Supplementary Material

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

Manoel T. Rodrigues Jr.,[a] Hugo Santos, [a] Lucas A. Zeoly,[a] Deborah A. Simoni,[b] Albert Moyano,[c] and Fernando Coelho*[a]

[a] Laboratory of Synthesis of Natural Products and Drugs, and [b] Laboratory of Crystallography, Institute of Chemistry, University of Campinas, UNICAMP, P.O. Box 6154, 13083-970, Campinas, SP, Brazil
[c] Secció de Química Orgànica, Departament de Química Inorgànica i Orgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Catalonia, Spain
E-mail: facoelho@unicamp.br

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^{1}H NMR and ^{13}C{^{1}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)

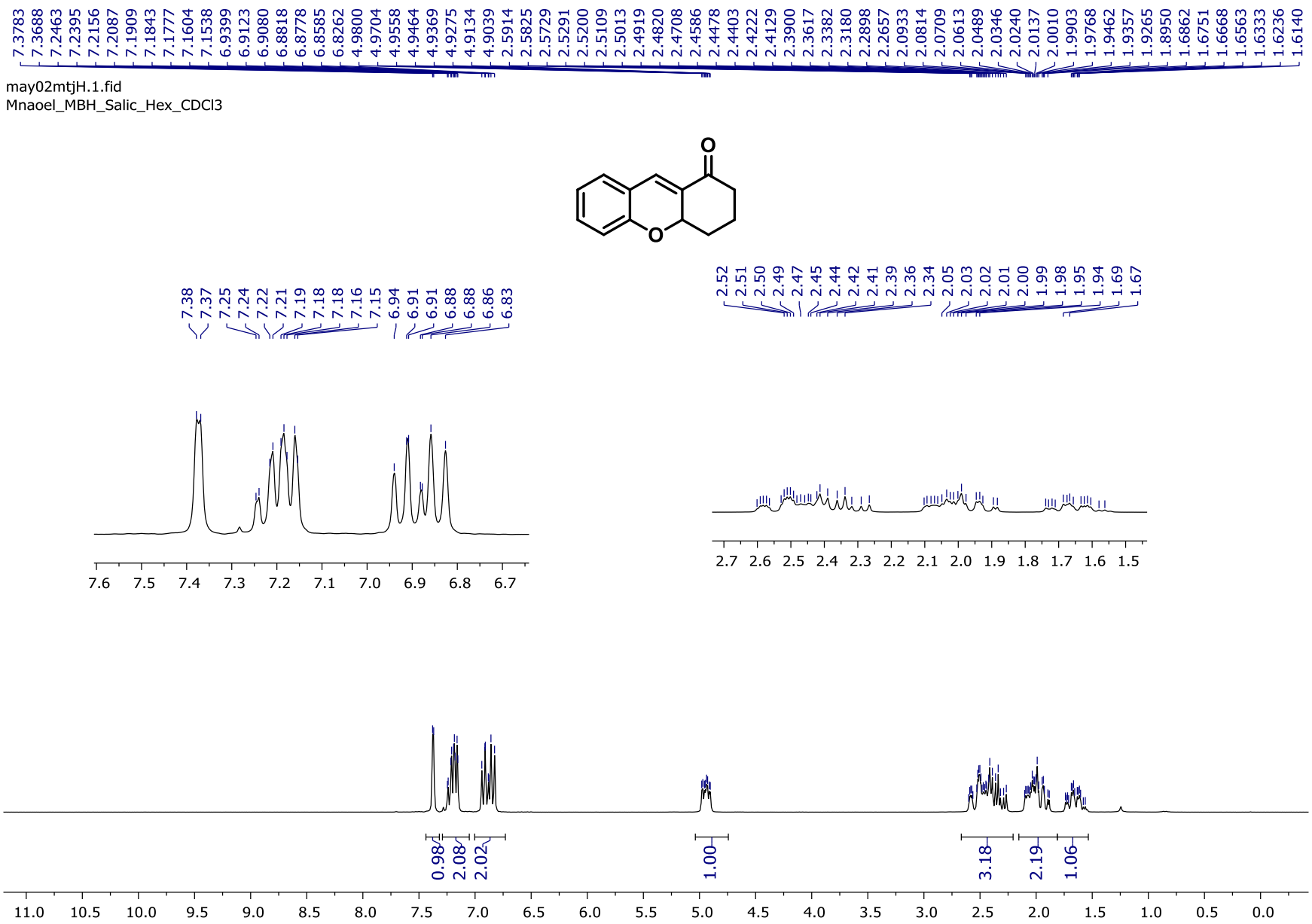

Figure S1. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3a.**

