

Solution and Solid-State Optical Properties of Trifluoromethylated 5-(alkyl/aryl/heteroaryl)-2-methyl-pyrazolo[1,5-*a*]pyrimidine System

Felipe S. Stefanello ¹, Jean C. B. Vieira¹, Juliane N. Araújo¹, Vitória B. Souza², Clarissa P. Frizzo¹, Marcos A. P. Martins¹, Nilo Zanatta¹, Bernardo A. Iglesias^{*2}, and Helio G. Bonacorso^{1*}

¹ Núcleo de Química de Heterociclos (NUQUIMHE), Departamento de Química, Universidade Federal de Santa Maria, 97105-900 – Santa Maria, RS – Brazil.

² Laboratório de Bioinorgânica e Materiais Porfirínicos, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 – Santa Maria, RS – Brazil.

* Corresponding Authors. E-mail addresses: helio.bonacorso@ufsm.br (H.G. Bonacorso) and bernardopgq@gmail.com (B.A. Iglesias)

1. General.....	2
2. NMR Spectra	4
3. Photophysical analysis.....	8
4. Thermal analysis.....	18
5. HRMS analysis	22
6. References.....	23

1. General

^1H and ^{13}C NMR spectra were acquired on a Bruker Avance III 600 MHz (**5a-q**) spectrometers for one-dimensional experiments, with 5-mm sample tubes, 298 K, and digital resolution of 0.01 ppm, in CDCl_3 as solvent, and using TMS as the internal reference. All spectra can be found in Figures S1–S8 in the *Supplementary information*. All results are reported with the chemical shift (δ), multiplicity, integration, and coupling constant (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and dd = double doublet. All NMR chemical shifts were reported in parts per million, which is relative to the internal reference. The HRMS analyses were performed on a hybrid high-resolution and high-accuracy (5 $\mu\text{L/L}$) micrOTOF-Q mass spectrometer (Bruker Scientific®, Billerica, MA, USA) at (Caxias do Sul University, UCS, Brazil) (Figures S34–S35) [1].

Electronic UV-Vis absorption analysis of compounds in CH_3CN , CHCl_3 , THF, toluene, EtOH, and DMSO solutions were done with a Shimadzu UV2600 spectrophotometer (data interval of 1.0 nm) at 250 to 500 nm range. Steady-state emission fluorescence analysis of samples in CH_3CN , CHCl_3 , THF, toluene, EtOH, and DMSO solutions were measured with a Varian Cary50 fluorescence spectrophotometer (slit of 5.0 mm; em/exc) and corrected according to the manufacturer's instructions. Fluorescence quantum yield values (Φ_{fl}) of the compounds in solution were determined by comparing the corrected fluorescence spectra with that of 9,10-diphenylanthracene (DPA) in chloroform ($\Phi_{\text{fl}} = 0.65$, $\lambda_{\text{ex}} = 366$ nm) as the standard for the fluorescence yield. All spectra can be found in Figures S9–S25 in this *Supplementary information*.

Thermogravimetric analyses (TGA) were performed using a TGA Q5000 instrument (TA Instruments Inc., USA) at a heating rate of 10 $^{\circ}\text{C min}^{-1}$, from 40 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ under a N_2 flux of 25 mL min^{-1} . The masses were approximately 1 mg for all samples. Data analysis was performed using the OriginPro 8.5 software. The confirmation of calibration of apparatus before analysis was done with $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (99.9%). All curves of TGA can be found in Figures S26–S29 in this *Supplementary information*.

Differential scanning calorimetry (DSC) analysis were carried out using a Q2000 DSC calorimeter (TA Instruments, USA) equipped with an RCS refrigeration accessory,

and with N₂ as purge gas (50 mL min⁻¹). The heating rate used was 5 °C min⁻¹. The calibration of instruments in standard DSC mode was verified with indium (99.99%). The masses of the samples (1–5 mg) were weighed on a Sartorius balance (M500P) with a precision of ±0.001 mg. All samples were subjected to three heating–cooling cycles, as follows: 25 to 250 °C. DSC curves of 3b and 3d can be found in [Figures S30–S33](#) in this *Supplementary information*.

2. NMR Spectra

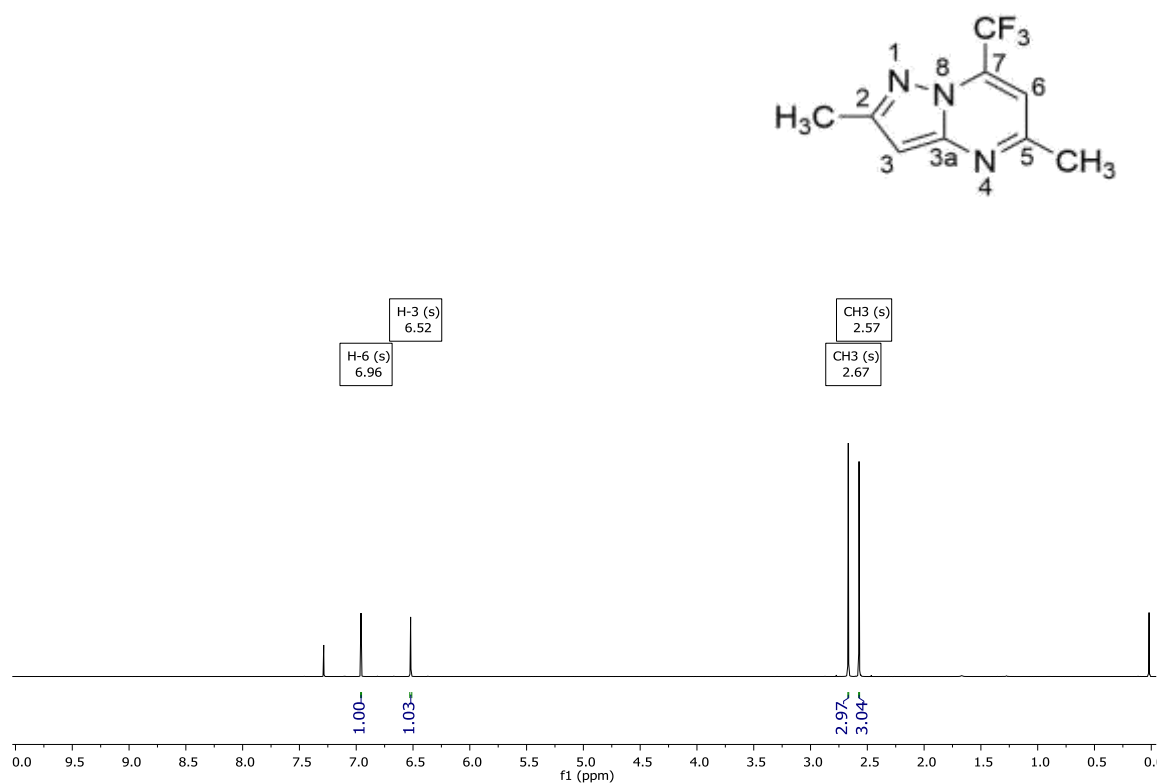


Figure S1. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3a**.

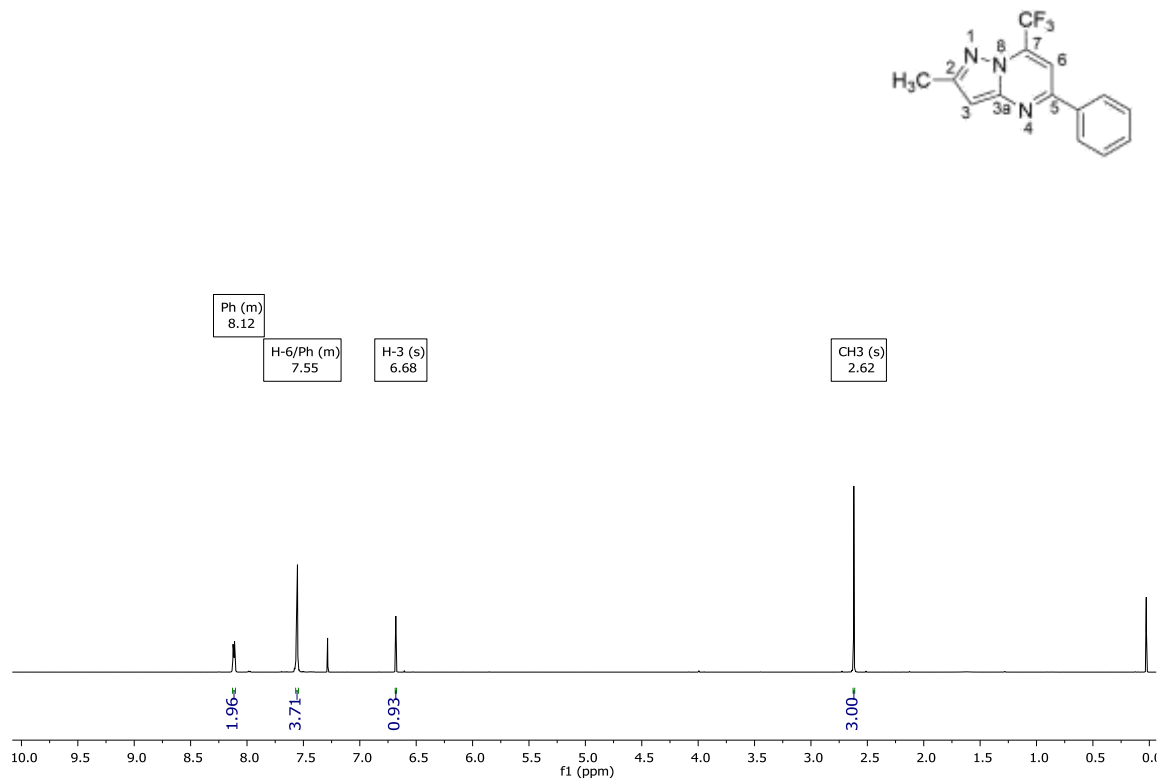


Figure S2. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3b**.

