

ortho-Arylation of 3,5-Di-*tert*-butylphenol with Aryllead(IV) Derivatives: A Facile Synthesis of Sterically Hindered Phenols

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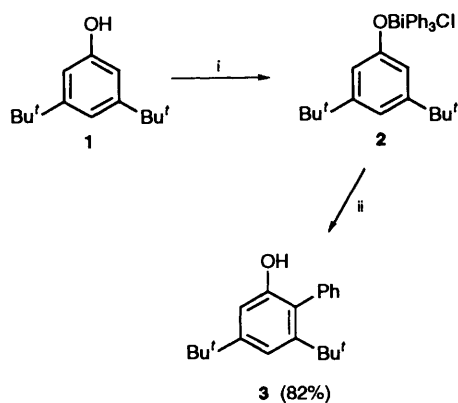
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The reaction of aryllead(IV) triacetates with 3,5-di-*tert*-butylphenol **1** has been shown to yield very hindered 2-aryl-3,5-di-*tert*-butylphenols and 2,6-diaryl-3,5-di-*tert*-butylphenols such as **15** and **16**. The mechanism of this arylation reaction with aryllead(IV) derivatives is discussed. A free radical pathway has been excluded. The favoured pathway must involve the occurrence of covalent aryl(aryloxy)lead(IV) diacetate intermediates, although they have not been detected. The required aryl cation behaviour of the lead reagents is supported by ¹³C NMR spectroscopic studies on aryllead triacetates.

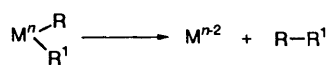
Aryllead triacetates are a class of organolead(IV) derivatives which have proved very efficient for the arylation of a variety of soft nucleophiles such as phenols, β -dicarbonyls and nitroalkanes under mild reaction conditions.^{1,2} These properties have been studied in depth by Pinhey *et al.* We have recently taken advantage of their efficiency to prepare a range of hindered β -dicarbonyl derivatives leading to flavonoid^{3,4} and biflavonoid⁵ natural products.

The utility of arylbismuth(V) compounds as aryl cation equivalents is also well established.⁶ Reaction of electron-rich phenols with pentavalent phenylbismuth derivatives led to 2,6-diphenylphenols.⁷ For example, 3,5-di-*tert*-butylphenol **1** was phenylated to its 2,6-diphenyl derivative **17** by Ph₃BiCl₂ in 77% yield.⁸ Mechanistic studies on these bismuth(V)-mediated phenylations of **1** led to the detection by ¹H NMR spectroscopy and isolation of an intermediate **2** which possesses a covalent Bi-O bond. The controlled thermal degradation of this intermediate led to the *ortho*-C-phenyl derivative, 3,5-di-*tert*-butyl-2-phenylphenol **3** (Scheme 1).⁸



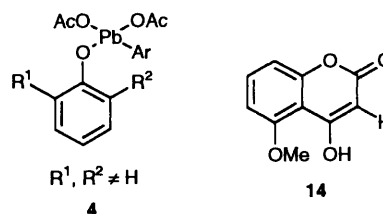
Scheme 1 Reagents and conditions: i, Ph₃BiCl₂-1,1,3,3-tetramethylguanidine, THF, room temp. and -20 °C; ii, toluene, heat

The aryloxybismuth intermediate is thought to undergo ligand coupling, a concept which implies that two groups attached to an atom couple together in a concerted manner without separating into radicals or ions (Scheme 2).⁹



Scheme 2

In their studies, Bell *et al.* have shown that *ortho*-substituted phenols lead to 6-arylcyclohexa-2,4-dienone derivatives.¹⁰ ¹H NMR monitoring of the reaction of 4-methoxyphenyllead triacetate with 2,6-dichloro-4-nitrophenol indicated a downfield shift of the signals of 2-H and 6-H of the 4-methoxyphenyl moiety. The presence of an aryloxylead intermediate **4** was thus suggested in the lead-mediated arylation of 2,6-disubstituted phenols.¹⁰ The exclusive *ortho*-arylation affording 6-arylcyclohexa-2,4-dienones ruled out the breakdown of **4** to phenoxide ion and aryl cation which could then recombine. A mechanism involving free-radical intermediates was also discarded by intermolecular and intramolecular trapping experiments.^{11,12}



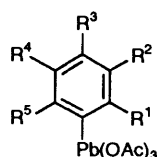
In view of the similarity between the reactivity patterns of organobismuth(V) compounds and aryllead triacetates, we decided to investigate further the reaction of aryllead triacetates with phenols. We had previously observed that 4-nitrophenol reacts with organobismuth reagents to form a stable, isolable covalent aryloxybismuth compound which is thermally decomposed only to the *O*-phenyl ether. In an attempt to observe a covalent aryloxylead intermediate, it seemed pertinent to use 3,5-di-*tert*-butylphenol **1** instead of the 4-nitrophenol derivative used by Bell *et al.*¹⁰

The reaction of the phenol **1** with 2,4,6-trimethoxyphenyllead triacetate **13** was first investigated as, in the arylation of the benzopyran-2-one **14**, the lead reagent **13** seemed to be the most reactive giving the highest yield.³ In view of the steric constraints, it was thought possible that the proposed intermediate might be stable enough to be detected although the formation of arylated products was not probable. ¹H NMR monitoring of the mixing of phenol **1** and lead reagent **13** at room temperature failed to afford any evidence of the proposed intermediate as the signals for *ortho*-H and *para*-H remained virtually unaltered. However, after a reaction time of 45 min, two new peaks were observed in the *tert*-butyl region. By analogy with the phenylation of 3,5-di-*tert*-butylphenol **1** with phenylbismuth(V) reagents,⁸ these peaks were assigned to the

Table 1 Arylation of phenol **1** with lead reagent **13**^{a,b}

13 (equiv.)	<i>T</i> /°C	DPE ^c (equiv.)	1 (%)	15 (%)	16 ^d (%)
1.1	25	0	35	21	24
1.1	25	2	40	18	23
1.1	25	10	42	22	18
1.1	40	0	28	30	18
2	40	0	11	12	52
3	40	0	12	16	44
4	25	0	24	32	15
4	40	0	14	34	24
4 ^e	25	0	Trace	10	87

^a Reactions carried out in the presence of pyridine in dry chloroform (0.3 mmol of **1** per cm³ of solvent), for 24 h at the indicated temperature. ^b Isolated yields based on **1**. ^c DPE = 1,1-diphenylethylene. ^d **16**, m.p. 216.5–218 °C, lit.,¹³ 216.5–218 °C. ^e After stirring for 24 h, the homogeneity of the reaction mixture was restored by addition of CHCl₃ and the reaction stirred for a further 24 h.

