

# CHEMPHOTOCHEM

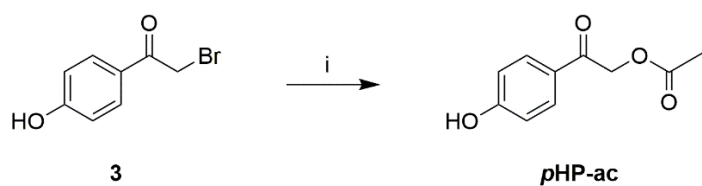
## Supporting Information

### **Coumarin-4-ylmethyl- and *p*-Hydroxyphenacyl-Based Photoacid Generators with High Solubility in Aqueous Media: Synthesis, Stability and Photolysis**

Karishma K. Adatia, Thomas Halbritter, Matiss Reinfelds, Andre Michele, Michael Tran, Sabine Laschat, Alexander Heckel, Günter E. M. Tovar,\* and Alexander Southan\*© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.

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## Supporting information



Scheme S 1: Synthesis of *p*-hydroxyphenylacetate (*p*HP-ac).<sup>1</sup> i) AcOH, NaOAc, H<sub>2</sub>O, 90 °C, 3 h, 73 %.

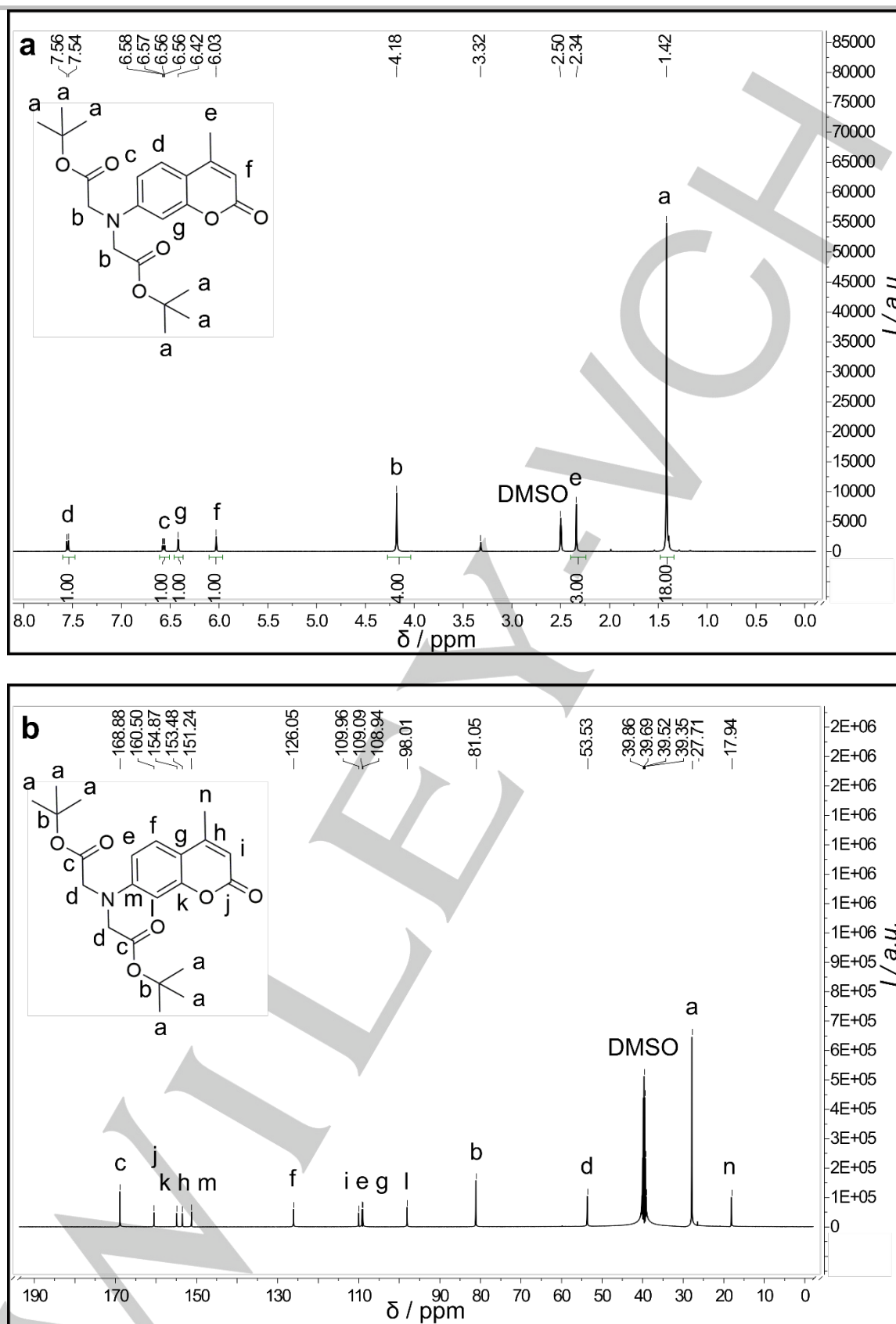


Figure S 1. a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 7-[bis(*tert*-butylcarboxymethyl)amino]-4-(methyl)coumarin (**1a**).

