Supporting Information

An Unprecedented Tandem Synthesis of Fluorescent Coumarin-Fused Pyrimidines *via* Copper-Catalyzed Cross-Dehydrogenative C*(sp^3)*–N Bond Coupling

Santosh Kumari,[a] S. M. Abdul Shakoor,[a] Sadhika Khullar,[b] Sanjay K. Mandal,[c] and Rajeev Sakhuja*[a]

[a]*Department of Chemistry, Birla Institute of Technology & Science, Pilani, Rajasthan, 333031, India*

[b]*Department of Chemistry, D.A.V. University, Jalandhar-Pathankot National Highway, Jalandhar-144012, Punjab, India*

[c]*Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector 81, S.A.S. Nagar, Manuali P.O., Punjab 140306, India*

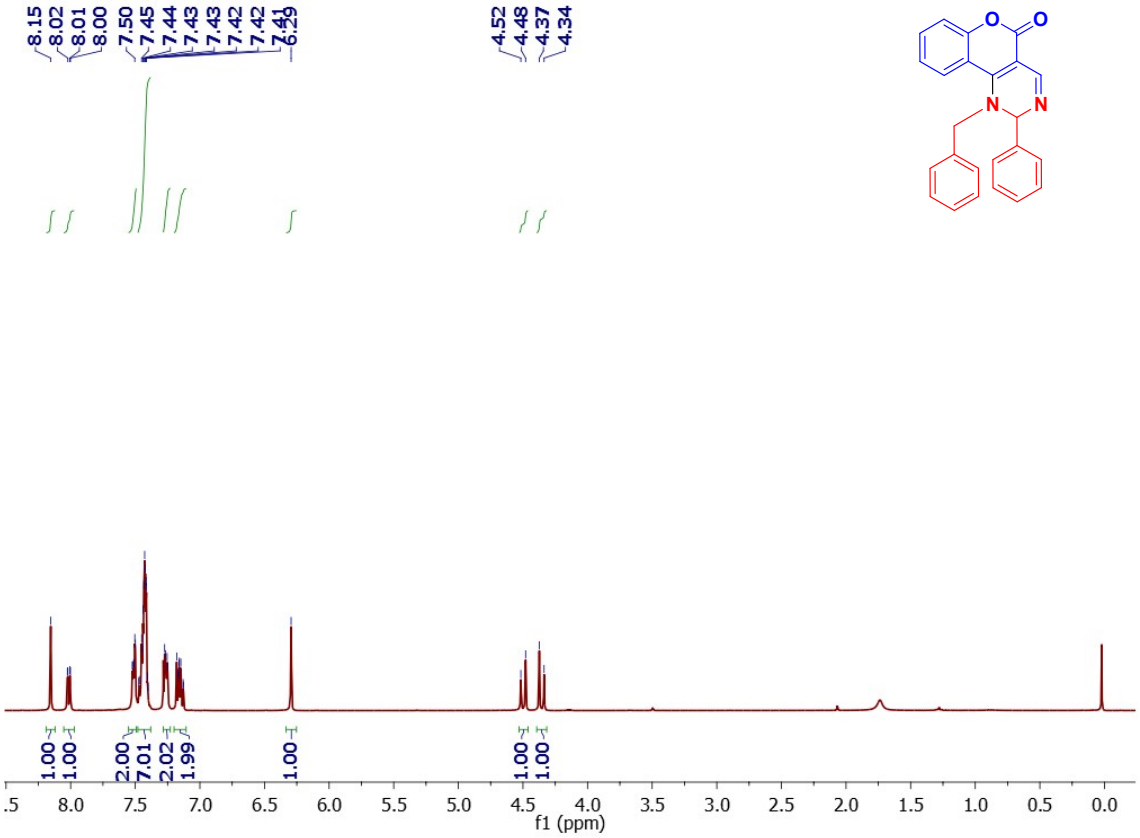
Fax: 91-1596-244183, Tel: 91-5196-515711