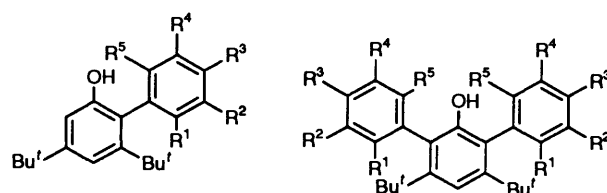


ArPb(OAc) ₃	R ¹	R ²	R ³	R ⁴	R ⁵
5	H	H	H	H	H
6	OMe	H	H	H	H
7	H	OMe	H	H	H
8	H	H	OMe	H	H
9	H	H	Me	H	H
10	OMe	H	OMe	H	H
11	OMe	H	H	OMe	H
12	H	H	OCH ₂ O	H	H
13	OMe	H	OMe	H	OMe

chemically non-equivalent *tert*-butyl groups of the monoarylated phenol. After 72 min, their intensity had increased so that the yield of monoarylated product rose from 5 to 9%. This improved to 28% after 20 h and a further *tert*-butyl resonance was observed which was assigned to the *tert*-butyl groups of the diarylated phenol. Further ¹H NMR studies at –31 °C failed to give any evidence of the proposed intermediate. In order to determine whether the proposed products had been formed, the reaction was repeated under the standard phenol arylation conditions.¹⁰ Thus, a molar concentration of phenol: aryllead triacetate: pyridine of 0.3:0.33:1 mol dm⁻³ at ambient temperature for 24 h afforded 3,5-di-*tert*-butyl-2-(2',4',6'-trimethoxyphenyl)phenol **15** and 3,5-di-*tert*-butyl-2,6-bis(2',4',6'-trimethoxyphenyl)phenol **16** in yields of 21 and 24%, respectively. It was in this fashion that the facile synthesis of such a hindered phenol as **16** was discovered and in a preliminary communication,¹³ we have described the preparation of **16** under optimised conditions. We will now report in more detail on further work in this area.

The possibility of a free-radical mediated mechanism in the arylation of phenol **1** with lead reagent **13** was investigated in the presence of 1,1-diphenylethylene. Again, the yields of arylated products were not affected by the presence of either a slight or a large excess of the radical trap (Table 1).

As phenyllead triacetate **5** appeared to be the least reactive reagent towards the benzopyran-2-one **14**, its reaction with **1** was monitored by ¹H NMR. But no evidence of the postulated intermediate could be obtained either at room temperature or at –31 °C. The intensities of the products peaks were observed to increase with time. After 18 h at room temperature *tert*-butyl resonances similar⁸ to those of 3,5-di-*tert*-butyl-2-phenylphenol



Biphenyl	Terphenyl	R ¹	R ²	R ³	R ⁴	R ⁵
3	17	H	H	H	H	H
18	19	OMe	H	H	H	H
20	21	H	OMe	H	H	H
22	23	H	H	OMe	H	H
24	25	H	H	Me	H	H
26	27	OMe	H	OMe	H	H
28	29	OMe	H	H	OMe	H
30	31	H		OCH ₂ O	H	H
15	16	OMe	H	OMe	H	OMe

3 and 3,5-di-*tert*-butyl-2,6-diphenylphenol **17** were observed. The reaction was carried out under standard conditions and the products **3** and **17** were isolated in yields of 25 and 16%, respectively. Increasing the number of phenyl groups borne by the lead phenylating agent led to a decrease in yields of products, in agreement with similar results using the benzopyran-2-one **14** as substrate.³ Only phenyllead triacetate and diphenyllead diacetate were found to phenylate. ¹H NMR monitoring of the mixing of phenol **1** with the latter reagent did not supply any evidence of a covalent aryloxylead intermediate.

The concentration of the reaction solutions employed in the arylation of phenols was more dilute than those used in the arylation of 4-hydroxy-5-methoxy-2*H*-1-benzopyran-2-ones. In addition, the former reactions were carried out at room temperature whilst it was shown for the latter reactions that higher temperatures afforded higher yields of arylated products. These observations were considered in an attempt to optimise the yield of 3,5-di-*tert*-butyl-2,6-bis(2',4',6'-trimethoxyphenyl)phenol **16** formed by the arylation of 3,5-di-*tert*-butylphenol **1** with **13**. Better yields of diarylated phenol **16** were obtained by using twice the number of equivalents of aryllead reagent **13** previously used and increasing the reaction temperature to 40 °C. However, further increases in the number of equivalents of aryllead triacetate **13** did not lead to higher yields of diarylated phenol **16**. Indeed the yields using 4 equiv. of reagent **13** were comparable to those obtained using 2 equiv. During reactions using 3 or 4 equiv. of lead reagent **13**, it was noticed that the reaction mixtures were not homogeneous. This had to be expected as 0.75 g of **13** was used in 1 cm³ of chloroform. When the reaction was repeated using 4 equiv. of lead reagent **13** at room temperature and the homogeneity of the reaction restored by the addition of a further cm³ of chloroform after 24 h and the resultant solution stirred for another 24 h, an 87% yield of diarylated phenol **16** was obtained. These conditions were considered the optimal phenol arylation conditions and they ought to be general for a range of aryllead triacetates. They were employed in the arylation of phenol **1** with a series of aryllead triacetates (Table 2). Diarylated phenols were obtained in good to excellent yields (63–89%). Monoarylated phenols were also isolated in poor yields. As the arylation of phenol **1** by **13** represented the limits of ligand coupling, it was not surprising that arylation with the less substituted aryllead triacetates proceeded smoothly. Complete regioselectivity in the *ipso*-substitution of the aryllead triacetate was observed.

