Supplemental Information

Precursor-directed Biosynthesis of Aminofulvenes: new Chalanilines from endophytic fungus *Chalara* sp.

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*All the experiments and their NMR data were collected at room temperature.

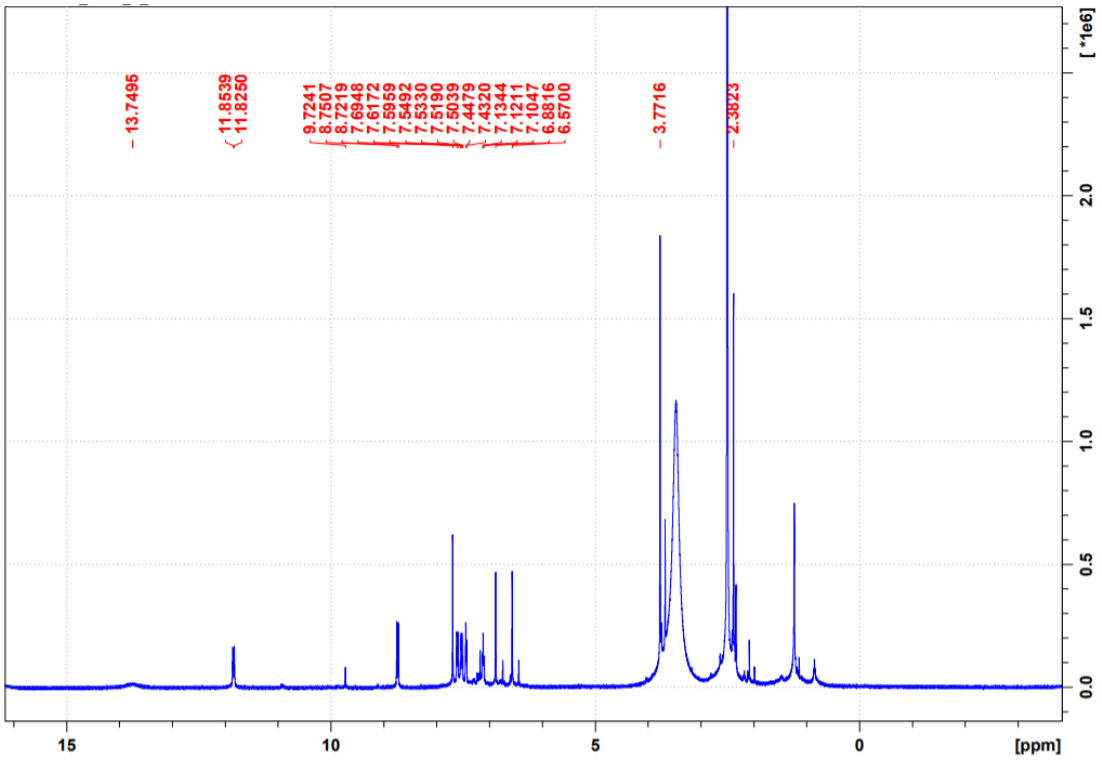


Figure S1. ^{1}H NMR spectrum (500 MHz, DMSO) of **1**.

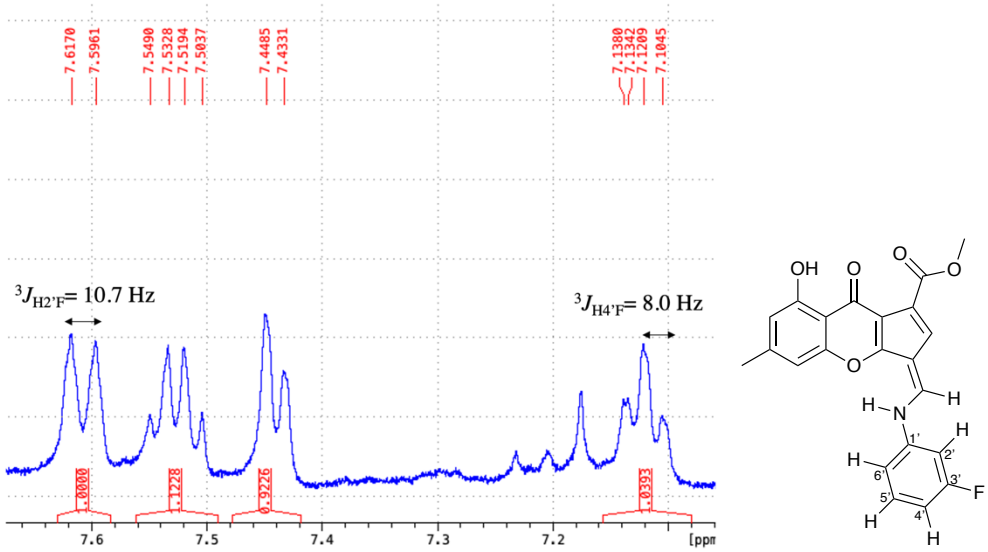


Figure S2. Expanded ^{1}H NMR spectrum of the H-F couplings of **1**.

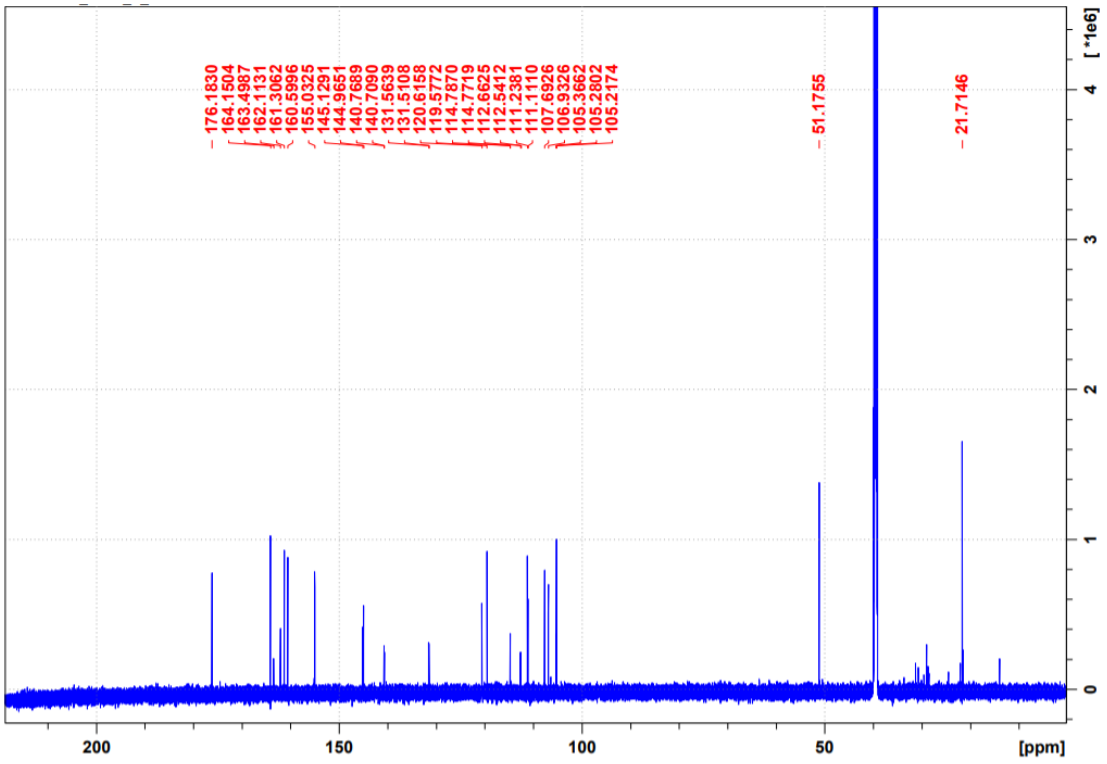


Figure S3. ^{13}C NMR spectrum (176 MHz, DMSO) of **1**.

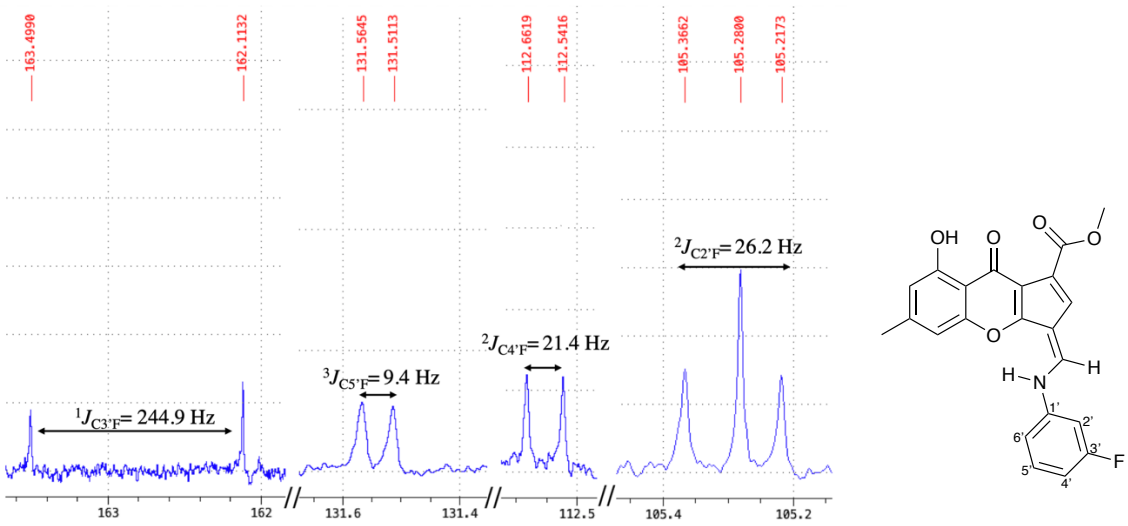


Figure S4. Expanded ^{13}C NMR spectrum of the C-F couplings of **1**.

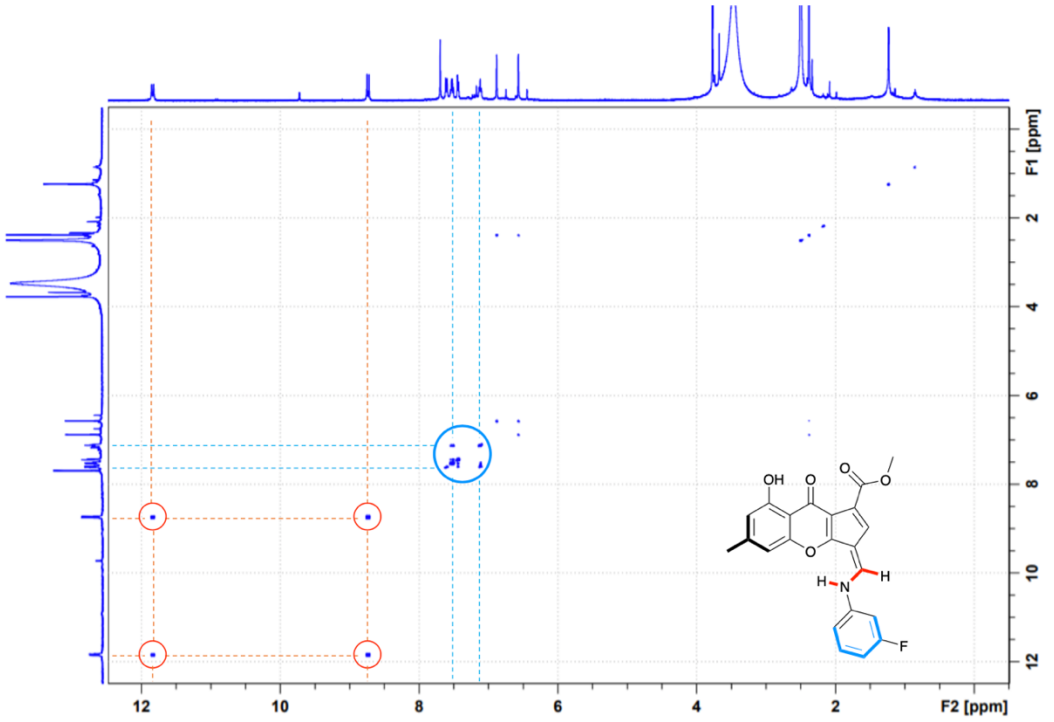


Figure S5. COSY NMR spectrum of **1**.

