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Synthesis of Benzophenone Glucopyranosides from *Phaleria macrocarpa* and Related Benzophenone Glucopyranosides

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The first total syntheses of benzophenone glucopyranosides reported from *Phaleria macrocarpa* and related benzophenone glucopyranosides were successfully carried out. The alkoxy groups present *ortho* to the carbonyl group in polyalkoxybenzophenones were selectively deprotected by $AlCl_3$–$PhNMe_2$ in high yields, leaving other alkoxy groups unaffected. It was concluded in the current synthetic study that all the reported benzophenone glucopyranosides possessed the same structure as 2,4′,6-trihydroxy-4-methoxybenzophenone 2-*O*-*β*-D-glucopyranoside.

Key words: benzophenone glucopyranoside; *Phaleria macrocarpa*; selective dealkylation; $AlCl_3$–$PhNMe_2$

Phaleria macrocarpa (Scheff.) Boerl. [mahkota dewa in Indonesian], which belongs to the family Thymelaeaceae, has been used for traditional medicine in Java Island, Indonesia. The phytochemical analysis of this plant has shown the presence of benzophenone glucosides (Fig. 1), 3,4,5-trihydroxy-4′-methoxybenzophenone 3-*O*-*β*-D-glucopyranoside (phalerin, proposed as **1**),[1] 2,4′,6-trihydroxy-4-methoxybenzophenone 2-*O*-*β*-D-glucopyranoside (**2**),[2,3] 2,4′,6-trihydroxy-4-methoxybenzophenone 2-*O*-*α*-D-glucopyranoside (**3**) reported by Tambunan *et al.*,[4] 2,4,4′-trihydroxy-6-methoxybenzophenone 2-*O*-*β*-D-glucopyranoside (mahkoside A, proposed as **4**), mangiferin, kaempferol 3-*O*-*β*-D-glucopyranoside, dodecanoic acid, palmitic acid, ethyl stearate and sucrose,[5] gallic acid,[6] desacetylfevicordin A, fevicordin A, fevicordin A glucoside and fevicordin D glucoside,[7] and the lignans, pinoresinol, lariciresinol and matairesinol.[8]

Benzophenone derivatives are a series of diphenyl ketones used primarily as photoinitiators and fragrance enhancers. They are also used in the manufacturing of insecticides, agricultural chemicals, hypnotics, antihistamines and other pharmaceuticals, ultraviolet curing agents in sunglasses and inks, as an additive in plastics, coatings and adhesive formulations, and in flavor ingredients.[9] This class of compounds has recently shown notable cytotoxicity against cancer cells and antioxidative activity.[1–3] It is necessary for *in vivo* experiments to obtain these compounds in sufficient quantity. We describe here total syntheses of the benzophenone glucopyranosides (**1**, **2** and **4**) reported as constituents of *P. macrocarpa*, and of related benzophenone glucopyranosides (**5** and **6**) for further investigation into the structure-activity relationship.

Results and Discussion

We chose the following reactions to synthesize the benzophenone glucopyranosides: i) Friedel-Crafts acylation for synthesis of the benzophenone skeleton and ii) regioselective dealkylation of alkyl aryl ethers by $AlCl_3$–$PhNMe_2$. Compound **1** was synthesized as shown in Scheme 1. 3,4,4′,5-Tetramethoxybenzophenone (**8**) was prepared by the Friedel-Crafts acylation of anisole with 3,4,5-trimethoxybenzoyl chloride (**7**),[10] and subsequent demethylation with boron tribromide at 0 °C gave 3,4,5-trihydroxy-4′-methoxybenzophenone (**9**).[11,12] Protection of the hydroxyl groups at C-4 and C-5 in **9** by using such protection reagents as *p*-anisaldehyde dimethyl acetal[13] and benzylidene dichloride[14] failed to give the desired compound, but eventually the reaction was successful by using benzaldehyde dimethyl acetal in refluxed toluene to yield **10**. Glucosylation of **10** with 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl bromide under a phase transfer-catalyzed condition[15] afforded **11** as a 1:1 mixture of diastereomers. Deacetylation of **11** in a mixture of MeOH/Et_3N (3:1) gave diastereomers of deacetylated glucopyranoside (**12**). Hydrogenolysis of **12** with palladium on charcoal as a catalyst in ethanol[16] led to 3,4,5-trihydroxy-4′-methoxybenzophenone 3-*O*-*β*-D-glucopyranoside (**1**).

A comparison of the NMR data for synthesized **1** with those for phalerin[1] showed they were different. In a current report,[3] another benzophenone glucopyranoside (**2**) was isolated from the same plant, and the structure of phalerin had been revised to that of **2**. Compound **2** had first been isolated from *Gnidia involucrata* (Thymelaeaceae).[17] The $[\alpha]_D$ value (+4° in MeOH) for **2** from *P. macrocarpa*,[3] however, was an opposite sign to that of originally reported **2** from *G. involucrata* with a $[\alpha]_D$ value of −23° in MeOH.[17] We therefore prepared **2** (Scheme 2). 2,4,6-Trimethoxy-4′-benzyloxybenzophenone (**15**) was obtained from 1,3,5-trimethoxybenzene and 4-benzyloxybenzoic acid (**14**) by triflouroacetic anhydride (TFAA) condensation.[18] A combination system of $AlCl_3$–$PhNMe_2$ was used to cleave the benzyl, allyl and methyl ethers.[19] We demonstrated that selective *ortho* monodemethylation of **15** occurred

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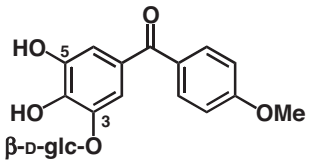
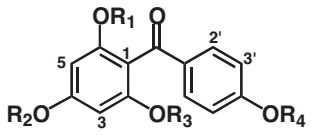
Abbreviations: DMAP, 4-*N*,*N*-dimethylaminopyridine; TFAA, trifluoroacetic anhydride; NBA, 3-nitrobenzylalcohol; TEA, triethanolamine

with the system at 0 °C to yield **16**. The resulting hydroxyl group was benzoylated, and subsequent product **17** was *ortho* monodemethylated by the same system. After debenzoylation of **18** in *N*,*N*-dimethyl-1,3-propanediamine, the product (**19**) was then subjected to glucosylation with 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl bromide in the presence of 18-crown-6 under an alkaline condition[20] to give **20**. Finally, deacetylation of **20** in MeOH/Et_3N (3:1) and subsequent hydrogenolysis yielded **2**.

The ^{13}C-NMR spectral data for phalerin (proposed as structure **1**)[1] and those for synthesized **2** were identical. The ^{1}H-NMR spectra of phalerin[1] and synthesized **2** closely resembled each other. However, the reported proton chemical shifts of phalerin[1] and those of synthesized **2** are quite different (Table 1). By moving all the proton signals of phalerin to the left around 0.17 ppm, we found that the signals of phalerin and those of synthesized **2** overlapped. We therefore consider that phalerin and synthesized **2** were same.



1 Phalerin (proposed)



2 R_1= H, R_2=Me, R_3= β-D-glc, R_4= H
3 R_1= H, R_2=Me, R_3= α-D-glc, R_4= H
4 R_1= Me, R_2=H, R_3= β-D-glc, R_4= H
Mahkoside A (proposed)
5 R_1= Me, R_2= H, R_3= H, R_4= β-D-glc
6 R_1= Me, R_2= β-D-glc, R_3= H, R_4= H

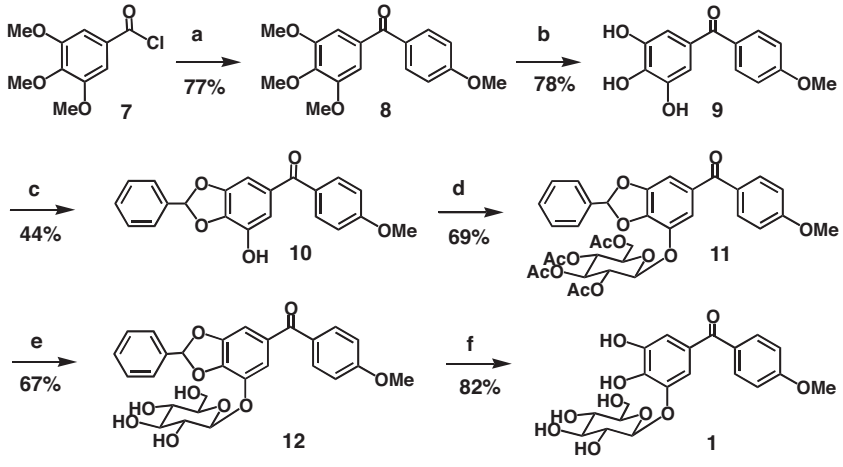
Fig. 1. Proposed Structures for Benzophenone Derivatives from *Phaleria macrocarpa* and Related Benzophenone Glucopyranosides.

The $[\alpha]_D$ value for phalerin (+0.53° in EtOH)[1] and isolated **2** (+4° in MeOH)[3] from the same plant showed an opposite sign and smaller values than those of synthesized **2** (−26° in MeOH, −15° in EtOH) and originally reported **2** (−23° in MeOH).[17] We therefore started to isolate compound **2** (phalerin) from the leaves and fruits of *P. macrocapra*. We found one constituent in the MeOH extract that had the same R_f value as synthesized **2**. This compound was obtained in a 0.98% yield from dried fruits and in 2.0% yield from dried leaves. The compound showed identical physiochemical data to those of synthesized **2**. The $[\alpha]_D$ values of the compound from the fruits and leaves were −18° in MeOH and −2.7° in EtOH, and −14° in MeOH and −2.8° in EtOH, respectively. These results indicate that phalerin was compound **2**.

We also confirmed that 2,4′,6-trihydroxy-4-methoxybenzophenone 2-*O*-*α*-D-glucopyranoside (**3**) reported from *P. macrocarpa*[4] should be revised to 2-*O*-*β*-D-glucopyranoside (**2**), because the coupling constant (J = 7.5 Hz) of the anomeric proton signal at δ 5.64 in pyridine-d_5 of **3** was characteristic of a *β*-anomer. We therefore measured synthesized **2** in pyridine-d_5 and found that compounds **3** and **2** were the same.

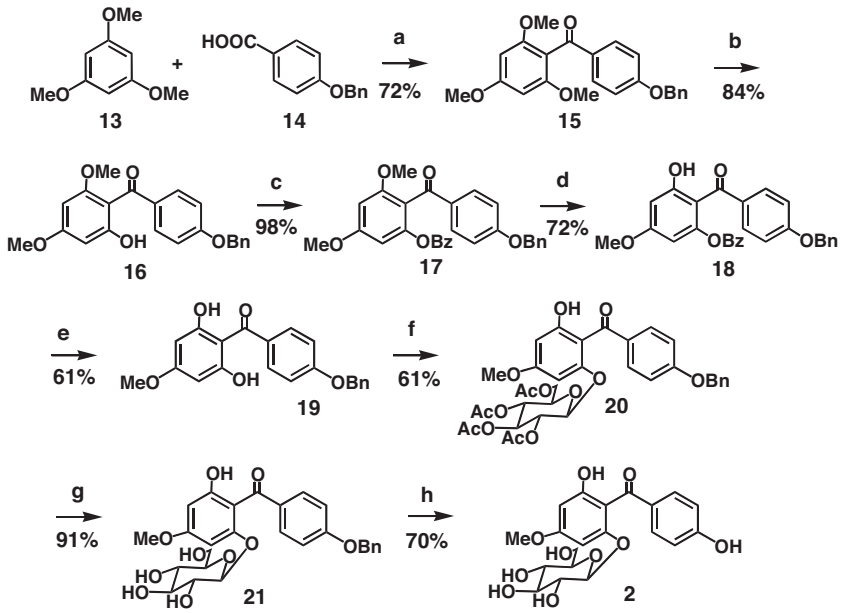
The synthetic route for mahkoside A (proposed as **4**)[5] is shown in Scheme 3. A coupling reaction of 1,3,5-tribenzyloxybenzene and **14** was established with TFAA to obtain benzophenone (**23**). Selective *ortho* monodebenzylation of **23** by $AlCl_3$–$PhNMe_2$ afforded **24** in a high yield. Methylation of **24** with dimethyl sulfate[21] gave **25** which was again selectively *ortho* monodebenzylated by $AlCl_3$–$PhNMe_2$ to yield **26** in a high yield.