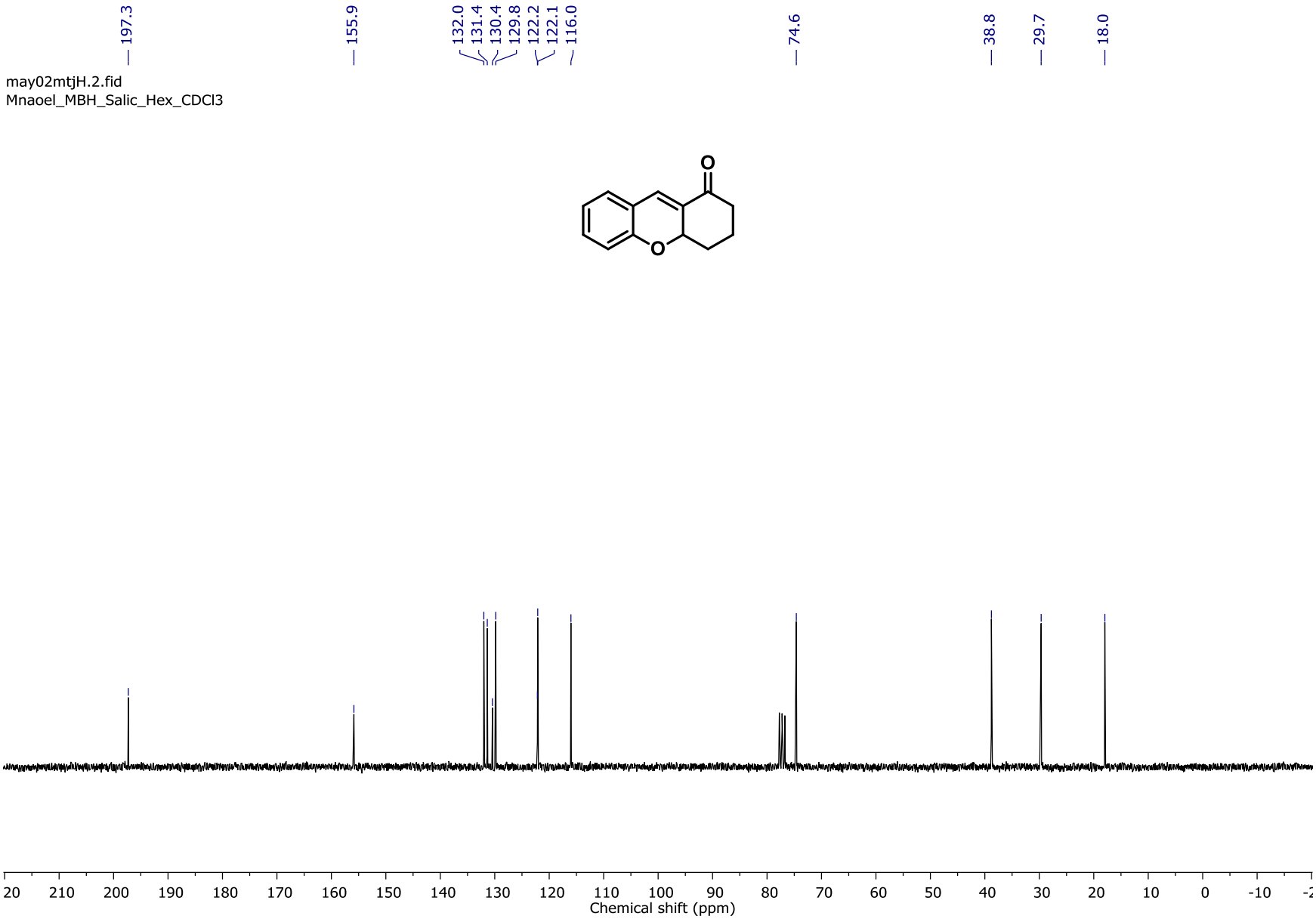

Figure S2. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3a.**

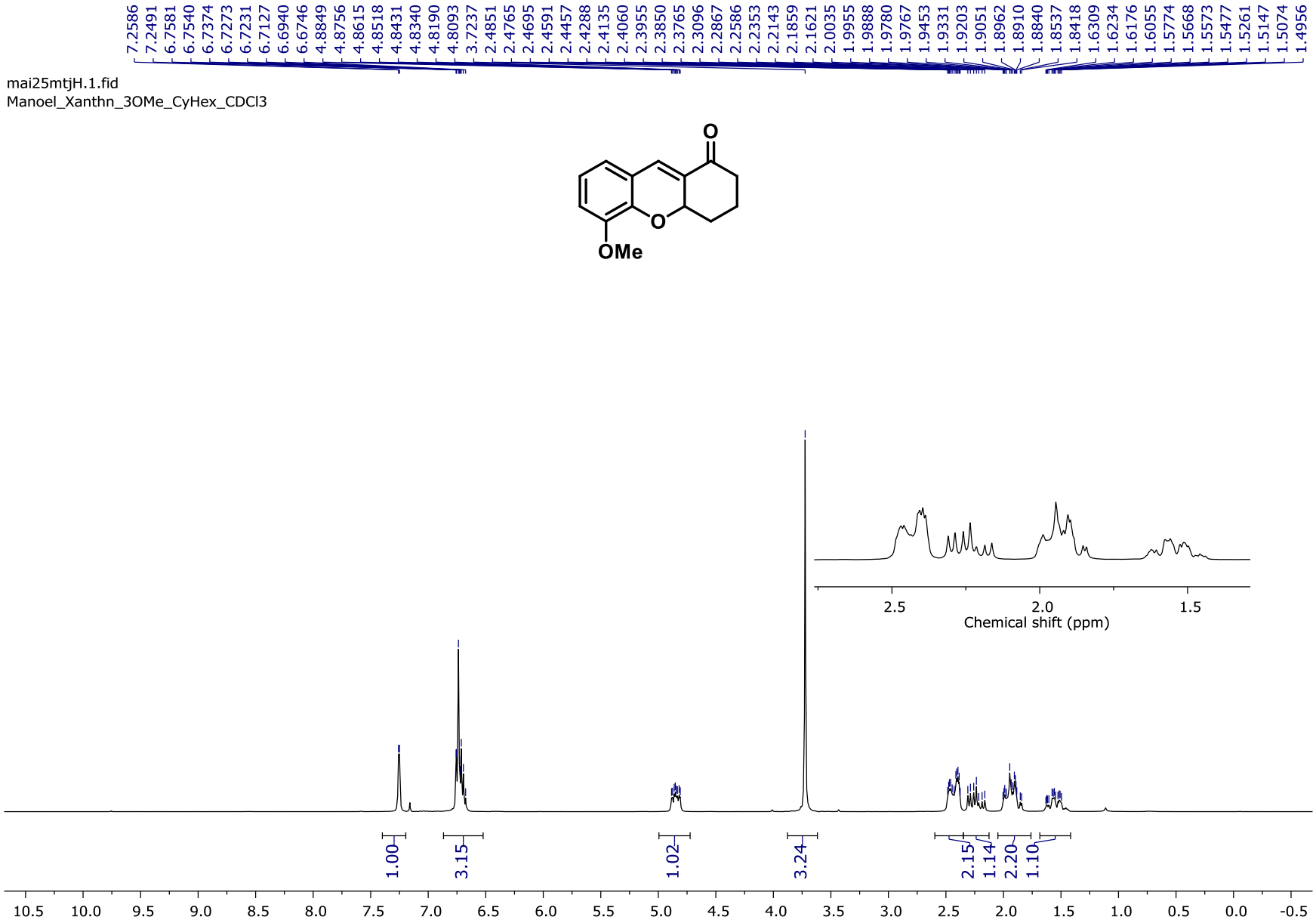

Figure S3. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3b.**

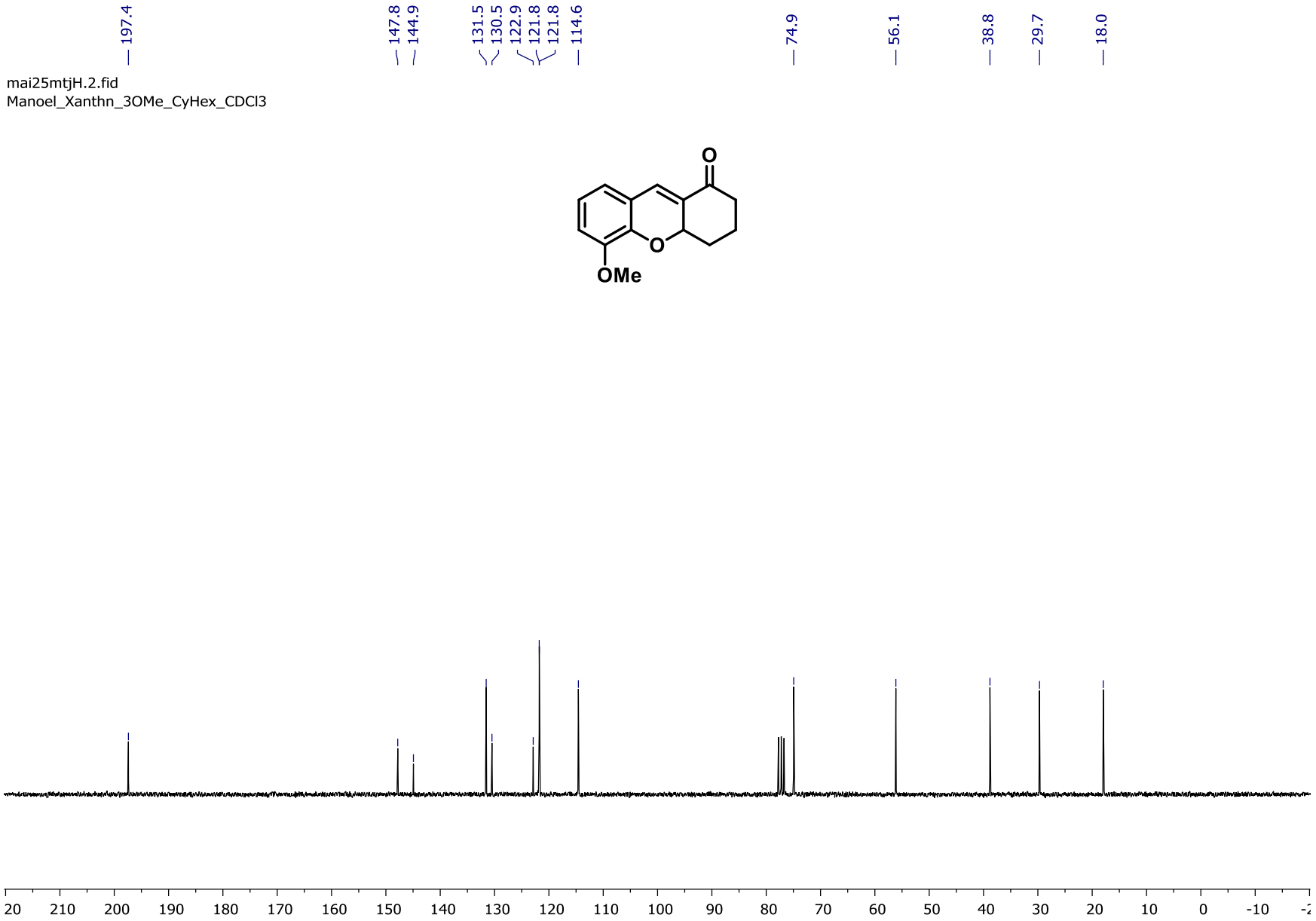

Figure S4. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3b.**

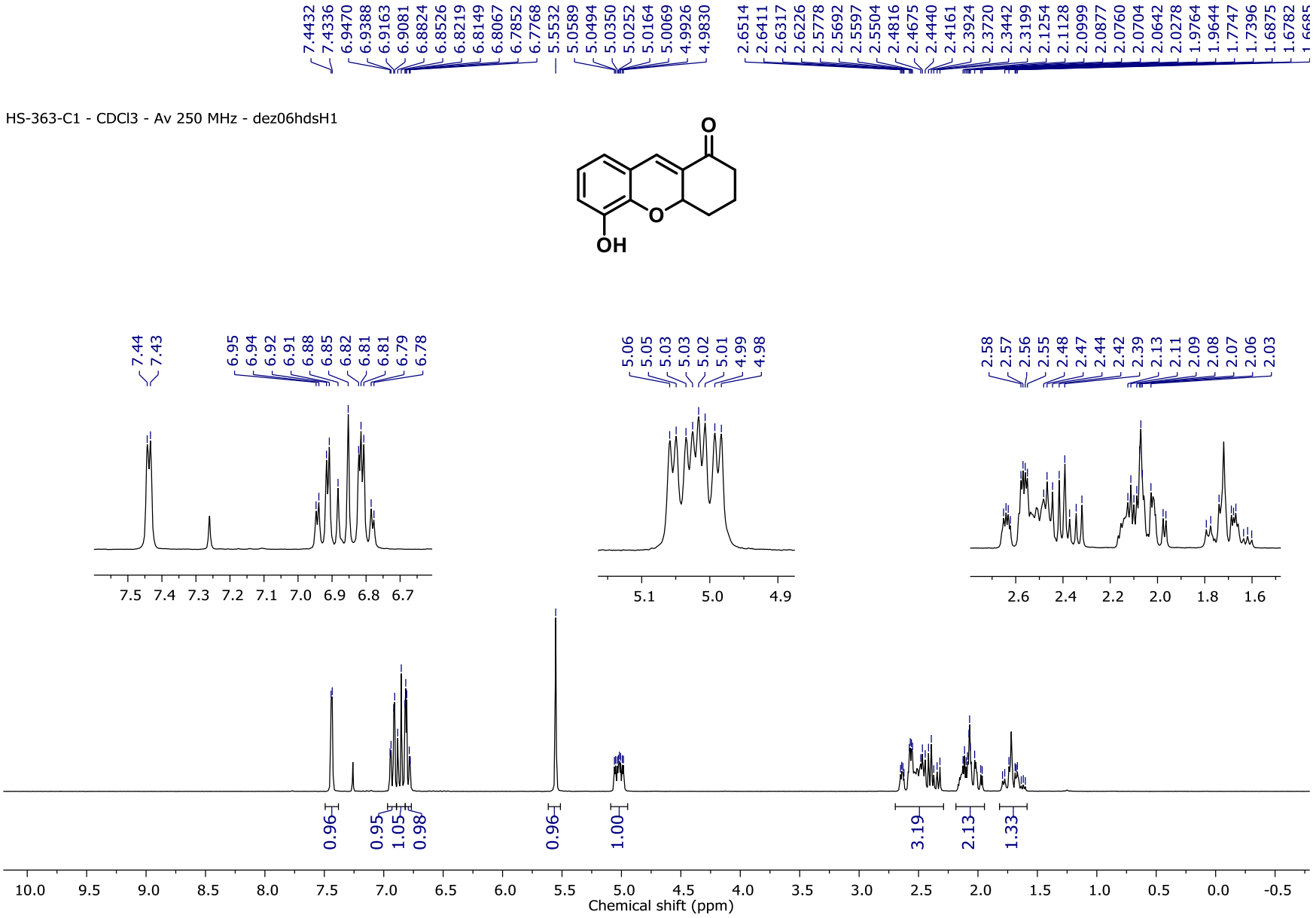

Figure S5. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3c.**

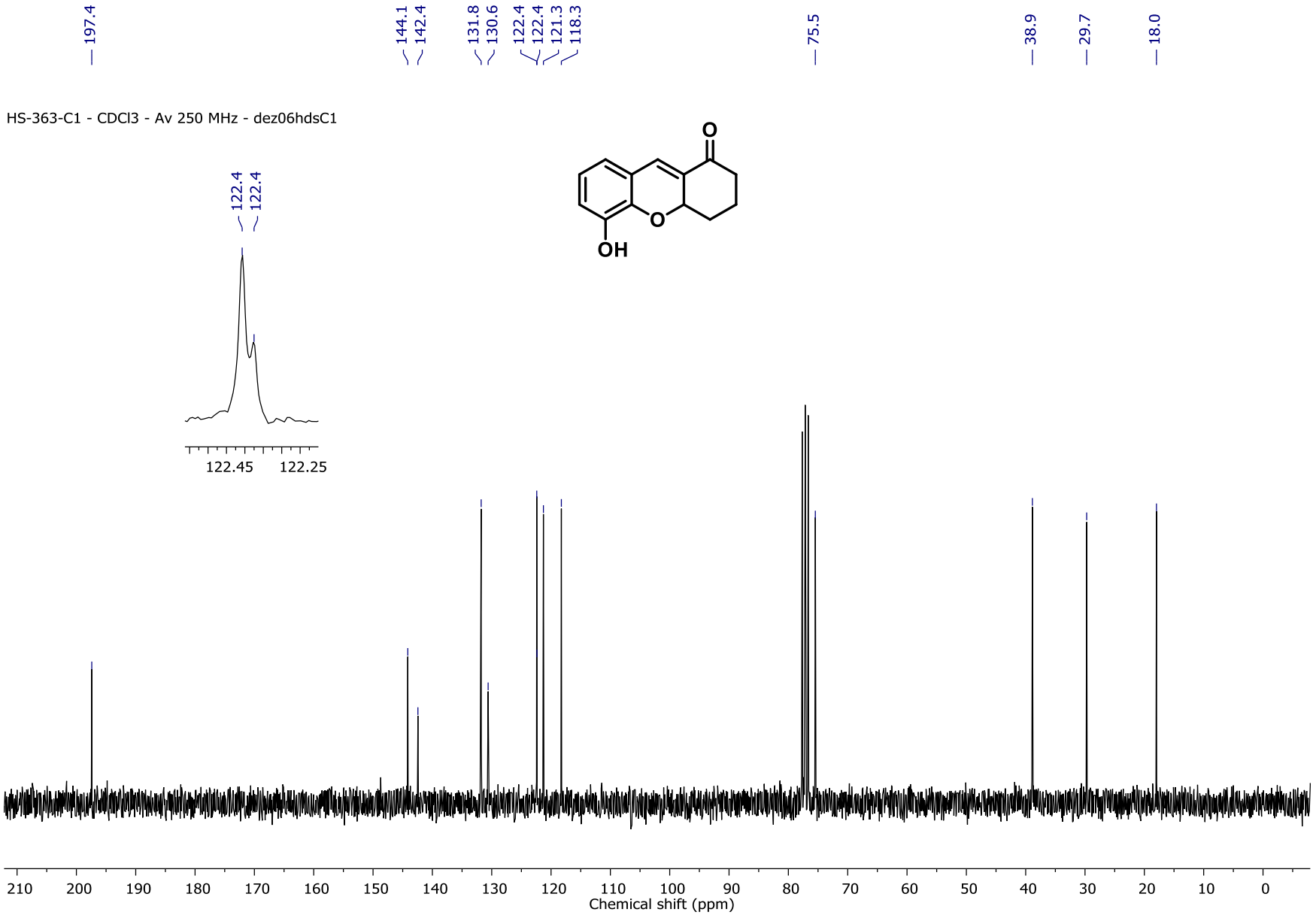

Figure S6. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3c.**

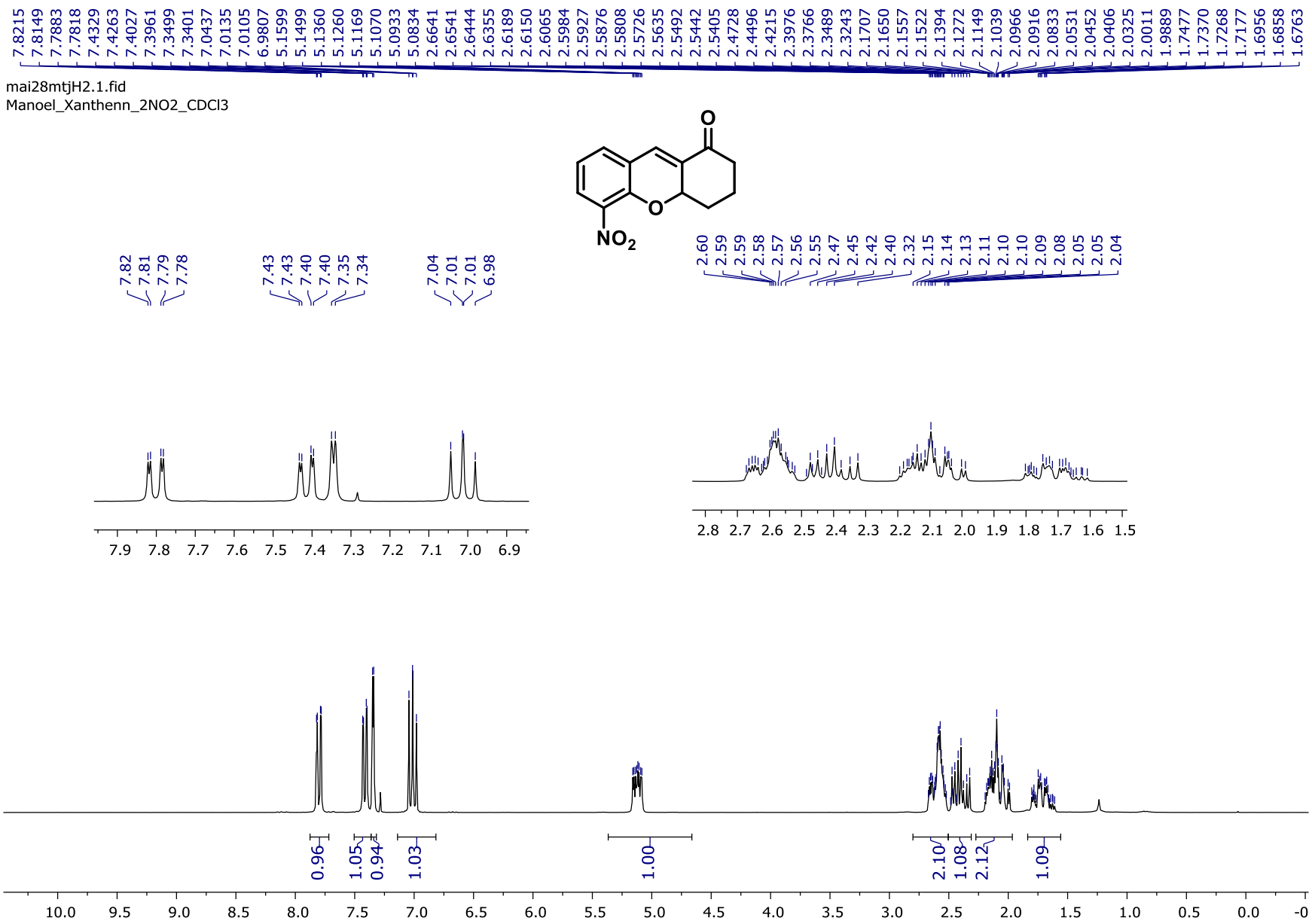

Figure S7. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3d.**

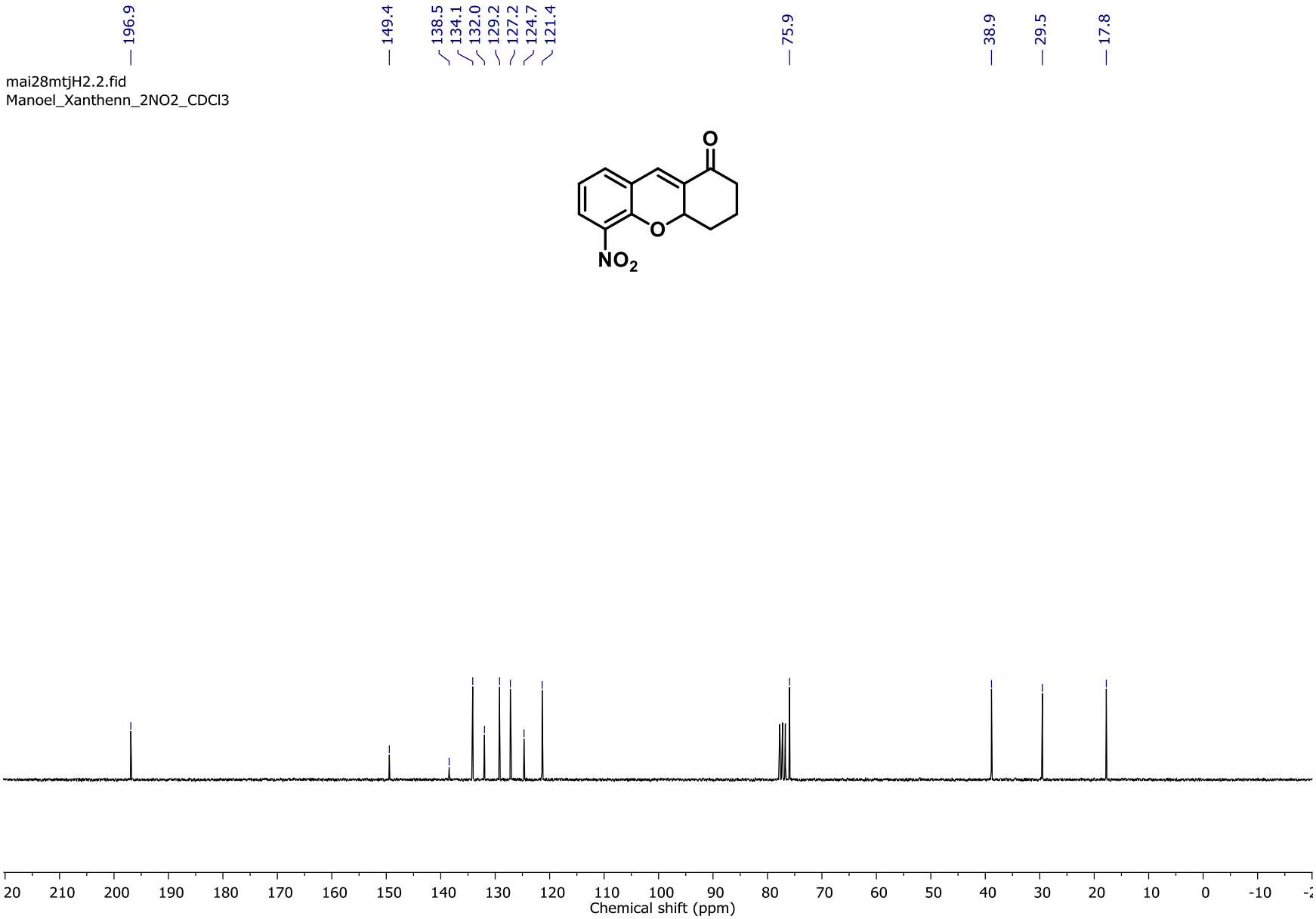

Figure S8. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3d.**

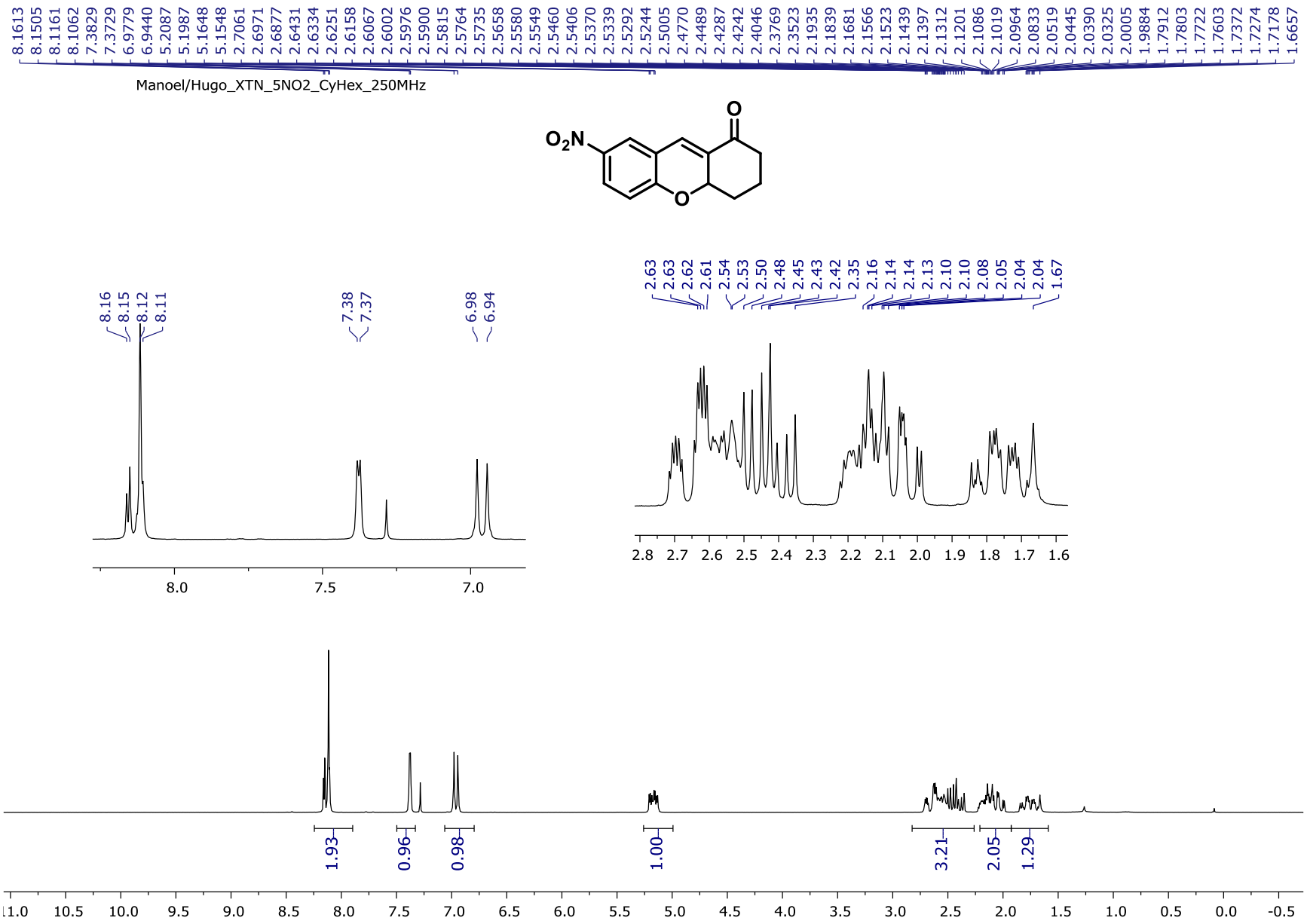

Figure S9. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3e.**