E-mail: sakhuja.rajeev@gmail.com

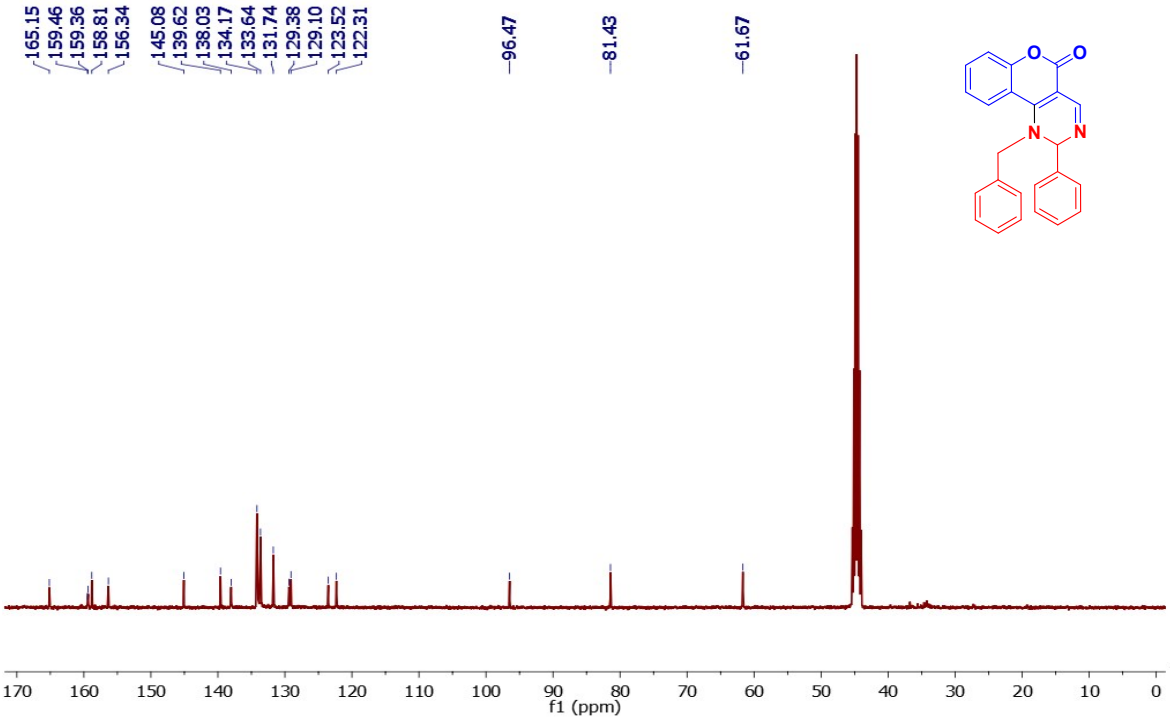
Contents **Page No.**

1. ^{1}H & ^{13}C NMR spectra of 3a-r, 3a′ & 3a″

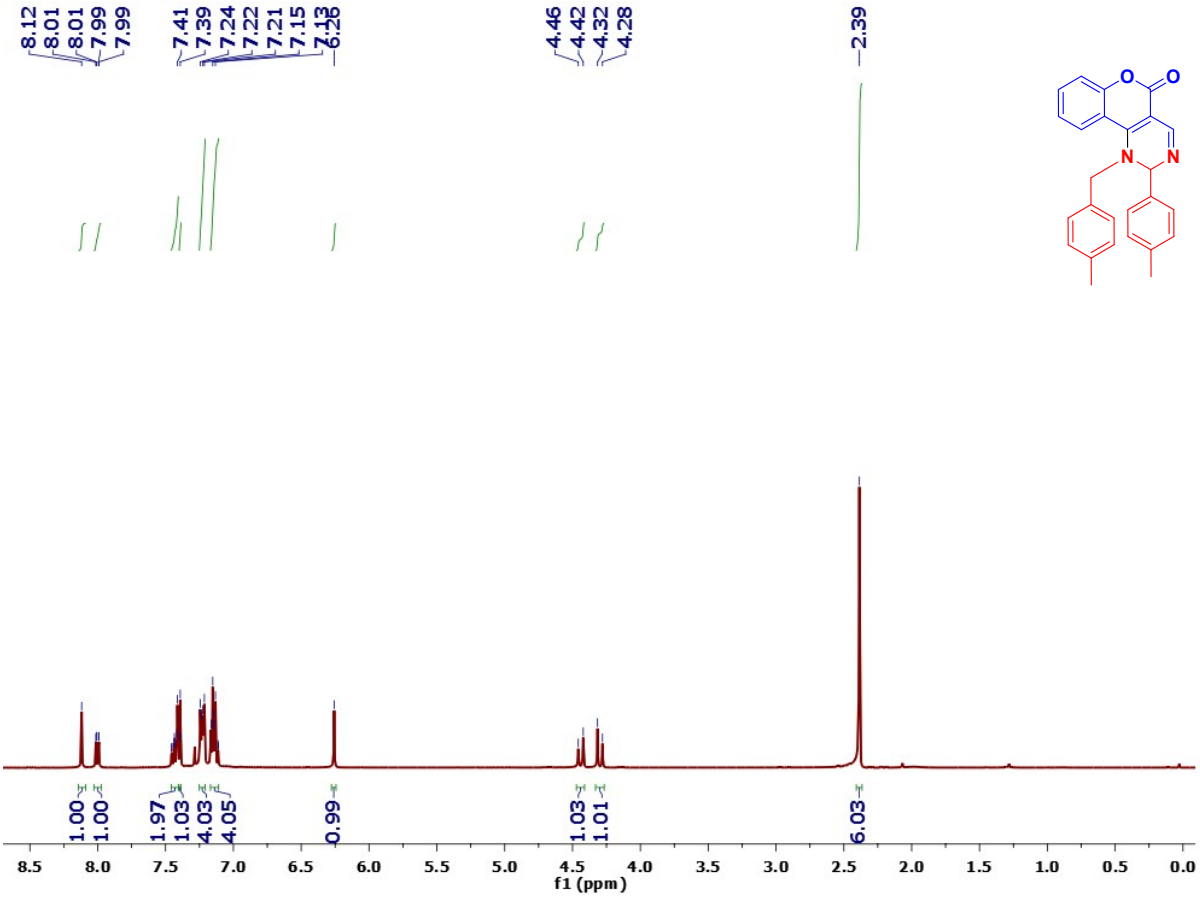
^{1} H NMR of **3a**



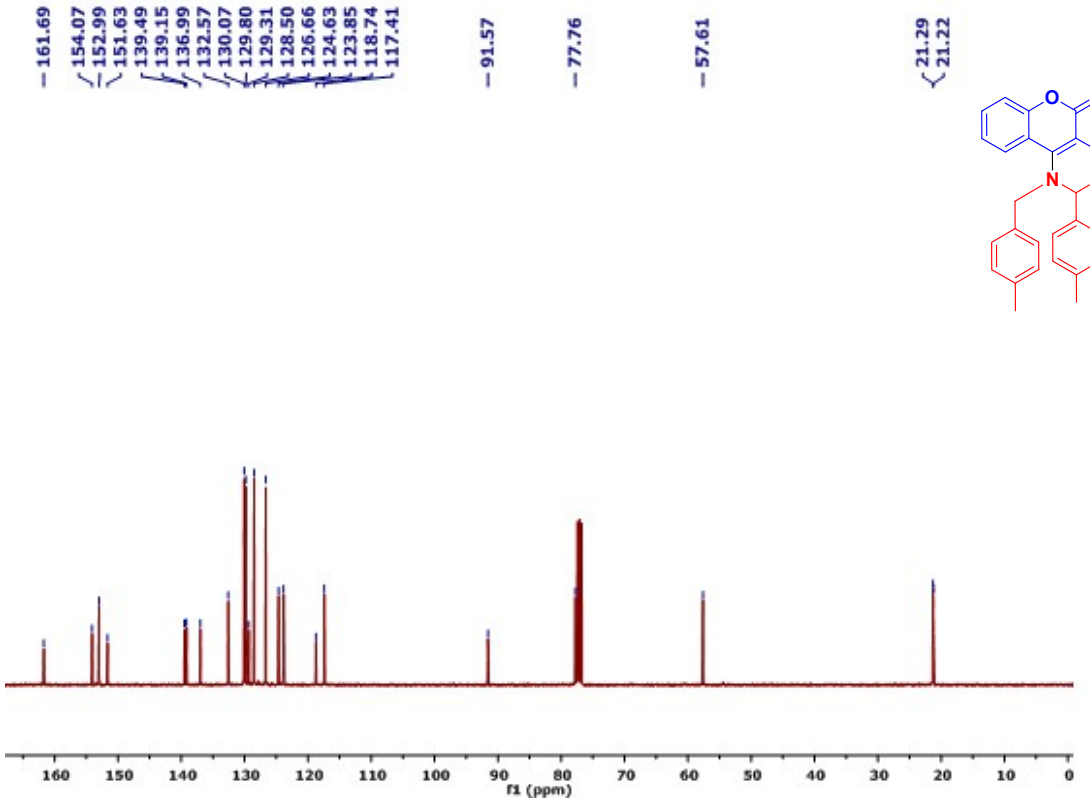
^{13} C NMR of **3a**



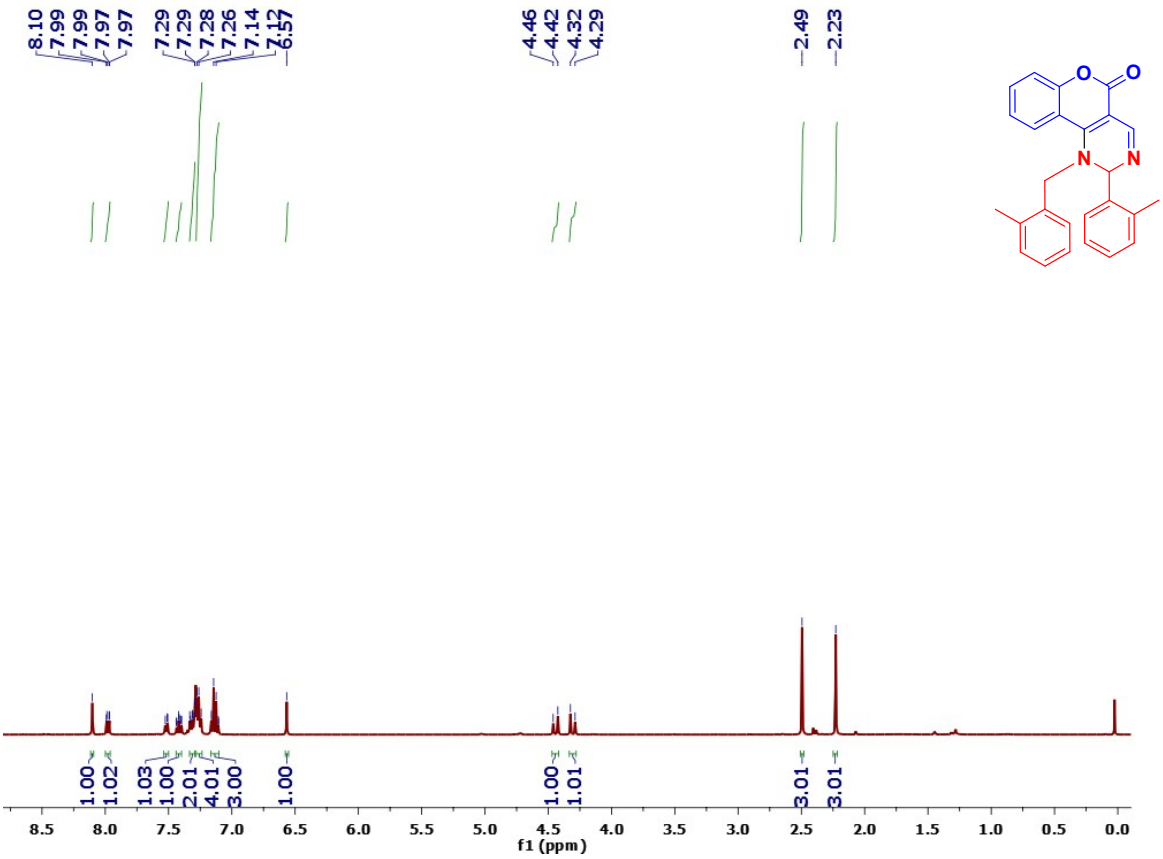
^{1}H NMR of **3b**



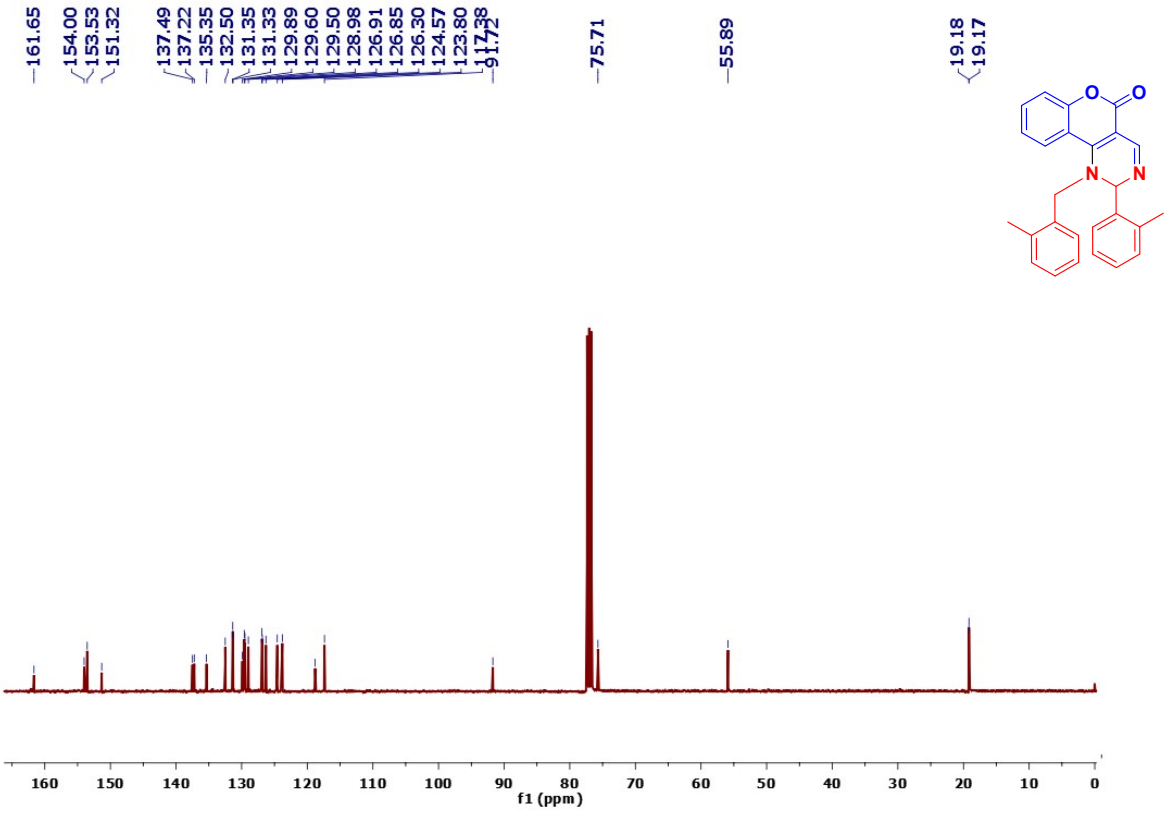
^{13}C NMR of **3b**



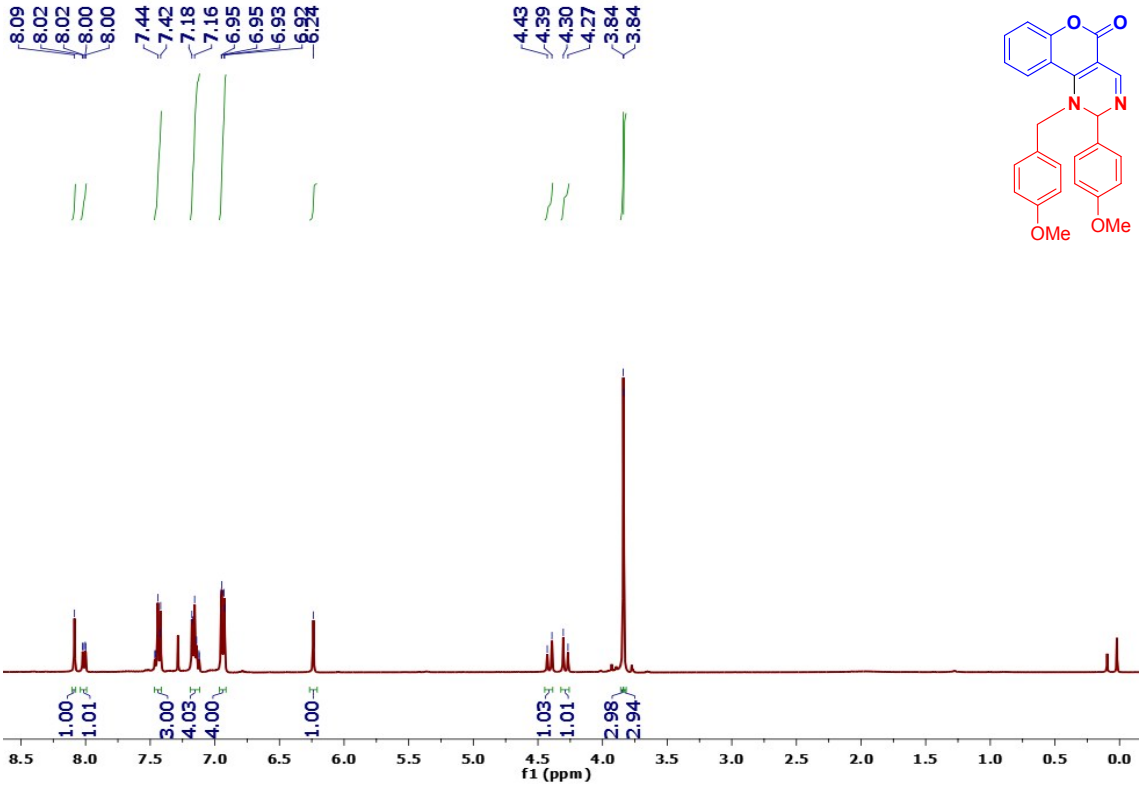
^{1}H NMR of **3c**



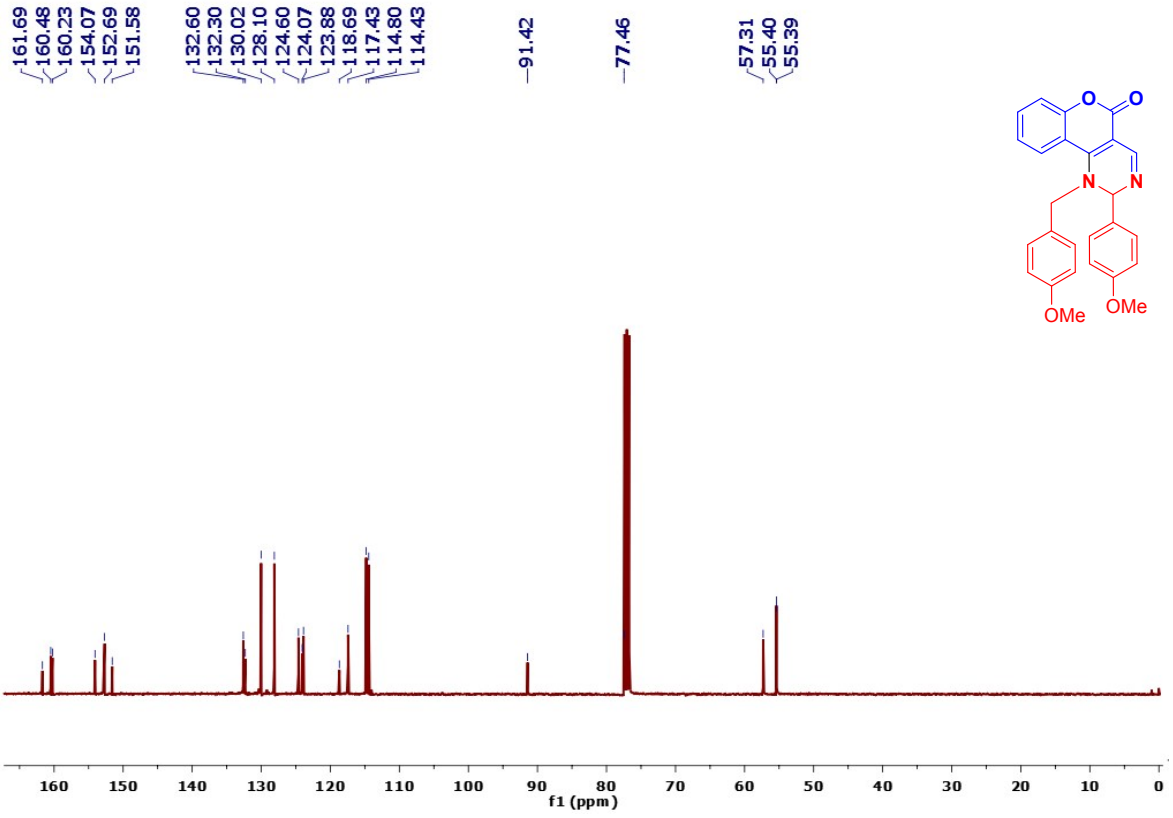
^{13}C NMR of **3c**



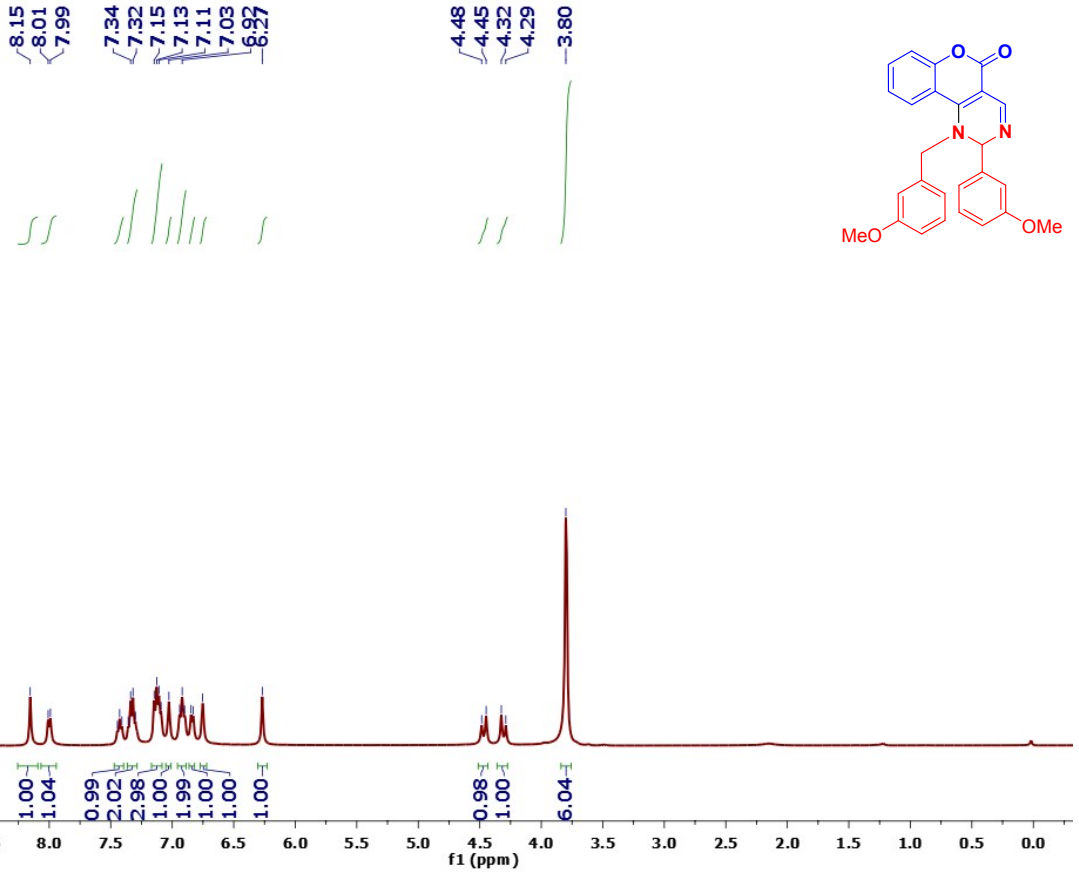
^{1}H NMR of **3d**



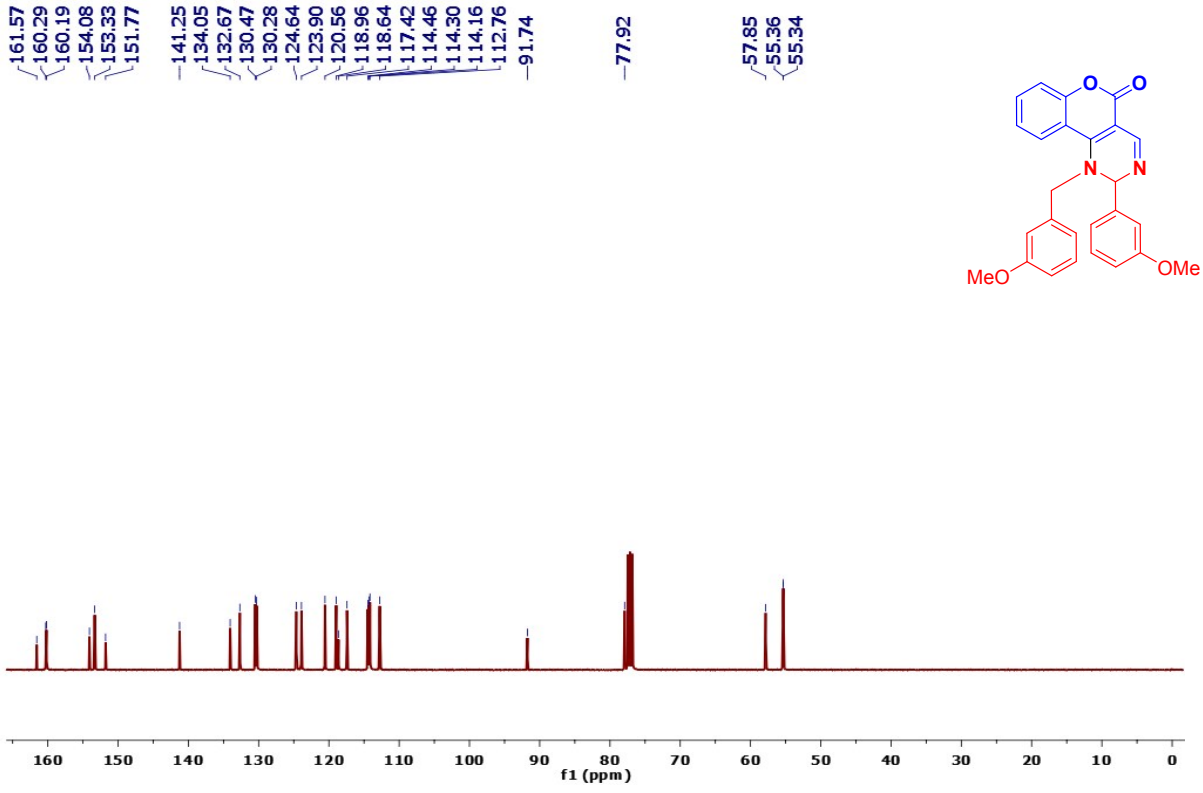
^{13}C NMR of **3d**



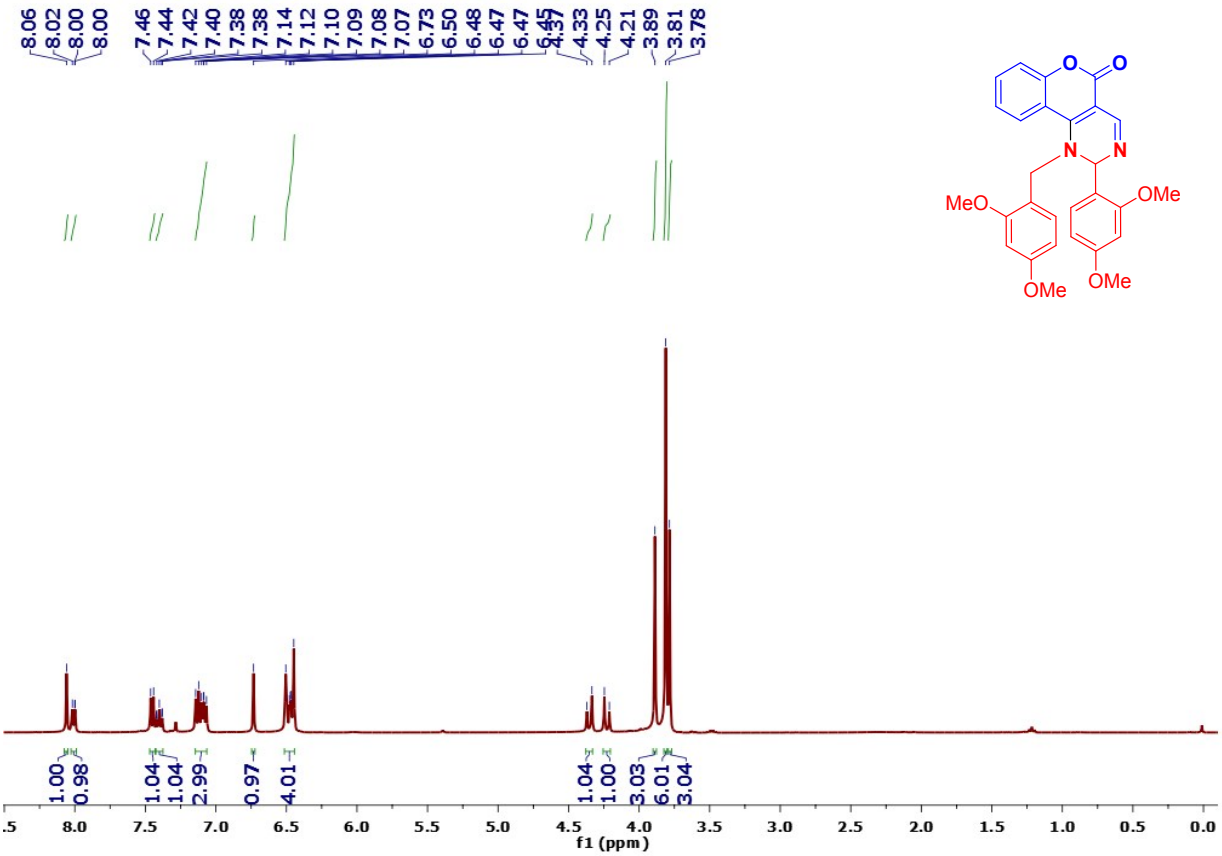
^{1}H NMR of **3e**



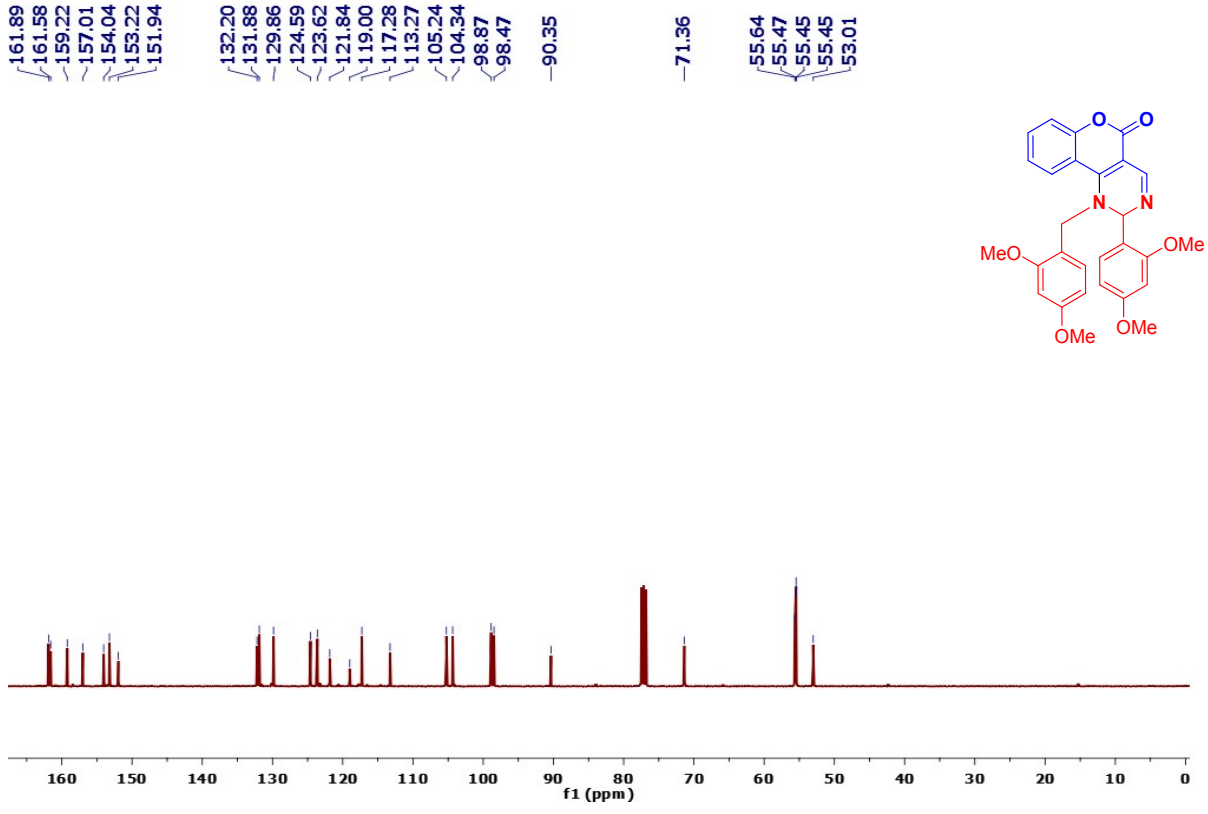
^{13}C NMR of 3**e**



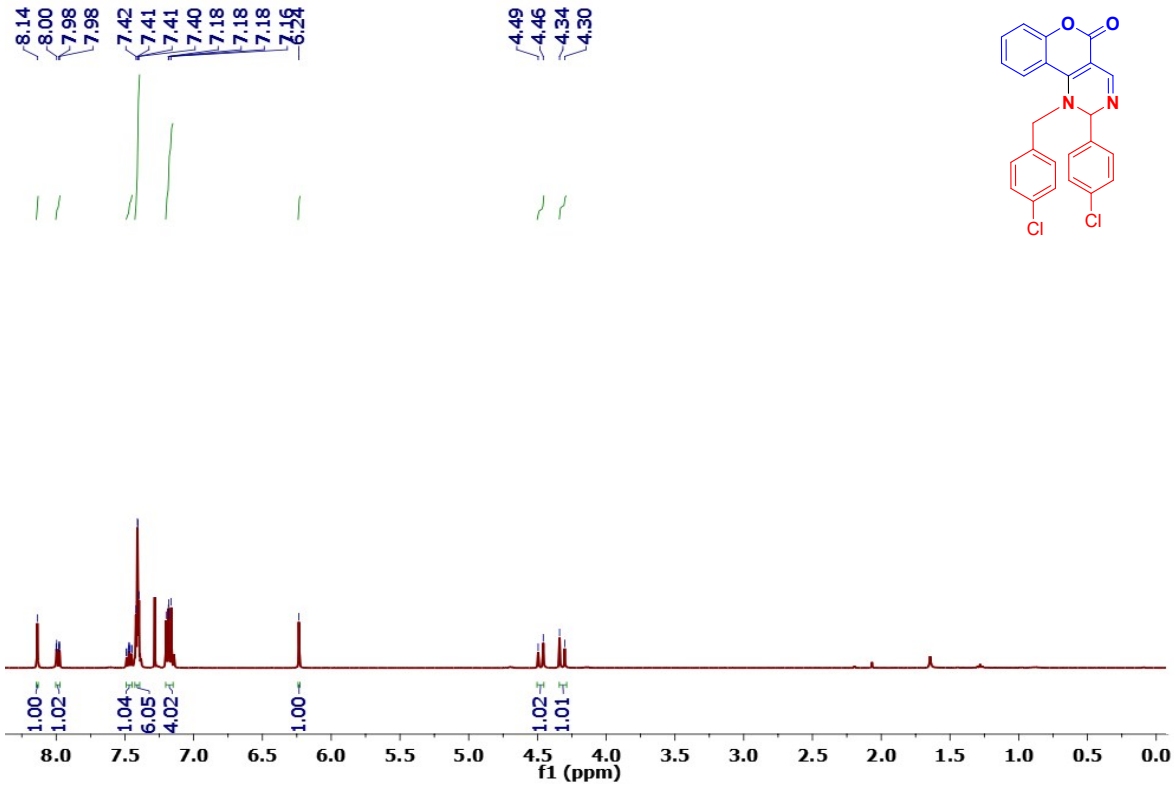
^{1}H NMR of **3f**



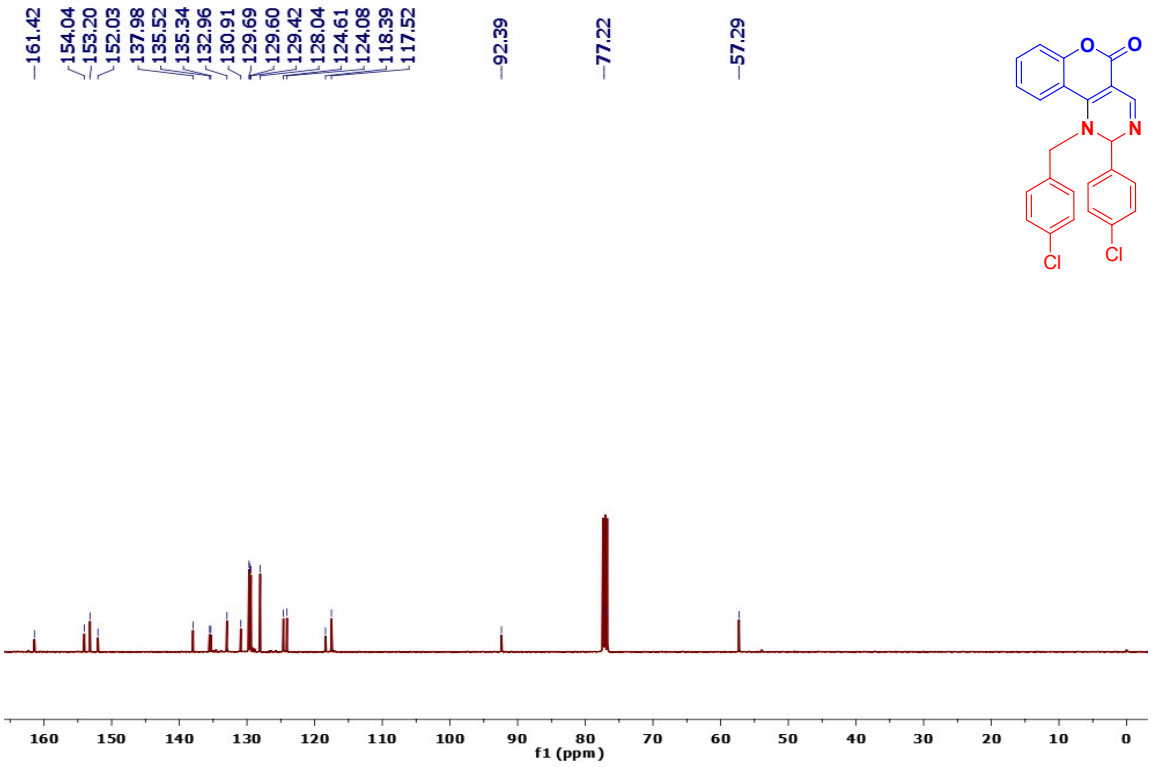
