 (OMe), 61.2 (OCH_2CH_3), 64.2 (C-2), 99.9 (C-3$'$), 104.5 (C-5$'$), 120.4 (C-1$'$), 127.8 (C-6$'$), 158.5 and 160.3 (C-2$'$ and C-4$'$), 171.7 (CO) and 206.6 (CO_2CH_2) ppm. $C_{17}H_{22}O_5$ (306.35): calc. C 66.65, H 7.24; found C 66.62, H 7.60%.

Ethyl 1-(2$'$,5$'$-dimethoxyphenyl)-2-oxocyclohexanecarboxylate (**28**): CC (ether/pentane, 3/7); colourless oil; 71%. ^{1}H NMR: $\delta = 1.22$ (t, 3H, $J = 7.2$ Hz, CH_2CH_3), 1.40–1.95 (m, 4H, 4-H and 5-H), 2.45–2.70 (m, 4H, 3-H and 6-H), 3.70 and 3.76 (s, 6H, OMe), 4.21 (dq, 2H, $J = 7.2$ and $J = 1.9$ Hz, OCH_2CH_3), 6.70 (d, 1H, $J = 2.6$ Hz, 6$'$-H) and 6.75–6.89 (m, 2H, 3$'$-H and 4$'$-H) ppm. ^{13}C NMR: $\delta = 14.0$ (OCH_2CH_3), 21.9 (C-5), 27.2 (C-4), 35.3 (C-6), 40.6 (C-3), 55.6 and 56.3 (OMe), 61.4 (OCH_2CH_3), 64.6 (C-1), 112.4, 113.3 and 114.5 (C-3$'$, C-4$'$ and C-6$'$), 129.4 (C-1$'$), 151.7 and 153.7 (C-2$'$ and C-5$'$), 171.2 (CO) and 205.9 (CO_2CH_2) ppm. $C_{17}H_{22}O_5$ (306.35): calc. C 66.65; H 7.24; found C 66.89, H 7.46%.

Ethyl 1-(3$'$,4$'$,5$'$-trimethoxyphenyl)-2- oxocyclohexanecarboxylate (**29**): PLC (pentane/ether, 7:3); colourless oil; 82%. ^{1}H NMR: $\delta = 1.23$ (t, 3H, $J = 7.1$ Hz, CH_3CH_2O), 1.64–2.00 (m, 4H, 4-H and 5-H), 2.26–2.78 (m, 4H, 3-H and 6-H), 3.80 (s, 6H, OMe), 3.86 (s, 3H, OMe), 4.20 (t, 2H, $J = 7.1$ Hz, OCH_2CH_3) and 6.42 (s, 2H, 2$'$-H and 6$'$-H) ppm. ^{13}C NMR: $\delta = 14.0$ (OCH_2CH_3), 22.2 (C-5), 27.5 (C-4), 35.3 (C-6), 40.9 (C-3), 56.1 (OMe), 60.7 (OMe), 60.7 (OCH_2CH_3), 66.2 (C-2), 105.4 (C-2$'$ and C-6$'$), 135.4 (C-1$'$), 132.0 and 152.9 (C-3$'$, C-5$'$ and C-4$'$), 171.1 (CO) and 206.5 (CO_2CH_2) ppm. $C_{18}H_{24}O_6$ (336.38): calc. C 64.27, H 7.19; found C 64.51, H, 7.42%.

4.5.3. With 4-hydroxy-5,7-dimethoxy-2H-1-benzopyrane-2-one (30)

3-(3$'$,4$'$-Dimethoxyphenyl)-4-hydroxy-5,7-dimethoxy-2H-1-benzopyrane-2-one (**31**): CC (ether) light yellow needles; m.p. 200 °C (EtOH); (lit. [17b] 200–202 °C); 31%. ^{1}H NMR: $\delta = 3.85$, 3.86, 3.88 and 4.01 (4s, 12H, OMe), 6.36 (d, 1H, $J = 2.2$ Hz, 6-H), 6.51 (d, 1H, $J = 2.2$ Hz, 8-H), 6.90 (d, 1H, $J = 8.1$ Hz, 6$'$-H), 7.05–7.10 (m, 2H, 2$'$-H and 5$'$-H) and 9.60 (s, 1H, OH) ppm. ^{13}C NMR: $\delta = 55.8$, 55.9, 56.0 (OMe), 94.3 (C-6), 95.6 (C-8), 99.0 (C-10), 103.2 (C-3), 110.8 (C-5$'$), 114.0 (C-2$'$), 123.2 (C-6$'$), 123.8 (C-1$'$), 148.4 (C-3$'$), 148.4 (C-4$'$), 155.7 (C-9), 157.0 (C-5), 161.2 (C-7), 162.8 (C-2) and 163.0 (C-4) ppm.

