

Supplementary Material

Synthesis of C4-substituted coumarins via Pechmann condensation catalyzed by sulfamic acid. Insights into the reaction mechanism by HRMS analysis

Maiara C. Moraes,^{a,b} Eder J. Lenardão,^c and Thiago Barcellos^{*a}

^a *Laboratório de Biotecnologia de Produtos Naturais e Sintéticos, Universidade de Caxias do Sul, 95070-560, Caxias do Sul, RS, Brazil*

^b *Instituto Federal de Ciência e Tecnologia do Rio Grande do Sul, Campus Caxias do Sul, 95043-700, Caxias do Sul, RS, Brazil*

^c *LASOL-CCQFA, Universidade Federal de Pelotas – UFPel, P.O. Box 354, 96010 900, Pelotas, RS, Brazil*

Email: thiago.barcellos@ucs.br

Table of Contents

HRMS spectral data of the mechanism elucidation	S2
Copies of the ¹ H and ¹³ C NMR spectra of the coumarins 3a-o	S4

1. HRMS spectral data of the mechanism elucidation

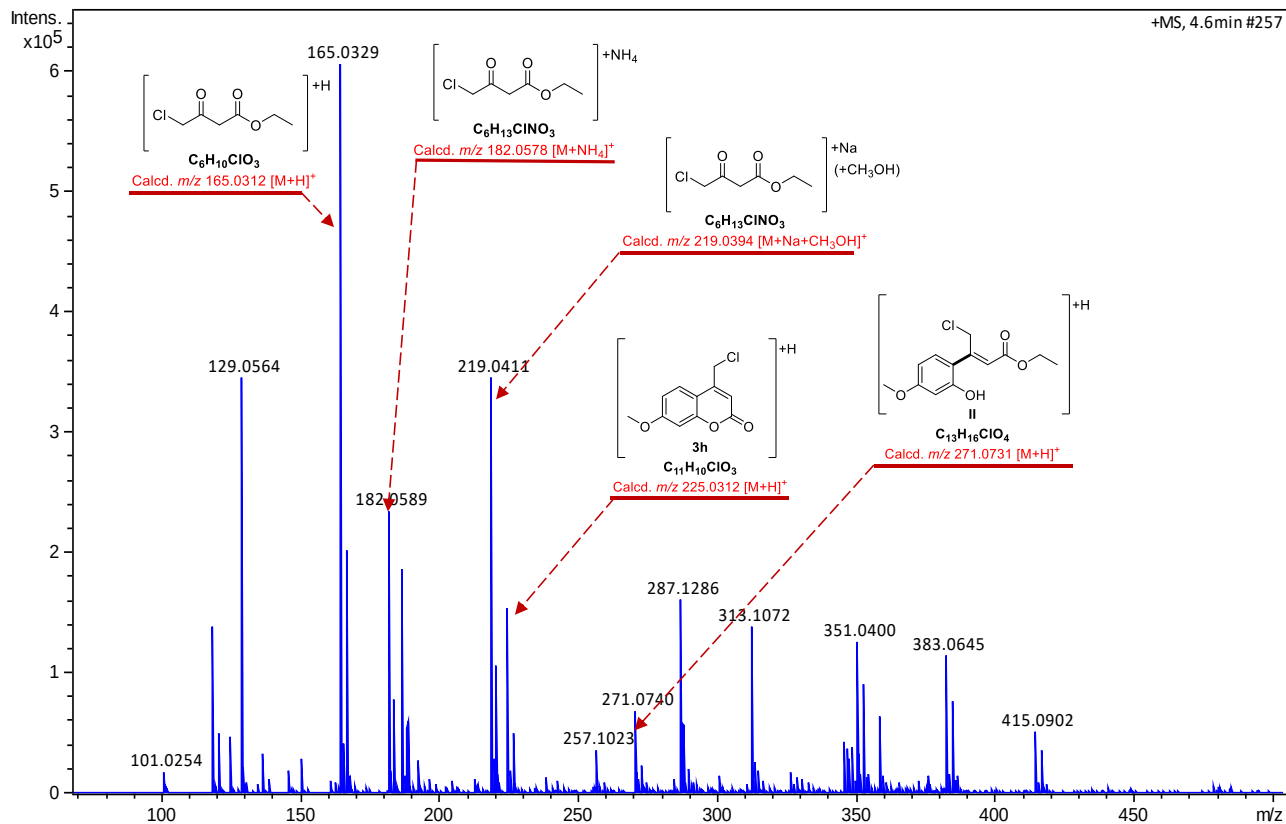
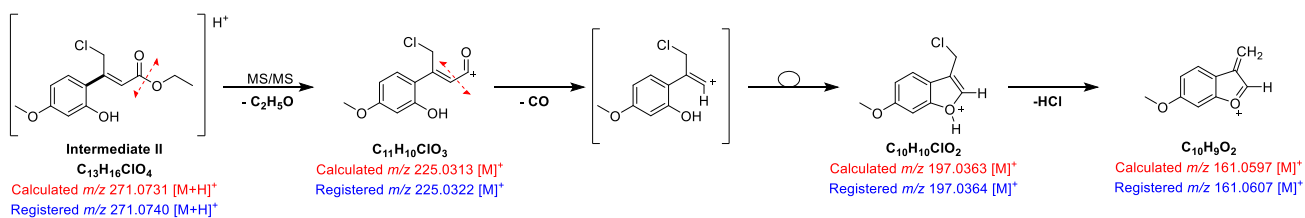


Figure S1. HRMS (ESI+) analysis of an aliquote of the reaction between *m*-cresol and ethyl 4-chloroacetoacetate to afford the coumarin **3h**.



Scheme S1. Plausible fragmentation of intermediate II into the product ion.

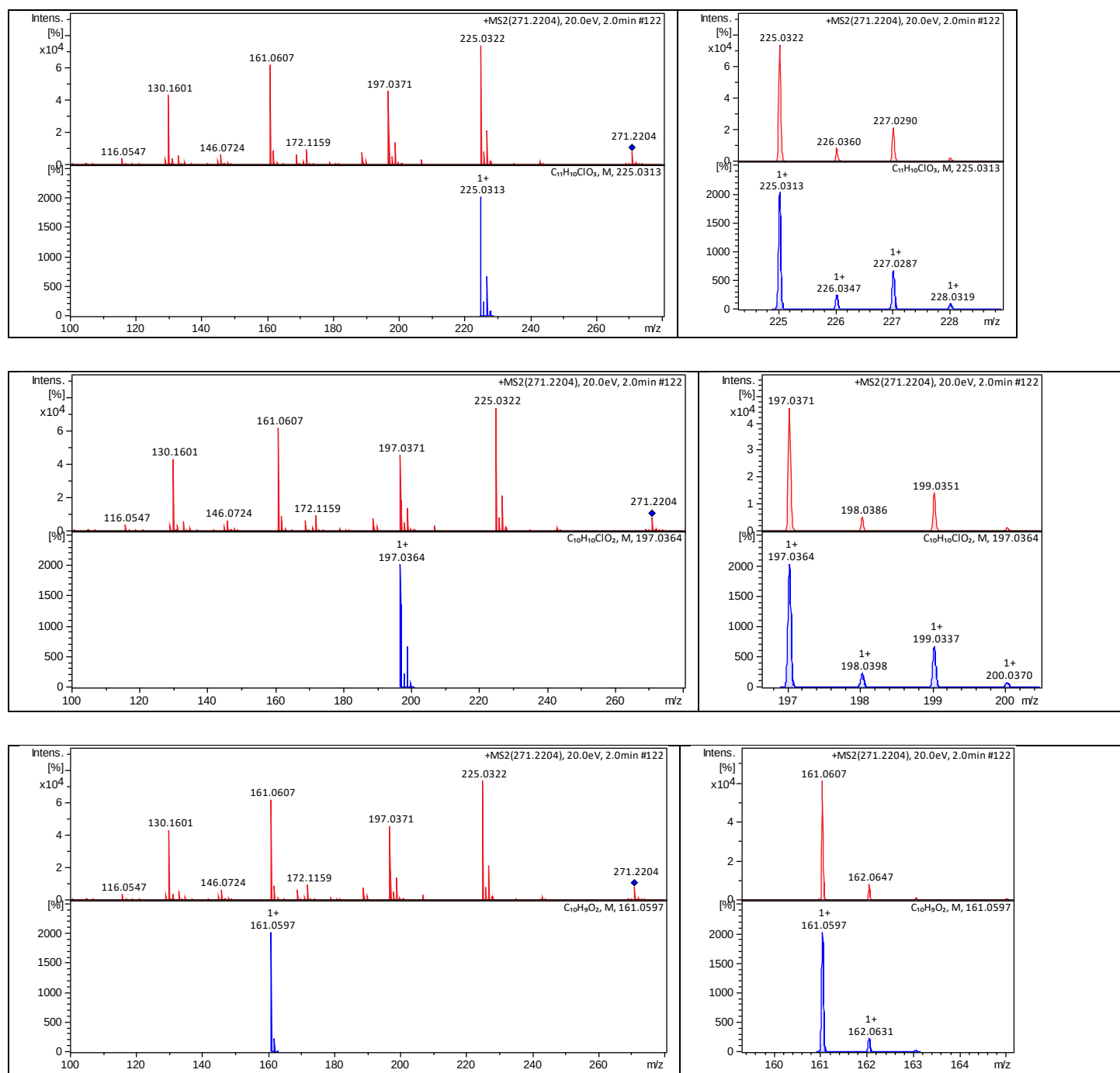
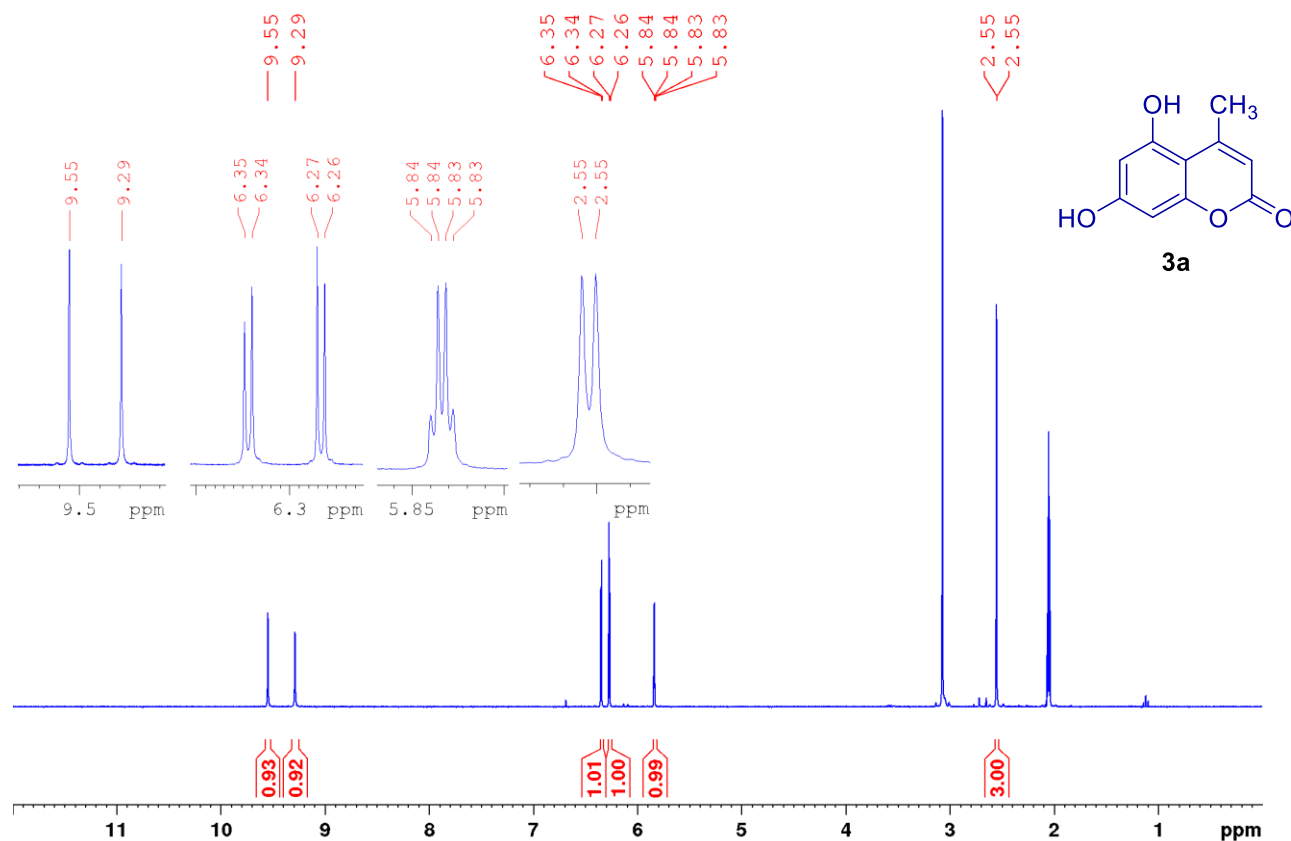
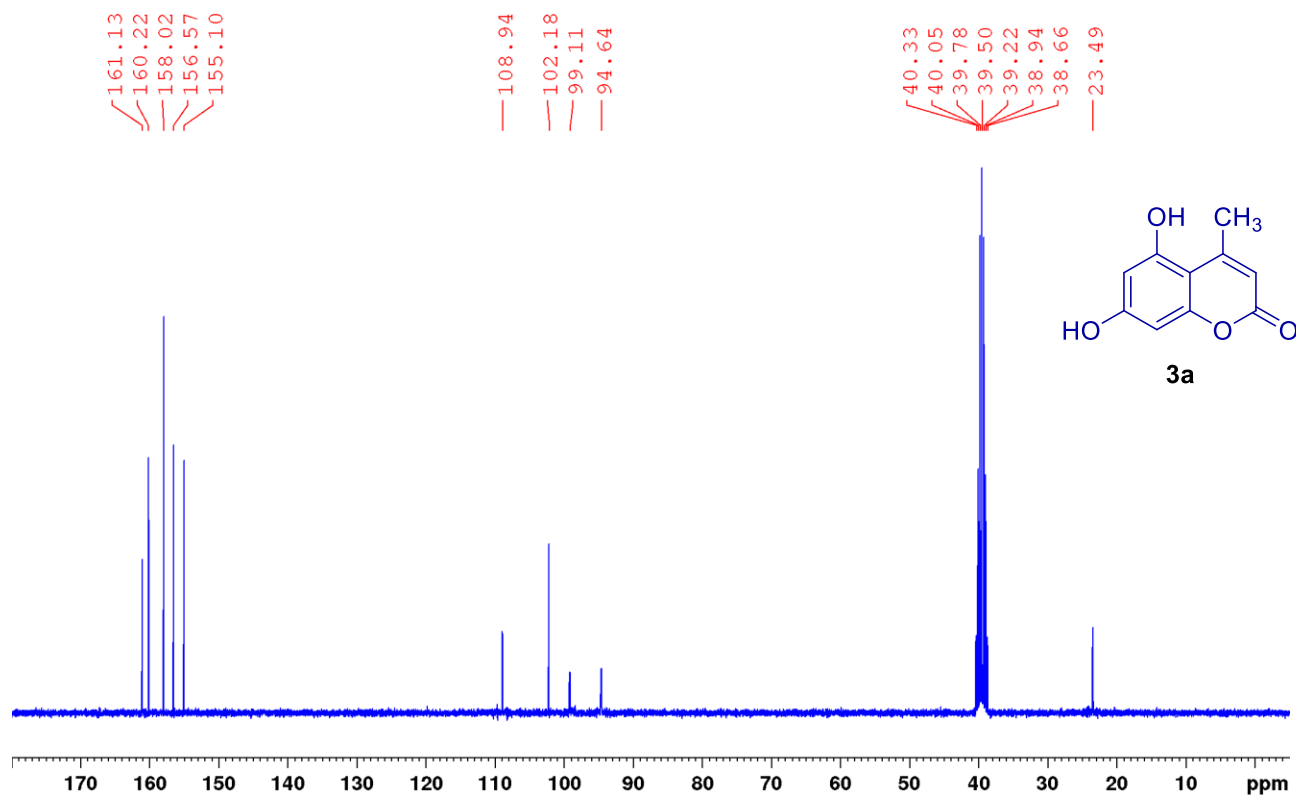


Figure S2. Tandem mass spectrometry (ESI-MS/MS) of the protonated molecule with m/z 271.0740 using N_2 as collision gas at 20 eV.

