

4-Formyl-5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 10.85 (s, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 1.67 (s, 6H), 1.36 (s, 9H), 1.34 (s, 9H).

4-(5,5'-Dimethyl-1,3-dioxane)-5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (3). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.61 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 6.08 (s, 1H), 3.82 (s, 4H), 1.63 (s, 6H), 1.37 (s, 3H), 1.36 (s, 9H), 1.34 (s, 9H), 0.85 (s, 3H).

4-(5,5'-Dimethyl-1,3-dioxane)-5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (4). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 8.10 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 5.75 (s, 1H), 3.83 (s, 4H), 1.67 (s, 6H), 1.36 (s, 18H), 1.30 (s, 3H), 0.85 (s, 3H).

4-Formyl-5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (5). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 10.16 (s, 1H), 8.24 (d, J = 2.4 Hz, 1H), 7.76 (d, J = 2.4 Hz, 1H), 7.72 (d, J = 2.4 Hz, 1H), 7.68 (d, J = 2.4 Hz, 1H), 1.71 (s, 6H), 1.41 (s, 9H), 1.38 (s, 9H).

4-Formyl-5-methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (6). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 10.79 (s, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.63 (d, J = 2.4 Hz, 1H), 3.99 (s, 3H), 1.69 (s, 6H), 1.38 (s, 9H), 1.37 (s, 9H).

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-

trimesitylporphyrin, $\text{H}_2(\text{HPX-CO}_2\text{Me})$ (7). ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 8.79 (d, J = 4.8 Hz, 2H), 8.62-8.72 (br, 6H), 7.90 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.27-7.38 (m, 6H), 2.67 (s, 3H), 2.66 (s, 6H), 2.13 (s, 3H), 1.99 (s, 6H), 1.98 (s, 6H), 1.88 (s, 6H), 1.76 (s, 3H), 1.52 (s, 9H), 1.31 (s, 9H), -0.08 (s, 3H), -2.37 (s, 2H). HRFABMS (M^+) calcd for $\text{C}_{72}\text{H}_{74}\text{N}_4\text{O}_3$ m/z , 1042.5761, found 1042.5759. Anal. Calcd for $\text{C}_{72}\text{H}_{74}\text{N}_4\text{O}_3$: C, 82.88; H, 7.15; N, 5.37. Found: C, 82.49; H, 7.10; N, 5.58.

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5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-

triphenylporphyrin, H₂(HTPPX-CO₂Me) (8). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.84 (d, *J* = 19 Hz, 9H), 8.21-8.30 (m, 6H), 8.01 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 2.5 Hz, 1H), 7.74-7.79 (m, 9H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 1.92 (s, 6H), 1.52 (s, 9H), 1.25 (s, 9H), -0.34 (s, 3H), -2.66 (s, 2H). HRFABMS (M⁺) calcd for C₆₃H₅₆N₄O₃ *m/z*, 916.4352, found 916.4355. Anal. Calcd for C₆₃H₅₆N₄O₃: C, 82.50; H, 6.15; N, 6.11. Found: C, 82.28; H, 6.52; N, 5.94.

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tri(2,6-

dichlorophenyl)porphyrin, H₂(HTDCPPX-CO₂Me) (9). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.83 (d, *J* = 4.5 Hz, 2H), 8.68 (br, 4H), 8.63 (d, *J* = 4.5 Hz, 2H), 7.69-7.85 (m, 11H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 1.92 (s, 6H), 1.47 (s, 9H), 1.25 (s, 9H), -0.02 (s, 3H), -2.46 (s, 2H). HRFABMS (M⁺) calcd for C₆₃H₅₀Cl₆N₄O₃ *m/z*, 1120.2014, found 1120.2014. Anal. Calcd for C₆₃H₅₀N₄O₃Cl₆: C, 67.33; H, 4.48; N, 4.99. Found: C, 67.50; H, 4.58; N, 5.11.

