

## Supporting Information to

### *meso*-Tetrahexyl-7,8-dihydroxychlorin and its Conversion to $\beta$ -Modified Derivatives

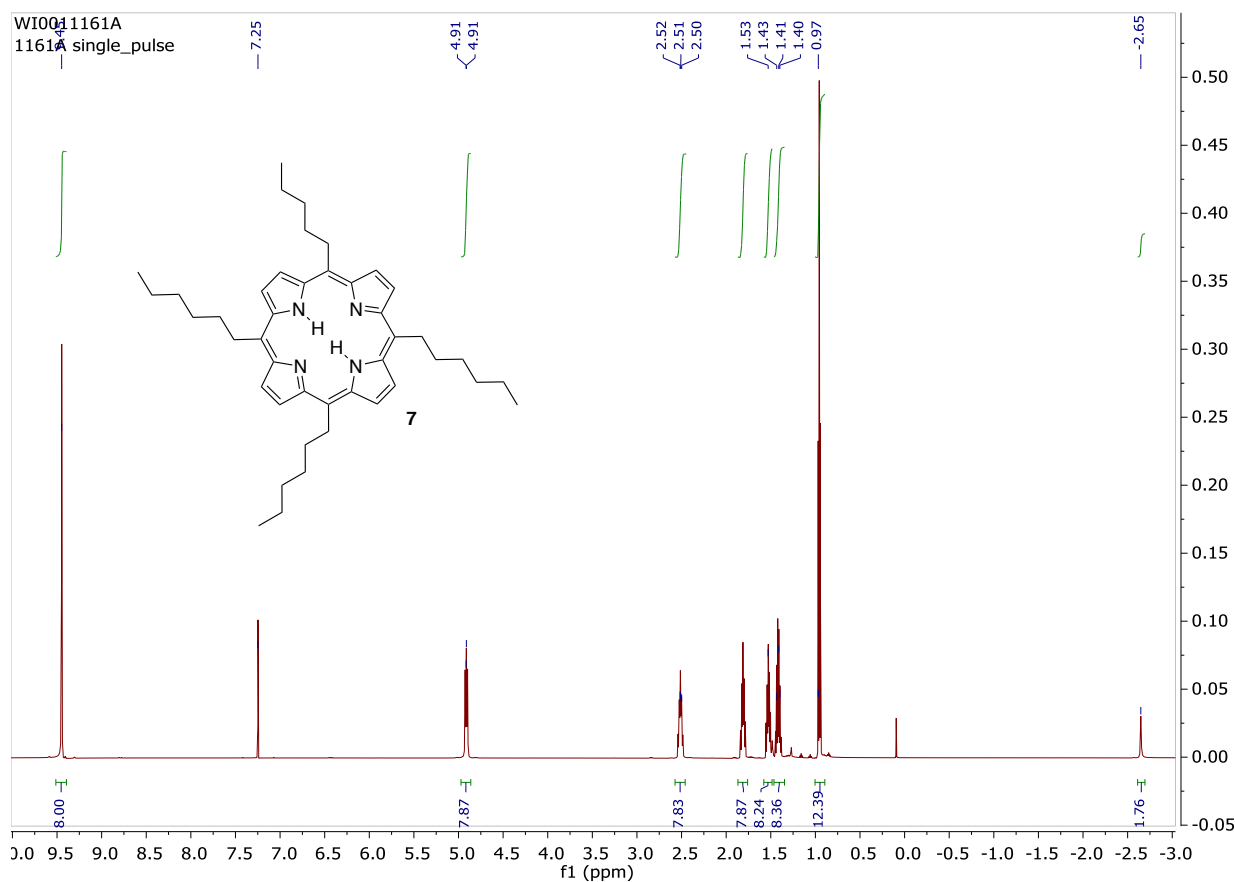
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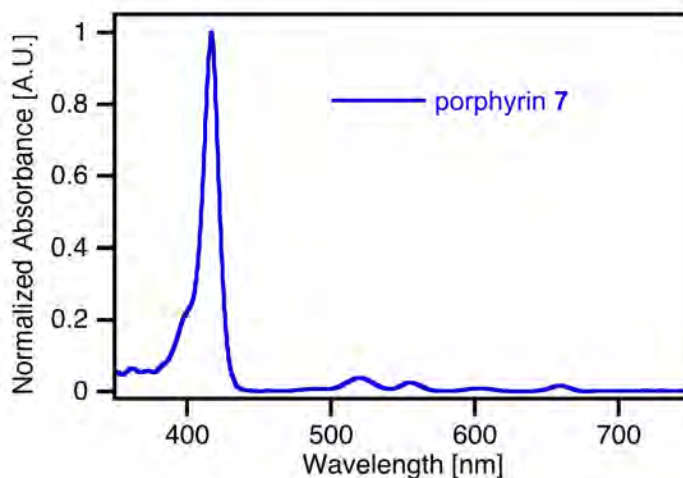
#### Select Reproduction of Spectroscopic Data for:

|  |    |
|--|----|
| <i>meso</i> -Tetrahexylporphyrin ( <b>7</b> ) Known compound; data included for comparison.          | 2  |
| 5,15-Dihexylporphyrin ( <b>15</b> ). Known compound; data included for comparison.                   | 4  |
| <i>meso</i> -Tetrahexyl-7,8- <i>cis</i> -dihydroxychlorin ( <b>8</b> )                               | 6  |
| <i>meso</i> -Tetrahexyl-7,8,17,18- <i>cis</i> -tetrahydroxybacteriochlorin ( <b>9</b> ).             | 11 |
| <i>meso</i> -Tetrahexylporphyrin-7,8-dione ( <b>10</b> ).  | 14 |
| <i>meso</i> -Tetrahexylchlorin-7-one ( <b>11</b> ).  | 18 |
| <i>meso</i> -Tetrahexyl-7-hydroxychlorin ( <b>12</b> ).  | 21 |
| <i>meso</i> -Tetrahexylporpholactone ( <i>meso</i> -Tetrahexyl-7-oxo-8-oxa-porphyrin) ( <b>13</b> ). | 24 |
| 5-(1'-Oxo-hexyl)-10,15,20-trihexylporphyrin ( <b>14</b> ).   | 27 |
| 5,15-Dihexyl-3-oxo-2-oxa-porphyrin) ( <b>16A</b> )   | 30 |
| 5,15-Dihexyl-7-oxo-8-oxa-porphyrin) ( <b>16B</b> ).  | 33 |
| <i>meso</i> -Tetrahexyl-7,8- <i>trans</i> -dihydroxychlorin ( <b>17</b> ).                           | 35 |
| <i>meso</i> -Tetrahexyl-8-hydroxy-8-methyl-chlorin-7-one ( <b>18</b> )                               | 38 |
| <i>meso</i> -Tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin ( <b>19</b> ).                            | 41 |
| <i>meso</i> -Tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one ( <b>18<sup>F</sup></b> ).         | 44 |
| <i>meso</i> -Tetrahexyl-7,8-dihydroxy-8-methyl-chlorin ( <b>20</b> ).                                | 48 |
| <i>meso</i> -Tetrahexyl-7,8-dihydroxy-8-trifluoromethyl-chlorin ( <b>20<sup>F</sup></b> ).           | 51 |

**meso-Tetrahexylporphyrin (7).** Known compound;<sup>1</sup> data included for comparison.

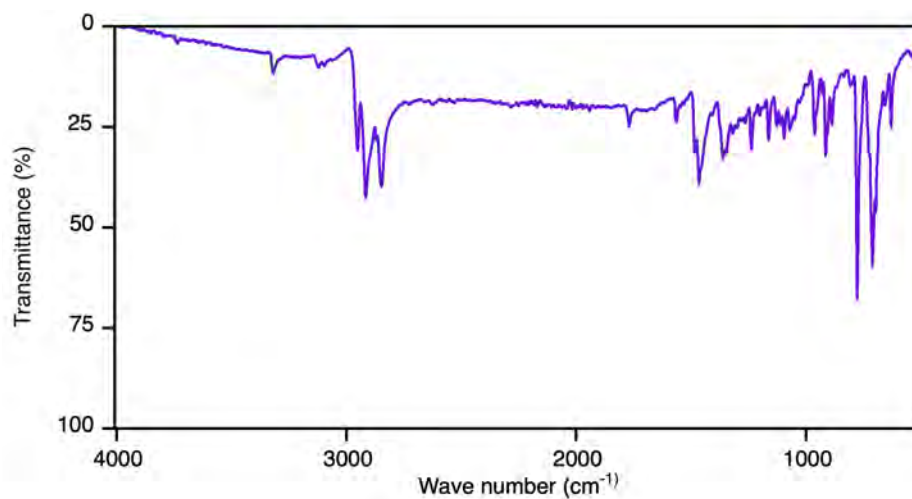


**Figure S-1.** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexylporphyrin **7**.



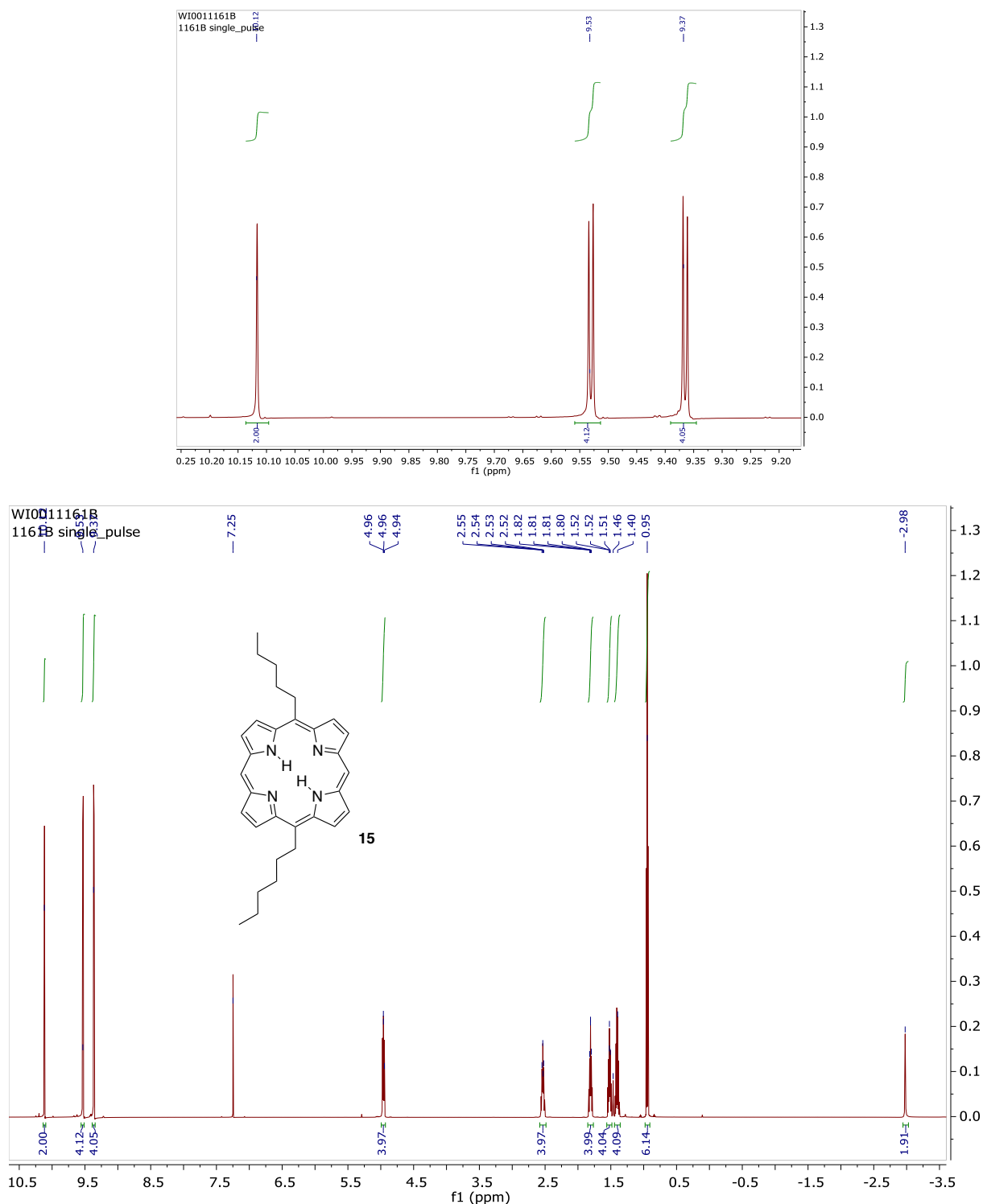
**Figure S-2.** UV-vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>) of *meso*-tetrahexylporphyrin **7**.

<sup>1</sup> (a) Senge, M.O.; Bischoff, I.; Nelson, N.Y.; Smith, K.M. Synthesis, reactivity and structural chemistry of 5,10,15,20-tetraalkylporphyrins. *J. Porphyrins Phthalocyanines* **1999**, *3*, 99–116. (b) Wiehe, A.; Shaker, Y.M.; Brandt, J.C.; Mebs, S.; Senge, M.O. Lead structures for applications in photodynamic therapy. Part 1: Synthesis and variation of *m*-THPC (Temoporfin) related amphiphilic A<sub>2</sub>BC-type porphyrins. *Tetrahedron* **2005**, *61*, 5535–5564. (c) Plamont, R.; Kikkawa, Y.; Takahashi, M.; Kanesato, M.; Giorgi, M.; Chan Kam Shun, A.; Roussel, C.; Balaban, T.S. Nanoscopic Imaging of *meso*-Tetraalkylporphyrins Prepared in High Yields Enabled by Montmorillonite K10 and 3 Å Molecular Sieves. *Chem.-Eur. J.* **2013**, *19*, 11293–11300.



**Figure S-3.** FT-IR (neat, diamond ATR) spectrum of *meso*-tetrahexylporphyrin **7**.

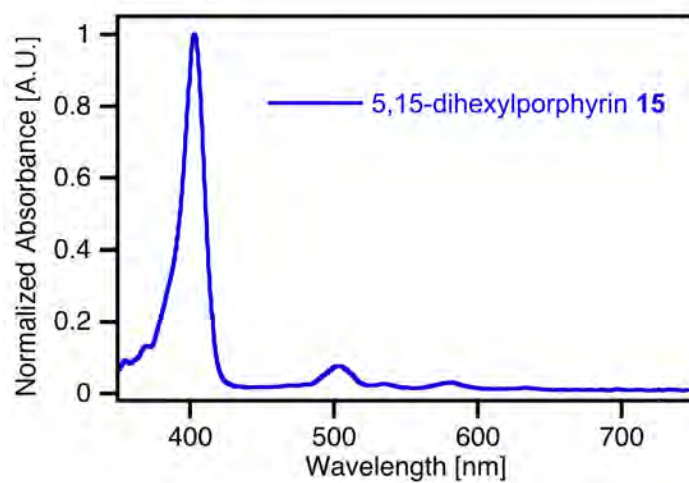
**5,15-Dihexylporphyrin (15).** Known compound;<sup>2</sup> data included for comparison.



**Figure S-1.** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 5,15-dihexylporphyrin **15** (full spectrum, bottom, and detail, top)

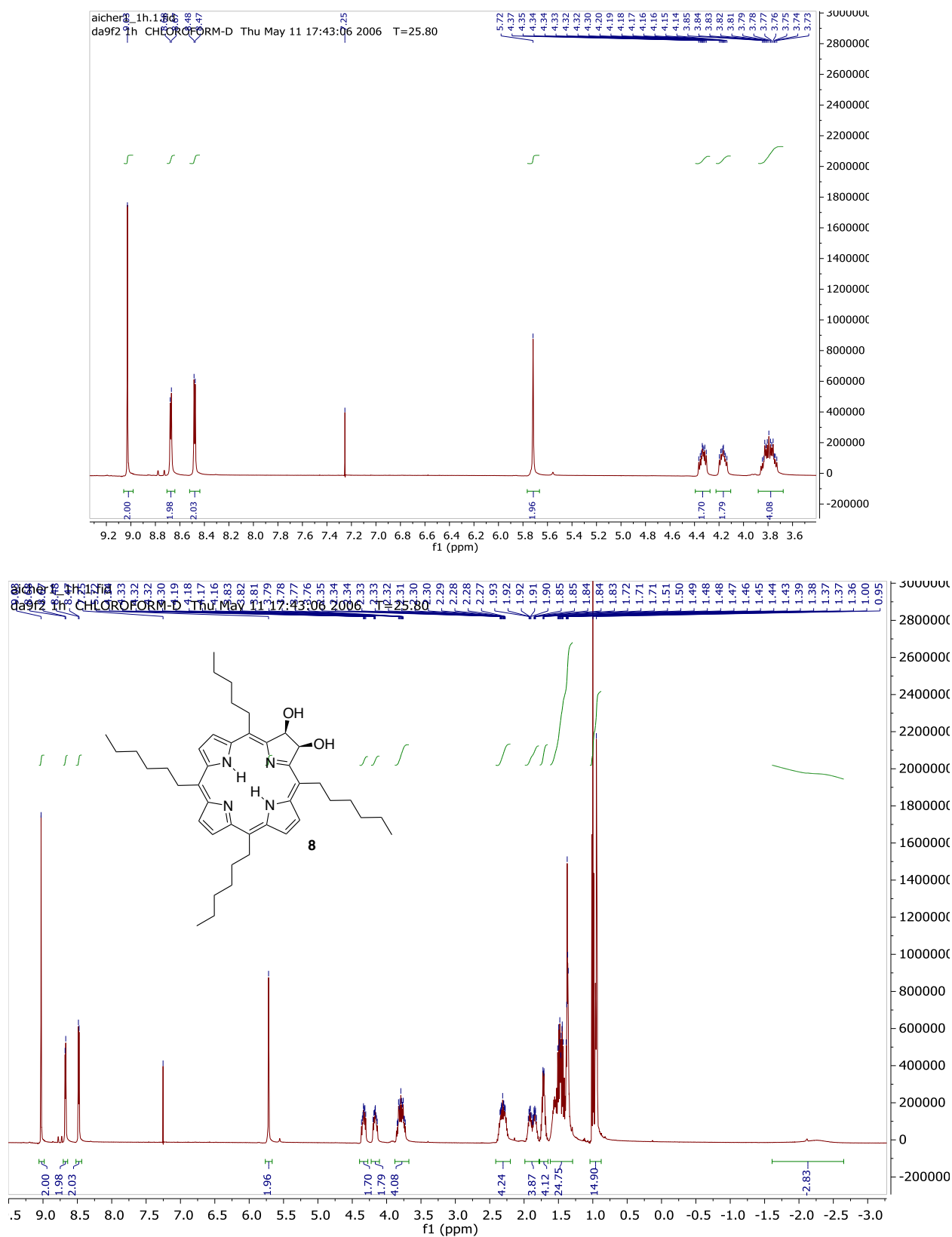
<sup>2</sup> Hiroto, S.; Osuka, A. Meso-Alkyl-Substituted meso-meso Linked Diporphyrins and meso-Alkyl-Substituted meso-meso, β-β, β-β Triply Linked Diporphyrins. *J. Org. Chem.* **2005**, *70*, 4054-4058.



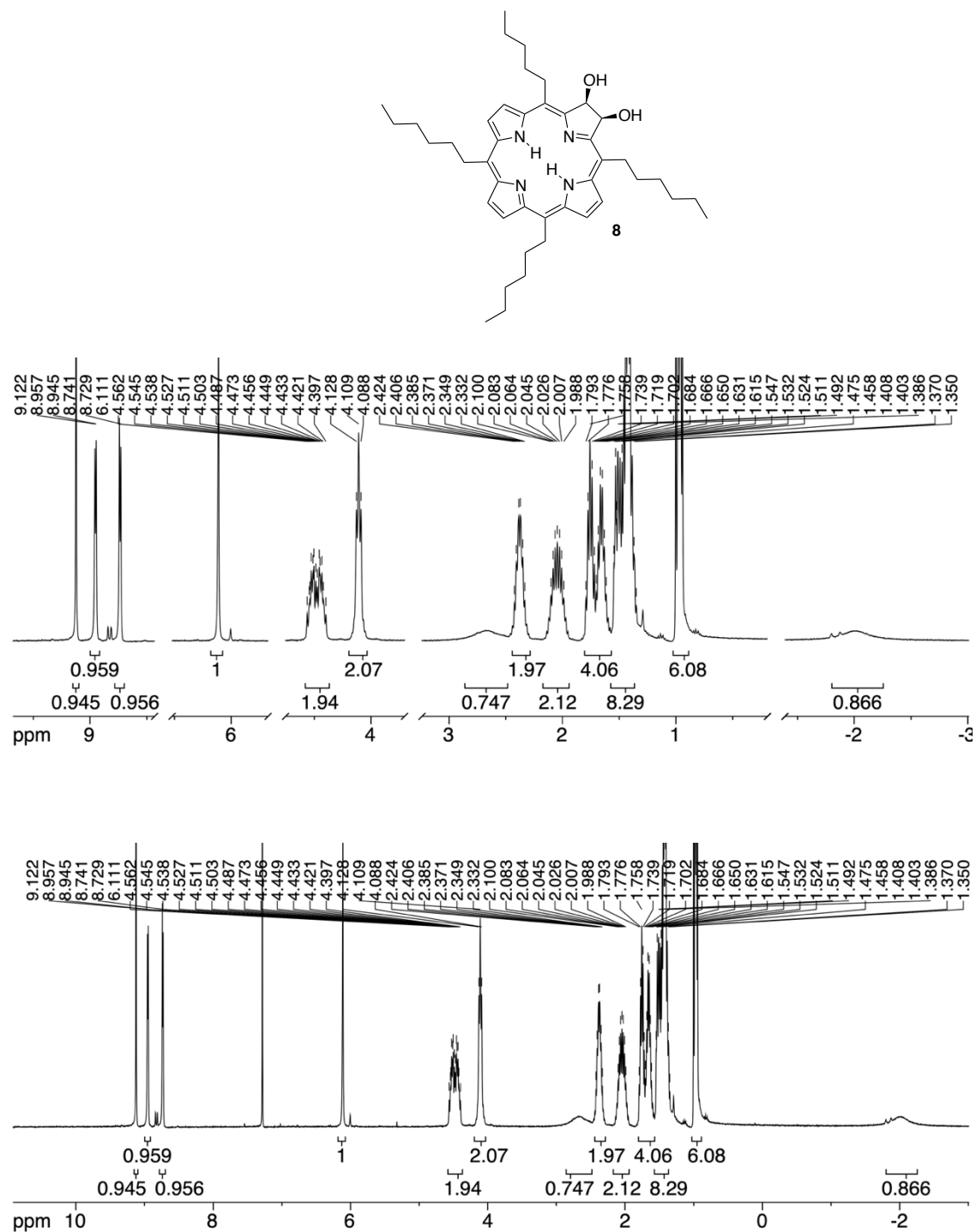


**Figure S-2.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of 5,15-dihexylporphyrin **15**.

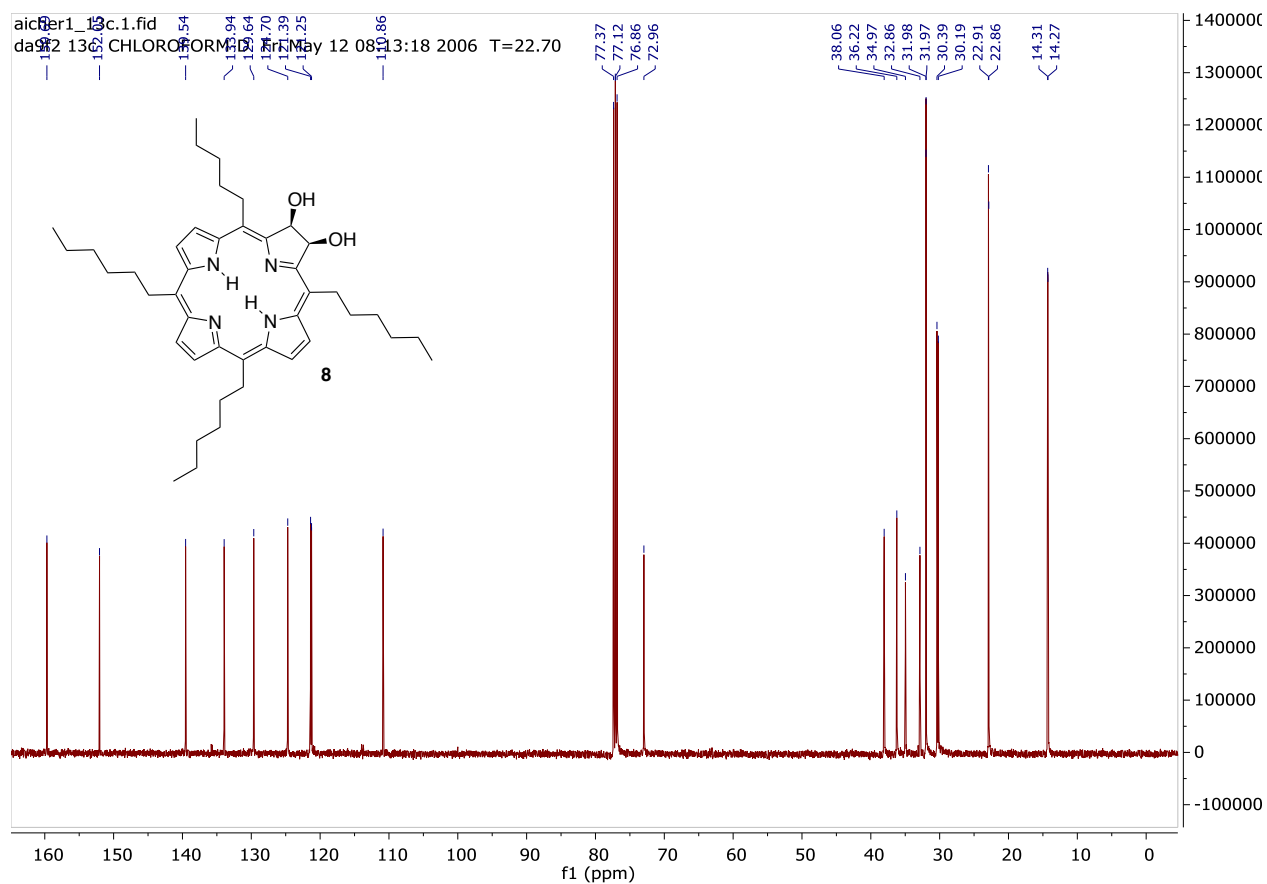
***meso*-Tetrahexyl-7,8-*cis*-dihydroxychlorin (8)**



