Supporting Information

Photocatalytic C(sp^3)-H Thiolation by a Double S_H2 Strategy Using Thiosulfonates

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I. General Remarks

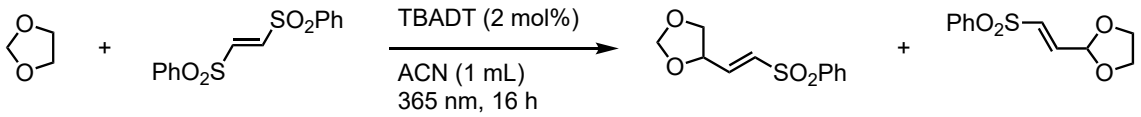
^{1}H NMR spectra were recorded using α-400 or ECZ500 (JEOL) spectrometer using CD_3CN as the solvent that is referenced at 0.00 ppm for tetramethylsilane. Chemical shifts are reported in parts per million (ppm). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; and, m, multiplet. GC analysis was performed on a Shimadzu GC-2014 instrument equipped with an FID detector using a J&W Scientific DB-1 column under the following conditions: initial oven temperature was held at 50 ºC for 5 min; and, the first ramp was 10 ºC/min to 250 ºC, which was held for 5 min. UV-visible absorption spectra were measured by V-630 Spectrometer (JASCO). The detector for the measurement of optical density was the UV power meter C9563_H9958-01 purchased from Hamamatsu Photonics. Cyclohexane, cyclopentane, cycloheptane, acetonitrile, sodium tungstate, and tetrabutylammonium bromide were purchased from Nacalai Tesque. Phenylthiobenzensulfonate **2a** was purchased from Aldrich. Tetrakis(tetrabutykammonium) decatunsgtate (TBADT) was prepared according to the reported procedure.[1] The blacklight (15W) was purchased from Toshiba. The photo flow system consisting of UV-LED (MiChS UV-LED-s equipped with Kyocera G5A (365 nm, 60-480 W)), a photo flow reactor (PFA tube: inner diameter = 1 mm, outer diameter = 1.56 mm, length = 3.82 m, total volume 3 mL), and a T-shape mixer MiChS α400 was provided from MiChS Inc: http://www.michs.jp.

II. Experimental Procedures

General Procedure for C(sp^3)–H Thiolation

To a 15 mL glass tube, cyclohexane **1.1** (5 mmol, 420 mg), phenylthiobenzensulfonate **2.1** (0.5 mmol, 125 mg) and TBADT (0.01 mmol, 33 mg) were added along with a solvent (CH_3CN, 1.0 mL). The mixture was stirred at room temperature and irradiated either by a blacklight (352 nm, 15 W) or UV-LED (365 nm, 480 W). After the reaction, ethyl acetate was added to the reaction mixture and filtered to remove the precipitated TBADT. An aliquot of the solution then was applied to GC analysis. Afterwards, the solution was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 95/5) to afford **3.1** (75 mg, 78% yield).

C(sp^3)–H Alkenylation of 3.21 Using 4.



3.21 **4** **5** **5'**

A magnetic stirring bar, 1,2-bis(phenylsulfonyl)ethylene (**4**) (0.25 mmol, 77 mg), 1,3-dioxolane (1.25 mmol, 93 mg), TBADT (2 mol%, 16.1 mg), MeCN (1.0 mL) were added in a 10 mL Pyrex tube. The tube was capped and irradiated by photoreactor 3.4 W, 365 nm for 16 h. Afterwards, the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 99/1) to afford the compound **5** (12 mg, 20% yield) and **5'** (9 mg, 15% yield) respectively.

Procedure for Scalable Synthesis of 3.1

To a 50 mL glass flask, cyclohexane **1.1** (25 mmol, 2.104 g), phenylthiobenzensulfonate **2.1** (5 mmol, 1.25 mg) and TBADT (0.1 mmol, 332 mg) were added along with a solvent (CH_3CN, 10 mL). The mixture was stirred at room temperature and irradiated by a UV-LED (365 nm, 480 W) for 1 h. After the reaction, ethyl acetate was added to the reaction mixture and filtered to remove the precipitated TBADT. Afterwards, the solution was

extracted with ethyl acetate (3 x 30 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 95/5) to afford **3.1** (685 mg, 71% yield).

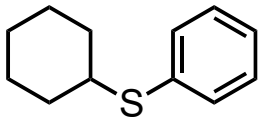
Procedure of Flow Photoreaction of 2.1

The flow-thiolation reaction was carried out using a photo flow reactor (tube reactor, PFA tube (inner diameter = 1 mm, outer diameter = 1.56 mm, length = 3.82 m, total volume 3 mL), and high power UV-LED (365 nm, 480 W). An acetonitrile solution containing **2.1** (0.5 M) and TBADT (2 mol%) was mixed to prepare the solution, which was placed in a syringe (SGE syringe, Trajan Scientific). Neat cyclohexane **1.1** was also placed in another syringe. These solutions were pumped by PHD ULTRA (Harvard Apparatus) at the rate of 0.075 mL/min (**2.1** solution) and 0.025 mL/min (cyclohexane) respectively and mixed using a MiChS α400 mixer (T-shape mixer with 400 μm inner diameter and introduced into a tubular photo flow reactor fitted with a back pressure regulator (5 psi). The distance was 4 cm between the light source and the reactor. Under photoirradiation using UV-LED-s (365 nm, 480 W), the reaction was carried out with a residence time of 30 min. The reaction solution was collected over 30 min, The reaction solution was poured into the mixture of ethyl acetate and sodium hydrogen carbonate solution and the organic layer was recovered. The aqueous layer was extracted twice with ethyl acetate. The organic extracts were combined and concentrated. The resulting material was chromatographed on a silica gel successively using a 100:1 hexane–ethyl acetate mixture, 10:1 hexane–ethyl acetate mixture as eluents to afford **3.1** (154 mg, 71% yield).

III. Characterization Data of Thiolation Products

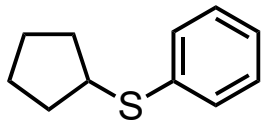
Known compounds are identified by comparison of the NMR data with those of the reported data, whose references are given.

Cyclohexyl phenyl sulfide (3.1)[2]



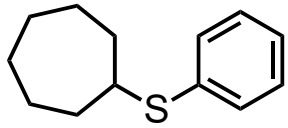
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21–1.41 (m, 5H), 1.59–1.62 (m, 2H), 1.74–1.78 (m, 2H), 1.96–1.99 (m, 1H), 3.07–3.13 (m, 1H), 7.19–7.29 (m, 3H), 7.38–7.40 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 25.7, 26.0, 33.3, 46.5, 126.5, 128.7, 131.8, 135.1.

Cyclopentyl phenyl sulfide (3.2)[3]



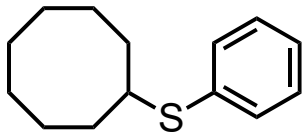
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60–1.78 (m, 6H), 2.04–2.06 (m, 2H), 3.58–3.61 (m, 2H), 7.15–7.49 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 28.2, 34.6, 48.0, 126.3, 128.8, 131.2, 136.2.

Cycloheptyl phenyl sulfide (3.3)[4]



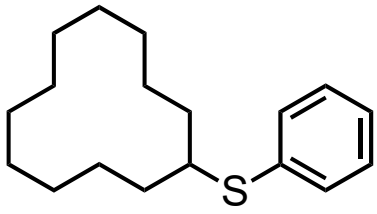
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44–1.63 (m, 10H), 1.69–1.76 (m, 2H), 1.99–2.05 (m, 2H), 3.31–3.36 (m, 1H), 7.17–7,21 (m, 1H), 7.25–7.29 (m, 2H), 7.35–7.37 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 28.2, 34.6, 47.9, 126.3, 128.7, 131.1, 136.2.

Cyclooctyl phenyl sulfide (3.4)[4]



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47–1.77 (m, 12H), 1.93–1.99 (m, 2H), 3.37–3.42 (m, 1H), 7.17–7.21 (m, 1H), 7.25–7.33 (m, 2H), 7.37–7.39 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 225.1, 25.8, 27.1, 32.0, 47.6, 126.3, 128.7, 131.4, 136.1.

Cyclododecyl phenyl sulfide (3.5)[4]

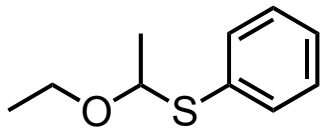


^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (m, 16H), 1.51–1.61 (m, 4H), 1.68–1.73 (m, 2H), 3.26–3.28 (m, 1H), 7.18–7.21 (m, 1H), 7.26–7.30 (m, 2H), 7.36–7.38 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 23.5, 23.9, 24.2, 29.9, 44.8, 126.4, 128.8, 131.3, 136.1.

***p*-Chlorobenzyl phenyl sulfide (3.6)[5]**

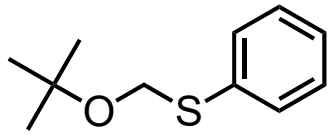
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (s, 2H), 6.89–6.90 (m, 2H), 7.26–7.33 (m, 5H), 7.47–7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.4, 117.5, 127.0, 127.4, 129.4, 130.7, 134.7, 155.2.

1-Ethoxy-1-(phenylthio)ethane (3.7)[6]



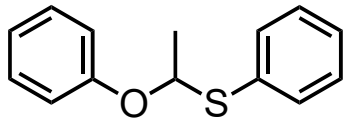
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.0 Hz, 3H), 1.51 (t, J = 7.0 Hz, 3H), 3.49 (dq, J = 9.0, 7.0 Hz, 1H), 3.95 (dq, J = 9.0, 7.0 Hz, 1H), 4.89 (q, J = 7.0 Hz, 1H), 7.27–7.31 (m, 2H), 7.46–7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 22.7, 63.3, 84.5, 127.5, 128.7, 132.9, 133.8.

tert-Butyl phenylthiomethyl ether (3.8)[7]



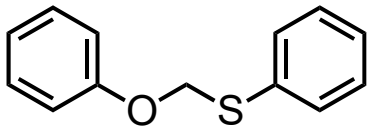
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 9H), 4.90 (s, 2H), 7.18–7.30 (m, 3H), 7.47–7.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 68.2, 75.3, 126.4, 128.7, 129.9, 136.6.

Phenyl 1-(phenylthio)ethyl ether (3.9)[8]



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.66 (d, J = 6.5 Hz, 3H), 5.64 (q, J = 6.5 Hz, 1H), 6.98–7.03 (m, 3H), 7.28–7.32 (m, 5H), 7.45–7.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 81.1, 116.9, 1219, 128.1, 128.7, 129.4, 131.5, 134.5, 156.6.

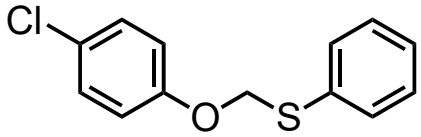
Phenyl phenylthiomethyl ether (3.10)[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 2H), 6.96–7.04 (m, 3H), 7.24–7.33 (m, 5H), 7.49–7.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.1, 116.1, 122.0, 127.2, 129.0, 129.5,

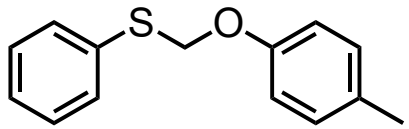
130.6, 135.2, 136.7.

_p_-Chlorophenyl phenylthiomethyl ether (3.11)[10]



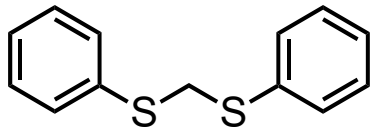
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (s, 2H), 6.89–6.90 (m, 2H), 7.26–7.33 (m, 5H), 7.47–7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.4, 117.5, 127.0, 127.4, 129.1, 129.4, 130.7, 134.7, 155.2.

_p_-Methoxybenzyl phenylsulfide (3.12)



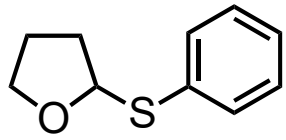
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 5.45 (s, 2H), 6.87–6.88 (m, 2H), 7.11 (*d*, *J* = 8.0 Hz, 2H), 7.25–7.32 (m, 4H), 7.49–7.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 73.4, 116.1, 127.1, 129.0, 130.0, 130.5, 131.5, 135.3, 154.5.
HRMS (ESI^+) m/z Calcd for $C_{14}H_{14}OSNa$ ($M + Na^+$): 253.0658. Found: 253.0656.

Diphenylthiomethane (3.13)[10]



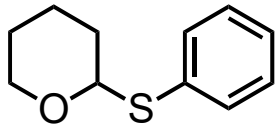
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (s, 2H), 7.23–7.27 (m, 2H), 7.30–7.33 (m, 4H), 7.41–7.44 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.5, 127.1, 129.0, 130.7, 134.9

2-(Phenylthio)tetrahydrofuran (3.14)[6]



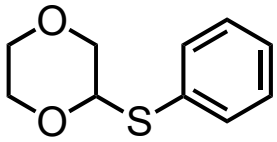
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85–2.02 (m, 3H), 2.33–2.37 (m, 1H), 3.94–4.05 (m, 2H), 5.65 (dd, J = 4.0, 7.5 Hz, 1H), 7.20–7.30 (m, 3H), 7.49–7.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.8, 32.6, 67.2, 87.1, 126.7, 128.7, 131.0, 135.6.

2-(Phenylthio)tetrahydropyran (3.15)[6]



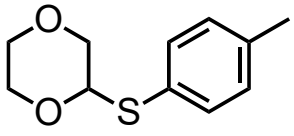
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69 (s, 3H), 1.58–1.67 (m, 3H), 1.80–1.89 (m, 2H), 2.00–2.06 (m, 1H), 3.56–3.63 (m, 1H), 4.15–4.19 (m, 1H), 5.21 (dd, J = 6.0, 4.0 Hz, 1H), 7.19–7.30 (m, 3H), 7.40–7.48 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 25.5, 31.5, 64.5, 85.2, 126.7, 128.7, 130.8, 135.4.

3-Phenylthio-1,4-dioxacyclohexane (3.16)[6]



^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65–3.74 (m, 4H), 3.98 (dd, J = 11.8, 3.0 Hz, 1H), 4.23 (td, J = 10.5, 6.8 Hz, 1H), 5.11 (dd, J = 6.0, 3.5 Hz, 1H),7.24–7.32 (m, 3H), 7.48–7.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.7, 66.4, 69.9, 83.2, 127.3, 128.9, 131.5, 133.9.

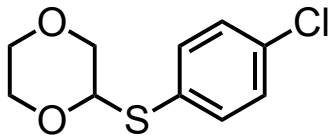
2-(4-Methylphenyl)thio-1,4-dioxacyclohexane (3.17)[6]



^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.64–3.71 (m, 4H), 3.96 (dd, J = 3.0, 11.8

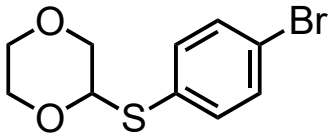
Hz, 1H), 4.18–4.22 (m, 1H), 5.03 (dd, J = 3.5, 5.8 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 63.9, 66.4, 83.4, 129.7, 129.8, 132.3, 137.6.

2-(4-Chlorophenyl)thio-1,4-dioxacyclohexane (3.18)[6]



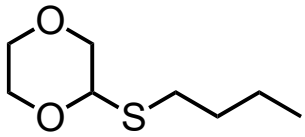
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65–3.74 (m, 4H), 3.98 (dd, J = 3.5, 11.5 Hz, 1H), 4.24 (td, J = 4.5, 11.5 Hz, 1H), 5.09 (dd, J = 3.0, 5.2 Hz, 1H), 7.26–7.29 (m, 2H), 7.42–7.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.5, 66.5, 69.8, 83.2, 129.1, 132.4, 132.9, 133.5

2-(4-Bromophenyl)thio-1,4-dioxacyclohexane (3.19)[11]



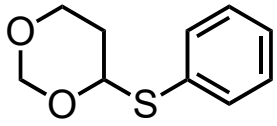
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65–3.74 (m, 4H), 3.98 (dd, J = 3.0, 11.5 Hz, 1H), 4.18 (td, J = 4.5, 11.5 Hz, 1H), 5.10 (dd, J = 3.0, 6.0 Hz, 1H), 7.35–7.38 (m, 2H), 7.41–7.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.4, 66.5, 70.0, 83.1, 121.5, 132.0, 133.0, 133.2.

2-Butylthio-1,4-dioxacyclohexane (3.20)



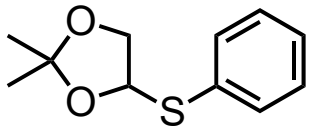
^{1}H NMR (500 MHz, $CDCl_3$) δ. 0.92 (t, J = 7.5 Hz, 3H), 1.38–1.45 (m, 2H), 1.58–1.64 (m, 2H), 2.61–2.73 (m, 2H), 3.57 (dd, J = 9.2, 11.5 Hz, 1H), 3.63–3.73 (m, 3H), 3.89 (dd, J =3.0, 11.5 Hz, 1H), 4.06–4.10 (m, 1H), 4.79 (dd, J = 2.4, 3.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 21.9, 30.1, 32.2, 64.4, 66.4, 69.9, 86.4.
HRMS (ESI$^+$) m/z Calcd for $C_8H_{16}O_2SNa$ ($M + Na^+$): 199.0763. Found: 199.0759.

4-Phenylthio-1,3-dioxacyclohexane (3.21)



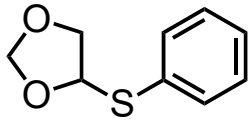
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93–1.99 (m, 1H), 2.15–2.21 (m, 1H), 3.82–3.87 (m, 1H), 4.07–4.11 (m, 1H), 4.77 (2 s, 1H), 5.30–5.33 (m, 2H), 7.24–7.32 (m, 3H), 7.48–7.50 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 65.1, 83.1, 90.4, 127.4, 128.9, 131.5, 133.8. HRMS (ESI$^+$) m/z Calcd for $C_{10}H_{12}O_2SNa$ (M + Na^+): 219.0450. Found: 219.0477.

2,2-Dimethyl-4-phenylthio-1,3-dioxacyclopentane (3.22)[12]



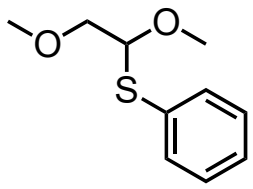
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 3H), 1.51 (s, 3H), 3.95 (dd, J = 9.5, 6.0 Hz, 1H), 4.34 (dd, J = 9.5, 6.0 Hz, 1H), 5.55 (dd, J = 6.0, 6.0 Hz, 1H), 7.25–7.33 (m, 3H), 7.50–7.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 26.2, 69.4, 83.6, 111.4, 127.3, 128.9, 131.7, 134.1.

4-Phenylthio-1,3-dioxacyclopentane (3.23)



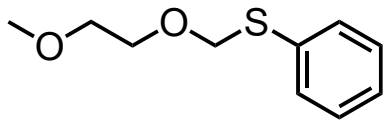
^{1}H NMR (500 MHz, $CDCl_3$) δ 3,74 (dd, J = 9.0, 5.0 Hz, 1H), 4.32 (dd, J = 9.0, 8.0 Hz, 1H), 5.05 (s, 1H), 5.14 (s, 1H), 5.63 (dd, J = 8.0, 5.0 Hz, 1H), 7.26–7.35 (m, 3H), 7.53–7.55 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 69.5, 83.6, 94.0, 127.6, 129.0, 131.6, 133.9. HRMS (ESI$^+$) m/z Calcd for $C_9H_{10}O_2SNa$ (M + Na^+): 205.0294. Found: 205.0243.

1,2-Dimethoxy-1-phenylthioethane (3.24)[6]



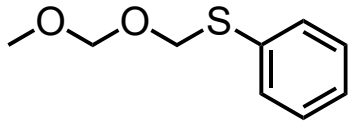
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.52 (dd, J = 7.5, 11 Hz, 1H), 3.57 (s, 3H), 3.60 (dd, J = 4.0, 11 Hz, 1H), 4.75 (dd, J = 3.6, 6.0 Hz, 1H), 7.30–7.32 (m, 3H), 7.49–7.50 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 56.4, 59.1, 74.7, 88.8, 127.9, 128.8, 132.2, 133.9.

1-Methoxy-2-phenylthiomethoxyethane (3.24')[6]



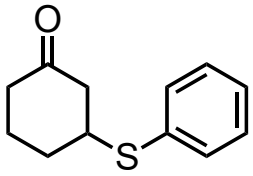
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (s, 3H), 3.57–3.59 (m, 2H), 3.78–3.79 (m, 2H), 5.07 (s, 2H), 7.26–7.30 (m, 3H), 7.47–7.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 59.0, 67.4, 71.5, 76.5, 126.6, 128.9, 130.1, 135.9.

