Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Synthesis of Benzochromenes and Dihydrophenanthridines with Helical Motif using Garratt-Braverman and Buchwald-Hartwig Reactions

Prabuddha Bhattacharya, Kalyan Senapati, Krishna Chattopadhyay, Santi M. Mandal and Amit Basak*

Department of Chemistry, Indian Institute of Technology Kharagpur 721302 India

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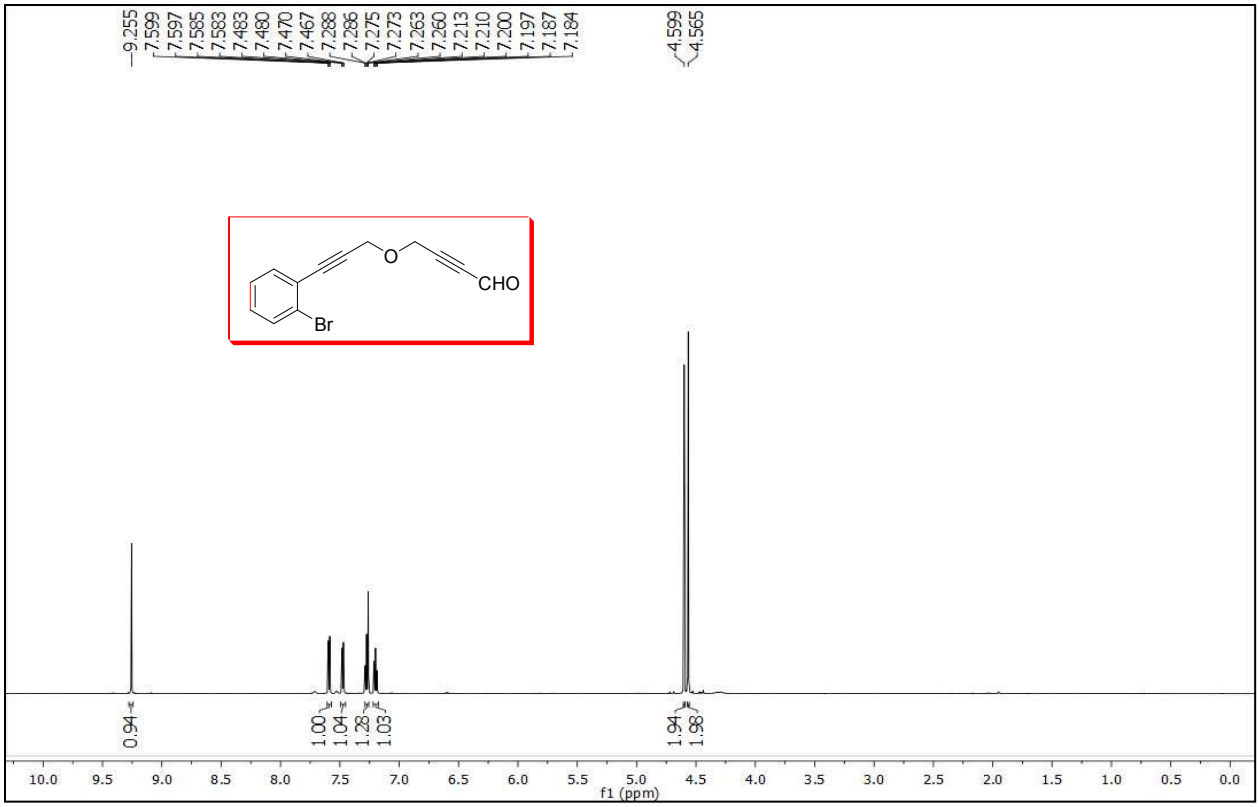
EXPERIMENTAL SECTION

General Aspects: All dry reactions were conducted with oven-dried glassware under an atmosphere of nitrogen (N_2). All common reagents were commercial grade reagents and used without further purification. The solvents were dried by standard methods and purified by distillation before use.

Silica gel (60–120 and 230–400 mesh) was used for column chromatography. TLC was performed on aluminum-backed plates coated with Silica gel 60 with F254 indicator. Locally available UV-lamp chamber and I_2-blower were used as the TLC spot indicator. HRMS were obtained using ESI-TOF mass spectrometer

The ^1H NMR spectra were recorded at 600, 400, 200 MHz and ^{13}C NMR spectra were measured at 150, 100, 50 MHz using $CDCl_3$. Proton and carbon spectra were referenced internally to solvent signals, using values of δ = 7.26 ppm for proton and δ = 77.2 for carbon (middle peak) in $CDCl_3$ and The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad signal, AB_q = AB quartet. All coupling constants (J) are given in Hz.