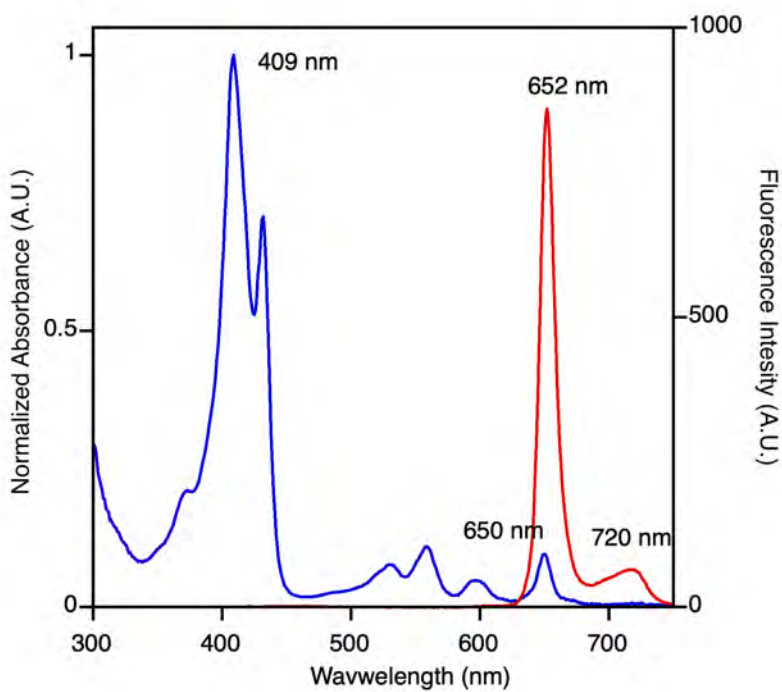
**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyldihydroxychlorin **8** (full spectrum, bottom, and detail, top)



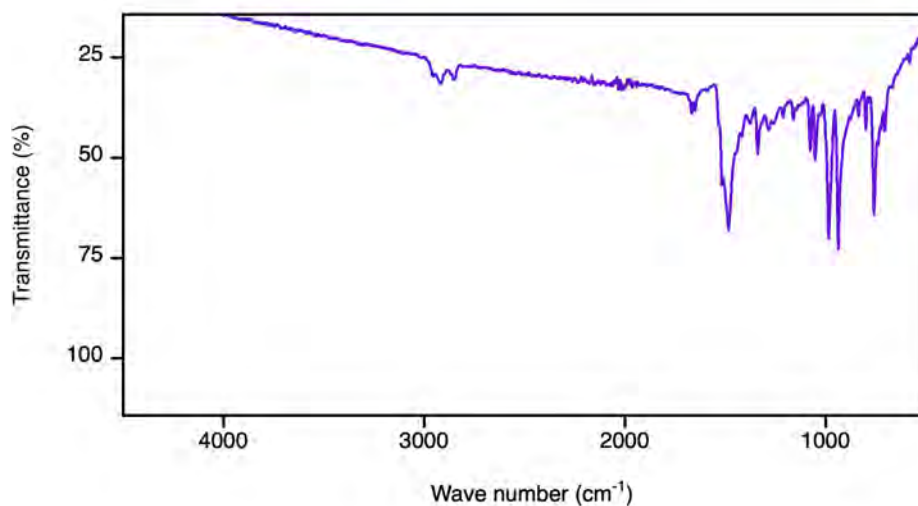
**Figure S-2.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexyldihydroxychlorin **8** (full spectrum, bottom, and detail, top)



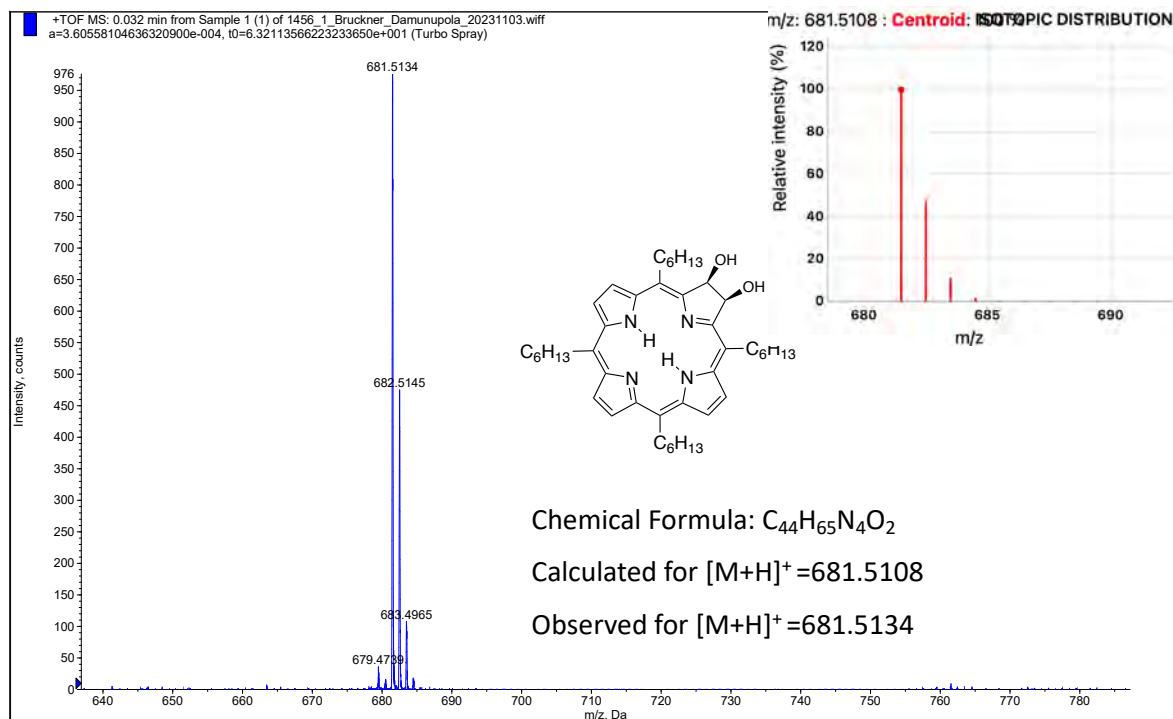
**Figure S-3.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyldihydroxychlorin **8**.



**Figure S-4.** UV-vis (blue) and fluorescence emission (red) spectra ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexyldihydroxychlorin **8**;  $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ .



**Figure S-5.** FT-IR spectrum (neat, ATR) of *meso*-tetrahexyldihydroxychlorin **8**.



**Figure S-6.** HR-MS spectrum (ESI<sup>+</sup>, CH<sub>3</sub>CN, TOF) of *meso*-tetrahexyldihydroxychlorin **8**.

Zentrale Meßabteilung Massenspektrometrie - Inst.f.Org.Chemie der Freien Universität Berlin

**Hochauflösung** - peak-match-Methode - Meßbedingungen: Massenspektrometer MAT 711 der Fa. Finnigan MAT, Bremen - Emission: 80 eV;  
Elektronenenergie: 0,8 mA; Ionenbeschleunigung: 8 kV; Ionenquellentemperatur: 150 °C - Aufnahmetemperatur: 170 °C - Auflösung: 12.500

Name: Biolitec / D. Aicher Probenbezeichnung: [DA 9 F 2] (10 % rel. Tal)

Bearbeitungs-Nr.: 7/28.445 Datum: 25.7.2006

| Referenzmasse:    | Dekade:   | Gefundene Masse: | Berechnete Masse | Summenformel:            | Zuordnung: |
|-------------------|-----------|------------------|------------------|--------------------------|------------|
| PFK<br>654,960125 | 1,0389980 | 680,50225        | 680,50293        | $[C_{44}H_{64}N_4O_2]^+$ | $[H]^+$    |

ATOMIC COMPOSITION REPORT (MANUAL)

Selected Isotopes:

| Symbol | Min | Max | Vcy | Name        |
|--------|-----|-----|-----|-------------|
| C      | 0   | 80  | 4   | Carbon-12   |
| H      | 0   | 90  | 1   | Hydrogen-1  |
| O      | 0   | 10  | 2   | Oxygen-16   |
| N      | 0   | 6   | 3   | Nitrogen-14 |

Allowable error = minimum of 5.0 ppm, 5.0 mmu.

MasCalculated ppmmmu Formula

|           |           |      |      |              |
|-----------|-----------|------|------|--------------|
| 680.50225 | 680.50159 | -1.0 | -0.7 | C43H68O6     |
| 680.50293 | 1.0       | 0.7  |      | C44H64O2N4 * |
| 680.50024 | -2.9      | -2.0 |      | C41H66O5N3   |
| 680.50427 | 3.0       | 2.0  |      | C46H66O3N    |
| 680.50476 | 3.7       | 2.5  |      | C32H68O9N6   |
| 680.49890 | -4.9      | -3.3 |      | C39H64O4N6   |

\*\*\*\* End of Atomic Composition Report \*\*\*\*

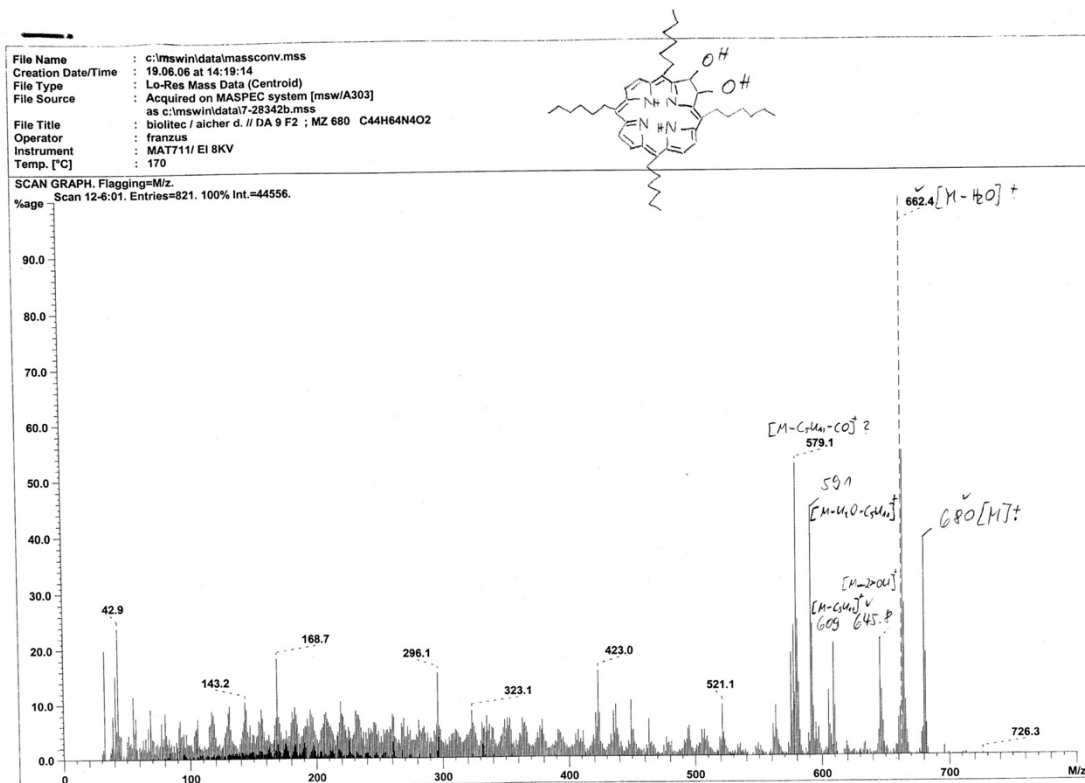
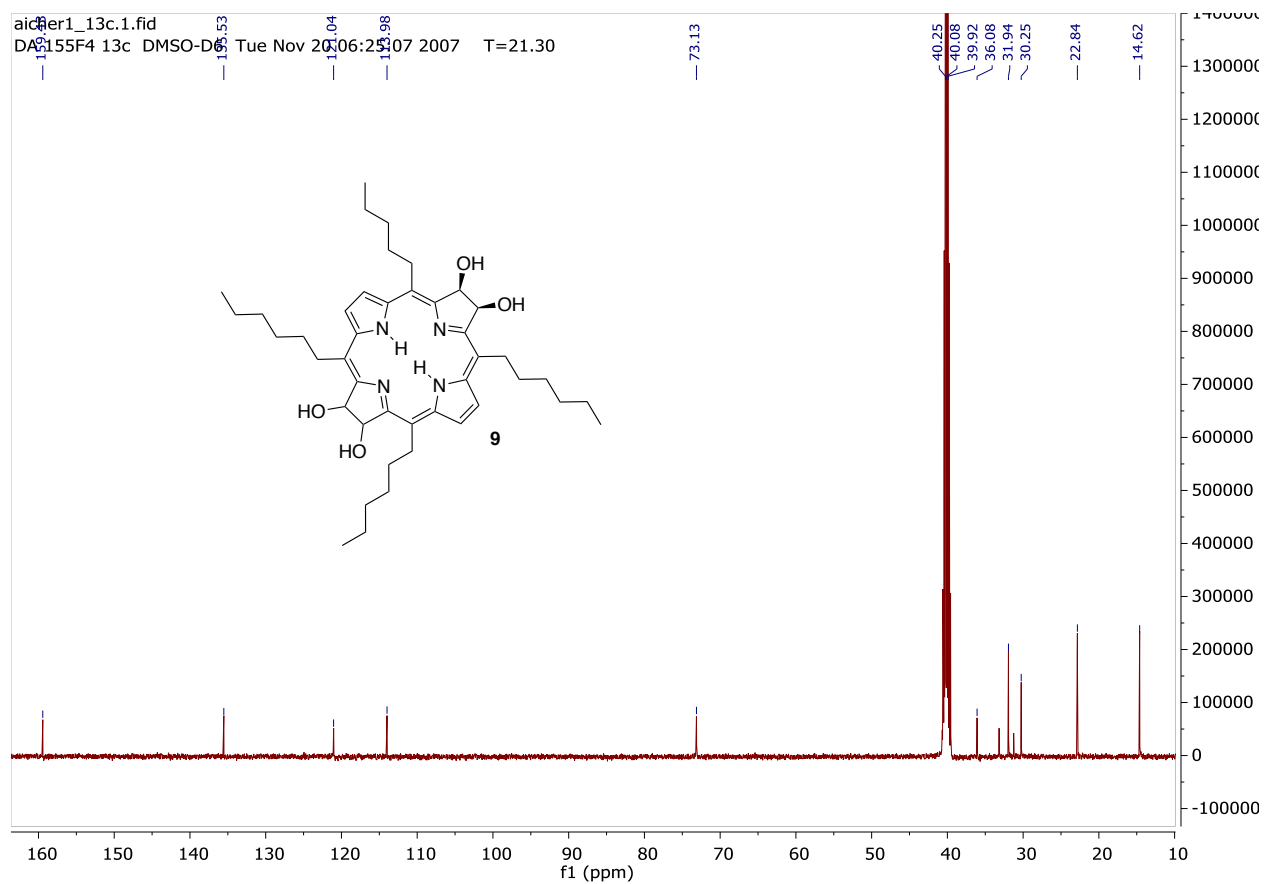


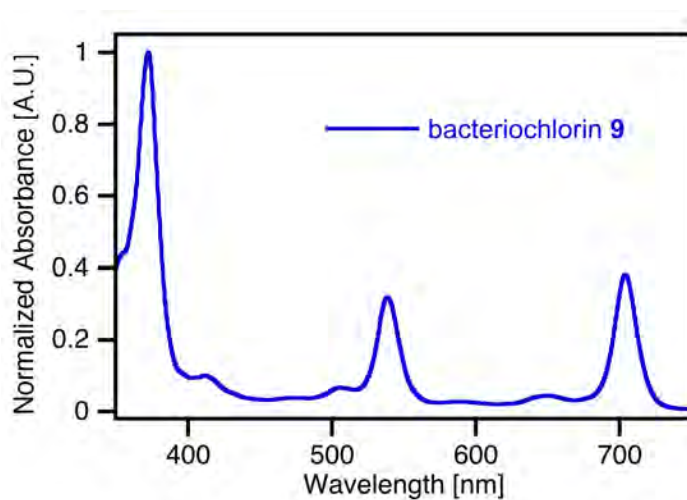
Figure S-7. High-resolution (top) and low-resolution (bottom) mass spectra (EI) of meso-tetrahexyldihydroxychlorin 8.

**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ) spectrum of *meso*-tetrahexyltetrahydroxybacteriochlorin **9** (full spectrum, bottom, and detail, top)



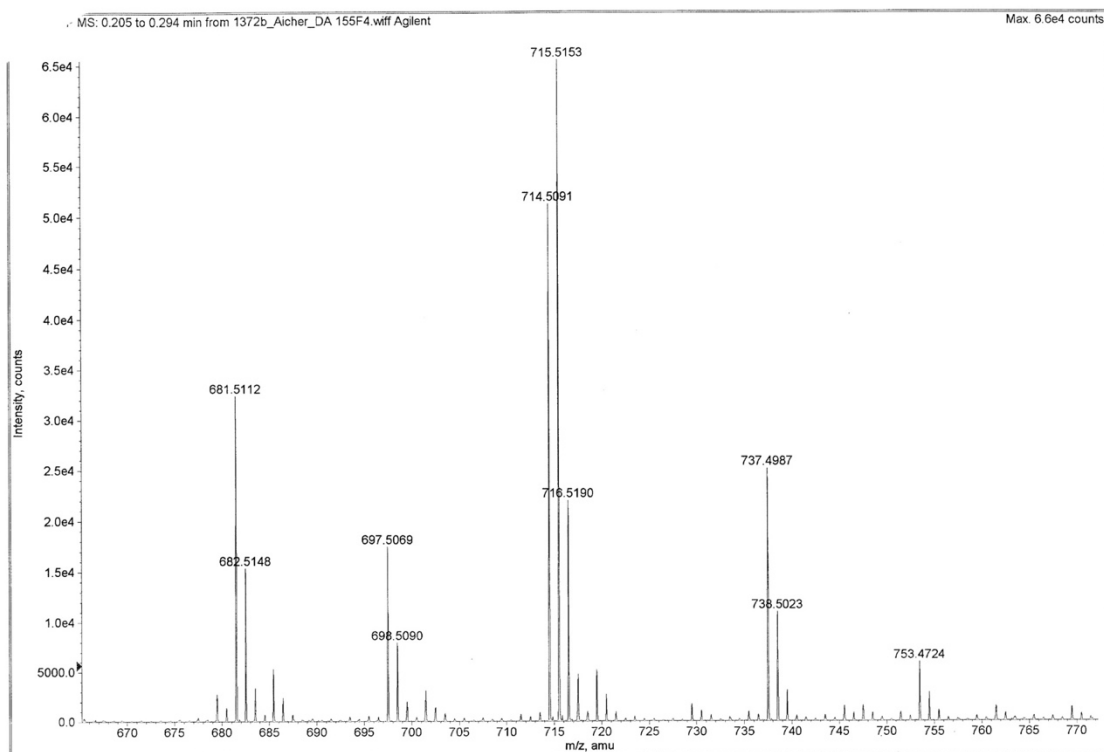


**Figure S-2.**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $\text{d}_6$ ) spectrum of *meso*-tetrahexyltetrahydroxybacteriochlorin **9**.



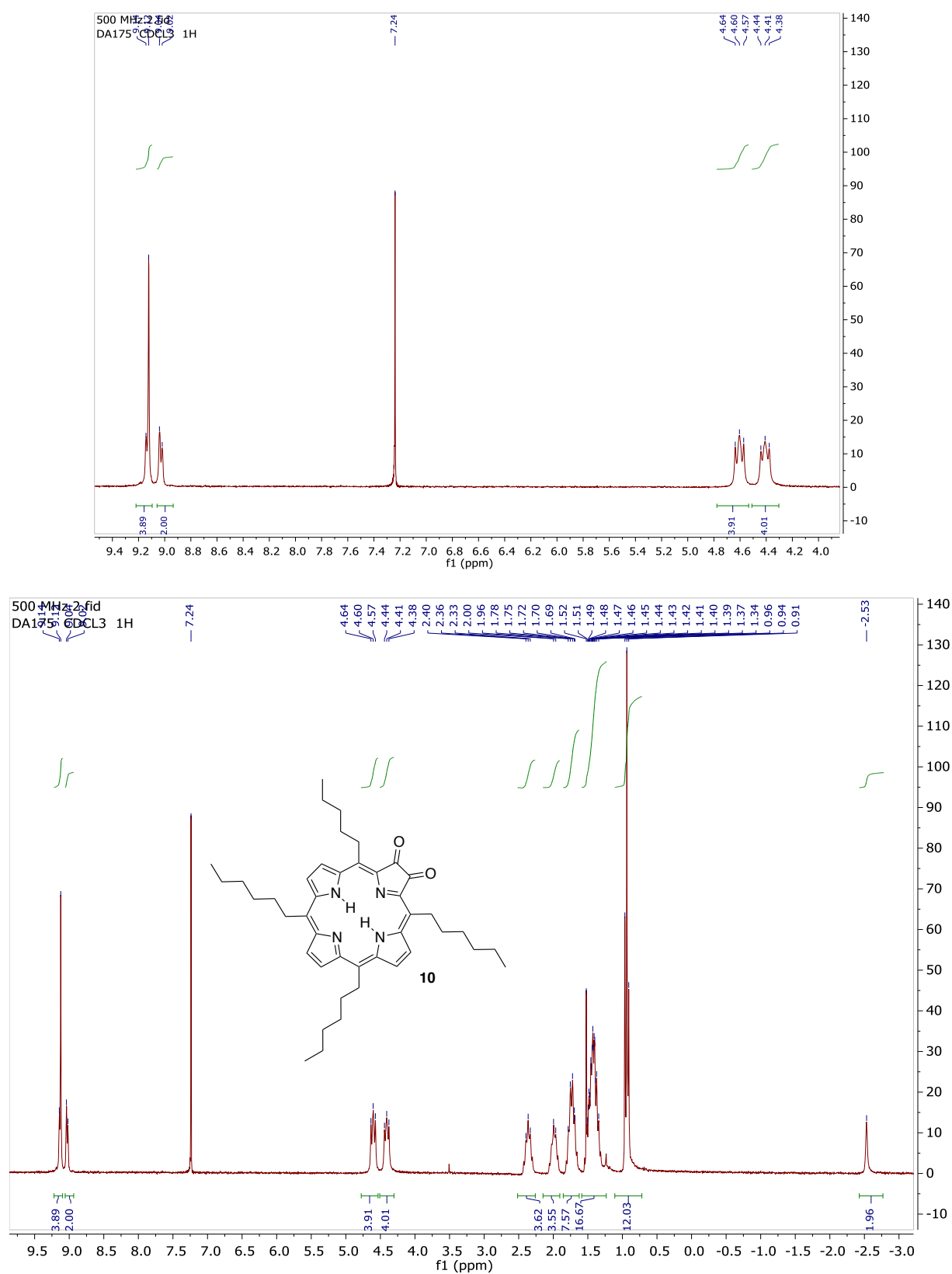
**Figure S-3.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexyltetrahydroxybacteriochlorin **9**.