1-Methoxy-1-phenylthiomethoxymethane (3.25)



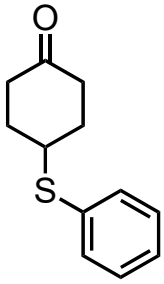
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (s, 3H), 4.82 (s, 2H), 5.06 (s, 2H), 7.21–7.31 (m, 3H), 7.47–7.48 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 55.8, 70.8, 93.0, 126.7, 128.9, 129.8, 135.6.
HRMS (ESI$^+$) m/z Calcd for $C_9H_{12}O_2SNa$ (M + Na^+): 207.0450. Found: 207.0455.

3-Phenylthiocyclohexanone (3.26)[13]



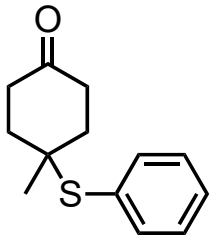
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69–1.76 (m, 2H), 2.12–2.19 (m, 2H), 2.30–2.41 (m, 2H), 2.67–2.71 (m, 2H), 3.40–3.45 (m, 1H), 7.27–7.34 (m, 3H), 7.41–7.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0, 31.2, 40.9, 46.1, 47.8, 127.8, 129.1, 133.0, 133.2, 209.8.

4-Phenylthiocyclohexanone (3.26')[14]



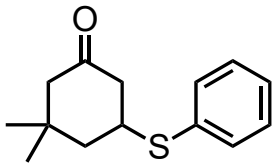
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90–1.97 (m, 2H), 2.20–2.26 (m, 2H), 2.31–2.37 (m, 2H), 2.56–2.61 (m, 2H), 3.53–3.57 (m, 1H), 7.27–7.35 (m, 3H), 7.45–7.48 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 32.0, 39.4, 44.1, 127.5, 129.1, 132.7, 133.9, 210.2.

4-Methyl-4-phenylthiocyclohexanone (3.27)



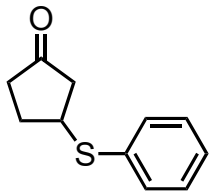
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.81–1.87 (m, 2H), 1.99–2.04 (m, 2H), 2.29–2.34 (m, 2H), 2.79–2.86 (m, 2H), 7.34–7.42 (m, 3H), 7.53–7.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.1, 37.7, 38.0, 48.5, 128.8, 129.2, 130.9, 137.4, 211.1.
HRMS (ESI$^+$) m/z Calcd for $C_{13}H_{16}OSNa$ (M + Na^+): 243.0814. Found: 243.0782.

3,3-Dimethyl-5-phenylthiocyclohexanone (3.28)[15]



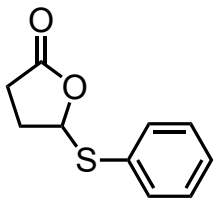
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.09 (s, 3H), 1.67 (t, J = 12.5 Hz, 1H), 1.93–1.97 (m, 1H), 2.09, 2.12 (2 t, J = 2.5 Hz, 1H), 2.19–2.29 (m, 2H), 2.62–2.66 (m, 1H), 3.43 (tt, J = 4.0, 12.5 Hz, 1H), 7.27–7.34 (m, 3H), 7.41–7.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.6, 31.7, 36.2, 42.4, 45.0, 47.6, 54.0, 127.8, 129.1, 132.8, 133.1, 209.0.

3-Phenylthiocyclopentane (3.29)[16]



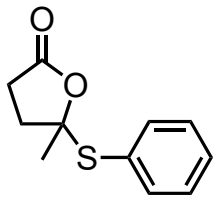
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99–2.06 (m, 1H), 2.19–2.38 (m, 3H), 2.45–2.52 (m, 1H), 2.61 (dd, J = 19.0, 7.0 Hz, 1H), 3.87–3.92 (m, 1H), 7.25–7.34 (m, 3H), 7.39–7.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.3, 36.7, 43.4, 45.2, 127.4, 129.1, 132.0, 134.2, 216.4.

γ-Phenylthio-γ-butyrolactone (3.30)[17]



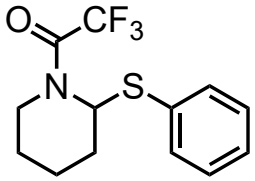
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21–2.28 (m, 1H), 2.52 (td, J = 8.0, 2.0 Hz, 2H), 2.64–2.70 (m, 1H), 5.82 (dd, J = 8.0, 6.0 Hz, 1H), 7.33–7.36 (m, 3H), 7.54–7.56 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 28.5, 86.5, 128.5, 129.2, 131.8, 132.9, 175.8.

5-Methyl-5-phenylthio-dihydrofuran-2(3H)-one (3.31)



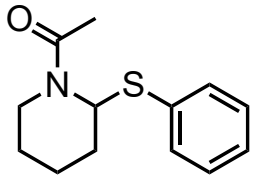
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 3H), 2.32–2.55 (m, 4H), 7.37–7.41 (m, 3H), 7.58–7.60 (m, 2H).m^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 29.5, 35.5, 94.0, 129.1, 129.5, 129.9, 136.4, 175.7.
HRMS (ESI$^+$) m/z Calcd for $C_{11}H_{12}O_2SNa$ (M + Na^+): 231.0450. Found: 231.0451.

***N*-Trifluoroacetyl-2-phenylthiopiperidine (3.32)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47–1.59 (m, 1H), 1.73-2.10 (m, 5H), 3.76 (m, 1H) 3.84 (td, J = 2.4, 10.4 Hz, 1H), 6.24–6.25 (m, 1H), 7.28–7.37 (m, 3H), 7.43–7.48 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 25.9, 30.1, 38.7, 40.9, 60.6, 128.6, 129.0, 133.9, 135.6, 155.3.
HRMS (ESI$^+$) m/z Calcd for $C_{13}H_{14}F_3NOSNa$ (M + Na^+): 312.0640. Found: 312.0598.

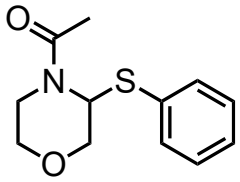
***N*-Acetyl-2-phenylthiopiperidine (3.33)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 1.95 (2 s, 3H), 1.68–2.15 (m, 6H), 3.24 3.64 (2 td, J = 13.0, 3.0 Hz, 1H), 3.53–3.56 4.52–4.55 (2 m, 1H), 5.35 6.46 (2 s, 1H), 7.22–7.38 (m,

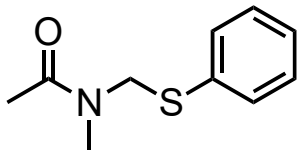
2H), 7.46–7.48 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 19.8, 20.4, 21.7, 25.2, 26.0, 30.1, 31.4, 36.1, 41.8, 58.4, 66.4, 127.4, 128.7, 129.1, 132.5, 133.3, 135.9, 168.9, 169.3. HRMS (ESI$^+$) m/z Calcd for $C_{13}H_{17}NOSNa$ (M + Na^+): 258.0923. Found: 258.0896.

4-Acetyl-3-phenylthiomorpholine (3.34)



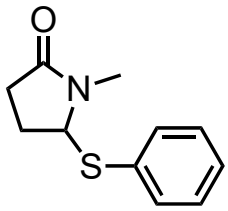
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47, 1.98 (2 s, 3H), 3.43–3.58 (m, 2H), 3.71–3.80 (m, 1H), 3.90–4.33 (m, 3H), 5.09, 6.11 (2 s, 1H), 7.27–7.44 (m, 3H), 7.51–7.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.7, 21.2, 36.5, 42.0, 58.4, 65.6, 66.6, 67.1, 69.8, 70.0, 128.0, 128.9, 129.6, 131.9, 132.7, 133.6, 136.0, 168.8, 169.3.

***N*-Methyl-*N*-phenylthiomethylacetamide (3.35)[18]**



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65, 2.03 (2 s, 3H), 2.97, 2.99 (2 s, 3H), 4.65 (s, 1H), 4.89 (s, 1H), 7.23–7.36 (m, 3H), 7.46–7.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 21.8, 32.8, 35.1, 51.6, 57.7, 127.2, 128.9, 129.3, 131.5, 132.3, 133.9, 134.9, 170.5, 170.6.

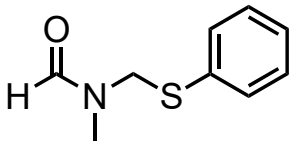
***N*-Methyl-5-phenylthio-2-pyrrolidone (3.36)[18]**



^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67–1.74 (m, 2H), 2.07–2.22 (m, 2H), 2.44–2.53 (m, 1H),

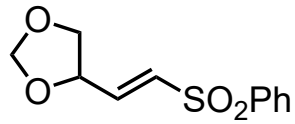
2.98 (s, 3H), 4.81 (dd, J = 2.5, 8.0 Hz, 1H), 7.33–7.46 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 28.0, 29.1, 69.6, 129.0, 129.3, 130.6, 135.2, 174.5.

_N_-Methyl-_N_-phenylthiomethylformamide (3.37)[18]



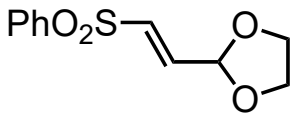
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.95 (s, 3H), 4.54, 4.81 (2 s, 2H), 7.24–7.35 (m, 3H), 7.40–7.46 (m, 2H), 7.52, 7.80 (2 s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 33.3, 48.2, 57.0, 127.3, 128.9, 129.0, 129.4, 131.2, 131.6, 133.1, 134.4, 161.5, 162.3.

(E)-4-(2-phenylsulfonyl)vinyl)-1,3-dioxolane (5)[19]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.68 – 7.61 (m, 1H), 7.59 – 7.52 (m, 2H), 6.92 (dd, J = 14.9, 4.4 Hz, 1H), 6.65 (dd, J = 14.9, 1.6 Hz, 1H), 5.04 (s, 1H), 4.95 (s, 1H), 4.66 (ddd, J = 7.1, 3.6, 2.1 Hz, 1H), 4.11 (dd, J = 8.3, 7.1 Hz, 1H), 3.68 (dd, J = 8.3, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.02, 139.84, 133.63, 131.73, 129.37, 127.78, 95.86, 73.38, 69.04.

(E)-2-(2-phenylsulfonyl)vinyl)-1,3-dioxolane (5')[19]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.73 – 7.59 (m, 1H), 7.60 – 7.48 (m, 2H), 6.81 (dd, J = 15.1, 3.5 Hz, 1H), 6.68 (dd, J = 15.1, 1.1 Hz, 1H), 5.50 (dd, J = 3.5, 1.1 Hz, 1H), 4.05 – 3.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.79, 139.60, 133.72, 133.61, 129.37, 127.94, 100.01, 65.15.

IV. References

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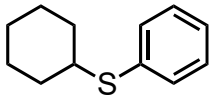
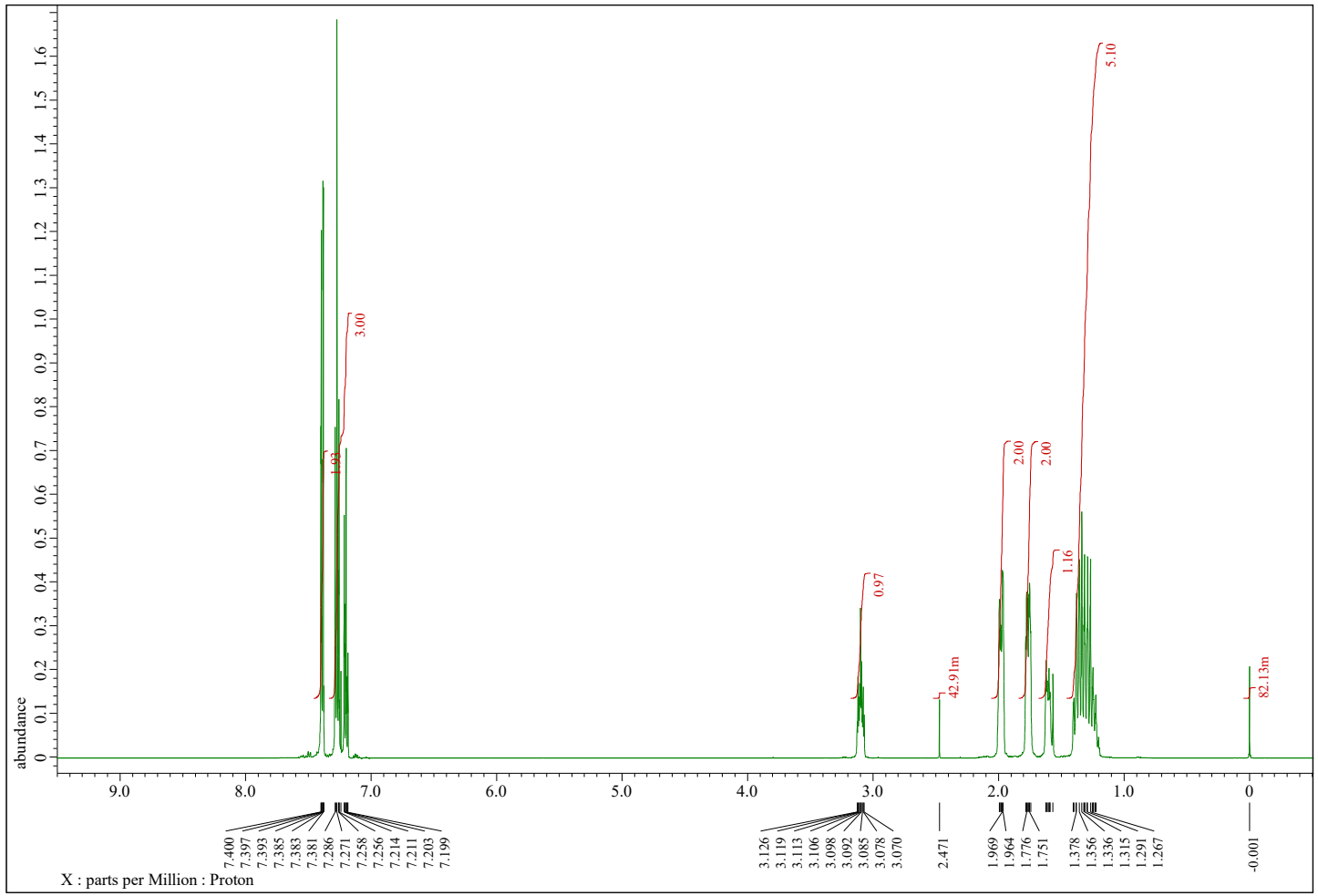
V. NMR Spectra

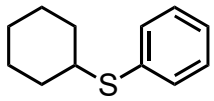
^{1}H NMR spectrum of the compound (3.1)



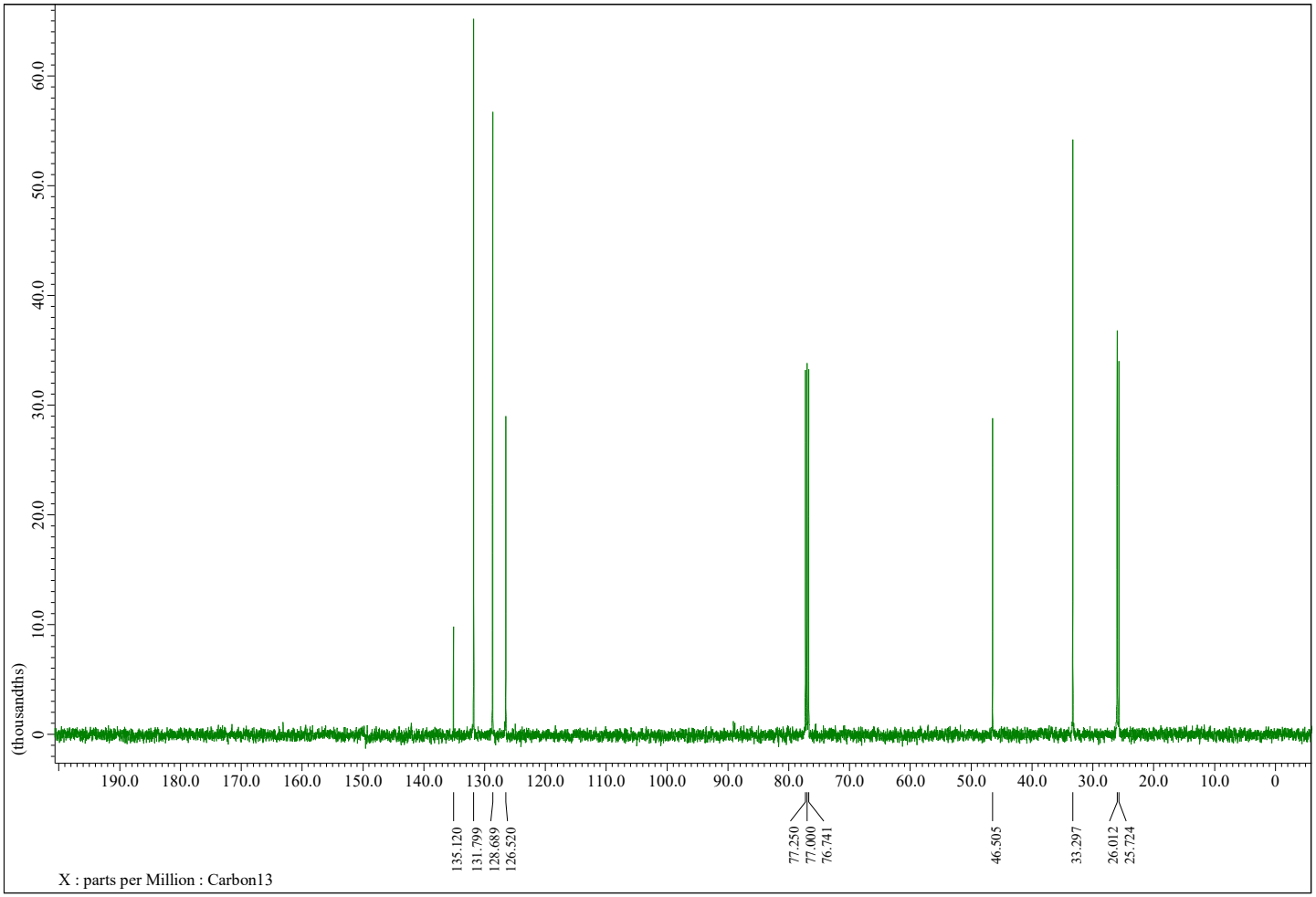
3.1



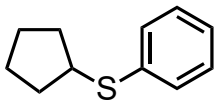
^{13}C NMR spectrum of the compound (3.1)



3.1



^{1}H NMR spectrum of the compound (3.2)



