Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information

On-water synthesis of 3,6-dihydro-2*H*-thiopyrans: Doyle-Kirmse reaction induced by blue-LED and ring-closing metathesis

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1. General information

The thin-layer chromatography was performed on silica 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. Unless otherwise stated, the Hexanes-EtOAc mixture was used as the eluent for the elution process. All air and moisture-sensitive reactions were carried out in oven-dried glassware under positive argon or nitrogen gas pressure using standard gas-tight syringes and septa with magnetic stirring. Grubbs' catalysts were purchased from commercial suppliers and used as provided.

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. ^{1}H, $^{13}C\{^{1}H\}$, $^{13}C\{^{1}H\}$ DEPT-135, [^{1}H, ^{1}H] COSY, [^{1}H, $^{13}C\{^{1}H\}$] HSQC, [^{1}H, $^{13}C\{^{1}H\}$] HMBC, [^{1}H, ^{1}H] NOESY, and 1D NOE NMR spectra were obtained on a 400 MHz Bruker Avance III 400 NMR spectrometer in the deuterated solvents indicated. Data are reported in the following order: Chemical shifts (δ) are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard; multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), td (triplet of doublets), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), ABq (AB quartet); coupling constants (*J*) are in Hertz (Hz). High-resolution mass analyses were performed using the electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. Optical rotations were determined on a JASCO P-2000 polarimeter and reported as follows: $[\alpha]_D^T$ (*c* g/100 mL, solvent). The diastereomeric ratios (*dr*) were determined from ^{1}H NMR.

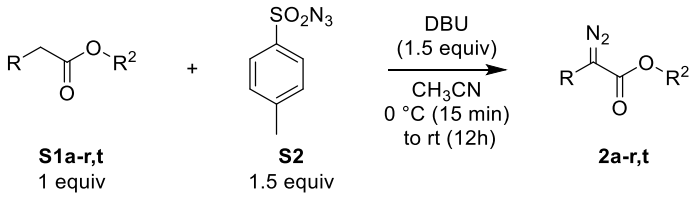
Two 470 nm LED lights are the light source used in the experiment, and the reaction vessel is between the two lights (the distance from the vessel to each light is about 10 cm). The irradiation intensity is ca. $12 Wm^{-2}$. The irradiation vessels used in the reaction are all borosilicate glass vials (screw cap). No filter is used in all cases.

2. Important safety notes

Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling diazoalkanes during this work, yet the reader should be aware of the described diazo compounds' carcinogenicity and explosiveness. Generally, sulfur analogues are foul-smell in nature, so all the sulfur reactions are carried out inside the fume cupboard. Any reactions described in this work should not be performed without strict risk assessment and proper safety precautions.

3. General synthetic procedure

3.1. General procedure for the preparation of diazoacetates 2a-r,t[1]

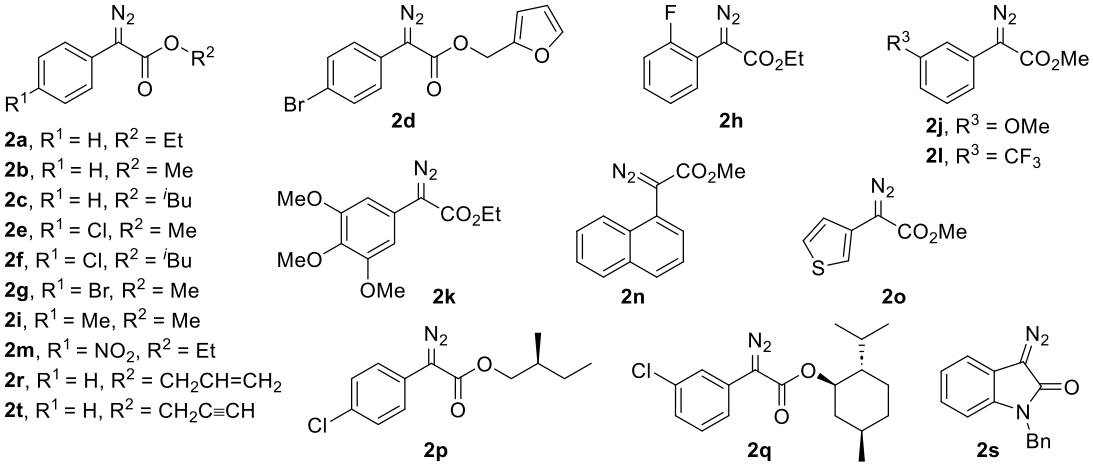


In an oven-dried round bottom flask, the appropriate precursors **S1a-r**,**t** (1 equiv) and *p*-toluenesulfonylazide **S2** (1.5 equiv) were dissolved in anhydrous acetonitrile and cooled to 0 ^{o}C under argon atmosphere. 1,8-Diazabicyclo(5.4.0)undec-7-ene (1.5 equiv) was added at once to a stirred mixture. After 15 minutes, the ice bath was removed and stirred overnight under the argon atmosphere. The reaction was quenched with saturated NH_4Cl and water. The layer was extracted with diethyl ether (3 x 20 mL) and the combined organics were washed with brine (3 x 10 mL), and dried over anhydrous $NaSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on neutral alumina, (Hexanes:EtOAc = 19:1) to give diazoacetates **2a-r**,**t** respectively (Table S1).

3.2. Preparation of diazoamide 2s

The diazoamide **2s** was prepared according to the literature.[2]

Table S1. Diazo compounds **2a-t**

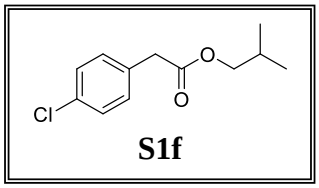


Diazo compounds: **2a-t** were prepared according to literature procedures. The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those previously reported.

The reports are (**2a,b,c,e,g,i,r**),[1] (**2d**),[3] (**2h,j**),[4] (**2k**),[5] (**2l**),[6] (**2m,n,o**),[7] (**2s**),[2] (**2t**).[8]

2-Methylpropyl (4-chlorophenyl)acetate (S1f)

(Spectra)



S1f

Yield 95%, colourless oil; R_f = 0.60 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2963, 1732, 1493, 1247, 1147, 1092, 1008, 806 cm^{-1}.

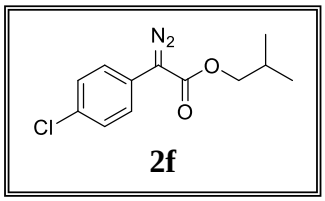
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.27-7.24 (m, 2H), 3.91 (d, J = 6.8 Hz, 2H), 3.63 (s, 2H), 2.00-1.90 (m, 1H), 0.93 (d, J = 6.8 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 133.0, 132.7, 130.7, 128.7, 71.1, 40.8, 27.7, 19.0 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{15}ClO_2+H]^+$ 227.0839; Found: 227.0818.

2-Methylpropyl (4-chlorophenyl)(diazo)acetate (2f)

(Spectra)



2f

Yield 89%, yellowish oil; R_f = 0.62 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2963, 2083, 1700, 1493, 1341, 1277, 1240, 1156, 1095, 1033, 821, 739 cm^{-1}.

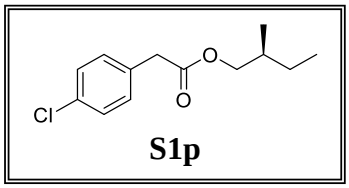
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H), 7.23-7.21 (m, 2H), 3.95 (d, J = 6.4 Hz, 2H), 1.95-1.85 (m, 1H), 0.87 (d, J = 6.8 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 131.3, 129.1, 125.0, 124.3, 71.1, 63.1, 27.9, 19.0 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{13}ClN_2O_2+H]^+$ 253.0744; Found: 253.0728.

(2*S*)-2-Methylbutyl (4-chlorophenyl)acetate (S1p)

(Spectra)



S1p

Yield 95%, colourless oil; R_f = 0.62 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{26}$ = +3.7 (*c* 0.388, $CHCl_3$).

IR (neat): ν_{max} = 2964, 1733, 1493, 1462, 1334, 1250, 1148, 1092, 1010, 807 cm^{-1}.

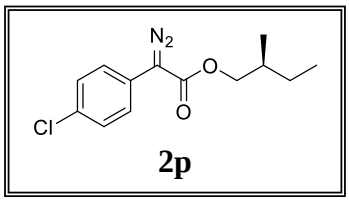
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.17 (m, 2H), 7.13-7.11 (m, 2H), 3.91-3.86 (m, 1H), 3.81-3.77 (m, 1H), 3.49 (s, 2H), 1.63-1.55 (m, 1H), 1.34-1.23 (m, 1H), 1.11-1.00 (m, 1H), 0.80-0.76 (m, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.2, 133.0, 132.7, 130.7, 128.7, 69.6, 40.8, 34.1, 26.0, 16.4 11.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{17}ClO_2+H]^+$ 241.0995; Found: 241.1001.

(2*S*)-2-Methylbutyl (4-chlorophenyl)(diazo)acetate (2p)

(Spectra)



2p

Yield 92%, yellowish oil; R_f = 0.70 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{26}$ = +4.3 (*c* 0.393, $CHCl_3$).

IR (neat): ν_{max} = 2964, 2085, 1700, 1492, 1462, 1341, 1276, 1239, 1157, 1093, 1034, 1008, 825, 739 cm^{-1}.

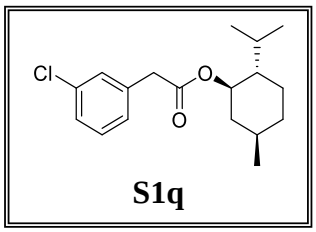
^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H), 7.24-7.21 (m, 2H), 4.08-4.04 (m, 1H), 3.99-3.95 (m, 1H), 1.74-1.62 (m, 1H), 1.41-1.31 (m, 1H), 1.19-1.08 (m, 1H), 0.87-0.82 (m, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.9, 131.3, 129.1, 125.0, 124.3, 69.6, 63.1, 34.3, 26.0, 16.4 11.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{15}ClN_2O_2+H]^+$ 267.0900; Found: 267.0921.

(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl (3-chlorophenyl)acetate (S1q)

(Spectra)



S1q

Yield 94%, colourless oil; R_f = 0.74 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{27}$ = -40.5 (*c* 0.55, $CHCl_3$).

IR (neat): ν_{max} = 2954, 1730, 1457, 1252, 1149, 1090, 986, 768, 686 cm^{-1}.

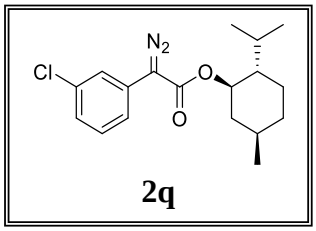
^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.27-7.26 (m, 2H), 7.20-7.18 (m, 1H), 4.71 (td, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 3.60 (s, 2H), 2.04-1.99 (m, 1H), 1.82-1.75 (m, 1H), 1.74-1.66 (m, 2H), 1.57-1.45 (m, 1H), 1.44-1.36 (m, 1H), 1.12-0.88 (m, 9H), 0.73 (d, *J* = 6.8 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.5, 136.3, 134.3, 129.7, 129.4, 127.4, 127.2, 75.0, 47.0, 41.4, 40.8, 34.2, 31.4, 26.2, 23.4, 22.0, 20.7, 16.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{18}H_{25}ClO_2+H]^+$ 309.1621; Found: 309.1618.

(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl (3-chlorophenyl)(diazo)acetate (2q)

(Spectra)



2q

Yield 91%, yellowish oil; R_f = 0.76 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{27}$ = -65.2 (*c* 0.42, $CHCl_3$).

IR (neat): ν_{max} = 2954, 2086, 1698, 1594, 1479, 1343, 1281, 1241, 1163, 1031, 778, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.61 (m, 1H), 7.38-7.30 (m, 2H), 7.18-7.16 (m, 1H), 4.91 (td, J_1 = 10.8 Hz, J_2 = 4.4 Hz, 1H), 2.17-2.12 (m, 1H), 1.98-1.91 (m, 1H), 1.78-1.73 (m, 2H), 1.62-1.45 (m, 2H), 1.20-1.06 (m, 2H), 0.98-0.95 (m, 7H), 0.85 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 135.0, 130.0, 128.1, 125.6, 123.7, 121.5, 75.4, 63.3, 47.1, 41.3, 34.2, 31.5, 26.6, 23.7, 22.0, 20.7, 16.6 ppm.

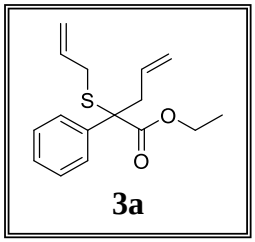
HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{18}H_{23}ClN_2O_2+H]^+$ 335.1526; Found: 335.1519.

4. General procedure for the synthesis of dienes 3 *via* Doyle-Kirmse reaction

The allyl sulfide (purchased from a commercial supplier and used as such) **1** (1.5 equiv) and a solution of diazo compounds **2** (0.5 mmol) in deionized H_2O (2 mL) were taken in a 5 mL screw cap vial. Then it was irradiated under 12W blue LEDs. The colour observed from pale yellowish/orange to colourless was an indication for the completion of the reaction. After the completion of reaction, the mixture was transferred to the separating funnel, 10 mL of CH_2Cl_2 was added to the mixture and the organic layers were collected (3 times), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was subjected to flash chromatography (silica gel 230-400 mesh, Hexanes:EtOAc = 19:1) to furnish the respective pure dienes **3a-u**.

Ethyl 2-phenyl-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3a)[9]

(Spectra)



3a

Yield 88%, colourless oil; R_f = 0.62 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2924, 2854, 1726, 1639, 1446, 1216, 1095, 1028, 919, 806, 701 cm^{-1}.

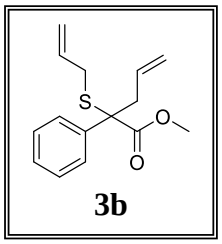
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.36-7.33 (m, 2H), 7.28-7.25 (m, 1H), 5.79-5.65 (m, 2H), 5.14-5.09 (m, 1H), 5.04-4.98 (m, 3H), 4.27 (q, J = 7.2 Hz, 2H), 3.07 (ddd, J_1 = 59.6 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.90-2.88 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 139.1, 133.3, 132.9, 128.2, 127.8, 127.4, 118.8, 117.9, 61.6, 60.8, 43.3, 33.6, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $[C_{16}H_{20}O_2S+Na]^+$ 299.1082; Found: 299.1075.

Methyl 2-phenyl-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3b)[10]

(**Spectra**)



3b

Yield 90%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2982, 1726, 1638, 1437, 1214, 1122, 991, 918, 698 cm^{-1}.

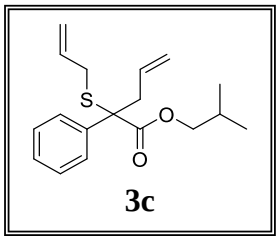
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.32 (m, 2H), 7.27-7.23 (m, 2H), 7.19-7.15 (m, 1H), 5.70-5.56 (m, 2H), 5.05-5.01 (m, 1H), 4.95-4.89 (m, 3H), 3.68 (s, 3H), 2.98 (ddd, J_1 = 51.2 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.83-2.81 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 139.0, 133.2, 132.8, 128.3, 127.8, 127.5, 118.9, 117.9, 60.8, 52.6, 43.2, 33.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{18}O_2S+H]^+$ 263.1106; Found: 263.1118.

2-Methylpropyl 2-phenyl-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3c)

(**Spectra**)



3c

Yield 69%, colourless oil; R_f = 0.64 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2963, 1723, 1638, 1467, 1440, 1210, 991, 917, 752, 699 cm^{-1}.

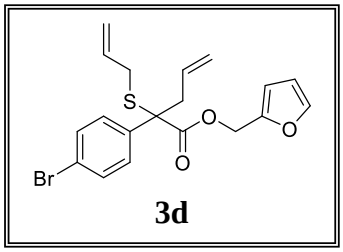
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 7.28-7.24 (m, 2H), 7.20-7.16 (m, 1H), 5.71-5.58 (m, 2H), 5.06-5.02 (m, 1H), 4.96-4.91 (m, 3H), 3.90 (d, J = 6.4 Hz, 2H), 2.99 (ddd, J_1 = 58.0 Hz, J_2 = 12.4 Hz, J_3 = 6.8 Hz, 2H), 2.84 (d, J = 7.2 Hz, 2H), 1.93-1.83 (m, 1H), 0.84-0.82 (m, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 139.1, 133.2, 133.0, 128.2, 127.9, 127.4, 118.7, 117.9, 71.8, 60.9, 43.1, 33.6, 27.8, 19.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{18}H_{24}O_2S+H]^+$ 305.1575; Found: 305.1577.

(Furan-2-yl)methyl 2-(4-bromophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3d)

(Spectra)



3d

Yield 94%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2926, 1728, 1637, 1489, 1204, 1006, 922, 821, 747 cm^{-1}.

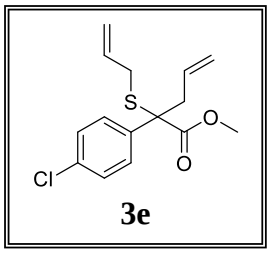
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 3H), 7.19-7.16 (m, 2H), 6.37-6.36 (m, 1H), 6.29-6.28 (m, 1H), 5.65-5.48 (m, 2H), 5.15-5.08 (m, 2H), 5.03-4.83 (m, 4H), 2.92 (ddd, J_1 = 59.2 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.75 (ddd, J_1 = 37.6 Hz, J_2 = 14.4 Hz, J_3 = 7.2 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 149.0, 143.3, 137.8, 132.8, 132.2, 131.3, 129.8, 121.5, 119.4, 118.2, 111.3, 110.7, 60.3, 59.0, 43.3, 33.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{19}BrO_3S+H]^+$ 407.0317; Found: 407.0319.

Methyl 2-(4-chlorophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3e)

(Spectra)



3e

Yield 70%, colourless oil; R_f = 0.60 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2924, 1728, 1639, 1490, 1436, 1218, 1094, 1011, 992, 921, 822 cm^{-1}.

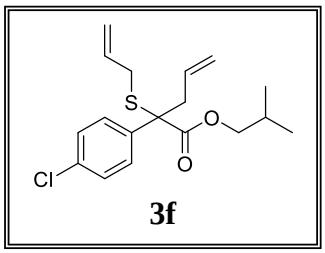
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.25-7.23 (m, 2H), 5.71-5.52 (m, 2H), 5.08-5.03 (m, 1H), 4.98-4.88 (m, 3H), 3.70 (s, 3H), 2.98 (ddd, J_1 = 50.4 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.85-2.72 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 137.5, 133.3, 132.9, 132.4, 129.4, 128.4, 119.2, 118.1, 60.2, 52.7, 43.1, 33.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}ClO_2S+H]^+$ 297.0716; Found: 297.0711.

2-Methylpropyl 2-(4-chlorophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3f)

(Spectra)



3f

Yield 65%, colourless oil; R_f = 0.64 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2963, 1723, 1639, 1490, 1209, 1094, 1003, 918, 821, 767 cm^{-1}.

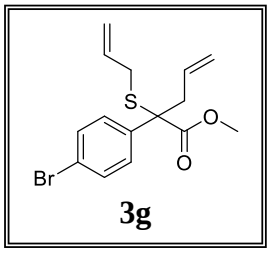
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.25-7.19 (m, 2H), 5.70-5.54 (m, 2H), 5.07-5.02 (m, 1H), 4.98-4.89 (m, 3H), 3.90 (d, J = 6.8 Hz, 2H), 2.98 (ddd, J_1 = 56.4 Hz, J_2 = 12.8 Hz, J_3 = 6.8 Hz, 2H), 2.80 (ddd, J_1 = 26.0 Hz, J_2 = 14.0 Hz, J_3 = 6.8 Hz, 2H), 1.93-1.83 (m, 1H), 0.85-0.83 (m, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 137.7, 133.2, 132.9, 132.5, 129.5, 128.3, 119.1, 118.1, 71.9, 60.3, 43.1, 33.6, 27.8, 19.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{18}H_{23}ClO_2S+H]^+$ 339.1186; Found: 339.1180.

Methyl 2-(4-bromophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3g)

(Spectra)



3g

Yield 78%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2982, 1726, 1638, 1486, 1435, 1214, 1071, 1002, 919, 818, 767 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.25-7.19 (m, 2H), 5.71-5.52 (m, 2H), 5.08-5.03 (m, 1H), 4.99-4.88 (m, 3H), 3.70 (s, 3H), 2.98 (ddd, J_1 = 50.0 Hz, J_2 = 12.4 Hz, J_3 = 6.8 Hz, 2H), 2.78 (ddd, J_1 = 28.0 Hz, J_2 = 14.4 Hz, J_3 = 6.8 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 138.0, 132.9, 132.4, 131.4, 129.7, 121.5, 119.3, 118.2, 60.3, 52.7, 43.1, 33.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{17}BrO_2S+H]^+$ 341.0211; Found: 341.0205.

Ethyl 2-(2-fluorophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3h)

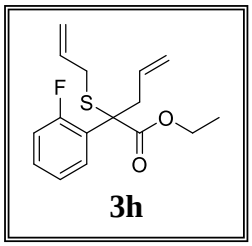
Yield 80%, colourless oil; R_f = 0.62 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2981, 1728, 1639, 1483, 1448, 1227, 1031, 922, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 1H), 7.25-7.19 (m, 1H), 7.11-7.07 (m, 1H), 6.99-

6.93 (m, 1H), 5.77-5.67 (m, 1H), 5.56-5.45 (m, 1H), 5.15-5.10 (m, 1H), 5.03-5.00 (m, 1H), 4.89-4.81 (m, 2H), 4.23-4.12 (m, 2H), 3.10 (ddd, J_1 = 28.8 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.90-2.76 (m, 2H), 1.18 (t, J = 7.2 Hz, 3H) ppm.

(Spectra)



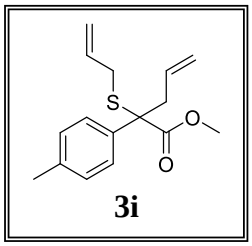
3h

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 171.4, 160.4 (d, $J_{C\text{-}F}$ = 248.1 Hz), 132.8, 132.4, 129.66 (d, $J_{C\text{-}F}$ = 3.5 Hz), 129.48 (d, $J_{C\text{-}F}$ = 8.8 Hz), 126.41 (d, $J_{C\text{-}F}$ = 12.2 Hz), 123.82 (d, $J_{C\text{-}F}$ = 3.1 Hz), 118.8, 118.3, 115.82 (d, $J_{C\text{-}F}$ = 22.8 Hz), 61.7, 56.90 (d, $J_{C\text{-}F}$ = 1.4 Hz), 41.40 (d, $J_{C\text{-}F}$ = 1.5 Hz), 33.4, 14.1 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{16}H_{19}FO_2S+H]^+$ 295.1168; Found: 295.1171.

Methyl 2-(4-methylphenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3i)

(Spectra)



3i

Yield 74%, colourless oil; R_f = 0.60 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2981, 1727, 1638, 1511, 1435, 1216, 1122, 992, 920, 814 cm^{-1}.

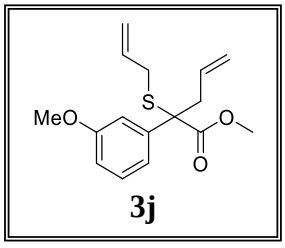
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22-7.18 (m, 2H), 7.09-7.07 (m, 2H), 5.72-5.57 (m, 2H), 5.07-5.02 (m, 1H), 4.97-4.92 (m, 3H), 3.69 (s, 3H), 2.98 (ddd, J_1 = 49.6 Hz, J_2 = 12.8 Hz, J_3 = 6.8 Hz, 2H), 2.82 (d, J = 7.2 Hz, 2H), 2.26 (s, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 172.9, 137.2, 136.0, 133.3, 133.0, 129.0, 127.6, 118.7, 117.8, 60.6, 52.6, 43.2, 33.5, 21.0 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{16}H_{20}O_2S+H]^+$ 277.1262; Found: 277.1255.

Methyl 2-(3-methoxyphenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3j)

(Spectra)



3j

Yield 93%, colourless oil; R_f = 0.51 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2949, 1727, 1637, 1593, 1488, 1431, 1216, 1047, 920, 779, 701 cm^{-1}.

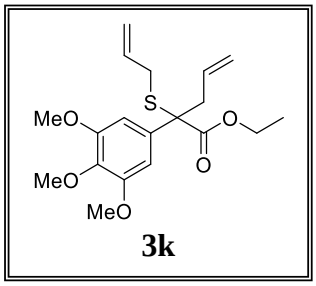
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.16 (m, 1H), 6.93-6.88 (m, 2H), 6.75-6.72 (m, 1H), 5.72-5.57 (m, 2H), 5.07-5.03 (m, 1H), 4.96-4.92 (m, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.00 (ddd, J_1 = 46.4 Hz, J_2 = 12.4 Hz, J_3 = 6.8 Hz, 2H), 2.82 (d, J = 6.8 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7, 159.5, 140.6, 133.2, 132.9, 129.2, 120.1, 118.8, 117.9, 113.9, 112.6, 60.8, 55.3, 52.6, 43.1, 33.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{20}O_3S+H]^+$ 293.1211; Found: 293.1218.

Ethyl 2-[(prop-2-en-1-yl)sulfanyl]-2-(3,4,5-trimethoxyphenyl)pent-4-enoate (3k)

(Spectra)



3k

Yield 79%, colourless oil; R_f = 0.28 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2937, 1723, 1638, 1587, 1507, 1456, 1414, 1238, 1125, 1008, 921, 772 cm^{-1}.

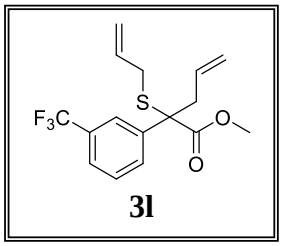
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 2H), 5.85-5.70 (m, 2H), 5.19-5.07 (m, 4H), 4.36-4.24 (m, 2H), 3.89 (s, 3H), 3.88 (s, 6H), 3.14 (ddd, J_1 = 48.0 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.91 (d, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 152.8, 137.3, 134.6, 133.3, 133.0, 118.7, 117.9, 105.3, 61.7, 61.0, 60.9, 56.2, 43.2, 33.7, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{26}O_5S+H]^+$ 367.1579; Found: 367.1563.

Methyl 2-[(prop-2-en-1-yl)sulfanyl]-2-[3-(trifluoromethyl)phenyl]pent-4-enoate (3l)

(Spectra)



3l

Yield 82%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2953, 1730, 1639, 1437, 1327, 1220, 1167, 1126, 1076, 922, 704 cm^{-1}.

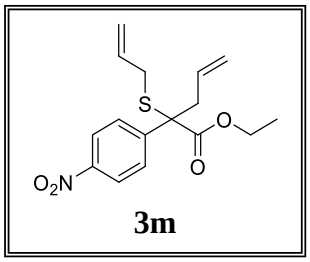
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.54-7.52 (m, 1H), 7.48-7.46 (m, 1H), 7.42-7.38 (m, 1H), 5.70-5.52 (m, 2H), 5.07-5.03 (m, 1H), 4.99-4.86 (m, 3H), 3.73 (s, 3H), 2.98 (ddd, J_1 = 52.0 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.82 (ddd, J_1 = 34.4 Hz, J_2 = 14.0 Hz, J_3 = 7.2 Hz, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.0, 140.1, 132.7, 132.1, 131.6, 131.10-130.14 (q, J_{C-F} = 32.32 Hz), 128.7, 128.09-119.96 (q, J_{C-F} = 273.71 Hz), 124.92-124.80 (q, J_{C-F} = 4.04 Hz), 124.45-124.33 (q, J_{C-F} = 4.04 Hz), 119.5, 118.3, 60.4, 52.8, 43.2, 33.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{17}F_3O_2S+H]^+$ 331.0980; Found: 331.0987.

Ethyl 2-(4-nitrophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3m)

(Spectra)



3m

Yield 72%, colourless oil; R_f = 0.46 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2983, 1727, 1640, 1602, 1523, 1350, 1220, 1114, 1023, 925, 856, 707 cm^{-1}.

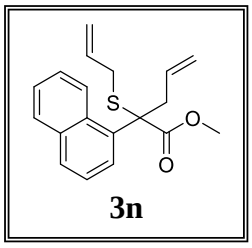
^1H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 7.57-7.55 (m, 2H), 5.70-5.51 (m, 2H), 5.09-4.85 (m, 4H), 4.22 (q, J = 7.2 Hz, 2H), 3.00 (ddd, J_1 = 59.2 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H) 2.90-2.72 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.9, 147.0, 146.5, 132.5, 131.8, 129.2, 123.3, 119.8, 118.5, 62.1, 60.3, 43.2, 33.7, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{19}NO_4S+H]^+$ 322.1113; Found: 322.1118.

Methyl 2-(naphthalen-1-yl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3n)

(Spectra)



3n

Yield 67%, colourless oil; R_f = 0.51 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2980, 1722, 1637, 1433, 1213, 1126, 1036, 990, 919, 778 cm^{-1}.

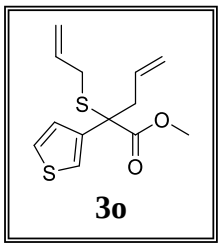
^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.72 (m, 4H), 7.41-7.17 (m, 3H), 5.71-5.52 (m, 2H), 5.07-5.02 (m, 1H), 4.97-4.87 (m, 3H), 3.57 (s, 3H), 3.13 (ddd, J_1 = 39.6 Hz, J_2 = 14.4 Hz, J_3 = 6.0 Hz, 2H), 2.96 (ddd, J_1 = 35.6 Hz, J_2 = 13.2 Hz, J_3 = 7.2 Hz, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.7, 134.5, 133.7, 133.2, 132.7, 130.9, 129.5, 129.2, 126.4, 126.2, 125.5, 124.7, 123.8, 118.5, 118.1, 60.4, 52.7, 41.5, 33.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{20}O_2S+H]^+$ 313.1262; Found: 313.1257.

Methyl 2-[(prop-2-en-1-yl)sulfanyl]-2-(thiophen-3-yl)pent-4-enoate (3o)

(Spectra)



3o

Yield 77%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2981, 1728, 1638, 1436, 1212, 1164, 992, 921, 785, 691 cm^{-1}.

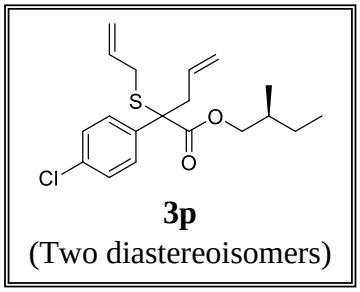
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.25 (m, 1H), 7.23-7.19 (m, 1H), 7.07-7.05 (m, 1H), 5.68-5.55 (m, 2H), 5.05-4.94 (m, 4H), 3.70 (s, 3H), 2.99 (ddd, J_1 = 40.8 Hz, J_2 = 12.8 Hz, J_3 = 6.8 Hz, 2H), 2.86 (ddd, J_1 = 26.8 Hz, J_2 = 14.4 Hz, J_3 = 7.2 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 139.8, 133.2, 132.8, 127.6, 125.6, 123.5, 118.8, 117.8, 57.2, 52.7, 42.6, 33.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{16}O_2S_2+H]^+$ 269.0670; Found: 269.0667.

(2*S*)-2-Methylbutyl 2-(4-chlorophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3p)

(Spectra)



3p

(Two diastereoisomers)

Yield 75%, *dr* 1.7:1, colourless oil; R_f = 0.69 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{25}$ = +1.9 (*c* 0.34, $CHCl_3$).

IR (neat): ν_{max} = 2964, 2929, 1724, 1639, 1490, 1462, 1212, 1095, 993, 921, 824, 765 cm^{-1}.

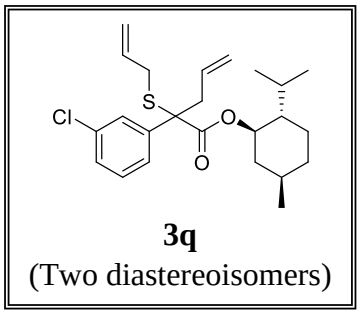
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.25-7.22 (m, 2H), 5.70-5.54 (m, 2H), 5.05 (dd, J_1 = 16.8 Hz, J_2 = 1.2 Hz, 1H), 4.98-4.89 (m, 3H), 4.02-3.98 (m, 1H), 3.94-3.90 (m, 1H), 2.97 (ddd, J_1 = 56.4 Hz, J_2 = 12.8 Hz, J_3 = 6.8 Hz, 2H), 2.79 (ddd, J_1 = 25.6 Hz, J_2 = 14.4 Hz, J_3 = 6.8 Hz, 2H), 1.69-1.61 (m, 1H), 1.35-1.26 (m, 1H), 1.15-1.06 (m, 1H), 0.84-0.79 (m, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 137.7, 133.2, 132.9, 132.5, 129.5, 128.3, 119.1, 118.1, 70.40, 70.38, 60.4, 43.1, 43.0, 34.14, 34.12, 33.6, 26.0, 16.54, 16.50, 11.20, 11.16 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{25}ClO_2S+H]^+$ 353.1342; Found: 353.1337.

(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl-2-(3-chlorophenyl)-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3q)

(Spectra)



3q
(Two diastereoisomers)

Yield 81%, *dr* 1.9:1, colourless oil; R_f = 0.69 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{27}$ = -47.0 (*c* 0.273, $CHCl_3$).

IR (neat): ν_{max} = 2955, 2926, 1718, 1639, 1458, 1218, 1186, 988, 958, 918, 777, 698 cm^{-1}.

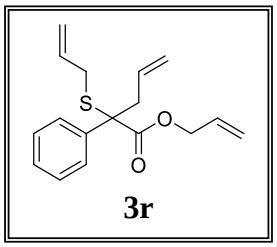
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.39-7.35 (m, 1H), 7.33-7.27 (m, 2H), 5.85-5.62 (m, 2H), 5.20-4.99 (m, 4H), 4.81 (ddd, J_1 = 21.6 Hz, J_2 = 10.8 Hz, J_3 = 4.4 Hz, 1H), 3.21-2.81 (m, 4H), 2.15-2.05 (m, 1H), 1.92-1.68 (m, 3H), 1.61-1.55 (m, 1H), 1.47-1.36 (m, 1H), 1.15-1.01 (m, 2H), 0.98-0.95 (m, 3H), 0.89-0.85 (m, 4H), 0.81-0.77 (m, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.1, 171.0, 141.8, 141.1, 134.2, 134.1, 133.0, 132.8, 132.6, 132.4, 129.4, 129.3, 128.3, 128.1, 127.6, 127.5, 126.3, 126.0, 119.1, 118.3, 118.1, 76.2, 76.0, 60.8, 60.3, 47.08, 47.05, 43.1, 42.1, 40.6, 40.4, 34.2, 34.1, 33.7, 33.3, 31.49, 31.45, 25.8, 25.7, 23.0, 22.9, 22.1, 20.9, 20.8, 15.82, 15.79 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{24}H_{33}ClO_2S+H]^+$ 421.1968; Found: 421.1978.

Prop-2-en-1-yl 2-phenyl-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3r)

(Spectra)



3r

Yield 77%, colourless oil; R_f = 0.58 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 3080, 1726, 1641, 1441, 1209, 1121, 990, 921, 754, 701 cm^{-1}.

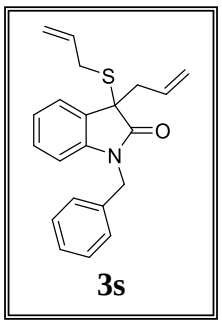
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.36-7.32 (m, 2H), 7.28-7.25 (m, 1H), 5.97-5.87 (m, 1H), 5.79-5.64 (m, 2H), 5.34-5.30 (m, 1H), 5.25-5.22 (m, 1H), 5.13-5.09 (m, 1H), 5.04-4.98 (m, 3H), 4.69 (d, *J* = 6.0 Hz, 2H), 3.07 (ddd, J_1 = 58.0 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.96-2.86 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9, 138.9, 133.2, 132.8, 131.7, 128.2, 127.8, 127.5, 118.9, 118.8, 117.9, 66.1, 60.8, 43.3, 33.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{17}H_{20}O_2S+H]^+$ 289.1262; Found: 289.1258.

1-Benzyl-3-(prop-2-en-1-yl)-3-[(prop-2-en-1-yl)sulfanyl]-1,3-dihydro-2*H*-indol-2-one (3s)

(Spectra)



3s

Yield 89%, colourless oil; R_f = 0.40 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2921, 1711, 1638, 1609, 1489, 1464, 1352, 1172, 995, 923, 749, 696 cm^{-1}.

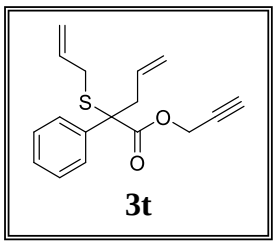
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.2 Hz, 1H), 7.23-7.16 (m, 5H), 7.12-7.08 (m, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 5.67-5.57 (m, 1H), 5.47-5.37 (m, 1H), 5.03-4.84 (m, 5H), 4.69-4.66 (m, 1H), 3.12-3.00 (m, 2H), 2.85-2.74 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.7, 142.5, 135.7, 133.7, 131.3, 128.9, 128.8, 127.7, 127.4, 124.4, 122.9, 119.9, 117.6, 109.2, 54.1, 43.9, 40.4, 32.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{21}H_{21}NOS+H]^+$ 336.1422; Found: 336.1414.

Prop-2-yn-1-yl 2-phenyl-2-[(prop-2-en-1-yl)sulfanyl]pent-4-enoate (3t)

(Spectra)



3t

Yield 78%, colourless oil; R_f = 0.50 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 3292, 3078, 1729, 1638, 1438, 1201, 1119, 992, 921, 753, 697, 640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.18 (m, 1H), 5.73-5.55 (m, 2H), 5.08-5.03 (m, 1H), 4.98-4.91 (m, 3H), 4.72-4.71 (m, 2H), 3.03 (ddd, J_1 = 68.0 Hz, J_2 = 12.8 Hz, J_3 = 7.2 Hz, 2H), 2.88-2.77 (m, 2H), 2.41 (t, J = 2.4 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 138.5, 133.1, 132.5, 128.3, 127.8, 127.6, 119.2, 118.1, 77.2, 75.3, 60.5, 52.8, 43.5, 33.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{17}H_{18}O_2S+H]^+$ 287.1106; Found: 287.1112.

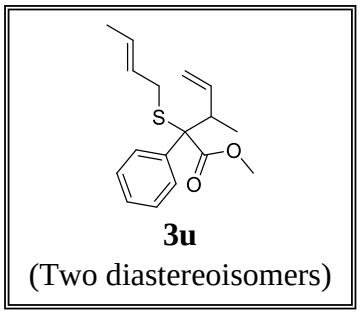
Methyl 2-{[(2*E*)-but-2-en-1-yl]sulfanyl}-3-methyl-2-phenylpent-4-enoate (3u)

Yield 68%, *dr* 1.2:1, colourless oil; R_f = 0.60 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2973, 1725, 1441, 1232, 1185, 1024, 965, 920, 756, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.28-7.24 (m, 2H), 7.23-7.19 (m, 1H), 5.72-5.44 (m, 2H), 5.37-5.27 (m, 1H), 4.98-4.90 (m, 2H), 3.77-3.73 (m, 3H), 3.10-2.92 (m, 2H), 2.91-2.81 (m, 1H), 1.57-1.51 (m, 3H), 0.92-0.89 (m, 3H) ppm.

(Spectra)



3u
(Two diastereoisomers)

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.4, 172.3, 139.3, 138.5, 136.11, 136.06, 135.3, 129.9, 129.7, 129.5, 128.7, 127.5, 127.4, 127.3, 125.29, 125.26, 124.0, 123.9, 116.8, 116.7, 116.3, 64.9, 64.5, 52.4, 52.2, 45.7, 45.6, 44.8, 44.7, 33.5, 33.4, 27.9, 27.7, 17.9, 17.71, 17.67, 15.8, 12.8 ppm.

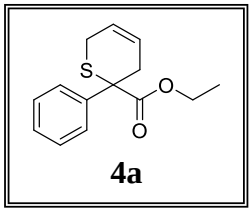
HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{22}O_2S+H]^+$ 291.1419; Found: 291.1415.

5. General procedure for the synthesis of thiopyrans 4 *via* ring-closing metathesis

A 5 mL screw cap vial was charged with dienes **3a-s**,**u** (0.2 mmol) and 2 mL of water was added. Then, 10 mol% of Grubbs' second-generation catalyst (G-II) was added. The reaction was monitored using TLC. The reaction was allowed to stir until the complete conversion of the starting material. Then, to the reaction mixture, CH_2Cl_2 was added and separated the organic layer (3 x 20 mL) and dried over anhydrous Na_2SO_4. The whole of the organic layer was concentrated under reduced pressure followed by purification using flash chromatography (silica gel, 230-400 mesh, Hexanes:EtOAc = 9:1) to afford the respective 3,6-dihydro-2*H*-thiopyrans **4a-s**,**u**.

Ethyl 2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4a)

(Spectra)



4a

Yield 89%, colourless oil; R_f = 0.46 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2977, 1728, 1447, 1226, 1187, 1093, 1034, 727, 696, 649 cm^{-1}.

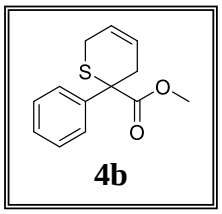
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.30-7.25 (m, 2H), 7.22-7.18 (m, 1H), 5.89-5.84 (m, 1H), 5.79-5.74 (m, 1H), 4.15-4.07 (m, 2H), 3.26-3.19 (m, 1H), 3.07-3.00 (m, 1H), 2.92-2.84 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.2, 139.9, 128.5, 127.7, 126.9, 126.7, 123.8, 62.0, 54.4, 34.6, 26.6, 14.0 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_2S+H]^+$ 249.0949; Found: 249.0944.

Methyl 2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4b)

(Spectra)



4b

Yield 88%, colourless crystalline solid; mp 98-100 °C; R_f = 0.40 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2923, 2853, 1729, 1493, 1438, 1229, 1032, 727, 694, 650 cm^{-1}.

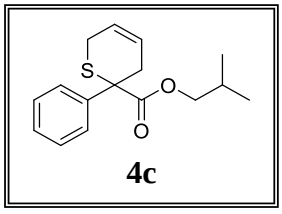
^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 1H), 5.85-5.81 (m, 1H), 5.75-5.71 (m, 1H), 3.60 (s, 3H), 3.22-3.17 (m, 1H), 3.04-2.98 (m, 1H), 2.89-2.81 (m, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.8, 139.8, 128.6, 127.8, 126.8, 126.7, 123.8, 54.5, 53.2, 34.6, 26.6 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{13}H_{14}O_2S+H]^+$ 235.0793; Found: 235.0790.

2-Methylpropyl 2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4c)

(Spectra)



4c

Yield 91%, colourless oil; R_f = 0.42 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2961, 2927, 1727, 1466, 1222, 1184, 1029, 994, 726, 696, 650 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.28-7.25 (m, 2H), 7.22-7.18 (m, 1H), 5.89-5.84 (m, 1H), 5.78-5.74 (m, 1H), 3.85-3.78 (m, 2H), 3.24-3.19 (m, 1H), 3.08-3.02 (m, 1H), 2.95-2.84 (m, 2H), 1.86-1.76 (m, 1H), 0.76 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.3, 139.8, 128.4, 127.7, 126.8, 123.9, 71.9, 54.6, 34.4, 27.7, 26.6, 18.9 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{16}H_{20}O_2S+H]^+$ 277.1262; Found: 277.1257.

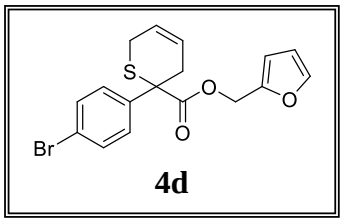
(Furan-2-yl)methyl 2-(4-bromophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4d)

Yield 80%, colourless oil; R_f = 0.38 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2924, 1731, 1490, 1220, 1076, 1014, 922, 816, 747, 648 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.30-7.25 (m, 3H), 6.29-6.26 (m, 2H), 5.83-5.80 (m, 1H), 5.74-5.72 (m, 1H), 5.03 (ABq, $\Delta\delta_{AB}$ = 0.02, J_{AB} = 13.2 Hz, 2H), 3.18-3.13 (m, 1H), 3.01-2.96 (m, 1H), 2.85-2.80 (m, 2H) ppm.

(Spectra)



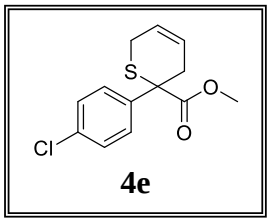
4d

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.5, 148.9, 143.3, 138.7, 131.6, 128.6, 126.4, 123.8, 121.9, 111.1, 110.6, 59.5, 54.0, 34.3, 26.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{17}H_{15}BrO_3S+H]^+$ 379.0004; Found: 379.0012.

Methyl 2-(4-chlorophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4e)

(Spectra)



4e

Yield 85%, colourless oil; R_f = 0.40 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2925, 2854, 1734, 1491, 1235, 1095, 1023, 814, 764, 732, 645 cm^{-1}.

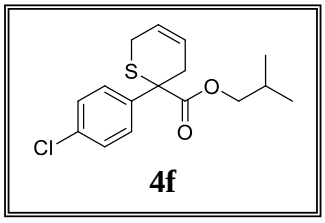
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.26-7.19 (m, 2H), 5.88-5.82 (m, 1H), 5.79-5.73 (m, 1H), 3.64 (s, 3H), 3.21-3.15 (m, 1H), 3.04-2.97 (m, 1H), 2.90-2.82 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5, 138.2, 133.7, 128.7, 128.3, 126.4, 123.9, 53.9, 53.3, 34.3, 26.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{13}ClO_2S+H]^+$ 269.0403; Found: 269.0398.

2-Methylpropyl 2-(4-chlorophenyl)-3,6-dihydro-2*H* -thiopyran-2-carboxylate (4f)

(Spectra)



4f

Yield 95%, colourless oil; R_f = 0.51 (9:1 *n*-hexanes:ethyl acetate).

IR (neat): ν_{max} = 2962, 2929, 1727, 1490, 1223, 1186, 1093, 1021, 992, 812, 761, 644 cm^{-1}.

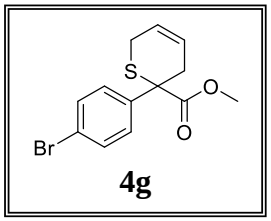
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.24-7.19 (m, 2H), 5.87-5.83 (m, 1H), 5.77-5.73 (m, 1H), 3.85-3.77 (m, 2H), 3.20-3.14 (m, 1H), 3.05-2.99 (m, 1H), 2.93-2.81 (m, 2H), 1.85-1.75 (m, 1H), 0.76 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 6H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.9, 138.3, 133.6, 128.6, 128.4, 126.4, 124.0, 72.1, 54.1, 34.1, 27.7, 26.4, 18.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{19}ClO_2S+H]^+$ 311.0873; Found: 311.0882.

Methyl 2-(4-bromophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4g)

(Spectra)



4g

Yield 87%, colourless oil; R_f = 0.42 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2949, 1728, 1486, 1434, 1226, 1076, 1033, 1006, 808, 756, 727, 643 cm^{-1}.

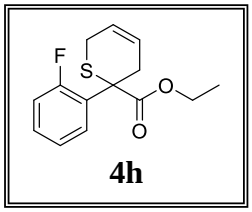
^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.35-7.32 (m, 2H), 5.86-5.82 (m, 1H), 5.78-5.73 (m, 1H), 3.64 (s, 3H), 3.21-3.14 (m, 1H), 3.03-2.97 (m, 1H), 2.89-2.82 (m, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.4, 138.8, 131.6, 128.7, 126.4, 123.9, 121.9, 54.0, 53.3, 34.2, 26.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{13}BrO_2S+H]^+$ 312.9898; Found: 312.9892.

Ethyl 2-(2-fluorophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4h)

(Spectra)



4h

Yield 79%, colourless oil; R_f = 0.39 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2980, 1729, 1485, 1451, 1218, 1093, 1031, 849, 753, 645 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.35-7.29 (m, 1H), 7.16 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.11-7.06 (m, 1H), 6.02-5.94 (m, 2H), 4.29-4.24 (m, 2H), 3.28-3.23 (m, 1H), 3.07-2.94 (m, 2H), 2.78-2.73 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.1, 160.1 (d, J_{C-F} = 249.6 Hz), 129.4 (d, J_{C-F} = 8.9 Hz), 128.87 (d, J_{C-F} = 11.7 Hz), 127.8 (d, J_{C-F} = 3.5 Hz), 126.9, 123.80 (d, J_{C-F} = 3.5 Hz), 123.6, 115.95 (d, J_{C-F} = 22.2 Hz), 62.0, 50.8, 34.4, 25.5, 14.0 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}FO_2S+H]^+$ 267.0855; Found: 267.0861.

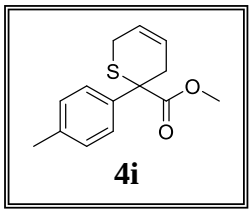
Methyl 2-(4-methylphenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4i)

Yield 80%, white solid; mp 88-90 °C; R_f = 0.47 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2949, 1732, 1512, 1437, 1234, 1188, 1034, 816, 745, 650 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.32 (m, 2H), 7.09-7.07 (m, 2H), 5.88-5.83 (m, 1H), 5.77-5.74 (m, 1H), 3.64 (s, 3H), 3.25-3.20 (m, 1H), 3.05-2.99 (m, 1H), 2.91-2.84 (m, 2H), 2.26 (s, 3H) ppm.

(**Spectra**)



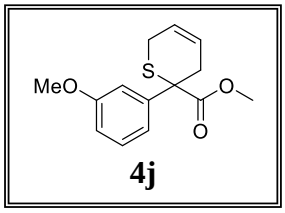
4i

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.9, 137.6, 136.7, 129.3, 126.8, 126.5, 123.7, 54.2, 53.2, 34.7, 26.6, 21.1 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_2S+H]^+$ 249.0949; Found: 249.0944.

Methyl 2-(3-methoxyphenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4j)

(**Spectra**)



4j

Yield 83%, colourless oil; R_f = 0.31 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2948, 1728, 1590, 1488, 1430, 1236, 1162, 1035, 778, 737, 692, 650 cm^{-1}.

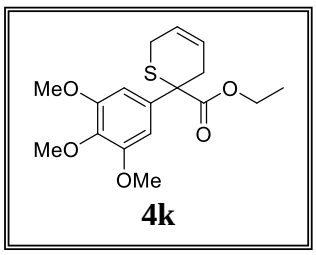
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 1H), 7.13-7.11 (m, 2H), 6.88-6.85 (m, 1H), 5.99-5.94 (m, 1H), 5.90-5.85 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.37-3.30 (m, 1H), 3.16-3.10 (m, 1H), 3.05-2.94 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7, 159.7, 141.3, 129.5, 126.8, 123.7, 119.0, 113.0, 112.9, 55.3, 54.4, 53.2, 34.7, 26.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_3S+H]^+$ 265.0898; Found: 265.0903.

Ethyl 2-(3,4,5-trimethoxyphenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4k)

(**Spectra**)



4k

Yield 78%, colourless oil; R_f = 0.14 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2933, 1726, 1586, 1507, 1456, 1414, 1244, 1188, 1126, 1009, 851, 662 cm^{-1}.

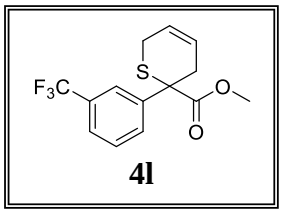
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 2H), 5.95-5.92 (m, 1H), 5.87-5.84 (m, 1H), 4.27-4.14 (m, 2H), 3.85 (s, 6H), 3.84 (s, 3H), 3.38-3.33 (m, 1H), 3.15-2.99 (m, 2H), 2.94-2.89 (m, 1H) 1.24 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.0, 153.0, 137.6, 135.4, 126.8, 123.7, 104.1, 62.0, 60.8, 56.2, 54.5, 34.9, 26.9, 14.1 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{22}O_5S+H]^+$ 339.1266; Found: 339.1261.

Methyl 2-[3-(trifluoromethyl)phenyl]-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4l)

(Spectra)



4l

Yield 81%, colourless oil; R_f = 0.47 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2953, 1732, 1435, 1324, 1232, 1164, 1121, 1077, 1034, 789, 698, 657 cm^{-1}.

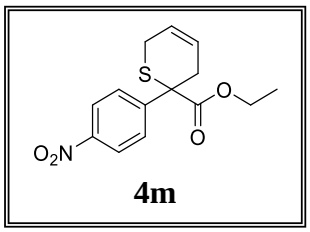
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 5.90-5.85 (m, 1H), 5.80-5.75 (m, 1H), 3.66 (s, 3H), 3.23-3.17 (m, 1H), 3.08-3.02 (m, 1H), 2.94-2.81 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 140.8, 130.87 (q, J_{C-F} = 32.32 Hz), 130.4, 129.0, 128.04-119.91 (q, J_{C-F} = 273.71 Hz), 126.3, 124.79-124.67 (q, J_{C-F} = 4.04 Hz), 124.0, 123.78-123.66 (q, J_{C-F} = 4.04 Hz), 54.1, 53.4, 34.2, 26.4 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{13}F_3O_2S+H]^+$ 303.0667; Found: 303.0665.

Ethyl 2-(4-nitrophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4m)

(Spectra)



4m

Yield 75%, colourless oil; R_f = 0.30 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2981, 1729, 1600, 1521, 1348, 1228, 1033, 857, 736, 649 cm^{-1}.

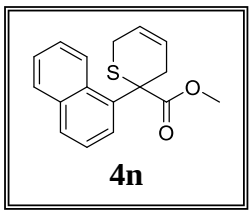
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.66-7.64 (m, 2H), 5.90-5.87 (m, 1H), 5.80-5.77 (m. 1H), 4.23-4.07 (m, 2H), 3.19-3.14 (m, 1H), 3.06-2.91 (m, 2H), 2.83-2.79 (m, 1H), 1.14 (t, J = 7.2 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 147.2, 147.1, 128.1, 126.1, 124.2, 123.5, 62.5, 54.3, 33.9, 26.2, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}NO_4S+H]^+$ 294.0800; Found: 294.0791.

Methyl 2-(naphthalen-1-yl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4n)

(Spectra)



4n

Yield 79%, white solid; mp 126-128 °C; R_f = 0.33 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2921, 1726, 1433, 1228, 1195, 1032, 778, 732, 645 cm^{-1}.

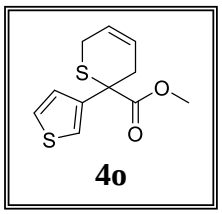
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.13 (m, 1H), 7.80-7.77 (m, 1H), 7.73-7.71 (m, 1H), 7.51-7.49 (m, 1H), 7.43-7.38 (m, 2H), 7.37-7.31 (m, 1H), 5.96-5.93 (m, 1H), 5.87-5.81 (m, 1H), 3.56 (s, 3H), 3.12-3.06 (m, 2H), 3.01-2.95 (m, 1H), 2.71-2.65 (m, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 134.8, 134.6, 130.8, 129.3, 129.2, 126.5, 126.0, 125.5, 125.0, 124.7, 124.6, 124.0, 53.9, 53.2, 36.0, 25.9 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $[C_{17}H_{16}O_2S+Na]^+$ 307.0769; Found: 307.0771.

Methyl 2-(thiophen-3-yl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4o)

(Spectra)



4o

Yield 84%, colourless oil; R_f = 0.38 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2949, 1728, 1433, 1219, 1086, 1033, 857, 775, 729, 646 cm^{-1}.

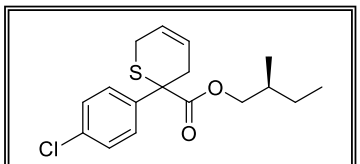
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.24-7.23 (m, 1H), 5.98-5.92 (m, 1H), 5.89-5.84 (m, 1H), 3.77 (s, 3H), 3.34-3.28 (m, 1H), 3.19-3.13 (m, 1H), 3.04-2.94 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 140.5, 126.7, 126.5, 125.9, 123.6, 122.6, 53.3, 51.4, 35.0, 26.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{11}H_{12}O_2S_2+H]^+$ 241.0357; Found: 241.0349.

(2*S*)-2-Methylbutyl 2-(4-chlorophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4p)

(Spectra)



4p

(Two diastereoisomers)

Yield 84%, *dr* 1.5:1, colourless oil; R_f = 0.56 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{26}$ = -2.0 (*c* 0.085, $CHCl_3$).

IR (neat): ν_{max} = 2964, 2928, 1730, 1492, 1462, 1225, 1096, 1020, 814, 761, 645 cm^{-1}.

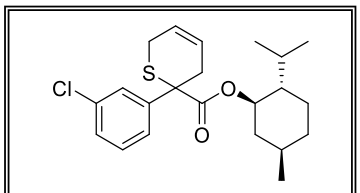
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.24-7.19 (m, 2H), 5.87-5.82 (m, 1H), 5.77-5.72 (m, 1H), 3.93-3.80 (m, 2H), 3.19-3.15 (m, 1H), 3.04-2.98 (m, 1H), 2.92-2.81 (m, 2H), 1.64-1.52 (m, 1H), 1.29-1.17 (m, 1H), 1.09-0.97 (m, 1H), 0.78-0.74 (m, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9, 138.3, 133.6, 128.5, 128.4, 126.41, 126.40, 124.0, 70.6, 54.1, 34.1, 34.05, 34.04, 26.4, 25.89, 25.86, 16.29, 16.27, 11.15, 11.13 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{17}H_{21}ClO_2S+H]^+$ 325.1029; Found: 325.1024.

(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl-2-(3-chlorophenyl)-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4q)

(**Spectra**)



4q
(Two diastereoisomers)

Yield 76%, *dr* 1.4:1, colourless oil; R_f = 0.59 (9:1 hexanes:ethyl acetate); $[\alpha]_D^{27}$ = -82.1 (*c* 0.234, $CHCl_3$).

IR (neat): ν_{max} = 2953, 2925, 2867, 1723, 1457, 1230, 1188, 1088, 1022, 989, 956, 772, 691, 649 cm^{-1}.

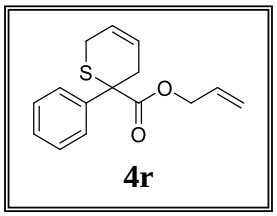
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42-7.40 (m, 1H), 7.26-7.24 (m, 2H), 5.94-5.91 (m, 1H), 5.86-5.83 (m, 1H), 4.68-4.61 (m, 1H), 3.31-3.22 (m, 1H), 3.12-2.87 (m, 3H), 1.93-1.89 (m, 1H), 1.66-1.62 (m, 2H), 1.46-1.42 (m, 1H), 1.39-1.30 (m, 1H), 1.28-1.26 (m, 1H), 1.01-0.87 (m, 5H), 0.84-0.70 (m, 4H), 0.64-0.56 (m, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 142.1, 142.0, 134.32, 134.29, 129.6, 129.5, 127.9, 127.8, 127.3, 127.1, 126.6, 126.2, 125.1, 124.9, 124.3, 123.8, 76.3, 76.2, 54.4, 54.3, 47.0, 46.8, 40.3, 40.1, 34.4, 34.2, 34.1, 33.7, 31.4, 26.5, 26.3, 25.8, 25.7, 23.1, 22.9, 22.0, 20.8, 20.6, 15.8, 15.7 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{22}H_{29}ClO_2S+H]^+$ 393.1655; Found: 393.1660.

Prop-2-en-1-yl 2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4r)

(Spectra)



4r

Yield 79%, colourless oil; R_f = 0.43 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2932, 1729, 1446, 1218, 1027, 992, 934, 730, 697, 651 cm^{-1}.

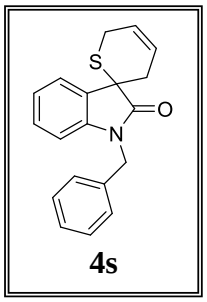
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.28-7.25 (m, 2H), 7.22-7.19 (m, 1H), 5.88-5.85 (m, 1H), 5.80-5.71 (m, 2H), 5.16-5.08 (m, 2H), 4.54 (d, J = 5.6 Hz, 2H), 3.25-3.21 (m, 1H), 3.08-3.03 (m, 1H), 2.92-2.86 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.9, 139.7, 131.6, 128.5, 127.8, 126.8, 126.7, 123.8, 118.4, 66.3, 54.5, 34.6, 26.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{16}O_2S+H]^+$ 261.0949; Found: 261.0959.

1-Benzyl-3',6'-dihydrospiro[indole-3,2'-thiopyran]-2(1*H*)-one (4s)

(Spectra)



4s

Yield 88%, colourless oil; R_f = 0.24 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2923, 1708, 1608, 1489, 1463, 1350, 1167, 747, 695, 651 cm^{-1}.

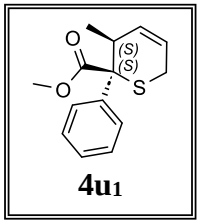
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.16 (m, 6H), 7.13-7.09 (m, 1H), 6.98-6.94 (m, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.09-6.03 (m, 1H), 5.96-5.91 (m, 1H), 4.84 (ABq, $\Delta\delta_{AB}$ = 0.14, J_{AB} = 15.6 Hz, 2H), 3.91-3.84 (m, 1H), 3.16-3.10 (m, 1H), 2.69-2.50 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.7, 141.8, 135.8, 131.1, 129.0, 128.9, 127.6, 127.2, 125.1, 123.8, 123.6, 122.8, 109.3, 45.0, 43.6, 31.0, 25.0 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{17}NOS+H]^+$ 308.1109; Found: 308.1105.

Methyl (2*S*,3*S*)-3-methyl-2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate ($4u_1$)

(Spectra)



$4u_1$

Yield 55%, white crystalline solid; mp 98-100 °C; R_f = 0.43 (19:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2924, 1734, 1449, 1238, 1198, 1039, 737, 702 cm^{-1}.

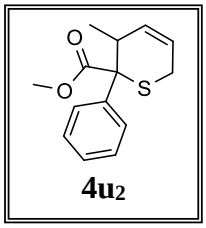
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.32-7.29 (m, 2H), 7.26-7.22 (m, 1H), 5.92-5.88 (m, 1H), 5.70-5.66 (m, 1H), 3.67 (s, 3H), 3.25-3.21 (m, 1H), 2.76 (dd, J_1 = 17.6 Hz, J_2 = 6.0 Hz, 1H), 2.52 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1H), 1.24 (d, J = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.7, 140.0, 132.3, 128.1, 127.6, 127.3, 123.6, 61.1, 52.8, 33.9, 25.5, 18.4 ppm.

HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_2S+H]^+$ 249.0949; Found: 249.0955.

Methyl 3-methyl-2-phenyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate (4u$_2$)

(Spectra)



4u$_2$

Yield 34%, colourless liquid; R_f = 0.37 (19:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2932, 1727, 1448, 1231, 1014, 749, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 4H), 7.30-7.29 (m, 1H), 5.96-5.92 (m, 1H), 5.79-5.75 (m, 1H), 3.69 (s, 3H), 3.39 (dd, J_1 = 17.6 Hz, J_2 = 2.0 Hz, 1H), 3.29-3.29 (m, 1H), 3.08 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 0.80 (d, J = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.5, 138.8, 134.7, 128.6, 127.7, 126.2, 120.9, 59.8, 53.2, 36.8, 26.7, 16.9 ppm.

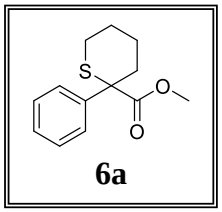
HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_2S+H]^+$ 249.0949; Found: 249.0946.

6. Synthetic procedure for the reduction of thiopyran 4b

3,6-Dihydro-2*H*-thiopyran **4b** (0.02 g, 0.09 mmol) and 10% palladium on carbon (0.009 g, 0.009 mmol) were dissolved in dry ethyl acetate (2 mL) and stirred under an atmosphere of hydrogen (balloon pressure) for 17 h. The reaction mixture was then filtered through a short pad of Celite® and the filtrate was concentrated *in vacuo*. The NMR analysis of the crude without additional purification yields pure tetrahydro-2*H*-thiopyran **6a** (0.02 g, 99%) as a colourless oil.

Methyl 2-phenylthiane-2-carboxylate (6a)

(Spectra)



6a

Yield 98%, colourless oil; R_f = 0.40 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2931, 1728, 1493, 1439, 1259, 1221, 1177, 1136, 1061, 1030, 997, 728, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 2H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 3.63 (s, 3H), 2.80-2.73 (m, 1H), 2.61-2.49 (m, 2H), 2.38-2.31 (m, 1H), 1.84-1.78 (m, 1H), 1.73-1.59 (m, 2H), 1.57-1.48 (m, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.2, 140.2, 128.7, 127.7, 126.7, 56.5, 53.0, 36.1, 28.8, 26.2, 23.1 ppm.

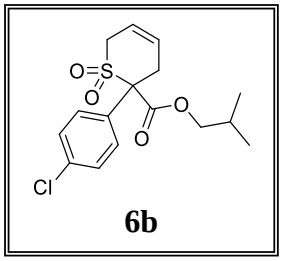
HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{16}O_2S+H]^+$ 237.0949; Found: 237.0941.

7. Synthetic procedure for the oxidation of thiopyran 4f

To a solution of thiopyran **4f** (0.02 g, 0.06 mmol) in dichloromethane (DCM) 2 mL was added *m*-Chloroperbenzoic acid (*m*-CPBA) (2 equiv) and the mixture was stirred at room temperature for 3 h. Reaction was monitored using TLC. After completion of the reaction, the reaction was quenched with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layers were dried over Na_2SO_4, concentrated, and purified by flash chromatography using silica gel (230-400 mesh; Hexanes:EtOAc = 6:4) to provide the product **6b** (0.018 g, 82%) as a white solid.

2-Methylpropyl 2-(4-chlorophenyl)-1,1-dioxo-1,2,3,6-tetrahydro-1λ^6-thiopyran-2-carboxylate (6b)

(Spectra)



6b

Yield 82%, white solid, mp 106-108 °C; R_f = 0.13 (9:1 hexanes:ethyl acetate).

IR (neat): ν_{max} = 2963, 2928, 1734, 1494, 1318, 1281, 1208, 1155, 1128, 1097, 1039, 1018, 846, 740, 654 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.35-7.32 (m, 2H), 5.95-5.90 (m, 1H), 5.63-5.59 (m, 1H), 4.02-3.87 (m, 3H), 3.55-3.50 (m, 2H), 3.27-3.21 (m, 1H), 1.90-1.80 (m, 1H), 0.79 (dd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 136.1, 130.2, 129.0, 127.6, 125.6, 120.9, 72.7, 71.6, 51.3, 34.3, 27.6, 18.9 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $[C_{16}H_{19}ClO_4S+Na]^+$ 365.0590; Found: 365.0600.

8. Crystal data and structure refinement for compound 4b

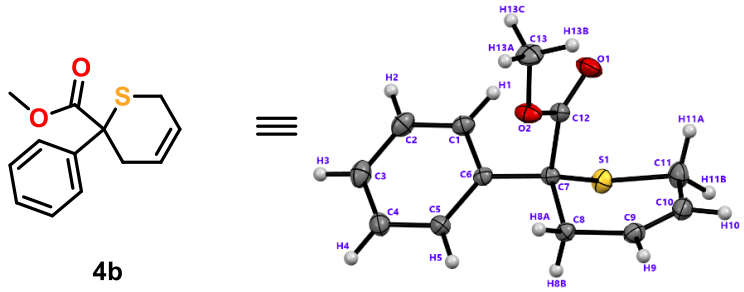


Figure S1. ORTEP diagram of compound **4b** showing thermal ellipsoids at the 50% probability level

Table S2. Crystal data and structure refinement for **4b**

CCDC	2332011
Empirical formula	$C_{13}H_{14}O_2S$
Formula weight	234.30
Temperature/K	159.(2)
Crystal system	Monoclinic
Space group	*P* 1 2_1/*n* 1
a (Å)	7.8862(3)
b (Å)	10.3502(4)
c (Å)	14.3311(5)
α (°)	90
β (°)	103.6680(10)
γ (°)	90
Volume ($Å^3$)	1136.63(7)
Z	4
ρ_{calc} (g cm^{-3})	1.369
μ (mm^{-1})	0.266
F(000)	496
Crystal size (mm)	0.560 (max) × 0.175 (mid) × 0.156 (min)
Radiation	MoKα (λ = 0.71073 Å)
Theta range for data collection (°)	2.45 to 39.44
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $-25 \le l \le 25$
Reflections collected / unique	39684 / 6788 [R_{int} = 0.0606]
Completeness to theta = 39.44	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.960 and 0.865
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6788/0/201
Goodness-of-fit on F^2	1.081
Final R indices [I>2σ (I)]	R_1 = 0.0432, wR_2 = 0.1040

R indices [all data]	R_1 = 0.0790, wR_2 = 0.1278
Largest diff. peak and hole (e $Å^{-3}$)	0.532 and -0.373

Table S3: Atomic parameters of compound **4b**

Atom	Wyck.	Site	x/a	y/b	z/c	U [$Å^2$]
S1	4e	1	0.99211(3)	0.72849(3)	0.61740(2)	
O1	4e	1	0.64990(12)	0.86700(8)	0.59284(6)	
O2	4e	1	0.49251(9)	0.73631(8)	0.48104(6)	
C1	4e	1	0.86710(13)	0.86232(9)	0.41580(7)	
C2	4e	1	0.90770(14)	0.90233(11)	0.33116(8)	
C3	4e	1	0.91552(14)	0.81250(12)	0.26020(8)	
C4	4e	1	0.88323(14)	0.68325(11)	0.27454(7)	
C5	4e	1	0.84248(13)	0.6427(1)	0.35925(7)	
C6	4e	1	0.83450(11)	0.73179(9)	0.43094(6)	
C7	4e	1	0.79431(11)	0.69241(8)	0.52603(6)	
C8	4e	1	0.75089(12)	0.54813(9)	0.53294(7)	
C9	4e	1	0.73054(14)	0.51172(10)	0.63135(7)	
C10	4e	1	0.80421(14)	0.57137(11)	0.71326(8)	
C11	4e	1	0.92022(16)	0.68689(12)	0.72419(8)	
C12	4e	1	0.64094(12)	0.77608(9)	0.53975(7)	
C13	4e	1	0.33815(15)	0.81133(13)	0.48187(10)	
H1	4e	1	0.863(2)	0.9215(16)	0.4656(11)	0.028(4)
H2	4e	1	0.932(2)	0.9899(18)	0.3229(12)	0.039(5)
H3	4e	1	0.942(2)	0.8370(18)	0.2031(14)	0.043(5)
H4	4e	1	0.888(2)	0.6212(16)	0.2260(12)	0.033(4)
H5	4e	1	0.8261(19)	0.5527(16)	0.3674(11)	0.028(4)
H9	4e	1	0.663(2)	0.4346(16)	0.6341(12)	0.032(4)
H8A	4e	1	0.6489(19)	0.5294(15)	0.4856(11)	0.024(4)
H8B	4e	1	0.8383(19)	0.4969(15)	0.5188(11)	0.024(4)
H10	4e	1	0.780(2)	0.5374(17)	0.7718(11)	0.032(4)
H11A	4e	1	0.869(2)	0.7627(16)	0.7450(13)	0.032(4)
H11B	4e	1	1.028(2)	0.6734(18)	0.7741(13)	0.039(4)
H13A	4e	1	0.245(2)	0.7751(17)	0.4365(13)	0.038(5)
H13B	4e	1	0.316(2)	0.8081(19)	0.5439(14)	0.042(5)
H13C	4e	1	0.354(2)	0.8999(18)	0.4631(12)	0.038(4)

Table S4: Anisotropic displacement parameters, in $Å^2$ of compound **4b**

Atom	U11	U22	U33	U12	U13	U23
S1	0.01836(10)	0.02458(12)	0.02047(11)	-0.00353(8)	-0.00021(8)	-0.00113(8)
O1	0.0328(4)	0.0267(4)	0.0296(4)	0.0065(3)	0.0042(3)	-0.0108(3)
O2	0.0153(3)	0.0246(3)	0.0317(4)	0.0034(2)	0.0024(3)	-0.0056(3)
C1	0.0210(4)	0.0179(4)	0.0240(4)	-0.0012(3)	0.0047(3)	0.0001(3)
C2	0.0245(4)	0.0238(4)	0.0290(5)	-0.0029(4)	0.0061(4)	0.0063(4)

Atom	U11	U22	U33	U12	U13	U23
C3	0.0217(4)	0.0348(5)	0.0231(4)	-0.0004(4)	0.0064(3)	0.0062(4)
C4	0.0248(4)	0.0298(5)	0.0197(4)	0.0033(4)	0.0059(3)	0.0004(4)
C5	0.0232(4)	0.0194(4)	0.0187(4)	0.0019(3)	0.0044(3)	-0.0011(3)
C6	0.0139(3)	0.0166(3)	0.0175(3)	0.0002(3)	0.0023(3)	0.0002(3)
C7	0.0148(3)	0.0154(3)	0.0171(3)	-0.0003(3)	0.0019(3)	-0.0013(3)
C8	0.0173(3)	0.0164(3)	0.0186(4)	-0.0008(3)	0.0035(3)	0.0005(3)
C9	0.0235(4)	0.0194(4)	0.0244(4)	0.0015(3)	0.0071(3)	0.0031(3)
C10	0.0262(4)	0.0268(5)	0.0209(4)	0.0039(4)	0.0063(3)	0.0038(3)
C11	0.0285(5)	0.0318(5)	0.0179(4)	-0.0015(4)	0.0003(4)	-0.0018(4)
C12	0.0191(4)	0.0168(3)	0.0184(4)	0.0012(3)	0.0049(3)	-0.0001(3)
C13	0.0197(4)	0.0311(5)	0.0360(6)	0.0084(4)	0.0076(4)	0.0018(4)

Table S5: Bond lengths [Å] for **4b**

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
S1—C11	1.8053(13)	C6—C7	1.5257(13)
S1—C7	1.8226(8)	C7—C12	1.5375(13)
O1—C12	1.2017(13)	C7—C8	1.5405(13)
O2—C12	1.3350(11)	C8—C9	1.5046(15)
O2—C13	1.4463(15)	C8—H8A	0.9418(135)
C1—C2	1.3888(16)	C8—H8B	0.9292(161)
C1—C6	1.4017(13)	C9—C10	1.3320(14)
C1—H1	0.9468(165)	C9—H9	0.9656(166)
C2—C3	1.3900(17)	C10—C11	1.4911(17)
C2—H2	0.9397(186)	C10—H10	0.9693(170)
C3—C4	1.3862(17)	C11—H11A	0.9616(174)
C3—H3	0.9264(207)	C11—H11B	0.9830(149)
C4—C5	1.3920(15)	C13—H13A	0.9366(154)
C4—H4	0.9540(173)	C13—H13B	0.9462(208)
C5—C6	1.3930(14)	C13—H13C	0.9717(187)
C5—H5	0.9514(166)	C3—C10^{i}	10.7191(15)

(i) 1/2-x, 1/2+y, 1/2-z.

