Supplementary Information

*Laminaria digitata* and *Palmaria palmata* Seaweeds as Natural Source of Catalysts for the Cycloaddition of CO₂ to Epoxides

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Table S1a) Conversion to styrene carbonate and diol by-product using metal halides and histidine co-catalyst

| Conversion % | Metal Halide |  |  |  |  |  |  |
|--------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|              | KI | KBr | KCl | NaI | NaBr | NaCl | CaCl₂ |
| Carbonate 2a | 75.2 | 76.3 | 61.7 | 49.8 | 67.2 | 77.5 | 80.0 |
| Diol 3a      | 0 | 23.7 | 21.0 | 3.9 | 32.8 | 8.3 | 17.6 |
| Epoxide 1a   | 24.8 | 0 | 17.3 | 18.6 | 0 | 42.1 | 2.4 |

Table S1b) Conversion to styrene carbonate and diol by-product using metal halides lysine co-catalyst

| Conversion % | Metal Halide |  |  |  |  |  |  |
|--------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|              | KI | KBr | KCl | NaI | NaBr | NaCl | CaCl₂ |
| Carbonate 2a | 63.9 | 44.1 | 8.0 | 56.2 | 58.8 | 12.1 | 18.7 |
| Diol 3a      | 14.6 | 3.5 | 5.1 | 16.8 | 3.5 | 6.5 | 13.9 |
| Epoxide 1a   | 21.5 | 52.4 | 86.9 | 27.0 | 37.7 | 81.4 | 67.4 |

Table S1c) Conversion to styrene carbonate and diol by-product using metal halides glycine co-catalyst

| Conversion % | Metal Halide |  |  |  |  |  |  |
|--------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|              | KI | KBr | KCl | NaI | NaBr | NaCl | CaCl₂ |
| Carbonate 2a | 79.5 | 10.2 | 0.8 | 97.1 | 41.2 | 0 | 11.8 |
| Diol 3a      | 11.5 | 2.4 | 1.6 | 2.9 | 3.7 | 1.7 | 9.1 |
| Epoxide 1a   | 9.0 | 87.4 | 97.6 | 0 | 55.1 | 98.3 | 79.1 |

Table S1d) Conversion to styrene carbonate and diol by-product using metal halides alone

| Conversion % | Metal Halide |  |  |  |  |  |  |
|--------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|              | KI | KBr | KCl | NaI | NaBr | NaCl | CaCl₂ |
| Carbonate 2a | 100 | 0.9 | 1.0 | 23.1 | 2.8 | 1.0 | 0 |
| Diol 3a      | 0 | 4.7 | 2.9 | 1.5 | 3.7 | 4.7 | 13.8 |
| Epoxide 1a   | 0 | 94.3 | 96.2 | 75.4 | 93.5 | 94.3 | 86.2 |

Table S1e) Conversion to styrene carbonate and diol by-product using amino acids alone

| Conversion % | Amino acid |  |  |  |
|--------------|------------|-------------------|-------------------|
|              | Histidine | Lysine | Glycine |
| Carbonate 2a | 39.1 | 9.7 | 0 |
| Diol 3a      | 15.2 | 9.4 | 0 |
| Epoxide 1a   | 45.7 | 80.9 | 100 |
**Figure S1.** Variation in Kelp catalyst loading in the synthesis of styrene carbonate

**Table S2.** Effect of CO₂ pressure on conversion to styrene carbonate using Kelp D <125 nm as a catalyst

| Pressure / bar | Carbonate / % | Diol / % | Epoxide / % | CPE / % | Selectivity / % |
|---------------|--------------|----------|-------------|---------|-----------------|
| 10            | 26.5         | 26.1     | 33.7        | 8.6     | 43.3            |
| 20            | 31.1         | 29.7     | 28.1        | 11.1    | 43.3            |
| 30            | 36.1         | 23.0     | 37.8        | 3.1     | 58.0            |
| 40            | 39.4         | 35.8     | 13.3        | 11.5    | 45.5            |