^{13}C NMR of 3**f**



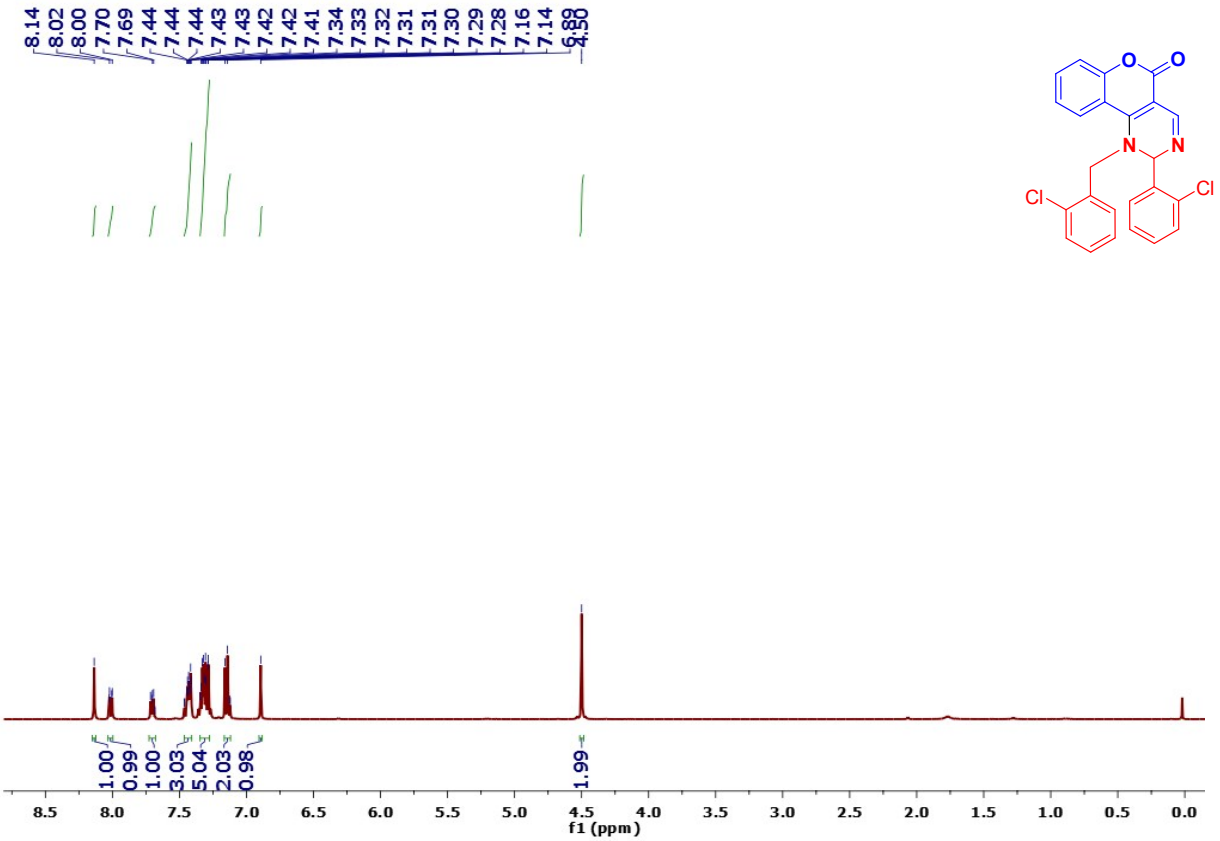
^{1} H NMR of **3g**



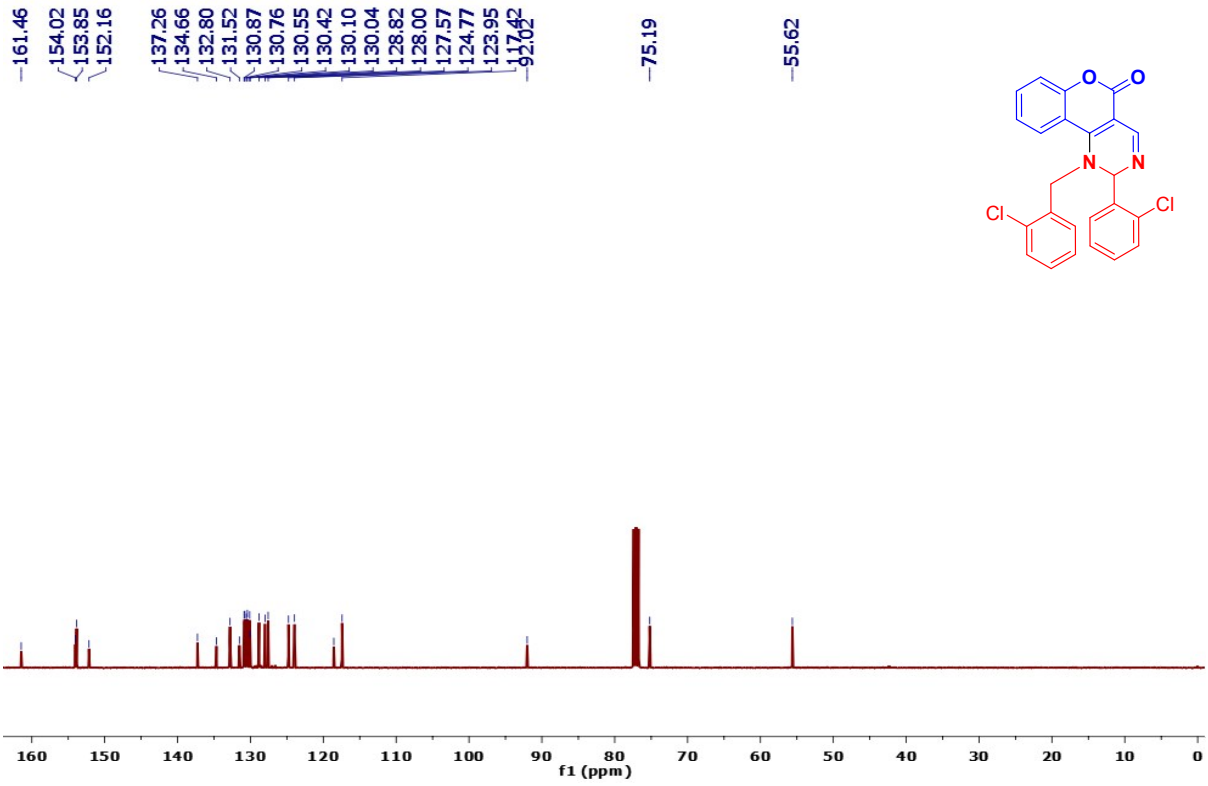
^{13} C NMR of 3g



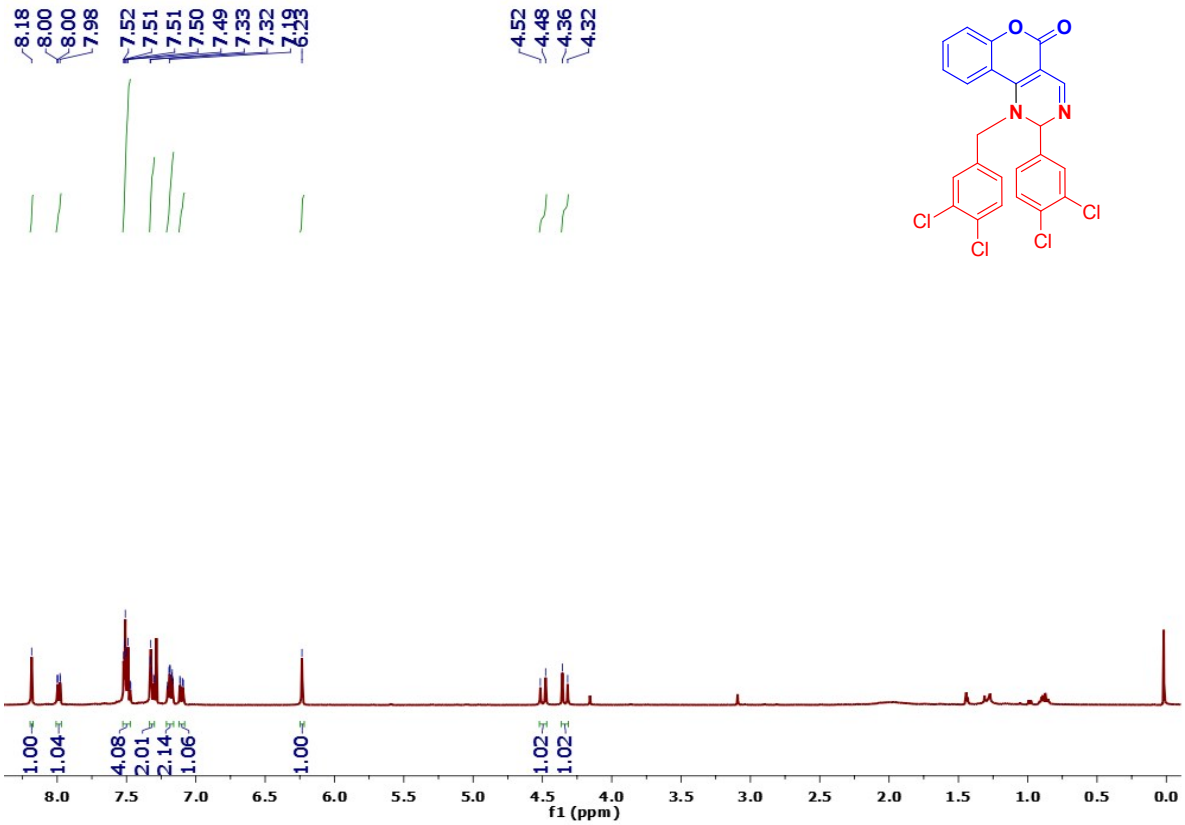
^{1}H NMR of **3h**



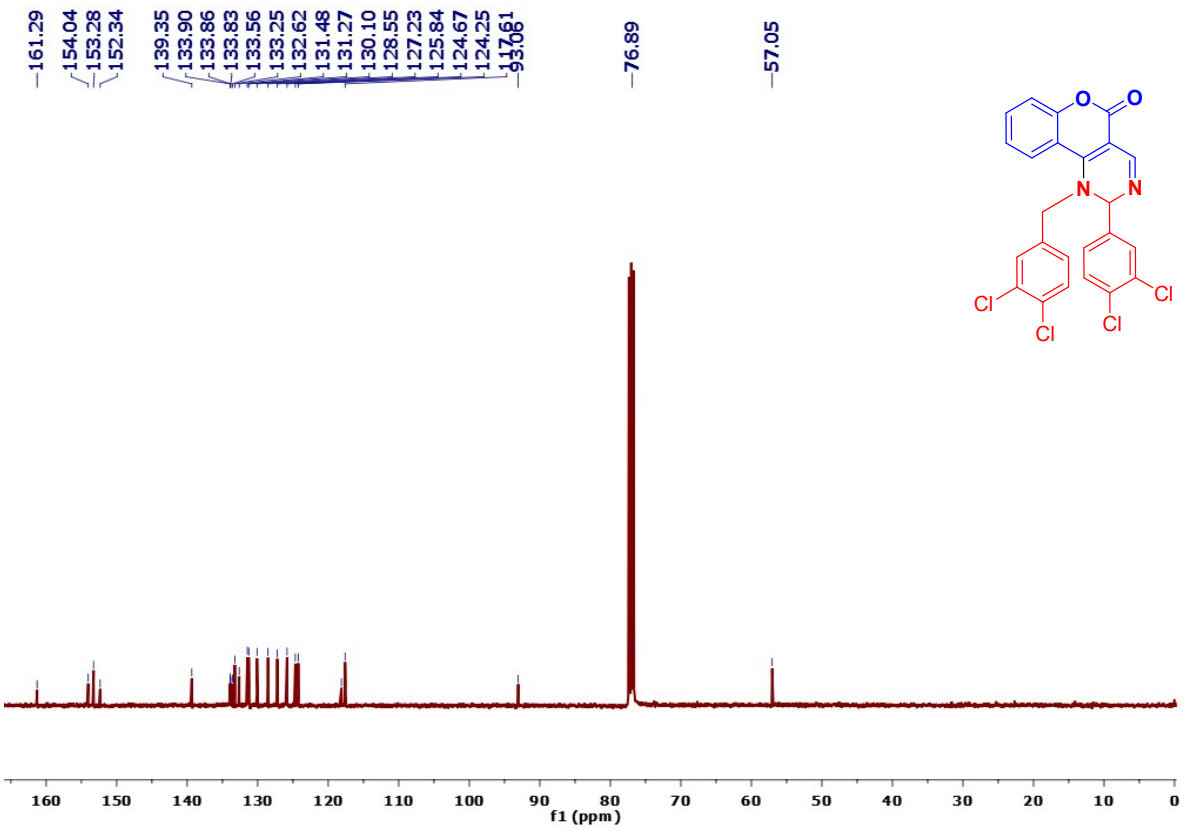
^{13} C NMR of **3h**



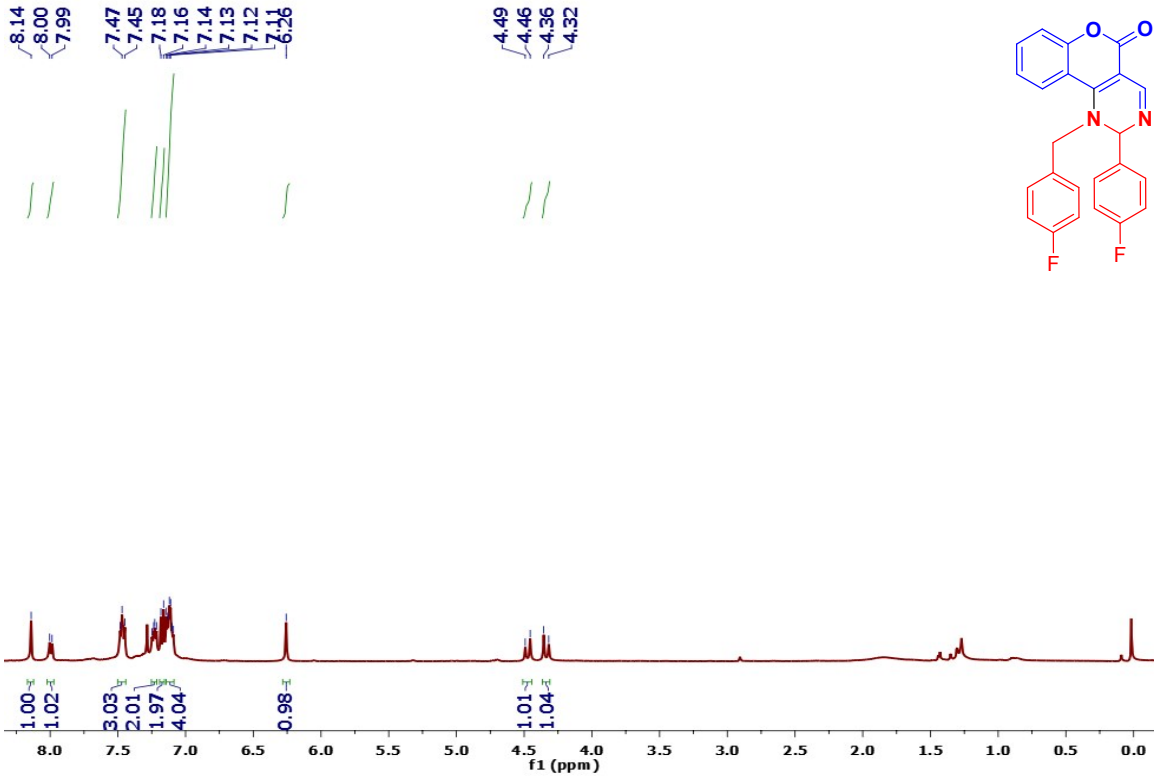
^{1}H NMR of **3i**



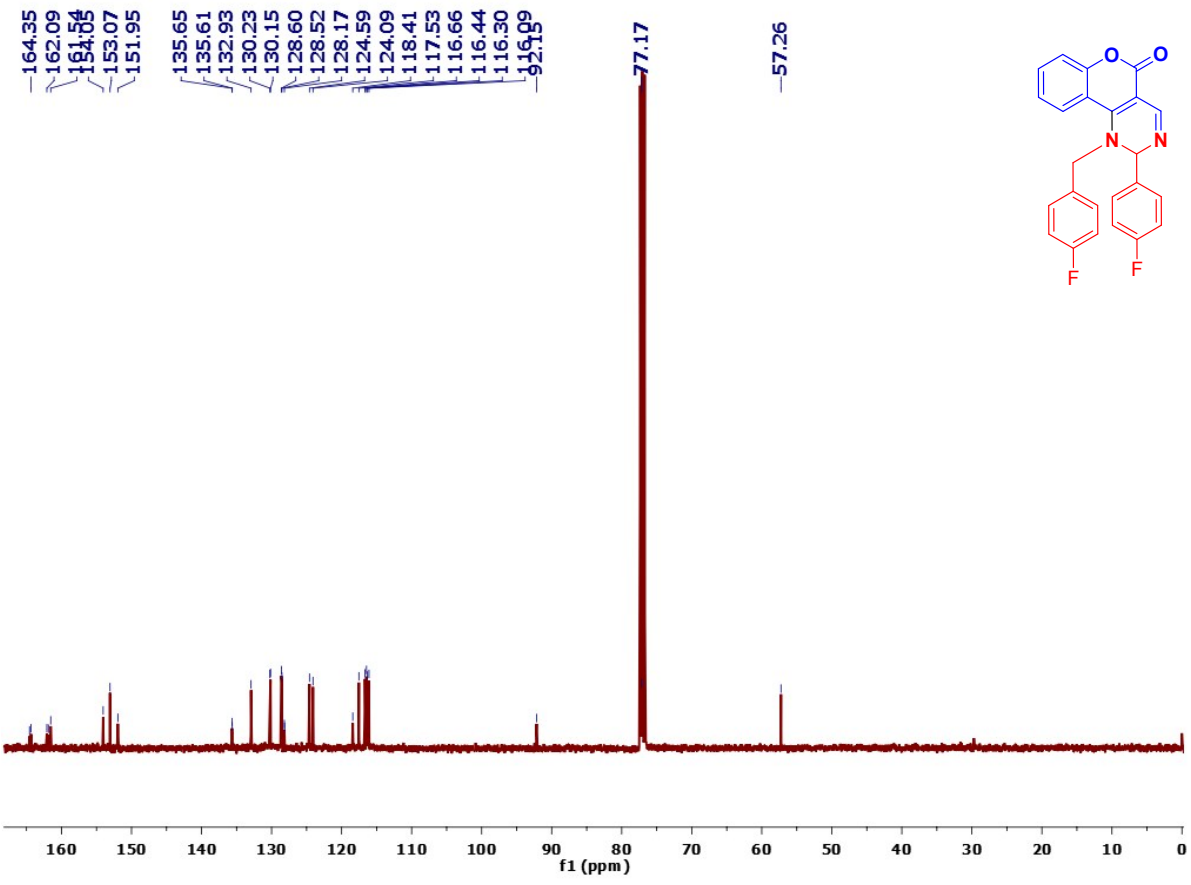
^{13}C NMR of **3i**



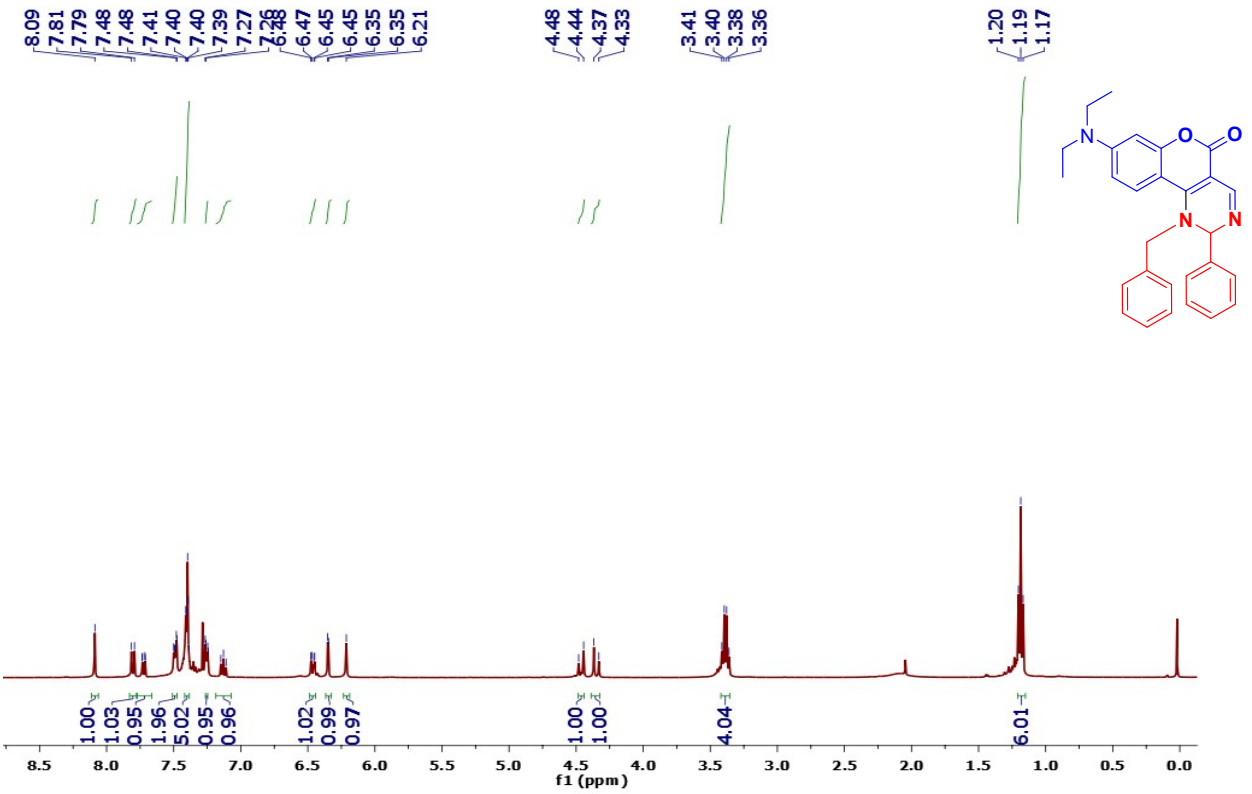
^{1}H NMR of **3j**



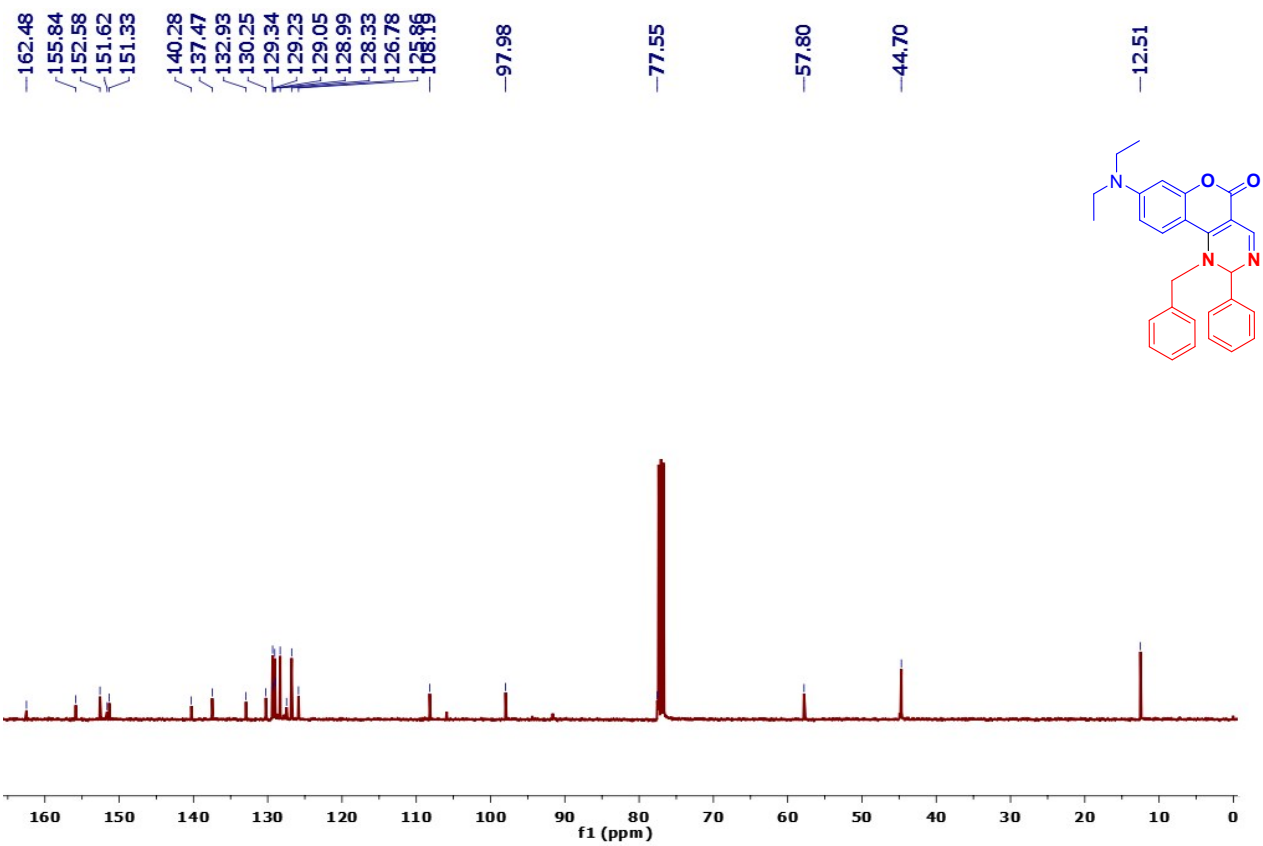
^{13}C NMR of **3j**



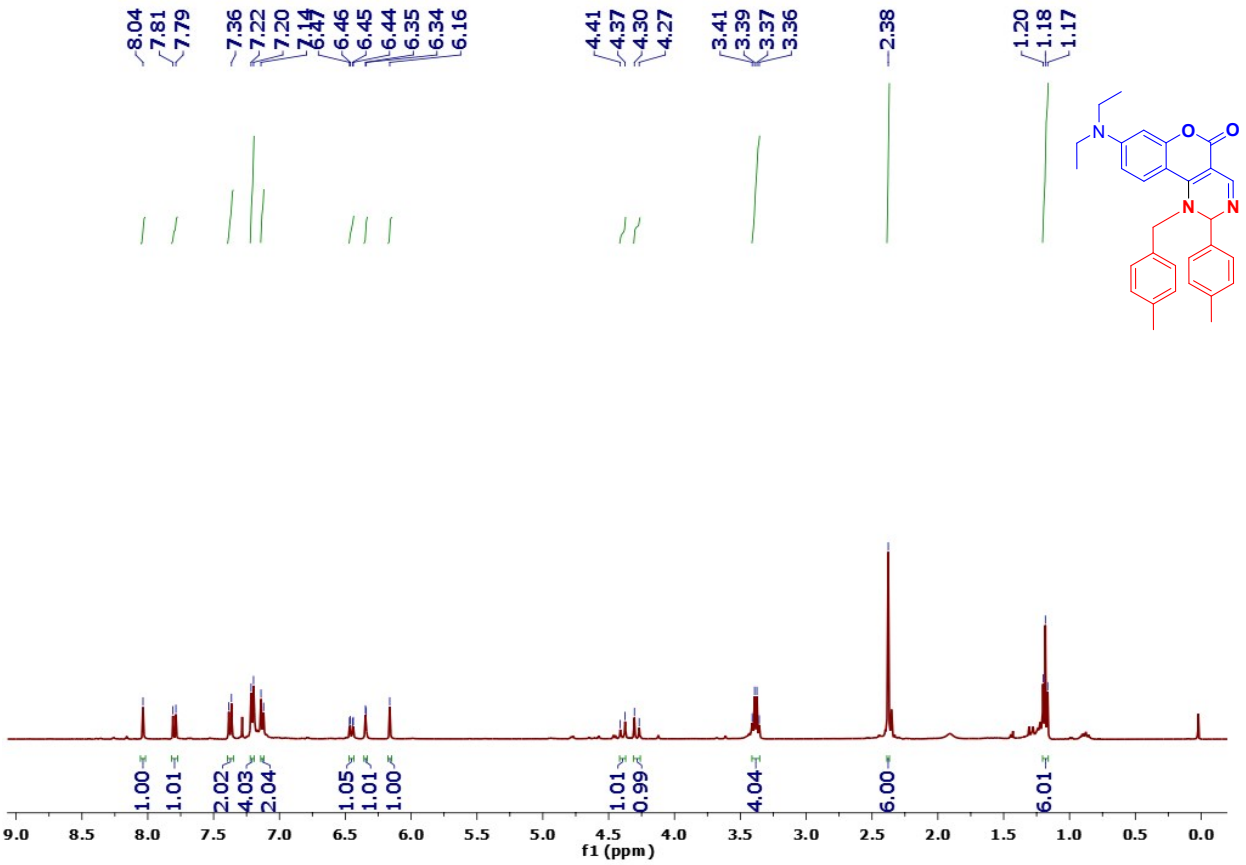
^{1}H NMR of **3k**



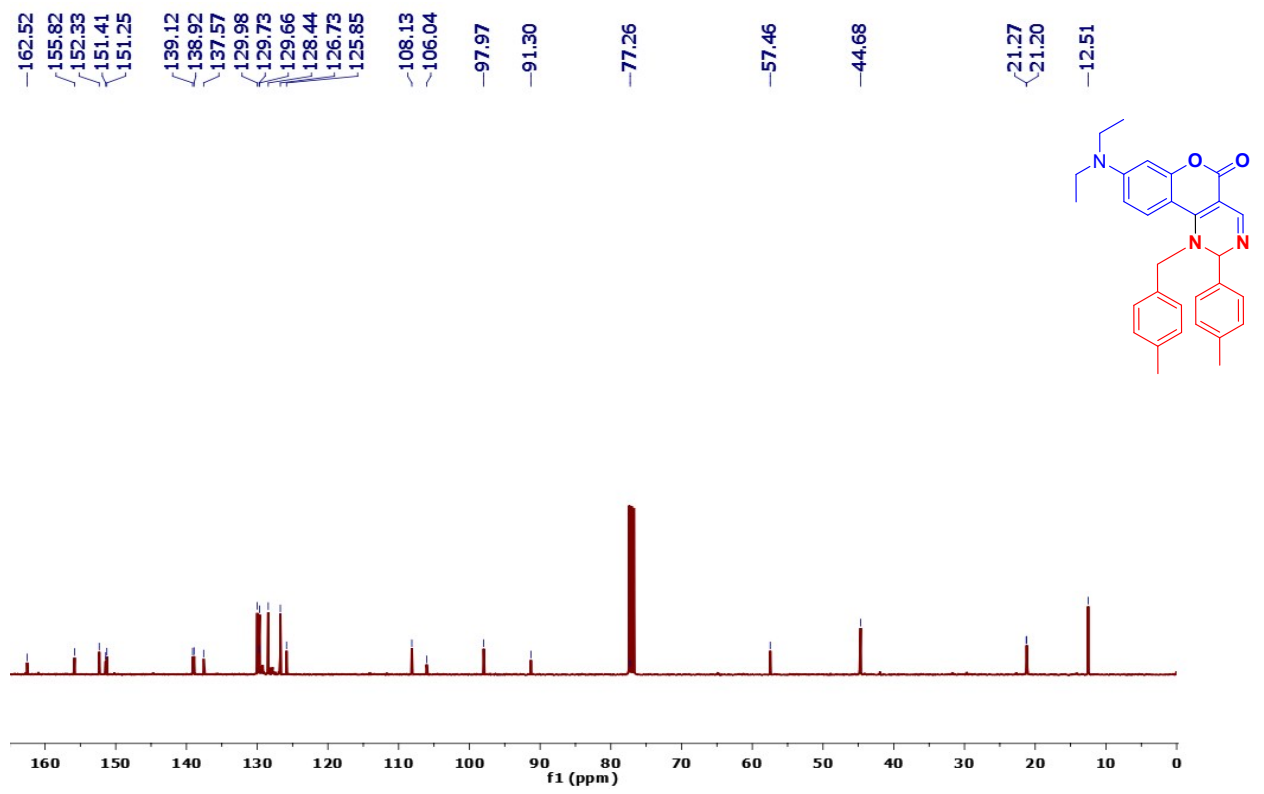
^{13}C NMR of **3k**



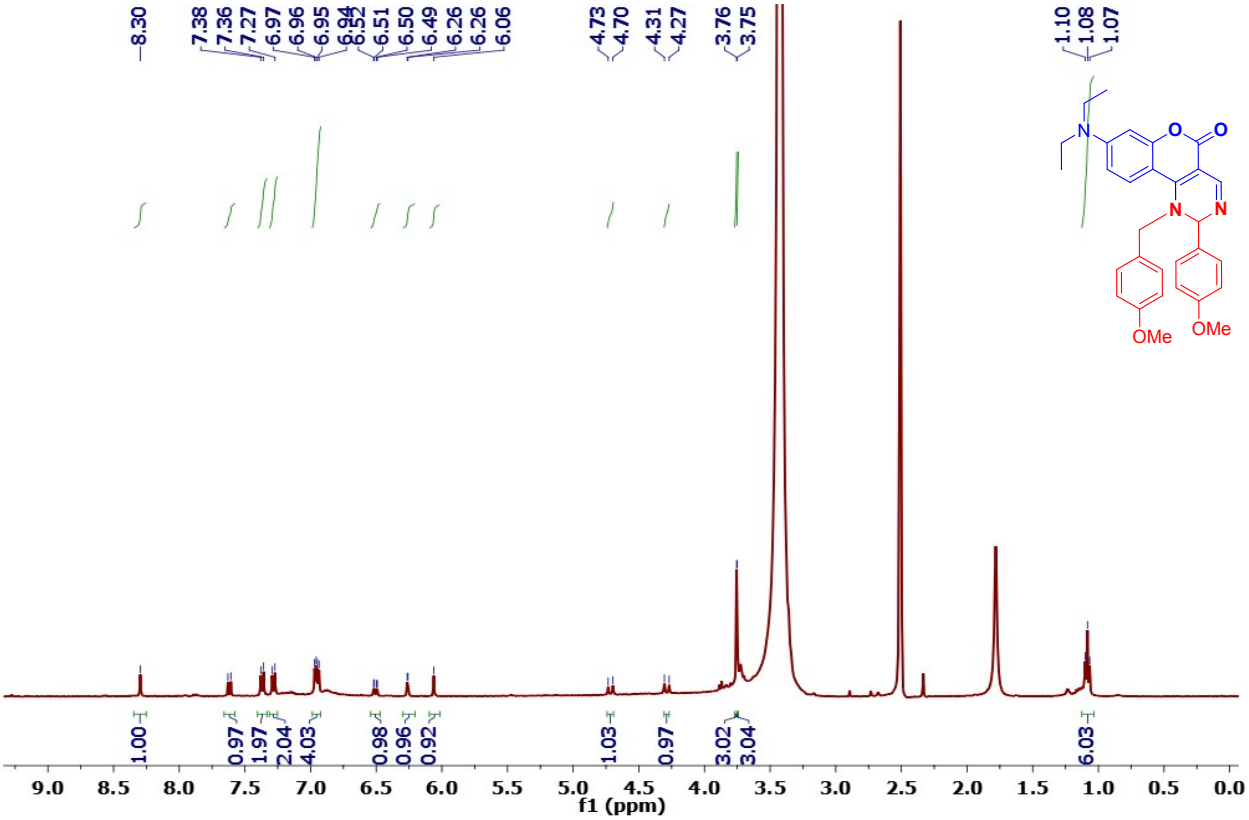
^{1}H NMR of **3l**



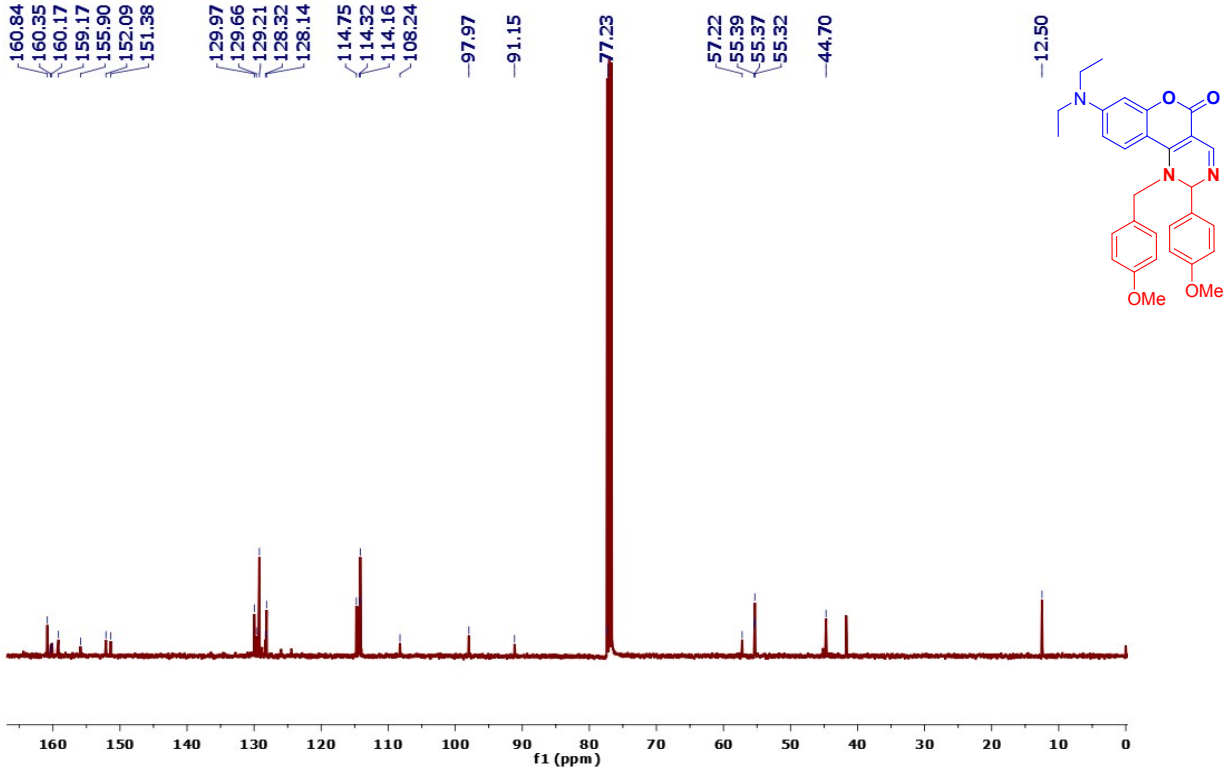
^{13}C NMR of **3l**



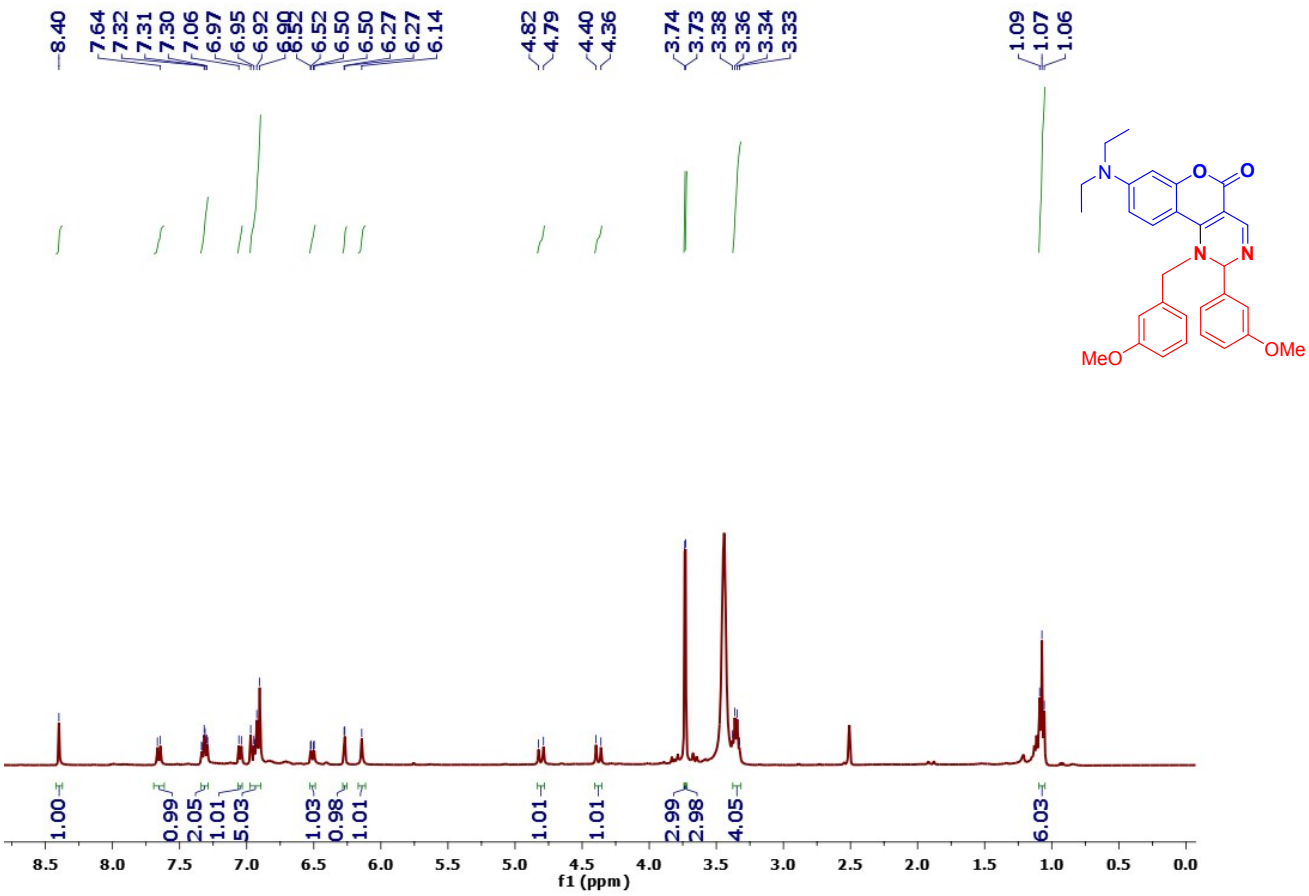
^{13}H NMR of **3m**



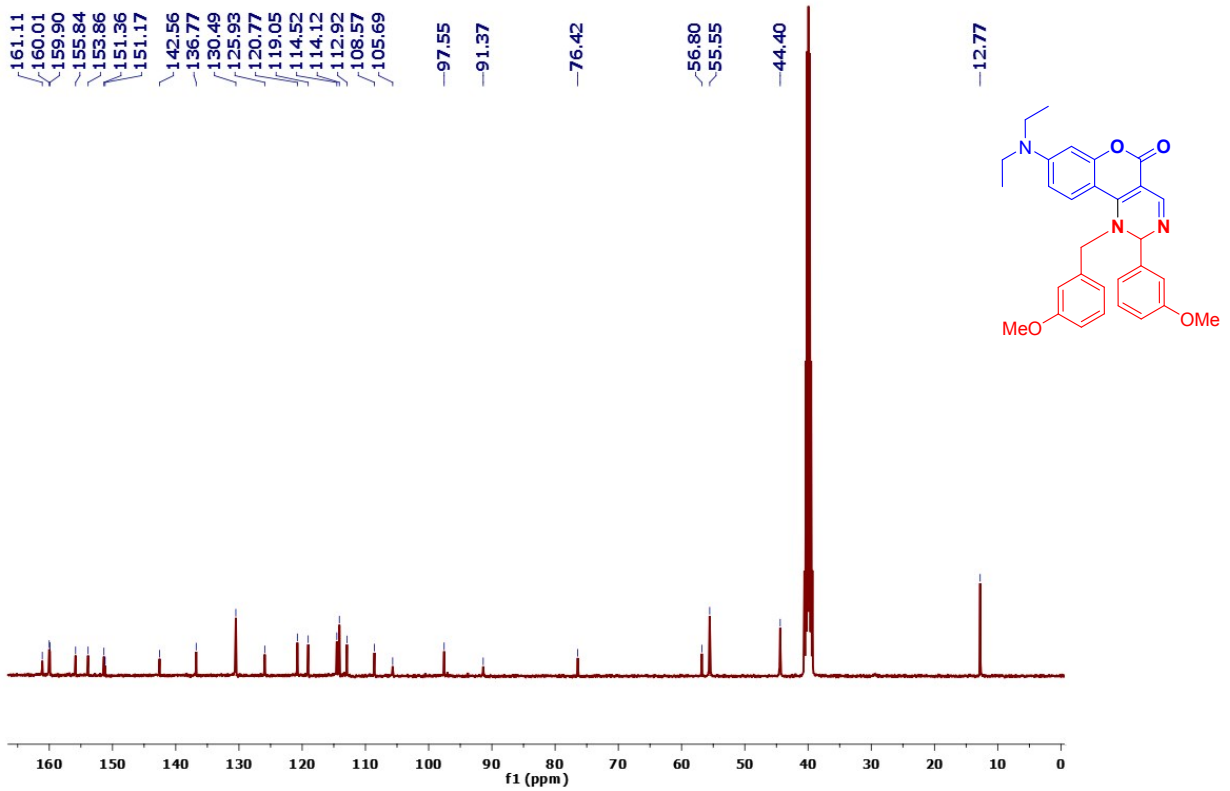
