New Journal of Chemistry

Microwave-Assisted Synthesis and Photophysical Studies of Novel Fluorescent N-acylhydrazone- and Semicarbazone-7-OH-Coumarin Dyes

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Supporting Information

Contents

^{1}H HMR , ^{13}C NMR, IV and Mass Spectra

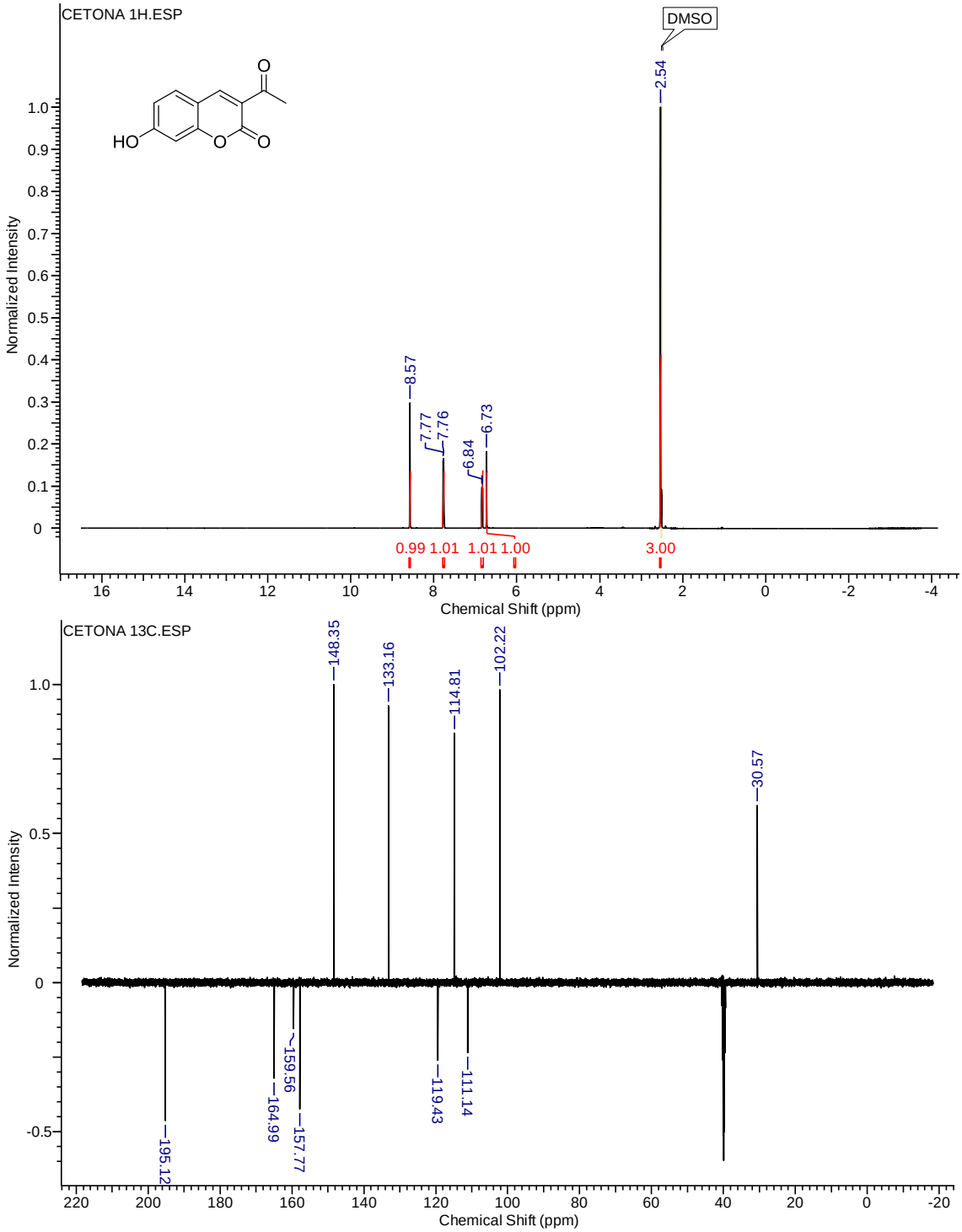

Fig. S1. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **1** in DMSO-d_6.

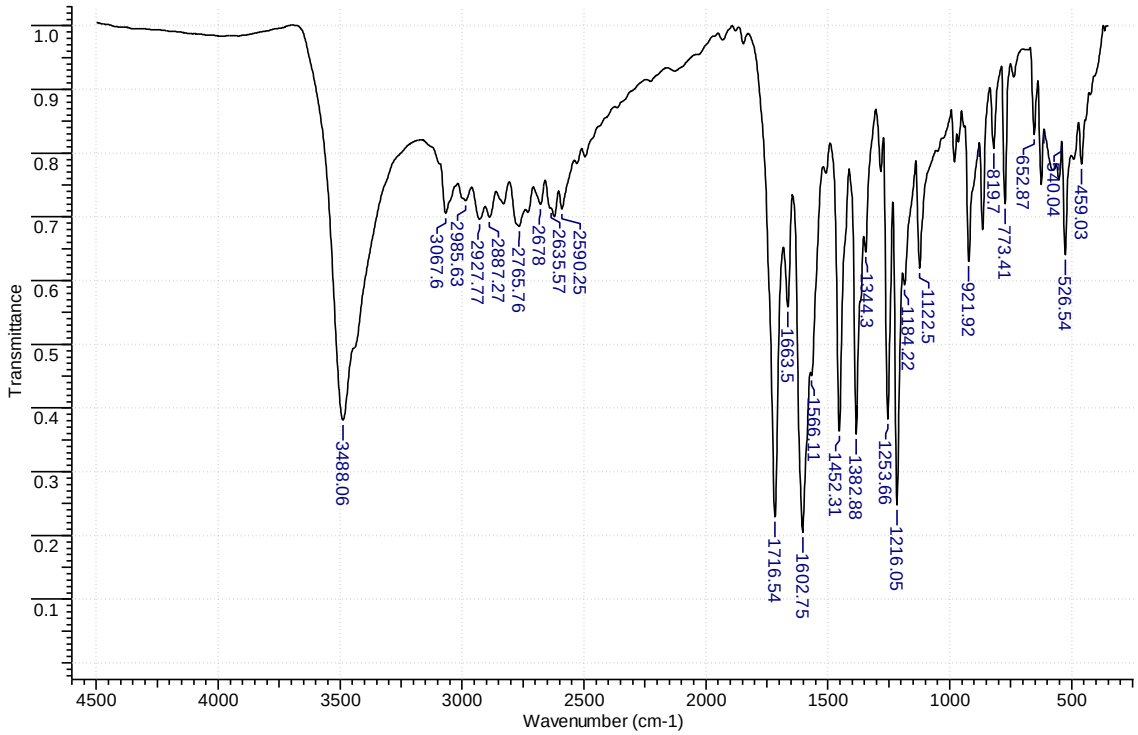

Fig. S2. IR spectra of **1** in KBr.

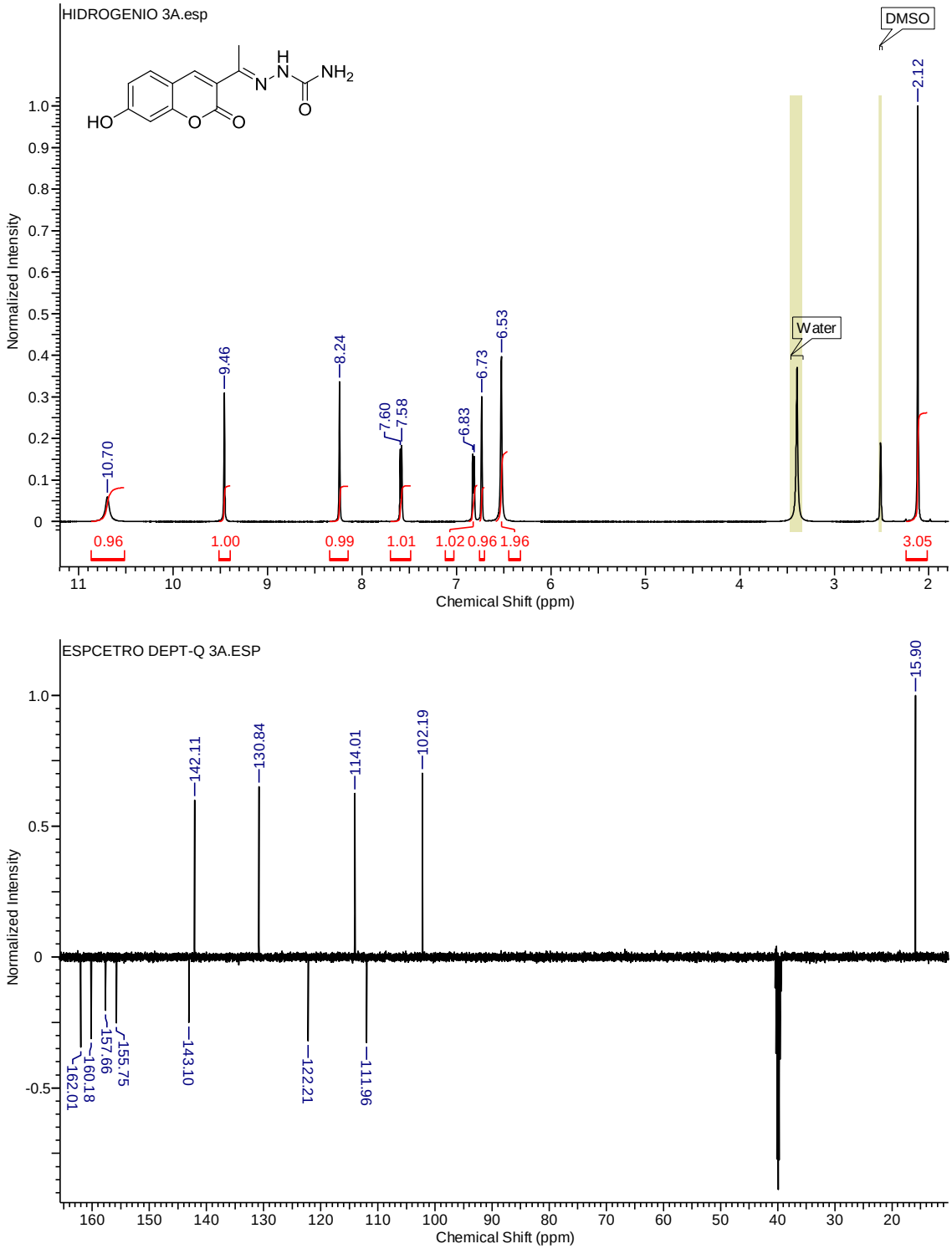

Fig. S3. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3a** in DMSO-d_6.

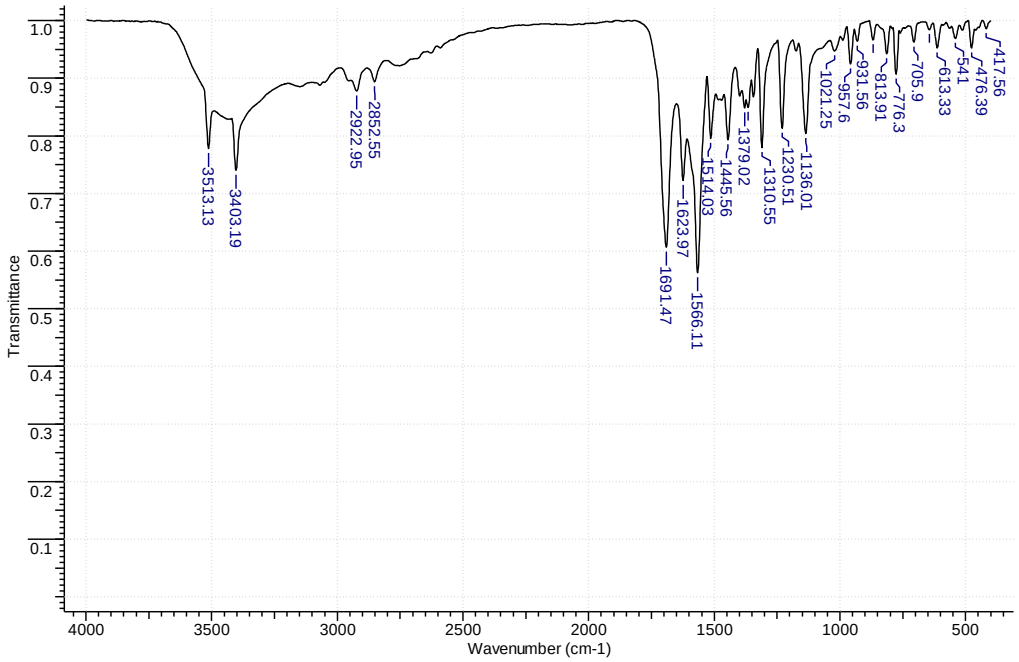

Fig. S4. IR spectra of **1** in KBr.