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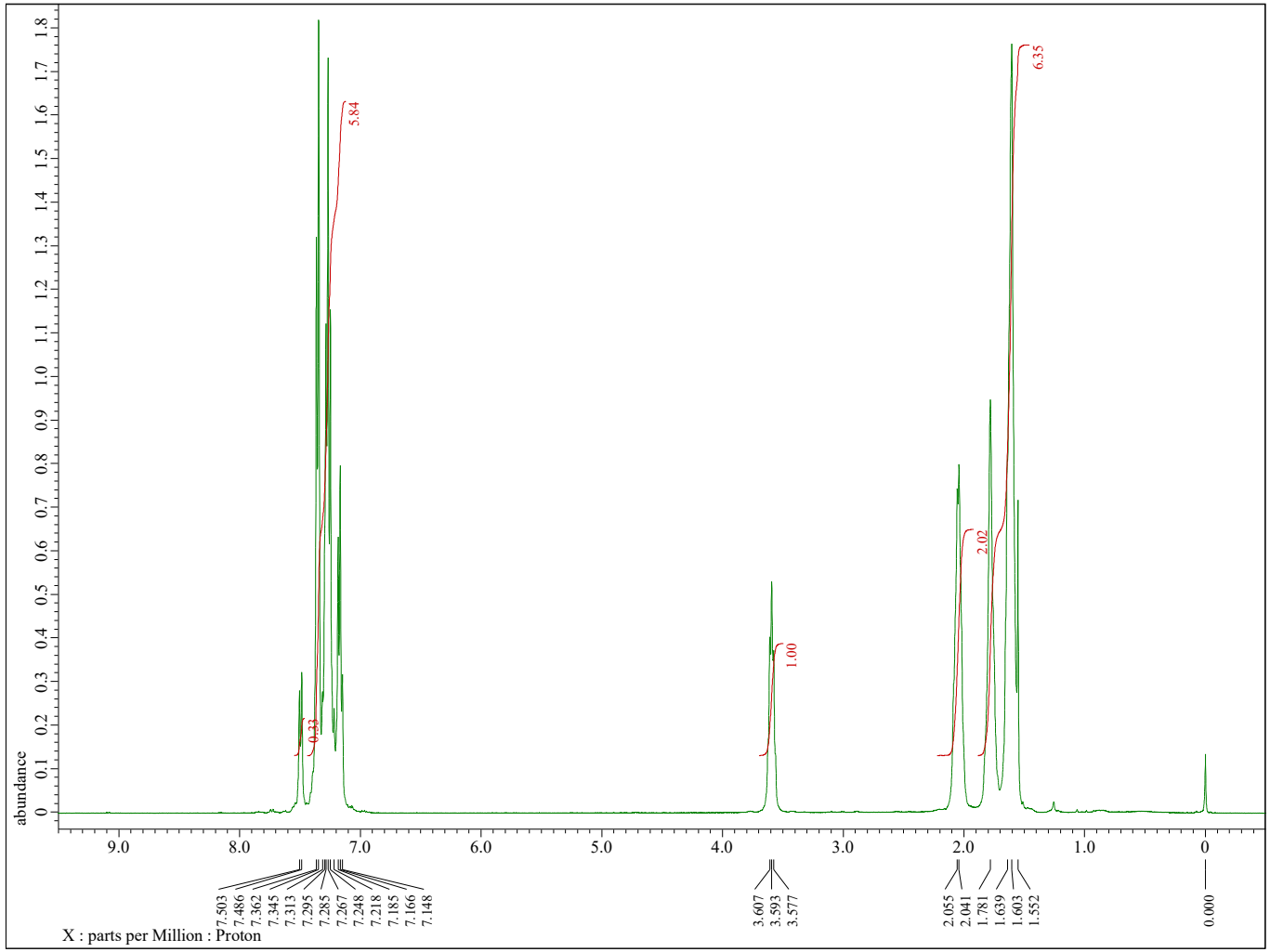
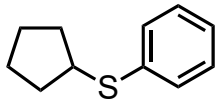
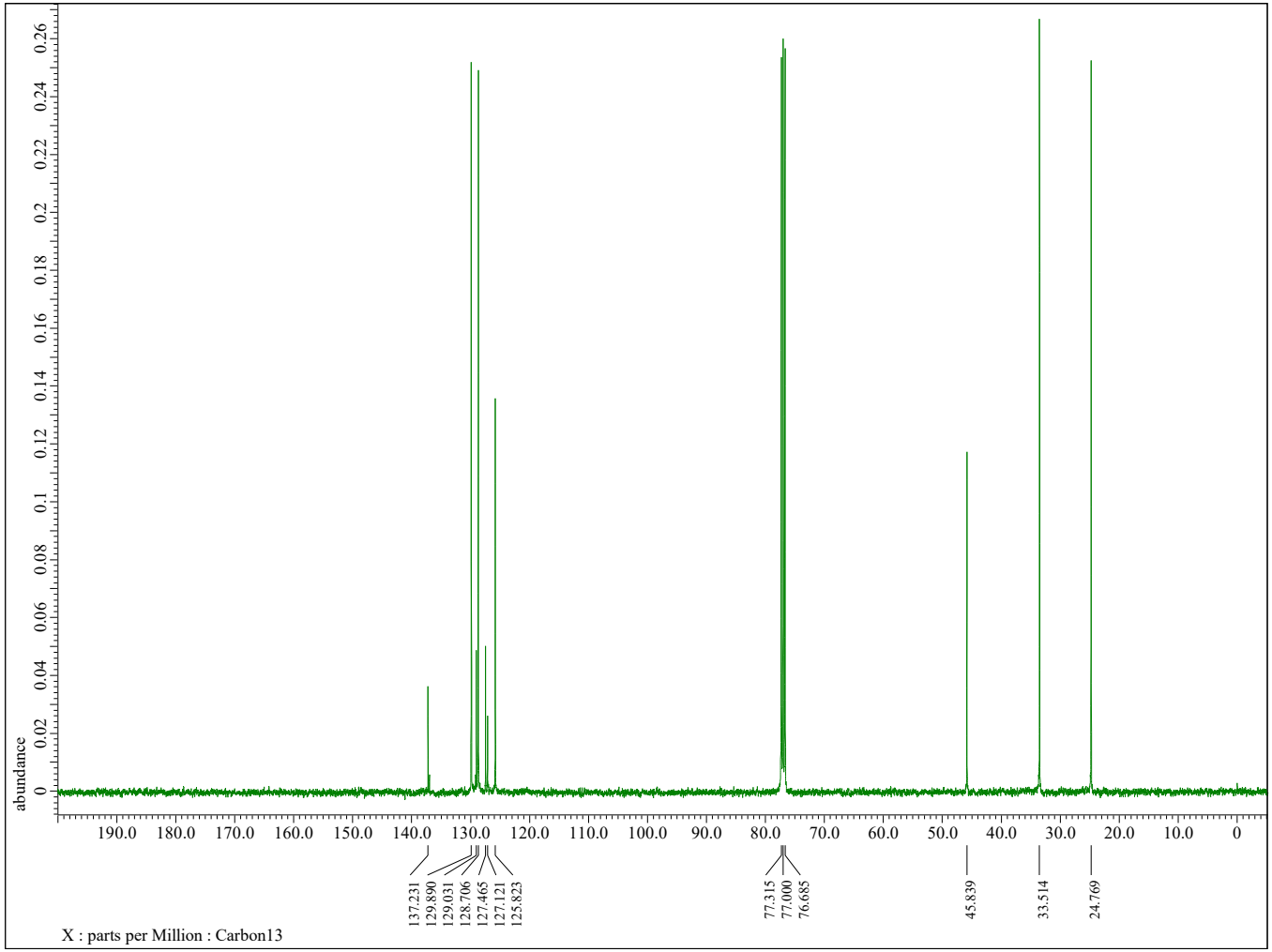


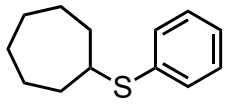
^{13}C NMR spectrum of the compound (3.2)



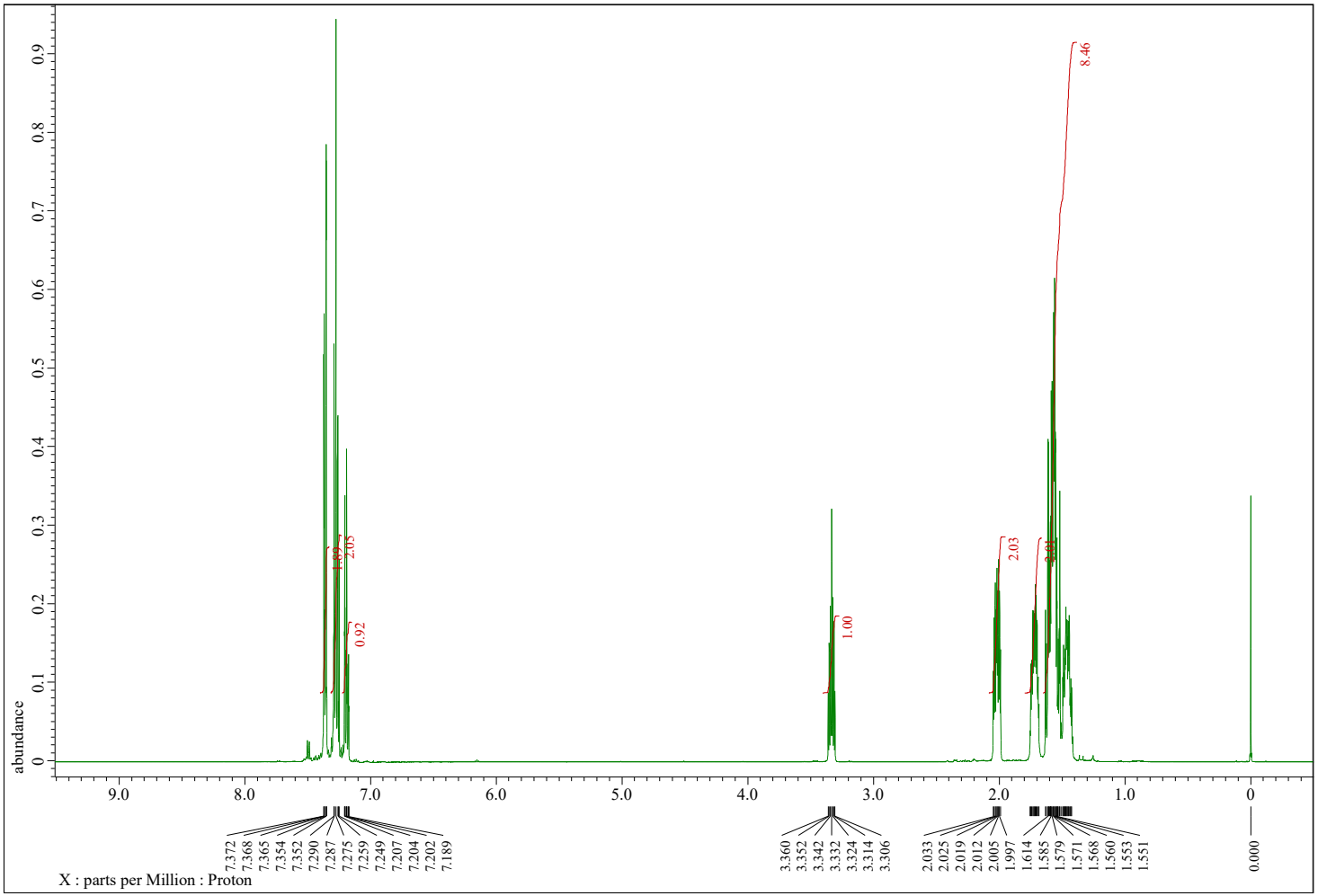
3.2



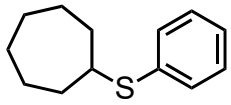
^{1}H NMR spectrum of the compound (3.3)



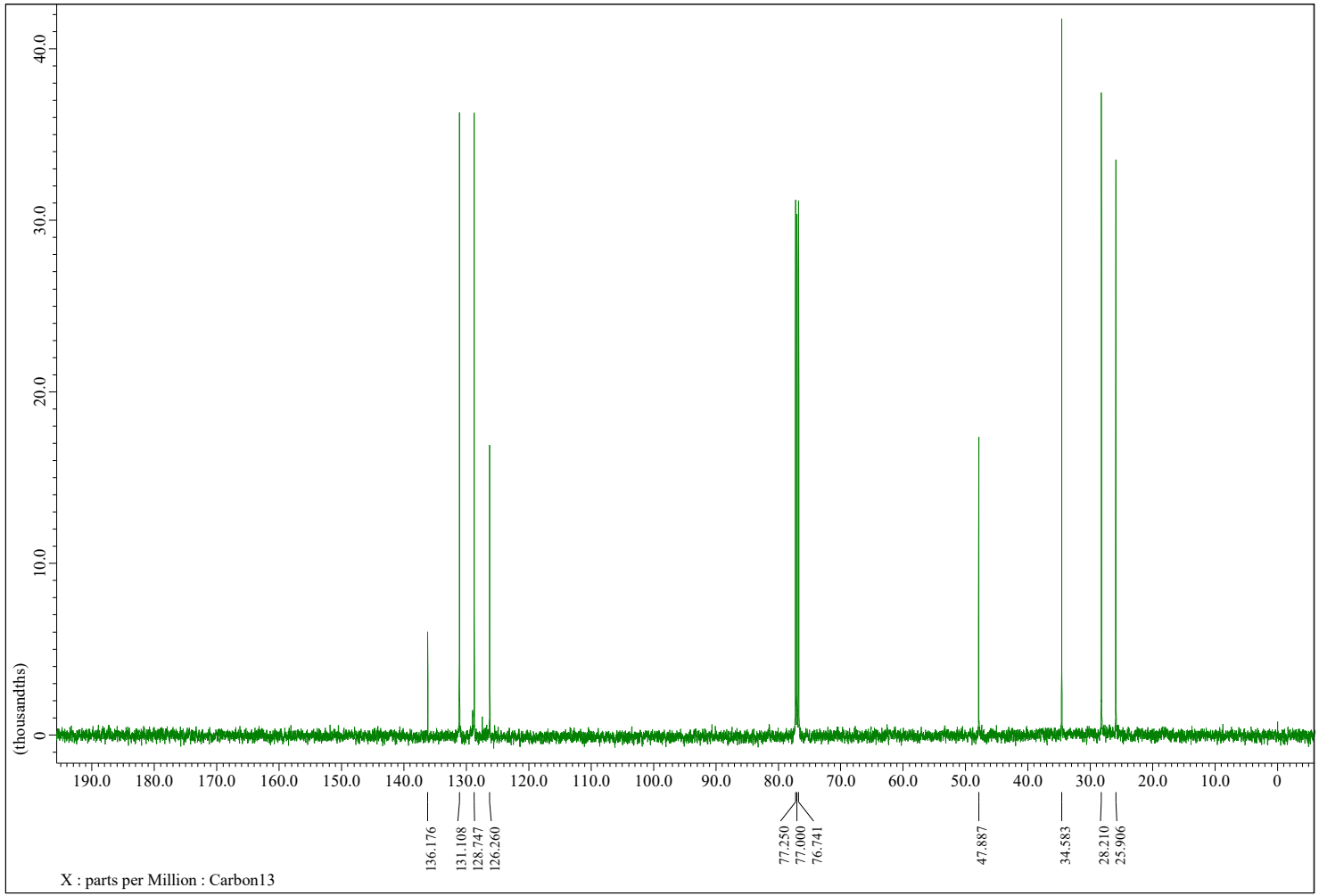
3.3



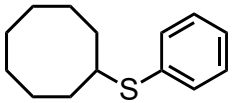
^{13}C NMR spectrum of the compound (3.3)



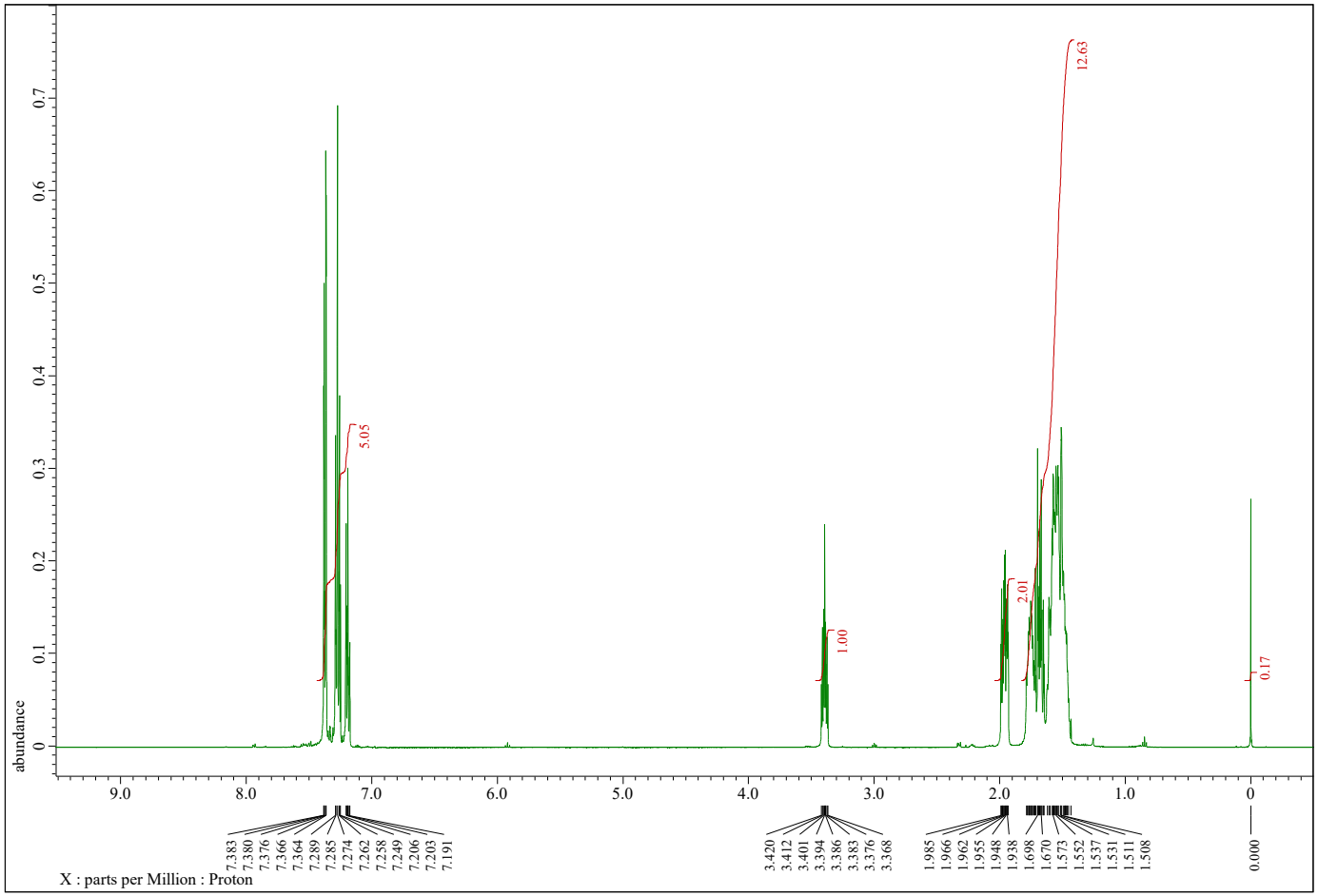
3.3



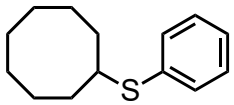
^{1}H NMR spectrum of the compound (3.4)



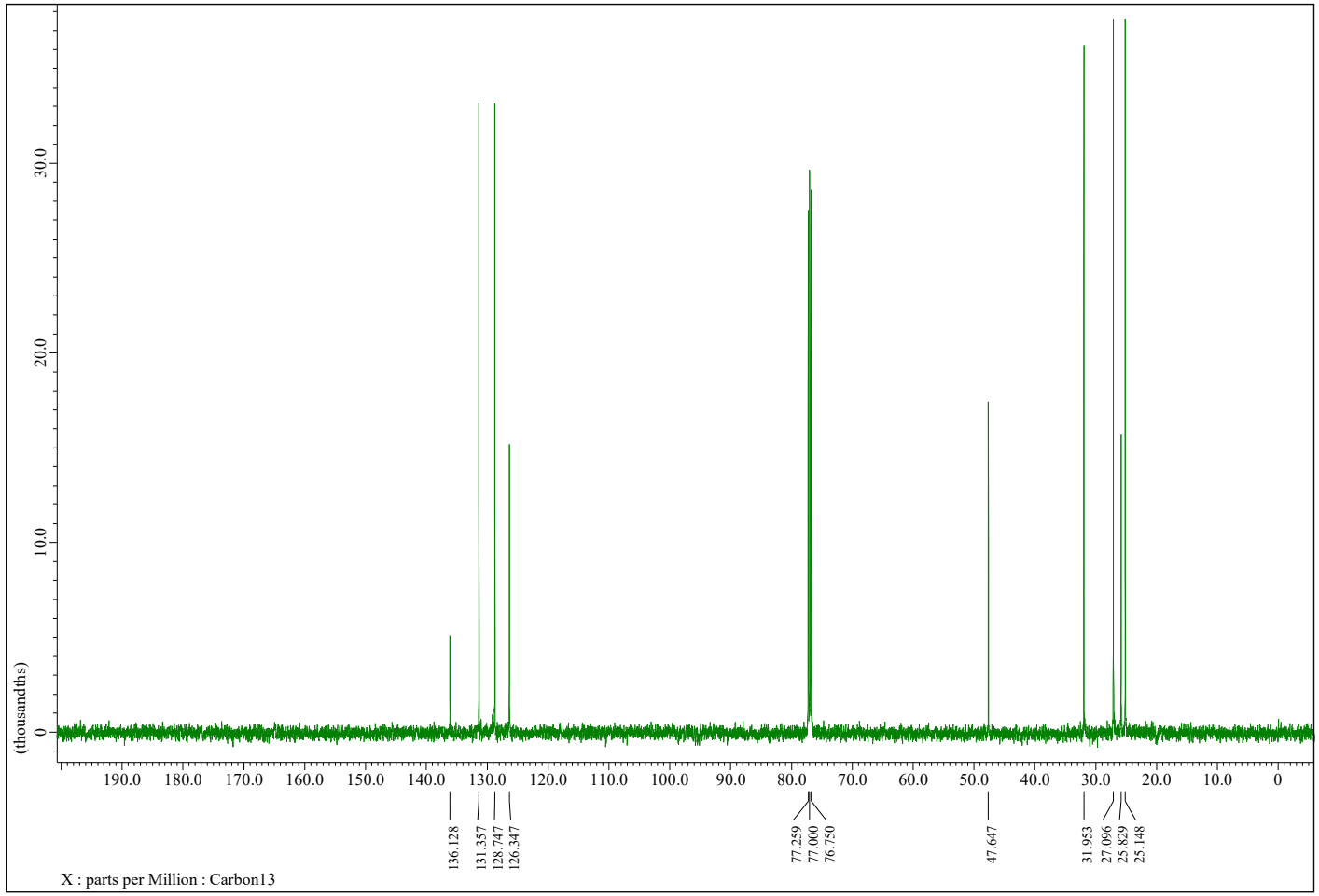
3.4



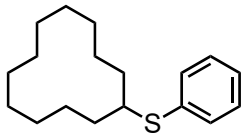
^{13}C NMR spectrum of the compound (3.4)