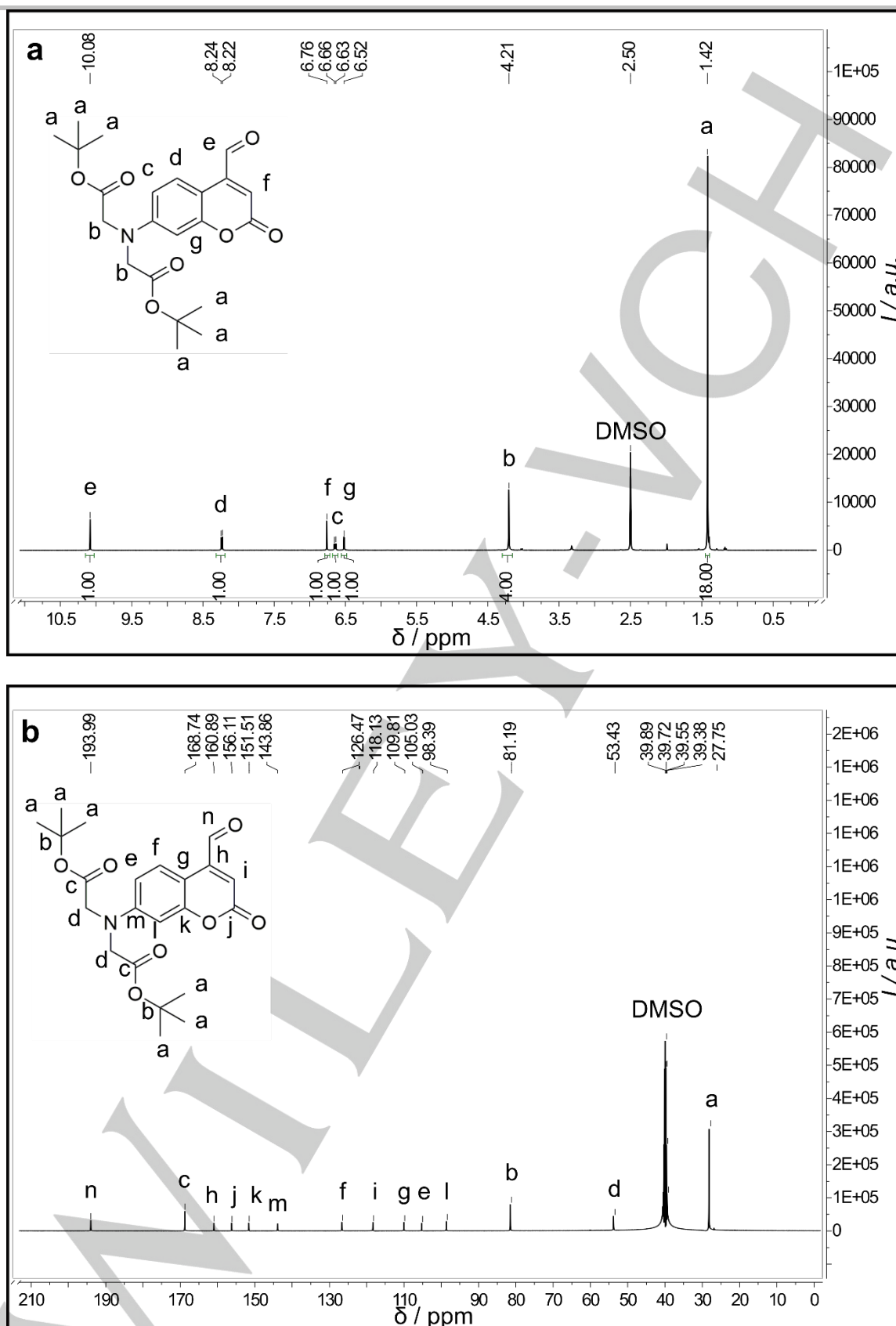


Figure S 2. a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 7-[bis(*tert*-butylcarboxymethyl)amino]-4-(formylmethyl)coumarin (1b).

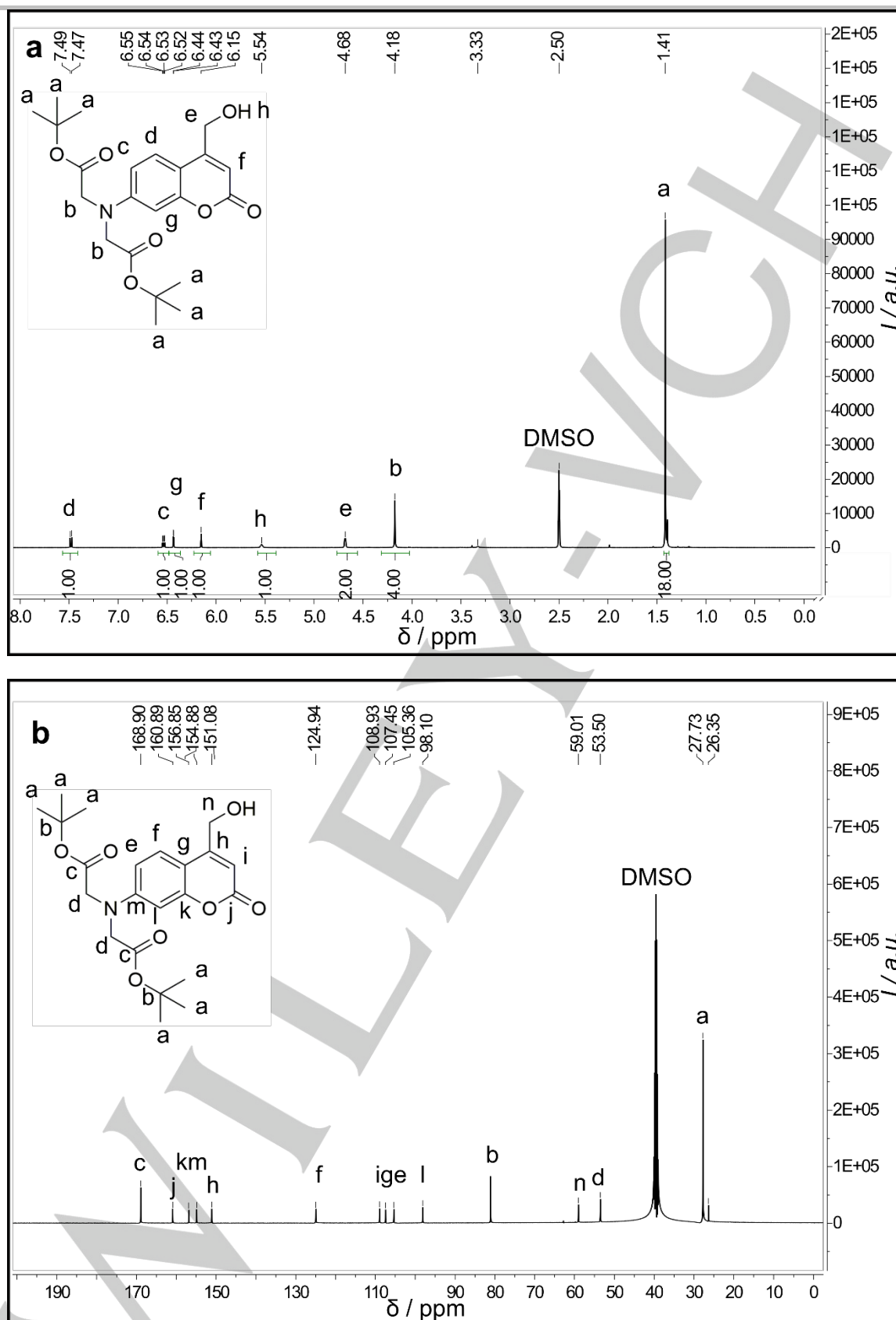


Figure S 3. a) <sup>1</sup>H NMR spectrum and b) <sup>13</sup>C NMR spectrum of 7-[bis(*tert*-butylcarboxymethyl)amino]-4-(hydroxymethyl)coumarin (1c).