Table S6: Bond Angles [°] for **4b**

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C11—S1—C7	99.978(47)	C9—C8—H8A	111.198(936)
C12—O2—C13	116.337(84)	C7—C8—H8A	108.555(947)
C2—C1—C6	120.74(9)	C9—C8—H8B	108.085(951)
C2—C1—H1	121.427(941)	C7—C8—H8B	110.581(961)
C6—C1—H1	117.818(1004)	H8A—C8—H8B	106.066(1340)
C1—C2—C3	119.919(101)	C10—C9—C8	126.089(93)
C1—C2—H2	119.577(1056)	C10—C9—H9	118.497(989)
C3—C2—H2	120.491(1109)	C8—C9—H9	115.301(989)
C4—C3—C2	119.710(109)	C9—C10—C11	126.387(104)
C4—C3—H3	118.866(1150)	C9—C10—H10	117.419(918)
C2—C3—H3	121.424(1178)	C11—C10—H10	116.192(1006)
C3—C4—C5	120.574(100)	C10—C11—S1	114.204(85)
C3—C4—H4	120.086(1001)	C10—C11—H11A	113.241(994)
C5—C4—H4	119.338(1004)	S1—C11—H11A	107.901(1043)

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C4—C5—C6	120.241(89)	C10—C11—H11B	111.477(1017)
C4—C5—H5	117.924(953)	S1—C11—H11B	105.068(1050)
C6—C5—H5	121.768(983)	H11A—C11—H11B	104.158(1447)
C5—C6—C1	118.813(87)	O1—C12—O2	123.514(94)
C5—C6—C7	122.484(78)	O1—C12—C7	126.279(89)
C1—C6—C7	118.696(78)	O2—C12—C7	110.173(79)
C6—C7—C12	107.427(72)	O2—C13—H13A	107.634(1019)
C6—C7—C8	114.370(72)	O2—C13—H13B	109.351(1047)
C12—C7—C8	110.137(71)	H13A—C13—H13B	110.453(1596)
C6—C7—S1	105.296(57)	O2—C13—H13C	109.915(1035)
C12—C7—S1	110.996(62)	H13A—C13—H13C	108.458(1477)
C8—C7—S1	108.538(60)	H13B—C13—H13C	110.965(1537)
C9—C8—C7	112.186(78)		

Table S7. Torsion angles [°] for **4b**

C(11)-S(1)-C(7)-C(6)	176.62(6)
C(11)-S(1)-C(7)-C(8)	-60.49(7)
C(11)-S(1)-C(7)-C(12)	60.68(7)
C(7)-S(1)-C(11)-C(10)	37.73(9)
C(13)-O(2)-C(12)-O(1)	1.6(1)
C(13)-O(2)-C(12)-C(7)	-176.38(8)
C(6)-C(1)-C(2)-C(3)	0.3(2)
C(2)-C(1)-C(6)-C(5)	-0.4(1)
C(2)-C(1)-C(6)-C(7)	178.70(9)
C(1)-C(2)-C(3)-C(4)	-0.2(2)
C(2)-C(3)-C(4)-C(5)	0.2(2)
C(3)-C(4)-C(5)-C(6)	-0.3(2)
C(4)-C(5)-C(6)-C(1)	0.4(1)
C(4)-C(5)-C(6)-C(7)	-178.66(9)
C(1)-C(6)-C(7)-S(1)	-64.06(9)
C(1)-C(6)-C(7)-C(8)	176.88(8)
C(1)-C(6)-C(7)-C(12)	54.3(1)
C(5)-C(6)-C(7)-S(1)	114.99(9)
C(5)-C(6)-C(7)-C(8)	-4.1(1)
C(5)-C(6)-C(7)-C(12)	-126.64(9)
S(1)-C(7)-C(8)-C(9)	56.90(9)
C(6)-C(7)-C(8)-C(9)	174.12(8)
C(12)-C(7)-C(8)-C(9)	-64.8(1)
S(1)-C(7)-C(12)-O(1)	10.7(1)
S(1)-C(7)-C(12)-O(2)	-171.43(6)
C(6)-C(7)-C(12)-O(1)	-104.0(1)
C(6)-C(7)-C(12)-O(2)	73.95(9)
C(8)-C(7)-C(12)-O(1)	130.9(1)
C(8)-C(7)-C(12)-O(2)	-51.2(1)
C(7)-C(8)-C(9)-C(10)	-26.0(1)
C(8)-C(9)-C(10)-C(11)	0.6(2)
C(9)-C(10)-C(11)-S(1)	-11.0(2)

Symmetry transformations used to generate equivalent atoms:

The following intermolecular interactions are present in compound **4b**

The molecules of compound **4b** was aligned involving a sulfur-arene (sulfur-π)[11,12] and three C-H---O intermolecular interactions.

(i) S1---π (sulfur- π)

Distance S1---C4(ring edge) = 3.484 Å

Distance S1---centroid:C1-C6 = 3.890 Å

Angle S1---cenroid:C1-C6---C4(ring plane) = 62.89°

(ii) C9-H9---O2

Distance H9---O2 = 2.530 Å; Angle C9-H9---O2 = 137.61°

(iii) C10-H10---O1

Distance H10---O1 = 2.583 Å; Angle C10-H10---O1 = 147.85°

(iv) C13-H13C---O1

Distance H13C---O1 = 2.540 Å; Angle C13-H13C---O1 = 172.14°

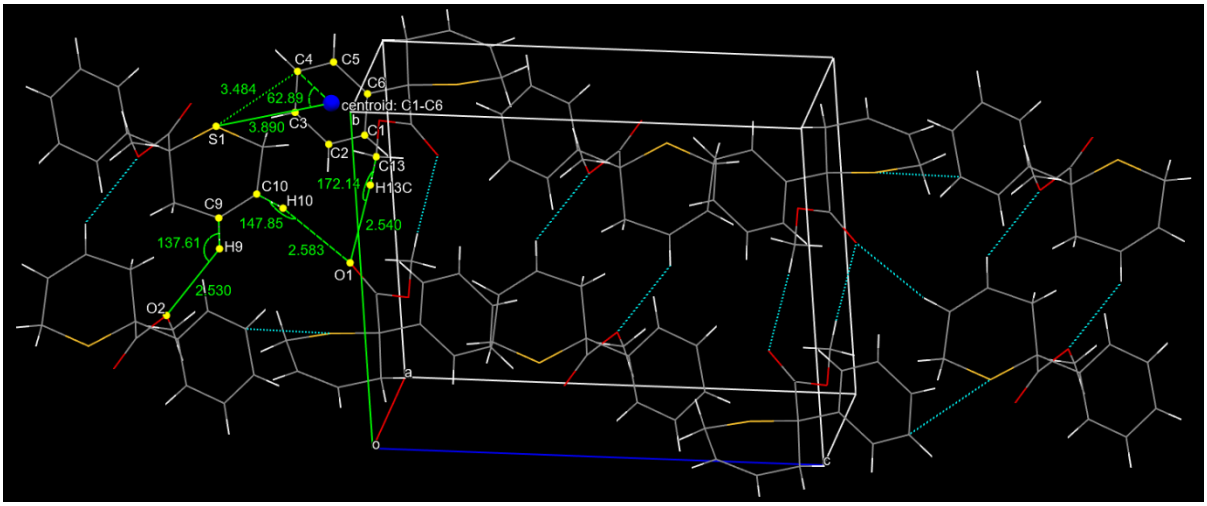


Figure S2. Sulfur---π and C-H---O intermolecular interactions of compound **4b**

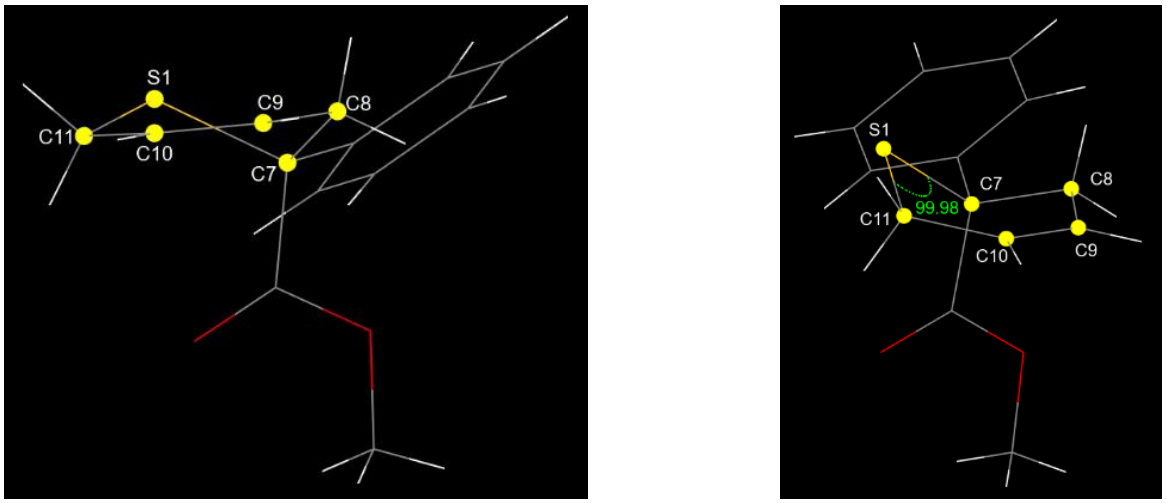


Figure S3. Thiopyran in compound **4b** exist as half-chair form with bond angle 99.98° of C-S-C

9. Crystal data and structure refinement for compound 4u*1*

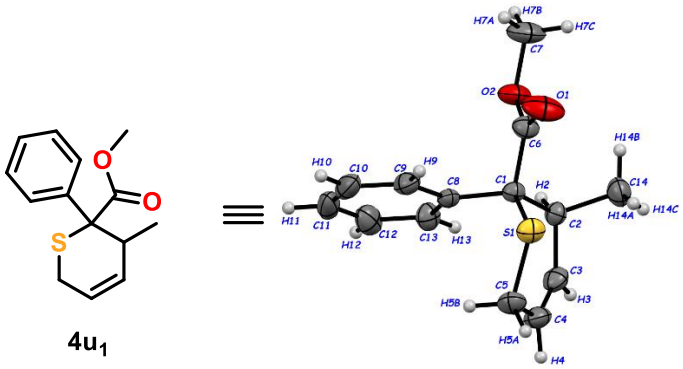


Figure S4. ORTEP diagram of compound **4u*1*** showing thermal ellipsoids at the 40% probability level

Table S8. Crystal data and structure refinement for **4u*1***

CCDC	2332012
Empirical formula	$C_{14}H_{16}O_2S$
Formula weight	248.33
Temperature/K	298(2)
Crystal system	Triclinic
Space group	*P* -1
a (Å)	7.7176(9)
b (Å)	8.7676(11)
c (Å)	10.6594(13)
α (°)	84.913(5)
β (°)	82.334(4)
γ (°)	65.082(4)
Volume (Å^3)	647.86(14)
Z	2
ρ_{calc} (mg m^{-3})	1.273
μ (mm^{-1})	0.237
F(000)	264
Crystal size (mm)	0.202 (max) × 0.127 (mid) × 0.074 (min)
Radiation	MoKα (λ = 0.71073Å)
Theta range for data collection (°)	3.329 to 27.128
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected / unique	27420 / 2847 [R_{int} = 0.0654]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.667
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2847/0/156

Goodness-of-fit on F^2	1.185
Final R indices [I>2σ (I)]	R_1 = 0.0614, wR_2 = 0.1614
R indices [all data]	R_1 = 0.0817, wR_2 = 0.1812
Largest diff. peak and hole (e $Å^{-3}$)	0.668 and -0.447

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4u*1*** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	5716(3)	6939(3)	2779(2)	32(1)
C(2)	3733(3)	7039(3)	3392(2)	36(1)
C(3)	2571(4)	6853(3)	2440(3)	46(1)
C(4)	2823(4)	7042(4)	1196(3)	50(1)
C(5)	4363(4)	7467(4)	472(3)	51(1)
C(6)	6629(4)	7532(3)	3709(2)	42(1)
C(7)	7779(6)	6997(5)	5712(3)	70(1)
C(8)	7143(3)	5166(3)	2382(2)	33(1)
C(9)	8928(4)	4955(4)	1747(2)	46(1)
C(10)	10284(4)	3386(5)	1406(3)	61(1)
C(11)	9891(5)	1983(4)	1670(3)	63(1)
C(12)	8149(5)	2169(4)	2292(3)	59(1)
C(13)	6780(4)	3745(3)	2644(3)	46(1)
C(14)	2530(4)	8657(4)	4113(3)	54(1)
O(1)	6983(4)	8738(3)	3544(2)	74(1)
O(2)	6971(3)	6524(2)	4742(2)	52(1)
S(1)	5358(1)	8443(1)	1417(1)	45(1)

Table S10. Bond lengths [Å] for **4u*1***

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
C(1)-C(6)	1.529(3)	C(7)-H(7A)	0.9600
C(1)-C(8)	1.535(3)	C(7)-H(7B)	0.9600
C(1)-C(2)	1.552(3)	C(7)-H(7C)	0.9600
C(1)-S(1)	1.839(2)	C(8)-C(13)	1.386(3)
C(2)-C(3)	1.502(3)	C(8)-C(9)	1.396(3)
C(2)-C(14)	1.535(3)	C(9)-C(10)	1.375(4)
C(2)-H(2)	0.9800	C(9)-H(9)	0.9300
C(3)-C(4)	1.321(4)	C(10)-C(11)	1.384(5)
C(3)-H(3)	0.9300	C(10)-H(10)	0.9300
C(4)-C(5)	1.491(4)	C(11)-C(12)	1.368(5)
C(4)-H(4)	0.9300	C(11)-H(11)	0.9300
C(5)-S(1)	1.802(3)	C(12)-C(13)	1.387(4)
C(5)-H(5A)	0.9700	C(12)-H(12)	0.9300
C(5)-H(5B)	0.9700	C(13)-H(13)	0.9300
C(6)-O(1)	1.192(3)	C(14)-H(14A)	0.9600
C(6)-O(2)	1.331(3)	C(14)-H(14B)	0.9600
C(7)-O(2)	1.448(3)	C(14)-H(14C)	0.9600

Symmetry transformations used to generate equivalent atoms:

Table S11. Bond angles [°] for **4u*1***

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C(6)-C(1)-C(8)	107.93(18)	O(2)-C(7)-H(7C)	109.5

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C(6)-C(1)-C(2)	109.62(18)	H(7A)-C(7)-H(7C)	109.5
C(8)-C(1)-C(2)	113.95(18)	H(7B)-C(7)-H(7C)	109.5
C(6)-C(1)-S(1)	105.31(15)	C(13)-C(8)-C(9)	117.7(2)
C(8)-C(1)-S(1)	110.61(15)	C(13)-C(8)-C(1)	123.7(2)
C(2)-C(1)-S(1)	109.05(15)	C(9)-C(8)-C(1)	118.6(2)
C(3)-C(2)-C(14)	109.1(2)	C(10)-C(9)-C(8)	121.0(3)
C(3)-C(2)-C(1)	112.15(19)	C(10)-C(9)-H(9)	119.5
C(14)-C(2)-C(1)	113.5(2)	C(8)-C(9)-H(9)	119.5
C(3)-C(2)-H(2)	107.2	C(9)-C(10)-C(11)	120.5(3)
C(14)-C(2)-H(2)	107.2	C(9)-C(10)-H(10)	119.8
C(1)-C(2)-H(2)	107.2	C(11)-C(10)-H(10)	119.8
C(4)-C(3)-C(2)	127.4(2)	C(12)-C(11)-C(10)	119.2(3)
C(4)-C(3)-H(3)	116.3	C(12)-C(11)-H(11)	120.4
C(2)-C(3)-H(3)	116.3	C(10)-C(11)-H(11)	120.4
C(3)-C(4)-C(5)	125.5(2)	C(11)-C(12)-C(13)	120.6(3)
C(3)-C(4)-H(4)	117.2	C(11)-C(12)-H(12)	119.7
C(5)-C(4)-H(4)	117.2	C(13)-C(12)-H(12)	119.7
C(4)-C(5)-S(1)	113.18(19)	C(8)-C(13)-C(12)	121.0(3)
C(4)-C(5)-H(5A)	108.9	C(8)-C(13)-H(13)	119.5
S(1)-C(5)-H(5A)	108.9	C(12)-C(13)-H(13)	119.5
C(4)-C(5)-H(5B)	108.9	C(2)-C(14)-H(14A)	109.5
S(1)-C(5)-H(5B)	108.9	C(2)-C(14)-H(14B)	109.5
H(5A)-C(5)-H(5B)	107.8	H(14A)-C(14)-H(14B)	109.5
O(1)-C(6)-O(2)	124.1(2)	C(2)-C(14)-H(14C)	109.5
O(1)-C(6)-C(1)	125.0(2)	H(14A)-C(14)-H(14C)	109.5
O(2)-C(6)-C(1)	110.86(19)	H(14B)-C(14)-H(14C)	109.5
O(2)-C(7)-H(7A)	109.5	C(6)-O(2)-C(7)	115.7(2)
O(2)-C(7)-H(7B)	109.5	C(5)-S(1)-C(1)	96.92(12)
H(7A)-C(7)-H(7B)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4u*1***. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
C(1)	36(1)	31(1)	31(1)	2(1)	-7(1)	-16(1)
C(2)	34(1)	36(1)	37(1)	0(1)	-2(1)	-14(1)
C(3)	35(1)	49(2)	58(2)	-1(1)	-7(1)	-20(1)
C(4)	47(1)	52(2)	53(2)	0(1)	-21(1)	-20(1)
C(5)	57(2)	57(2)	38(1)	2(1)	-16(1)	-21(1)
C(6)	49(1)	41(1)	42(1)	0(1)	-8(1)	-25(1)
C(7)	101(3)	76(2)	59(2)	6(2)	-40(2)	-55(2)
C(8)	32(1)	37(1)	28(1)	1(1)	-10(1)	-12(1)
C(9)	37(1)	62(2)	41(1)	-1(1)	-7(1)	-22(1)
C(10)	36(1)	84(2)	45(2)	-6(2)	-7(1)	-6(1)
C(11)	61(2)	51(2)	46(2)	-6(1)	-16(1)	11(1)
C(12)	78(2)	38(2)	53(2)	2(1)	-12(2)	-15(1)
C(13)	51(2)	35(1)	50(2)	2(1)	-5(1)	-15(1)
C(14)	52(2)	50(2)	52(2)	-11(1)	3(1)	-13(1)
O(1)	124(2)	74(2)	65(1)	14(1)	-33(1)	-77(2)
O(2)	76(1)	52(1)	45(1)	9(1)	-29(1)	-38(1)
S(1)	54(1)	42(1)	42(1)	11(1)	-12(1)	-24(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4u*1***

	x	y	z	U(eq)
H(2)	3975	6093	4008	43
H(3)	1558	6573	2764	55
H(4)	1968	6898	732	60
H(5A)	3839	8223	-237	61
H(5B)	5386	6447	133	61
H(7A)	8952	7074	5357	105
H(7B)	8040	6164	6393	105
H(7C)	6881	8069	6029	105
H(9)	9205	5888	1552	55
H(10)	11472	3269	995	73
H(11)	10801	926	1426	76
H(12)	7880	1230	2481	71
H(13)	5600	3850	3063	56
H(14A)	2372	9617	3555	81
H(14B)	3174	8686	4816	81
H(14C)	1292	8679	4420	81

Table S14. Torsion angles [°] for **4u*1***

C(6)-C(1)-C(2)-C(3)	167.1(2)
C(8)-C(1)-C(2)-C(3)	-71.9(2)
S(1)-C(1)-C(2)-C(3)	52.2(2)
C(6)-C(1)-C(2)-C(14)	42.8(3)
C(8)-C(1)-C(2)-C(14)	163.9(2)
S(1)-C(1)-C(2)-C(14)	-72.0(2)
C(14)-C(2)-C(3)-C(4)	108.4(3)
C(1)-C(2)-C(3)-C(4)	-18.2(4)
C(2)-C(3)-C(4)-C(5)	0.8(5)
C(3)-C(4)-C(5)-S(1)	-21.1(4)
C(8)-C(1)-C(6)-O(1)	118.9(3)
C(2)-C(1)-C(6)-O(1)	-116.4(3)
S(1)-C(1)-C(6)-O(1)	0.7(3)
C(8)-C(1)-C(6)-O(2)	-61.5(3)
C(2)-C(1)-C(6)-O(2)	63.2(3)
S(1)-C(1)-C(6)-O(2)	-179.63(17)
C(6)-C(1)-C(8)-C(13)	116.4(2)
C(2)-C(1)-C(8)-C(13)	-5.6(3)
S(1)-C(1)-C(8)-C(13)	-128.9(2)
C(6)-C(1)-C(8)-C(9)	-62.1(3)
C(2)-C(1)-C(8)-C(9)	175.9(2)
S(1)-C(1)-C(8)-C(9)	52.7(2)
C(13)-C(8)-C(9)-C(10)	-0.6(4)
C(1)-C(8)-C(9)-C(10)	177.9(2)
C(8)-C(9)-C(10)-C(11)	1.0(4)
C(9)-C(10)-C(11)-C(12)	-1.0(4)
C(10)-C(11)-C(12)-C(13)	0.7(5)
C(9)-C(8)-C(13)-C(12)	0.3(4)
C(1)-C(8)-C(13)-C(12)	-178.1(2)
C(11)-C(12)-C(13)-C(8)	-0.4(4)
O(1)-C(6)-O(2)-C(7)	1.6(4)
C(1)-C(6)-O(2)-C(7)	-178.0(2)
C(4)-C(5)-S(1)-C(1)	47.5(2)

C(6)-C(1)-S(1)-C(5)	178.55(17)
C(8)-C(1)-S(1)-C(5)	62.19(17)
C(2)-C(1)-S(1)-C(5)	-63.87(18)

The following intermolecular interactions are present in compound **4u*1***

The molecules of compound **4u*1*** was aligned by di-hydrogen (C-H---H-C)[13–15] and C-H---O intermolecular interactions.

(i) C7-H7B---H3-C3

Distance H7B---H3 = 2.394 Å; Angle C7-H7B---H3 = 151.01°

Angle C3-H3---H7B = 123.94°

(ii) C12-H12---O1

Distance H12---O1 = 2.676 Å; Angle C12-H12---O1 = 167.50°

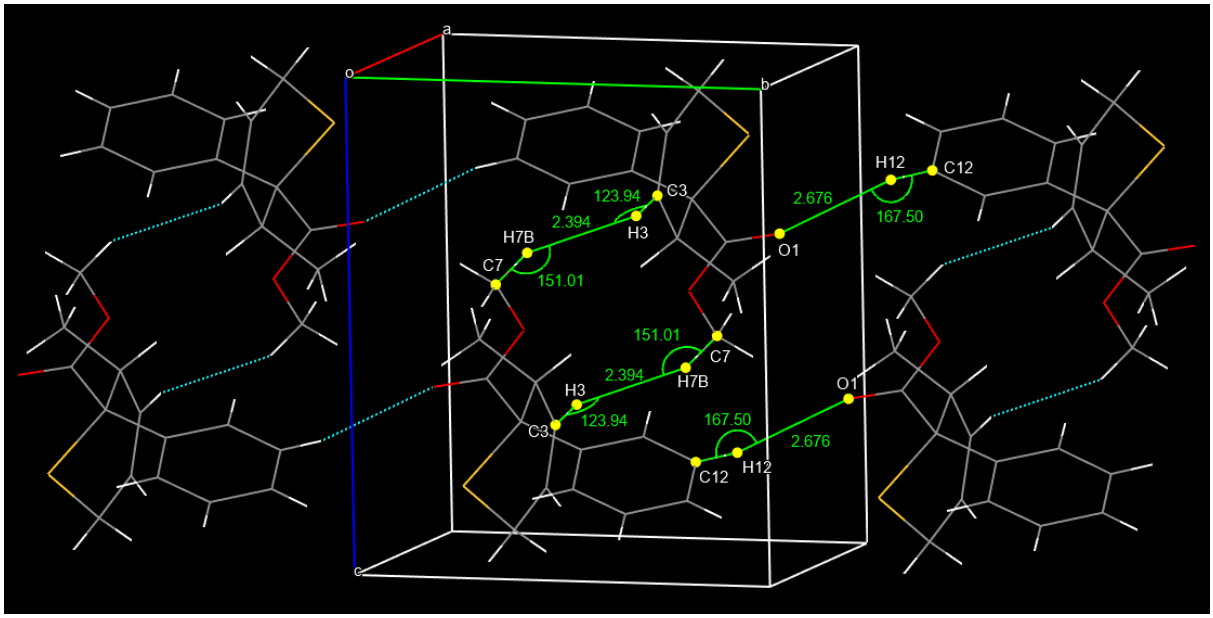


Figure S5. C-H---H-C and C-H---O intermolecular interactions of compound **4u1**

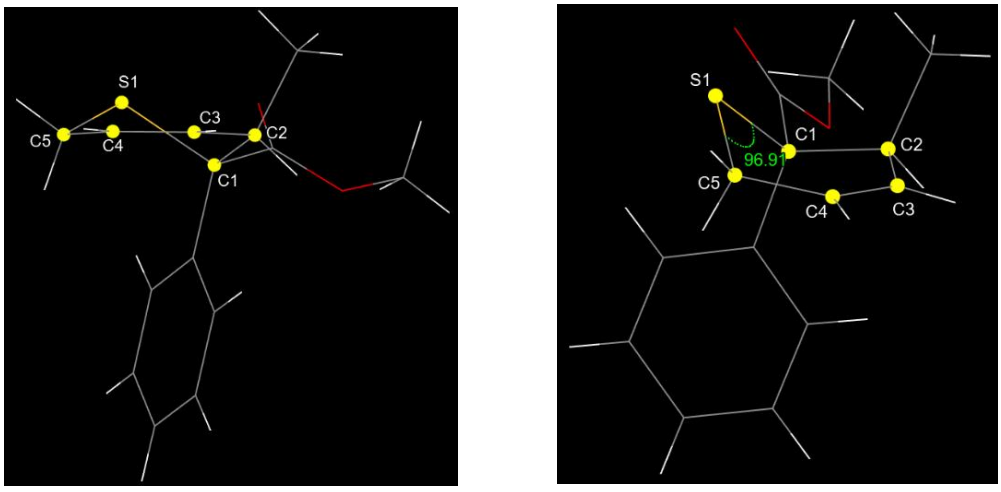


Figure S6. Thiopyran in compound **4u1** exist as half-chair form with bond angle 96.91° of C-S-C

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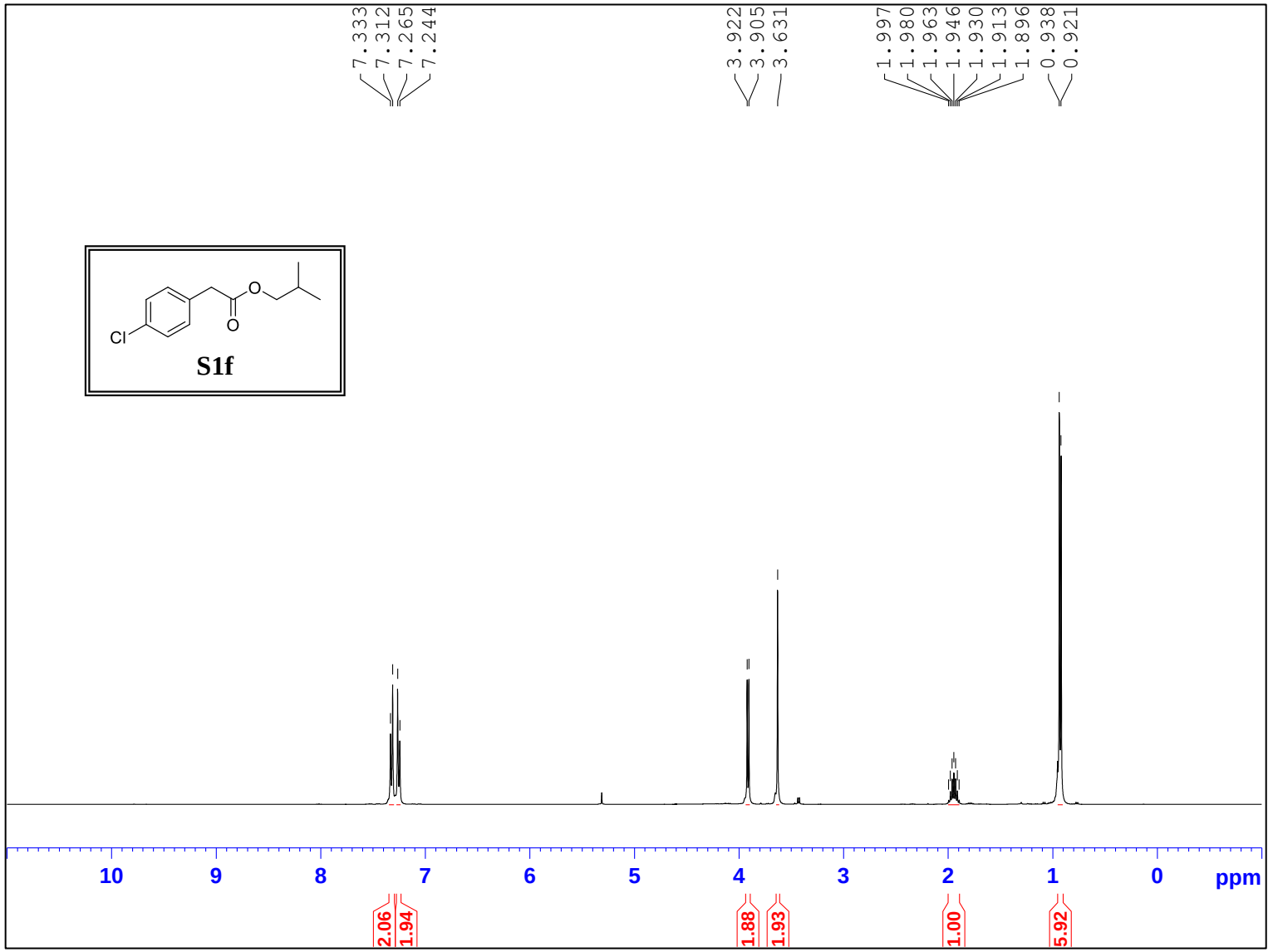
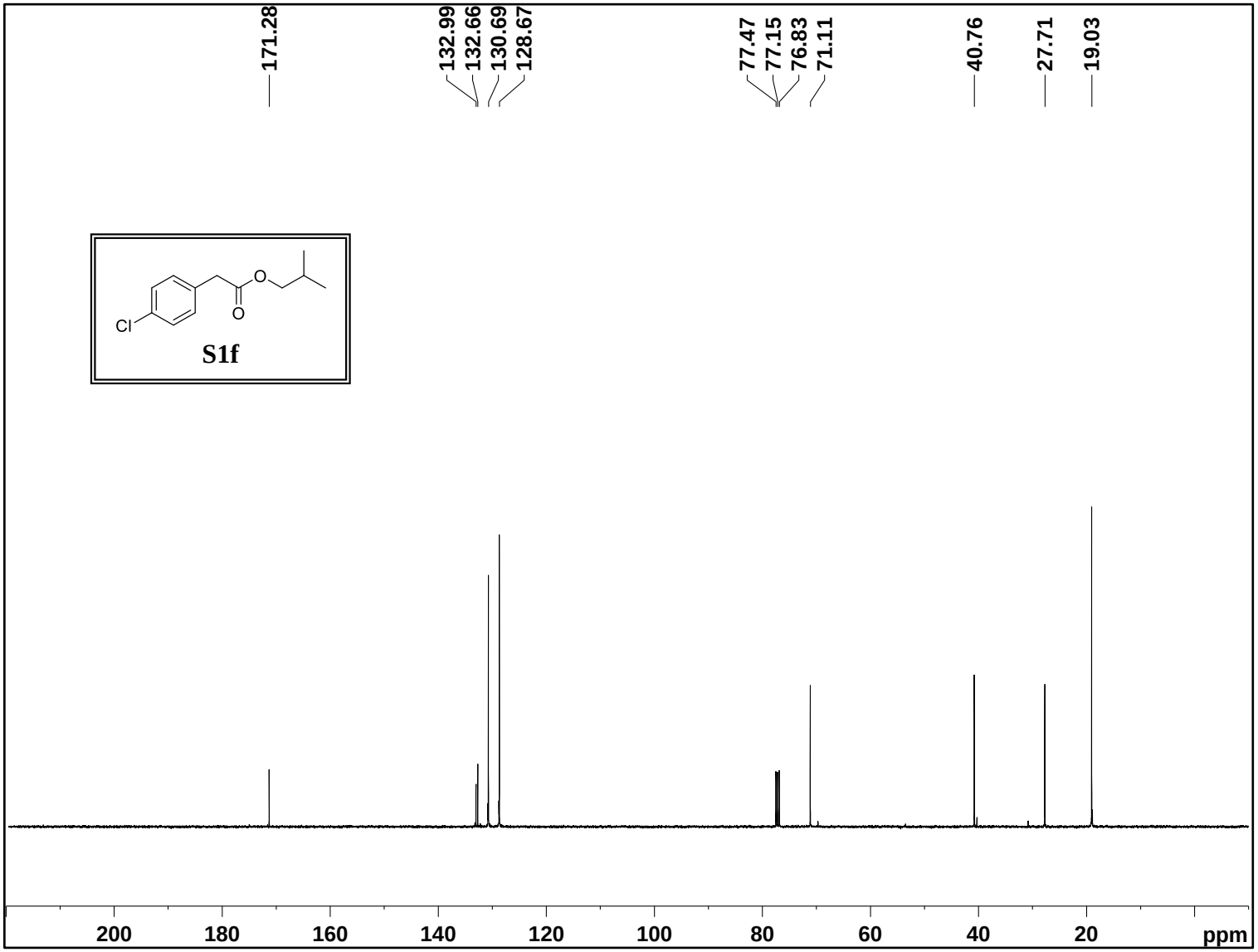
11. Copies of ^{1}H, ^{13}C, selected [DEPT-135, COSY, HSQC, HMBC, NOESY, and 1D-NOE] NMR spectra for compounds **S1**,**2**-**4**,**6**

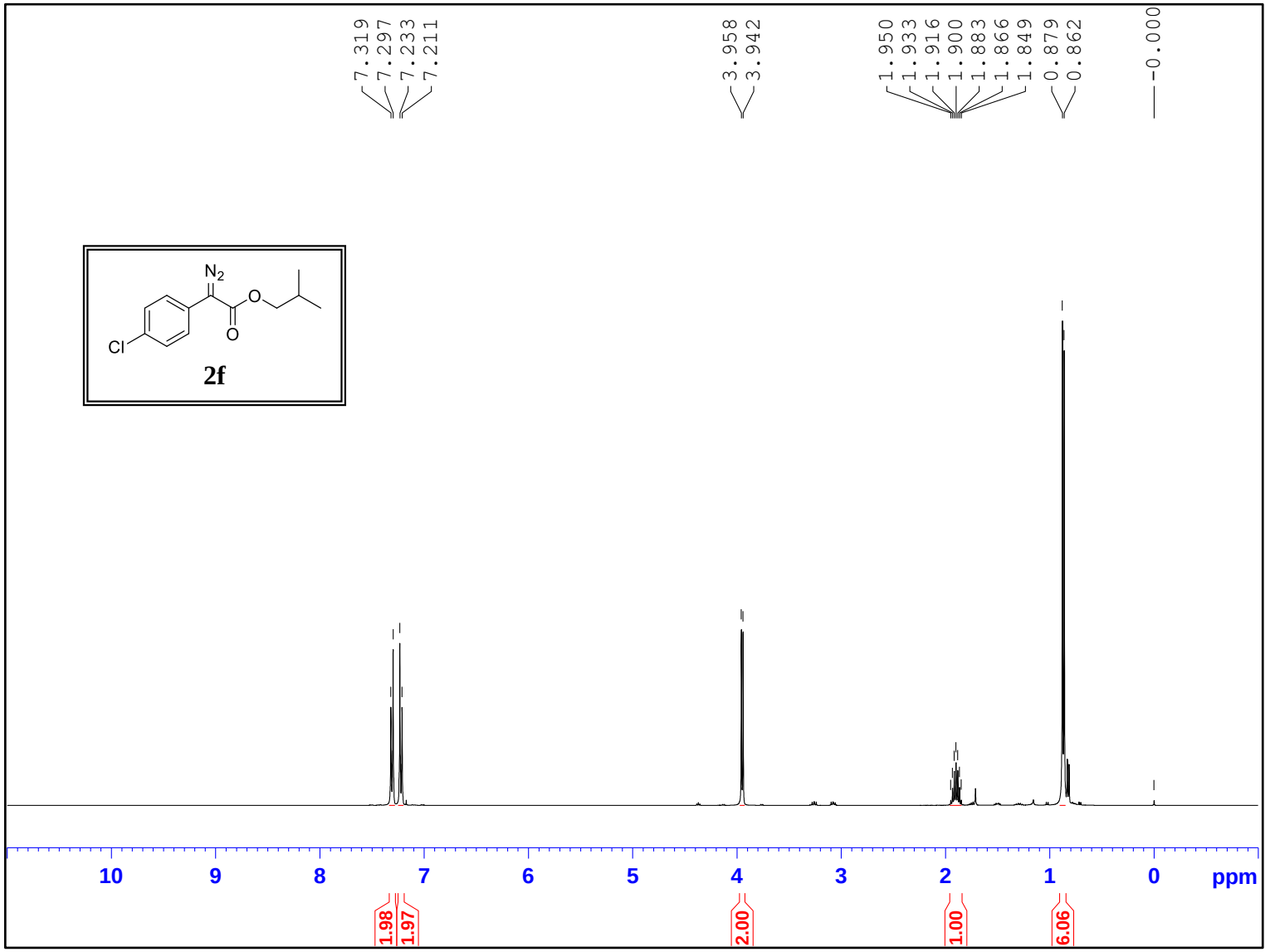
^{1}H NMR for compound **S1f** (400 MHz, $CDCl_3$) (**data**)



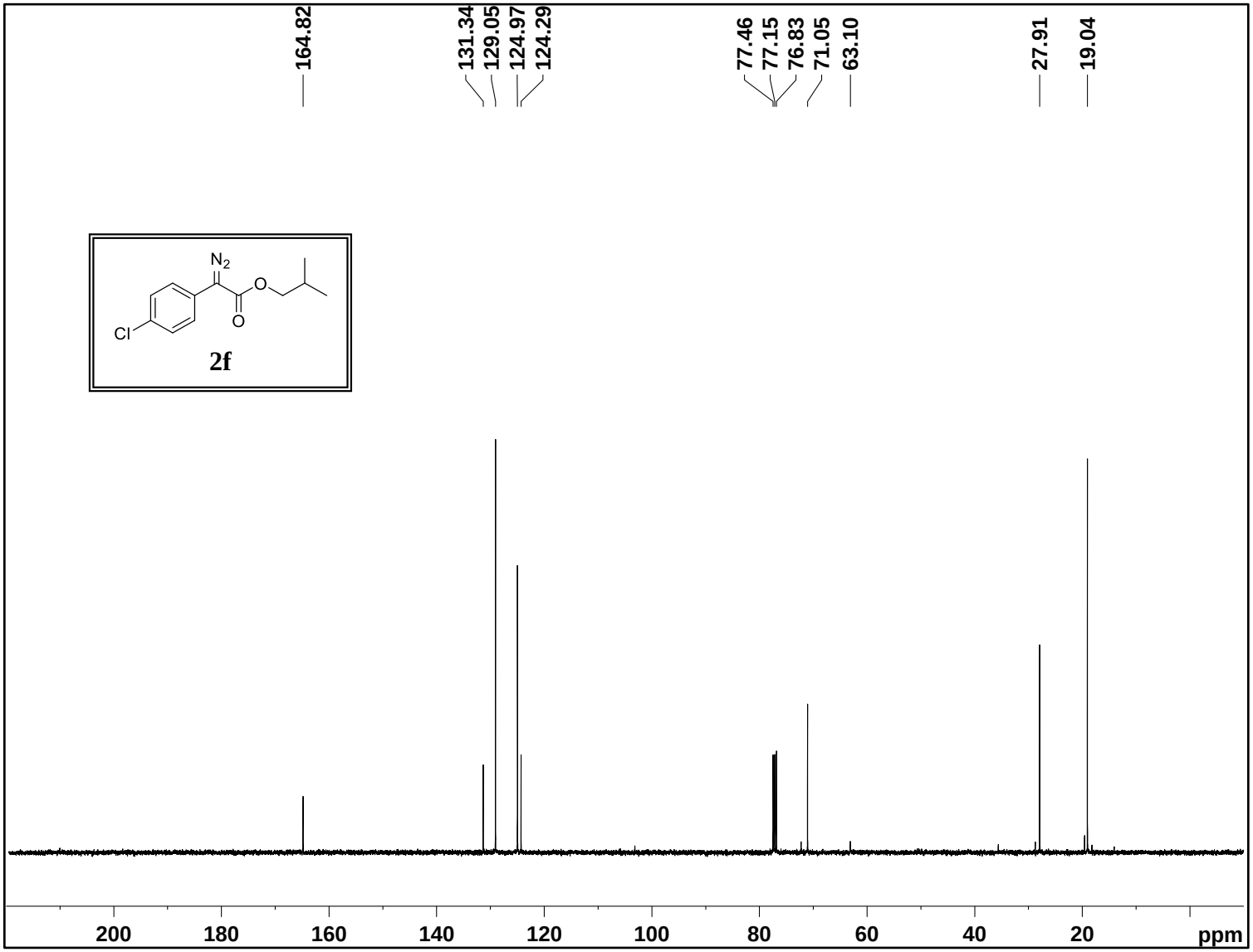
$^{13}C\{^{1}H\}$-NMR for compound **S1f** (101 MHz, $CDCl_3$)



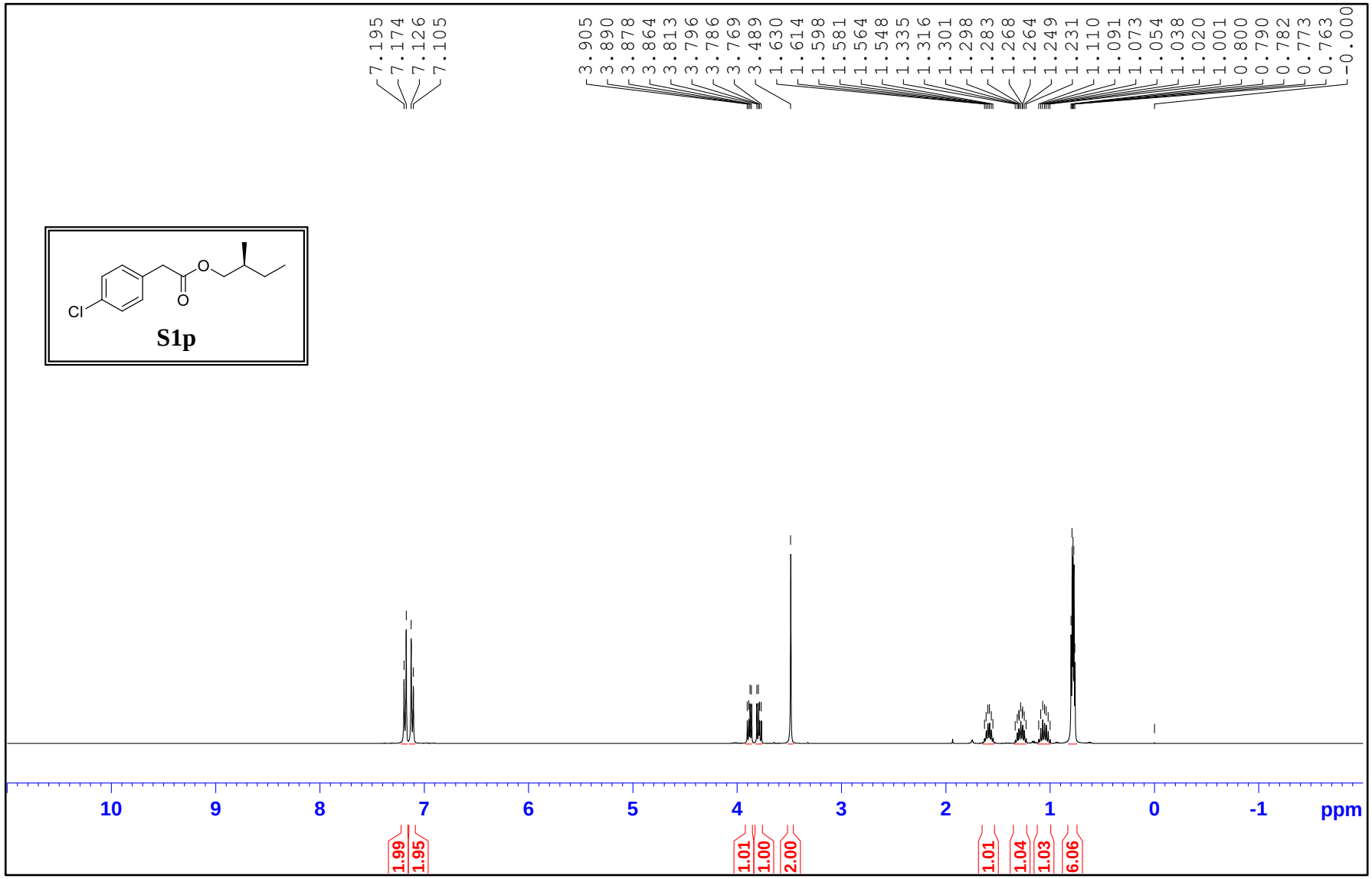
^{1}H NMR for compound **2f** (400 MHz, $CDCl_3$) (**data**)



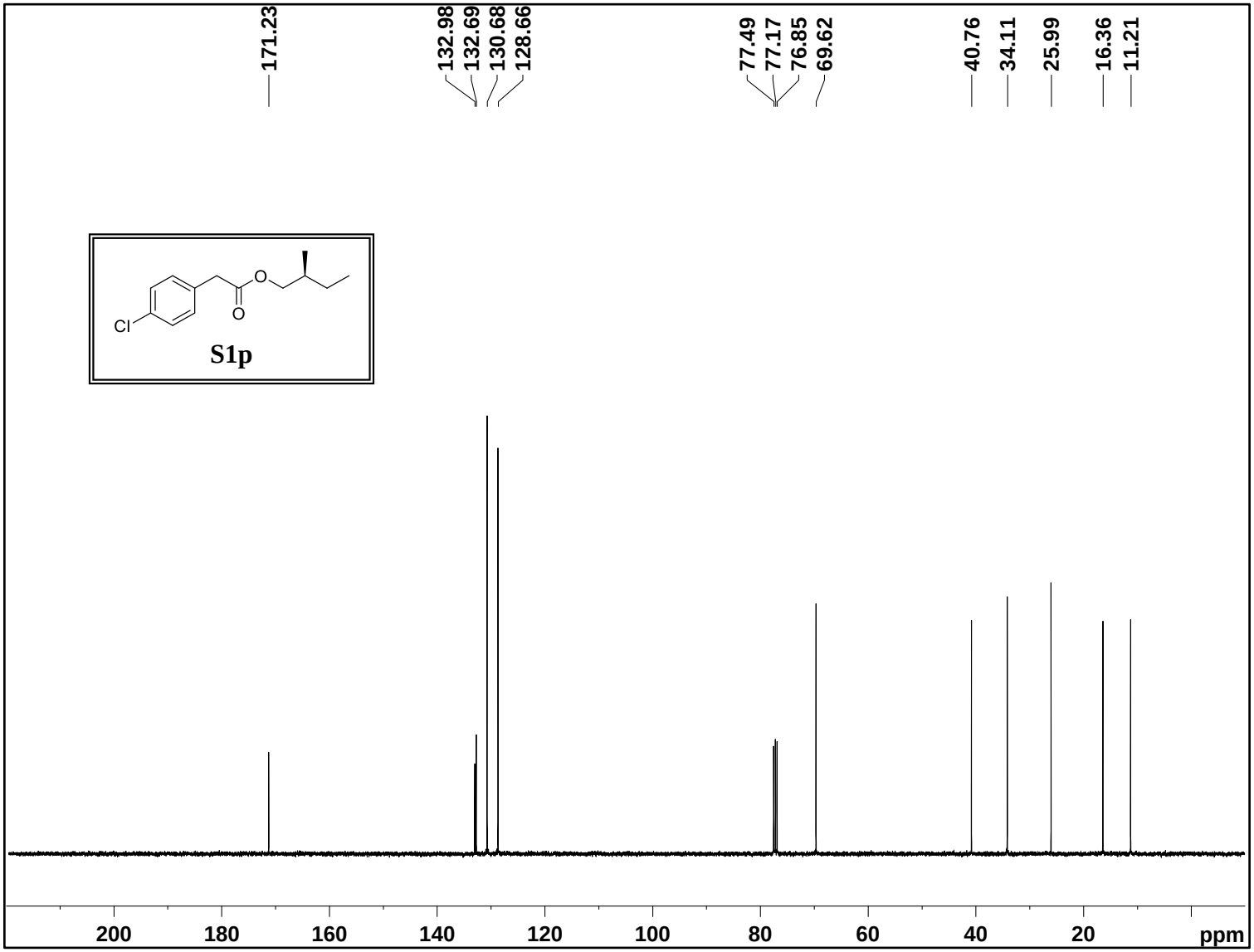
$^{13}C\{^{1}H\}$ NMR for compound **2f** (101 MHz, $CDCl_3$)



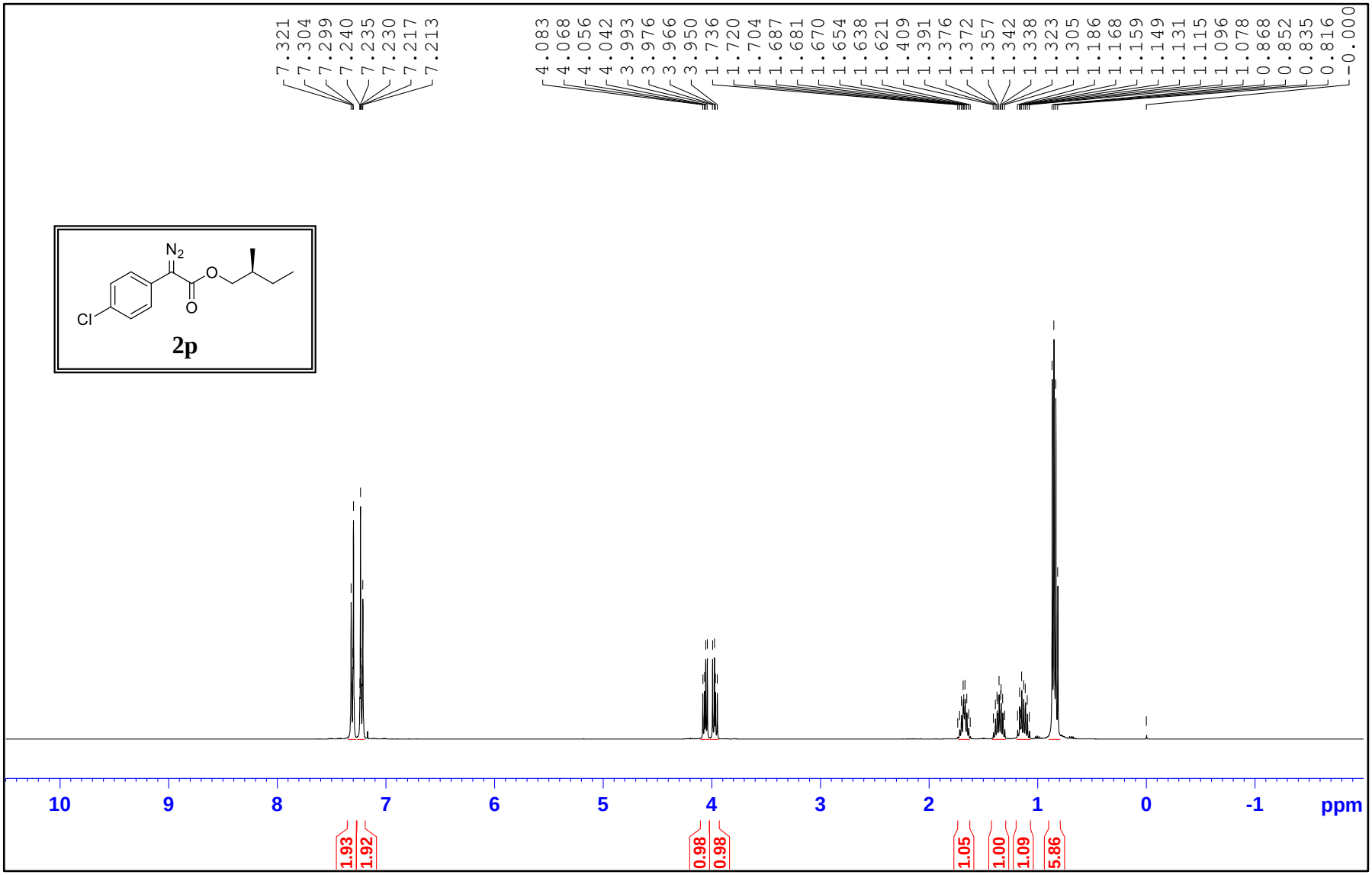
^{1}H NMR for compound **S1p** (400 MHz, $CDCl_3$) (**data**)



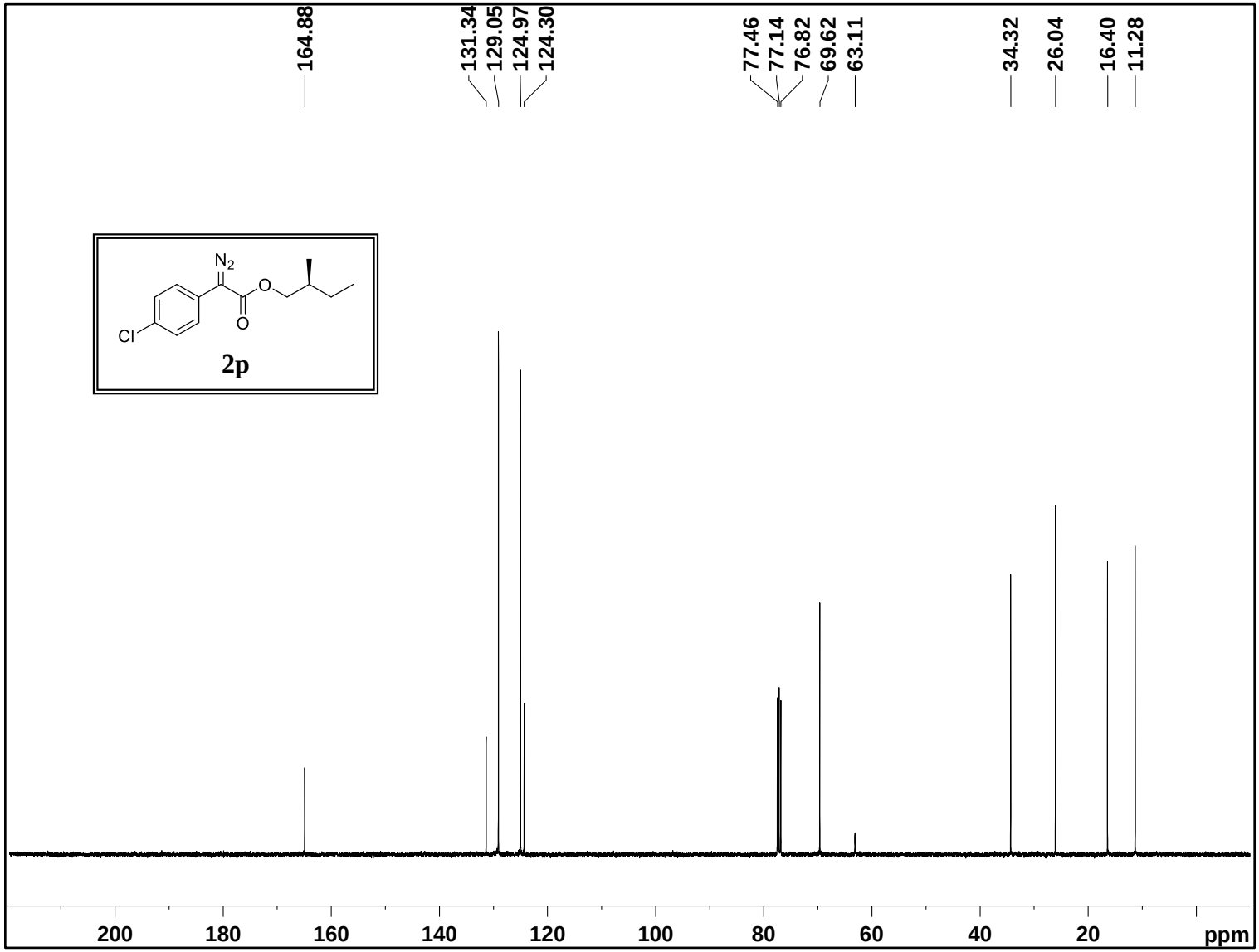
$^{13}C\{^{1}H\}$ NMR for compound **S1p** (101 MHz, $CDCl_3$)



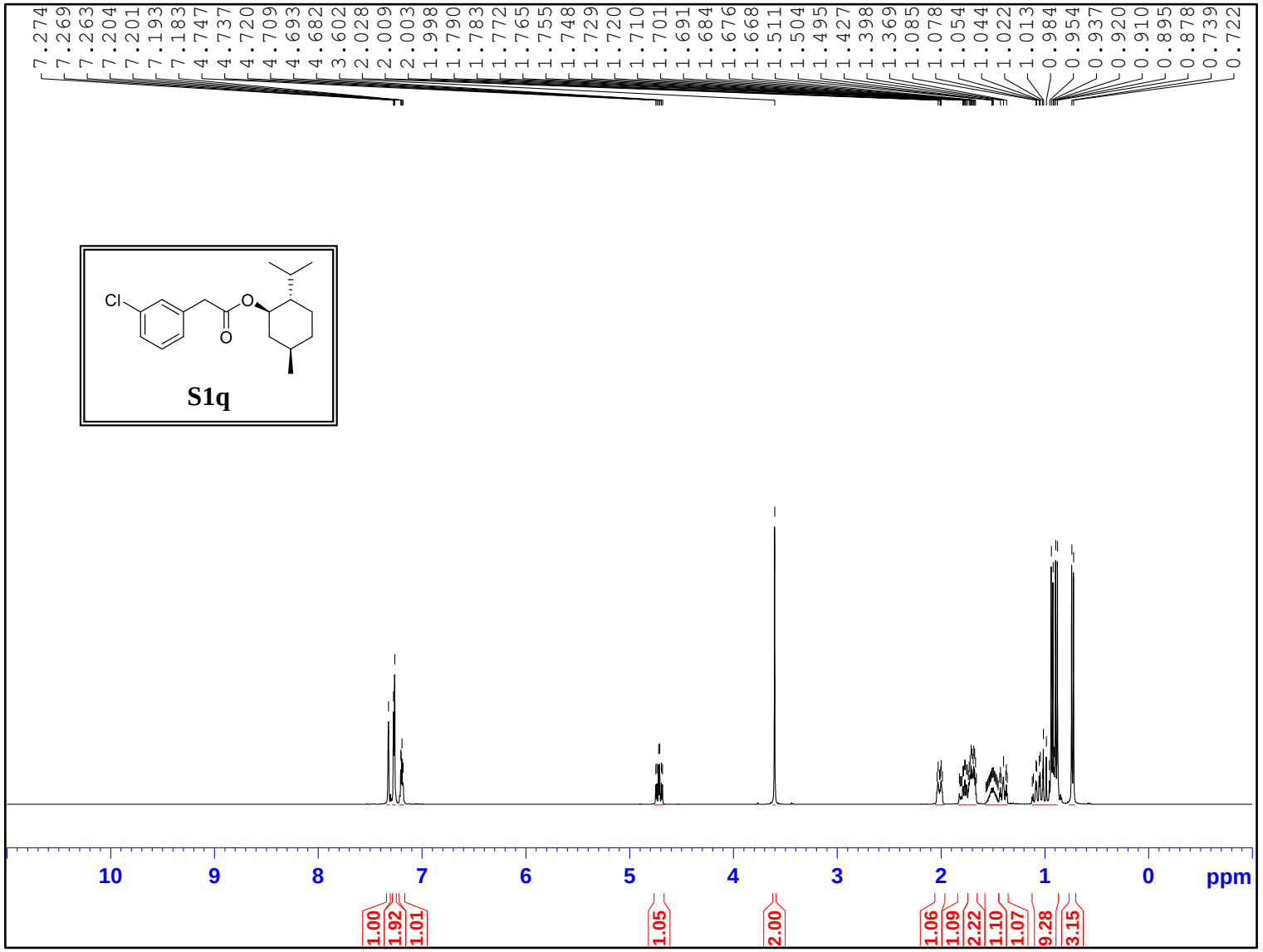
^{1}H NMR for compound **2p** (400 MHz, $CDCl_3$) (**data**)



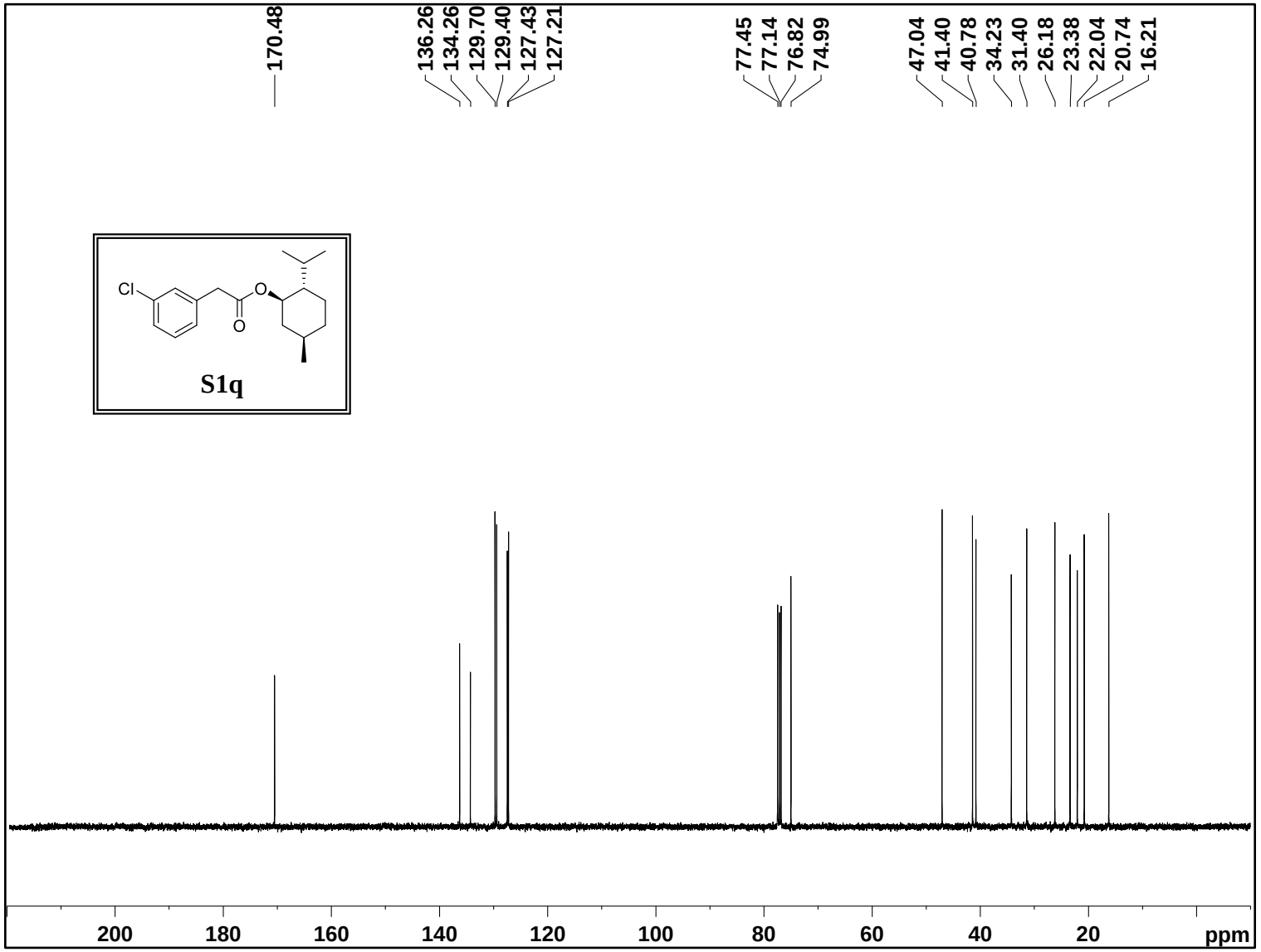
$^{13}C\{^{1}H\}$ NMR for compound **2p** (101 MHz, $CDCl_3$)



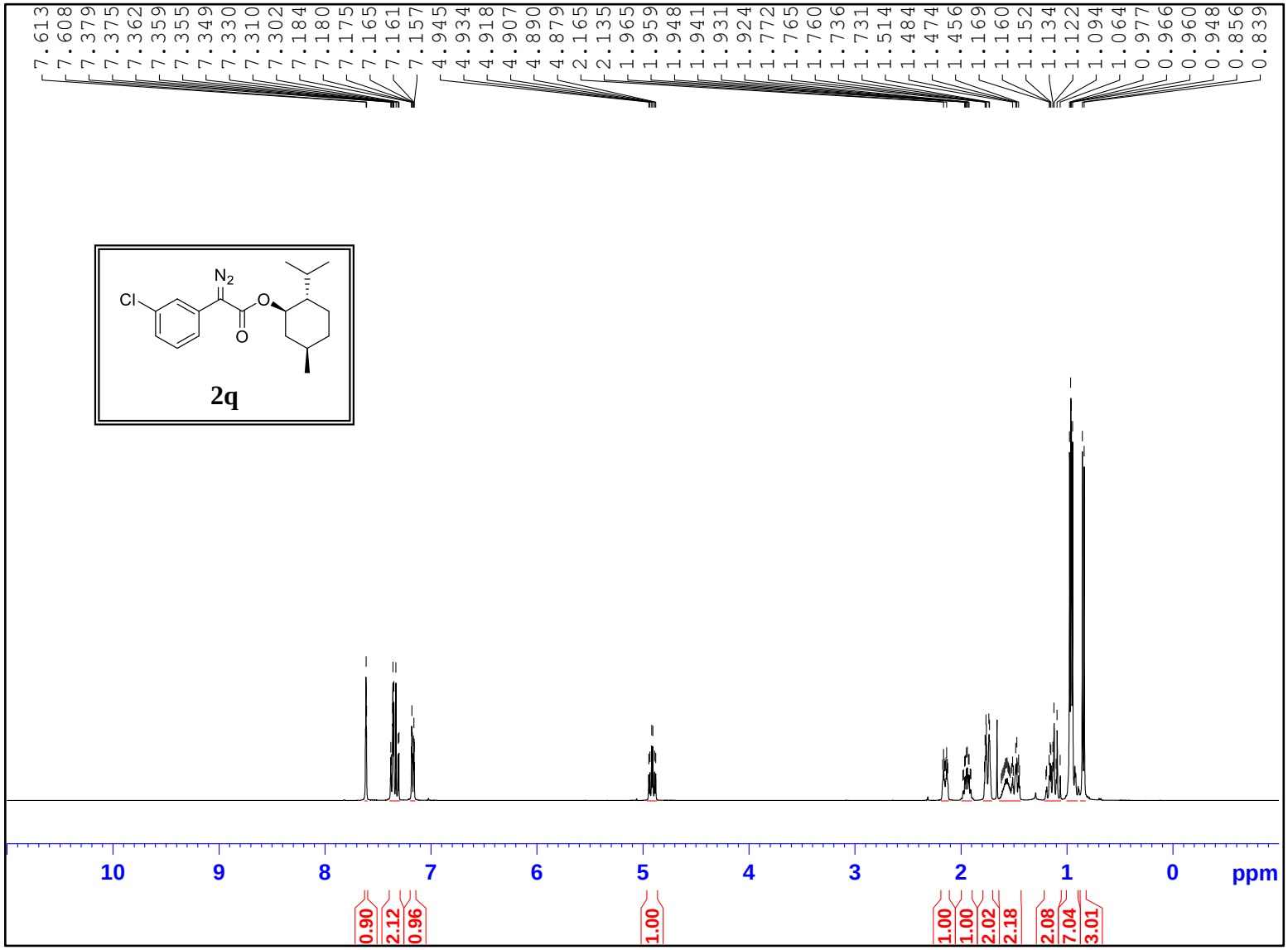
^{1}H NMR for compound **S1q** (400 MHz, $CDCl_3$) (**data**)



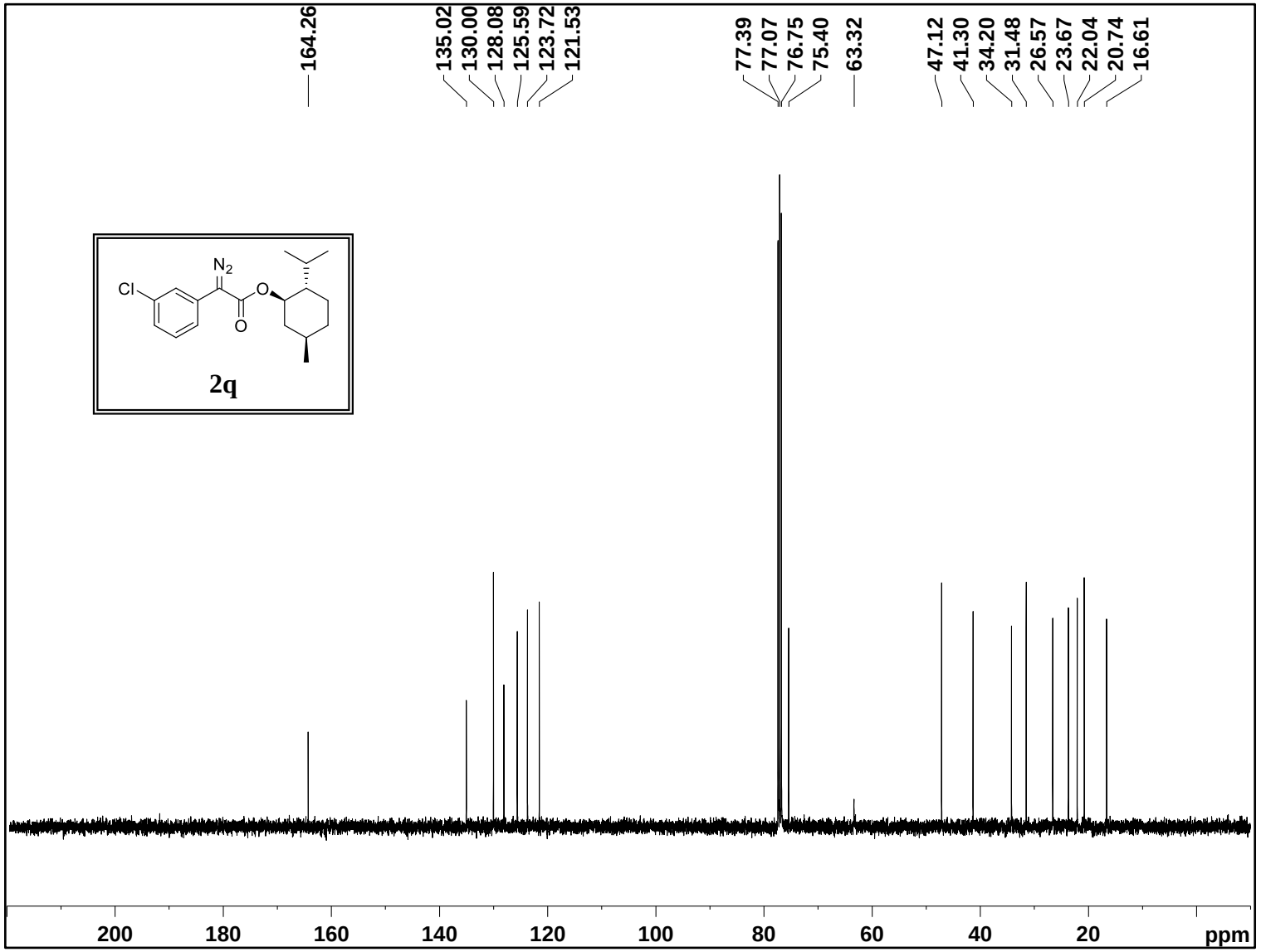
$^{13}C\{^{1}H\}$ NMR for compound **S1q** (101 MHz, $CDCl_3$)



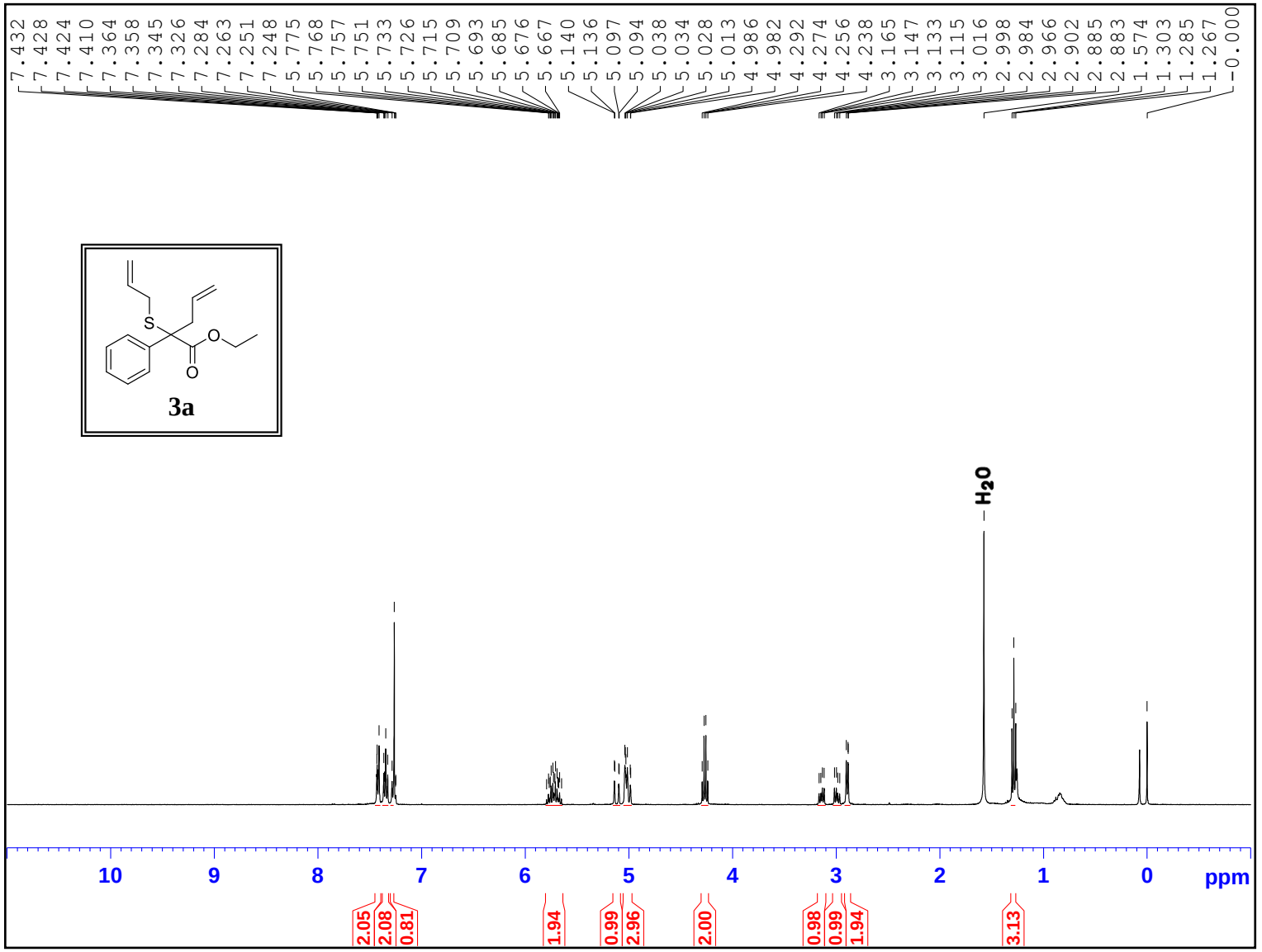
^{1}H NMR for compound **2q** (400 MHz, $CDCl_3$) (**data**)



