*Electronic Supplementary Information*

# Base-mediated cascade synthesis of indole diolefins: a route to spiro[cyclopentene-indole]thiones and thiepino[2,3-*b*]indoles

Sengodagounder Muthusamy,* Ramasamy Naveen and Muniyappankovilthottam Devaraj Senthil Kumar

*School of Chemistry, Bharathidasan University*
*Tiruchirappalli – 620024, India. E-mail: muthu@bdu.ac.in*

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## 1. General information

Capillary melting point apparatus was used to determine the melting points which are uncorrected. Infrared spectra were recorded as neat (ATR) on a Bruker Alpha FT-IR spectrophotometer ($cm^{-1}$). $^{1}H$ and $^{13}C$ NMR spectra were recorded in Bruker Avance III 400 NMR spectrometer operating at 400 MHz ($^{1}H$) and 101 MHz ($^{13}C$) at ambient temperature. The chemical shift ($\delta$) values are given in parts per million (ppm) and coupling constants ($J$) in Hertz (Hz). All NMR studies used $CDCl_3$ ($^{1}H$ NMR: $\delta$ 7.26 ppm; $^{13}C$ NMR: $\delta$ 77.16 ppm) as a solvent and Tetramethylsilane (TMS) as an internal standard ($\delta$ 0.00 ppm). The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; ABq, AB quartet. High-resolution mass analyses were performed using the electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. The diastereomeric ratios (dr) were determined from $^{1}H$ NMR.

Solvents were purified by distillation according to usual methods. DCM was dried using $P_2O_5$. DMF was purified through vacuum distillation using $CaH_2$ and stored over 4Å molecular sieves. Toluene was dried by downward distillation and stored with sodium wire. Ultimate care has been taken while using sodium for solvent drying purposes. Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine or UV light at 254 nm. Crude samples were purified by either column (silica gel, 100-200 mesh) or flash (silica gel, 230-400 mesh) chromatography. For the elution process *n*-hexanes-EtOAc mixture was used as the eluent unless otherwise stated. All air and moisture-sensitive reactions were carried out in oven-dried glassware under a positive argon or nitrogen gas pressure using standard gas-tight syringes and septa with magnetic stirring. Anhydrous chloroform and Grubbs' catalysts were purchased from M/s Sigma Aldrich Co. and used as provided. $K_2CO_3$ was dried by heating at 110 ℃ in a hot air oven for 12 h and left to cool under a nitrogen atmosphere.

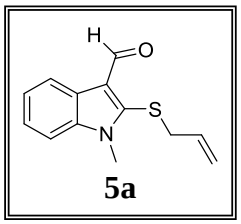
***Important**: In general, compounds **5** and **8** were highly decomposing nature. Quick purification and characterization are mandatory for substrates **5** and **8**.*

## 2. General procedure for the synthesis of compounds 5

An oven-dried flask under an inert atmosphere was charged with the appropriate aldehyde **4** (1.0 equiv) and anhydrous powdered $K_2CO_3$ (1.2 equiv) in dry dimethylformamide (25 mL) and stirred at 0 ℃ for 10 min, the appropriate alkyl/aryl halide (1.2 equiv) and tetrabutylammonium iodide (TBAI) (0.1 equiv) were added to the above reaction mixture. The reaction mixture was stirred at room temperature overnight. Water (100 mL) was added

to the reaction and extracted with dichloromethane (3 x 25 mL). The entire organic layers were combined and washed with water (100 mL). Finally, the organic layer was dried over $Na_2SO_4$, evaporated, and purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 4:1) to afford the respective *N*-alkylated products **5**.

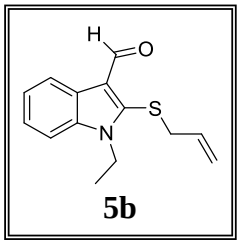
**1-Methyl-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5a)**




**5a**

Yellowish oil (87%); **IR** (neat): $\nu_{max}$ 2825, 1670, 915, 866, 798, 751, 707, 689, 652, 610 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.23 (s, 1H), 8.34 (d, $J$ = 7.6 Hz, 1H), 7.32-7.29 (m, 3H), 5.84-5.73 (m, 1H), 4.98-4.83 (m, 2H), 3.85 (s, 3H), 3.40 (d, $J$ = 7.2 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.3, 141.7, 138.0, 132.3, 125.0, 124.6, 123.2, 121.8, 120.8, 119.2, 110.0, 40.8, 30.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{13}H_{13}NOS+H]^+$ 232.0796; Found: 232.0802.

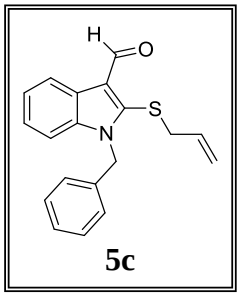
**1-Ethyl-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5b)**




**5b**

Yellowish oil (83%); **IR** (neat): $\nu_{max}$ 2906, 1672, 985, 906, 778, 747, 697, 677, 652, 619 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.27 (s, 1H), 8.38-8.36 (m, 1H), 7.41-7.29 (m, 3H), 5.86-5.80 (m, 1H), 5.04-4.89 (m, 2H), 4.46 (q, $J$ = 7.2 Hz, 2H), 3.48-3.46 (m, 2H), 1.44 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.4, 140.8, 136.8, 132.3, 125.5, 124.5, 123.1, 122.0, 120.8, 119.4, 110.1, 41.4, 38.9, 15.3 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}NOS+H]^+$ 246.0953; Found: 246.0957.

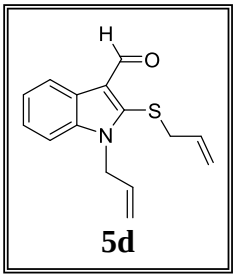
**1-Benzyl-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5c)**




**5c**

Yellowish oil (78%); **IR** (neat): $\nu_{max}$ 2921, 1671, 975, 968, 788, 756, 709, 675, 655 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.21 (s, 1H), 8.34-8.31 (m, 1H), 7.25-7.17 (m, 6H), 6.99-6.97 (m, 2H), 5.70-5.60 (m, 1H), 5.56 (s, 2H), 4.90 (d, $J$ = 10.0 Hz, 1H), 4.70 (dd, $J_1$ = 16.8 Hz, $J_2$ = 1.2 Hz, 1H), 3.15 (d, $J$ = 7.6 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.7, 141.5, 137.8, 136.5, 132.2, 129.0, 127.9, 126.3, 125.3, 124.9, 123.3, 122.0, 121.5, 119.6, 110.8, 47.3, 40.9 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{17}NOS+H]^+$ 308.1109; Found: 308.1114.

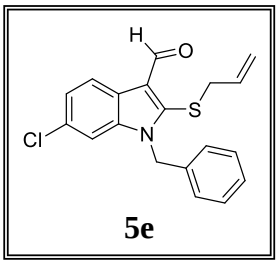
**1-(Prop-2-en-1-yl)-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5d)**




**5d**

Yellowish oil (81%); **IR** (neat): $\nu_{max}$ 1656, 1454, 1381, 1333, 1199, 990, 921, 746 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.18 (s, 1H), 8.30-8.28 (m, 1H), 7.25-7.18 (m, 3H), 5.94-5.85 (m, 1H), 5.77-5.67 (m, 1H), 5.15-5.13 (m, 1H), 4.96-4.75 (m, 5H), 3.35 (d, $J$ = 7.6 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.7, 141.3, 137.5, 132.4, 132.3, 125.2, 124.7, 123.3, 122.0, 121.2, 119.5, 117.5, 110.7, 46.1, 40.9 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{15}NOS+H]^+$ 258.0953; Found: 258.0944.

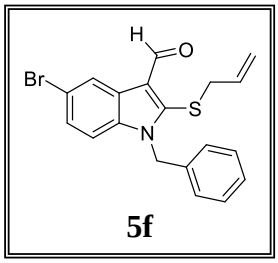
**1-Benzyl-6-chloro-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5e)**




**5e**

Yellowish amorphous solid (76%); **IR** (neat): $\nu_{max}$ 1723, 1653, 1606, 1452, 1378, 1334, 1071, 859, 807, 699 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.25 (s, 1H), 8.32-8.30 (m, 1H), 7.32-7.26 (m, 5H), 7.06-7.04 (m, 2H), 5.78-5.67 (m, 1H), 5.59 (s, 2H), 4.99 (d, $J$ = 10.0 Hz, 1H), 4.78 (dd, $J_1$ = 16.8 Hz, $J_2$ = 1.2 Hz, 1H), 3.22 (d, $J$ = 7.6 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.5, 142.1, 138.2, 136.0, 132.0, 131.0, 129.1, 128.1, 126.2, 124.1, 123.7, 123.0, 121.6, 119.8, 110.7, 47.3, 40.8 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{16}ClNOS+H]^+$ 342.0719; Found: 342.0713.

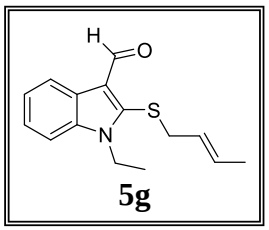
**1-Benzyl-5-bromo-2-[(prop-2-en-1-yl)sulfanyl]-1*H*-indole-3-carbaldehyde (5f)**




**5f**

Yellowish amorphous solid (79%); **IR** (neat): $\nu_{max}$ 2923, 1725, 1658, 1606, 1442, 1384, 1338, 1264, 1189, 804, 731, 701 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.14 (s, 1H), 8.48 (s, 1H), 7.28-7.17 (m, 4H), 7.04-7.02 (m, 1H), 6.95-6.94 (m, 2H), 5.69-5.56 (m, 1H), 5.52 (s, 2H), 4.90 (d, $J$ = 10.0 Hz, 1H), 4.71-4.67 (m, 1H), 3.15 (d, $J$ = 7.2 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.4, 142.3, 136.4, 136.0, 132.0, 129.1, 128.1, 127.9, 126.6, 126.2, 124.6, 120.9, 119.8, 117.1, 112.2, 47.4, 40.8 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{16}BrNOS+H]^+$ 386.0214; Found: 386.0221.

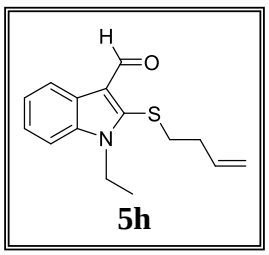
**2-{[(2*E*)-But-2-en-1-yl]sulfanyl}-1-ethyl-1*H*-indole-3-carbaldehyde (5g)**




**5g**

Yellowish oil (73%); **IR** (neat): $\nu_{max}$ 2926, 1676, 977, 915, 865, 777, 731, 689, 625 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.14 (s, 1H), 8.32-8.30 (m, 1H), 7.34-7.22 (m, 3H), 5.43-5.37 (m, 1H), 5.26-5.18 (m, 1H), 4.42-4.36 (m, 2H), 3.34 (d, $J$ = 7.6 Hz, 2H), 1.50 (dd, $J_1$ = 6.4 Hz, $J_2$ = 0.8 Hz, 3H), 1.36 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.4, 141.4, 136.8, 131.1, 125.4, 125.1, 124.4, 123.0, 122.0, 120.8, 110.1, 41.0, 38.8, 17.7, 15.3 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}NOS+H]^+$ 260.1109; Found: 260.1106.

**2-[(But-3-en-1-yl)sulfanyl]-1-ethyl-1*H*-indole-3-carbaldehyde (5h)**




**5h**

Yellowish oil (78%); **IR** (neat): $\nu_{max}$ 3060, 2672, 1338, 1104, 998, 966, 916, 790, 731, 654, 611 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.32 (s, 1H), 8.37 (d, $J$ = 7.2 Hz, 1H), 7.40-7.26 (m, 3H), 5.81-5.71 (m, 1H), 5.09-5.05 (m, 2H), 4.44 (q, $J$ = 7.2 Hz, 2H), 2.94-2.90 (m, 2H),

2.36-2.33 (m, 2H), 1.43 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 187.1, 141.8, 136.9, 135.3, 125.5, 124.5, 123.2, 122.0, 120.6, 117.2, 110.2, 38.9, 37.6, 33.7, 15.3 ppm; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}NOS+H]^+$ 260.1109; Found: 260.1114.

### 3. NMR Studies for the transformation of products 5 to 8

The reaction pathway for the formation of alcohols **8** *via* intermediate **7** was monitored using NMR spectral studies. In figures S1-S3, spectrum A represented the NMR spectrum for aldehyde **5e**. Spectrum B was recorded at a reaction time of 2 h. It indicates that the aldehyde's starting material completely converted and formed as a mixture of intermediate **7** and product **8e**. It was identified using the mixture of peaks from intermediate **7** and peaks from respective alcohol **8e**. Spectrum C was recorded at a reaction time of 4 h indicating the interconversion of intermediate **7** [minor] to respective alcohol **8e** [major]. Spectrum D was recorded after 5 h, which indicated the complete conversion of intermediate **7** into corresponding alcohol **8e**.

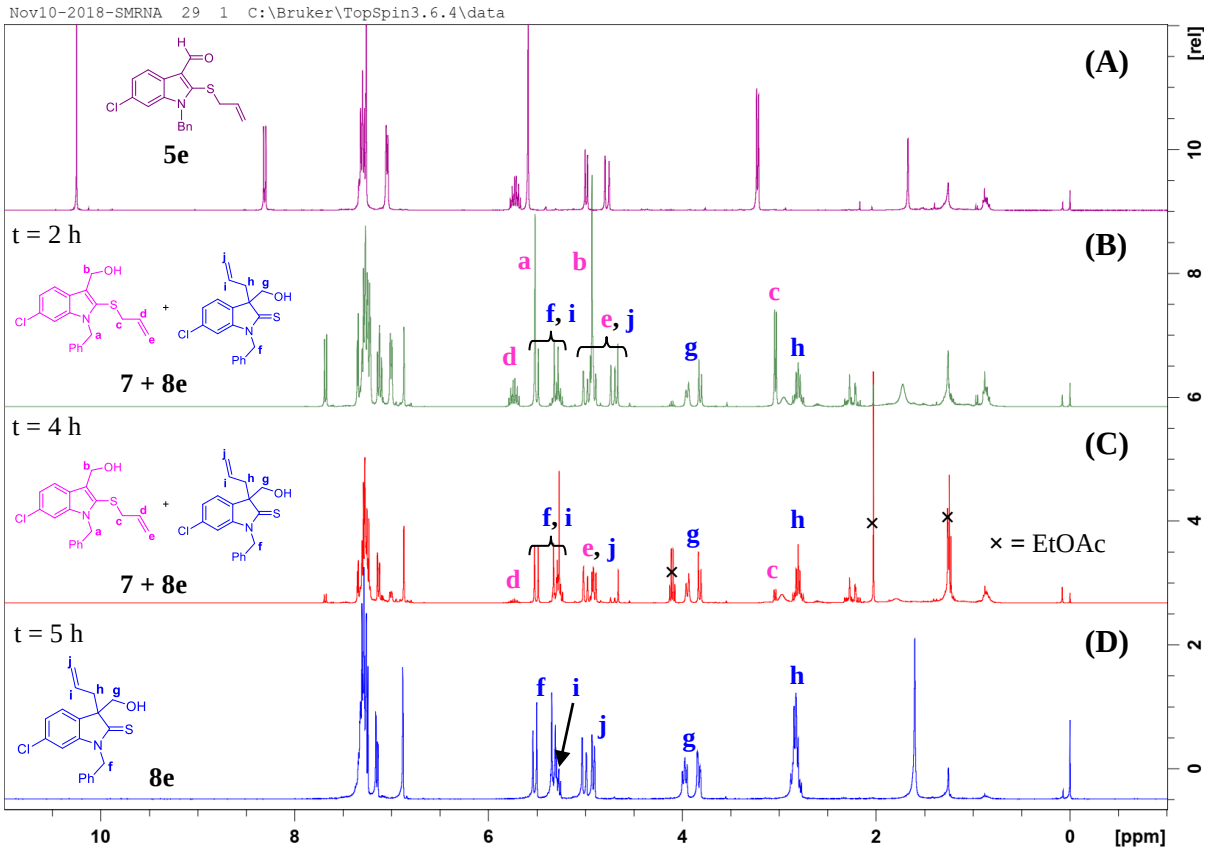



**Figure S1:** $^1$H NMR studies for the formation of alcohol **8** *via* intermediate **7**

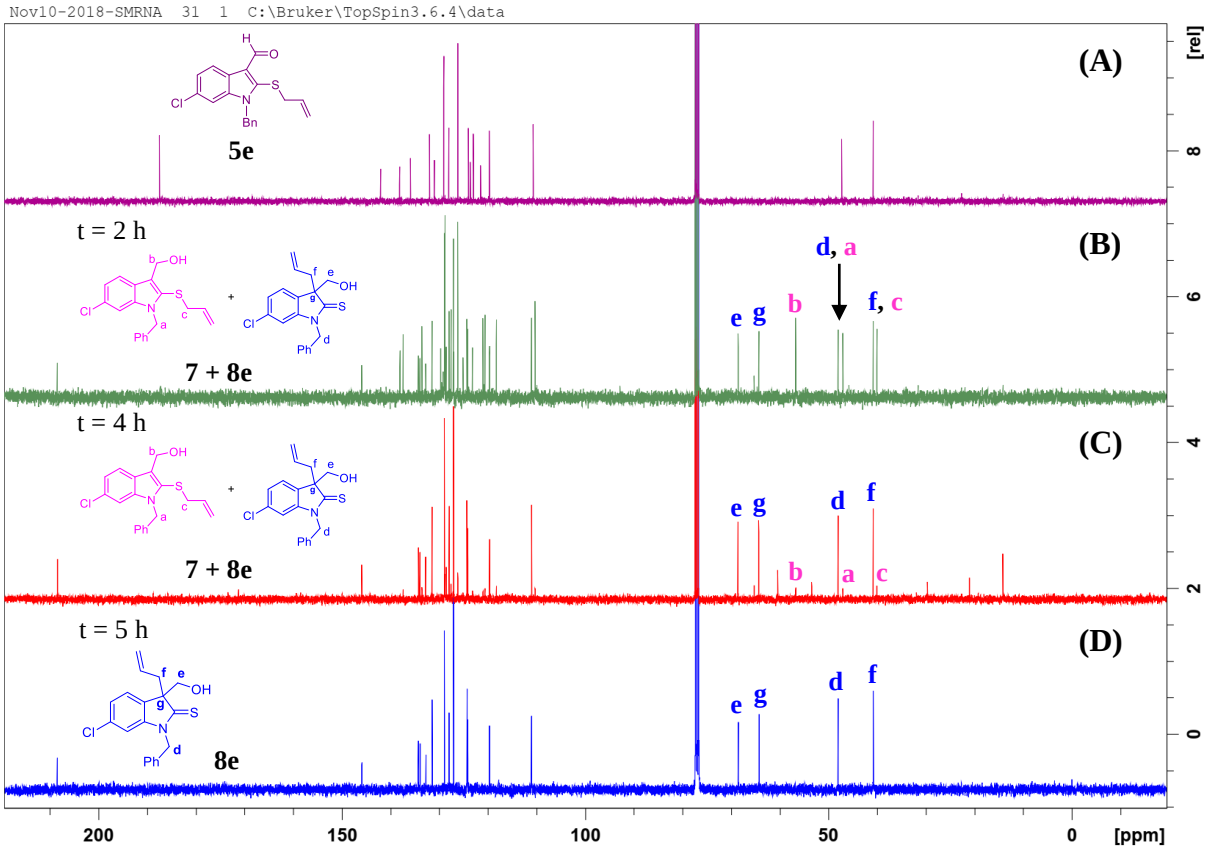



**Figure S2:** $^{13}$C NMR studies for the formation of alcohol **8** *via* intermediate **7**

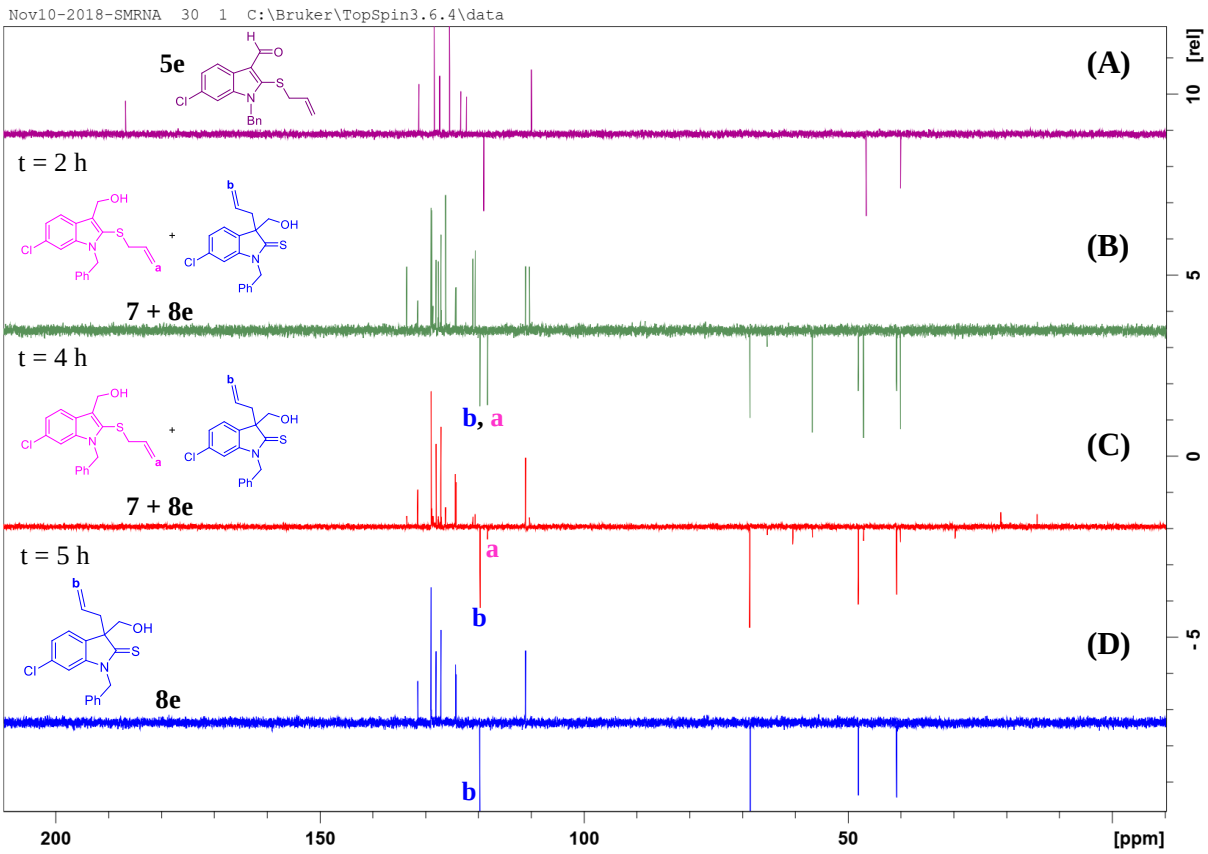
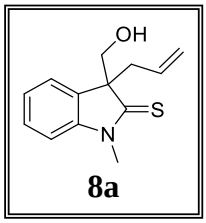



**Figure S3:** DEPT-135 NMR studies for the formation of alcohol **8** *via* intermediate **7**

## 4. General procedure for the synthesis of alcohols 8/9

To the stirred solution of aldehyde **5** (1 equiv) in MeOH (5 mL) was added $NaBH_4$ (1.1 equiv) slowly at 0 ℃ under a nitrogen atmosphere. The reaction mixture was allowed to stir for 5 h at 0 ℃ to room temperature and after completion of the reaction, the solvent is evaporated under reduced pressure. To the residue, the water was added, then adjusts the *p*H to 3 using dil. HCl and extracted with DCM (3 x 50 mL). The combined organic layers were dried over $Na_2SO_4$, and concentrated. The crude residue was purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 7:3) to furnish the corresponding alcohols **8**/**9**.

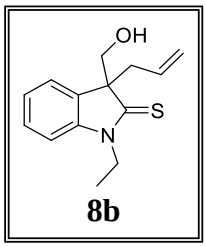
**3-(Hydroxymethyl)-1-methyl-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8a)**




**8a**

Pale yellowish oil (66%); **IR** (neat): $\nu_{max}$ 3061, 2926, 1676, 995, 966, 906, 798, 751, 707, 685, 652, 620 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32-7.25 (m, 2H), 7.19-7.12 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.26-5.18 (m, 1H), 4.92-4.78 (m, 2H), 3.87-3.85 (m, 1H), 3.69-3.66 (m, 1H), 3.56 (s, 3H), 3.08 (br s, 1H), 2.73 (d, *J* = 7.2 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 205.9, 144.3, 133.3, 130.8, 127.5, 123.3, 122.5, 118.1, 108.6, 66.9, 63.0, 39.6, 30.2 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{13}H_{15}NOS+H]^+$ 234.0953; Found: 234.0957.

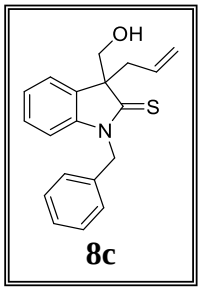
**1-Ethyl-3-(hydroxymethyl)-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8b)**




**8b**

Pale yellowish oil (62%); **IR** (neat): $\nu_{max}$ 3068, 2921, 1681, 989, 954, 780, 756, 707, 688, 655, 624 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38-7.32 (m, 2H), 7.22-7.18 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.32-5.21 (m, 1H), 4.98-4.84 (m, 2H), 4.39-4.30 (m, 1H), 4.21-4.12 (m, 1H), 3.95-3.90 (m, 1H), 3.76-3.72 (m, 1H), 3.19-3.16 (m, 1H), 2.87-2.75 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 206.0, 144.4, 134.7, 131.7, 128.5, 124.2, 123.7, 119.1, 109.7, 68.0, 63.9, 40.7, 39.3, 11.4 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{17}NOS+H]^+$ 248.1109; Found: 248.1116.

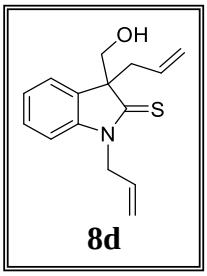
**1-Benzyl-3-(hydroxymethyl)-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8c)**




**8c**

Pale yellowish oil (56%); **IR** (neat): $\nu_{max}$ 3055, 2920, 1686, 1005, 959, 916, 783, 751, 707, 683, 652, 615 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34-7.14 (m, 8H), 6.89 (d, $J$ = 7.6 Hz, 1H), 5.57-5.53 (m, 1H), 5.37-5.27 (m, 2H), 5.03-4.98 (m, 1H), 4.90-4.86 (m, 1H), 3.99-3.94 (m, 1H), 3.82-3.79 (m, 1H), 3.16-3.14 (m, 1H), 2.91-2.79 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.7, 144.8, 134.5, 134.4, 131.9, 128.9, 128.5, 127.8, 127.2, 124.4, 123.6, 119.4, 110.7, 68.6, 64.4, 48.0, 40.8 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{19}NOS+H]^+$ 310.1266; Found: 310.1270.

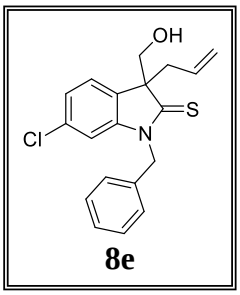
**3-(Hydroxymethyl)-1,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8d)**




**8d**

Yellowish oil (65%); **IR** (neat): $\nu_{max}$ 3419, 3056, 2918, 1720, 1643, 1610, 1459, 1387, 1223, 1023, 920, 802, 734, 623 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28-7.24 (m, 2H), 7.16-7.12 (m, 1H), 6.95-6.93 (m, 1H), 5.83-5.72 (m, 1H), 5.28-5.09 (m, 3H), 4.93-4.86 (m, 2H), 4.82-4.77 (m, 1H), 4.73-4.69 (m, 1H), 3.91-3.86 (m, 1H), 3.72-3.69 (m, 1H), 3.01-2.99 (m, 1H), 2.82-2.70 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.0, 144.7, 134.3, 131.8, 129.4, 128.5, 124.3, 123.5, 119.3, 118.2, 110.4, 68.3, 64.2, 46.6, 40.7 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}NOS+H]^+$ 260.1109; Found: 260.1101.

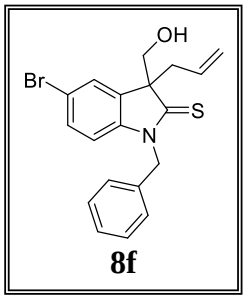
**1-Benzyl-6-chloro-3-(hydroxymethyl)-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8e)**




**8e**

Yellowish oil (63%); **IR** (neat): $\nu_{max}$ 3418, 2922, 2858, 1606, 1487, 1431, 1381, 1220, 1069, 1023, 854, 734, 698 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35-7.24 (m, 6H), 7.16-7.14 (m, 1H), 6.89-6.88 (m, 1H), 5.54-5.50 (m, 1H), 5.36-5.26 (m, 2H), 5.04-4.99 (m, 1H), 4.93-4.91 (m, 1H), 4.00-3.95 (m, 1H), 3.85-3.81 (m, 1H), 2.88-2.77 (m, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 208.5, 145.9, 134.3, 134.0, 132.8, 131.5, 129.0, 128.0, 127.1, 124.3, 124.2, 119.7, 111.1, 68.6, 64.3, 48.1, 40.9 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}ClNOS+H]^+$ 344.0876; Found: 344.0869.

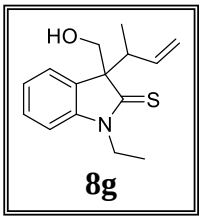
**1-Benzyl-5-bromo-3-(hydroxymethyl)-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (8f)**




**8f**

Yellowish oil (68%); **IR** (neat): $\nu_{max}$ 3432, 2923, 2857, 1722, 1607, 1431, 1385, 1336, 1216, 1062, 995, 922, 809, 736, 700 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.47-7.46 (m, 1H), 7.37-7.35 (m, 1H), 7.30-7.26 (m, 5H), 6.75 (d, $J$ = 8.4 Hz, 1H), 5.56-5.52 (m, 1H), 5.36-5.26 (m, 2H), 5.07-5.02 (m, 1H), 4.95-4.92 (m, 1H), 4.01-3.96 (m, 1H), 3.86-3.83 (m, 1H), 2.89-2.77 (m, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.4, 143.9, 136.6, 134.1, 131.5, 131.4, 128.9, 128.0, 127.1, 126.9, 119.8, 117.8, 111.8, 68.6, 64.7, 48.1, 40.8 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}BrNOS+H]^+$ 388.0371; Found: 388.0381.

**3-(But-3-en-2-yl)-1-ethyl-3-(hydroxymethyl)-1,3-dihydro-2*H*-indole-2-thione (8g)**

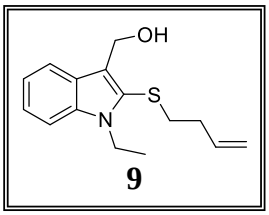



**8g**

Pale yellowish oil (58%); dr = >95:5; **IR** (neat): $\nu_{max}$ 3056, 2914, 1663, 984, 963, 906, 785, 746, 717, 685, 652, 623 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40-7.32 (m, 2H), 7.21-7.16 (m, 1H), 7.08-7.03 (m, 1H), 6.14-6.05 (m, 1H), 5.30-5.26 (m, 2H), 4.46-4.36 (m, 1H), 4.21-4.02 (m, 2H), 3.69-3.65 (m, 1H), 3.40 (dd, $J_1$ = 9.6 Hz, $J_2$ = 3.6 Hz, 1H), 3.28 (quint, $J$ = 7.2 Hz, 1H), 1.34 (t, $J$ = 7.2 Hz, 3H), 0.48 (d, $J$ = 6.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 206.9, 144.7, 138.1, 133.0, 128.6, 124.5, 124.0, 117.7, 109.6, 66.8, 66.6, 43.0, 39.4, 13.7,

11.3 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{19}NOS+H]^+$ 262.1266; Found: 262.1263.

**{2-[(But-3-en-1-yl)sulfanyl]-1-ethyl-1*H*-indol-3-yl}methanol (9)**




**9**

Pale yellowish oil (63%); **IR** (neat): $\nu_{max}$ 3053, 2929, 1681, 994, 972, 914, 786, 729, 654, 628 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.75 (d, *J* = 8.0 Hz, 1H), 7.36-7.34 (m, 1H), 7.29-7.27 (m, 1H), 7.18-7.14 (m, 1H), 5.84-5.74 (m, 1H), 5.10-5.01 (m, 4H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.33-2.28 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 136.7, 136.0, 128.6, 126.7, 123.1, 121.3, 119.9, 119.3, 116.5, 109.9, 56.9, 38.5, 36.8, 33.7, 15.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{19}NOS+H]^+$ 262.1266; Found: 262.1263.

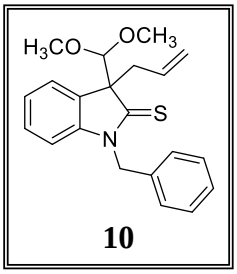
## 5. Experimental procedure for products 10-12

*Procedure for product **10***: A solution of aldehyde **5c** (0.33 mmol), trimethyl orthoformate (0.99 mmol) and *p*-toluenesulfonic acid monohydrate (3 mg, 0.017 mmol) in methanol (20 mL) was stirred at room temperature. After 8 h, the solution was diluted with ethyl acetate and the organic solvent was removed under vacuum. The resulting mixture was workup with ethyl acetate (3 x 20 mL) and washed with saturated aqueous $NaHCO_3$. The combined organics were dried over $Na_2SO_4$ and concentrated *in vacuo*. The resulting mixture was purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 9:1) to provide product **10**.

*Procedure for product **11***: *n*-BuLi (1.6M in hexane, 0.3 mL, 0.49 mmol) was added dropwise to a stirred solution of methyltriphenylphosphonium bromide (0.49 mmol) in dry THF (20 mL) at -30 ℃ (immersion cooler). The mixture was stirred at -30 ℃ for 10 min then at room temperature for 2 h. The mixture was cooled again to -30 ℃ (immersion cooler) and was treated slowly with a solution of the aldehyde **5c** (0.325 mmol) in dry THF (5 mL). The reaction mixture was allowed to warm to room temperature and stir 6 h. The mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 9:1) to provide product **11**.

*Procedure for product **12***: In a 50 mL RB flask equipped with a magnetic stirrer placed 0.4 mmol of aldehyde **5b** and 0.44 mmol of 1,2-ethanedithiol in 20 mL of dichloromethane. To the stirred solution are added 2 drops of boron trifluoride etherate. The mixture is stirred at room temperature for 4 h. Then the mixture was quenched with water and workup with dichloromethane (3 x 20 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 9:1) to furnish the corresponding product **12**.

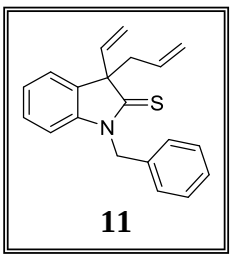
**1-Benzyl-3-(dimethoxymethyl)-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (10)**




**10**

Colorless oil (62%); **IR** (neat): $\nu_{max}$ 3040, 2926, 1071, 1006, 869, 755, 723, 692, 635, 621, 596, 552 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55-7.53 (m, 1H), 7.28-7.12 (m, 7H), 6.81 (d, $J$ = 7.6 Hz, 1H), 5.46 (ABq, $\Delta\delta_{AB}$ = 0.32, $J_{AB}$ = 15.6 Hz, 2H), 5.18-5.08 (m, 1H), 4.97-4.92 (m, 1H), 4.81-4.77 (m, 2H), 3.65 (s, 3H), 3.38 (s, 3H), 3.02-2.89 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 205.1, 145.3, 134.7, 133.2, 131.8, 128.6, 128.2, 127.5, 127.0, 125.5, 124.0, 118.9, 112.4, 109.9, 67.9, 59.6, 58.9, 47.8, 41.1 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{21}H_{23}NO_2S+H]^+$ 354.1528; Found: 354.1530.

**1-Benzyl-3-ethenyl-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (11)**

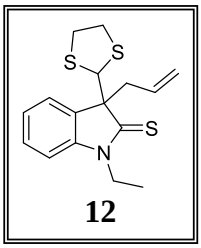



**11**

Colorless oil (56%); **IR** (neat): $\nu_{max}$ 3042, 2923, 1078, 1026, 869, 723, 692, 642, 621, 595, 555 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.25-7.07 (m, 8H), 6.83 (d, $J$ = 7.6 Hz, 1H), 6.13-6.06 (m, 1H), 5.50-5.44 (m, 1H), 5.31-5.24 (m, 2H), 5.09 (d, $J$ = 10.4 Hz, 1H), 4.94-4.81 (m, 2H), 4.84-4.81 (m, 1H), 2.82 (d, $J$ = 7.2 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.5, 144.5, 140.3, 134.8, 134.4, 132.3, 128.8, 128.2, 127.7, 127.2, 125.2, 123.9, 119.3, 115.1,

110.6, 65.5, 48.1, 44.7 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{20}H_{19}NS+H]^+$ 306.1316; Found: 306.1302.

**3-(1,3-Dithiolan-2-yl)-1-ethyl-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (12)**



**12**

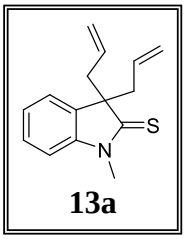
Yellowish oil (48%); **IR** (neat): $\nu_{max}$ 3047, 2916, 1071, 1026, 955, 869, 755, 722, 692, 646, 627, 596, 552 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 7.6 Hz, 1H), 7.33-7.29 (m, 1H), 7.09-7.06 (m, 1H), 6.96 (d, $J$ = 8.0 Hz, 1H), 5.17 (s, 1H), 4.99-4.89 (m, 1H), 4.84-4.80 (m, 1H), 4.64 (dd, $J_1$ = 10.0 Hz, $J_2$ = 2.0 Hz, 1H), 4.33-4.20 (m, 1H), 4.19-4.10 (m, 1H), 3.09-3.05 (m, 2H), 2.91-2.86 (m, 1H), 2.82-2.75 (m, 2H), 2.36-2.30 (m, 1H), 1.25 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 204.9, 145.7, 133.4, 131.7, 128.7, 125.6, 123.3, 118.8, 109.2, 67.3, 63.0, 44.5, 40.1, 39.5, 37.4, 11.3 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{16}H_{19}NS_3+H]^+$ 322.0758; Found: 322.0760.

**6. General procedure for the synthesis of diolefins 13/14**

An oven-dried flask under an inert atmosphere was charged with the appropriate alcohol **8** (1.0 equiv) and anhydrous powdered $K_2CO_3$ (1.2 equiv) in dry dimethylformamide (25 mL) and stirred at 0 °C for 10 min. Alkyl/alkenyl/alkynyl halide (1.2 equiv) and tetrabutylammonium iodide (TBAI, 0.1 equiv) was added to the above reaction mixture. The reaction mixture was stirred at room temperature for overnight. Water (50 mL) was added to the reaction mixture and extracted with dichloromethane (3 x 25 mL). The entire organic layers were combined and washed with water (50 mL). Finally, the organic layer was dried over $Na_2SO_4$, evaporated, and purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 9:1) to afford the respective diolefin product **13**/**14a-g**.

*Procedure for products **14h,i***: An oven-dried flask, alcohol **8b** (1.0 equiv.) and appropriate carboxylic acid (1.2 equiv) in dichloromethane were charged under inert atmosphere. *N,N'*-Dicyclohexylcarbodiimide (DCC) (1.2 equiv) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added to the above reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 8 h. Progress of the reaction was monitored using TLC. Finally, the solid obtained in the reaction was filtered. The filtrate was concentrated and purified by column chromatography using silica gel (100-200 mesh; *n*-hexanes:EtOAc = 7:3) to furnish the corresponding esterification products **14h,i**.

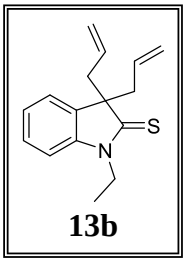
**1-Methyl-3,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13a)**



**13a**

Colorless oil (87%); **IR** (neat): $\nu_{max}$ 3043, 2932, 1623, 975, 781, 741, 737, 611 $cm^{-1}$; **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34-7.29 (m, 2H), 7.20-7.18 (m, 1H), 7.01-6.99 (m, 1H), 5.27-5.19 (m, 2H), 4.94-4.79 (m, 4H), 3.61 (s, 3H), 2.73-2.71 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.9, 145.3, 135.9, 132.3, 128.0, 123.9, 123.7, 118.7, 109.2, 63.0, 44.7, 31.3 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}NS+H]^+$ 244.1160; Found: 244.1171.

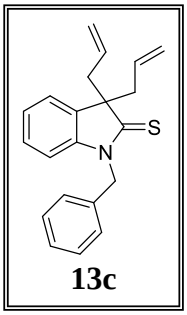
**1-Ethyl-3,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13b)**



**13b**

Colorless oil (82%); **IR** (neat): $\nu_{max}$ 3070, 2925, 1674, 991, 961, 902, 792, 750, 706, 610 $cm^{-1}$; **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.26-7.22 (m, 2H), 7.12-7.08 (m, 1H), 6.92 (d, $J$ = 7.6 Hz, 1H), 5.18-5.07 (m, 2H), 4.86-4.81 (m, 2H), 4.73-4.70 (m, 2H), 4.17 (q, $J$ = 7.2 Hz, 2H), 2.69-2.59 (m, 4H), 1.20 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 206.9, 144.3, 136.2, 132.2, 127.9, 123.8, 123.7, 118.7, 109.2, 62.7, 44.7, 39.3, 11.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{16}H_{19}NS+H]^+$ 258.1316; Found: 258.1323.

**1-Benzyl-3,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13c)**

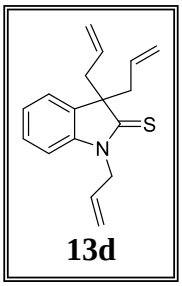


**13c**

Colorless oil (79%); **IR** (neat): $\nu_{max}$ 3051, 2916, 1656, 985, 956, 916, 788, 717, 675, 642, 630 $cm^{-1}$; **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31-7.12 (m, 8H), 6.86 (d, $J$ = 7.6 Hz, 1H), 5.45 (s, 2H), 5.31-5.20 (m, 2H), 4.98-4.94 (m, 2H), 4.86-4.83 (m, 2H), 2.79-2.76 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 208.8, 144.7, 135.9, 134.9, 132.4, 128.7, 127.9, 127.7, 127.4,

123.9, 123.7, 119.0, 110.2, 63.1, 48.2, 45.1 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{21}H_{21}NS+H]^+$ 320.1473; Found: 320.1477.

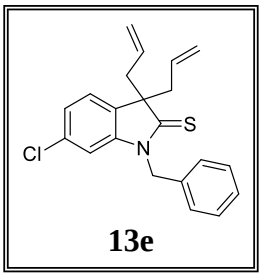
**1,3,3-Tri(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13d)**




**13d**

Colorless oil (85%); **IR** (neat): $\nu_{max}$ 2921, 2853, 1709, 1609, 1462, 1433, 1383, 1043, 919, 799, 747 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.24-7.19 (m, 2H), 7.13-7.09 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.80-5.71 (m, 1H), 5.21-5.09 (m, 4H), 4.88-4.84 (m, 2H), 4.79-4.73 (m, 4H), 2.68-2.65 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.9, 144.5, 135.8, 132.3, 129.8, 127.9, 123.9, 123.7, 118.9, 117.9, 110.0, 63.1, 46.8, 44.9 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{19}NS+H]^+$ 270.1316; Found: 270.1313.

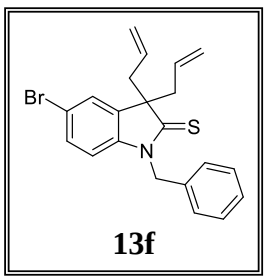
**1-Benzyl-6-chloro-3,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13e)**




**13e**

Colorless oil (79%); **IR** (neat): $\nu_{max}$ 3073, 2922, 2855, 1640, 1605, 1429, 1375, 1346, 1221, 1073, 988, 921, 853, 813, 734, 698 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32-7.26 (m, 5H), 7.21-7.20 (m, 1H), 7.13-7.10 (m, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 5.41 (s, 2H), 5.30-5.19 (m, 2H), 4.99-4.94 (m, 2H), 4.88-4.85 (m, 2H), 2.81-2.70 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 209.5, 145.8, 134.3, 134.2, 133.7, 132.0, 128.8, 127.9, 127.3, 124.4, 123.8, 119.4, 110.7, 63.0, 48.2, 45.1 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{21}H_{20}ClNS+H]^+$ 354.1083; Found: 354.1076.

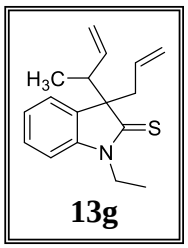
**1-Benzyl-5-bromo-3,3-di(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13f)**




**13f**

Colorless oil (85%); **IR** (neat): $\nu_{max}$ 3073, 2924, 2853, 1640, 1607, 1429, 1382, 1331, 1223, 1191, 990, 921, 806, 735, 699 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.34 (s, 1H), 7.24-7.20 (m, 6H), 6.63 (d, $J$ = 8.4 Hz, 1H), 5.34 (s, 2H), 5.23-5.12 (m, 2H), 4.94-4.90 (m, 2H), 4.82-4.80 (m, 2H), 2.74-2.62 (m, 4H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 208.4, 143.7, 138.1, 134.4, 131.9, 130.9, 128.8, 127.9, 127.3, 126.8, 119.6, 117.4, 111.5, 63.4, 48.3, 45.0 ppm; **HRMS** (ESI) $m/z$: $[M+H]^+$ Calcd for $[C_{21}H_{20}BrNS+H]^+$ 398.0578; Found: 398.0569.

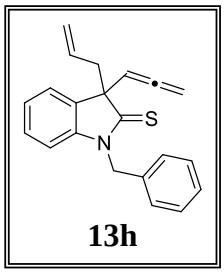
**3-(But-3-en-2-yl)-1-ethyl-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13g)**




**13g**

Colorless oil (77%); dr = 86:14; **IR** (neat): $\nu_{max}$ 2962, 1767, 995, 976, 960, 789, 715, 658, 625, 602 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35-7.30 (m, 2H), 7.18-7.14 (m, 1H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.03-5.96 (m, 1H), 5.24-5.20 (m, 2H), 5.00-4.96 (m, 1H), 4.85-4.80 (m, 1H), 4.68-4.65 (m, 1H), 4.31-4.24 (m, 2H), 2.89-2.80 (m, 1H), 2.78-2.76 (m, 2H), 1.30 (t, $J$ = 7.2 Hz, 3H), 0.49 (d, $J$ = 6.8 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.4, 144.8, 138.7, 134.7, 132.6, 127.9, 124.6, 123.5, 118.2, 117.5, 109.1, 65.8, 47.9, 43.6, 39.4, 14.7, 11.4 ppm; **HRMS** (ESI) $m/z$: $[M+H]^+$ Calcd for $[C_{17}H_{21}NS+H]^+$ 272.1473; Found: 272.1469.

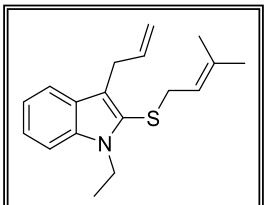
**1-Benzyl-3-propadienyl-3-(prop-2-en-1-yl)-1,3-dihydro-2*H*-indole-2-thione (13h)**




**13h**

Colourless oil (73%); **IR** (neat): $\nu_{max}$ 3067, 2921, 1670, 964, 891, 716, 692, 641, 620, 596, 557 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33-7.26 (m, 5H), 7.25-7.23 (m, 1H), 7.21-7.19 (m, 1H), 7.16-7.12 (m, 1H), 6.88 (d, $J$ = 8.0 Hz, 1H), 5.60-5.56 (m, 2H), 5.35-5.29 (m, 2H), 5.01-4.96 (m, 1H), 4.93-4.87 (m, 2H), 4.76-4.71 (m, 1H), 2.89-2.86 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 207.8, 207.2, 144.1, 135.0, 134.7, 132.2, 128.8, 128.2, 127.7, 127.3, 125.0, 123.8, 119.4, 110.3, 95.3, 78.9, 61.8, 48.3, 45.3 ppm; **HRMS** (ESI) $m/z$: $[M+H]^+$ Calcd for $[C_{21}H_{19}NS+H]^+$ 318.1316; Found: 318.1317.

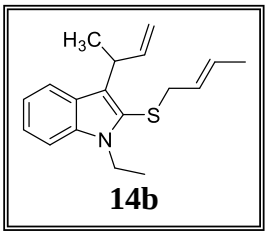
**1-Ethyl-2-[(3-methylbut-2-en-1-yl)sulfanyl]-3-(prop-2-en-1-yl)-1*H*-indole (14a)**



**14a**

Colorless oil (78%); **IR** (neat): $\nu_{max}$ 3016, 2962, 1667, 959, 906, 789, 751, 707, 658, 623 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 (dd, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.03-5.99 (m, 1H), 5.27-5.23 (m, 1H), 5.13-5.00 (m, 2H), 4.37 (q, $J$ = 7.2 Hz, 2H), 3.71-3.69 (m, 2H), 3.30 (d, $J$ = 8.0 Hz, 2H), 1.66 (s, 3H), 1.40 (s, 3H), 1.35 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 137.8, 136.63, 136.56, 127.4, 127.2, 122.5, 120.2, 119.7, 119.4, 118.9, 114.7, 109.7, 38.3, 35.7, 30.3, 25.7, 17.4, 15.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{18}H_{23}NS+H]^+$ 286.1629; Found: 286.1637.

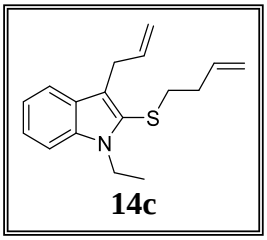
**3-(But-3-en-2-yl)-2-{[(2*E*)-but-2-en-1-yl]sulfanyl}-1-ethyl-1*H*-indole (14b)**



**14b**

Colorless oil (68%); **IR** (neat): $\nu_{max}$ 3058, 2920, 1676, 995, 969, 906, 798, 751, 707, 685, 655, 615 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.68 (d, $J$ = 8.0 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 1H), 7.24-7.18 (m, 1H), 7.05-7.01 (m, 1H), 6.29-6.19 (m, 1H), 5.54-5.35 (m, 2H), 5.14-5.02 (m, 2H), 4.41-4.33 (m, 2H), 4.19-4.13 (m, 1H), 3.35-3.24 (m, 2H), 1.60-1.58 (m, 2H), 1.54-1.51 (m, 3H), 1.45-1.43 (m, 1H), 1.38-1.33 (m, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 143.0, 137.0, 129.1, 128.0, 126.5, 125.8, 125.4, 122.3, 120.9, 118.6, 112.7, 109.8, 40.1, 38.4, 35.9, 20.1, 17.8, 15.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{18}H_{23}NS+H]^+$ 286.1629; Found: 286.1623.

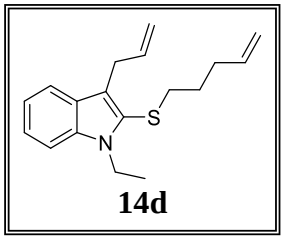
**2-[(But-3-en-1-yl)sulfanyl]-1-ethyl-3-(prop-2-en-1-yl)-1*H*-indole (14c)**



**14c**

Colorless oil (76%); **IR** (neat): $\nu_{max}$ 3050, 2916, 1676, 995, 778, 751, 707, 685, 657, 632 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 7.6 Hz, 1H), 7.32 (d, $J$ = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.10-7.06 (m, 1H), 6.07-5.97 (m, 1H), 5.83-5.77 (m, 1H), 5.11-5.00 (m, 4H), 4.37 (q, $J$ = 7.2 Hz, 2H), 3.72-3.69 (m, 2H), 2.73-2.70 (m, 2H), 2.30-2.25 (m, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 137.6, 136.7, 136.3, 127.3, 127.2, 122.6, 119.9, 119.7, 119.1, 116.3, 114.8, 109.7, 38.5, 36.5, 33.8, 30.3, 15.6 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{21}NS+H]^+$ 272.1473; Found: 272.1478.

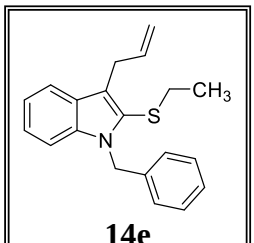
**1-Ethyl-2-[(pent-4-en-1-yl)sulfanyl]-3-(prop-2-en-1-yl)-1*H*-indole (14d)**




**14d**

Colorless oil (68%); **IR** (neat): $\nu_{max}$ 3060, 2925, 1675, 994, 965, 905, 797, 750, 706, 684, 651, 619 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 8.0 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 7.24-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.06-5.97 (m, 1H), 5.77-5.67 (m, 1H), 5.11-4.94 (m, 4H), 4.37 (q, $J$ = 7.2 Hz, 2H), 3.70 (d, $J$ = 5.6 Hz, 2H), 2.68-2.64 (m, 2H), 2.16-2.10 (m, 2H), 1.63 (quint, $J$ = 7.6 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 137.6, 137.5, 136.7, 127.4, 127.3, 122.6, 119.8, 119.7, 119.0, 115.4, 114.8, 109.7, 38.4, 36.7, 32.7, 30.3, 28.8, 15.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{18}H_{23}NS+H]^+$ 286.1629; Found: 286.1634.

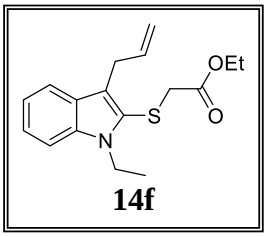
**1-Benzyl-2-(ethylsulfanyl)-3-(prop-2-en-1-yl)-1*H*-indole (14e)**




**14e**

Colorless oil (83%); **IR** (neat): $\nu_{max}$ 3077, 2930, 1679, 1036, 973, 901, 733, 725, 701, 651, 641, 606 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 (d, $J$ = 7.6 Hz, 1H), 7.18-7.07 (m, 5H), 7.06-6.99 (m, 1H), 6.94-6.92 (m, 2H), 6.02-5.92 (m, 1H), 5.49 (s, 2H), 5.06-4.94 (m, 2H), 3.67 (dt, $J_1$ = 6.0 Hz, $J_2$ = 1.6 Hz, 2H), 2.41 (q, $J$ = 7.2 Hz, 2H), 1.02 (t, $J$ = 7.6 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 138.4, 137.62, 137.56, 128.7, 128.1, 127.3, 127.2, 126.2, 123.0, 120.7, 119.7, 119.4, 114.9, 110.4, 47.0, 31.2, 30.4, 14.7 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{20}H_{21}NS+H]^+$ 308.1473; Found: 308.1476.

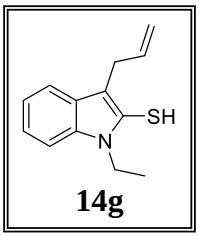
**Ethyl {[1-ethyl-3-(prop-2-en-1-yl)-1*H*-indol-2-yl]sulfanyl}acetate (14f)**




**14f**

Colourless oil (76%); **IR** (neat): $\nu_{max}$ 3077, 2930, 1730, 1679, 1036, 943, 901, 733, 715, 701, 651, 641, 606 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 8.0 Hz, 1H), 7.32 (d, $J$ = 8.4 Hz, 1H), 7.26-7.22 (m, 1H), 7.10-7.06 (m, 1H), 6.06-5.96 (m, 1H), 5.10-5.00 (m, 2H), 4.39 (q, $J$ = 7.2 Hz, 2H), 4.09 (q, $J$ = 7.2 Hz, 2H), 3.72-3.69 (m, 2H), 3.40 (s, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H), 1.16 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 169.4, 137.4, 136.9, 127.1, 125.5, 123.1, 120.9, 120.0, 119.2, 114.9, 109.9, 61.5, 39.3, 38.5, 30.1, 15.6, 14.0 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{21}NO_2S+H]^+$ 304.1371; Found: 304.1372.

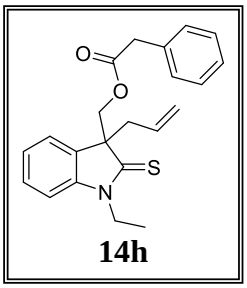
**1-Ethyl-3-(prop-2-en-1-yl)-1*H*-indole-2-thiol (14g)**




**14g**

Brownish liquid (72%); **IR** (neat): $\nu_{max}$ 3078, 2931, 1036, 974, 901, 735, 702, 651, 631, 616, 567 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, $J$ = 8.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.09-7.05 (m, 1H), 5.65-5.55 (m, 1H), 4.81 (d, $J$ = 17.2 Hz, 1H), 4.72 (d, $J$ = 9.6 Hz, 1H), 4.20-4.14 (m, 2H), 3.08 (d, $J$ = 5.6 Hz, 2H), 1.33 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 137.5, 137.0, 126.8, 126.4, 124.0, 123.4, 120.4, 119.3, 114.6, 109.9, 38.3, 29.4, 15.2 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{13}H_{15}NS+H]^+$ 218.1003; Found: 218.1005.

**[1-Ethyl-3-(prop-2-en-1-yl)-2-sulfanylidene-2,3-dihydro-1*H*-indol-3-yl]methyl phenylacetate (14h)**

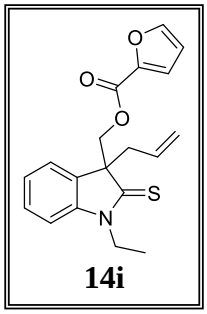



**14h**

Colourless liquid (84%); **IR** (neat): $\nu_{max}$ 1737, 1608, 1458, 1394, 1253, 1131, 754, 706 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.22-7.19 (m, 3H), 7.14-7.06 (m, 2H), 6.96-6.93 (m, 3H), 5.17-5.09 (m, 1H), 4.93-4.89 (m, 1H), 4.82-4.79 (m,

1H), 4.71 (d, $J$ = 10.4 Hz, 1H), 4.27-4.20 (m, 2H), 4.17-4.10 (m, 1H), 3.39 (ABq, $\Delta\delta_{AB}$ = 0.03, $J_{AB}$ = 15.2 Hz, 2H), 2.66 (d, $J$ = 7.2 Hz, 2H), 1.25 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 204.1, 170.6, 144.4, 133.9, 133.6, 130.8, 129.1, 128.5, 128.4, 126.9, 124.2, 123.9, 119.4, 109.3, 69.6, 62.1, 41.2, 41.1, 39.4, 11.3 ppm; **HRMS** (ESI) $m/z$: $[M+H]^+$ Calcd for $[C_{22}H_{23}NO_2S+H]^+$ 366.1528; Found: 366.1520.

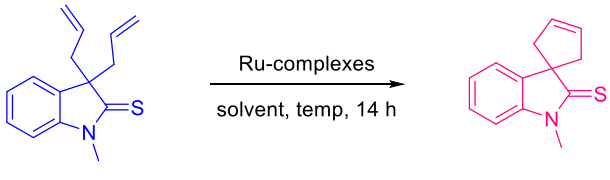
**[1-Ethyl-3-(prop-2-en-1-yl)-2-sulfanylidene-2,3-dihydro-1*H*-indol-3-yl]methyl furan-2-carboxylate (14i)**



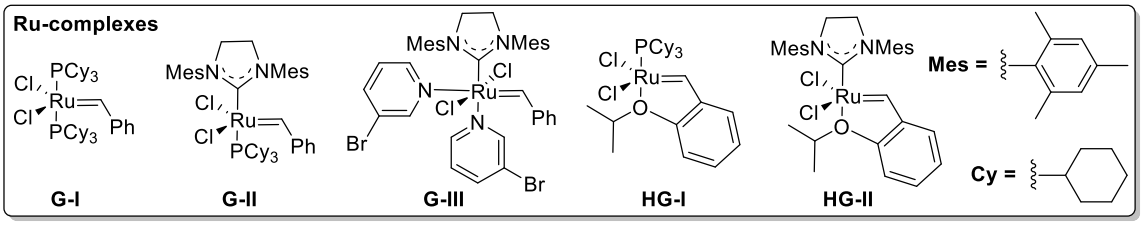
**14i**

Colourless liquid (78%); **IR** (neat): $\nu_{max}$ 1743, 1602, 1551, 1472, 1259, 1125, 1022, 860, 835, 775, 593, 555 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.50 (d, $J$ = 0.8 Hz, 1H), 7.44 (d, $J$ = 7.6 Hz, 1H), 7.36-7.32 (m, 1H), 7.19-7.15 (m, 1H), 7.03 (d, $J$ = 7.6 Hz, 1H), 6.89 (d, $J$ = 3.6 Hz, 1H), 6.43-6.41 (m, 1H), 5.25-5.16 (m, 1H), 4.97 (d, $J$ = 17.2 Hz, 1H), 4.86-4.82 (m, 2H), 4.45 (d, $J$ = 10.4 Hz, 1H), 4.34-4.20 (m, 2H), 2.88-2.75 (m, 2H), 1.32 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 203.8, 157.9, 146.5, 144.5, 144.1, 134.0, 130.9, 128.6, 124.4, 124.1, 119.5, 117.9, 111.7, 109.3, 69.8, 62.1, 41.1, 39.4, 11.4 ppm; **HRMS** (ESI) $m/z$: $[M+H]^+$ Calcd for $[C_{19}H_{19}NO_3S+H]^+$ 342.1164; Found: 342.1162.

## 7. Optimization table for ring-closing metathesis reaction of di-olefin 13a[a]




**13a** **16a**




| Entry | Ru-Complexes | Solvent | Temperature[b] [°C] | Yield of 16a (%)[c] |
|---|---|---|---|---|
| **1** | G-I | $CH_2Cl_2$ | rt | n.r |
| **2** | G-I | $CH_2Cl_2$ | 40 | trace |
| **3** | G-II | $CH_2Cl_2$ | rt | trace |

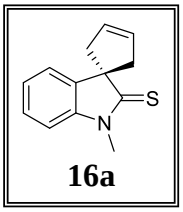
| Entry | Ru-Complexes | Solvent | Temperature[b] [°C] | Yield of 16a (%)[c] |
|---|---|---|---|---|
| **4** | G-II | $CH_2Cl_2$ | 40 | 29 |
| **5** | G-III | $CH_2Cl_2$ | rt | trace |
| **6** | G-III | $CH_2Cl_2$ | 40 | 25 |
| **7** | HG-I | $CH_2Cl_2$ | rt | n.r |
| **8** | HG-I | $CH_2Cl_2$ | 40 | trace |
| **9** | HG-II | $CH_2Cl_2$ | rt | trace |
| **10** | HG-II | $CH_2Cl_2$ | 40 | 26 |
| **11** | G-II | THF | 65 | 52 |
| **12** | G-II | $CH_3CN$ | 80 | 60 |
| **13** | **G-II** | **$PhCH_3$** | **110** | **78** |
| **14** | G-II[d] | $PhCH_3$ | 110 | 79 |
| **15** | G-II[e] | $PhCH_3$ | 110 | 73 |
| **16** | G-II | $PhCH_3$[f] | 110 | 28 |

[a]Reaction conditions unless noted: **13a** (0.35 mmol) and Ru-complexes (10 mol %) in 5 mL of dry solvent for 14 h under $N_2$ atmosphere. [b]Unless rt was carried out in oil bath using glass reflux condenser. [c]Isolated Yield. [d]G-II (15 mol %). [e]G-II (5 mol %). [f]Commercial toluene. rt = room temperature. n.r = no reaction.

## 8. General procedure for the ring-closing metathesis reaction for products 16/17

In an oven-dried flask, di-olefin **13** or **14** (0.35 mmol) in dry toluene (5 mL) with magnetic stir bar were charged under a nitrogen atmosphere. Then, 10 mol% of Grubbs' second-generation catalyst (G-II) in dry toluene (5 mL) was slowly added (30 min) at 110 °C (oil bath) and allowed to stir the above mixture for 14 h. The completion of starting material was monitored using TLC. Then, the reaction mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash chromatography using silica gel (230-400 mesh; *n*-hexanes:EtOAc = 9:1) to afford the respective compound **16**/**17**.

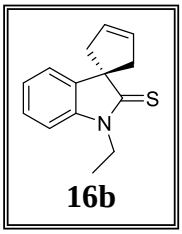
**1'-Methylspiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16a)**




**16a**

White crystalline solid (78%); mp 138-140 °C; **IR** (neat): $\nu_{max}$ 3048, 2921, 1671, 1026, 964, 946, 899, 713, 692, 645, 621, 596, 557 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.18-7.13 (m, 1H), 7.03-7.01 (m, 1H), 5.84 (s, 2H), 3.67 (s, 3H), 3.15-3.11 (m, 2H), 2.68-2.63 (m, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 211.9, 143.5, 142.3, 128.7, 127.8, 124.7, 121.9, 109.3, 63.4, 49.5, 31.7 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{13}H_{13}NS+H]^+$ 216.0847; Found: 216.0839.

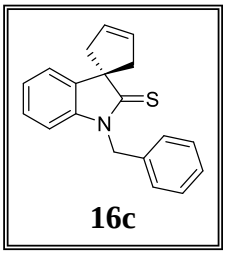
**1'-Ethylspiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16b)**



**16b**

Colorless oil (75%); **IR** (neat): $\nu_{max}$ 3048, 2921, 1671, 1026, 964, 946, 896, 716, 692, 645, 621, 595, 556 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 (d, $J$ = 6.8 Hz, 1H), 7.33-7.29 (m, 1H), 7.16-7.12 (m, 1H), 7.02 (d, $J$ = 8.0 Hz, 1H), 5.84 (s, 2H), 4.28 (q, $J$ = 7.2 Hz, 2H), 3.12 (d, $J$ = 14.8 Hz, 2H), 2.64 (d, $J$ = 14.8 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 211.0, 142.6, 142.5, 128.7, 127.7, 124.5, 122.1, 109.4, 63.4, 49.5, 39.7, 11.4 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}NS+H]^+$ 230.1004; Found: 230.1020.

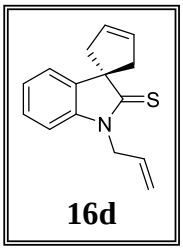
**1'-Benzylspiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16c)**



**16c**

Colorless oil (71%); **IR** (neat): $\nu_{max}$ 3049, 2921, 1671, 1126, 964, 956, 899, 713, 692, 645, 611, 595, 567 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.32-7.30 (d, $J$ = 7.2 Hz, 1H), 7.27-7.24 (m, 2H), 7.22-7.17 (m, 3H), 7.14-7.10 (m, 1H), 7.06-7.02 (m, 1H), 6.82 (d, $J$ = 7.6 Hz, 1H), 5.80 (s, 2H), 5.42 (s, 2H), 3.14 (d, $J$ = 14.4 Hz, 2H), 2.64 (d, $J$ = 14.8 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 212.9, 142.8, 142.2, 134.9, 128.9, 128.7, 127.8, 127.7, 127.2, 124.6, 121.9, 110.2, 63.6, 49.8, 48.4 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{19}H_{17}NS+H]^+$ 292.1160; Found: 292.1166.

**1'-(Prop-2-en-1-yl)spiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16d)**

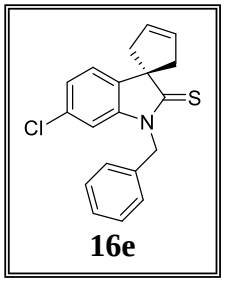


**16d**

Colorless oil (64%); **IR** (neat): $\nu_{max}$ 3070, 2925, 2854, 1613, 1465, 1386, 1224, 800, 752, 681 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 (d, $J$ = 7.2 Hz, 1H), 7.31-7.29 (m, 1H), 7.16-7.12 (m, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 5.95-5.87 (m, 1H), 5.85 (s, 2H), 5.27-5.18 (m, 2H), 4.89 (d, $J$ = 5.2 Hz, 2H), 3.15 (d, $J$ = 14.4 Hz, 2H), 2.67 (d, $J$ = 14.4 Hz, 2H) ppm; **$^{13}$C NMR** (101

MHz, $CDCl_3$) $\delta$ 212.0, 142.7, 142.2, 129.8, 128.7, 127.7, 124.6, 122.0, 118.2, 110.0, 63.4, 49.7, 47.1 ppm; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{15}NS+H]^+$ 242.1003; Found: 242.0998.