^{13}C NMR of **3m**



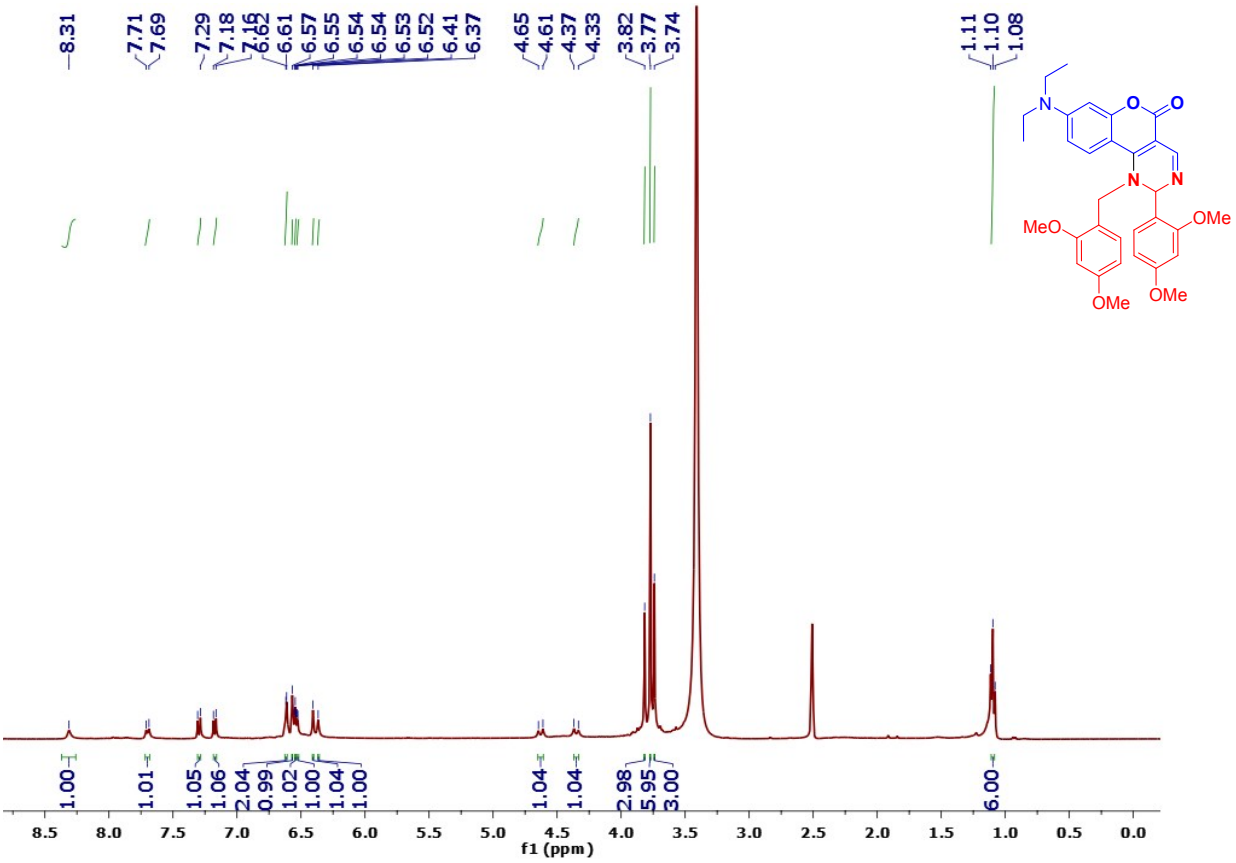
^{1}H NMR of **3n**



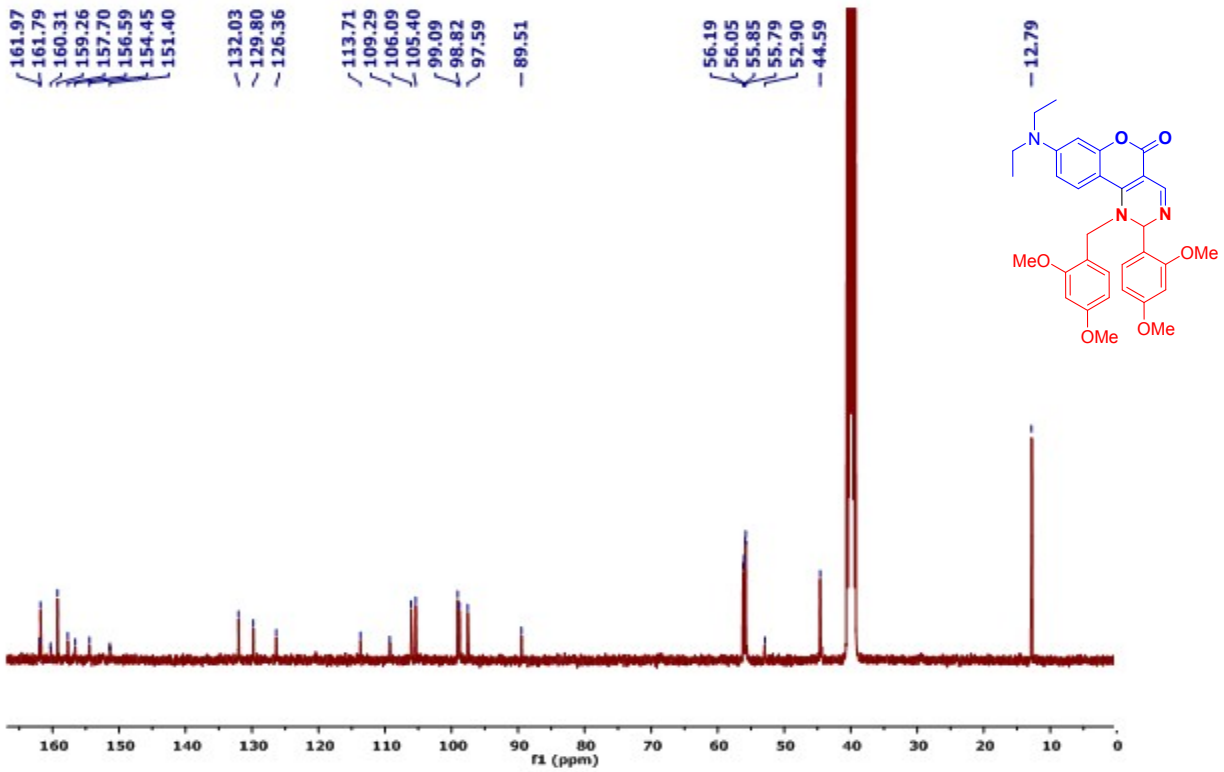
^{13}C NMR of **3n**



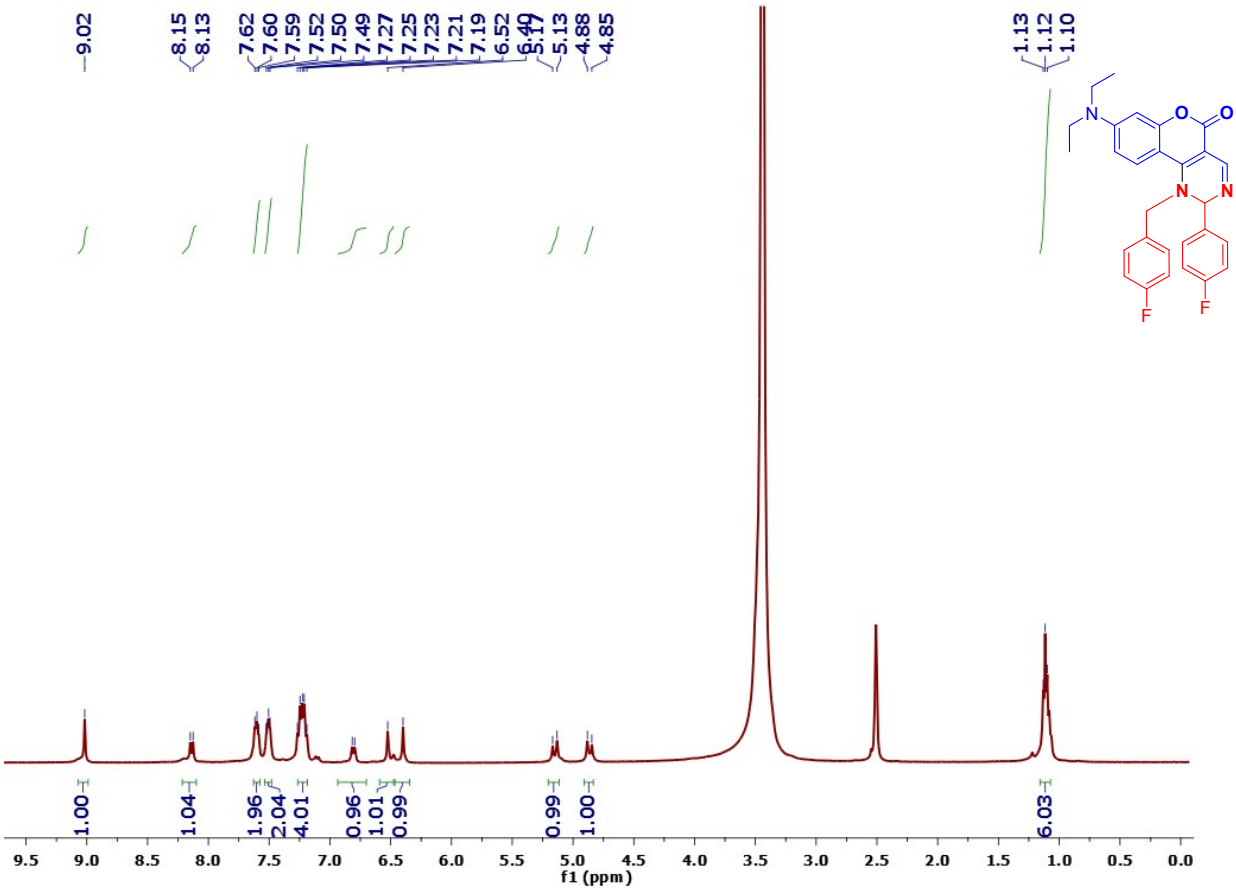
^{13}H NMR of **3o**



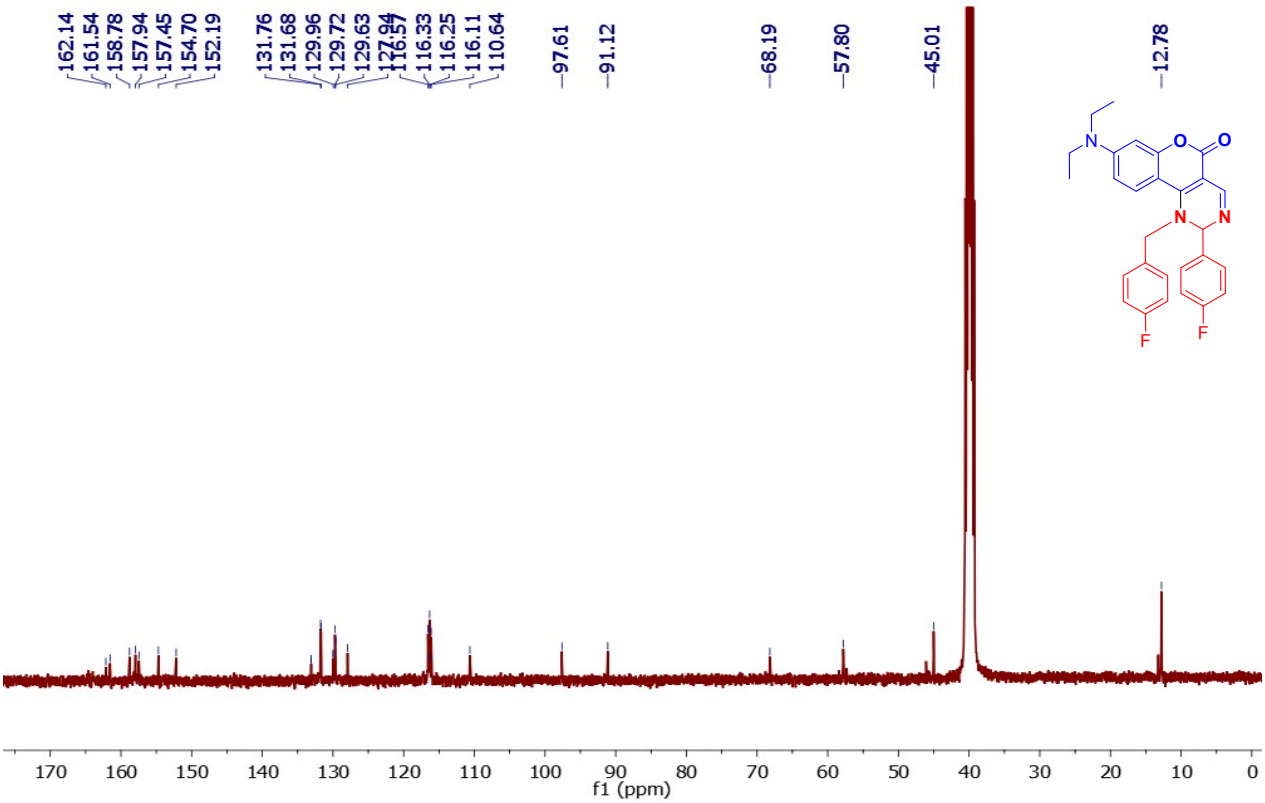
^{13}C NMR of **3o**



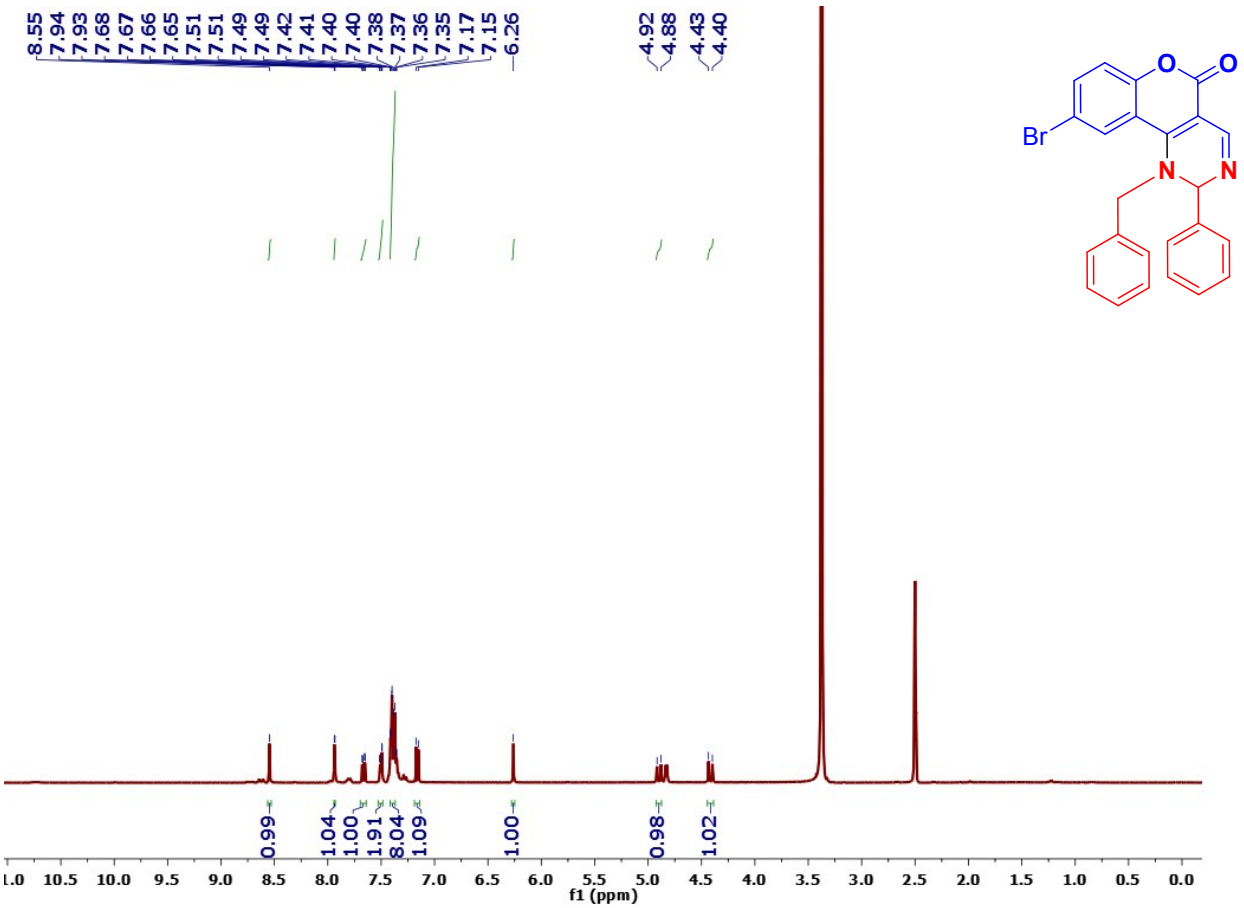
^{1}H NMR of **3p**



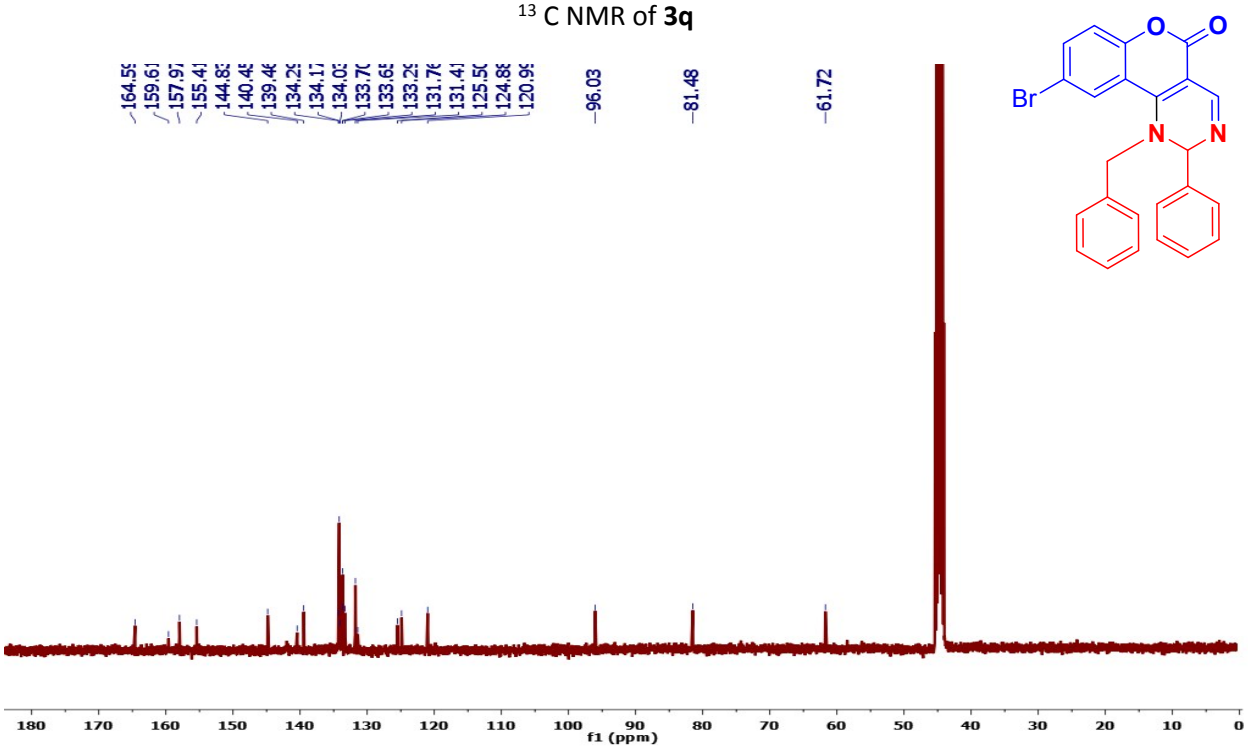
^{13}C NMR of **3p**



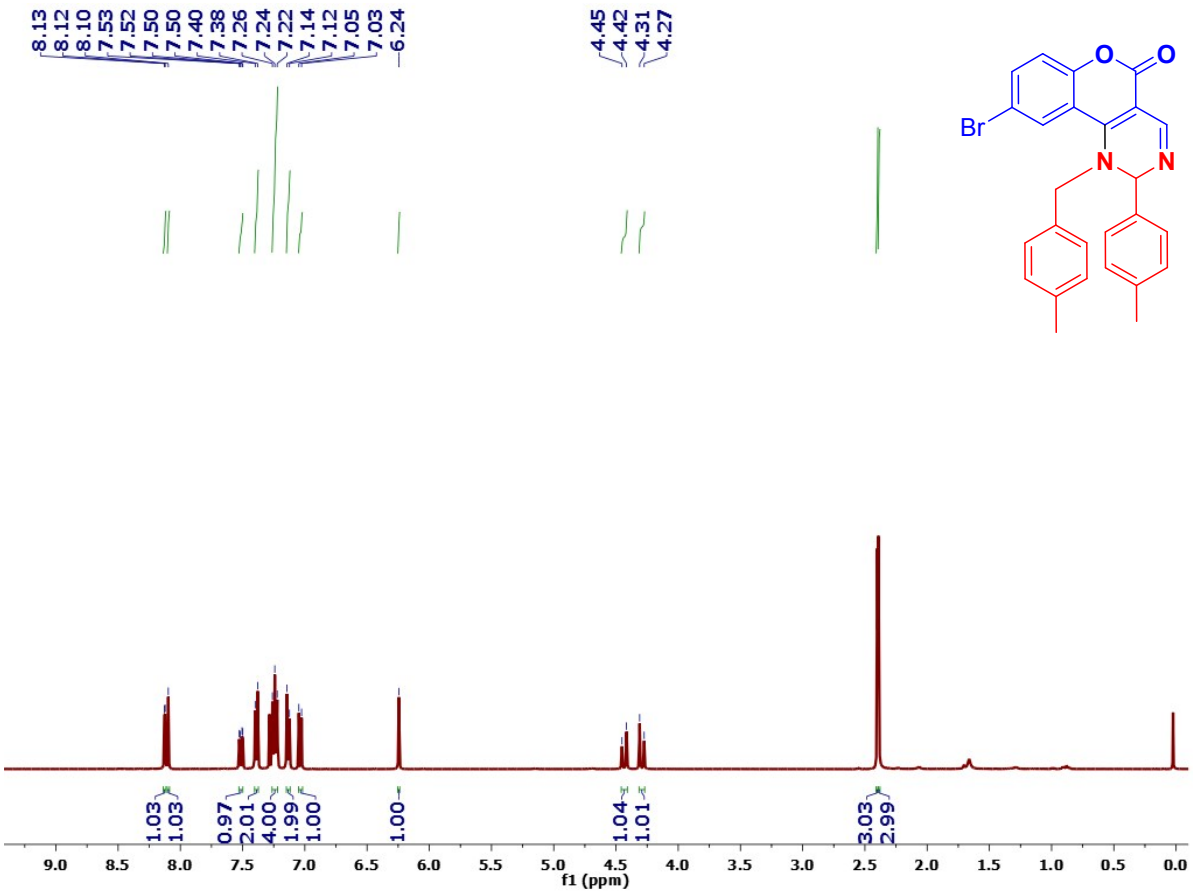
^{1}H NMR of **3q**



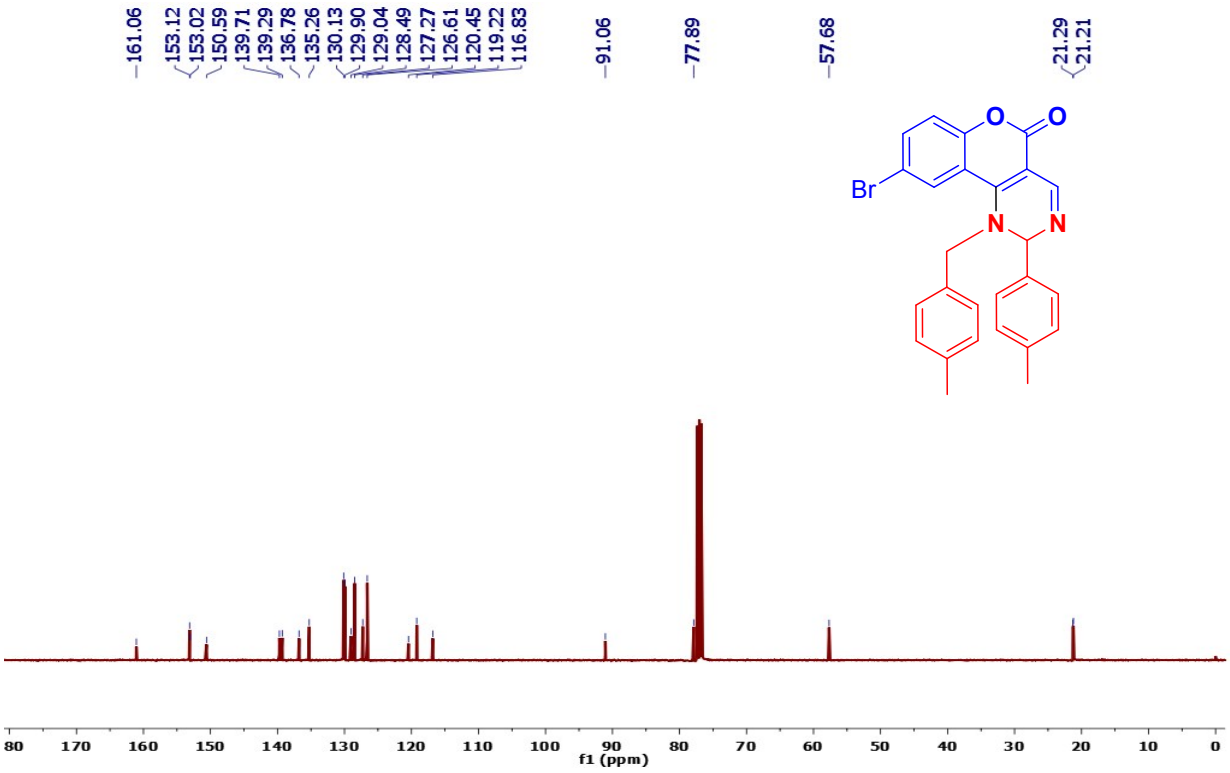
^{13}C NMR of **3q**



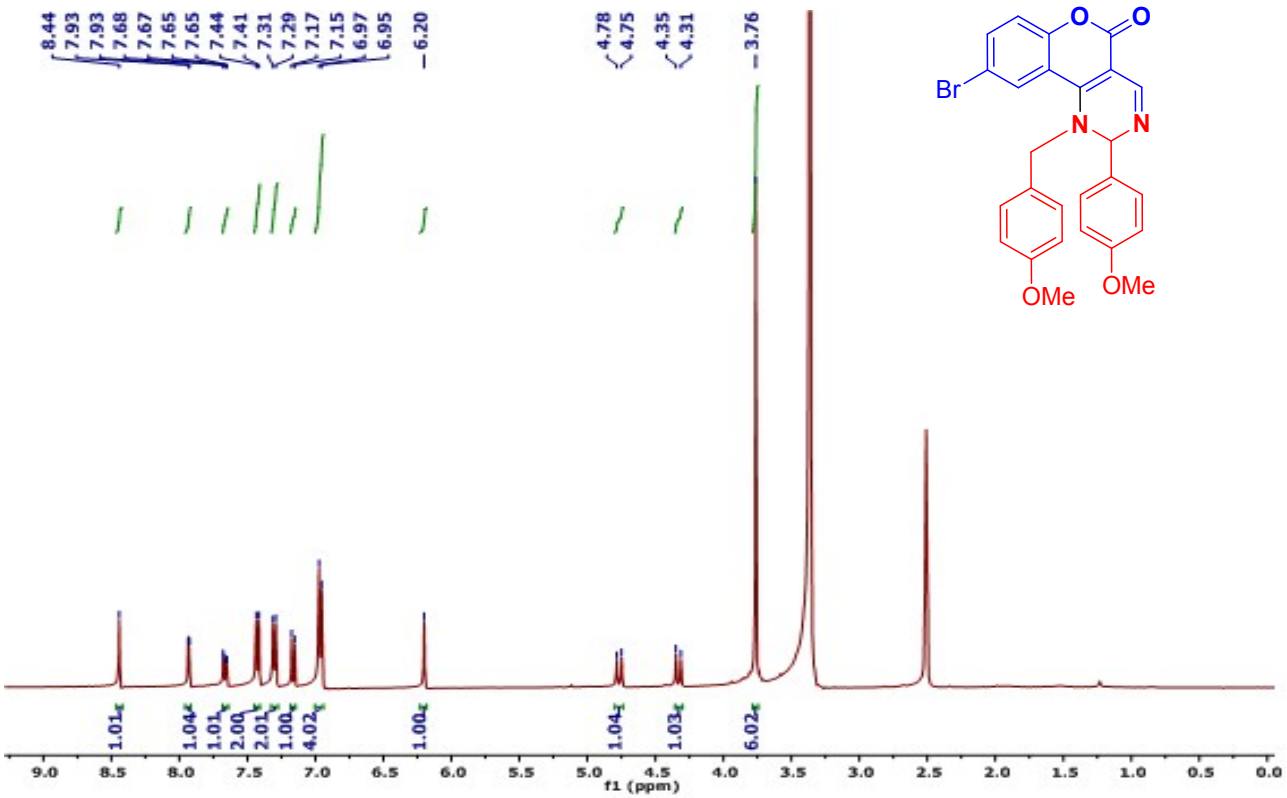
^{1}H NMR of **3r**



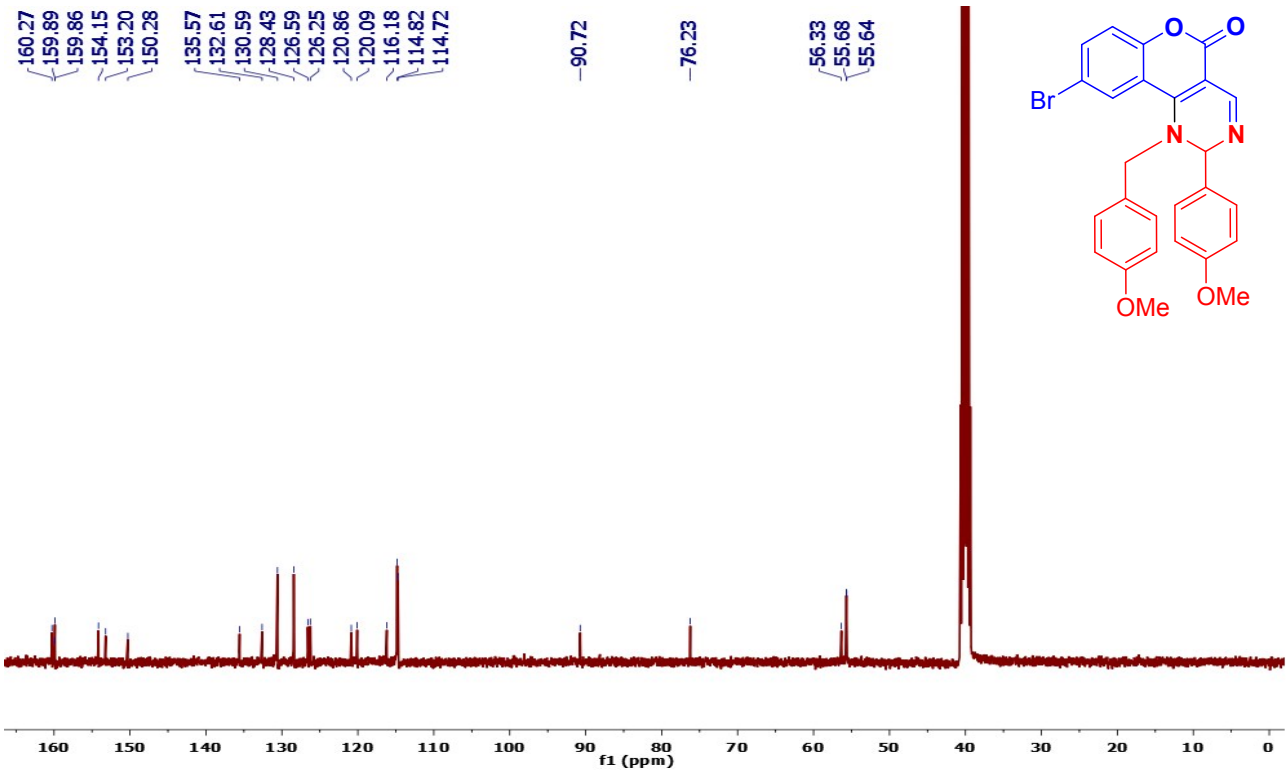
^{13}C NMR of **3r**



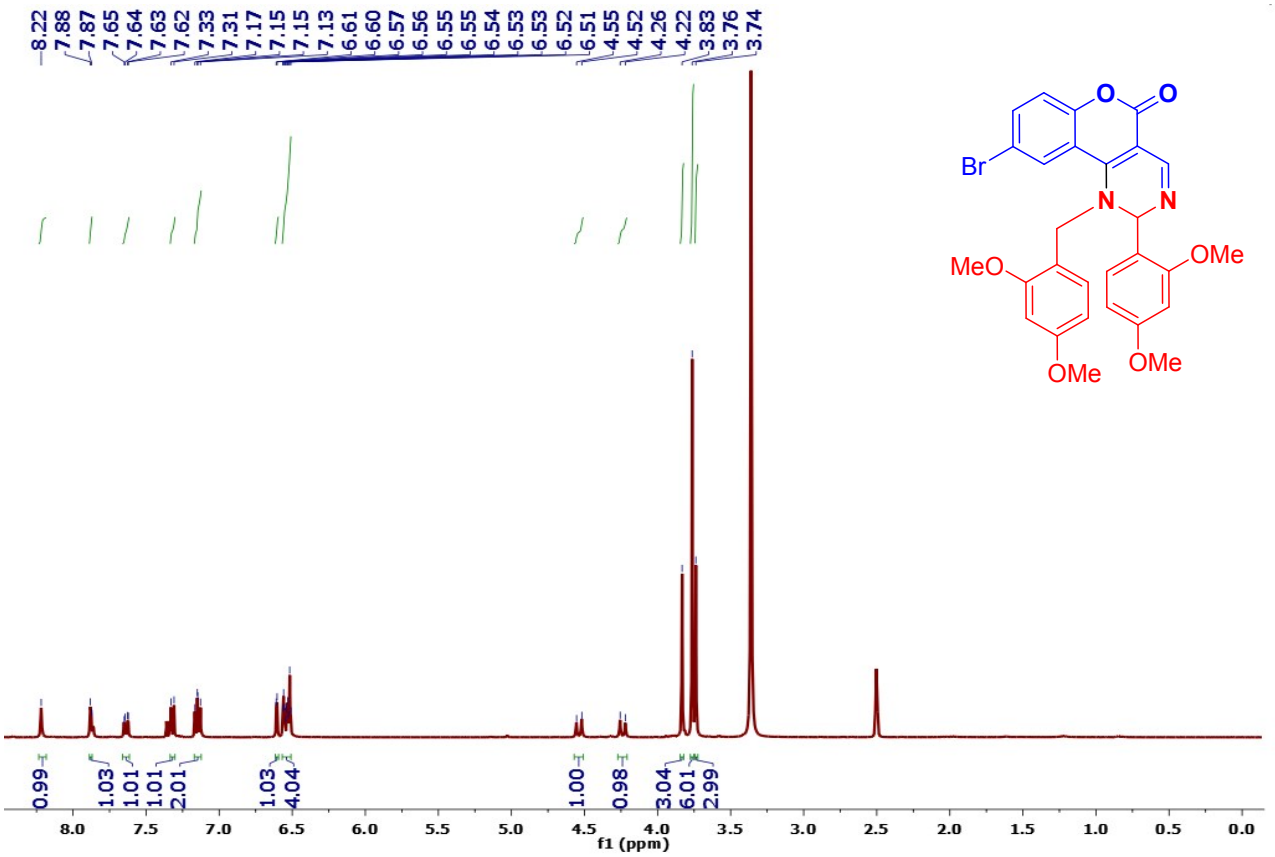
^{1}H NMR of **3s**



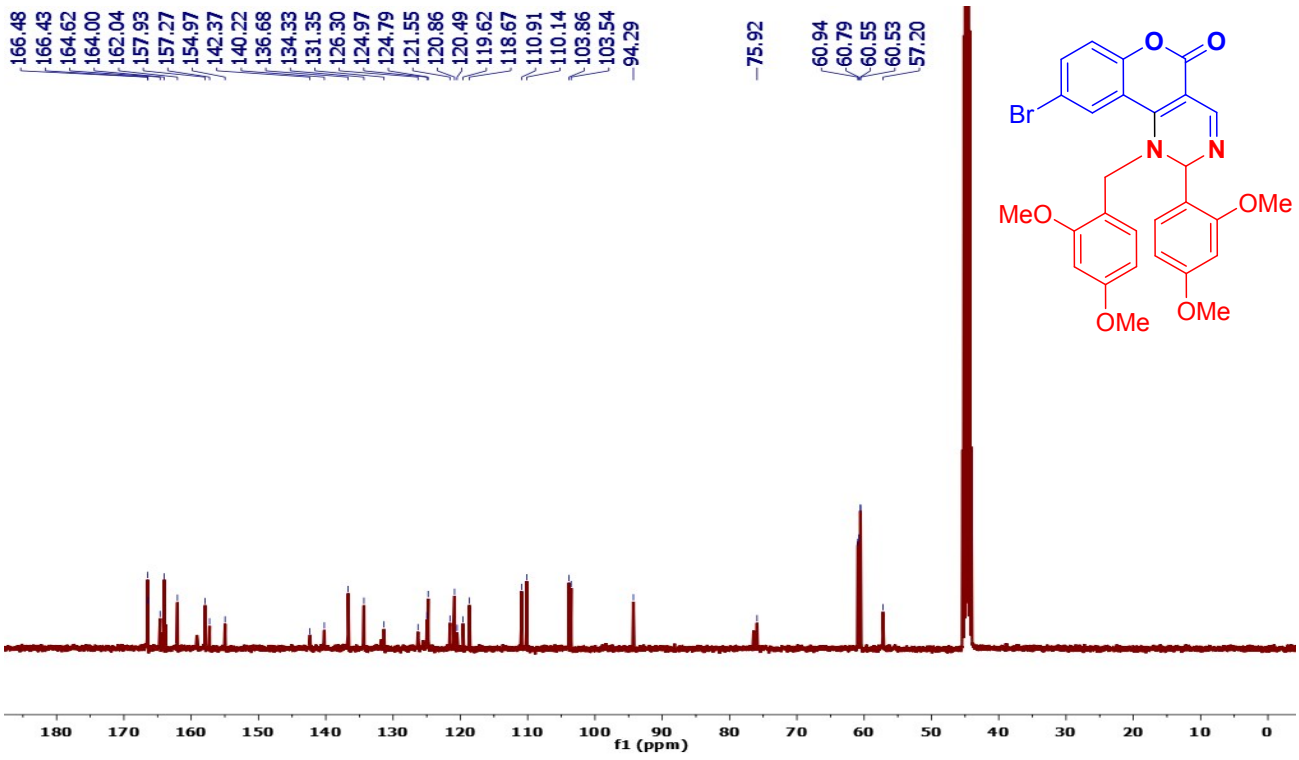
^{13}C NMR of **3s**



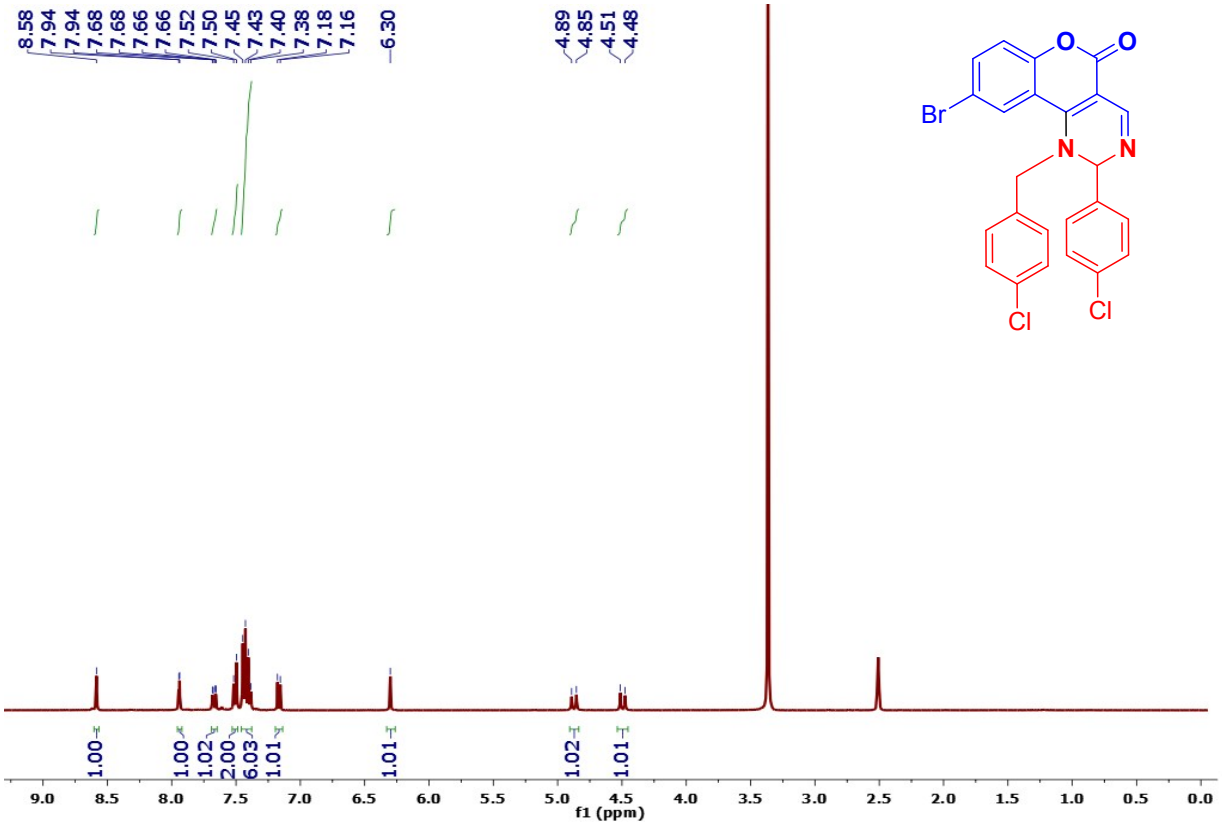
^{1}H NMR of **3t**



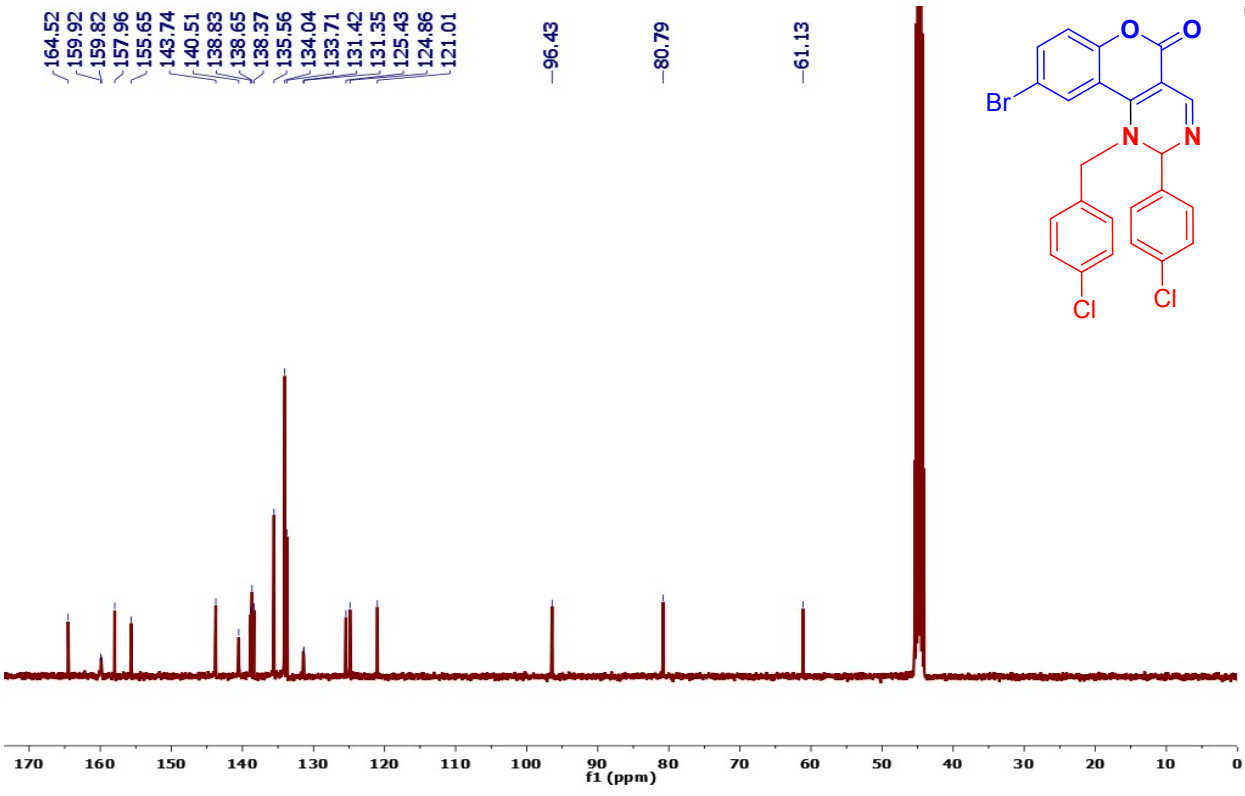