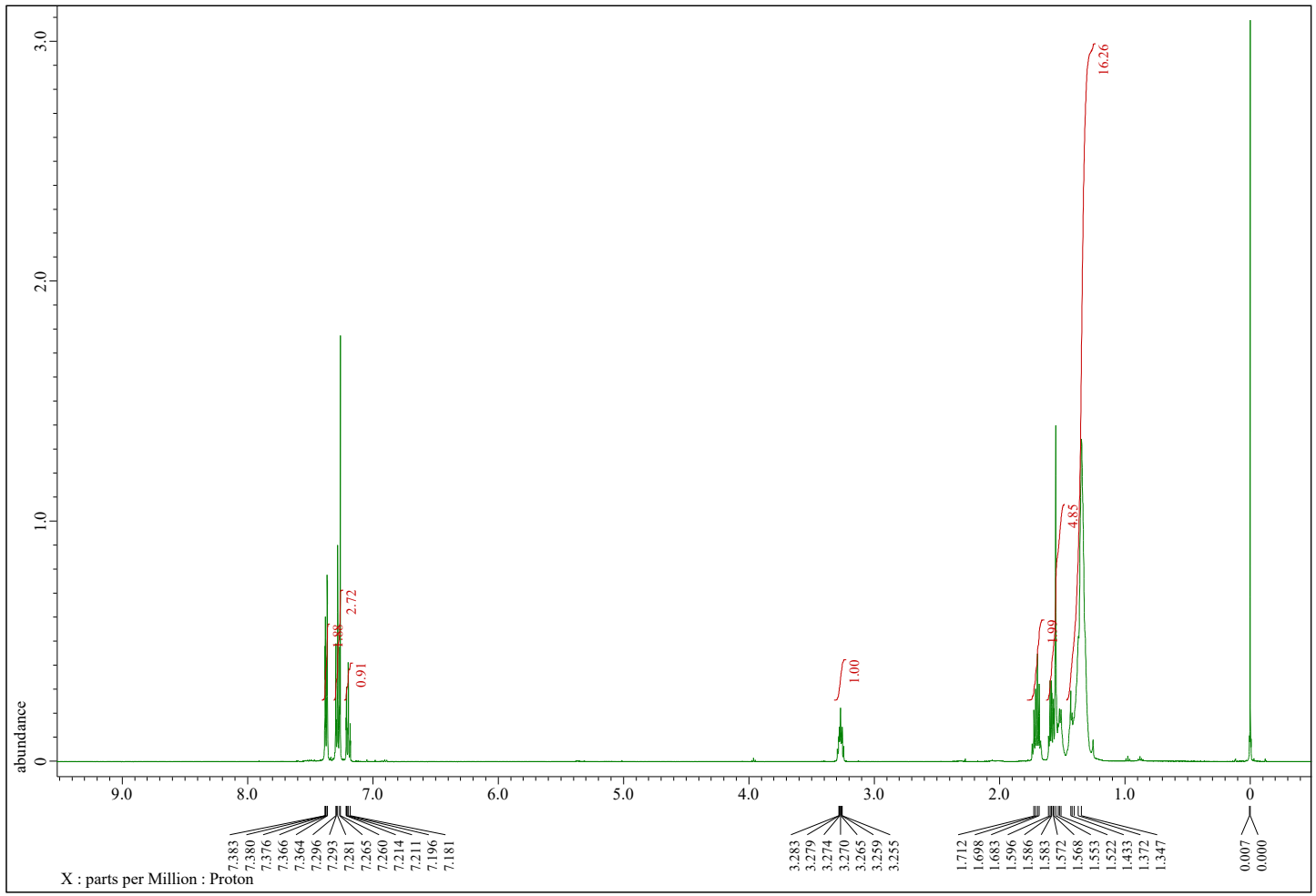
3.4



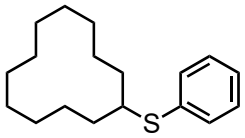
^{1}H NMR spectrum of the compound (3.5)



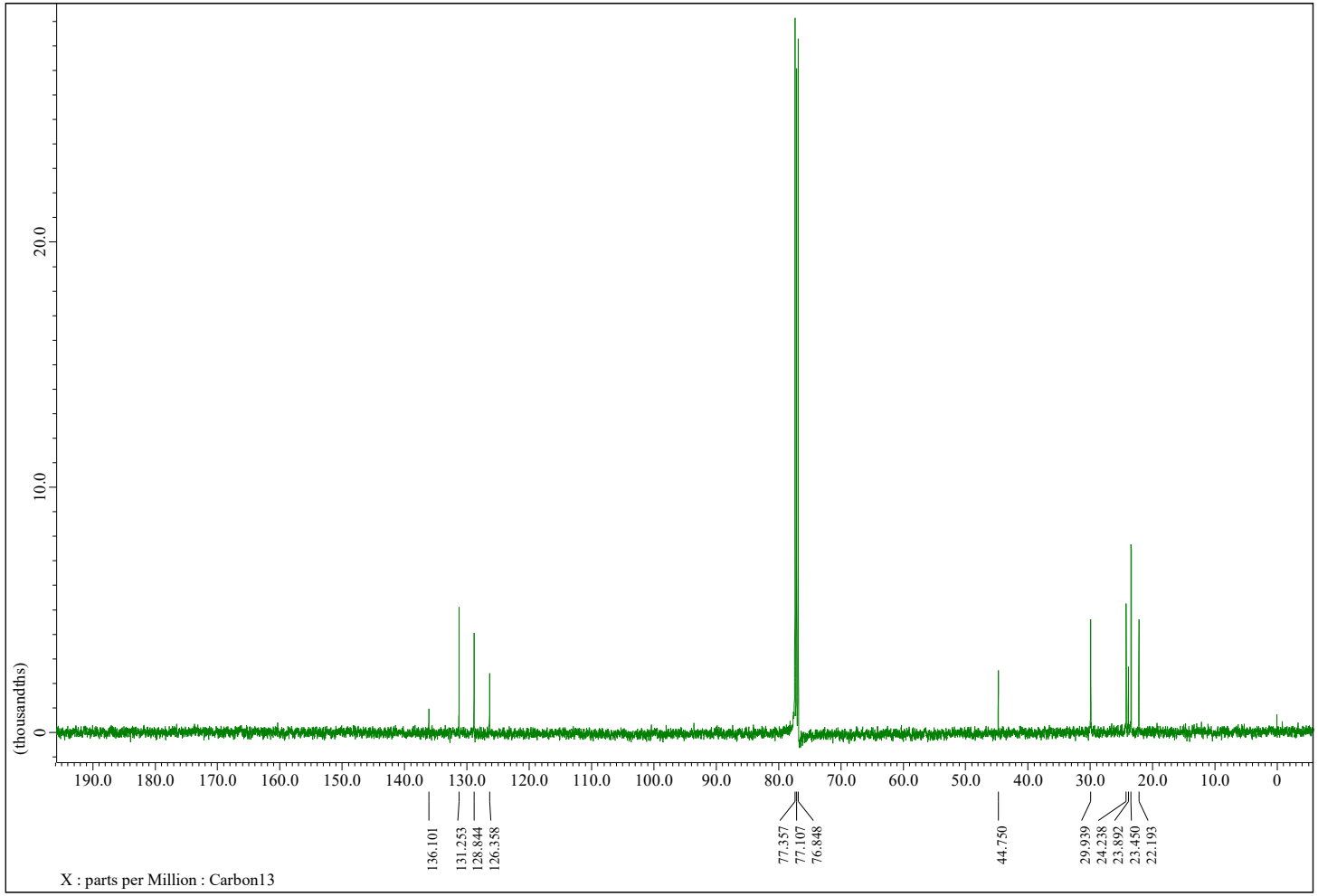
3.5



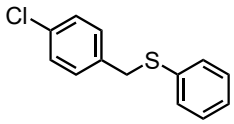
^{13}C NMR spectrum of the compound (3.5)



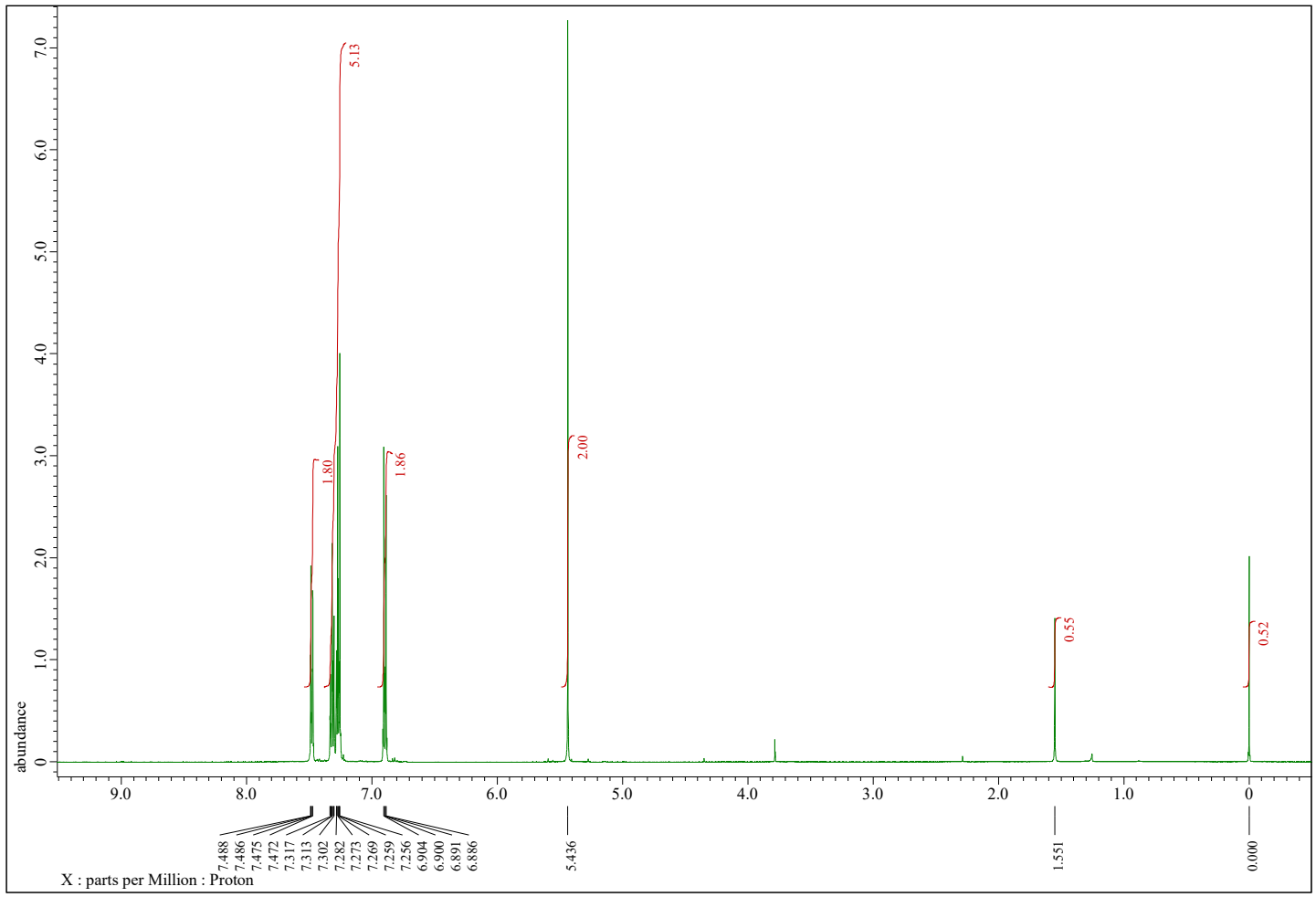
3.5



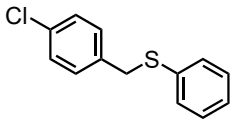
^{1}H NMR spectrum of the compound (3.6)



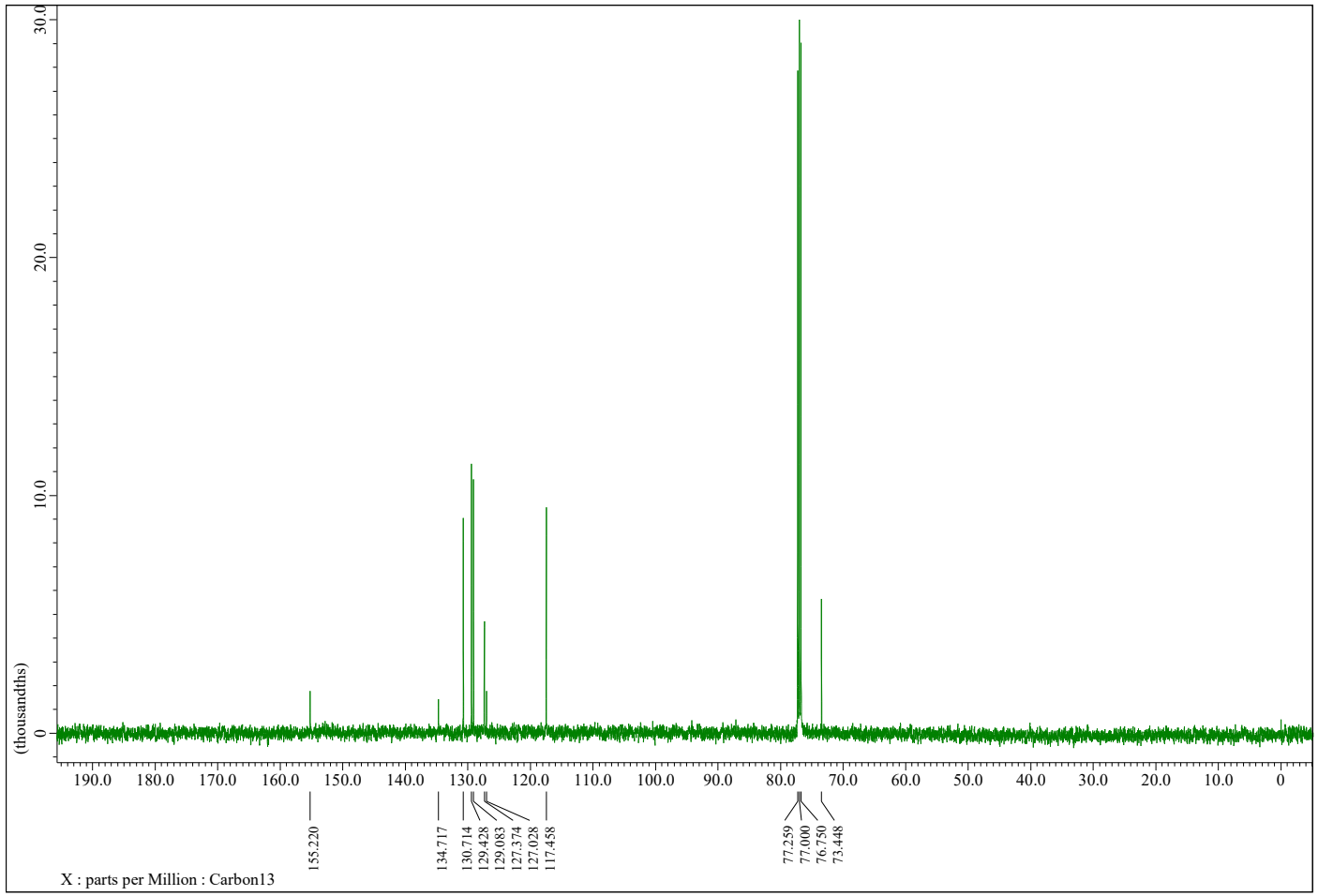
3.6



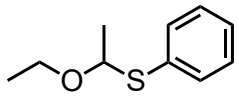
^{13}C NMR spectrum of the compound (3.6)



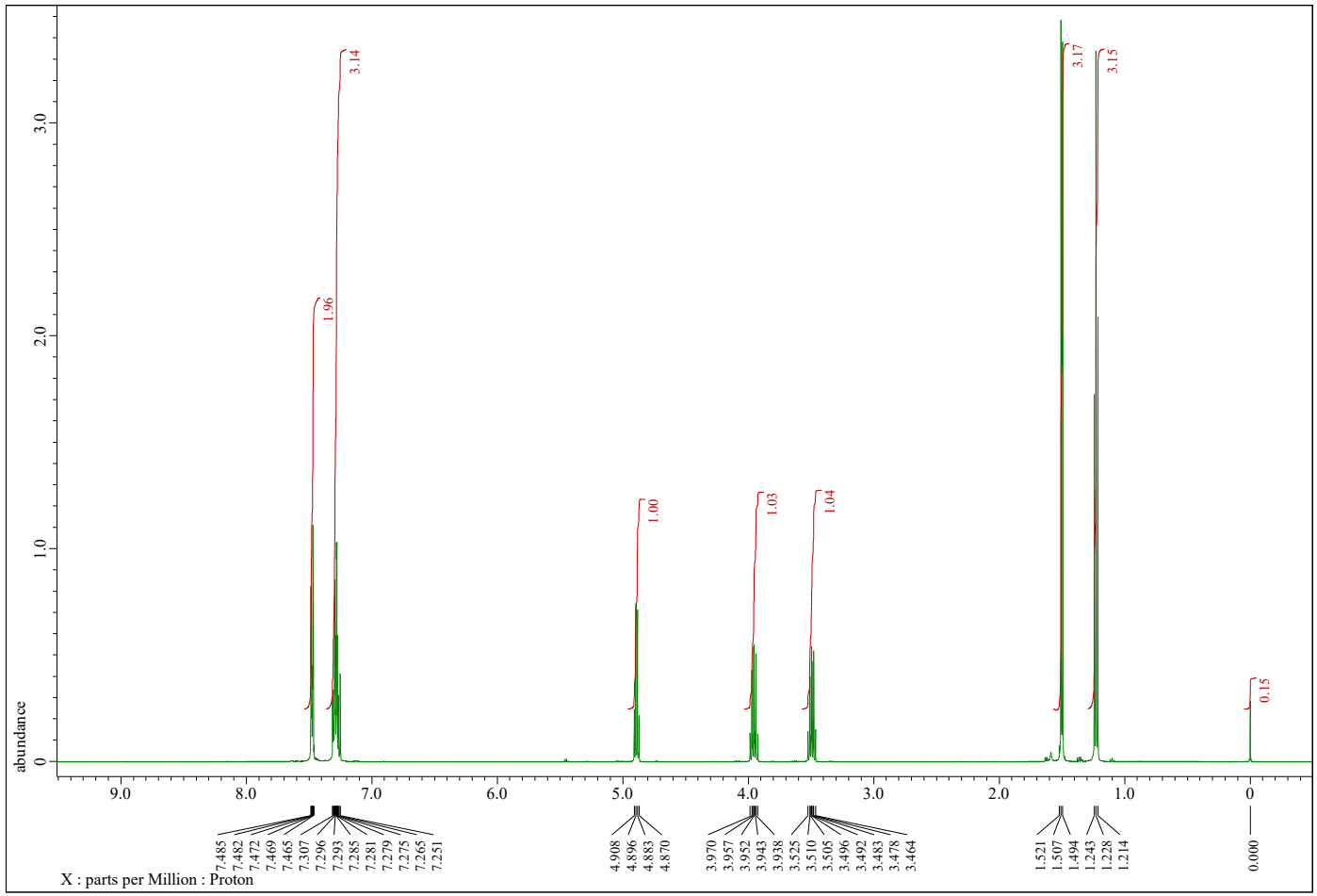
3.6



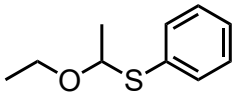
^{1}H NMR spectrum of the compound (3.7)