**Figure S2.** Conversion to styrene carbonate over time using Kelp D catalyst and larger reaction scale of 20 mmols in a single Parr reactor.
### Table S3. Calculation of water content from TGIR analysis of unused Kelp seaweeds B-D<125

| Kelp     | Water content TGIR (% wt) | Particle Size (µm) | Conversion to Diol 6a (%) | Diol (mmol) | H₂O in Kelp Sample (mmol) | H₂O converted to diol (%) |
|----------|---------------------------|--------------------|---------------------------|-------------|---------------------------|---------------------------|
| B (18/09/17) | 8.2                       | < 125              | 26.2                      | 1.31        | 2.17                      | 60.4                      |
| C (15/11/17) | 8.5                       | < 125              | 27.4                      | 1.37        | 2.25                      | 60.9                      |
| D (20/11/17) | 8.4                       | < 125              | 35.2                      | 1.76        | 2.22                      | 79.2                      |

### Table S4. % organic vs inorganic content for Kelp seaweeds B, C and D

| Kelp | % Weight of residual inorganics | % Weight organic material lost |
|------|---------------------------------|------------------------------|
| B    | Unused                          | 24.0                         | 76.0                         |
|      | Used                            | 33.0                         | 67.0                         |
| C    | Unused                          | 22.1                         | 77.9                         |
|      | Used                            | 32.7                         | 67.3                         |
| D    | Unused                          | 23.8                         | 76.2                         |
|      | Used                            | 32.6                         | 67.4                         |
Figure S3. TGIR Analysis of Kelp B (Green), C (Blue) and D (Red). TG used to assess residual moisture content of the dried seaweeds.
Figure S4. TGIR to measure residual water in Kelp B (top), Kelp C (middle) and Kelp D (bottom)
Conversion to carbonate (19.9) = $100 \times \frac{H1 (13.78)}{H1 (13.78) + H2 (7.17) + H3 (16.16) + H5 (30.11) + H6 (0.38) + H7 (1.55)}$

Figure S5. $^1$H NMR of conversion to styrene carbonate using Kelp B 300-500 nm particle size as shown in table 3.
Figure S6. GC/MS Chromatogram of conversion to styrene carbonate using Kelp D <125 nm particle size as shown in table 3.
Figure S7. M/S of Peak 1 - Benzaldehyde
Figure S8. M/S of Peak 1 – Styrene Oxide
Figure S9. M/S of Peak 3 – 1-Phenyl-2-chloroethanol
**Figure S10.** M/S of Peak 4 – 1-Phenyl-1,2-ethanediol
Figure S11. M/S of Peak 5 – Styrene carbonate
Figure S12. High resolution M/S of reaction mixture showing phenylacetaldehyde, 1-phenyl-1,2-ethanediol and styrene carbonate
## Figure S13. ICP-MS raw data

| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|---------------|---------|-------------|-----------|
| Blank     | Al 396.153   | 56913.40945| 0.78103        | 444.51304     |               |         |             |           |
| 0.01 ppm M4| Al 396.153   | 1559.31457 | 86.22568       | 1344.52961    |               |         |             |           |
| 0.05 ppm M4| Al 396.153   | 3274.73052 | 48.09511       | 1574.98518    |               |         |             |           |
| 0.1 ppm M4 | Al 396.153   | 6194.72994 | 10.58408       | 655.65499     |               |         |             |           |
| 0.5 ppm M4 | Al 396.153   | 34537.18784| 1.04251        | 360.05218     |               |         | mg metal / 100ml | mg Metal / g seaweed |
| Kelp D    | Al 396.153   | 10402.29670| 10.32365       | 1073.89719    | 0.15077       | 10.37040| 0.01564     | 0.99924   | 0.01508     | 0.36138   |
| Kelp C    | Al 396.153   | 8493.08945 | 7.05515        | 599.20011     | 0.12297       | 7.09432 | 0.00872     | 0.99924   | 0.01230     | 0.27176   |
| Kelp B    | Al 396.153   | 6412.83655 | 15.57553       | 998.83339     | 0.09268       | 15.69025| 0.01454     | 0.99924   | 0.00927     | 0.22099   |
| M6 x 100  | Al 396.153   | 82684.57059 | 5.89266       | 4872.32164    | 1.20316       | 5.89600 | 0.07094     | 0.99924   |             |           |
| SLRS-4    | Al 396.153   | 11190.60560| 15.03809       | 1682.85377    | 0.16225       | 15.10137| 0.02450     | 0.99924   |             |           |