3-(2$'$,4$'$-Dimethoxyphenyl)-4-hydroxy-5,7-dimethoxy-2H-1- benzopyrane-2-one (**32**): PLC (CHCl$_3$/ether, 2:3); colourless powder; m.p. 194 °C; 29%. ^{1}H NMR: $\delta = 3.77$, 3.80, 3.84 and 3.97 (4s, 12H, OMe), 6.34 (d, 1H, $J = 2.2$ Hz,

6-H), 6.50–6.58 (m, 3H, 7-H, 3′-H and 5′-H), 7.17 (d, 1H, $J = 8.90$ Hz, 6′-H) and 9.44 (s, 1H, OH) ppm. ^{13}C NMR: $\delta = 55.3$, 55.8, 55.9 and 56.9 (OMe), 91.1 (C-1′), 94.3 and 95.4 (C-6 and C-3′), 99.2 (C-8), 102.3 (C-3), 104.7 (C-5′), 113.0 (C-10), 132.5 (C-6′), 155.8 (C-9), 157.0 (C-5), 158.7 (C-7), 160.9 (C-4′), 161.8 (C-2′), 162.5 (C-2) and 162 (C-4) ppm. $C_{19}H_{18}O_7$ (358.34): calc. C 63.68, H 5.06; found C 63.91, H 5.17%.

3-(2′,5′-Dimethoxyphenyl)-4-hydroxy-5,7-dimethoxy-2H-1-benzopyrane-2-one (**33**): CC (CHCl$_3$/pentane/MeOH, 25:24:1), then PLC (CHCl$_3$–pentane–MeOH, 25:24:1); colourless powder; m.p. 195 °C; 58%. ^{1}H NMR: $\delta = 3.77$, 3.86 and 3.98 (s, 12H, OMe), 6.36 (d, 1H, $J = 2.2$ Hz, 6-H), 6.52 (d, 1H, $J = 2.2$ Hz, 8-H), 6.85–6.99 (m, 3H, 3′-H, 4′-H and 6′-H) and 9.51 (s, 1H, OH) ppm. ^{13}C NMR: $\delta = 55.6$, 55.9, 56.6 and 56.9 (OMe), 94.2 (C-6), 95.4 (C-8), 98.9 (C-1′), 100.4 (C-3), 112.7, 114.4 and 117.6 (C-3′, C-4′ and C-6′), 121.5 (C-10), 152.0, 153.4, 155.8 and 157.1 (C-5, C-7, C-2′ and C-5′), 161.8 (C-2), 162.0 (C-9) and 163.0 (C-4) ppm. $C_{19}H_{18}O_7$ (358.34): calc. C 63.68, H 5.06; found C 63.84; H 5.19%.

3-(3′,4′,5′-Trimethoxyphenyl)-4-hydroxy-5,7-dimethoxy-2H-1-benzopyrane-2-one (**34**): CC (CHCl$_3$/Et$_2$O 1:1), then PLC (CHCl$_3$/ether, 1:1); colourless powder; m.p. 244 °C; 25%. ^{1}H NMR: $\delta = 3.83$, 3.86, 4.01 (3s, 15 H, OMe), 6.36 (d, 1H, $J = 2.2$ Hz, 6-H), 6.50 (d, 1H, $J = 2.2$ Hz, 8-H), 6.72 (s, 2H, 2′-H and 6′-H) and 9.66 (s, 1H, OH) ppm. ^{13}C NMR: $\delta = 55.9$, 56.1, 57.0 and 60.7 (OMe), 94.2 (C-6), 94.4 (C-8), 98.8 (C-10), 103.3 (C-3), 107.9 (C-2′ and C-6′), 126.7 (C-1′), 137.3 (C-4′), 152.7 (C-3′ and C-5′), 155.5 and 157.4 (C-5 and C-7), 161.4 (C-9), 162.5 (C-2) and 163.2 (C-4) ppm. $C_{20}H_{20}O_8$ (388.37): calc. C 61.85, H 5.19; found C 61.95, H, 5.14%.

