**Supplemantary Information**

**Synthesis of fluorinated acid-functionalized electron rich nickel porphyrins**

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Contents

[1. Mass spectrometry 2](#_Toc172291994)

[2. NMR spectroscopy 2](#_Toc172291995)

[3 Synthesis 3](#_Toc172291996)

[3.1 General procedure for benzylidation of 1-3 3](#_Toc172291997)

[3.2 General procedure for oxidation of 4-6 9](#_Toc172291998)

[3.3 General procedure for the esterification of 7, 8 and 9 15](#_Toc172291999)

[3.4 General procedure for the deprotection of 10, 11 and 12 23](#_Toc172292000)

[3.5 General procedure for the tosylation of 13, 14 and 15 29](#_Toc172292001)

[3.6 Synthesis of 2-Iodo-3,4,5-trimethoxybenzaldehyde (20) 36](#_Toc172292002)

[3.7 Synthesis of 2-Hydroxy-3,4,5-trimethoxybenzaldehyde (21) 38](#_Toc172292003)

[3.8 General procedure for the ethers 22, 23 and 24 39](#_Toc172292004)

[3.9 General procedure for the metal free porphyrins 25, 26 and 27 46](#_Toc172292005)

[3.10 General procedure for the nickel porphyrins 28, 29 and 30 53](#_Toc172292006)

[3.11 General procedure of nickel porphyrins 31, 32 and 33 (free acid) 61](#_Toc172292007)

**Experimental Section**

**1. Mass spectrometry**

Electron ionization mass spectra were measured at 70 eV ionization energy using a Jeol Accu-TOF 4G mass spectrometer (EI). Electrospray ionization mass spectra (ESI-MS) were recorded using a Finnigan LCQ Deca quadrupole ion trap mass spectrometer.

# 2. NMR spectroscopy

All NMR spectra were recorded in deuterated solvents from Deutero. Two-dimensional NMR techniques were used to assign the signals (COSY, HSQC, HMBC). The following table indicates both the degree of deuteration of each solvent and the solvent signal. Tetramethylsilane (TMS) was used as the internal standard for referencing the spectra.

|  |  |  |  |
| --- | --- | --- | --- |
| solvent | deuteration level | 1H-Signal / ppm | 13C-Signal / ppm |
| CDCl3 | 99.8 % | 7.26 (singlet) | 77.16 (triplet) |

The following spectrometers were used:

|  |  |  |  |
| --- | --- | --- | --- |
|  | frequency / MHz | | |
| device name | 1H-NMR spectra | 13C-NMR spectra | 19F-NMR spectra |
| Bruker DRX 500  Bruker AV 600 | 500  600 | 125  150 | 470 |

For the evaluation of the NMR spectra of the porphyrins, the carbon atoms were numbered as follows:



Starting from the *meso* position of the porphyrin, the porphyrin was numbered consecutively. The substituent at the *meso* position of the porphyrin follows the scheme above. The symmetry of the molecules was considered in the numbering.

Some carbon atoms of certain porphyrins could be assigned via the heteronuclear single quantum coherence (HSQC) and the heteronuclear multiple bond correlation (HMBC) spectra. Since the porphyrins are mixtures of atrop isomers assignment of the signal was not possible in all cases.

# 3 Synthesis

The syntheses of the fluorinated alkyl chains of different lengths are given as general procedures.

## **3.1 General procedure for benzylidation of 1-3**

Under nitrogen atmosphere 1 eq. of the corresponding diol (**1**-**3**) was mixed with potassium carbonate (2 eq.). Then abs. acetonitrile (100 ml) and benzyl bromide (1 eq.) were added and stirred for 18 h under reflux. Afterwards the solution was filtered over Celite® 545 and the solvent was removed in vacuo. The crude product was then purified by flash column chromatography (cyclohexane/ethyl acetate, gradient 5%‑60% ethyl acetate). A colorless oil was obtained.

**4-benzyloxy-2,2,3,3-tetrafluorobutan-1-ol (4)**



**Yield:** 65%.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 7.39-7.31 (m, 5 H, *H*-7, *H*-7‘, *H*-8, *H*-8‘,*H*-9), 4.66 (s, 2 H, *H*‑5), 3.98 (tt, 3*J*=13.7 Hz, 4*J*=1.5 Hz, 2 H, *H*-1), 3.89 (tt, 3*J*=13.2 Hz, 4*J*=1.6 Hz, 2 H, *H*-4), 2.63 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 136.1 (*C*-6), 128.7 (*C*-8), 128.5 (*C*-9), 128.0 (*C*‑7),116.1 (*C*-2), 116.0 (*C*-3), 74.6 (*C*-5), 66.7 (*C*-4), 60.6 (*C*-1) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -122.4 (s, 2 F, *F*-2), -125.0 (s, 2 *F*, F-3) ppm.

**FT-IR:** = 3414 (br, w), 2880 (br, w), 2249 (w), 1741 (w), 1498 (w), 1455 (w), 1370 (w), 1216 (m), 1184 (m), 1111 (s), 1027 (m), 932 (m), 913 (m), 781 (m), 751 (s), 740 (s), 698 (s), 672 (m), 649 (m), 595 (m), 555 (m), 569 (m), 526 (s) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = 252.08 (29) [M]+·, 107.05 (40) [C7H7O]+·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C11H12F4O2 *m/z* = calc.: 252.07734, found: 252.07719, diff.: -0.60 ppm.𝜈~

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**Figure S1:** 1H-NMR spectrum of compound **4**, measured in CDCl3 at 300 K.

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**Figure S2:** 13C-NMR spectrum of compound **4**, measured in CDCl3 at 300 K.

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**Figure S3:** 19F-NMR spectrum of compound **4**, measured in CDCl3 at 300 K.

**6-benzyloxy-2,2,3,3,4,4,5,5-octafluorohexan-1-ol (5)**



**Yield:** 50%.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 7.40-7.31 (m, 5 H, *H*-9, *H*-9‘, *H*-10, *H*-10‘, *H*-11),

4.68 (s, 2 H, *H*-7), 4.08 (tt, 3*J* = 14.2 Hz, 4*J* = 1.5 Hz, 2 H, *H*-1), 3.94 (tt, 3*J* = 14.1 Hz,   
4*J* = 1.6 Hz, 2 H, *H*-6), 1.80 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 136.5 (*C*-8), 128.6 (*C*-10), 128.3 (*C*-11),

127.8 (*C*-9), 117.8 (*C*-3), 115.6 (*C*-5), 115.4 (*C*-2), 113.6 (*C*-4), 74.4 (*C*-7), 66.7 (*C*-6), 60.7 (*C*‑1) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -120.0 (td, 3*J* = 13.3 Hz,   
4*J* = 3.0 Hz, 2F, *F*-5), ‑123.1 to -123.2 (m, 2 F, *F*-2),   
-124.2 to -124.3 (m, 2 F, *F*-4), -124.5 to -124.6 (m, 2 F, *F*-3) ppm.

**FT-IR:** = 2883 (br, w), 2190 (w), 1705 (w), 1498 (w), 1456 (m), 1370 (w), 1168 (s), 1121 (s), 1030 (m), 992 (m), 937 (m), 866 (m), 821 (m), 738 (s), 698 (s) cm−1.  
**MS** (EI, 70 eV): *m/z* (%) = 352.08 (21) [M]+·, 107.05 (9) [C7H7O]+·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C13H12F8O2 *m/z* = calc.: 352.07095, found: 352.07089, diff.: -0.19 ppm.



**Figure S4:** 1H-NMR spectrum of compound **5**, measured in CDCl3 at 300 K.

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**Figure S5:** 13C-NMR spectrum of compound **5**, measured in CDCl3 at 300 K.

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**Figure S6:** 19F-NMR spectrum of compound **5**, measured in CDCl3 at 300 K.

