Reaction of β-Vinyl-*meso*-tetraphenylporphyrin with *o*-Quinone Methides

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Abstract: The hetero-Diels–Alder reaction of β-vinyl-*meso*-tetraphenylporphyrinatozinc(II) with quinone methides generated in situ from Knoevenagel reaction of 2-hydroxy-1,4-naphthoquinone, 4-hydroxycoumarin, and 4-hydroxy-6-methylcoumarin with paraformaldehyde and directly from *o*-hydroxybenzyl alcohol derivatives is reported.

Key words: porphyrin, *o*-quinone methide, naphthoquinone, coumarin, *o*-hydroxybenzyl alcohol, hetero-Diels–Alder

Porphyrins demonstrate promising applications in various scientific fields such as supramolecular chemistry, biomimetic models for photosynthesis, catalysis, and medicinal applications, namely as photosensitizers in the photodynamic therapy of tumors, in the treatment of age-related macular degeneration, and in the diagnosis of neoplastic diseases.[1] The modification of a porphyrin macrocycle leading to new derivatives, using functionalization procedures, especially pericyclic reactions,[2] plays a key role in finding promising compounds with potential use as photodynamic agents. 5,10-Dioxobenzo[*g*]chromene, 5,6-dioxobenzo[*h*]chromene,[3a] pyrano[3,2-*c*]coumarin,[4] and benzopyran[5] features are found in many natural products and are associated with antitumor,[3a] the treatment of Chagas disease,[3b] molluscicidal,[4a] K_{ATP} channel opening,[5a] and myocardial ischemia[5b] activities. Such motifs are being incorporated into newer scaffolds using the domino Knoevenagel hetero-Diels–Alder reaction.[6] In this context, the synthesis of molecules by coupling entities containing well-established pharmacological activities with porphyrins may be a good strategy for the discovery of new molecules with dual function potential.

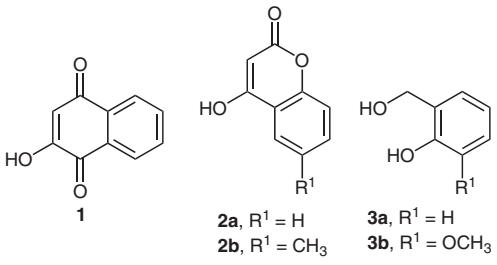

Figure 1 Precursors of *o*-quinone methides

Porphyrins have been shown to be versatile reagents in Diels–Alder reactions wherein a peripheral double bond acts as a dienophile[7] or the β-vinyl substituent of the macrocycle and the neighboring peripheral double bond act as a diene.[8] We report herein the hetero-Diels–Alder reaction of several *o*-quinone methides (*o*-QM) generated from 2-hydroxy-1,4-naphthoquinone (**1**, Lawsone), 4-hydroxycoumarin (**2a**), 4-hydroxy-6-methylcoumarin (**2b**), *o*-hydroxybenzyl alcohol (**3a**), and 2-hydroxy-3-methoxybenzyl alcohol (**3b**, Figure 1), with β-vinyl-*meso*-tetraphenylporphyrinatozinc(II) (**4**, Scheme 1).

The reaction of β-vinyl-*meso*-tetraphenylporphyrinatozinc(II)[9] (**4**) with the quinone methide **5**, generated in situ from 2-hydroxy-1,4-naphthoquinone (**1**) and paraformaldehyde, was performed in refluxing dioxane until complete disappearance of **4** (monitored by TLC).[10] Starting the reaction with one equivalent of **1** and eight equivalents of paraformaldehyde, it was observed that gradual addition of another two equivalents of **1** (1 equiv each time after 12 and 36 h of reaction) and paraformaldehyde, in the same ratio, was required for the reaction to reach completion after 48 hours. On workup of the reaction mixture and its purification by column and preparative thin-layer chromatography two new compounds were isolated; these were identified as the porphyrin derivatives **8** and **9** in 44% and 22% yield, respectively (entry 1, Table 1).

Table 1 Products and Yields of Reaction Using Vinyl Porphyrin **4** with *o*-Quinone Methides **5**, **6a**,**b**, and **7a**,**b**

Entry	Product	*o*-QM	Solvent	Time (h)	Yields (%)
1	**8** **9**	**5**	dioxane	48	44 22
2	**8** **9**	**5**	dioxane[a]	24	50 22
3	**10a**	**6a**	dioxane	1	88
4	**10b**	**6b**	dioxane	1	95
5	**11a** **11c**	**7a**	*o*-DCB[b]	26	49 8
6	**11b**	**7b**	*o*-DCB[b]	6	86

[a] Catalytic AcOH.
[b] *o*-DCB = *o*-Dichlorobenzene.

