Synthesis of 5*H*-chromeno[3,4-*b*]pyridines via DABCO-catalyzed [3+3] annulation of 3-nitro-2*H*-chromenes and allenoates

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Electronic Supplementary Information

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Copies of ^{1}H, ^{13}C, ^{19}F RMN and 2D NMR Spectra for New Compounds

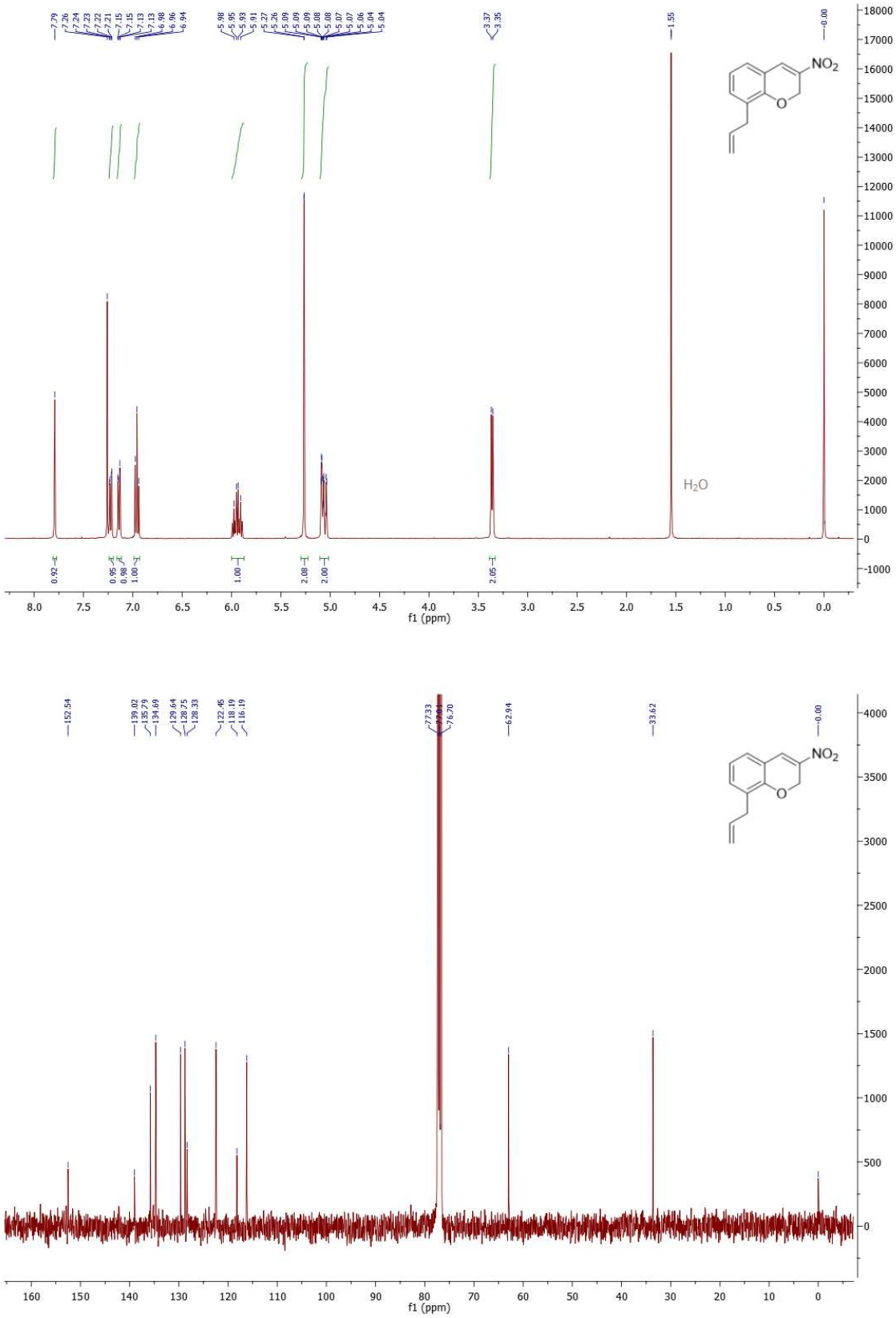


Figure S1: ^{1}H and ^{13}C NMR spectra of compound **1c** ($CDCl_3$).

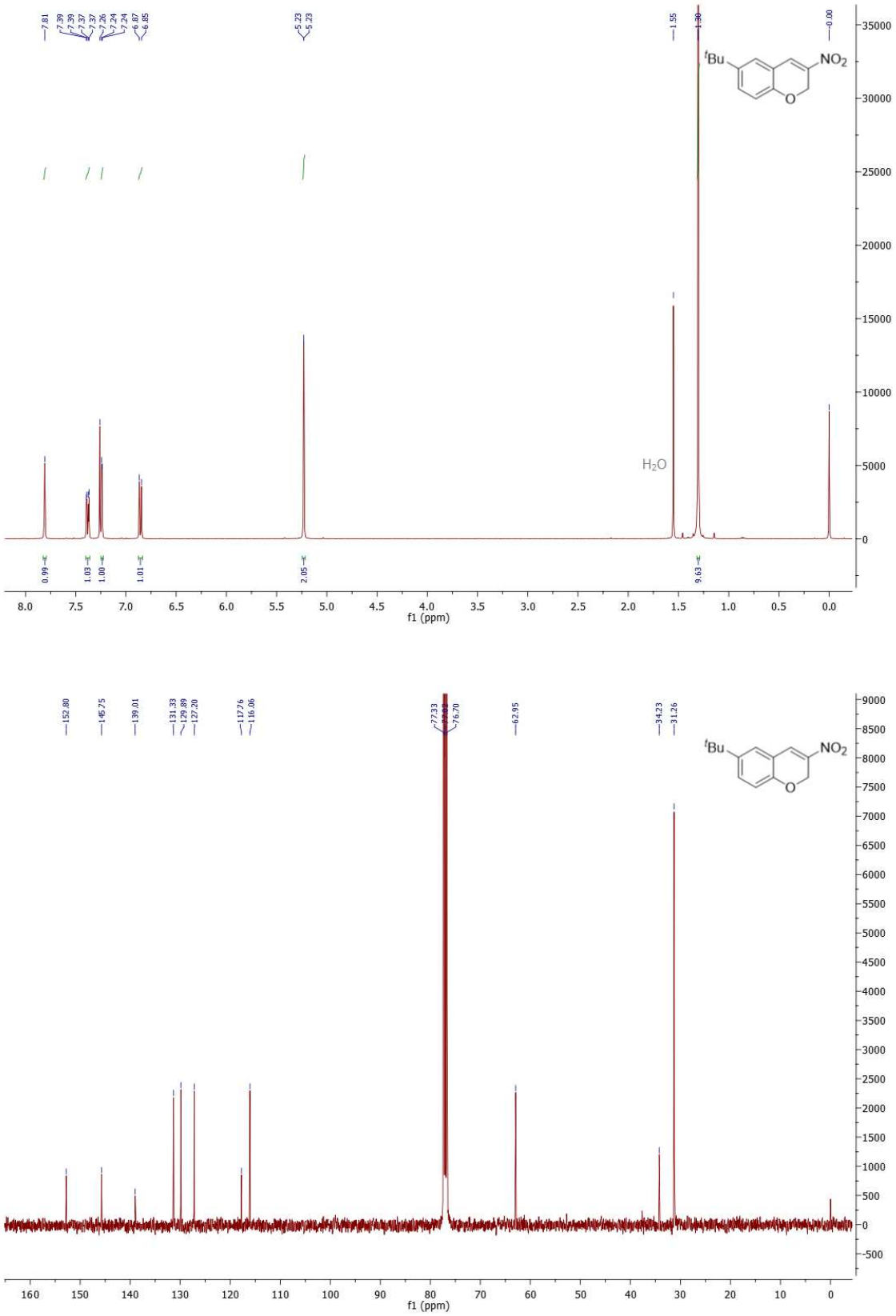


Figure S2: ^{1}H and ^{13}C NMR spectra of compound **1i** ($CDCl_3$).

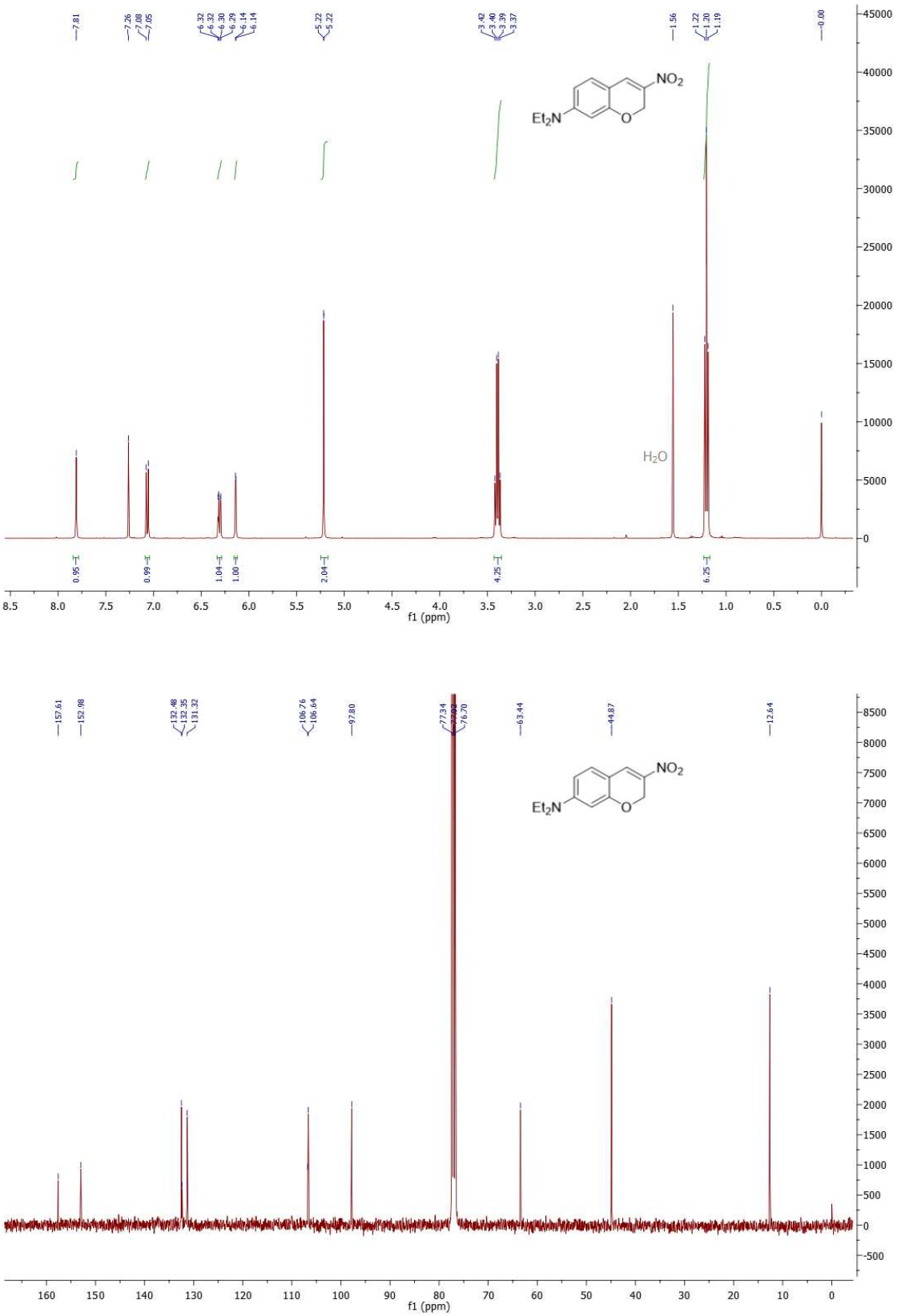


Figure S3: ^{1}H and ^{13}C NMR spectra of compound **1k** ($CDCl_3$).

