Facile preparation of novel β-substituted metalloporphyrins via Suzuki cross-coupling reaction

Rainer Gauler, Ralf Keuper, Andreas Winter*, and Nikolaus Risch

Department Chemie, Fakultät für Naturwissenschaften, Universität Paderborn,
Warburger Straße 100, D-33098 Paderborn, Germany
E-mail: awi@chemie.uni-paderborn.de

Dedicated to Prof. Dr. Karsten Krohn on the occasion of his 60th birthday

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Abstract

The Suzuki cross-coupling reaction of the porphyrin-zinc(II) complexes **1** and **2** and boronic ester **3a** and various boronic acids **3b–l** provided novel substituted porphyrins. These have been designed as building blocks in the synthesis of new photosensitizers for the photodynamic therapy (PDT) and for the preparation of porphyrin-containing supramolecular assemblies.

Keywords: Porphyrins, boronic acids, Suzuki cross-coupling, palladiumPd(0)-catalyzed C-C coupling

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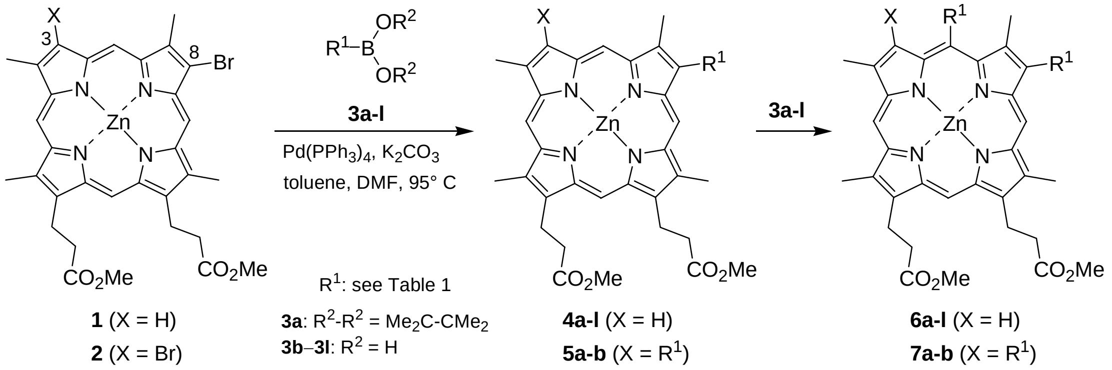
Introduction

The continuing interest in porphyrins and metalloporphyrins has encompassed areas in organometallic chemistry,[1] material sciences,[2] and photodynamic therapy (PDT).[3] In the field of PDT research C–C linked porphyrin-oligomers have been shown to be efficient photosensitizers in vivo,[4-6] especially those possessing a substitution pattern related to that of the natural tetrapyrrole derivatives (e.g. hemato- or protoporphyrin).[5,6]

Palladium-mediated cross-coupling reactions of aryl halides with arylboronic acids (Suzuki coupling) are versatile methods for the synthesis of biaryls under mild reaction conditions.[7] Furthermore, the Suzuki cross-coupling is largely unaffected by the presence of water, the reaction tolerates a broad range of functionalities, and yields non-toxic by-products. In spite of all these advantages only a few examples[8] of this coupling reaction in the field of porphyrin synthesis have been described in the literature.

Results and Discussion

To the best of our knowledge we describe the first application of the Suzuki reaction for the modification of such "natural porphyrins".[9] The metalloporphyrins **1** (ZnBrDPDME, zinc(II)-monobromodeuteroporphyrin dimethylester) and **2** ($ZnBr_2DPDME$, zinc(II)-dibromodeutero-porphyrin dimethylester) easily obtainable from heme (inexpensive natural porphyrin source)[10,11] were subjected to the reaction with boronic ester **3a** and boronic acids **3b–l** (Scheme 1).



Scheme 1. Suzuki reaction of ZnBrDPDME (**1**) and $ZnBr_2DPDME$ (**2**).

The results of our experiments are summarized in Table 1. It is desirable to synthesize tetrapyrroles **4–7** with a great diversity of functional groups. Porphyrins linked by aryl spacers are the subject of many reports.[11,12] In this connection **4g,h,j** represent important key intermediates in the preparation of dimeric or oligomeric porphyrins by cross-coupling reactions.