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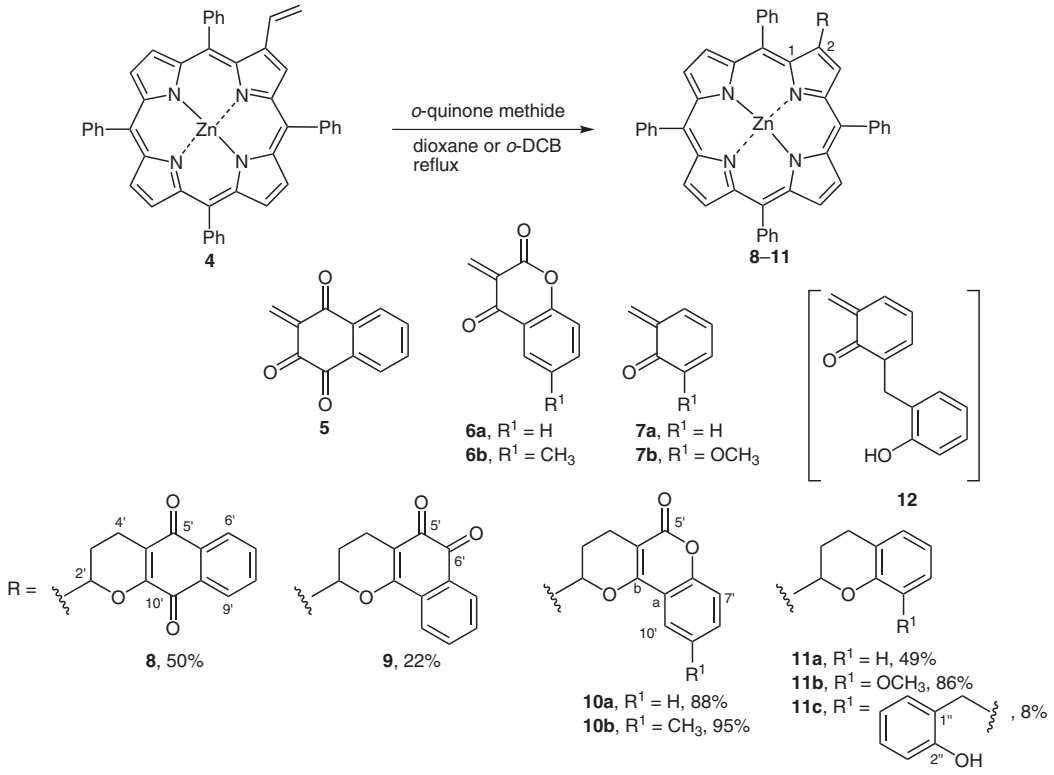

Scheme 1 Reactions of porphyrin **4** with the *o*-quinone methides

Attempts were carried out to reduce the reaction time of **4** with **5**. It was found that, by addition of a few drops of acetic acid[6c] and also by one addition, after 6 hours, of *o*-quinone methide precursors (**1** and paraformaldehyde, 1:8), the reaction was completed in 24 hours giving rise to compounds **8** and **9** in 50% and 22% yields, respectively (entry 2, Table 1).

This result shows that this reaction is highly regioselective and site-selective, as observed for similar systems.[6c,d,11]

The structures of the new porphyrin derivatives **8** and **9** were confirmed by NMR and UV/vis spectroscopy and high-resolution mass spectrometry.[12] The mass spectra of **8** and **9** show the same peak at *m/z* = 889.2143 and 889.2122, respectively, corresponding to the $[M + H]^+$ ion. The ^{1}H NMR of isomer **8** shows multiplets in the region δ = 2.12–2.79 ppm for the H-3′ and H-4′ protons and a doublet at δ = 4.95 ppm for the H-2′ proton. In the HSQC spectrum, the H-2′ proton correlates with the resonance at δ = 75.8 ppm which indicates the presence of a dihydropyran ring. The ^{1}H NMR spectrum of isomer **9** shows similarities with the one from **8** concerning the porphyrin macrocycle, pyran ring, and the aromatic signals of naphthoquinone part. Detailed analysis of the NMR spectra allowed us to assign the product with higher R_f as being isomer **8** and the other as the isomer **9**. The 2D HMBC clearly showed correlations of the aromatic protons (H-6′ and H-9′) of the naphthalene moiety with the carbonyl groups (C-5′ and C-10′) in **8** and the aliphatic (H-4′) and aromatic proton (H-7′) with the carbonyl groups (C-5′ and C-6′) in **9**.

