Facile preparation of novel $\beta$-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
(received 21 Apr 04; accepted 13 Sept 04; published on the web 16 Sept 04)

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

Introduction
The continuing interest in porphyrins and metalloporphyrins has encompassed areas in organometallic chemistry, material sciences, and photodynamic therapy (PDT). In the field of PDT research C–C linked porphyrin-oligomers have been shown to be efficient photosensitizers in vivo, especially those possessing a substitution pattern related to that of the natural tetrapyrrole derivatives (e.g. hemato- or protoporphyrin). 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. 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 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”. The metalloporphyrins 1 (ZnBrDPDME, zinc(II)-monobromodeuteroporphyrin dimethylester) and 2 (ZnBr₂DPDME, zinc(II)-dibromodeuteroporphyrin dimethylester) easily obtainable from heme (inexpensive natural porphyrin source) were subjected to the reaction with boronic ester 3a and boronic acids 3b–l (Scheme 1).

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. 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 (C₆₇H₆₆N₈O₈Zn₂ (1242.07); FAB-MS (NBA): m/z (%) 1238.32 (17) [M⁺, ⁶⁴Zn]). 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.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metallo-porphyrin</th>
<th>Boronic acid 3, R¹ (R² = H, except 3a)</th>
<th>Reaction conditions</th>
<th>Product / Yield [%]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3a b</td>
<td>95 °C / 15 h</td>
<td>4a / 46</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3b, -CH=CH-C₅H₁₁</td>
<td>95 °C / 10 h</td>
<td>4b / 79</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3c, phenyl</td>
<td>95 °C / 15 h</td>
<td>4c / 60</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>3d, 1-naphthyl</td>
<td>95 °C / 14 h</td>
<td>4d / 46</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>3e, 3-nitrophenyl</td>
<td>95 °C / 48 h</td>
<td>4e / 35</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>3f, 3-(trifluoromethyl)phenyl</td>
<td>95 °C / 48 h</td>
<td>4f / 55</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>3g, 3-bromophenyl</td>
<td>95 °C / 48 h</td>
<td>4g / 21</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>3h, 4-bromophenyl</td>
<td>95 °C / 48 h</td>
<td>4h / 27</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>3i, 4-fluorophenyl</td>
<td>95 °C / 14 h</td>
<td>4i / 66</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>3j, 4-vinylphenyl</td>
<td>95 °C / 24 h</td>
<td>4j / 41</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>3k, 4-methoxyphenyl</td>
<td>95 °C / 18 h</td>
<td>4k / 35</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>3l</td>
<td>95 °C / 48 h</td>
<td>– c</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>3j, 4-vinylphenyl</td>
<td>95 °C / 18 h</td>
<td>5a / 35</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>3k, 4-methoxyphenyl</td>
<td>95 °C / 15 h</td>
<td>5b / 68</td>
</tr>
</tbody>
</table>

a Isolated yield after flash column chromatography on SiO₂ (elucent: CH₂Cl₂).
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 R₇ values in comparison with porphyrins 4 and 5. The ¹H 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 R¹. Comparison with recently published experimental data (COSY NMR) leads us to
suggest that position 5 has been substituted selectively.\textsuperscript{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-pyrole 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.\textsuperscript{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 (\textsuperscript{1}H at 200 MHz, \textsuperscript{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\textsubscript{2}Cl\textsubscript{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.). 1H NMR (200 MHz, CDCl3): δ 3.01–3.12 (m, 4 H, 132/172-CH2), 3.25–3.54 (m, 12 H, CH3,pyr), 3.64–3.67 (m, 6 H, CO2CH3), 4.04–4.21 (m, 4 H, 131/171-CH2), 4.41–4.59 (m, 2 H, 83/1-CH2), 5.10–5.31 (m, 2 H, 83/1-ABX-CH2,vinyl), 6.36–6.49 (m, 1 H, 83/2-ABX-CH2,vinyl), 8.66, 8.77 (s, 1 H, 3(8)-CH β-pyr), 9.21–9.47 (m, 4 H, Hmeso). 13C NMR (50 MHz, CDCl3): δ 11.36, 11.42, 11.64, 11.74 (q, 2 1/71, 121, 171-CH3), 13.65, 13.68 (q, 71/21-CH3), 21.85, 21.98 (t, 131/171-CH2), 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, 138.34, 138.49, 139.34, 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, Cquart), 174.11, 174.14 (13 3/173-CO2Me). UV/VIS (CH2Cl2): λmax (lg ε) 567 (4.326), 531 (4.222), 402 (5.559), 326 (4.251). FAB-MS (NBA): m/z (%) 640.12 (100) [M+, 64Zn]. Anal. Calcd for C35H36N4O4Zn (642.07) C, 65.52; H, 5.73; N, 8.69. Found C, 65.18; H, 5.53; N, 8.39.