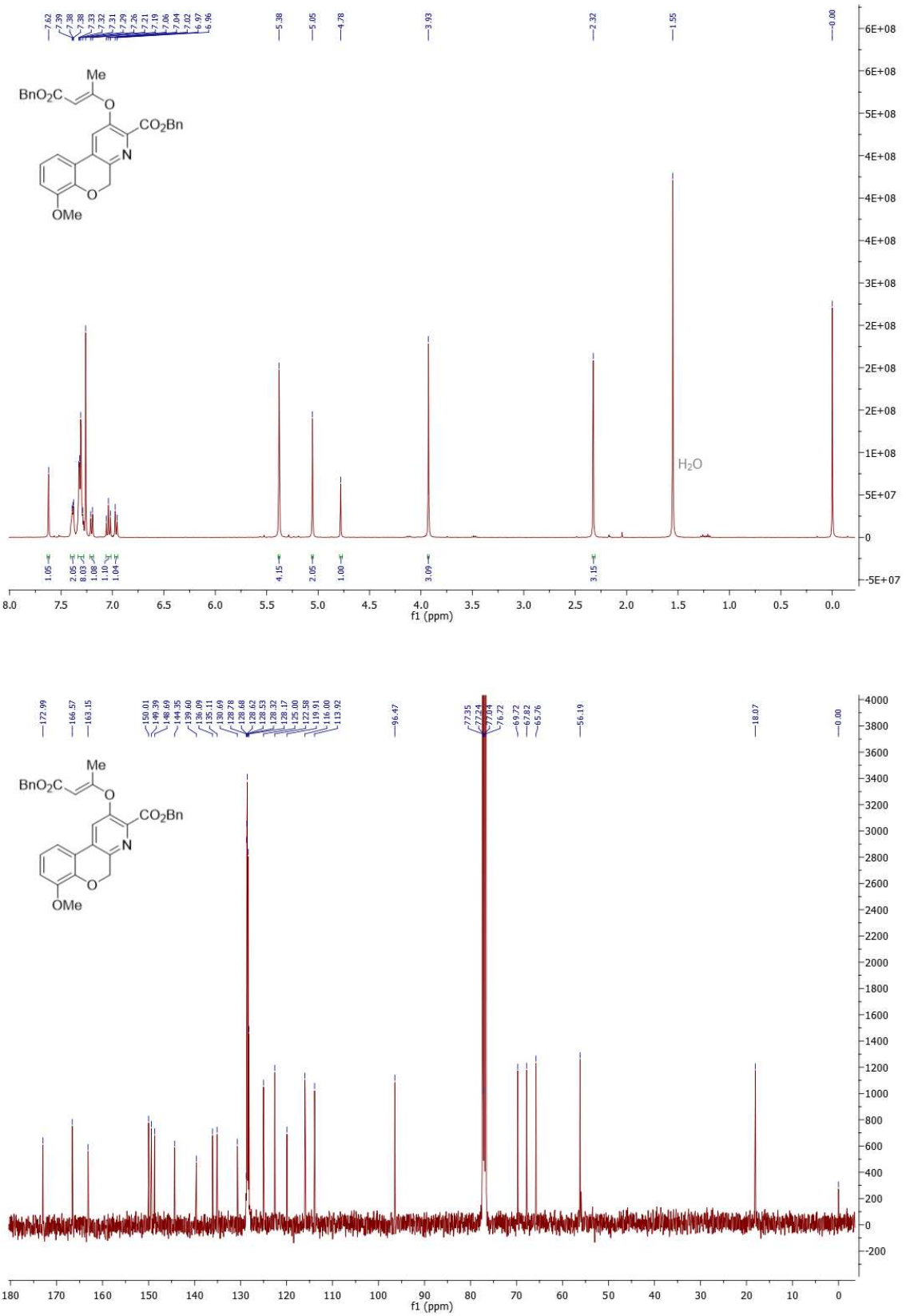


Figure S4: ^{1}H and ^{13}C NMR spectra of compound **3a** ($CDCl_3$).

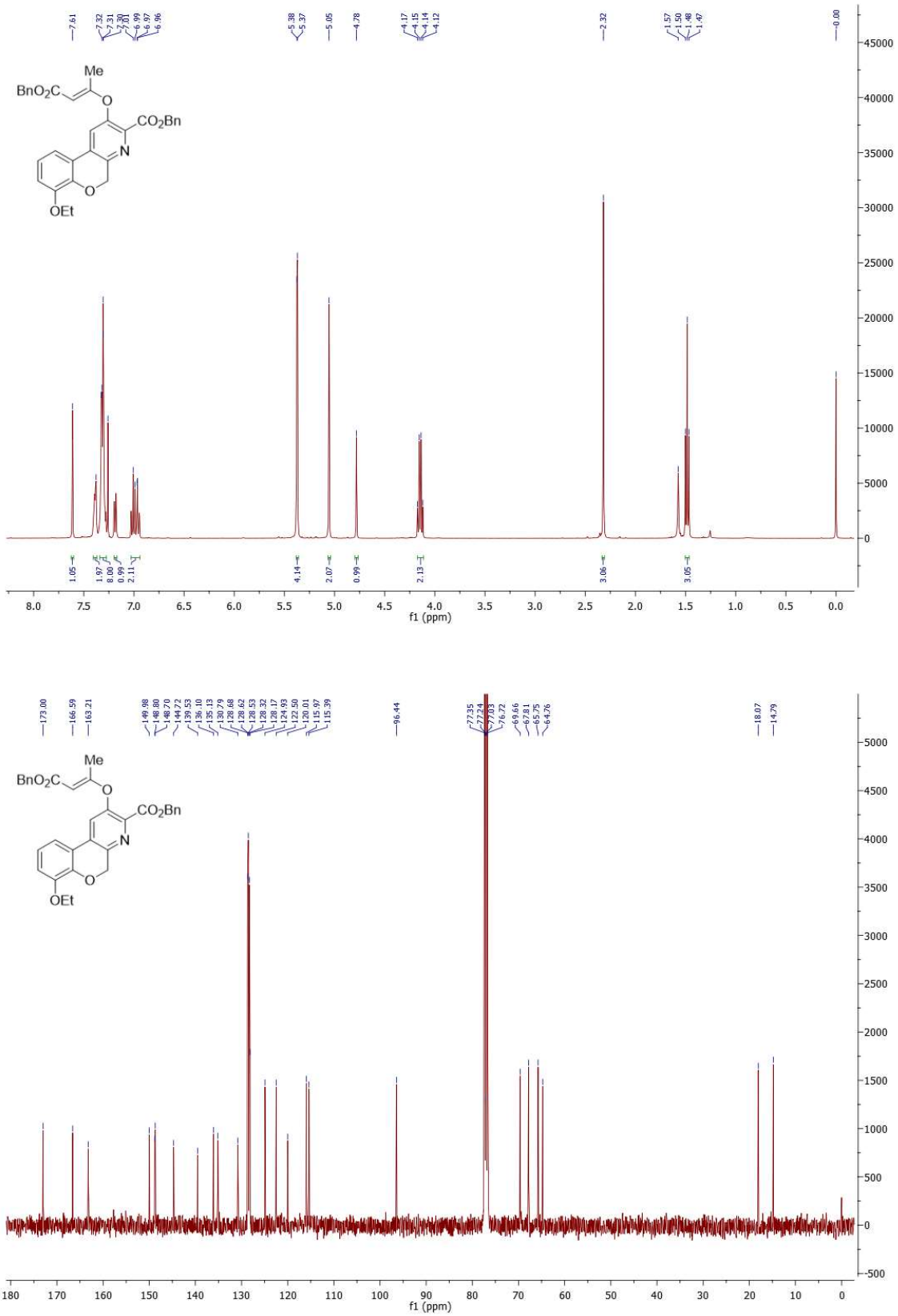


Figure S5: ^{1}H and ^{13}C NMR spectra of compound **3b** ($CDCl_3$).

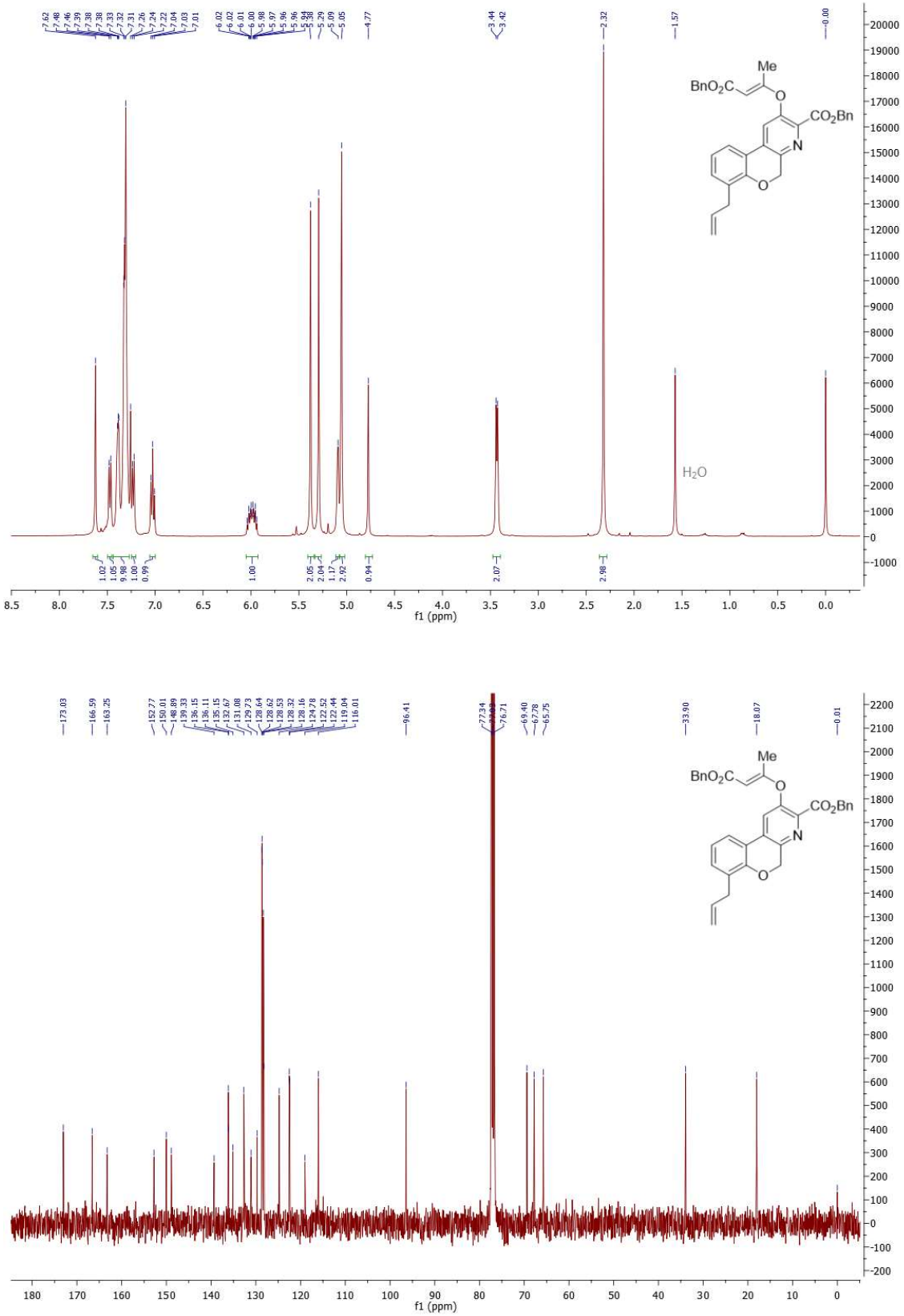


Figure S6: ^{1}H and ^{13}C NMR spectra of compound **3c** ($CDCl_3$).