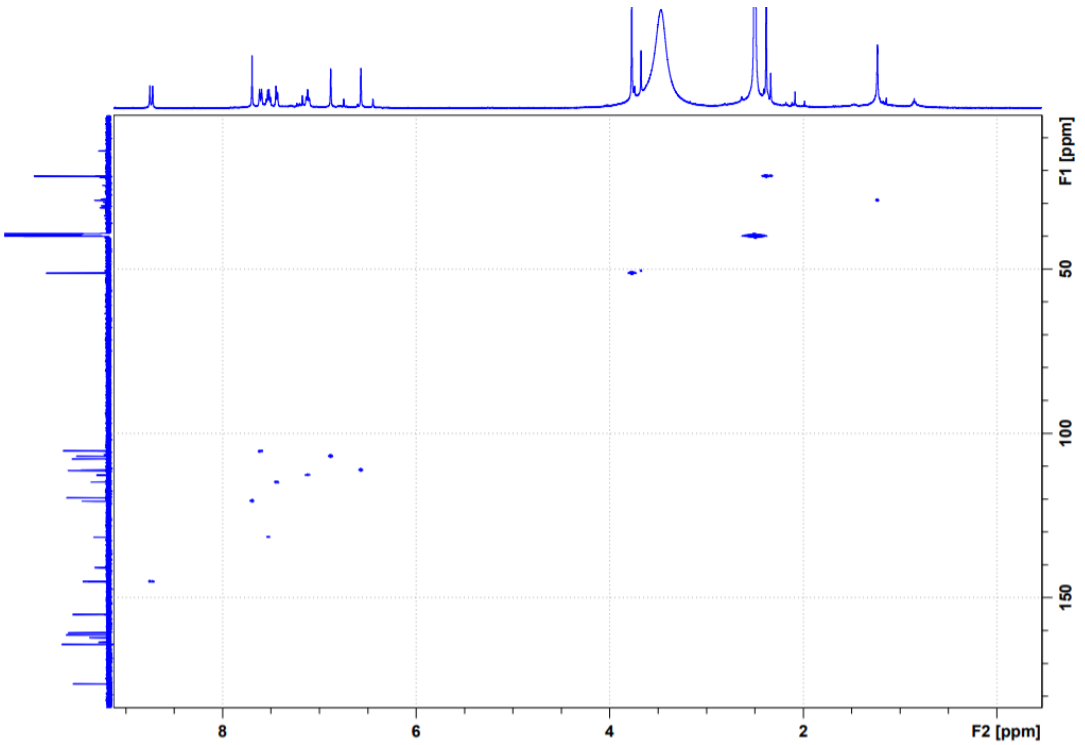


Figure S6. HSQC NMR spectrum of **1**.

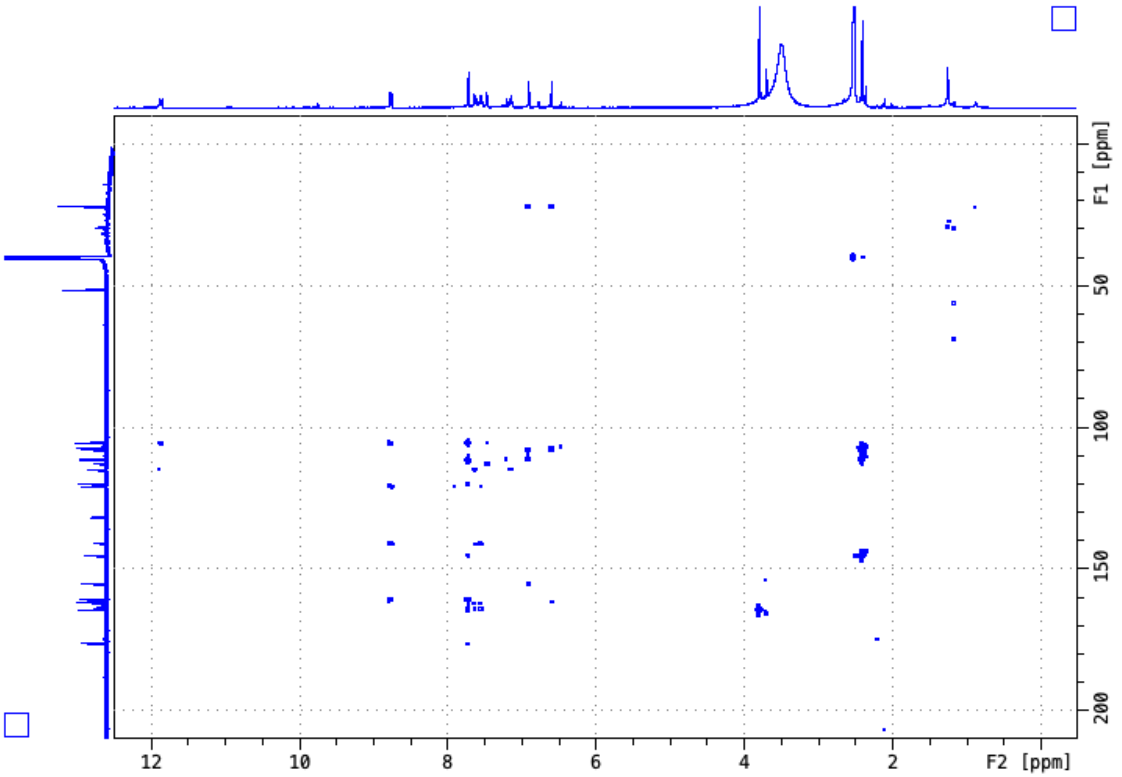


Figure S7. ^{1}H-^{13}C HMBC NMR spectrum of **1**.

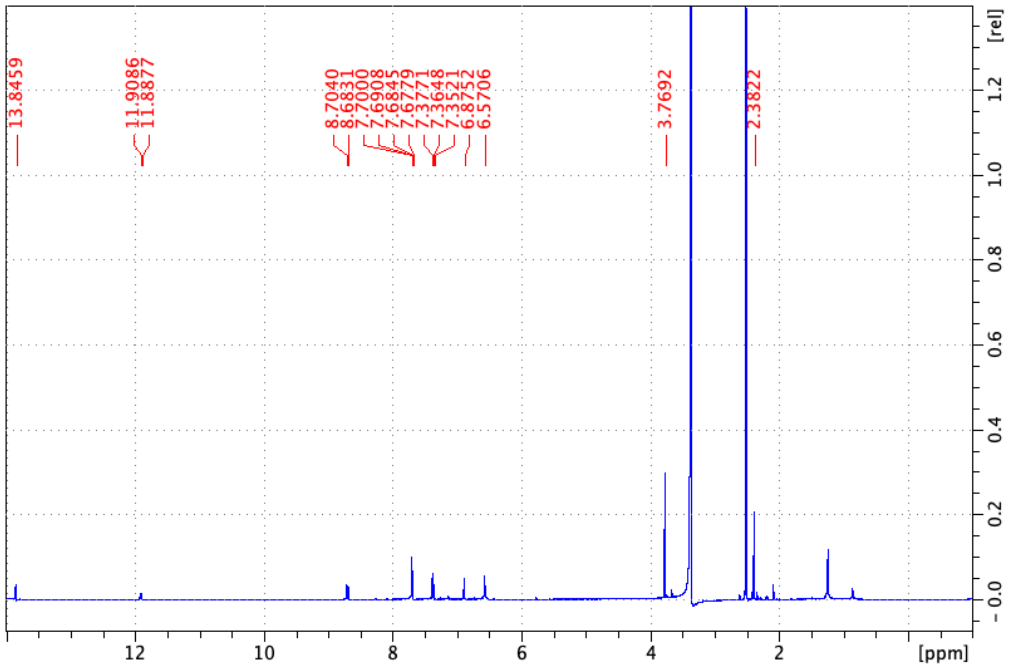
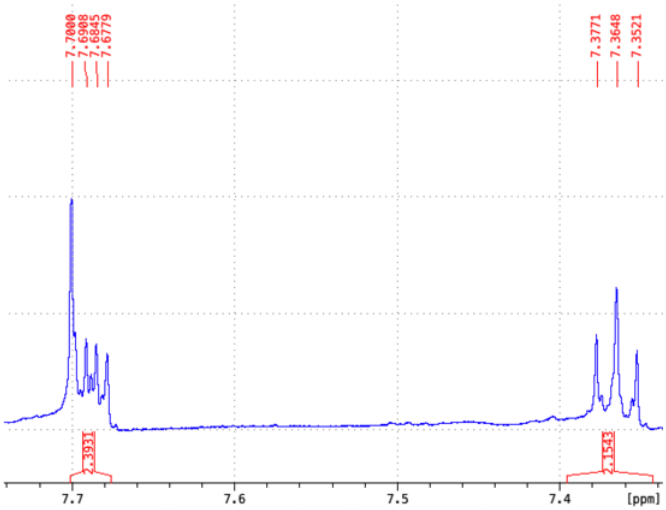
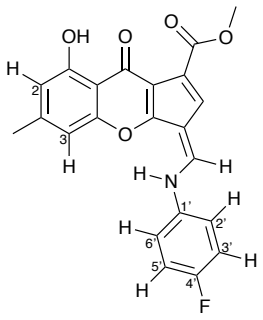


Figure S8. ^{1}H NMR spectrum (700 MHz, DMSO) of **2**.





