

Supplementary Material

Preparation of tetrahydro-1*H*-xanthen-1-one and chromen-1-one derivatives via a Morita-Baylis-Hillman/oxa-Michael/elimination cascade

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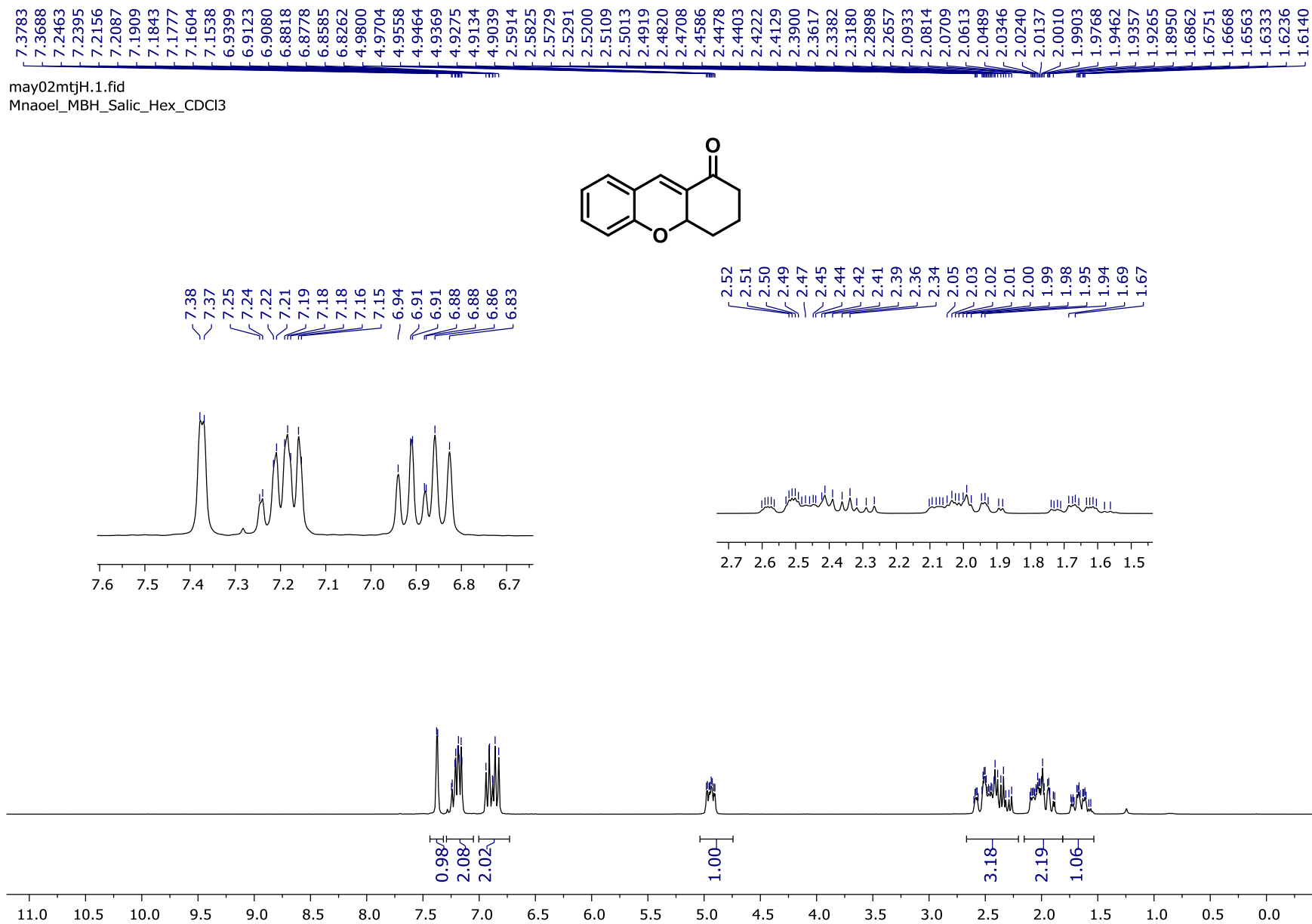
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^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for compounds 3a-m, 4a-c and 5a-b (only resonance signals associated with each compound have been integrated and/or assigned chemical shift values)

Figure S1. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3a**.

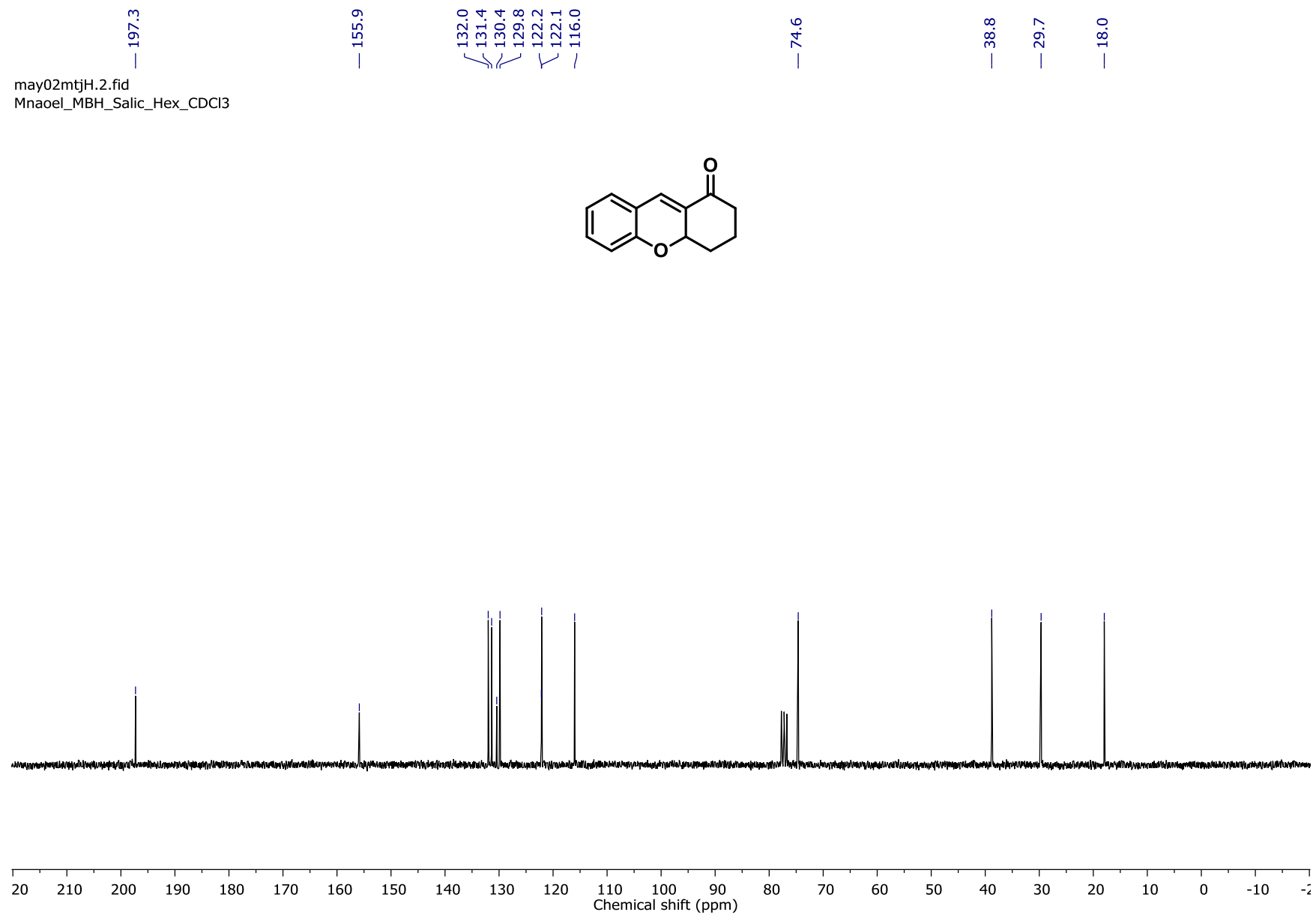


Figure S2. ^{13}C NMR spectrum (63 MHz, CDCl_3) of compound **3a**.

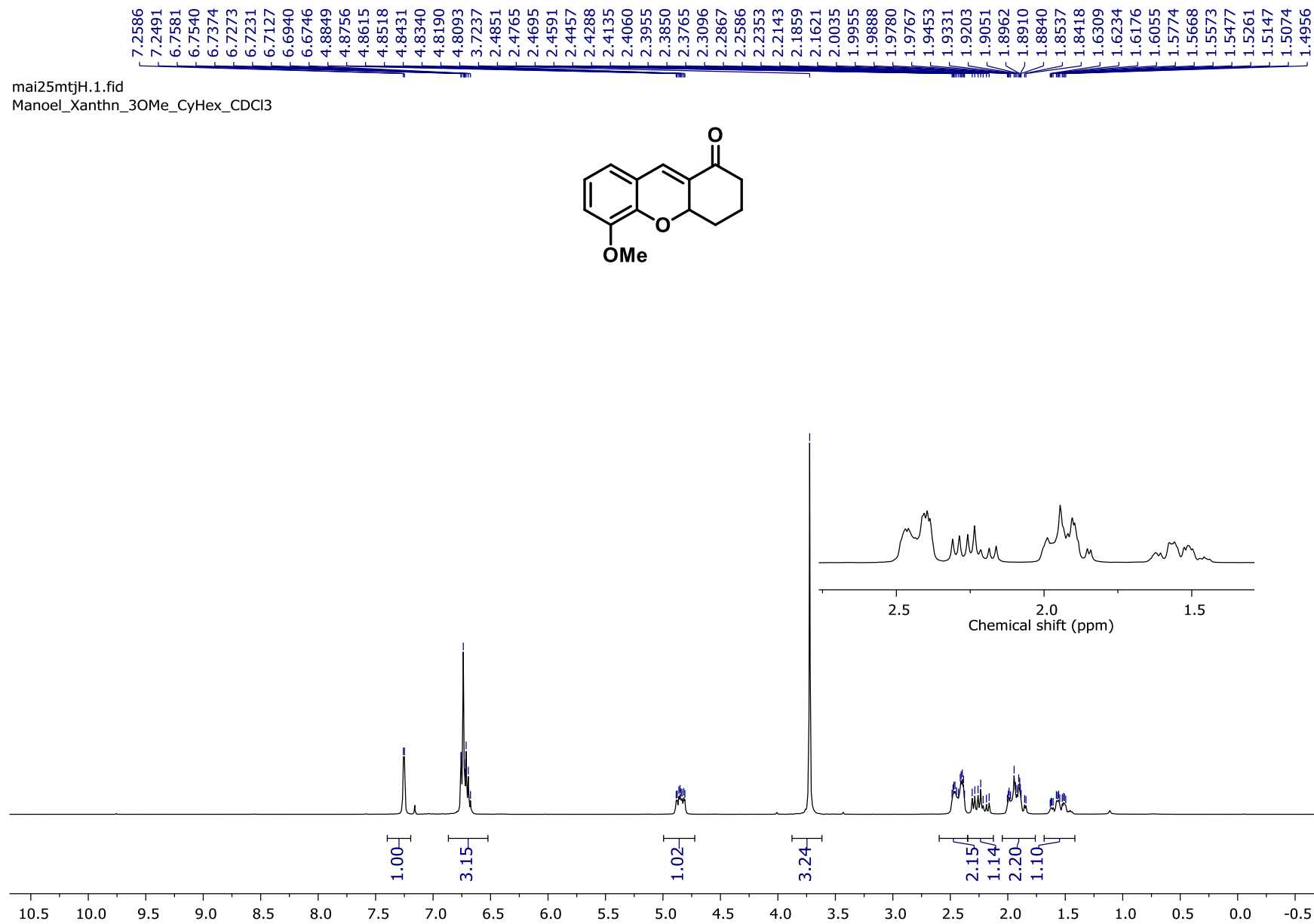
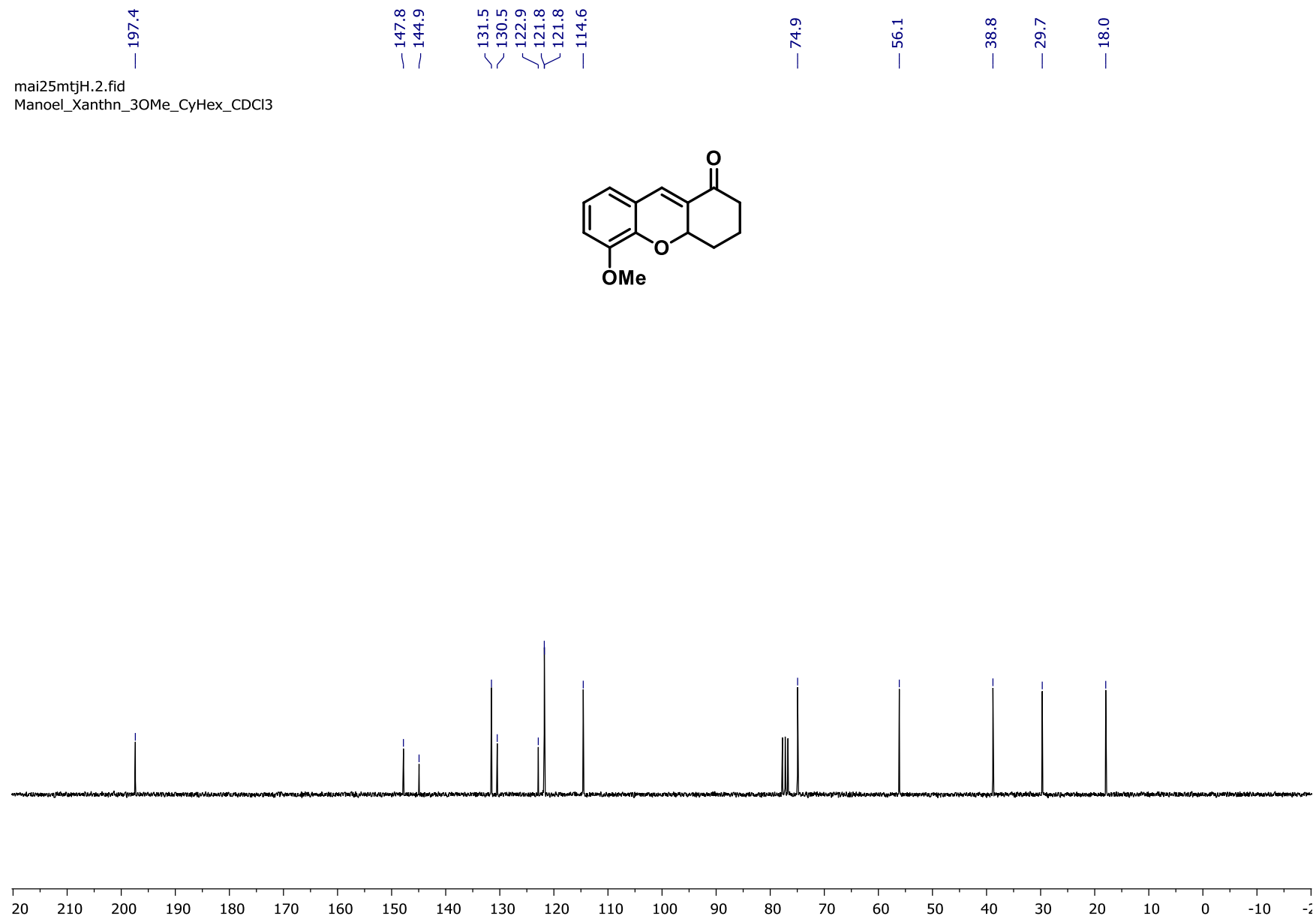
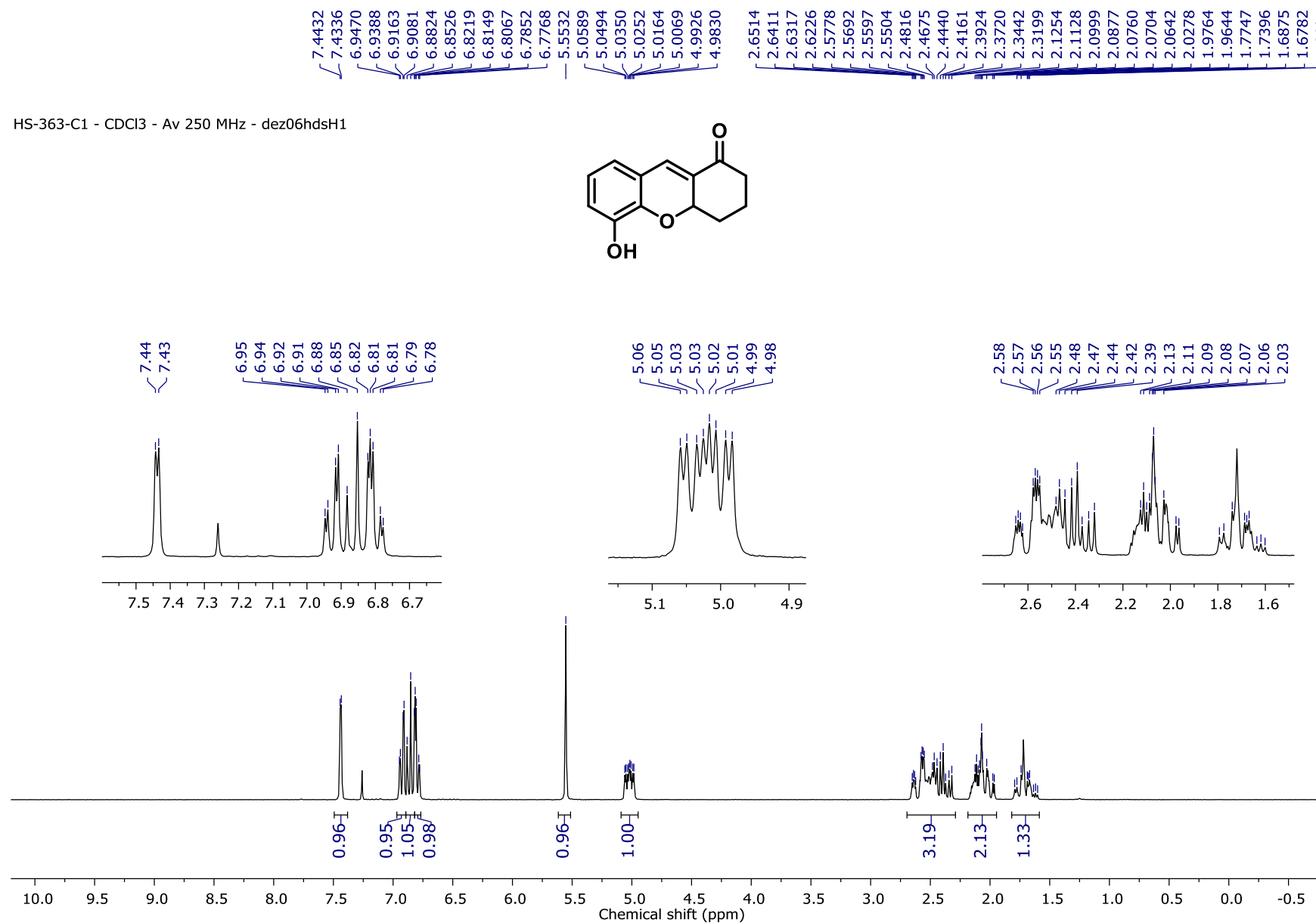


Figure S3. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3b**.



Figure S5. ¹H NMR spectrum (250 MHz, CDCl₃) of compound 3c.

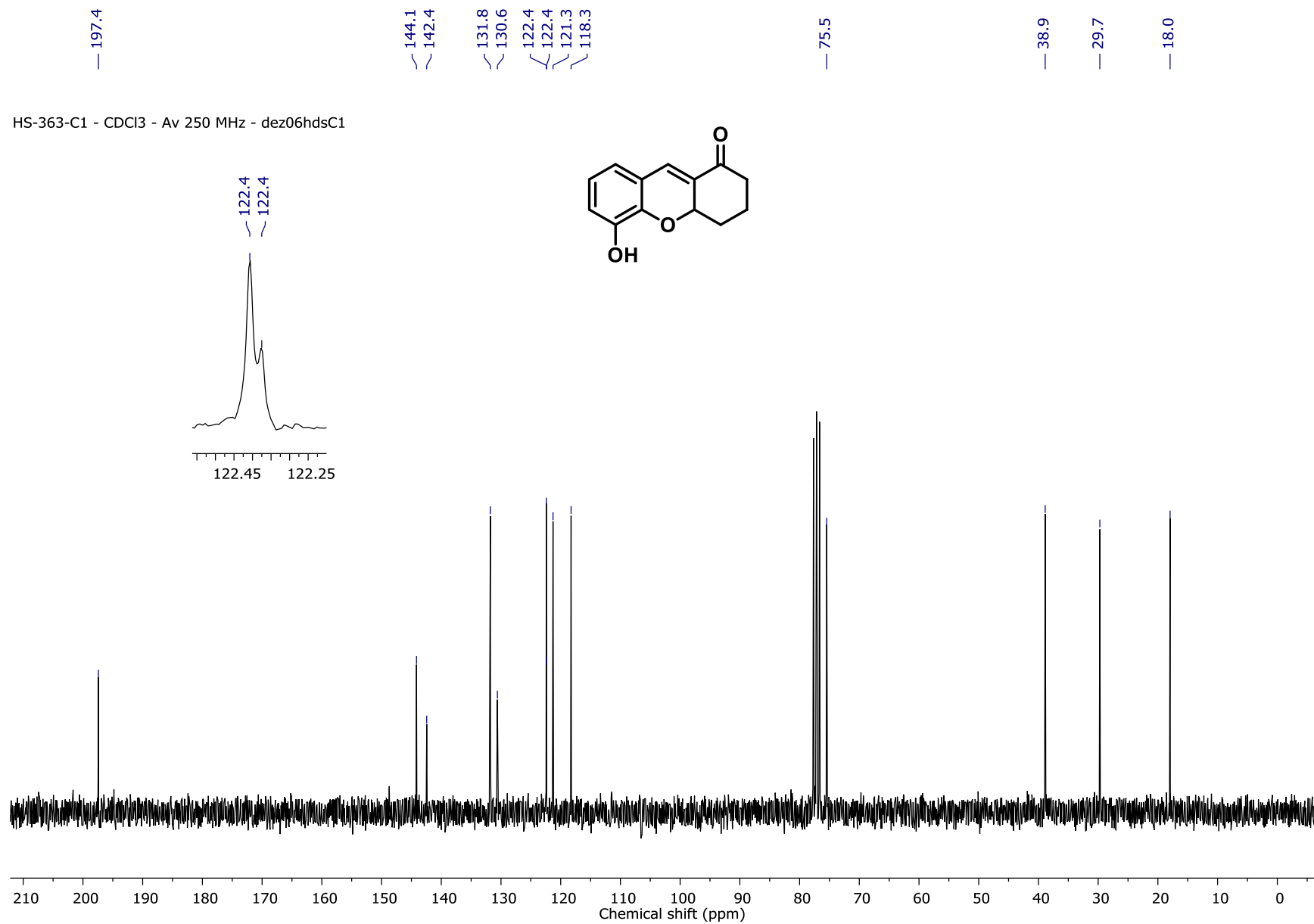


Figure S6. ¹³C NMR spectrum (63 MHz, CDCl₃) of compound **3c**.