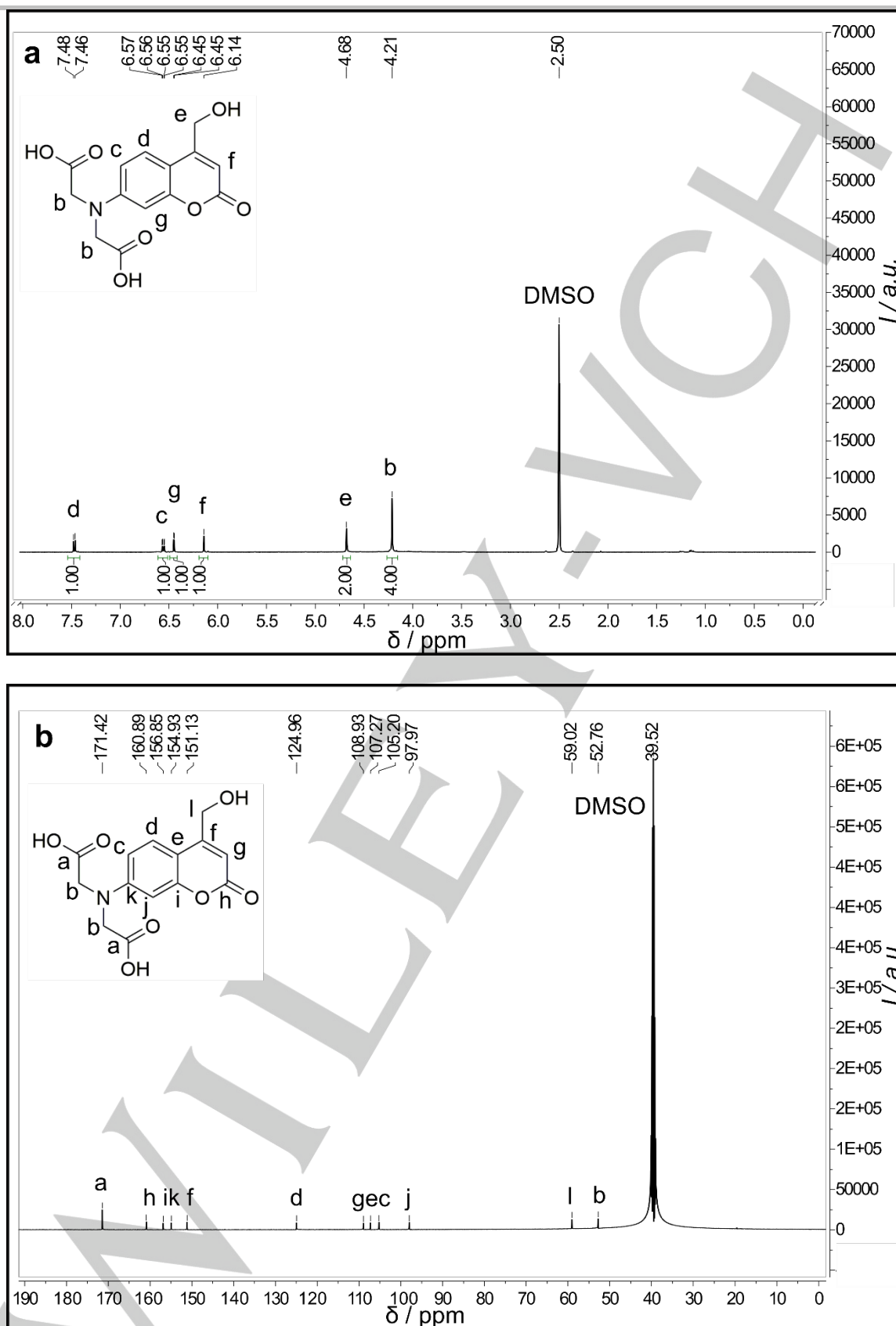


Figure S 4. a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 7-bis(carboxymethyl)amino-4-(hydroxymethyl)coumarin (**1d**).

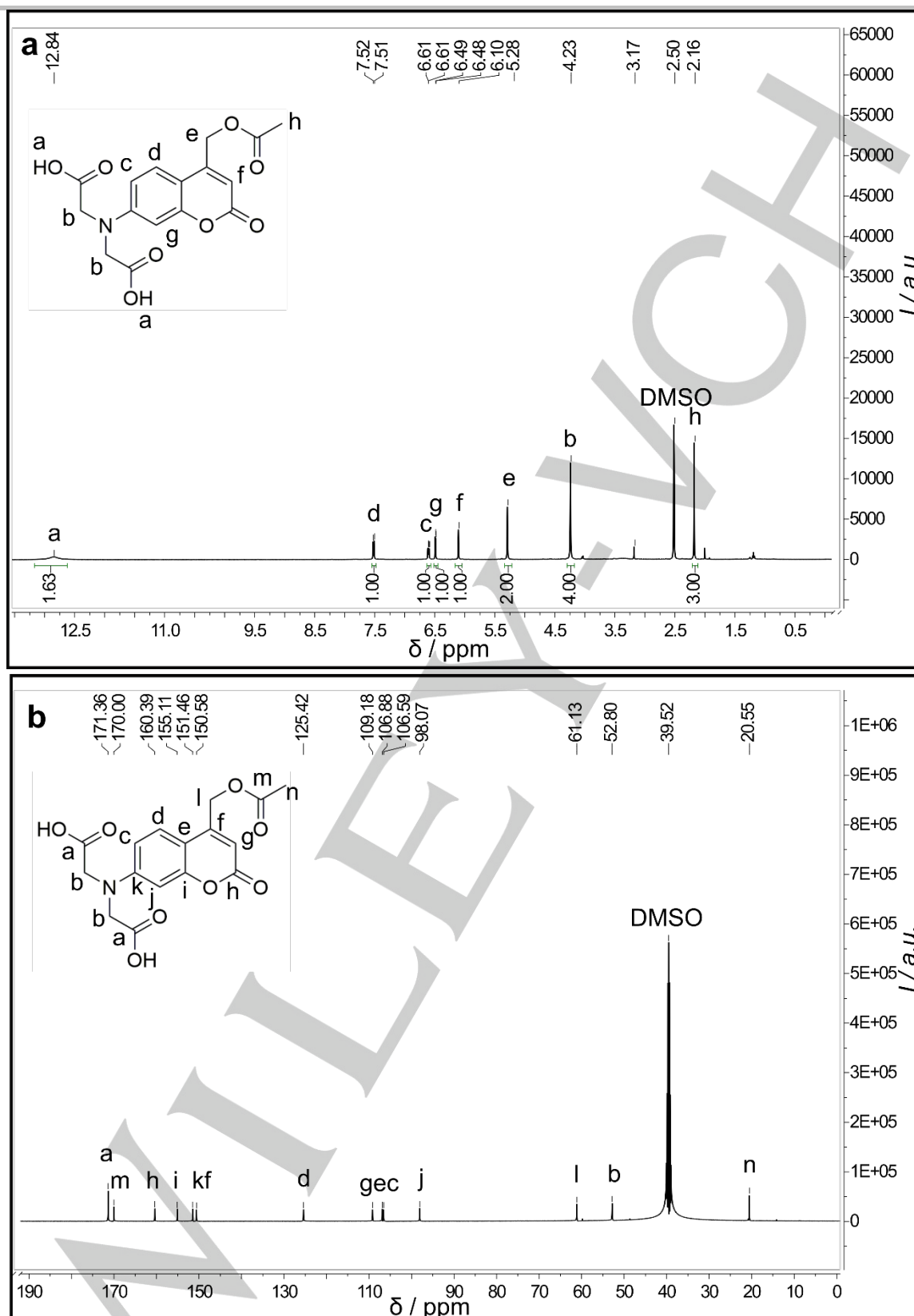


Figure S 5. a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 7-[bis(carboxymethyl)amino]-4-(acetoxymethyl)coumarin (c4m-ac).