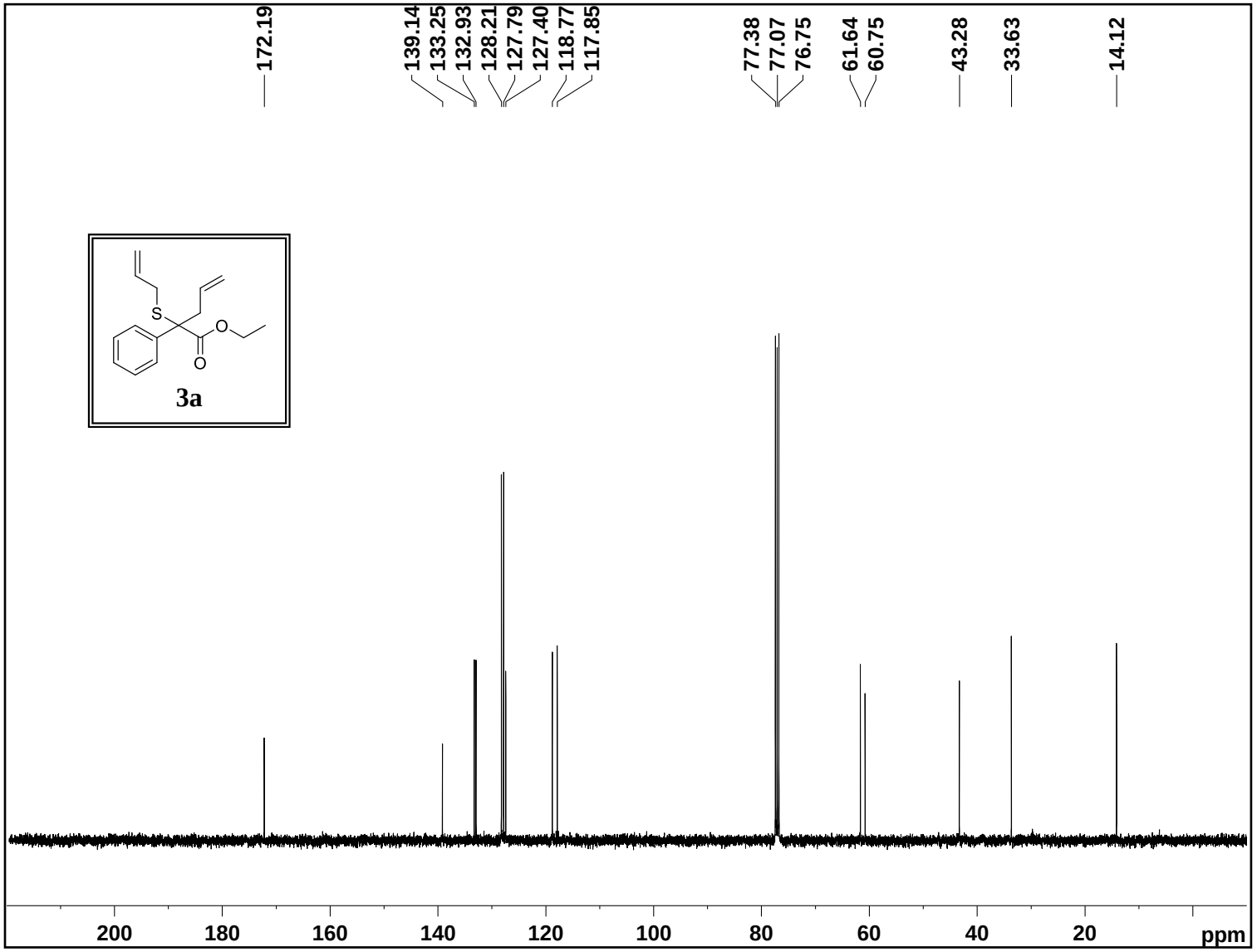
$^{13}C\{^{1}H\}$ NMR for compound **2q** (101 MHz, $CDCl_3$)



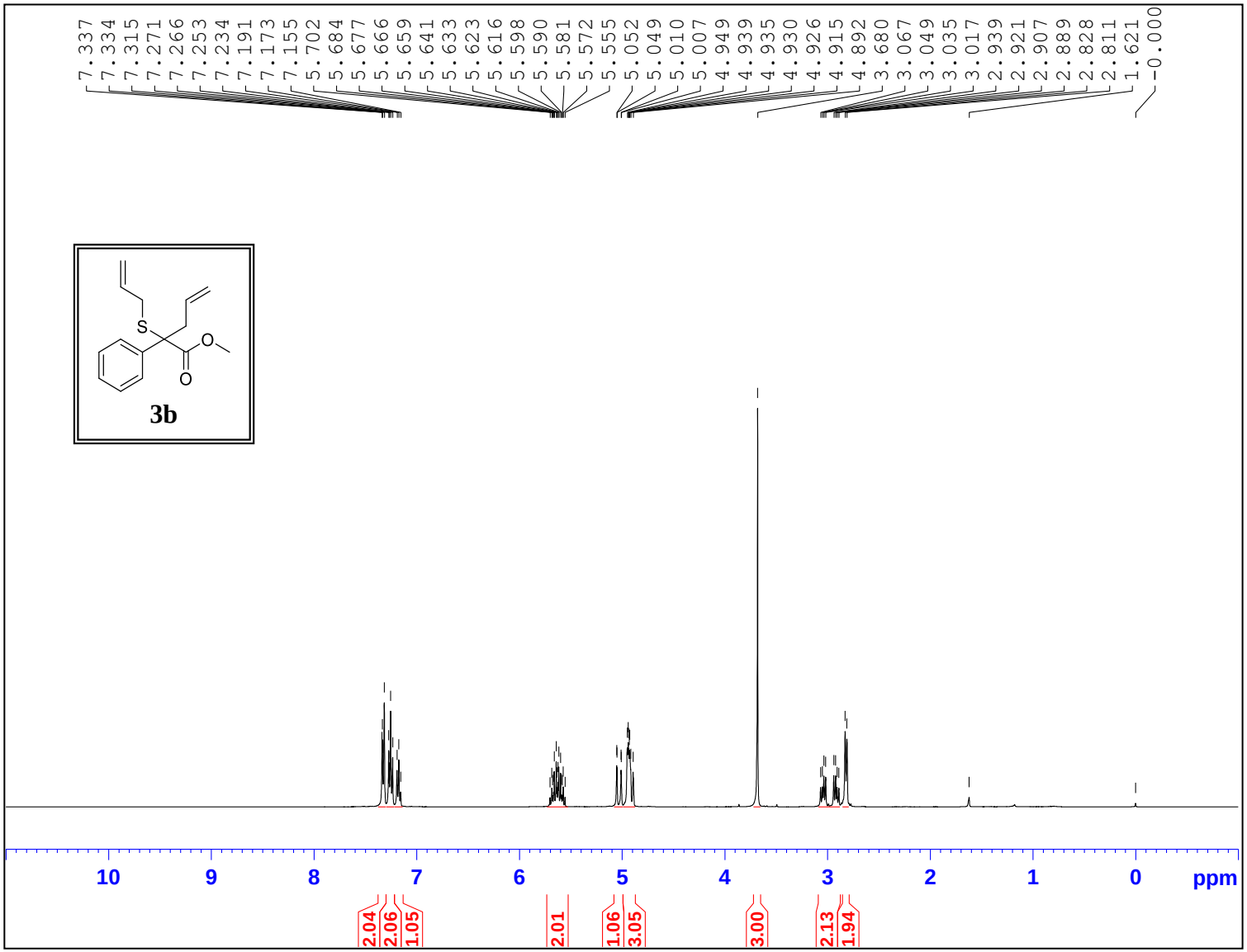
^{1}H NMR for compound **3a** (400 MHz, $CDCl_3$) (**data**)



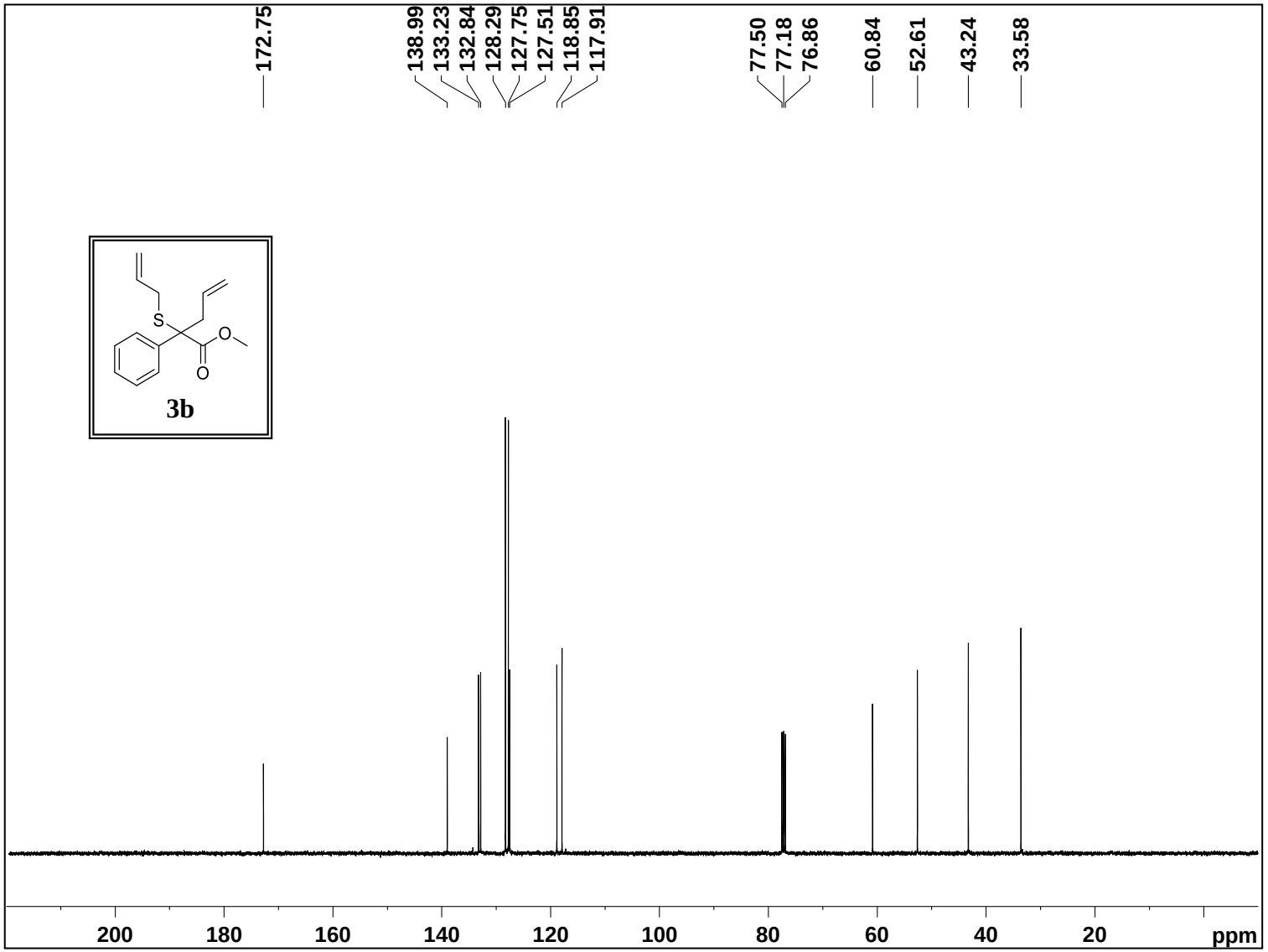
$^{13}C\{^{1}H\}$ NMR for compound **3a** (101 MHz, $CDCl_3$)



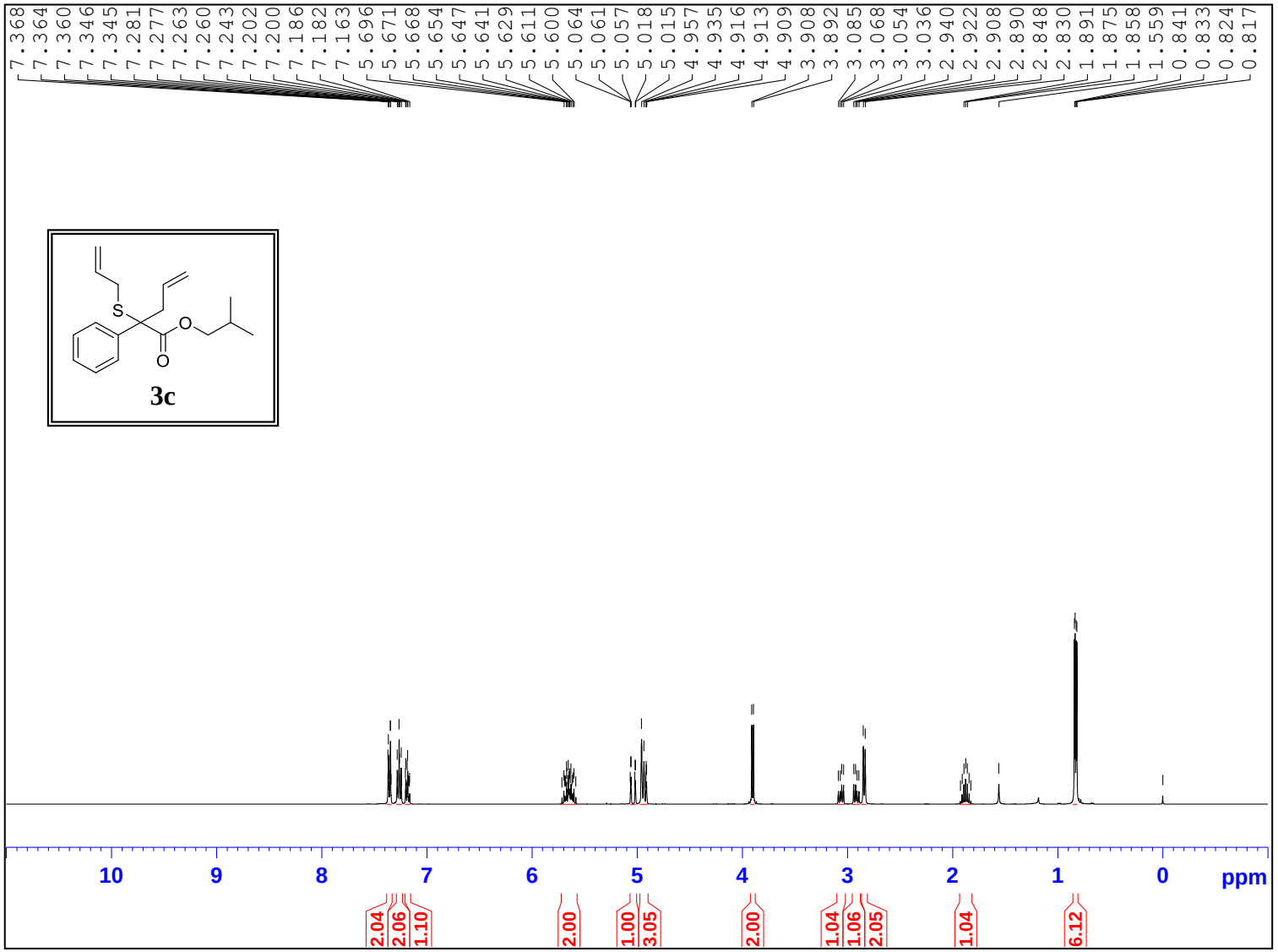
^{1}H NMR for compound **3b** (400 MHz, $CDCl_3$) (**data**)



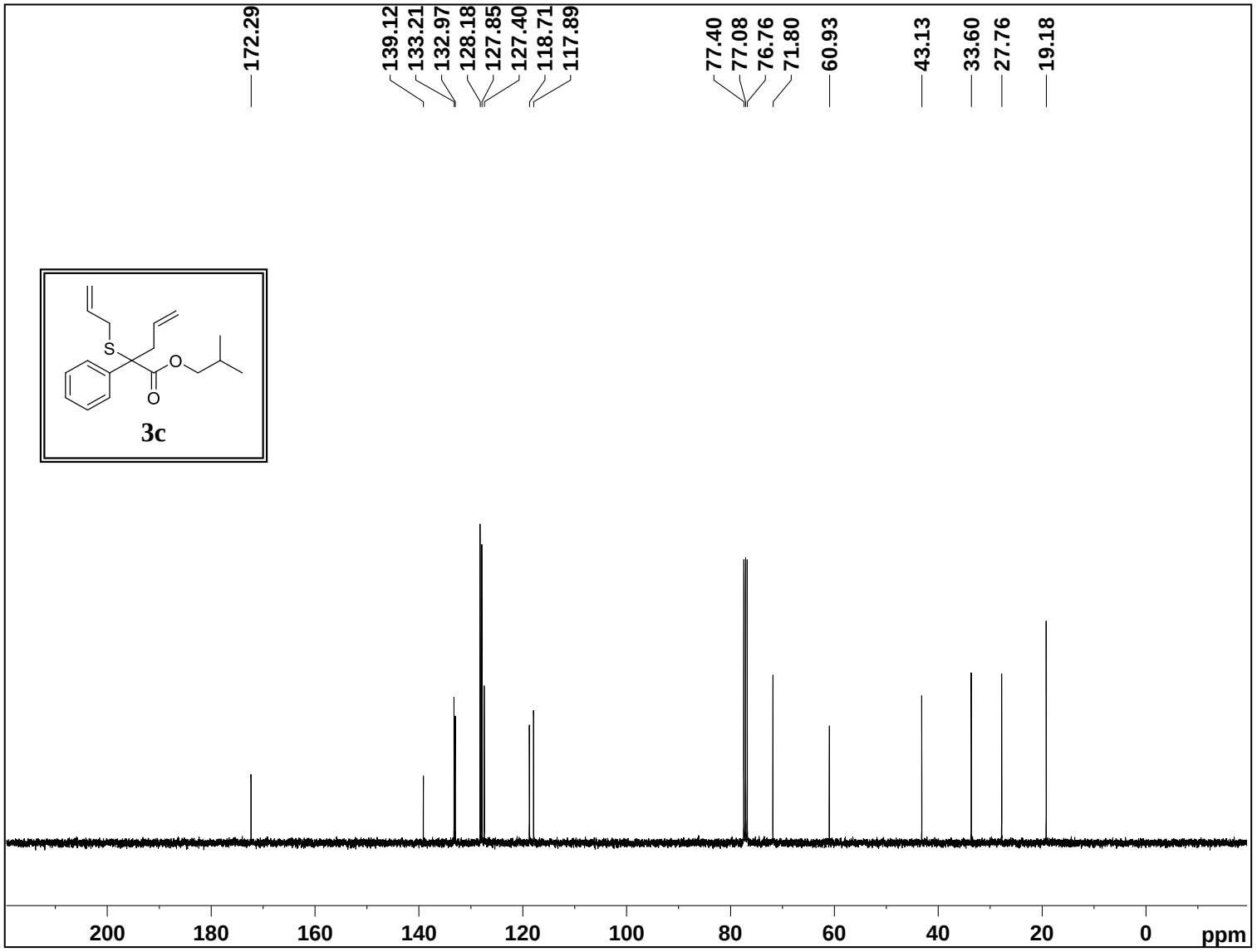
$^{13}C\{^{1}H\}$ NMR for compound **3b** (101 MHz, $CDCl_3$)



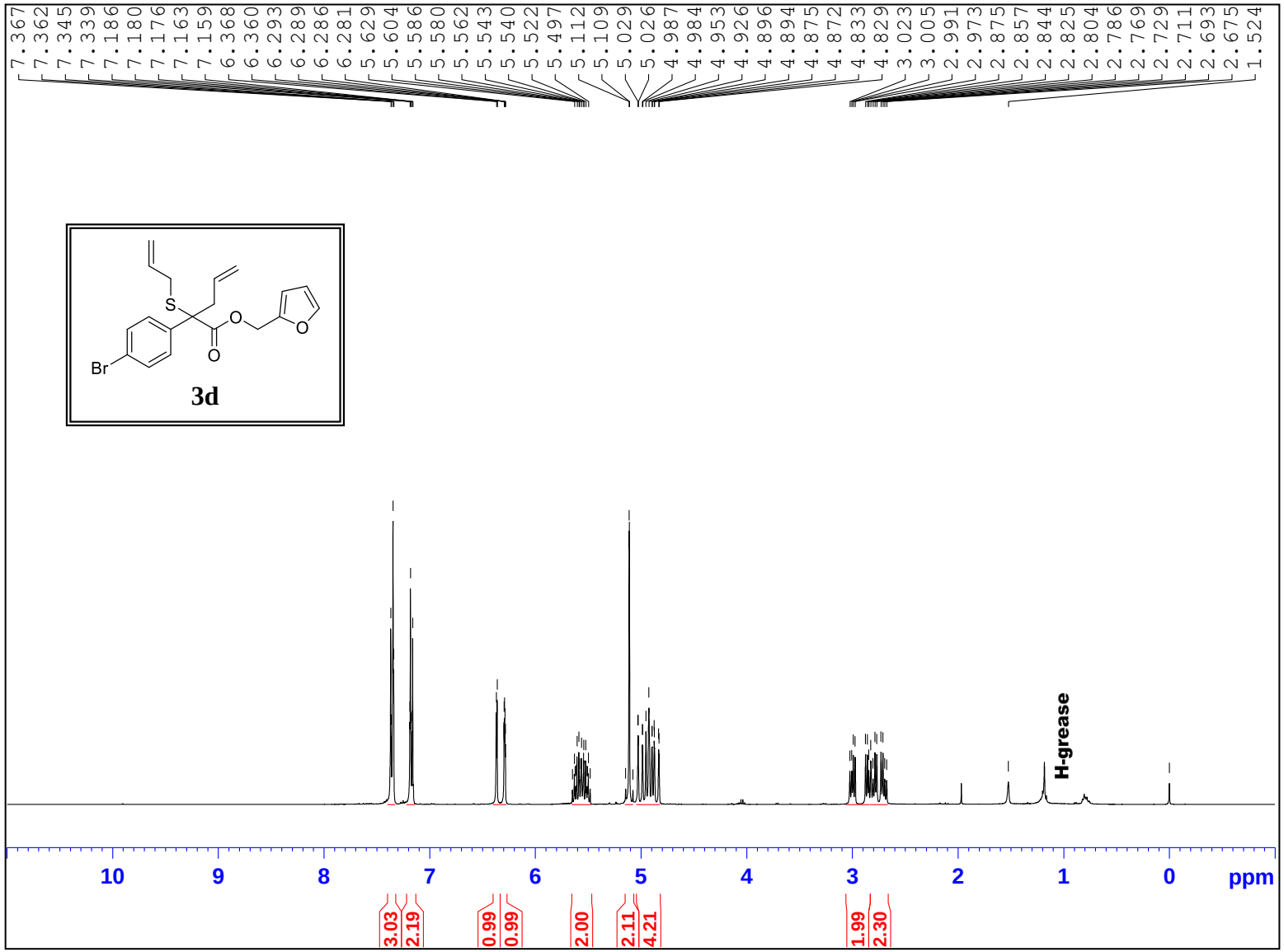
^{1}H NMR for compound **3c** (400 MHz, $CDCl_3$) (**data**)



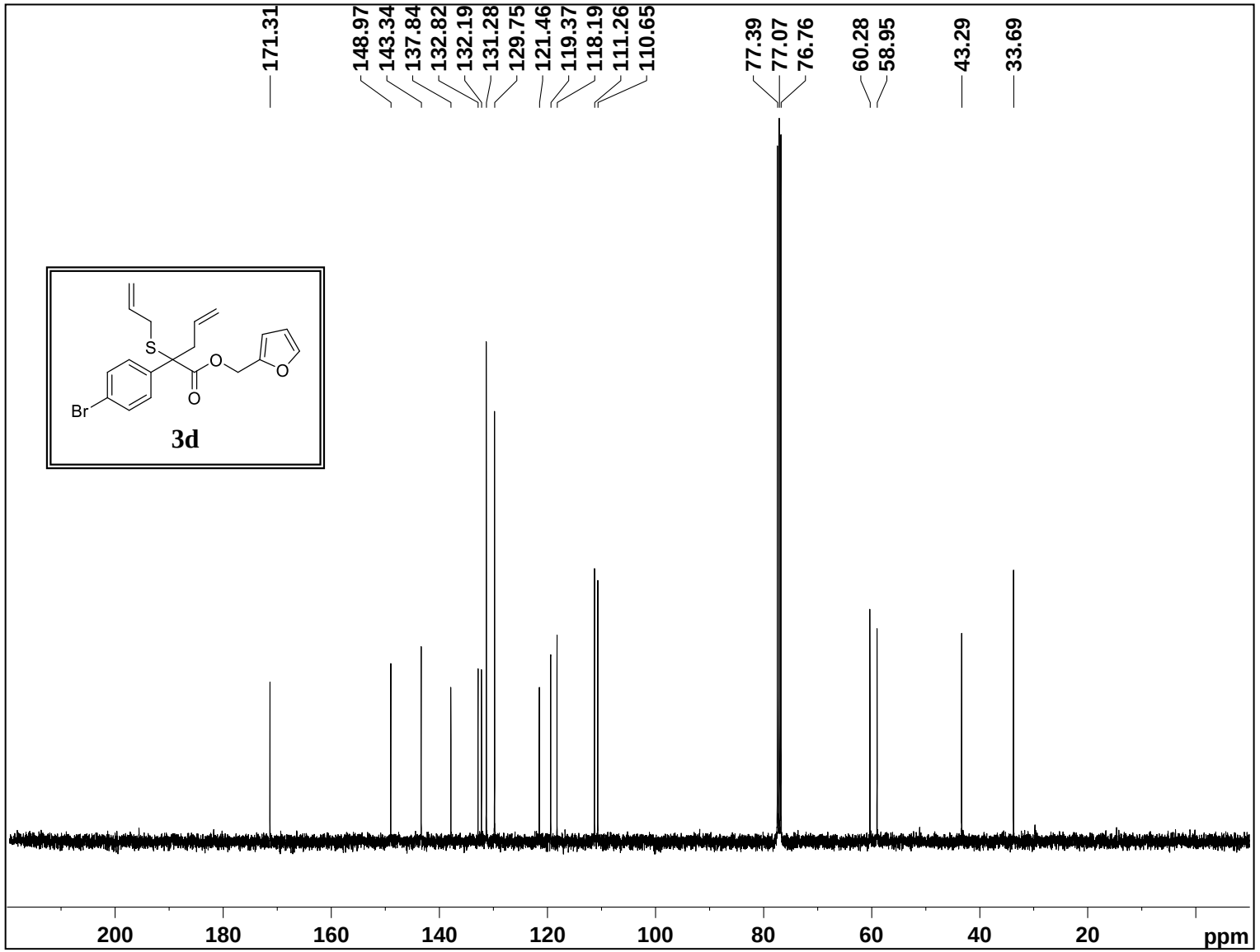
$^{13}C\{^{1}H\}$ NMR for compound **3c** (101 MHz, $CDCl_3$)



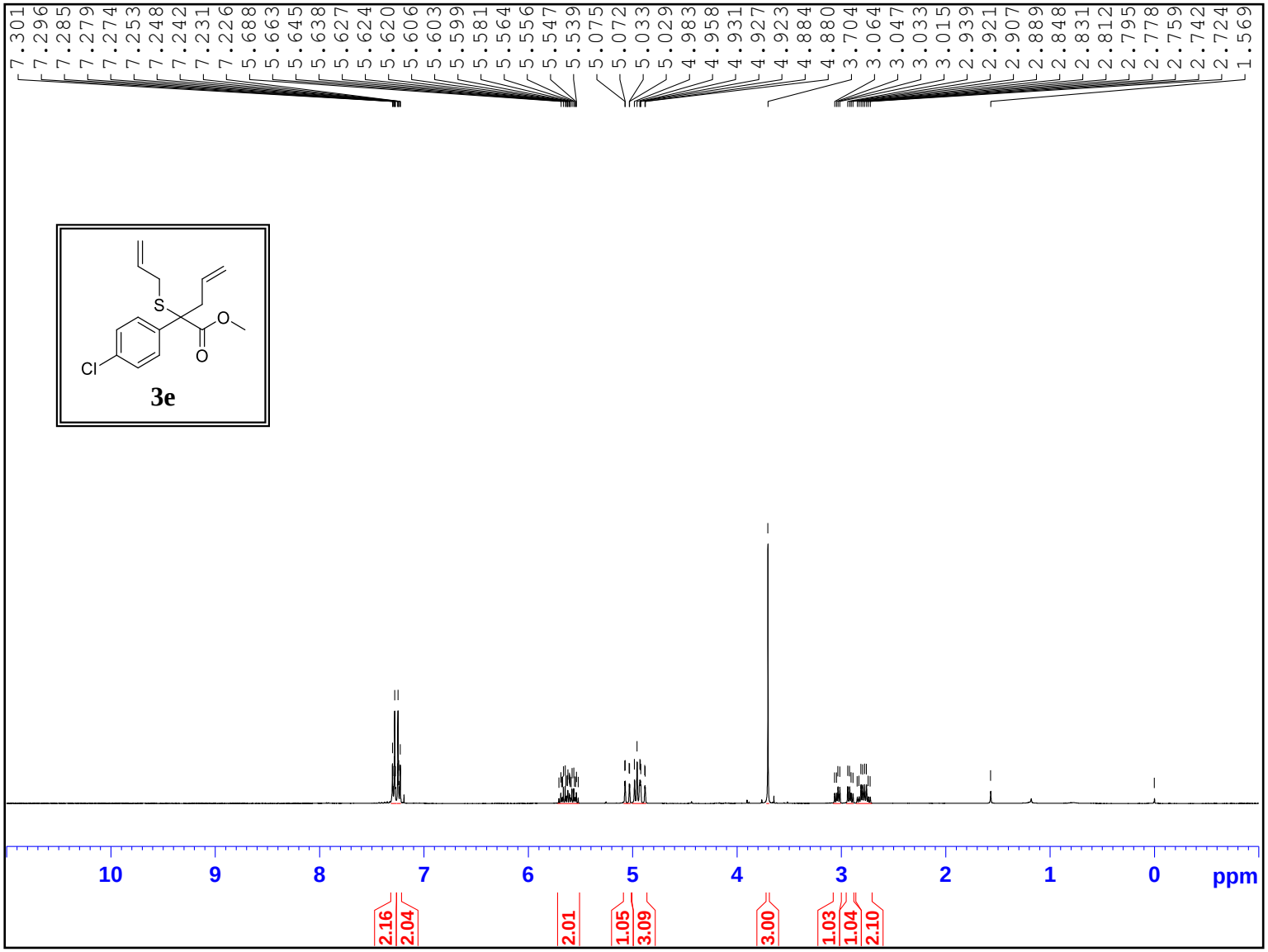
^{1}H NMR for compound **3d** (400 MHz, $CDCl_3$) (**data**)



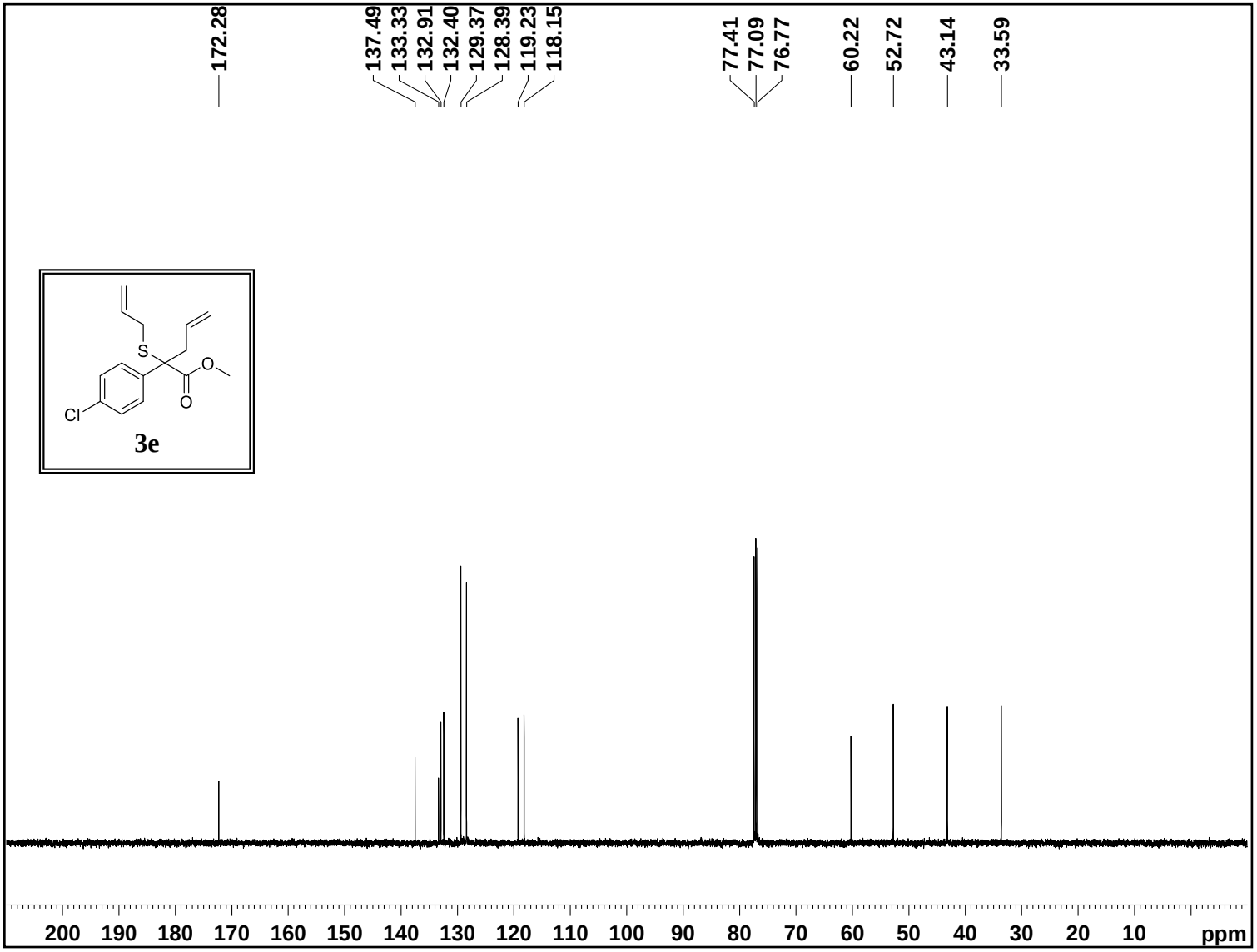
$^{13}C\{^{1}H\}$ NMR for compound **3d** (101 MHz, $CDCl_3$)



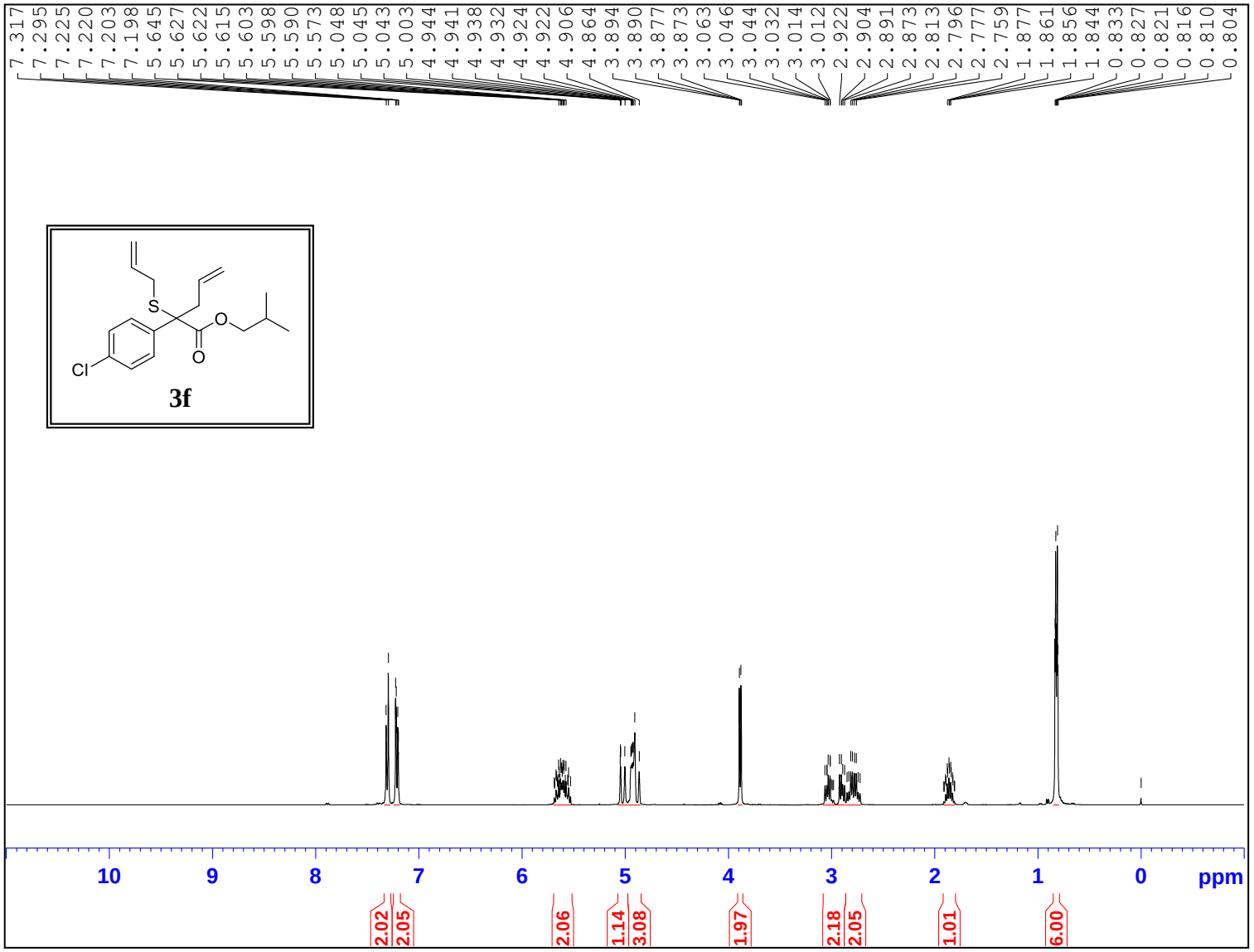
^{1}H NMR for compound **3e** (400 MHz, $CDCl_3$) (**data**)



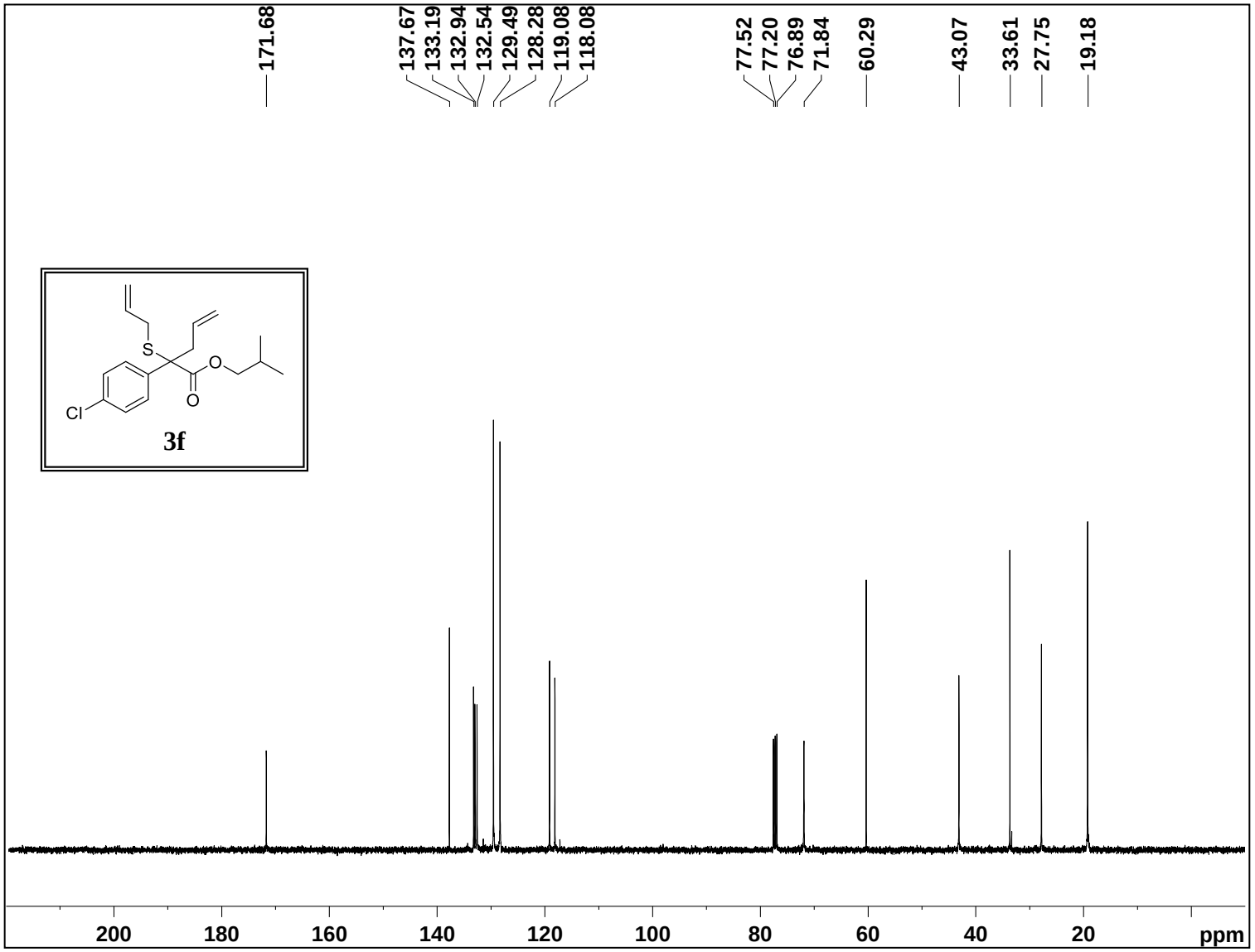
$^{13}C\{^{1}H\}$ NMR for compound **3e** (101 MHz, $CDCl_3$)



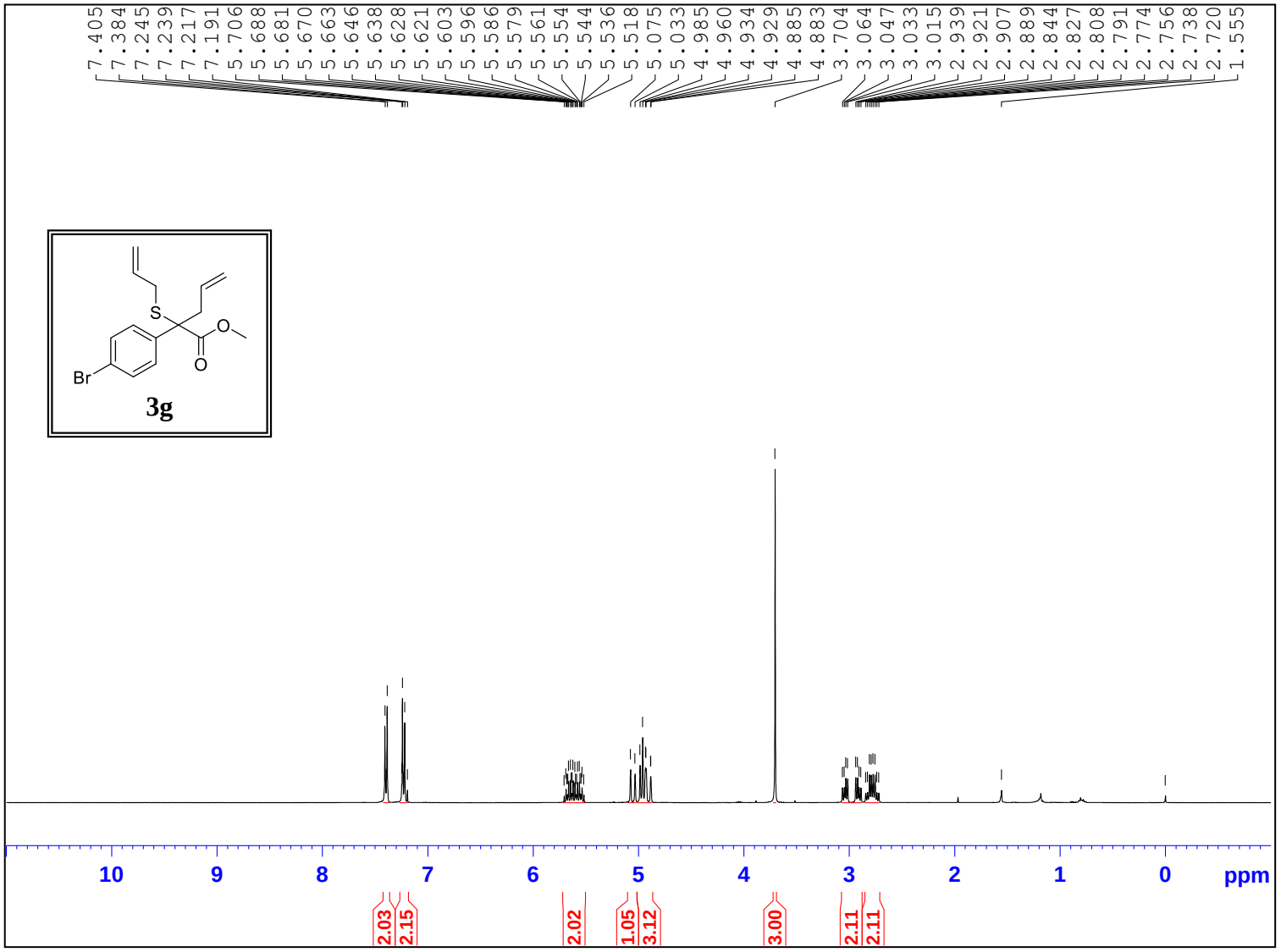
^{1}H NMR for compound **3f** (400 MHz, $CDCl_3$) (**data**)



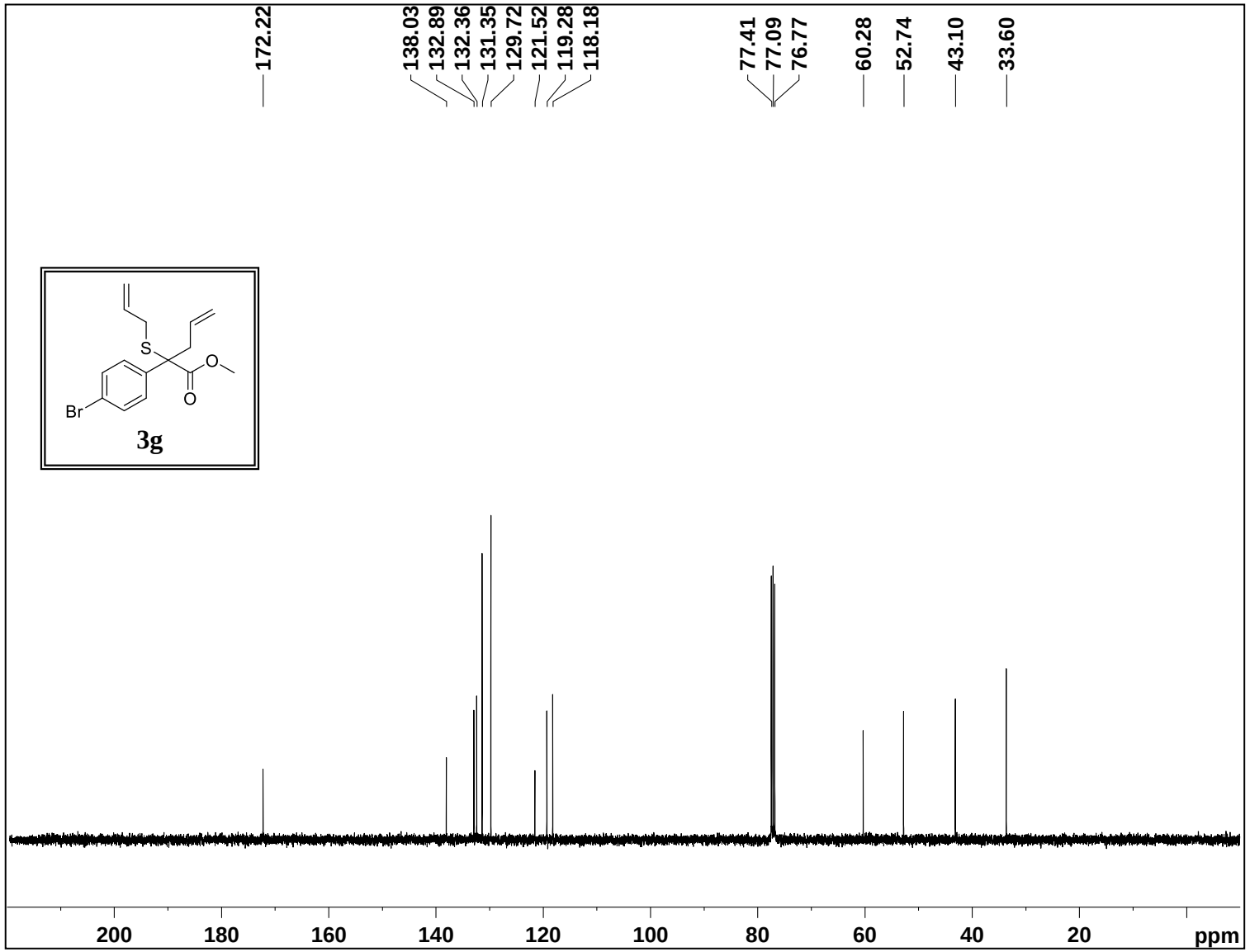
$^{13}C\{^{1}H\}$ NMR for compound **3f** (101 MHz, $CDCl_3$)



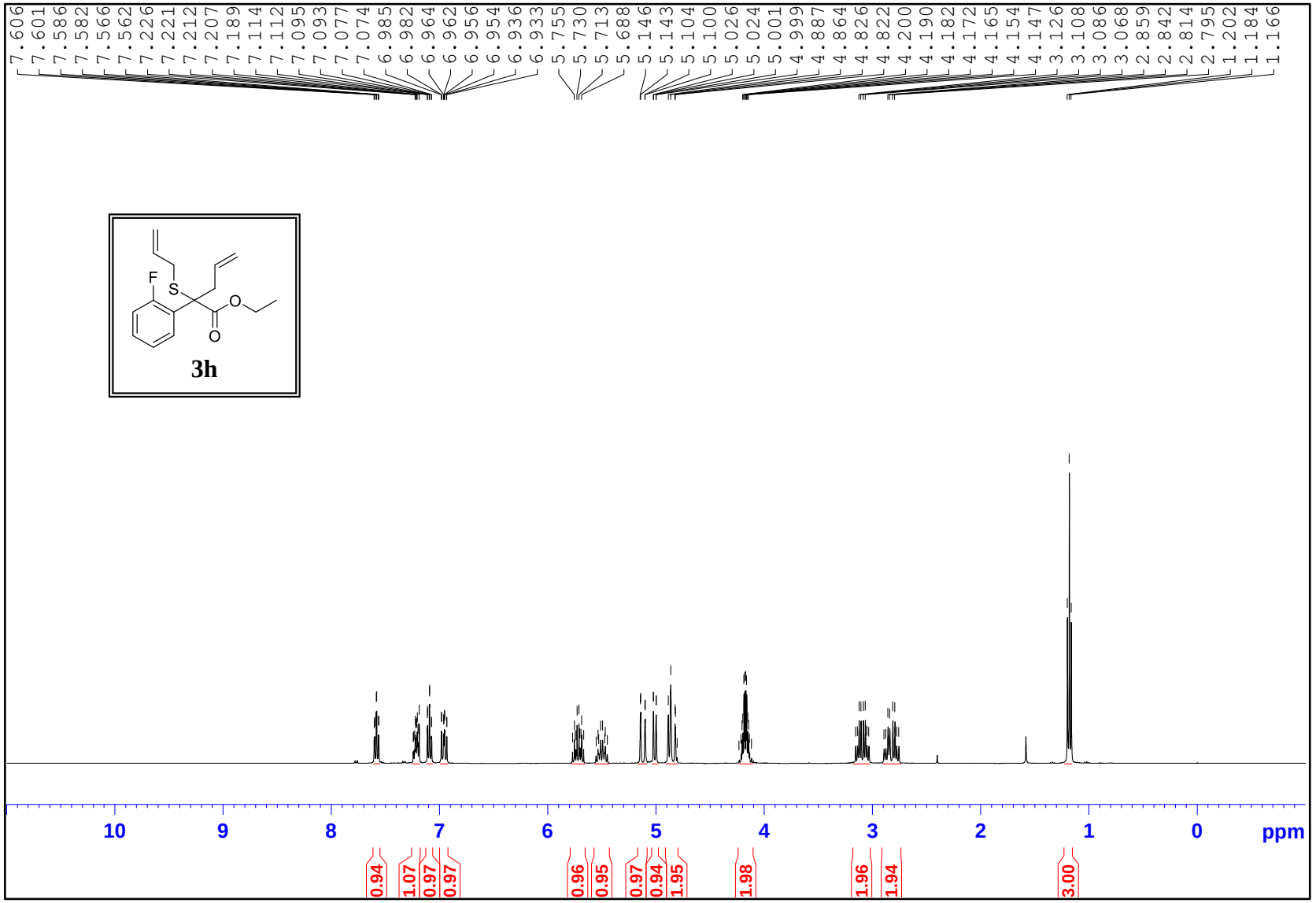
^{1}H NMR for compound **3g** (400 MHz, $CDCl_3$) (**data**)



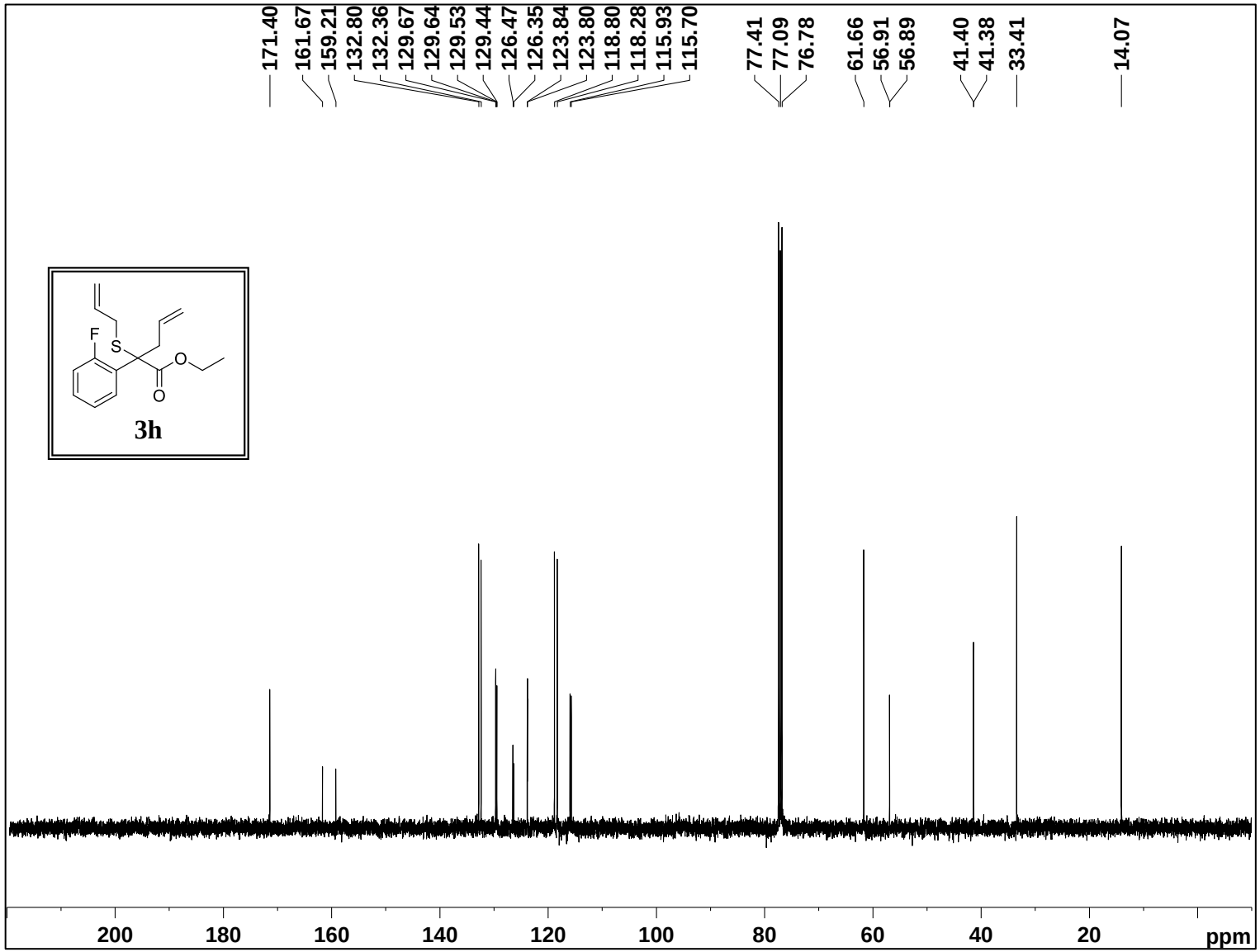
$^{13}C\{^{1}H\}$ NMR for compound **3g** (101 MHz, $CDCl_3$)



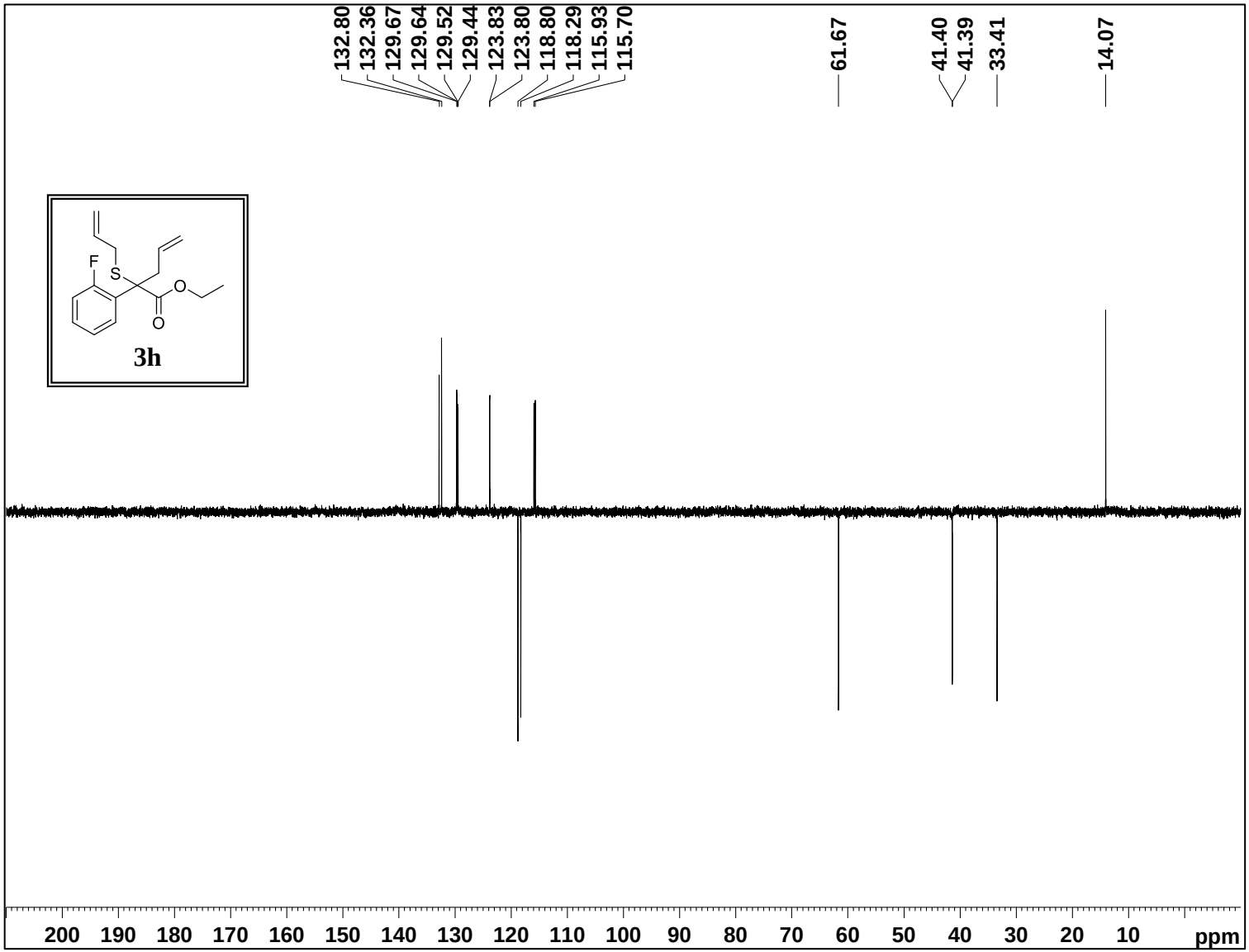
^{1}H NMR for compound **3h** (400 MHz, $CDCl_3$) (**data**)



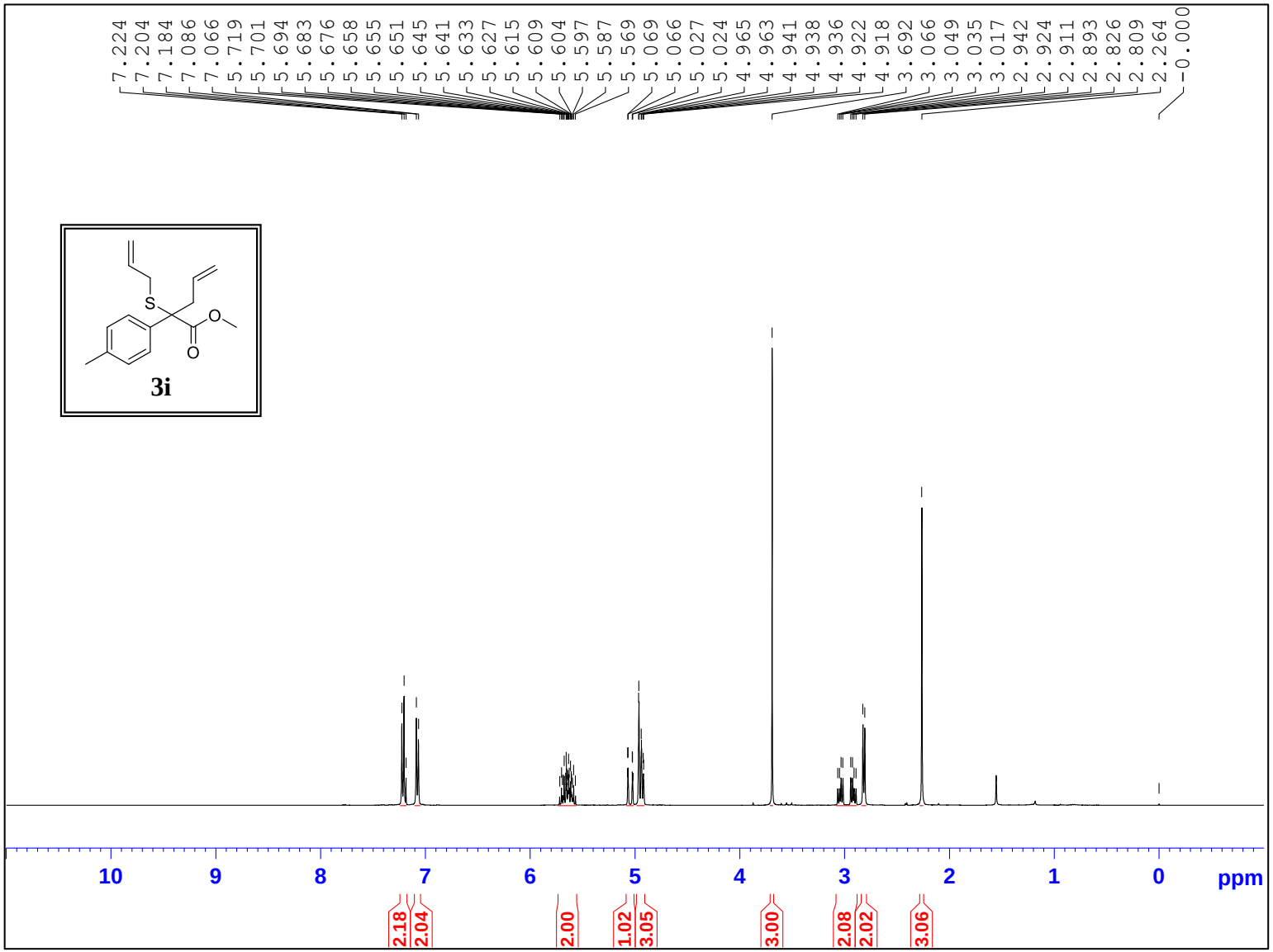
$^{13}C\{^{1}H\}$ NMR for compound **3h** (101 MHz, $CDCl_3$)



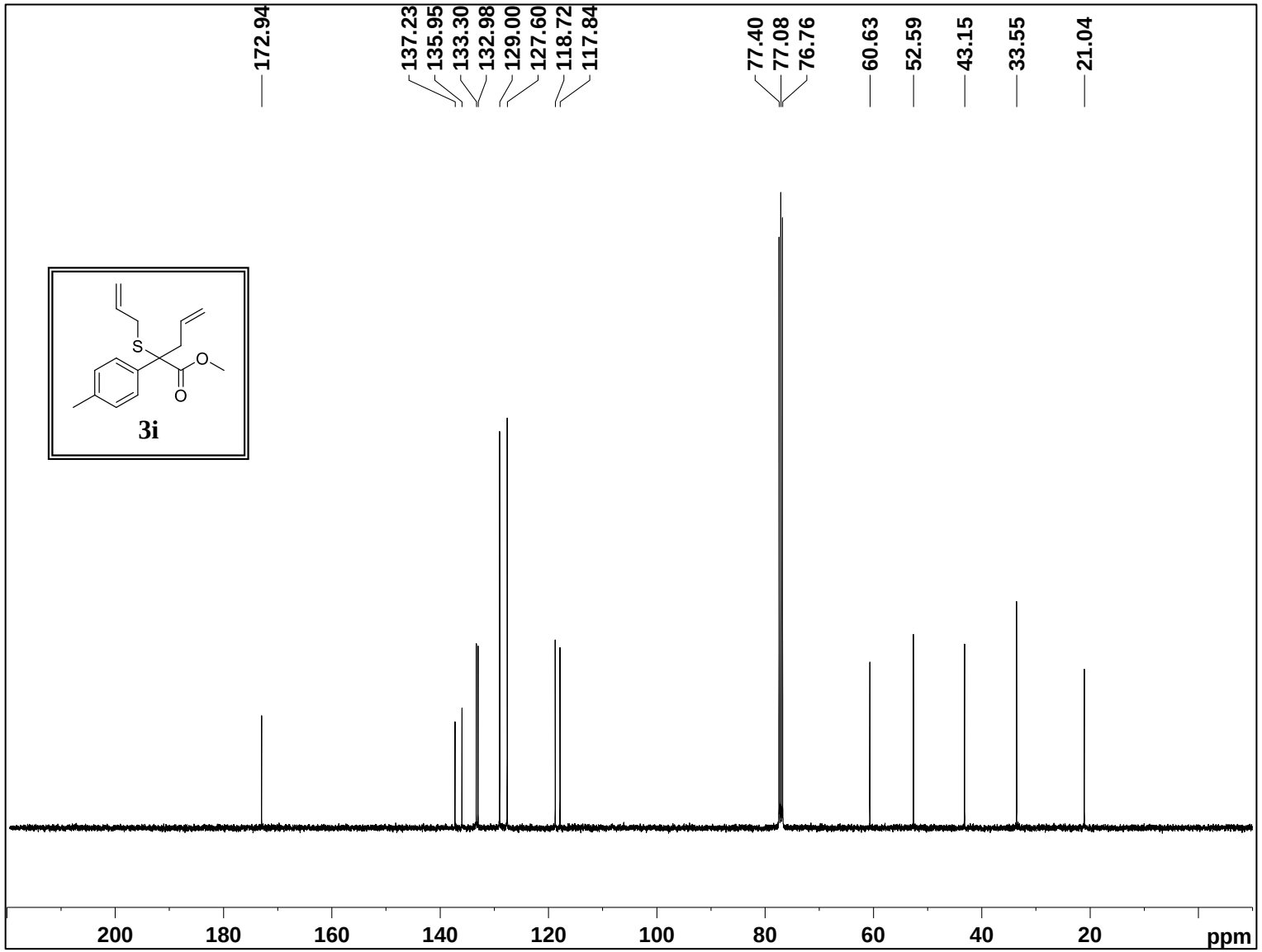
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3h** (101 MHz, $CDCl_3$)



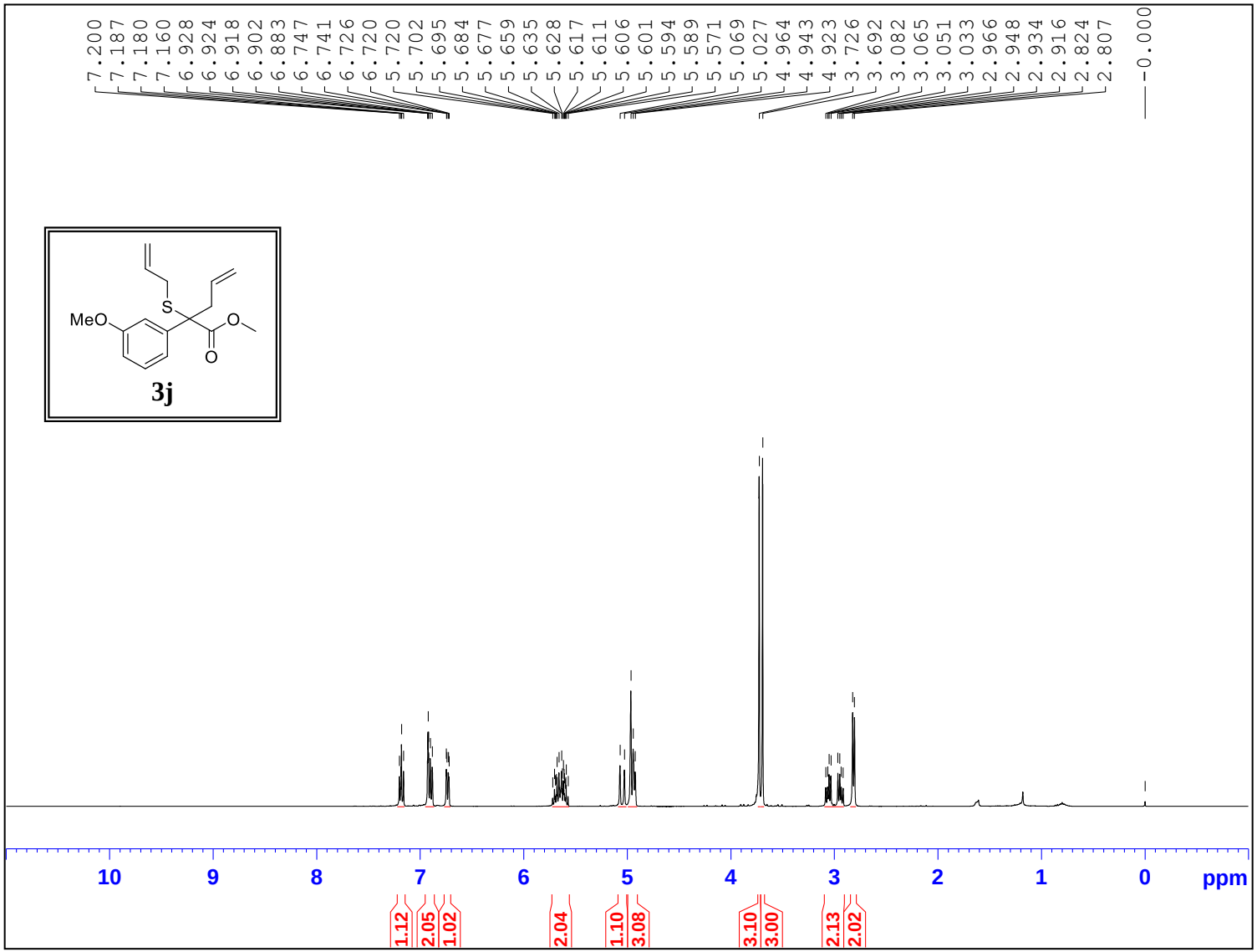
^{1}H NMR for compound **3i** (400 MHz, $CDCl_3$) (**data**)