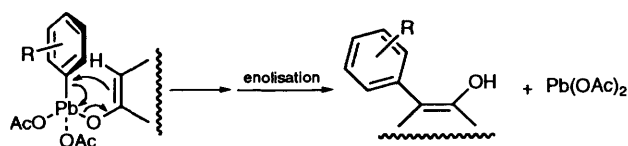
In spite of the high steric hindrance, the methyl groups of the 3- and 5-*tert*-butyl substituents always gave rise, in the ¹³C NMR spectra, to two signals in the 2-monosubstituted series and a single signal in the 2,6-disubstituted series. The high symmetry of the 2,6-diarylphenol, which had been observed in

Table 2 Arylation of phenol **1** by various aryllead triacetates^{a,b}

ArPb(OAc) ₃	1 (%)	Substituted biphenyl (%)	Substituted terphenyl (%)
5	14	3 ^c (15)	17 ^c (64)
6	7	18 (18)	19 (71)
7	11	20 (16)	21 (65)
8	13	22 (14)	23 (67)
9	8	24 (9)	25 (73)
10	Trace	26 (4)	27 (89)
11	12	28 (13)	29 (67)
12	14	30 (11)	31 (63)

^a Reactions carried out in dry chloroform (0.15 mmol of **1** per cm³ of solvent) at 25 °C for 24 h. Molar ratio of 1/aryllead triacetate/pyridine = 1/4/10. After 24 h, chloroform (1 cm³ per 0.15 mmol of **1**) was added and the reaction stirred for a further 24 h. ^b Isolated yields based on **1**. ^c **3**, m.p. 99–100 °C, lit.,⁸ 99–101 °C; **17**, m.p. 211–213 °C, lit.,⁸ 212–213 °C.

the X-ray crystallographic structure of **16** and in the ¹H NMR and ¹³C NMR spectra of **16** in solution, was also present for all the new 2,6-diarylphenols, as the ¹³C NMR spectra of their solutions always showed the minimum number of signals. In spite of our failure to detect any intermediate in a combination of reagents leading to *ortho* C-arylation, we believe that an intermediate such as **4** breaks down by ligand coupling, like the aryloxybismuth analogue **2**. This involves the overlap of the π-system of the aryl and phenolate ligands (Scheme 3). It requires

**Scheme 3**

aryl cation behaviour for the aryl group in aryllead triacetates and this should reflect in the ¹³C NMR of the aryllead compounds.

In view of the relatively limited number of ¹³C NMR studies on organolead triacetates, we have investigated the ¹³C NMR spectra of the aryllead reagents used in our arylation reactions. In parallel to our work, a number of related ¹³C NMR data were recently reported by Huber *et al.* as part of their X-ray crystallographic structural studies on aryllead triacetates.¹⁴

As in the ¹H NMR spectra of organolead compounds, the ¹³C NMR spectra show satellites associated with the aryllead species containing the ²⁰⁷Pb nuclide, which are symmetrically grouped around the main peaks from the aryllead species containing non-magnetic lead isotopes. ²⁰⁷Pb, ¹³C coupling constants are much larger than ¹H, ¹H coupling constants. In previous ¹³C NMR investigations of organolead compounds, considerable emphasis was placed on the determination and explanation of the size of these ²⁰⁷Pb, ¹³C coupling constants. In the series Ar_nPbMe_{4-n} (*n* = 0–4), it was found that the value of *J*(²⁰⁷Pb, ¹³C) depended on the number and nature of the aryl group where replacement of methyl by aryl groups increased *J*(²⁰⁷Pb, ¹³C).¹⁵ Similarly, the number and nature of the alkyl group R in the series Ph_nPbR_{4-n} (*n* = 0–4) affected the value of *J*(²⁰⁷Pb, ¹³C).¹⁶ ¹³C Chemical shifts and ²⁰⁷Pb, ¹³C coupling constants were also determined for the compounds Ph_nPb(OAc)_{4-n} (*n* = 1–4).¹⁷ The ¹³C chemical shifts are in good agreement with those obtained in the present study (Table 3).

The downfield resonances of the C-1 signals are noteworthy as they are indicative of electron-deficient carbon atoms, e.g. the ¹³C chemical shift for C-1 of fluorobenzene is δ 163.6.¹⁸

Table 3 ¹³C Chemical shifts^a of compounds (C₆H₅)_nPb(OAc)_{4-n} (*n* = 1–4)

<i>n</i>	C-1	C-2,6	C-3,5	C-4	C(C=O)	C(CH ₃)
4	150.51	137.97	129.86	128.92	—	—
3	158.08	136.82	130.21	129.47	178.04	21.31
2	163.27	134.20	131.09	131.72	181.67	21.80
1	161.25	131.32	131.20	132.08	180.51	20.65

^a Spectra were determined in CDCl₃ at 50 MHz on a Varian Gemini 200E spectrometer with tetramethylsilane as internal reference.

Replacement of three of the phenyl groups of tetraphenyllead by acetate ligands causes a downfield shift for C-1 of ~10 ppm. In each of the above three series of organolead compounds, (Ar)_nPb(Me)_{4-n} (*n* = 0–4), (C₆H₅)_nPb(R)_{4-n} (R = alkyl) (*n* = 0–4), and (C₆H₅)_nPb(OAc)_{4-n} (*n* = 1–4), the change in the magnitude of the ²⁰⁷Pb, ¹³C coupling constants was ascribed to changes in hybridisation of the lead–carbon bonds and effective nuclear charge on the lead atom.¹⁷ For the latter, an increase in *J*(²⁰⁷Pb, ¹³C) corresponds to an increase in the positive charge on the lead atom. This trend is in keeping with the decreasing ¹³C chemical shift of C-1 on replacement of phenyl groups by acetate ligands as outlined above.

Next to the effect of substitution at the lead atom, the influence of the substitution in the aromatic nucleus on the ¹³C NMR chemical shifts and coupling constants was investigated for compounds of general formula Ar₄Pb.¹⁹ It was found that the ¹³C chemical shifts varied in the expected way with the nature of the substituent on the aryl ring and the position of the substituent greatly influenced the size of *J*(²⁰⁷Pb, ¹³C (ring)). In the present study, ¹³C NMR spectra were determined for variously substituted aryllead triacetates (Table 4). As for the ¹H NMR spectra obtained for these compounds, coupling constants involving the ²⁰⁷Pb nuclide were not investigated due to their magnitude. Thus, the ¹³C NMR spectra obtained can be considered to be first-order as satellite signals were not investigated.