## Additional Table

| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|---------------|---------|-------------|-----------|
| Blank     | Ca 317.933   | 2967.10570 | 1.50992        | 44.80098      |               |         |             |           |
| 0.01 ppm M4| Ca 317.933   | 870.59020  | 5.68091        | 49.45744      |               |         |             |           |
| 0.05 ppm M4| Ca 317.933   | 3944.34839 | 4.36552        | 172.19138     |               |         |             |           |
| 0.1 ppm M4 | Ca 317.933   | 7585.59997 | 1.81528        | 137.70015     |               |         |             |           |
| 0.5 ppm M4 | Ca 317.933   | 35112.42619| 1.38776        | 487.27515     |               |         |             |           |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|----------------|---------|-------------|-----------|
| Blank     | Fe 239.562   | 825.59447  | 7.20401        | 59.47593      |                 |         |             |           |
| 0.01 ppm M4 | Fe 239.562 | 68.20726   | 15.97451       | 10.89577      |                 |         |             |           |
| 0.05 ppm M4 | Fe 239.562 | 1409.20400 | 0.91541        | 12.89995      |                 |         |             |           |
| 0.1 ppm M4 | Fe 239.562  | 3121.33455 | 1.56229        | 48.76423      |                 |         |             |           |
| 0.5 ppm M4 | Fe 239.562  | 16491.41643 | 0.82424       | 135.92827     |                 |         |             |           |
| Kelp D    | Fe 239.562  | 2746.88444 | 3.48247        | 95.65939      | 0.08783        | 3.26968 | 0.00287     | 0.99988   | 0.00878  | 0.21053 |
| Kelp C    | Fe 239.562  | 1373.45272 | 56.35865       | 774.05938     | 0.04660        | 49.86780 | 0.02324     | 0.99988   | 0.00466  | 0.10298 |
| Kelp B    | Fe 239.562  | 1337.03477 | 1.66993        | 22.32755      | 0.04551        | 1.47298 | 0.00067     | 0.99988   | 0.00455  | 0.10851 |
| M6 x 100  | Fe 239.562  | 321508.12650 | 2.40486   | 7731.81342    | 9.65763        | 2.40352 | 0.23212     | 0.99988   |           |           |
| SLRS-4    | Fe 239.562  | 3758.87094 | 1.49273        | 56.10963      | 0.11822        | 1.42496 | 0.00168     | 0.99988   |           |           |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|----------------|----------|-------------|-----------|
| Blank     | K 766.490    | 39411.7775 | 0.60793        | 239.59536     |                |          |             |           |
| 0.01 ppm M4  | K 766.490    | 834.34351  | 79.27820       | 661.45255     |                |          |             |           |
| 0.05 ppm M4  | K 766.490    | 7799.79558 | 13.91678       | 1085.48006    |                |          |             |           |
| 0.1 ppm M4   | K 766.490    | 18395.20590 | 3.37716       | 621.23569     |                |          |             |           |
| 0.5 ppm M4   | K 766.490    | 121343.38290 | 1.18965      | 1443.56055    |                |          |             |           |
| 1 ppm M4     | K 766.490    | 269818.74600 | 1.24409      | 3356.79652    |                |          |             |           |
| 5 ppm M4     | K 766.490    | 1553987.3690 | 0.12814     | 1991.25890    |                |          |             |           |
| 10 ppm M4    | K 766.490   | 3447665.6020 | 0.74695      | 25752.28945   | mg metal / 100ml |          | mg Metal / g seaweed |           |
| Kelp D      | K 766.490   | 3592594.1290 | 1.92802      | 69265.82656   | 10.61271       | 1.90984  | 0.20269     | 0.99890   | 1.06127  | 25.43794  |
| Kelp C      | K 766.490   | 2202196.2930 | 0.45530      | 10026.70899   | 6.54413        | 0.44834  | 0.02934     | 0.99890   | 0.65441  | 14.46216  |
| Kelp B      | K 766.490   | 2166705.1830 | 3.73589      | 80945.68037   | 6.44027        | 3.67785  | 0.23686     | 0.99890   | 0.64403  | 15.35592  |
| M6 x 100    | K 766.490   | 321884.13760 | 3.06666      | 9871.08468    | 1.04195        | 2.77218  | 0.02888     | 0.99890   | 15.35592  |
| SLRS-4      | K 766.490   | 165143.70500 | 4.01746      | 6634.58766    | 0.58330        | 3.32833  | 0.01941     | 0.99890   |           |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|----------------|----------|-------------|-----------|
| Blank     | Li 670.784   | 34214.85071 | 1.65450       | 566.08502     |                |          |             |           |
| 0.01 ppm M4  | Li 670.784   | 76763.87060 | 5.79995       | 4452.26712    |                |          |             |           |
| 0.05 ppm M4  | Li 670.784   | 356810.23520 | 1.56885      | 5597.82175    |                |          |             |           |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|--------------|---------------|---------|-------------|-----------|
| Blank     | Mg 279.077   | 947.55371  | 2.48345        | 23.53202     |               |         |             |           |
| 0.01 ppm M4 | Mg 279.077 | 103.97117  | 11.33641       | 11.78660     |               |         |             |           |
| 0.05 ppm M4 | Mg 279.077 | 460.50814  | 3.34628        | 15.40989     |               |         |             |           |
| 0.1 ppm M4  | Mg 279.077 | 883.57931  | 8.55461        | 75.58680     |               |         |             |           |
| 0.5 ppm M4  | Mg 279.077 | 4601.51856 | 0.27202        | 12.51700     |               |         |             |           |
| 1 ppm M4    | Mg 279.077 | 9255.24152 | 0.85013        | 78.68118     |               |         |             |           |
| 5 ppm M4    | Mg 279.077 | 43245.81425| 0.54501        | 235.69615    |               |         |             |           |