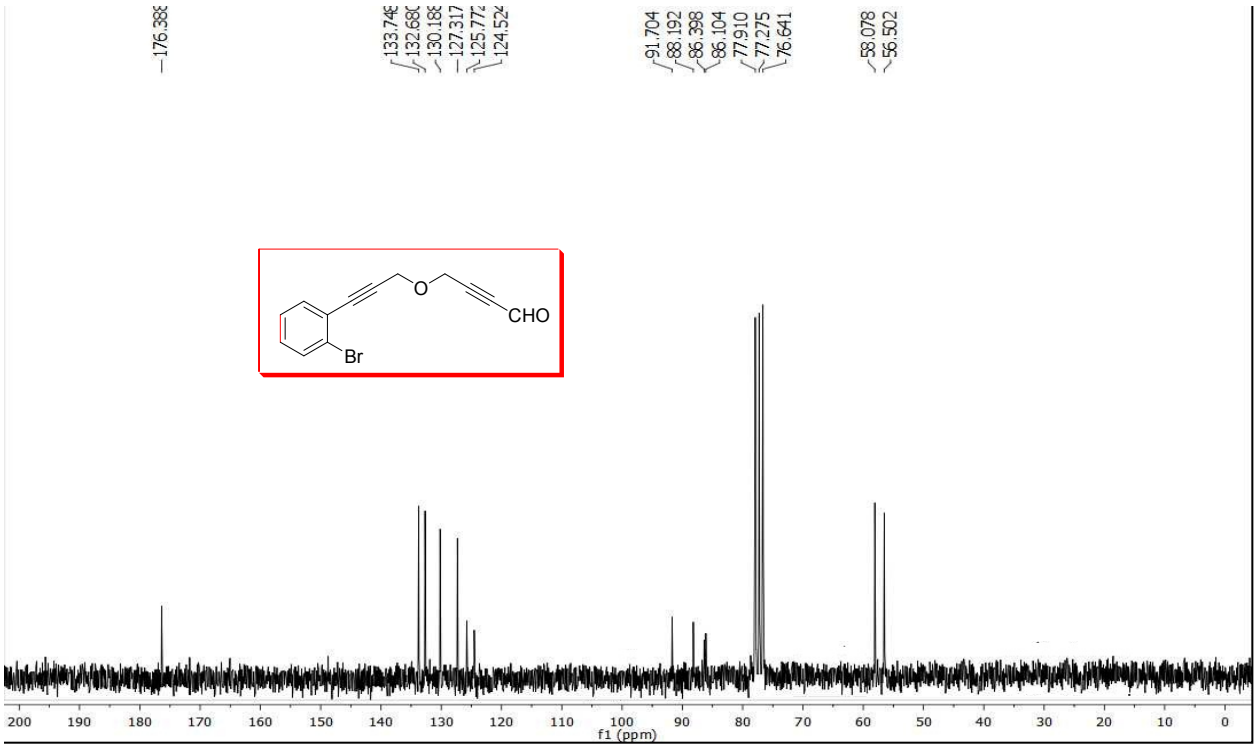


Figure S1. ^{1}H and ^{13}C NMR spectra of **4a** in $CDCl_3$

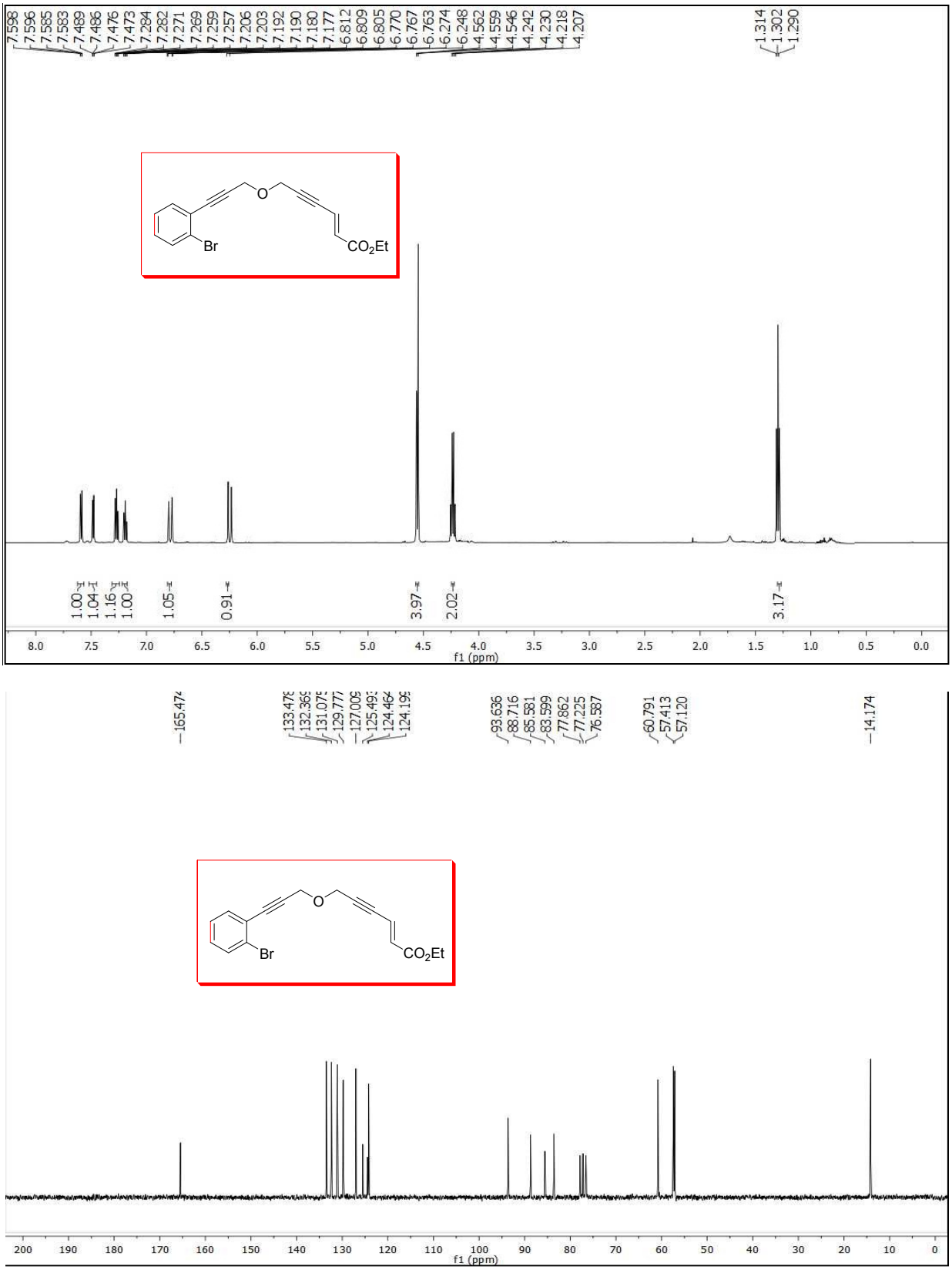


Figure S2. ^{1}H and ^{13}C NMR spectra of **5a** in $CDCl_3$

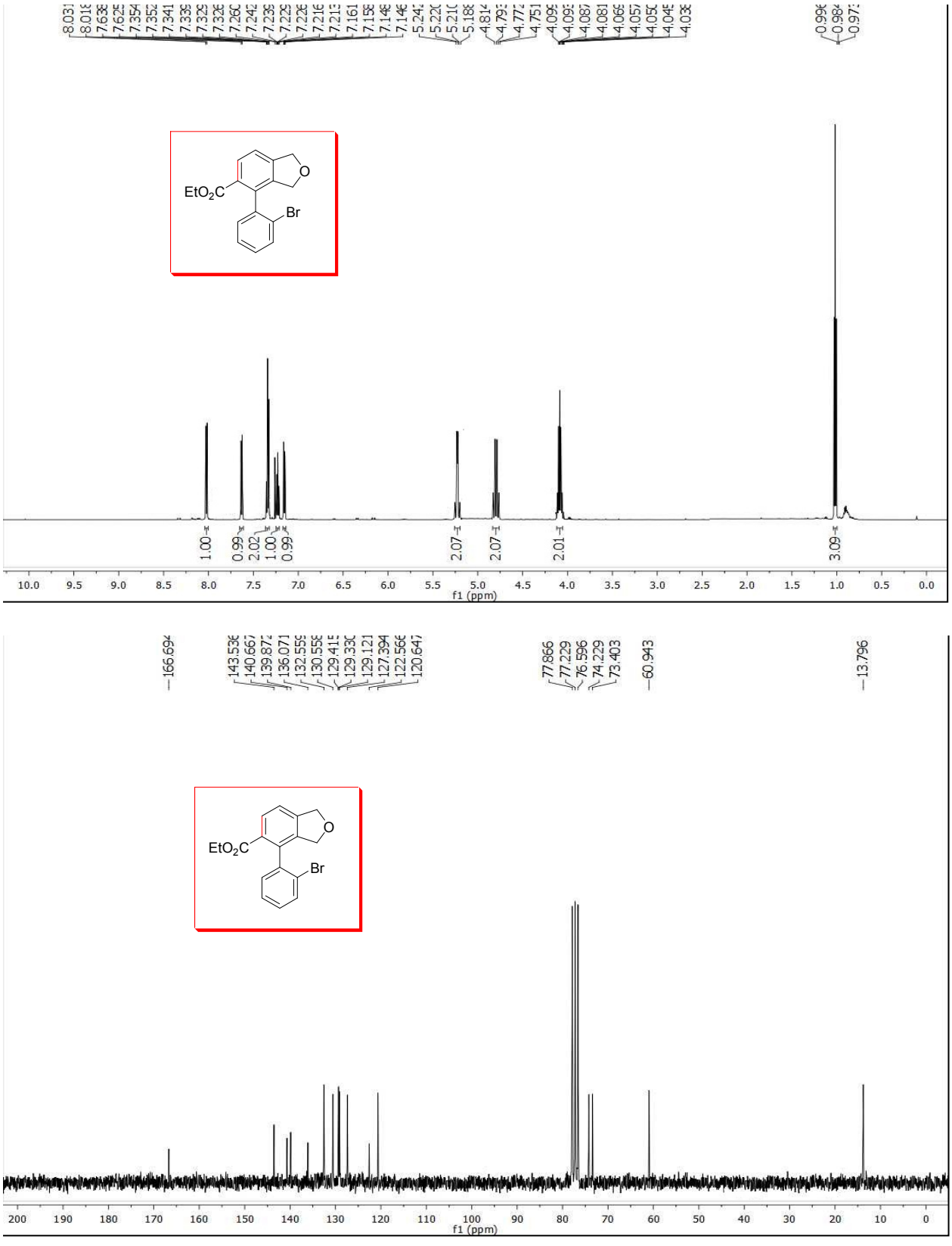


Figure S3. ^{1}H and ^{13}C NMR spectra of **6a** in $CDCl_3$

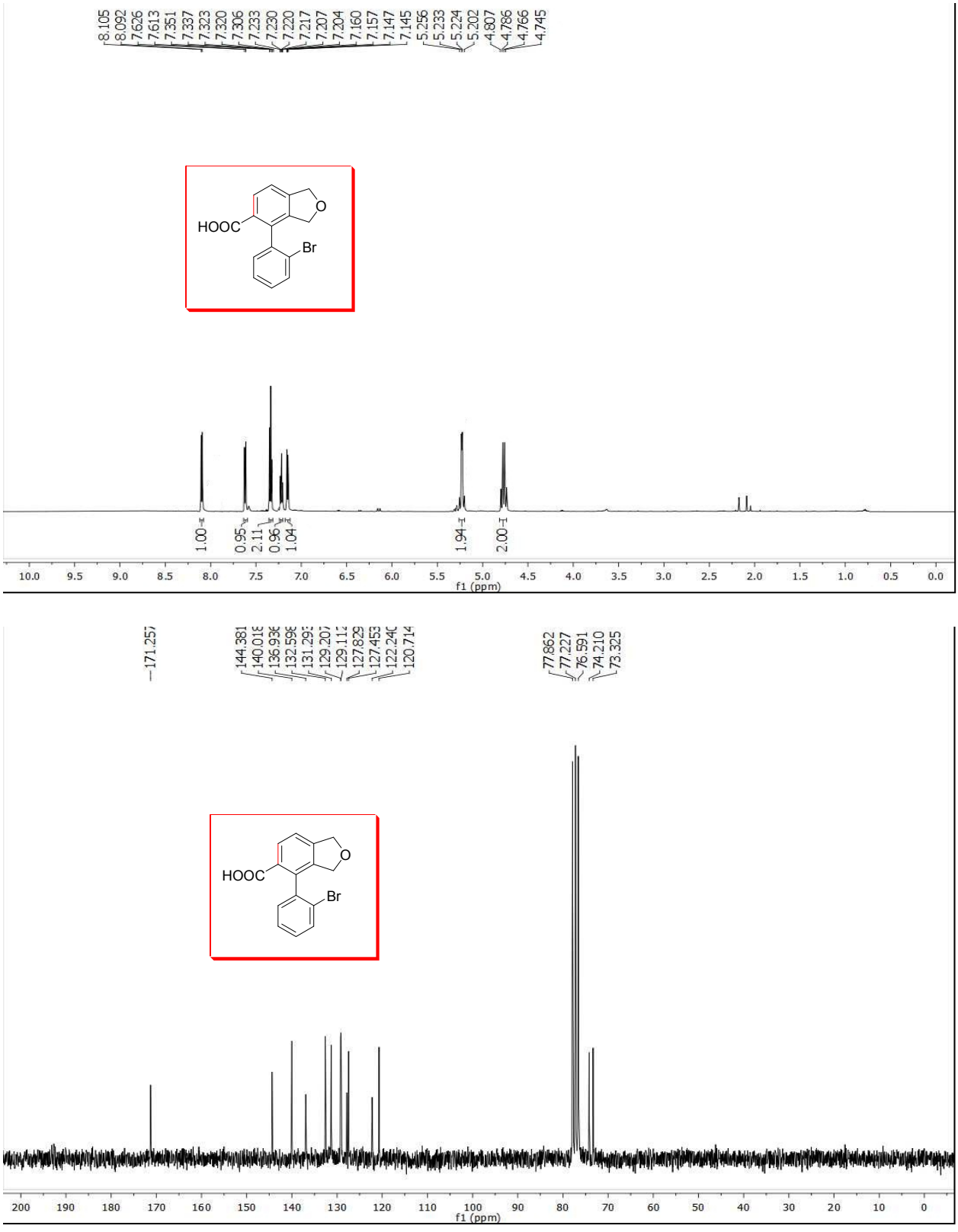


Figure S4. ^{1}H and ^{13}C NMR spectra of **7a** in $CDCl_3$

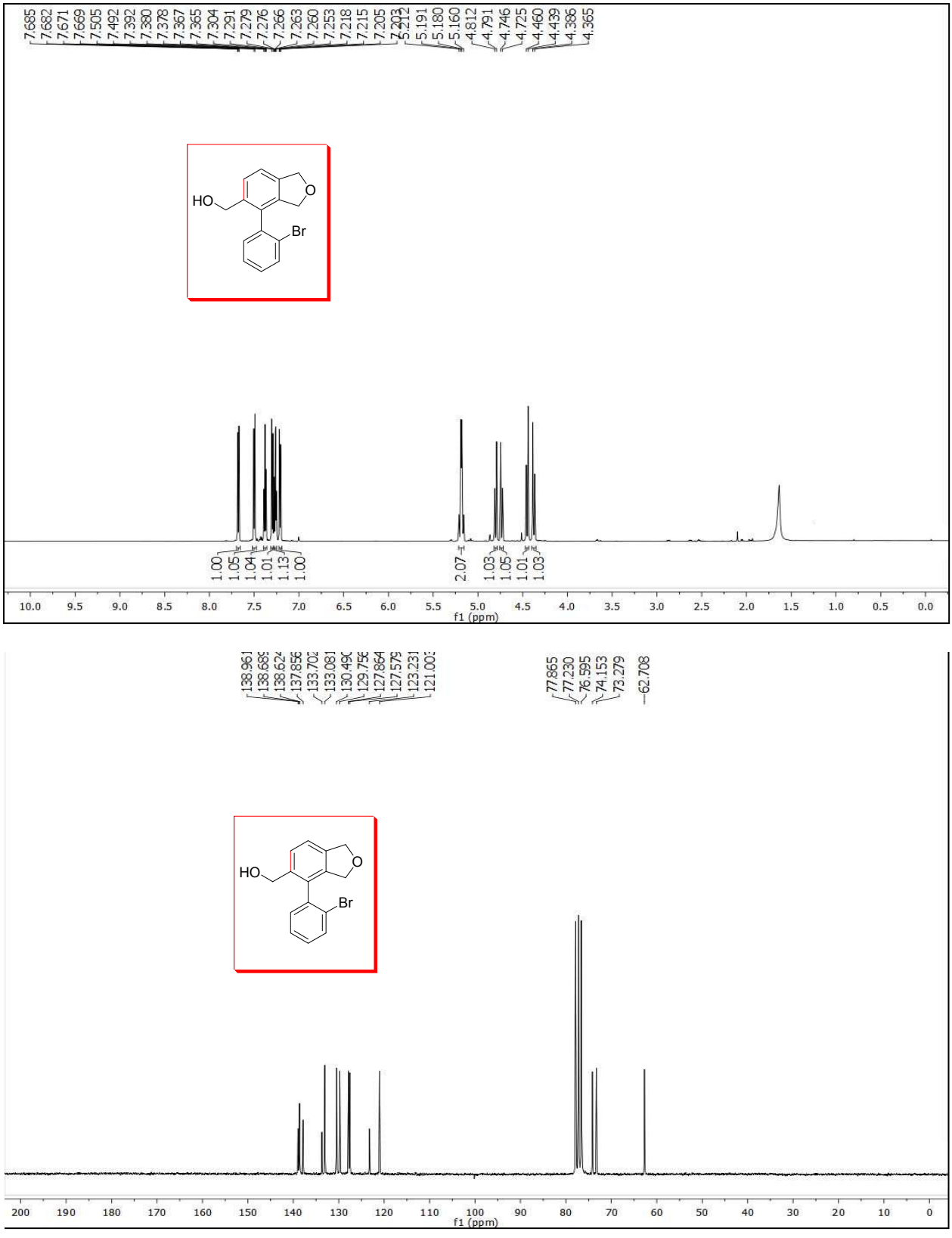


Figure S5. ^{1}H and ^{13}C NMR spectra of **8a** in $CDCl_3$

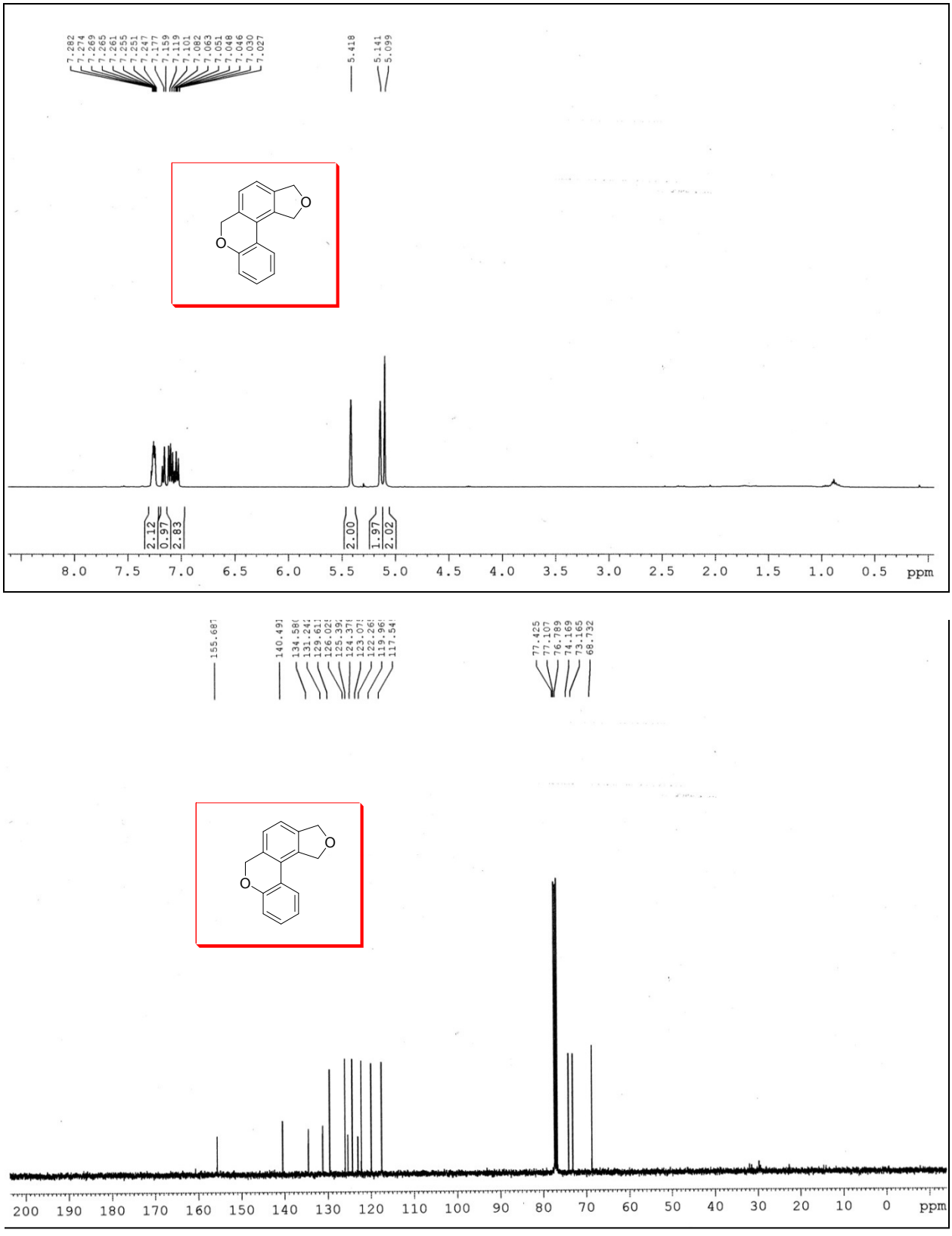


Figure S6. ^{1}H and ^{13}C NMR spectra of **9a** in $CDCl_3$

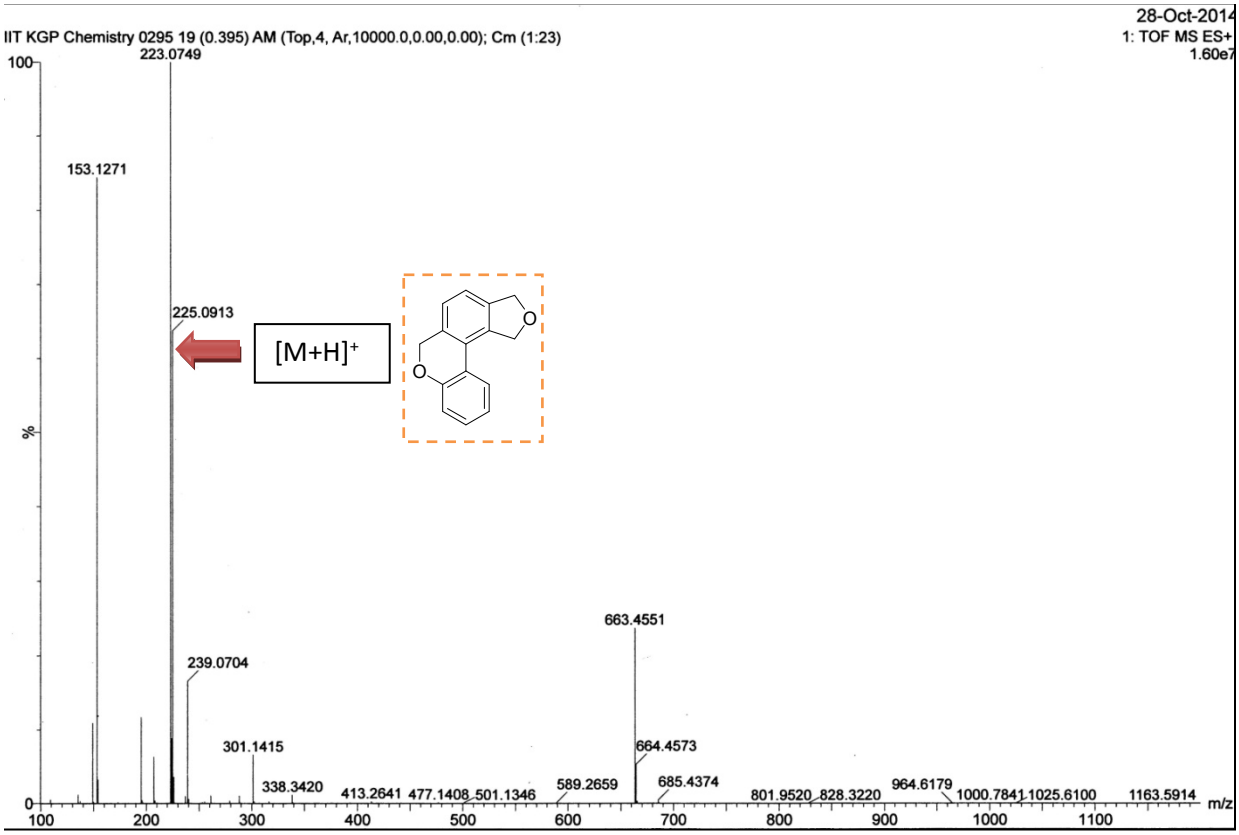


Figure S7. HRMS spectrum of **9a**

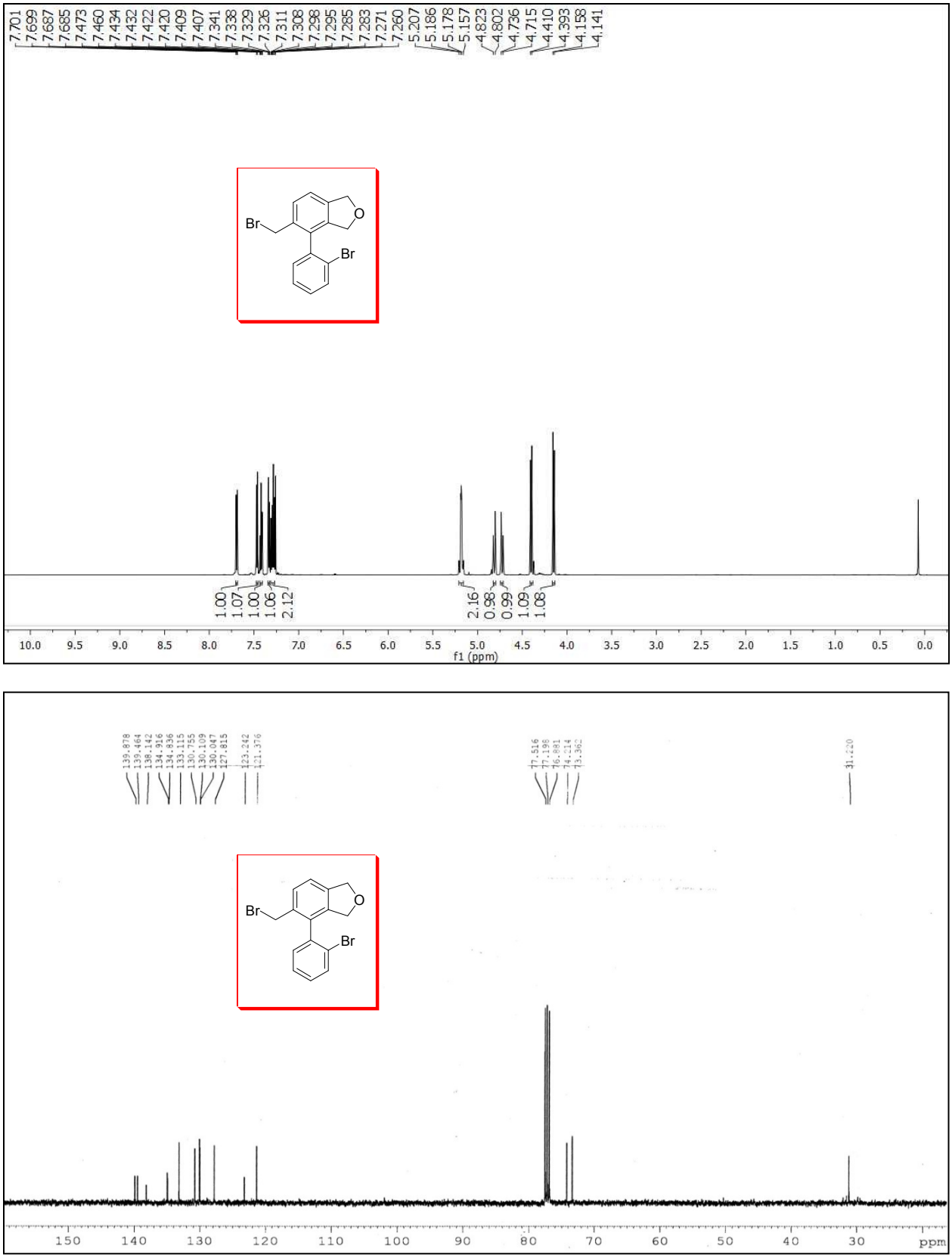


Figure S8. ^{1}H and ^{13}C NMR spectra of **10a** in $CDCl_3$

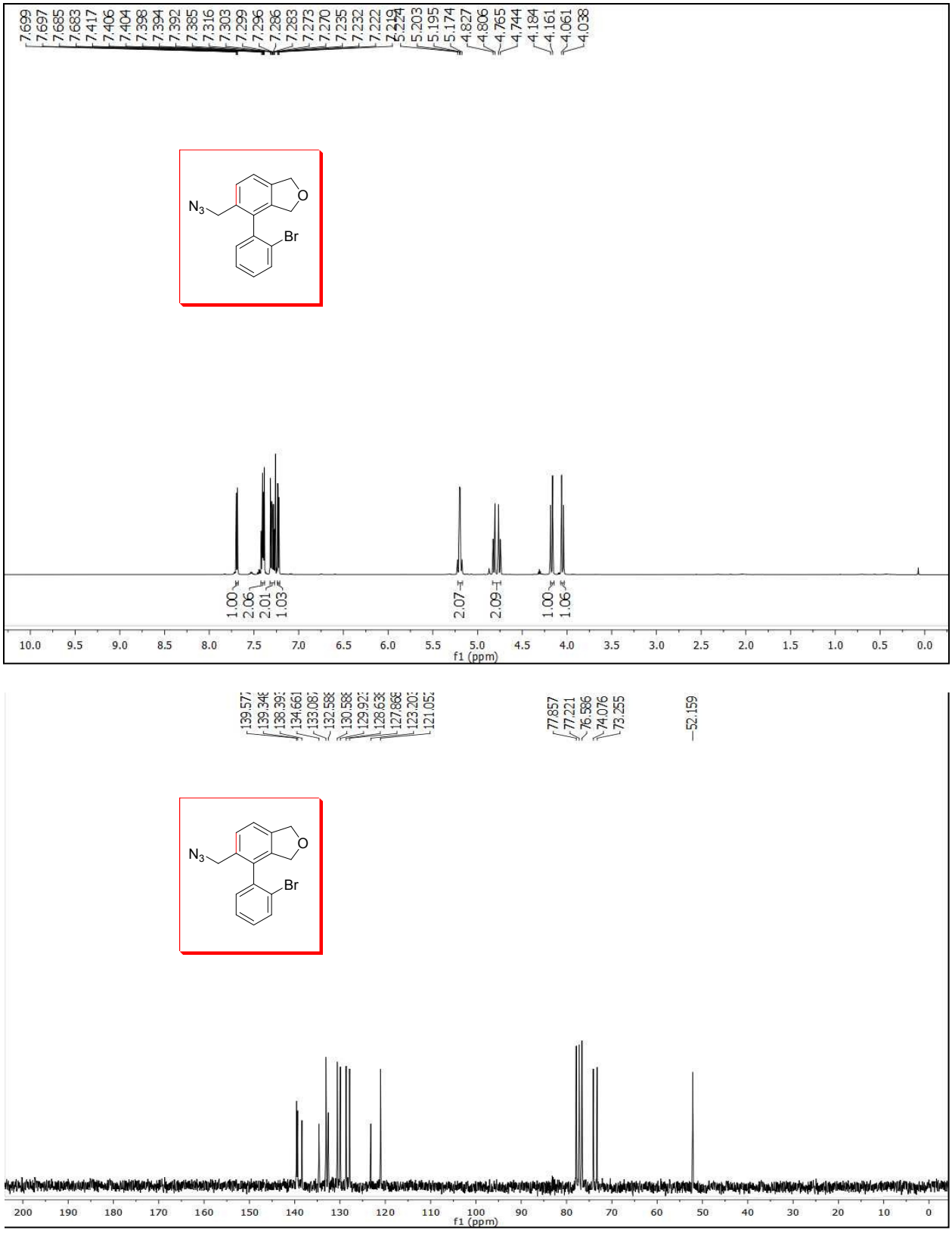


Figure S9. ^{1}H and ^{13}C NMR spectra of **11a** in $CDCl_3$

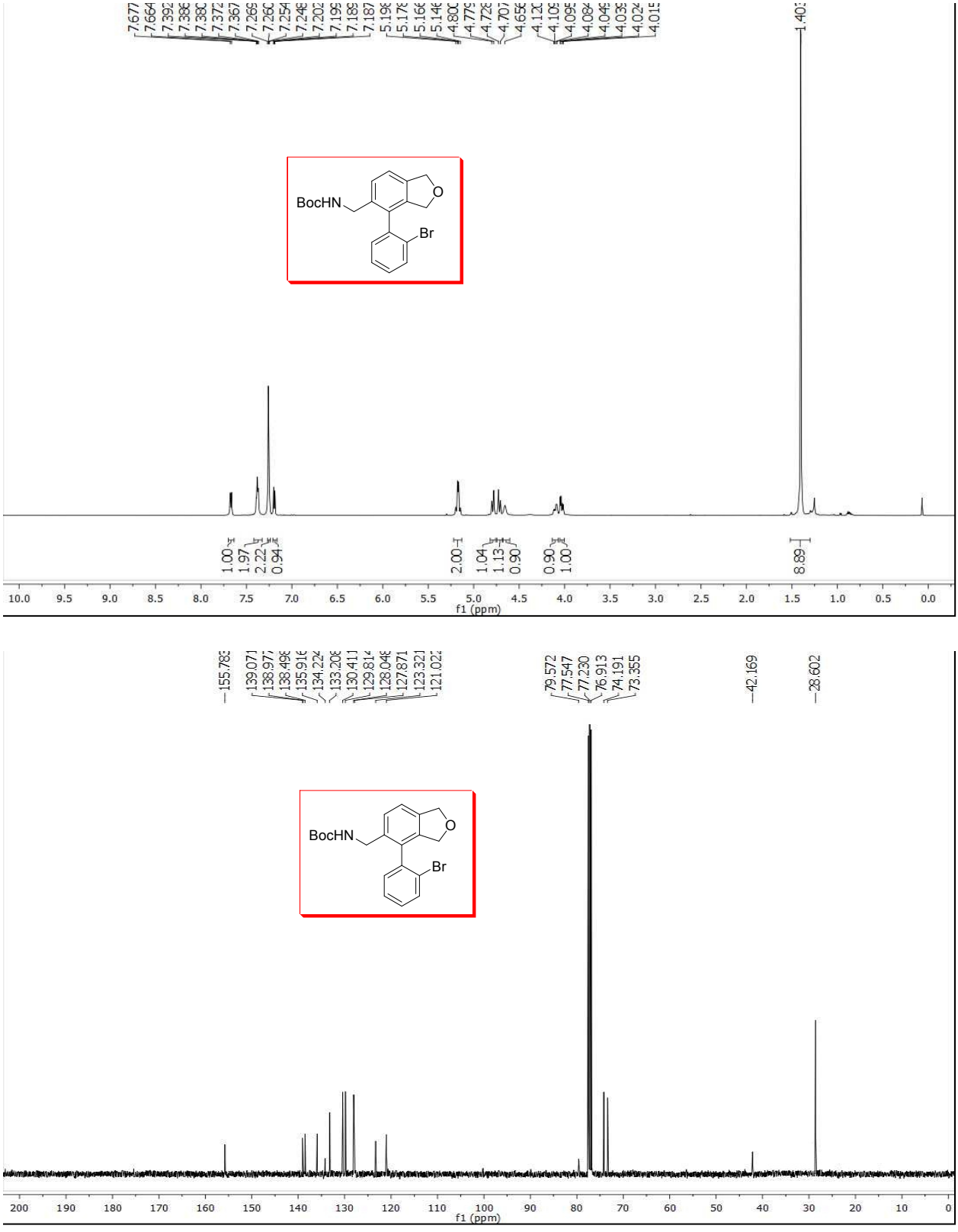
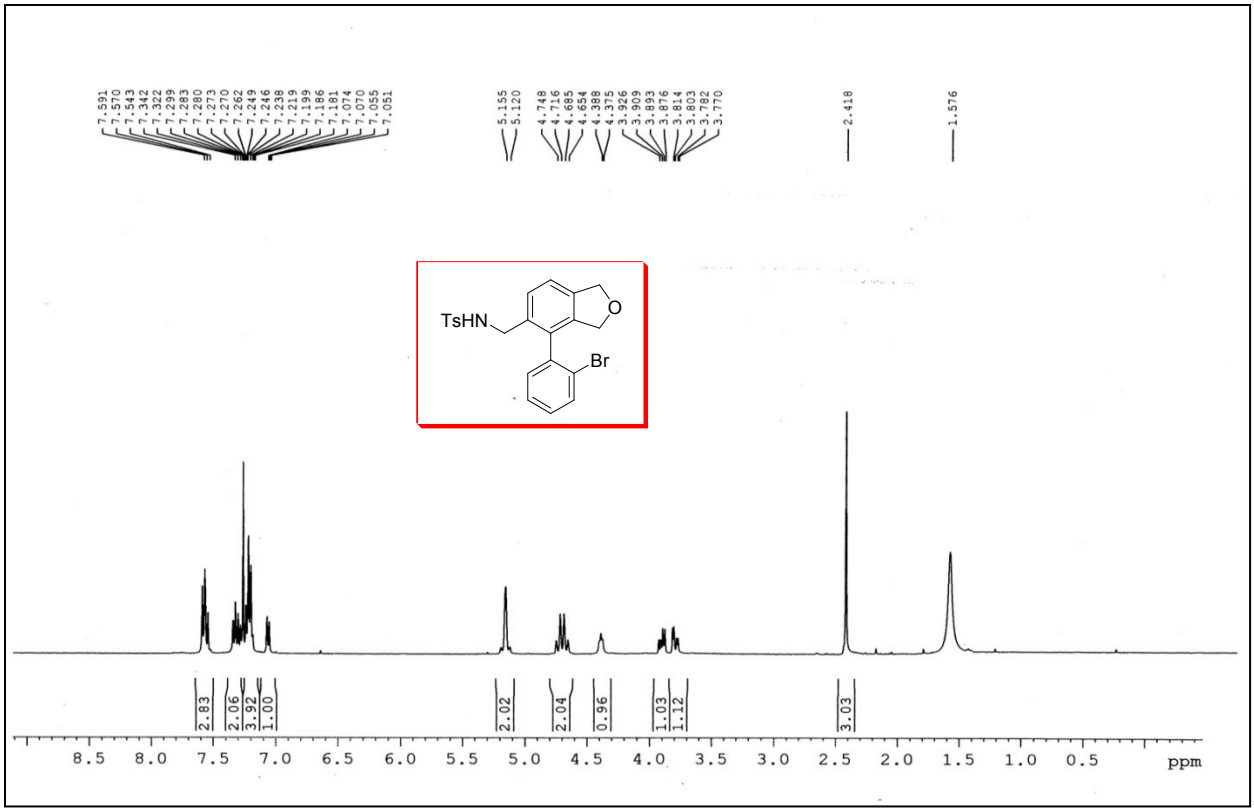