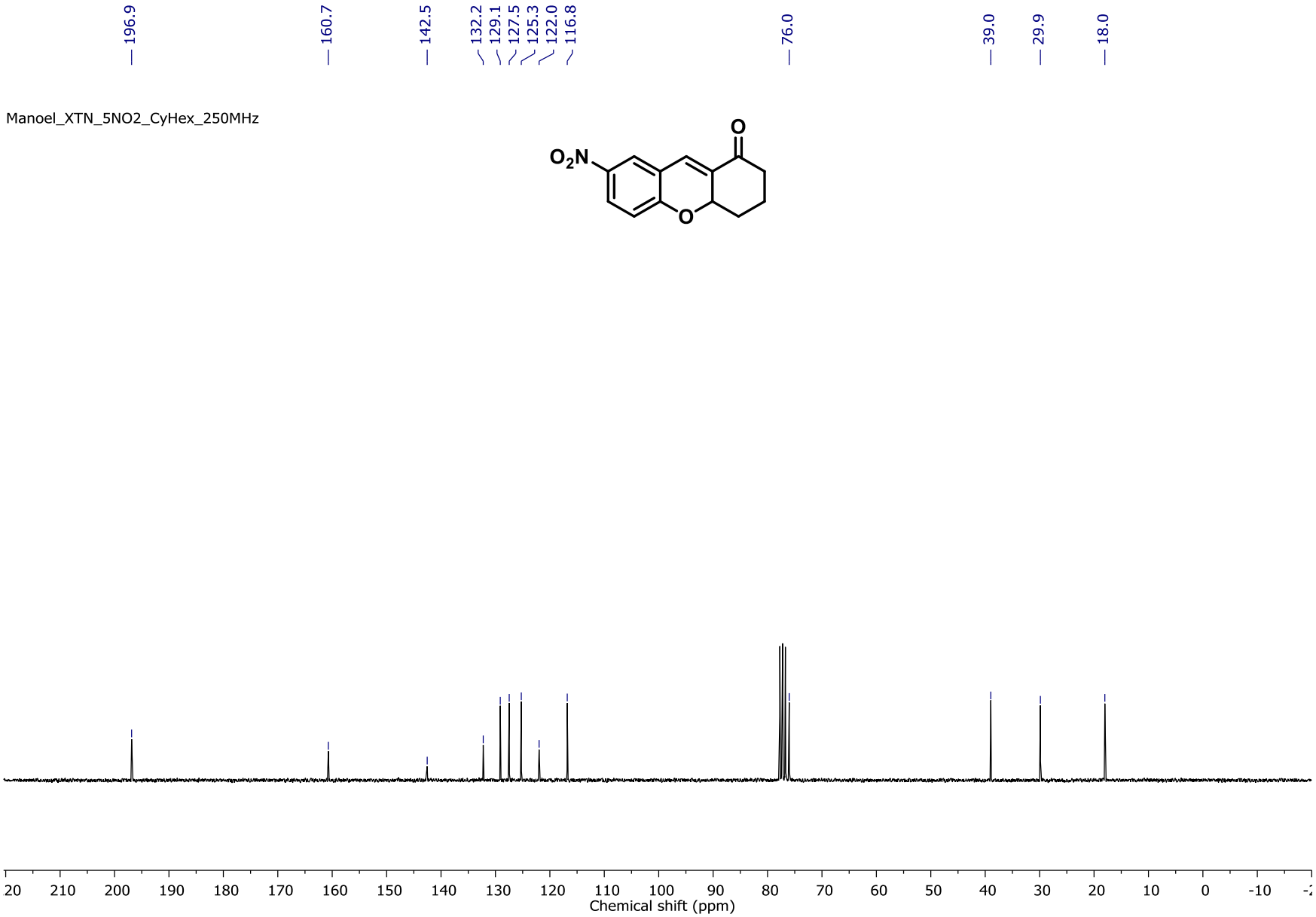

Figure S10. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3e.**

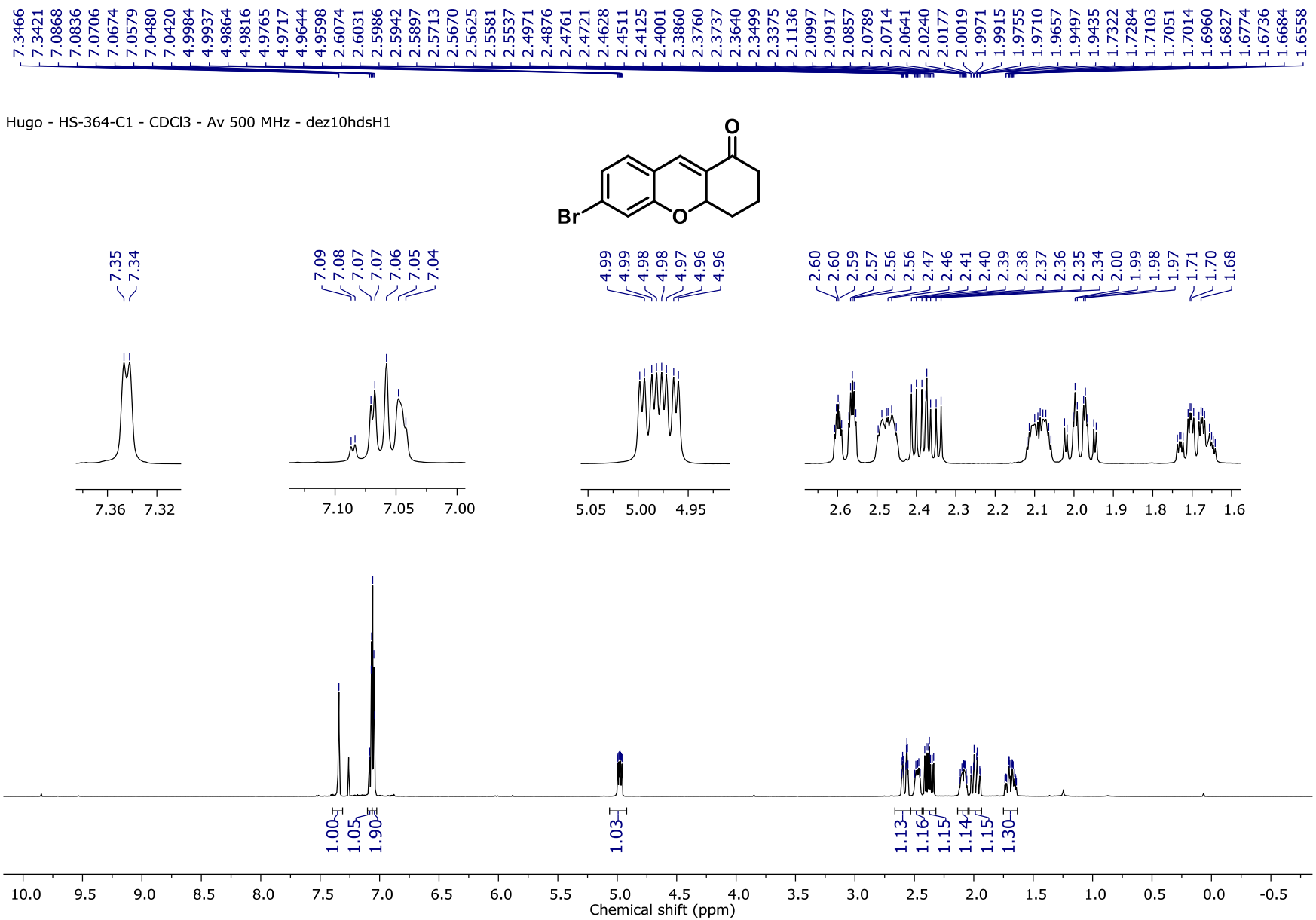

Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3f.**

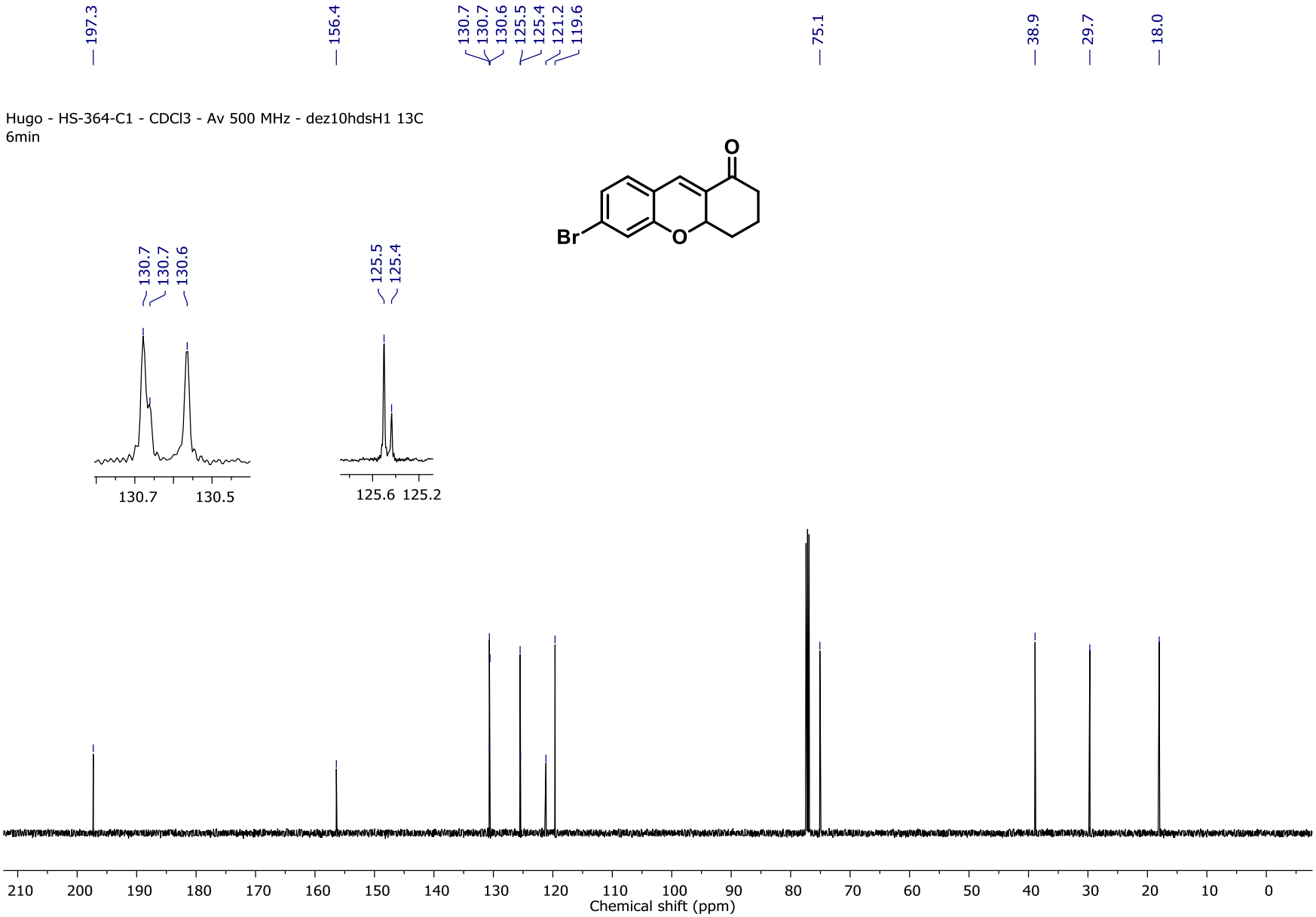

Figure S12. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **3f.**

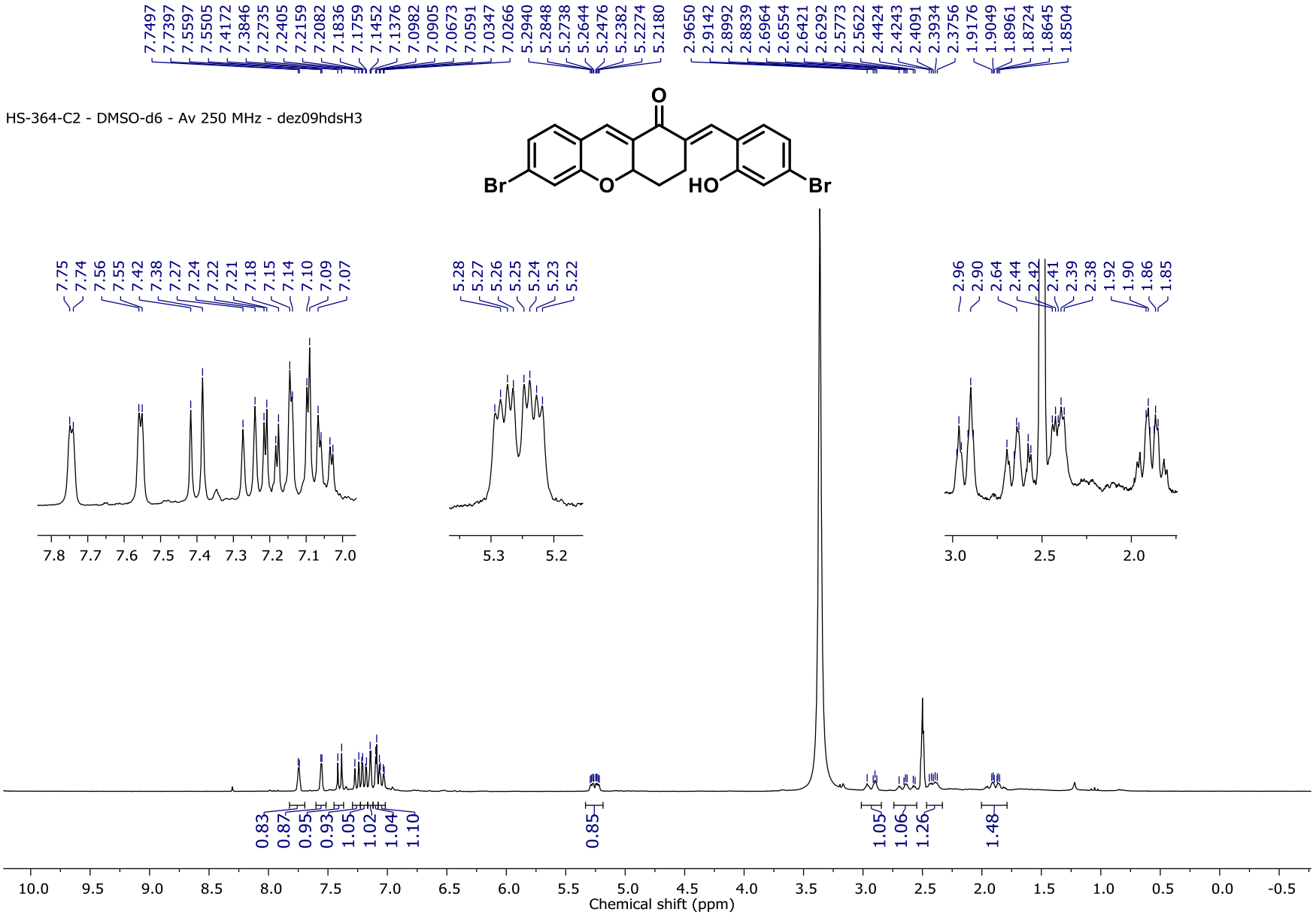

Figure S13. ^{1}H NMR spectrum (250 MHz, DMSO-d_6) of compound **4a.**

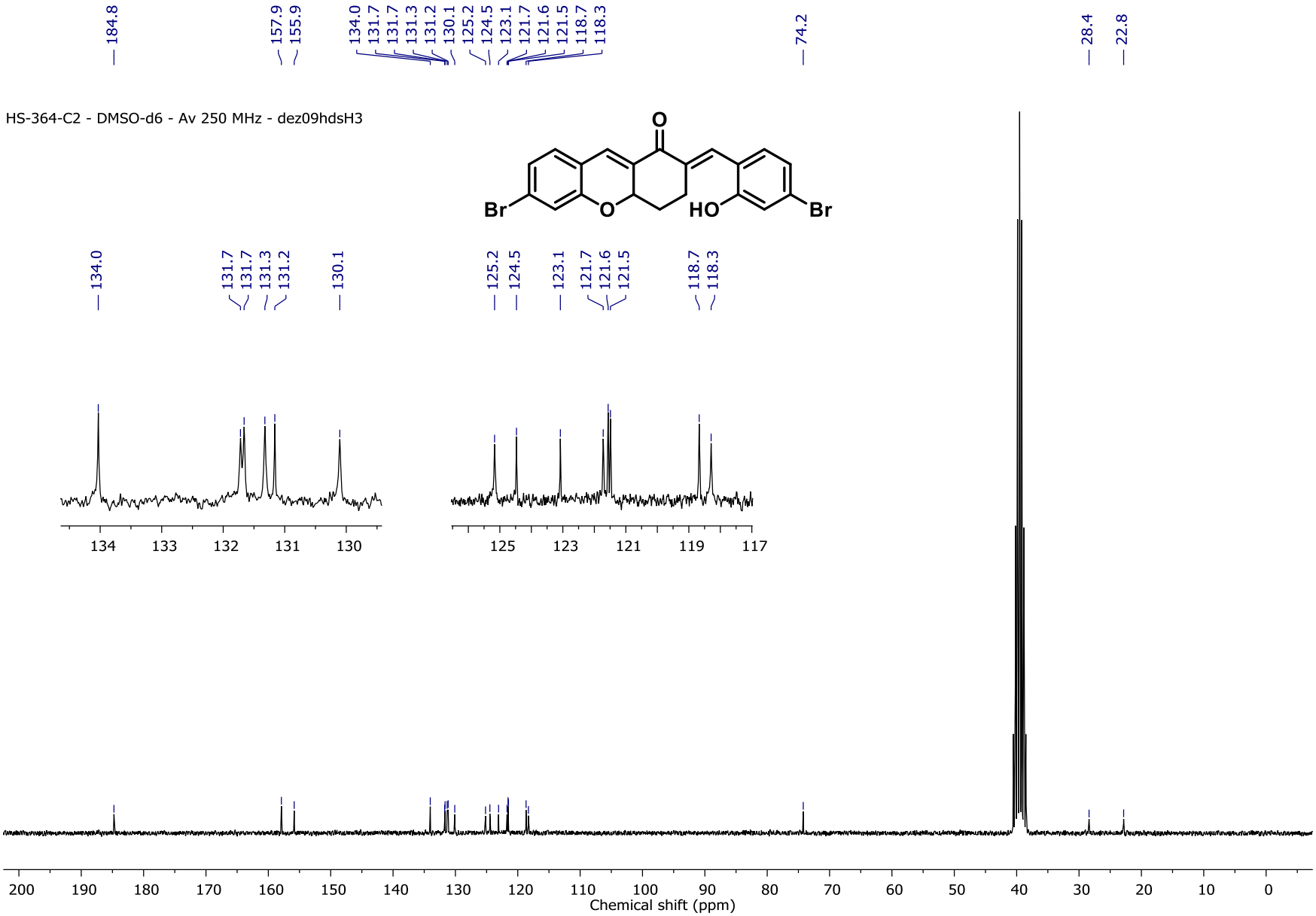

Figure S14. ^{13}C NMR spectrum (63 MHz, DMSO-d_6) of compound **4a.**

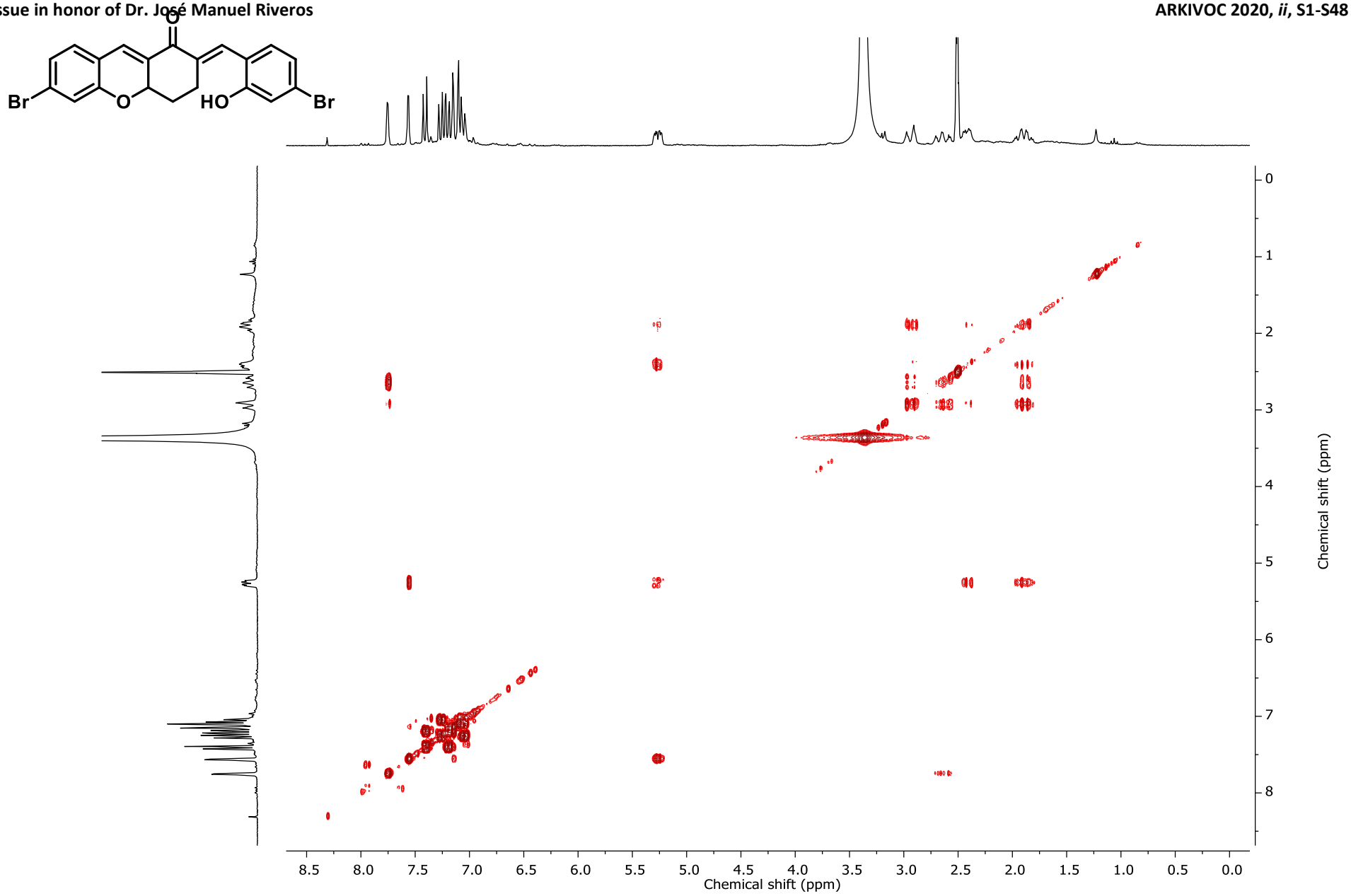

Figure S15. ^{1}H-^{1}H COSY NMR contour plot (250 MHz, DMSO-d_6) of compound **4a.**

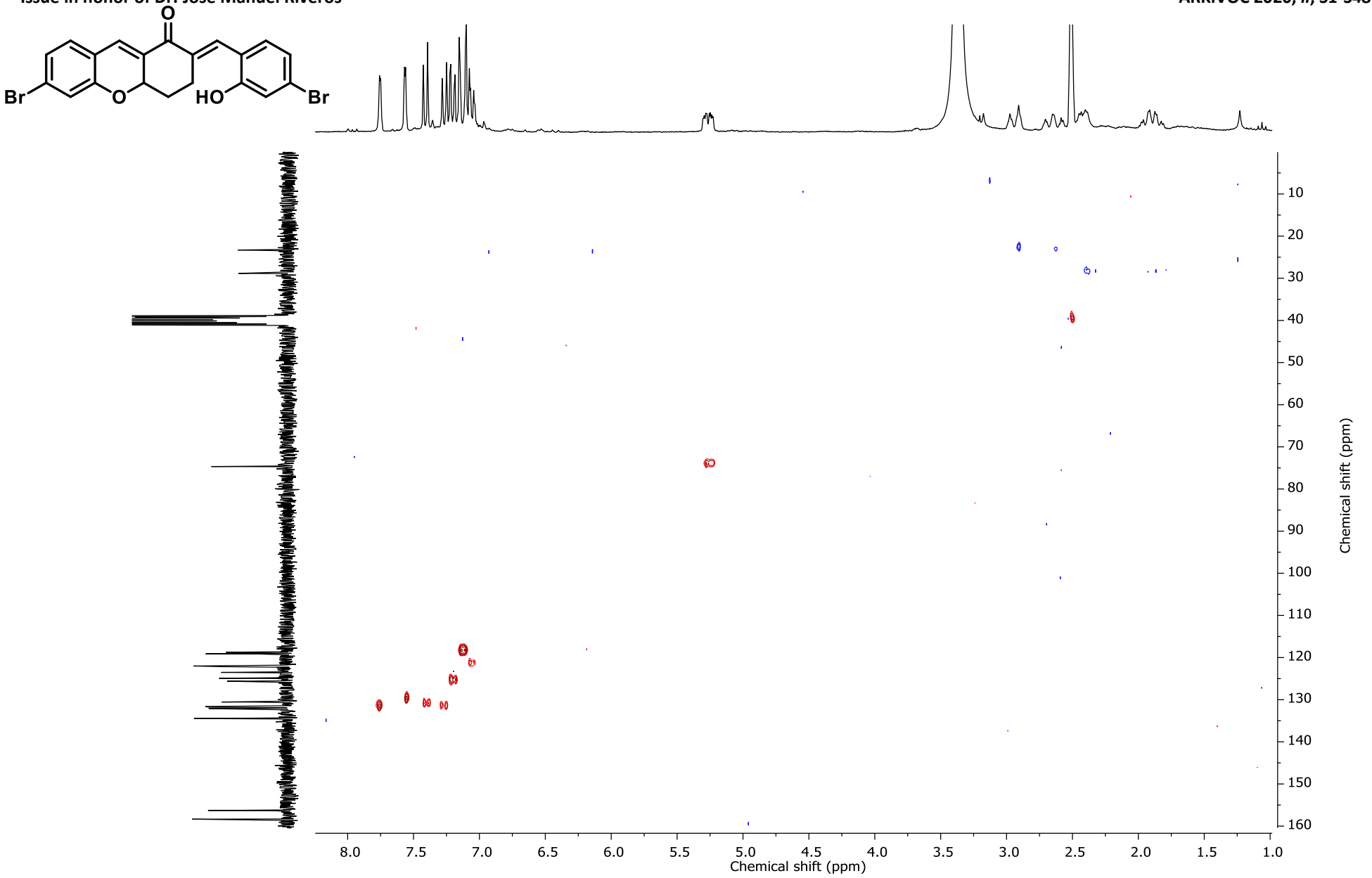

Figure S16. ^{1}H-^{13}C HSQC NMR contour plot (250 MHz, DMSO-d_6) of compound **4a.**