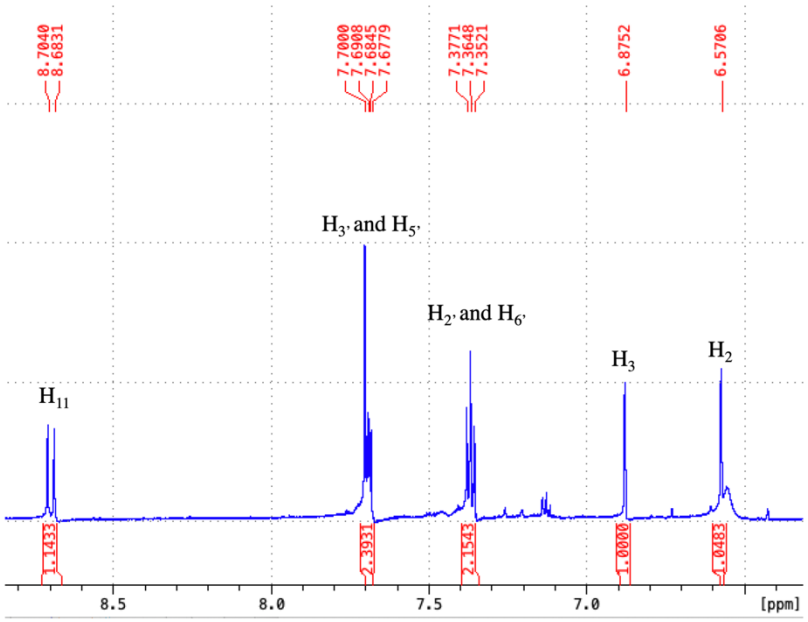


Figure S9. Expanded ^{1}H NMR spectrum of the H-F couplings of **2**.

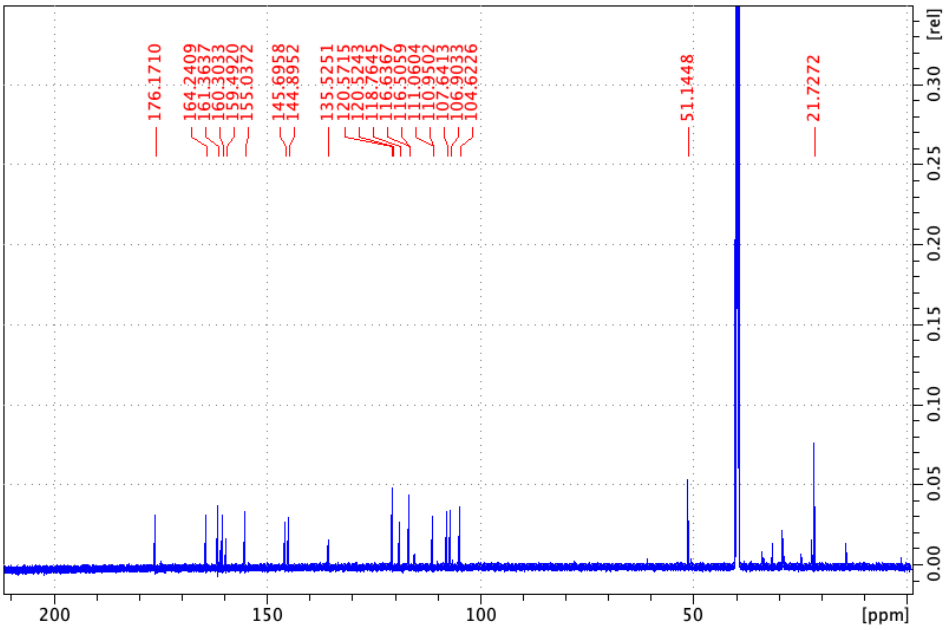


Figure S10. ^{13}CNMR spectrum (176 MHz, DMSO) of **2**.

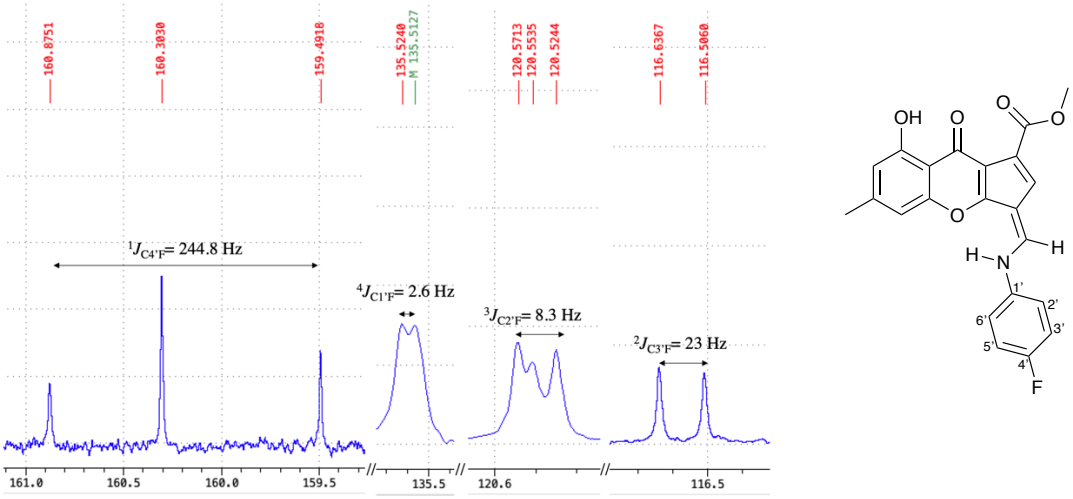


Figure S11. Expanded ^{13}C NMR spectrum of the C-F couplings of **2**.

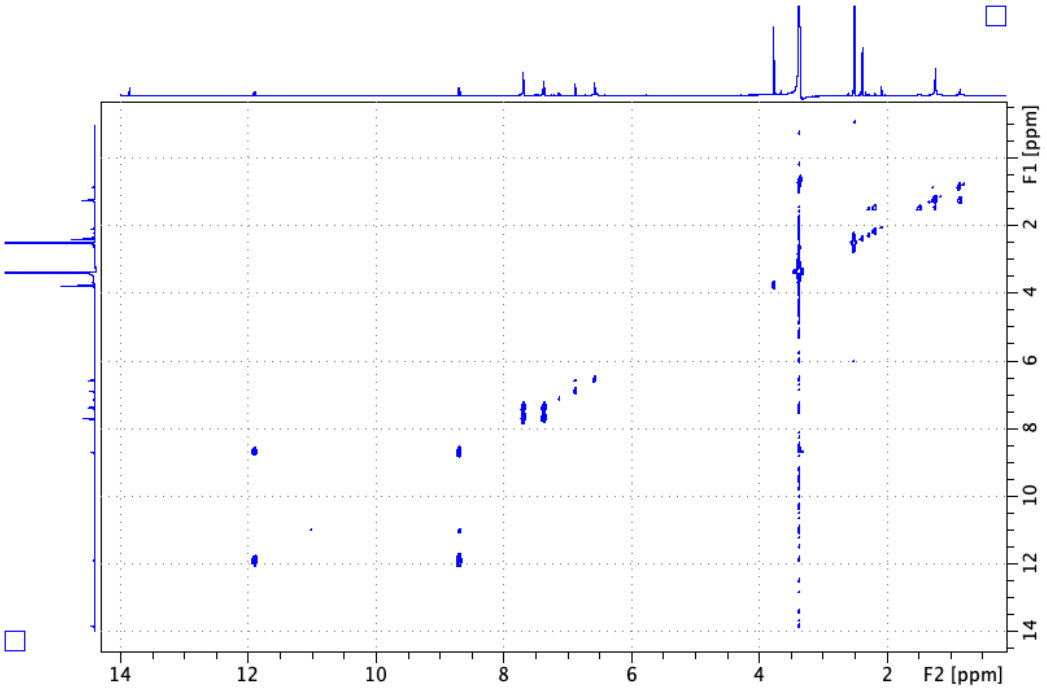


Figure S12. COSY NMR spectrum of **2**.

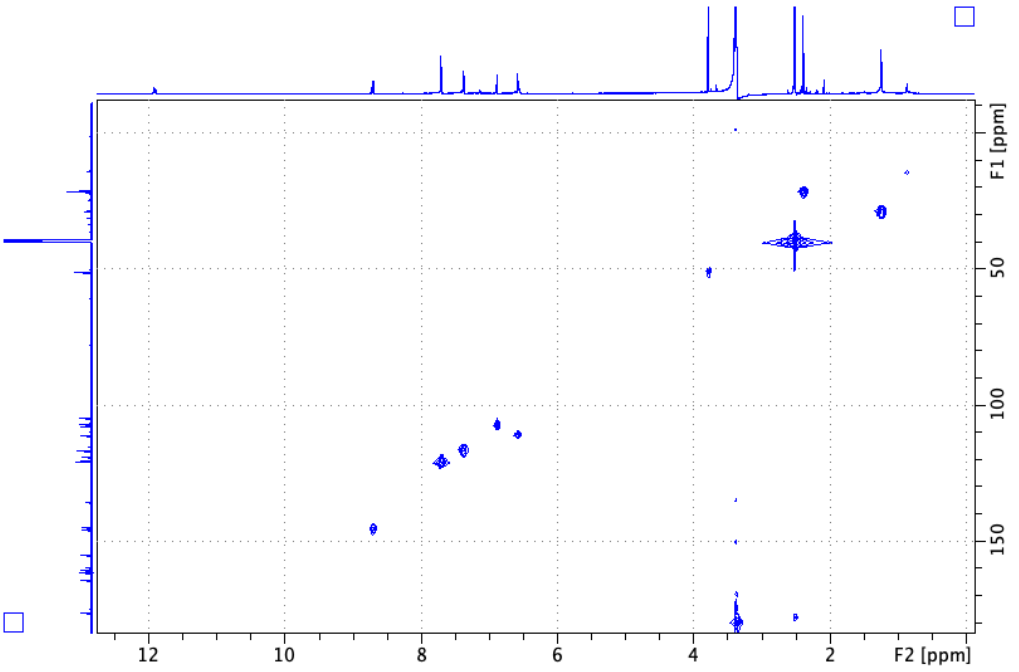


Figure S13. HSQC NMR spectrum of **2.**

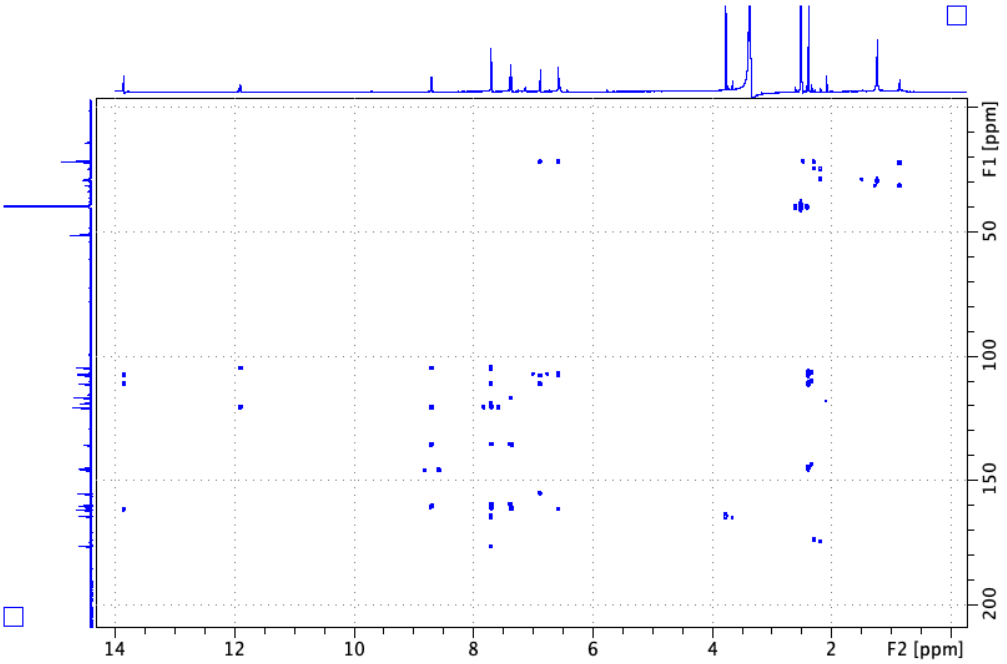


Figure S14. ^{1}H-^{13}C HMBC NMR spectrum of **2**.