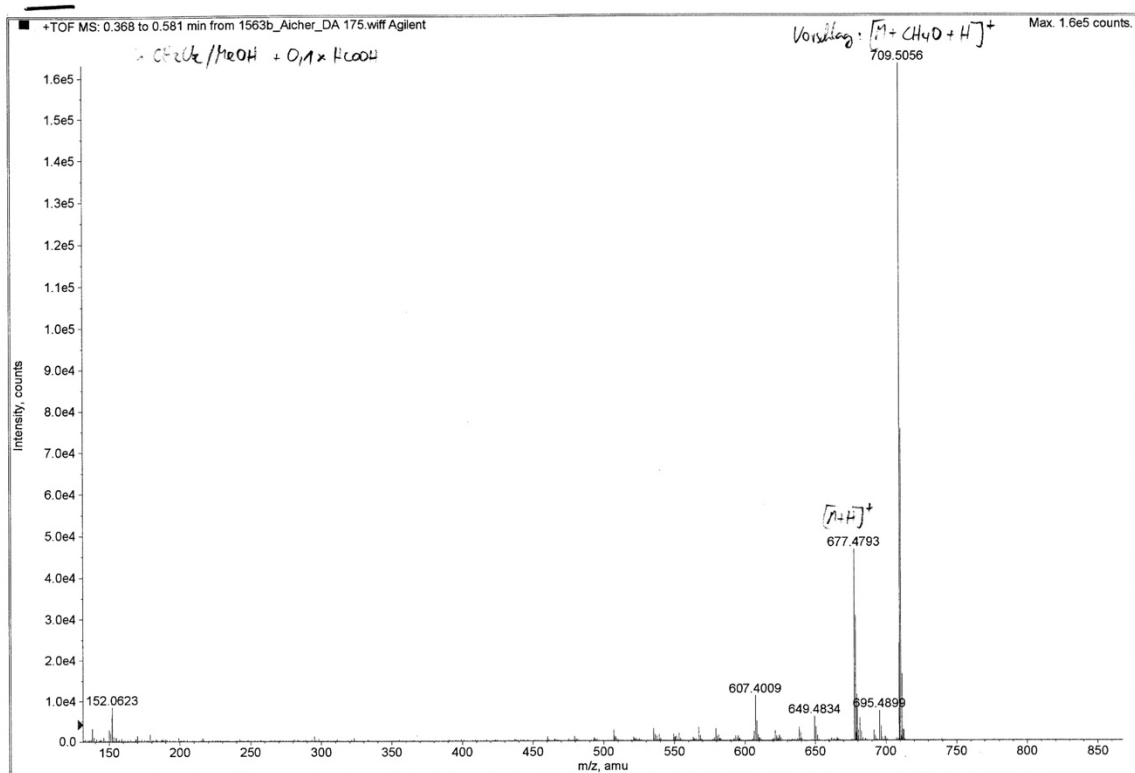
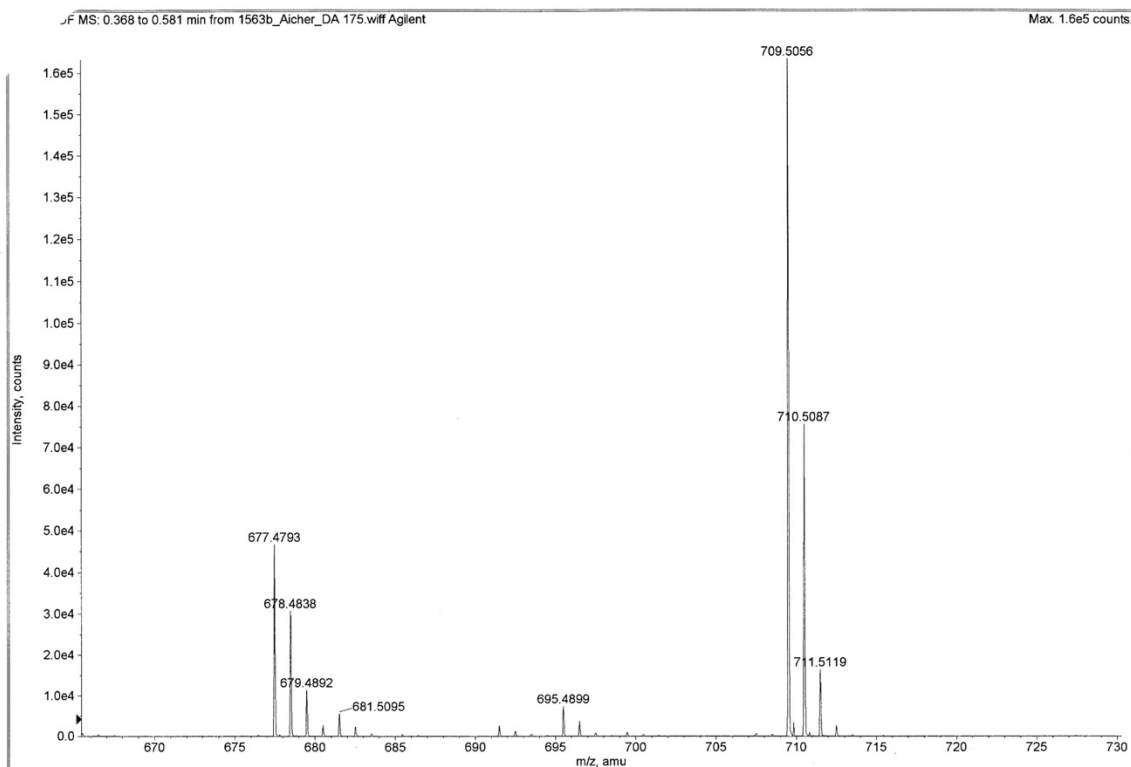
**Figure S-4.** HR-MS spectrum (ESI+, TOF, CH<sub>3</sub>OH) of *meso*-tetrahexyltetrahydroxybacteriochlorin (**9**).

***meso*-Tetrahexylporphyrin-7,8-dione (10).**

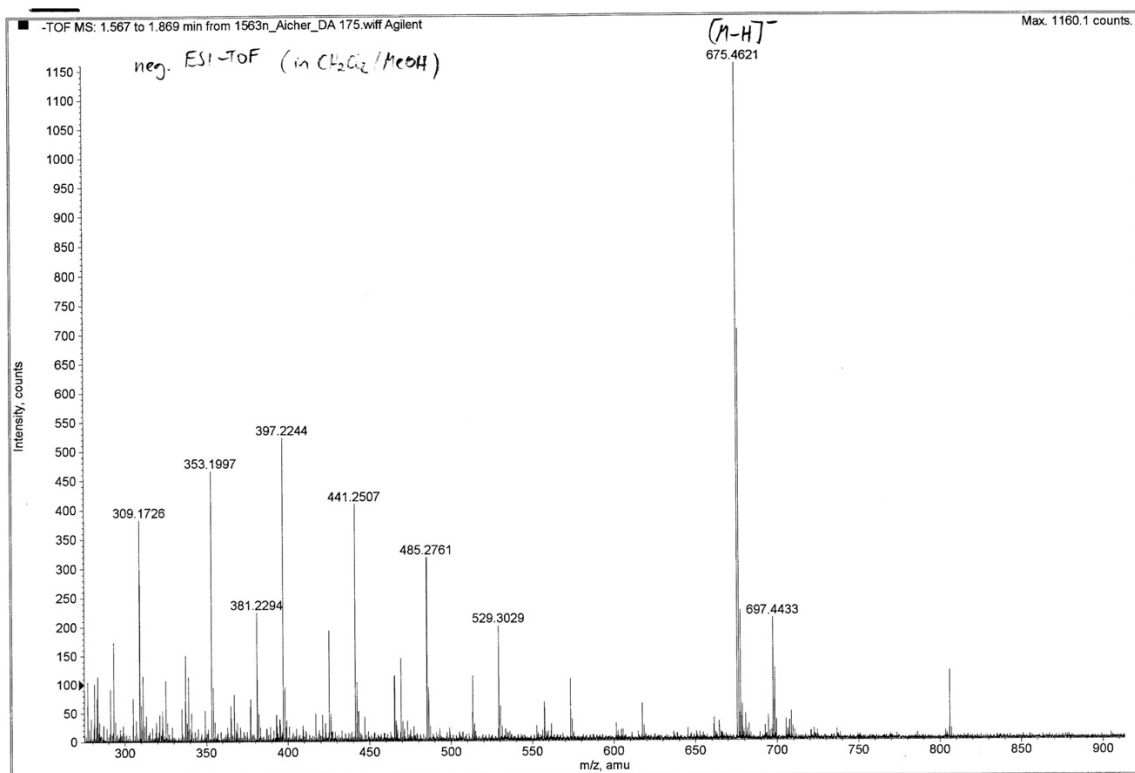
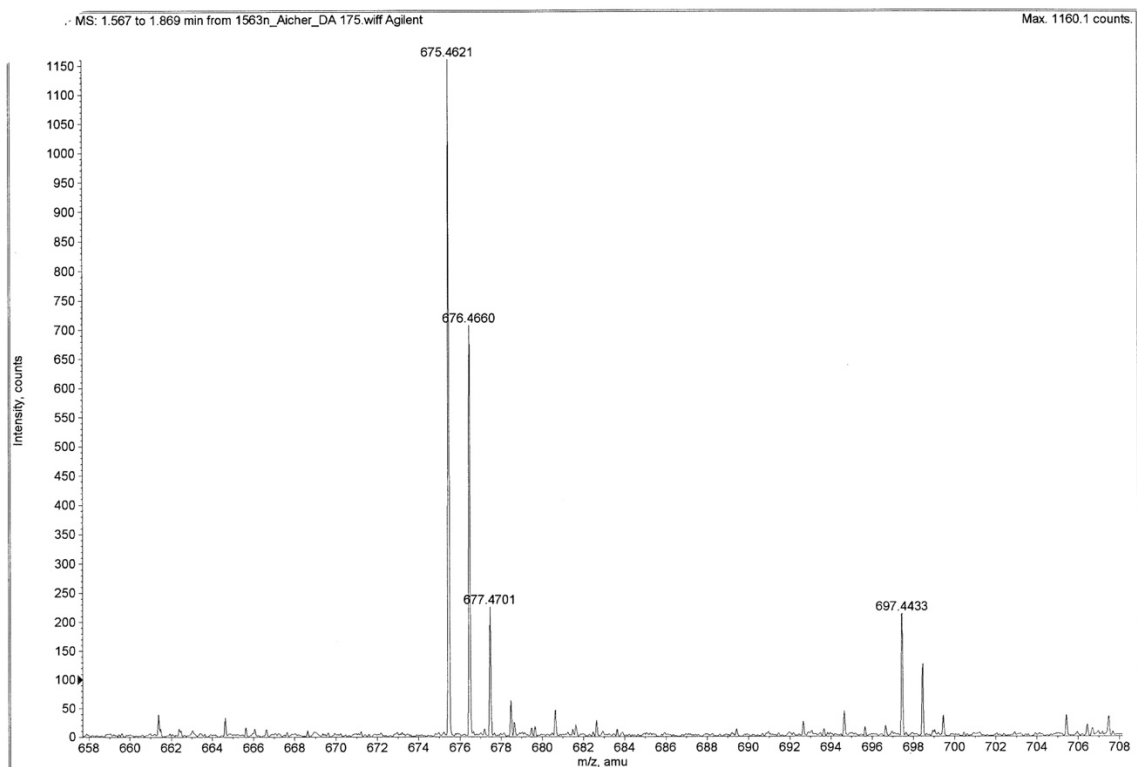


**Figure S-1.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexylporphyrin-7,8-dione (10) (full spectrum, bottom, and detail, top)



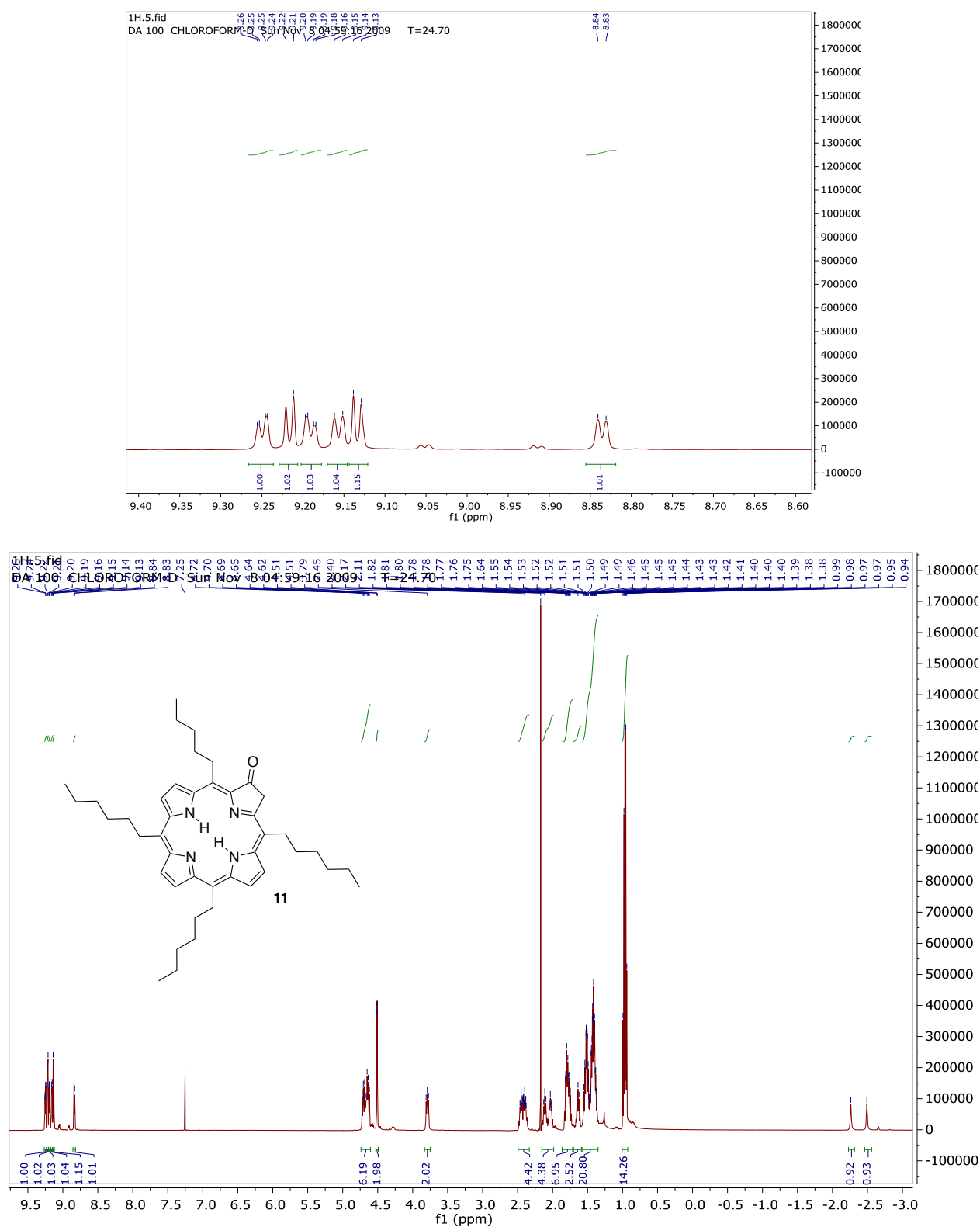


**Figure S-4.** HR-MS spectrum (ESI+, TOF, MeOH) (full and detail) of *meso*-tetrahexyl-porphyrin-7,8-dione (**10**)

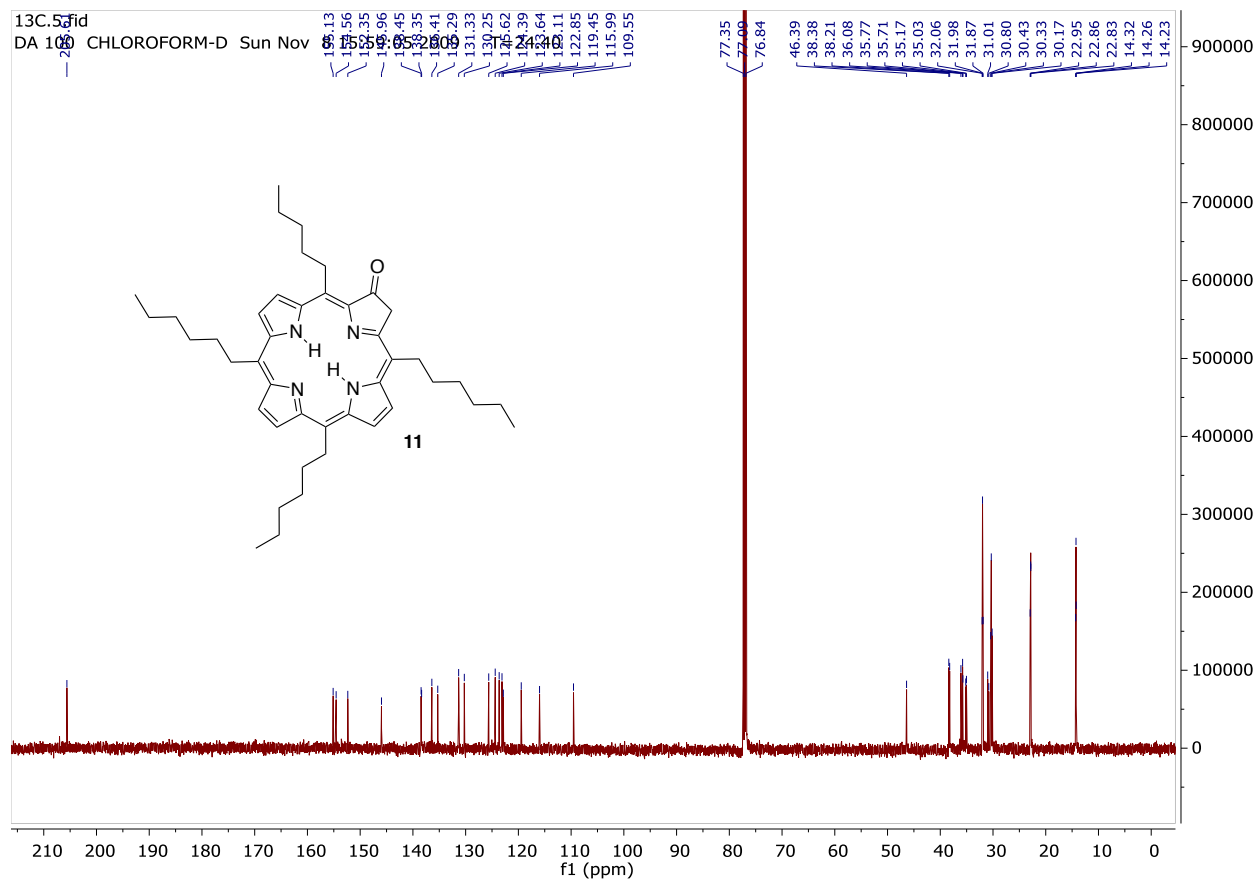


**Figure S-5.** HR-MS spectrum (ESI<sup>-</sup>, TOF, CH<sub>2</sub>Cl<sub>2</sub>/MeOH) (full and detail) of *meso*-tetrahexylporphyrin-7,8-dione (**10**).

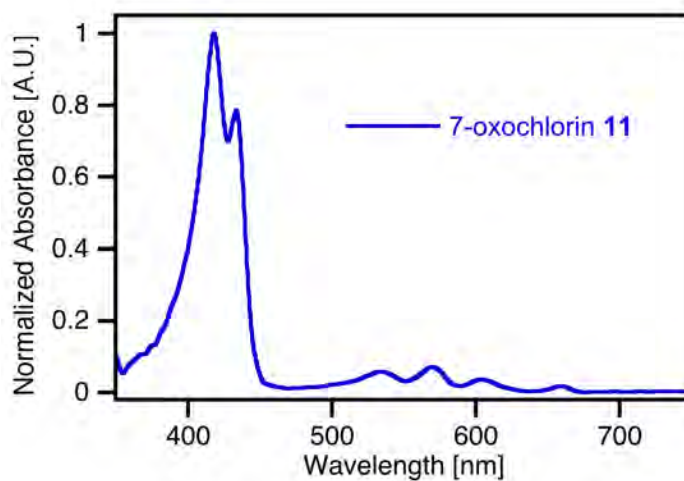
***meso*-Tetrahexylchlorin-7-one (11).**



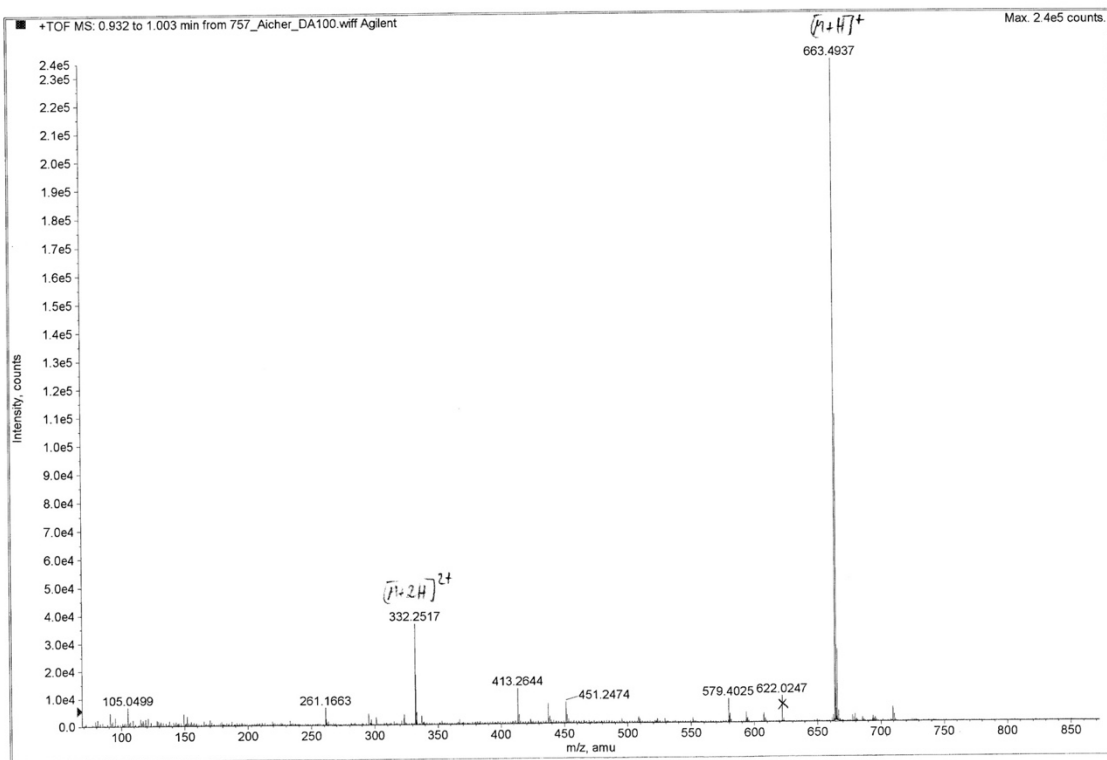
**Figure S-1.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexylchlorin-7-one (**11**) (full spectrum, bottom, and detail, top).



**Figure S-2.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexylchlorin-7-one (**11**).



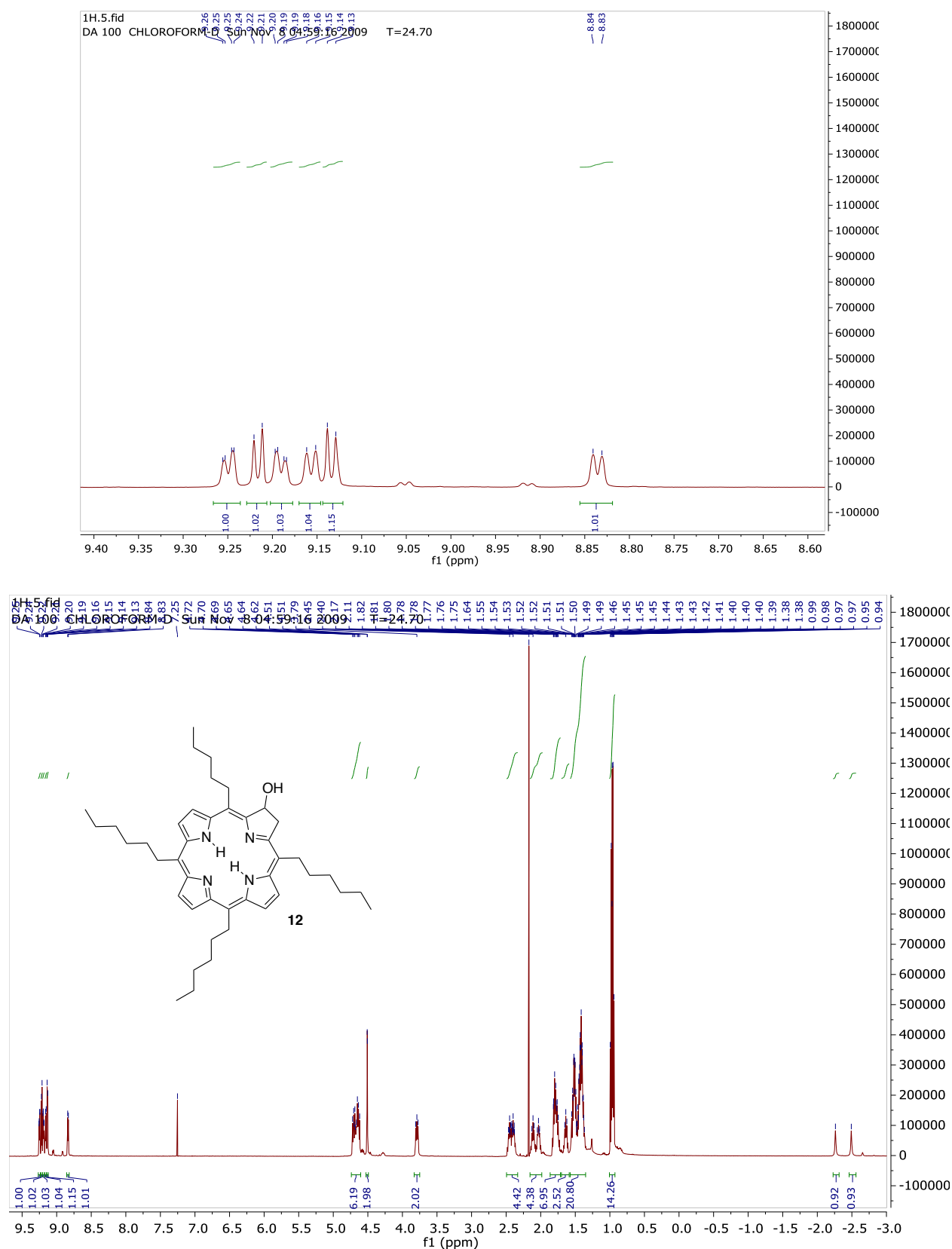
**Figure S-3.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexylchlorin-7-one (**11**).