Upon reaction of **1** with 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **3a** (entry 1, Table 1) a polar by-product was obtained, the porphyrin dimer **8** (Figure 1) as revealed by FAB mass spectrometry ($C_{67}H_{66}N_8O_8Zn_2$ (1242.07); FAB-MS (NBA): *m/z* (%) 1238.32 (17) [M^+, ^{64}Zn]). The unexpected formation of **8** can be explained by a Heck reaction of the Suzuki cross-coupling product **4a** with boronic ester **3a**. Remarkably, this reaction occurred using a stochiometric mixture of **1** and **3a** indicating, that in this case the Heck reaction is much faster than the desired Suzuki cross-coupling reaction. Further investigations will show whether this method is suited for a highly efficient one-pot synthesis of coupled porphyrins.

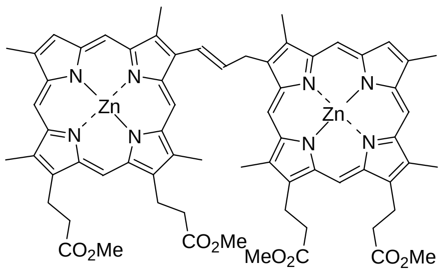


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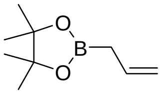
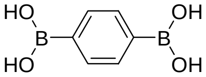
Figure 1. Dimeric metalloporphyrin **8** formed by Suzuki cross-coupling and Heck reactions.

Table 1. Results of the Suzuki cross-coupling reaction of **1** and **2** with boronic ester **3a** and boronic acids **3b–l**

Entry	Metallo-porphyrin	Boronic acid **3**, R^1 (R^2 = H, except **3a**)	Reaction conditions	Product / Yield [%][a]
1	**1**	**3a**[b] 	95 °C / 15 h	**4a** / 46
2	**1**	**3b**, $\text{-CH=CH-C}_5\text{H}_{11}$	95 °C / 10 h	**4b** / 79
3	**1**	**3c**, phenyl	95 °C / 15 h	**4c** / 60
4	**1**	**3d**, 1-naphthyl	95 °C / 14 h	**4d** / 46 **6d** / 49
5	**1**	**3e**, 3-nitrophenyl	95 °C / 48 h	**4e** / 35
6	**1**	**3f**, 3-(trifluoromethyl)phenyl	95 °C / 48 h	**4f** / 55 **6f** / 42
7	**1**	**3g**. 3-bromophenyl	95 °C / 48 h	**4g** / 21
8	**1**	**3h**, 4-bromophenyl	95 °C / 48 h	**4h** / 27
9	**1**	**3i**, 4-fluorophenyl	95 °C / 14 h	**4i** / 66 **6i** / 32
10	**1**	**3j**, 4-vinylphenyl	95 °C / 24 h	**4j** / 41 **6j** / 35
11	**1**	**3k**, 4-methoxyphenyl	95 °C / 18 h	**4k** / 99
12	**1**	**3l** 	95 °C / 48 h	–[c]
13	**2**	**3j**, 4-vinylphenyl	95 °C / 18 h	**5a** / 35 **7a** / 28
14	**2**	**3k**, 4-methoxyphenyl	95 °C / 15 h	**5b** / 68 **7b** / 19

[a] Isolated yield after flash column chromatography on SiO_2 (eluent: CH_2Cl_2).

[b] Boronic ester, 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

[c] No 1,4-phenyl-tethered product could be isolated.

Using boronic acids **3d**, **3f**, **3i–k** (Table 1, entries 4, 6, 9, 10, 13 and 14) in the reactions with **1** and **2** we were able to isolate compounds **6** and **7** from the crude product mixture by flash chromatography (Scheme 1). These products show greater R_f values in comparison with porphyrins **4** and **5**. The ^{1}H NMR spectra of these compounds indicate unequivocally that one of the four possible *meso*-positions (positions 5, 10, 15 or 20) has been substituted by an aromatic substituent R^1. Comparison with recently published experimental data (COSY NMR) leads us to suggest that position 5 has been substituted selectively.[13] Obviously, substitution is only possible if the reactivity of the metalloporphyrins **1** and **2** is enhanced by a preceding substitution at the 3- and/or 8-position (β-pyrrole position). This observation was verified by the failure of the reaction of Zn(II)-deuteroporphyrin dimethylester (ZnDPDME) and **3j**; in this case a Pd(0)-catalyzed substitution occurred in neither position.

The direct formation of a phenyl-tethered bis(porphyrin) by using 4-(dihydroxyboryl)-phenylboronic acid (**3l**) failed (Table 1, entry 12). We isolated only a mixture of oligomeric porphyrinoids; the elucidation of their constitution is still under investigation.