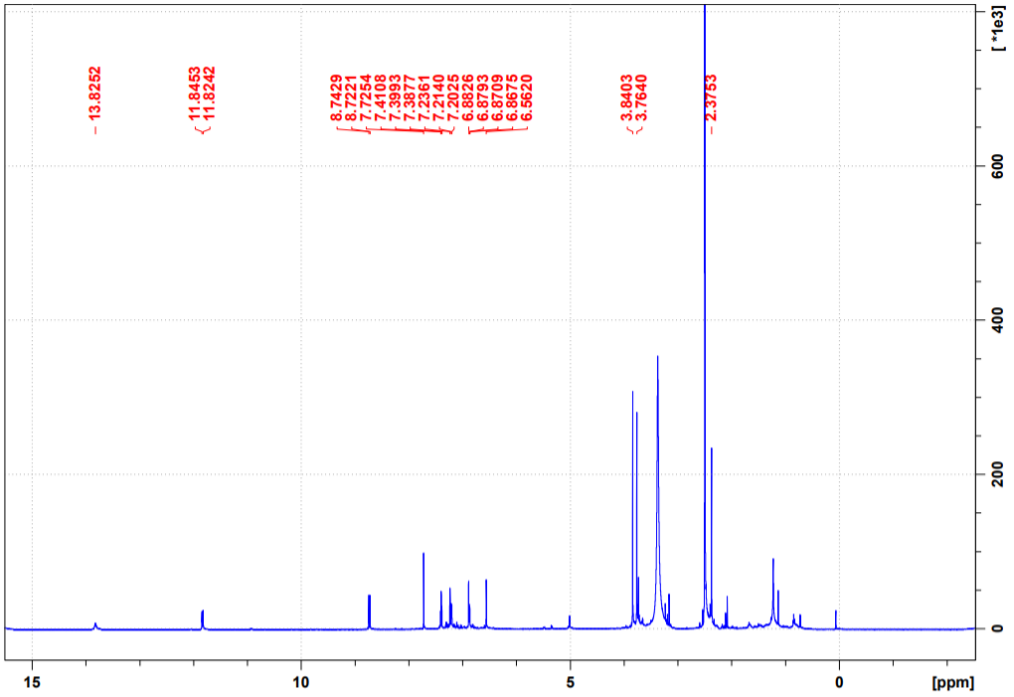


Figure S15. ^{1}H NMR spectrum (700 MHz, DMSO) of **3**.

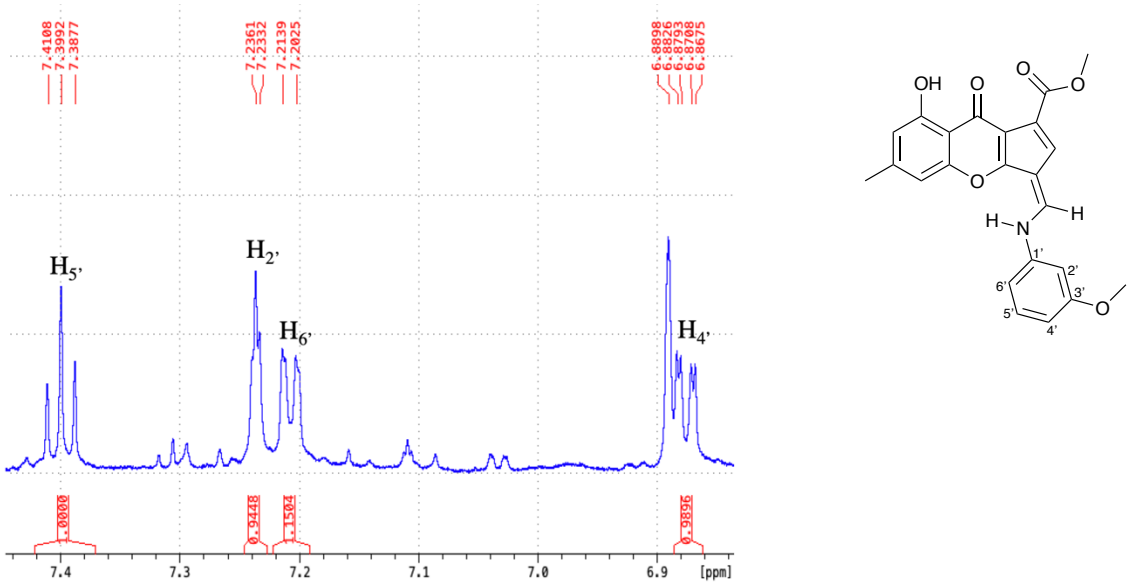


Figure S16. Expanded aromatic region of the ^{1}H NMR spectrum of **3**.

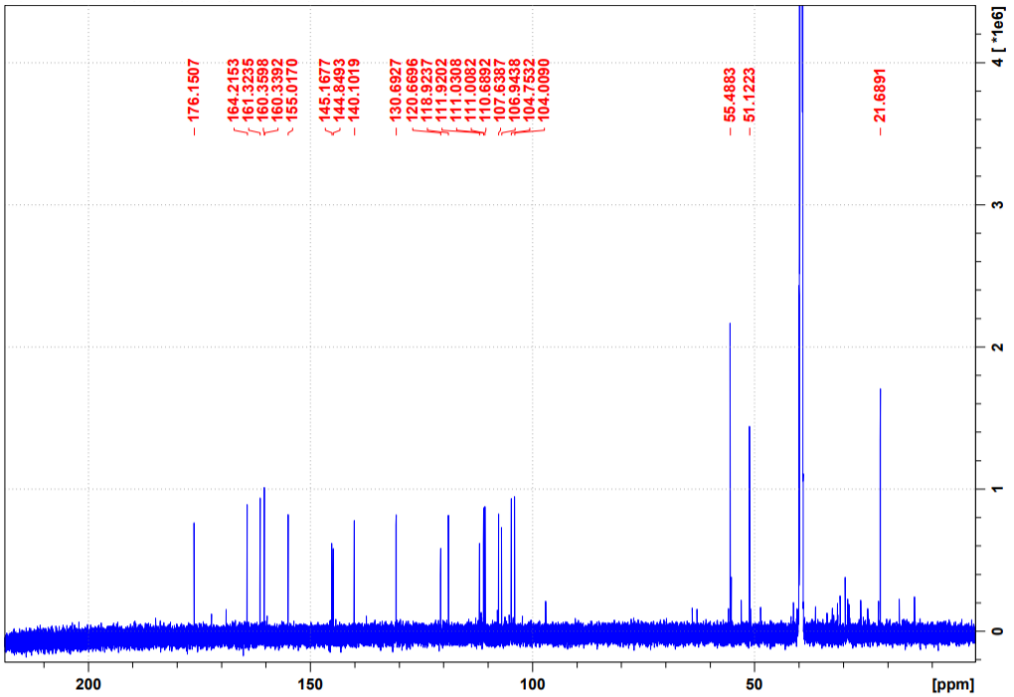


Figure S17. ^{13}C NMR spectrum (176 MHz, DMSO) of **3**.

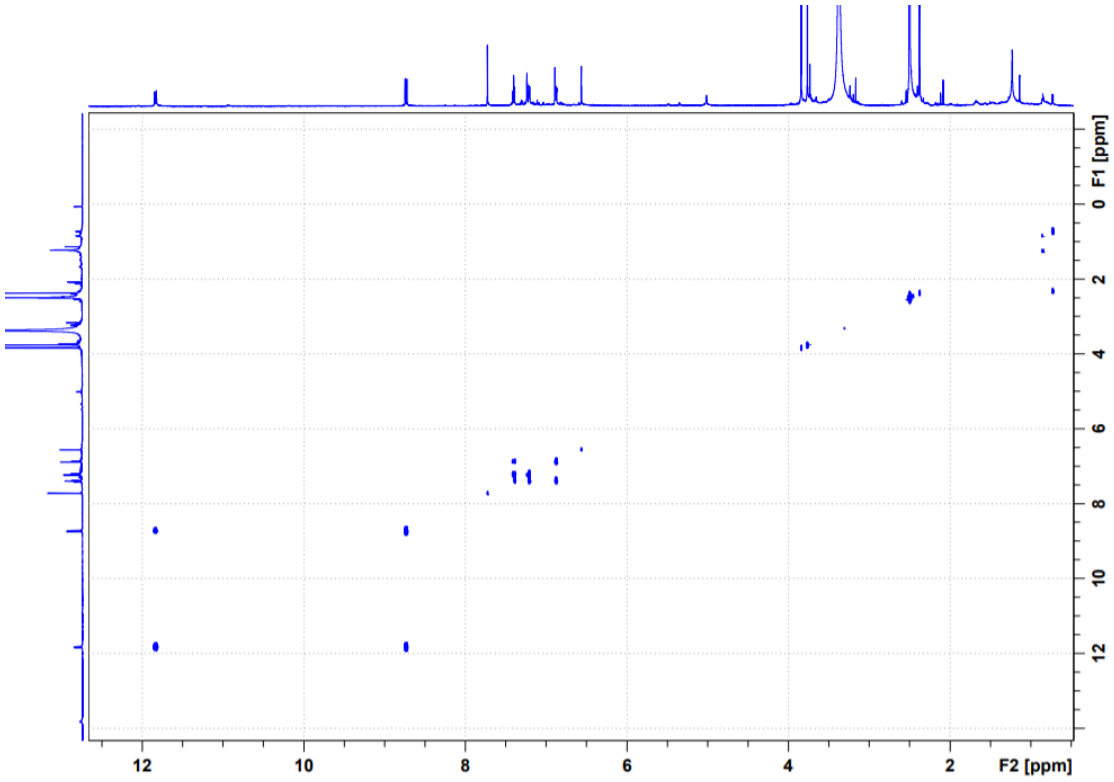


Figure S18. COSY NMR spectrum of **3**.

