Supplementary Material

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

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1. HRMS spectral data of the mechanism elucidation

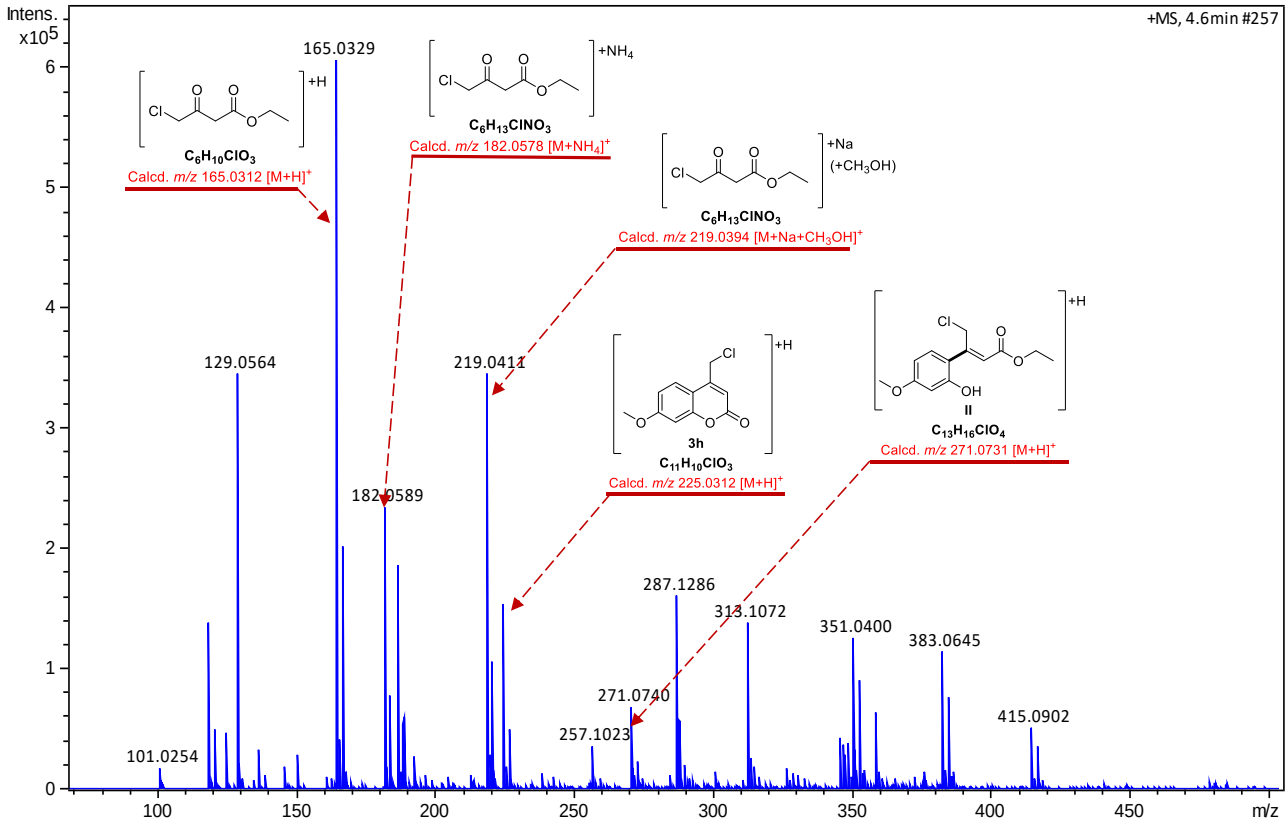
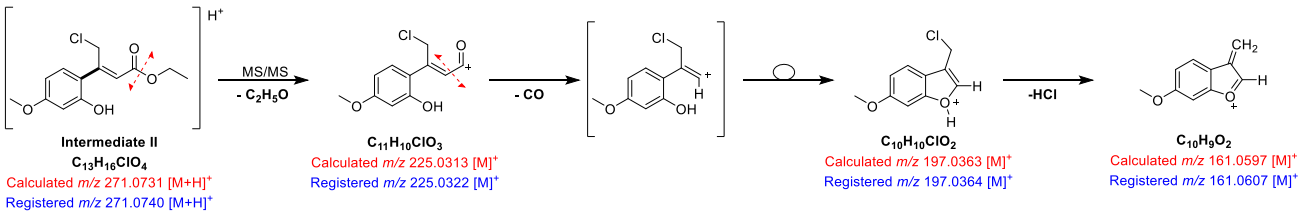


Figure S1. HRMS (ESI+) analysis of an aliquote of the reaction between *m*-cresol and ethyl 4-chloroacetoacetate to afford the coumarin **3h**.



Scheme S1. Plausive fragmentation of intermediate **II** into the product ion.

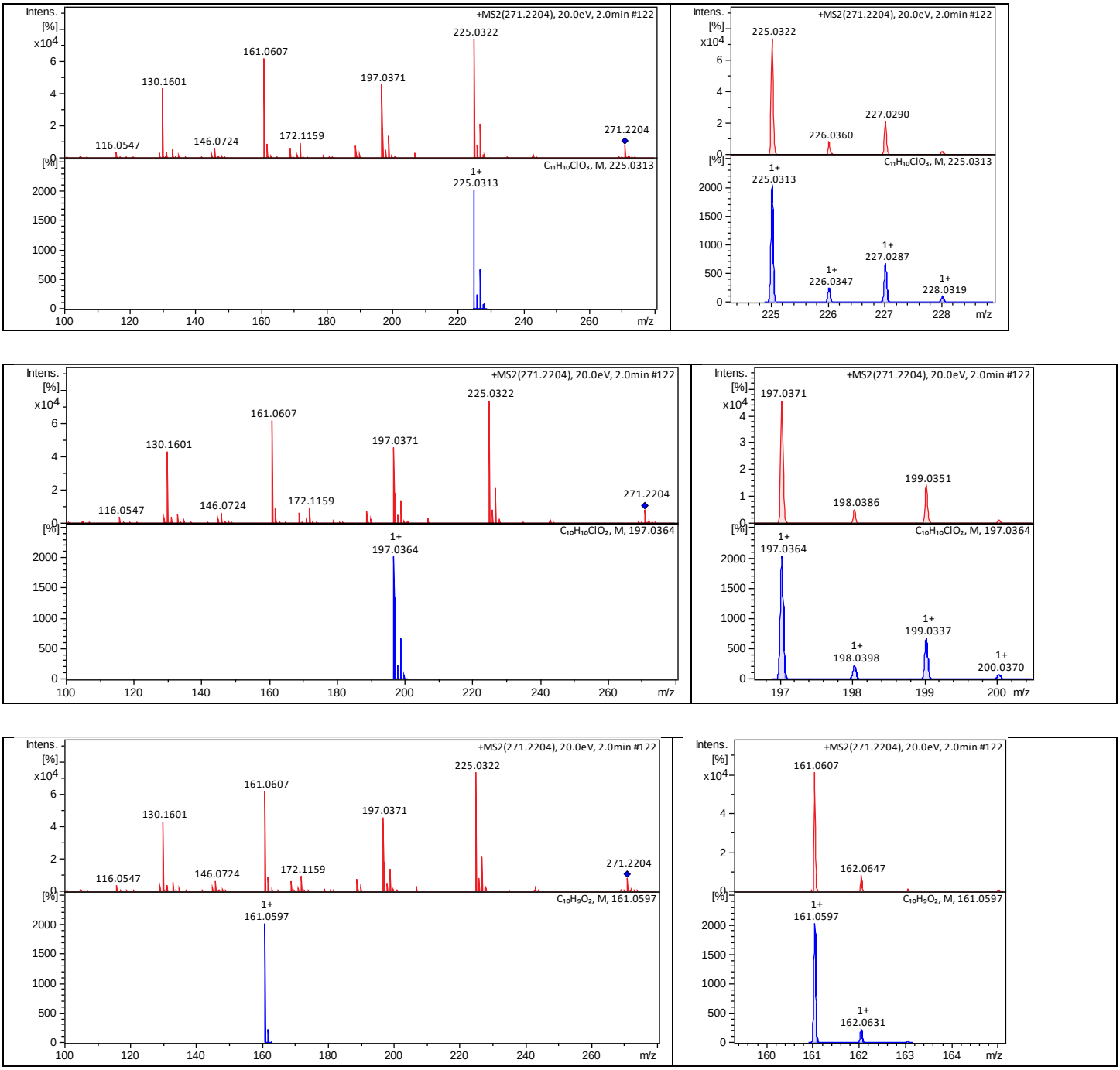


Figure S2. Tandem mass spectrometry (ESI-MS/MS) of the protonated molecule with *m/z* 271.0740 using N_2 as collision gas at 20 eV.

2. Copies of ^{1}H and ^{13}C NMR Spectra of products 3a-o

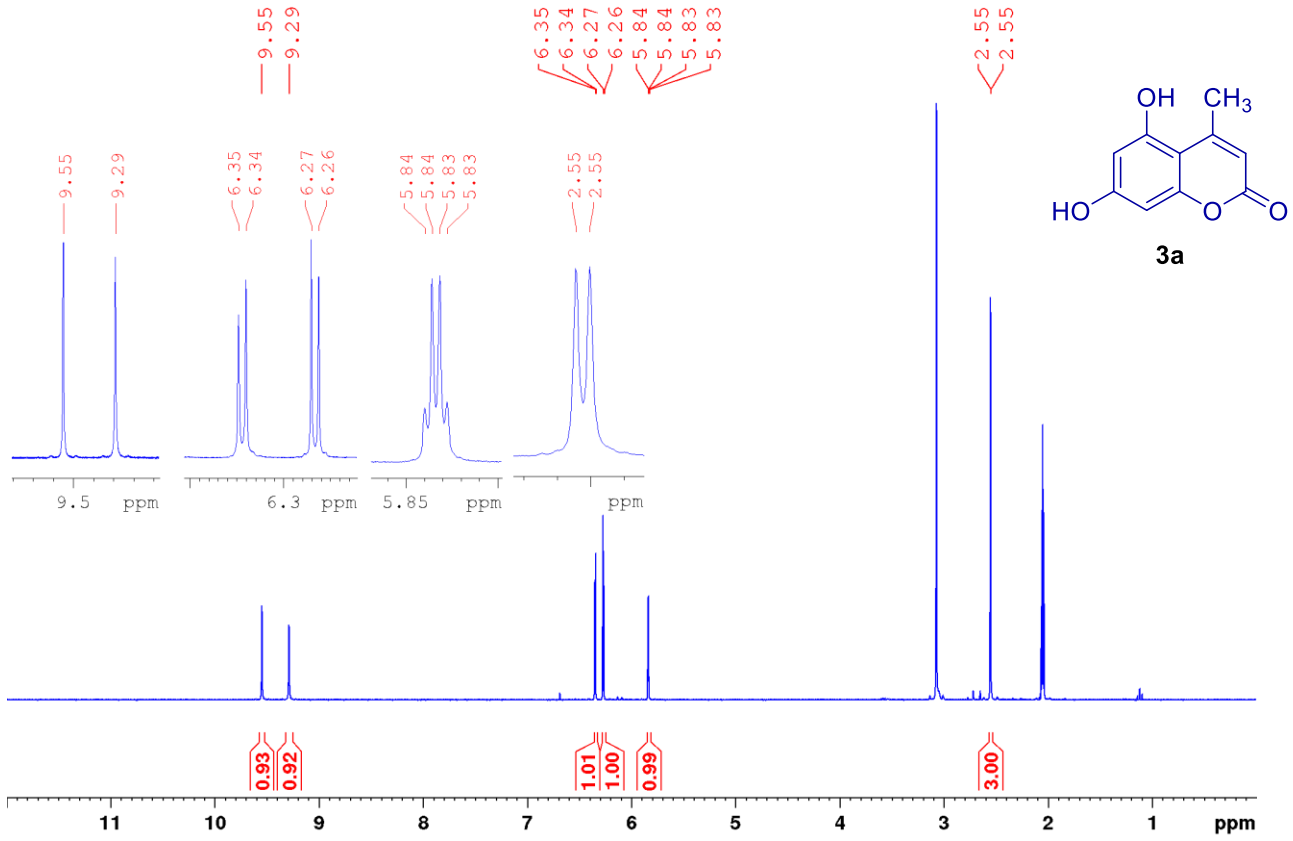


Figure S3. ^{1}H NMR spectrum (300 MHz, acetone-d_6) of the product **3a**.

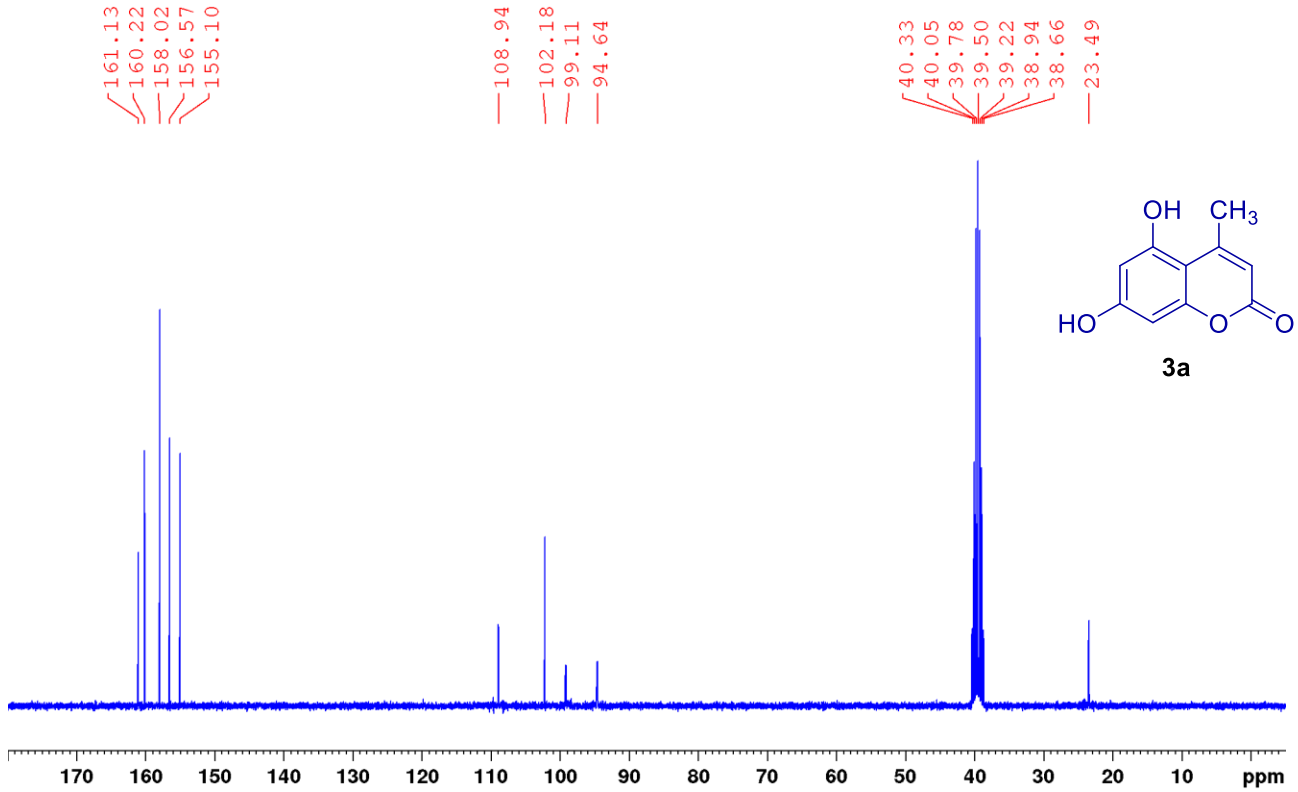


Figure S4. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3a**.