The dealkylation reaction of **25** was examined by using $AlCl_3$, BBr_3 and $AlCl_3$–$PhNMe_2$ (Table 2). Deprotection of the alkyl group of **25** by using $AlCl_3$ at 0 °C and then for 3 h at room temperature, failed to give the desired benzophenone (**26**; entry 1). Dealkylation of **25** with BBr_3 (1 eq.) at low temperature gave a mixture of **26** and **24** (4.6:1) as determined by ^{1}H-NMR (entry 2). Akiyama *et al.*[19] have reported that a combination system of $AlCl_3$ (3 eq.) and $PhNMe_2$



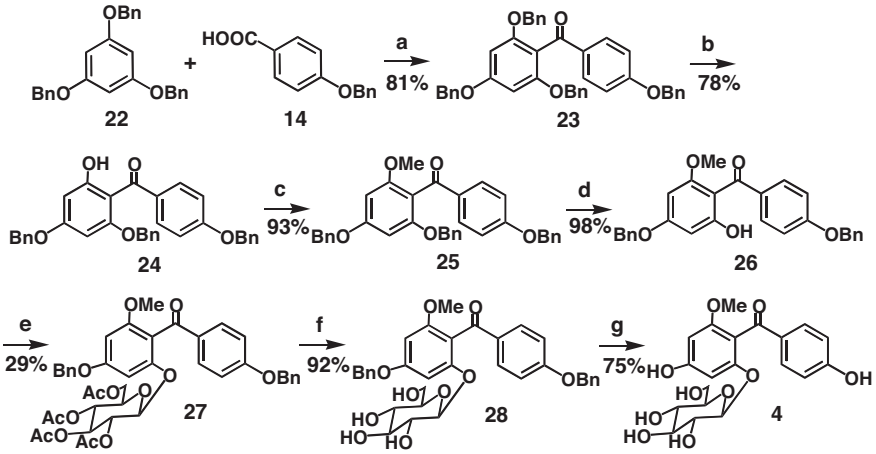
Scheme 1. Synthesis of 3,4,5-Trihydroxy-4′-methoxybenzophenone 3-*O*-*β*-D-Glucopyranoside (**1**).

Reagents and conditions: (a) anisole, $CHCl_3$, $AlCl_3$, 0 °C → r.t., 2 h; (b) BBr_3, CH_2Cl_2, 0 °C, 1 h; (c) benzaldehyde dimethyl acetal, *p*-TsOH, toluene, refl., 2 h; (d) 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl bromide, $BnBu_3NCl$, K_2CO_3, $CHCl_3$, r.t., 72 h; (e) MeOH/Et_3N (3:1), r.t., 72 h; (f) H_2, Pd–C, EtOH, r.t., 15 h.



Scheme 2. Synthesis of 2,4′,6-Trihydroxy-4-methoxybenzophenone 2-*O*-*β*-D-Glucopyranoside (**2**).

Reagents and conditions: (a) $(CF_3CO)_2O$, CH_2Cl_2, 0 °C → r.t., overnight; (b) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 20 min; (c) BzCl, Et_3N, DMAP, CH_2Cl_2, r.t., 20 min; (d) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 15 min; (e) $NH_2(CH_2)_3NMe_2$, r.t., 1 h; (f) 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl bromide, 18-crown-6, K_2CO_3, CH_3CN, r.t., 24 h; (g) MeOH/Et_3N (3:1), r.t., 15 h; (h) H_2, Pd–C, dioxane, r.t., 15 h.



Scheme 3. Synthesis of 2,4,4′-Trihydroxy-6-methoxybenzophenone 2-*O*-*β*-D-Glucopyranoside (**4**).

Reagents and conditions: (a) $(CF_3CO)_2O$, CH_2Cl_2, 0 °C → r.t., overnight; (b) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 10 min; (c) $(MeO)_2SO_2$, K_2CO_3, 18-crown-6, CH_3CN, refl., 1 h; (d) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 10 min; (e) *O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl) trichloroacetimidate, $BF_3 \cdot OEt_2$, CH_2Cl_2, 0 °C → r.t., 6 h; (f) MeOH/Et_3N (3:1), r.t., 15 h; (g) H_2, Pd–C, dioxane, r.t., 15 h.

Table 1. Comparison of ^{1}H-NMR Data for the Aglycon Moieties of Synthesized **1**, **2**, **4**-**6** and Proposed **1**, **3** and **4**

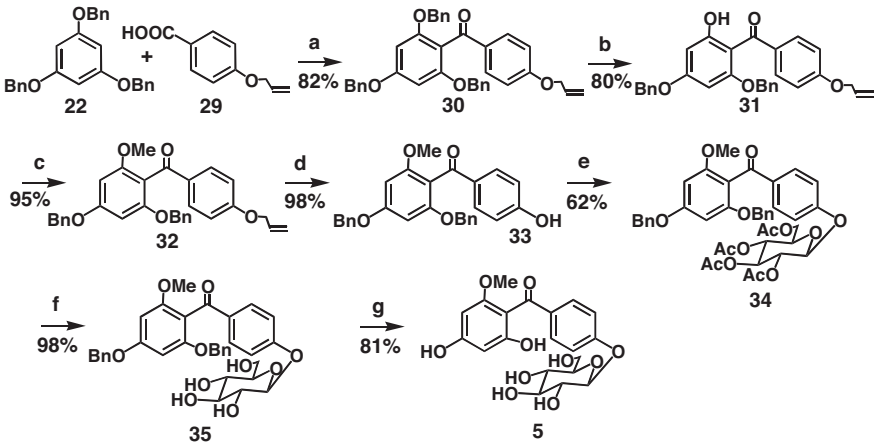
Position	Synthesized **1**	Proposed **1**[ref.1]	Synthesized **2**			Proposed **3**[ref.4]	Proposed **4**[ref.5]	Synthesized **4**		Synthesized **5**	Synthesized **6**
	CD_3OD 500 MHz	CD_3OD* 500 MHz	CD_3OD 500 MHz	DMSO-d_6 500 MHz	Pyridine-d_5 500 MHz	Pyridine-d_5 500 MHz	DMSO-d_6 400 MHz	CD_3OD 500 MHz	DMSO-d_6 270 MHz	CD_3OD 500 MHz	CD_3OD 500 MHz
H-2′ and H-6′	7.75 (8.6)	6.60 (8)	7.68 (8.7)	7.57 (8.7)	8.23 (8.6)	8.26 (8.5)	7.57 (8.6)	7.66 (8.7)	7.55 (8.0)	7.62 (8.8)	7.63 (8.8)
H-3′ and H-5′	7.03 (8.6)	7.52 (8)	6.78 (8.7)	6.78 (8.7)	7.12 (8.6)	7.13 (8.5)	6.80 (8.7)	6.78 (8.7)	6.77 (8.0)	7.10 (8.8)	6.78 (8.8)
H-6	7.03 (2)	6.19									
H-5			6.17 (1.7)	6.12 (2)	6.60	6.60	6.30 (1.9)	6.22 (1.9)	6.26	5.99	6.35 (2)
H-3			6.39 (1.7)	6.29 (2)	7.02	7.05	6.12 (1.9)	6.37 (1.9)	6.16	5.99	6.30 (2)
H-2	7.20 (2)	6.00									
OCH_3	3.88	3.55	3.79	3.72	3.73	3.76	3.73	3.62	3.55	3.54	3.63

*$CDCl_3$ was described as NMR solvent in ref. 1. CD_3OD signals, however, were detected in ^{13}C-NMR spectra.

Table 2. Results of the Cleavage of Benzophenone **25** in CH_2Cl_2 under Different Reaction Conditions

Entry	Conditions	Product ratio*		Yield of **26** (%)
		24 (%)	**26** (%)	
1	$AlCl_3$ (3 eq.), 0 °C → r.t. 3 h	—	—	0
2	BBr_3 (1 eq.), −78 °C 2 h → −60 °C 30 min	18	82	41
3	$AlCl_3$ (3 eq.)-$PhNMe_2$ (6 eq.), 0 °C 10 min	0	>99	98
4	$AlCl_3$ (3 eq.)-$PhNMe_2$ (6 eq.), 0 °C 10 min → r.t. 2 h	0	>99	96

*determined by ^{1}H NMR



Scheme 4. Synthesis of 2,4,4′-Trihydroxy-6-methoxybenzophenone 4′-*O*-*β*-D-Glucopyranoside (**5**).

Reagents and conditions: (a) $(CF_3CO)_2O$, CH_2Cl_2, 0 °C → r.t., 48 h; (b) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 5 min; (c) $(MeO)_2SO_2$, K_2CO_3, 18-crown-6, acetone, refl., 2 h; (d) $Pd(PPh_3)_4$, K_2CO_3, dioxane, MeOH, r.t., 20 h; (e) 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl bromide, $BnBu_3NCl$, K_2CO_3, CH_2Cl_2, r.t., 24 h; (f) MeOH/Et_3N (3:1), r.t., 30 h; (g) H_2, Pd–C, dioxane, r.t., 15 h.

(4 eq.) was available to cleave general aliphatic and aromatic benzyl ethers mostly in less than 1 h at room temperature. The cleavage reaction, however, didn't proceed at 0 °C, except for the *p*-methoxybenzyl ethers.[19] Chemo- and regioselective monodebenzylation of **25** occurred by using the combination system at 0 °C to give **26** (entry 3 in Scheme 3). Although the reaction was continued for 2 h at room temperature, no other product was obtained (entry 4).

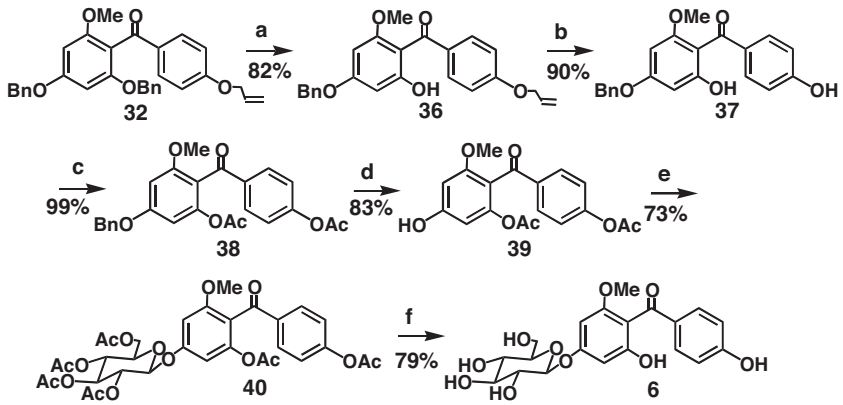
Glucosylation of **26** with *O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl) trichloroacetimidate[22] afforded **27**. Deacetylation of **27** in MeOH/Et_3N and subsequent hydrogenolysis gave **4**.

The spectral data did not match those of mahkoside A and synthesized **4** (Table 1). The distinguishable differences between them were the chemical shifts of the methoxy and H-3 and H-5 aromatic proton signals. The methoxy proton signal of mahkoside A resonated at δ 3.73 in DMSO-d_6. Synthesized **4** however showed the signal at δ 3.55 in the same solvent. The *ortho* methoxy protons in **4** may have been affected by the shielding effect of another benzene ring of the benzophenone skeleton. The downfield appearance of the methoxy signal (δ 3.73) of mahkoside A indicates that the methoxyl group was located at the *para* position of benzophenone. Therefore, we also compared the reported ^{1}H-NMR data of mahkoside A with those of synthesized **2** in DMSO-d_6 (Table 1), and found that their data were indistinguishable. Consequently, the correct structure of mahkoside A should be 2,4′,6-trihydroxy-4-methoxybenzophenone 2-*O*-*β*-D-glucopyranoside (**2**).

Details for the synthesis of **5** are depicted in Scheme 4. Benzophenone (**30**) was prepared from 1,3,5-tribenzyloxybenzene and 4-allyloxybenzoic acid, using TFAA as a condensing agent. After *ortho* monodebenzylation of **30** by $AlCl_3$–$PhNMe_2$, product **31** was methylated and then subjected to a cleaving reaction of the allyl group with $Pd(PPh_3)_4$[23] in the presence of potassium carbonate to afford **33**. Glucosylation of **33** yielded **34**. Deacetylation of **34** and subsequent hydrogenolysis led to **5**.

Compound **6** was synthesized as shown in Scheme 5. Selective *ortho* debenzylation of **32** by $AlCl_3$–$PhNMe_2$ and subsequent deallylation yielded **37**. The resulting hydroxyl groups of **37** were acetylated, and **38** was subsequently hydrogenated into **39**. Glucosylation of **39** afforded **40**. Deacetylation of **40** in MeOH/Et_3N gave product **6**.

The structures of compounds **1**, **2** and **4**–**6** were determined by 2D-NMR analyses (Fig. 2). We made it possible to provide five synthetically pure benzophenone glucopyranosides. Enough of each glucoside was available for a bioassay by scaling up the reactions. In addition, we found that selective *ortho* monodealkylation to polyalkoxybenzophenones could be achieved by $AlCl_3$–$PhNMe_2$. $AlCl_3$–$PhNMe_2$ may selectively cleave the alkoxy groups located at the *ortho* carbonyl group in the substrate. Thus, we could synthesize some benzophenone glucopyranosides related with the reported benzophenone glucopyranosides from *P. macrocarpa*. Comparing the NMR data of the four benzophenone glucopyranosides (for proposed structures **1**–**4**) from *P. macrocarpa* with those of the synthesized material



Scheme 5. Synthesis of 2,4,4′-Trihydroxy-6-methoxybenzophenone 4-*O*-*β*-D-Glucopyranoside (**6**).
Reagents and conditions: (a) $AlCl_3$, $PhNMe_2$, CH_2Cl_2, 0 °C, 20 min; (b) $Pd(PPh_3)_4$, K_2CO_3, dioxane, MeOH, r.t., 20 h; (c) Ac_2O, Et_3N, CH_2Cl_2, r.t., 1 h; (d) H_2, Pd-C, dioxane, r.t., overnight; (e) *O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl) trichloroacetimidate, $BF_3 \cdot OEt_2$, CH_2Cl_2, 0 °C → r.t., 6 h; (f) MeOH/Et_3N (3:1), r.t., 15 h.