3.7



^{13}C NMR spectrum of the compound (3.7)



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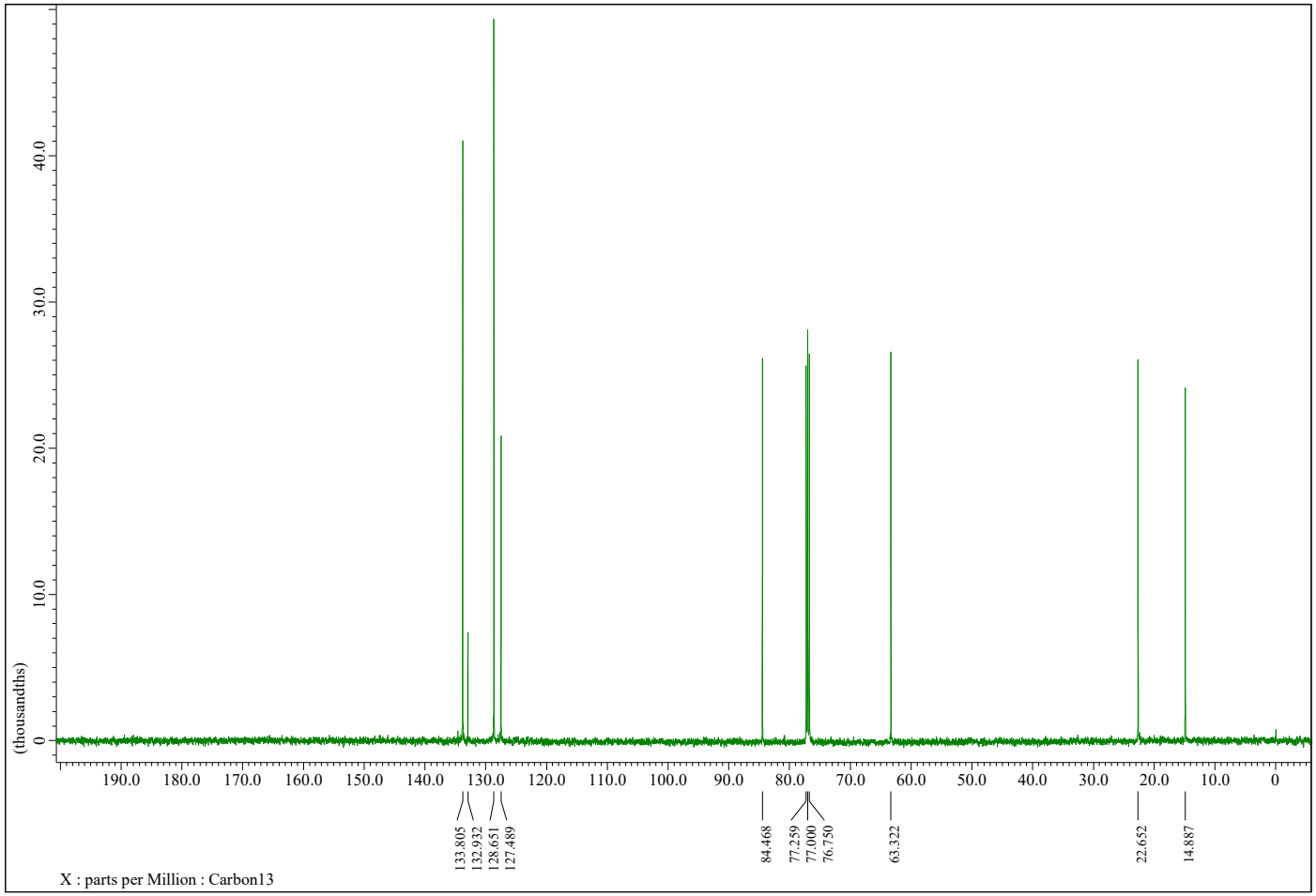
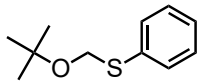


^{1}H NMR spectrum of the compound (3.8)



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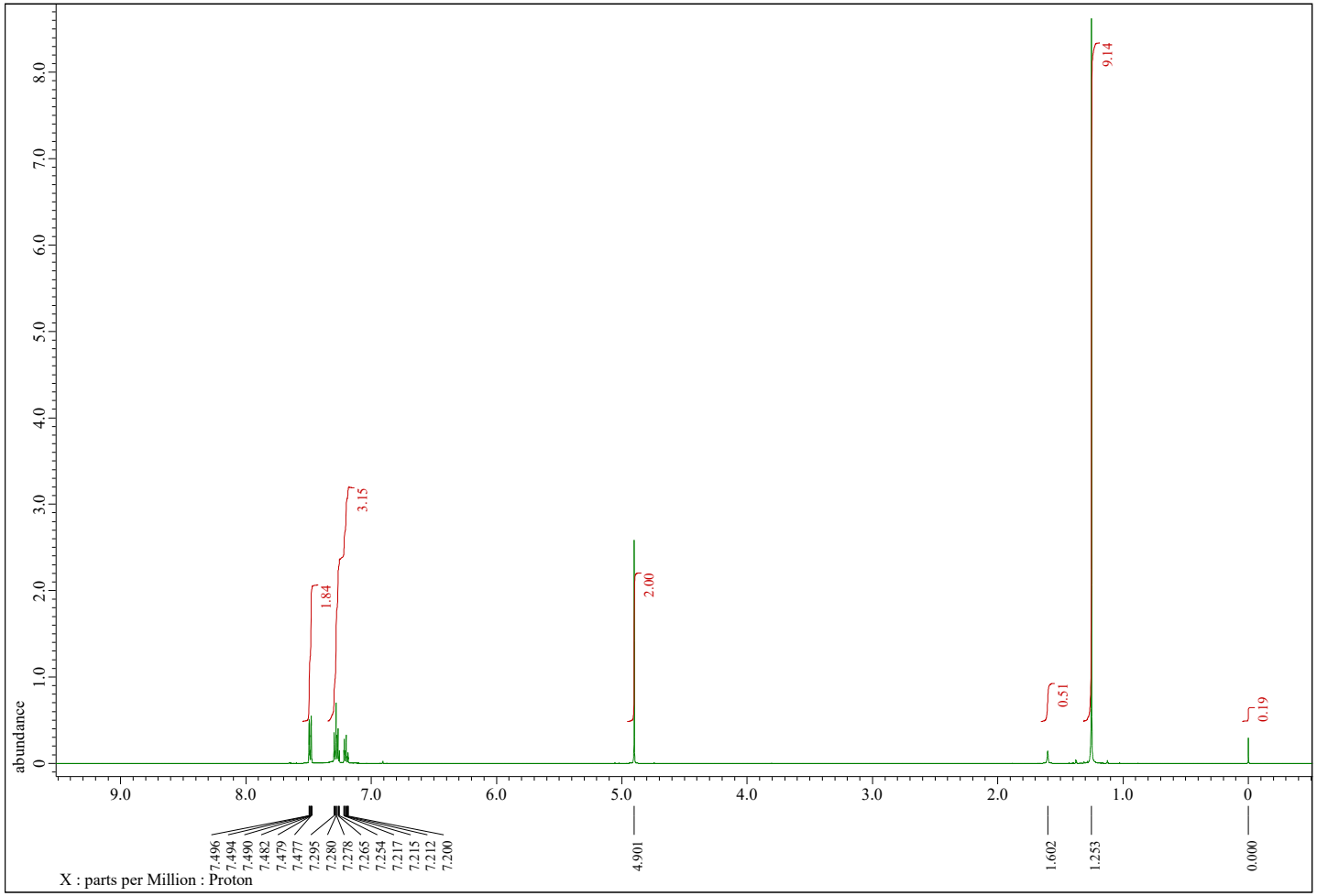
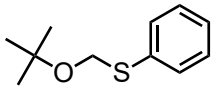


^{13}C NMR spectrum of the compound (3.8)



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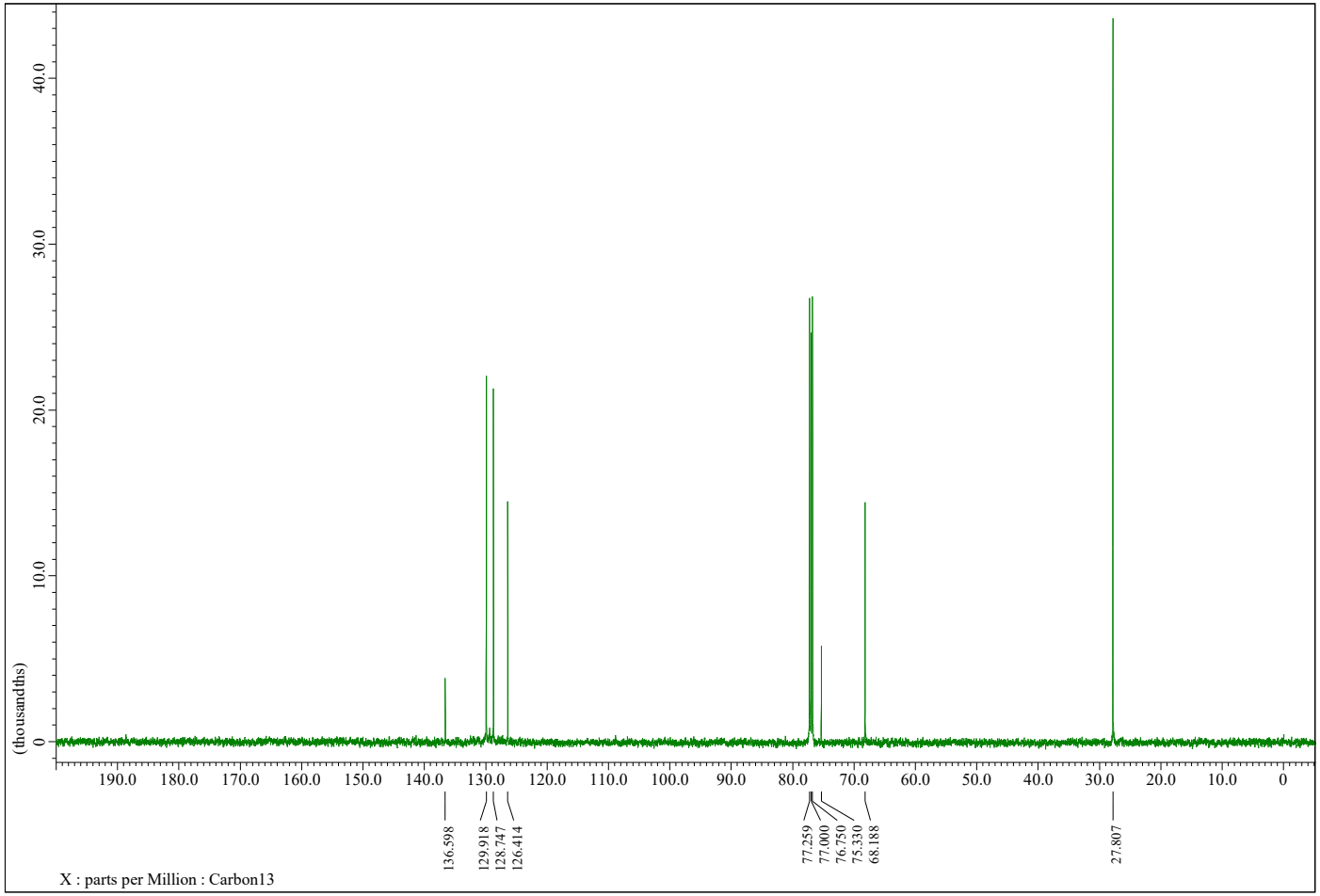
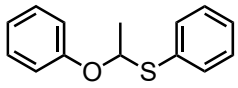
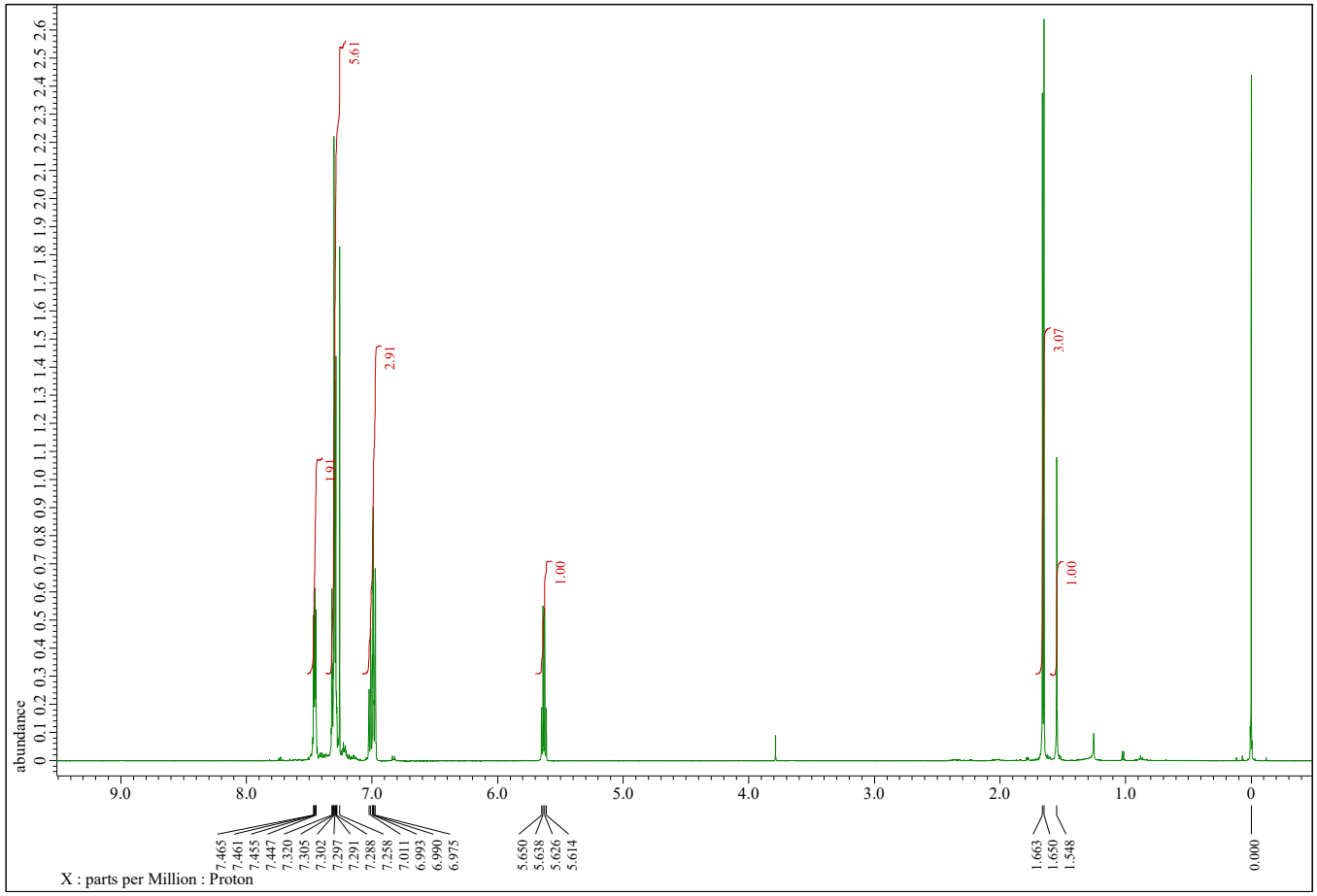


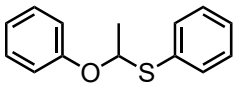
^{1}H NMR spectrum of the compound (3.9)



3.9



^{13}C NMR spectrum of the compound (3.9)



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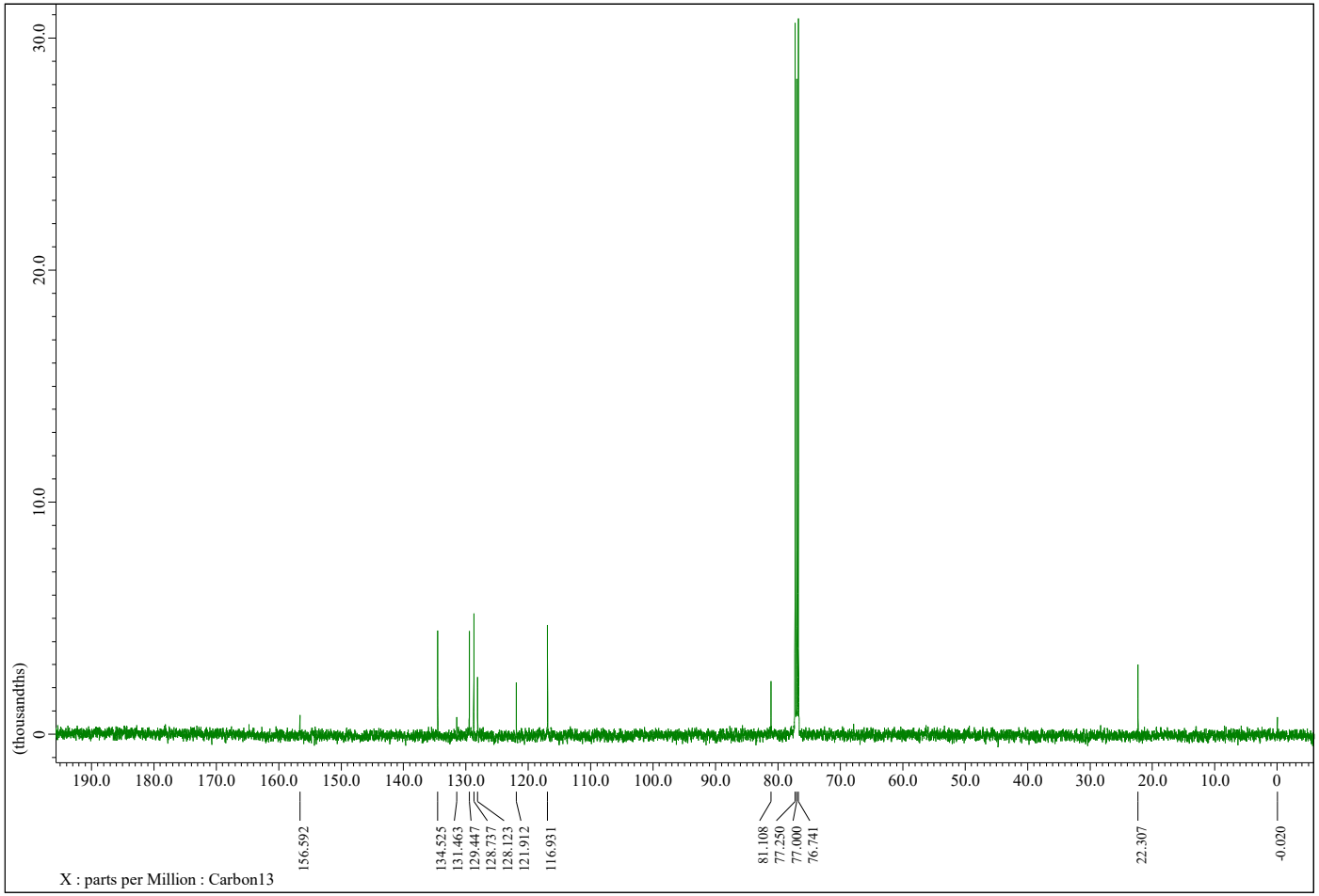
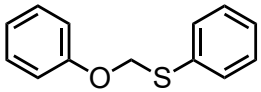
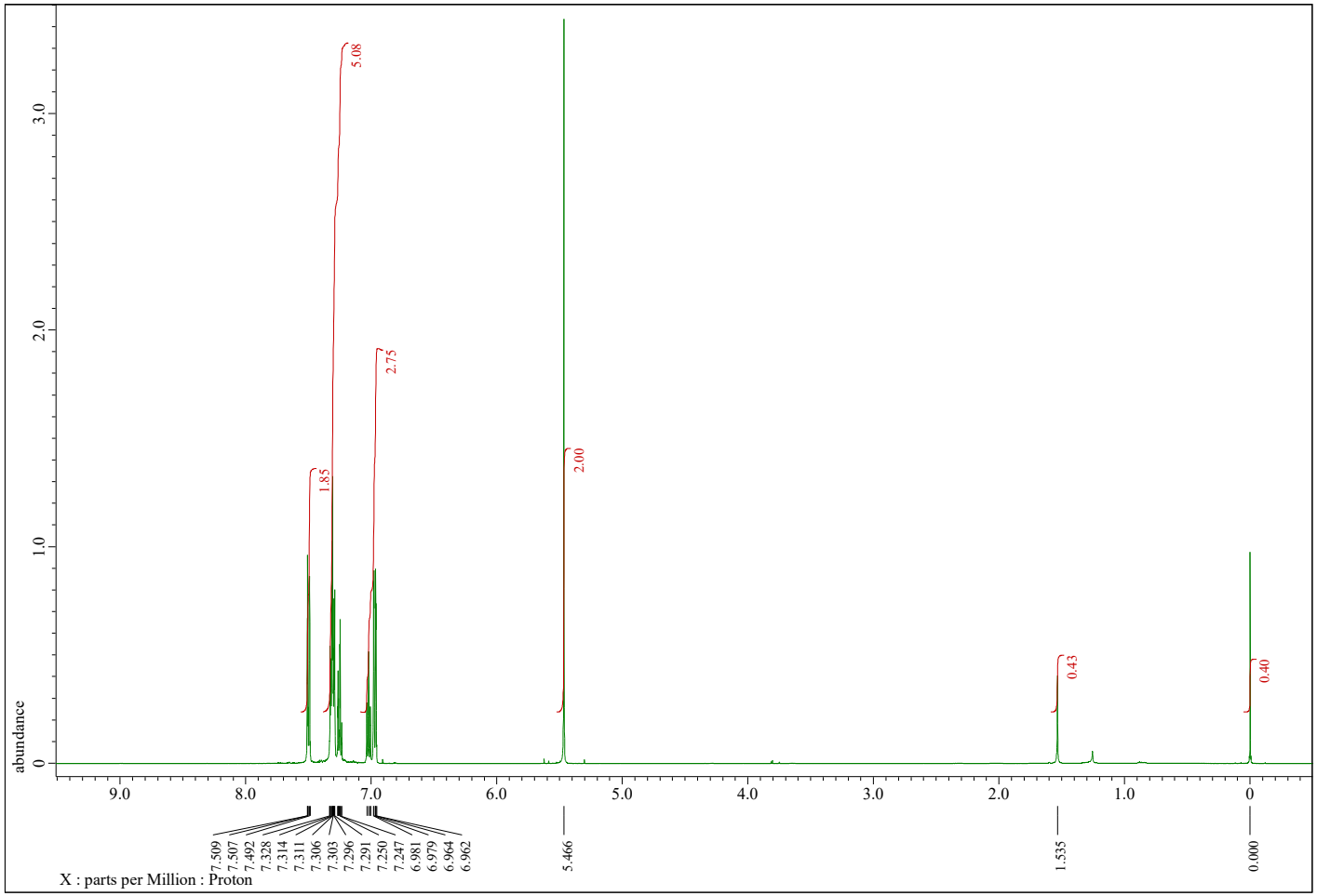