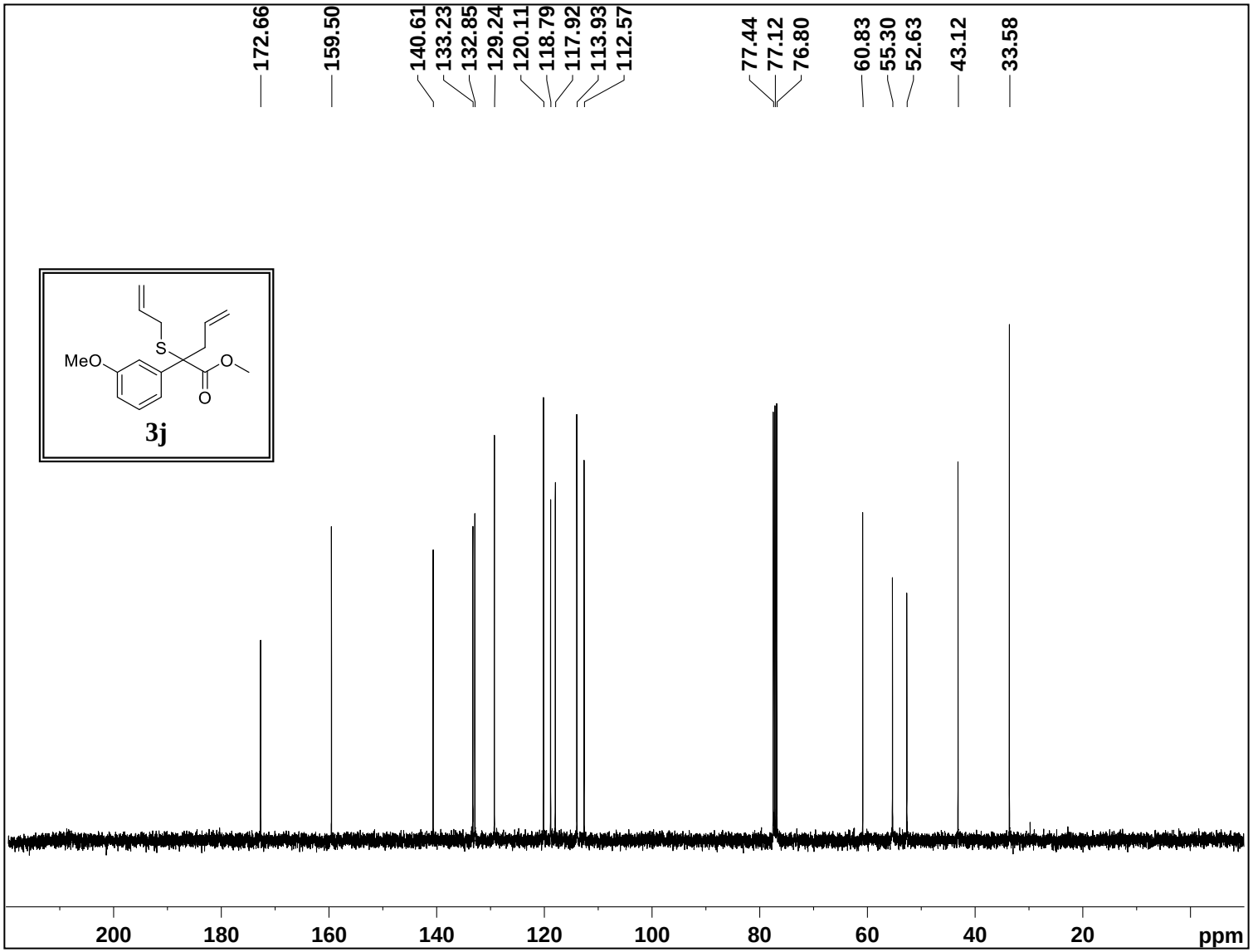
$^{13}C\{^{1}H\}$ NMR for compound **3i** (101 MHz, $CDCl_3$)



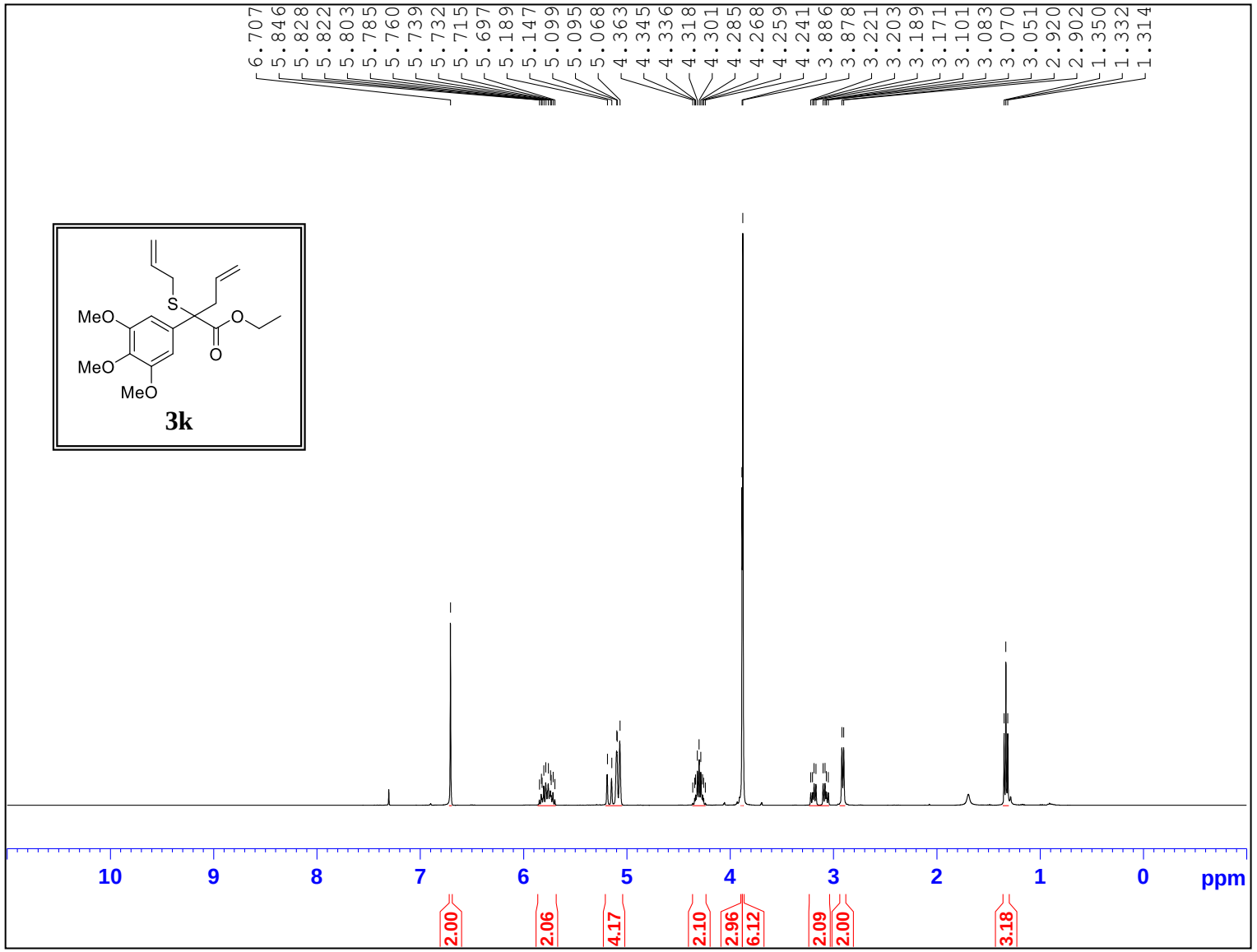
^{1}H NMR for compound **3j** (400 MHz, $CDCl_3$) (**data**)



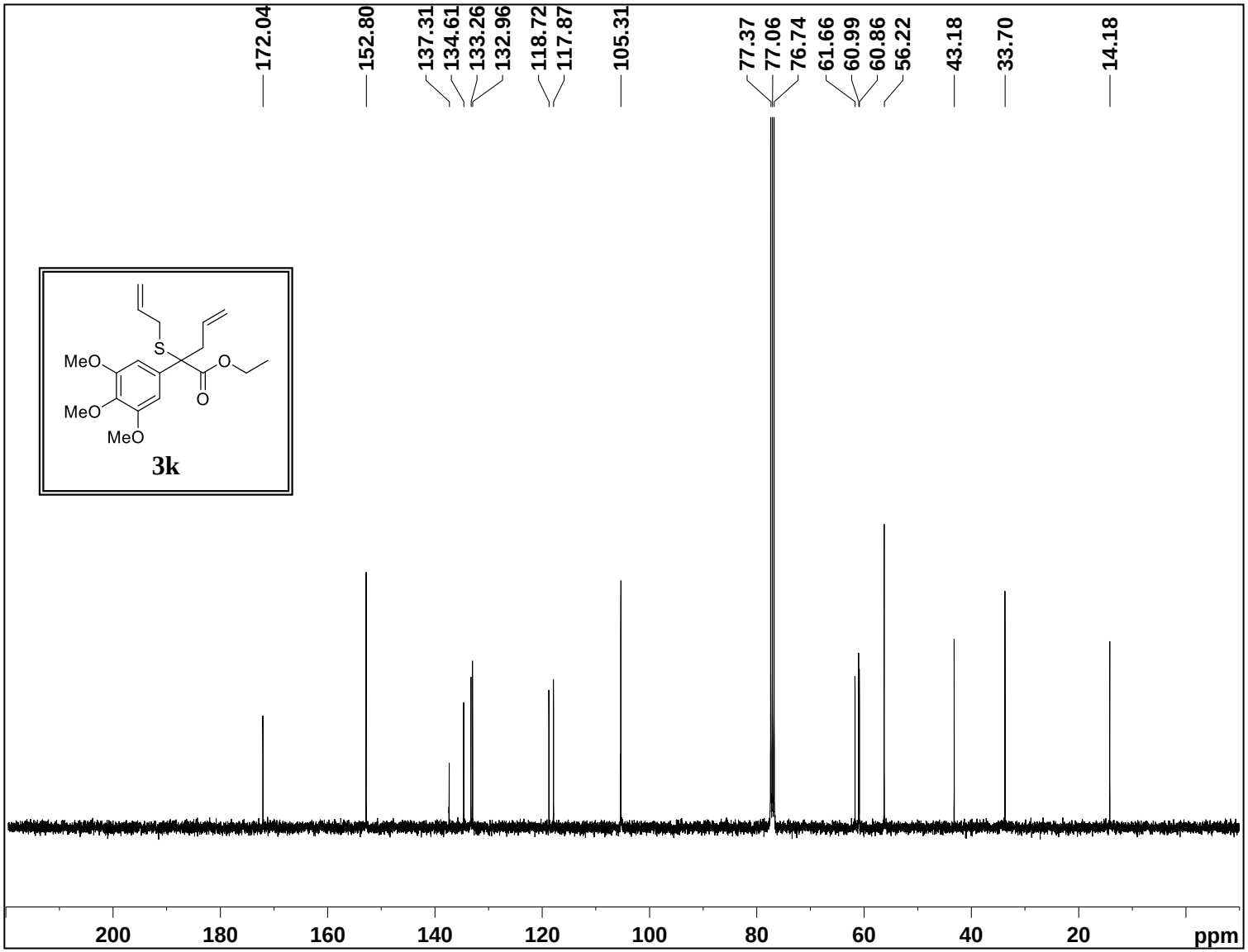
$^{13}C\{^{1}H\}$ NMR for compound **3j** (101 MHz, $CDCl_3$)



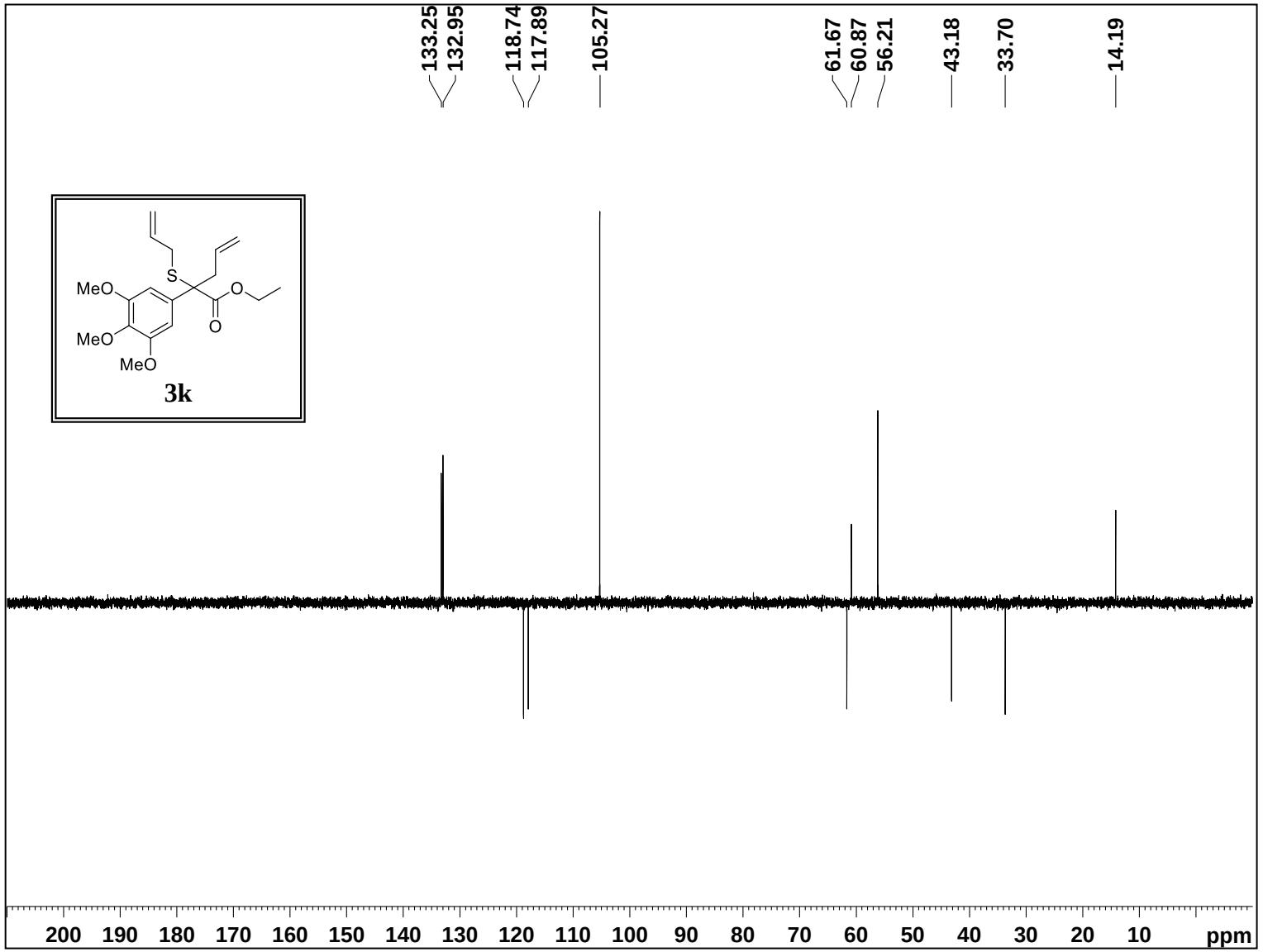
^{1}H NMR for compound **3k** (400 MHz, $CDCl_3$) (**data**)



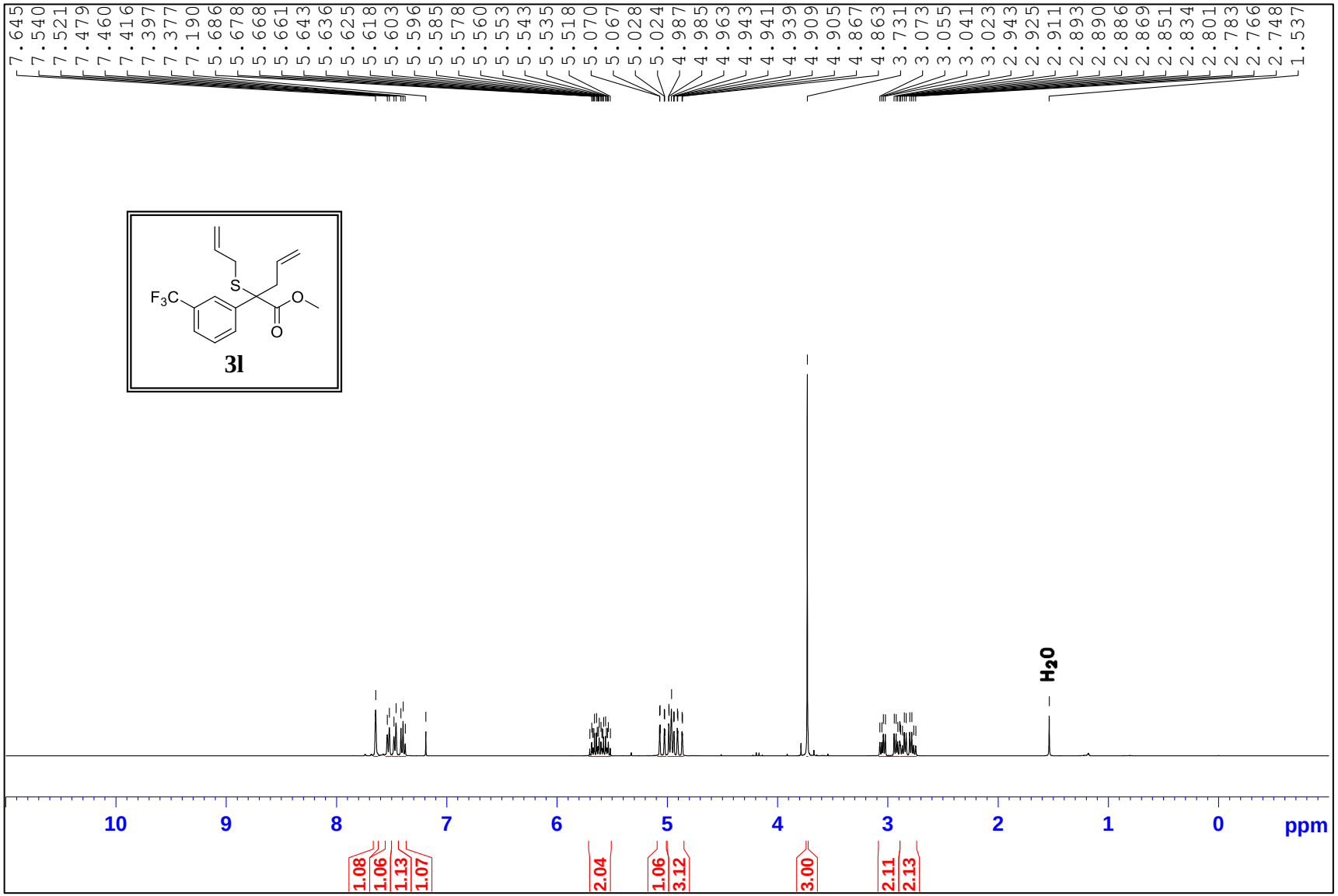
$^{13}C\{^{1}H\}$ NMR for compound **3k** (101 MHz, $CDCl_3$)



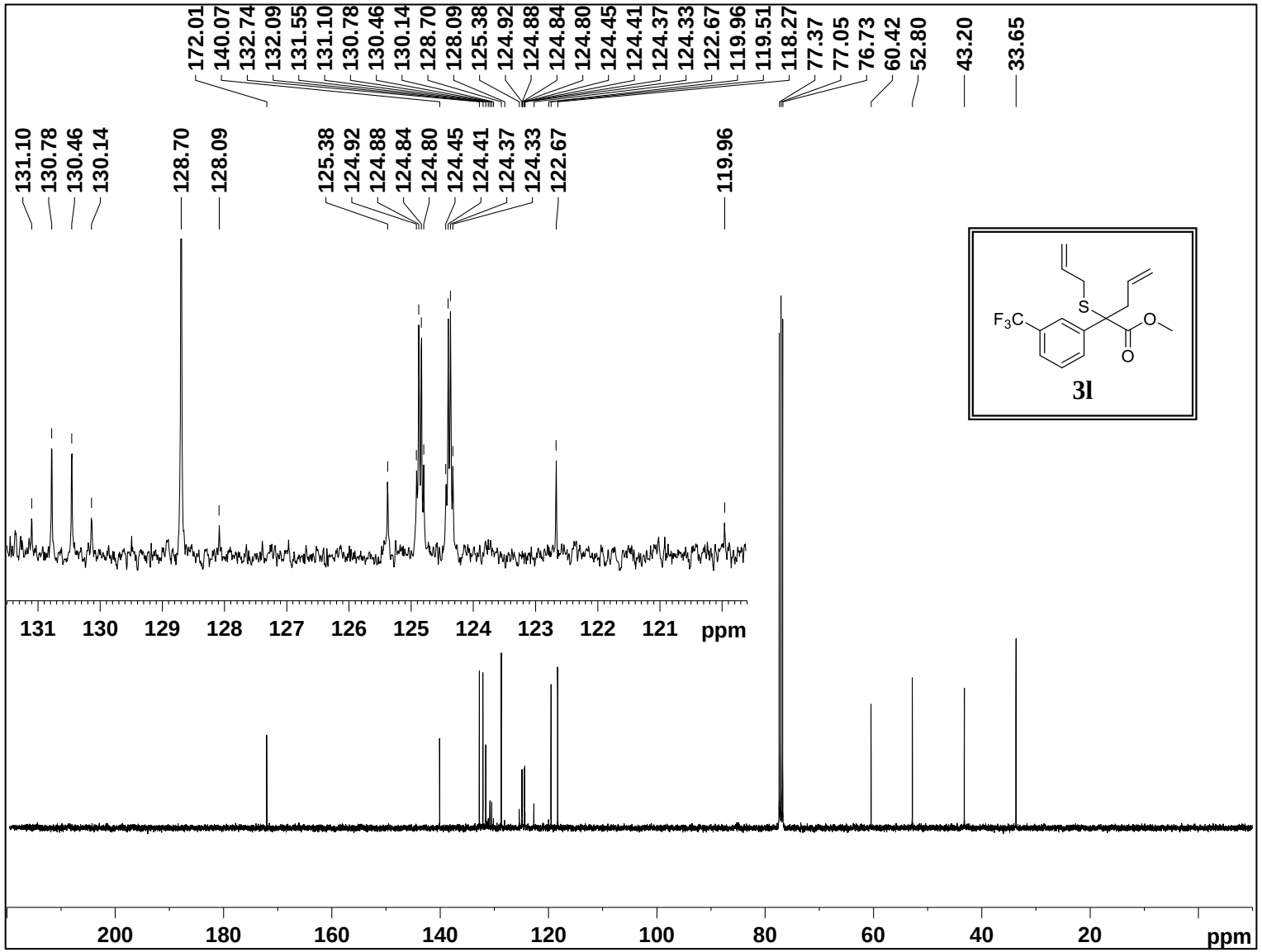
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3k** (101 MHz, $CDCl_3$)



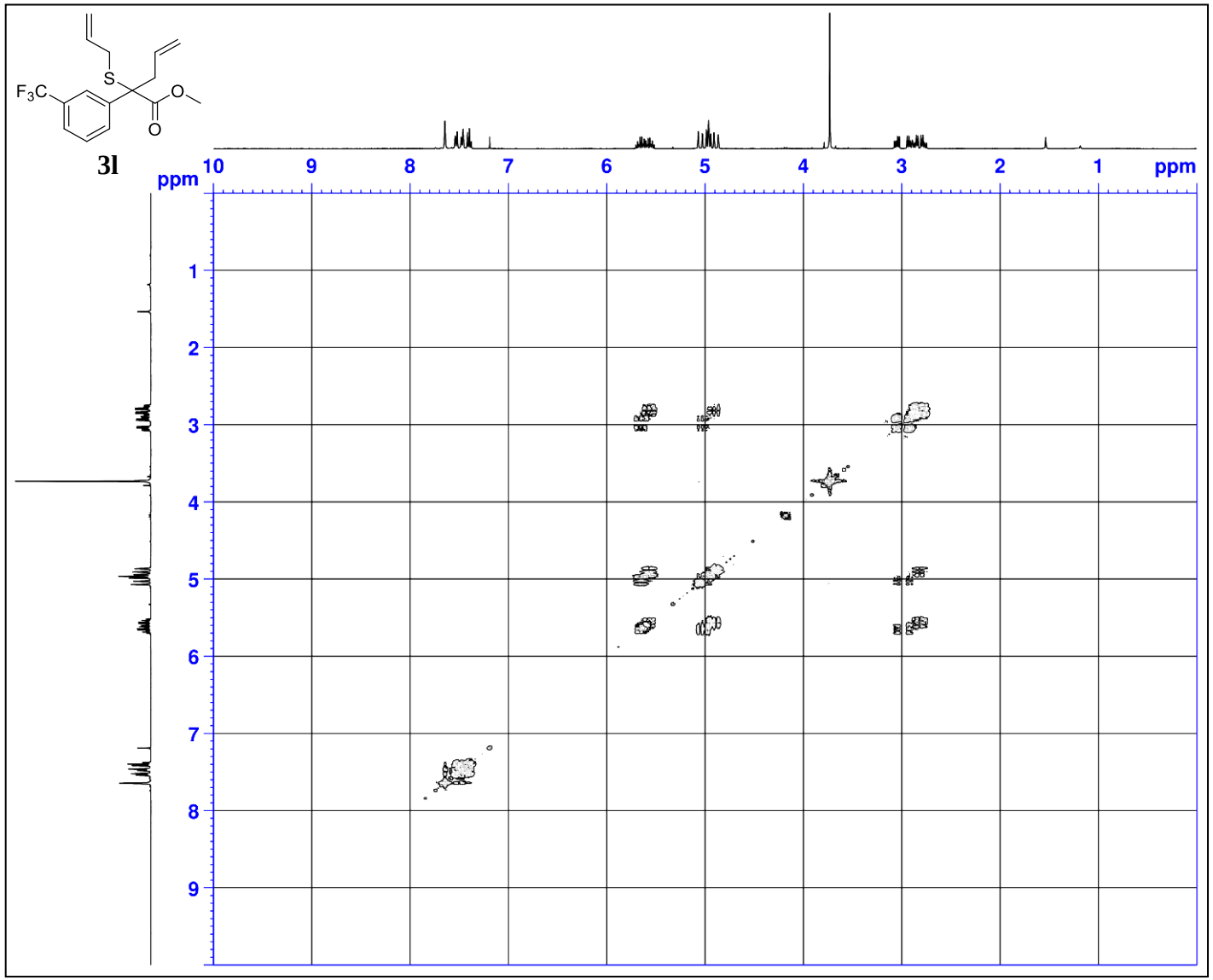
^{1}H NMR for compound **3l** (400 MHz, $CDCl_3$) (**data**)



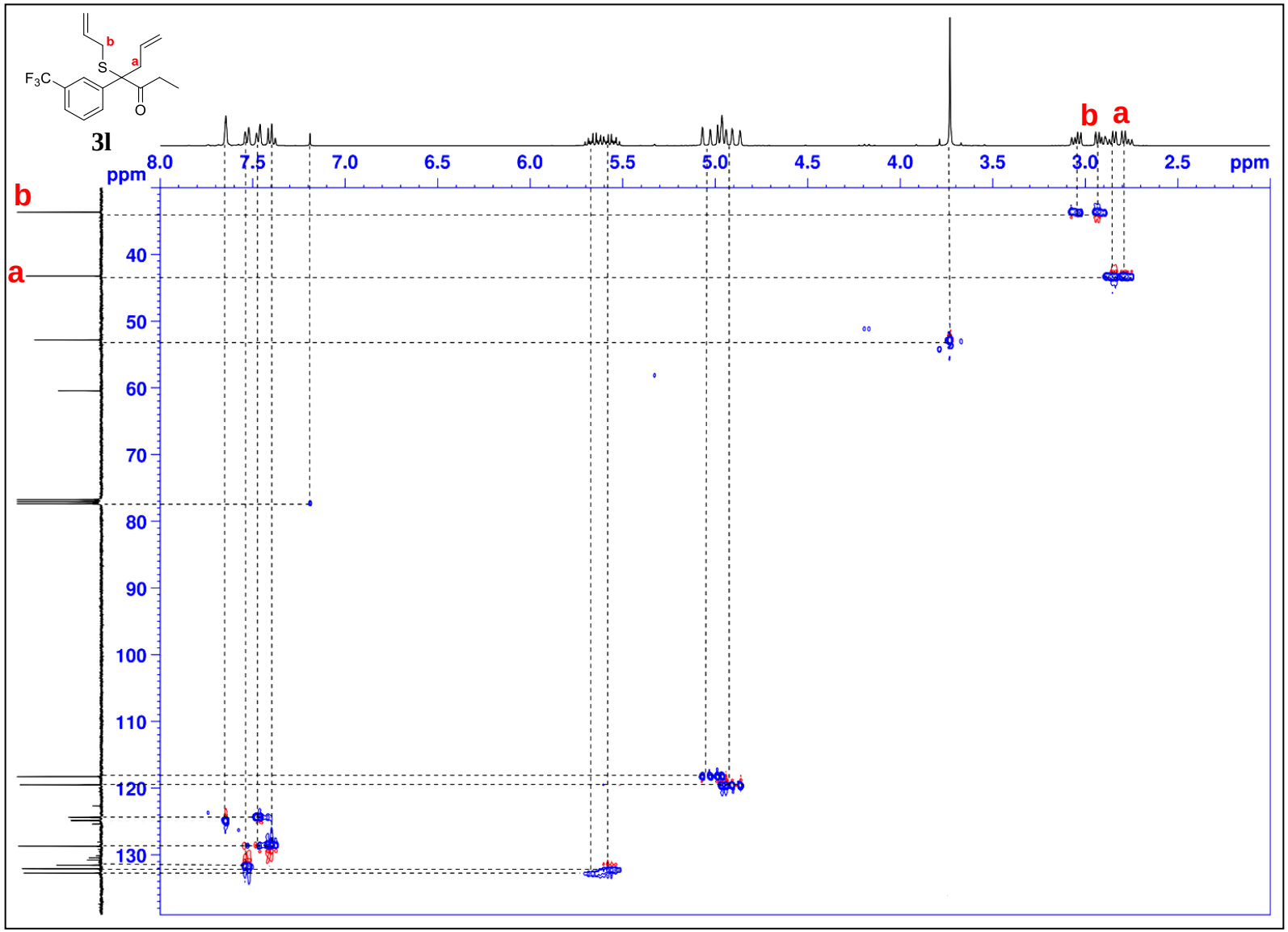
$^{13}C\{^{1}H\}$ NMR for compound **3l** (101 MHz, $CDCl_3$)



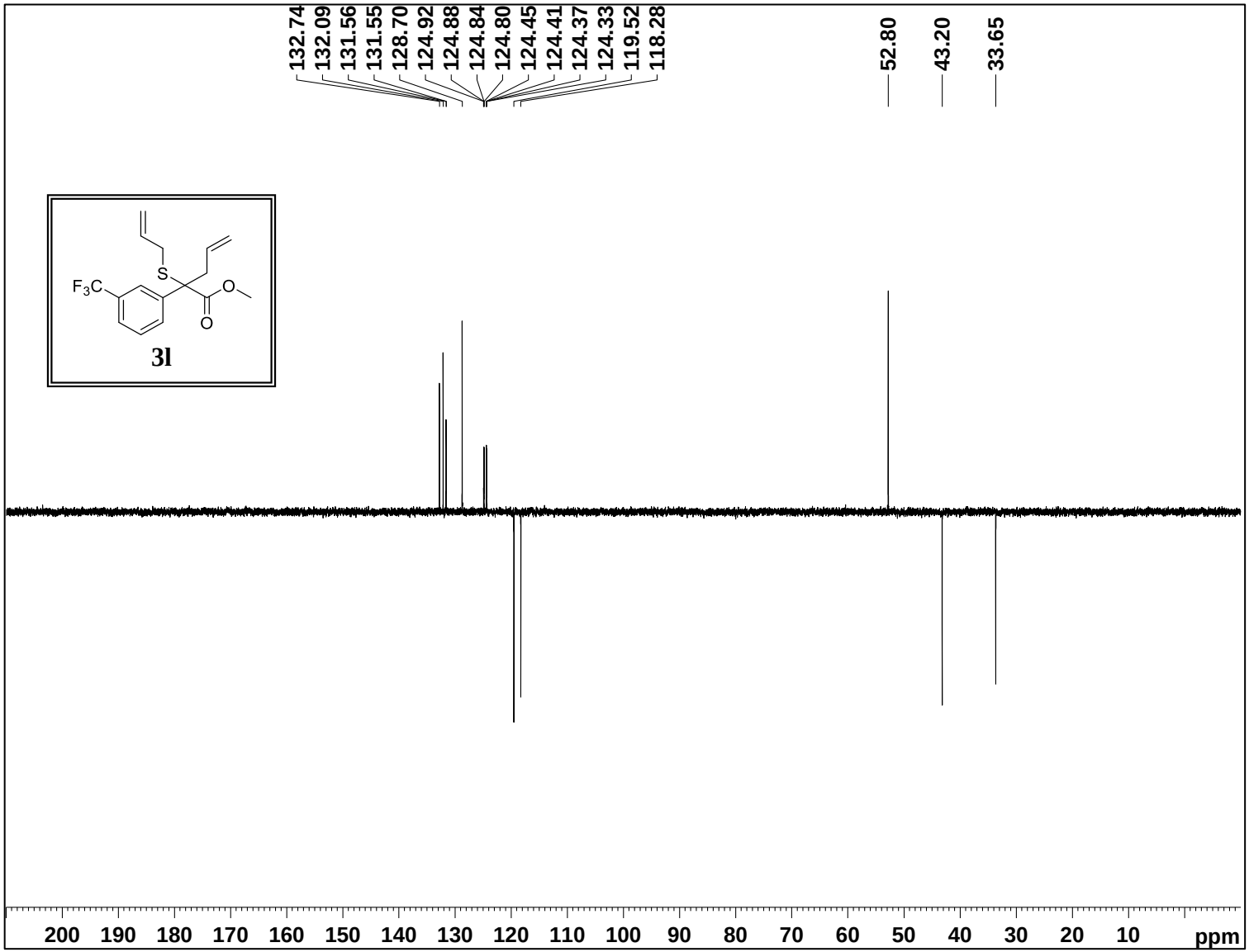
[^{1}H, ^{1}H] COSY for compound **3l** (400 MHz, $CDCl_3$)



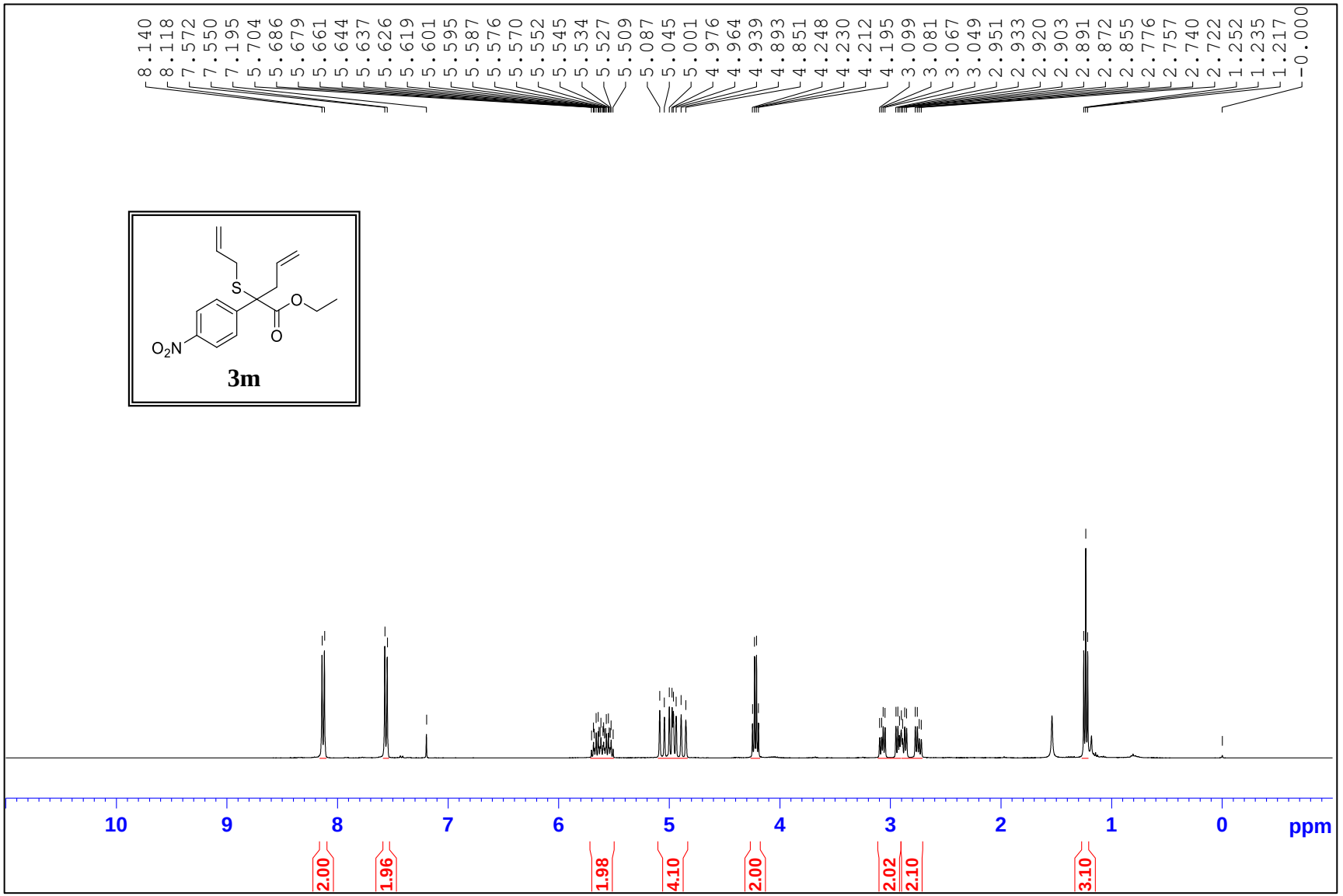
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **3l** (400 MHz, $CDCl_3$)



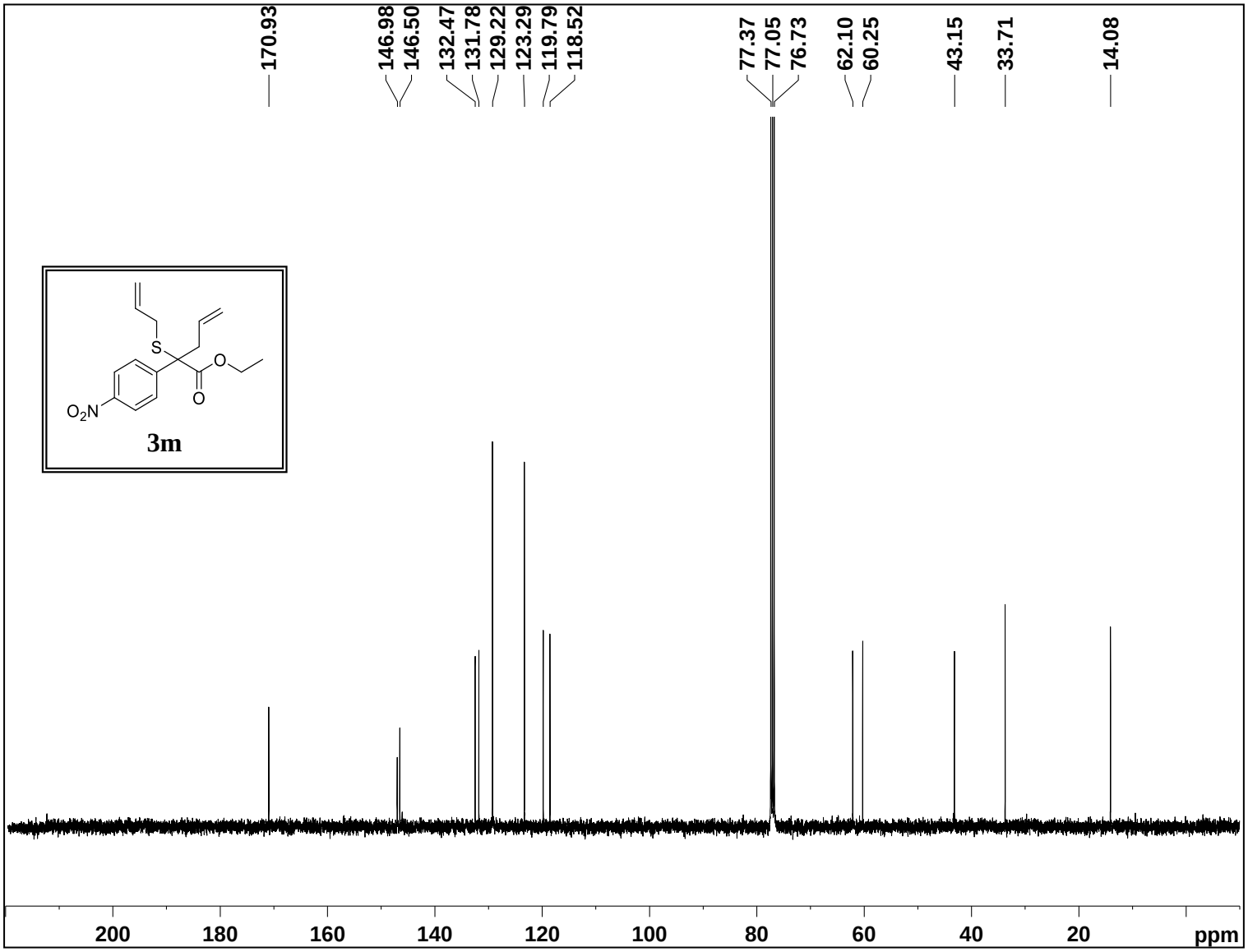
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3l** (101 MHz, $CDCl_3$)



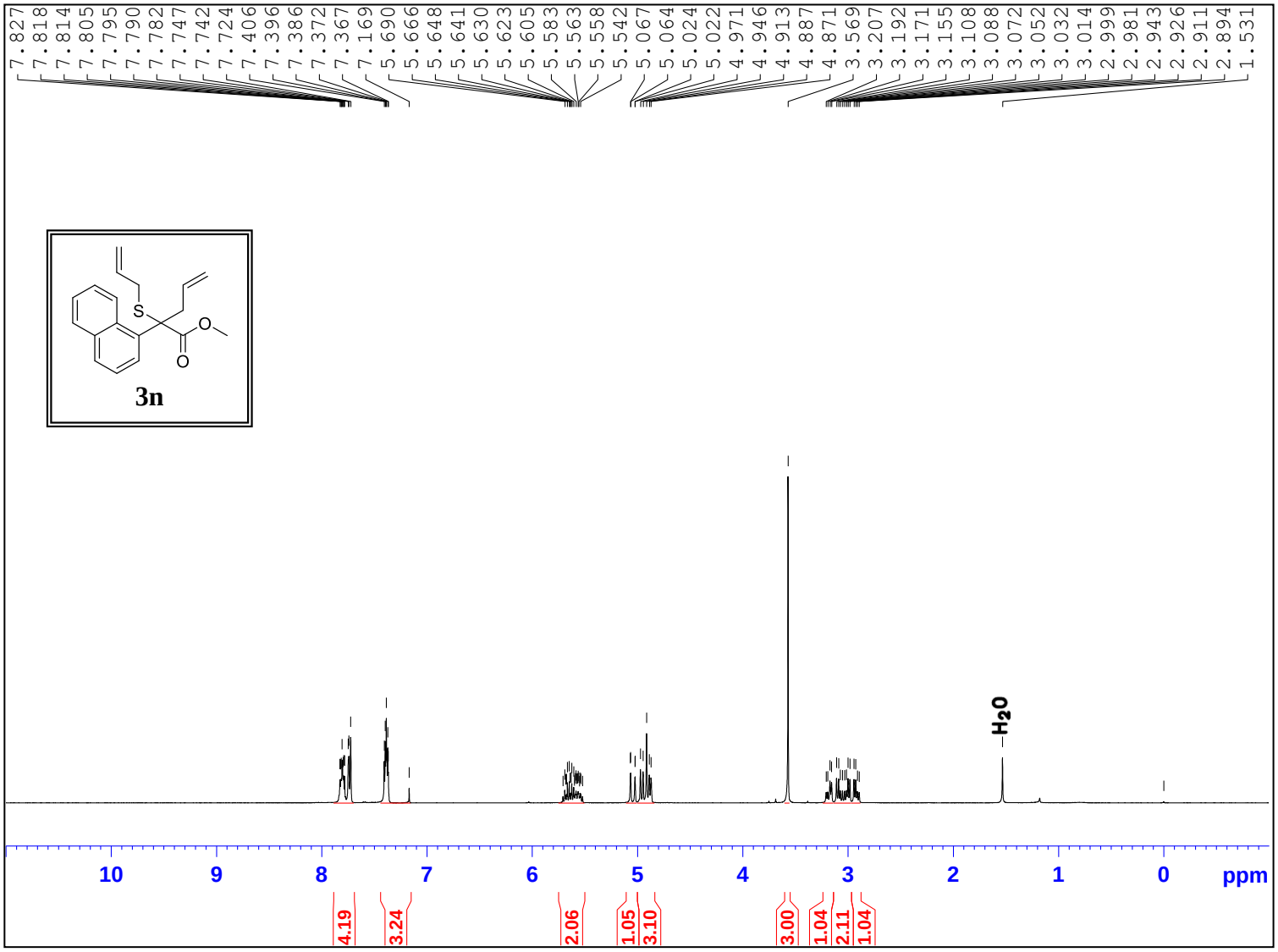
^{1}H NMR for compound **3m** (400 MHz, $CDCl_3$) (**data**)



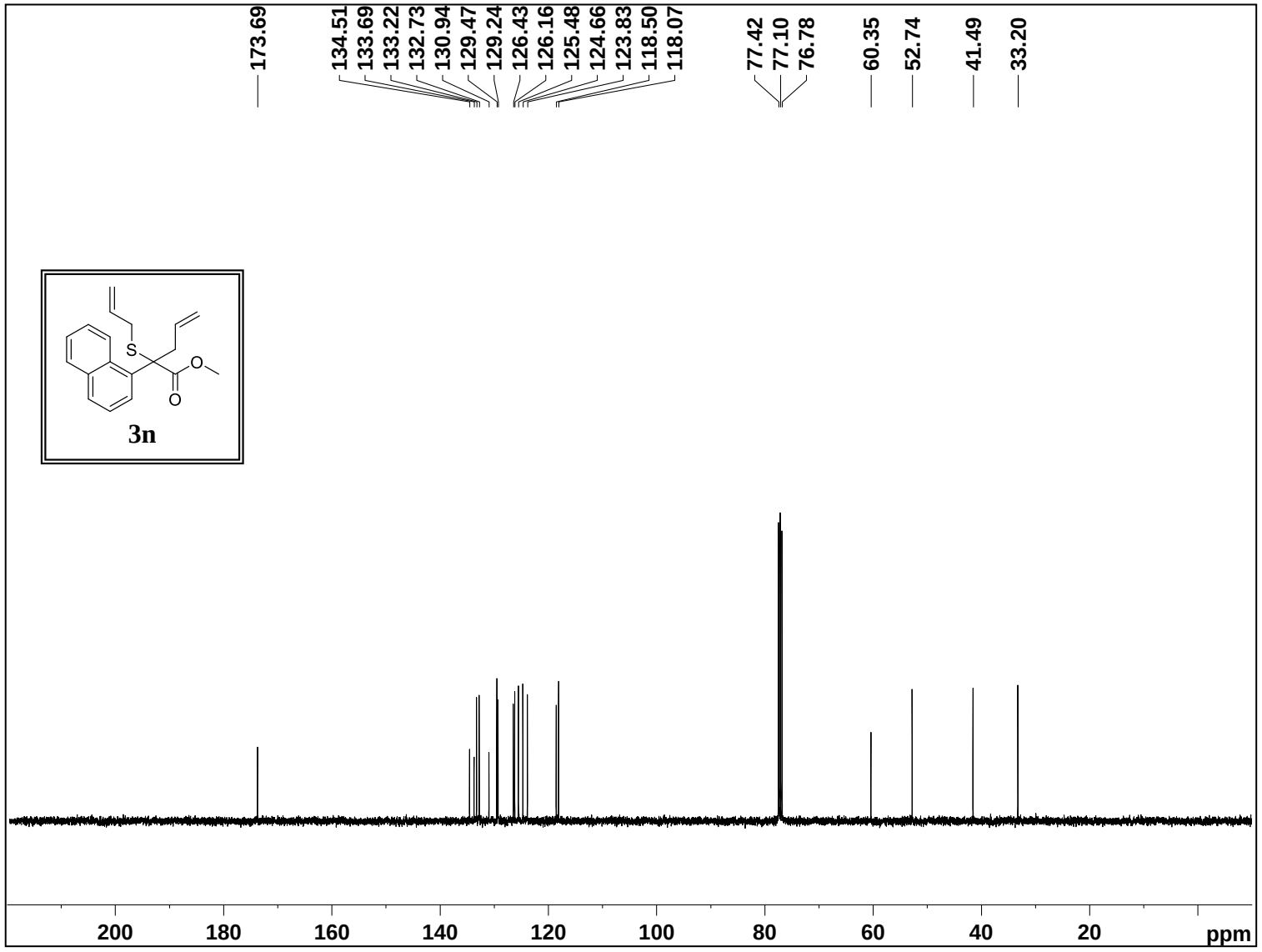
$^{13}C\{^{1}H\}$ NMR for compound **3m** (101 MHz, $CDCl_3$)



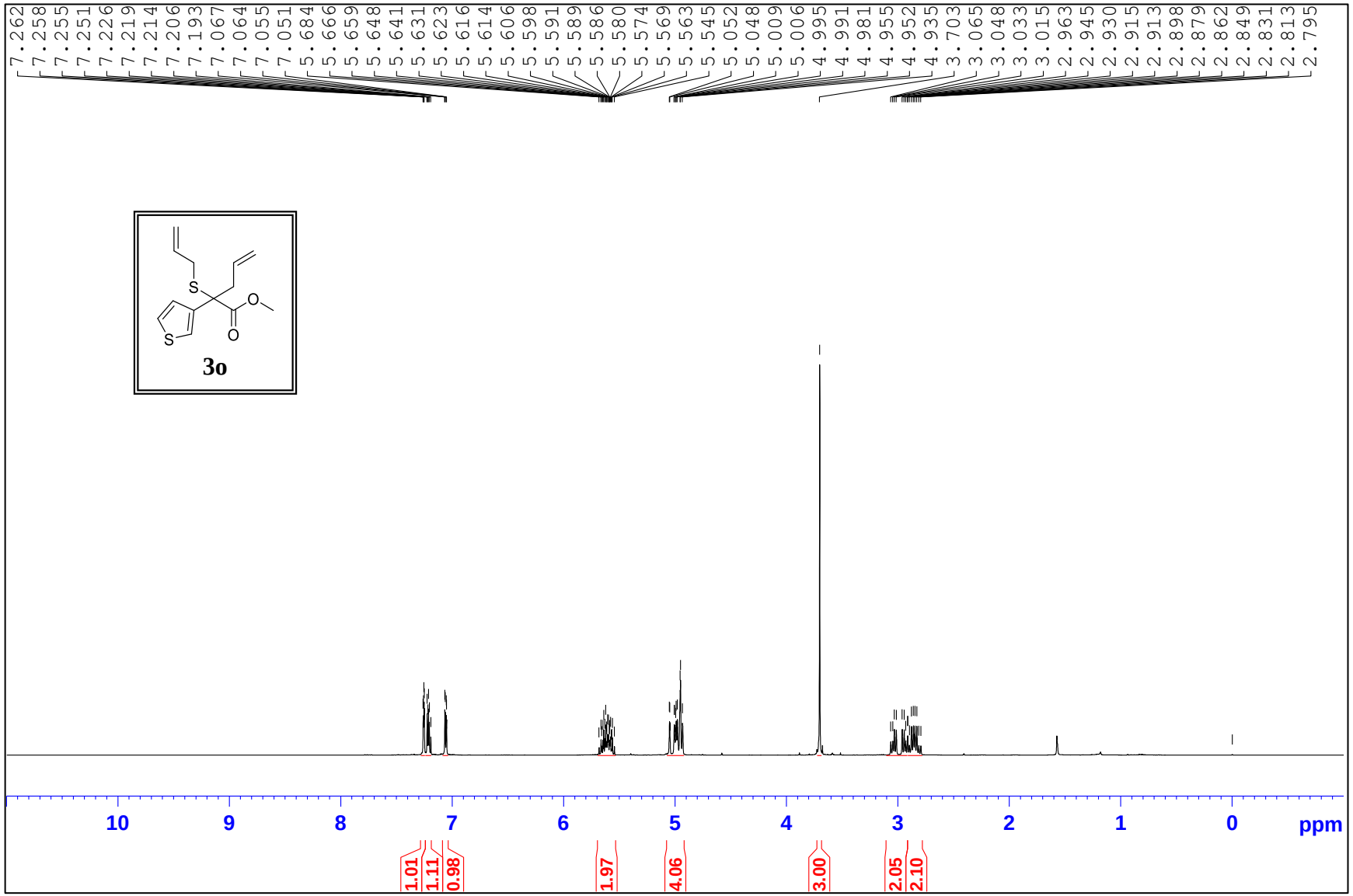
^{1}H NMR for compound **3n** (400 MHz, $CDCl_3$) (**data**)



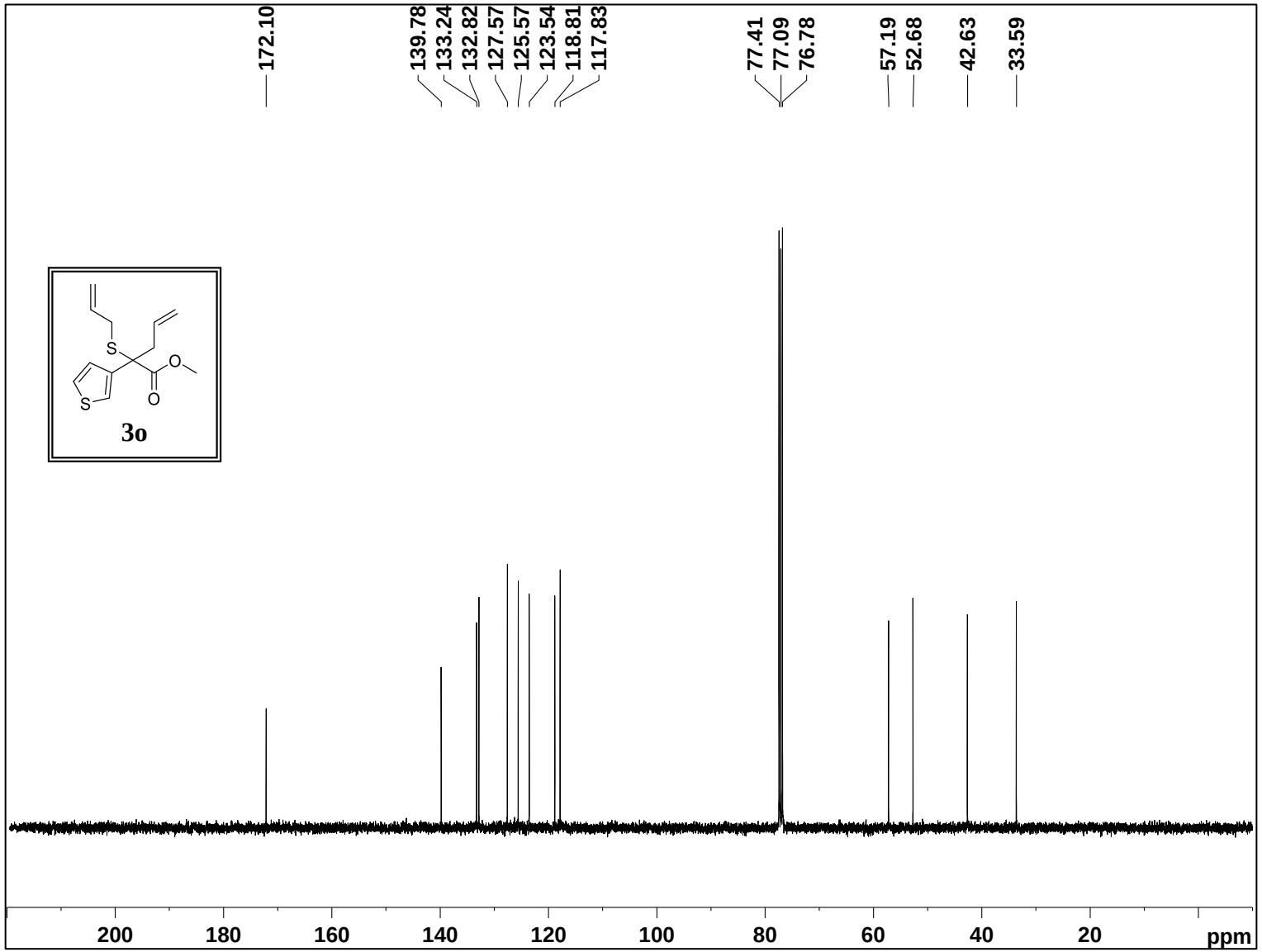
$^{13}C\{^{1}H\}$ NMR for compound **3n** (101 MHz, $CDCl_3$)



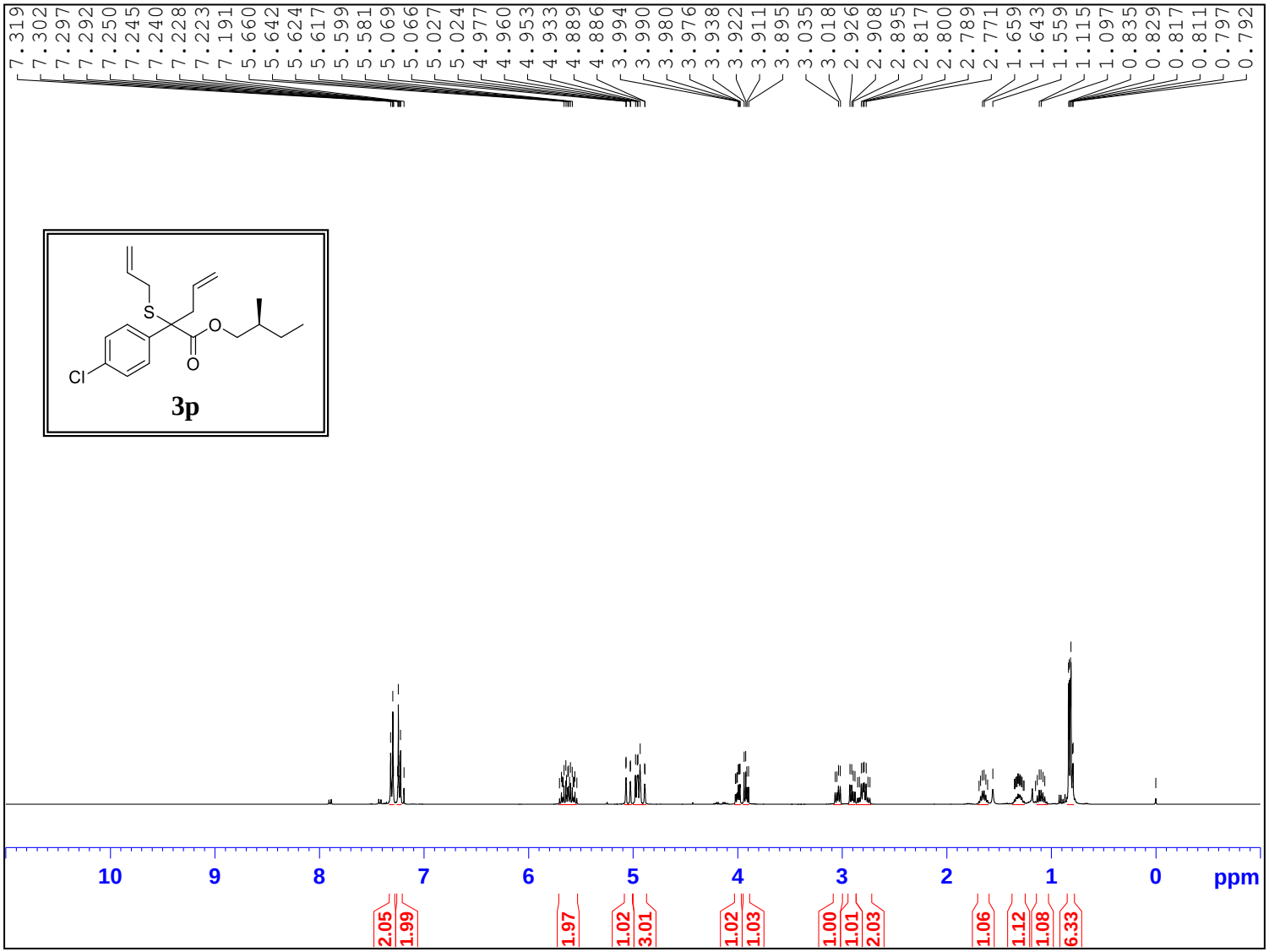
^{1}H NMR for compound **3o** (400 MHz, $CDCl_3$) (**data**)



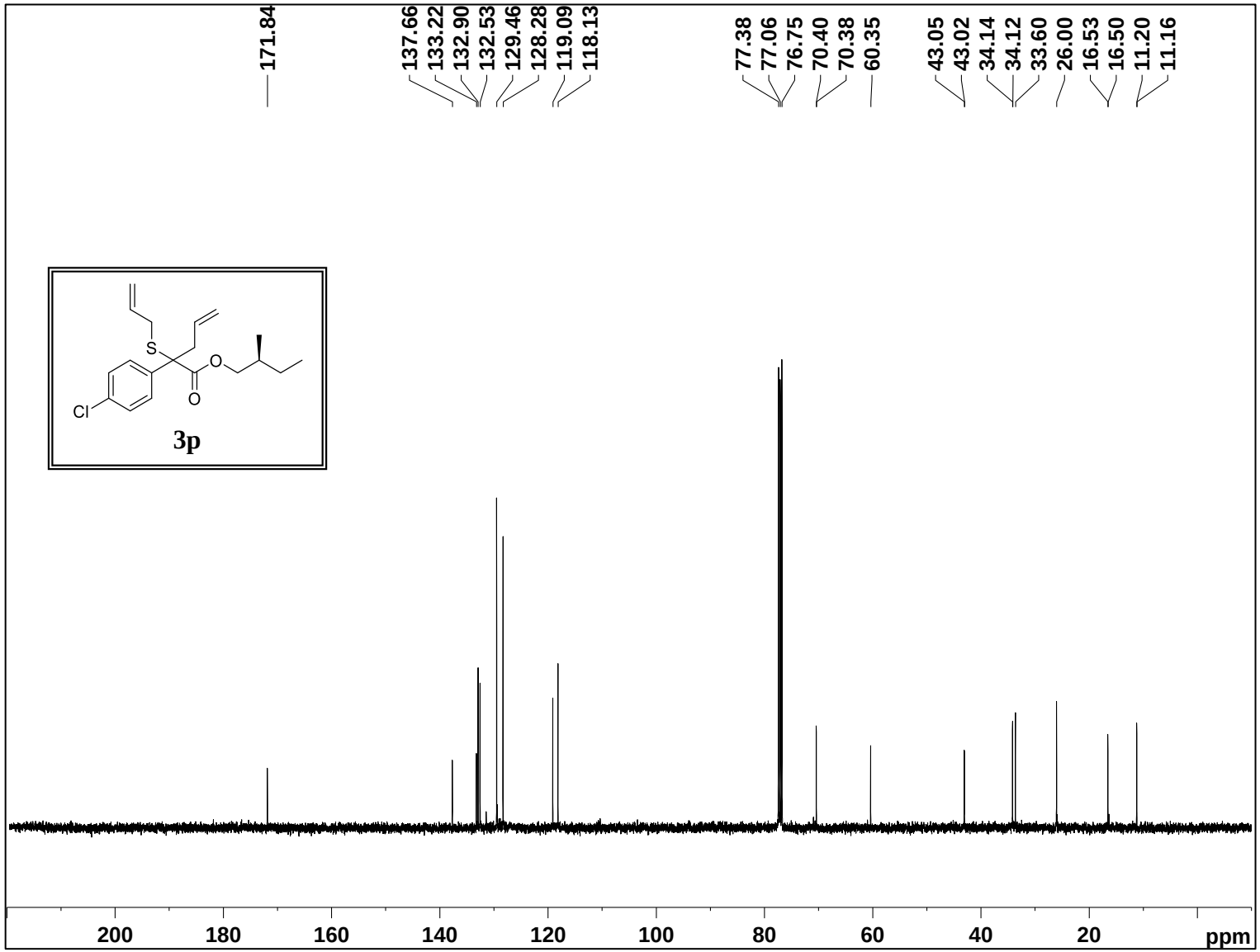
$^{13}C\{^{1}H\}$ NMR for compound **3o** (101 MHz, $CDCl_3$)



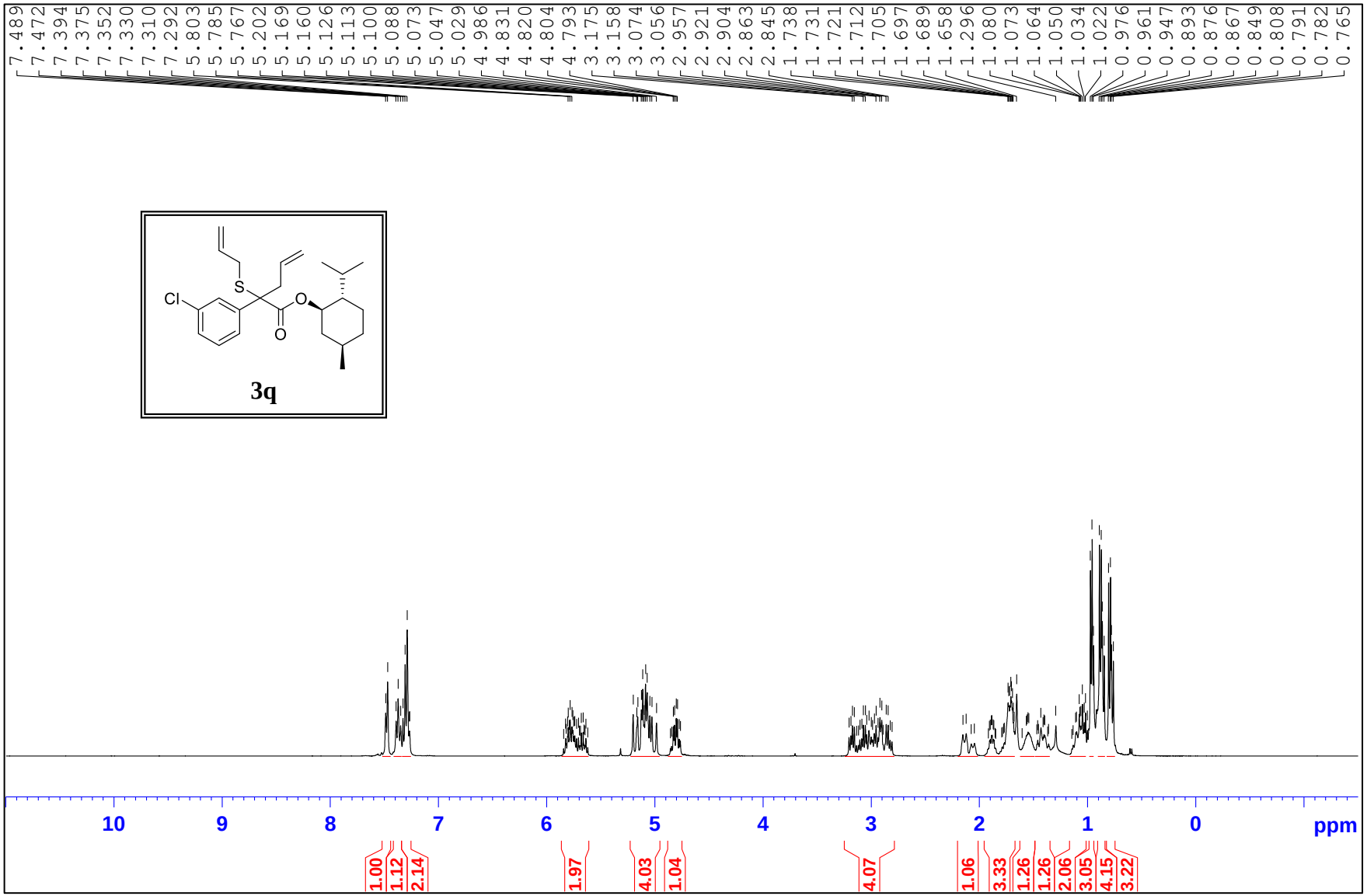
^{1}H NMR for compound **3p** (400 MHz, $CDCl_3$) (**data**)



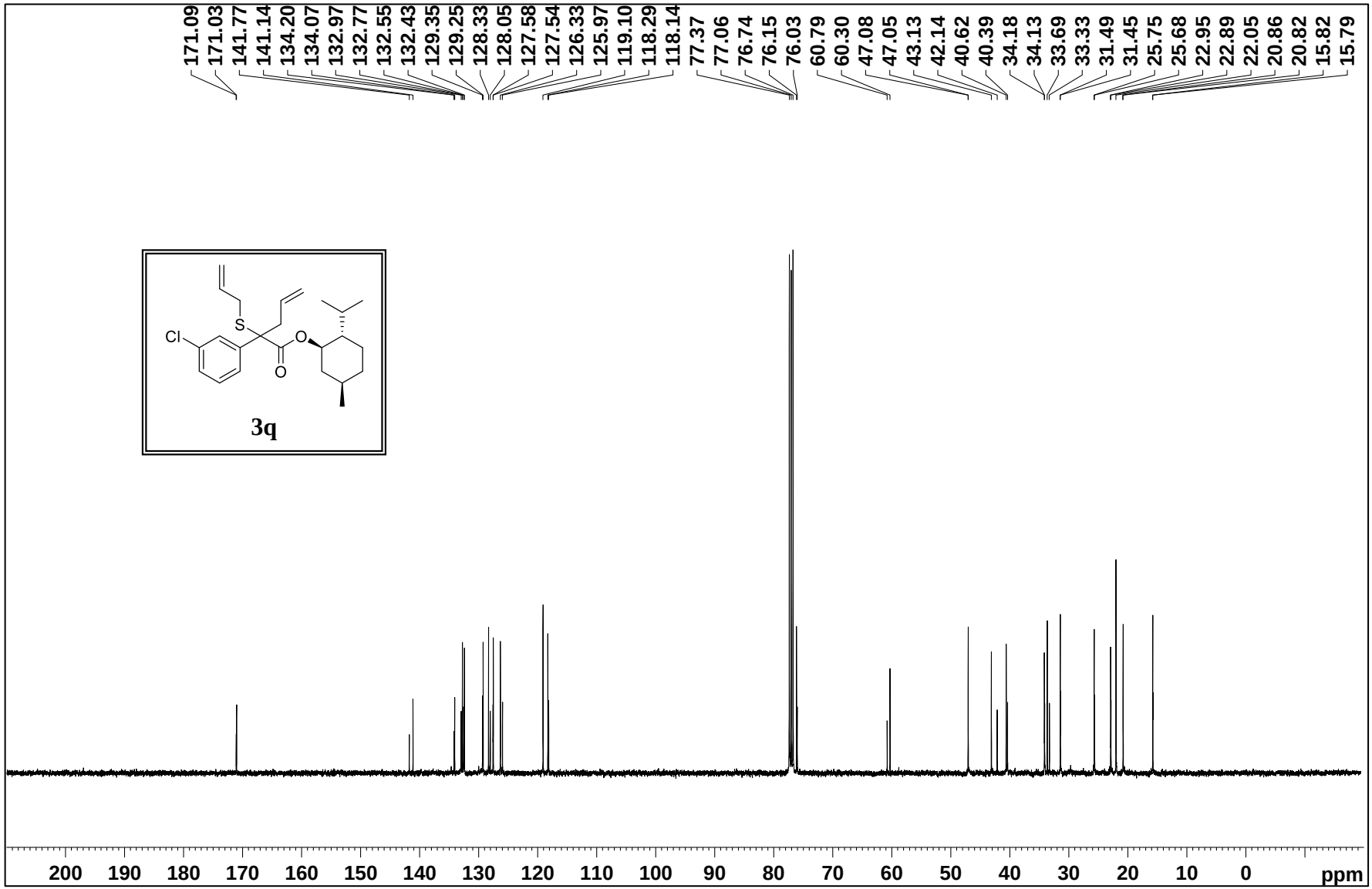
$^{13}C\{^{1}H\}$ NMR for compound **3p** (101 MHz, $CDCl_3$)



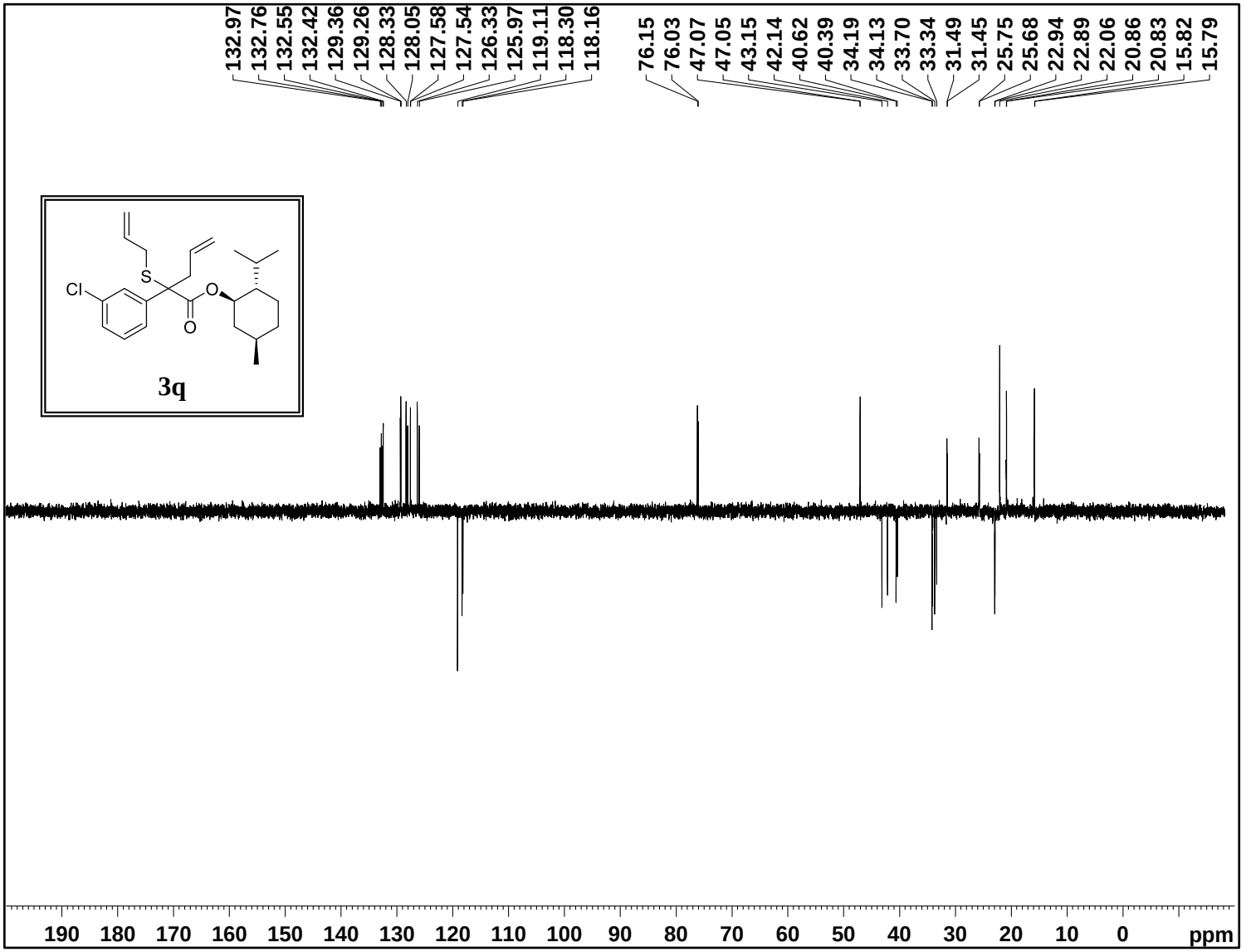
^{1}H NMR for compound **3q** (400 MHz, $CDCl_3$) (**data**)