2. Copies of ^1H and ^{13}C NMR Spectra of products 3a-oFigure S3. ^1H NMR spectrum (300 MHz, acetone- d_6) of the product **3a**.Figure S4. ^{13}C NMR spectrum (75 MHz, DMSO- d_6) of the product **3a**.

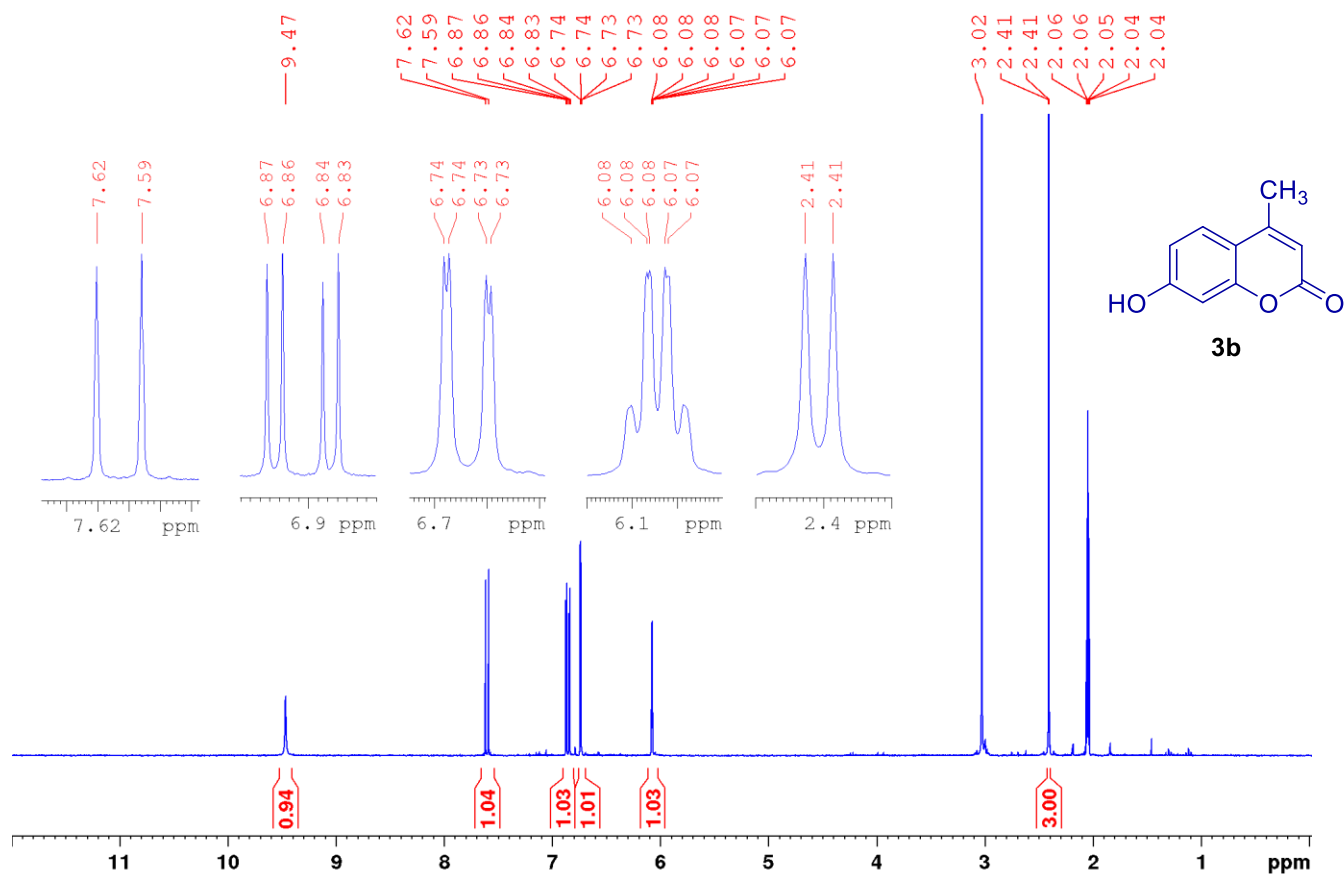


Figure S5. ¹H NMR spectrum (300 MHz, acetone-d₆) of the product **3b**.

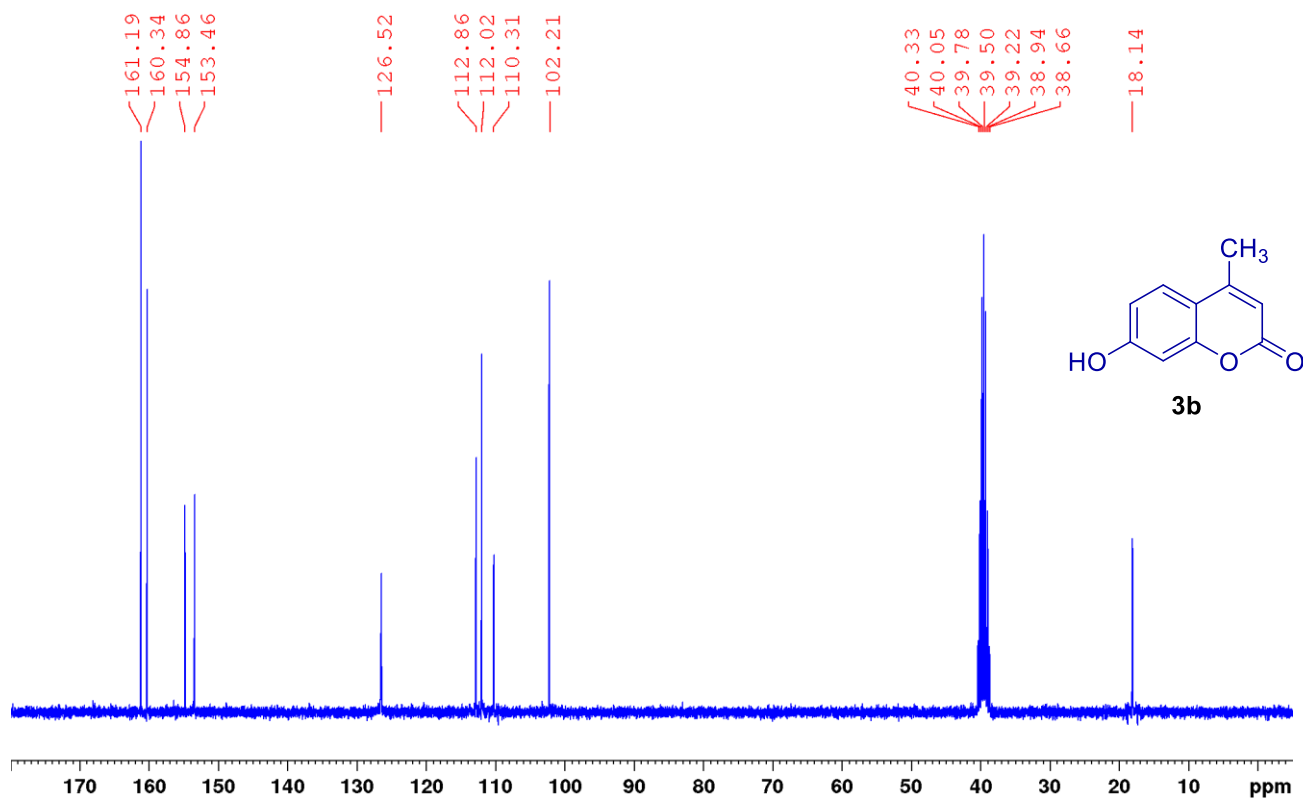


Figure S6. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3b**.

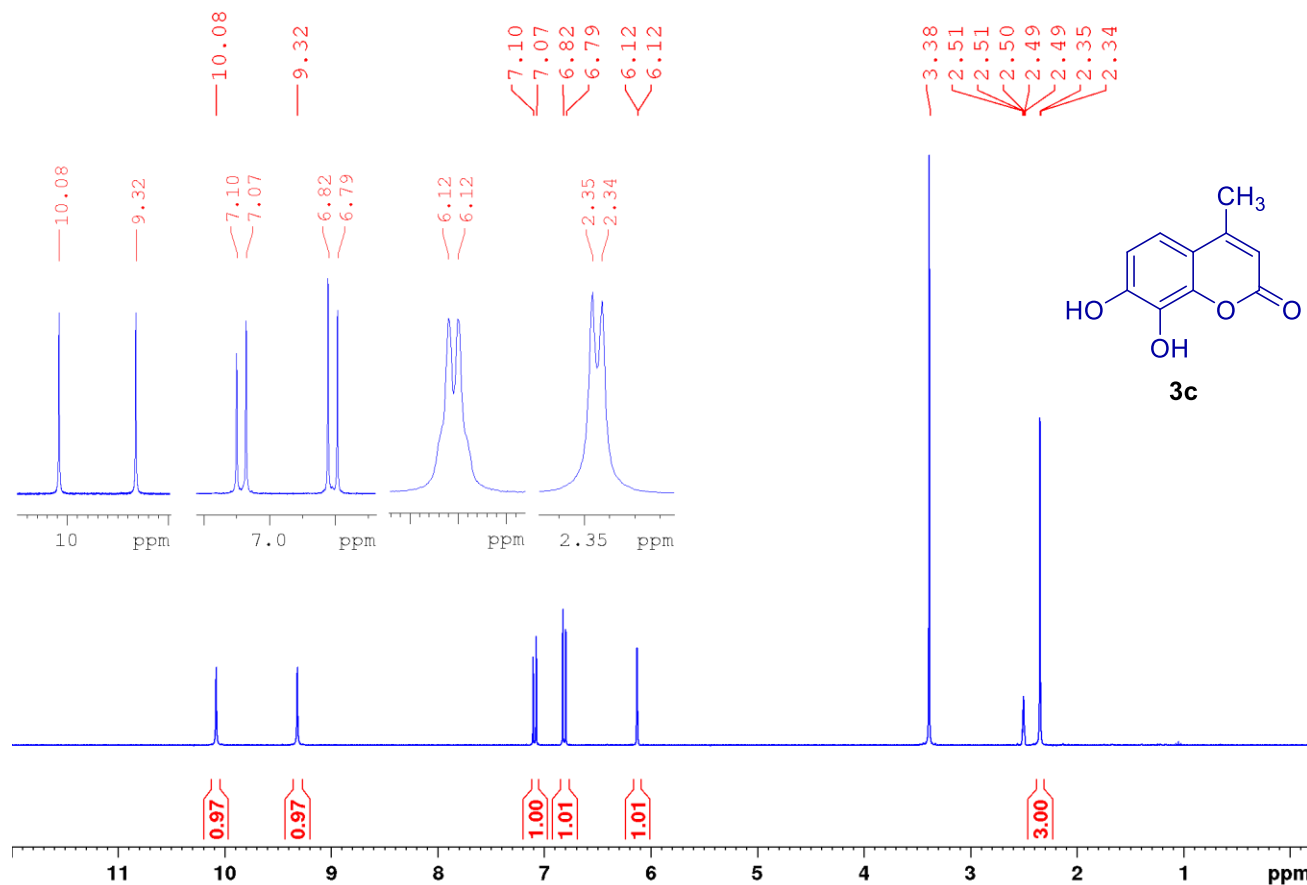


Figure S7. ¹H NMR spectrum (300 MHz, DMSO-d₆) of product **3c**.