Figure S10. ^{1}H and ^{13}C NMR spectra of **12a** in $CDCl_3$



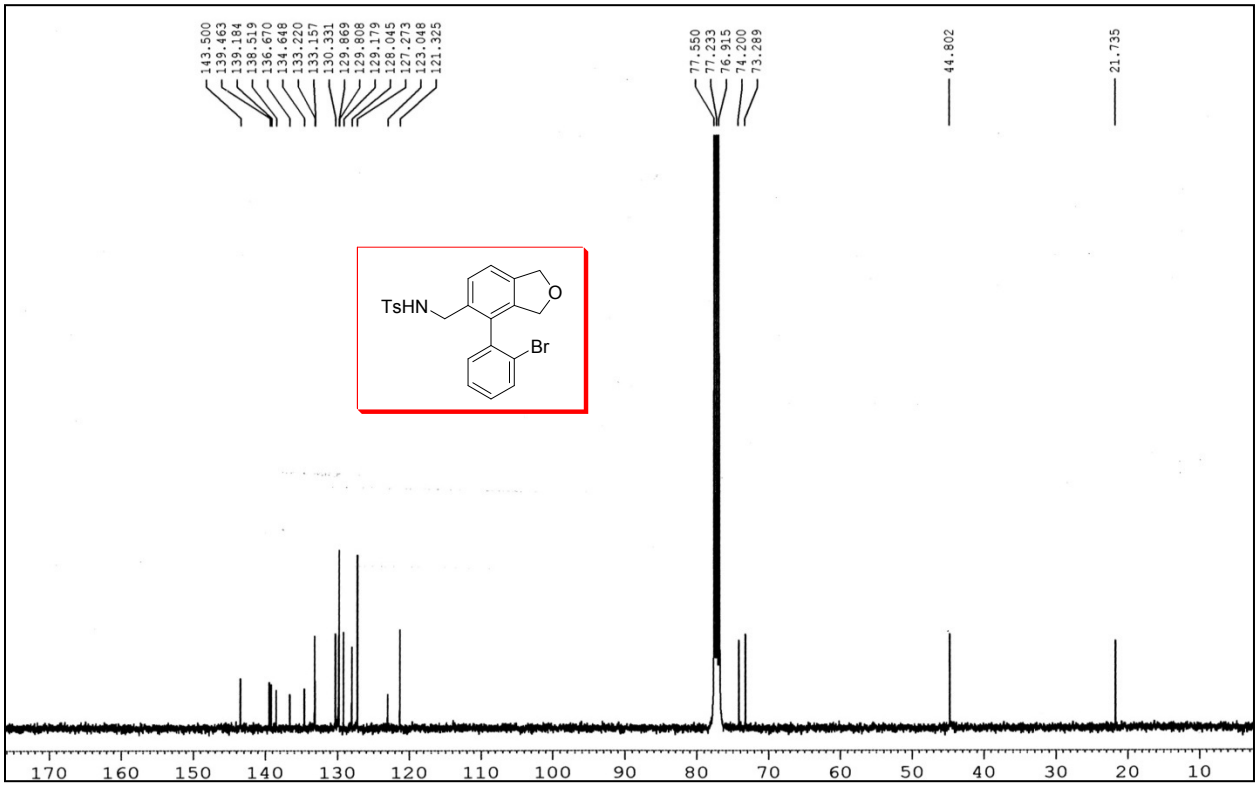


Figure S11. ^{1}H and ^{13}C NMR spectra of **13a** in $CDCl_3$

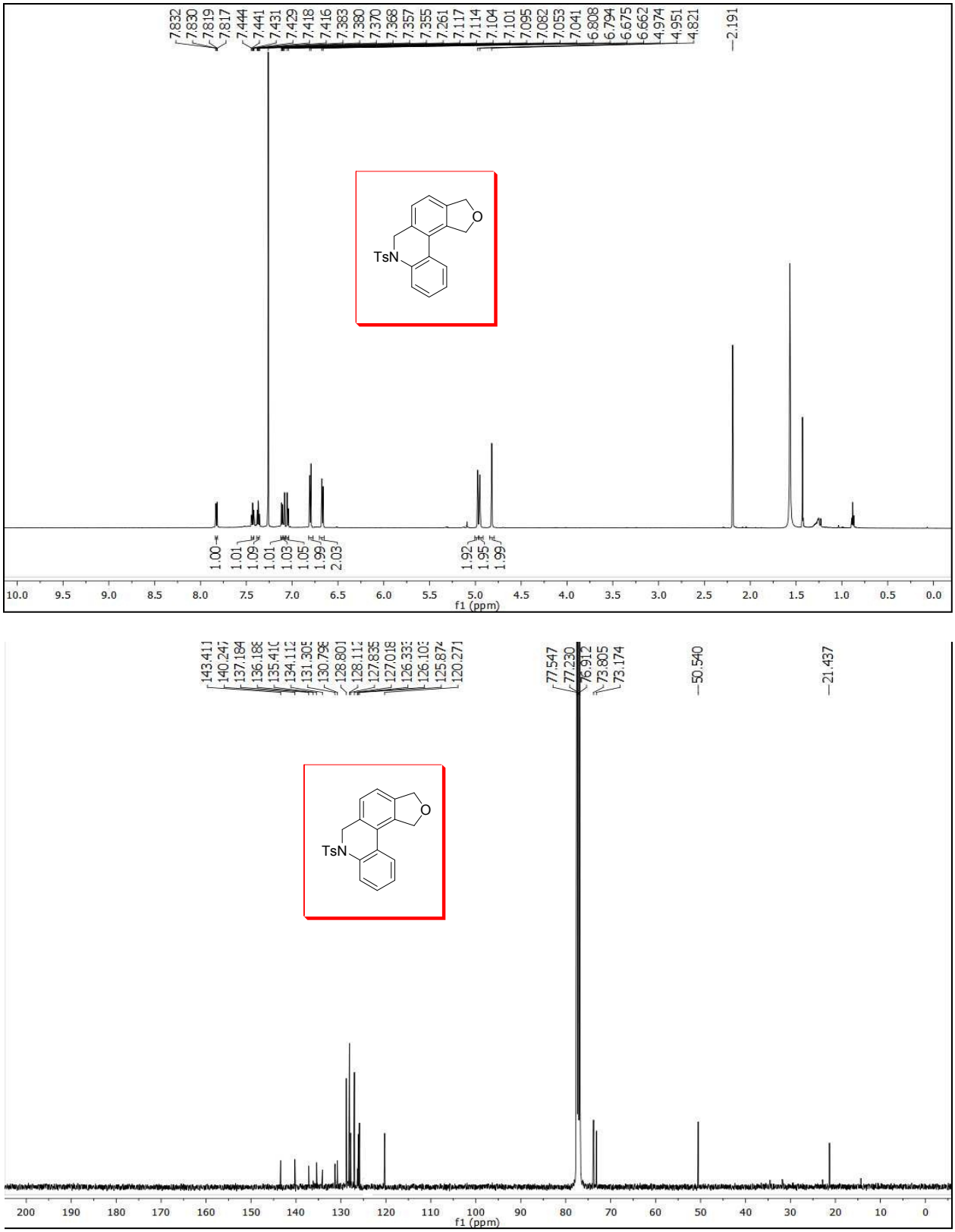


Figure S12. ^{1}H and ^{13}C NMR spectra of **14a** in $CDCl_3$

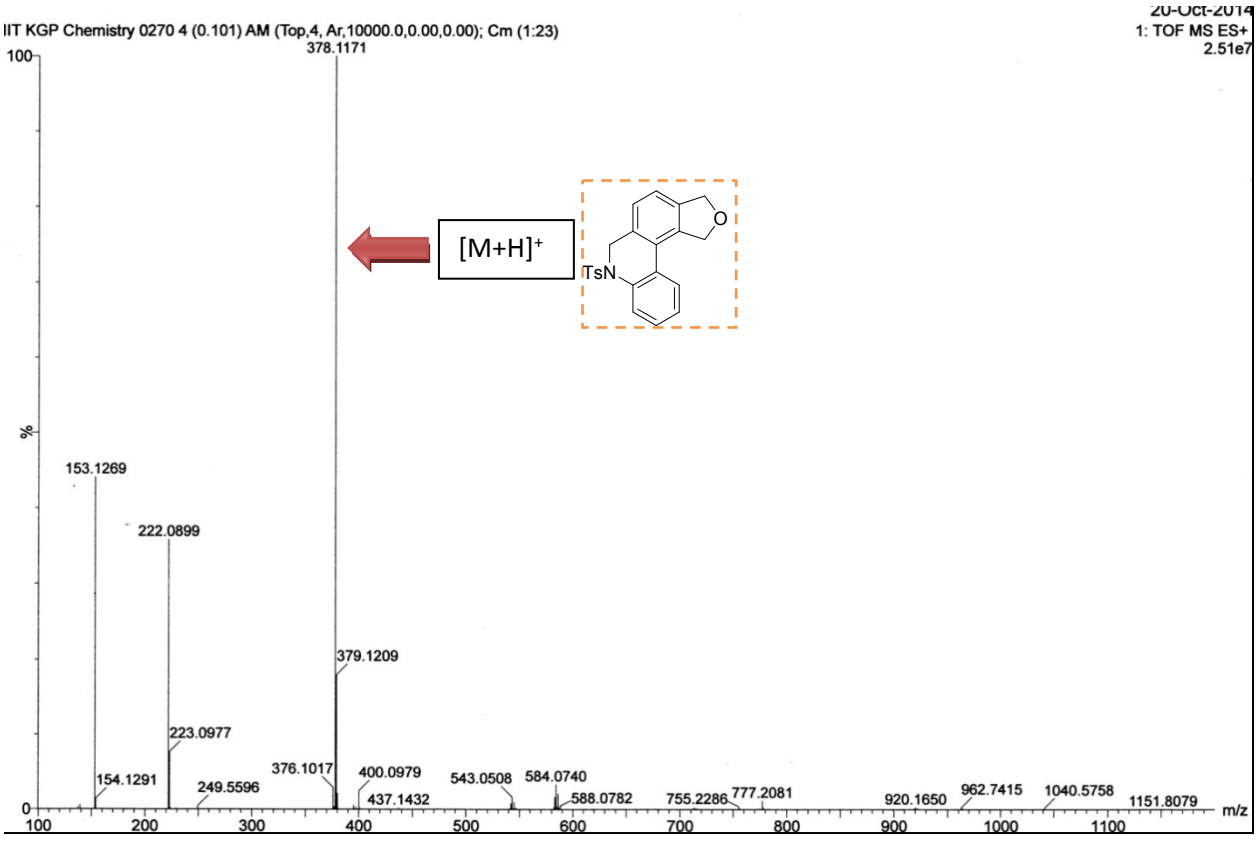


Figure S13. HRMS spectrum of **14a**

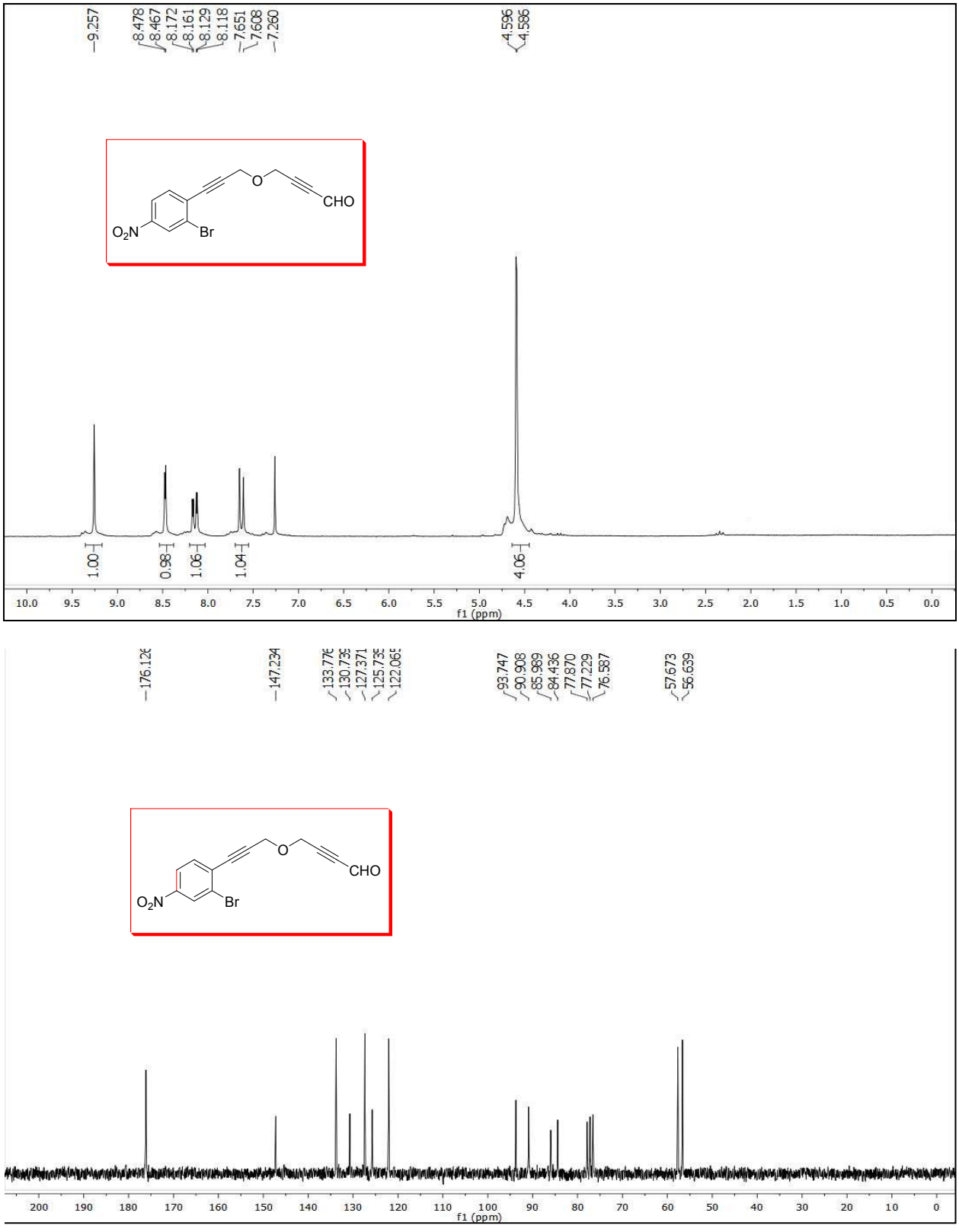


Figure S14. ^{1}H and ^{13}C NMR spectra of **4b** in $CDCl_3$

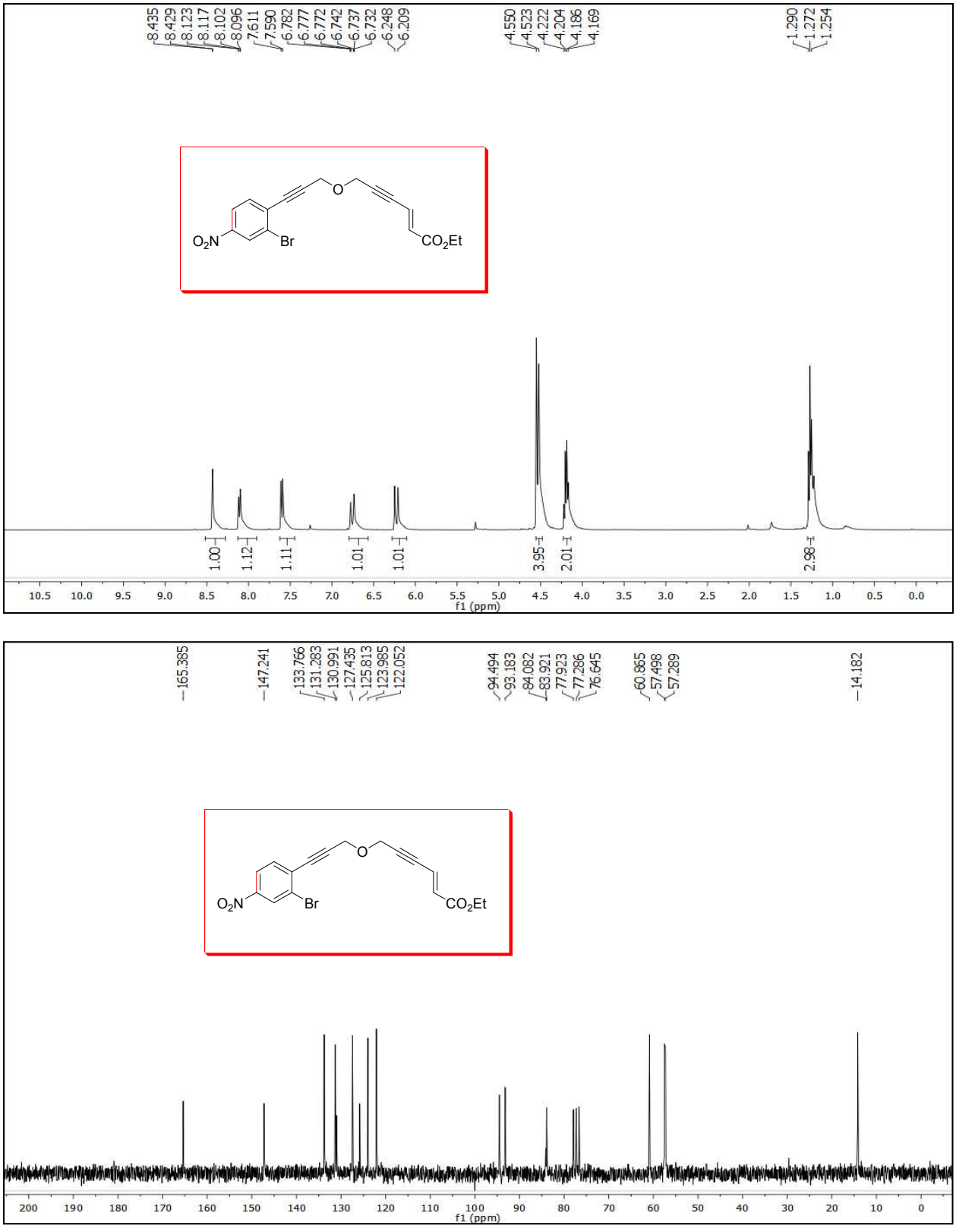


Figure S15. ^{1}H and ^{13}C NMR spectra of **5b** in $CDCl_3$

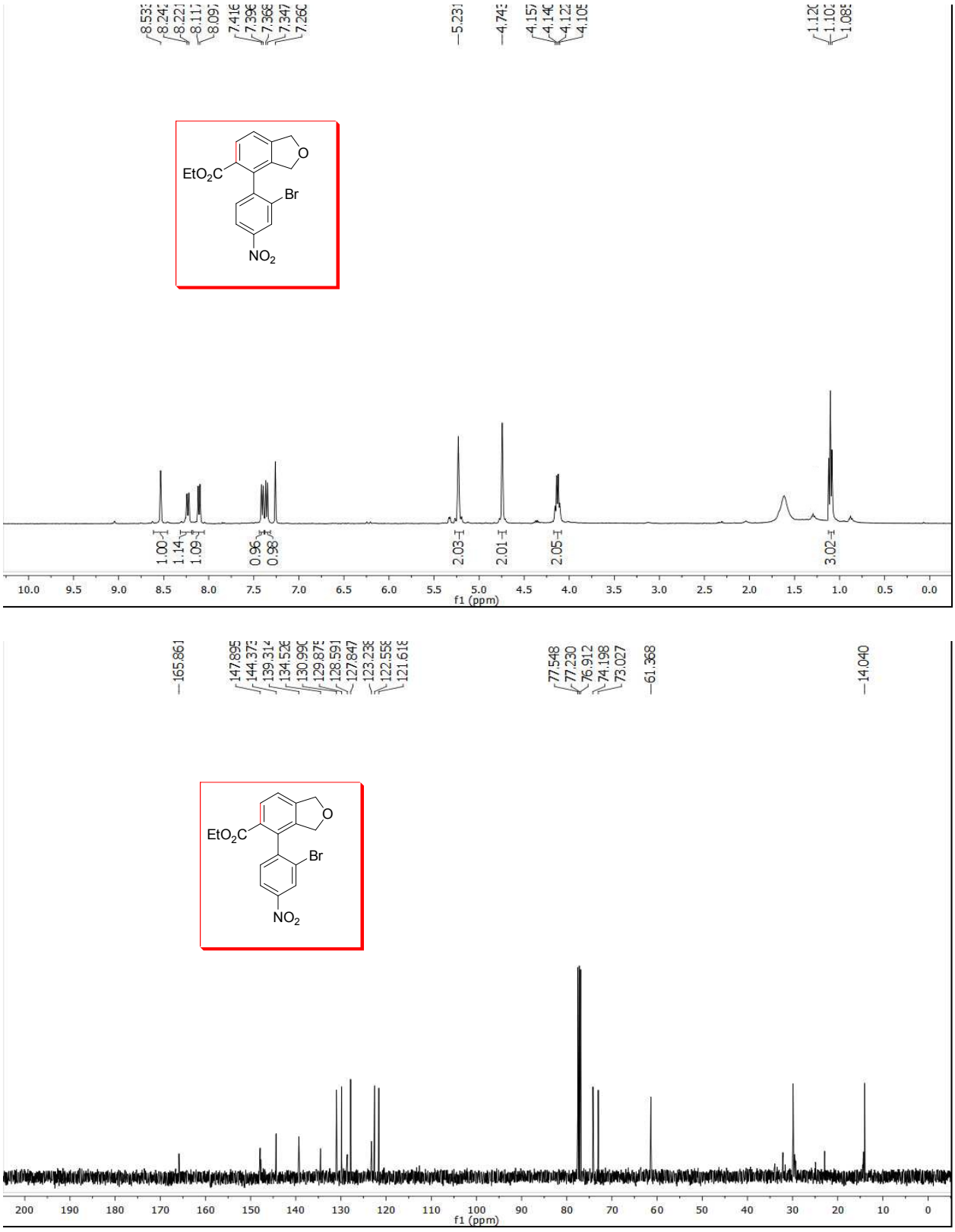


Figure S16. ^{1}H and ^{13}C NMR spectra of **6b** in $CDCl_3$

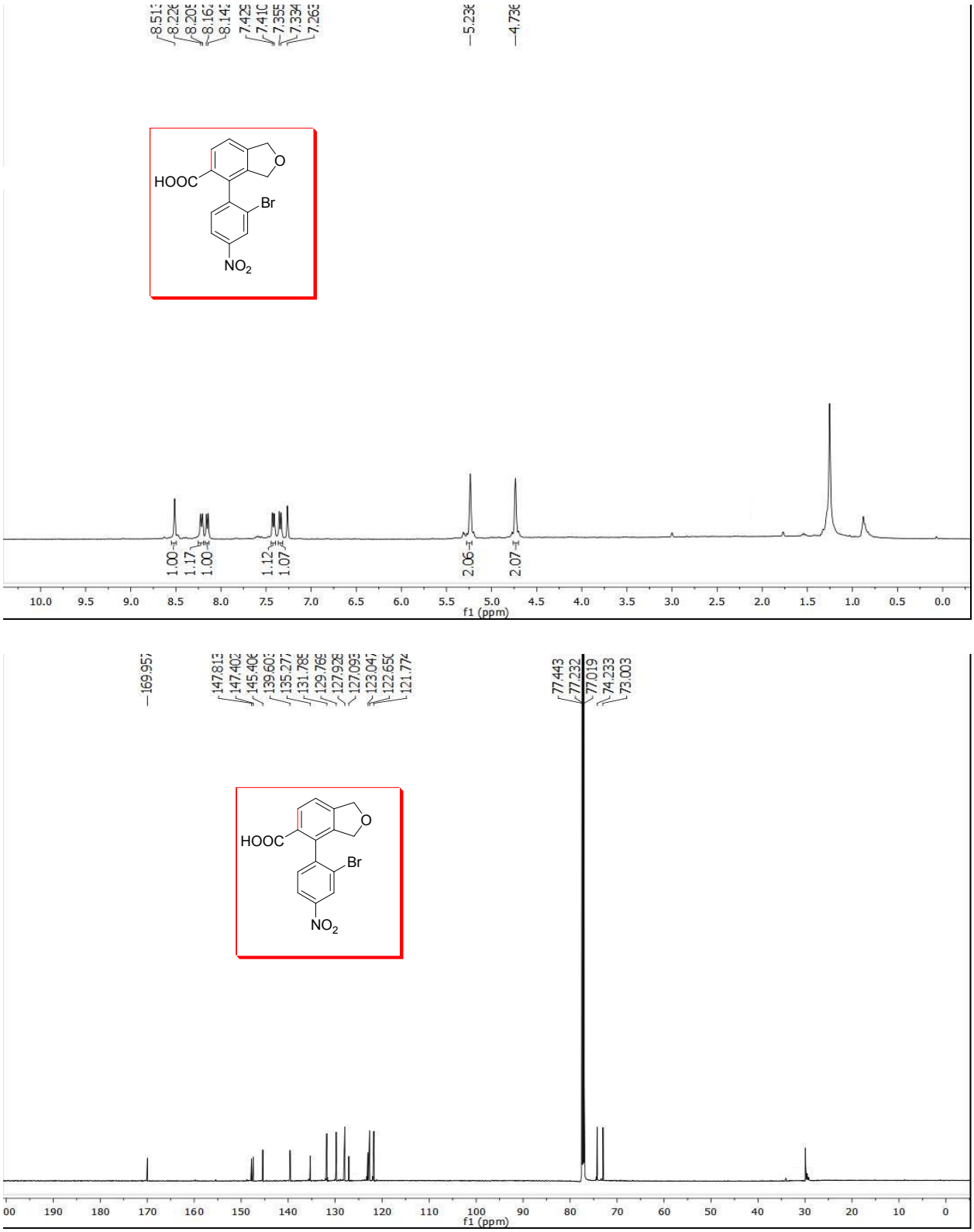