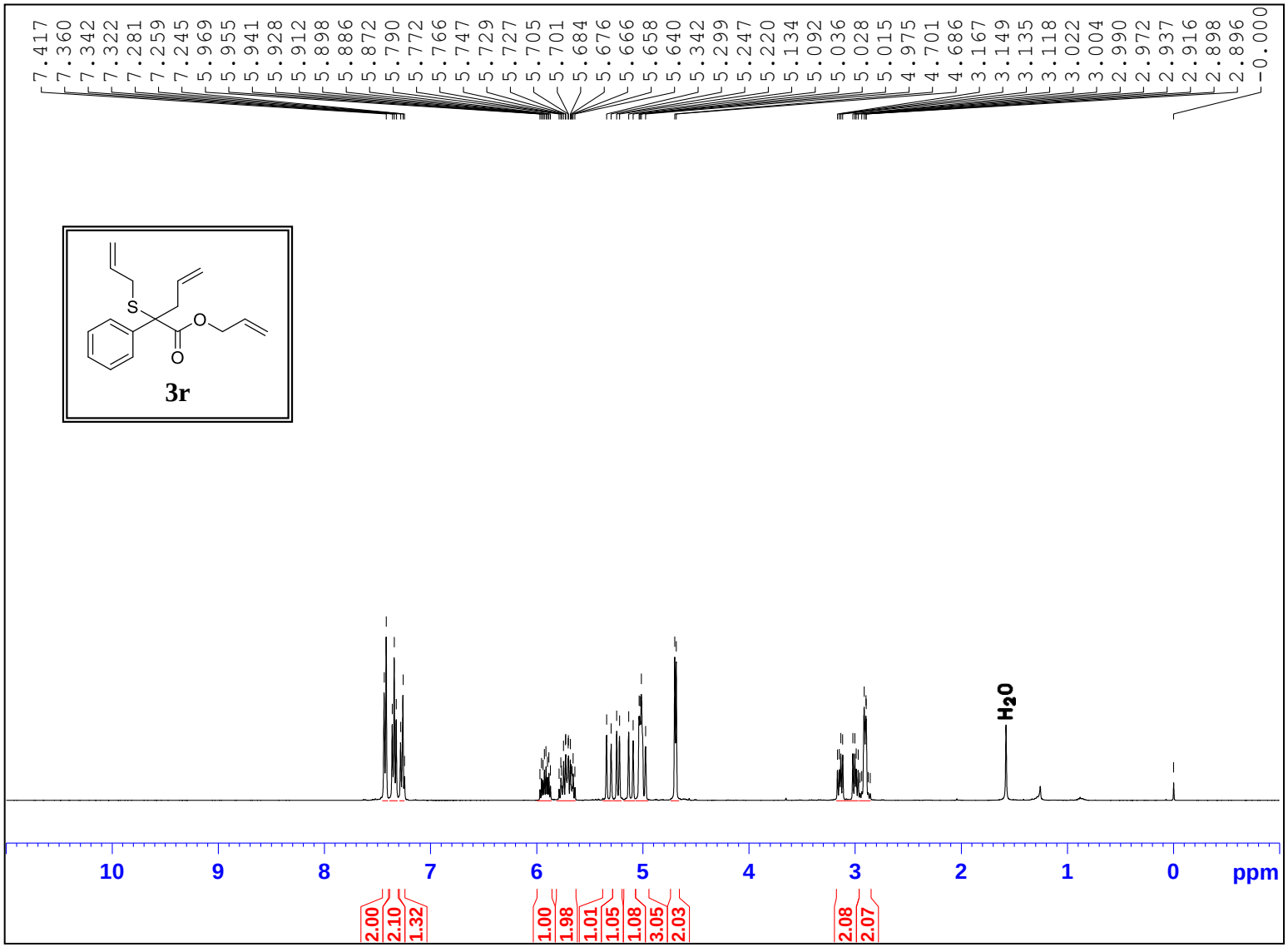
$^{13}C\{^{1}H\}$ NMR for compound **3q** (101 MHz, $CDCl_3$)



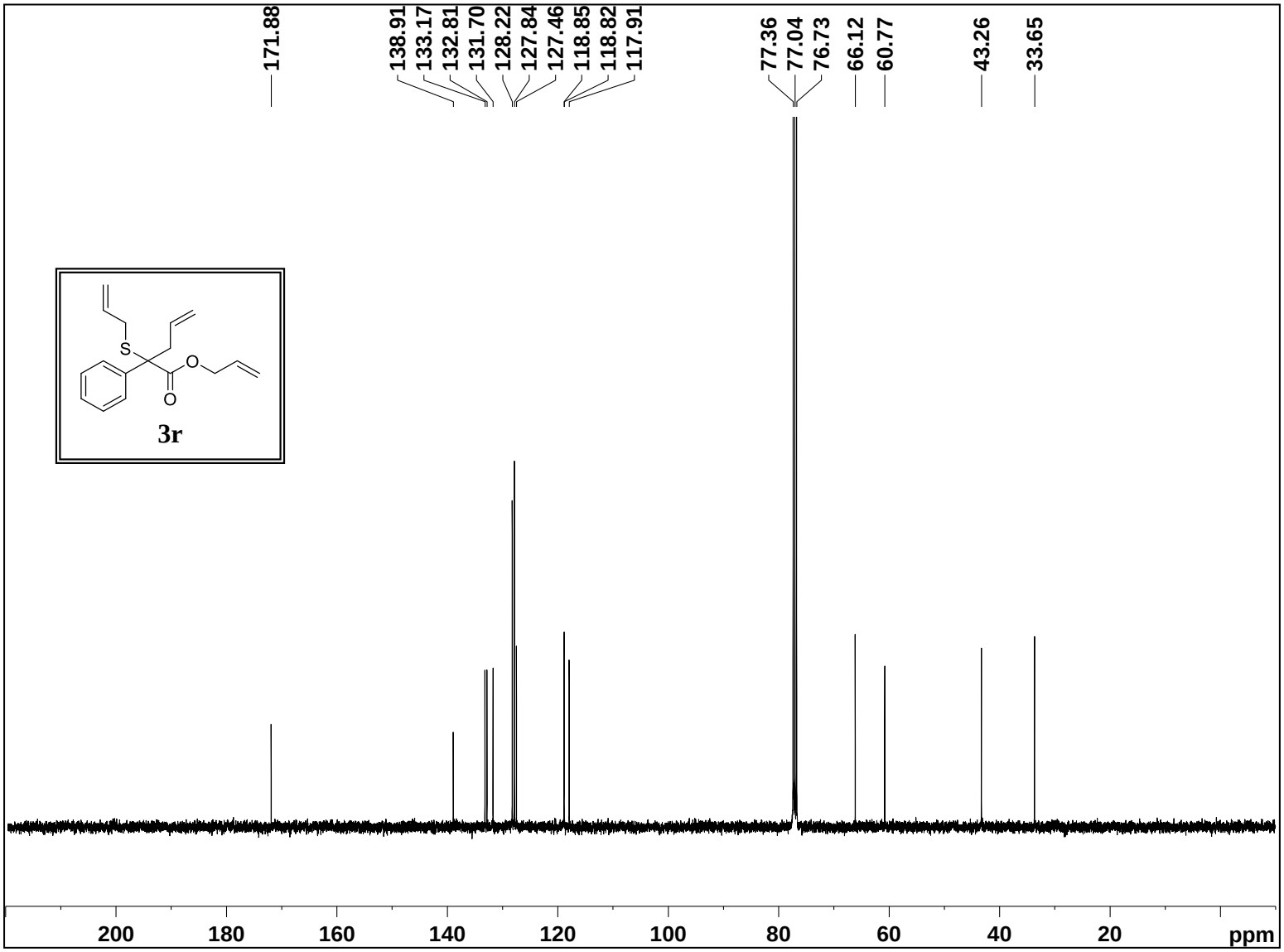
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3q** (101 MHz, $CDCl_3$)



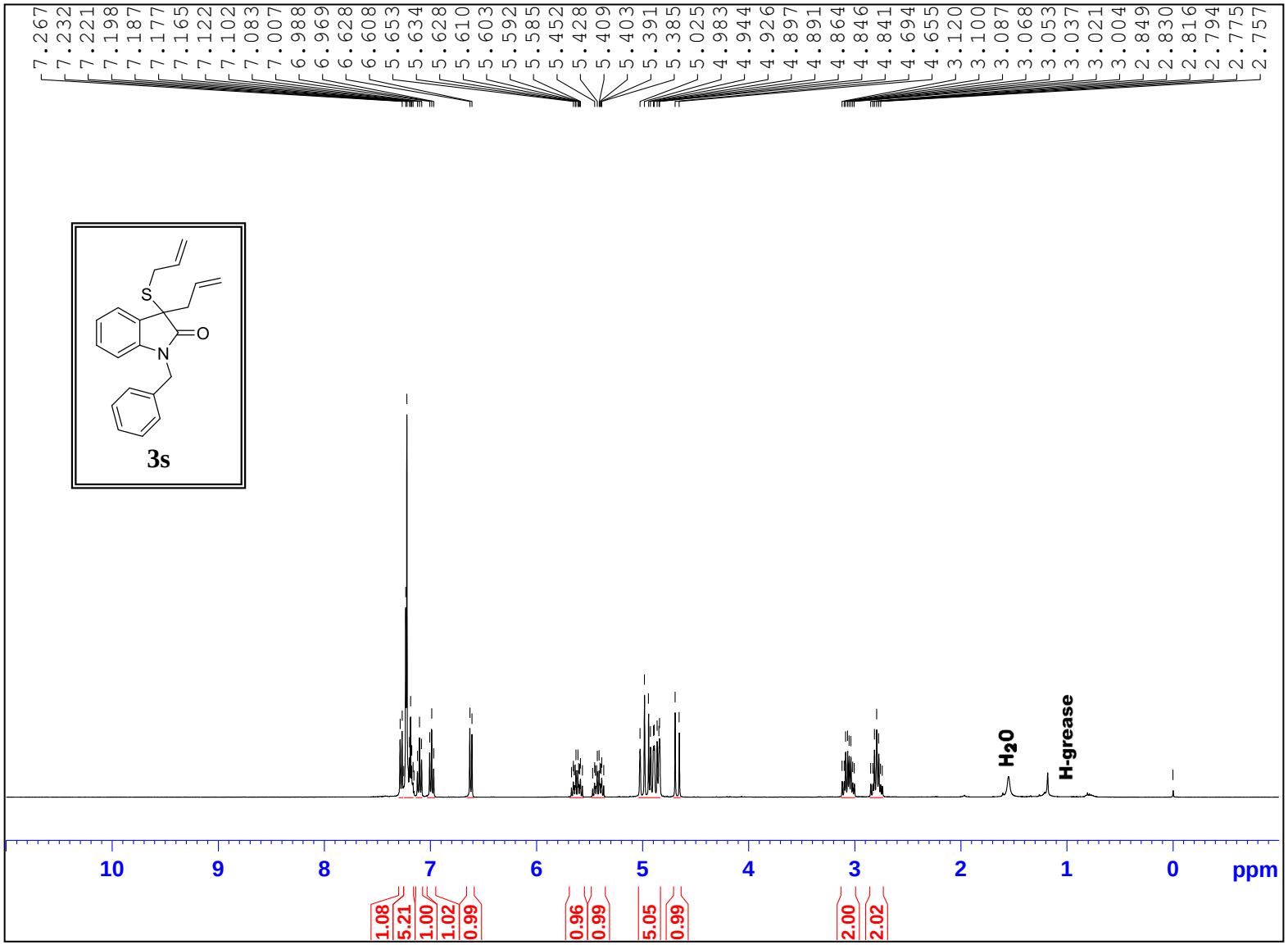
^{1}H NMR for compound **3r** (400 MHz, $CDCl_3$) (**data**)



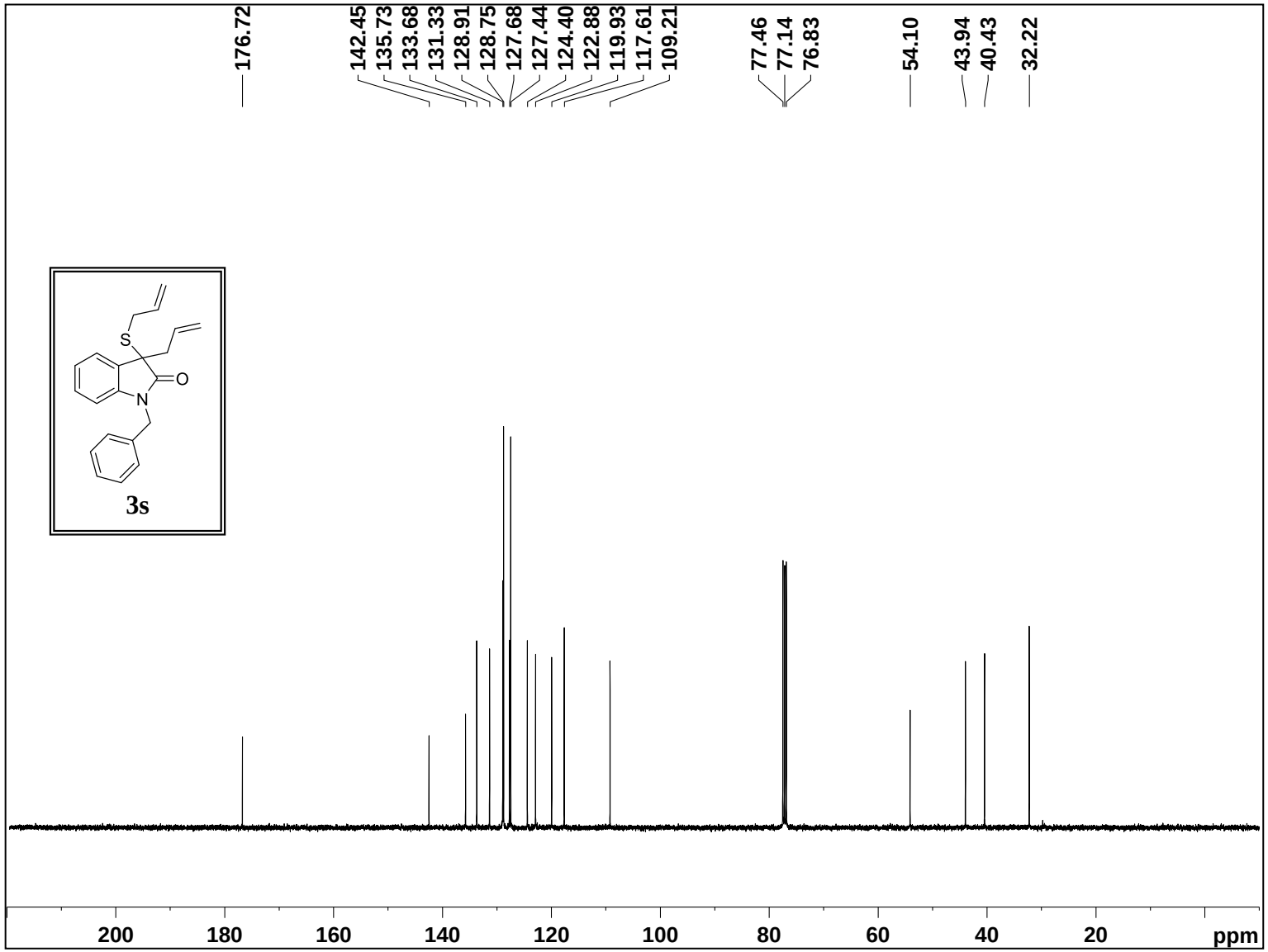
$^{13}C\{^{1}H\}$ NMR for compound **3r** (101 MHz, $CDCl_3$)



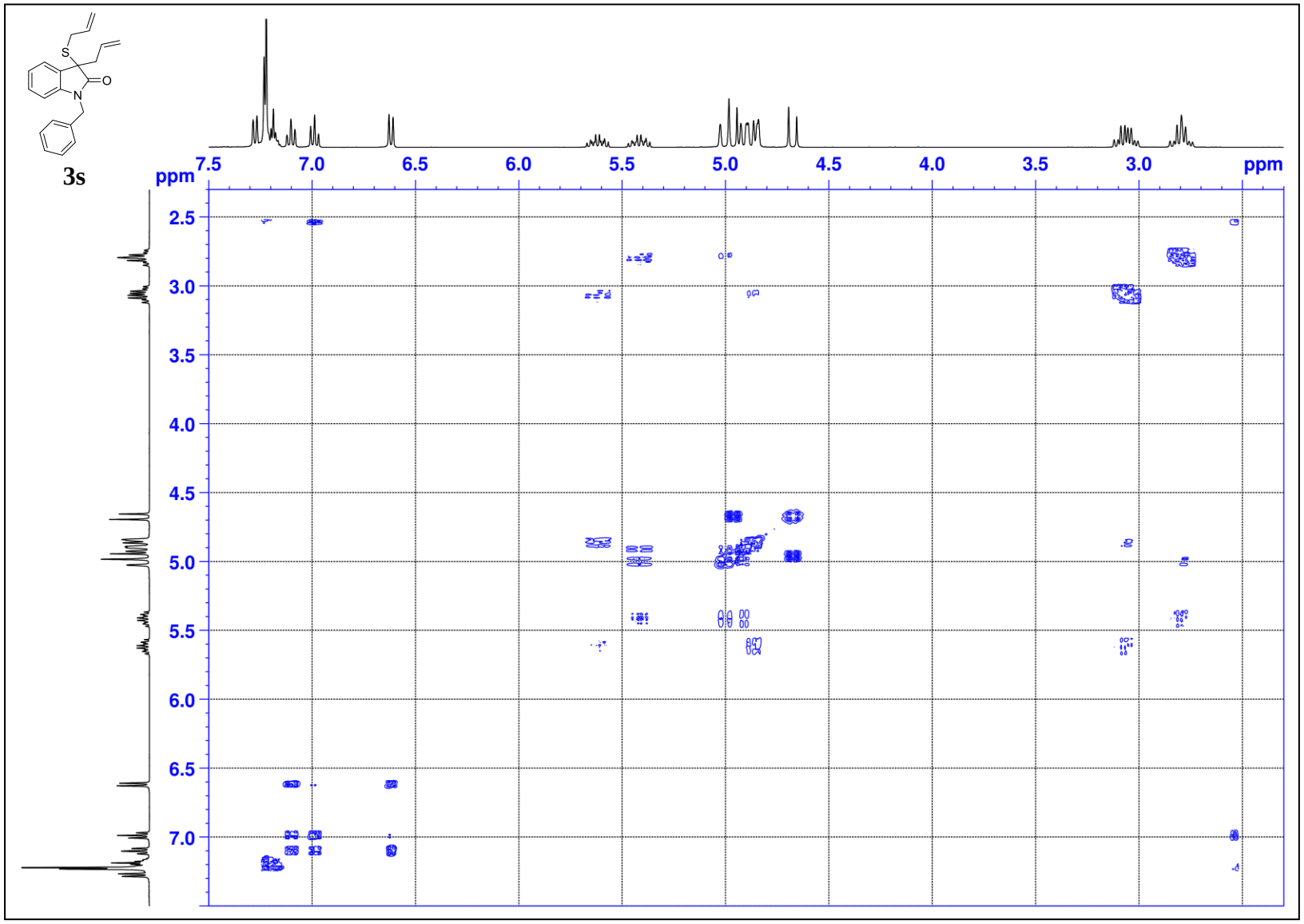
^{1}H NMR for compound **3s** (400 MHz, $CDCl_3$) (**data**)



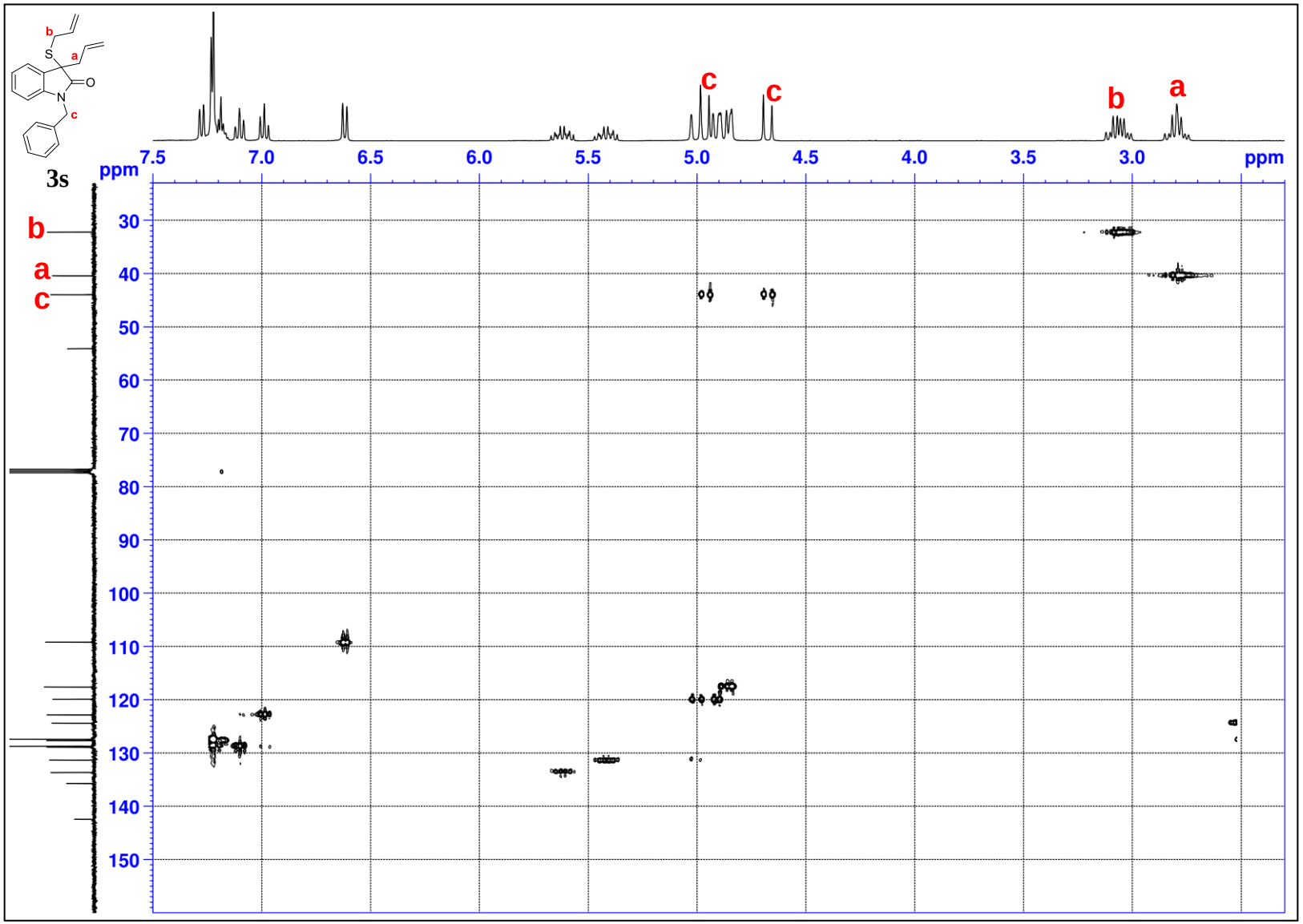
$^{13}C\{^{1}H\}$ NMR for compound **3s** (101 MHz, $CDCl_3$)



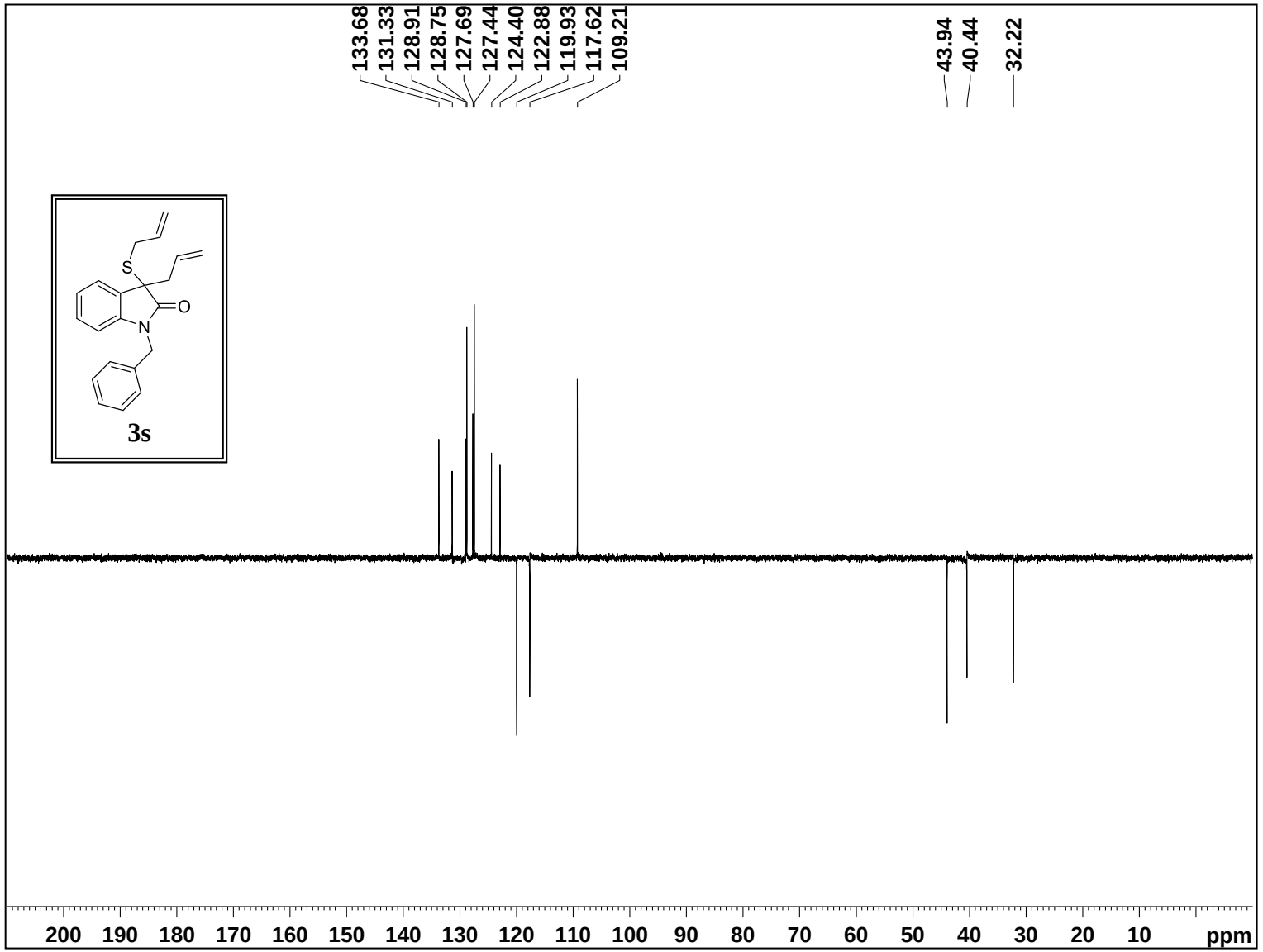
[^{1}H, ^{1}H] COSY for compound **3s** (400 MHz, $CDCl_3$)



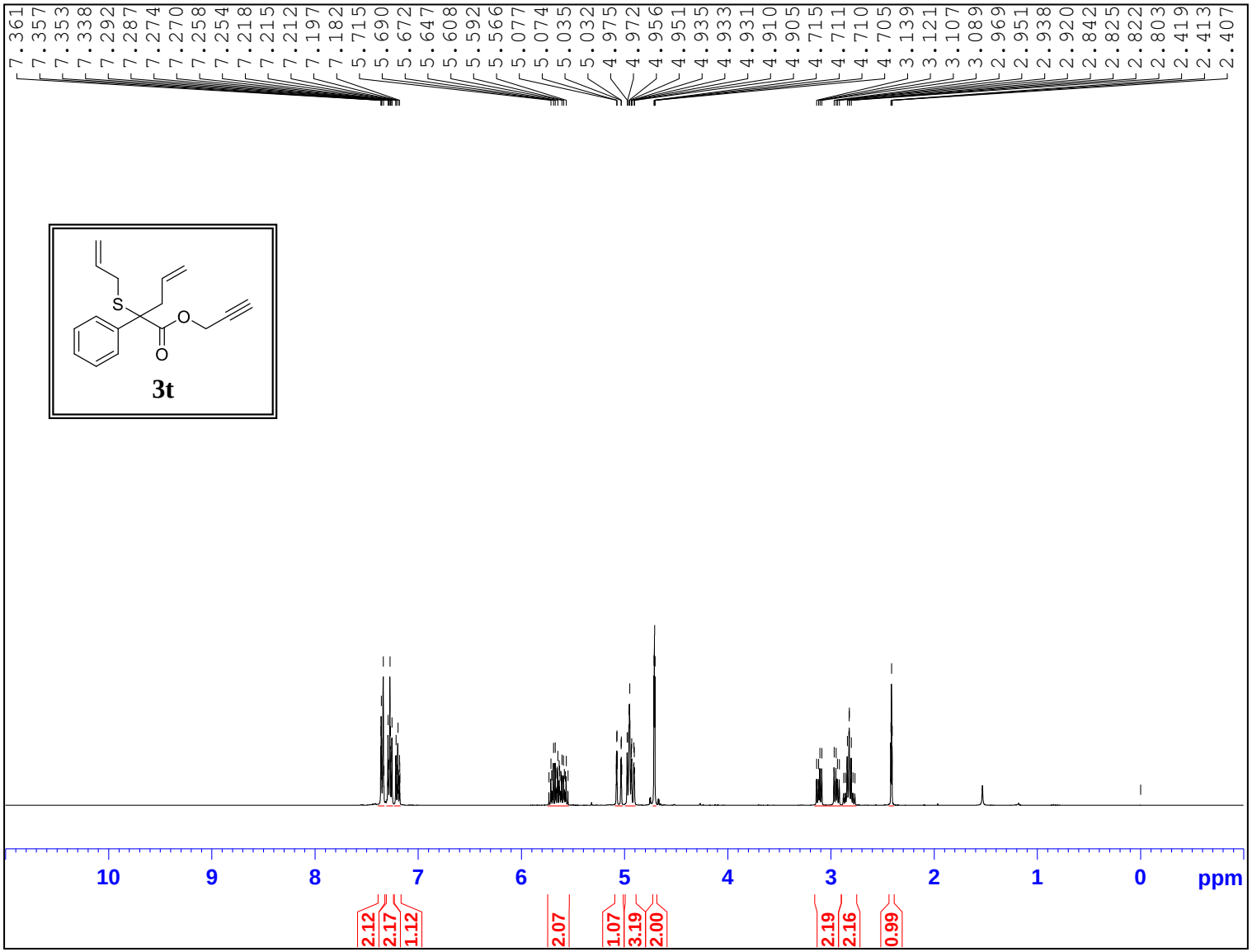
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **3s** (400 MHz, $CDCl_3$)



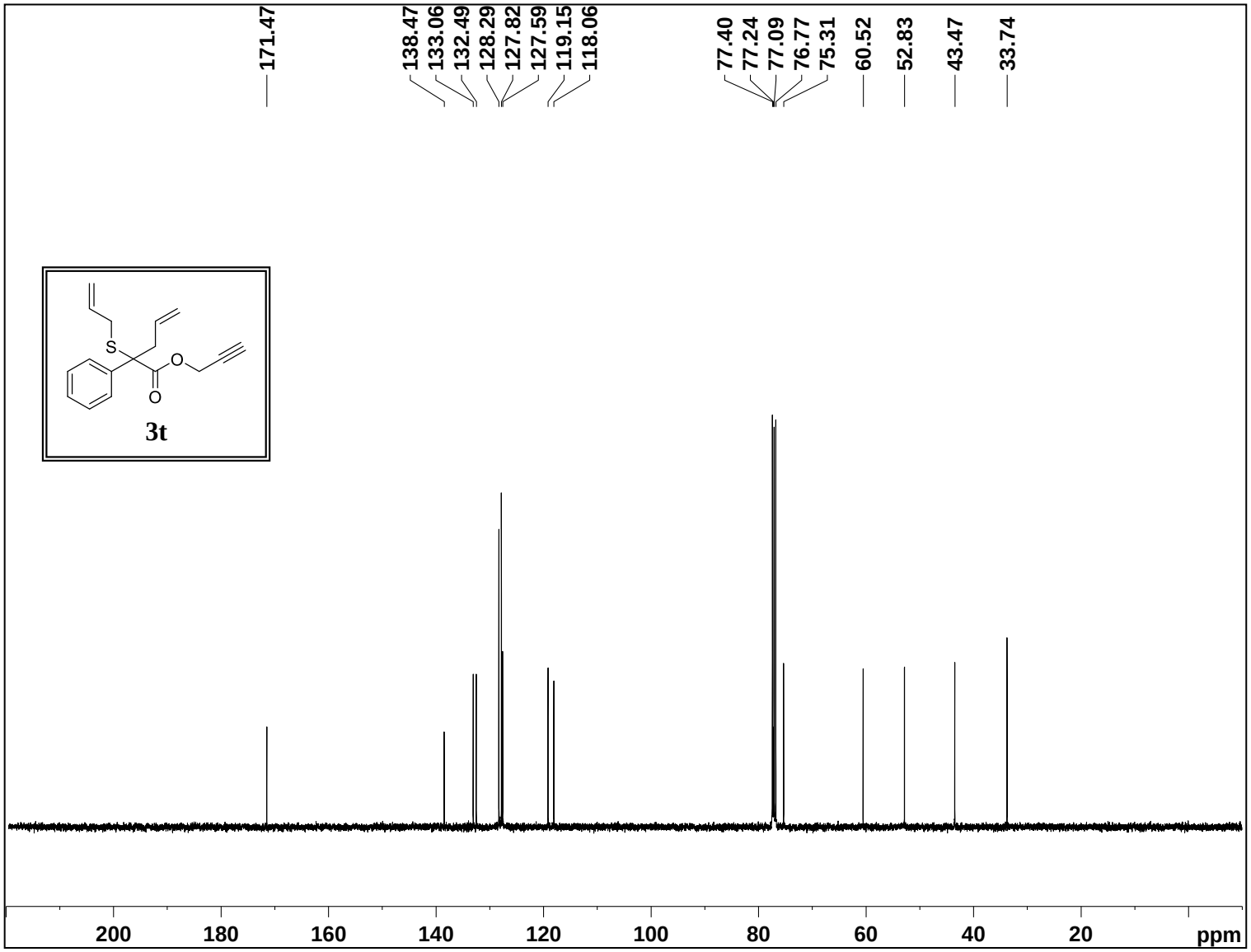
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3s** (101 MHz, $CDCl_3$)



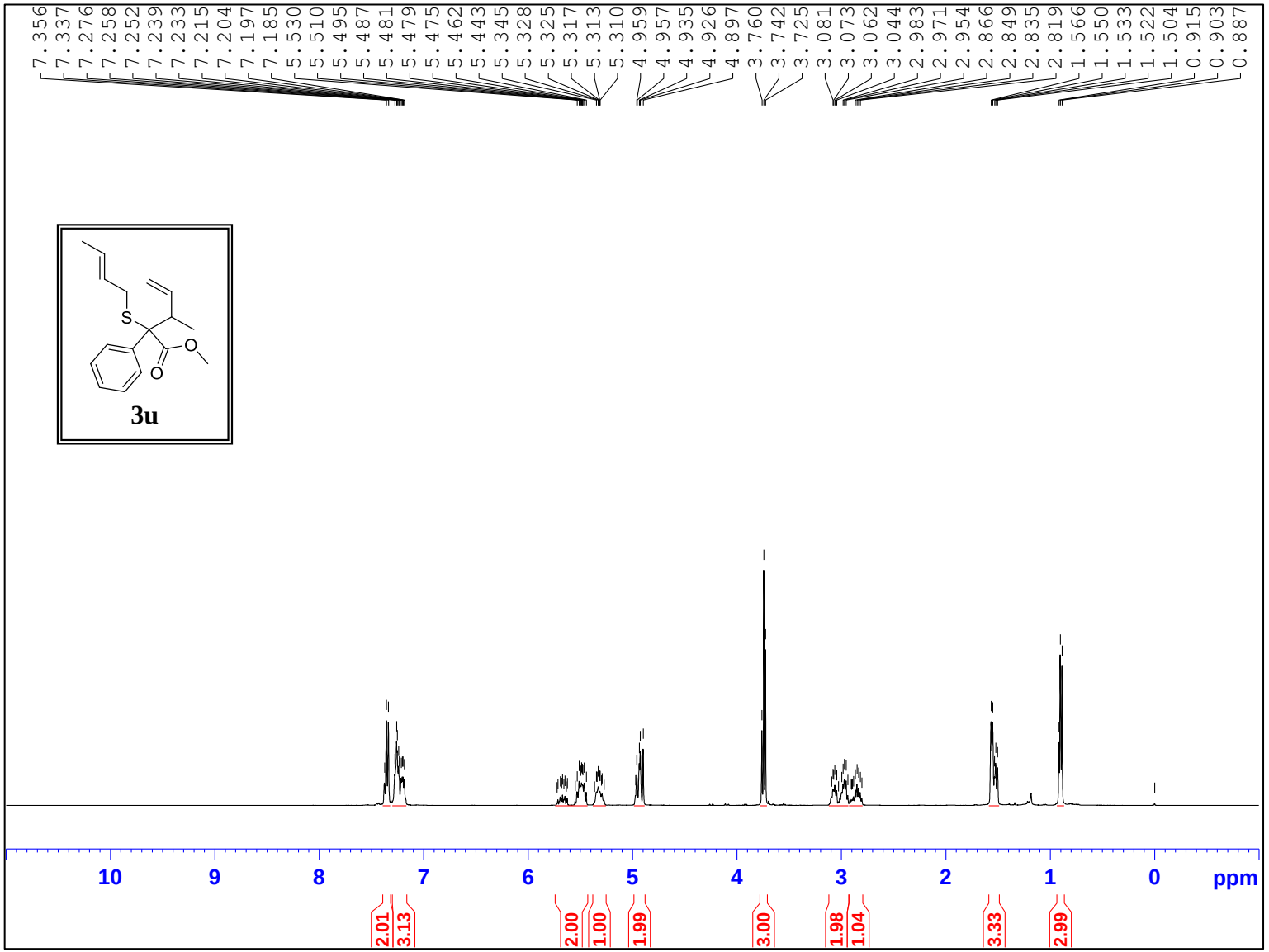
^{1}H NMR for compound **3t** (400 MHz, $CDCl_3$) (**data**)



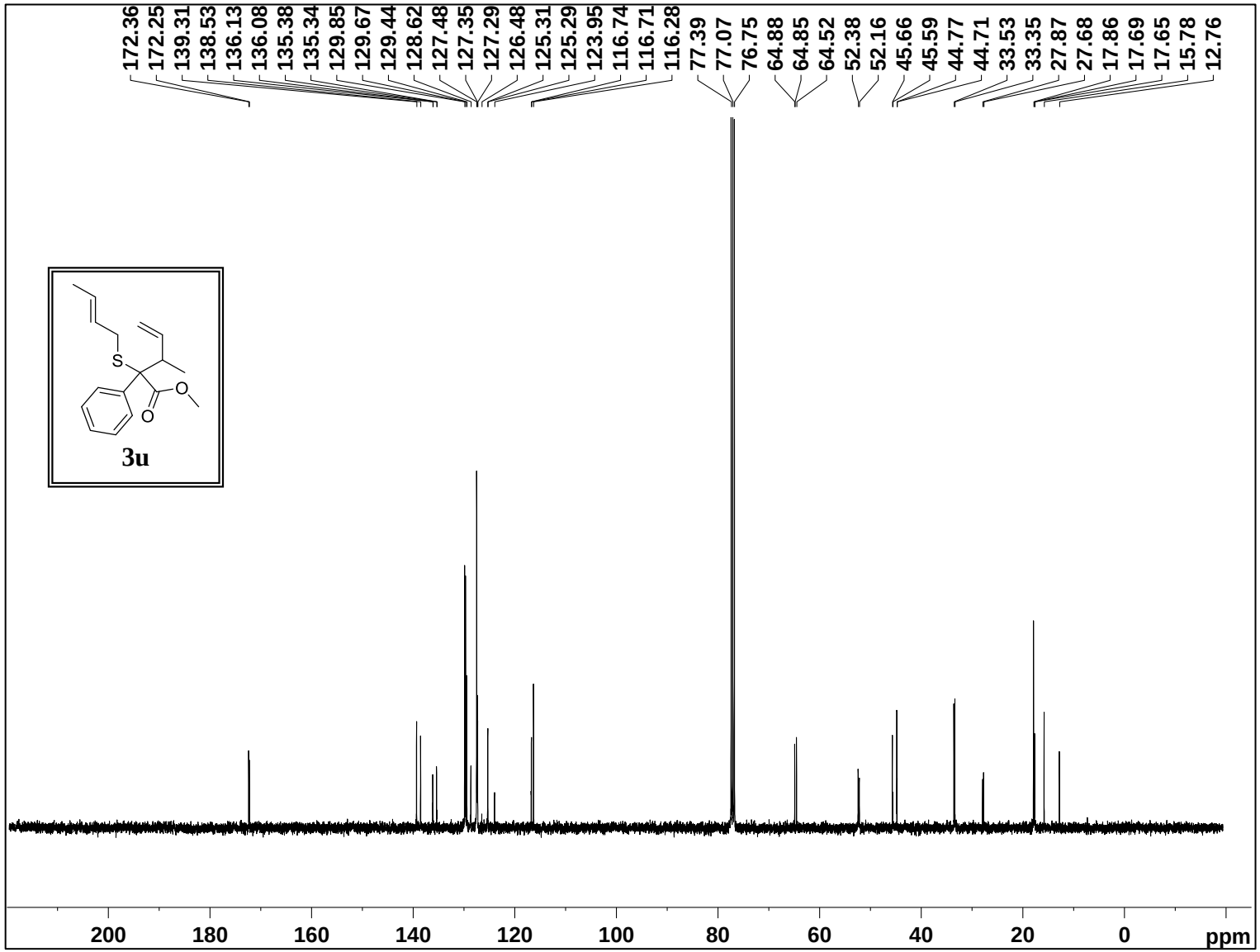
$^{13}C\{^{1}H\}$ NMR for compound **3t** (101 MHz, $CDCl_3$)



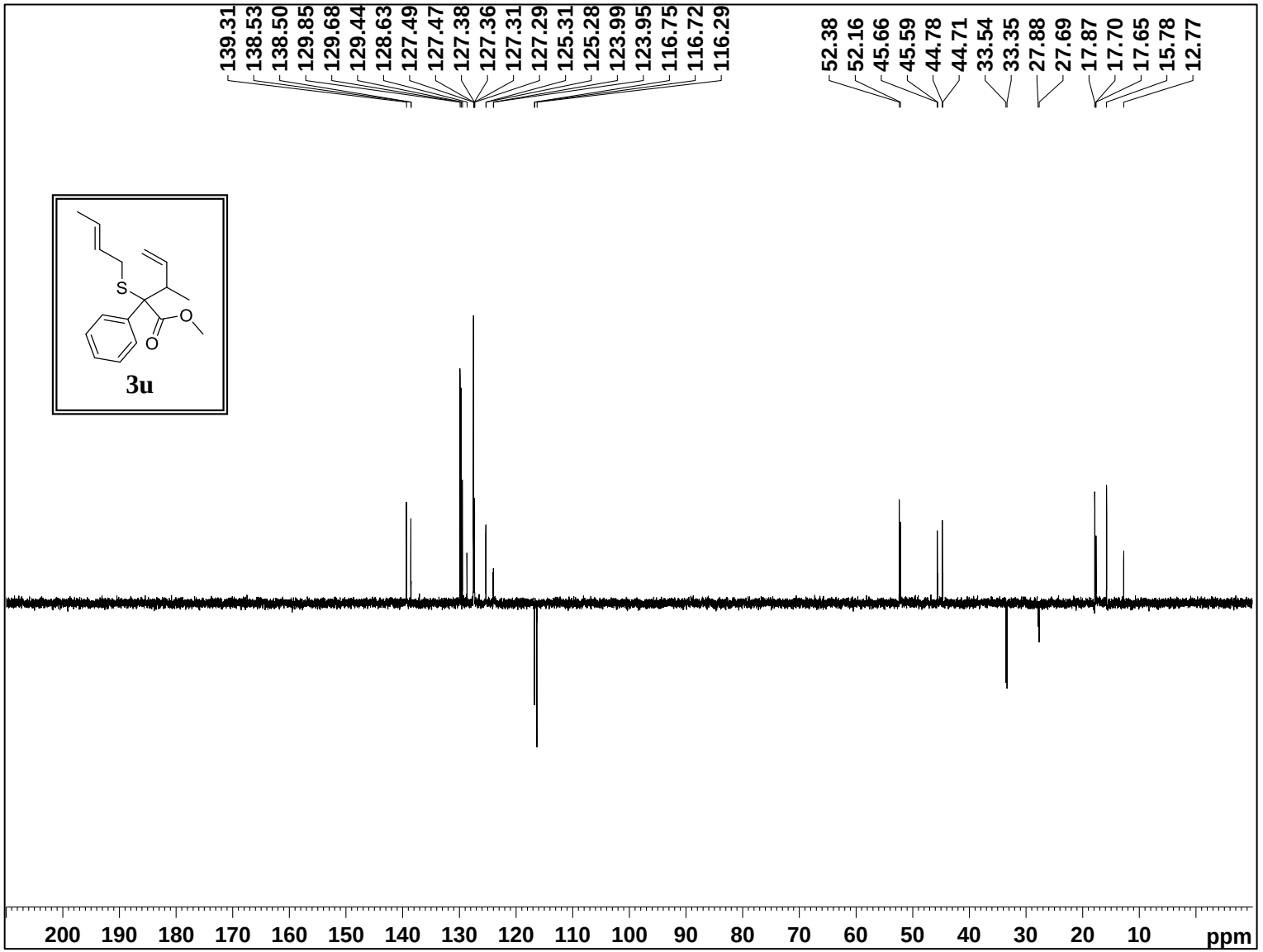
^{1}H NMR for compound **3u** (400 MHz, $CDCl_3$) (**data**)



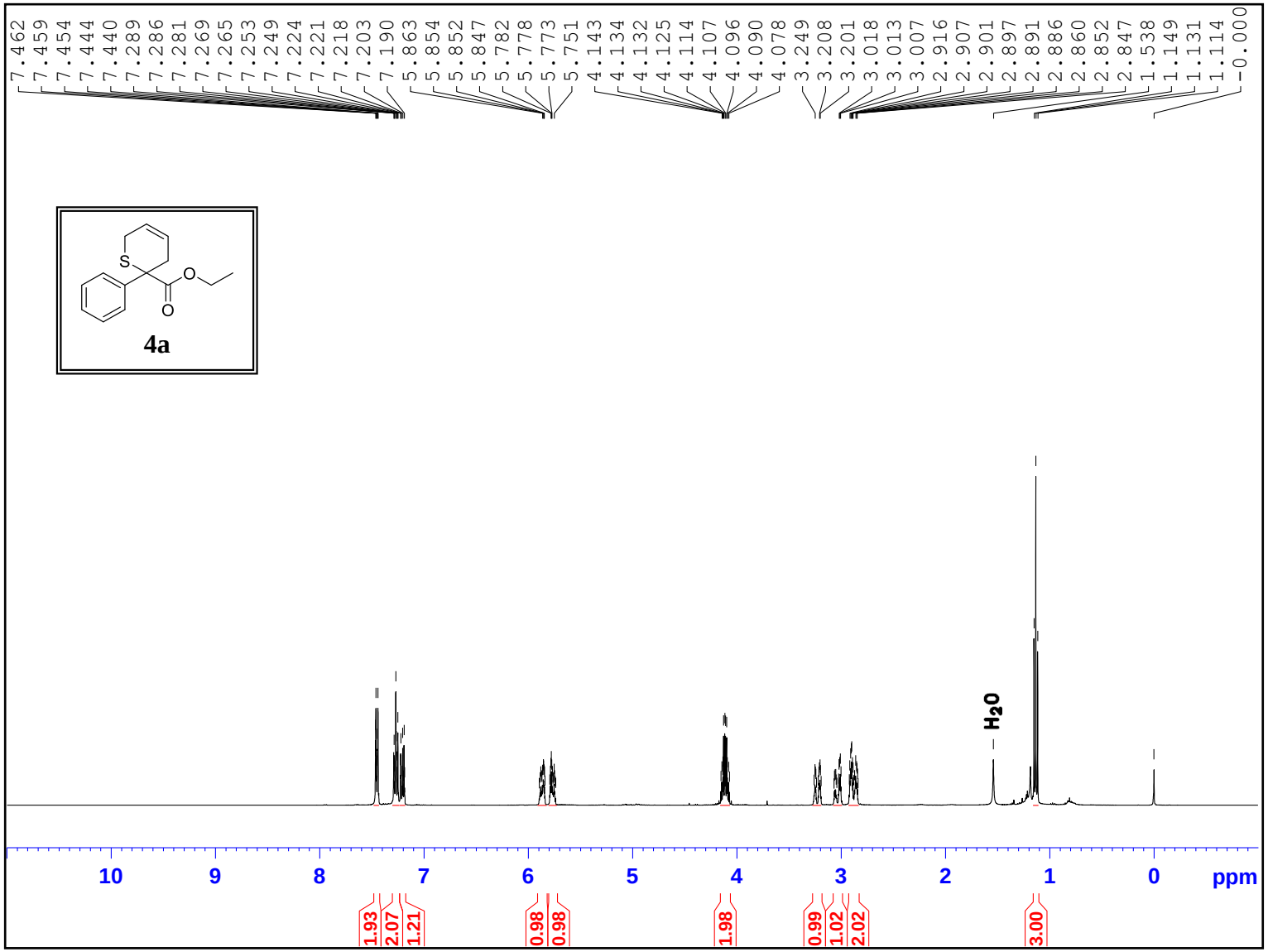
$^{13}C\{^{1}H\}$ NMR for compound **3u** (101 MHz, $CDCl_3$)



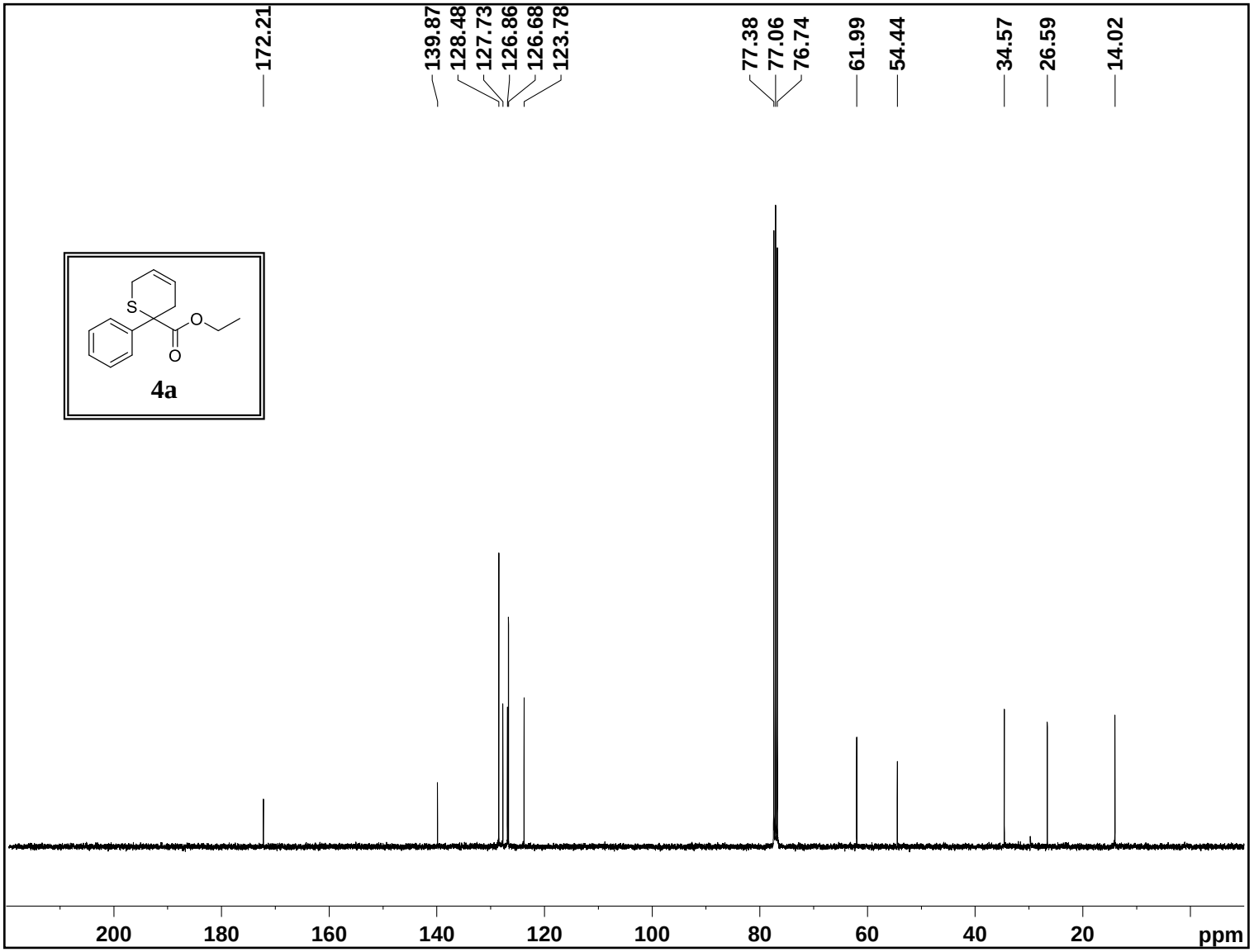
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **3u** (101 MHz, $CDCl_3$)



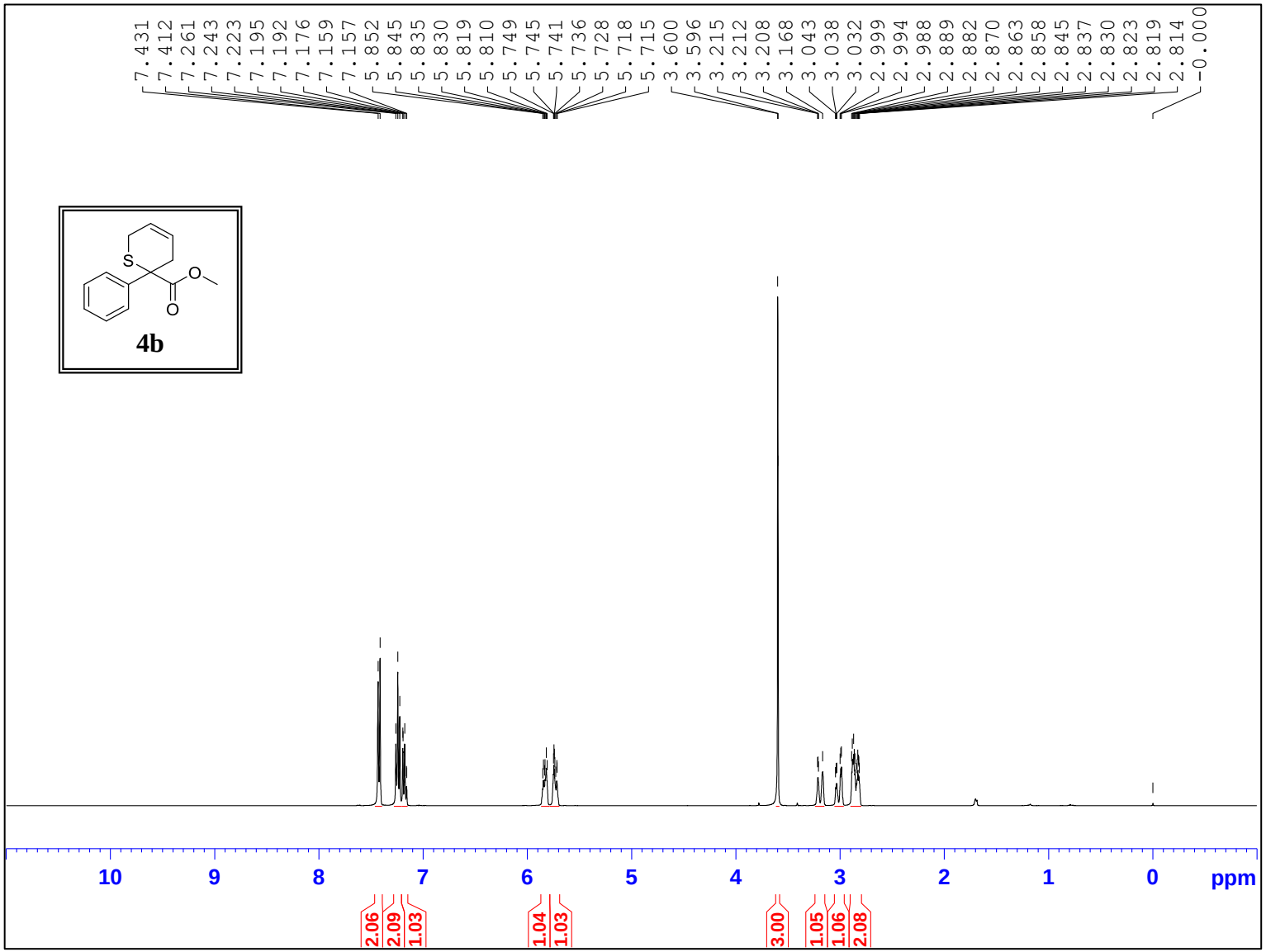
^{1}H NMR for compound **4a** (400 MHz, $CDCl_3$) (**data**)



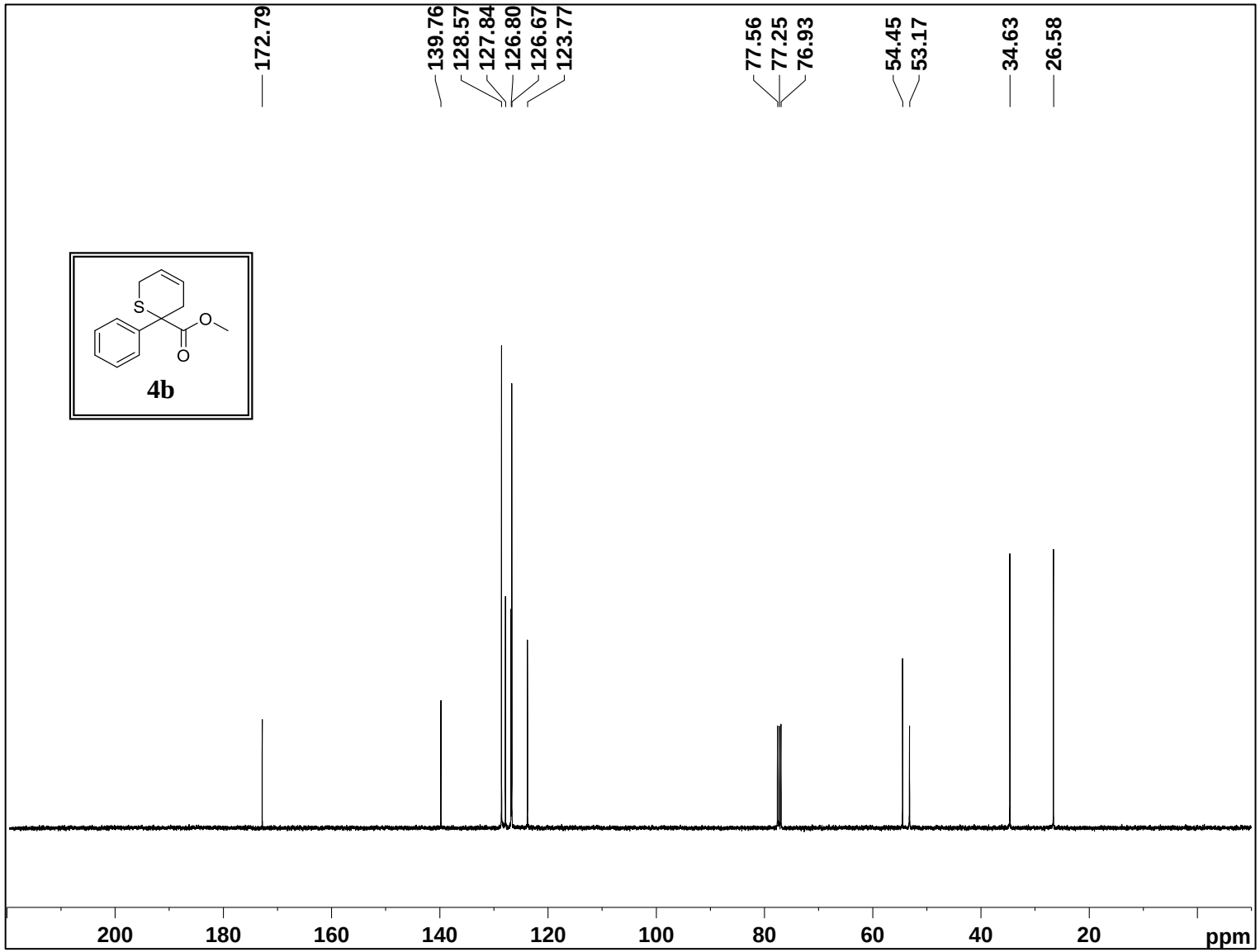
$^{13}C\{^{1}H\}$ NMR for compound **4a** (101 MHz, $CDCl_3$)



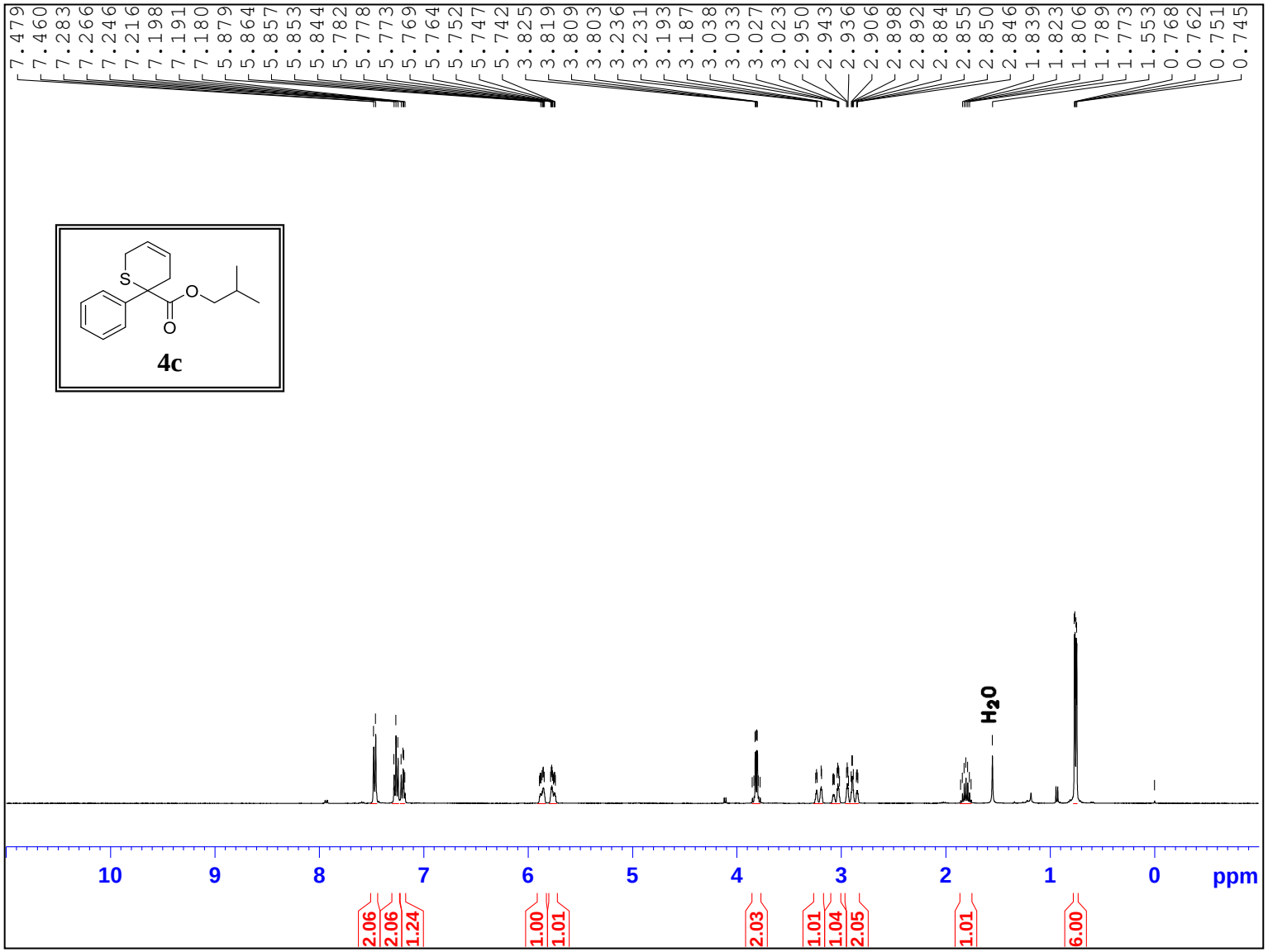
^{1}H NMR for compound **4b** (400 MHz, $CDCl_3$) (**data**)



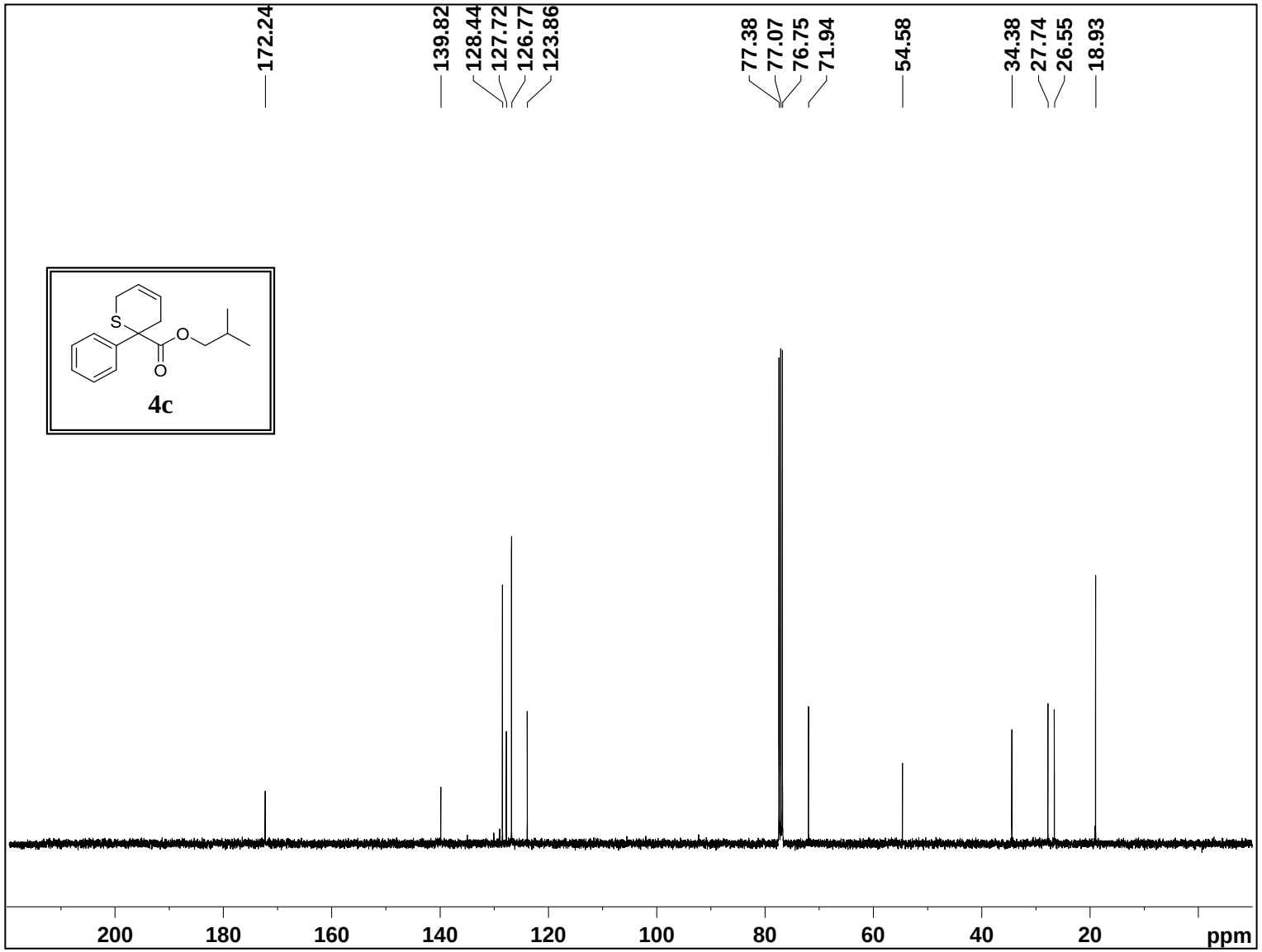
$^{13}C\{^{1}H\}$ NMR for compound **4b** (101 MHz, $CDCl_3$)



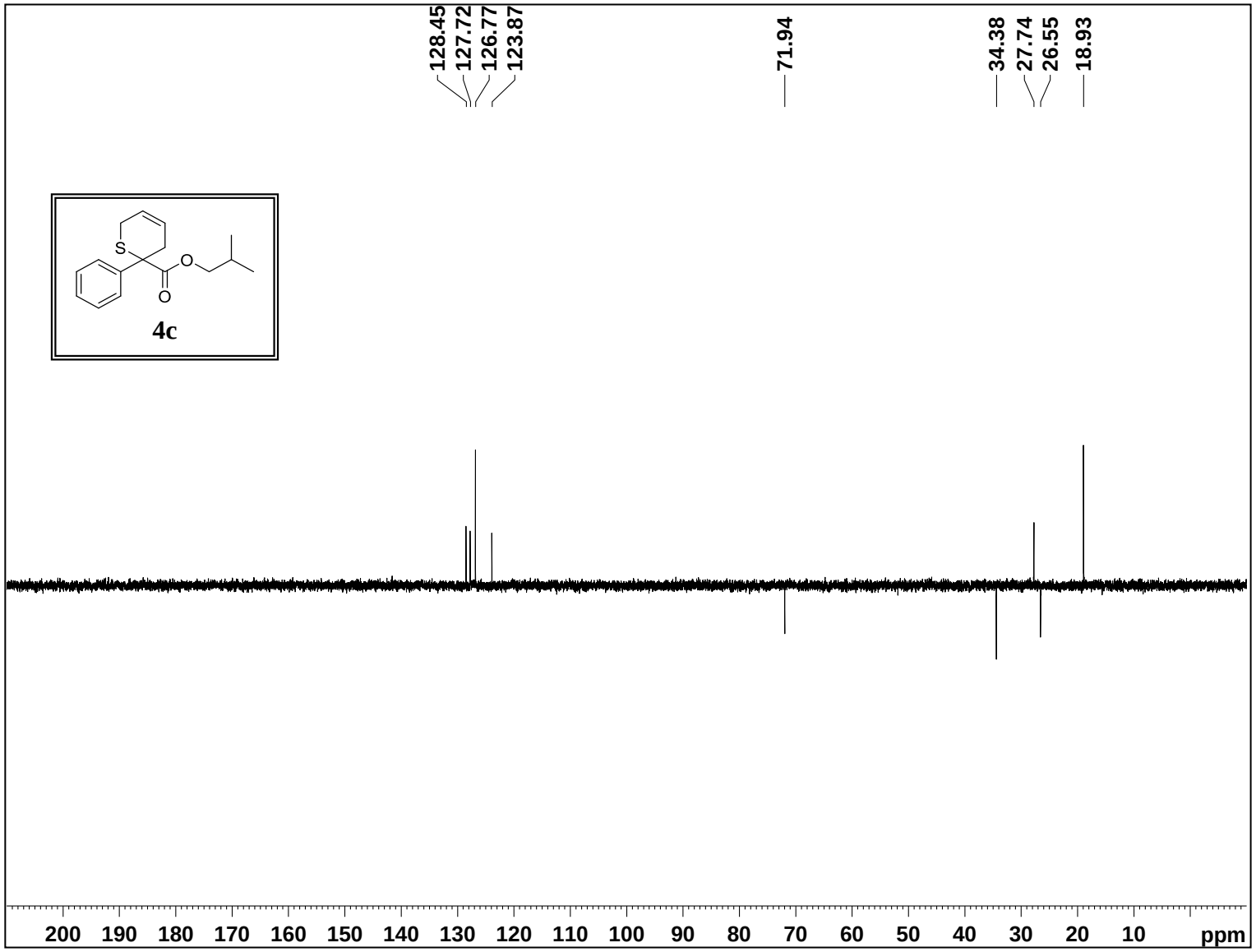
^{1}H NMR for compound **4c** (400 MHz, $CDCl_3$) (**data**)