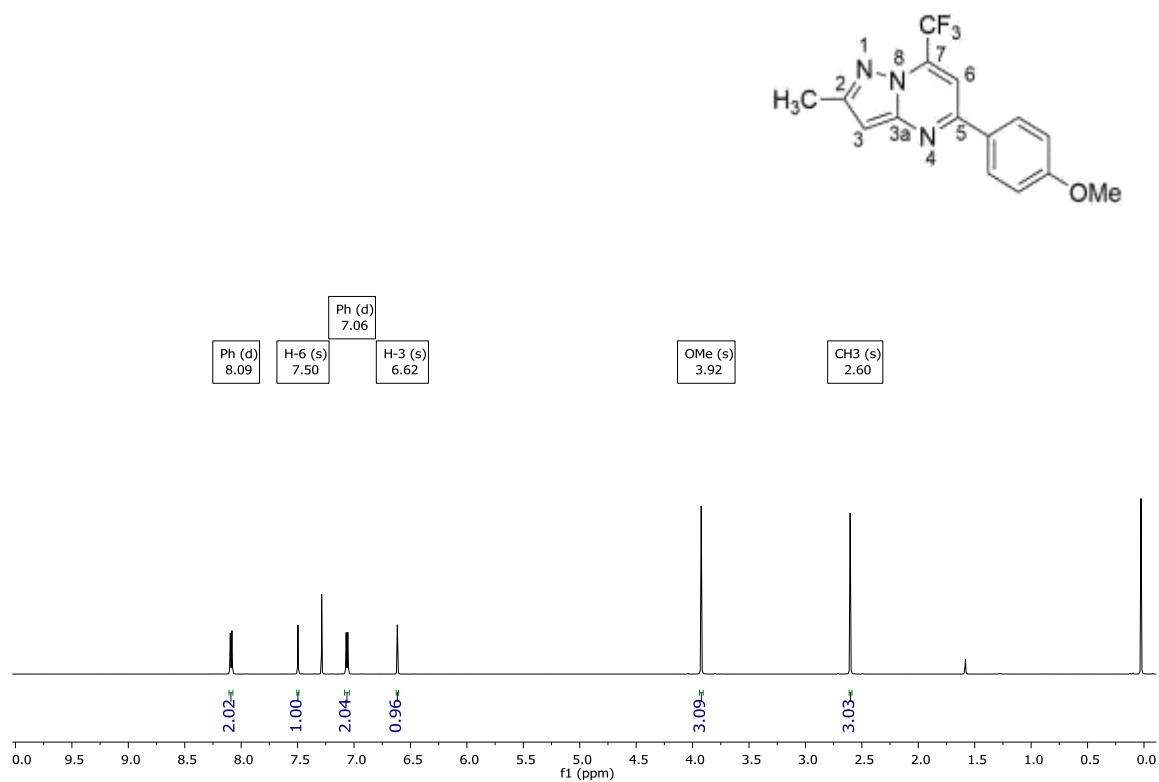


Figure S3. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3c**.

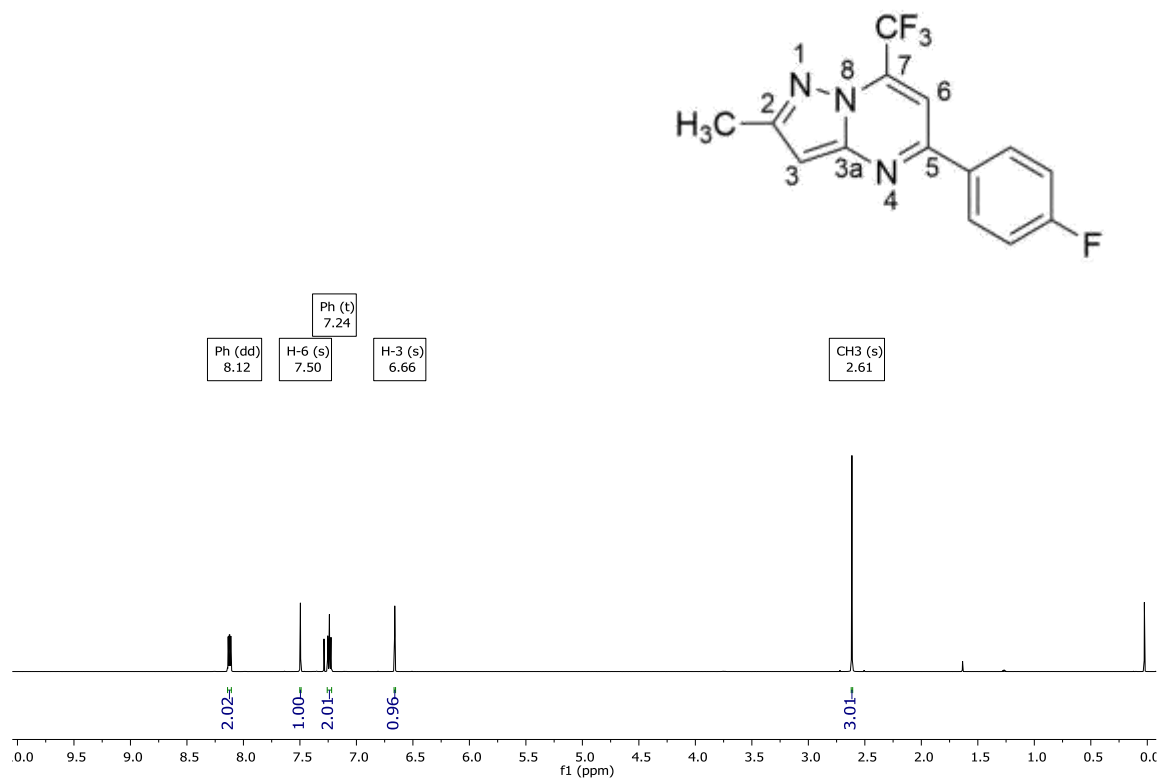


Figure S4. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3d**.

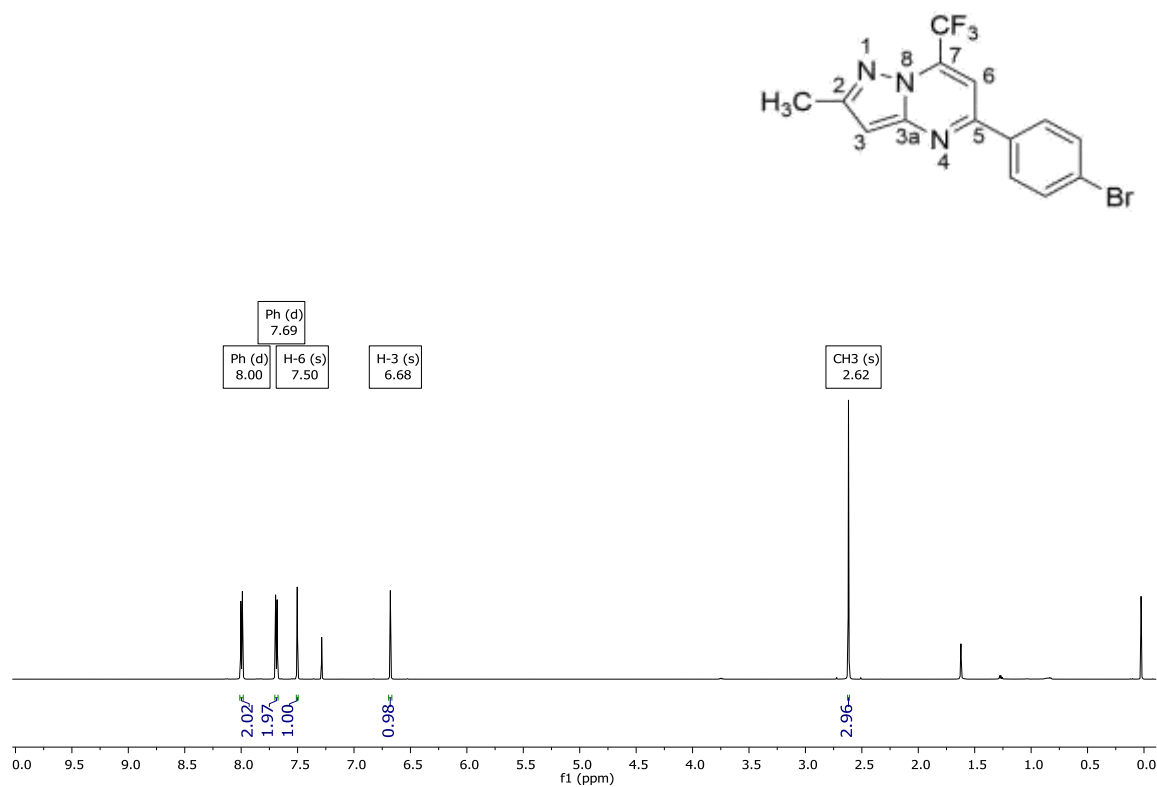


Figure S5. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3e**.

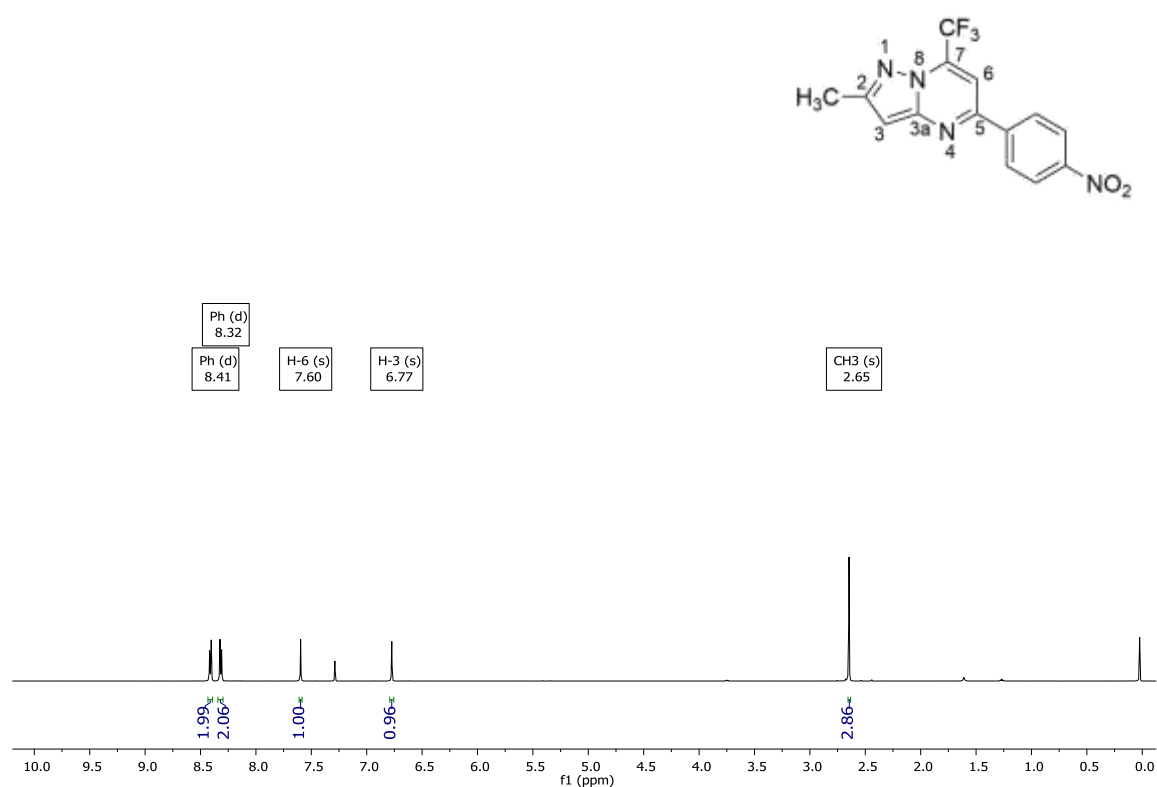


Figure S6. ^1H NMR spectra at 600 MHz in CDCl_3 of compound **3f**.