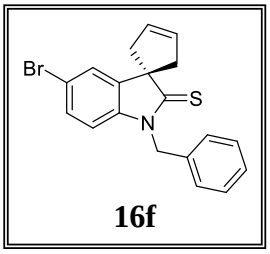
**1'-Benzyl-6'-chlorospiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16e)**




**16e**

Colorless oil (76%); **IR** (neat): $\nu_{max}$ 3059, 2923, 2850, 1722, 1606, 1431, 1375, 1266, 1214, 1073, 1026, 848, 806, 733, 694 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29-7.19 (m, 6H), 7.02-6.99 (m, 1H), 6.80 (s, 1H), 5.78 (s, 2H), 5.38 (s, 2H), 3.12 (d, *J* = 14.8 Hz, 2H), 2.60 (d, *J* = 14.4 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 212.5, 142.9, 139.4, 133.3, 132.4, 128.0, 127.6, 126.9, 126.0, 123.4, 121.6, 109.6, 62.3, 48.9, 47.3 ppm; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{16}ClNS+H]^+$ 326.0770; Found: 326.0762.

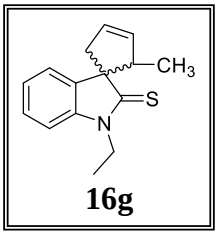
**1'-Benzyl-5'-bromospiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16f)**




**16f**

White crystalline solid (90%); mp 156-158 °C; **IR** (neat): $\nu_{max}$ 3062, 2924, 2846, 1719, 1608, 1428, 1382, 1267, 1216, 809, 731, 688 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.50 (d, *J* = 2.0 Hz, 1H), 7.34-7.25 (m, 6H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.86 (s, 2H), 5.46 (s, 2H), 3.20 (d, *J* = 14.8 Hz, 2H), 2.70 (d, *J* = 14.4 Hz, 2H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 212.4, 144.1, 141.8, 134.5, 130.7, 129.0, 128.7, 127.9, 127.1, 125.2, 117.9, 111.5, 63.7, 49.8, 48.4 ppm; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{16}NSBr+H]^+$ 370.0265; Found: 370.0260.

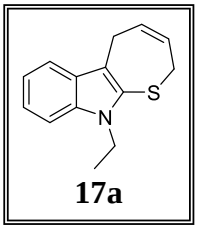
**1'-Ethyl-2-methylspiro[cyclopent-3-ene-1,3'-indole]-2'(1'*H*)-thione (16g)**




**16g**

Colorless oil (63%); dr = 90:10; **IR** (neat): $\nu_{max}$ 3042, 2821, 1671, 1035, 964, 946, 899, 713, 645, 625, 596, 554 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 7.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.16-7.09 (m, 1H), 7.03 (d, $J$ = 8.0 Hz, 1H), 5.85-5.82 (m, 1H), 5.68-5.66 (m, 1H), 4.38-4.31 (m, 1H), 4.28-4.21 (m, 1H), 3.63-3.61 (m, 1H), 3.27-3.22 (m, 1H), 2.59 (d, $J$ = 16.4 Hz, 1H), 1.35 (t, $J$ = 7.2 Hz, 3H), 0.61 (d, $J$ = 7.6 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 209.6, 143.1, 138.4, 135.1, 127.8, 127.6, 123.8, 123.6, 109.4, 69.4, 54.4, 48.5, 39.8, 14.6, 11.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}NS+H]^+$ 244.1160; Found: 244.1153.

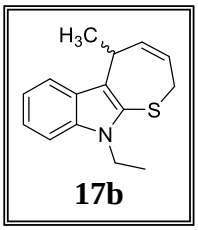
**10-Ethyl-5,10-dihydro-2*H*-thiepino[2,3-*b*]indole (17a)**




**17a**

Colorless oil (68%); **IR** (neat): $\nu_{max}$ 3041, 2921, 1671, 1326, 965, 946, 899, 755, 692, 645, 621, 596, 552 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 (d, $J$ = 7.2 Hz, 1H), 7.24-7.22 (m, 1H), 7.15-7.05 (m, 2H), 6.05-6.03 (m, 2H), 4.13 (q, $J$ = 7.2 Hz, 2H), 3.69-3.68 (m, 2H), 3.62-3.61 (m, 2H), 1.31 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 135.2, 130.5, 130.1, 128.2, 126.7, 120.7, 118.9, 116.8, 108.3, 107.8, 38.1, 28.0, 22.5, 15.2 ppm; **HRMS** (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}NS+H]^+$ 230.1003; Found: 230.1004.

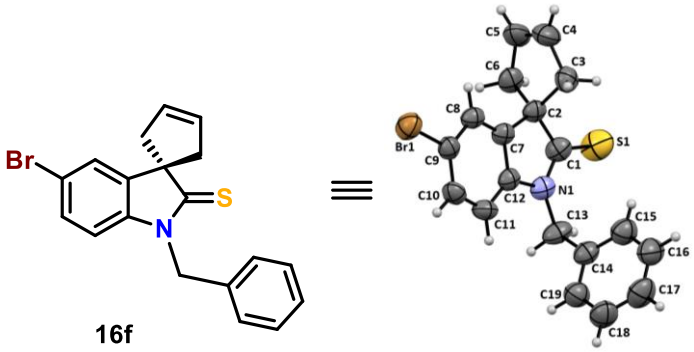
**10-Ethyl-5-methyl-5,10-dihydro-2*H*-thiepino[2,3-*b*]indole (17b)**




**17b**

Colorless oil (62%); **IR** (neat): $\nu_{max}$ 3043, 2931, 1671, 1326, 965, 899, 755, 692, 635, 621, 596, 532 $cm^{-1}$; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.48 (d, $J$ = 8.0 Hz, 1H), 7.25 (d, $J$ = 2.4 Hz, 1H), 7.18-7.14 (m, 1H), 7.10-7.06 (m, 1H), 5.98-5.90 (m, 2H), 4.21 (q, $J$ = 7.2 Hz, 2H), 4.05-3.95 (m, 1H), 3.48-3.34 (m, 2H), 1.53 (d, $J$ = 7.2 Hz, 3H), 1.32 (t, $J$ = 7.2 Hz, 3H) ppm; **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 135.6, 135.3, 129.6, 127.7, 126.1, 121.2, 119.0, 117.6, 117.3, 108.8, 38.2, 31.4, 29.4, 23.1, 15.5 ppm; **HRMS** (ESI) *m*/*z*: $[M+Na]^+$ Calcd for $[C_{15}H_{17}NS+Na]^+$ 266.0979; Found: 266.0977.

## 9. Single crystal X-ray analysis of compound 16f




ORTEP view of compound **16f** with thermal ellipsoids shown at 50% probability level. [There are two molecules in the asymmetric unit, but only one is shown]

**Table S1**. Summary of X-ray crystallographic data for compound **16f**

| | |
|---|---|
| CCDC | 2254000 |
| Empirical formula | $C_{19}H_{16}BrNS$ |
| Formula weight | 369.0187 |
| Temperature/K | 303.(2) |
| Crystal system | Triclinic |
| Space group | *P* -1 |
| a (Å) | 9.382(2) |
| b (Å) | 10.472(2) |
| c (Å) | 17.945(4) |
| α (°) | 88.563(6) |
| β (°) | 78.673(6) |
| γ (°) | 72.965(6) |
| Volume ($Å^3$) | 1651.9(6) |
| Z | 2 |
| $\rho_{calc}$ (g $cm^{-3}$) | 1.489 |
| μ ($mm^{-1}$) | 2.610 |
| F(000) | 752 |
| Crystal size ($mm^3$) | 0.163 (max) × 0.093 (mid) × 0.085 (min) |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073 Å) |
| Theta range for data collection (°) | 2.31 to 32.54 |
| Index ranges | $-14 \le h \le 14$, $-15 \le k \le 15$, $-26 \le l \le 26$ |
| Reflections collected / unique | 65104 / 11747 [$R_{int}$ = 0.1559] |
| Completeness to theta = 32.54 | 98.0 % |
| Data/restraints/parameters | 11747/0/397 |
| Goodness-of-fit on $F^2$ | 0.931 |
| Final R indexes [I>2σ (I)] | $R_1$ = 0.0637, $wR_2$ = 0.1534 |
| Final R indexes [all data] | $R_1$ = 0.2098, $wR_2$ = 0.2212 |
| Largest diff. peak and hole (e $Å^{-3}$) | 0.544 and -0.592 |

The single crystal of the product **16f** was obtained by slow evaporation of the solvent when the compound was dissolved in *n*-hexanes/few drops of ethyl acetate mixture. The crystal data of product **16f** has already been deposited at Cambridge Crystallographic Data Centre.

The following intermolecular interactions are present in compound **16f**,

(i) C-Br---$\pi$

C28–Br2---(centroid C7-C12) Bond length Br2–(C7-C12) = 3.752 Å

Bond angle C28–Br2---(C7-C12) = 164.79 °

(ii) C-H---Br

C35–H35---Br2 Bond length H35–Br2 = 3.033 Å

Bond angle C35–H35---Br2 = 139.28 °

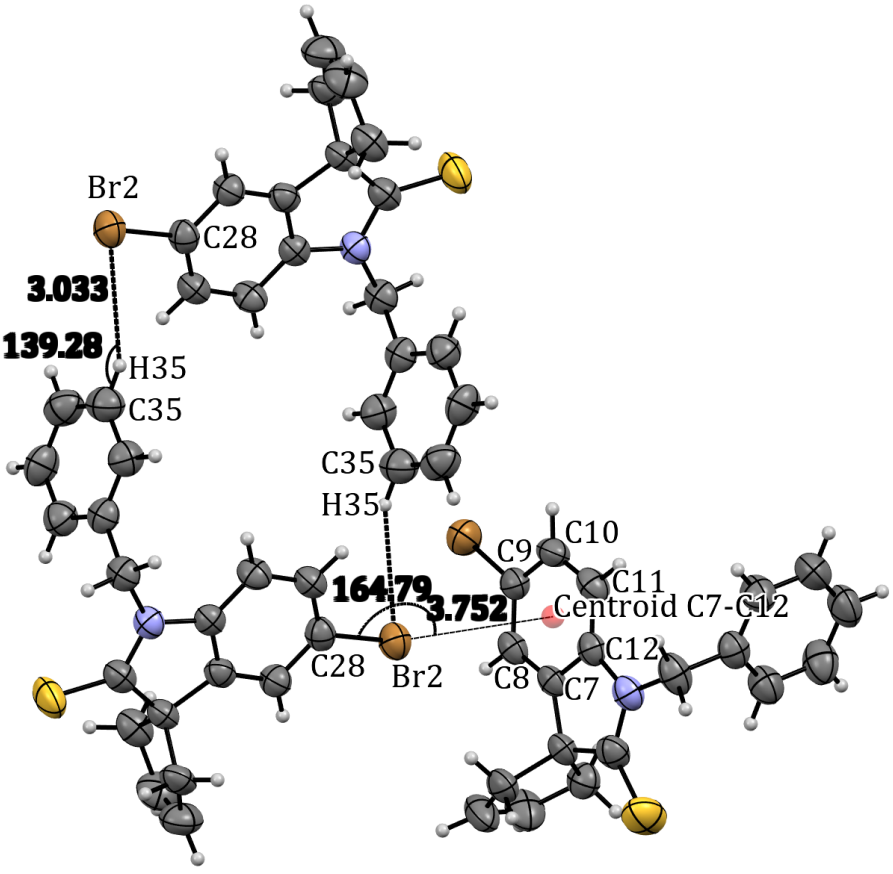
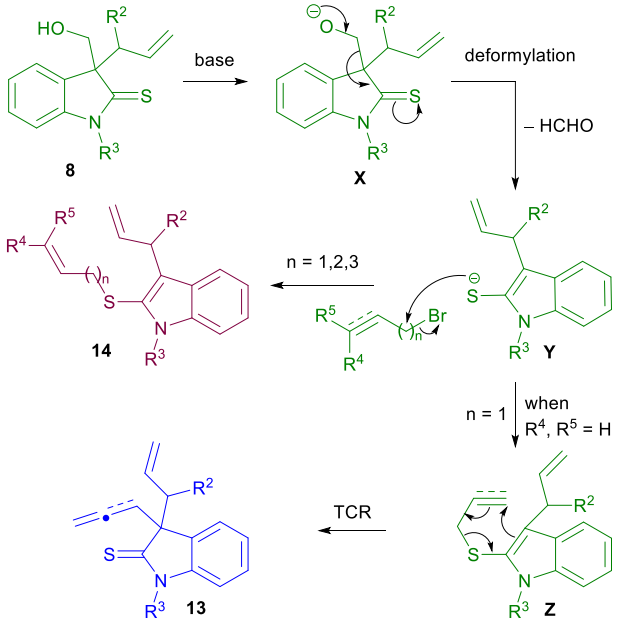



**Figure S4**. Intermolecular interactions present in compound **16f**

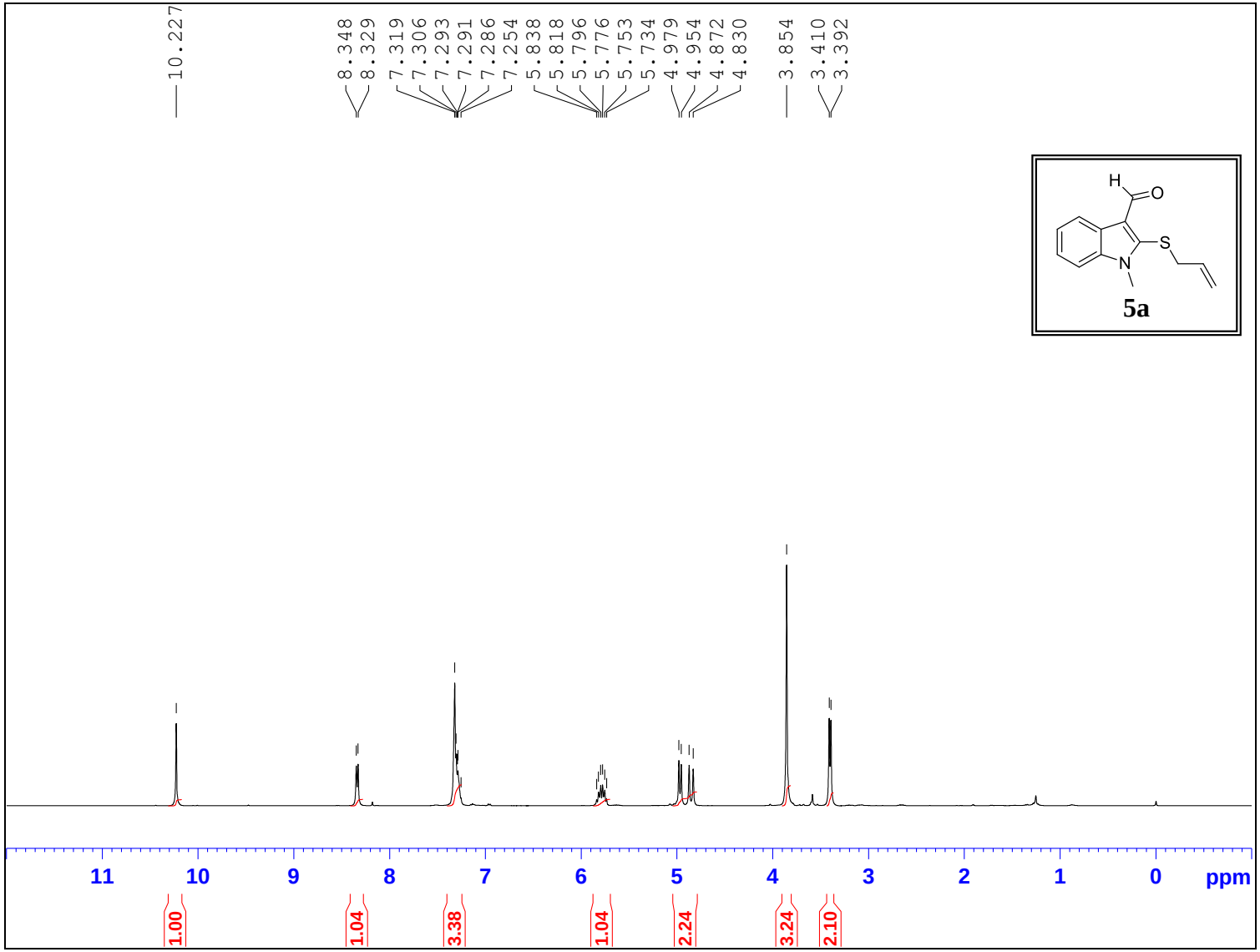
## 10. Proposed cascade pathway for the formation of diolefins 13/14



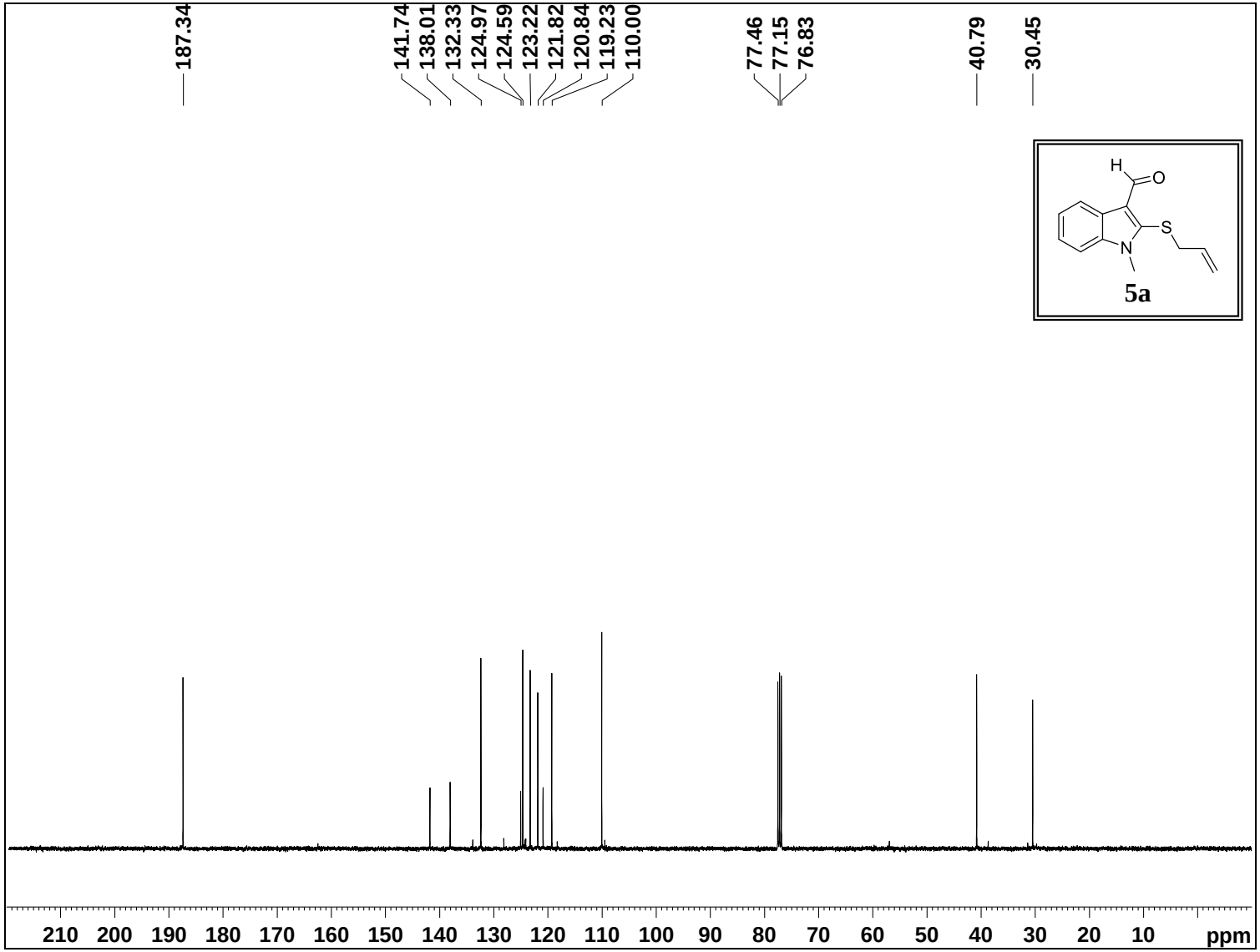

**Scheme S1**. Proposed cascade pathway for the formation of diolefins **13**/**14**

**11.** $^{1}H$, $^{13}C$ & selected DEPT-135 NMR copies of compounds **5, 8-14, 16,17**

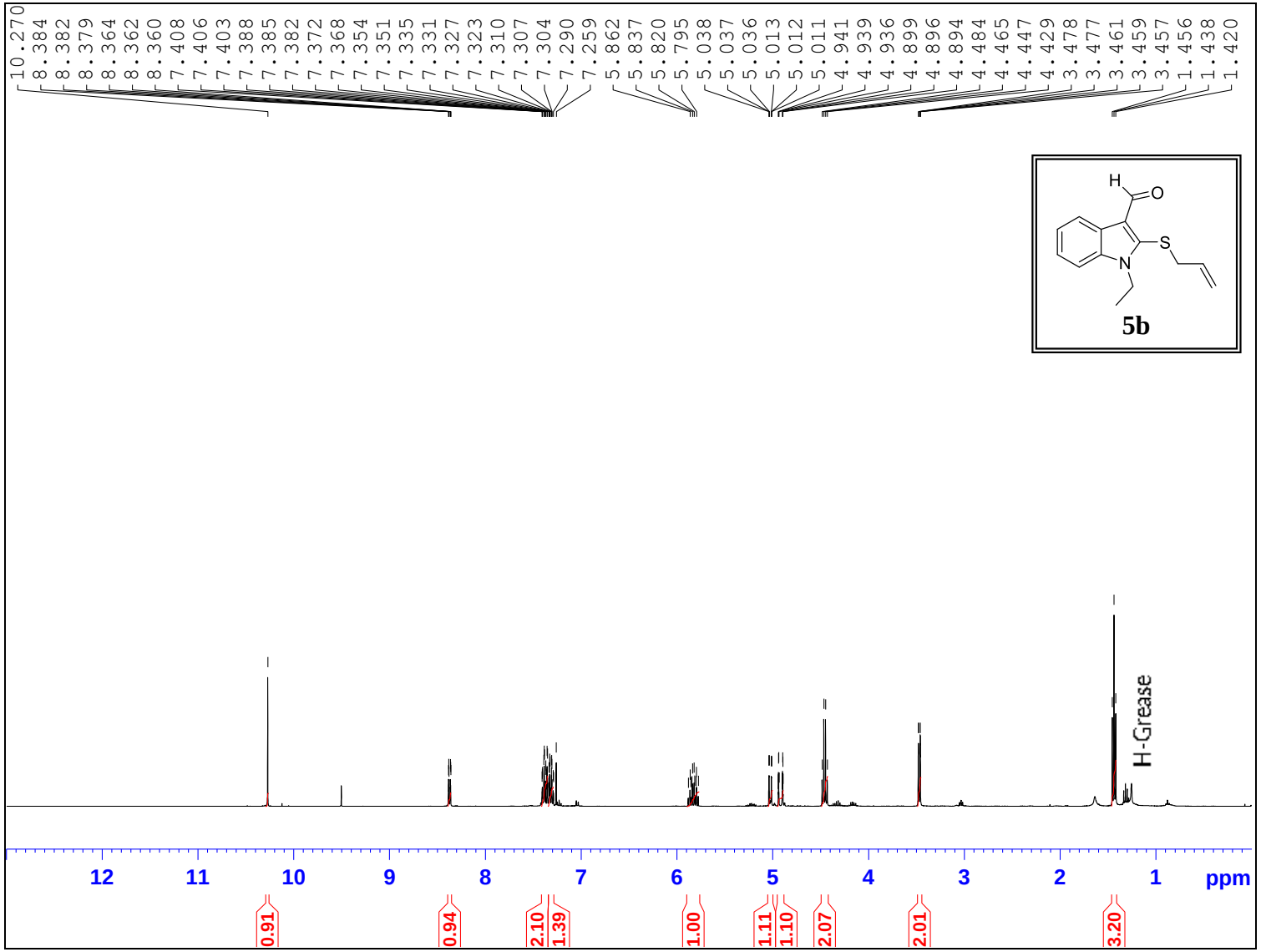
$^{1}$H NMR for compound **5a** (400 MHz, $CDCl_3$)



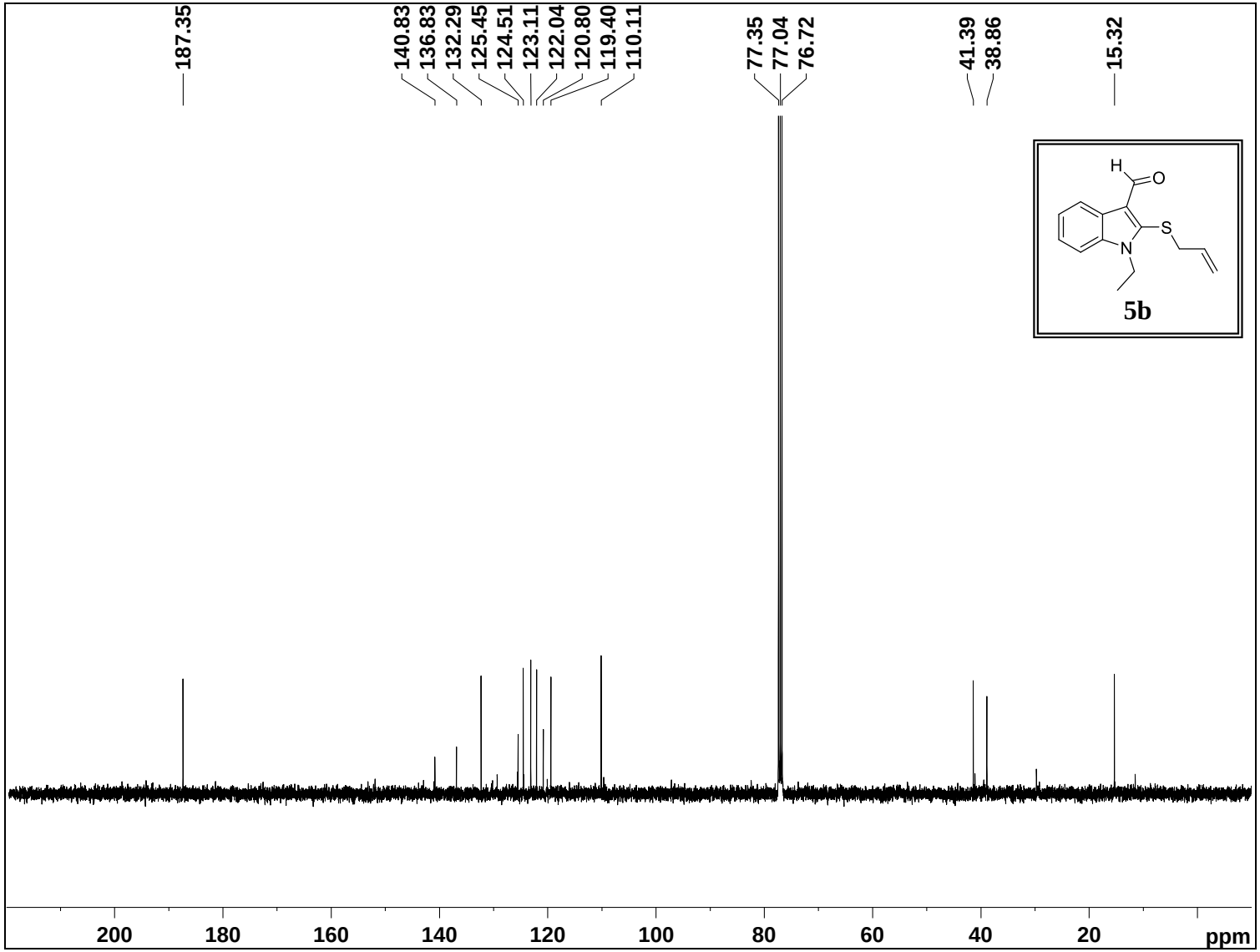
$^{13}C$ NMR for compound **5a** (101 MHz, $CDCl_3$)



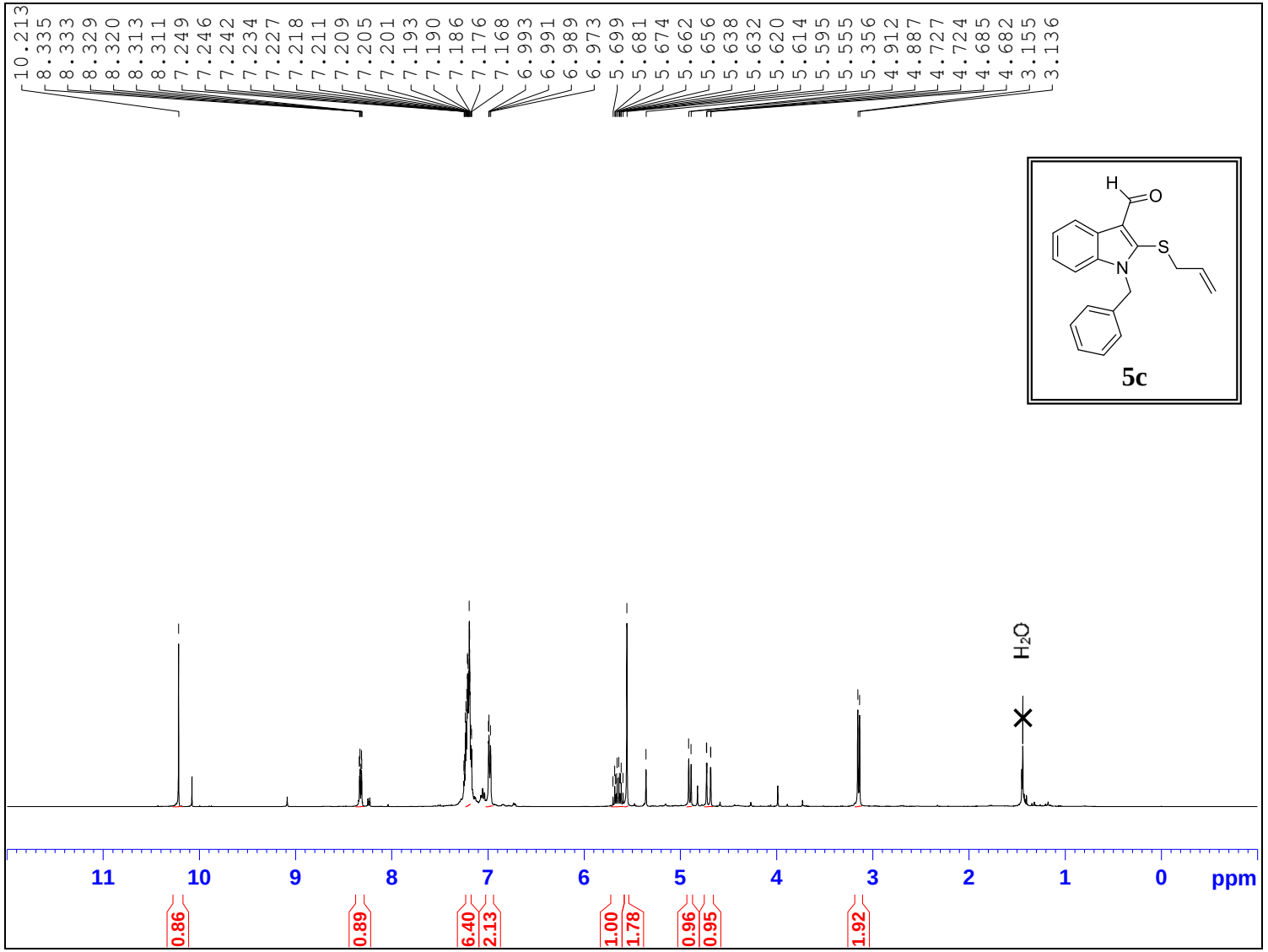
$^{1}$H NMR for compound **5b** (400 MHz, $CDCl_3$)



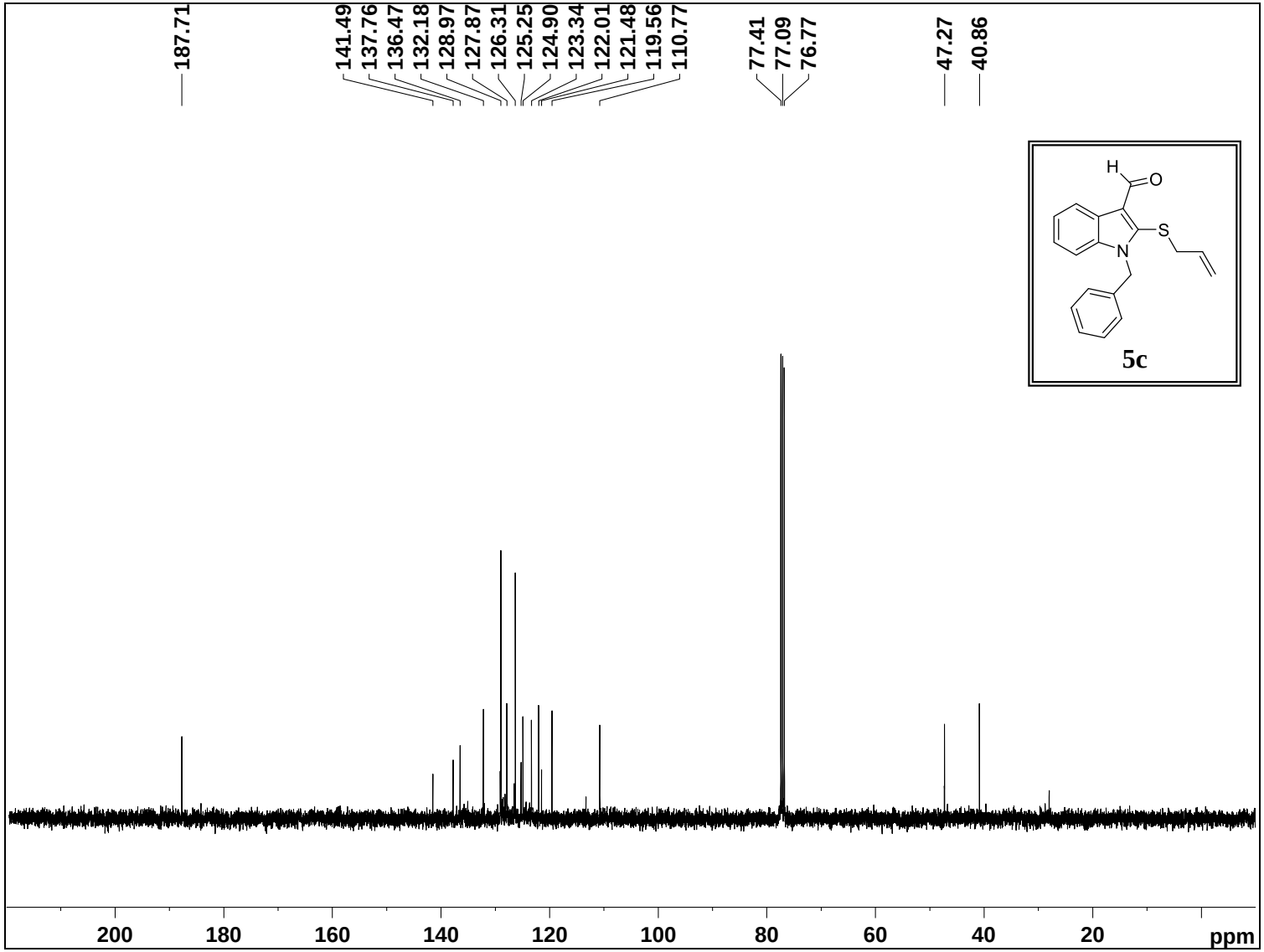
$^{13}C$ NMR for compound **5b** ($101$ MHz, $CDCl_3$)



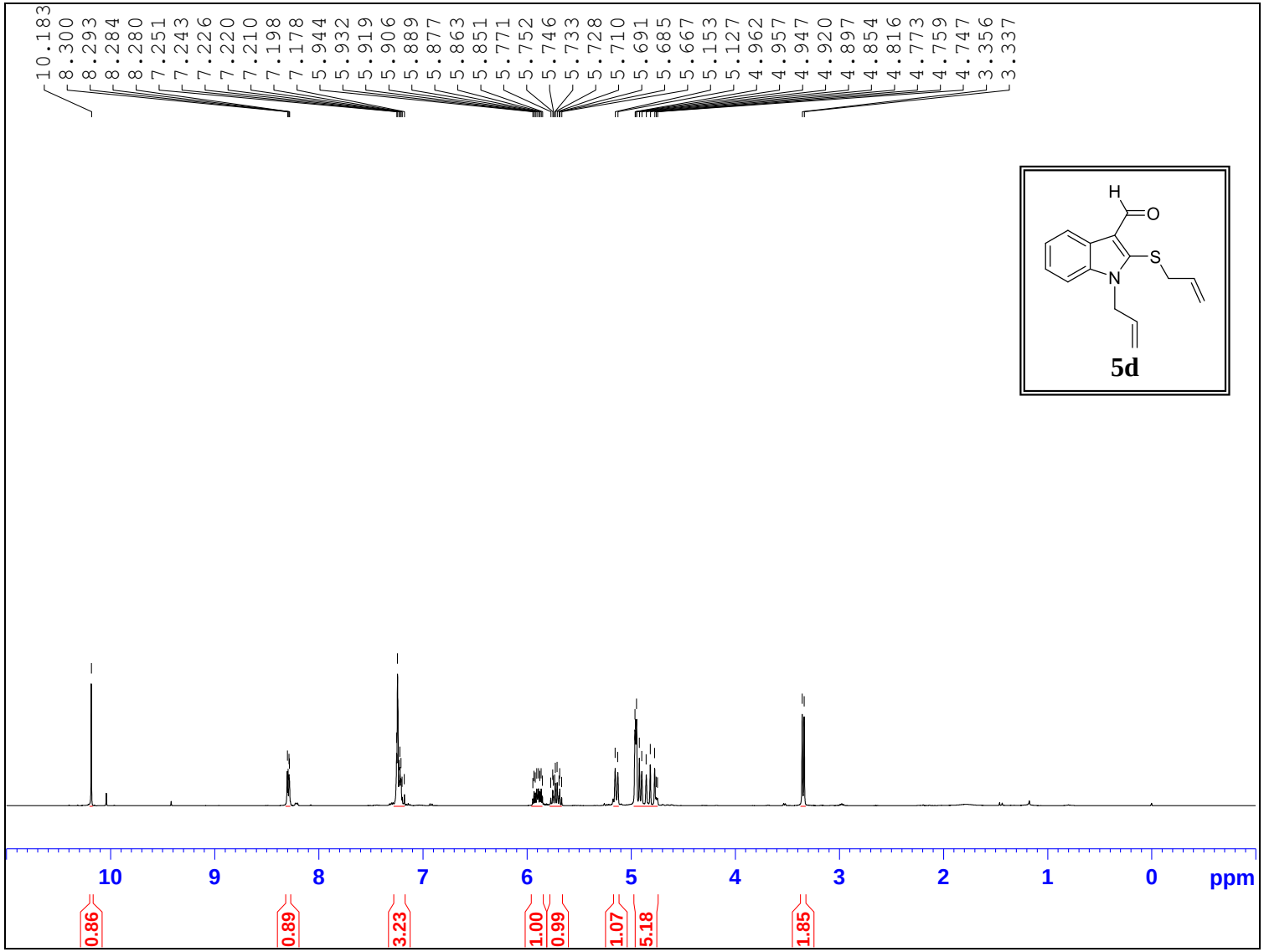
$^{1}$H NMR for compound **5c** (400 MHz, $CDCl_3$)



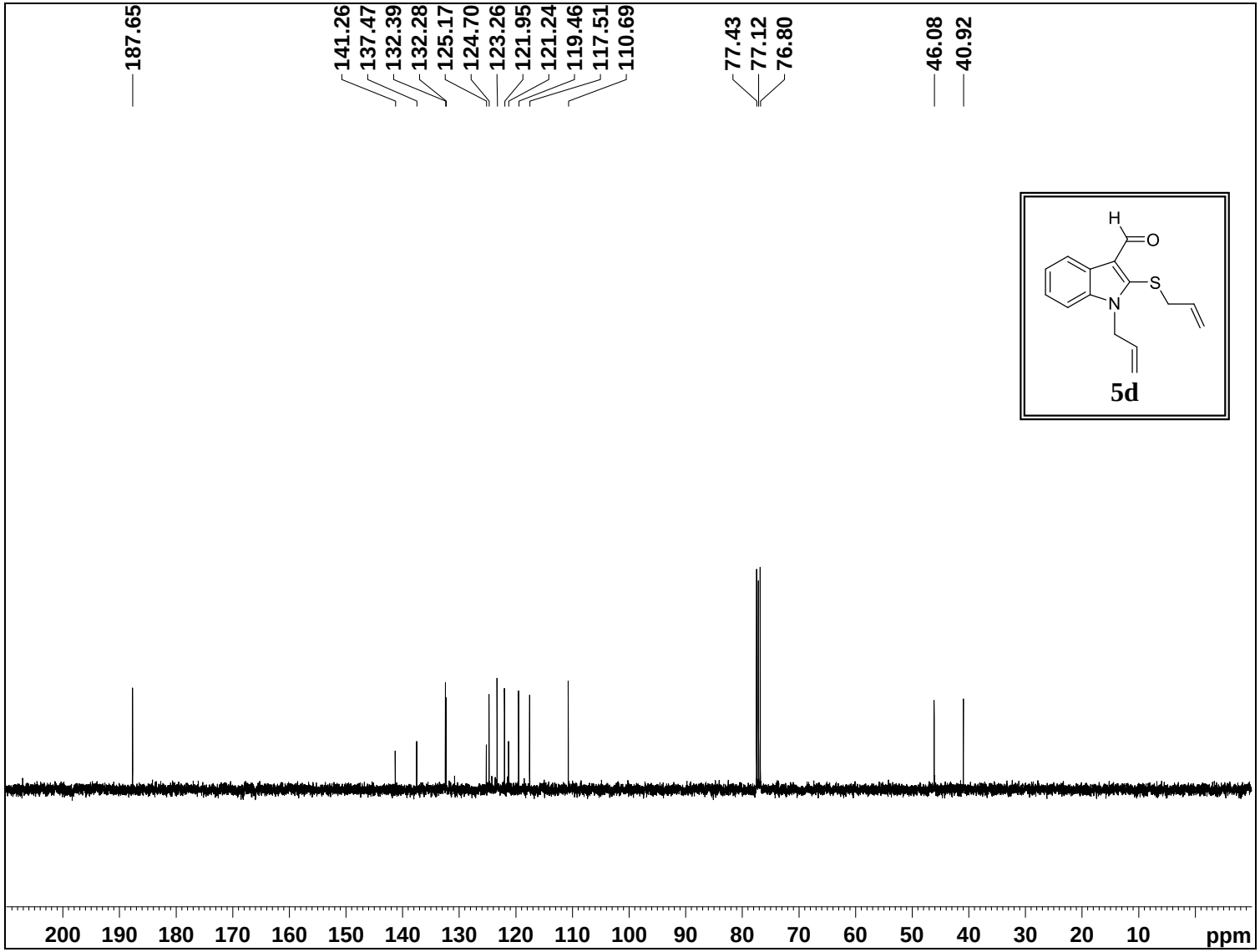
$^{13}C$ NMR for compound **5c** (101 MHz, $CDCl_3$)



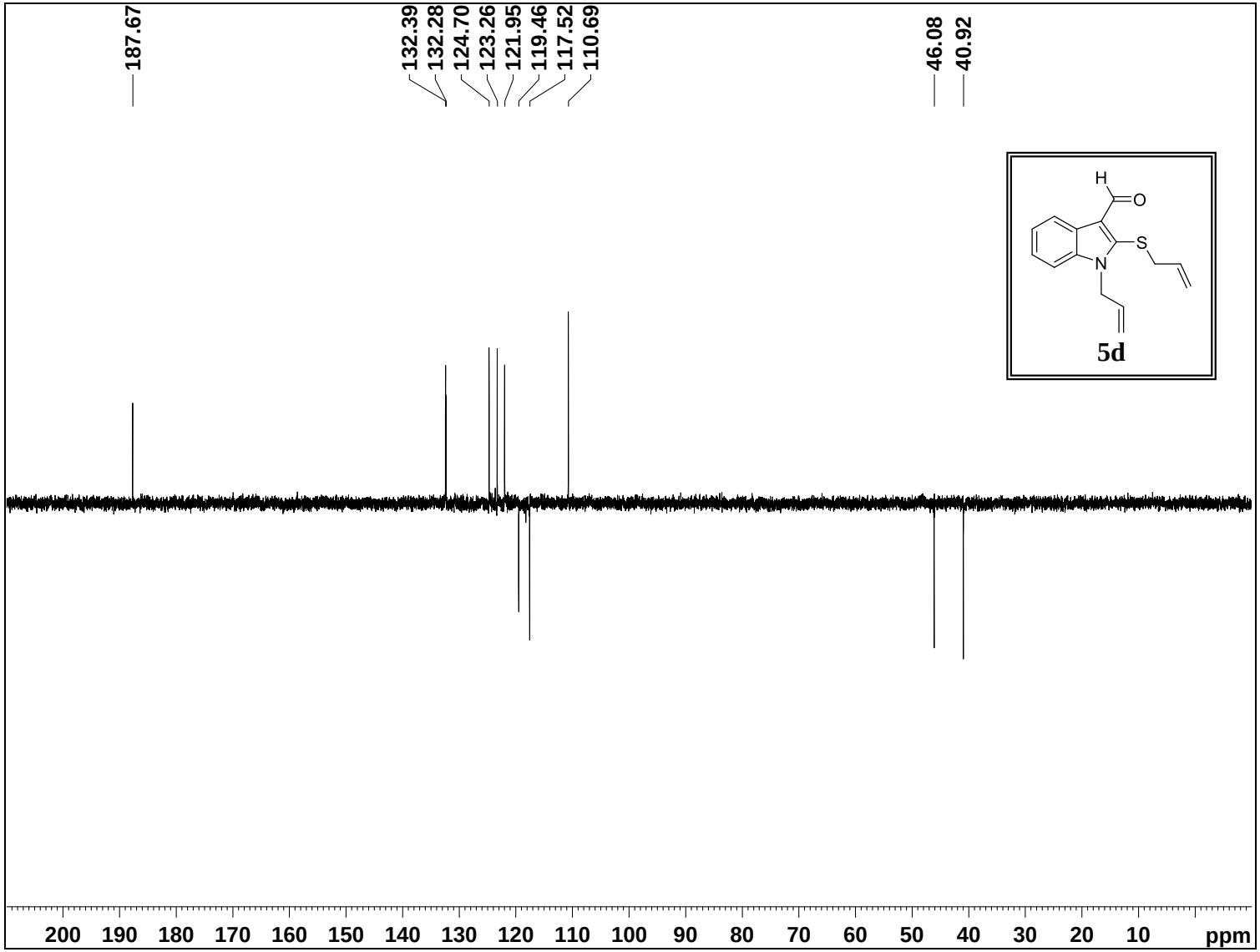
$^{1}$H NMR for compound **5d** (400 MHz, $CDCl_3$)



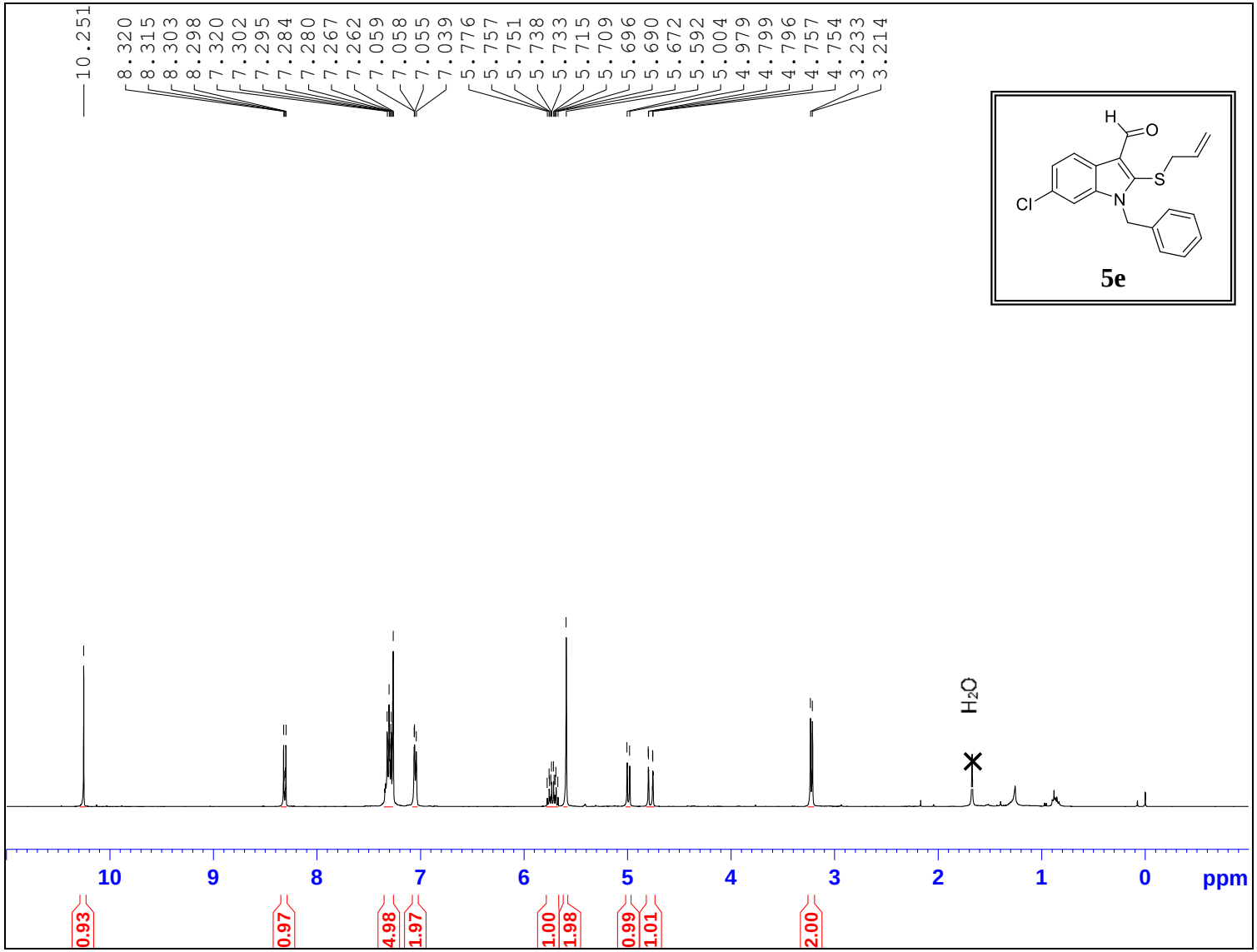
$^{13}C$ NMR for compound **5d** ($101$ MHz, $CDCl_3$)



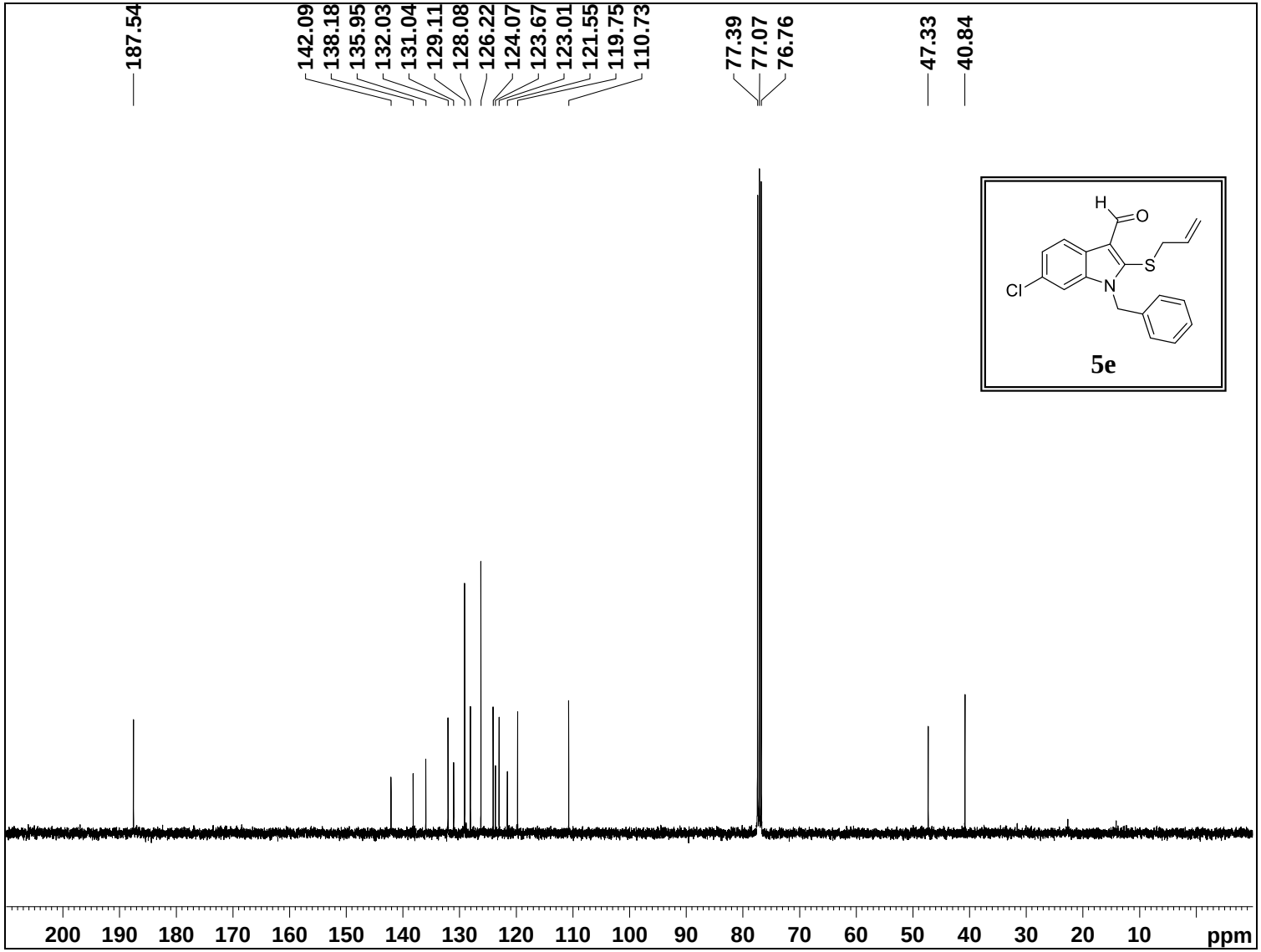
DEPT-135 NMR for compound **5d** (101 MHz, $CDCl_3$)



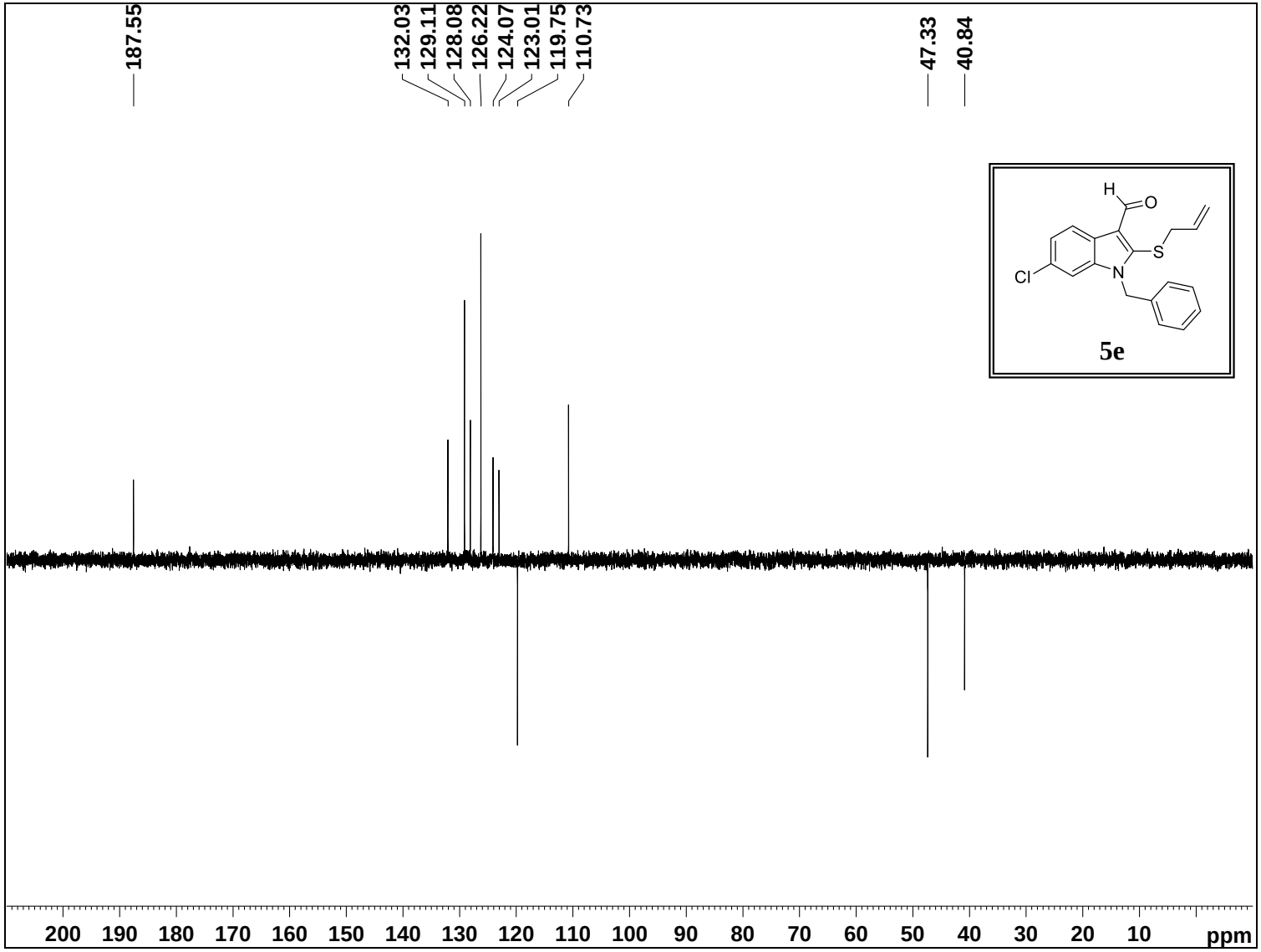
$^{1}$H NMR for compound **5e** (400 MHz, $CDCl_3$)



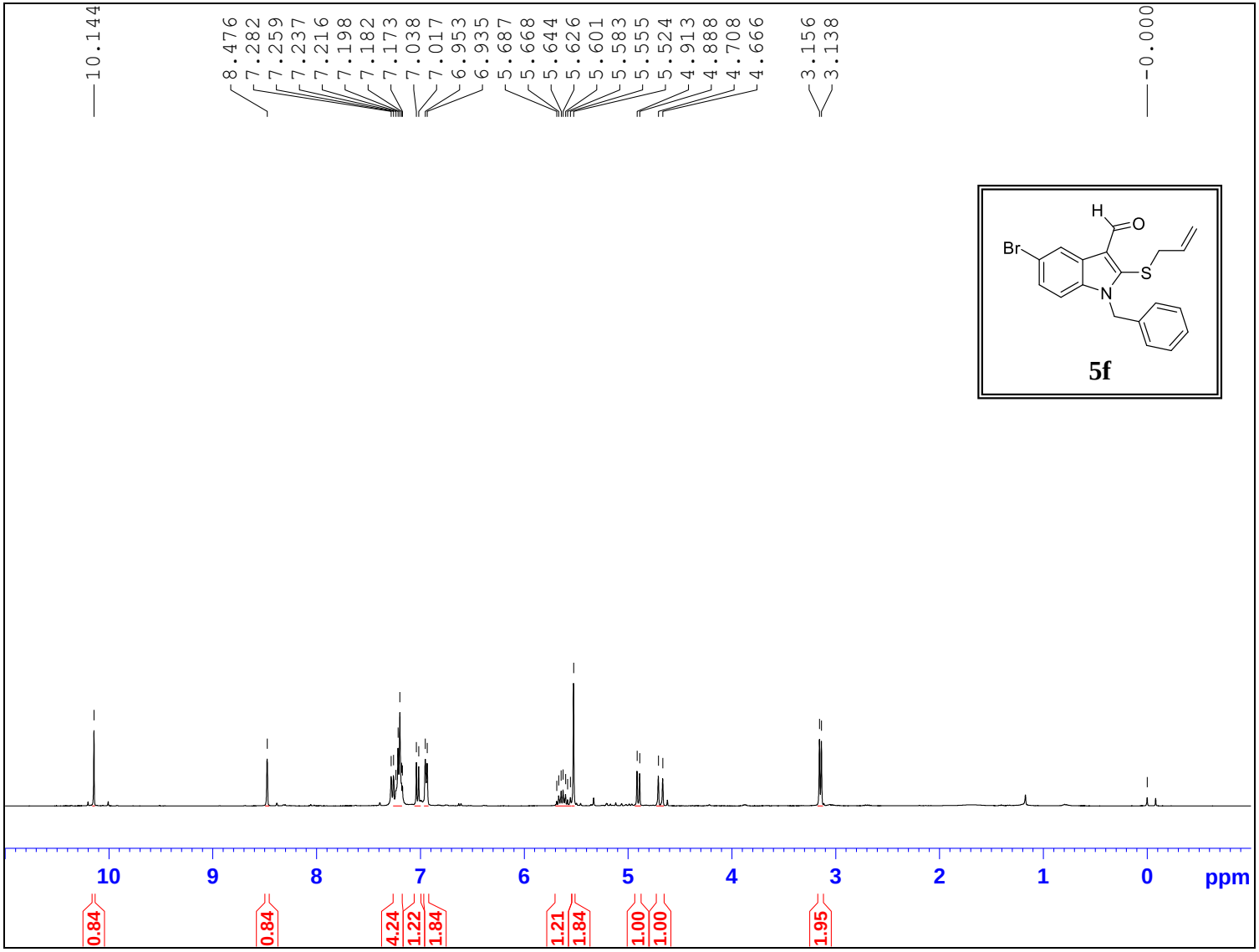
$^{13}C$ NMR for compound **5e** (101 MHz, $CDCl_3$)



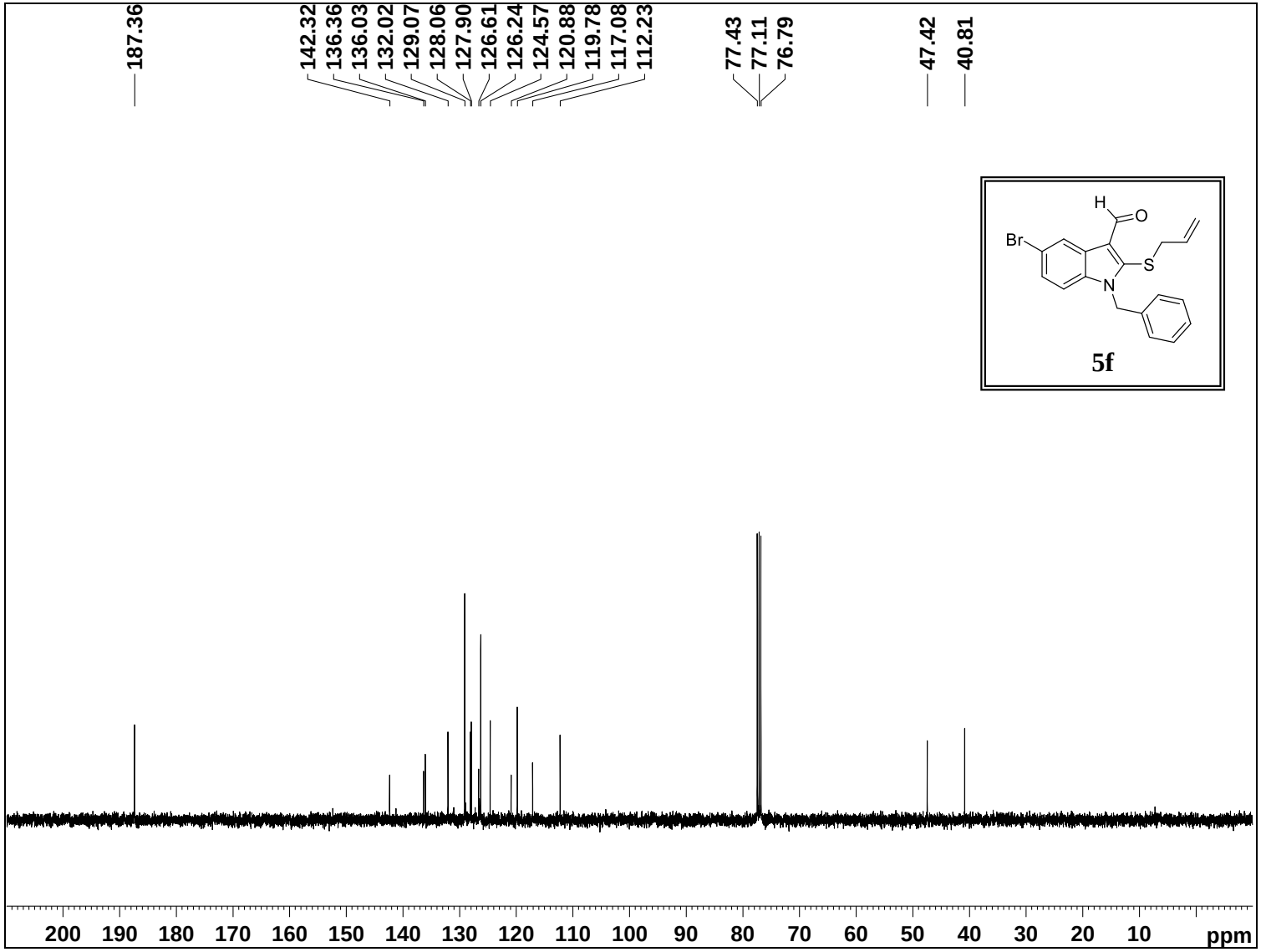
DEPT-135 NMR for compound **5e** (101 MHz, $CDCl_3$)



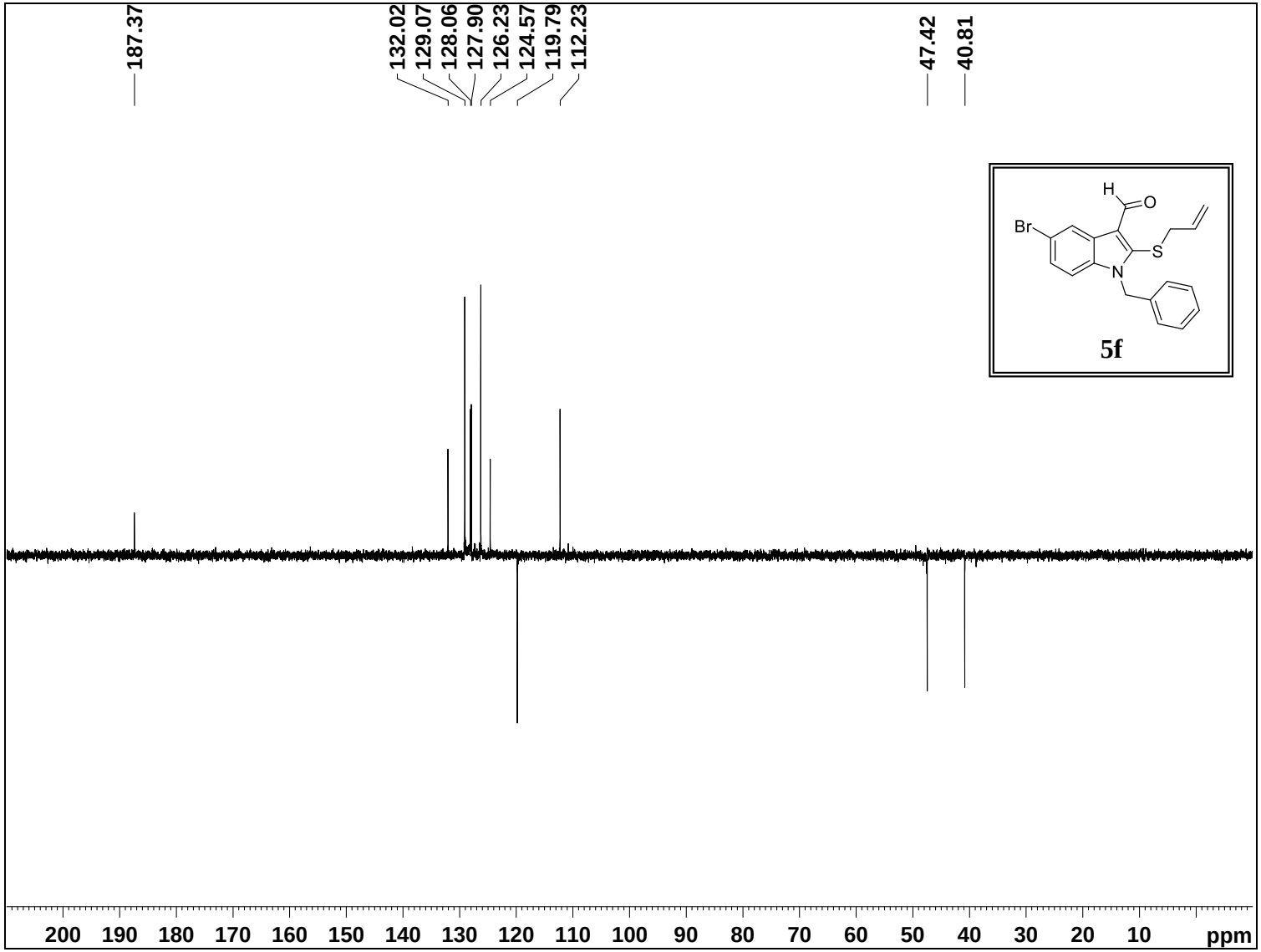
$^{1}$H NMR for compound **5f** (400 MHz, $CDCl_3$)