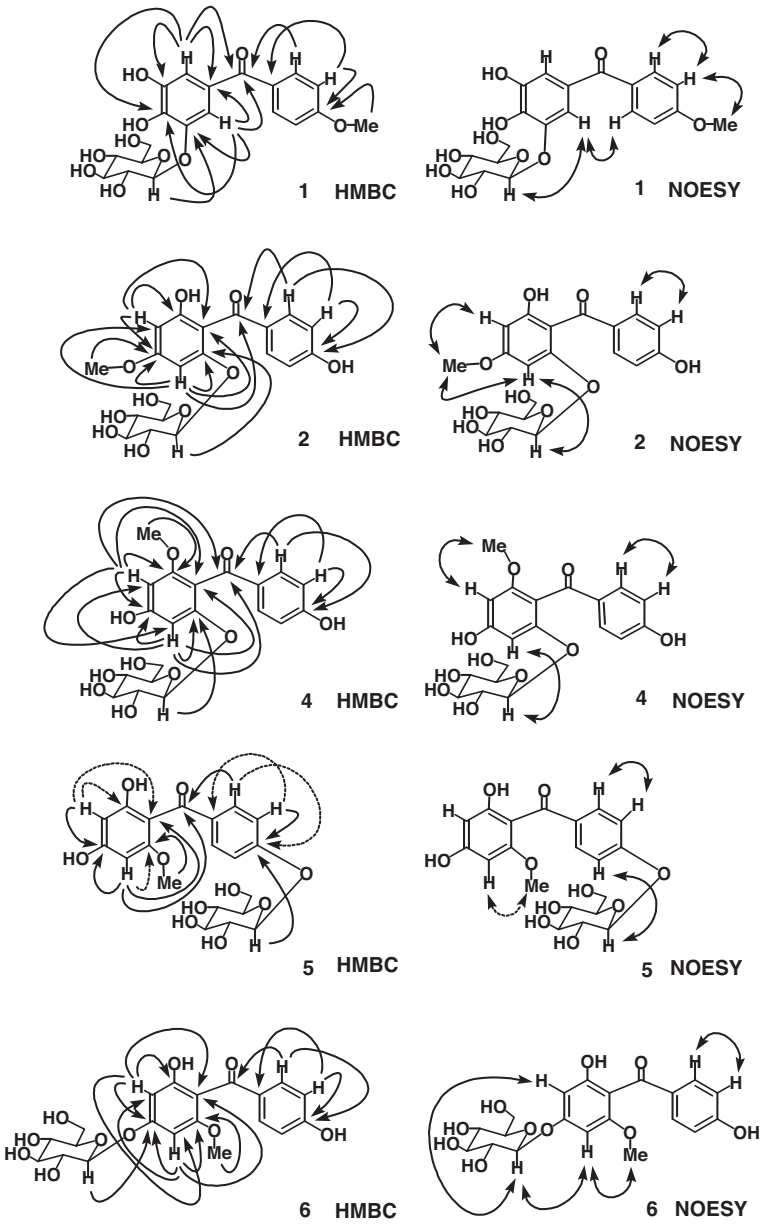


Fig. 2. Selected NOESY and HMBC Correlations for **1**, **2** and **4**-**6**.
Dashed arrows are correlations with overlapping signals.

(**1**, **2** and **4**) showed that the proposed structures for the natural products of the four benzophenone glucopyranosides were all **2**.

Experimental

General procedures. The solvent and reagents used were each a pure grade of the commercial product. Unless otherwise stated, they were used without purification. NMR spectra were recorded at 270 MHz/67.5 MHz ($^1H/^{13}C$) in $CDCl_3$, using tetramethylsilane as an internal standard, unless otherwise stated. Compounds **1**, **2** and **4**–**6** were recorded at 500 MHz/126 MHz ($^1H/^{13}C$), and the chemical shifts were calculated from the residual solvent signals of δ_H 3.30 ppm and δ_C 49.0 ppm in CD_3OD, δ_H 2.49 ppm and δ_C 39.5 ppm in DMSO-d_6, δ_H 2.04 ppm and δ_C 29.0 ppm in acetone-d_6, and δ_H 8.71 ppm and δ_C 149 ppm in pyridine-d_5. Complete attribution was performed on the basis of 2D-NMR (COSY, NOESY, HMBC and HMQC) experiments.

*3,4,5,4′-Tetramethoxybenzophenone (**8**).* To a stirred solution of 3,4,5-trimethoxybenzoyl chloride (**7**; 4.6 g, 20 mmol) and anisole (2.8 ml, 28 mmol) in $CHCl_3$ (20 ml) was added powdered $AlCl_3$ (2.9 g, 22 mmol) at 0 °C. The solution was stirred for 2 h at room temperature. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated, washed with aq. sat. $NaHCO_3$ and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 20:1) afforded **8** (4.6 g, 77%).

8: colorless prisms; mp 81.0–81.5 °C (EtOH), lit. 72–73 °C;[10] NMR δ_H ($CDCl_3$): 7.83 (2H, d, J = 8.9 Hz), 7.02 (2H, s), 6.97 (2H, d, J = 8.9 Hz), 3.93 (3H, s), 3.90 (3H, s), 3.88 (6H, s); NMR δ_C ($CDCl_3$): 194.4, 162.9, 152.7, 141.5, 133.2, 132.3, 130.2, 113.4, 107.4, 61.0, 56.3, 55.5; EIMS m/z (rel. int. %): 303 (M^+ +1, 18), 302 (M^+, 100), 287 (16), 271 (11), 259 (25), 195 (17), 135 (52), 92 (10), 77 (15).

*3,4,5-Trihydroxy-4′-methoxybenzophenone (**9**).* To a stirred solution of **8** (1.51 g, 4.99 mmol) in CH_2Cl_2 (20 ml) was added boron tribromide (15.0 ml of 1 M in hexane, 15 mmol) at 0 °C. The solution was stirred for 1 h at 0 °C. The reaction mixture was decomposed by ice-cold aq. 2 M HCl and diluted with EtOAc. The organic layer was separated and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel ($CHCl_3$/MeOH 10:0.5) to afford **9** (1.02 g, 78%).

9: colorless prisms; mp 182.0–184.0 °C (acetone); NMR δ_H (acetone-d_6): 7.73 (2H, d, J = 8.9 Hz), 7.03 (2H, d, J = 8.9 Hz), 6.88 (2H, s), 3.89 (3H, s); NMR δ_C (acetone-d_6): 183.7, 163.6, 148.2, 147.0, 145.9, 132.6, 131.9, 130.0, 114.2, 110.6, 55.8; EIMS m/z (rel. int. %): 261 (M^+ +1, 16), 260 (M^+, 100), 243 (21), 229 (21), 153 (21), 135 (87); HREIMS m/z (M^+) calcd. for $C_{14}H_{12}O_5$, 260.0685; found, 260.0722.

*3,4-(Benzylidenedioxy)-5-hydroxy-4′-methoxybenzophenone (**10**).* A flask equipped with a Dean-Stark trap and water condenser was charged with **9** (0.91 g, 3.5 mmol), benzaldehyde dimethyl acetal (0.52 ml, 3.4 mmol) and *p*-toluene-sulfonic acid monohydrate (3 mg) in toluene (50 ml). The reaction mixture was refluxed for 2 h. The solvent collected from the side arm of the Dean-Stark trap was continuously removed. The reaction mixture was then diluted with EtOAc and washed with aq. sat. Na_2CO_3. The organic layer was separated and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (toluene/EtOAc 10:1) to afford **10** (0.54 g, 44%).

10: amorphous white solid; mp 162.5–164.5 °C (EtOAc); NMR δ_H ($CDCl_3$): 7.80 (2H, d, J = 8.8 Hz), 7.46–7.62 (5H, m), 7.10 (1H, d, J = 1.5 Hz), 7.07 (1H, d, J = 1.5 Hz), 6.96 (1H, s), 6.94 (2H, d, J = 8.8 Hz), 5.67 (OH, brs), 3.88 (3H, s); NMR δ_C ($CDCl_3$): 194.3, 163.1, 148.7, 138.9, 138.0, 135.3, 132.6, 132.4, 130.6, 130.2, 128.7, 126.4, 114.8, 113.5, 111.8, 103.8, 56.3, 55.5; EIMS m/z (rel. int. %): 349 (M^+ +1, 21), 348 (M^+, 100), 347 (17), 241 (15), 135 (44); HREIMS m/z (M^+) calcd. for $C_{21}H_{16}O_5$, 348.0998; found, 348.0962.

*3,4-(Benzylidenedioxy)-5-hydroxy-4′-methoxybenzophenone 5-(2,3,4,6-tetra-O-acetyl)-β-D-glucopyranoside (**11**).* A mixture of **10** (0.70 g, 2.0 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (1.66 g, 4.0 mmol), K_2CO_3 (1.38 g, 10 mmol) and benzyltributylammonium chloride (0.12 g, 0.4 mmol) were added to $CHCl_3$ (30 ml), and the solution stirred for 72 h at room temperature. The reaction mixture was acidified with aq. 2 M HCl and diluted with EtOAc. The organic layer was separated, washed with aq. sat. $NaHCO_3$ and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 5:1) gave **11** (0.93 g, 69%) as a 1:1 mixture of diastereomers as determined by ^{1}H-NMR.

11: white solid; $[\alpha]_D^{27}$ −15° (*c* 0.3, MeOH); NMR δ_H (500 MHz, $CDCl_3$): 7.77 (4H, d, J = 8.9 Hz), 7.54–7.56 (4H, m), 7.45–7.47 (6H, m), 7.18 (1H, d, J = 1.5 Hz), 7.16 (1H, d, J = 1.5 Hz), 7.08 (2H, d, J = 2.3 Hz), 7.06 (2H, d, J = 2.3 Hz), 6.94 (4H, d, J = 8.9 Hz), 5.22–5.25 (6H, m), 5.13 (2H, dd, J = 9.8, 7.3 Hz), 4.23 (1H, dd, J = 12.3, 4.9 Hz), 4.16 (1H, dd, J = 12.3, 4.8 Hz), 4.08 (1H, dd, J = 12.3, 2.4 Hz), 3.94 (1H, dd, J = 12.3, 2.3 Hz), 3.87 (6H, s), 3.76 (1H, m), 3.70 (1H, m), 2.01 (3H, s), 2.00 (6H, s), 1.99 (6H, s), 1.98 (3H, s), 1.97 (3H, s), 1.92 (3H, s); NMR δ_C ($CDCl_3$): 193.2, 170.6, 170.2, 169.3, 169.24, 169.22, 169.18, 163.2, 149.3, 140.1, 139.8, 139.0, 138.9, 135.4, 135.2, 132.9, 132.8, 132.3, 130.75, 130.71, 130.1, 128.8, 126.4, 126.3, 116.8, 116.5, 113.6, 111.9, 111.87, 106.1, 106.0, 99.8, 96.1, 72.7, 72.6, 72.2, 71.1, 71.0, 68.2, 68.1, 61.8, 61.5, 55.5, 20.6, 20.57, 20.5; FABMS (positive, NBA matrix) m/z (rel. int. %): 701 [M + Na]$^+$ (6), 679 [M + H]$^+$ (14); HRFABMS m/z [M + H]$^+$ calcd. for $C_{35}H_{35}O_{14}$, 679.2027; found, 679.2018.

*3,4-(Benzylidenedioxy)-5-hydroxy-4′-methoxybenzophenone 5-O-β-D-glucopyranoside (**12**).* Compound **11** (204 mg, 0.301 mmol) was dissolved in MeOH (6 ml) and triethylamine (2 ml), and the solution stirred for 72 h at room temperature. To the reaction mixture was added toluene, before evaporating to dryness. Purification by flash column chromatography on silica gel ($CHCl_3$/MeOH 5:1) afforded **12** (103 mg, 67%) as a 1:1 mixture of diastereomers as determined by ^{1}H-NMR.

