SUPPORTING INFORMATION

Synthesis and Magnetic Properties of Novel Azamacrocyclic Ln(III), Cu(II), Fe(III) and Sr(II) Complexes and Conformational Analysis of the Ligands

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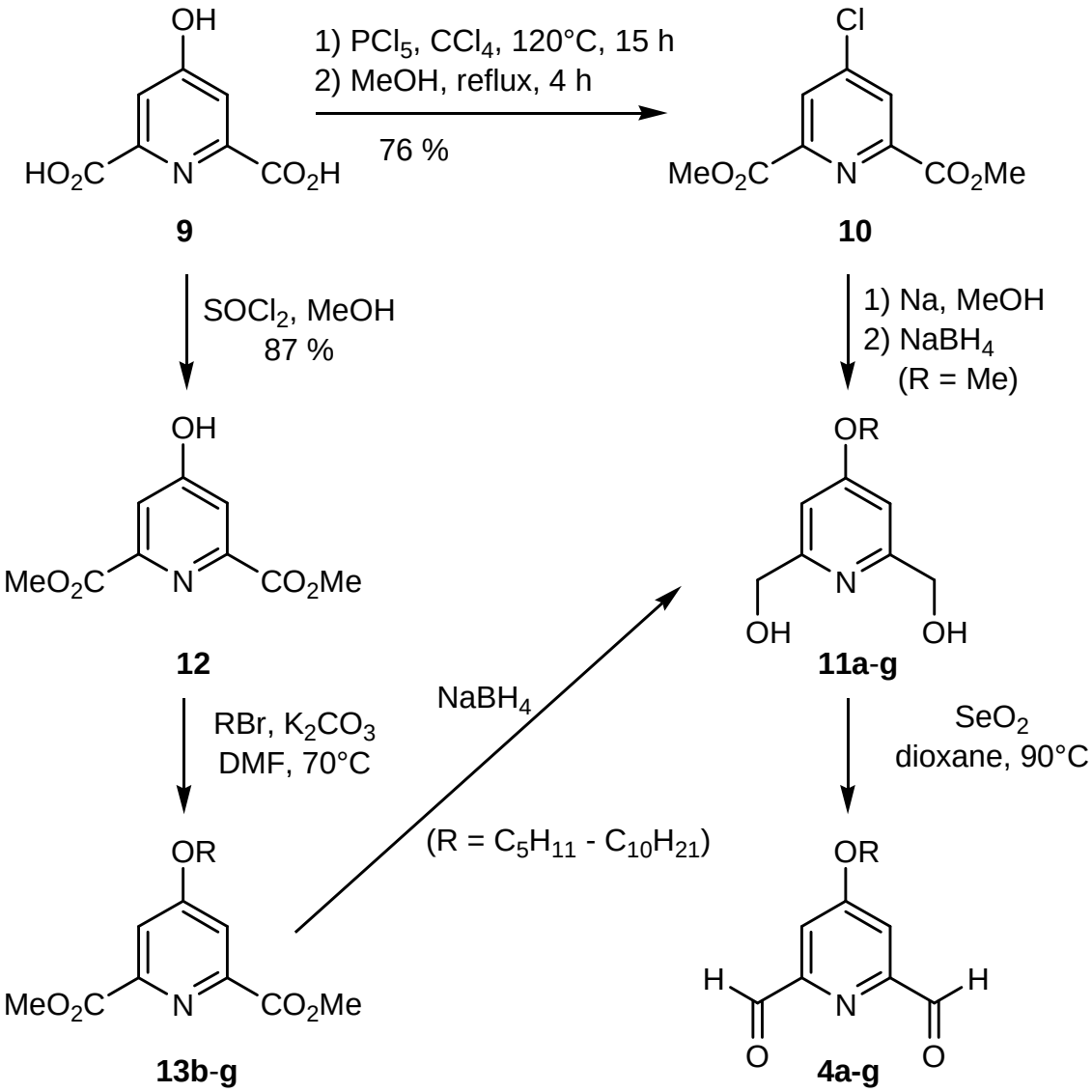
Following a procedure by *Piguet* [1a] and *Battacharya* [1b] chelidamic acid **9** was treated with phosphorous pentachloride in CCl_4 and subsequently refluxed with MeOH to give 4-chloro-pyridine-2,6-dicarboxylic acid dimethylester **10** in 76 % yield (Scheme). Replacement of chloride was achieved by reaction of diester **10** with freshly prepared sodium methoxide according to a method by *Lüning* [2]. Further reduction of the ester moieties with $NaBH_4$ yielded the diol **11a** in 48 %. Diol **11a** was then oxidized with selenium dioxide to the corresponding dialdehyde **4a** in 95 % yield. The dialdehydes **4b**-**g** with longer alkoxy substituents in the 4-position were synthesized by a different route. According to the procedure by *Chessa* [3] chelidamic acid **9** was reacted with thionyl chloride in MeOH to give the dimethylester **12** in 87 % yield.



R	**4**, **11**, **13**	**4** [%]	**11** [%]	**13** [%]
CH_3	**a**	95	48	--
C_5H_{11}	**b**	81	87	96
C_6H_{13}	**c**	89	81	81
C_7H_{15}	**d**	85	83	81
C_8H_{17}	**e**	95	83	85
C_9H_{19}	**f**	85	97	80
$C_{10}H_{21}$	**g**	80	86	87

Scheme

Etherification of the 4-hydroxy group under classical Williamson conditions yielded the diesters **13b-g** , which were subsequently reduced with $NaBH_4$ to the diols **11b-g** and finally oxidized with selenium dioxide to the dialdehydes **4b-g**.

