Supporting Informations

A Toolset of Functionalized Porphyrins with Different Linker Strategies for Application in Bioconjugation

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Table of Contents

1. Synthesis of porphyrins 1d, 2a-f, 2h-i, 4, and 5c

2. $^1$H, $^{13}$C, and $^{19}$F-NMR of porphyrins 1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d, 11, 13a-b, and 14a-b

3. ESI-MS of porphyrins 1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d, and 11
1. Synthesis of porphyrins 1d, 2a-f, 2h-i, 4, and 5c

{5,10,15-Tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrinato}-zinc (II) (1d) In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (1c) (42.0 mg, 55.8 µmol) was dissolved in 5 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (120 mg, 547 µmol) was added to the stirred solution. The solution was stirred for 2 h at RT. The crude product was diluted with 100 mL of ethyl acetate and washed three times with 50 mL of H₂O. Afterwards the organic layer was dried over Na₂SO₄ and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/n-hexane to obtain {5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrinato}-zinc (II) (1d) (46.0 mg, 56.4 µmol, quant. yield) as a pink solid.

¹H NMR (Acetone-D₆, 700 MHz): δ = 9.04 (d, 3J(H,H) = 4.5 Hz, 2H, 2,1β), 9.01 (d, 3J(H,H) = 4.5 Hz, 2H, 3,17β), 8.97 (d, 3J(H,H) = 4.5 Hz, 2H, 7,13β), 8.95 (d, 3J(H,H) = 4.5 Hz, 2H, 8,12β), 8.80 (s, 3H, OH), 7.74–7.72 (m, 3H, 5,10,15-meso-2-Ar), 7.70 (d, 3J(H,H) = 7.2 Hz, 3H, 5,10,15-meso-6-Ar), 7.62–7.58 (m, 3H, 5,10,15-meso-5-Ar), 7.32–7.29 ppm (m, 3H, 5,10,15-meso-4-Ar). ¹³C NMR (Acetone-D₆, 176 MHz): δ = 156.55, 156.52, 151.33, 150.90, 150.73, 150.39, 148.31, 146.92, 145.25, 145.16, 139.31, 137.92, 133.79, 132.86, 132.49, 130.63, 128.26, 128.23, 127.25, 123.20, 122.01, 118.68, 115.47, 101.30 ppm. ¹⁹F NMR (Acetone-D₆, 376 MHz): δ = −139.45 (−139.87) (m, 2F, m-ArF), −156.90 (q, 3J(F,F) = 19.7 Hz, 1F, p-ArF), −165.22 (−165.49) ppm (m, 2F, o-ArF). m.p.: 143 °C. HRMS (ESI): calc. for C₄₄H₂₄F₅N₄O₃Zn⁺ ([M + H]⁺): 815.1060 found: 815.1127. UV/Vis (Ethanol): λ_max (ε [M⁻¹cm⁻¹]) = 596 (5000), 555 (19 000), 422 nm (412 000).
5,10,15-Tris(3-hydroxyphenyl)-20-[4-((2-((2-aminoethyl)disulfanyl)ethyl)amino)tetrafluorophenyl]porphyrin (2a) In a 100 mL flask with magnetic stirrer sodium hydroxide (99%, 1.55 g, 38.4 mmol) was dissolved in 20 mL of H₂O. To the stirred solution cystamine dihydrochloride (97%, 2.71 g, 11.7 mmol) was added. After 10 min of stirring the aqueous solution was extracted four times with 100 mL of DCM. Afterwards the organic layer was dried over Na₂SO₄. The product was evaporated to dryness and the remaining residue was dissolved in 1.5 mL of DMSO (Roth). 5,10,15-Tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (1c) (151 mg, 177 µmol) was added. The solution was stirred at 100 °C for 30 min in the microwave oven (300 W). The crude product was diluted with 100 mL of ethyl acetate and washed once with 50 mL of saturated NaCl-solution and twice with H₂O. Afterwards the organic layer was dried over Na₂SO₄. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 85/15, v/v, Fluka) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-((2-((2-aminoethyl)disulfanyl)ethyl)amino)tetrafluorophenyl]porphyrin (2a) (136 mg, 154 µmol, 87% yield) as a purple solid.

¹H NMR (THF-D₈, 700 MHz): δ = 9.04–8.81 (m, 11H, β + 5,10,15-meso-3-Ar-OH), 7.69–7.60 (m, 6H, 5,10,15-meso-2,6-Ar), 7.58–7.44 (m, 3H, 5,10,15-meso-5-Ar), 7.20 (d, ³J(H,H) = 8.2 Hz, 1H, 10-meso-4-Ar), 7.18 (dd, ³J(H,H) = 8.9, ⁴J(H,H) = 2.1 Hz, 1H, 10-meso-4-Ar), 6.21–6.17 (bs, 1H, NH), 3.99 (q, ³J(H,H) = 6.6 Hz, 2H, NHCH₂), 3.50 (t, ³J(H,H) = 7.2 Hz, 2H, CH₂NH₂), 3.35 (t, ³J(H,H) = 7.2 Hz, 2H, SCH₂), 3.24 (t, ³J(H,H) = 6.8 Hz, 2H, SCH₂), −2.73 ppm (s, 2H, pyrrole-NH). ¹³C NMR (THF-D₈, 176 MHz): δ = 157.41, 148.83, 147.46, 144.37, 144.20, 138.86, 137.57, 130.01, 128.44, 128.39, 127.13, 123.16, 122.40, 121.50, 115.93, 108.36, 103.65, 45.62, 40.00, 39.80, 35.57 ppm. ¹⁹F NMR (THF-D₈, 376 MHz): δ = −142.15–(−143.15) (m, 2F, m-ArF), −161.73–(−162.85) ppm (m, 2F, o-ArF). m.p.: > 230 °C. HRMS (ESI): calc. for C₄₈H₂₇F₄N₆O₅S₂⁺ ([M + H]^+): 885.2305 found: 885.2342. UV/Vis
(Ethanol): $\lambda_{\text{max}}$ (ε [M$^{-1}$cm$^{-1}$]) = 645 (2000), 589 (4000), 547 (5000), 512 (14 000), 416 nm (257 000).