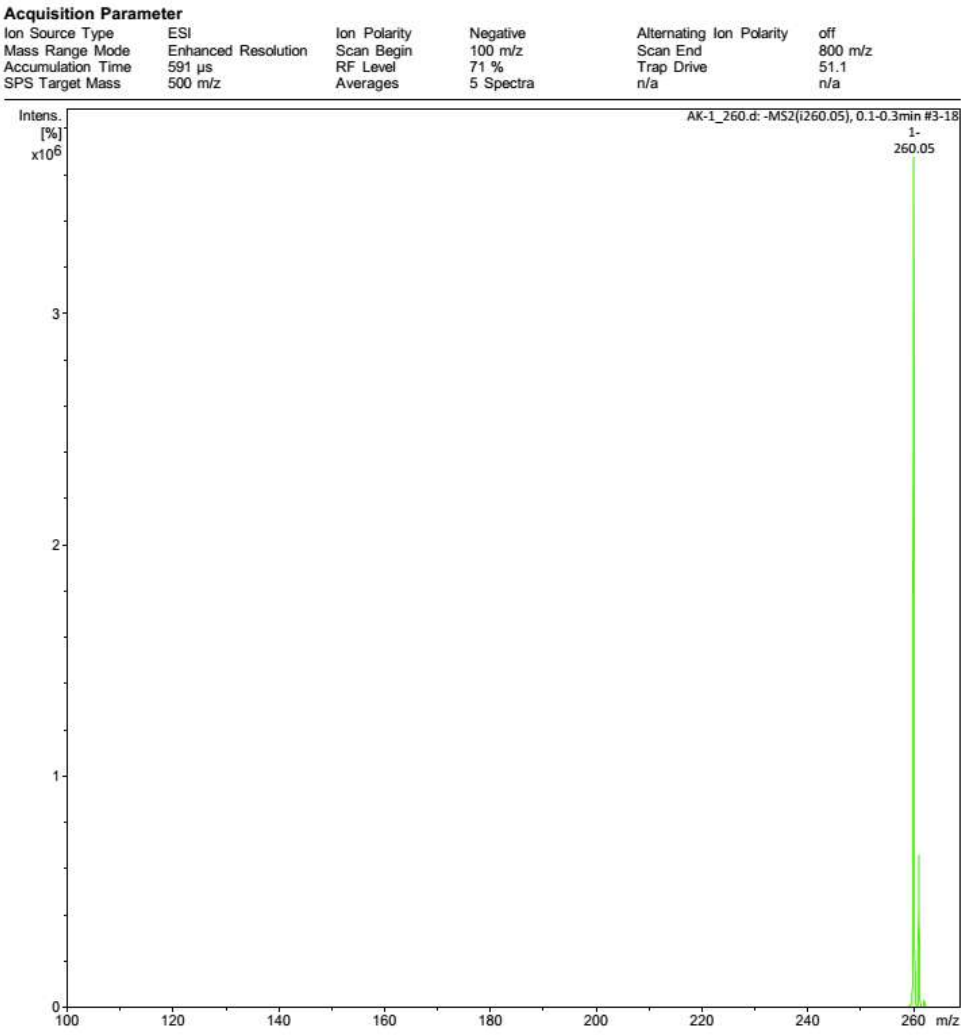

Fig. S5. EM spectra of **3a**.

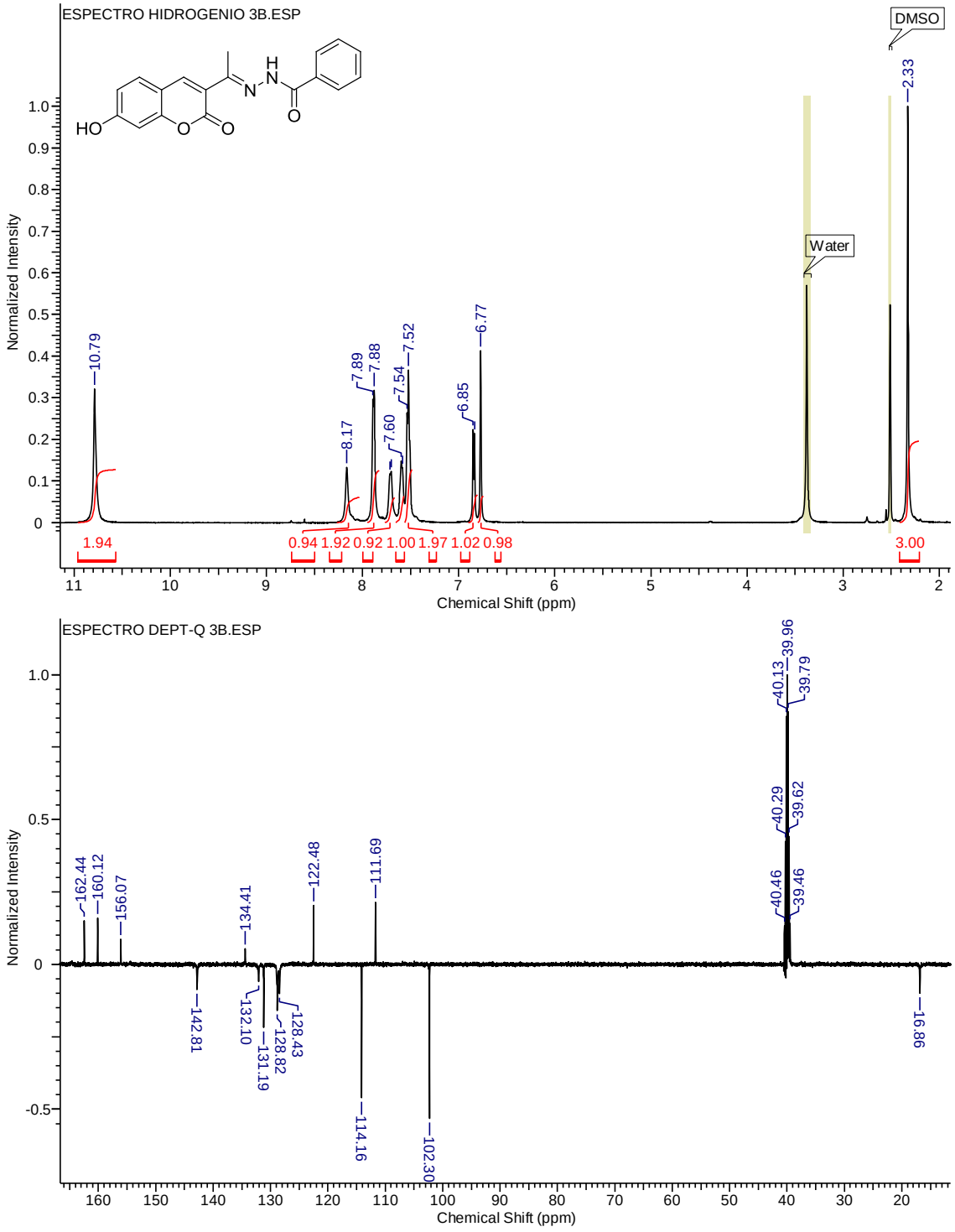

Fig. S6. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3b** in DMSO-d_6.

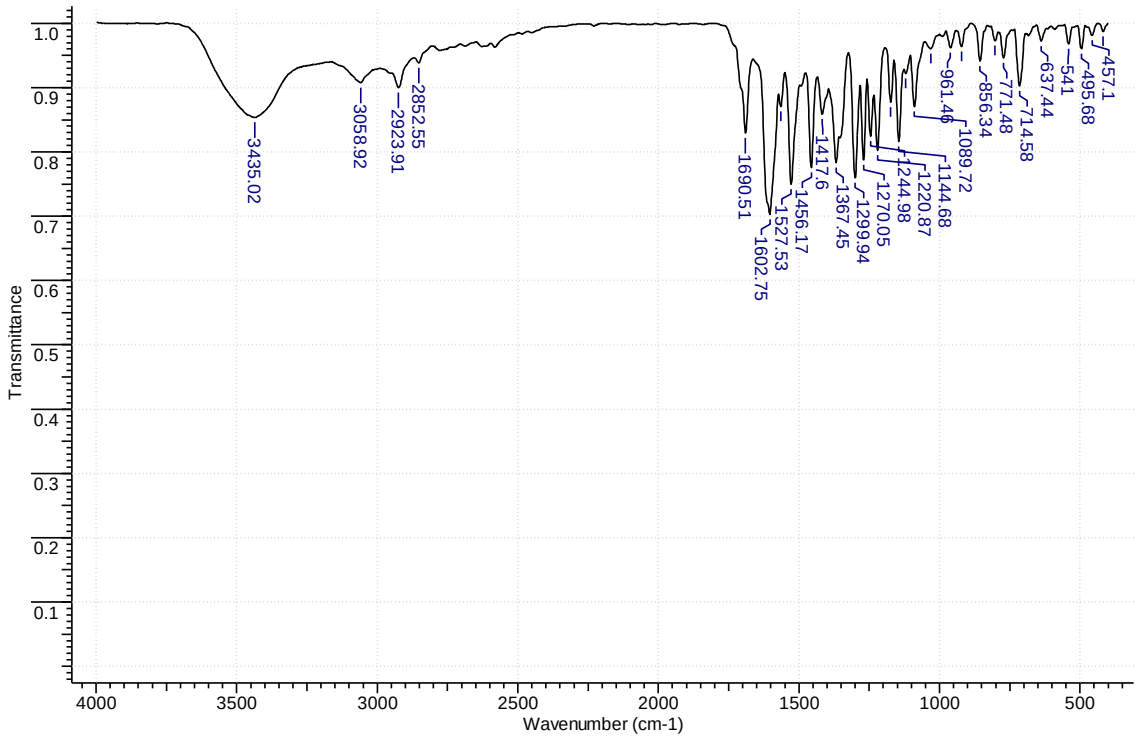

Fig. S7. IR spectra of **3b** in KBr.

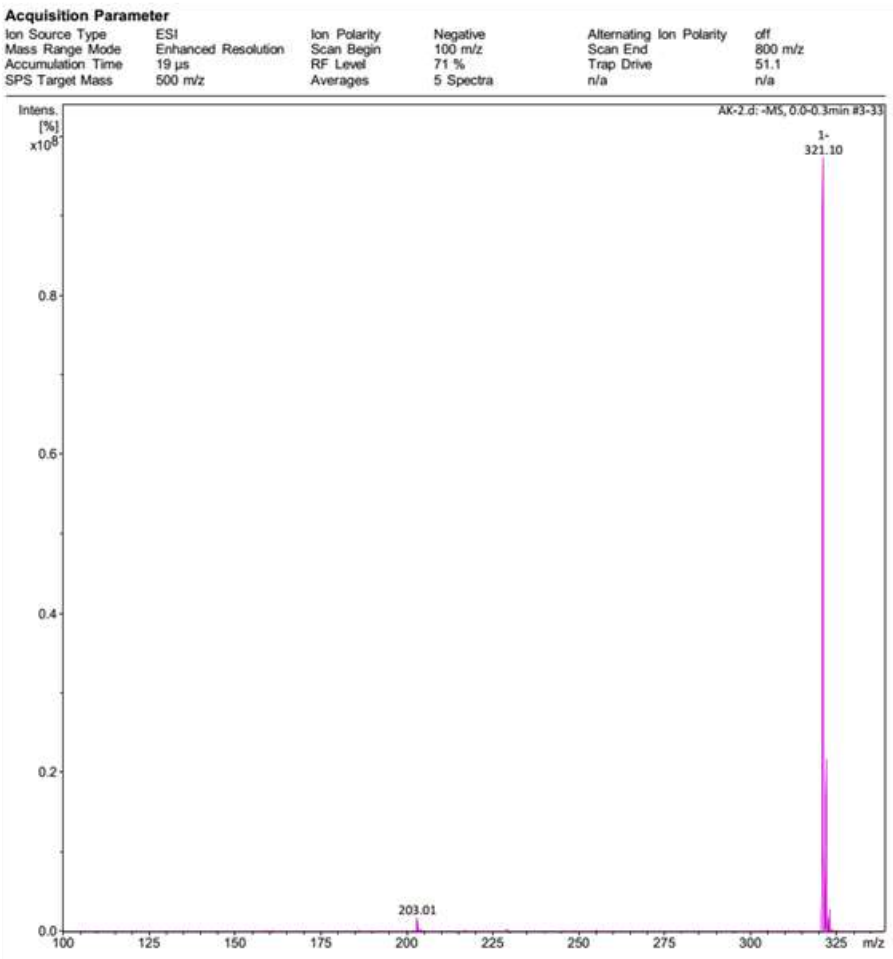

Fig. S8. EM spectra of **3b**.