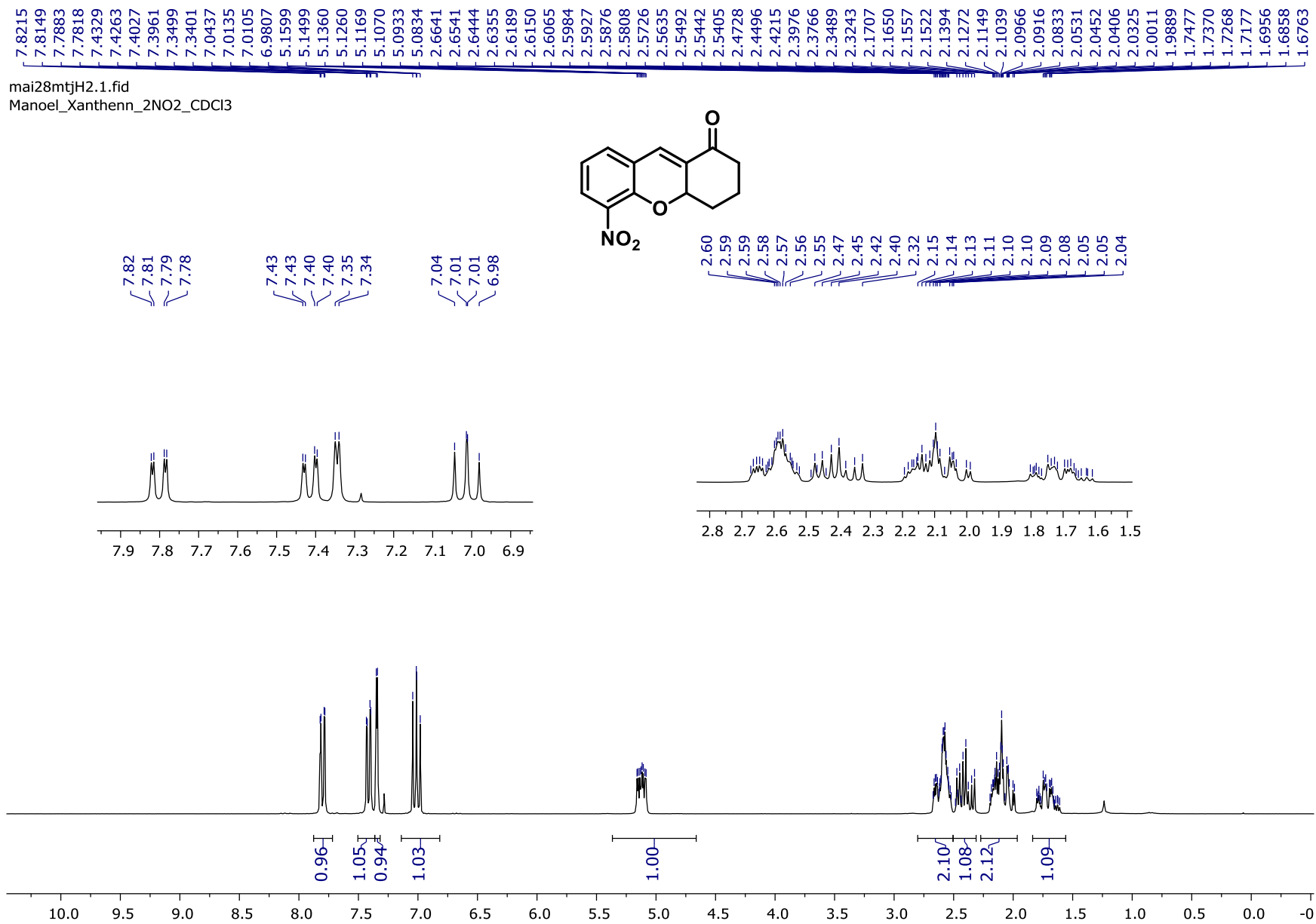


Figure S7. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3d**.

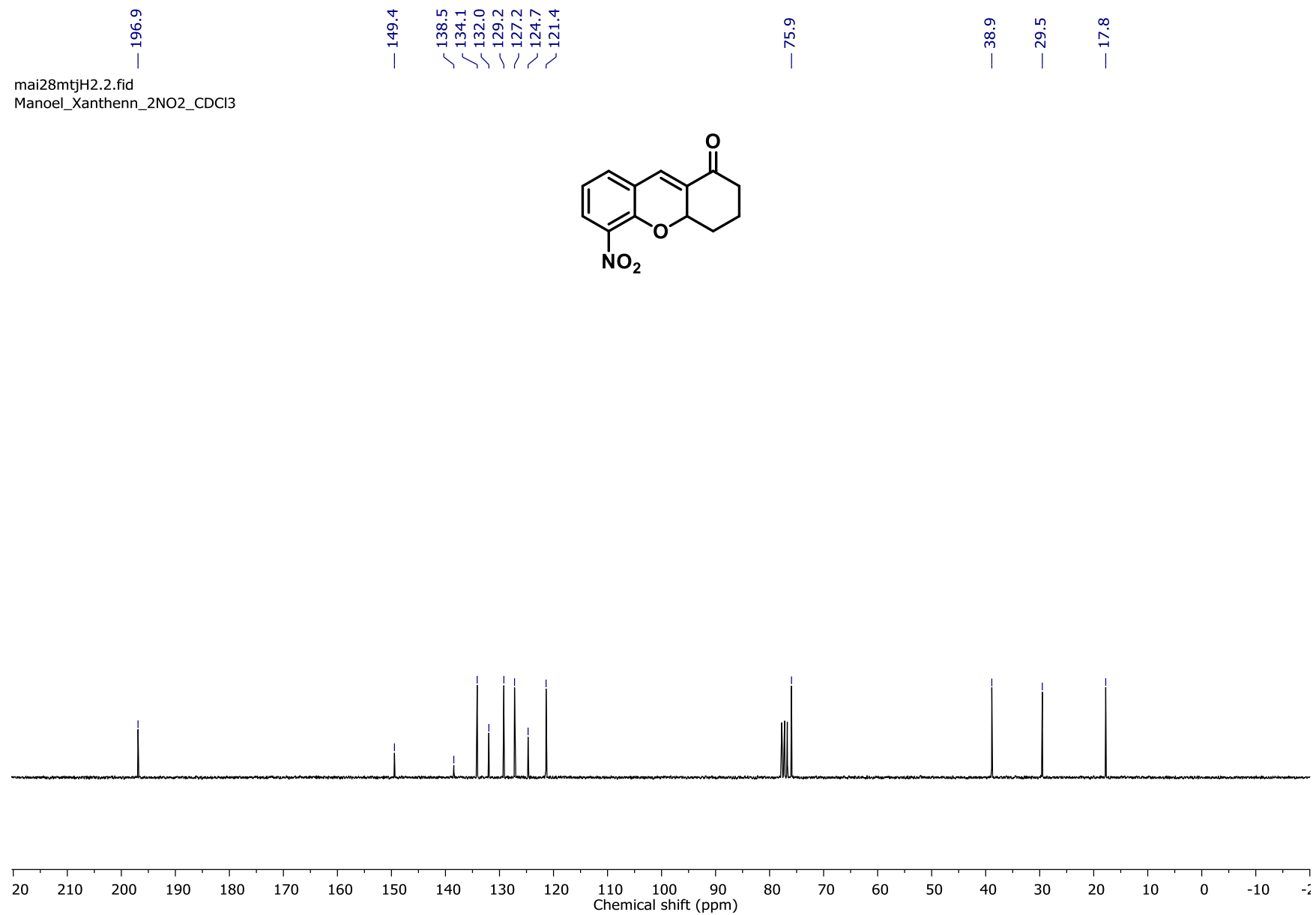
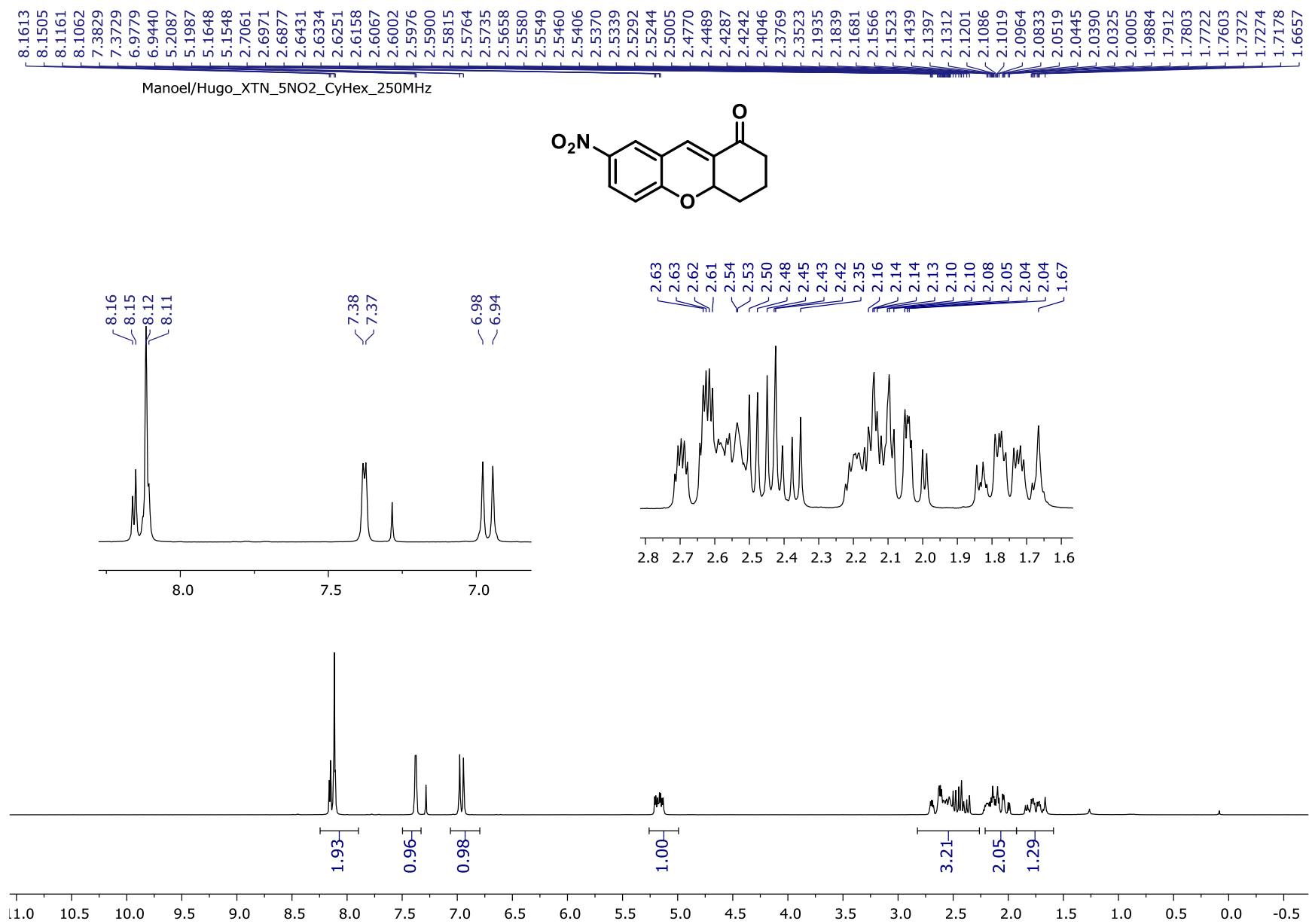


Figure S8. ^{13}C NMR spectrum (63 MHz, CDCl_3) of compound **3d**.

Figure S9. ^1H NMR spectrum (250 MHz, CDCl_3) of compound 3e.

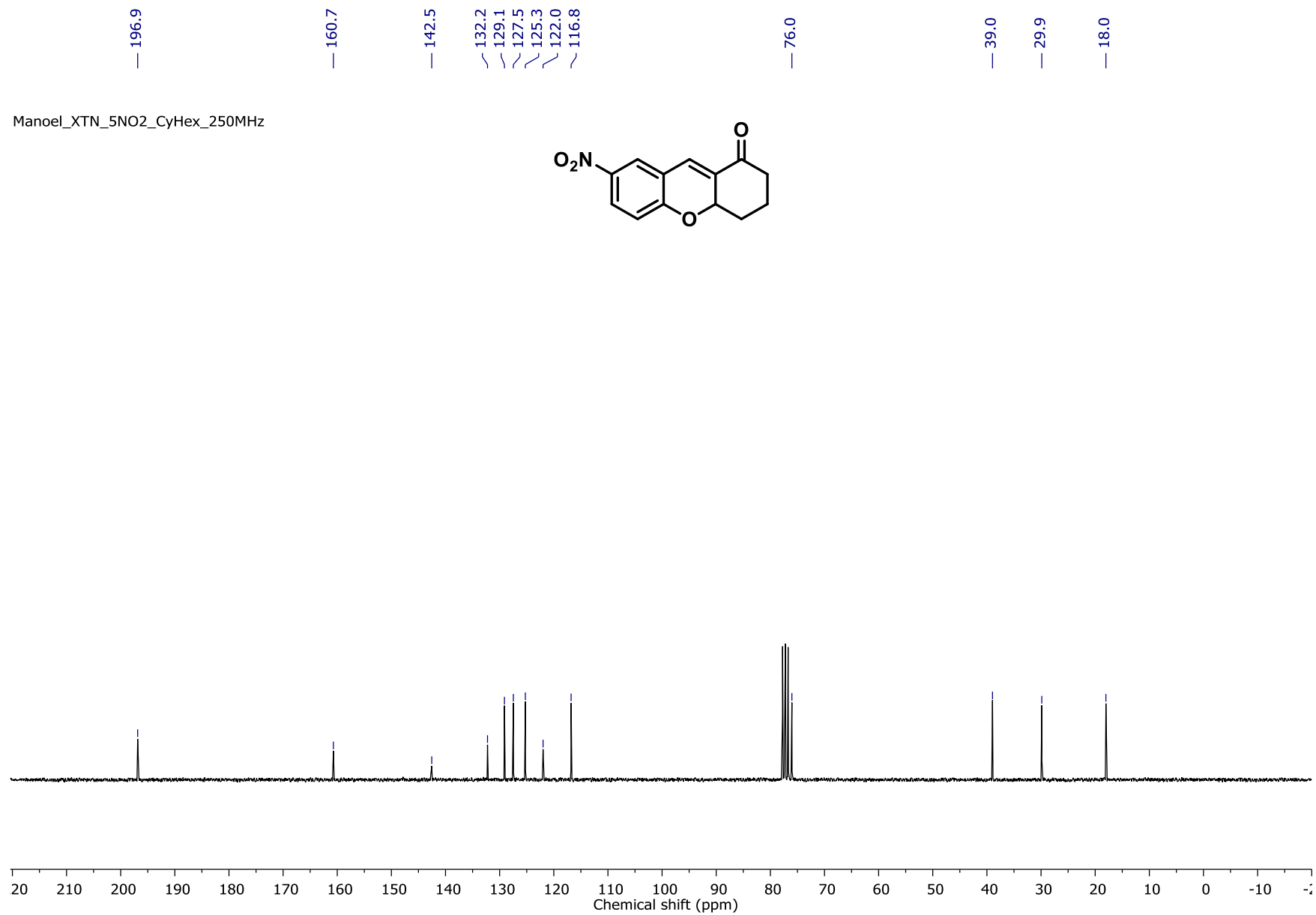
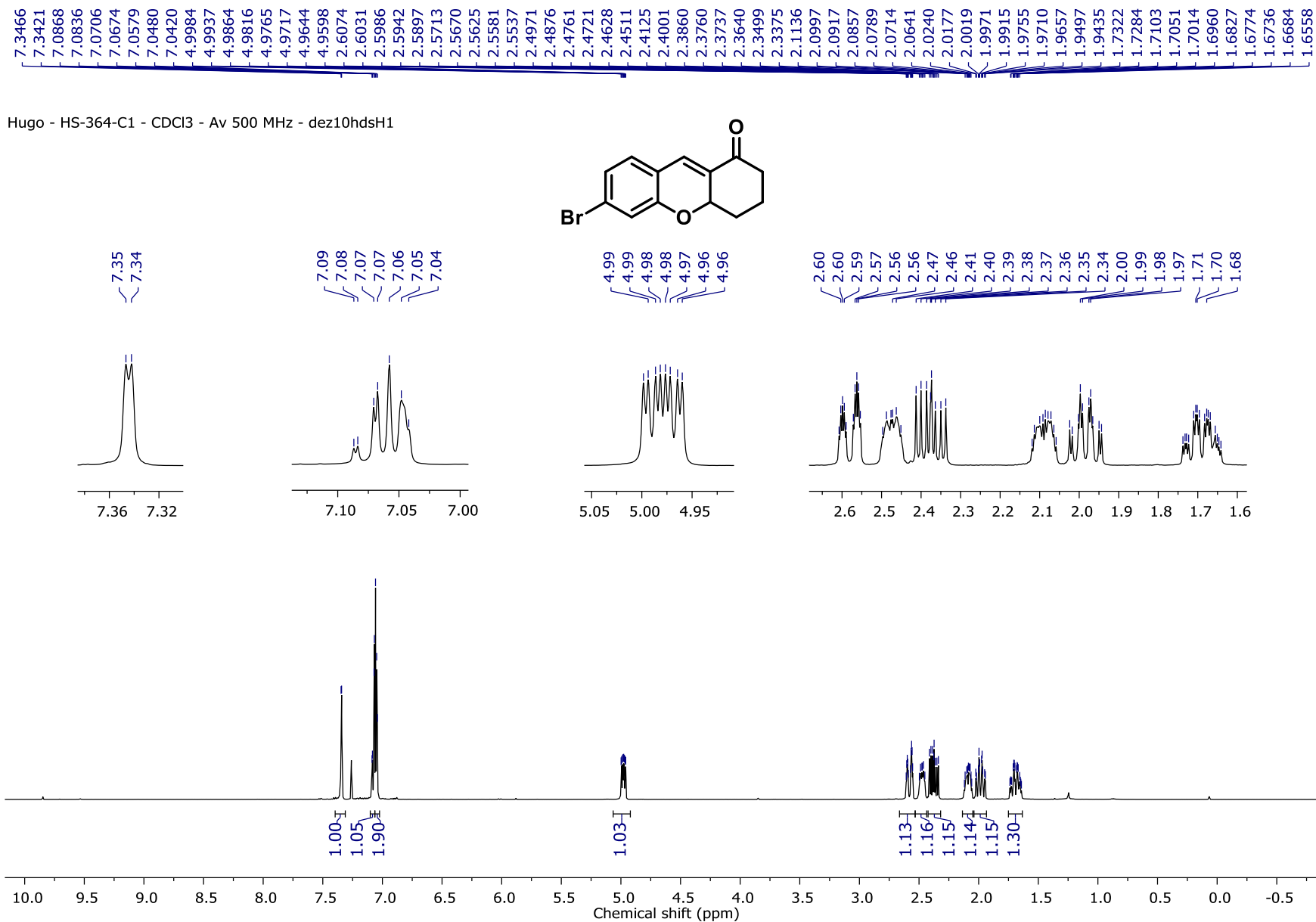


Figure S10. ^{13}C NMR spectrum (63 MHz, CDCl_3) of compound **3e**.

Figure S11. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **3f**.