**8-benzyloxy-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctan-1-ol (6)**



**Yield:** 40%.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 7.40-7.31 (m, 5 H, *H*-11, *H*-11‘, *H*-12, *H*-12‘, *H*-13), 4.68 (s, 2 H, *H*-9), 4.08 (tt, 3*J* = 14.1 Hz, 4*J* = 1.4 Hz, 2 H, *H*-1), 3.94 (tt, 3*J* = 13.9 Hz, 4*J* = 1.5 Hz, 2 H, *H*-8), 1.87 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 136.3 (*C*-10), 128.6 (*C*-12), 128.3 (*C*-13),

127.8 (*C*-11), 117.5 (*C*-5), 117.8 (*C*-4), 115.6 (*C*-7), 115.4 (*C*-2), 113.2 (*C*-6), 113.6 (*C*-3), 74.4 (*C*-9), 66.7 (*C*-8), 60.7 (*C*-1) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -119.8 to -119.9 (m, 2 F, *F*-7), -122.5 to 122.7 (m, 4 F, *F*-4, *F*-5), -122.9 to 123.0 (m, 2 F, *F*-2), -123.8 to -123.9 (m, 2 F, *F*-6), -124.1 to ‑124.2 (m, 2 F, *F*-3) ppm.  
**FT-IR:** = 1707 (m), 1498 (w), 1456 (m), 1370 (m), 1191 (s), 1139 (s) 1029 (w), 939 (w), 908 (w), 837 (w), 791 (w), 745 (m), 698 (m), 657 (s) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 452.06 (21) [M]+·, 107.05 (3) [C7H7O]+·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C15H12F12O2 *m/z* = calc.: 452.06457, found: 452.06435, diff.: -0.48 ppm.



**Figure S7:** 1H-NMR spectrum of compound **6**, measured in CDCl3 at 300 K.

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**Figure S8:** 13C-NMR spectrum of compound **6**, measured in CDCl3 at 300 K.

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**Figure S9:** 19F-NMR spectrum of compound **6**, measured in CDCl3 at 300 K.

## **3.2 General procedure for oxidation of 4-6**

1 equivalent of the corresponding alcohol (**4-6**) was dissolved in acetonitrile (100 ml) and 2,2,6,6-tetramethylpiperidinyloxyl (0.029 eq.) (TEMPO) and potassium bromide (0.136 eq.) were added with stirring. Separately, a solution of sodium hypochloride (4.2 eq.) and sodium bicarbonate (4.2 eq.) was prepared. This solution was added in three portions. The first addition was made at -10 °C, the second after 16 h at room temperature and the third after a further 6 h, also at room temperature. The reaction mixture was then stirred for a further 54 h at room temperature before the reaction was stopped by adding conc. sulphuric acid (5 ml), and dist. water (100 ml). Subsequently, the reaction was extracted with diethyl ether (3 x 100 ml), the organic phases were dried over magnesium sulfate, filtered and the solvent was removed in vacuo. A clear, yellowish liquid was obtained. The raw product was not further worked up and was used without purification in the next stage.

**4-benzyloxy-2,2,3,3-tetrafluorobutanoic acid (7)**



**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 7.37-7.28 (m, 5 H, *H*-7, *H*-7‘, *H*-8, *H*-8‘, *H*-9), 4.63 (s, 2 H, *H*-5), 3.93 (tt, 3*J* = 13.1 Hz, 4*J* = 1.5 Hz, 2 H, *H*-4), 2.00 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 162.7 (*C*-1), 136.2 (*C*-6), 128.6 (*C*-8), 128.4 (*C*‑9), 128.0 (*C*-7), 115.3 (*C*-2), 108.7 (*C*-3), 74.6 (*C*-5), 66.7 (*C*-4) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -121.2 (s, 2 F, *F*-2), -122.4 (s, 2 F, *F*-3) ppm.

**FT-IR:** = 3490 (br, w), 2879 (br, w), 2526 (br, w), 1763 (m), 1497 (w), 1455 (m), 1370 (m), 1246 (m), 1209 (m), 1127 (s), 1031 (m), 987 (m), 777 (m), 750 (m), 714 (m), 698 (s), 594 (m), 537 (m) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = 266.06 (26) [M]+·, 159.01 (9) [M-C7H7O]+, 107.05 (42) [C7H7O]·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C11H10F4O3 *m/z* = calc.: 266.05661, found: 266.05651, diff.: -0.35 ppm.

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**Figure S10:** 1H-NMR spectrum of compound **7**, measured in CDCl3 at 300 K. The reaction was not worked up and an NMR of the crude product was measured. The additional signals in the aromatic region can be assigned to side product **34** (see below).



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**Figure S11:** 13C-NMR spectrum of compound **7**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **34** (see above).

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**Figure S12:** 19F-NMR spectrum of compound **7**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **34** (see above).

**6-Benzyloxy-2,2,3,3,4,4,5,5-octafluorohexanoic acid (8)**



**1H-NMR** (500 MHz, CDCl3, 300 K): = 7.40-7.31 (m, 5 H, *H*-9, *H*-9‘, *H*-10, *H*-10‘, *H*-11), 4.68 (s, 2 H, *H*-7), 3.94 (tt, 3*J* = 13.9 Hz, 4*J* = 1.5 Hz, 2 H, *H*-6), 2.23 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 160.7 (*C*-1), 136.3 (*C*-8), 128.3 (*C*-10), 128.3 (*C*‑11), 127.9 (*C*-9), 117.7 (*C*-3), 115.6 (*C*-5), 113.6 (*C*-4), 74.5 (*C*-7), 66.6 (*C*‑6) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -119.7 (t, 3*J* = 10.7 Hz, 2 F, *F*-2), -119.9 to -120.0 (m, 2 F, *F*-5), -123.5 to -123.7 (m, 4 F, *F*-3, F-4) ppm.

**FT-IR:** = 2946 (br, w), 1774 (m), 1456 (w), 1272 (m), 1179 (s), 1122 (s), 1029 (m), 951 (w), 867 (m), 846 (m), 750 (m), 698 (s) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 366 (21) [M]+·, 107.05 (8) [C7H7O]+·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C13H10F8O3 *m/z* = calc.: 366.05022, found: 366.05018, diff.: -0.11 ppm.

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**Figure S13:** 1H-NMR spectrum of compound **8**, measured in CDCl3 at 300 K. The reaction was not worked up and an NMR of the crude product was measured. The additional signals in the aromatic region can be assigned to side product **35** (see below).



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**Figure S14:** 13C-NMR spectrum of compound **8**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **35** (see above).

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**Figure S15:** 13C-NMR spectrum of compound 8, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **35** (see above).

**8-Benzyloxy-2,2,3,3,4,4,4,5,5,6,6,7,7-dodecafluoroctanoic acid (9)**



**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 7.40-7.31 (m, 5 H, *H*-11, *H*-11‘, *H*-12, *H*-12‘,

*H*-13), 4.70 (s, 2 H, *H*-9), 3.96 (tt, 3*J* = 13.9 Hz, 4*J* = 1.5 Hz, 2 H, *H*-8), 2.04 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 177.7 (*C*-1), 136.3 (*C*-10), 128.4 (*C*-12),

128.3 (*C*-13), 127.9 (*C*-11), 117.8 (*C*-5), 115.7 (*C*-7), 113.6 (*C*-6), 74.5 (*C*-9), 66.6 (*C*-8) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -119.5 to -119.6 (m, 2 F, *F*-2), -119.8 to -119.9 (m, 2 F, *F*‑7), ‑122.0 to -122.2 (m, 2 F, *F*-4), -122.5 to -122.7 (m, 2 F, *F*-5) -123.2 to -123.3 (m, 2 F, *F*-3), -123.8 to 123.9 (m, 2 F, *F*-6) ppm.