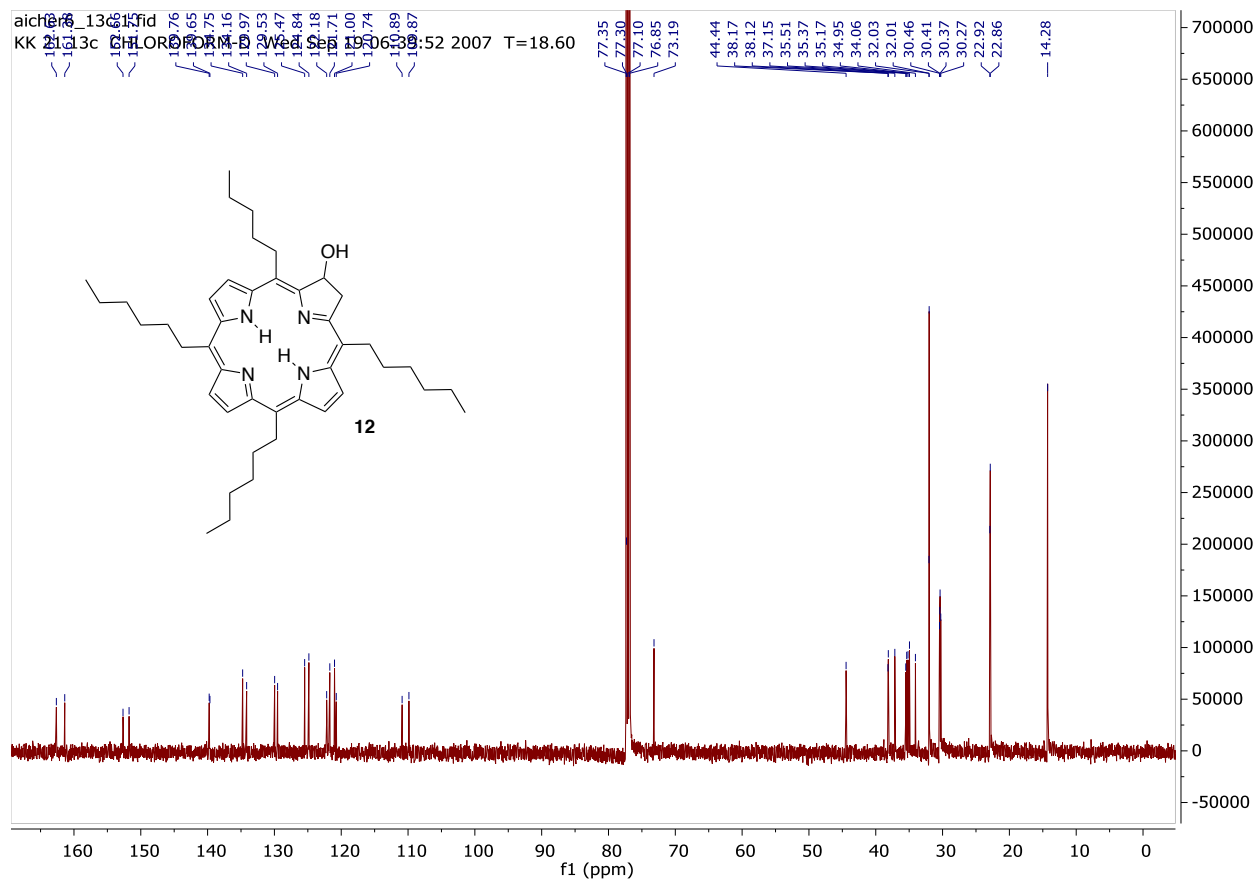
**Figure S-4.** HR-MS (ESI+, TOF) of *meso*-tetrahexylchlorin-7-one (**11**).



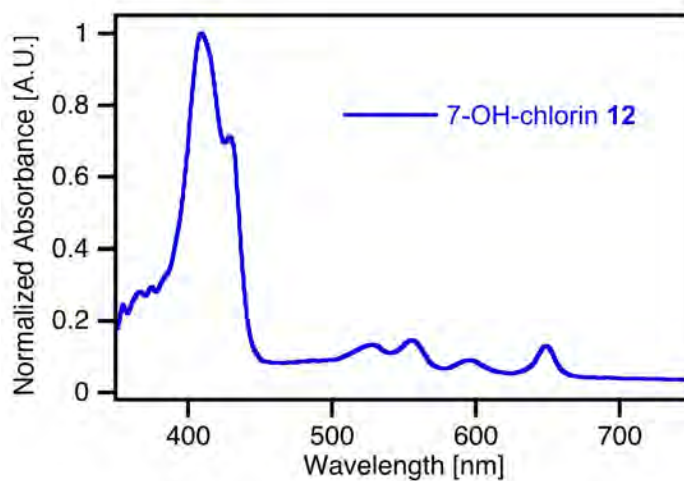
***meso*-Tetrahexyl-7-hydroxychlorin (12).**



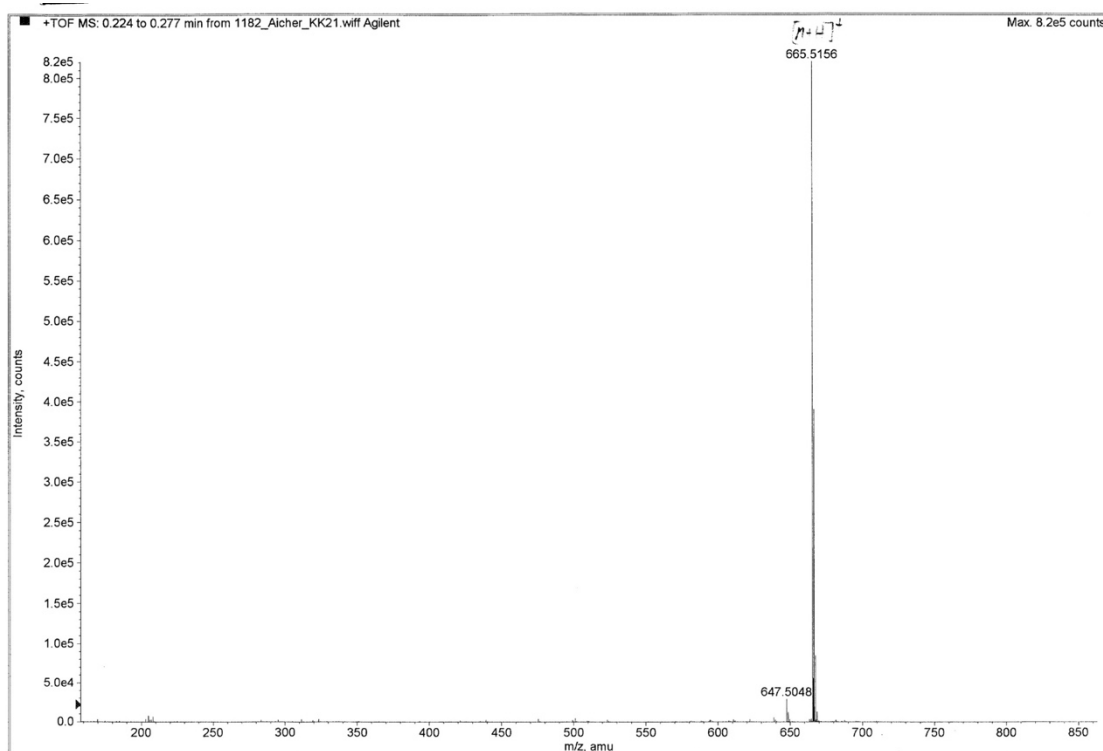
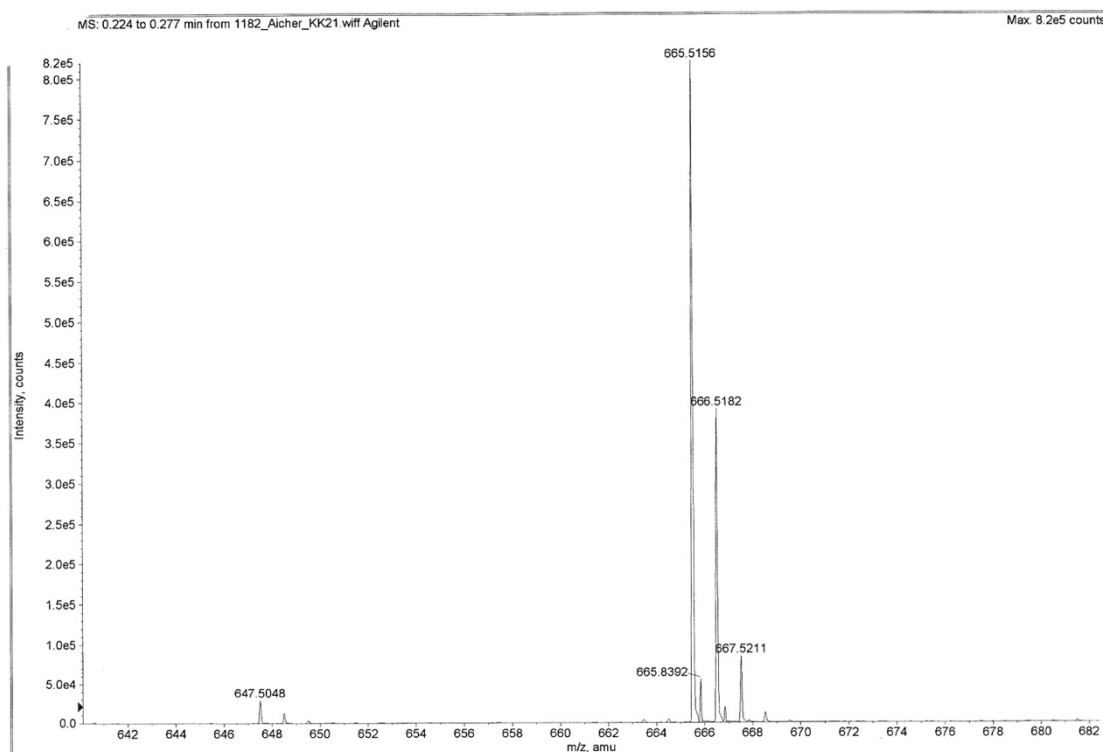
**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyl-7-hydroxychlorin (**12**) (full spectrum, bottom, and detail, top).



**Figure S-2.** <sup>13</sup>C NMR spectrum (126 MHz, CDCl<sub>3</sub>) of *meso*-tetrahexyl-7-hydroxychlorin (**12**).

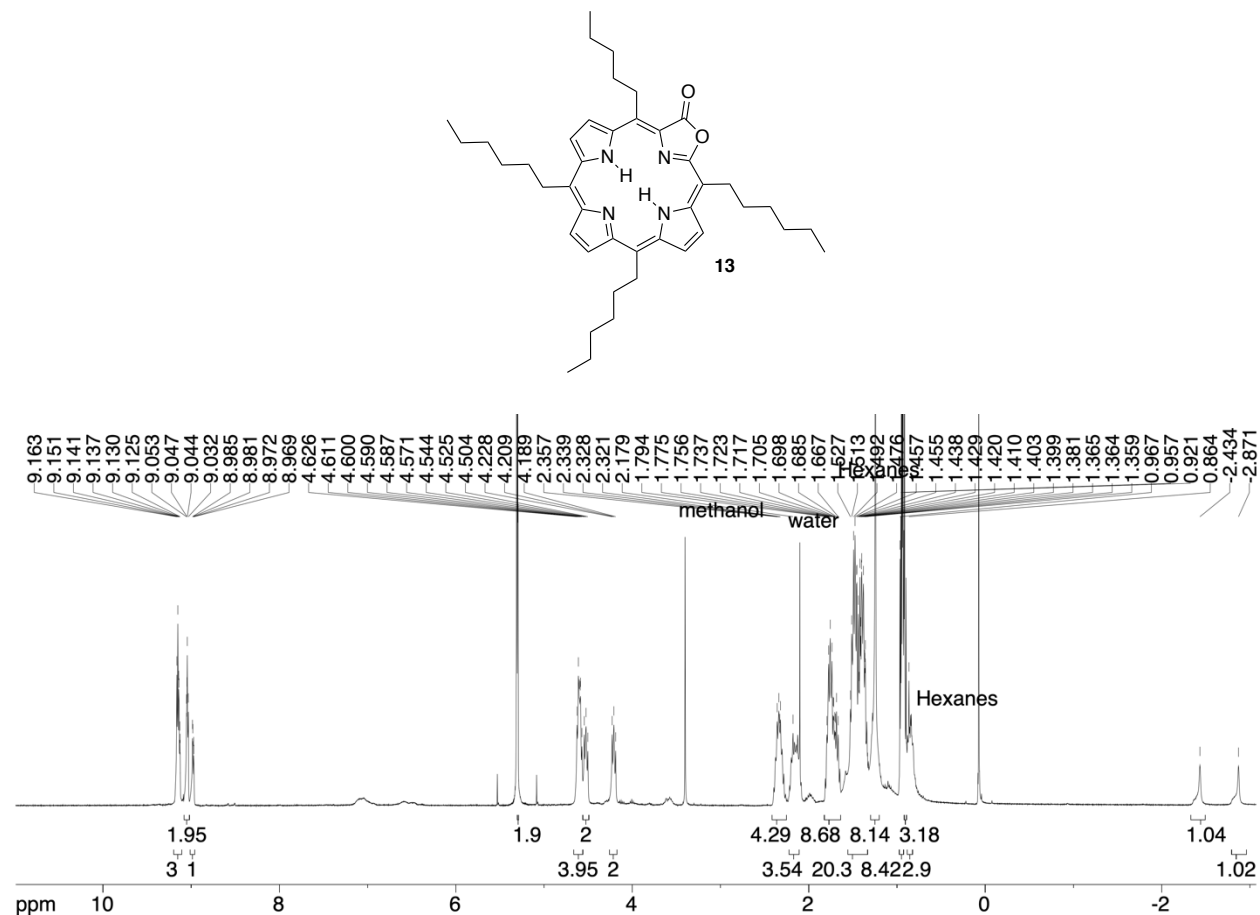


**Figure S-3.** UV-vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>) of *meso*-tetrahexyl-7-hydroxychlorin (**12**).

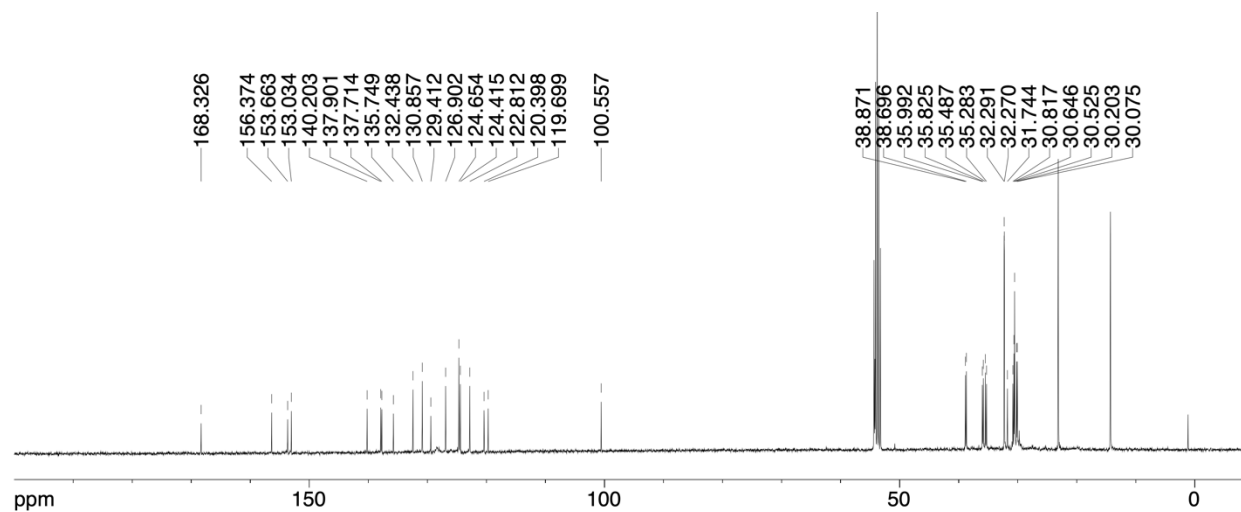


**Figure S-4.** Mass spectrum (ESI+, TOF) of *meso*-tetrahexyl-7-hydroxychlorin (**12**) (full and detail).

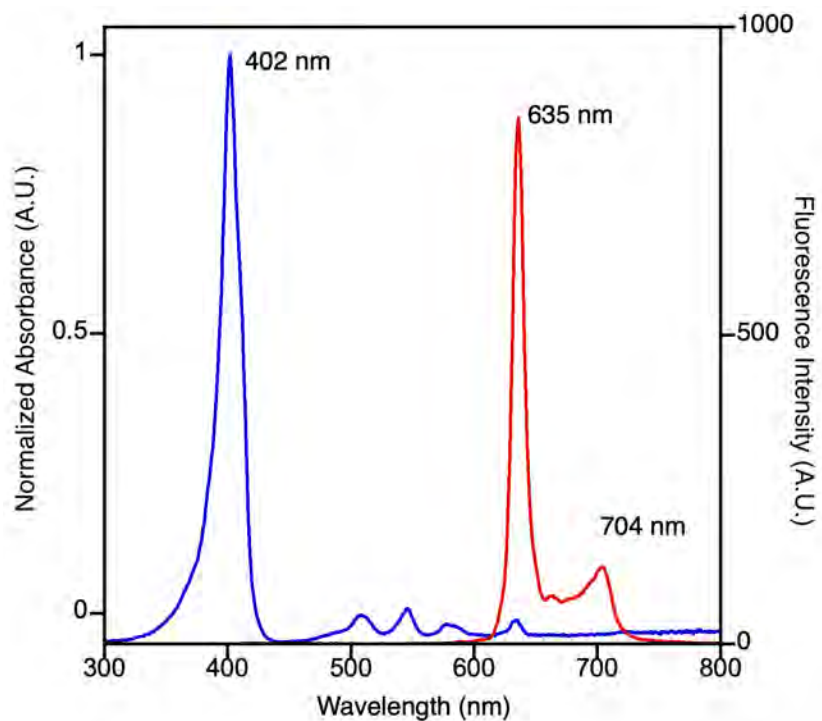
***meso*-Tetrahexylporpholactone (*meso*-Tetrahexyl-7-oxo-8-oxa-porphyrin) (13).**



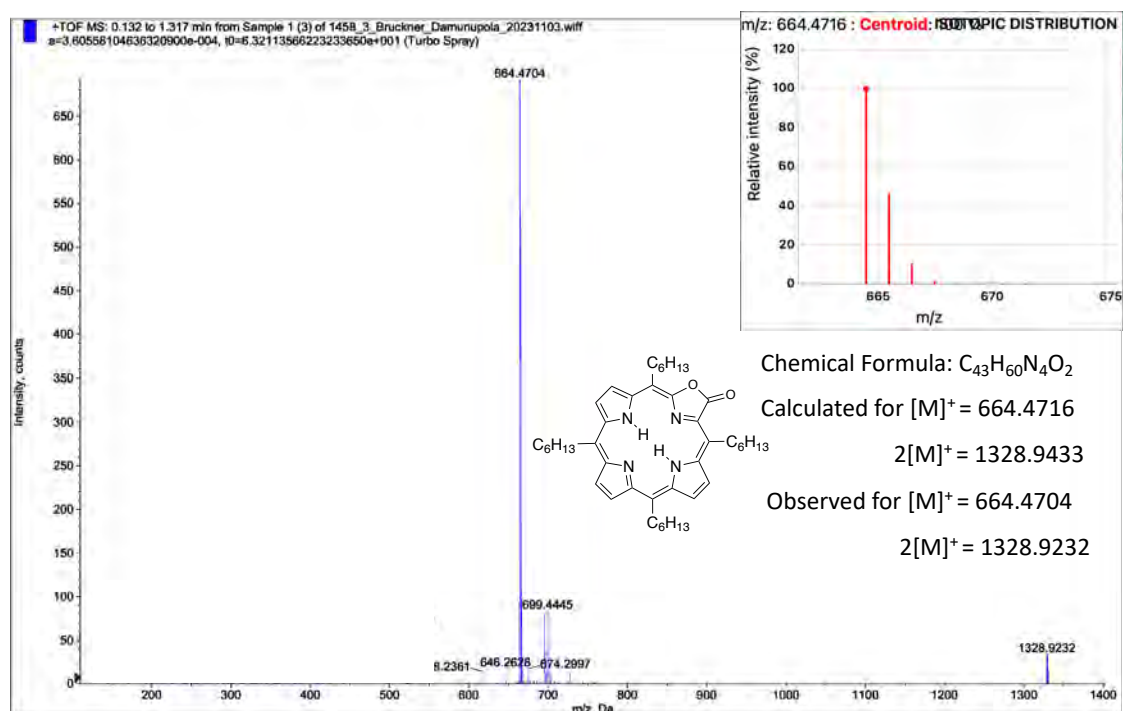
**Figure S-1.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexylporpholactone (13).



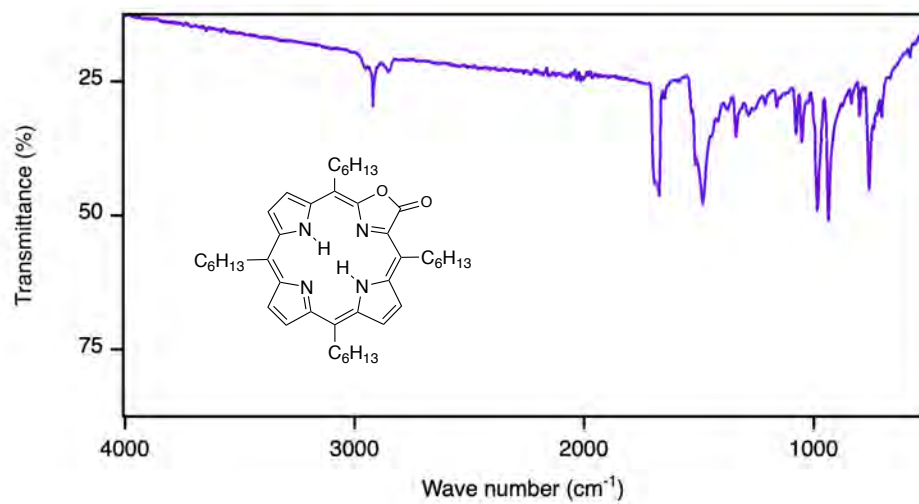
**Figure S-2.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of *meso*-tetrahexylporpholactone (13).



**Figure S-3.** UV-vis (blue) and fluorescence emission (red) spectra ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexylporpholactone (**13**);  $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ .



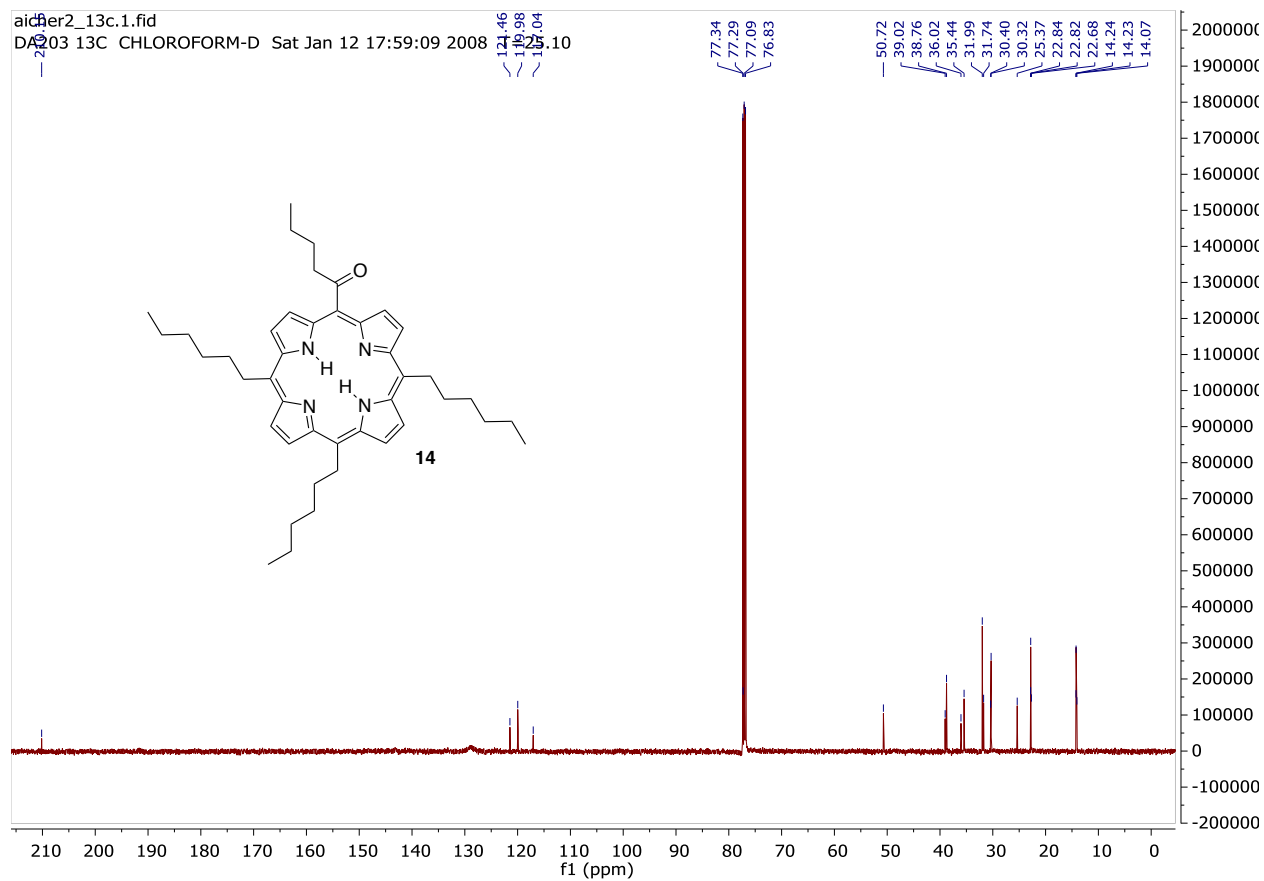
**Figure S-4.** HR-MS  $\text{ESI}^+$  ( $\text{CH}_3\text{CN}$ , TOF) of *meso*-tetrahexylporpholactone (**13**).



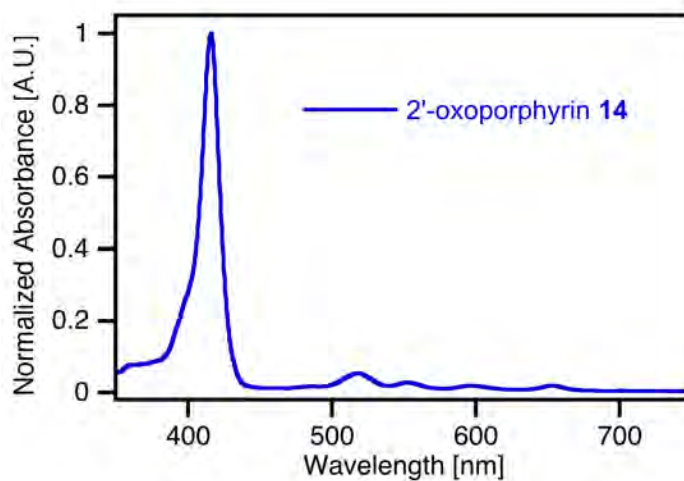
**Figure S-5.** FT-IR spectrum (neat, ATR) of *meso*-tetrahexylporpholactone (**13**).