^{13}C NMR of **3t**



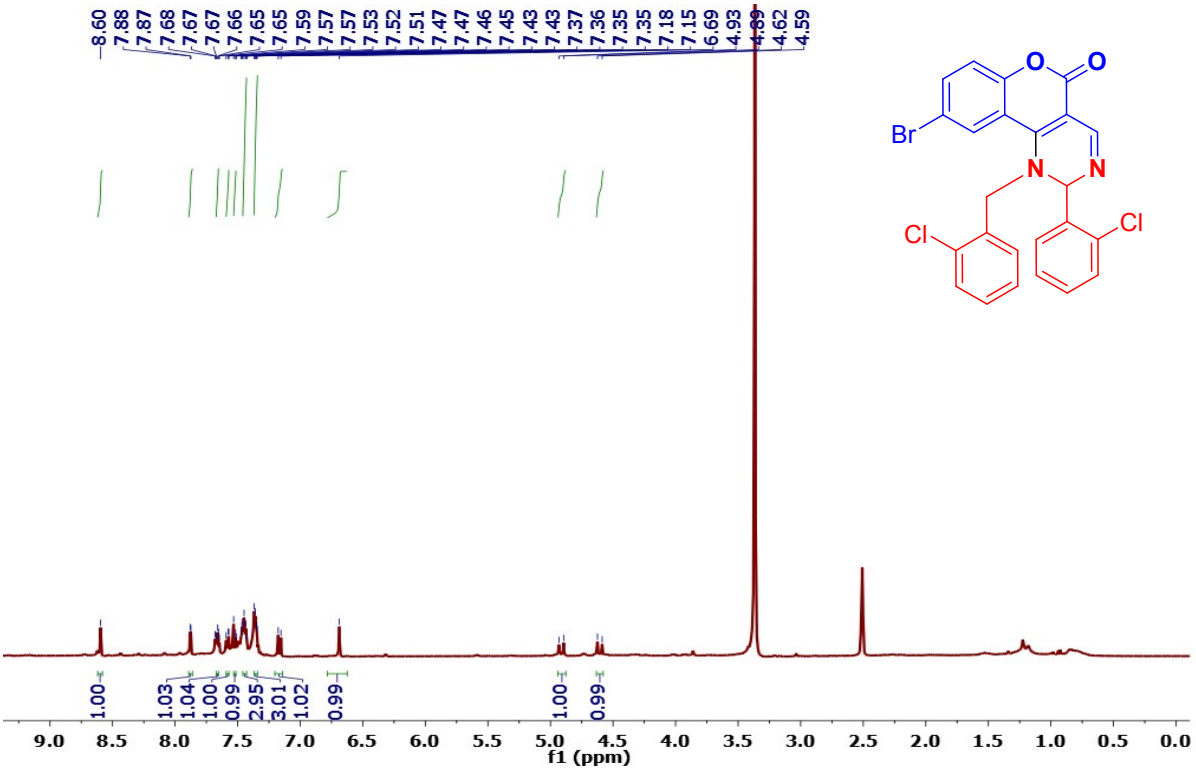
^{1}H NMR of **3u**



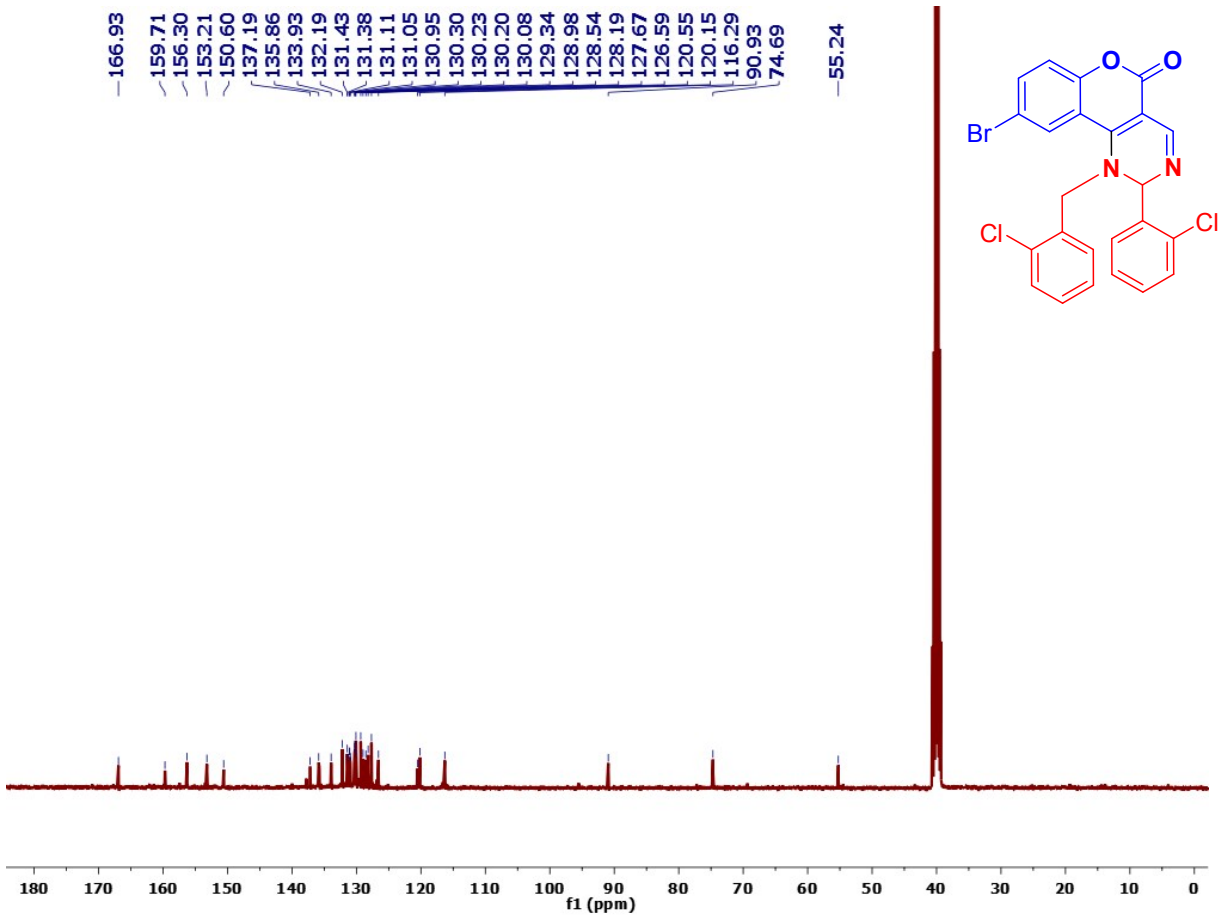
^{13}C NMR of **3u**



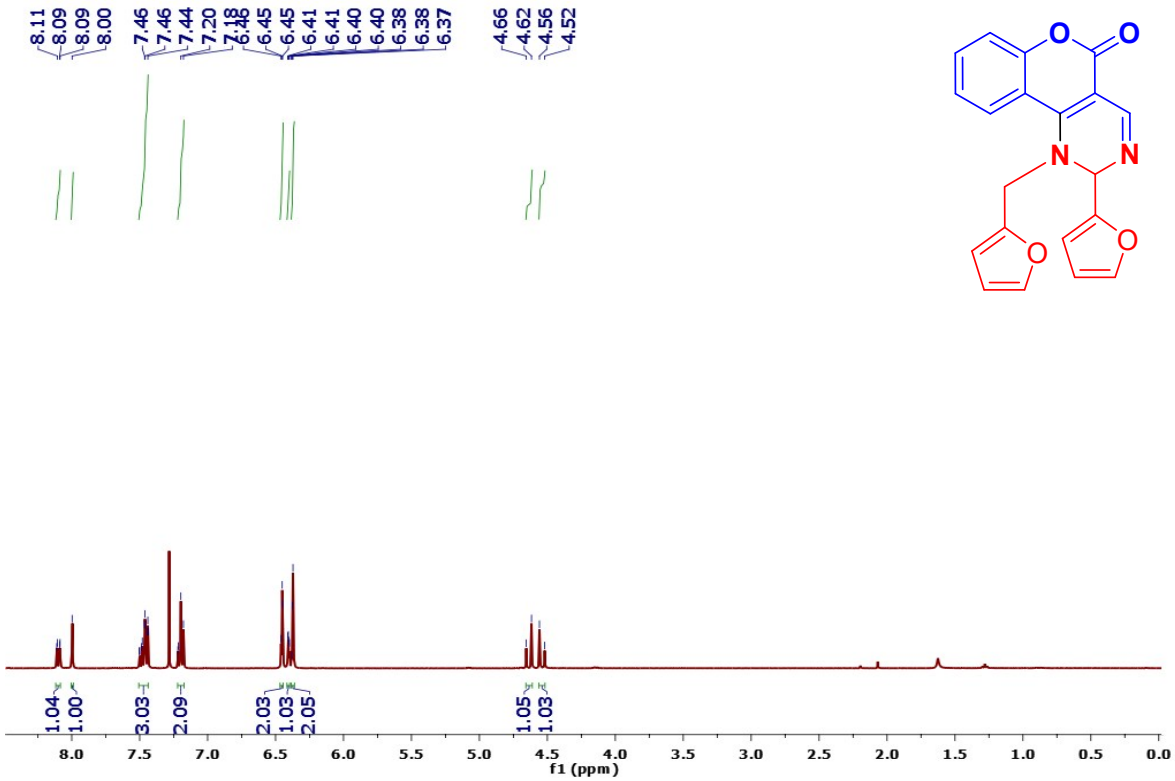
^{1}H NMR of **3v**



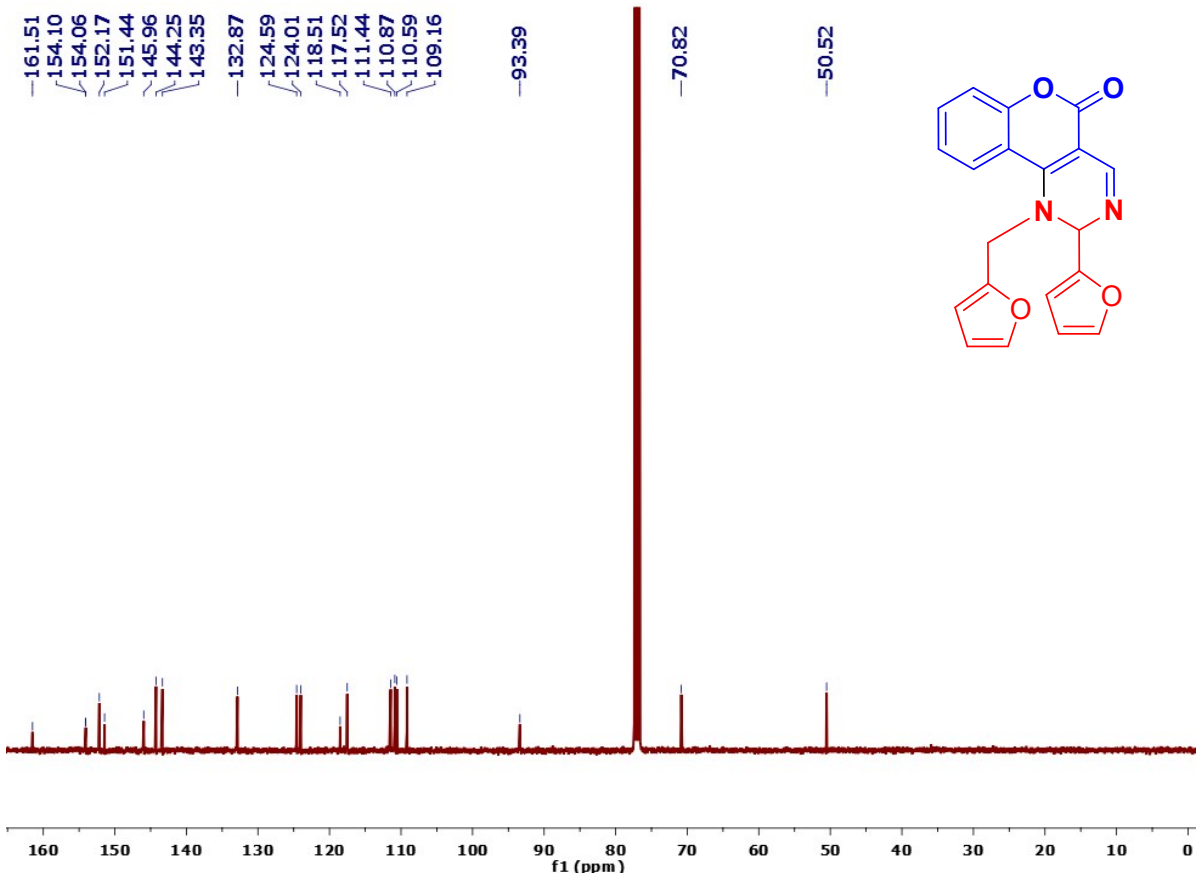
^{13}C NMR of **3v**



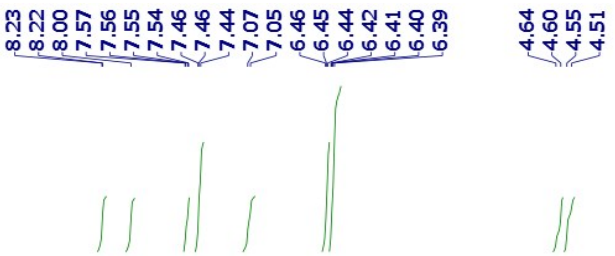
^{1}H NMR of **3w**

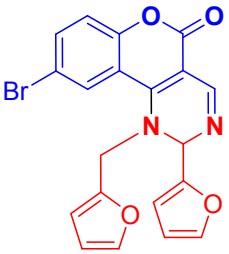


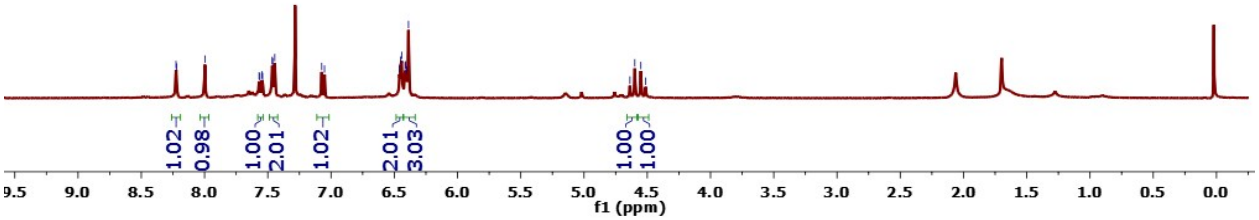
^{13}C NMR of **3w**



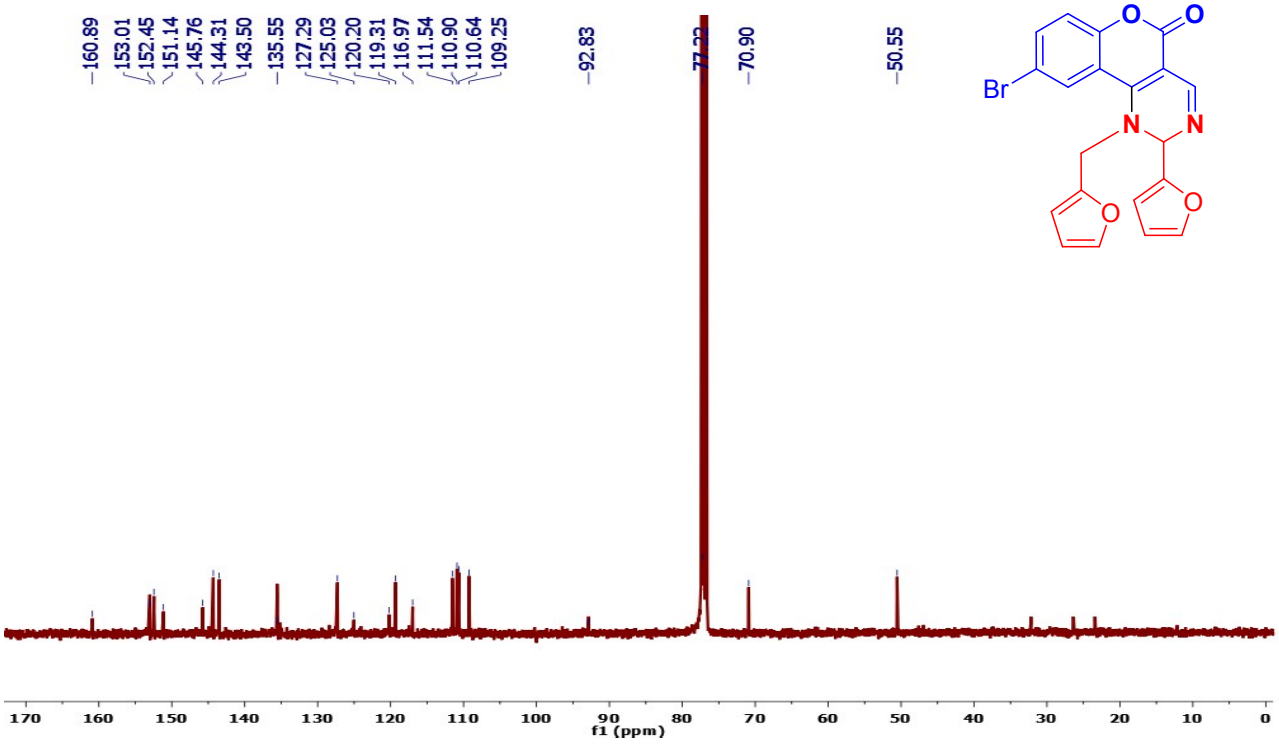
^{1}H NMR of **3y**



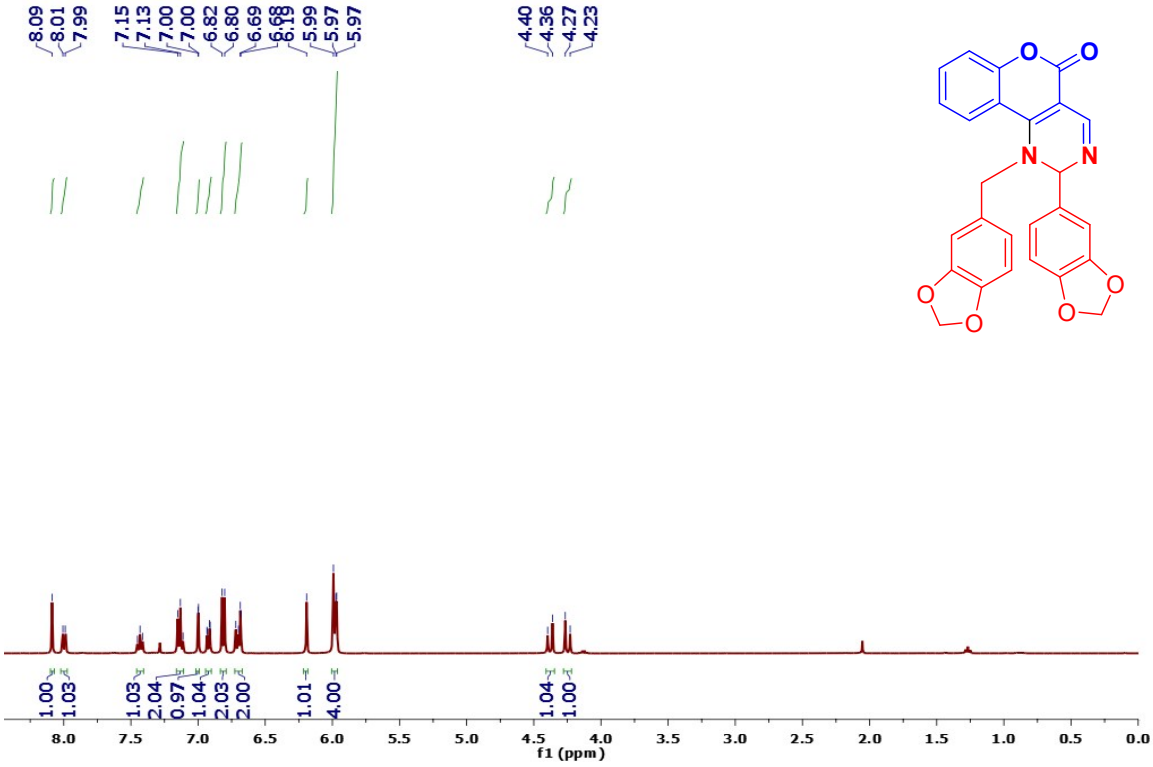




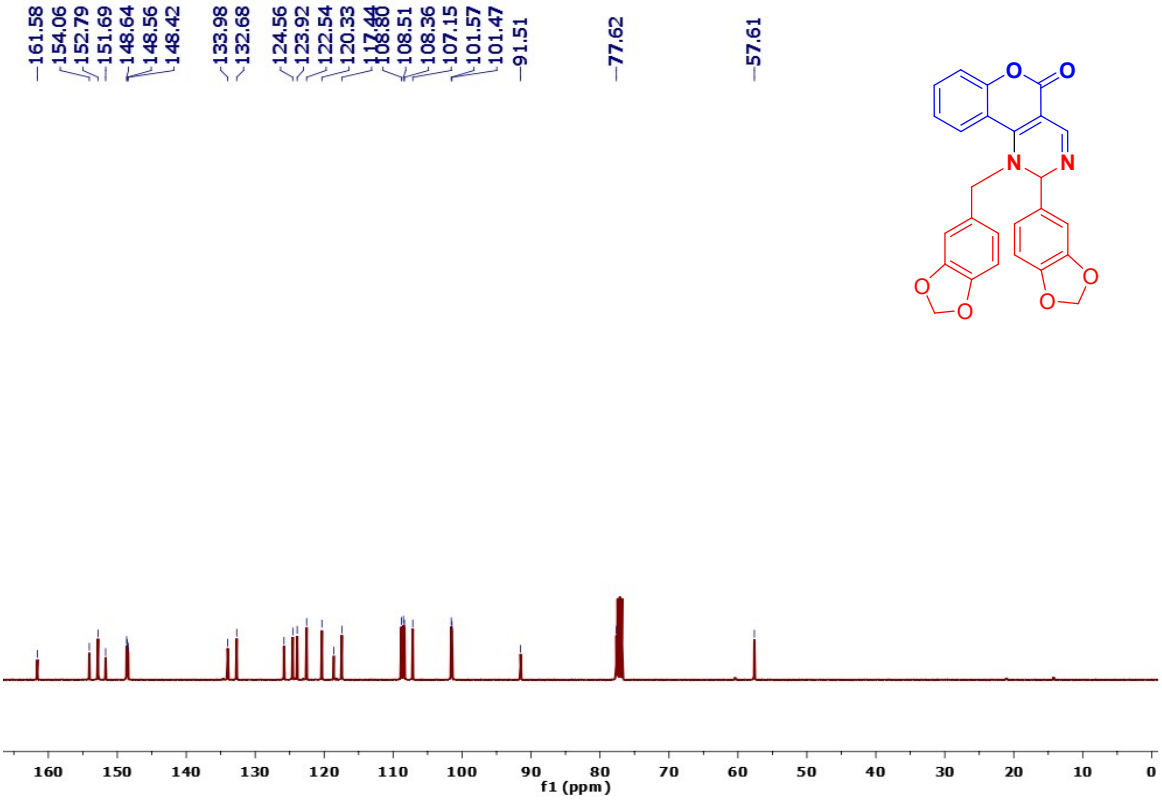
^{13}C NMR of **3y**



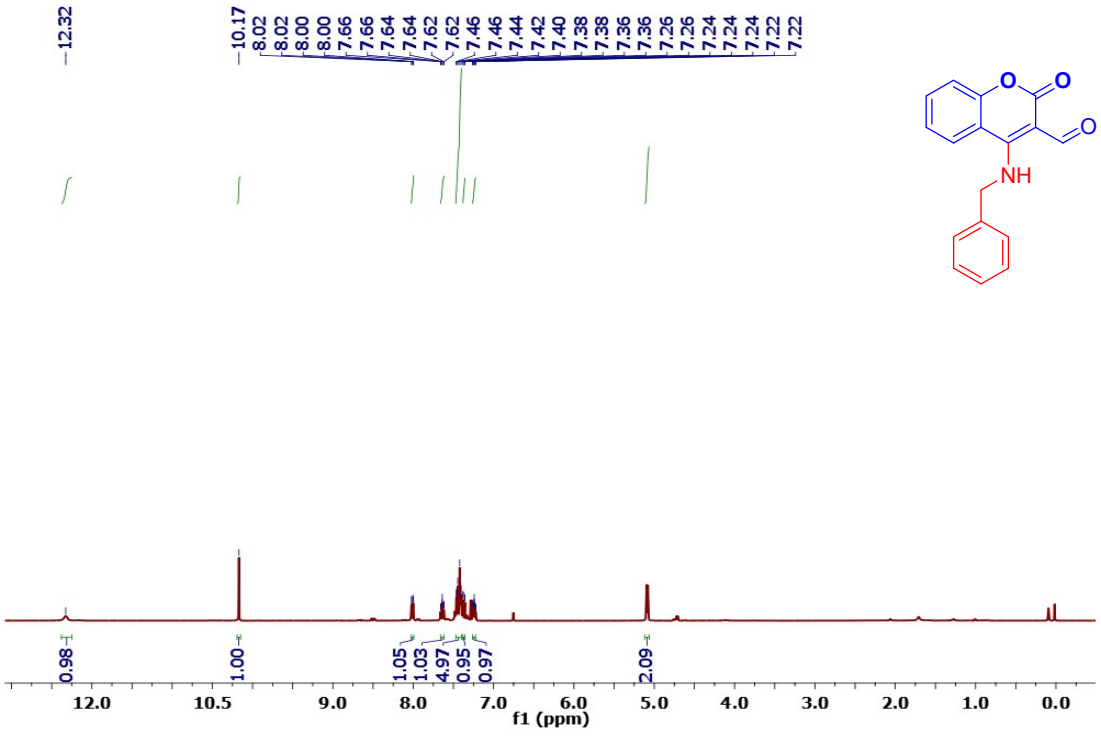
^{1}H NMR of **3y**



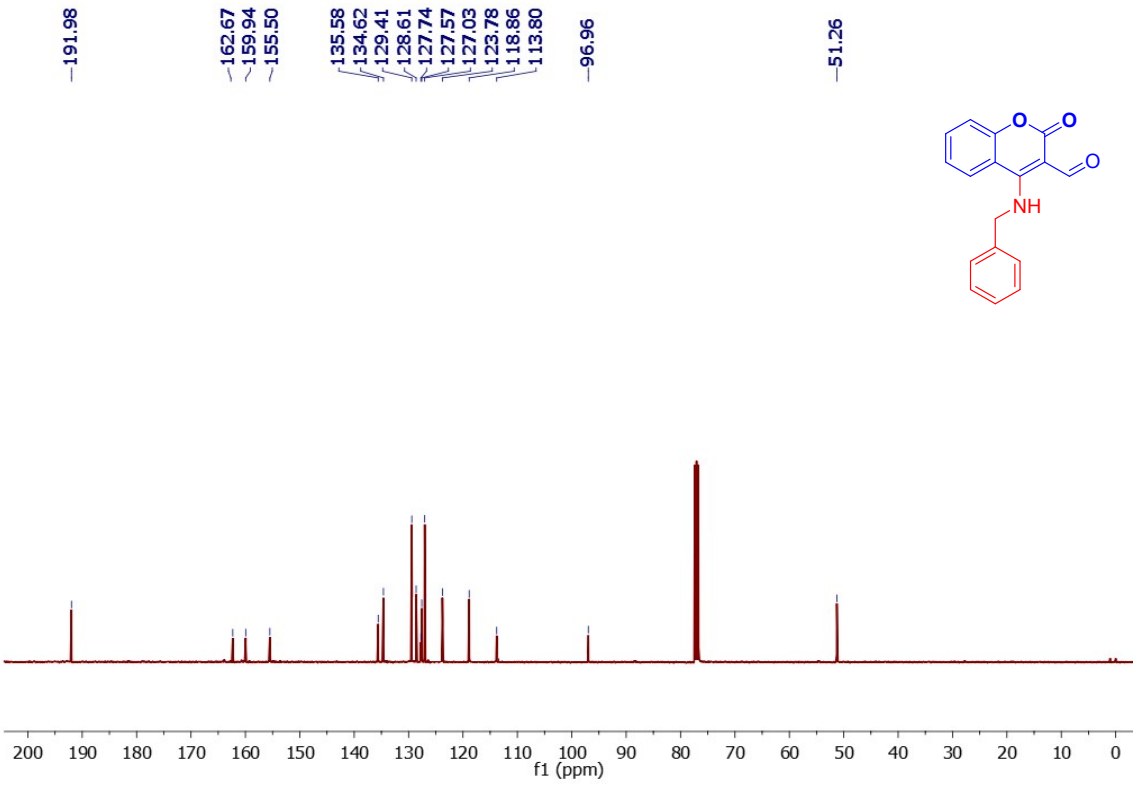
^{13}C NMR of **3y**



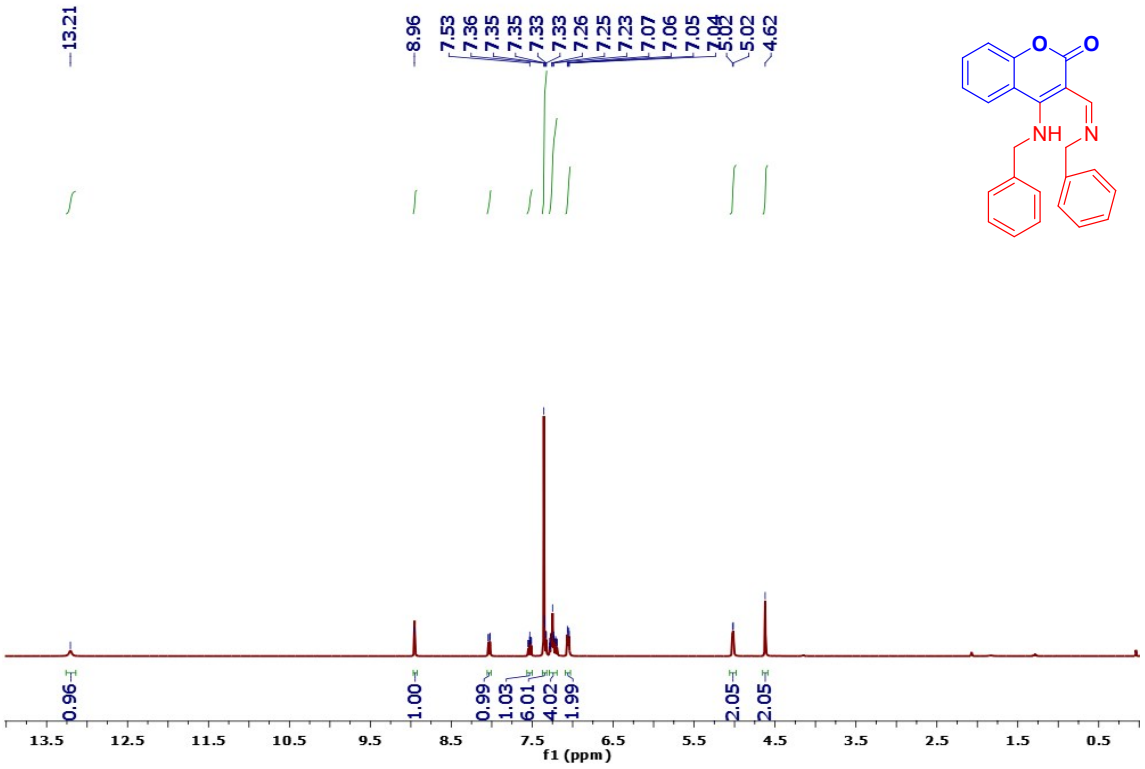
^{1}H NMR of **3a' (or A)**



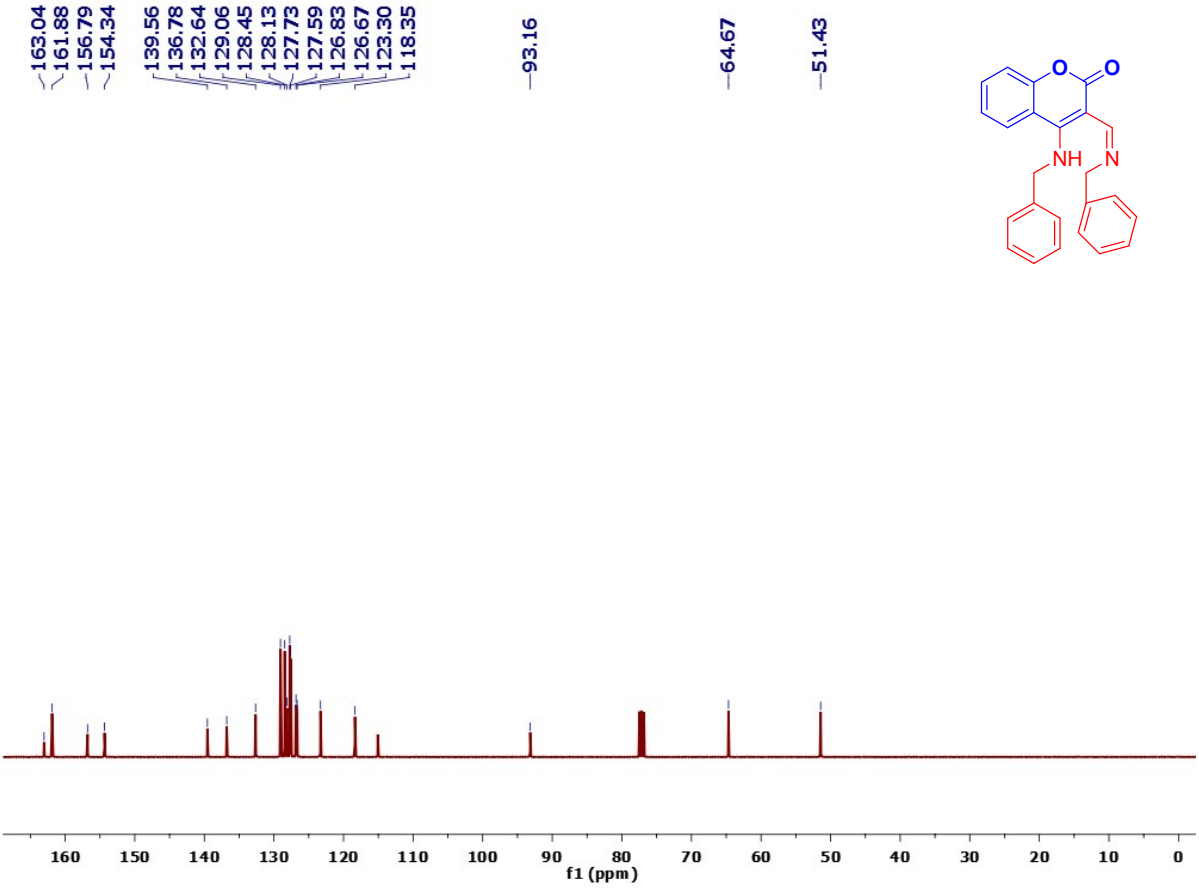
^{13}C NMR of **3a' (or A)**