General: Mass spectrometry was performed on a Varian MAT 711 mass spectrometer with EI ionization (70 eV).

***Preparation of* 4-chloropyridine-2,6-dicarboxylic acid dimethylester (10)**

A mixture of chelidamic acid monohydrate **9** (11.4 g, 62.6 mmol) and PCl_5 (32.1 g, 0.15 mol) in 48 mL CCl_4 was heated at 120°C for 15 h and cooled to room temperature. Dry MeOH (48 mL) was added to this mixture over a period of 30 min, and the resulting mixture was refluxed for 4 h. The solvents were evaporated to afford a solid which was dissolved in EtOAc and treated with activated charcoal (5.0 g) under boiling conditions. The green resulting mixture was filtered over Celite, the EtOAc was evaporated. Repeated crystallizations from MeOH gave colorless crystals (10.9 g, 76 %). Mp. 209°C, ref.[4c]: mp. 210°C (HOAc). Spectroscopic data were in accordance with ref. [4].

***Preparation of* 2,6-bis(hydroxymethyl)-4-methoxy-pyridine (11a)**

Na (0.51 g, 10.5 mmol) was dissolved in dry methanol (75 mL) and **10** (3.36 g, 15.0 mmol) was slowly added in small quantities and the mixture was refluxed for 3 h. After completion of the reaction (controlled by TLC), the mixture was cooled to 0°C, and $NaBH_4$ (3.00 g, 90.0 mmol) was added in portions during 15 min, followed by stirring at 20°C (1.5 h) and at reflux temperature (16 h). Then acetone (20 mL) was added, the

mixture was refluxed for 1 h, the solvents were removed, and the residue was heated with 22 mL of a sat. $NaHCO_3/Na_2CO_3$ solution. After dilution with 15 mL of water, the mixture was continuously extracted with $CHCl_3$ for 2 days. The organic phase was dried over $MgSO_4$, evaporation of the solvent yielded a pale yellow solid (1.25 g, 48 %). Mp. 121°C, ref. [2]: mp. 121-122°C ($CHCl_3$). Spectroscopic data were in accordance with ref. [2].

***Preparation of* 4-methoxy-pyridine-2,6-dicarbaldehyde (4a)**:

11a (0.57 g, 3.37 mmol) was suspended in 1,4-dioxane (17 mL) and SeO_2 (0.374 g, 3.37 mmol) added. After refluxing for 7 h, the hot solution was filtered through celite und sand, the solvent was evaporated to yield 0.58 g of pale yellow solid. The mixture was dissolved in a small volume of CH_2Cl_2 and purified by column chromatography (SiO_2 with 5 % H_2O; hexanes/EtOAc = 45 : 10). Evaporation of the solvent yielded a colorless solid (0.53 g, 95 %). Mp. 138°C, ref. [2]: mp. 137°C (CH_2Cl_2/hexanes). Spectroscopic data were in accordance with ref. [2].

***Preparation of* 4-hydroxypyridine-2,6-dicarboxylic acid dimethylester (12)**:

Chelidamic acid monohydrate **9** (1.10 g, 5.46 mmol) was added at -10°C to a cooled solution of $SOCl_2$ (3.2 mL, 43.7 mmol) and methanol (11 mL). The mixture was stirred 24 h at room temperature and than refluxed for additional 3.5 h. After cooling, the mixture was concentrated under reduced pressure to give a residue, which was treated with water at 0°C. The resulting suspension was neutralized with 10% $NaCO_3$ solution and filtered. The solid was dried and recrystallized from water to yield colorless crystals

(1.00 g, 87 %). Mp. 168°C, ref. [3b]: mp. 170-171°C. Spectroscopic data were in accordance with ref. [3].

***General procedure for the preparation of* 4-alkyloxy-pyridine-2,6-dicarboxylic acid dimethylesters (13b-g)**:

A mixture of 2 equiv. K_2CO_3, 1 equiv. of 4-hydroxypyridine-2,6-dicarboxylic acid dimethylester **12** and 1 equiv. of 1-alkyl bromide (R = C_5H_{11}-$C_{10}H_{21}$) in DMF (10-35 mL) was refluxed for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature, water (10 mL) was added and the mixture was washed with EtOAc (3 x 20 mL) (**13b**,**g**), the organic phase was dried over $MgSO_4$, concentrated and dried *in vacuo*. In case of **13c-f** the precipitate was filtered and dried *in vacuo* and was then recrystallized.

4-Pentyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13b): According to the general procedure, K_2CO_3 (0.27 g, 2.0 mmol), **12** (0.21 g, 1.0 mmol) and *n*-pentyl bromide (0.12 mL, 1.0 mmol) in DMF (26 mL) were used. Colorless solid (0.27 g, 96 %). Mp: 73°C, ref. [5]: mp. 72.5-73°C (MeOH). Spectroscopic data were in accordance with ref.[5].