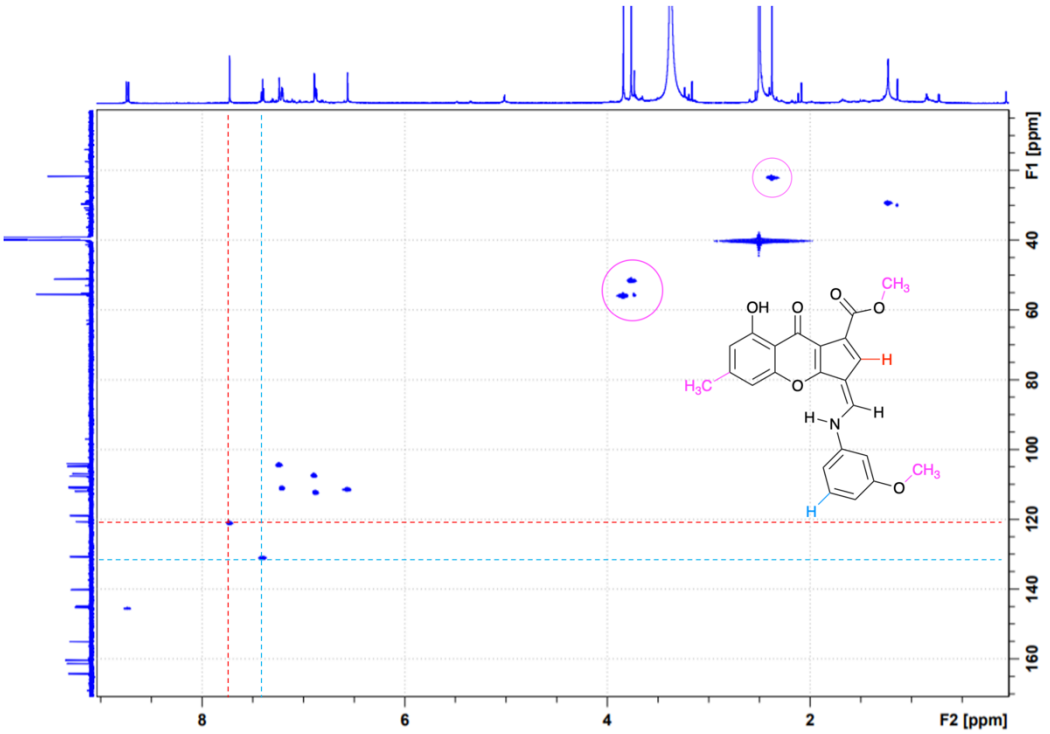


Figure S19. HSQC NMR spectrum of **3**.

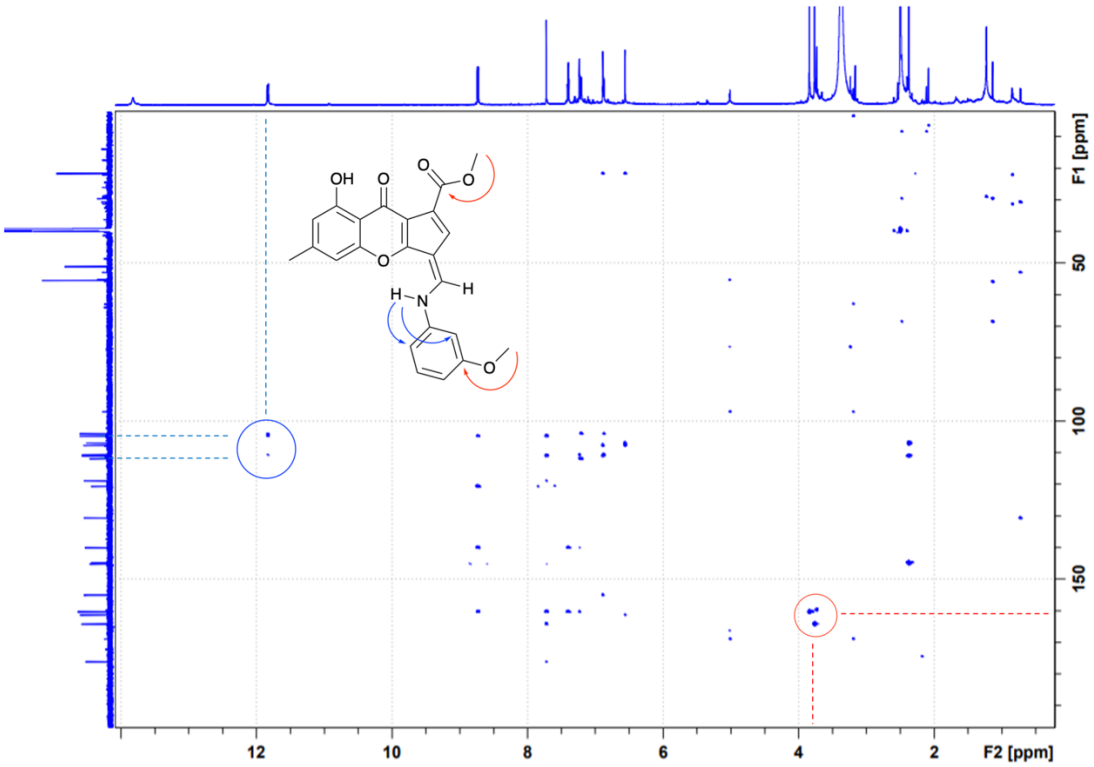


Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of **3**.

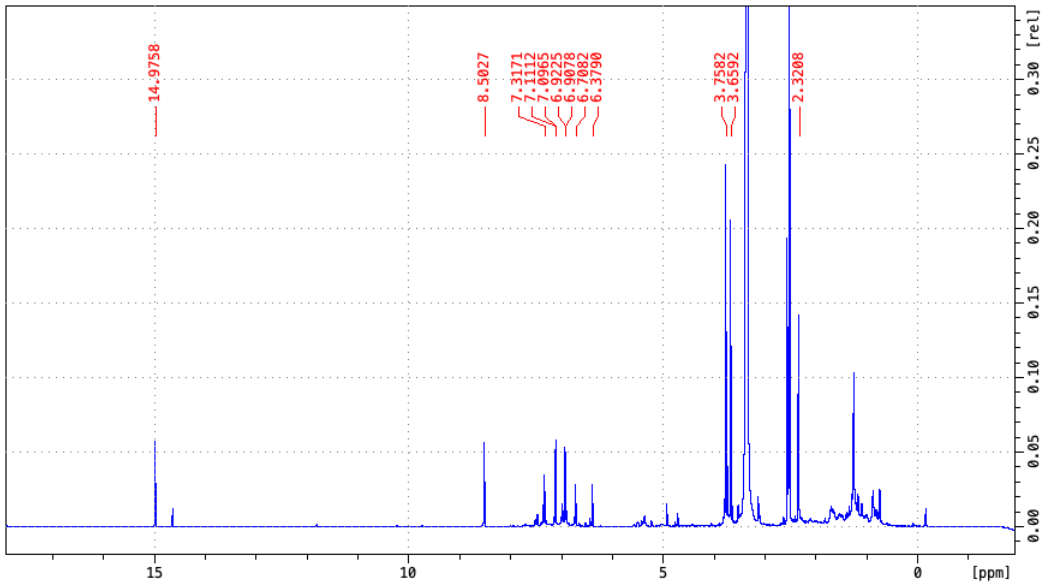


Figure S21. ^{1}H NMR spectrum (600 MHz, DMSO) of **4**.

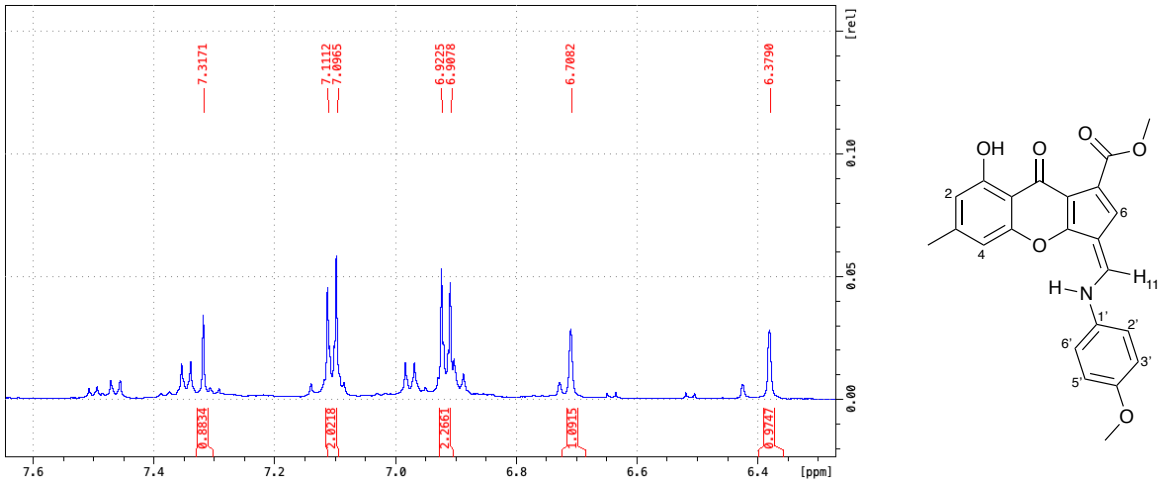


Figure S22. Expanded aromatic region of the ^{1}H NMR spectrum of **4**.

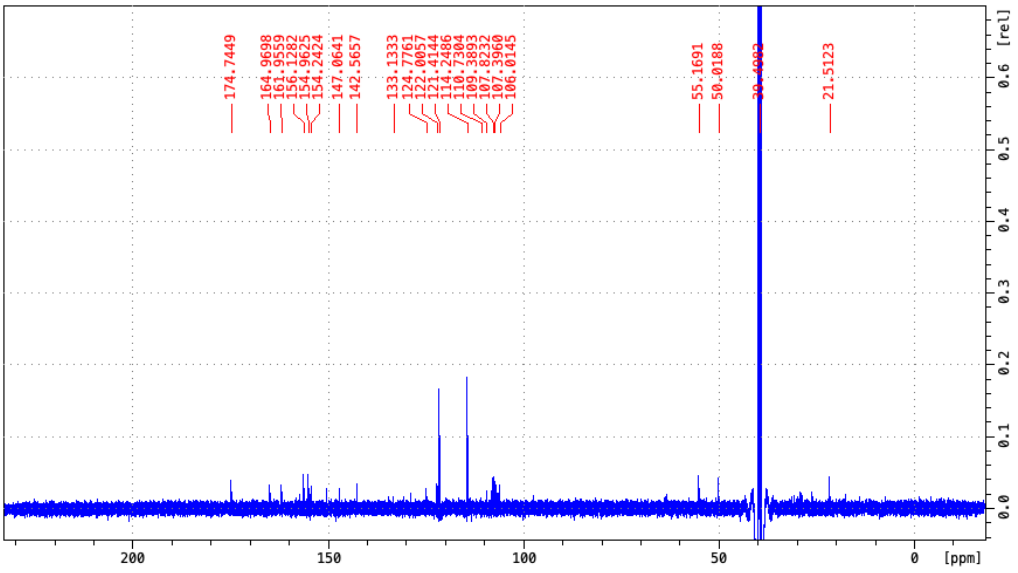


Figure S23. ^{13}C NMR spectrum (150 MHz, DMSO) of **4**.