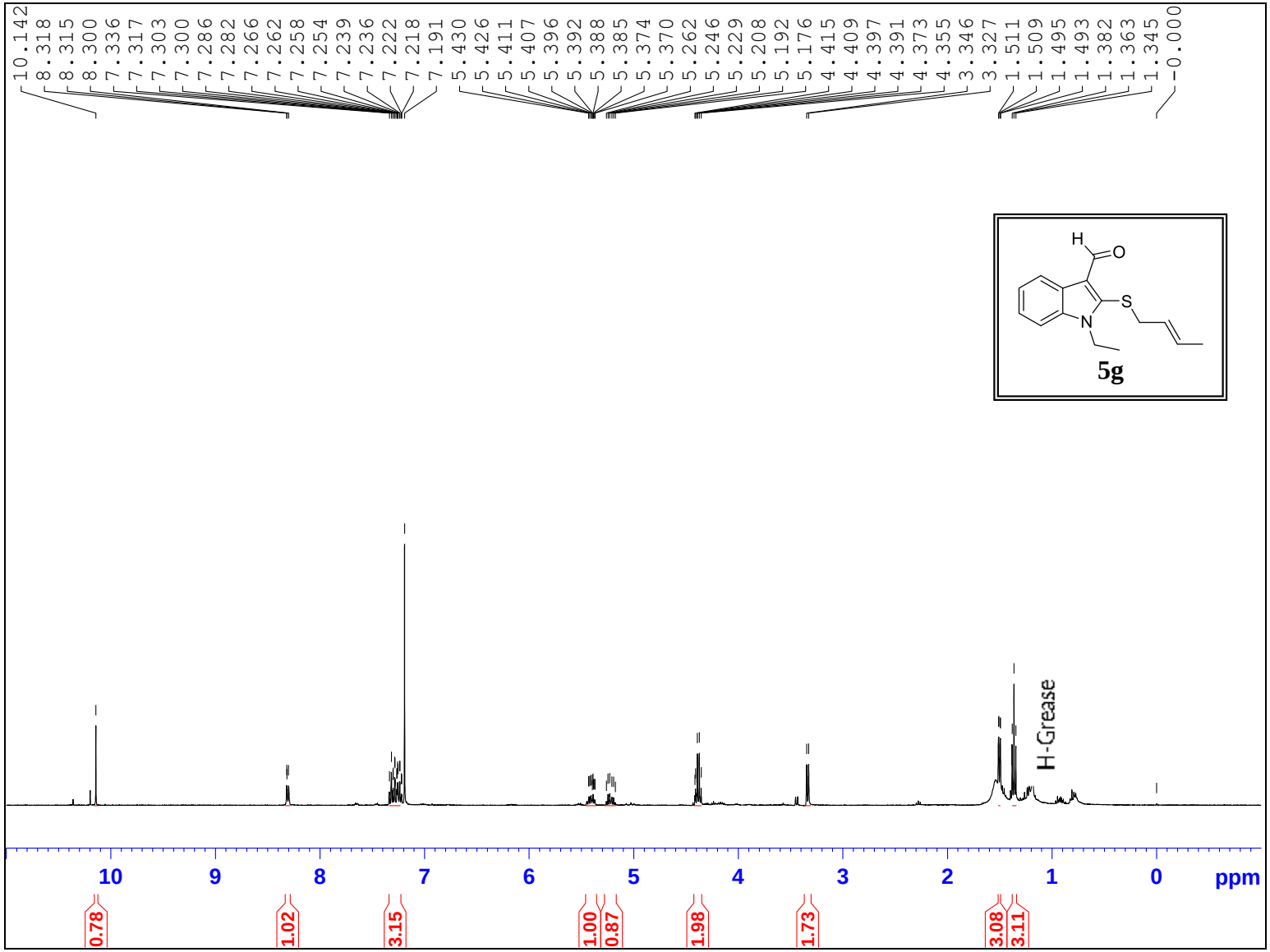
$^{13}C$ NMR for compound **5f** (101 MHz, $CDCl_3$)



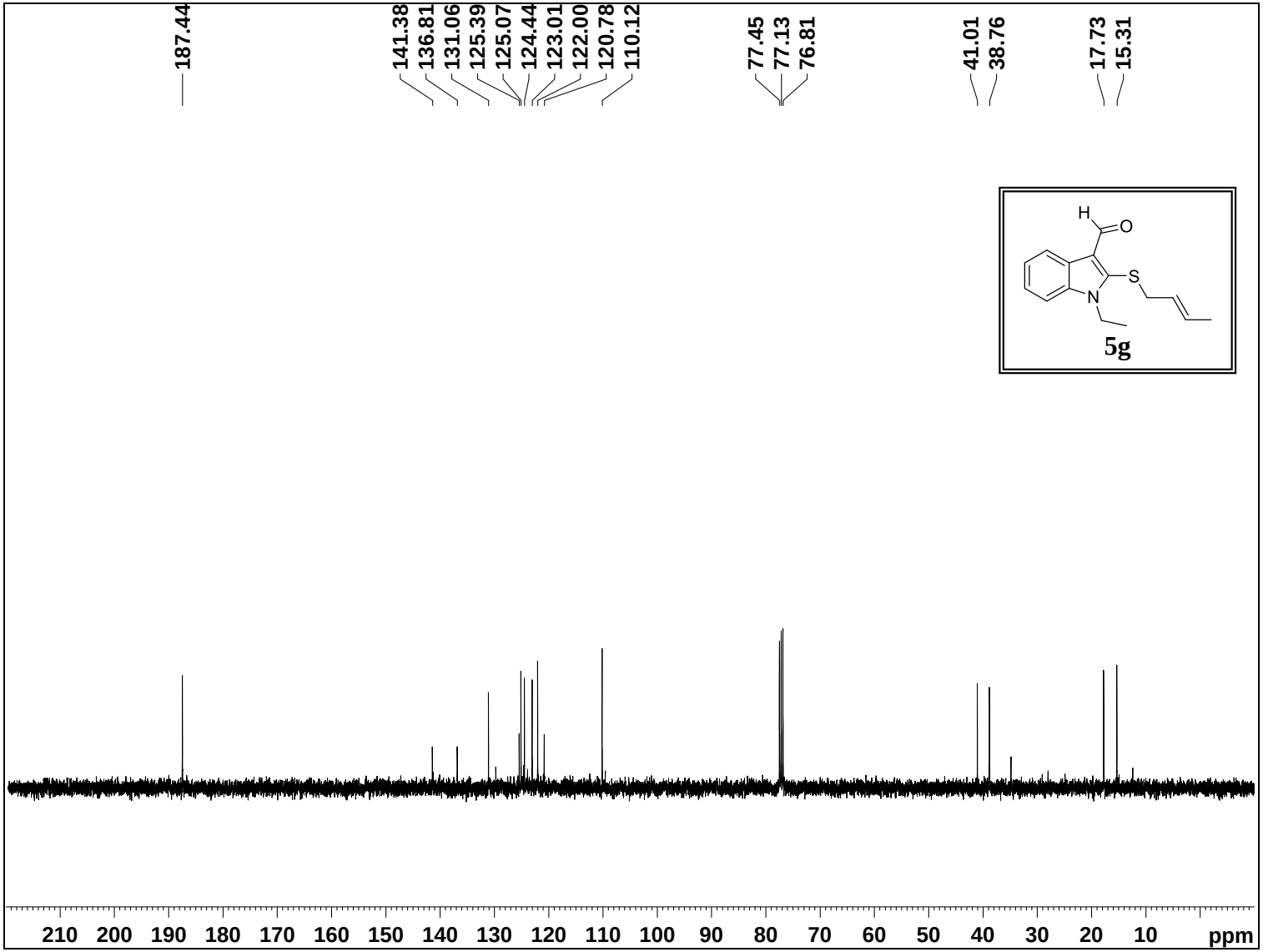
DEPT-135 NMR for compound **5f** (101 MHz, $CDCl_3$)



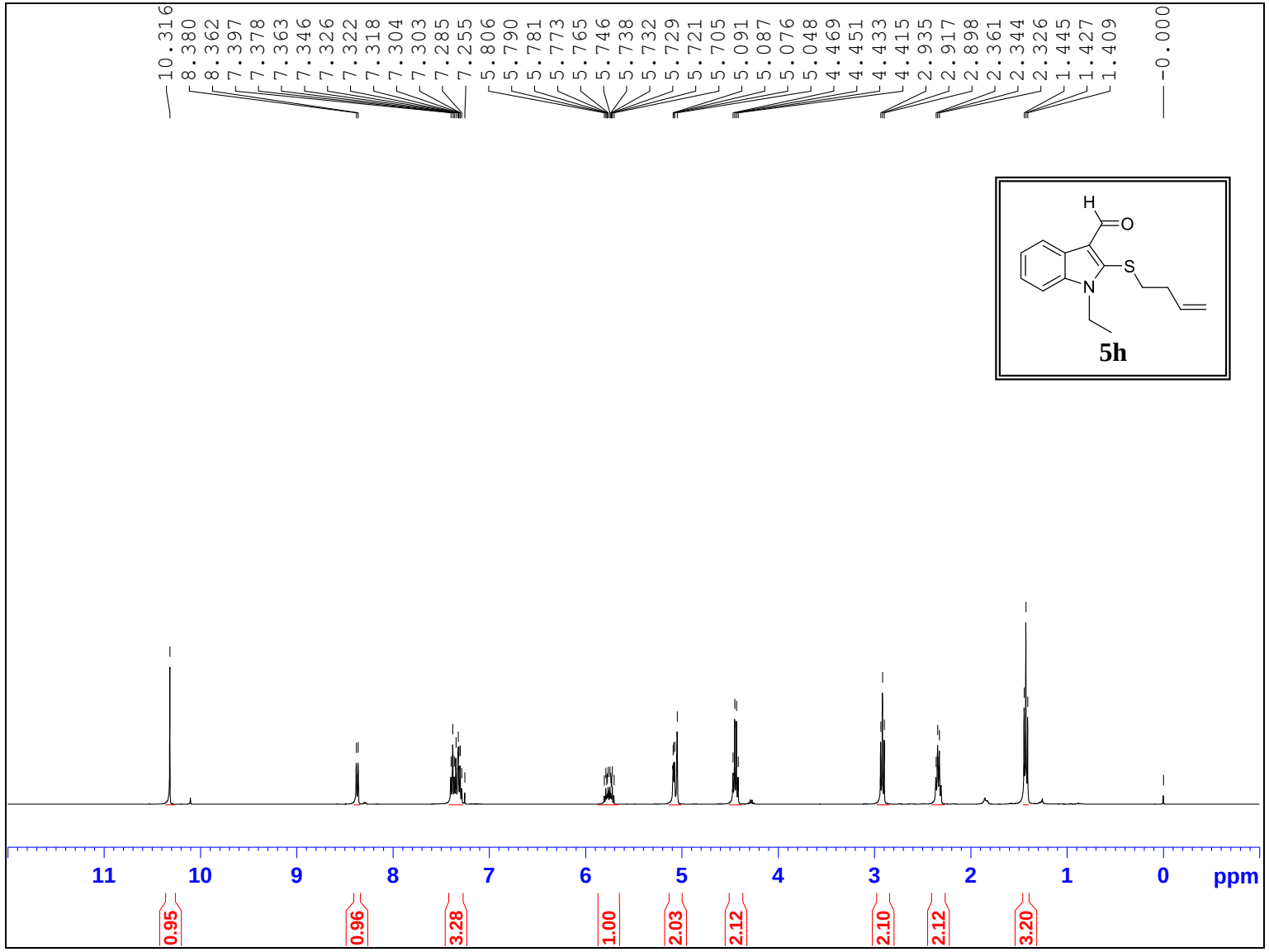
$^{1}$H NMR for compound **5g** (400 MHz, $CDCl_3$)



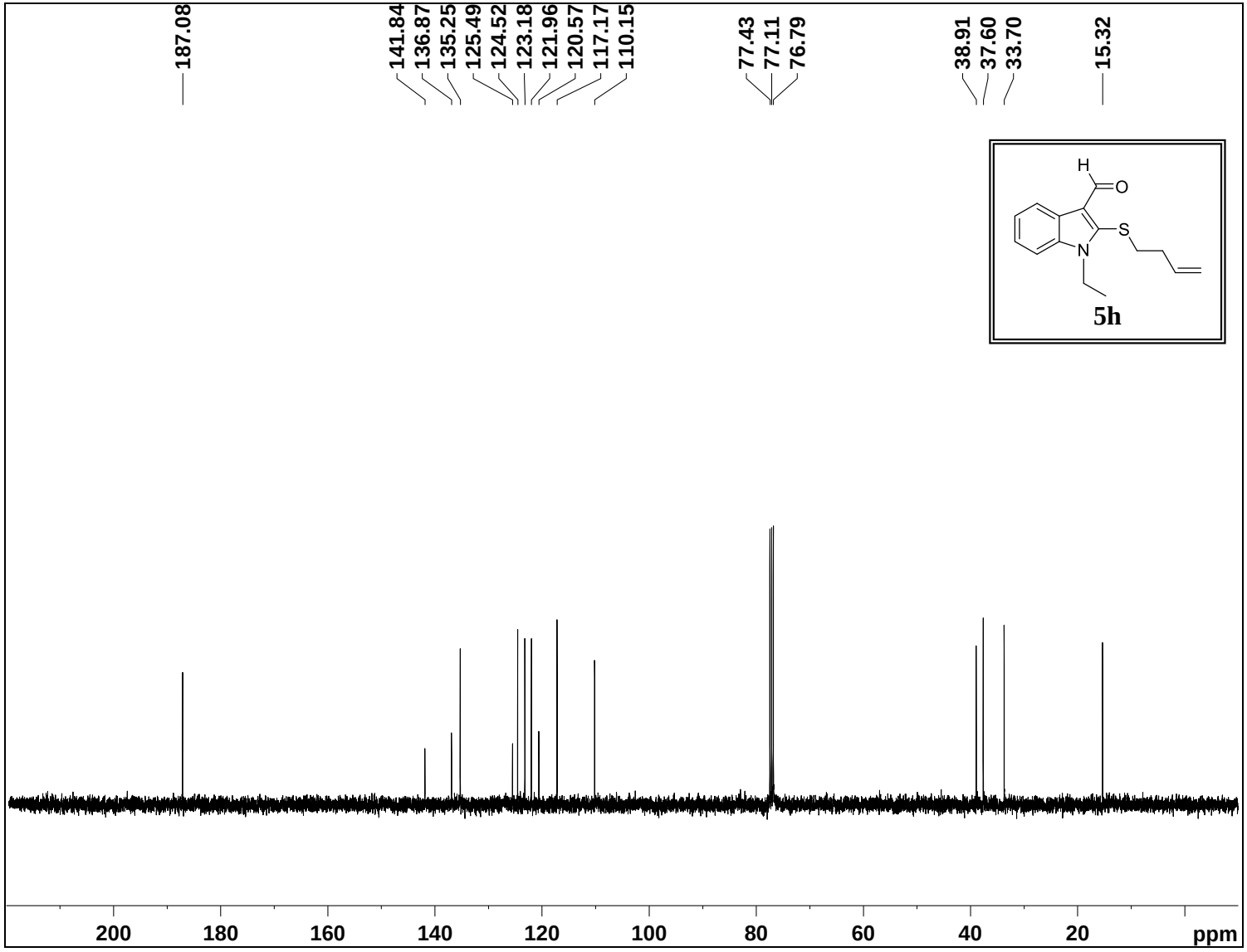
$^{13}C$ NMR for compound **5g** ($101$ MHz, $CDCl_3$)



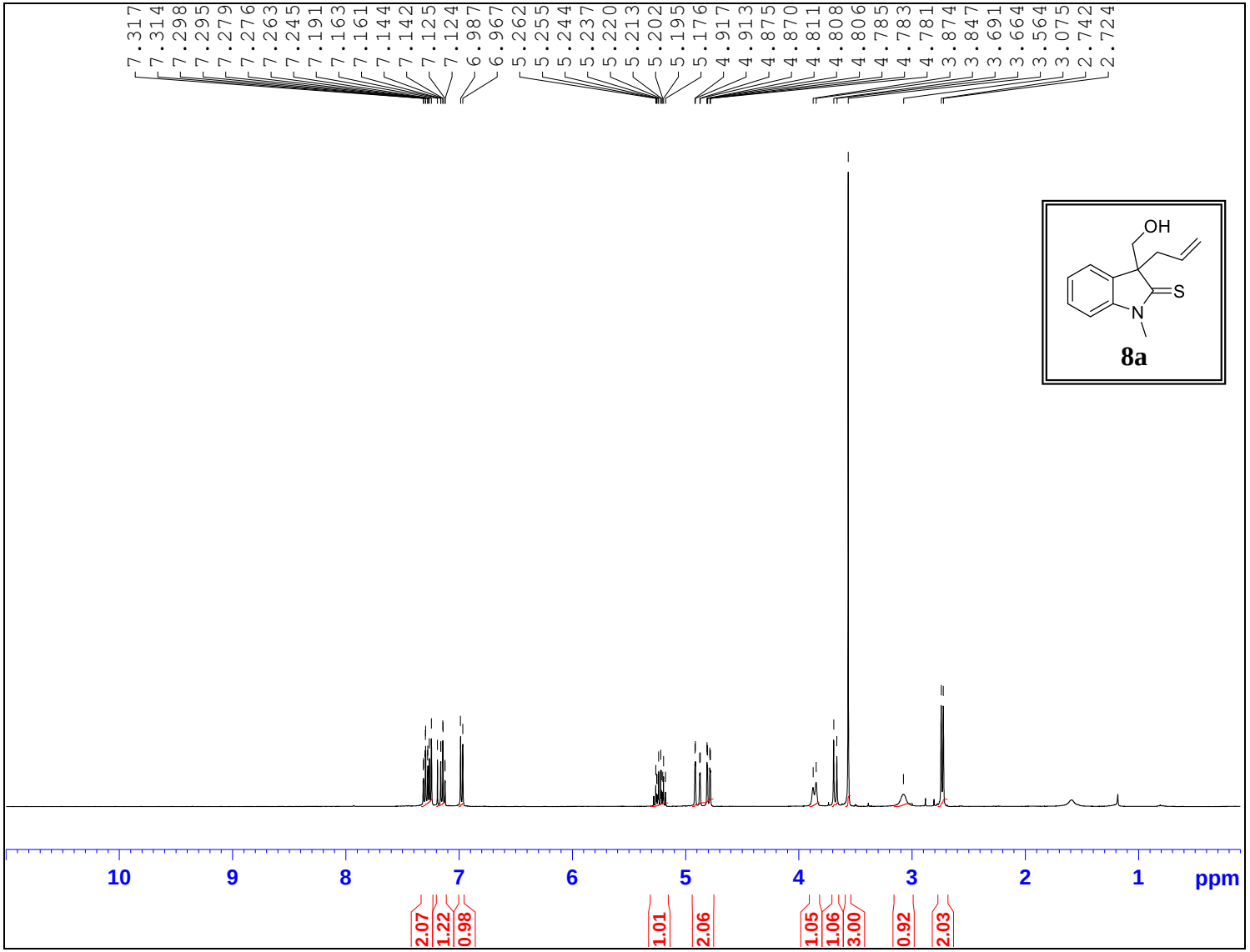
$^{1}$H NMR for compound **5h** (400 MHz, $CDCl_3$)



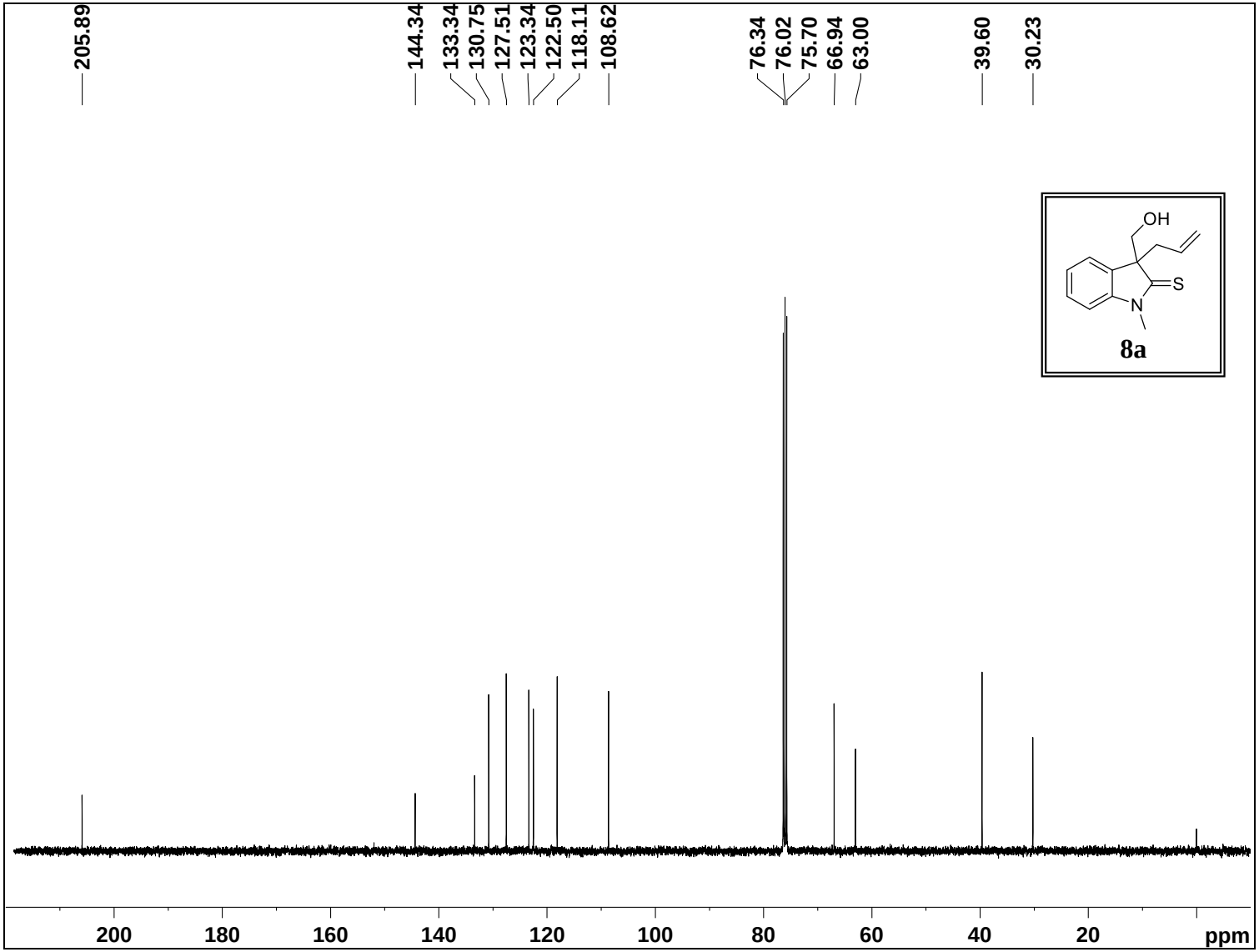
$^{13}C$ NMR for compound **5h** ($101$ MHz, $CDCl_3$)



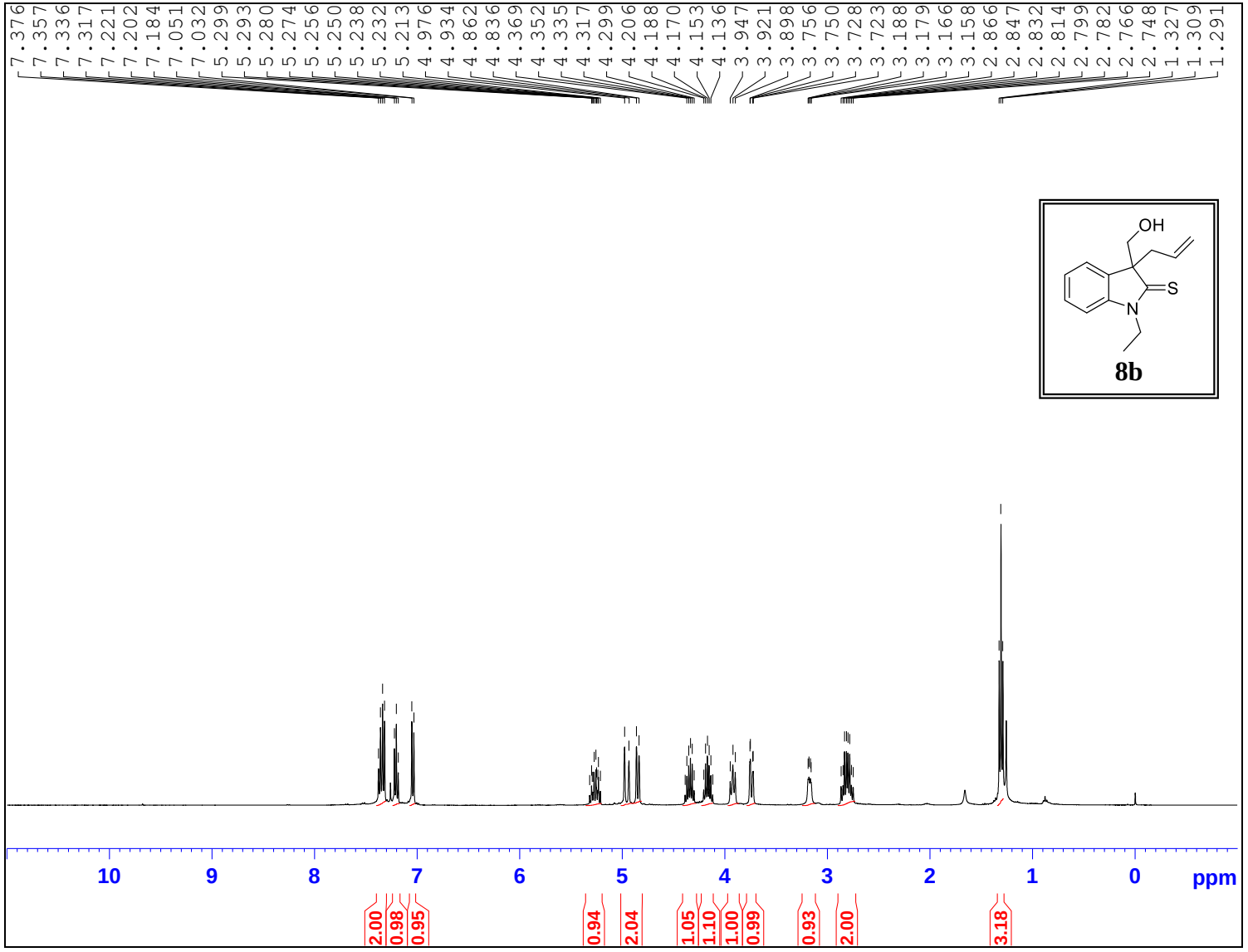
$^{1}$H NMR for compound **8a** (400 MHz, $CDCl_3$)



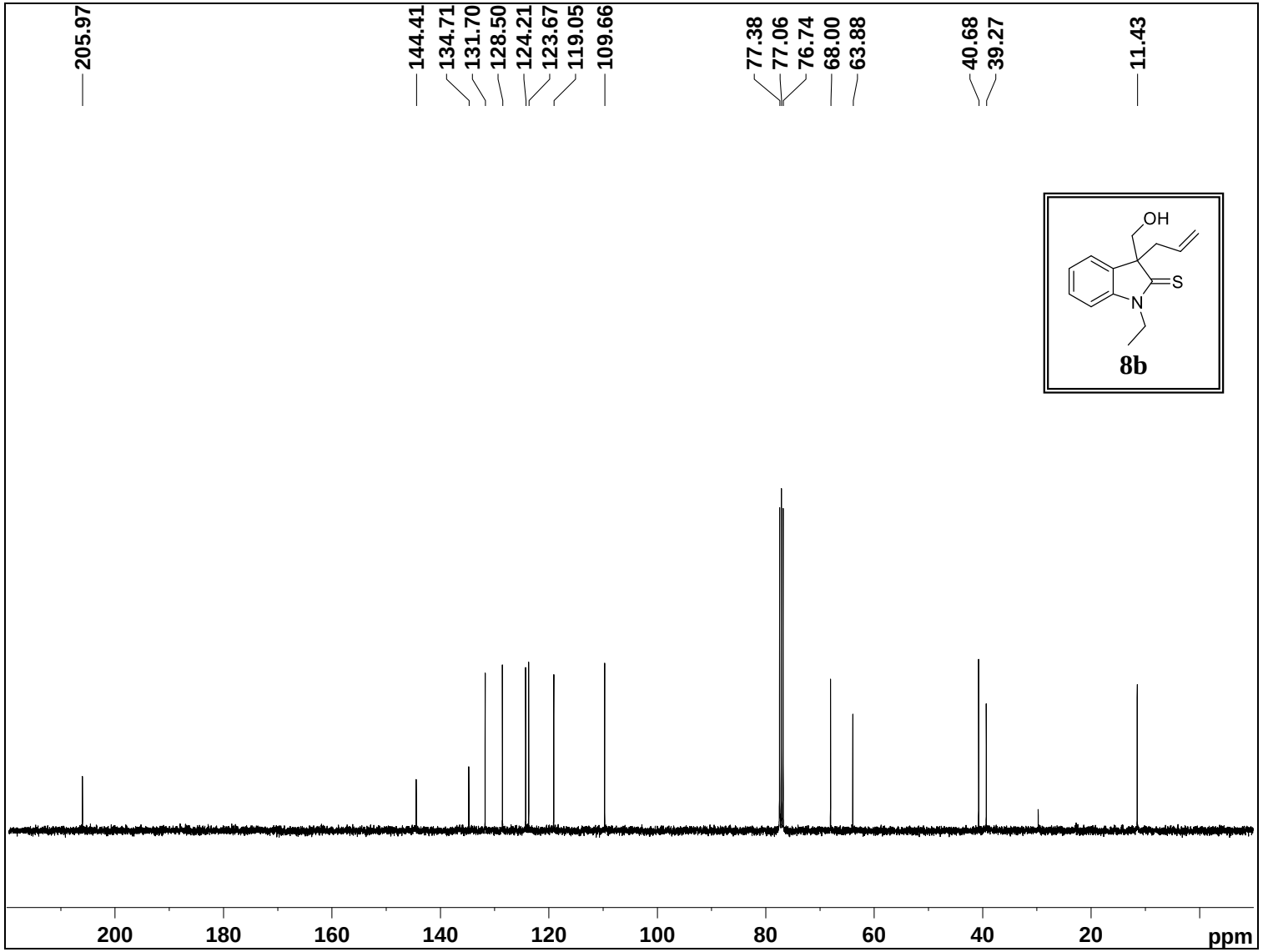
$^{13}C$ NMR for compound **8a** (101 MHz, $CDCl_3$)



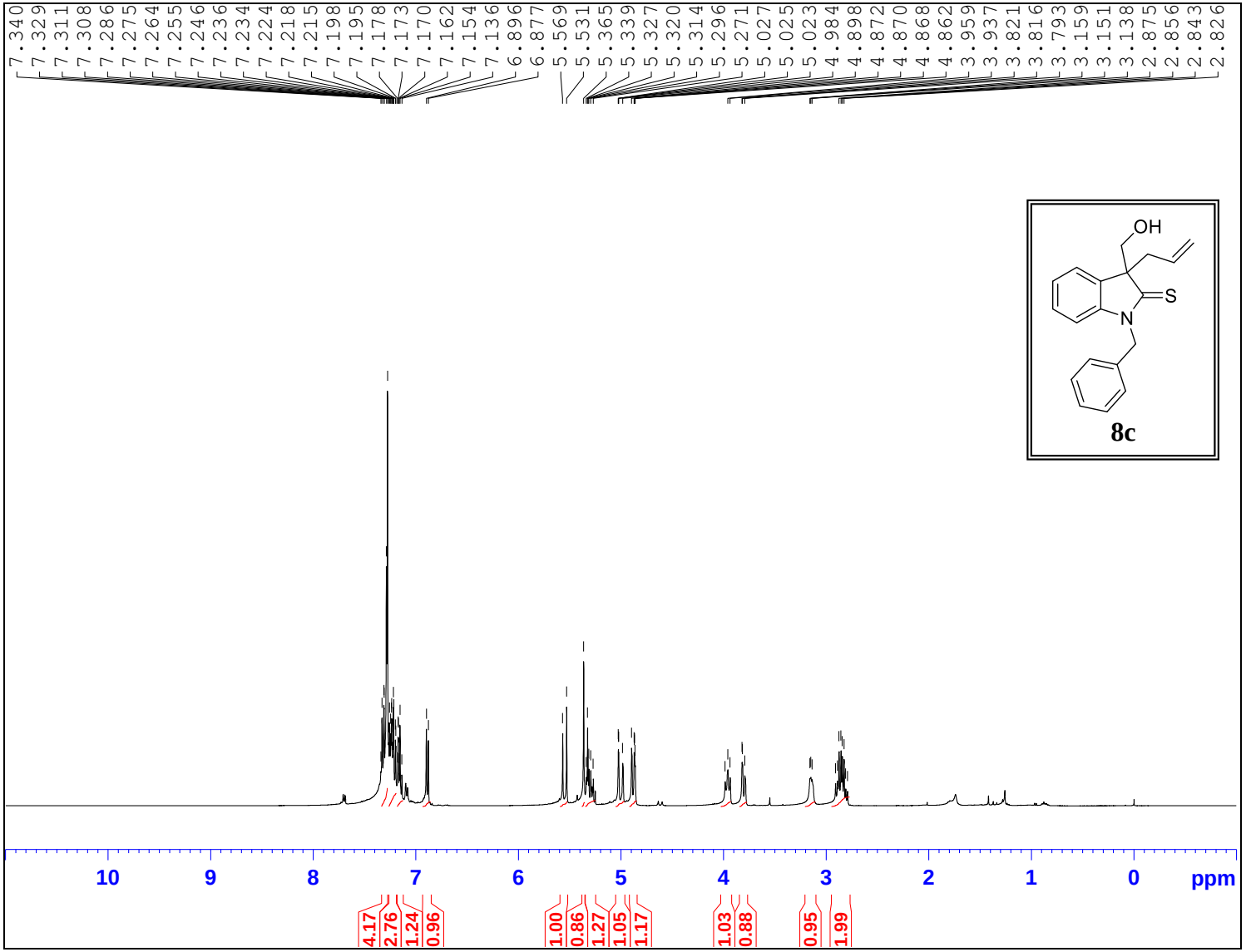
$^{1}$H NMR for compound **8b** (400 MHz, $CDCl_3$)



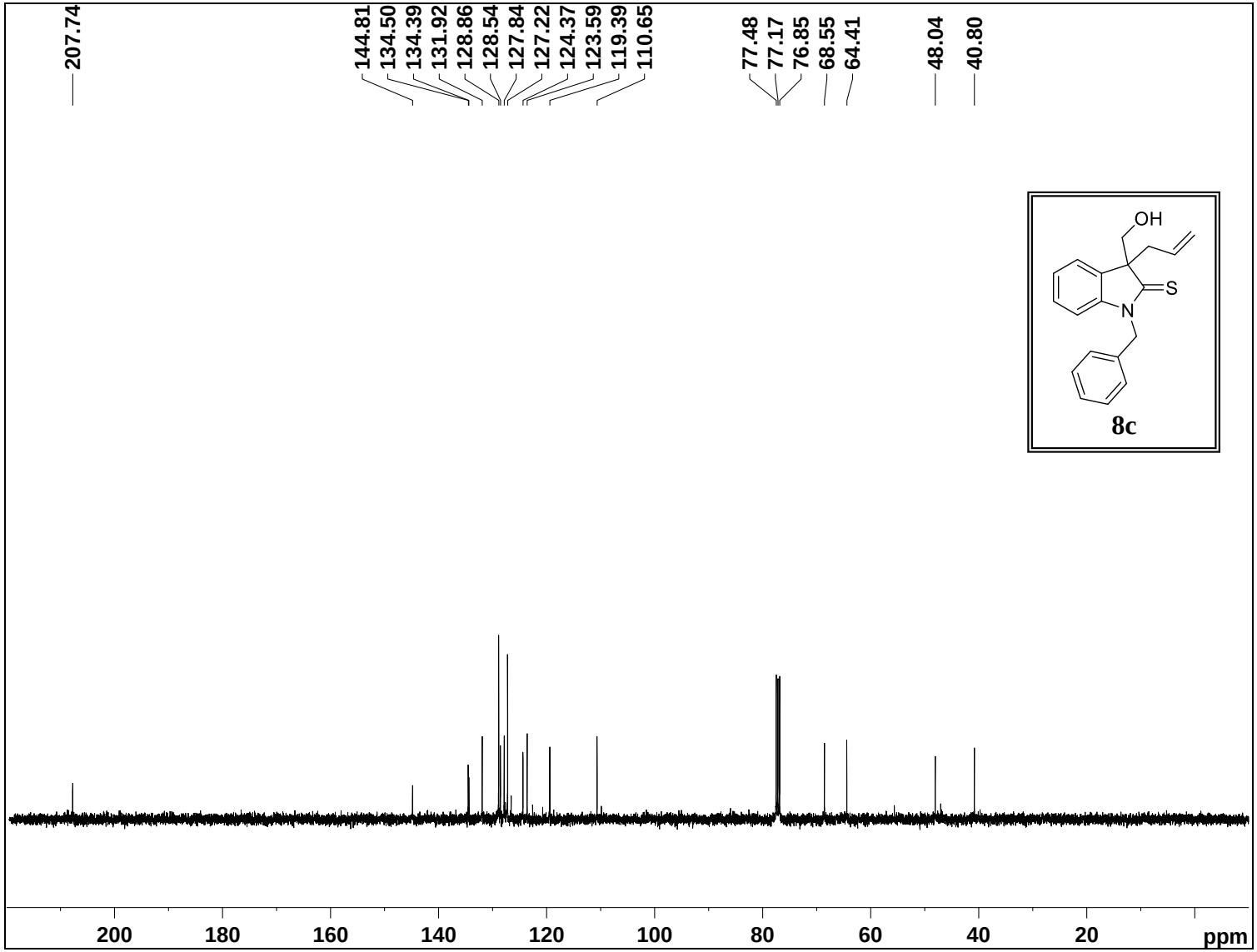
$^{13}C$ NMR for compound **8b** (101 MHz, $CDCl_3$)



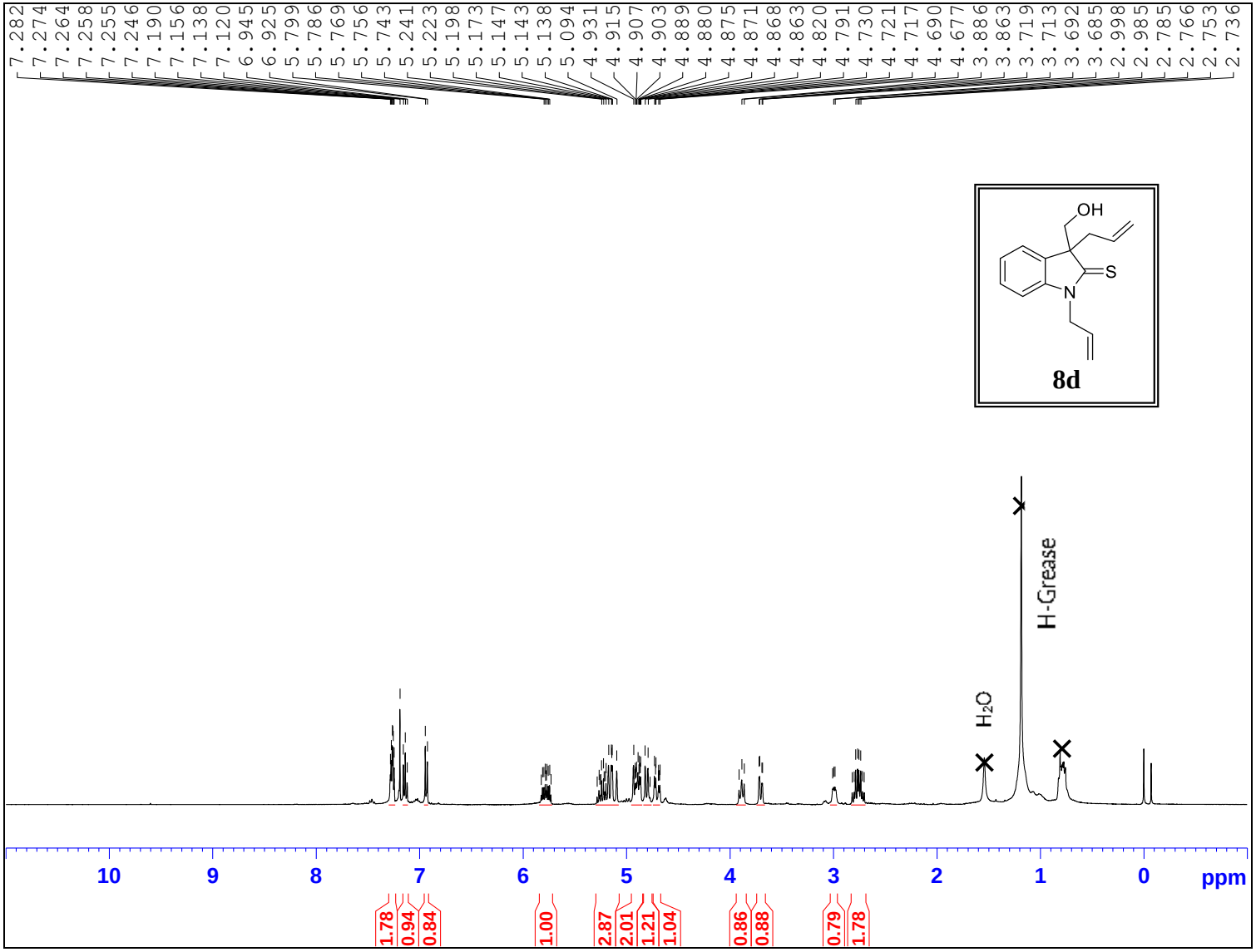
$^{1}$H NMR for compound **8c** (400 MHz, $CDCl_3$)



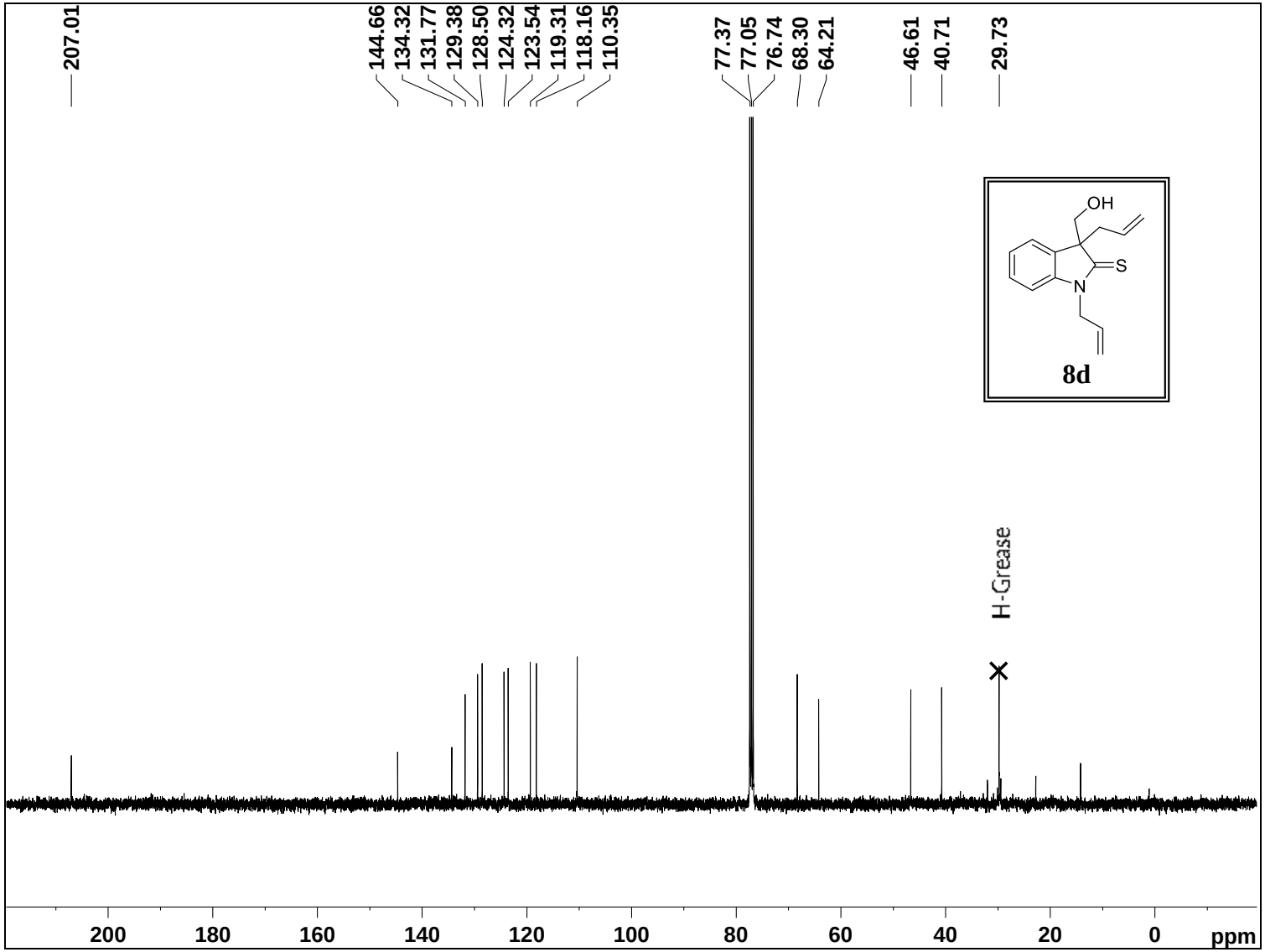
$^{13}C$ NMR for compound **8c** (101 MHz, $CDCl_3$)



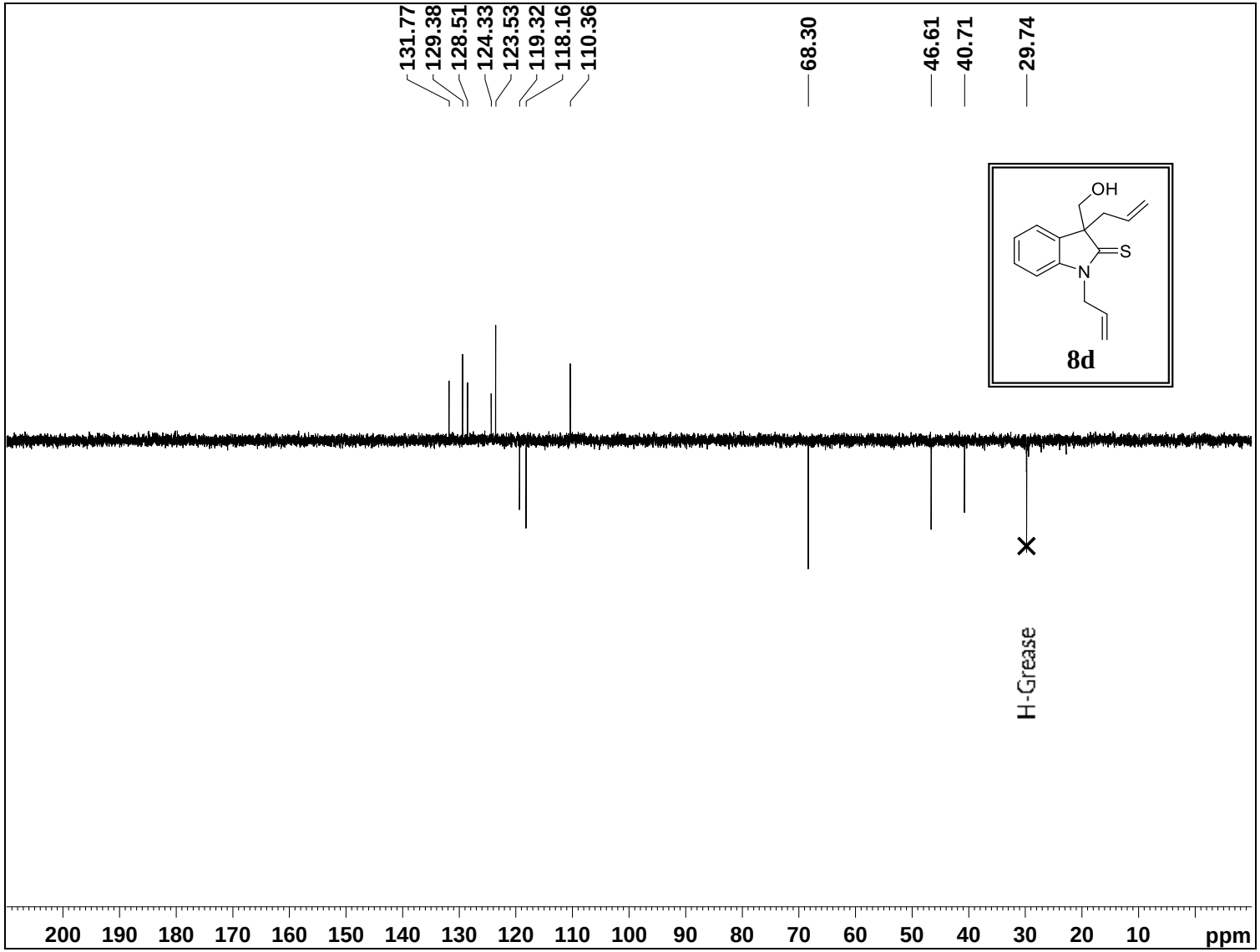
$^{1}$H NMR for compound **8d** (400 MHz, $CDCl_3$)



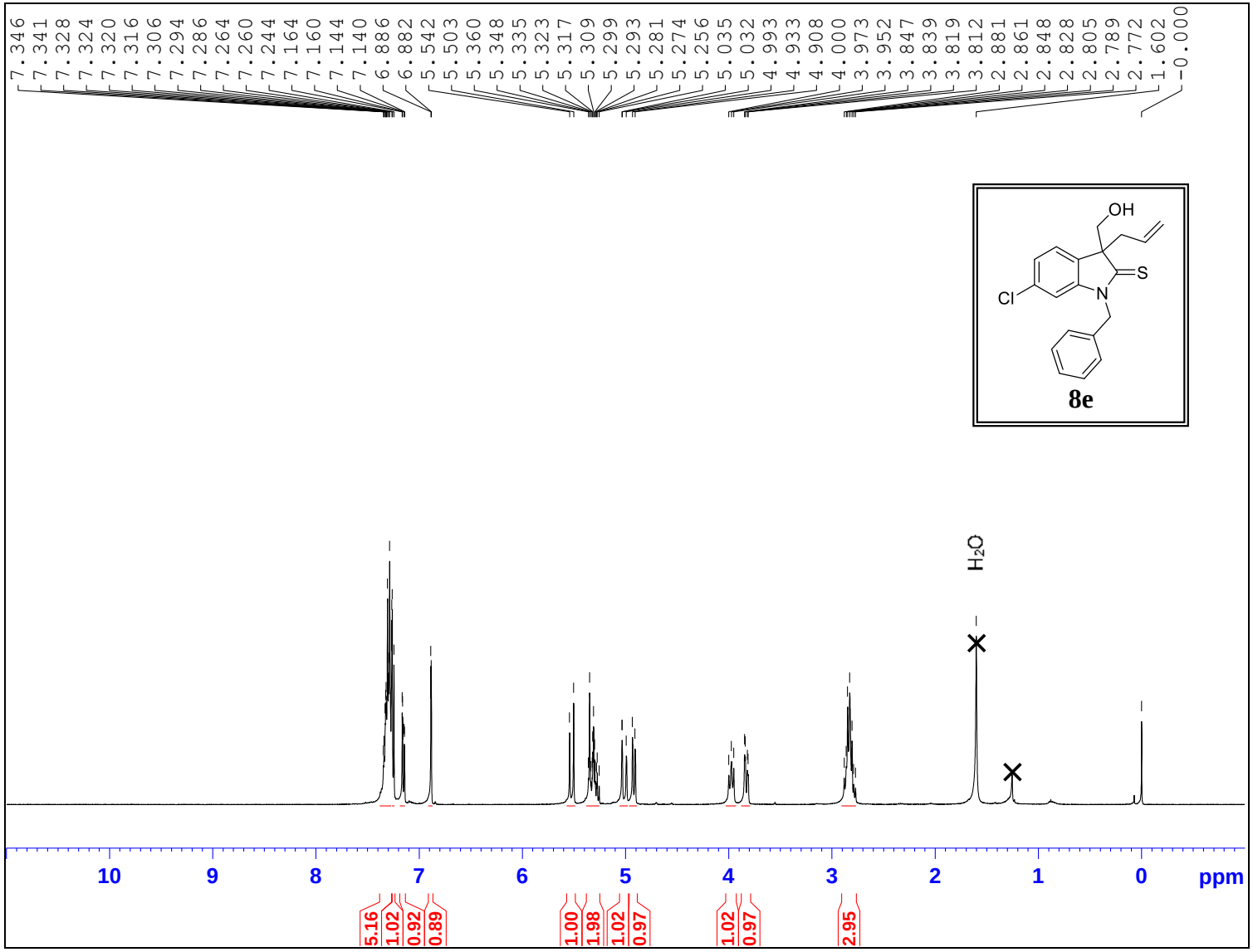
$^{13}C$ NMR for compound **8d** ($101$ MHz, $CDCl_3$)



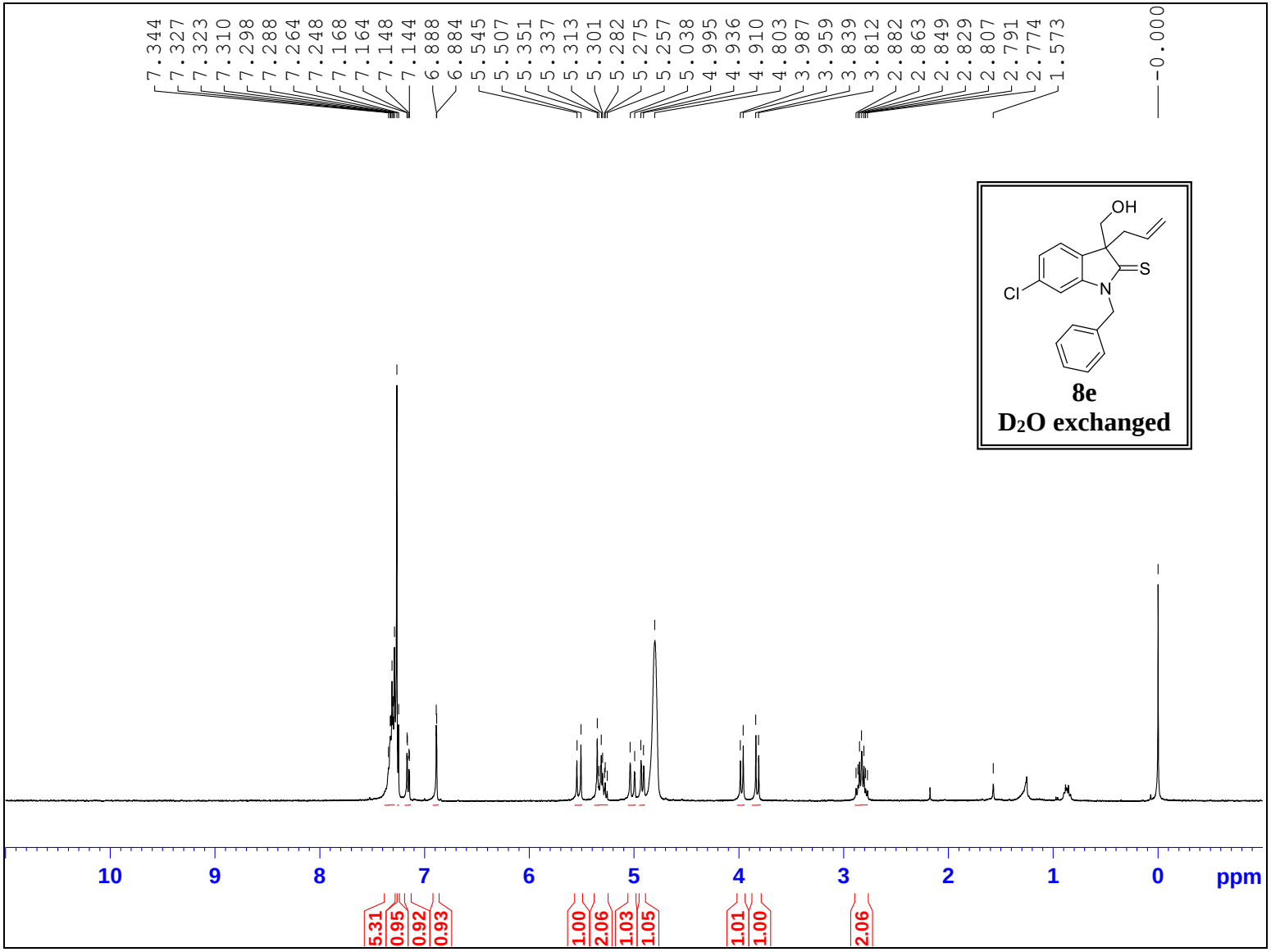
DEPT-135 NMR for compound **8d** (101 MHz, $CDCl_3$)



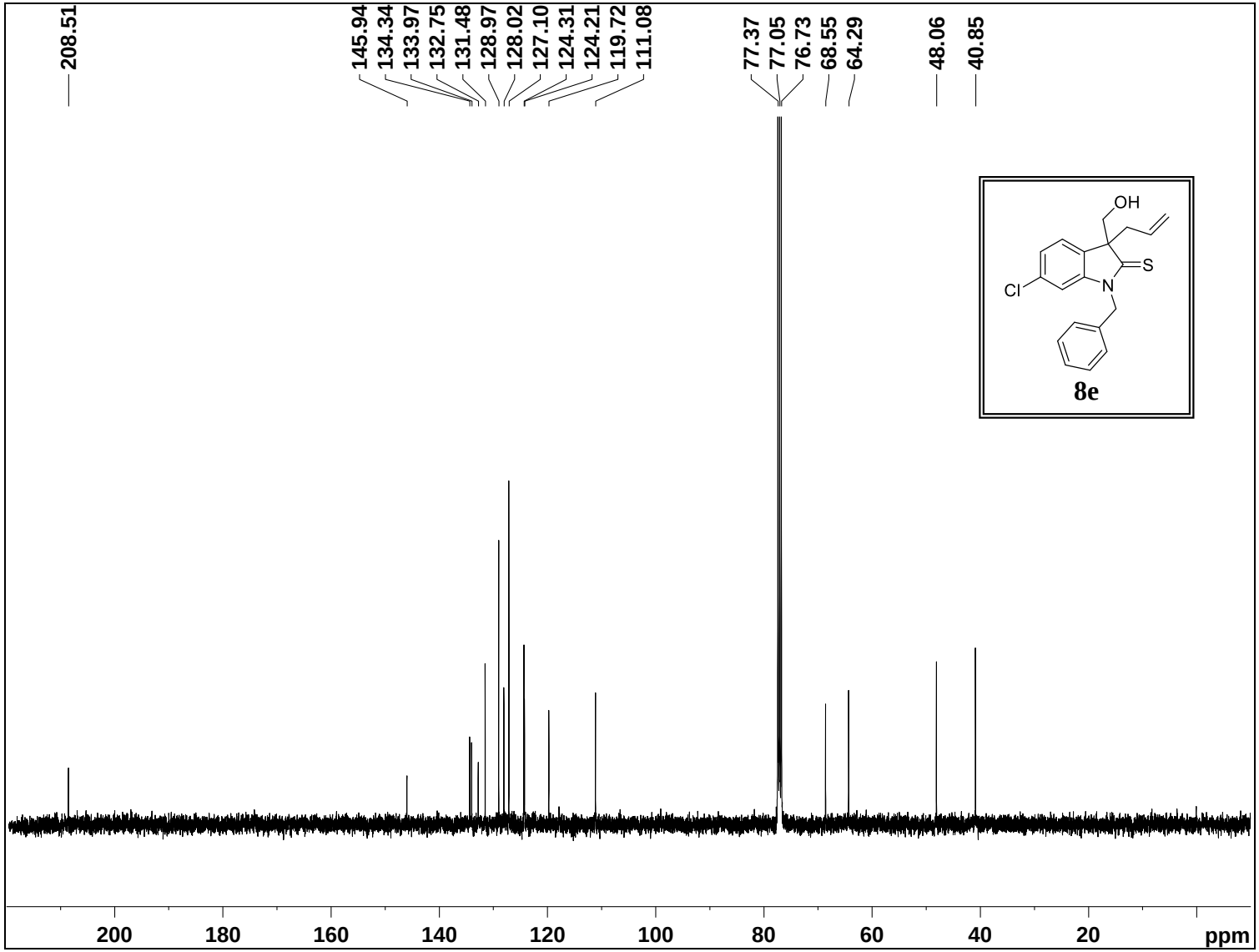
$^{1}$H NMR for compound **8e** (400 MHz, $CDCl_3$)



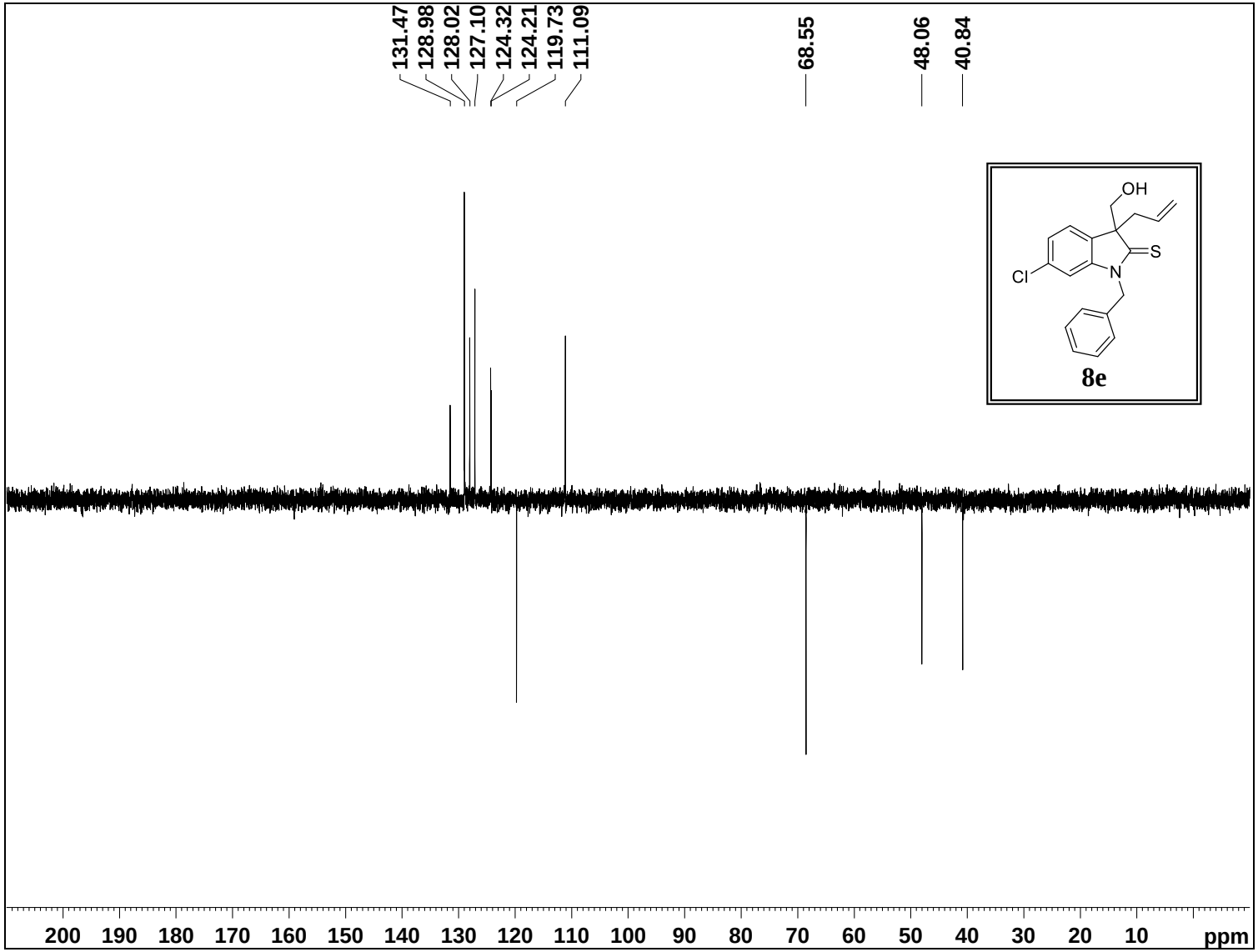
$^{1}$H NMR for compound **8e** (400 MHz, $CDCl_3$)



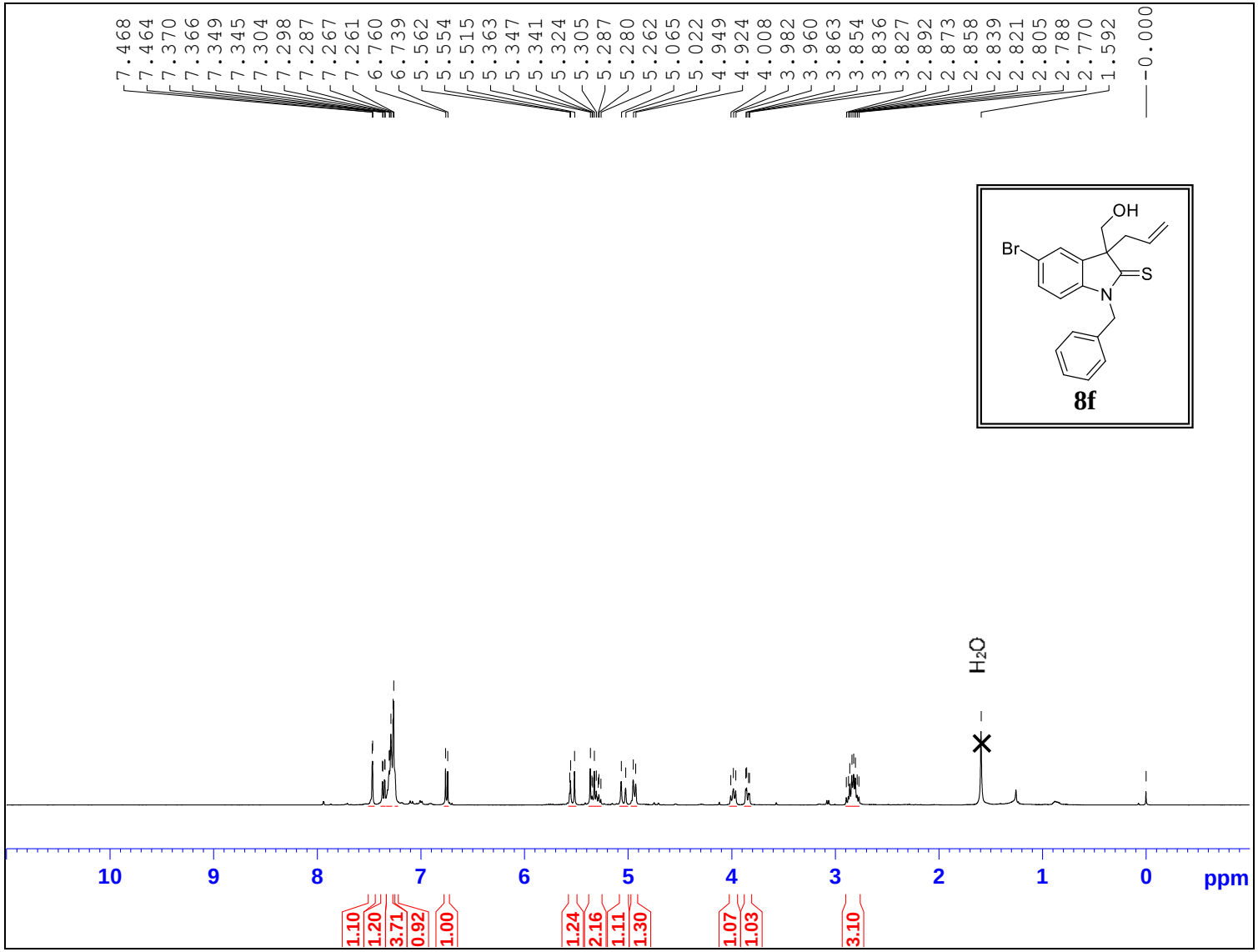
$^{13}C$ NMR for compound **8e** (101 MHz, $CDCl_3$)