4.6. Copper-catalyzed arylation reactions with triarylbismuth diacetates: general procedure

A mixture of the substrate (1 equiv.), copper diacetate (0.1 equiv.) and the triarylbismuth diacetate (1.1 equiv.) in THF (5 mL/mmol of substrate) was stirred at the temperature and for the time indicated in Table 3. The solvent was distilled off and the residue was purified by chromatography (eluent indicated below) to afford the reaction products.

4.6.1. With 3,4-dimethylaniline (35)

N-(3,4-Dimethylphenyl)-N-(3′,4′-dimethoxyphenyl)amine (**36**): PLC (ether/CH$_2$Cl$_2$/pentane, 3:2:5), colourless oil; 83%. ^{1}H NMR: $\delta = 2.21$ (s, 6H, Me), 3.81 and 3.83 (2s, 6H, OMe), 6.50–6.81 (m, 6H, 2-H, 6-H, 2′-H, 5′-H, 6′-H and N–H) and 7.00 (d, 1H, $J = 7.8$ Hz, 5-H) ppm. ^{13}C NMR: $\delta = 18.8$ and 19.8 (Me); 55.7 and 56.3 (OMe), 104.4 (C-2′), 110.9 (C-6′), 112.3 (C-5′), 114.3, 118.5 and 130.2 (C-2, C-5 and C-6), 128.3 (C-1′), 137.2 (C-1), 137.4 and 142.3 (C-3 and C-4) and 144.1 and 146.6 (C-3′ and C-4′) ppm. $C_{16}H_{19}NO_2$ (257.33): calc. C 74.68, H 7.44, N 5.44; found C 74.73, H 7.55, N 5.37%.

N-(3,4-Dimethylphenyl)-N-(2′,5′-dimethoxyphenyl) amine (**37**): CC (ether/pentane, 1:19); colourless oil; 78%. ^{1}H NMR: $\delta = 2.20$ and 2.22 (2s, 6H, Me), 3.70 and 3.82 (2s, 6H, OMe), 6.08 (s, 1H, NH), 6.28 (dd, 1H, $J = 8.7$ and $J = 2.9$ Hz, 4′-H), 6.75 (d, 1H, $J = 8.7$ Hz, 3′-H), 6.82 (d, 1H, $J = 3.0$ Hz, 6′-H), 6.90–6.98 (m, 2H, 2-H and 6-H) and 7.04 (d, 1H, $J = 7.8$ Hz, 5-H) ppm. ^{13}C NMR: $\delta = 19.0$ and 19.9 (Me), 55.5 and 56.1 (OMe), 100.8 and 102.0 (C-4′ and C-6′), 111.0 (C-3′), 117.3, 121.5 and 130.25 (C-2, C-5 and C-6), 130.1 and 135.0 (C-3 and C-4), 137.4 (C-1), 139.7 and 142.2 (C-2′ and C-5′) and 154.2 (C-1′) ppm. $C_{16}H_{19}NO_2$ (257.33): calc. C 74.68, H 7.44, N 5.44; found C 74.60, H 7.59, N 5.44%.

N-(3,4-Dimethylphenyl)-N-(3′,4′,5′-trimethoxyphenyl)-amine (**38**): PLC (ether/CH$_2$Cl$_2$/pentane, 3:2:5); yellow plates; m.p. 89 °C; 86%. ^{1}H NMR: $\delta = 2.21$ (s, 6H, Me), 3.78 and 3.80 (s, 9H, OMe), 5.91 (s (large), 1H, NH), 6.26 (s, 2H, 2′-H and 6′-H), 6.79–6.84 (m, 2H, 2-H and 6-H) and 7.02 (d, 1H, $J = 7.8$ Hz, 5-H) ppm. ^{13}C NMR: $\delta = 18.9$ and 19.9 (Me), 55.9 and 61.0 (OMe), 95.1 (C-2′ and C-6′), 115.7, 119.9 and 130.3 (C-2, C-5 and C-6), 129.3 (C-1′), 132.9 (C-1), 137.5 and 140.1 (C-3 and C-4) and 141.0 and 153.7 (C-3′ and C-5′) ppm. $C_{17}H_{21}NO_3$ (287.35): calc. C 71.06, H 7.37, N 4.87; found C 70.78, H 7.35, N 4.90%.