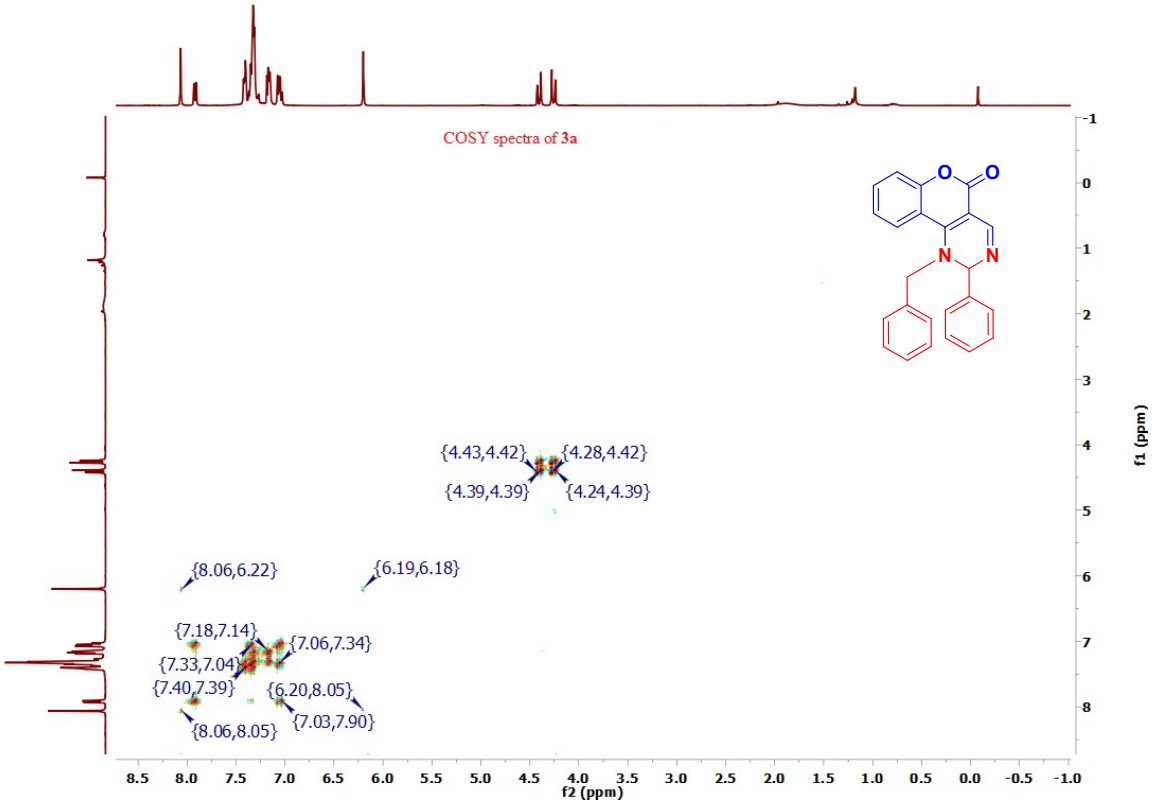
[1] H NMR of **3a'' (or B)**

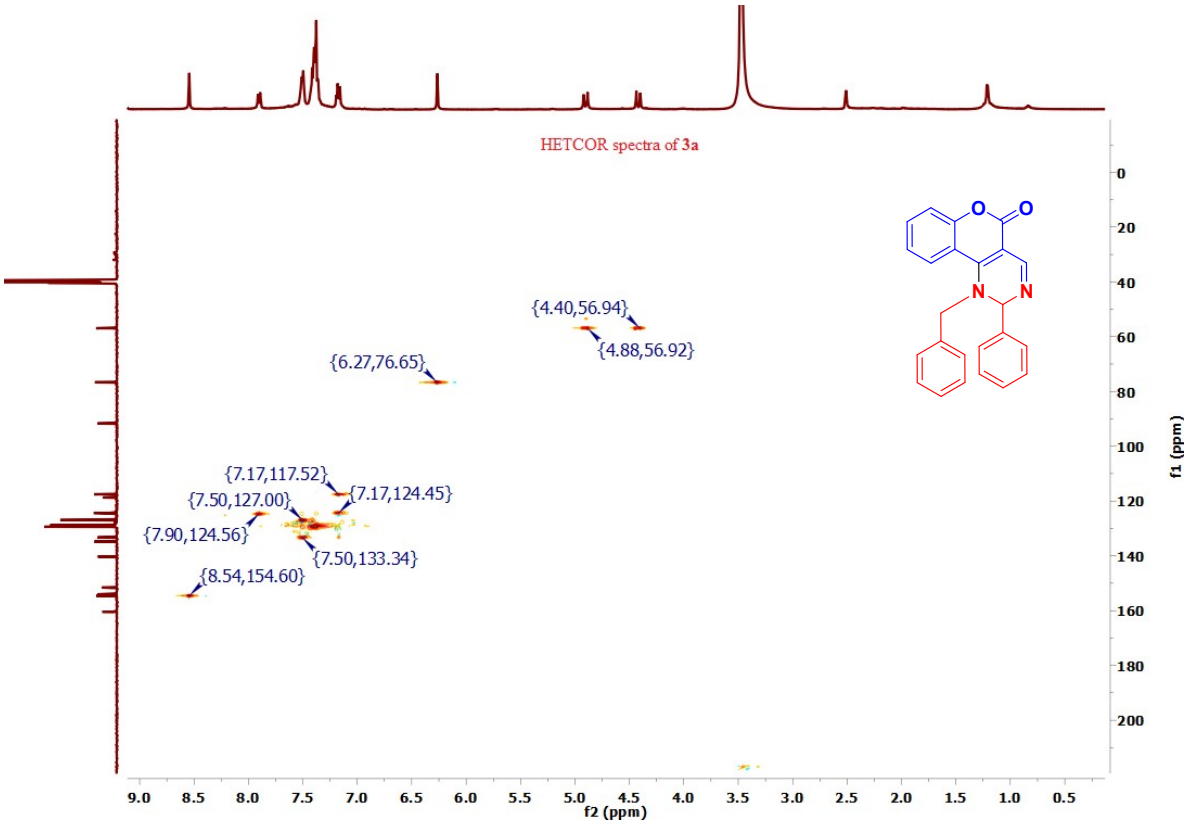


[13] C NMR of **3a'' (or B)**

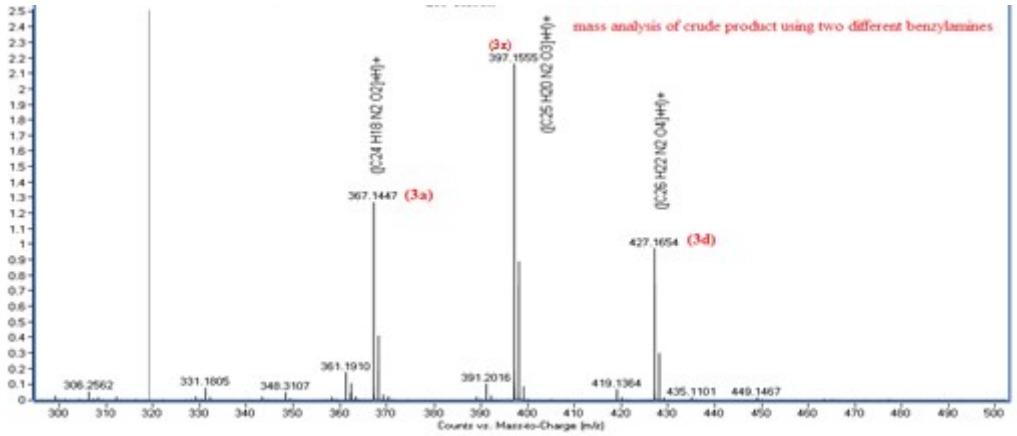


2. ^{1}H & ^{13}C NMR spectra of **3a-r4. 2D (COSY & HETCOR) spectra of 3a**

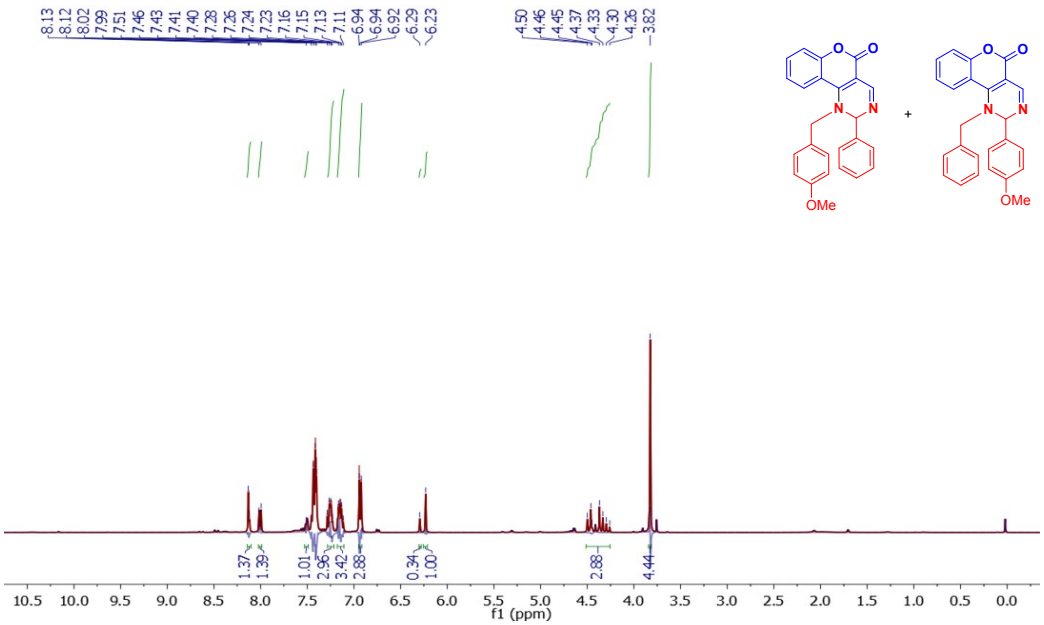


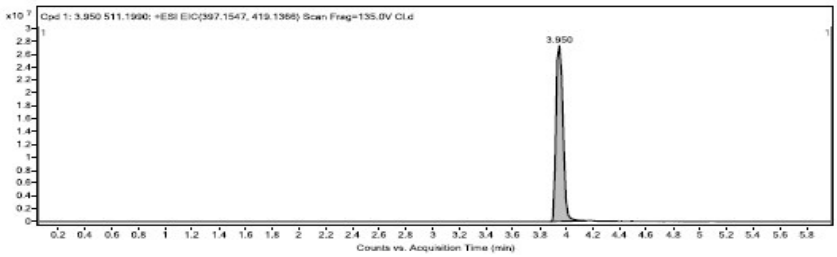


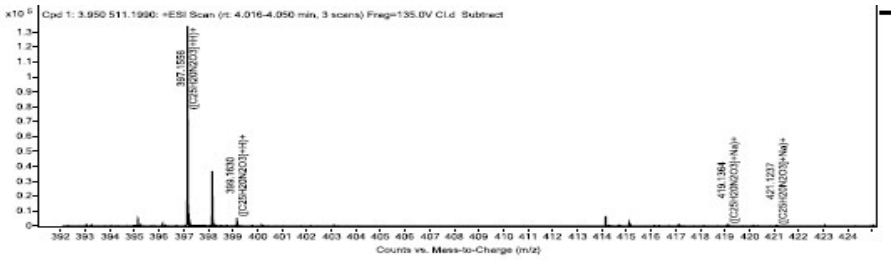
3. Mass analysis of mixture of cross-coupled product (3z) and homo-coupled products (3a & 3d) using two different benzyl amines



^{1}H NMR and Mass analysis of 3z+3z′





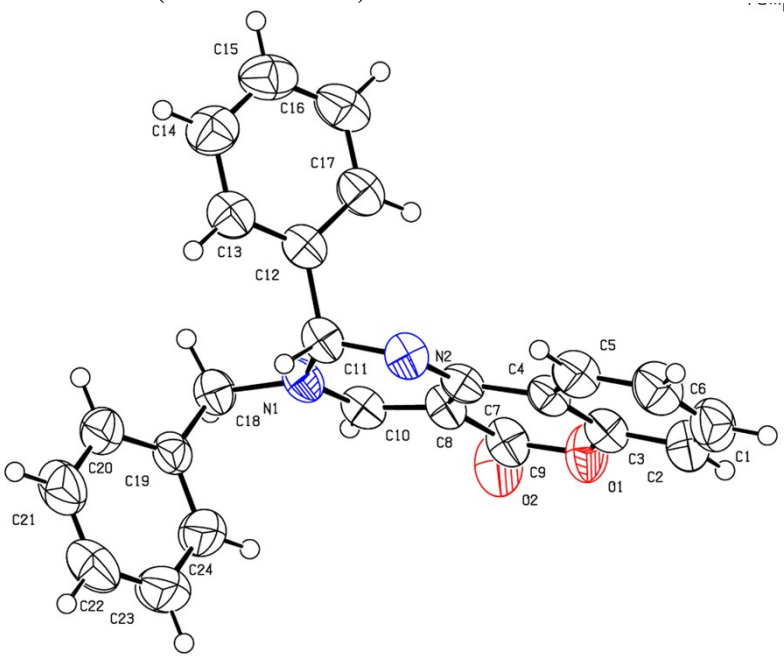


4. X-ray Crystallography Studies of 3a

Crystals of **3a** were screened under a microscope for mounting in a nylon loop attached to a goniometer head. Initial crystal evaluation and data collection were performed on a Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated MoKα radiation using the program APEX2.