With boronic acids **3g** and **3h** the yields of the expected products **4g** and **4h** are rather low (Table 1, entries 7 and 8), presumably due to a further Suzuki cross-coupling reaction of the bromophenyl-substituted metalloporphyrins. The appearance of small amounts of a 3-/8-bromobiphenyl-substituted porphyrin supports this assumption.

Experimental Section

General Procedures. All reagents were purchased from commercial sources and used without prior purification unless specified. ZnBrDPDME (**1**) and ZnBr2DPDME (**2**) were obtained from heme as published previously.[10,11] All solvents were dried and distilled according to standard procedures and stored under argon. Chromatographic separation was performed on silica gel (Merck, 0.04–0.063 mm). Melting points were obtained on a Büchi SMP-20 mp apparatus. NMR spectra were recorded on a Bruker ARX 200 instrument (^{1}H at 200 MHz, ^{13}C at 50 MHz) with TMS as internal standard. FAB mass spectrometry was carried out using a VG Autospec apparatus (glycerine/NBA/CsI-matrix, 30 keV). UV/Vis-spectra were measured on a Shimadzu 2101 spectrometer. Elemental analyses were obtained on a Perkin-Elmer M2400 analyzer.

General procedure for Suzuki cross-coupling reaction

The solution of the metalloporphyrin **1** or **2** (0.21 mmol), potassium carbonate (136 mg, 1.6 mmol), tetrakis(triphenylphosphine)palladium(0) (23 mg, 10 mol%) and boronic acid ester **3a** or a boronic acid **3b–l** (0.8 mmol) in a mixture of dry DMF (5 mL) and toluene (5 mL) was heated at 95 °C for 18 h in an atmosphere of argon. After cooling to room temperature water (40 mL) was added, and the solution was extracted with dichloromethane (4 x 50 mL). The combined organic layers were washed with water (3 x 30 mL), dried over sodium sulphate, and the solvent was removed under reduced pressure. Small amounts of DMF and toluene in the oily residue were removed under high vacuum. The resulting crude product, a brown solid was dissolved in a minimal volume of dichloromethane and purified by flash chromatography on silica gel (eluent: CH_2Cl_2) collecting fractions of approx. 10 mL.

Zinc(II) 8-allyldeuteroporphyrin dimethylester (4a). According to the conditions of the General Procedure the reaction of metalloporphyrin **1** (136 mg, 0.21 mmol) and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**) (51 mg, 0.3 mmol) resulted in the isolation of **4a** (58 mg, 46%) as a red-violet solid, mp 189–191 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.01–3.12 (m, 4 H, $13^{2}/17^{2}$-CH_2), 3.25–3.54 (m, 12 H, $CH_{3,pyr}$), 3.64–3.67 (m, 6 H, CO_2CH_3), 4.04–4.21 (m, 4 H, $13^{1}/17^{1}$-CH_2), 4.41–4.59 (m, 2 H, $8^{1}/3^{1}$-CH_2), 5.10–5.31 (m, 2 H, $8^{3}/3^{3}$-ABX-$CH_{2,vinyl}$), 6.36–6.49 (m, 1 H, $8^{2}/3^{2}$-ABX-$CH_{,vinyl}$), 8.66, 8.77 (s, 1 H, 3(8)-$CH_{\beta\text{-}pyr}$), 9.21–9.47 (m, 4 H, H_{meso}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.36, 11.42, 11.64, 11.74 (q, $2^{1}/7^{1}$, 12^{1}, 17^{1}-CH_3), 13.65, 13.68 (q, $7^{1}/2^{1}$-CH_3), 21,85, 21.98 (t, $13^{1}/17^{1}$-CH_2), 30.61, 30.89 (t, $3^{1}/8^{1}$-CH_2), 37.34 (t, $13^{2}/17^{2}$-CH_2), 52.12 (q, $13^{3}/17^{3}$-OCH_3), 95.47, 95.63, 96.22, 96.46, 96.72, 96.97, 99.67 (d, 5, 10, 15, 20-CH), 115.34, 115.49 (t, $3^{3}/8^{3}$-CH_2), 128.65, 128.82 (d, 8/3-CH), 138.58, 138.65 (d, $8^{2}/3^{2}$-CH), 135.94, 136.01, 136.12, 136.20, 136.46, 136.62, 136.71, 136.82, 136.91, 137.72, 137.92, 138.11, 138.20, 139.43, 139.43, 139.64, 140.02, 145.65, 145.71, 145.83, 145.95, 146.17, 146.54, 146.66, 146.92, 147.05, 147.18, 147,28 (s, C_{quart}), 174.11, 174.14 ($13^{3}/17^{3}$-CO_2Me). UV/VIS (CH_2Cl_2): λ_{max} (lg ε) 567 (4.326), 531 (4.222), 402 (5.559), 326 (4.251). FAB-MS (NBA): *m/z* (%) 640.12 (100) [M^{+}, ^{64}Zn]. Anal. Calcd for $C_{35}H_{36}N_4O_4Zn$ (642.07) C, 65.52; H, 5.73; N, 8.69. Found C, 65.18; H, 5.53; N, 8.39.