Figure S17. ^{1}H and ^{13}C NMR spectra of **7b** in $CDCl_3$

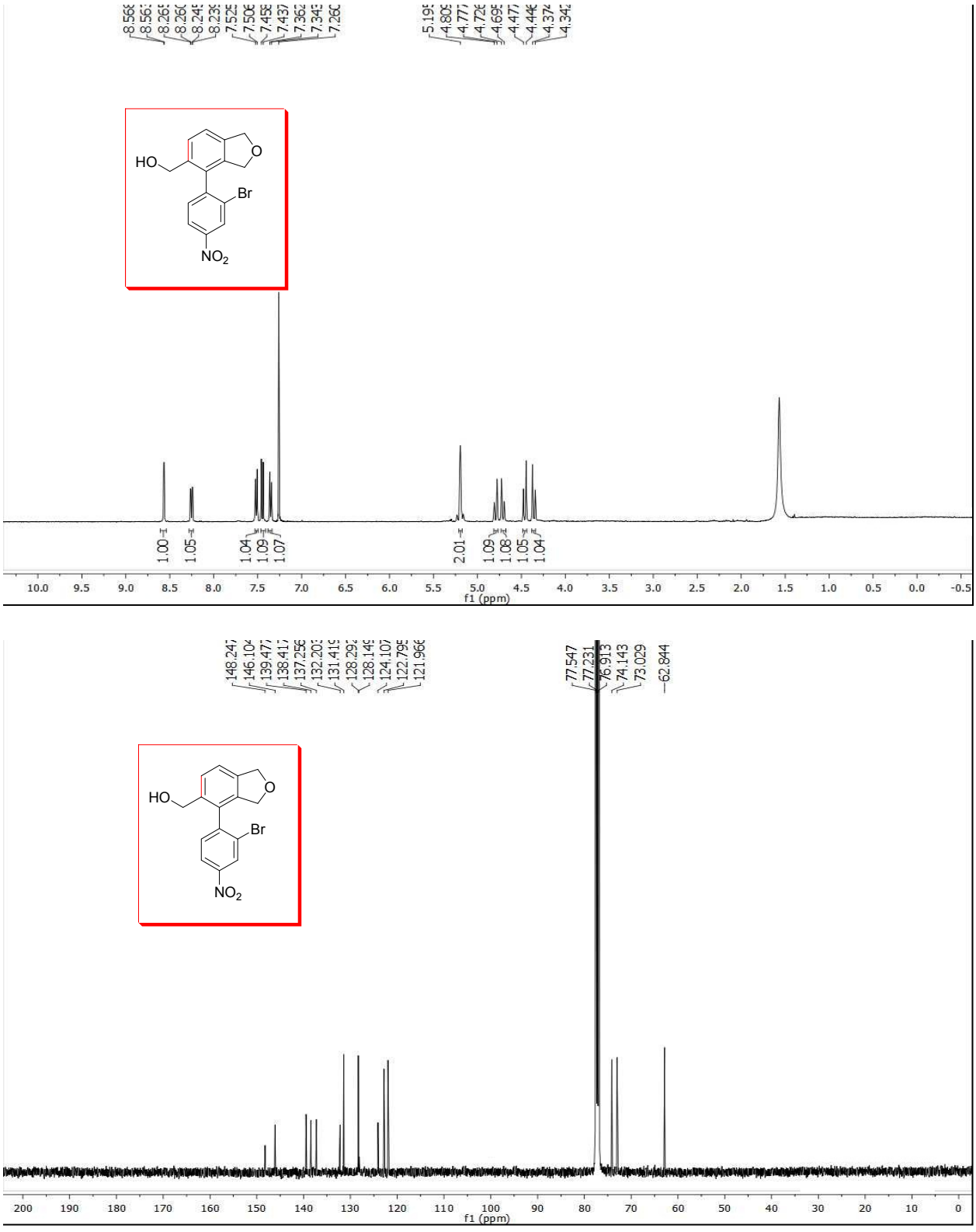


Figure S18. ^{1}H and ^{13}C NMR spectra of **8b** in $CDCl_3$

Figure S19. ^{1}H and ^{13}C NMR spectra of **9b** in $CDCl_3$

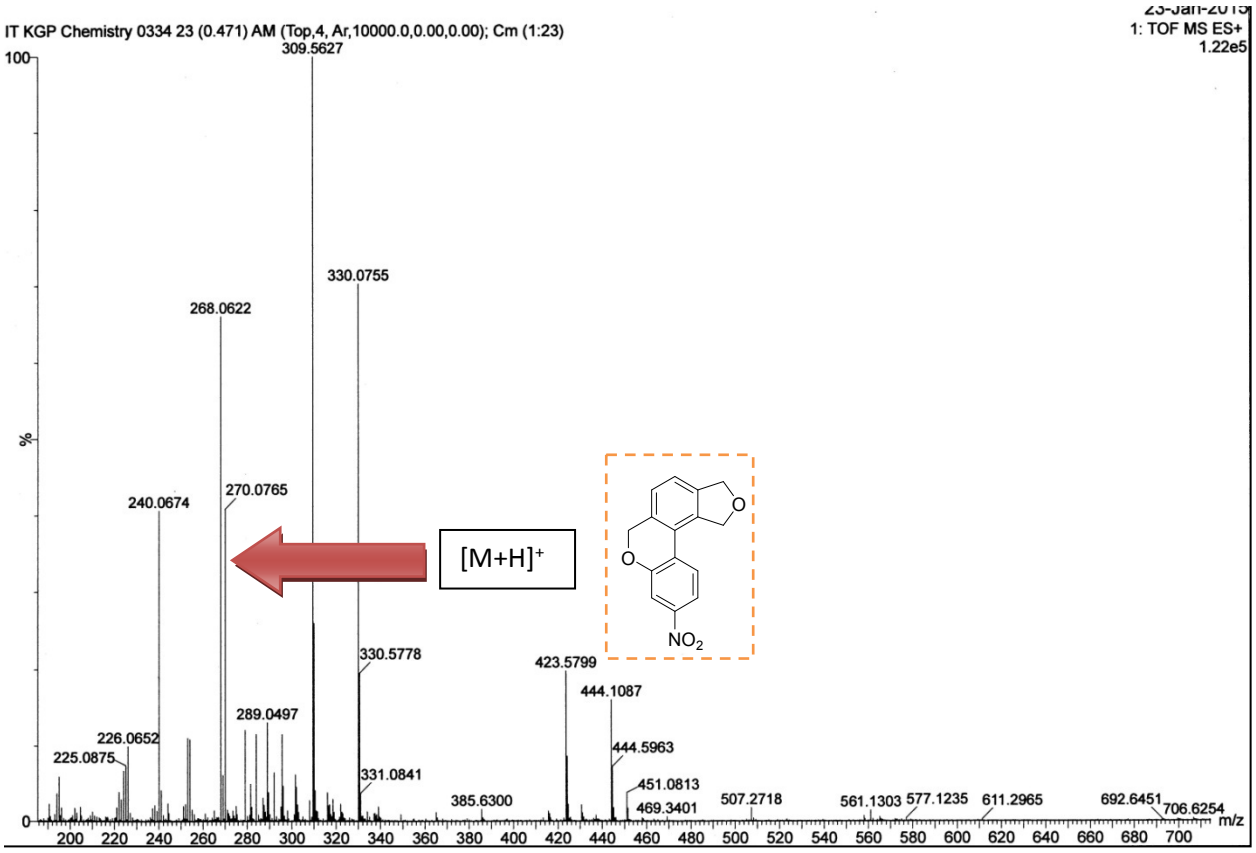


Figure S20. HRMS spectrum of **9b**

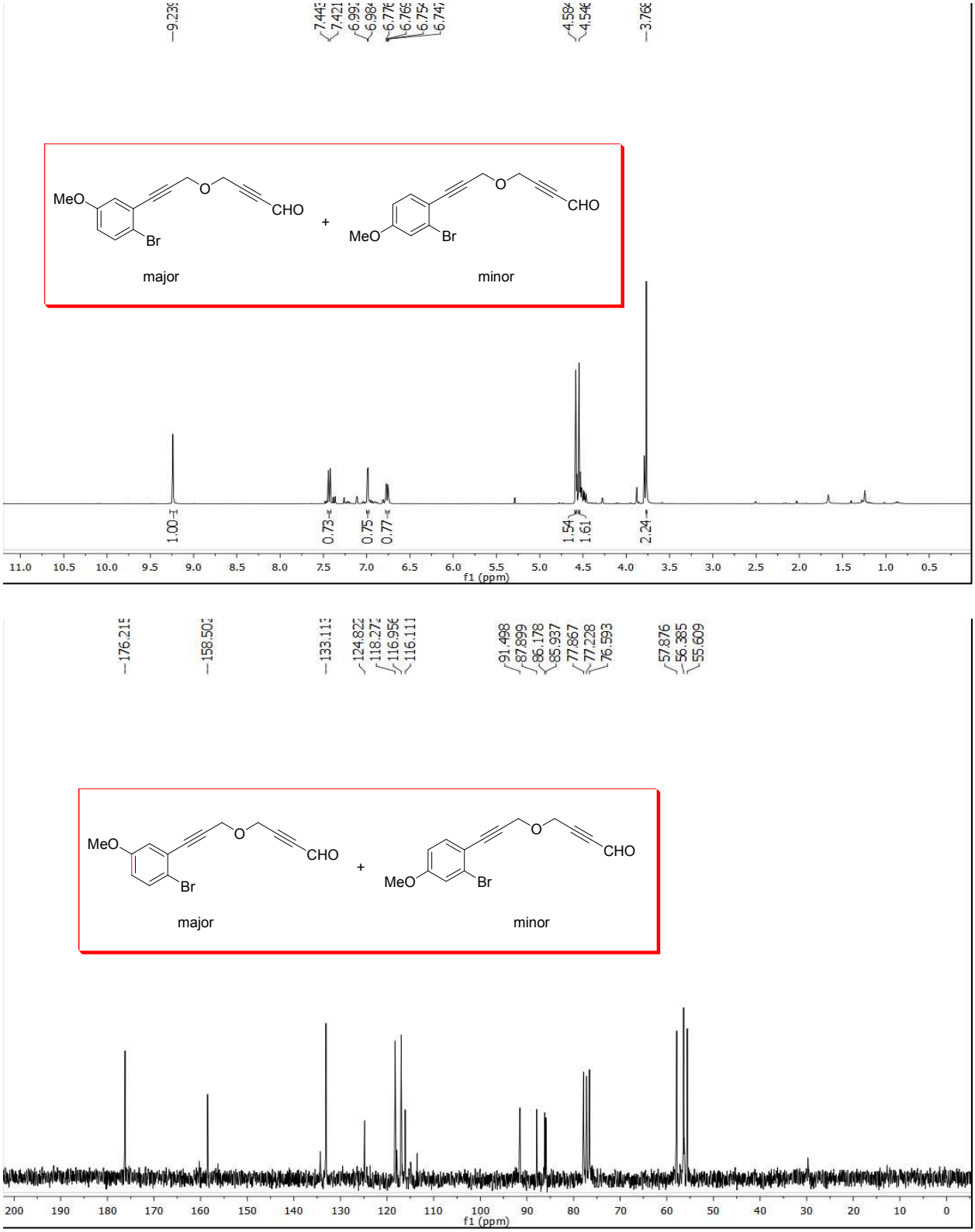


Figure S21. ^{1}H and ^{13}C NMR spectra of **4c** (major isomer) in $CDCl_3$

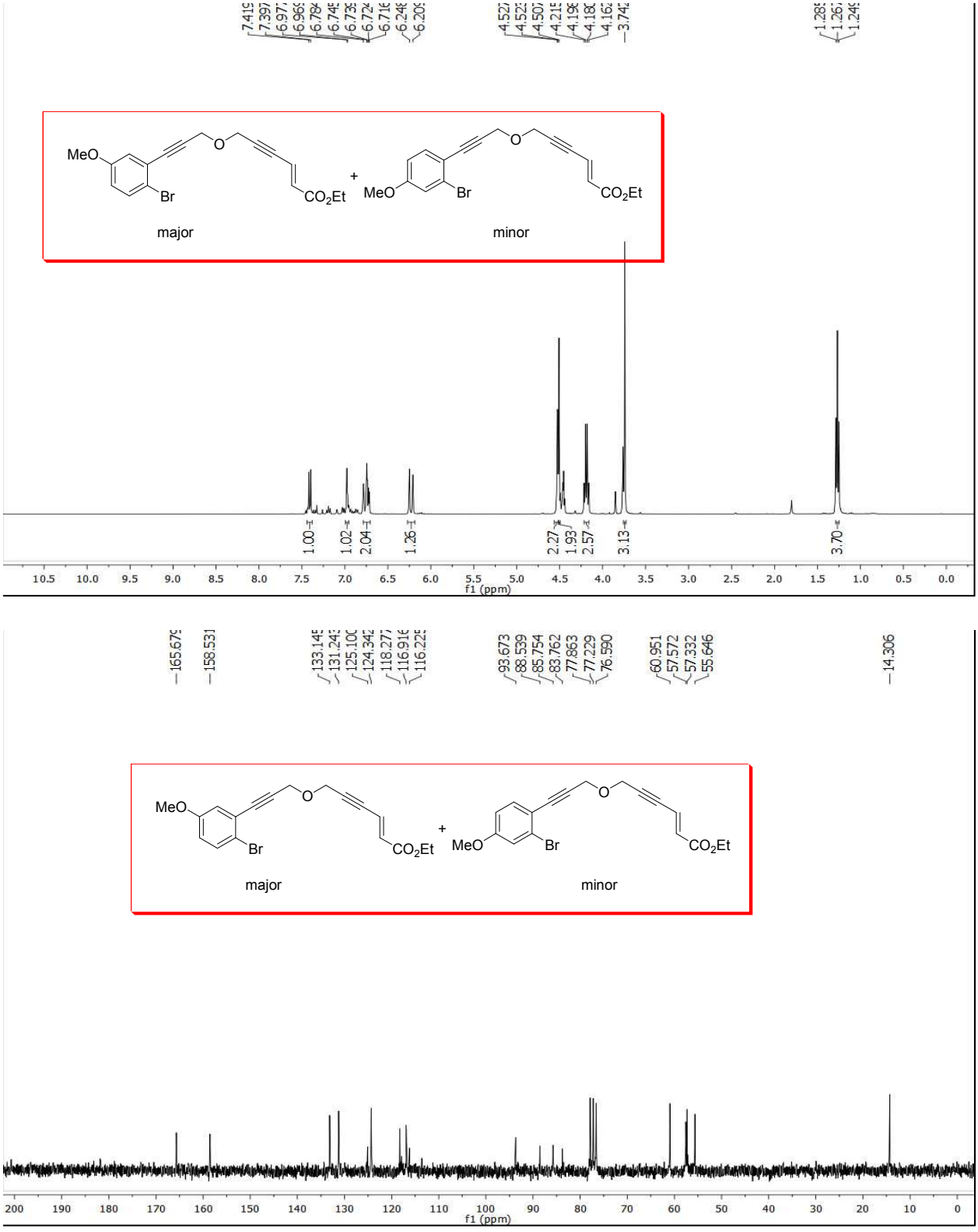
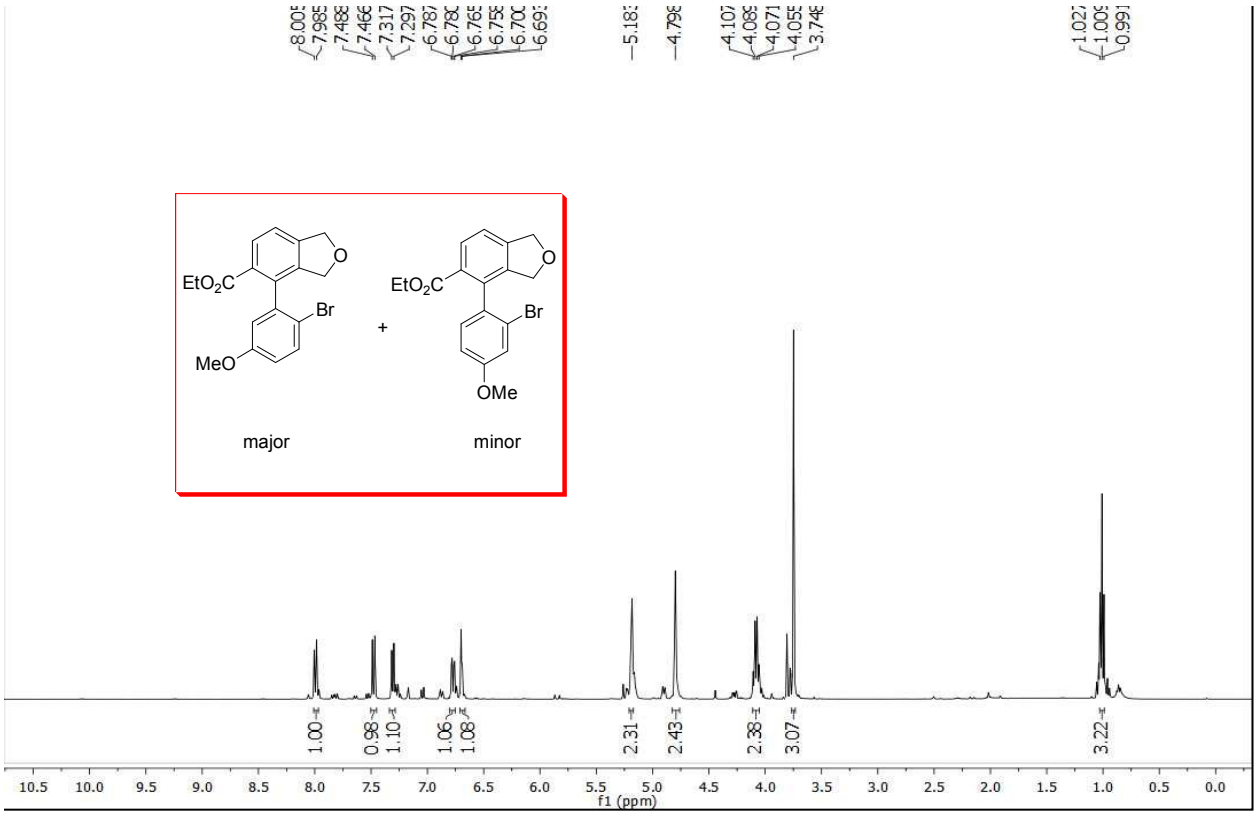


Figure S22. ^{1}H and ^{13}C NMR spectra of **5c** (major isomer) in $CDCl_3$



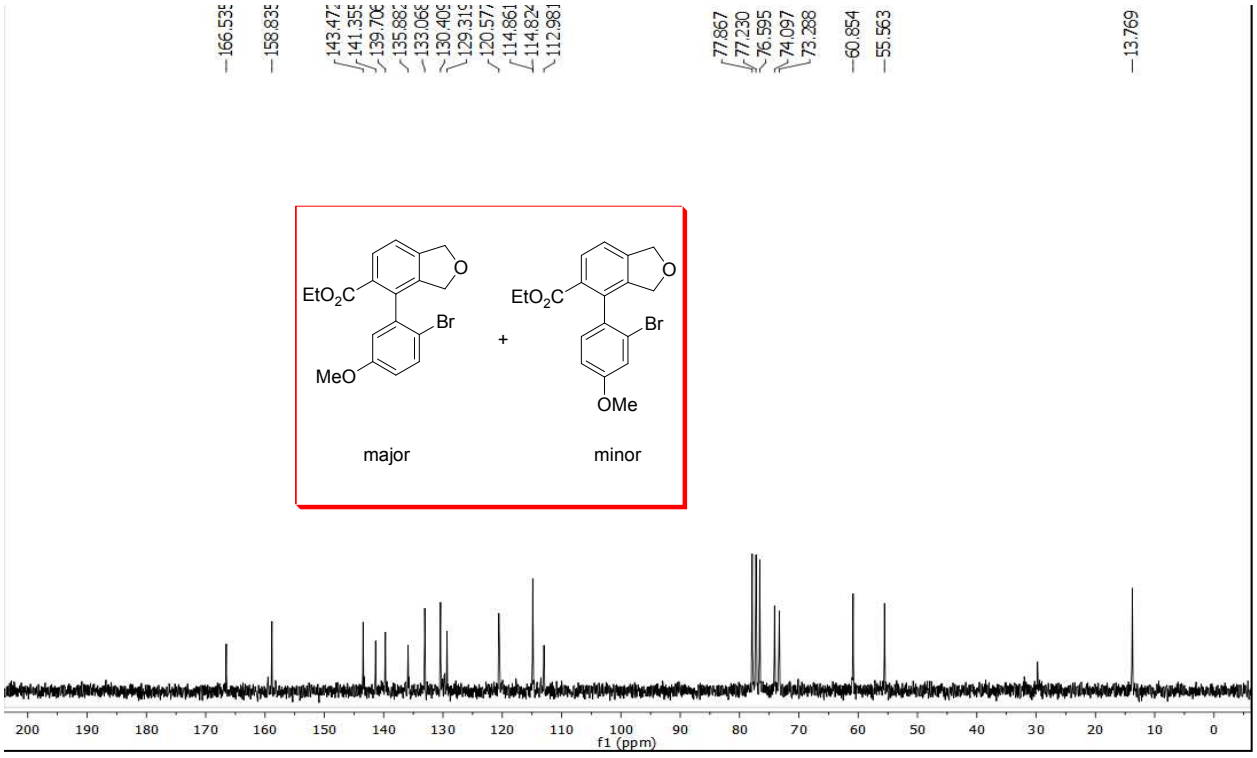
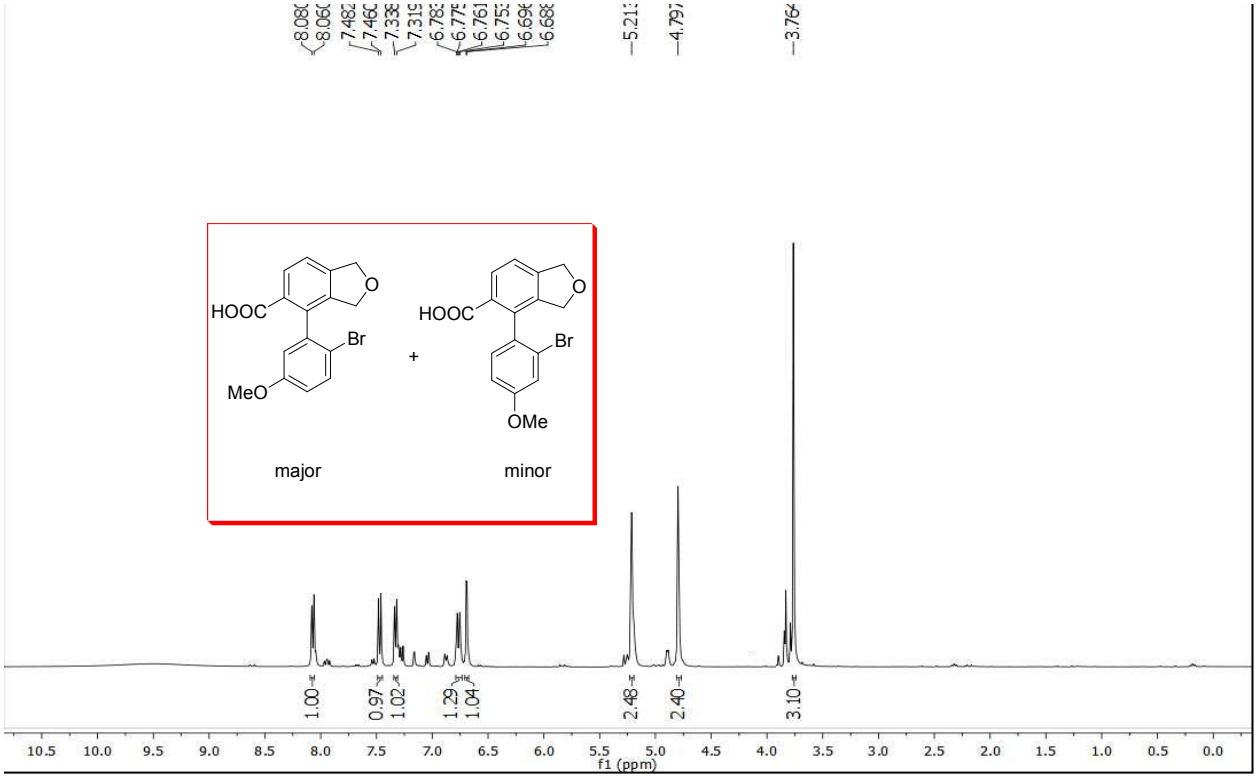


