

Supporting Information for:

**Total Synthesis Campaigns Toward Chlorophylls and Related Natural Hydroporphyrins –
Diverse Macrocycles, Unrealized Opportunities**

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Scaling of reaction steps for cRME calculations.

Considering steps 8 and 9 in the chlorophyll *a* synthesis, the reported scale is as follows:

Step 8:

Reactants = 100 g of compound **7**, 32.5 g of CH₃NO₂

Product = 77 g of compound **8**

Step 9:

Reactants = 307 g of compound **8**, 51.0 g of NaBH₄

Product = 270.1 g of compound **9**

Because step 9 used 307 g of compound **8** but step 8 only described the synthesis of 77 g of **8**, step 8 must have been carried out multiple times. To calculate the cRME, step 8 needs to be rescaled to match the required amount of **8** in step 9; thus, the rescaled step 8 would give 307 g of product, which requires 399 g of **7** and 130 g of CH₃NO₂. The cRME for these two steps is given in equation S1 (amounts are given in grams):

$$\begin{aligned} cRME_8^9 &= \frac{\text{step 9 product mass}}{\sum_{i=8}^{i=9} (\text{mass of newly added material in step } i)} \\ &= \frac{270.1}{51.0 + 399 + 130} = 46.5\% \end{aligned} \tag{S1}$$