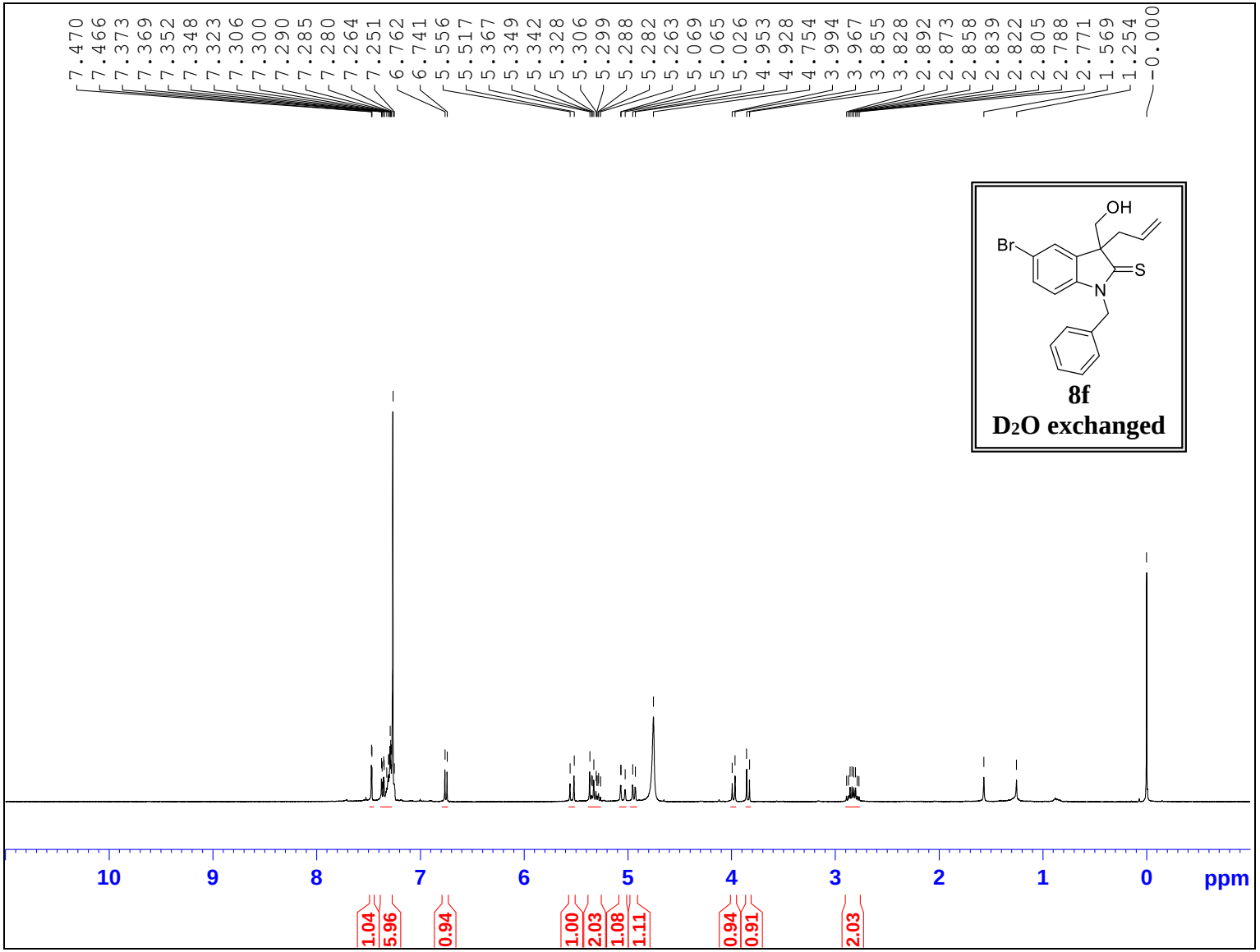
DEPT-135 NMR for compound **8e** (101 MHz, $CDCl_3$)



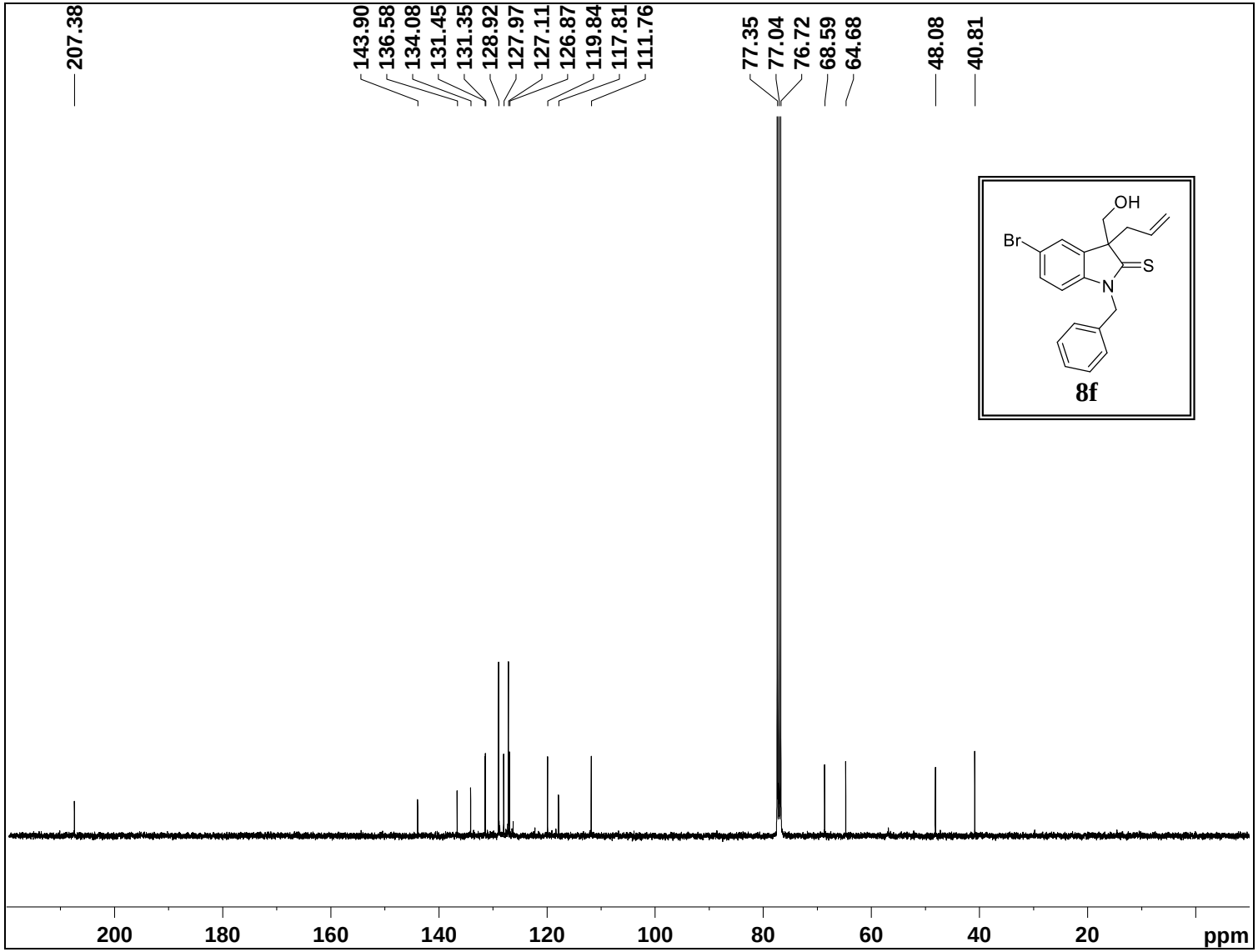
$^{1}$H NMR for compound **8f** (400 MHz, $CDCl_3$)



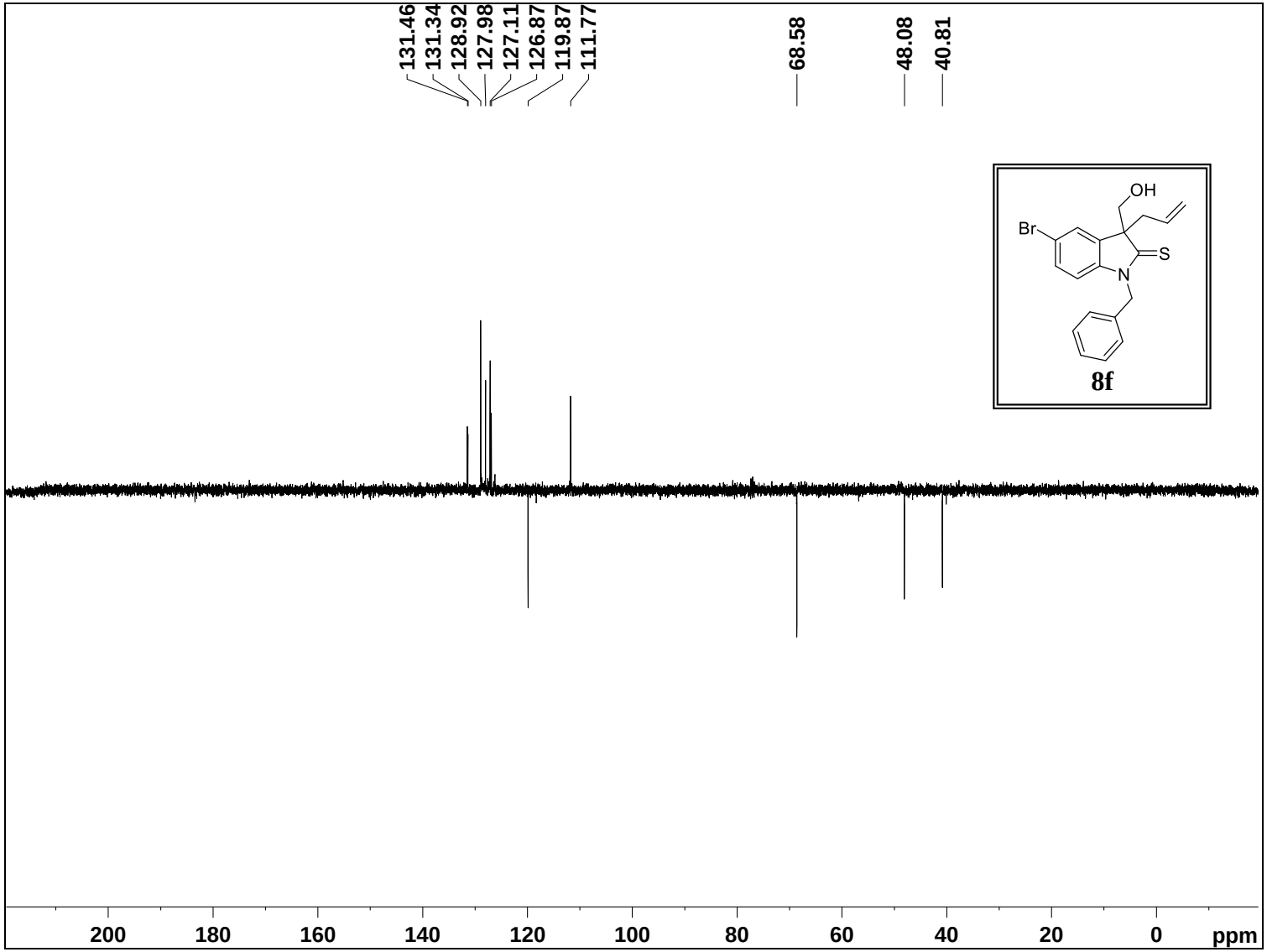
$^{1}$H NMR for compound **8f** (400 MHz, $CDCl_3$)



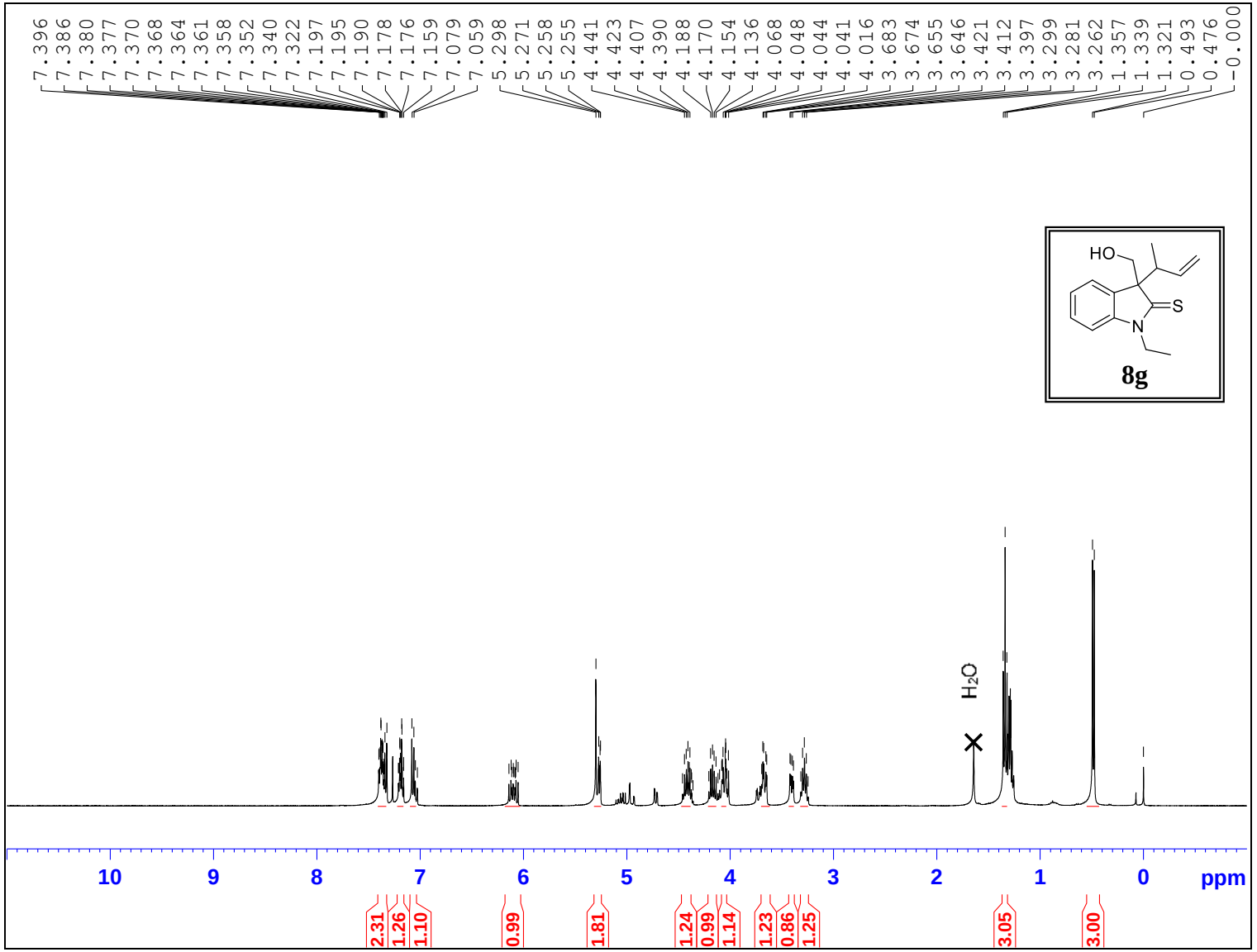
$^{13}C$ NMR for compound **8f** (101 MHz, $CDCl_3$)



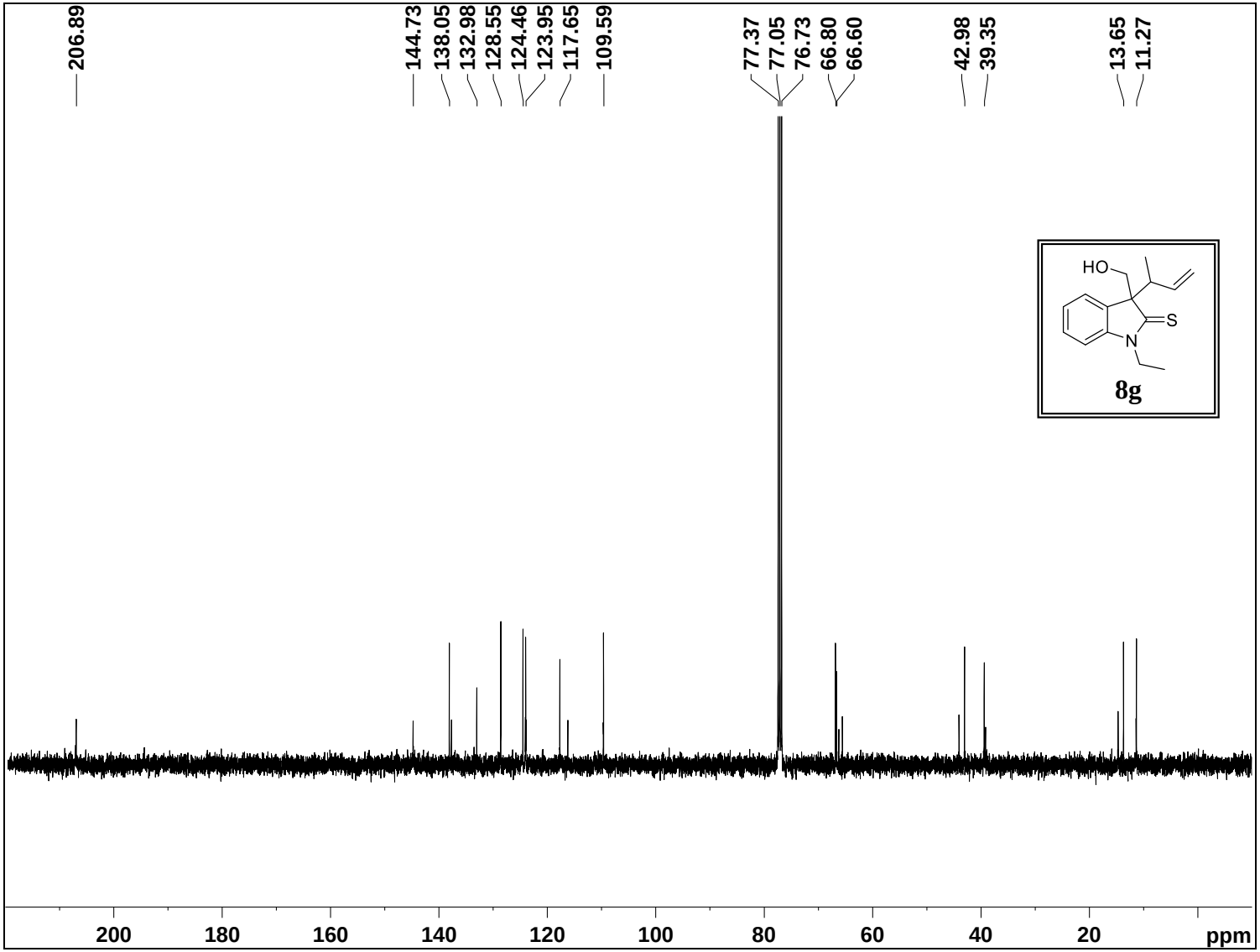
DEPT-135 NMR for compound **8f** (101 MHz, $CDCl_3$)



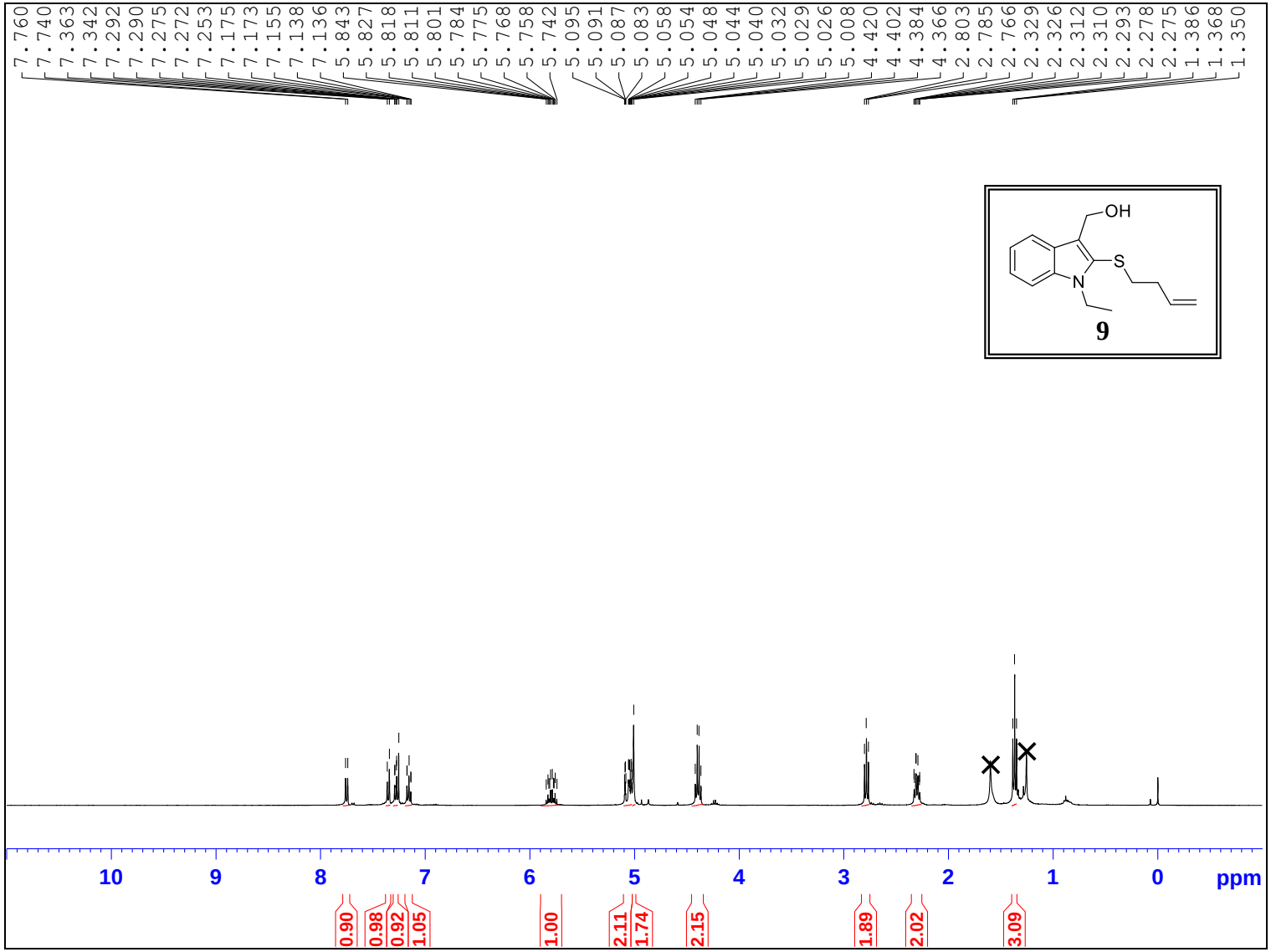
$^{1}$H NMR for compound **8g** (400 MHz, $CDCl_3$)



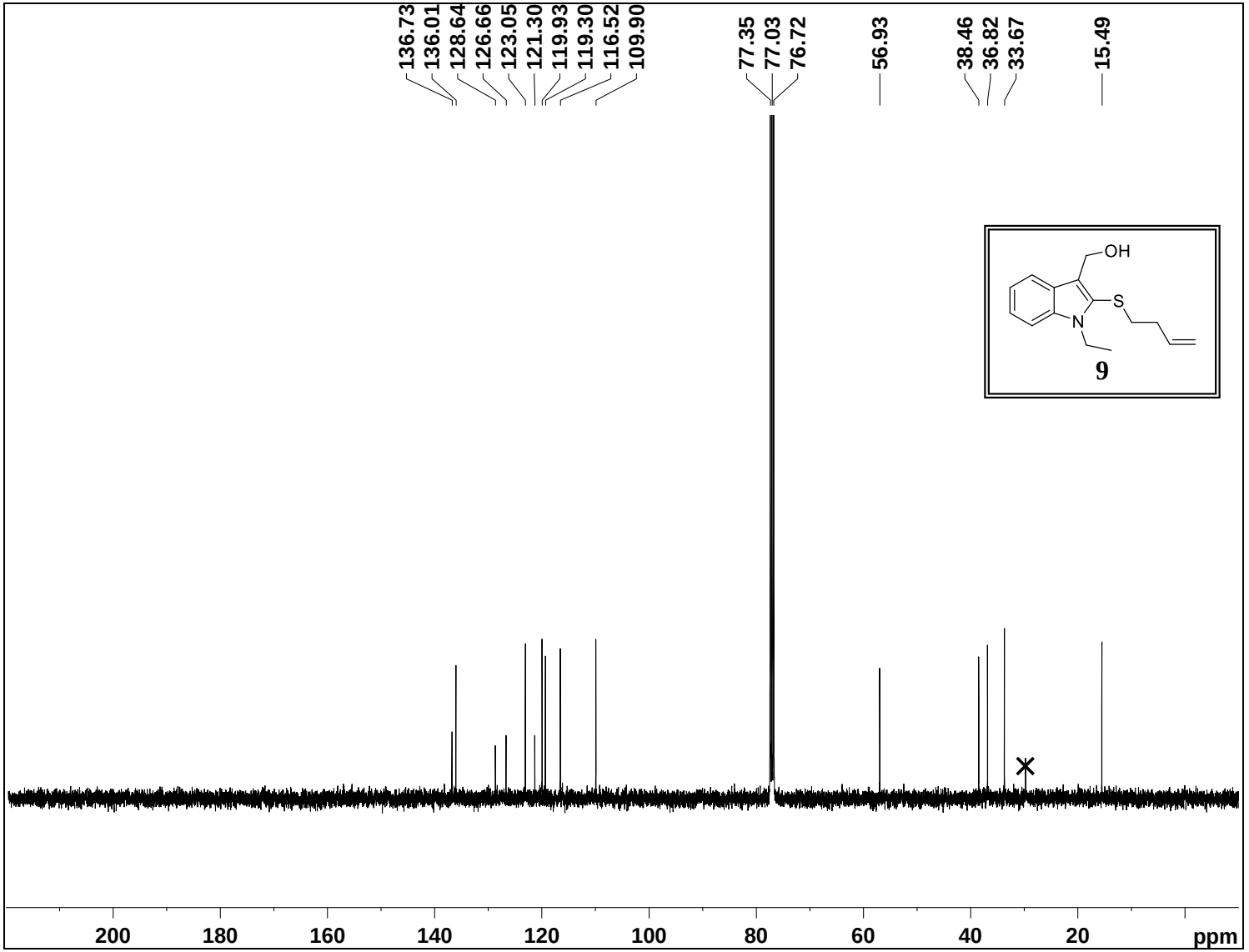
$^{13}C$ NMR for compound **8g** ($101$ MHz, $CDCl_3$)



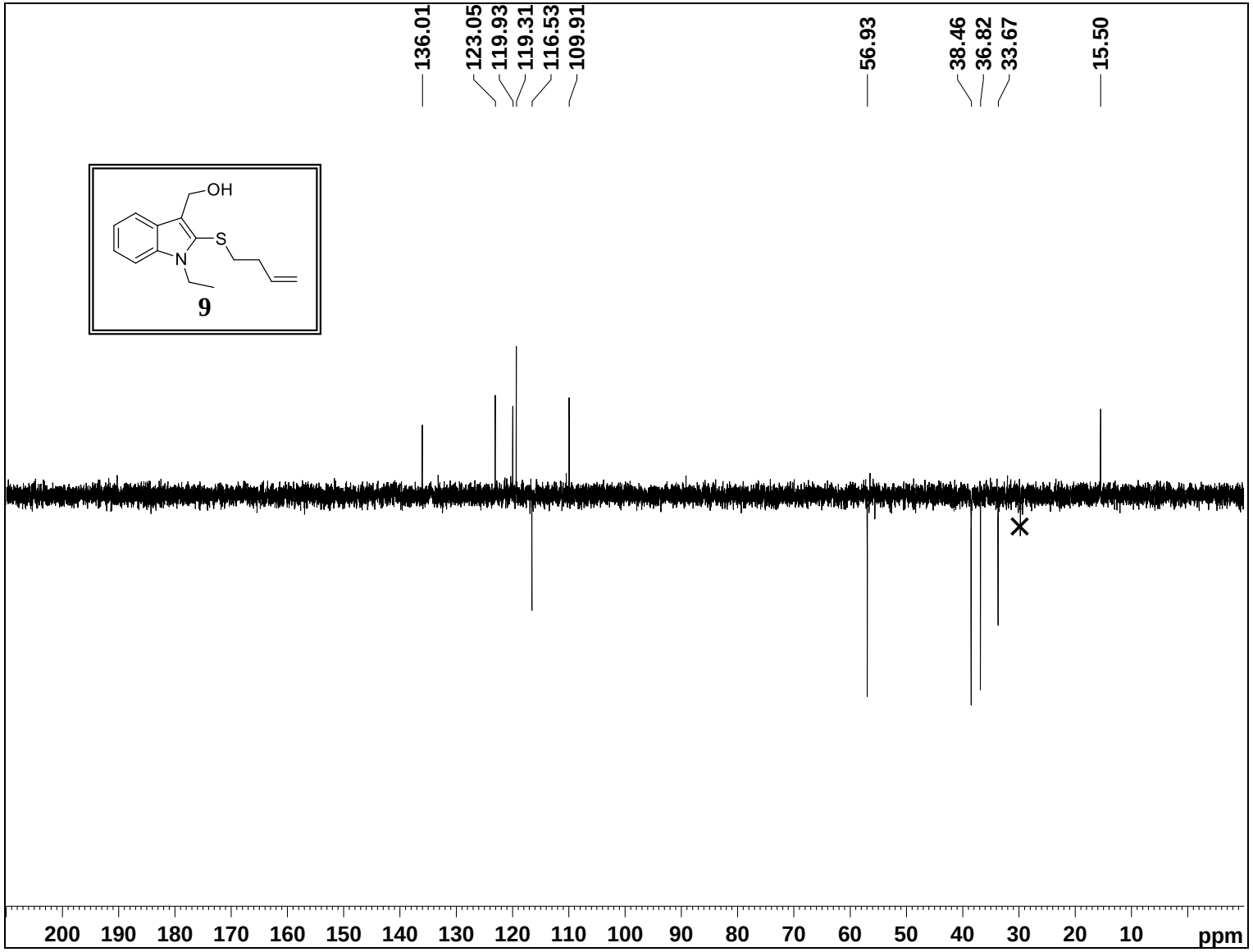
$^{1}$H NMR for compound **9** (400 MHz, $CDCl_3$)



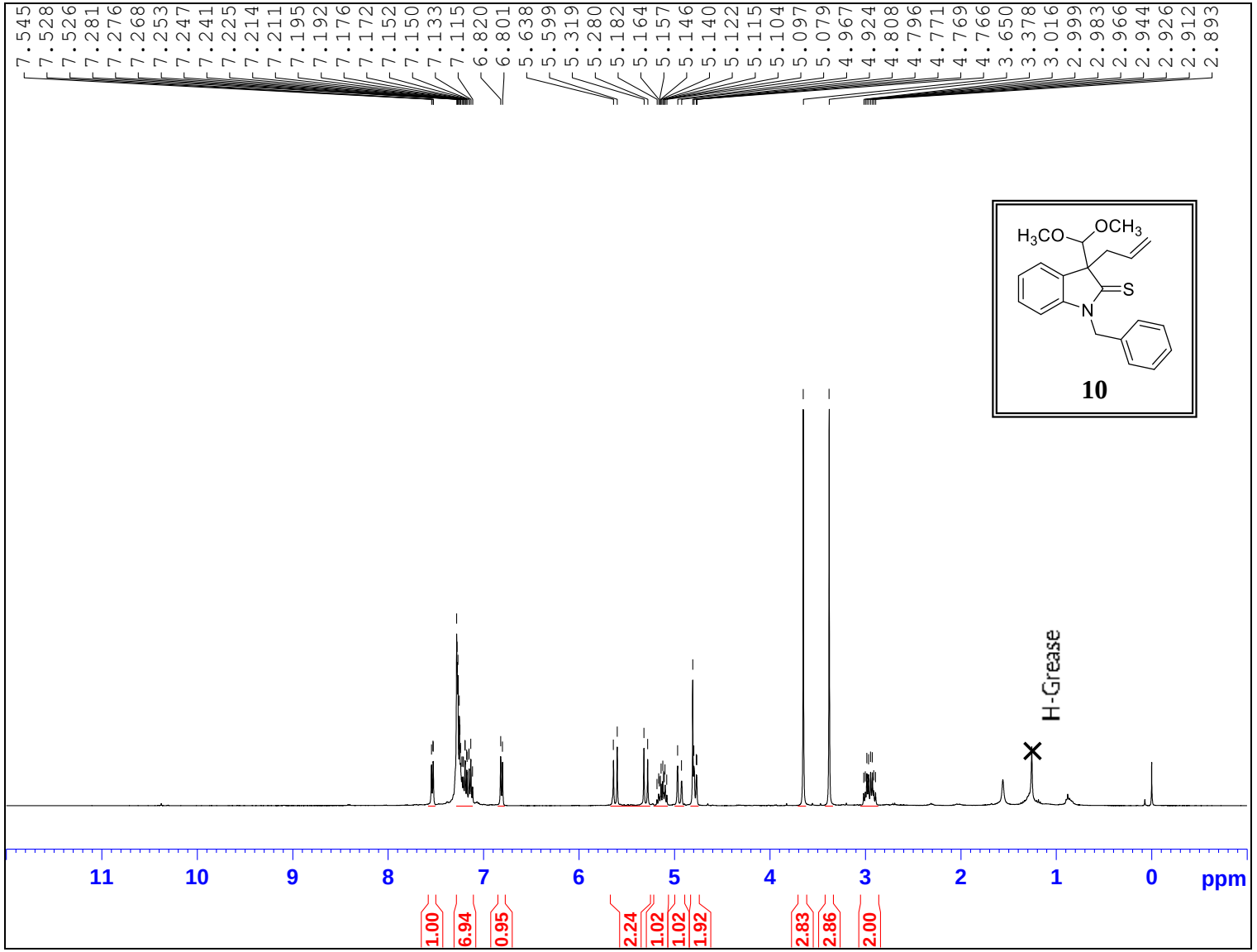
$^{13}C$ NMR for compound **9** ($CDCl_3$)



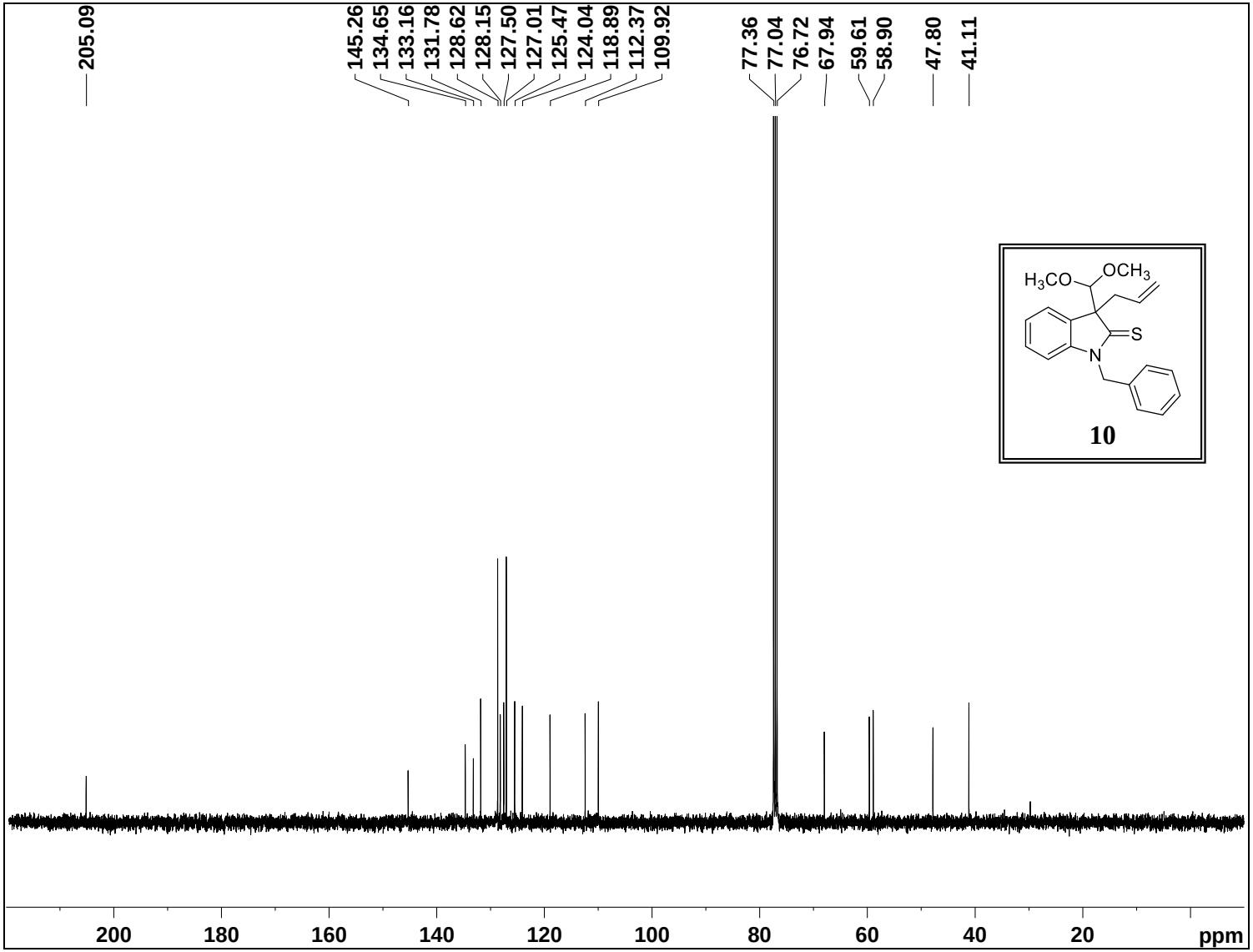
DEPT-135 NMR for compound **10** (101 MHz, $CDCl_3$)



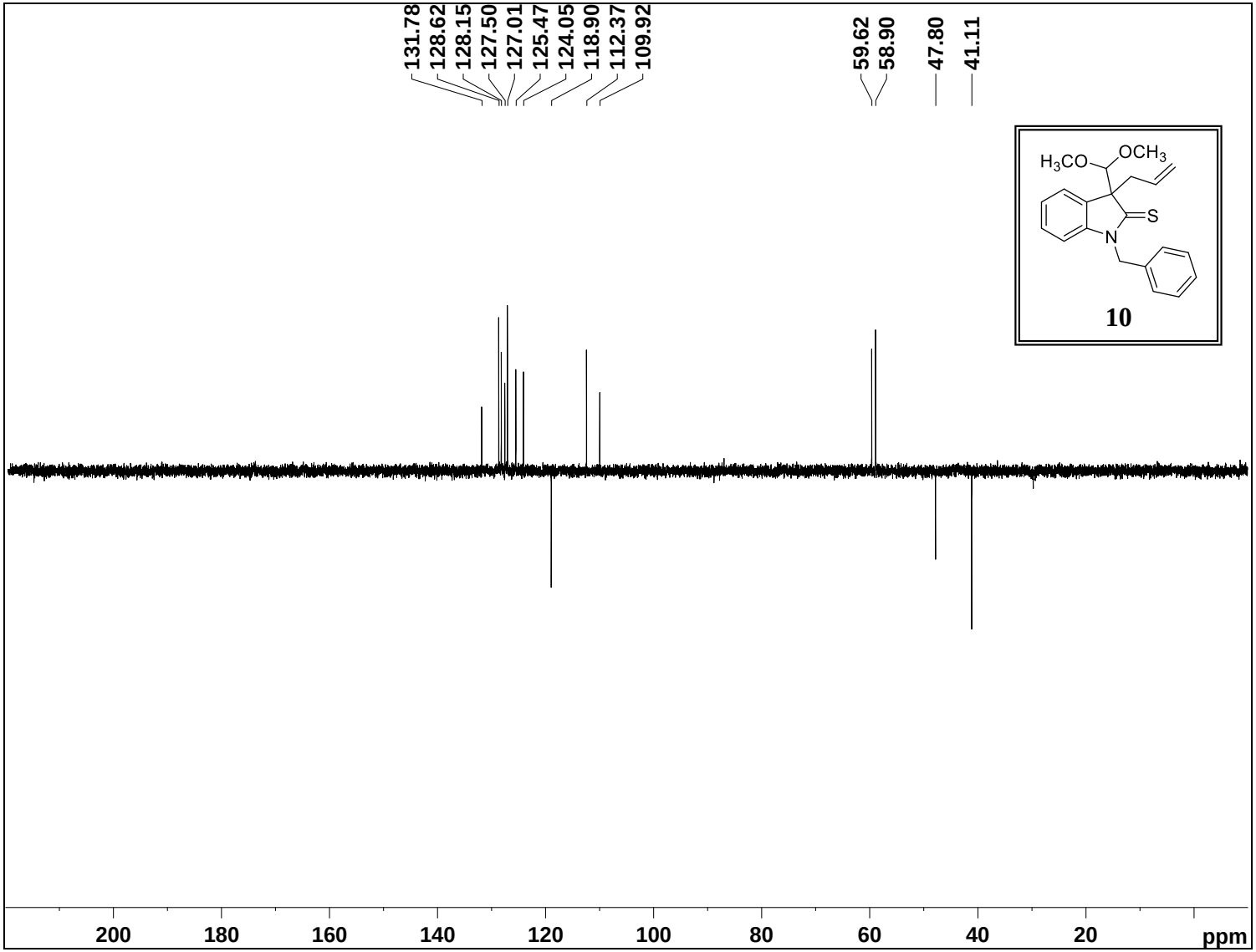
$^{1}$H NMR for compound **10** (400 MHz, $CDCl_3$)



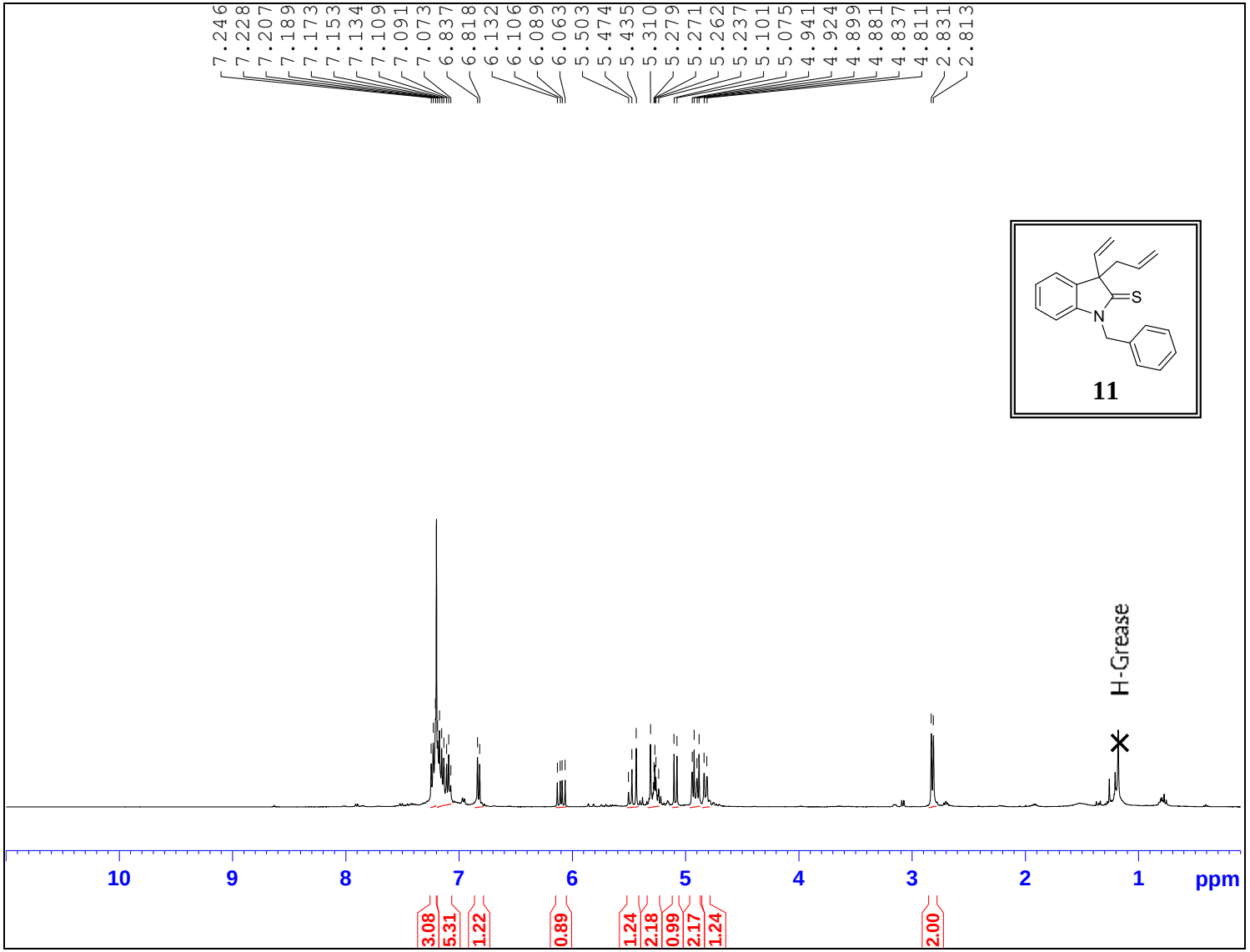
$^{13}C$ NMR for compound **10** ($101$ MHz, $CDCl_3$)



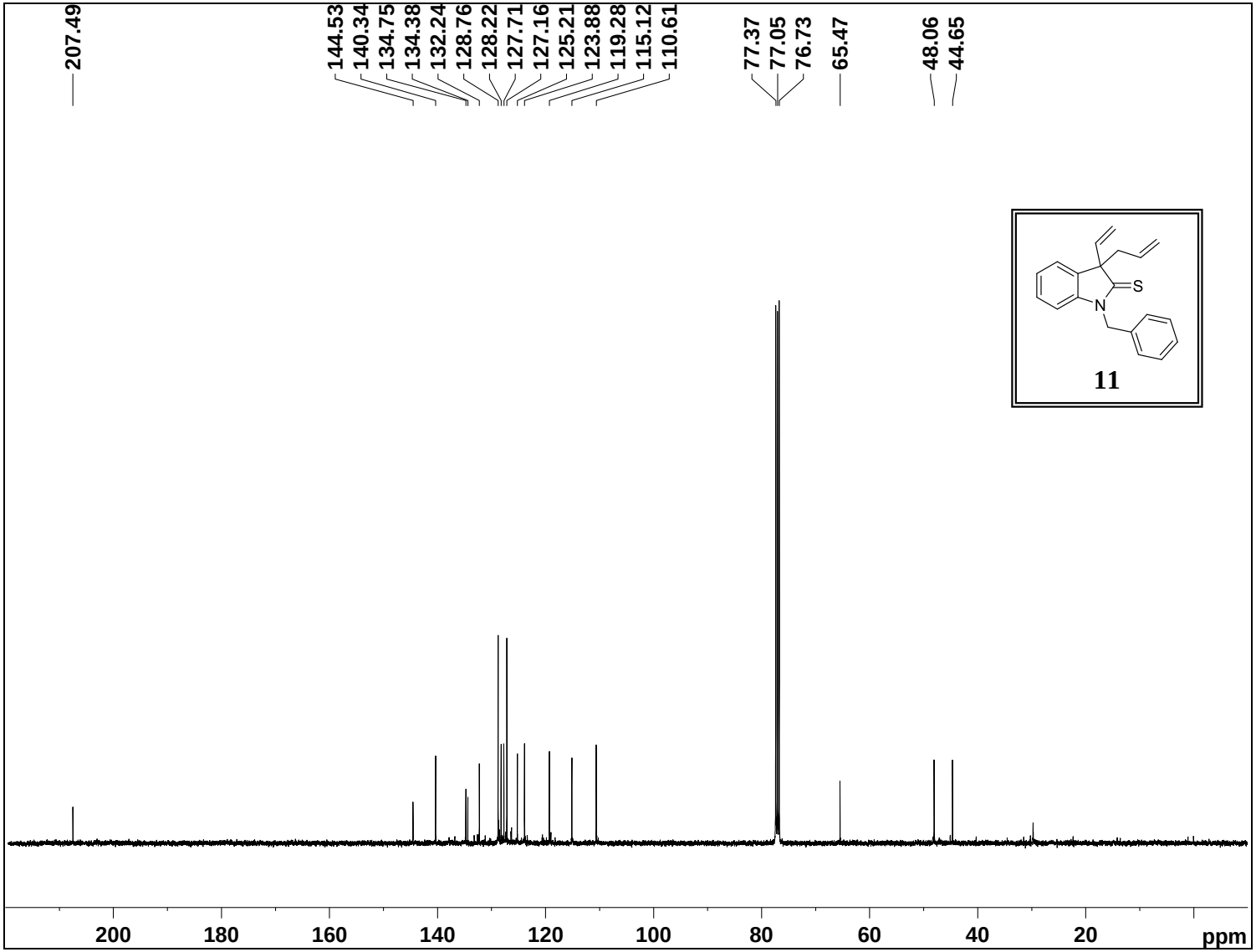
DEPT-135 NMR for compound **10** (101 MHz, $CDCl_3$)



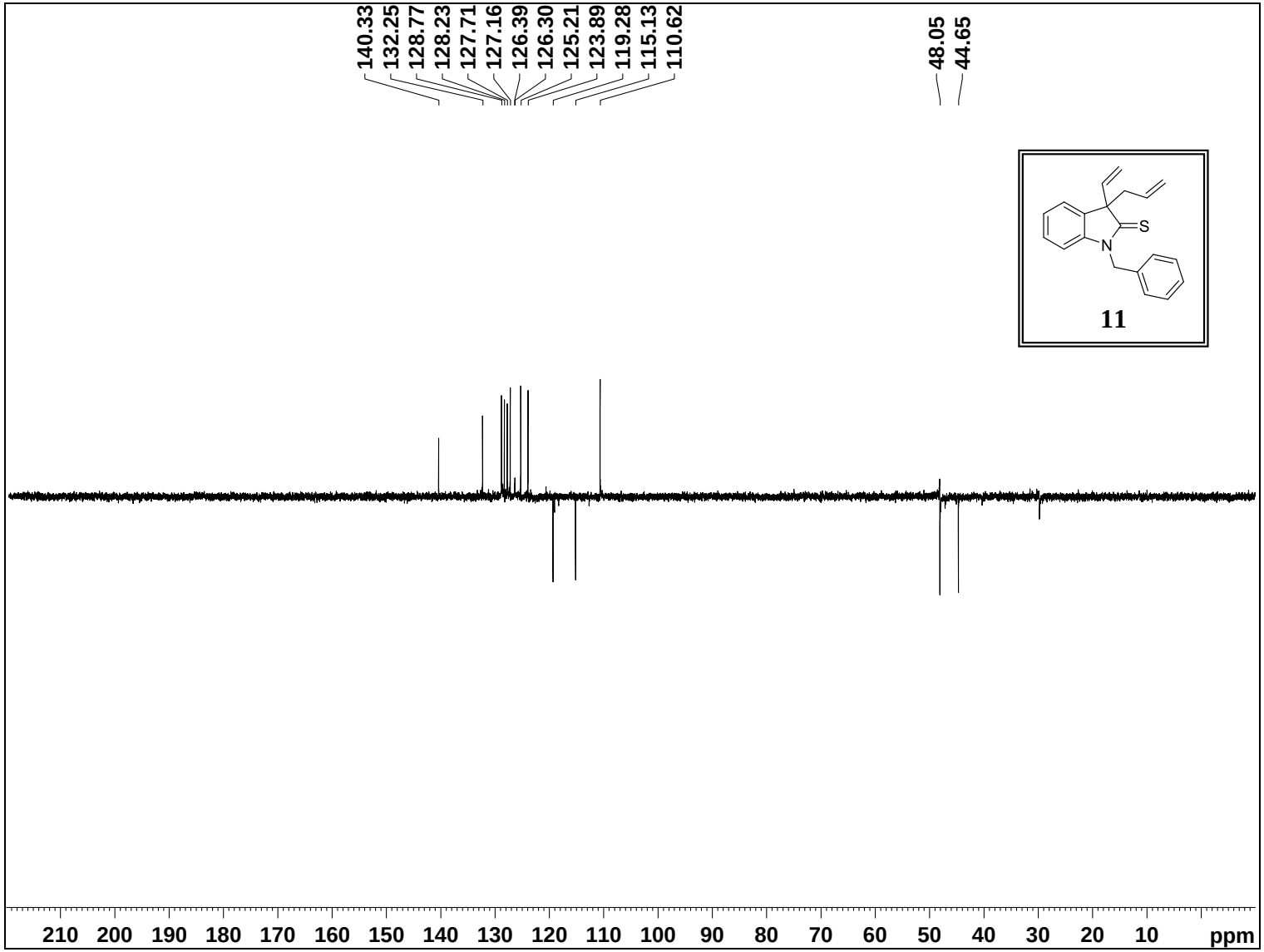
$^{1}$H NMR for compound **11** (400 MHz, $CDCl_3$)



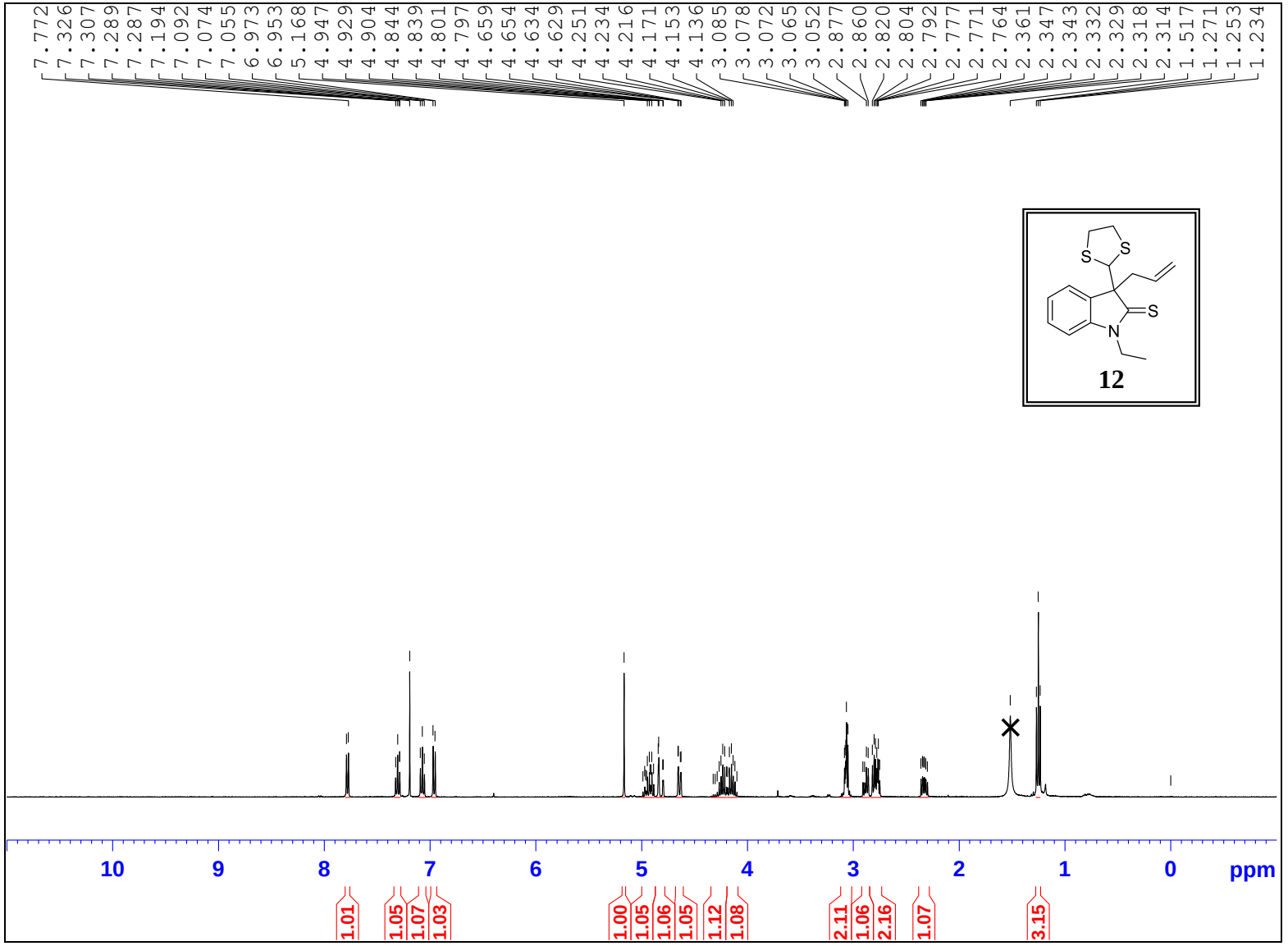
$^{13}C$ NMR for compound **11** ($101$ MHz, $CDCl_3$)



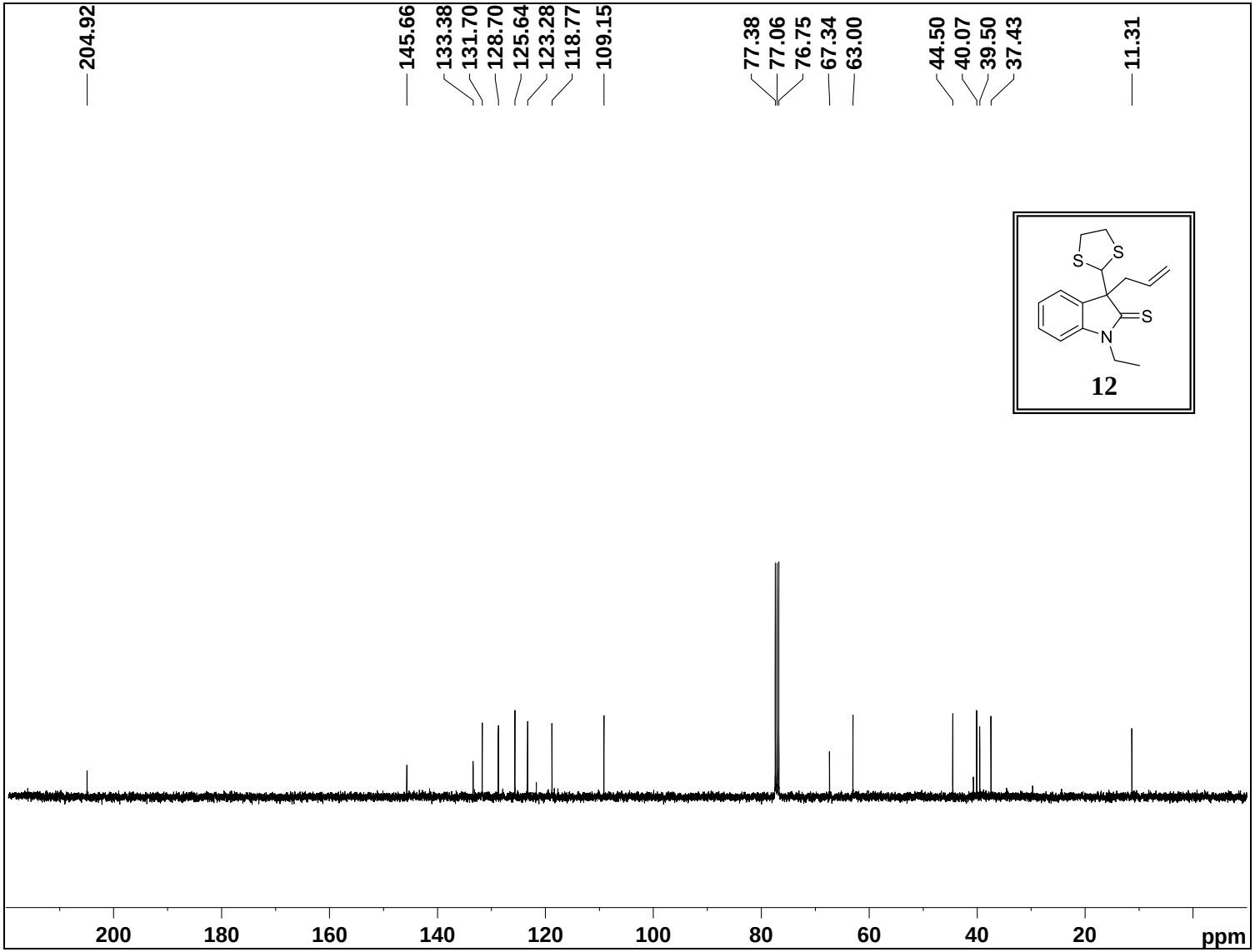
DEPT-135 NMR for compound **15f** (101 MHz, $CDCl_3$)



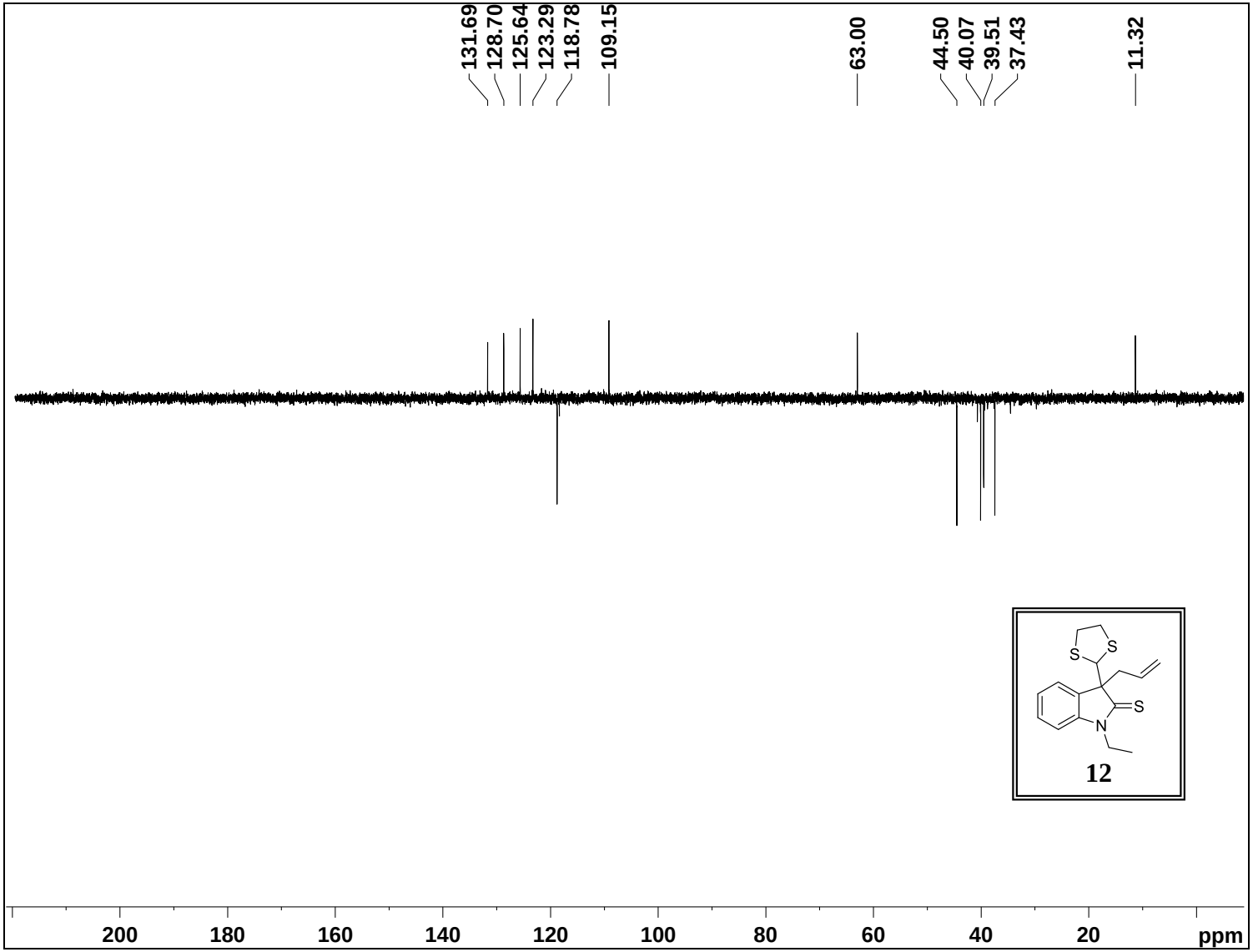
$^{1}$H NMR for compound **12** (400 MHz, $CDCl_3$)