**FT-IR:** = 1774 (m), 1498 (w), 1456 (m), 1196 (s), 1137 (s), 1028 (m) 905 (w), 836 (w), 779 (w), 732 (m), 714 (w), 698 (m), 656 (m) cm−1.

**MS** (ESI): *m/z* (%) = 465 (100) [M-H]−·, 374.99 (30) [M-C7H7]-·.

**MS** (ESI, HR): C15H9F12O3 *m/z* = calc.: 465.03656, found: 465.03706 diff.: -1.09 ppm.



**Figure S16:** 1H-NMR spectrum of compound **9**, measured in CDCl3 at 300 K. The reaction was not worked up and an NMR of the crude product was measured. The additional signals in the aromatic region can be assigned to side product **36** (see below).



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**Figure S17:** 13C-NMR spectrum of compound **9**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **36** (see above).

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**Figure S18:** 19F-NMR spectrum of compound **9**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **36** (see above).

## **3.3 General procedure for the esterification of 7, 8 and 9**

The corresponding crude product (**7**-**9**)(1 eq.) from the synthesis above and conc. sulfuric acid (300 µl) were dissolved in MeOH (100 ml) and stirred under reflux for 18 h. After cooling to room temperature, dist. water (100 ml) and saturated sodium chloride solution (100 ml) were added, extracted with diethyl ether (3 x 100 ml) and the organic phases were washed with dist. water (2 x 50 ml) and saturated sodium chloride solution (2 x 50 ml). The organic phase was dried over magnesium sulfate, filtered and the solvent removed in vacuo. The crude product was separated by flash column chromatography on silica gel (cyclohexane/ethyl acetate, gradient: 8%-60% ethyl acetate). A colorless liquid was obtained.

**4-benzyloxy-2,2,3,3-tetrafluoromethylbutanoate (10)**



**Yield (2 steps):** 54 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 7.39-7.30 (m, 5 H, *H*-7, *H*-7‘, *H*-8, *H*-8‘, *H*-9), 4.60 (s, 2 H, *H*-5), 3.91 (tt, 3*J* = 13.7 Hz, 4*J* = 1.5 Hz, 2 H, *H*-4), 3.79 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 160.9 (*C*-1), 136.3 (*C*-6), 128.6 (*C*-8), 128.3 (*C*‑9), 128.0 (*C*-7), 115.3 (*C*-2), 108.7 (*C*-3), 74.4 (*C*-5), 66.7 (*C*-4), 53.9 (*C*-10) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -121.3 (t, 3*J* = 2.6 Hz, 2 F, *F*-2), -122.2 (t, 3*J* = 2.6 Hz, 2 F, *F*-3) ppm.

**FT-IR:** = 2960 (br, w), 1774 (s), 1498 (w), 1455 (m), 1442 (m), 1331 (m), 1309 (m), 1244 (m), 1205 (m), 1163 (s), 1116 (s), 1039 (s), 1000 (m), 929 (m), 816 (m), 742 (s), 698 (s), 594 (m), 571 (m) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = 280 (24) [M]+·, 173.06 (34) [M-C7H7O]+, 107.07 (41) [C7H7O]·, 91.07 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C12H12F4O3 *m/z* = calc.: 280.07226, found: 280.07226, diff.: -0.00 ppm.

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**Figure S19:** 1H-NMR spectrum of compound **10**, measured in CDCl3 at 300 K.

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**Figure S20:** 13C-NMR spectrum of compound **10**, measured in CDCl3 at 300 K.

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**Figure S21:** 19F-NMR spectrum of compound **10**, measured in CDCl3 at 300 K.

**6-Benzyloxy-2,2,3,3,4,4,5,5-octafluoromethylhexanoate (11)**



**Yield (2 steps):** 52 %.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 7.40-7.31 (m, 5 H, *H*-9, *H*-9‘, *H*-10, *H*-10‘, *H*-11),

4.67 (s, 2 H, *H*-7), 3.97 (s, 3 H, *H*-12), 3.92 (tt, 3*J* = 14.0 Hz, 4*J* = 1.6 Hz, 2 H, *H*-6) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 159.3 (*C*-1), 136.4 (*C*-8), 128.6 (*C*-10), 128.3

(*C*-11), 127.8 (*C*-9), 117.7 (*C*-3), 115.6 (*C*-5), 113.5 (*C*-4), 74.4 (*C*-7), 66.7 (*C*-6), 54.5

(*C*-12) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -119.1 to -119.2 (m, 2 F, *F*-2), -120.0 (td, 3*J* = 13.1 Hz, 4*J* = 3.20 Hz, 2 F, *F*-5), -123.6 to -123.7 (m, 2 F, *F*-3), -123.8 to -123.9 (m, 2 F, *F*-4) ppm.

**FT-IR:** = 2964 (br, w), 1782 (s), 1498 (w), 1456 (m), 1442 (m), 1370 (w) 1322 (m), 1266 (w), 1187 (s), 1137 (s), 1048 (m), 1029 (w), 959 (m), 868 (m), 807 (m), 746 (m), 699 (m) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 380 (23) [M]+·, 273.02 (3) [M-C7H7O]+, 107.05 (14) [C7H7O]·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C14H12F8O3 *m/z* = calc.: 380.06587, found: 380.06576, diff.: -0.29 ppm.

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**Figure S22:** 1H-NMR spectrum of compound **11**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **37** (see below) and could not be separated from each other by column chromatography.



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**Figure S23:** 13C-NMR spectrum of compound **11**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

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**Figure S24:** 19F-NMR spectrum of compound **11**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

**8-Benzyloxy-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluormethyloctanoate (12)**



**Yield (2 steps):** 46 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 7.40-7.31 (m, 5 H, *H*-11, *H*-11‘, *H*-12, *H*-12‘, *H*-13), 4.68 (s, 2 H, *H*-9), 3.99 (s, 3 H, *H*-14), 3.94 (tt, 3*J* = 13.9 Hz, 4*J* = 1.4 Hz, 2 H, *H*-8) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 159.0 (*C*-1), 136.4 (*C*-10), 128.6 (*C*-12),

128.3 (*C*-13), 127.8 (*C*-11), 117.7 (*C*-5), 115.7 (*C*-7), 113.7 (*C*-6), 74.4 (*C*-9), 66.6 (*C*‑8), 54.6 (*C*-14) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2, *C*-3 and *C*-4 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -118.9 to -119.0 (m, 2 F, *F*-2), -119.8 to -119.9 (m, 2 F, *F*-7), -122.2 to -122.4 (m, 2 F, *F*-4), -122.5 to -122.7 (m, 2 F, *F*-5), -123.2 to -123.4 (m, 2 F, *F*-3), -123.7 to -123.9 (m, 2 F, *F*-6) ppm.

**FT-IR:** = 2965 (br, w), 2189 (w), 1784 (s), 1498 (w), 1456 (m), 1443 (m) 1323 (m), 1198 (s), 1138 (s), 1030 (w), 963 (w), 909 (w), 840 (w), 816 (w), 804 (w), 788 (w), 751 (m), 716 (w), 698 (m), 663 (m) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 480 (22) [M]+·, 465.04 (4) [M-CH3]+·, 91.06 (100) [C7H7]+·.

**MS** (EI, HR, 70 eV): C16H12F12O3 *m/z* = calc.: 480.05948, found: 480.05953, diff.: -0.09 ppm.

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**Figure S25:** 1H-NMR spectrum of compound **12**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **38** (see below) and could not be separated from each other by column chromatography.



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**Figure S26:** 13C-NMR spectrum of compound **12**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **38** (see above).

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**Figure S27:** 19F-NMR spectrum of compound **12**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **38** (see above).