12: white solid; $[\alpha]_D^{26}$ −23° (*c* 0.3, MeOH); NMR δ_H (500 MHz, CD_3OD): 7.76 (2H, d, J = 8.9 Hz), 7.75 (2H, d, J = 8.9 Hz), 7.59–7.62 (4H, m), 7.30–7.49 (6H, m), 7.21 (1H, d, J = 1.8 Hz), 7.20 (1H, d, J = 2.0 Hz), 7.18 (1H, s), 7.16 (1H, s), 7.033 (1H, d, J = 2.0 Hz), 7.030 (4H, d, J = 8.9 Hz), 7.027 (1H, d, J = 1.8 Hz), 5.12 (1H, d, J = 7.0 Hz), 5.10 (1H, d, J = 7.4 Hz), 3.89 (3H, s), 3.88 (3H, s), 3.80 (1H, dd, J = 12.2, 2.6 Hz), 3.77 (1H, dd, J = 12.2, 2.5 Hz), 3.70 (2H, dd, J = 12.2, 4.5 Hz), 3.38–3.53 (6H, m), 3.32–3.34 (2H, m); NMR δ_C (CD_3OD): 195.9, 195.8, 165.0, 164.7, 150.84, 150.81, 147.0, 146.6, 141.5, 141.1, 137.2, 137.1, 133.72, 133.70, 133.5, 133.4, 131.7, 131.3, 129.9, 129.83, 127.8, 127.5, 117.0, 114.8, 114.6, 113.2, 113.0, 105.5, 105.4, 104.6, 104.3, 102.44, 102.4, 78.2, 78.1, 77.9, 77.6, 74.85, 74.82, 71.0, 70.9, 62.3, 62.1, 56.5, 56.1; FABMS (positive, NBA matrix) m/z (rel. int. %): 533 [M + Na]$^+$ (12), 511 [M + H]$^+$ (32); HRFABMS m/z [M + H]$^+$ calcd. for $C_{27}H_{27}O_{10}$, 511.1604; found, 511.1597.

*3,4,5-Trihydroxy-4′-methoxybenzophenone 3-O-β-D-glucopyranoside (**1**).* To a solution of **12** (20 mg, 0.039 mmol) in EtOH (5 ml) was added 10% Pd/C (20 mg), and the resulting suspension was stirred vigorously under a hydrogen atmosphere for 15 h at room temperature. The catalyst was filtered off through Celite, and the filtrate was evaporated under reduced pressure. The crude product was suspended in EtOH and filtered to afford **1** (13.6 mg, 82%).

1: colorless prisms; mp 117.5–119.5 °C (EtOH); $[\alpha]_D^{27}$ −38° (*c* 0.3, MeOH); NMR δ_H (500 MHz, CD_3OD): 7.75 (2H, d, J = 8.6 Hz, H-2′ and 6′), 7.20 (1H, d, J = 2.0 Hz, H-2), 7.03 (1H, d, J = 2.0 Hz, H-6), 7.03 (2H, d, J = 8.6 Hz, H-3′ and H-5′), 4.81 (1H, d, J = 7.5 Hz, H-1″), 3.88 (3H, s, OCH_3), 3.77 (1H, dd, J = 12.1, 2.2 Hz, H-6″b), 3.70 (1H, dd, J = 12.1, 4.6 Hz, H-6″a), 3.52 (1H, m, H-2″), 3.48 (1H, m, H-4″), 3.45 (1H, m, H-3″), 3.34 (1H, m, H-5″); NMR δ_C (CD_3OD): 196.7 (C=O), 164.7 (C-4′), 147.0 (C-5), 146.6 (C-3), 141.6 (C-4), 133.4 (C-2′ and C-6′), 131.6 (C-1′), 129.7 (C-1), 114.6 (C-3′ and C-5′), 113.9 (C-6), 112.9 (C-2), 104.2 (C-1″), 78.2 (C-5″), 77.5 (C-3″), 74.8 (C-2″), 70.9 (C-4″), 62.0 (C-6″), 56.0 (OCH_3); FABMS (positive, NBA matrix) m/z (rel. int. %): 445 [M + Na]$^+$ (37), 423 [M + H]$^+$ (22); HRFABMS m/z [M + H]$^+$ calcd. for $C_{20}H_{23}O_{10}$, 423.1291; found, 423.1299.

*4′-Benzyloxy-2,4,6-trimethoxybenzophenone (**15**).* To a suspension of 4-benzyloxybenzoic acid (2.28 g, 10 mmol) in CH_2Cl_2 (15 ml) cooled to 0 °C was added trifluoroacetic anhydride (1.81 ml, 13 mmol), and the mixture was stirred for 10 min to give a clear solution. To this solution was added 1,3,5-trimethoxybenzene **13** (2.19 g, 13 mmol), and the mixture stirred overnight at room temperature. The reaction mixture was diluted with EtOAc, ice water and aq. sat. Na_2CO_3, and stirred vigorously again to yield a suspension. Sodium 4-benzyloxybenzoate was filtered off through Celite, and the organic layer was separated and successively washed with aq. sat. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was suspended in EtOH and filtered to afford **15** (2.72 g, 72%).

15: colorless prisms; mp 120.5–122.0 °C (EtOH); NMR δ_H ($CDCl_3$): 7.81 (2H, d, $J = 8.9$ Hz), 7.32–7.43 (5H, m), 6.96 (2H, d, $J = 8.9$ Hz), 6.15 (2H, brs), 5.10 (2H, s), 3.85 (3H, s), 3.68 (6H, s); NMR δ_C ($CDCl_3$): 193.4, 162.7, 162.2, 158.5, 136.3, 131.8, 131.6, 128.6, 128.2, 127.5, 114.3, 111.2, 96.1, 90.7, 70.1, 55.8, 55.40, 55.36; EIMS m/z (rel. int. %): 379 ($M^+ +1$, 10), 378 (M^+, 40), 361 (12), 258 (35), 195 (11), 91 (100); HREIMS m/z (M^+) calcd. for $C_{23}H_{22}O_5$, 378.1467; found, 378.1491.

*4′-Benzyloxy-2-hydroxy-4,6-dimethoxybenzophenone (**16**).* To a stirred solution of **15** (2.22 g, 5.87 mmol) and $PhNMe_2$ (4.45 ml, 35.2 mmol) in CH_2Cl_2 (40 ml) was added powdered $AlCl_3$ (5.48 g, 41.1 mmol) at 0 °C. The solution was stirred for 20 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated, washed with brine and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 3:1) afforded **16** (1.79 g, 84%).

16: colorless prisms; mp 119.0–120.5 °C (EtOH); NMR δ_H ($CDCl_3$): 11.85 (OH, brs), 7.56 (2H, d, $J = 8.8$ Hz), 7.32–7.45 (5H, m), 6.94 (2H, d, $J = 8.8$ Hz), 6.15 (1H, d, $J = 2.3$ Hz), 5.93 (1H, d, $J = 2.3$ Hz), 5.11 (2H, s), 3.83 (3H, s), 3.49 (3H, s); NMR δ_C ($CDCl_3$): 197.4, 165.9, 165.2, 161.51, 161.47, 136.4, 134.0, 130.8, 128.6, 128.1, 127.5, 113.7, 105.8, 93.7, 91.3, 70.1, 55.6, 55.1; EIMS m/z (rel. int. %): 365 ($M^+ +1$, 6), 364 (M^+, 27), 363 (17), 244 (14), 91 (100); HREIMS m/z (M^+) calcd. for $C_{22}H_{20}O_5$, 364.1311; found, 364.1310.

*2-Benzoyloxy-4′-benzyloxy-4,6-dimethoxybenzophenone (**17**).* To a stirred solution of **16** (1.62 g, 4.45 mmol), triethylamine (0.92 ml, 6.6 mmol) and 4-*N*,*N*-dimethylaminopyridine (DMAP, 5 mg, 0.04 mmol) in CH_2Cl_2 (20 ml) was added benzoyl chloride (0.62 ml, 5.3 mmol) at room temperature. The solution was stirred for 20 min. The reaction mixture was then diluted with $CHCl_3$, successively washed with aq. 2 M HCl, aq. sat. $NaHCO_3$ and brine, and then dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 3:1) afforded **17** (2.04 g, 98%).

17: colorless oil; NMR δ_H ($CDCl_3$): 8.15 (2H, dd, $J = 7.3$, 1.3 Hz), 7.83 (1H, t, $J = 7.3$ Hz), 7.79 (2H, d, $J = 8.9$ Hz), 7.67 (2H, dd, $J = 7.6$, 7.3 Hz), 7.46–7.55 (2H, m), 7.30–7.38 (3H, m), 6.90 (2H, d, $J = 8.9$ Hz), 6.52 (1H, d, $J = 2.0$ Hz), 6.44 (1H, d, $J = 2.0$ Hz), 5.05 (2H, s), 3.85 (3H, s), 3.72 (3H, s); NMR δ_C ($CDCl_3$): 191.5, 164.2, 162.8, 162.2, 161.7, 158.7, 149.8, 136.2, 134.5, 133.6, 133.4, 131.8, 131.3, 130.5, 130.2, 130.1, 128.8, 128.6, 128.4, 128.3, 128.2, 127.4, 115.4, 114.3, 99.8, 96.7, 96.1, 70.0, 55.9, 55.6; EIMS, m/z (rel. int. %): 469 ($M^+ +1$, 12), 468 (M^+, 38), 243 (28), 105 (100), 91 (66), 77 (24); HREIMS m/z (M^+) calcd. for $C_{29}H_{24}O_6$, 468.1573; found, 468.1539.

*2-Benzoyloxy-4′-benzyloxy-6-hydroxy-4-methoxybenzophenone (**18**).* To a stirred solution of **17** (2.0 g, 4.3 mmol) and $PhNMe_2$ (3.1 ml, 25 mmol) in CH_2Cl_2 (30 ml) was added powdered $AlCl_3$ (2.19 g, 16.4 mmol) at 0 °C. The solution was stirred for 15 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated, washed with brine and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 3:1) afforded **18** (1.40 g, 72%).

18: colorless needles; mp 117.5–119.0 °C (EtOH); NMR δ_H ($CDCl_3$): 11.48 (OH, brs), 7.43–7.54 (5H, m), 7.47 (2H, d, $J = 8.9$ Hz), 7.24–7.38 (5H, m), 6.71 (2H, d, $J = 8.9$ Hz), 6.47 (1H, d, $J = 2.5$ Hz), 6.35 (1H, d, $J = 2.5$ Hz), 4.79 (2H, s), 3.87 (3H, s); NMR δ_C ($CDCl_3$): 196.9, 164.9, 164.5, 163.9, 161.8, 151.7, 136.2, 133.3, 133.2, 130.6, 129.8, 128.6, 128.5, 128.2, 127.9, 127.3, 114.1, 108.9, 102.5, 99.4, 96.2, 70.0, 55.7; EIMS m/z (rel. int. %): 455 ($M^+ +1$, 11), 454 (M^+, 37), 105 (100), 91 (53), 77 (21); HREIMS m/z (M^+) calcd. for $C_{28}H_{22}O_6$, 454.1416; found, 454.1409.

*4′-Benzyloxy-2,6-dihydroxy-4-methoxybenzophenone (**19**).* Compound **18** (0.70 g, 1.5 mmol) was added to *N*,*N*-dimethyl-1,3-propanediamine (2.0 ml) at 0 °C, and then the solution was stirred for 1 h at room temperature. The reaction mixture was diluted with EtOAc and aq. 2 M HCl, and then mixed. The organic layer was separated, washed with brine and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 3:1) afforded **19** (0.33 g, 61%).

19: amorphous white solid; mp 110.0–112.0 °C (EtOH); NMR δ_H ($CDCl_3$): 8.68 (OH, brs), 7.67 (2H, d, $J = 8.6$ Hz), 7.34–7.42 (5H, m), 7.06 (2H, d, $J = 8.6$ Hz), 6.03 (2H, s), 5.13 (2H, s), 3.82 (3H, s); NMR δ_C ($CDCl_3$): 195.8, 166.5, 162.5, 161.9, 135.9, 131.7, 130.9, 128.7, 128.3, 127.5, 115.3, 104.6, 96.1, 94.9, 70.3, 55.1; EIMS m/z (rel. int. %): 351 ($M^+ +1$, 8), 350 (M^+, 33), 259 (5), 230 (5), 166 (7), 121 (5), 91 (100), 65 (5); HREIMS m/z (M^+) calcd. for $C_{21}H_{18}O_5$, 350.1154; found, 350.1109.

*4′-Benzyloxy-2,6-dihydroxy-4-methoxybenzophenone 2-(2,3,4,6-tetra-O-acetyl)-β-D-glucopyranoside (**20**).* A mixture of **19** (55 mg, 0.16 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (110 mg, 0.268 mmol), 18-crown-6 (10 mg, 0.038 mmol), K_2CO_3 (108 mg, 0.781 mmol) and CH_3CN (5 ml) was stirred at room temperature for 24 h. The reaction mixture was acidifed with aq. 2 M HCl and diluted with EtOAc. The organic layer was separated, washed with aq. sat. $NaHCO_3$ and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel ($CHCl_3$/acetone 15:1) gave **20** (107 mg, 61%).