4-Hexyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13c): According to the general procedure, K_2CO_3 (3.32 g, 24.0 mmol), **12** (2.5 g, 12.0 mmol) and *n*-hexyl bromide (1.71 mL, 12.0 mmol) in DMF (30 mL) were used. Recrystallization from hexanes/Et_2O yielded a colorless solid (2.87 g, 81 %). Mp: 69°C. $C_{15}H_{21}NO_5$ (295.14): calcd.: C, 61.00; H, 7.17; N 4.74; found: C, 60.95; H, 7.09; N 4.67. ^{1}H-NMR (300 MHz,

DMSO-[D_6]): δ = 0.87 (t, *J* = 6.8 Hz, 3H, *CH_3*), 1.23-1.46 (m, 6H, CH_3*$CH_2CH_2CH_2$*), 1.69-1.79 (m, 2H, *CH_2*CH_2*O*), 3.90 (s, 6H, 2 x O*CH_3*), 4.20 (t, *J* = 6.4 Hz, 2H, O*CH_2*), 7.71 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): δ = 13.7 (*C*H_3), 21.9 (CH_3*C*H_2), 24.8, 28.0, 30.7 (OCH_2*C*H_2), 52.6 (2 x O*C*H_3), 68.6 (O*C*H_2), 113.9 (*C*H, py), 149.2, 164.5, 166.3 (2 x *C*O) ppm. MS (CI, CH_4): *m/z* (%) = 296 (100) [M^+ + H], 212 (60) [M^+ - C_6H_{12}]. FT-IR (ATR): ? = 2924 (m), 2855 (w, CH), 1748 (vs), 1717 (vs, C=O), 1591 (vs), 1565 (s, C=C), 1439 (vs), 1340 (vs, C-H), 1256 (s), 1227 (vs), 1154 (s), 1102 (s), 1034 (s, C-O-C), 987 (s), 782 (s), 732 (s) cm^{-1}. UV-VIS (CH_2Cl_2): $?_{max}$ (log e) = 249 (2.66).

4-Heptyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13d): According to the general procedure, K_2CO_3 (3.32 g, 24.0 mmol), **12** (2.8 g, 12.0 mmol) and *n*-heptyl bromide (2.0 mL, 12.0 mmol) in DMF (30 mL) were used. Recrystallization from hexanes/$CHCl_3$ yielded a colorless solid (3.06 g, 81 %). Mp: 75°C. $C_{16}H_{23}NO_5$ (309.16): calcd.: C, 62.12; H, 7.49; N 4.53; found: C, 62.04; H, 7.38; N 4.54. ^{1}H-NMR (300 MHz, DMSO-[D_6]): δ = 0.8 (t, 3H, *CH_3*, *J* = 6.3, 6.9 Hz), 1.2-1.4 (m, 8H, CH_3(*CH_2)$_4$*), 1.70-1.79 (m, 2H, *CH_2*CH_2O), 3.9 (s, 6H, 2 x O*C*H_3), 4.2 (t, 2H, O*CH_2*, *J* = 6.4 Hz), 7.7 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): δ = 13.8 (*C*H_3), 21.9, 25.1, 28.0, 28.2, 31.1, 52.5 (2 x O*C*H_3), 68.6 (O*C*H_2), 113.9 (*C*H, py), 149.2, 164.5, 166.3 (2 x *C*O) ppm. MS (CI, CH_4): *m/z* (%) = 310 (100) [M^+ + H], 212 (40) [M^+ - C_7H_{14}]. FT-IR (ATR): ? = 2947 (w), 2920 (w, CH), 1748 (vs), 1716 (vs, C=O), 1591 (vs, C=C), 1442 (vs), 1343 (vs, C-H), 1254 (s), 1227 (vs), 1103 (s), 1035 (s, C-O-C), 997 (s), 878 (m), 781 (s) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 253 (3.15), 197 (0.33).

4-Octyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13e): According to the general procedure, K_2CO_3 (3.02 g, 22.0 mmol), **12** (2.34 g, 11.09 mmol) and *n*-octyl bromide (2.1 mL, 11.0 mmol) in DMF (30 mL) were used. Recrystallization from *n*-pentane yielded a colorless solid (3.08 g, 9.3 mmol, 85 %). Mp. 77°C. $C_{17}H_{25}NO_5$ (309.16): calcd.: C, 63.14; H, 7.79; N 4.33; found: C, 63.21; H, 7.85; N 4.28. ^{1}H-NMR (300 MHz, DMSO-[D_6]): δ = 0.8 (t, 3H, *CH*$_3$, *J* = 6.7, 7.1 Hz), 1.2-1.4 (m, 10 H, $CH_3(CH_2)_5$), 1.71-1.78 (m, 2H, *CH*$_2$$CH_2O$), 3.8 (s, 6H, 2 x O*CH*$_3$), 4.1 (t, 2H, O*CH*$_2$, *J* = 6.5 Hz), 7.7 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): δ = 13.8 (*C*H_3), 22.0, 25.1, 28.0, 28.5, 31.1, 52.6 (2 x O*C*H_3), 68.6 (O*C*H_2), 113.9 (*C*H, py), 149.2, 164.5, 166.43 (2 x *C*O) ppm. MS (CI, CH_4): *m/z* (%) = 323 (100) [M^+ + H], 212 (10) [M^+ - C_8H_{15}]. FT-IR (ATR): ? = 2955 (m), 2919 (m), 2850 (s, CH), 1748 (vs), 1719 (vs, C=O), 1596 (vs, C=C), 1442 (vs), 1359 (vs, C-H), 1254 (s), 1104 (s), 1034 (s, C-O-C), 990 (s), 885 (w), 786 (s) cm^{-1}. UV/VIS (CH_2Cl_2): ?$_{max}$ (log e) = 245 (1.78).

