Photochemical & Photobiological Sciences

Electronic Supplementary Information (ESI)

Photolabile acetals as profragrances: the effect of structural modifications on the light-induced release of volatile aldehydes on cotton

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General

Instrumentation for the spectroscopic characterisation of compounds

Nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance III 400, 500 or 600 spectrometers; the chemical displacements δ are indicated in ppm with respect to $Si(CH_3)_4$ (TMS) as the internal standard. Multiplets indicated together with the chemical shifts obtained from decoupled ^{13}C NMR spectra were determined by distortionless enhancement of polarization transfer (DEPT) measurements; two sets of spectra (DEPT-90 and DEPT-135, data not shown) were systematically recorded. Ultraviolet/Visible (UV/Vis) absorption spectra were measured on a Perkin Elmer Lambda 14 spectrometer, with λ indicated in nm (ε in L mol^{-1} cm^{-1}) and sh = shoulder. Infrared (IR) spectra were measured on a Perkin Elmer 1600 FTIR spectrometer, with $\tilde{\nu}_{max}$ given in cm^{-1} and the intensities of the IR bands indicated as strong (*s*), medium (*m*) or weak (*w*) and br. = broad band. High resolution mass spectra (HRMS) were recorded on a Waters Acquity I-Class ultra-performance liquid chromatography (UPLC) system composed of a binary solvent manager (UPIBSM), a sample manager with fixed loop (UPISMFL, 10 µL), a column manager (UPCMA) and a PDA detector (UPPDATC). Samples were eluted at 0.5 mL min^{-1} from a Waters Acquity UPLC® BEH C18 column (1.7 µm, 50 mm × 2.1 mm inner diameter), thermostatted at 30.0°C ± 0.1°C, with a gradient of water/acetonitrile (both containing 0.1% of formic acid) at 98:2 for 1 min, then to 0:100 in 5 min. Electrospray ionisation (ESI) mass spectra were recorded on a Thermo Fisher Scientific Q-Exactive system (0726020) equipped with an H-ESI probe source in the full scan mode (m/z from 100 to 1500) with the H-ESI probe source in the positive or negative mode, depending on the ionization potential of the molecule, and at a spray voltage of 3500 V with a resolution of 70'000. Direct solvent injections were performed at a flow rate of 0.5 mL min^{-1} with acetonitrile (containing 0.1% of formic acid) for 5 min, using the same setup of the Q-Exactive system.

Instrumentation and conditions for dynamic headspace analysis

Tenax® cartridges (each filled with 100 mg of Tenax® TA [= poly(2,6-diphenyl-*p*-phenylene oxide)] adsorbent resin) were thermally desorbed on a Perkin Elmer TurboMatrix ATD desorber, connected to an Agilent Technologies 7890A gas chromatograph (GC) equipped with a HP-1 capillary column (30 m, 0.32 mm inner diameter, film thickness 0.25 µm) and a flame ionisation detector. The volatiles were eluted with a one-step temperature gradient from 60°C to 200°C at 15°C min^{-1} using He as the carrier gas. The thermodesorber was operated at a pressure of 70 kPa. Cartridges were heated at 240°C for 5 min. The volatiles were desorbed at 20 mL min^{-1} and trapped at -30°C. The trap was then heated to 240°C (at 40°C s^{-1}) and held for 2 min. The transfer tube to the GC was heated at 200°C and an outlet split of 30 mL min^{-1} was used.

Quantitative headspace concentrations (in ng L^{-1} of air) were determined by external standard calibration. Ethanol solutions (0.2 µL) of the aldehydes to be released at different concentrations were directly injected onto clean Tenax® cartridges, which were immediately desorbed and analysed as described above.

Table S1 Dynamic headspace concentrations (with standard deviations) for the light-induced release of 10-undecenal from profragrances **1–12** and **25** as compared to unmodified 10-undecenal (reference) on dry cotton (indirect deposition) after line drying for 1 day (average values of at least two measurements)

10-Undecenal released from	Measured headspace concentrations of 10-undecenal with standard deviations (in parentheses) [ng L^{-1} of air] on dry cotton after drying for 1 day and sampling for					
	25 min	55 min	85 min	115 min	145 min	175 min
1a	2.5 (±3.2)	4.3 (±0.6)	5.2 (±2.3)	3.2 (±2.8)	4.7 (±0.4)	2.6 (±0.8)
2a	2.8 (±4.9)	2.5 (±2.6)	2.4 (±2.1)	3.0 (±2.3)	2.9 (±2.5)	2.4 (±1.6)
3a	4.2 (±2.5)	6.9 (±3.3)	8.9 (±3.1)	10.8 (±4.4)	12.0 (±4.2)	11.2 (±2.8)
4a	545.3 (±296.4)	837.1 (±340.4)	854.9 (±263.5)	849.6 (±317.7)	750.6 (±359.6)	650.1 (±387.2)
5a	325.3 (±25.5)	477.0 (±18.4)	515.1 (±9.1)	458.6 (±54.2)	416.6 (±92.4)	344.7 (±64.3)
6a	250.8 (±72.4)	403.1 (±69.3)	413.2 (±14.7)	399.4 (±3.9)	366.0 (±3.5)	345.9 (±23.4)
7a	294.0 (±109.3)	520.0 (±100.5)	587.6 (±56.8)	524.2 (±12.1)	466.4 (±44.9)	397.6 (±54.1)
8a	10.7 (±2.8)	20.9 (±4.5)	19.5 (±13.7)	24.5 (±6.0)	25.8 (±0.1)	21.6 (±1.2)
9a	27.3 (±41.7)	122.5 (±97.2)	161.9 (±115.2)	181.4 (±131.6)	188.9 (±124.4)	186.7 (±121.5)
10a	74.8 (±54.1)	129.7 (±87.5)	141.6 (±78.3)	133.7 (±63.3)	123.5 (±44.7)	111.4 (±32.0)
11a	7.5 (±8.2)	10.8 (±5.3)	12.5 (±8.7)	14.9 (±10.0)	16.1 (±11.5)	14.9 (±11.3)
12a	79.2 (±68.6)	148.8 (±118.0)	191.3 (±138.3)	186.1 (±112.8)	187.9 (±107.2)	205.4 (±128.4)
25	148.1 (±23.9)	235.9 (±43.9)	227.6 (±34.1)	217.2 (±14.5)	252.3 (±22.6)	172.4 (±21.5)
Reference	2.9 (±2.7)	5.5 (±4.8)	7.6 (±5.6)	9.1 (±7.6)	8.6 (±5.2)	9.4 (±6.2)

Table S2 Amount of remaining acetal (**7a–12a**) or 2-oxo-2-phenylacetate (**25**) after photoirradiation in undegassed deuterated acetonitrile with a xenon lamp. Data from quantitative ^{1}H NMR analysis based on the disappearance of the proton at C(2) using DMSO as the internal standard.

Irradiated compound	Amount of remaining profragrance[a] after photoirradiation for				
	30 min	60 min	90 min	120 min	150 min
7a	55.2%	34.2%	22.3%	12.0%	11.3%
8a	96.4%	92.4%	89.4%	87.9%	87.6%
9a	88.8%	80.6%	72.6%	66.3%	61.9%
10a	98.5%	95.7%	94.0%	88.8%	87.2%
11a	98.7%	98.1%	96.5%	93.8%	90.3%
12a	87.6%	79.5%	70.0%	62.7%	56.7%
25	23.9%	3.8%	0.0%	0.0%	0.1%

[a] the ^{1}H NMR spectrum recorded before irradiation was taken as corresponding to 100%.

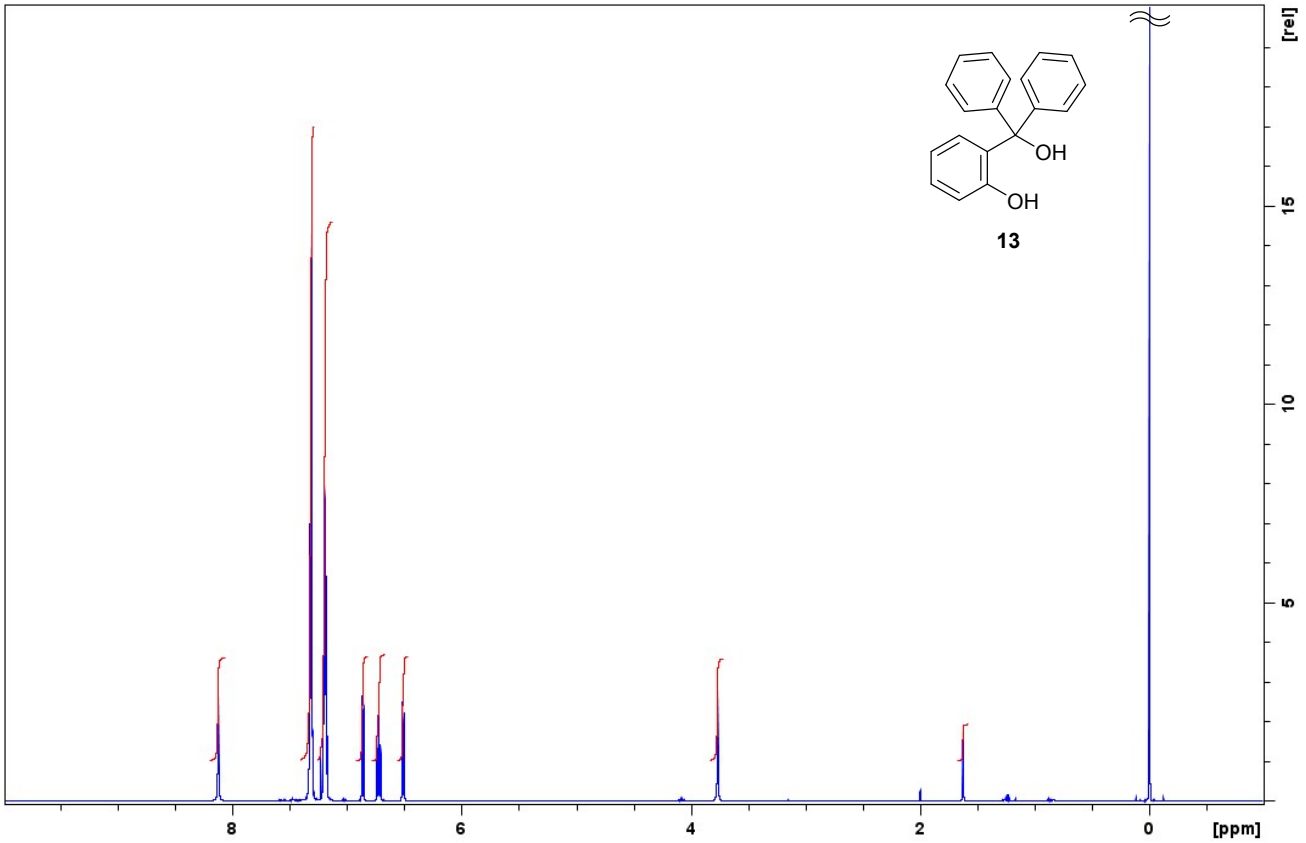
Table S3 Dynamic headspace concentrations (with standard deviations) for the light-induced release of (±)-6-methoxy-2,6-dimethylheptanal from profragrances **2b–4b**, of (±)-3-phenylbutanal from profragrances **3c** and **4c** and of (±)-3,5,5-trimethylhexanal from profragrance **4d** as compared to the corresponding unmodified reference aldehyde on dry cotton (indirect deposition) after line drying for 1 day (average values of at least two measurements)

(±)-6-methoxy-2,6-dimethylheptanal released from	Measured headspace concentrations of (±)-6-methoxy-2,6-dimethylheptanal with standard deviations (in parentheses) [ng L^{-1} of air] on dry cotton after drying for 1 day and sampling for					
	25 min	55 min	85 min	115 min	145 min	175 min
2b	3.1[a]	4.5[a]	4.7[a]	4.3[a]	4.2[a]	3.9[a]
3b	12.2 (±6.7)	19.6 (±11.4)	21.1 (±10.4)	23.0 (±11.3)	23.7 (±11.0)	24.4 (±11.9)
4b	311.2 (±123.2)	342.9 (±89.6)	275.1 (±54.0)	232.1 (±41.1)	196.6 (±30.5)	149.4 (±33.4)
Reference	0.9 (±0.9)	1.7 (±1.7)	2.1 (±2.2)	2.1 (±2.2)	2.0 (±2.1)	1.7 (±1.9)
(±)-3-phenylbutanal released from	Measured headspace concentrations of (±)-3-phenylbutanal with standard deviations (in parentheses) [ng L^{-1} of air] on dry cotton after drying for 1 day and sampling for					
	25 min	55 min	85 min	115 min	145 min	175 min
3c	0.9 (±0.0)	2.1 (±1.4)	3.0 (±1.4)	3.6 (±1.5)	4.4 (±2.0)	4.7 (±1.6)
4c	121.9 (±48.1)	159.4 (±62.0)	148.1 (±63.3)	128.0 (±47.5)	109.3 (±36.5)	90.8 (±30.0)
Reference	2.0 (±1.3)	2.9 (±1.5)	3.5 (±1.8)	3.9 (±1.9)	4.0 (±2.2)	3.9 (±2.0)
(±)-3,5,5-trimethylhexanal released from	Measured headspace concentrations of (±)-3,5,5-trimethylhexanal with standard deviations (in parentheses) [ng L^{-1} of air] on dry cotton after drying for 1 day and sampling for					
	25 min	55 min	85 min	115 min	145 min	175 min
4d	1038.5 (±118.4)	579.5 (±37.7)	415.6 (±8.4)	327.9 (±37.9)	279.7 (±25.6)	237.0 (±27.4)
Reference	1.6 (±0.1)	2.8 (±0.4)	2.8 (±0.5)	3.2 (±0.1)	3.6 (±0.4)	5.0 (±2.8)

[a] single measurement.

Table S4 Dynamic headspace concentrations (with standard deviations) for the light-induced release of 10-undecenal from profragrances **1a–12a** and **25** as compared to unmodified 10-undecenal (reference) on dry cotton (direct deposition) after line drying for 1 day (average values of at least two measurements)

10-Undecenal released from	Measured headspace concentrations of 10-undecenal with standard deviations (in parentheses) [ng L^{-1} of air] on dry cotton after drying for 1 day and sampling for					
	25 min	55 min	85 min	115 min	145 min	175 min
1a	7.5 (±9.0)	4.6 (±3.1)	4.6 (±1.5)	5.7 (±1.1)	6.0 (±1.2)	3.6 (±0.3)
2a	8.7 (±12.2)	24.4 (±0.7)	28.2 (±1.1)	29.1 (±2.1)	27.1 (±0.5)	25.6 (±0.2)
3a	13.7 (±10.1)	24.5 (±11.0)	41.3 (±5.8)	43.9 (±11.8)	49.2 (±10.4)	58.1 (±14.3)
4a	2998.5 (±1461.6)	7561.4 (±3172.4)	9888.8 (±3408.0)	10041.6 (±2728.8)	9447.3 (±1802.8)	8790.0 (±1189.1)
5a	2250.7 (±146.0)	5441.9 (±540.9)	7230.6 (±90.3)	6123.9 (±980.4)	5268.1 (±1195.2)	4722.4 (±1534.1)
6a	1410.7 (±468.3)	4286.7 (±437.0)	6363.7 (±469.7)	7364.9 (±202.2)	7491.0 (±150.8)	7483.5 (±487.3)
7a	3139.5 (±3073.9)	6907.0 (±5089.9)	8599.0 (±4504.5)	9027.5 (±3784.6)	8541.9 (±2977.2)	7349.8 (±2076.4)
8a	74.6 (±16.1)	149.7 (±23.7)	206.9 (±6.6)	218.1 (±6.1)	226.3 (±17.4)	211.0 (±18.8)
9a	397.2 (±391.1)	1108.0 (±980.6)	1396.0 (±1077.7)	1696.4 (±1170.3)	1723.3 (±1070.7)	1697.0 (±1000.8)
10a	495.4 (±225.1)	952.4 (±436.4)	1014.1 (±422.4)	910.4 (±294.1)	798.5 (±218.3)	724.3 (±148.6)
11a	18.7 (±6.1)	59.2 (±19.7)	92.4 (±38.4)	110.7 (±33.7)	107.3 (±28.9)	103.8 (±27.2)
12a	888.5 (±585.7)	2153.2 (±1564.4)	2558.2 (±1739.8)	2496.6 (±1555.7)	2006.3 (±1875.0)	1889.1 (±1686.8)
25	772.8 (±64.8)	1108.7 (±69.4)	1169.0 (±106.4)	1078.9 (±137.4)	971.6 (±122.3)	894.0 (±72.1)
Reference	89.4 (±127.1)	207.5 (±326.5)	451.3 (±737.2)	623.2 (±960.1)	650.6 (±960.0)	603.9 (±866.7)