**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 5-(1'-oxo-hexyl)-10,15,20-trihexylporphyrin (14)



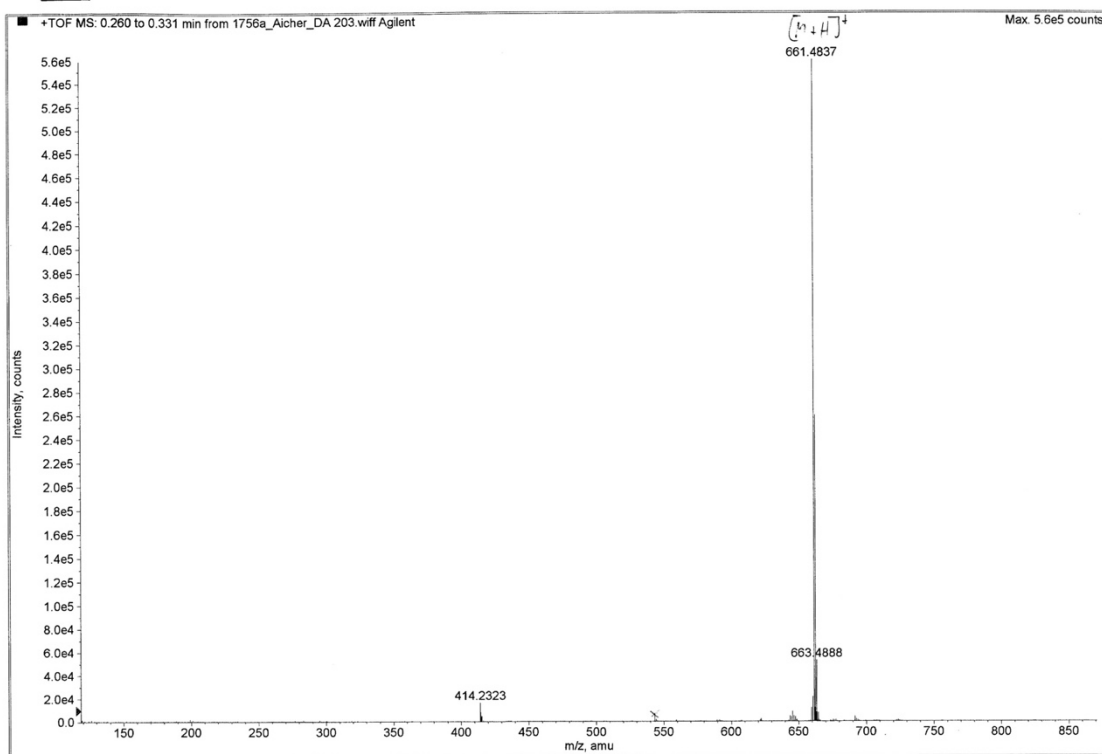
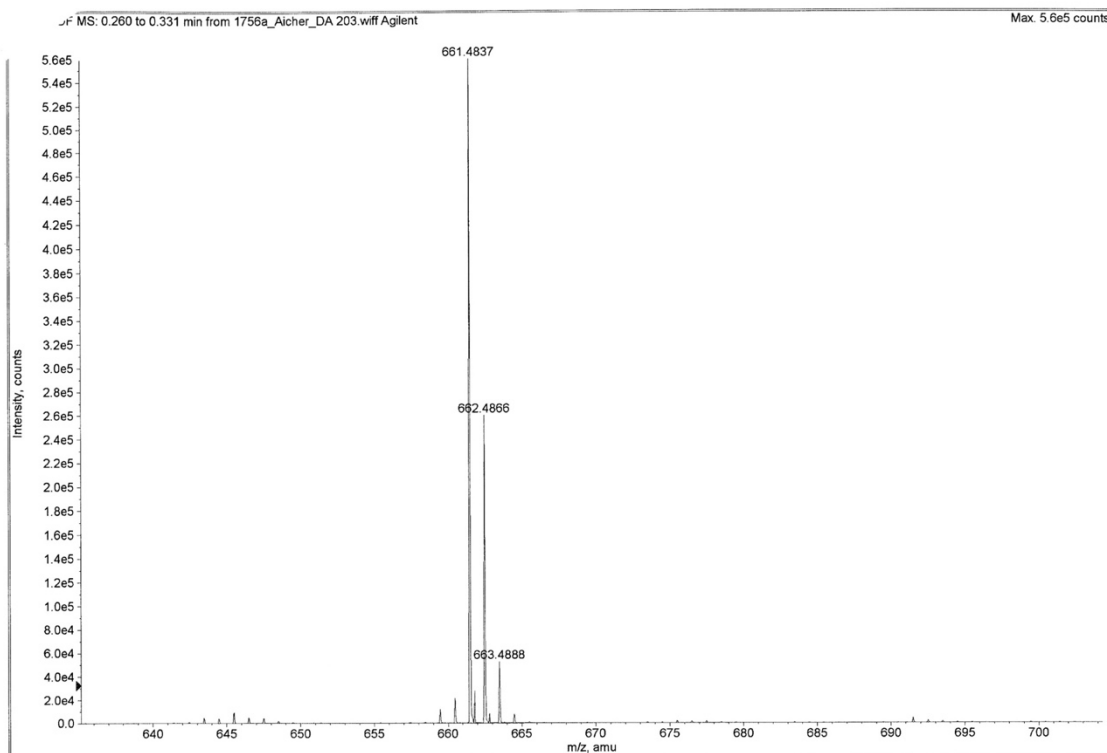


**Figure S-2.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 5-(1'-oxo-hexyl)-10,15,20-trihexylporphyrin (**14**)



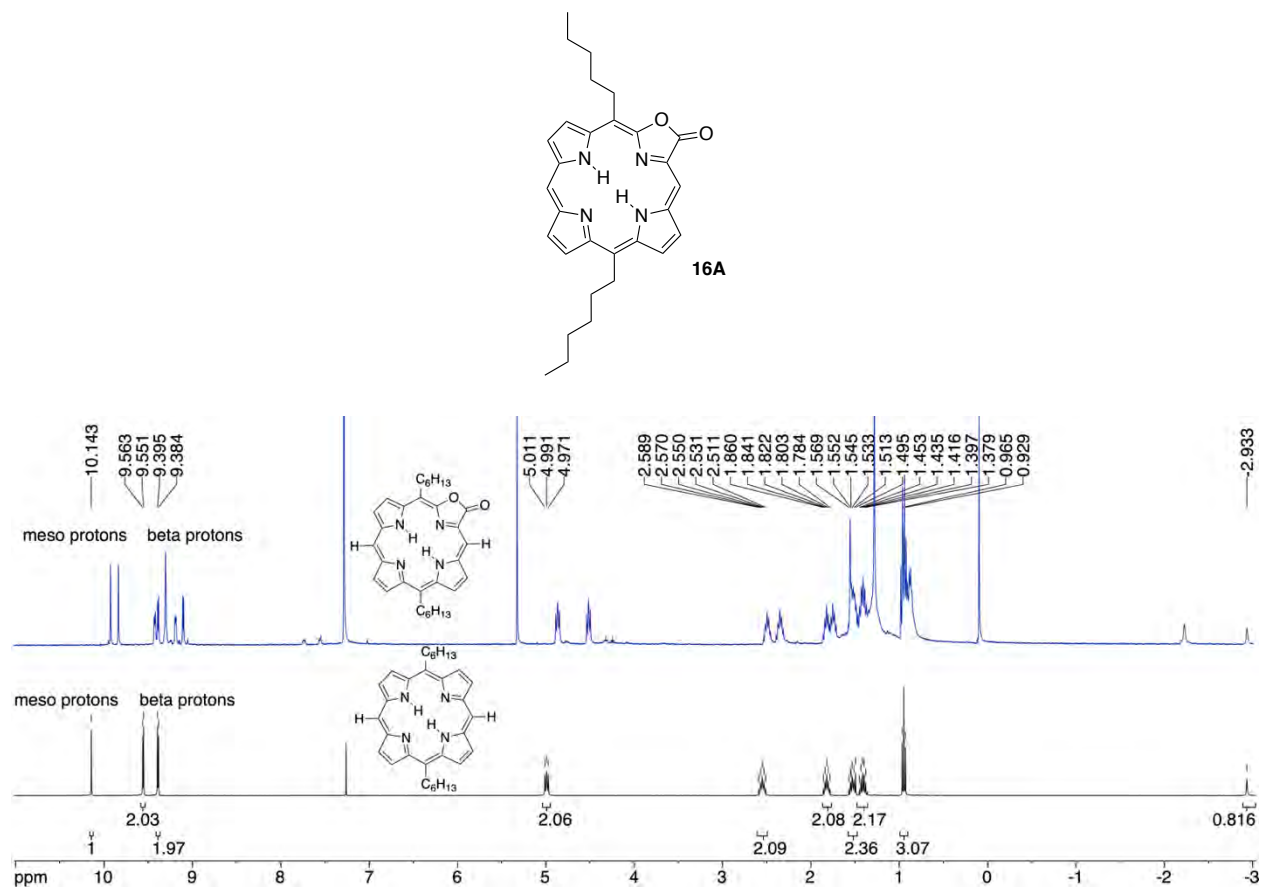
**Figure S-3.** UV-vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>) of 5-(1'-oxo-hexyl)-10,15,20-trihexylporphyrin (**14**).



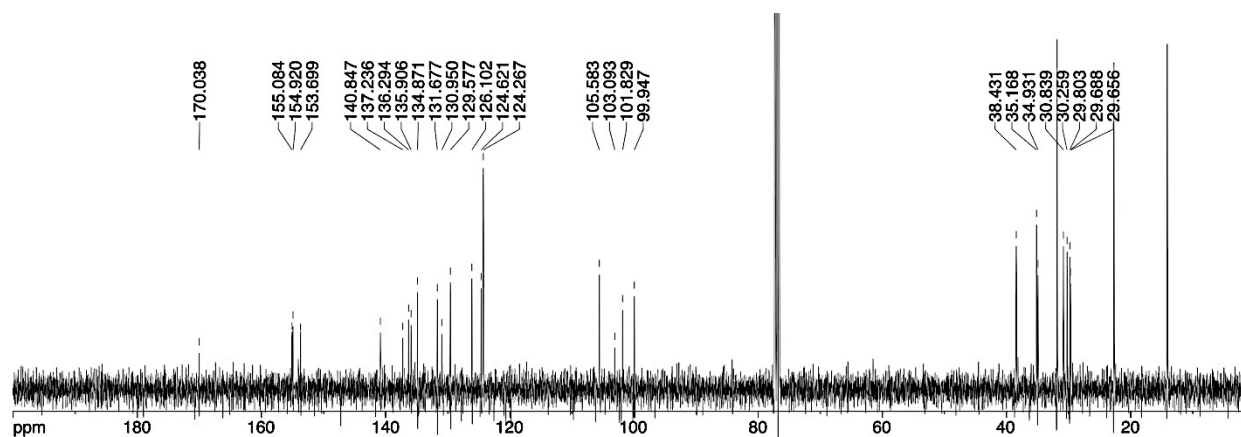


**Figure S-4.** Mass spec of 5-(1'-oxo-hexyl)-10,15,20-trihexylporphyrin (**14**)

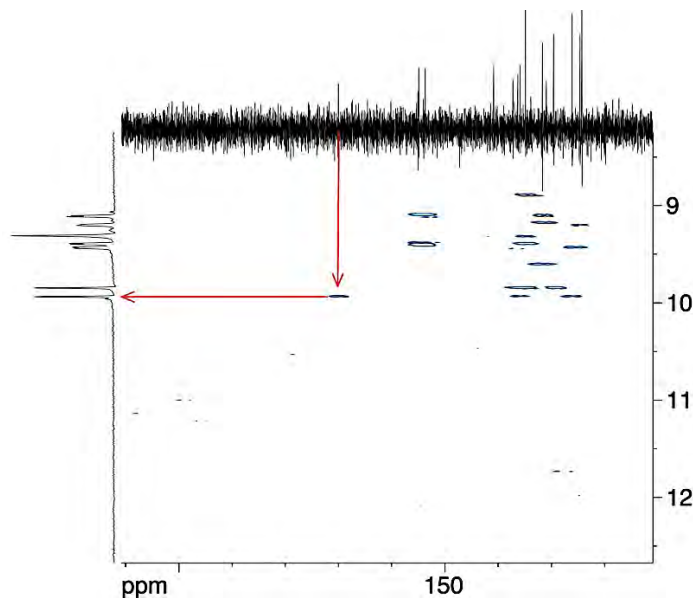
## 5,15-Dihexyl-3-oxo-2-oxa-porphyrin) (16A)



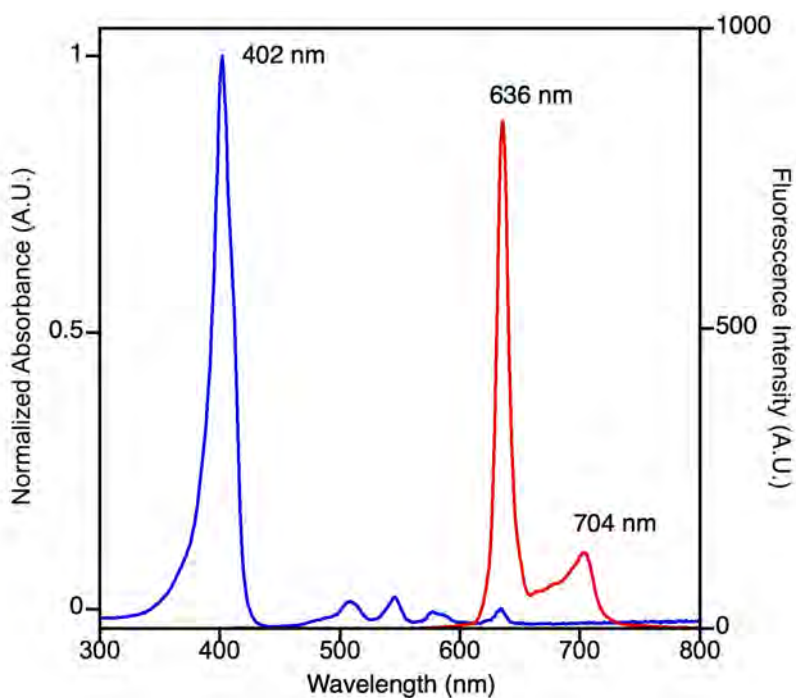
**Figure S-1.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 5,15-dihexyl-3-oxo-2-oxa-porphyrin) (16A) in comparison to that of the parent porphyrin 15.



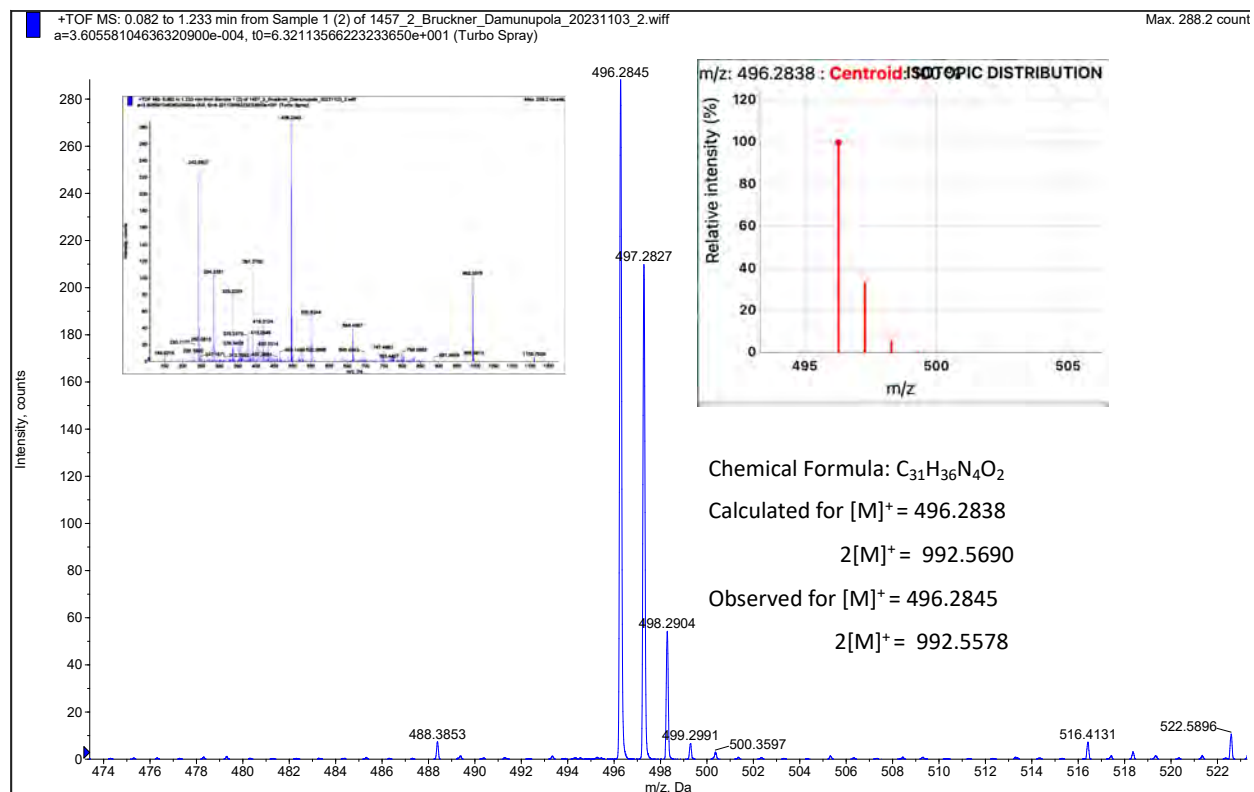
**Figure S-2.**  $\{^1\text{H}\}^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of meso-dihexyl-3-oxo-2-oxa-porphyrin) (16A)



**Figure S-3.**  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC NMR spectrum (400, 100 MHz,  $\text{CDCl}_3$ ) of *meso*-dihexyl-3-oxo-2-oxa-porphyrin) (**16A**)

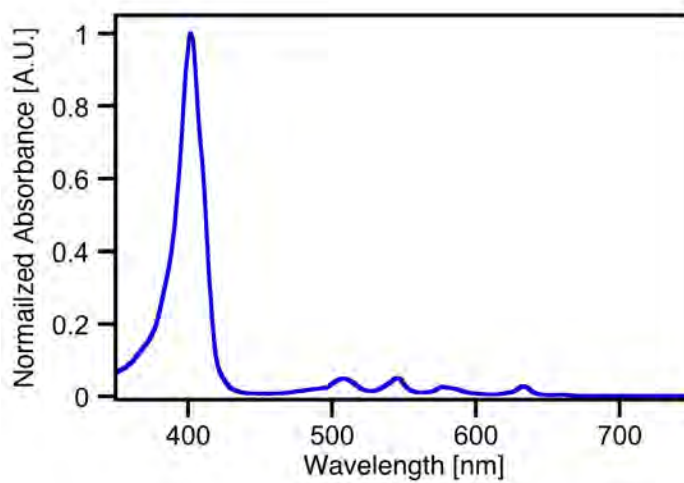
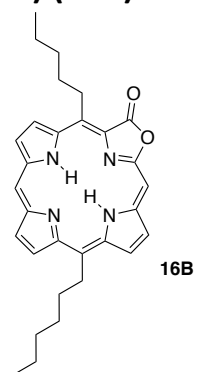


**Figure S-4.** UV-vis (blue) and fluorescence emission spectra ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-dihexyl-3-oxo-2-oxa-porphyrin) (**16A**);  $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ .

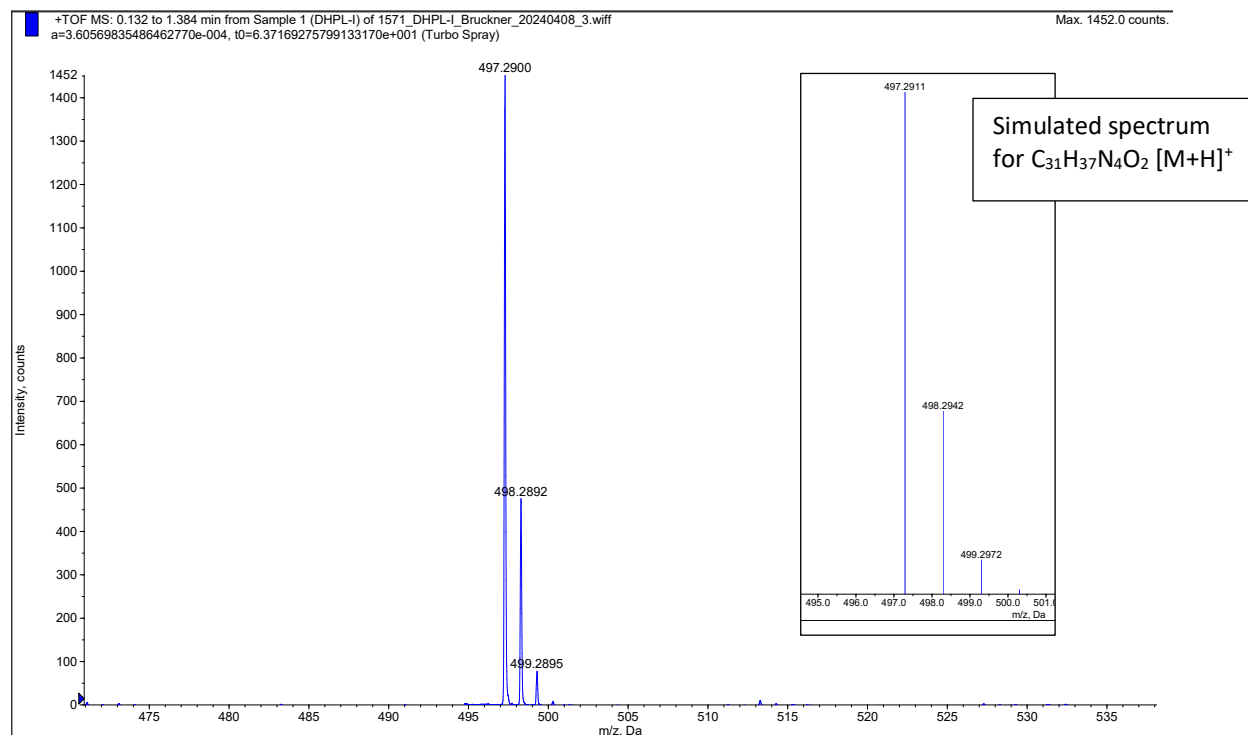
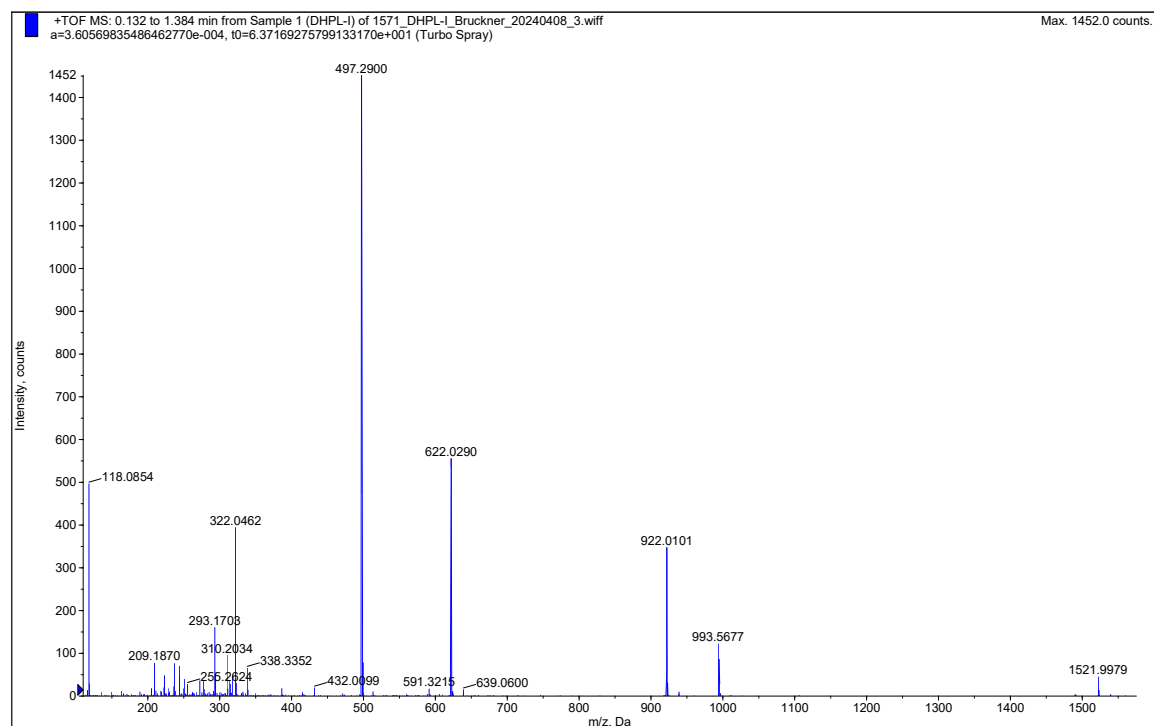


**Figure S-5.** HR-MS spectrum (ESI<sup>+</sup>, CH<sub>3</sub>CN, TOF) of *meso*-dihexyl-3-oxo-2-oxa-porphyrin) (**16A**).