4-Nonyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13f): According to the general procedure, K_2CO_3 (0.41 g, 3.0 mmol), **12** (0.31 g, 1.50 mmol) and 1-nonyl bromide (0.28 mL, 1.5 mmol) in DMF (10 mL) were used. Recrystallization from *n*-pentane yielded a colorless solid (0.4 g, 80 %). Mp: 73°C. $C_{18}H_{27}NO_5$ (337.19): calcd.: $C_{18}H_{27}NO_5$ (337.19): C, 64.07; H, 8.07; N 4.1; found: C, 64.01; H, 7.96; N 4.08. ^{1}H-NMR (300 MHz, DMSO-[D_6]): δ = 0.8 (t, 3H, C*H*$_3$, *J* = 6.3, 6.8 Hz), 1.1-1.4 (m, 12 H, $CH_3(CH_2)_6$), 1.6-1.7 (m, 2H, *CH*$_2$$CH_2O$), 3.8 (s, 6H, 2 x O*CH*$_3$), 4.1 (t, 2H, O*CH*$_2$, *J* = 6.4 Hz), 7.7 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): δ = 13.8 (*C*H_3), 22.0, 28.0, 28.5, 28.8, 29.25, 31.1, 42.9, 52.5 (2 x O*C*H_3), 68.7 (O*C*H_2), 114.0 (*C*H, py), 149.2, 164.5, 166.3 (2 x *C*O) ppm. MS (CI, CH_4): *m/z* (%) = 338 (30) [M^+ + H], 337

(100) [M^+], 212 (70) [M^+ - C_9H_{17}]. FT-IR (ATR): ? = 2947 (m), 2920 (m), 2851 (s, CH), 1746 (vs), 1716 (vs, C=O), 1592 (vs, C=C), 1442 (vs), 1341(vs, C-H), 1253 (s), 1227 (m), 1103 (s, C-O-C), 998 (s), 785 (s) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 244 (1.64), 197 (0.18).

4-Decyloxy-pyridine-2,6-dicarboxylic acid dimethylester (13g): According to the general procedure, K_2CO_3 (0.41 g, 3.0 mmol), **12** (0.31 g, 1.5 mmol) and *n*-decyl bromide (0. 31 mL, 1.5 mmol) in DMF (10 mL) were used. Colorless solid (0.5 g, 87 %). Mp: 68 °C. $C_{19}H_{29}NO_5$ (351.44): calcd.: C, 64.93; H, 8.32; N 3.99; found: C, 64.81; H, 8.33; N 4.07. ^{1}H-NMR (300 MHz, DMSO-[D_6]): δ = 0.8 (t, 3H, *CH*$_3$, *J* = 6.1, 6.8 Hz), 1.2-1.4 (m, 12H, CH_3(*CH*$_2$)$_7$), 1.6-1.7 (m, 2H, *CH*$_2$$CH_2O$), 3.8 (s, 6H, 2 x O*CH*$_3$), 4.1 (t, 2H, O*CH*$_2$, *J* = 6.4 Hz) , 7.7 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): δ = 13.8 (*C*H_3), 22.0, 25.1, 28.0, 28.5, 28.6, 28.85, 28.88, 31.2, 52.5 (2 x O*C*H_3), 68.7 (O*C*H_2), 114.0 (*C*H, py), 149.2, 164.5, 166.3 (2 x *C*O) ppm. MS (EI): *m/z* (%) = 351 (30) [M^+], 293 (35) [M^+ - $COOCH_3$], 211 (40) [M^+ - $C_{10}H_{21}$], 153 (100). FT-IR (ATR): ? = 2955 (m), 2916 (m), 2852 (m, CH), 1715 (vs, C=O), 1595 (vs, C=C), 1442 (vs), 1363 (vs, C-H), 1267 (s), 1255 (s), 1106 (s), 1033 (s, C-O-C), 990 (s), 883 (w), 786 (s) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 242 (0.66).

***General procedure for the preparation of* 4-alkyloxy-2,6-dihydroxymethylpyridines (11b-g)**:

A solution of 1 equiv. 4-alkyloxypyridine-2,6-dicarboxylic acid dimethylester **13b-g** in MeOH (5-31 mL) was cooled to 0°C, and 4.8 equiv. $NaBH_4$ was added in portions during 15 min followed by stirring at 25°C (for 1.5 h) and subsequent refluxing (for 16

h). Then acetone (20-36 mL) was added, the mixture was heated under reflux for 1 h and the solvents were removed. The residue was treated with 10-20 mL of K_2CO_3 solution (60 g/150 mL H_2O) and heated for 2 h under reflux. The residual mixture was extracted continuously with $CHCl_3$ (30 mL) for 1½ h. The organic phase was dried over $MgSO_4$, concentrated and dried *in vacuo*.

4-Pentyloxy-2,6-dihydroxymethylpyridine (11b): According to the general procedure, **13b** (3.00 g, 10.7 mmol) and $NaBH_4$ (1.95 g, 51.7 mmol) in MeOH (32 mL) were used. Recrystallization from Et_2O/acetone yielded a colorless solid (2.15 g, 87 %). Mp: 79°C. $C_{12}H_{19}NO_3$ (225.14) calcd.: C, 63.98; H, 8.50; N 6.22; found: C, 63.74; H, 8.36; N 6.21. ^{1}H-NMR (500 MHz, DMSO-[D_6]): d = 0.9 (t, 3H, *CH*$_3$, *J* = 5.8, 6.3 Hz), 1.1-1.5 (m, 4H, CH_3*(*CH_2*)*$_2$), 1.6-1.8 (m, 2H, OCH_2*CH*$_2$), 3.9 (s, 2H, O*CH*$_2$), 4.6 (d, 4H, 2 x *CH*$_2$OH, *J* = 5.8 Hz), 5.4 (t, 2 H, OH, *J* = 5.8 Hz), 6.6 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): d = 13.8 (CH_3), 21.7 (CH_3*C*H_2), 27.5, 27.9, 63.9 (*CH*$_2$OH), 67.3 (O*C*H_2), 104.2 (CH, py), 125.6, 162.8, 165.9 ppm. MS (EI): *m/z* (%) = 225 (50) [M^+], 224 (100) [M^+ - H], 196 (5) [M^+ - OCH_3 + H], 154 (35) [M^+ - C_5H_{11}], 137 (25), 108 (10). FT-IR (ATR): ? = 3325 (m), 3064 (w, OH), 2958 (w), 2776 (w, CH), 1597 (vs), 1566 (s, C=C), 1432 (s), 1315 (vs, C-H), 1156 (m), 1090 (m), 1032 (s, C-O-C), 851 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): ?$_{max}$ (log e) = 241 (1.04).