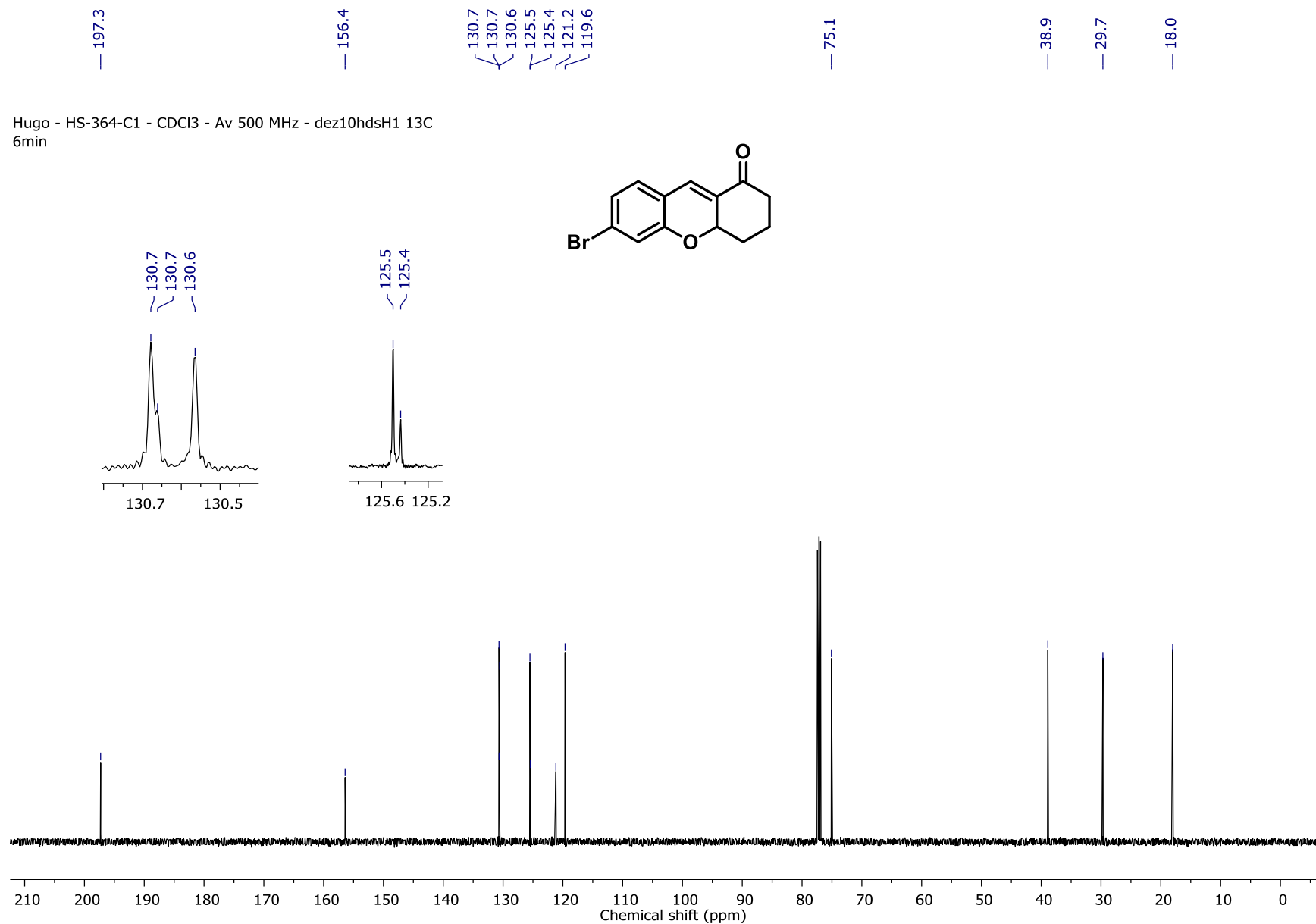


Figure S12. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound **3f**.

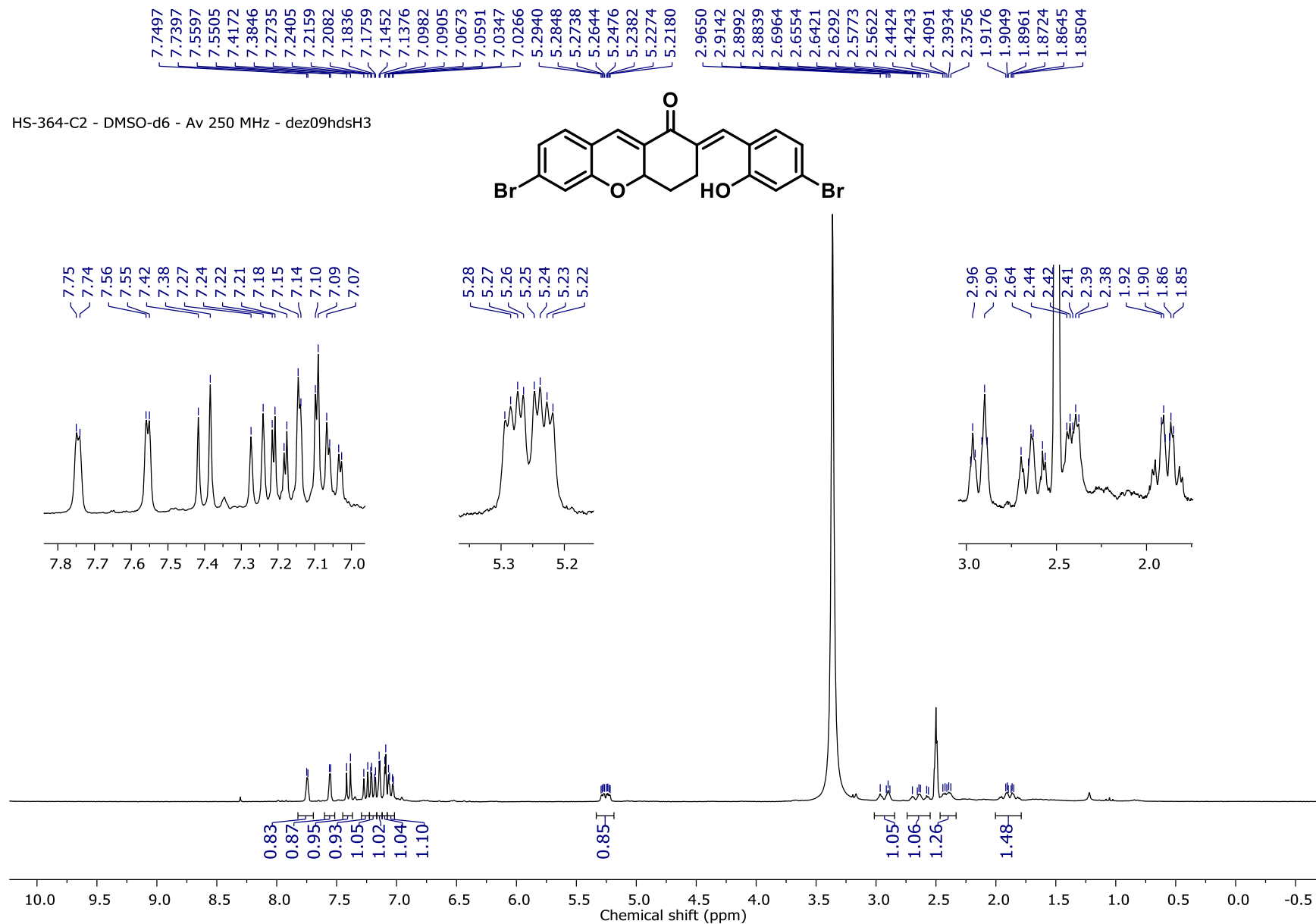


Figure S13. ¹H NMR spectrum (250 MHz, DMSO-d₆) of compound 4a.

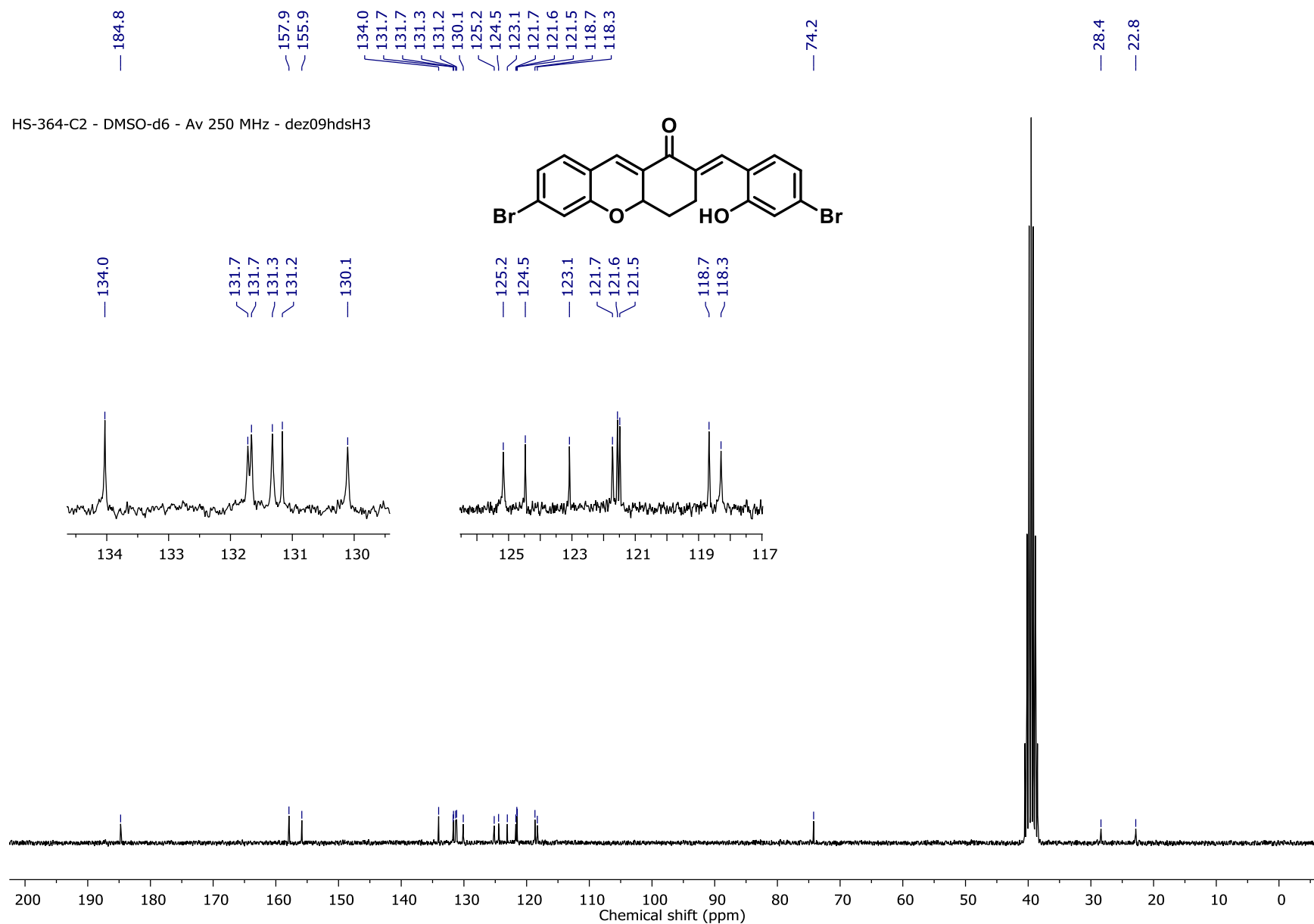
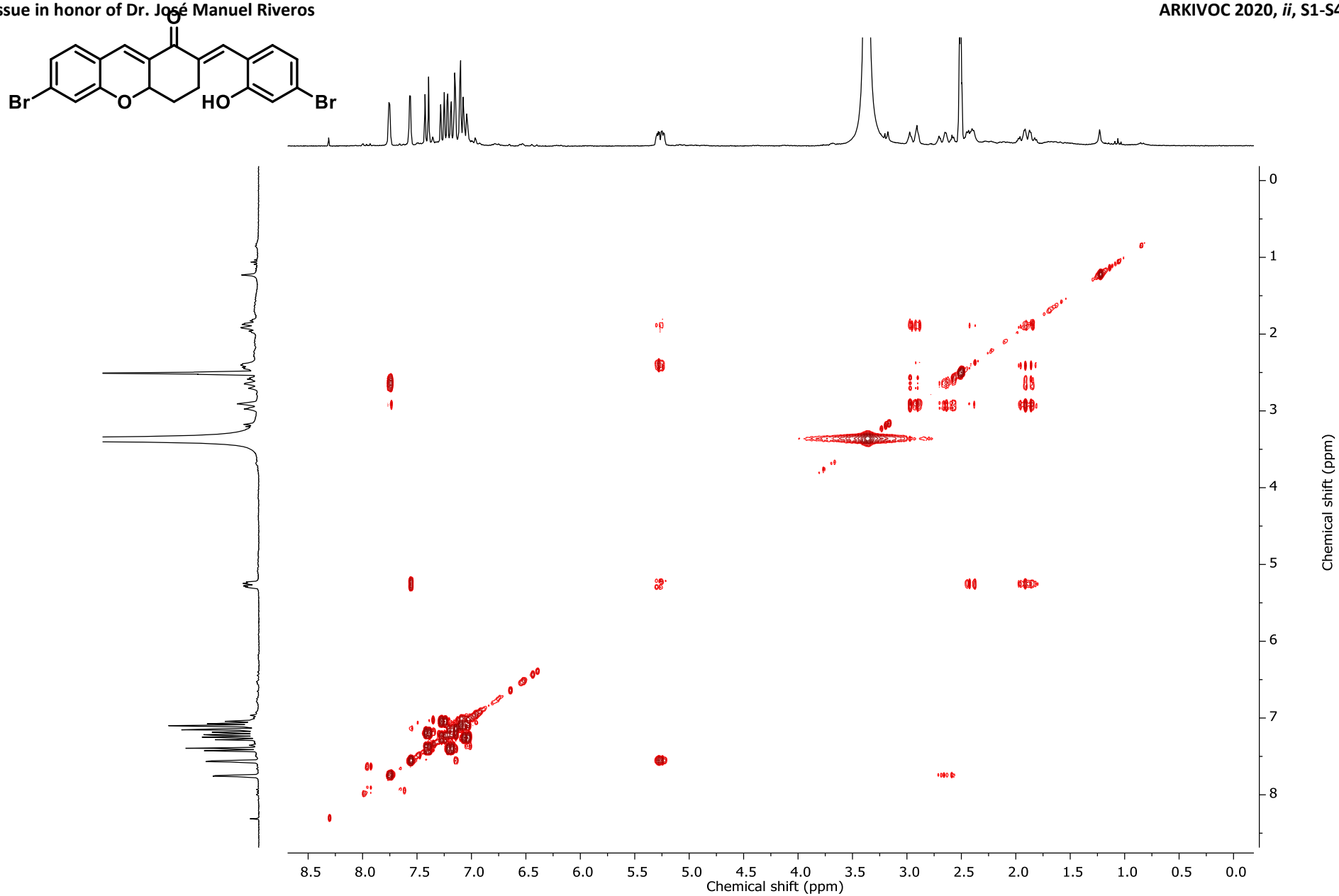


Figure S14. ¹³C NMR spectrum (63 MHz, DMSO-*d*₆) of compound **4a**.



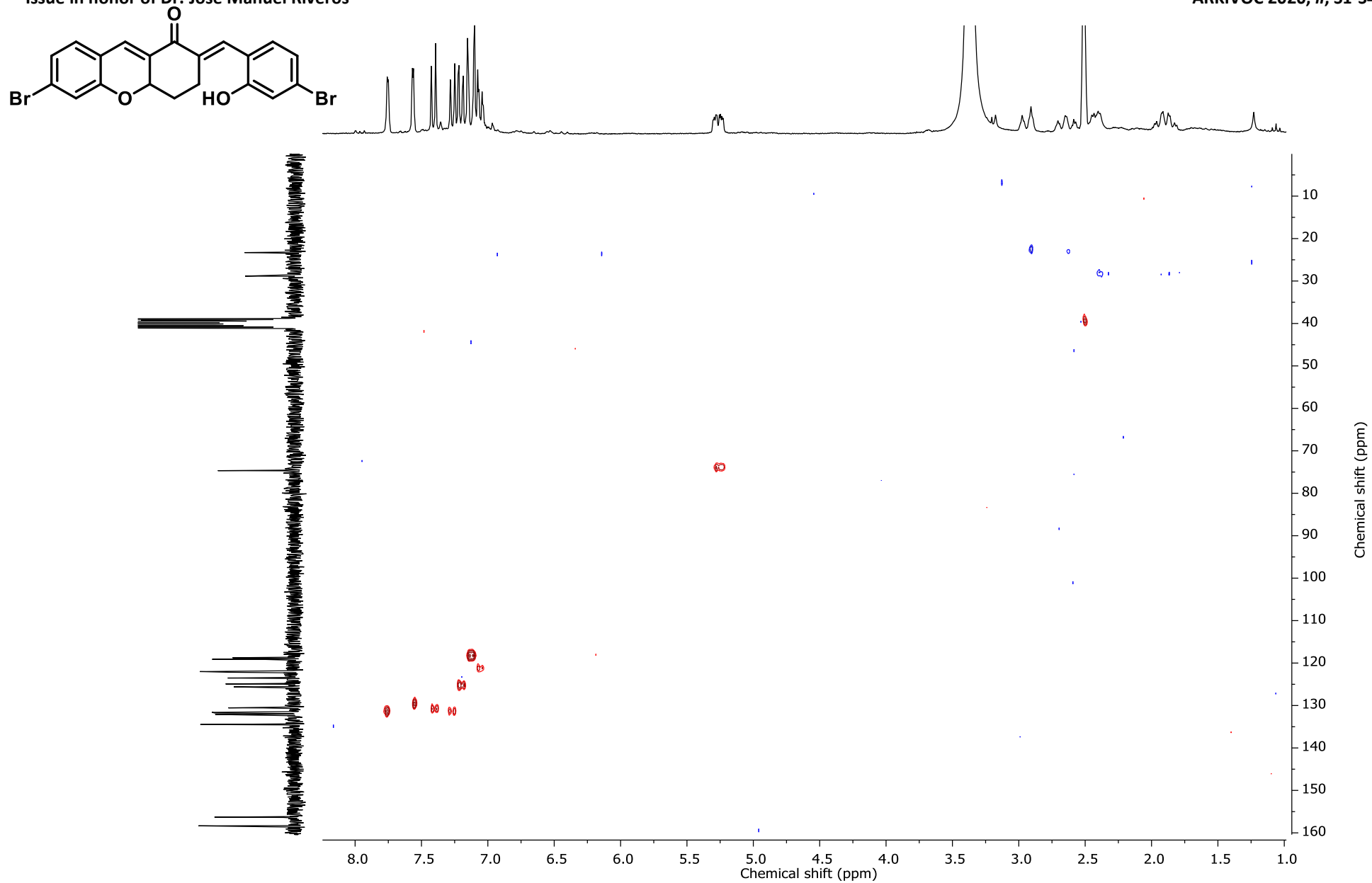


Figure S16. ^1H - ^{13}C HSQC NMR contour plot (250 MHz, $\text{DMSO}-d_6$) of compound **4a**.