20: colorless prisms; mp 65.0–67.0 °C (EtOH); $[\alpha]_D^{28}$ −19° (*c* 0.3, $CHCl_3$); NMR δ_H ($CDCl_3$): 11.3 (OH, brs), 7.60 (2H, d, $J = 8.7$ Hz), 7.32–7.48 (5H, m), 6.94 (2H, d, $J = 8.7$ Hz), 6.27 (1H, d, $J = 2.1$ Hz), 6.15 (1H, d, $J = 2.1$ Hz), 5.18 (2H, s), 5.05 (1H, dd, $J = 9.3$, 8.8 Hz), 4.98 (1H, dd, $J = 9.3$, 9.3 Hz), 4.88 (1H, d, $J = 7.5$ Hz), 4.40 (1H, dd, $J = 8.8$, 7.5 Hz), 4.20 (1H, dd, $J = 12.4$, 6.3 Hz), 4.11 (1H, dd, $J = 12.4$, 2.3 Hz), 3.74 (1H, m), 3.82 (3H, s), 2.09 (3H, s), 2.00 (3H, s), 1.91 (3H, s), 1.87 (3H, s); NMR δ_C ($CDCl_3$): 196.6, 170.5, 170.0, 169.3, 168.3, 165.0, 164.3, 162.3, 157.6, 136.5, 132.9, 131.3, 128.6, 128.1, 127.5, 114.0, 107.2, 98.5, 96.1, 95.9, 95.6, 91.7, 72.9, 72.2, 70.8, 70.1, 67.9, 62.0, 55.6, 20.6; FABMS (negative, TEA matrix) m/z (rel. int. %) 679 $[M-H]^-$ (8); HRFABMS m/z $[M-H]^-$ calcd. for $C_{35}H_{35}O_{14}$, 679.2027; found, 679.2033.

*4′-Benzyloxy-2,6-dihydroxy-4-methoxybenzophenone 2-O-β-D-glucopyranoside (**21**).* Compound **20** (41 mg, 0.060 mmol) was dissolved in MeOH (3 ml) and triethylamine (1 ml) and stirred for 15 h at room temperature. To the reaction mixture was added toluene, before being evaporated to dryness. The crude product was suspended in hexane and diethyl ether and then filtered to afford **21** (39 mg, 91%).

21: colorless plates; mp 74.5–76.0 °C (EtOH); $[\alpha]_D^{27}$ −27° (*c* 0.3, $CHCl_3$); NMR δ_H ($CDCl_3$): 7.55 (2H, d, $J = 8.7$ Hz), 7.25–7.33 (5H, m), 6.90 (2H, d, $J = 8.7$ Hz), 6.18 (1H, d, $J = 2.0$ Hz), 6.06 (1H, d, $J = 2.0$ Hz), 5.05 (2H, s), 4.62 (1H, d, $J = 7.5$ Hz), 3.74 (3H, s), 3.60–3.80 (3H, m), 3.25–3.34 (3H, m), 2.56 (OH, brs); NMR δ_C ($CDCl_3$): 197.1, 165.4, 164.3, 161.8, 157.5, 136.1, 134.1, 130.8, 128.7, 128.2, 127.4, 114.1, 107.0, 100.1, 96.1, 95.9, 95.2, 75.7, 74.7, 73.2, 70.2, 69.8, 62.1, 55.7; FABMS (negative, TEA matrix) m/z (rel. int. %) 511 $[M-H]^-$ (2); HRFABMS m/z $[M-H]^-$ calcd. for $C_{27}H_{27}O_{10}$, 511.1604; found, 511.1584.

*2,4′,6-Trihidroxy-4-methoxybenzophenone 2-O-β-D-glucopyranoside (**2**).* To a solution of **21** (20 mg 0.039 mmol) in dioxane (3 ml) was added 10% Pd/C (20 mg), and the resulting suspension was stirred vigorously under a hydrogen atmosphere for 15 h at room temperature. The catalyst was filtered off through Celite, and the filtrate was evaporated under reduced pressure. The crude product was suspended in $CHCl_3$ and filtered to afford **2** (11.5 mg, 70%).

2: colorless prisms; mp 103.5–104.5 °C (EtOH), lit. 202–204 °C,[2)]

133–135 °C,[17] 103–105 °C;[5] $[\alpha]_D^{27}$ −26° (*c* 0.1, MeOH), −15° (*c* 0.5, EtOH), lit. −23° (*c* 0.1, MeOH),[17] +4° (*c* 0.9, MeOH),[3] +0, 53° (*c* 0.15, EtOH);[1] NMR δ_H (500 MHz, CD_3OD): 7.68 (2H, d, $J = 8.7$ Hz, H-2′ and H-6′), 6.78 (2H, d, $J = 8.7$ Hz, H-3′ and H-5′), 6.39 (1H, d, $J = 1.7$ Hz, H-3), 6.17 (1H, d, $J = 1.7$ Hz, H-5), 4.86 (1H, d, $J = 7.9$ Hz, H-1″), 3.84 (1H, brd, $J = 12.0$ Hz, H-6″b), 3.79 (3H, s, OC*H*$_3$), 3.63 (1H, dd, $J = 12.0$, 6.0 Hz, H-6″a), 3.37 (1H, m, H-5″), 3.37 (1H, m, H-3″), 3.24 (1H, dd, $J = 9.5$, 9.2 Hz, H-4″), 3.12 (1H, dd, $J = 8.9$, 7.9 Hz, H-2″); NMR δ_H (500 MHz, DMSO-d_6): 10.26 (O*H*, brs), 9.70 (O*H*, brs), 7.57 (2H, d, $J = 8.7$ Hz, H-2′ and H-6′), 6.78 (2H, d, $J = 8.7$ Hz, H-3′ and H-5′), 6.29 (1H, d, $J = 2.0$ Hz, H-3), 6.12 (1H, d, $J = 2.0$ Hz, H-5), 4.96 (O*H*, d, $J = 5.3$ Hz, OH-C-4″), 4.92 (O*H*, d, $J = 5.2$ Hz, OH-C-3″), 4.78 (1H, d, $J = 8.0$ Hz, H-1″), 4.54 (O*H*, d, $J = 5.7$ Hz, OH-C-6″), 4.52 (O*H*, d, $J = 5.0$ Hz, OH-C-2″), 3.72 (3H, s, OC*H*$_3$), 3.66 (1H, ddd, $J = 11.0$, 5.7, 5.2 Hz, H-6″a), 3.38 (1H, brdd, $J = 11.0$, 5.7 Hz, H-6″b), 3.27 (1H, m, H-5″), 3.17 (1H, ddd, $J = 9.2$, 8.8, 5.2 Hz, H-3″), 3.01 (1H, ddd, $J = 9.3$, 9.2, 5.3 Hz, H-4″), 2.91 (1H, ddd, $J = 8.8$, 8.0, 5.0 Hz, H-2″); NMR δ_H (500 MHz, pyridine-d_5): 8.23 (2H, d, $J = 8.6$ Hz, H-2′ and H-6′), 7.12 (2H, d, $J = 8.6$ Hz, H-3′ and H-5′), 7.02 (1H, s, H-3), 6.60 (1H, s, H-5), 5.60 (1H, d, $J = 8.2$ Hz, H-1″), 4.54 (1H, brd, $J = 12.0$ Hz, H-6″b), 4.30 (1H, dd, $J = 12.0$, 6.0 Hz, H-6″a), 4.25 (1H, dd, $J = 10.0$, 8.7 Hz, H-3″), 4.13 (1H, dd, $J = 9.6$, 8.7 Hz, H-4″), 4.06 (1H, m, H-5″), 4.03 (1H, dd, $J = 10.0$, 8.2 Hz, H-2″), 3.73 (3H, s); NMR δ_C (CD_3OD): 197.1 (C=O), 164.3 (C-4), 163.8 (C-4′), 159.0 (C-6), 158.4 (C-2), 133.6 (C-2′ and C-6′), 131.9 (C-1′), 115.9 (C-3′ and C-5′), 111.7 (C-1), 102.5 (C-1″), 96.8 (C-5), 94.9 (C-3), 78.3 (C-5″), 77.8 (C-3″), 74.8 (C-2″), 71.2 (C-4″), 62.6 (C-6″), 55.9 (O*C*H$_3$); NMR δ_C (DMSO-d_6): 192.5, 161.9, 161.0, 156.3, 156.1, 131.7, 129.8, 114.9, 110.6, 100.6, 95.1, 92.9, 77.2, 76.7, 73.2, 69.8, 60.8, 55.1; NMR δ_C (pyridine-d_5): 194.1, 163.1, 162.2, 158.0, 157.8, 132.5, 115.4, 107.9, 102.5, 96.2, 93.6, 78.6, 77.9, 74.2, 70.7, 62.0, 54.8; FABMS (negative, TEA matrix) *m/z* (rel. int. %) 421 $[M-H]^-$ (8); HRFABMS *m/z* $[M-H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1138.

*2,4,6,4′-Tetrabenzyloxybenzophenone (**23**).* To a suspension of 4-benzyloxybenzoic acid (2.32 g, 10.2 mmol) in CH_2Cl_2 (20 ml) cooled to 0 °C was added trifluoroacetic anhydride (1.67 ml, 12.0 mmol), and the mixture was stirred for 10 min to gave a clear solution. To this solution was added 1,3,5-tribenzyloxybenzene **22** (3.0 g, 7.6 mmol), and the mixture stirred overnight at room temperature. The reaction mixture was diluted with EtOAc, ice water and aq. sat. Na_2CO_3, and stirred vigorously to yield a suspension again. Sodium 4-benzyloxybenzoate was filtered off through Celite, and the organic layer was separated and successively washed with aq. sat. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was suspended in diethyl ether and filtered to afford **23** (3.71 g, 81%).

23: amorphous white solid; mp 119.0–121.0 °C (EtOH); NMR δ_H ($CDCl_3$): 7.82 (2H, d, $J = 8.9$ Hz), 7.32–7.43 (10H, m), 7.18–7.24 (5H, m), 7.07–7.10 (5H, m), 6.95 (2H, d, $J = 8.9$ Hz), 6.24 (2H, s), 5.11 (2H, s), 4.97 (2H, s), 4.96 (4H, s); NMR δ_C ($CDCl_3$): 193.3, 162.6, 161.4, 161.1, 157.6, 137.0, 136.6, 136.5, 136.4, 132.1, 131.8, 128.9, 128.7, 128.3, 128.2, 127.9, 127.8, 127.6, 127.54, 127.45, 126.7, 114.3, 93.6, 70.3, 70.1; EIMS *m/z* (rel. int. %): 606 (M^+, 3), 273 (9), 91 (100), 44 (15); HREIMS *m/z* (M^+) calcd. for $C_{41}H_{34}O_5$, 606.2406; found, 606.2403.

*2,4,4′-Tribenzyloxy-6-hydroxybenzophenone (**24**).* To a stirred solution of **23** (4.35 g, 7.17 mmol) and $PhNMe_2$ (5.43 ml, 43.0 mmol) in CH_2Cl_2 (30 ml) was added powdered $AlCl_3$ (2.87 g, 21.5 mmol) at 0 °C. The solution was stirred for 10 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured to ice-cold aq. 2 M HCl and mixed. The organic layer was separated, and the aqueous phase was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad; the filtrate was evaporated under reduced pressure. The crude product was suspended in EtOAc and filtered to afford **24** (2.90 g, 78%).

24: amorphous white solid; mp 146.0–148.0 °C (EtOH); NMR δ_H ($CDCl_3$): 11.79 (OH, brs), 7.57 (2H, d, $J = 8.7$ Hz), 7.31–7.42 (10H, m), 7.08–7.20 (5H, m), 6.84 (2H, d, $J = 8.7$ Hz), 6.26 (1H, d, $J = 2.1$ Hz), 6.12 (1H, d, $J = 2.1$ Hz), 5.08 (2H, s), 4.99 (2H, s), 4.80 (2H, s); NMR δ_C ($CDCl_3$): 197.9, 165.2, 164.9, 161.6, 160.5, 136.5, 135.9, 135.6, 134.4, 130.6, 128.7, 128.6, 128.3, 128.11, 128.06, 127.7, 127.5, 127.4, 126.5, 113.8, 106.2, 96.1, 94.8, 92.9, 70.3, 70.1, 70.0; EIMS *m/z* (rel. int. %): 516 (M^+, 10), 425 (5), 211 (8), 91 (100); HREIMS *m/z* (M^+) calcd. for $C_{34}H_{28}O_5$, 516.1937; found, 516.1929.

*2,4,4′-Tribenzyloxy-6-methoxybenzophenone (**25**).* A mixture of **24** (3.49 g, 6.76 mmol), dimethyl sulfate (1.11 g, 8.80 mmol), potassium carbonate (1.39 g, 10.1 mmol) and 18-crown-6 (0.10 mg, 0.38 mmol) as a catalyst in CH_3CN (15 ml) was refluxed for 1 h. To the reaction mixture was added conc. NH_4OH (0.5 ml), and the solution stirred for 10 min, EtOAc subsequently added and the whole washed with brine. The organic layer was separated, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel (hexane/EtOAc 6:1) gave **25** (3.20 g, 93%).