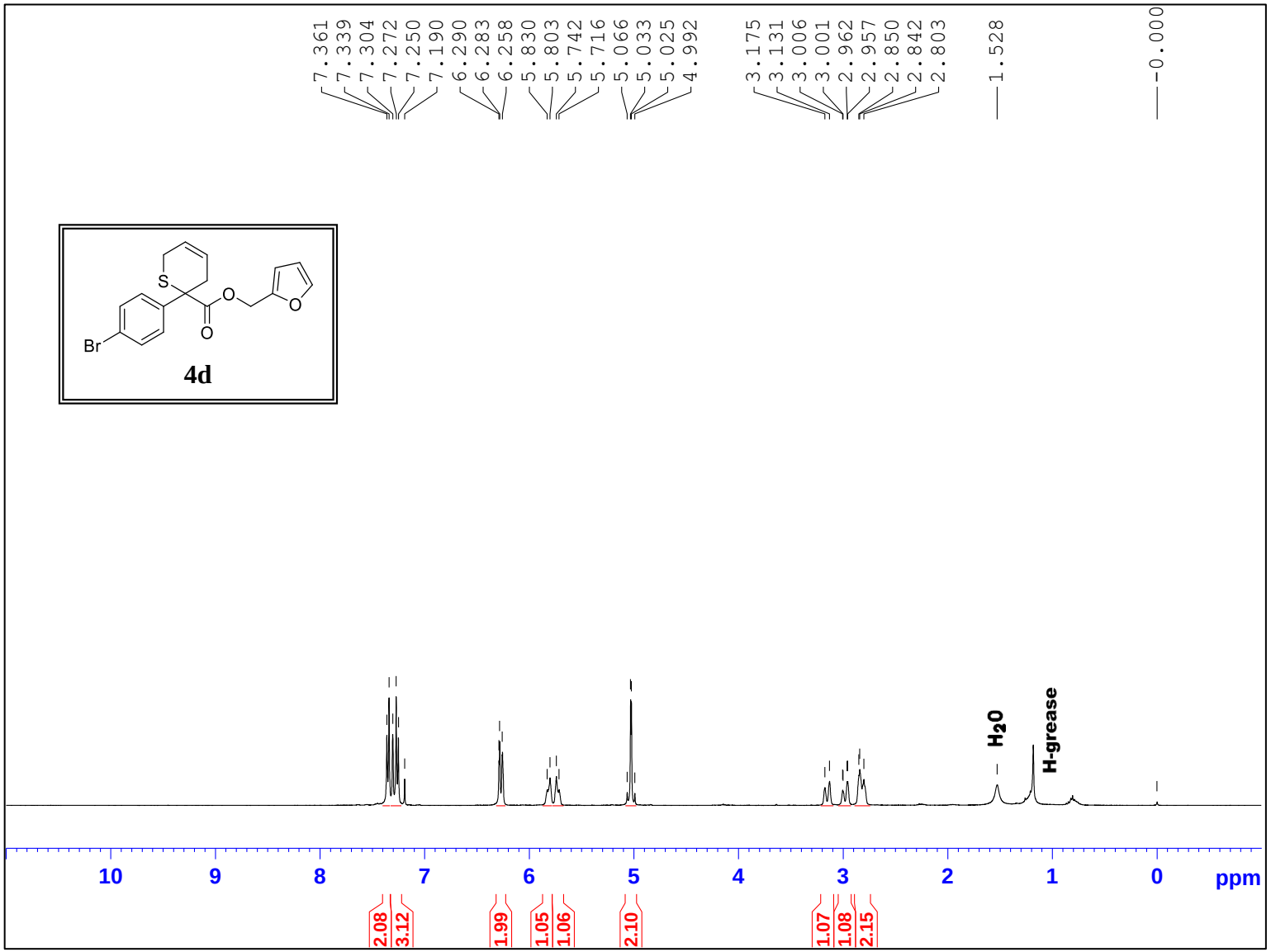
$^{13}C\{^{1}H\}$ NMR for compound **4c** (101 MHz, $CDCl_3$)



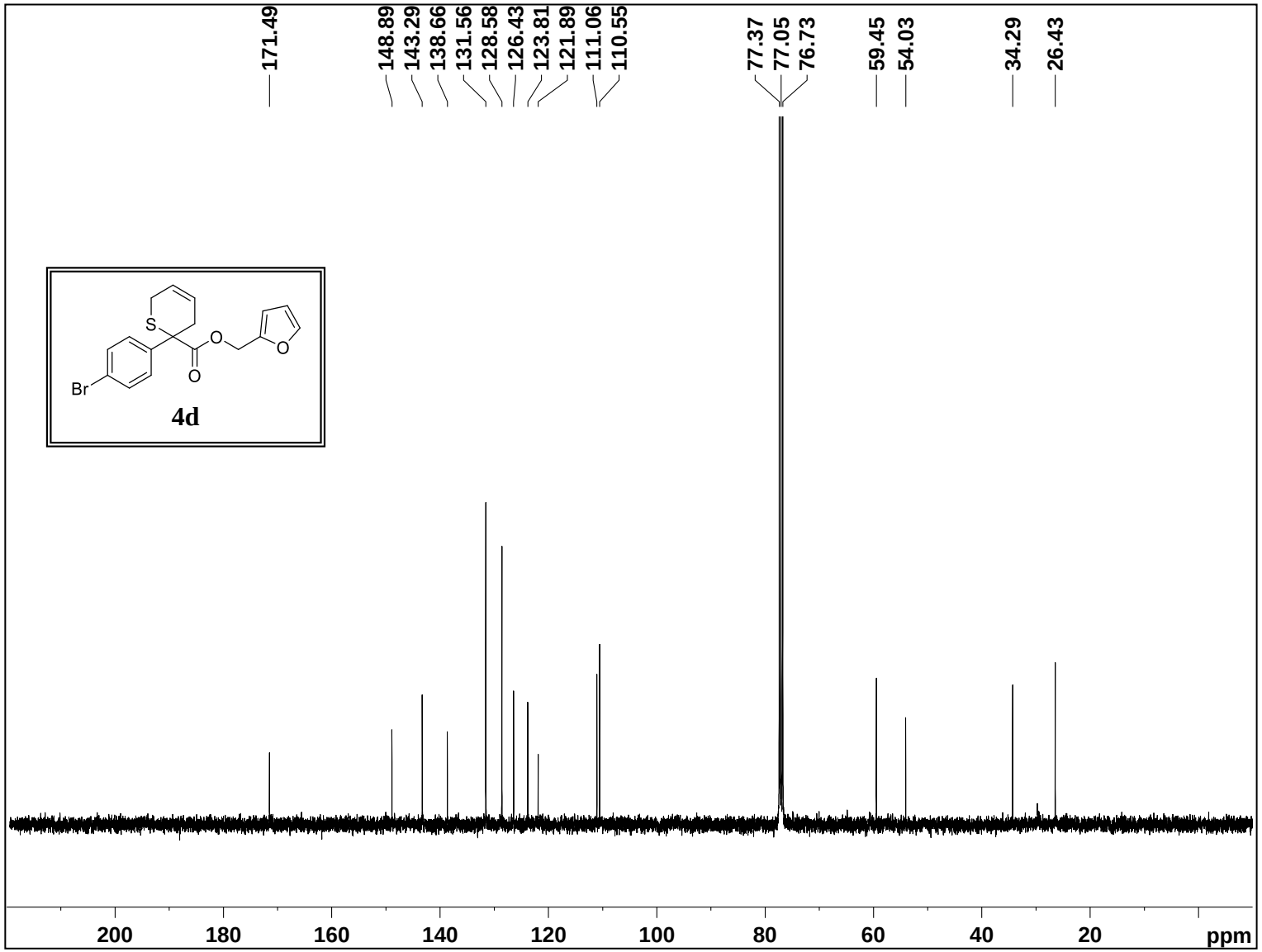
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4c** (101 MHz, $CDCl_3$)



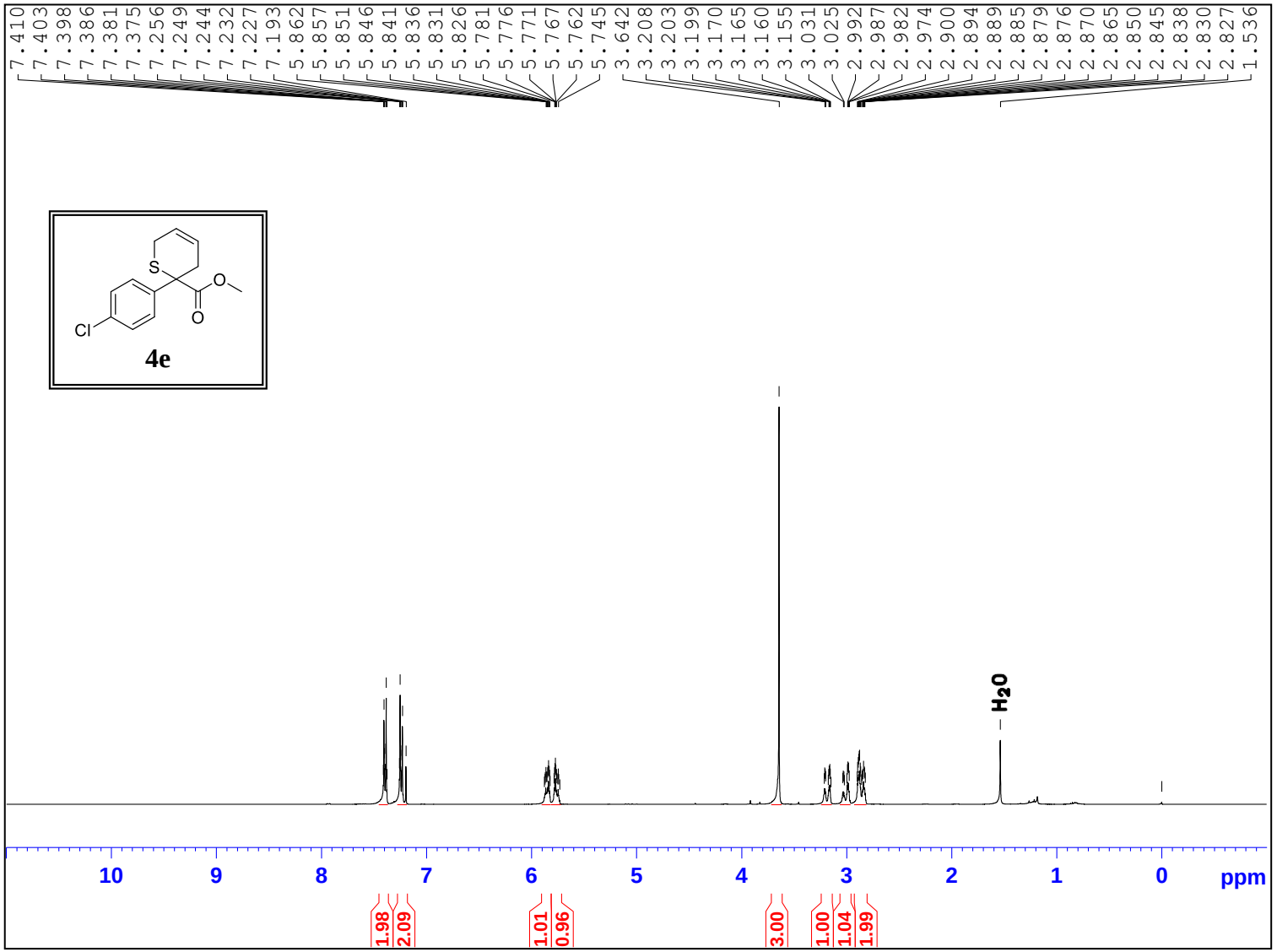
^{1}H NMR for compound **4d** (400 MHz, $CDCl_3$) (**data**)



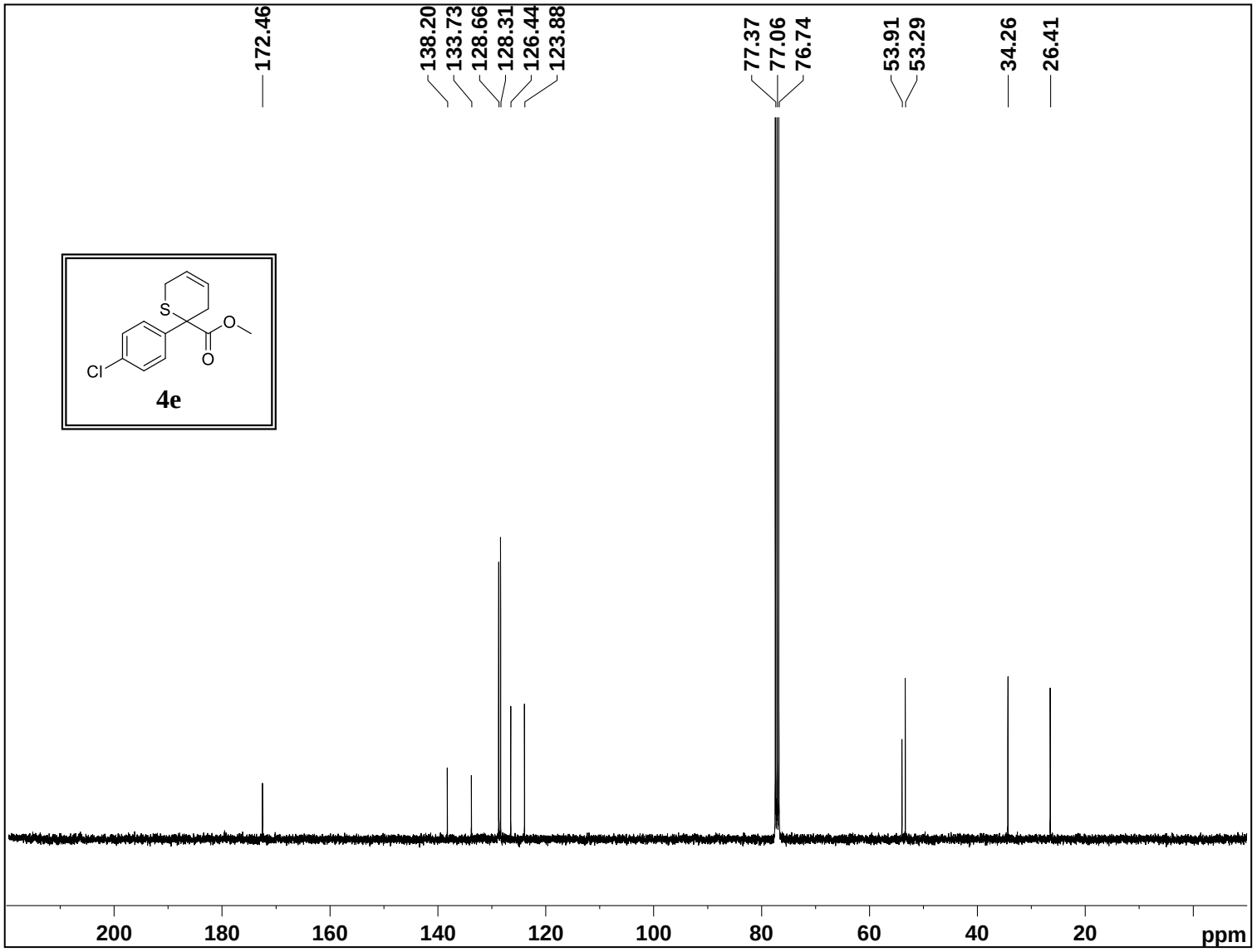
$^{13}C\{^{1}H\}$ NMR for compound **4d** (101 MHz, $CDCl_3$)



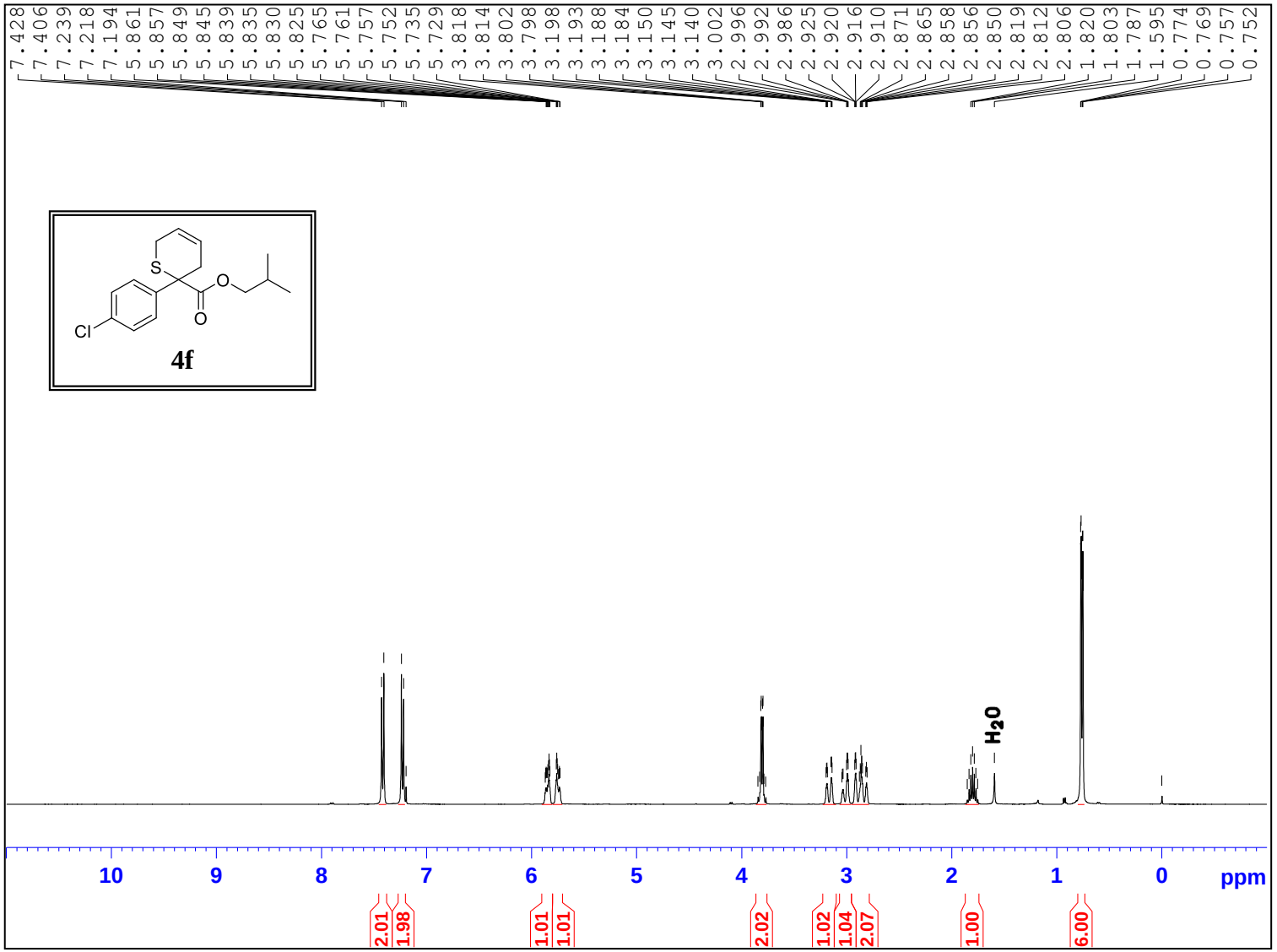
^{1}H NMR for compound **4e** (400 MHz, $CDCl_3$) (**data**)



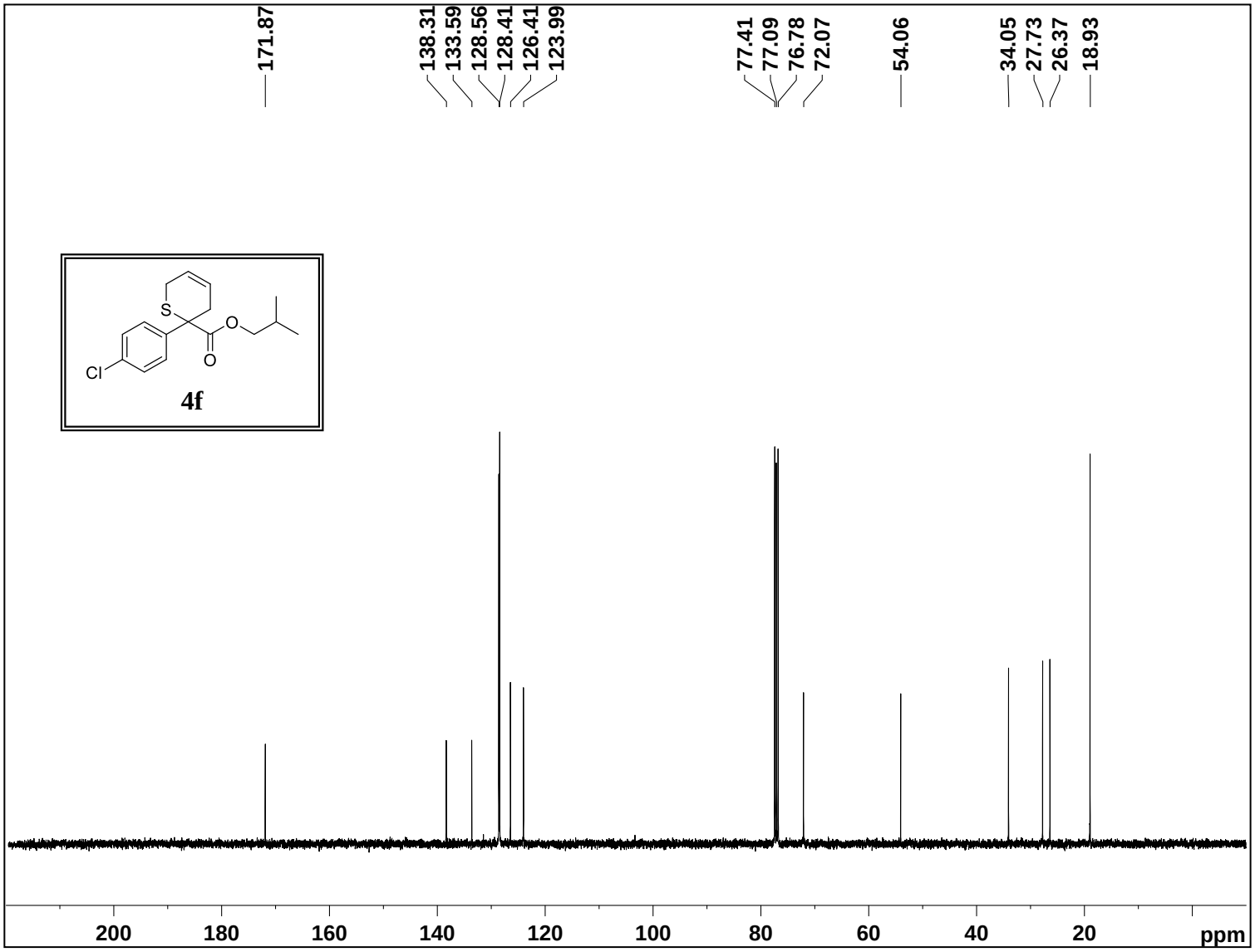
$^{13}C\{^{1}H\}$ NMR for compound **4e** (101 MHz, $CDCl_3$)



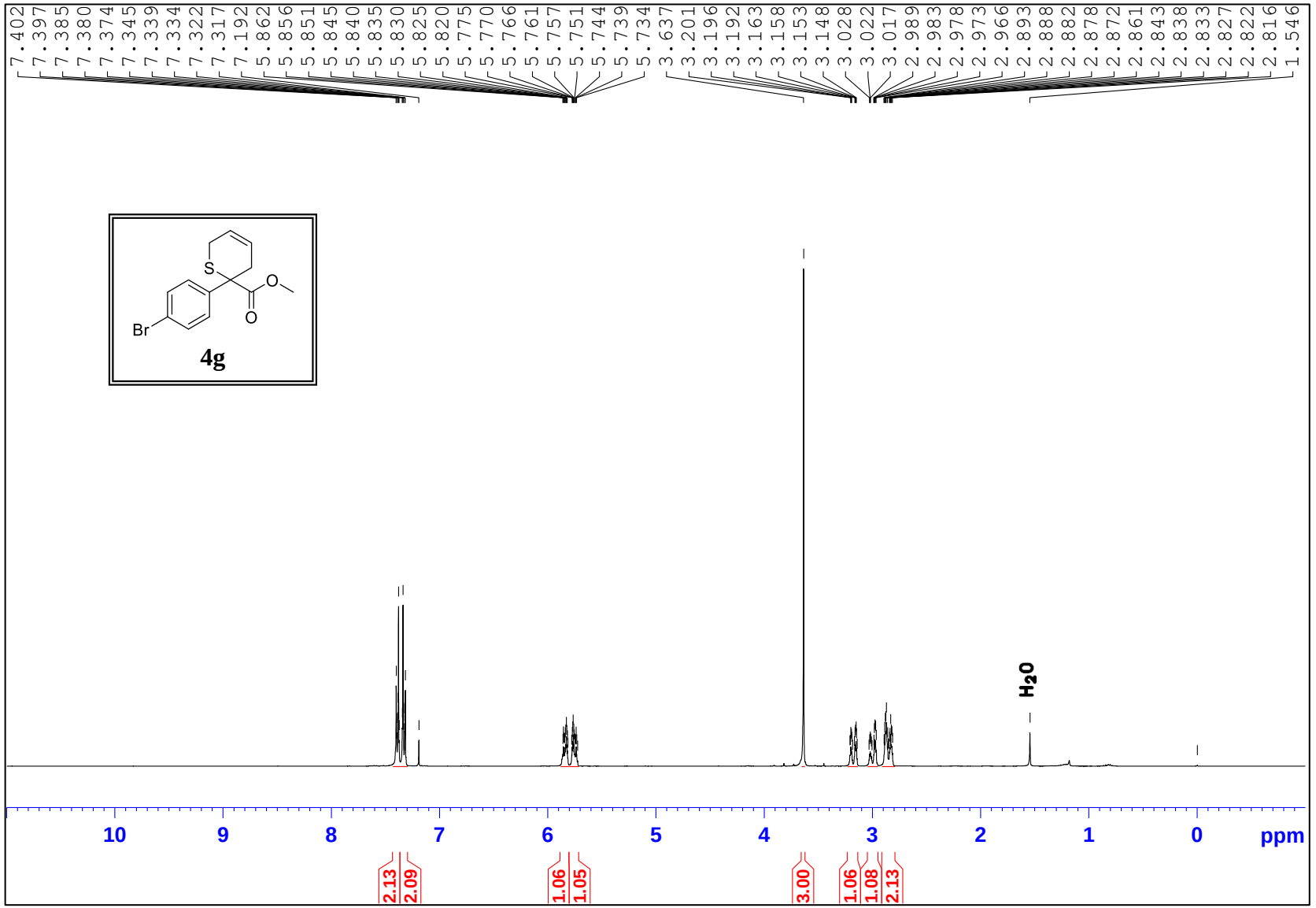
^{1}H NMR for compound **4f** (400 MHz, $CDCl_3$) (**data**)



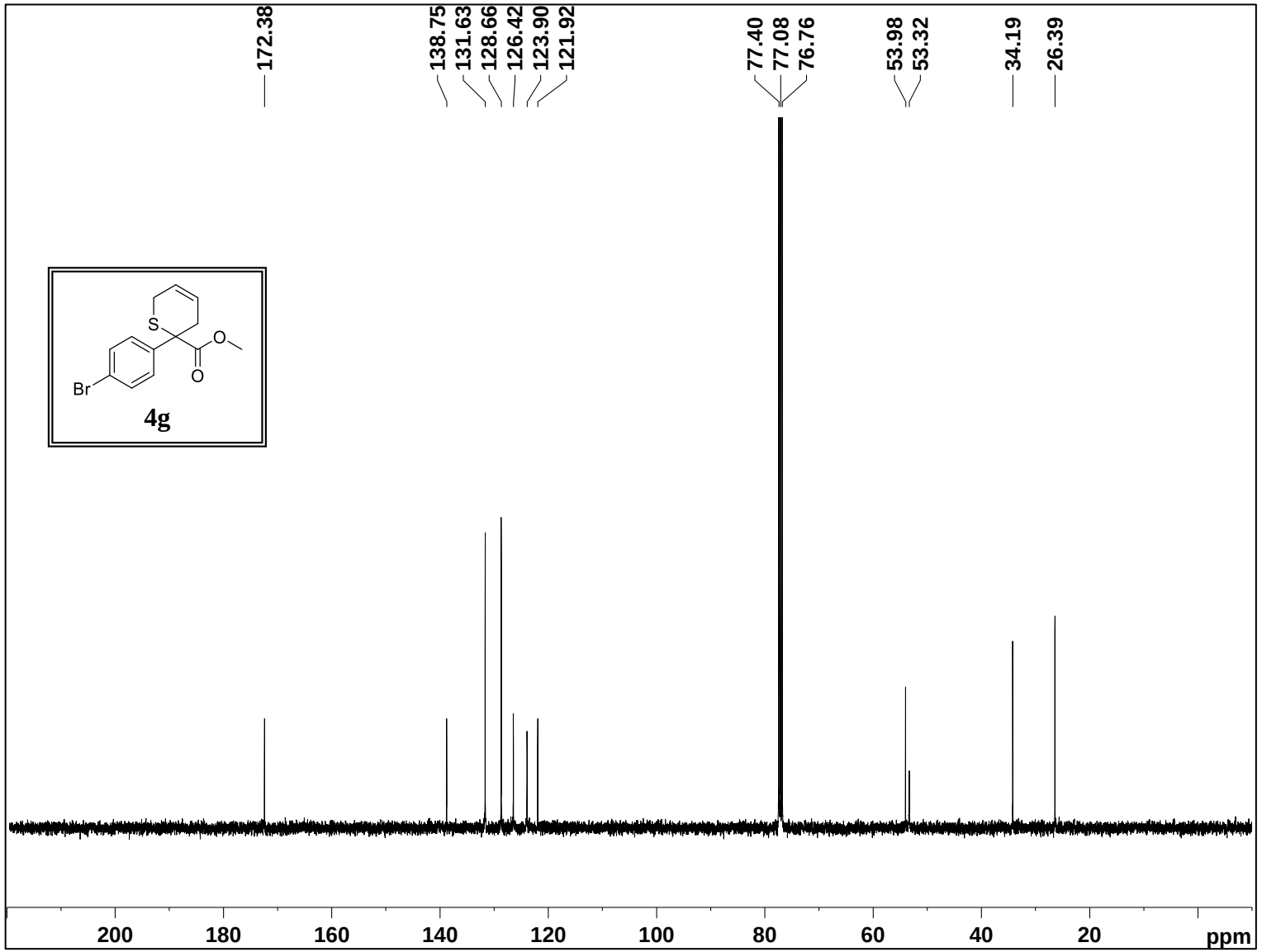
$^{13}C\{^{1}H\}$ NMR for compound **4f** (101 MHz, $CDCl_3$)



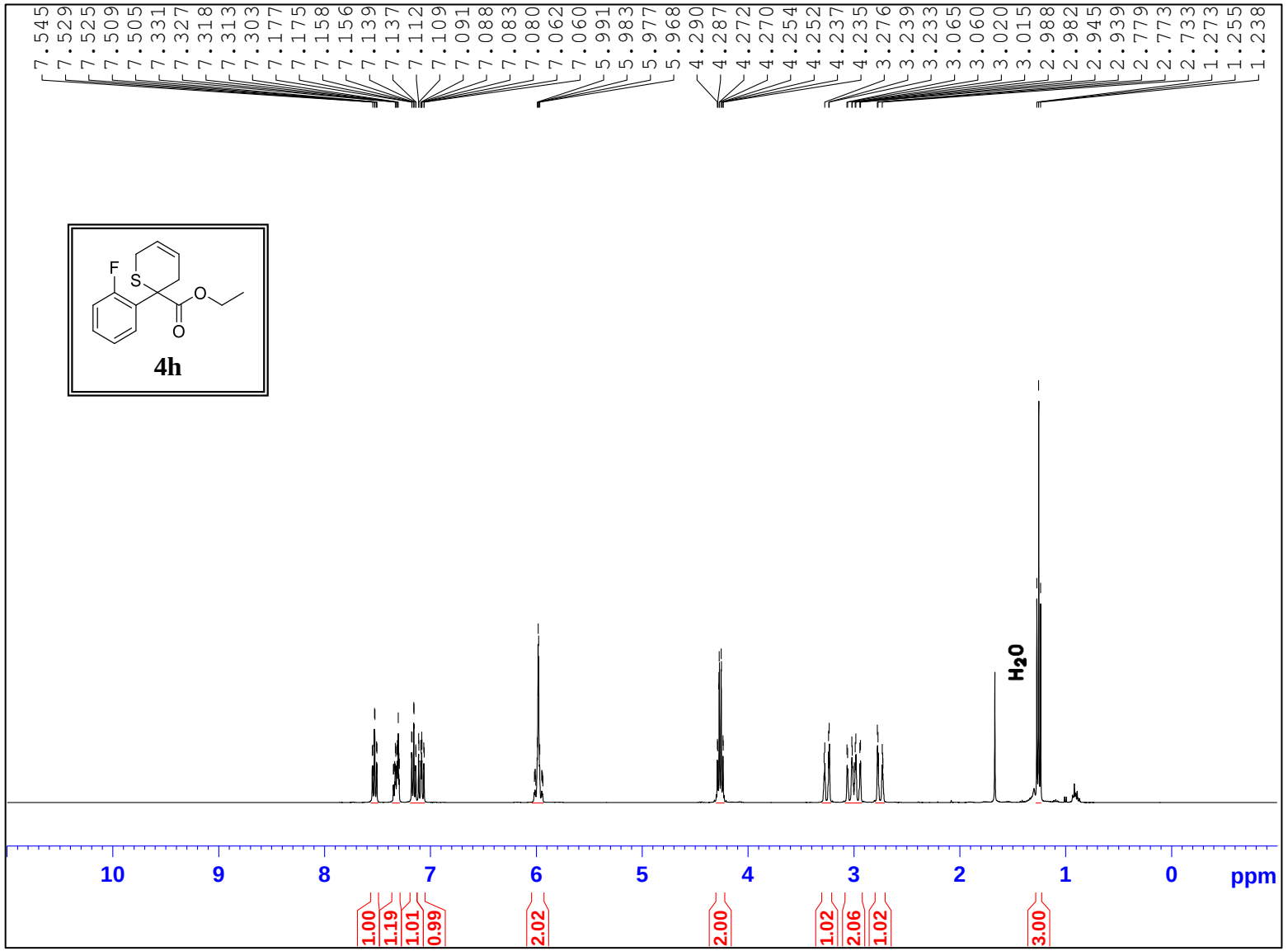
^{1}H NMR for compound **4g** (400 MHz, $CDCl_3$) (**data**)



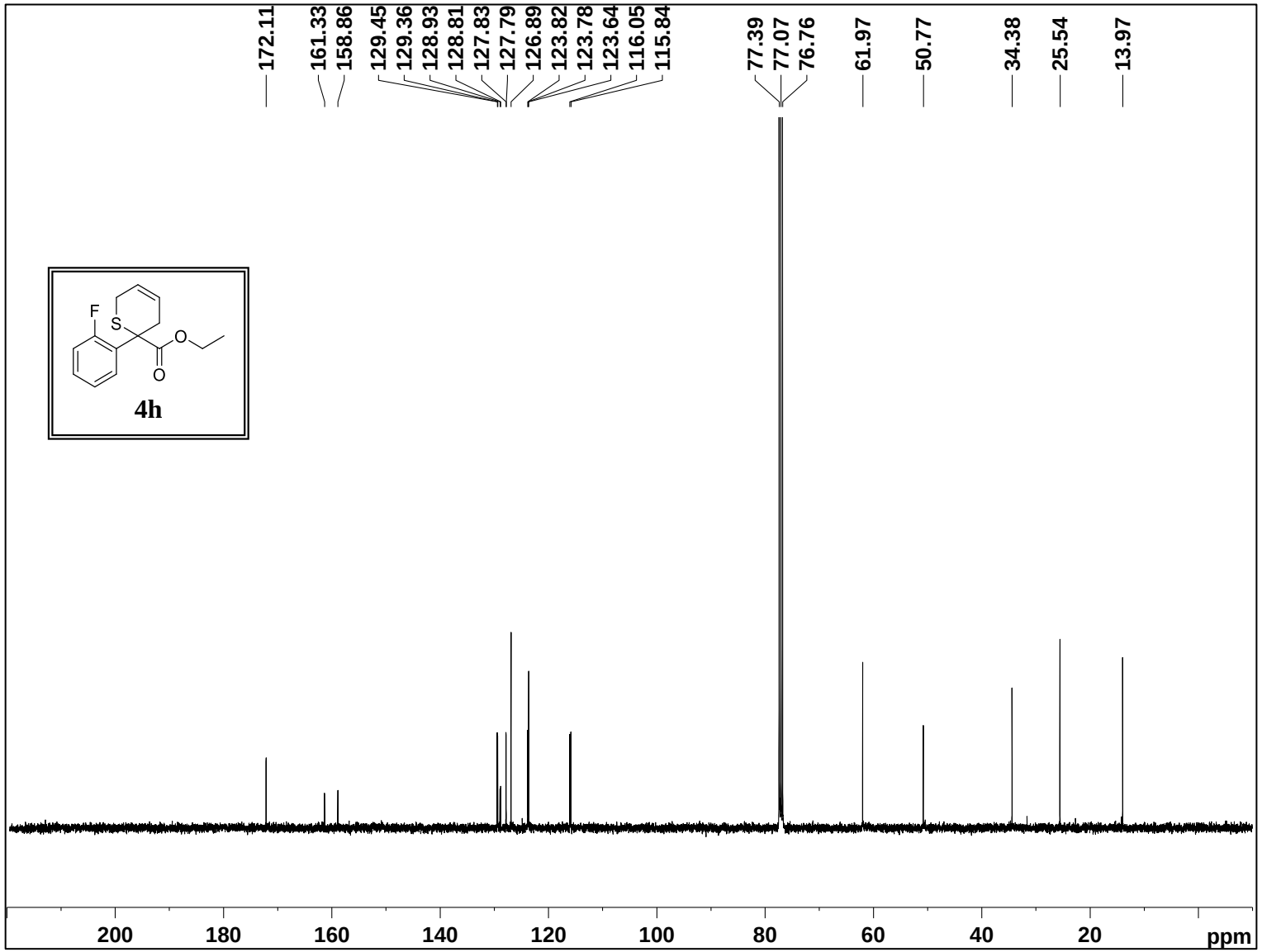
$^{13}C\{^{1}H\}$ NMR for compound **4g** (101 MHz, $CDCl_3$)



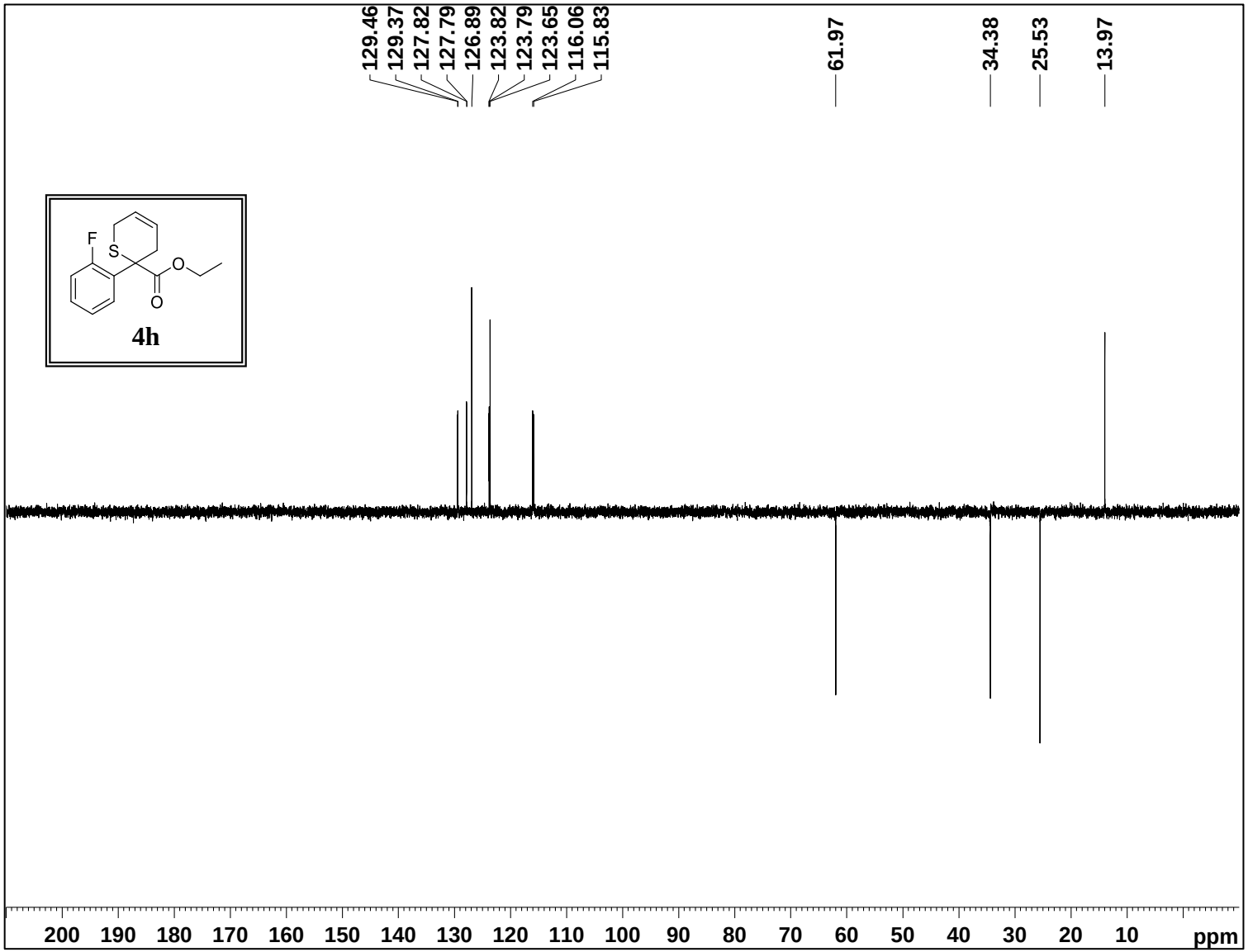
^{1}H NMR for compound **4h** (400 MHz, $CDCl_3$) (**data**)



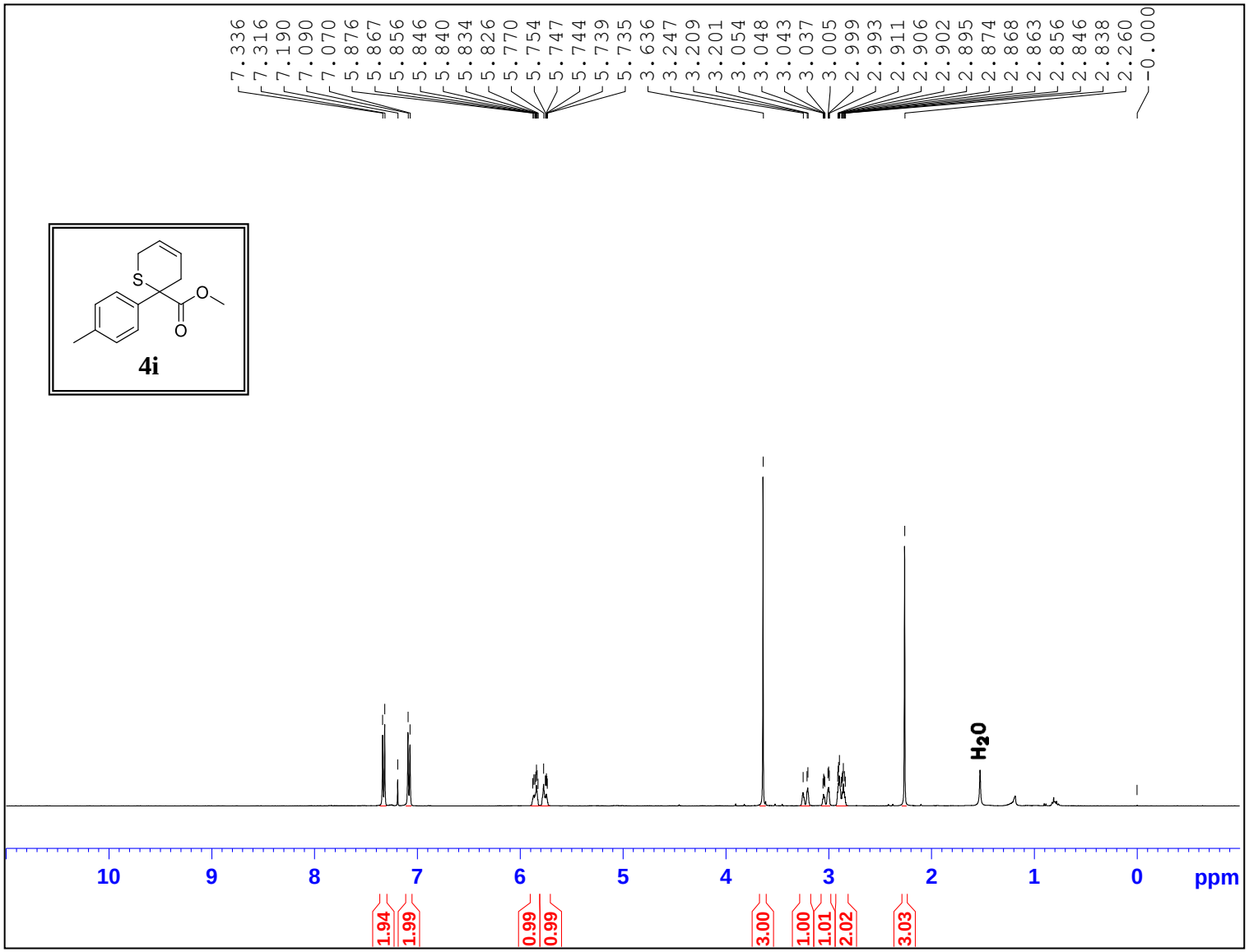
$^{13}C\{^{1}H\}$ NMR for compound **4h** (101 MHz, $CDCl_3$)



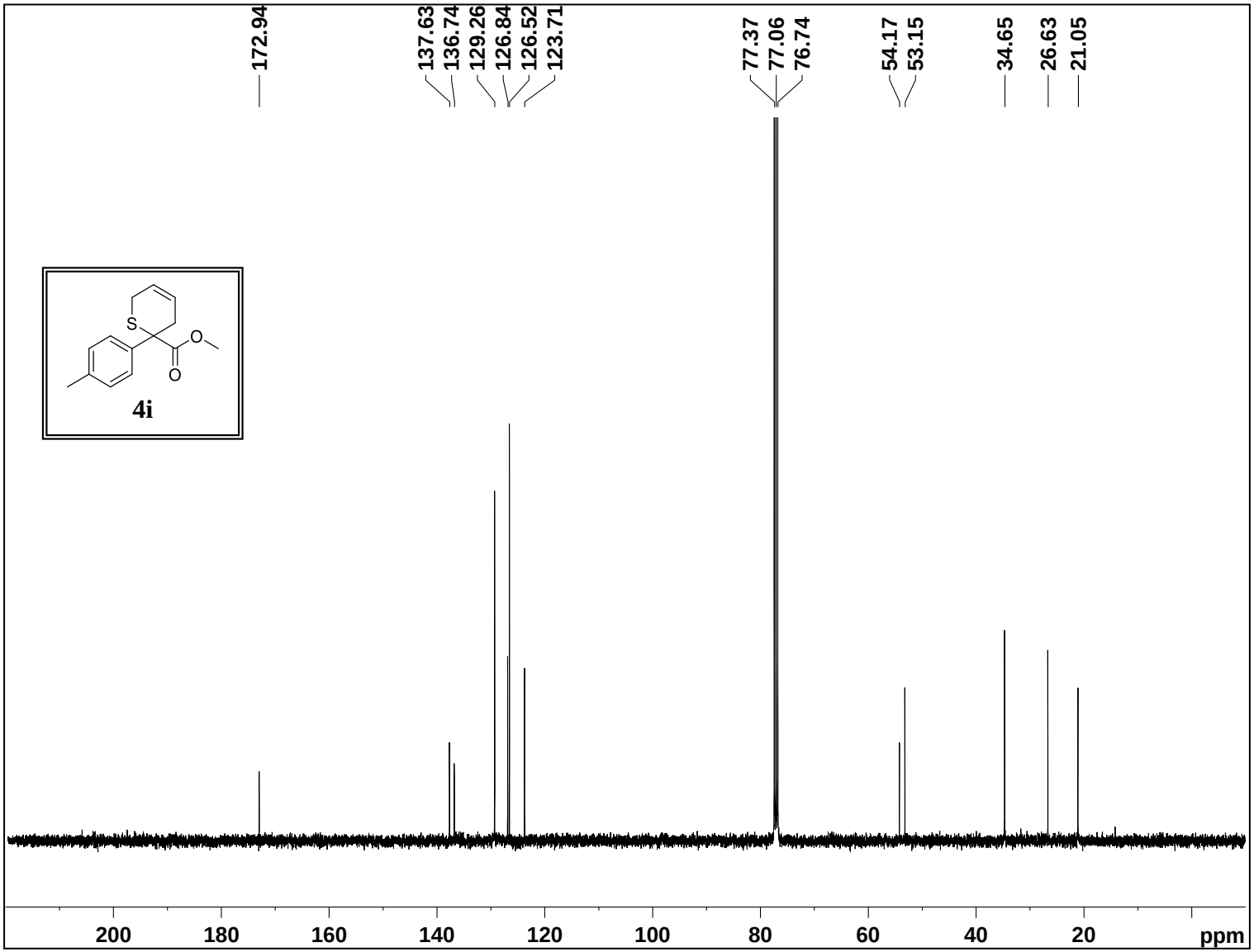
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4h** (101 MHz, $CDCl_3$)



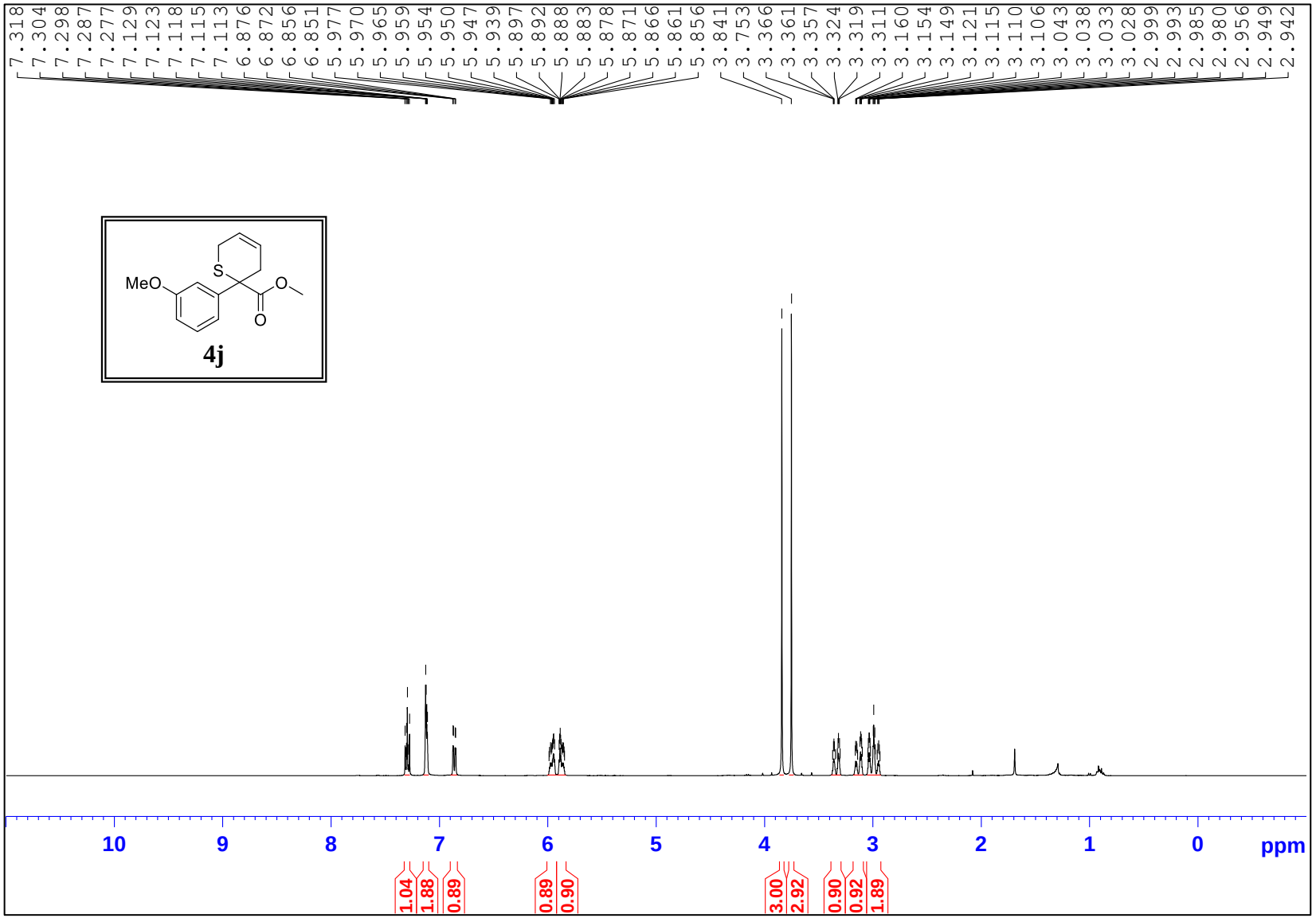
^{1}H NMR for compound **4i** (400 MHz, $CDCl_3$) (**data**)



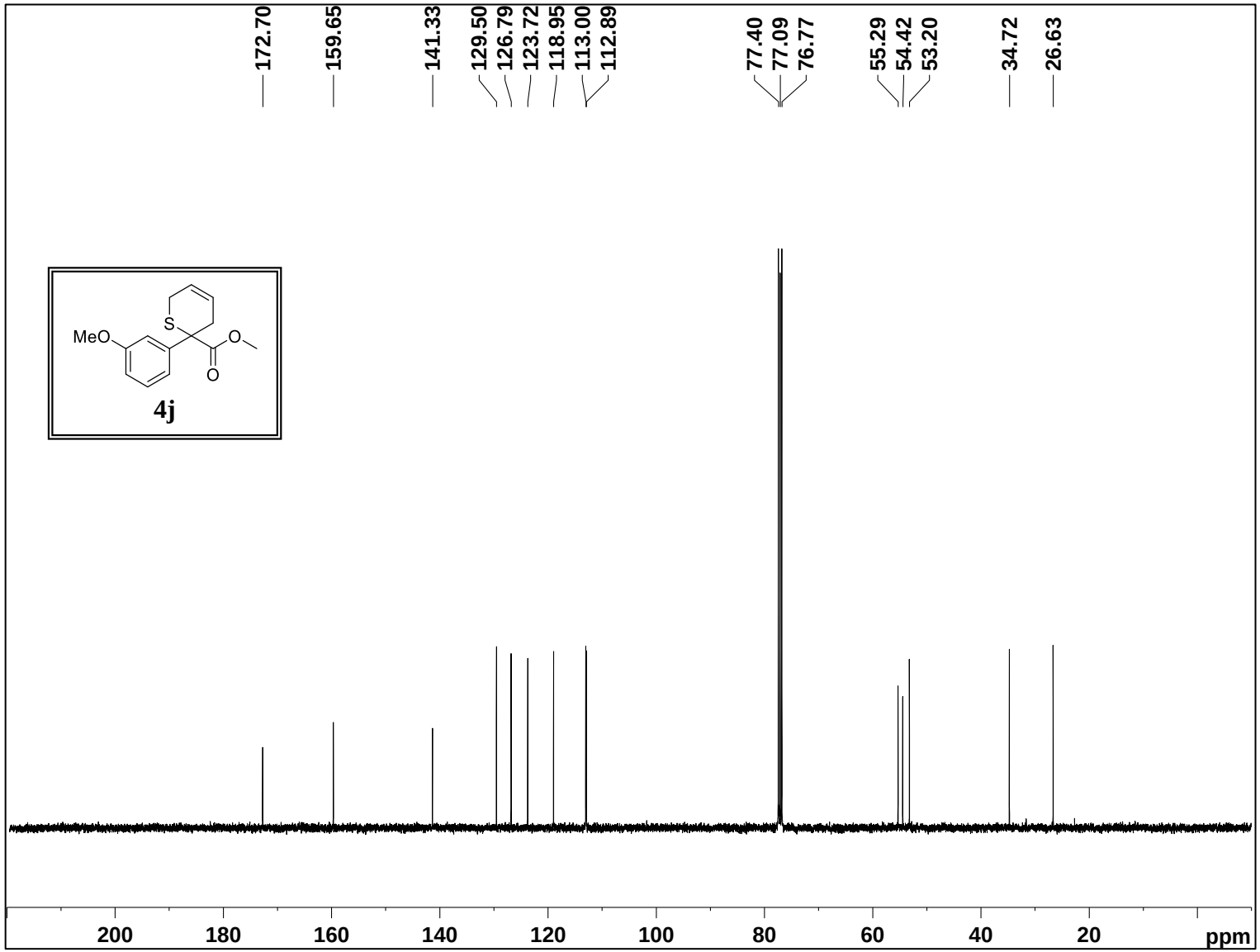
$^{13}C\{^{1}H\}$ NMR for compound **4i** (101 MHz, $CDCl_3$)



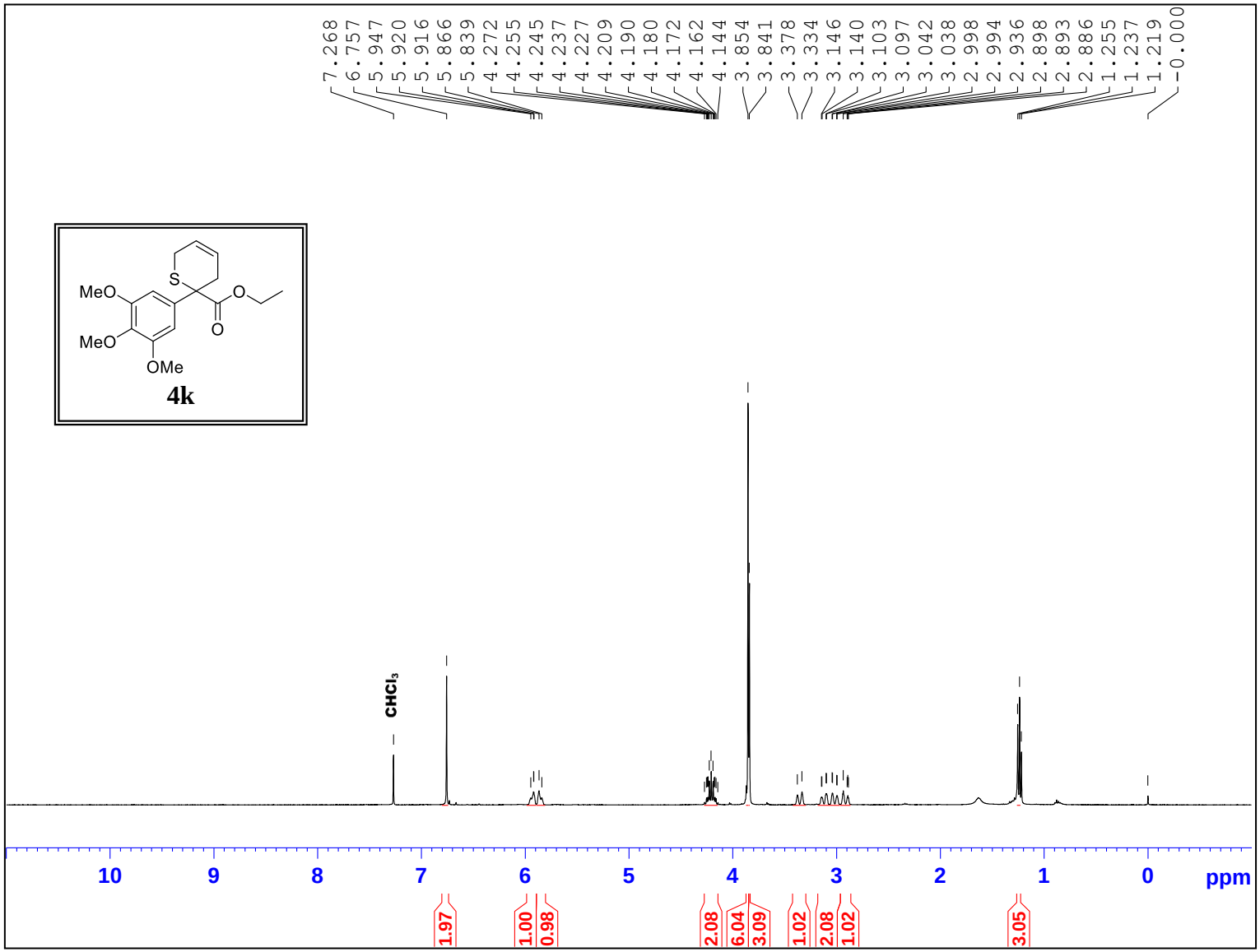
^{1}H NMR for compound **4j** (400 MHz, $CDCl_3$) (**data**)



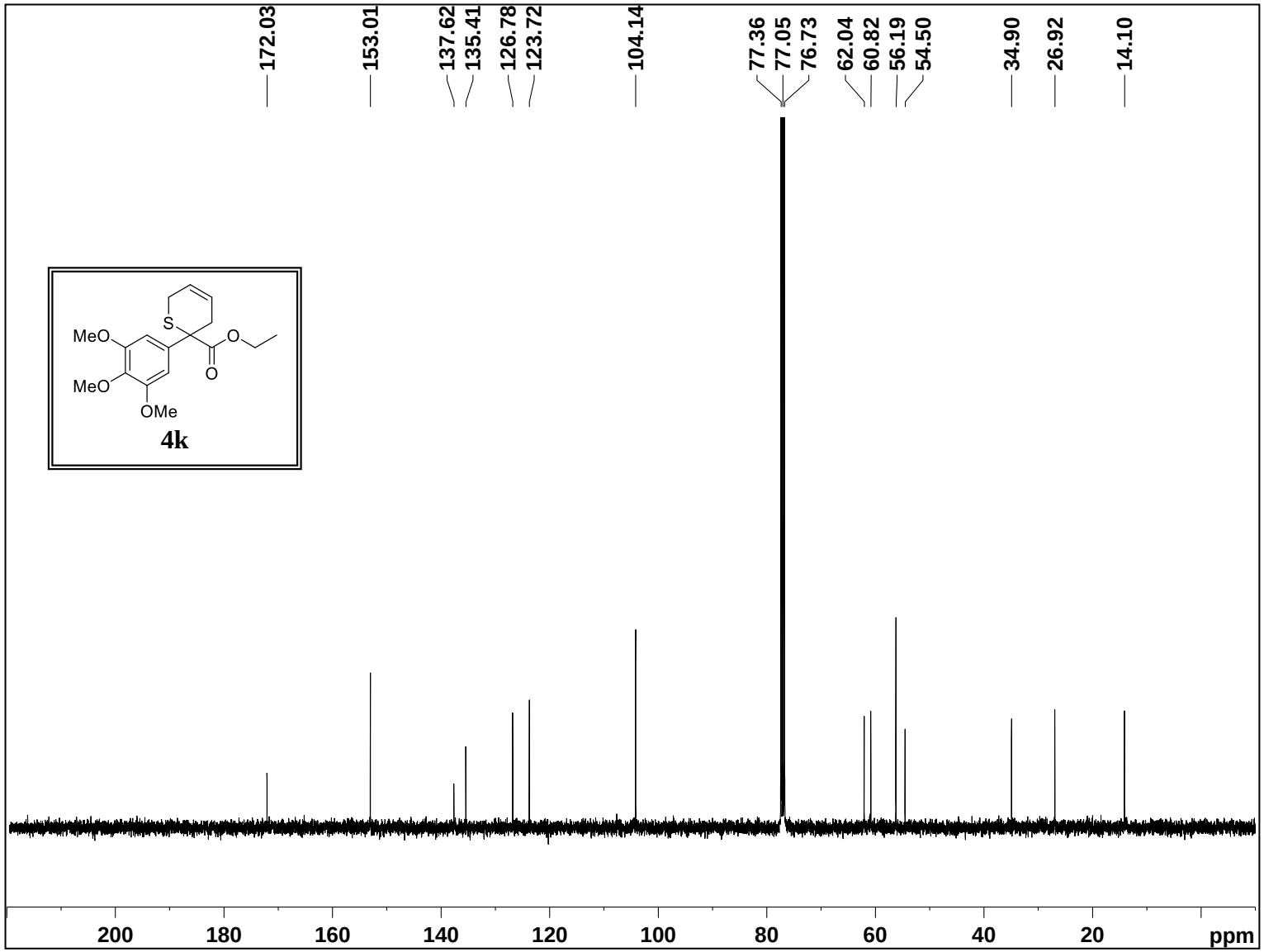
$^{13}C\{^{1}H\}$ NMR for compound **4j** (101 MHz, $CDCl_3$)



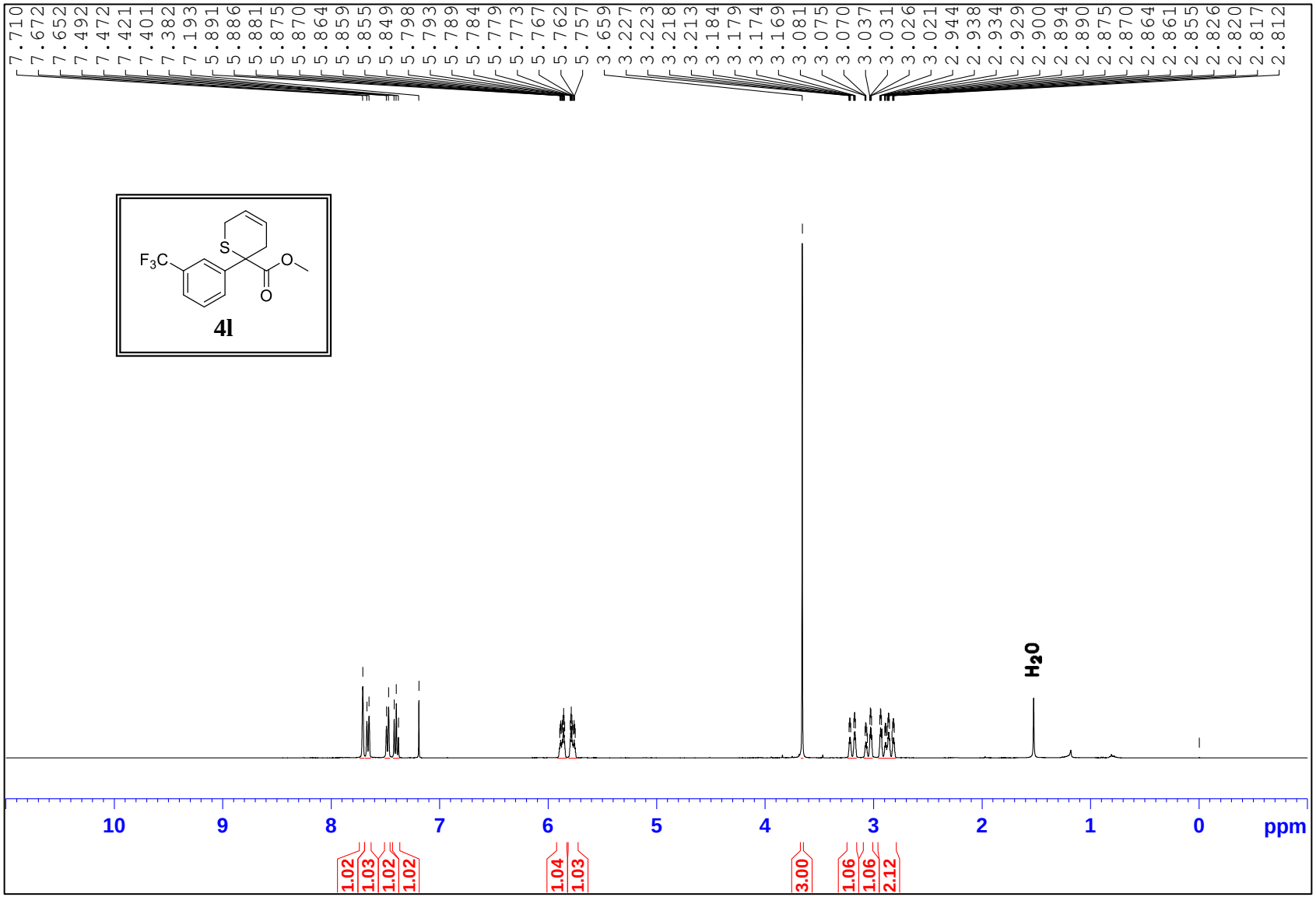
^{1}H NMR for compound **4k** (400 MHz, $CDCl_3$) (**data**)



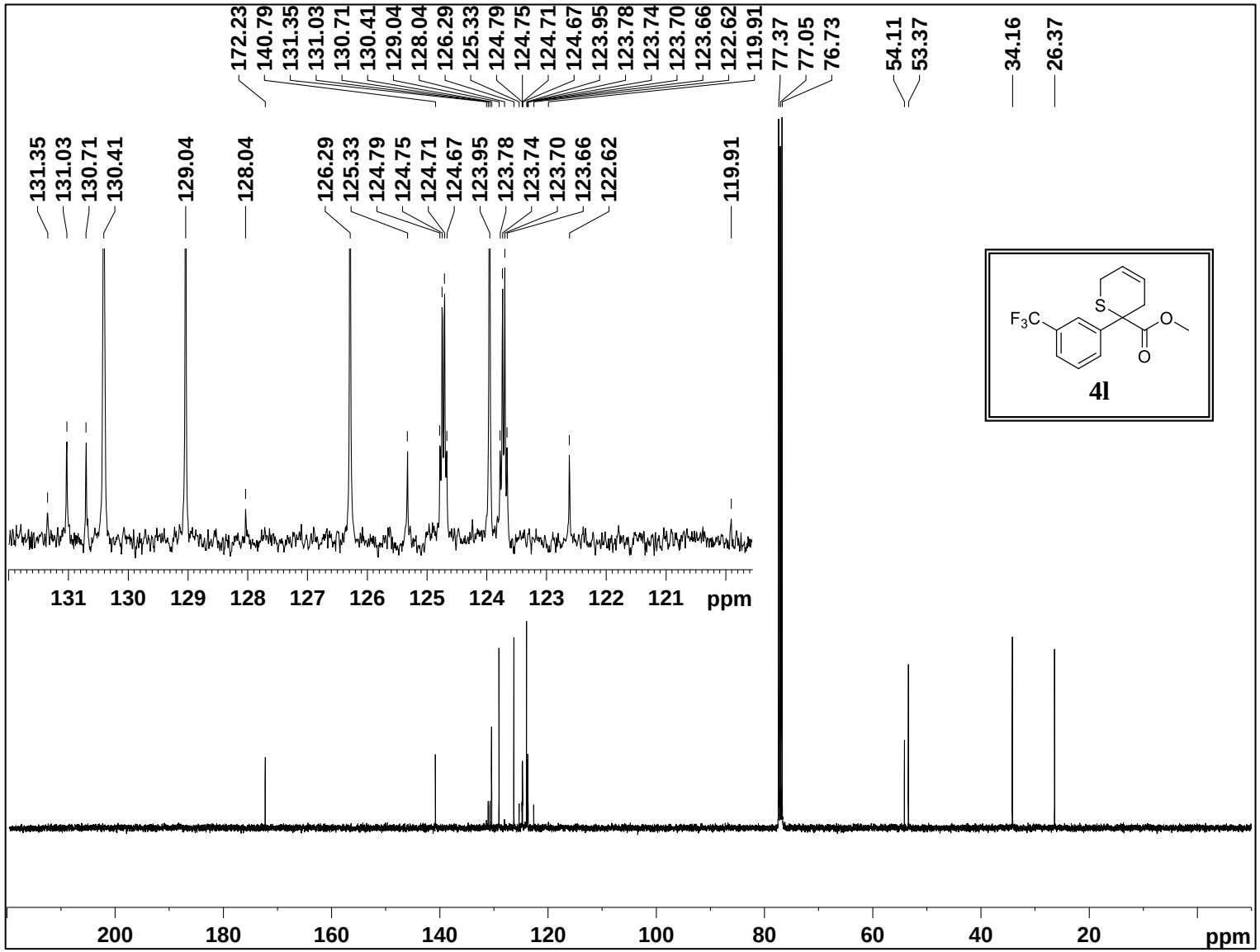
$^{13}C\{^{1}H\}$ NMR for compound **4k** (101 MHz, $CDCl_3$)



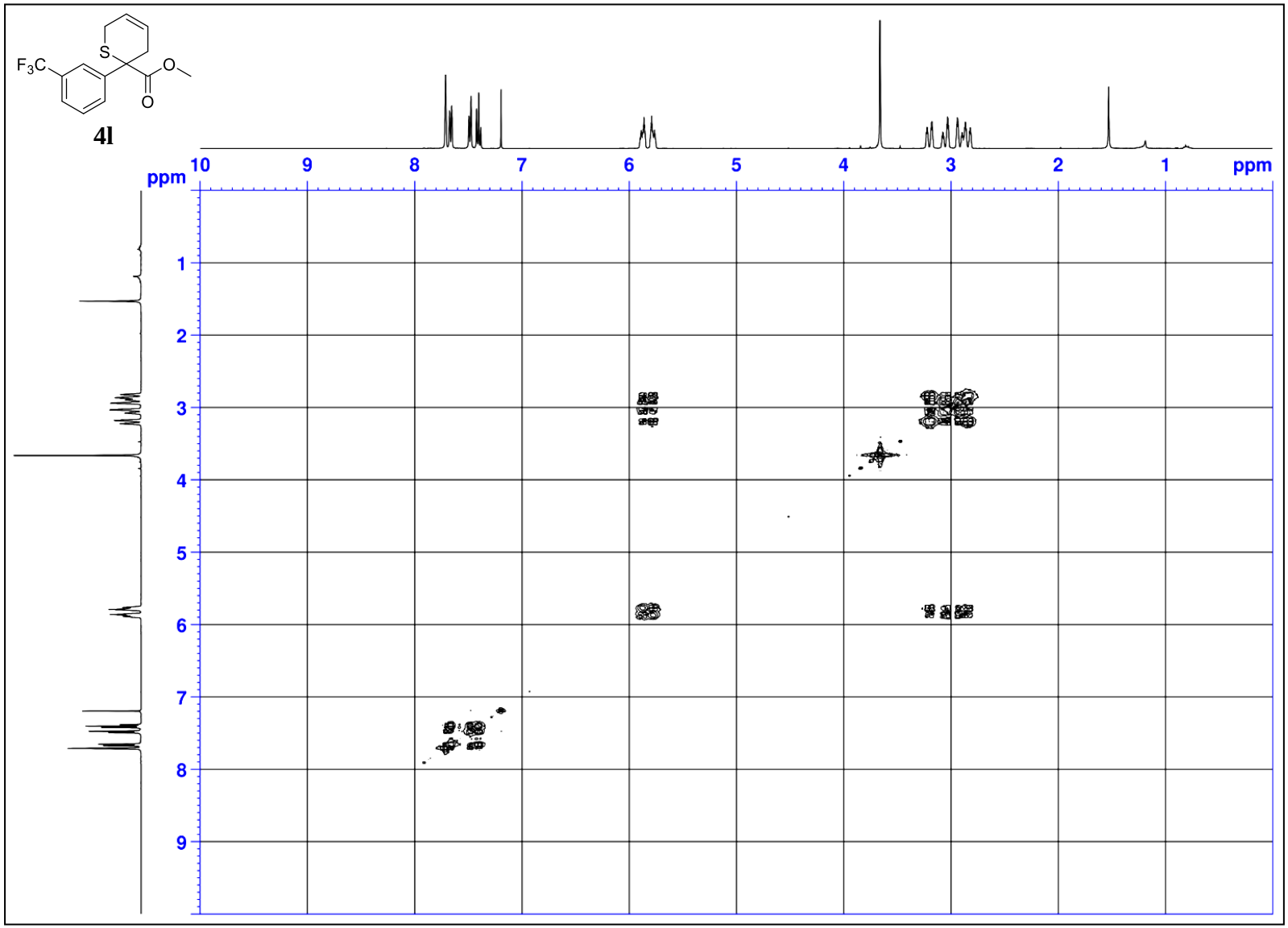
^{1}H NMR for compound **4l** (400 MHz, $CDCl_3$) (**data**)