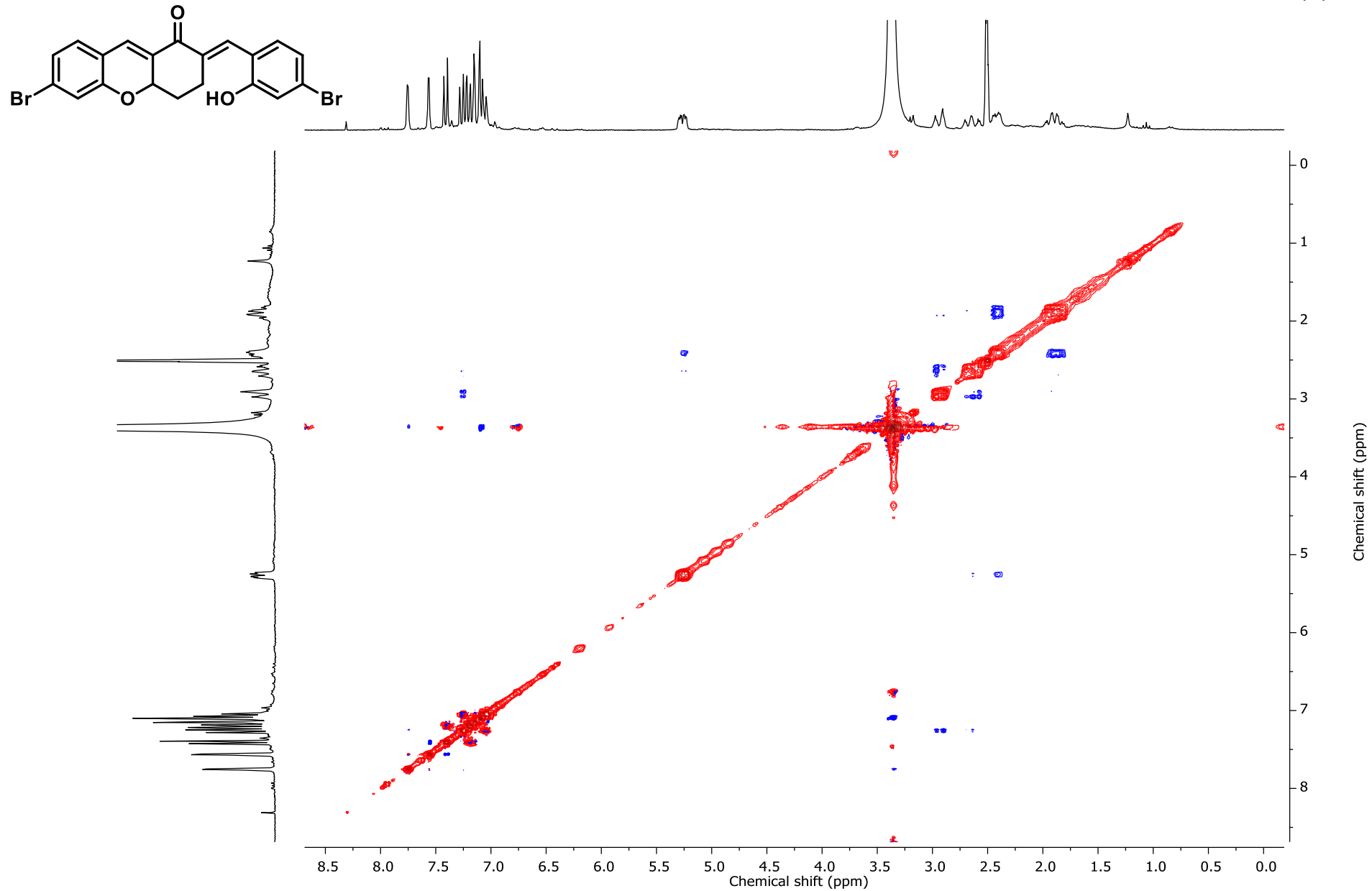
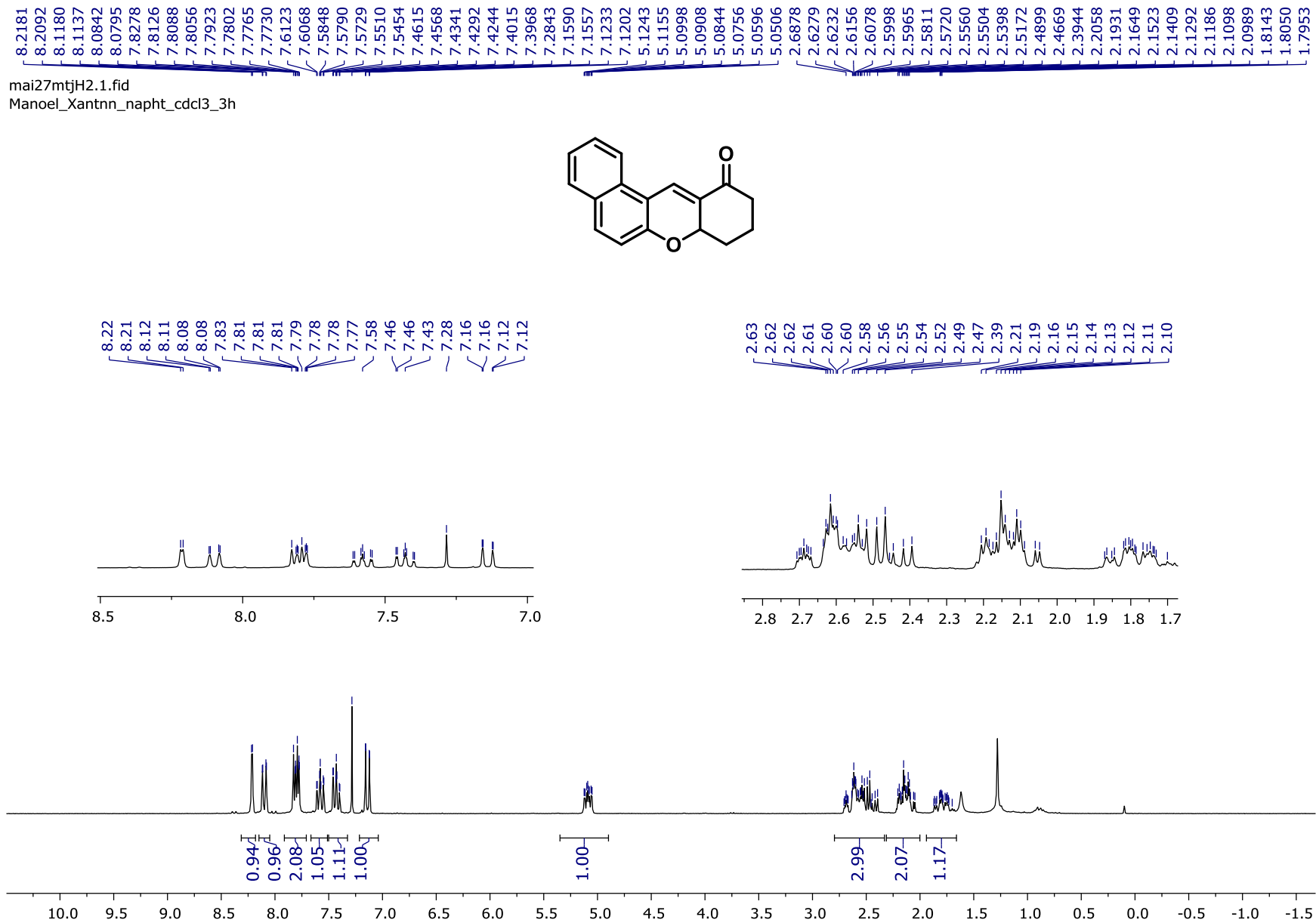
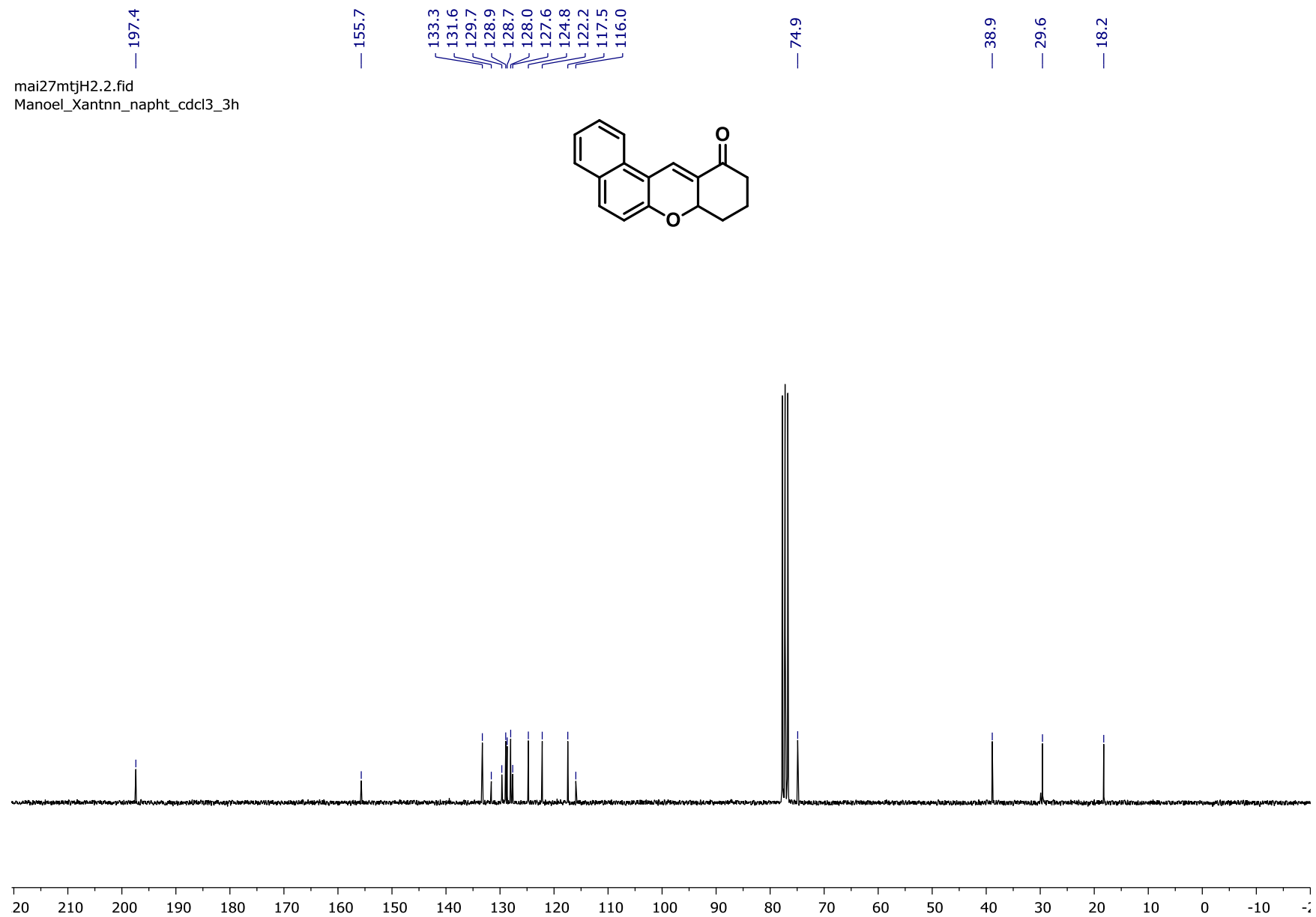


Figure S17. ^1H - ^1H NOESY NMR contour plot (250 MHz, $\text{DMSO}-d_6$) of compound **4a**.

Figure S18. ¹H NMR spectrum (250 MHz, CDCl₃) of compound **3g**.



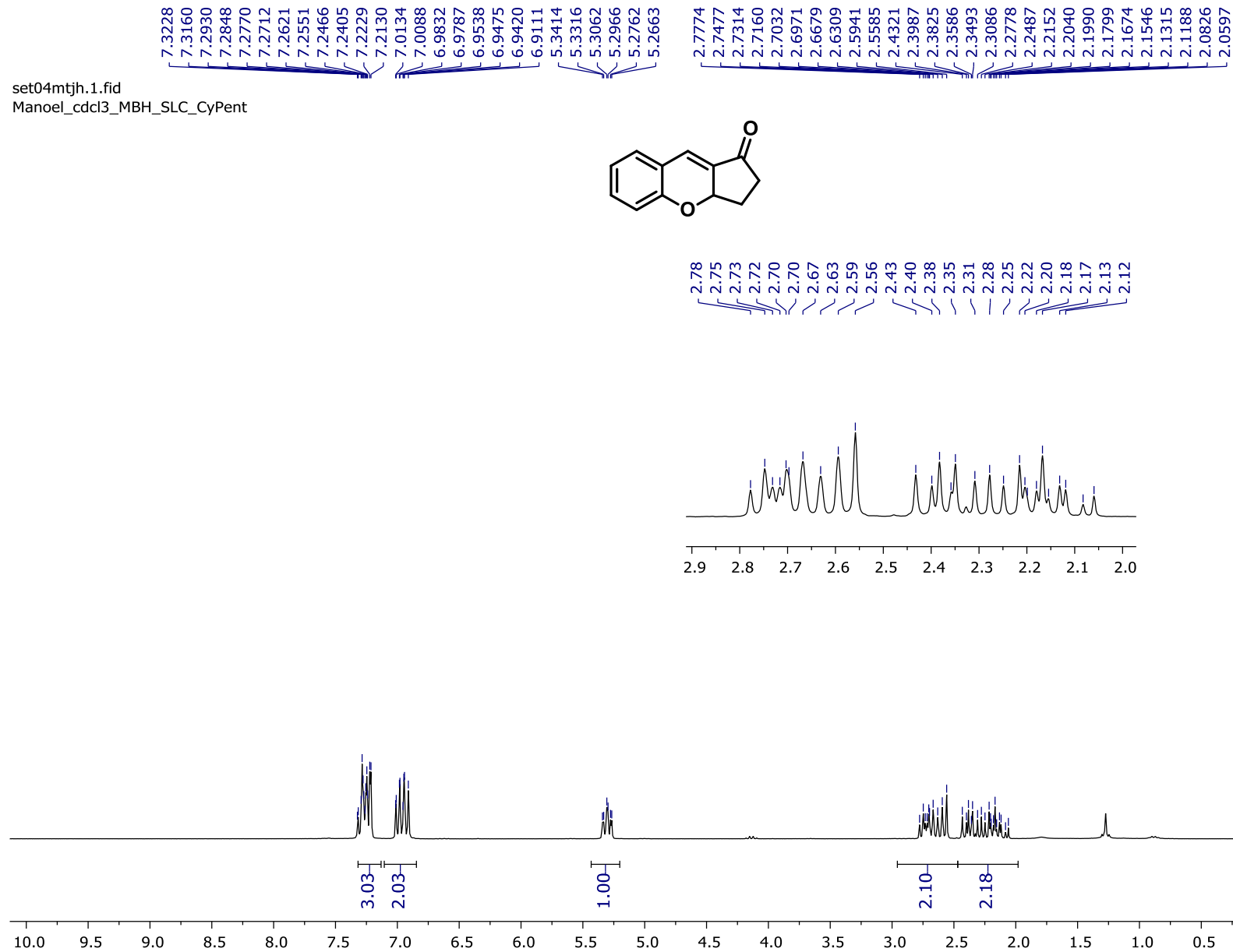
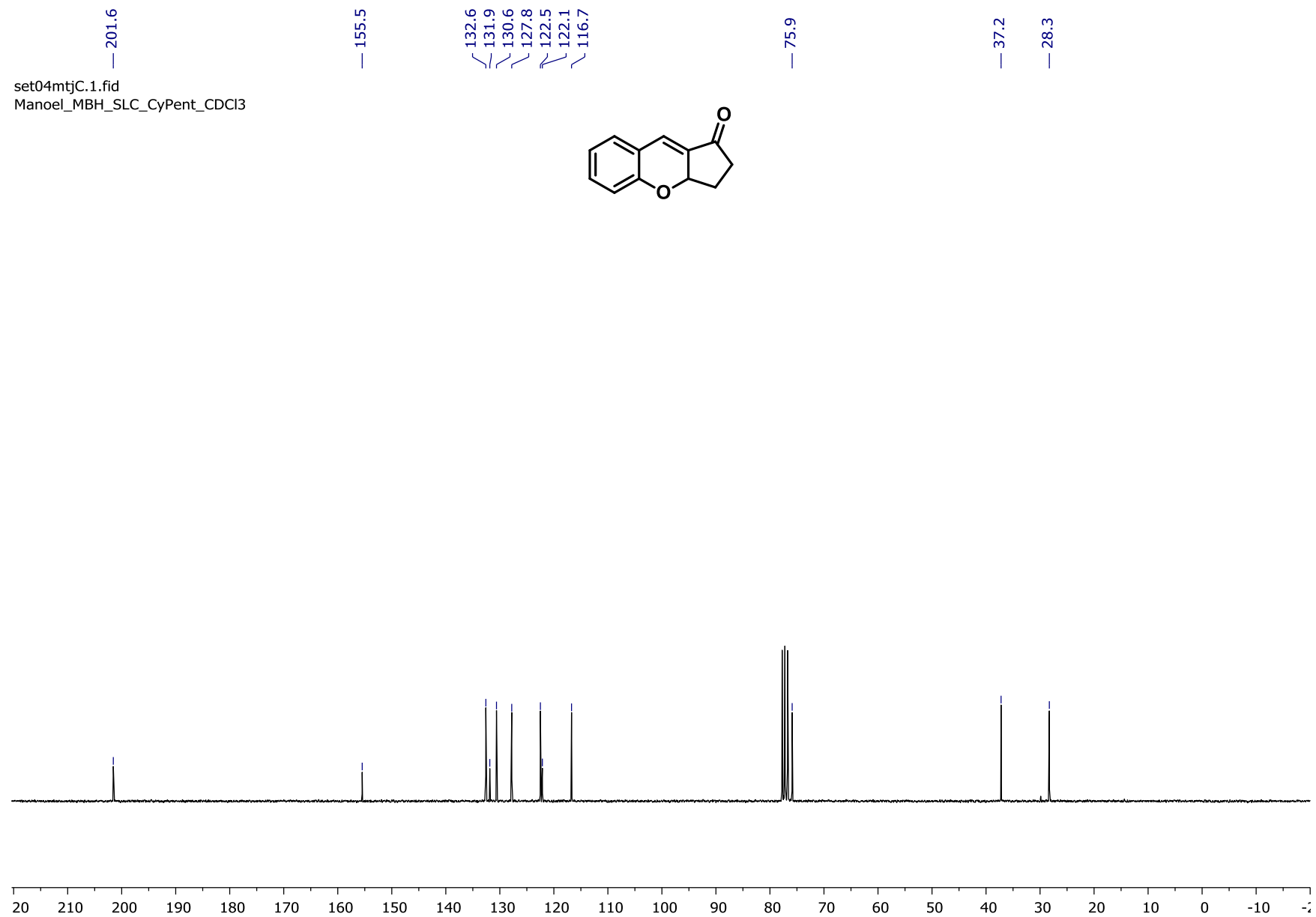


Figure S20. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3h**.



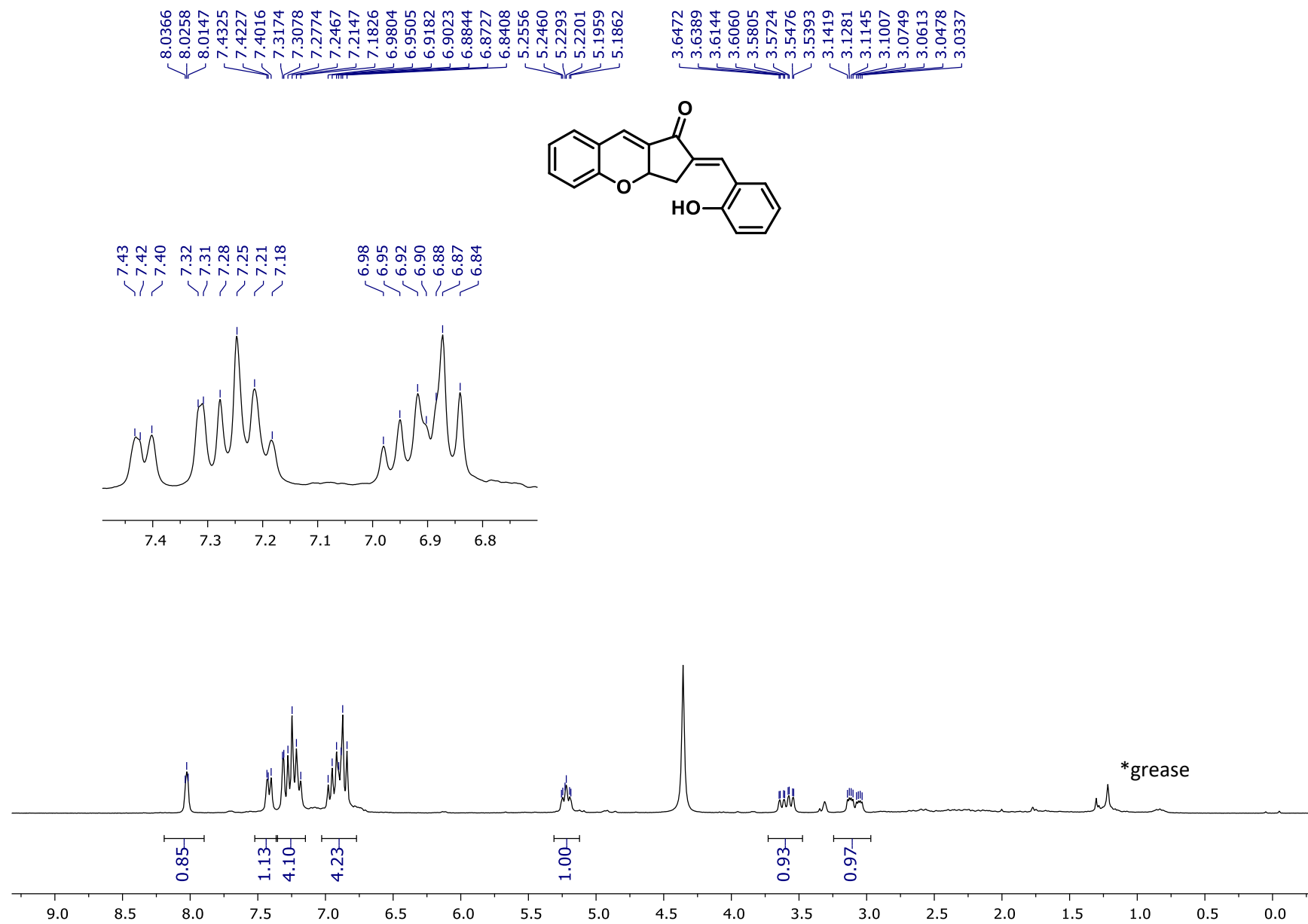


Figure S22. ¹H NMR spectrum (250 MHz, CDCl₃/MeOH-*d*₄ 6:1) of compound **4b**.

