Figure S96. $^1$H-$^1$H COSY NMR spectrum of tert-butyl benzoselenacarbaporphyrin 15e in CDCl$_3$.
Figure S97. HSQC NMR spectrum of tert-butyl benzoselenacarbaporphyrin 15c in CDCl$_3$. 
Figure S98. Selected nOe difference proton NMR spectra of 15c in CDCl$_3$. 
Figure S99. DEPT-135 NMR spectrum of 15c in CDCl₃.

Figure S100. 125 MHz carbon-13 NMR spectrum of 15c in CDCl₃ at 50 °C.
Figure S101. 500 MHz proton NMR spectrum of phenyl benzoselenacarbaporphyrin 15d in CDCl₃.
Figure S102. $^1$H-$^1$H COSY NMR spectrum of phenyl benzoselenacarbaporphyrin 15d in CDCl$_3$. 
Figure S103. Selected nOe difference proton NMR spectra of 15d in CDCl₃.
Figure S104. HSQC NMR spectrum of phenyl benzoselenacarbaporphyrin 15d in CDCl₃.
Figure S105. DEPT-135 NMR spectrum of 15d in CDCl₃.

Figure S106. 125 MHz carbon-13 NMR spectrum of phenyl benzoselenacarbaporphyrin 15d in CDCl₃ at 50 °C.
Figure S107. 500 MHz proton NMR spectrum of phenyl benzoselenacarbaporphyrin aldehyde 16d in CDCl$_3$ at 50 °C.
Figure S108. $^1$H-$^1$H COSY NMR spectrum of phenyl benzoselenacarbaporphyrin aldehyde 16d in CDCl$_3$.
Figure S109. Selected nOe difference proton NMR spectra of 16d in CDCl₃.
Figure S110. HSQC NMR spectrum of selenacarbaporphyrin aldehyde 16d in CDCl$_3$. 
**Figure S111.** DEPT-135 NMR spectrum of 16d in CDCl₃.

**Figure S112.** 125 MHz carbon-13 NMR spectrum of selenacarbaporphyrin aldehyde 16d in CDCl₃ at 50 °C.
Figure S113. 500 MHz proton NMR spectrum of oxa-azuliporphyrin 12a.2HCl in methanol-\textit{d}_4 at 50 °C. * = solvent impurities.
Figure S114. $^1$H-$^1$H COSY NMR spectrum of 12a.2HCl in methanol-$d_4$.

Figure S115. HSQC NMR spectrum of 12a.2HCl in methanol-$d_4$. 
Figure S116. DEPT-135 NMR spectrum of 12a.2HCl in methanol-$d_4$.

Figure S117. 125 MHz carbon-13 NMR spectrum of 12a.2HCl in methanol-$d_4$ at 50 °C. The poor quality of the spectrum is due to the very poor solubility of this sample.
Figure S118. 500 MHz proton NMR spectrum of 12a.2HCl in TFA-CDCl3.

Figure S119. ¹H-¹H COSY (left) and HSQC (right) NMR spectra of 12a.2HCl in TFA-CDCl3.
Figure S120. DEPT-135 NMR spectrum of 12a.2HCl in TFA-CDCl$_3$.

Figure S121. 125 MHz proton NMR spectrum of 12a.2HCl in TFA-CDCl$_3$. 
Figure S122. 500 MHz proton NMR spectrum of tert-butyl oxa-azuliporphyrin 12b.2HCl in methanol-$d_4$. * = solvent impurities.

Figure S123. HSQC NMR spectrum of 12b.2HCl in methanol-$d_4$. 
Figure S124. DEPT-135 NMR spectrum of 12b.2HCl in methanol-$d_4$.

Figure S125. 125 MHz carbon-13 NMR spectrum of 12b.2HCl in methanol-$d_4$. The poor quality of the spectrum is due to the very poor solubility of this sample.
**Figure S126.** 500 MHz proton NMR spectrum of tert-butyl oxa-azuliporphyrin 12b.2HCl in TFA-CDCl₃.

**Figure S127.** HSQC NMR spectrum of 12b.2HCl in TFA-CDCl₃.
**Figure S128.** DEPT-135 NMR spectrum of 12b.2HCl in TFA-CDCl₃.

**Figure S129.** 125 MHz carbon-13 NMR spectrum of 12b.2HCl in TFA-CDCl₃.
Figure S130. 500 MHz proton NMR spectrum of phenyl oxa-azuliporphyrin 12c.2HCl in methanol-$d_4$. * = solvent impurities.

Figure S131. $^1$H-$^1$H COSY (left) and HSQC (right) NMR spectra of 12c.2HCl in methanol-$d_4$. 
**Figure S132.** DEPT-135 NMR spectrum of 12c.2HCl in methanol-$d_4$.

**Figure S133.** 125 MHz carbon-13 NMR spectrum of 12c.2HCl in methanol-$d_4$. The poor quality of the spectrum is due to the very poor solubility of this sample.
Figure S134. 500 MHz proton NMR spectrum of phenyl oxa-azuloporphyrin 12c.2HCl in TFA-CDCl₃.

Figure S135. ¹H-¹H COSY (left) and HSQC (right) NMR spectra of 12c.2HCl in TFA-CDCl₃.
Figure S136. DEPT-135 NMR spectrum of 12c.2HCl in TFA-CDCl₃.

Figure S137. 125 MHz carbon-13 NMR spectrum of 12c.2HCl in TFA-CDCl₃.
Figure S138. Partial 500 MHz proton NMR spectrum of 12a.2HCl in DBU-CDCl₃. The free base oxa-azuliporphyrin is very unstable and rapidly decomposes.

Figure S139. Partial 500 MHz proton NMR spectrum of 12b.2HCl in DBU-CDCl₃. The free base oxa-azuliporphyrin is very unstable and rapidly decomposes.
Figure S140. ESI MS of tert-butyl thia-azuliporphyrin 8b.

Figure S141. ESI MS of phenyl thia-azuliporphyrin 8c.
Figure S142. ESI MS of tert-butyl selena-azuliporphyrin 9b.

Figure S143. ESI MS of phenyl selena-azuliporphyrin 9c.
Figure S144. ESI (top) and electron impact (bottom) mass spectra of tert-butyl benzothiacarbaporphyrin 15a.
Figure S145. ESI (top) and electron impact (bottom) mass spectra of phenyl benzothiocabaporphyrin 15b.
Figure S146. ESI (top) and electron impact (bottom) mass spectra of phenyl benzothiacarbaporphyrin aldehyde 16b.
Figure S147. ESI (top) and electron impact (bottom) mass spectra of tert-butyl benzoselenacarbaporphyrin 15c.
Figure S148. ESI (top) and electron impact mass spectra of phenyl benzoselenacarbaporphyrin 15d.
Figure S149. ESI (top) and electron impact mass spectra of phenyl benzoselenacarbaporphyrin aldehyde 16d.
Figure S150. Electrospray ionization mass spectrum of oxa-azuliporphyrin 12a.
Figure S151. Electrospray ionization mass spectrum of tert-butyl oxa-azuliporphyrin 12b.
**Figure S152.** Electrospray ionization mass spectrum of phenyl oxa-azuliporphyrin 12c.