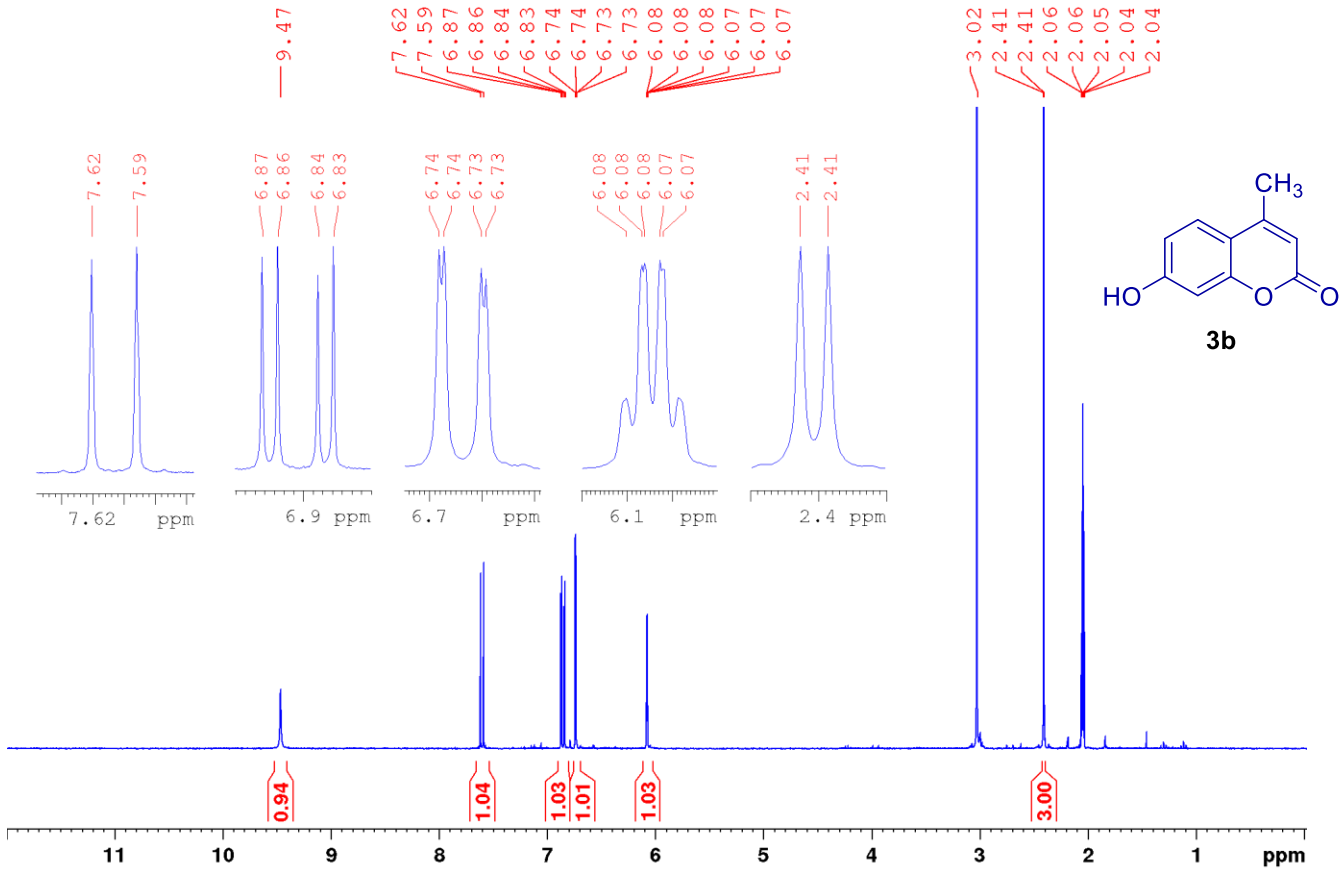


Figure S5. ^{1}H NMR spectrum (300 MHz, acetone-d_6) of the product **3b**.

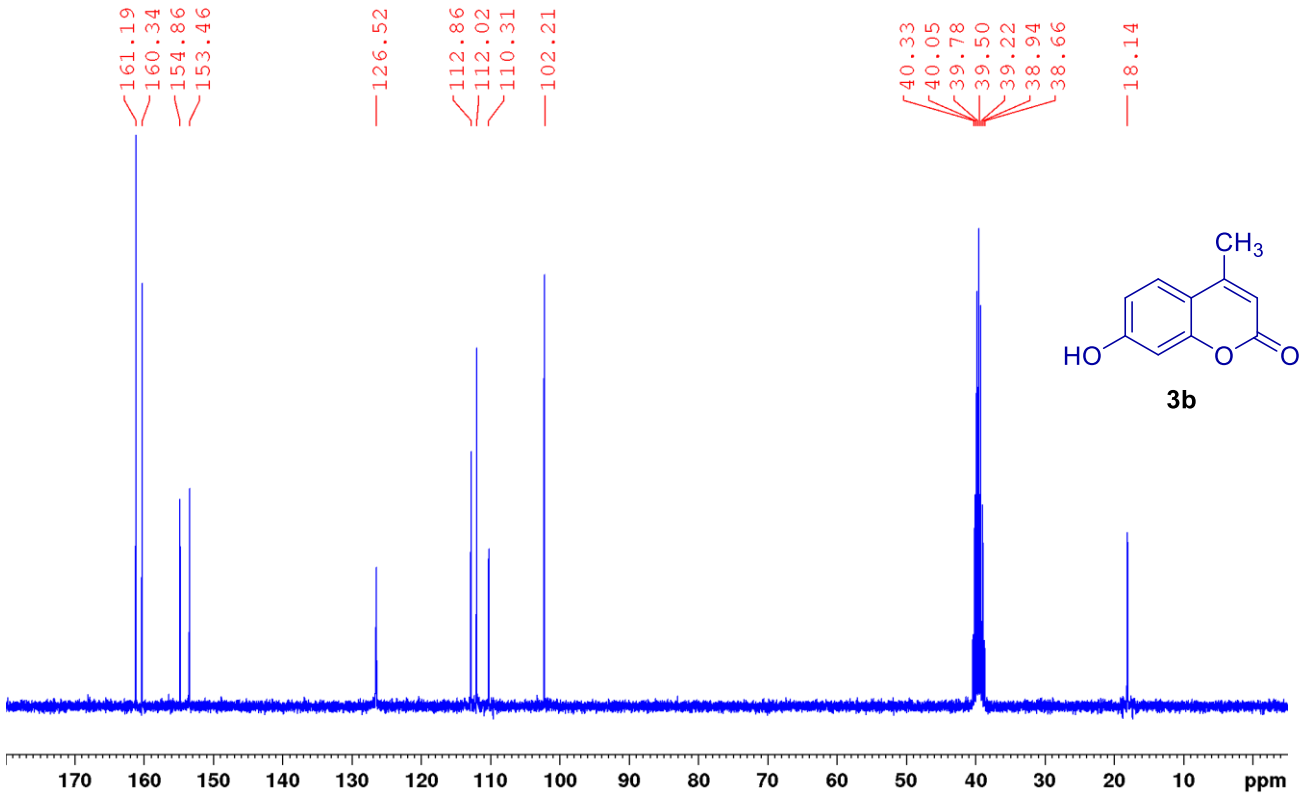


Figure S6. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3b**.

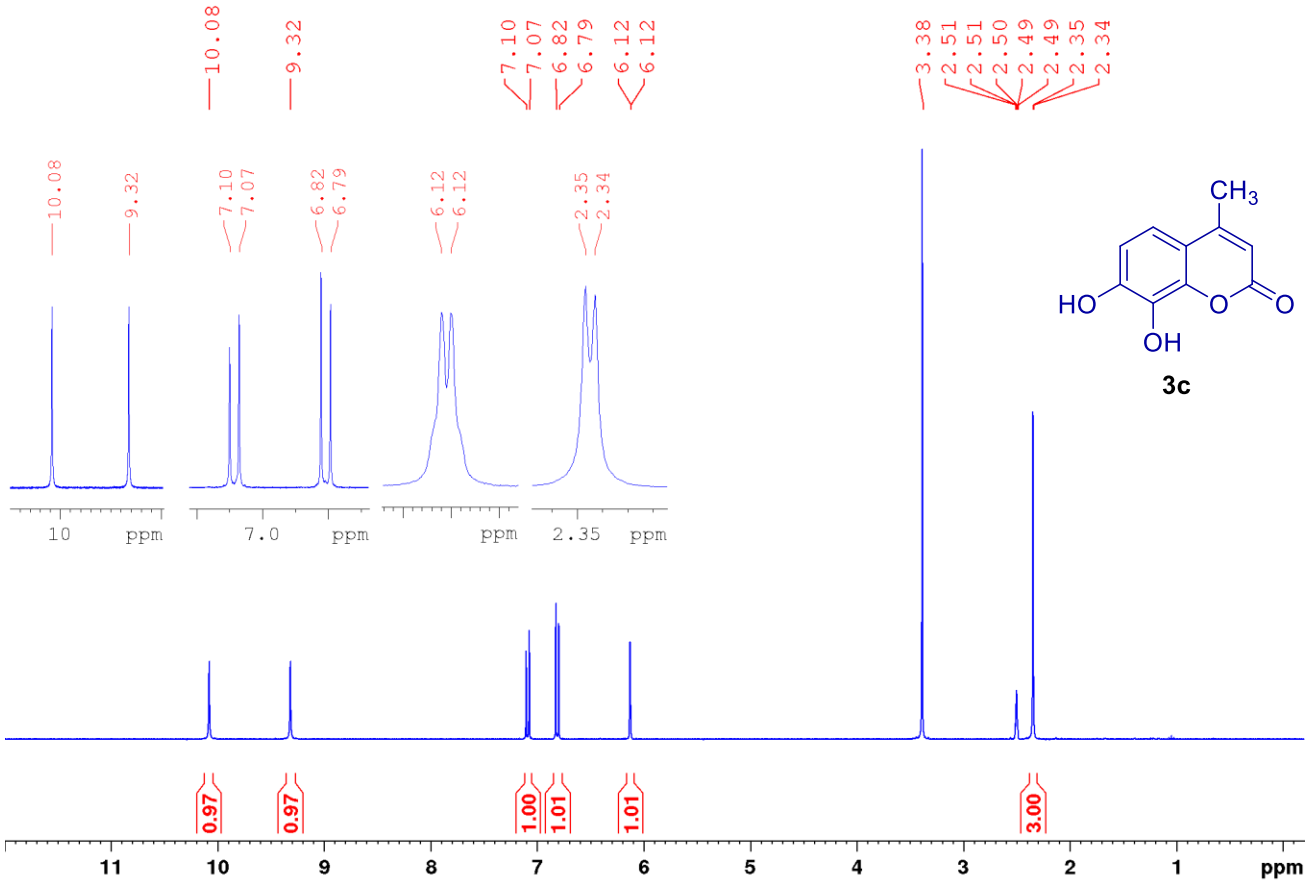


Figure S7. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of product **3c**.

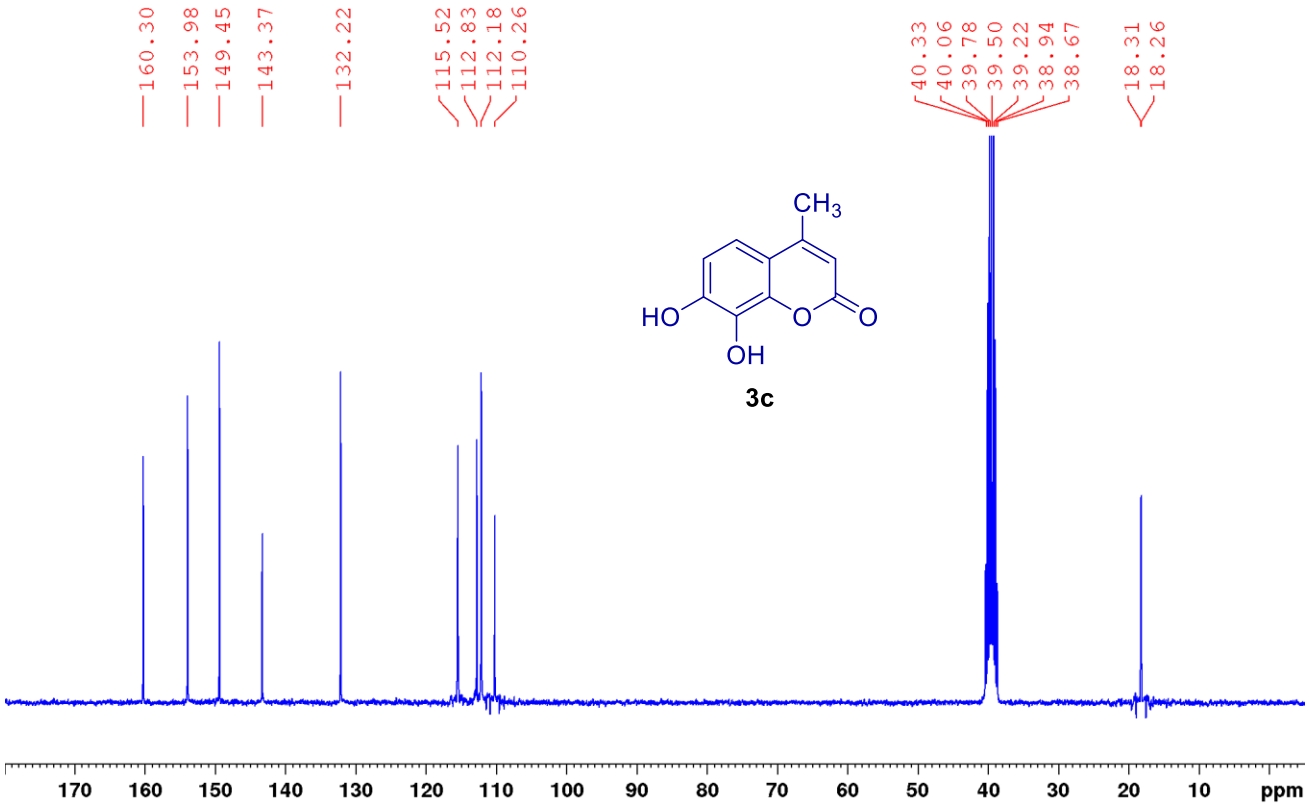


Figure S8. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3c**.