**Zinc(II) 8-allyldederoporphyrin 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.). 1H NMR (200 MHz, CDCl3): δ 1.13 (t, 3 H, J = 7 Hz, 3 7/87-CH3), 1.61–1.83 (m, 4 H, 3 5/85, 36/86-CH2) 1.88–1.95 (m, 2 H, 3 4/84-CH2), 2.71–2.89 (m, 2 H, 3 3/83-CH2), 3.00–3.14 (m, 4 H, 13 2/172-CH2), 3.31–3.55 (m, 12 H, CH3,pyr), 3.64–3.66 (m, 6 H, CO2CH3), 4.08–4.24 (m, 4 H, 131/171-CH2), 6.62–6.86 (m, 1 H, 82/32-CHvinyl), 7.61, 7.70 (d, 1 H, J = 16.87 Hz, 8/3-CH β-pyr), 9.17–9.52 (m, 4 H, Hmeso). 13C NMR (50 MHz, CDCl3): δ 11.40, 11.49, 11.67, 11.90, 12.49, 12.59, 13.54 (q, CH3,Pyr), 14.87 (q, 3 7/87-CH3), 21.72 (t, 13 1/171-CH2), 23.41 (t, 3 6/86-CH2), 30.61 (t, 3 5/85-CH2), 32.41 (t, 3 4/84-CH2), 35.16, 35.23 (t, 3 3/83-CH2), 37.27 (t, 13 2/172-CH2), 52.04 (q, 13 3/173-OCH3), 95.04, 95.19, 96.10, 96.27, 96.89, 99.54 (d, CHmeso), 123.35, 123.58 (d, 3 2/82-CHvinyl), 128.35, 128.47 (d, 8/3-CHβ-pyr), 137.04, 137.22 (d, 8/3-CHvinyl), 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, 145.52, 145.80, 145.96. 146.00, 146.36, 146.58, 146.74, 146.84, 146.99, 147.04 (s, Cquart), 174.06, 174.09 (13 1/172-CO2Me). UV/VIS (CH2Cl2): λmax (lg ε) 572 (4.028), 535 (3.903), 404 (5.051). FAB-MS (NBA): m/z (%) 696.14 (23) [M+, 64Zn]. Anal. Calcd for C39H44N4O4Zn (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 dimethylster (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.). 1H NMR (200 MHz, CDCl3): δ 3.10–3.18 (t, 4 H, J = 7.72 Hz, 132/172-CH2), 3.42–3.65 (m, 18 H, CO2CH3, CH3,pyr), 4.10–4.32 (m, 4 H, 131/171-CH2), 7.76 (d, 1 H, J = 7.46 Hz, CHaryl), 7.90 (dd, 2 H, J = 7.46, J = 7.12 Hz, CHaryl), 8.20 (d, 2 H, J = 7.12 Hz, CHaryl), 8.96 (s, 1 H, 8/3-CHβ-pyr), 9.58, 9.74, 9.89, 9.97 (s, 4 H, Hmeso). 13C NMR (50 MHz, CDCl3): δ 11.64, 11.66, 13.99, 14.22 (q, 2 1, 7 1, 71/21-CH3), 21.72 (t, 131/171-CH2), 37.15 (t, 132/172-CH2), 52.06 (q, OCH3), 95.18, 97.11, 99.82, 100.26 (d, 5, 10, 15, 20-CH), 127.58, 129.18, 132.82 (d, CHaryl), 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, 148.24 (s, C<sub>quar</sub>), 174.02 (13<sup>3</sup>/17<sup>3</sup>-CO<sub>2</sub>Me). UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (lg ε) 570 (4.316), 533 (4.235), 405 (5.325). FAB-MS (NBA): m/z (%) 676.08 (29) [M<sup>+</sup>, 64Zn]. Anal. Calcd for C<sub>38</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>Zn (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-violent solid, mp 221–227 °C (dec.).