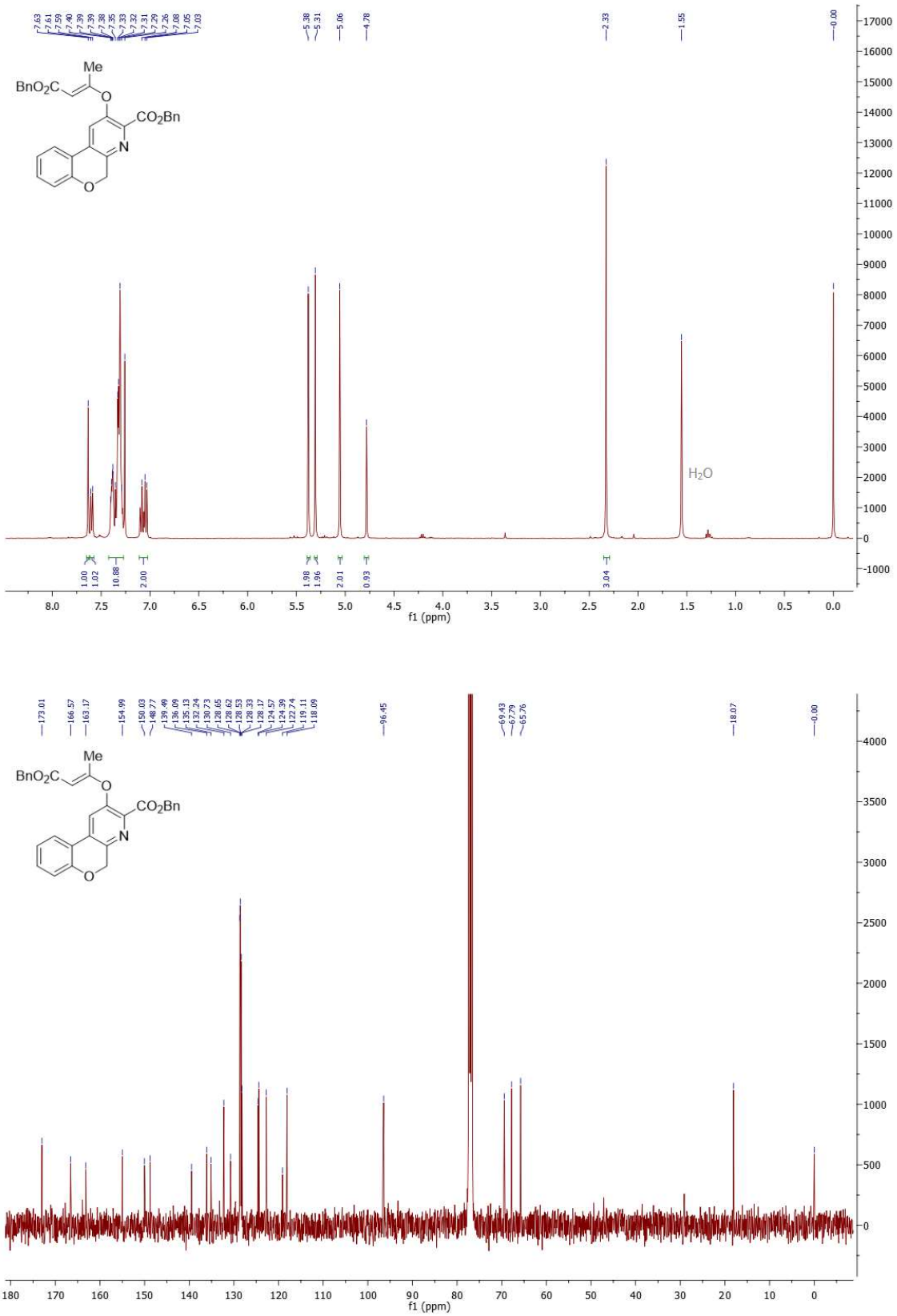


Figure S7: ^{1}H and ^{13}C NMR spectra of compound **3d** ($CDCl_3$).

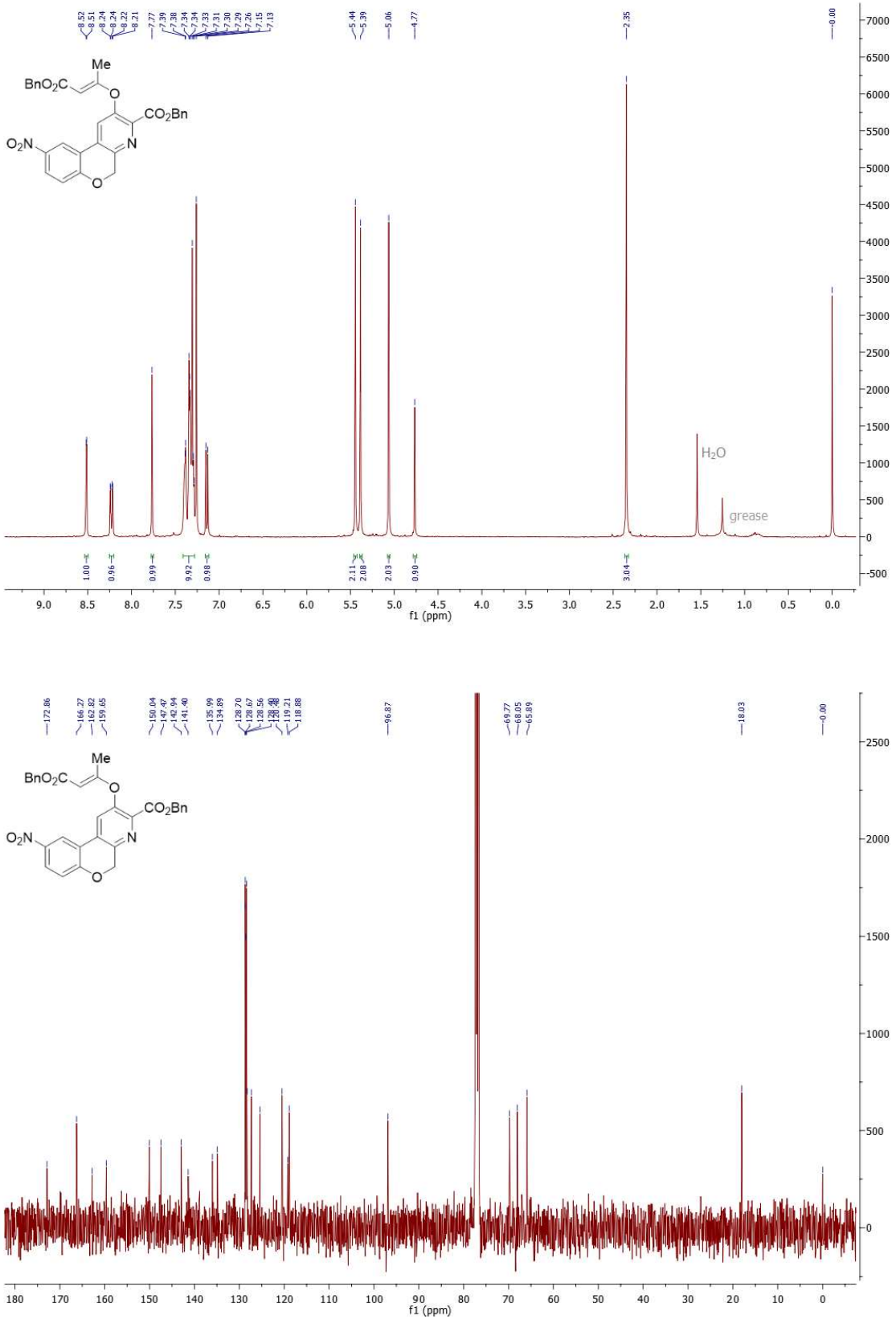


Figure S8: ^{1}H and ^{13}C NMR spectra of compound **3e** ($CDCl_3$).

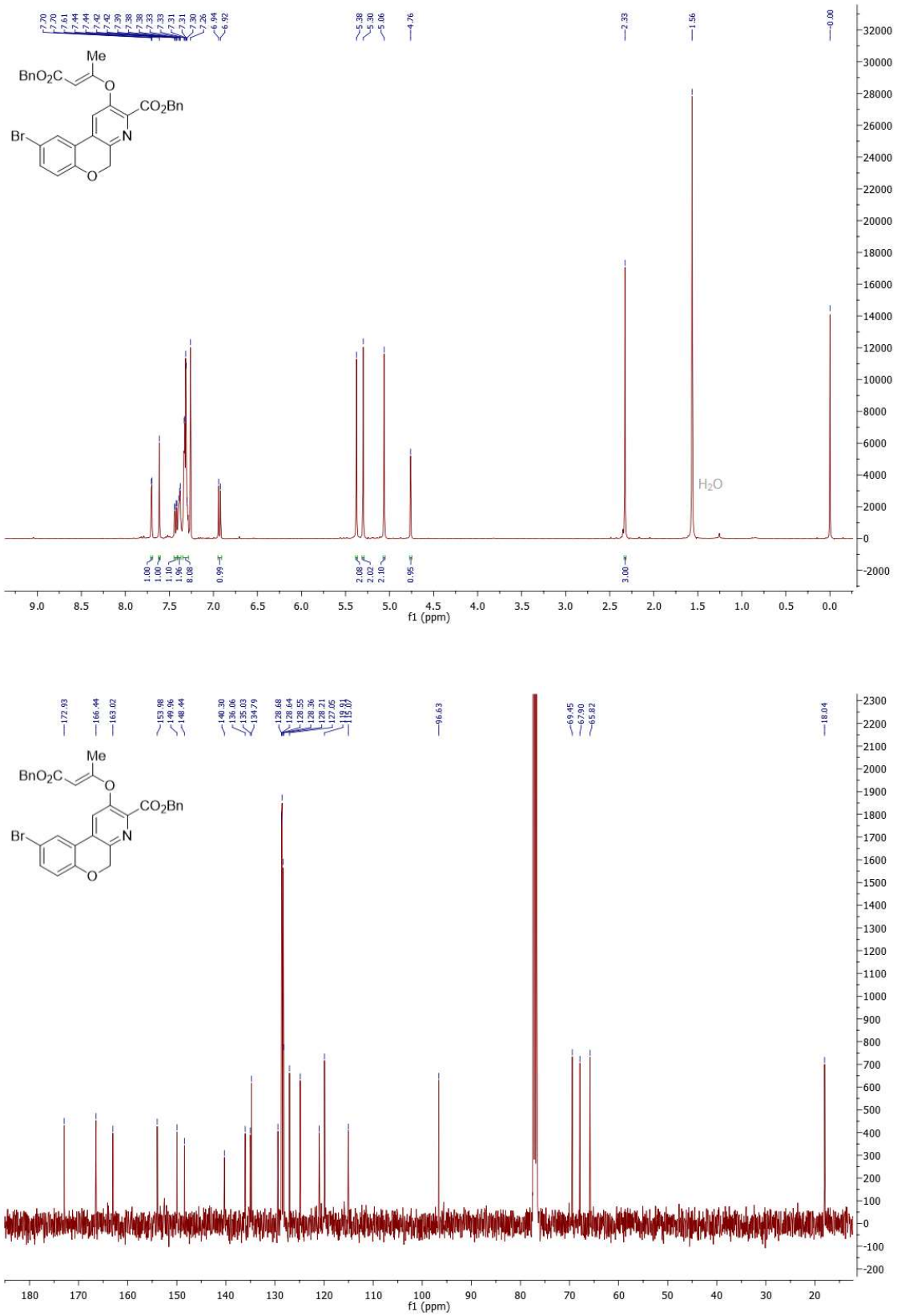


Figure S9: ^{1}H and ^{13}C NMR spectra of compound **3f** ($CDCl_3$).

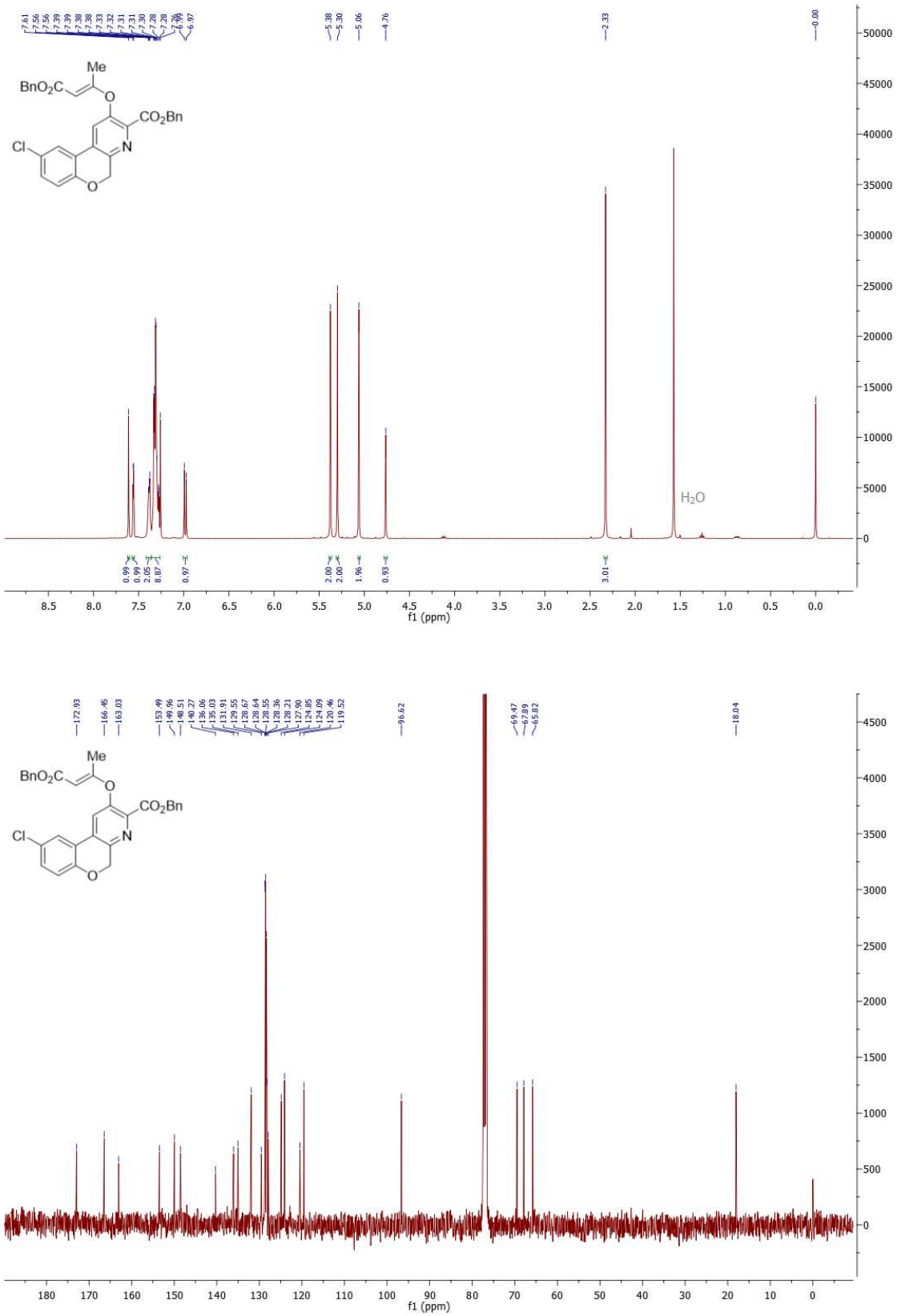


Figure S10: ^{1}H and ^{13}C NMR spectra of compound **3g** ($CDCl_3$).