5,10,15-Tris(3-hydroxyphenyl)-20-[4-(4-aminobutylamino)tetrafluorophenyl]porphyrin (2b)

In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (1c) (197 mg, 262 µmol) was dissolved in 7 mL of anhydrous DMSO (Acros) under argon. To the stirred solution 1,4-diaminobutane (99%, 4.00 g, 44.9 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 200 mL of ethyl acetate and washed twice with 300 mL of saturated NaCl-solution and twice with 300 mL of H$_2$O. Afterwards the organic layer was dried over Na$_2$SO$_4$. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, Fluka) to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(4-aminobutylamino)tetrafluorophenyl]porphyrin (2b) (145 mg, 177 µmol, 69% yield) as a purple solid.

$^1$H NMR (CD$_3$OD, 700 MHz): δ = 9.21–8.66 (bs, 8H, β), 7.70–7.61 (m, 6H, 5,10,15-meso-2,6-Ar), 7.55 (q, $^3$J(H,H) = 7.2 Hz, 3H, 5,15-meso-5-Ar), 7.24 (d, $^3$J(H,H) = 8.4 Hz, 3H, 5,15-meso-4-Ar), 3.62 (t, $^3$J(H,H) = 6.8 Hz, 2H, NHCH$_2$), 2.84 (t, $^3$J(H,H) = 7.3 Hz, 2H, NHCH$_2$), 1.83 ppm (quin, $^3$J(H,H) = 7.2 Hz, 2H, NHCH$_2$CH$_2$), 1.72 ppm (quin, $^3$J(H,H) = 7.5 Hz, 2H, NHCH$_2$CH$_2$).

$^{13}$C NMR (CD$_3$OD, 176 MHz): δ = 157.24, 157.19, 149.01, 147.67, 144.35, 144.23, 139.03, 137.67, 130.82, 128.78, 128.72, 127.52, 127.48, 123.23, 123.19, 122.78, 121.84, 116.12, 108.04, 104.03, 46.23, 41.74, 29.27 ppm.

$^{19}$F NMR (CD$_3$OD, 376 MHz): δ = −143.75–(−143.99) (m, 2F, $m$-Ar$_F$), −163.31 ppm (d, $^3$J(F,F) = 16.3 Hz, 2F, $o$-Ar$_F$).

m.p.: > 300 °C. HRMS (ESI): calc. for C$_{48}$H$_{37}$F$_4$N$_6$O$_3$$^+$ ([M + H]$^+$): 821.2858; found: 821.2884.

UV/Vis (Acetone): $\lambda_{\text{max}}$ (ε [M$^{-1}$cm$^{-1}$]) = 644 (3000), 589 (5000), 545 (6000), 512 (16 000), 416 nm (251 000).
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(5-aminopentylamino)tetrafluorophenyl]porphyrin (2c) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (1c) (120 mg, 160 µmol) was dissolved in 4 mL of anhydrous DMSO (Acros) under argon. To the stirred solution 1,5-diaminopentane (98%, 2.80 mL, 2.44 g, 23.4 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 100 mL of ethyl acetate and washed twice with 150 mL of saturated NaCl-solution and twice with 150 mL of H₂O. Afterwards the organic layer was dried over Na₂SO₄. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, Fluka) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(5-aminopentylamino)tetrafluorophenyl]porphyrin (2c) (71.3 mg, 85.4 µmol, 54% yield) as a purple solid.