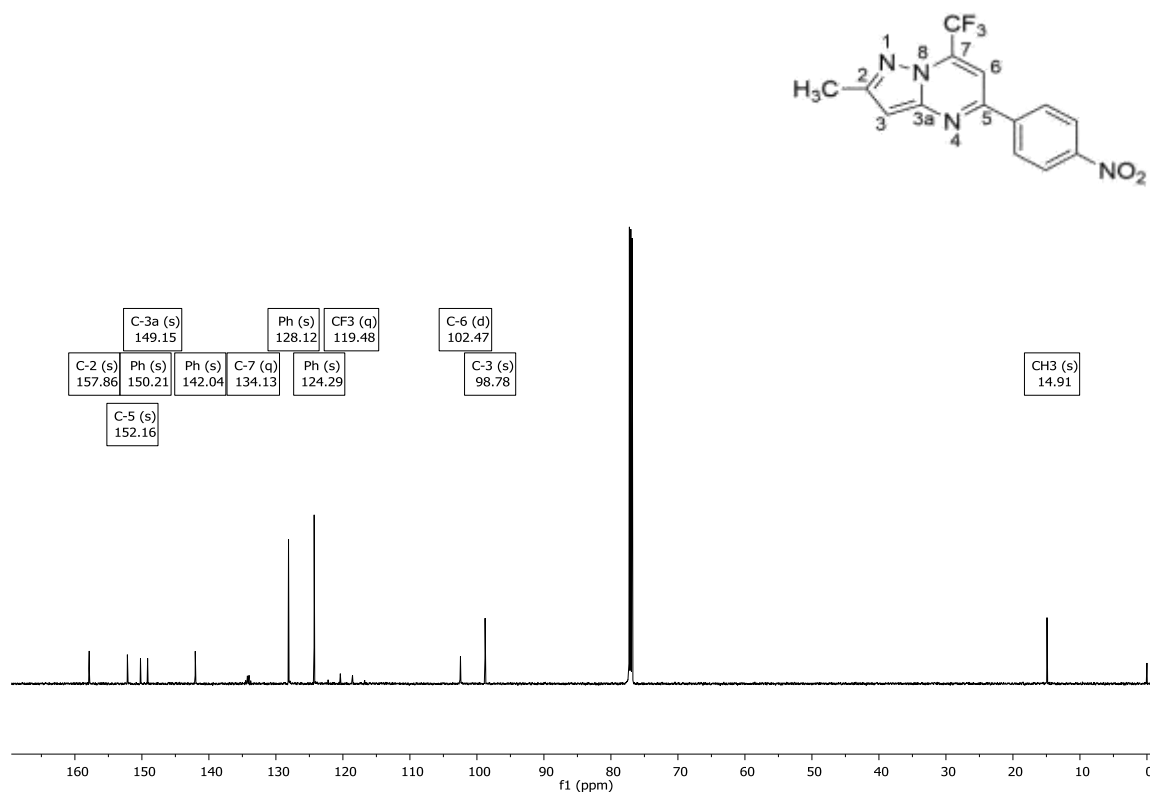


Figure S7. ¹³C NMR spectra at 600 MHz in CDCl₃ of compound **3f**.

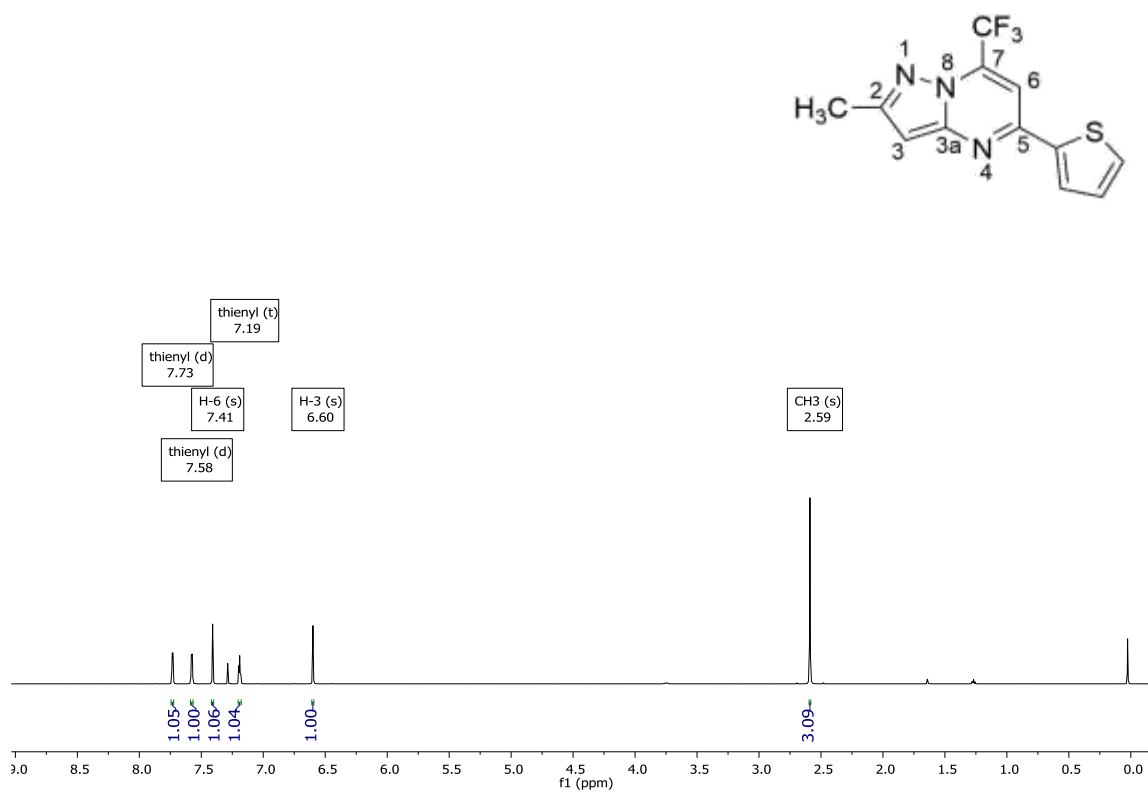


Figure S8. ¹H NMR spectra at 600 MHz in CDCl₃ of compound **3g**.

3. Photophysical analysis

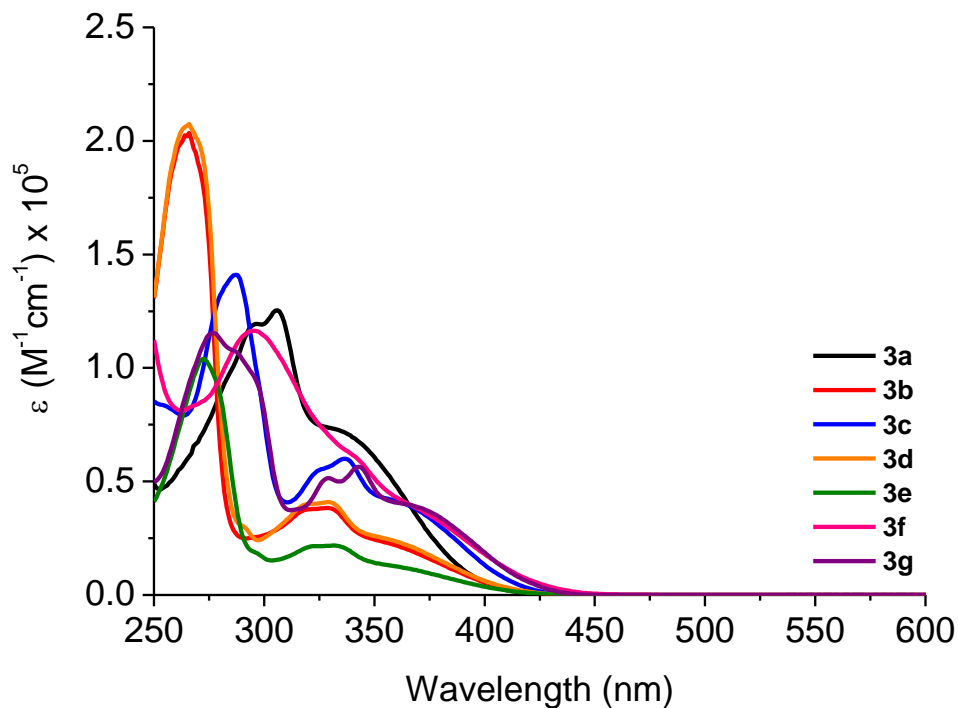


Figure S9. UV-Vis spectra of compounds **3a-g** in CH_3CN solution.

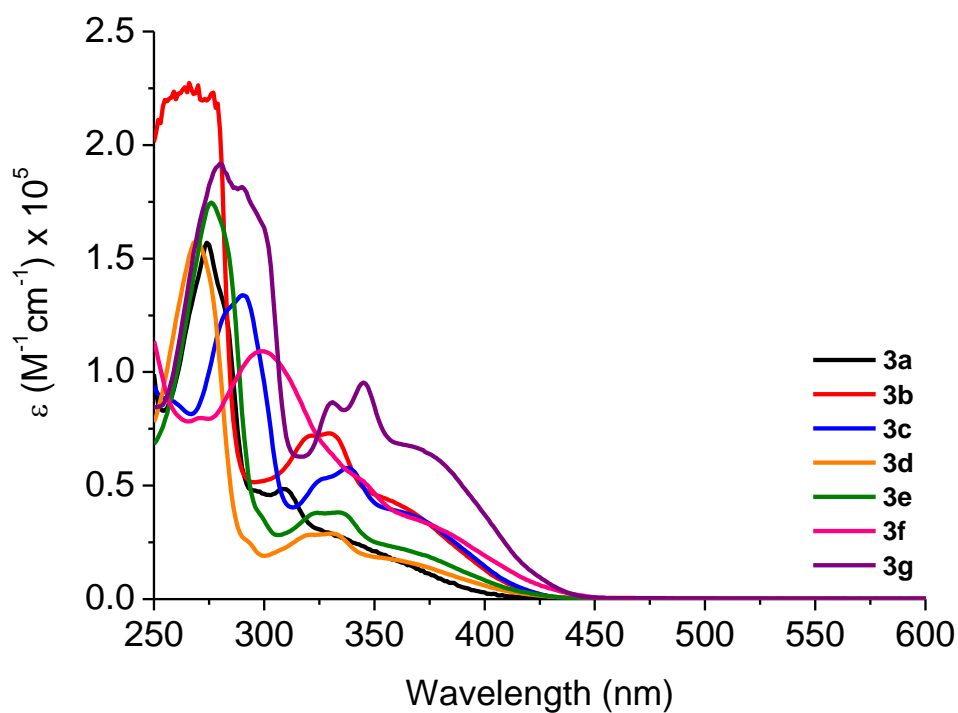


Figure S10. UV-Vis spectra of compounds **3a-g** in CHCl_3 solution.