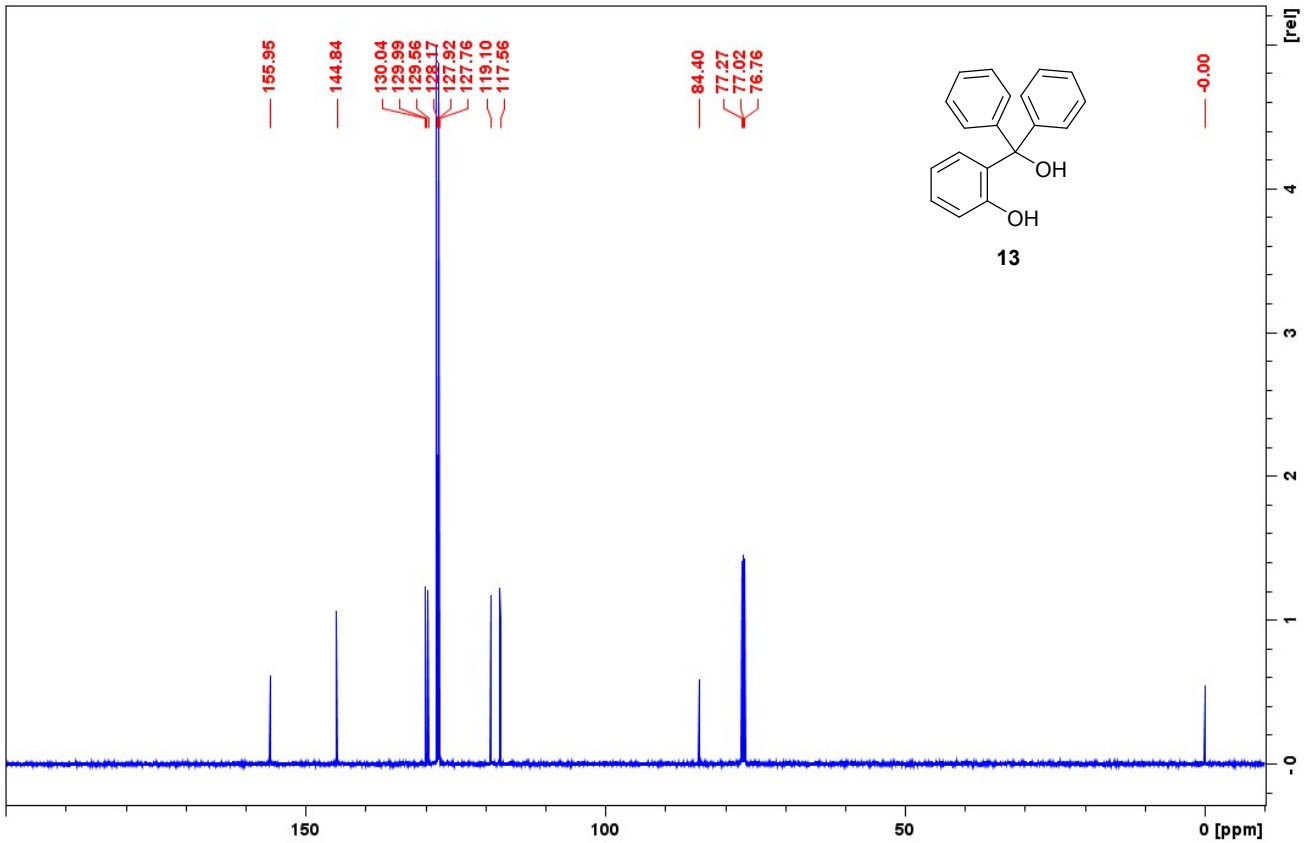


Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **13** in $CDCl_3$.

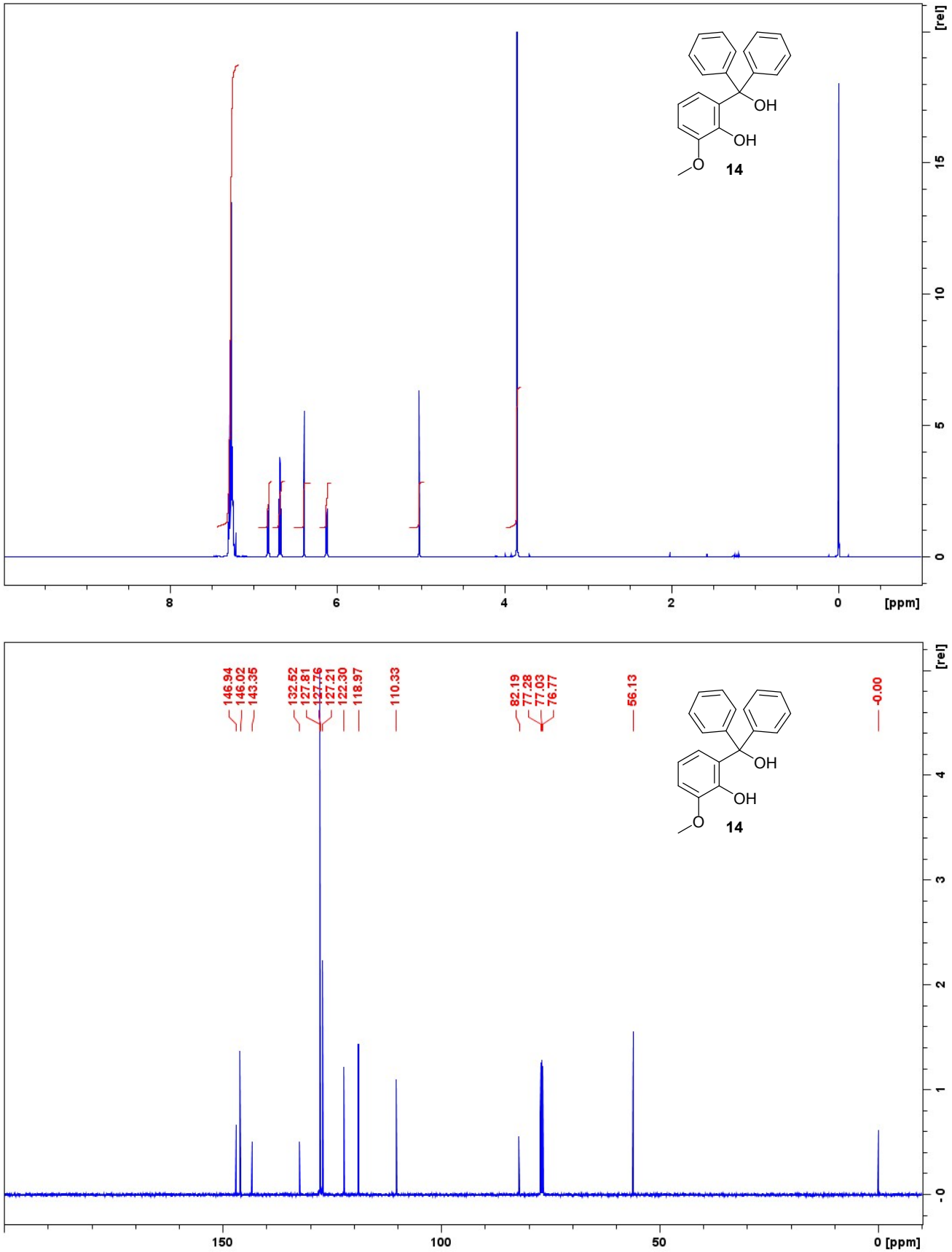


Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **14** in $CDCl_3$.

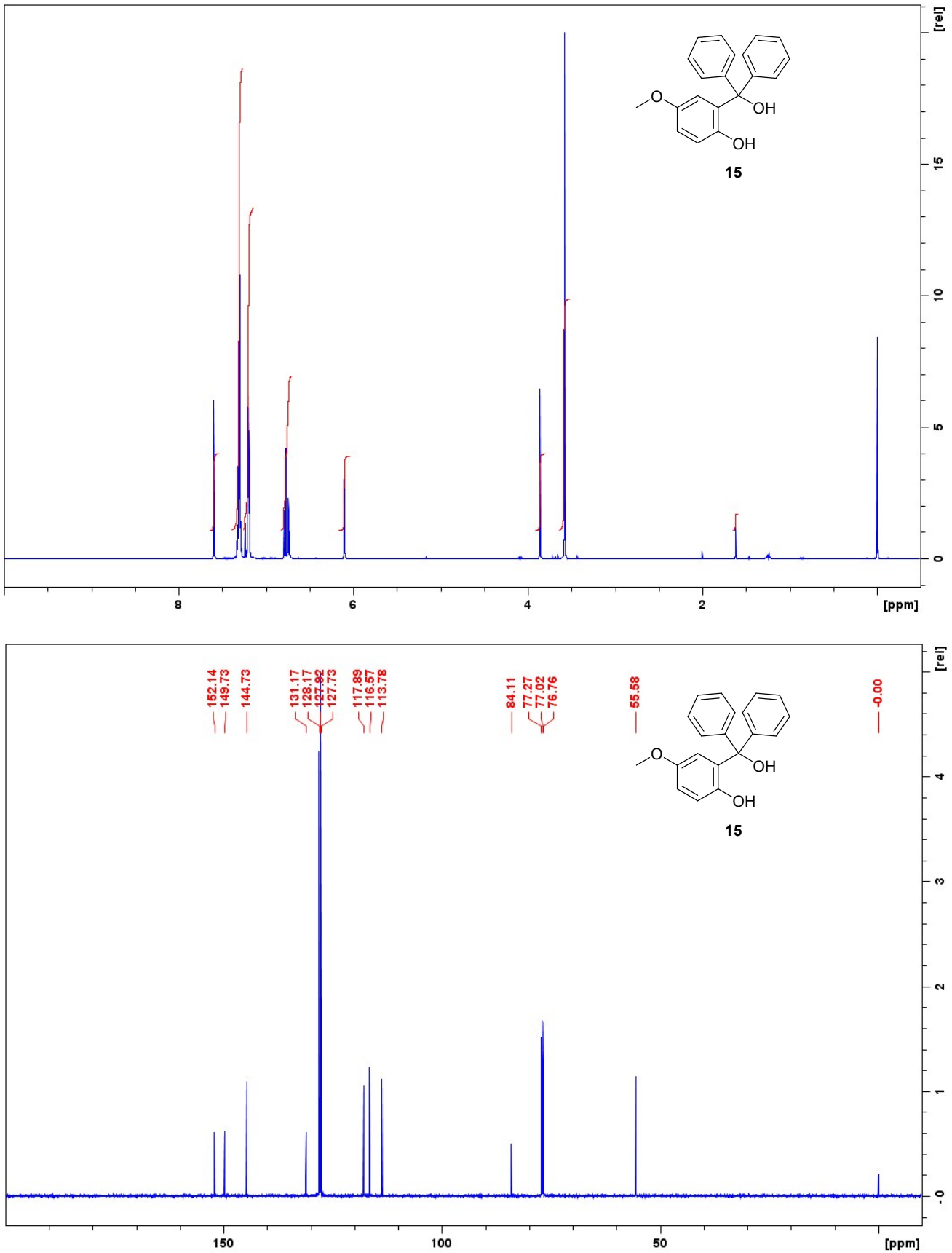


Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **15** in $CDCl_3$.

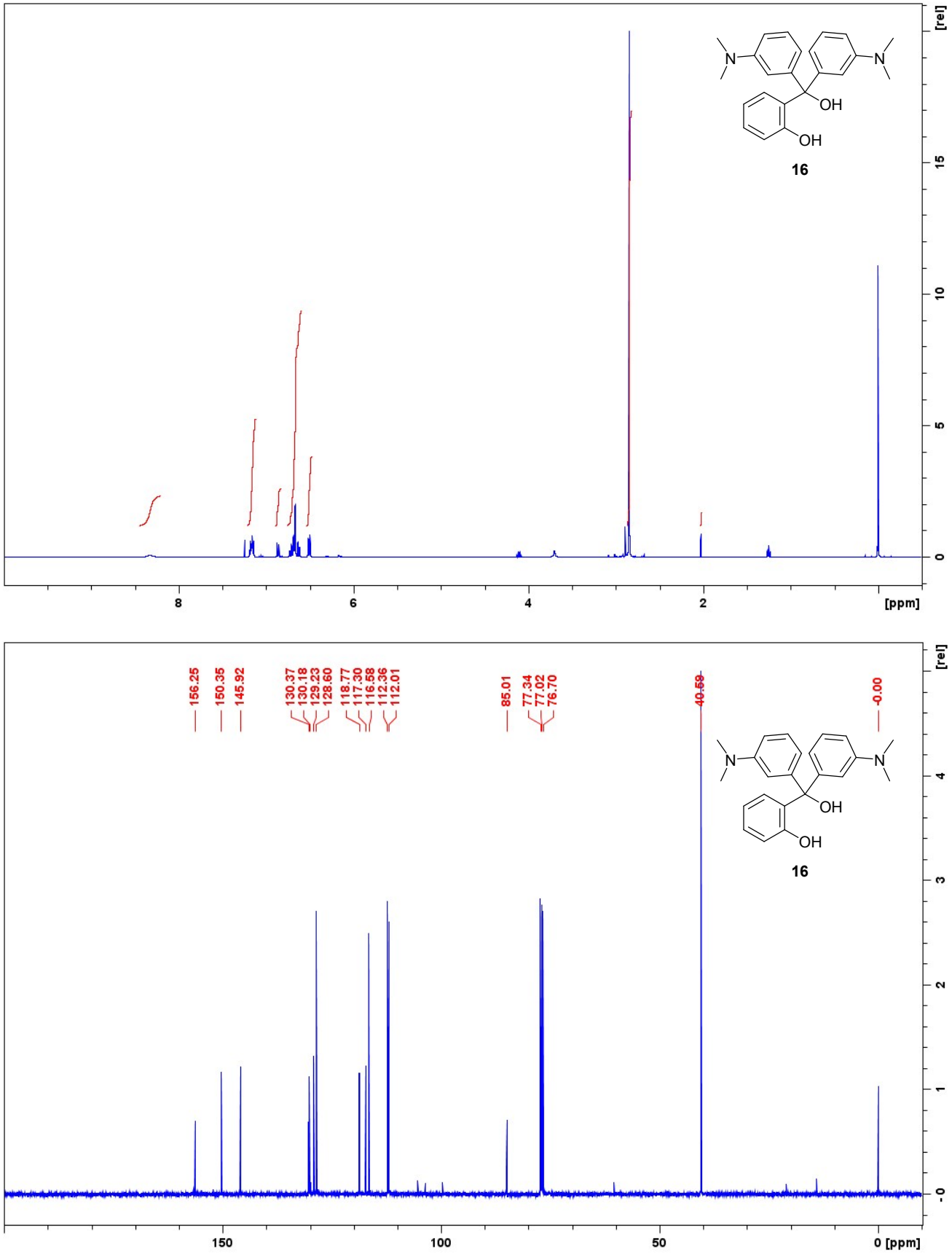


Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **16** in $CDCl_3$.

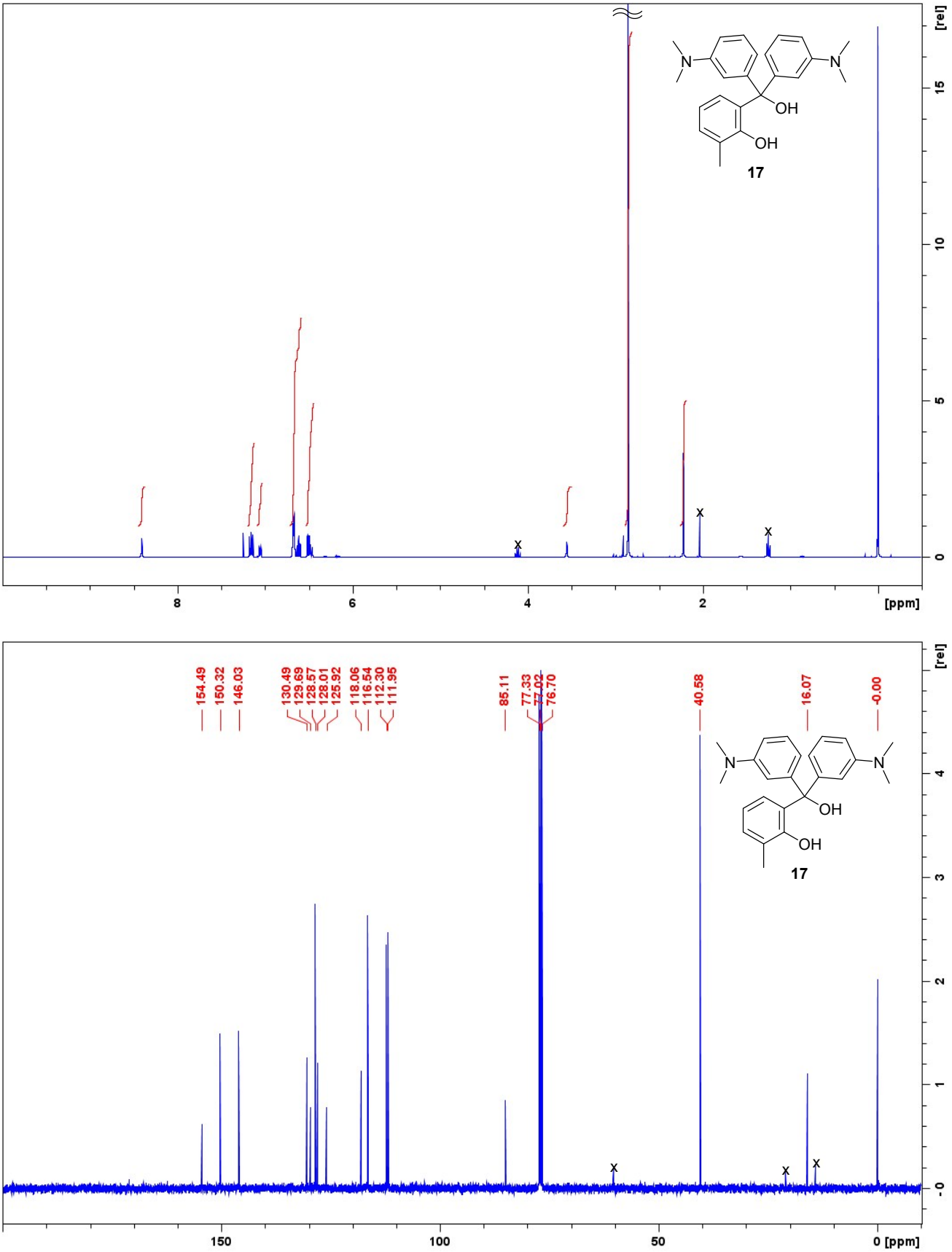


Fig. S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **17** in $CDCl_3$ (x = AcOEt).