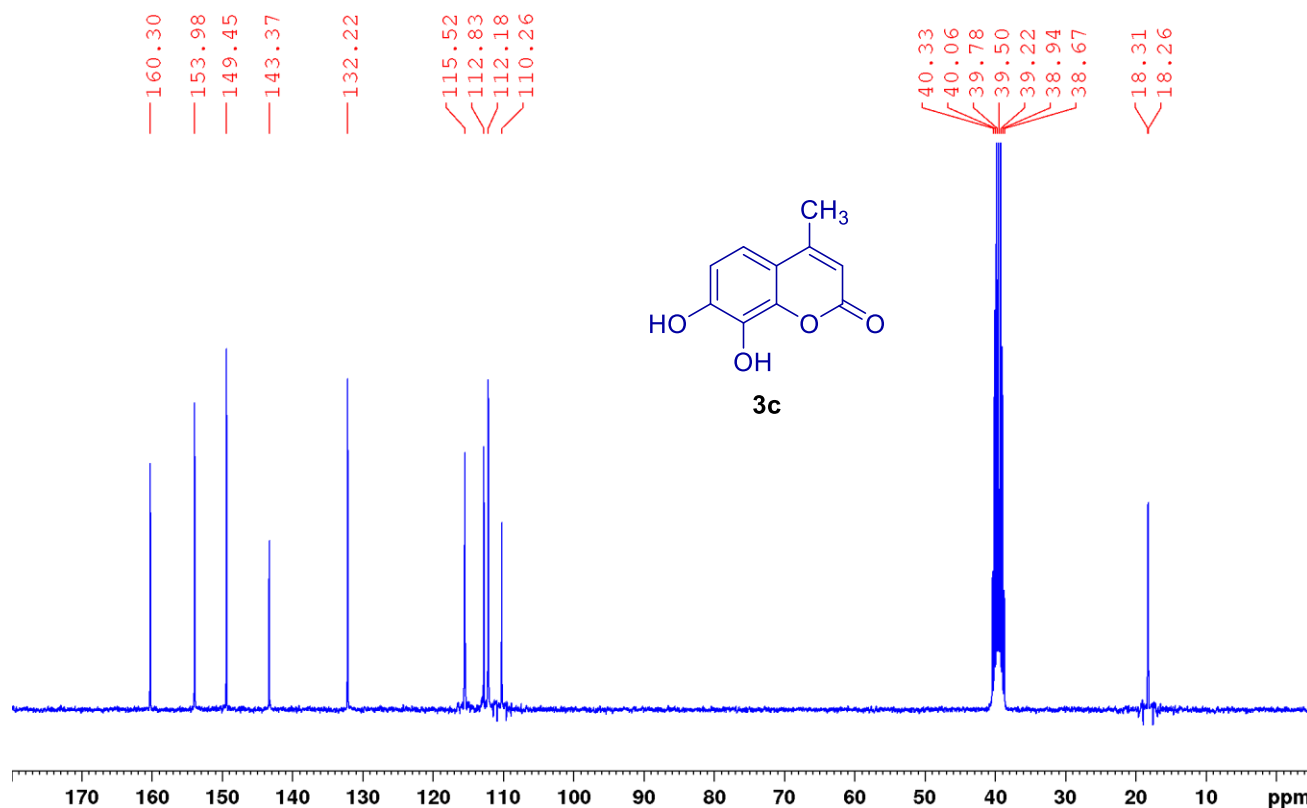


Figure S8. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3c**.

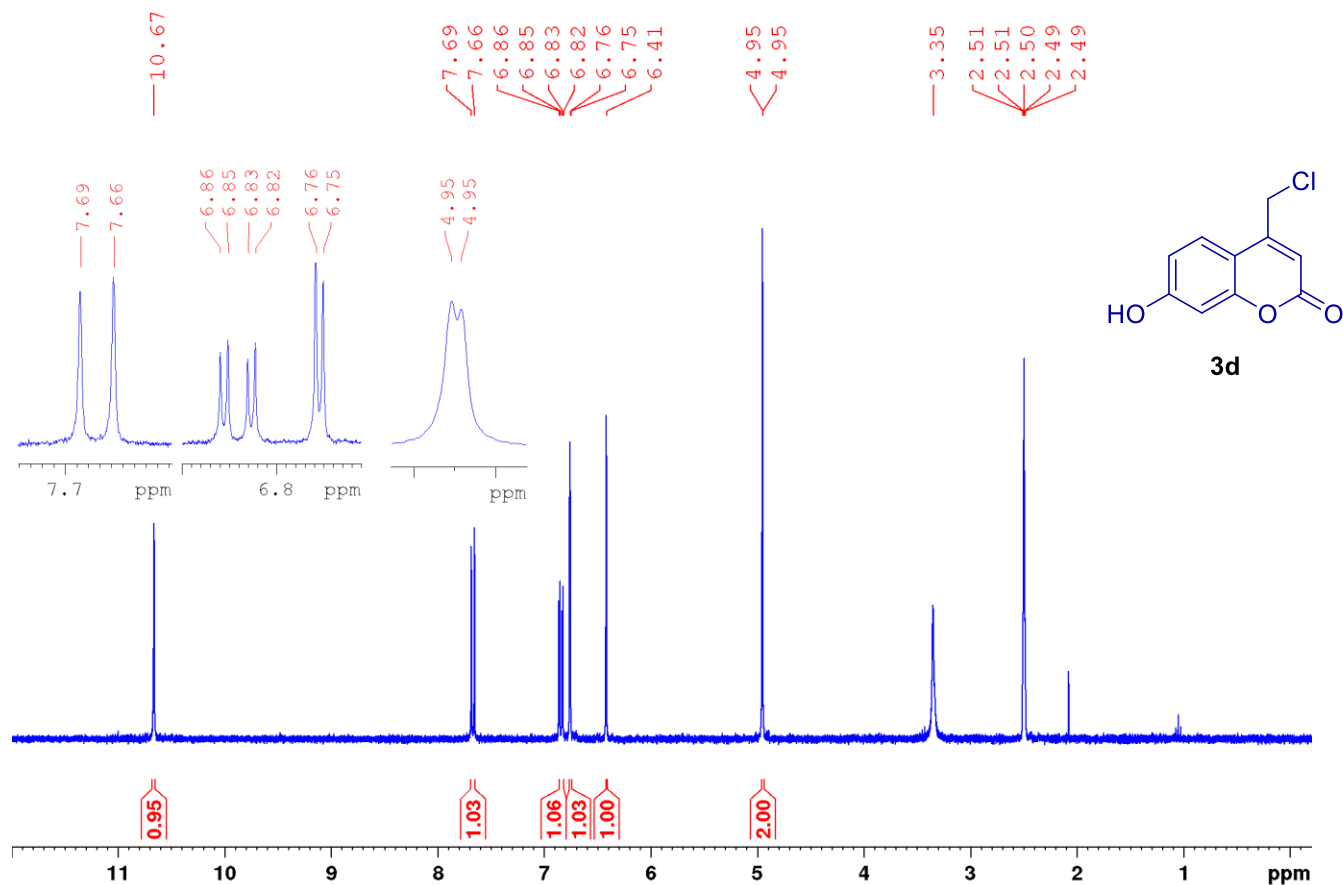


Figure S9. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3d**.

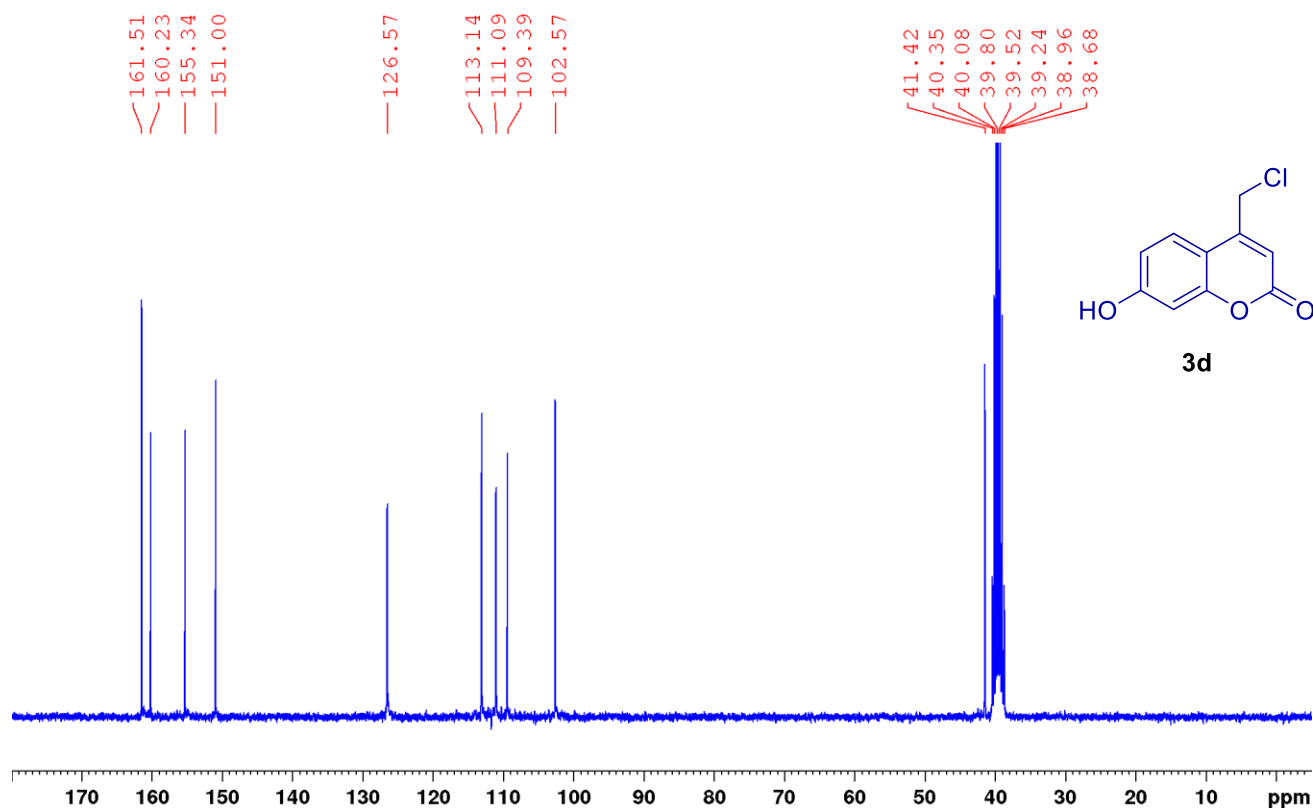


Figure S10. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3d**.

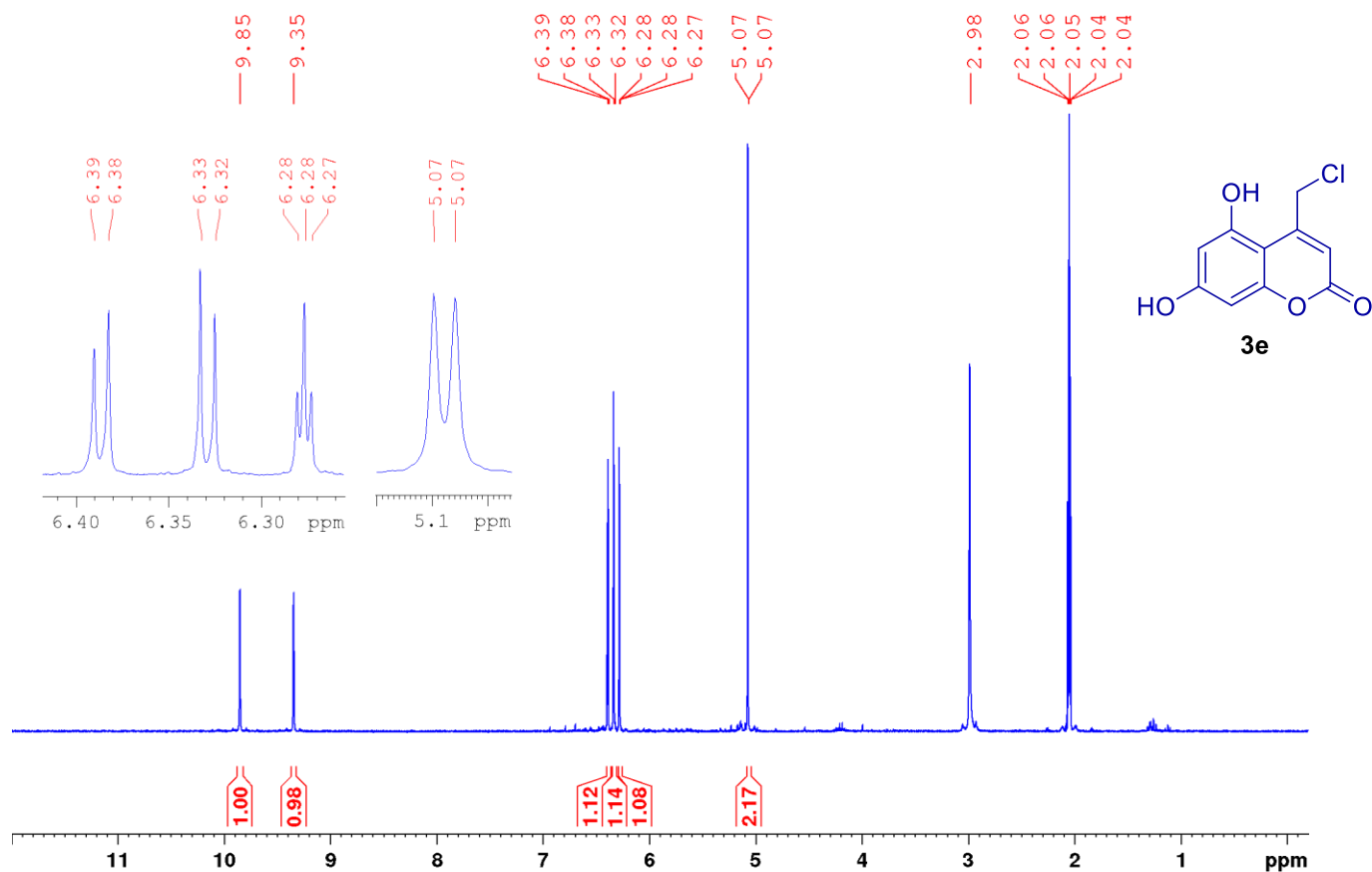


Figure S11. ¹H NMR Spectrum (300 MHz, DMSO-d₆) of the product 3e.