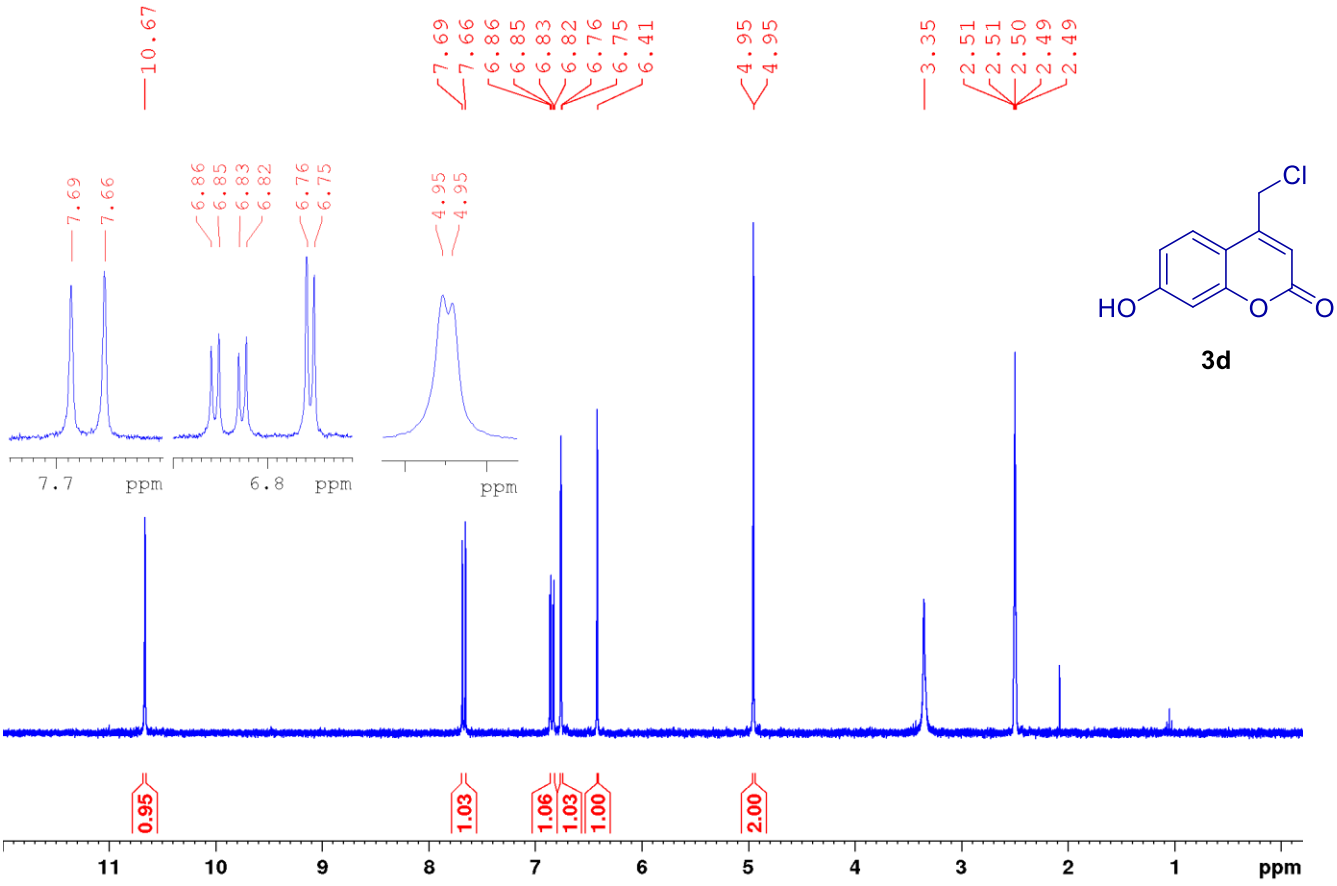


Figure S9. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3d**.

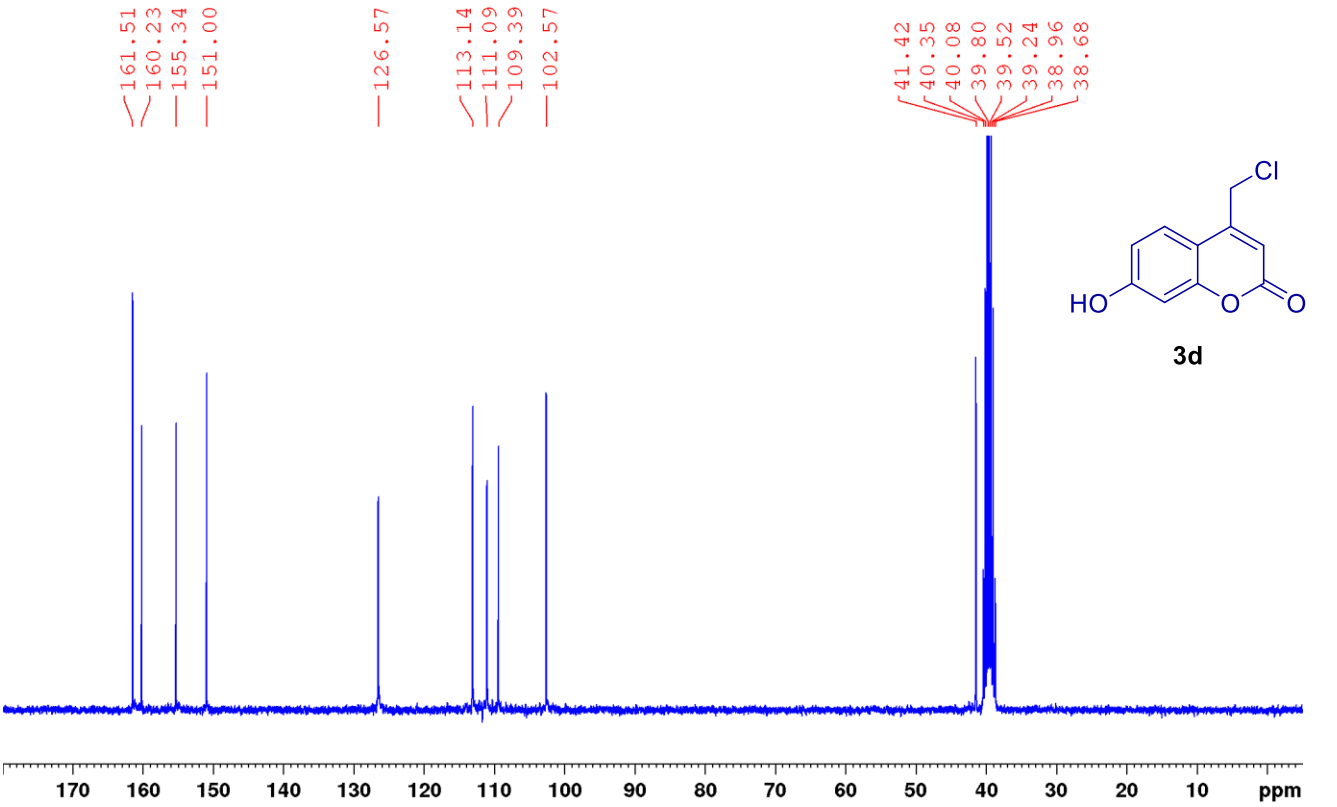


Figure S10. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3d**.

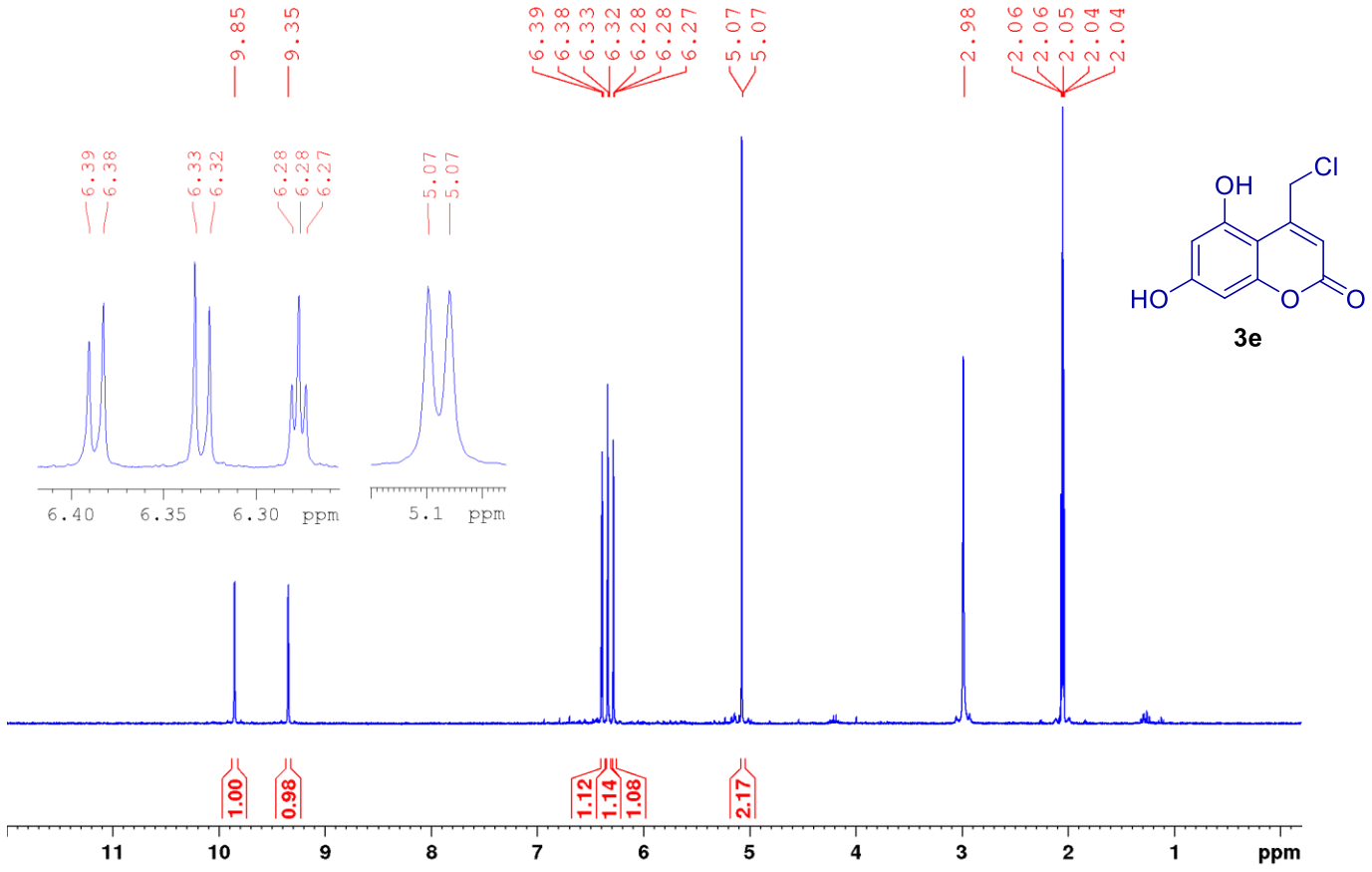


Figure S11. ^{1}H NMR Spectrum (300 MHz, DMSO-d_6) of the product **3e**.

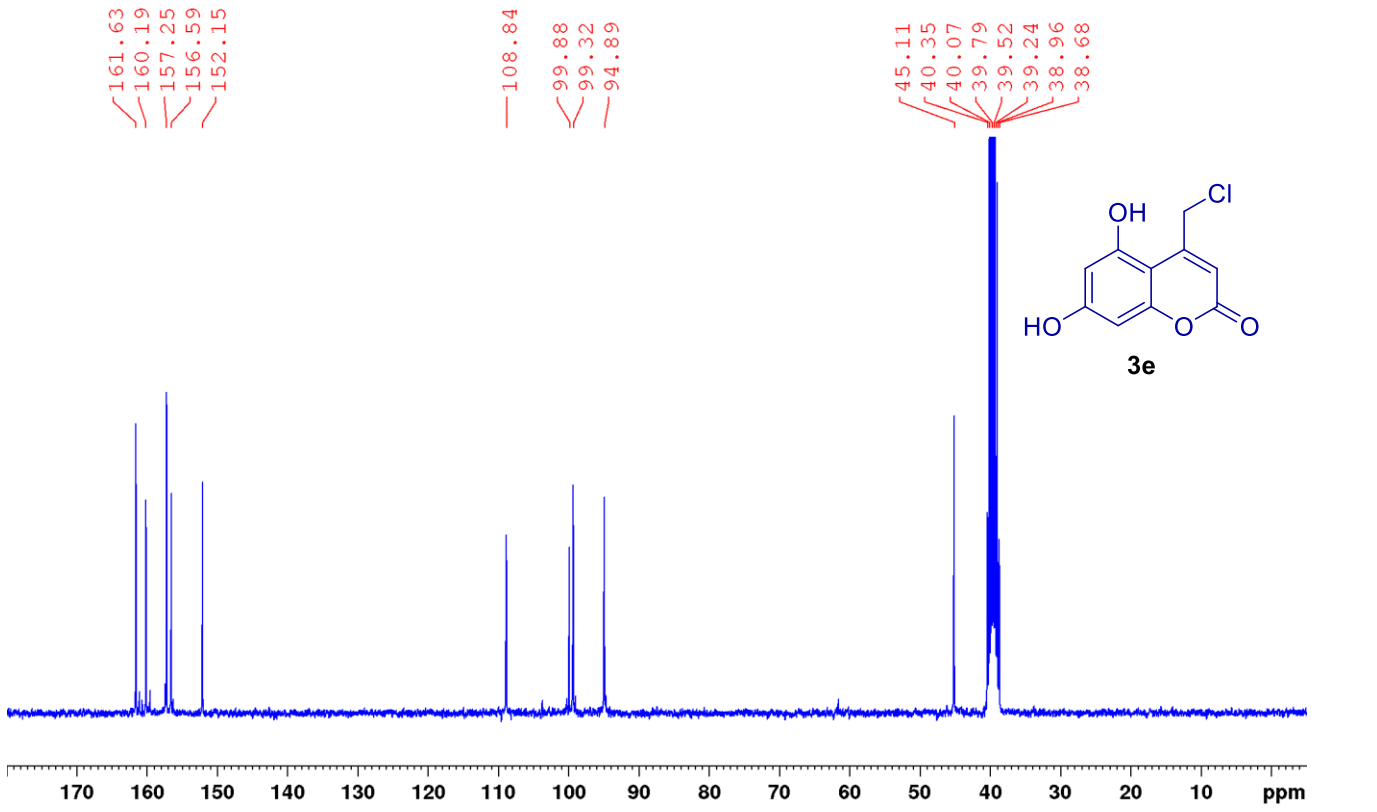


Figure S12. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3e**.