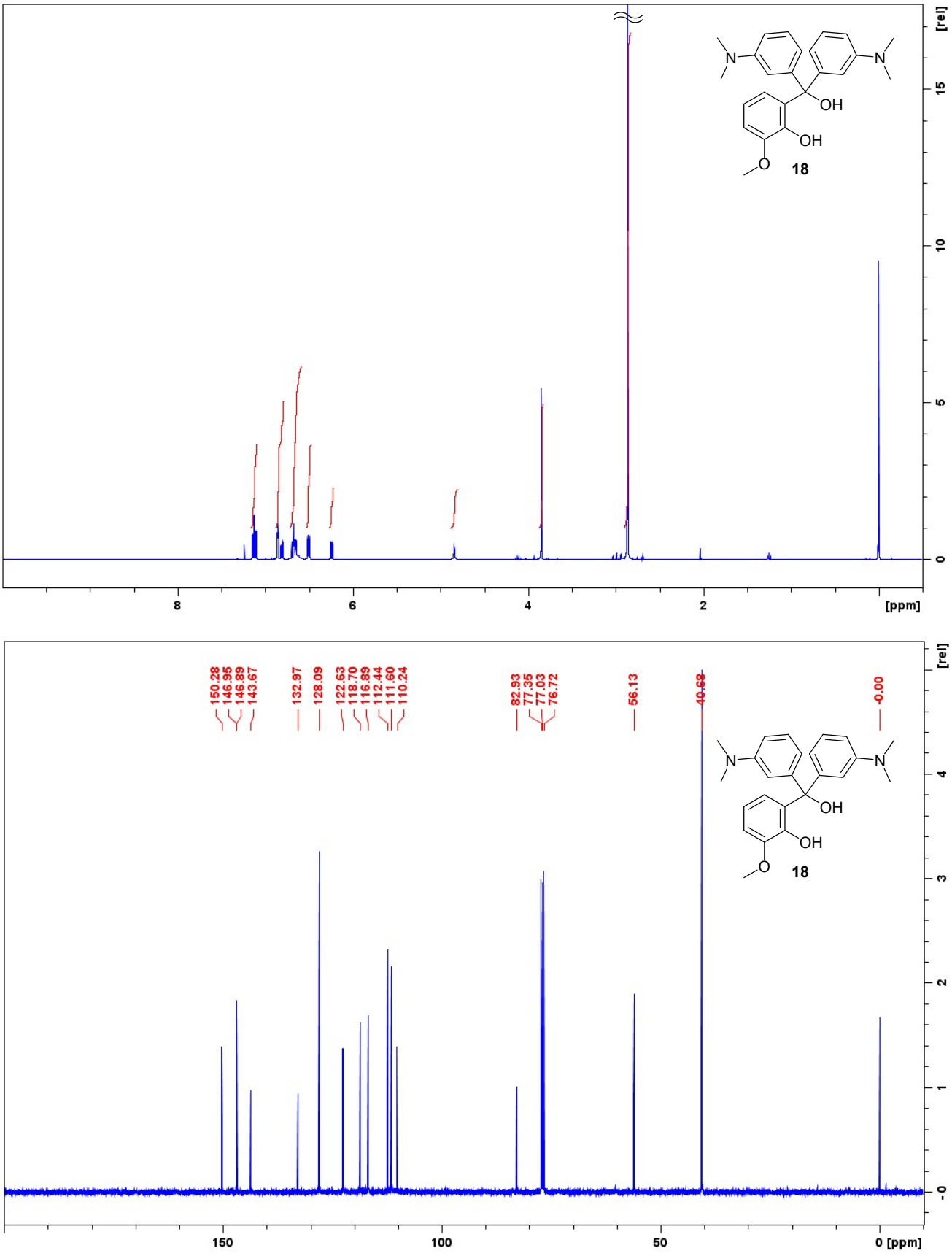


Fig. S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **18** in $CDCl_3$.

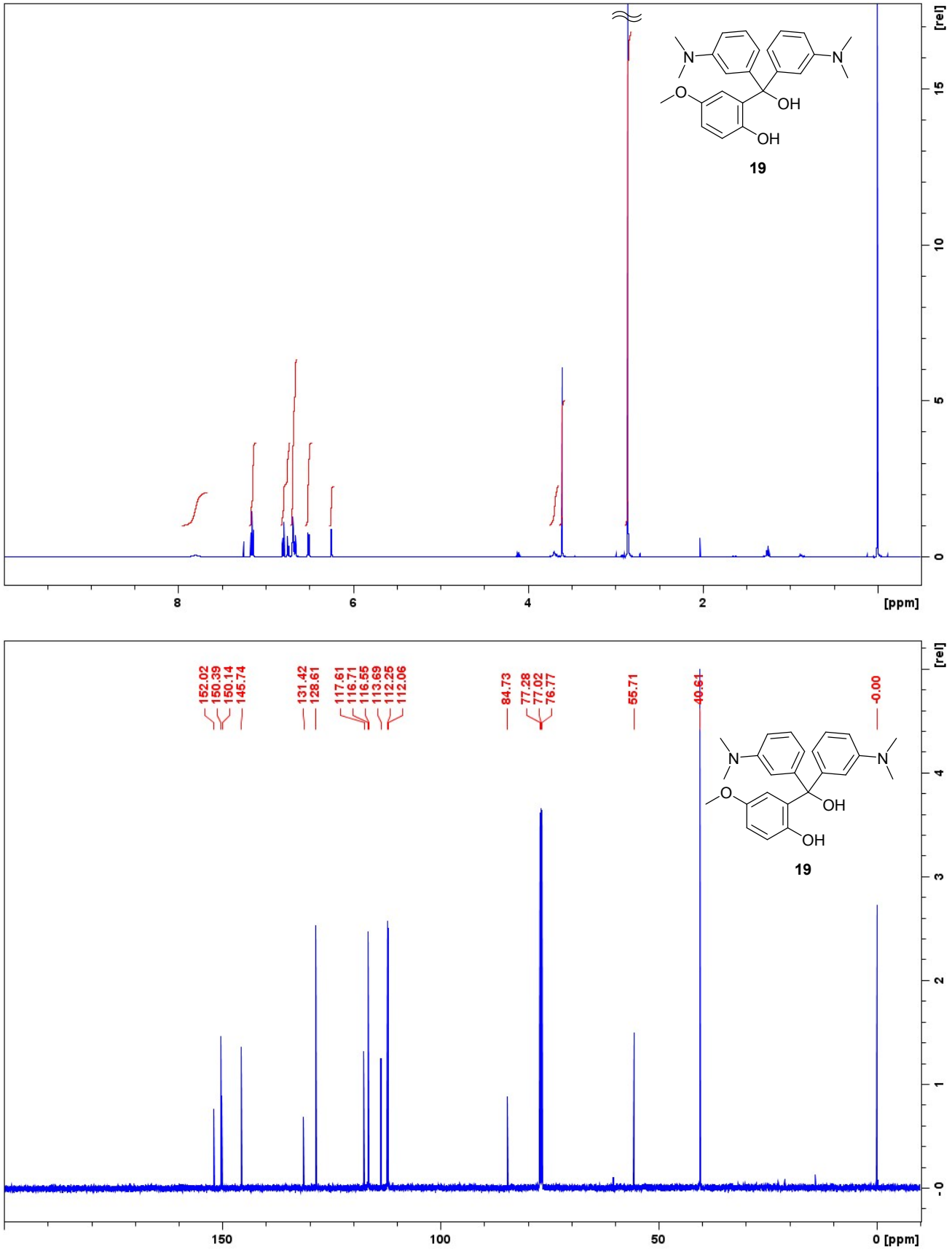


Fig. S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **19** in $CDCl_3$.

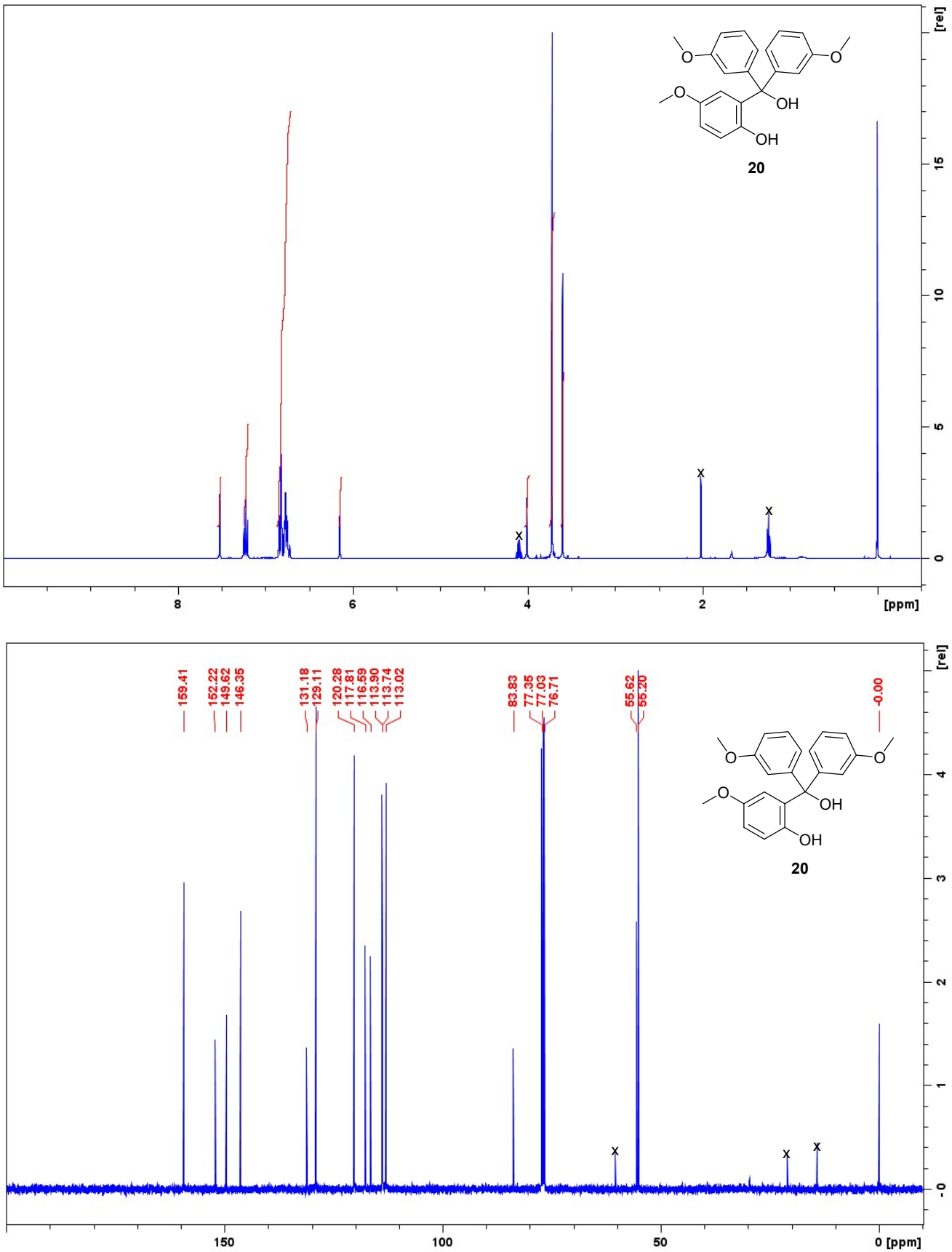


Fig. S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **20** in $CDCl_3$ (x = AcOEt).

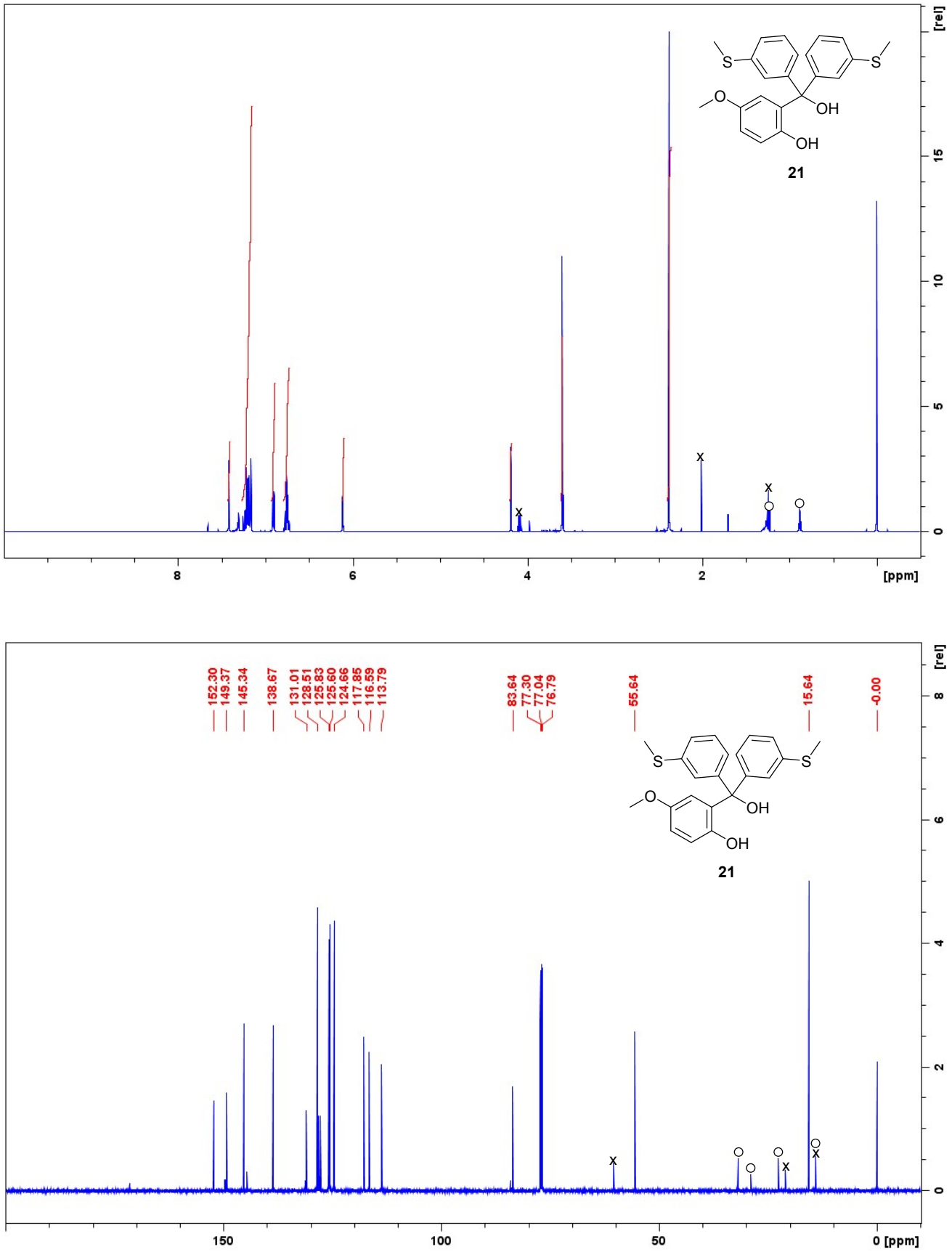


Fig. S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **21** in $CDCl_3$ (x = AcOEt, ○ = *n*-heptane).