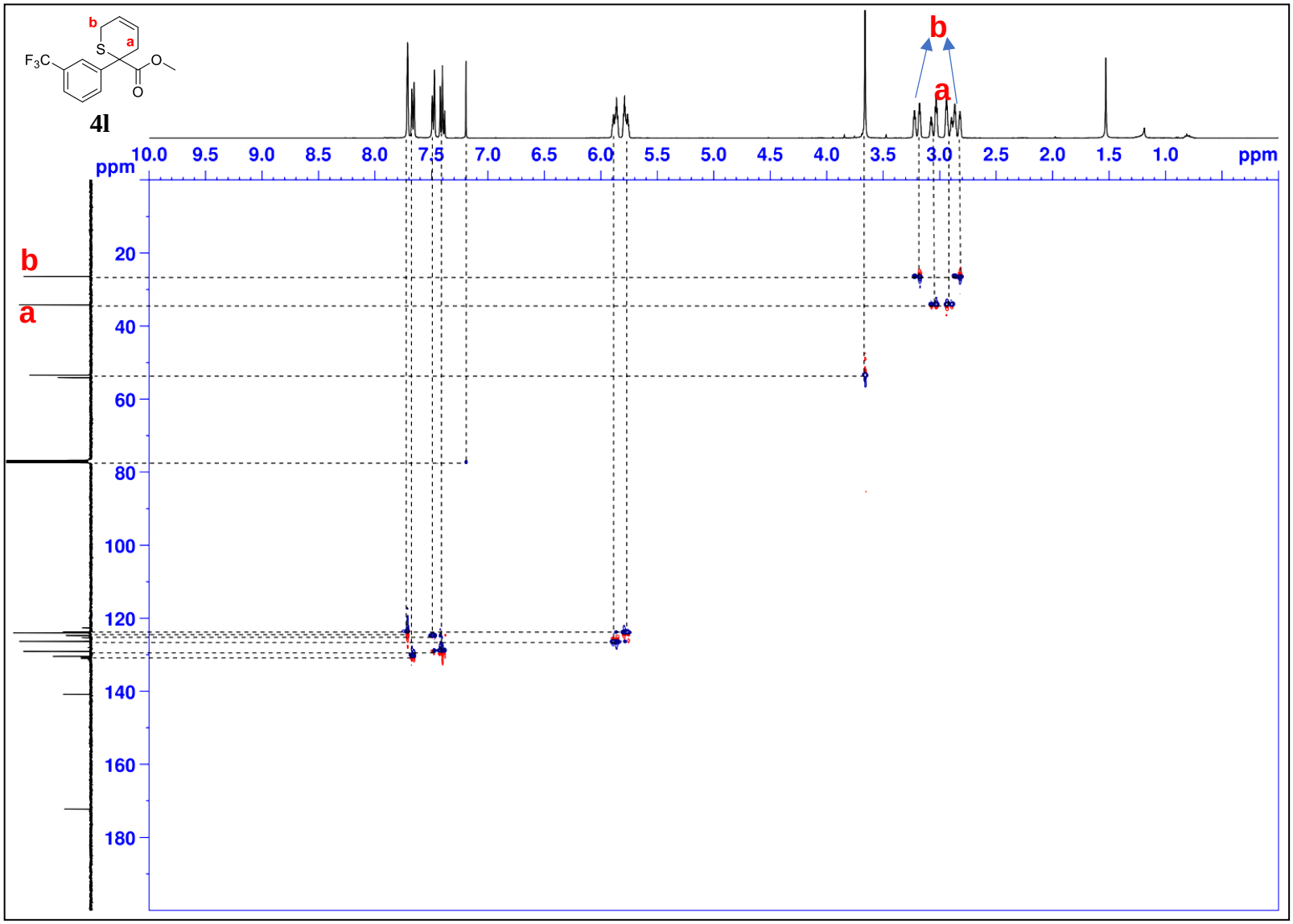
$^{13}C\{^{1}H\}$ NMR for compound **4l** (101 MHz, $CDCl_3$)



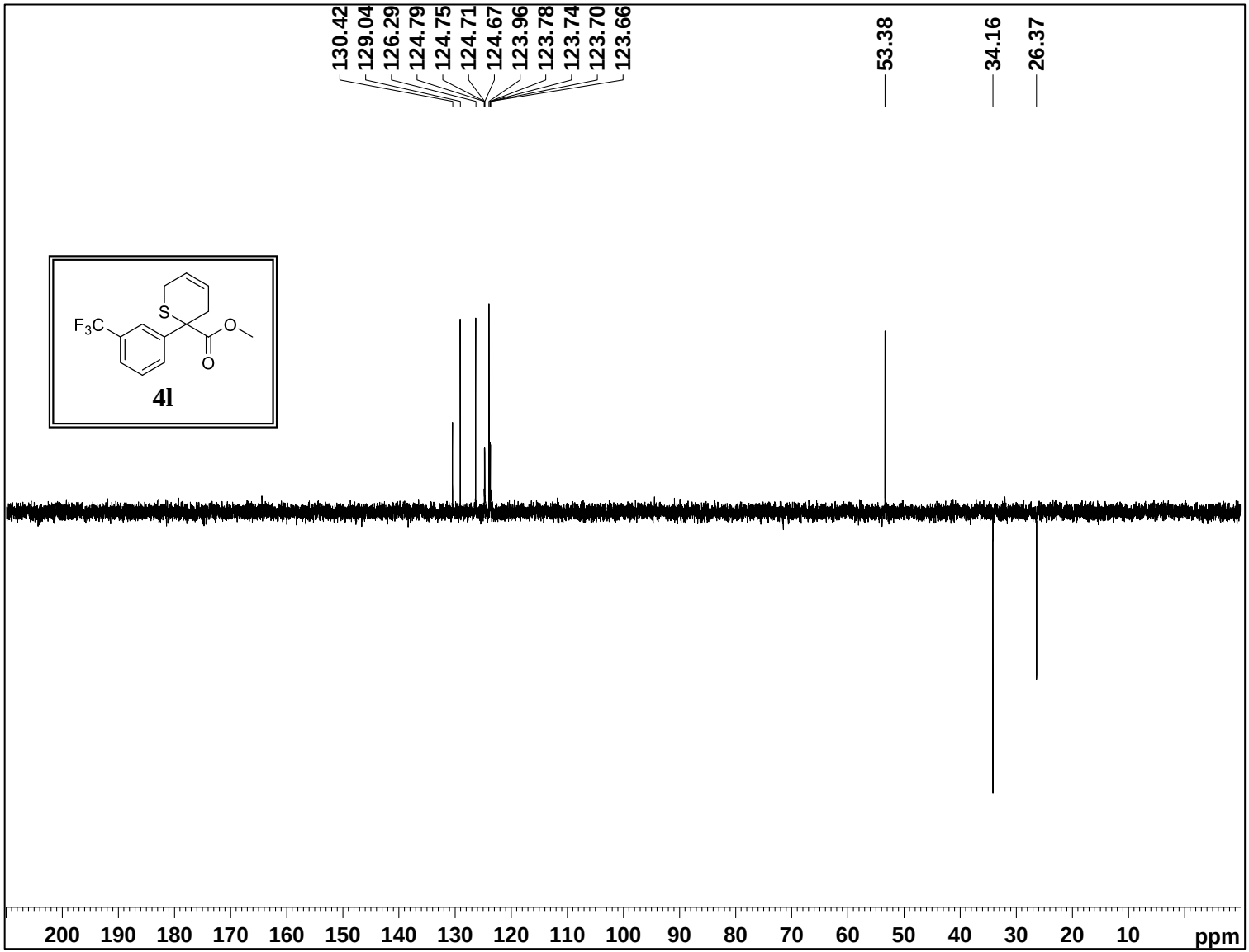
[^{1}H, ^{1}H] COSY for compound **4l** (400 MHz, $CDCl_3$)



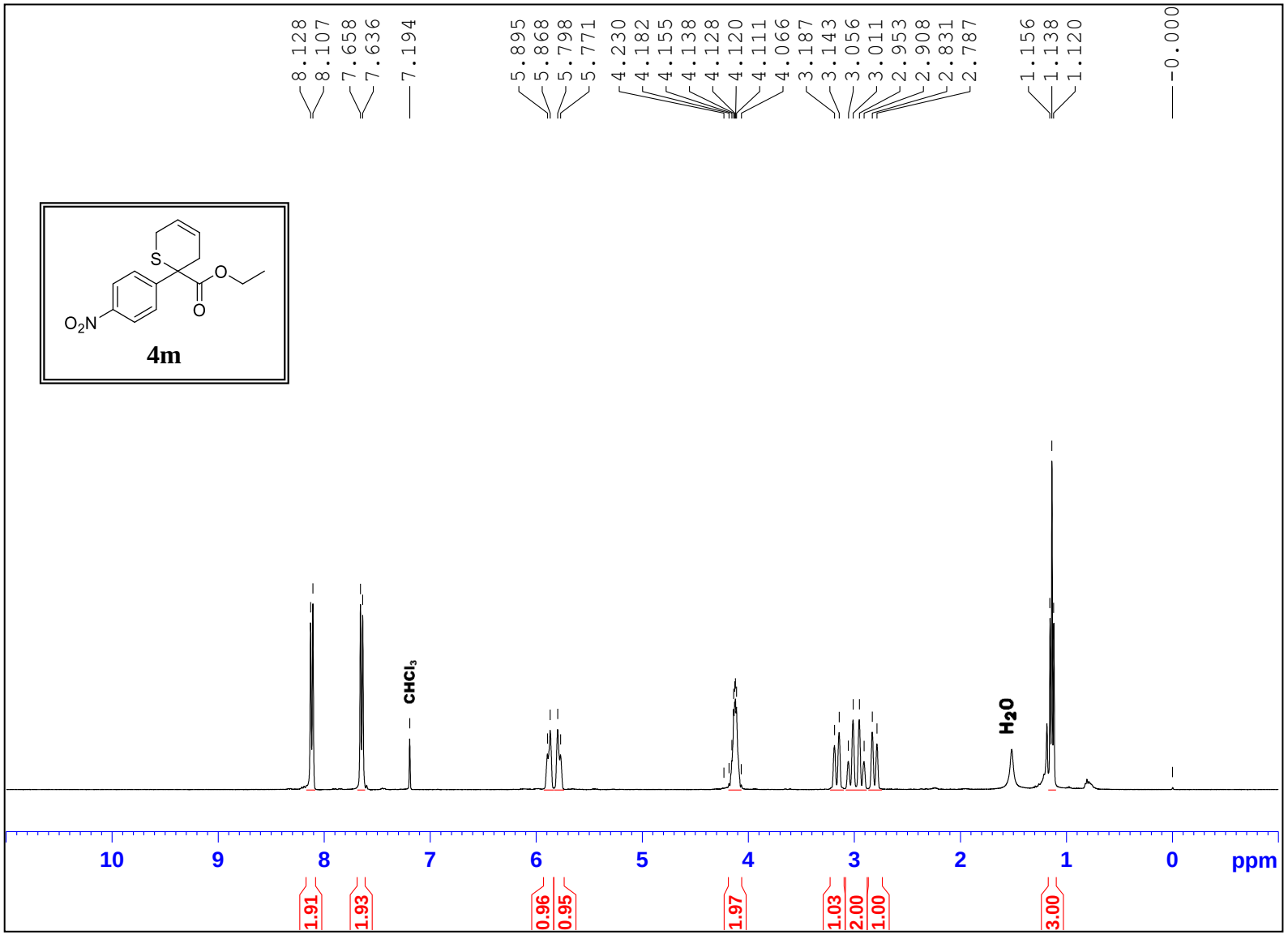
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **4l** (400 MHz, $CDCl_3$)



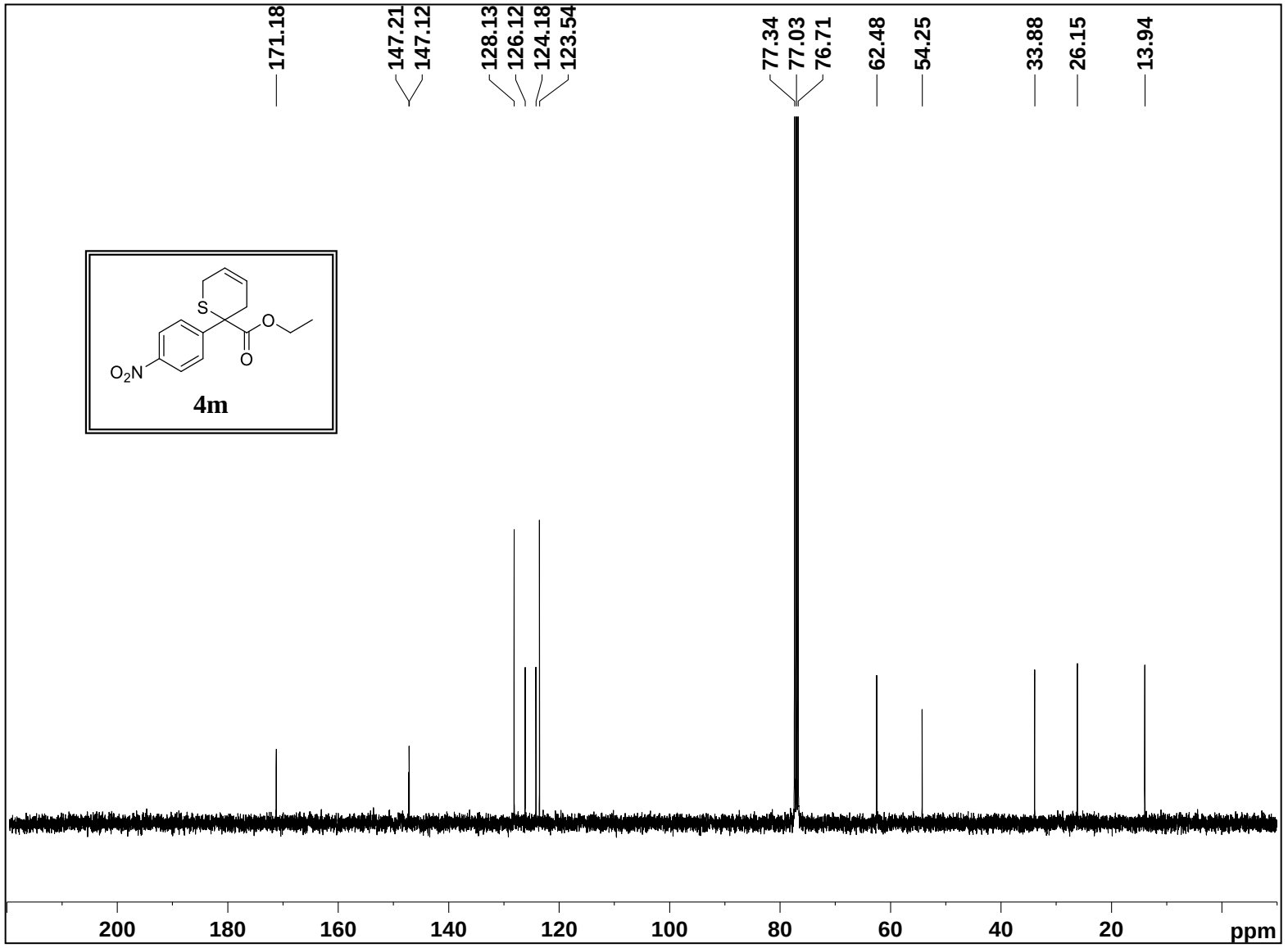
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4l** (101 MHz, $CDCl_3$)



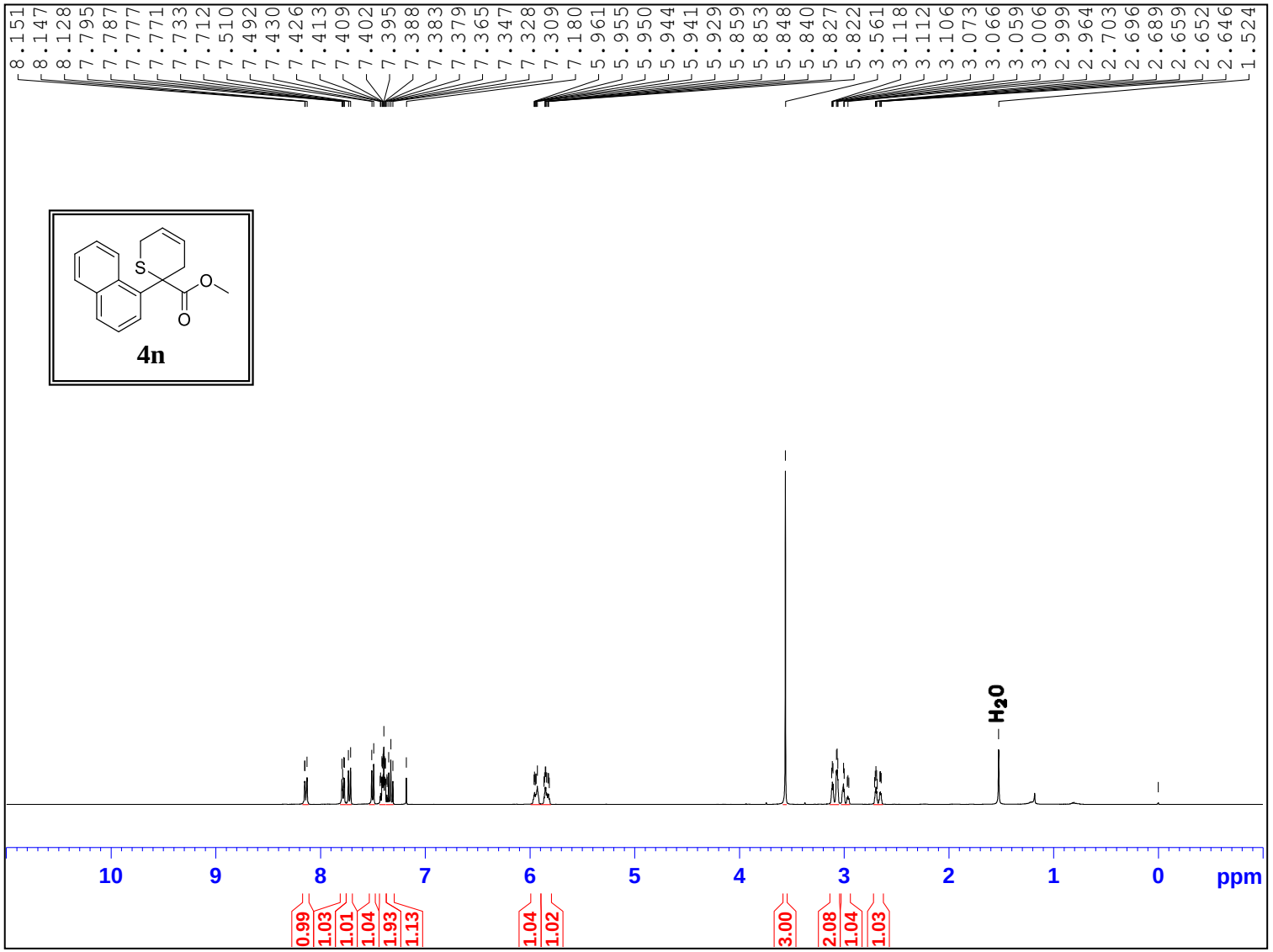
^{1}H NMR for compound **4m** (400 MHz, $CDCl_3$) (**data**)



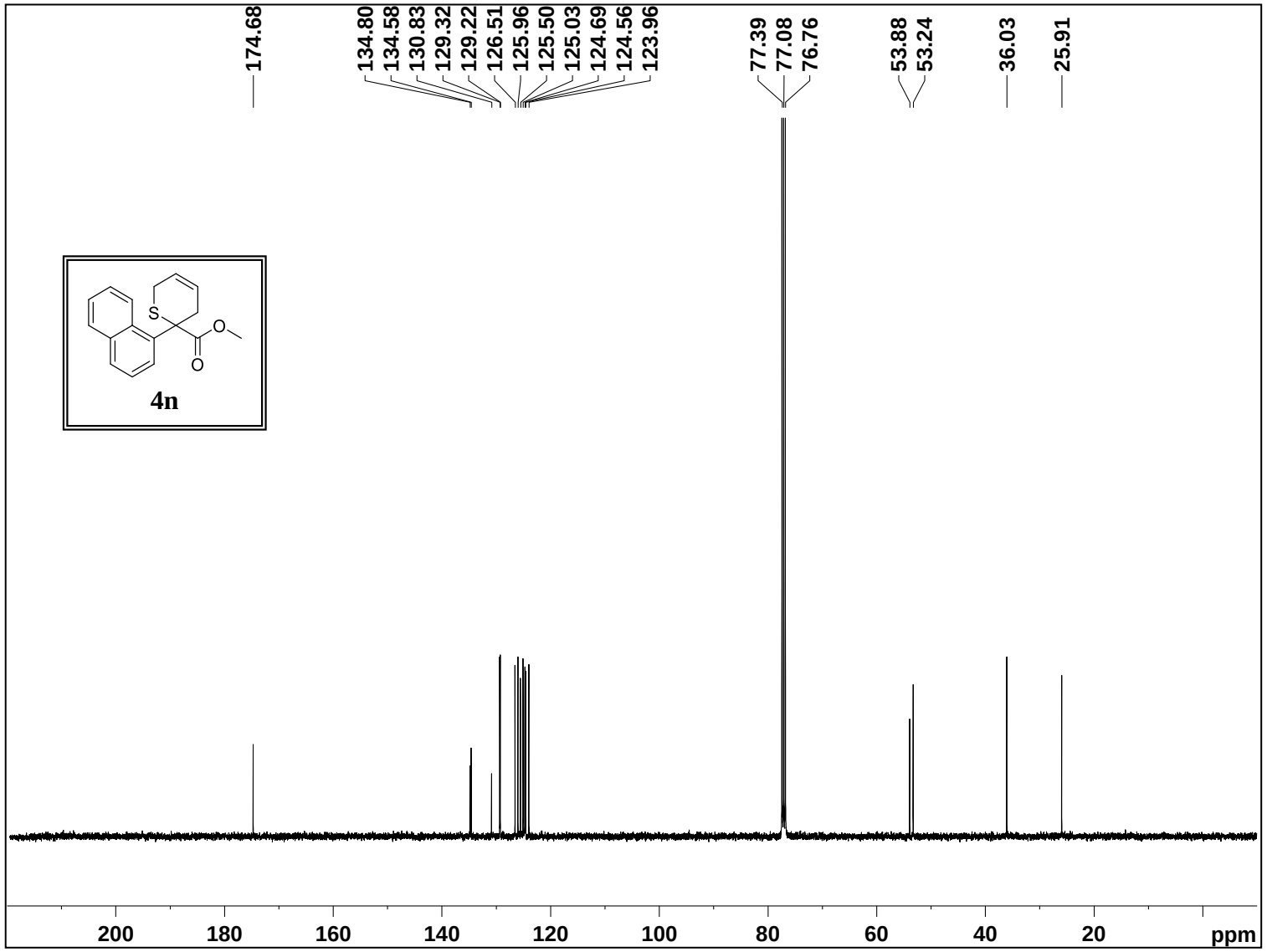
$^{13}C\{^{1}H\}$ NMR for compound **4m** (101 MHz, $CDCl_3$)



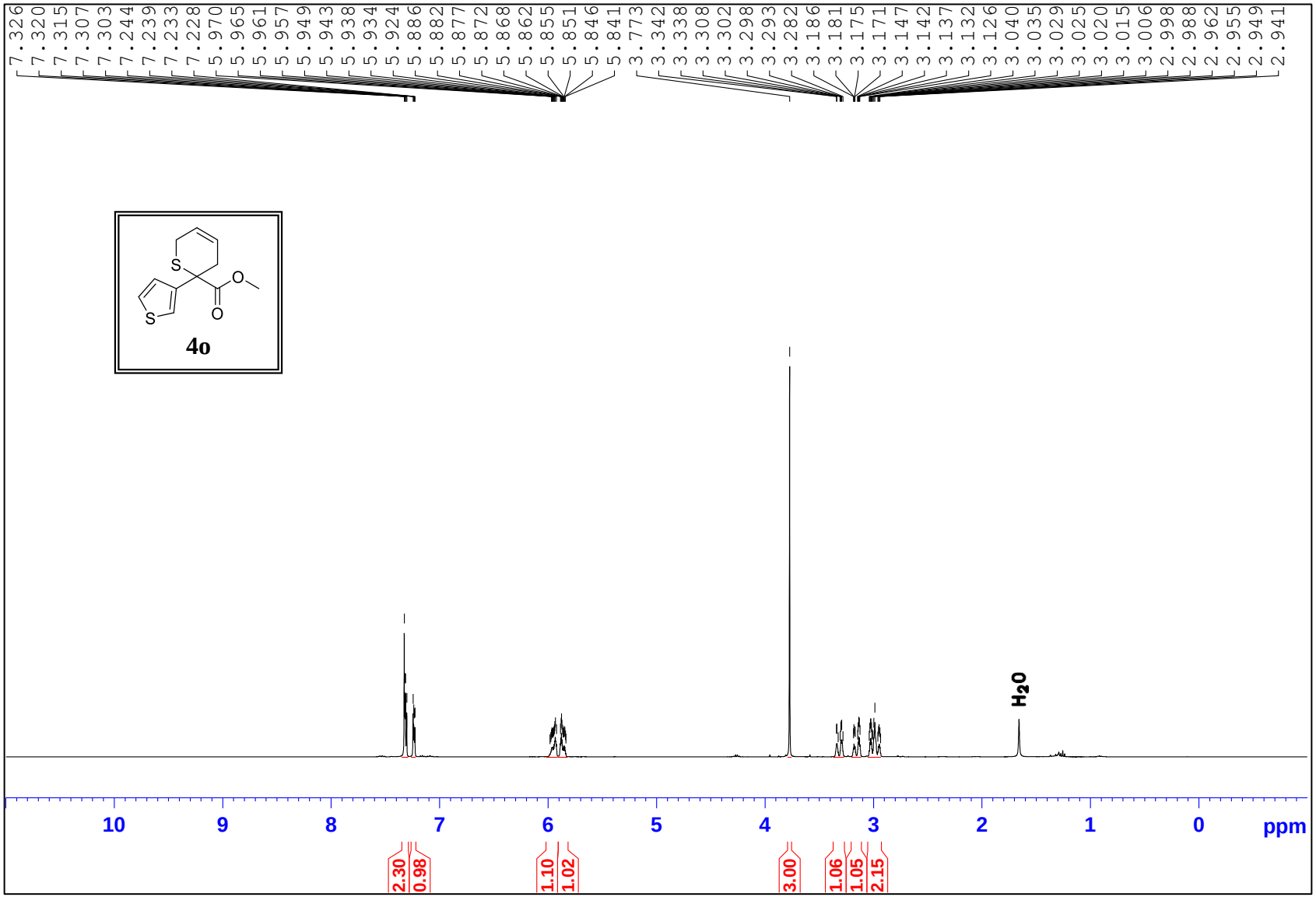
^{1}H NMR for compound **4n** (400 MHz, $CDCl_3$) (**data**)



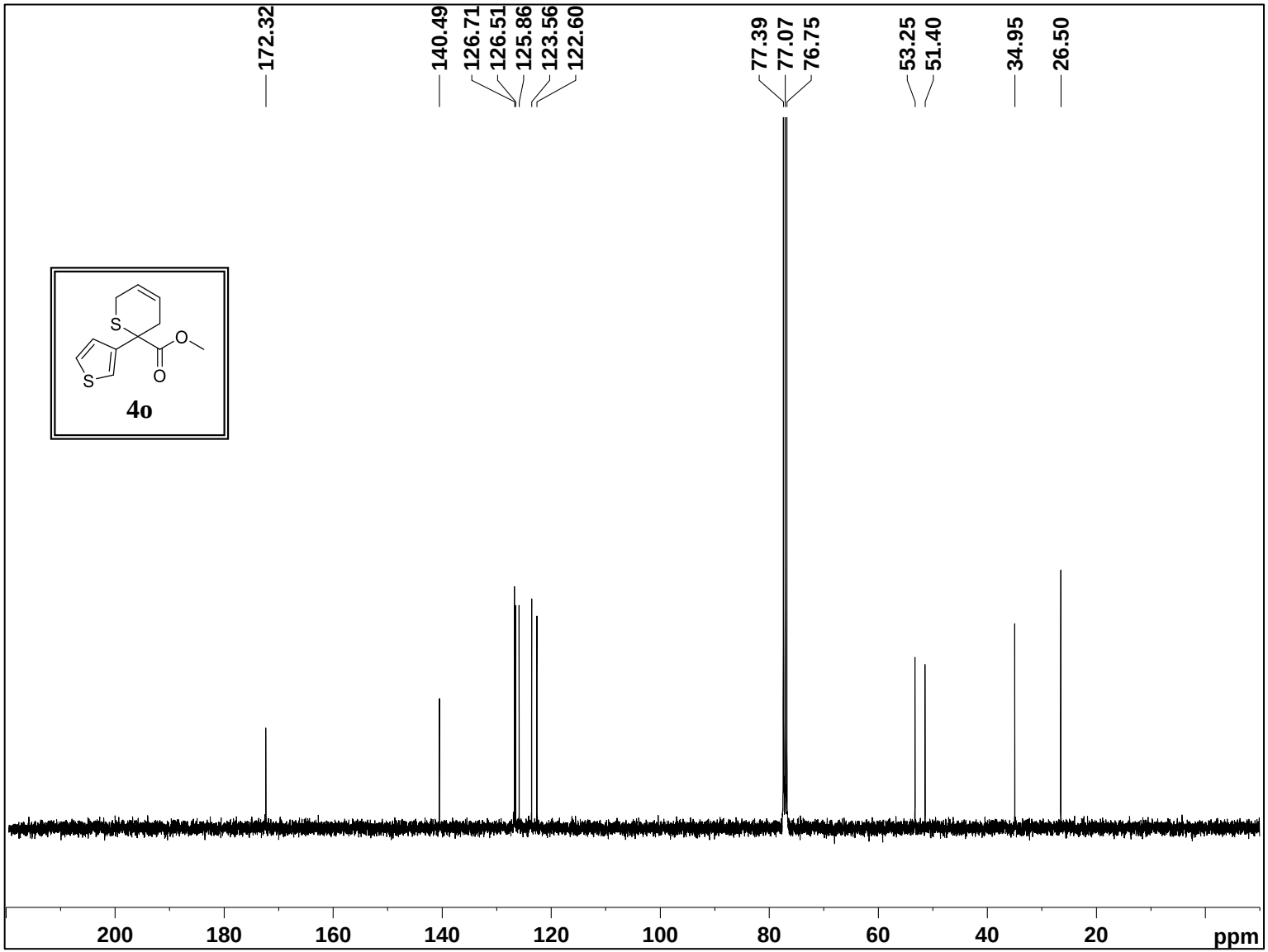
$^{13}C\{^{1}H\}$ NMR for compound **4n** (101 MHz, $CDCl_3$)



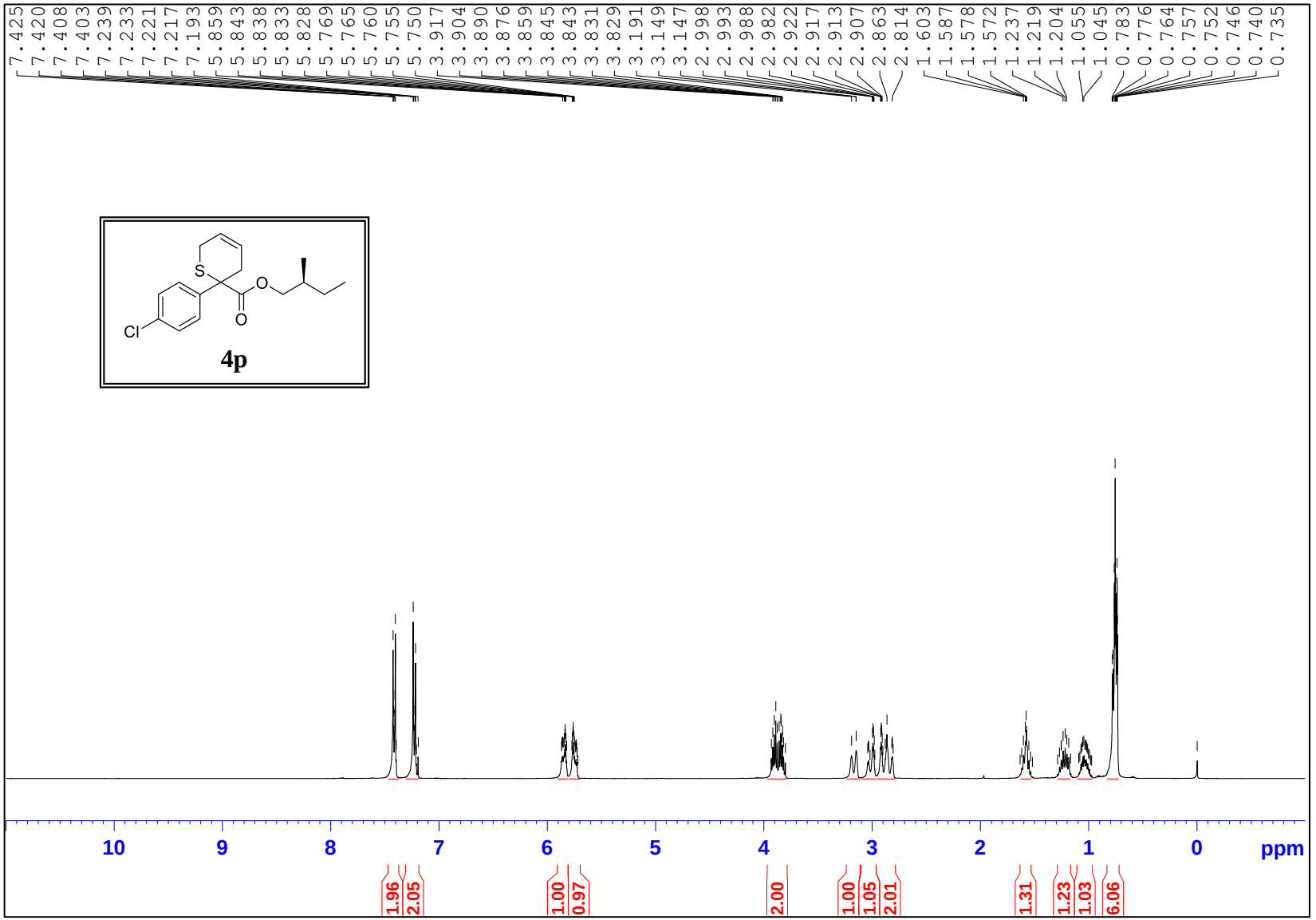
^{1}H NMR for compound **4o** (400 MHz, $CDCl_3$) (**data**)



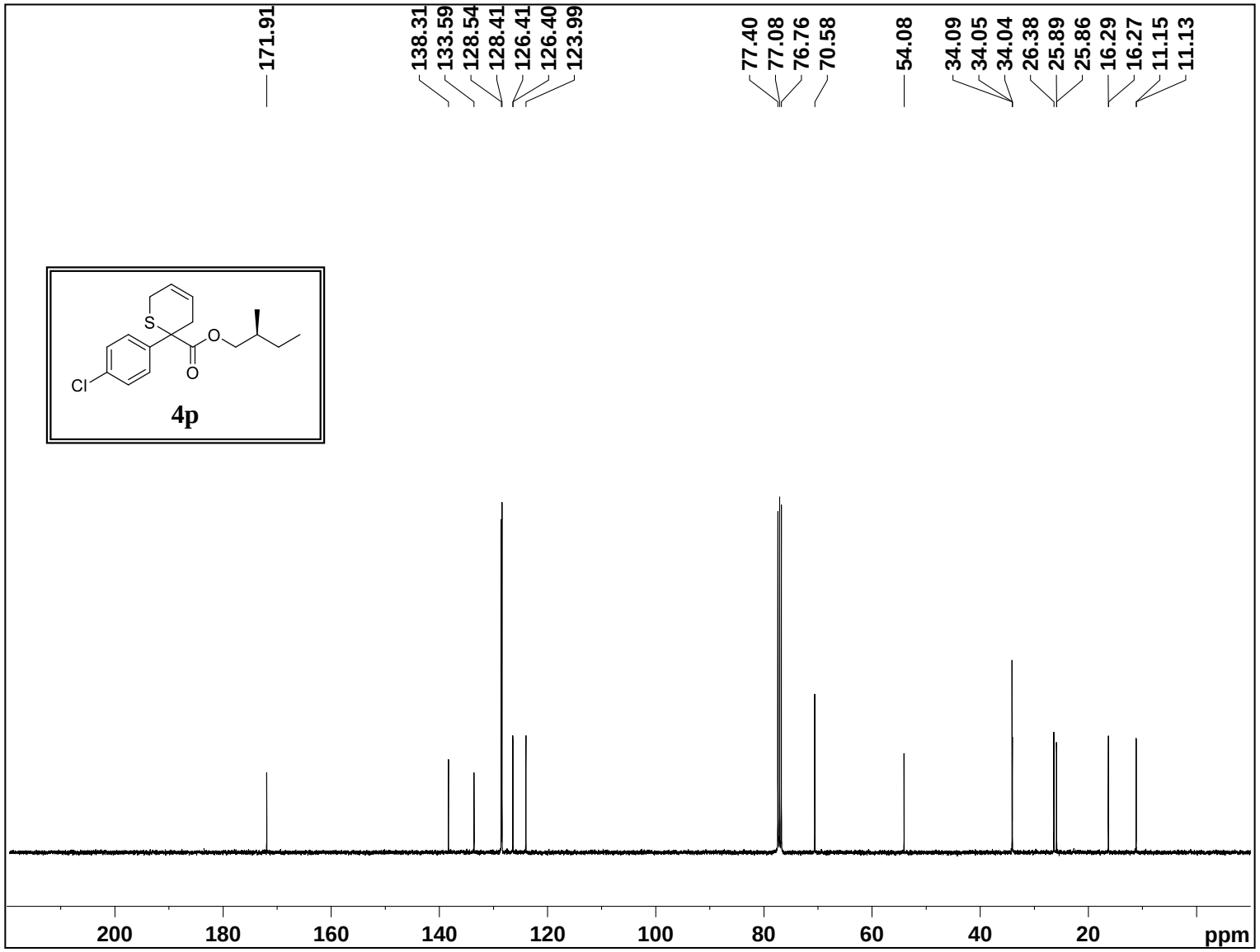
$^{13}C\{^{1}H\}$ NMR for compound **4o** (101 MHz, $CDCl_3$)



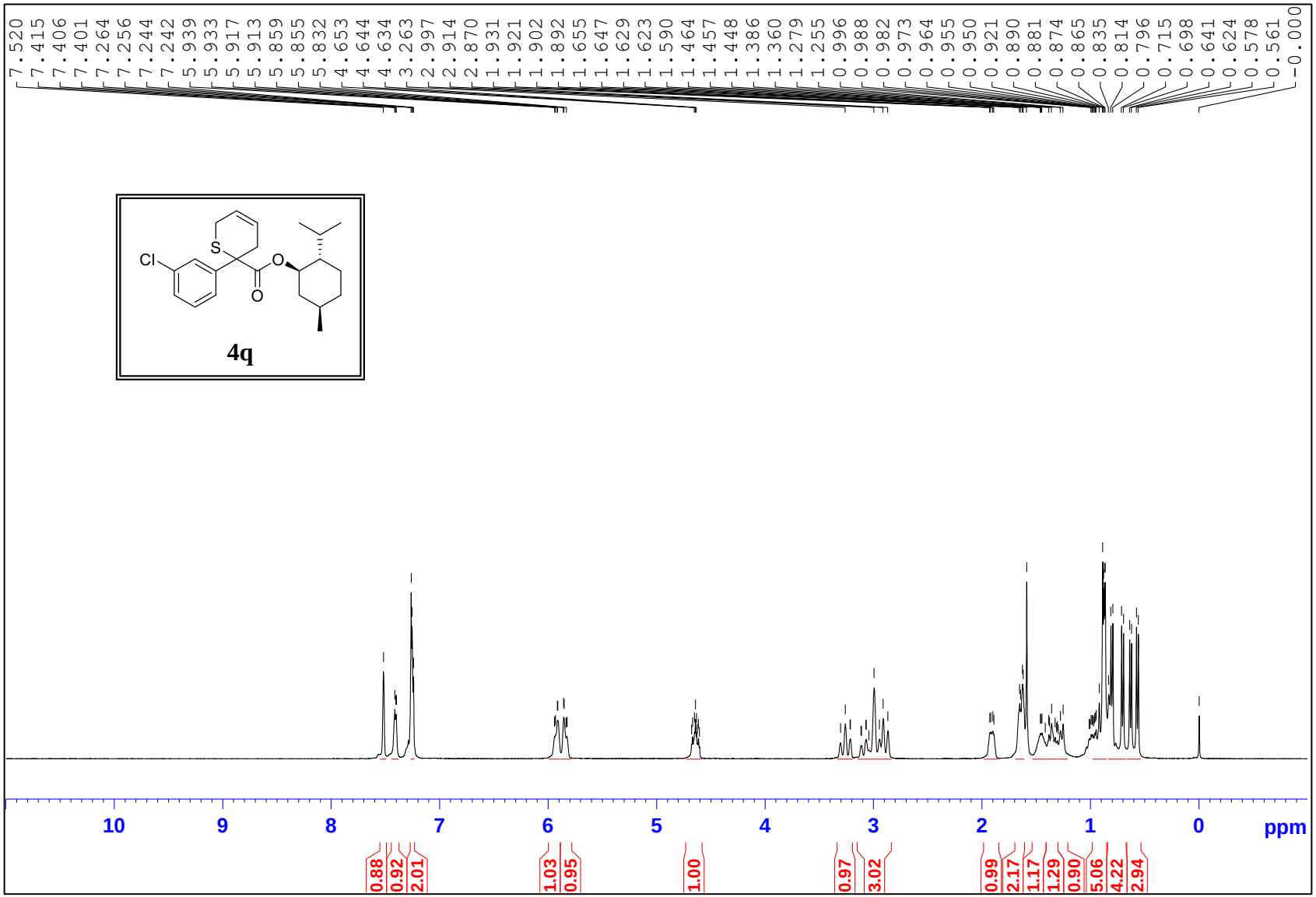
^{1}H NMR for compound **4p** (400 MHz, $CDCl_3$) (**data**)



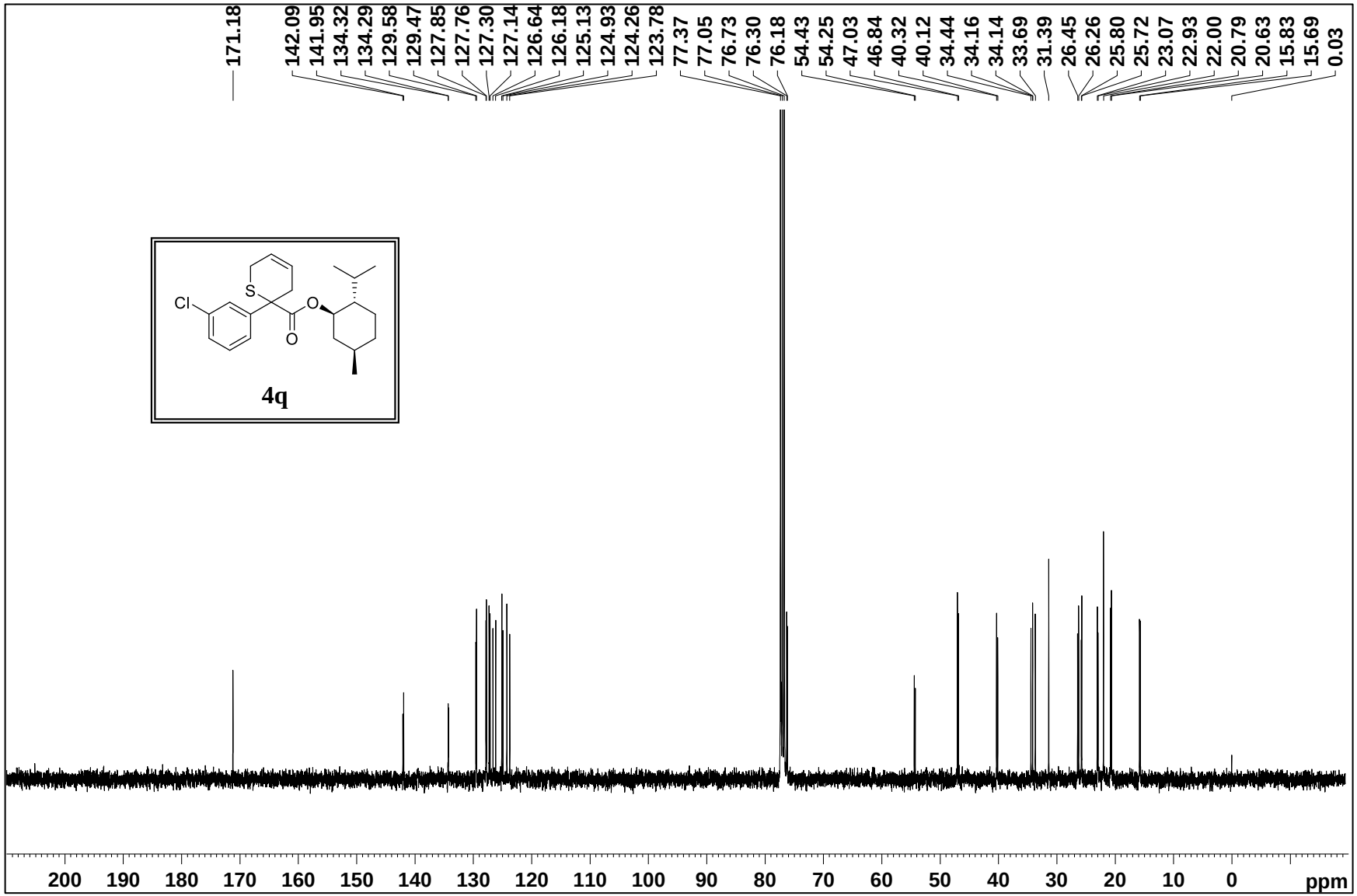
$^{13}C\{^{1}H\}$ NMR for compound **4p** (101 MHz, $CDCl_3$)



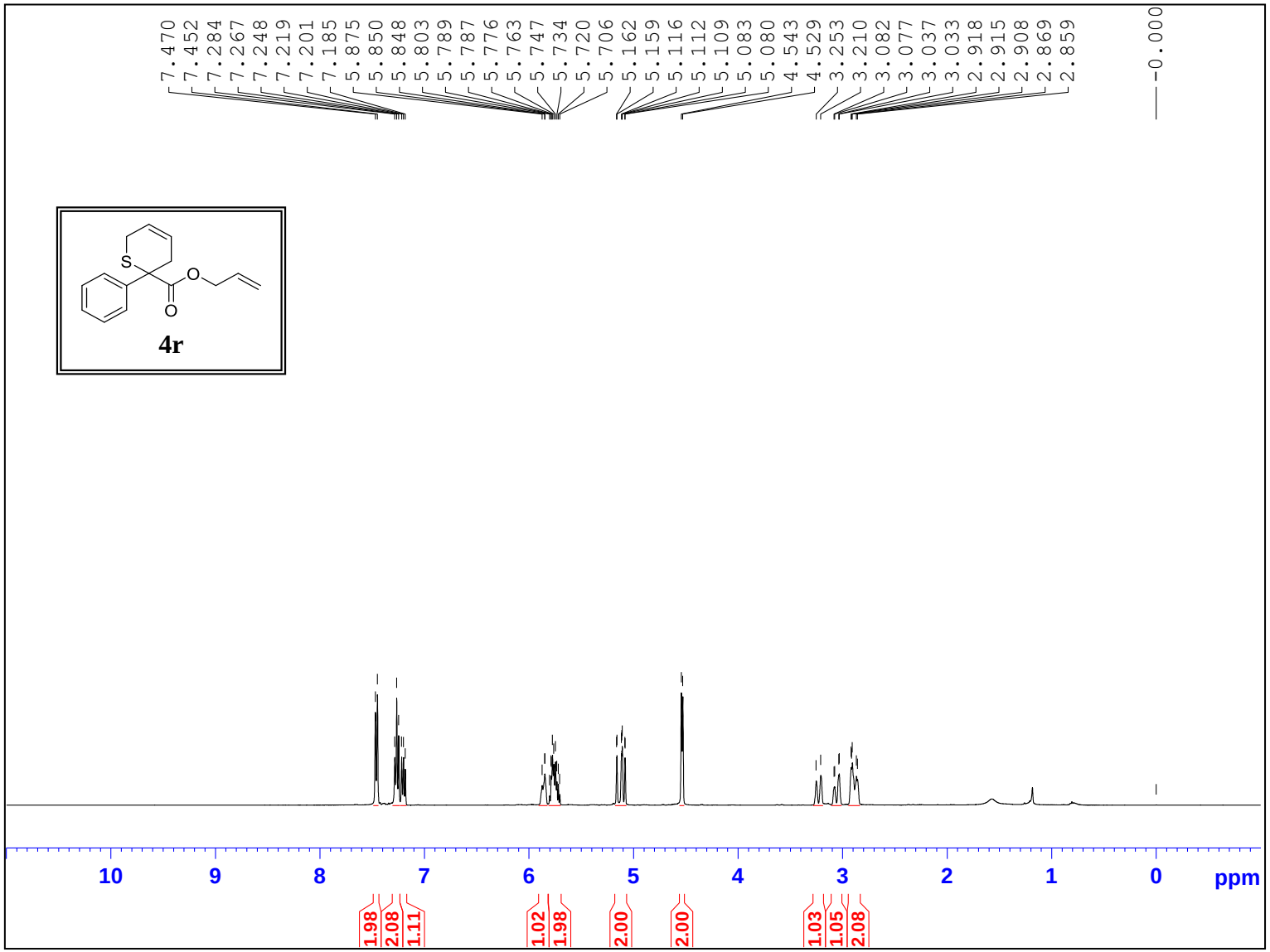
^{1}H NMR for compound **4q** (400 MHz, $CDCl_3$) (**data**)



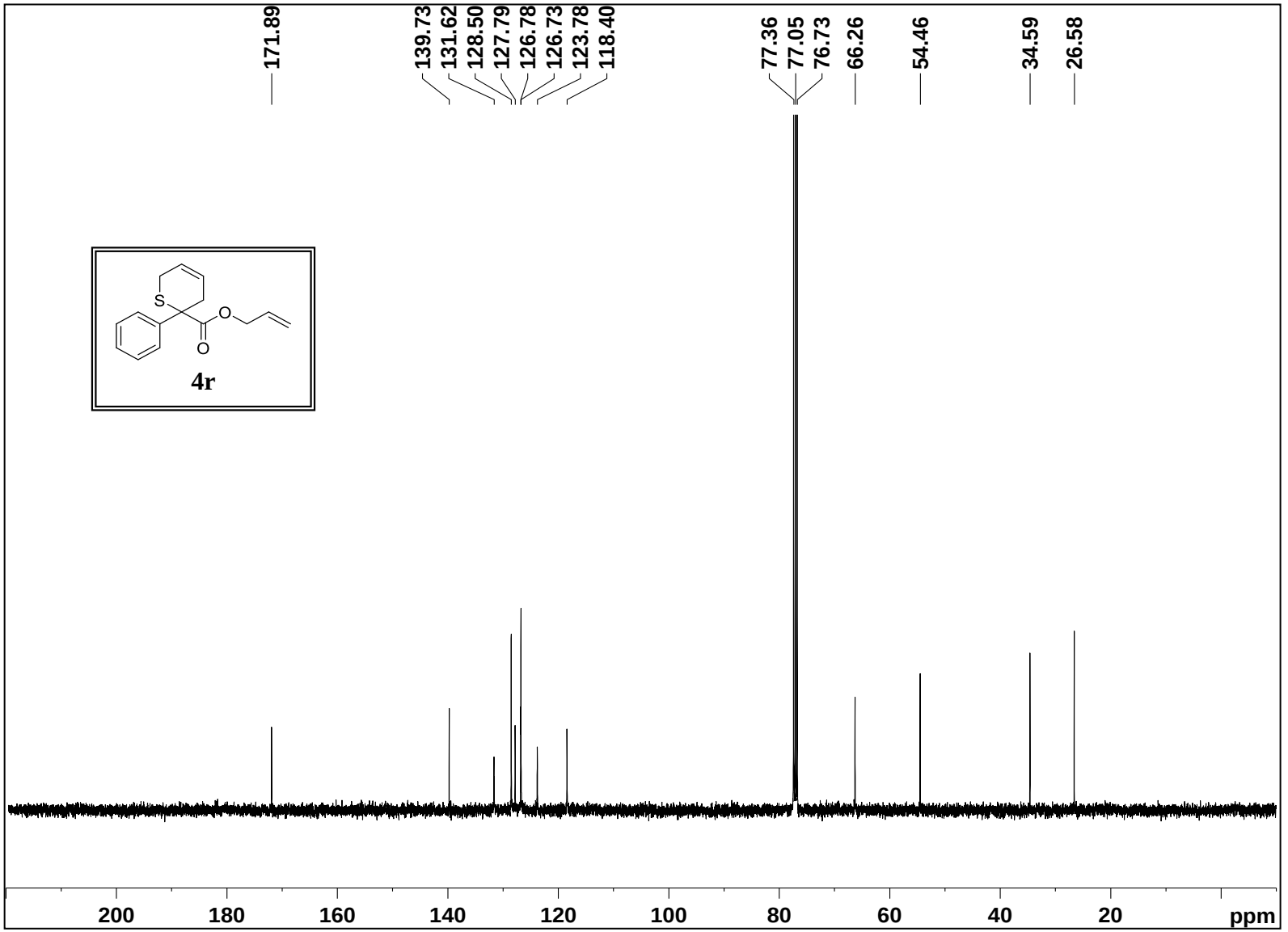
$^{13}C\{^{1}H\}$ NMR for compound **4q** (101 MHz, $CDCl_3$)



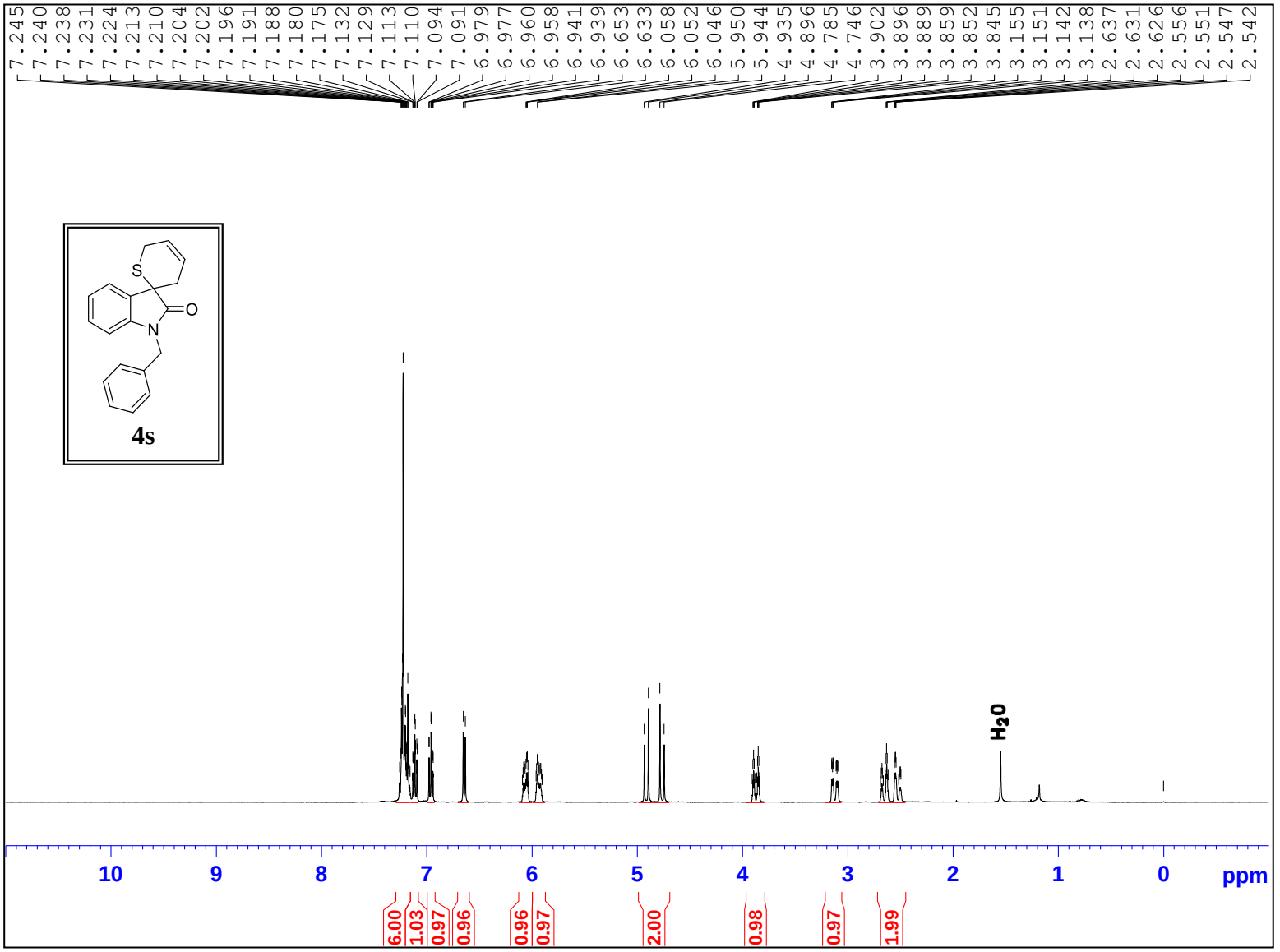
^{1}H NMR for compound **4r** (400 MHz, $CDCl_3$) (**data**)



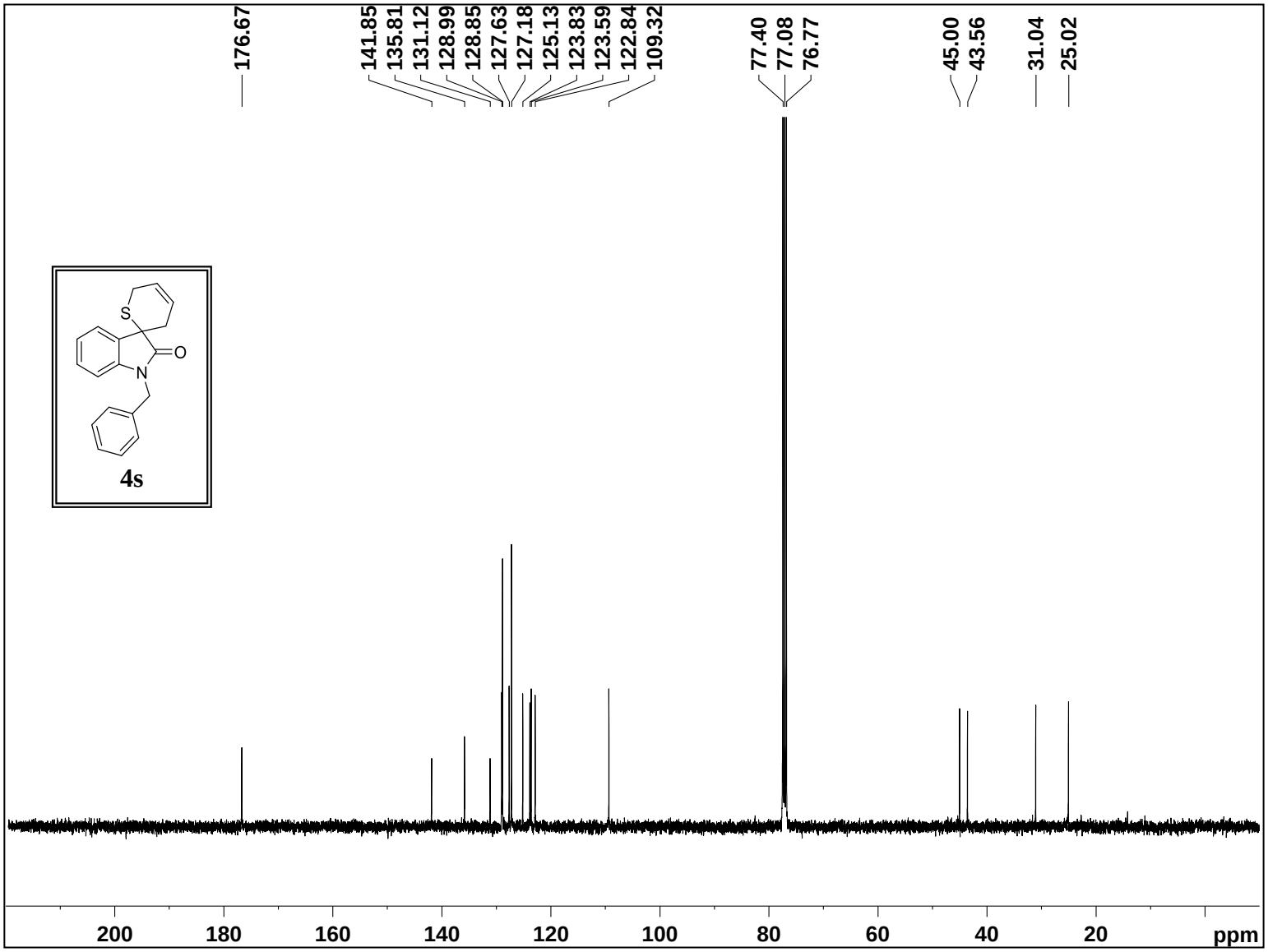
$^{13}C\{^{1}H\}$ NMR for compound **4r** (101 MHz, $CDCl_3$)



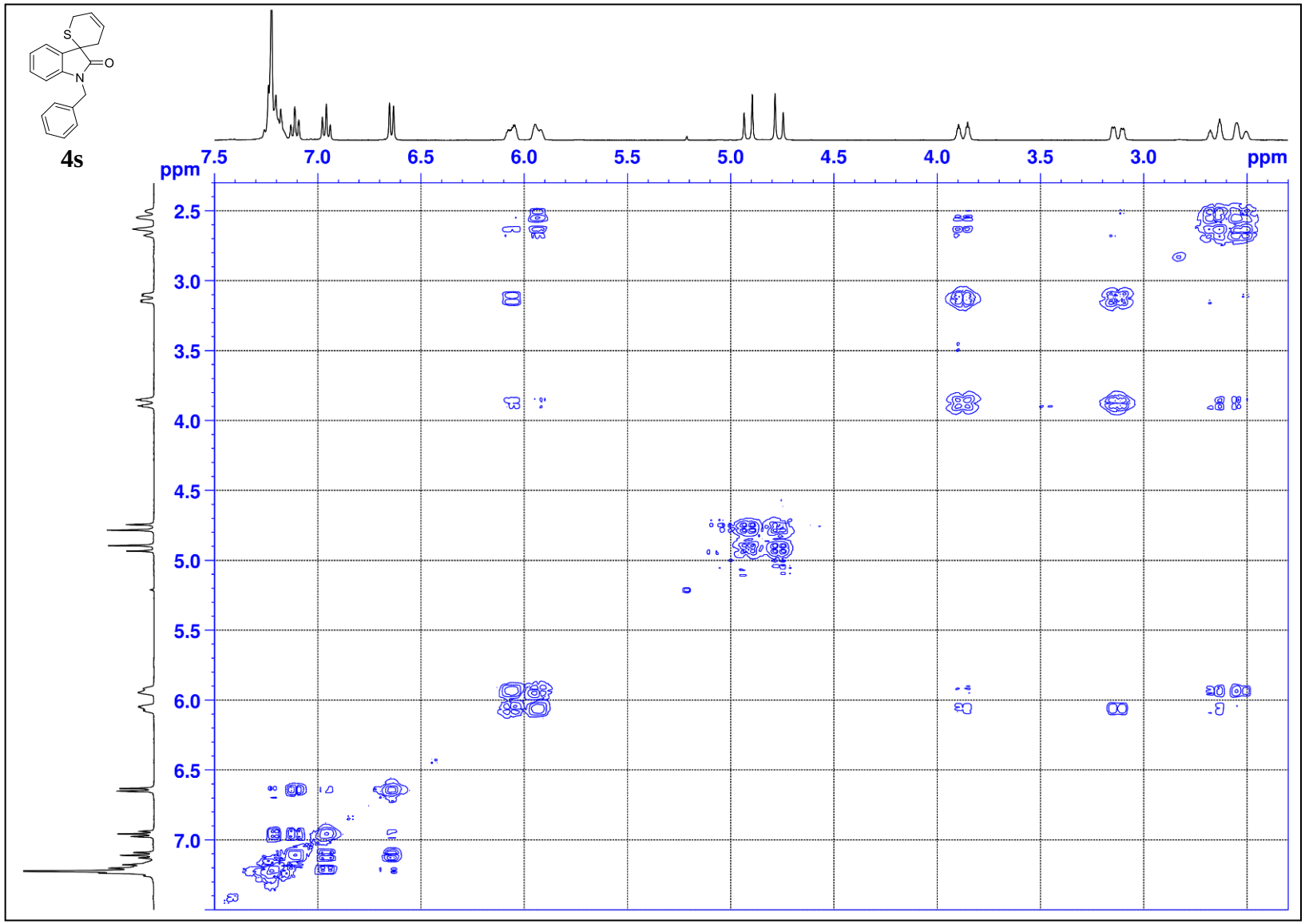
^{1}H NMR for compound **4s** (400 MHz, $CDCl_3$) (**data**)



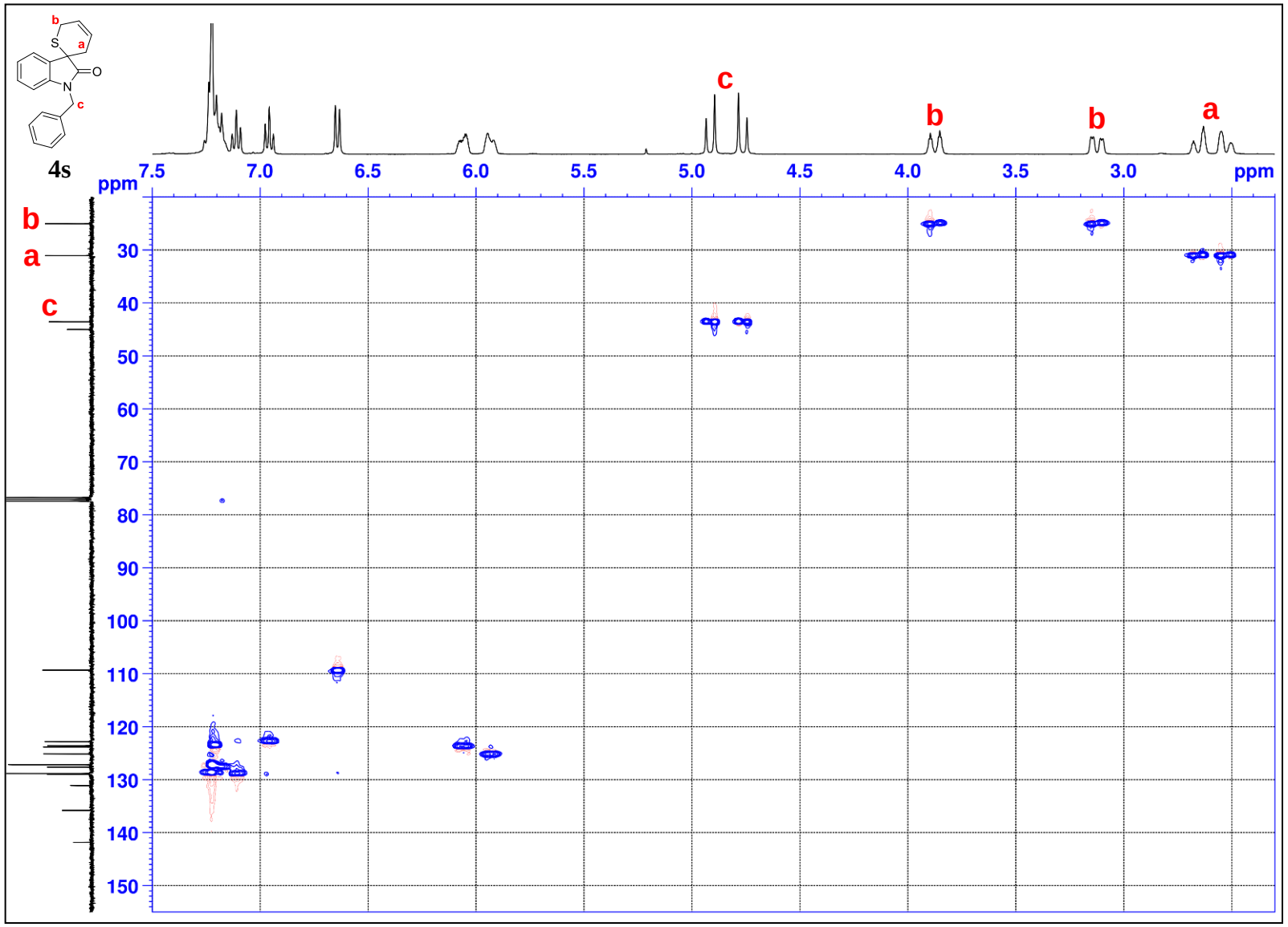
$^{13}C\{^{1}H\}$ NMR for compound **4s** (101 MHz, $CDCl_3$)



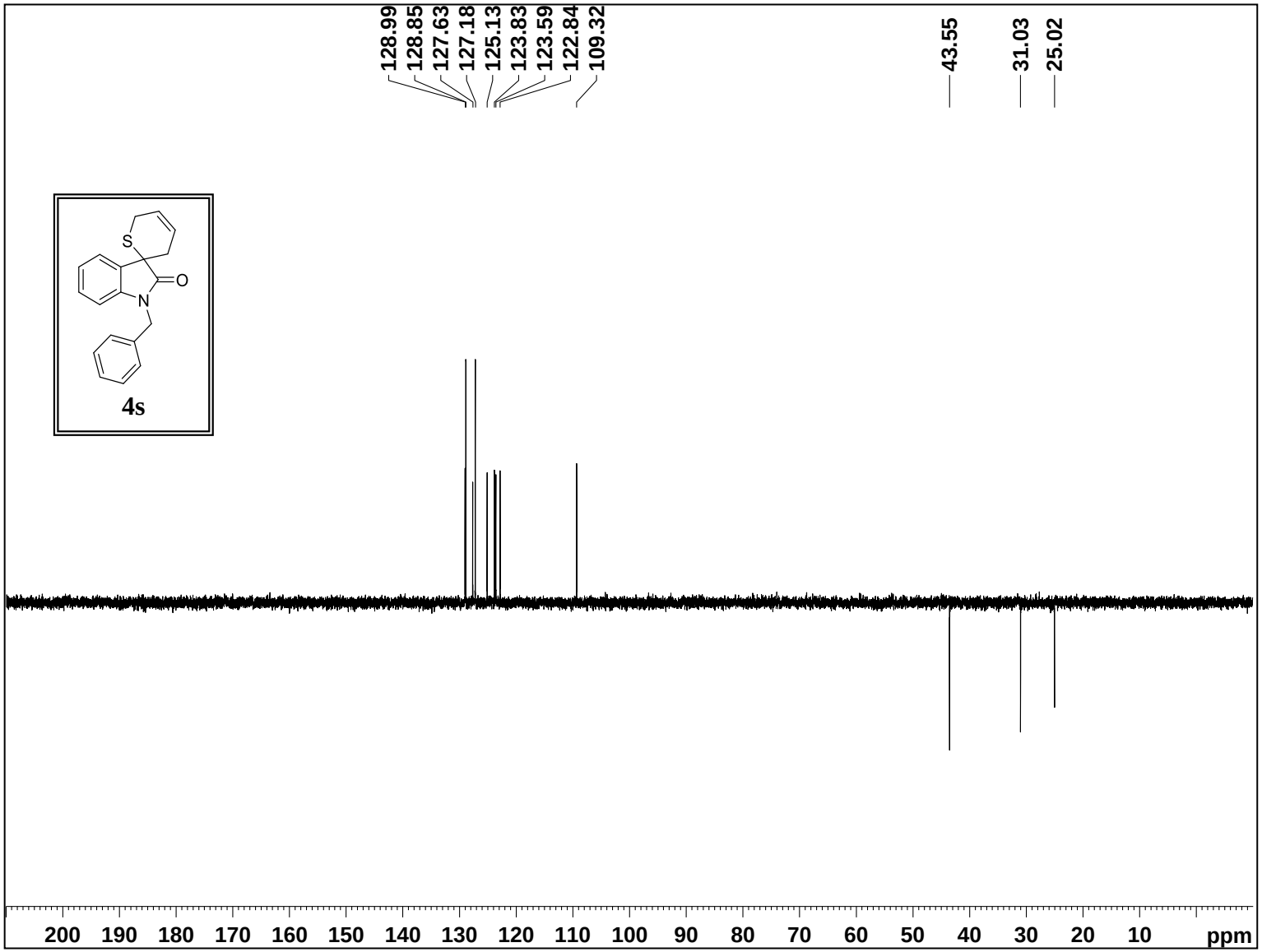
[^{1}H, ^{1}H] COSY for compound **4s** (400 MHz, $CDCl_3$)