¹H NMR (CD₃OD, 500 MHz): δ = 9.25–8.62 (bs, 8H, β), 7.70–7.59 (m, 6H, 5,10,15-meso-2,6-Ar), 7.58–7.49 (m, 3H, 5,10,15-meso-5-Ar), 7.27–7.18 (m, 3H, 5,10,15-meso-4-Ar), 3.54 (t, 3J(H,H) = 7.0 Hz, 2H, ArF-NHCH₂), 2.62 (t, 3J(H,H) = 7.1 Hz, 2H, CH₂NH₂), 1.74 (quin, 3J(H,H) = 7.4 Hz, 2H, ArF-NHCH₂CH₂), 1.55–1.44 ppm (m, 4H, ArF-CH₂CH₂NH₂). ¹³C NMR (CD₃OD, 126 MHz): δ = 157.45, 157.39, 149.29, 147.39, 144.37, 144.24, 139.39, 128.77, 128.72, 127.44, 127.40, 123.34, 123.29, 122.80, 121.88, 116.19, 104.07, 46.45, 42.14, 32.70, 31.78, 25.10 ppm. ¹⁹F NMR (CD₃OD, 376 MHz): δ = −143.80−(−144.17) (m, 2F, m-ArF), −163.38 ppm (d, 3J(F,F) = 15.6 Hz, 2F, o-ArF). m.p.: >300 °C. HRMS (ESI): calc. for C₄₉H₃₉F₄N₆O₅⁺ ([M + H]⁺): 835.3020; found: 835.3018. UV/Vis (Methanol): λmax (ε [M⁻¹cm⁻¹]) = 644 (2000), 588 (5000), 547 (6000), 512 (15 000), 415 nm (186 000).
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(6-aminohexylamino)tetrafluorophenyl]porphyrin (2d) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (1c) (120 mg, 159 µmol) was dissolved in 4 mL of anhydrous DMSO (Acros) under argon. To the stirred solution 1,6-diaminohexane (98%, 3.60 mL, 2.99 g, 25.5 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 100 mL of ethyl acetate and washed twice with 150 mL of saturated NaCl solution and twice with 150 mL of H2O. Afterwards the organic layer was dried over Na2SO4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, Fluka) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(6-aminohexylamino)tetrafluorophenyl]porphyrin (2d) (107 mg, 127 µmol, 79% yield) as a purple solid.

1H NMR (CD3OD, 500 MHz): δ = 8.96–8.92 (bs, 8H, β), 7.68–7.64 (m, 3H, 5,10,15-meso-2-Ar), 7.63 (t, 3J(H,H) = 8.0 Hz, 3H, 5,10,15-meso-6-Ar), 7.543 (t, 3J(H,H) = 7.7 Hz, 2H, 5,15-meso-5-Ar), 7.537 (t, 3J(H,H) = 7.9 Hz, 1H, 10-meso-5-Ar), 7.24 (dd, 3J(H,H) = 8.3, 4J(H,H) = 1.6 Hz, 3H, 5,15-meso-4-Ar), 3.52 (t, 3J(H,H) = 7.3 Hz, 2H, NHCH2), 2.62 (t, 3J(H,H) = 7.2 Hz, 2H, NHCH2), 1.73 (quin, 3J(H,H) = 7.3 Hz, 2H, NHCH2CH2), 1.52–1.31 ppm (m, 6H, NHCH2CH2CH2CH2).

13C NMR (CD3OD, 126 MHz): δ = 157.50, 157.43, 144.36, 144.24, 128.77, 128.72, 127.42, 127.38, 123.37, 123.32, 122.81, 121.88, 116.21, 104.08, 46.49, 42.15, 32.90, 31.92, 27.65 ppm.

19F NMR (CD3OD, 471 MHz): δ = −143.95 (d, 3J(F,F) = 16.1 Hz, 2F, m-ArF), −163.40 ppm (d, 3J(F,F) = 16.1 Hz, 2F, o-ArF). m.p.: > 300 °C. HRMS (ESI): calc. for C50H41F4N6O3+ ([M + H]+): 849.3176; found: 849.3184. UV/Vis (Methanol): λ max (ε [M⁻¹cm⁻¹]) = 644 (2000), 588 (5000), 545 (6000), 512 (16 000), 415 nm (178 000).
In a 10 mL flask with magnetic stirrer, 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin 1c (49 mg, 65.1 µmol) was dissolved in 0.5 mL of anhydrous DMSO (Acros) under argon. To the stirred solution, N-Boc-cadaverine (97%, 60 µL, 58 mg, 280 µmol) was added. The solution was stirred at 100 °C for 4 h. The crude product was diluted with 100 mL of ethyl acetate and washed three times with 50 mL of H₂O. Afterwards, the organic layer was dried over Na₂SO₄. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/acetone = 9/1, v/v, Machery-Nagel) and recrystallization from DCM/n-hexane to obtain N-Boc protected 5,10,15-tris(3-hydroxyphenyl)-20-[4-(6-aminopentylamino)tetrafluorophenyl]porphyrin (2e) (42 mg, 127 µmol, 69% yield) as a purple solid.