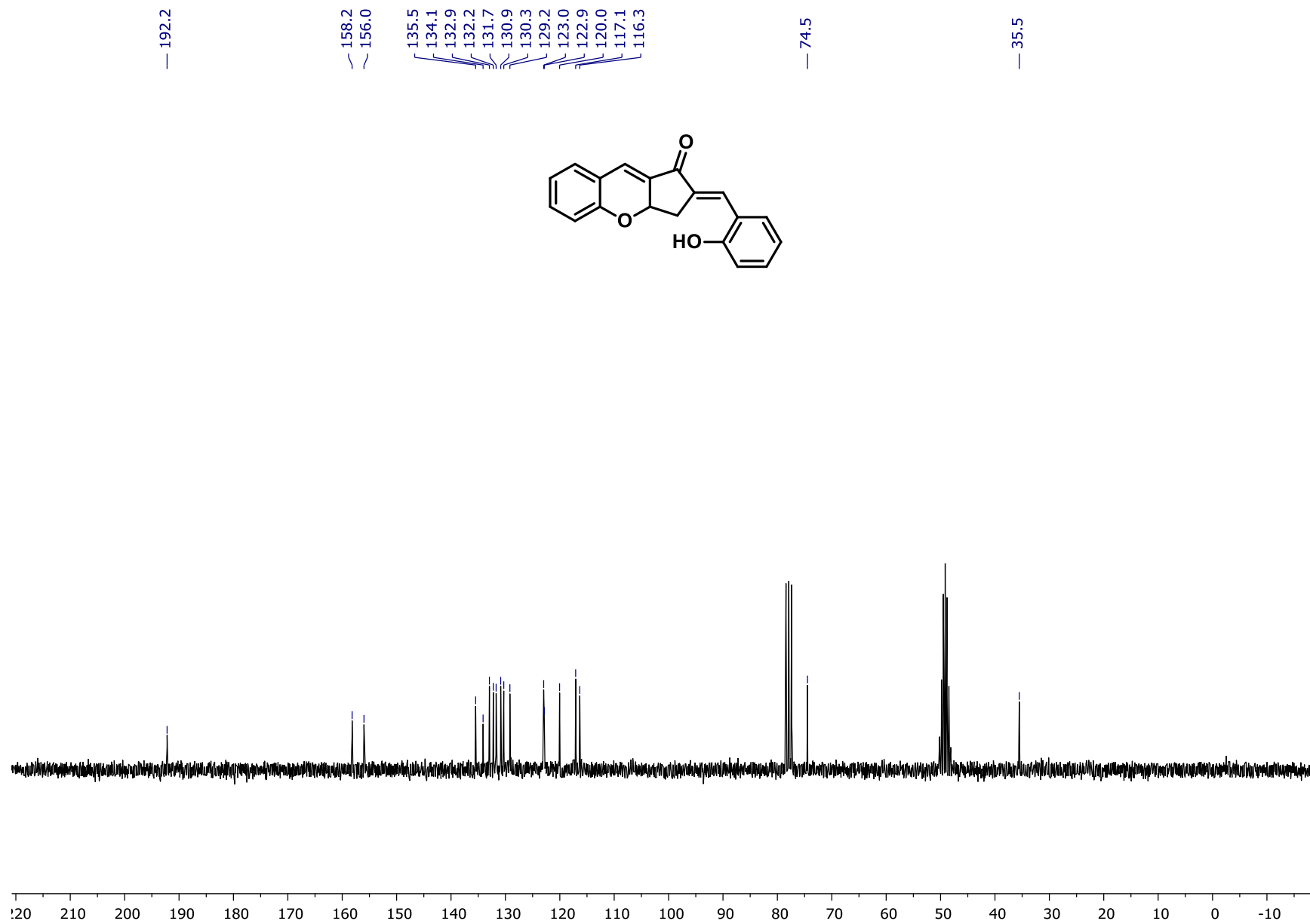
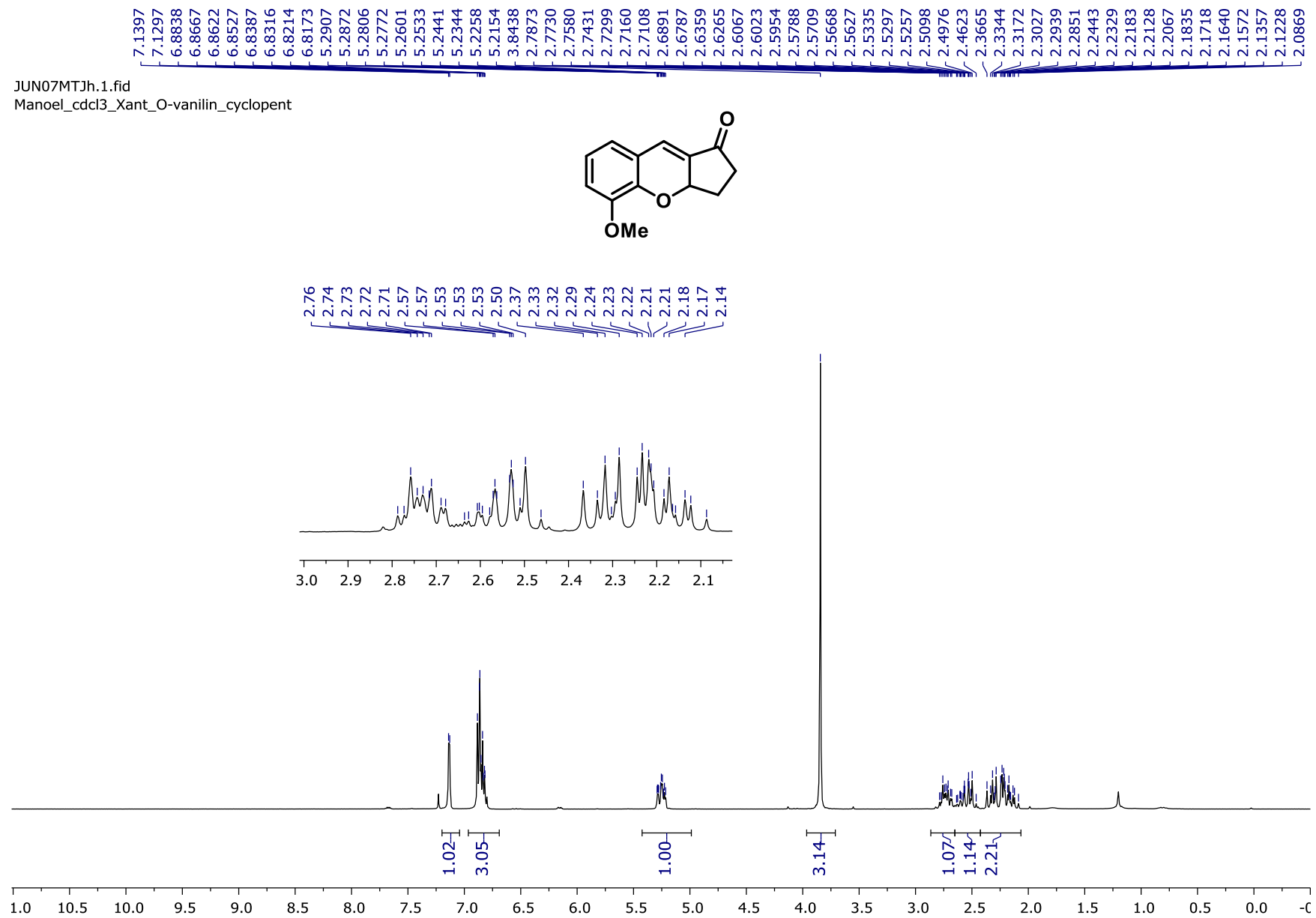
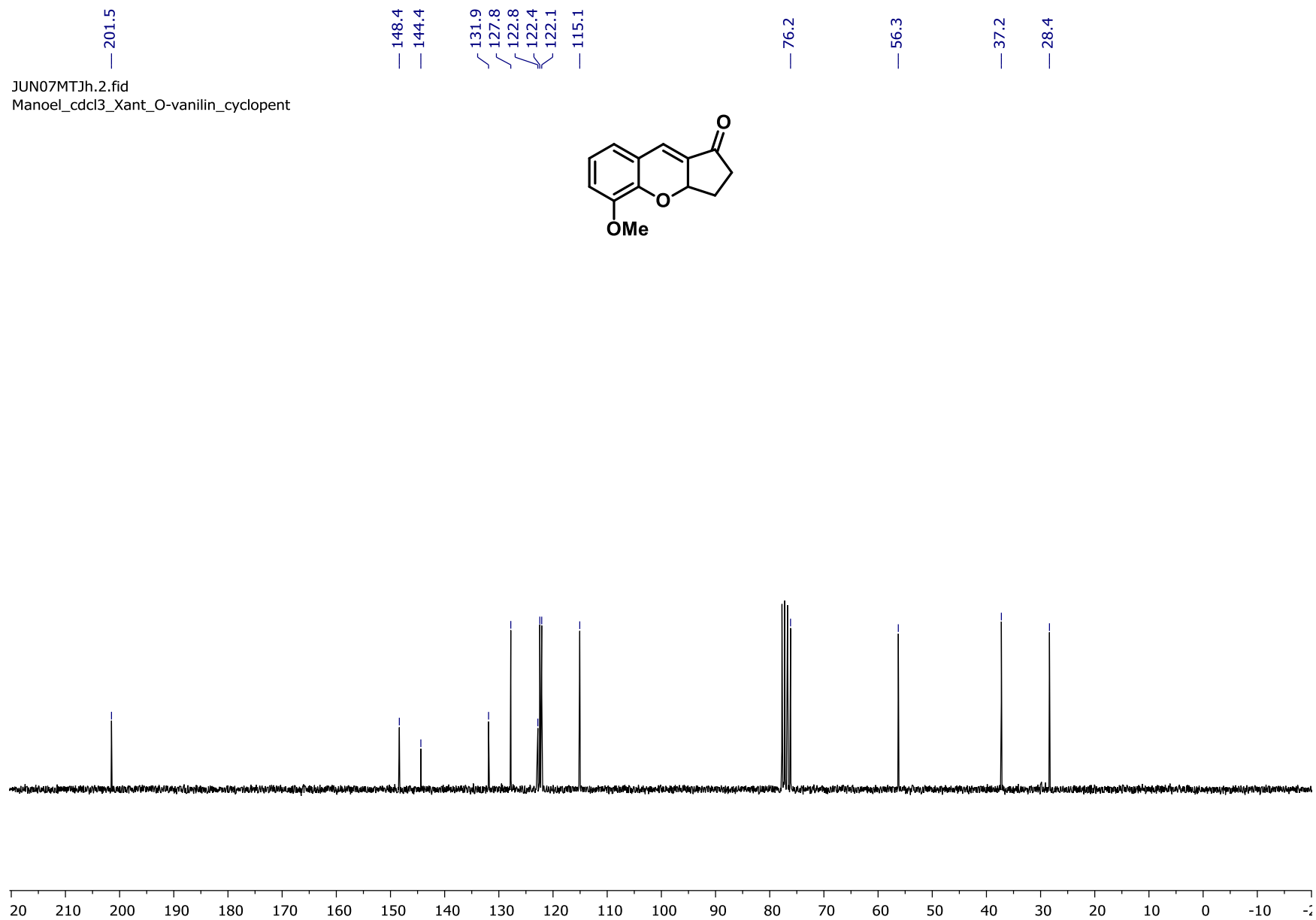
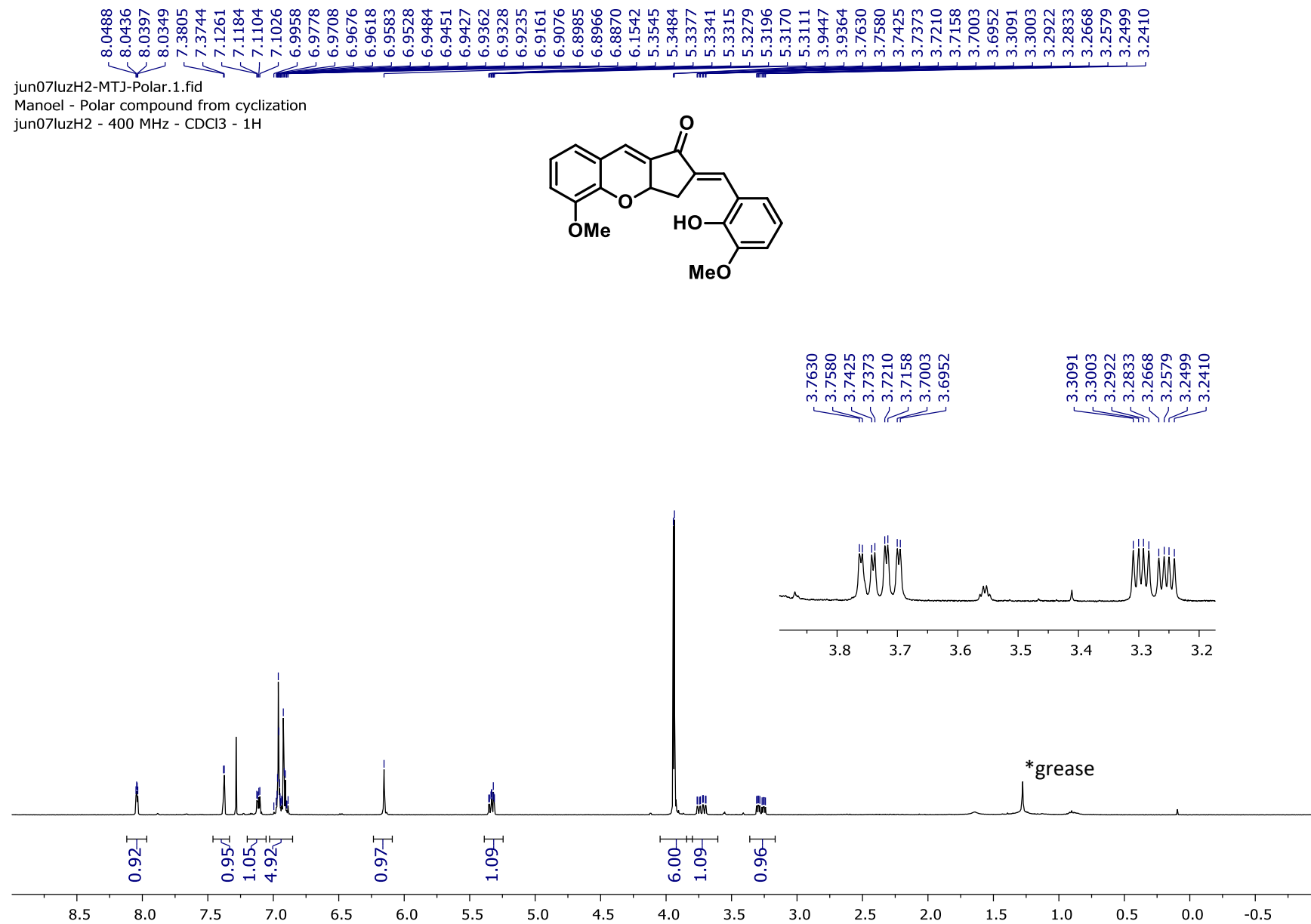


Figure S23. ¹³C NMR spectrum (63 MHz, CDCl₃/MeOH-*d*₄ 6:1) of compound **4b**.

Figure S24. ^1H NMR spectrum (250 MHz, CDCl_3) of compound 3i.



Figure S26. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 4c.

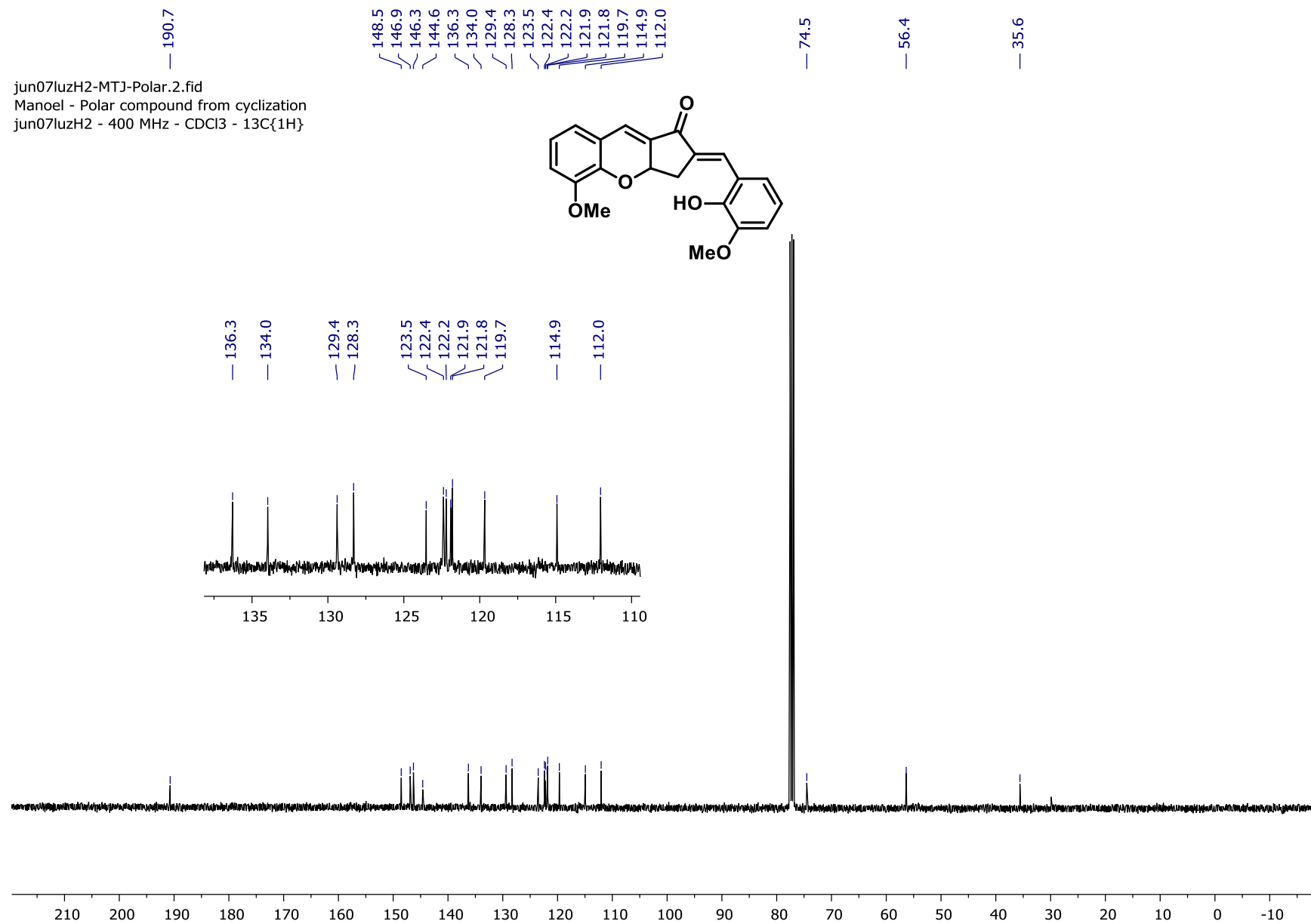


Figure S27. ¹³C NMR spectrum (101 MHz, CDCl₃) of compound **4c**.