4.6.2. With 2.2-dimethyl-1,3-propanediol (39)

3-(3′,4′-Dimethoxyphenoxy)-2,2-dimethylpropan-1-ol (**40**): CC (pentane/ether, 1:1) colourless plates; m.p. 67–68 °C; 67%. ^{1}H NMR: $\delta = 1.02$ (s, 6H, Me), 2.02 (s, 1H, OH), 3.54 (s, 2H, 1-H), 3.72 (s, 2H, 3-H), 3.82 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.39 (dd, 1H, $J = 8.7$ and $J = 2.8$ Hz, 6′-H), 6.51 (d, 1H, $J = 2.7$ Hz, 2′-H) and 6.76 (d, 1H, $J = 8.7$ Hz, 5′-H) ppm. ^{13}C NMR: $\delta = 21.7$ (Me) 36.3 (C-2), 55.8 and 56.5 (OMe), 70.1 (C-1), 75.7 (C-3), 100.8 (C-2′), 103.9 (C-6′), 111.9 (C-5′), 143.6 (C-1′), 149.7 (C-4′) and 153.7 (C-3′) ppm. $C_{13}H_{20}O_4$ (240.30): calc. C 64.98, H 8.39; found C 64.77, H 8.35%.

3-(2′,5′-Dimethoxyphenoxy)-2,2-dimethylpropan-1-ol (**41**): CC (ether/pentane, 2:3); colourless oil; 68%. ^{1}H NMR: $\delta = 1.04$ (s, 6H, Me), 3.55 (s, 2H, CH$_2$), 3.75 and 3.79 (s, 8H, OMe and 3-CH$_2$), 6.43 (dd, 1H, $J = 8.7$ and $J = 2.3$ Hz, 4′-H), 6.51 (d, 1H, $J = 2.3$ Hz, H-6′) and 6.79 (d, 1H, $J = 8.9$ Hz, 3′-H) ppm. ^{13}C NMR: $\delta = 21.8$ (Me), 36.30 (C-2), 55.6 and 56.7 (OMe), 71.1 (C-1); 78.3 (C-3), 102.31 and 104.4 (C-3′ and C-4′), 112.7 (C-6′), 144.0 and 149.3 (C-2′ and C-5′) and 154.3 (C-1′) ppm. $C_{13}H_{20}O_4$ (240.30): calc. C 64.98, H 8.39; found C 64.74, H 8.46%.

3-(3′,4′,5′-Trimethoxyphenoxy)-2,2-dimethylpropan-1-ol (**42**): CC (pentane/ether, 1:1); colourless plates; m.p. 88 °C; 78%. ^{1}H NMR: $\delta = 1.00$ (s, 6H, Me), 1.95 (s, 1H, OH), 3.51 (s, 2H, 1-H), 3.70 (s, 2H, 3-H), 3.75 and 3.81 (s, 9H, OMe) and 6.12 (s, 2H, 2′-H and 6′H) ppm. ^{13}C NMR: $\delta = 21.6$ (Me), 36.4 (C-2), 56.1 and 61.0 (OMe), 69.8 (C-1), 75.1 (C-3), 92.3 (C-2′ and C-6′), 132.4 (C-1′), 153.7 (C-3′ and C-5′) and 155.7 (C-4′) ppm. $C_{14}H_{22}O_5$ (270.32): calc. C 62.20, H 8.20; found C 62.49, H 8.48%.

References

[1] (a) N.M. Leonard, L.C. Wieland, R.S. Mohan, Tetrahedron 58 (2002) 8373;
(b) H. Gaspard-Iloughmane, C. Le Roux, Eur. J. Org. Chem. (2004) 2517.