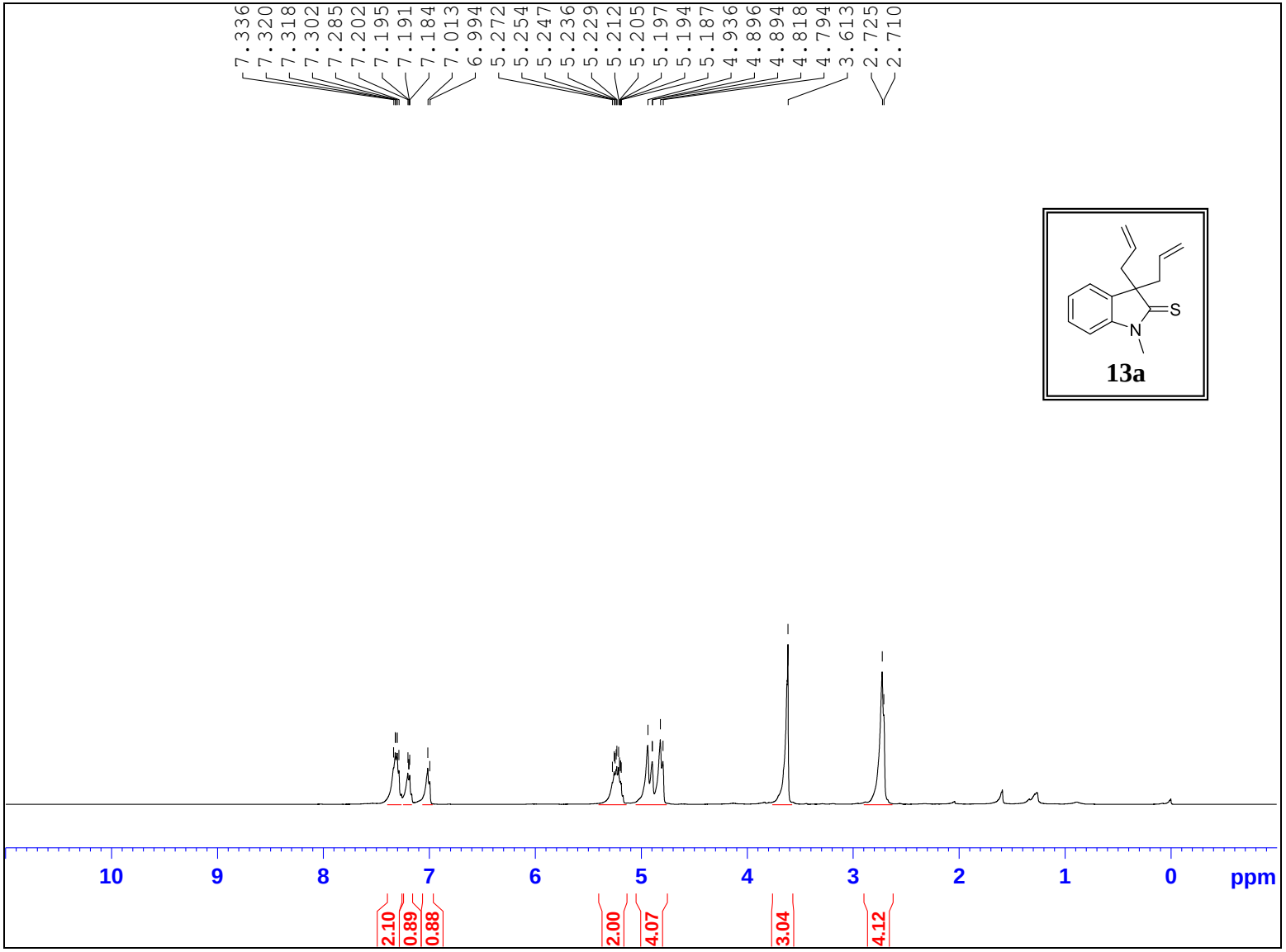
$^{13}C$ NMR for compound **12** ($101$ MHz, $CDCl_3$)



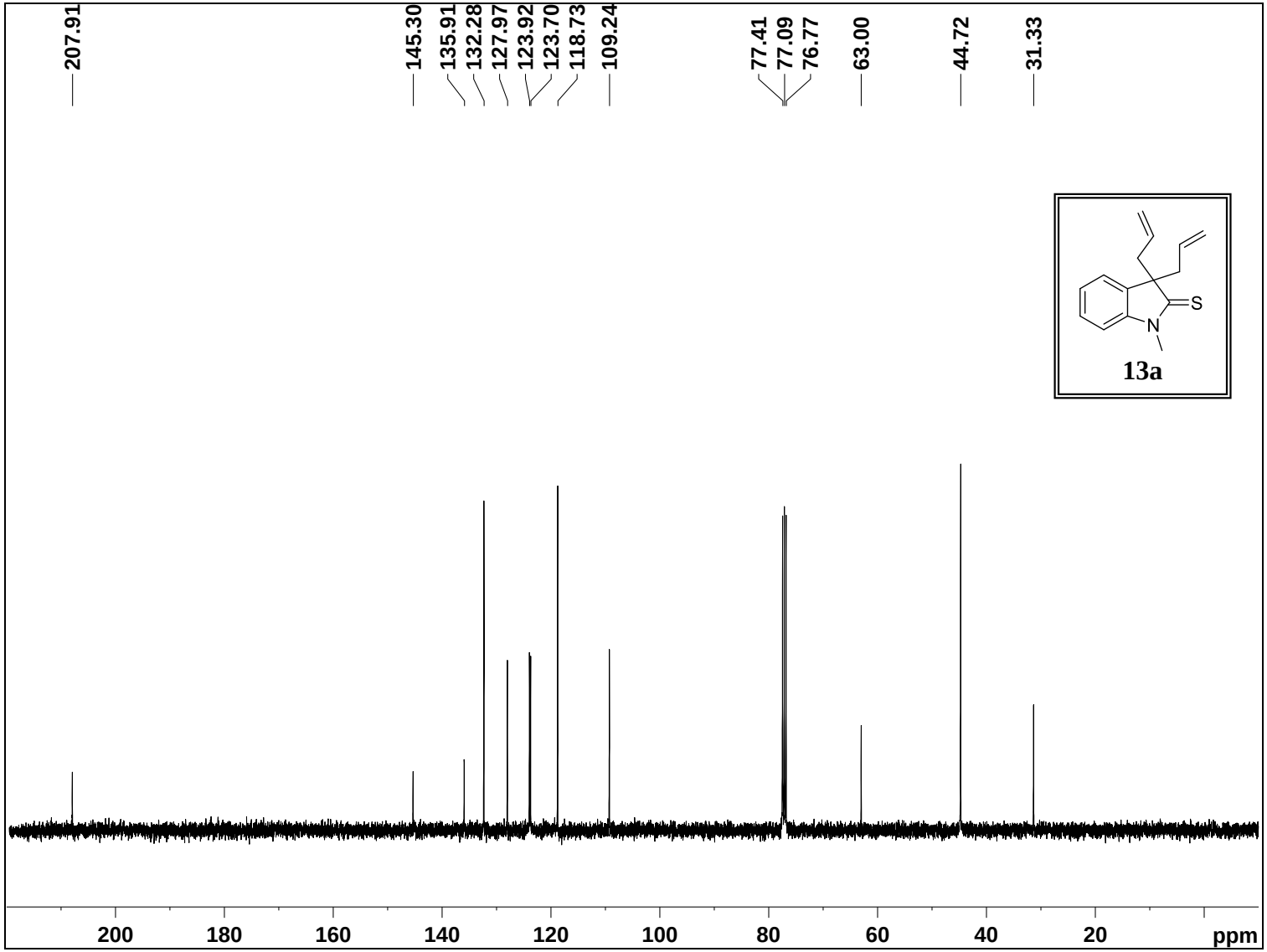
DEPT-135 NMR for compound **12** (101 MHz, $CDCl_3$)



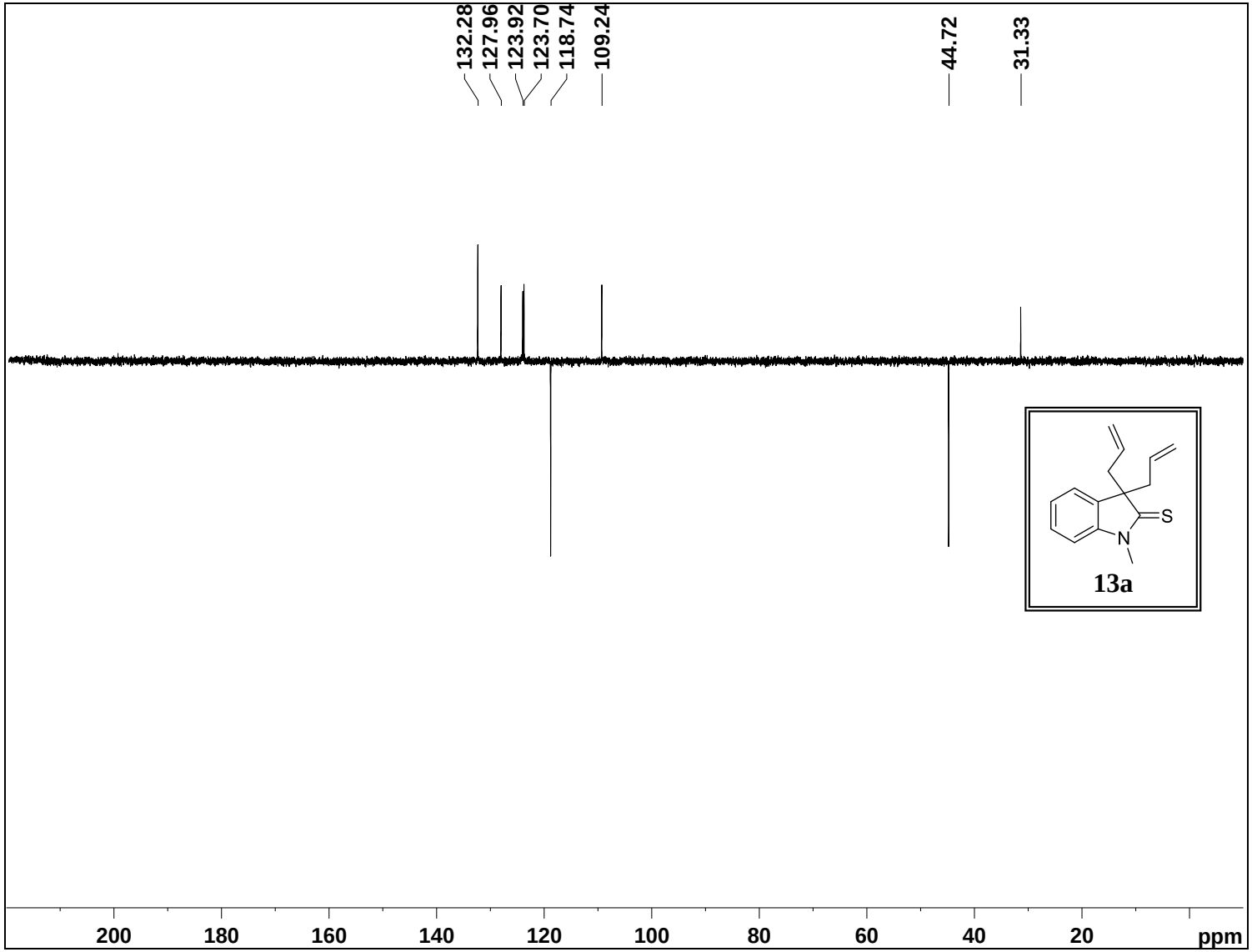
$^{1}$H NMR for compound **13a** (400 MHz, $CDCl_3$)



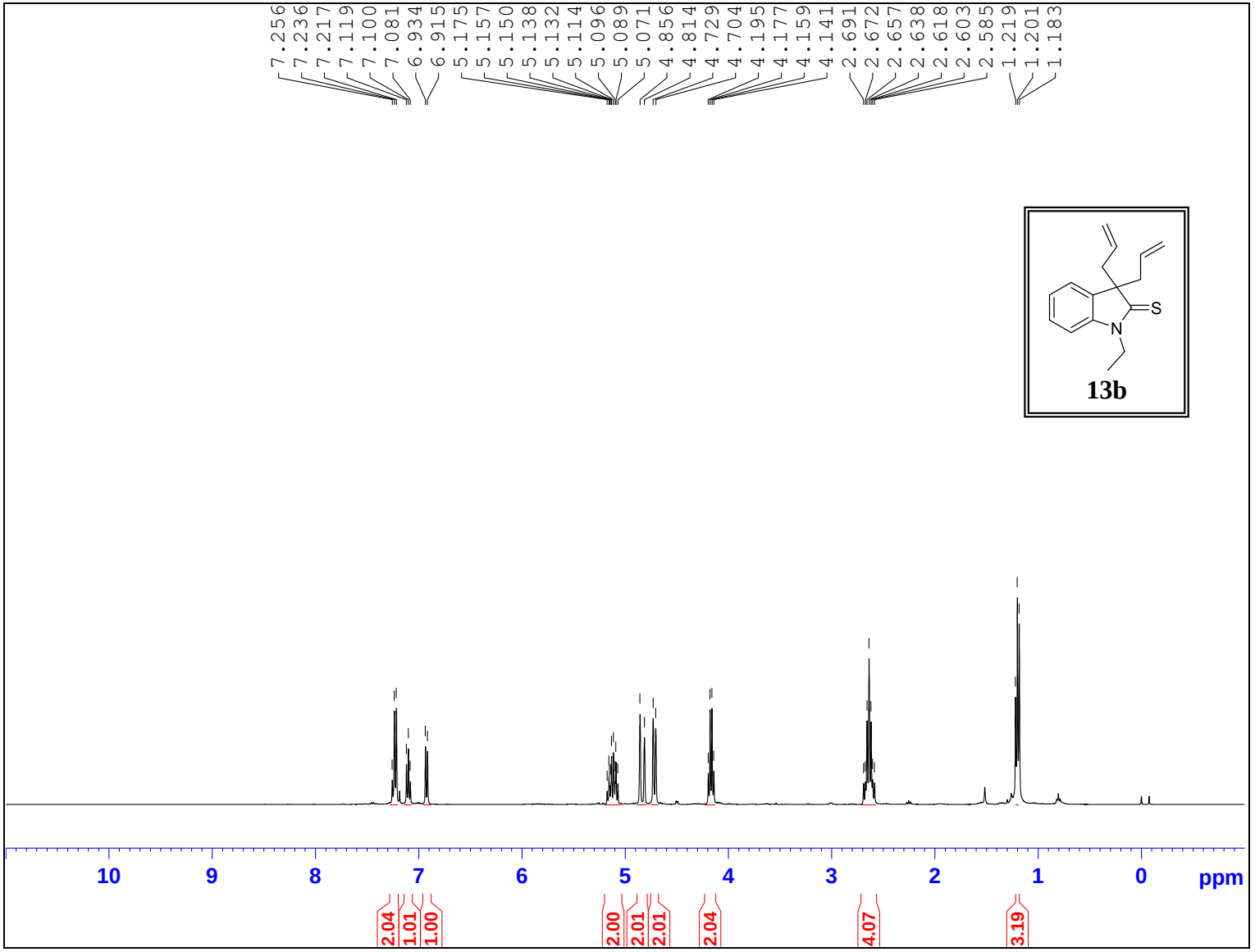
$^{13}C$ NMR for compound **13a** ($101$ MHz, $CDCl_3$)



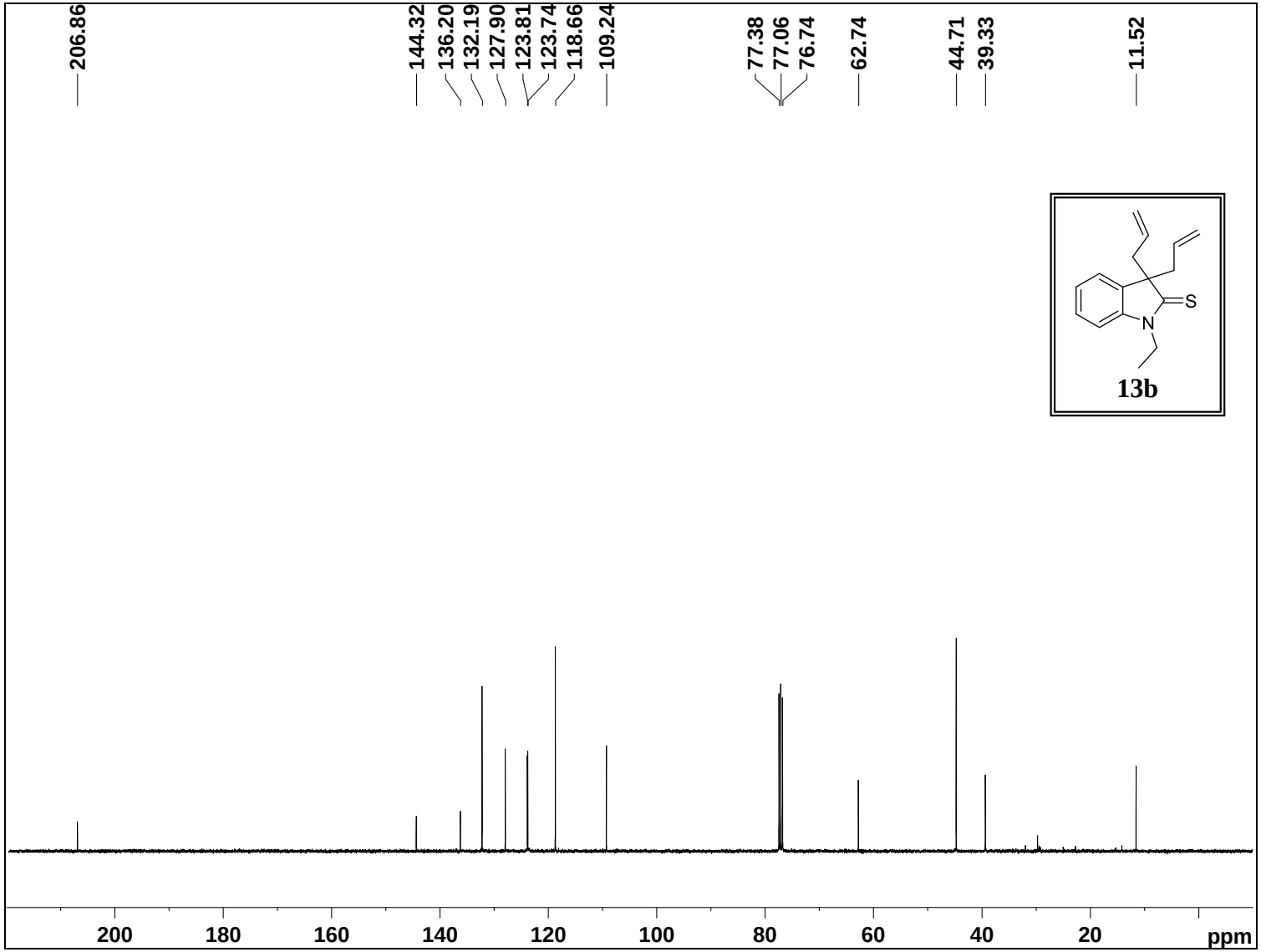
DEPT-135 NMR for compound **13a** (101 MHz, $CDCl_3$)



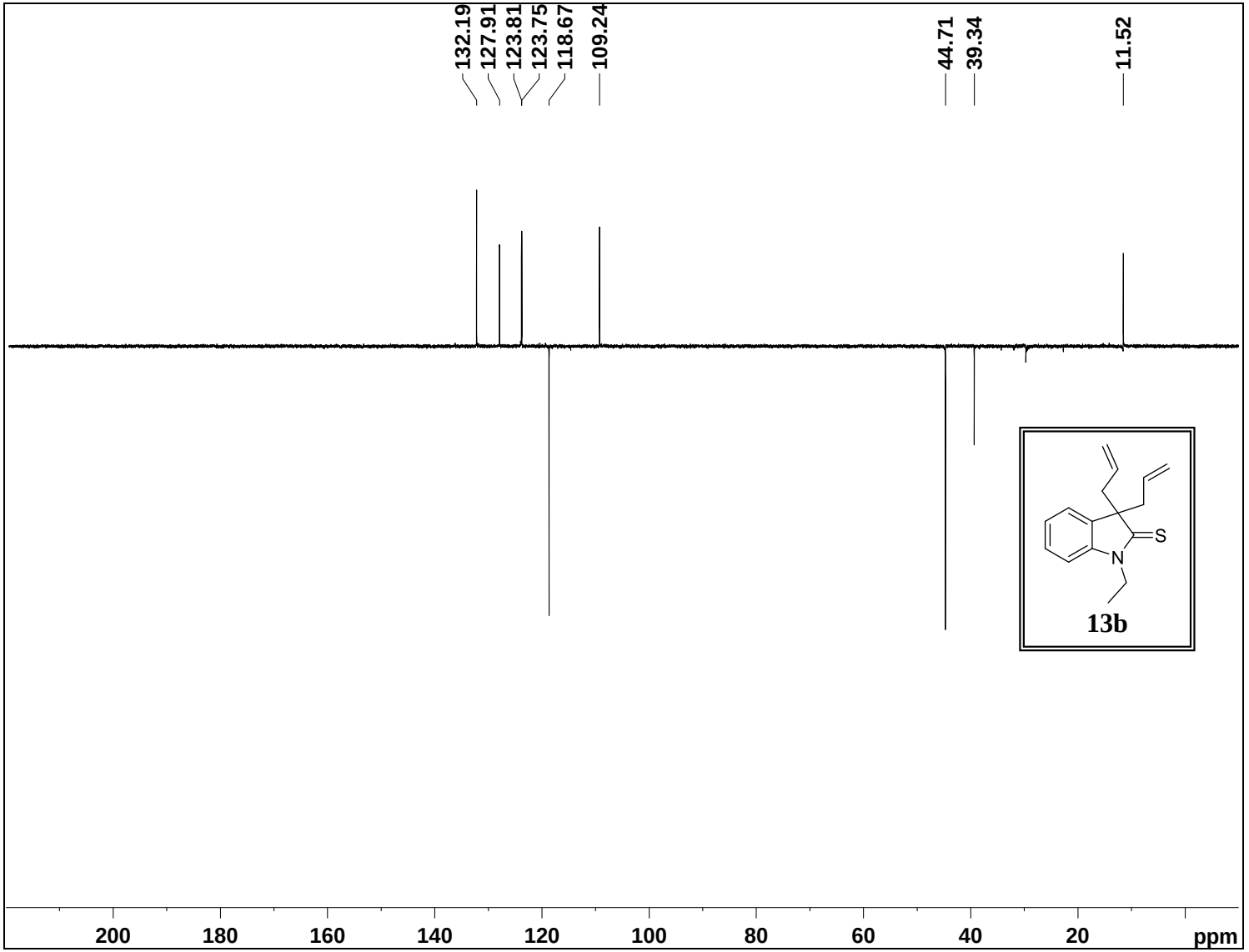
$^{1}$H NMR for compound **13b** (400 MHz, $CDCl_3$)



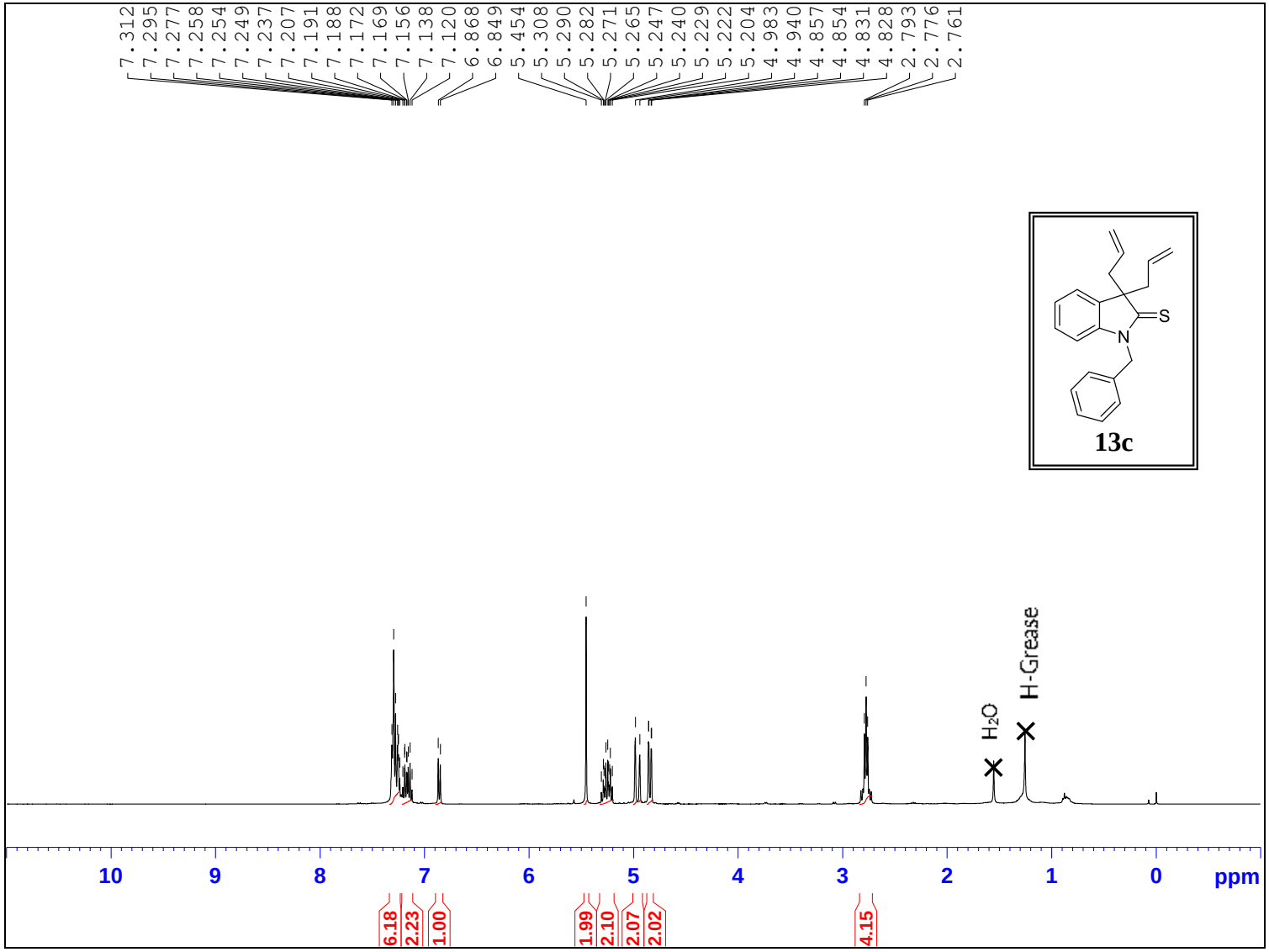
$^{13}C$ NMR for compound **13b** ($101$ MHz, $CDCl_3$)



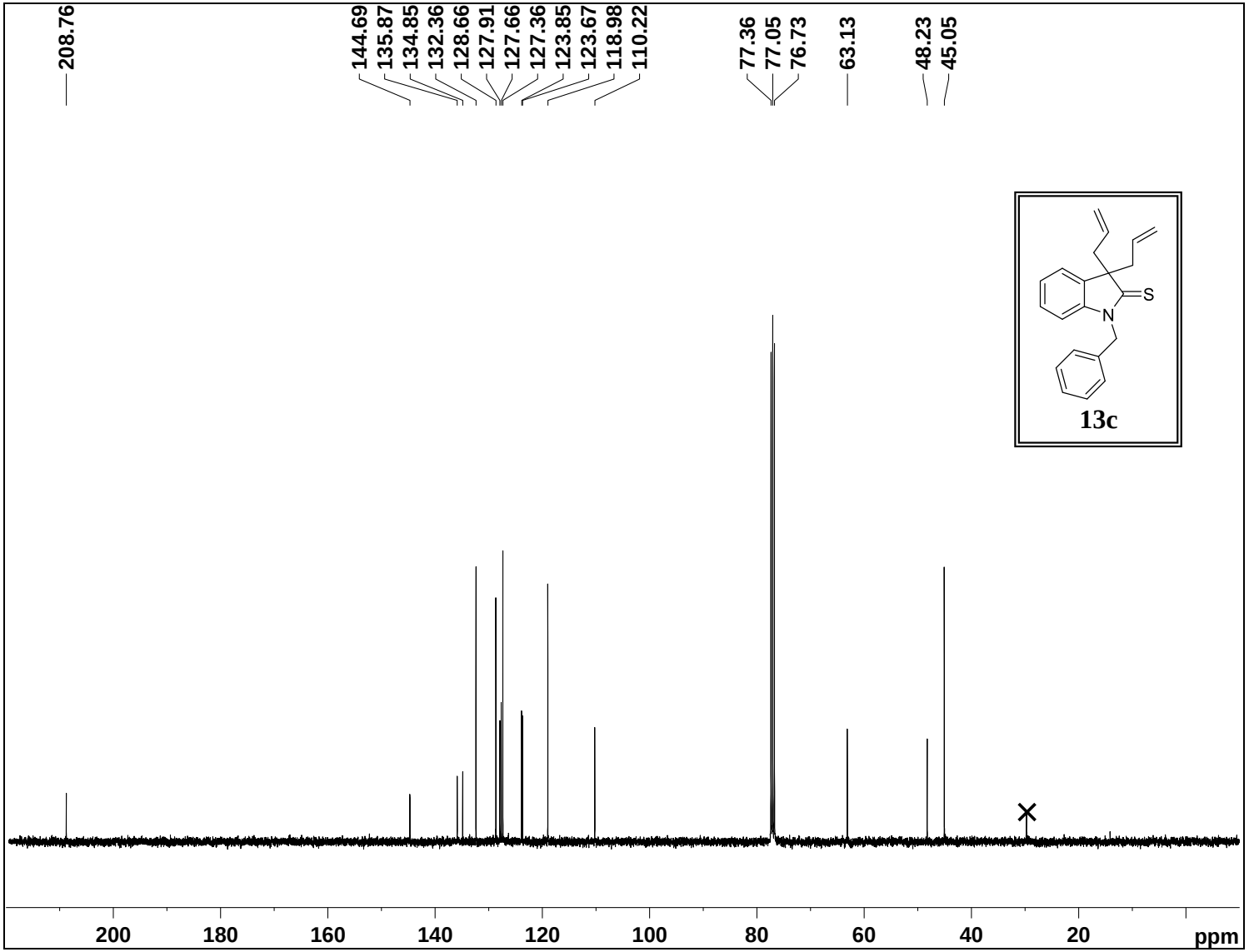
DEPT-135 NMR for compound **13b** (101 MHz, $CDCl_3$)



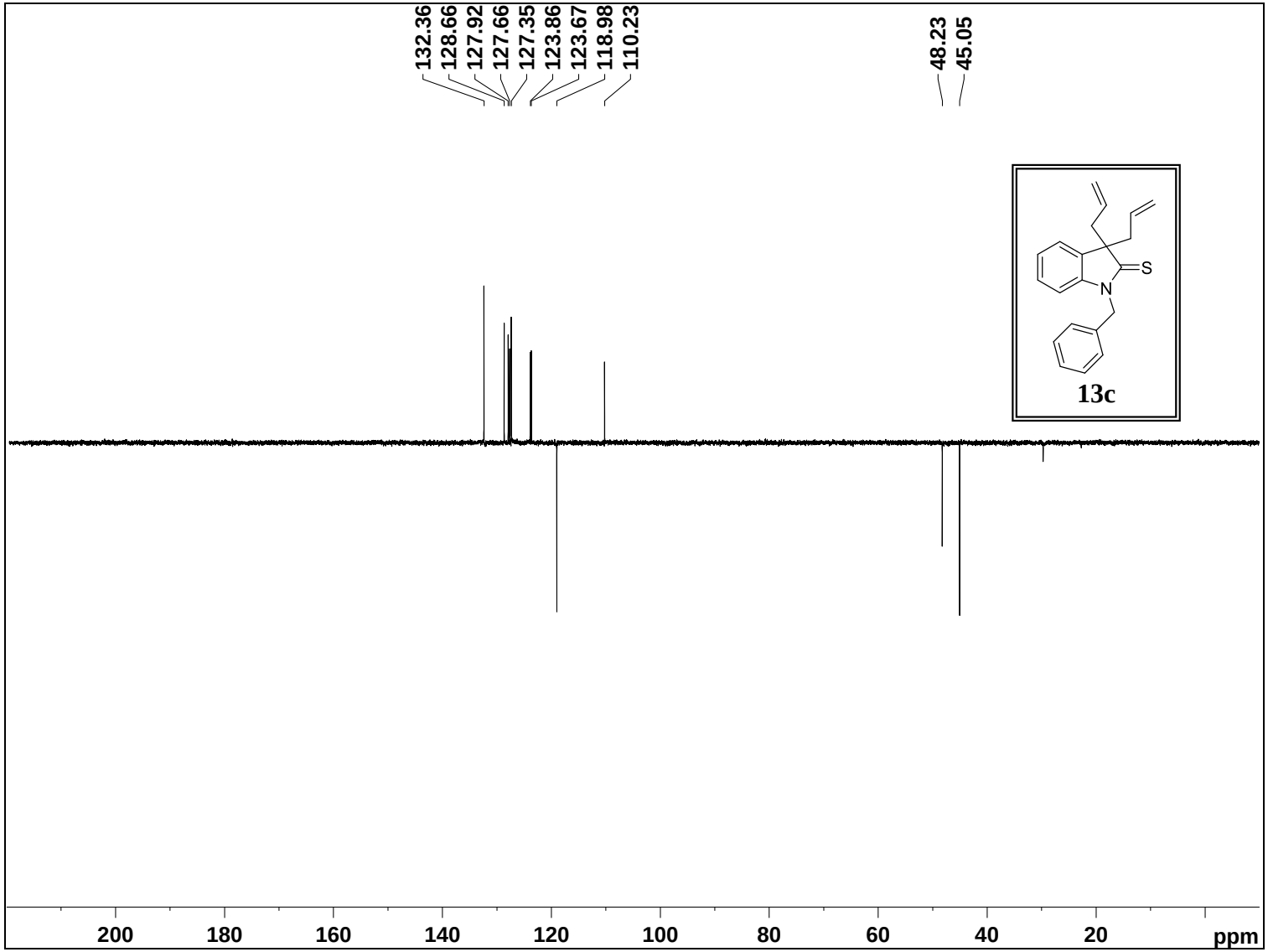
$^{1}$H NMR for compound **13c** (400 MHz, $CDCl_3$)



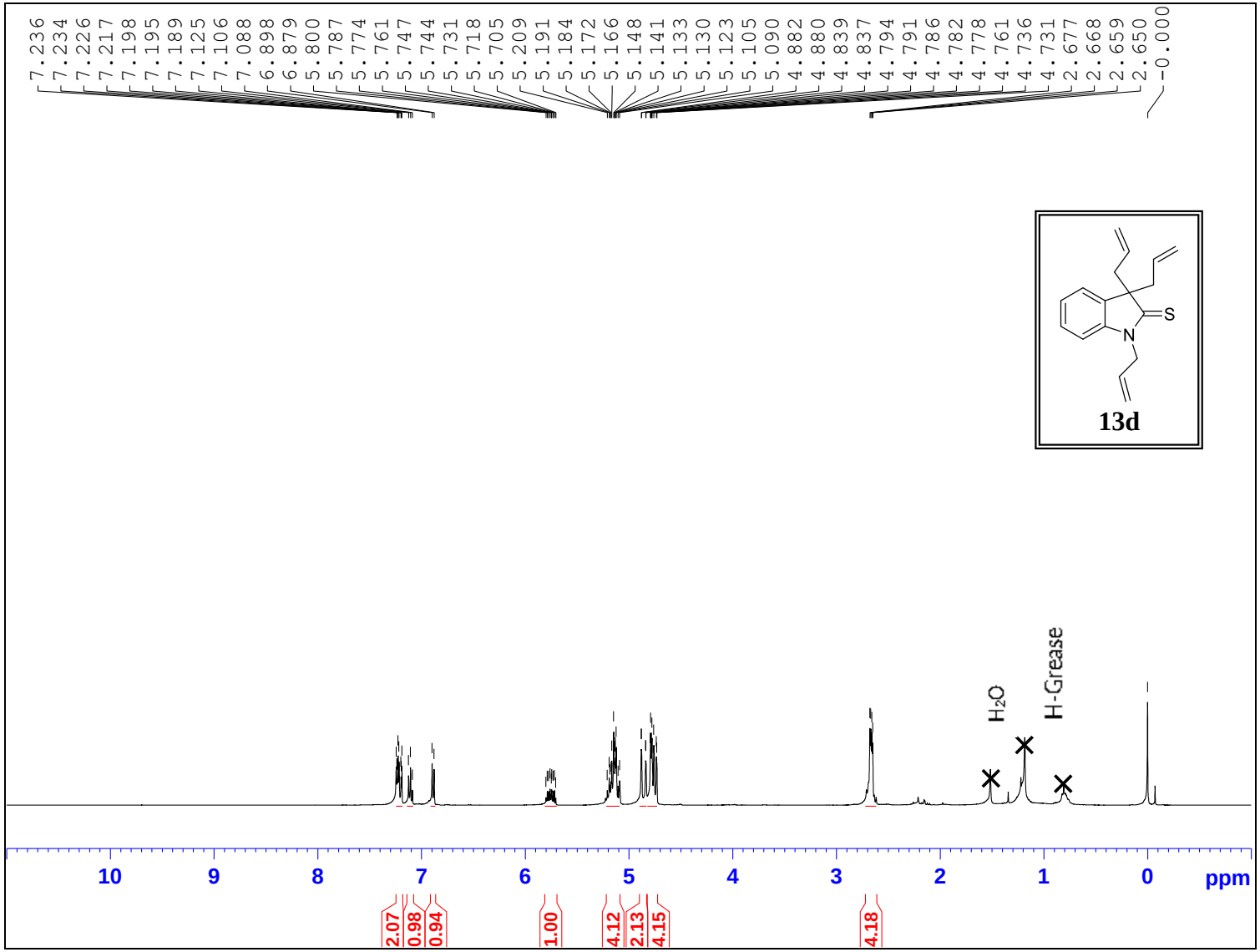
$^{13}C$ NMR for compound **13c** ($101$ MHz, $CDCl_3$)



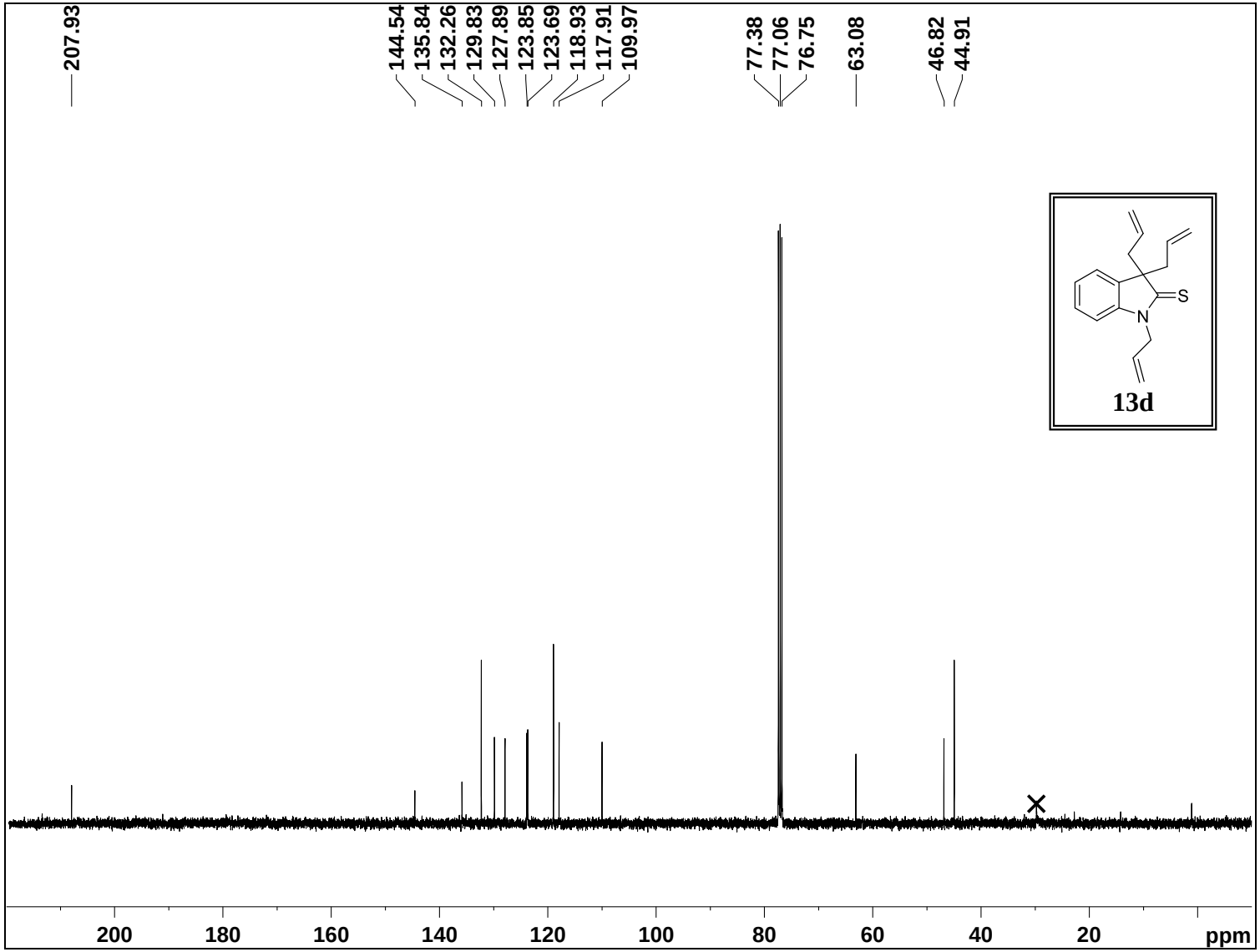
DEPT-135 NMR for compound **13c** (101 MHz, $CDCl_3$)



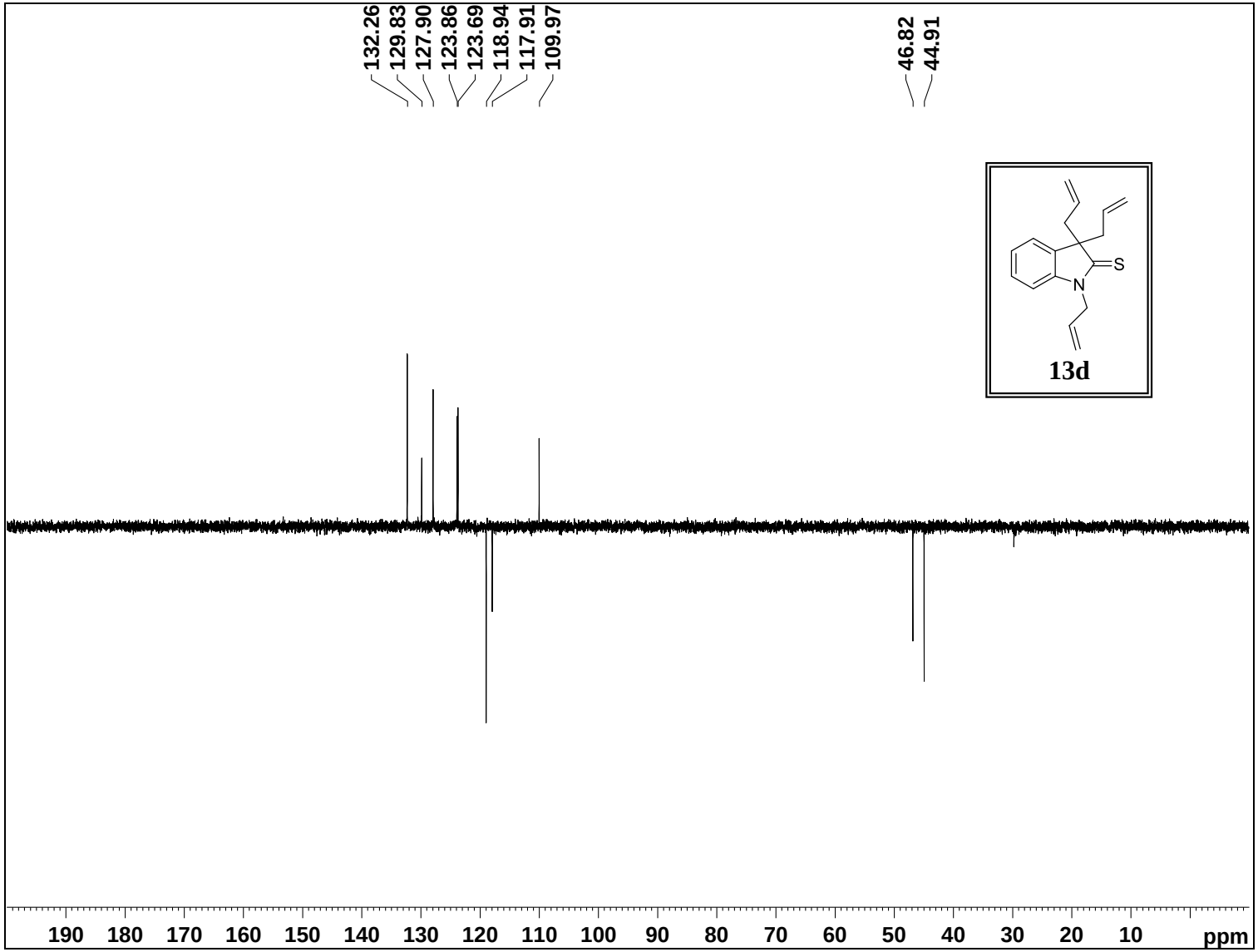
$^{1}$H NMR for compound **13d** (400 MHz, $CDCl_3$)



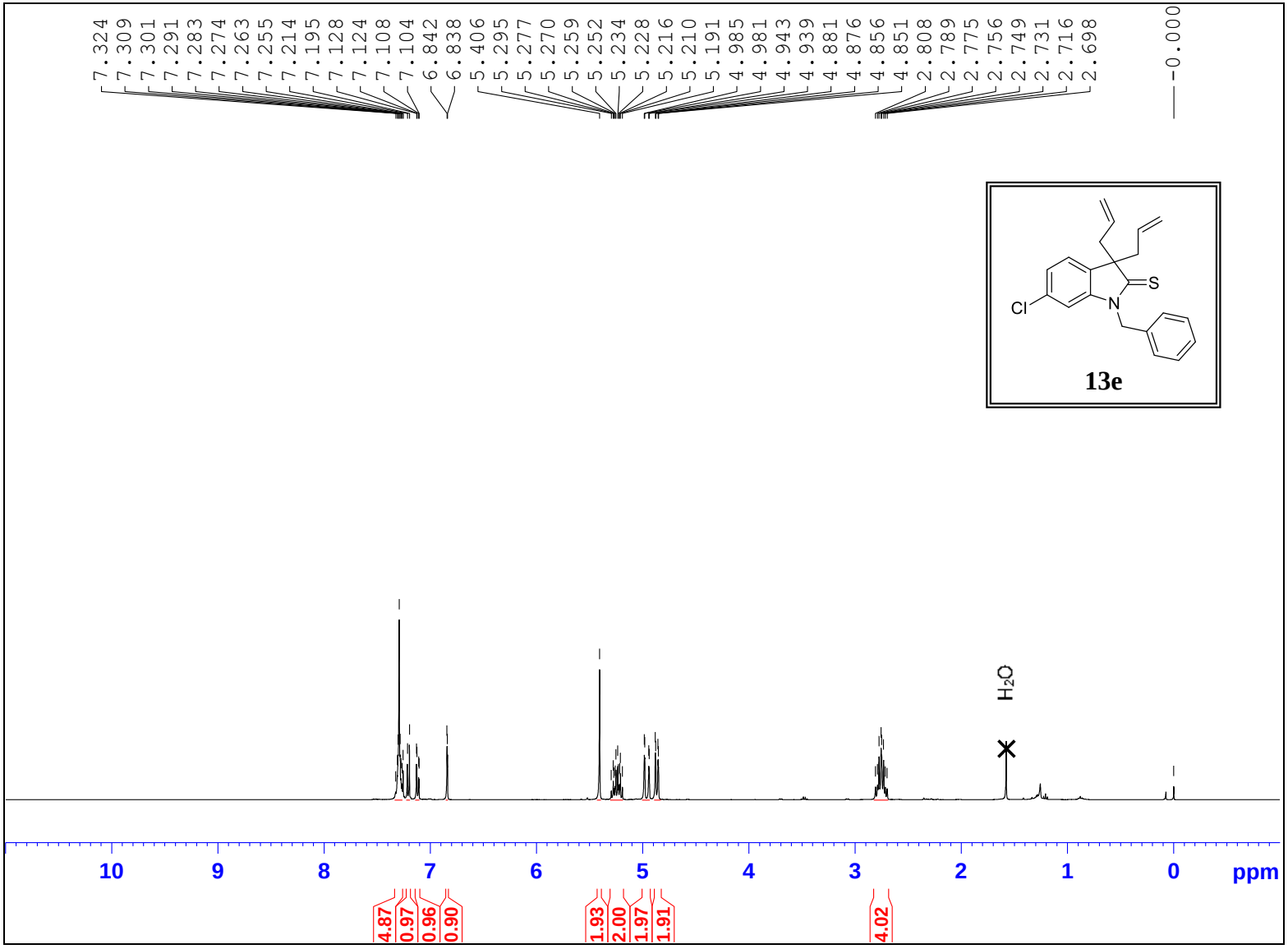
$^{13}C$ NMR for compound **13d** ($101$ MHz, $CDCl_3$)



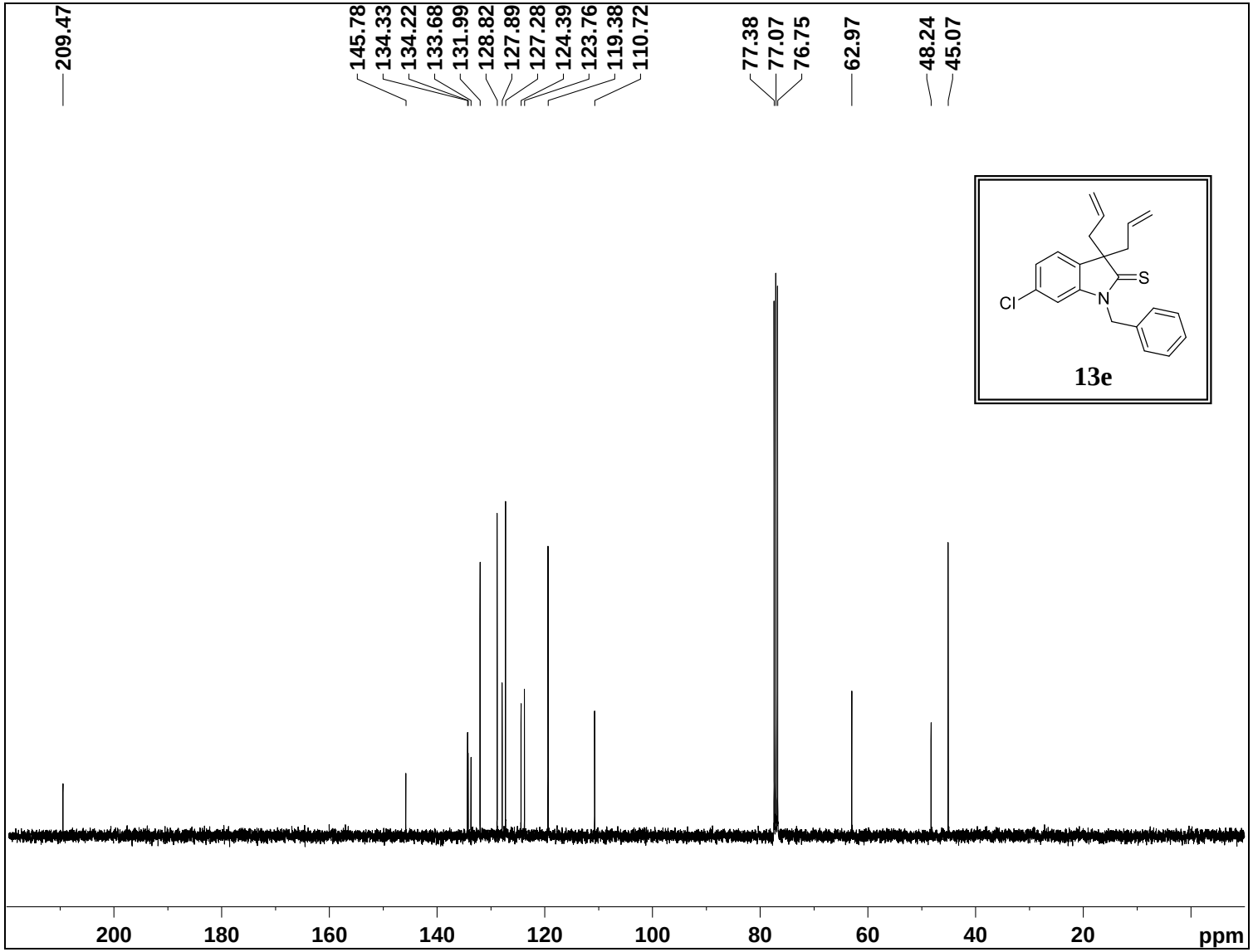
DEPT-135 NMR for compound **13d** (101 MHz, $CDCl_3$)



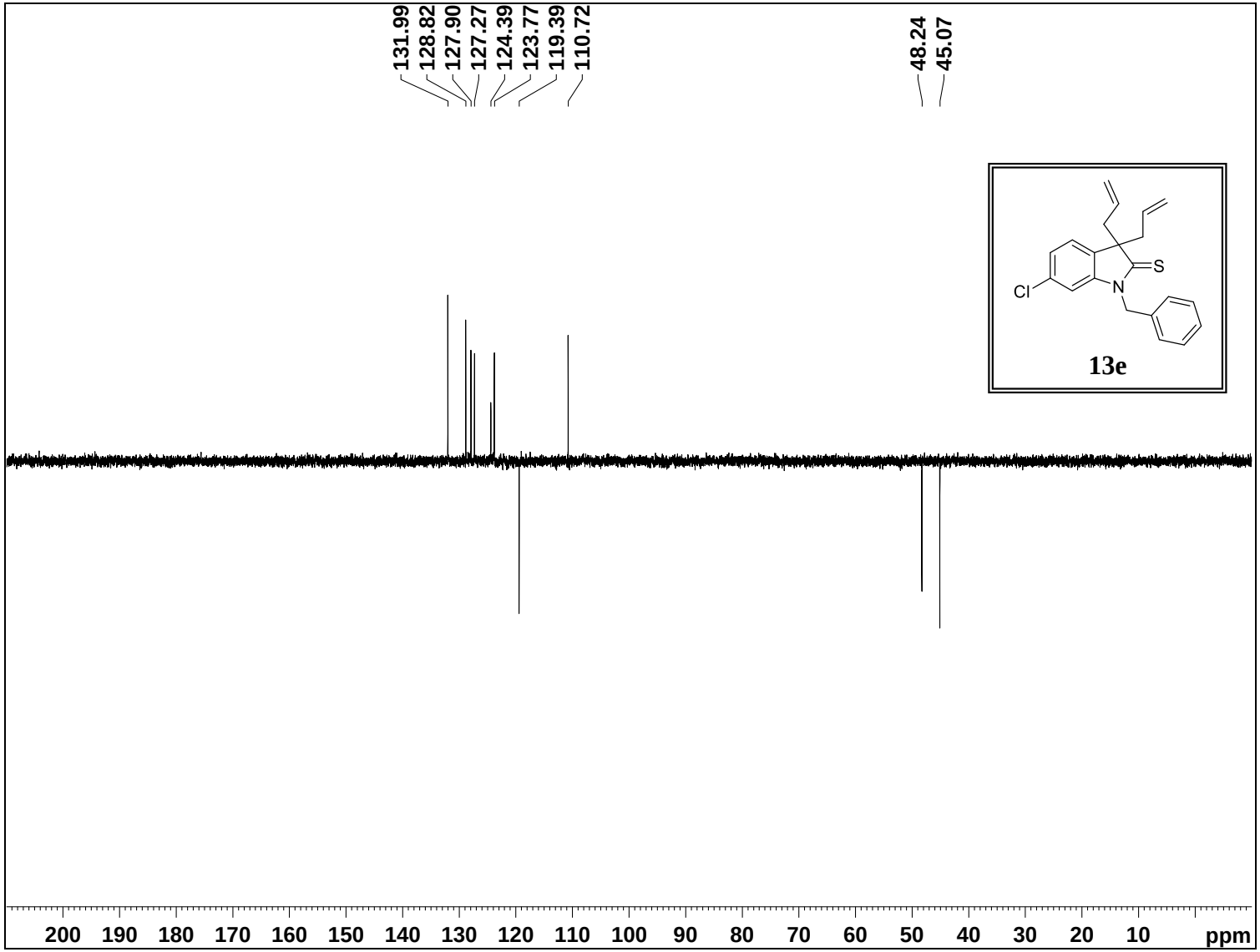
$^{1}$H NMR for compound **13e** (400 MHz, $CDCl_3$)



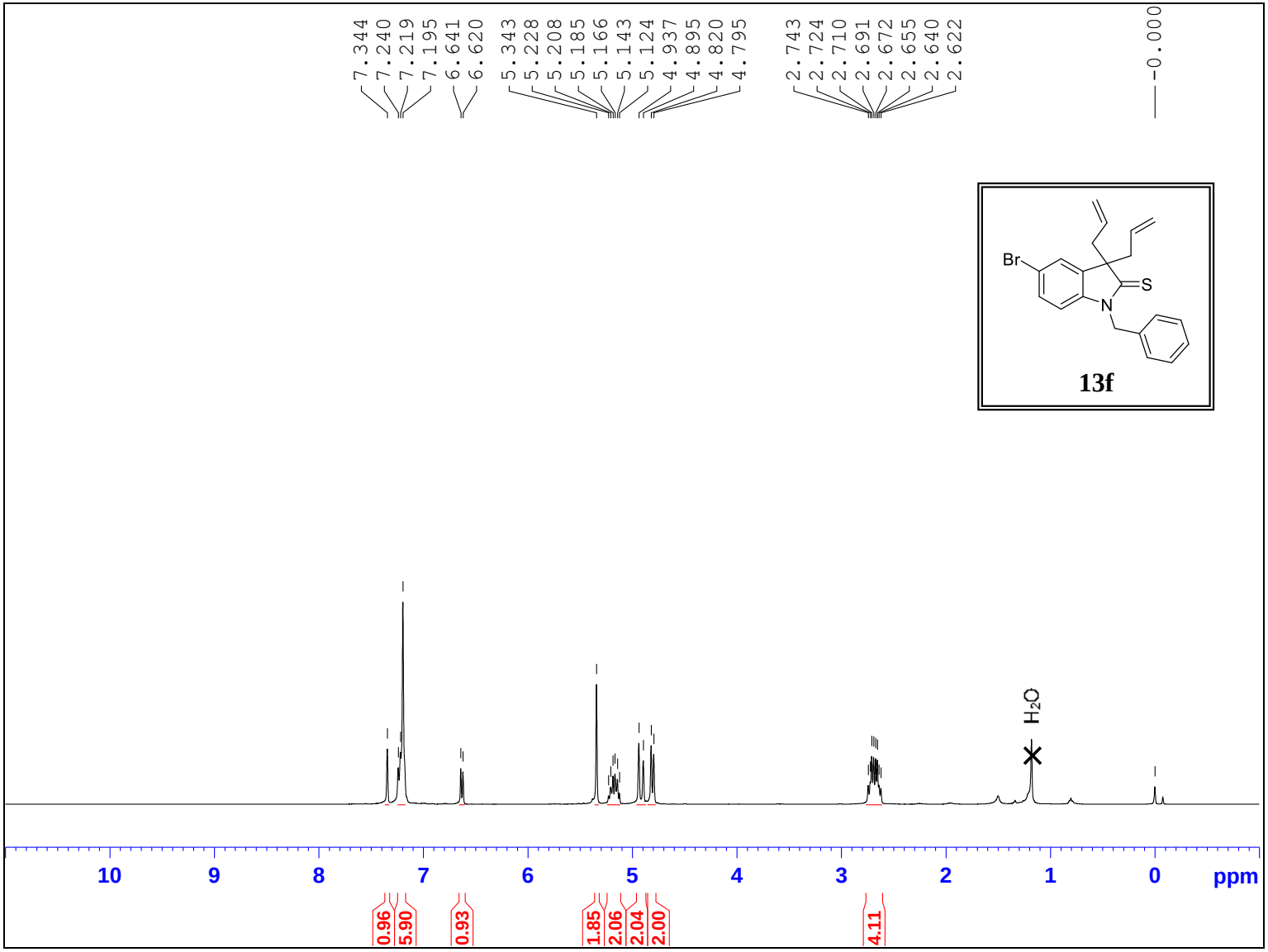
$^{13}C$ NMR for compound **13e** (101 MHz, $CDCl_3$)



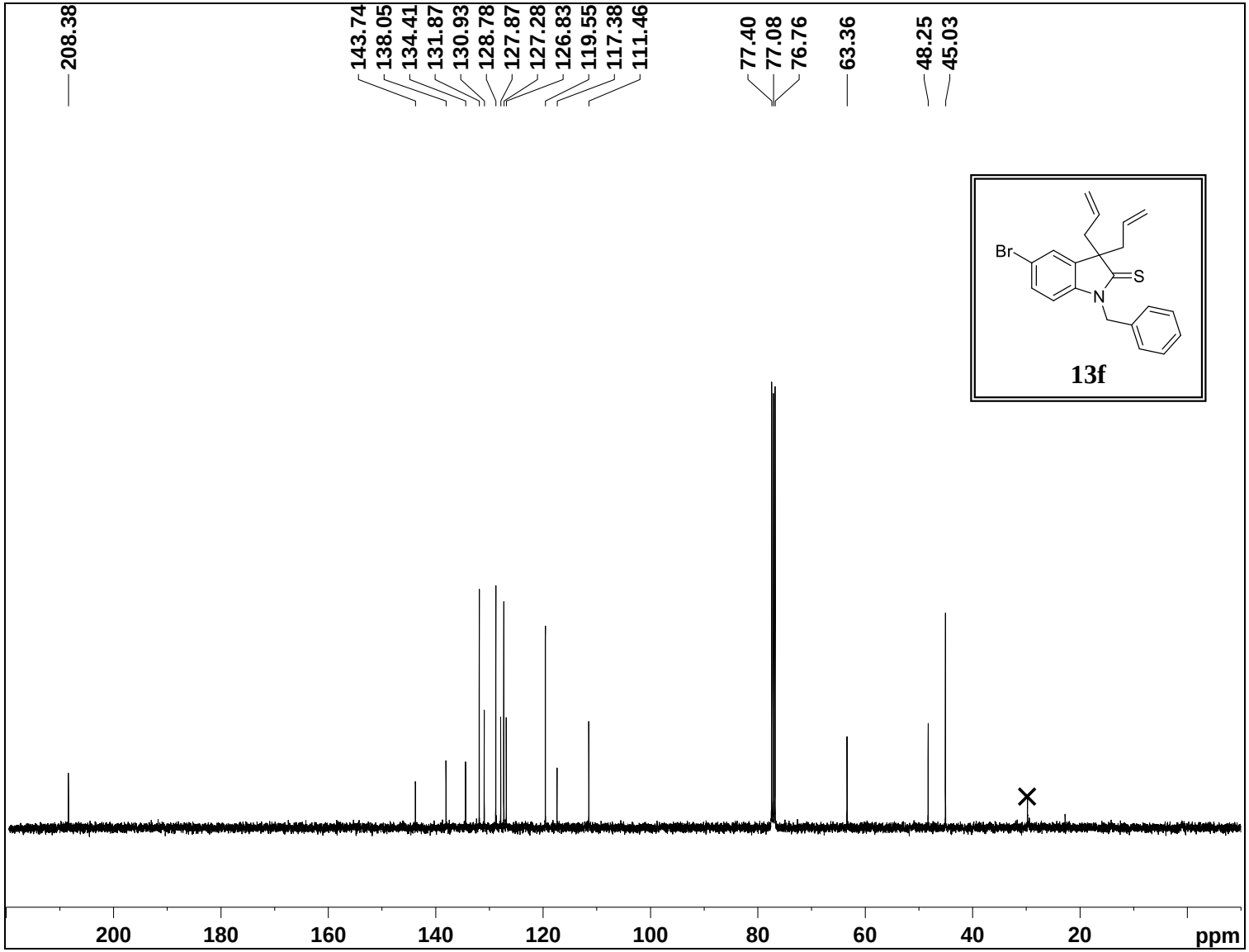
DEPT-135 NMR for compound **13e** (101 MHz, $CDCl_3$)



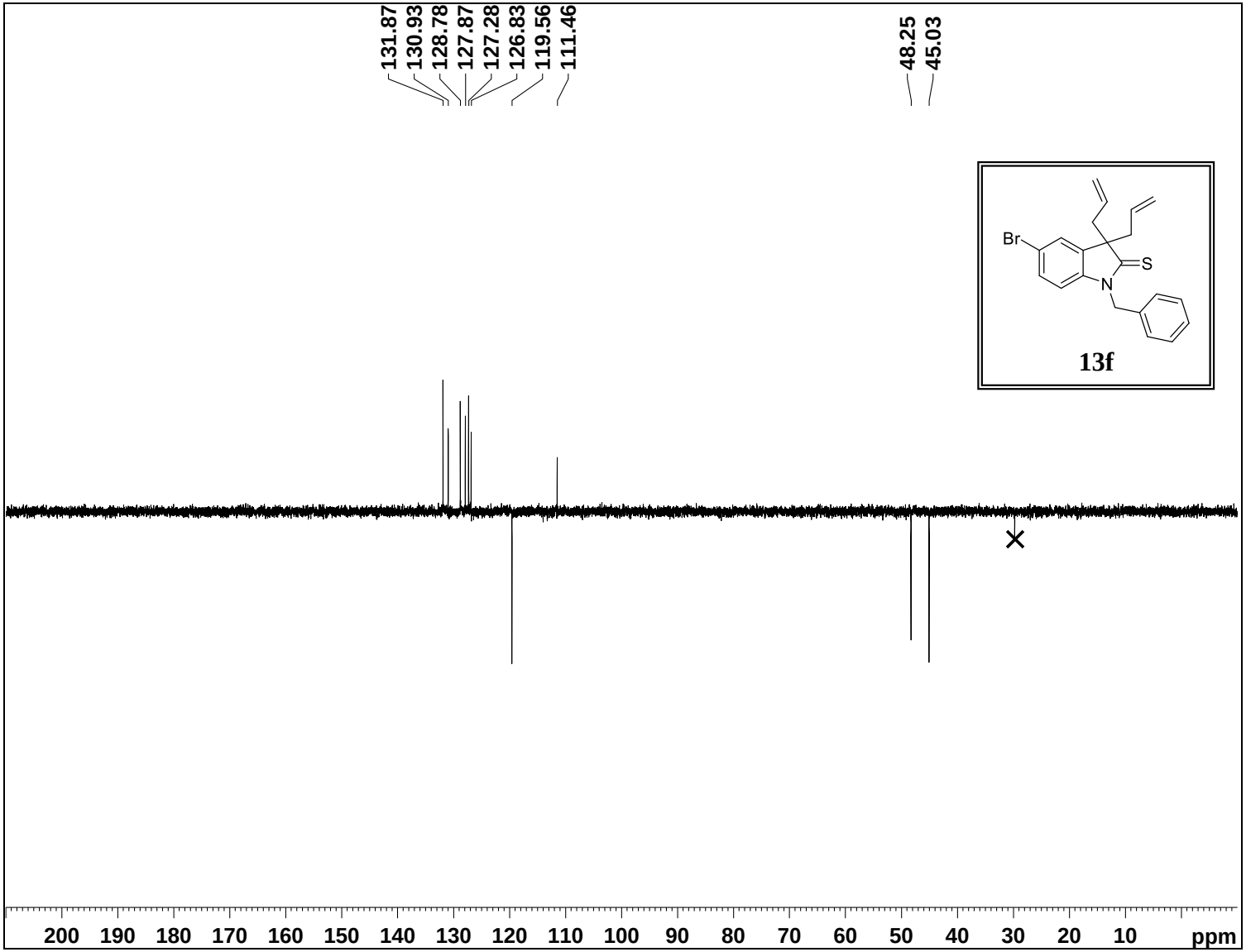
$^{1}$H NMR for compound **13f** (400 MHz, $CDCl_3$)