Figure S23. ^{1}H and ^{13}C NMR spectra of **6c** (major isomer) in $CDCl_3$



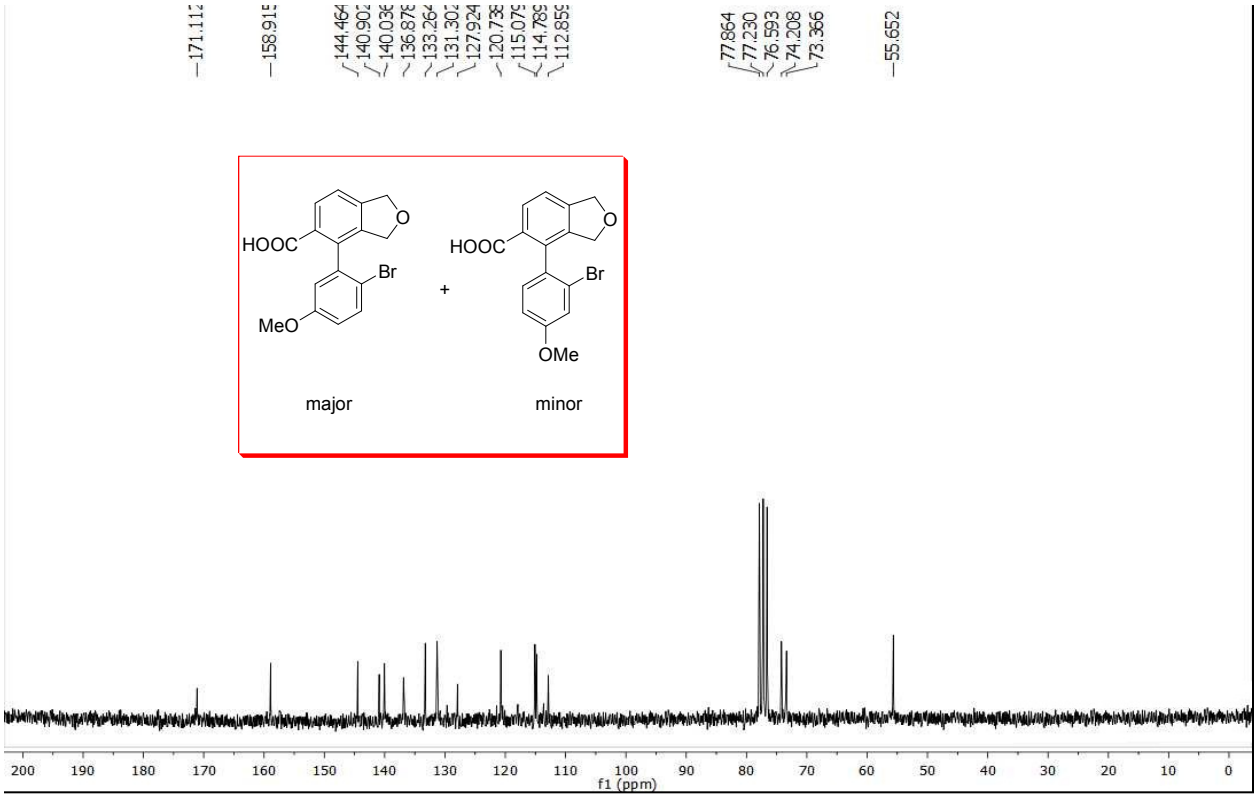


Figure S24. ^{1}H and ^{13}C NMR spectra of **7c** (major isomer) in $CDCl_3$

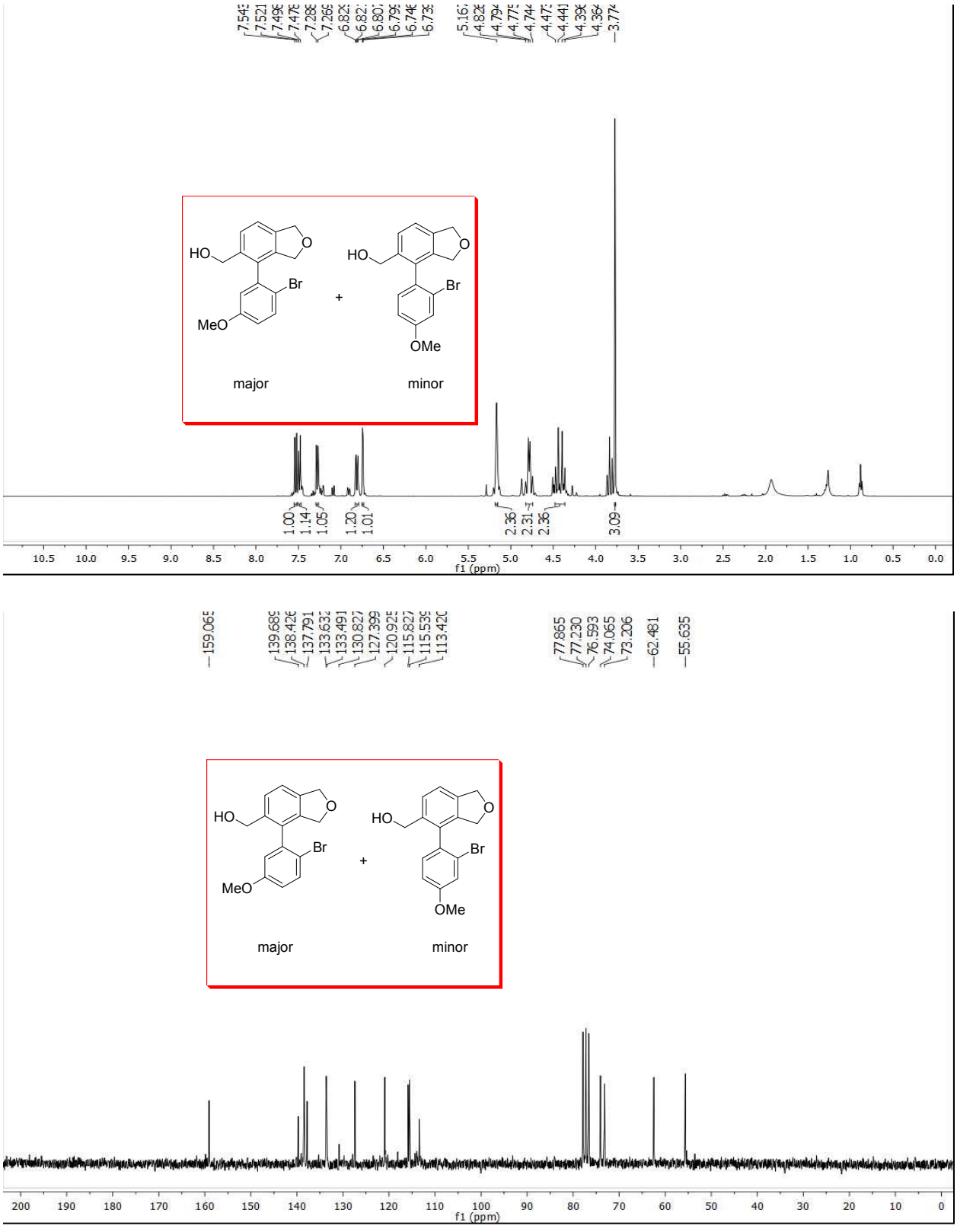


Figure S25. ^{1}H and ^{13}C NMR spectra of **8c** (major isomer) in $CDCl_3$

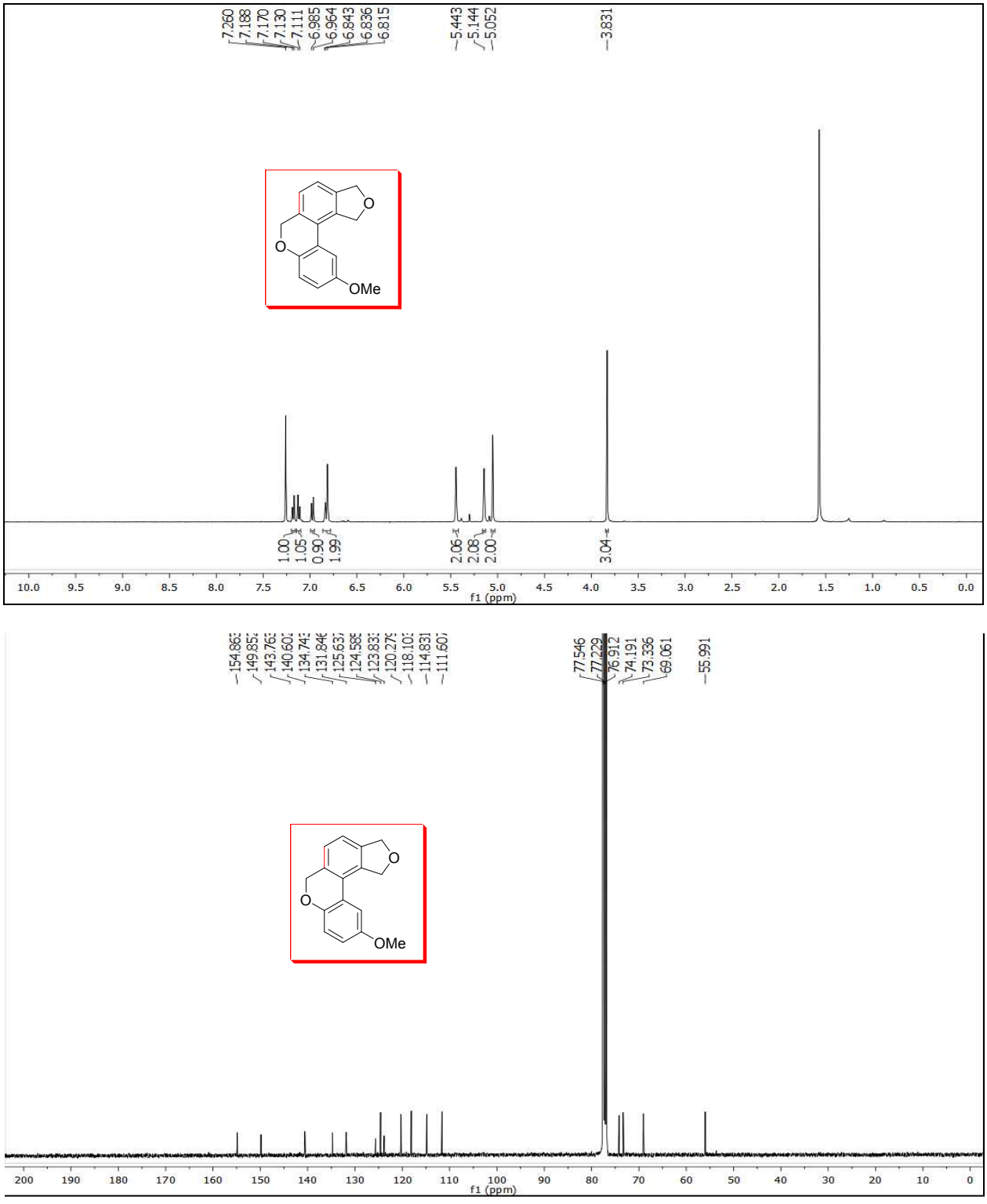


Figure S26. ^{1}H and ^{13}C NMR spectra of **9c** (major isomer) in $CDCl_3$

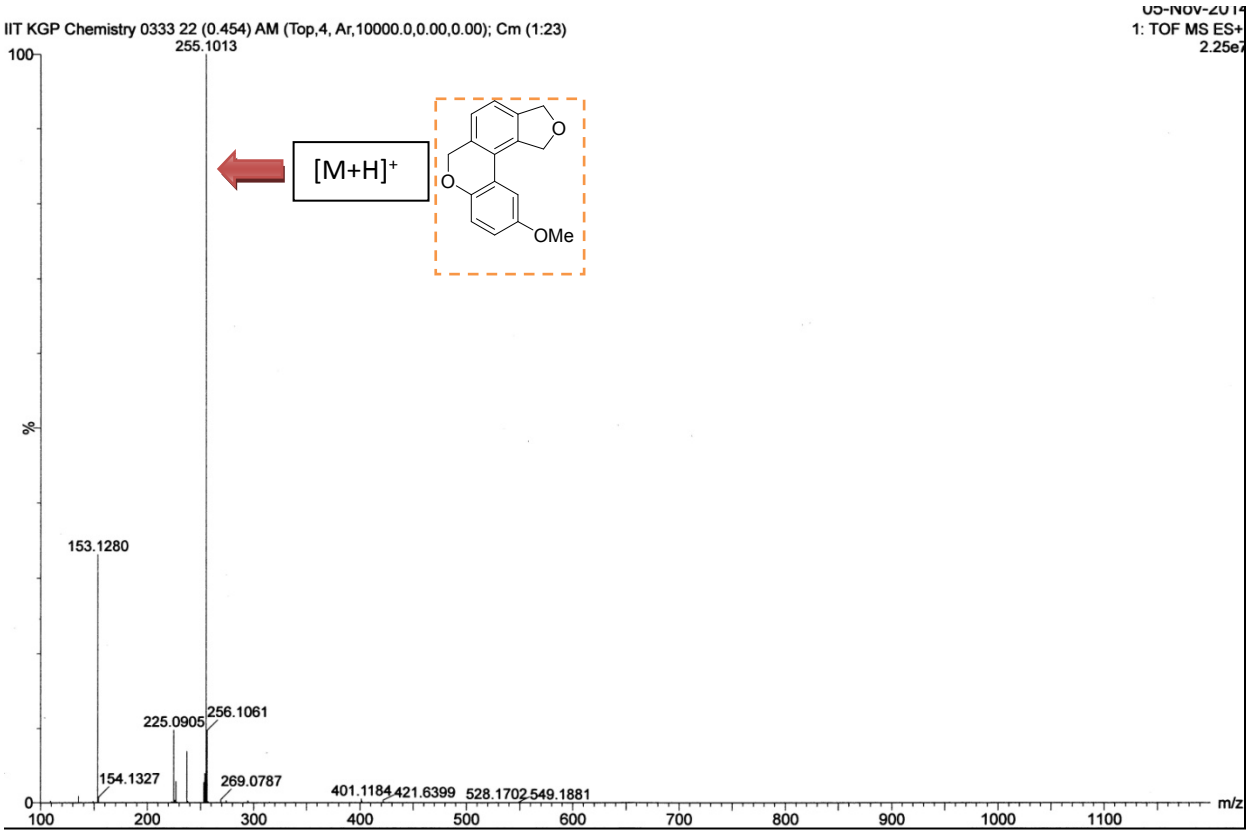
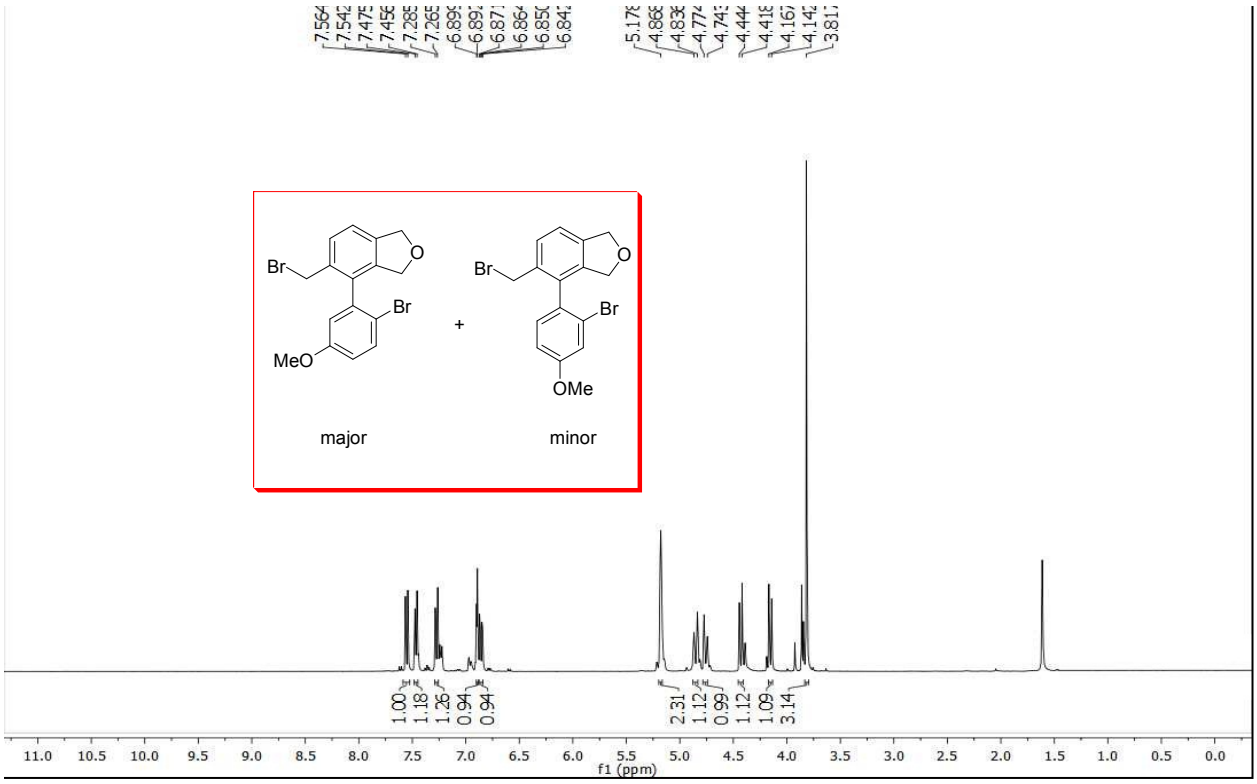


Figure S27. HRMS spectrum of **9c**



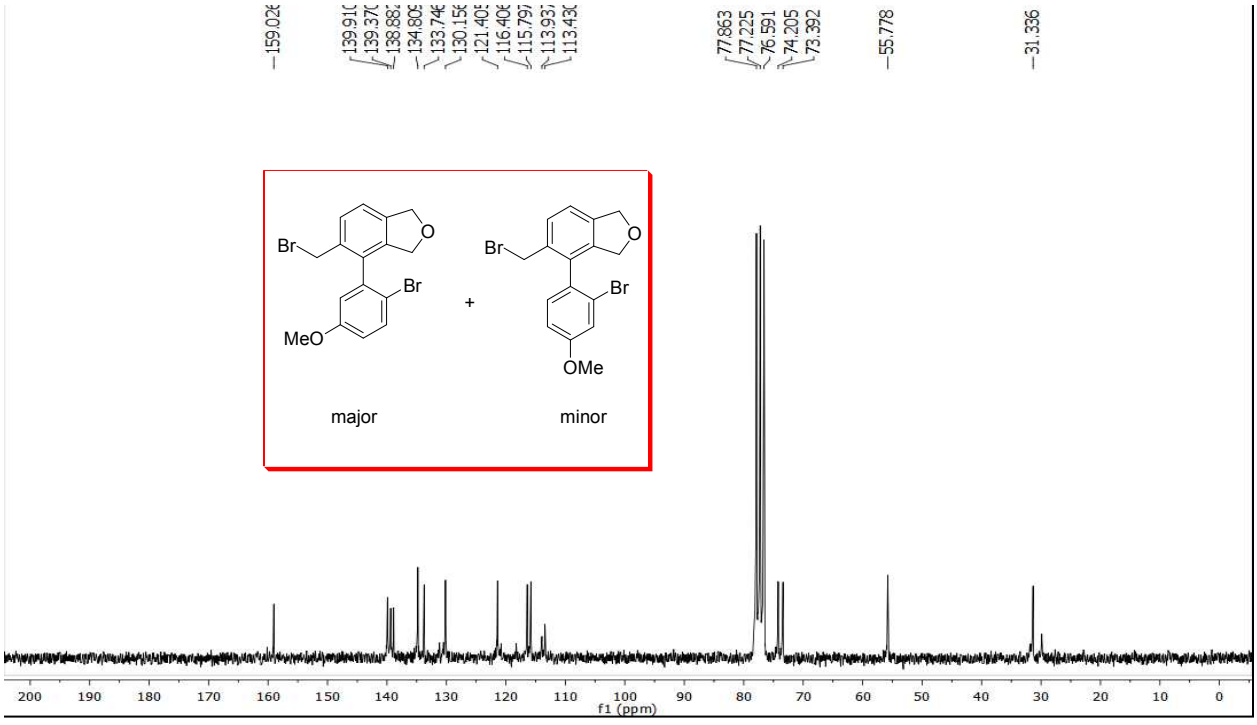


Figure S28. ^{1}H and ^{13}C NMR spectra of **10c** (major isomer) in $CDCl_3$

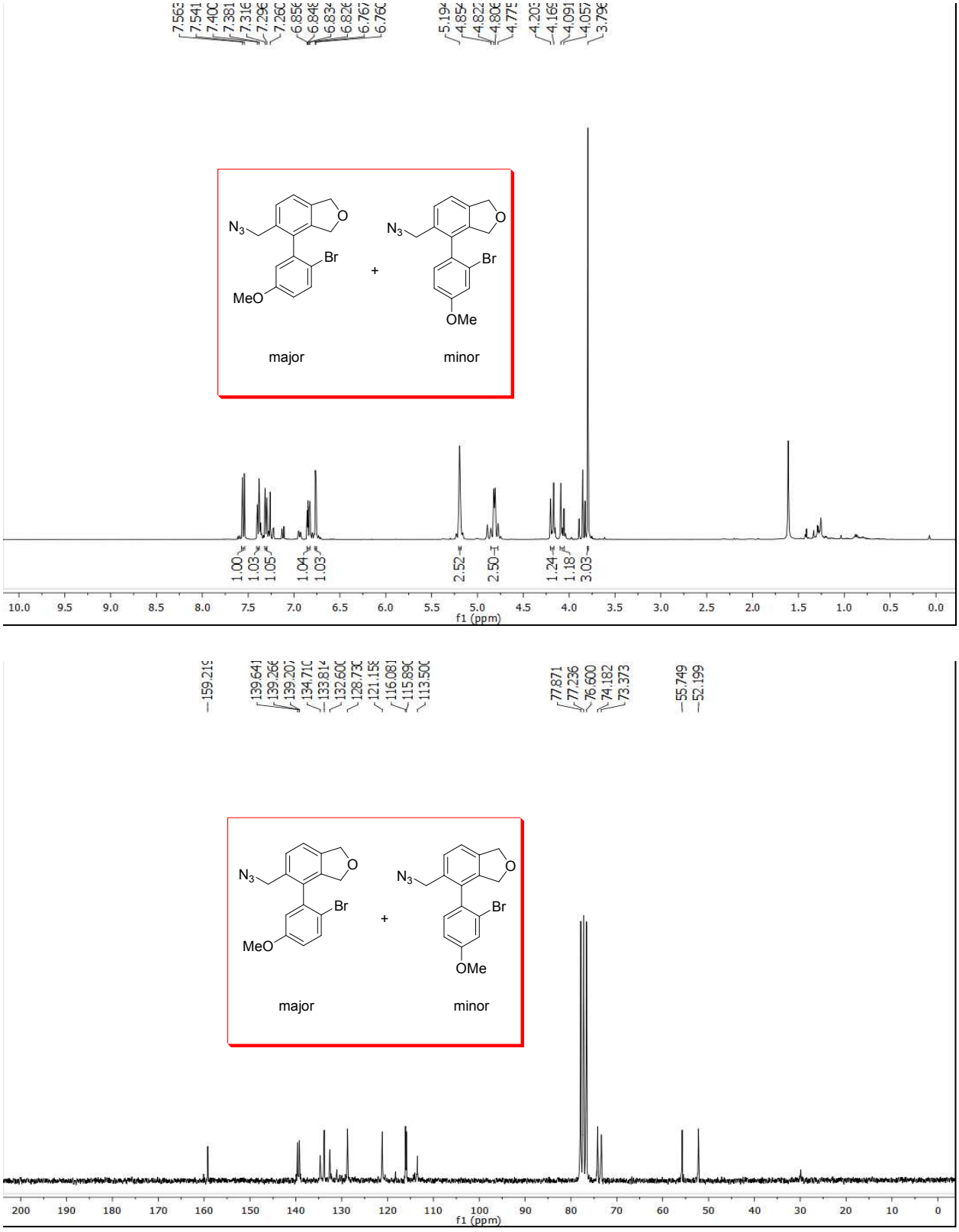
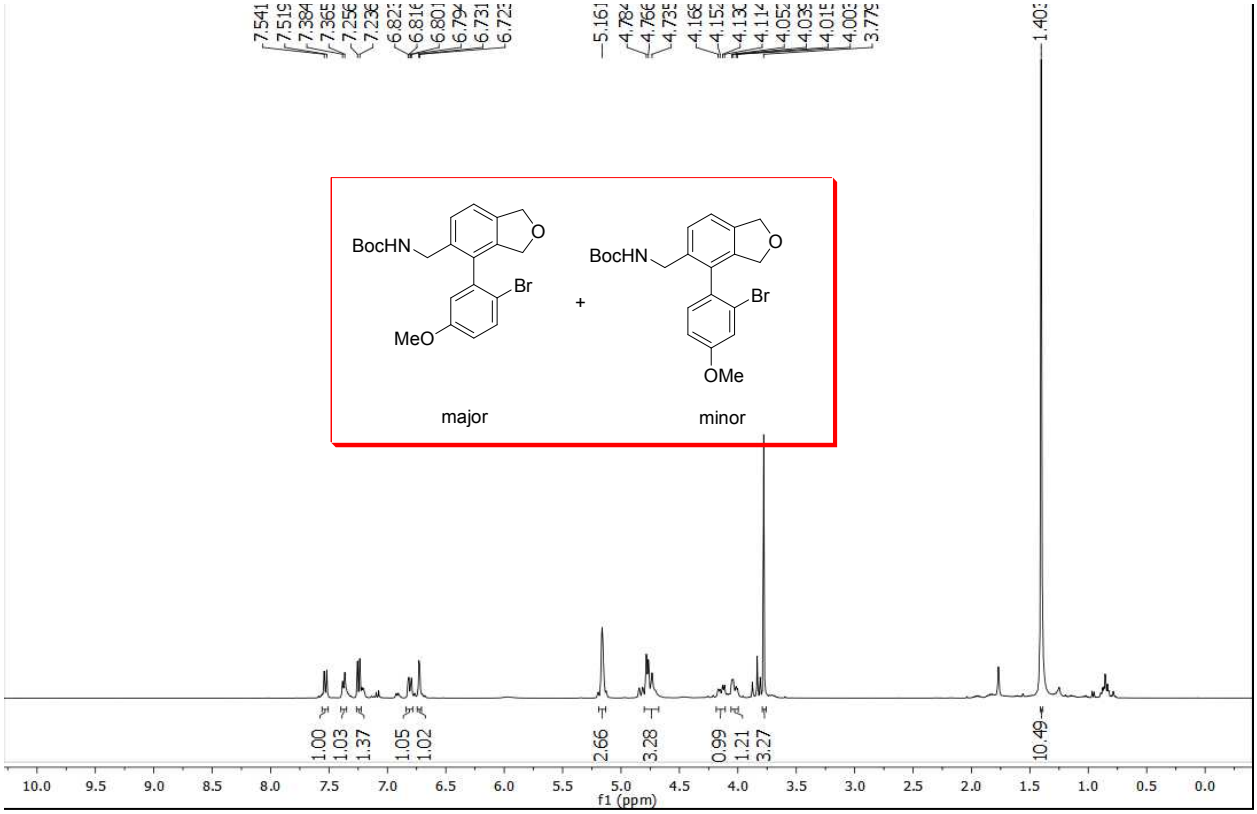