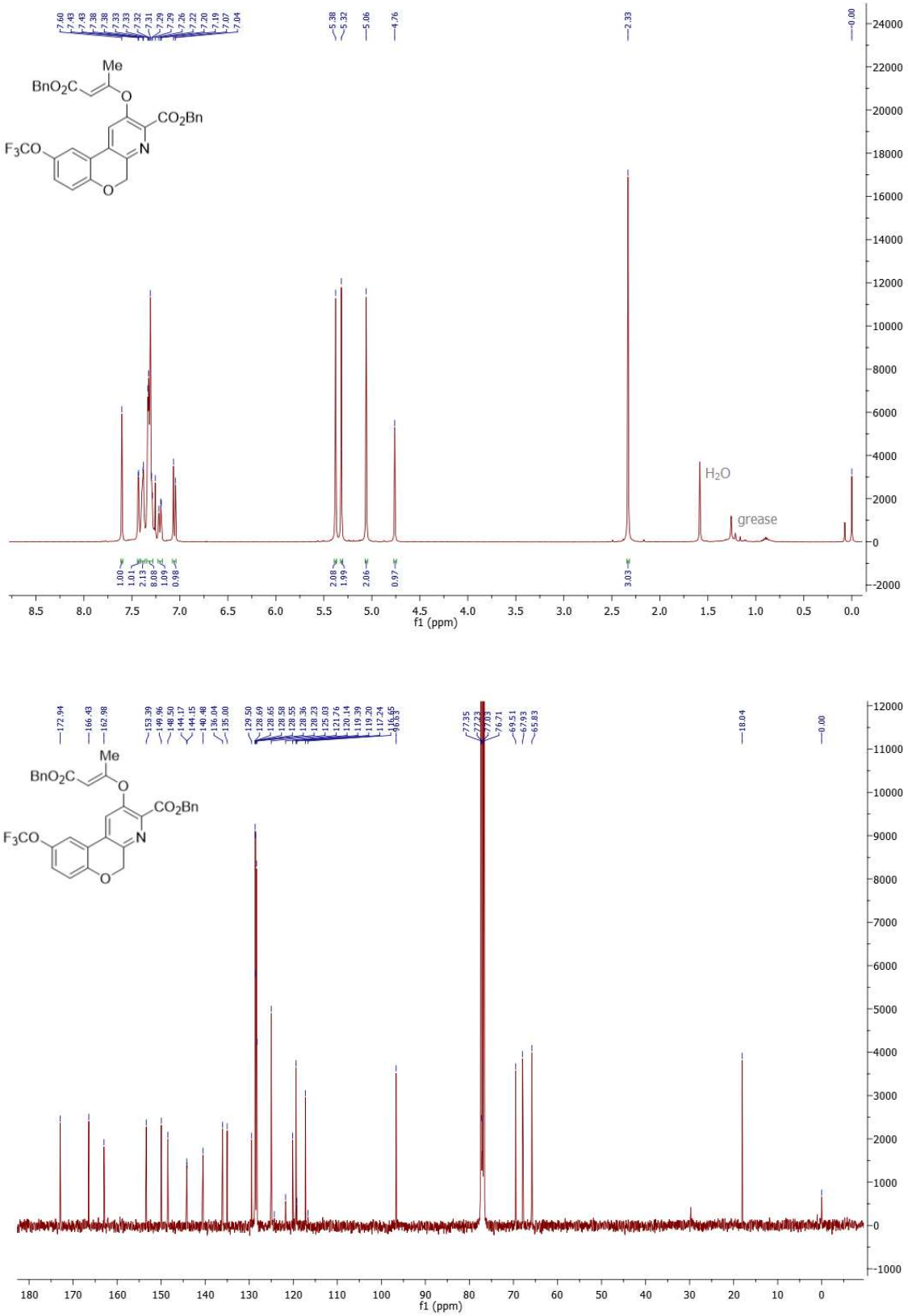


Figure S11a: ^{1}H and ^{13}C spectra of compound **3h** ($CDCl_3$).

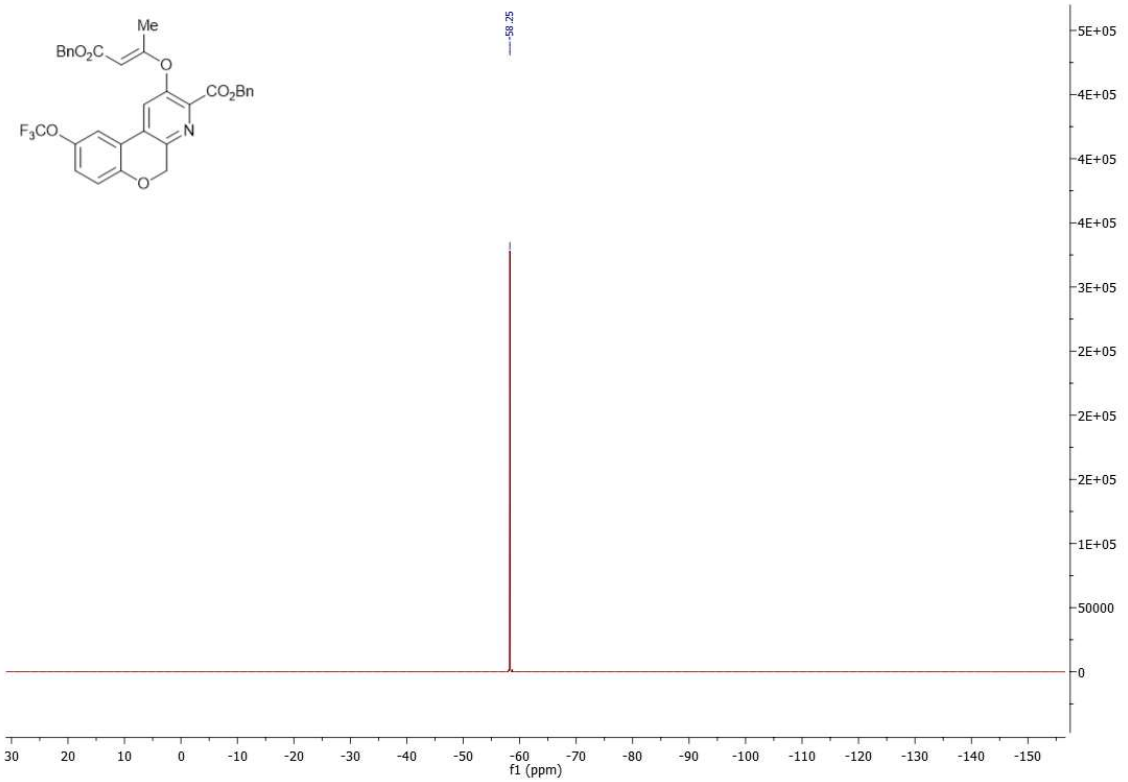


Figure S11b: ^{19}F NMR spectrum of compound **3h** ($CDCl_3$).

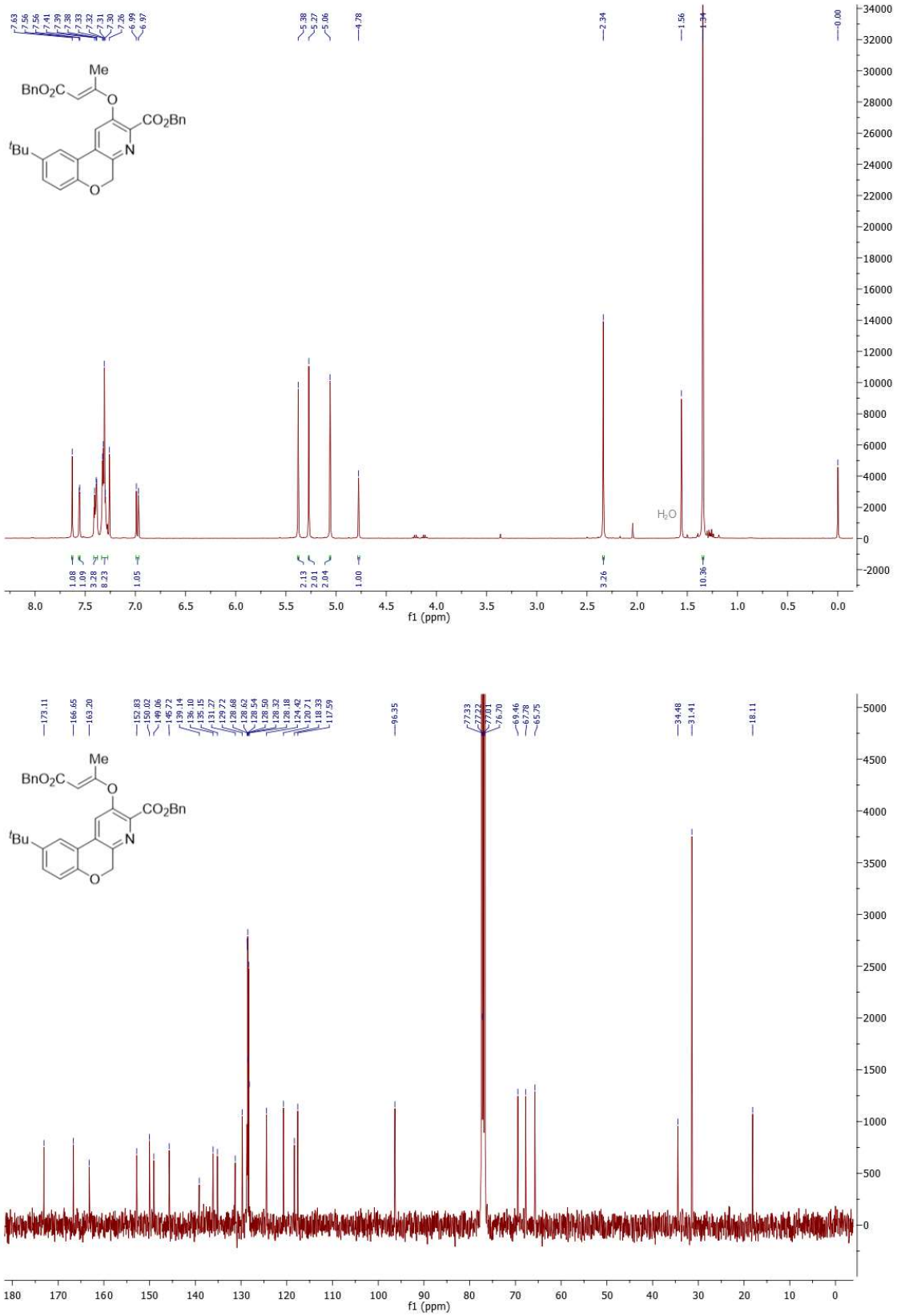


Figure S12: ^{1}H and ^{13}C NMR spectra of compound **3i** ($CDCl_3$).