## **3.4 General procedure for the deprotection of 10, 11 and 12**

Under a nitrogen atmosphere, the corresponding ester (**7**-**9**)(1 eq.) was dissolved in ethanol (300 ml) in a chicane flask and placed under a nitrogen atmosphere. In counter stream, palladium on activated carbon (10 mg, 10 %) was added. The reaction solution was evacuated and placed under a hydrogen atmosphere; it was stirred vigorously for 24 h at room temperature. The catalyst was removed by filtration over Celite®545 and the solvent was removed in vacuo. A yellowish oil was obtained.

**4-Hydroxy-2,2,3,3-tetrafluoromethylbutanoate (13)**



**Yield:** 85 %.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 4.07 (tt, 3*J* = 13.4 Hz, 4*J* = 1.4 Hz, 2 H, *H*-4), 3.96 (s, 3 H, *H*-5), 1.95 (s, 1H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 161.0 (*C*-1), 115.2 (*C*-2), 109.0 (*C*-3), 60.5 (*C*-4), 54.3 (*C*-5) ppm.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -121.5 (t, 3*J* = 1.8 Hz, 2 F, *F*-2), -123.9 (t, 3*J* = 1.8 Hz, 2 F, *F*-3) ppm.

**FT-IR:** = 3382 (br, w), 1771 (s), 1445 (w), 1335 (m), 1119 (s), 1078 (m), 1033 (m), 979 (w), 936 (w), 817 (w), 774 (w), 746 (w), 542 (w), 522 (w), 493 (w), 473 (w), 454 (w), 433 (w), 416 (w), 403 (m) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = no result.

**MS** (ESI): *m/z* (%) = no result.



**Figure S28:** 1H-NMR spectrum of compound **13**, measured in CDCl3 at 300 K.

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**Figure S29:** 13C-NMR spectrum of compound **13**, measured in CDCl3 at 300 K.

****

**Figure S30:** 19F-NMR spectrum of compound **13**, measured in CDCl3 at 300 K.

**6-Hydroxy-2,2,3,3,4,4,5,5-octafluoromethylhexanoate (14)**



**Yield:** 65 %.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 4.08 (tt, 3*J* = 14.4 Hz, 4*J* = 1.5 Hz, 2 H, *H*-6), 3.99 (s, 3 H, *H*-7), 2.01(s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 159.3 (*C*-1), 117.5 (*C*-3), 115.2 (*C*-5), 113.2

(*C*-4), 60.6 (*C*-6), 54.5 (*C*-7) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -119.1 to -119.2 (m, 2 F, *F*-2), -123.0 to -123.1 (m, 2 F, *F*-5), -123.6 to -123.7 (m, 2 F, *F*-3), -124.1 to -124.2 (m, 2 F, *F*-4) ppm.

**FT-IR:** = 2968 (w), 1779 (s), 1444 (m), 1325 (m), 1270 (m), 1179 (s), 1139 (s), 1045 (w), 1014 (w), 941 (m), 867 (m), 854 (w), 833 (w), 808 (m), 755 (m), 712 (m), 651 (w), 617 (w) cm−1.

**MS** (ESI): *m/z* (%) = 324.99 (100) [M+Cl]−.

**MS** (ESI, HR): C7H6F8O3Cl *m/z* = calc.: 324.98832, found: 324.98888 diff.: -1.73 ppm.

****

**Figure S31:** 1H-NMR spectrum of compound **14**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **37** (see above) and could not be separated from each other by column chromatography.

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**Figure S32:** 13C-NMR spectrum of compound **14**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

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**Figure S33:** 19F-NMR spectrum of compound **14**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

**8-Hydroxy-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluormethyloctanoate (15)**



**Yield:** 99 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 4.09 (tt, 3*J* = 14.2 Hz, 4*J* = 1.4 Hz, 2 H, *H*-8), 4.00 (s, 3 H, *H*-9), 1.93 (s, 1 H, *OH*) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 159.0 (*C*-1), 117.5 (*C*-5), 115.6 (*C*-7), 113.6 (*C*-6), 60.7 (*C*-8), 54.6 (*C*-9) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2, *C*-3 and *C*-4 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -118.9 to -119.0 (m, 2 F, *F*-2), -122.2 to 122.4 (m, 2 F, *F*-4), -122.5 to -122.7 (m, 2 F, *F*-5), -122.9 to -123.0 (m, 2 F, *F*-7), -123.2 to -123.4 (m, 2 F, *F*-3), -124.0 to -124.2 (m, 2 F, *F*-6) ppm.

**FT-IR:** = 3376 (w), 2921 (w), 2851 (w), 1752 (w), 1444 (w), 1348 (w), 1276 (w), 1257 (w), 1195 (m), 1173 (m), 1146 (m), 1135 (m), 1118 (m), 1083 (w), 1026 (w), 988 (w), 764 (w), 748 (w), 729 (w), 715 (w), 674 (w), 646 (w), 626 (w), 572 (w), 534 (m), 516 (w), 409 (w) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = 391.02 (13) [M+H]+·.

**MS** (EI, HR, 70 eV): C9H7F12O3 *m/z* = calc.: 391.02036, found: 391.02059, diff.: -0.60 ppm.

****

**Figure S34:** 1H-NMR spectrum of compound **15**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **38** (see above) and could not be separated from each other by column chromatography.

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**Figure S35:** 13C-NMR spectrum of compound **15**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **38** (see above).

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**Figure S36:** 19F-NMR spectrum of compound **15**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **38** (see above).

## **3.5 General procedure for the tosylation of 13, 14 and 15**

The corresponding alcohol (**13**-**15**) (1 eq.) and pyridine (1 eq.) were dissolved in dichloromethane (25 ml), the reaction solution was stirred at room temp. for 30 min. A seperate solution was prepared from trifluoromethanesulfonic anhydride (2 eq.) and dichloromethane (10 ml), which was added to the reaction solution over the course of one hour. After stirring for 18 h at room temperature, the solution was washed with dist. water (3 x 50 ml). The organic phase was dried over magnesium sulfate, filtered and the solvent was removed in vacuo. The crude product was then purified by flash column chromatography (cyclohexane/ethyl acetate, gradient: 5%-60%). A yellowish oil was obtained.

**2,2,3,3-Tetrafluor-4-(trifluormethylsulfonyloxy)methylbutanoat (16)**



**Yield:** 28 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 4.88 (t, 3J = 12.8 Hz, 2 H, *H*-4), 4.00 (s, 3 H, *H*-5) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 159.8 (*C*-1), 112.8 (*C*-2), 68.6 (*C*-4), 54.7

(*C*-5) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-3 and *C*-6 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -74.5 (t, 3*J* = 1.4 Hz, 3 F, *F*-6), -120.3 (t, 3*J* = 1.3 Hz, 2 F, *F*-3), -121.7 (s, 2 F, *F*-2) ppm.

**FT-IR:** = 2970 (w), 1773 (m), 1425 (m), 1338 (m), 1272 (w), 1250 (m), 1241 (s), 1136 (s), 1046 (m), 1011 (m), 984 (m), 953 (m), 922 (w), 815 (m), 751 (w), 713 (w), 610 (m) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = no result.

**MS** (ESI): *m/z* (%) = no result.



**Figure S37:** 1H-NMR spectrum of compound **16**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **39** (see below) and could not be separated from each other by column chromatography.





**Figure S38:** 13C-NMR spectrum of compound **16**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **39** (see above).

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**Figure S39:** 19F-NMR spectrum of compound **16**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **39** (see above).

**2,2,3,3,4,4,5,5-Oktafluor-6-(trifluoromethylsulfonyloxy)-methylhexanoate (17)**



**Yield:** 41 %.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 4.81 (t, 3*J* = 12.5 Hz, 2 H, *H*-6), 4.00 (s, 3 H,

*H*-7) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 159.3(*C*-1), 115.0 (*C*-3), 112.8 (*C*-5), 110.8

(*C*-4) 68.2 (*C*-6), 54.7 (*C*-7) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2 and *C*-8 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -74.4 (br. s, 3 F, *F*-8), -118.9 to -119.0 (m, 2 F, *F*-2), -120.3 to -120.4 (m, 2 F, *F*-5), -123.2 to -123.3 (m, 2 F, *F*-4), -123.5 to -123.6 (m, 2 F, *F*-3) ppm.