Zinc(II) 8-allyldeuteroporphyrin dimethylester (4b). Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3b** (114 mg, 0.8 mmol) afforded **4b** (110 mg, 79%) as a red-violet solid, mp 178–180 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.13 (t, 3 H, *J* = 7 Hz, $3^{7}/8^{7}$-CH_3), 1.61–1.83 (m, 4 H, $3^{5}/8^{5}$, $3^{6}/8^{6}$-CH_2) 1.88–1.95 (m, 2 H, $3^{4}/8^{4}$-CH_2), 2.71–2.89 (m, 2 H, $3^{3}/8^{3}$-CH_2), 3.00–3.14 (m, 4 H, $13^{2}/17^{2}$-CH_2), 3.31–3.55 (m, 12 H, $CH_{3,pyr}$), 3.64–3.66 (m, 6 H, CO_2CH_3), 4.08–4.24 (m, 4 H, $13^{1}/17^{1}$-CH_2), 6.62–6.86 (m, 1 H, $8^{2}/3^{2}$-CH_{vinyl}), 7.61, 7.70 (d, 1 H, *J* = 16.87 Hz, *J* = 16.63 Hz, $3^{1}/8^{1}$-CH_{vinyl}), 8.61, 8.72 (s, 1 H, 8/3-$CH_{\beta\text{-}pyr}$), 9.17–9.52 (m, 4 H, H_{meso}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.40, 11.49, 11.67, 11.90, 12.49, 12.59, 13.54 (q, $CH_{3,Pyr}$), 14.87 (q, $3^{7}/8^{7}$-CH_3), 21.77 (t, $13^{1}/17^{1}$-CH_2), 23.41 (t, $3^{6}/8^{6}$-CH_2), 30.61 (t, $3^{5}/8^{5}$-CH_2), 32.41 (t, $3^{4}/8^{4}$-CH_2), 35.16, 35.23 (t, $3^{3}/8^{3}$-CH_2), 37.27 (t, $13^{2}/17^{2}$-CH_2), 52.04 (q, $13^{3}/17^{3}$-OCH_3), 95.04, 95.19, 96.10, 96.27, 96.89, 99.54 (d, CH_{meso}), 123.35, 123.58 (d, $3^{2}/8^{2}$-CH_{vinyl}), 128.35, 128.47 (d, 8/3-$CH_{\beta\text{-}pyr}$), 137.04, 137.22 (d, $8^{1}/3^{1}$-CH), 134.35, 134.83, 135.71, 135.75, 136.03, 136.13, 136,34, 136.55, 137.51, 137.96, 139.21, 139.75, 145.09, 145.19, 145.40, 140.52, 145.52, 145.80, 145.96. 146.00, 146.36, 146.58, 146.74, 146.84, 146.99, 147.04 (s, C_{quart}), 174.06, 174.09 ($13^{3}/17^{3}$-CO_2Me). UV/VIS (CH_2Cl_2): λ_{max} (lg ε) 572 (4.028), 535 (3.903), 404 (5.051). FAB-MS (NBA): *m/z* (%) 696.14 (23) [M^{+}, ^{64}Zn]. Anal. Calcd for $C_{39}H_{44}N_4O_4Zn$ (698.18) C, 67.09; H, 6.35; N, 8.02. Found C, 66.78; H, 6.24; N, 8.07.