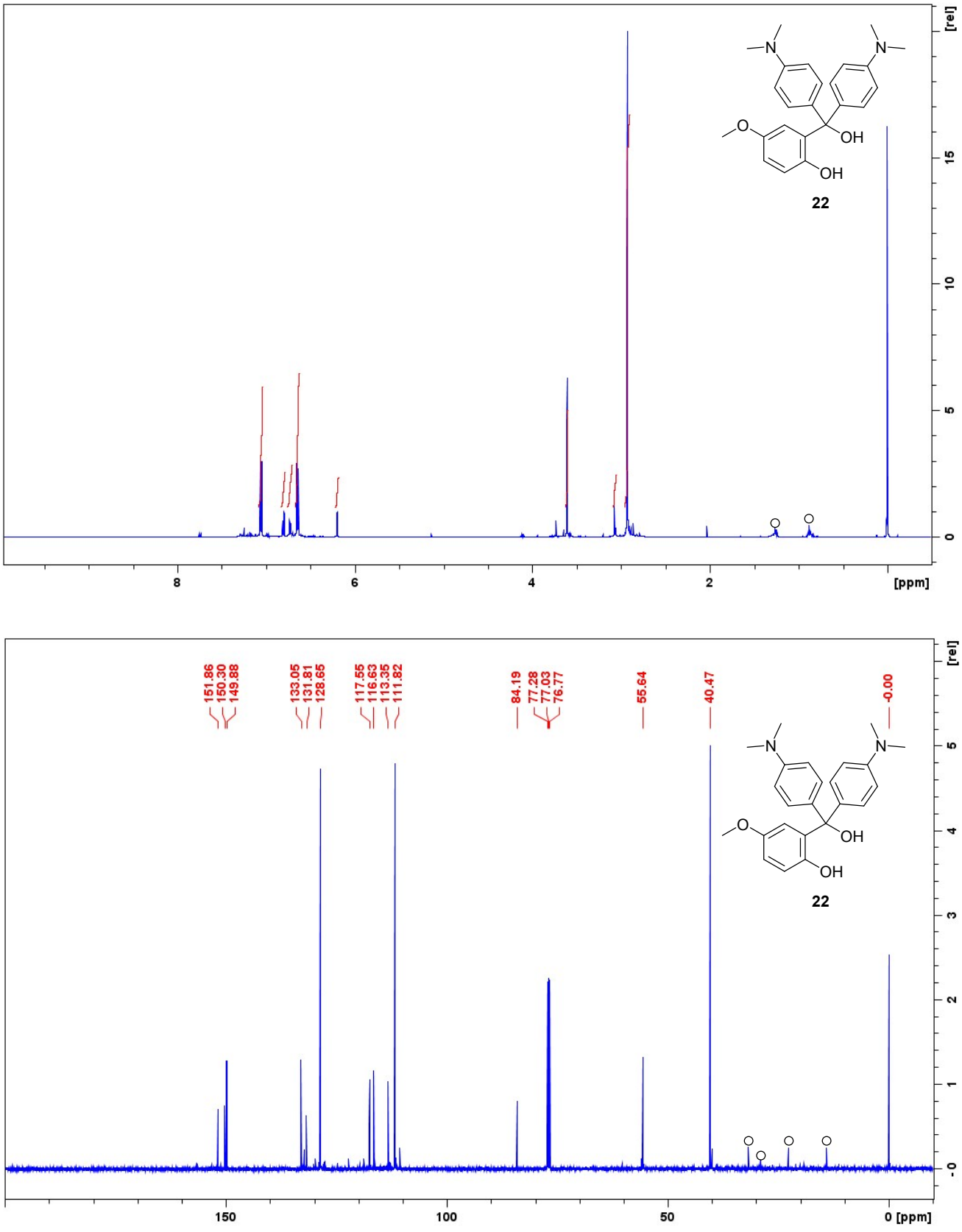


Fig. S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **22** in $CDCl_3$ (○ = *n*-heptane).

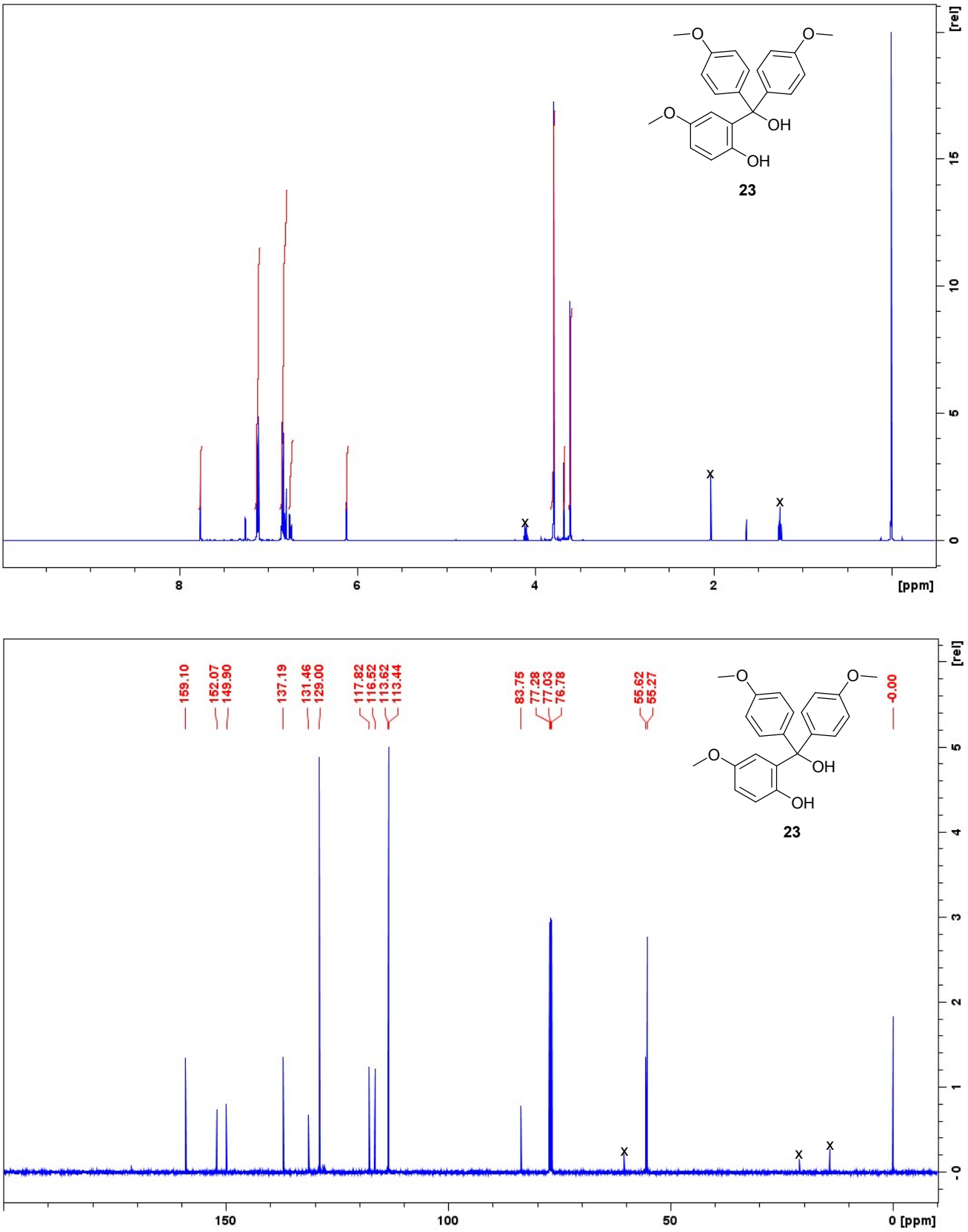


Fig. S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **23** in $CDCl_3$ (x = AcOEt).

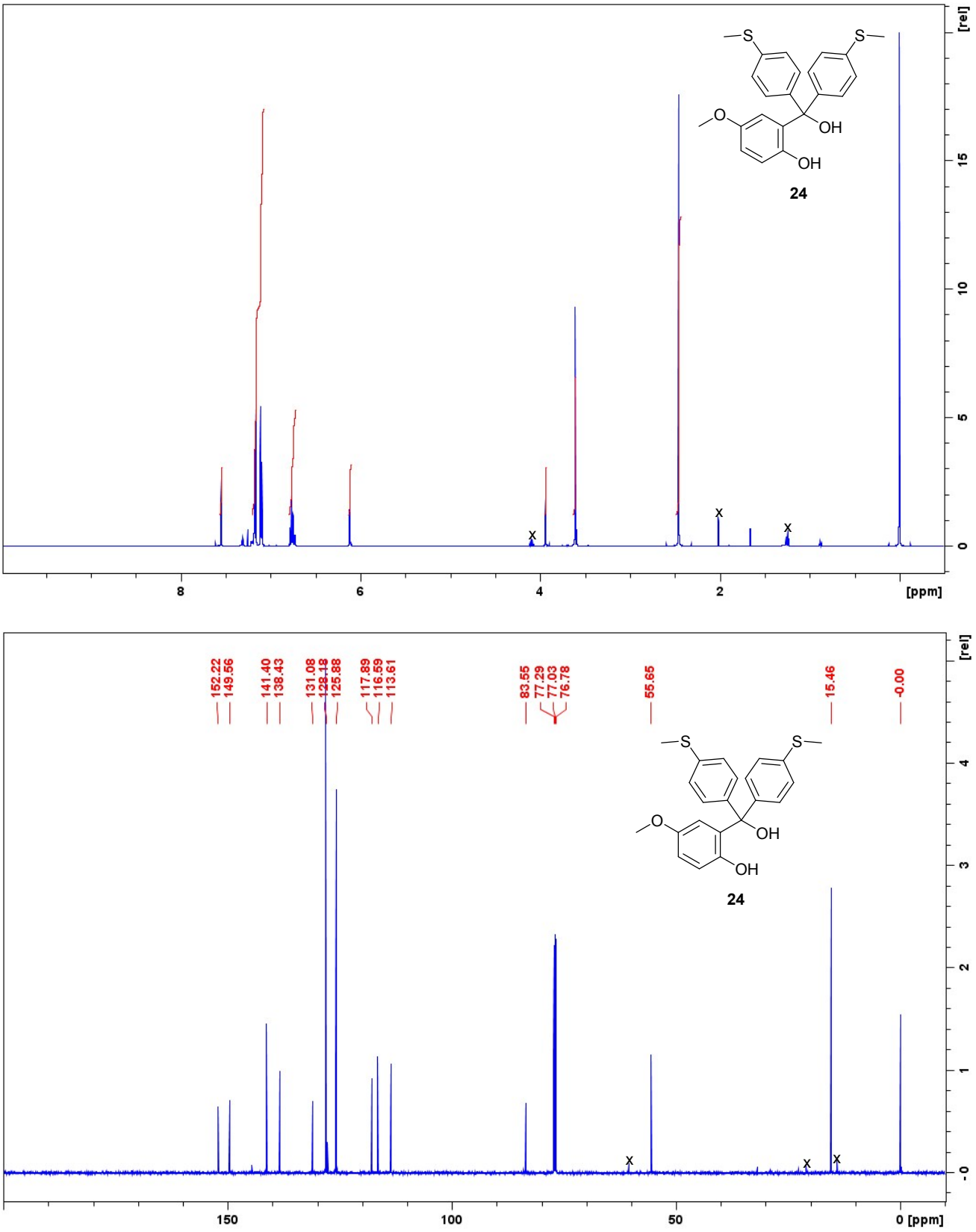


Fig. S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **24** in $CDCl_3$ (x = AcOEt).

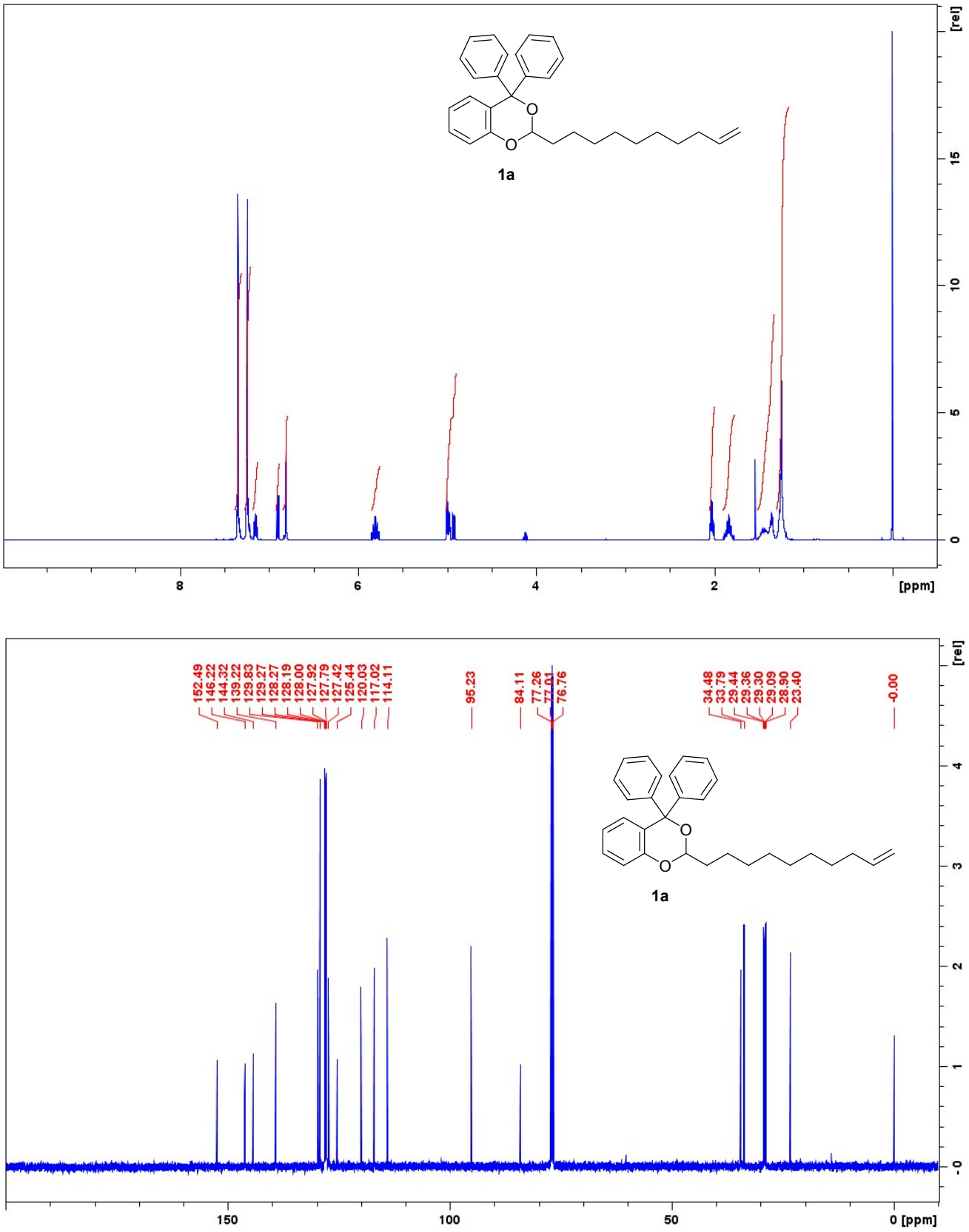


Fig. S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1a** in $CDCl_3$.