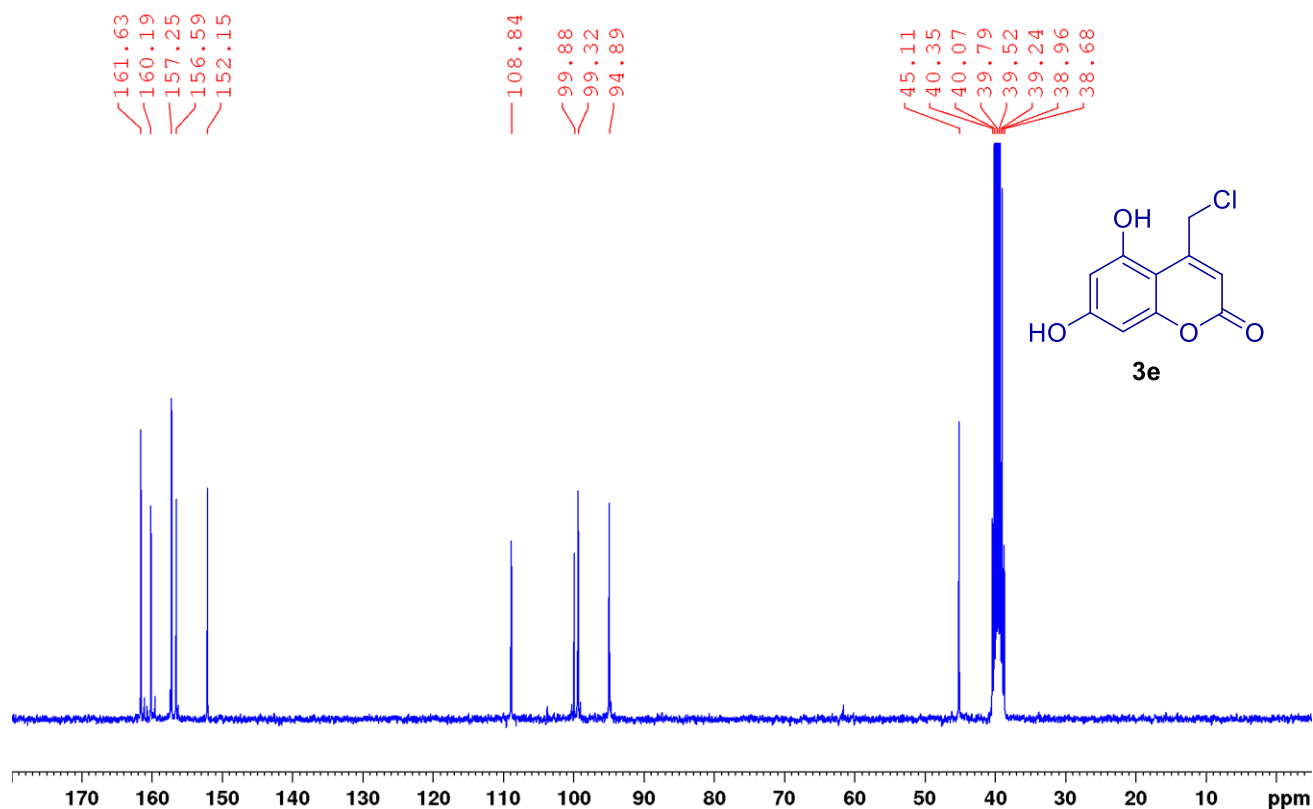


Figure S12. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product 3e.

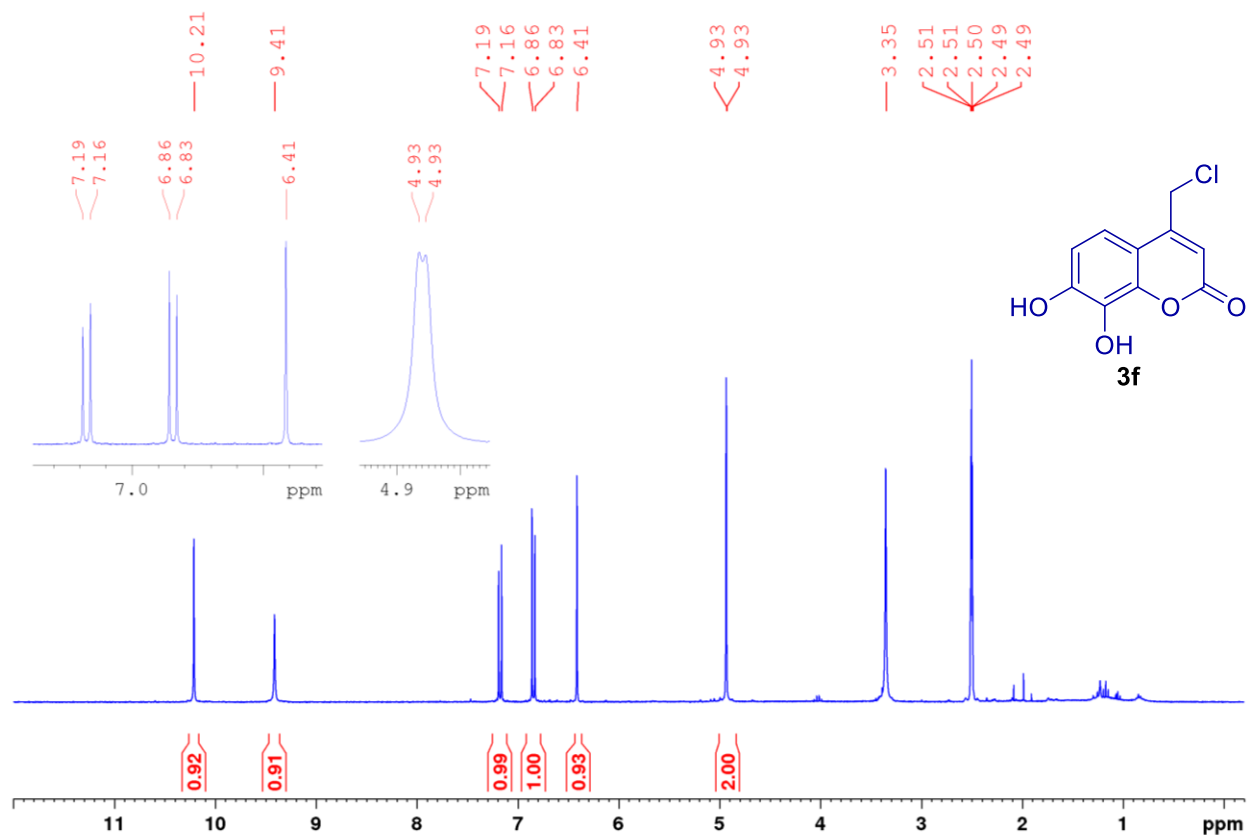


Figure S13. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3f**.

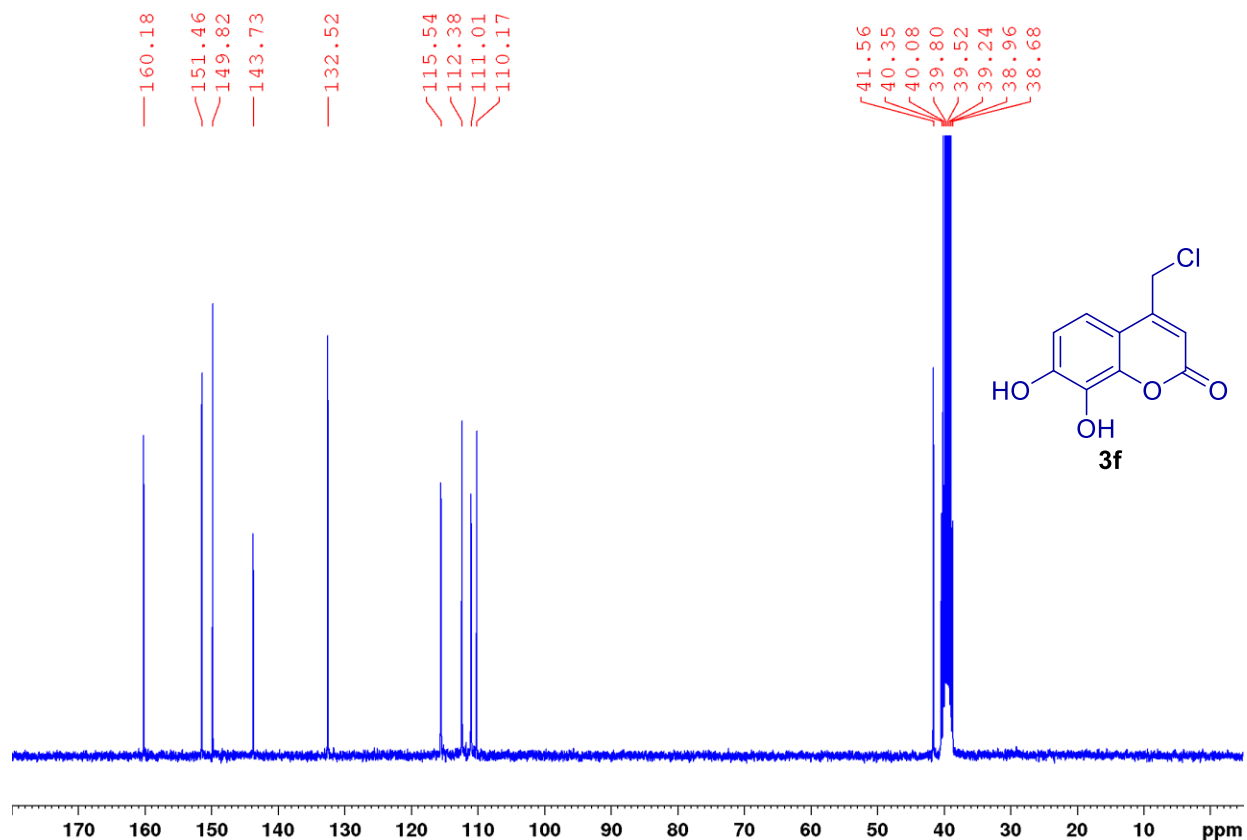


Figure S14. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3f**.

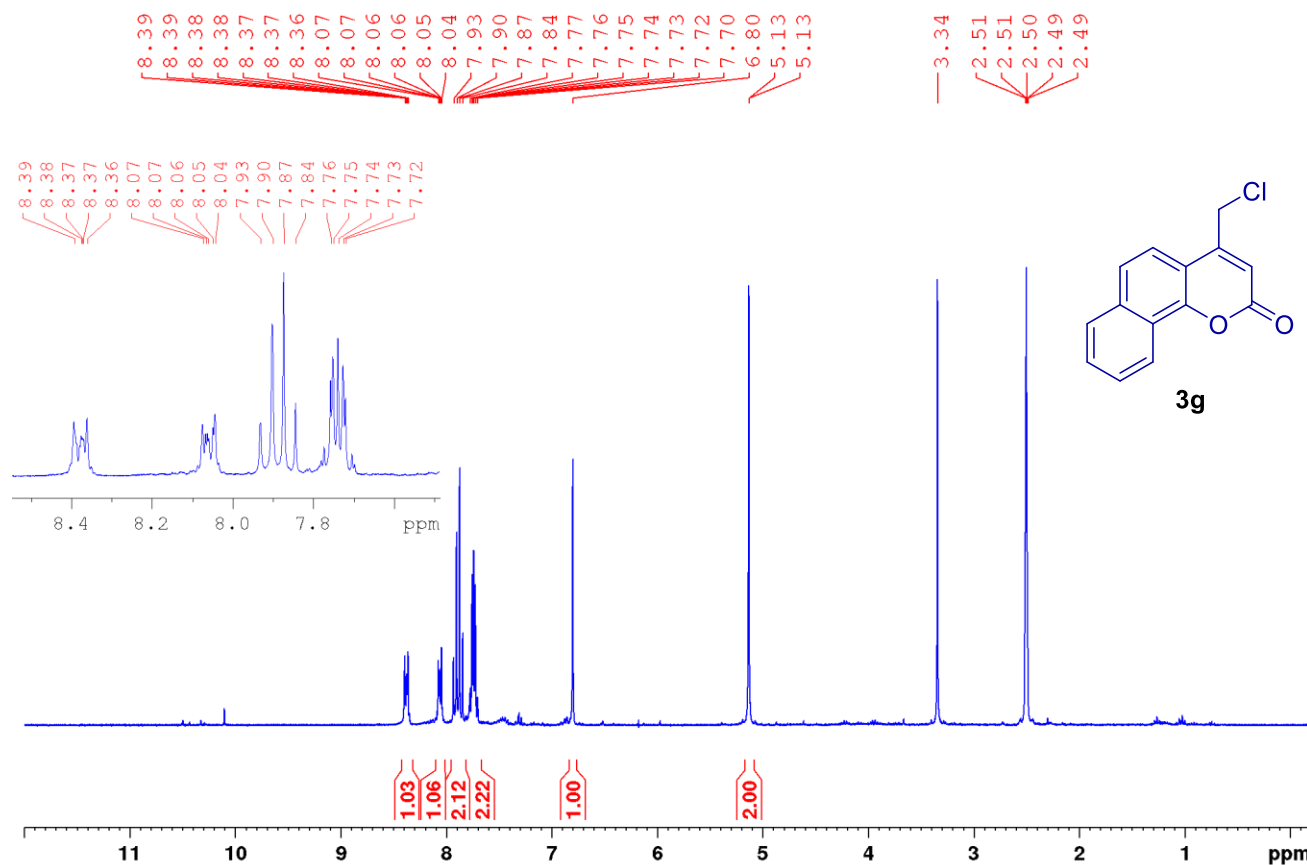


Figure S15. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3g**.

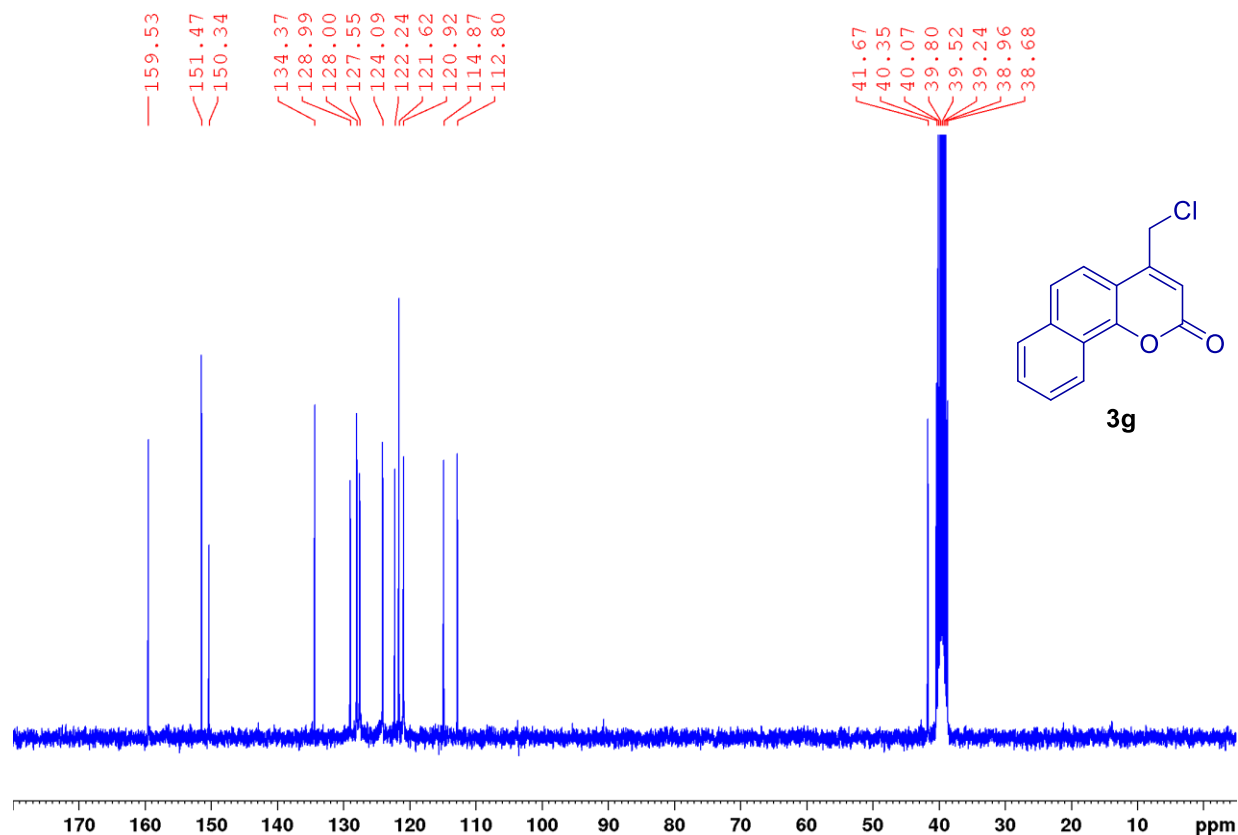


Figure S16. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3g**.