This reaction was extended to 4-hydroxycoumarin (**2a**) and 4-hydroxy-6-methylcoumarin (**2b**). In these cases we observed that the *o*-quinone methides (**6a** and **6b**, Scheme 1) of these coumarins are more reactive than the *o*-quinone methide **5**. This is evident from the shorter reaction times and higher yields (entries 3 and 4, Table 1). The reaction of porphyrin **4** with intermediates **6a** and **6b** showed complete consumption of **4** in one hour (TLC), and after workup and column purification the adducts **10a**[13] (88% yield) and **10b** (95% yield) were isolated. In both cases just one equivalent of the corresponding quinone methide precursor was sufficient for reaction completion. The ^{1}H NMR spectra show similarities except for the appearance of a singlet for the methyl group at δ = 2.33 ppm in **10b**. The analysis of the ^{13}C NMR spectrum of **10a** indicated a peak at δ = 163.4 ppm for the coumarin carbonyl group. This shows that the addition occurred selectively at the 3,4-position of the coumarin nucleus. This was confirmed by HMBC correlation of the H-4′ protons with the carbonyl carbon C-5′ (δ = 163.4 ppm), the quaternary carbon C-10′b (δ = 160.7 ppm) and the C-2′ (δ = 75.9 ppm) of the dihydropyran ring.

A simple hetero-Diels–Alder reaction wherein the quinone methide can be formed in situ from the appropriately substituted *o*-hydroxybenzyl alcohols[14] was also studied. The reaction of porphyrin **4** with *o*-hydroxybenzyl alcohol (**3a**), which generates quinone methide **7a** (Scheme 1), in refluxing *o*-dichlorobenzene (*o*-DCB) and subsequent gradual addition of a further equivalent of the alcohol **3a** after 6 and 24 hours showed complete consumption of starting porphyrin **4** (26 h) and gave two new compounds,

which were separated by column and preparative thin-layer chromatography.[15]

The major product (with higher R_f) was identified as being the adduct **11a**[16] (49% yield). The product with lower R_f **11c**[17] (8% yield) showed a molecular ion at *m/z* = 914.2583. Its ^{1}H NMR spectrum shows a multiplet for 4 H at δ = 2.17–2.75 ppm, two doublets at δ = 3.79 and 3.92 ppm for 1 H each (J = 14.4 Hz) and a double doublet at δ = 4.97 ppm for 1 H. The aromatic region shows a double doublet at δ = 6.47 ppm (1 H), a double triplet at δ = 6.75 ppm (1 H), a triplet at δ = 6.84 ppm (1 H), a singlet for a phenolic proton at δ = 6.87 ppm, multiplet at δ = 6.93–6.97 ppm (2 H), and two double doublets at δ = 7.12 ppm and δ = 7.20 ppm for 1 H each, indicating there was addition of a second molecule of **3a**.

It was observed by TLC that compound **11c** is formed in the reaction mixture within two hours of reaction time. Therefore a reaction of compound **11a** with excess of alcohol **3a** was carried out under similar conditions, but it resulted in total recovery of starting material, thus indicating that **11a** is not a precursor of **11c**. Therefore the formation of this compound under the observed experimental conditions can be justified by the formation of the condensation dimer, 2,2′-dihydroxy-3-(hydroxymethyl)diphenylmethane, which has been previously identified by GC-MS analysis[18] as a product on heating alcohol **3a** above 200 °C. This dimer may form the quinone methide **12** in situ which can react with porphyrin **4** to give product **11c**.

Reaction of **4** and 2-hydroxy-3-methoxybenzyl alcohol **3b**, followed by three additions of one equivalent of that alcohol after one, three, and five hours gave compound **11b** (86% yield) after six hours reaction time.

In conclusion, the hetero-Diels–Alder reaction has been successfully used in the derivatization of β-vinyl-*meso*-tetraphenylporphyrin leading to macrocycles containing 5,10-dioxobenzo[*g*]chromene, 5,6-dioxobenzo[*h*]-chromene, pyrano[3,2-*c*]coumarin, and benzopyran motifs at the β-position. Studies on the reaction of these *o*-quinone methides with natural vinylporphyrins are under investigation in our laboratory.