Figure S29. ^{1}H and ^{13}C NMR spectra of **11c** (major isomer) in $CDCl_3$



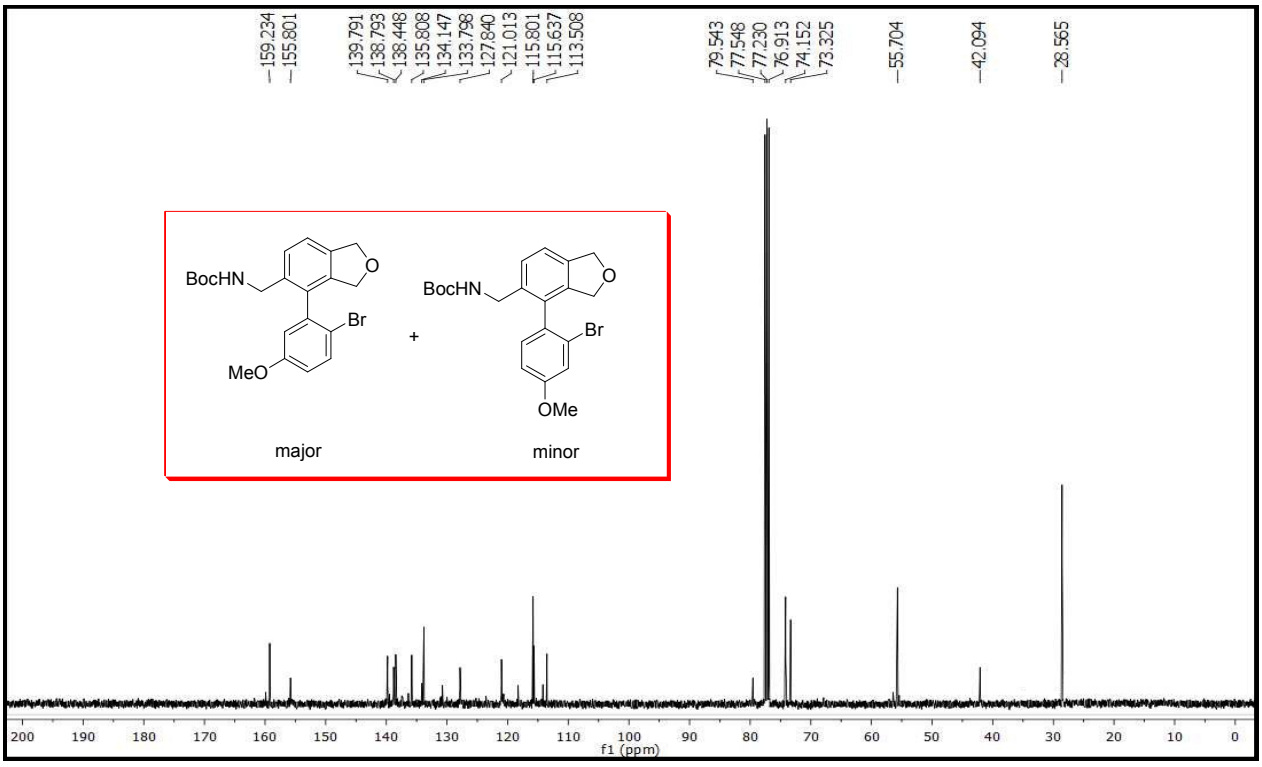


Figure S30. ^{1}H and ^{13}C NMR spectra of **12c** (major isomer) in $CDCl_3$

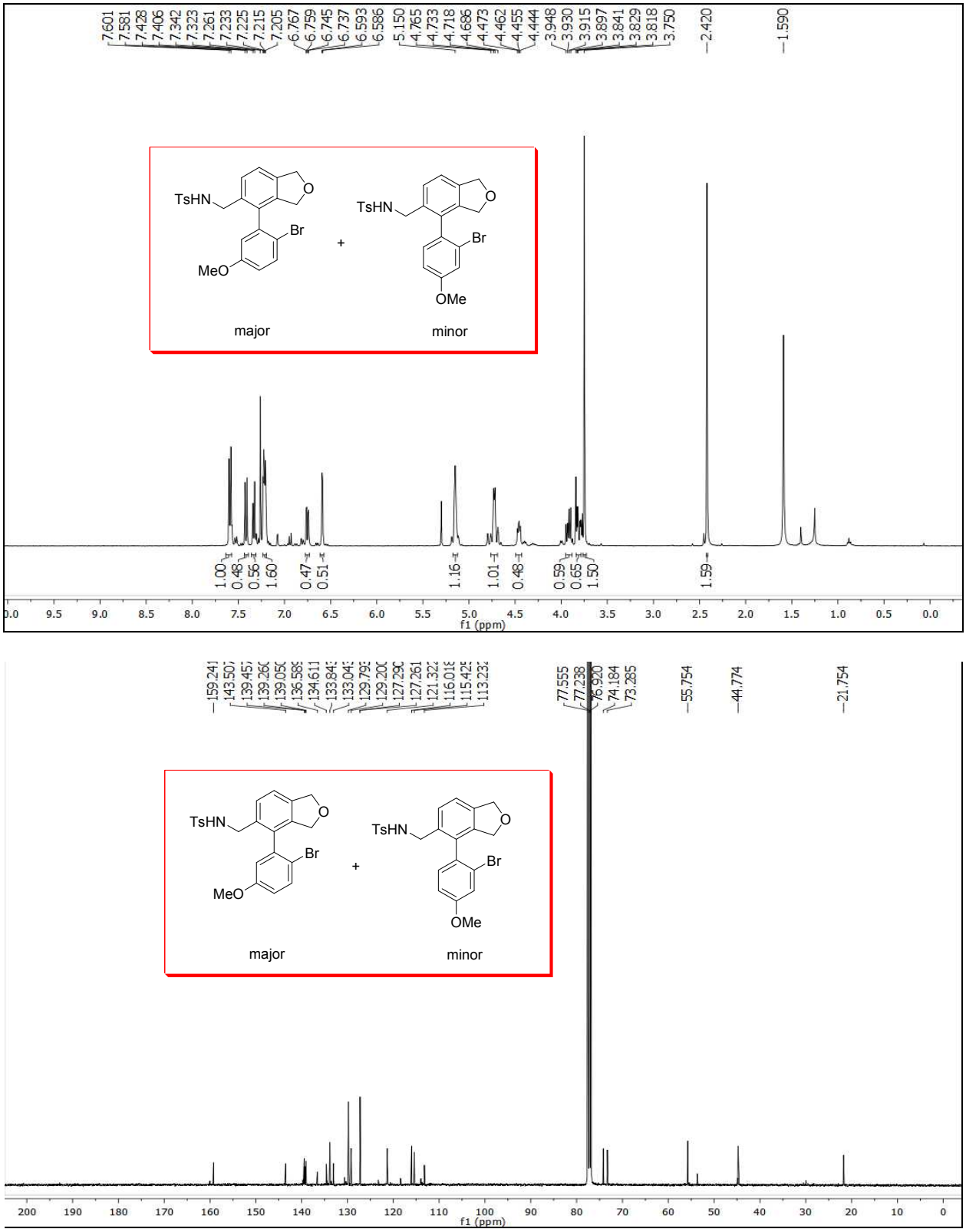


Figure S31. ^{1}H and ^{13}C NMR spectra of **13c** (major isomer) in $CDCl_3$

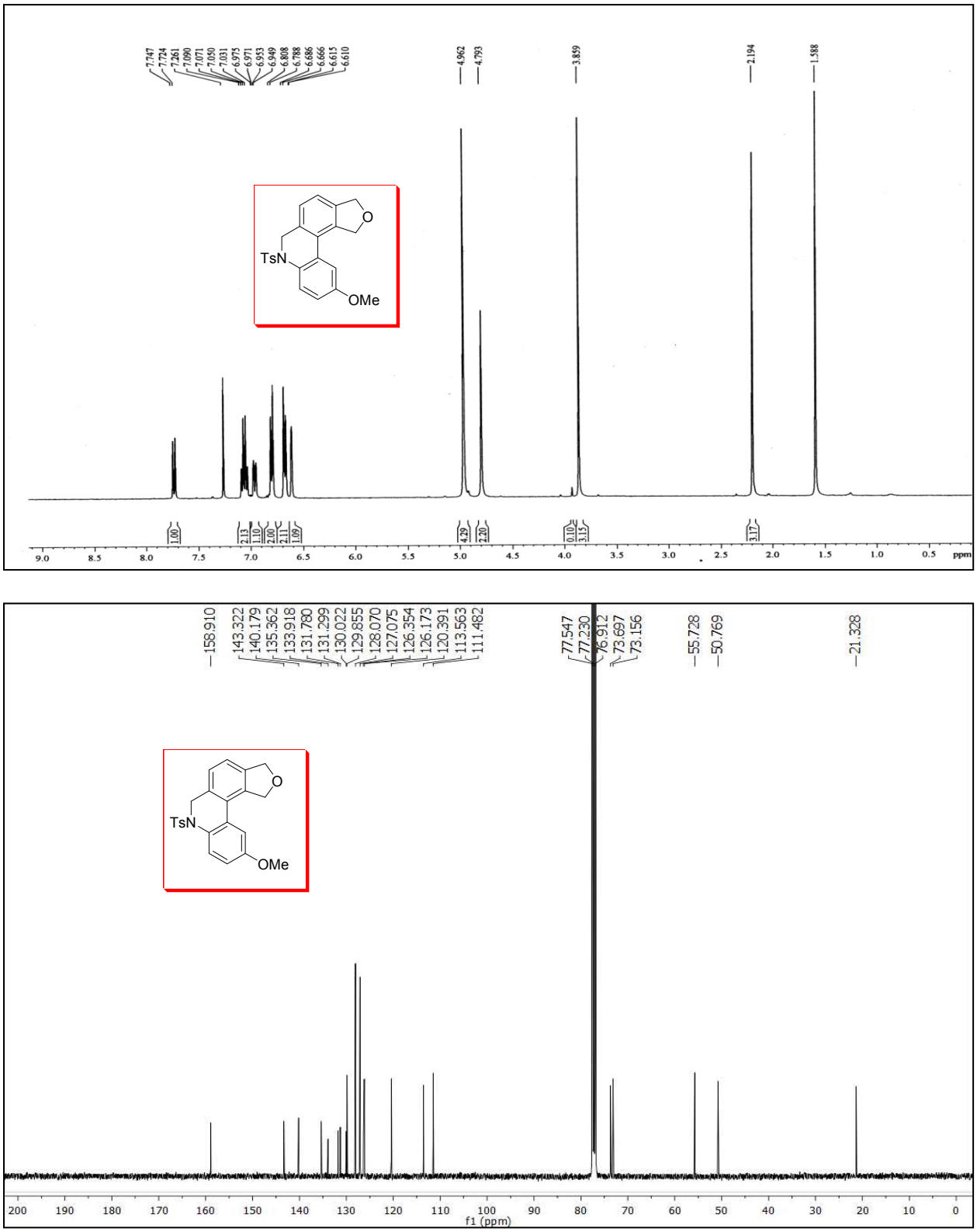


Figure S32. ^{1}H and ^{13}C NMR spectra of **14c** in $CDCl_3$

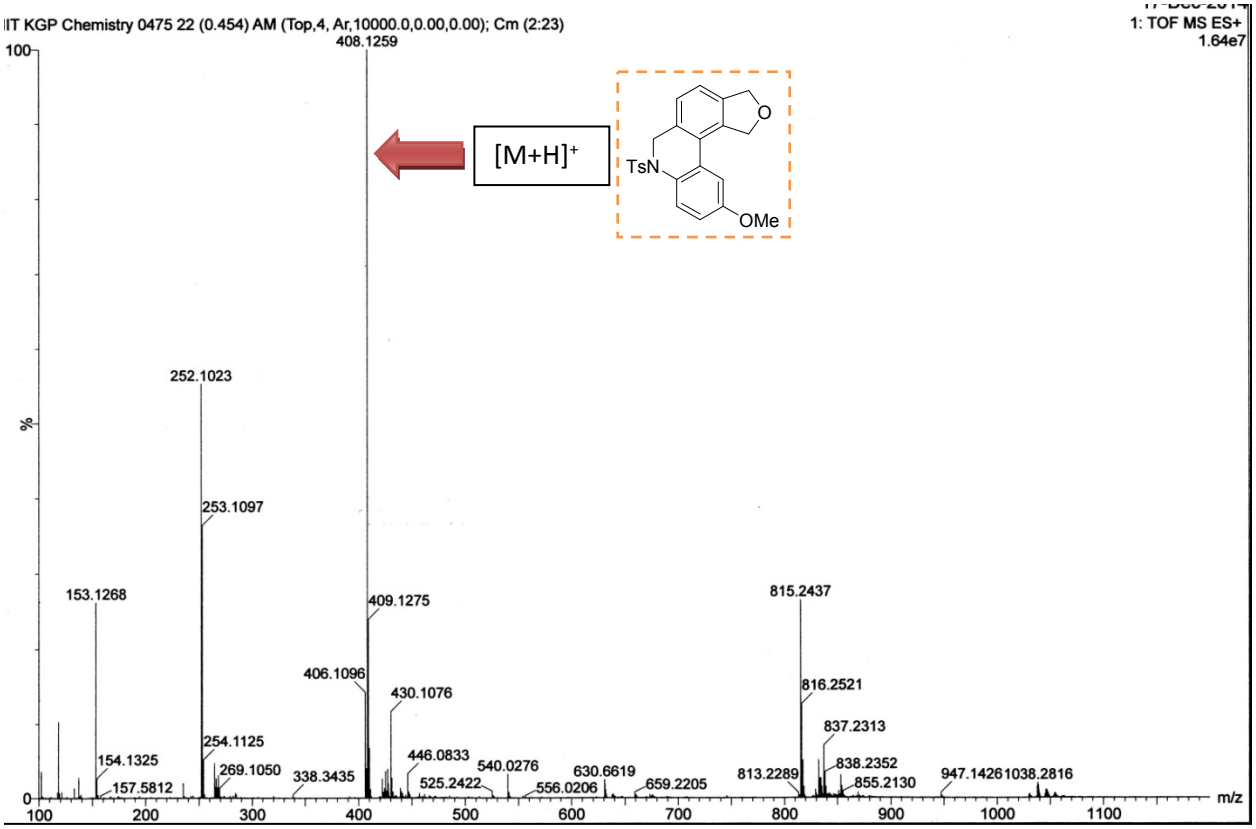


Figure S33. HRMS spectrum of **14c**

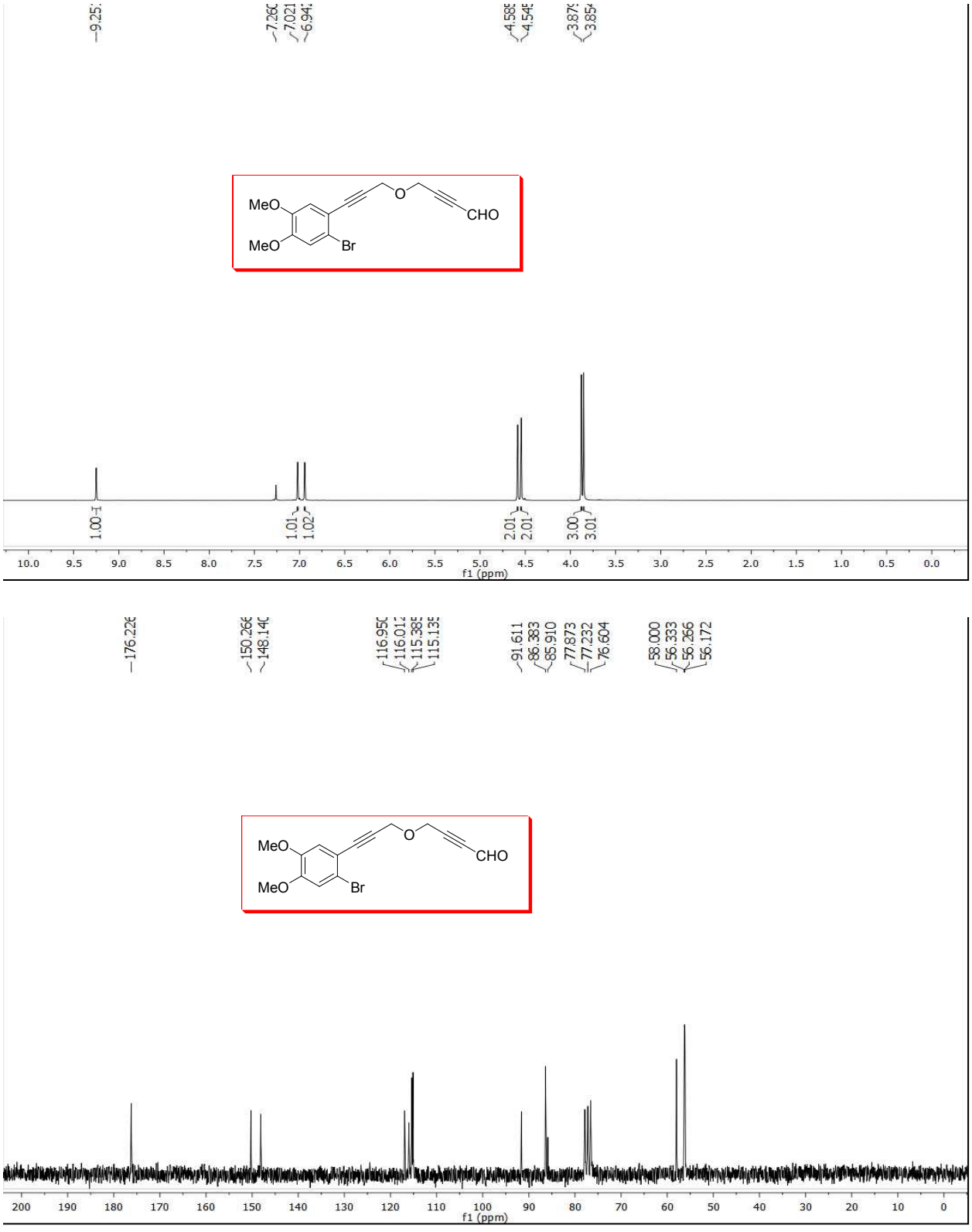


Figure S34. ^{1}H and ^{13}C NMR spectra of **4d** in $CDCl_3$

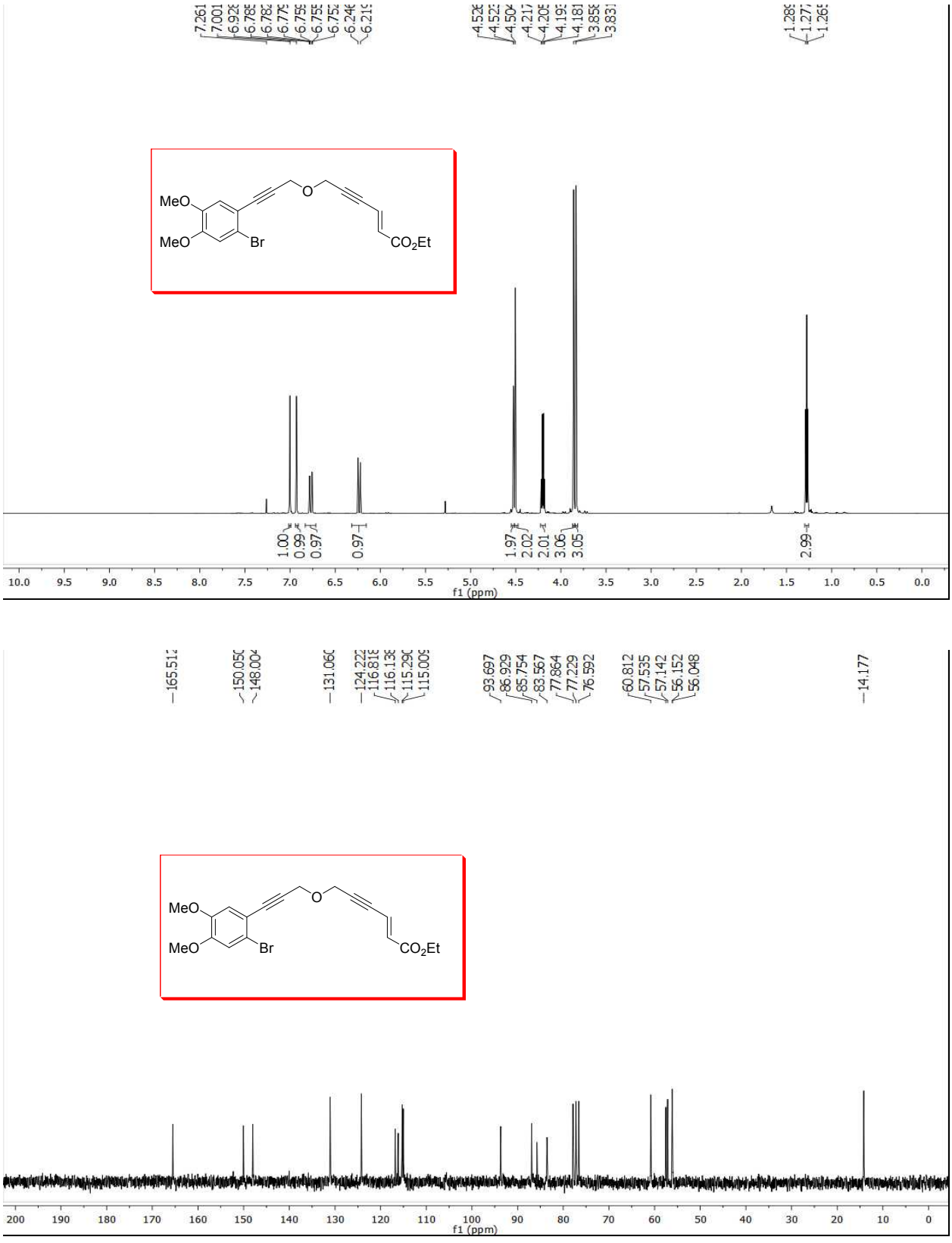


Figure S35. ^{1}H and ^{13}C NMR spectra of **5d** in $CDCl_3$