¹H NMR (Acetone-D₆, 500 MHz): δ = 9.13–9.08 (m, 2H, 2,18-β), 9.02 (d, ³J(H,H) = 4.5 Hz, 2H, 3,17-β), 8.99–8.94 (bs, 4H, 7,8,12,13-β), 8.83 (s, 3H, 5,10,15-meso-3-Ar-OH), 7.79–7.70 (m, 6H, 5,10,15-meso-2,6-Ar), 7.66–7.61 (m, 3H, 5,10,15-meso-5-Ar), 7.36–7.32 (m, 3H, 5,10,15-meso-4-Ar), 6.00 (s, 1H, NH), 5.66 (s, 1H, NH), 3.72 (t, ³J(H,H) = 6.9 Hz, 2H, NHCH₂), 3.17 (t, ³J(H,H) = 6.5 Hz, 2H, NHCH₂), 1.91 (quin, ³J(H,H) = 7.3 Hz, 2H, NHCH₂CH₂), 1.68–1.55 ppm (m, 4H, NHCH₂CH₂CH₂), 1.43 (s, 9H, CH₃), −2.74 ppm (s, 2H, pyrrole-NH). ¹³C NMR (Acetone-D₆, 126 MHz): δ = 156.85, 156.80, 148.91, 147.02, 144.03, 143.89, 139.08, 137.04, 132.21, 130.66, 128.69, 128.65, 127.29, 127.25, 122.91, 122.87, 122.31, 121.38, 116.01, 107.46, 103.79, 78.40, 46.45, 41.08, 35.26, 31.40, 30.72, 28.72, 24.79 ppm. ¹⁹F NMR (Acetone-D₆, 471 MHz): δ = −143.34 (−143.51) (m, 2F, m-ArF), −162.44 (−162.61) (m, 2F, o-ArF). m.p.: 190 °C. HRMS (ESI): calc. for C₅₄H₄₇F₅N₆O₅⁺ ([M + H]⁺): 935.3544; found: 935.3536. UV/Vis (ethanol): λ_max (ε [M⁻¹·cm⁻¹]) = 645 (4000), 589 (8000), 546 (9000), 512 (25 000), 416 nm (445 000).
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (2f) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-acetoxyphenyl)-20-pentafluorophenylporphyrin (1a) (203 mg, 231 µmol) was dissolved in 2 mL of anhydrous DMSO (Roth) under argon. Propargylamine (98%, 300 µL, 258 mg, 4.59 mmol) was added and the solution was stirred at 83 °C for 3 h. The crude product was diluted with 150 mL of ethyl acetate and washed three times with 30 mL of H2O. Afterwards the organic layer was dried over Na2SO4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/acetone = 9/1, v/v, Machery-Nagel) and recrystallization from DCM/n-hexane to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (2f) (170 mg, 216 µmol, 94% yield) as a purple solid.

1H NMR (Acetone-D6, 500 MHz): δ = 9.13–9.06 (m, 2H, 2,18-β), 9.03 (d, 3J(H,H) = 4.8 Hz, 2H, 3,17-β), 9.00–8.92 (bs, 4H, 7,8,12,13-β), 8.87 (s, 3H, 5,10,15-meso-3-Ar-OH), 7.77 (t, 4J(H,H) = 2.0 Hz, 2H, 5,15-meso-2-Ar), 7.76–7.71 (m, 4H, 10-meso-2-Ar + 5,10,15-meso-6-Ar), 7.66–7.61 (m, 3H, 5,10,15-meso-5-Ar), 7.36–7.32 (m, 3H, 5,10,15-meso-4-Ar), 6.15 (t, 3J(H,H) = 7.2 Hz, 1H, ArF-NH), 4.49–4.46 (m, 2H, CH2), 2.98 (t, 4J(H,H) = 2.5 Hz, 1H, C≡C-H), −2.75 ppm (s, 2H, pyrrole-NH). 13C NMR (Acetone-D6, 126 MHz): δ = 156.83, 156.78, 148.78, 146.83, 143.97, 143.82, 139.72, 137.82, 132.39, 129.38, 128.70, 128.65, 127.27, 127.23, 122.88, 122.84, 122.42, 121.45, 116.00, 109.58, 103.30, 81.88, 73.55, 35.75 ppm. 19F NMR (Acetone-D6, 471 MHz): δ = −142.99 (d, 3J(F,F) = 20.5 Hz, 2F, m-ArF), −160.83 ppm (d, 3J(F,F) = 19.3 Hz, 2F, o-ArF). m.p.: 135 °C. HRMS (ESI): calc. for C47H30F4N5O3+ ([M + H]+): 788.2285 found: 788.2270. UV/Vis (Ethanol): λmax (ε [M−1cm−1]) = 645 (3000), 589 (5000), 546 (6000), 512 (17000), 416 (283000).
In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (2f) (181 mg, 230 µmol) was dissolved in 10 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (506 mg, 2.31 mmol) was added to the stirred solution. The solution was stirred for 1 h at RT. The crude product was diluted with 150 mL of ethyl acetate and washed three times with 50 mL of H2O. Afterwards the organic layer was dried over Na2SO4 and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/n-hexane to obtain {5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrinato}zinc(II) (2h) (186 mg, 219 µmol, 95% yield) as a pink solid.