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(10) **General Procedure for Preparing Compounds 8, 9, and 10a,b**
In a round-bottom flask, equipped with a magnetic stirring bar, a solution of 2-hydroxy-1,4-naphthoquinone (**1**, 6.2 mg, 35.5 μmol) [or 4-hydroxycoumarins (**2a**, 5.7 mg; **2b**, 6.2 mg; 35.5 μmol)], 1,4-dioxane (5 mL), paraformaldehyde (8.5 mg, 284 μmol), and porphyrin **4** (25 mg, 35.5 μmol) was heated at reflux until consumption of the starting porphyrin **4** (1–48 h). Quinone methide precursors were added at regular intervals. Dioxane was then removed under reduced pressure, $CHCl_3$ (50 mL) was added to the residue, and the mixture was washed with sat. aq $NaHCO_3$ (2 × 20 mL). The organic phase was concentrated under vacuum, and the residual crude product was purified by column chromatography on silica gel and subsequently by preparative TLC using $CHCl_3$ as the eluent.

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(12) Unequivocal proton and carbon assignments for all compounds were based on two-dimensional COSY, HSQC, and HMBC experiments.
Data for {2-(5,10-Dioxo-3,4,5,10-tetrahydro-2*H*-benzo[*g*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (8)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12–2.32 (m, 2 H, H-3′ and H-4′), 2.54–2.79 (m, 2 H, H-3′ and H-4′), 4.95 (d, J = 8.3 Hz, 1 H, H-2′), 7.49–7.54 (m, 1 H, H*p*-Ph), 7.65–7.76 (m, 13

H, H*m*,*p*-Ph, H-7′ and H-8′), 8.07–8.11 (m, 2 H, H-6′ and H-9′), 8.14–8.23 (m, 8 H, H*o*-Ph), 8.73 (d, *J* = 4.8 Hz, 1 H, H-β), 8.89 (d, *J* = 4.8 Hz, 1 H, H-β), 8.92 (d, *J* = 4.8 Hz, 1 H, H-β), 8.93 (s, 2 H, H-12 and H-13), 8.95 (d, *J* = 4.8 Hz, 1 H, H-β), 9.12 (s, 1 H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2 (C-4′), 29.4 (C-3′), 75.8 (C-2′), 120.4, 121.1, 121.2, 121.5, 121.7 (C-4′a and 2 C-quat), 126.0, 126.2, 126.3, 126.4, 126.6, 126.65, 126.7, 127.5, 128.3 (C*o*-Ph, C*m*,*p*-Ph, C-6′, C-9′), 131.1; 131.6, 132.0, 132.2, 132.2, 132.5 (C-β), 132.9 (C*o*-Ph, C-3), 133.0, 133.3, 133.8, 134.4, 134.42, 134.7 (C-7′, C-8′, C*o*-Ph, C*m*,*p*-Ph), 142.5, 142.6, 142.7,143.3 (C-1), 145.8, 147.9, 150.3, 150.4, 150.5, 150.6, 150.9, 156.2 (C-10a′), 179.5 (C-5′), 184.5 (C-10′); UV/vis ($CHCl_3$): λ_{max} (log ε) = 424 (4.94), 554 (4.57), 597 (3.96) nm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{57}H_{37}N_4O_3Zn$: 889.2152; found: 889.2143.