| 10 ppm M4   | Mg 279.077 | 85647.67687| 0.35866        | 307.18094    |               |         |             |           |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|---------------|----------|-------------|---------|
| Blank     | Na 589.592   | 95057.20193| 1.88720        | 1793.91672    |               |          |             |         |
| 0.01 ppm M4 | Na 589.592  | 4077.88123 | 101.1203       | 4123.56888    |               |          |             |         |
| 0.05 ppm M4 | Na 589.592  | 19024.14446| 25.22180       | 4798.23091    |               |          |             |         |
| 0.1 ppm M4  | Na 589.592  | 42461.04606| 5.16732        | 2194.09761    |               |          |             |         |
| 0.5 ppm M4  | Na 589.592  | 249823.22100| 3.09198       | 7724.47814    |               |          |             |         |
| 1 ppm M4    | Na 589.592  | 522859.85670| 1.36570       | 7140.71527    |               |          |             |         |
| 5 ppm M4    | Na 589.592  | 3146361.088 | 0.72796         | 22904.11598   |               |          |             |         |
| 10 ppm M4   | Na 589.592  | 6824688.653 | 0.51667        | 35261.12651   |               |          |             |         |
| Kelp D     | Na 589.592  | 11639595.610| 0.39904        | 64646.57274   | 17.24786      | 0.39694 | 0.06846    | 0.99923 |
| Kelp C     | Na 589.592  | 13419144.840| 0.14953        | 20065.51438   | 19.87096      | 0.14885 | 0.02958    | 0.99923 |
| Kelp B     | Na 589.592  | 13779426.880| 0.67480        | 92984.01208   | 20.40202      | 0.67180 | 0.13706    | 0.99923 |
| M6 x 100   | Na 589.592  | 642577.239 | 4.45447        | 28623.42983   | 1.03803       | 4.06457 | 0.04219    | 0.99923 |
| SLRS-4     | Na 589.592  | 1117909.105 | 1.27592        | 14263.64454   | 1.73868       | 1.20925 | 0.02102    | 0.99923 |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|---------------|---------|-------------|-----------|
| Blank     | Zn 202.548   | 68.40420   | 11.52839       | 7.88590       |               |         |             |           |
| 0.01 ppm M4 | Zn 202.548 | 170.52294  | 5.87456        | 10.01747      |               |         |             |           |
| 0.05 ppm M4 | Zn 202.548 | 905.69475  | 1.06340        | 9.63114       |               |         |             |           |
| 0.1 ppm M4   | Zn 202.548  | 1767.78131 | 2.19623        | 38.82454      |               |         |             |           |
| 0.5 ppm M4   | Zn 202.548  | 9086.78076 | 0.60040        | 54.55745      |               |         |             |           |
| Kelp D      | Zn 202.548   | 1953.92914 | 0.74491        | 14.55509      | 0.10824       | 0.73918 | 0.00080     | 0.99999   | 0.01082   | 0.25945   |
| Kelp C      | Zn 202.548   | 2703.58040 | 15.50297       | 419.13530     | 0.14945       | 15.41652 | 0.02304     | 0.99999   | 0.01494   | 0.33027   |
| Kelp B      | Zn 202.548   | 5078.83806 | 1.03871        | 52.75454      | 0.28002       | 1.03562 | 0.00290     | 0.99999   | 0.02800   | 0.66766   |
| M6 x 100    | Zn 202.548   | 165916.34310 | 1.66175      | 2757.11030    | 9.12132       | 1.66160 | 0.15156     | 0.99999   |           |           |
| SLRS-4      | Zn 202.548   | 302.28066  | 7.89095        | 23.85281      | 0.01745       | 7.51409 | 0.00131     | 0.99999   |           |           |
| Sample ID   | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
| Blank       | Sr 460.733    | 448.46187  | 29.57393       | 132.62778     |               |         |             |           |
| 0.01 ppm M4 | Sr 460.733    | 4681.59424 | 5.69415        | 266.57699     |               |         |             |           |
| 0.05 ppm M4 | Sr 460.733    | 23046.01900 | 4.43156       | 1021.29870    |               |         |             |           |
| 0.1 ppm M4  | Sr 460.733    | 46258.34326 | 0.90296       | 417.69295     |               |         |             |           |
| 0.5 ppm M4  | Sr 460.733    | 240906.09410 | 2.95058       | 7108.12851    |               |         |             |           | mg metal / 100ml | mg Metal / g seaweed |
| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|----------------|----------|-------------|-----------|
| Blank     | Cu 324.752   | 7581.41265 | 1.39837        | 106.01653     |                |          |             |           |
| 0.01 ppm M4 | Cu 324.752  | 1852.48140 | 11.17210       | 206.96108     |                |          |             |           |
| 0.05 ppm M4 | Cu 324.752  | 11822.95445 | 5.27419        | 623.56545     |                |          |             |           |
| 0.1 ppm M4 | Cu 324.752  | 23795.80573 | 0.26927        | 64.07606      |                |          |             |           |
| 0.5 ppm M4 | Cu 324.752  | 123464.46870 | 0.92309       | 1139.68702    |                |          |             |           |
| Kelp D    | Cu 324.752   | 12070.18814 | 2.25050        | 271.63975     | 0.05081        | 2.15790  | 0.00110     | 0.99998   |
| Kelp C    | Cu 324.752   | 9495.19873  | 1.64382        | 156.08416     | 0.04041        | 1.55879  | 0.00063     | 0.99998   |
| Kelp B    | Cu 324.752   | 13418.59768 | 1.43810        | 192.97286     | 0.05625        | 1.38465  | 0.00078     | 0.99998   |
| M6 x 100  | Cu 324.752   | 249633.41230 | 2.48710      | 6208.64271    | 1.00963        | 2.48195  | 0.02506     | 0.99998   |
| SLRS-4    | Cu 324.752   | -716.00074  | 13.43241       | 96.17614      | -0.00080       | 48.56552 | 0.00039     | 0.99998   |