4-Hexyloxy-2,6-dihydroxymethylpyridine (11c): According to the general procedure, **13c** (2.50 g, 8.50 mmol) and $NaBH_4$ (1.55 g, 41.11 mmol) in MeOH (25 mL) were used. Recrystallization from acetone/Et_2O yielded a colorless solid (1.66 g, 81 %). Mp: 70°C. $C_{13}H_{21}NO_3$ (239.15): calcd.: C, 65.25; H, 8.84; N 5.85; found: C, 64.99; H, 8.83; N,

5.77. ^{1}H-NMR (500 MHz, DMSO-[D_6]): d = 0.87 (t, *J* = 7.0 Hz, 3H, *CH_3*), 1.26-1.43 (m, 6H, CH_3*$CH_2CH_2CH_2$*), 1.69-1.74 (m, 2H, OCH_2*CH_2*), 4.04 (t, *J* = 6.5 Hz, 2H, O*CH_2*), 4.45 (d, *J* = 5.7 Hz, 4H, 2 x *CH_2*OH), 5.33 (t, *J* = 5.8 Hz, 2H, 2 x O*H*), 6.84 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): d = 13.8 (*C*H_3), 22.0 (*C*H_2), 25.0 (*C*H_2), 28.2 (*C*H_2), 30.8 (OCH_2*C*H_2), 63.9 (2 x *CH_2*OH), 67.3 (O*C*H_2), 104.2 (*C*H, py), 162.8, 165.9 ppm. MS (CI, CH_4): *m/z* (%) = 240 (50) [M^+ + H], 184 (10), 156 (22) [M^+ - C_6H_{12}]. FT-IR (ATR): ? = 3316 (m, OH), 2952 (w), 2853 (w, CH), 1616 (s), 1552 (w, C=C), 1402 (m), 1298 (s, C-H), 1208 (w), 1020 (s), 999 (w, C-O-C), 847 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): ?$_{max}$ (log e) = 254 (1.18), 248 (1.19), 242 (1.21).

4-Heptyloxy-2,6-dihydroxymethylpyridine (11d): According to the general procedure, **13d** (2.17 g, 7.03 mmol) and $NaBH_4$ (1.28 g, 33.72 mmol) in MeOH (21 mL) were used. Recrystallization from Et_2O/acetone yielded a colorless solid (1.53 g, 83 %). Mp: 70°C. $C_{14}H_{23}NO_3$ (253.17) calcd.: C, 66.37; H, 9.15; N 5.53; found: C, 66.02; H, 9.09; N, 5.38. ^{1}H-NMR (300 MHz, DMSO-[D_6]): d = 0.85 (t, *J* = 6.3 Hz, 3H, *CH_3*), 1.13-1.46 (m, 8H, CH_3*$CH_2CH_2CH_2CH_2$*), 1.67-1.76 (m, 2H, OCH_2*CH_2*), 4.03 (t, *J* = 6.4 Hz, 2H, O*CH_2*), 4.44 (d, *J* = 5.7 Hz, 4H, 2 x *CH_2*OH), 5.33 (t, *J* = 5.8 Hz, 2H, 2 x O*H*), 6.83 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): d = 13.8 (*C*H_3), 22.0 (*C*H_2), 25.3 (*C*H_2), 28.3 (*C*H_2), 28.6 (*C*H_2), 31.2 (OCH_2*C*H_2), 63.9 (2 x *C*H_2OH), 67.3 (O*C*H_2), 104.2 (CH, py), 162.8, 165.9 ppm. MS (CI, CH_4): *m/z* (%) = 254 (100) [M^+ + H], 184 (10), 156 (75) [M^+ - C_7H_{14}]. HRMS (EI): *m/z* [M^+ - H] calcd. for $C_{14}H_{22}NO_3$: 252.1600; found: 252.1600. FT-IR (ATR): ? = 3341 (m), 3064 (w, OH), 2954 (w), 2924 (w), 2848 (w, CH), 1598 (vs), 1568 (s, C=C), 1434 (s), 1319 (vs, C-H), 1156 (s), 1034 (vs, C-O-C), 860 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): ?$_{max}$ (log e) = 240 (0.65).

4-Octyloxy-2,6-dihydroxymethylpyridine (11e): According to the general procedure, **13e** (2.17 g, 7.03 mmol) and $NaBH_4$ (1.28 g, 33.7 mmol) in 21 mL of MeOH were used. Recrystallization from Et_2O/acetone yielded a colorless solid (1.53 g, 83 %). Mp: 78°C, ref. [6]: mp. 80-81°C. Spectroscopic data were in accordance with ref. [6].