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tri(2,6-

dimethoxyphenyl)porphyrin, H₂(HTDMPPX-CO₂Me) (10). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.68-8.71 (m, 6H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.68-7.73 (m, 4H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.04 (d, *J* = 9.5 Hz, 1H), 6.97-7.00 (m, 6H), 3.68 (s, 3H), 3.55 (s, 6H), 3.51 (s, 6H), 3.47 (s, 3H), 1.92 (s, 6H), 1.46 (s, 9H), 1.25 (s, 9H), 0.05 (s, 3H), -2.46 (s, 2H). HRFABMS (M⁺) calcd for C₆₉H₆₈N₄O₉ *m/z*, 1096.4986, found 1096.4929. Anal. Calcd for C₆₉H₆₈N₄O₉: C, 75.53; H, 6.25; N, 5.11. Found: C, 75.28; H, 6.52; N, 4.94.

Zinc(II) 5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-

trimesitylporphyrin, Zn(HPX-CO₂Me) (11). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.83 (d, *J* = 4.8 Hz, 2H), 8.68-8.74 (m, 6H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.31 (br, 1H), 7.22-7.30 (m, 6H), 2.64 (s, 3H), 2.62 (s, 6H), 2.05 (s, 3H), 1.97 (s, 6H), 1.94 (s, 6H), 1.77 (s, 6H), 1.72 (s, 3H), 1.47 (s, 9H), 1.26 (s, 9H), 0.30 (s, 3H). HRFABMS

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(M⁺) calcd for C₇₂H₇₂N₄O₃Zn *m/z*, 1104.4896, found 1104.4900. Anal. Calcd for C₇₂H₇₄N₄O₃Zn: C, 78.14; H, 6.56; N, 5.06. Found: C, 78.53; H, 7.47; N, 4.81.

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-

trimesitylporphyrin, H₂(HPX-CO₂H) (12). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.60-8.67 (br, 6H), 8.04 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.24-7.34 (m, 6H), 2.65 (s, 3H), 2.62 (s, 6H), 2.00 (s, 3H), 1.97 (s, 6H), 1.92 (s, 6H), 1.89 (s, 3H), 1.85 (s, 6H), 1.54 (s, 9H), 1.27 (s, 9H), -2.44 (s, 2H). HRFABMS (M⁺) calcd for C₇₁H₇₂N₄O₃ *m/z*, 1028.5604, found 1028.5579. Anal. Calcd for C₇₁H₇₂N₄O₃: C, 82.84; H, 7.05; N, 5.44. Found: C, 82.47; H, 7.19; N, 5.71.

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-triphenyl-

porphyrin, H₂(HTPPX-CO₂H) (13). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.77-8.85 (m, 9H), 8.19-8.31 (m, 6H), 8.08 (d, *J* = 2.5 Hz, 1H), 7.93 (d, *J* = 2.5 Hz, 1H), 7.72-7.80 (m, 9H), 7.66 (d, *J* = 2.5 Hz, 1H), 1.97 (s, 6H), 1.27 (s, 9H), 1.25 (s, 9H), -2.69 (s, 2H). HRESI-MS (MH⁺) calcd for C₆₂H₅₅N₄O₃ *m/z*, 903.4269, found 903.4286. Anal. Calcd for C₆₂H₅₄N₄O₃: C, 82.45; H, 6.03; N, 6.20. Found: C, 82.44; H, 6.13; N, 6.07.

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tri(2,6-

dichlorophenyl)porphyrin, H₂(HTDCPPX-CO₂H) (14). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.78 (d, *J* = 4.5 Hz, 2H), 8.63-8.68 (m, 5H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.77-7.83 (m, 6H), 7.65-7.72 (m, 6H), 1.95 (s, 6H), 1.53 (s, 9H), 1.25 (s, 9H), -2.46 (s, 2H). HRESI-MS (MH⁺) calcd for C₆₂H₄₉Cl₆N₄O₃ *m/z*, 1107.1930, found 1107.1922. Anal. Calcd for C₆₂H₄₈N₄O₃Cl₆: C, 67.10; H, 4.36; N, 5.05. Found: C, 67.28; H, 4.12; N, 5.25.