¹³C Chemical shifts are predominantly determined by mesomeric and inductive effects with electron donating substituents inducing a shielding relative to benzene (δ_{C(o,p)} < 128.5), whereas electron withdrawing substituents induce a deshielding relative to benzene (δ_{C(o,p)} > 128.5). Examination of the C-1 chemical shift data is particularly useful for the information it gives on the role the lead atom plays in the lead–aryl bond. The C-1 chemical shift of 2,4,6-trimethoxyphenyllead triacetate **13** is worthy of particular mention as even with good electron donating substituents *ortho* and *para* to this position, a resonance of δ 131.38 is observed. In comparison to the strongly shielded resonance (δ 92.42) of C-3 and C-5, this gives some indication as to the strength of this electron withdrawing power (δ 131.38 compared to 92.42). In 2,4-dimethoxyphenyllead triacetate **10**, a C-1 resonance of δ 142.25 is observed which again is further downfield than that expected for an aryl ring containing electron donating substituents *ortho* and *para* to this position. The reported ²⁰⁷Pb, ¹³C-1 coupling constant for this aryllead triacetate is 2199 Hz,¹⁷ and that magnitude indicates an electropositive lead atom thus making it a powerful withdrawer of π electrons from the aryl ring, resulting in the observed downfield C-1 resonance.

The reported C-1 resonance in (4-MeOC₆H₄)₄Pb is δ 140.4¹⁹ whereas in (4-MeOC₆H₄)Pb(OAc)₃ **8** a more downfield resonance of δ 153.84 is observed. This is in keeping with the observation that replacement of a phenyl group by an acetate group in the series (C₆H₅)_nPb(OAc)_{4-n} (*n* = 1–4) leads to an increase in the C-1 resonance, e.g. δ 150.51 in tetraphenyllead compared to δ 161.25 in phenyllead triacetate **5**. The establishment of the electron-withdrawing power of the lead

Table 4 ^{13}C NMR chemical shifts of variously substituted aryllead triacetates^a

Ar in ArPb(OAc) ₃	C-1	C-2	C-3	C-4	C-5	C-6	C(C=O)	C(CH ₃)	Others
2-MeOC ₆ H ₄	150.95	158.24	113.10	132.16	123.96	133.64	180.55	20.46	56.75
3-MeOC ₆ H ₄	162.23	118.61	161.79	116.38	131.65	123.30	181.05	20.67	55.95
4-MeOC ₆ H ₄	153.84	132.81	116.62	162.70	116.62	132.81	181.01	20.67	55.81
4-MeC ₆ H ₄	159.60	132.22	131.34	143.23	131.34	132.22	180.79	20.74	21.37
2,4-(MeO) ₂ C ₆ H ₃	142.25	163.93	99.88	159.16	107.31	132.49	179.86	20.32	55.85(4) 56.43(2)
3,4-(MeO) ₂ C ₆ H ₃	154.26	112.00	150.19	150.71	115.93	126.76	181.02	21.92	55.82(4) 56.14(3)
2,5-(MeO) ₂ C ₆ H ₃	151.05	156.25	116.23	113.63	152.37	119.86	186.59	20.56	57.43(5) 56.41(2)
3,4-(OCH ₂ O)C ₆ H ₃	153.49	109.82	150.69	149.25	111.24	125.18	180.26	20.78	102.09
2,4,6-(MeO) ₃ C ₆ H ₂	131.38	161.27	92.42	165.39	92.42	161.27	180.01	26.30	56.65(2, 6) 55.96(4)

^a Spectra were determined in CDCl₃ at 50 MHz on a Varian Gemini 200E spectrometer with tetramethylsilane as internal reference.

atom facilitated the assignment of the remaining resonances which varied in the expected way with the nature of the substituents.

In conclusion, the reaction of 3,5-di-*tert*-butylphenol **1** with aryllead(IV) derivatives affords mono- and di-arylated phenols in high yield under mild reaction conditions. Reaction homogeneity was shown to be very important. The mechanism of this arylation is believed to proceed by ligand coupling and was conclusively shown not to involve free-radicals.

Experimental

M.p.s were determined on a Kofler hot stage apparatus and are uncorrected. 200 MHz ^1H NMR and 50 MHz ^{13}C NMR were determined on a Varian Gemini-200 spectrometer. Tetramethylsilane was used as the internal standard in all NMR spectra recorded. All *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer and UV spectra were recorded on a Beckman DU-7 spectrophotometer. Mass spectra were determined on a VG Analytical 705 high resolution double focusing magnetic sector mass spectrometer with attached VG 11/2505 data system in the EI mode. Merck Kieselgel PF₂₅₄₊₃₃₆ was used for preparative layer chromatography (PTLC). Aryllead triacetates were prepared as previously reported.²⁰ Ether refers to diethyl ether.

General Procedure for the Arylation of 3,5-Di-*tert*-butylphenol.—*Method A.* Pyridine (3.3 mol equiv.) was added to a well-stirred solution of 3,5-di-*tert*-butylphenol (1 mol equiv.) and aryllead triacetate (1.1 mol equiv.) in dry chloroform (1 cm³ per 0.3 mmol of phenol) and was stirred at room temperature for 24 h. The reaction mixture was successively diluted with chloroform (60 cm³), washed with 3 mol dm⁻³ aq. H₂SO₄ (2 × 50 cm³), dried (MgSO₄), concentrated, and then the residue was purified by PTLC.

Method B. Pyridine (10 mol equiv.) was added to a well-stirred solution of 3,5-di-*tert*-butylphenol (1 mol equiv.) and aryllead triacetate (4 mol equiv.) in dry chloroform (1 cm³ per 0.15 mmol of phenol) and was stirred at room temperature for 24 h. After this time, chloroform (1 cm³ per 0.15 mmol of phenol) was added and the solution stirred for a further 24 h. The work-up was the same as in method A.