[1] By using the program SAINT[1] for the integration of the data, reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP[1] was used for the processing of data that included determination of space group, application of an absorption correction (SADABS)[1], merging of data, and generation of files necessary for solution and refinement. The crystal structure was solved and refined using SHELX 97.[2] In each case, the space group was chosen based on systematic absences and confirmed by the successful refinement of the structure. Positions of most of the non-hydrogen atoms were obtained from a direct methods solution. Several full-matrix least-squares/difference Fourier cycles were performed, locating the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. All figures were drawn using MERCURY V 3.0[3] and Platon.[4]

Crystal data for **3a**. $C_{24}H_{18}N_2O_2$, Mr = 366.40 g/mol, monoclinic, space group *C*2/*c*, a = 21.348(4) Å, b = 9.871(2) Å, c = 17.745(4) Å, α = 90°, β = 92.423(5)°, γ = 90°, V = 3736(1) $Å^3$, Z = 8, T = 296(2) K, D_{calcd} = 1.303 g/cm^3; Full matrix least-square on F^2; R_1 = 0.046, wR_2 = 0.1064 for 2274 observed reflections [$I > 2\sigma(I)$] and R_1 = 0.073, wR_2 = 0.1199 for all 3294 reflections; GOF = 1.024. CCDC No. 1575437.

Fully labelled ORTEP of **3a** (*R* stereoisomer) is shown below:



References

1. *APEX2*, *SADABS and SAINT*; Bruker AXS inc: Madison, WI, USA, **2008**.
2. Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112.
3. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edginton, P. R.; McCabe, P.; Pidocck, E.; Rodriguez-Monge, L.; Taylor, T.; Van de Streek, J.; Wood, P. A. *J. Appl. Cryst.,*2008, **41**, 466.
4. Spek, A. L. *PLATON, Version 1.62*, University of Utrecht, 1999.