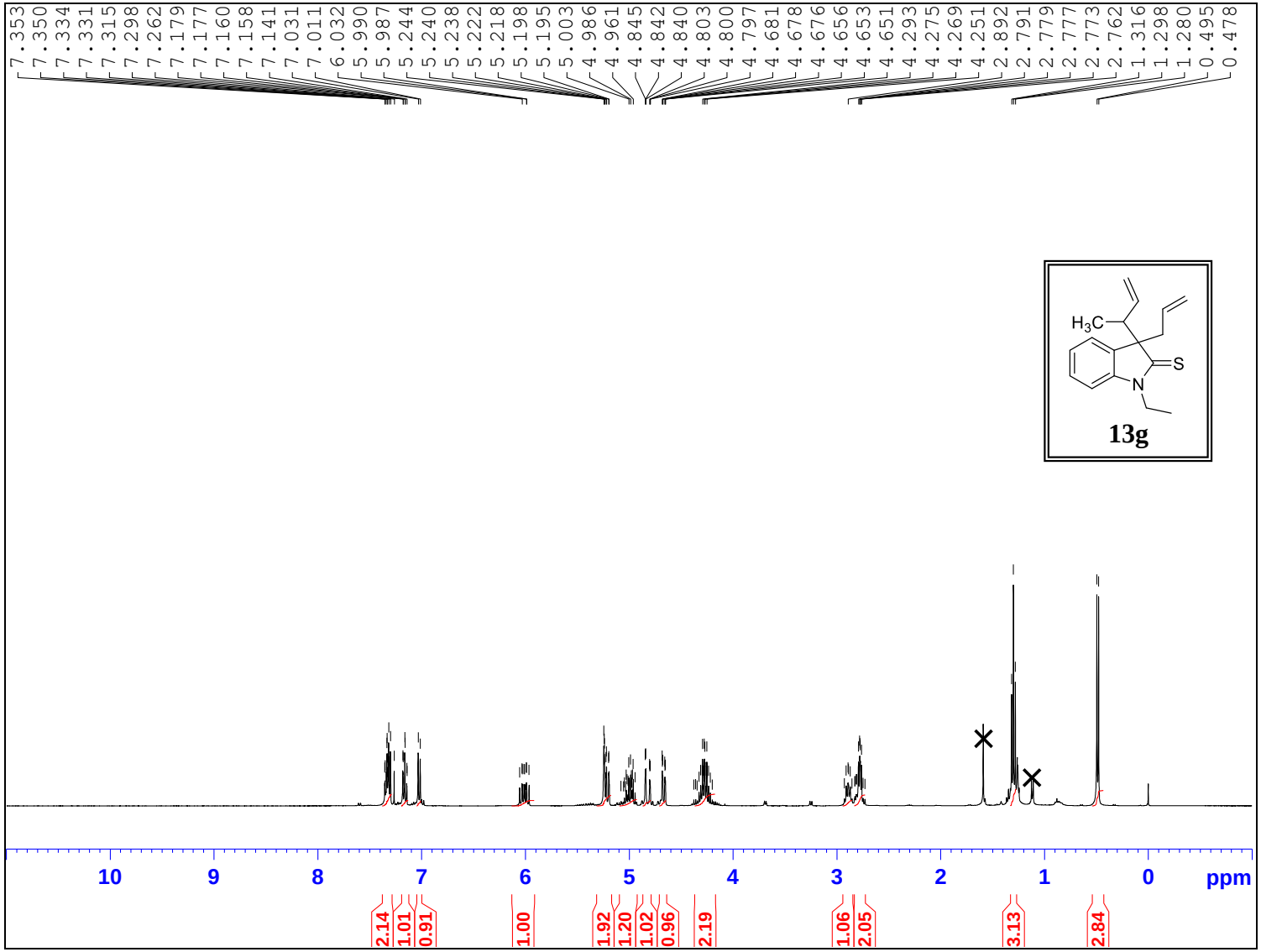
$^{13}C$ NMR for compound **13f** (101 MHz, $CDCl_3$)



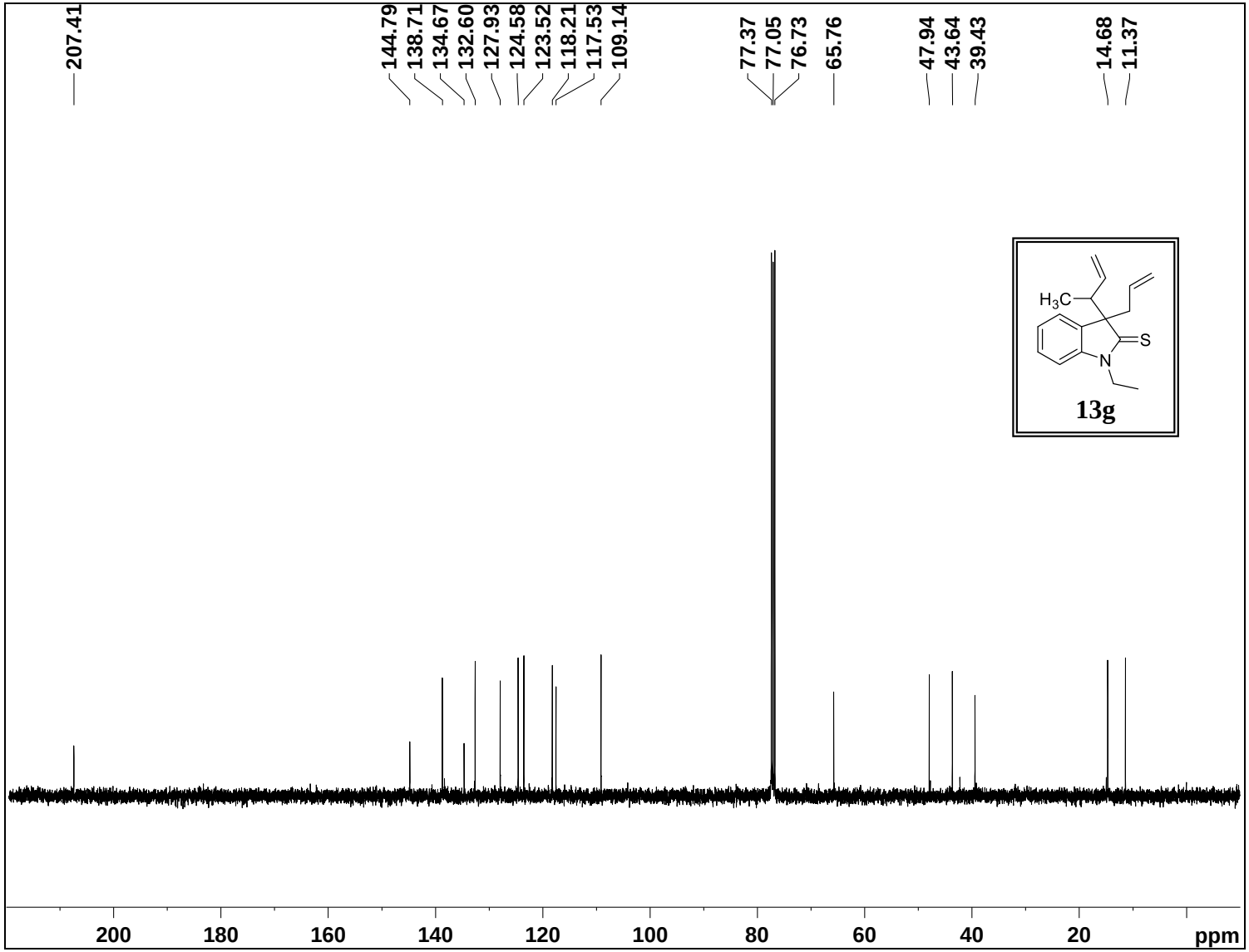
DEPT-135 NMR for compound **13f** (101 MHz, $CDCl_3$)



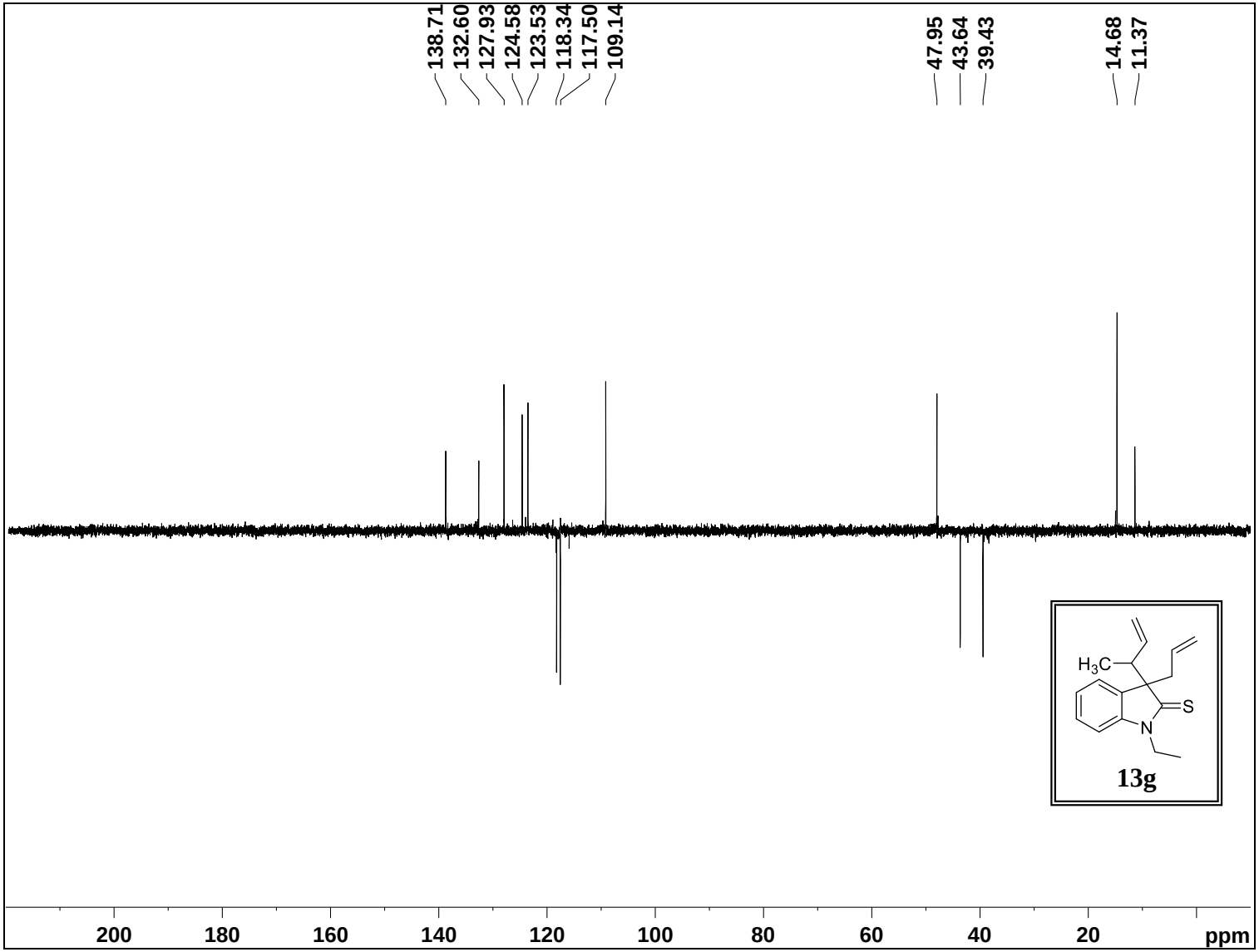
$^{1}$H NMR for compound **13g** (400 MHz, $CDCl_3$)



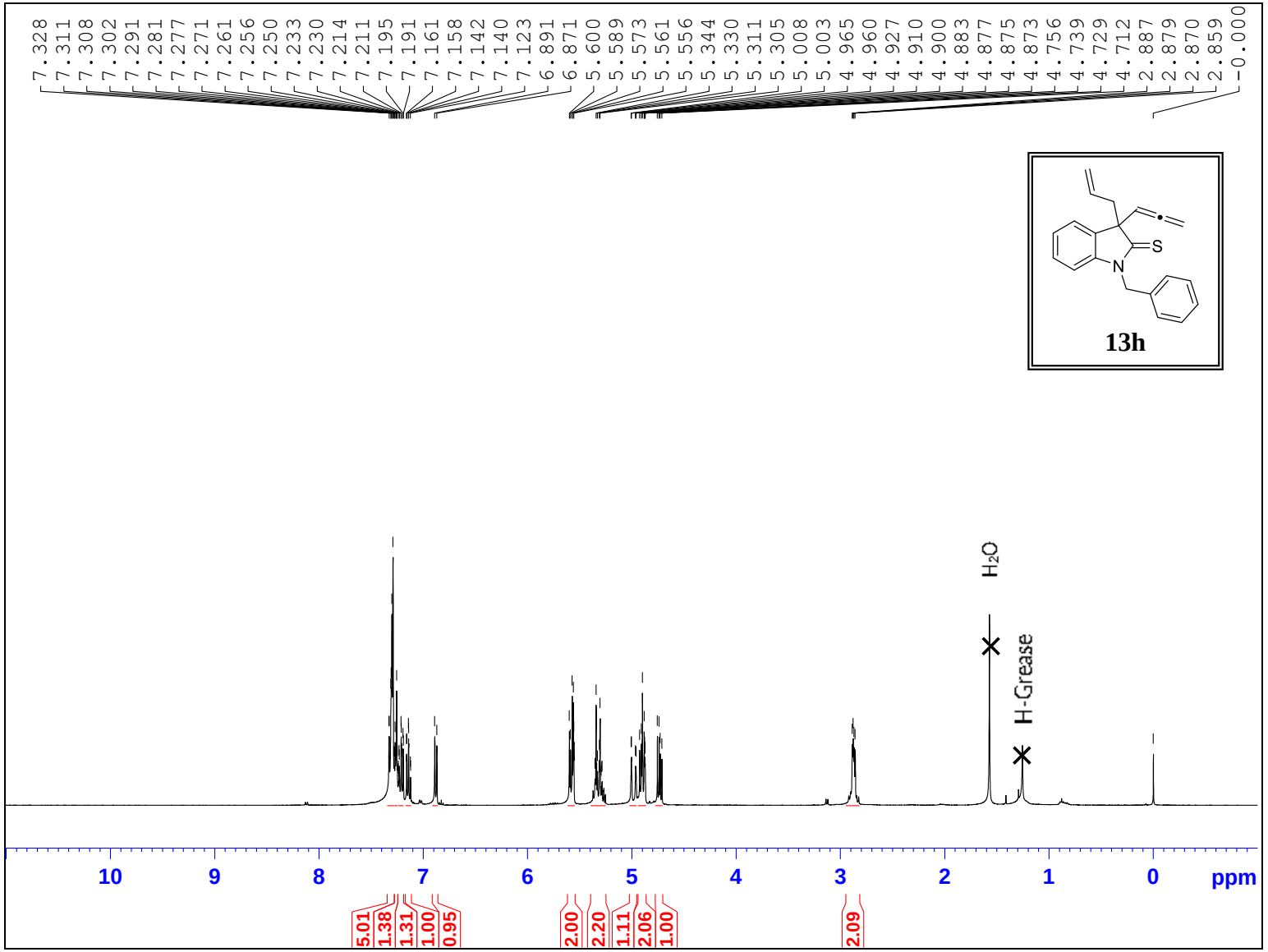
$^{13}C$ NMR for compound **13g** (101 MHz, $CDCl_3$)



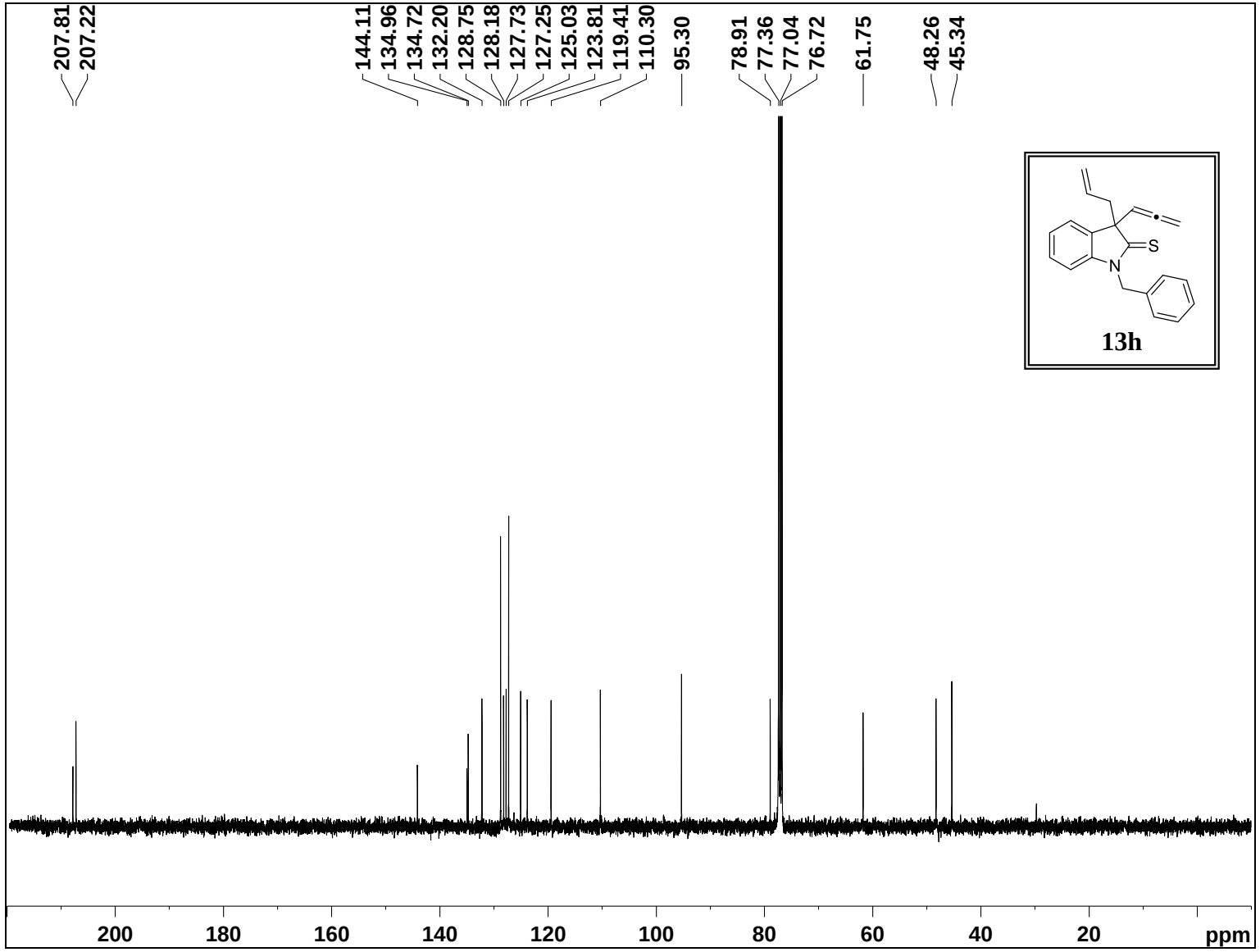
DEPT-135 NMR for compound **13g** (101 MHz, $CDCl_3$)



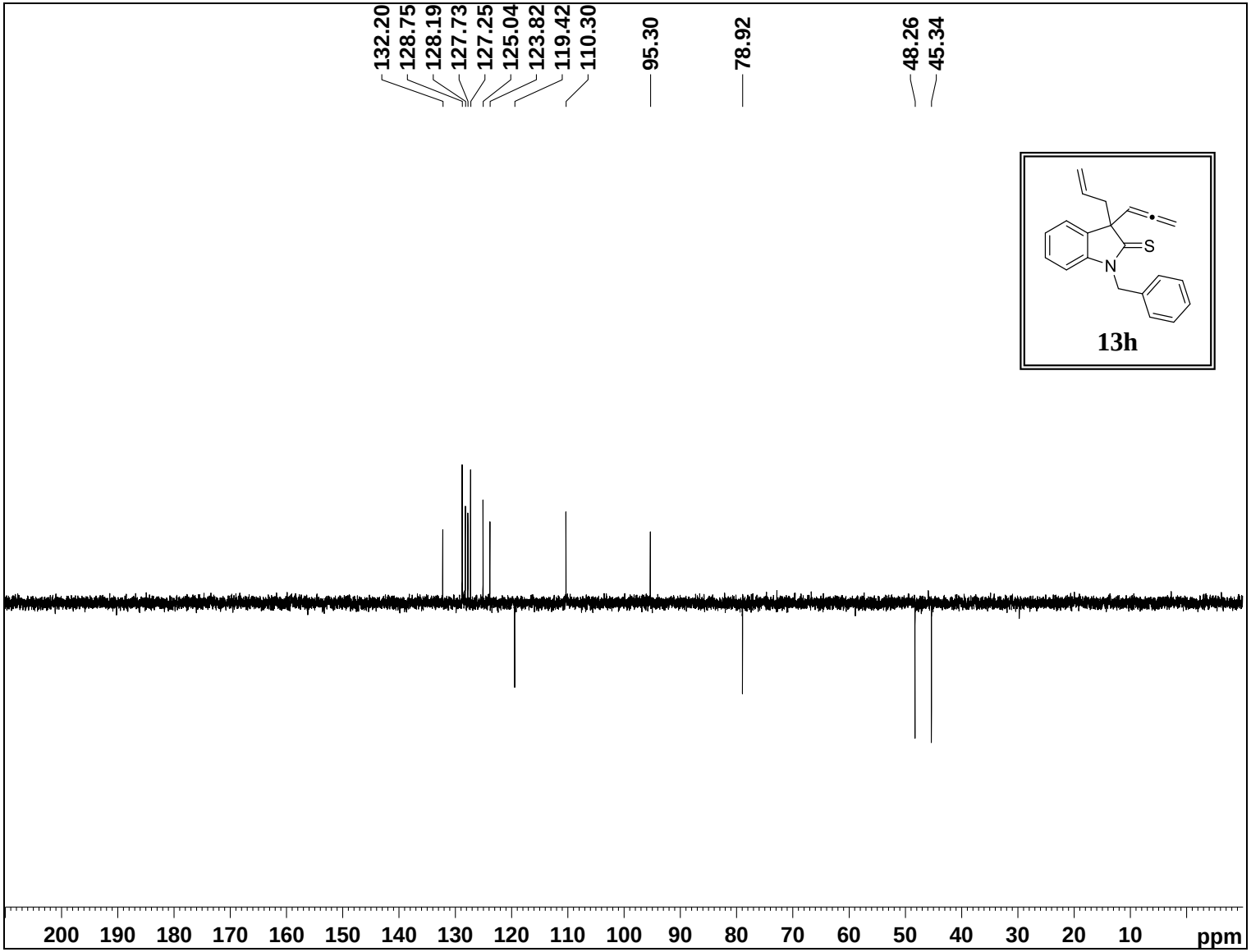
$^{1}$H NMR for compound **13h** (400 MHz, $CDCl_3$)



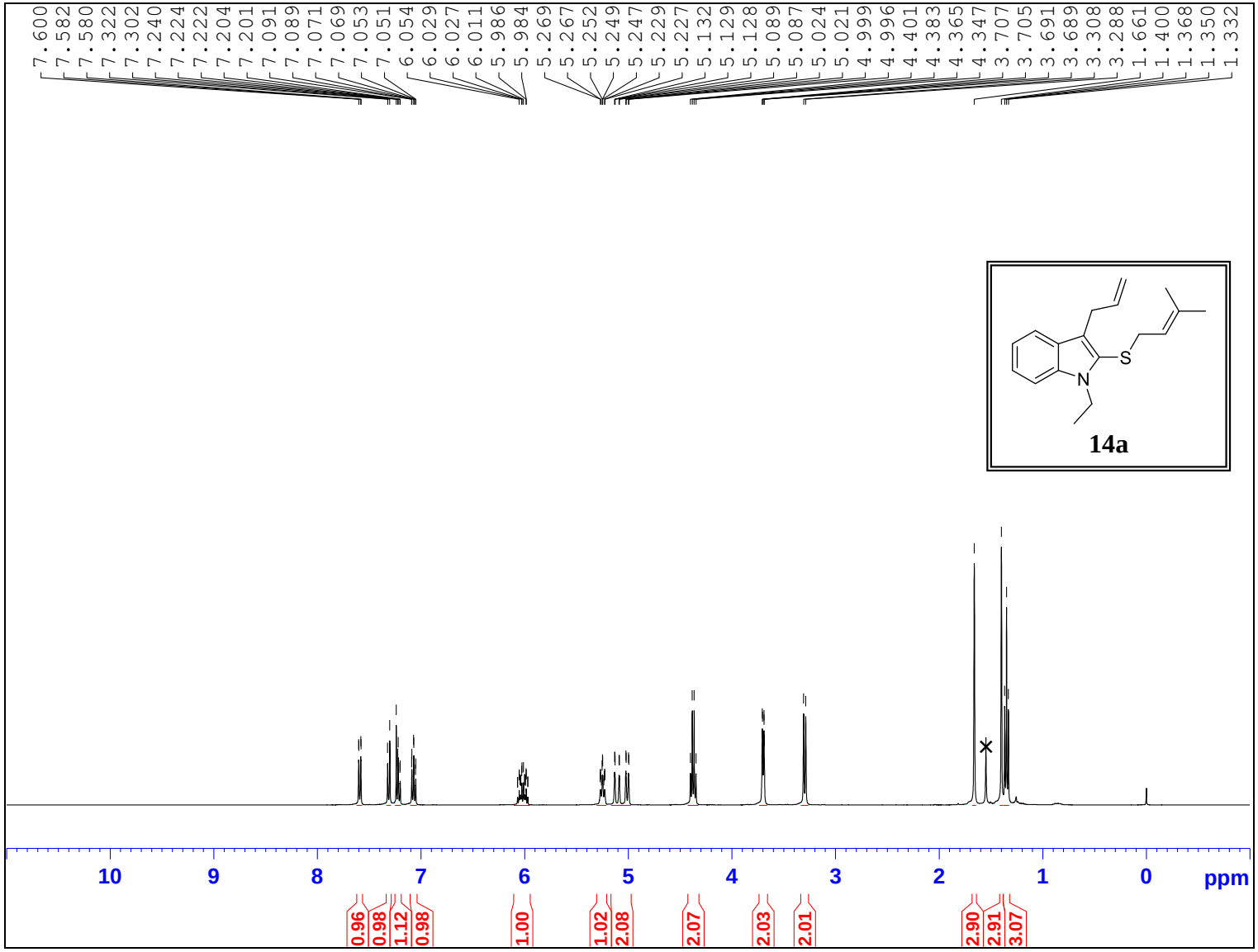
$^{13}C$ NMR for compound **13h** ($101$ MHz, $CDCl_3$)



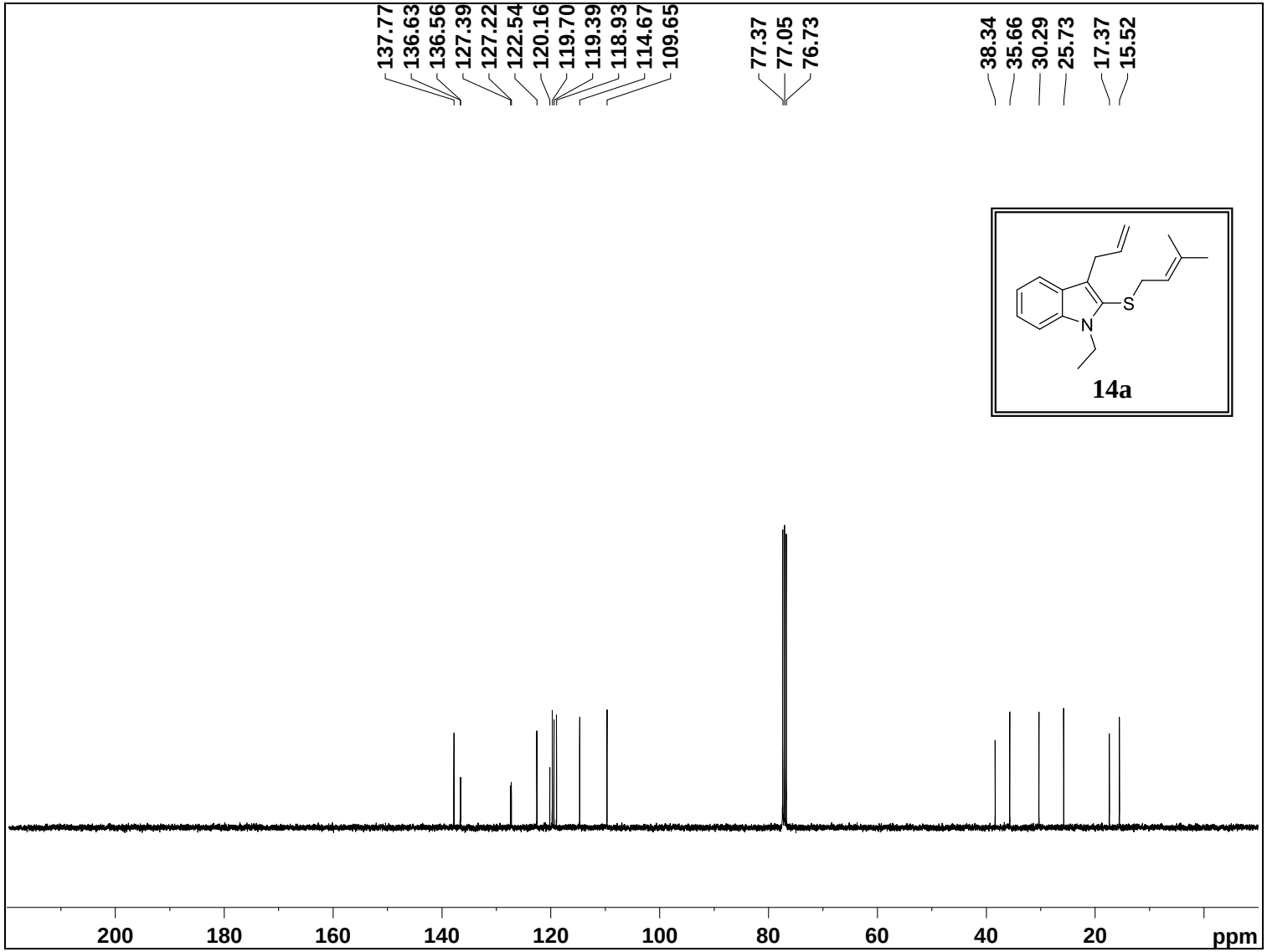
DEPT-135 NMR for compound **13h** (101 MHz, $CDCl_3$)



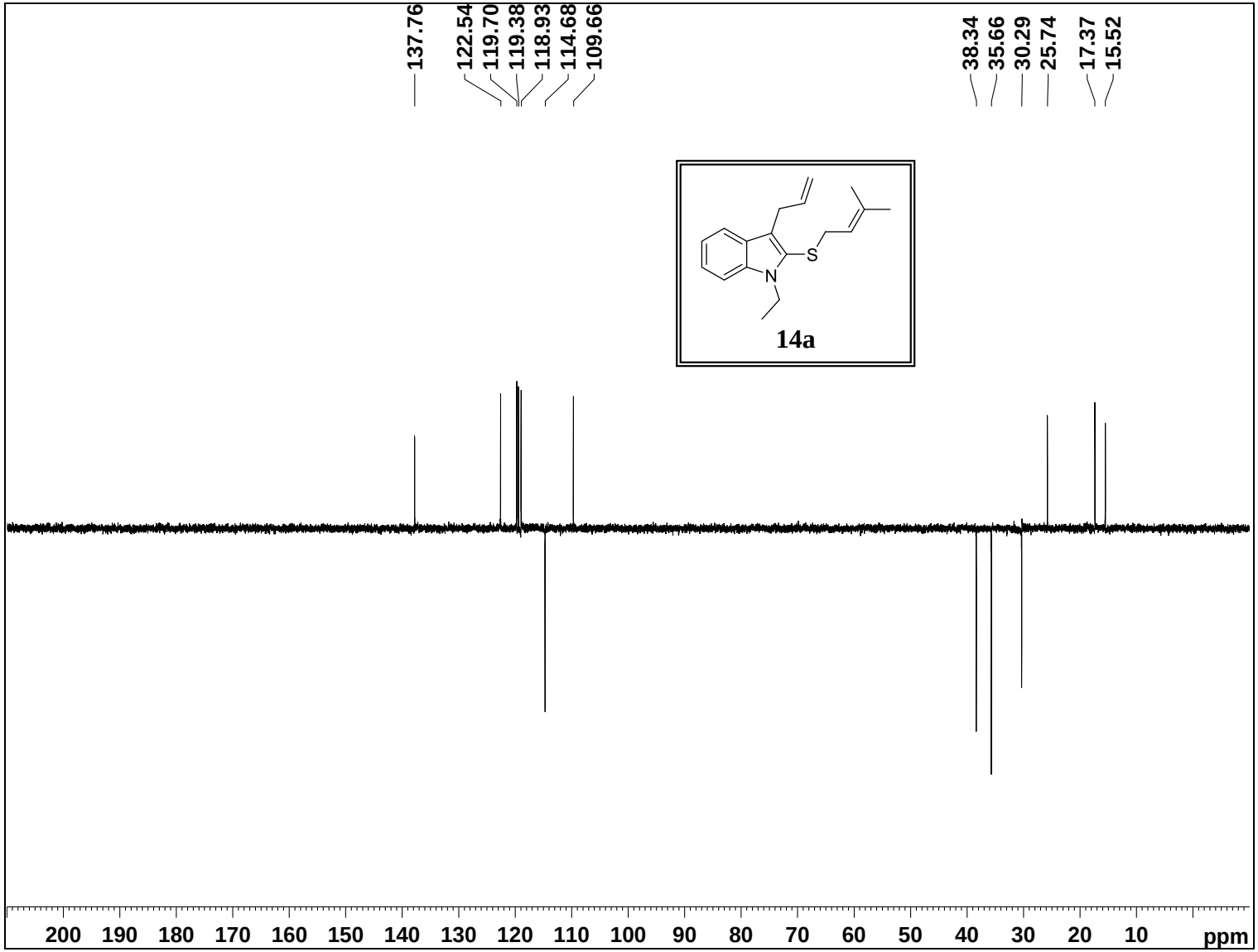
$^{1}$H NMR for compound **14a** (400 MHz, $CDCl_3$)



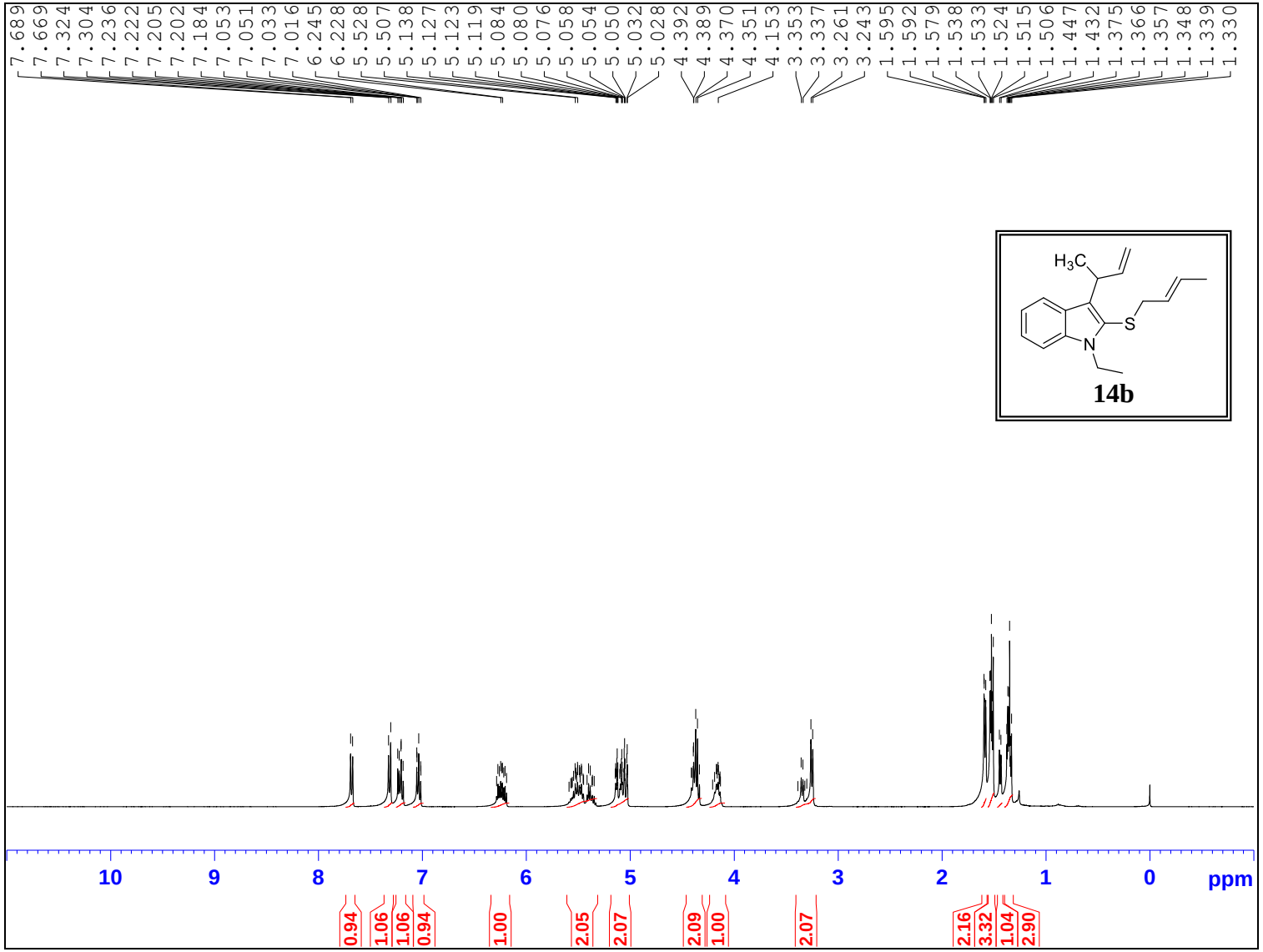
$^{13}C$ NMR for compound **14a** (101 MHz, $CDCl_3$)



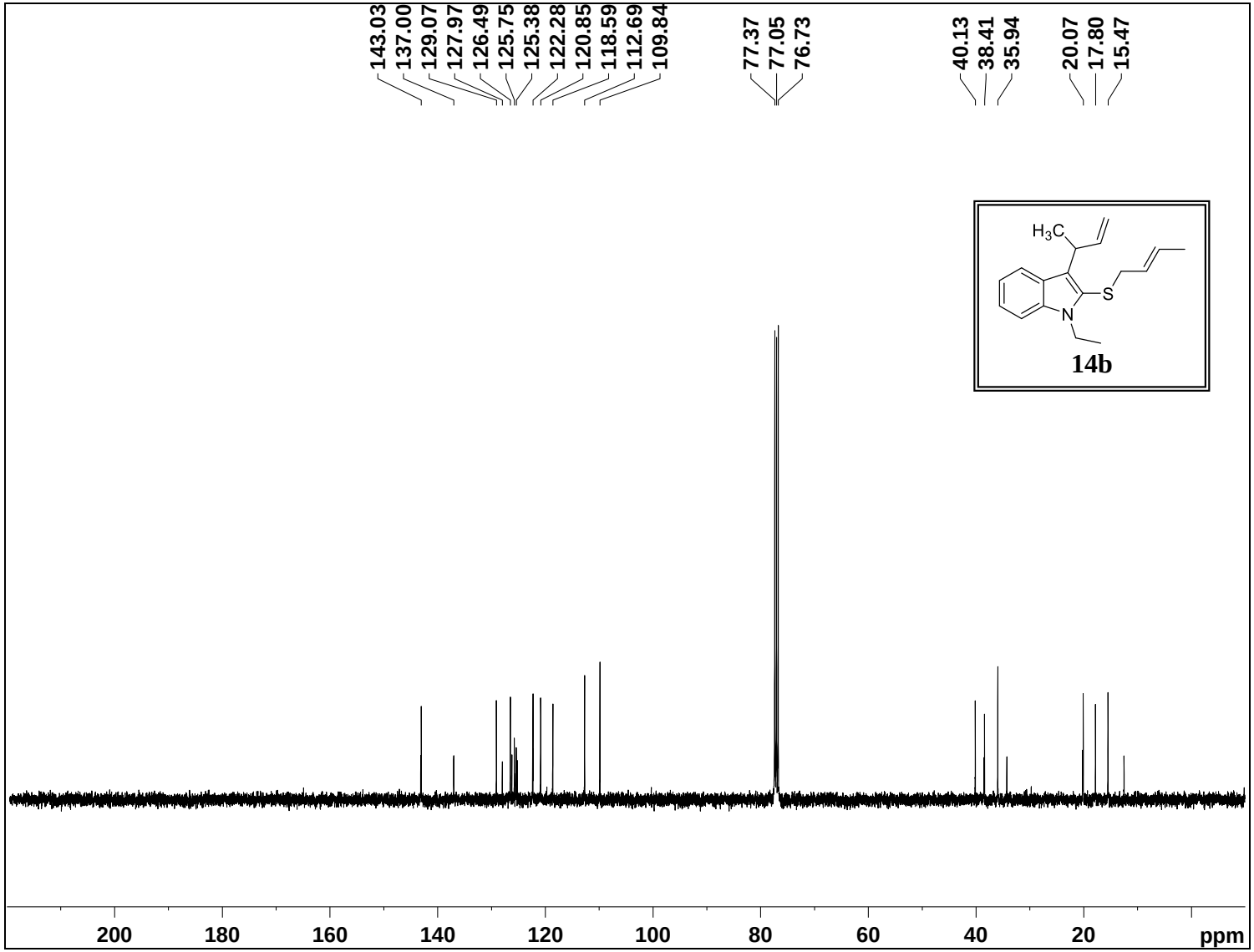
DEPT-135 NMR for compound **14a** (101 MHz, $CDCl_3$)



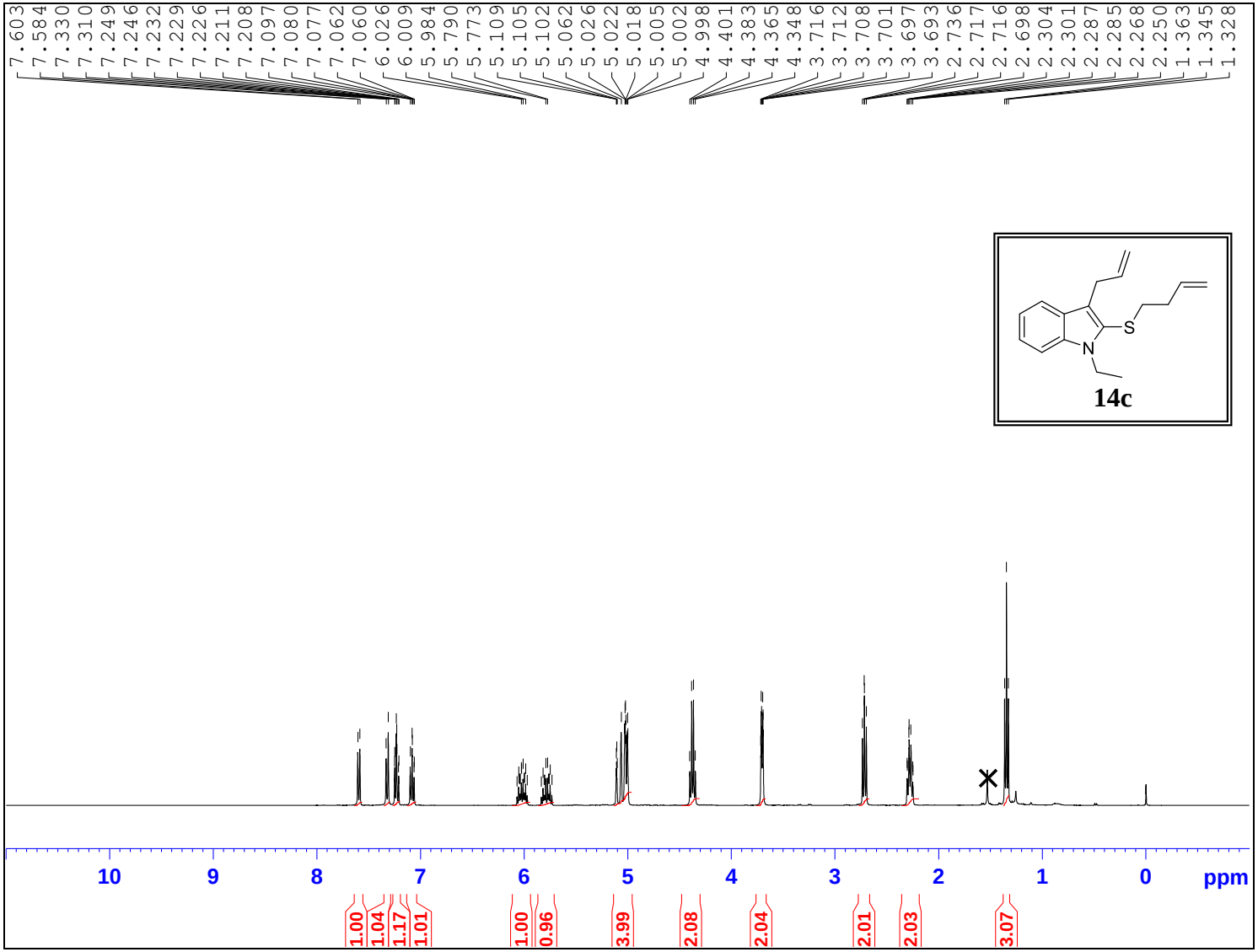
$^{1}$H NMR for compound **14b** (400 MHz, $CDCl_3$)



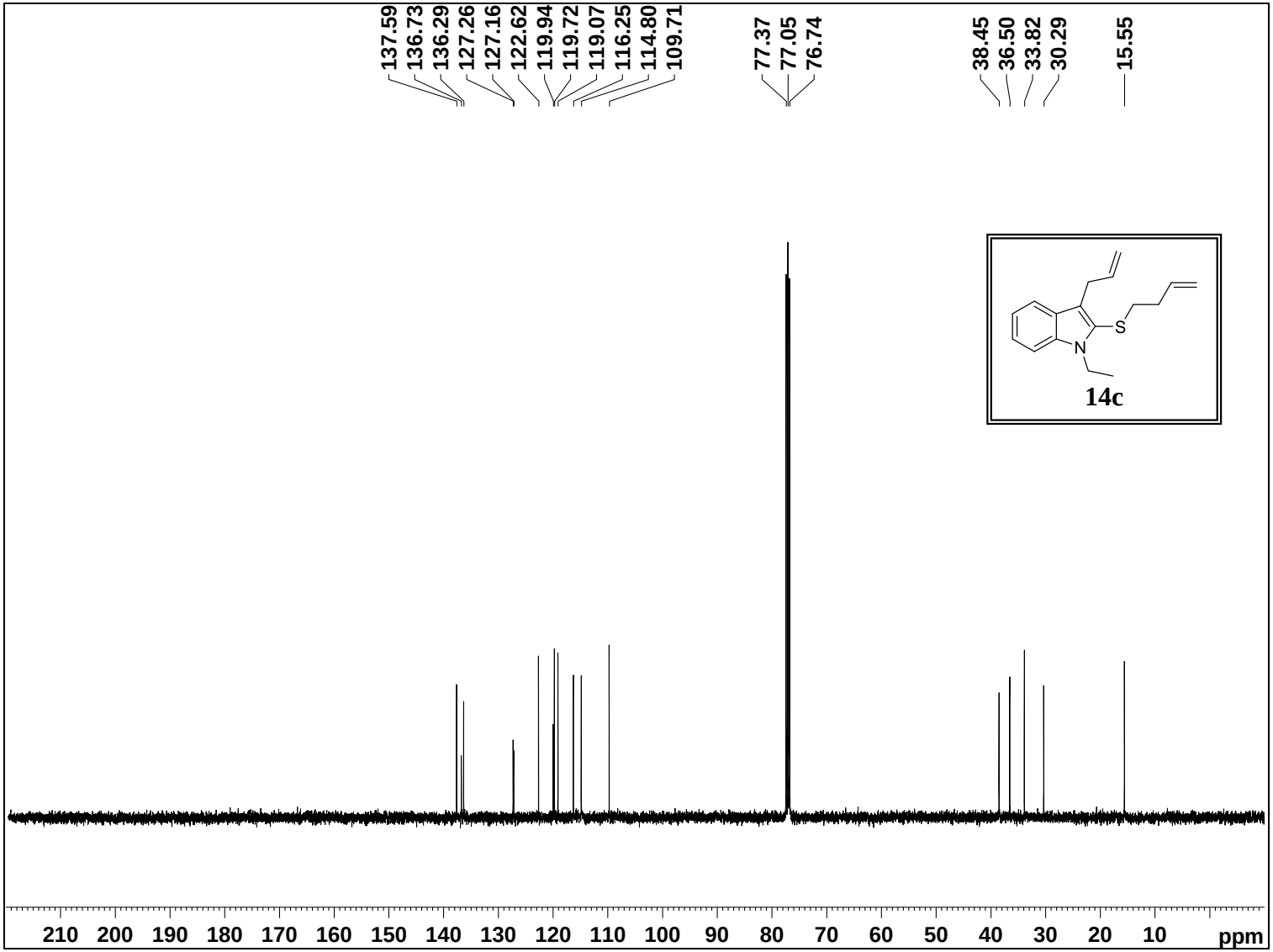
$^{13}C$ NMR for compound **14b** ($101$ MHz, $CDCl_3$)



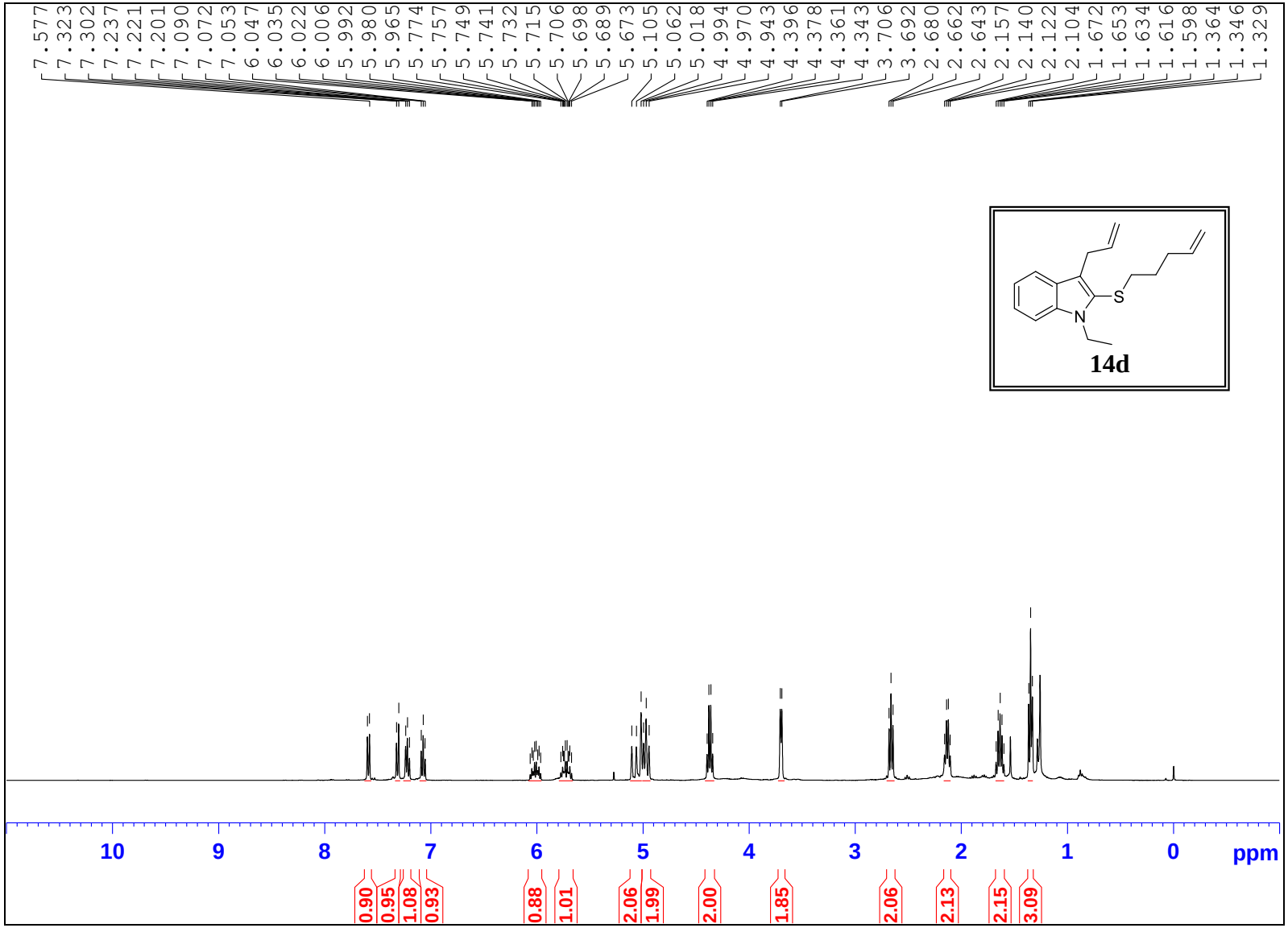
$^{1}$H NMR for compound **14c** (400 MHz, $CDCl_3$)



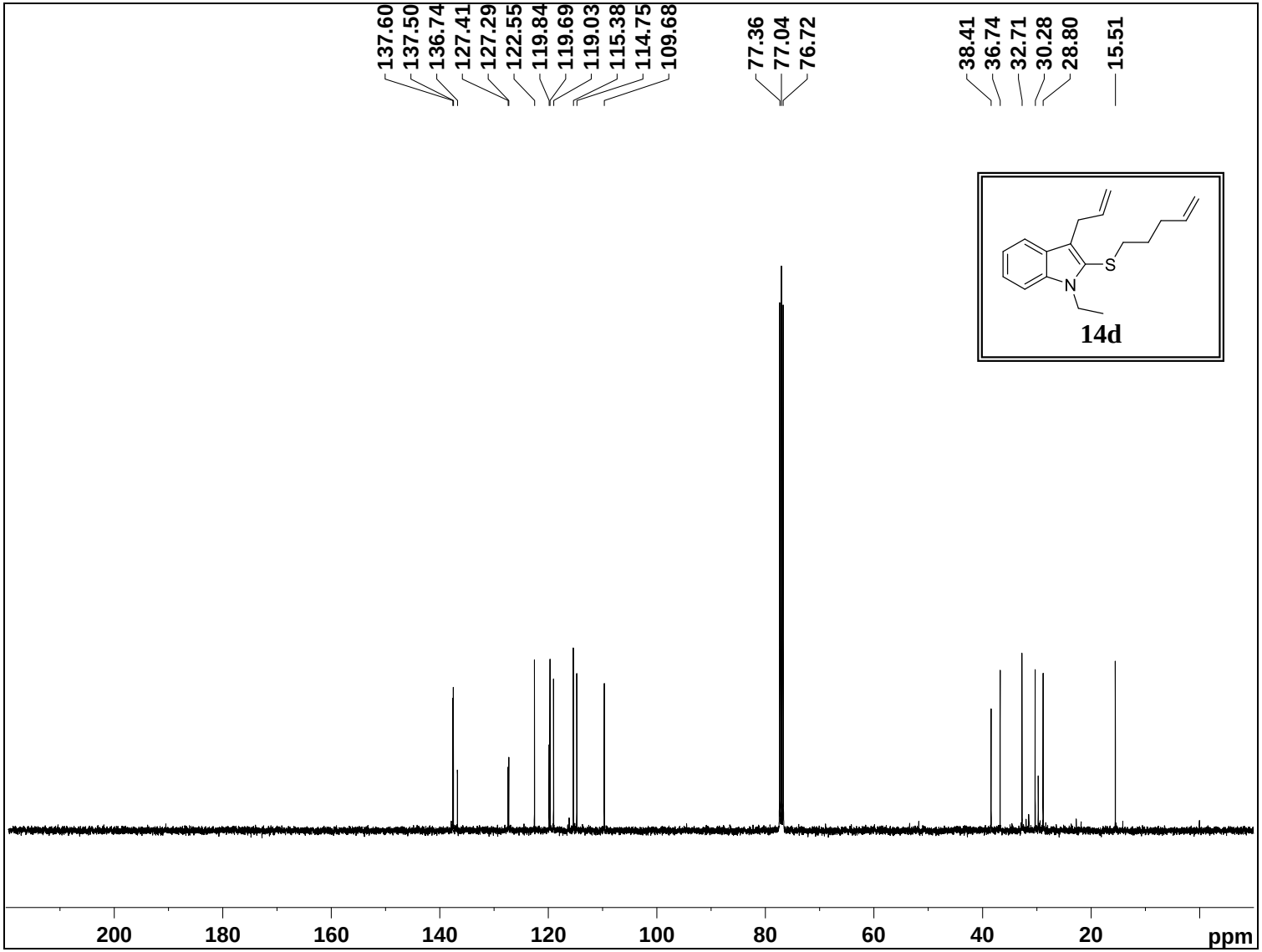
$^{13}C$ NMR for compound **14c** (101 MHz, $CDCl_3$)



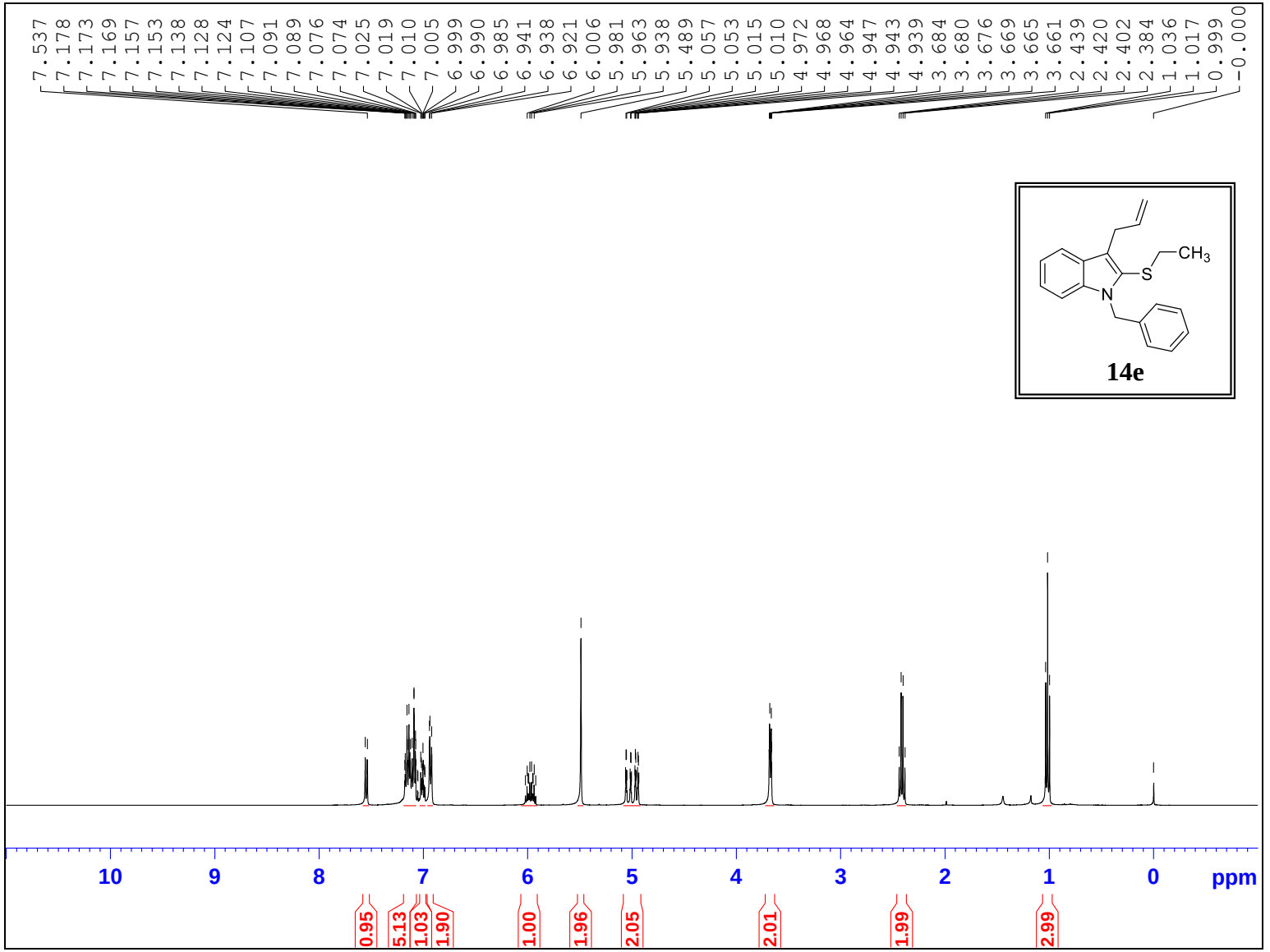
$^{1}$H NMR for compound **14d** (400 MHz, $CDCl_3$)



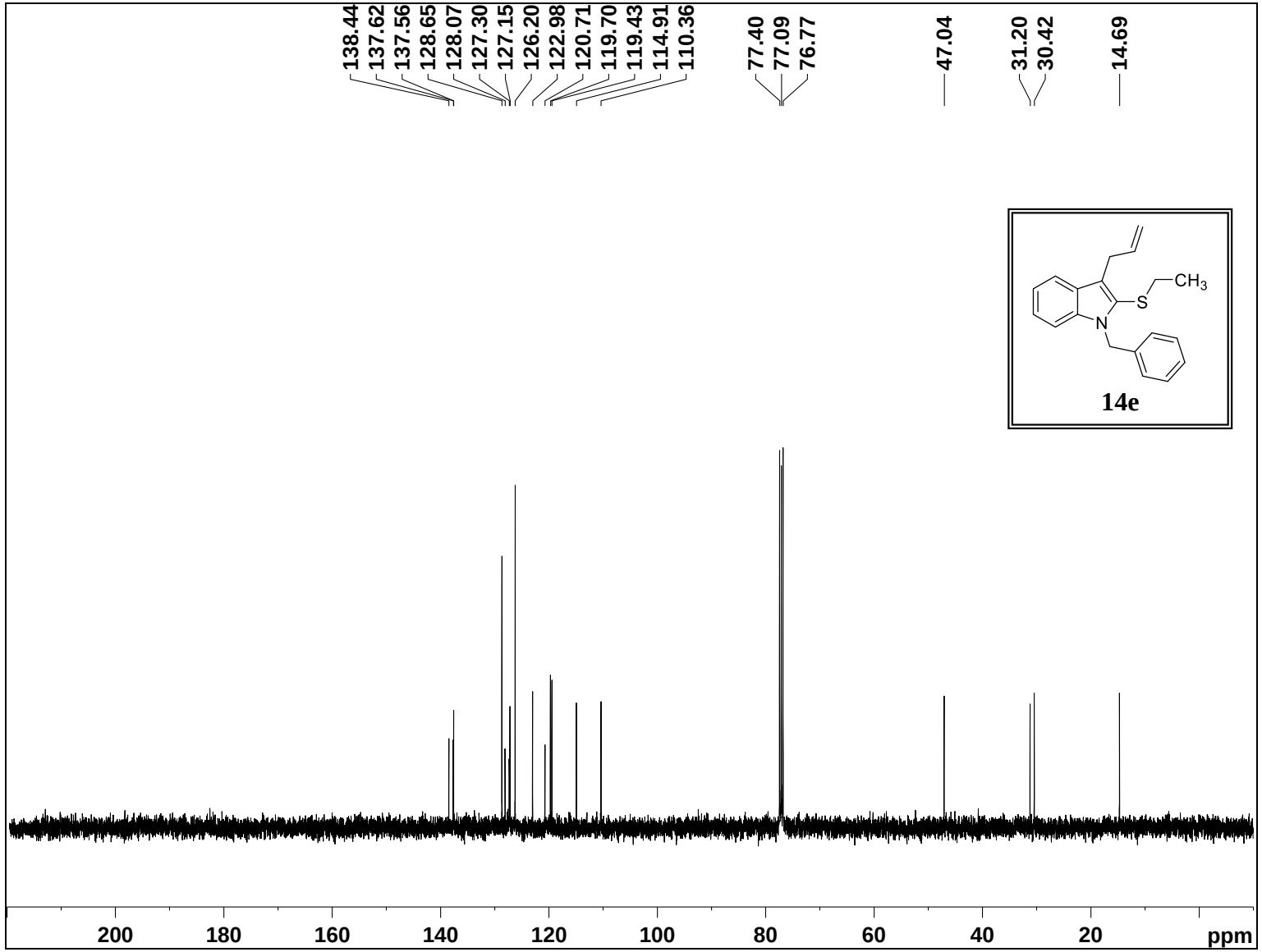
$^{13}C$ NMR for compound **14d** ($101$ MHz, $CDCl_3$)



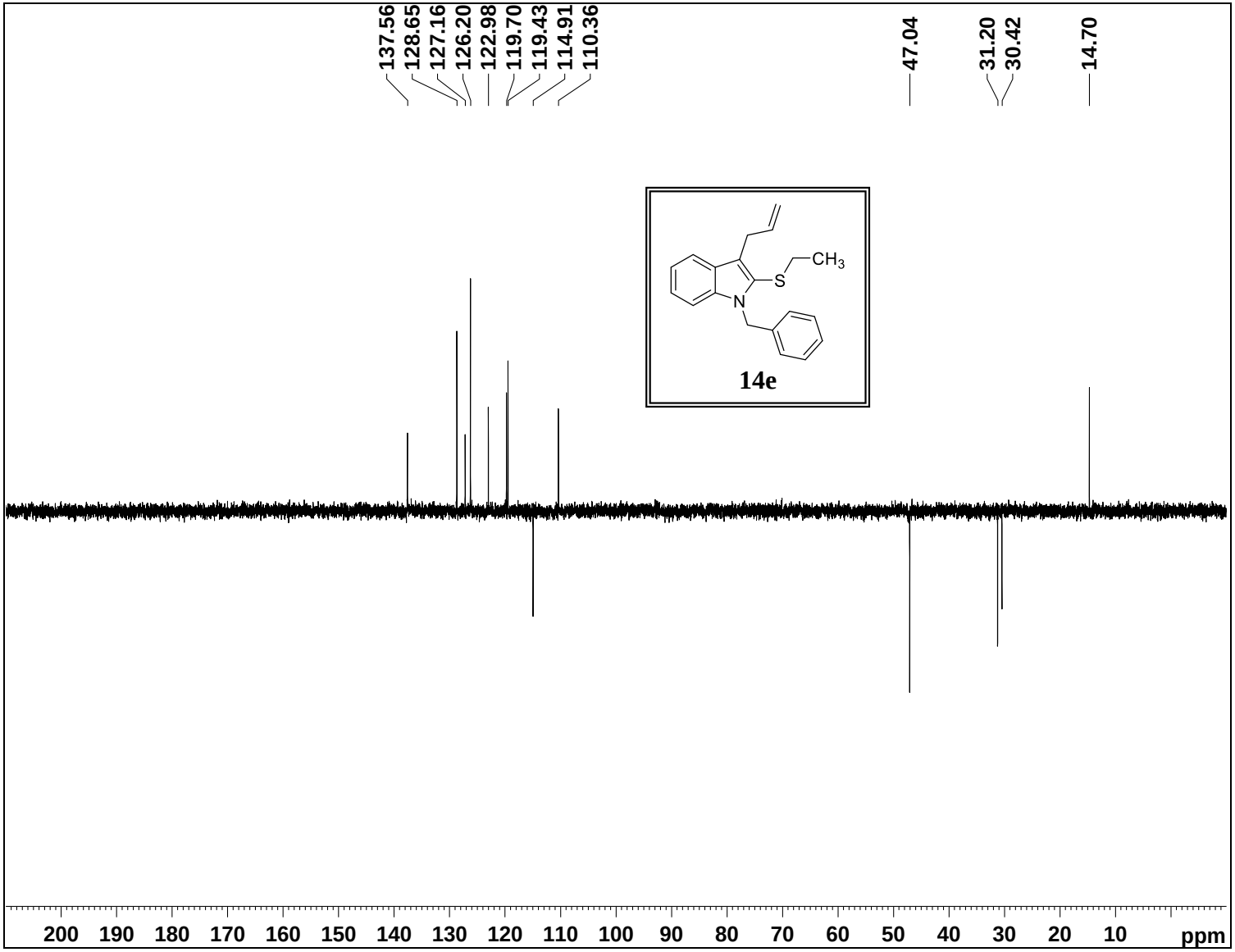
$^{1}$H NMR for compound **14e** (400 MHz, $CDCl_3$)