Phenylation of 3,5-Di-*tert*-butylphenol with Diphenyllead Diacetate.—Using method A, pyridine (0.19 cm³), 3,5-di-*tert*-butylphenol (0.114 g) and diphenyllead diacetate (0.295 g) after work-up and PTLC [developer: hexane–ether (5:2)] gave 3,5-di-*tert*-butylphenol (0.062 g, 50%), 3,5-di-*tert*-butyl-2-phenylphenol (0.042 g, 25%) and 3,5-di-*tert*-butyl-2,6-diphenylphenol (0.023 g, 20%).

Products of the Arylation of 3,5-Di-*tert*-butylphenol with Aryllead Triacetates 5–12.—3,5-Di-*tert*-butyl-2-(2',4',6'-trimethoxyphenyl)phenol **15**. [PTLC developer: hexane–ether (3:2)], m.p. 146.5–148 °C (from MeOH), $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3025, 2935, 1579, 1209, 736 and 660; $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 214.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 33 525) and 276 (4113); δ_{H} 7.11 (1 H, d, *J* 1.82, 4-H), 6.87 (1 H, d, *J* 1.83, 6-H), 6.22 (2 H, s, 3'- and 5'-H), 4.58 (1 H, s, OH), 3.88 (3 H, s, 4'-OMe), 3.69 (6 H, s, 2'- and 6'-OMe), 1.33 (9 H, s, 5-Bu') and 1.12 (9 H, s, 3-Bu'); δ_{C} 162.60 (C-4'), 160.18 (C-2' and -6'), 153.46 (C-1), 151.18 (C-3), 149.82 (C-5), 116.49 (C-4), 116.16 (C-6), 109.44 (C-2), 106.02 (C-1'), 91.16 (C-3' and -5'), 55.63 (2'- and 6'-MeO), 55.50 (4'-MeO), 36.61 [5-(CMe₃)], 34.87 [3-(CMe₃)] and 31.49 (CMe₃); *m/z* 372 (M⁺, 100%), 357 (29), 342 (2), 326 (8), 301 (10), 270 (10), 269 (11), 241 (7), 168 (6), 69 (7), 57 (44) and 41 (17) (Found: C, 74.45; H, 8.45%; M⁺, 372.2289. C₂₃H₃₂O₄ requires C, 74.15; H, 8.65%; M, 372.2300).

3,5-Di-*tert*-butyl-2-(2'-methoxyphenyl)phenol **18**. [PTLC developer: dichloromethane–hexane (4:1)], m.p. 120–121.5 °C (from MeOH), $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3534, 2947, 2345, 1273, 1126, 756 and 609; $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 207.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 29 136) and 276 (5702); δ_{H} 7.43–7.19 (2 H, m, 4'- and 6'-H), 7.15 (1 H, d, *J* 1.87, 6-H), 7.08–6.95 (2 H, m, 3'- and 5'-H), 6.89 (1 H, d, *J* 1.83, 4-H), 4.40 (1 H, s, OH), 3.75 (3 H, s, 2'-OMe), 1.34 (9 H, s, 5-Bu') and 1.14 (9 H, s, 3-Bu'); δ_{C} 158.08 (C-2'), 152.91 (C-1), 151.14 (C-5), 148.67 (C-3), 133.66 (C-4'), 130.07 (C-6'), 125.65 (C-1'), 120.79 (C-5'), 120.54 (C-2), 116.13 (C-4), 111.30 (C-3'), 109.66 (C-6), 55.32 (2'-MeO), 36.74 [5-(CMe₃)], 34.81 [3-(CMe₃)], 31.94 [5-(CMe₃)] and 31.37 [3-(CMe₃)]; *m/z* 313 (M⁺ + 1, 25%), 312 (100), 297 (62), 241 (61), 226 (21), 131 (11), 105 (12), 57 (87) and 40 (90) (Found: C, 80.8; H, 8.7%; M⁺, 312.2115. C₂₁H₂₈O₂ requires C, 80.7; H, 9%; M, 312.2084).

3,5-Di-*tert*-butyl-2,6-bis(2'-methoxyphenyl)phenol **19**. [PTLC developer: dichloromethane–hexane (4:1)], m.p. 188–189 °C (from hexane), $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3526, 2947, 1466, 1119, 756 and 609; $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 208.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 36 073) and 276 (10 274); δ_{H} 7.26 (1 H, s, 4-H), 7.34–7.18 (4 H, m, 2 × 4'- and 6'-H), 7.02–6.90 (4 H, m, 2 × 3'- and 5'-H), 4.35 (1 H, s, OH), 3.74 (6 H, s, 2 × 2'-OMe) and 1.20 (18 H, s, 3- and 5-Bu'); δ_{C} 158.03 (C-2'), 151.34 (C-1), 147.49 (C-3 and -5), 133.03 (C-6'), 129.17 (C-4'), 127.67 (C-2 and -6), 121.27 (C-1'), 120.37 (C-5'), 117.16 (C-4), 111.44 (C-3'), 55.47 (2'-MeO), 36.81 (CMe₃) and 31.91 (CMe₃); *m/z* 419 (M⁺ + 1, 31%), 418 (100), 348 (20), 347 (82), 332 (10), 317 (8), 57 (40) and 41 (12) (Found: C, 80.0; H, 8.0%; M⁺, 418.2472. C₂₈H₃₄O₃ requires C, 80.35; H, 8.2%; M, 418.2499).