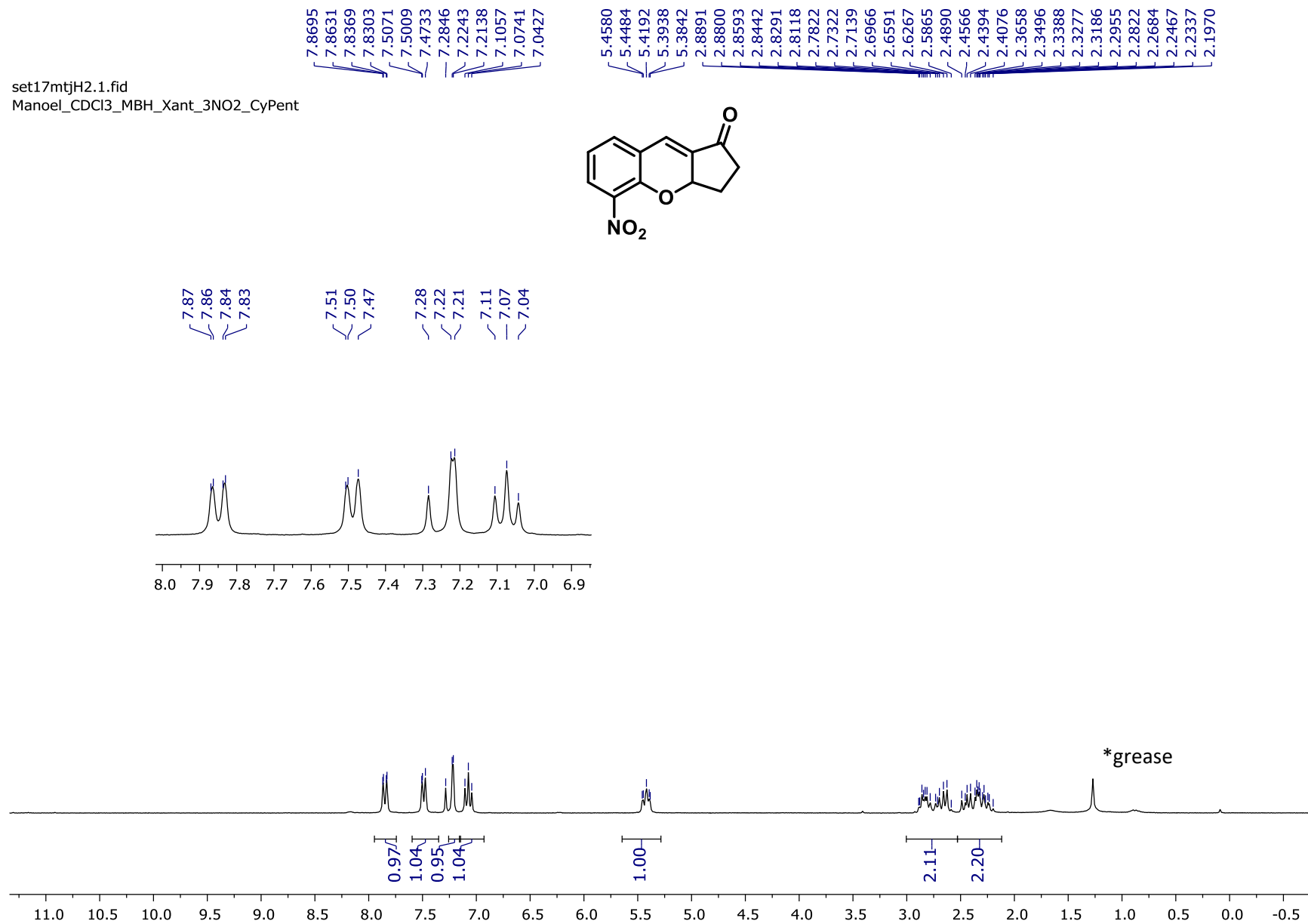
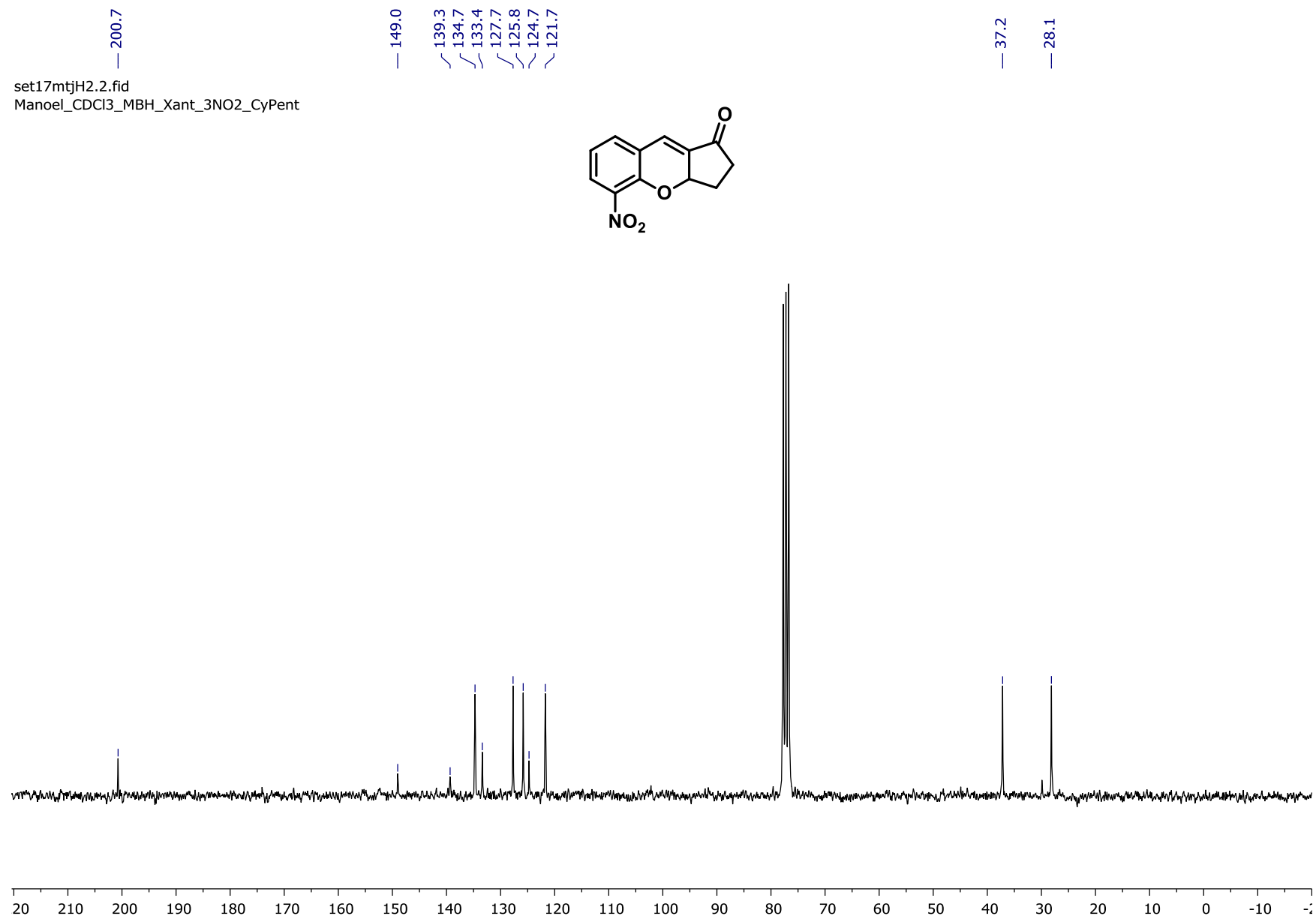
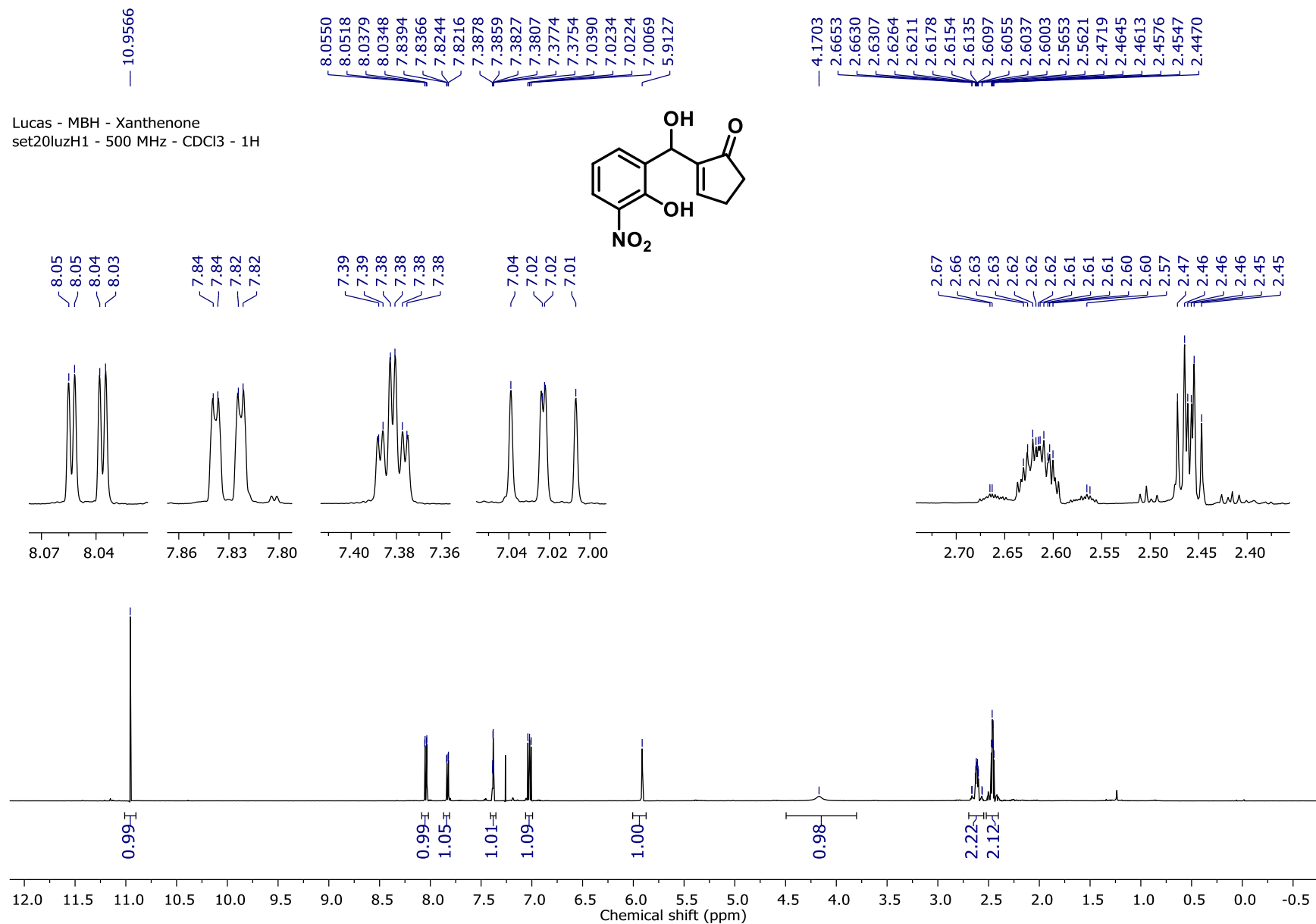


Figure S28. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3j**.



Figure S30. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 5a.

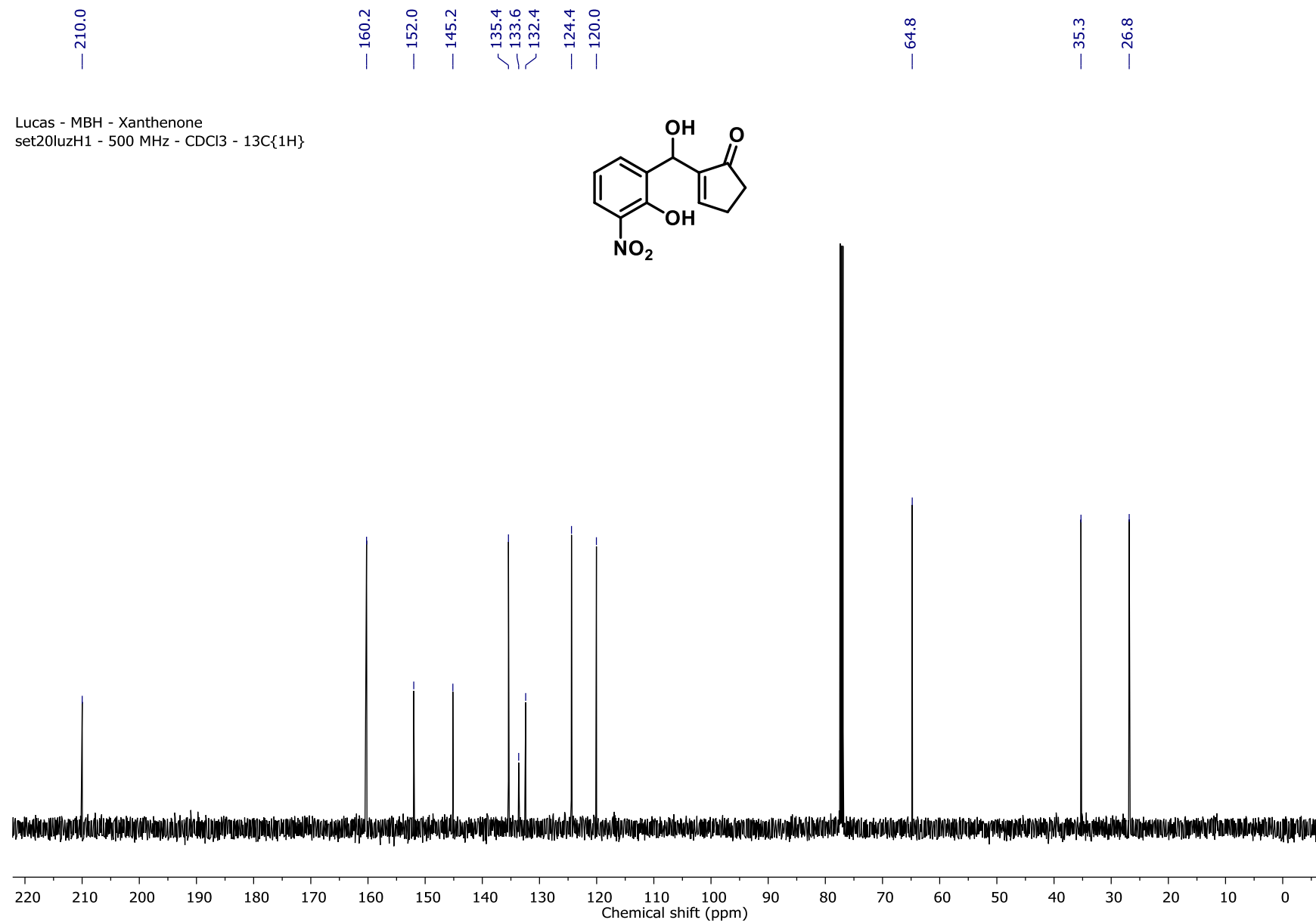


Figure S31. ¹³C NMR spectrum (126 MHz, CDCl₃) of compound 5a.

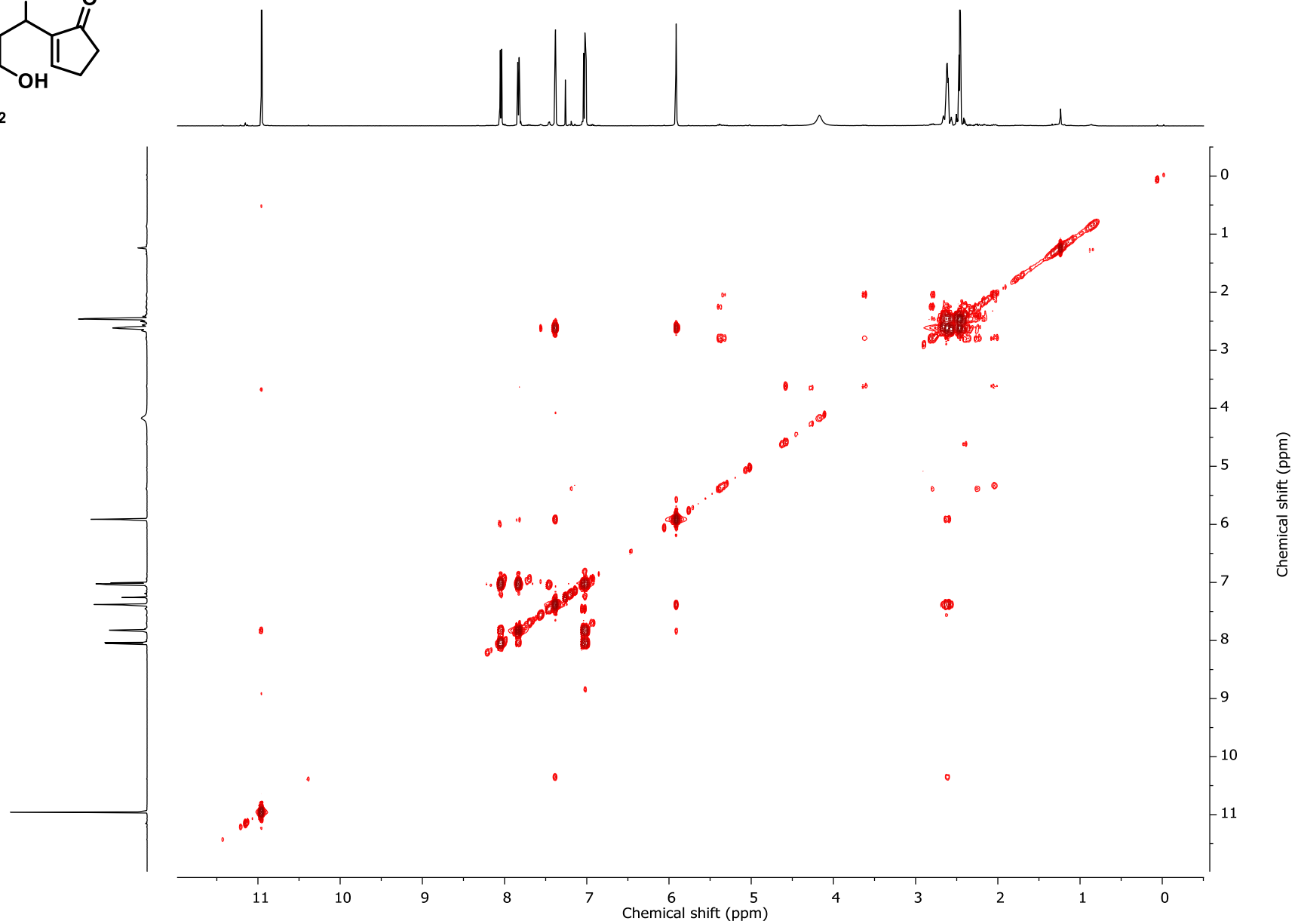
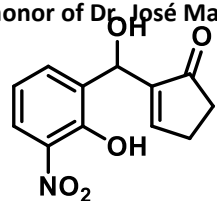


Figure S32. ¹H-¹H COSY NMR contour plot (500 MHz, CDCl₃) of compound 5a.

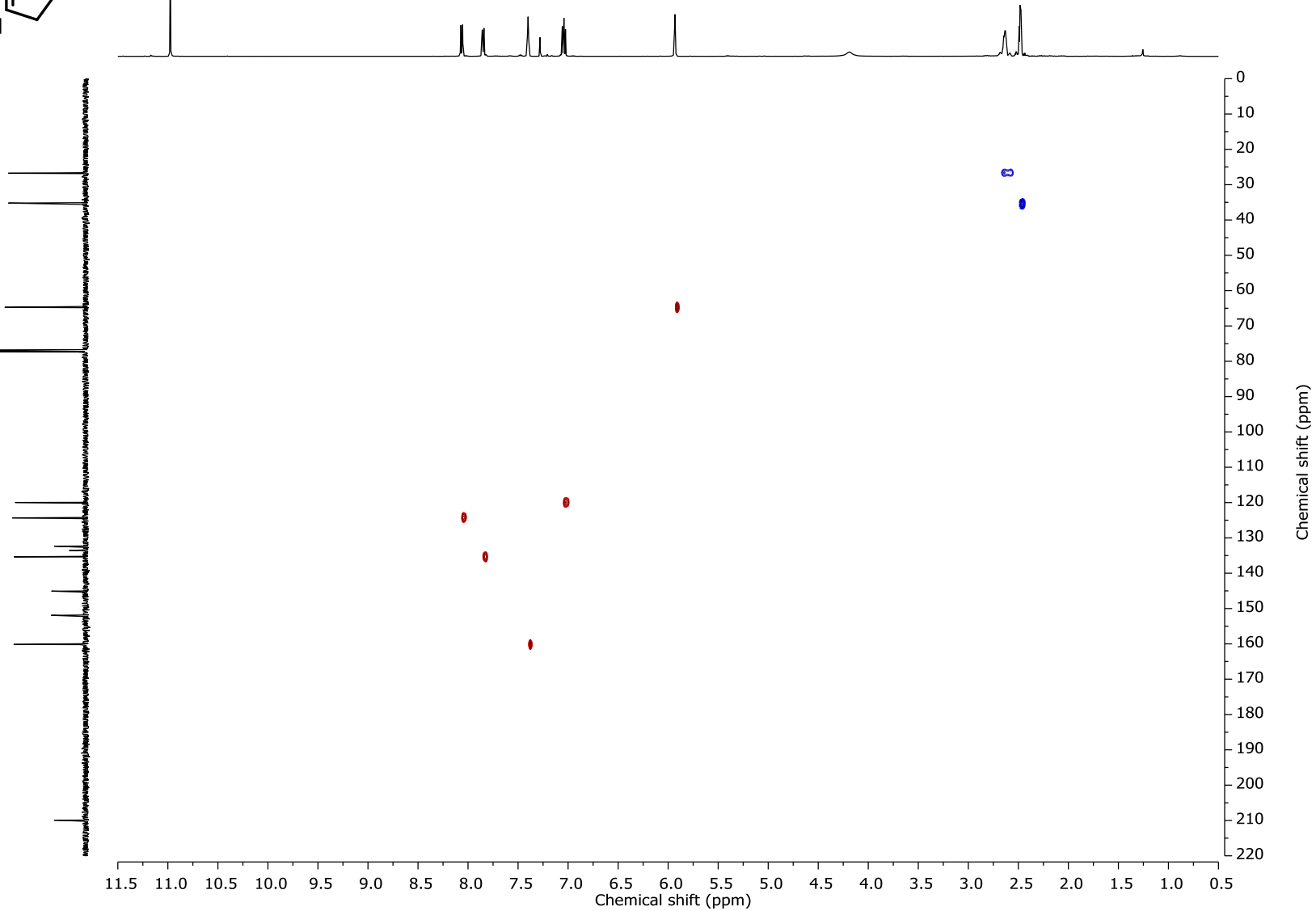
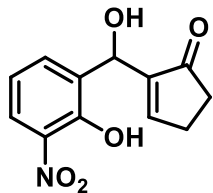


Figure S33. ^1H - ^{13}C HSQC NMR contour plot (500 MHz, CDCl_3) of compound 5a.