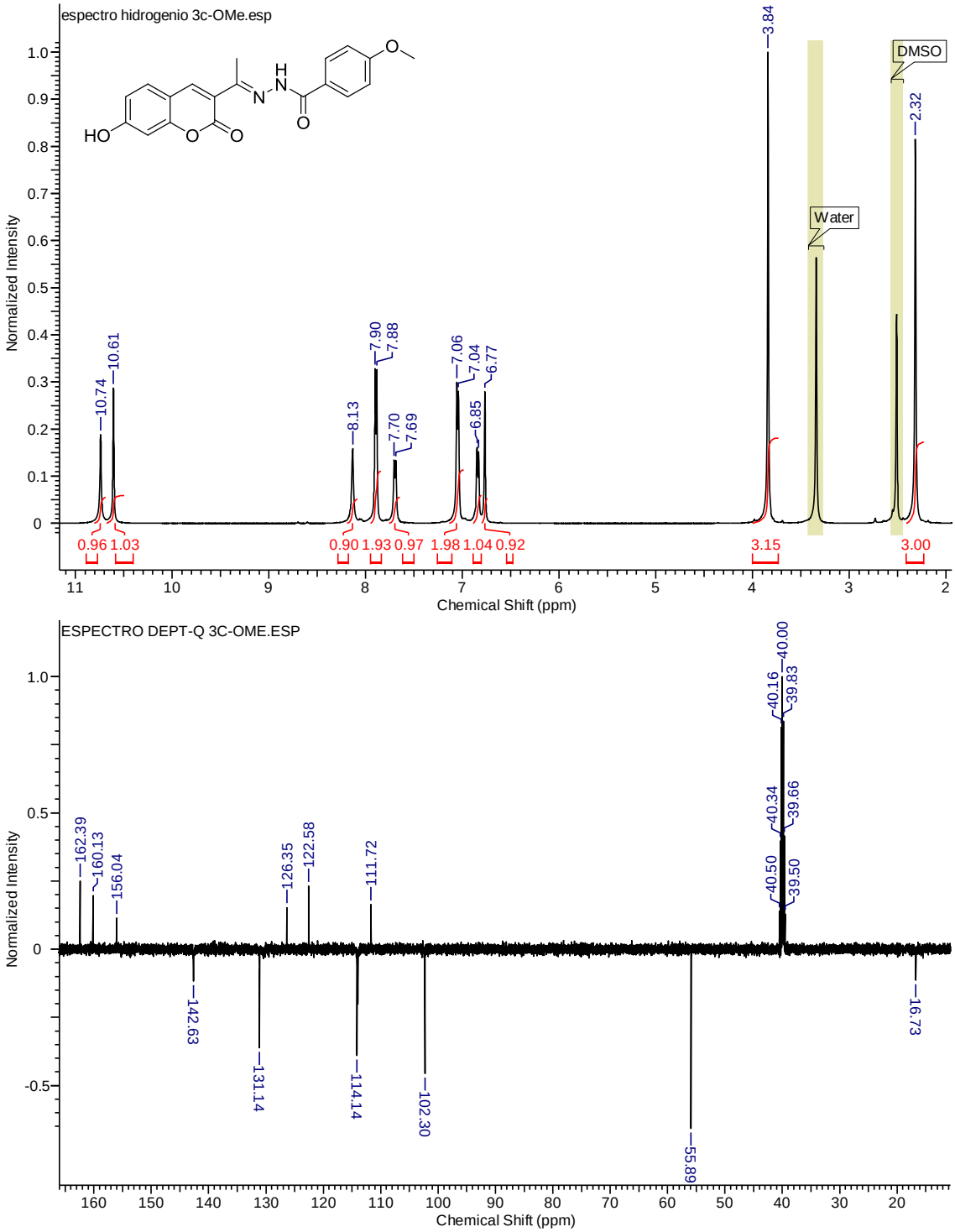

Fig. S9. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3c** in DMSO-d_6.

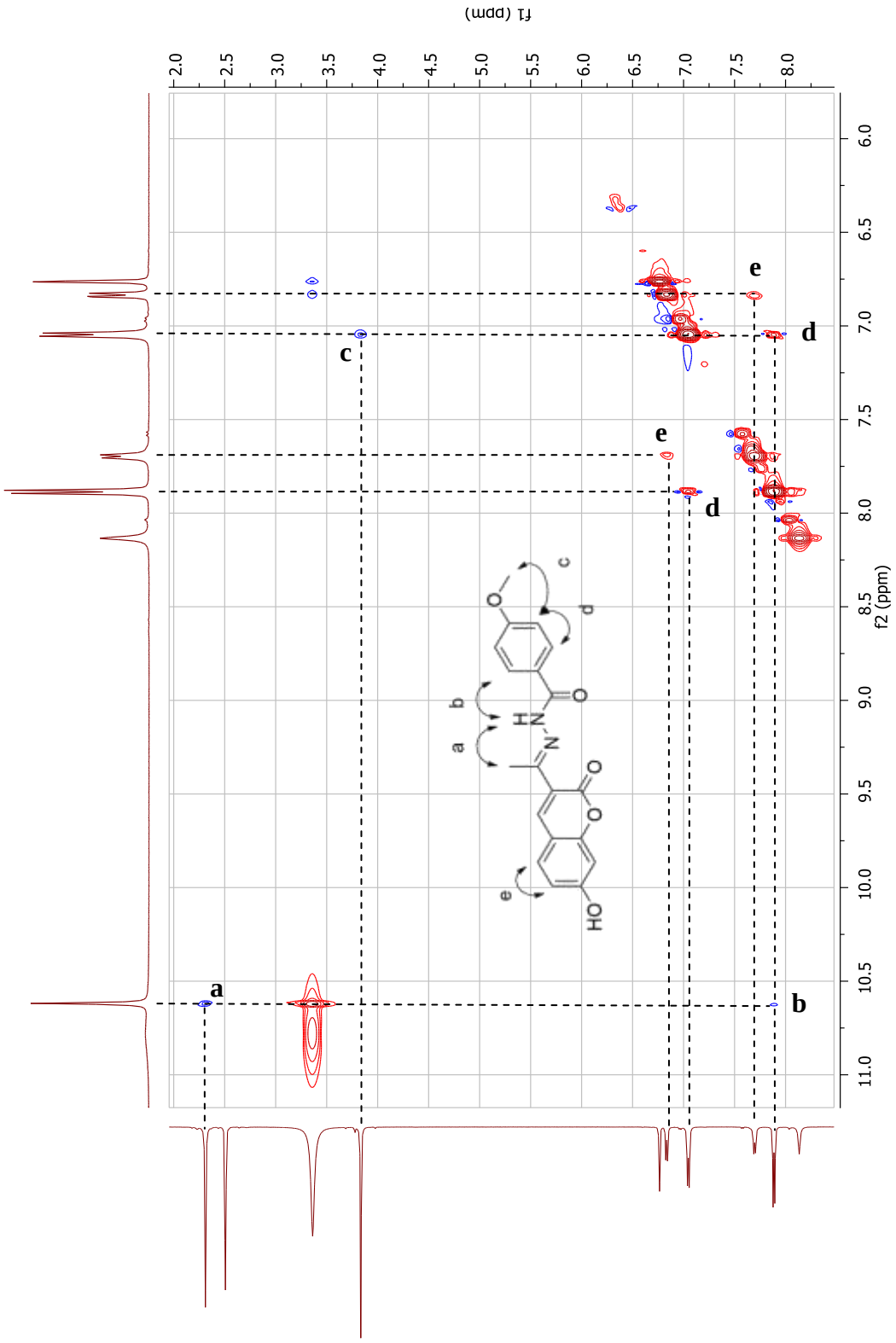

Fig. S10. NOESY spectrum of **3c** in DMSO-d_6 and correlations indicating the (*E*)-isomer.

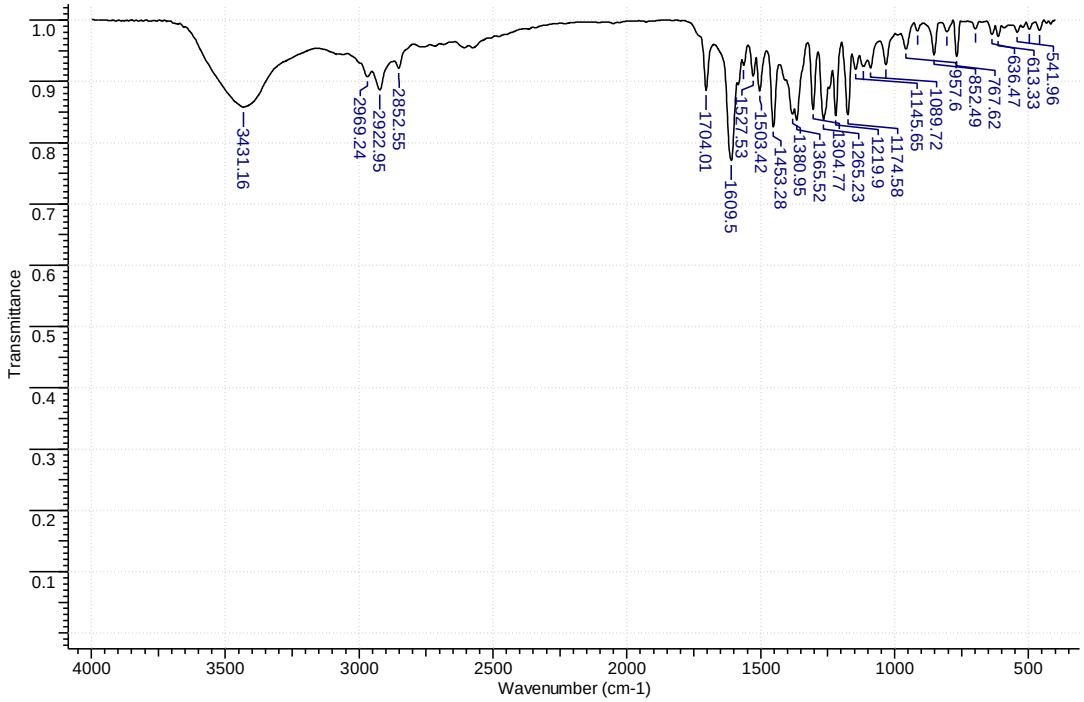

Fig. S11. IR spectra of **3c** in KBr.