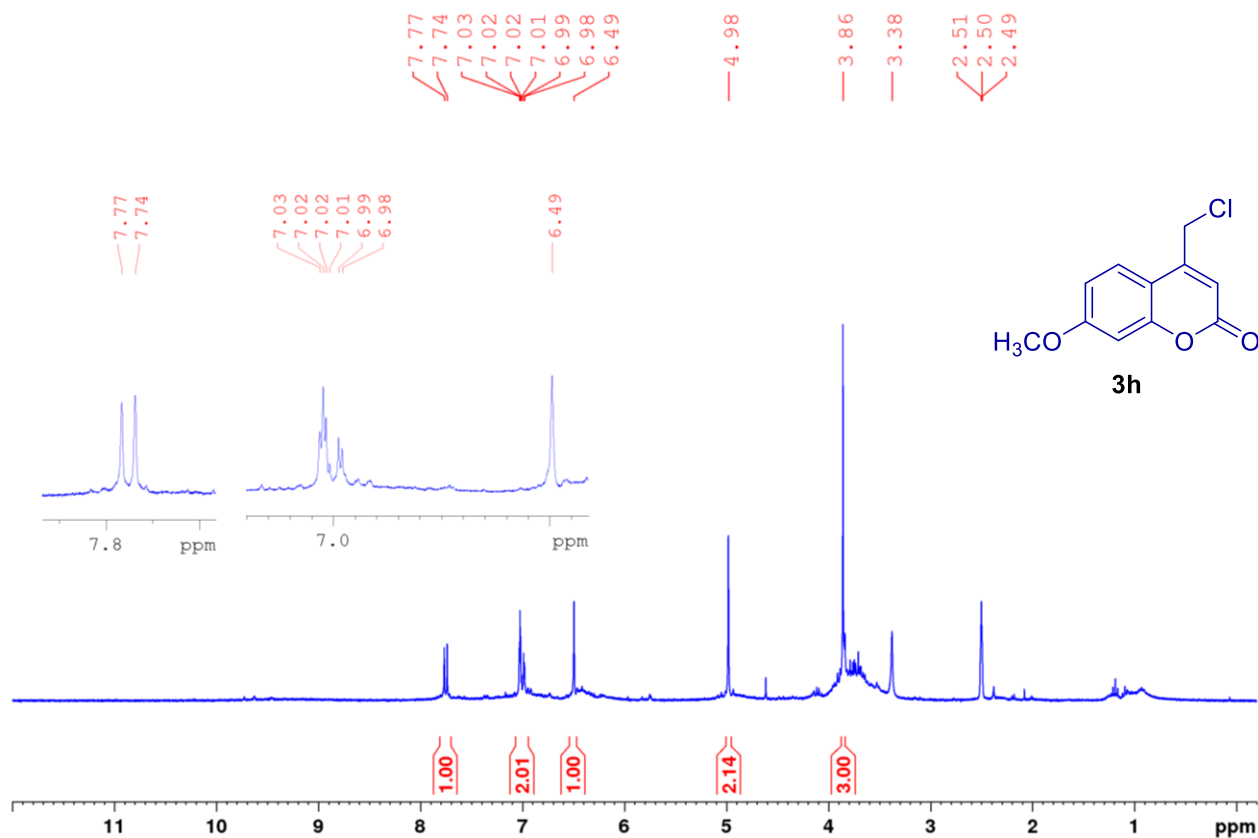


Figure S17. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3h**.

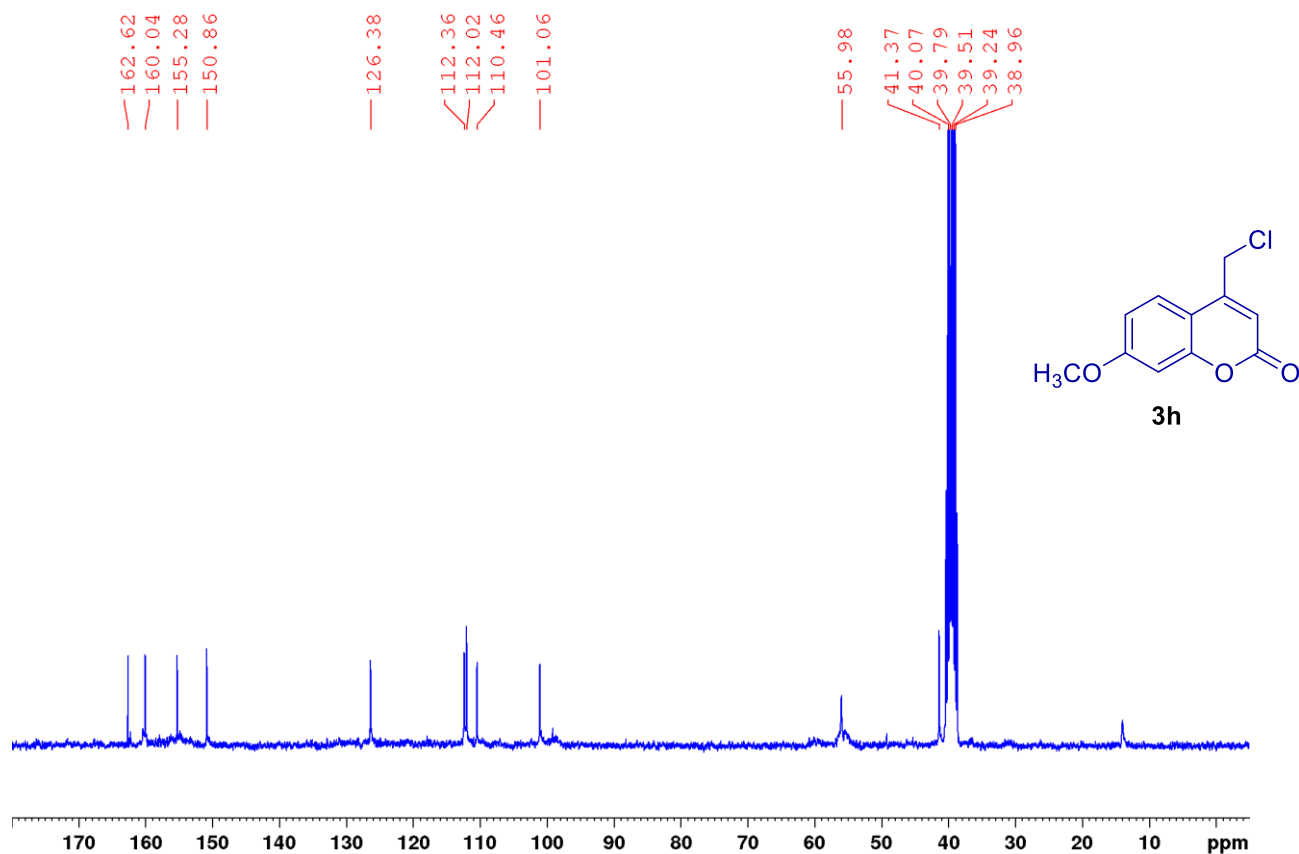


Figure S18. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3h**.

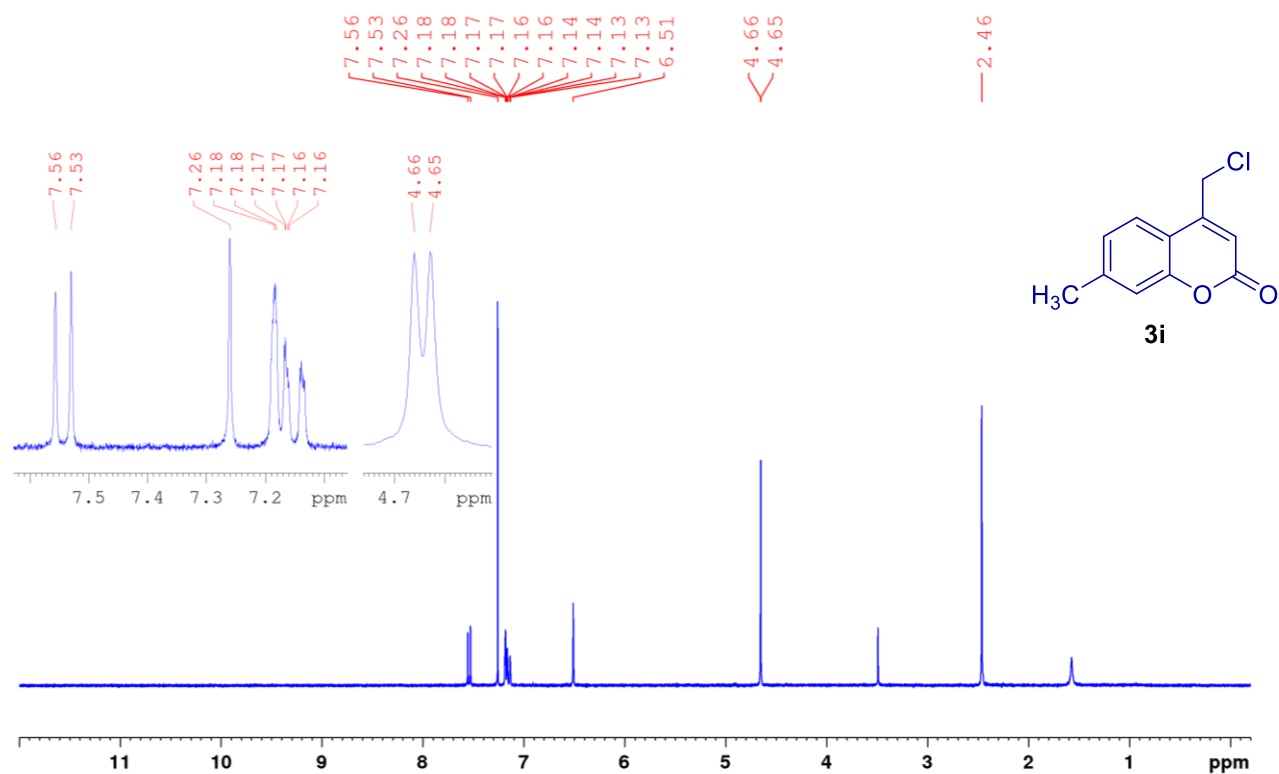


Figure S19. ¹H NMR spectrum (300 MHz, CDCl₃) of the product **3i**.

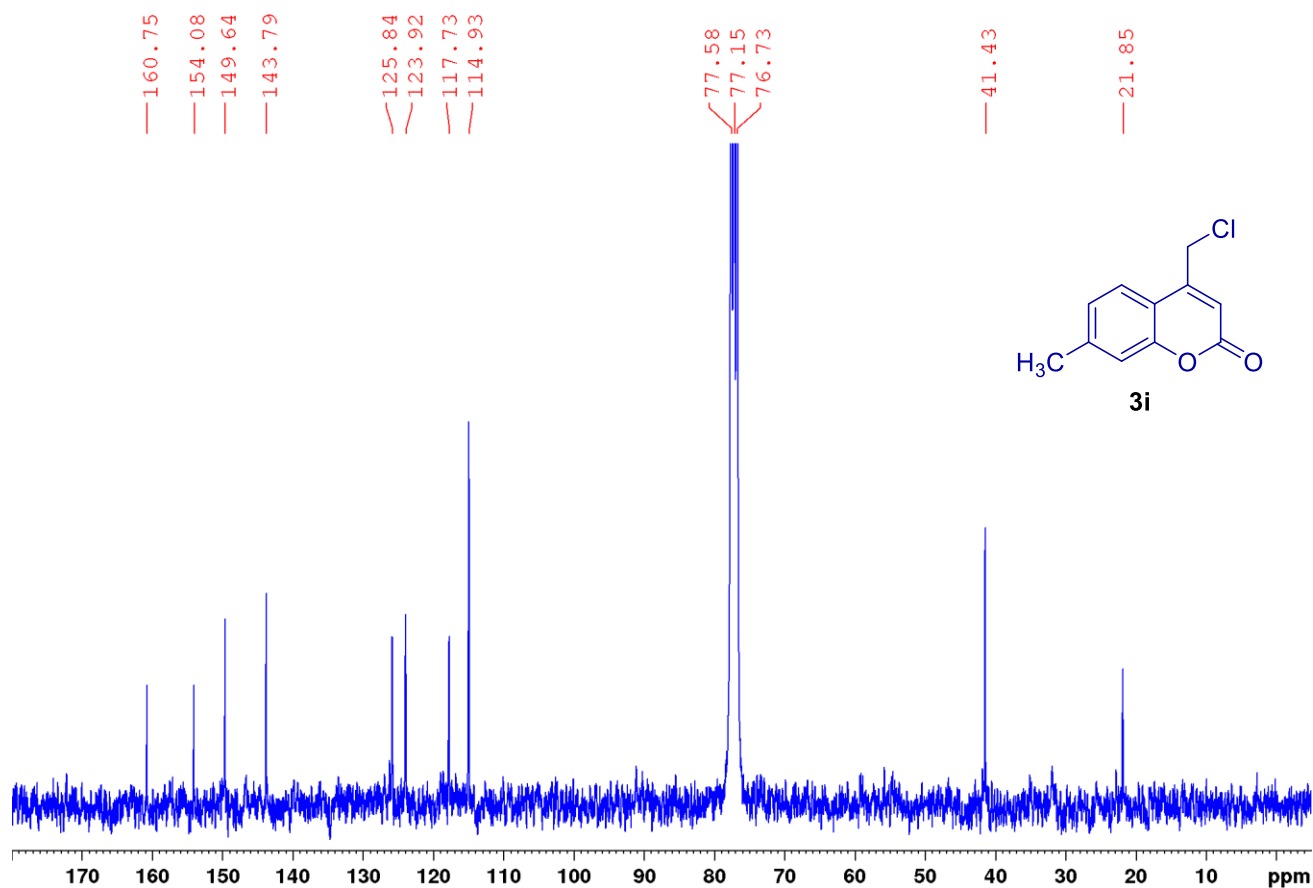


Figure S20. ¹³C NMR spectrum (75 MHz, CDCl₃) of the product **3i**.