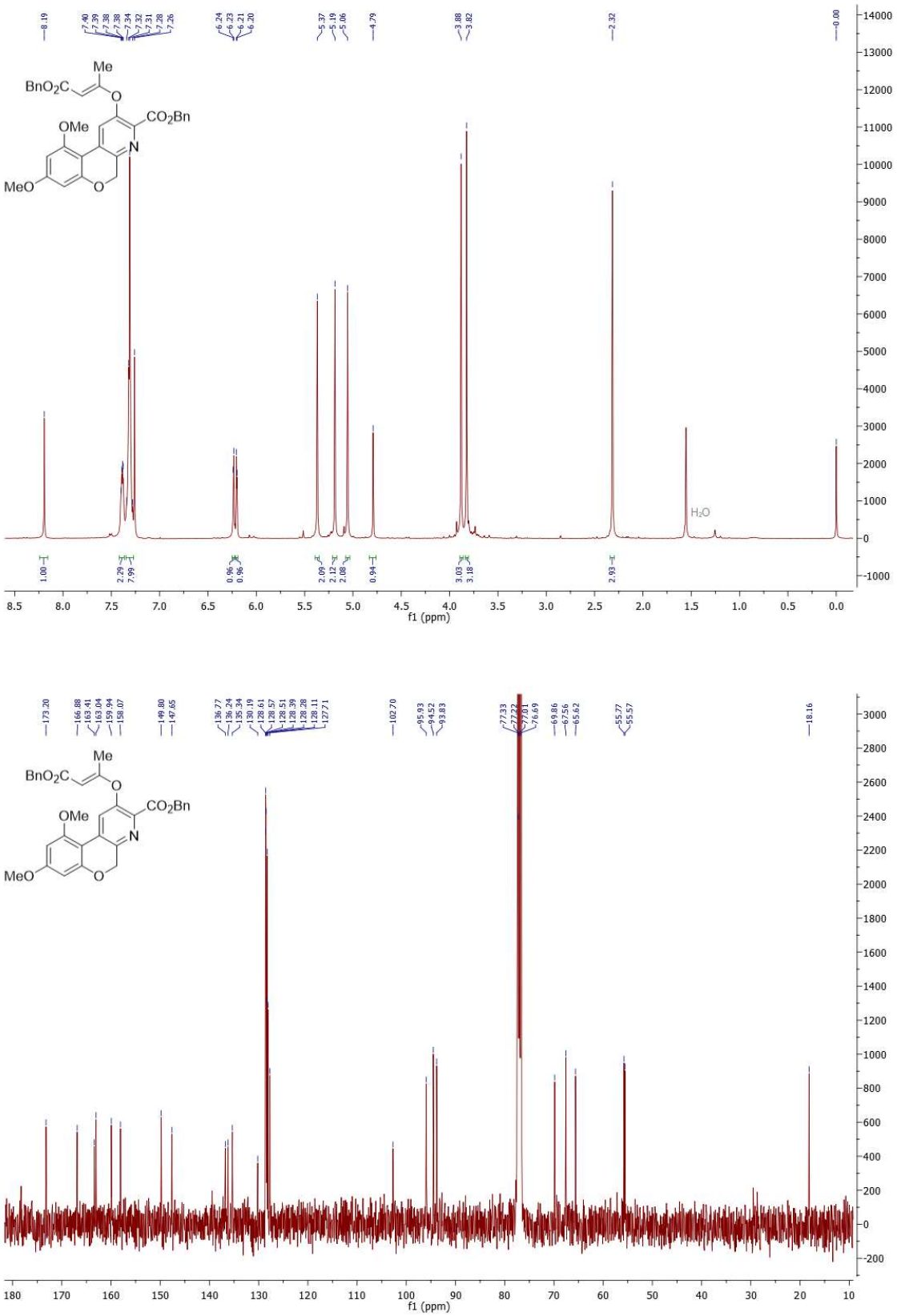


Figure S13: ^{1}H and ^{13}C NMR spectra of compound **3j** ($CDCl_3$).

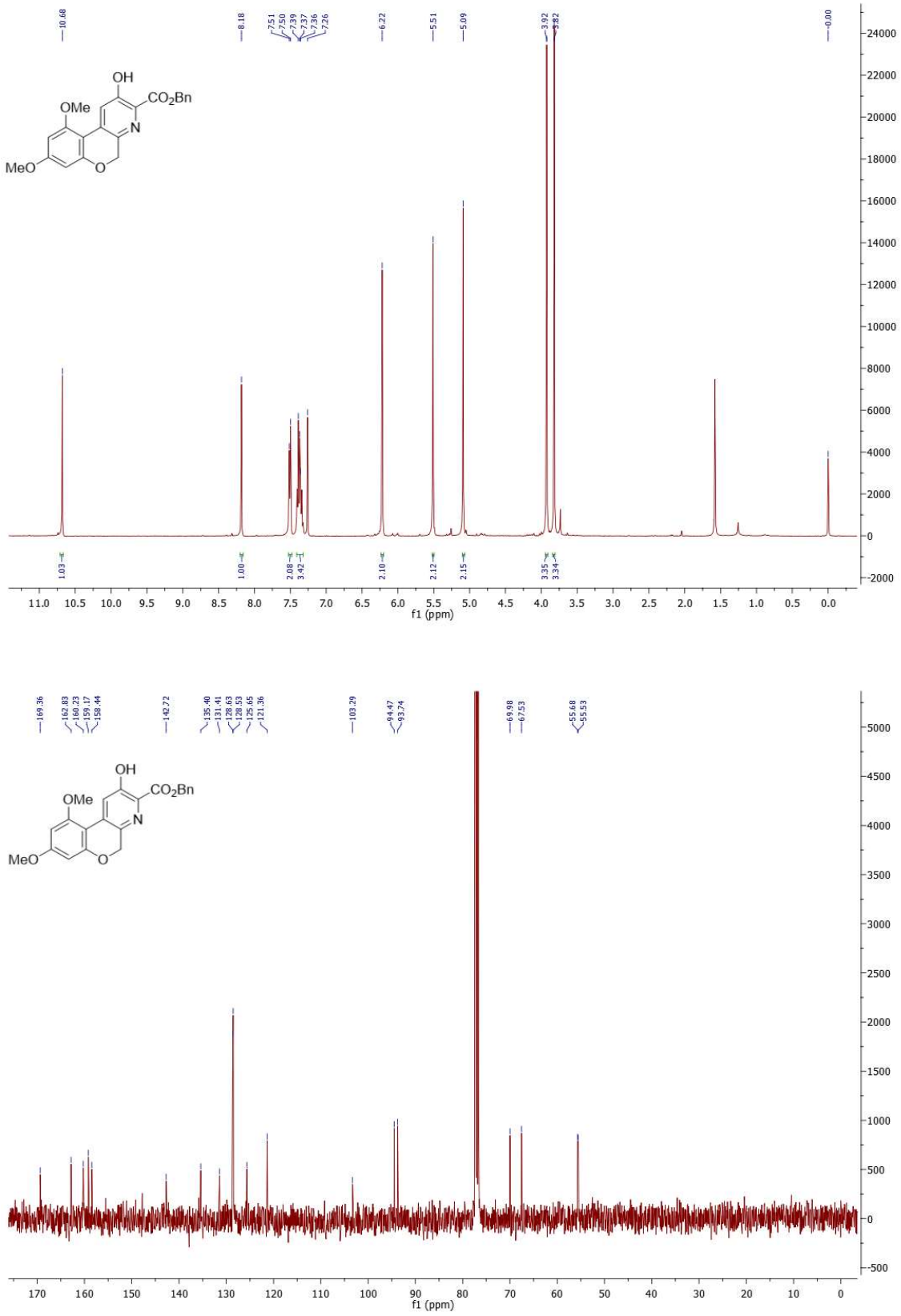


Figure S14: ^{1}H and ^{13}C NMR spectra of compound **4** ($CDCl_3$).

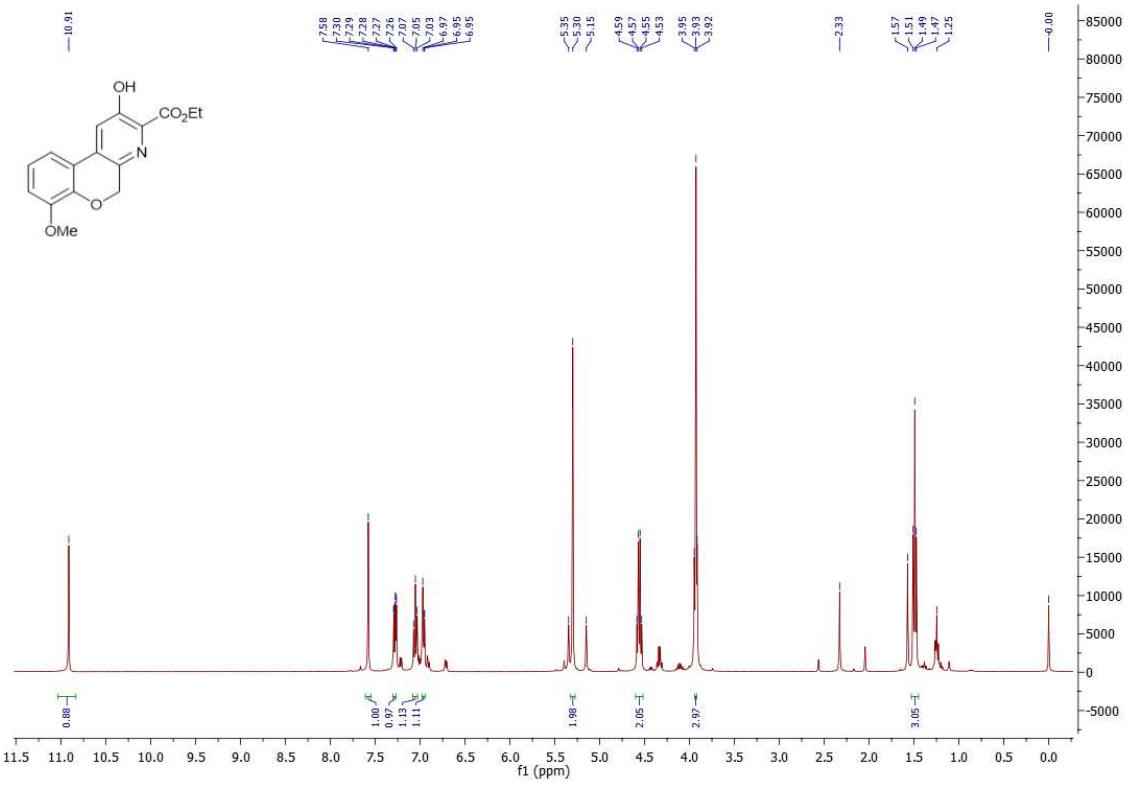


Figure S15: ^{1}H NMR spectrum of compound **6** ($CDCl_3$).

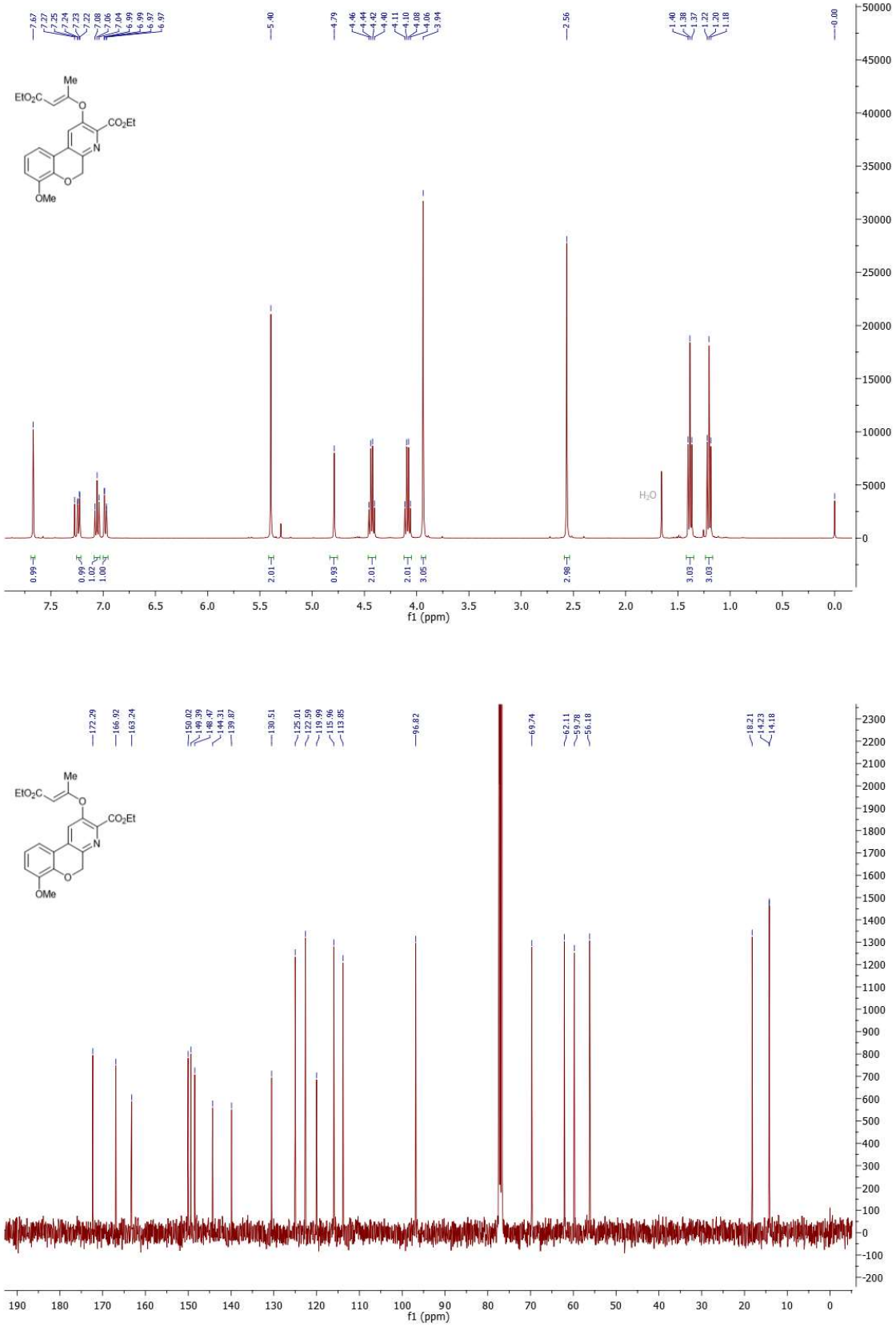


Figure S16a: ^{1}H and ^{13}C NMR spectra of compound **7** ($CDCl_3$).