**FT-IR:** = 2969 (w), 1783 (m), 1718 (w), 1427 (m), 1324 (w), 1250 (w) 1190 (s), 1138 (s), 1037 (m), 1017 (m), 956 (m), 871 (w), 840 (m), 806 (s), 769 (m), 746 (w), 713 (m), 610 (s) cm−1.

**MS** (ESI): *m/z* (%) = 456.94 (100) [M+Cl]−.

**MS** (ESI, HR): C8H5F8O5Cl *m/z* = calc.: 456.93761, found: 456.93860 diff.: -2.17 ppm.

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**Figure S40:** 1H-NMR spectrum of compound **17**, measured in CDCl3 at 300 K. The additional signals in the aromatic range can be assigned to side product **37** (see below) and could not be separated from each other by column chromatography.

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**Figure S41:** 13C-NMR spectrum of compound **17**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

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**Figure S42:** 19F-NMR spectrum of compound **17**, measured in CDCl3 at 300 K. The additional signals can be assigned to side product **37** (see above).

**2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluor-8-(trifluoromethylsulfonyloxy)-methyl-octanoate (18)**



**Yield:** 63 %.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 4.82 (t, 3*J* = 12.3 Hz, 2 H, *H*-8), 4.00 (s, 3 H,

*H*-9) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 158.83 (*C*-1), 114.95 (*C*-5), 112.89 (*C*-7), 110.87 (*C*-6) 68.13 (*C*-8), 54.67 (*C*-9) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-2, *C*-3, *C*-4 and *C*-10 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K): = -74.5 (br. s, 3 F, *F*-10), -118.9 to -119.0 (m, 2 F, *F*‑2), ‑120.1 to -120.2 (m, 2 F, *F*-7), -122.1 to -122.4 (m, 4 F, *F*-4, *F*-5), -123.1 to -123.3 (m, 2 F, *F*-6), -123.3 to -123.5 (m, 2 F, *F*-3) ppm.

**FT-IR:** = 2970 (w), 1785 (s), 1428 (s), 1325 (m), 1249 (w), 1199 (s) 1137 (s), 1015 (s), 958 (w), 904 (w), 816 (m), 763 (m), 716 (w), 691 (w), 657 (w), 610 (s) cm−1.

**MS** (ESI): *m/z* (%) = 544.95 (100) [M+Na]+·.

**MS** (ESI, HR): C10H5F15O5NaS *m/z* = calc.: 544.95104, found: 544.95095, diff.: -0.17 ppm.

****

**Figure S43:** 1H-NMR spectrum of compound **18**, measured in CDCl3 at 300 K.

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**Figure S44:** 13C-NMR spectrum of compound **18**, measured in CDCl3 at 300 K.

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**Figure S45:** 19F-NMR spectrum of compound **18**, measured in CDCl3 at 300 K.

## **3.6 Synthesis of 2-Iodo-3,4,5-trimethoxybenzaldehyde (20)**



3,4,5-Trimethoxybenzaldehyde (3.00 g, 15.3 mmol) was dissolved in acetonitrile (20 ml), then *N*-iodosuccinimide (6.87 g, 30.6 mmol) and three drops of trifluoroacetic acid were added and the solution was refluxed for 18 h. After cooling the reaction mixture, sodium sulfit (1.92 g, 15.3 mmol) was added and stirred for a further 2 h at room temperature. Then dichloromethane (150 ml) was added and diluted with sodium chloride solution (2 x 50 ml) and dist. water (1 x 50 ml). The crude product was dried over magnesium sulphate, filtered, the solvent removed in vacuo and flashes were analyzed by column chromatography (cyclohexane/ethyl acetate, gradient: 5%-60% ethyl acetate) purification. A yellow solid was obtained.

**Yield:** 4.39 g (13.7 mmol,89 %) (Lit.1: 99 %).

**Melting Point:** 66.7 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 10.05 (s, 1 H, *H*-7), 7.35 (s, 1 H, *H*-6), 3.97 (s, 3 H, *H*-9), 3.92 (s, 3 H, *H*-8), 3.90 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 195.3 (*C*-7), 154.0 (*C*-5), 153.0 (*C*-3), 147.8 (*C*-4), 130.6 (*C*-1), 108.6 (*C*-6), 91.5 (*C*-2), 61.2 (*C*-9), 61.0 (*C*-8), 56.3 (*C*-10) ppm.

**FT-IR:** = 2936 (m), 2853 (m), 2249 (w), 1685 (s), 1573 (m), 1424 (m), 1446 (m), 1398 (m), 1378 (s), 1320 (s), 1283 (m), 1242 (m), 1197 (s), 1161 (s), 1100 (s), 1041 (m), 997 (s), 978 (s), 920 (s), 862 (s), 808 (m), 773 (m), 750 (w), 722 (m), 663 (m), 637 (m), 577 (m), 522 (m) cm-1.

**MS** (EI, 70 eV): *m/z* (%) = 321.97 (100) [M]+·.

**MS** (EI, HR, 70 eV): C10H11O4I *m/z* = calc.: 321.97020, found: 321.97020, diff.: 0.00 ppm.



**Figure S46:** 1H-NMR spectrum of compound **20**, measured in CDCl3 at 300 K.



**Figure S47:** 13C-NMR spectrum of compound **20**, measured in CDCl3 at 300 K.

## **3.7 Synthesis of 2-Hydroxy-3,4,5-trimethoxybenzaldehyde (21)**



2-Iodo-3,4,5-trimethoxybenzaldehyde (**44**) (4.04 g, 12.6 mmol) was placed in a three-necked flask under a nitrogen atmosphere. Copper(I) oxide (90.0 mg, 630 µmol), pyridine-2-aldoxime (154 mg, 1.26 mmol), tetrabutylammonium bromide (811 mg, 2.52 mmol) and caesium hydroxide monohydrate (9.41 g, 63.0 mmol) were added countercurrently. Then dist. water (20 ml) was added and stirred for 18 h at room temperature. Afterwards the reaction mixture was heated to 60 °C for 4 h and DMSO (10 ml) was added for a better solubility. Then the reaction was stirred another 65 h at room temperature. A pH value of 2 was adjusted with 1 m hydrochloric acid. The organic phase was extracted with dichloromethane (4 x 60 ml) and dried over magnesium sulfate. The solvent was then removed in vacuo and analyzed by flash column chromatography (cyclohexane/ethyl acetate, gradient: 5%-60% ethyl acetate). A yellow solid was obtained.

**Yield:** 1.73g (8.15 mmol, 65 %) (Lit.1: 83 %).

**Melting Point:** 44.8 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 10.99 (s, 1 H, *OH*), 9.77 (s, 1 H, *H*-7), 6.78 (s, 1 H, *H*-6), 4.05 (s, 3 H, *H*-9), 3.94 (s, 3 H, *H*-8), 3.86 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K): = 194.9 (*C*-7), 151.8 (*C*-5), 150.4 (*C*-3), 146.3

(*C*-4), 141.0 (*C*-1), 115.2 (*C*-2), 109.3 (*C*-6), 61.4 (*C*-9), 61.1 (*C*-8), 56.5 (*C*-10) ppm.

**FT-IR:** = 2947 (m), 2841 (m), 1642 (s), 1586 (w), 1488 (s), 1454 (s), 1432 (s), 1392 (s), 1319 (s), 1274 (s), 1217 (w), 1199 (m), 1140 (s), 1097 (s), 1032 (m), 987 (m), 935 (m), 897 (s), 844 (m), 781 (m), 733 (m), 610 (m) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 212.07 (100) [M]+·.