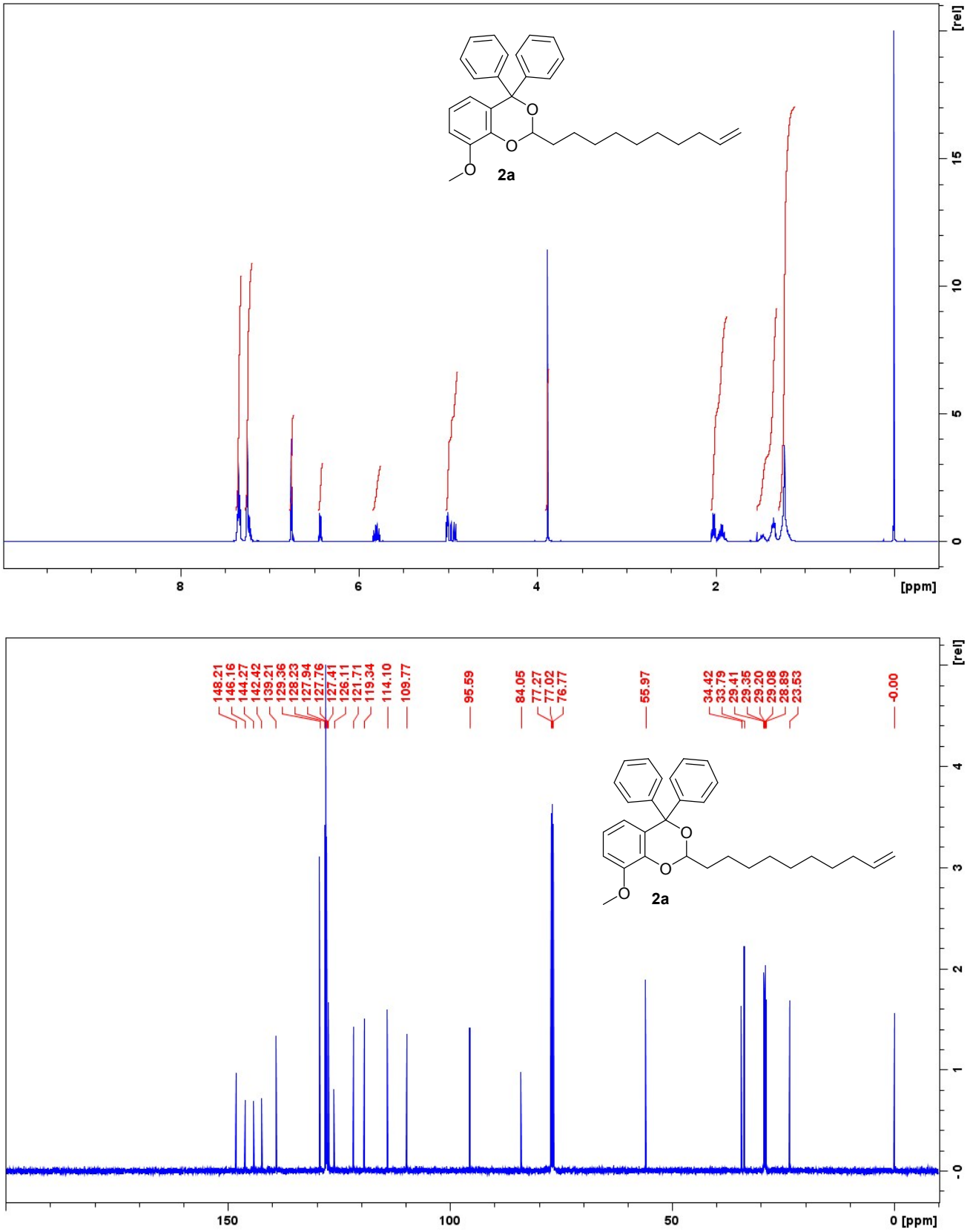


Fig. S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** in $CDCl_3$.

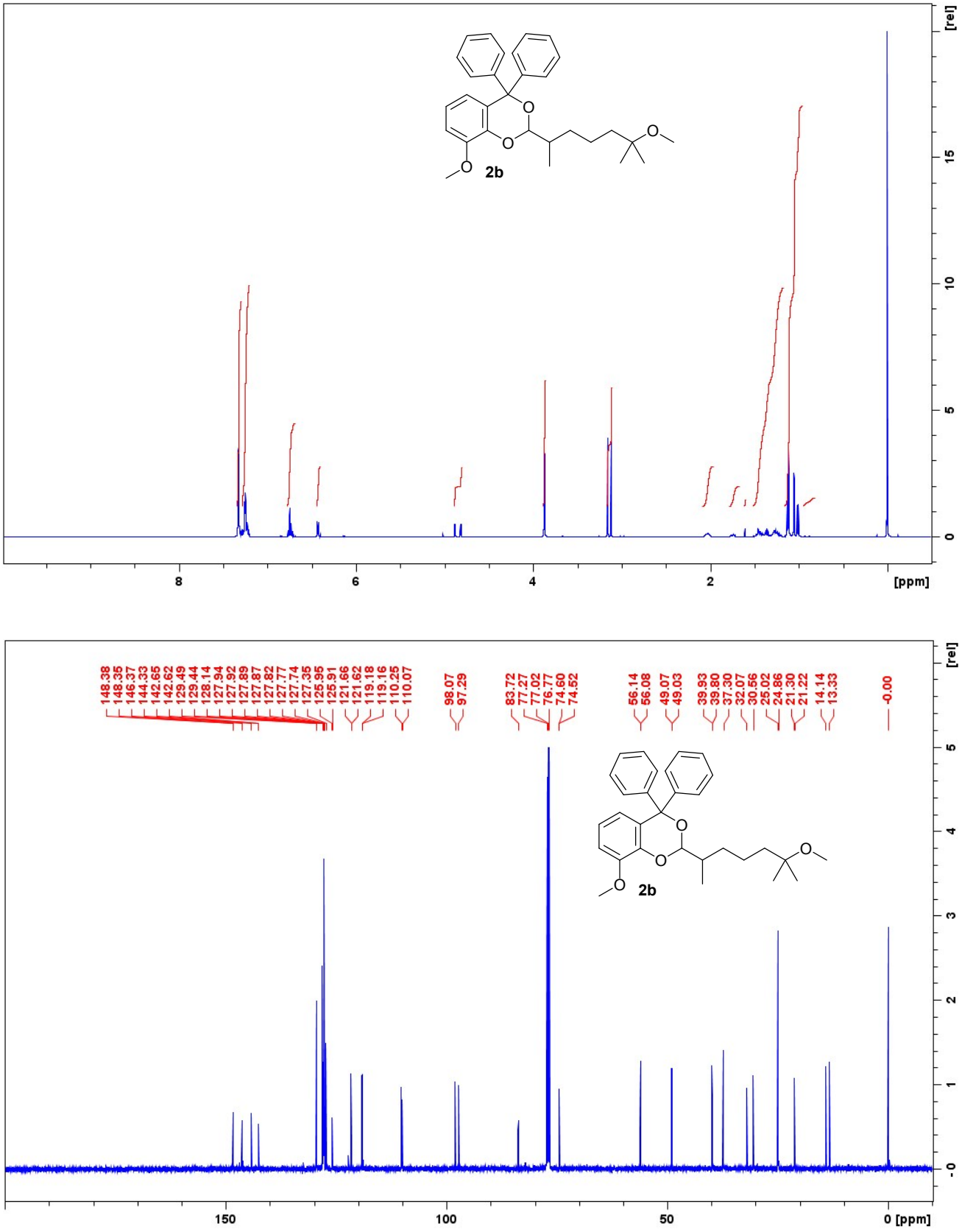


Fig. S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b** in $CDCl_3$.

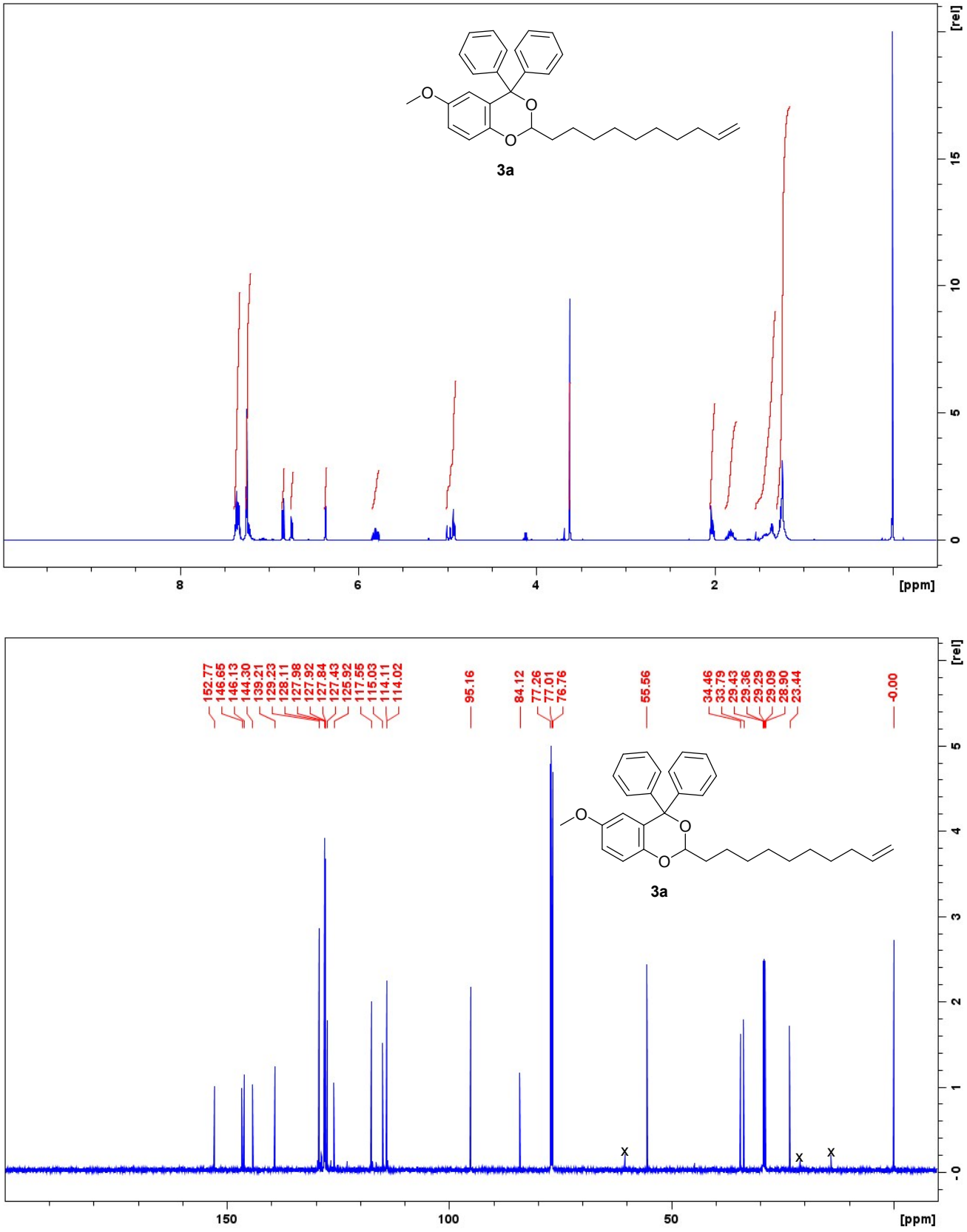


Fig. S16 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3a** in $CDCl_3$ (x = AcOEt).

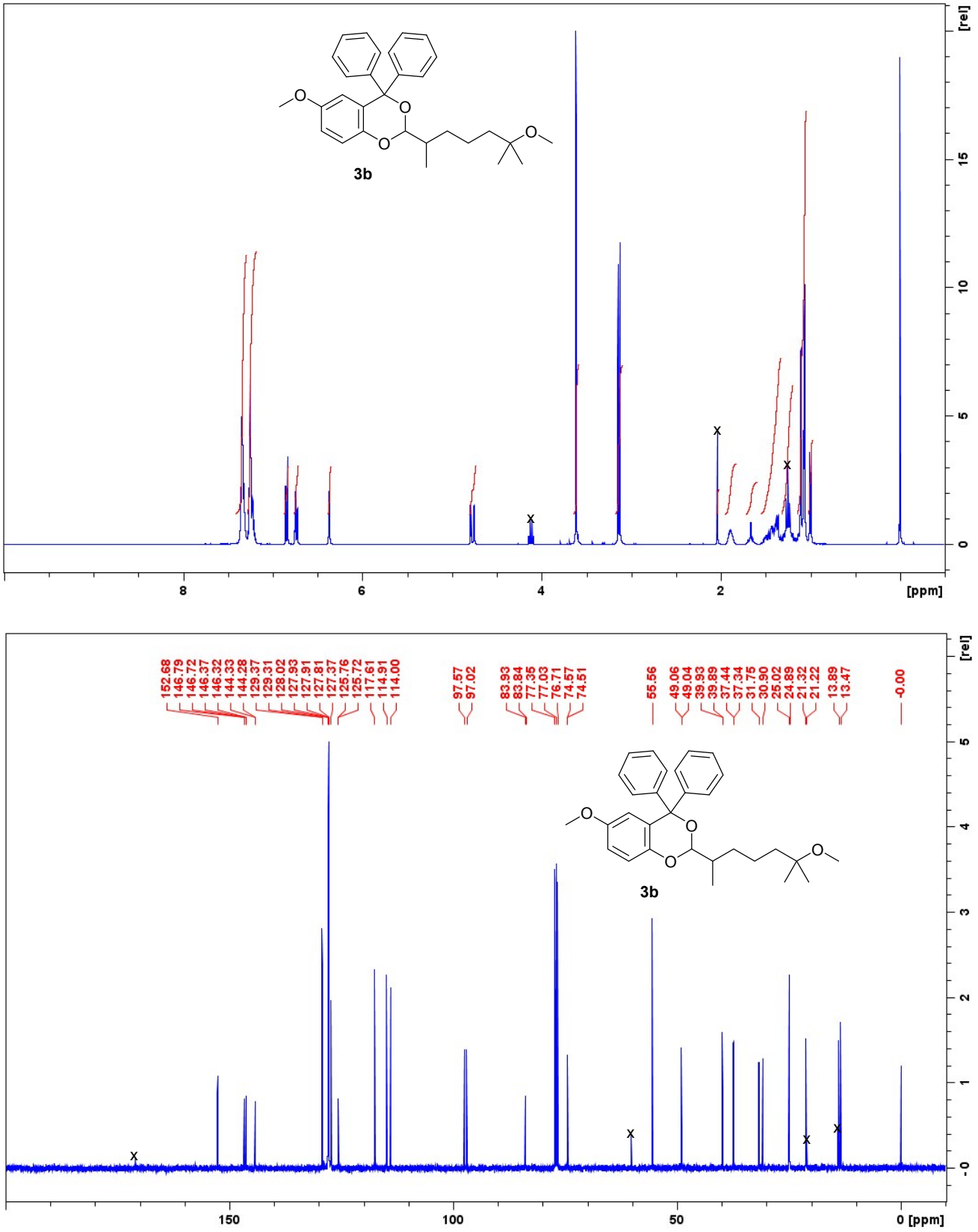


Fig. S17 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3b** in $CDCl_3$ (x = AcOEt).

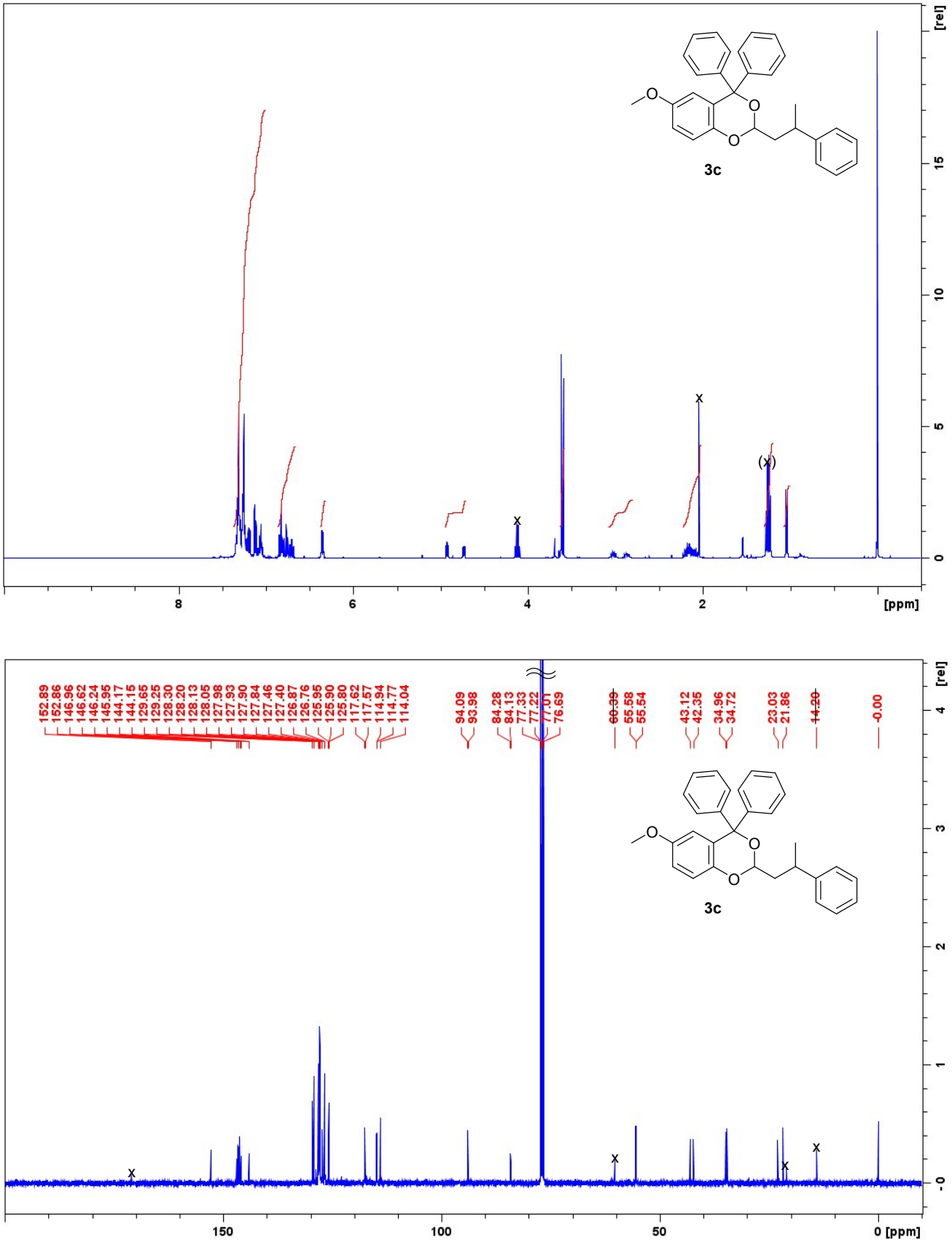


Fig. S18 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3c** in $CDCl_3$ (x = AcOEt).