[2] (a) R.J. Lewis, Sax's Dangerous Properties of Industrial Materials, eighth ed., Van Nostrand Reinhold, New York, 1992;
(b) R.E. Lenga, The Sigma-Aldrich Library of Chemical Safety, second ed., Sigma-Aldrich, Milwaukee, 1988.

[3] (a) For reviews on the use of organobismuth compounds in organic synthesis, see: H. Suzuki, T. Ikegami, Y. Matano, Synthesis (1997) 249;
(b) H. Suzuki, Y. Matano, Organobismuth compounds: synthesis, properties and uses in organic transformations, in: N.C. Norman (Ed.), Chemistry of Arsenic, Antimony and Bismuth, Blackie Academic and Professional, London, 1998, p. 283 (Chapter 6);
(c) H. Suzuki, Y. Matano (Eds.), Organobismuth Chemistry, Elsevier, Amsterdam, 2001, p. 619;
(d) Y. Matano, in: H. Yamamoto, K. Oshima (Eds.), Main Group Metals in Organic Synthesis, vol. 2, Wiley–VCH, Weinheim, 2004, p. 753.

[4] (a) D.H.R. Barton, J.-P. Finet, Pure Appl. Chem. 59 (1987) 937;
(b) J.-P. Finet, Chem. Rev. 89 (1989) 1487.

[5] J.-P. Finet, Ligand Coupling Reactions with Heteroatomic Compounds, Pergamon Press, Oxford, 1998, pp. 159–204 (Chapter 6).

[6] C.I. Elliott, J.P. Konopelski, Tetrahedron 57 (2001) 5683.

[7] J.-P. Finet, A.Yu. Fedorov, S. Combes, G. Boyer, Curr. Org. Chem. 6 (2002) 597.

[8] S.V. Ley, A. Thomas, Angew. Chem., Int. Ed. 42 (2003) 5400.

[9] (a) P.J. Sinclair, F. Wong, M. Wyvratt, M.J. Staruch, F. Dumont, Bioorg. Med. Chem. Lett. 5 (1995) 1035;
(b) P.J. Sinclair, F. Wong, M.J. Staruch, G. Wiederrecht, W.H. Parsons, F. Dumont, M. Wyvratt, Bioorg. Med. Chem. Lett. 6 (1996) 2193;
(c) K.M.J. Brands, U.-H. Dolling, R.B. Jobson, G. Marchesini, R.A. Reamer, J.M. Williams, J. Org. Chem. 63 (1998) 6721;
(d) G.S. Sheppard, Synlett (1999) 1207;
(e) S. Pietri, T. Liebgott, J.-P. Finet, M. Culcasi, L. Billottet, C. Bernard-Henriet, Drug Dev. Res. 54 (2001) 191.

[10] D.H.R. Barton, N.Y. Bhatnagar, J.-P. Finet, W.B. Motherwell, Tetrahedron 42 (1986) 3111.

[11] (a) T. Ogawa, T. Hikasa, T. Ikegami, N. Ono, H. Suzuki, Chem. Lett. 22 (1993) 815;
(b) T. Ogawa, T. Hikasa, T. Ikegami, N. Ono, H. Suzuki, J. Chem. Soc., Perkin Trans. 1 (1994) 3473;
(c) T. Ogawa, T. Ikegami, T. Hikasa, N. Ono, H. Suzuki, J. Chem. Soc., Perkin Trans. 1 (1994) 3479;
(d) H. Suzuki, T. Ikegami, N. Azuma, J. Chem. Soc., Perkin Trans. 1 (1997) 1609;
(e) Y. Matano, H. Nomura, J. Am. Chem. Soc. 123 (2001) 6443.

[12] S. Combes, J.-P. Finet, Tetrahedron 54 (1998) 4313.

[13] R.J. Sorenson, J. Org. Chem. 65 (2000) 7747.