1H NMR (Acetone-D6, 400 MHz): δ = 8.99 (s, 4H, 2,3,17,18-β), 8.97–8.91 (m, 4H, 7,8,12,13-β), 8.82–8.70 (bs, 3H, 5,10,15-meso-3-Ar-OH), 7.76–7.71 (m, 6H, 5,10,15-meso-2,6-Ar), 7.58 (t, 3J(H,H) = 7.8 Hz, 3H, 5,10,15-meso-5-Ar), 7.287 (dd, 3J(H,H) = 8.2 Hz; 4J(H,H) = 1.2 Hz, 2H, 5,15-meso-4-Ar), 7.281 (dd, 3J(H,H) = 8.1 Hz; 4J(H,H) = 1.0 Hz, 1H, 10-meso-4-Ar), 6.04–5.94 (m, 1H, ArF-NH), 4.43–4.36 (m, 2H, CH2), 2.95 ppm (t, 4J(H,H) = 2.4 Hz, 1H, C≡C). 13C NMR (Acetone-D6, 126 MHz): δ = 156.54, 156.51, 151.17, 151.05, 150.86, 150.69, 148.70, 146.81, 145.32, 145.25, 139.76, 137.84, 133.58, 132.74, 132.44, 130.93, 128.78, 128.73, 128.28, 128.25, 127.29, 122.91, 122.81, 121.82, 115.44, 111.25, 103.43, 81.91, 73.53, 35.81 ppm. 19F NMR (Acetone-D6, 471 MHz): δ = -142.68 (d, 3J(F,F) = 22.9 Hz, 2F, m-ArF), -160.99 ppm (d, 3J(F,F) = 20.7 Hz, 2F, o-ArF). m.p.: > 230 °C. HRMS (ESI): calc. for C47H27F4N5O3Zn+: 849.1341 found: 849.1331. UV/Vis (Ethanol): λmax (ε [M−1 cm−1]) = 597 (5000), 556 (20 000), 423 nm (435 000).
{5,10,15-Tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (2i) In a 100 mL flask with magnetic stirrer 5,10,15-tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrin (2g) (444 mg, 420 µmol) was dissolved in 10 mL of DCM. A point of a spatula of sodium acetate and zinc acetate dihydrate (99.5%, 1.02 g, 4.60 mmol) were dissolved in 500 µL methanol and added to the stirred solution. The solution was stirred at RT for 18 h. The crude product was diluted with 70 mL of DCM and washed twice with 70 mL of H₂O. Afterwards the organic layer was dried over Na₂SO₄. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/n-hexane = 3/1, v/v, Machery-Nagel) and recrystallization from DCM/n-hexane to obtain {5,10,15-tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (2i) (343 mg, 306 µmol, 73% yield) as a pink solid.

¹H NMR (CDCl₃, 500 MHz): δ = 9.09–9.00 (m, 6H, 3,7,8,12,13,17-β), 8.77 (s, 2H, 2,18-β), 7.94–7.80 (m, 6H, Ar), 7.67–7.58 (m, 3H, Ar), 7.38–7.28 (m, 3H, Ar), 7.20–6.84 (m, 15H, Ar), 4.99–4.82 (m, 9H, C₆H₂ + ArF-NH), 1.95 ppm (s, 1H, C≡C). ¹³C NMR (CDCl₃, 126 MHz): δ = 157.06, 150.59, 150.15, 150.04, 149.91, 146.91, 146.60, 144.72, 144.13, 144.04, 138.30, 136.69, 136.61, 133.24, 132.55, 132.25, 130.55, 128.27, 128.22, 128.16, 127.68, 127.62, 127.54, 127.29, 127.24, 127.20, 127.16, 122.31, 121.47, 121.43, 121.29, 114.76, 102.50, 78.61, 72.82, 70.04, 34.06 ppm. ¹⁹F NMR (CDCl₃, 471 MHz): δ = −139.59–(−140.24) (m, 2F, m-ArF), −157.91–(−158.49) ppm (m, 2F, o-ArF). m.p.: 100 °C. HRMS (ESI): calc. for C₆₈H₄₅F₄N₅O₃Zn⁺ ([M]⁺): 1119.2750 found: 1119.2767. UV/Vis (DCM): λ_max (ε [M⁻¹cm⁻¹]) = 584 (3000), 548 (20000), 420 nm (296000).
In a 25 mL flask with magnetic stirrer, {5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato}-zinc(II) (3) (43.0 mg, 39.5 µmol) was dispensed in 5 mL of anhydrous DMSO (Roth) and 5 mL of anhydrous THF (Acros) under argon. Propargylamine (98%, 100 µL, 1.53 mmol) was added and the solution was stirred at 100 °C for 90 min. The crude product was diluted with 100 mL of DCM and washed three times with 30 mL of H₂O. Afterwards the organic layer was dried over Na₂SO₄. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/n-hexane = 2/1, v/v, Machery-Nagel) and recrystallization from DCM/methanol to obtain the main product {5,10,15-tris(pentafluorophenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (4) (10.0 mg, 9.32 µmol, 22% yield) and the by-product {bis(pentafluorophenyl)-bis[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (cis/trans mixture) (8.0 mg, 7.22 μmol, 18% yield) as purple solids.