Zinc(II) 8-phenyldeuteroporphyrin dimethylester (4c). Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3c** (98 mg, 0.8 mmol) yielded **4c** (81 mg, 60%) as a red-violet solid, mp 186–187 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.10–3.18 (t, 4 H, *J* = 7.72 Hz, $13^{2}/17^{2}$-CH_2), 3.42–3.65 (m, 18 H, CO_2CH_3, $CH_{3,pyr}$), 4.10–4.32 (m, 4 H, $13^{1}/17^{1}$-CH_2), 7.76 (d, 1 H, *J* = 7.46 Hz, CH_{aryl}), 7.90 (dd, 2 H, *J* = 7.46 , *J* = 7.12 Hz, CH_{aryl}), 8.20 (d, 2 H, *J* = 7.12 Hz, CH_{aryl}), 8.96 (s, 1 H, 8/3-$H_{\beta\text{-}pyr}$), 9.58, 9.74, 9.89, 9.97 (s, 4 H, H_{meso}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.64, 11.66, 13.99, 14.22 (q, 2^{1}, 7^{1}, 12^{1}, 17^{1}-CH_3), 21.72 (t, $13^{1}/17^{1}$-CH_2), 37.15 (t, $13^{2}/17^{2}$-CH_2), 52.06 (q, OCH_3), 95.18, 97.11, 99.82, 100.26 (d, 5, 10, 15, 20-CH), 127.58, 129.18, 132.82 (d, CH_{aryl}), 129.06 (d, 8(3)-CH), 136.18, 136.37, 136.55, 137.16, 137.93, 138.20, 141.41, 145.89, 146.02, 146.11, 146.75, 146.86, 147.27, 147.38, 148.24 (s, $\mathrm{C_{quart}}$), 174.02 ($13^3/17^3$-$\mathrm{CO_2Me}$). UV/VIS ($\mathrm{CH_2Cl_2}$): λ_{max} (lg ε) 570 (4.316), 533 (4.235), 405 (5.325). FAB-MS (NBA): *m/z* (%) 676.08 (29) [$\mathrm{M^+}$, $^{64}\mathrm{Zn}$]. Anal. Calcd for $\mathrm{C_{38}H_{36}N_4O_4Zn}$ (678.11) C, 67.31; H, 5.35; N, 8.26. Found C, 66.98; H, 5.14; N, 8.05.

Zinc(II) 8-(naphth-1-yl)deuteroporphyrin dimethylester (4d) and **Zinc(II) 5,8-di(naphth-1-yl)deuteroporphyrin dimethylester (6d).** Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3d** (138 mg, 0.8 mmol) gave **4d** (82 mg, 46%) as a brown-violet solid, mp 197–201 °C (dec.) and **6d** (100 mg, 49%) as a brown-violet solid, mp 221–227 °C (dec.).

4d. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.26–3.35 (m, 4 H, $13^2/17^2$-$\mathrm{CH_2}$), 3.49–3.82 (m, 18 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.41–4.55 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.36–7.46 (m, 1 H, $\mathrm{CH_{aryl}}$), 7.54–7.74 (m, 1 H, $\mathrm{CH_{aryl}}$), 7.92–8.03 (m, 2 H, $\mathrm{CH_{aryl}}$), 8.13–8.32 (m, 3 H, $\mathrm{CH_{aryl}}$), 9.09 (s, 1 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$), 9.85, 10.07, 10.15, 10.33 (s, 4 H, $\mathrm{H}_{\mathit{meso}}$).

6d. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.28 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.32–3.46 (m, 7 H, $13^2/17^2$-$\mathrm{CH_2}$, $\mathrm{CH_{3,pyr}}$), 3.64 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.74–3.81 (m, 9 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.42–4.56 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.20–8.35 (m, 14 H, $\mathrm{CH_{aryl}}$), 9.86, 10.05, 10.21, 10.39 (s, 4 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$, $\mathrm{H}_{\mathit{meso}}$).

Zinc(II) 8-(3-nitrophenyl)deuteroporphyrin dimethylester (4e). Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3e** (136 mg, 0.8 mmol) furnished **4e** (50 mg, 35%) as a red-violet solid, mp 188–193 °C (dec.). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.12–3.19 (m, 4 H, $13^2/17^2$-$\mathrm{CH_2}$), 3.39–3.61 (m, 18 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.08–4.33 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.41–7.47 (m, 1 H, $\mathrm{CH_{aryl}}$), 7.66–7.69 (m, 1 H, $\mathrm{CH_{aryl}}$), 8.01–8.05 (m, 1 H, $\mathrm{CH_{aryl}}$), 8.17 (s, 1 H, $\mathrm{CH_{aryl}}$), 8.95 (s, 1 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$), 9.55, 9.71, 9.91, 9.94 (s, 4 H, $\mathrm{H_{meso}}$).

Zinc(II) 8-(3-trifluoromethylphenyl)deuteroporphyrin dimethylester (4f) and **zinc(II) 5,8-di(3-trifluoromethylphenyl)deutoroporphyrin dimethylester (6f).** Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3f** (152 mg, 0.8 mmol) gave **4f** (82 mg, 55%) as a red-violet solid, mp 191–194 °C (dec.) and **6f** (74 mg, 42%) as a red-violet solid, mp 201–206 °C (dec.).