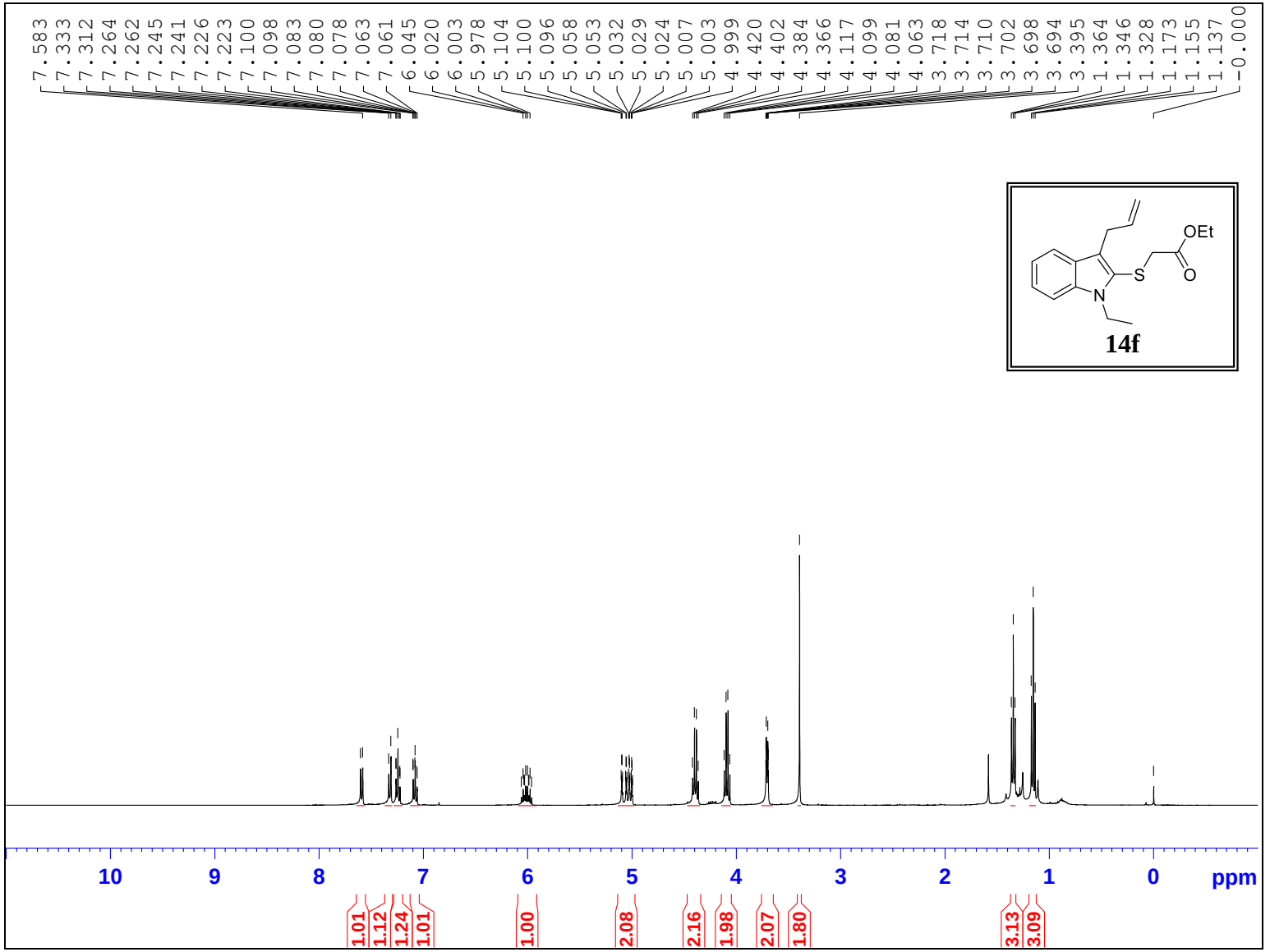
$^{13}C$ NMR for compound **14e** (101 MHz, $CDCl_3$)



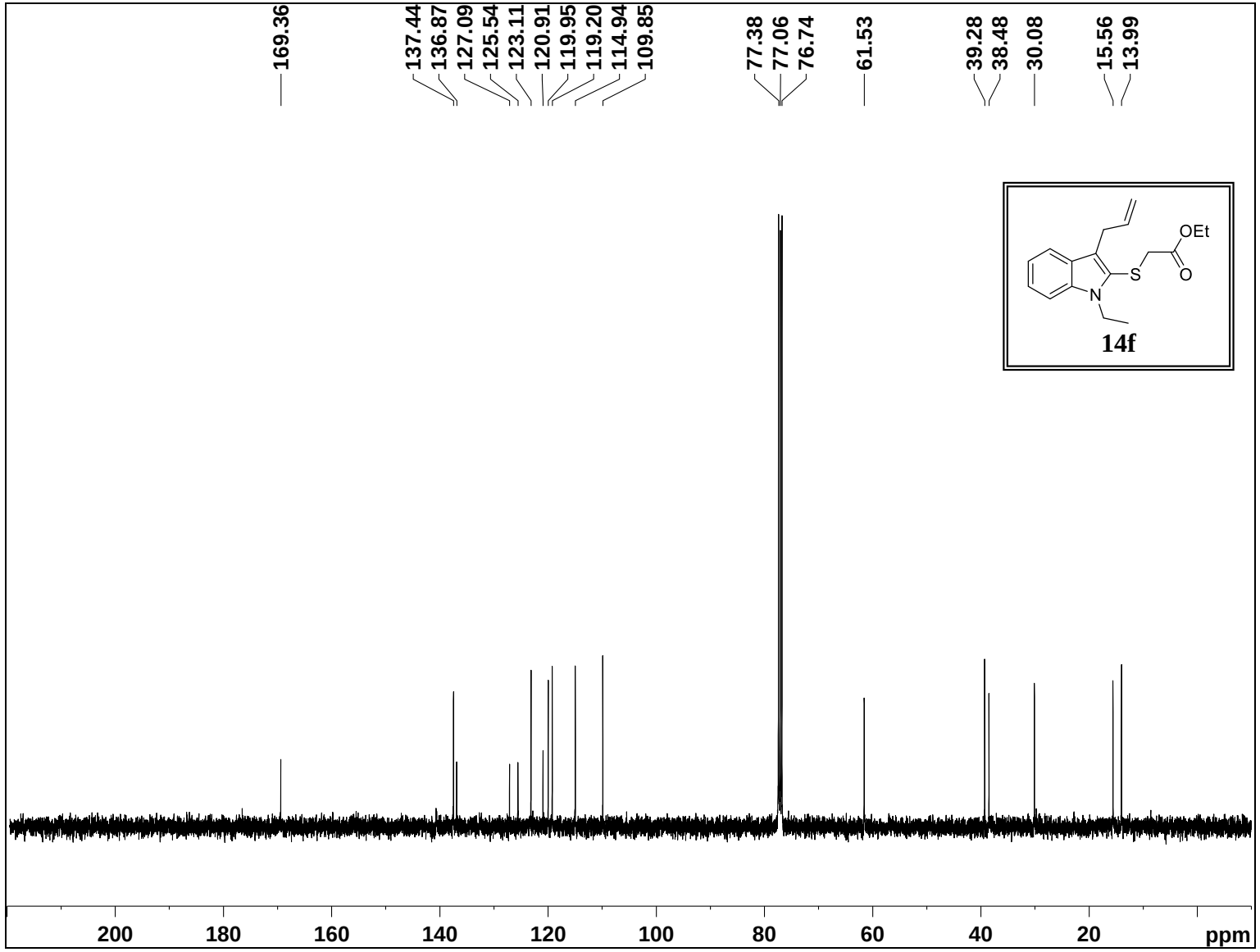
DEPT-135 NMR for compound **14e** (101 MHz, $CDCl_3$)



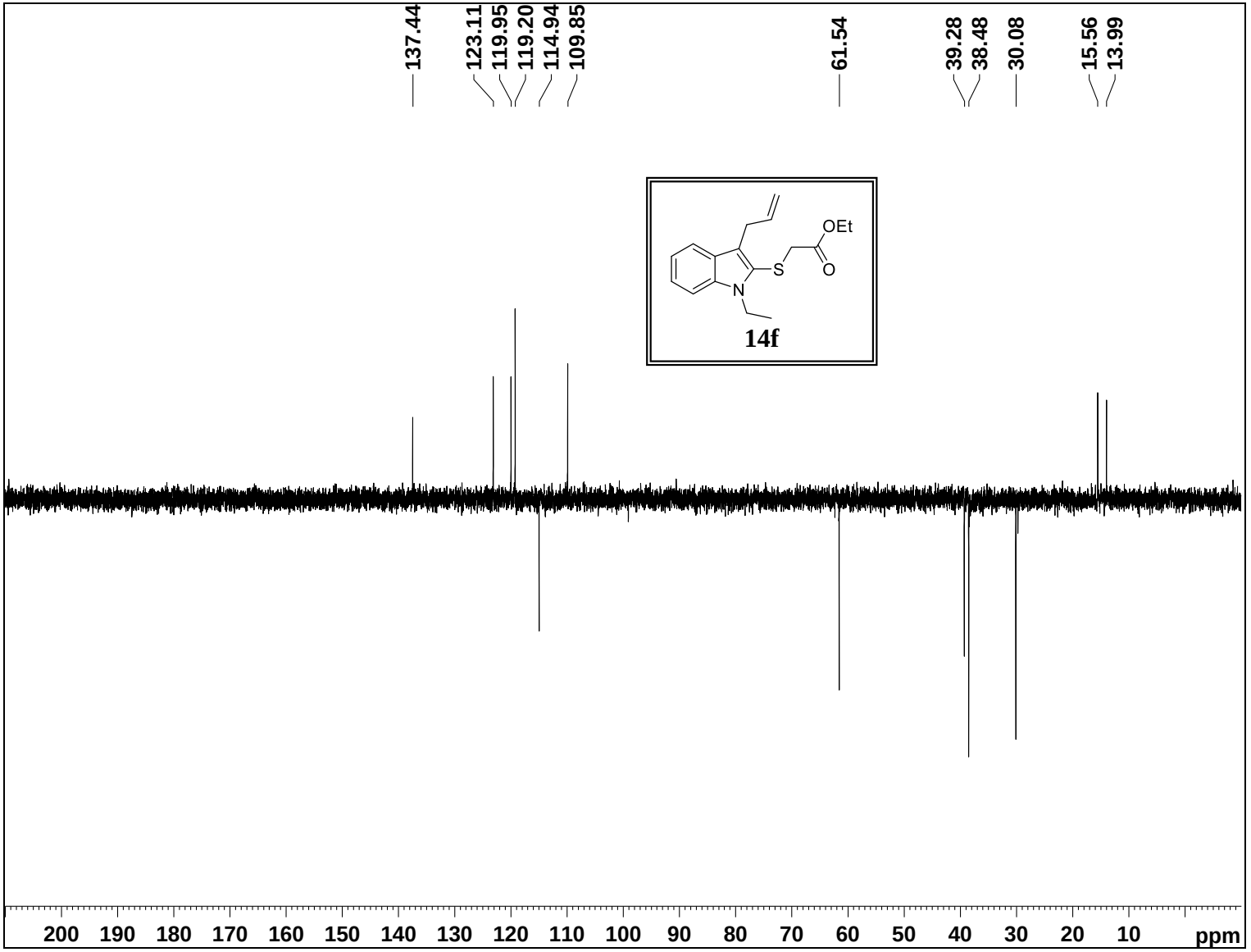
$^{1}$H NMR for compound **14f** (400 MHz, $CDCl_3$)



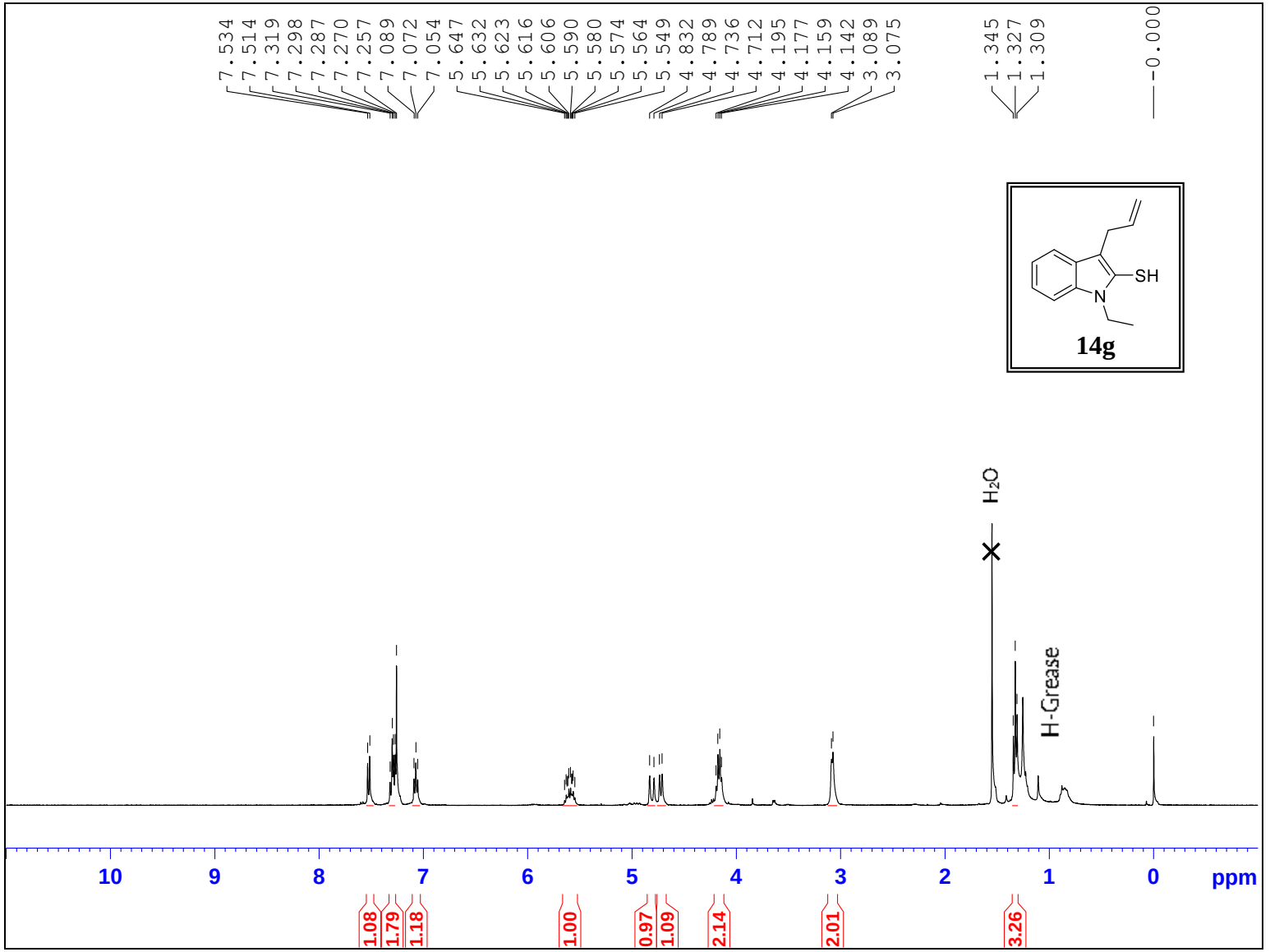
$^{13}C$ NMR for compound **14f** (101 MHz, $CDCl_3$)



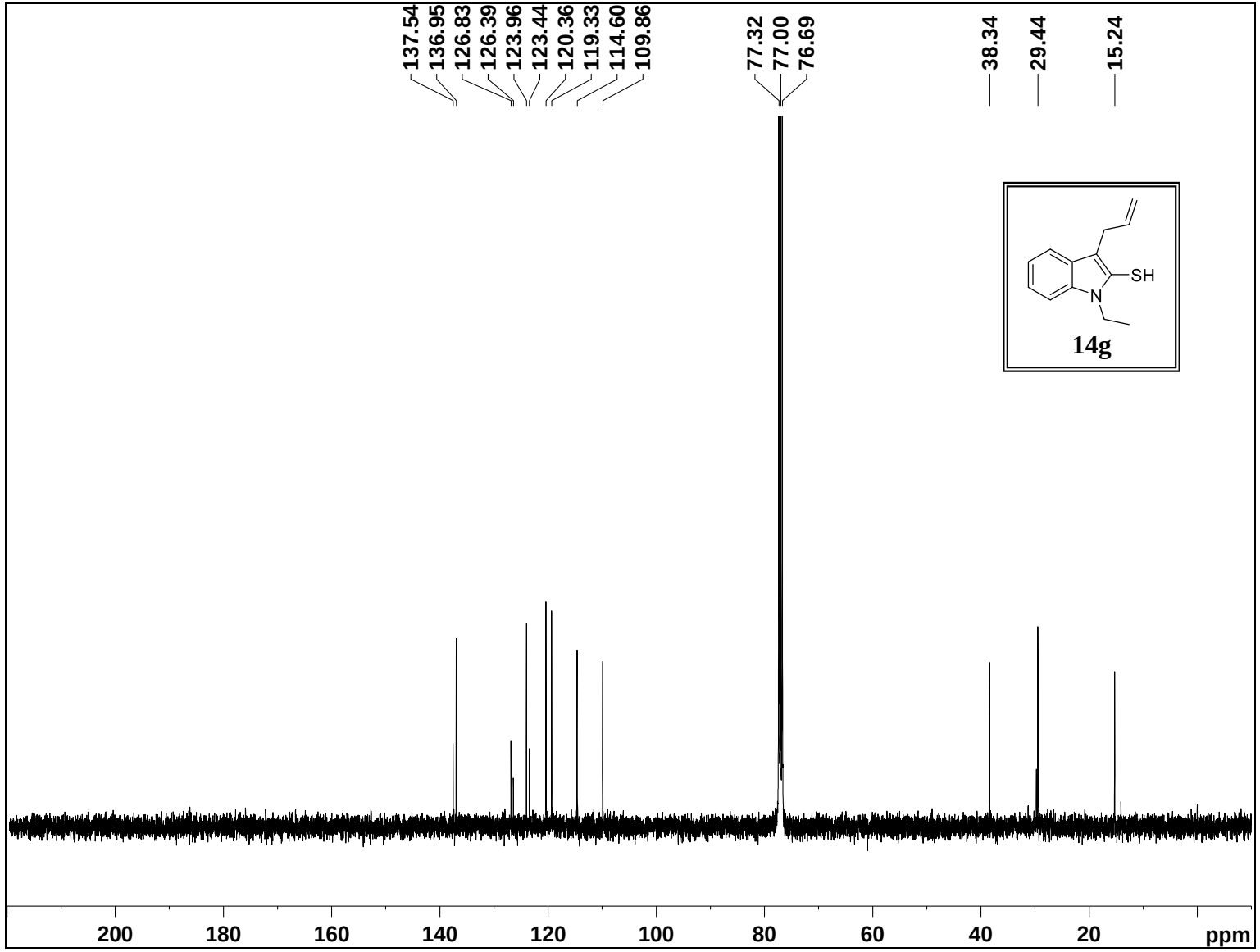
DEPT-135 NMR for compound **14f** (101 MHz, $CDCl_3$)



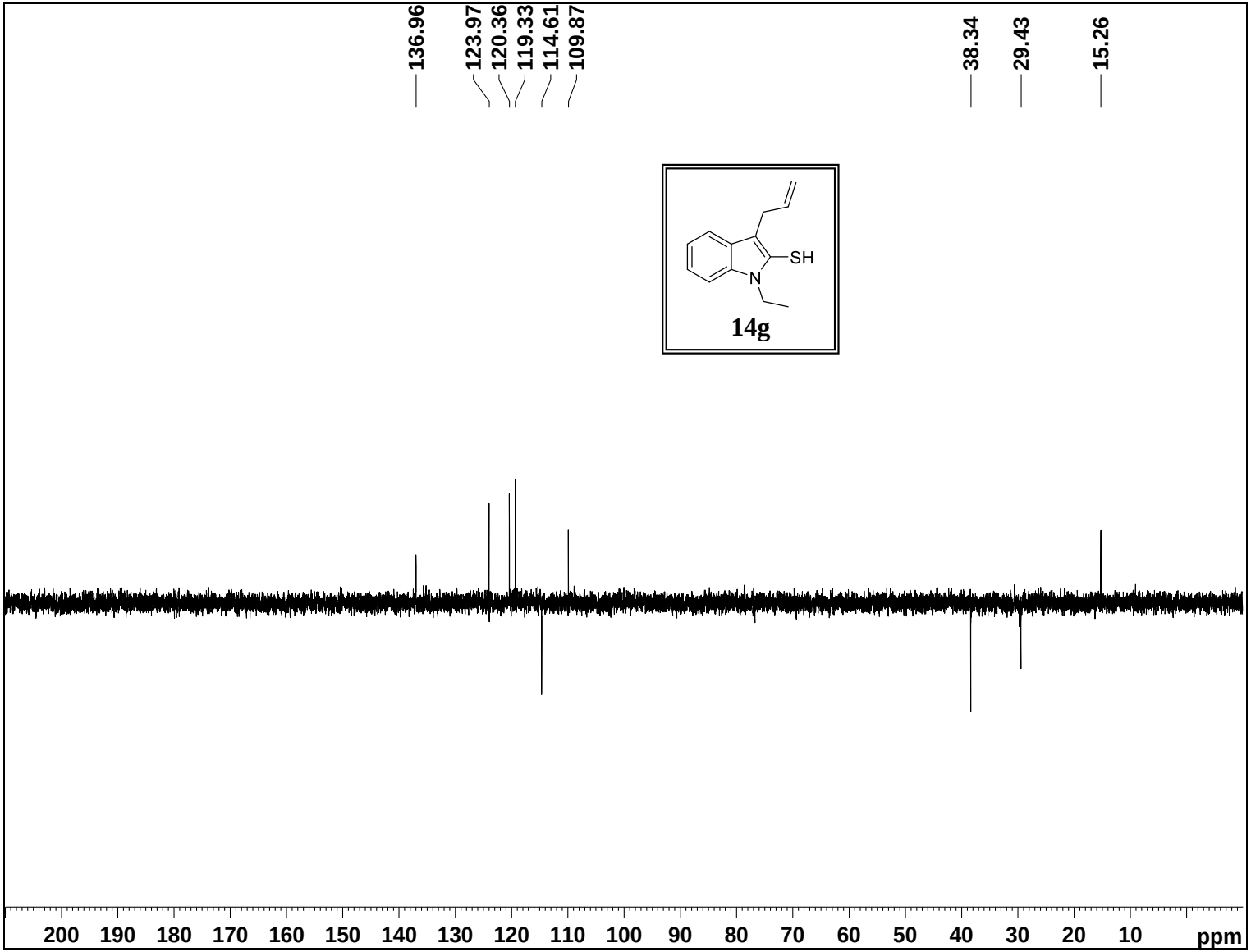
$^{1}$H NMR for compound **14g** (400 MHz, $CDCl_3$)



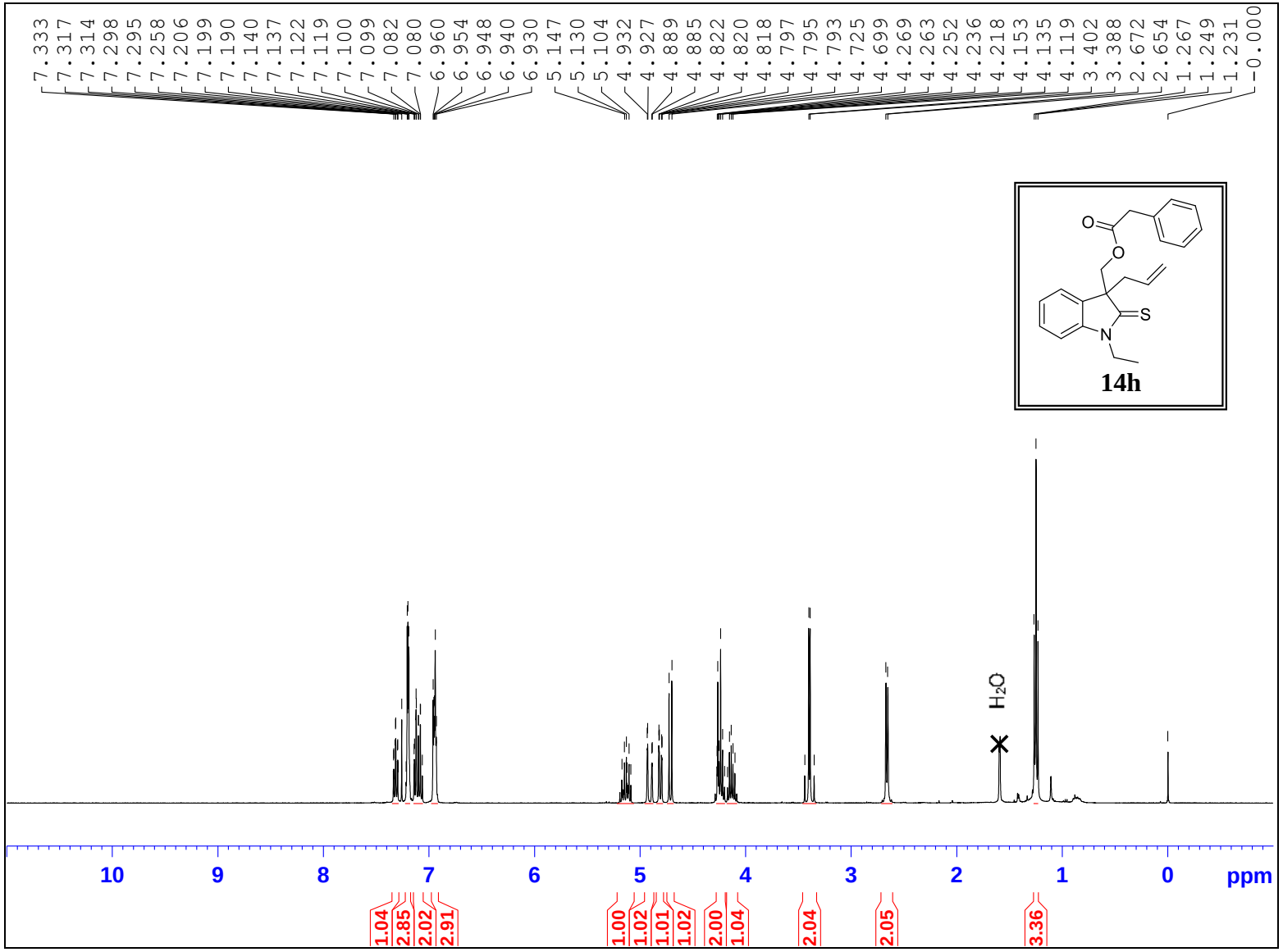
$^{13}C$ NMR for compound **14g** (101 MHz, $CDCl_3$)



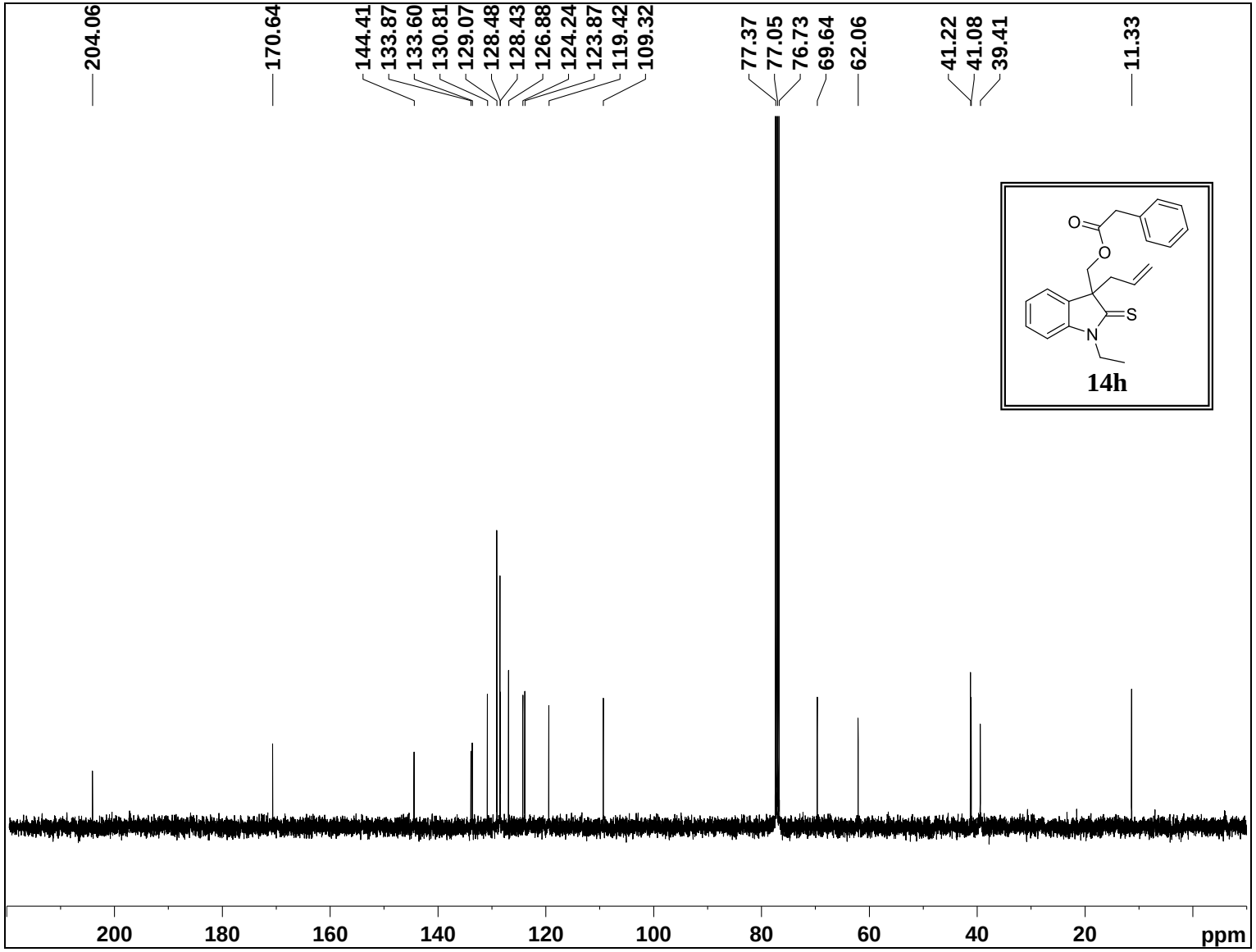
DEPT-135 NMR for compound **14g** (101 MHz, $CDCl_3$)



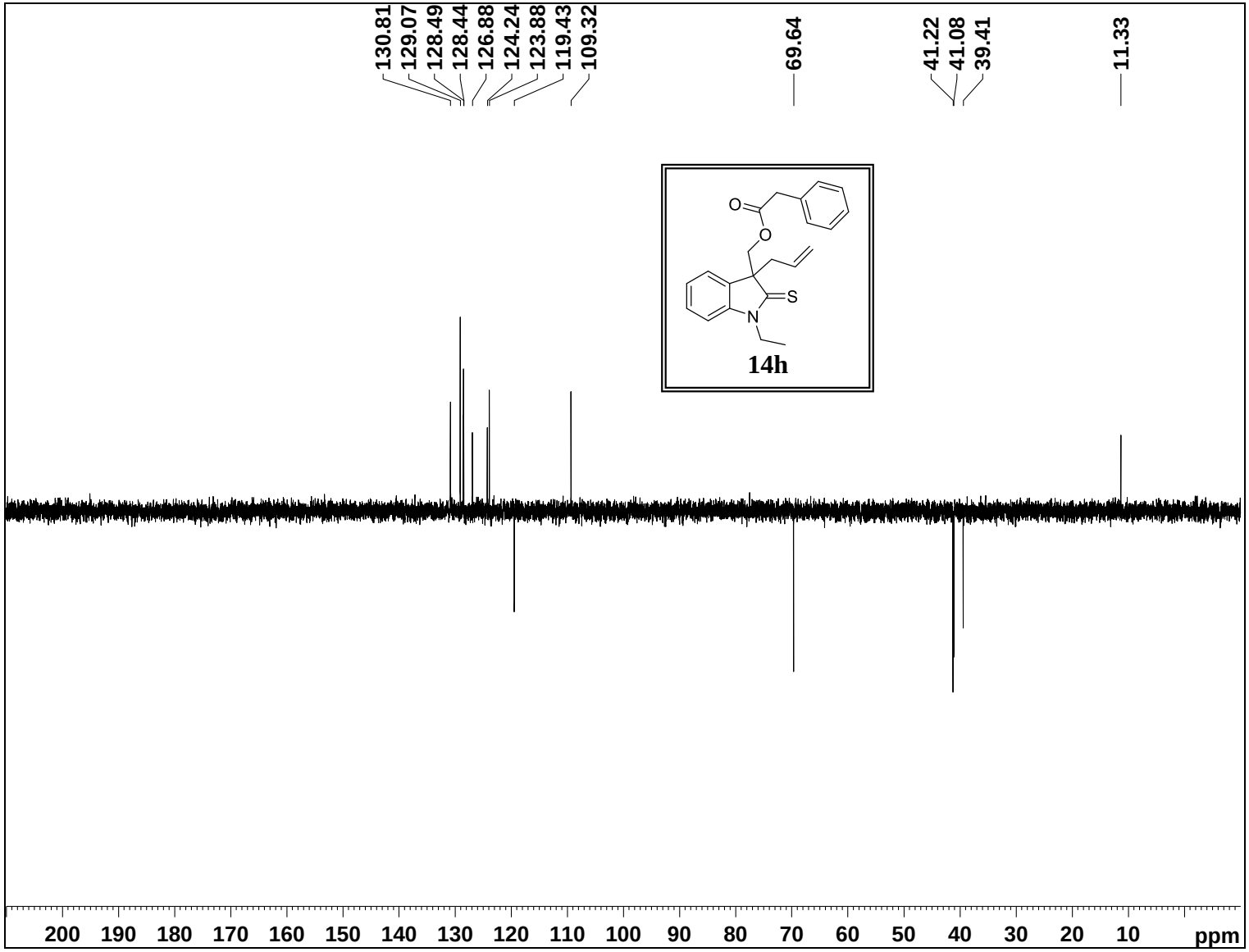
$^{1}$H NMR for compound **14h** (400 MHz, $CDCl_3$)



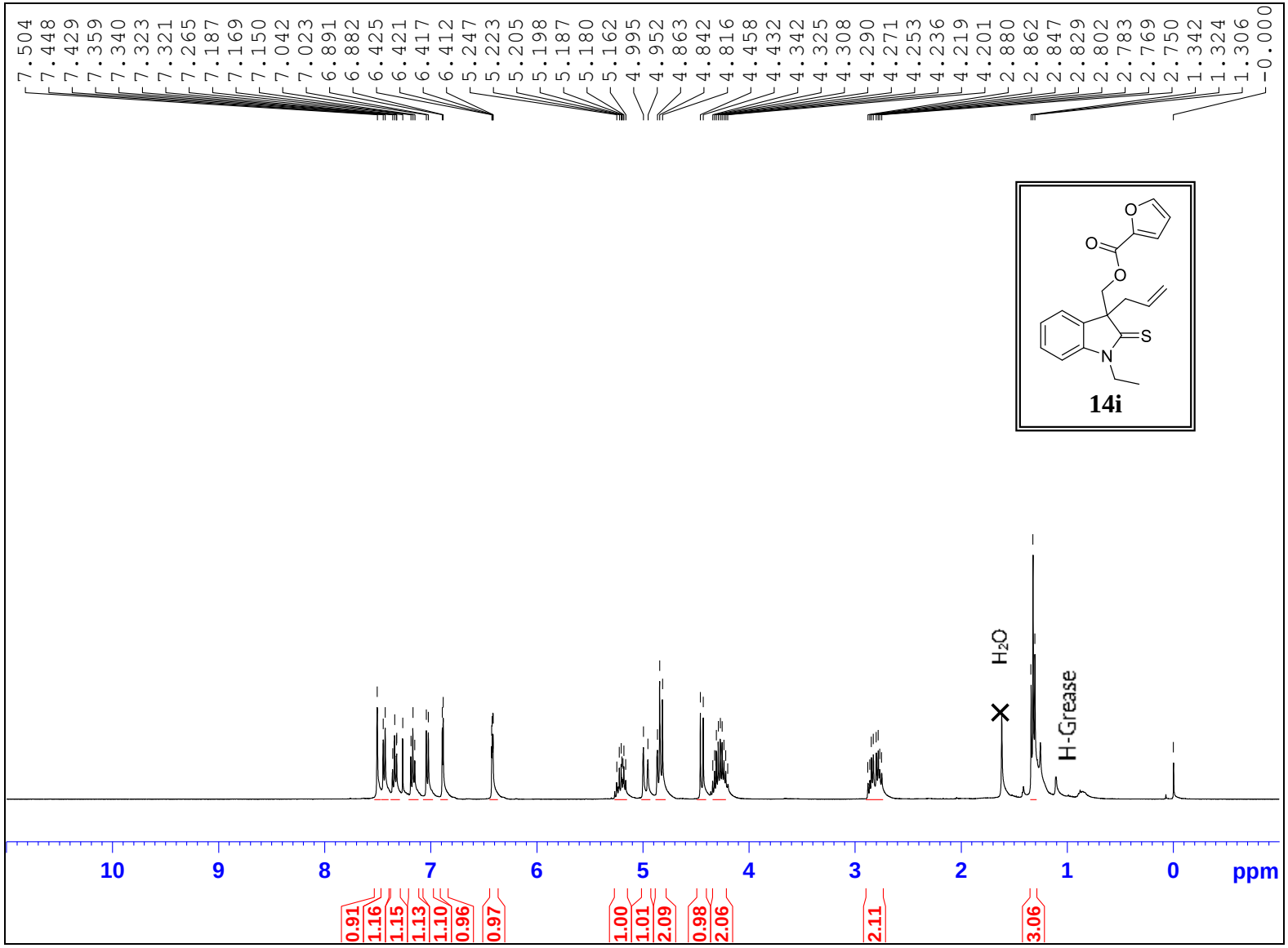
$^{13}C$ NMR for compound **14h** ($101$ MHz, $CDCl_3$)



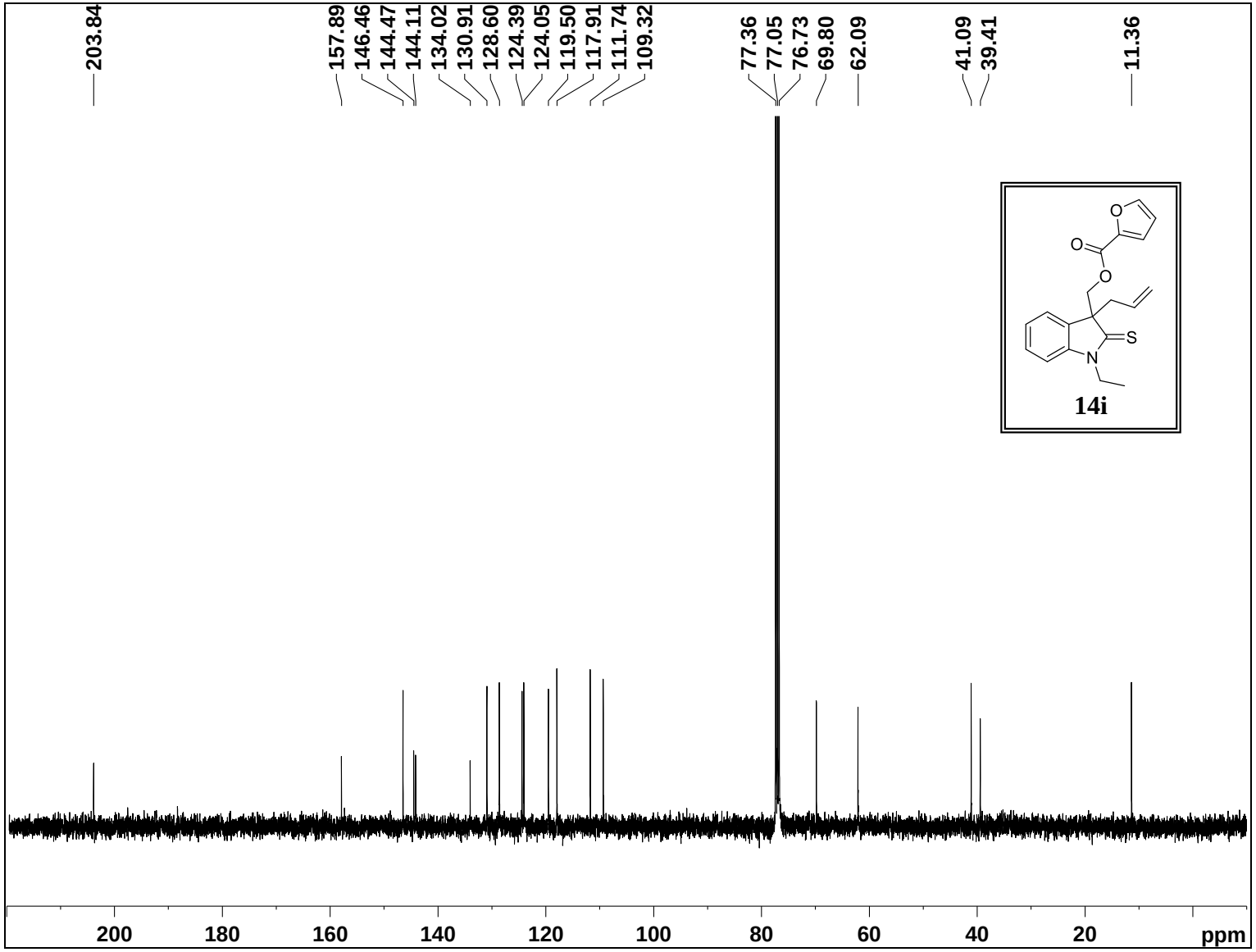
DEPT-135 NMR for compound **14h** (101 MHz, $CDCl_3$)



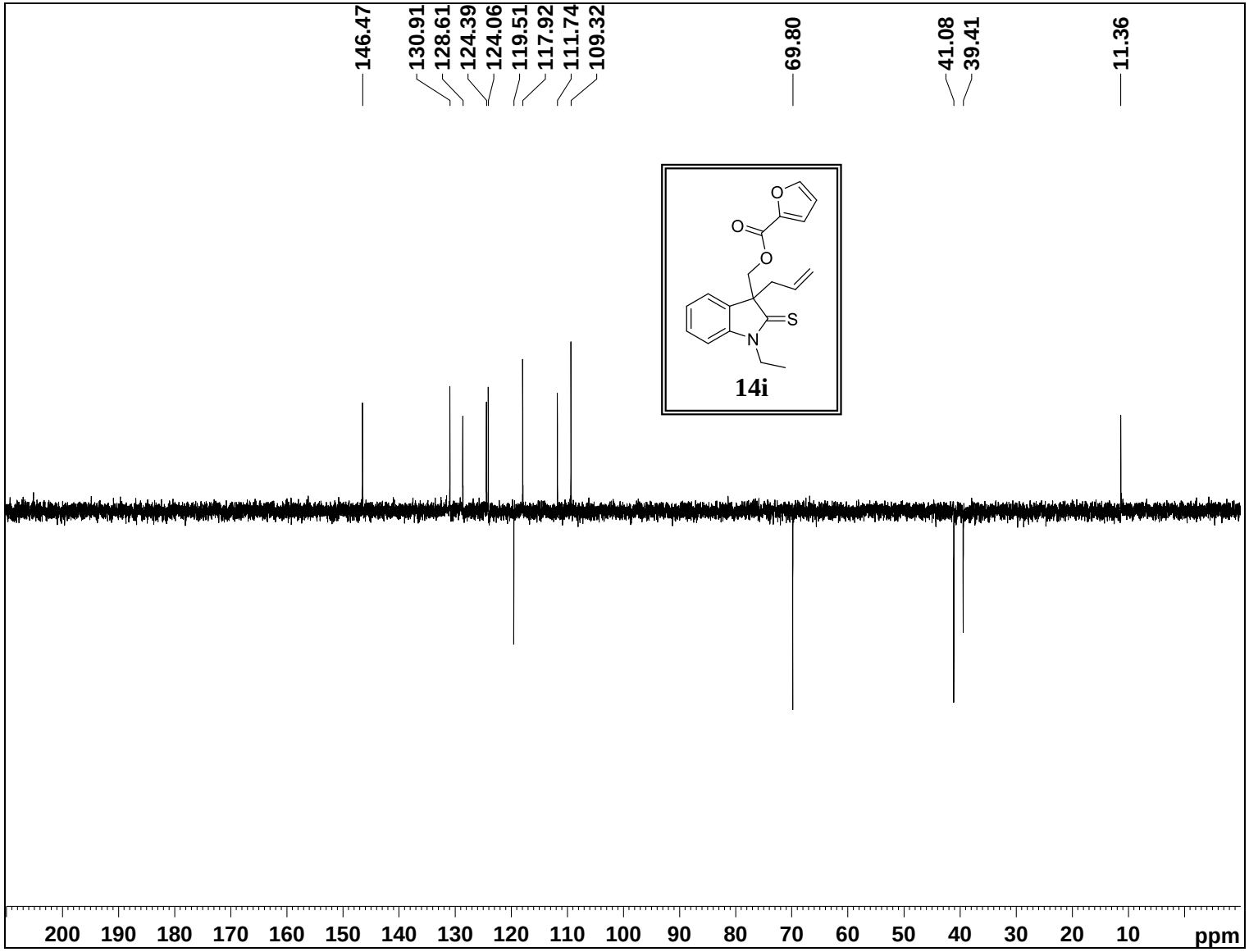
$^{1}$H NMR for compound **14i** (400 MHz, $CDCl_3$)



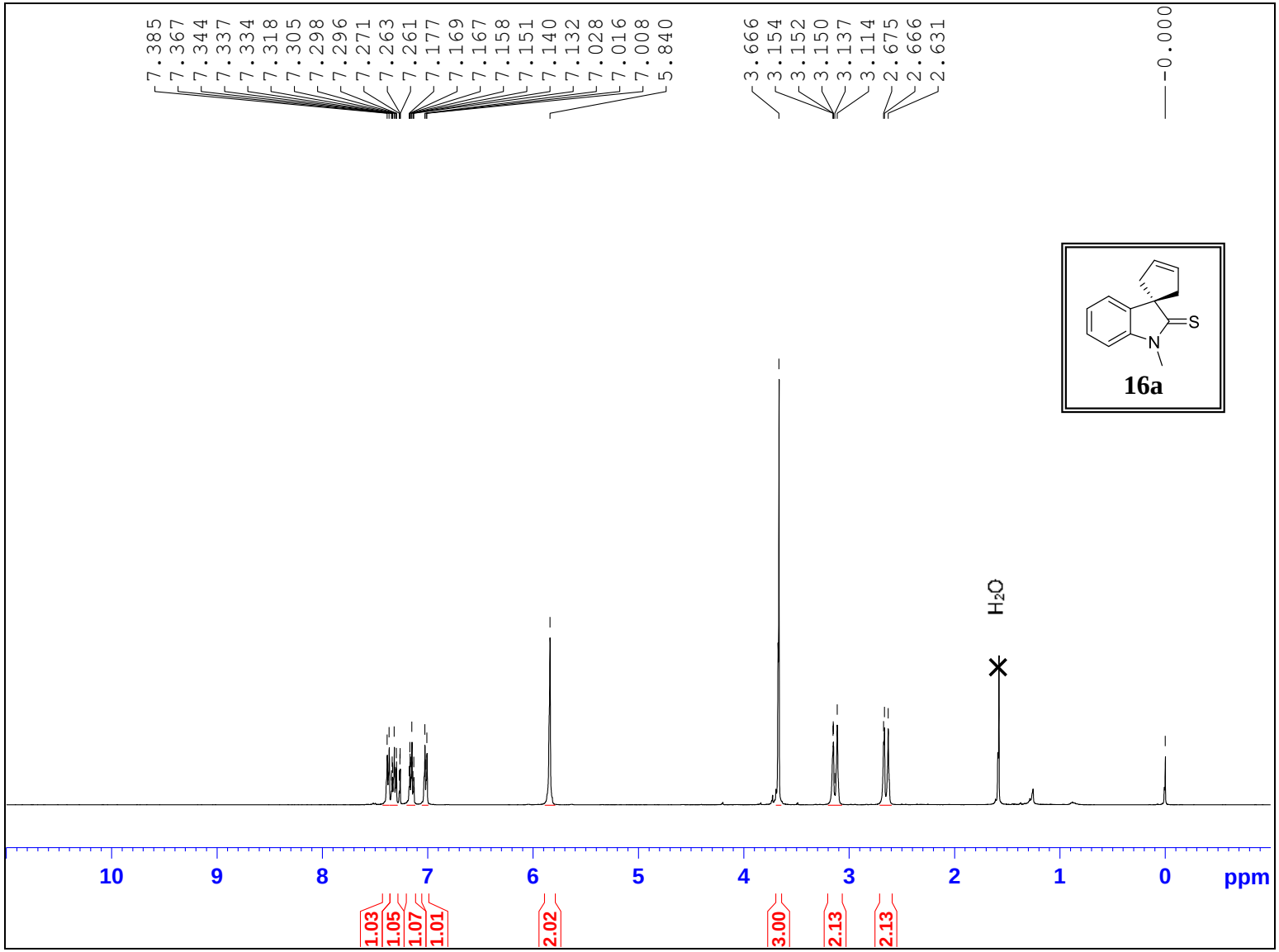
$^{13}C$ NMR for compound **14i** (101 MHz, $CDCl_3$)



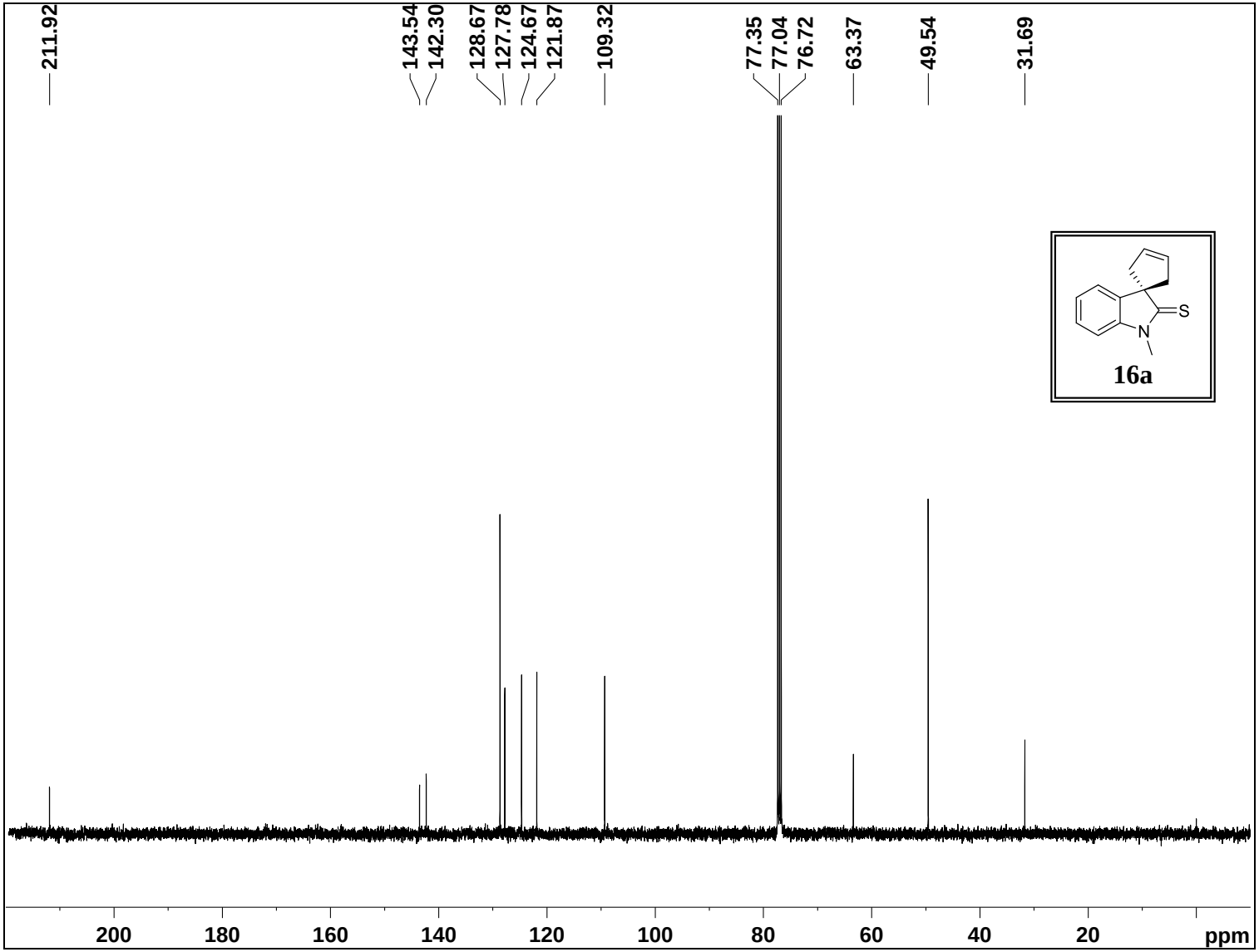
DEPT-135 NMR for compound **14i** (101 MHz, $CDCl_3$)



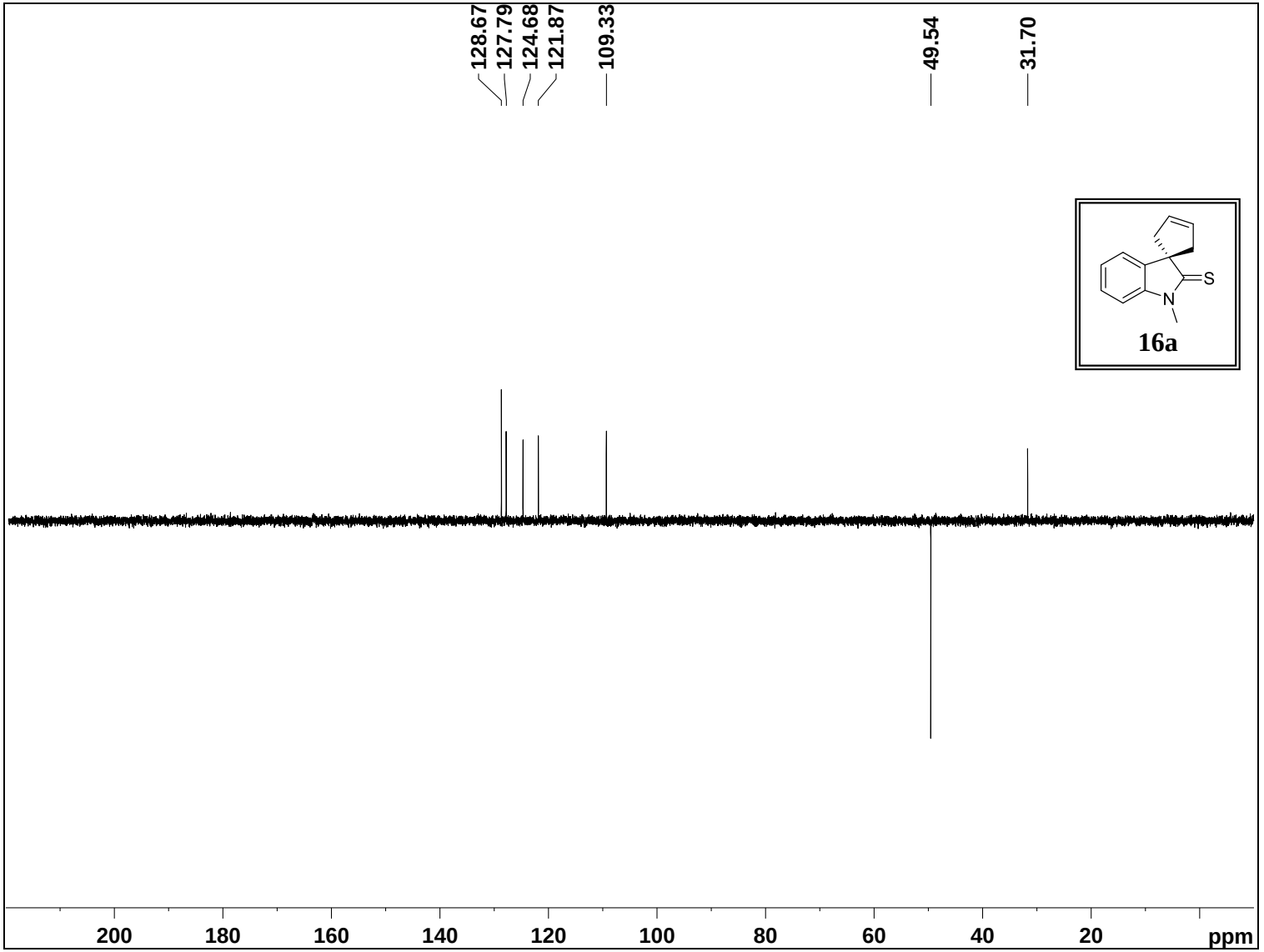
$^{1}$H NMR for compound **16a** (400 MHz, $CDCl_3$)



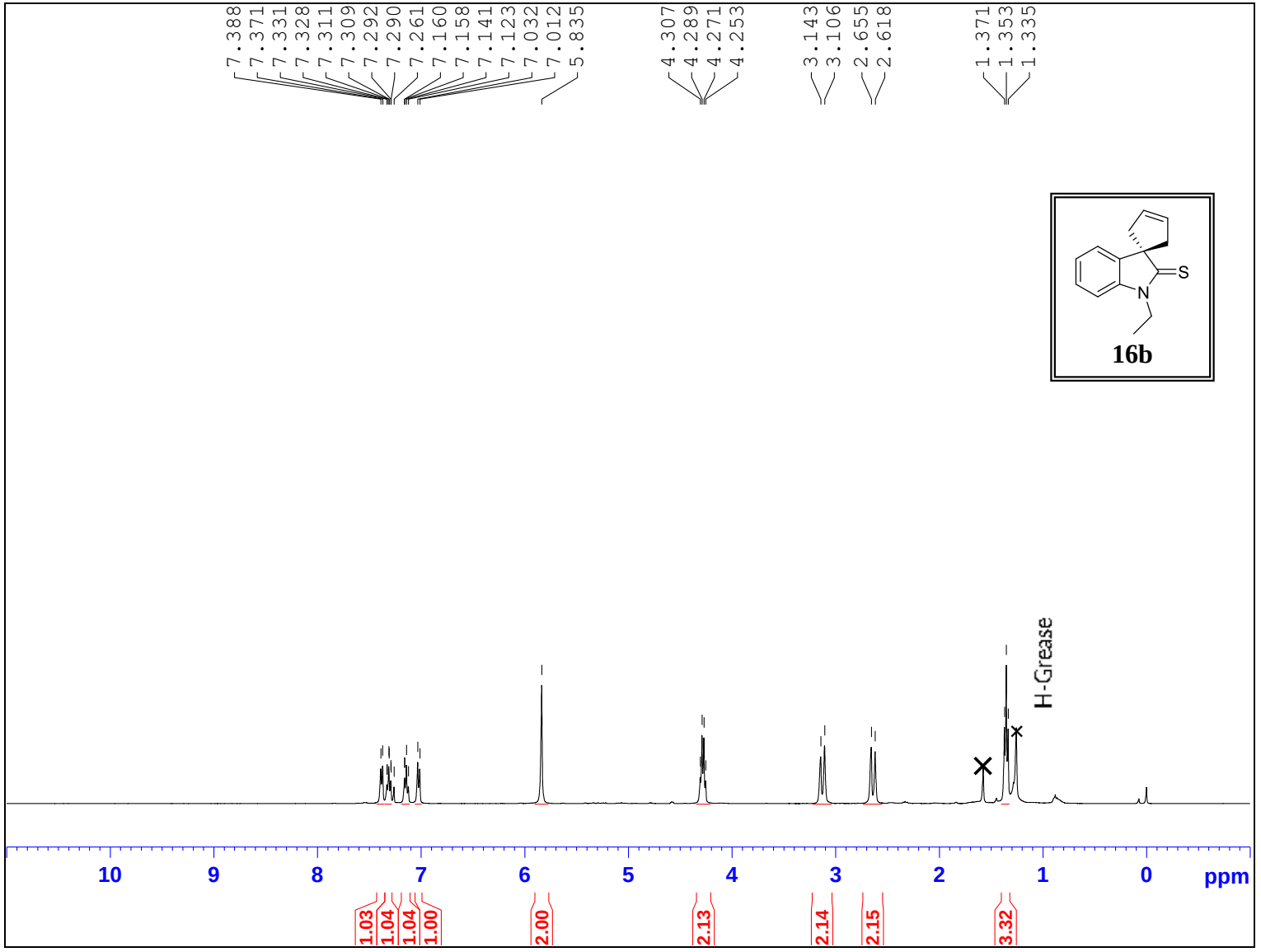
$^{13}C$ NMR for compound **16a** (101 MHz, $CDCl_3$)



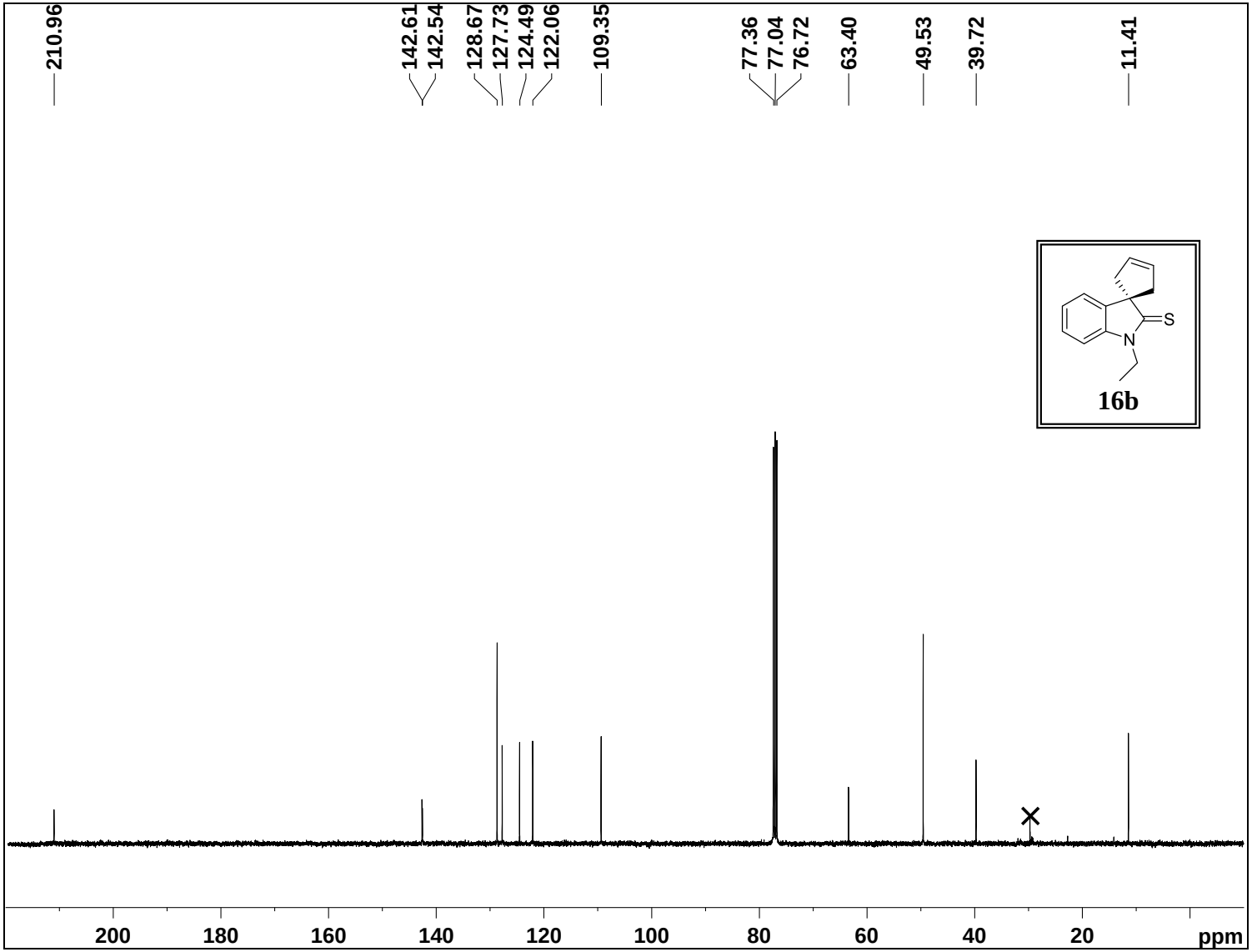
DEPT-135 NMR for compound **16a** (101 MHz, $CDCl_3$)



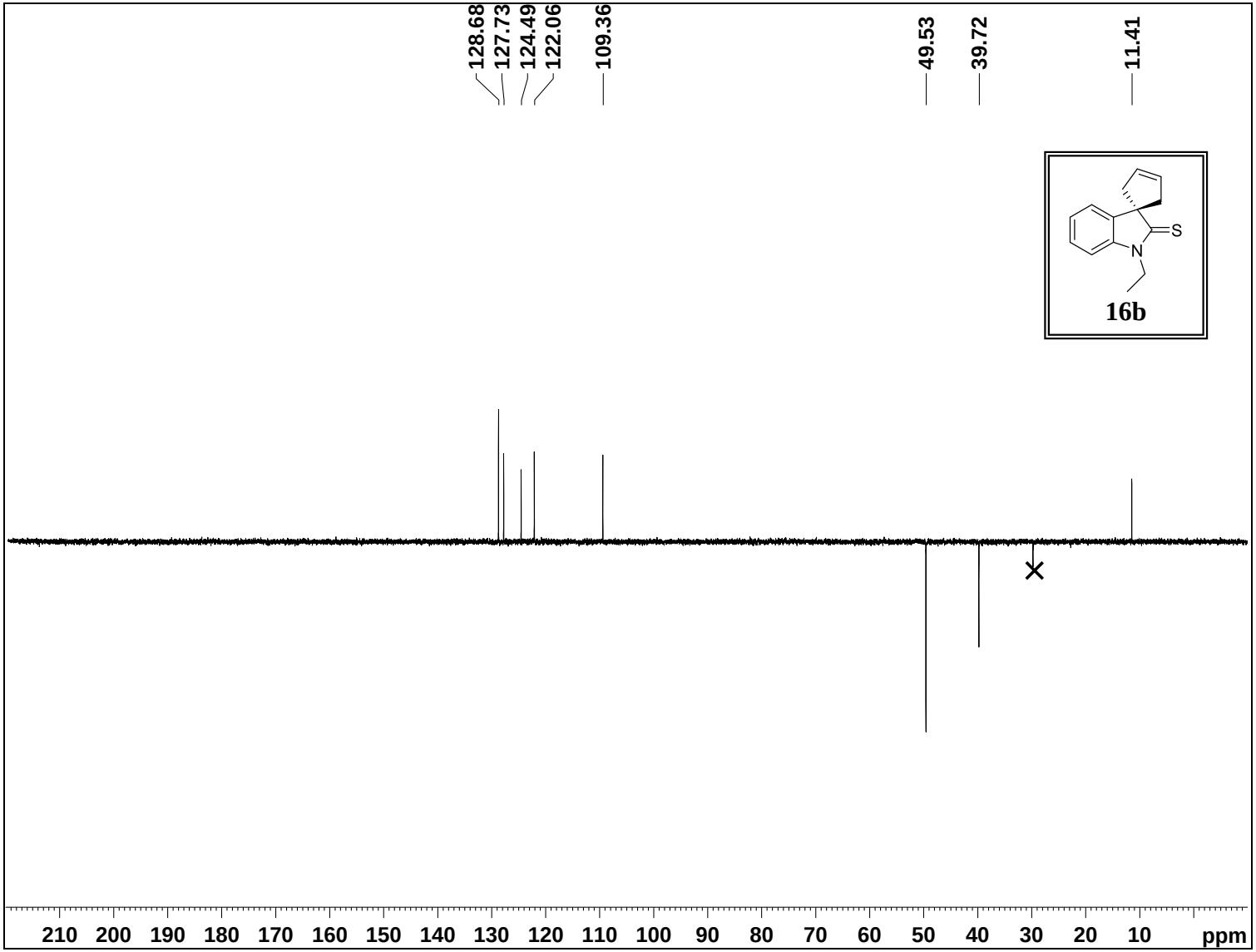
$^{1}$H NMR for compound **16b** (400 MHz, $CDCl_3$)