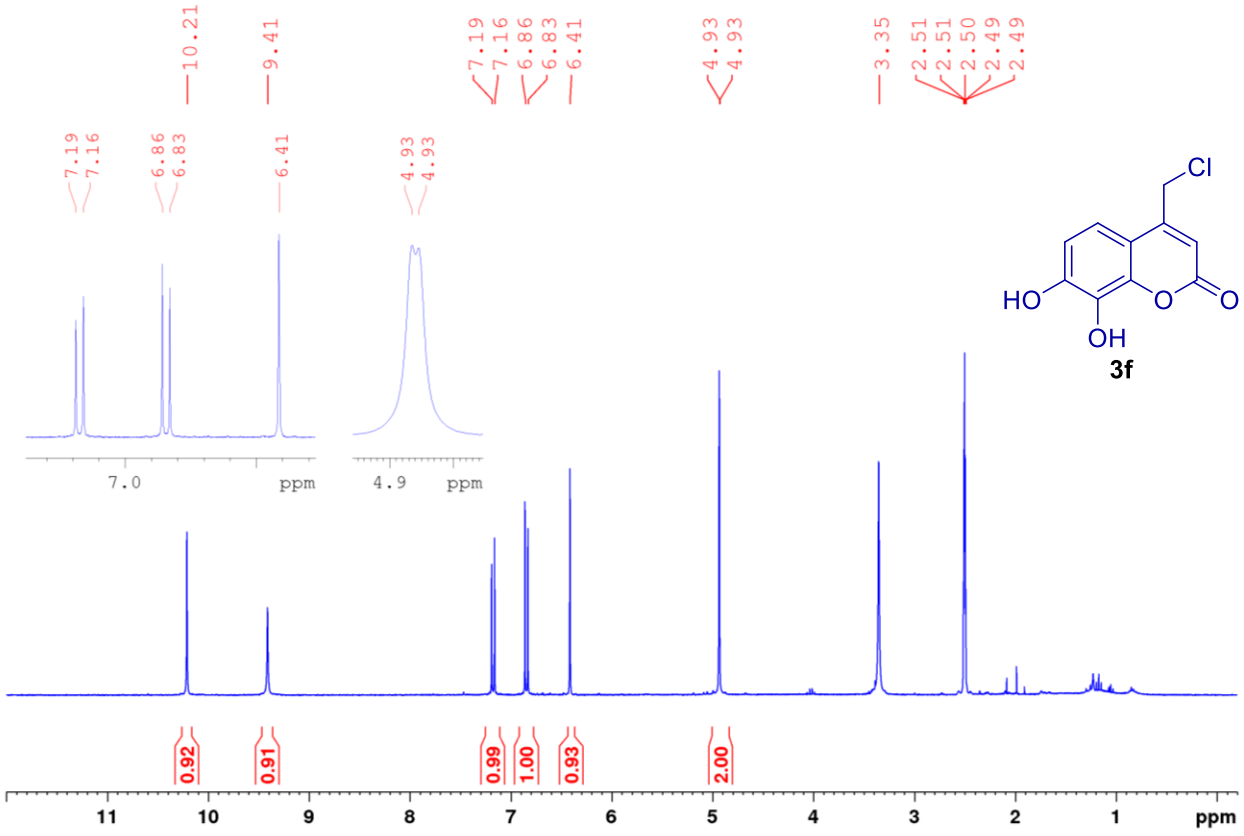


Figure S13. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3f**.

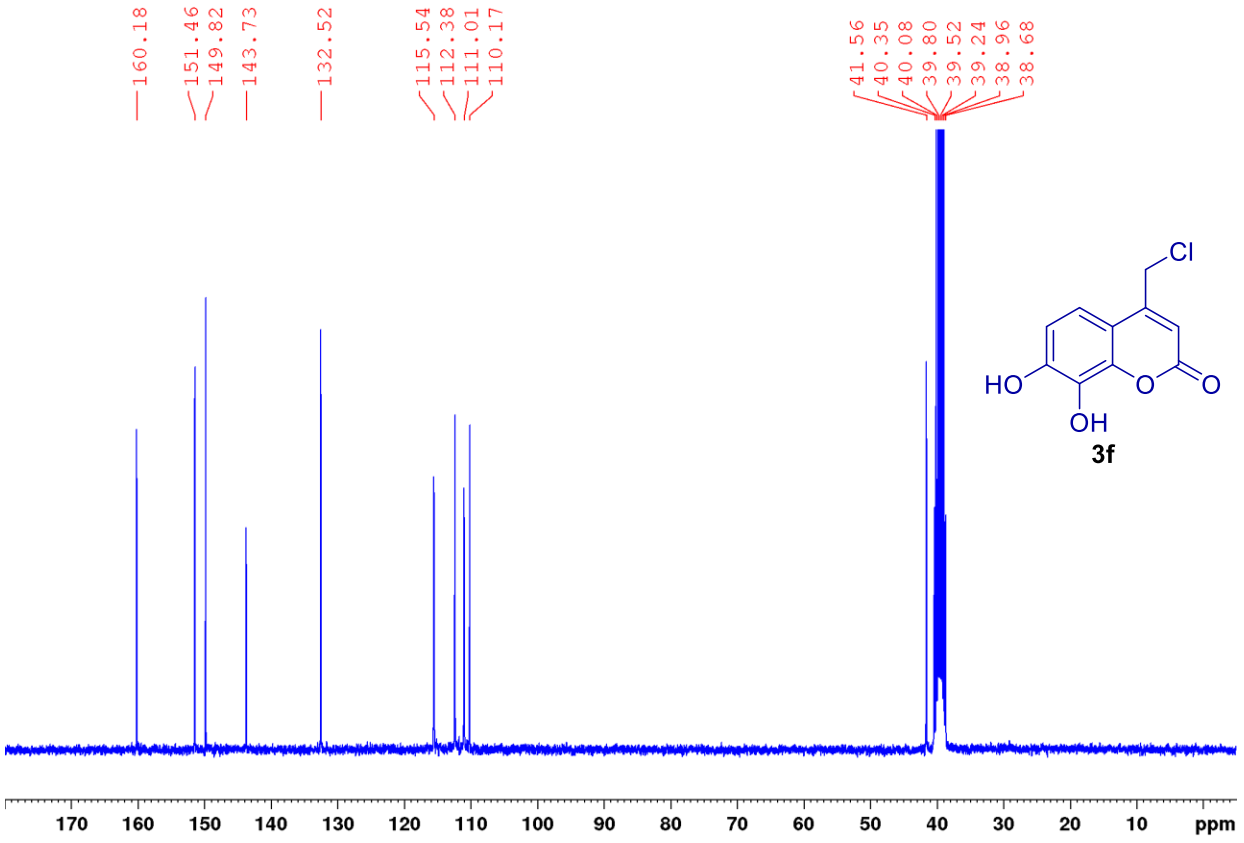


Figure S14. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3f**.

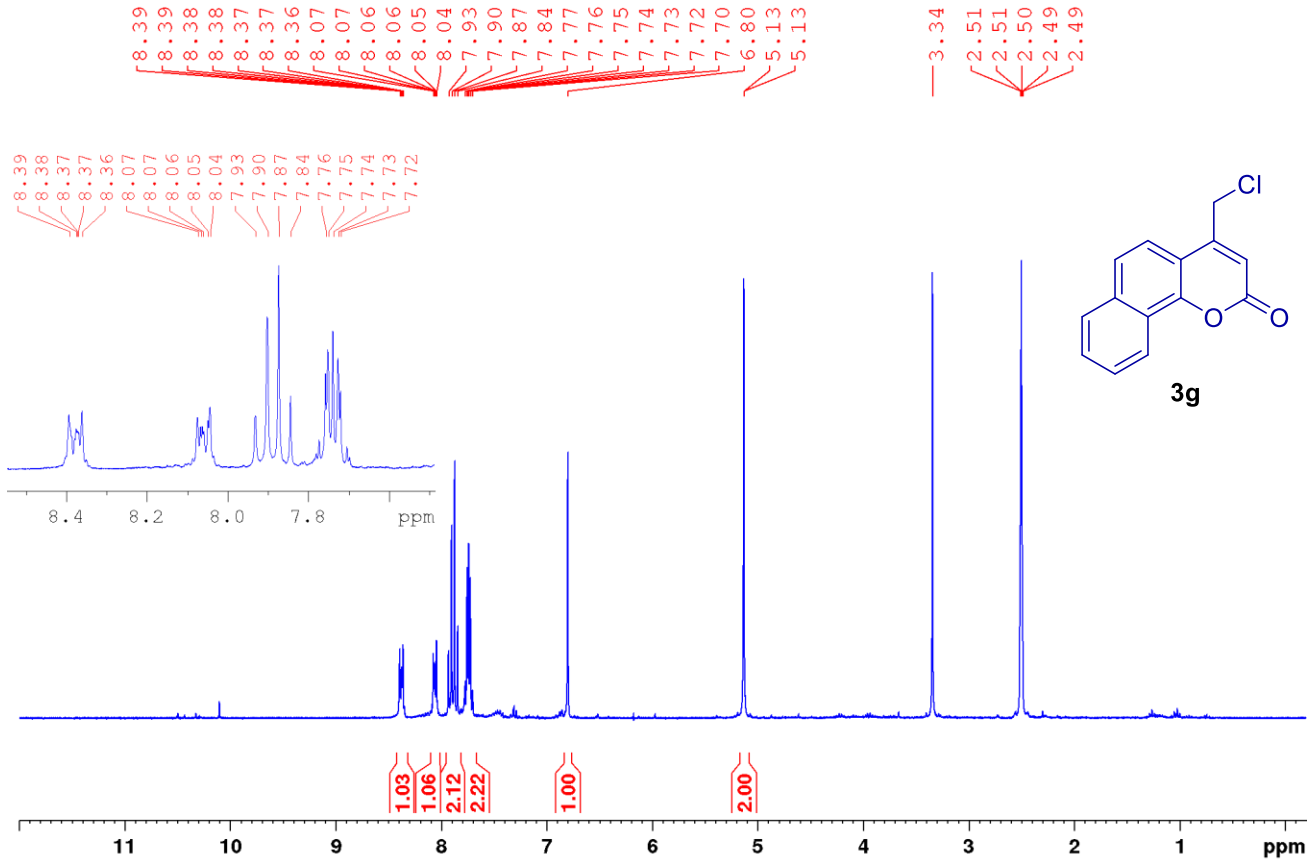


Figure S15. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3g**.

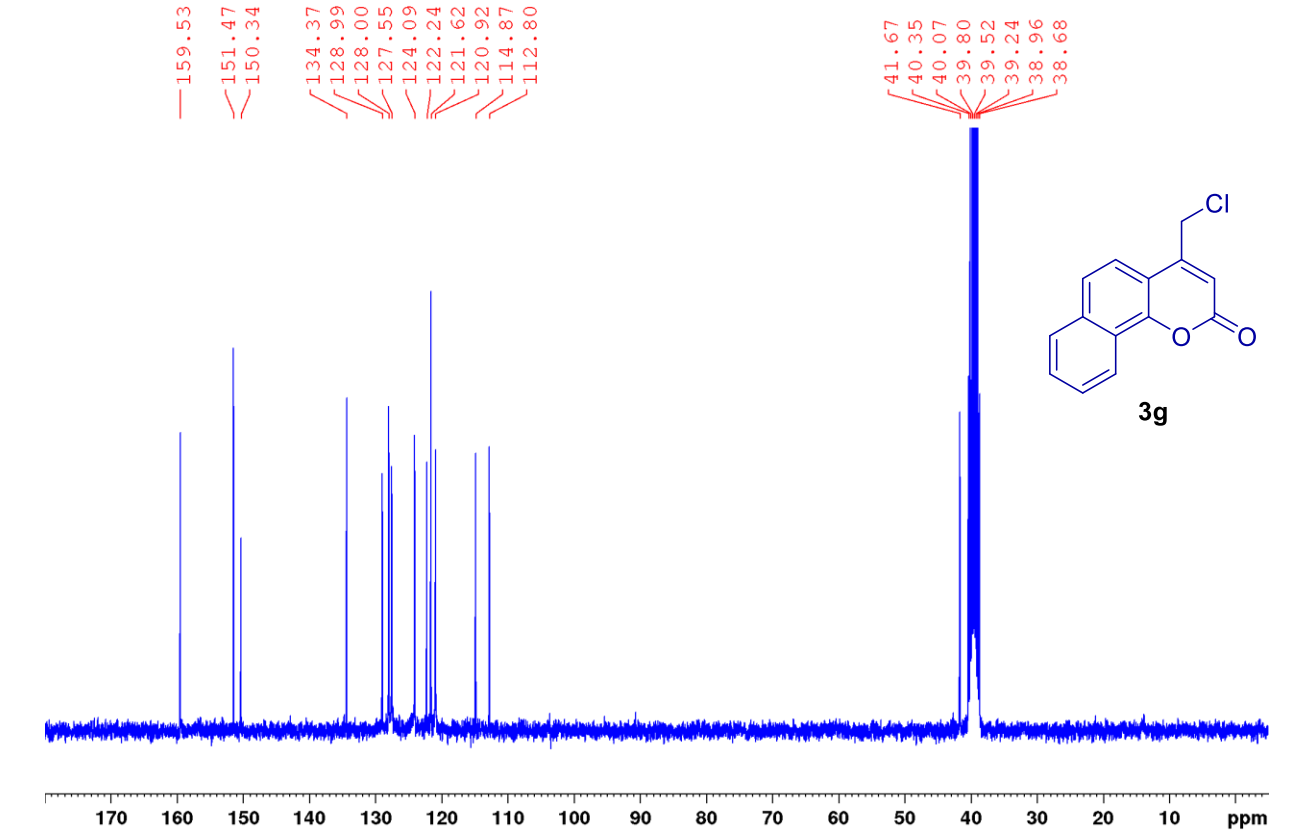


Figure S16. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3g**.