4-Nonyloxy-2,6-dihydroxymethylpyridine (11f): According to the general procedure, **13f** (3.26 g, 9.70 mmol) and $NaBH_4$ (1.77 g, 46.8 mmol) in MeOH (29 mL) were used. Recrystallization from hexanes/acetone yielded a colorless solid (2.8 g, 97 %). Mp: 75°C. $C_{16}H_{27}NO_3$ (281.20) calcd.: C, 68.29; H, 9.67; N 4.98; found: C, 68.13; H, 9.62; N, 4.87. ^{1}H-NMR (300 MHz, DMSO-[D_6]): d = 0.85 (t, *J* = 6.4 Hz, 3H, CH_3), 1.17-1.46 (m, 12H, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2$), 1.67-1.76 (m, 2H, OCH_2CH_2), 4.03 (t, *J* = 6.4 Hz, 2H, OCH_2), 4.44 (d, *J* = 5.7 Hz, 4H, 2 x CH_2OH), 5.33 (t, *J* = 5.8 Hz, 2H, 2 x OH), 6.83 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): d = 13.8 (CH_3), 22.0 (CH_2), 25.3 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 31.2 (OCH_2CH_2), 63.9 (2 x CH_2OH), 67.2 (OCH_2), 104.2 (CH, py), 162.8, 165.9 ppm. MS (CI, CH_4): *m/z* (%) = 282 (100) [M^+ + H], 264 (10), 184 (12), 156 (30) [M^+ - C_9H_{18}]. FT-IR (ATR): ? = 3326 (m, OH), 2956 (w), 2924 (w), 2850 (w), 2656 (w, CH), 1598 (vs), 1566 (s, C=C), 1434 (s), 1319 (vs, C-H), 1155 (s), 1060 (s), 1037 (vs, C-O-C), 856 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 286 (0.24), 254 (1.12), 240 (0.81).

4-Decyloxy-2,6-dihydroxymethylpyridine (11g): According to the general procedure, **13g** (3.00 g, 8.54 mmol) and $NaBH_4$ (1.56 g, 41.3 mmol) in MeOH (25 mL) were used. The resulting mixture was recrystallized from Et_2O/CH_2Cl_2/MeOH. Colorless crystals

(2.34 g, 86 %). Mp: 78.5°C. $C_{17}H_{29}NO_3$ (295.21) calcd.: C, 69.12; H, 9.89; N 4.74; found: C, 68.95; H, 9.86; N, 4.62. ^{1}H-NMR (300 MHz, $CDCl_3$): d = 0.85 (t, *J* = 6.3 Hz, 3H, *CH*$_3$), 1.14-1.46 (m, 14H, CH_3*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$), 1.67-1.76 (m, 2H, OCH_2*CH*$_2$), 4.03 (t, *J* = 6.4 Hz, 2H, O*CH*$_2$), 4.44 (d, *J* = 5.7 Hz, 4H, 2 x *CH*$_2$OH), 5.33 (t, *J* = 5.8 Hz, 2H, 2 x *OH*), 6.83 (s, 2H, py) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 14.1 (*C*H_3), 22.6 (*C*H_2), 25.8 (*C*H_2), 28.8 (*C*H_2), 29.27 (*C*H_2), 29.28 (*C*H_2), 29.5 (*C*H_2), 29.6 (*C*H_2), 31.8 (OCH_2*C*H_2), 64.2 (2 x *C*H_2OH), 68.3 (O*C*H_2), 105.7 (*C*H, py), 160.1, 166.8 ppm. MS (EI): *m/z* (%) = 295 (100) [M^+], 294 (40) [M^+ - H], 266 (10), 168 (15), 155 (75) [M^+ - $C_{10}H_{20}$]. HRMS (EI): *m/z* [M^+ - H] calcd. for $C_{17}H_{29}NO_3$: 295.2147; found: 295.2147. FT-IR (ATR): ? = 3322 (m, OH), 2922 (w), 2847 (w, CH), 1600 (vs), 1568 (s, C=C), 1463 (m), 1435 (s), 1324 (vs, C-H), 1155 (s), 1089 (s), 1035 (vs, C-O-C), 865 (vs), 729 (m) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 239 (0.55).

***General procedure for the preparation of* 4-alkoxy-pyridine-2,6-dicarbaldehydes (4b-g)**:

A suspension of 1 equiv. 4-alkyloxy-2,6-dihydroxymethylpyridine **11b-g** und 1 equiv. of SeO_2 in 1,4-dioxane (35-50 mL) was heated for 20 min at 70°C and then refluxed for further 4 h at 90°C. After filtration of the hot solution through celite and sand, the solvent was evaporated to yield a yellow powder. The mixture was purified by column chromatography (SiO_2 with 5 % H_2O). Evaporation of the solvent yielded a colorless powder.