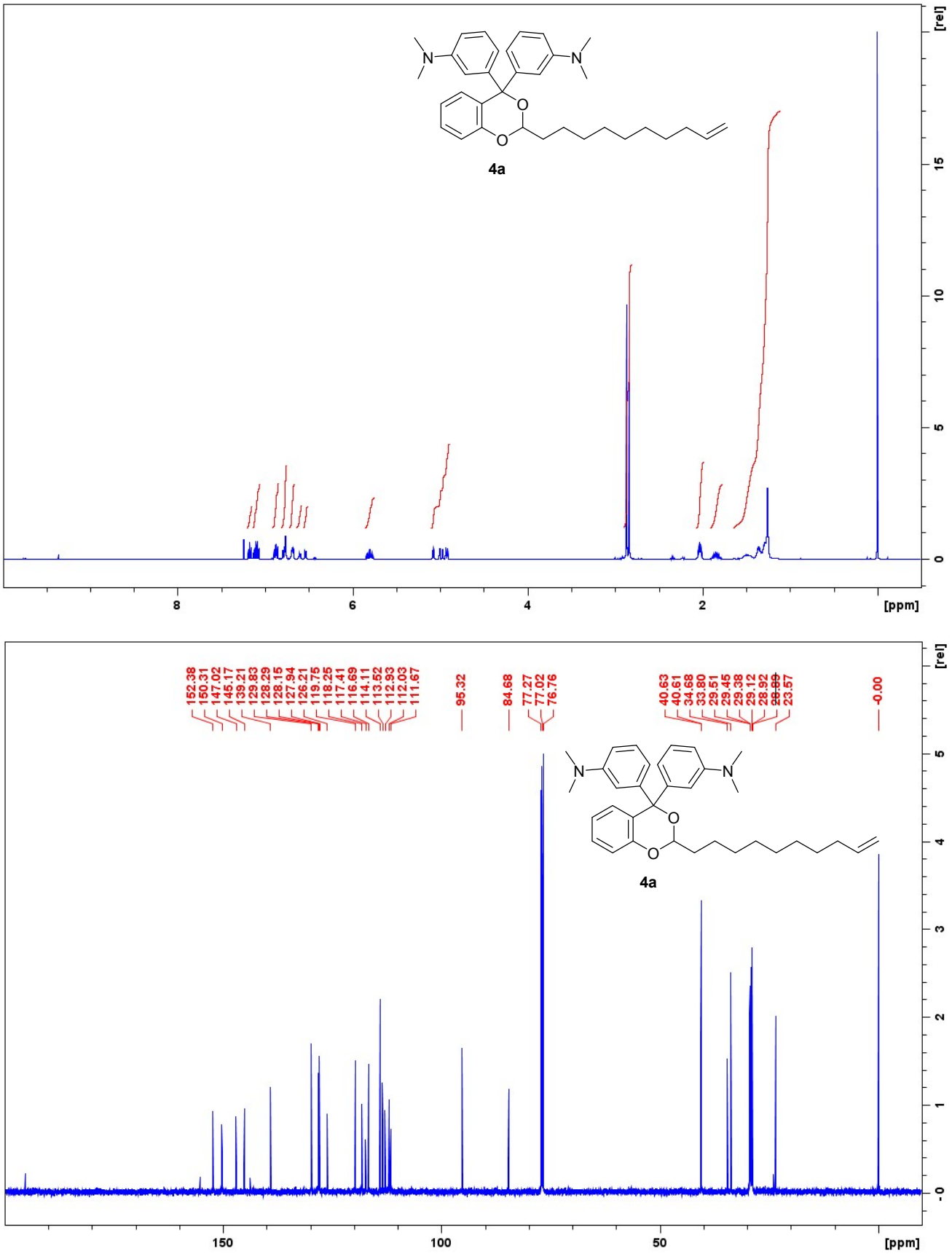


Fig. S19 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4a** in $CDCl_3$.

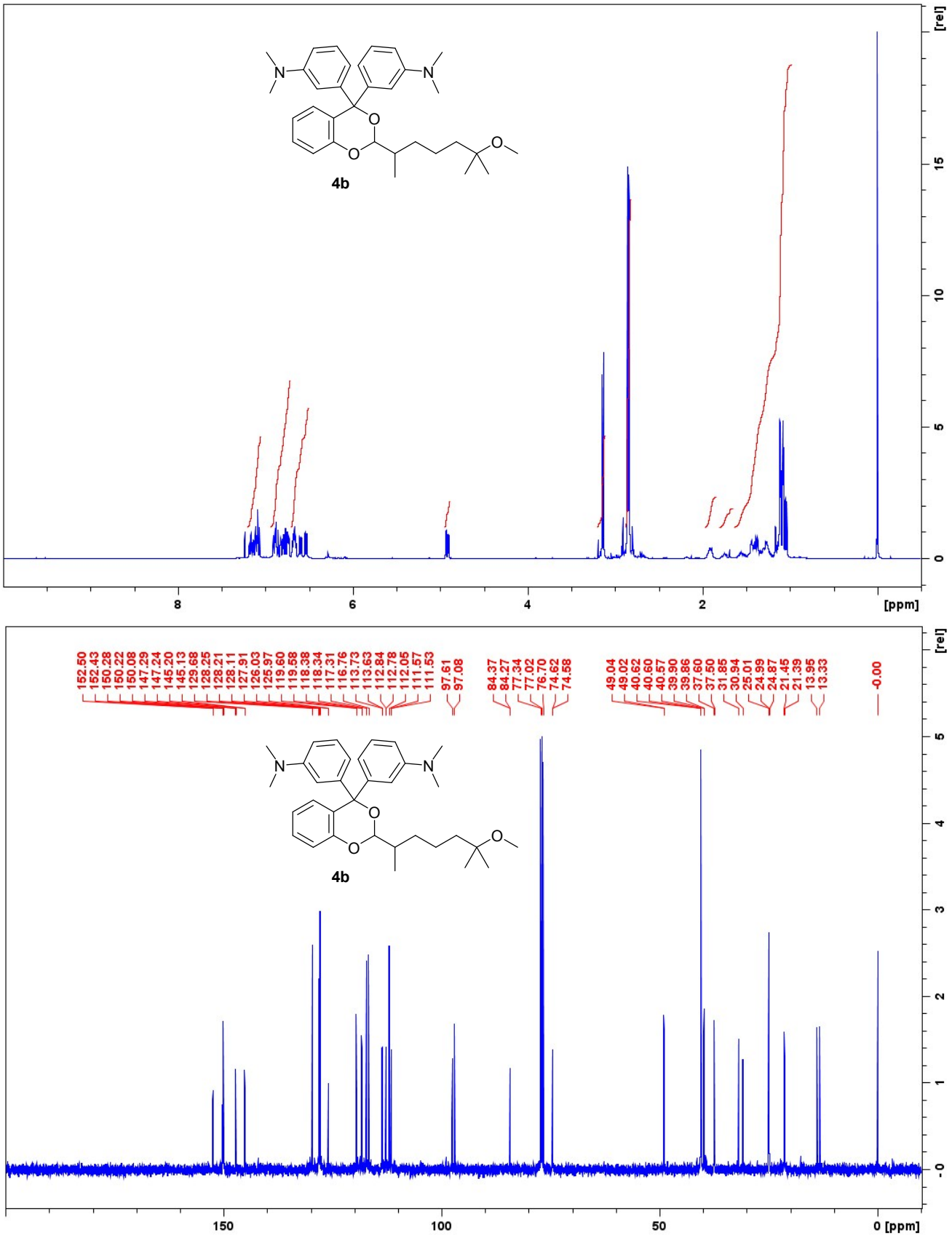


Fig. S20 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4b** in $CDCl_3$.

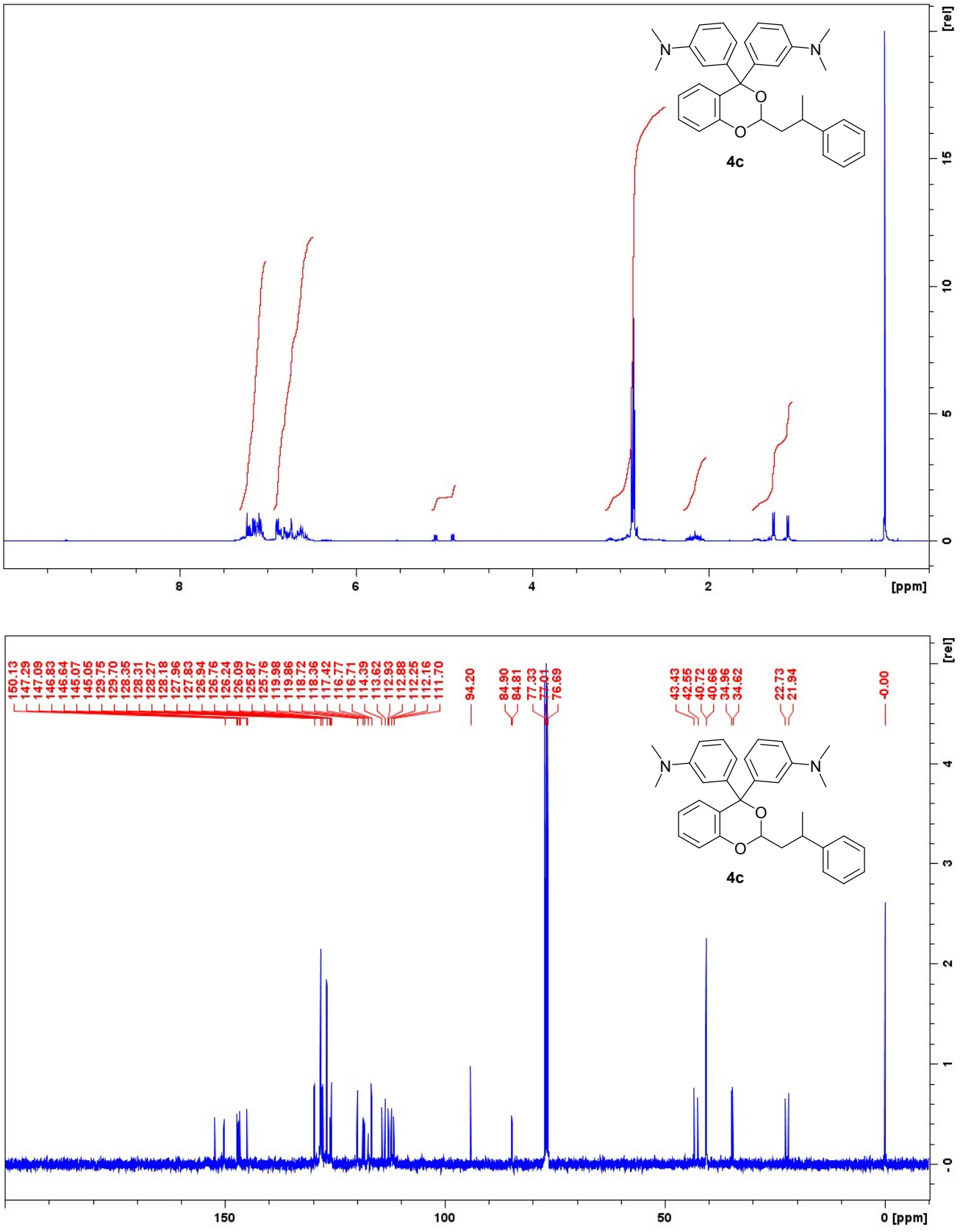


Fig. S21 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4c** in $CDCl_3$.

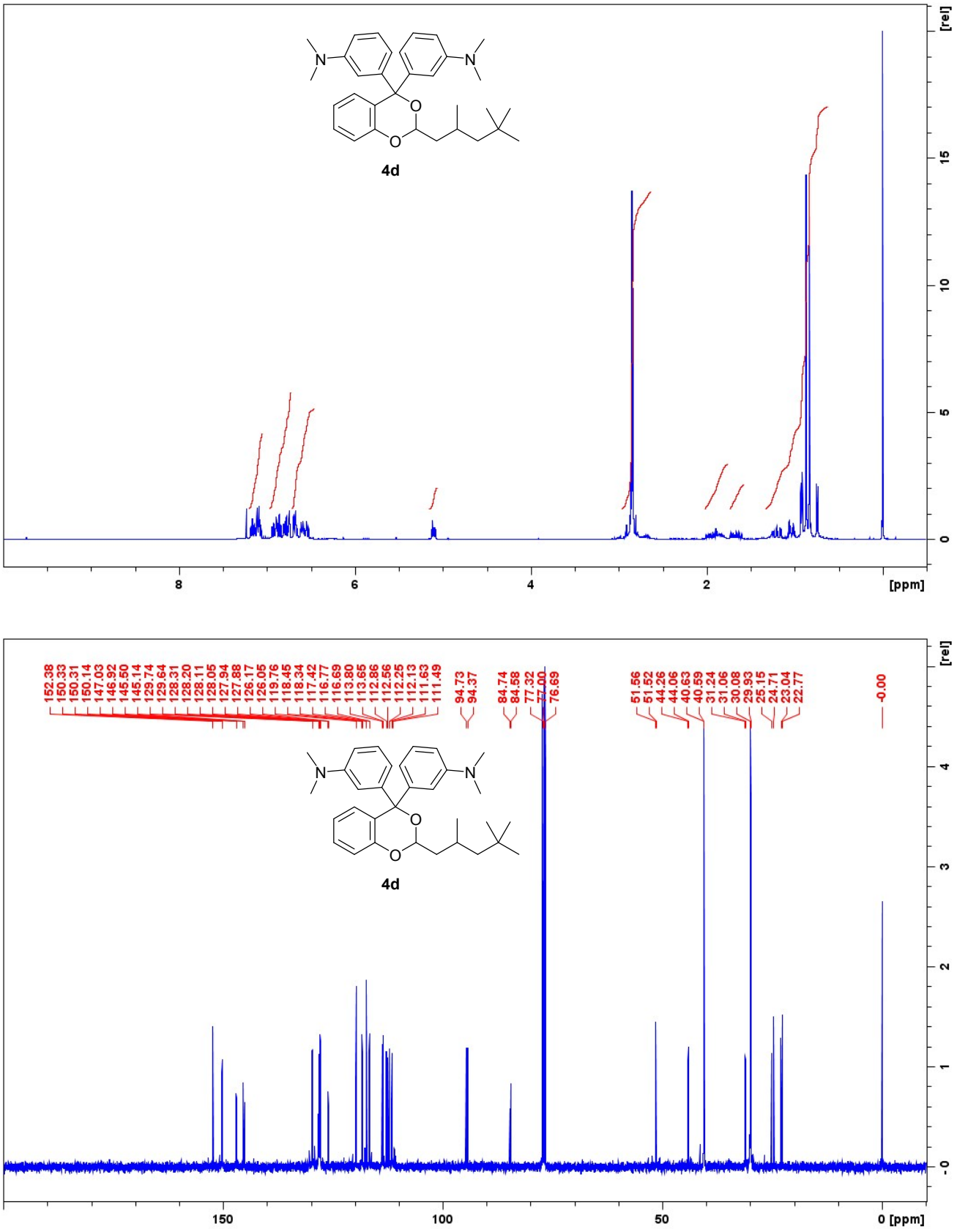


Fig. S22 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4d** in $CDCl_3$.