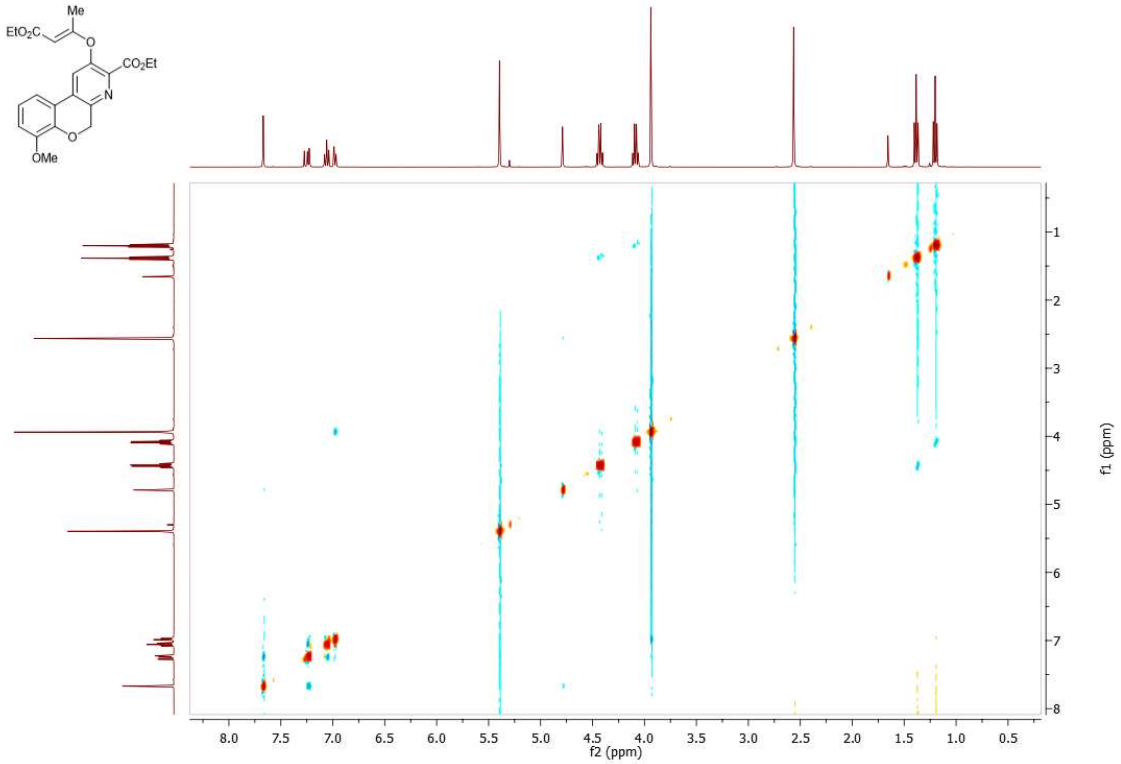


Figure S16b: NOESY spectrum of compound **7** ($CDCl_3$).

Crystallographic Data for Compounds 3b and 4

Table S1: Crystallographic data and details about refinement for structures **3b** and **4**.

	Compound 3b	**Compound 4**
Formula	C_{33} H_{29} N O_7	C_{22} H_{19} N O_6
M	551.57	393.38
λ (Å)	0.71073	0.71073
T (K)	296 (2)	296(2)
crystal system	Triclinic	Triclinic
space group	*P* -1	*P* -1
a (Å)	10.646(2)	8.708(2)
b (Å)	11.634(3)	13.624(4)
c (Å)	12.087(3)	17.004(5)
α (°)	101.823(13)	66.753(6)
β (°)	109.747(10)	79.781(7)
γ (°)	91.715(13)	88.762(7)
V (Å^3)	1371.0(6)	1821.5(9)
Z	2	4
ρ_{calc} (g.cm^{-3})	1.336	1.434
μ (mm^{-1})	0.094	0.105
Crystal size	0.20 x 0.20 x 0.12	0.60 x 0.20 x 0.20
Crystal colour	Yellow	Yellow
Crystal description	Block	Prism
θ_{max} (°)	26.357	25.350
total data	33320	64553
unique data	5500	6676
R_{int}	0.1499	0.2185
R [*I*>2σ(*I*)]	0.0422	0.0946
R_w	0.0985	0.1675
Goodness of fit	1.028	1.025
ρ_{min}	-0.655	-0.284
ρ_{max}	0.184	0.259

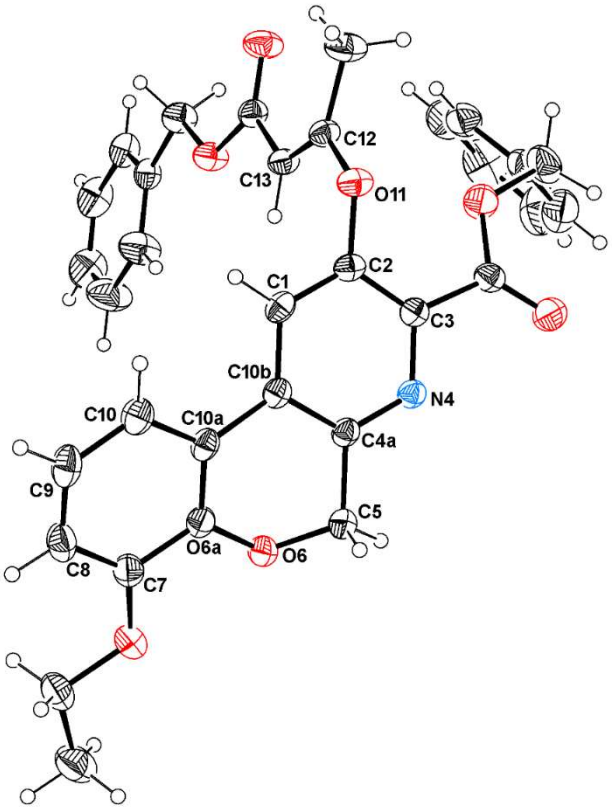


Figure S17. ORTEP-3 representation of compound **3b**, using 30% probability level ellipsoids (CCDC 2079932).

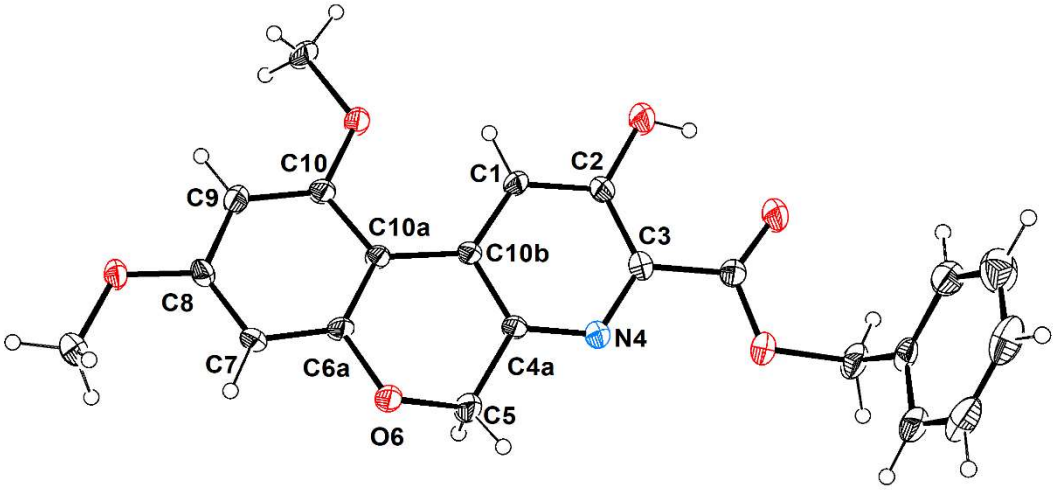
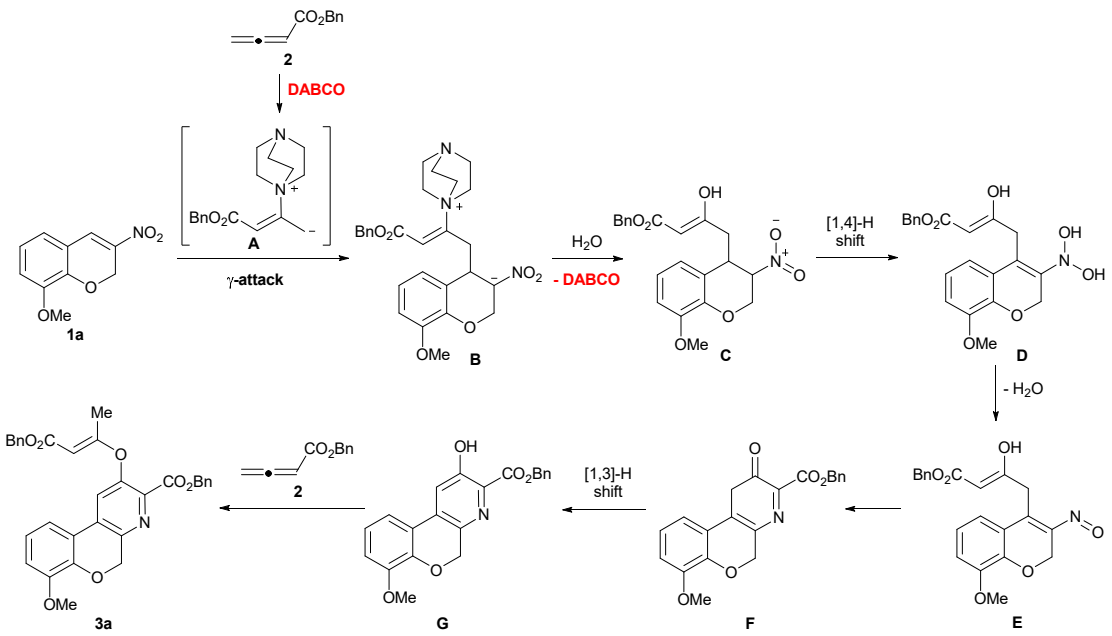


Figure S18. ORTEP-3 representation of compound **4**, using 30% probability level ellipsoids (CCDC 2079933).

Study of the Reaction Mechanism via Mass Spectrometry Analysis



Scheme S1. Proposed mechanism for the synthesis of 5*H*-chromeno[3,4-*b*]pyridines.

Table S2. Characterization of allene **2**, intermediates and final product **3a** by HRMS.