4f. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.19–3.36 (m, 4 H, $13^2/17^2$-$\mathrm{CH_2}$), 3.54 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.56 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.64, 3.66, 3.73, 3.76 (s, 12 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.28–4.40 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.47–7.87 (m, 1 H, $\mathrm{CH_{aryl}}$), 7.95–8.16 (m, 2 H, $\mathrm{CH_{aryl}}$), 8.28–8.35 (m, 1 H, $\mathrm{CH_{aryl}}$), 8.56 (s, 1 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$), 9.88, 9.92, 10.01, 10.04 (s, 4 H, $\mathrm{H}_{\mathit{meso}}$).

6f. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 2.93 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.00 (s, 3 H, $\mathrm{CH_{3,pyr}}$), 3.26–3.39 (m, 4 H, $13^2/17^2$-$\mathrm{CH_2}$, $\mathrm{CH_{3,pyr}}$), 3.60–3.77 (m, 9 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.39–4.55 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.47–8.87 (m, 4 H, $\mathrm{CH_{aryl}}$), 8.00–8.06 (m, 2 H, $\mathrm{CH_{ary}}$), 8.38 (s, 1 H, $\mathrm{CH_{ary}}$), 8.52 (s, 1 H, $\mathrm{CH_{ary}}$), 9.89, 10.08, 10.17, 10.26 (s, 4 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$, $\mathrm{H}_{\mathit{meso}}$).

Zinc(II) 8-(3-bromophenyl)deuteroporphyrin dimethylester (4g). From metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3g** (161 mg, 0.8 mmol) was isolated **4g** (32 mg, 21%) as a red-violet solid, mp 192–197 °C (dec.). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ 3.15–3.43 (m, 10 H, $13^2/17^2$-$\mathrm{CH_2}$, $\mathrm{CH_{3,pyr}}$), 3.47–3.77 (m, 12 H, $\mathrm{CO_2CH_3}$, $\mathrm{CH_{3,pyr}}$), 4.22–4.38 (m, 4 H, $13^1/17^1$-$\mathrm{CH_2}$), 7.67–7.83 (m, 1 H, $\mathrm{CH_{aryl}}$), 7.90–8.04 (m, 2 H, $\mathrm{CH_{aryl}}$), 8.38 (m, 1 H, $\mathrm{CH_{aryl}}$), 9.05 (s, 1 H, 8/3-$\mathrm{H_{ß\text{-}pyr}}$), 9.87–10.00 (m, 4 H, $\mathrm{H}_{\mathit{meso}}$).

Zinc(II) 8-(4-bromophenyl)deuteroporphyrin dimethylester (4h). Metalloporphyrin **1** (136 mg, 0.21 mmol) boronic acid **3h** (161 mg, 0.8 mmol) yielded **4h** (41 mg, 27%) as a red-violet solid, mp 195–199 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.16–3.55 (m, 13 H, $13^{2}/17^{2}$-CH_2, $CH_{3,pyr}$), 3.66–3.80 (m, 9 H, CO_2CH_3, $CH_{3,pyr}$), 4.13–4.29 (m, 4 H, $13^{1}/17^{1}$-CH_2), 7.83–7.99 (m, 4 H, CH_{aryl}), 9.02 (s, 1 H, 8/3-$H_{ß\text{-}pyr}$), 9.60–9.97 (m, 4 H, H_{meso}).

Zinc(II) 8-(4-fluorophenyl)deuteroporphyrin dimethylester (4i) and **zinc(II) 5,8-di-(4-fluorophenyl)deuteroporphyrin dimethylester (6i).** Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3i** (112 mg, 0.8 mmol afforded **4i** (92 mg, 66%) as a red-violet solid, mp 192–197 °C (dec.) and **6i** (67 mg, 32%) as a red-violet solid, mp 207–212 °C.

4i. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.31 (t, J = 7.6 Hz, 4 H, $13^{2}/17^{2}$-CH_2), 3.59 (s, 3 H, $CH_{3,pyr}$), 3.59 (s, 3 H, $CH_{3,pyr}$), 3.62 (s, 3 H, $CH_{3,pyr}$), 3.68, 3.72, 3.74 (s, 9 H, CO_2CH_3, $CH_{3,pyr}$), 4.39 (q, 4 H, J = 7.6 Hz, $13^{1}/17^{1}$-CH_2), 7.55–7.63 (m, 2 H, CH_{aryl}), 8.06–8.12 (m, 2 H, CH_{aryl}), 9.08 (s, 1 H, 8/3-$H_{ß\text{-}pyr}$), 9.94, 9.99, 10.00, 10.10 (s, 4 H, H_{meso}).