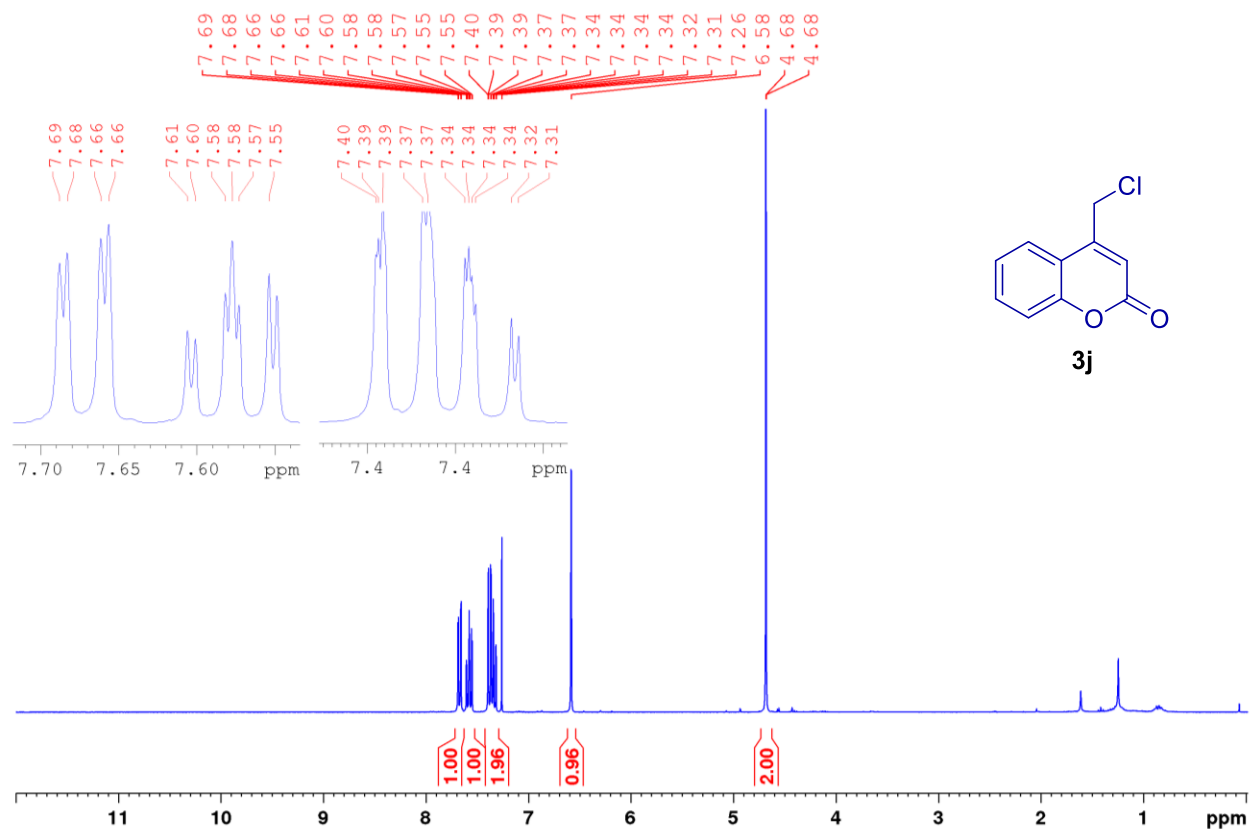


Figure S21. ¹H NMR spectrum (300 MHz, CDCl₃) of the product **3j**.

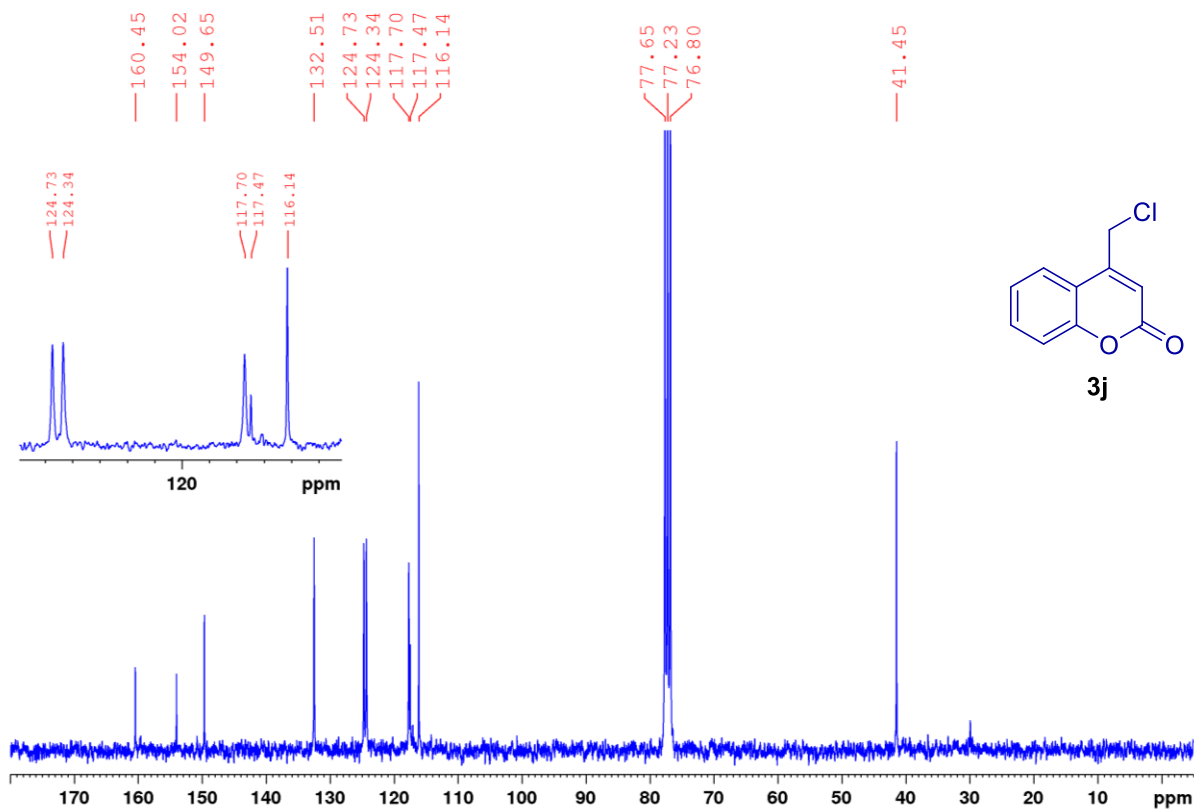


Figure S22. ¹³C NMR spectrum (75 MHz, CDCl₃) of the product **3j**.

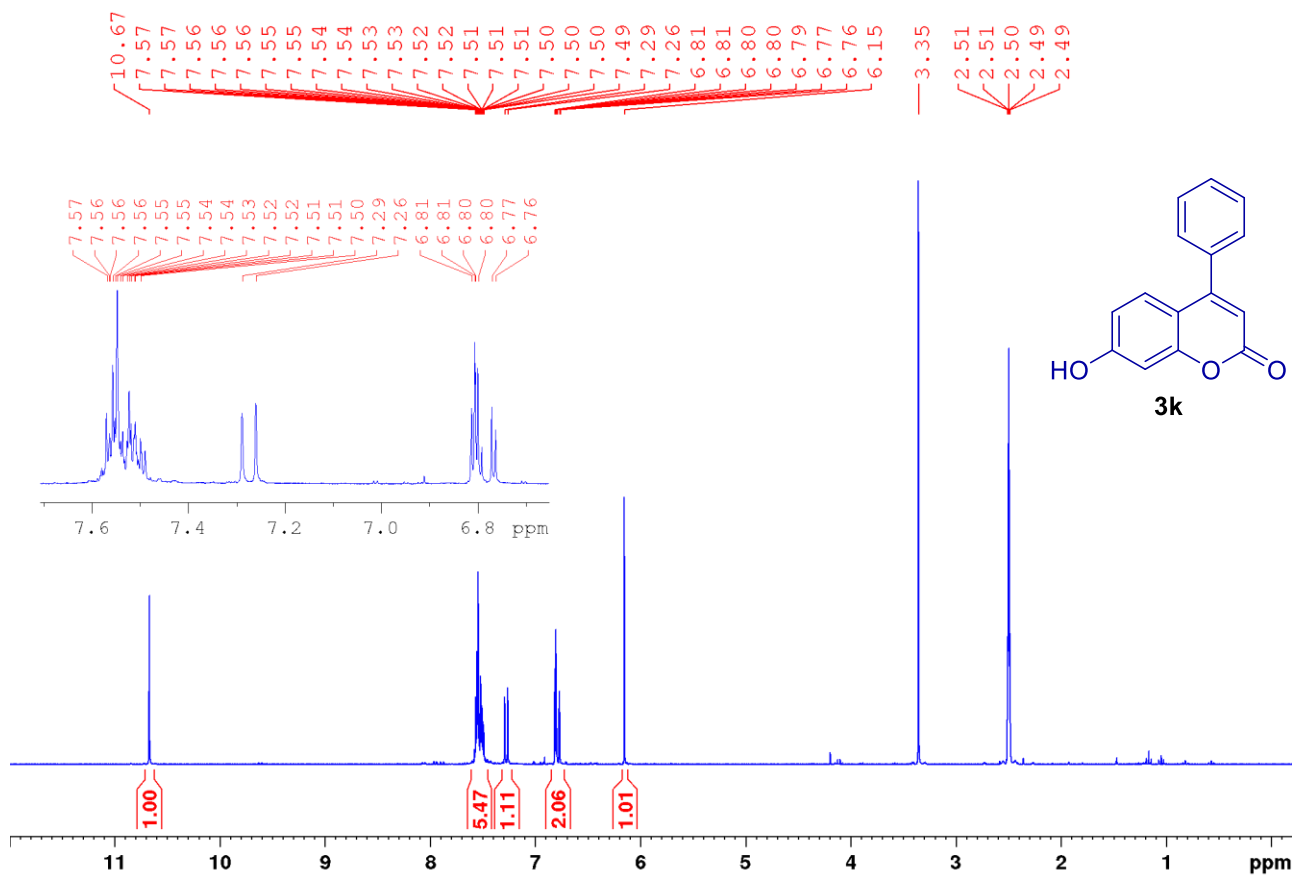


Figure S23. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3k**.

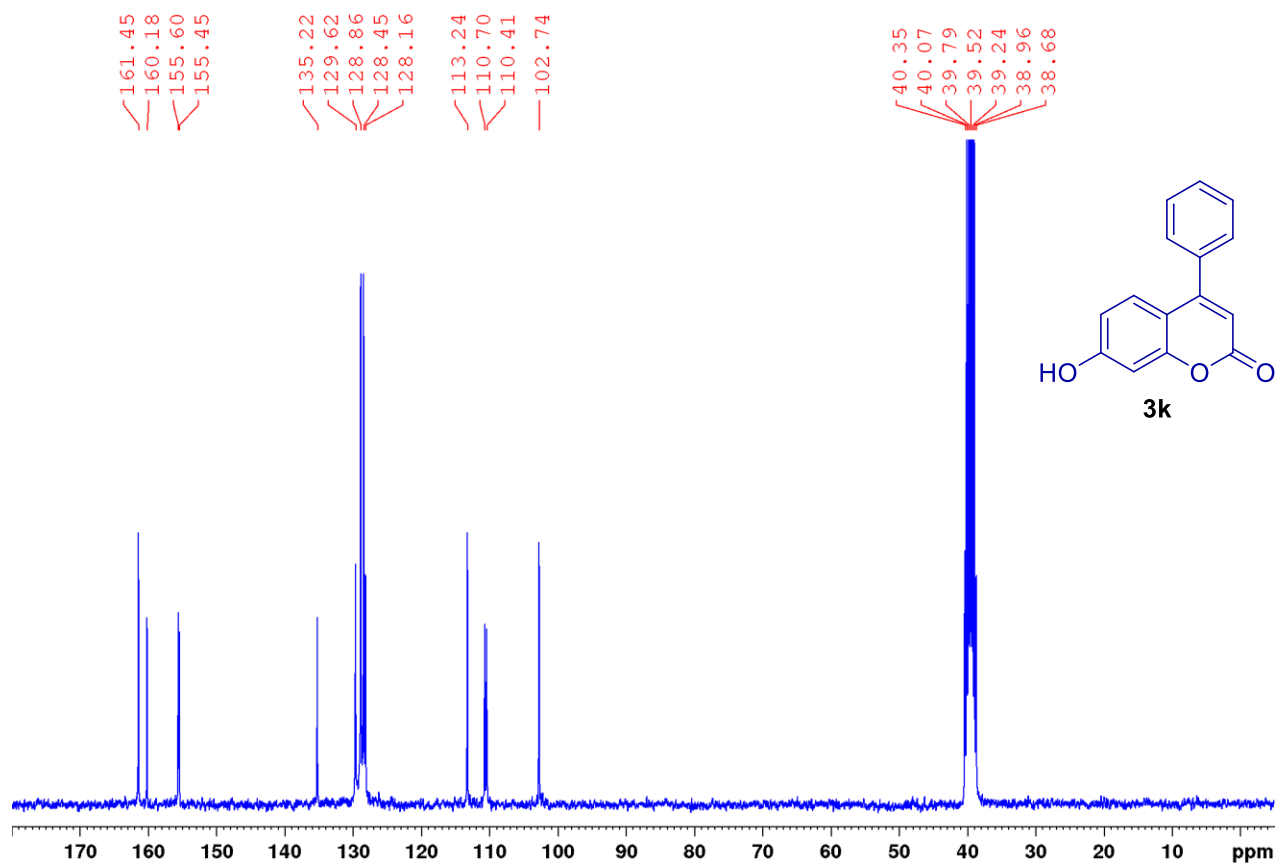


Figure S24. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3k**.