Compound			HRMS results			
Number/ Reference	Formula	Exact mass	Accurate mass	Ion formula	Exact mass	Err (ppm)
2	$C_{11}H_{10}O_2$	174.0681	175.0767	$C_{11}H_{11}O_2$	175.0765	-1.1
A	$C_{17}H_{22}N_2O_2$	286.1681	287.1764	$C_{17}H_{23}N_2O_2$	287.1754	-3.3
B	$C_{27}H_{31}N_3O_6$	493.2213	494.2300	$C_{27}H_{32}N_3O_6$	494.2286	-2.8
C/D	$C_{21}H_{21}NO_7$	399.1318	398.1243	$C_{21}H_{20}NO_7$	398.1245	+0.5
E	$C_{21}H_{19}NO_6$	381.1212	380.1136	$C_{21}H_{18}NO_6$	380.1140	+0.9
F/G	$C_{21}H_{17}NO_5$	363.1108	362.1046	$C_{21}H_{16}NO_5$	362.1034	-3.3
3a	$C_{32}H_{27}NO_7$	537.1788	576.1439	$C_{32}H_{27}KNO_7$	576.1419	-3.4

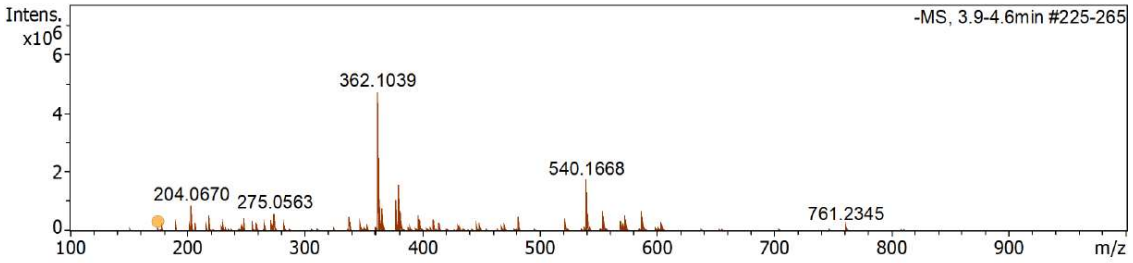


Figure S19. ESI(-)/HRMS spectrum of allene **2**.

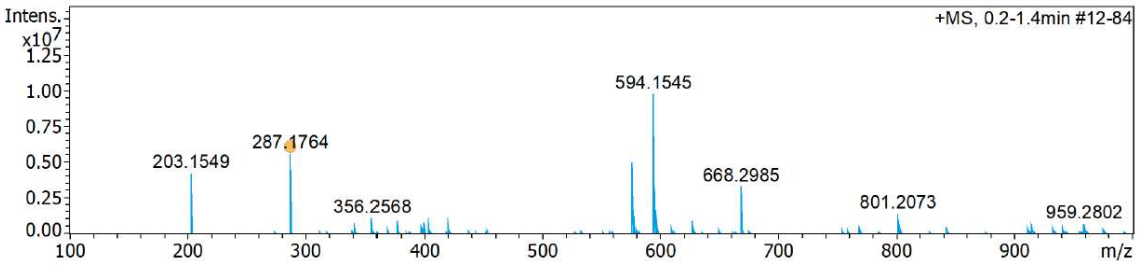


Figure S20. ESI(+)/HRMS spectrum of intermediate **A**.

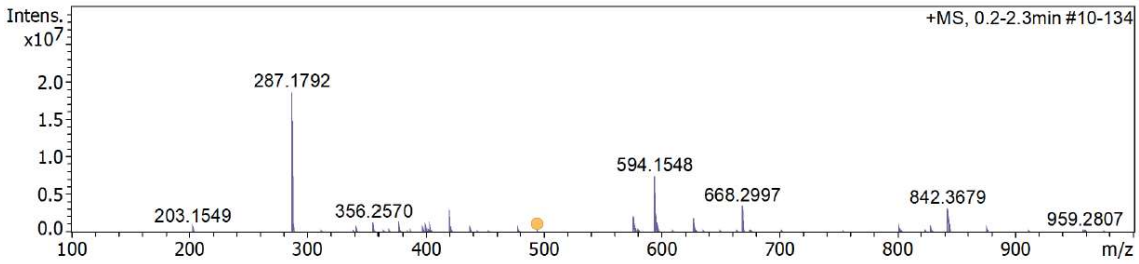


Figure S21. ESI(+)/HRMS spectrum of intermediate **B**.

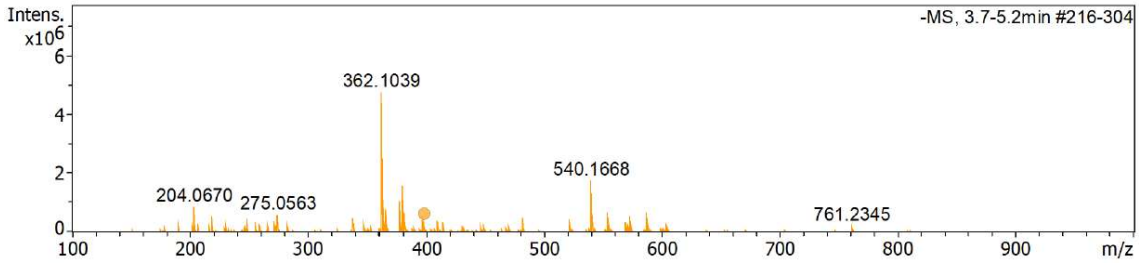


Figure S22. ESI(-)/HRMS spectrum of intermediate **C/D**.

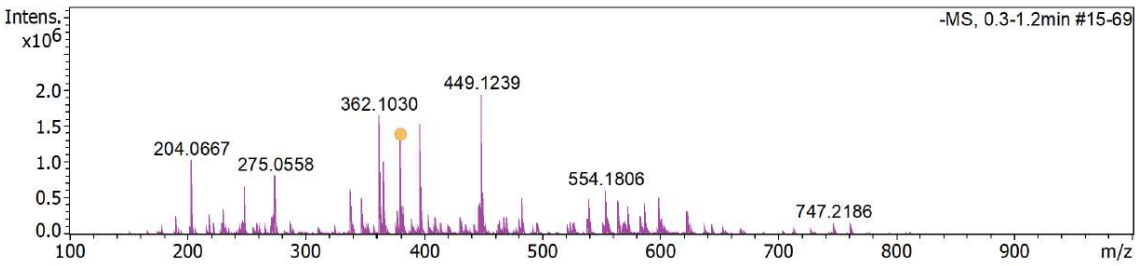


Figure S23. ESI(-)/HRMS spectrum of intermediate **E**.

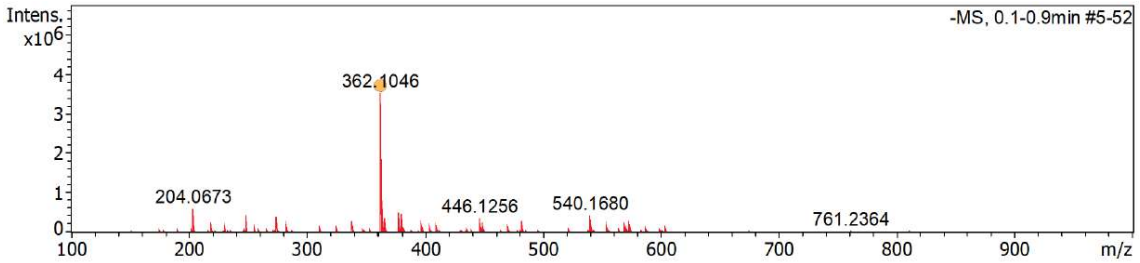


Figure S24. ESI(-)/HRMS spectrum of intermediate **F/G**.

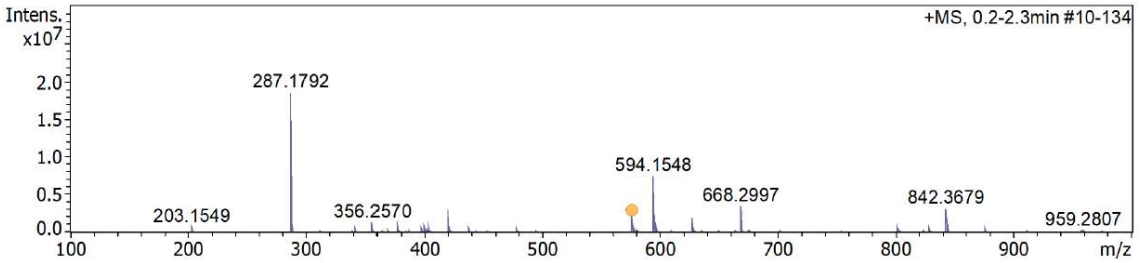


Figure S25. ESI(+)/HRMS spectrum of **3a**.

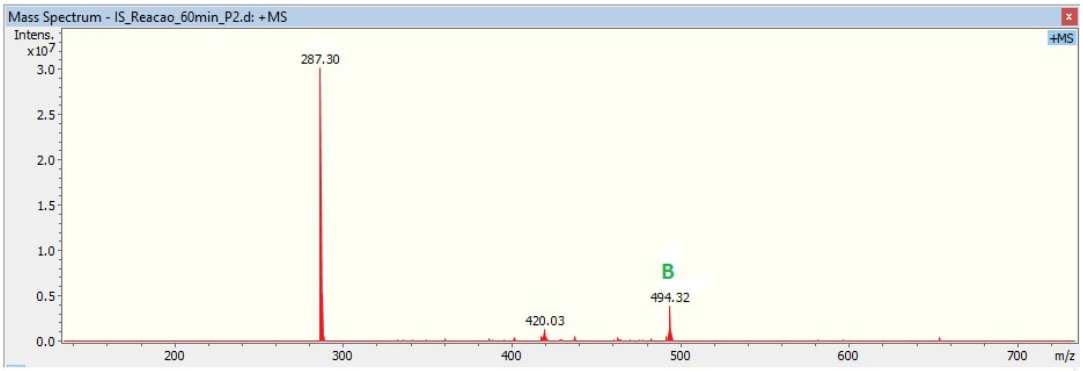


Figure S26. Full scan mass spectrum obtained in the ESI positive mode for the reactional mixture, at 60 min. The peak at *m/z* 494 was assigned to the protonated molecule of intermediate **B**. This precursor ion was isolated in the QIT mass analyser and CID experiments were done in order to obtain the MS^2 spectrum.

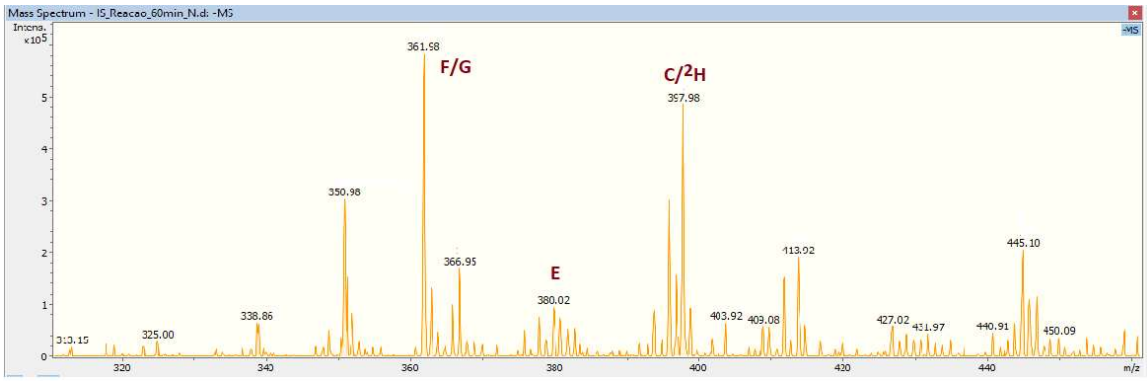


Figure S27. Full scan mass spectrum obtained in the ESI negative mode for the reactional mixture, at 60 min. The peaks at *m/z* 398, 380 and 362 were assigned to the deprotonated molecules of intermediates **C/D, E** and **F/G**, respectively. These precursor ions were isolated in the QIT analyser and CID experiments were performed in order to obtain the MS^2 spectra.

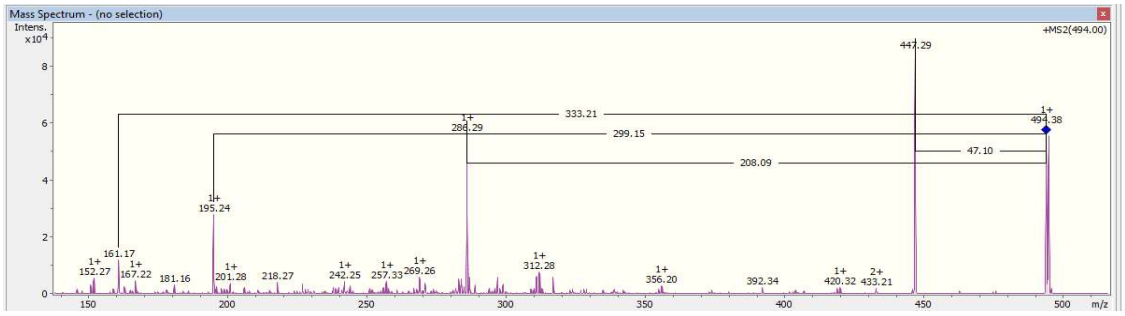


Figure S28. ESI(+)/MS^2 spectrum of precursor ion *m/z* 494.