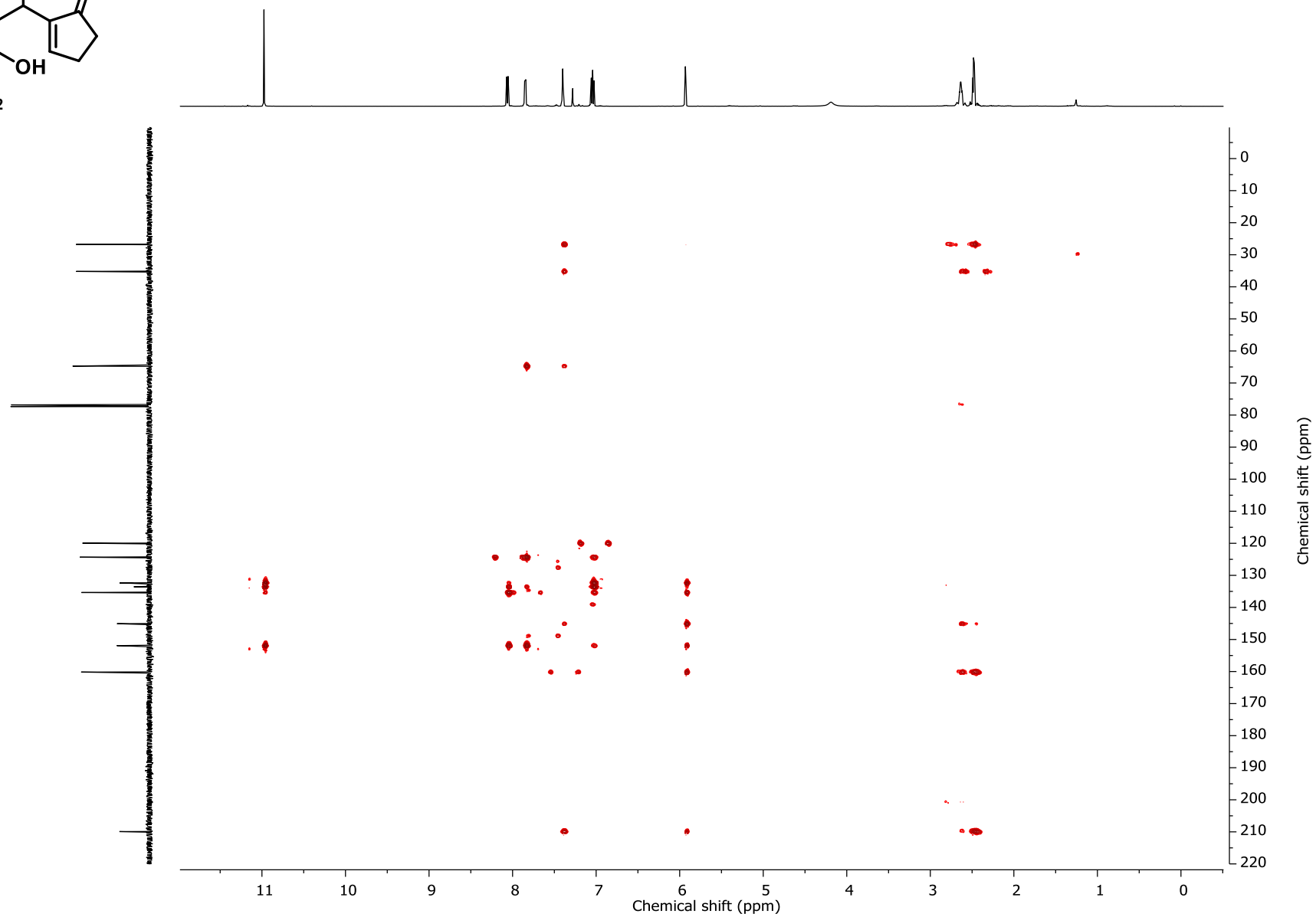
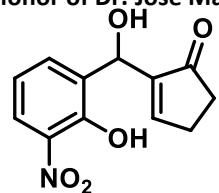


Figure S34. ^1H - ^{13}C HMBC NMR contour plot (500 MHz, CDCl_3) of compound **5a**.

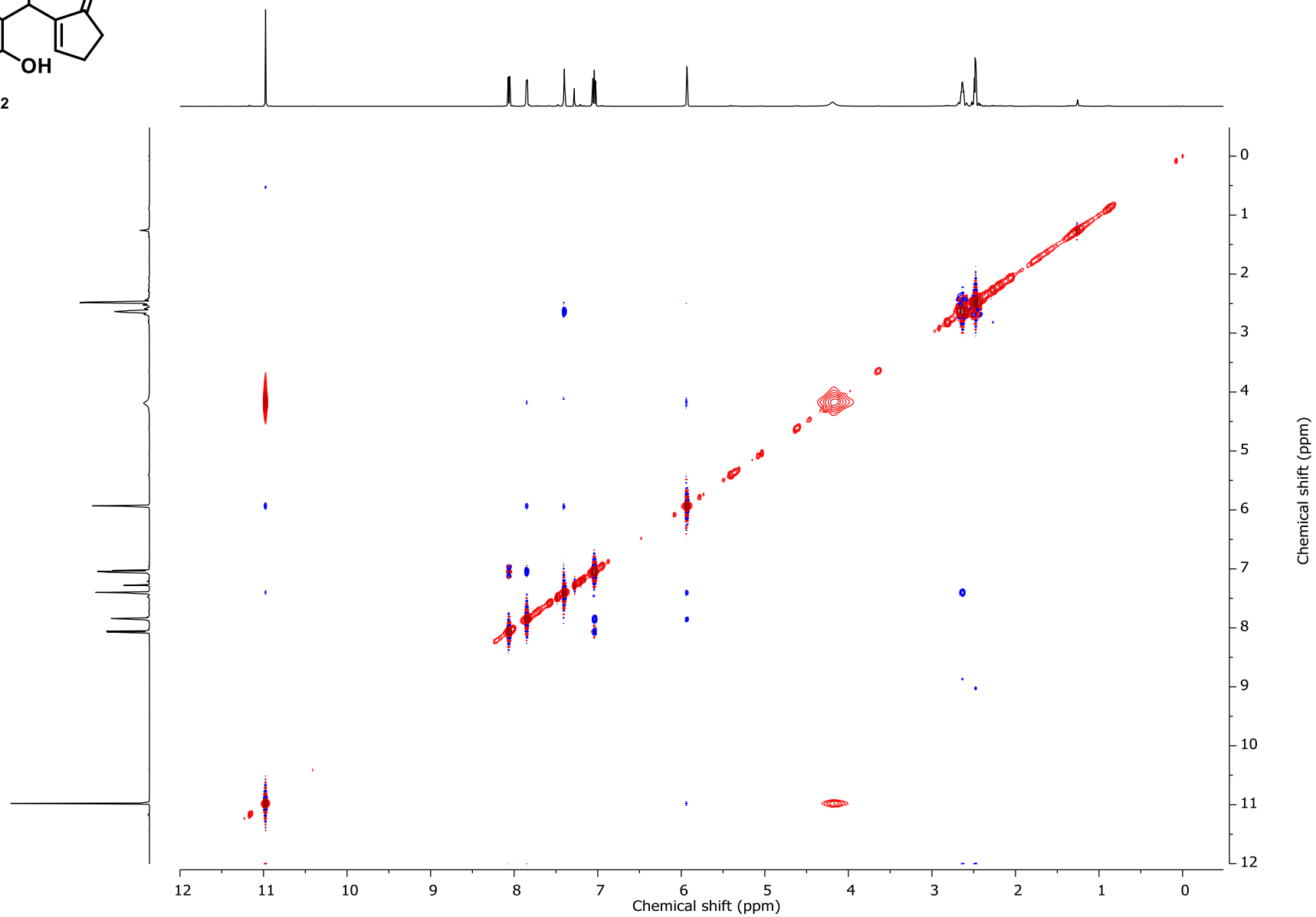
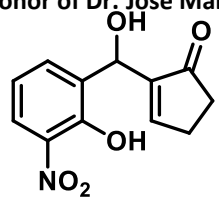


Figure S35. ^1H - ^1H NOESY NMR contour plot (500 MHz, CDCl_3) of compound 5a.

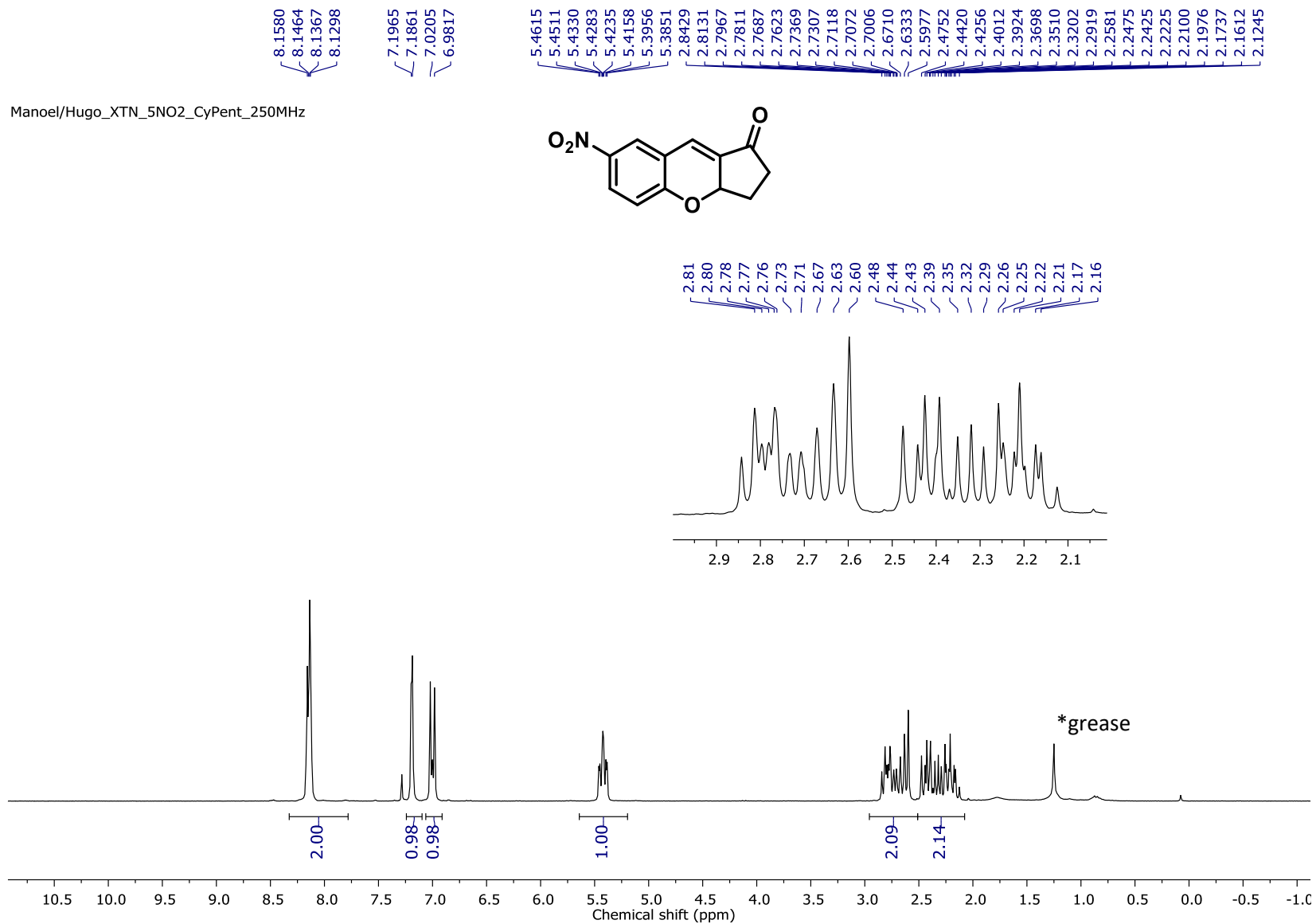
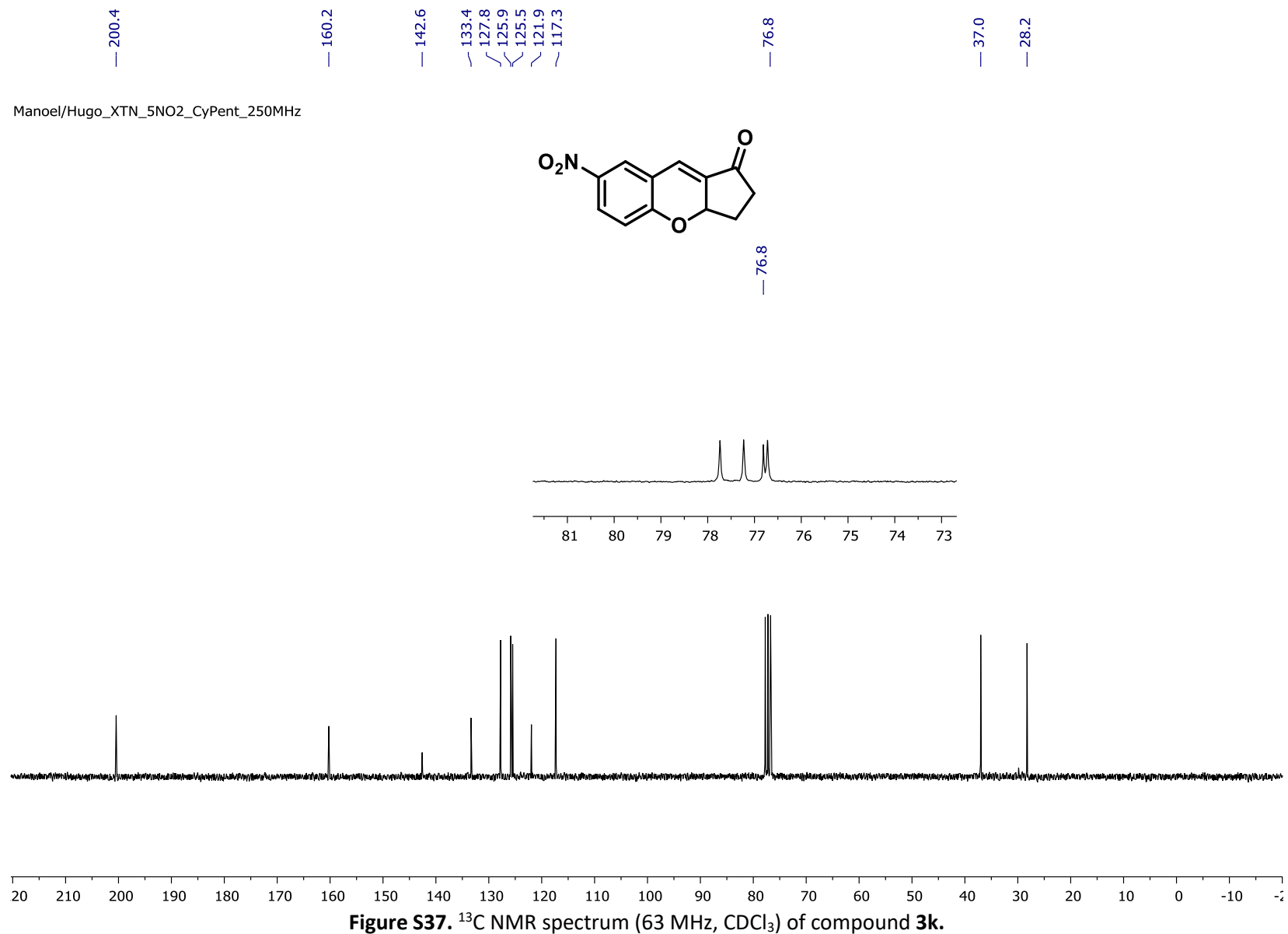
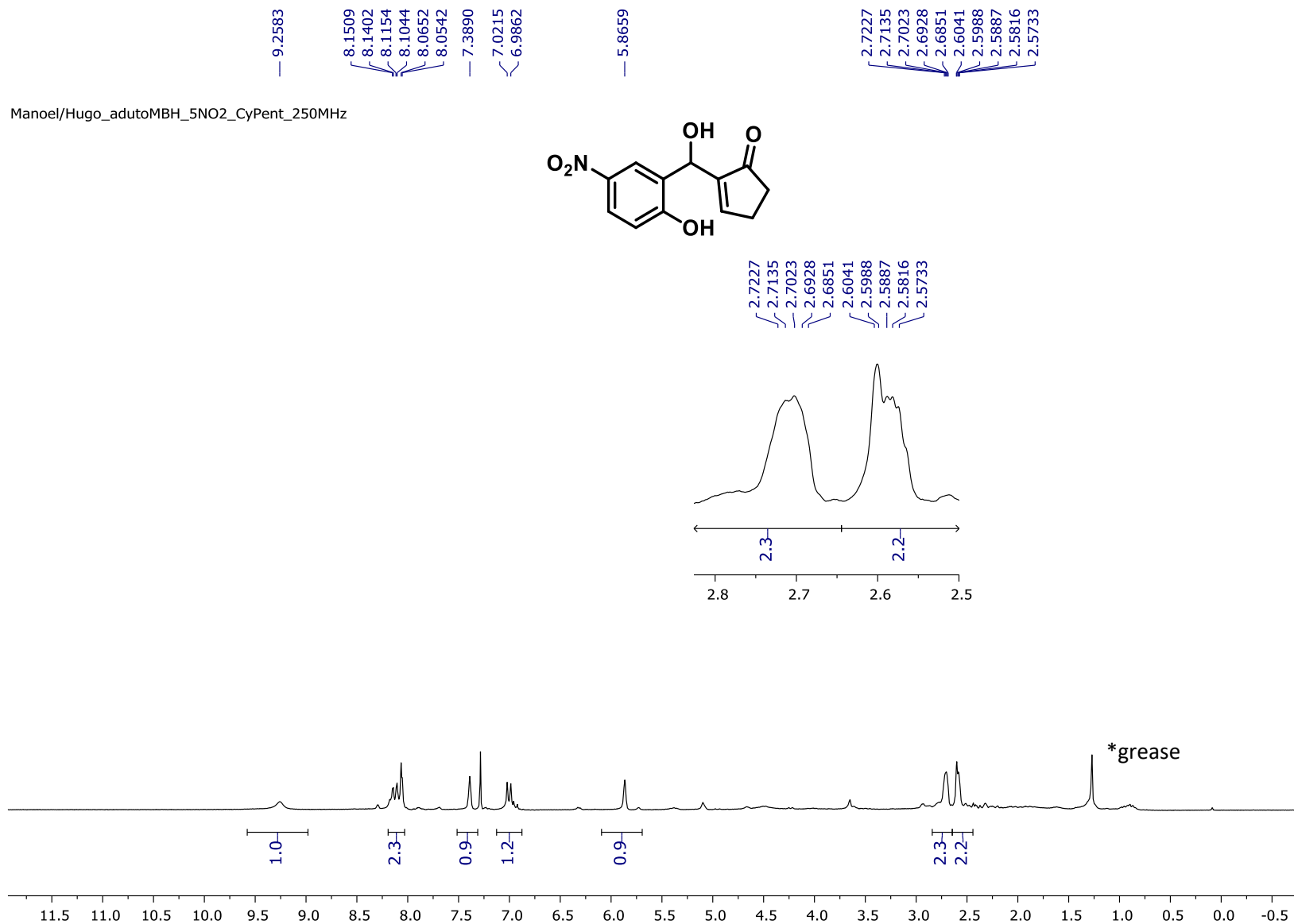
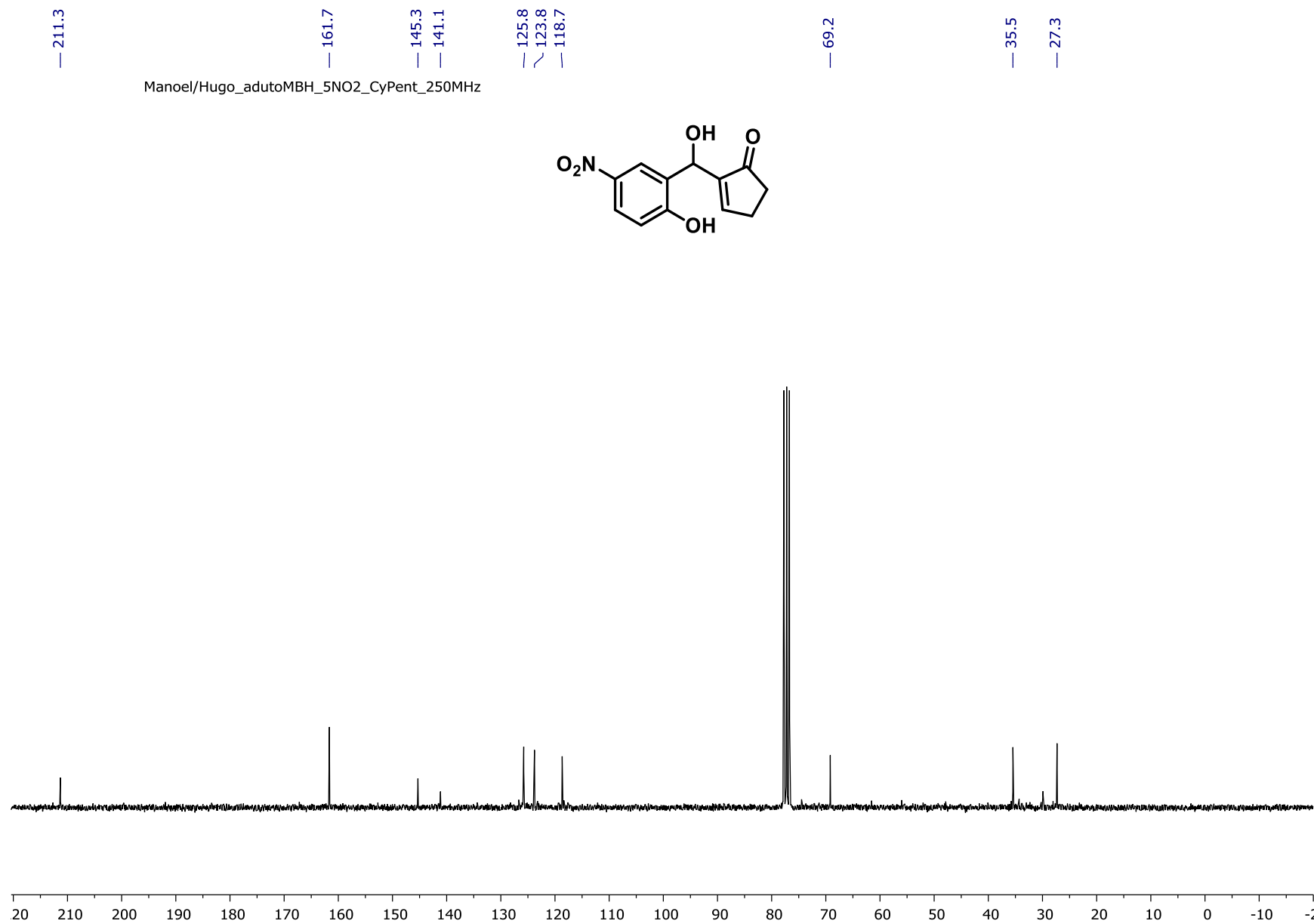
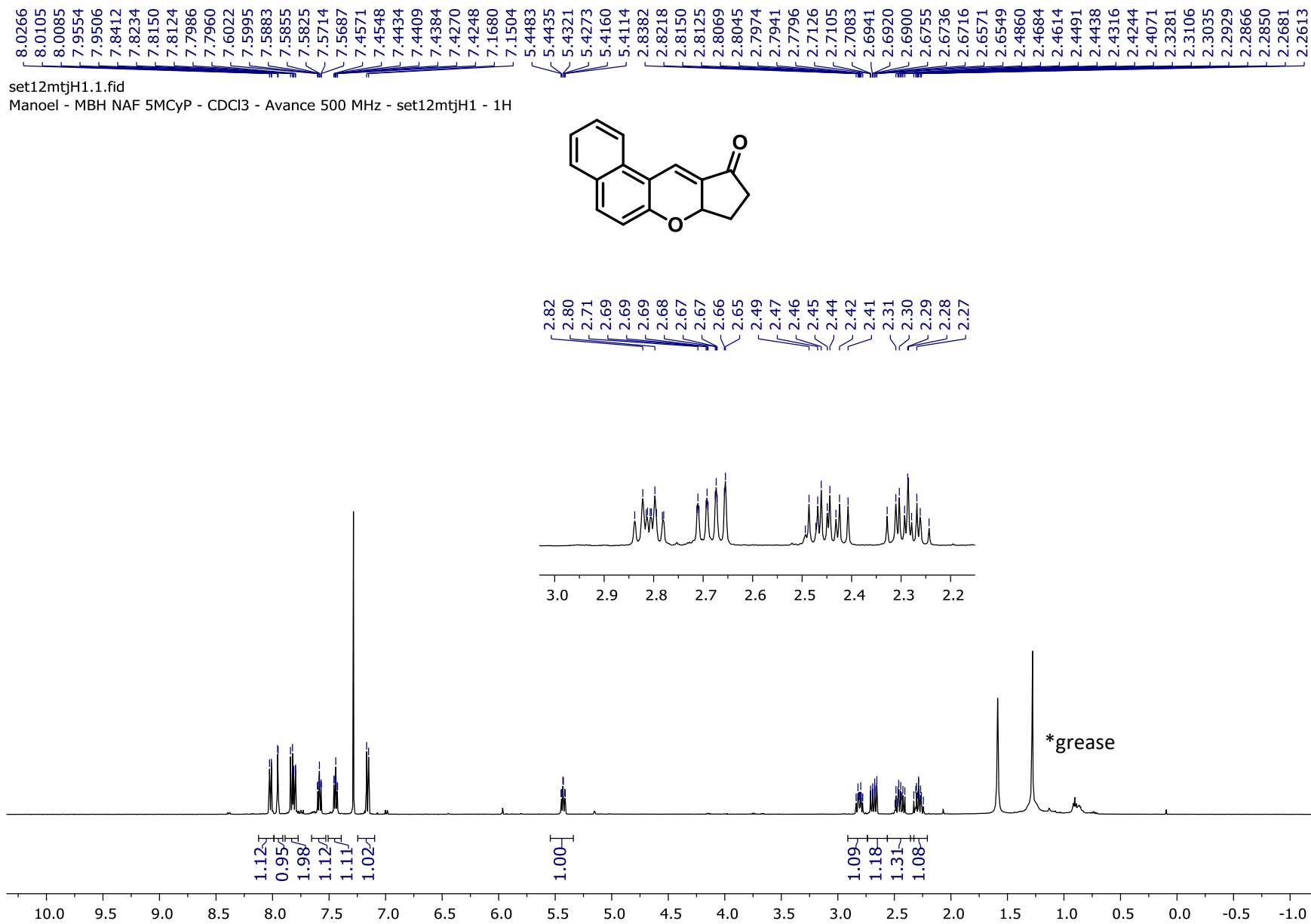