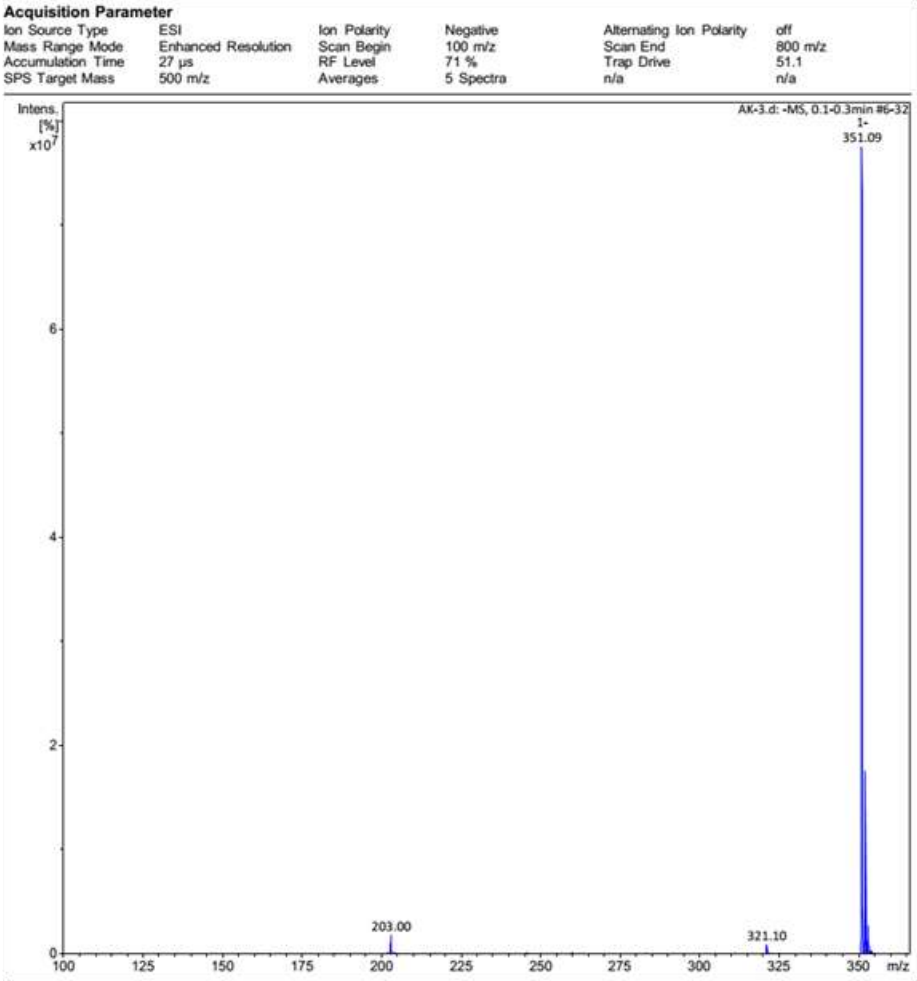

Fig. S12. EM spectra of **3c**.

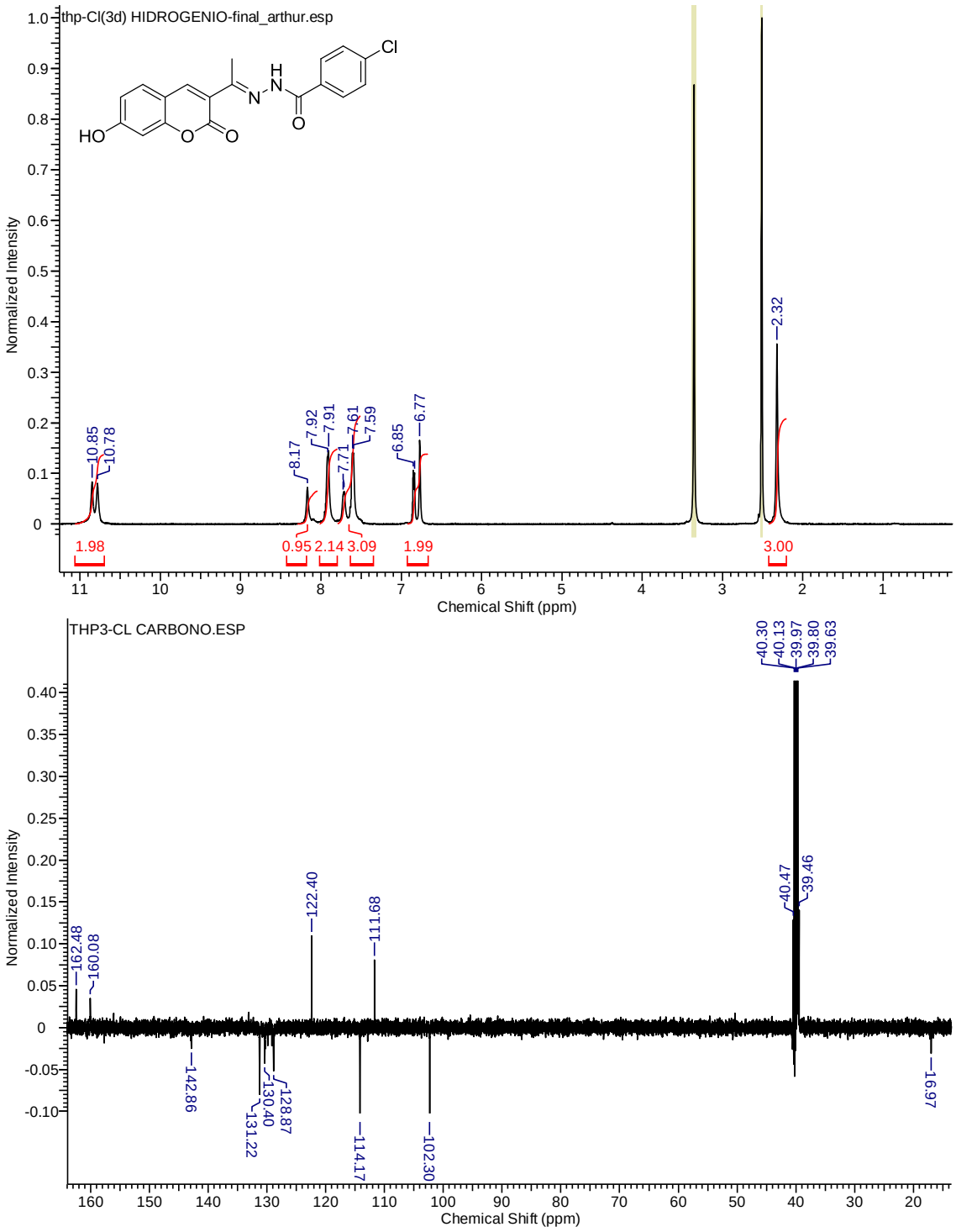

Fig. S13. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3d** in DMSO-d_6.

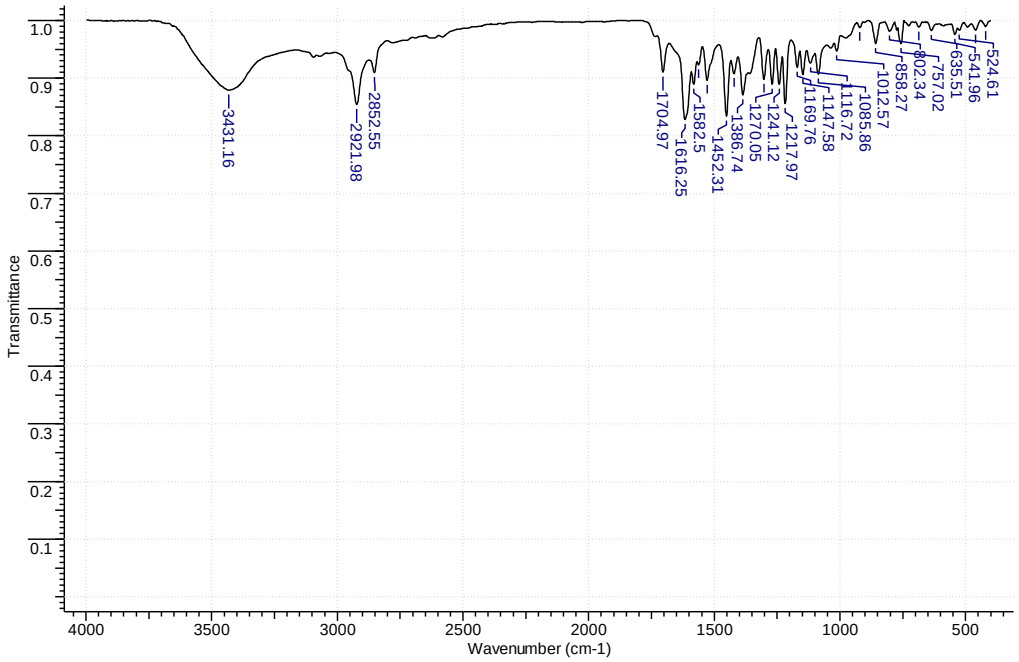

Fig. S14. IR spectra of **3d** in KBr.

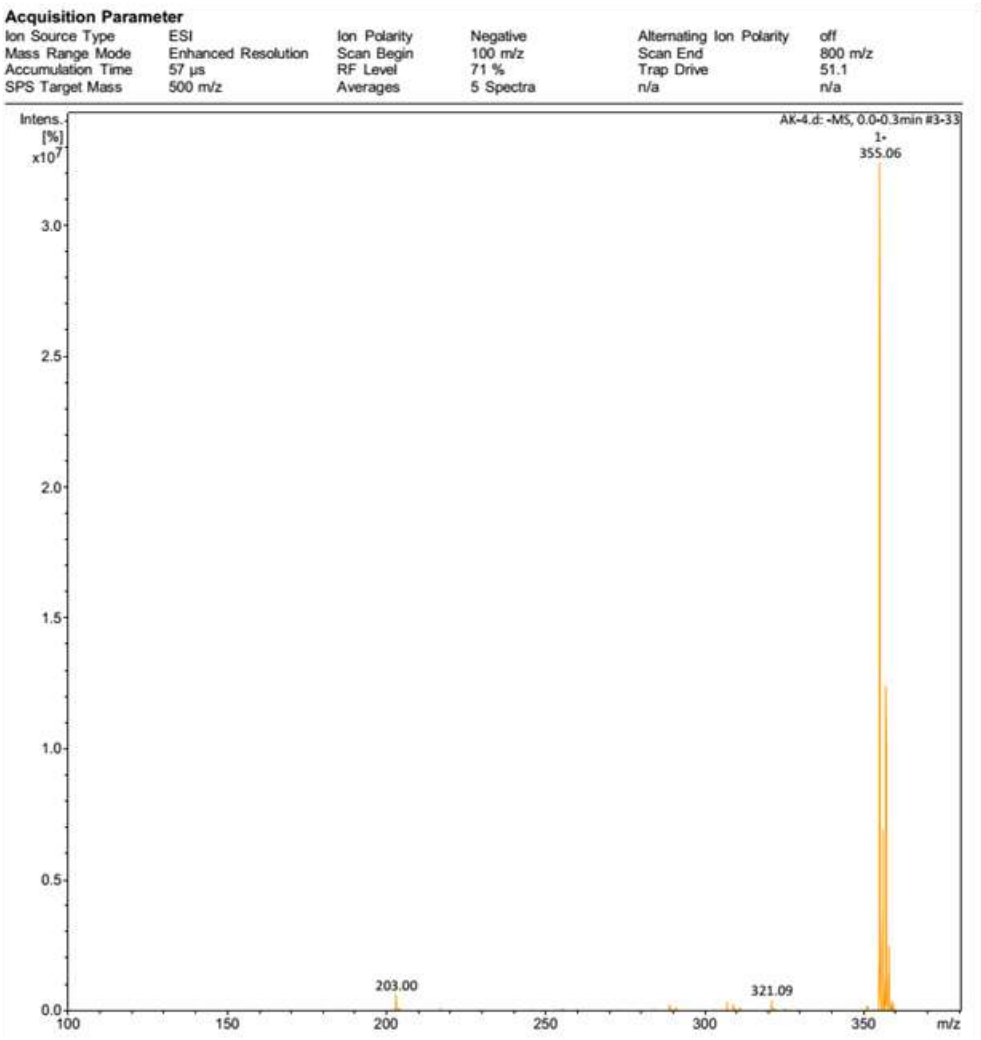

Fig. S15. EM spectra of **3d**.