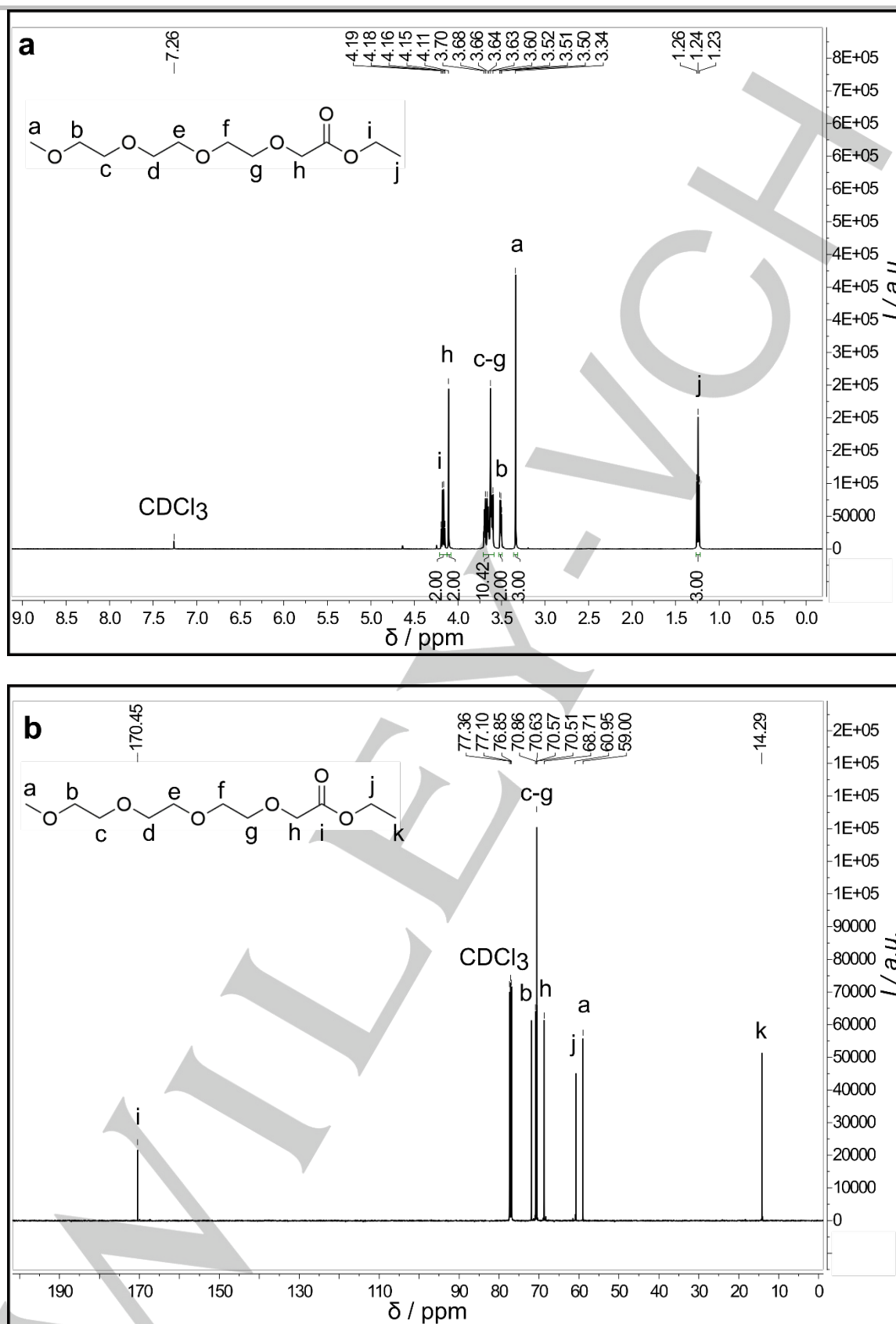


Figure S 6.  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of ethyl-2,5,8,11-tetraoxatridecan-13-oate (**2a**).



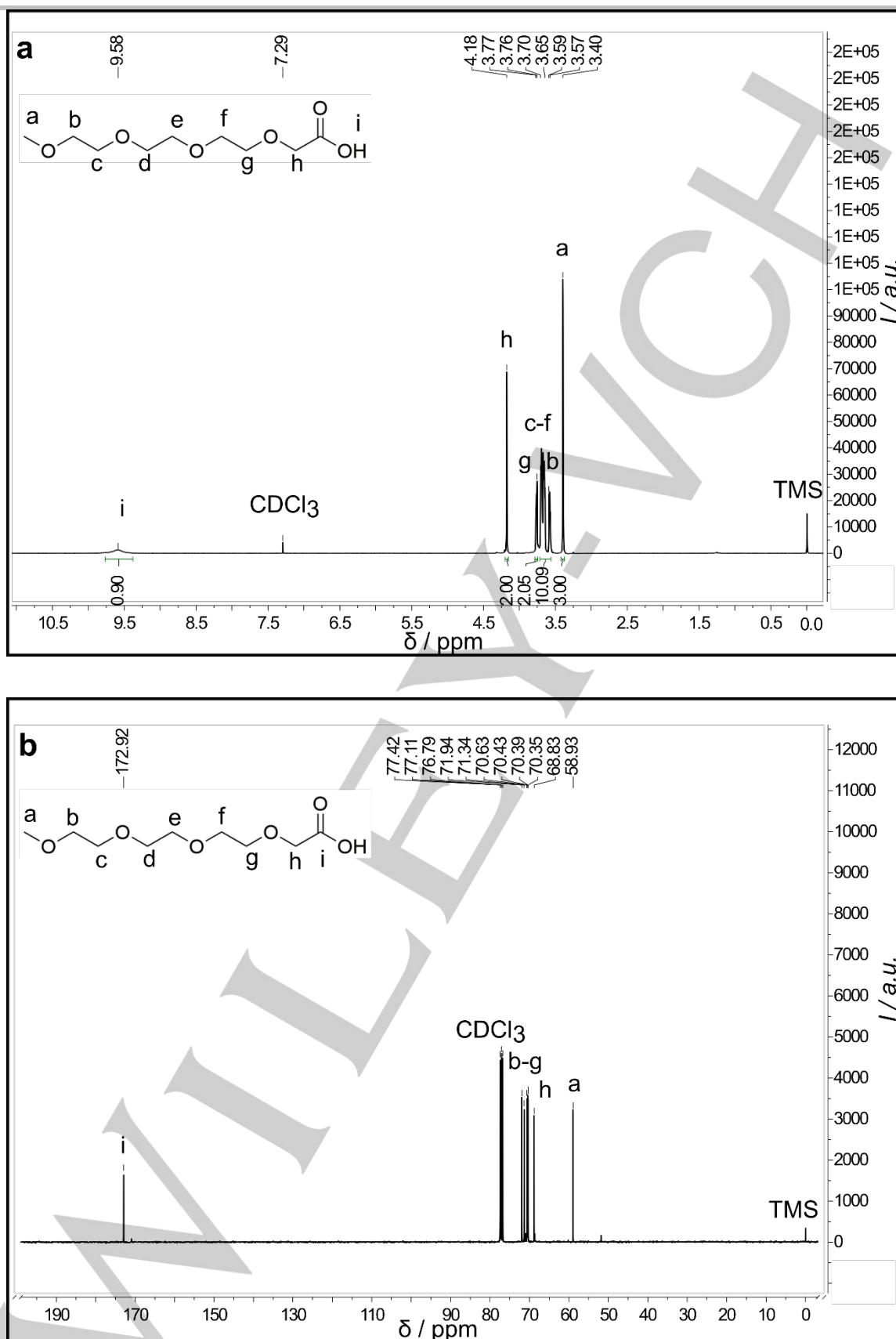


Figure S 7.  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 2,5,8,11-tetraoxatridecan-13-oic acid (**2b**).