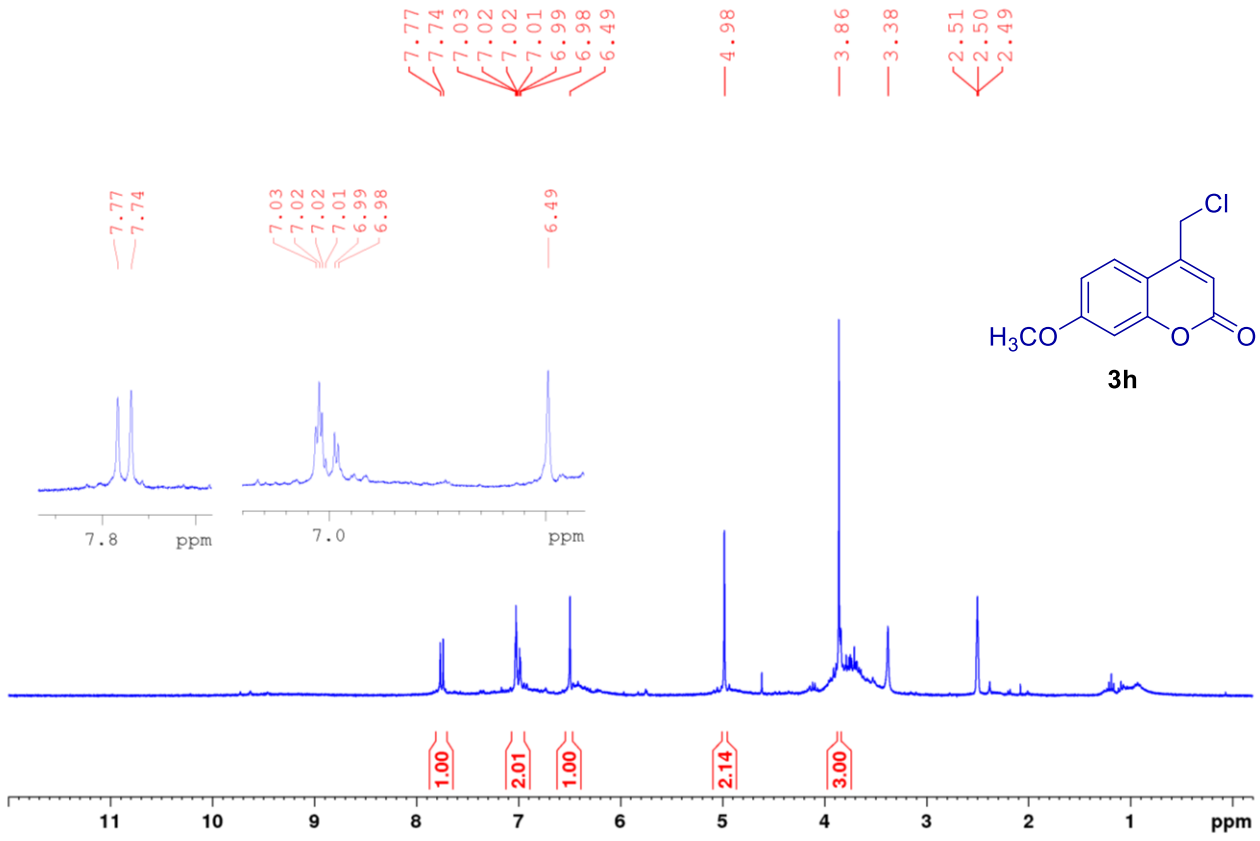


Figure S17. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3h**.

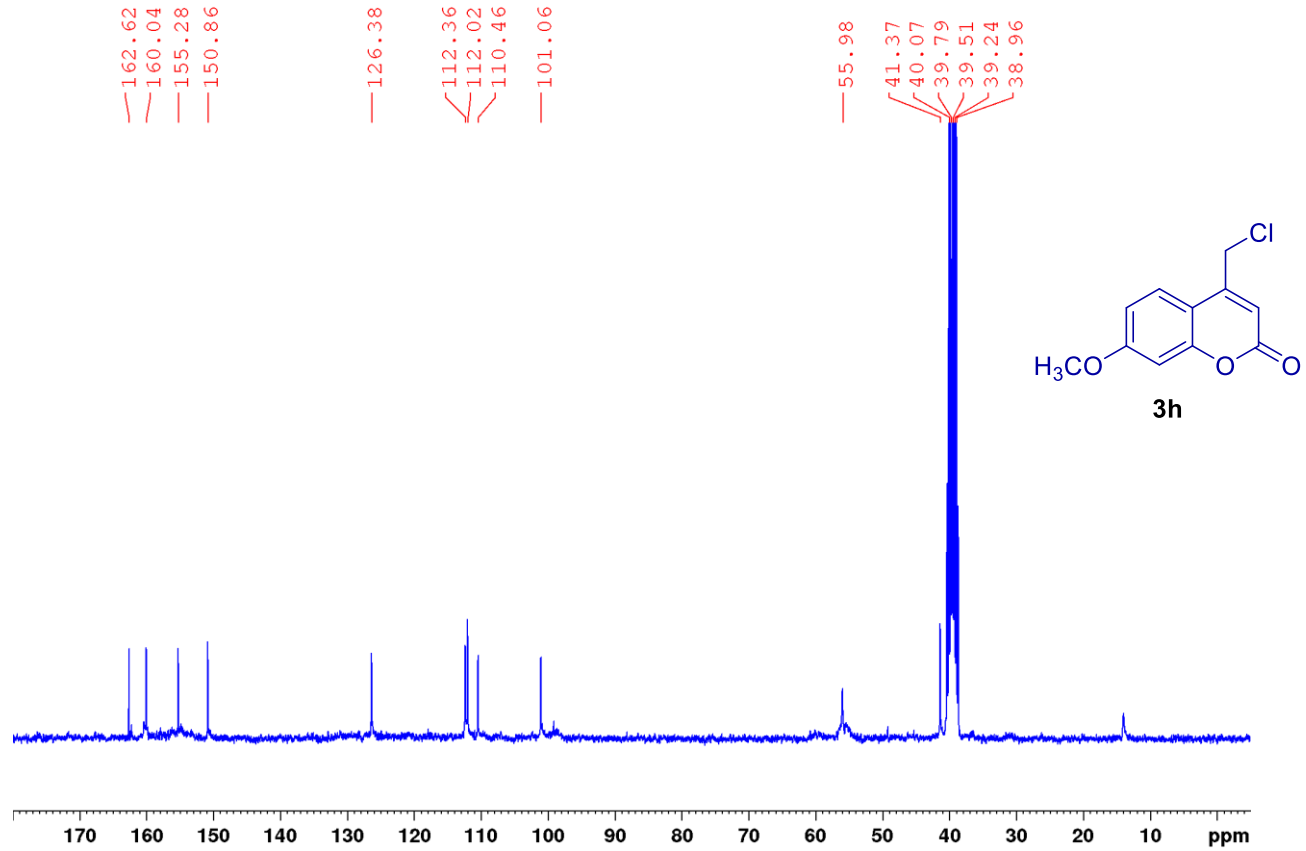


Figure S18. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3h**.

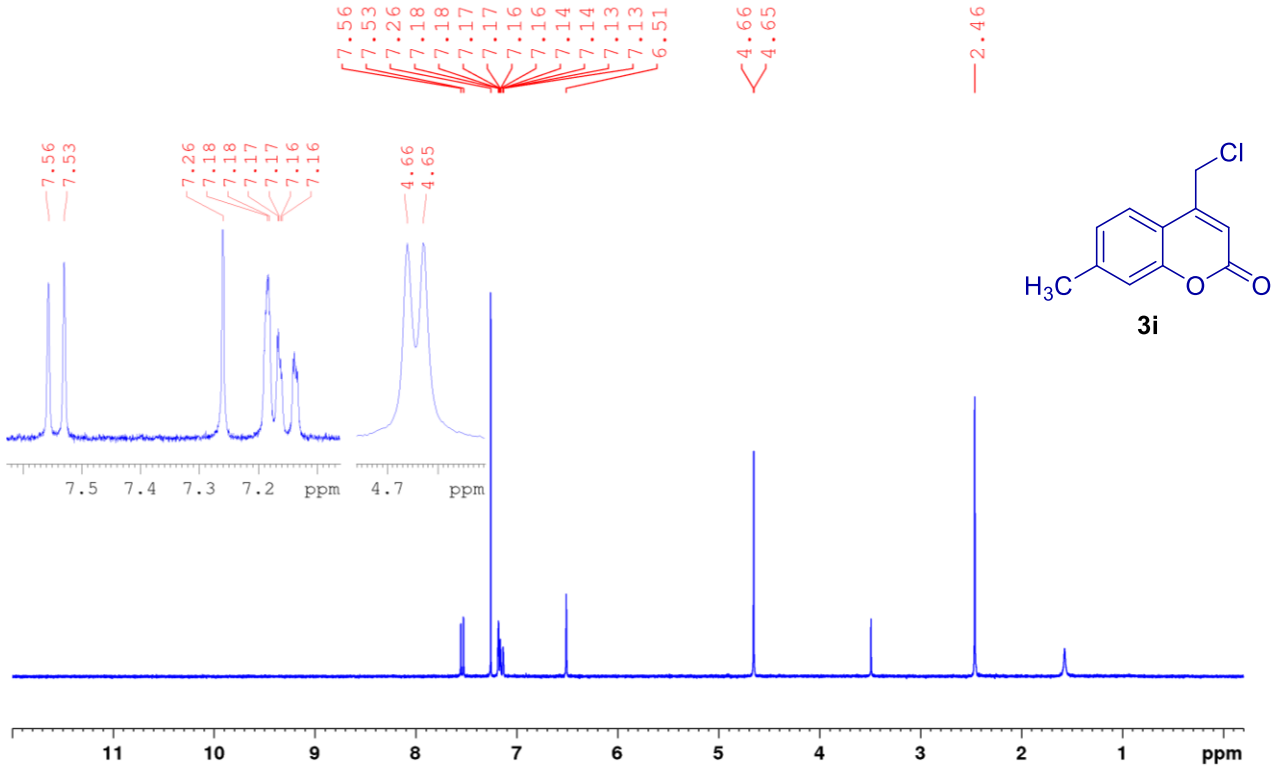


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the product **3i**.

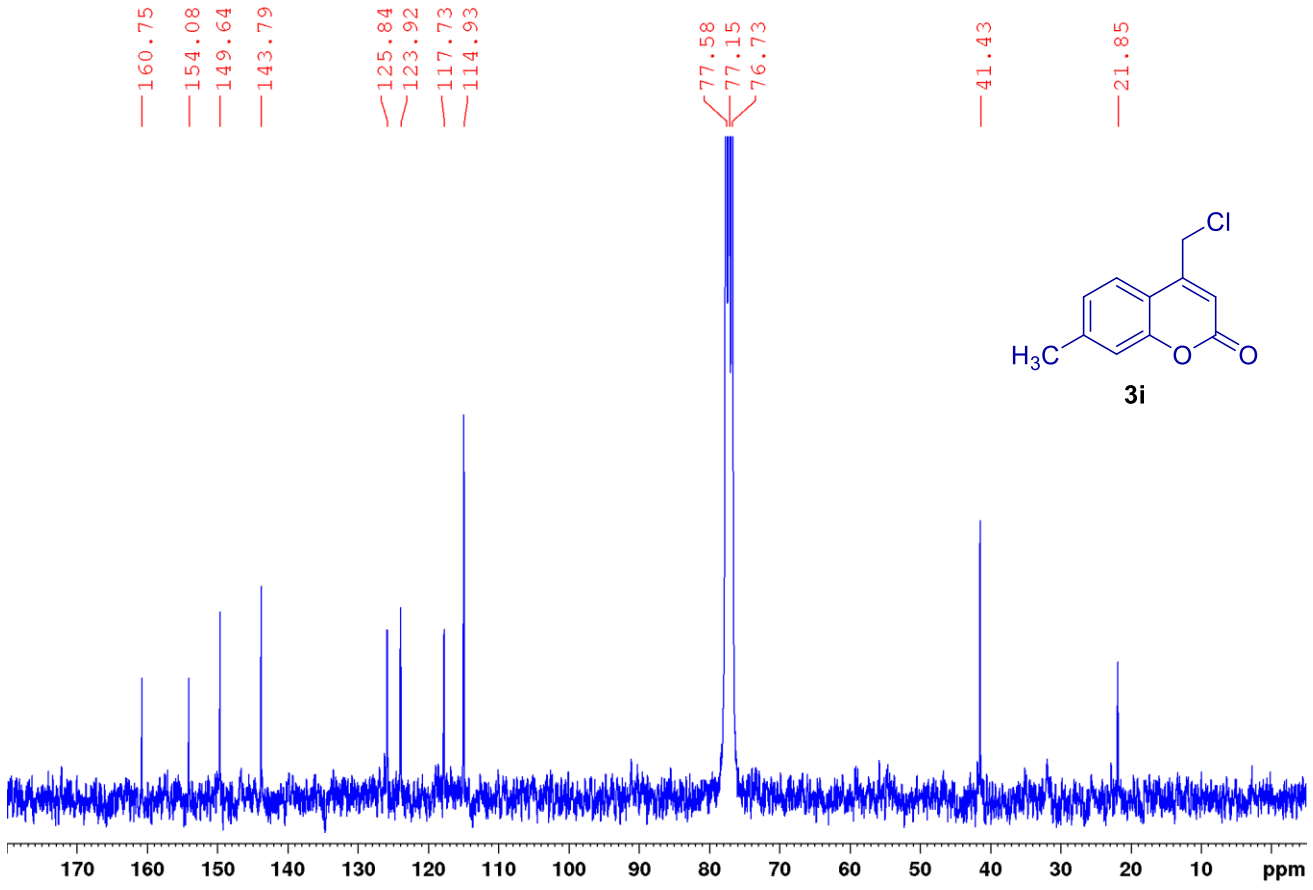


Figure S20. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of the product **3i**.