Data for {2-(5,6-Dioxo-3,4,5,6-tetrahydro-2*H*-benzo[*h*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (9)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.16–2.24 (m, 2 H, H-3′ and H-4′), 2.58–2.61 (m, 1 H, H-3′), 2.71–2.75 (m, 1 H, H-4′), 5.08 (d, *J* = 10.2 Hz, 1 H, H-2′), 7.47–7.51 (m, 2 H, H-8′, 1 H*p*-Ph), 7.55 (dt, *J* = 7.6, 1.6 Hz, 1 H, H-9′), 7.71–7.81 (m, 12 H, H*m*,*p*-Ph, H-10′), 8.09 (dd, *J* = 7.6, 1.3 Hz, 1 H, H-7′), 8.16–8.24 (m, 8 H, H*o*-Ph), 8.76 (d, *J* = 4.6 Hz, 1 H, H-β), 8.91 (d, *J* = 4.6 Hz, 1 H, H-β), 8.95 (s, 2 H, H-12 and H-13), 8.96 (d, *J* = 4.6 Hz, 1 H, H-β), 8.97 (d, *J* = 4.6 Hz, 1 H, H-β), 9.14 (d, *J* = 0.7 Hz, 1 H, H-3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.8 (C-4′), 29.8 (C-3′), 76.9 (C-2′), 114.2 (C-4′a), 120.4, 121.1, 121.4, 121.7, 124.2 (C-10′), 126.4, 126.5, 126.6, 126.7, 127.6, 127.7 (C*m*,*p*-Ph), 128.6, 128.7 (C*m*,*p*-Ph, C-7′), 129.9 (C-6′a), 130.6 (C-8′), 131.8, 132.27, 132.30, 132.33, 132.4, 132.43 (C-β), 132.6 (C-3, C-10′a), 133.4, 133.5, 134.36, 134.4, 134.42; 134.5 (C-*o*), 134.75 (C-9′), 142.3, 142.5, 142.7, 143.2 (C-1), 145.5, 147.7, 150.21, 150.4, 150.57, 150.6, 150.7, 150.8, 163.6 (C-10b′), 178.7 (C-5′), 179.7 (C-6′); UV/vis ($CHCl_3$): λ_{max} (log ε): 424 (4.85), 552 (4.52), 596 (3.96) nm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{57}H_{37}N_4O_3Zn$: 889.2152; found: 889.2122.

(13) **Data for {2-(5-Oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (10a)**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25–2.29 (m, 2 H, H-3′ and H-4′), 2.61–2.67 (m, 2 H, H-3′ and H-4′), 5.04 (d, *J* = 8.5 Hz, 1 H, H-2′), 7.19 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1 H, H-9′), 7.34 (dd, *J* = 8.5, 1.0 Hz, 1 H, H-7′), 7.40–7.45 (m, 1 H, H*p*-Ph), 7.49 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1 H, H-8′), 7.71–7.81 (m, 12 H, H*m*,*p*-Ph, H-10′), 8.16–8.23 (m, 8 H, H*o*-Ph), 8.75 (d, *J* = 4.6 Hz, 1 H, H-β), 8.90 (d, *J* = 4.6 Hz, 1 H, H-β), 8.94 (s, 2 H, H-12 and H-13), 8.95 (d, *J* = 4.6 Hz, 1 H, H-β), 8.97 (d, *J* = 4.6 Hz, 1 H, H-β), 9.15 (d, *J* = 0.5 Hz, 1 H, H-3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9 (C-3′), 30.0 (C-4′), 75.9 (C-2′), 101.2 (C-4′a), 115.9 (C-10′a), 116.5 (C-7′), 120.5, 121.1, 121.3, 121.6, 122.5 (C-10′), 123.7 (C-9′), 126.4, 126.5, 126.6, 126.7, 127.6, 127.7, 128.5 (C*m*,*p*-Ph), 131.2 (C-8′), 131.7, 132.3, 132.35, 132.6 (C-β), 133.4, 133.5, 134.37, 134.4, 134.42, 134.47, 134.5 (C*o*-Ph), 142.3, 142.4, 142.5, 142.7, 143.5 (C-1), 145.6, 147.8, 150.2, 150.4, 150.5, 150.6, 150.9, 152.4 (C-6′a), 160.7 (C-10′b), 163.4 (C-5′). UV/vis ($CHCl_3$): λ_{max} (log ε): 425 (4.94), 555 (4.54), 596 (4.00) nm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{56}H_{37}N_4O_3Zn$: 877.2152; found: 877.2116.

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(15) **General Procedure for Preparing 11a–c**

A mixture of porphyrin **4** (10 mg, 14.2 μmol) and appropriate benzyl alcohol (**3a**, 1.7 mg; **3b**, 2.2 mg; 14.2 μmol) was refluxed in *o*-dichlorobenzene (3 mL) in a sealed tube until consumption of starting porphyrin **4** (monitored by TLC) with addition of quinone methide precursors at regular intervals. After completion of reaction (6–26 h) the mixture was loaded on a silica column or preparative TLC plate and eluted with PE. Further elution with $CHCl_3$ gave the corresponding adducts.