25: amorphous white solid; mp 104.0–105.0 °C (EtOH); NMR δ_H ($CDCl_3$): 7.82 (2H, d, $J = 8.9$ Hz), 7.31–7.39 (10H, m), 7.04–7.18 (5H, m), 6.95 (2H, d, $J = 8.9$ Hz), 6.24 (2H, s), 5.10 (2H, s), 5.03 (2H, s), 4.94 (2H, s), 3.67 (3H, s); NMR δ_C ($CDCl_3$): 193.3, 162.6, 161.2, 158.6, 157.4, 136.6, 136.5, 136.4, 131.9, 131.8, 128.7, 128.3, 128.2, 127.5, 127.4, 126.7, 117.4, 114.3, 112.1, 96.2, 93.1, 92.2, 70.2, 70.1, 55.8; EIMS *m/z* (rel. int. %): 530 (M^+, 17), 439 (7), 333 (5), 257 (4), 211 (5), 910 (100), 65 (5), 44 (5); HREIMS *m/z* (M^+) calcd. for $C_{35}H_{30}O_5$, 530.2093; found, 530.2071.

*4,4′-Dibenzyloxy-2-hydroxy-6-methoxybenzophenone (**26**).* To a stirred solution of **25** (1.80 g, 3.39 mmol) and $PhNMe_2$ (2.57 ml, 20.3 mmol) in CH_2Cl_2 (15 ml) was added powdered $AlCl_3$ (1.36 g, 10.2 mmol) at 0 °C. The solution was stirred for 10 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated, and the aqueous phase was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad; the solvent was evaporated under reduced pressure to give a white solid. The crude product was suspended in EtOAc and filtered to afford **26** (1.48 g, 98%).

26: amorphous white solid; mp 111.0–113.0 °C (EtOH); NMR δ_H ($CDCl_3$): 11.82 (OH, brs), 7.56 (2H, d, $J = 8.9$ Hz), 7.32–7.44 (10H, m), 6.94 (2H, d, $J = 8.9$ Hz), 6.23 (1H, d, $J = 2.1$ Hz), 6.02 (1H, d, $J = 2.1$ Hz), 5.11 (2H, s), 5.08 (2H, s), 3.48 (3H, s); NMR δ_C ($CDCl_3$): 197.4, 165.2, 164.9, 161.5, 136.4, 136.0, 134.0, 130.8, 128.7, 128.6, 128.3, 128.1, 127.7, 127.5, 113.7, 106.0, 94.6, 91.9, 70.3, 70.1, 55.2; EIMS *m/z* (rel. int. %): 440 (M^+, 30), 349 (7), 320 (4), 91 (100), 65 (5); HREIMS *m/z* (M^+) calcd. for $C_{28}H_{24}O_5$, 440.0998; found, 440.1659.

*Dealkylation reaction of **25** with Lewis acids ($AlCl_3$ and BBr_3).*

(a) Reaction with $AlCl_3$

To a stirred solution of **25** (200 mg, 0.38 mmol) in CH_2Cl_2 (5 ml) was added powdered $AlCl_3$ (151 mg, 1.13 mmol) at 0 °C. The solution was stirred for 3 h at room temperature. No reaction occurred.

(b) Reaction with BBr_3

To a stirred solution of **25** (206 mg, 0.39 mmol) in CH_2Cl_2 (5 ml) was added BBr_3 (0.39 ml of 1 M in hexane, 0.39 mmol) at −78 °C. The solution was stirred for 2 h at −78 °C and then for 30 min at −60 °C. The reaction mixture was decomposed by ice-cold aq. 2 M HCl and diluted with EtOAc. The organic layer was separated and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. A product with the same *Rf* value as that of **26** was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1). This product suspended in hexane gave a white solid (86 mg). ^{1}H-NMR indicated this to be a mixture of **26** (68 mg, 41%) and **24** (18 mg, 9%).

(c) Reaction with $AlCl_3$ and $PhNMe_2$ at room temperature

To a stirred solution of **25** (200 mg, 0.39 mmol) and $PhNMe_2$ (0.29 ml, 2.26 mmol) in CH_2Cl_2 (5 ml) was added powdered $AlCl_3$ (150 mg, 1.1 mmol) at 0 °C. The solution was stirred for 10 min at 0 °C and then for 2 h at room temperature. The reaction mixture diluted with EtOAc was poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated, and the aqueous phase was extracted twice with $CHCl_3$. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad; the solvent was evaporated under reduced pressure to give a white solid. The

crude product was suspended in EtOAc and filtered to afford **26** (160 mg, 96%).

*4,4′-Dibenzyloxy-2-hydroxy-6-methoxybenzophenone 2-(2,3,4,6-tetra-O-acetyl)-β-D-glucopyranoside (**27**).* To a stirred solution of **26** (200 mg, 0.454 mmol) and *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) trichloroacetimidate (447 mg, 0.91 mmol) in dry CH_2Cl_2 (5 ml) was added $BF_3 \cdot OEt_2$ (1 drop) at 0 °C. The solution was stirred for 6 h at room temperature. The reaction mixture was diluted with EtOAc and successively washed with aq. sat. NH_4Cl and brine. The organic layer was separated and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. Purification by flash column chromatography on silica gel ($CHCl_3$/acetone 15:1) afforded **27** (100.5 mg, 29%) and **26** (122.5 mg, 61%).

27: colorless prisms; mp 77.5–78.5 °C (EtOH); $[\alpha]_D^{27}$ −16° (*c* 0.3, $CHCl_3$); NMR δ_H ($CDCl_3$): 7.75 (2H, d, J = 8.6 Hz), 7.26–7.40 (10H, m), 6.95 (2H, d, J = 8.6 Hz), 6.45 (1H, d, J = 1.9 Hz), 6.34 (1H, d, J = 1.9 Hz), 5.16 (1H, dd, J = 9.9, 9.2 Hz), 5.11 (2H, s), 5.09 (2H, s), 5.02 (1H, dd, J = 9.9, 9.6 Hz), 4.93 (1H, dd, J = 9.6, 7.6 Hz), 4.88 (1H, d, J = 7.6 Hz) , 4.19 (1H, dd, J = 12.4, 5.2 Hz), 4.10 (1H, dd, J = 12.4, 2.9 Hz), 3.73 (1H, m), 3.67 (3H, s), 2.04 (3H, s), 2.00 (3H, s), 1.95 (3H, s), 1.90 (3H, s); NMR δ_C ($CDCl_3$): 193.7, 171.9, 171.5, 170.7, 170.5, 164.3, 162.4, 159.6, 156.7, 137.7, 133.3, 132.6, 130.12, 130.07, 129.7, 129.6, 129.0, 128.9, 115.8, 101.4, 98.0, 97.5, 95.6, 74.0, 73.4, 71.8, 71.7, 71.5, 69.4, 57.3, 22.00, 21.97, 21.7; FABMS (negative, TEA matrix) m/z (rel. int. %) 769 $[M-H]^-$ (1); HRFABMS m/z $[M-H]^-$ calcd. for $C_{42}H_{41}O_{14}$, 769.2496; found, 769.2519.

*4,4′-Dibenzyloxy-2-hydroxy-6-methoxybenzophenone 2-O-β-D-glucopyranoside (**28**).* Compound **27** (70 mg, 0.091 mmol) was dissolved in MeOH (6 ml) and triethylamine (2 ml), and then stirred at room temperature for 15 h. To the reaction mixture was added toluene, and the solution evaporated to dryness. The crude product was suspended in hexane and diethyl ether, and filtered to afford **28** (50 mg, 92%).

28: colorless prisms; mp 79.5–81.5 °C (EtOH); $[\alpha]_D^{27}$ −6° (*c* 0.1, MeOH); NMR δ_H ($CDCl_3$): 7.78 (2H, d, J = 8.4 Hz), 7.39–7.42 (10H, m), 6.94 (2H, d, J = 8.4 Hz), 6.45 (1H, d, J = 1.9 Hz), 6.32 (1H, d, J = 1.9 Hz), 5.09 (4H, brs), 4.73 (1H, d, J = 7.5 Hz), 3.75–3.86 (2H, m), 3.71 (3H, s), 3.51–3.57 (3H, m), 3.41 (1H, m), 2.34 (OH, brs); NMR δ_C ($CDCl_3$): 194.1, 163.1, 161.7, 158.7, 157.1, 136.2, 132.1, 131.5, 128.8, 128.7, 128.3, 128.2, 127.5, 114.4, 103.9, 96.3, 96.1, 94.5, 75.9, 73.7, 70.4, 70.2, 70.2, 69.9, 62.4, 55.8; FABMS (negative, TEA matrix) m/z (rel. int. %) 601 $[M-H]^-$ (1); HRFABMS m/z $[M-H]^-$ calcd. for $C_{34}H_{33}O_{10}$, 601.2074; found, 601.2075.

*2,4,4′-Trihydroxy-6-methoxybenzophenone 2-O-β-D-glucopyranoside (**4**).* To a solution of **28** (53 mg, 0.088 mmol) in dioxane (4 ml) was added 10% Pd/C (50 mg), and the resulting suspension was stirred vigorously under a hydrogen atmosphere for 15 h at room temperature. The catalyst was filtered off through Celite, and the filtrate was evaporated under reduced pressure. The crude product was suspended in $CHCl_3$ and filtered to afford **4** (28 mg, 75%).

4: colorless plates; mp 136.0–138.0 °C (EtOH); $[\alpha]_D^{28}$ −10° (*c* 0.1, MeOH); NMR δ_H (DMSO-d_6): 10.26 (O*H*, brs), 9.81 (O*H*, brs), 7.55 (2H, d, J = 8.0 Hz), 6.77 (2H, d, J = 8.0 Hz), 6.26 (1H, brs), 6.16 (1H, brs), 4.94 (O*H*, d, J = 4.9 Hz), 4.90 (O*H*, d, J = 5.3 Hz), 4.73 (1H, d, J = 7.0 Hz), 4.52 (O*H*, d, J = 4.6 Hz), 4.46 (O*H*, d, J = 5.0 Hz), 3.63 (1H, m), 3.55 (3H, s), 3.48 (1H, m), 3.20 (1H, m), 3.17 (1H, m), 3.06 (1H, m), 2.89 (1H, m); NMR δ_H (500 MHz, CD_3OD): 7.66 (2H, d, J = 8.7 Hz, H-2′ and H-6′), 6.78 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 6.37 (1H, d, J = 1.9 Hz, H-3), 6.22 (1H, d, J = 1.9 Hz, H-5), 4.83 (1H, d, J = 7.9 Hz, H-1″), 3.84 (1H, dd, J = 12.0, 2.1 Hz, H-6″b), 3.66 (1H, dd, J = 12.0, 5.5 Hz, H-6″a), 3.62 (3H, s, OCH_3), 3.37 (1H, dd, J = 9.3, 9.0 Hz, H-3″), 3.36 (1H, m, H-5″), 3.28 (1H, dd, J = 9.3, 9.3 Hz, H-4″), 3.19 (1H, dd, J = 9.0, 7.9 Hz, H-2″); NMR δ_C (CD_3OD): 196.4 (C=O), 164.1 (C-4′), 161.9 (C-4), 160.2 (C-6), 157.9 (C-2), 133.5 (C-2′ and C-6′), 131.6 (C-1′), 116.0 (C-3′ and C-5′), 112.1 (C-1), 102.8 (C-1″), 96.9 (C-3), 94.6 (C-5), 78.2 (C-5″), 77.8 (C-3″), 74.7 (C-2″), 71.1 (C-4″), 62.5 (C-6″), 56.1 (O*C*H$_3$); FABMS (negative, TEA matrix) m/z (rel. int. %) 421 $[M-H]^-$ (7); HRFABMS m/z $[M-H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1138.

*4′-Allyloxy-2,4,6-tribenzyloxybenzophenone (**30**).* To a suspension of 4-allyloxybenzoic acid (2.14 g, 12.0 mmol) in CH_2Cl_2 (20 ml) cooled to 0 °C was added trifluoroacetic anhydride (1.81 ml, 13.0 mmol), and the mixture was stirred for 10 min. To the solution was added 1,3,5-tribenzyloxybenzene (**22**; 3.96 g, 10.0 mmol) and the mixture stirred at room temperature for 48 h. The reaction mixture was diluted with EtOAc, ice-cooled water and aq. sat. Na_2CO_3, and then stirred vigorously. The organic layer was separated, successively washed with aq. sat. $NaHCO_3$ and brine, dried over $MgSO_4$ and filtered through a silica-gel pad. The solvent was evaporated under reduced pressure. The crude product was suspended in EtOH and filtered to afford **30** (4.57 g, 82%).

30: colorless prisms; mp 121.5–123.5 °C (EtOH); NMR δ_H ($CDCl_3$): 7.83 (2H, d, J = 8.7 Hz), 7.35–7.38 (5H, m), 7.20–7.22 (5H, m), 7.08–7.11 (5H, m), 6.90 (2H, d, J = 8.7 Hz), 6.25 (2H, s), 6.04 (1H, ddt, J = 18.8, 11.8, 5.3 Hz), 5.43 (1H, ddt, J = 18.8, 2.5, 2.0 Hz), 5.31 (1H, ddt, J = 11.8, 2.5, 1.0 Hz), 4.98 (4H, s), 4.97 (2H, s), 4.58 (2H, ddt, J = 5.3, 2.0, 1.0 Hz); NMR δ_C ($CDCl_3$): 193.1, 162.4, 161.1, 157.6, 155.6, 136.6, 132.7, 132.0, 131.7, 128.7, 128.4, 128.2, 127.6, 127.5, 126.7, 118.0, 114.2, 112.8, 96.1, 93.6, 70.3, 68.8, 25.0; EIMS m/z (rel. int. %): 557 (M^+ +1, 6), 556 (M^+, 16), 223 (29), 161 (15), 91 (100); HREIMS m/z (M^+) calcd. for $C_{37}H_{32}O_5$, 556.2250; found, 556.2209.