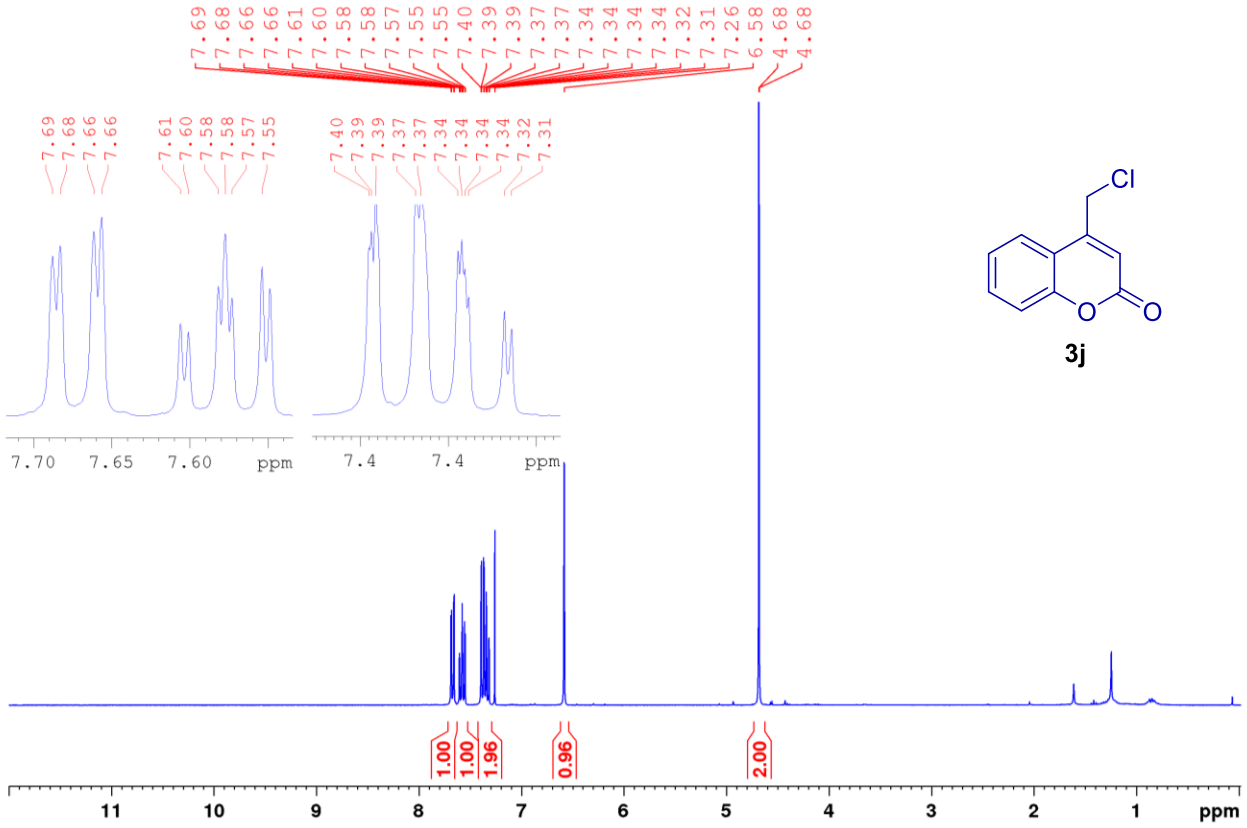


Figure S21. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the product **3j**.

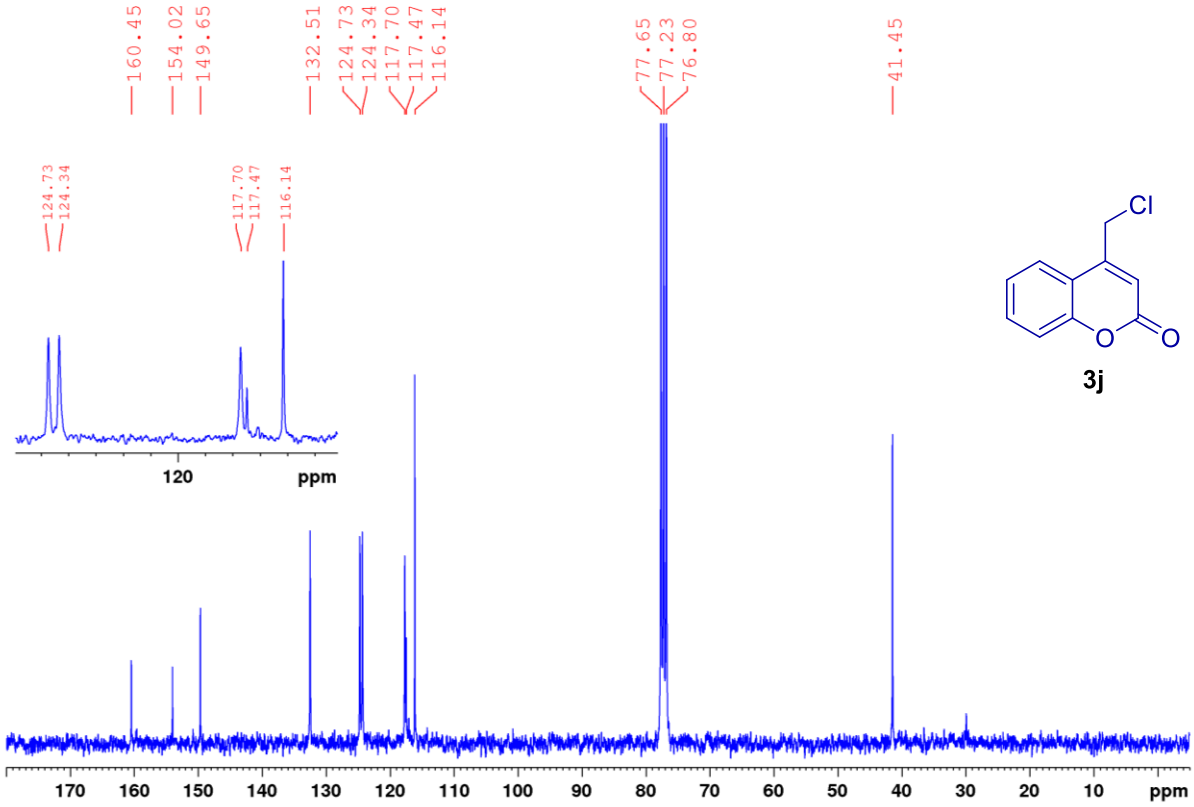


Figure S22. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of the product **3j**.

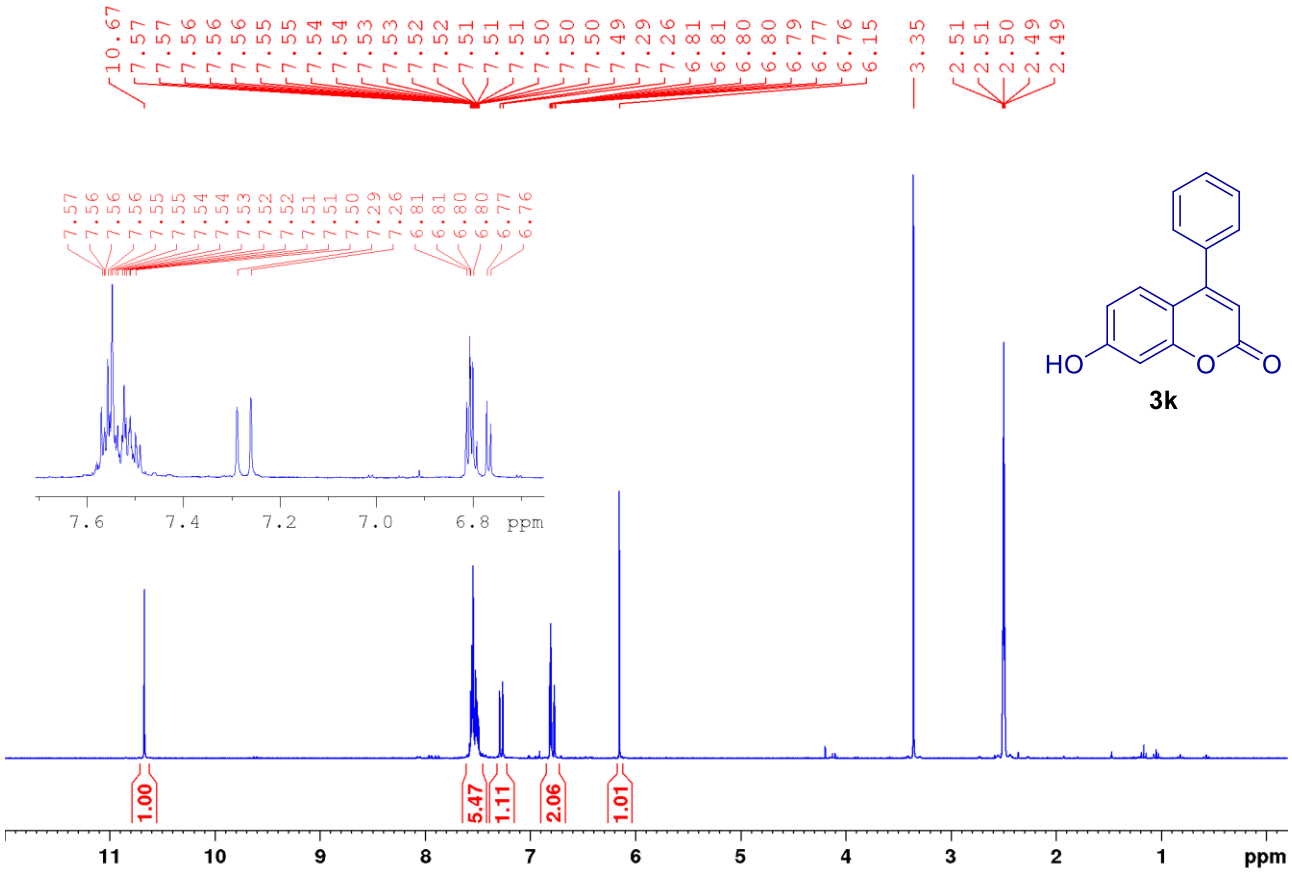


Figure S23. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3k**.

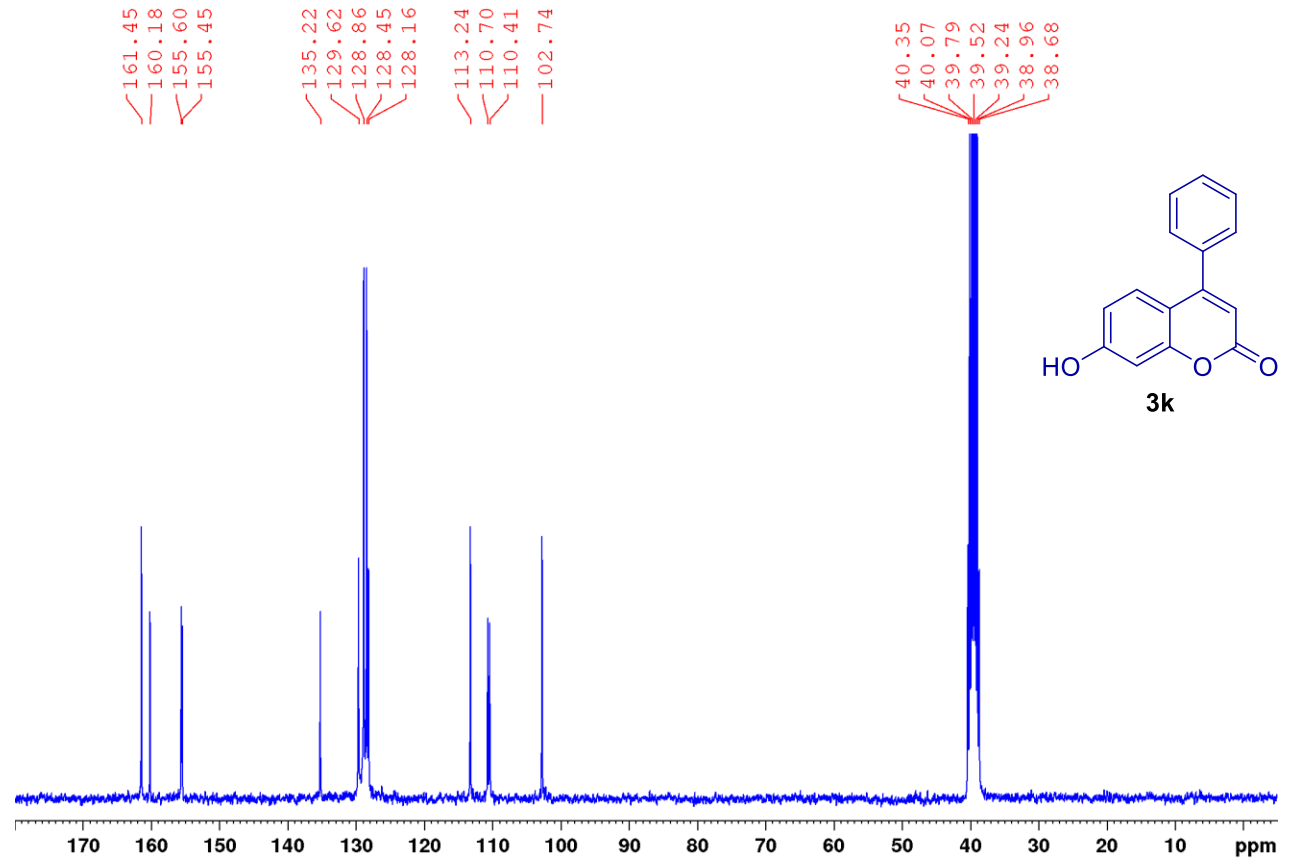


Figure S24. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3k**.