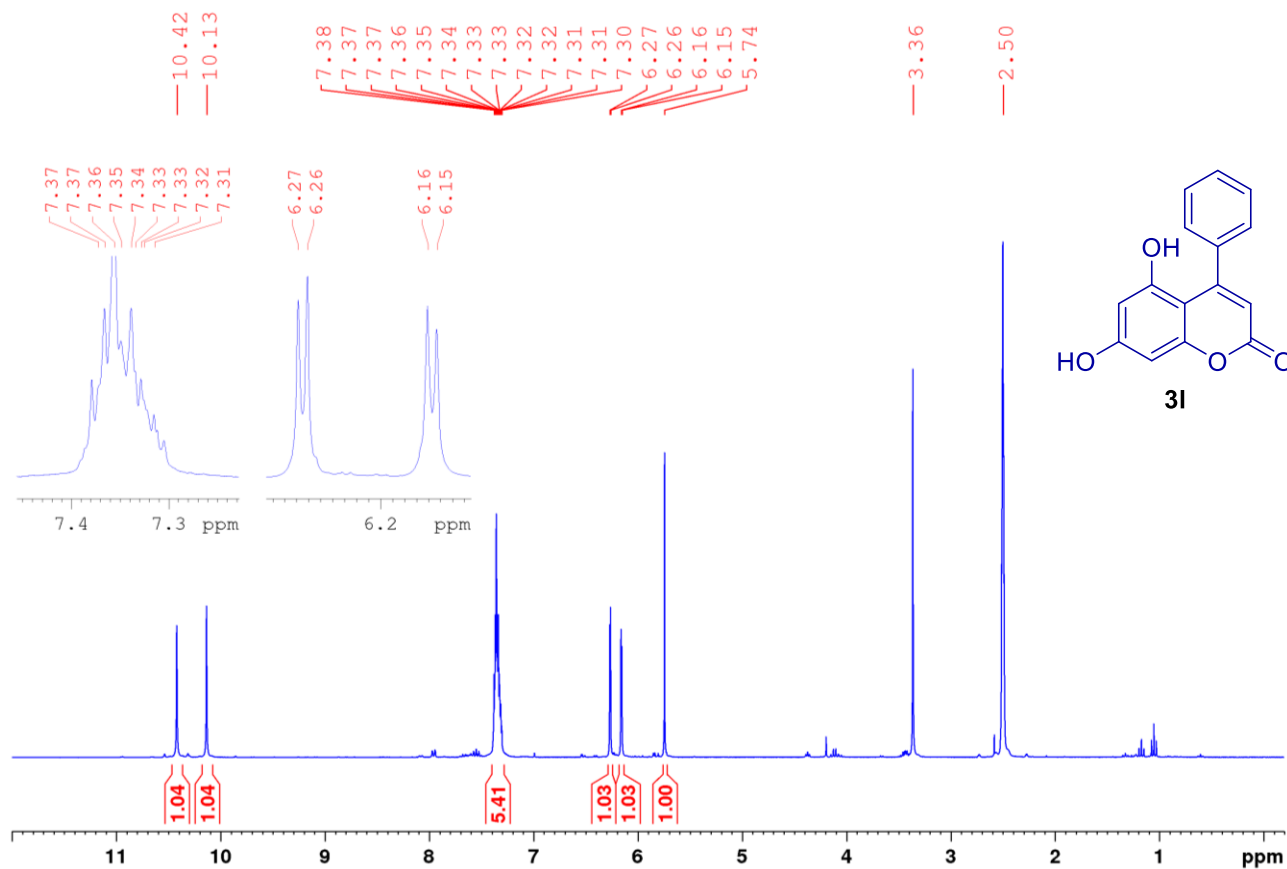


Figure S25. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3I**.

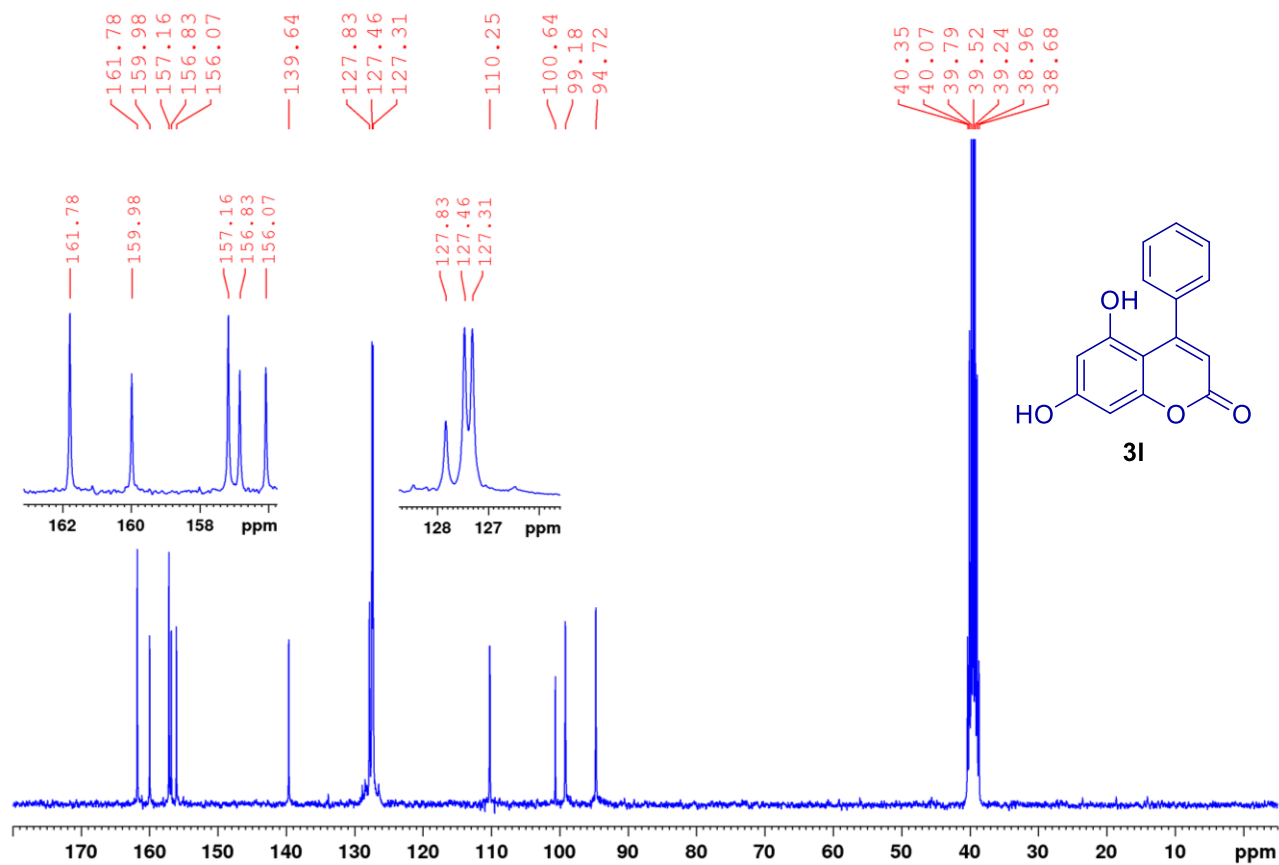


Figure S26. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3I**.

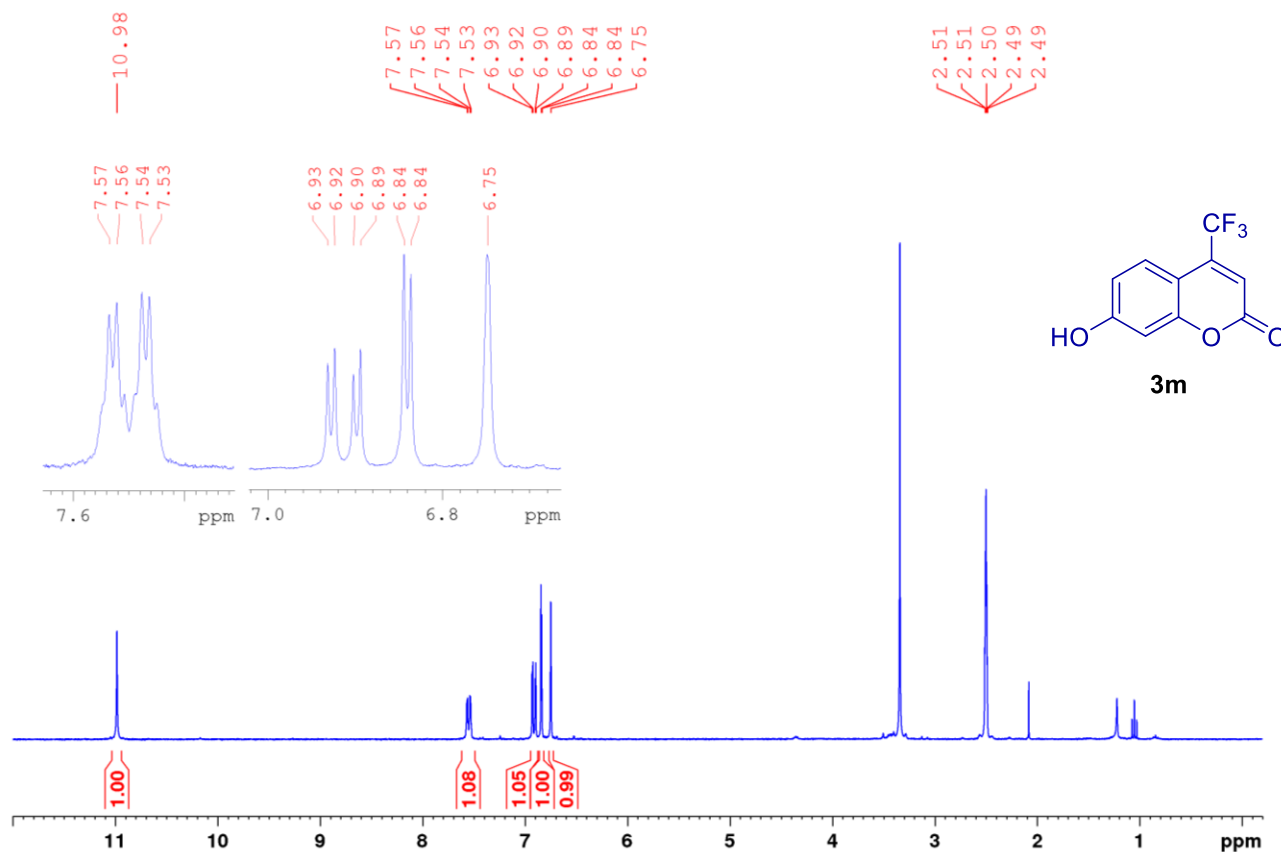


Figure S27. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3m**.

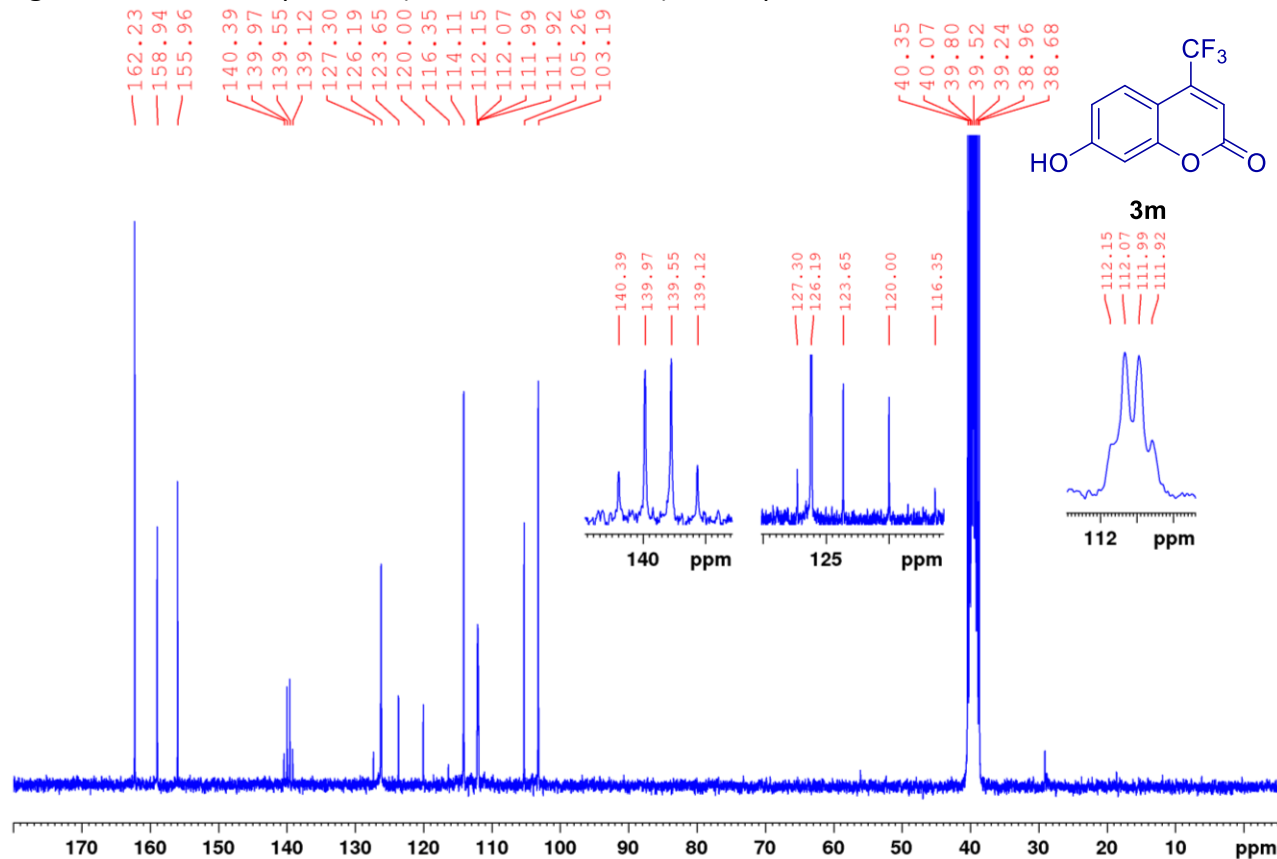


Figure S28. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3m**.