**MS** (EI, HR, 70 eV): C10H12O5 *m/z* = calc.: 212.06847, found: 212.06843, diff.: -0.22 ppm.



**Figure S48:** 1H-NMR spectrum of compound **21**, measured in CDCl3 at 300 K.

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**Figure S49:** 1H-NMR spectrum of compound **21**, measured in CDCl3 at 300 K.

## **3.8 General procedure for the ethers 22, 23 and 24**

Under a nitrogen atmosphere, 2-hydroxy-3,4,5-trimethoxybenzaldehyde (**21**, 1 eq.), the corresponding fluorinated alcohol (**16**-**18**)(1 eq.)and cesium carbonate (1 eq.) were dissolved in *N*,*N*-dimethylacetamide (25 ml). The solution was stirred at room temperature for 2 h and then combined with dist. water (75 ml). It was extracted with ethyl acetate (3 x 50 ml) and the organic phases were separated with dist. water (2 x 50 ml) and saturated sodium chloride solution (2 x 50 ml). The organic phase was dried over magnesium sulfate, filtered and the solvent removed in vacuo. A dark yellow oil was obtained.

**2-(2,2,3,3-Tetrafluor-4-methylbutanoat-1-oxy)-3,4,5-trimethoxybenzaldehyd (22)**



**Yield:** 78 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 10.32 (s, 1 H, *H*-7), 7.14 (s, 1 H, *H*-6), 4.64 (t, 3*J*= 13.2 Hz, 2 H, *H*-11), 4.00 (s, 3 H, *H*-9), 3.96 (s, 3 H, *H*-15), 3.92 (s, 3 H, *H*-8), 3.88 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 188.3 (*C*-7), 160.4 (*C*-14), 150.4 (*C*-5), 149.5 (*C*-2), 149.3 (*C*-4), 145.8 (*C*-3), 123.7 (*C*-1), 115.0 (*C*-13), 104.1 (*C*-6), 69.9 (*C*-11), 61.5 (*C*-8), 61.3 (*C*-9), 56.2 (*C*-10), 54.4 (*C*-15) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-12 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -120.5 (s, 2 F, *F*-12), -121.7 (s, 2 F, *F*-13) ppm.

**FT-IR:** = 2947 (w), 2250 (w), 1776 (m), 1682 (m), 1591 (m), 1486 (m), 1466 (m), 1421 (m), 1388 (m), 1342 (m), 1284 (m), 1257 (m), 1199 (m), 1127 (s), 1084 (s), 1032 (s), 986 (m), 956 (m), 922 (m), 856 (w), 818 (m), 800 (w), 750 (m), 641 (m), 596 (w) cm-1.

**MS** (ESI): *m/z* (%) = 407.07 (100) [M+Na]+.

**MS** (ESI, HR): C15H16F4O7Na *m/z* = calc.: 407.07244, found: 407.07177, diff.: -1.64 ppm.



**Figure S50:** 1H-NMR spectrum of compound **22**, measured in CDCl3 at 300 K.

****

**Figure S51:** 13C-NMR spectrum of compound **22**, measured in CDCl3 at 300 K.

****

**Figure S52:** 19F-NMR spectrum of compound **22**, measured in CDCl3 at 300 K.

**2-(2,2,3,3,4,4,5,5-Oktafluor-6-methylhexanoat-1-oxy)-3,4,5-trimethoxy-benzaldehyd (23)**



**Yield:** 44 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 10.32 (s, 1 H, *H*-7), 7.14 (s, 1 H, *H*-6), 4.63 (t, 3*J* = 14.1 Hz, 2 H, *H*-11), 4.01 (s, 3 H, *H*-9), 3.99 (s, 3 H, *H*-17), 3.92 (s, 3 H, *H*-8), 3.88 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 188.1 (*C*-7), 159.2 (*C*-16), 150.4 (*C*-5), 149.3 (*C*-2), 149.2 (*C*-4), 145.5 (*C*-3), 123.5 (*C*-1), 117.2 (*C*-13), 115.2 (*C*-12), 113.1 (*C*-14), 104.1 (*C*-6), 69.9 (*C*-11), 61.5 (*C*-8), 61.3 (*C*-9), 56.2 (*C*-10), 54.6 (*C*-17) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-15 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -119.1 (t, 3J= 11.7 Hz, 2 F, *F*-15), -120.9 (dt, 3J= 14.3 Hz, 4J= 2.80 Hz, 2 F, *F*-12), -123.4 to -123.5 (m, 2 F, *F*-13), -123.7 to -123.9 (m, 2 F, *F*-14) ppm.

**FT-IR:** = 2946 (m), 1782 (m), 1684 (m), 1591 (m), 1486 (m), 1467 (m), 1421 (m), 1389 (m), 1343 (s), 1283 (m), 1187 (s), 1133 (s), 1086 (s), 1046 (m), 987 (w), 960 (w), 925 (w), 868 (m), 809 (m), 757 (m), 711 (w), 637 (m) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 484 (90) [M]+·, 211.06 (100) [M-C7H5F8O2]+·.

**MS** (EI, HR, 70 eV): C17H16F8O7 *m/z* = calc.: 484.07683, found: 484.07686, diff.: 0.06 ppm.



**Figure S53:** 1H-NMR spectrum of compound **23**, measured in CDCl3 at 300 K.

****

**Figure S54:** 13C-NMR spectrum of compound **23**, measured in CDCl3 at 300 K.

****

**Figure S55:** 19F-NMR spectrum of compound **22**, measured in CDCl3 at 300 K.

**2-(2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluor-8-methyloktanoat-1-oxy)-3,4,5-trimethoxybenzaldehyd (24)**



**Yield:** 44 %.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 10.32 (s, 1 H, *H*-7), 7.15 (s, 1 H, *H*-6), 4.64 (t, 3*J* = 14.0 Hz, 2 H, *H*-11), 4.01 (s, 3 H, *H*-9), 4.00 (s, 3 H, *H*-17), 3.92 (s, 3 H, *H*-8), 3.89 (s, 3 H, *H*-10) ppm.

**13C-NMR** (125 MHz, CDCl3, 300 K, TMS): = 188.0 (*C*-7), 159.0 (*C*-18), 150.5 (*C*-5), 149.3 (*C*-2), 149.2 (*C*-4), 145.6 (*C*-3), 123.4 (*C*-1), 117.1 (*C*-13), 115.3 (*C*-12), 113.3 (*C*-14), 104.2 (*C*-6), 69.9 (*C*-11), 61.5 (*C*-8), 61.3 (*C*-9), 56.2 (*C*-10), 54.7 (*C*-19) ppm.

Due to the large number of 19F-coupled C atoms, it was not possible to obtain sufficient signal intensity for the *C*-15, *C*-16 and *C*-17 atom.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -118.9 to -118.0 (m, 2 F, *F*-17), -120.8 to -120.9 (m, 2 F, *F*-12), -122.1 to -122.3 (m, 2 F, *F*-15), -122.3 to -122.5 (m, 2 F, *F*-14), -123.2 to -123.3 (m, 2 F, *F*-13), -123.6 to -123.8 (m, 2 F, *F*-16) ppm.

**FT-IR:** = 2946 (m), 1784 (m), 1685 (m), 1591 (m), 1487 (m), 1467 (m), 1432 (w), 1421 (m), 1389 (m), 1344 (m), 1283 (w), 1198 (s), 1133 (s), 1087 (s), 1036 (m), 986 (w), 962 (w), 925 (w), 842 (w), 805 (w), 755 (m), 716 (m), 640 (m) cm−1.

**MS** (EI, 70 eV): *m/z* (%) = 584.07 (82) [M]+·, 211.06 (100) [M-C9H5F12O2]+·.

**MS** (EI, HR, 70 eV): C19H16F12O7 *m/z* = calc.: 584.07044, found: 584.07020, diff.: -0.42 ppm.



**Figure S56:** 1H-NMR spectrum of compound **24**, measured in CDCl3 at 300 K.

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**Figure S57:** 13C-NMR spectrum of compound **24**, measured in CDCl3 at 300 K.