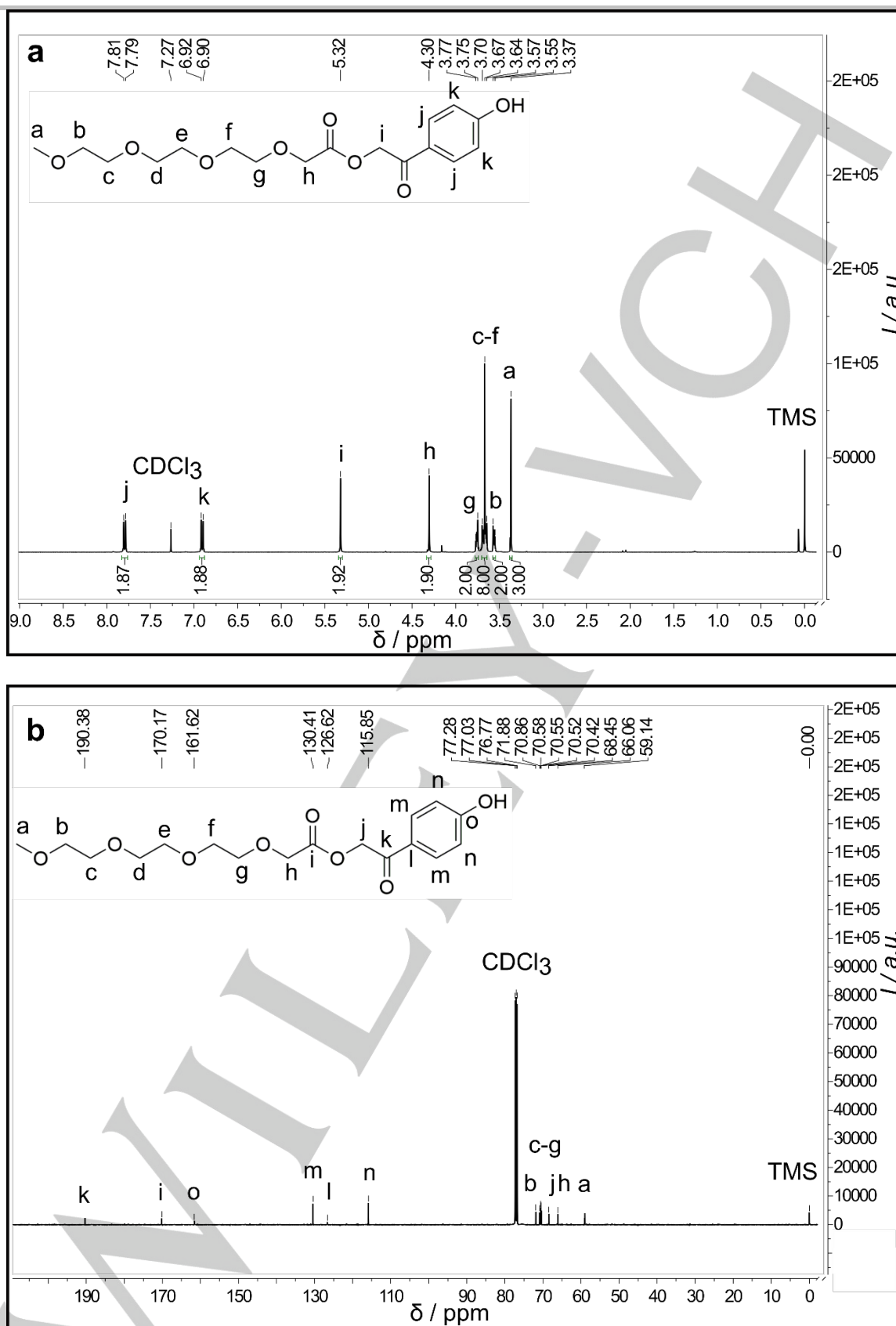
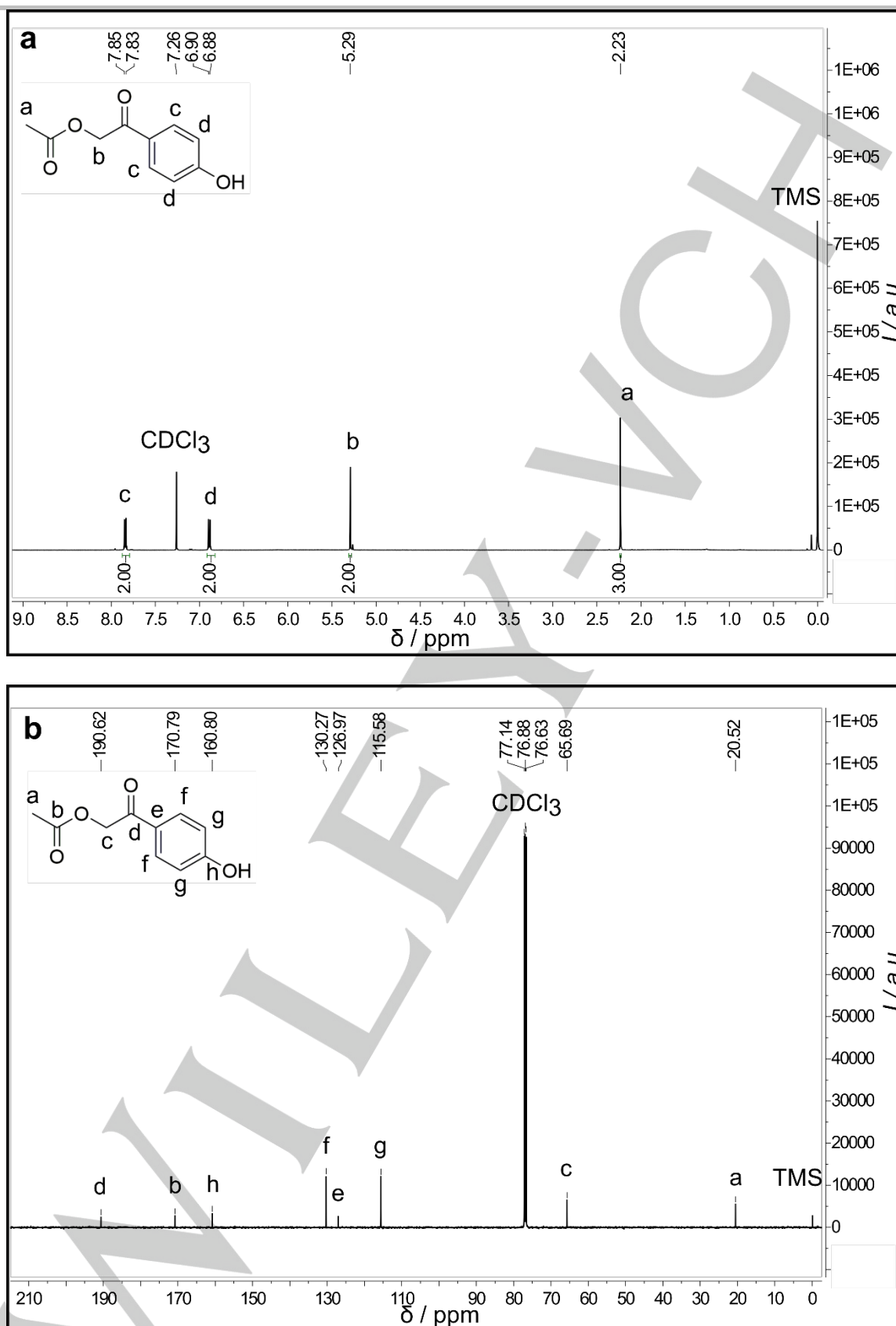
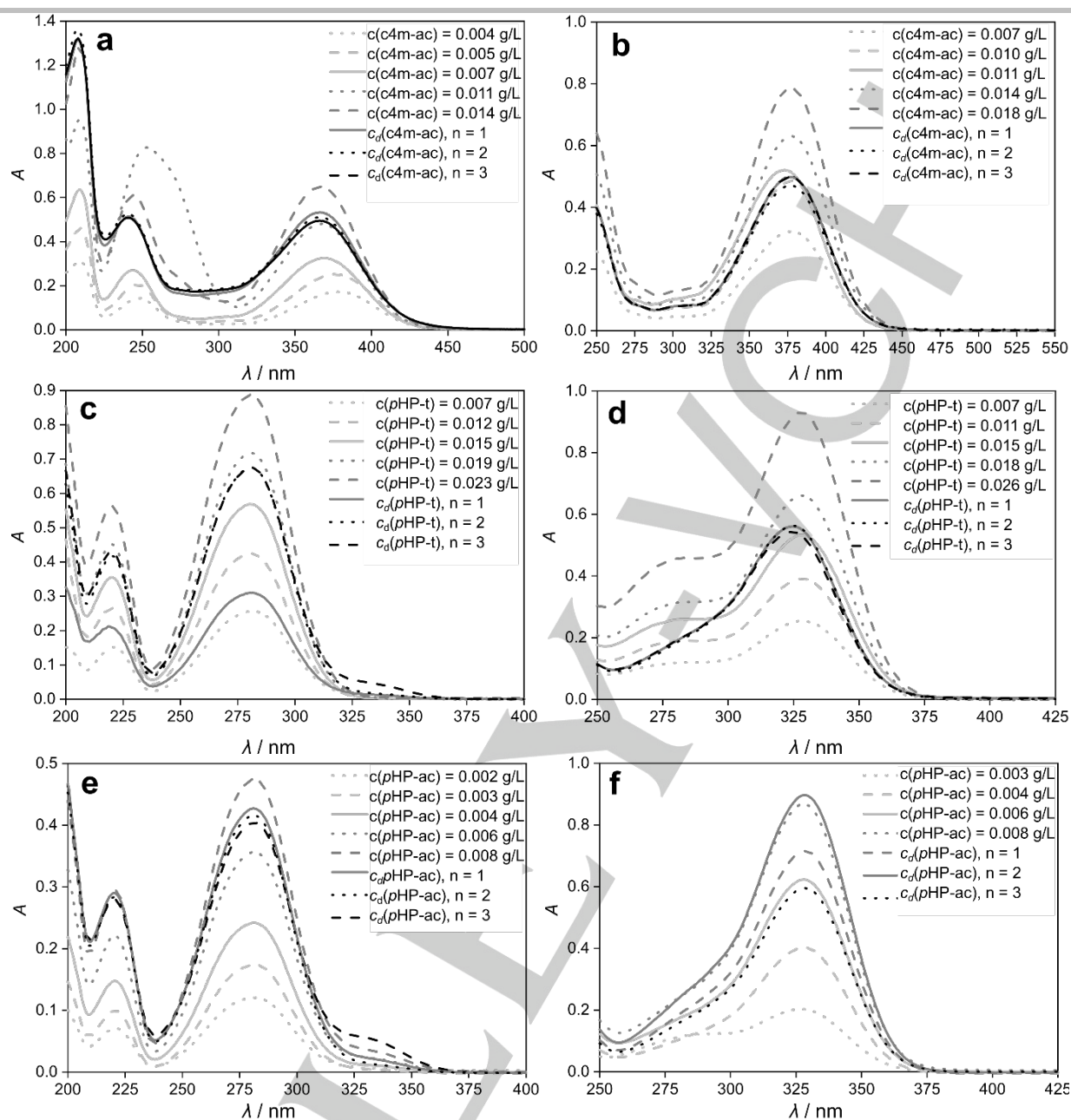