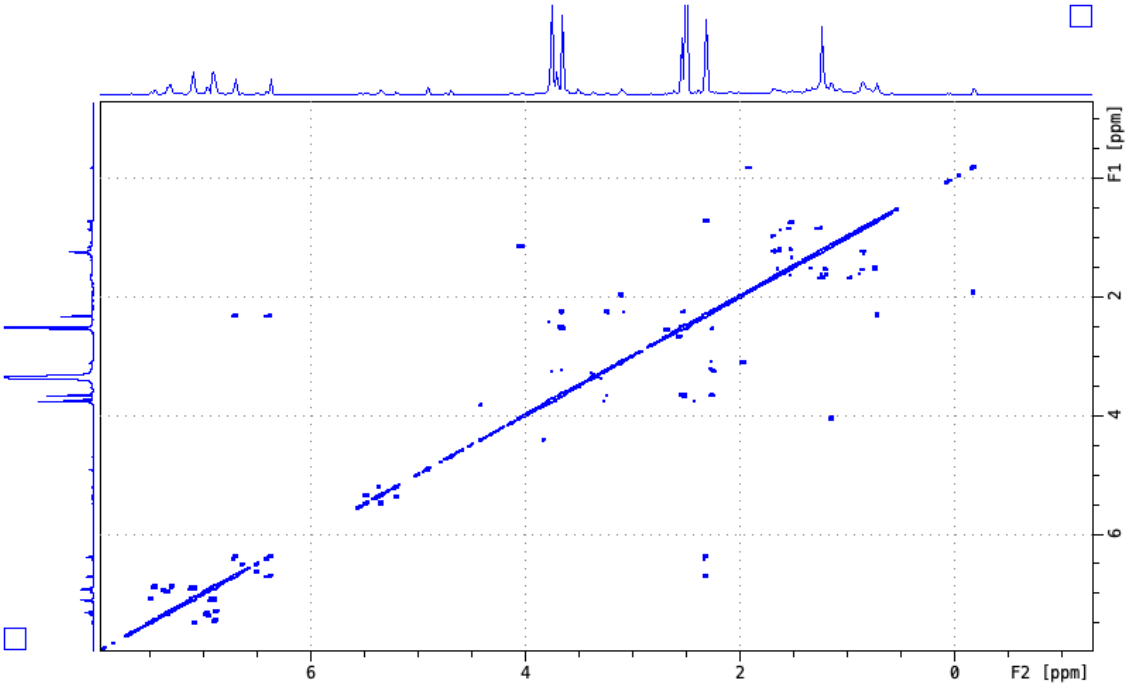


Figure S24. COSY NMR spectrum of **4**.

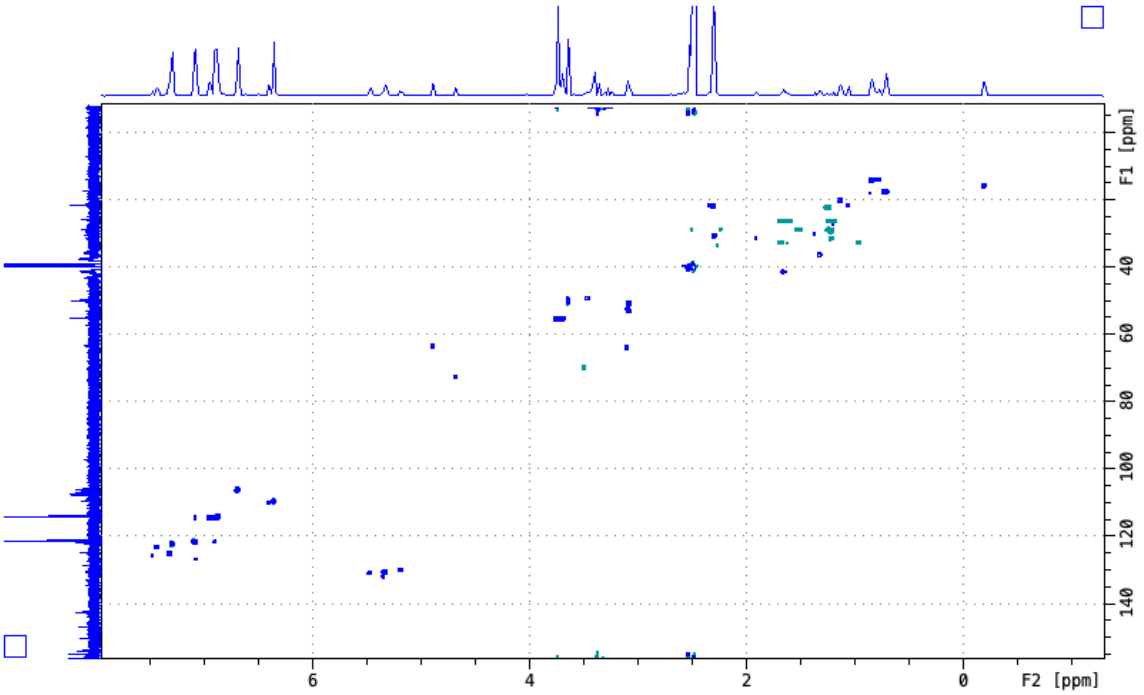


Figure S25. HSQC NMR spectrum of **4**.

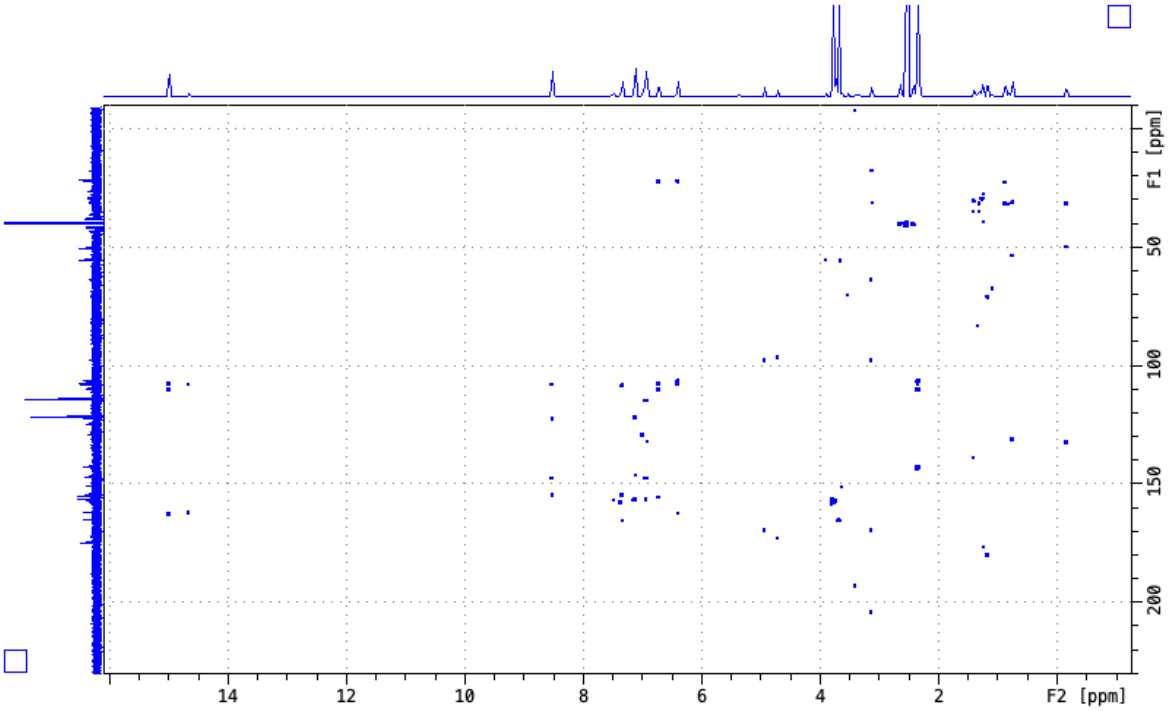


Figure S26. ^{1}H-^{13}C HMBC NMR spectrum of **4**.

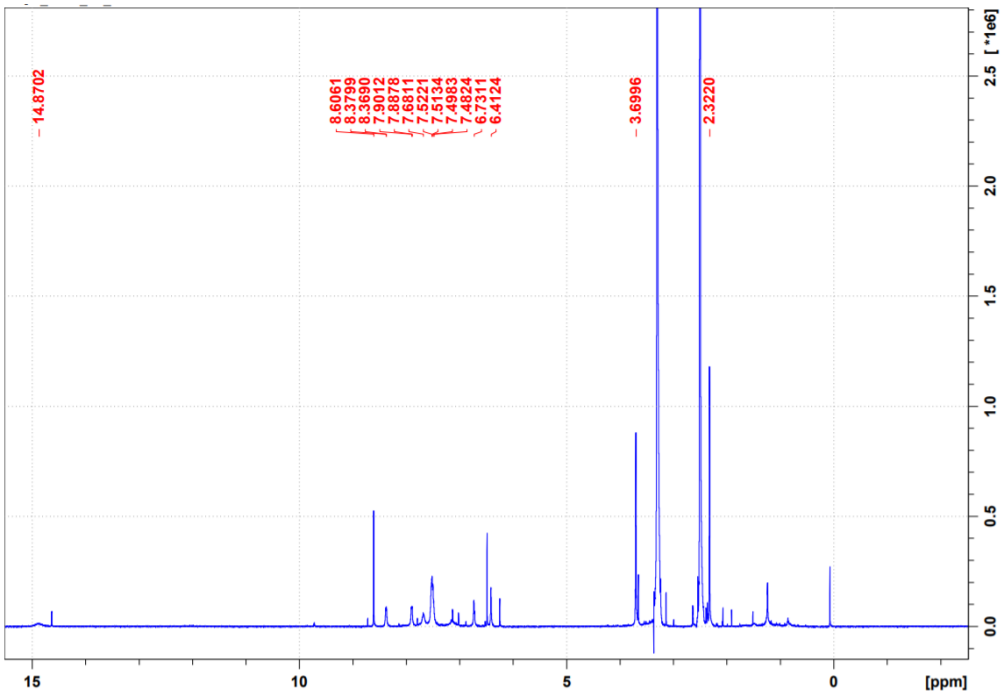
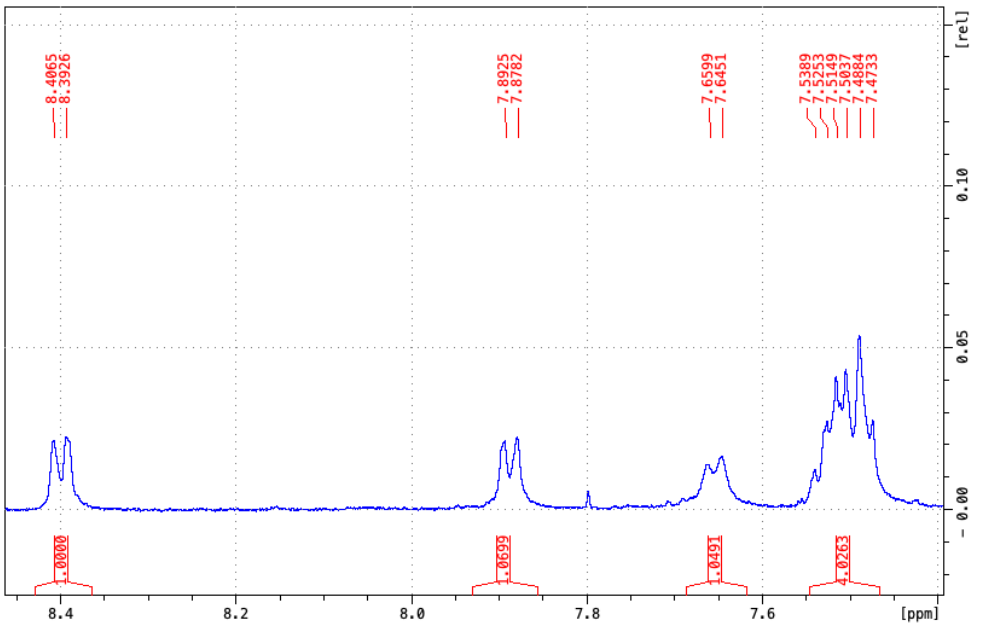


Figure S27. ^{1}H NMR spectrum (500 MHz, DMSO) of **5**.