****

**Figure S58:** 19F-NMR spectrum of compound **24**, measured in CDCl3 at 300 K.

## **3.9 General procedure for the metal free porphyrins 25, 26 and 27**

Under a nitrogen atmosphere, the corresponding aldehyde (**22-24**) (1 eq.) and trifluoroacetic acid (0.31 eq.) were introduced into abs. dichloromethane (50 ml) and the solution was refluxed for 30 min. Pyrrole (1 eq.) was added and the reaction mixture was stirred under reflux for a further 2.5 h. After the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.48 eq.) (DDQ) it was again refluxed for 2 h. The crude product was purified on silica gel by column chromatography (Cyclohexane/ethyl acetate, 1:1). Afterwards the product was dissolved in dichloromethane (50 ml), washed with saturated sodium carbonate solution (3 x 50 ml), dried over magnesium sulfate and the solvent was removed in vacuo. A purple, crystalline solid was obtained.

**5,10,15,20-Tetrakis-(2-(2,2,3,3-tetrafluor-4-methylbutanoate-1-oxy)-3,4,5-trimethoxyphenyl)-21*H*,23*H*-porphyrin (25)**



**Yield:** 9 %.

**Melting Point:** 61.8 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 8.56-8.39 (m, 8 H, *H*-3), 7.65-7.32 (m, 4 H, *H*-9), 4.29-3.71 (m, 44 H, *H*-10, *H*-15, *H*-16, *H*-17), 3.35-2.03 (m, 12 H, *H*-14), -2.71 to -2.76 (m, 2H, N-*H*) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2923 (m), 2249 (w), 1774 (m), 1583 (m), 1492 (m), 1457 (m), 1413 (m), 1367 (m), 1228 (m), 1120 (s), 1034 (s), 954 (m), 804 (m), 750 (m), 594 (m) cm-1.

**MS** (ESI): *m/z* (%) = 1727.42 (100) [M+H]+.

**MS** (ESI, HR): C76H70F16N4O24 *m/z* = calc.: 1727.41973, found: 1727.42122, diff.: 0.87 ppm.

****

**Figure S59:** 1H-NMR spectrum of compound **25**, measured in CDCl3 at 300 K.

****

**Figure S60:** 13C-NMR spectrum of compound **25**, measured in CDCl3 at 300 K.

****

**Figure S61:** 19F-NMR spectrum of compound **25**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5-oktafluor-6-methylhexanoate-1-oxy)-3,4,5-trimethoxyphenyl)-21*H*,23*H*-porphyrin (26)**



**Yield:** 18 %.

**Melting Point:** 181-185 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 8.87-8.79 (m, 8 H, *H*-3), 7.43-7.26 (m, 4 H, *H*-9), 4.25-2.42 (m, 44 H, *H*-10, *H*-17, *H*-18, *H*-19), 3.45-2.04 (m, 12 H, *H*-16), -2.69 to -2.84 (m, 2 H, N-*H*) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 3184 (w), 2943 (w), 2255 (w), 1780 (m), 1575 (w), 1492 (w), 1452 (m), 1413 (w), 1357 (w), 1324 (w), 1268 (w), 1183 (m), 1137 (m), 1103 (m), 1073 (m), 1037 (m), 1007 (w), 957 (w), 922 (w), 886 (w), 867 (w), 803 (w), 775 (w), 744 (w), 688 (w), 618 (w) cm-1.

**MS** (ESI): *m/z* (%) = 2127.39 (100) [M-H]+.

**MS** (ESI, HR): C84H71O24N4F32: calc.: 2127.39418, found: 2127.39382, diff.: -0.17 ppm.

****

**Figure S62:** 1H-NMR spectrum of compound **26**, measured in CDCl3 at 300 K.

****

**Figure S63:** 13C-NMR spectrum of compound **26**, measured in CDCl3 at 300 K.

****

**Figure S64:** 19F-NMR spectrum of compound **26**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluor-8-methyloktanoat-1-oxy)-3,4,5-Trimethoxyphenyl)-21*H*,23*H*-porphyrin (27)**



**Yield:** 21 %.

**Melting Point:** 72.5 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.89-8.80 (m, 8 H, *H*-3), 7.46-7.21 (m, 4 H, *H*-9), 4.25-2.09 (m, 56 H, *H*-10, *H*-18, *H*-19, *H*-20, *H*-21), -2.68 to -2.75 (m, 2 H, N-*H*) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2917 (w), 2849 (w), 1782 (w), 1690 (w), 1577 (w),1491 (w),1459 (w), 1434 (w), 1413 (w), 1356 (w), 1324 (w), 1195 (m), 1137 (m), 1103 (m), 1038 (w), 1011 (w), 956 (w), 923 (w), 899 (w), 803 (w), 744 (w), 717 (w), 653 (w), 624 (w) cm-1.

**MS** (ESI): *m/z* (%) = 2527.37 (100) [M]+.

**MS** (ESI, HR): C92H71F48N4O24 *m/z* = calc.: 2527.36863, found: 2527.36760, diff.: -0.41 ppm.



**Figure S65:** 1H-NMR spectrum of compound **27**, measured in CDCl3 at 300 K.

****

**Figure S66:** 13C-NMR spectrum of compound **27**, measured in CDCl3 at 300 K.

****

**Figure S67:** 19F-NMR spectrum of compound **27**, measured in CDCl3 at 300 K.

## **3.10 General procedure for the nickel porphyrins 28, 29 and 30**

The corresponding porphyrin (**25-27**) (1 eq.) was dissolved in toluene (25 ml), nickel(II) acetylacetonate (10 eq.) was added and refluxed for 20 h. The solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 1:1) by dry loading. A brown, crystalline solid was obtained.

**5,10,15,20-Tetrakis-(2-(2,2,3,3-tetrafluoro-4-methylbutanoate-1-oxy)-3,4,5-trimethoxyphenyl)-nickel(II)porphyrin (28)**



**Yield:** 78 %.

**Melting Point:** 84.9 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.78-8.70 (m, 8 H, *H*-3), 7.35-6.95 (m, 4 H, *H*-9),

4.15-3.77 (m, 44 H, *H*-10,15,16,17), 3.05-2.52 (m, 12 H, *H*-14) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR and 19F-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR spectrum was not possible.

**19F-NMR** (500 MHz, CDCl3, 300 K, TMS): = -121.3 to -122.3 (m, 2 F, *F*-11), -122.5 to -123.5 (m, 2 F, *F*-12) ppm.

**FT-IR:** = 2937 (w), 2252 (w), 1982 (w), 1774 (m), 1490 (m), 1456 (m), 1412 (m), 1366 (s), 1110 (s), 1075 (s), 1036 (s), 1006 (s), 751 (s), 632 (m) cm-1.

**MS** (ESI): *m/z* (%) = 1782.33 (100) [M]+.

**MS** (ESI, HR): C76H68F16N4O24Ni *m/z* = calc.: 1782.33160, found: 1782.33356,

diff.: 1.10 ppm.

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**Figure S68:** 1H-NMR spectrum of compound **28**, measured in CDCl3 at 300 K.

****

**Figure S69:** 13C-NMR spectrum of compound **28**, measured in CDCl3 at 300 K.

****

**Figure S70:** 19F-NMR spectrum of compound **28**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5-oktafluor-6-methylhexanoate-1-oxy)-3,4,5-trimethoxyphenyl)-nickel(II)-porphyrin (29)**



**Yield:** 97 %.

**Melting Point:** 86.7 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K): = 8.86-8.70 (m, 8 H, *H*-3), 7.22-7.09 (m, 4 H, *H*-9), 4.20-3.00 (m, 44 H, *H*-10, *H*-17, *H*-18, *H*-19), 3.56-3.00 (m, 12 H, *H*-16) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2925 (w), 2851 (w), 1780 (w), 1578 (w), 1490 (w), 1456 (w), 1434 (w),1413 (w), 1366 (m), 1323 (w), 1253 (w), 1183 (m), 1141 (m), 1109 (s), 1074 (m), 1039 (m), 1005 (m), 967 (w), 897 (w), 867 (w), 827 (w), 770 (w), 750 (w), 731 (w), 710 (w) cm-1.