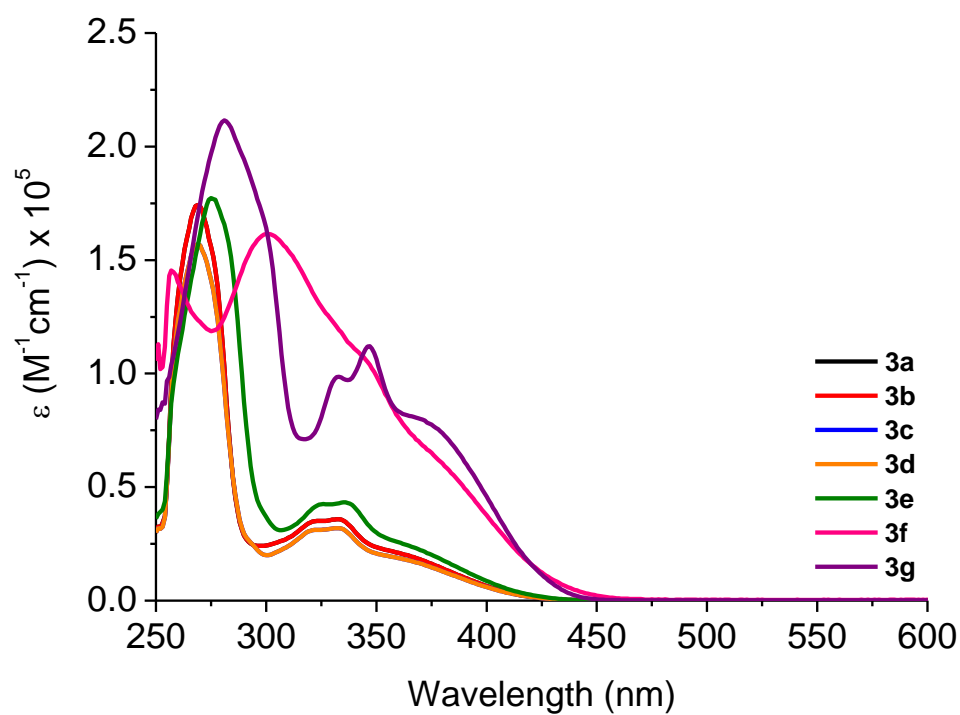


Figure S11. UV-Vis spectra of compounds **3a-g** in DMSO solution.

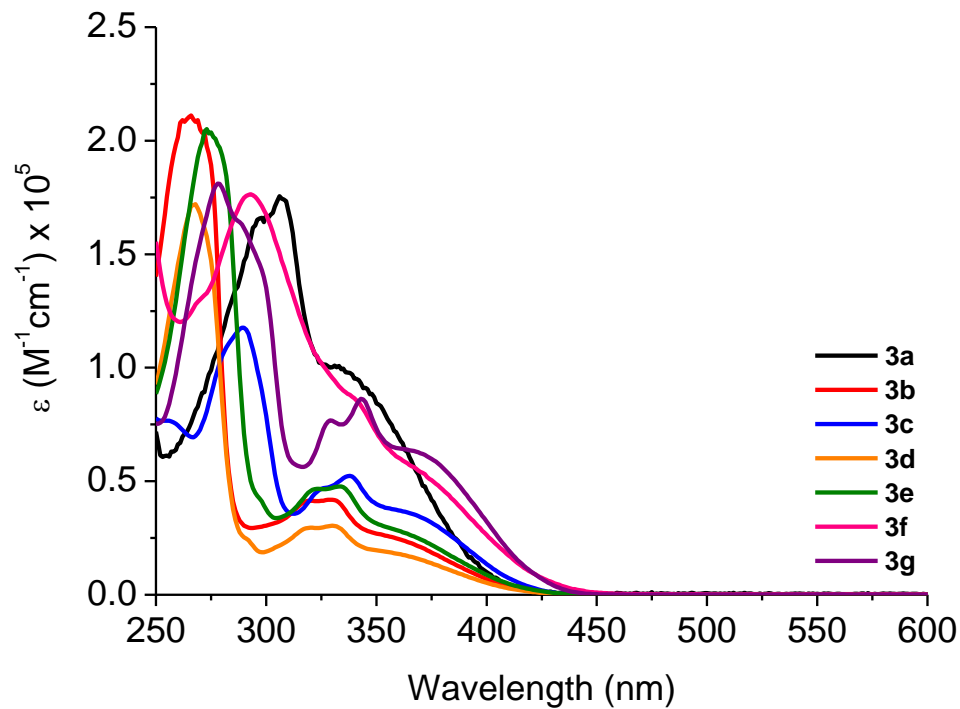


Figure S12. UV-Vis spectra of compounds **3a-g** in EtOH solution.

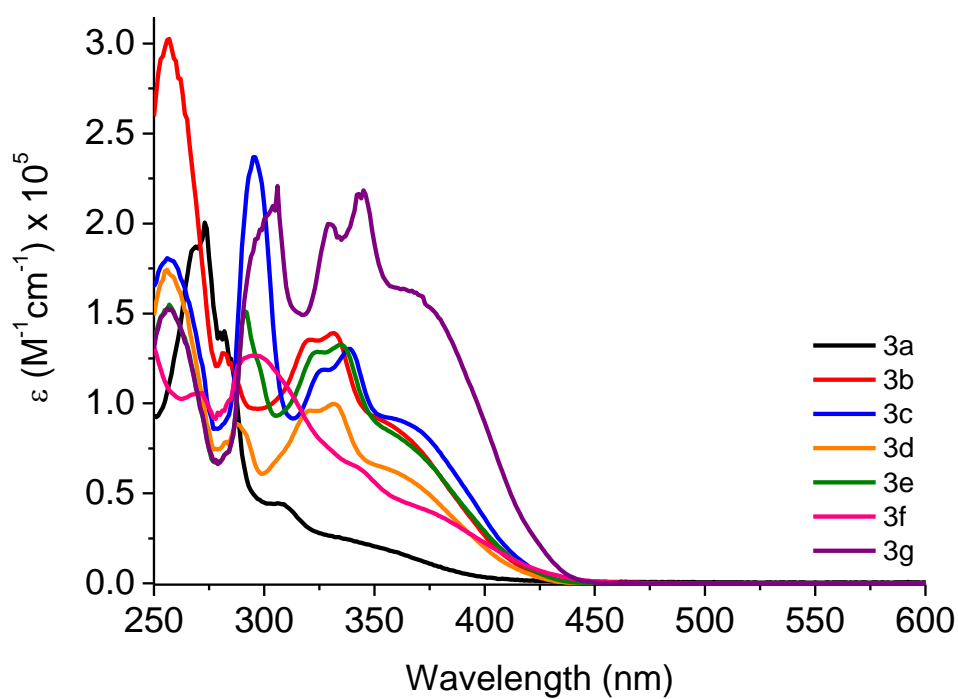


Figure S13. UV-Vis spectra of compounds **3a-g** in THF solution.

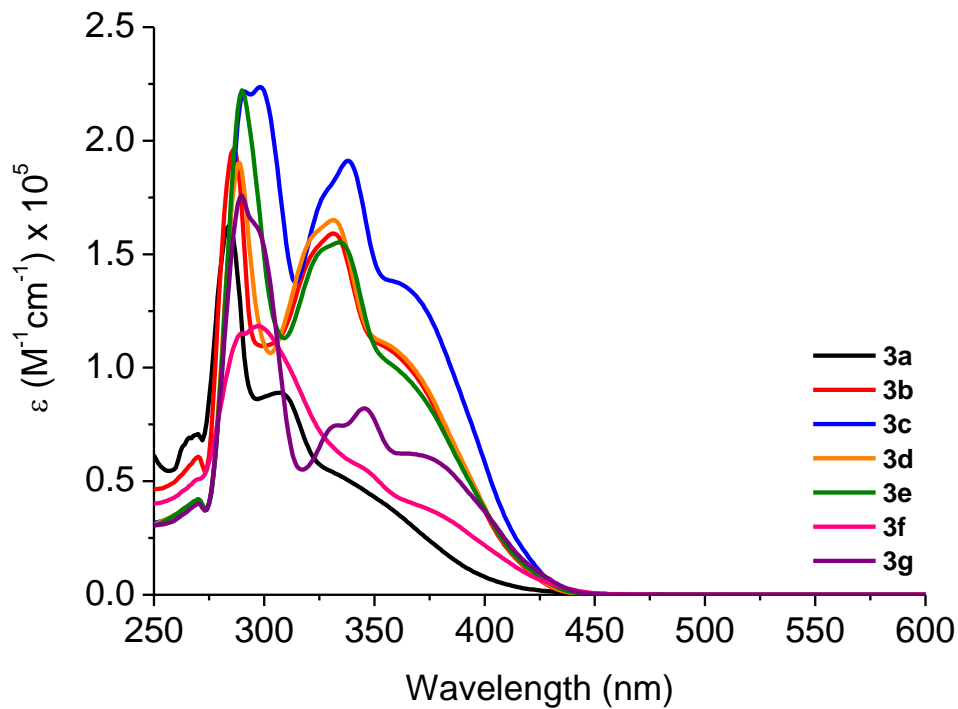


Figure S14. UV-Vis spectra of compounds **3a-g** in Toluene solution.

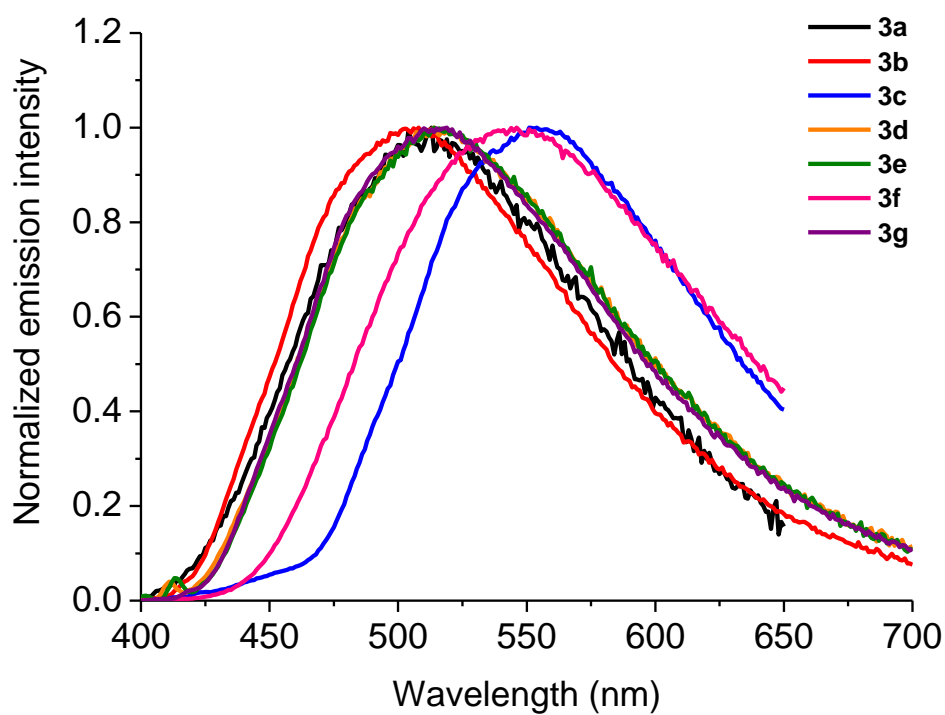


Figure S15. Steady-state fluorescence emission spectra of compounds **3a-g** in CH_3CN solution.