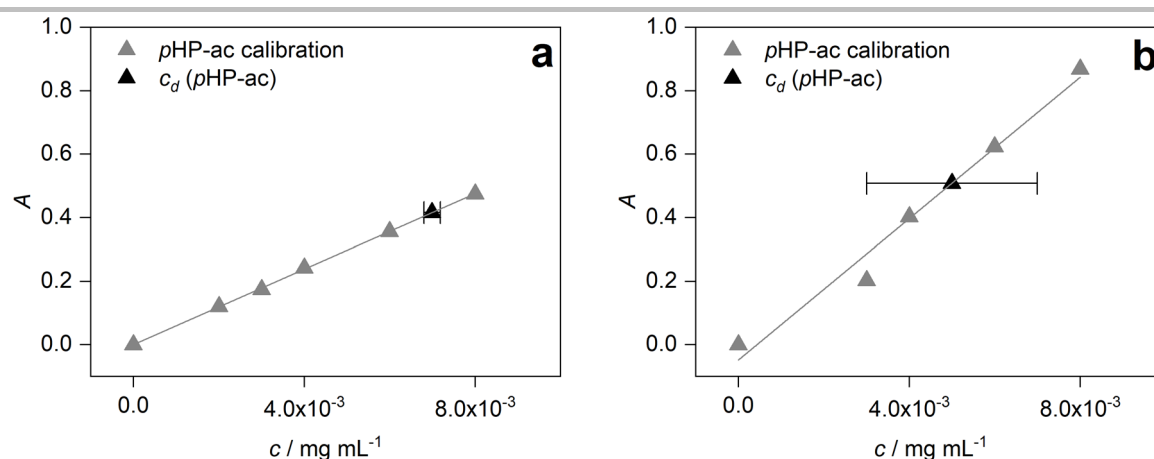
Figure S 8. a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum of 2-(4-hydroxyphenyl)-2-oxoethyl-2,5,8,11-tetraoxatridecan-13-oate (pHP-t).