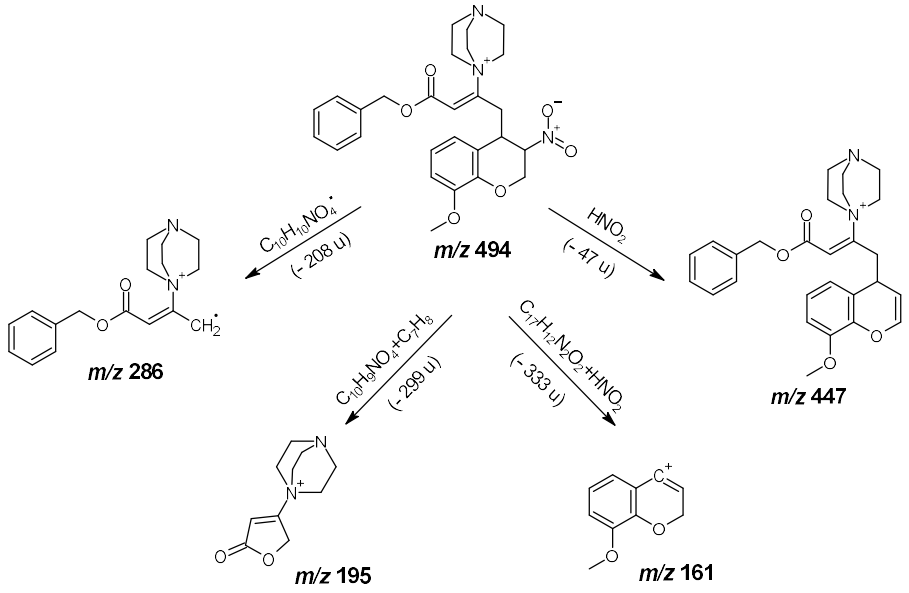


Figure S29. Proposed fragmentation patterns for the protonated molecule *m/z* 494 of intermediate **B**.

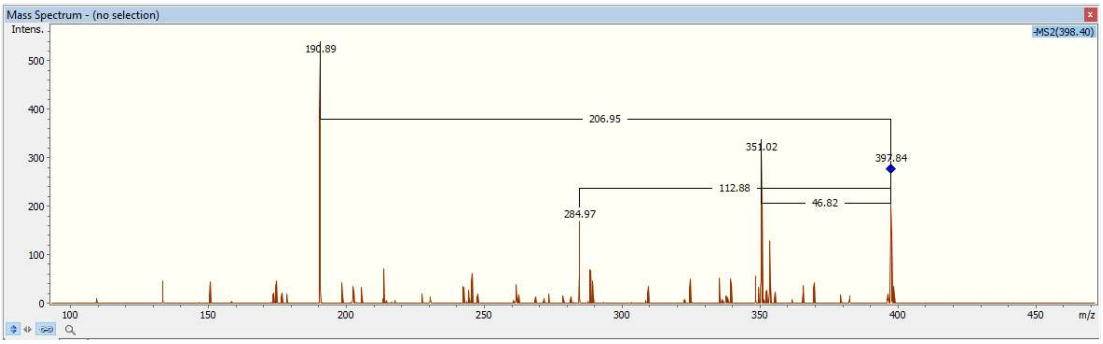


Figure S30. ESI(-)/MS^2 spectrum of precursor ion *m/z* 398.

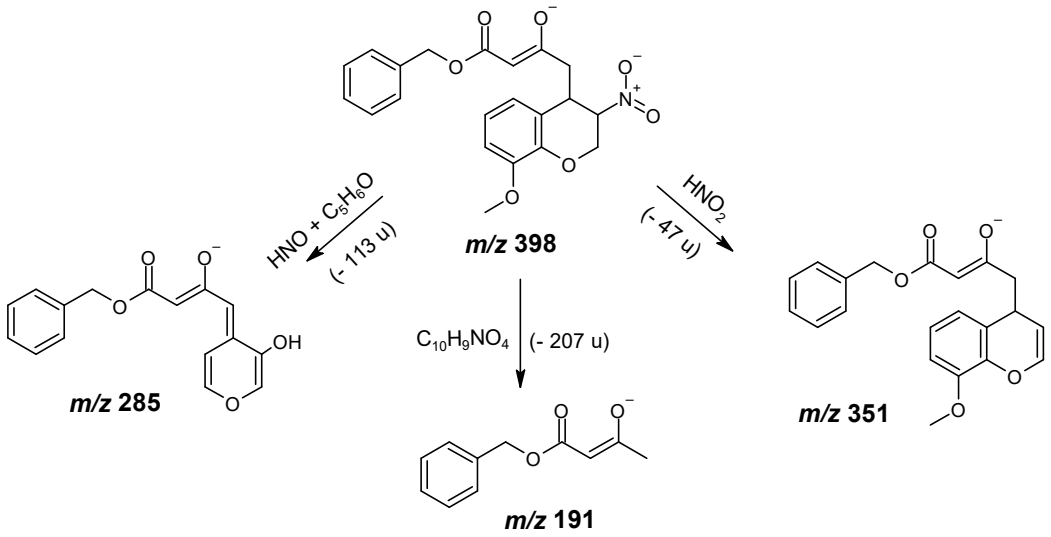


Figure S31. Proposed fragmentation patterns for the deprotonated molecule *m/z* 398 of intermediates **C/D**.

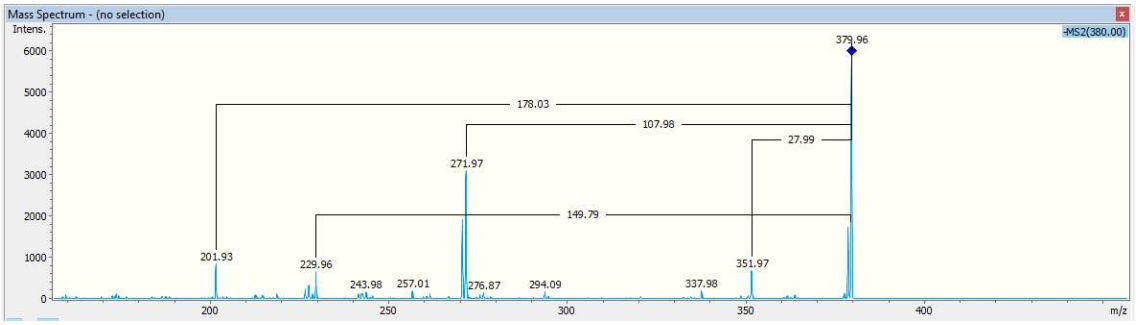


Figure S32. ESI(-)/MS^2 spectrum of precursor ion *m/z* 380.

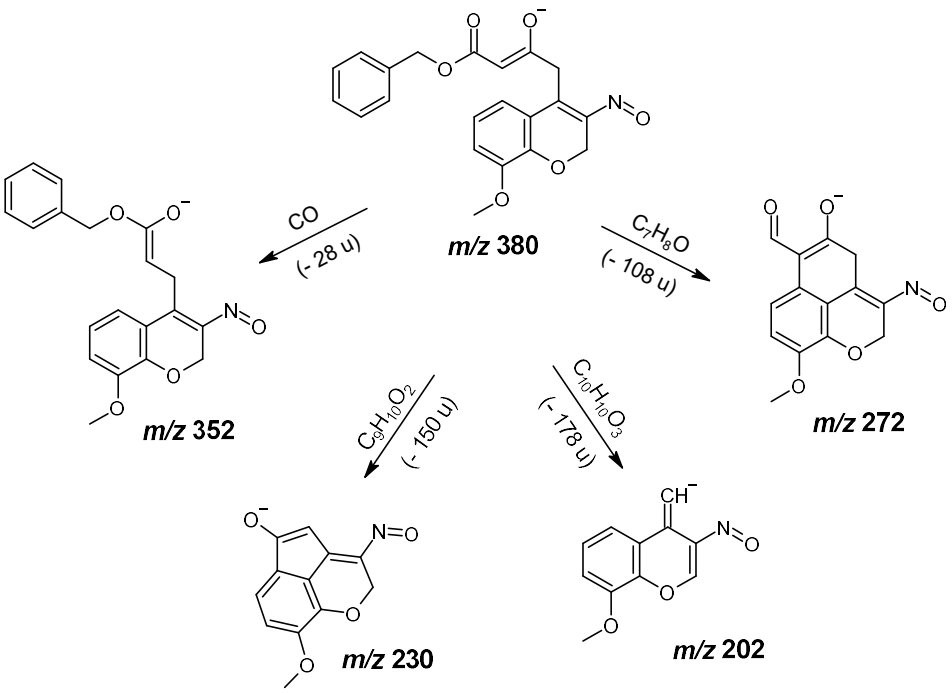


Figure S33. Proposed fragmentation patterns for the deprotonated molecule *m/z* 380 of intermediate **E**.

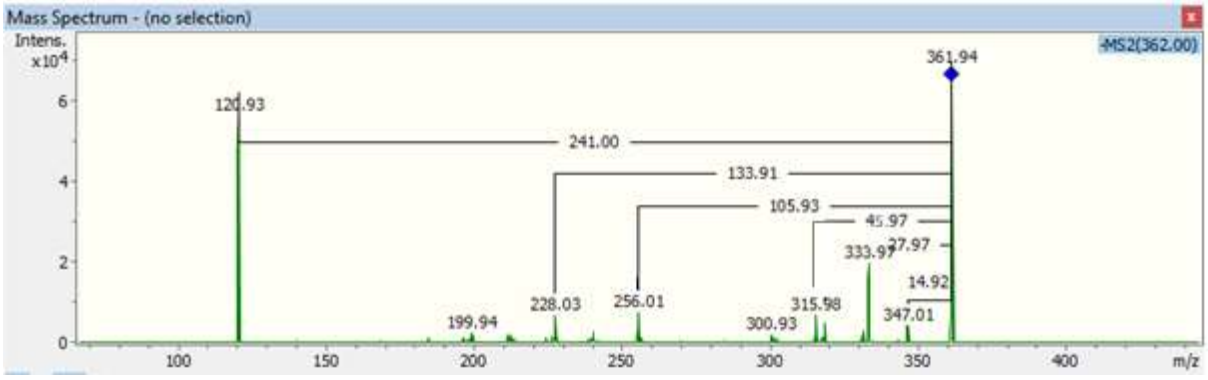


Figure S34. ESI(-)/MS^2 spectrum of precursor ion *m/z* 362.

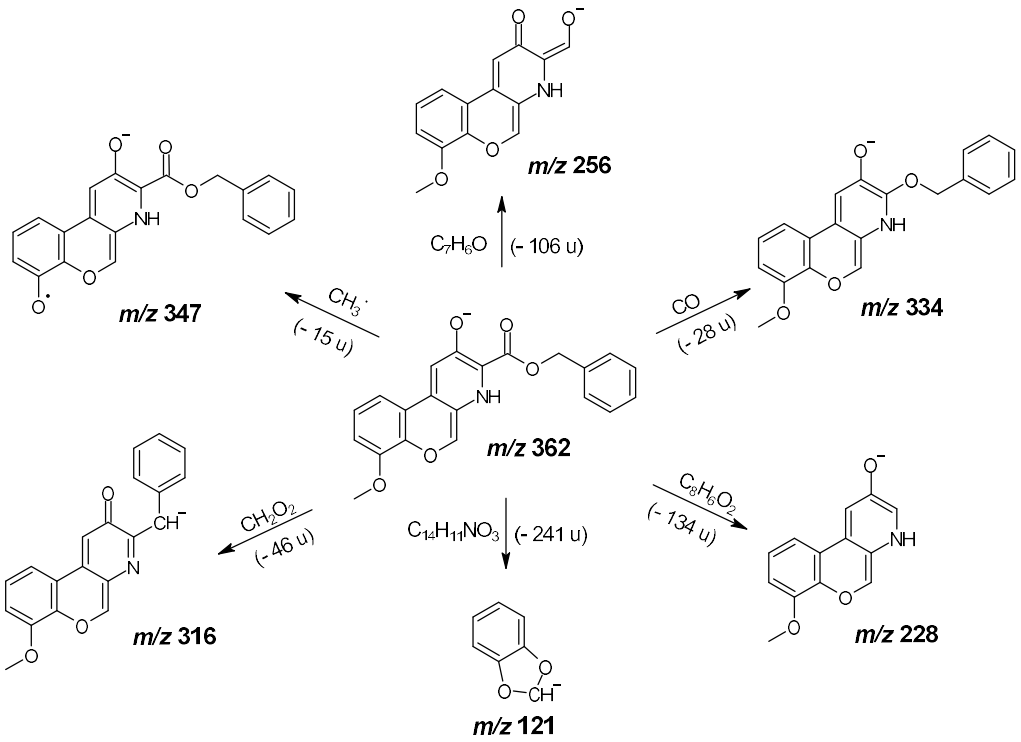


Figure S35. Proposed fragmentation patterns for the deprotonated molecule *m/z* 362 of intermediates **F/G**.