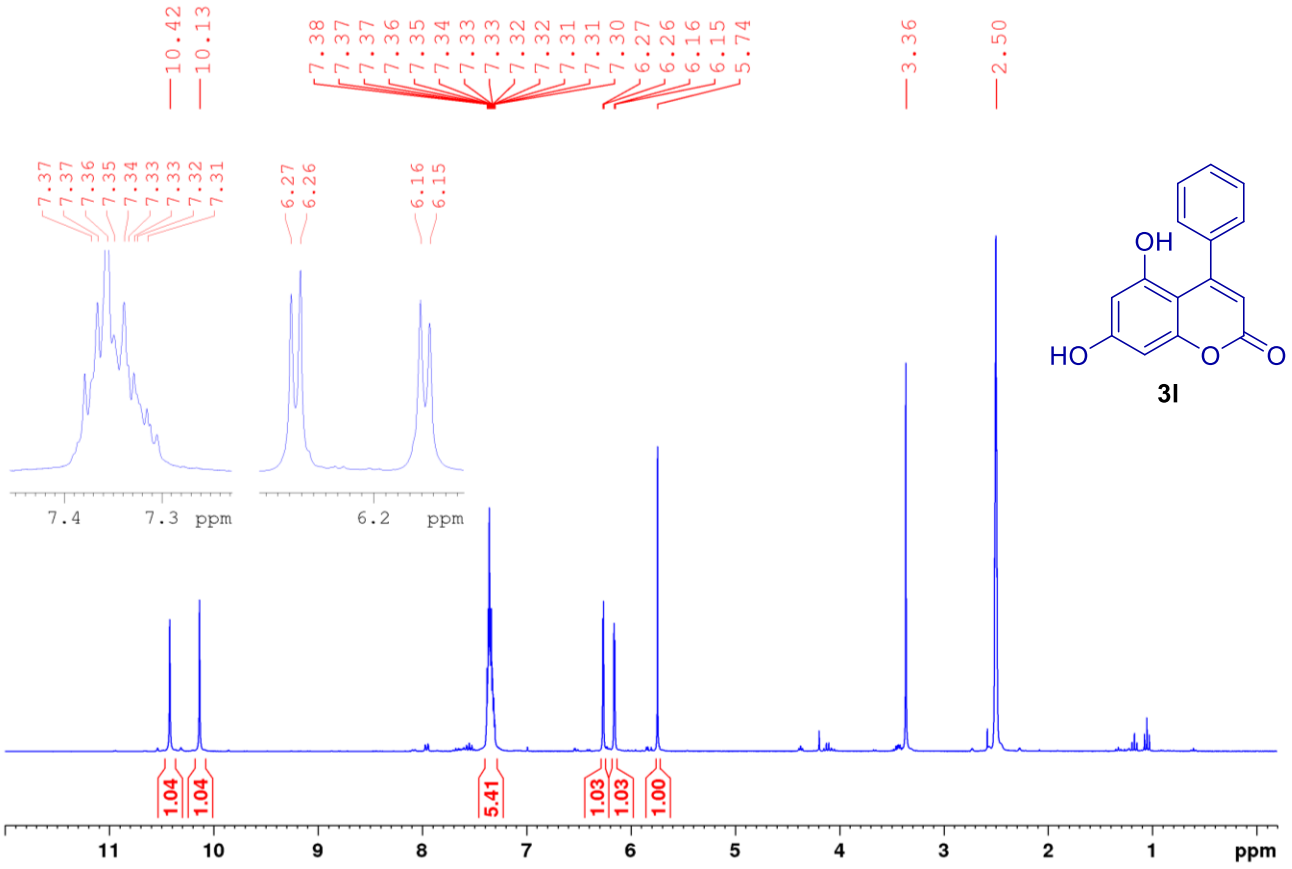


Figure S25. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3l**.

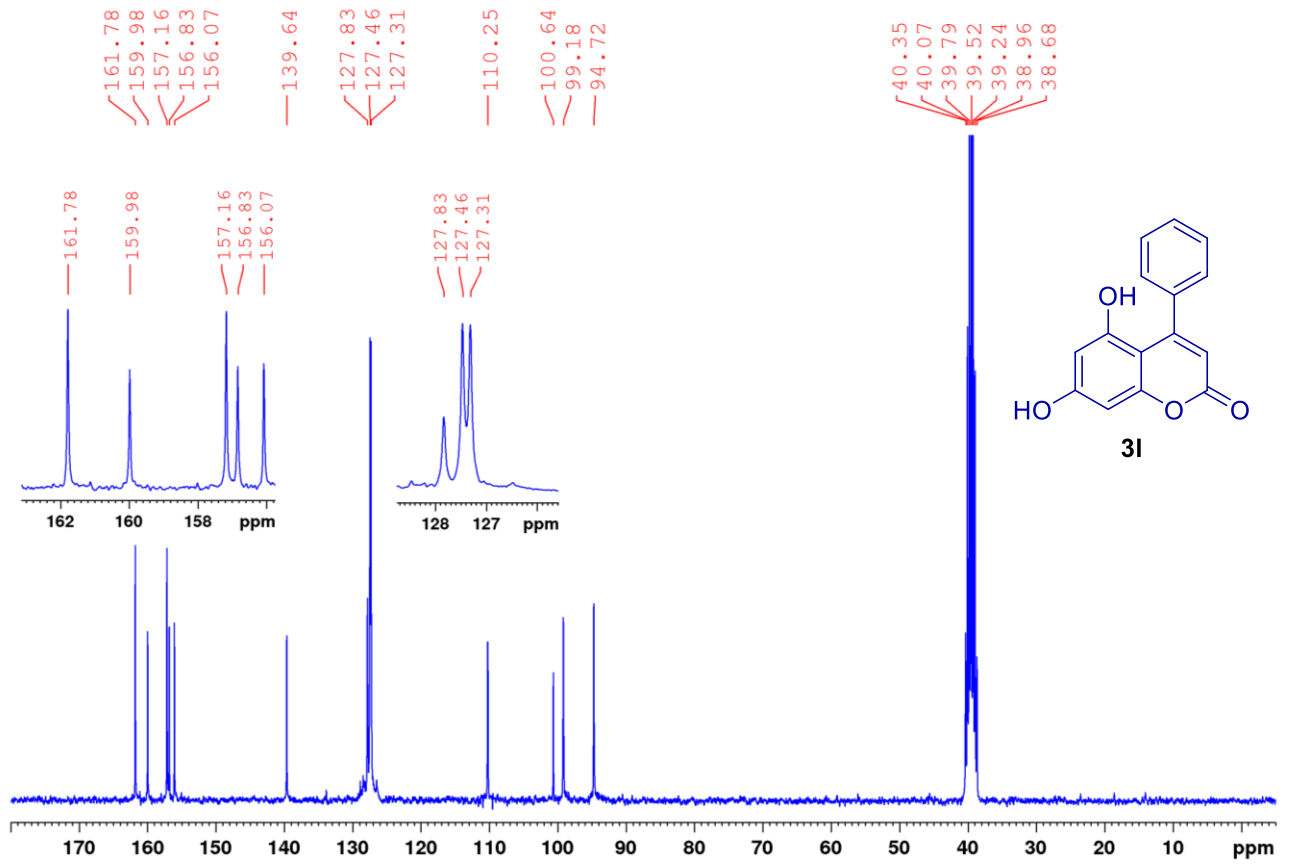


Figure S26. ^{13}C NMR spectrum (75 MHz, DMSO-d_6)of the product **3l**.

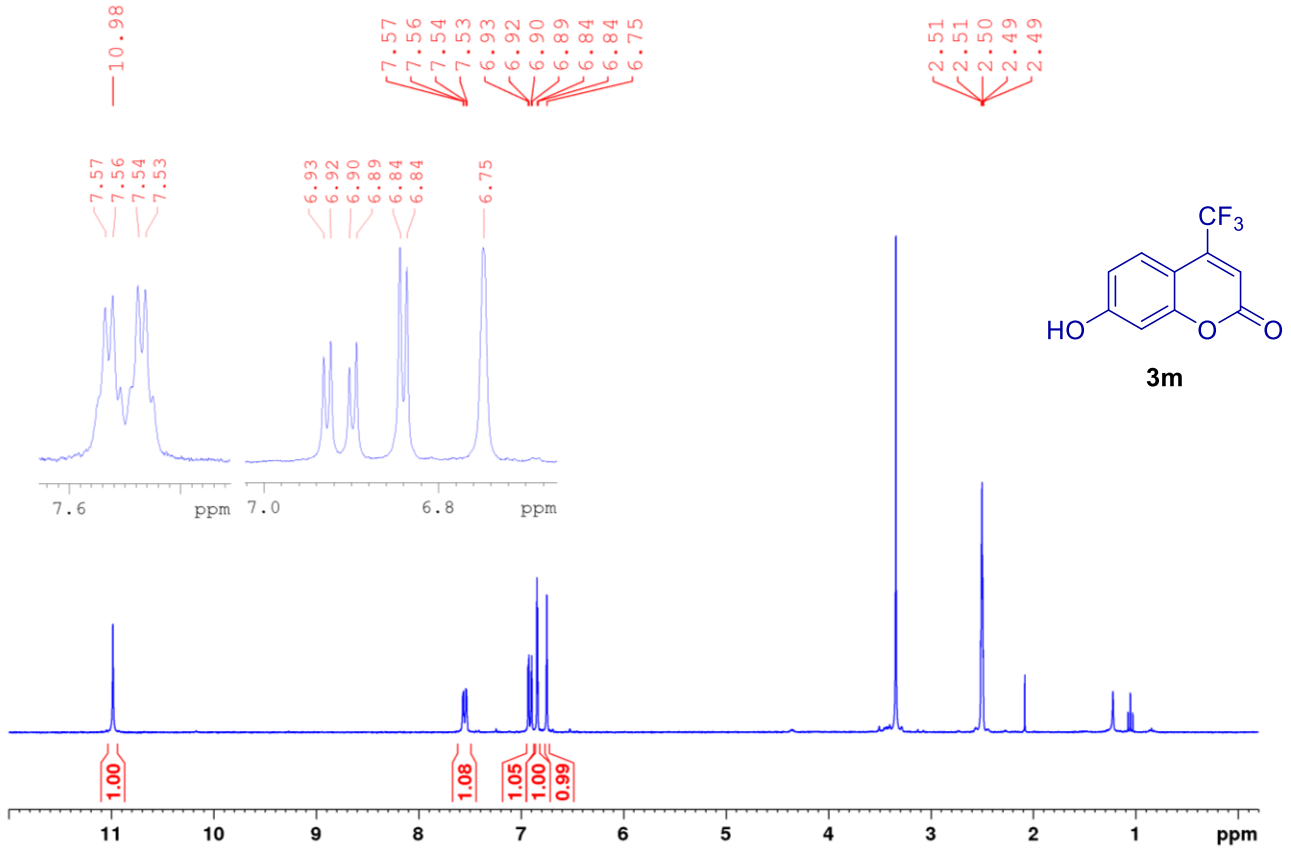


Figure S27. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3m**.

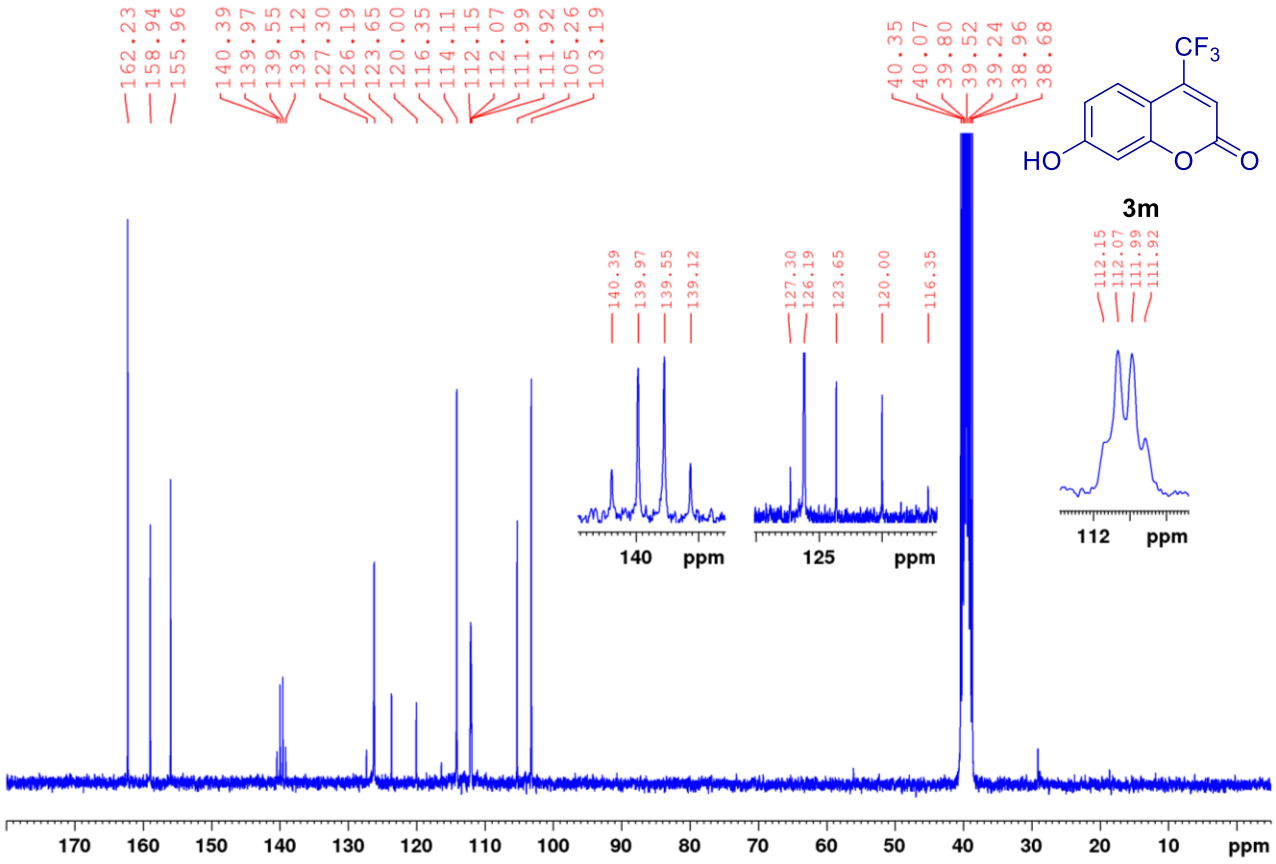


Figure S28. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3m**.