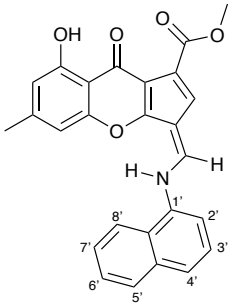


Figure S28. Expanded ^{1}H NMR spectrum of the naphthyl group of **5**.

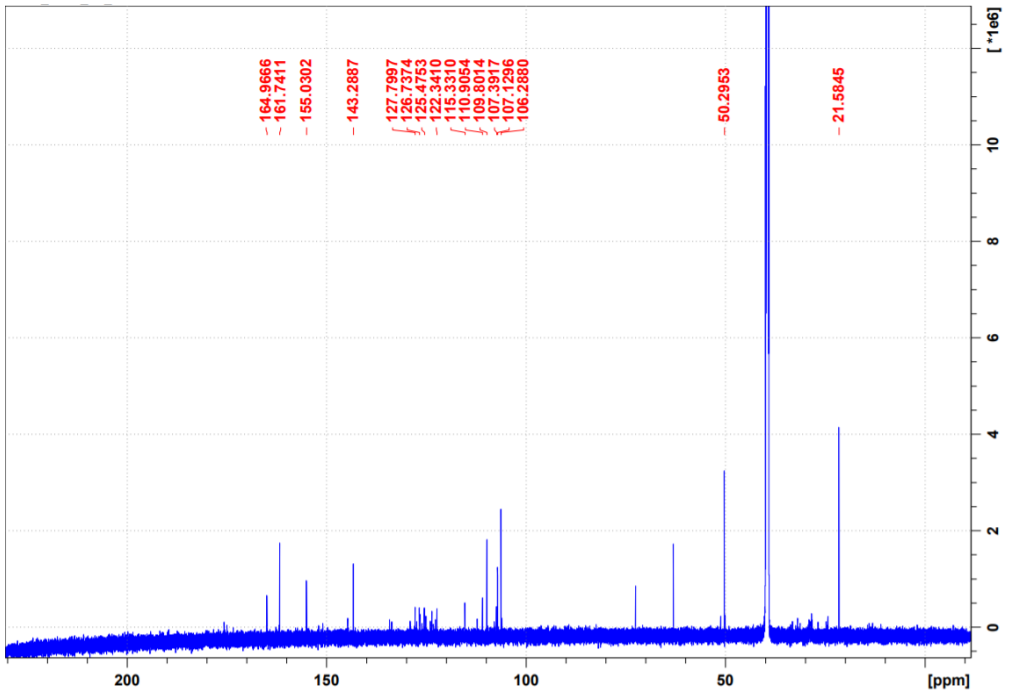


Figure S29. ^{13}C NMR spectrum (176 MHz, DMSO) of **5**.

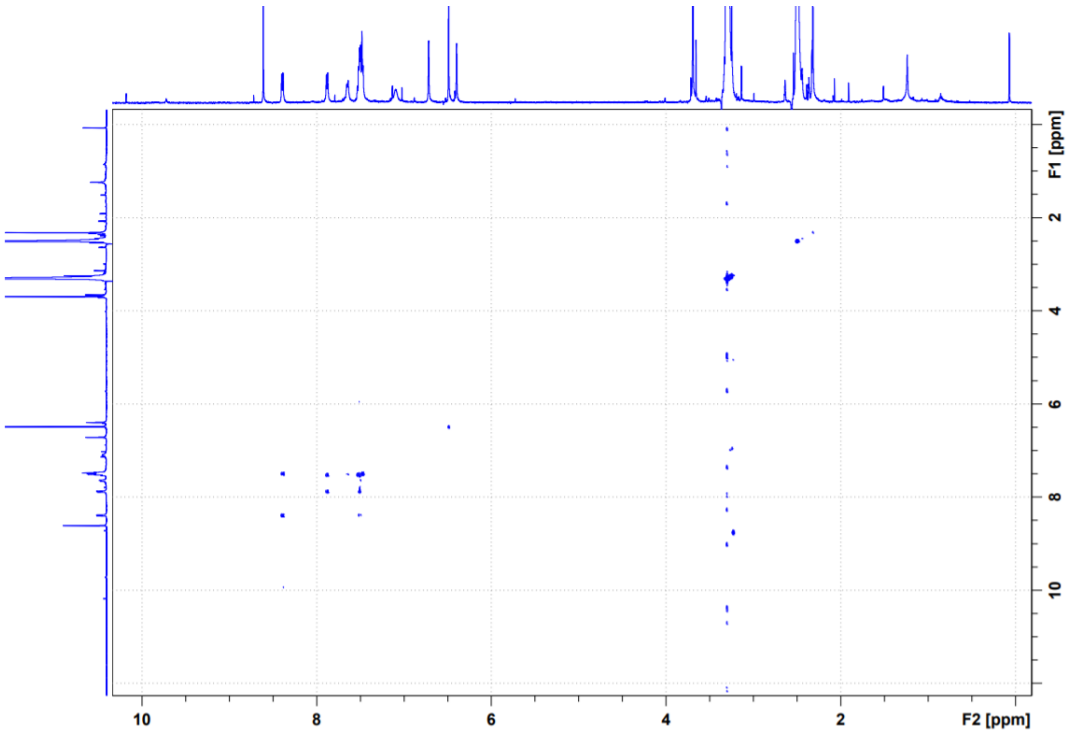


Figure S30. COSY NMR spectrum of **5.**

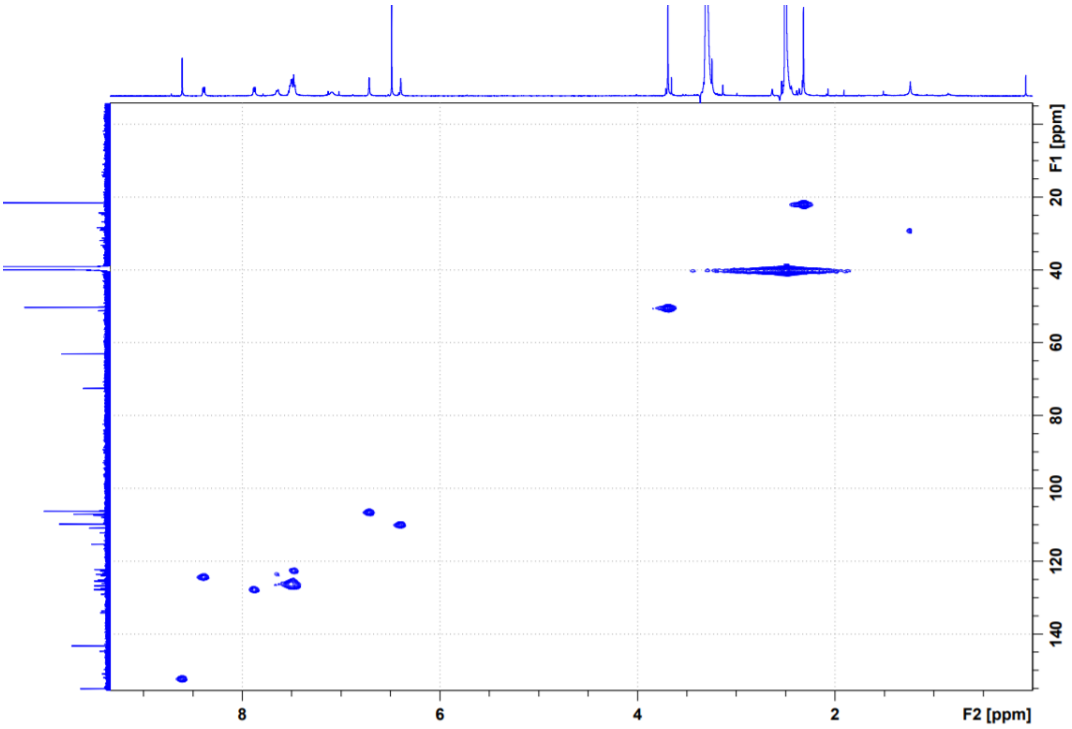


Figure S31. HSQC NMR spectrum of **5**.

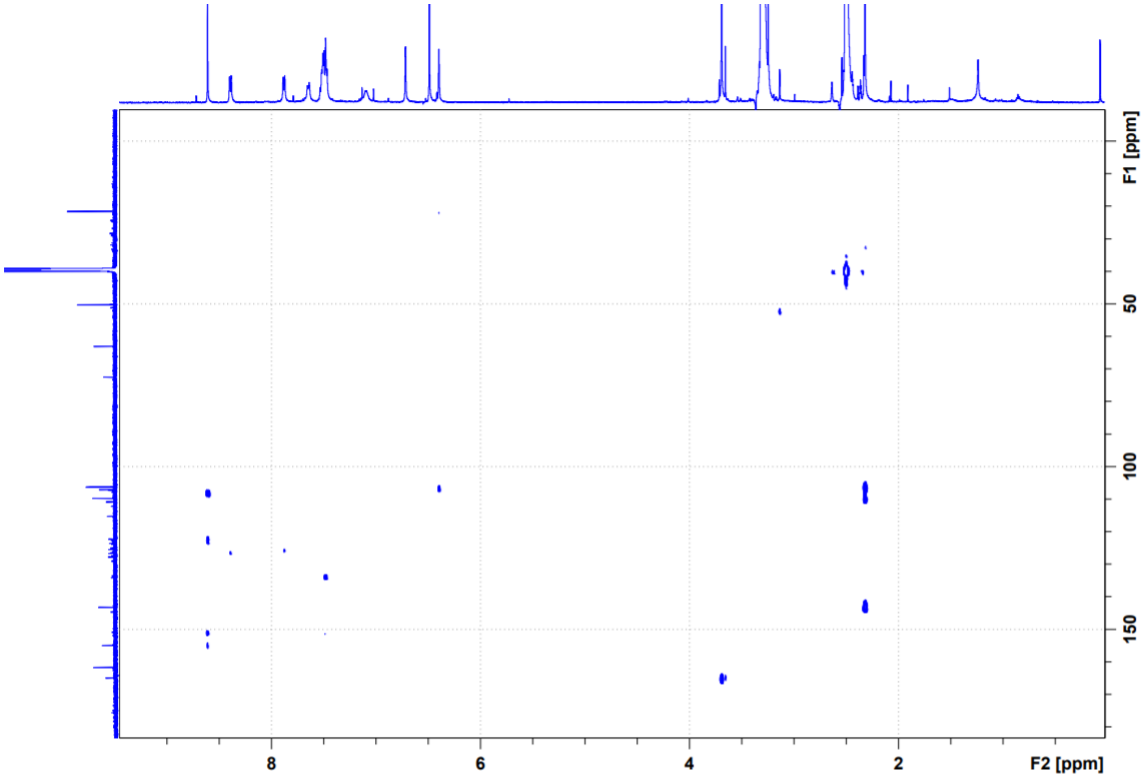


Figure S32. ^{1}H-^{13}C HMBC NMR spectrum of **5**.