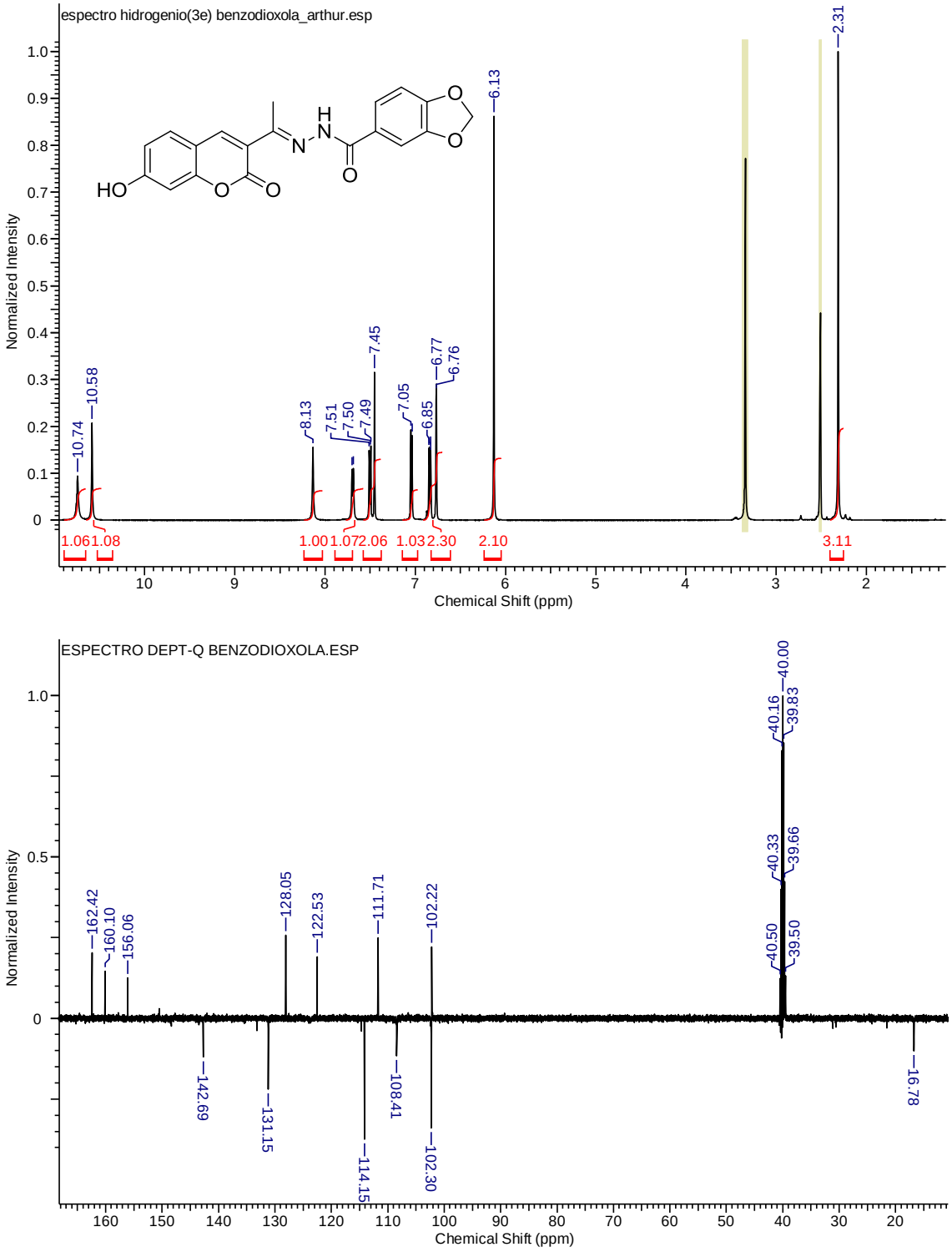

Fig. S16. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3e** in DMSO-d_6.

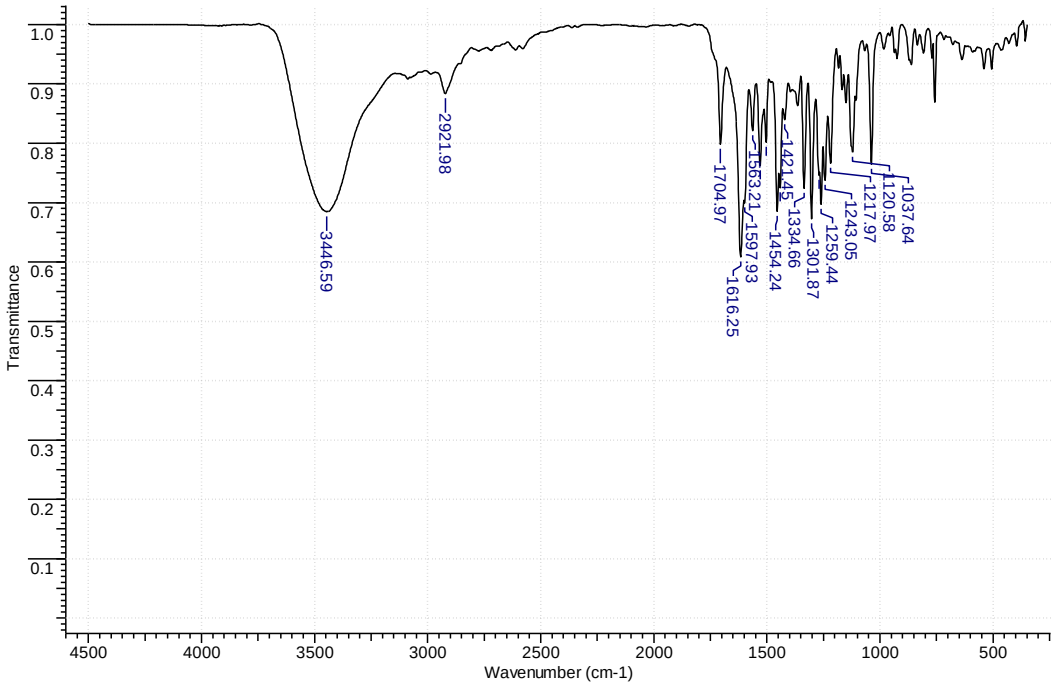

Fig. S17. IR spectra of **3e** in KBr.

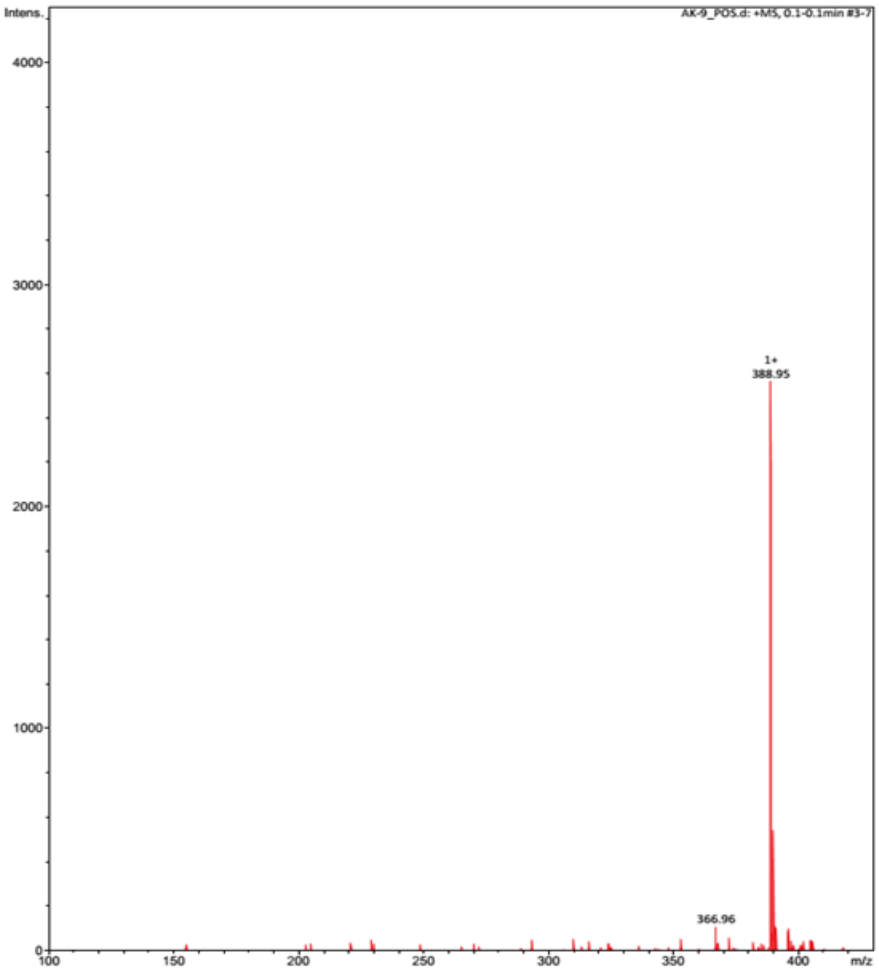

Fig. S18. EM spectra of **3e**.

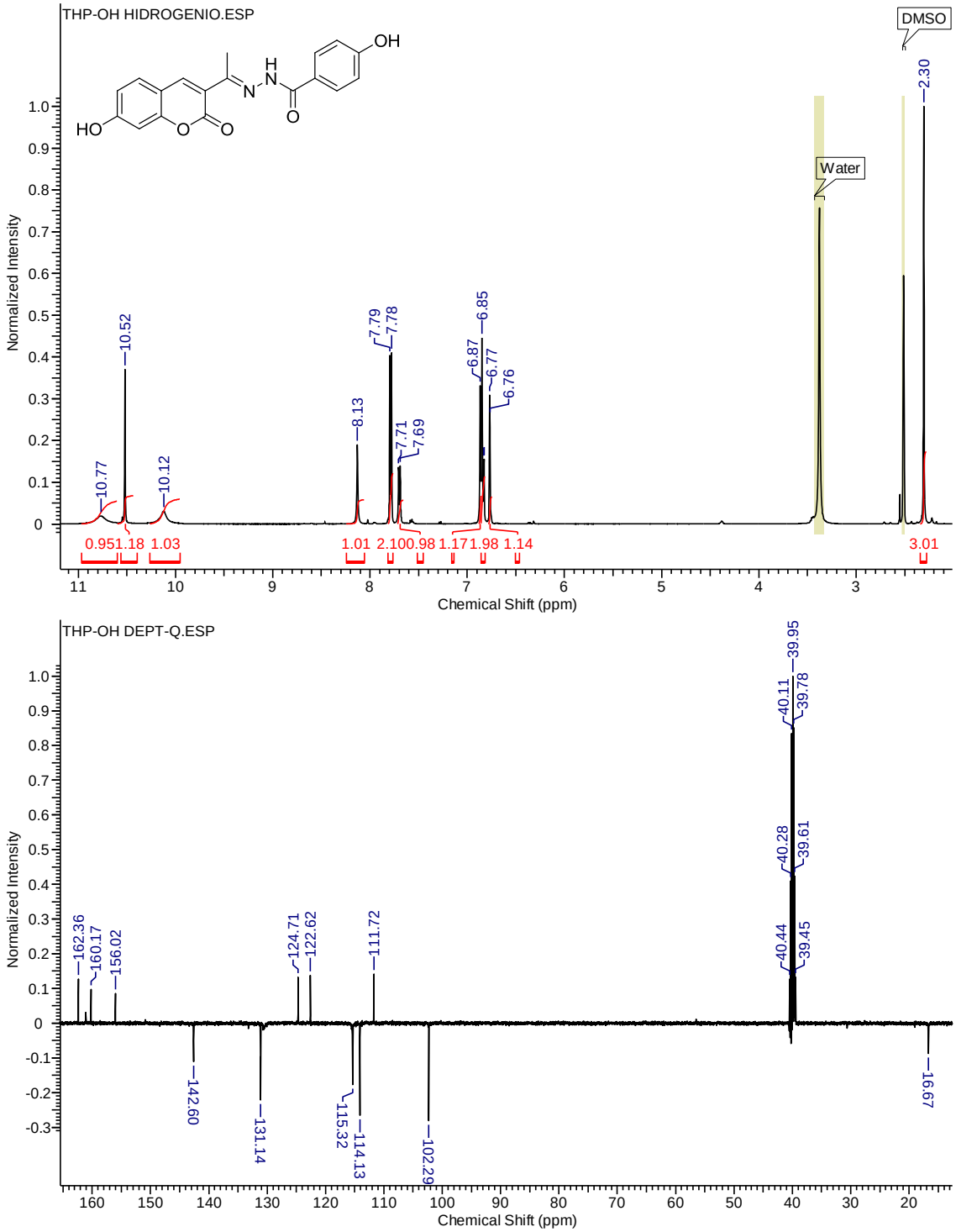

Fig. S19. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3f** in DMSO-d_6.