**5,15-Dihexyl-7-oxo-8-oxa-porphyrin) (16B).**

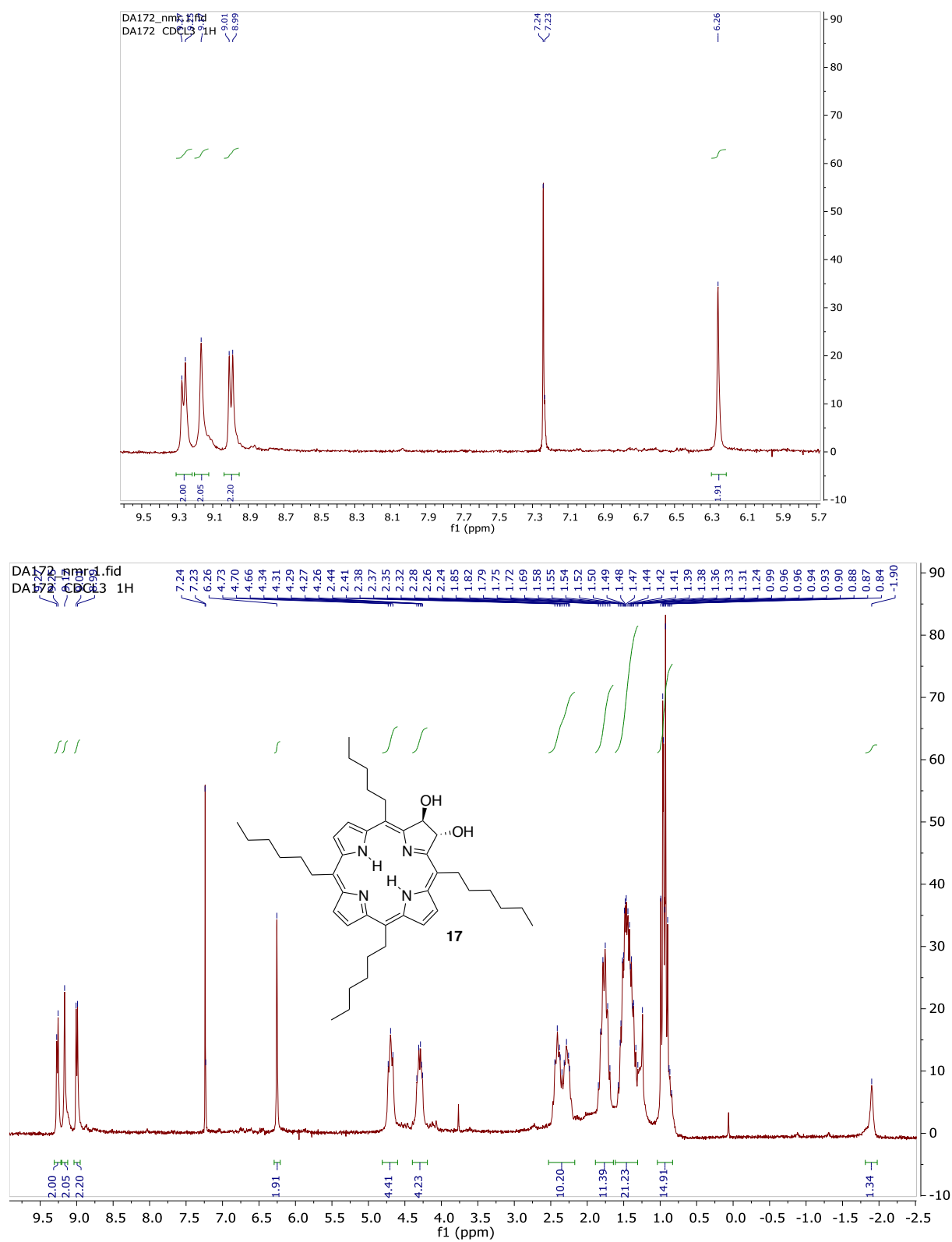


**Figure S-1.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-dihexyl-7-oxo-8-oxa-porphyrin) (**16B**).

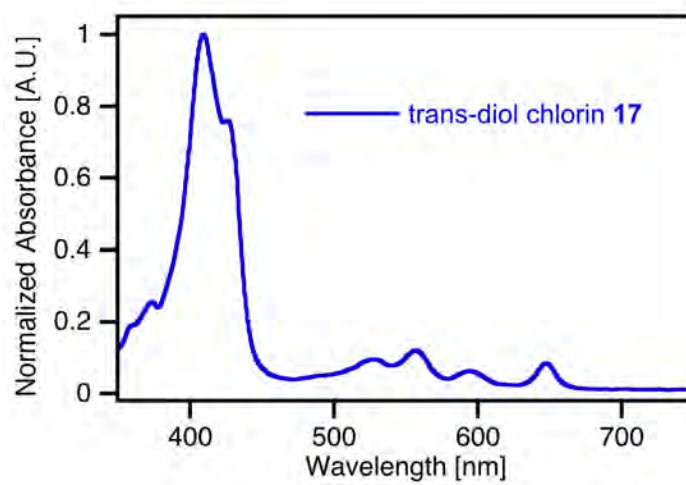


**Figure S-2.** HR-MS (ESI+, CH<sub>3</sub>OH, TOF) of *meso*-dihexyl-7-oxo-8-oxa-porphyrin) (**16B**); full spectrum to, expansion with simulation, bottom.

***meso*-Tetrahexyl-7,8-*trans*-dihydroxychlorin (17).**

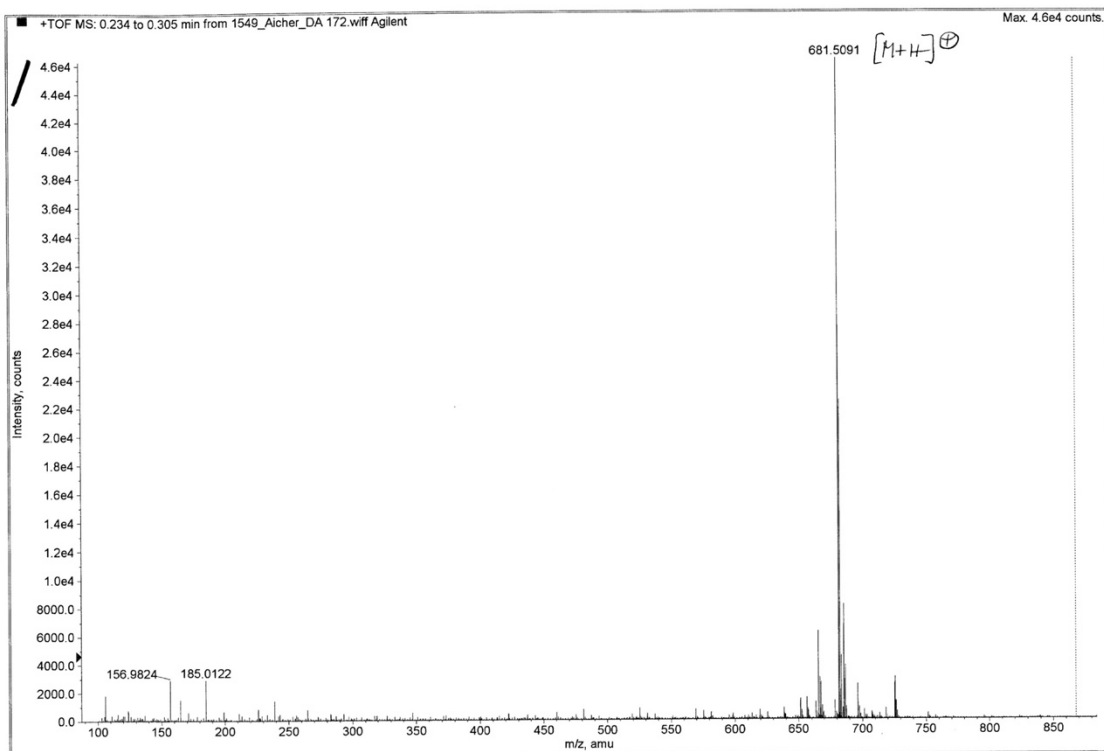
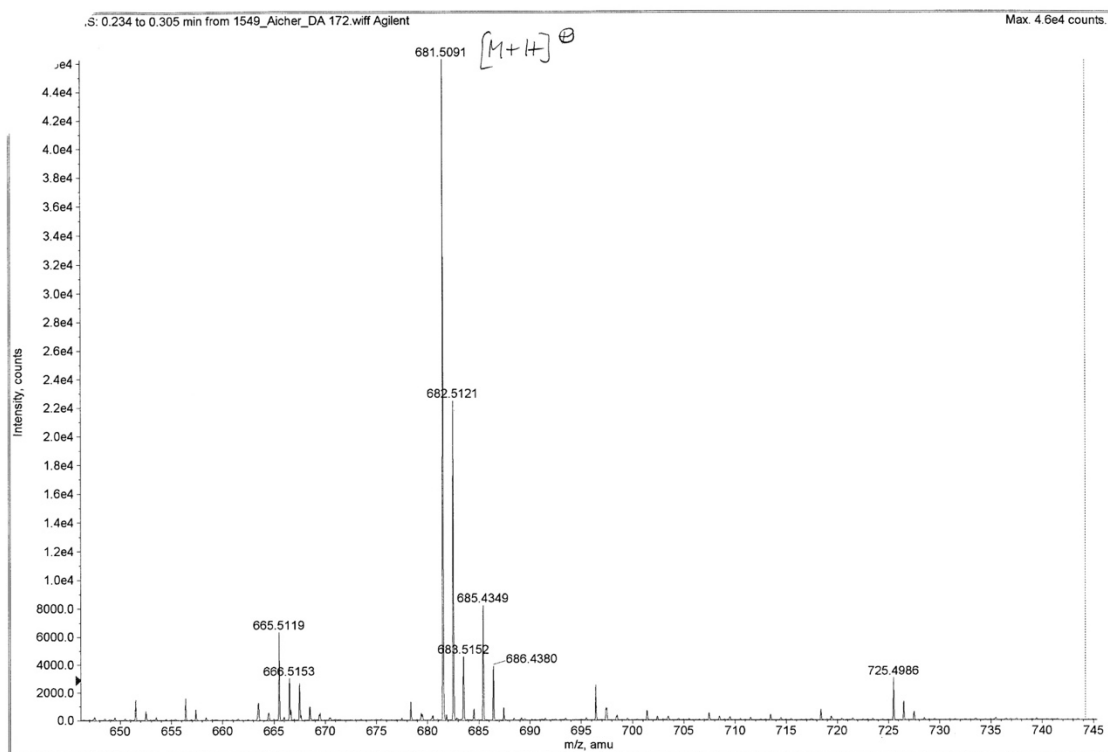


**Figure S-1.**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyl-7,8-*trans*-dihydroxychlorin (**17**).



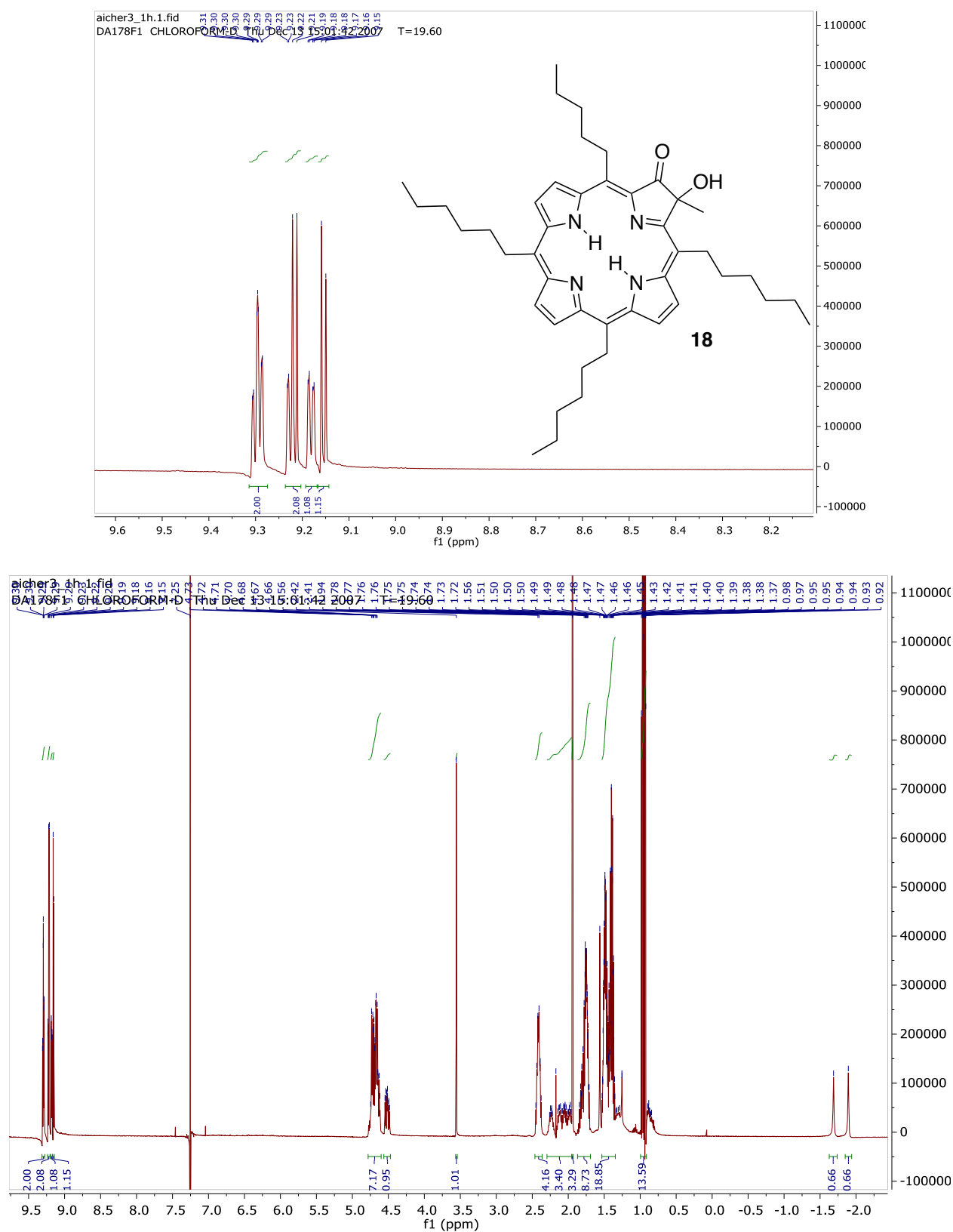
**Figure S-2.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexyl-7,8-*trans*-dihydroxychlorin (**17**).





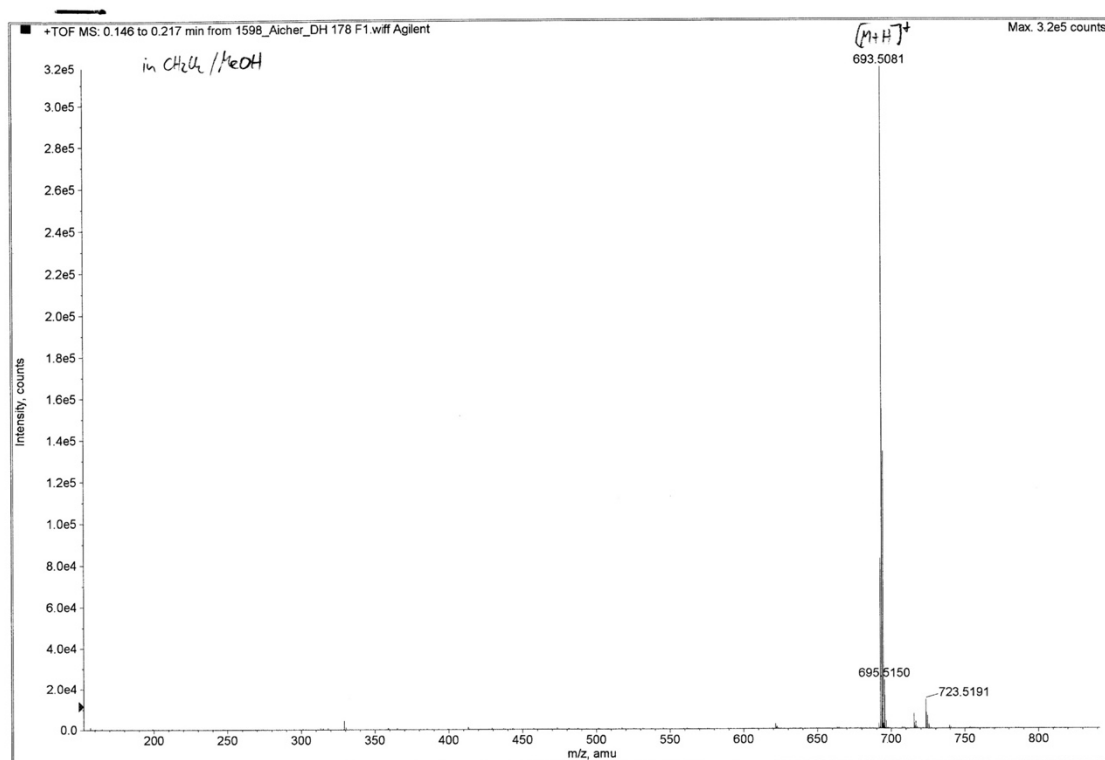
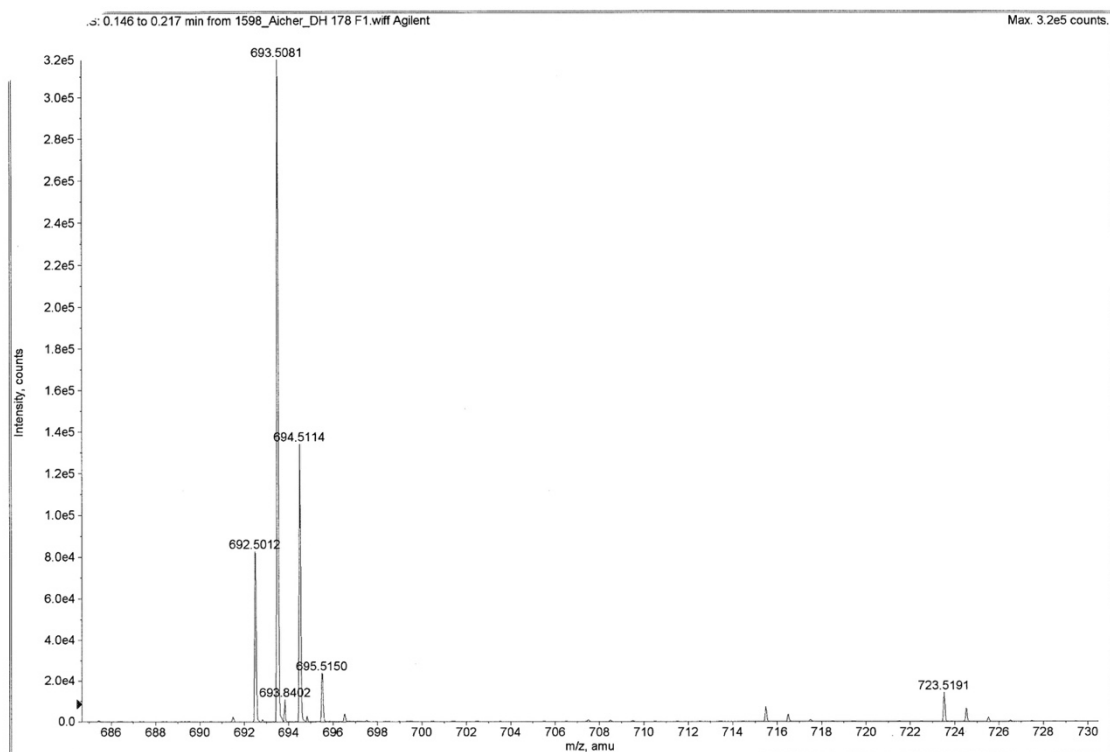
**Figure S-3.** HR-MS (ESI+, TOF) of *meso*-tetrahexyl-7,8-*trans*-dihydroxychlorin (**17**) (full and detail).

***meso*-Tetrahexyl-8-hydroxy-8-methyl-chlorin-7-one (18)**



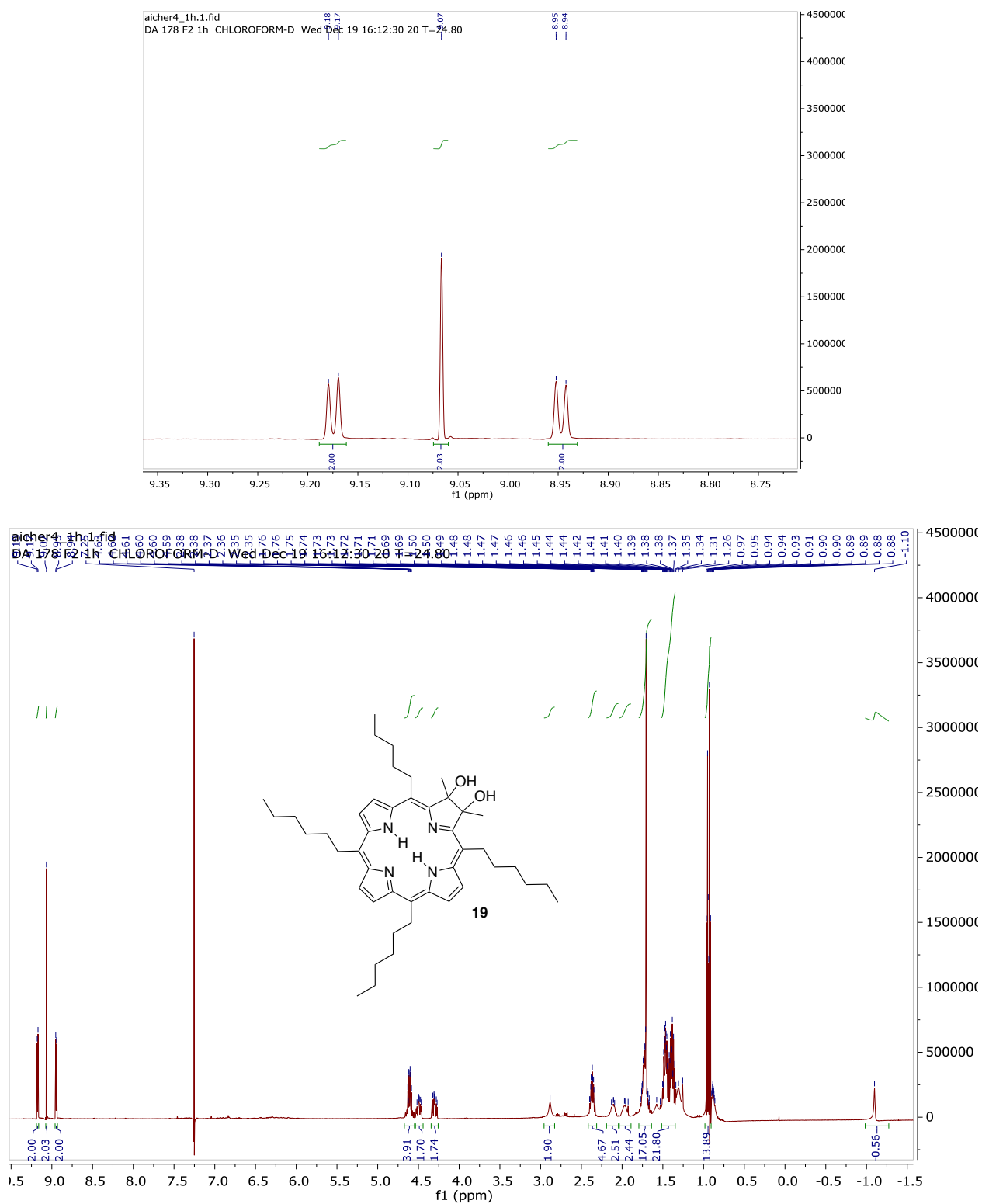
**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyl-8-hydroxy-8-methyl-chlorin-7-one (**18**).