4-Pentyloxy-pyridine-2,6-dicarbaldehyde (4b): According to the general procedure, **11b** (1.00 g, 4.44 mmol) and SeO_2 (0.49 g, 4.44 mmol) in 1,4-dioxane (35 mL) were

used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/EtOAc = 95 : 1) yielded a colorless solid (0.79 g, 81 %). Mp: 53°C. $C_{12}H_{15}NO_3$ (221.11) calcd.: C, 65.14; H, 6.83; N 6.33; found: C, 65.17; H, 6.81; N 6.29. ^{1}H-NMR (300 MHz, $CDCl_3$): d = 0.92 (t, *J* = 6.9 Hz, 3H, *CH*$_3$), 1.31-1.49 (m, 4H, $CH_3CH_2CH_2$), 1.78-1.88 (m, 2H, OCH_2CH_2), 4.12 (t, *J* = 6.5 Hz, 2H, OCH_2), 7.60 (s, 2H, py), 10.08 (s, 2H, 2 x CHO) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 13.9 (CH_3), 22.2 (CH_3CH_2), 27.8 ($CH_3CH_2CH_2$), 28.3 (OCH_2CH_2), 69.2 (OCH_2), 111.4 (*C*H, py), 154.6, 167.0, 192.4 (2 x *C*HO) ppm. MS (CI, CH_4): *m/z* (%) = 222 (100) [M^+ + H], 152 (38) [M^+ - C_5H_{11}]. FT-IR (ATR): ? = 3075 (w), 2951 (m), 2926 (m), 2853 (w, CH), 1706 (vs, C=O), 1595 (vs, C=C), 1449 (s), 1367 (vs), 1310 (s, C-H), 1156 (m, C-O-C), 1088 (w), 1034 (s), 940 (s), 865 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 266 (3.61), 192 (0.48).

4-Hexyloxy-pyridine-2,6-dicarbaldehyde (4c): According to the general procedure, **11c** (1.0 g, 4.17 mmol) und SeO_2 (0.46 g, 4.17 mmol) in 1,4-dioxane (35 mL) were used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/EtOAc = 80 : 1) yielded a colorless solid (0.87 g, 81 %). Mp: 37°C. $C_{13}H_{17}NO_3$ (235.12) calcd.: C, 66.36; H, 7.28; N 5.95; found: C, 66.25; H, 7.26; N 5.93. ^{1}H-NMR (300 MHz, $CDCl_3$): d = 0.89 (t, *J* = 7.0 Hz, 3H, *CH*$_3$), 1.30-1.50 (m, 6H, $CH_3CH_2CH_2CH_2$), 1.78-1.87 (m, 2H, OCH_2CH_2), 4.12 (t, *J* = 6.5 Hz, 2H, OCH_2), 7.61 (s, 2H, py), 10.09 (s, 2H, 2 x *CH*O) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 13.9 (CH_3), 22.4 (CH_3CH_2), 25.4 (CH_2), 28.5 (CH_2), 31.3 (OCH_2CH_2), 69.3 (OCH_2), 111.4 (*C*H, py), 154.6, 167.0, 192.4 (2 x *C*HO) ppm. MS (CI, CH_4): *m/z* (%) = 236 (70) [M^+ + H], 180 (10), 152 (100) [M^+ - C_6H_{12}]. FT-IR (ATR): ? = 3087 (w), 2931 (m), 2854 (m), 2852 (m, CH), 1711 (vs,

C=O), 1595 (vs, C=C), 1452 (s), 1366 (vs), 1319 (s, C-H), 1162 (m, C-O-C), 1033 (s), 936 (s), 725 (m), 701 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 256 (3.29).

4-Heptyloxy-pyridine-2,6-dicarbaldehyde (4d): According to the general procedure, **11d** (1.00 g, 3.94 mmol) und SeO_2 (0.43 g, 3.94 mmol) in 1,4-dioxane (35 mL) were used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/EtOAc = 80 : 1) yielded a colorless solid (0.83 g, 81 %). Mp: 44°C. $C_{14}H_{19}NO_3$ (249.14) calcd.: C, 67.45; H, 7.68; N 5.62; found: C, 66.93; H, 7.65; N 5.42. ^{1}H-NMR (300 MHz, $CDCl_3$): d = 0.88 (t, *J* = 6.6 Hz, 3H, *CH*$_3$), 1.24-1.50 (m, 8H, CH_3*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$), 1.78-1.88 (m, 2H, OCH_2*CH*$_2$), 4.13 (t, *J* = 6.5 Hz, 2H, O*CH*$_2$), 7.61 (s, 2H, py), 10.09 (s, 2H, 2 x *CH*O) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 14.0 (*C*H_3), 22.5 (CH_3*C*H_2), 25.7 (*C*H_2), 28.6 (*C*H_2), 28.8 (*C*H_2), 31.6 (OCH_2*C*H_2), 69.3 (O*C*H_2), 111.4 (*C*H, py), 154.6, 167.1, 192.4 (2 x *C*HO) ppm. MS (CI, CH_4): *m/z* (%) = 250 (100) [M^+ + H], 152 (15) [M^+ - C_7H_{14}]. HRMS (EI): *m/z* [M^+] calcd. for $C_{14}H_{19}NO_3$: 249.1365; found: 249.1359. FT-IR (ATR): ? = 3081 (w), 2951 (m), 2914 (m), 2831 (w, CH), 1708 (vs, C=O), 1591 (vs, C=C), 1452 (s), 1362 (vs), 1310 (s, C-H), 1196 (m), 1158 (m, C-O-C), 1035 (s), 941 (s), 889 (s), 719 (vs), 703 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 258 (3.45), 203 (0.45).