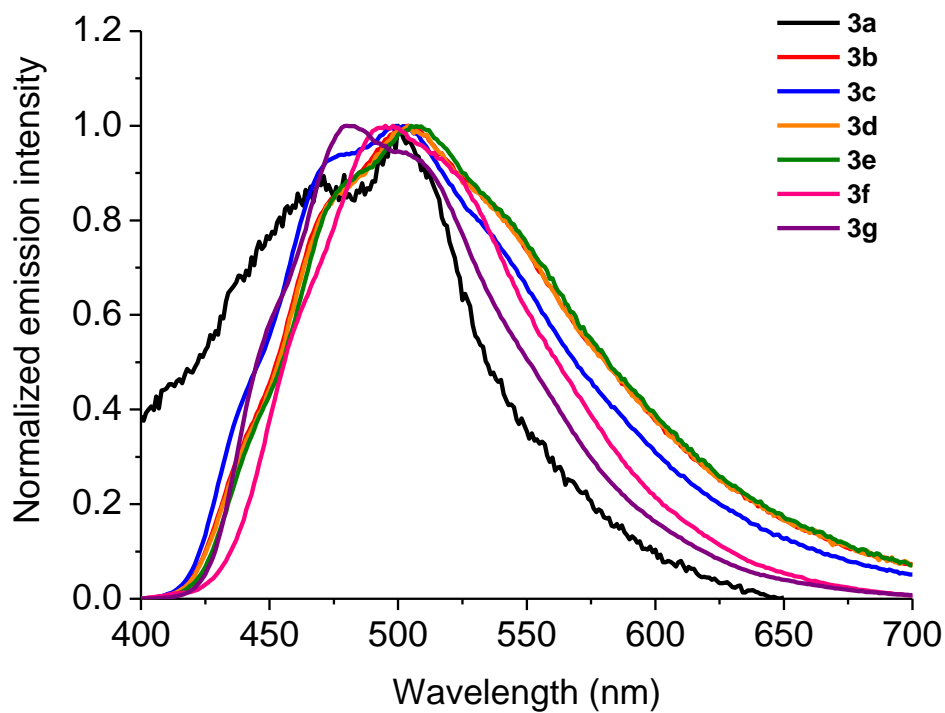


Figure S16. Steady-state fluorescence emission spectra of compounds **3a-g** in CHCl_3 solution.

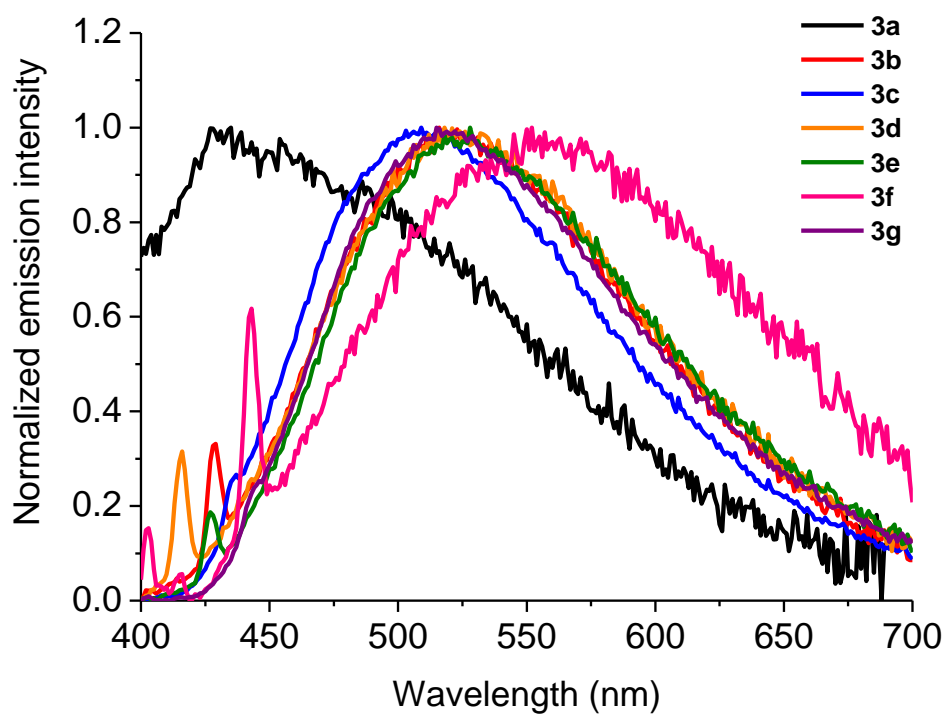


Figure S17. Steady-state fluorescence emission spectra of compounds **3a-g** in DMSO solution.

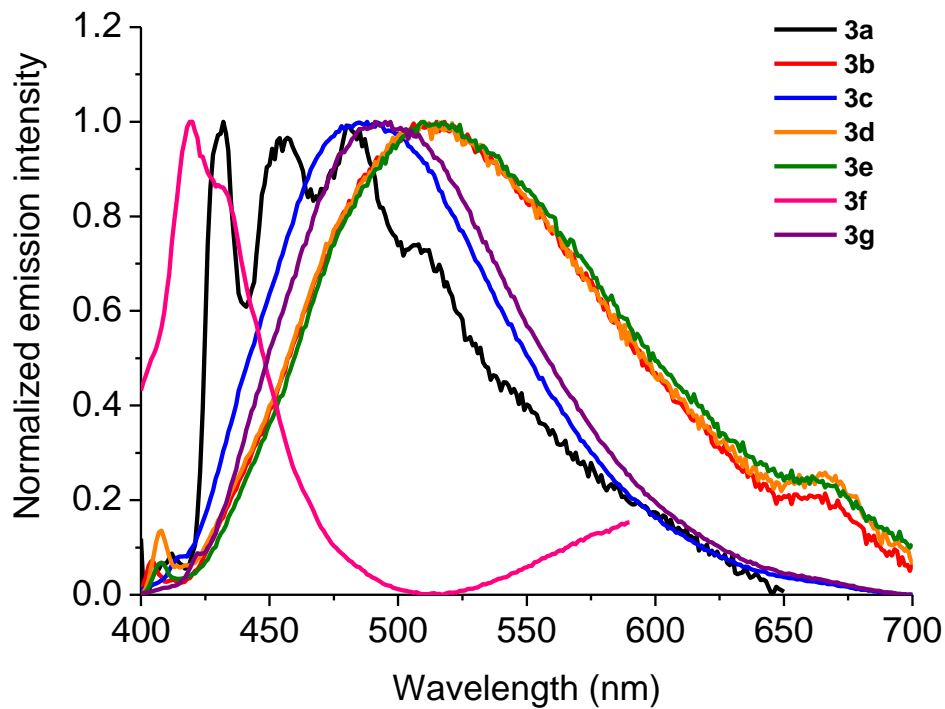


Figure S18. Steady-state fluorescence emission spectra of compounds **3a-g** in EtOH solution.

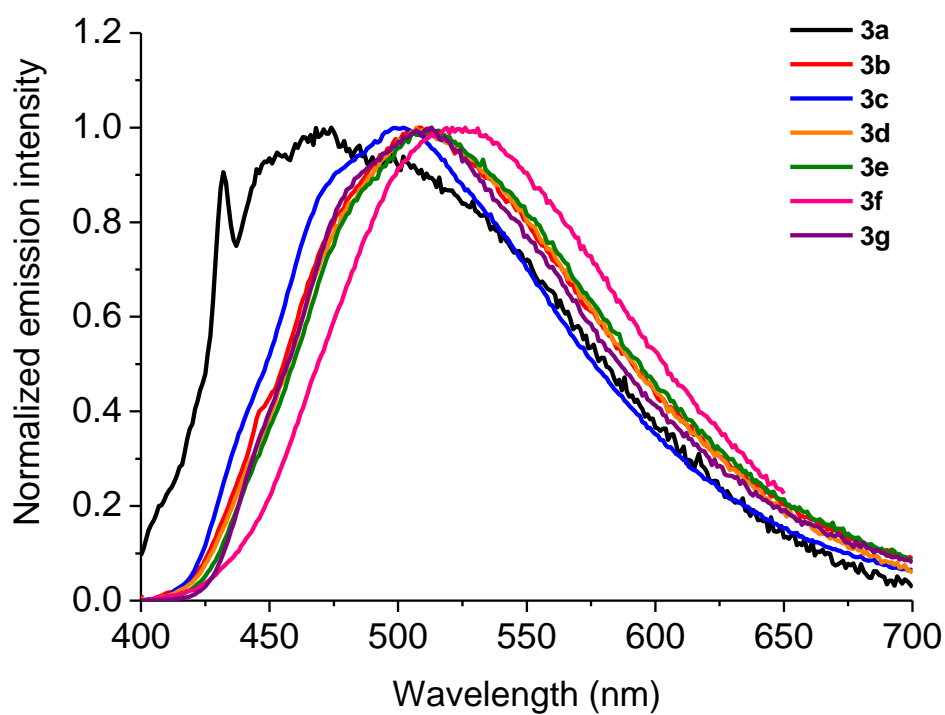


Figure S19. Steady-state fluorescence emission spectra of compounds **3a-g** in THF solution.

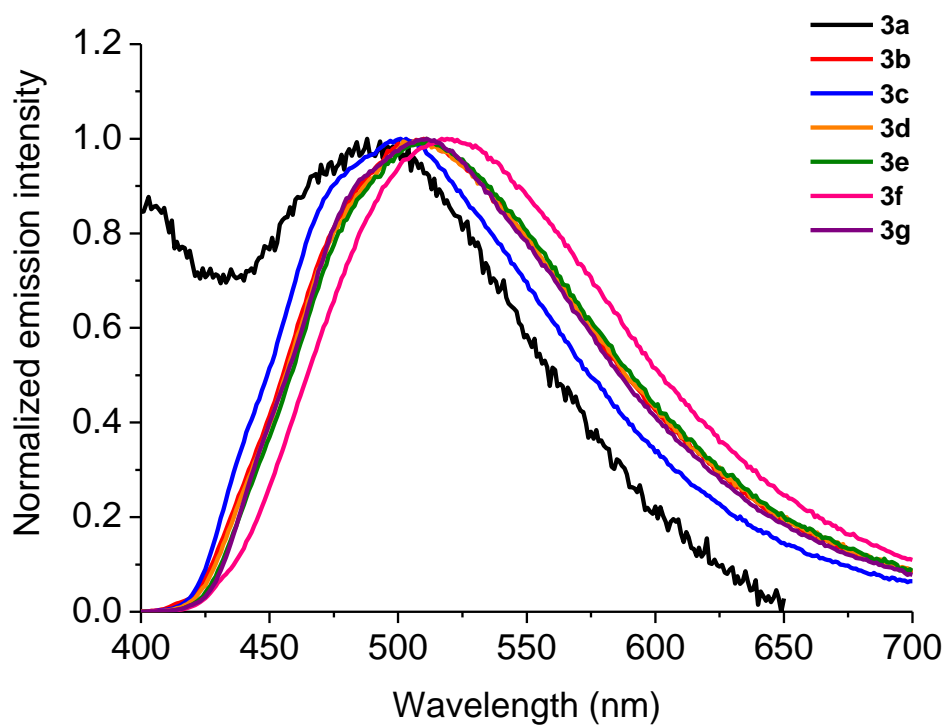


Figure S20. Steady-state fluorescence emission spectra of compounds **3a-g** in Toluene solution.