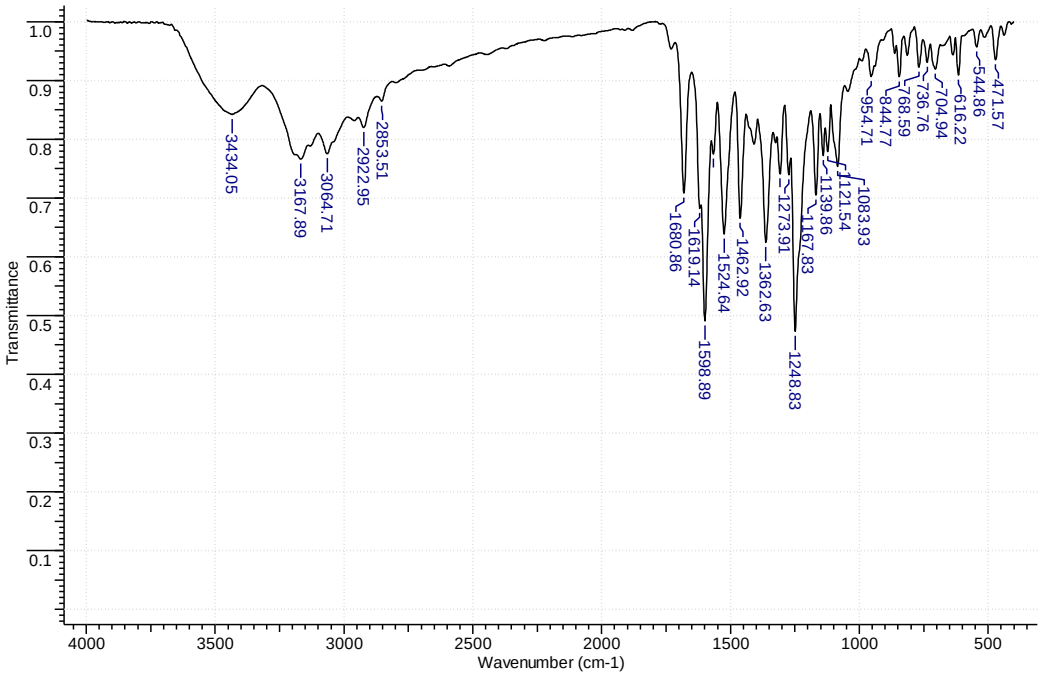

Fig. S20. IR spectra of **3f** in KBr.

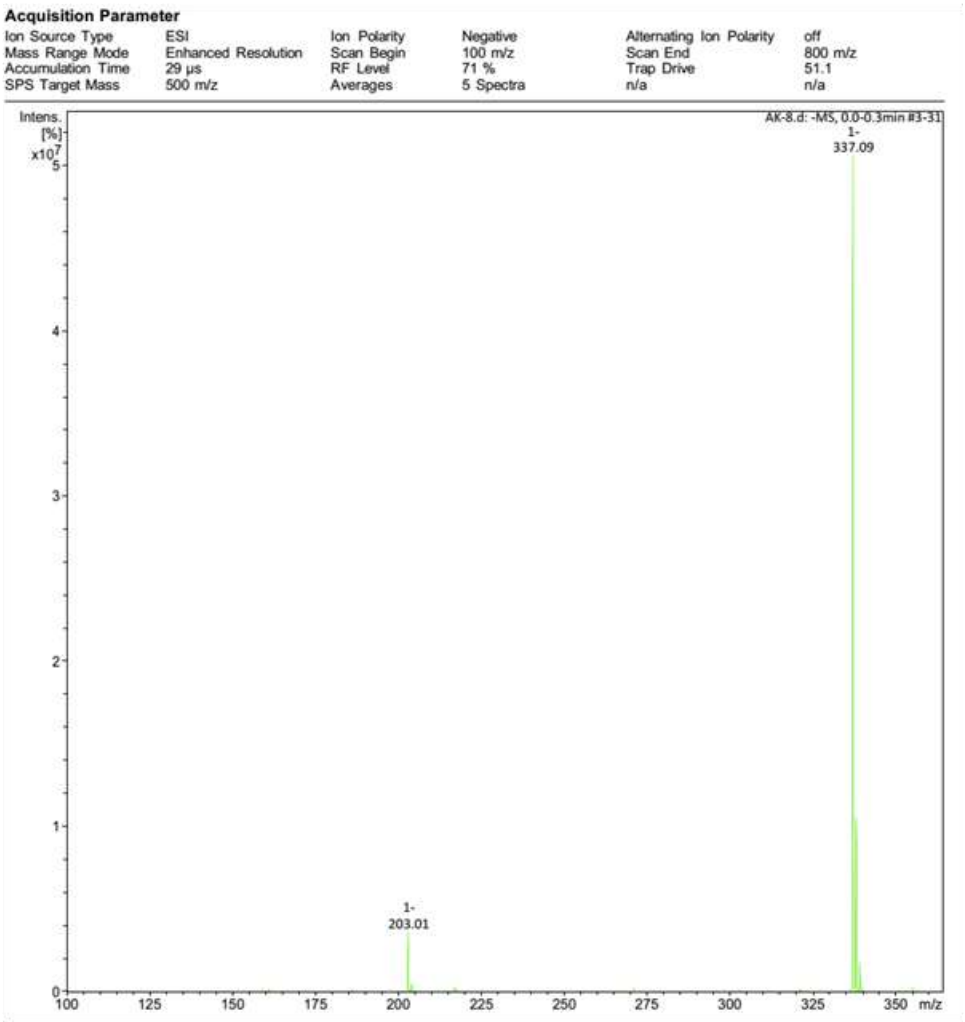

Fig. S21. EM spectra of **3f**.

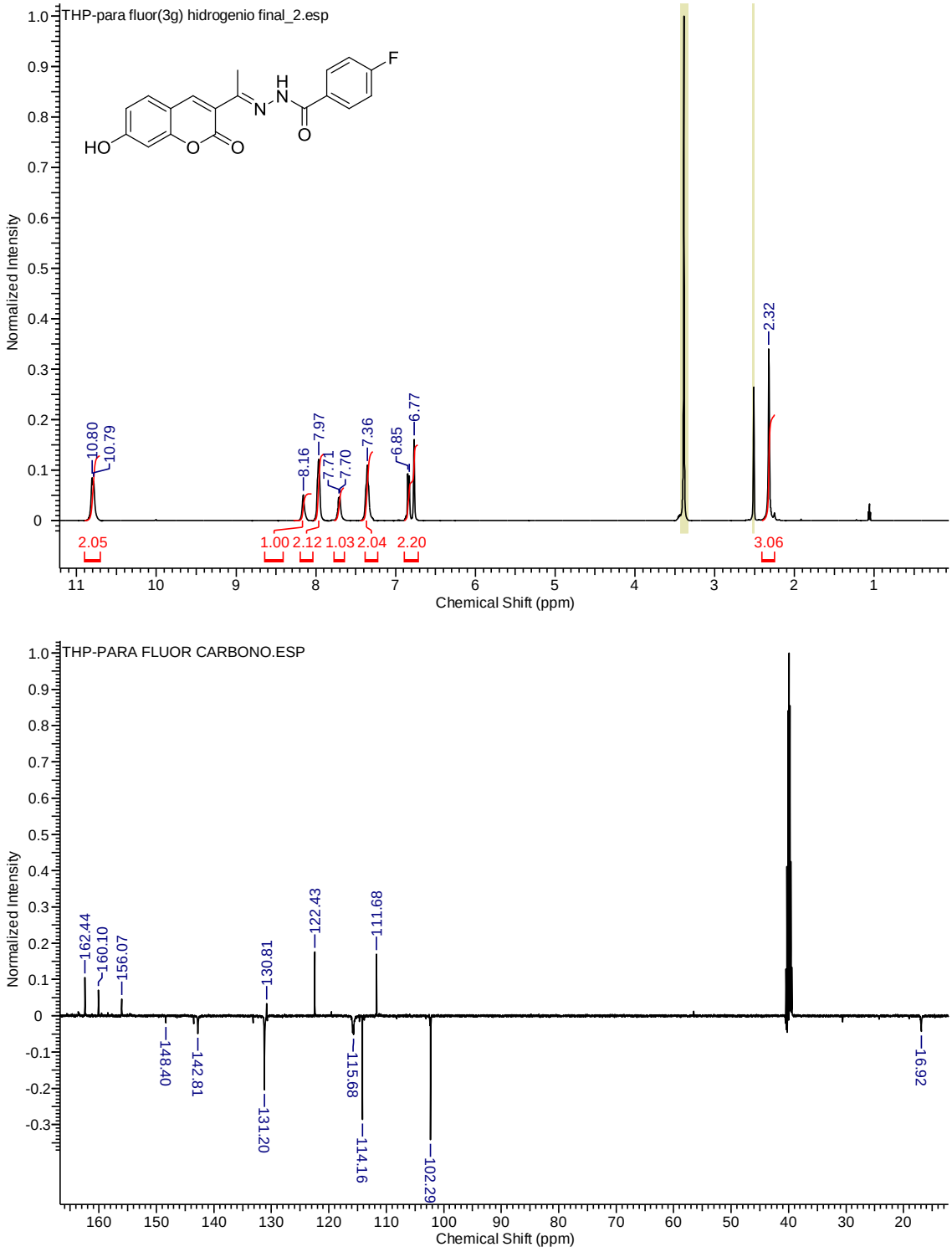

Fig. S22. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3g** in DMSO-d_6.

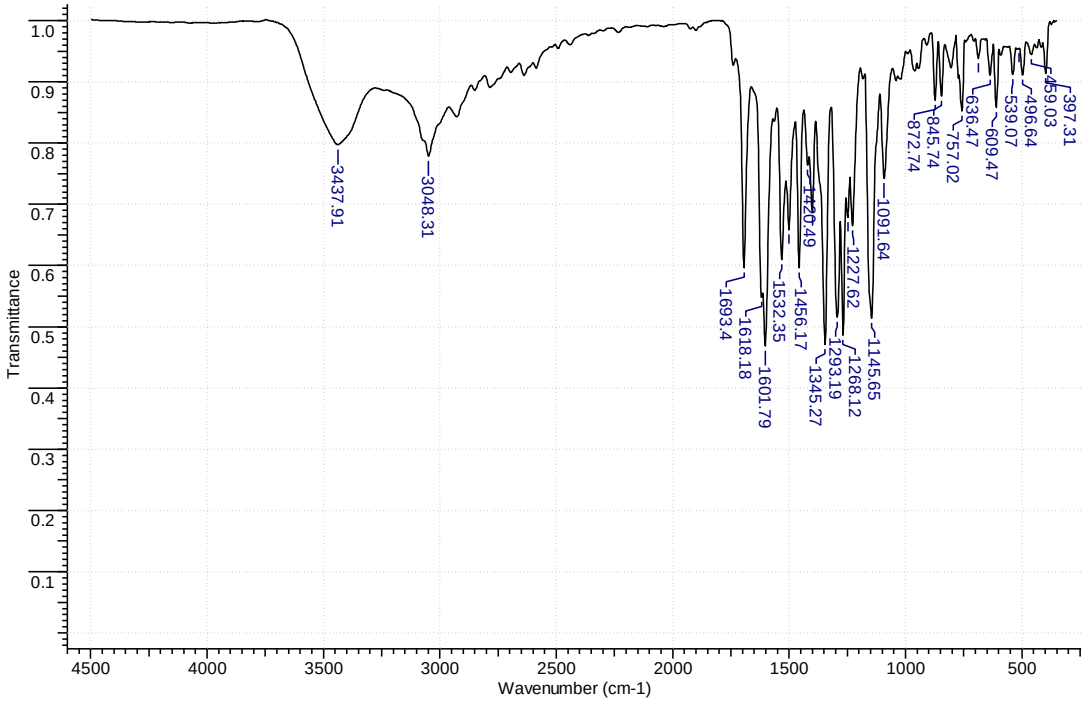

Fig. S23. IR spectra of **3g** in KBr.