1H NMR (Acetone-D₆, 500 MHz): δ = 9.26–9.22 (m, 6H, 3,7,8,12,13,17-β), 9.21–9.19 (m, 2H, 2,18-β), 6.11 (t, 3J(H,H) = 7.0 Hz, 1H, ArF-NH), 4.47 (d, 3J(H,H) = 7.2 Hz, 2H, NHCH₂), 2.95 ppm (t; 4J(H,H) = 2.4 Hz, 1H, C≡CH). 13C NMR (Acetone-D₆, 126 MHz): δ = 151.99, 151.22, 151.17, 151.12, 148.63, 146.69, 144.03, 142.04, 139.72, 137.73, 133.33, 133.00, 132.94, 132.83, 129.31, 117.77, 109.96, 106.70, 104.36, 104.17, 81.90, 73.50, 35.75 ppm. 19F NMR (Acetone-D₆, 471 MHz): δ = −139.74 (dd, 3J(F,F) = 24.1 Hz; 4J(F,F) = 7.3 Hz, 2H, 5,10,15-o-ArF), −142.78–(−142.93) (m, 2F, 20-m-ArF), −156.32 (dd, 3J(F,F) = 20.2 Hz; 4J(F,F) = 9.6 Hz, 3H, 5,10,15-p-ArF), −160.95 (d, 3J(F,F) = 16.1 Hz, 2F, o-ArF), −164.96–(−165.14) ppm (m, 6F, 5,10,15-m-ArF). m.p.: > 230 °C. HRMS (ESI): calc. for C₄₇H₁₂F₁₉N₅Zn⁺ ([M]+): 1071.0081 found: 1071.0035. UV/Vis (DCM): λmax (ε [M⁻¹cm⁻¹]) = 578 (4000), 544 (19 000), 415 nm (271 000).
{Bis(pentafluorophenyl)-bis[4-(prop-2-ynamino)tetrafluorophenyl]porphyrinato}·zinc(II) (cis/trans mixture) $^1$H NMR (Acetone-D$_6$, 250 MHz): $\delta = 9.35–9.08$ (m, 8H, $\beta$), 6.17 (t, $^3 J(H,H) = 7.0$ Hz, 2H, ArF-NH), 4.48 (d, $^3 J(H,H) = 6.0$ Hz, 4H, NHCH$_2$), 2.97 ppm (s, 2H, C≡CH). HRMS (ESI): calc. for C$_{50}$H$_{17}$F$_{18}$N$_6$Zn$^+$ ([M + H]$^+$): 1107.0519 found: 1107.0469.

![Structure](image)

{5,10,15-Tris(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(N-(2-((2-aminoethyl)disulfanyl)ethyl propyneamido))-phenyl]porphyrinato}·zinc(II) (5c) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(N-(2-((2-aminoethyl)disulfanyl)ethyl-propyneamido))phenyl]porphyrin (5b) (56.0 mg, 59.8 µmol) was dissolved in 2 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (138 mg, 629 µmol) was added to the stirred solution. The solution was stirred for 30 min at RT. The crude product was dissolved in 100 mL of ethyl acetate and washed three times with 50 mL of H$_2$O. Afterwards the organic layer was dried over Na$_2$SO$_4$ and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/n-hexane to obtain {5,10,15-tris-(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(N-(2-((2-aminoethyl)disulfanyl)ethyl propyneamido))phenyl]porphyrinato}·zinc(II) (5c) (58.0 mg, 58.0 µmol, 97% yield) as a pink solid.

$^1$H NMR (Acetone-D$_6$, 700 MHz): $\delta = 9.02$ (d, $^3 J(H,H) = 4.5$ Hz, 2H, 2,18-$\beta$), 8.98 (d, $^3 J(H,H) = 4.5$ Hz, 2H, 3,17-$\beta$), 8.95 (d, $^3 J(H,H) = 4.5$ Hz, 2H, 6,13-$\beta$), 8.94 (d, $^3 J(H,H) = 4.5$ Hz, 2H, 8,12-$\beta$), 8.91–8.87 (bs, 3H, 5,10,15-meso-3-Ar-OH), 8.10–8.07 (bs, 1H, NHC(O)), 7.72 (s, 3H, 5,10,15-meso-2-Ar), 7.69 (d, $^3 J(H,H) = 7.2$ Hz, 3H, 5,10,15-meso-6-Ar), 7.62–7.57 (m, 3H, 5,10,15-meso-5-Ar), 7.29 (dd, $^3 J(H,H) = 8.6, ^4 J(H,H) = 2.6$ Hz, 3H, 5,10,15-meso-4-Ar), 5.79 (t, $^3 J(H,H) = 6.6$ Hz, 1H, ArF-NHCH$_2$), 4.01 (q, $^3 J(H,H) = 6.8$ Hz, 2H, ArF-NHCH$_2$CH$_2$), 3.67 (q, $^3 J(H,H) = 6.5$ Hz, 2H, CH$_2$NHC(O)), 3.52 (s, 1H, C≡CH), 3.25 (t, $^3 J(H,H) = 6.7$ Hz, 2H, ArF-NHCH$_2$CH$_2$), 3.01 ppm (t, $^3 J(H,H) = 6.8$ Hz, 2H,
$CH_2CH_2NHC(O))$. $^{13}$C NMR (Acetone-$D_6$, 176 MHz): $\delta = 156.54, 156.52, 152.89, 151.17, 151.09, 150.82, 150.60, 148.55, 147.20, 145.39, 145.32, 138.85, 137.52, 133.44, 132.61, 132.32, 131.04, 129.32, 128.18, 128.15, 127.21, 122.88, 122.67, 121.68, 115.37, 109.94, 103.57, 78.66, 74.45, 45.49, 39.56, 39.42, 37.93$ ppm. $^{19}$F NMR (Acetone-$D_6$, 376 MHz): $\delta = -142.72$ (d, $^3J(F,F) = 21.3$ Hz, 2F, $m$-ArF), $-161.99$ (−162.12) ppm (m, 2F, $o$-ArF). m.p.: > 230 °C. HRMS (ESI): calc. for C$_{51}$H$_{34}$F$_6$N$_6$O$_4$S$_2$Zn$^+$ ([M]$^+$): 998.1311 found: 998.1294. UV/Vis (Ethanol): $\lambda_{\text{max}} (\varepsilon [M^{-1} \text{cm}^{-1}]) = 597$ (5000), 556 (18 000), 423 nm (411 000).
2. $^1$H, $^{13}$C, and $^{19}$F-NMR of porphyrins 1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d, 11, 13a-b, and 14a-b