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tri(2,6-

dimethoxyphenyl)porphyrin, H₂(HTDMPPX-CO₂H) (15). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.71-8.74 (m, 6H), 8.08 (d, *J* = 2.5 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.67-7.74 (m, 4H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 6.98-7.01 (m, 6H), 3.56 (s, 6H), 3.53 (s, 6H), 3.52 (s, 6H), 1.92 (s, 6H), 1.52 (s, 9H), 1.24 (s, 9H), -2.46 (s, 2H). HRESI-MS (MH⁺) calcd for

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$C_{68}H_{67}N_4O_9$ m/z , 1083.4903, found 1083.4899. Anal. Calcd for $C_{68}H_{66}N_4O_9$: C, 75.39; H, 6.14; N, 5.17. Found: C, 75.40; H, 4.12; N, 5.07.

5-(4-(5-Aminocarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-

trimesitylporphyrin, $H_2(HPX-CONH_2)$ (16). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.78 (d, J = 4.8 Hz, 2H), 8.70-8.63 (m, 6H), 8.12 (d, J = 2.4 Hz, 1H), 7.90 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.34-7.25 (m, 6H), 2.65 (s, 3H), 2.62 (s, 6H), 2.05 (s, 3H), 1.94 (s, 6H), 1.87 (s, 15H), 1.56 (s, 9H), 1.22 (s, 9H), -2.53 (s, 2H); HRFABMS (MH^+) calcd for $C_{71}H_{74}N_5O_2$ m/z , 1028.5843, found 1028.5810. Anal. Calcd for $C_{71}H_{73}N_5O_2$: C, 82.92; H, 7.15; N, 6.81. Found: C, 82.69; H, 6.96; N, 7.08.

5,15-Bis-(4-(5-methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,20-

dimesitylporphyrin, $H_2(HPBX-CO_2Me)$ (17a and 17b). **17a:** 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.77 (d, J = 4.5 Hz, 4H), 8.66 (d, J = 4.5 Hz, 4H), 7.94 (d, J = 2.5 Hz, 2H), 7.86 (d, J = 2.5 Hz, 2H), 7.65 (d, J = 2.5 Hz, 2H), 7.34 (d, J = 2.5 Hz, 2H), 7.65 (d, J = 22 Hz, 4H), 2.61 (s, 6H), 2.01 (s, 6H), 1.94 (s, 12H), 1.82 (d, J = 4 Hz, 6H), 1.49 (s, 18H), 1.26 (s, 18H), -0.202 (s, 6H), -2.41 (s, 2H). HRFABMS (M^+) calcd for $C_{88}H_{94}N_4O_6$ m/z , 1302.7173, found 1302.7169. Anal. Calcd for $C_{88}H_{94}N_4O_6$: C, 81.07; H, 7.27; N, 4.30. Found: C, 80.80; H, 6.87; N, 4.22. The α,β -atropisomer eluted first on the column. **17b:** 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.77 (d, J = 4.5 Hz, 4H), 8.64 (d, J = 4.5 Hz, 4H), 8.10 (d, J = 2.5 Hz, 2H), 7.85 (d, J = 2.5 Hz, 2H), 7.61 (d, J = 2.5 Hz, 2H), 7.26 (d, J = 2.5 Hz, 6H), 2.60 (s, 6H), 1.92 (s, 12H), 1.90 (s, 12H), 1.53 (s, 18H), 1.23 (s, 18H), -0.492 (s, 6H), -2.39 (s, 2H). HRFABMS (M^+) calcd for $C_{88}H_{94}N_4O_6$ m/z , 1302.7173, found 1302.7168. Anal. Calcd for $C_{88}H_{94}N_4O_6$: C, 81.07; H, 7.27; N, 4.30. Found: C, 80.93; H, 7.00; N, 4.53.