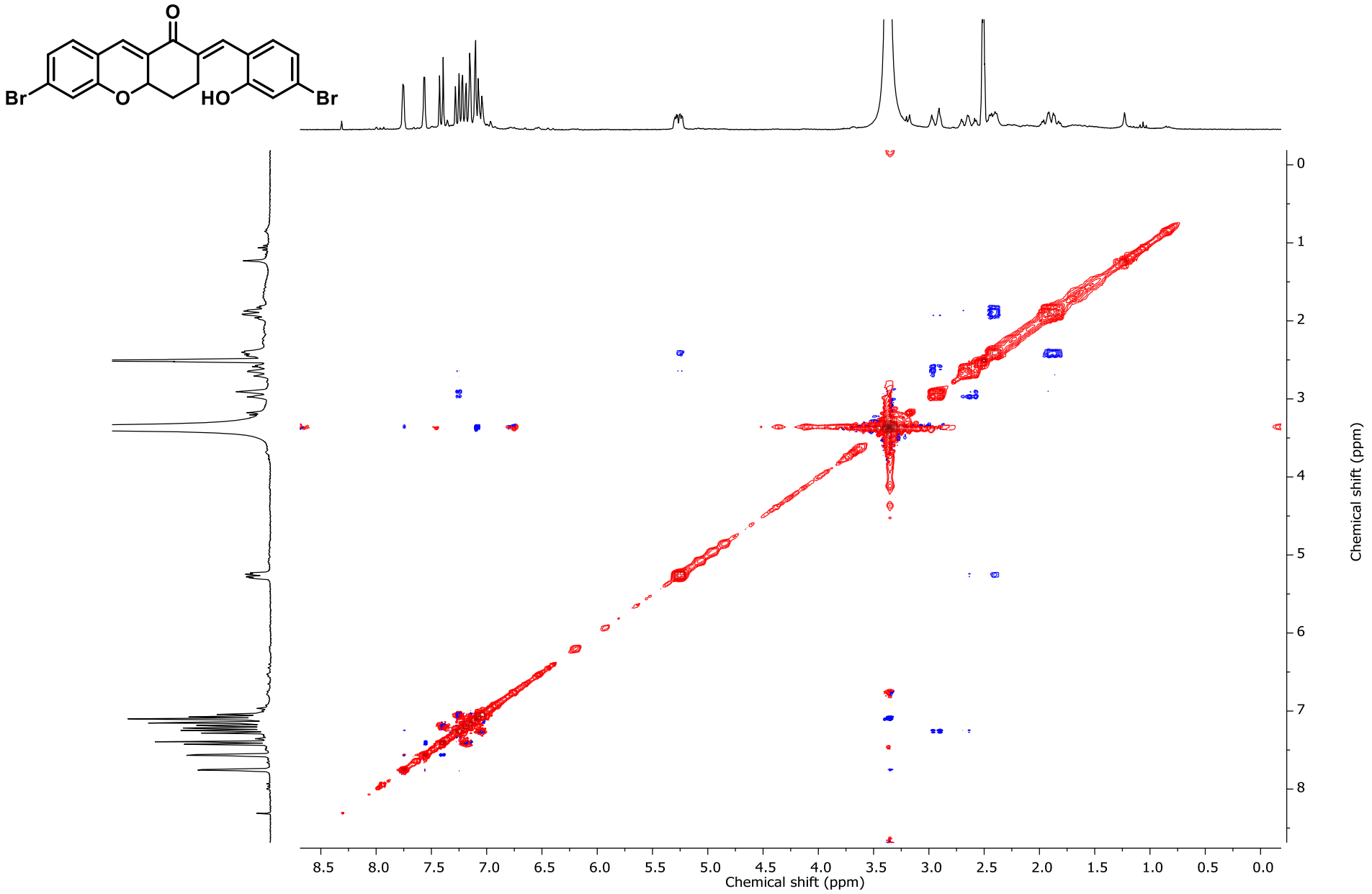

Figure S17. ^{1}H-^{1}H NOESY NMR contour plot (250 MHz, DMSO-d_6) of compound **4a.**

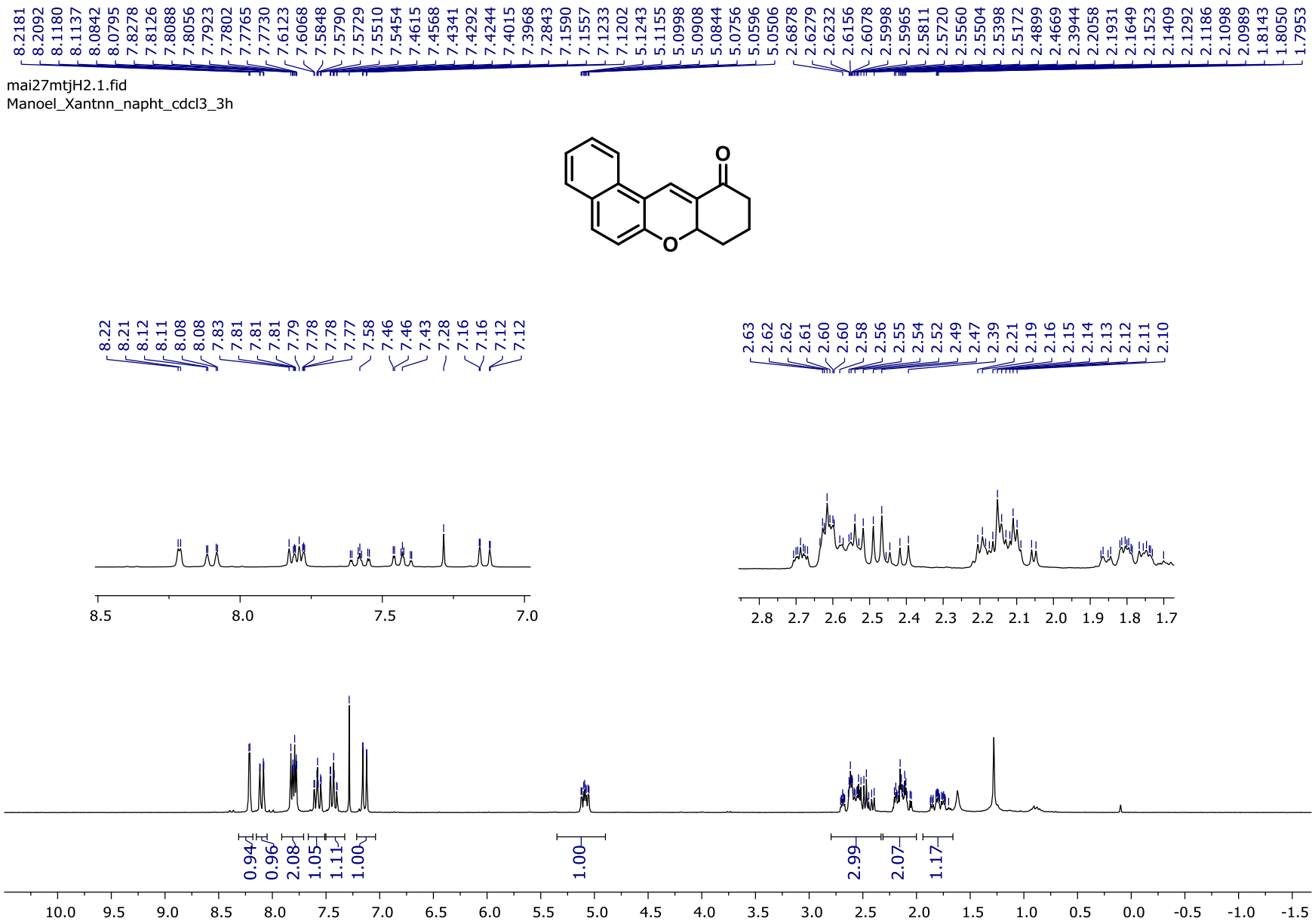

Figure S18. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3g.**

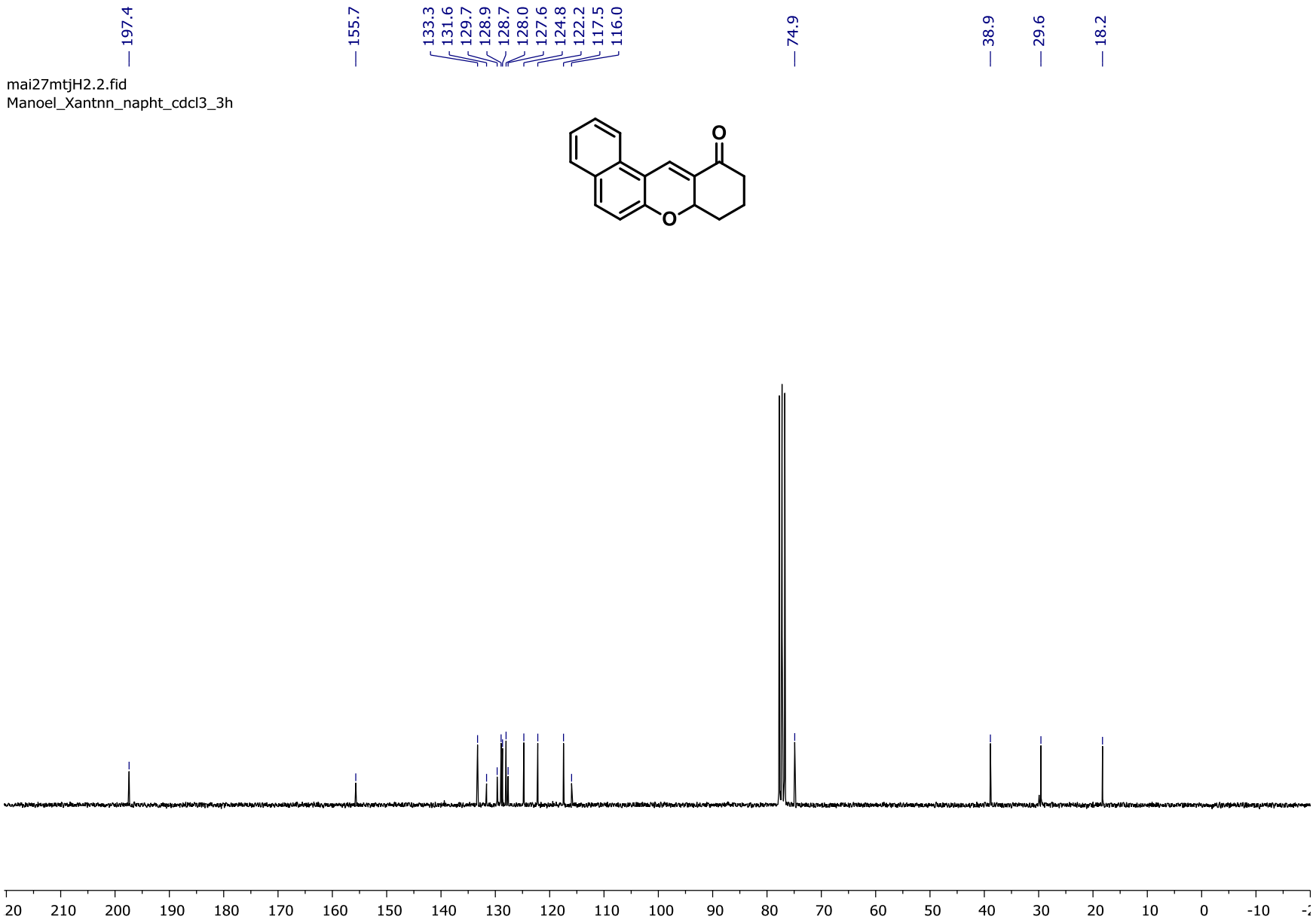

Figure S19. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3g.**

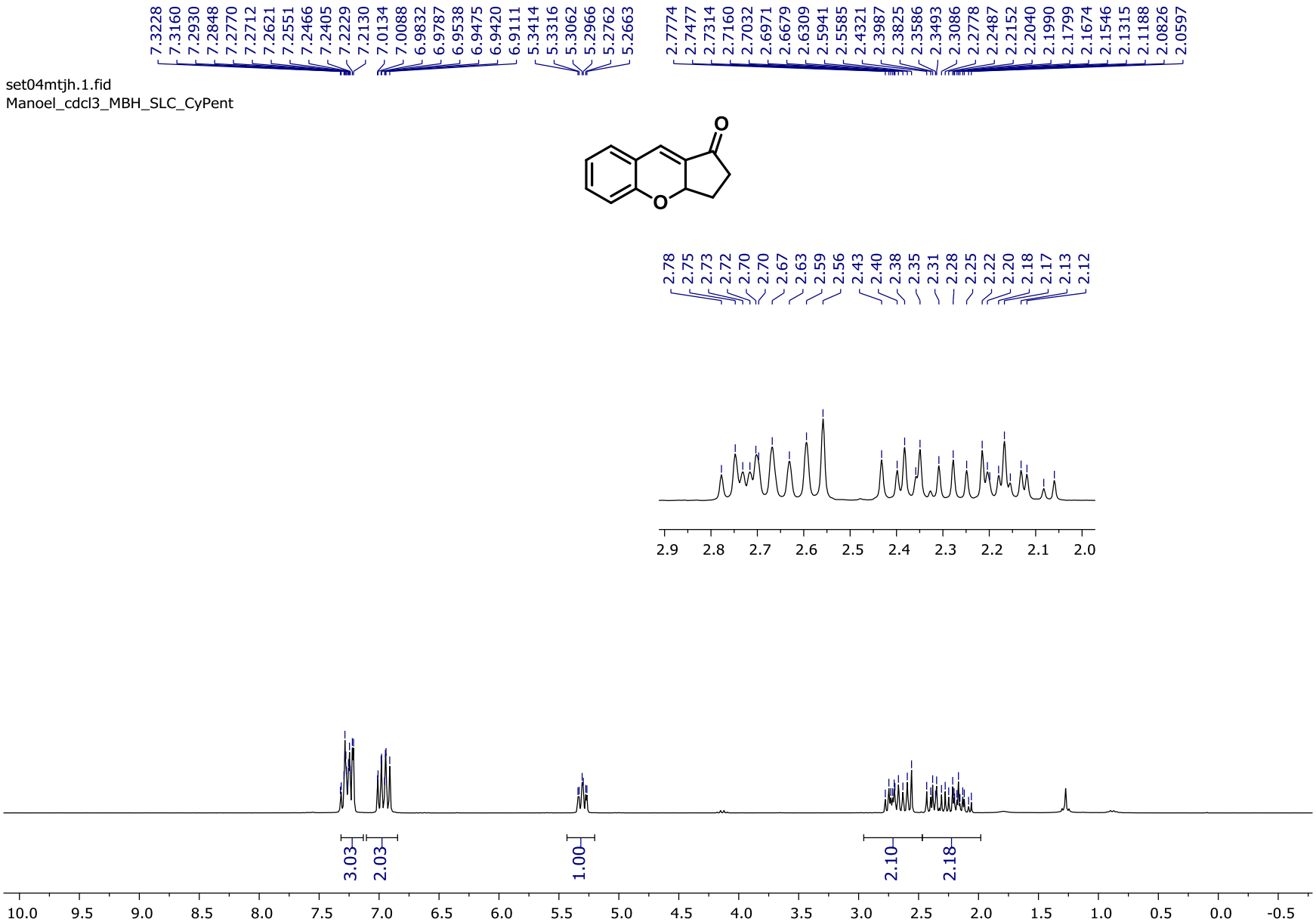

Figure S20. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3h.**

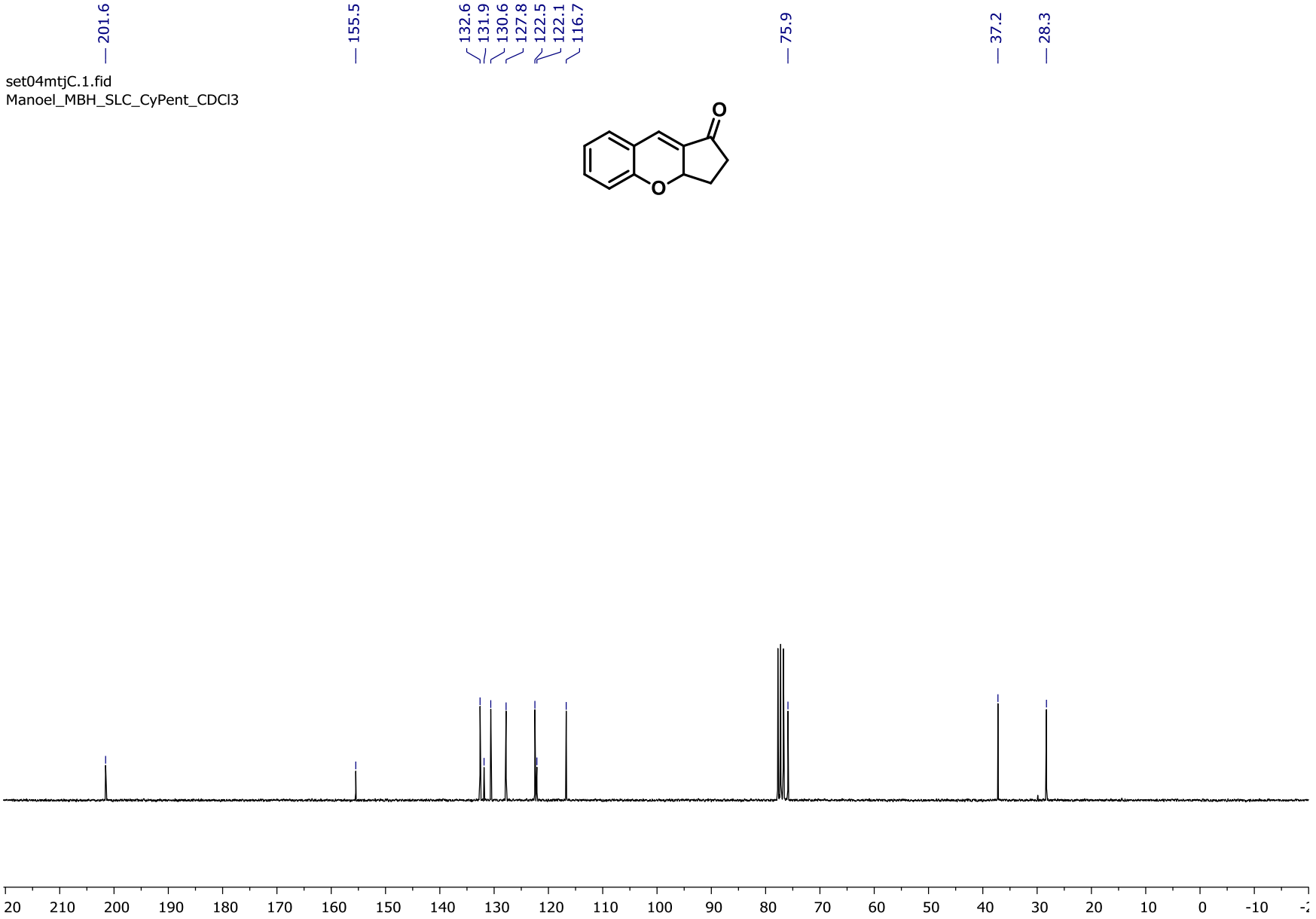

Figure S21. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3h.**

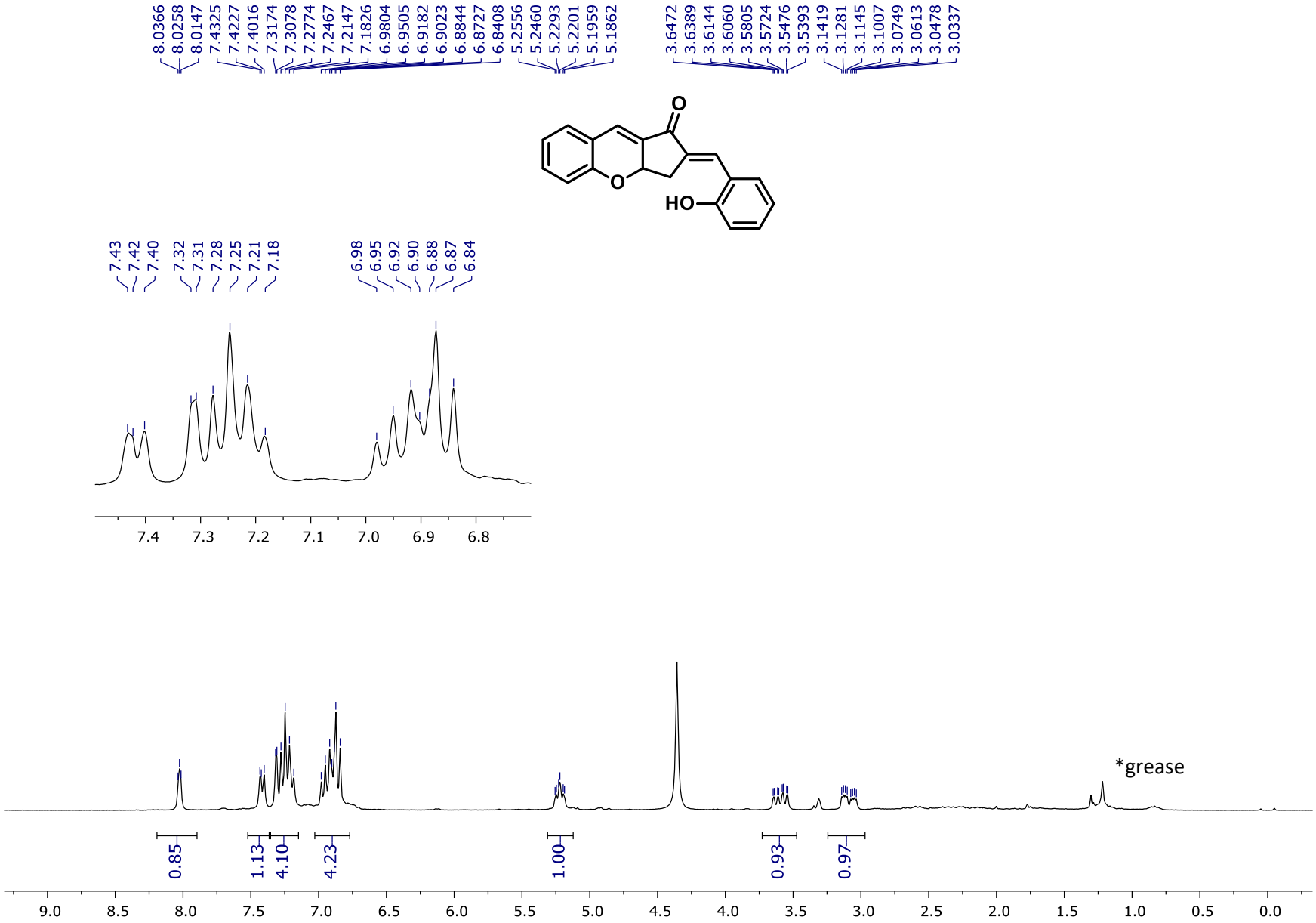

Figure S22. ^{1}H NMR spectrum (250 MHz, $CDCl_3$/MeOH-d_4 6:1) of compound **4b.**