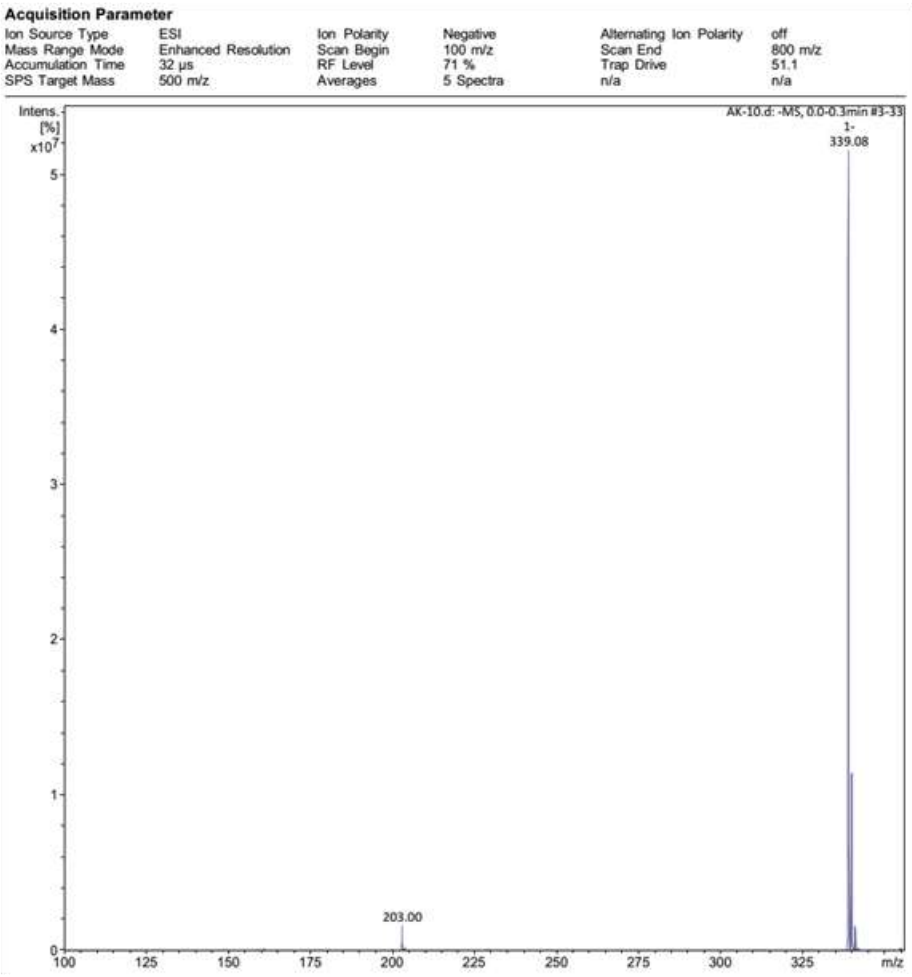

Fig. S24. EM spectra of **3g**.

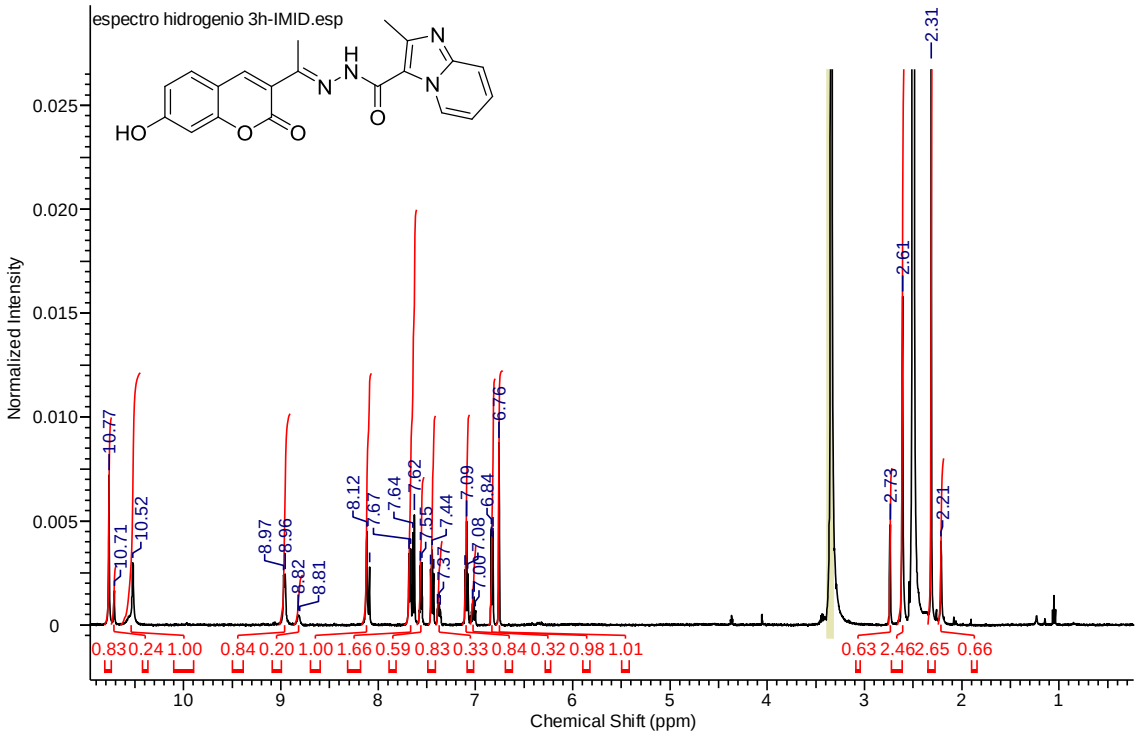

Fig. S25. ^{1}H NMR (500 MHz), spectra of **3h** in DMSO-d_6.

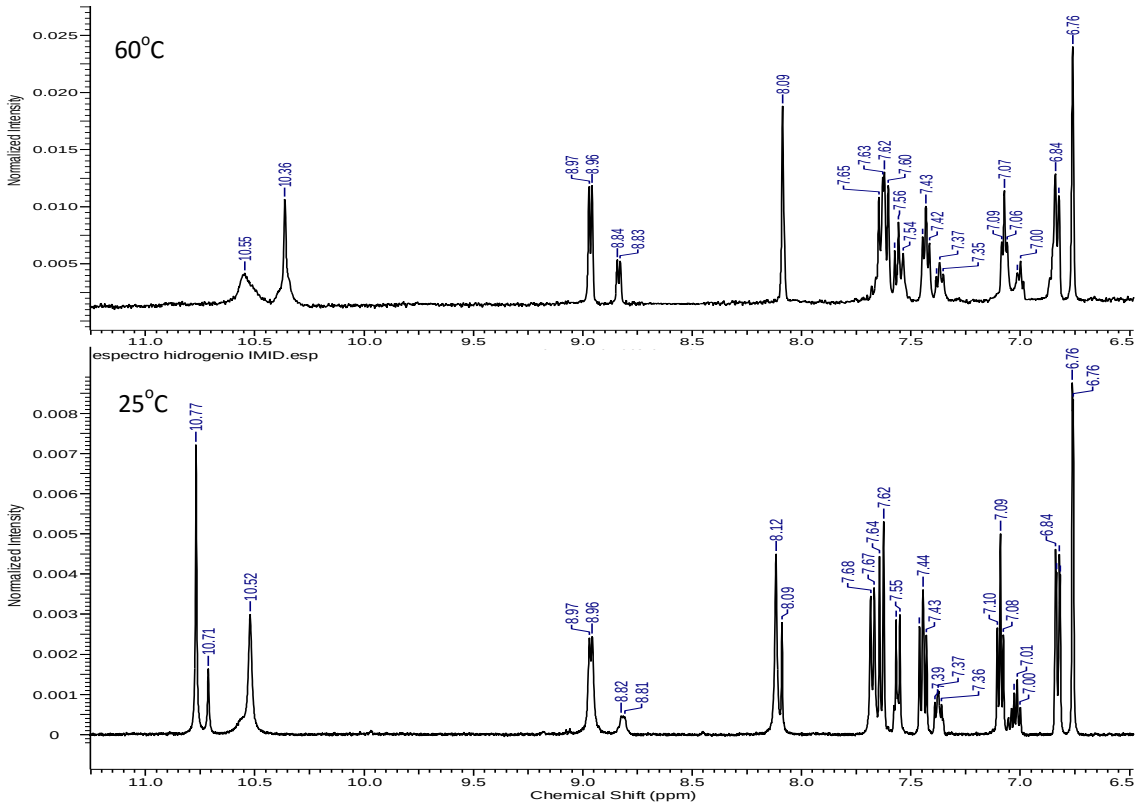

Fig. S26. ^{1}H NMR, expanded aromatic region of **3h** in DMSO-d_6 at 25 and 60°C.

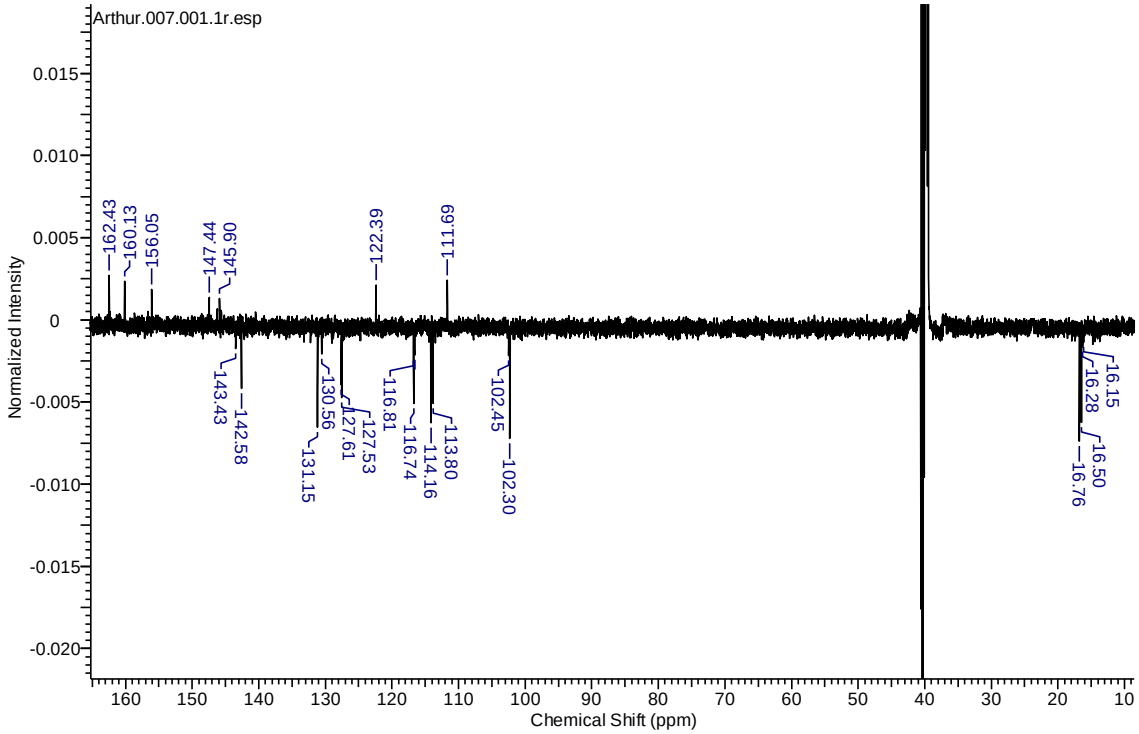

Fig. S27. ^{13}C NMR (125 MHz) spectrum of **3h** in DMSO-d_6 (poor quality due to low solubility).

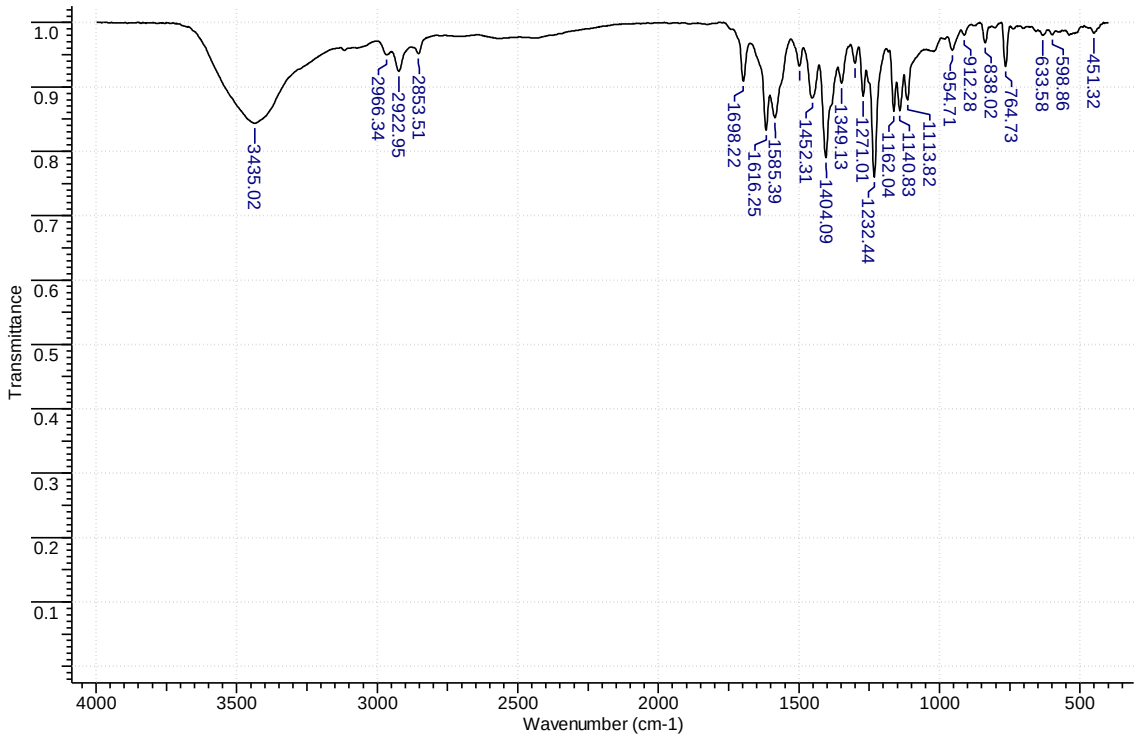

Fig. S28. IR spectra of **3h** in KBr.