*4′-Allyloxy-2,4-dibenzyloxy-6-hydroxybenzophenone (**31**).* To a stirred solution of **30** (1.04 g, 1.87 mmol) and $PhNMe_2$ (1.42 ml, 11.2 mmol) in CH_2Cl_2 (10 ml) was added powdered $AlCl_3$ (0.75 g, 5.6 mmol) at 0 °C. The solution was stirred for 5 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated and washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad. The solvent was evaporated under reduced pressure to give a white solid. The crude product was suspended in EtOH and filtered to afford **31** (0.70 g, 80%).

31: colorless needles; mp 114.0–115.5 °C (EtOH); NMR δ_H ($CDCl_3$): 11.76 (OH, brs), 7.56 (2H, d, J = 8.9 Hz), 7.35–7.45 (5H, m), 7.10–7.18 (3H, m), 6.79 (2H, d, J = 8.9 Hz), 6.73–6.80 (2H, m), 6.27 (1H, d, J = 2.3 Hz), 6.13 (1H, d, J = 2.3 Hz), 6.01 (1H, ddt, J = 18.8, 11.8, 5.3 Hz), 5.39 (1H, ddt, J = 18.8, 2.5, 2.0 Hz), 5.29 (1H, ddt, J = 11.8, 2.5, 1.0 Hz), 5.09 (2H, s), 4.81 (2H, s), 4.48 (2H, ddt, J = 5.3, 2.0, 1.0 Hz); NMR δ_C ($CDCl_3$): 197.9, 165.1, 164.9, 161.4, 160.5, 135.9, 135.6, 134.2, 132.8, 130.6, 128.7, 128.3, 128.1, 127.7, 127.5, 126.5, 117.9, 113.7, 106.3, 96.1, 94.8, 92.9, 70.3, 70.1, 68.8; EIMS m/z (rel. int. %): 467 (M^+ +1, 7), 466 (M^+, 24), 375 (6), 243 (6), 224 (5), 161 (18), 91 (100); HREIMS m/z (M^+) calcd. for $C_{30}H_{26}O_5$, 466.1780; found, 466.1775.

*4′-Allyloxy-2,4-dibenzyloxy-6-methoxybenzophenone (**32**).* A suspension of **31** (3.45 g, 7.40 mmol), potassium carbonate (1.42 g, 10.3 mmol), 18-crown-6 (0.10 g, 0.38 mmol), and dimethyl sulfate (1.08 g, 8.56 mmol) in acetone (30 ml) was refluxed for 2 h. To the reaction mixture was added conc. NH_4OH (2 ml), EtOAc and water. The organic layer was separated, washed with brine and dried over $MgSO_4$; the solvent was evaporated under reduced pressure. The crude product was suspended in hexane and filtered to afford **32** (3.36 g, 95%).

32: colorless needles; mp 83.0–84.0 °C (EtOH); NMR δ_H ($CDCl_3$): 7.82 (2H, d, J = 8.4 Hz), 7.33–7.41 (5H, m), 7.18–7.24 (3H, m), 7.04–7.07 (2H, m), 6.89 (2H, d, J = 8.4 Hz), 6.25 (2H, s), 6.03 (1H, ddt, J = 17.5, 10.6, 5.3 Hz), 5.40 (1H, ddt, J = 17.5, 2.1, 1.9 Hz), 5.29 (1H, ddt, J = 10.6, 2.1, 1.1 Hz), 5.04 (2H, s), 4.95 (2H, s), 4.57 (2H, ddt, J = 5.3, 1.9, 1.1 Hz), 3.67 (3H, s); NMR δ_C ($CDCl_3$): 193.3, 162.5, 161.2, 158.6, 157.4, 136.6, 136.5, 132.6, 131.7, 128.6, 128.3, 128.1, 127.5, 126.7, 118.0, 114.2, 112.1, 96.1, 93.0, 92.2, 70.3, 70.2, 68.8, 55.8; EIMS m/z (rel. int. %): 481 (M^+ +1, 16), 480 (M^+, 51), 463 (8), 439 (10), 257 (9), 161 (14), 91 (100), 43 (11); HREIMS m/z (M^+) calcd. for $C_{31}H_{28}O_5$, 480.1937; found, 480.1958.

*2,4-Dibenzyloxy-4′-hydroxy-6-methoxybenzophenone (**33**).* To a solution of **32** (0.53 g, 1.0 mmol) in dioxane (3 ml) and MeOH (3 ml) was added $Pd(PPh_3)_4$ (34 mg, 0.029 mmol) under an N_2 atmosphere. The solution was stirred for 10 min, K_2CO_3 (0.41 g, 3.0 mmol) was added, and stirring was continued for 20 h. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed.

The organic layer was separated and washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad. The solvent was evaporated under reduced pressure. The crude product was suspended in hexane and filtered to afford **33** (0.43 g, 98%).

33: amorphous white solid; mp 195.0–197.0 °C (EtOH); NMR δ_H (acetone-d_6): 9.12 (OH, brs), 7.70 (2H, d, $J = 8.7$ Hz), 7.35–7.51 (5H, m), 7.15–7.24 (5H, m), 6.90 (2H, d, $J = 8.7$ Hz), 6.51 (1H, d, $J = 2.0$ Hz), 6.44 (1H, d, $J = 2.0$ Hz), 5.17 (2H, s), 5.06 (2H, s), 3.69 (3H, s); NMR δ_C (acetone-d_6): 192.6, 162.6, 162.1, 159.4, 158.2, 138.0, 132.4, 131.9, 129.6, 129.3, 129.0, 128.8, 128.6, 128.3, 127.8, 115.9, 113.1, 94.0, 92.9, 70.8, 70.7, 56.1; EIMS m/z (rel. int. %): 441 ($M^+ +1$, 8), 440 (M^+, 30), 349 (7), 320 (4), 91 (100), 65 (5); HREIMS m/z (M^+) calcd. for $C_{28}H_{24}O_5$, 440.0998; found, 440.1659.

*2,4-Dibenzyloxy-4′-hydroxy-6-methoxybenzophenone 4′-(2,3,4,6-tetra-*O*-acetyl)-β-*D*-glucopyranoside (**34**).* A mixture of **33** (350 mg, 0.795 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bromide (653 mg, 1.59 mmol), $BnBu_3NCl$ (10.2 mg), K_2CO_3 (529 mg, 3.97 mmol) and CH_2Cl_2 (8 ml) was stirred at room temperature for 24 h. The reaction mixture was acidifed with aq. 2 M HCl and diluted with EtOAc. The organic layer was separated, washed with aq. sat. $NaHCO_3$, dried over $MgSO_4$, and evaporated under reduced pressure. Purification by flash column chromatography on silica gel ($CHCl_3$/acetone 15:1) afforded **34** (380 mg, 62%).

34: amorphous white solid; mp 152.5–154.5 °C (EtOH); $[\alpha]_D^{27}$ −11° (*c* 0.3, $CHCl_3$); NMR δ_H ($CDCl_3$): 7.82 (2H, d, $J = 8.9$ Hz), 7.33–7.41 (5H, m), 7.20–7.22 (3H, m), 7.04–7.07 (2H, m), 6.97 (2H, d, $J = 8.9$ Hz), 6.25 (2H, brs), 5.29 (1H, d, $J = 7.7$ Hz), 5.22 (2H, m) 5.16 (1H, dd, $J = 9.6$, 9.0 Hz), 5.05 (2H, s), 4.95 (2H, s), 4.28 (1H, dd, $J = 12.2$, 5.6 Hz), 4.15 (1H, dd, $J = 12.2$, 2.3 Hz), 3.89 (1H, m), 3.68 (3H, s), 2.10 (3H, s), 2.04 (9H, s); NMR δ_C ($CDCl_3$): 193.4, 170.5, 170.2, 169.3, 169.2, 161.4, 160.2, 158.7, 157.5, 136.4, 133.8, 131.6, 128.7, 128.3, 128.2, 127.7, 127.6, 126.7, 116.0, 106.1, 98.2, 96.1, 93.0, 92.1, 72.6, 72.2, 71.0, 70.3, 68.2, 63.9, 61.8, 55.8, 20.7, 20.6; FABMS (negative, TEA matrix) m/z (rel. int. %) 679 $[M - H]^-$ (8); HRFABMS m/z $[M - H]^-$ calcd. for $C_{35}H_{35}O_{14}$, 679.2027; found, 679.2033.

*2,4-Dibenzyloxy-4′-hydroxy-6-methoxybenzophenone 4′-O-β-*D*-glucopyranoside (**35**).* Compound **34** (100 mg, 0.130 mmol) was dissolved in MeOH (6 ml) and triethylamine (2 ml), and the solution stirred at room temperature for 30 h. To the reaction mixture was added toluene, and the solution evaporated to dryness. The crude product was suspended in $CHCl_3$ and filtered to afford **35** (78 mg, 98%).

35: colorless plates; mp 83.0–85.0 °C (EtOH); $[\alpha]_D^{27}$ −35° (*c* 0.3, $CHCl_3$); NMR δ_H ($CDCl_3$): 7.73 (2H, d, $J = 8.0$ Hz), 7.30–7.35 (5H, m), 7.08–7.11 (3H, m), 6.97 (2H, d, $J = 8.0$ Hz), 6.94–6.98 (2H, m), 6.20 (1H, brs), 6.18 (1H, brs), 4.98 (3H, s), 4.84 (2H, s), 3.75–3.82 (2H, m), 3.60–3.74 (3H, m), 3.52 (3H, s), 3.36–3.40 (1H, m); NMR δ_C ($CDCl_3$): 193.6, 161.4, 160.8, 158.6, 157.5, 136.5, 136.4, 133.2, 131.7, 128.6, 128.4, 128.1, 127.6, 126.7, 116.0, 105.4, 99.8, 96.1, 93.2, 92.2, 75.9, 75.1, 73.2, 70.2, 69.3, 65.5, 60.9, 55.7; FABMS (negative, TEA matrix) m/z (rel. int. %) 601 $[M - H]^-$ (1); HRFABMS m/z $[M - H]^-$ calcd. for $C_{34}H_{33}O_{10}$, 601.2074; found, 601.2092.

*2,4,4′-Trihydroxy-6-methoxybenzophenone 4′-O-β-*D*-glucopyranoside (**5**).* To a solution of **35** (57 mg, 0.095 mmol) in dioxane (3 ml) was added 10% Pd/C (20 mg), and the resulting suspension was stirred vigorously under a hydrogen atmosphere for 15 h at room temperature. The catalyst was filtered off through Celite, and the filtrate was evaporated under reduced pressure. The crude product was suspended in $CHCl_3$ and filtered to afford **5** (32.2 mg, 81%).

5: colorless prisms; mp 245.5–247.5 °C (EtOH); $[\alpha]_D^{27}$ −55° (*c* 0.3, MeOH); NMR δ_H (500 MHz, CD_3OD): 7.62 (2H, d, $J = 8.8$ Hz, H-2′ and H-6′), 7.10 (2H, d, $J = 8.8$ Hz, H-3′ and H-5′), 5.99 (2H, s, H-3 and H-5), 5.01 (1H, d, $J = 7.4$ Hz, H-1″), 3.89 (1H, dd, $J = 12.1$, 2.0 Hz, H-6″b), 3.69 (1H, dd, $J = 12.1$, 5.6 Hz, H-6″a), 3.54 (3H, s, OC*H*$_3$), 3.47–3.48 (3H, m, H-2″, H-3″ and H-5″), 3.39 (1H, dd, $J = 9.4$, 9.1 Hz, H-4″); NMR δ_C (CD_3OD): 198.1 (C=O), 164.2 (C-4[a]), 162.28 and 162.25 (C-2[a] and C-6[b]), 162.21 (C-4′[b]), 135.7 (C-1′), 132.0 (C-2′ and C-6′), 116.7 (C-3′ and C-5′), 107.7 (C-1), 101.6 (C-1″), 96.7 (C-5[c]), 92.2 (C-3[c]), 78.2 (C-5″), 77.9 (C-3″[d]), 74.8 (C-2″[d]), 71.3 (C-4″), 62.4 (C-6″), 55.8 (O*C*H$_3$) [signals with the same superscript may be interchangeable]; FABMS (negative, TEA matrix) m/z (rel. int. %) 421 $[M - H]^-$ (8); HRFABMS m/z $[M - H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1130.