| Sample ID | Analyte Name | Int (Corr) | RSD (Corr Int) | SD (Corr Int) | Conc (mg l⁻¹) | RSD (%) | SD (mg l⁻¹) | Corr Coef |
|-----------|--------------|------------|----------------|---------------|----------------|----------|-------------|-----------|
| Blank     | Ba 233.527   | 129.40965  | 7.43261        | 9.61852       |                |          |             |           |
| 0.01 ppm M4 | Ba 233.527  | 706.23876  | 2.23855        | 15.80951      |                |          |             |           |
| 0.05 ppm M4 | Ba 233.527  | 3548.79451 | 1.35061        | 47.93030      |                |          |             |           |
| Sample     | Ba 233.527 | mg metal / 100ml | mg Metal / g seaweed |
|------------|------------|-------------------|----------------------|
| 0.1 ppm M4 | Ba 233.527 | 7124.22001        | 79.94551             |
| 0.5 ppm M4 | Ba 233.527 | 34344.81833       | 358.09862            |
| Kelp D     | Ba 233.527 | 1996.79511        | 19.75450             |
| Kelp C     | Ba 233.527 | 2964.02210        | 52.06314             |
| Kelp B     | Ba 233.527 | 1902.37748        | 22.82429             |
| M6 x 100   | Ba 233.527 | 65934.11422       | 1123.75821           |
| SLRS-4     | Ba 233.527 | 954.11327         | 14.62872             |
**Method S1.** Detailed HPLC method for amino acid analysis

An Agilen HPLC infinity 1200 was used to perform the chromatography and a Poroshell 120 EC-C18 4.6 x 100 mm, 2.7 μm diameter. Temperature of the oven was set at 45 °C, a quaternary pump (G7111B) was used to pump eluents through the column with a pressure limit of 600 bar and a flow set at 0.4 mL/min. A DAD detector (G7115A) was set at wavelength 263 nm (FMOC) and 338 nm (OPA). Settings of the sampler (G7129A) were the following: draw speed-200 μL/min, eject speed-400 μL/min.