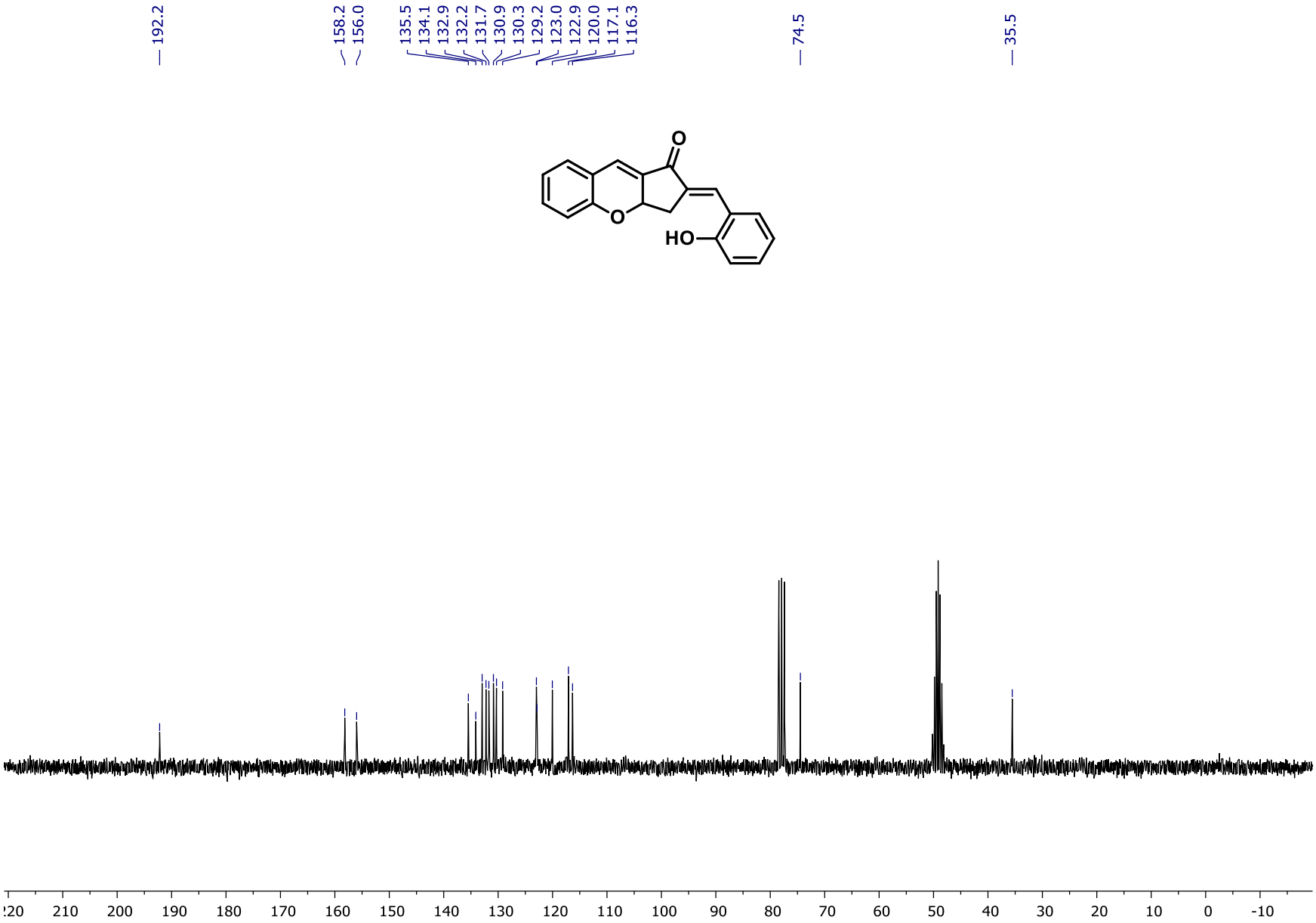

Figure S23. ^{13}C NMR spectrum (63 MHz, $CDCl_3$/MeOH-d_4 6:1) of compound **4b.**