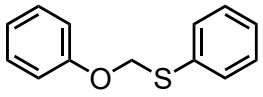
^{1}H NMR spectrum of the compound (3.10)



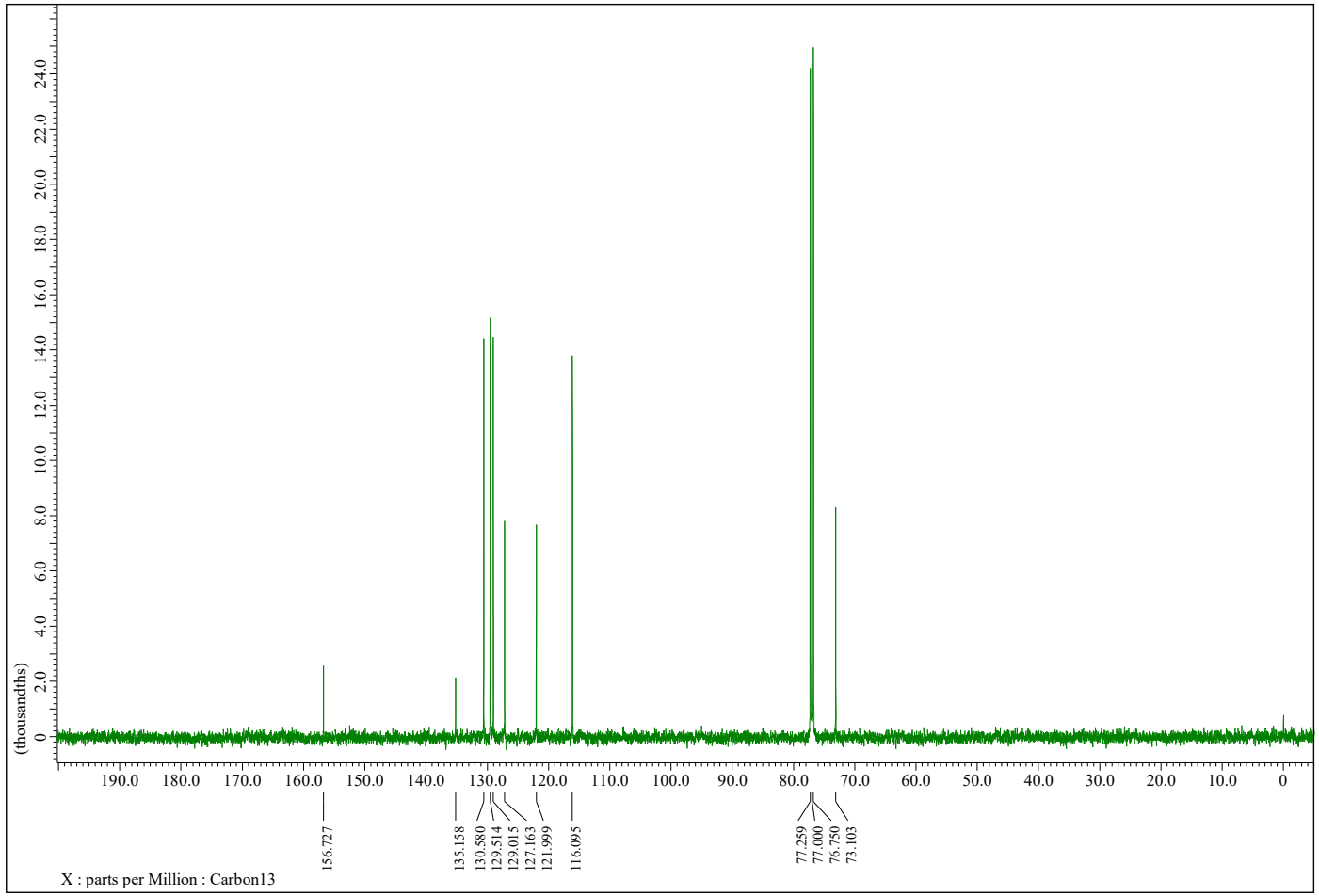
3.10



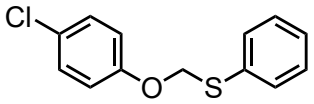
^{13}C NMR spectrum of the compound (3.10)



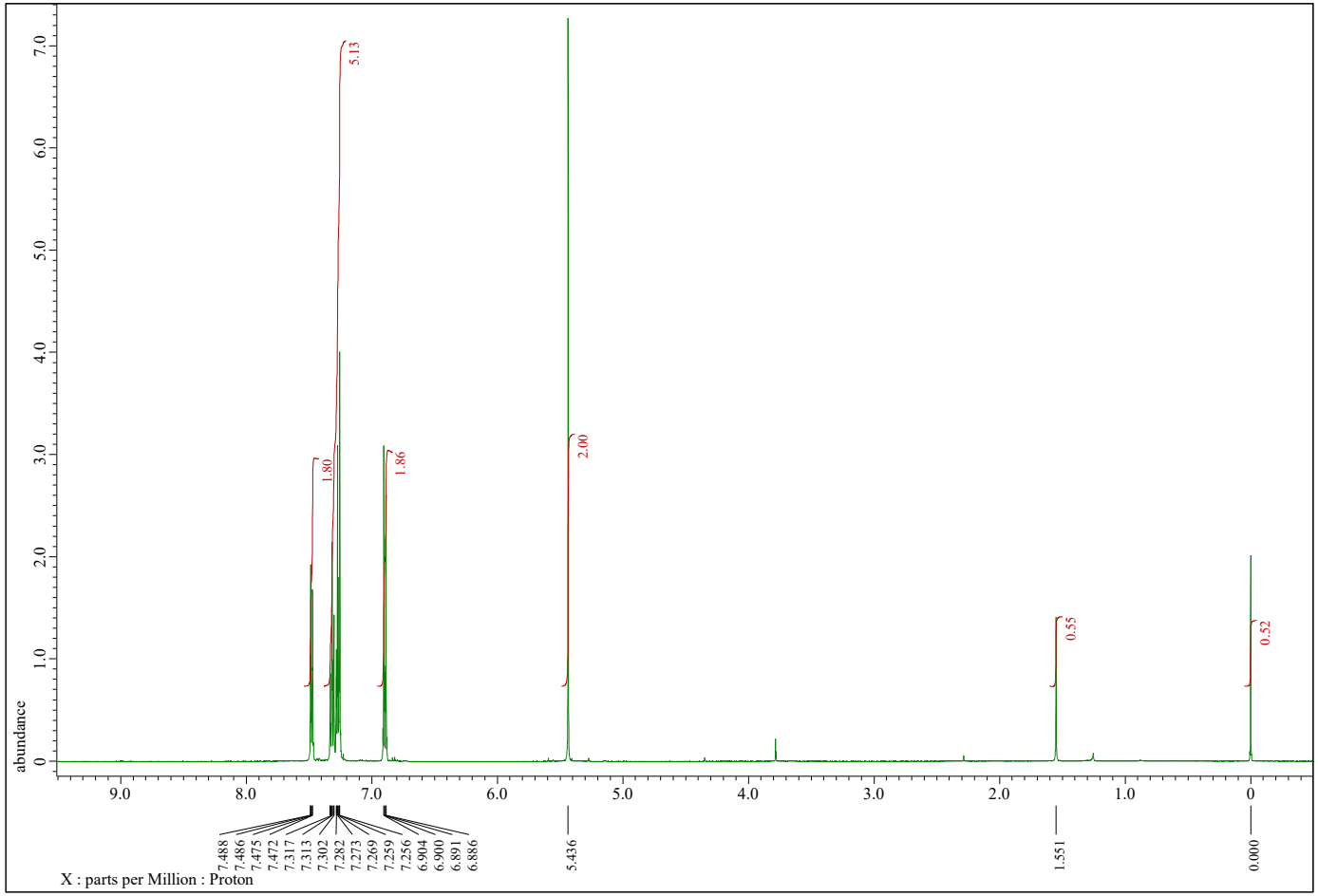
3.10



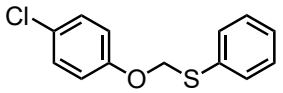
^{1}H NMR spectrum of the compound (3.11)



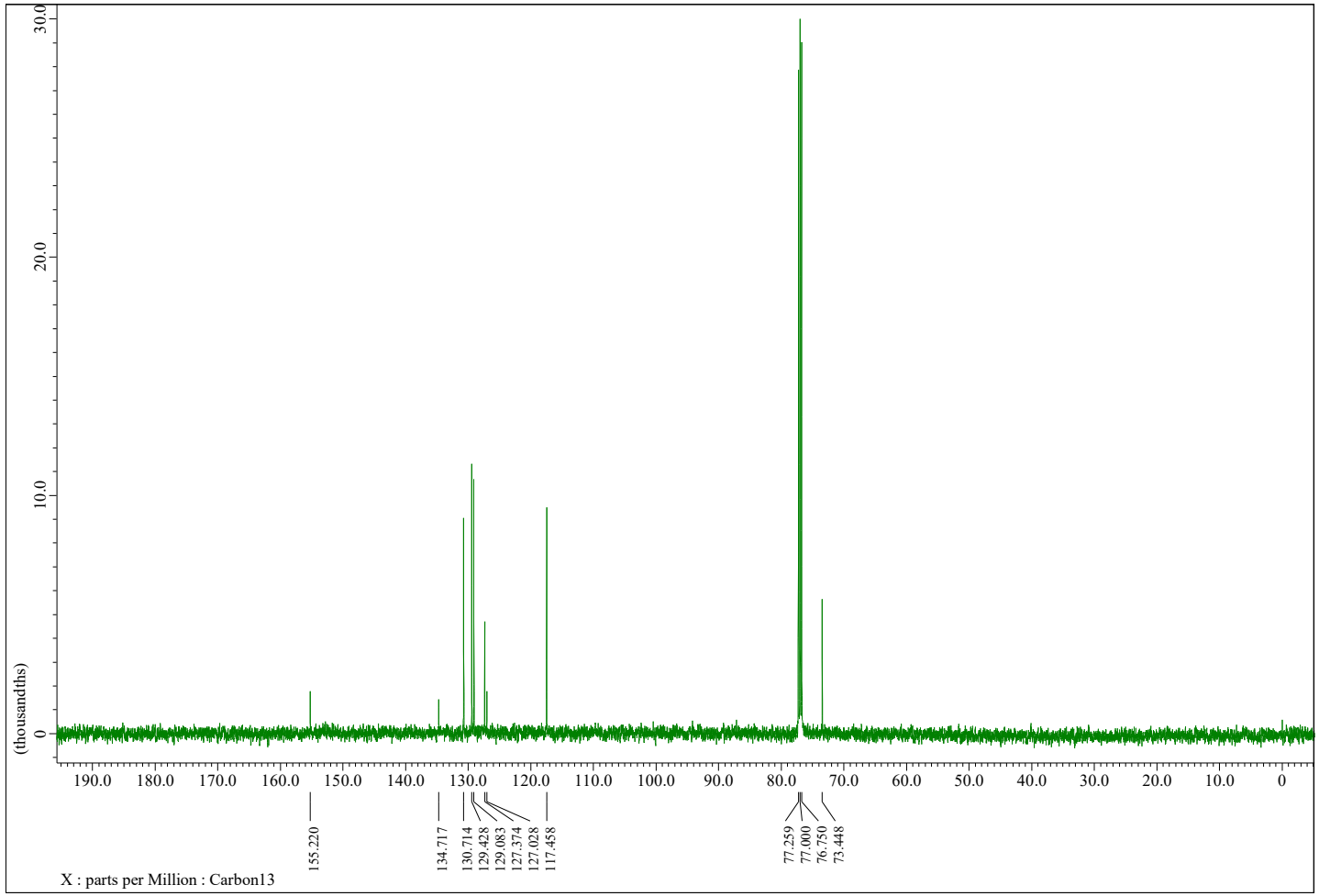
3.11



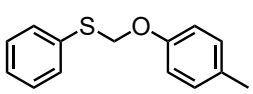
^{13}C NMR spectrum of the compound (3.11)



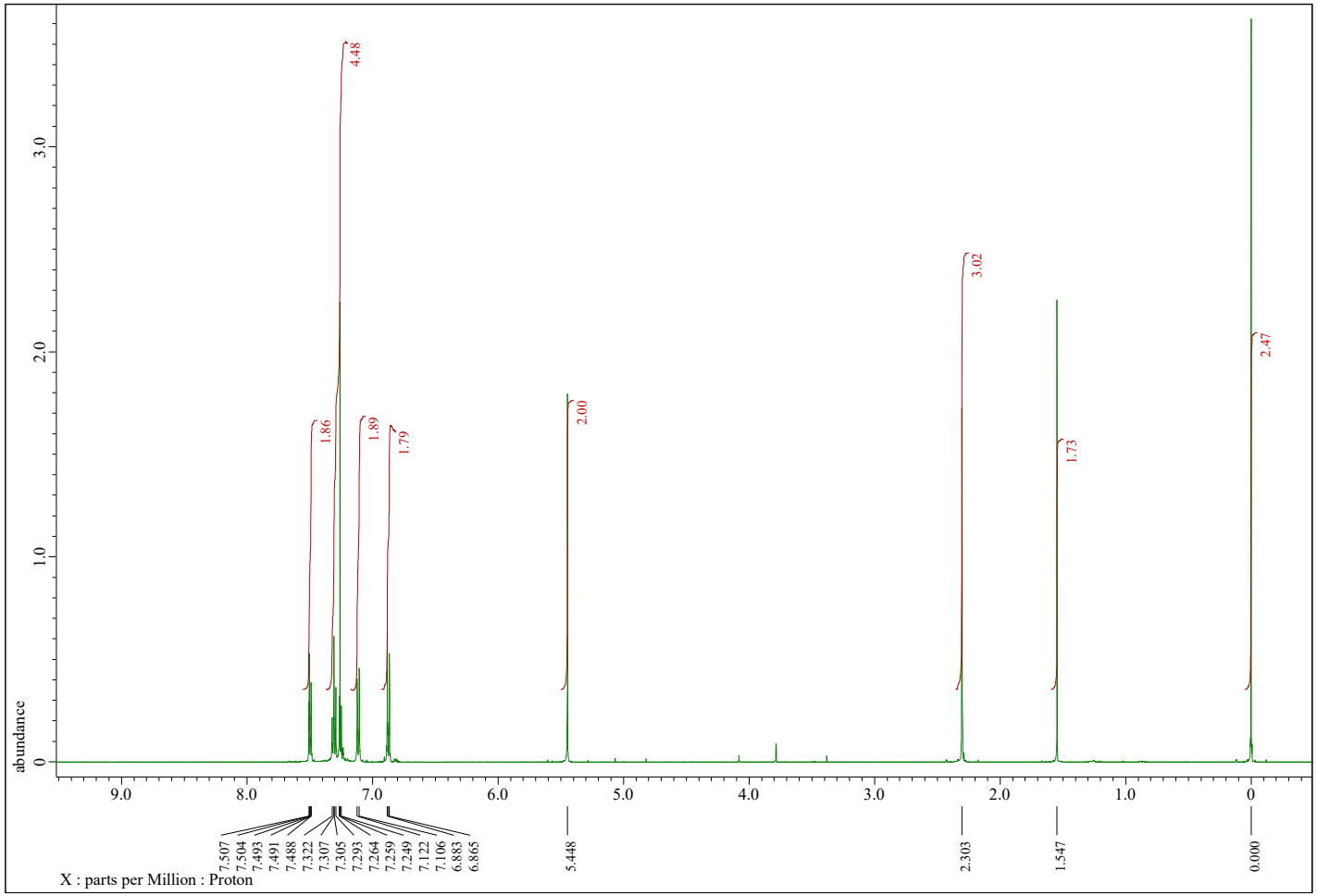
3.11



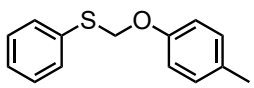
^{1}H NMR spectrum of the compound (3.12)