**Figure S 9.** a) <sup>1</sup>H NMR spectrum and b) <sup>13</sup>C NMR spectrum of *p*-hydroxyphenylacetate (pHP-ac). The labile phenoxide proton is not always visible in the <sup>1</sup>H NMR spectrum.



**Figure S 10.** UV Vis spectra for the calibration and determination of the maximum solubility of c4m-ac, pHP-t and pHP-ac in a), c), e) water as well as in b), d), f) alkaline solution. The diluted samples for the determination of maximum solubility ( $c_{\max,d}$ ) were measured in triplicates ( $n = 3$ ).



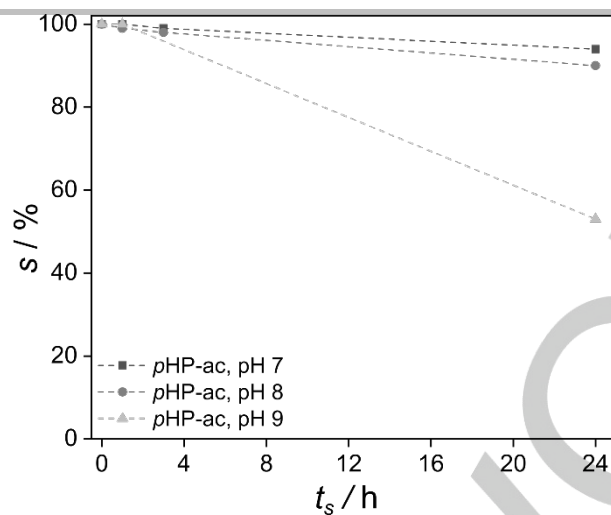
**Figure S 11.** Photometric determination of the solubility ( $c_{max}$ ) of pHP-ac in a) water as well as in b) alkaline solution at pH 9.  $c_{max}$  is calculated according to equation 2. The diluted concentration ( $c_d$ ) with the respective dilution factor ( $d_i$ ) are summarized in Table S 1. Fehler! Verweisquelle konnte nicht gefunden werden..

**Table S 1.** Diluted concentrations  $c_d$  and dilution factor  $d_i$  of the photoacid generators c4m-ac, pHP-t and pHP-ac. The subscript 'w' indicates measurements in water and 'a' refers to alkaline solution.

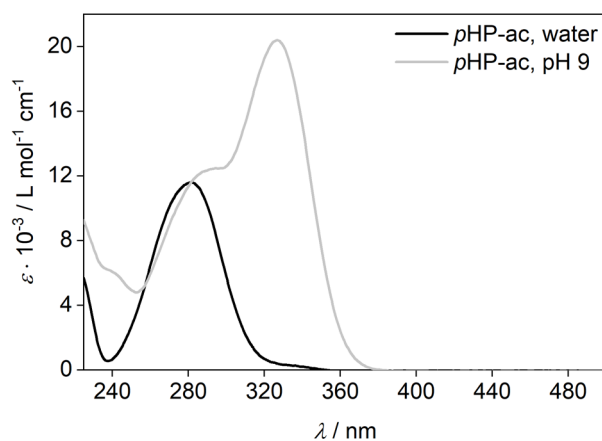
| PAG    | $d_{f,w}$ | $c_{d,w}$ [g L <sup>-1</sup> ] | $d_{f,a}$ | $c_{d,a}$ [g L <sup>-1</sup> ] |
|--------|-----------|--------------------------------|-----------|--------------------------------|
| c4m-ac | 86        | 0.01                           | 20 000    | 0.01                           |
| pHP-t  | 2 500     | 0.02                           | 800       | 0.02                           |
| pHP-ac | 400       | 0.01                           | 833       | 0.01                           |

**Table S 2.** Stabilities (s) of the photoacid generators (PAG) c4m-ac, pHP-t and pHP-ac after 1 h ( $s_{1h}$ ), 3 h ( $s_{3h}$ ) and 24 h ( $s_{24h}$ ) at pH 7, pH 8, and pH 9, as well as in water without pH adjustment after dissolution. The stabilities were determined via HPLC. n.d. = not determined.

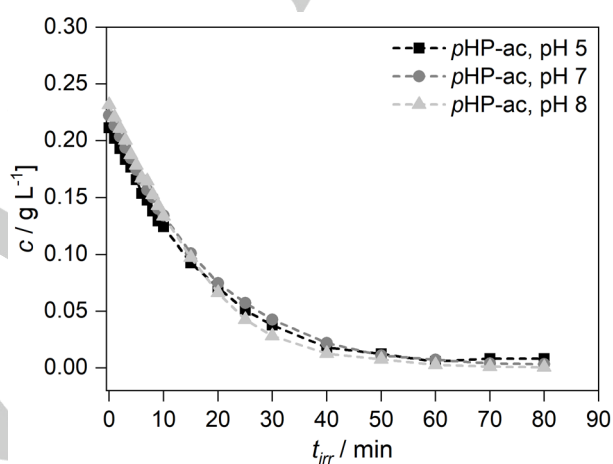
| PAG    | pH | $s_{1h}$ [%] | $s_{3h}$ [%] | $s_{24h}$ [%] |
|--------|----|--------------|--------------|---------------|
| c4m-ac | 3  | 100          | 100          | 100           |
| c4m-ac | 7  | 100          | 99           | 99            |
| c4m-ac | 8  | 100          | 95           | 96            |
| c4m-ac | 9  | 96           | 90           | 11            |
| pHP-t  | 6  | 97           | 96           | 95            |
| pHP-t  | 7  | 92           | 90           | 85            |
| pHP-t  | 8  | 73           | 65           | 48            |
| pHP-t  | 9  | 56           | 17           | 0             |
| pHP-ac | 5  | 100          | 100          | 99            |
| pHP-ac | 7  | 100          | 99           | 94            |
| pHP-ac | 8  | 99           | 99           | 94            |
| pHP-ac | 9  | 100          | n.d.         | 53            |



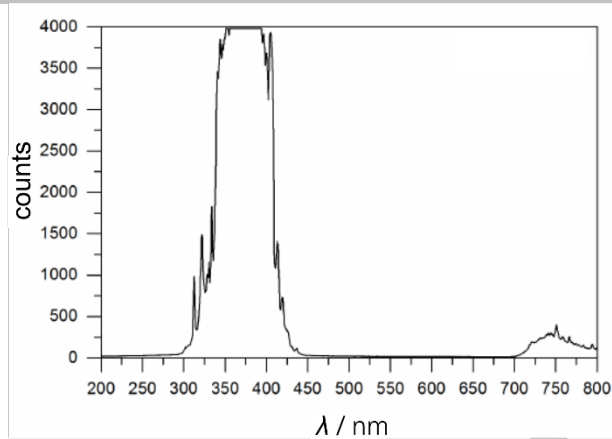
**Figure S 12.** HPLC determined stabilities ( $s$ ) of  $p\text{HP-ac}$  after a storage time ( $t_s$ ) of 1 h, 3 h and 24 h at pH 7, pH 8 and pH 9.. The lines are only for the guidance of the eye.