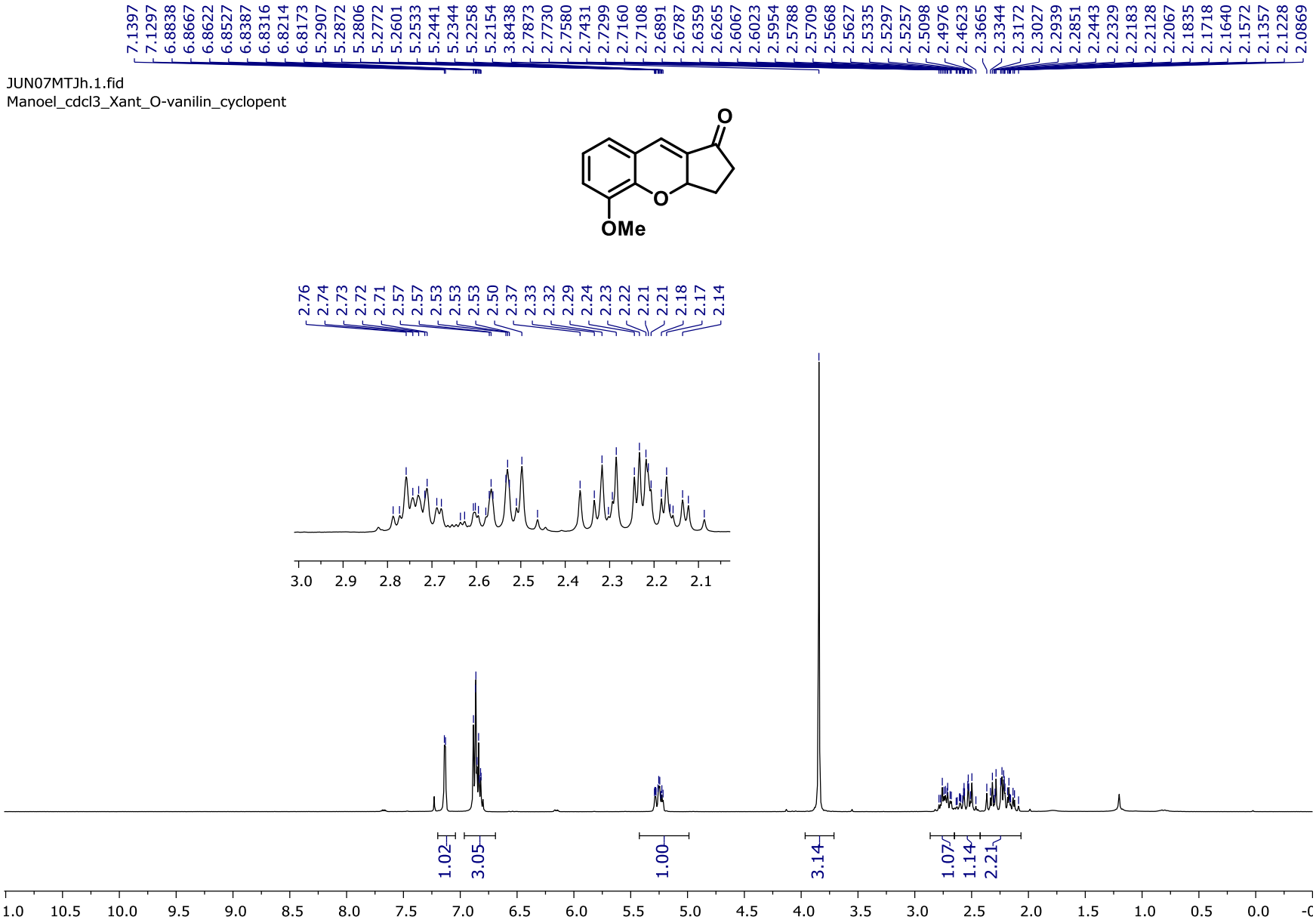

Figure S24. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3i.**

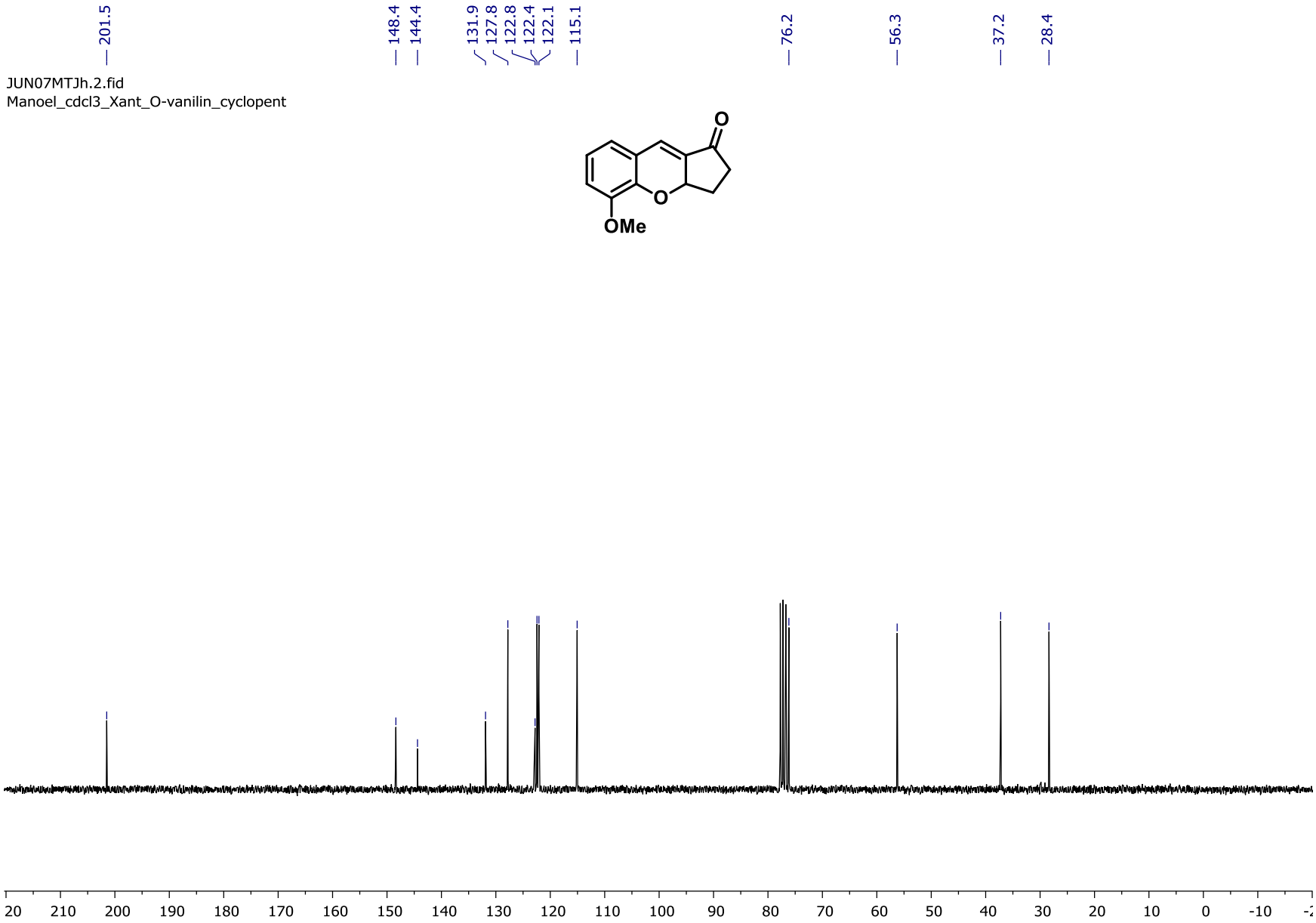

Figure S25. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3i.**

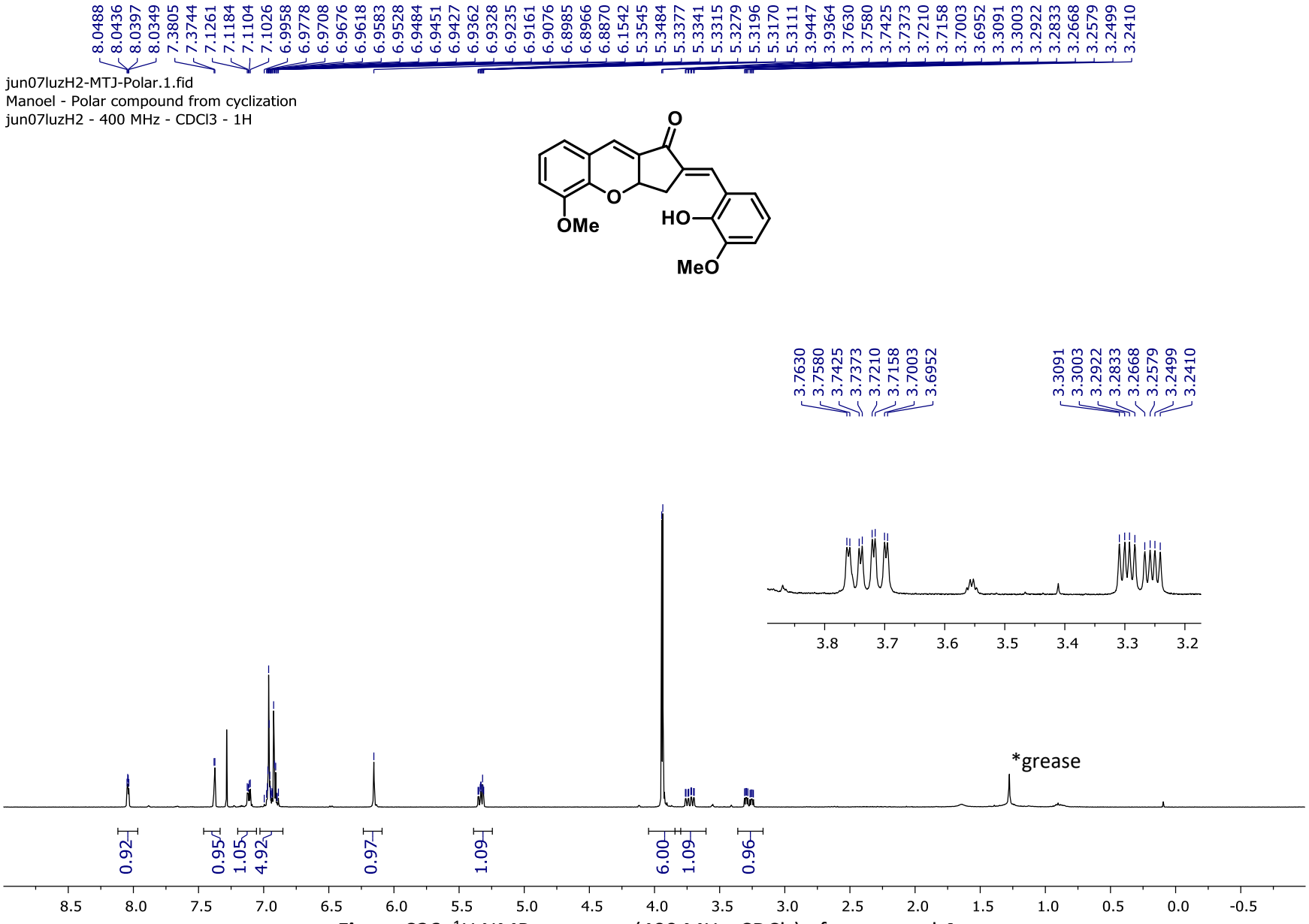

Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c.**

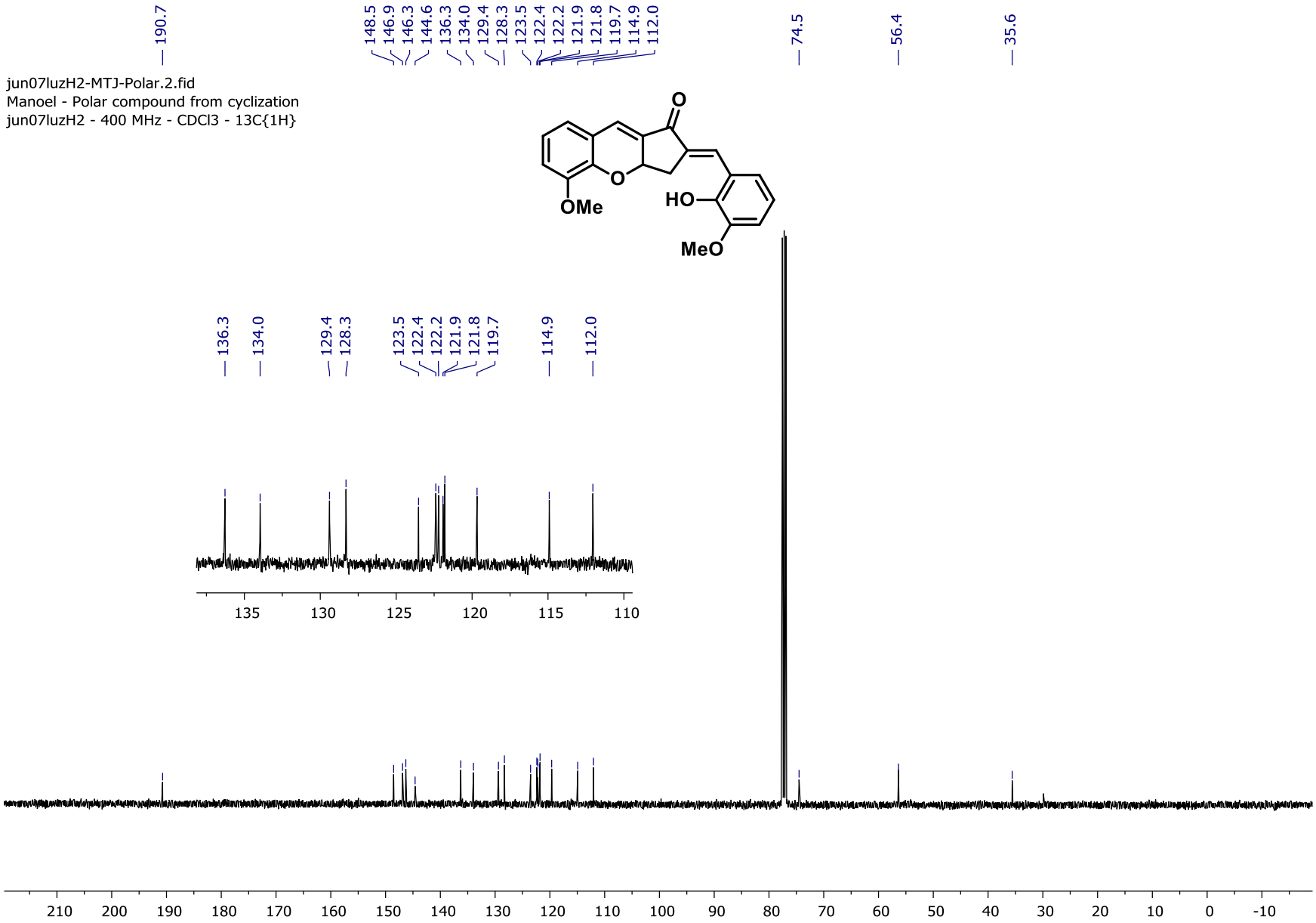

Figure S27. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4c.**

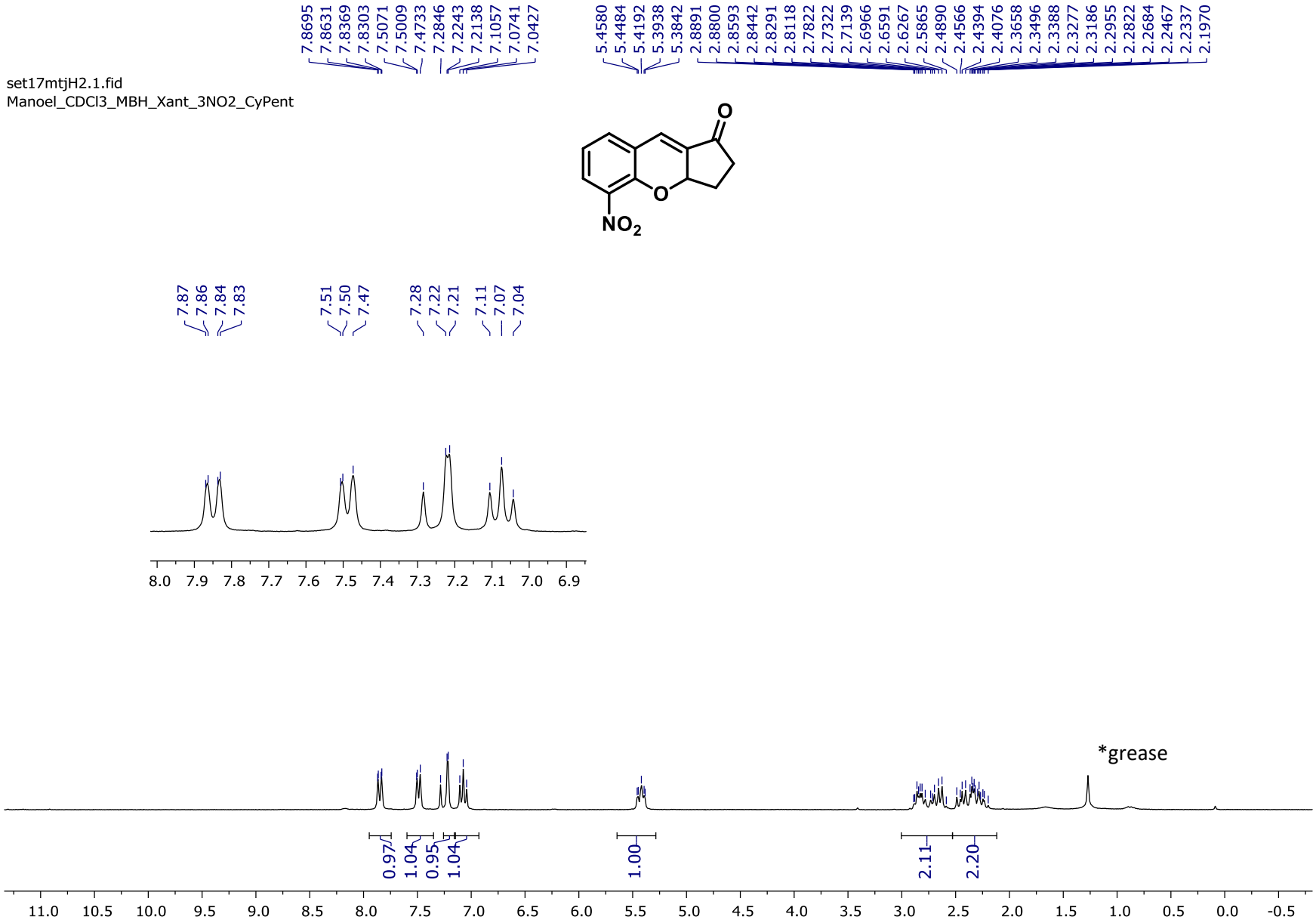

Figure S28. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3j.**

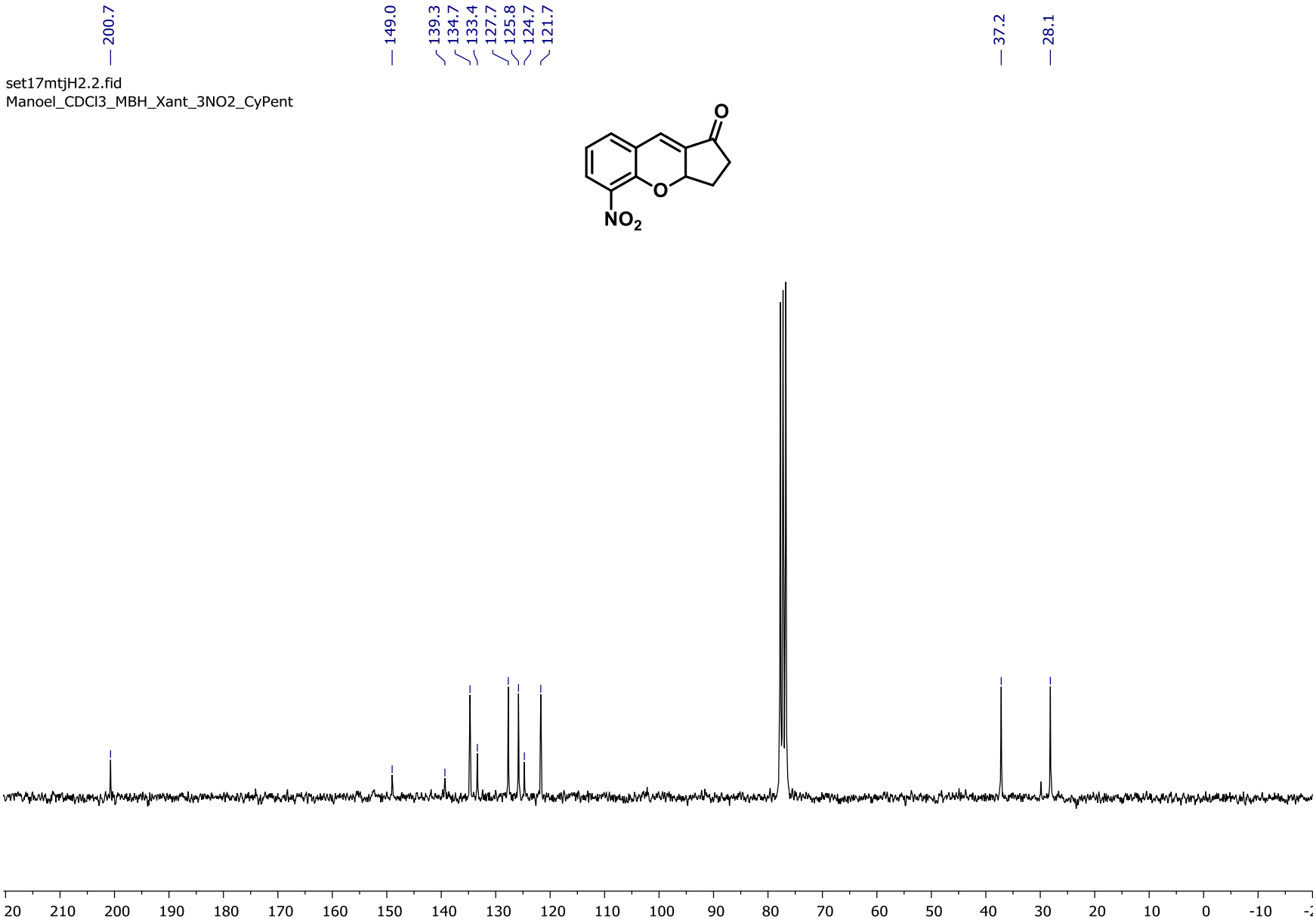

Figure S29. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3j.**

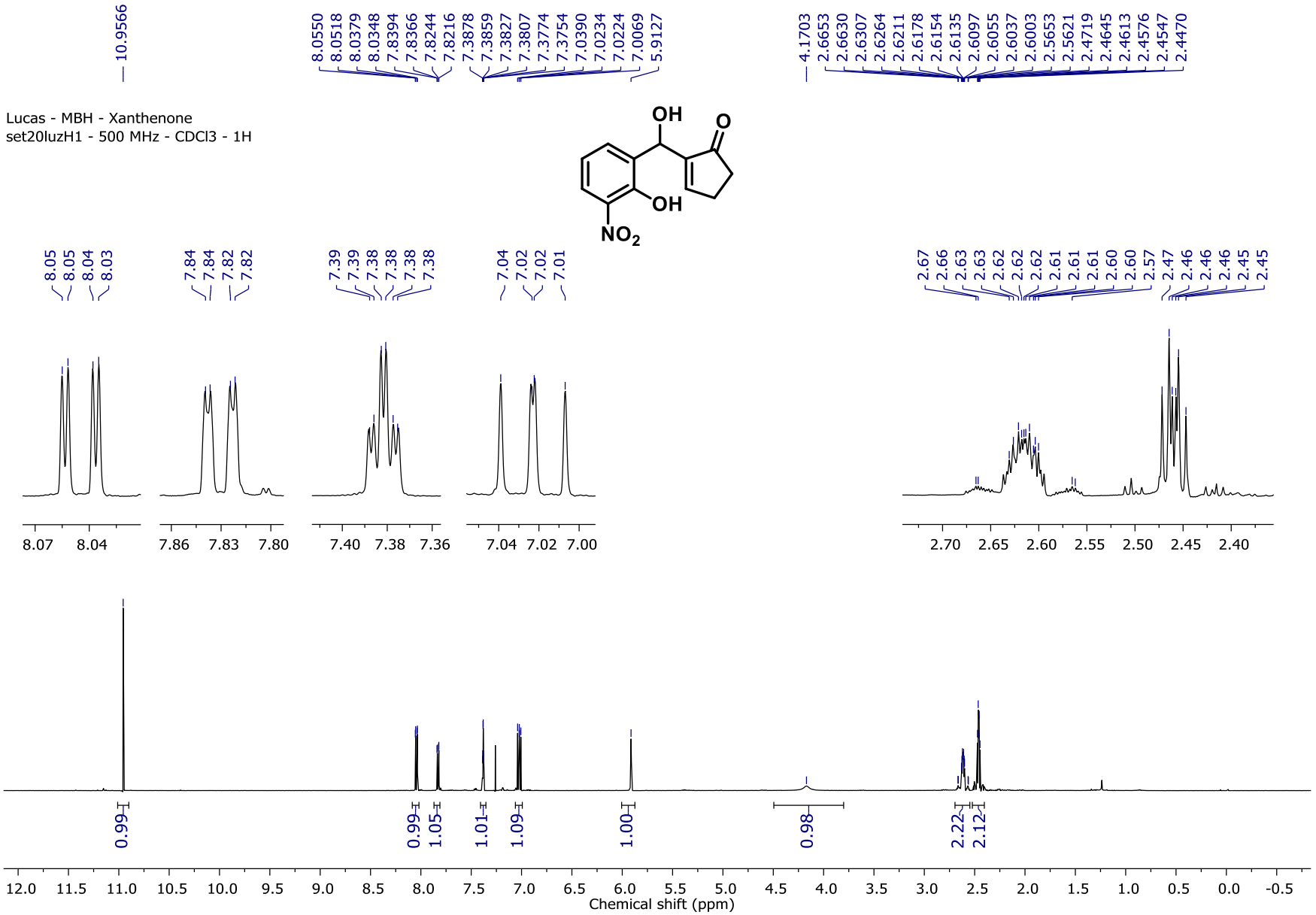

Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5a.**

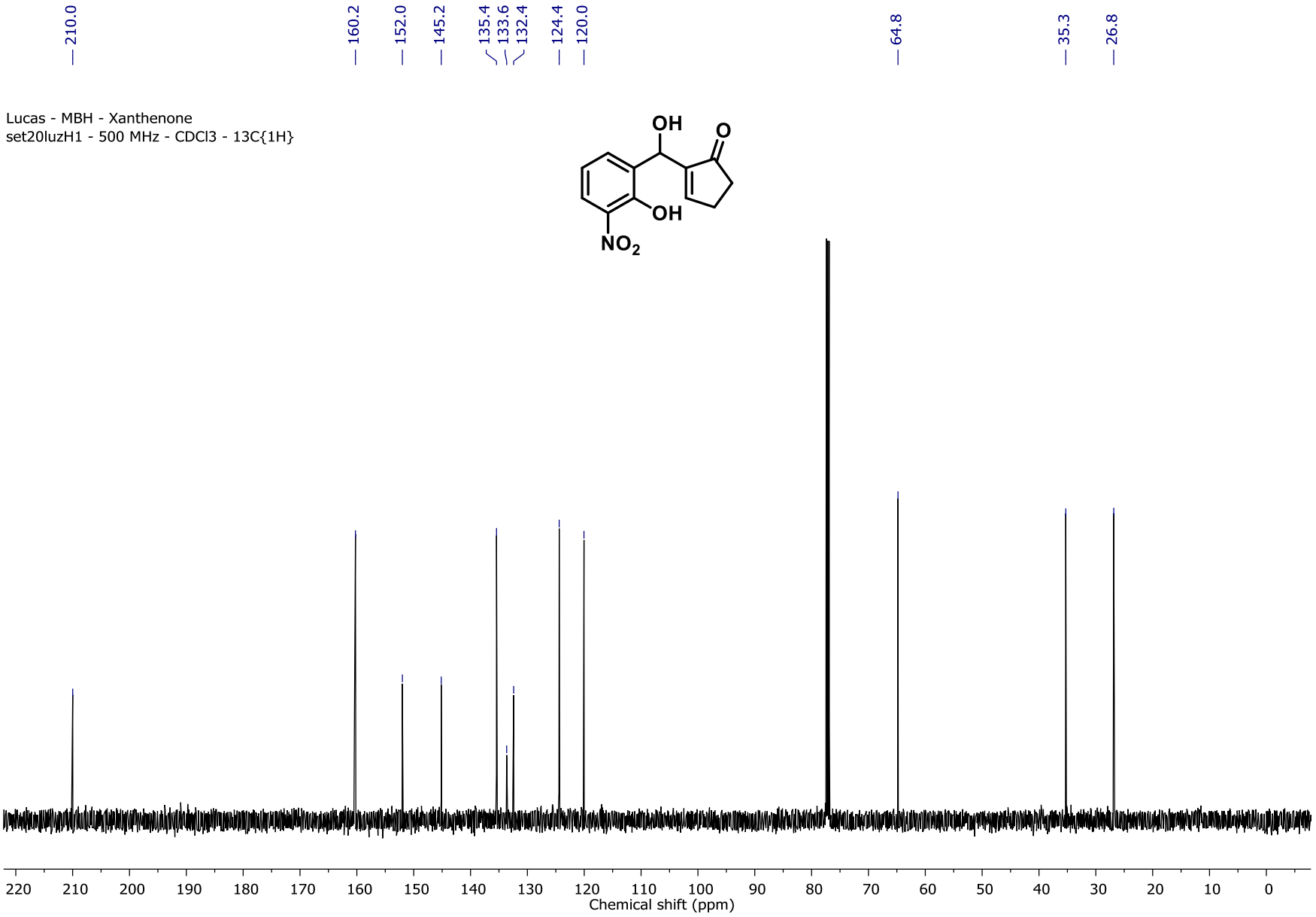

Figure S31. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **5a.**

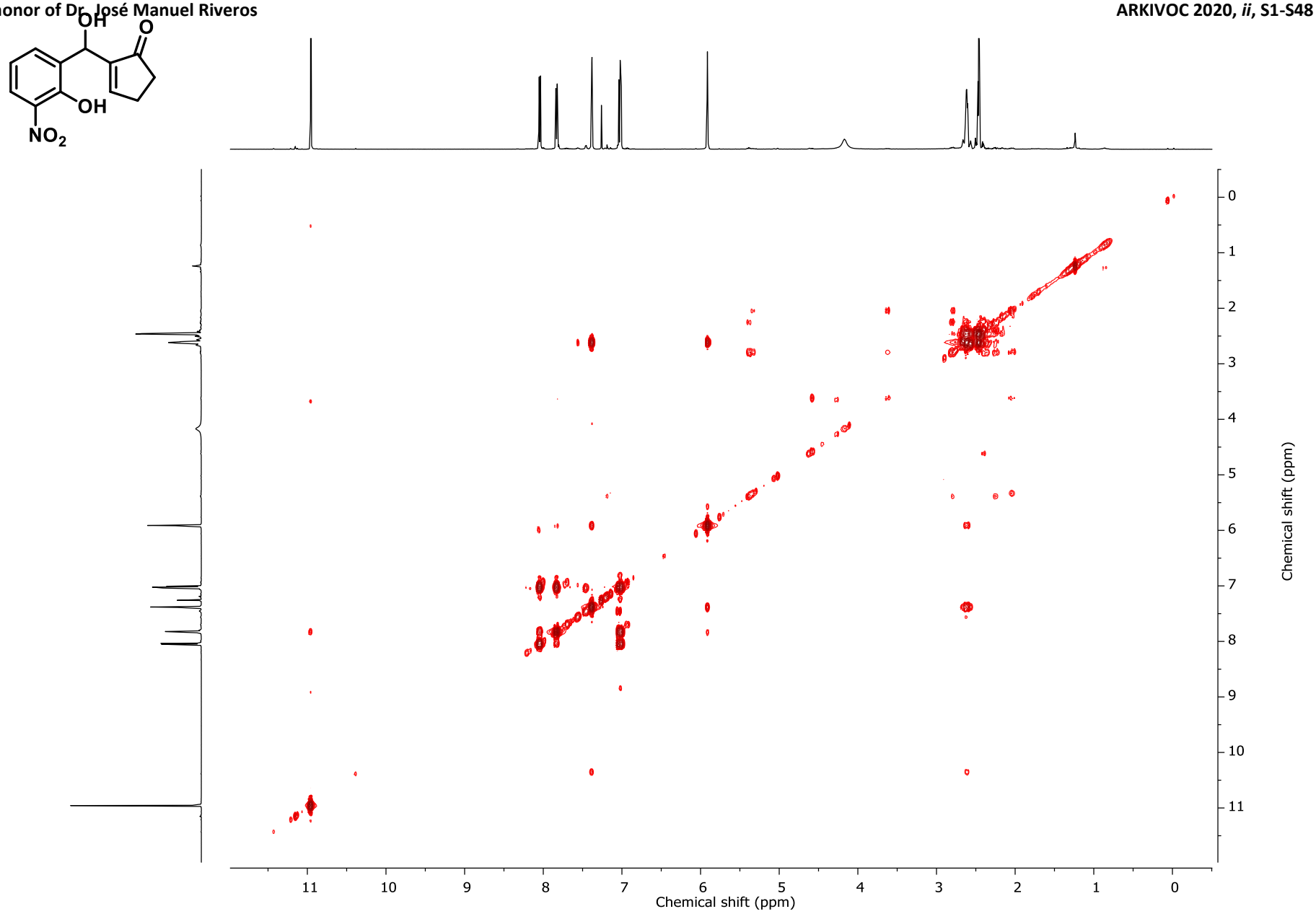

Figure S32. ^{1}H-^{1}H COSY NMR contour plot (500 MHz, $CDCl_3$) of compound **5a.**

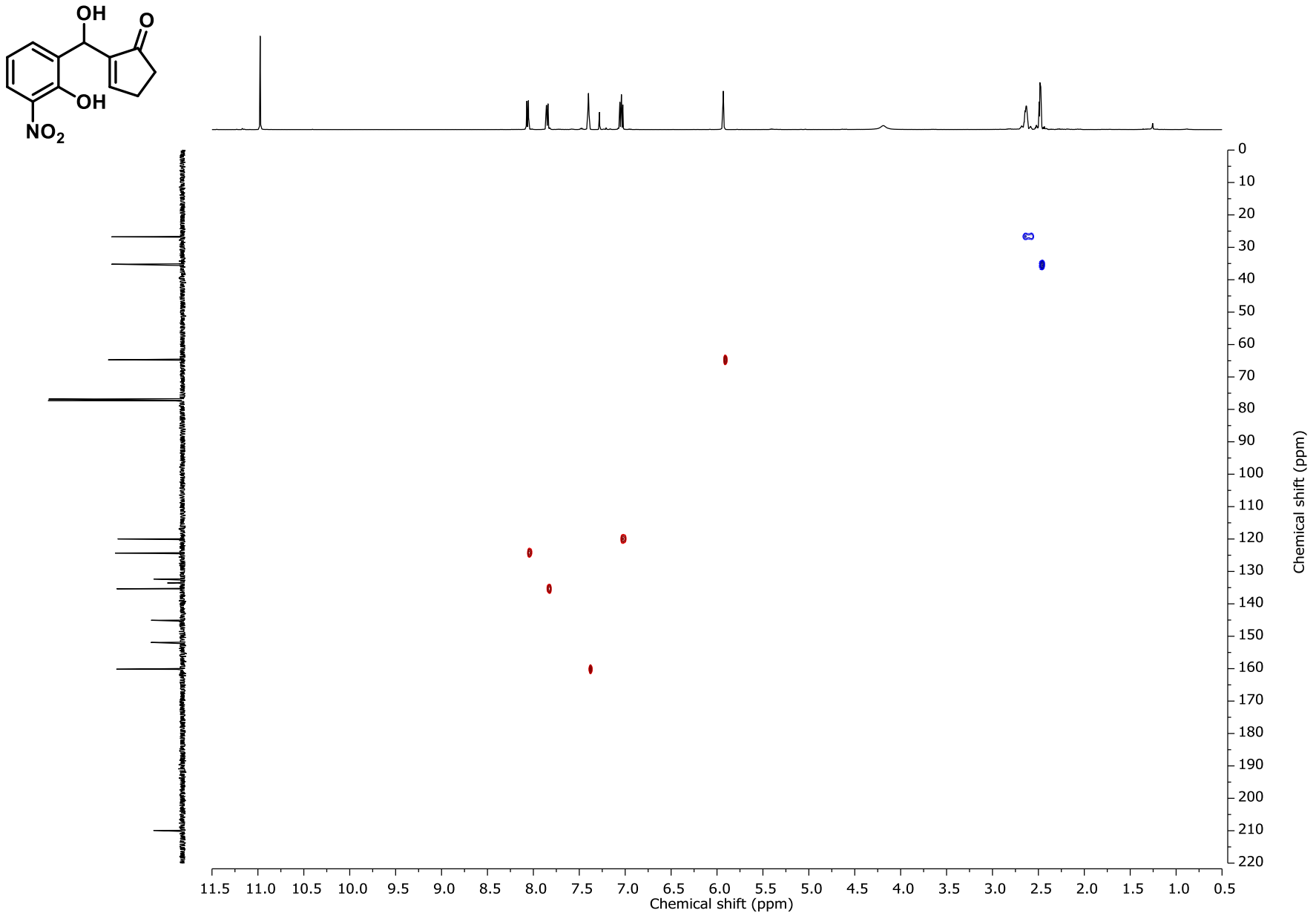

Figure S33. ^{1}H-^{13}C HSQC NMR contour plot (500 MHz, $CDCl_3$) of compound **5a.**