4d. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.26–3.35 (m, 4 H, 13<sup>2</sup>/17<sup>2</sup>-CH<sub>2</sub>), 3.49–3.82 (m, 18 H, CO<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>pyr), 7.36–7.46 (m, 1 H, CH<sub>aryl</sub>), 7.54–7.74 (m, 1 H, CH<sub>aryl</sub>), 7.92–8.03 (m, 2 H, CH<sub>aryl</sub>), 8.13–8.32 (m, 3 H, CH<sub>aryl</sub>), 9.09 (s, 1 H, 8/3-H<sub>ß</sub>-pyr), 9.85, 10.07, 10.15, 10.33 (s, 4 H, H<sub>meso</sub>).

6d. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.28 (s, 3 H, CH<sub>3</sub>pyr), 3.32–3.46 (m, 7 H, 13<sup>2</sup>/17<sup>2</sup>-CH<sub>2</sub>, CH<sub>3</sub>pyr), 3.64 (s, 3 H, CH<sub>3</sub>pyr), 3.74–3.81 (m, 9 H, CO<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>pyr), 4.42–4.56 (m, 4 H, 13<sup>1</sup>/17<sup>1</sup>-CH<sub>2</sub>), 7.20–8.35 (m, 14 H, CH<sub>aryl</sub>), 9.86, 10.05, 10.21, 10.39 (s, 4 H, 8/3-H<sub>ß</sub>-pyr, H<sub>meso</sub>).

**Zinc(II) 8-(3-nitrophenyl)deuteroporphyrin dimethylester (4e)**. Metalloporphyrin 1 (136 mg, 0.21 mmol) and boronic acid 3e (138 mg, 0.8 mmol) furnished 4e (50 mg, 35%) as a red-violet solid, mp 188–193 °C (dec.). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.12–3.19 (m, 4 H, 13<sup>2</sup>/17<sup>2</sup>-CH<sub>2</sub>), 3.39–3.61 (m, 18 H, CO<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>pyr), 4.08–4.33 (m, 4 H, 13<sup>1</sup>/17<sup>1</sup>-CH<sub>2</sub>), 7.41–7.47 (m, 1 H, CH<sub>aryl</sub>), 7.66–7.69 (m, 1 H, CH<sub>aryl</sub>), 8.01–8.05 (m, 1 H, CH<sub>aryl</sub>), 8.17 (s, 1 H, CH<sub>aryl</sub>), 8.95 (s, 1 H, 8/3-H<sub>ß</sub>-pyr), 9.55, 9.71, 9.91, 9.94 (s, 4 H, H<sub>meso</sub>).
Zinc(II) 8-(4-bromophenyl)deuteroporphyrin dimethylester (4h). Metallocorphyrin 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, 132/172-CH\(_2\), CH\(_3\),pyr), 3.66–3.80 (m, 9 H, CO\(_2\)CH\(_3\), CH\(_3\),pyr), 4.13–4.29 (m, 4 H, 13/17\(^{1}\)-CH\(_2\)), 7.83–7.99 (m, 4 H, CHaryl), 9.02 (s, 1 H, 8/3-Hß-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\(_2\)CH\(_3\), 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, CHaryl), 8.06–8.12 (m, 2 H, CHaryl), 9.08 (s, 1 H, 8/3-Hß-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\(_2\)CH\(_3\)), 4.33–4.42 (m, 4 H, 13\(^{1}/17^{1}\)-CH\(_2\)), 7.55–7.64 (m, 4 H, CHaryl), 8.07–8.14 (m, 4 H, CHaryl), 9.94, 10.01, 10.04, 10.10 (s, 4 H, 8/3-Hß-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-violet 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\(_2\)CH\(_3\), 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, CHvinyl), 7.95 (d, 2 H, \(J = 8.1\) Hz, CHaryl), 8.17 (d, 2 H, \(J = 8.1\) Hz, CHaryl), 9.14 (s, 1 H, 8/3-Hß-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\(_2\)CH\(_3\), 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, CHvinyl), 7.92–8.01 (m, 4 H, CHaryl), 8.14–8.21 (m, 4 H, CHaryl), 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 metallocorphyrin 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\(_2\)), 3.55–3.81 (m, 18 H, CO\(_2\)CH\(_3\), 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, CHvinyl), 7.92–8.01 (m, 4 H, CHaryl), 8.14–8.21 (m, 4 H, CHaryl), 10.07, 10.13, 10.17, 10.23 (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 metallocorphyrin 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, 13²/17²-CH₂), 2.98 (t, J = 7.7 Hz, 2 H, 13²/17²-CH₂), 3.12 (s, 3 H, CH₃pyr), 3.39 (s, 3 H, CH₃pyr), 3.41 (s, 3 H, CH₃pyr), 3.59, 3.61, 3.68 (s, 9 H, CO₂CH₃, CH₃pyr), 3.78–3.91 (m, 2 H, 13¹/17¹-CH₂), 4.00–4.11 (m, 2 H, 13¹/17¹-CH₂), 5.53–5.65 (m, 2 H, CH₂vinyl), 6.09–6.23 (m, 2 H, CH₂vinyl), 7.10–7.30 (m, 2 H, CHvinyl), 7.98–8.23 (m, 8 H, CHary), 8.69, 8.87, 9.68, 9.72 (s, 4 H, Hmeso).