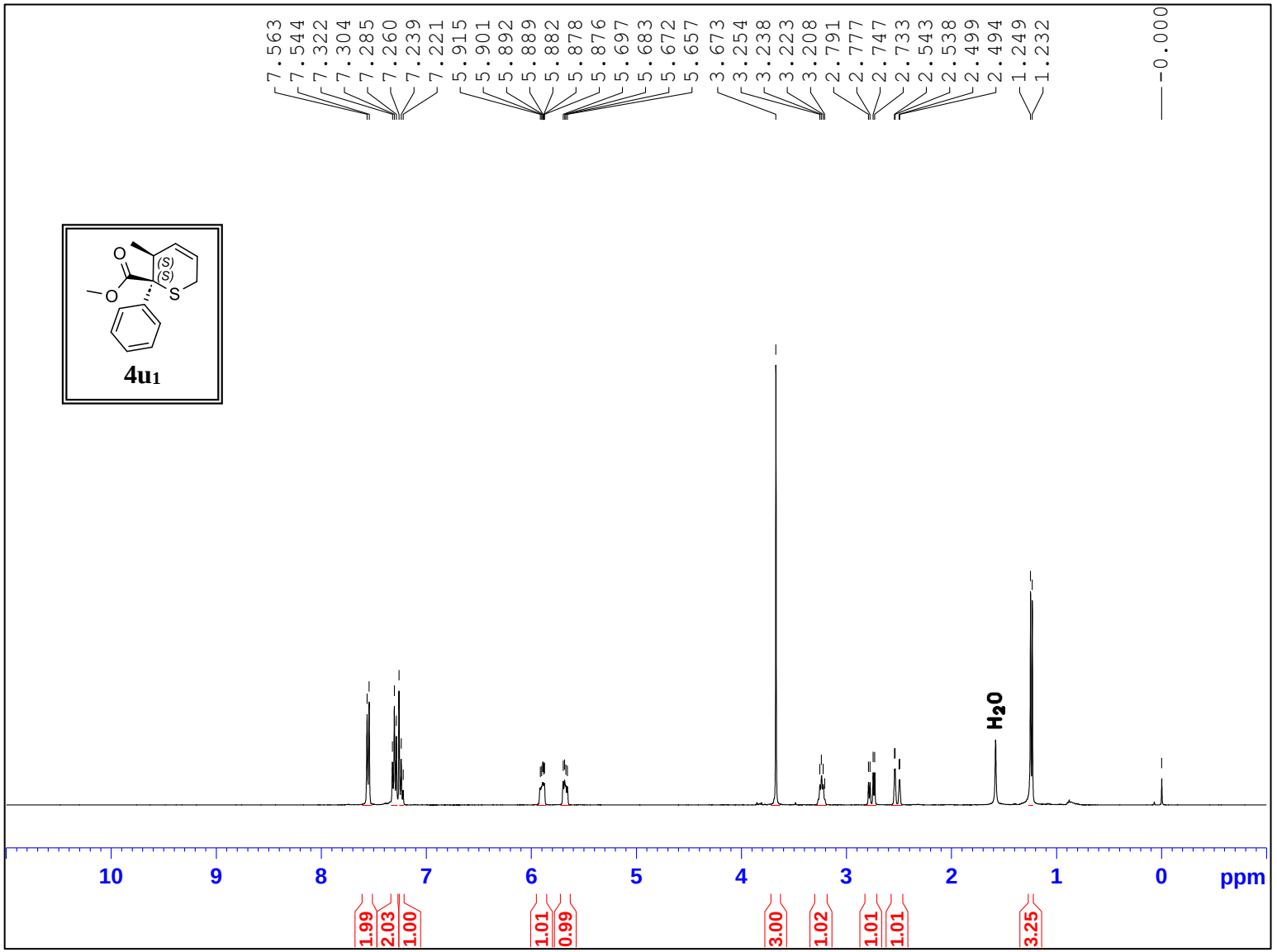
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **4s** (400 MHz, $CDCl_3$)



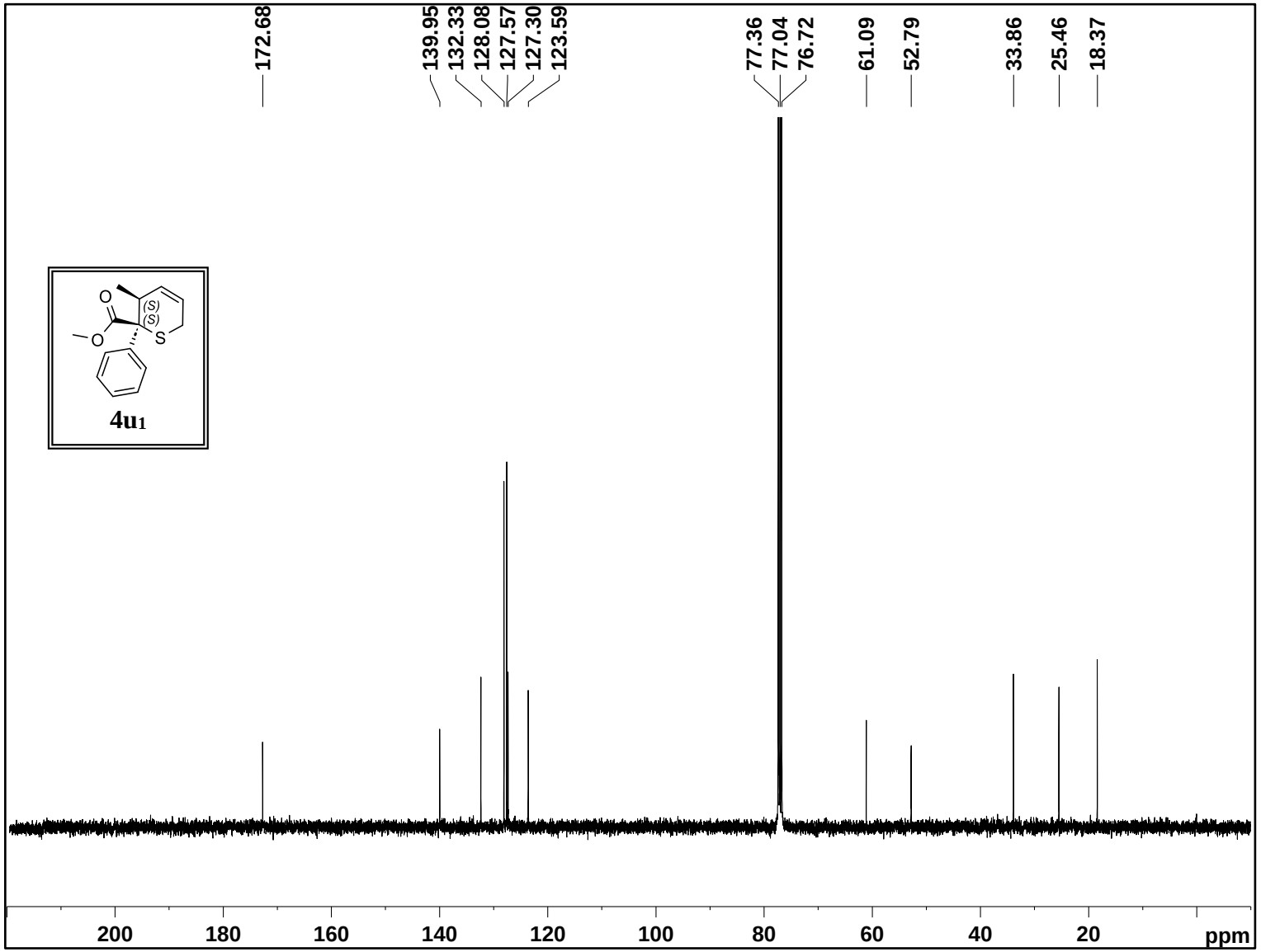
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4s** (101 MHz, $CDCl_3$)



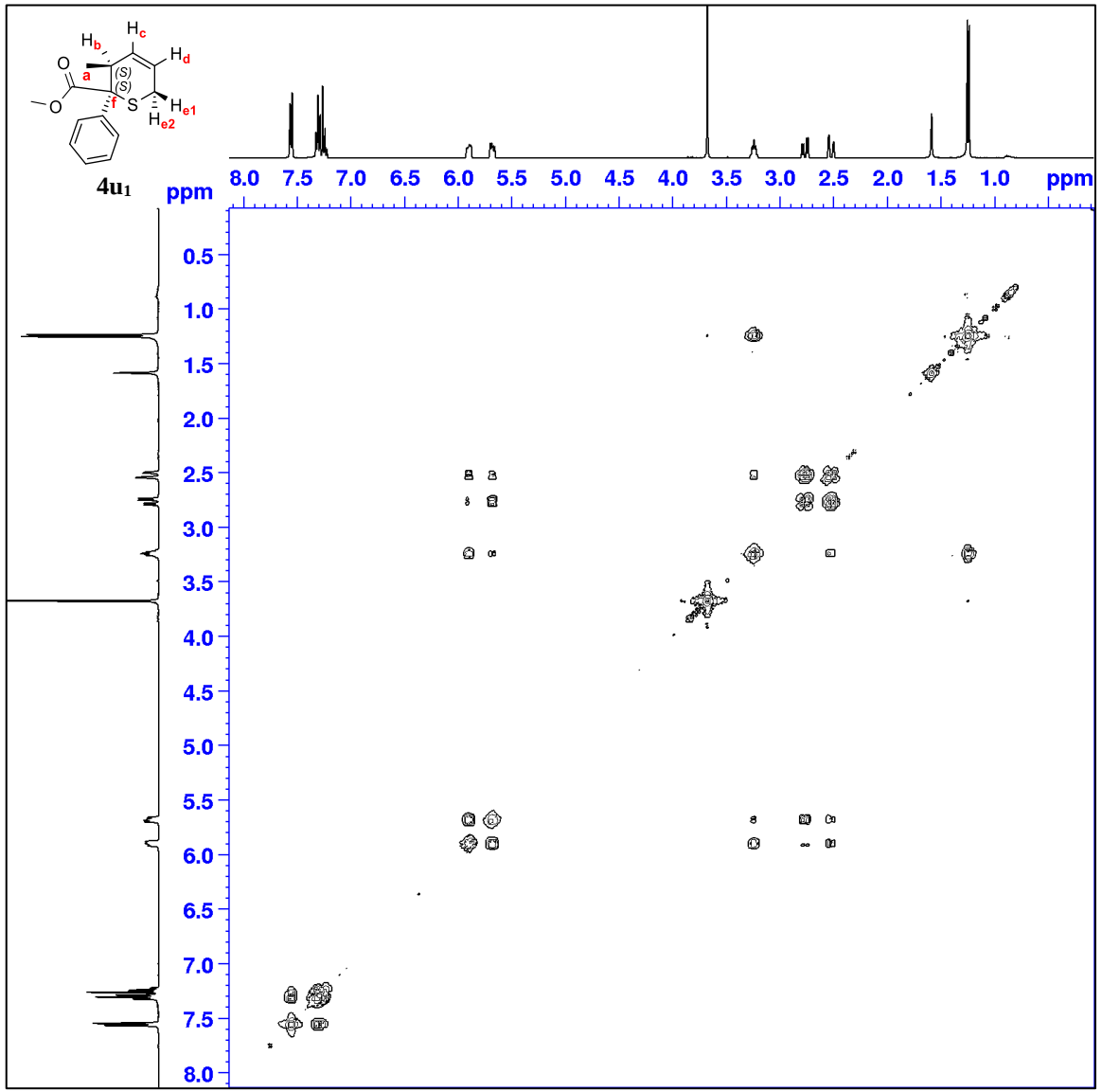
^{1}H NMR for compound **4u$_1$** (400 MHz, $CDCl_3$) (**data**)



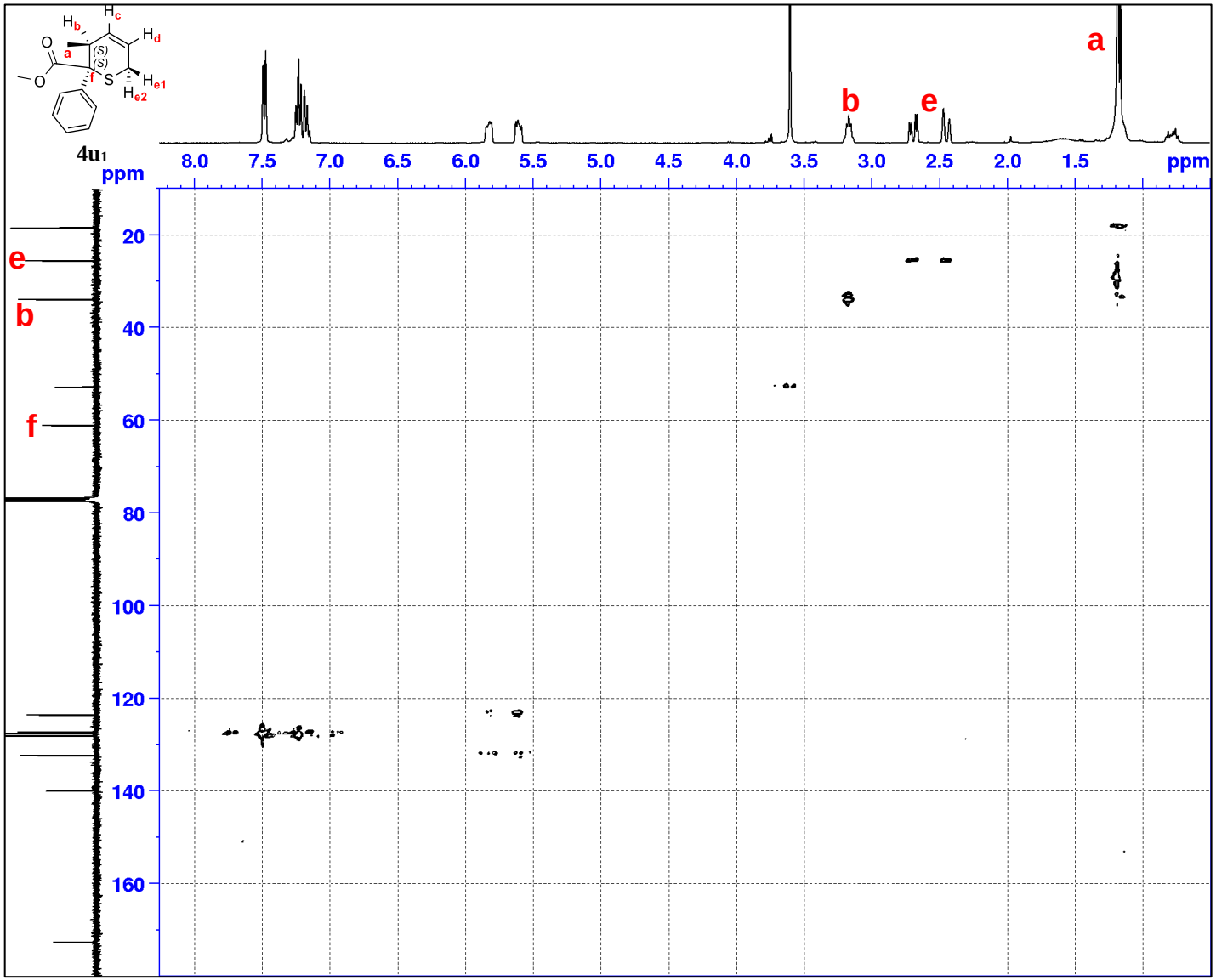
$^{13}C\{^{1}H\}$ NMR for compound **4u$_1$** (101 MHz, $CDCl_3$)



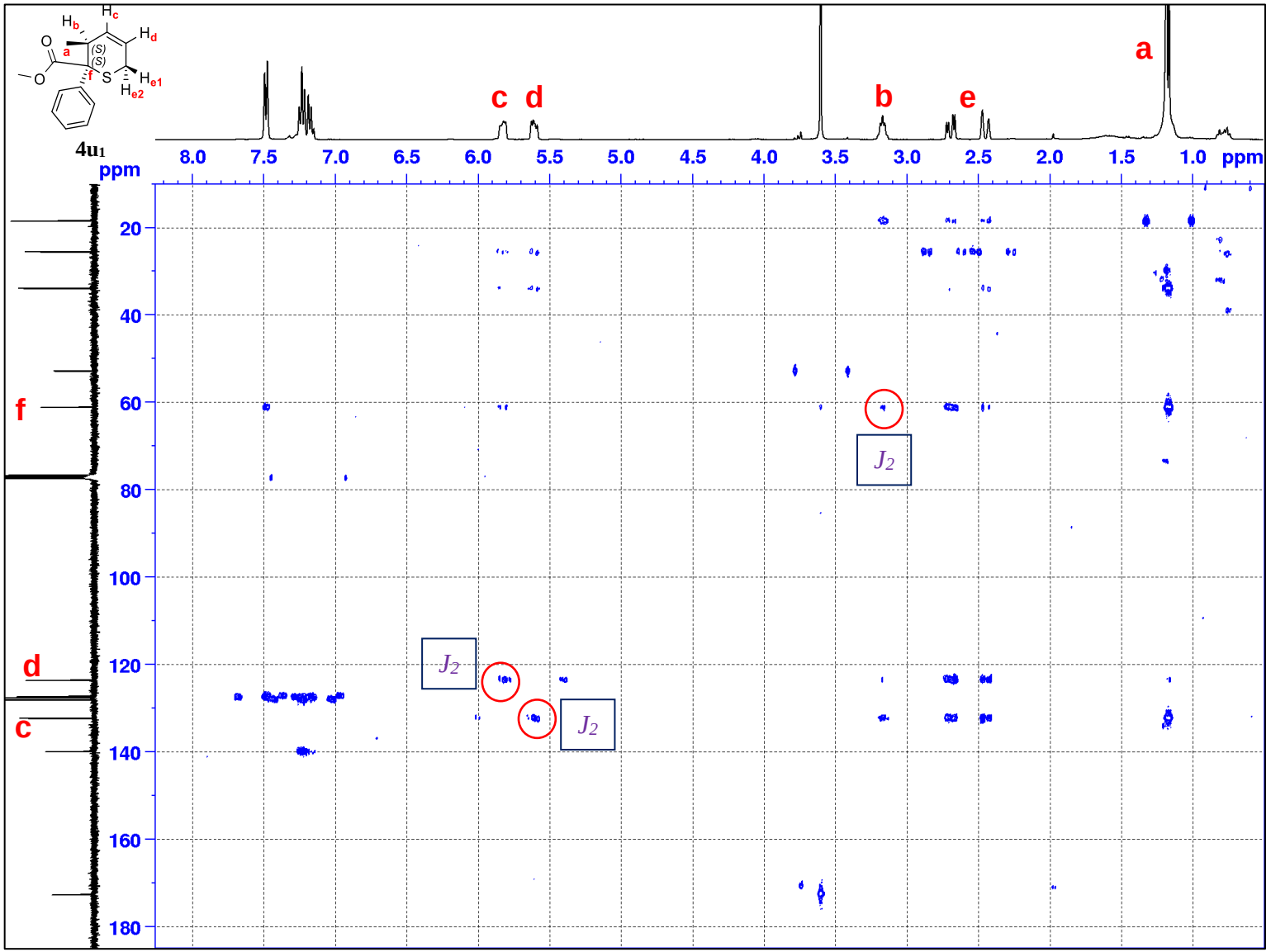
[^{1}H, ^{1}H] COSY for compound **4u$_1$** (400 MHz, $CDCl_3$)



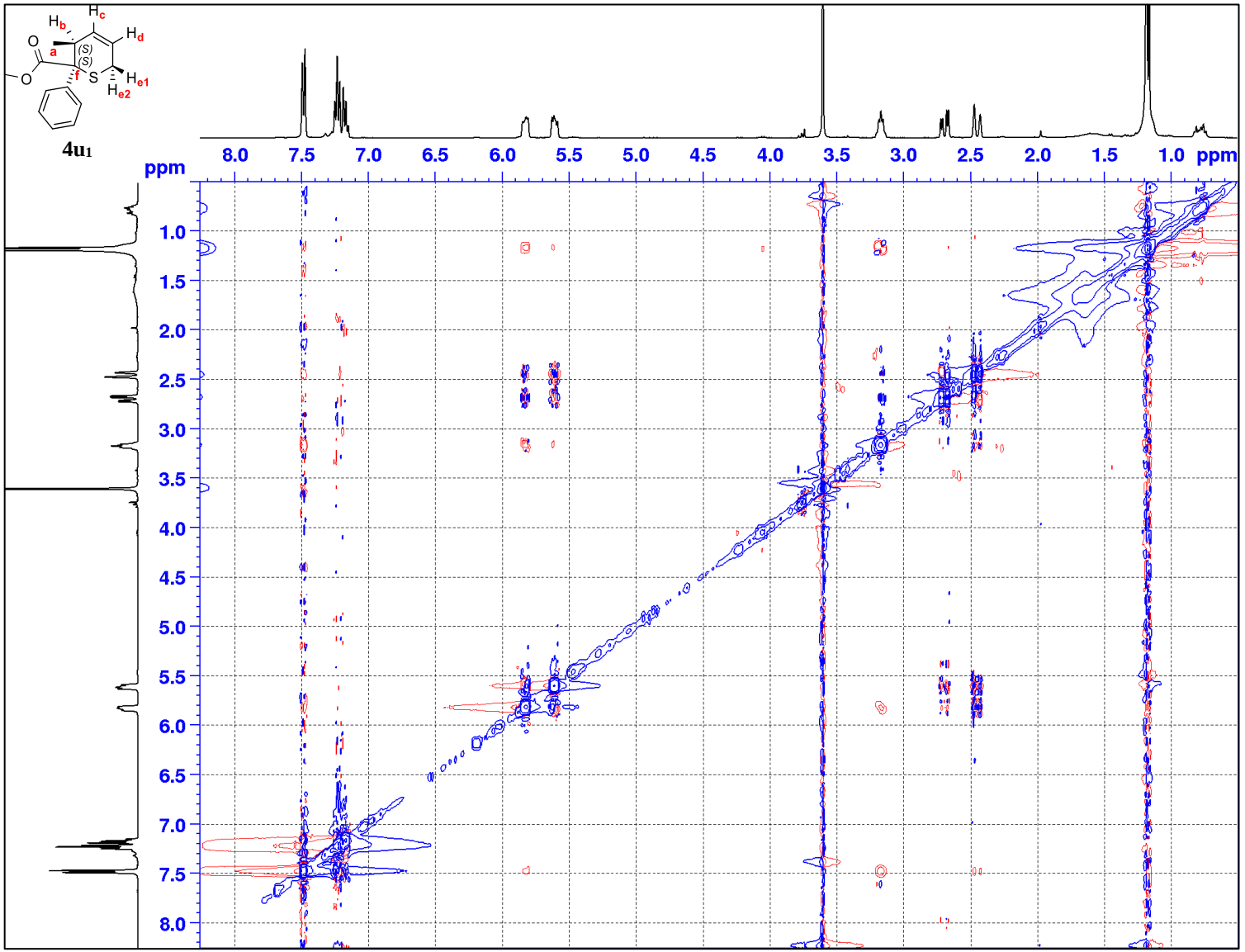
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **4u$_1$** (400 MHz, $CDCl_3$)



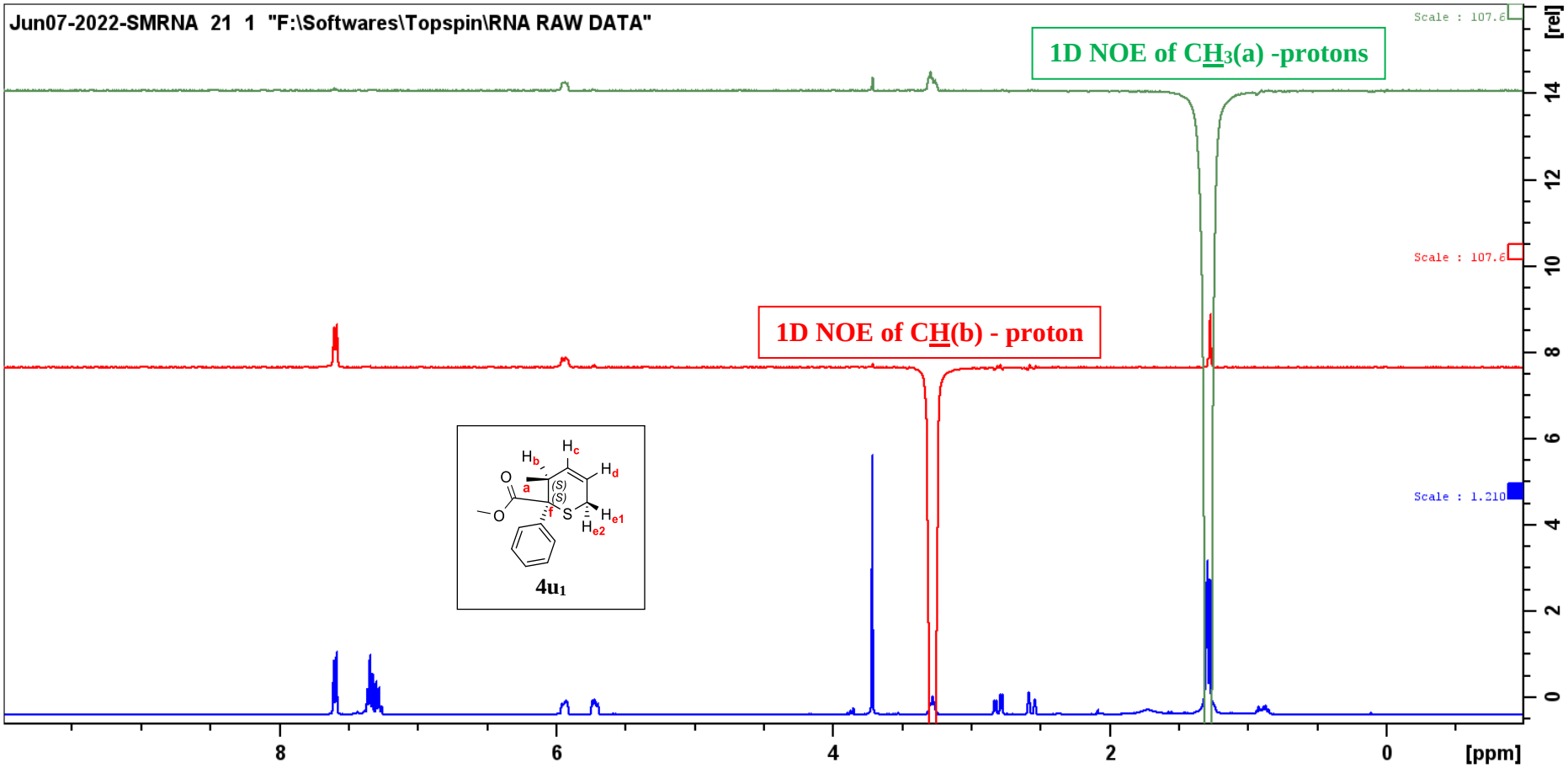
[^{1}H, ^{13}C{^{1}H}] HMBC for compound **4u$_1$** (400 MHz, $CDCl_3$)



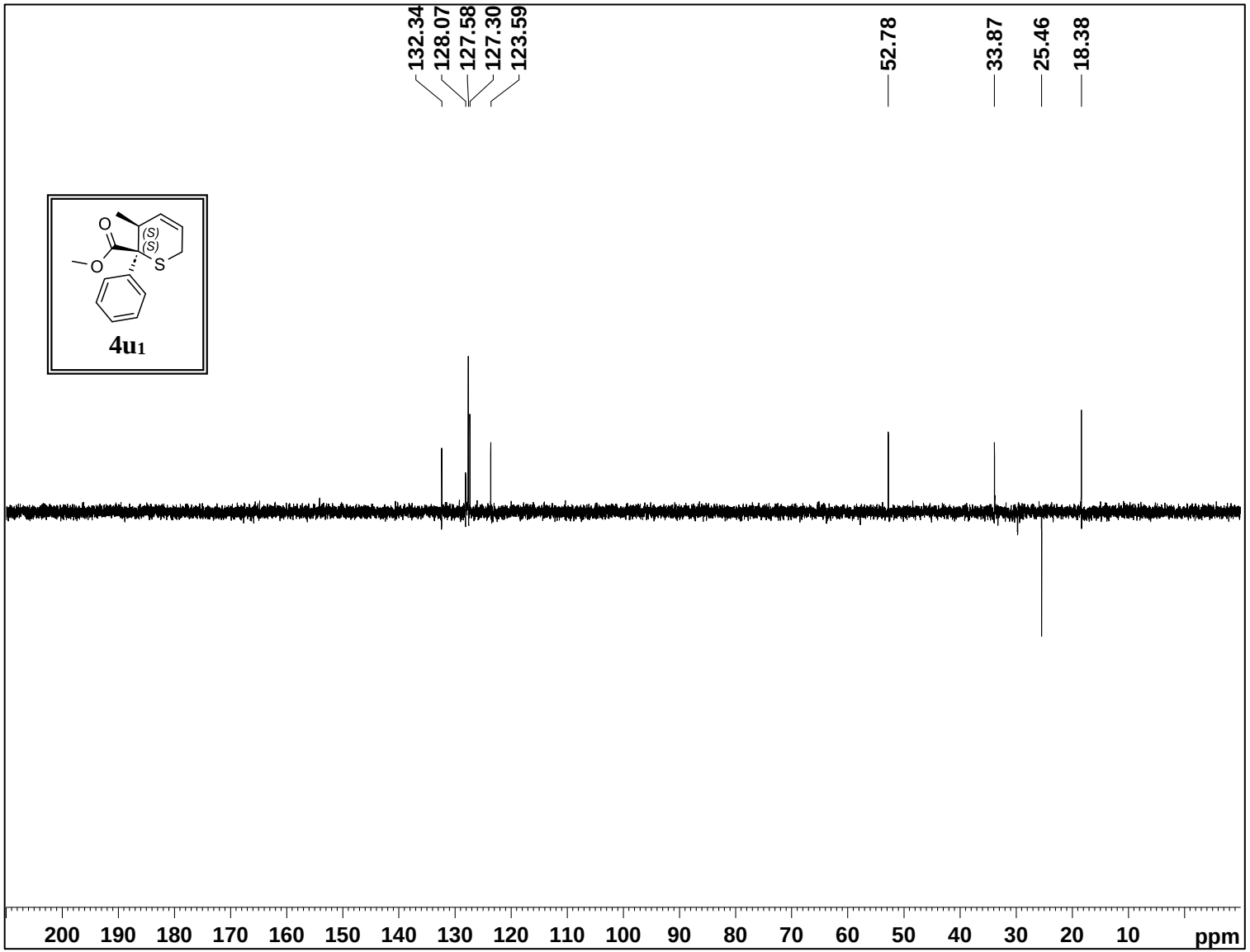
[^{1}H, ^{1}H] NOESY for compound **4u$_1$** (400 MHz, $CDCl_3$)



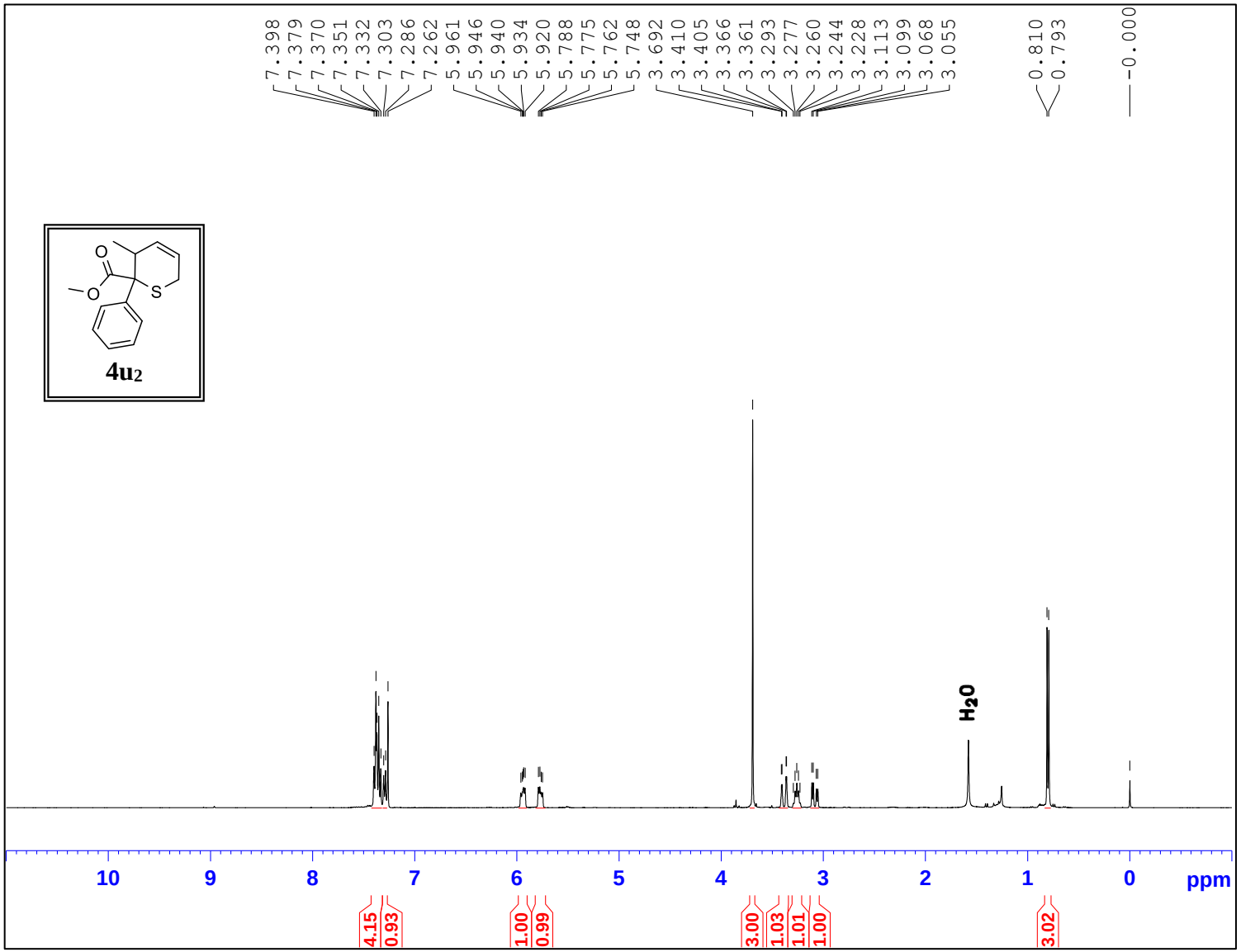
[^{1}H, ^{1}H] SELNOGP (1D NOE) for compound **4u$_1$** (400 MHz, $CDCl_3$)



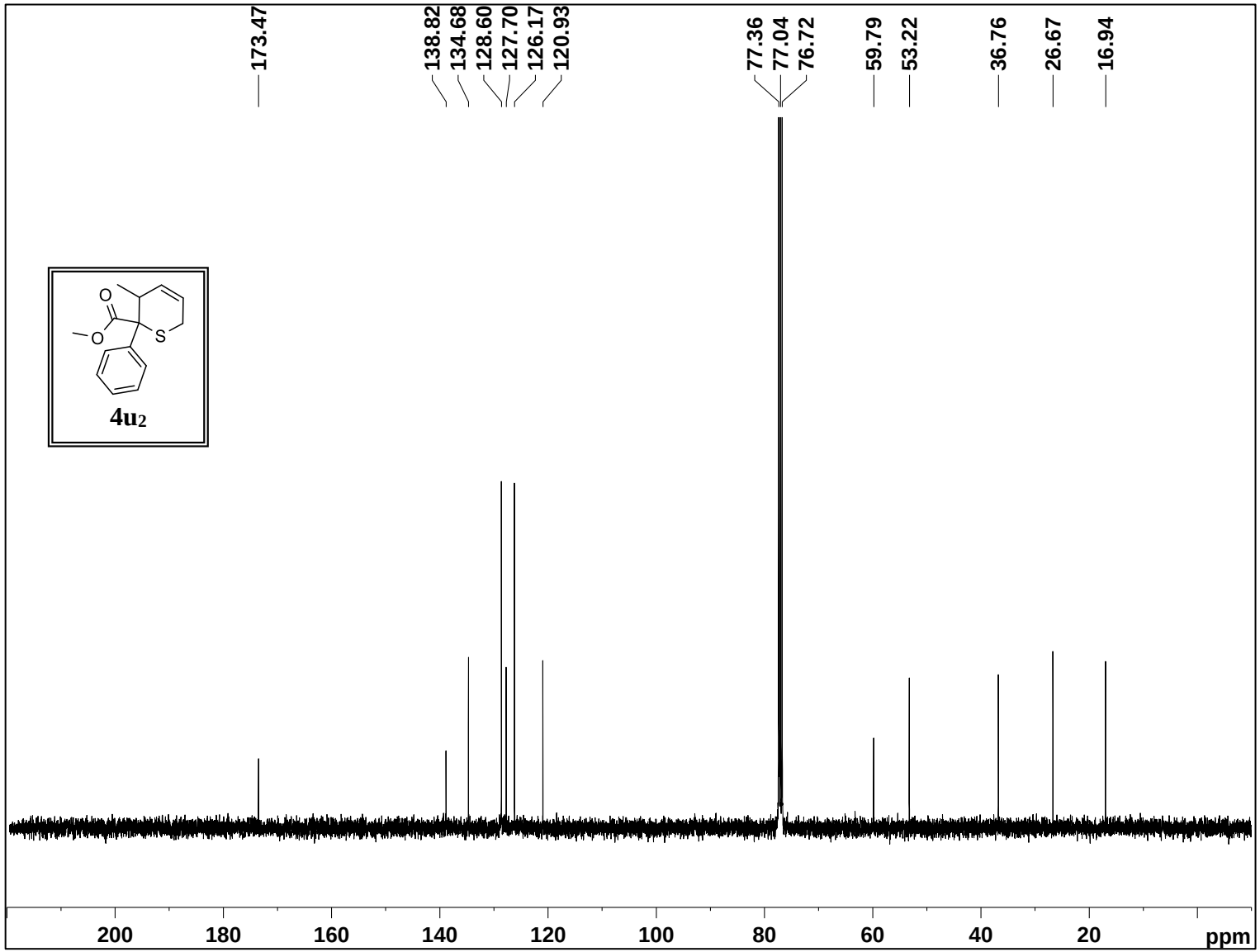
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4u₁** (101 MHz, $CDCl_3$)



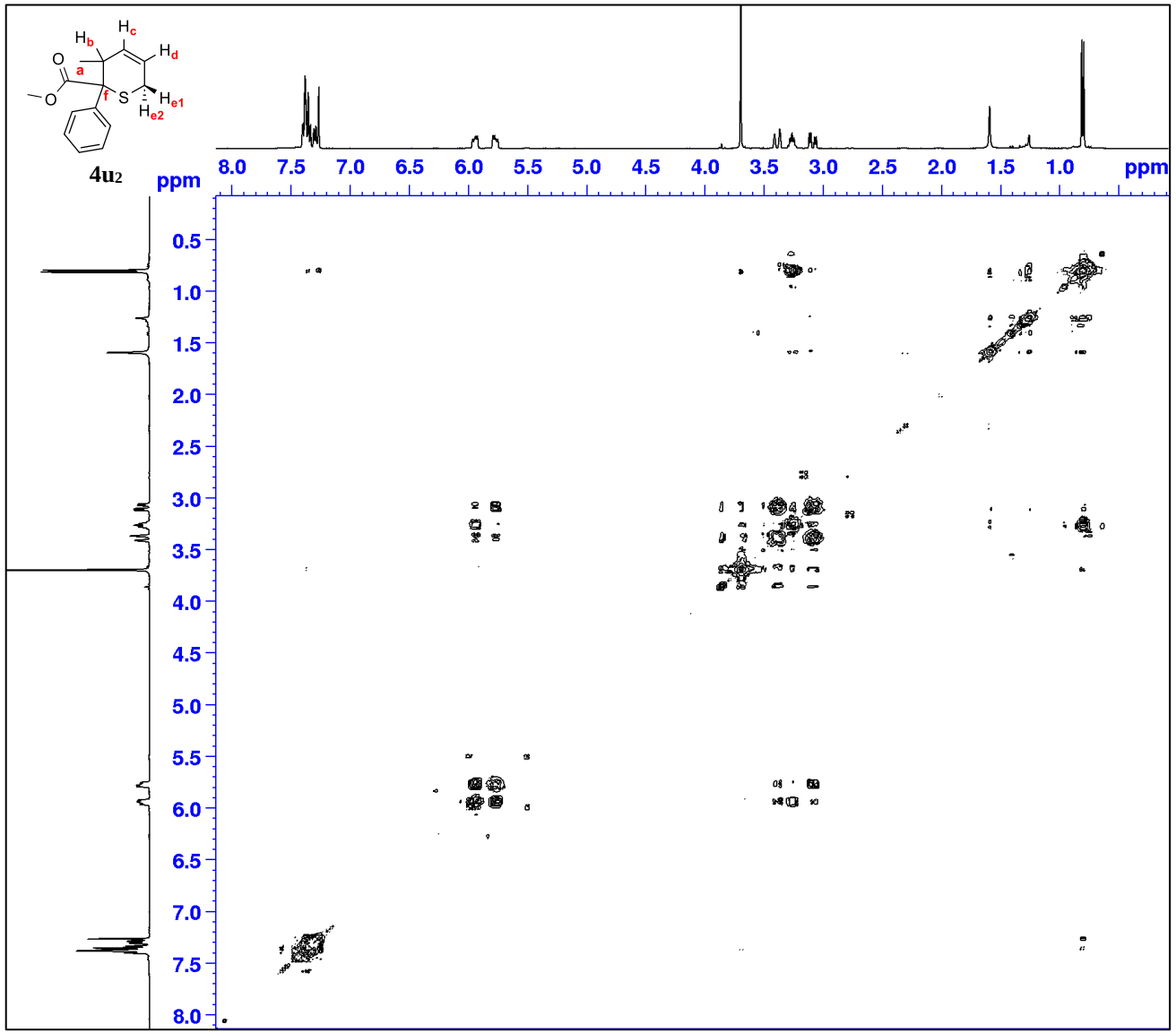
^{1}H NMR for compound **4u$_2$** (400 MHz, $CDCl_3$) (**data**)



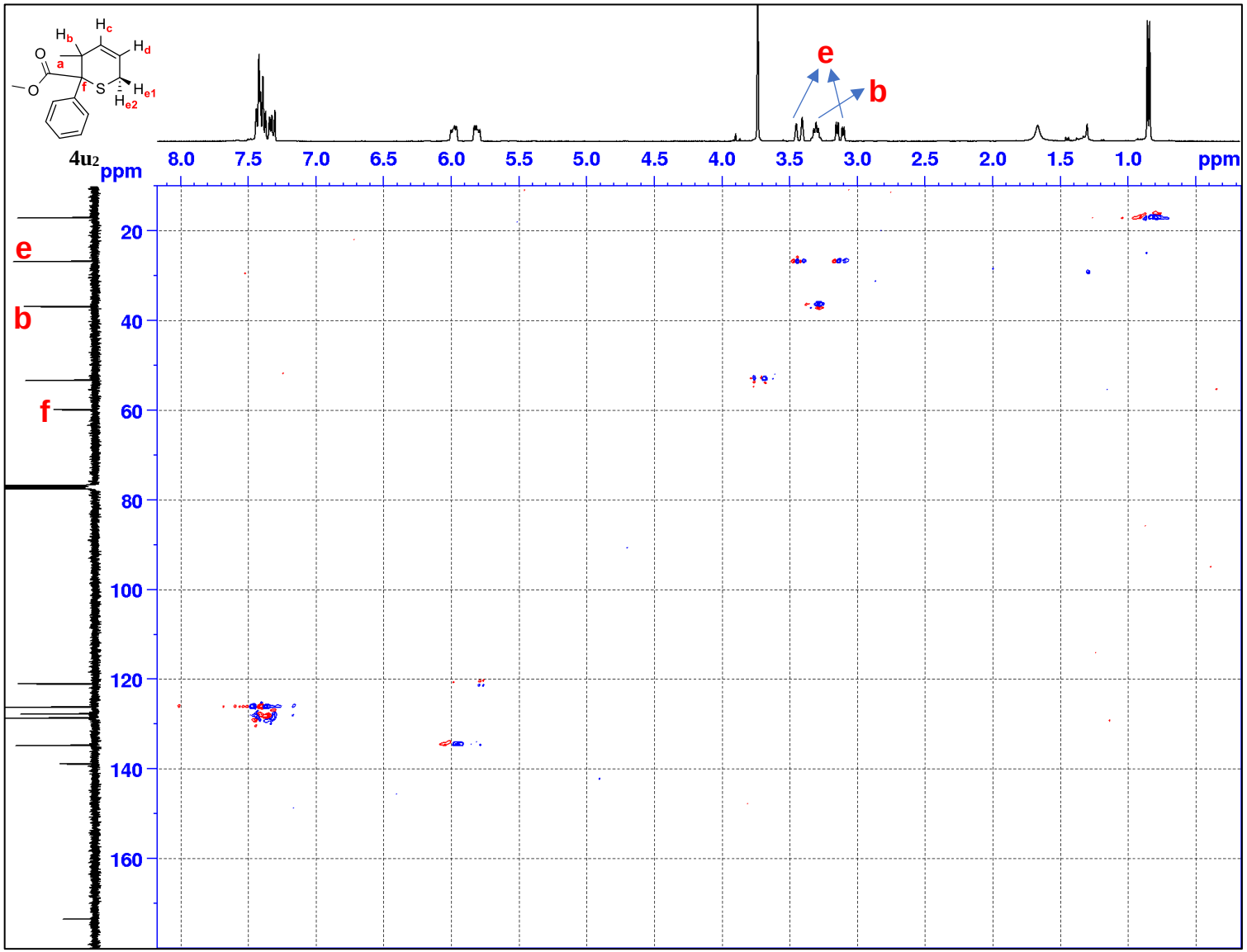
$^{13}C\{^{1}H\}$ NMR for compound **4u₂** (101 MHz, $CDCl_3$)



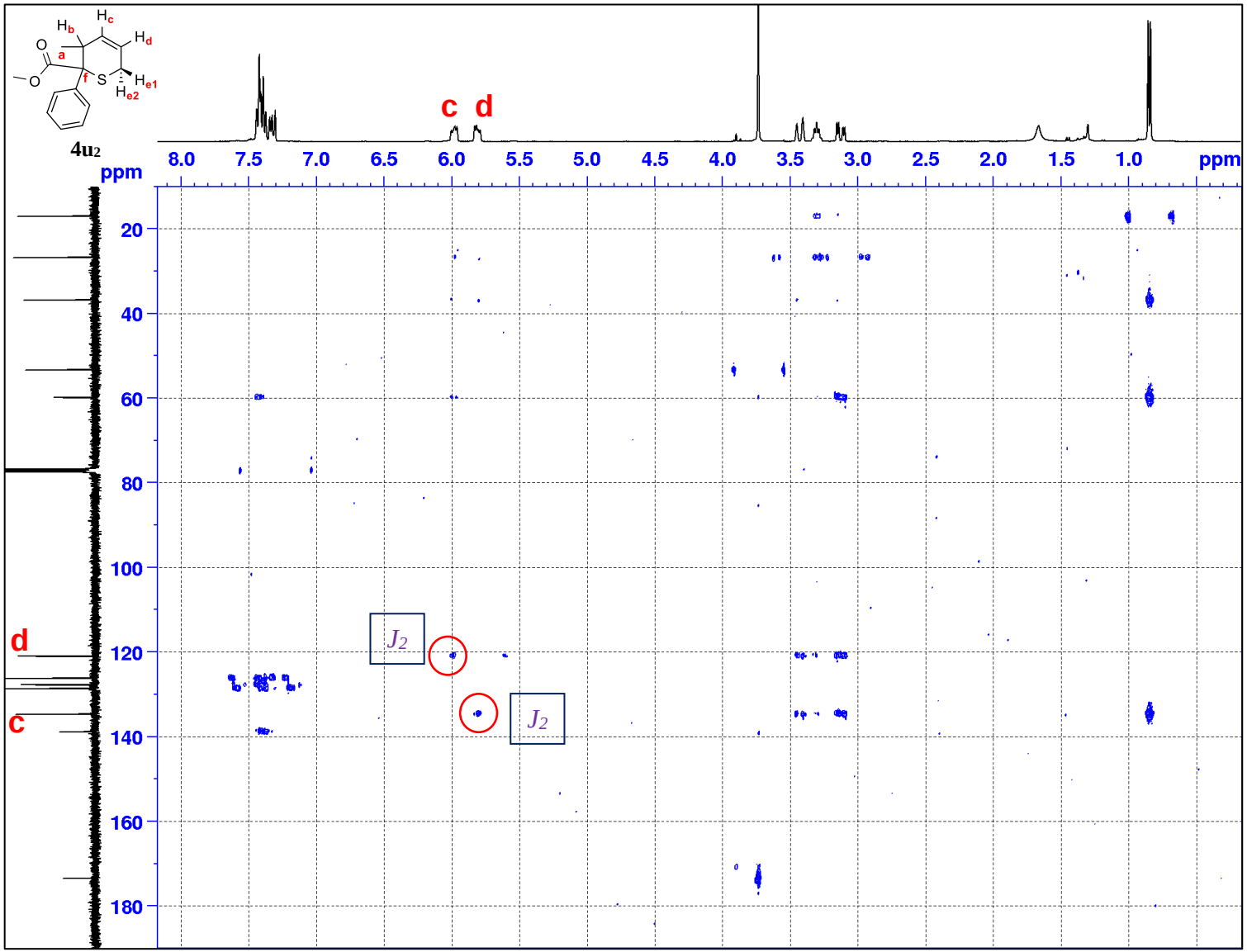
[^{1}H, ^{1}H] COSY for compound **4u$_2$** (400 MHz, $CDCl_3$)



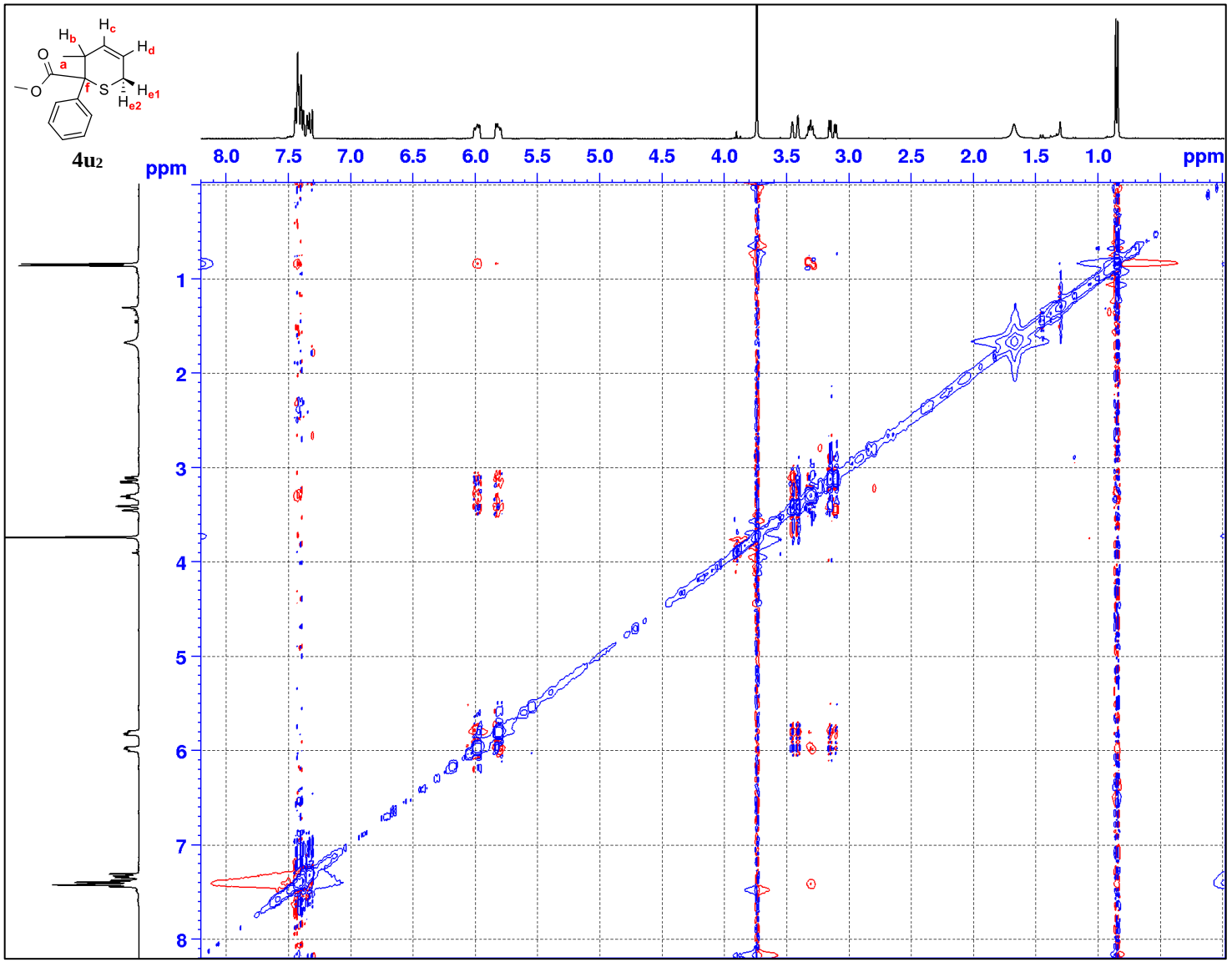
[^{1}H, ^{13}C{^{1}H}] HSQC for compound **4u$_2$** (400 MHz, $CDCl_3$)



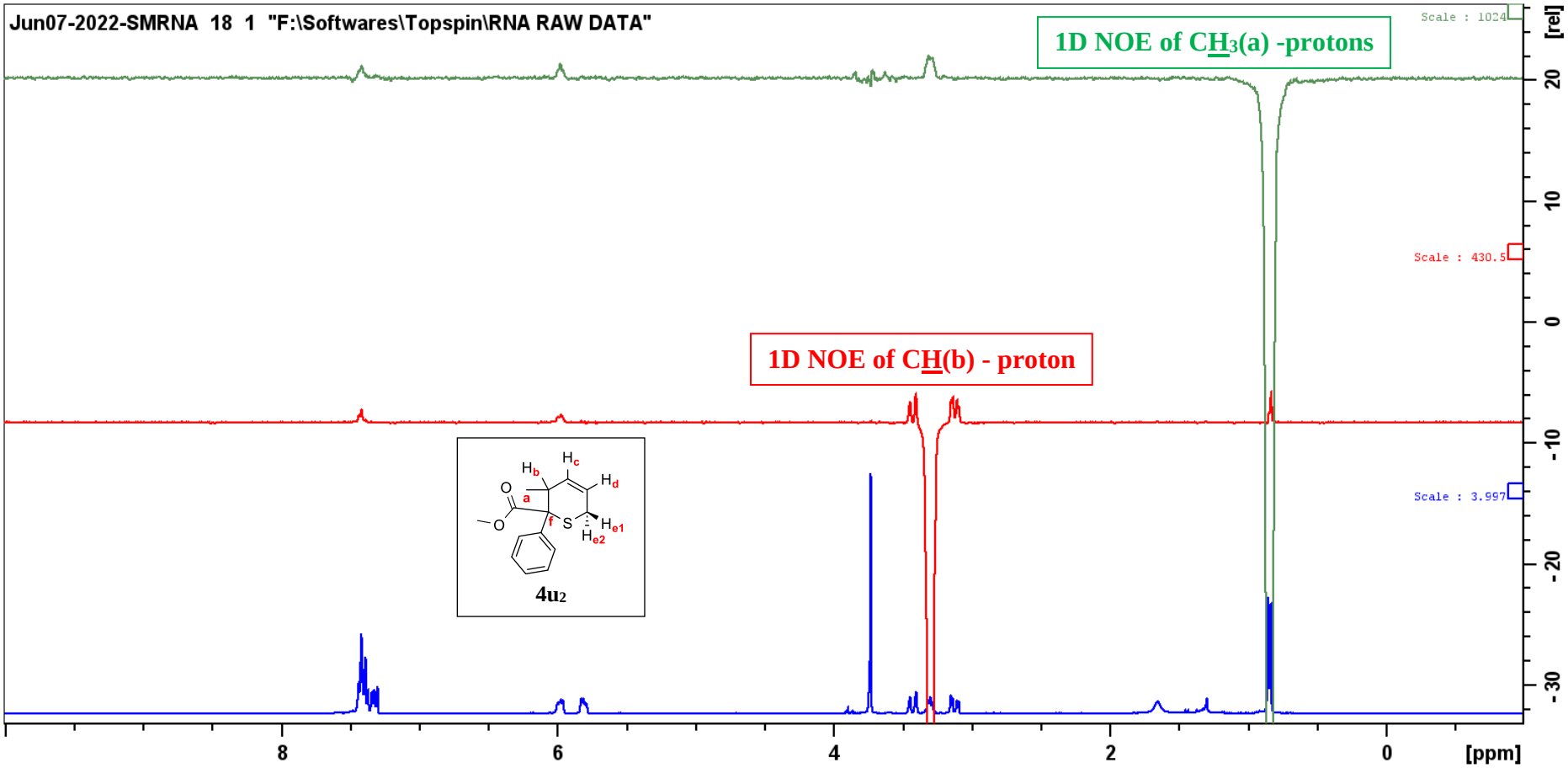
[^{1}H, ^{13}C{^{1}H}] HMBC for compound **4u$_2$** (400 MHz, $CDCl_3$)



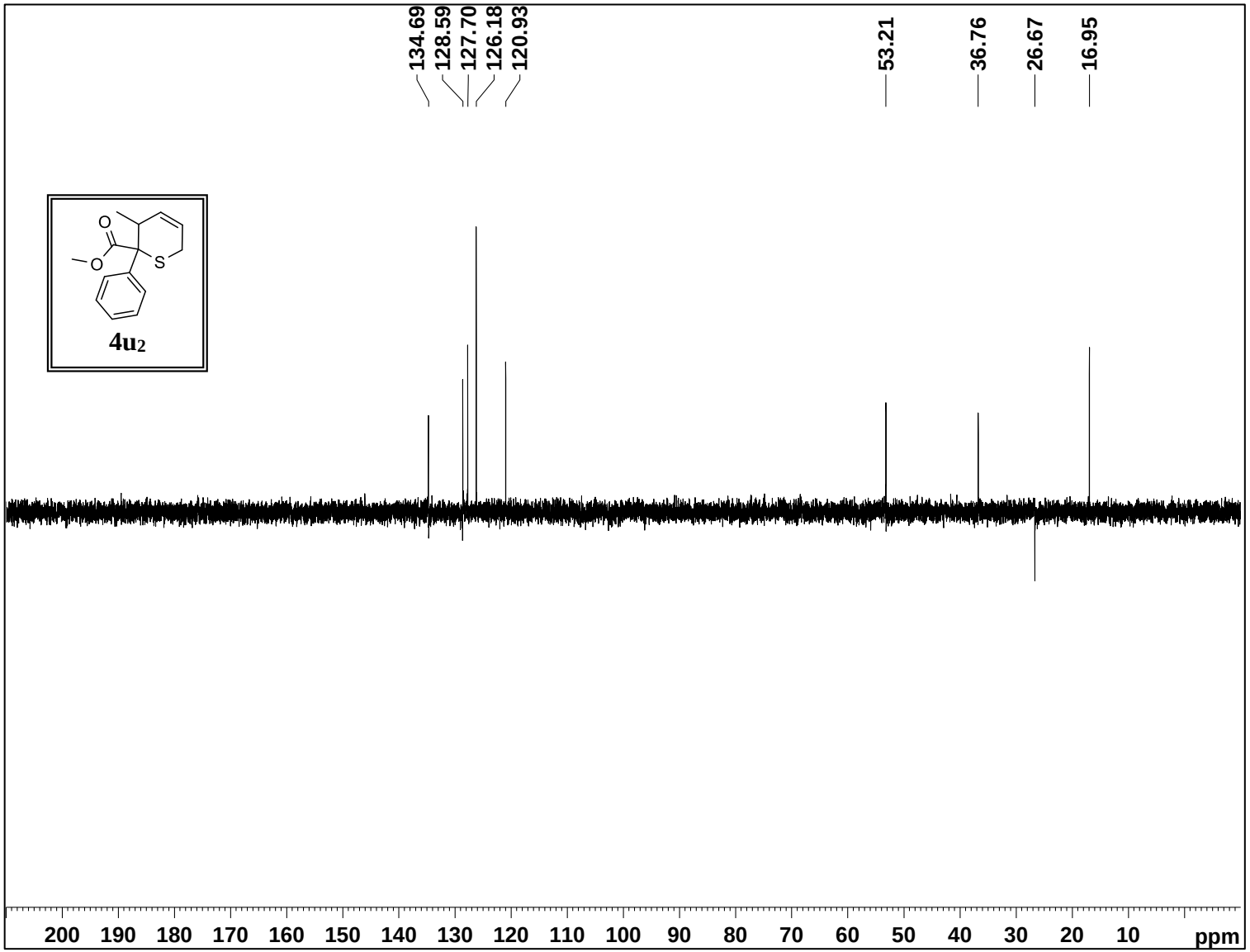
[^{1}H, ^{1}H] NOESY for compound **4u$_2$** (400 MHz, $CDCl_3$)



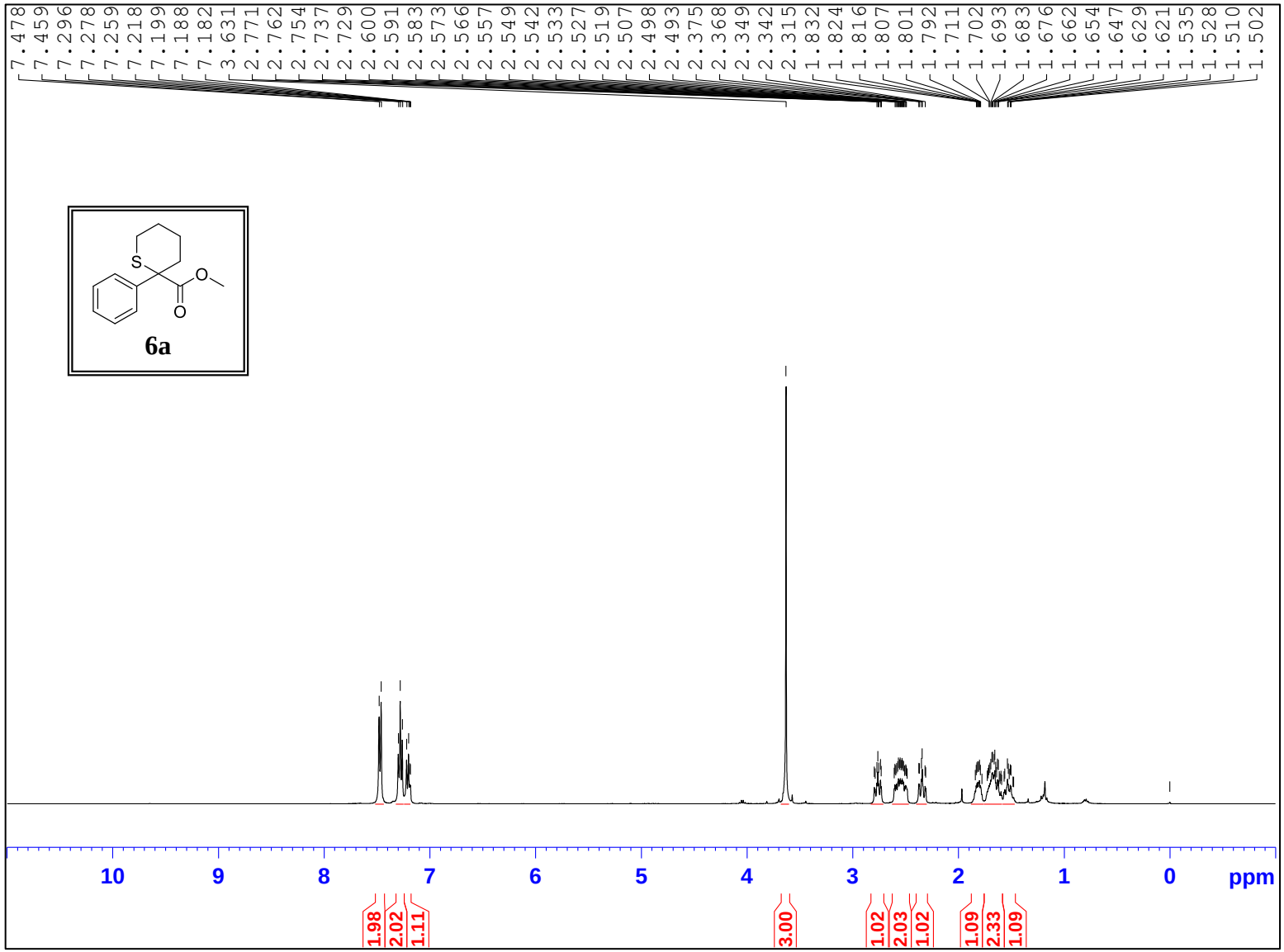
[^{1}H, ^{1}H] SELNOGP (1D NOE) for compound **4u$_2$** (400 MHz, $CDCl_3$)



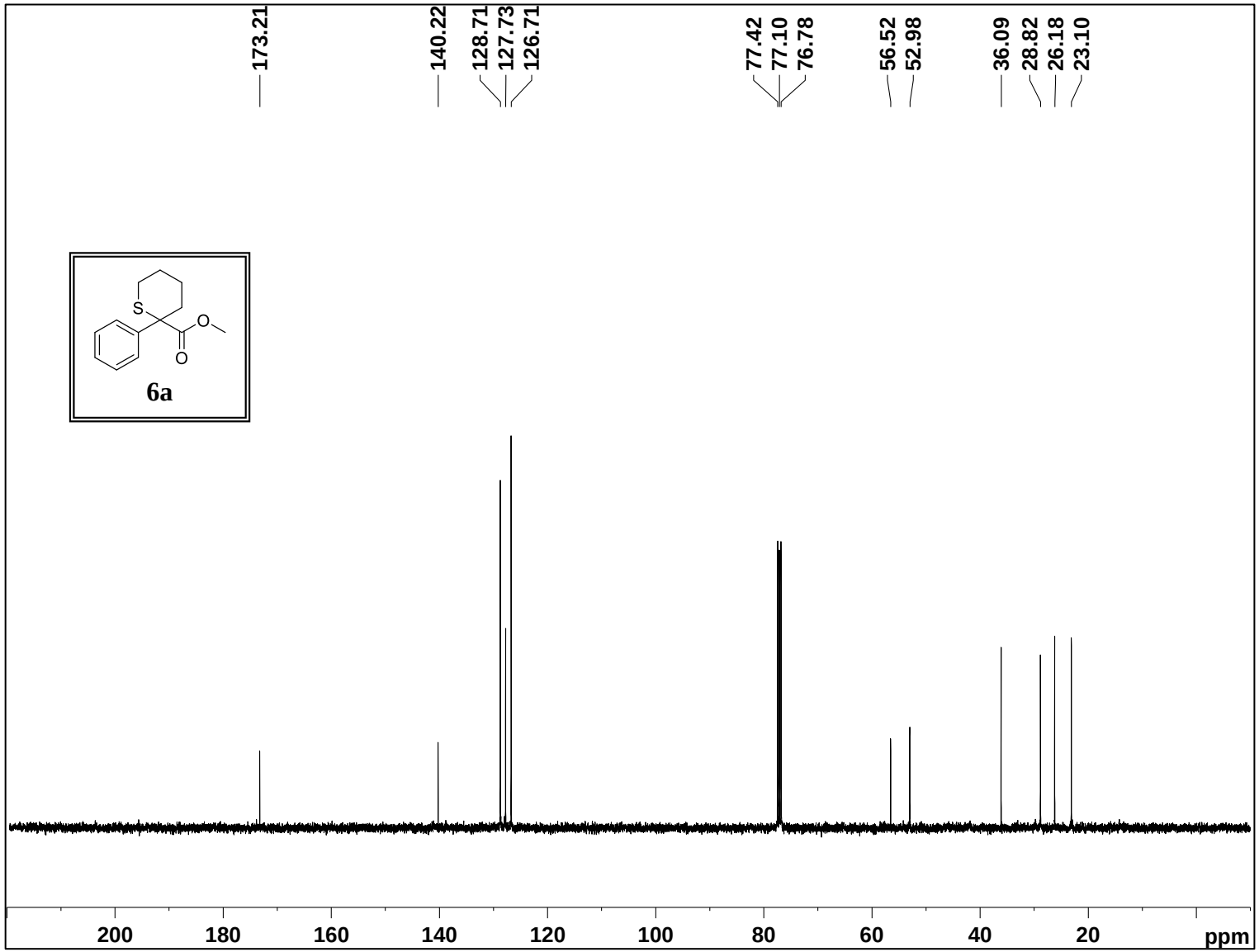
$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **4u₂** (101 MHz, $CDCl_3$)



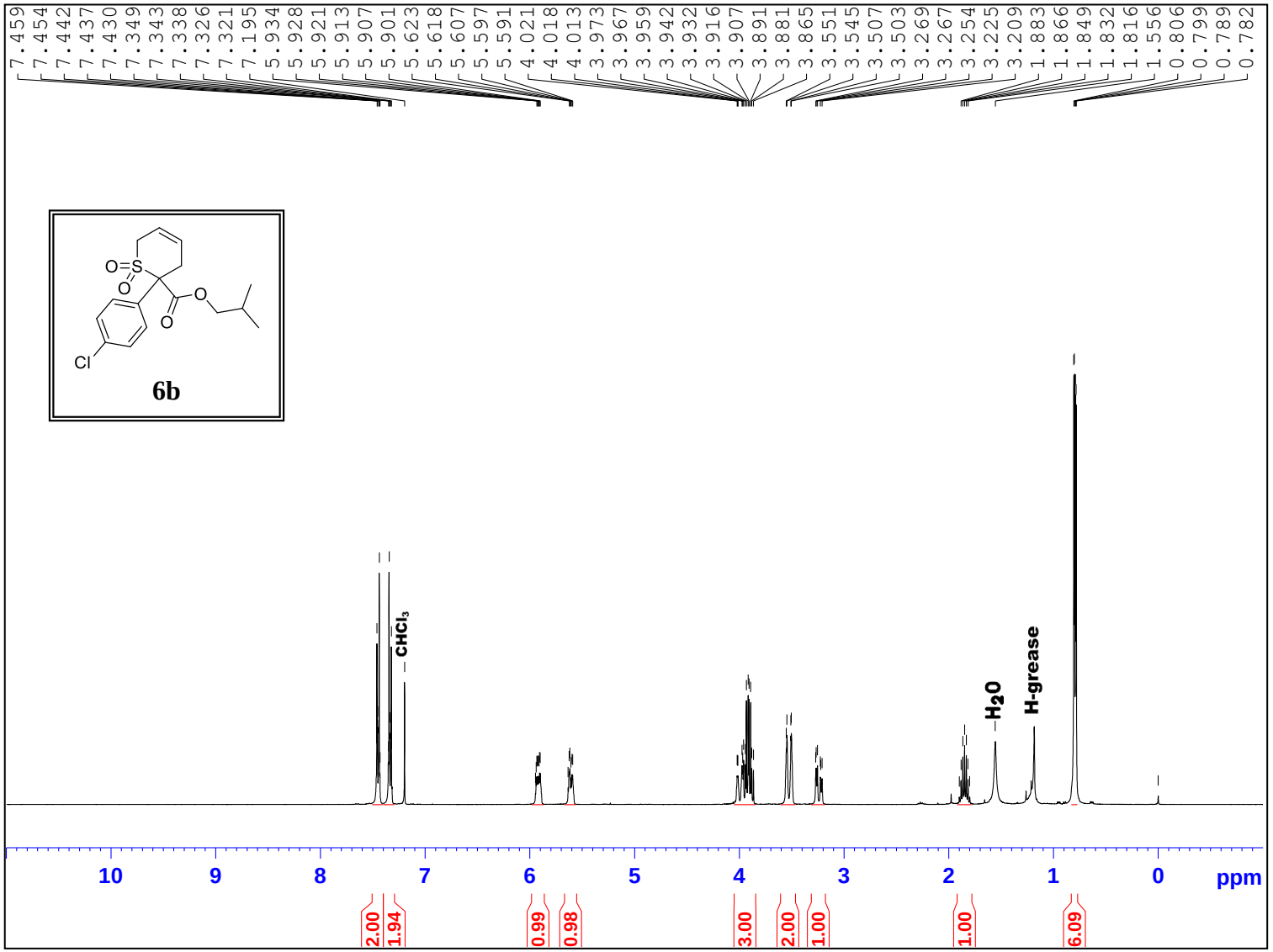
^{1}H NMR for compound **6a** (400 MHz, $CDCl_3$) (**data**)



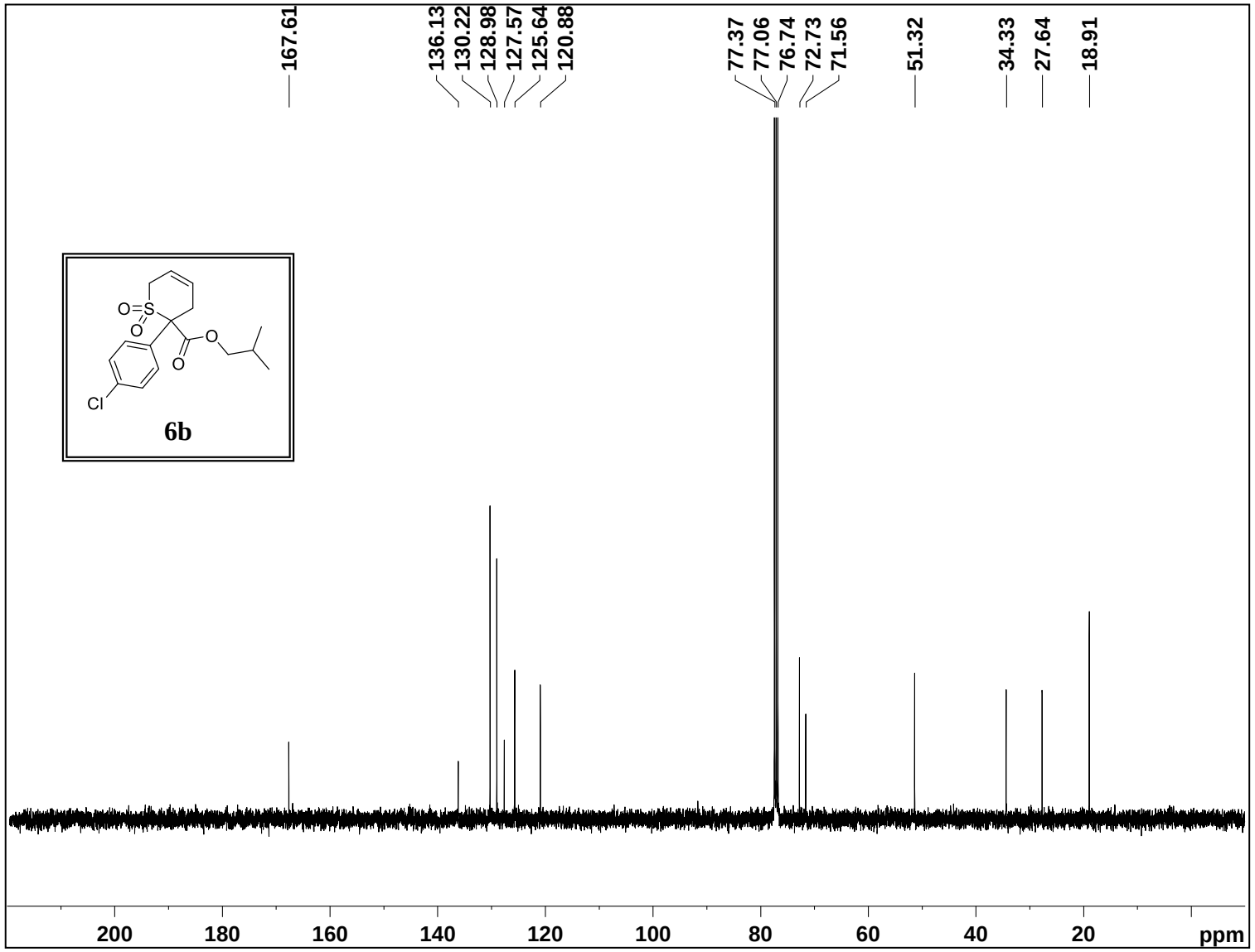
$^{13}C\{^{1}H\}$ NMR for compound **6a** (101 MHz, $CDCl_3$)



^{1}H NMR for compound **6b** (400 MHz, $CDCl_3$) (**data**)



$^{13}C\{^{1}H\}$ NMR for compound **6b** (101 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ DEPT-135 NMR for compound **6b** (101 MHz, $CDCl_3$)