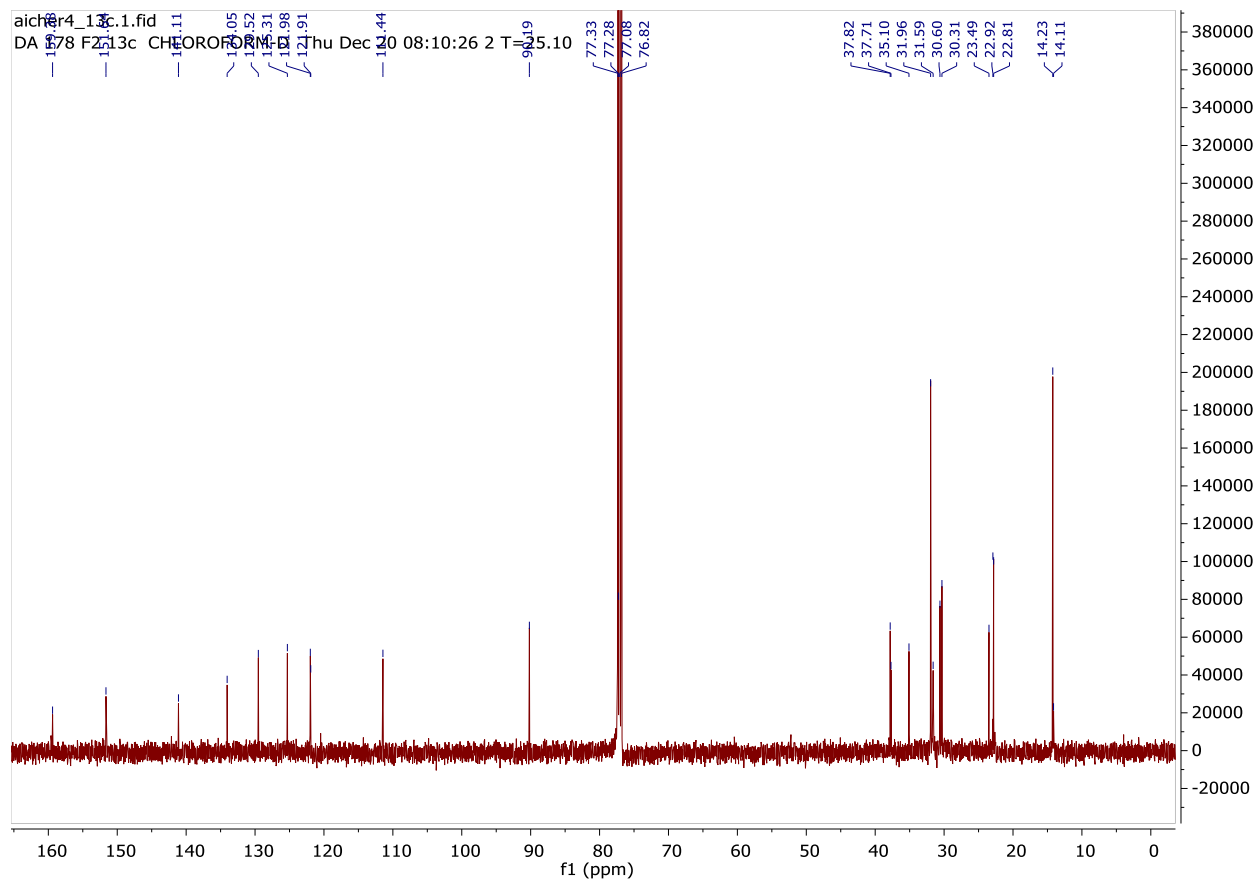


**Figure S-4.** Mass spec of *meso*-tetrahexyl-8-hydroxy-8-methyl-chlorin-7-one (**18**).

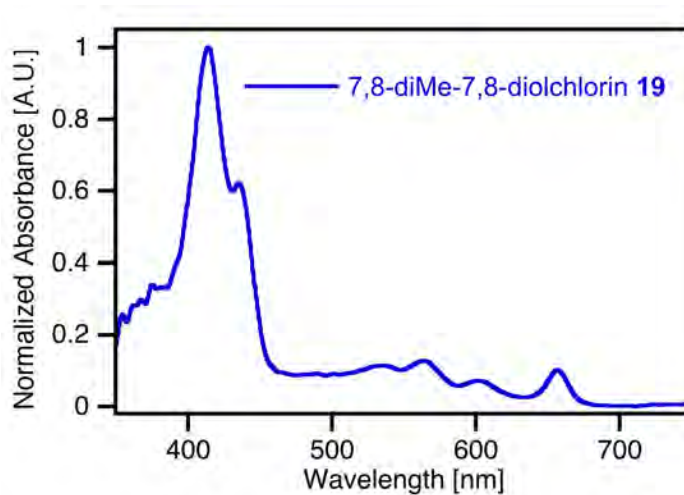
***meso*-Tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin (19).**



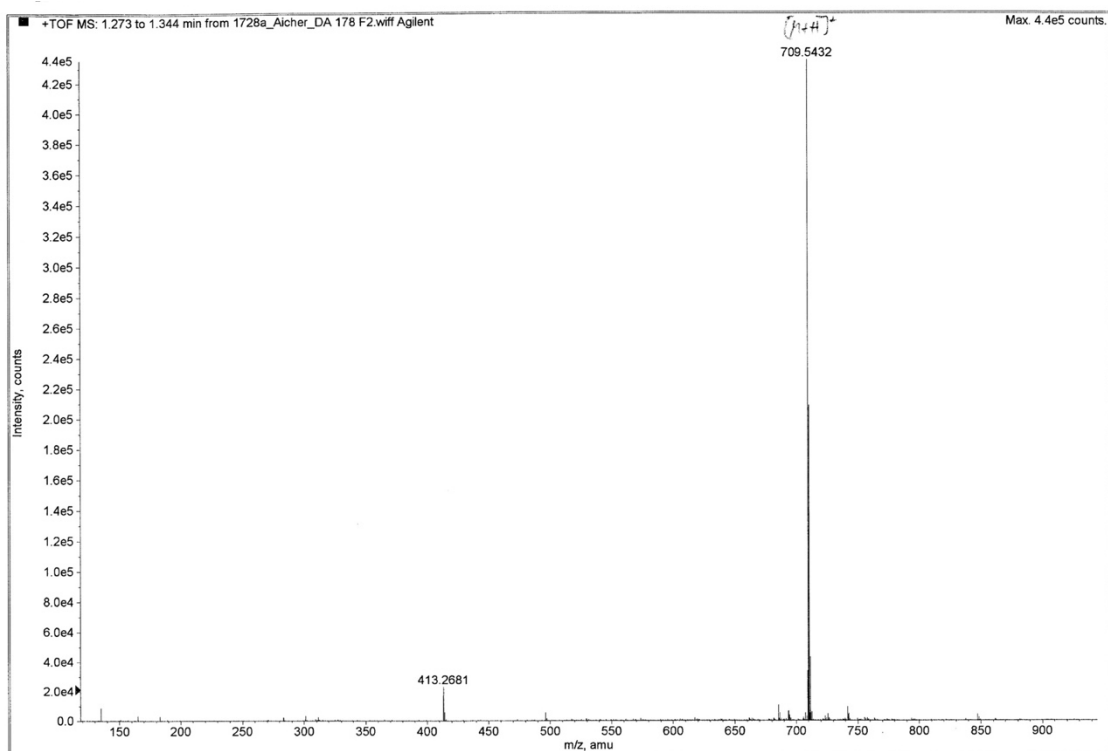
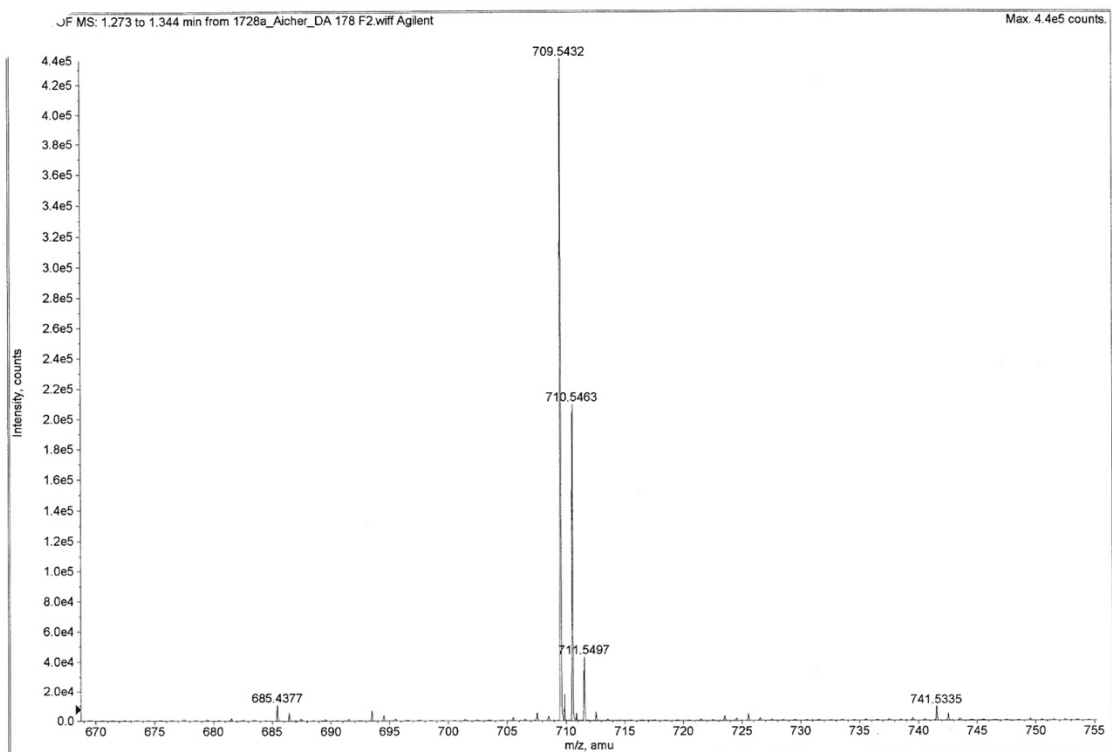
**Figure S-1.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin (19).



**Figure S-2.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of *meso*-tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin (19).

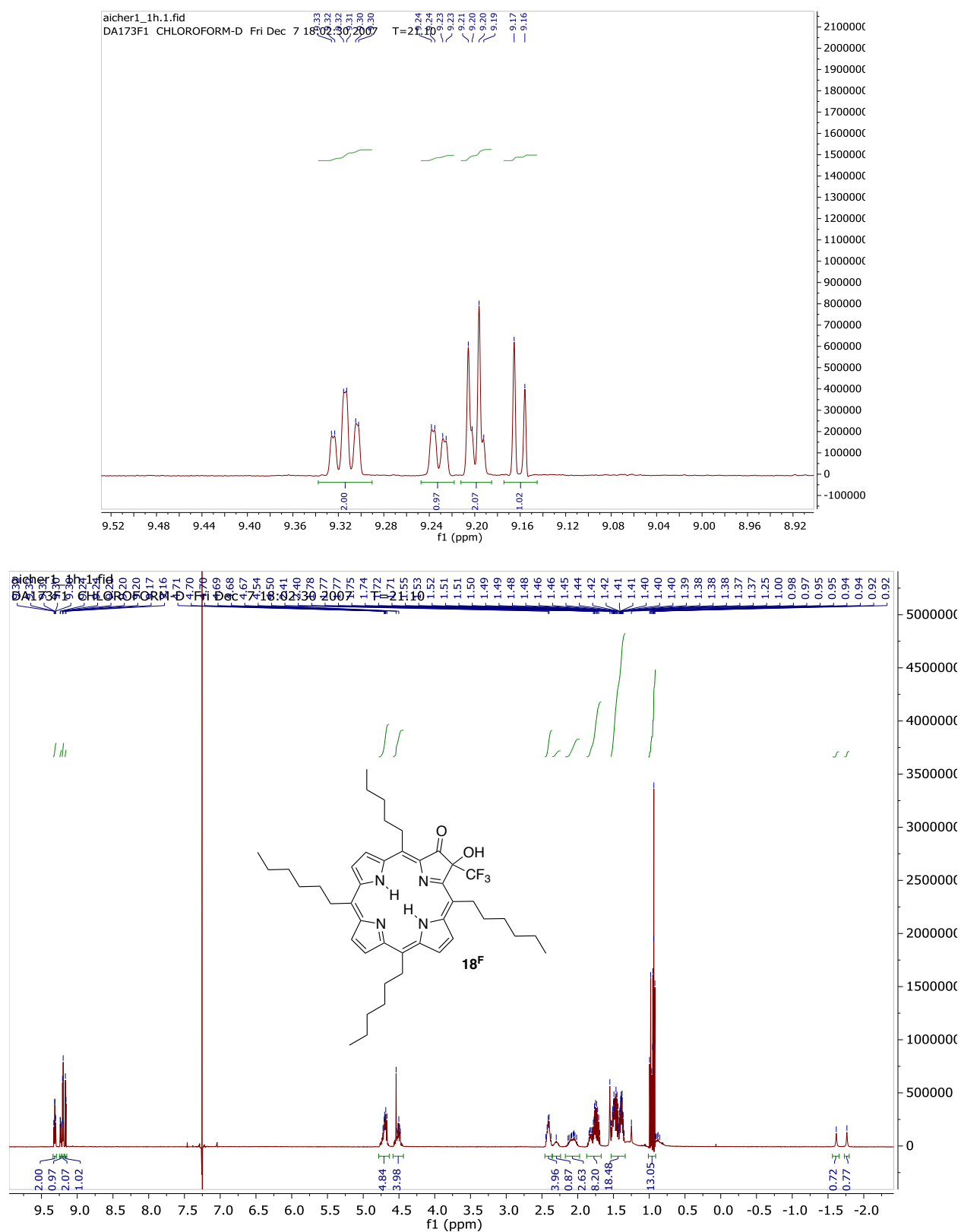


**Figure S-3.** UV-vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>) of *meso*-tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin (19).



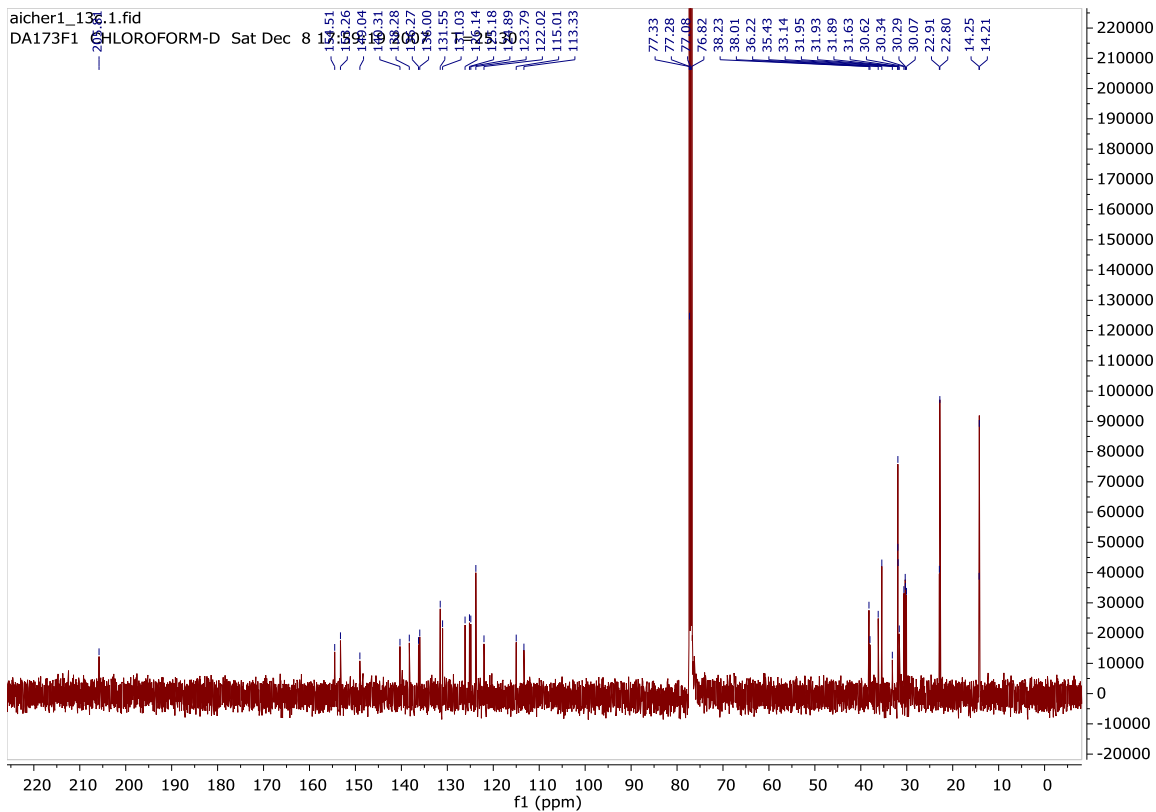
**Figure S-4.** Mass spec of *meso*-tetrahexyl-7,8-dihydroxy-7,8-dimethyl-chlorin (**19**).

***meso*-Tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one ( $18^F$ ).**

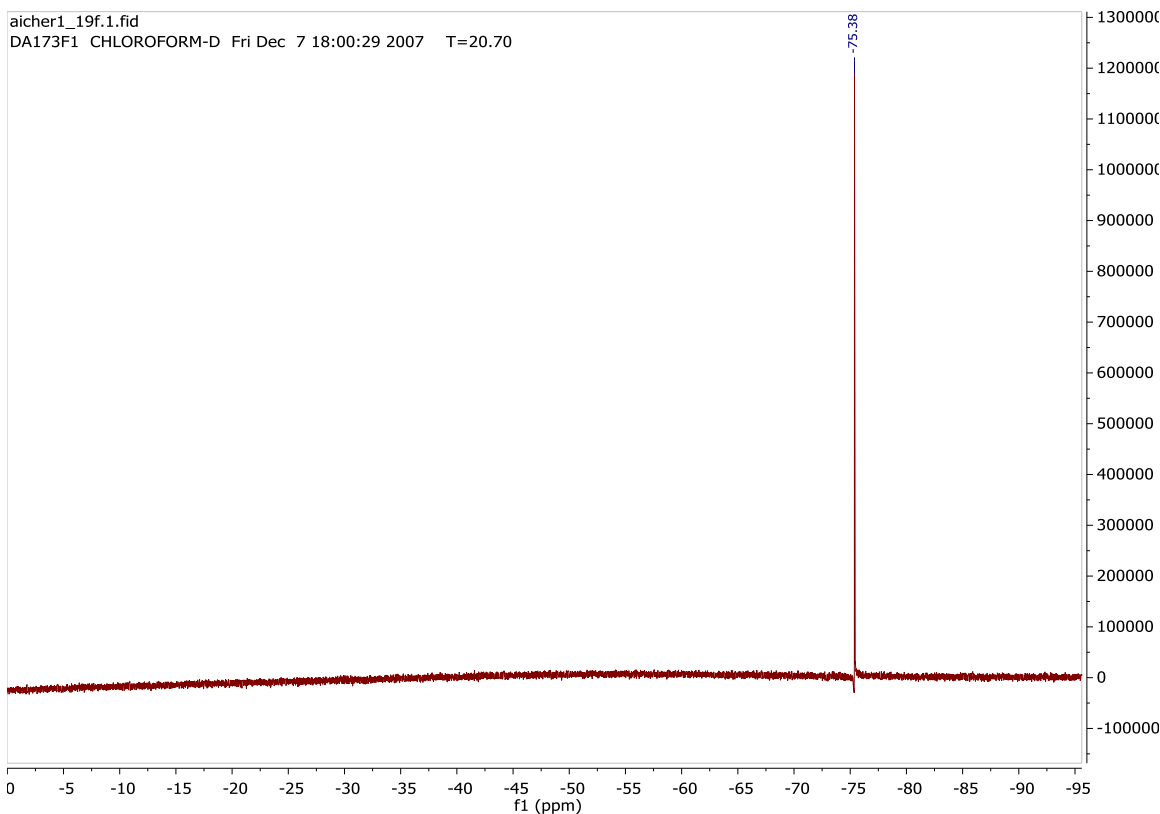


**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one ( $18^F$ ).

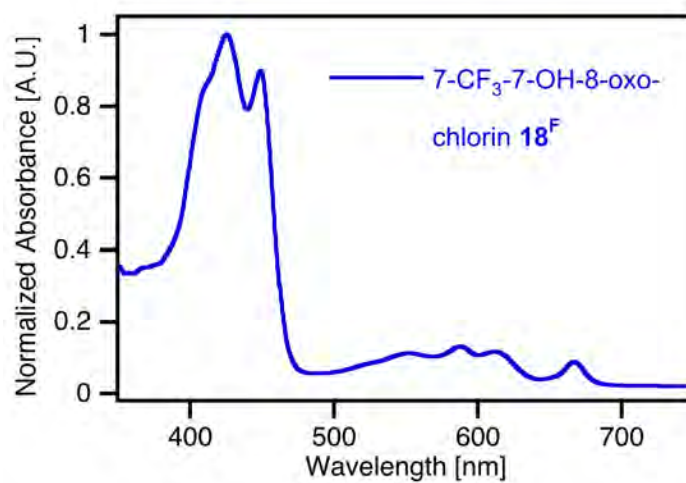




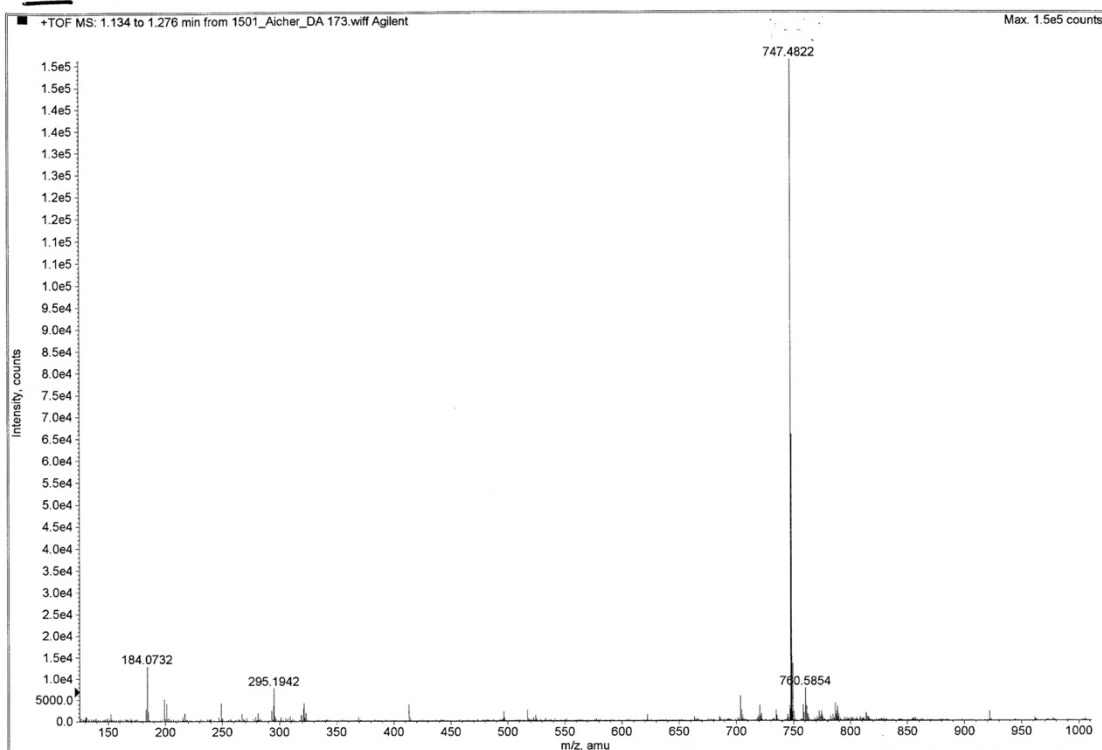
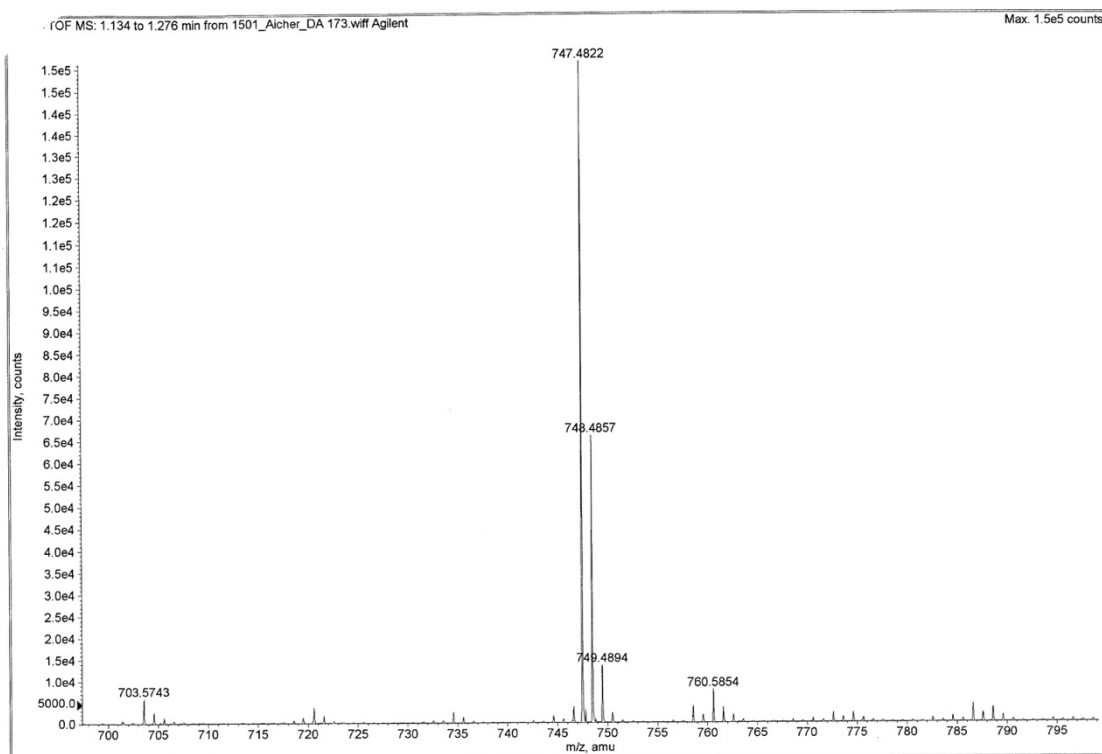
**Figure S-2.**  $^{13}\text{C}$  NMR of *meso*-tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one (**18<sup>F</sup>**).



**Figure S-3.**  $^{19}\text{F}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of *meso*-tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one (**18<sup>F</sup>**).