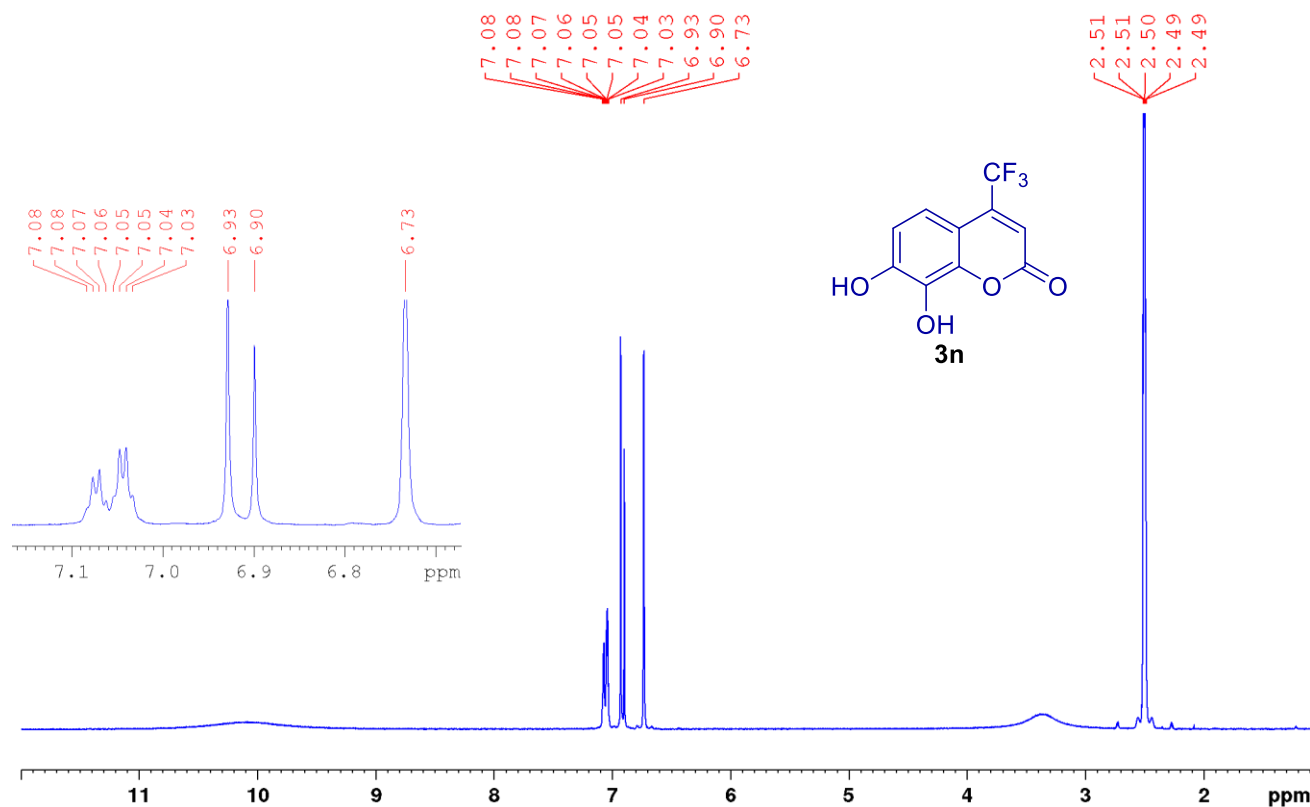


Figure S29. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product 3n.

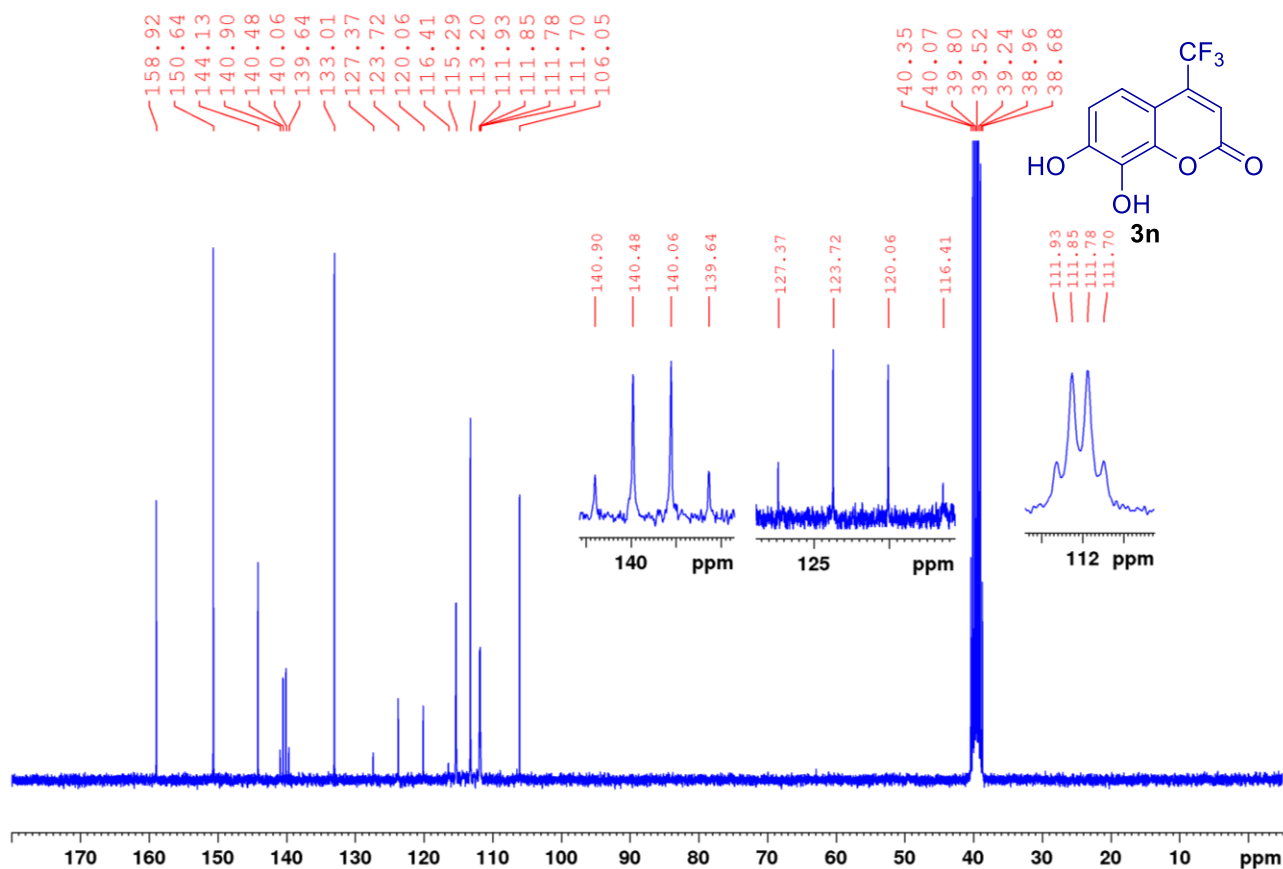
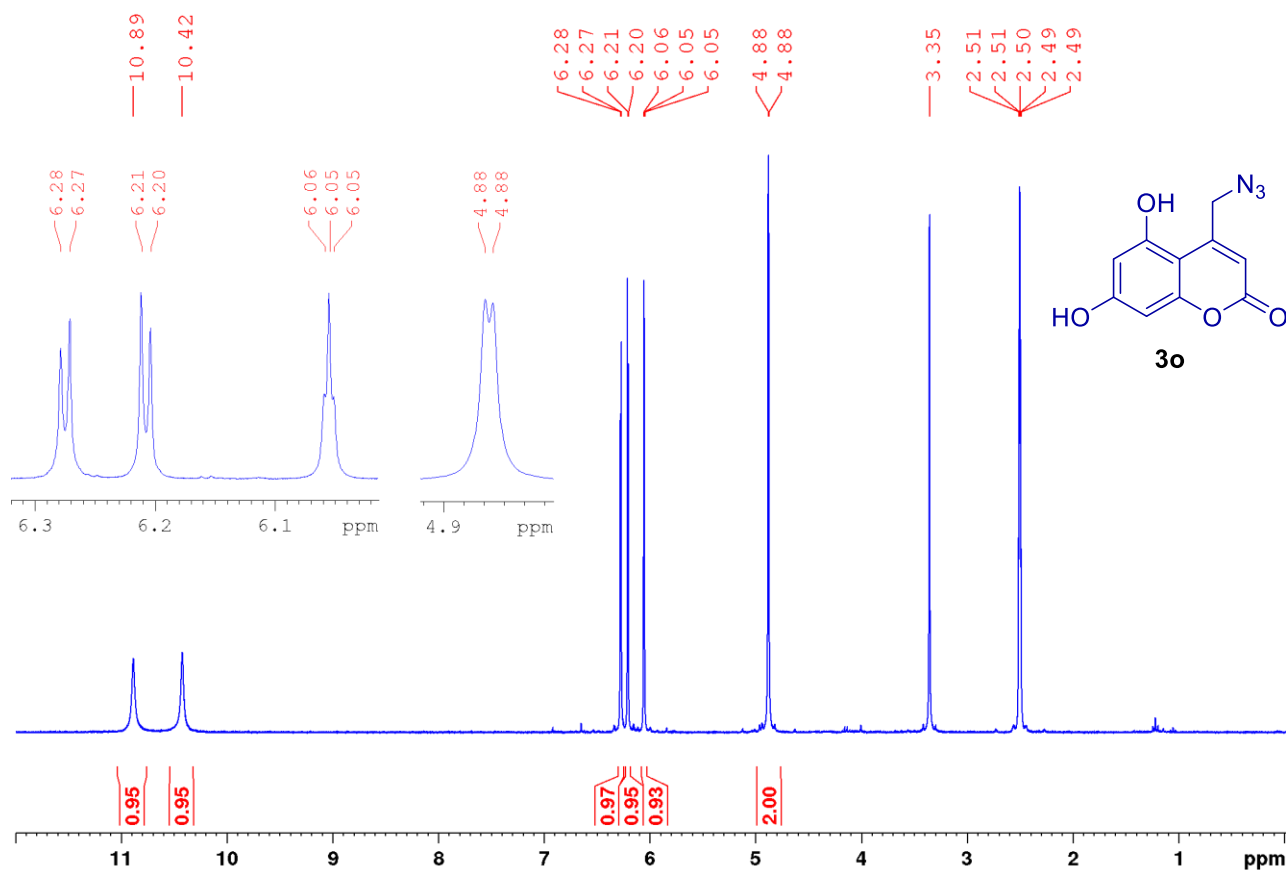
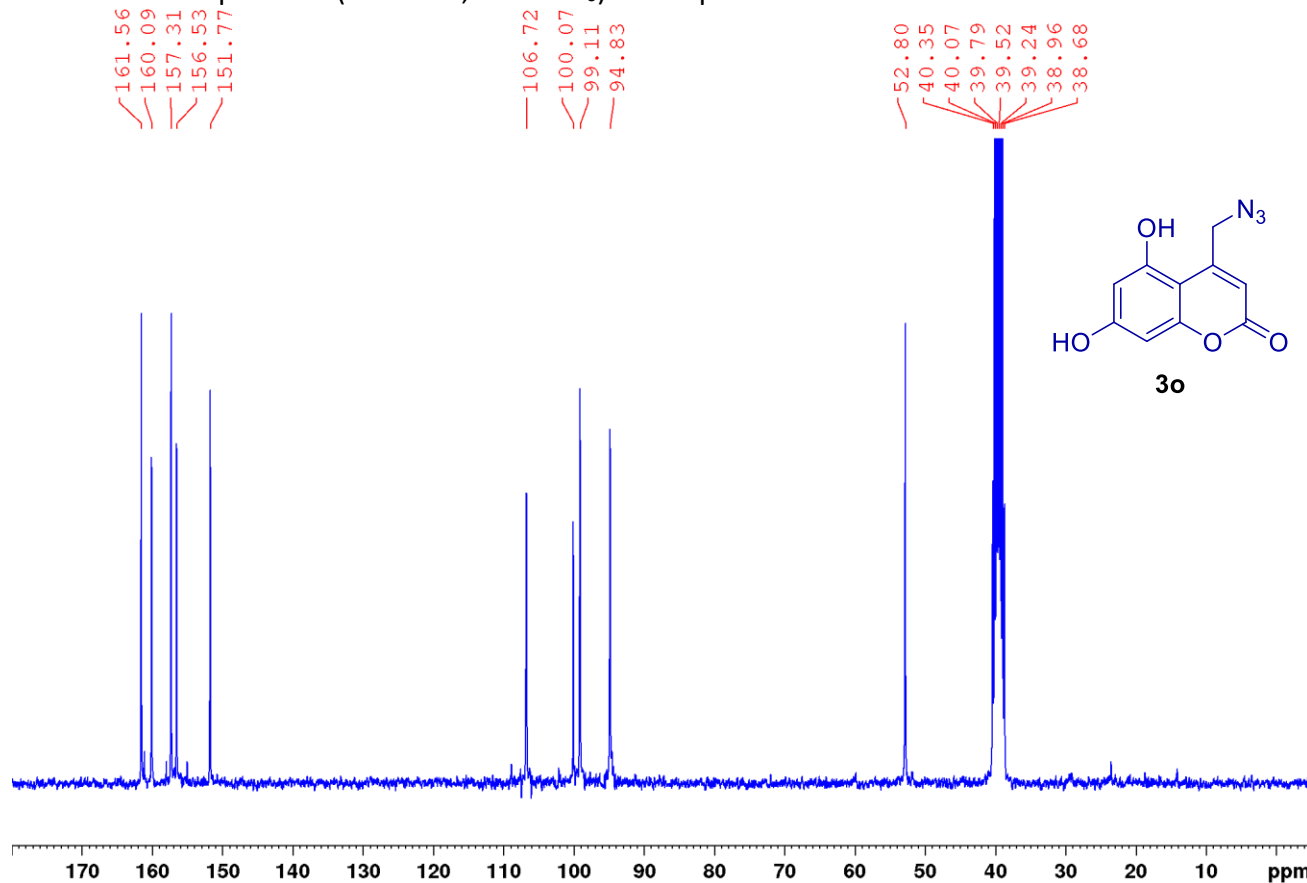


Figure S30. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product 3n.

Figure S31. ¹H NMR spectrum (300 MHz, DMSO-d₆) of the product **3o**.Figure S32. ¹³C NMR spectrum (75 MHz, DMSO-d₆) of the product **3o**.