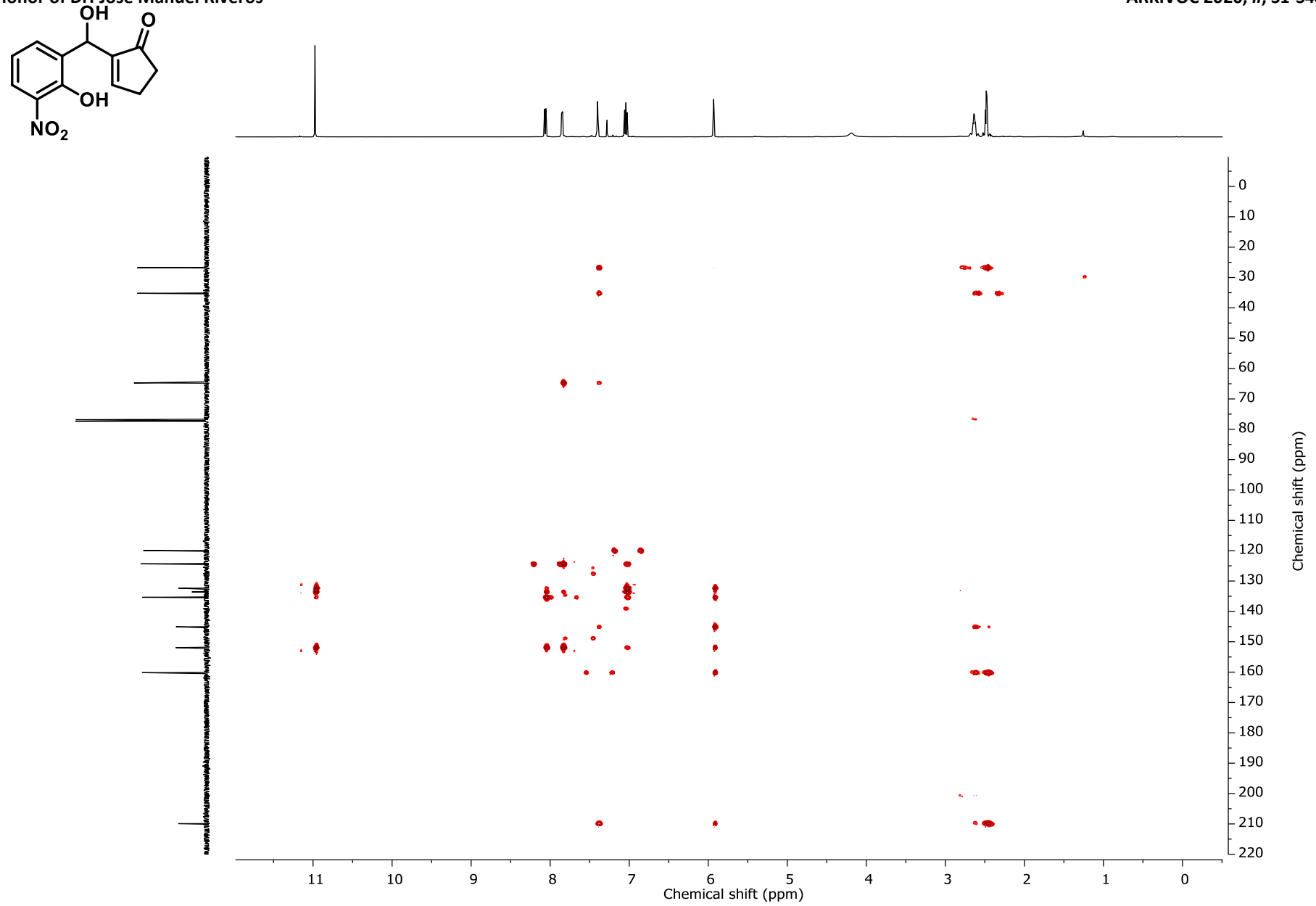

Figure S34. ^{1}H-^{13}C HMBC NMR contour plot (500 MHz, $CDCl_3$) of compound **5a.**

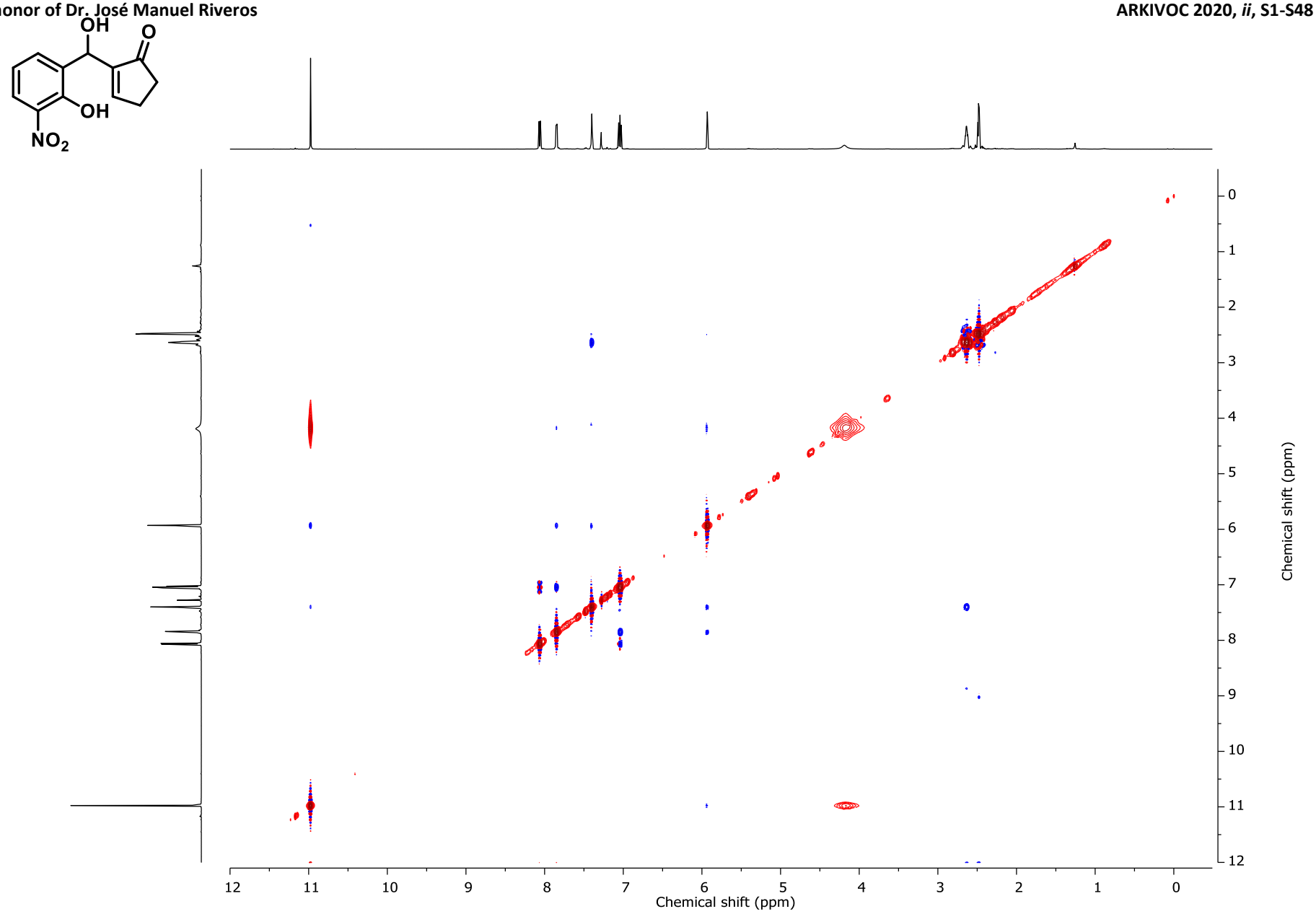

Figure S35. ^{1}H-^{1}H NOESY NMR contour plot (500 MHz, $CDCl_3$) of compound **5a.**