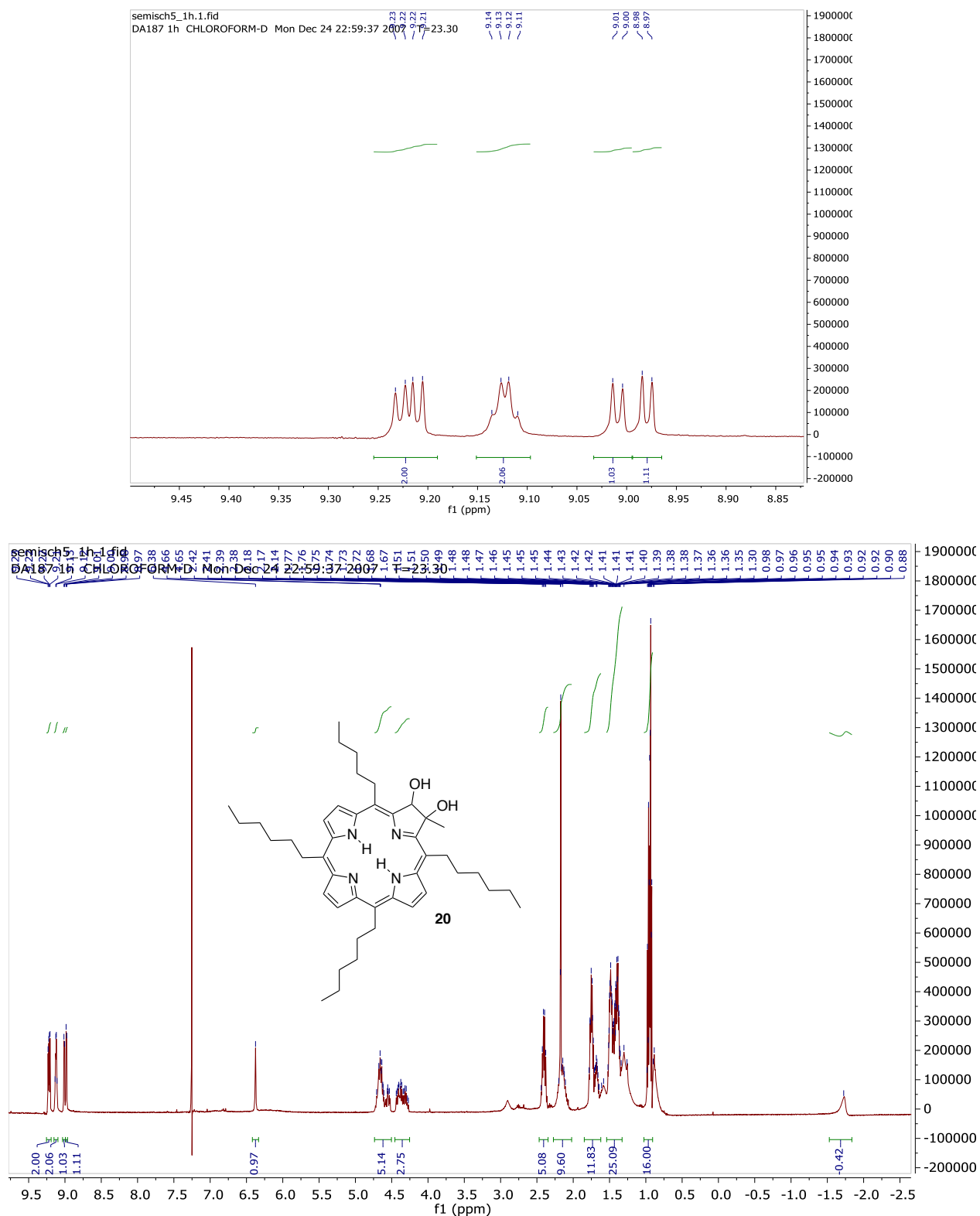


**Figure S-4.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one (**18<sup>F</sup>**).

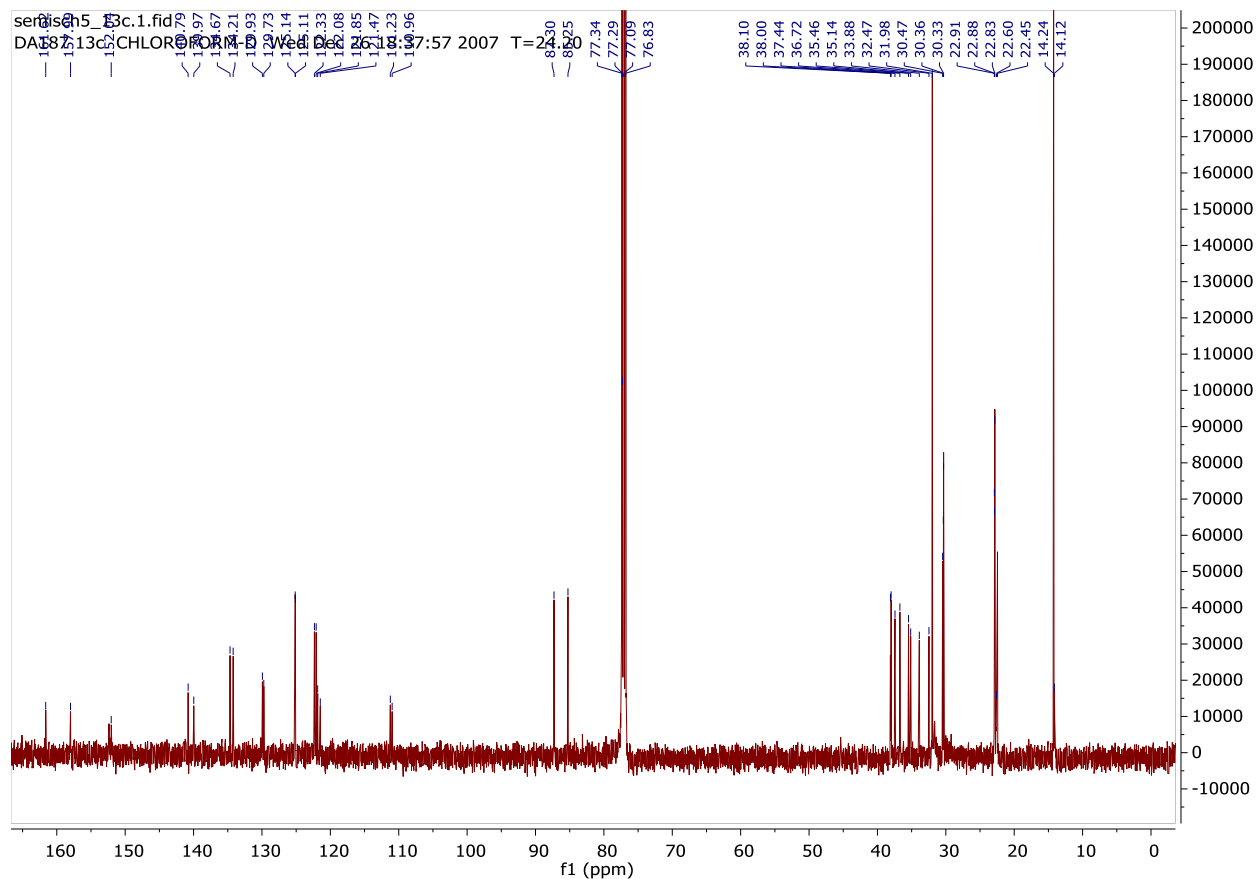


**Figure S-5.** Mass spec of *meso*-tetrahexyl-8-hydroxy-8-trifluoromethyl-chlorin-7-one (**18<sup>F</sup>**).

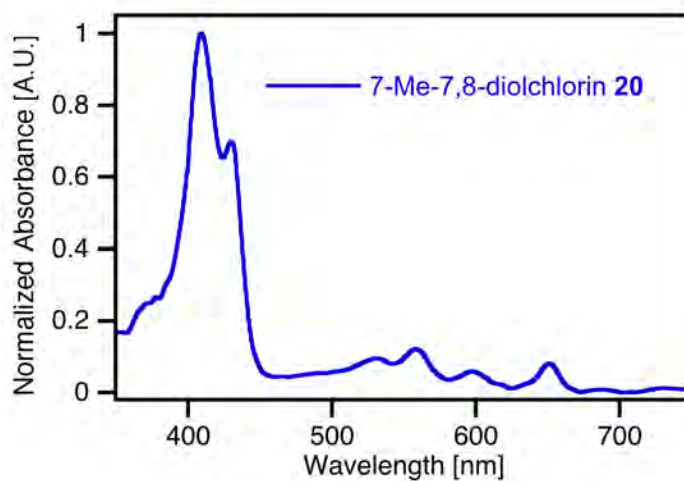
***meso*-Tetrahexyl-7,8-dihydroxy-8-methyl-chlorin (20).**



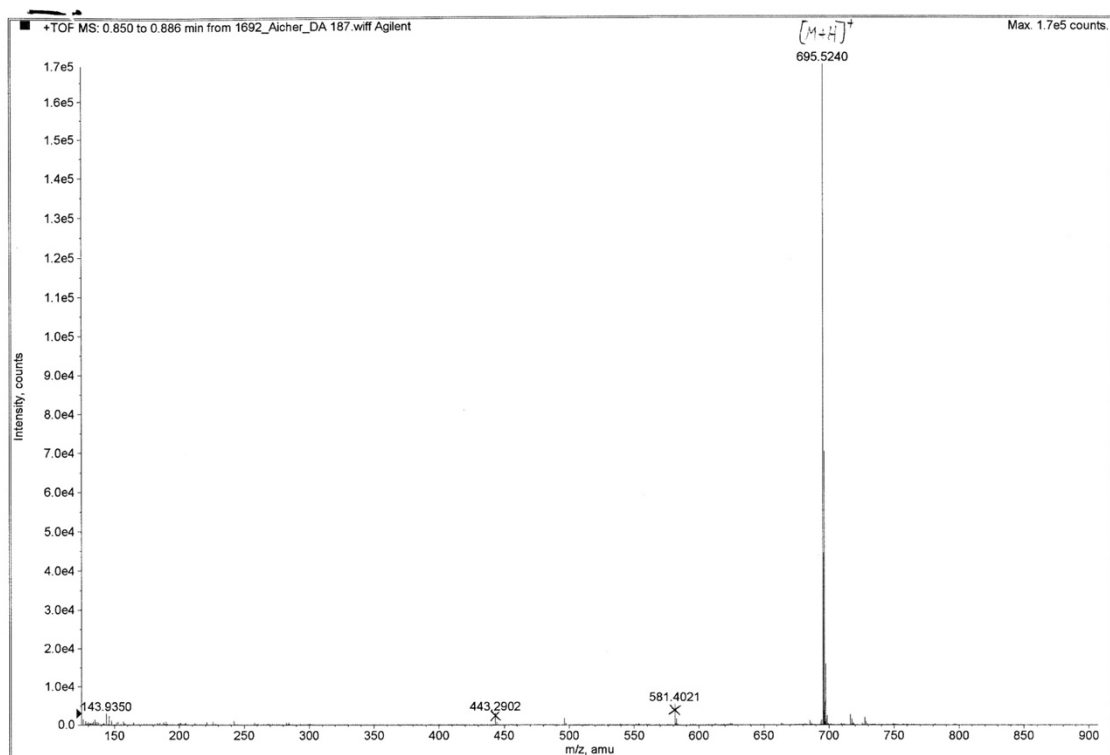
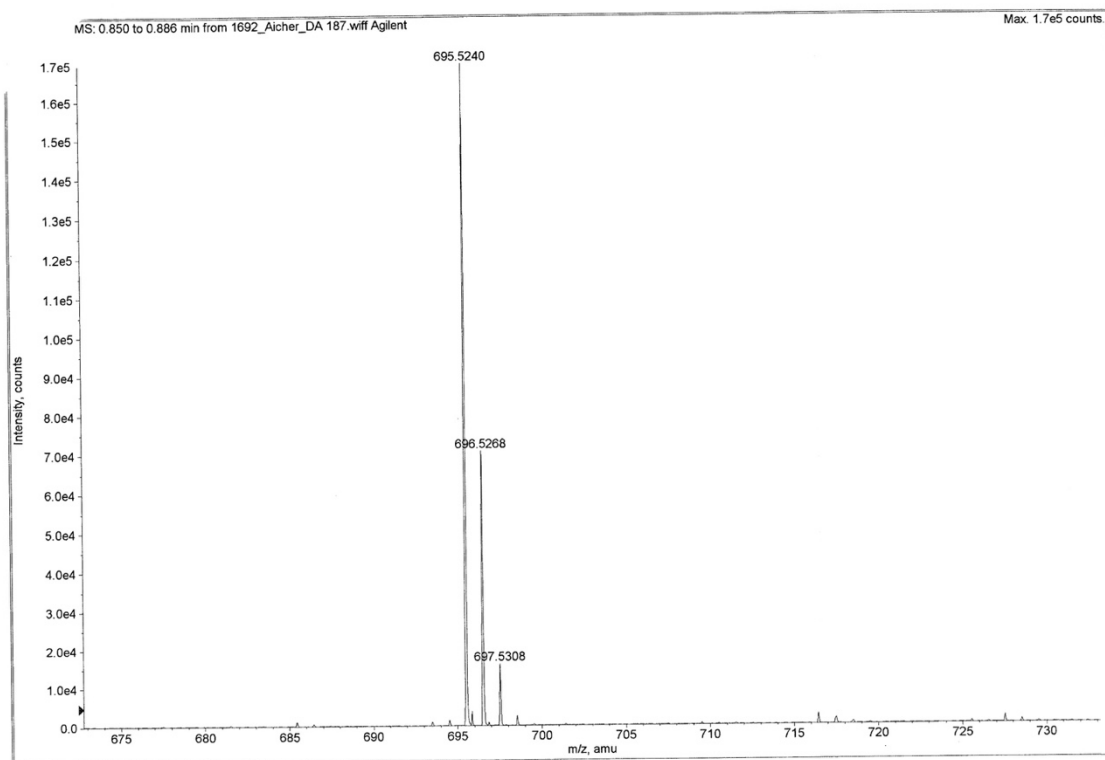
**Figure S-1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of *meso*-tetrahexyl-7,8-dihydroxy-8-methyl-chlorin (20).



**Figure S-2.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of *meso*-tetrahexyl-7,8-dihydroxy-8-methyl-chlorin (**20**).

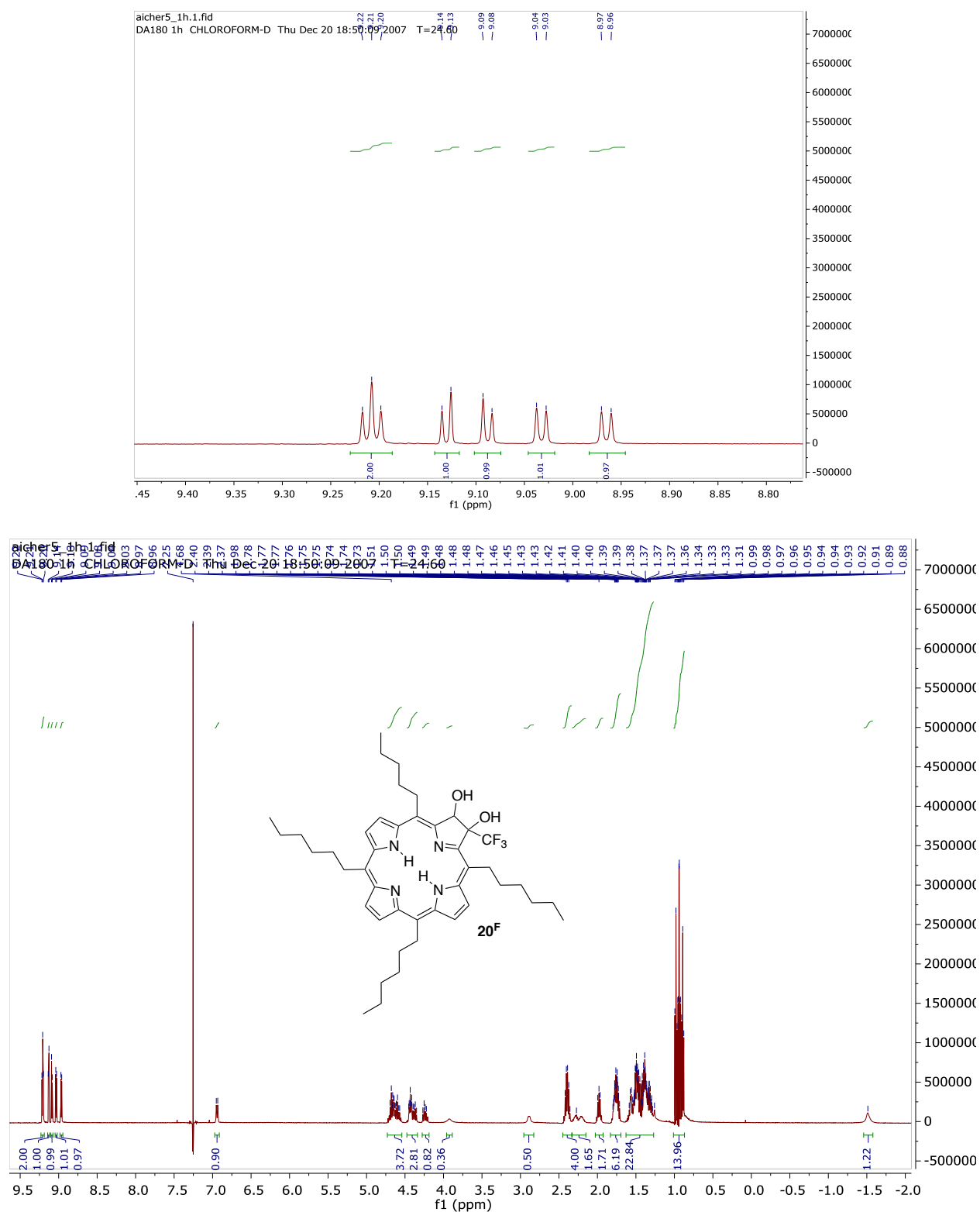


**Figure S-3.** UV-vis spectrum ( $\text{CH}_2\text{Cl}_2$ ) of *meso*-tetrahexyl-7,8-dihydroxy-8-methyl-chlorin (**20**).

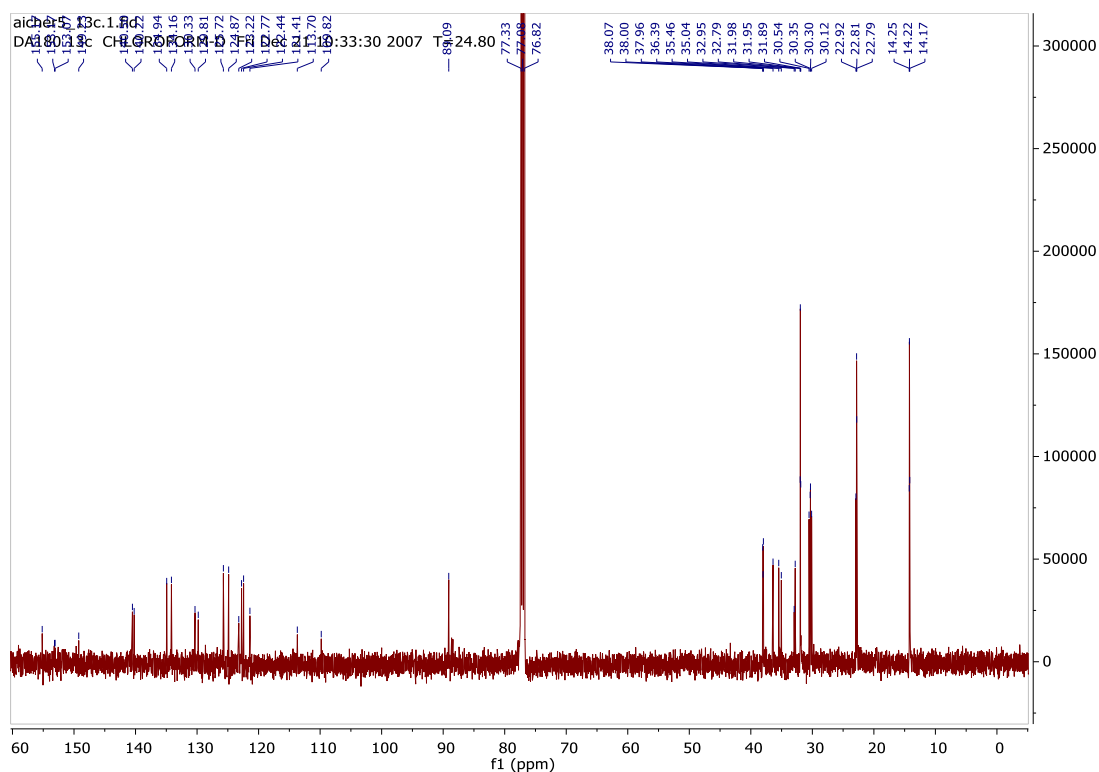


**Figure S-4.** Mass spec of *meso*-tetrahexyl-7,8-dihydroxy-8-methyl-chlorin (**20**).

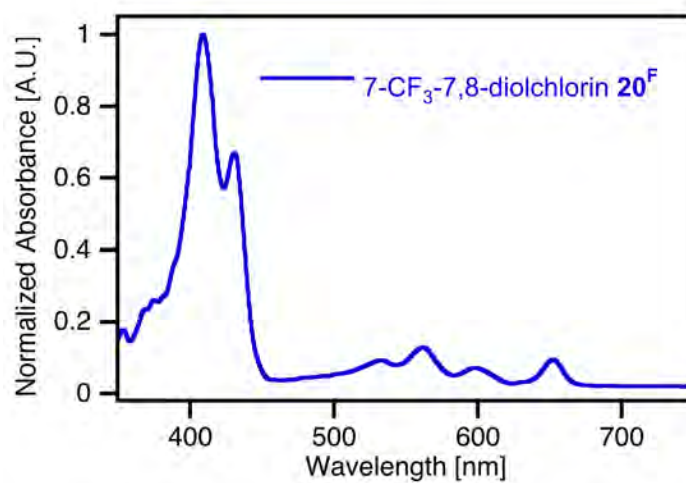
***meso*-Tetrahexyl-7,8-dihydroxy-8-trifluoromethyl-chlorin (**20<sup>F</sup>**).**



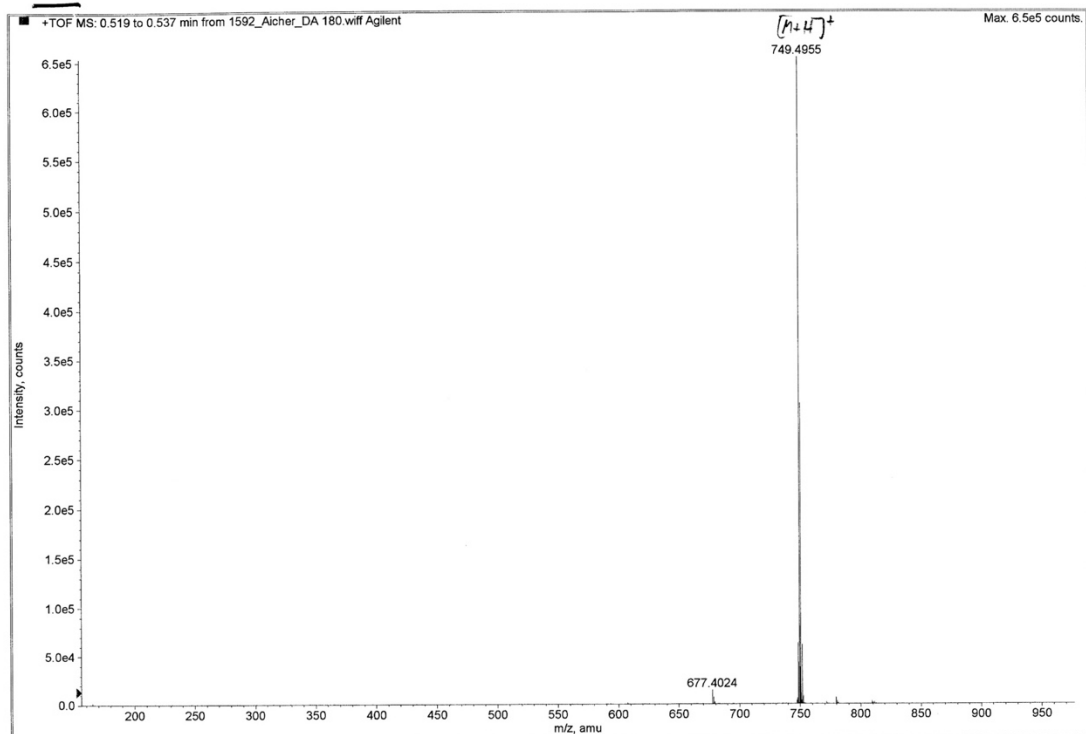
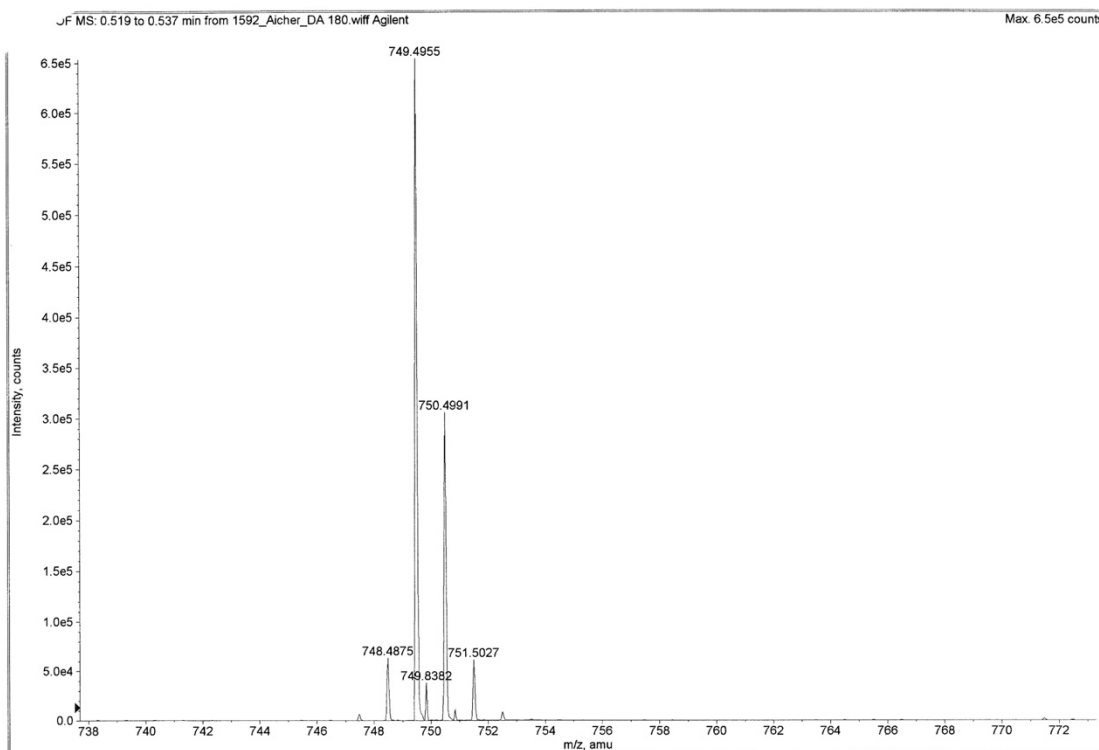
**Figure S-1.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of *meso*-tetrahexyl-7,8-dihydroxy-8-trifluoromethyl-chlorin (**20<sup>F</sup>**) (full and detail).







**Figure S-4.** UV-vis spectrum (CH<sub>2</sub>Cl<sub>2</sub>) of *meso*-tetrahexyl-7,8-dihydroxy-8-trifluoromethyl-chlorin (**20<sup>F</sup>**).



**Figure S-5.** HR-MS (ESI+, TOF) of *meso*-tetrahexyl-7,8-dihydroxy-8-trifluoromethyl-chlorin (**20<sup>F</sup>**) (full and detail).