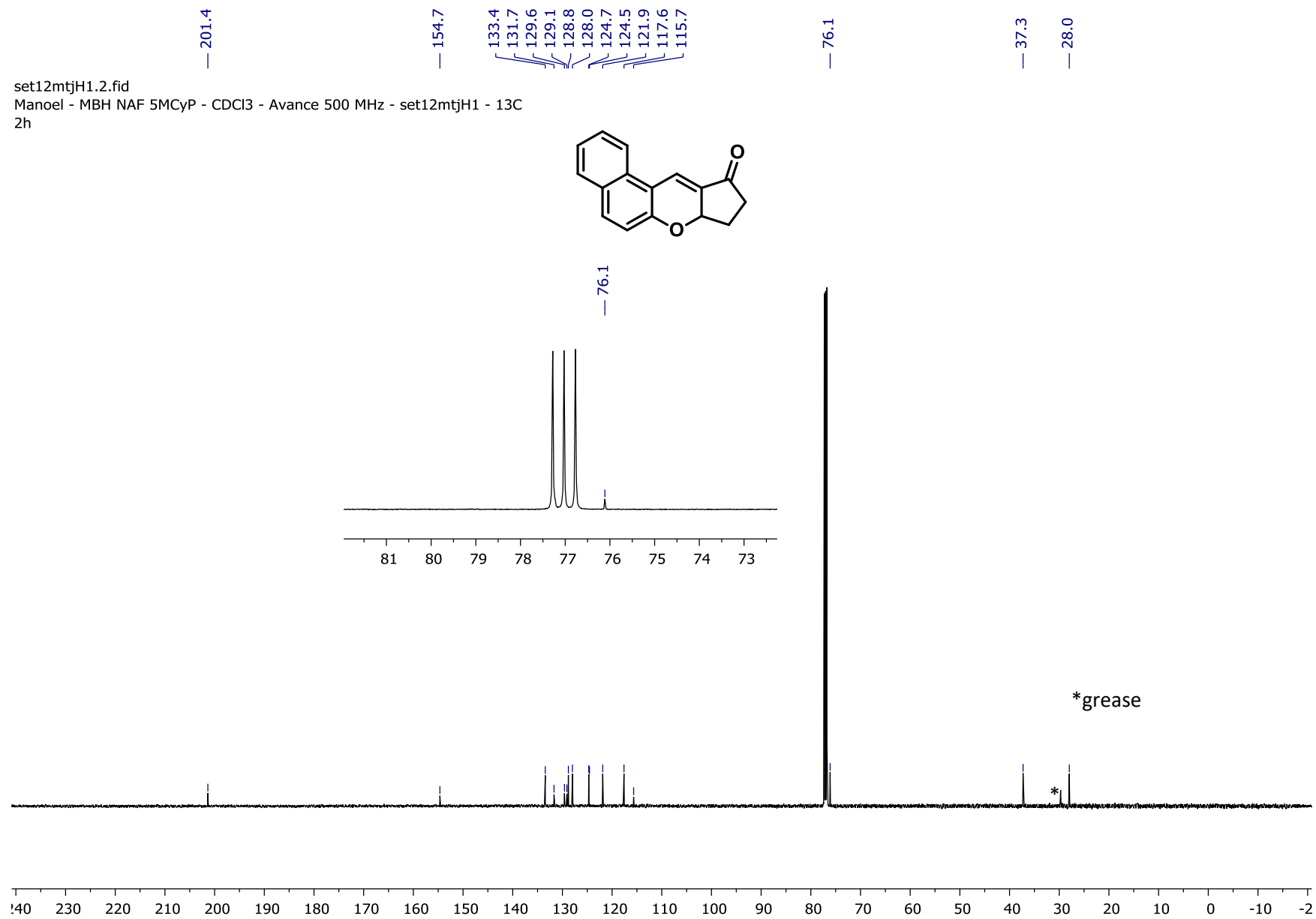
Figure S36. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3k**.



Figure S38. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **5b**.



Figure S40. ¹H NMR spectrum (500 MHz, CDCl₃) of compound **3I**.



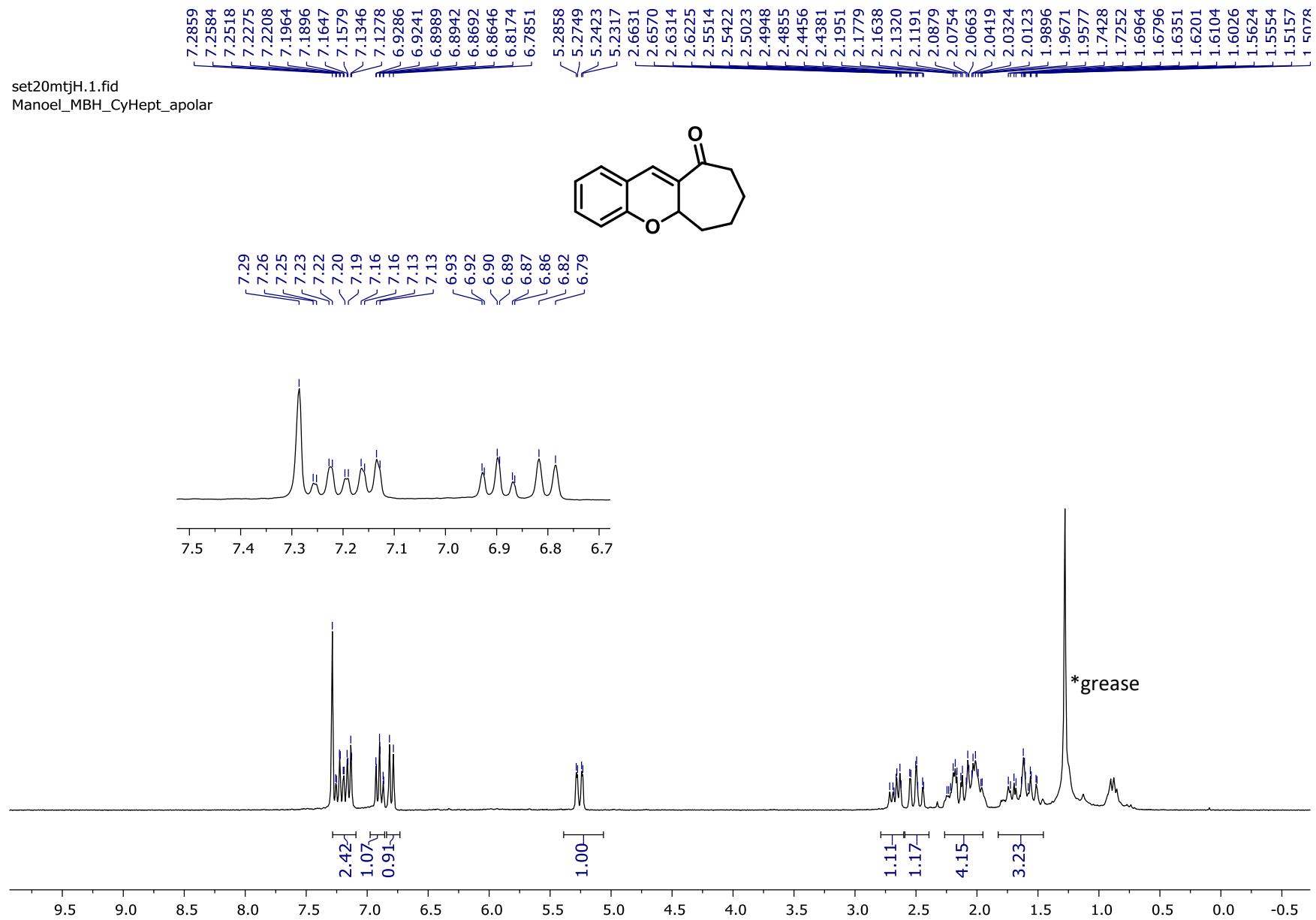


Figure S42. ^1H NMR spectrum (250 MHz, CDCl_3) of compound **3m**.

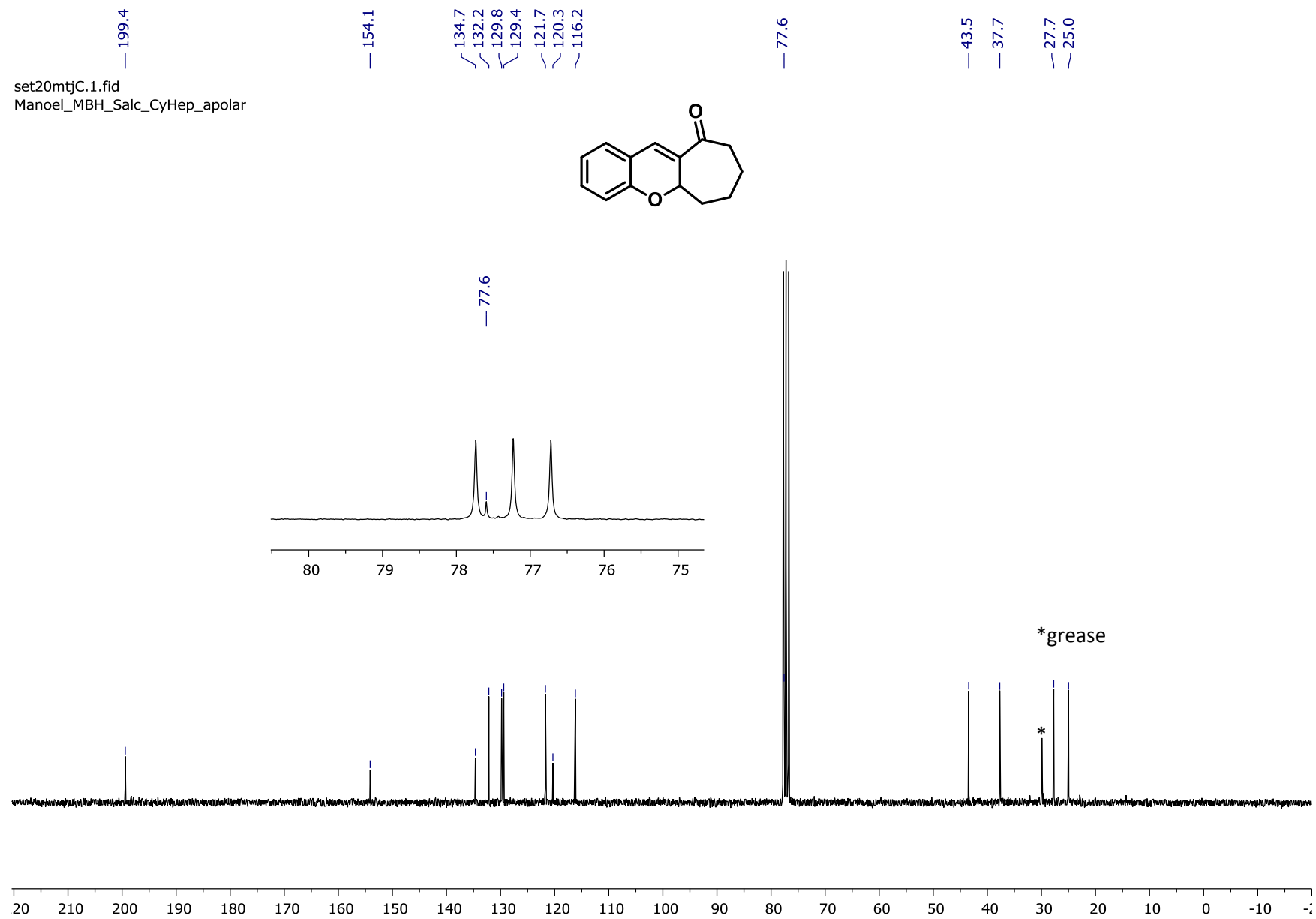


Figure S43. ^{13}C NMR spectrum (63 MHz, CDCl_3) of compound **3m**.

X-Ray Crystallographic Data for Compound 4c

Crystal structure of *(2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one* (**4c**) (**Figure S44**) was determined by single crystal X-ray diffraction analysis using a crystal that had been obtained by slow evaporation of a ethyl acetate/chloroform mixture (1:1 v/v) of **4c**. Data collection was performed on a Bruker APEX II DUO area diffractometer, at low temperature (150 K, CRYOSTREAM 700 - Oxford Cryosystem), based on a strategy combining omega and phi scans, with 0.5° width and 10 s of acquisition time per frame, operating with a Mo fine-focus sealed tube source of radiation ($K\alpha \lambda = 0.71073 \text{ \AA}$).

Cell refinement and data reduction were done using SAINT¹ and multi-scan absorption correction was applied using SADABS-2014/5¹. Solution structure was obtained by primary atom site location by structure-invariant direct methods SHELXS97². SHELXL2014/7³ was chosen to perform structure refinement using least squares methods against F^2 and hydrogen atoms were placed during the refinement, with their location inferred from neighbouring sites. All non-hydrogen atoms were refined anisotropically, while H-atom parameters were not refined. 311 parameters were refined (0 restraints), $R[F^2 > 2 \sigma(F^2)] = 0.033$, $wR(F^2) = 0.079$, $S = 1.02$, with maximum and minimum residual electron density of 0.65 e \AA^{-3} and -0.47 e \AA^{-3} , respectively. Details about the analyzed crystal and data collection are presented in **Table S1** and **Table S2**, respectively.

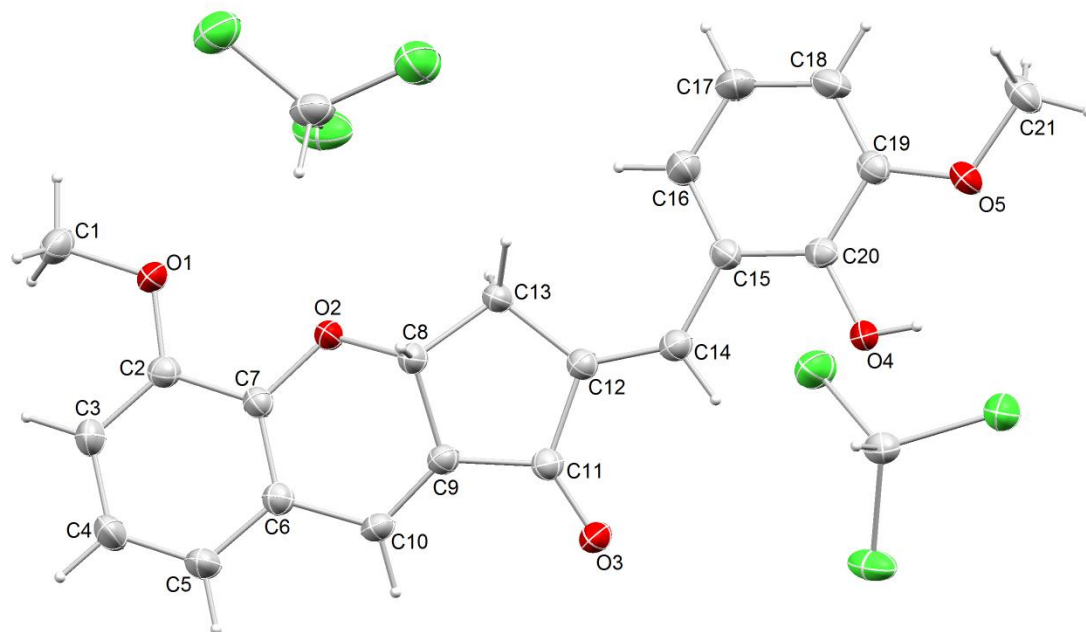


Figure S44. The molecular structure of *(2E)*-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1*H*,2*H*,3*H*,3*aH*-cyclopenta[*b*]chromen-1-one (**4c**) with 50% probability displacement ellipsoids.

Table S1. Selected crystallographic data for (2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one (**4c**) crystal

$C_{21}H_{18}O_5 \cdot 2(CHCl_3)$	$Z = 2$
$M_r = 589.09$	$F(000) = 600$
Triclinic, $P1$	$D_x = 1.536 \text{ Mg m}^{-3}$
$a = 8.8569 (8) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 10.8992 (11) \text{ \AA}$	Cell parameters from 134 reflections
$c = 14.8123 (14) \text{ \AA}$	$\theta = 3.2\text{--}24.4^\circ$
$\alpha = 71.700 (2)^\circ$	$\mu = 0.71 \text{ mm}^{-1}$
$\beta = 79.556 (2)^\circ$	$T = 150 \text{ K}$
$\gamma = 70.333 (2)^\circ$	Block, yellow
$V = 1273.8 (2) \text{ \AA}^3$	$0.22 \times 0.12 \times 0.08 \text{ mm}$

Table S2. Selected crystallographic data for data collection

Absorption correction: multi-scan	$R_{\text{int}} = 0.037$
$T_{\text{min}} = 0.684$, $T_{\text{max}} = 0.745$	$\theta_{\text{max}} = 26.8^\circ$, $\theta_{\text{min}} = 1.5^\circ$
35447 measured reflections	$h = -11 \rightarrow 11$
5395 independent reflections	$k = -13 \rightarrow 13$
4302 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 18$

References

1. Bruker (2010). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
3. Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.