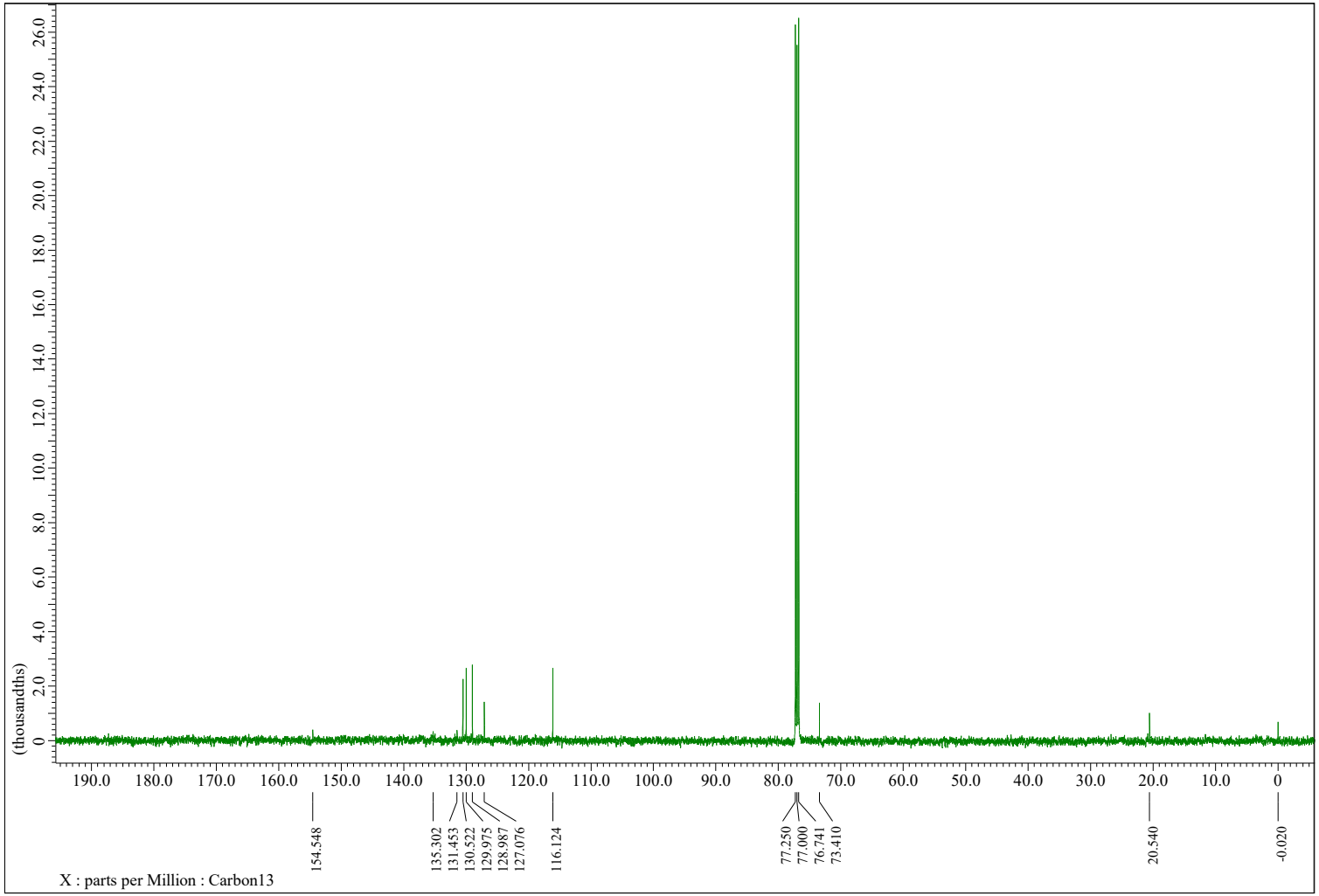
3.12



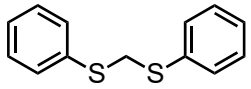
^{13}C NMR spectrum of the compound (3.12)



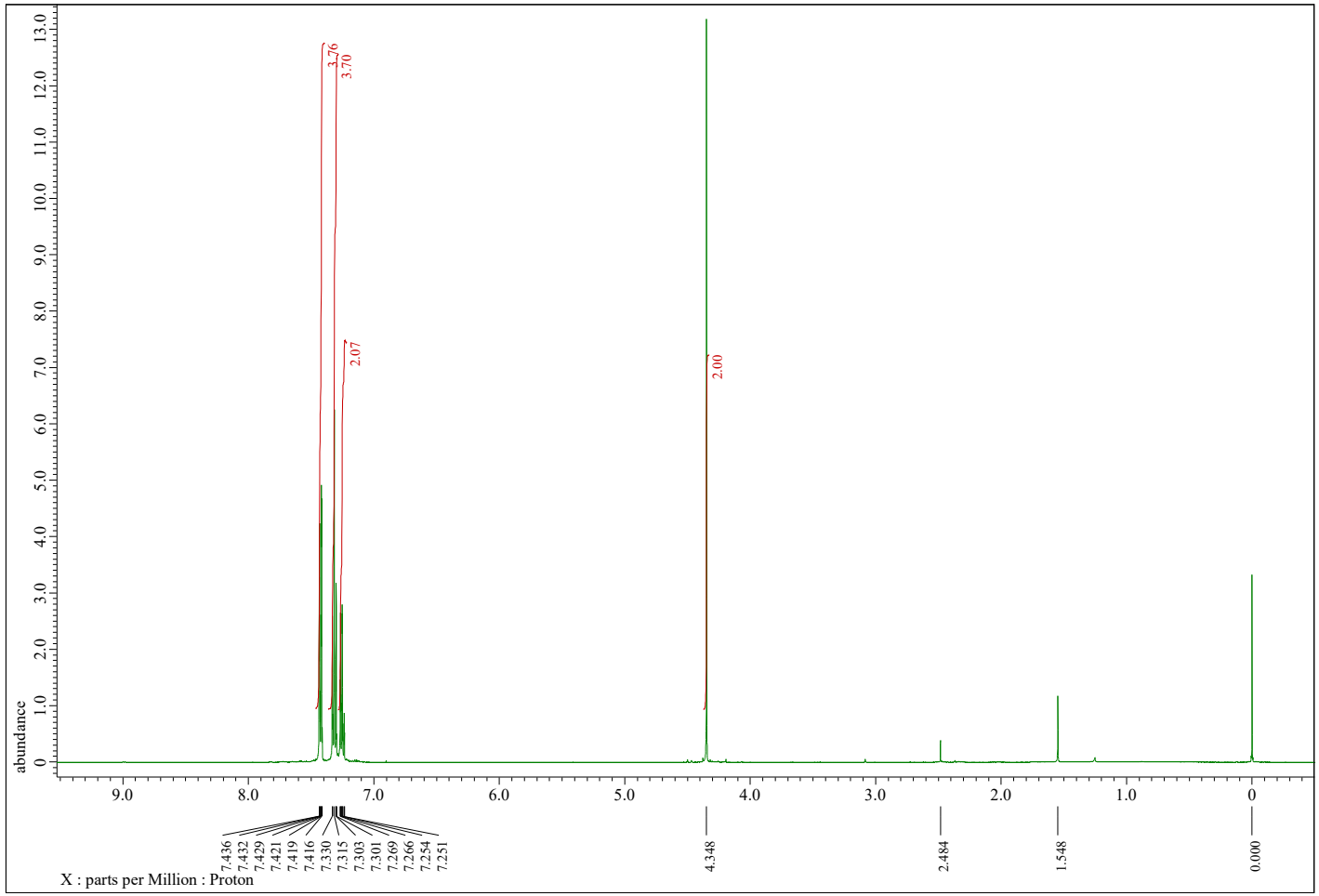
3.12



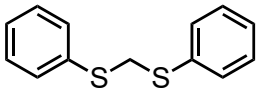
^{1}H NMR spectrum of the compound (3.13)



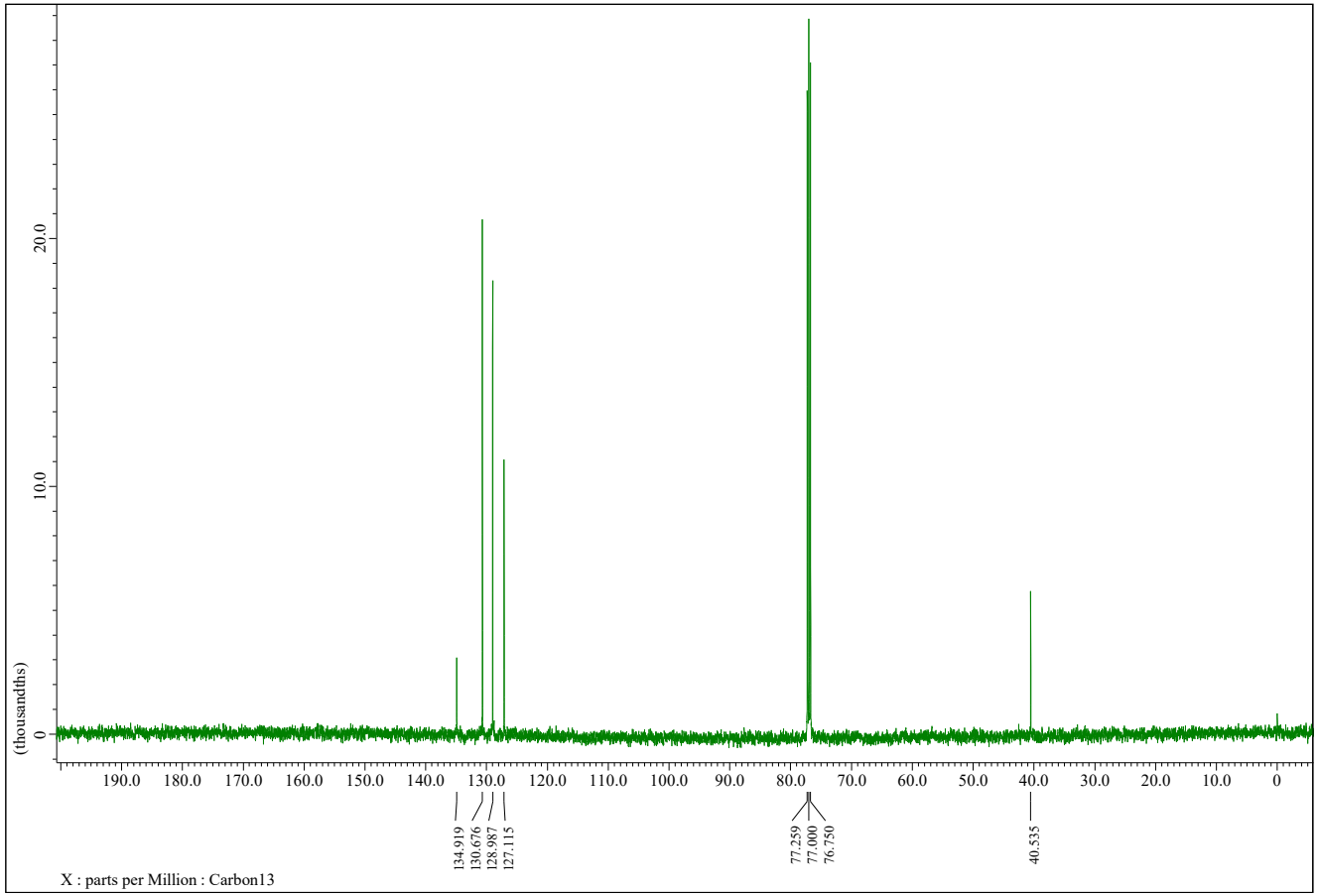
3.13



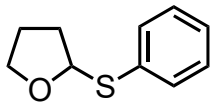
^{13}C NMR spectrum of the compound (3.13)



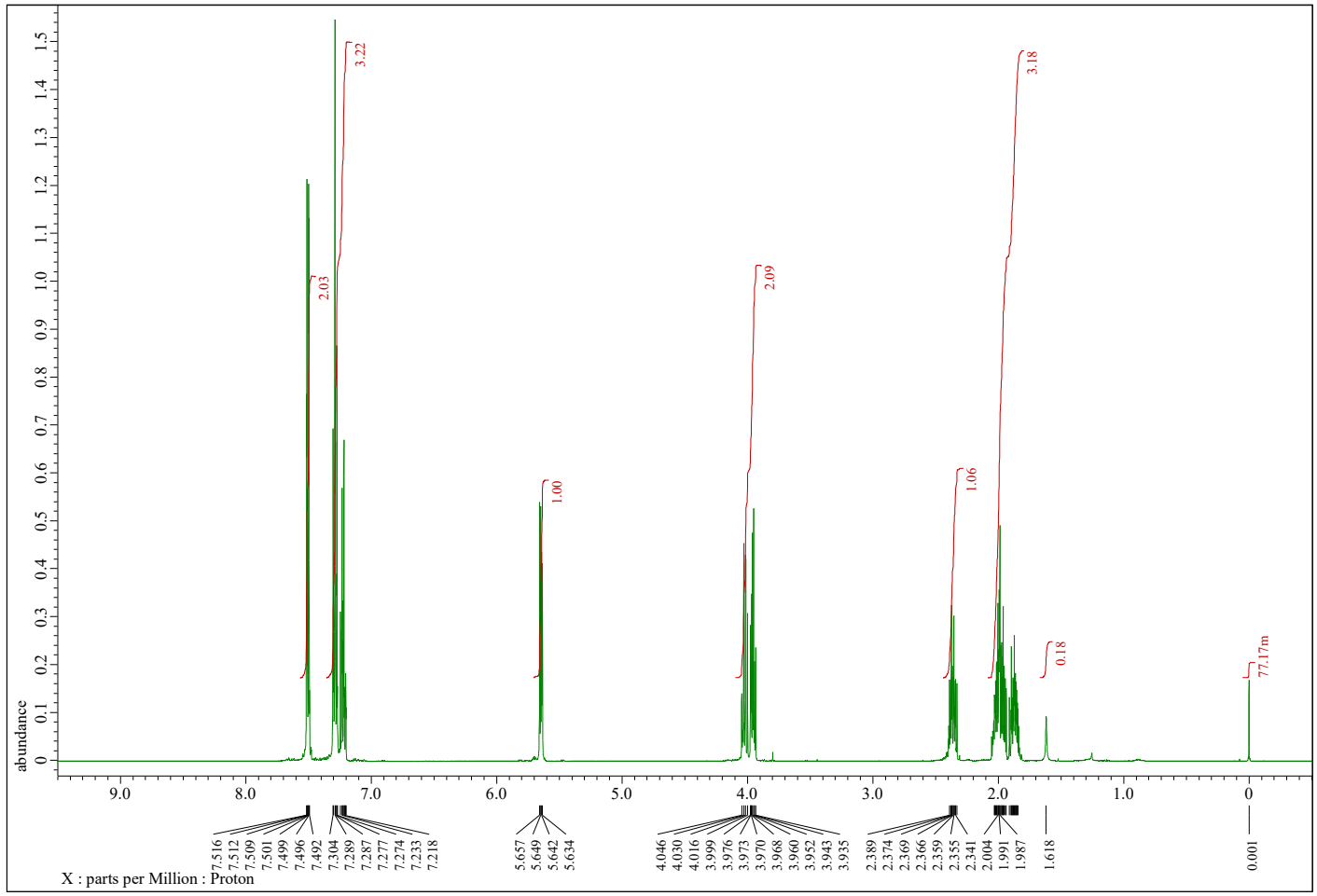
3.13



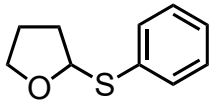
^{1}H NMR spectrum of the compound (3.14)



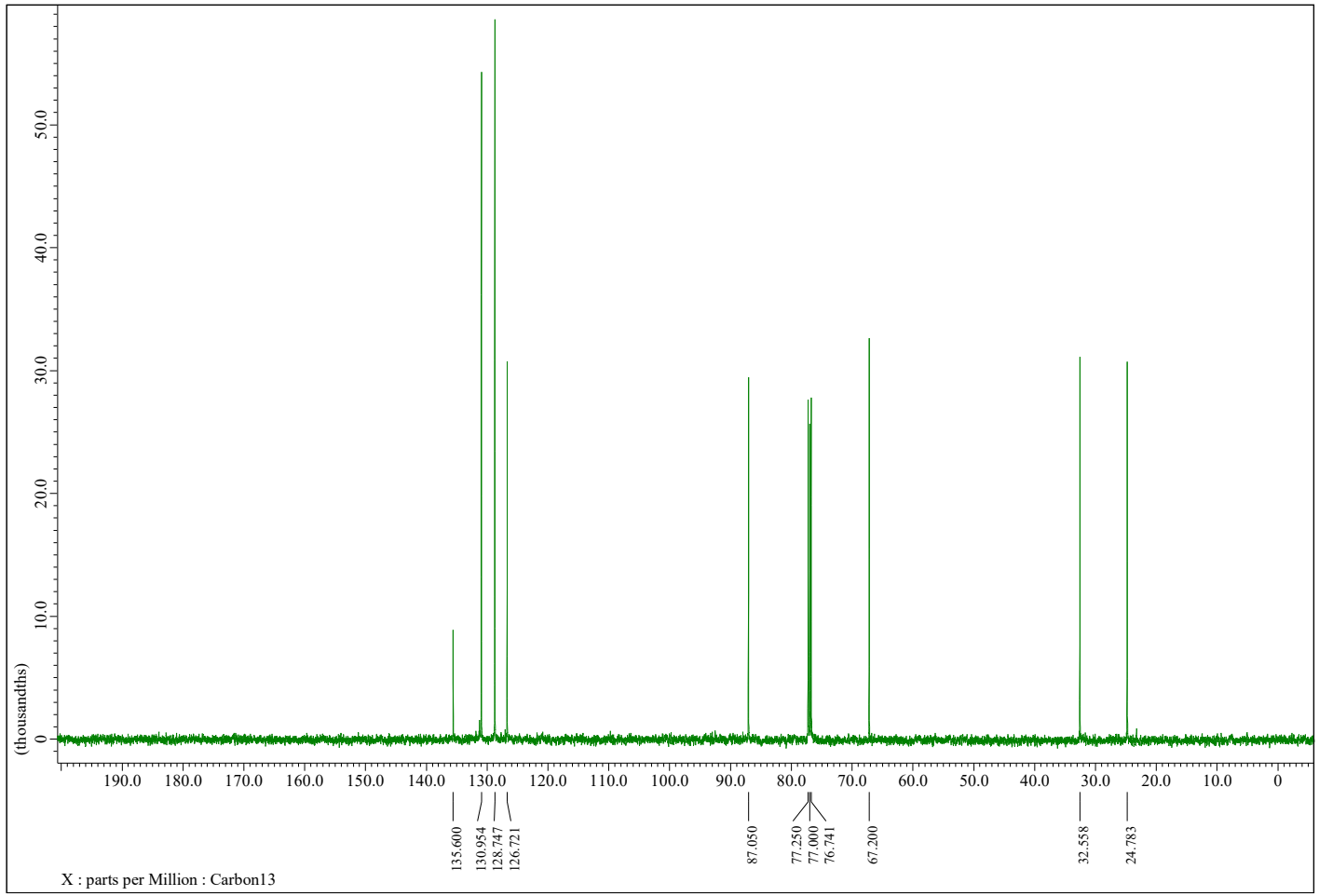
3.14



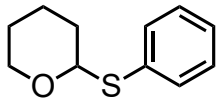
^{13}C NMR spectrum of the compound (3.14)



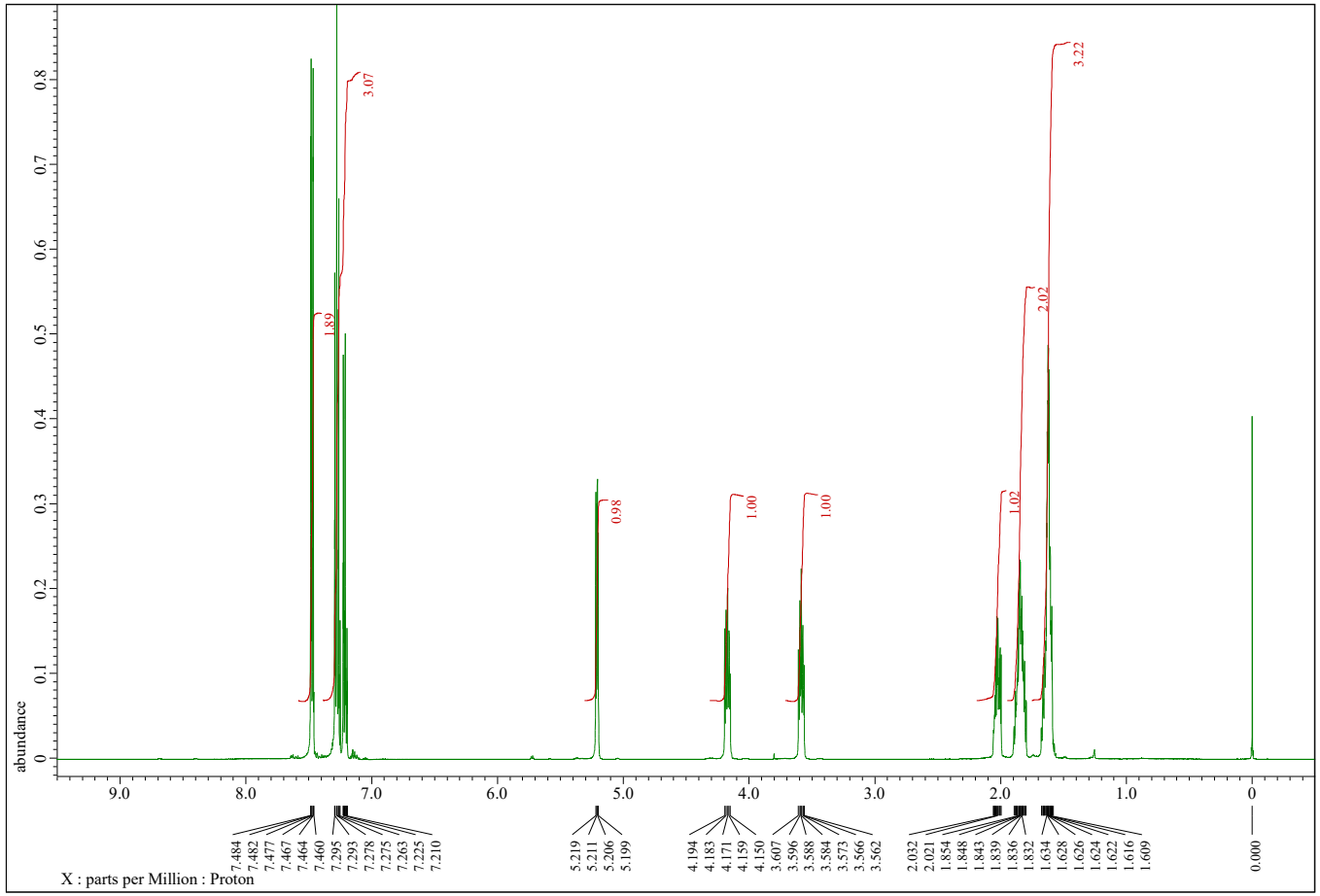
3.14



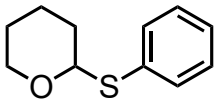
^{1}H NMR spectrum of the compound (3.15)