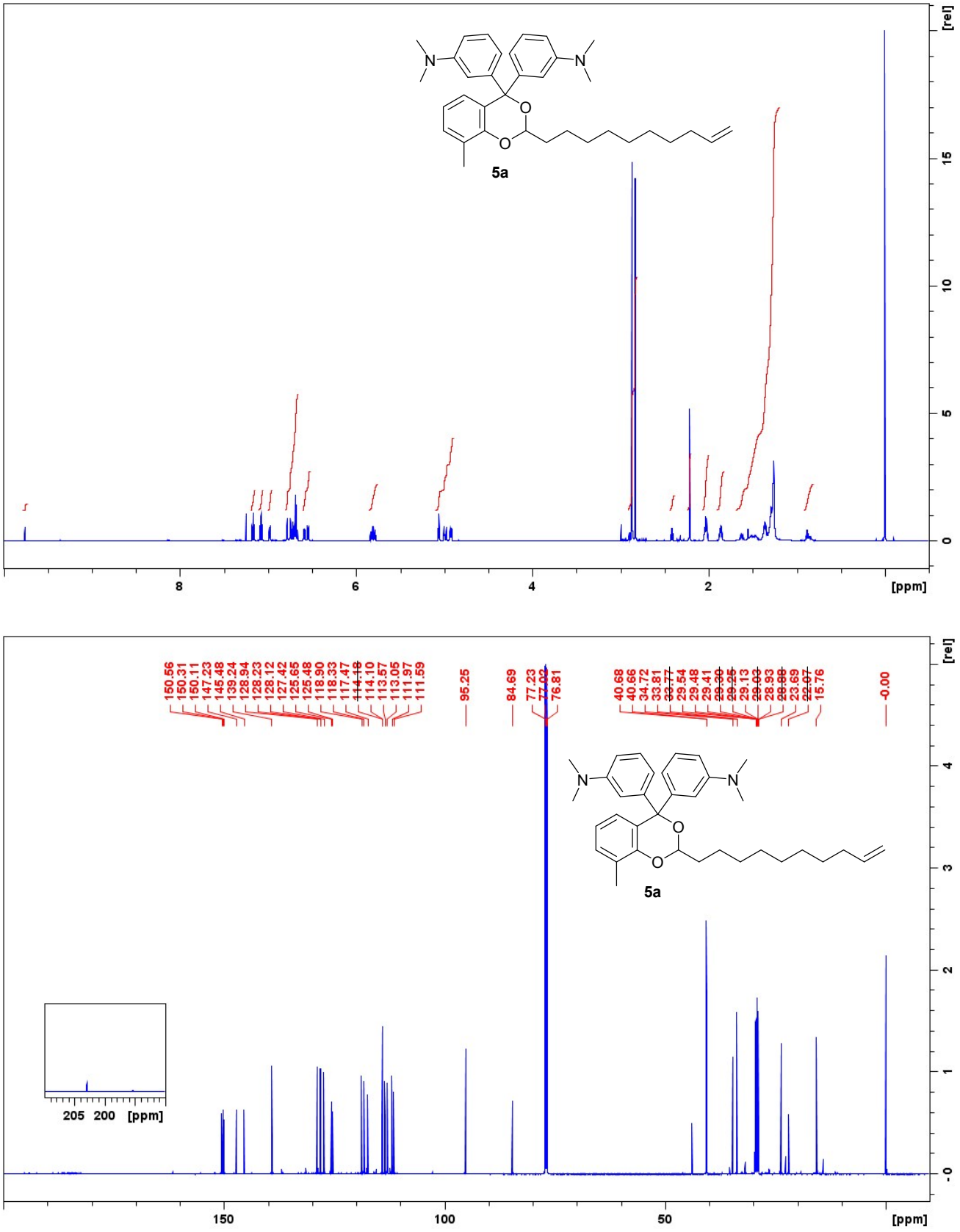


Fig. S23 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **5a** in $CDCl_3$. The sample contains *ca*. 25 mol-% of unreacted 10-undecenal.

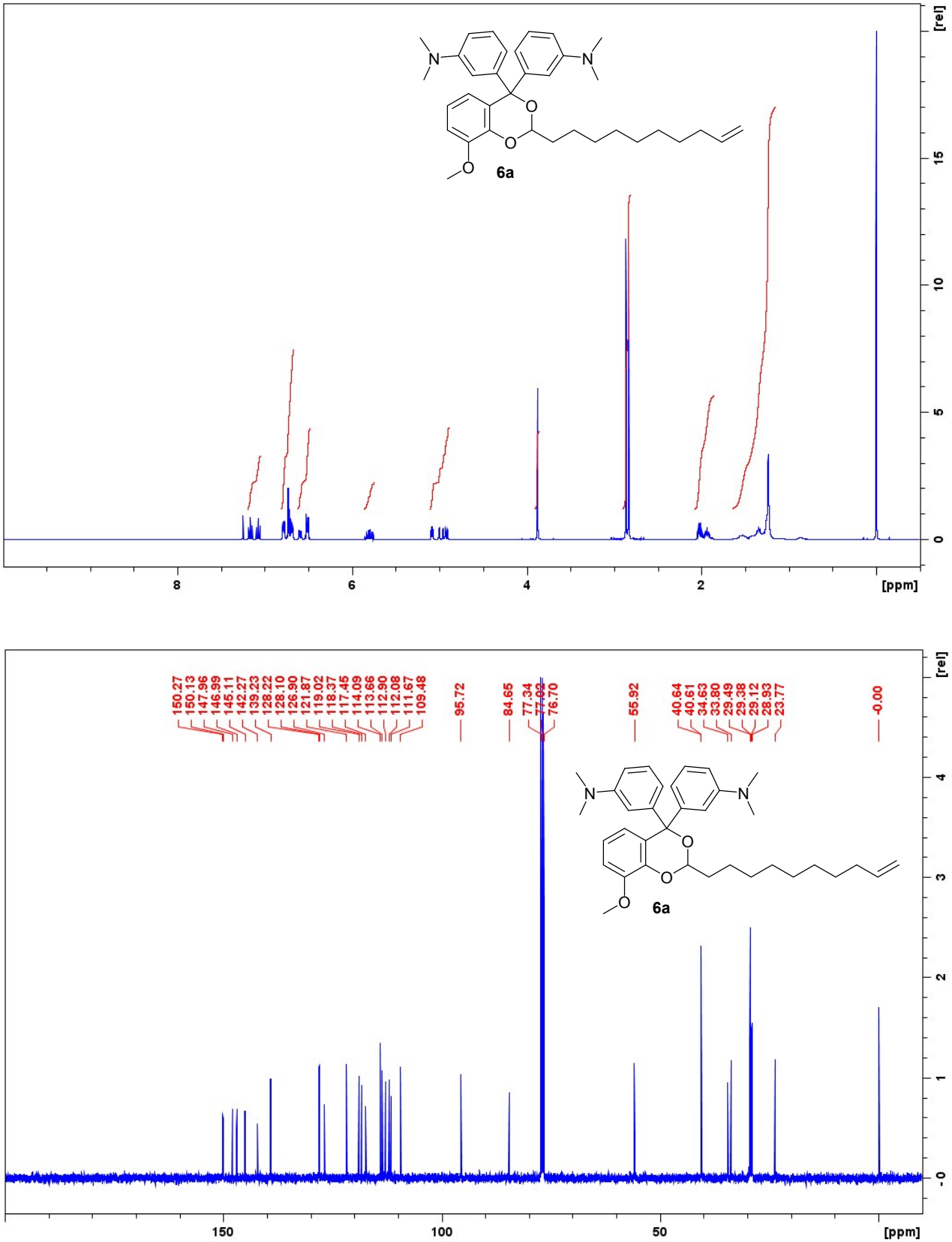


Fig. S24 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **6a** in $CDCl_3$.

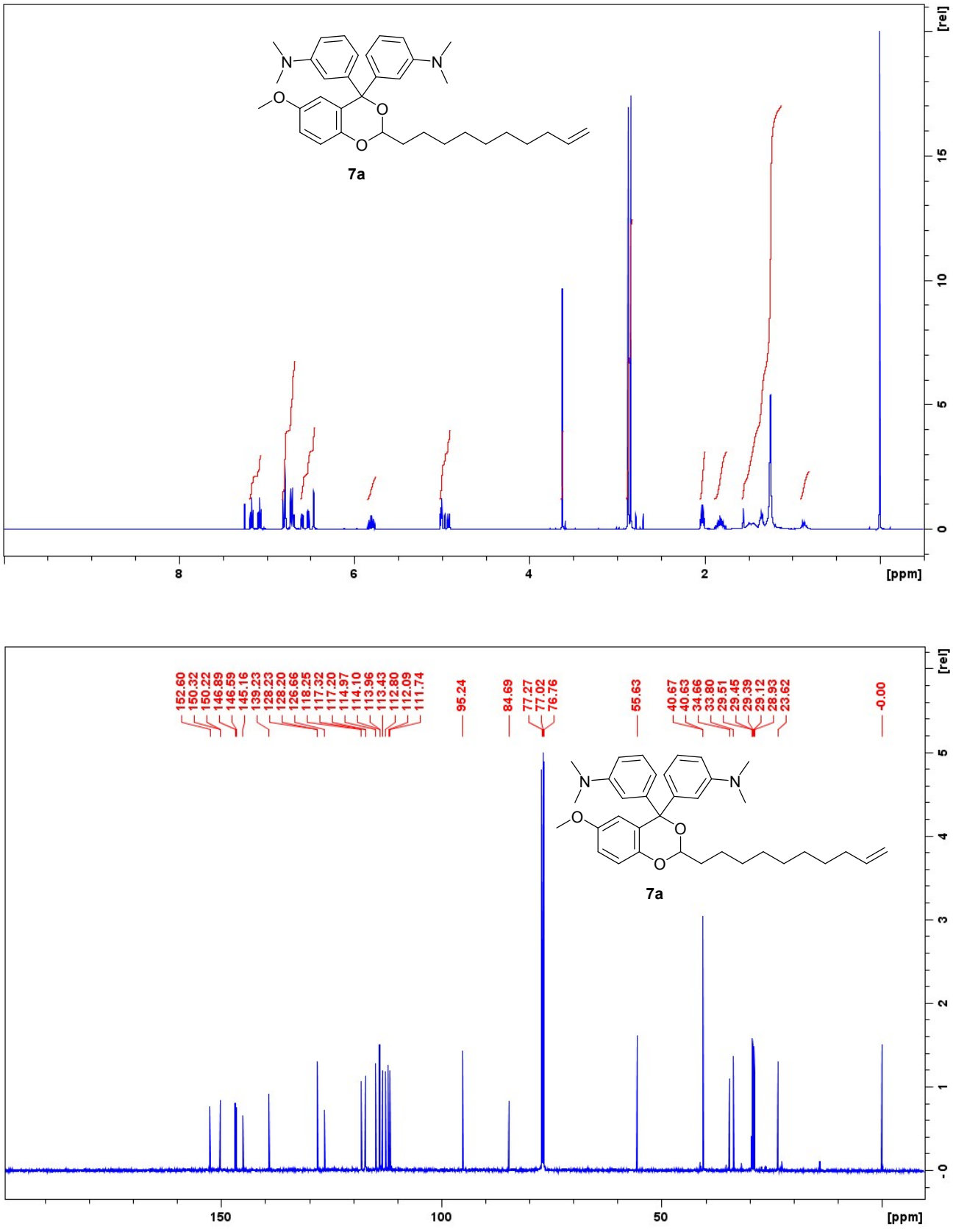


Fig. S25 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **7a** in $CDCl_3$.

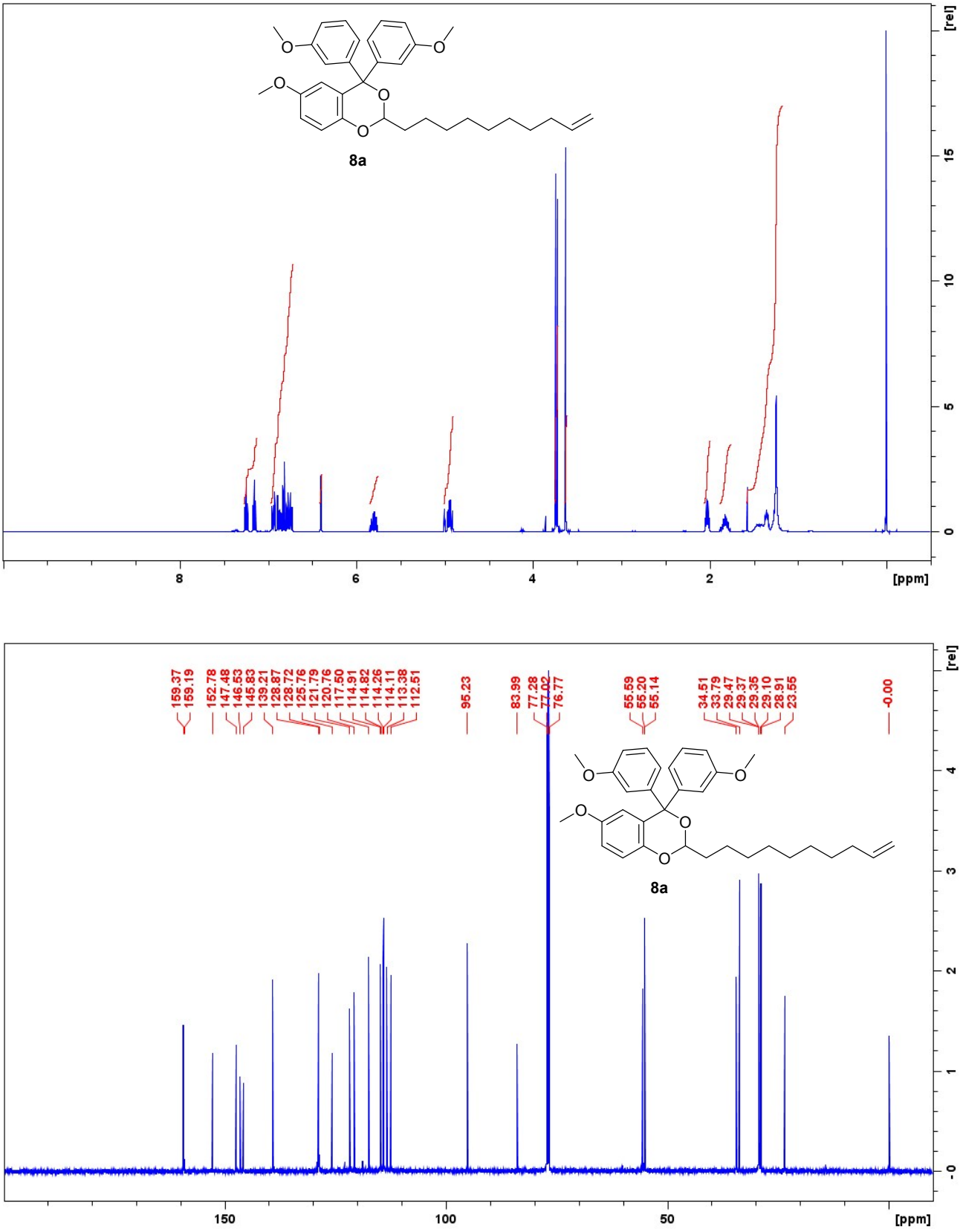


Fig. S26 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **8a** in $CDCl_3$.

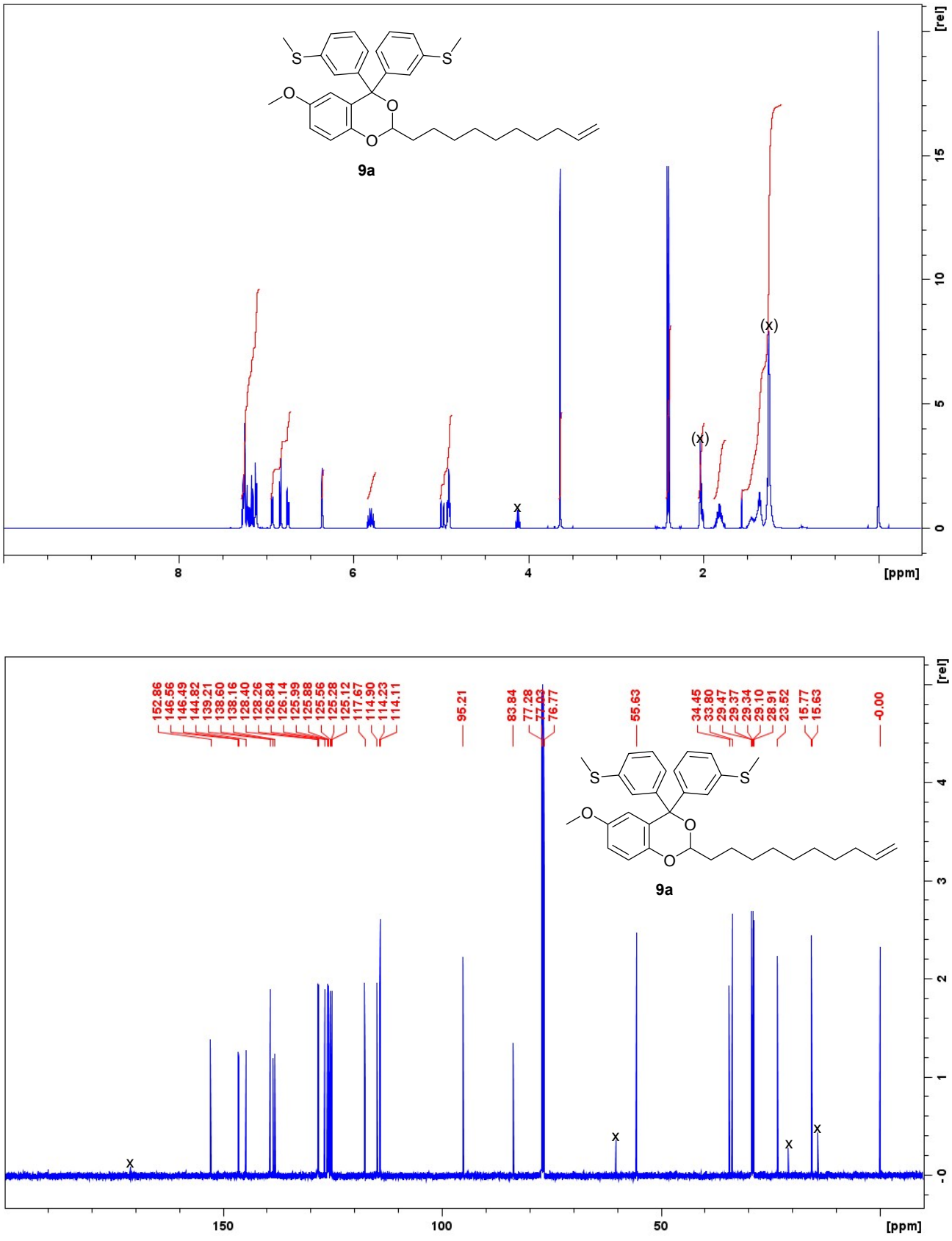


Fig. S27 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **9a** in $CDCl_3$ (x = AcOEt).