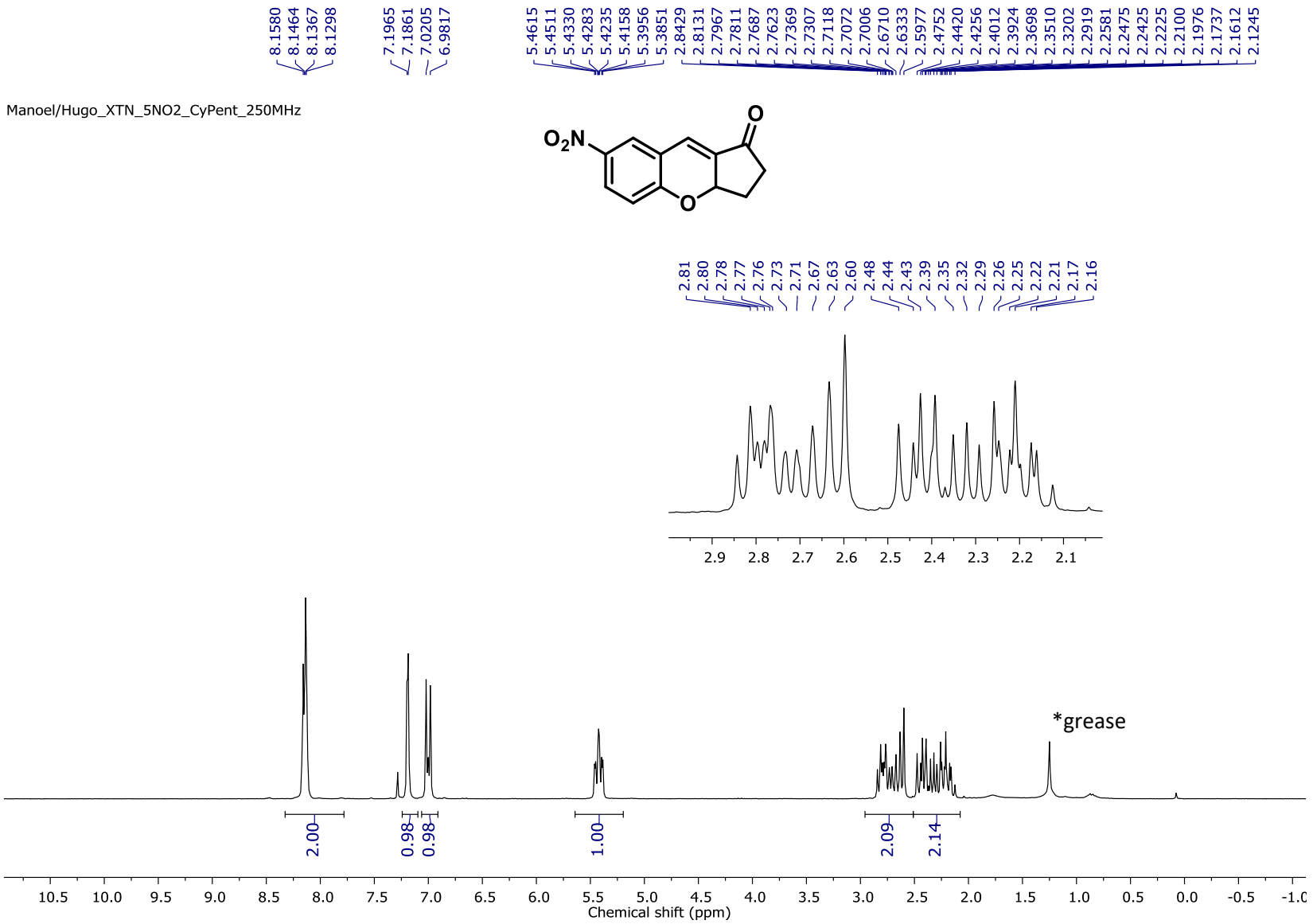

Figure S36. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3k.**

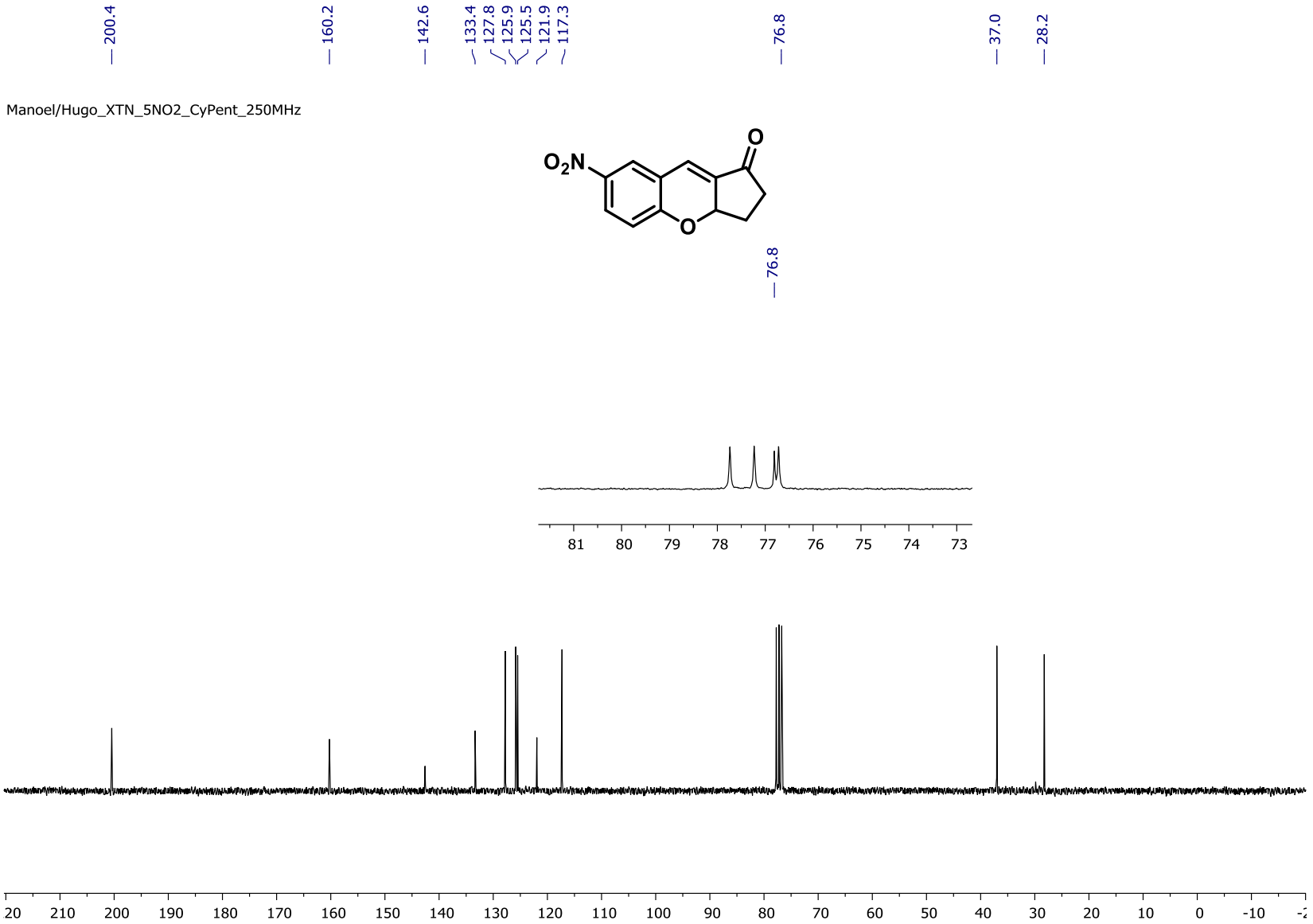

Figure S37. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3k.**

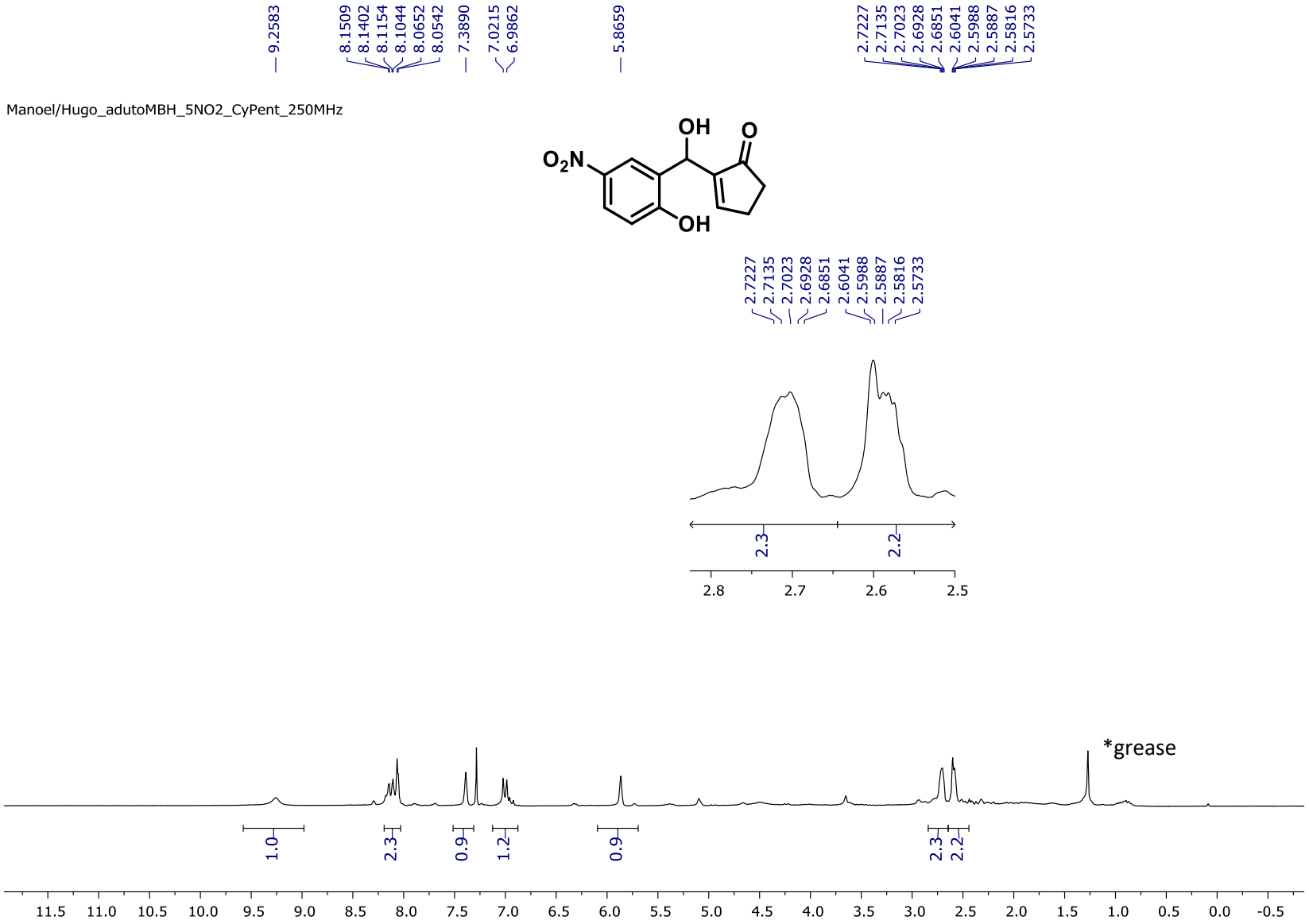

Figure S38. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **5b.**

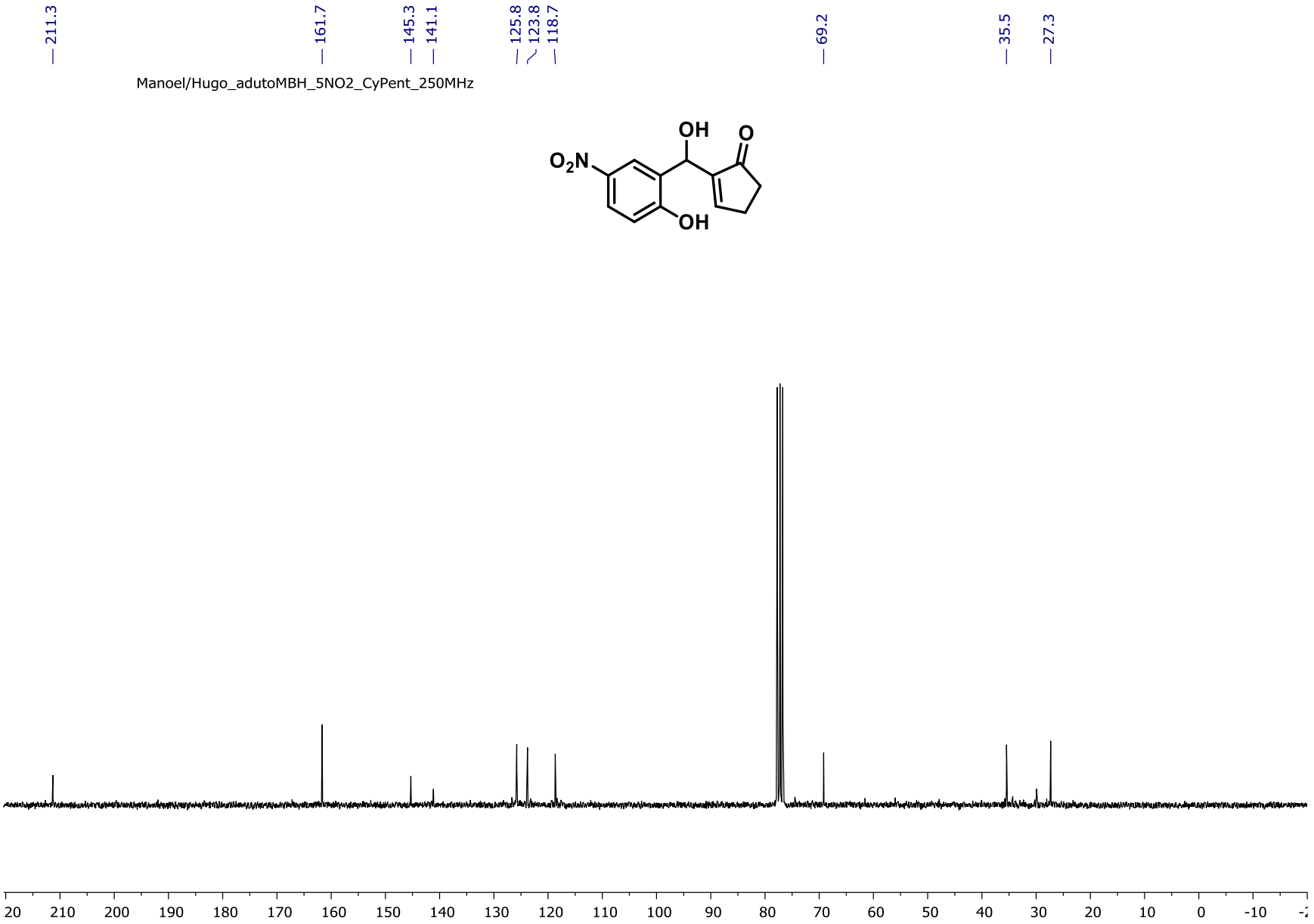

Figure S39. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **5b.**

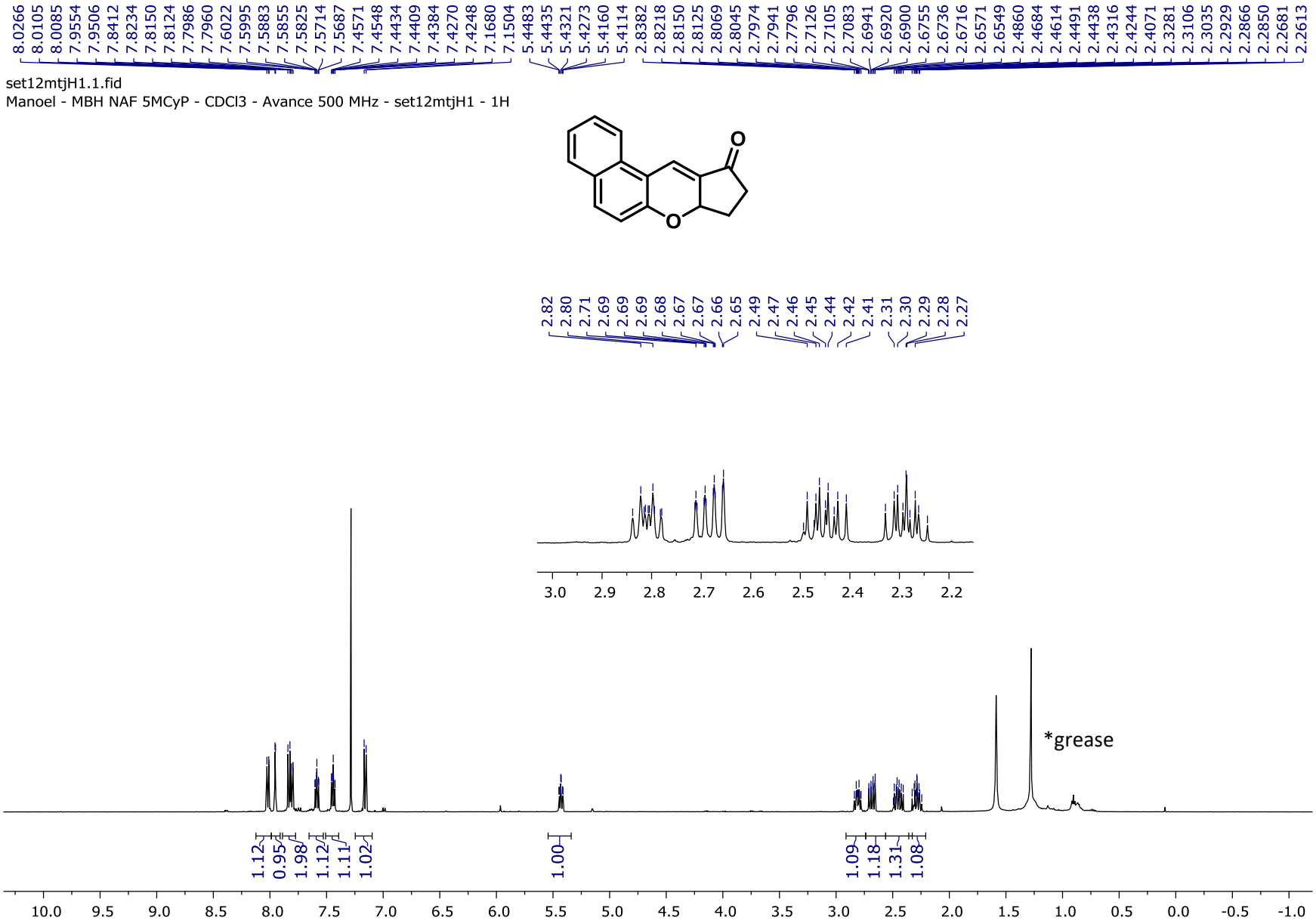

Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3l.**

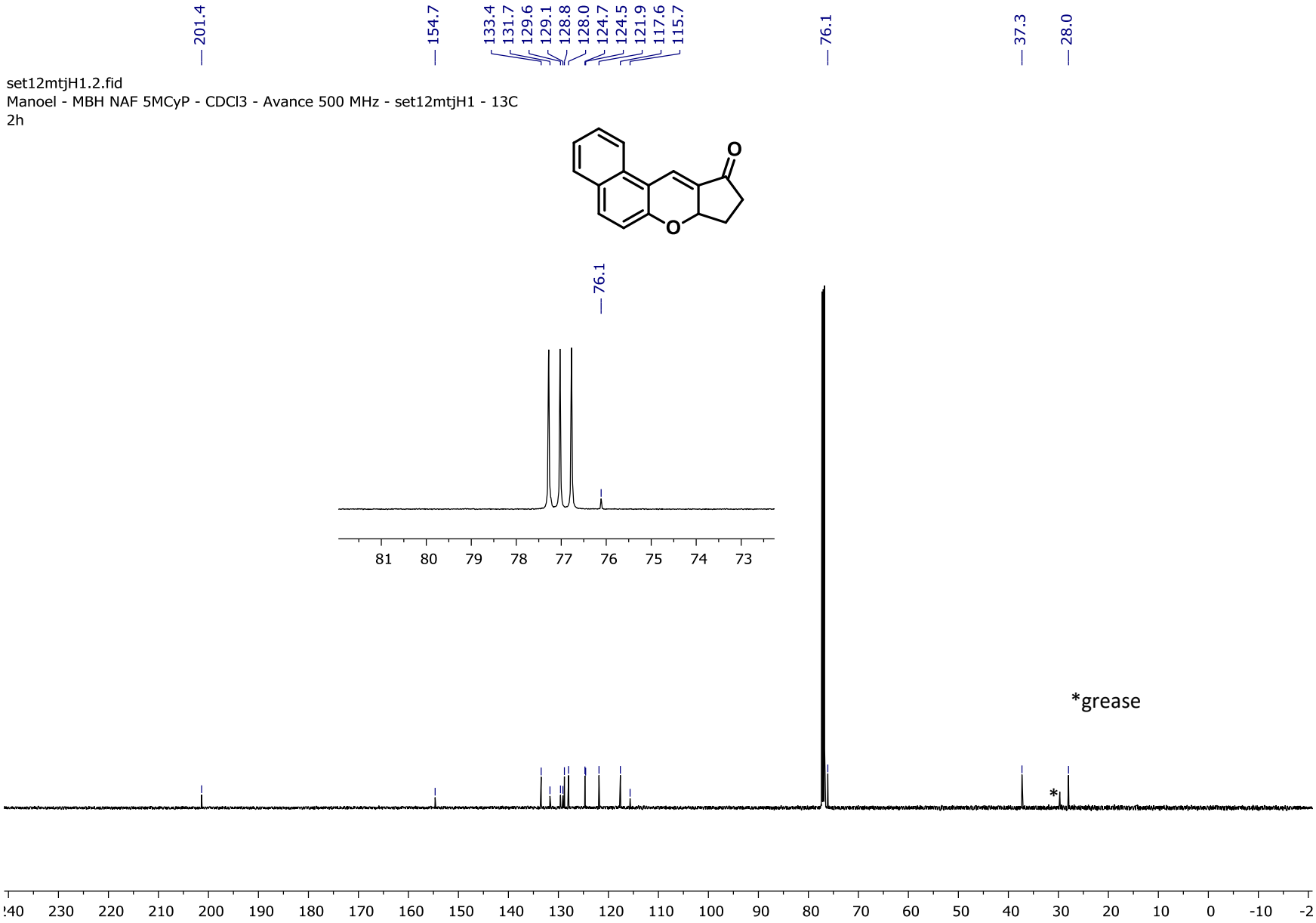

Figure S41. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **3l.**

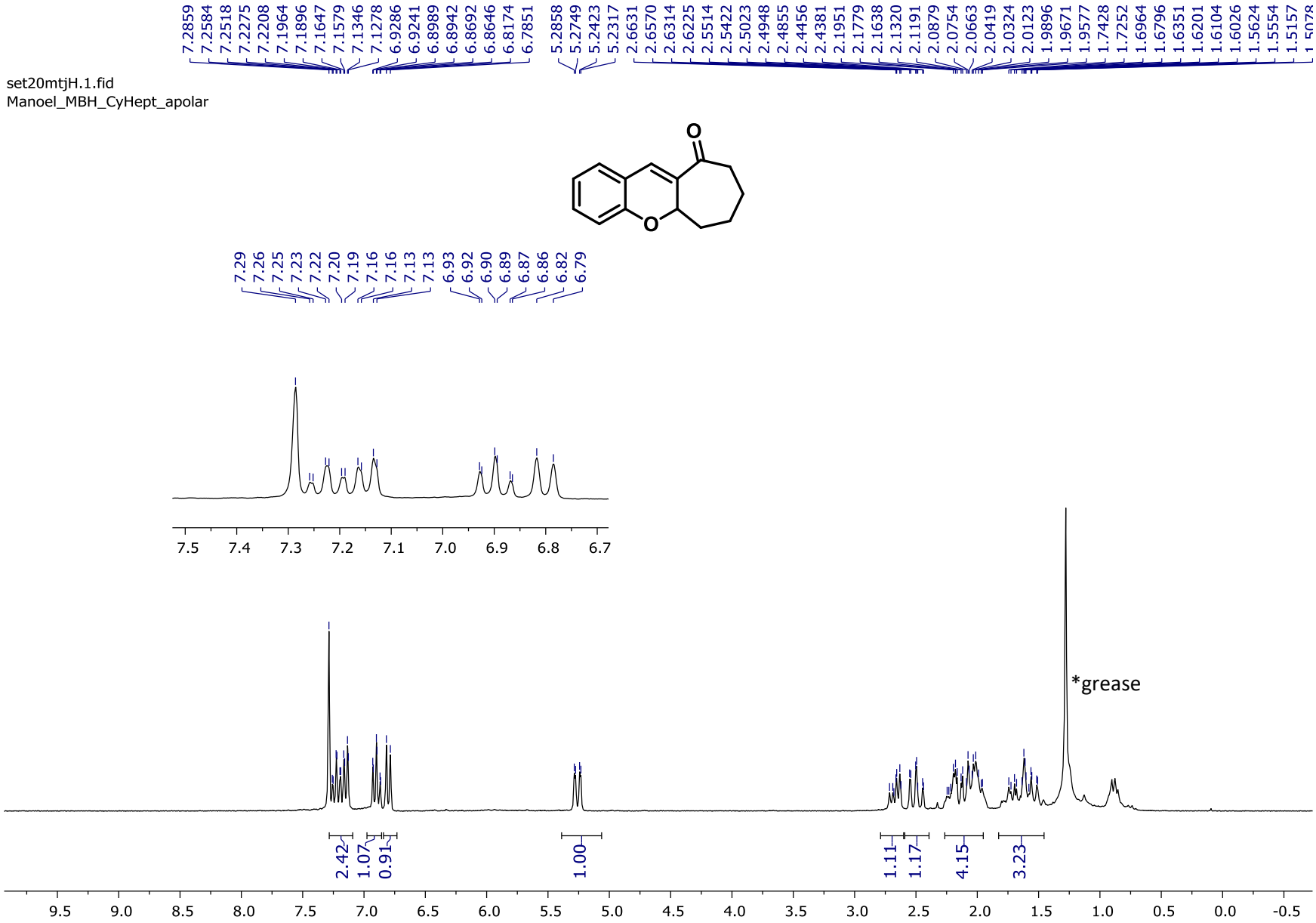

Figure S42. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3m.**

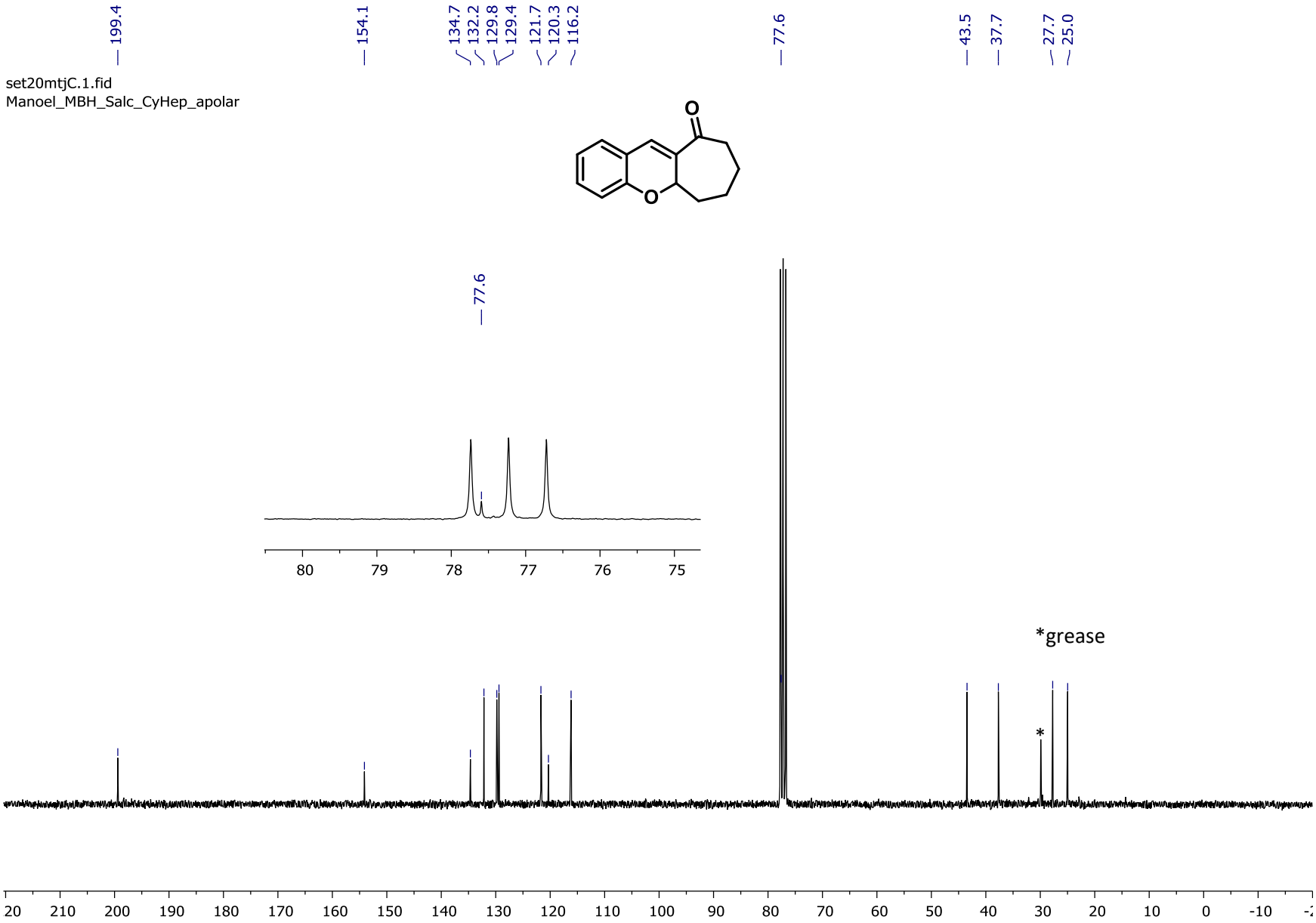

Figure S43. ^{13}C NMR spectrum (63 MHz, $CDCl_3$) of compound **3m.**

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 0.5º width and 10 s of acquisition time per frame, operating with a Mo fine-focus sealed tube source of radiation (*K*α λ = 0.71073 Å).

Cell refinement and data reduction were done using SAINT[1] and multi-scan absorption correction was applied using SADABS-2014/5[1]. Solution structure was obtained by primary atom site location by structure-invariant direct methods SHELXS97[2]. SHELXL2014/7[3] 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 restrains), $R[F^2 > 2\,\sigma(F^2)] = 0.033$, $wR(F^2) = 0.079$, $S = 1.02$, with maximum and minimum residual electron density of 0.65 e $Å^{-3}$ and -0.47 e $Å^{-3}$, respectively. Details about the analyzed crystal and data collection are presented in **Table S1** and **Table S2**, respectively.

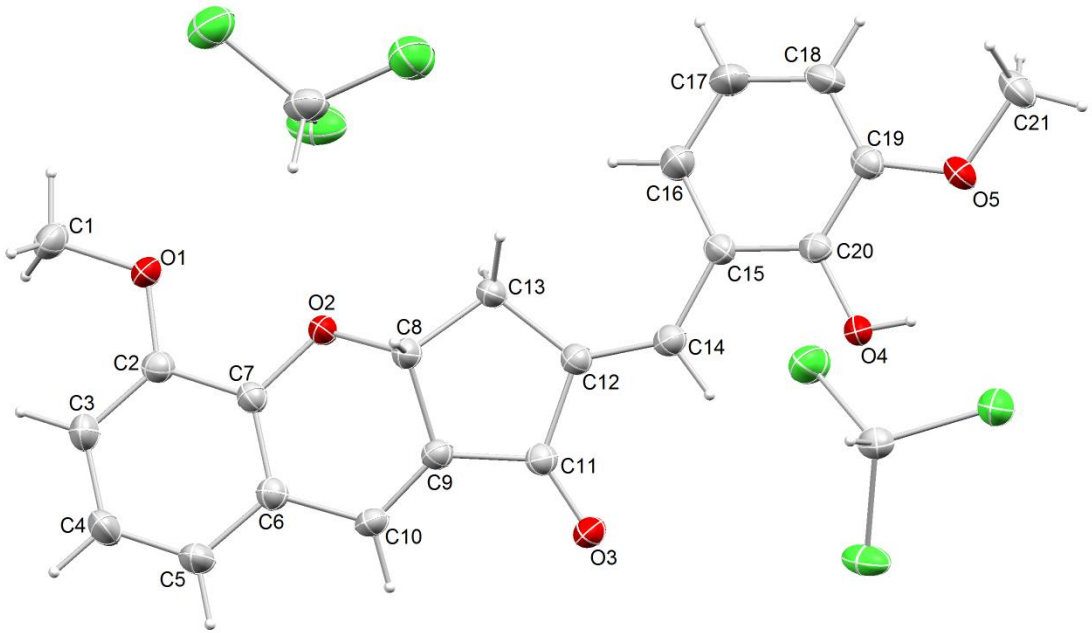

Figure S44. The molecular structure of *(2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one (**4c**)* with 50% probability displacement ellipsoids.

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
Mr = 589.09	F(000) = 600
Triclinic, *P1*	Dx = 1.536 Mg m^{-3}
a = 8.8569 (8) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 10.8992 (11) Å	Cell parameters from 134 reflections
c = 14.8123 (14) Å	θ = 3.2–24.4°
α = 71.700 (2)°	μ = 0.71 mm^{-1}
β = 79.556 (2)°	T = 150 K
γ = 70.333 (2)°	Block, yellow
V = 1273.8 (2) Å^3	0.22 × 0.12 × 0.08 mm

Table S2. Selected crystallographic data for data collection

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

References

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