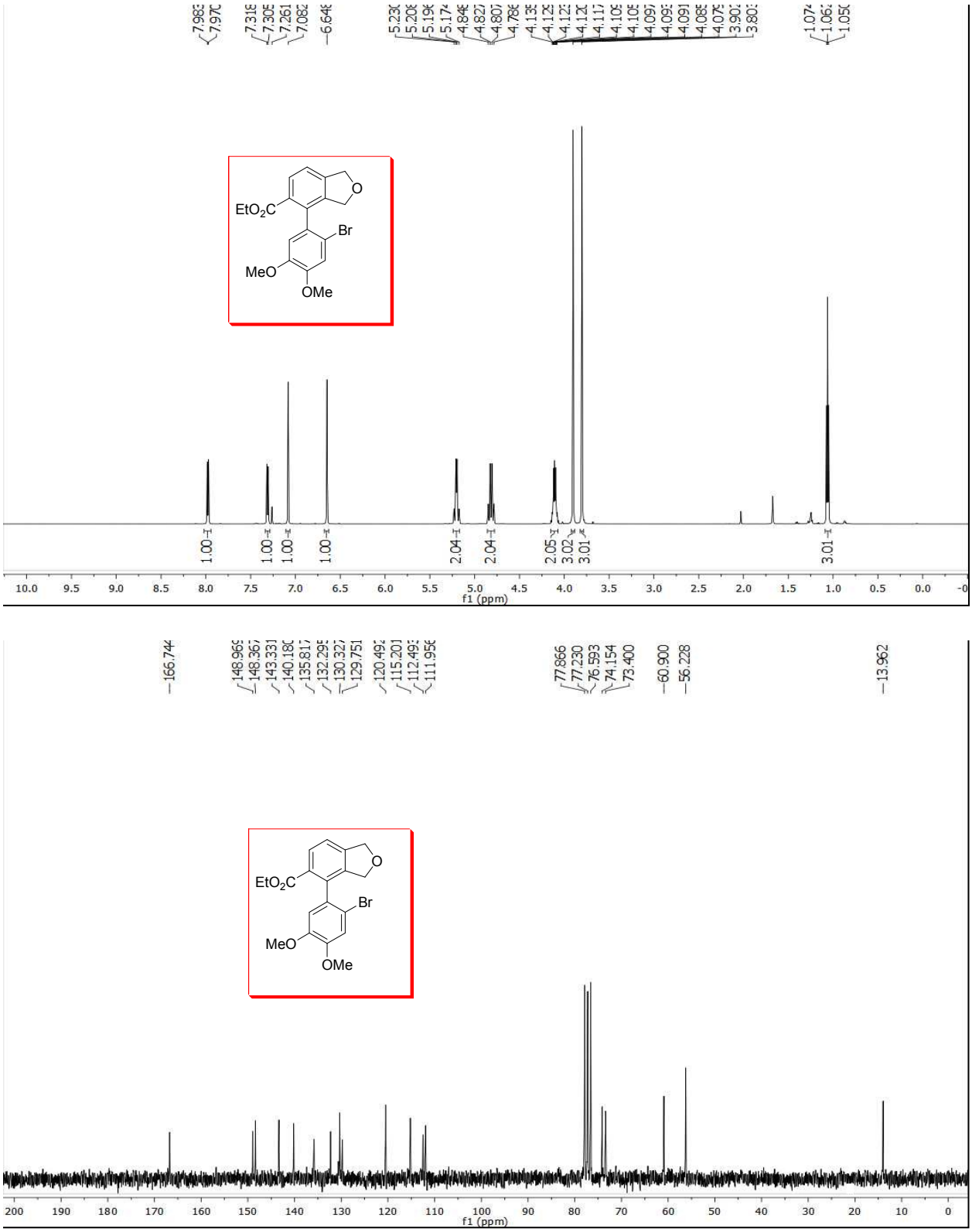


Figure S36. ^{1}H and ^{13}C NMR spectra of **6d** in $CDCl_3$

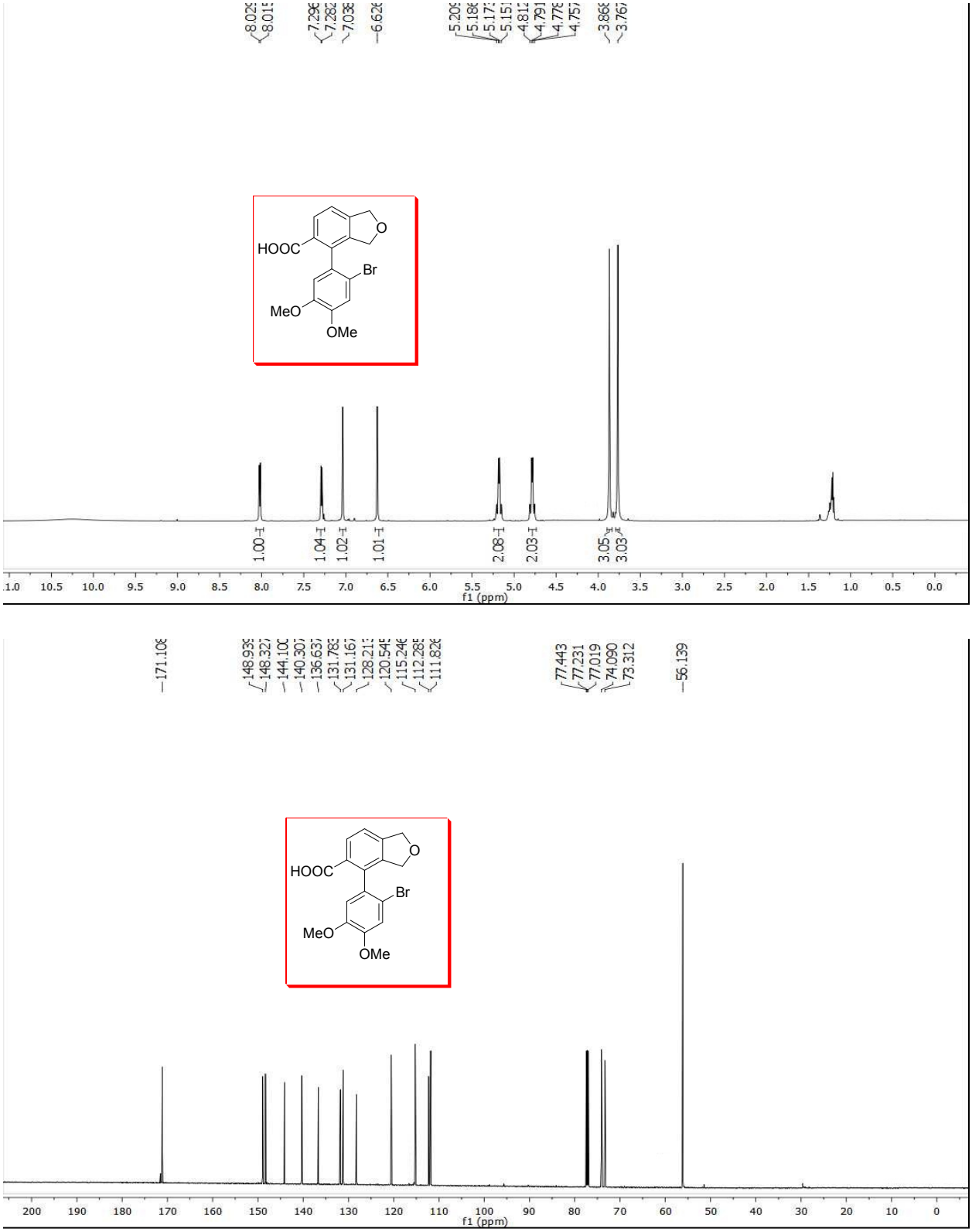


Figure S37. ^{1}H and ^{13}C NMR spectra of **7d** in $CDCl_3$

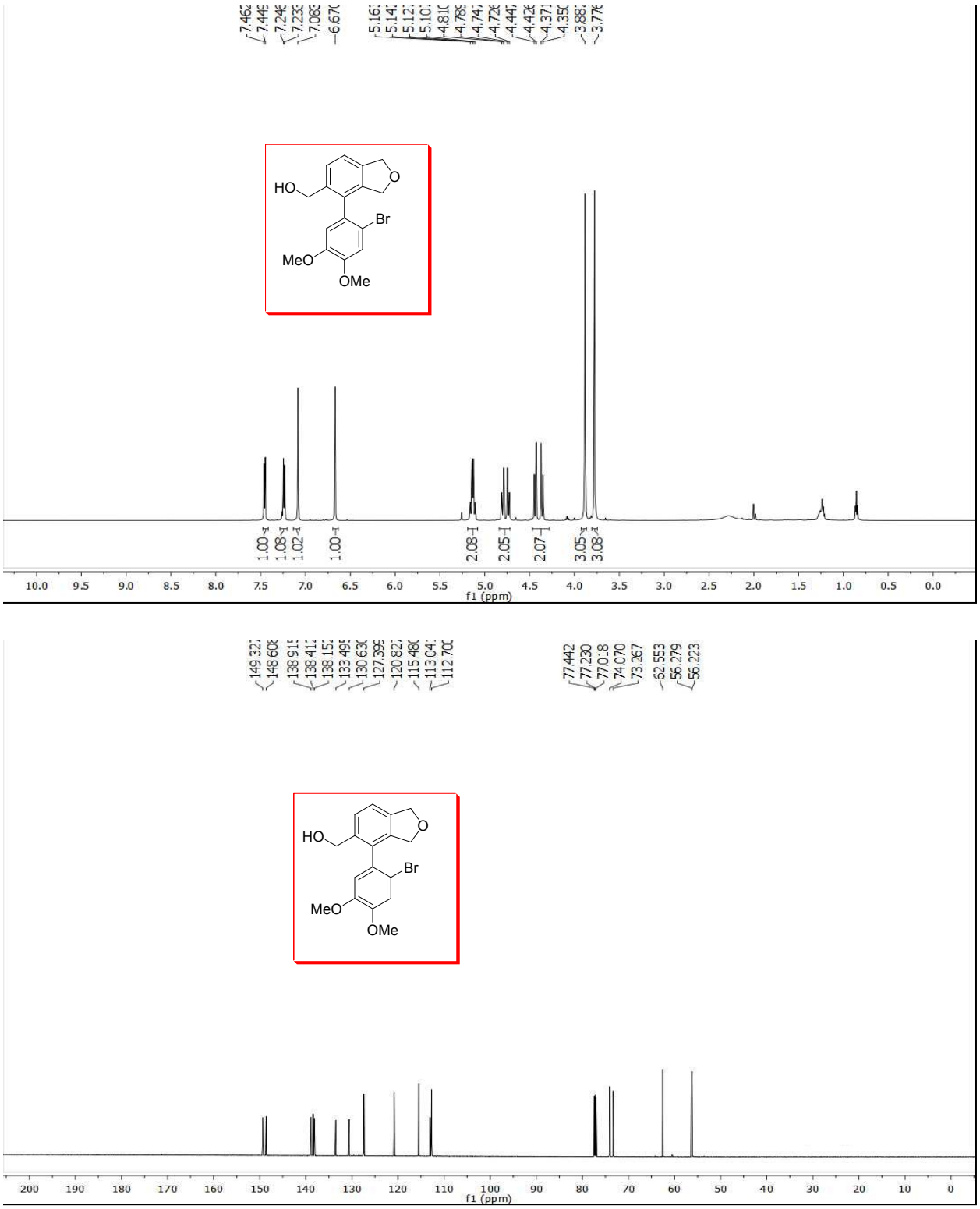


Figure S38. ^{1}H and ^{13}C NMR spectra of **8d** in $CDCl_3$

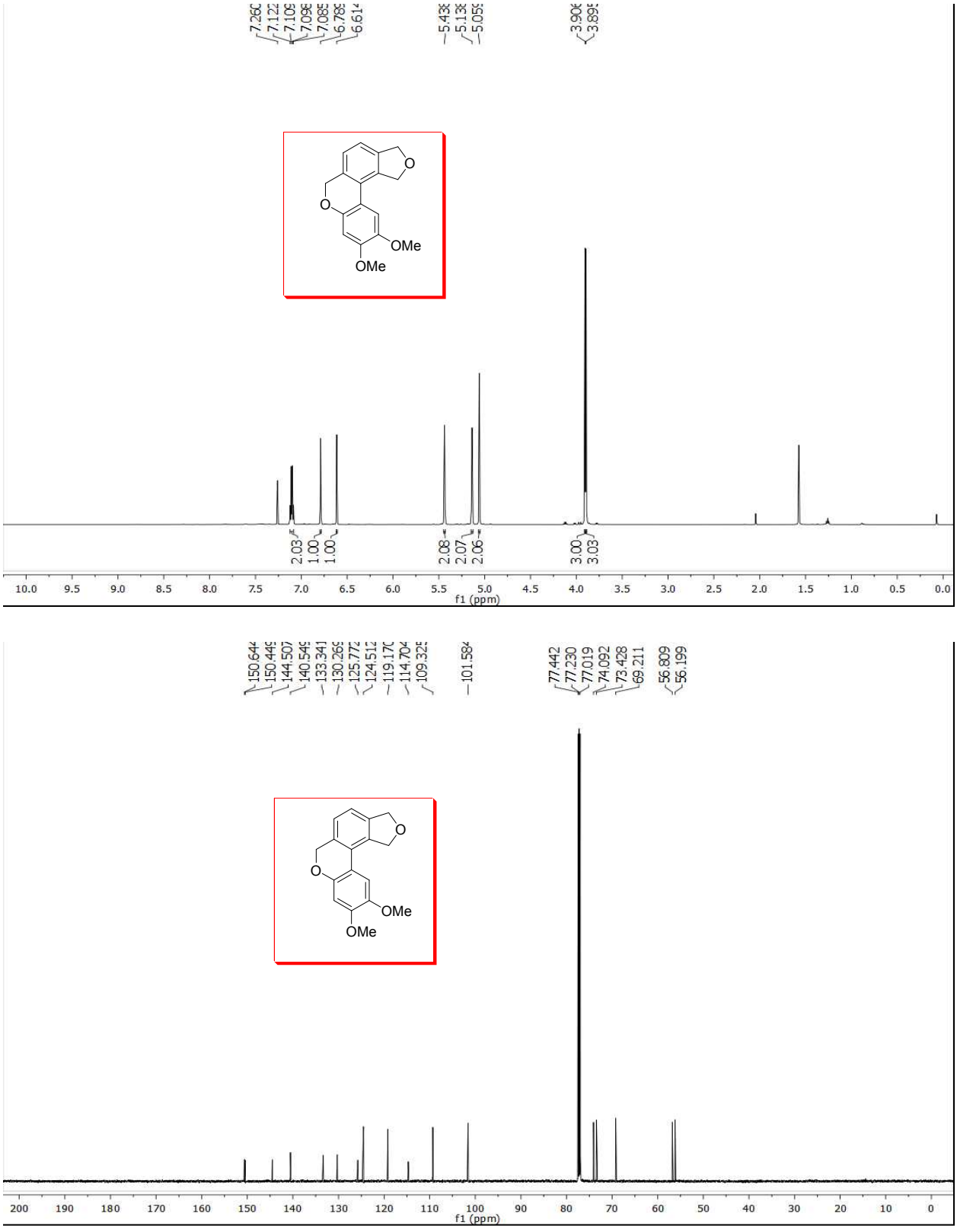


Figure S39. ^{1}H and ^{13}C NMR spectra of **9d** in $CDCl_3$

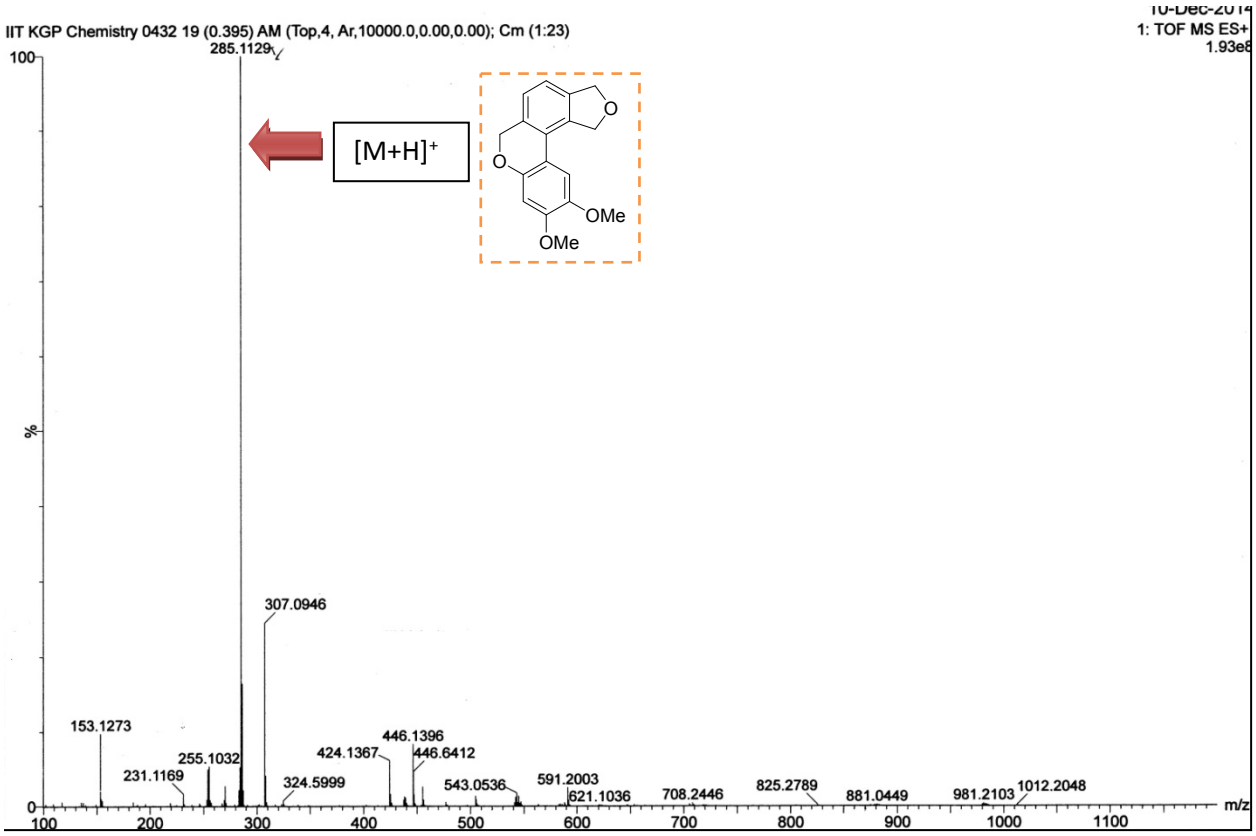


Figure S40. HRMS spectrum of **9d**

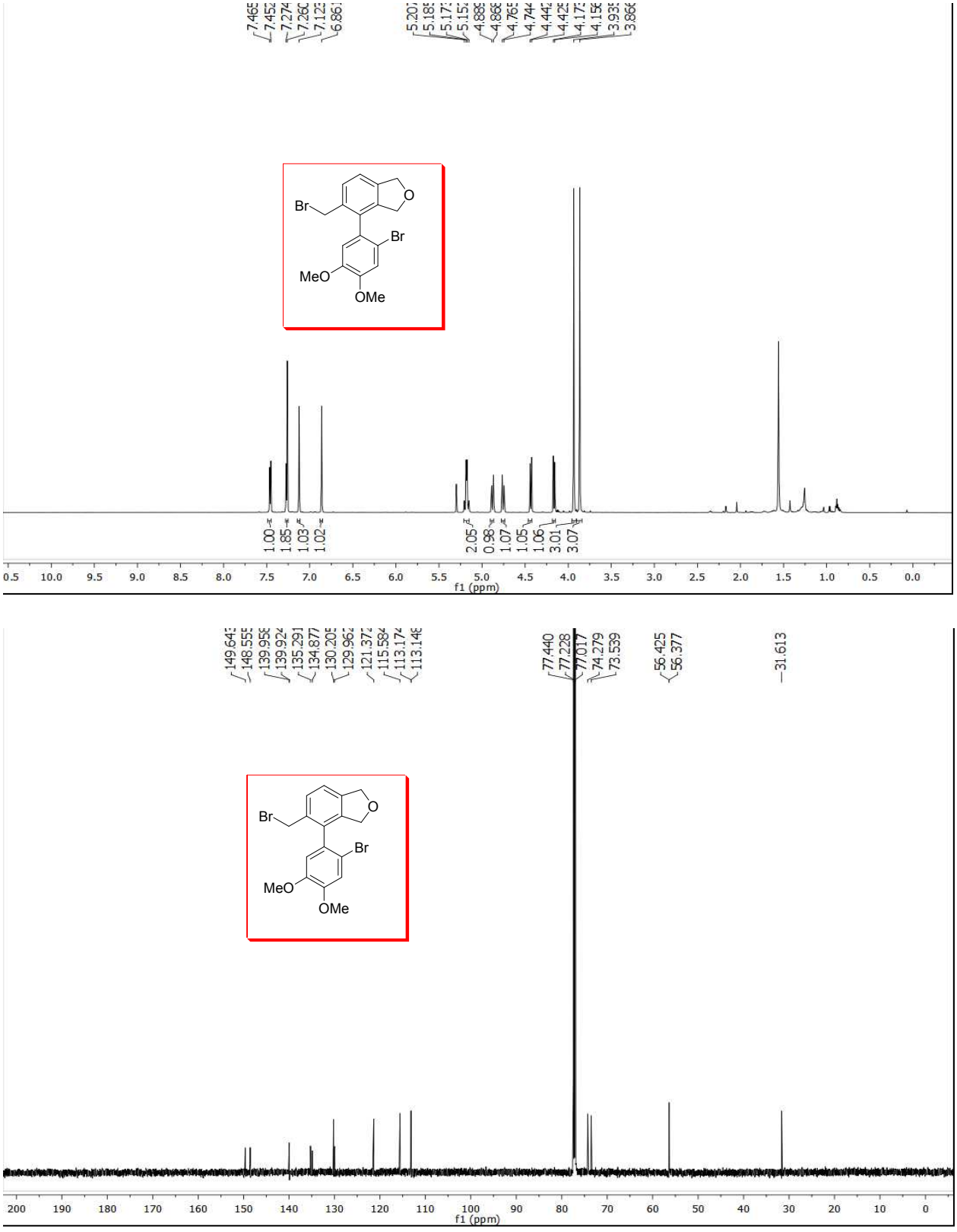


Figure S41. ^{1}H and ^{13}C NMR spectra of **10d** in $CDCl_3$

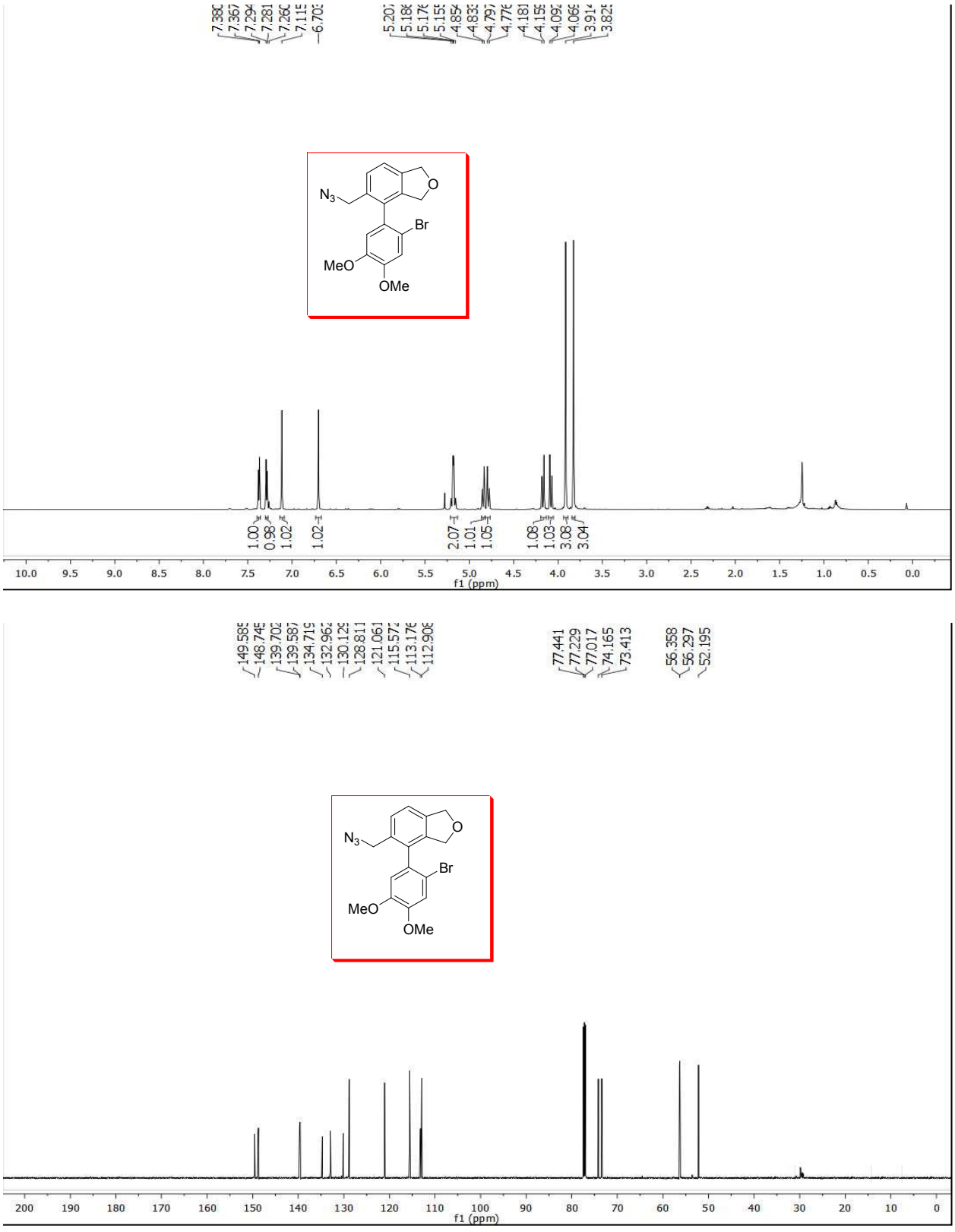
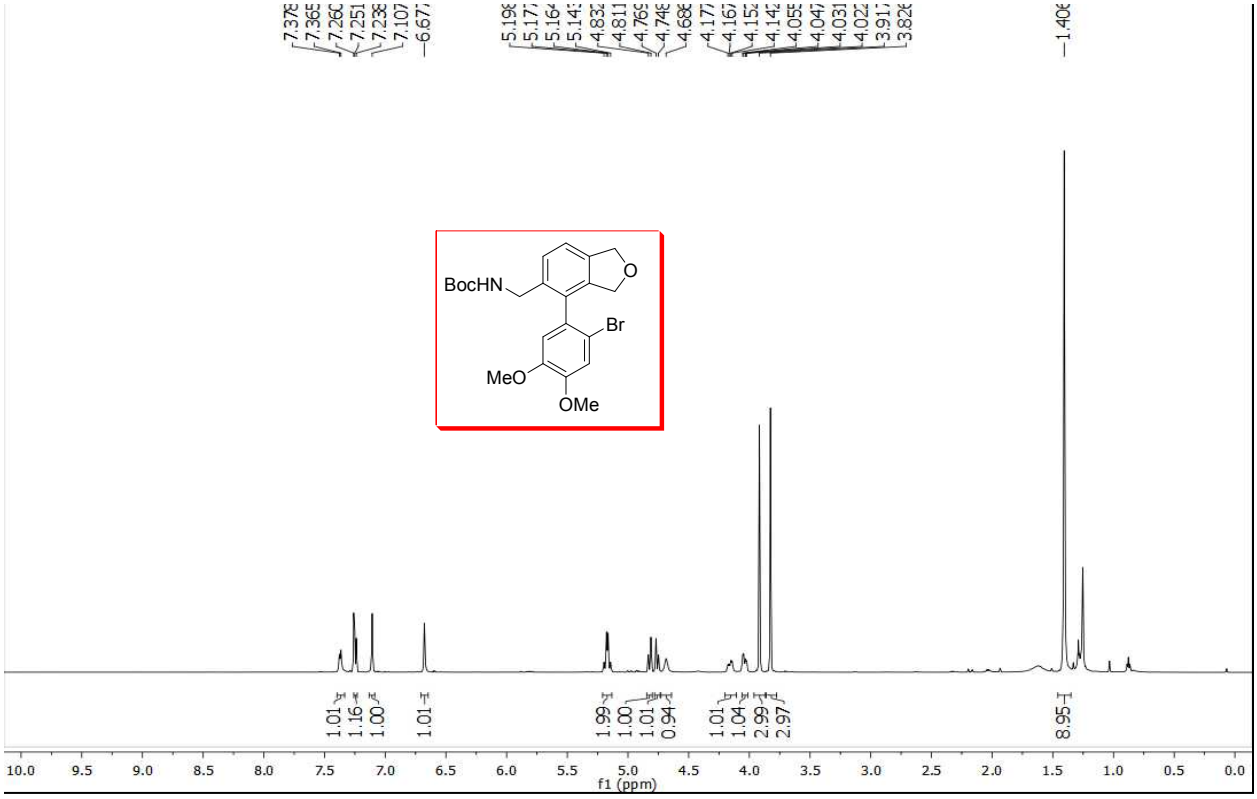