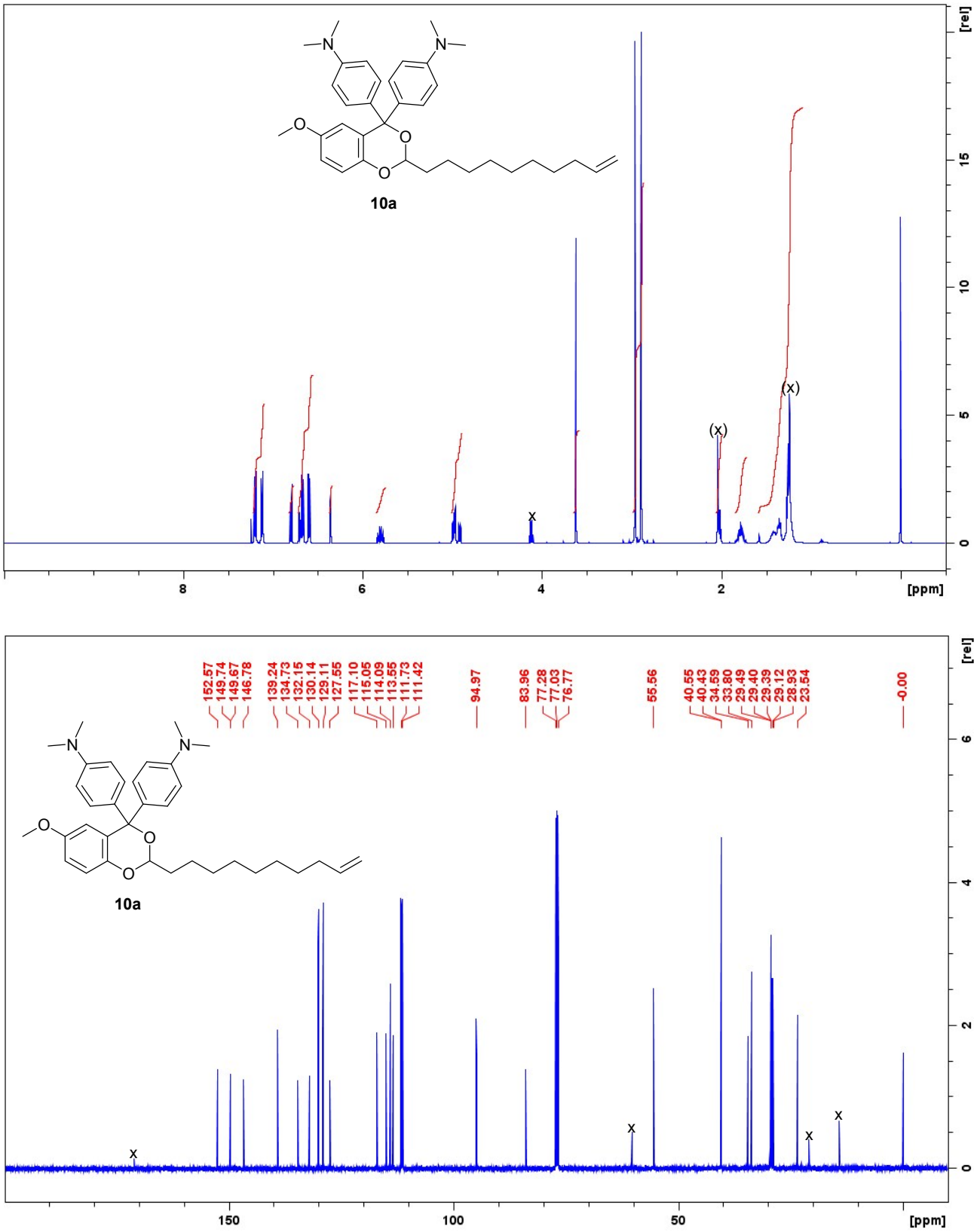


Fig. S28 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **10a** in $CDCl_3$ (x = AcOEt).

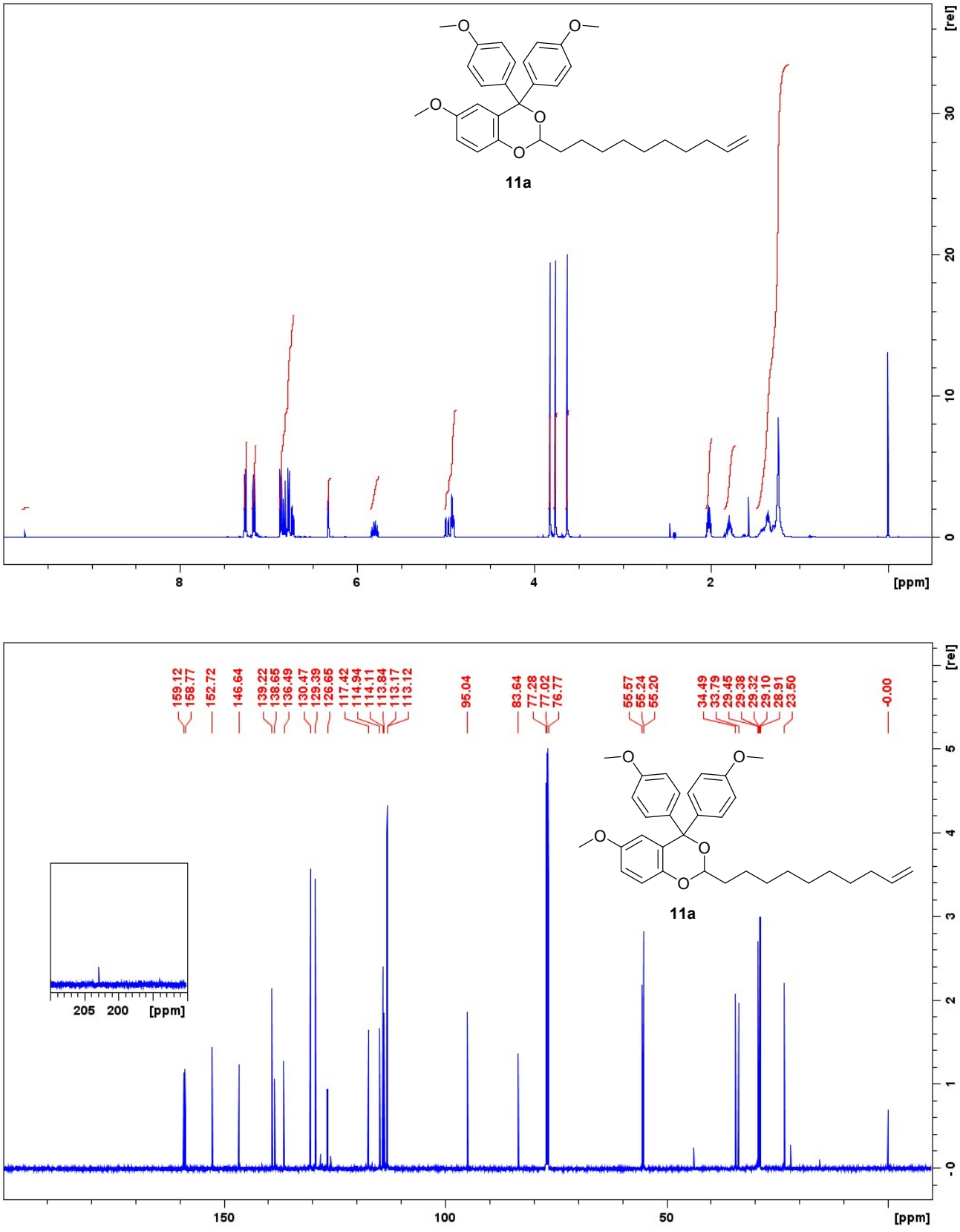


Fig. S29 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **11a** in $CDCl_3$. The sample contains *ca*. 5 mol-% of unreacted 10-undecenal.

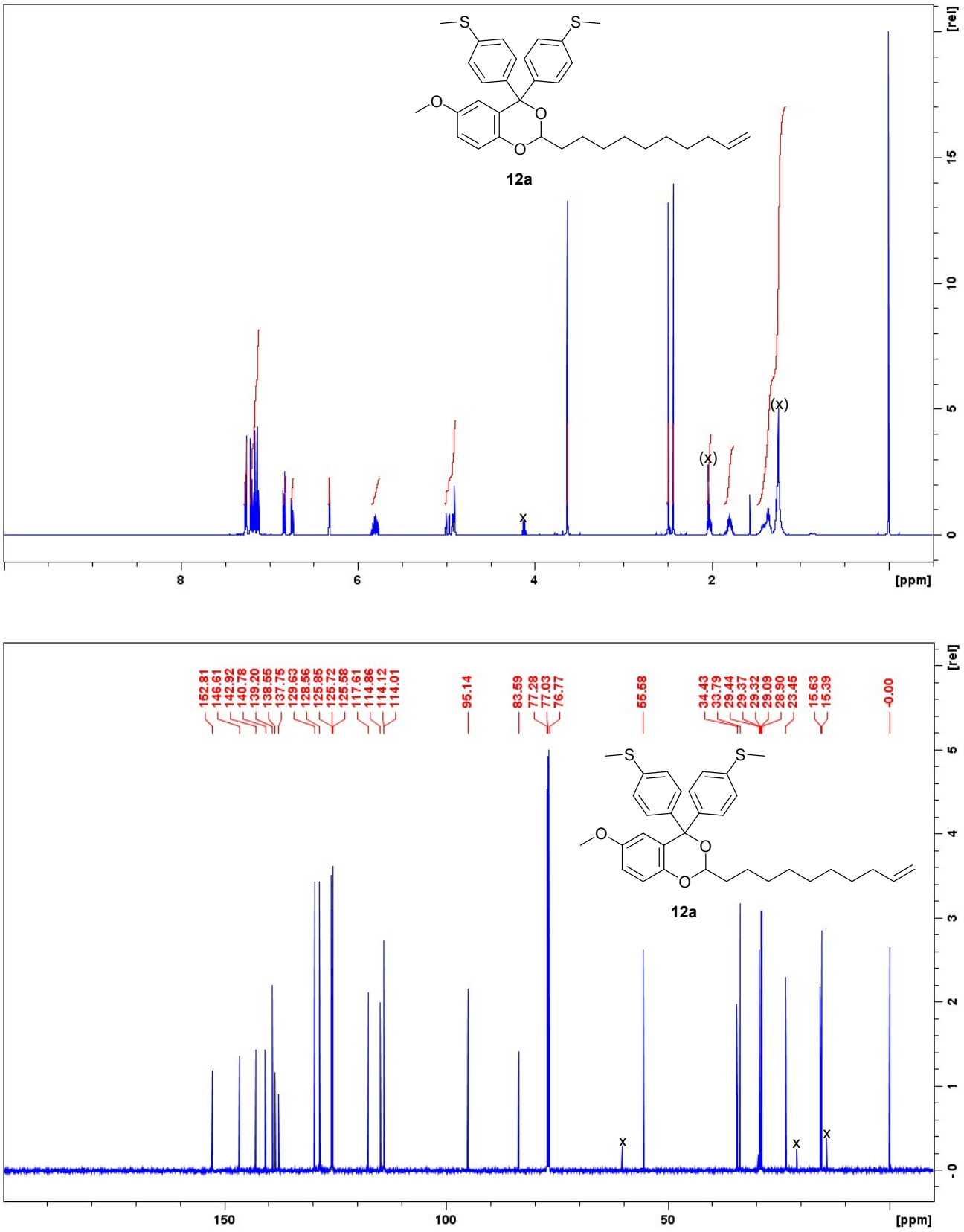


Fig. S30 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **12a** in $CDCl_3$ (x = AcOEt).

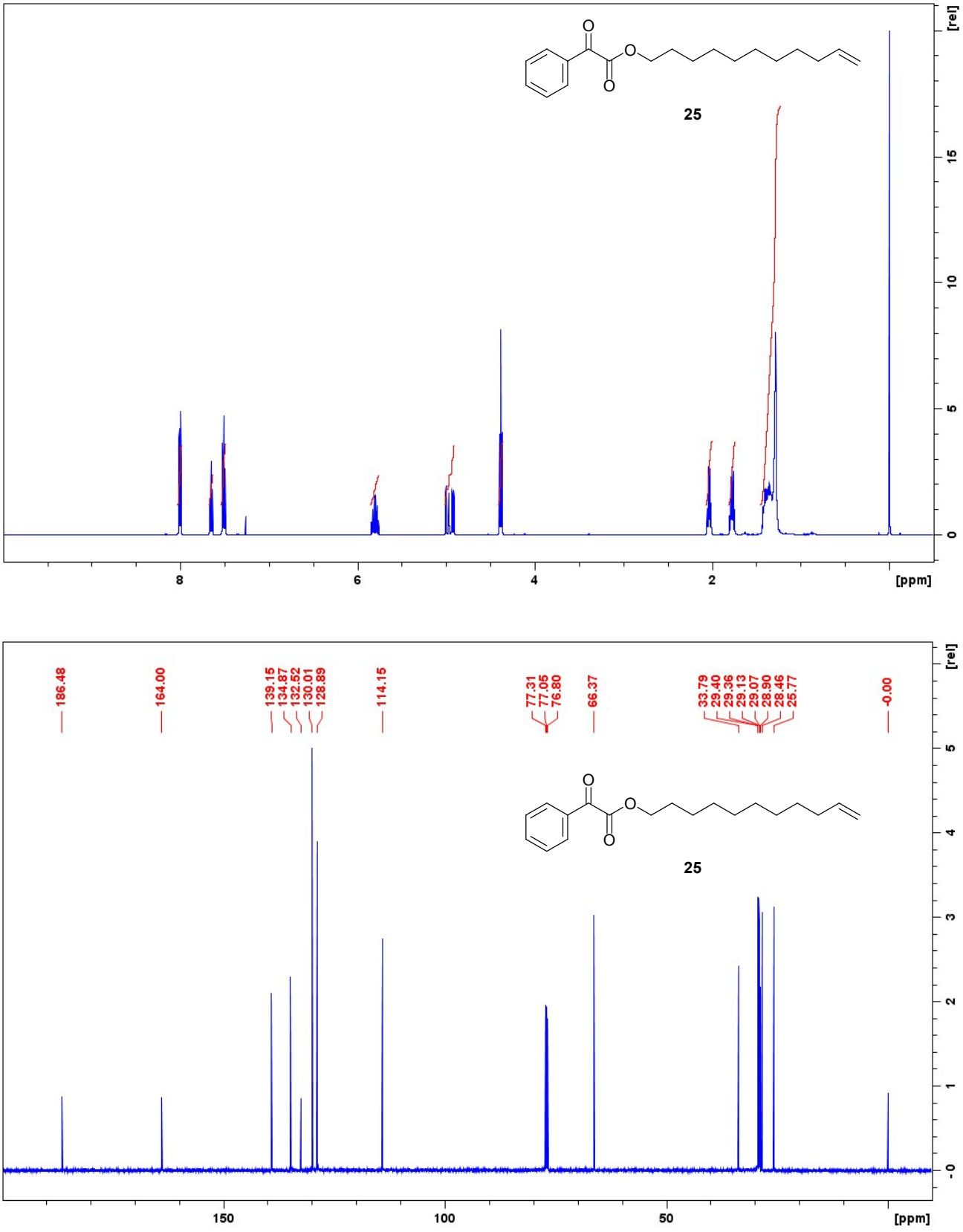


Fig. S31 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **25** in $CDCl_3$.