The following eluent gradient was used:

| Time (min) | A (%) | B (%) |
|-----------|-------|-------|
| 12.00     | 80.0  | 20.0  |
| 13.00     | 65.0  | 35.0  |
| 17.00     | 60.0  | 40.0  |
| 19.00     | 55.0  | 45.0  |
| 21.40     | 44.7  | 55.3  |
| 25.00     | 40.0  | 60.0  |
| 28.00     | 30.0  | 70.0  |
| 29.20     | 25.0  | 75.0  |
| 30.00     | 15.0  | 85.0  |
| 32.00     | 10.0  | 90.0  |
| 34.00     | 5.0   | 95.0  |
| 36.00     | 0.0   | 100.0 |
| 37.00     | 40.0  | 60.0  |
| 40.00     | 80.0  | 20.0  |

Eluent A (2L) was prepared as follow: 2.839 g of Na₂HPO₄ and 4.024 g of Na₂B₄O₇ were dissolved in 2 L DI water and adjusted to pH 7.9 with conc. HCl (37%) and 1M HCl.

Eluent B consisted (1 L) in a MeOH: MeCN: H₂O 20:60:20 solution.

Borate Buffer (BB) solution was made by dissolving 1.24 g of Boric Acid and 1.49 g of KCl in 50 mL DI water adjusted to pH 10.5 with NaOH ground pellets.

Ethanethiol solution (ETSH) consisted of 500 μL Ethanethiol, 20mL BB and 80 mL MeOH.

FMOC solution was prepared dissolving 25 mg of FMOC Chloride in 10 mL MeCN. OPA/ET was done dissolving 40 mg of OPA in 10 mL ET solution.

Diluent was prepared by mixing 48.5 mL of eluent A with 1.5 mL concentrated phosphoric acid.

Internal standard solution consisted (ISTDsol) in a 1.5 mM Norleucine solution in water.

The pre-column derivatisation was done in the HPLC needle by an automated procedure as follows:
Auto-sampler program for pre-column derivatisation

| Function | Parameter |
|----------|-----------|
| Draw     | Draw 50.00 μL from location "P2-A1" with default speed using default offset |
| Draw     | Draw 1.00 μL from air with default speed |
| Draw     | Draw 2.00 μL from location "P2-A2" with default speed using default offset |
| Draw     | Draw 2.00 μL from sample with default speed using default offset |
| Draw     | Draw 12.00 μL from air with default speed |
| Mix      | Mix 4.00 μL from air with default speed for 5 times |
| Wait     | Wait 1 min |
| Eject    | Eject 12.00 μL to seat with default speed |
| Wash     | Wash needle in flushport for 5 s |
| Draw     | Draw 2.00 μL from location "P2-A3" with default speed using default offset |
| Draw     | Draw 12.00 μL from air with default speed |
| Mix      | Mix 6.00 μL from air with default speed for 5 times |
| Wait     | Wait 0.15 min |
| Eject    | Eject 12.00 μL to seat with default speed |
| Wash     | Wash needle in flushport for 5 s |
| Draw     | Draw 4.00 μL from location "P2-A4" with default speed using default offset |
| Draw     | Draw 12.00 μL from air with default speed |
| Mix      | Mix 10.00 μL from air with default speed for 5 times |
| Eject    | Eject 12.00 μL to seat with default speed |
| Inject   | Inject |

Hydrolysis of the microalgae samples was done as follow: 20 mg of algal powder in 25 mL 6M HCl with 1% (w/v phenol) were heated at 150 °C for 30 min in a CEM discover microwave. The resulting mixture was filtered and evaporated under reduce pressure. The resulting solid was re-suspended in 30 mL of suspension solution consisting of Water:MeOH:ISTDsol (5:4:1). The suspension was sonicated for 10 s and filtered through 0.22 um Whatman filters.