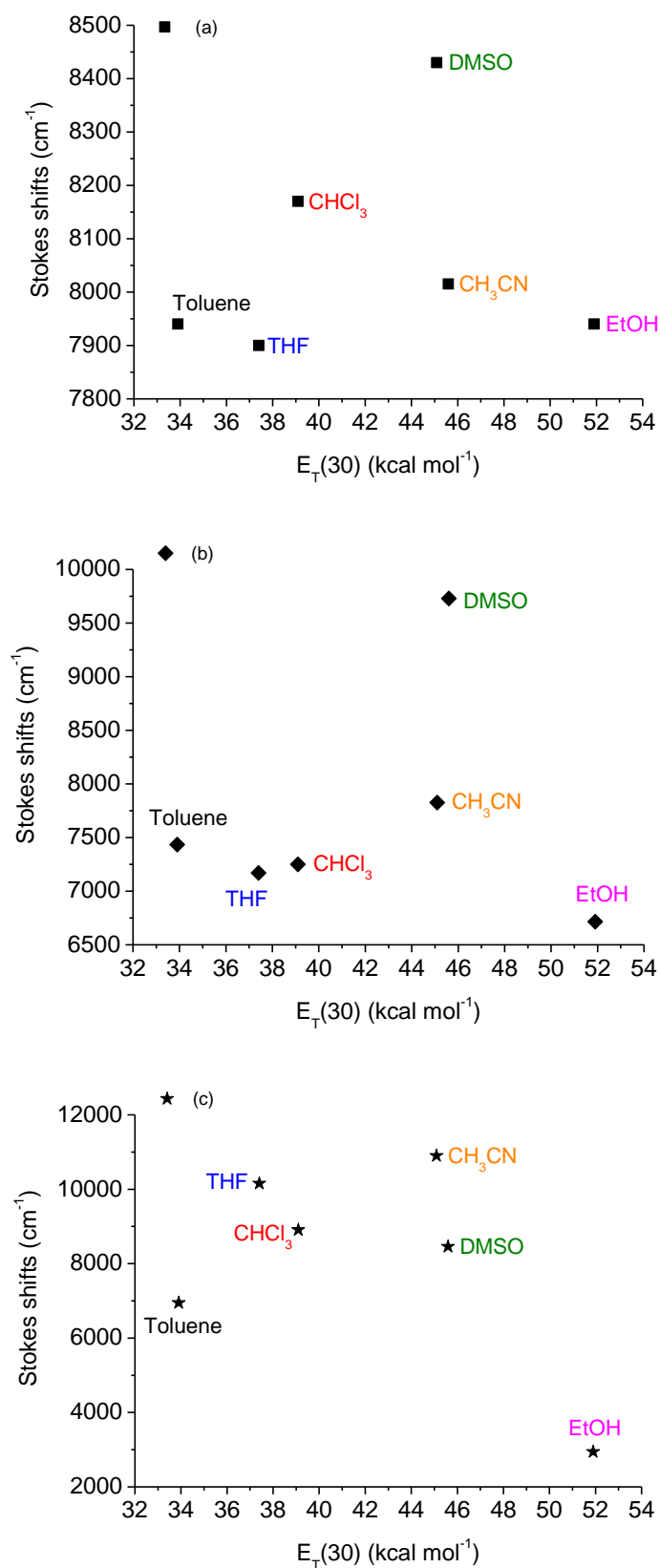


Figure S21. Lippert-Mataga plots relationship of $E_T(30)$ versus Stokes shifts (cm^{-1}) of compounds (a) 3b, (b) 3c and (c) 3f, respectively.

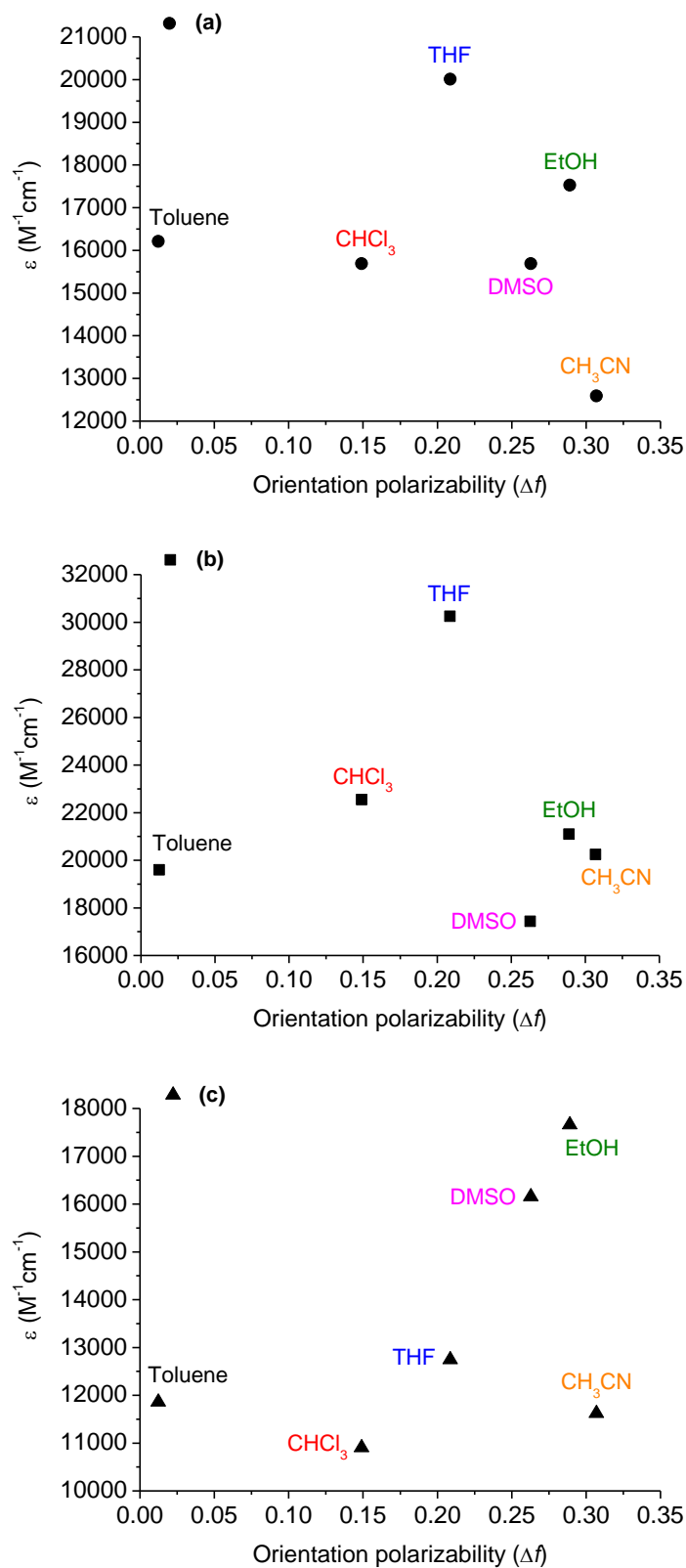


Figure S22. Lippert-Mataga plots relationship of orientation polarizability (Δf) versus ϵ ($M^{-1} cm^{-1}$) of compounds (a) **3b**, (b) **3c** and (c) **3f**, respectively.

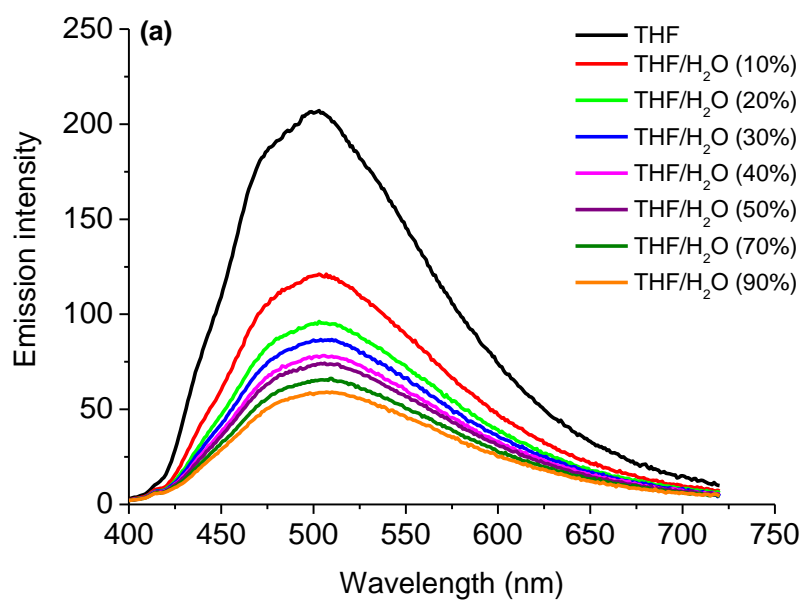


Figure S23. (a) Fluorescence emission spectra of compound **3c** and (b) photograph of compound **3c** solutions in THF/water mixture different water fractions (0 to 90%) under illumination of UV lamp (365 nm) light.

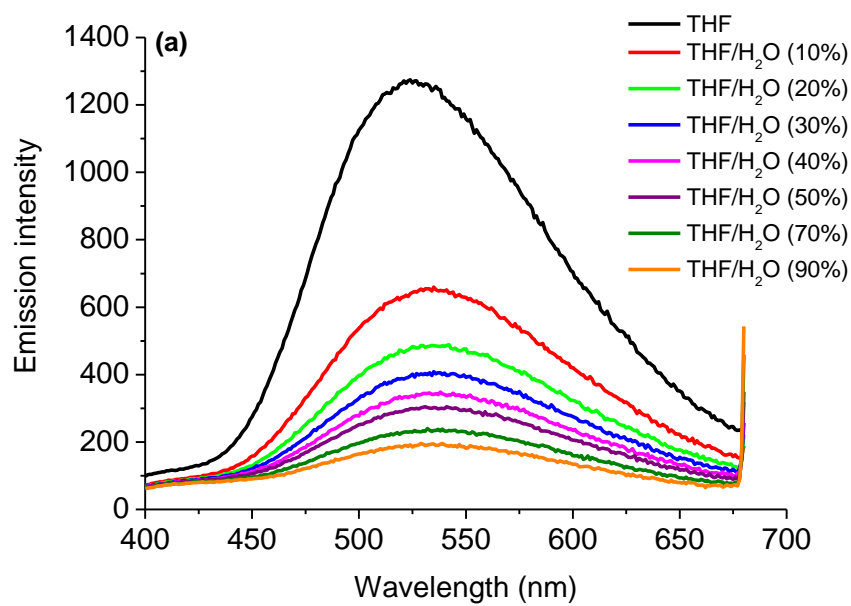


Figure S24. (a) Fluorescence emission spectra of compound **3f** and (b) photograph of compound **3f** solutions in THF/water mixture different water fractions (0 to 90%) under illumination of UV lamp (365 nm) light.