3,5-Di-*tert*-butyl-2-(3'-methoxyphenyl)phenol **20**. [PTLC developer: dichloromethane–hexane (1:1)], m.p. 116–117 °C (from hexane); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3526, 3024, 1427, 1219, 787, 733 and 671; $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$ 215.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 21 923) and 281.5 (5905); δ_{H} 7.39 (1 H, t, *J* 7.97, 5'-H), 7.16 (1 H, d, *J* 1.87,

4-H), 6.91 (1 H, d, J 1.81, 6-H), 7.02–6.85 (3 H, m, 2', 4'- and 6'-H), 4.47 (1 H, s, OH), 3.81 (3 H, s, 3'-OMe), 1.34 (9 H, s, 5-Bu') and 1.18 (9 H, s, 3-Bu'); δ_C 159.87 (C-3'), 153.09 (C-1), 151.47 (C-5), 148.16 (C-3), 138.59 (C-5), 129.93 (C-1'), 124.36 (C-6'), 124.27 (C-2'), 117.37 (C-4), 115.86 (C-4'), 113.99 (C-2), 109.86 (C-6), 55.28 (3'-MeO), 36.98 [5-(CMe₃)], 34.85 [3-(CMe₃)], 32.61 [5-(CMe₃)] and 31.35 [3-(CMe₃)]; m/z 313 ($M^+ + 1$, 20%), 312 (86), 297 (100), 241 (24), 217 (14), 57 (84) and 41 (18) (Found: C, 80.5%; H, 9.2%; M^+ , 312.2071. C₂₁H₂₈O₂ requires C, 80.7%; H, 9.05%; M , 312.2084).

3,5-Di-tert-butyl-2,6-bis(3'-methoxyphenyl)phenol 21. [PTLC developer: dichloromethane–hexane (1 : 1)], m.p. 204.5–206 °C (from MeOH), ν_{\max} (CHCl₃)/cm⁻¹ 3595, 3518, 2947, 1458, 1280, 1126, 756 and 609; λ_{\max} (MeOH)/nm 217.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 38 911) and 276 (11 269); δ_H 7.36–7.29 (2 H, m, 2 × 5'-H), 7.27 (1 H, s, 4-H), 6.95–6.85 (6 H, m, 2 × 2', 4'- and 6'-H), 4.46 (1 H, s, OH), 3.79 (6 H, s, 2 × 3'-OMe) and 1.23 (18 H, s, 3- and 5-Bu'); δ_C 159.83 (C-3'), 151.69 (C-1), 147.67 (C-3 and -5), 140.31 (C-5'), 129.59 (C-2 and -6), 125.66 (C-1'), 124.51 (C-6'), 124.46 (C-4'), 117.59 (C-4), 113.61 (C-2'), 55.66 (3'-MeO), 37.57 (CMe₃) and 33.07 (CMe₃); m/z 419 ($M^+ + 1$, 30%), 418 (100), 404 (15), 403 (52), 347 (27), 57 (52) and 41 (12) (Found: C, 79.75%; H, 8.0%; M^+ , 418.2492. C₂₈H₃₄O₃ requires C, 80.35%; H, 8.2%; M , 418.2499).

3,5-Di-tert-butyl-2-(4'-methoxyphenyl)phenol 22. [PTLC developer: dichloromethane–hexane (4 : 1)], m.p. 151–153 °C (from hexane), ν_{\max} (CHCl₃)/cm⁻¹ 3685, 3021, 2400, 1223, 1208, 788, 732 and 669; λ_{\max} (MeOH)/nm 225.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 19 066) and 277 (5118); δ_H 7.23 (2 H, d, J 8.05, 2'- and 6'-H), 7.14 (1 H, d, J 1.84, 4-H), 7 (2 H, d, J 8.79, 3'- and 5'-H), 6.9 (1 H, d, J 2, 6-H), 4.46 (1 H, s, OH), 3.87 (3 H, s, 4'-OMe), 1.34 (9 H, s, 5-Bu') and 1.16 (9 H, s, 3-Bu'); δ_C 159.46 (C-4'), 153.64 (C-1), 151.36 (C-5), 148.67 (C-3), 133.18 (C-2' and -6'), 128.62 (C-2), 124.01 (C-1'), 115.61 (C-4), 114.23 (C-3' and -5'), 109.54 (C-6), 54.99 (4'-MeO), 36.54 [5-(CMe₃)], 34.52 [3-(CMe₃)], 32.17 [5-(CMe₃)] and 31 [3-(CMe₃)]; m/z 313 ($M^+ + 1$, 23%), 312 (99), 298 (13), 297 (59), 241 (50), 226 (18), 127 (8), 57 (100) and 41 (15) (Found: C, 80.8%; H, 9.0%; M^+ , 312.2086. C₂₁H₂₈O₂ requires C, 80.7%; H, 9.05%; M , 312.2082).

3,5-Di-tert-butyl-2,6-bis(4'-methoxyphenyl)phenol 23. [PTLC developer: dichloromethane–hexane (4 : 1)], m.p. 199.5–201 °C (from hexane), ν_{\max} (CHCl₃)/cm⁻¹ 3524, 2961, 2363, 1726, 1132, 777 and 615; λ_{\max} (MeOH)/nm 227.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 30 207) and 277.5 (6341); δ_H 7.30 (1 H, s, 4-H), 7.22 (4 H, d, J 8.75, 2 × 2'- and 6'-H), 6.94 (4 H, d, J 8.8, 2 × 3'- and 5'-H), 4.44 (1 H, s, OH), 3.83 (6 H, s, 2 × 4'-OMe) and 1.21 (18 H, s, 2 × Bu'); δ_C 159.44 (C-4'), 153.34 (C-1), 148.14 (C-3 and -5), 133.19 (C-2' and -6'), 130.88 (C-2 and -6), 125.39 (C-1'), 117.12 (C-4), 114.09 (C-3' and -5'), 55.50 (4'-MeO), 37.26 (CMe₃) and 32.77 (CMe₃); m/z 419 ($M^+ + 1$, 10%), 418 (32), 347 (16), 332 (6), 312 (97), 297 (57), 241 (49), 226 (16), 57 (100) and 41 (14) (Found: C, 79.9%; H, 8.05%; M^+ , 418.2487. C₂₈H₃₄O₃ requires C, 80.35%; H, 8.2%; M , 418.2499).