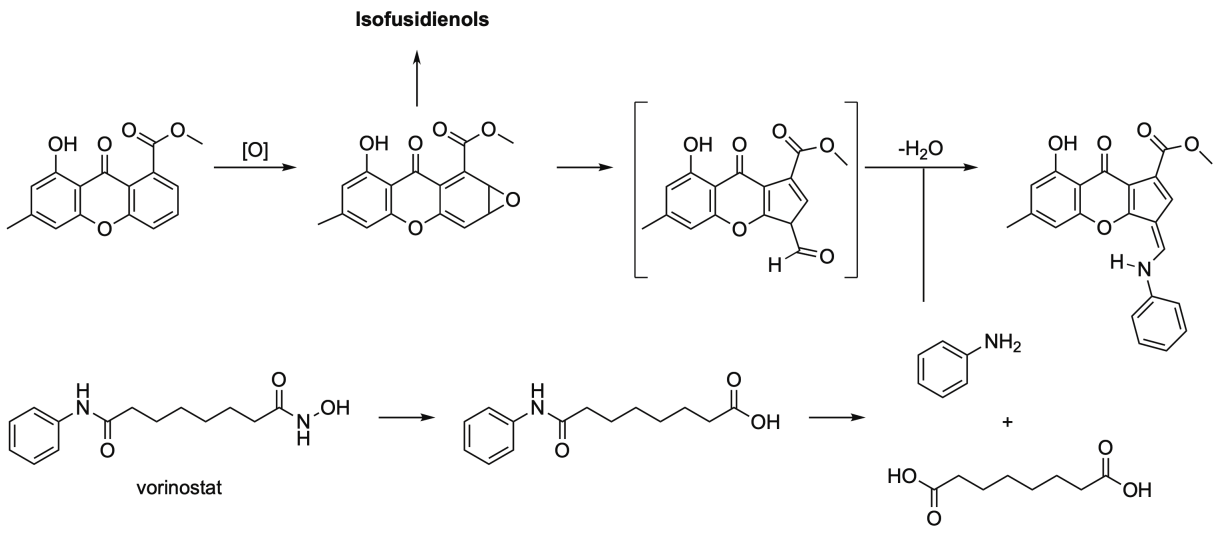


Figure S33. Biosynthetic proposal of the formation of chalanilines. Modified from [12].

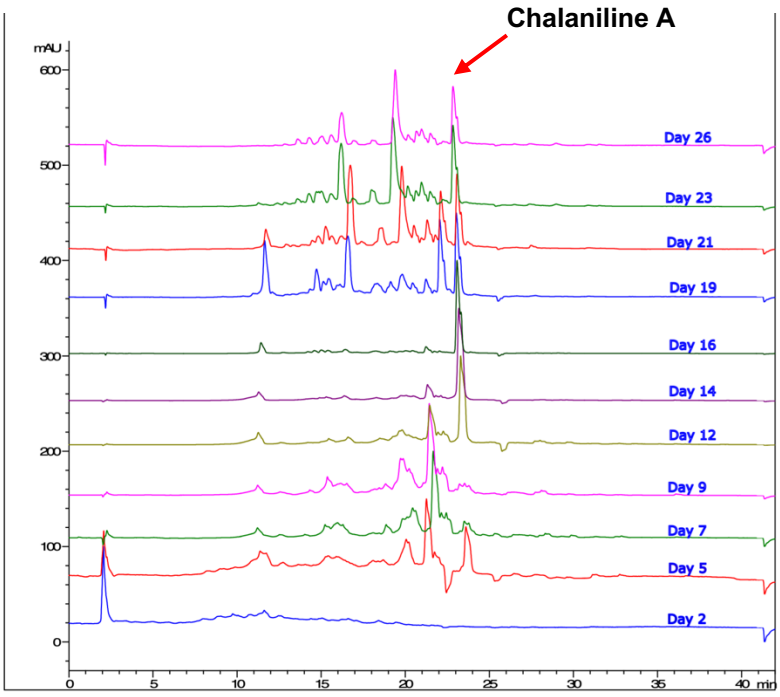


Figure S34. Assessment of chalaniline A (rt 24 min) production from day 2 to 26 of precursor addition with LCMS (UV observed at 360 nm). Highest amount of chalaniline A was observed at day 16.

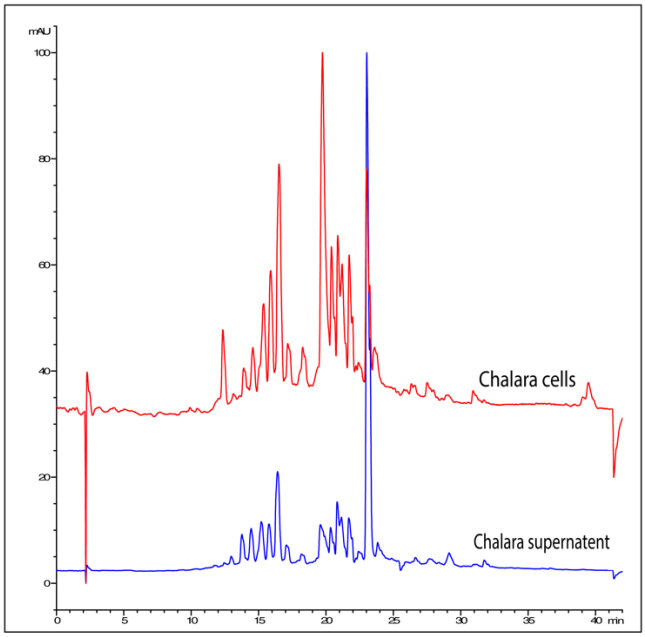


Figure S35. Chalaniline A (rt 24 min) is mainly found in the culture broth (blue) and to a lesser amount in the fungal cells (red).

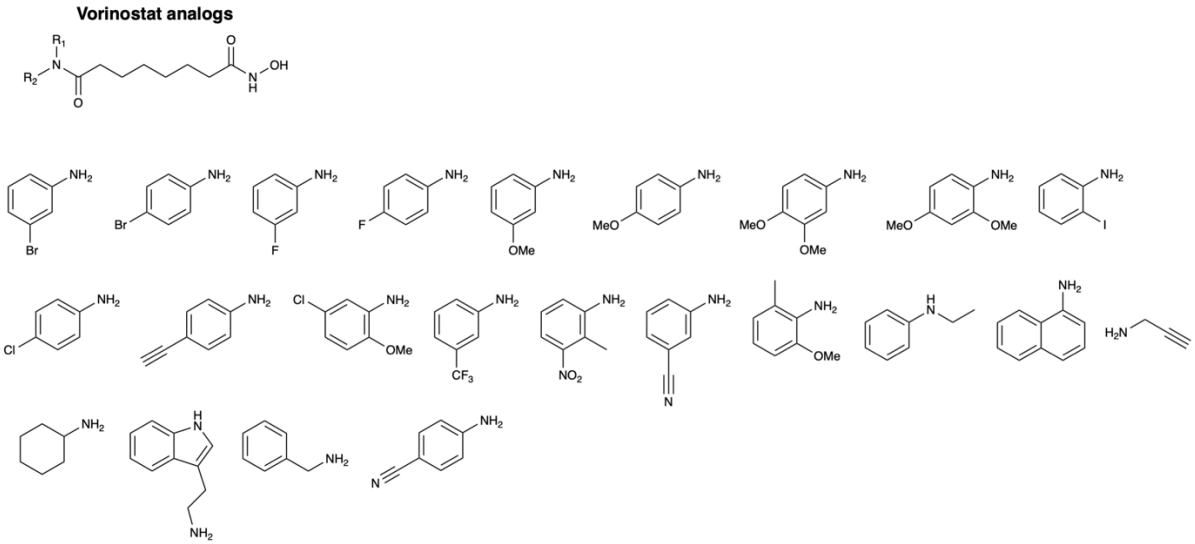


Figure S36. 23 Vorinostat derivatives prepared in this study.

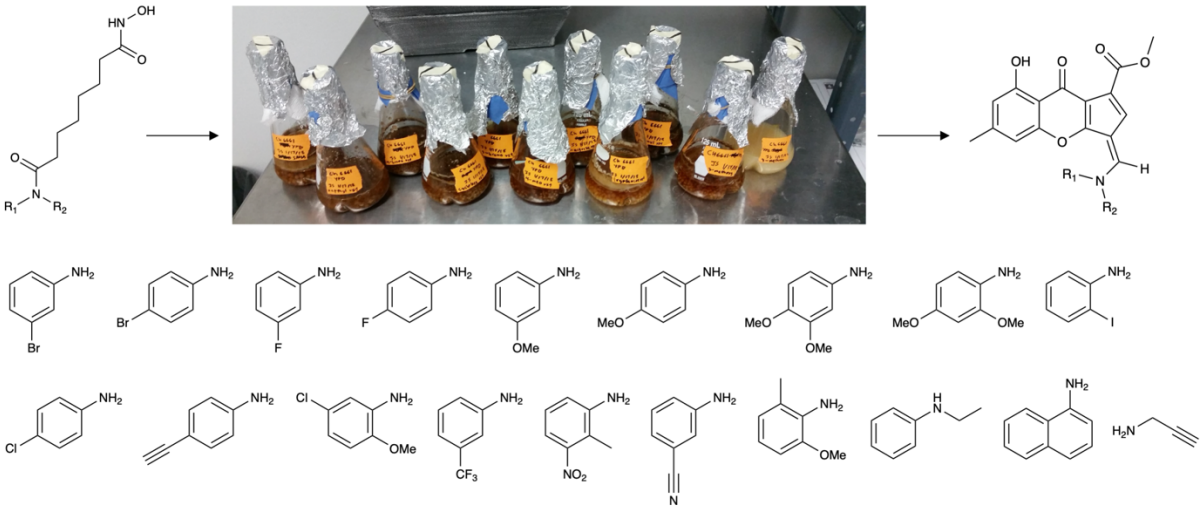


Figure S37. 19 Vorinostat analogs which were successfully incorporated into the chalaniline A structure.