Figure S42. ^{1}H and ^{13}C NMR spectra of **11d** in $CDCl_3$



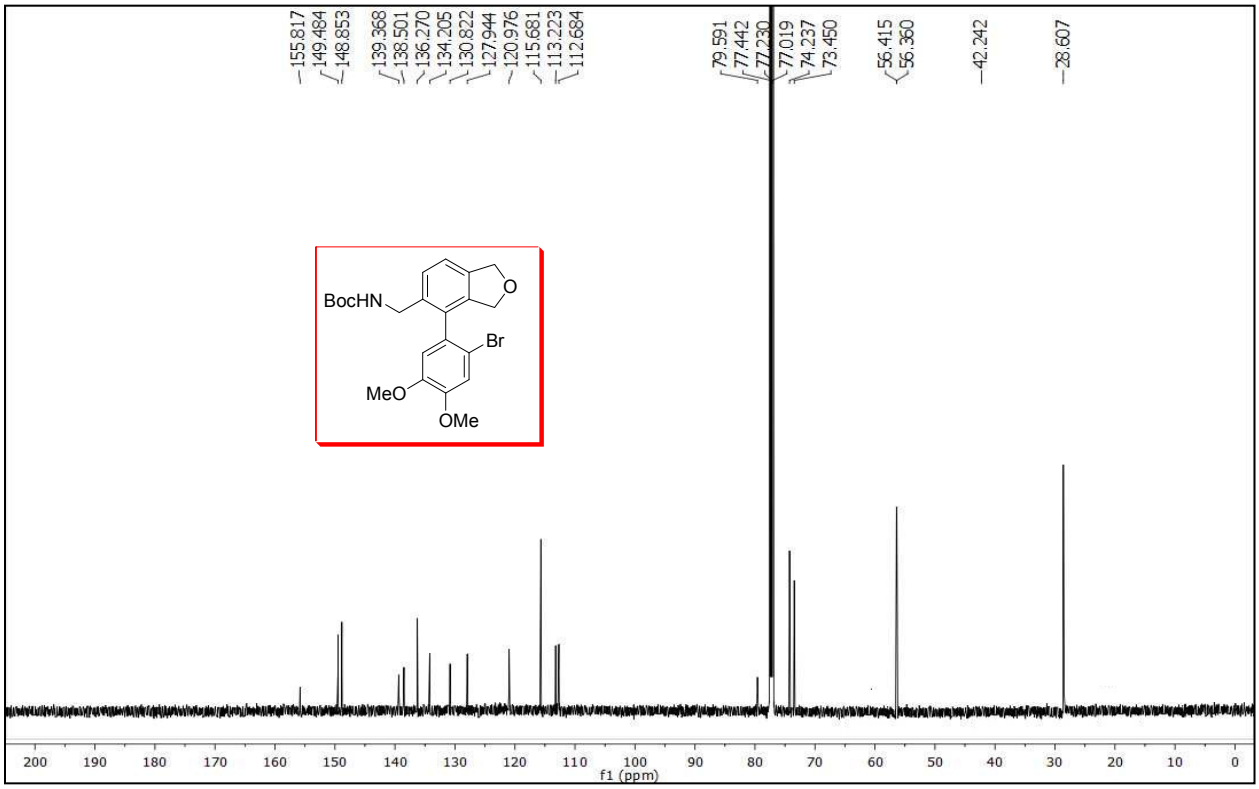


Figure S43. ^{1}H and ^{13}C NMR spectra of **12d** in $CDCl_3$

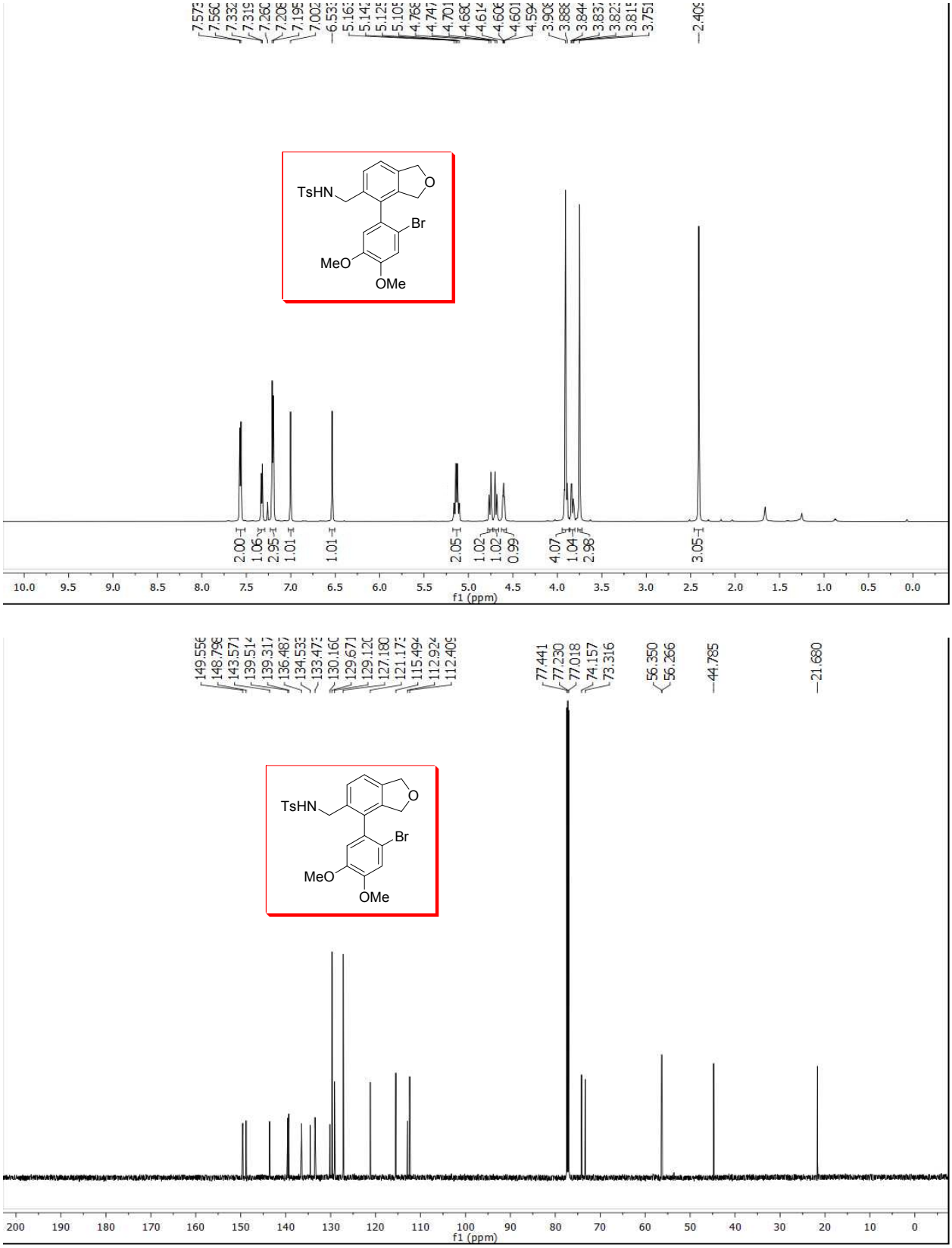


Figure S44. ^{1}H and ^{13}C NMR spectra of **13d** in $CDCl_3$

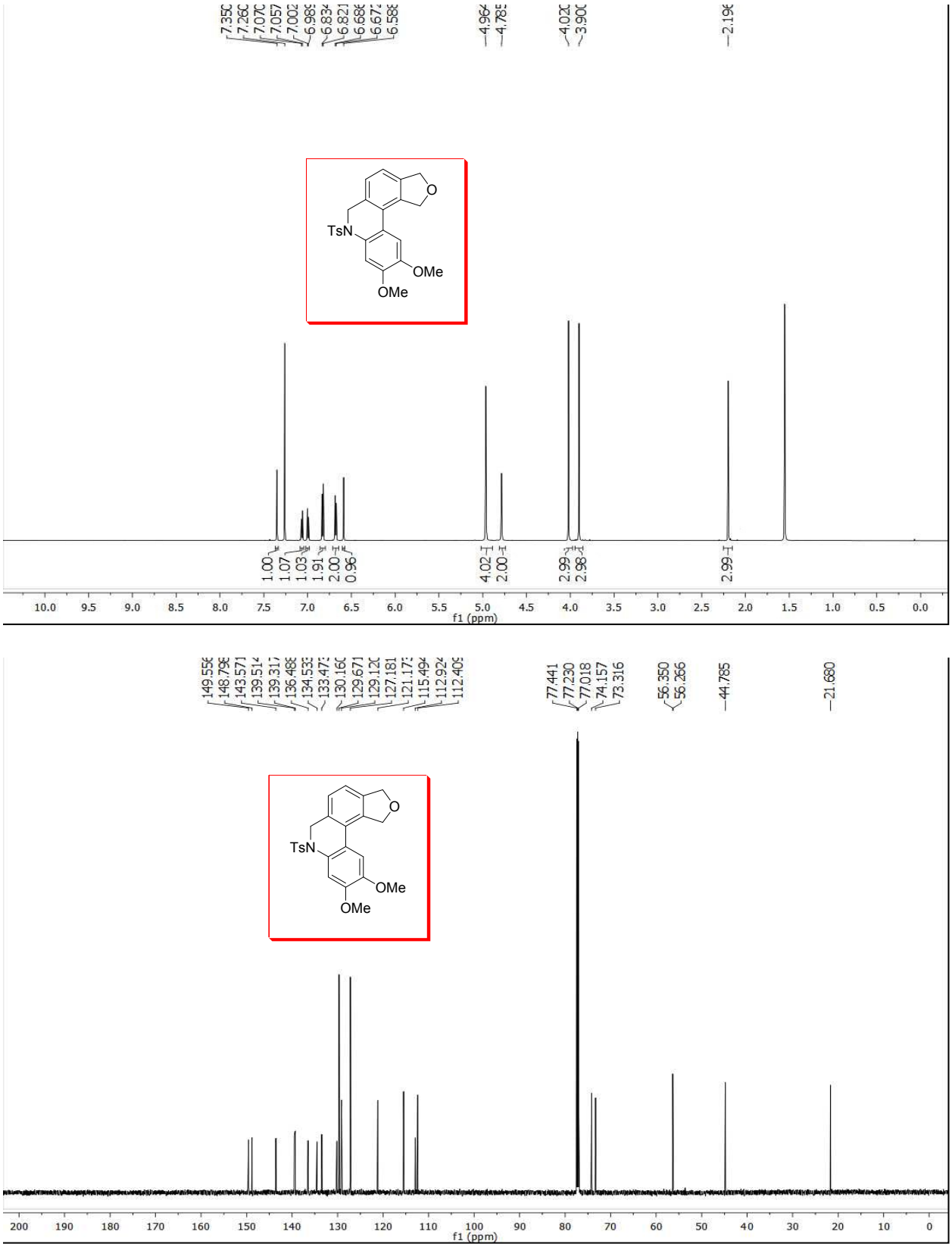


Figure S45. ^{1}H and ^{13}C NMR spectra of **14d** in $CDCl_3$

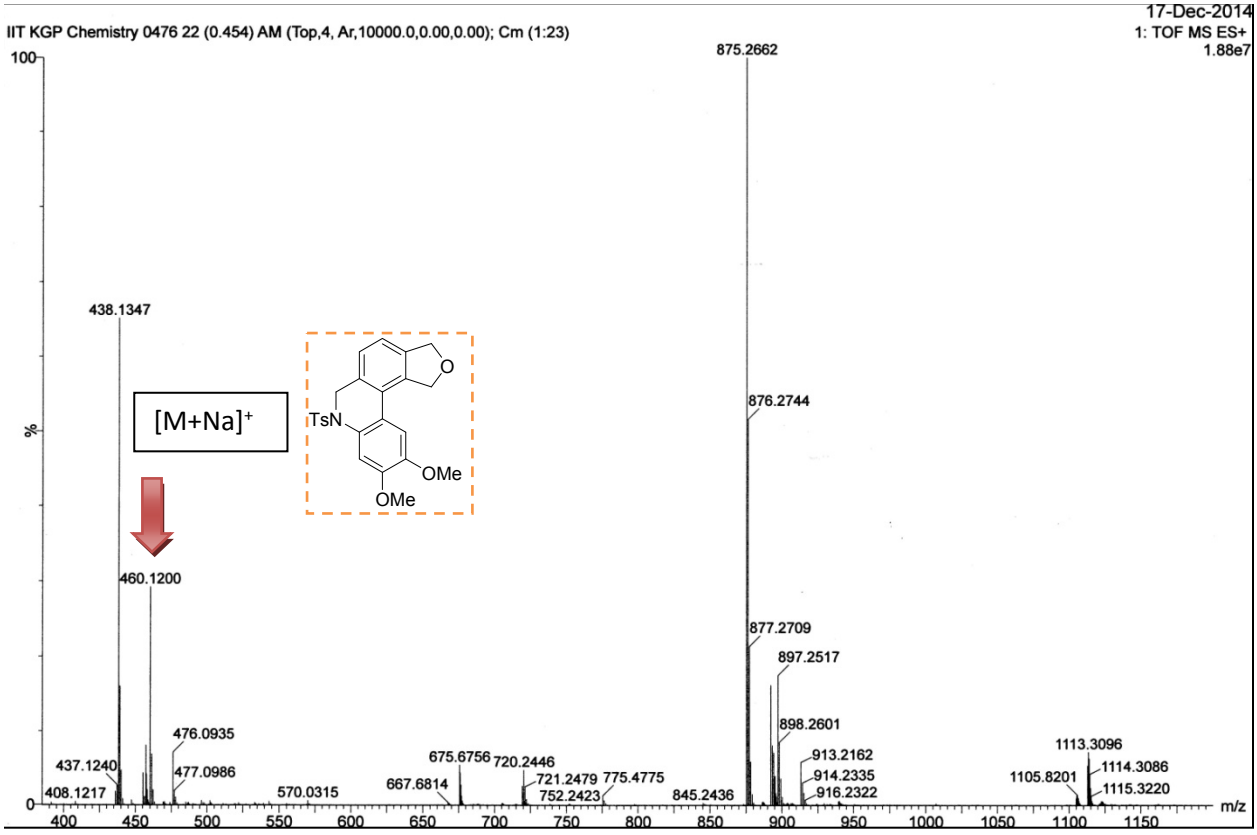


Figure S46. HRMS spectrum of **14d**

Crystallographic data:

Compounds	**14c**	**14d**	**9d**
CCDC No.	**1041545**	**1041544**	**1041542**
Formula	$C_{23}H_{21}NO_4S$	$C_{24}H_{23}NO_5S$	$C_{17}H_{16}O_4$
F.W.	407.47	437.49	284.30
crystal system	monoclinic	monoclinic	Triclinic
space group	*P* 21/*c*	*P* 21/*c*	*P*-1
Crystal color	White	White	White
Crystal size/mm^3	0.34x0.26x0.15	0.31x0.23x0.17	0.30x0.23x0.16
a/ Å	8.508(2)	8.243(2)	7.541(4)
b/ Å	12.301(3)	19.740(6)	8.769(5)
c/ Å	20.778(4)	12.654(4)	10.636(6)
α/ deg	90.00	90.00	98.434(18)
β/ deg	114.172(7)	103.100(8)	106.104(18)
γ/ deg	90.00	90.00	93.644(18)
V/ Å^3	1983.9(8)	2005.4(10)	664.4(6)
Z	4	4	2
D_c/g cm^{-3}	1.364	1.449	1.421
μ (mm^{-1})	0.193	0.200	0.101
F(000)	856	920	
T/K	293(2)	293(2)	293(2)
Total reflns	22705	22879	7588
R(int)	0.0383	0.0684	0.0707
Unique reflns	3489	3514	2327
Observed reflns	2694	2787	1431
Parameters	264	283	192
R_1; wR_2 ($I > 2\sigma(I)$)	0.0407, 0.0751	0.0479, 0.1028	0.0688, 0.1641
GOF (F^2)	2.111	1.827	1.386
Largest diff peak and hole (e Å^{-3})	0.265, -0.353	0.427, -0.493	0.346, -0.343

ORTEP diagram of the obtained crystals :

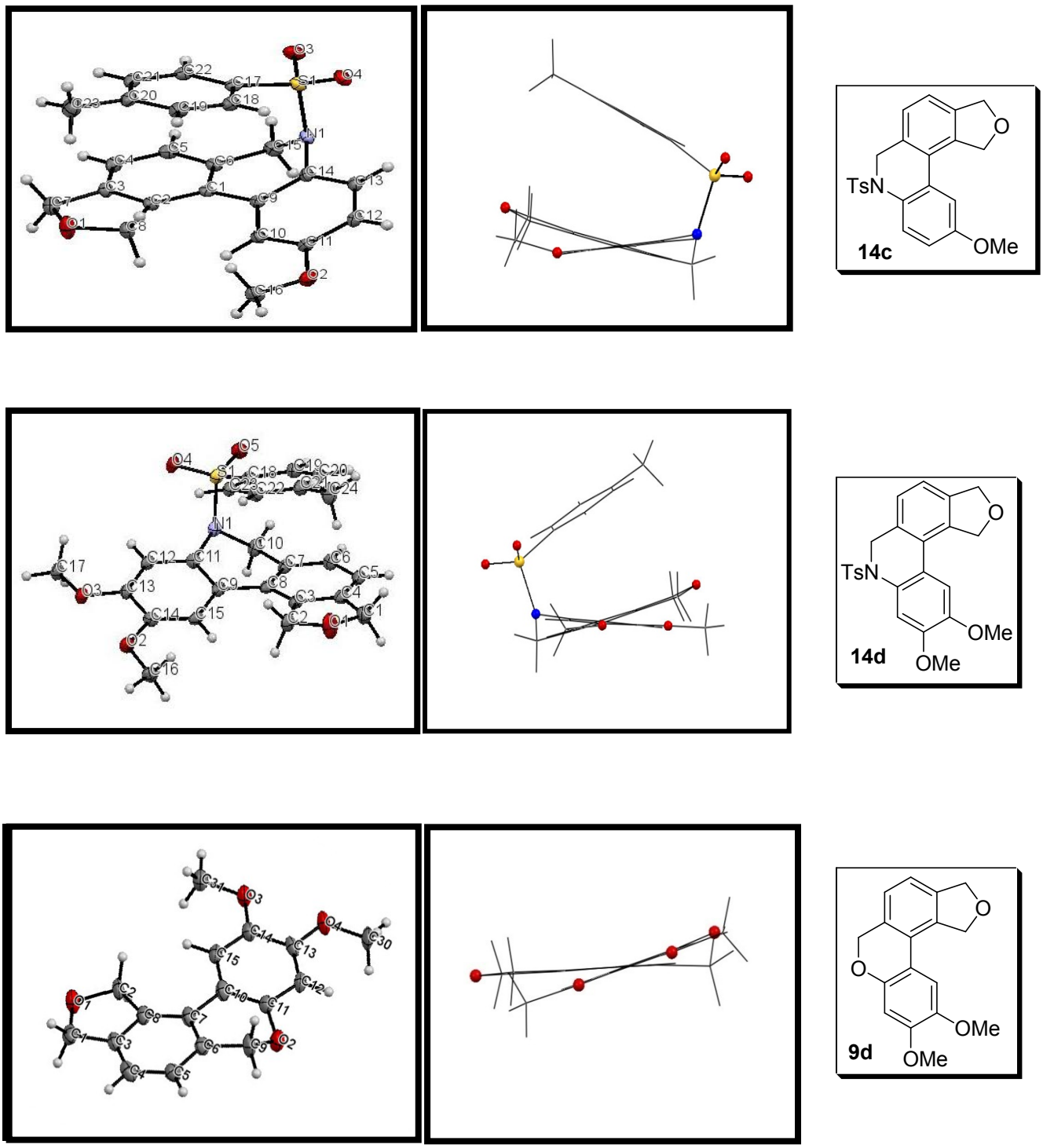


Figure S47

DNA binding studies:

Methods

Ethidium Bromide Displacement Assay:

Six µg (6 µl of 1 mg/ml solution, [DNA base pair]=3.0 µM)[1] of DNA was prepared and diluted in Tris-Cl buffer (pH 7.2) containing 40 mM NaCl. Ethidium bromide (EtBr) displacement fluorescence assay[2] was employed to determine whether compounds are intercalates to DNA or not. Fluorescence emission spectra (λ_{max} = 600 nm, excitation wavelength 546 nm) were obtained at 30 °C on a Beckman fluorescence spectrophotometer. The assays were performed using different concentrations (0-2.0 µM) of compounds in 3 mL of buffer. F/F_0 is plotted along with Y axis against the concentrations of compounds where F_0 and F are the fluorescence intensities of EB-DNA complex in presence and absence of compounds, respectively.

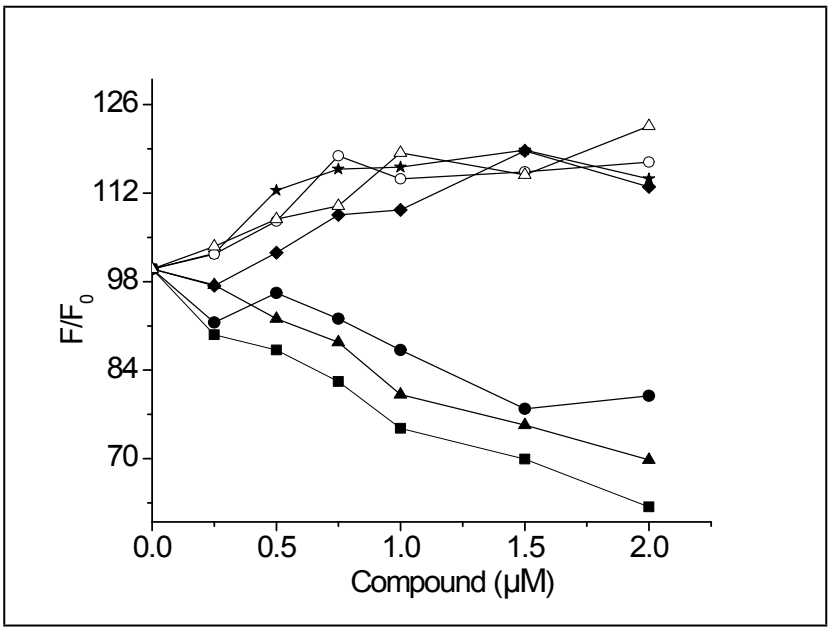


Figure S48

Figure S48: Relative fluorescence intensity measurement after EtBr replacement induced by synthesized compounds. A fixed concentration of DNA (6 µl of 1 mg/ mL) and EtBr (3 µl of 0.5 mg/ mL) was used to make a final volume of 3 mL solution. Fluorescence emission spectra (λ_{max} = 600 nm, excitation wavelength 546 nm) were recorded from each concentrations (0-2.0 µM) of compounds. The relative fluorescence intensities are plotted as line graph show **9a** (closed square); **9b** (closed circle); **9c** (closed triangle); **9d** (closed rhombus); **14a** (closed star); **14c** (open circle) and **14d** (open triangle).

UV-Vis spectroscopy:

A Shimadzu Pharmaspec (Shimadzu Corporation, Kyoto, Japan) was used for absorption spectral studies. For this purpose, a constant concentration (3.3×10^{-3} μM) of the DNA was treated with increasing concentration of the compounds in one cm path length matched quartz cells. The value of the binding constant (K) was obtained from spectrophotometric titration considering the DNA absorption at 260 nm according to equation $1/A\text{-}A_0 = 1/A\infty\text{-}A_0 + 1/ K(A\infty\text{-}A_0) \times 1/ [\text{compound}]^3$ where A_0 is the absorbance of DNA at 260 nm in the absence of compounds, A∞ is the final absorbance of compound-DNA and A is the recorded absorbance at different compound concentrations. The linearity of the double reciprocal plot of $1/(A\text{-}A_0)$ versus 1/[compound] and the binding constant (K) can be estimated from the ratio of intercept to the slope[4]. The non-linear binding isotherms are also observed which was also fitted to a theoretical curve drawn according to the excluded site model of McGhee and von Hippel[5].

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