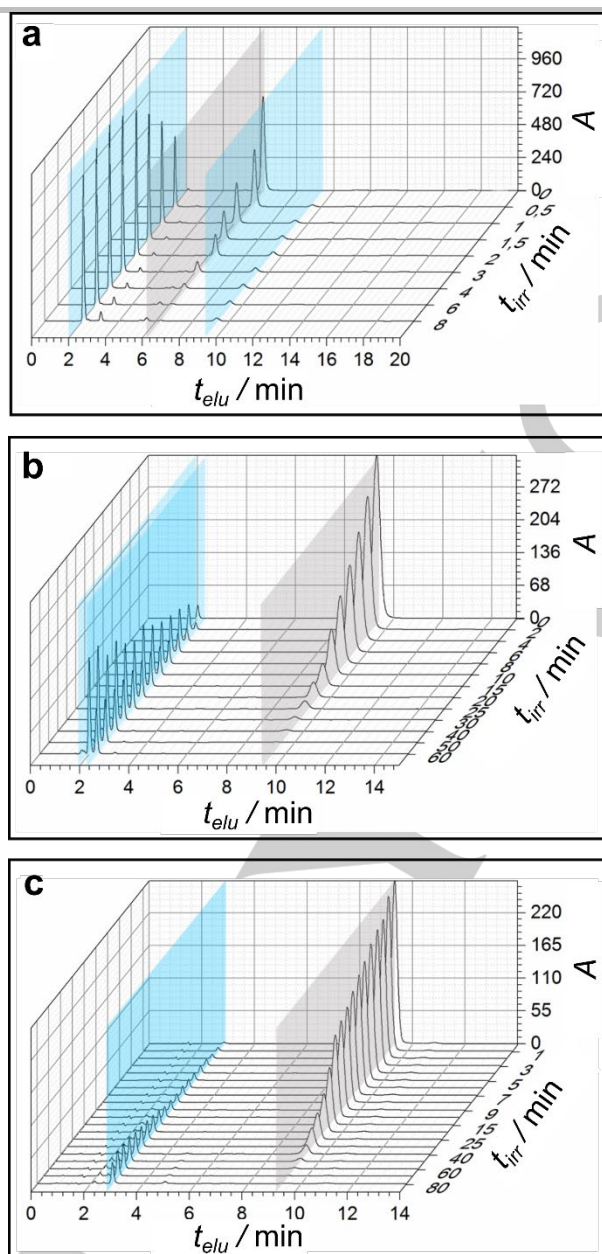
**Figure S 13.** UV-vis spectra of  $p\text{HP-ac}$  in water and alkaline solution at pH 9.



**Figure S 14.** Photolysis under UV irradiation of  $p\text{HP-ac}$  in water (pH 5), neutral (pH 7) and alkaline conditions (pH 8). The lines are only for the guidance of the eye

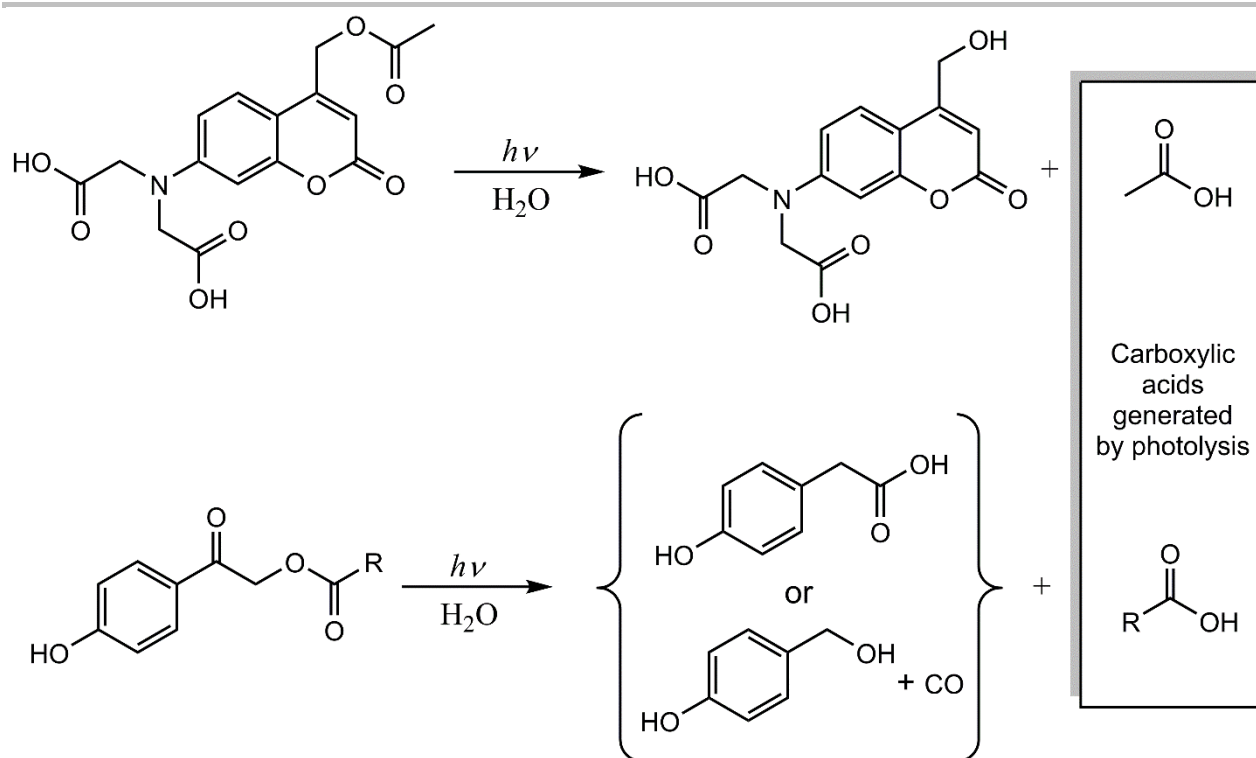


**Figure S 15.** Emission spectrum of a UV-H 255 UV chamber from Hartmann Feinwerkbau GmbH for the photolysis experiments.



**Figure S 16.** HPLC monitored photolysis of a) c4m-ac, b) pHP-t and c) pHP-ac under UV irradiation.  $t_{elu}$  is the elution time during the HPLC measurement,  $t_{irr}$  is the irradiation time under UV light and A is the absorbance at the respective wavelength. The absorbance of c4m-ac is shown at 360 nm and of pHP-t and pHP-ac at 300 nm. The photoacid generator is marked in gray and the photolysis products are marked in blue.





**Figure S 17.** Reaction pathways for the photolysis of c4m-ac (top) and pHP-ac as well as pHP-t (bottom). By photolysis, carboxylic acids are obtained, as depicted on the right.