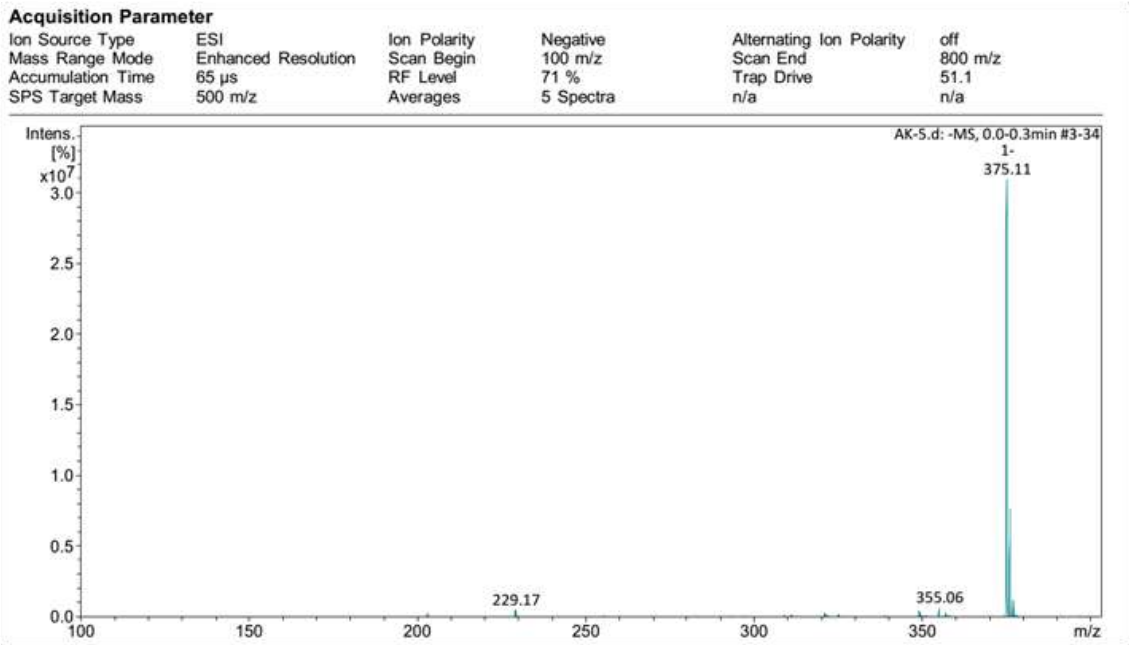

Fig. S29. EM spectra of **3h**.

==== Shimadzu LCsolution Analysis Report ====

C:\Lab[illegible]lutio[illegible]\D[illegible]\Dados HPLC\Marina\2016\Marco\AK-5.lcd

Acquired by	: Admin
Sample Name	: AK-5
Sample ID	:
Tray#	: 1
Vail #	: 64
Injection Volume	: 40 uL
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Method File Name	: MET_60ACN_40AGUA_T10.lcm
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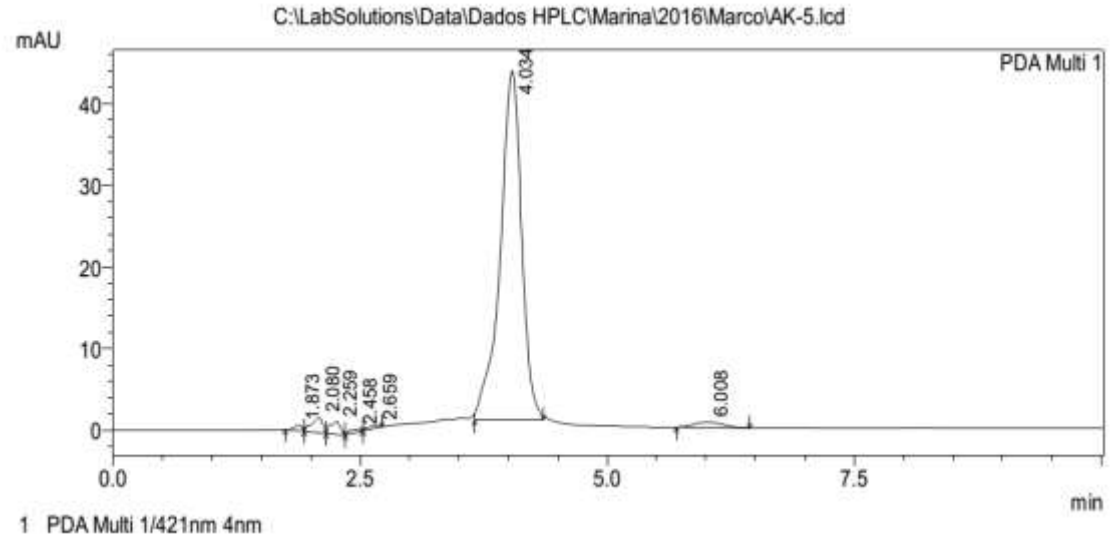
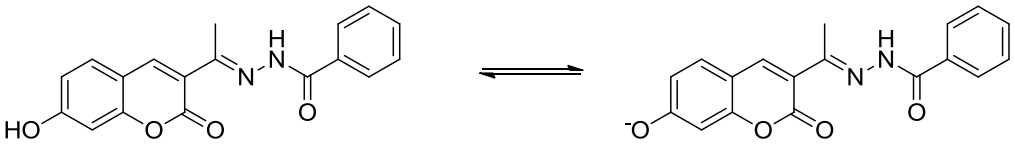


Fig. S30. RP-HPLC analysis of **3h**.

pKa determination:



The spectral change from pH 5 to pH 8 is ascribed to the deprotonation of the hydroxyl group in the coumarin nucleus, as typical for other hidroxycoumarins, and lead to a well-defined isosbestic point around 375 nm. By the relationship between the pH and $\log[(A - A_f)/(A_0 - A)]$, the pKa constant for the deprotonation of the **3b** hydroxycoumarin was calculated to be 6.7.

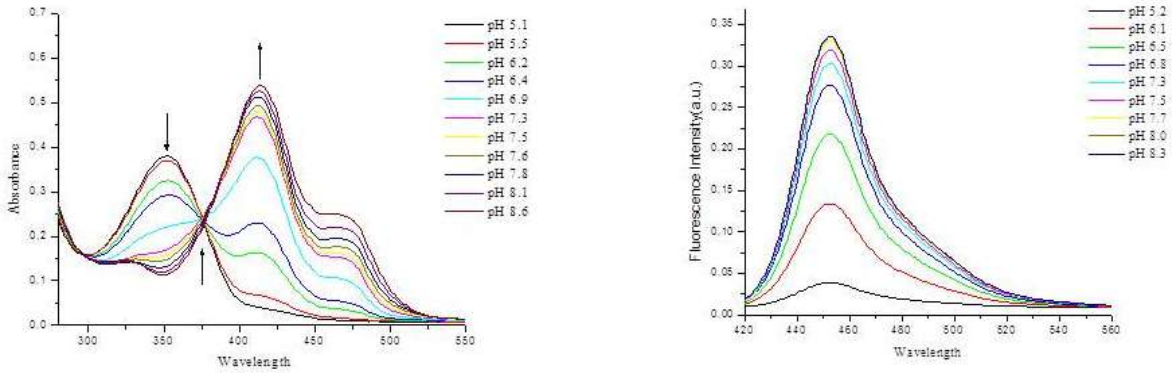


Fig.S31. pH titrations of **3b**. Absorption and emission spectrum.

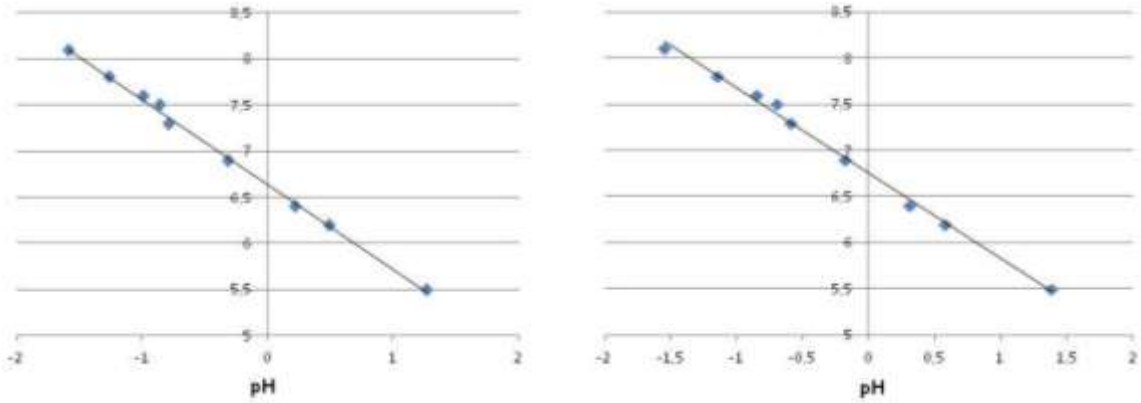


Fig. S32. pKa determination of **3b** considering 412nm and 351nm wavelengths.

pKa ≈ 6.7.

Table S1. Photophysical parameters in water (pH = 3.0) at 298 K.

Compound	ϕ_F [a]
3a	0.048
3b	0.068
3c	0.068
3d	0.066
3h	0.065

[a]Quantum yields were measured by the relative method against the standard compound ethyl-7-OH-coumarin-3-carboxylate (ϕ = 0.83 in water) [32].

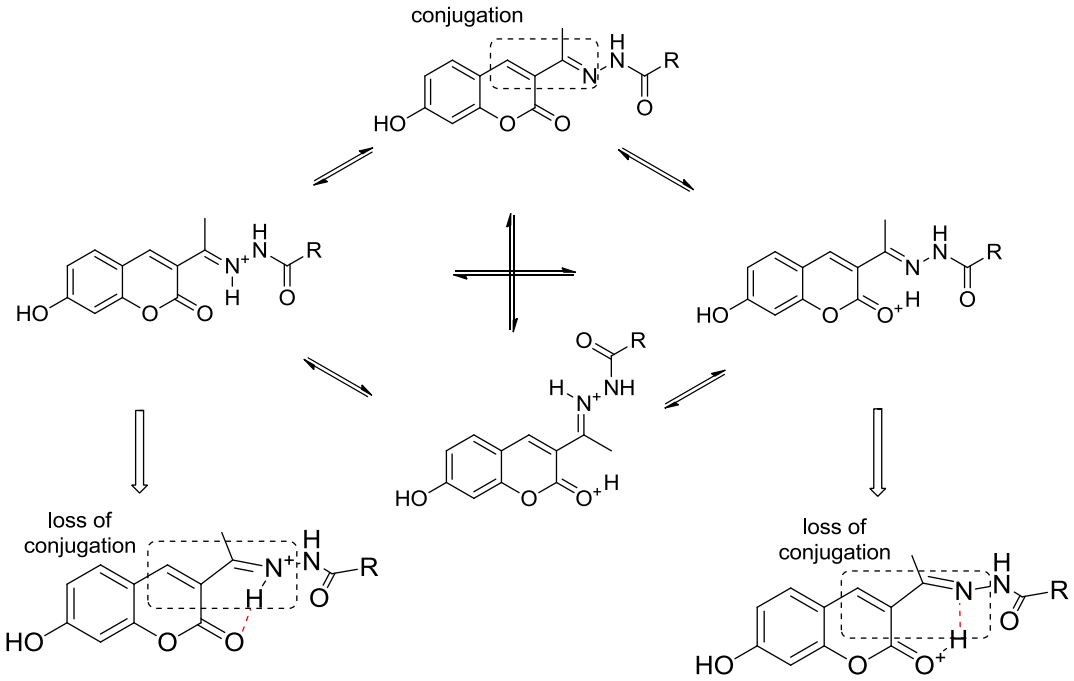


Fig. S33. Proposition of protonated states of *N*-acylhydrazone- and Semicarbazone-7-OH-Coumarins