*4′Allyloxy-4-benzyloxy-2-hydroxy-6-methoxybenzophenone (**36**).* To a stirred solution of **32** (1.06 g, 2.21 mmol) and $PhNMe_2$ (1.51 ml, 12.0 mmol) in CH_2Cl_2 (10 ml) was added powdered $AlCl_3$ (0.80 g, 6.0 mmol) at 0 °C. The solution was stirred for 20 min at 0 °C. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated and washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad. The solvent was evaporated under reduced pressure. The crude product was suspended in EtOH and filtered to afford **36** (0.71 g, 82%).

36: colorless needles; mp 118.5–119.5 °C (EtOH); NMR δ_H ($CDCl_3$): 11.81 (OH, brs), 7.57 (2H, d, $J = 8.9$ Hz), 7.33–7.45 (5H, m), 6.88 (2H, d, $J = 8.9$ Hz), 6.23 (1H, d, $J = 2.1$ Hz), 6.05 (1H, ddt, $J = 18.8$, 11.9, 5.3 Hz), 6.02 (1H, d, $J = 2.1$ Hz), 5.43 (1H, ddt, $J = 18.8$, 2.0, 1.5 Hz), 5.31 (1H, ddt, $J = 11.9$, 2.0, 1.3 Hz), 5.09 (2H, s), 4.59 (2H, ddt, $J = 5.3$, 1.5, 1.3 Hz), 3.51 (3H, s); NMR δ_C ($CDCl_3$): 197.3, 165.2, 164.9, 161.5, 161.4, 136.0, 133.9, 132.8, 130.8, 128.7, 128.3, 127.7, 118.0, 114.5, 113.5, 96.2, 94.6, 91.9, 70.3, 68.8, 55.1; EIMS m/z (rel. int. %): 391 ($M^+ +1$, 11), 390 (M^+, 46), 389 (21), 299 (8), 91 (100); HREIMS m/z (M^+) calcd. for $C_{24}H_{22}O_5$, 390.1467; found, 390.1462.

*4-Benzyloxy-2,4′-dihydroxy-6-methoxybenzophenone (**37**).* To a solution of **36** (0.55 g, 1.4 mmol) in dioxane (5 ml) and MeOH (5 ml) was added $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) under an N_2 atmosphere. The solution was stirred for 10 min, K_2CO_3 (0.97 g, 7.0 mmol) was added, and stirring was continued for 20 h. The reaction mixture was then diluted with EtOAc, poured into ice-cold aq. 2 M HCl and mixed. The organic layer was separated and washed with brine, dried over $MgSO_4$ and filtered through a silica-gel pad. The solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1) afforded **37** (0.44 g, 90%).

37: colorless prisms; mp 59.0–61.0 °C (EtOH); NMR δ_H ($CDCl_3$): 11.83 (OH, brs), 7.53 (2H, d, $J = 8.7$ Hz), 7.33–7.43 (5H, m), 6.80 (2H, d, $J = 8.7$ Hz), 6.24 (1H, d, $J = 2.3$ Hz), 6.03 (1H, d, $J = 2.3$ Hz), 5.43 (OH, brs), 5.09 (2H, s), 3.51 (3H, s); NMR δ_C ($CDCl_3$): 197.4, 165.2, 165.0, 161.5, 158.7, 135.9, 134.0, 131.1, 128.7, 128.4, 127.7, 114.4, 96.1, 94.6, 92.0, 70.3, 55.1; EIMS m/z (rel. int. %): 351 ($M^+ +1$, 11), 350 (M^+, 50), 349 (16), 259 (14), 91 (100); HREIMS m/z (M^+) calcd. for $C_{21}H_{18}O_5$, 350.1154; found, 350.1152.

*4′,6-Diacetoxy-4-benzyloxy-6-methoxybenzophenone (**38**).* A mixture of **37** (0.40 g, 1.14 mmol), triethylamine (0.80 ml, 5.7 mmol), DMAP (5 mg, 0.04 mmol) and acetic anhydride (0.30 ml, 3.4 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 1 h. The reaction mixture was added with toluene and evaporated to dryness. The crude product purified by flash column chromatography on silica gel (hexane/EtOAc 2:1) afforded **38** (0.50 g, 99%).

38: colorless prisms; mp 115.0–117.0 °C (hexane); NMR δ_H ($CDCl_3$): 7.65 (2H, d, $J = 8.0$ Hz), 7.20–7.27 (5H, m), 6.97 (2H, d, $J = 8.0$ Hz), 6.29 (2H, brs), 4.89 (2H, s), 3.47 (3H, s), 1.86 (3H, s), 1.79 (3H, s); NMR δ_C ($CDCl_3$): 191.2, 168.2, 161.0, 158.7, 154.1, 149.7, 135.9, 135.5, 130.5, 128.4, 128.0, 127.3, 121.2, 114.7, 100.9, 97.0, 95.9, 70.1, 57.5, 55.5, 20.1, 18.1; EIMS m/z (rel. int. %): 434 (M^+, 20), 392 (36), 259 (16), 91 (100); HREIMS m/z (M^+) calcd. for $C_{25}H_{22}O_7$, 434.1366; found, 434.1392.

*2,4′-Diacetoxy-4-hydroxy-6-methoxybenzophenone (**39**).* To a solution of **38** (0.47 g, 1.1 mmol) in dioxane (20 ml) was added 10% Pd/C (57 mg), and the resulting suspension was stirred vigorously overnight under a hydrogen atmosphere at room temperature. The catalyst was filtered off through Celite, and the filtrate was evaporated under reduced pressure. The crude product was suspended in hexane and filtered to afford **39** (0.31 g, 83%).

39: amorphous white solid; mp 132.0–134.0 °C (EtOH); NMR δ_H ($CDCl_3$): 7.82 (2H, d, $J = 8.6$ Hz), 7.15 (2H, d, $J = 8.6$ Hz), 6.28 (1H, brs), 6.24 (1H, brs), 3.56 (3H, s), 2.32 (3H, s), 1.98 (3H, s); NMR δ_C ($CDCl_3$): 192.9, 169.6, 168.9, 159.5, 159.2, 154.4, 149.7, 135.7, 131.1, 121.6, 113.6, 102.8, 97.3, 96.1, 55.8, 21.2, 20.6; EIMS m/z (rel. int.

%): 344 (M^+, 29), 259 (100), 167 (20), 43 (27); HREIMS m/z (M^+) calcd. for $C_{18}H_{16}O_7$, 344.0896; found, 344.0888.

*2,4′-Diacetoxy-4-hydroxy-6-methoxybenzophenone 4-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (**40**).* To a stirred solution of **39** (200 mg, 0.581 mmol) and *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) trichloroacetimidate (458 mg, 0.930 mmol) in dry CH_2Cl_2 (5 ml) was added $BF_3 \cdot OEt_2$ (1 drop) at 0 °C. The solution was stirred for 6 h at room temperature. The reaction mixture was diluted with EtOAc and successively washed with NH_4Cl and brine. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure. Purification by flash column chromatography on silica gel ($CHCl_3$/acetone 15:1) afforded **40** (284 mg, 73%).

40: colorless plates; mp 66.5–68.0 °C (EtOH); $[\alpha]_D^{27}$ −19° (*c* 0.3, MeOH); NMR δ_H ($CDCl_3$): 7.82 (2H, d, $J = 8.6$ Hz), 7.15 (2H, d, $J = 8.6$ Hz), 6.50 (1H, d, $J = 1.6$ Hz), 6.45 (1H, d, $J = 1.6$ Hz), 5.25–5.35 (2H, m), 5.17 (1H, d, $J = 7.6$ Hz), 5.12–5.21 (1H, m), 4.27 (1H, dd, $J = 12.3$, 5.4 Hz), 4.18 (1H, dd, $J = 12.3$, 2.0 Hz), 3.91 (1H, m), 3.68 (3H, s), 2.31 (3H, s), 2.09 (3H, s), 2.07 (3H, s), 2.06 (3H, s), 2.04 (3H, s), 1.98 (3H, s); NMR δ_C ($CDCl_3$): 191.4, 170.4, 170.1, 169.34, 169.3, 168.7, 168.5, 158.8, 158.7, 154.5, 149.6, 135.2, 130.9, 121.6, 117.1, 103.2, 99.1, 96.1, 72.6, 72.3, 71.0, 68.2, 62.0, 56.1, 21.5, 21.2, 20.7, 20.6; FABMS (negative, TEA matrix) m/z (rel. int. %) 674 $[M-H]^-$ (5); HRFABMS m/z $[M-H]^-$ calcd. for $C_{32}H_{34}O_{16}$, 674.1847; found, 674.17780.

*2,4,4′-Trihydroxy-6-methoxybenzophenone 4-O-β-D-glucopyranoside (**6**).* Compound **40** (136 mg, 0.20 mmol) was dissolved in MeOH (3 ml) and triethylamine (1 ml), and stirred at room temperature for 15 h. To the reaction mixture was added toluene, and the mixture evaporated to dryness. Purification by flash column chromatography on silica gel ($CHCl_3$/MeOH 5:1) afforded **6** (67 mg, 79%).

6: colorless plates; mp 110.0–112.0 °C (EtOH); $[\alpha]_D^{25}$ −35° (*c* 0.3, MeOH); NMR δ_H (500 MHz, CD_3OD): 7.63 (2H, d, $J = 8.8$ Hz, H-2′ and H-6′), 6.78 (2H, d, $J = 8.8$ Hz, H-3′ and H-5′), 6.35 (1H, d, $J = 2.0$ Hz, H-5), 6.30 (1H, d, $J = 2.0$ Hz, H-3), 4.92 (1H, d, $J = 7.4$ Hz, H-1″), 3.92 (1H, dd, $J = 12.0$, 2.2 Hz, H-6″b), 3.69 (1H, dd, $J = 12.0$, 6.1 Hz, H-6″a), 3.63 (3H, s, OCH_3), 3.44–3.49 (3H, m, H-2″, H-3″ and H-5″), 3.37 (1H, dd, $J = 9.4$, 9.1 Hz, H-4″); NMR δ_C (CD_3OD): 197.1 (C=O), 164.0 (C-4′), 162.1 (C-4), 160.6 (C-6), 158.8 (C-2), 133.2 (C-2′ and C-6′), 131.6 (C-1′), 116.0 (C-3′ and C-5′), 111.6 (C-1), 102.1 (C-1″), 97.8 (C-3), 93.3 (C-5), 78.4 (C-5″), 78.0 (C-3″), 74.8 (C-2″), 71.4 (C-4″), 62.6 (C-6″), 56.1 (OCH_3); FABMS (negative, TEA matrix) m/z (rel. int. %) 421 $[M-H]^-$ (4); HRFABMS m/z $[M-H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1138.

Extraction and isolation of phalerin from the fruits and leaves of P. macrocarpa.

(a) Plant material

Sliced dry fruits of *P. macrocarpa* were purchased from a local market in Yogyakarta, Indonesia, in 2006. The leaves of *P. macrocarpa* were collected in Yogyakarta, Indonesia, in 2009 and air dried. A voucher specimen was deposited at the Laboratory of Pharmacognosy-Phytochemistry, Faculty of Pharmacy, Sanata Dharma University, Yogyakarta.

(b) Extraction and isolation of phalerin

The sliced dry fruits of *P. macrocarpa* (2.94 g) were extracted with MeOH (10 ml) for 2 weeks at room temperature and filtered. The filtrate was concentrated to give a residue (0.444 g). The MeOH extract and synthesized **1**, **2** and **4**–**6** were developed on a silica gel TLC plate ($CHCl_3$/MeOH 3:1) by the technique of double spotting. One spot with the same R_f value of synthesized **2** was observed in the MeOH extract. There was, however, no corresponding spot to compounds **1** and **4**–**6** in the MeOH extract. By using synthesized **2** as a reference compound, the residue (0.444 g) was subjected to flash column chromatography on silica gel ($CHCl_3$/MeOH 3:1), and then applied to preparative TLC (1 mm thickness) on silica gel ($CHCl_3$/MeOH 3:1) to afford a white solid (28.8 mg):

colorless prisms; mp 101.8–103.5 °C (EtOH); $[\alpha]_D^{27}$ −18° (*c* 0.9, MeOH), −2.7° (*c* 0.15, EtOH); FABMS (negative, TEA matrix) m/z (rel. int. %) 421 $[M-H]^-$ (8); HRFABMS m/z $[M-H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1123. The ^{1}H- and ^{13}C-NMR data for the constituent were identical with those of synthesized **2**.

The dried leaves of *P. macrocarpa* (1.49 g) were extracted with MeOH (10 ml) for 2 weeks at room temperature and filtered. The filtrate was concentrated to give a residue (0.389 g). Under essentially the same conditions, the same compound (30.3 mg) was obtained:

colorless prisms; mp 101.5–103.2 °C (EtOH); $[\alpha]_D^{27}$ −14° (*c* 0.3, MeOH), −2.8° (*c* 0.3, EtOH); FABMS (negative, TEA matrix) m/z (rel. int. %) 421 $[M-H]^-$ (13); HRFABMS m/z $[M-H]^-$ calcd. for $C_{20}H_{21}O_{10}$, 421.1135; found, 421.1138. The ^{1}H- and ^{13}C-NMR data for the constituent were identical with those of synthesized **2**.

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