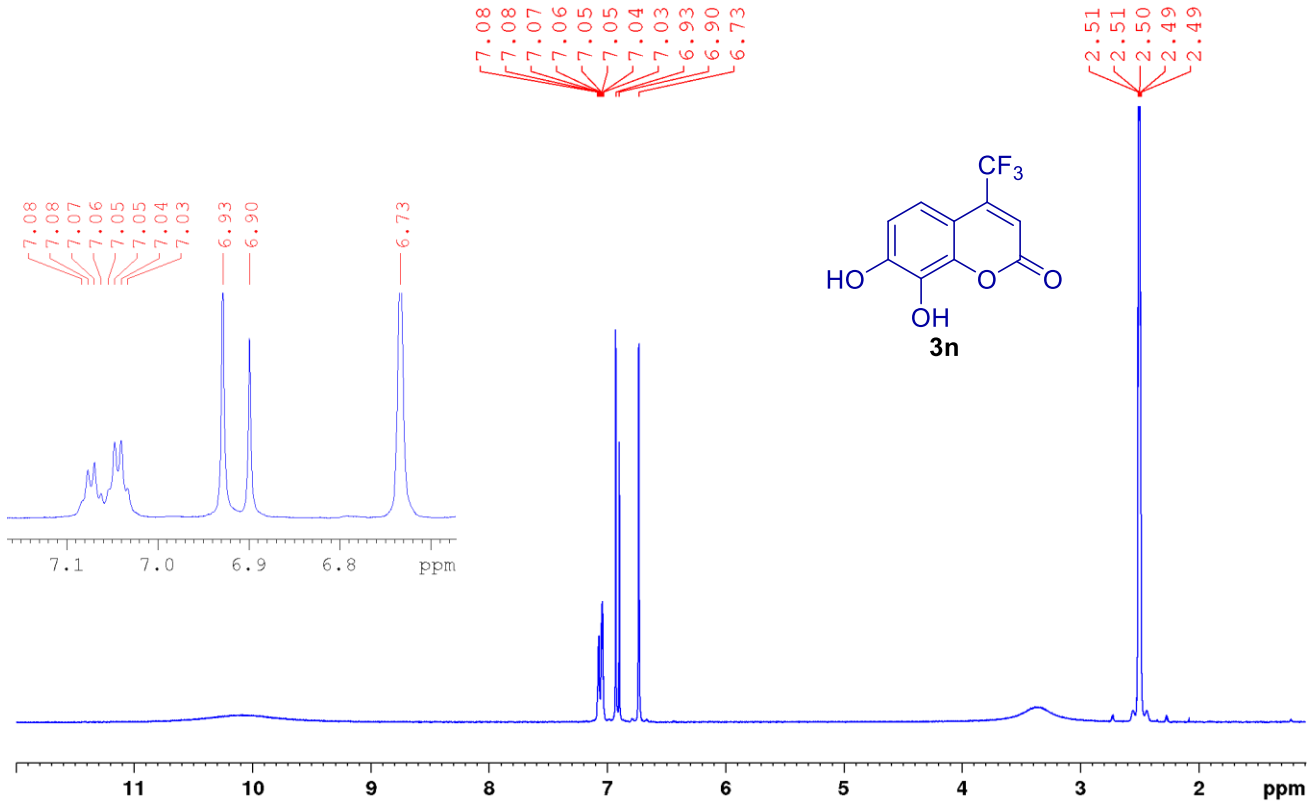


Figure S29. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3n**.

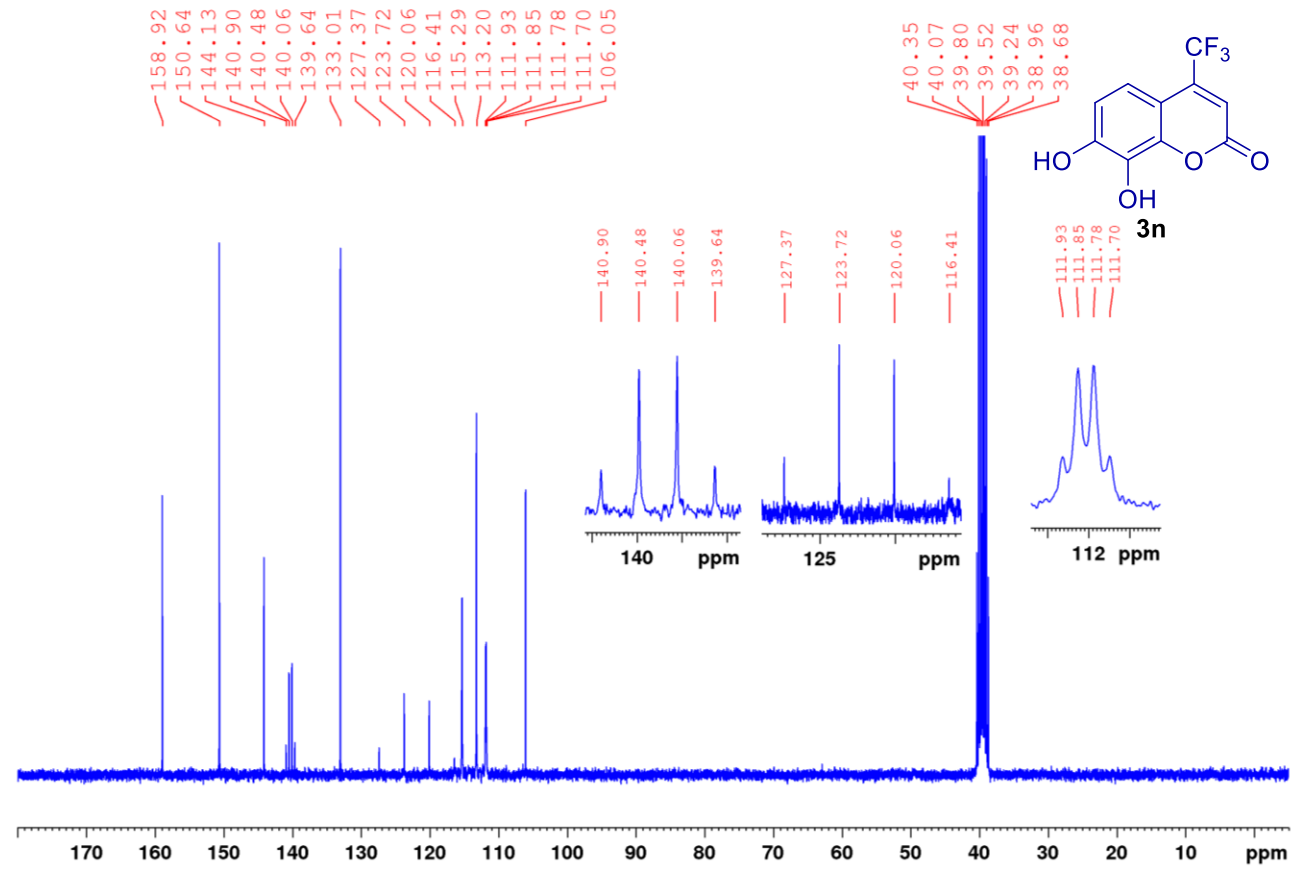


Figure S30. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3n**.

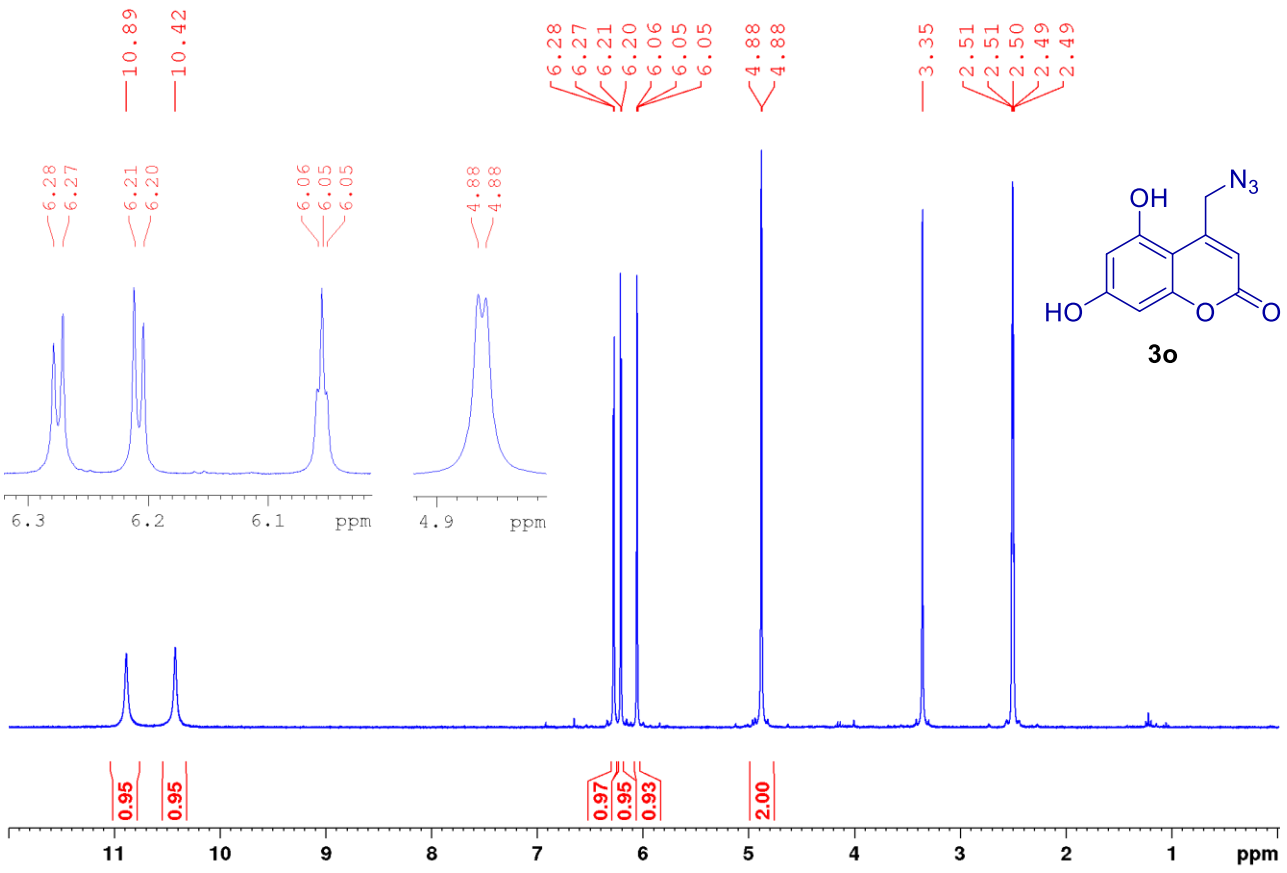


Figure S31. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of the product **3o**.

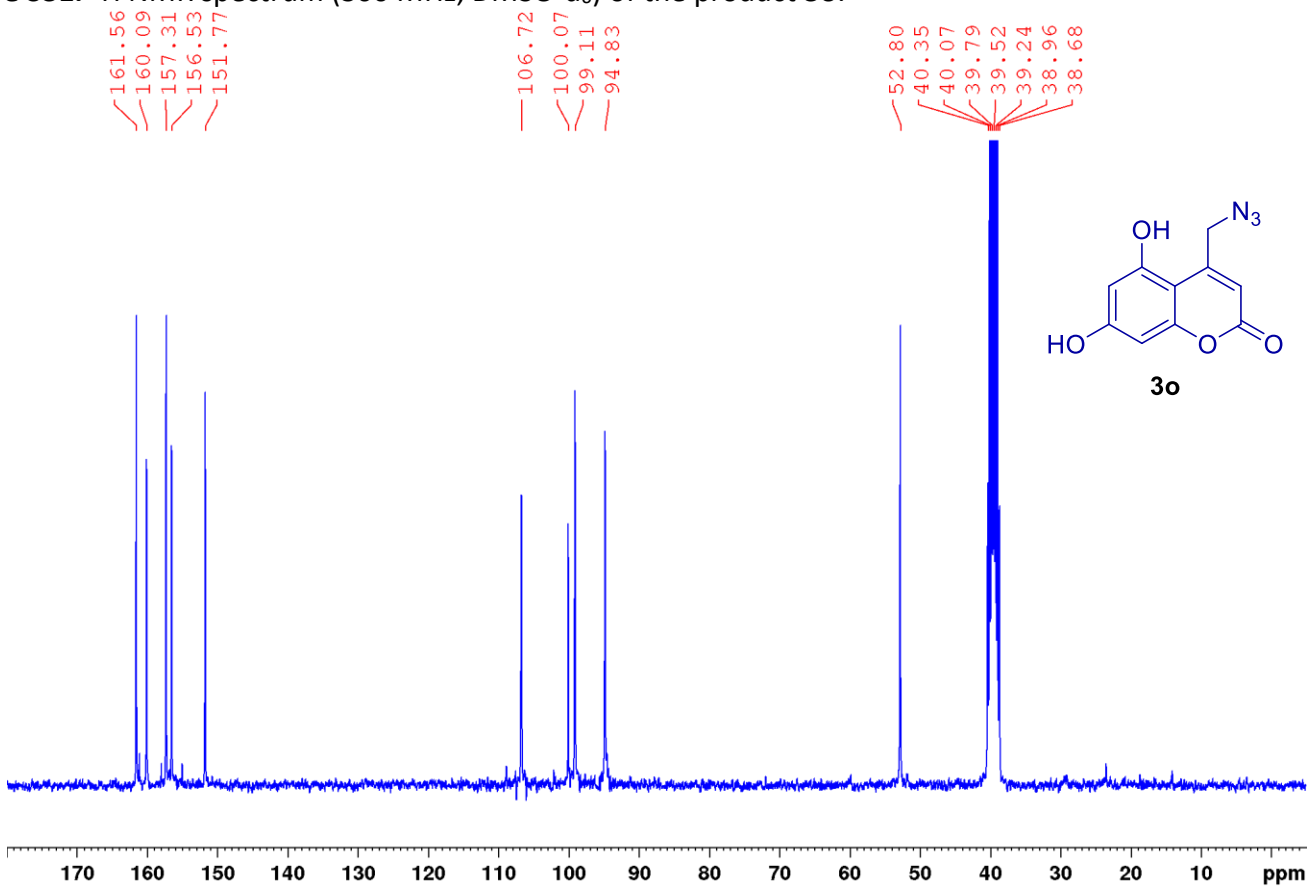


Figure S32. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of the product **3o**.