3,5-Di-tert-butyl-2-(4'-methylphenyl)phenol 24. [PTLC developer: dichloromethane–hexane (2 : 1)], m.p. 112.5–114 °C (from hexane), ν_{\max} (CHCl₃)/cm⁻¹ 3022, 1213, 772 and 671; λ_{\max} (MeOH)/nm 220.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 16 762) and 281 (4182); δ_H 7.26 (2 H, d, J 7.87, 2'- and 6'-H), 7.19 (2 H, d, J 7.84, 3'- and 5'-H), 7.14 (1 H, d, J 1.94, 4-H), 6.89 (1 H, d, J 1.94, 6-H), 4.42 (1 H, s, OH), 2.42 (3 H, s, 4'-Me), 1.34 (9 H, s, 5-Bu') and 1.16 (9 H, s, 3-Bu'); δ_C 153.33 (C-1), 151.27 (C-5), 148.36 (C-3), 137.88 (C-4'), 133.88 (C-2), 131.92 (C-2' and -6'), 129.61 (C-3' and -5'), 124.46 (C-1'), 115.69 (C-4), 109.70 (C-6), 36.89 [5-(CMe₃)], 34.84 [3-(CMe₃)], 32.51 [5-(CMe₃)], 31.35 [3-(CMe₃)] and 21.28 (4'-Me); m/z 297 ($M^+ + 1$, 23%), 296 (100), 282 (16), 281 (71), 225 (43), 119 (8) and 57 (76) (Found: C, 84.8%; H, 9.25%; M^+ , 296.2165. C₂₁H₂₈O requires C, 85.1%; H, 9.5%; M , 296.2133).

3,5-Di-tert-butyl-2,6-bis(4'-methylphenyl)phenol 25. [PTLC developer: dichloromethane–hexane (2 : 1)], m.p. 207.5–209 °C, ν_{\max} (CHCl₃)/cm⁻¹ 3020, 1212, 740 and 669; λ_{\max} (MeOH)/nm 207.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 43 224) and 256.5 (16 042); δ_H 7.30 (1 H, s, 4-H), 7.19 (8 H, s, 2 × 2', 3', 5'- and 6'-H), 4.38 (1 H, s, OH), 2.37 (6 H, s, 2 × 4'-Me) and 1.21 (18 H, s, 3- and 5-Bu'); δ_C 152.21 (C-1), 147.70 (C-3 and -5), 137.43 (C-4'), 135.87 (C-2 and -6), 131.94 (C-2' and -6'), 129.35 (C-3' and -5'), 125.74 (C-1'), 117.09 (C-4), 37.50 (CMe₃), 32.59 (CMe₃) and 21.73 (4'-Me); m/z 387 ($M^+ + 1$, 31%), 386 (100), 316 (14), 315 (55) and 57 (32) (Found: C, 86.8%; H, 9%; M^+ , 386.2628. C₂₈H₃₄O requires C, 87%; H, 8.85%; M , 386.2601).

3,5-Di-tert-butyl-2-(2',4'-dimethoxyphenyl)phenol 26. [PTLC developer: dichloromethane–hexane (4 : 1)], m.p. 205.5–207 °C, ν_{\max} (CHCl₃)/cm⁻¹ 3688, 3024, 2400, 1520, 1219, 787 and 671; λ_{\max} (MeOH)/nm 212.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 29 780) and 280.5 (8476); δ_H 7.13 (1 H, d, J 1.95, 4-H), 7.11 (1 H, d, J 8.65, 6'-H), 6.88 (1 H, d, J 1.95, 6-H), 6.61 (2 H, m, 3'- and 5'-H), 4.50 (1 H, s, OH), 3.87 (3 H, s, 4'-OMe), 3.72 (3 H, s, 2'-OMe), 1.34 (9 H, s, 5-Bu') and 1.14 (9 H, s, 3-Bu'); δ_C 161.87 (C-4'), 159.58 (C-2'), 153.81 (C-1), 151.52 (C-5), 149.55 (C-3), 134.41 (C-6'), 120.53 (C-1'), 117.81 (C-2), 116.30 (C-4), 109.77 (C-6), 104.90 (C-5'), 99.43 (C-3'), 55.54 (2'-MeO), 55.49 (4'-MeO), 36.79 [5-(CMe₃)], 34.90 [3-(CMe₃)], 31.99 [5-(CMe₃)] and 31.47 [3-(CMe₃)]; m/z 343 ($M^+ + 1$, 23%), 342 (100), 327 (32), 295 (14), 271 (20), 256 (18), 239 (7), 57 (38) and 41 (10) (Found: C, 76.95%; H, 8.85%; M^+ , 342.2193. C₂₂H₃₀O₃ requires C, 77.15%; H, 8.85%; M , 342.2194).

3,5-Di-tert-butyl-2,6-bis(2',4'-dimethoxyphenyl)phenol 27. [PTLC developer: dichloromethane–hexane (4 : 1)], m.p. 169.5–171.5 °C (from hexane), ν_{\max} (CHCl₃)/cm⁻¹ 3688, 3024, 2400, 1520, 1219, 785, 733 and 671; λ_{\max} (MeOH)/nm 210.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 41 400) and 281 (9420); δ_H 7.26 (1 H, s, 4-H), 7.08 (2 H, d, J 8.51, 2 × 6'-H), 6.55 (4 H, m, 2 × 3'- and 5'-H), 4.48 (1 H, s, OH), 3.82 (6 H, s, 2 × 4'-OMe), 3.70 (6 H, s, 2 × 2'-OMe) and 1.19 (18 H, s, 3- and 5-Bu'); δ_C 161.14 (C-6'), 159.43 (C-4'), 152.45 (C-1), 148.29 (C-3 and -5), 133.59 (C-6'), 121.15 (C-4), 120.18 (C-2 and -6), 117.28 (C-1'), 104.42 (C-5'), 99.48 (C-3'), 55.58 (2'-MeO), 55.46 (4'-MeO), 36.87 (CMe₃) and 31.97 (CMe₃); m/z 479 ($M^+ + 1$, 33%), 478 (100), 407 (27), 375 (6), 91 (6), 81 (6), 57 (44), 55 (14), 44 (25), 43 (10), 41 (20) and 40 (30) (Found: C, 75.45%; H, 8.25%; M^+ , 478.2711. C₃₀H₃₈O₅ requires C, 75.3%; H, 8%; M , 478.2719).