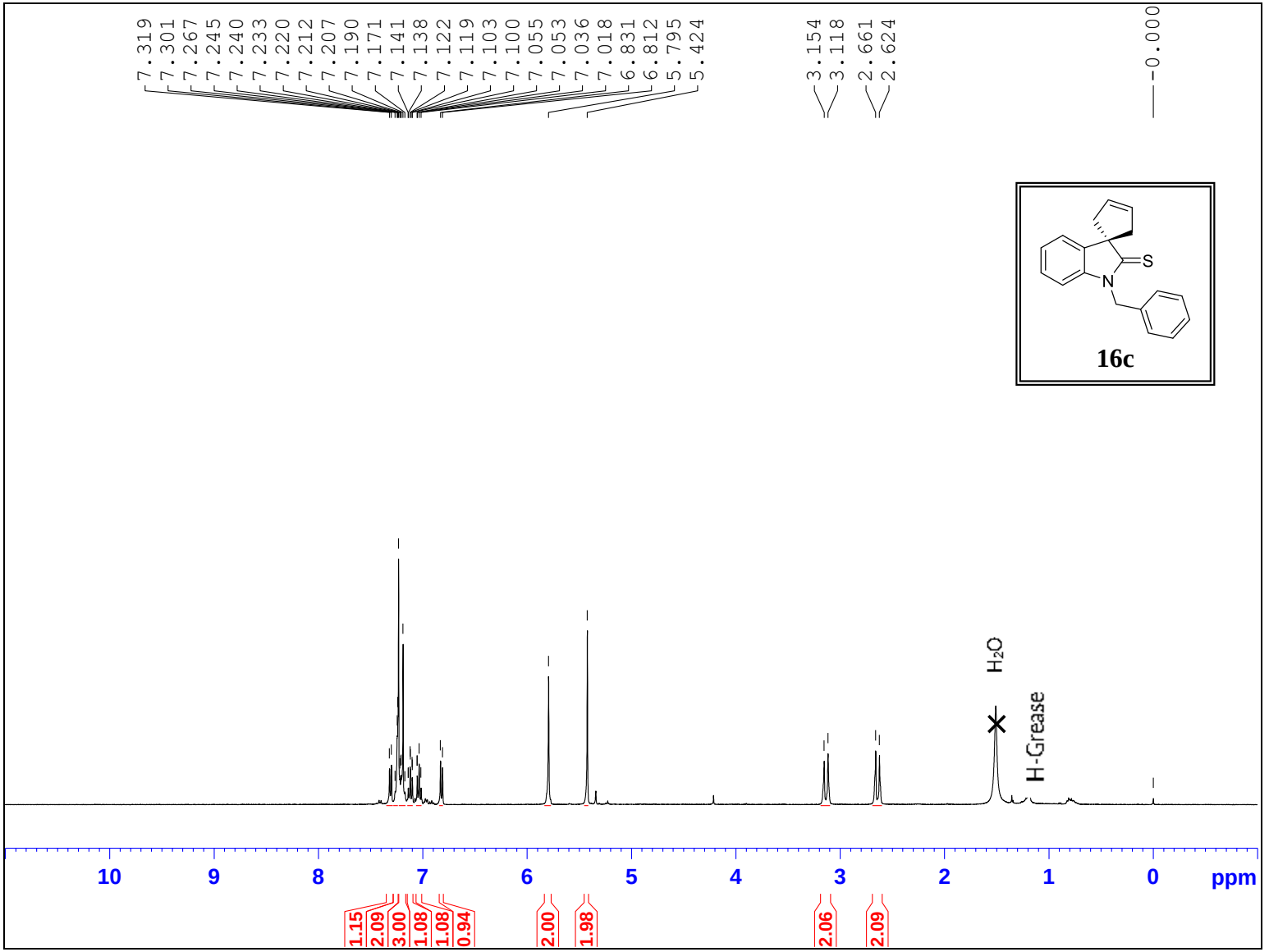
$^{13}C$ NMR for compound **16b** ($101$ MHz, $CDCl_3$)



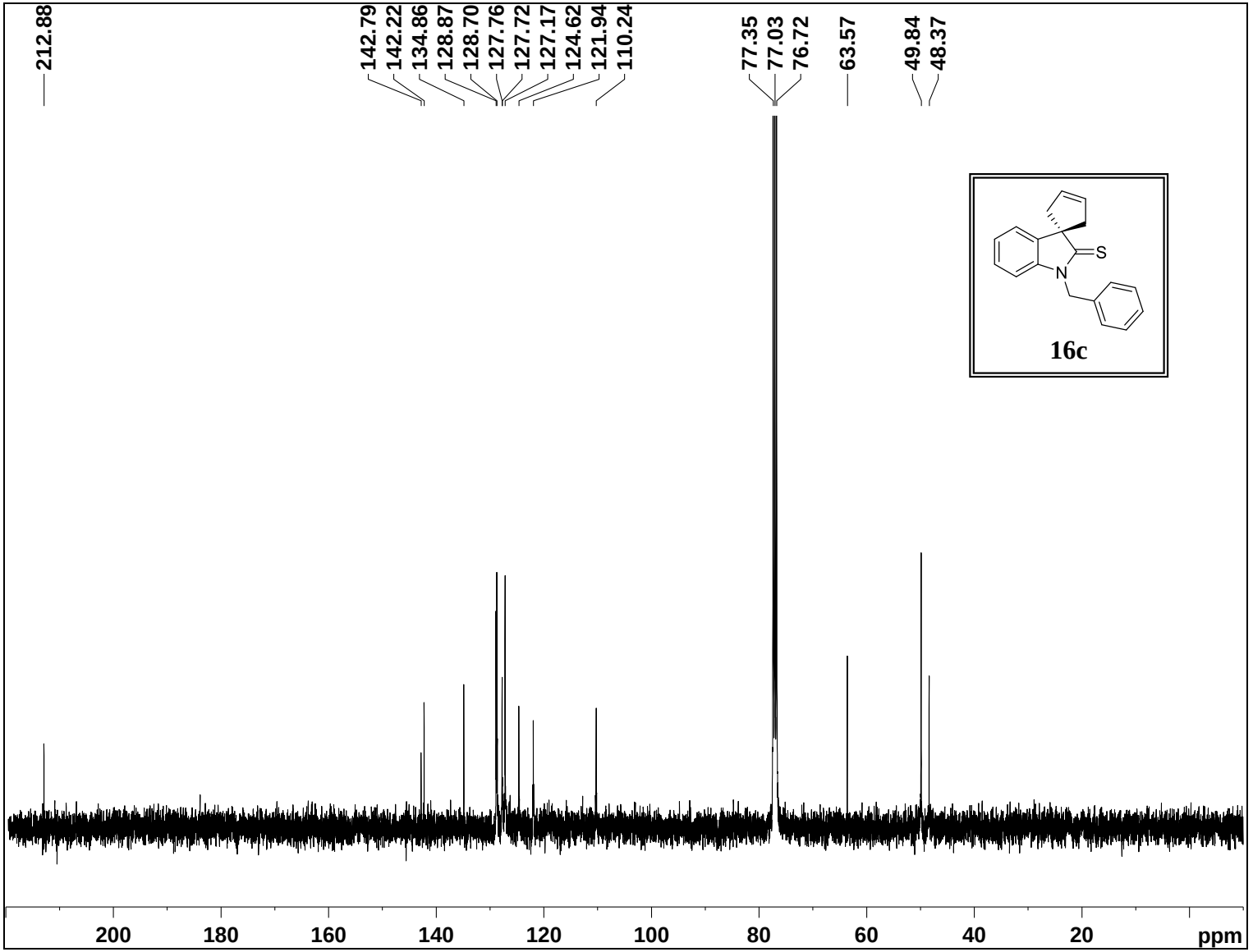
DEPT-135 NMR for compound **16b** (101 MHz, $CDCl_3$)



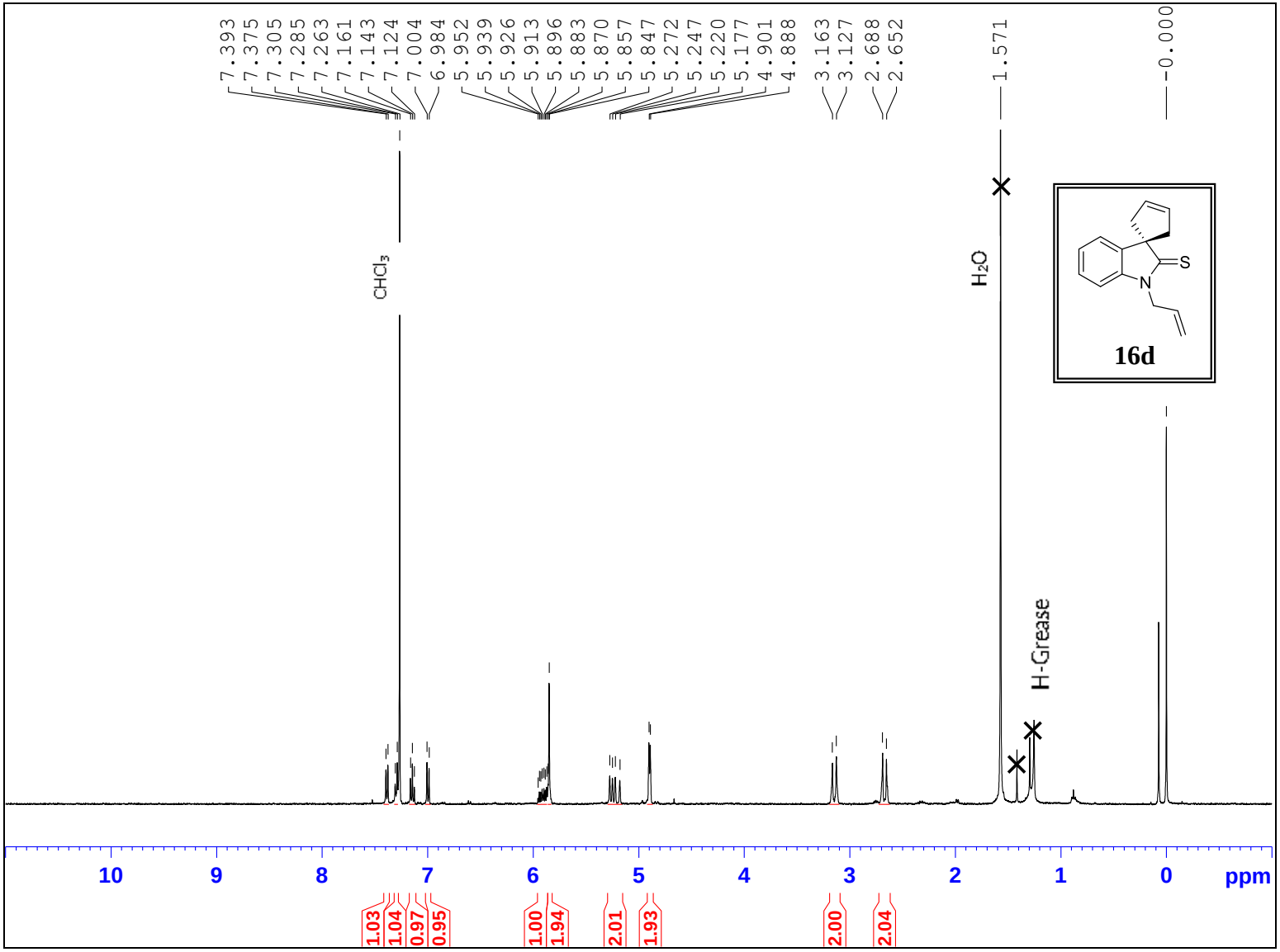
$^{1}$H NMR for compound **16c** (400 MHz, $CDCl_3$)



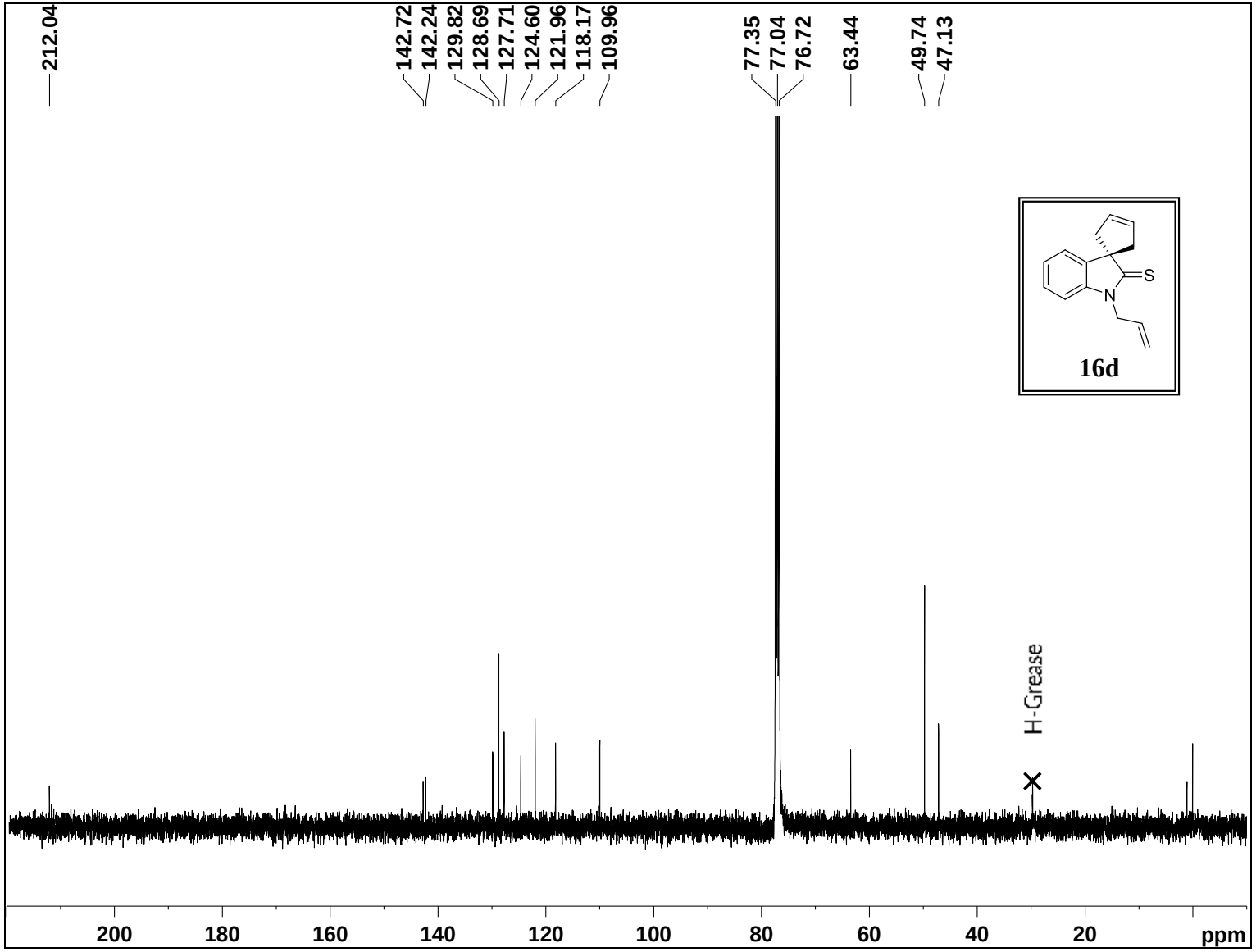
$^{13}C$ NMR for compound **16c** (101 MHz, $CDCl_3$)



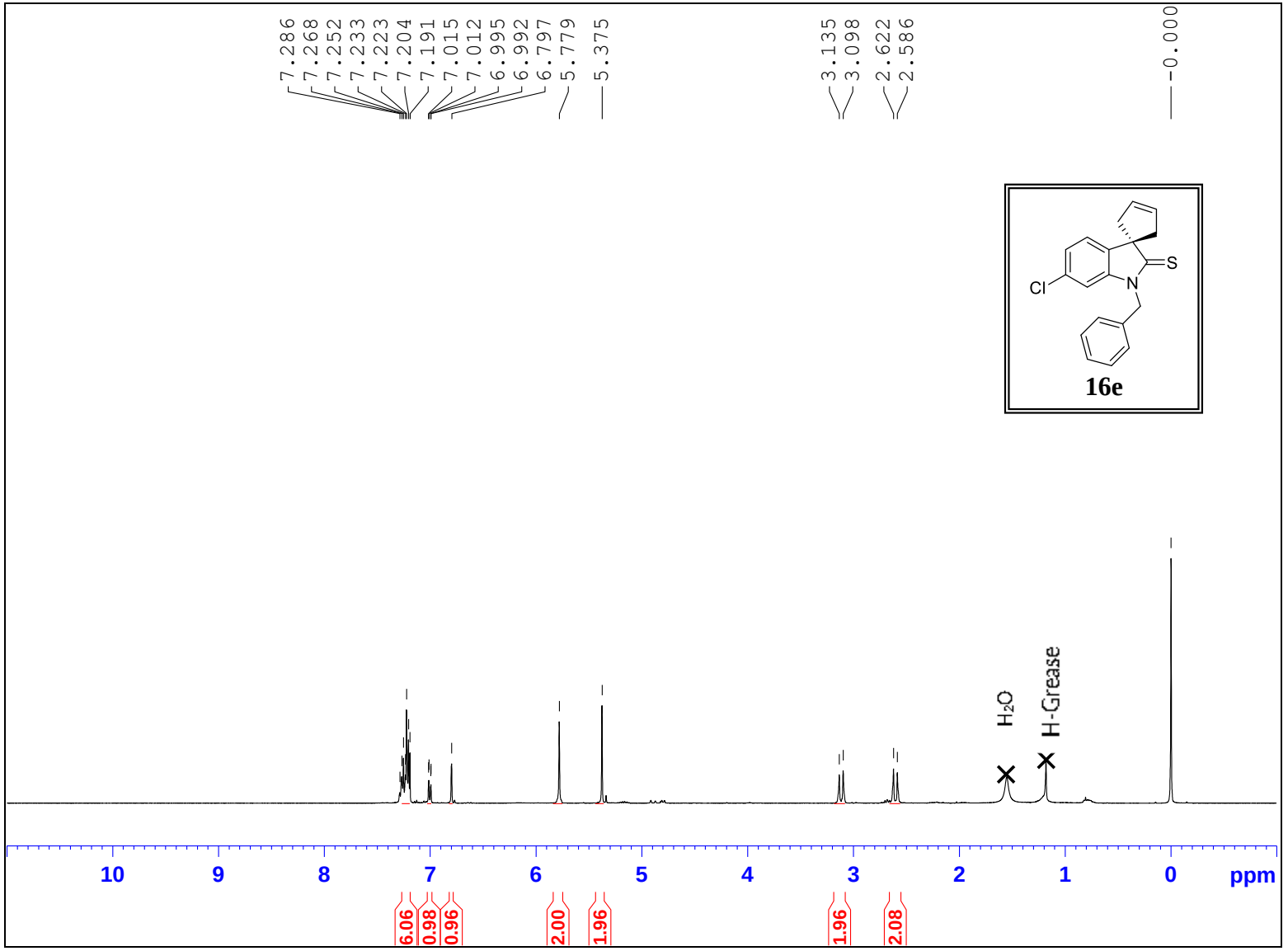
$^{1}$H NMR for compound **16d** (400 MHz, $CDCl_3$)



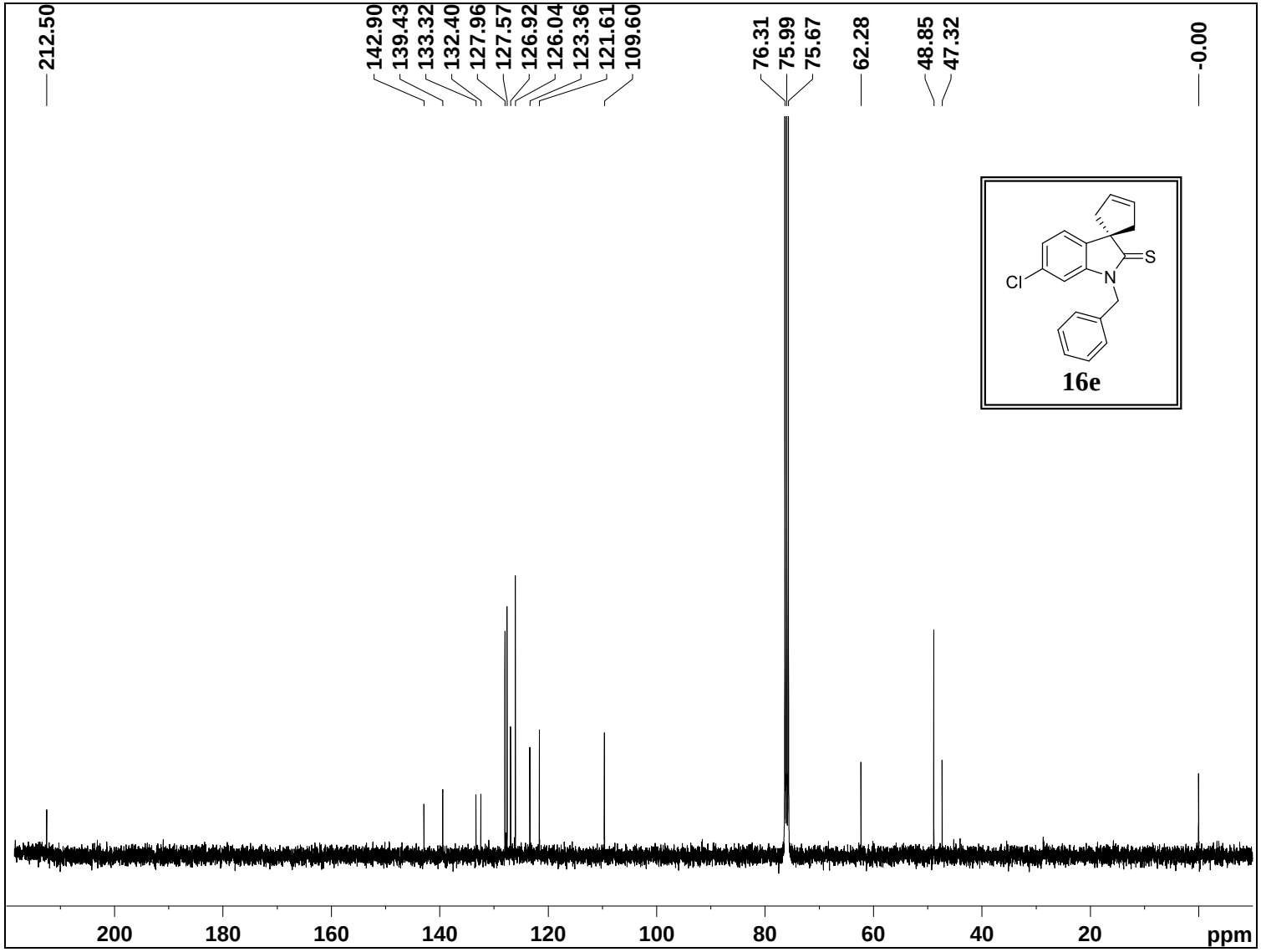
$^{13}C$ NMR for compound **16d** ($101$ MHz, $CDCl_3$)



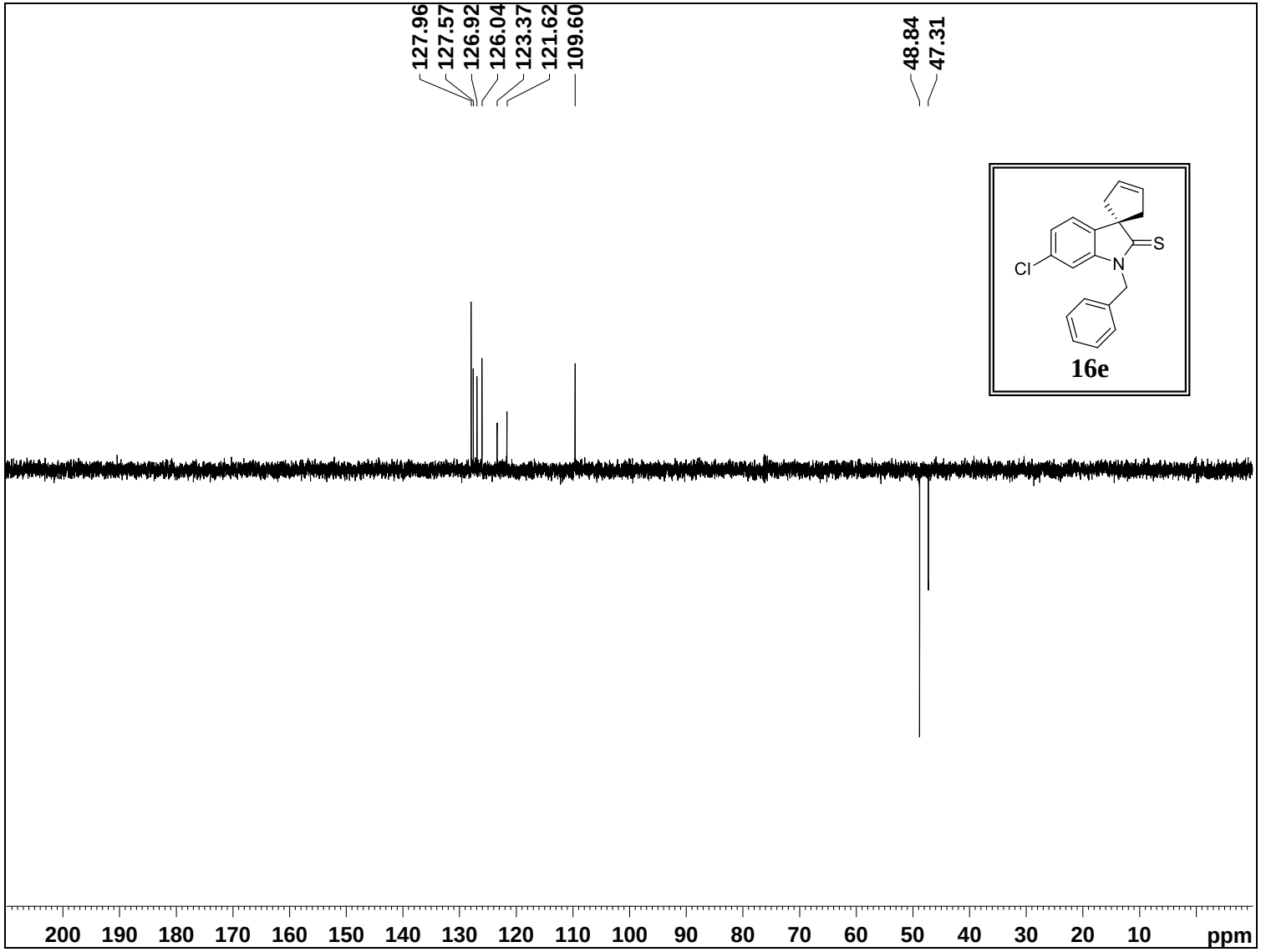
$^{1}$H NMR for compound **16e** (400 MHz, $CDCl_3$)



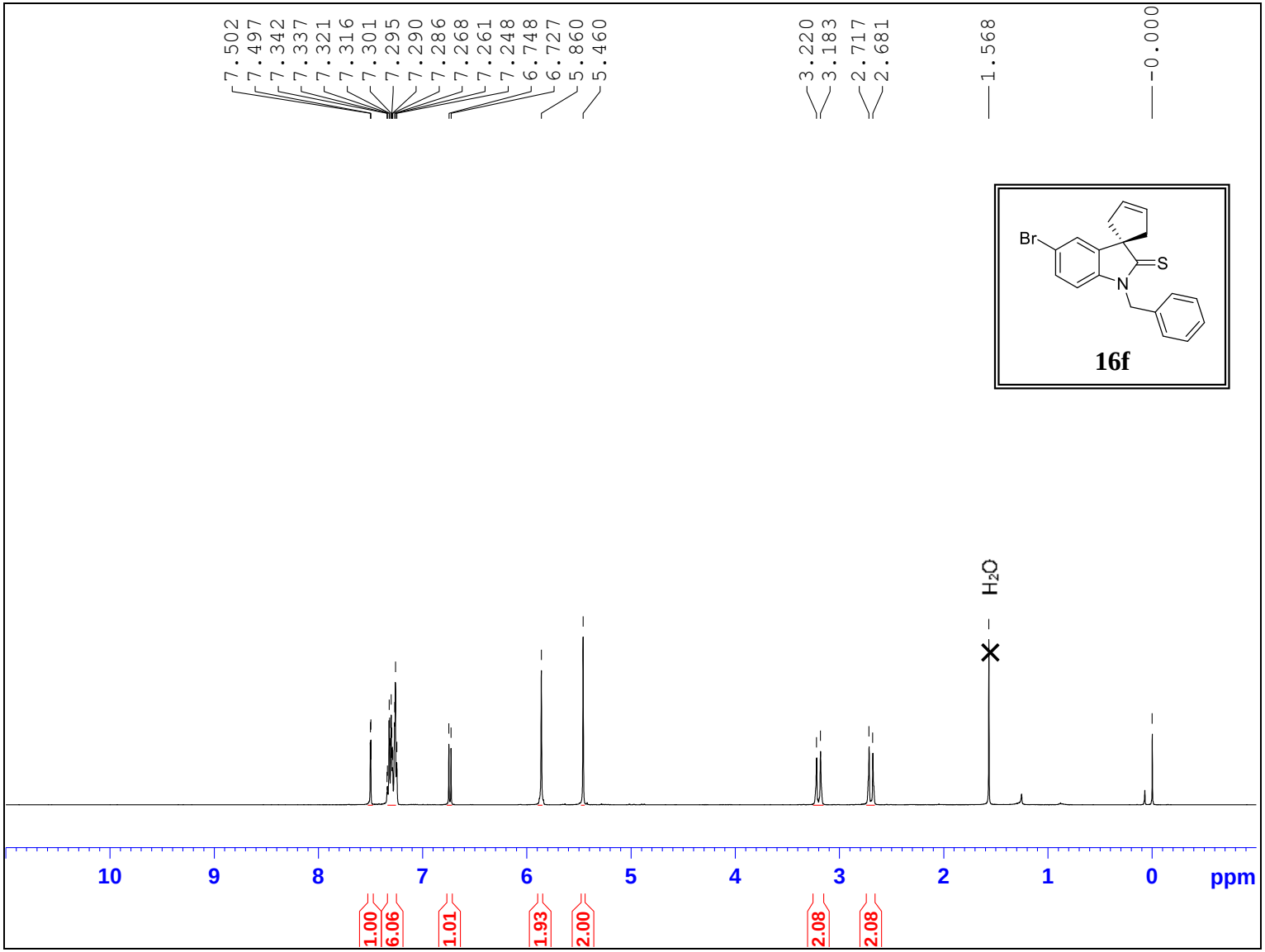
$^{13}C$ NMR for compound **16e** (101 MHz, $CDCl_3$)



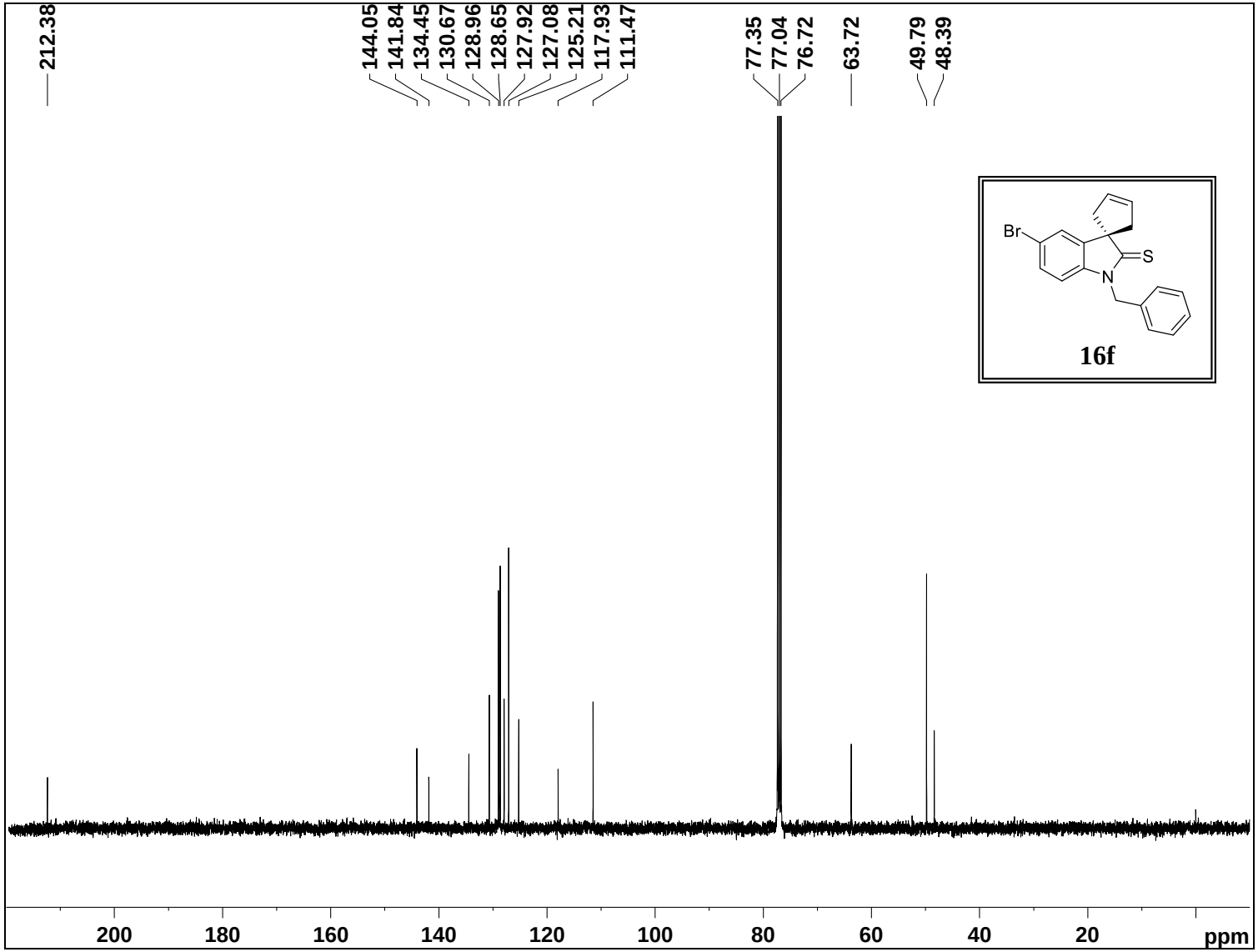
DEPT-135 NMR for compound **16e** (101 MHz, $CDCl_3$)



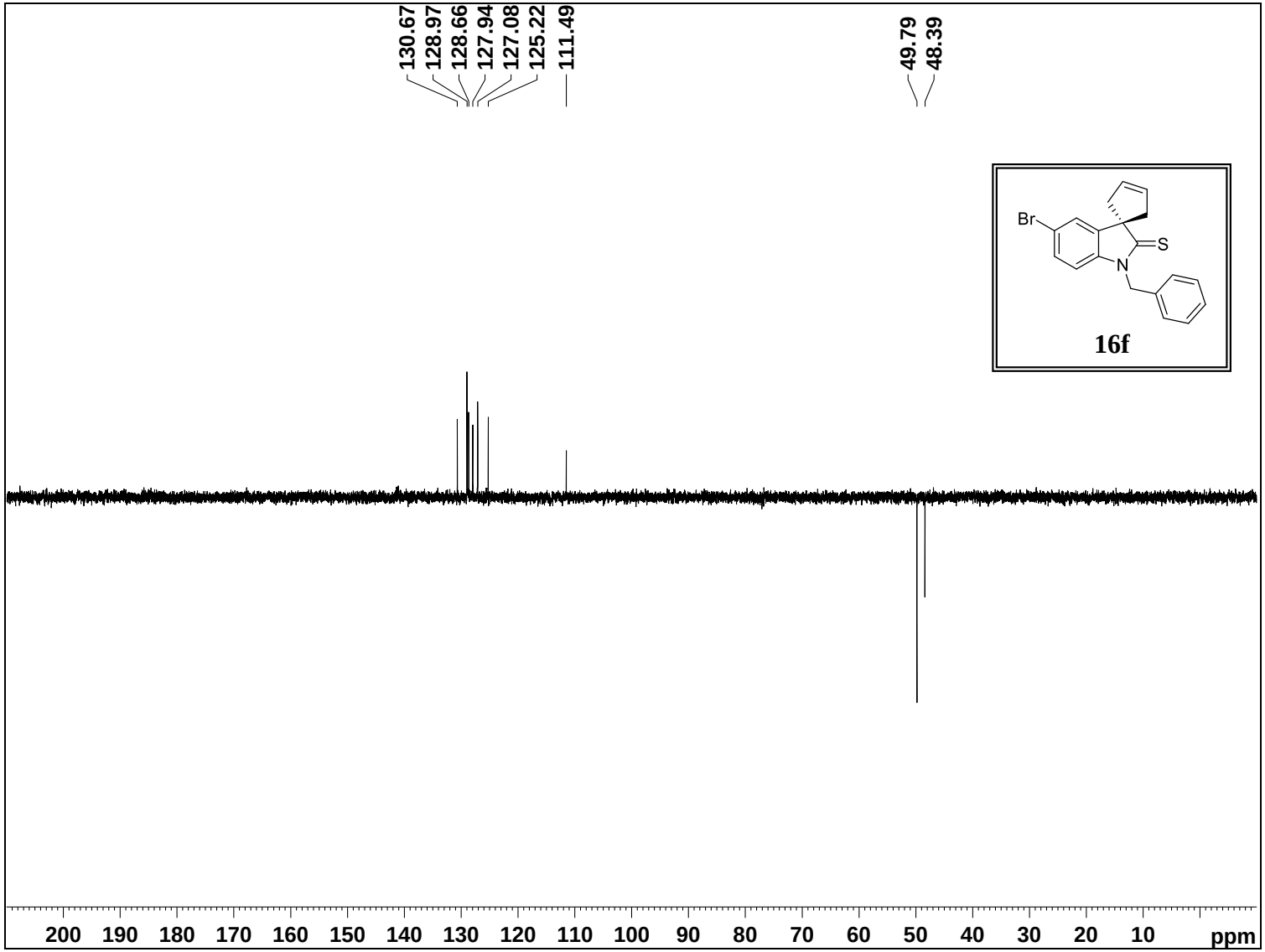
$^{1}$H NMR for compound **16f** (400 MHz, $CDCl_3$)



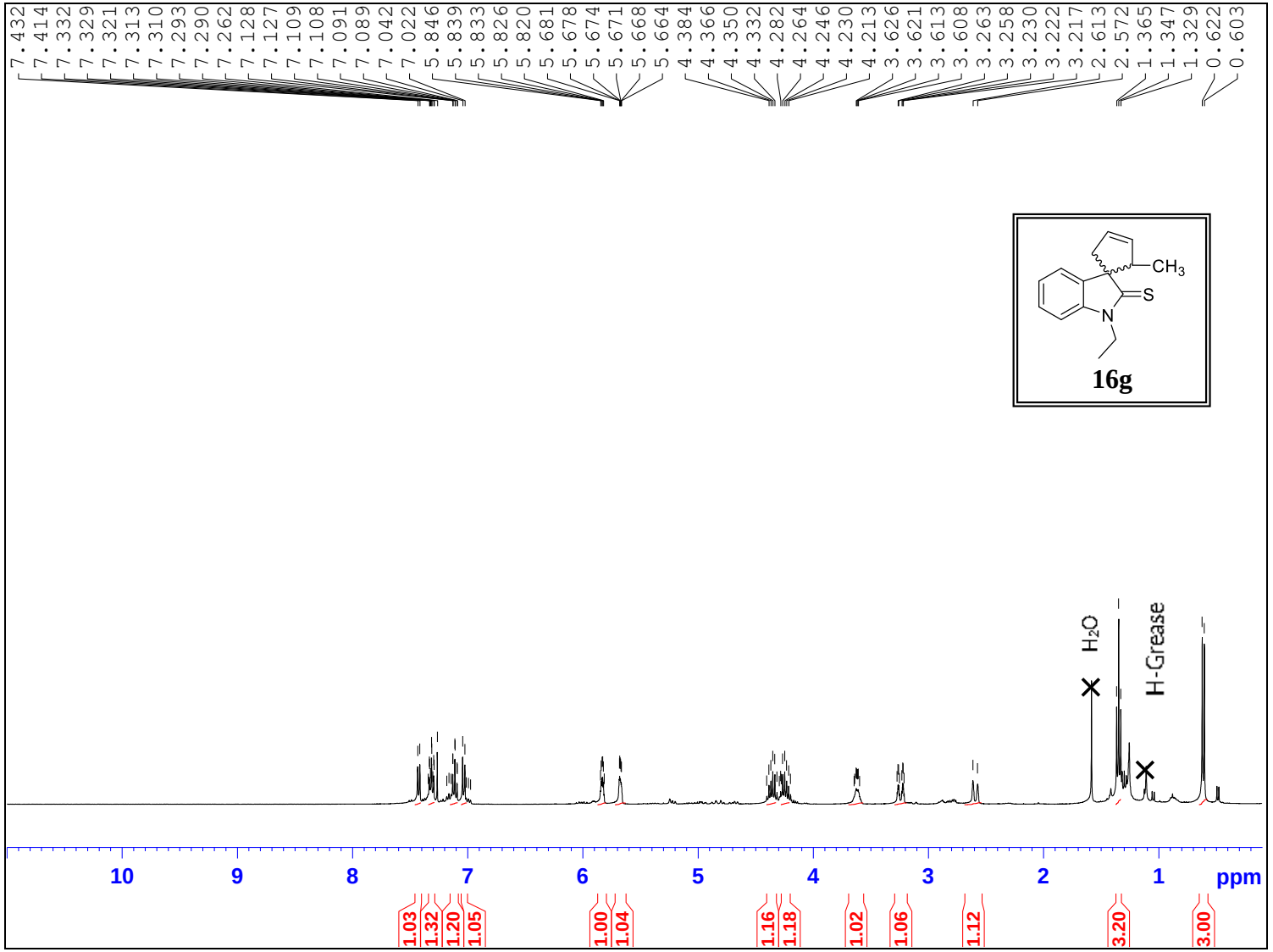
$^{13}C$ NMR for compound **16f** (101 MHz, $CDCl_3$)



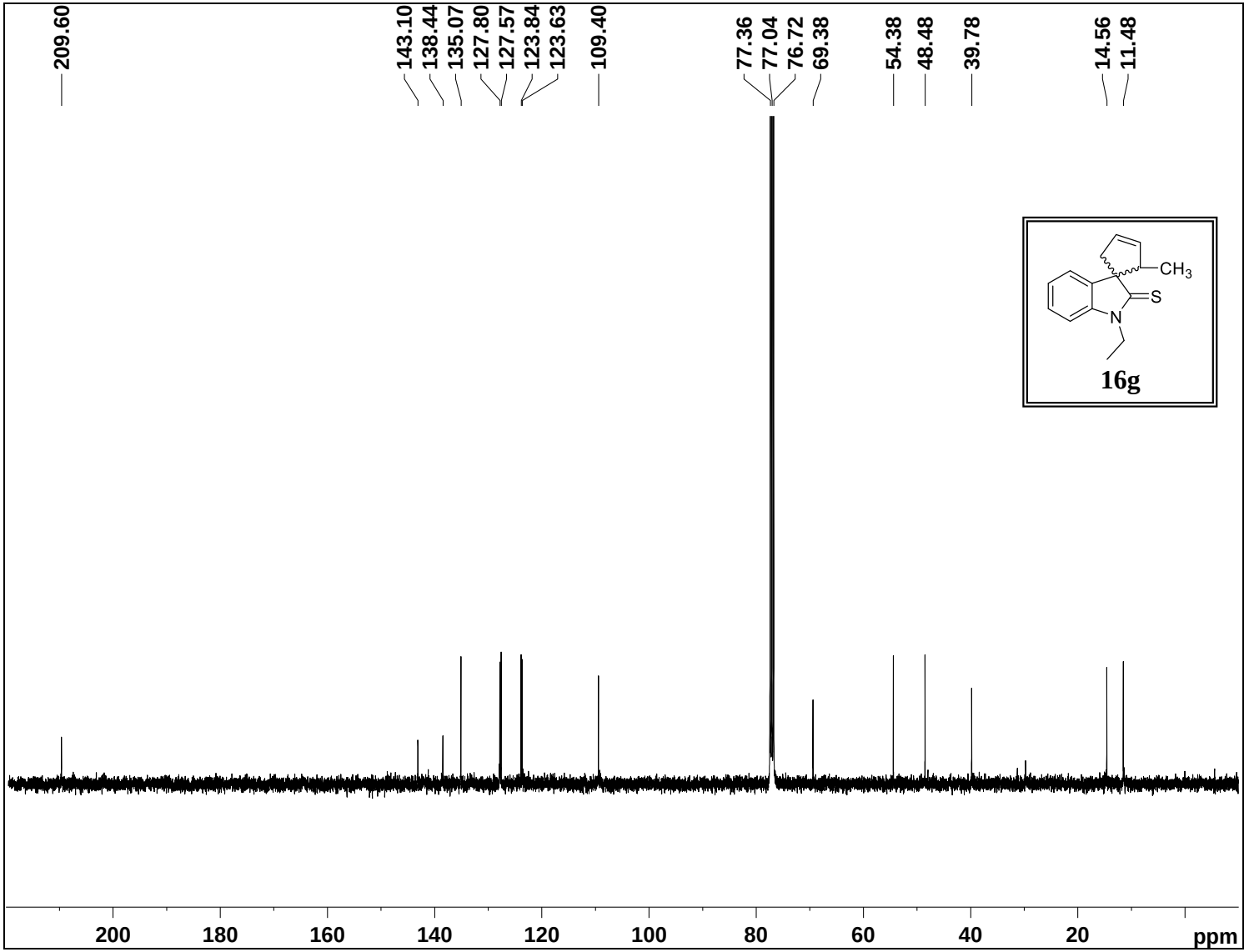
DEPT-135 NMR for compound **16f** (101 MHz, $CDCl_3$)



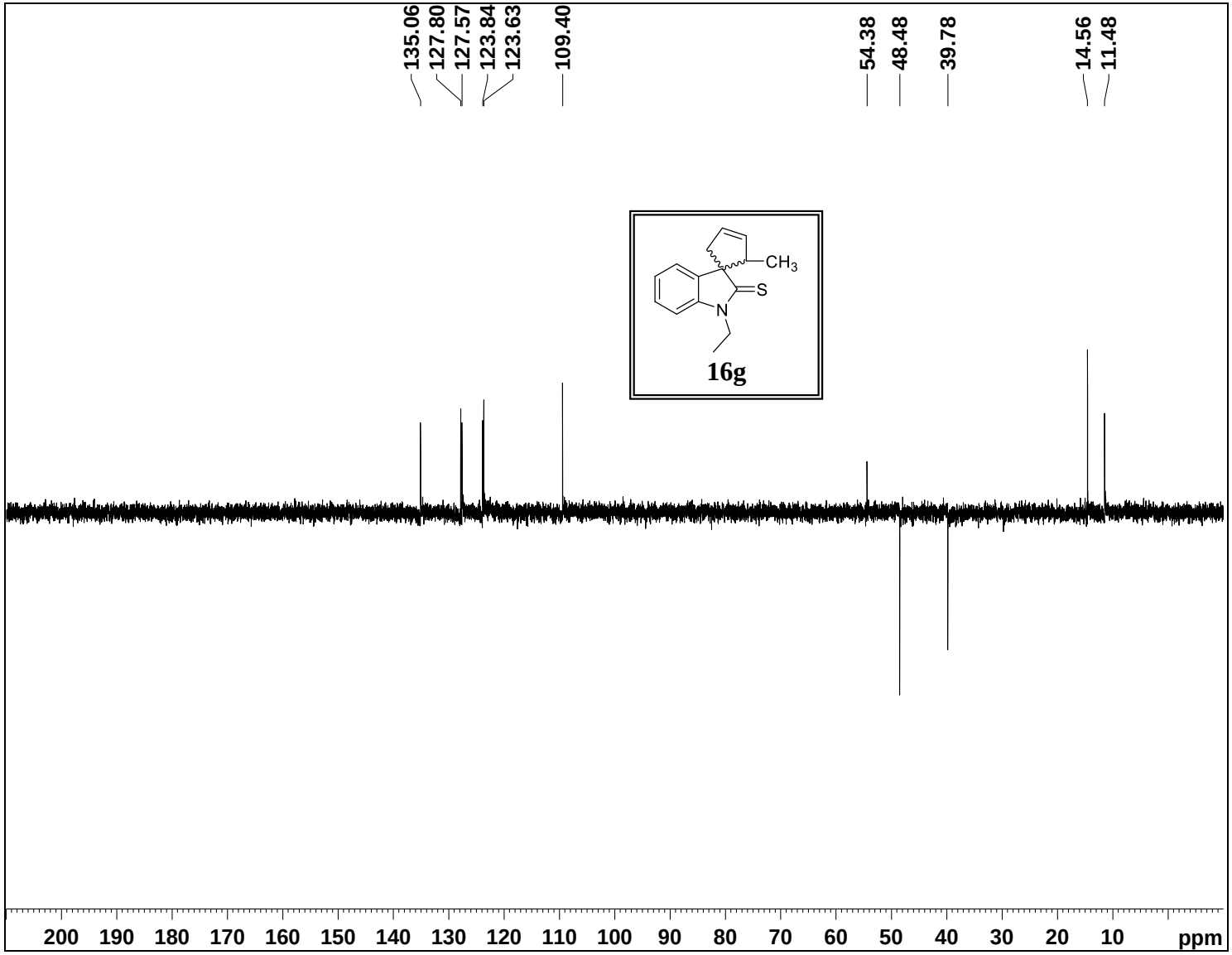
$^{1}$H NMR for compound **16g** (400 MHz, $CDCl_3$)



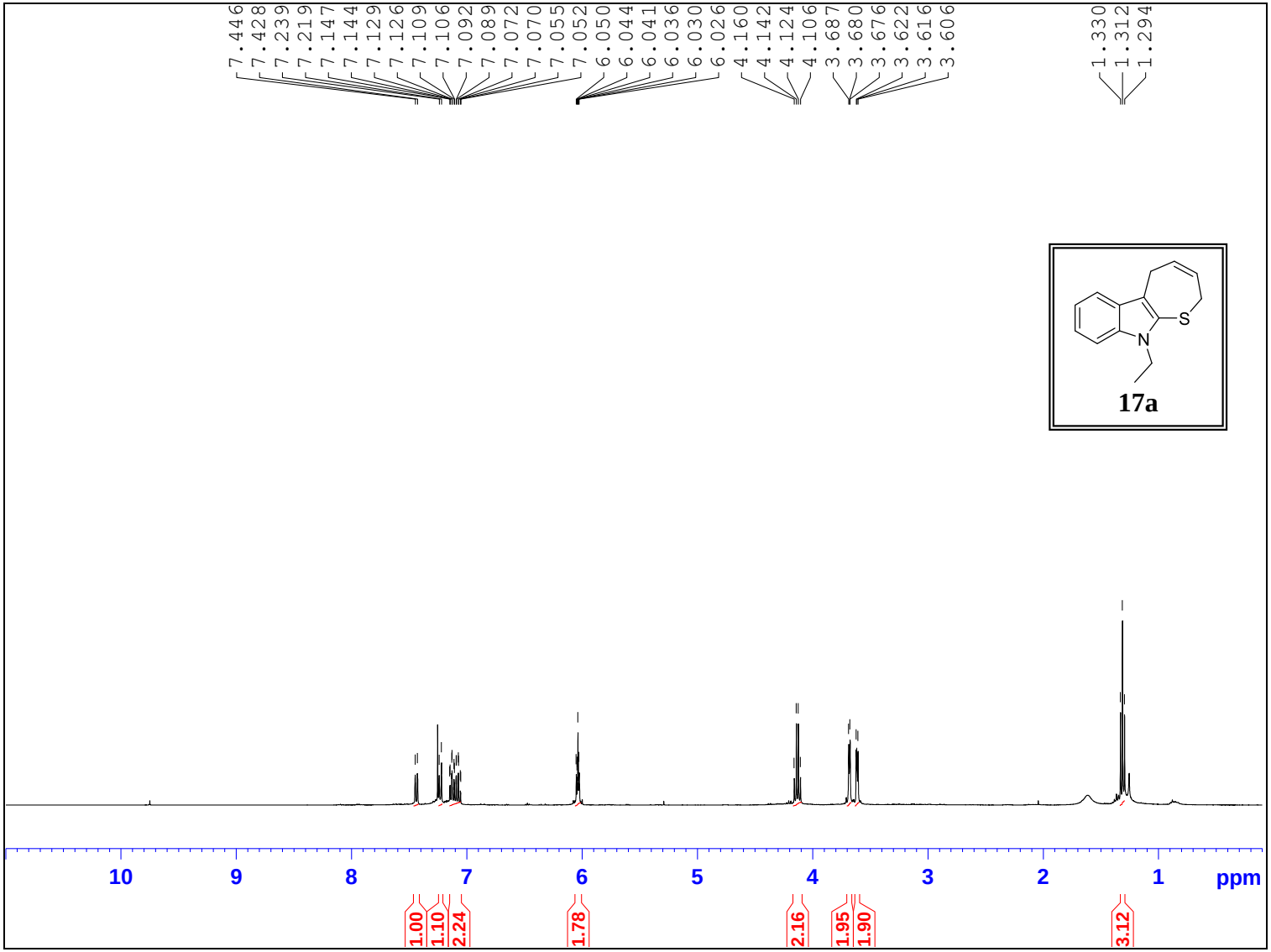
$^{13}C$ NMR for compound **16g** (101 MHz, $CDCl_3$)



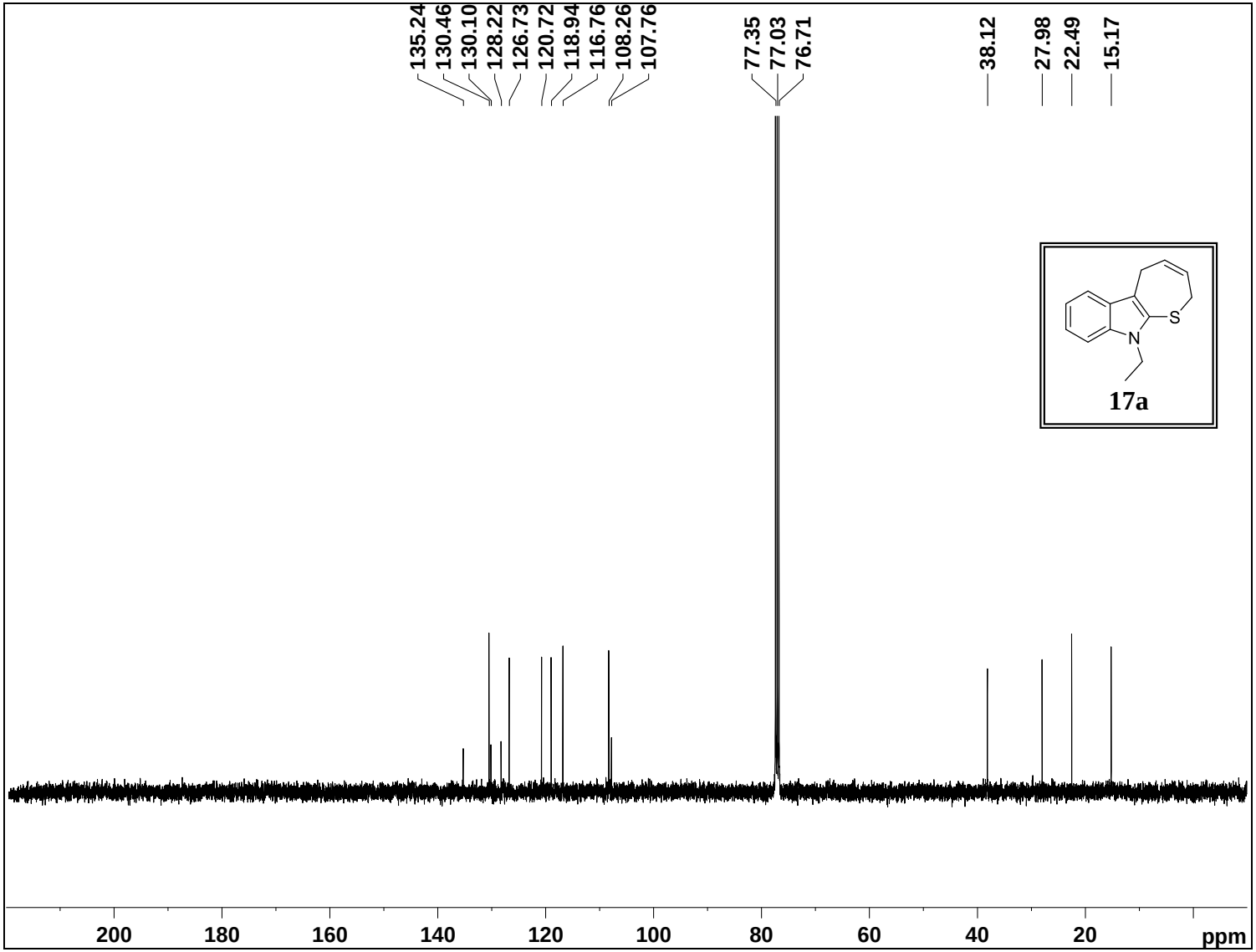
DEPT-135 NMR for compound **16g** (101 MHz, $CDCl_3$)



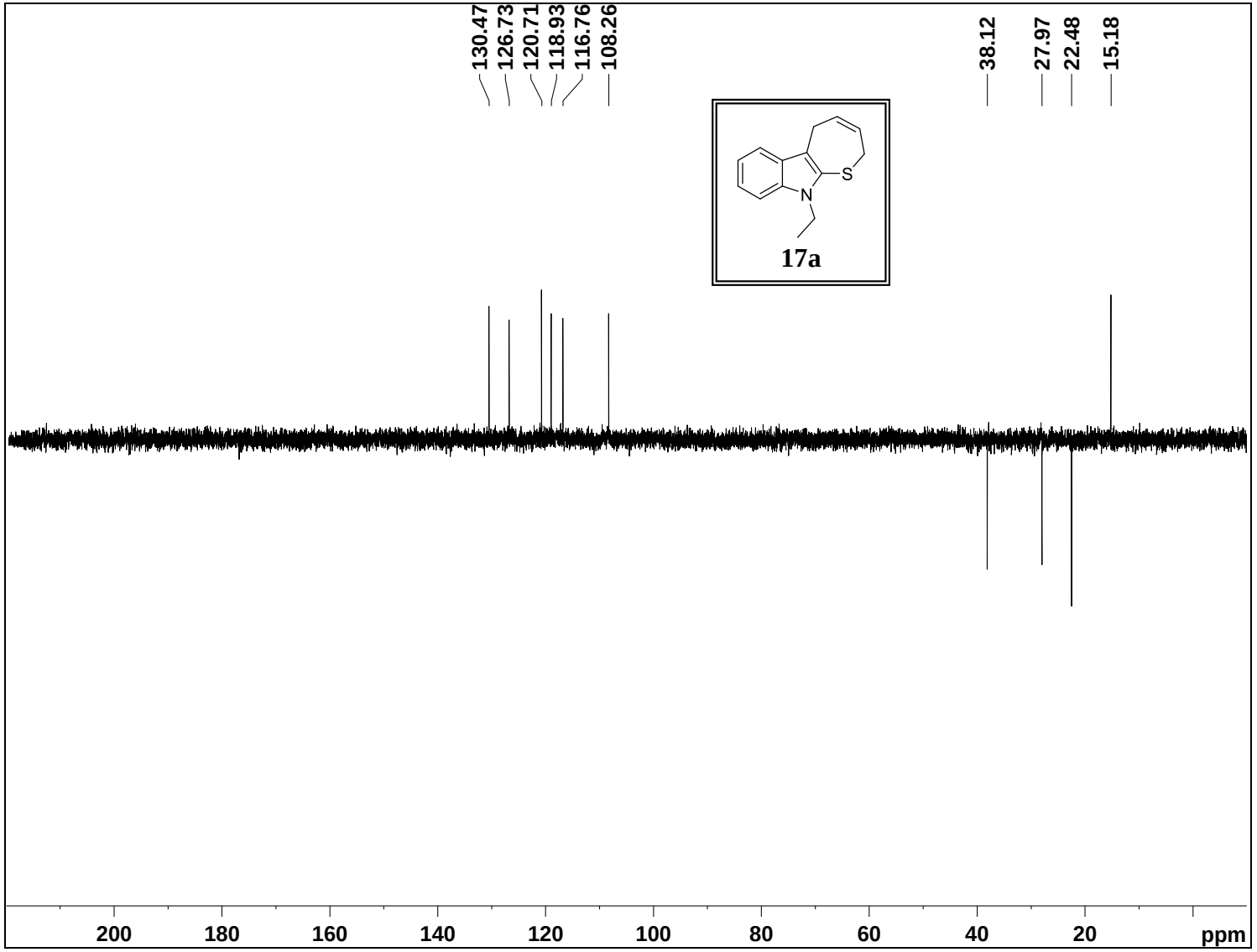
$^{1}$H NMR for compound **17a** (400 MHz, $CDCl_3$)



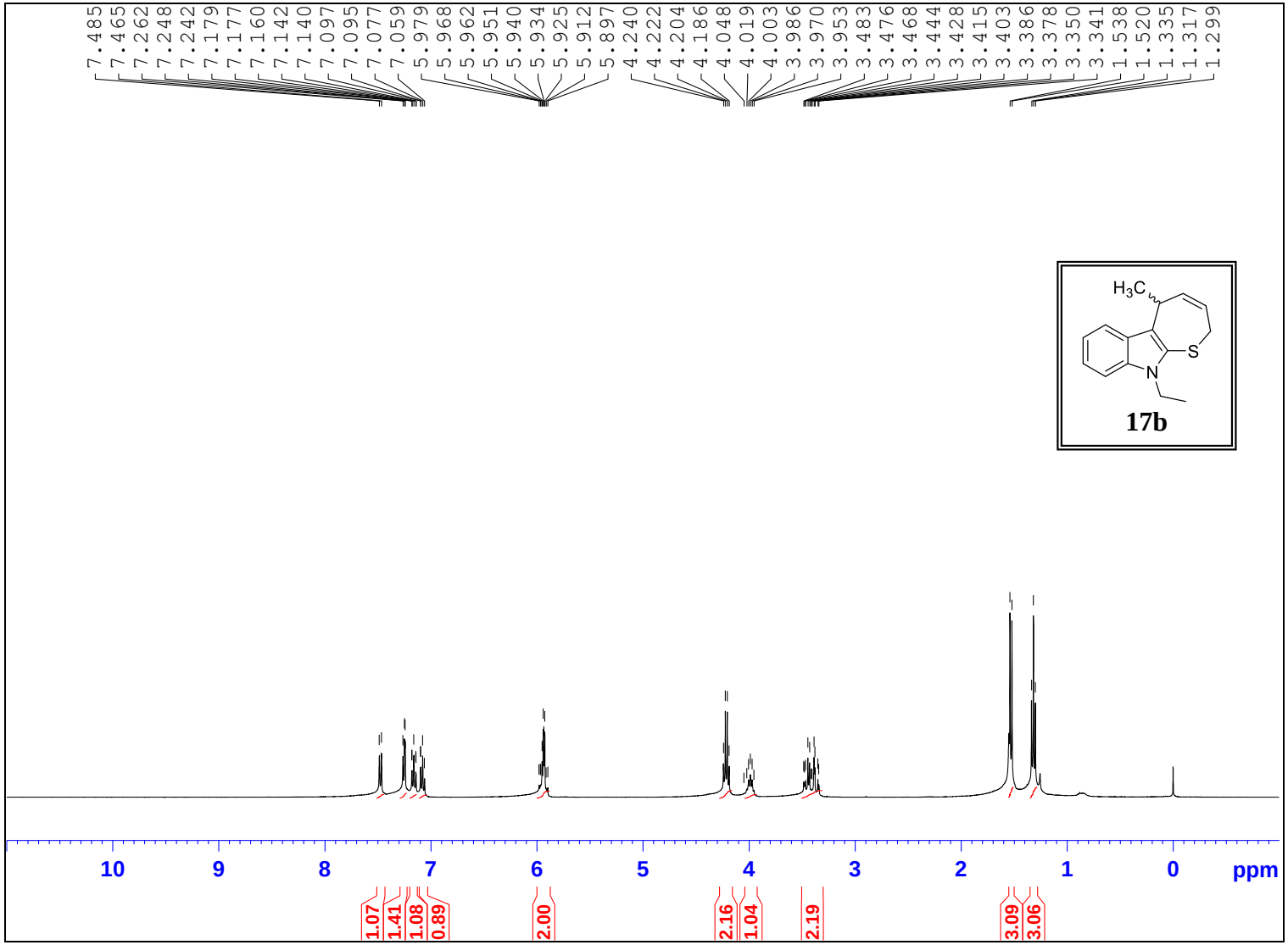
$^{13}C$ NMR for compound **17a** ($101$ MHz, $CDCl_3$)



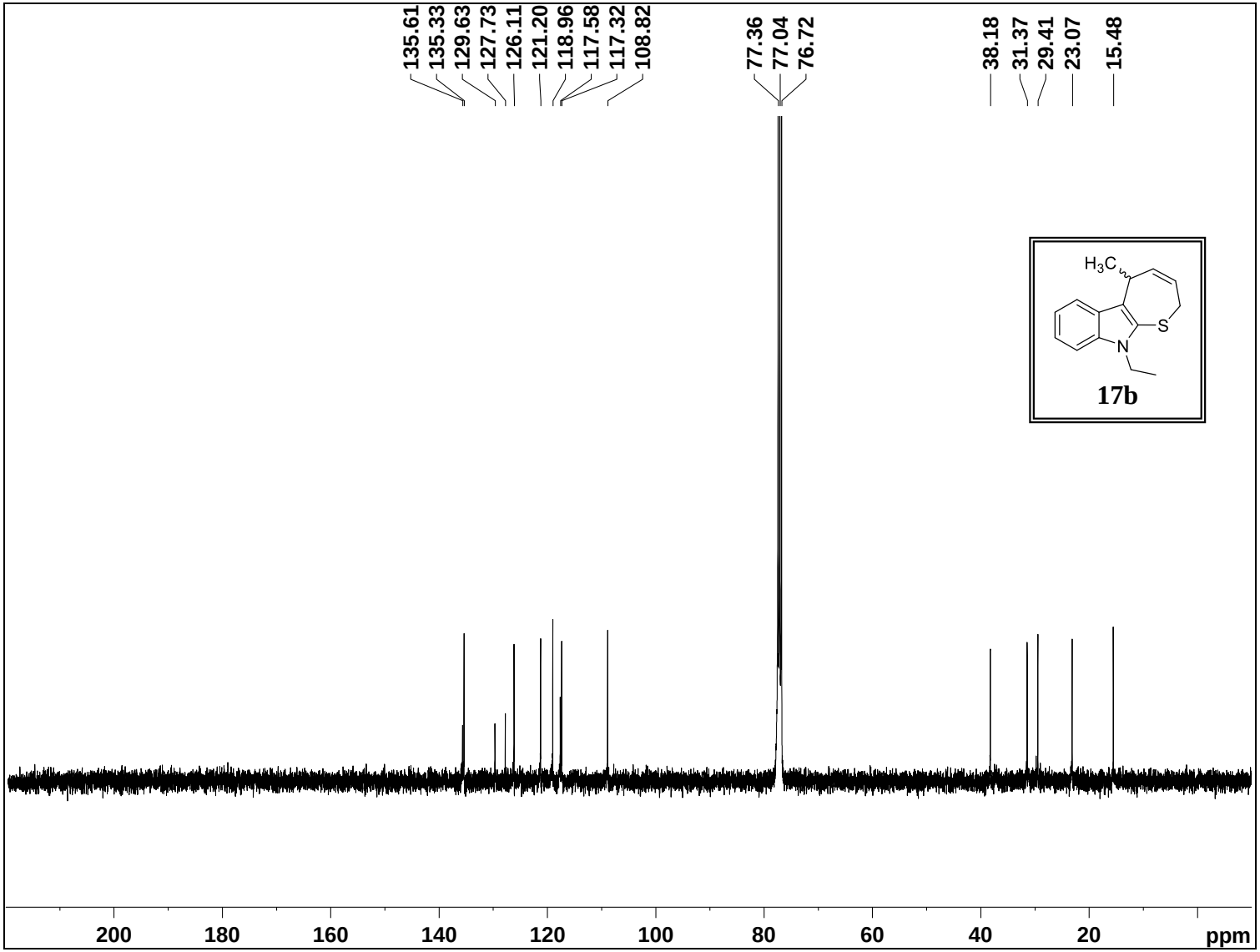
DEPT-135 NMR for compound **17a** (101 MHz, $CDCl_3$)



$^{1}$H NMR for compound **17b** (400 MHz, $CDCl_3$)



$^{13}C$ NMR for compound **17b** ($101$ MHz, $CDCl_3$)



DEPT-135 NMR for compound **17b** (101 MHz, $CDCl_3$)