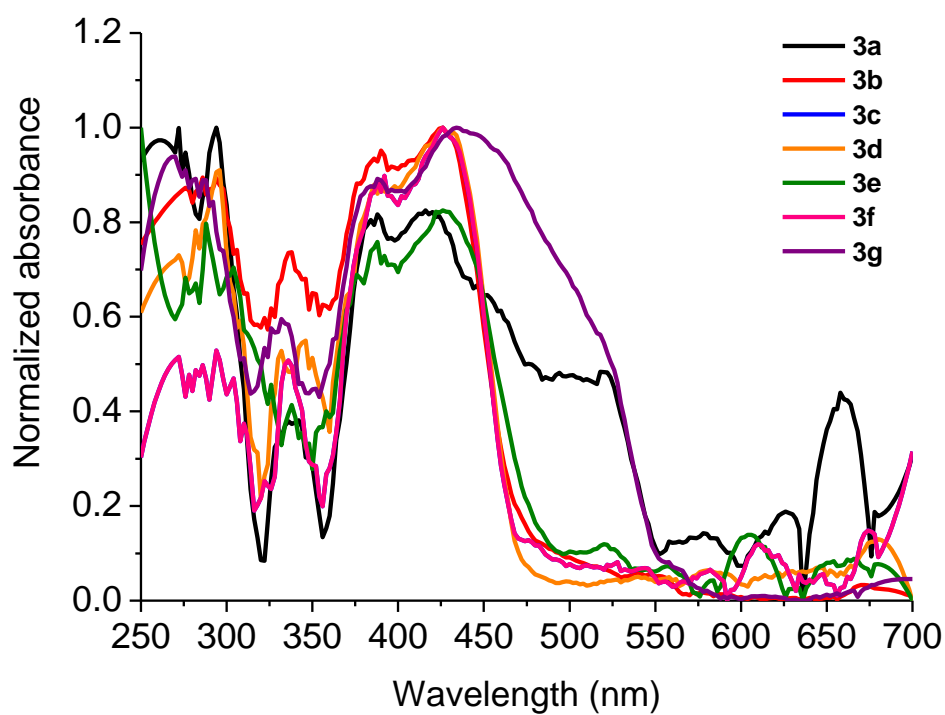


Figure S25. Normalized absorbance spectra of compounds **3a-g** in solid state.

4. Thermal stability

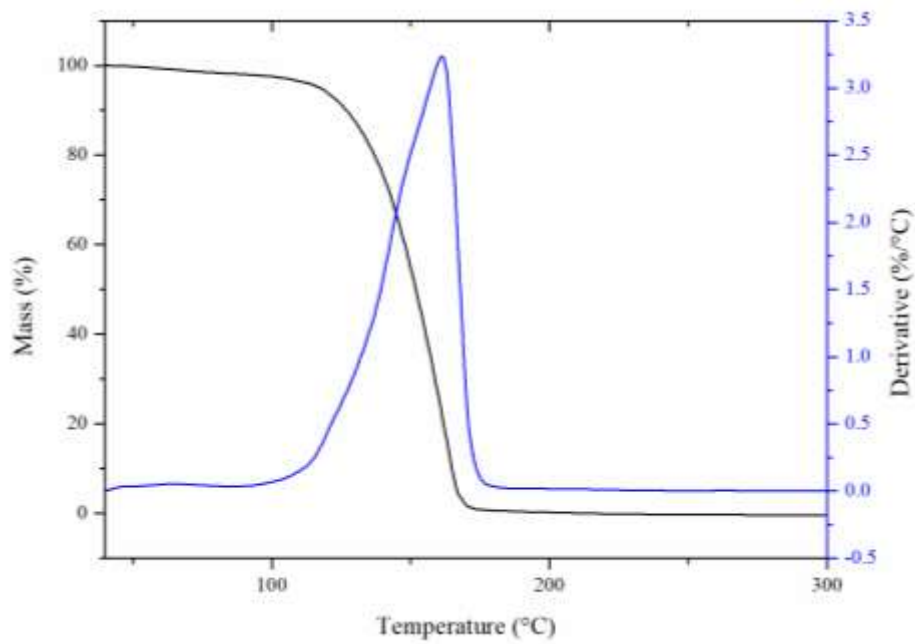


Figure S26. TGA curve of compound **3b**.

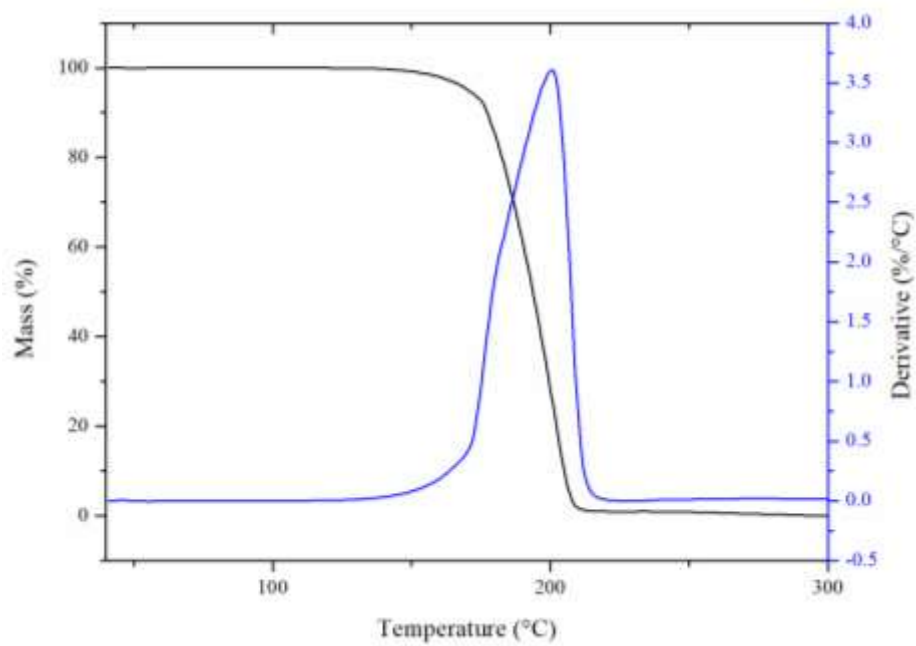


Figure S27. TGA curve of compound **3c**.

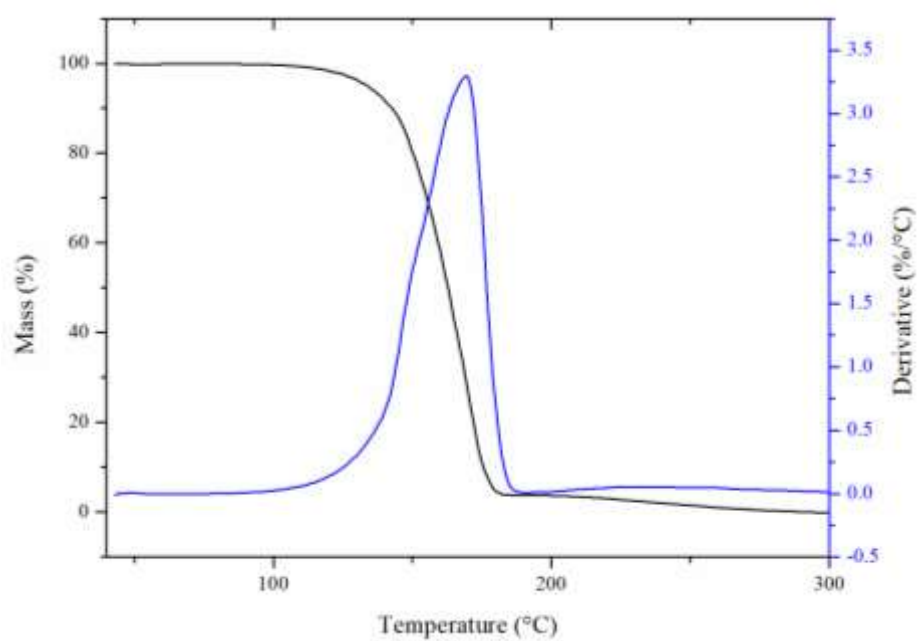


Figure S28. TGA curve of compound **3d**.

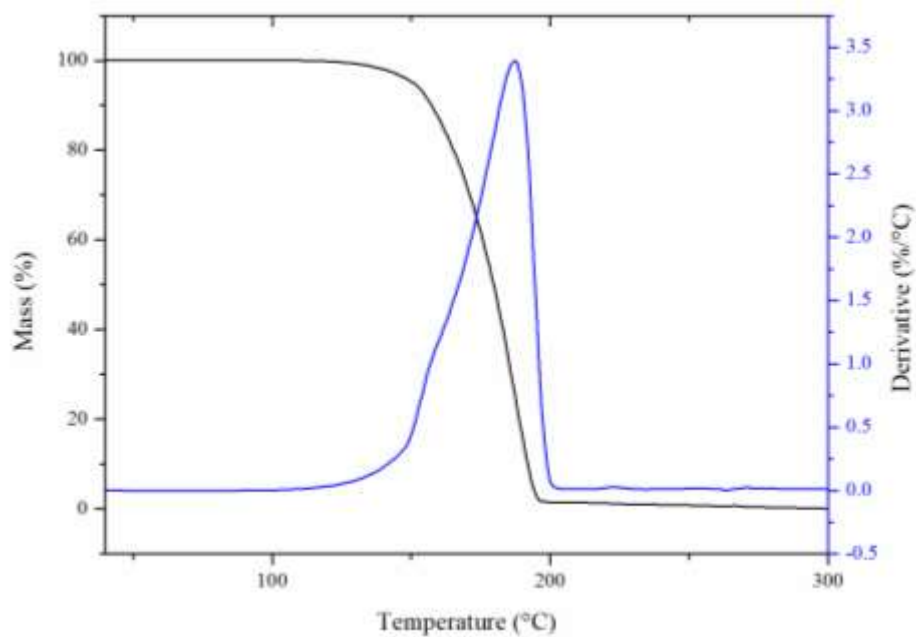


Figure S29. TGA curve of compound **3g**.