[14] (a) A. Huwe, R. Mazitschek, A. Giannis, Angew. Chem., Int. Ed. 42 (2003) 2122;
(b) F.T. Boyle, G.F. Costello, Chem. Soc. Rev. 27 (1998) 251;
(c) M. Roberti, D. Pizzirani, D. Simoni, R. Rondanin, R. Baruchello, C. Bonora, F. Buscemi, S. Grimaudo, M. Tolomeo, J. Med. Chem. 46 (2003) 3546;
(d) C. Bailly, C. Bal, P. Barbier, S. Combes, J.-P. Finet, M.-P. Hildebrand, V. Peyrot, N. Wattez, J. Med. Chem. 46 (2003) 5437;
(e) A. Saito, A. Tanaka, M. Ubukata, N. Nakajima, Synlett (2004) 2040;
(f) J. Zielonka, J. Gebicki, G. Grynkiewich, Free Rad. Biol. Med. 35 (2003) 958.

[15] S. Combes, J.-P. Finet, Synth. Commun. 26 (1996) 4569.

[16] V.A. Dodonov, A.V. Gushchin, Russ. Chem. Bull. 42 (1993) 1955.

[17] (a) G.B. Deacon, W.R. Jackson, J.M. Pfeiffer, Aust. J. Chem. 37 (1984) 527;
(b) T. Arnauld, D.H.R. Barton, E. Doris, Tetrahedron Lett. 38 (1997) 365.

[18] A.H. Gilbert, A. McGooking, A. Robertson, J. Chem. Soc. (1957) 3740.

[19] (a) D.H.R. Barton, D.M.X. Donnelly, J.-P. Finet, P.J. Guiry, J. Chem. Soc., Perkin Trans. 1 (1992) 1365;
(b) S. Combes, J.-P. Finet, D. Siri, J. Chem. Soc., Perkin Trans. 1 (2002) 38.

[20] A.Yu. Fedorov, S. Combes, J.-P. Finet, Tetrahedron 55 (1999) 1341.

[21] (a) D.H.R. Barton, N.Y. Bhatnagar, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, D.J. Lester, W.B. Motherwell, M.T.B. Papoula, S.P. Stanforth, J. Chem. Soc., Perkin Trans. 1 (1985) 2657;
(b) D.H.R. Barton, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, W.B. Motherwell, M.T.B. Papoula, S.P. Stanforth, J. Chem. Soc., Perkin Trans. 1 (1985) 2667.

[22] Y. Matano, T. Miyamatsu, H. Suzuki, Chem. Lett. 27 (1998) 127.

[23] (a) D.M.X. Donnelly, B.M. Fitzpatrick, B.A. O'Reilly, J.-P. Finet, Tetrahedron 49 (1993) 7967;
(b) D.M.X. Donnelly, B.M. Fitzpatrick, S.M. Ryan, J.-P. Finet, J. Chem. Soc., Perkin Trans. 1 (1994) 1797.

[24] D.H.R. Barton, J.-P. Finet, C. Pichon, J. Chem. Soc., Chem. Commun. (1986) 65.

[25] (a) A.R. Muci, S.L. Buchwald, Top. Curr. Chem. 219 (2002) 131;
(b) B.Y. Yang, S.L. Buchwald, J. Organomet. Chem. 576 (1999) 125;
(c) J.P. Wolfe, S. Wagaw, J.F. Marcoux, S.L. Buchwald, Acc. Chem. Res. 31 (1998) 805;
(d) D. Prim, J.-M. Campagne, D. Joseph, B. Andrioletti, Tetrahedron 58 (2002) 2041.

[26] (a) J.F. Hartwig, in: E.-I. Negishi, A. de Meijere (Eds.), Handbook of Organopalladium Chemistry for Organic Synthesis, vol. 1, Wiley, New York, 2002, pp. 1051–1096;
(b) J.F. Hartwig, Angew. Chem., Int. Ed. 37 (1998) 2046;
(c) J.F. Hartwig, Acc. Chem. Res. 31 (1998) 852.

[27] M.G. Moloney, Main Group Met. Chem. 24 (2001) 653.

[28] K. Kunz, U. Scholz, D. Ganzer, Synlett (2003) 2428.

[29] (a) J. Lindley, Tetrahedron 40 (1984) 1433;
(b) I.P. Beletskaya, A.V. Cheprakov, Coord. Chem. Rev. 248 (2004) 2337.