4-Octyloxy-pyridine-2,6-dicarbaldehyde (4e): According to the general procedure, **11e** (1.00 g, 3.74 mmol)) und SeO_2 (0.41 g, 3.74 mmol) in 1,4-dioxane (35 mL) were used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/EtOAc = 30 : 1) yielded a colorless solid (0.94 g, 81 %). Mp: 36°C. $C_{15}H_{21}NO_3$ (263.15) calcd.: C, 68.42; H, 8.08; N 5.32; found: C, 68.39; H, 7.98; N 5.32. ^{1}H-NMR (300 MHz,

$CDCl_3$): d = 0.87 (t, *J* = 6.5 Hz, 3H, *CH*$_3$), 1.27-1.49 (m, 10H, CH_3*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$), 1.78-1.87 (m, 2H, OCH_2*CH*$_2$), 4.12 (t, *J* = 6.5 Hz, 2H, O*CH*$_2$), 7.60 (s, 2H, py), 10.08 (s, 2H, 2 x *CH*O) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 14.0 (*C*H_3), 22.5 (CH_3*C*H_2), 25.7 (*C*H_2), 28.6 (*C*H_2), 29.12 (*C*H_2), 29.15 (*C*H_2), 31.7 (OCH_2*C*H_2), 69.3 (O*C*H_2), 111.4 (*C*H, py), 154.6, 167.0, 192.4 (2 x *C*HO) ppm. MS (CI, CH_4): *m/z* (%) = 263 (20) [M^+], 234 (30) [M^+ - H - CO], 152 (70) [M^+ - C_8H_{15}], 124 (25), 57 (100). FT-IR (ATR): ? = 3081 (w), 2952 (m), 2927 (m), 2857 (w, CH), 1710 (vs, C=O), 1590 (vs, C=C), 1451 (s), 1365 (vs), 1310 (s, C-H), 1160 (m, C-O-C), 1038 (s), 939 (s), 864 (vs), 721 (vs), 700(s) cm^{-1}. UV/VIS (CH_2Cl_2): ?$_{max}$ (log e) = 257 (3.34), 193 (0.37).

4-Nonyloxy-pyridine-2,6-dicarbaldehyde (4f): According to the general procedure, **11f** (1.14 g, 4.05 mmol) und SeO_2 (0.45 g, 4.05 mmol) in 1,4-dioxane (50 mL) were used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/EtOAc = 8 : 1) yielded a colorless solid (0.95 g, 81 %). Mp: 36°C. $C_{16}H_{23}NO_3$ (277.17) calcd.: C, 69.29; H, 8.36; N 5.05; found: C, 69.30; H, 8.37; N 4.89. ^{1}H-NMR (300 MHz, $CDCl_3$): d = 0.87 (t, *J* = 6.5 Hz, 3H, *CH*$_3$), 1.26-1.50 (m, 12H, CH_3*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$), 1.78-1.87 (m, 2H, OCH_2*CH*$_2$), 4.12 (t, *J* = 6.5 Hz, 2H, O*CH*$_2$), 7.61 (s, 2H, py), 10.09 (s, 2H, 2 x *CH*O) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): d = 14.0 (*C*H_3), 22.6 (CH_3*C*H_2), 25.7 (*C*H_2), 28.6 (*C*H_2), 29.1 (*C*H_2), 29.2 (*C*H_2), 29.4 (*C*H_2), 31.8 (OCH_2*C*H_2), 69.3 (O*C*H_2), 111.4 (CH, py), 154.6, 167.1, 192.4 (2 x *C*HO) ppm. MS (CI, CH_4): *m/z* (%) = 278 (100) [M^+ + H], 248 (15) [M^+ - H - CO], 152 (45) [M^+ - C_9H_{18}], 124 (5), 57 (15). FT-IR (ATR): ? = 3079 (w), 2954 (m), 2917 (m), 2851 (w, CH), 1708 (vs, C=O), 1590 (vs,

C=C), 1452 (s), 1365 (vs), 1310 (s, C-H), 1156 (m, C-O-C), 1040 (s), 939 (s), 864 (vs), 718 (s), 702 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 261 (3.55), 193 (0.44).

4-Decyloxy-pyridine-2,6-dicarbaldehyde (4g): According to the general procedure, **11g** (1.01 g, 3.38 mmol) und SeO_2 (0.37 g, 3.38 mmol) in 1,4-dioxane (50 mL) were used. Purification by column chromatography (SiO_2 with 5 % H_2O; CH_2Cl_2/hexanes = 10 : 1) yielded a colorless solid (0.78 g, 80 %). Mp: 52°C. $C_{17}H_{25}NO_3$ (291.18) calcd.: C, 70.07; H, 8.65; N 4.81; found: C, 70.25; H, 8.64; N 4.65. ^{1}H-NMR (300 MHz, DMSO-[D_6]): d = 0.86 (t, *J* = 6.4 Hz, 3H, CH_3), 1.25-1.47 (m, 14H, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2$), 1.79-1.85 (m, 2H, OCH_2CH_2), 4.12 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.60 (s, 2H, py), 10.08 (s, 2H, 2 x *CH*O) ppm. ^{13}C-NMR (75 MHz, DMSO-[D_6]): d = 14.0 (CH_3), 22.6 (CH_3CH_2), 25.7 (CH_2), 28.6 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 31.8 (OCH_2CH_2), 69.3 (OCH_2), 111.4 (*C*H, py), 154.7, 167.1, 192.4 (2 x *C*HO) ppm. MS (EI): *m/z* (%) = 278 (100) [M^+], 262 (60) [M^+ - CH_4], 152 (80) [M^+ - C_9H_{18}], 151 (18), 124 (18), 57 (30), 43 (45). FT-IR (ATR): ? = 2913 (w), 2849 (w, CH), 1706 (vs, C=O), 1580 (s, C=C), 1450 (s), 1406 (m), 1337 (vs, C-H), 1159 (m, C-O-C), 1018 (s), 850 (vs), 785 (s), 714 (vs) cm^{-1}. UV/VIS (CH_2Cl_2): $?_{max}$ (log e) = 240 (0.26), 211 (0.07).

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