7a. δ 3.27–3.39 (m, 4 H, 13²/17²-CH₂), 3.54 (s, 3 H, CH₃pyr), 3.60 (s, 3 H, CH₃pyr), 3.66 (s, 3 H, CH₃pyr), 3.71–3.73 (m, 9 H, CO₂CH₃, CH₃pyr), 4.33–4.59 (m, 4 H, 13¹/17¹-CH₂), 5.14 (d, 1 H, J = 11.2 Hz, CH₂vinyl), 5.51–5.65 (m, 3 H, CH₂vinyl), 6.11 (d, 1 H, J = 13.1 Hz, CH₂vinyl), 6.59–6.64 (m, 3 H, CHvinyl, CHary), 7.02–7.16 (m, 3 H, CHvinyl), 7.92–8.01 (m, 4 H, CHary), 8.13–8.20 (m, 4 H, CHary), 10.05, 10.06, 10.15 (s, 3 H, Hmeso).

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-violet solid, mp 234–238 °C (dec.).

5b. δ 2.85 (t, J = 7.6 Hz, 2 H, 13²/17²-CH₂), 2.99 (t, J = 7.8 Hz, 2 H, 13²/17²-CH₂), 3.17 (s, 3 H, CH₃pyr), 3.42 (s, 3 H, CH₃pyr), 3.45 (s, 3 H, CH₃pyr), 3.56, 3.62, 3.67 (s, 9 H, CO₂CH₃, CH₃pyr), 3.98–4.35 (m, 4 H, 13¹/17¹-CH₂), 4.14 (s, 3 H, OCH₃), 4.19 (s, 3 H, OCH₃), 7.25–7.52 (m, 4 H, CHary), 7.99–8.20 (m, 4 H, CHary), 8.75, 9.05, 9.72, 9.84 (s, 4 H, Hmeso).

7b. δ 3.19–3.40 (m, 4 H, 13²/17²-CH₂), 3.56 (s, 3 H, CH₃pyr), 3.60 (s, 3 H, CH₃pyr), 3.68 (s, 3 H, CH₃pyr), 3.72, 3.74, 3.78 (s, 9 H, CO₂CH₃, CH₃pyr), 3.33–4.53 (m, 4 H, 13¹/17¹-CH₂), 3.97 (s, 3 H, OCH₃), 4.01 (s, 3 H, OCH₃), 4.13 (s, 3 H, OCH₃), 6.60–6.80 (m, 4 H, CHary), 7.33–7.47 (m, 4 H, CHary), 8.01–8.16 (m, 4 H, CHary), 10.06, 10.15, 10.19 (s, 4 H, Hmeso).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Grünenthal GmbH for their financial support.

References