Figure 1. $^1$H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 1d

Figure 2. $^{13}$C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 1d
Figure 3. $^{19}$F spectrum ($JEOL^{TM}$ ECX 400, 376 MHz, acetone-$d_6$) of porphyrin 1d

Figure 4. $^1$H spectrum ($Bruker$ BioSpin AVANCE700, 700 MHz, THF-$d_8$) of porphyrin 2a
Figure 5. $^{13}$C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, THF-$d_8$) of porphyrin 2a

Figure 6. $^{19}$F spectrum (*JEOL* $^{TM}$ ECX 400, 376 MHz, THF-$d_8$) of porphyrin 2a
Figure 7. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, CD$_3$OD) of porphyrin 2b

Figure 8. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 126 MHz, CD$_3$OD) of porphyrin 2b
Figure 9. $^{19}$F spectrum ($JEOL^TM$ ECX 400, 376 MHz, CD$_3$OD) of porphyrin 2b

Figure 10. $^1$H spectrum ($JEOL^TM$ ECP 500, 500 MHz, CD$_3$OD) of porphyrin 2c
Figure 11. $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, CD$_3$OD) of porphyrin 2c

Figure 12. $^{19}$F spectrum ($JEOL^{TM}$ ECX 400, 376 MHz, CD$_3$OD) of porphyrin 2c
Figure 13. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, CD$_3$OD) of porphyrin 2d

Figure 14. $^{13}$C spectrum (JEOL$^{TM}$ ECP 500, 126 MHz, CD$_3$OD) of porphyrin 2d
Figure 15. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, CD$_3$OD) of porphyrin 2d

Figure 16. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 2e
Figure 17. $^{13}\text{C}$ spectrum (JEOL$^{\text{TM}}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 2e

Figure 18. $^{19}\text{F}$ spectrum (JEOL$^{\text{TM}}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 2e
**Figure 19.** $^1$H spectrum (JEOL$^\text{TM}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 2f

**Figure 20.** $^{13}$C spectrum (JEOL$^\text{TM}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 2f
Figure 21. $^{19}$F spectrum ($JEOL^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 2f

Figure 22. $^1$H spectrum ($Bruker BioSpin$ AVANCE700, 700 MHz, CDCl$_3$) of porphyrin 2g
Figure 23. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 176 MHz, CDCl$_3$) of porphyrin 2g

Figure 24. $^{19}$F spectrum (JEOL$^\text{TM}$ ECP 500, 471 MHz, CDCl$_3$) of porphyrin 2g
Figure 25. $^1$H spectrum (JEOL$^{TM}$ ECX 400, 400 MHz, acetone-$d_6$) of porphyrin 2h

Figure 26. $^{13}$C spectrum (JEOL$^{TM}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 2h
Figure 27. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 2h

Figure 28. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, CDCl$_3$) of porphyrin 2i
Figure 29. $^{13}$C spectrum (JEOL$^{\text{TM}}$ ECP 500, 126 MHz, CDCl$_3$) of porphyrin 2i

Figure 30. $^{19}$F spectrum (JEOL$^{\text{TM}}$ ECP 500, 471 MHz, CDCl$_3$) of porphyrin 2i
Figure 31. $^1$H spectrum ($JEOL^{TM}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 4

Figure 32. $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 4
Figure 33. $^{19}$F spectrum ($JEOL^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 4

Figure 34. $^1$H spectrum ($JEOL^{TM}$ ECP 500, 500 MHz, THF-$d_8$) of porphyrin 5a
**Figure 35.** $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, THF-$d_8$) of porphyrin 5a

**Figure 36.** $^{19}$F spectrum ($JEOL^{TM}$ ECX 400, 376 MHz, THF-$d_8$) of porphyrin 5a
Figure 37. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 5b

Figure 38. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 5b
Figure 39. $^{19}$F spectrum (JEOL™ ECX 400, 376 MHz, acetone-$d_6$) of porphyrin 5b

Figure 40. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 5c
**Figure 41.** $^{13}$C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 5c

**Figure 42.** $^{19}$F spectrum (*JEOL*™ ECX 400, 376 MHz, acetone-$d_6$) of porphyrin 5c
Figure 43. $^1$H spectrum ($JEOLECP$ 500, 500 MHz, THF-$d_8$) of porphyrin 6a

Figure 44. $^{13}$C spectrum ($JEOLECP$ 500, 126 MHz, THF-$d_8$) of porphyrin 6a
Figure 45. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, THF-$d_8$) of porphyrin 6a

Figure 46. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, THF-$d_8$) of porphyrin 6b
Figure 47. $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, THF-$d_8$) of porphyrin 6b

Figure 48. $^{19}$F spectrum ($JEOL^{TM}$ ECX 400, 376 MHz, THF-$d_8$) of porphyrin 6b
Figure 49. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, THF-$d_8$) of porphyrin 6c

Figure 50. $^{13}$C spectrum (JEOL$^{TM}$ ECP 500, 126 MHz, THF-$d_8$) of porphyrin 6c
Figure 51. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, THF-$d_8$) of porphyrin 6c

Figure 52. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 8a
Figure 53. $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 8a