3,5-Di-tert-butyl-2-(2',5'-dimethoxyphenyl)phenol 28. [PTLC developer: dichloromethane–hexane (3 : 1)], m.p. 120–122 °C, ν_{\max} (CHCl₃)/cm⁻¹ 3534, 2959, 1728, 1485, 1284, 1126, 744 and 610; λ_{\max} (MeOH)/nm 208.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 36 188) and 285.5 (7439); δ_H 7.14 (1 H, d, J 1.95, 4-H), 6.95–6.92 (2 H, m, 3'- and 6'-H), 6.88 (1 H, d, J 1.89, 6-H), 6.80 (1 H, dd, J 2.56 and 0.5, 4'-H), 4.46 (1 H, s, OH), 3.76 (3 H, s, 5'-OMe), 3.71 (3 H, s, 2'-OMe), 1.34 (9 H, s, 5-Bu') and 1.16 (9 H, s, 3-Bu'); δ_C 153.48 (C-1), 152.78 (C-5'), 152.13 (C-5), 151.24 (C-2'), 148.59 (C-3), 126.37 (C-2), 120.43 (C-1'), 118.92 (C-4), 116.19 (C-3'), 114.97 (C-4'), 112.27 (C-6'), 109.72 (C-6), 55.78 (2'-MeO), 55.74 (5'-MeO), 36.77 [5-(CMe₃)], 34.81 [3-(CMe₃)], 32 [5-(CMe₃)] and 31.36 [3-(CMe₃)]; m/z 343 ($M^+ + 1$, 24%), 342 (100), 326 (28), 271 (11), 256 (13), 164 (7) and 57 (13) (Found: C, 77.1%; H, 8.75%; M^+ , 342.2195. C₂₂H₃₀O₃ requires C, 77.15%; H, 8.85%; M , 342.2187).

3,5-Di-tert-butyl-2,6-bis(2',5'-dimethoxyphenyl)phenol 29. [PTLC developer: dichloromethane–hexane (3 : 1)], m.p. 139–141 °C (from hexane), ν_{\max} (CHCl₃)/cm⁻¹ 3522, 2955, 2357, 1728, 1127, 771 and 609; λ_{\max} (MeOH)/nm 215.5 (ϵ /dm³ mol⁻¹ cm⁻¹ 36 465) and 292 (11 531); δ_H 7.32 (1 H, s, 4-H), 6.88–6.79 (6 H, m, 2 × 3', 4'- and 6'-H), 4.43 (1 H, s, OH), 3.75 (6 H, s, 2 × 5'-OMe), 3.68 (6 H, s, 2 × 2'-OMe) and 1.22 (18 H, s, 3- and 5-Bu'); δ_C 153.30 (C-1), 152.19 (C-2'), 150.87 (C-5'), 147.57 (C-3 and -5), 128.49 (C-3'), 121.13 (C-2 and -6), 118.47 (C-4), 117.32 (C-1'), 114.0 (C-4'), 112.69 (C-6'), 56.12 (2'-MeO), 55.69 (5'-

MeO), 36.85 (CMe₃) and 31.96 (CMe₃); *m/z* 478 (M⁺, 78%), 400 (7), 359 (29), 358 (100), 287 (15) and 57 (40) (Found: C, 75.3; H, 7.8%; M⁺, 478.2674. C₃₀H₃₈O₅ requires C, 75.3; H, 8%; M, 478.2709).

3,5-Di-tert-butyl-2-(3',4'-methylenedioxyphenyl)phenol 30. [PTLC developer: dichloromethane-hexane (1:1)], m.p. 121–122.5 °C, $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3530, 2959, 1728, 1477, 1127, 771 and 610; $\lambda_{\max}(\text{MeOH})/\text{nm}$ 206.5 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 31 177) and 285 (4674); δ_{H} 7.13 (1 H, d, *J* 1.93, 4-H), 6.94–6.87 (2 H, m, 6- and 2'-H), 6.75–6.79 (2 H, m, 5'- and 6'-H), 6.04 (2 H, s, OCH₂O), 4.53 (1 H, s, OH), 1.34 (9 H, s, 5-Bu^t) and 1.18 (9 H, s, 3-Bu^t); δ_{C} 153.51 (C-1), 151.52 (C-5), 148.58 (C-3'), 148.07 (C-3), 147.55 (C-4'), 130.22 (C-2), 125.32 (C-6'), 123.94 (C-1'), 115.89 (C-4), 112.46 (C-2'), 109.79 (C-6), 108.73 (C-5'), 101.32 (OCH₂O), 36.97 [5-(CMe₃)], 34.86 [3-(CMe₃)], 32.65 [5-(CMe₃)] and 31.34 [3-(CMe₃)]; *m/z* 327 (M⁺ + 1, 22%), 326 (M⁺, 100), 311 (49), 281 (30), 255 (7), 225 (11), 156 (6), 91 (2), 57 (81) and 41 (15) (Found: C, 78.8; H, 7.35%; M⁺, 326.1903. C₂₁H₂₆O₃ requires C, 78.85; H, 7.5%; M, 326.1875).

3,5-Di-tert-butyl-2,6-bis(3',4'-methylenedioxyphenyl)phenol 31. [PTLC developer: dichloromethane-hexane (1:1)], m.p. 163–165 °C, $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3532, 1729, 1128, 771 and 610; $\lambda_{\max}(\text{MeOH})/\text{nm}$ 207 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 42 318) and 285 (5312); δ_{H} 7.29 (1 H, s, 4-H), 6.90–6.71 (6 H, m, 2 × 2'-, 5'- and 6'-H), 6.01 (2 H, dd, *J* 1.47 and 0.55, OCH₂O), 5.97 (2 H, dd, *J* 1.47 and 0.55, OCH₂O), 4.53 (1 H, s, OH) and 1.23 (18 H, s, 3- and 5-Bu^t); δ_{C} 152.01 (C-1), 147.68 (C-3 and -5), 147.49 (C-3), 146.88 (C-4), 131.73 (C-2), 129.26 (C-1'), 124.79 (C-6'), 116.97 (C-4), 112.18 (C-2'), 108.15 (C-5'), 100.97 (OCH₂O), 37.11 [3- or 5-(CMe₃)] and 32.63 [3- or 5-(CMe₃)]; *m/z* 446 (M⁺, 70%), 431 (2), 401 (16), 386 (6), 191 (10), 69 (11), 57 (57) and 40 (100) (Found: C, 75.6; H, 6.65%; M⁺, 446.2094. C₂₈H₃₀O₅ requires C, 75.3; H, 6.75; M, 446.2085).

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