6i. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.32 (t, J = 7.3 Hz, 4 H, $13^{2}/17^{2}$-CH_2), 3.52 (s, 3 H, $CH_{3,pyr}$), 3.57 (s, 3 H, $CH_{3,pyr}$), 3.58 (s, 3 H, $CH_{3,pyr}$), 3.65 (s, 3 H, $CH_{3,pyr}$), 3.74 (s, 6 H, CO_2CH_3), 4.33–4.42 (m, 4 H, $13^{1}/17^{1}$-CH_2), 7.55–7.64 (m, 4 H, CH_{aryl}), 8.07–8.14 (m, 4 H, CH_{aryl}), 9.94, 10.01, 10.04, 10.10 (s, 4 H, 8/3-$H_{ß\text{-}pyr}$, H_{meso}).

Zinc(II) 8-(4-vinylphenyl)deuteroporphyrin dimethylester (4j) and **zinc(II) 5,8-di(4-vinylphenyl)deuteroporphyrin dimethylester (6j).** Metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3j** (118 mg, 0.8 mmol) yielded **4j** (58 mg, 41%) as a brown-violet solid, mp 204–207 °C (dec.) and **6j** (57 mg, 35%) as a brown-violett solid, mp 221–226 °C (dec.).

4j. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.38 (t, J = 7.5 Hz, 4 H, $13^{2}/17^{2}$-CH_2), 3.61–3.81 (m, 18 H, CO_2CH_3, $CH_{3,pyr}$), 4.46 (q, 4 H, J = 7.5 Hz, $13^{1}/17^{1}$-CH_2), 5.53 (d, 1 H, J = 11.1 Hz, $CH_{2,vinyl}$), 6.11 (d, 1 H, J = 11.1 Hz, $CH_{2,vinyl}$), 7.02–7.16 (m, 1 H, CH_{vinyl}), 7.95 (d, 2 H, J = 8.1 Hz, CH_{aryl}), 8.17 (d, 2 H, J = 8.1 Hz, CH_{aryl}), 9.14 (s, 1 H, 8/3-$H_{ß\text{-}pyr}$), 10.07, 10.08, 10.12, 10.24 (s, 4 H, H_{meso}).

6j. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.26–3.38 (m, 4 H, $13^{2}/17^{2}$-CH_2), 3.55–3.81 (m, 18 H, CO_2CH_3, $CH_{3,pyr}$), 4.35–4.53 (m, 4 H, $13^{1}/17^{1}$-CH_2), 5.53 (d, 2 H, J = 10.8 Hz, $CH_{2,vinyl}$), 6.12 (d, 2 H, J = 10.8 Hz, $CH_{2,vinyl}$), 7.02–7.16 (m, 2 H, CH_{vinyl}), 7.92–8.01 (m, 4 H, CH_{aryl}), 8.14–8.21 (m, 4 H, CH_{aryl}), 10.07, 10.13, 10.17, 10.23 (s, 4 H, H_{meso}).

Zinc(II) 8-(4-methoxyphenyl)deuteroporphyrin dimethylester (4k). From the reaction of metalloporphyrin **1** (136 mg, 0.21 mmol) and boronic acid **3k** (122 mg, 0.8 mmol) was isolated **4k** (148 mg, 99%) as a red-violet solid, mp 179–185 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.33 (t, J = 6.0 Hz, 4 H, $13^{2}/17^{2}$-CH_2), 3.55 (s, 3 H, $CH_{3,pyr}$), 3.62 (s, 3 H, $CH_{3,pyr}$), 3.66 (s, 3 H, $CH_{3,pyr}$), 3.70, 3.72, 3.73 (s, 9 H, CO_2CH_3, $CH_{3,pyr}$), 4.13 (s, 3 H, OCH_3), 4.37–4.46 (m, 4 H, $13^{1}/17^{1}$-CH_2), 7.43 (d, 2 H, J = 7.4 Hz, CH_{ary}), 8.11 (d, 2 H, J = 7.4 Hz, CH_{aryl}), 9.10 (s, 1 H, 8/3-$H_{ß\text{-}pyr}$), 10.03, 10.06, 10.14, 10.18 (s, 4 H, H_{meso}).

Zinc(II) 3,8-di(4-vinylphenyl)deuteroporphyrin dimethylester (5a) and **zinc(II) 3,5,8-tri(4-vinylphenyl) deuteroporphyrin dimethylester (7a).** Following the General Procedure the reaction of metalloporphyrin **2** (152 mg, 0.2 mmol) and boronic acid **3j** (237 mg, 1.6 mmol) led to the isolation of **5a** (57 mg, 35%) as a red-violet solid, mp 217–223 °C (dec.) and of **7a** (50 mg, 28%) as a brown-violet solid, mp >250 °C.