Figure 54. $^{19}$F spectrum ($JEOL^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 8a
Figure 5. $^1$H spectrum (JEOL$^{\text{TM}}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 8b

Figure 6. $^{13}$C spectrum (JEOL$^{\text{TM}}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 8b
Figure 57. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 8b

Figure 58. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, acetone-$d_6$) of porphyrin 8c
Figure 59. $^{13}$C spectrum (JEOL$^{TM}$ ECP 500, 126 MHz, acetone-$d_6$) of porphyrin 8c

Figure 60. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 8c
Figure 61. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 9

Figure 62. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 9
Figure 63. $^{19}$F spectrum (JEOL$^{TM}$ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 9

Figure 64. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, THF-$d_8$) of porphyrin 10a
Figure 65. $^{13}$C spectrum (*Bruker BioSpin AVANCE700, 176 MHz, THF-$_d^8$*) of porphyrin 10a

Figure 66. $^{19}$F spectrum (*JEOL$^{TM}$ ECX 400, 376 MHz, THF-$_d^8$*) of porphyrin 10a
Figure 67. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 10b

Figure 68. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 10b
Figure 69. $^{19}$F spectrum (*JEOL*™ ECP 500, 471 MHz, acetone-$d_6$) of porphyrin 10b

Figure 70. $^1$H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-$d_6$) of porphyrin 10c
Figure 71. $^{13}$C spectrum (*Bruker BioSpin AVANCE700, 176 MHz, acetone-$d_6$) of porphyrin 10c

Figure 72. $^{19}$F spectrum (*JEOL$^\text{TM}$ ECX 400, 376 MHz, acetone-$d_6$) of porphyrin 10c
Figure 73. $^1$H spectrum (JEOL$^\text{TM}$ ECP 500, 500 MHz, CD$_3$OD) of porphyrin 10d

Figure 74. $^{13}$C spectrum (JEOL$^\text{TM}$ ECP 500, 126 MHz, CD$_3$OD) of porphyrin 10d
Figure 75. $^{19}$F spectrum (JEOL$^{TM}$ ECX 400, 376 MHz, CD$_3$OD) of porphyrin 10d

Figure 76. $^1$H spectrum (JEOL$^{TM}$ ECP 500, 500 MHz, CDCl$_3$) of porphyrin 11
**Figure 77.** $^{13}$C spectrum ($JEOL^{TM}$ ECP 500, 126 MHz, CDCl$_3$) of porphyrin 11

**Figure 78.** $^{19}$F spectrum ($JEOL^{TM}$ ECP 500, 471 MHz, CDCl$_3$) of porphyrin 11
**Figure 79.** $^1$H spectrum (*Bruker BioSpin AVANCE700, 700 MHz, acetone-$d_6$/D$_2$O = 5/1, v/v*) of conjugate 13a

**Figure 80.** $^{13}$C spectrum (*Bruker BioSpin AVANCE700, 176 MHz, acetone-$d_6$/D$_2$O = 5/1, v/v*) of conjugate 13a
Figure 81. $^1$H spectrum (Bruker BioSpin AVANCE700, 700 MHz, D$_2$O) of conjugate 13b

Figure 82. $^{13}$C spectrum (Bruker BioSpin AVANCE700, 176 MHz, D$_2$O) of conjugate 13b
**Figure 83.** $^1$H spectrum (*Bruker BioSpin AVANCE700, 700 MHz, D$_2$O*) of conjugate 14a

**Figure 84.** $^{13}$C spectrum (*Bruker BioSpin AVANCE700, 176 MHz, D$_2$O*) of conjugate 14a
**Figure 8.** $^1$H spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-$d_6$/D$_2$O = 5/1, v/v) of conjugate 14b

**Figure 86.** $^{13}$C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-$d_6$/D$_2$O = 5/1, v/v) of conjugate 14b
3. ESI-MS of porphins 1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d, and 11

**Figure 87.** HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 1d

**Figure 88.** Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 1d
Figure 89. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2a

Figure 90. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2a
**Figure 91.** HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2b

**Figure 92.** Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2b
Figure 93. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2c

Figure 94. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2c
Figure 95. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2d

Figure 96. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2d
Figure 97. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2e

Figure 98. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2e
**Figure 99.** HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2f

**Figure 100.** Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2f
Figure 101. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2g

Figure 102. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2g
Figure 103. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2h

Figure 104. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2h
Figure 105. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2i

Figure 106. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 2i
Figure 107. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 4

Figure 108. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 4
Figure 109. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5a

Figure 110. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5a
Figure 111. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5b

Figure 112. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5b
Figure 113. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5c

Figure 114. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 5c
Figure 115. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6a

Figure 116. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6a
**Figure 117.** HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6b

**Figure 118.** Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6b
Figure 119. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6c

Figure 120. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 6c
Figure 121. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 8a

Figure 122. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 8b
Figure 123. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 8b

Figure 124. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 8c
Figure 125. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 8c

Figure 126. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 9
Figure 127. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 9

Figure 128. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10a
Figure 129. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10a

Figure 130. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10b
Figure 131. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10b

Figure 132. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10c
**Figure 133.** Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin 10c

**Figure 134.** HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin 10d
Figure 135. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 10d

Figure 136. HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 11
Figure 137. Zoomed HRMS spectrum (Agilent 6210, Agilent Technologies) of porphyrin 11