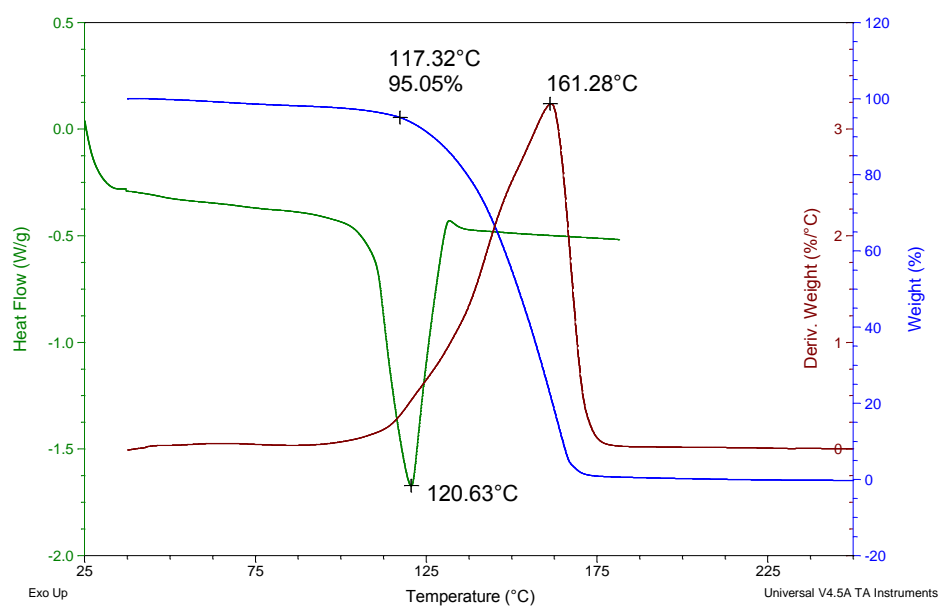


Figure S30. DSC/TGA/DTG curve of **3b** (first cycle).

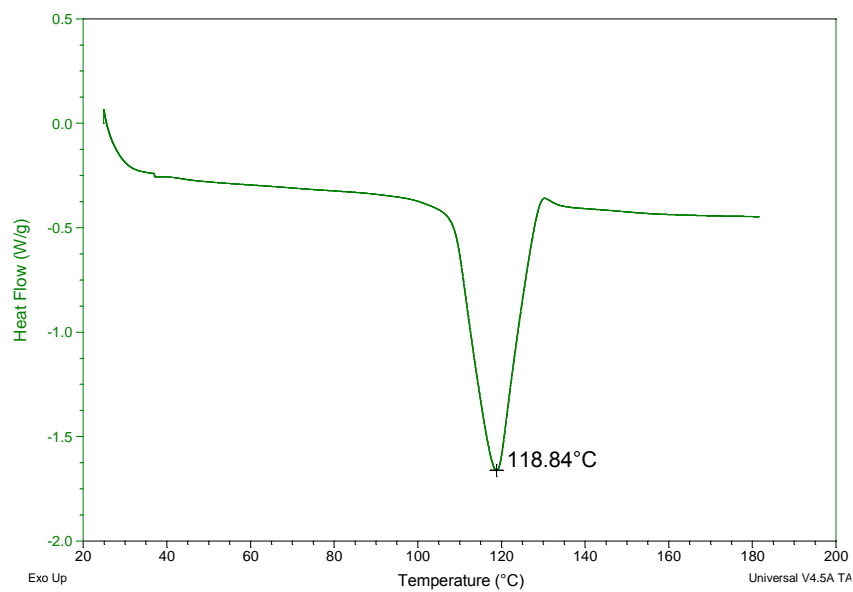


Figure S31. DSC curve of **3b** (second cycle).

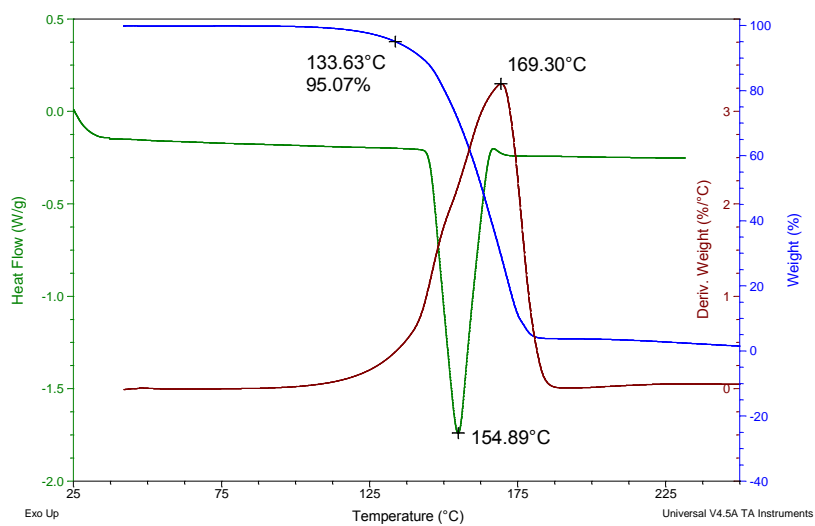


Figure S32. DSC/TGA/DTG curve of **3d** (first cycle).

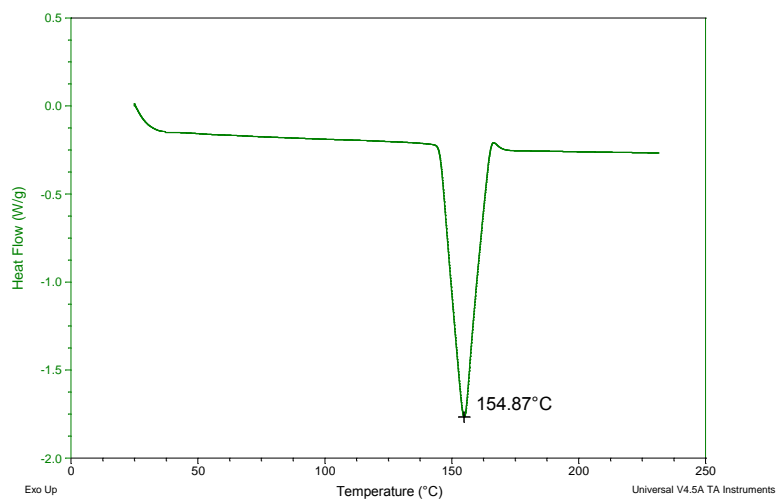


Figure S33. DSC curve of **3d** (second cycle).

5. HRMS analysis of compound 3f.

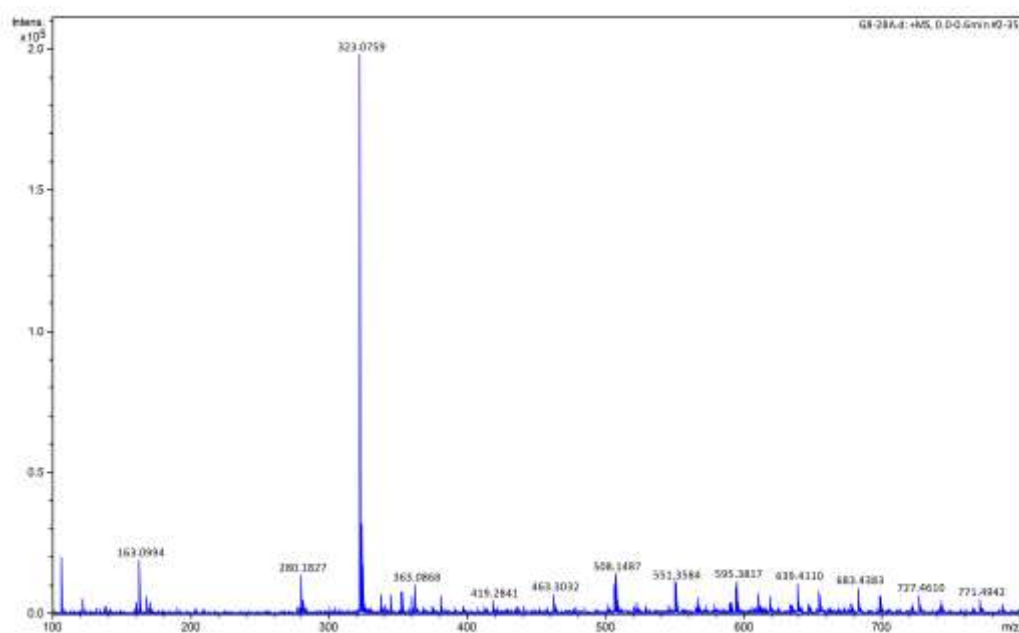


Figure S34. Spectrum obtained from compound 3f.

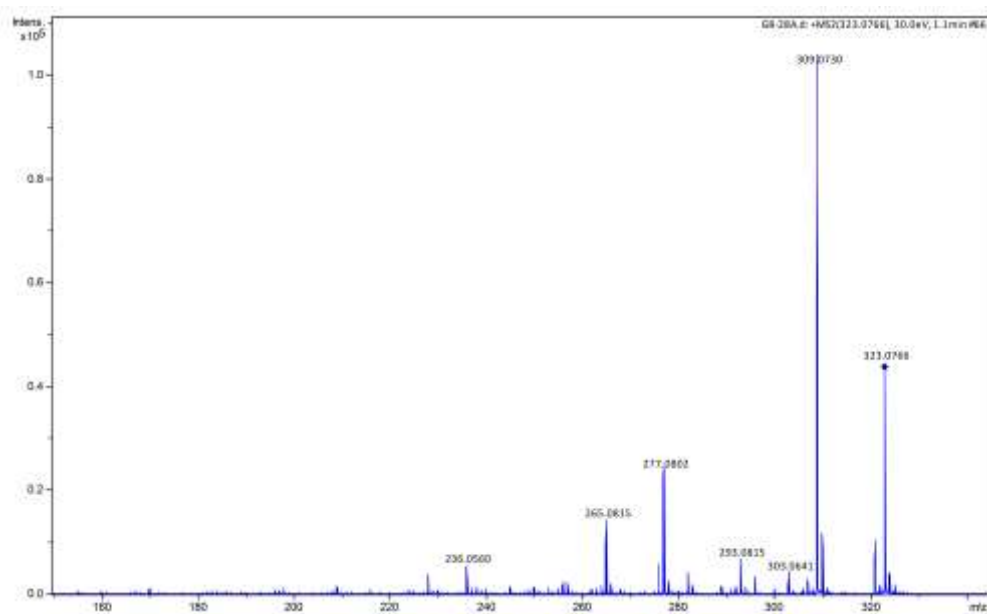


Figure S35. Spectrum obtained from the fragmentation of the m/z 323 ion of compound 3f.

6. References

- [1] A.W.T. Bristow, K.S. Webb, Intercomparison study on accurate mass measurement of small molecules in mass spectrometry, *J. Am. Soc. Mass Spectrom.* 14 (2003) 1086–1098. [https://doi.org/10.1016/S1044-0305\(03\)00403-3](https://doi.org/10.1016/S1044-0305(03)00403-3).