**MS** (MALDI-TOF, matrix: ClCCA): *m/z* (%) = 2182.2 (99).

**Figure S71:** 1H-NMR spectrum of compound **29**, measured in CDCl3 at 300 K.

****

**Figure S72:** 13C-NMR spectrum of compound **29**, measured in CDCl3 at 300 K.

****

**Figure S73:** 19F-NMR spectrum of compound **29**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluor-8-methyloktanoat-1-oxy)-3,4,5-Trimethoxyphenyl)-nickel(II)porphyrin (30)**



**Yield:** 57 %.

**Melting Point:** 63.2 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.78-8.70 (m, 8 H, *H*-3), 7.23-7.04 (m, 4 H, *H*-9), 4.20-3.71 (m, 56 H, *H*-10, *H*-18, *H*-19, *H*-20, *H*-21) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2942 (w), 2852 (w), 1781 (w), 1578 (w), 1491 (w), 1456 (w), 1434 (w), 1414 (w), 1366 (w), 1322 (w), 1195 (m), 1139 (m), 1109 (m), 1075 (m), 1040 (w), 1006 (w), 968 (w), 899 (w), 826 (w), 803 (w), 765 (w), 715 (w), 697 (w), 655 (w), 613 (w) cm-1.

**MS** (ESI): *m/z* (%) = 2582.29 (100) [M]+.

**MS** (ESI, HR): C92H68F48N4O24Ni *m/z* = calc.: 2582.28050, found: 2582.28562, diff.: 1.98 ppm.



**Figure S74:** 1H-NMR spectrum of compound **30**, measured in CDCl3 at 300 K.

****

**Figure S75:** 13C-NMR spectrum of compound **30**, measured in CDCl3 at 300 K.

****

**Figure S76:** 19F-NMR spectrum of compound **30**, measured in CDCl3 at 300 K.

## **3.11 General procedure of nickel porphyrins 31, 32 and 33 (free acid)**

The corresponding nickel porphyrin (**28-30**) (1 eq.) was dissolved in methanol (40 ml) and lithiumhydroxide (10 eq.) was added. This reaction mixture was stirred for 18 h at room temperature, then the solvent was removed in vacuo and water was added until everything was dissolved (30 ml). Afterwards 2 m HCl (20 ml) was added and a red solid precipitated and the aqueos phase turned colorless. The precipitate was filtered in vacuo and then dissolved in acetone (40 ml). After three cycles of freeze pump thaw (to remove HCl) the solvent was removed in vacuo to obtain a red solid.

**5,10,15,20-Tetrakis-(2-(2,2,3,3-tetrafluoro-butan-4-acid-1-oxy)-3,4,5-trimethoxyphenyl)-nickel(II)porphyrin (31)**



**Yield:** 94 %.

**Melting Point:** 127.5 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.79-8.65 (m, 8 H, *H*-3), 7.47-6.96 (m, 4 H, *H*-9), 4.26-3.64 (m, 44 H, *H*-10, *H*-14, *H*-15, *H*-16), 3.59 (br. s, 4 H, O-*H*) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2921 (br, m), 2849 (w), 2041 (w), 1765 (br, m), 1578 (w), 1491 (m), 1458 (m), 1412 (m), 1365 (s), 1251 (m), 1226 (m), 1106 (s), 1075 (s), 1006 (s), 966 (m), 823 (m), 804 (m), 732 (m) cm-1.

**MS** (ESI): *m/z* (%) = 431.17 (100) [M]4-.

**MS** (ESI, HR): C72H56F16N4O24Ni *m/z* = calc.: 430.56011, found: 430.56032, diff.: 0.49.

****

**Figure S77:** 1H-NMR spectrum of compound **31**, measured in CDCl3 at 300 K.

****

**Figure S78:** 13C-NMR spectrum of compound **31**, measured in CDCl3 at 300 K.

****

**Figure S79:** 19F-NMR spectrum of compound **31**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5-octafluoro-hexan-6-acid-1-oxy)-3,4,5-trimethoxyphenyl)-nickel(II)porphyrin (32)**



**Yield:** 39 %.

**Melting Point:** 86.4 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.85-8.63 (m, 8 H, *H*-3), 7.61-6.65 (m, 4 H, *H*-9), 6.34 (s, 4 H, O-*H*), 4.24-3.05 (m, 44 H, *H*-10, *H*-16, *H*-17, *H*-18) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2920 (w), 2850 (w), 2358 (w), 1772 (w), 1578 (w), 1489 (w), 1456 (w), 1433 (w), 1413 (w), 1365 (w), 1250 (w), 1179 (m), 1147 (w), 1108 (m), 1072 (m), 1034 (w), 1004 (w), 964 (w), 895 (w), 867 (w), 827 (w), 801 (w), 766 (w), 746 v 727 (w), 609 (w), 541 (w), 494 (w), 475 (w), 457 (w), 434 (w), 425 (w), 415 (w), 403 (w) cm-1.

**MS** (ESI): *m/z* (%) = 530.55 (100) [M]4-.

**MS** (ESI, HR): C80H56F32N4O24Ni *m/z* = calc.:530.55372, found: 530.55399, diff.: 0.51.

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**Figure S80:** 1H-NMR spectrum of compound **32**, measured in CDCl3 at 300 K.

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**Figure S81:** 13C-NMR spectrum of compound **32**, measured in CDCl3 at 300 K.

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**Figure S82:** 19F-NMR spectrum of compound **32**, measured in CDCl3 at 300 K.

**5,10,15,20-Tetrakis-(2-(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-octan-8-acid-1-oxy)-3,4,5-trimethoxyphenyl)-nickel(II)porphyrin (33)**



**Yield:** 45 %.

**Melting Point:** 112.4 °C.

**1H-NMR** (500 MHz, CDCl3, 300 K, TMS): = 8.78-8.67 (m, 8 H, *H*-3), 7.47-7.04 (m, 4 H, *H*-9), 4.19-3.37 (m, 48 H, *H*-10, *H*-18, *H*-19, *H*-20, O-*H*) ppm.

Due to atropisomers, an exact evaluation of the 1H-NMR spectrum was not possible and only the ranges of the signals were given. A qualitative evaluation of the 13C-NMR and 19F-NMR spectrum was not possible.

**FT-IR:** = 2921 (w), 2850 (w), 1773 (w), 1578 (w), 1490 (w), 1458 (w), 1434 (w), 1414 (w), 1366 (w), 1275 (w), 1260 (w), 1196 (m), 1138 (m), 1108 (m), 1034 (w), 1005 (w), 965 (w), 897 (w), 828 (w), 801 (w), 764 (m), 749 (m), 707 (w), 653 (w), 536 (w), 494 (w), 480 (w), 443 (w), 434 (w), 419 (w) cm-1.

**MS** (ESI): *m/z* (%) = 630.55 (100) [M]4-.

**MS** (ESI, HR): C88H56F48N4O24Ni *m/z* = calc.:630.54734, found: 630.54785, diff.: 0.81.



**Figure S83:** 1H-NMR spectrum of compound **33**, measured in CDCl3 at 300 K.

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**Figure S84:** 13C-NMR spectrum of compound **33**, measured in CDCl3 at 300 K.

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**Figure S85:** 19F-NMR spectrum of compound **33**, measured in CDCl3 at 300 K.

References

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