5a. δ 2.82 (t, *J* = 7.7 Hz, 2 H, $13^2/17^2$-CH_2), 2.98 (t, *J* = 7.7 Hz, 2 H, $13^2/17^2$-CH_2), 3.12 (s, 3 H, $CH_{3,pyr}$), 3.39 (s, 3 H, $CH_{3,pyr}$), 3.41 (s, 3 H, $CH_{3,pyr}$), 3.59, 3.61, 3.68 (s, 9 H, CO_2CH_3, $CH_{3,pyr}$), 3.78–3.91 (m, 2 H, $13^1/17^1$-CH_2), 4.00–4.11 (m, 2 H, $13^1/17^1$-CH_2), 5.53–5.65 (m, 2 H, $CH_{2,vinyl}$), 6.09–6.23 (m, 2 H, $CH_{2,vinyl}$), 7.10–7.30 (m, 2 H, CH_{vinyl}), 7.98–8.23 (m, 8 H, CH_{ary}), 8.69, 8.87, 9.68, 9.72 (s, 4 H, H_{meso}).

7a. δ 3.27–3.39 (m, 4 H, $13^2/17^2$-CH_2), 3.54 (s, 3 H, $CH_{3,pyr}$), 3.60 (s, 3 H, $CH_{3,pyr}$), 3.66 (s, 3 H, $CH_{3,pyr}$), 3.71–3.73 (m, 9 H, CO_2CH_3, $CH_{3,pyr}$), 4.33–4.59 (m, 4 H, $13^1/17^1$-CH_2), 5.14 (d, 1 H, *J* = 11.2 Hz, $CH_{2,vinyl}$), 5.51–5.65 (m, 3 H, $CH_{2,vinyl}$), 6.11 (d, 1 H, *J* = 13.1 Hz, $CH_{2,vinyl}$), 6.59–6.64 (m, 3 H, CH_{vinyl}, CH_{ary}), 7.02–7.16 (m, 3 H, CH_{vinyl}), 7.92–8.01 (m, 4 H, CH_{ary}), 8.13–8.20 (m, 4 H, CH_{ary}), 10.05, 10.06, 10.15 (s, 3 H, H_{meso}).

Zinc(II)-3,8-di(4-methoxyphenyl)-deuteroporphyrin dimethylester (5b) and **zinc(II)-3,5,8-tri(4-methoxyphenyl)-deuteroporphyrin dimethylester (7b).** Similarly, from the reaction of metalloporphyrin **2** (152 mg, 0.2 mmol) and boronic acid **3j** (244 mg, 1.6 mmol) were isolated **5b** (110 mg, 68%) as a red-violet solid, mp 208–213 °C (dec.) and **7b** (34 mg, 19%) as a red-violett solid, mp 234–238 °C (dec.).

5b. δ 2.85 (t, *J* = 7.6 Hz, 2 H, $13^2/17^2$-CH_2), 2.99 (t, *J* = 7.8 Hz, 2 H, $13^2/17^2$-CH_2), 3.17 (s, 3 H, $CH_{3,pyr}$), 3.42 (s, 3 H, $CH_{3,pyr}$), 3.45 (s, 3 H, $CH_{3,pyr}$), 3.56, 3.62, 3.67 (s, 9 H, CO_2CH_3, $CH_{3,pyr}$), 3.98–4.35 (m, 4 H, $13^1/17^1$-CH_2), 4.14 (s, 3 H, OCH_3), 4.19 (s, 3 H, OCH_3), 7.25–7.52 (m, 4 H, CH_{ary}), 7.99–8.20 (m, 4 H, CH_{ary}), 8.75, 9.05, 9.72, 9.84 (s, 4 H, H_{meso}).

7b. δ 3.19–3.40 (m, 4 H, $13^2/17^2$-CH_2), 3.56 (s, 3 H, $CH_{3,pyr}$), 3.60 (s, 3 H, $CH_{3,pyr}$), 3.68 (s, 3 H, $CH_{3,pyr}$), 3.72, 3.74, 3.78 (s, 9 H, CO_2CH_3, $CH_{3,pyr}$), 3.33–4.53 (m, 4 H, $13^1/17^1$-CH_2), 3.97 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 4.13 (s, 3 H, OCH_3), 6.60–6.80 (m, 4 H, CH_{ary}), 7.33–7.47 (m, 4 H, CH_{ary}), 8.01–8.16 (m, 4 H, CH_{ary}), 10.06, 10.15, 10.19 (s, 4 H, H_{meso}).

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