(16) **Data for [2-(Chroman-2-yl)-5,10,15,20-tetraphenylporphyrinato]zinc(II) (11a)**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14–2.26 (m, 1 H, H-3′), 2.43–2.55 (m, 1 H, H-3′), 2.56–2.74 (m, 2 H, H-4′), 4.95 (d, *J* = 9.6 Hz, 1 H, H-2′), 6.85–6.94 (m,2 H, H-6′ and H-8′), 7.07–7.21 (m, 2 H, H-5′ and H-7′), 7.53–7.59 (m, 1 H, H*p*-Ph), 7.68–7.80 (m, 11 H, H*m*,*p*-Ph), 8.15–8.23 (m, 8 H, H*o*-Ph), 8.73 (d, *J* = 4.7 Hz, 1 H, H-β), 8.89 (d, *J* = 4.7 Hz, 1 H, H-β), 8.91 (d, *J* = 4.7 Hz, 1 H, H-β), 8.92 (s, 2 H, H-12 and H-13), 8.95 (d, *J* = 4.7 Hz, 1 H, H-β), 9.16 (s, 1 H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2 (C-4′), 31.7 (C-3′), 74.2 (C-2′), 117.1 (C-8′), 120.0 (C-6′), 120.6, 120.9, 121.1, 121.5, 122.1 (C-4′a), 126.1, 126.5, 126.55, 127.0, 127.5, 128.1 (C-7′, C*m*,*p*-Ph), 129.5 (C-5′), 131.5, 131.9, 132.0, 132.1, 132.4, 132.5 (C-β), 133.3, 133.7, 134.3, 134.4, 134.42, 134.6 (C*o*-Ph), 142.6, 142.7, 142.8, 145.9, 146.5 (C-1), 148.4, 150.0, 150.2, 150.3, 150.5, 150.9, 155.6 (C-8′a). UV/vis ($CHCl_3$): λ_{max} (log ε): 420 (4.98), 548 (4.59) nm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{53}H_{37}N_4Ozn$: 809.2253; found: 809.2273.

(17) **Data for {2-[8-(2-Hydroxybenzyl)chroman-2-yl)]-5,10,15,20-tetraphenylporphyrinato}zinc(II) (11c)**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17–2.75 (m, 4 H, H-3′and H-4′), 3.79 (d, *J* = 14.4 Hz, 1 H, CH_2), 3.92 (d, *J* = 14.4 Hz, 1 H, CH_2), 4.97 (dd, *J* = 10.4, 1.1 Hz, 1 H, H-2′), 6.47 (dd, *J* = 8.0, 1.1 Hz, 1 H, H-3″), 6.75 (dt, *J* = 7.5, 1.1 Hz, 1 H, H-5″), 6.84 (t, *J* = 7.4 Hz, 1 H, H-6′), 6.87 (s, 1 H, OH), 6.93–6.97 (m, 2 H, H-5′ and H-4″), 7.12 (dd, *J* = 7.4, 1.4 Hz, 1 H, H-7′), 7.20 (dd, *J* = 7.5, 1.6 Hz, 1 H, H-6″), 7.52–7.55 (m, 1 H, H*p*-Ph), 7.66–7.76 (m, 11 H, H*m*,*p*-Ph), 8.17–8.33 (m, 8 H, H*o*-Ph), 8.77 (d, *J* = 4.7 Hz, 1 H, H-β), 8.89 (d, *J* = 4.7 Hz, 1 H, H-β), 8.93 (s, 2 H, H-β), 8.95 (s, 2 H, H-β), 9.26 (s, 1 H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.3 (C-4′), 30.5 (CH_2), 31.2 (C-3′), 75.3 (C-2′), 116.4 (C-3″), 120.3 (C-5″), 120.6, 120.8 (C-6′), 121.07, 121.13, 121.4, 122.2 (C-4′a), 126.2, 126.4, 126.5 (C*m*,*p*-Ph), 127.0 (C*m*,*p*-Ph, C-1″), 127.5, 127.6, 127.8 (C-8′), 128.1 (C-4″, C-7′, C-5′, C*m*,*p*-Ph), 128.2, 130.4 (C-6″), 130.5; 131.5, 132.06, 132.1, 132.2, 132.4 (C-β), 132.8 (C-3), 133.4, 133.6, 134.4, 134.5, 134.9 (C*o*-Ph), 142.8, 142.9, 144.9, 145.8, 148.1, 150.2, 150.2, 150.4, 150.4, 150.5, 150.8, 151.6 (C-8′a), 154.0 (C-2″). UV/vis ($CHCl_3$): λ_{max} (log ε): 420 (5.72), 547 (4.59) nm. HRMS (ESI$^+$): *m/z* [M]$^+$ calcd for $C_{60}H_{42}N_4O_2Zn$: 914.2594; found: 914.2583.

(18) Dorrestijn, E.; Kranenburg, M.; Ciriano, M. V.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 3012.