3.15



^{13}C NMR spectrum of the compound (3.15)



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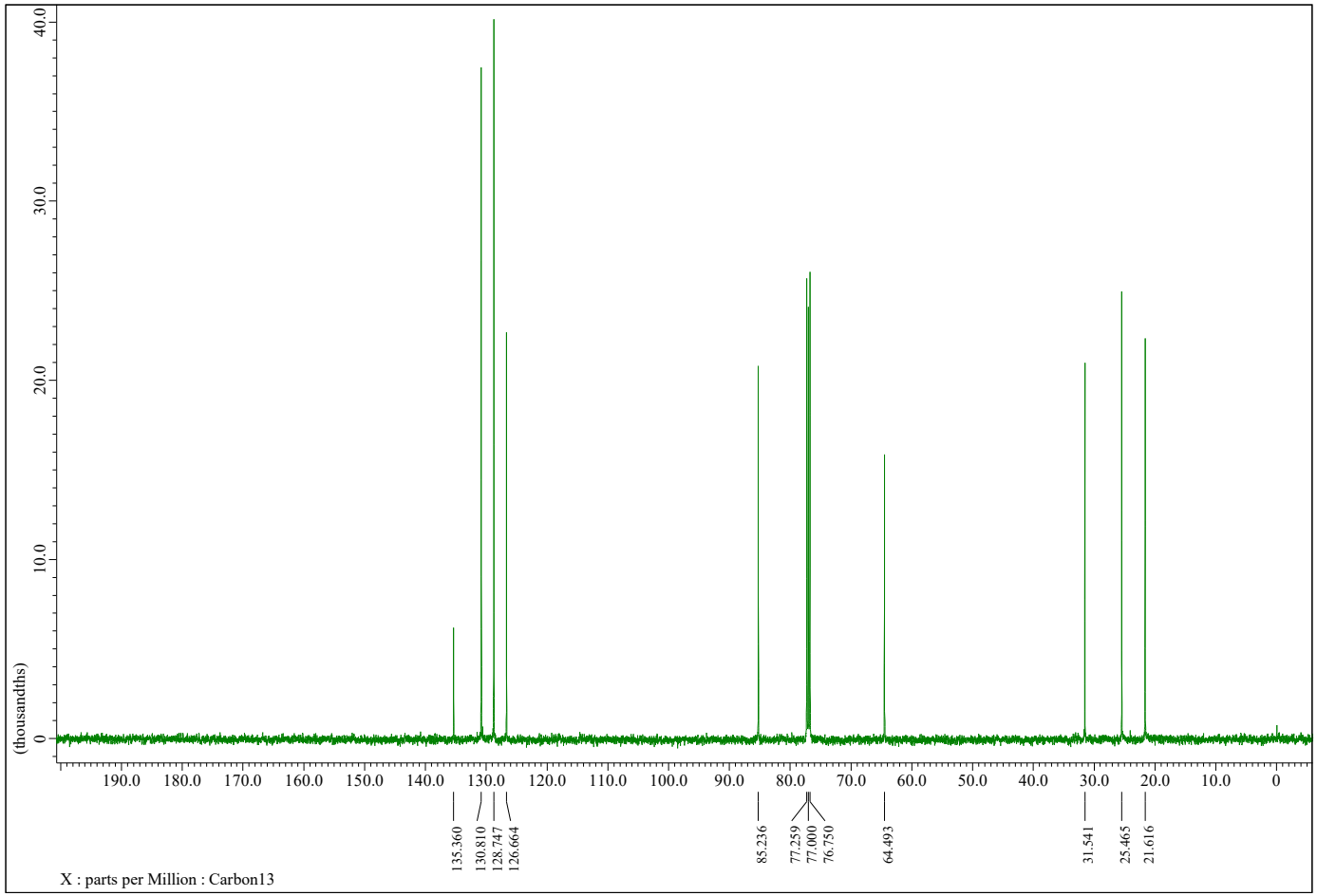
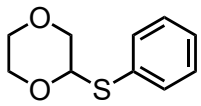


^{1}H NMR spectrum of the compound (3.16)



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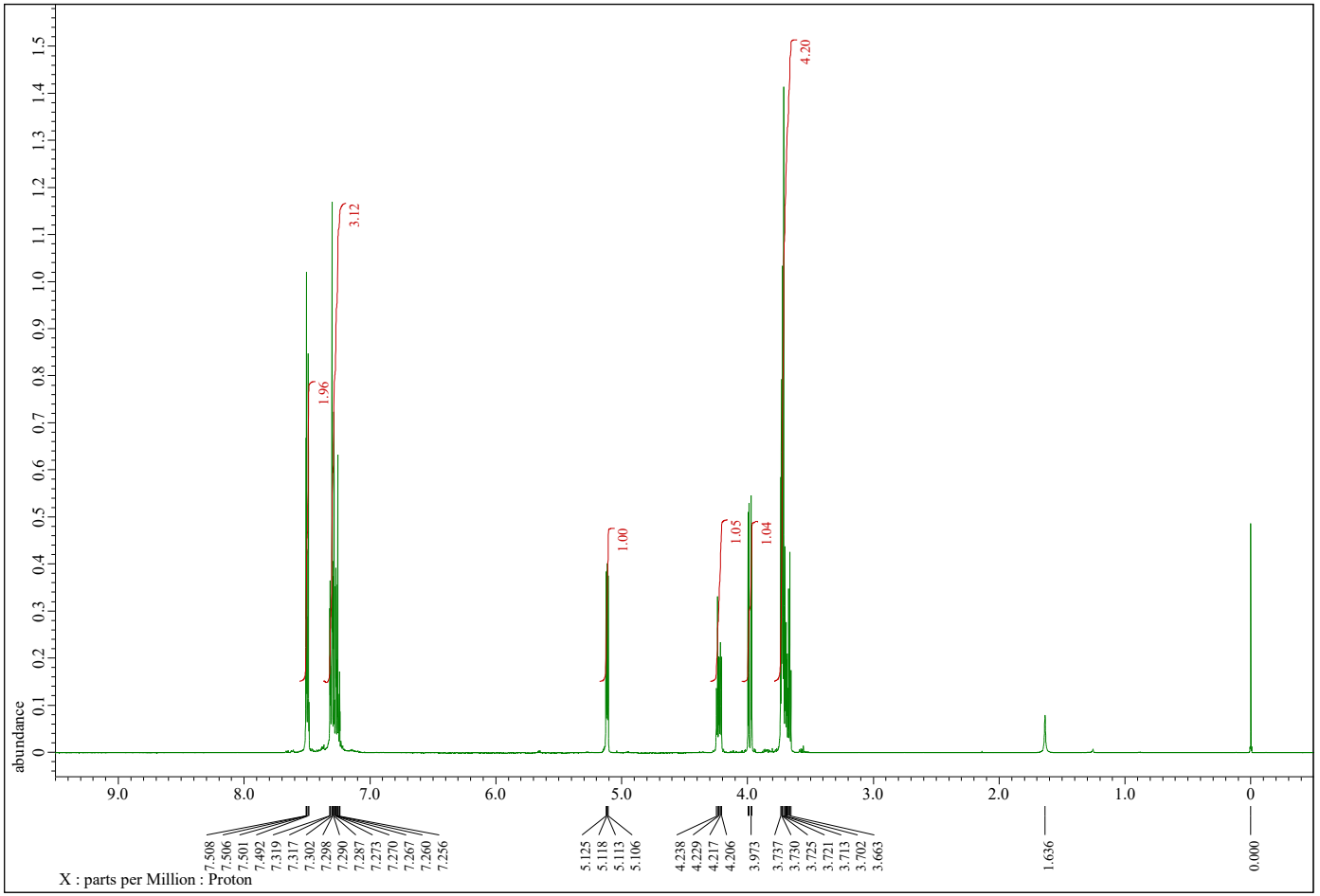
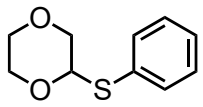


^{13}C NMR spectrum of the compound (3.16)



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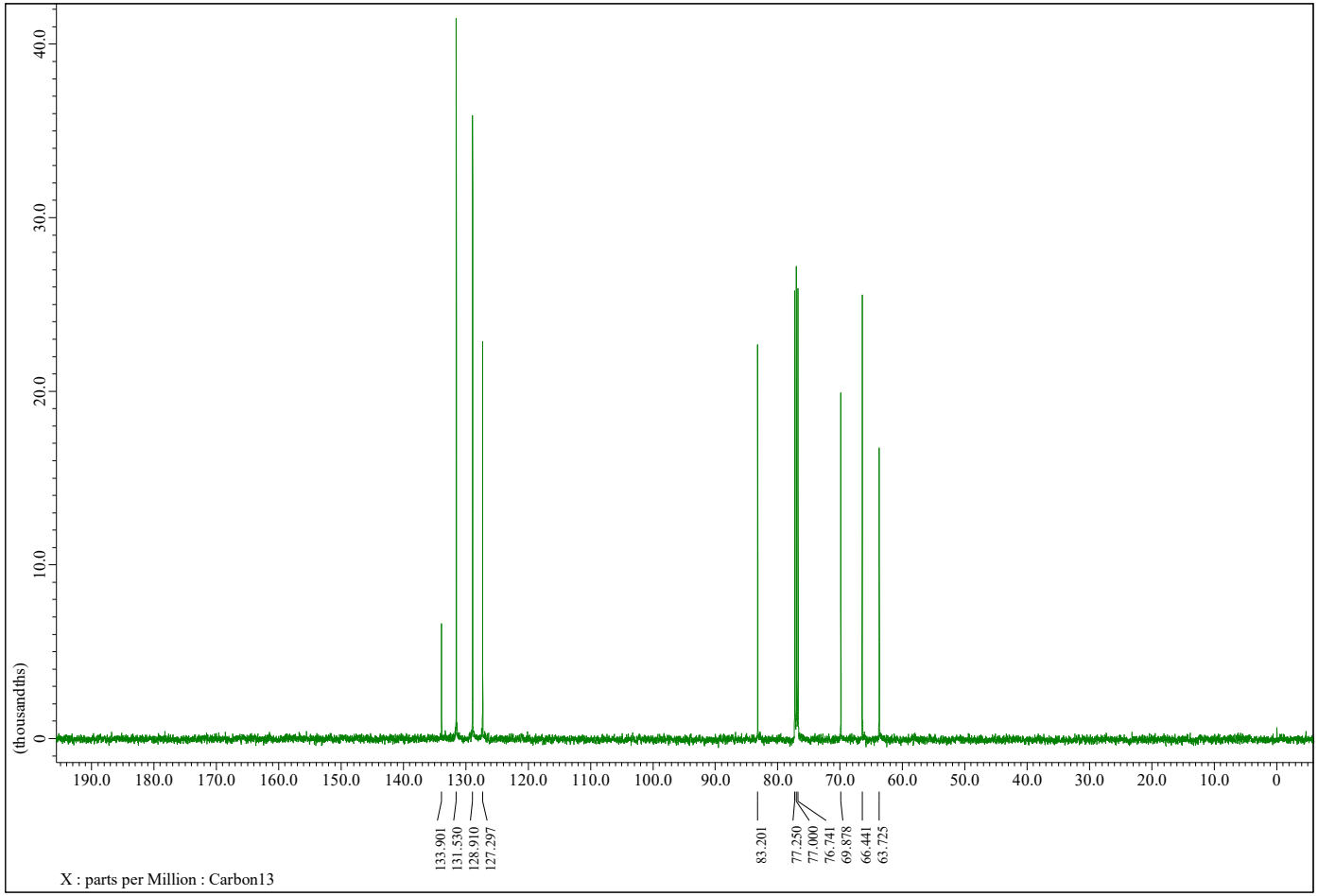
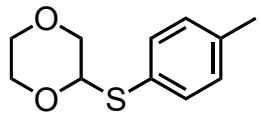


^{1}H NMR spectrum of the compound (3.17)



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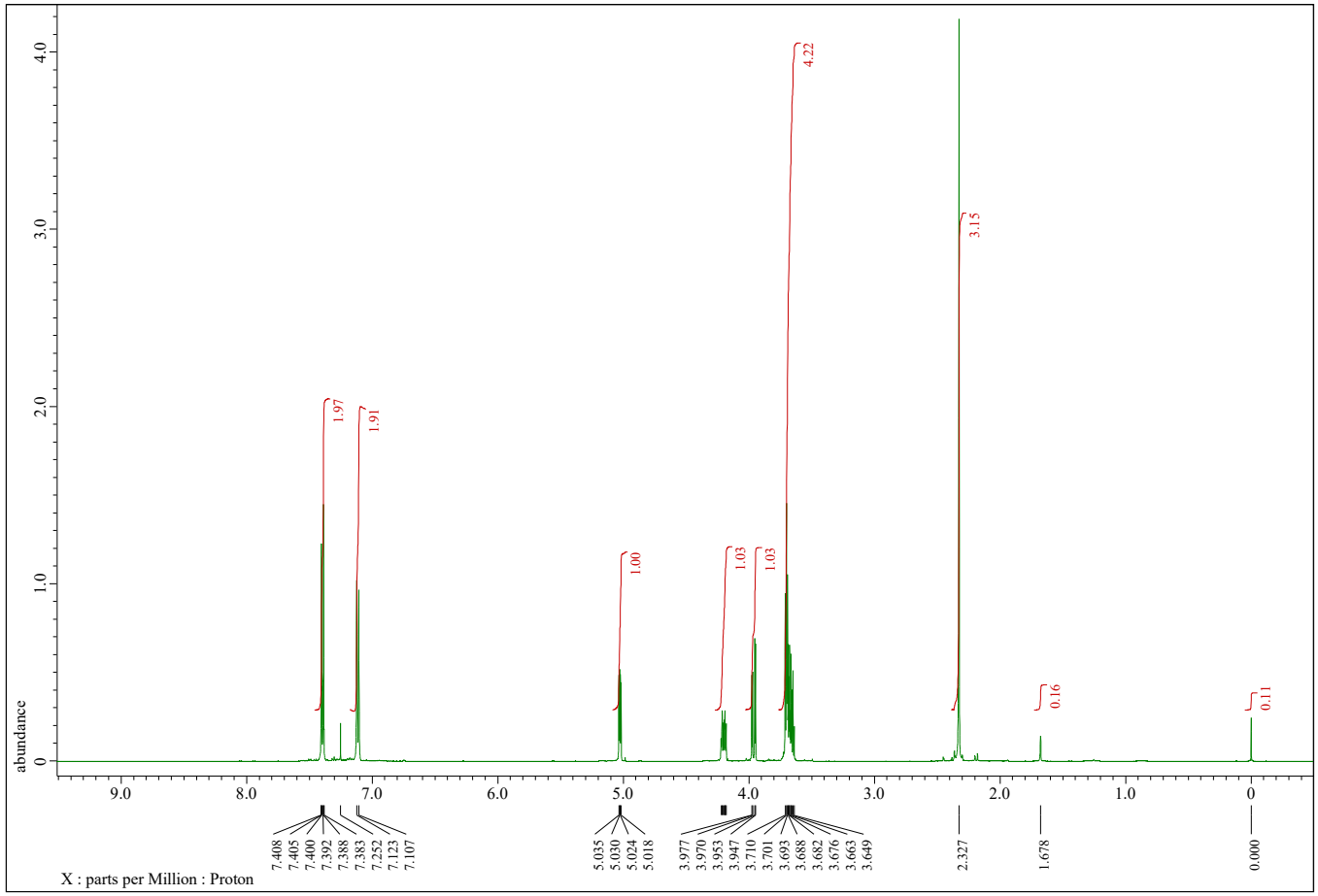
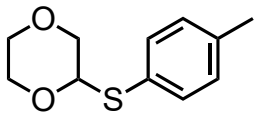


^{13}C NMR spectrum of the compound (3.17)



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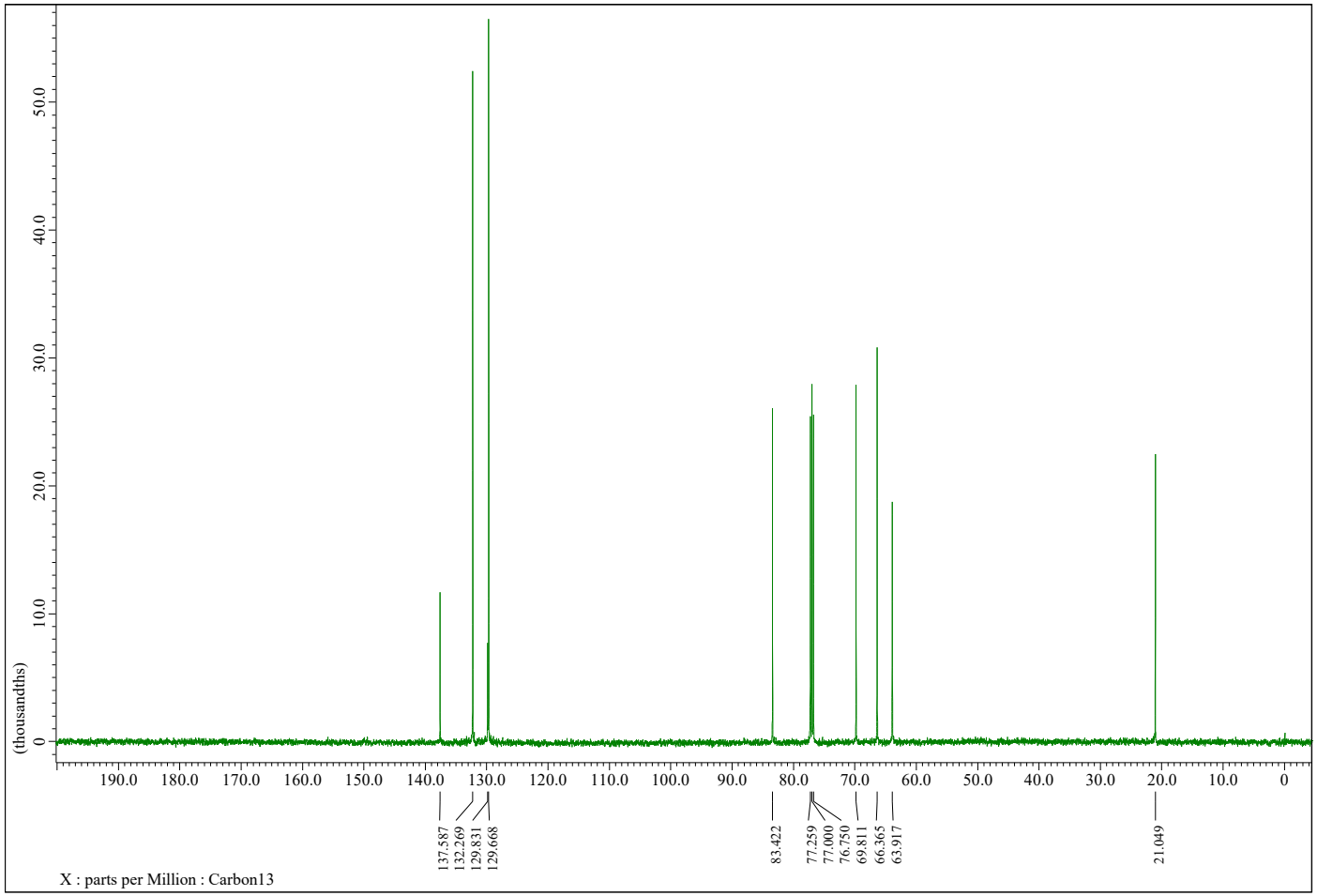
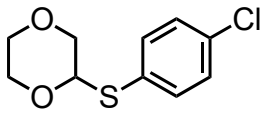


^{1}H NMR spectrum of the compound (3.18)



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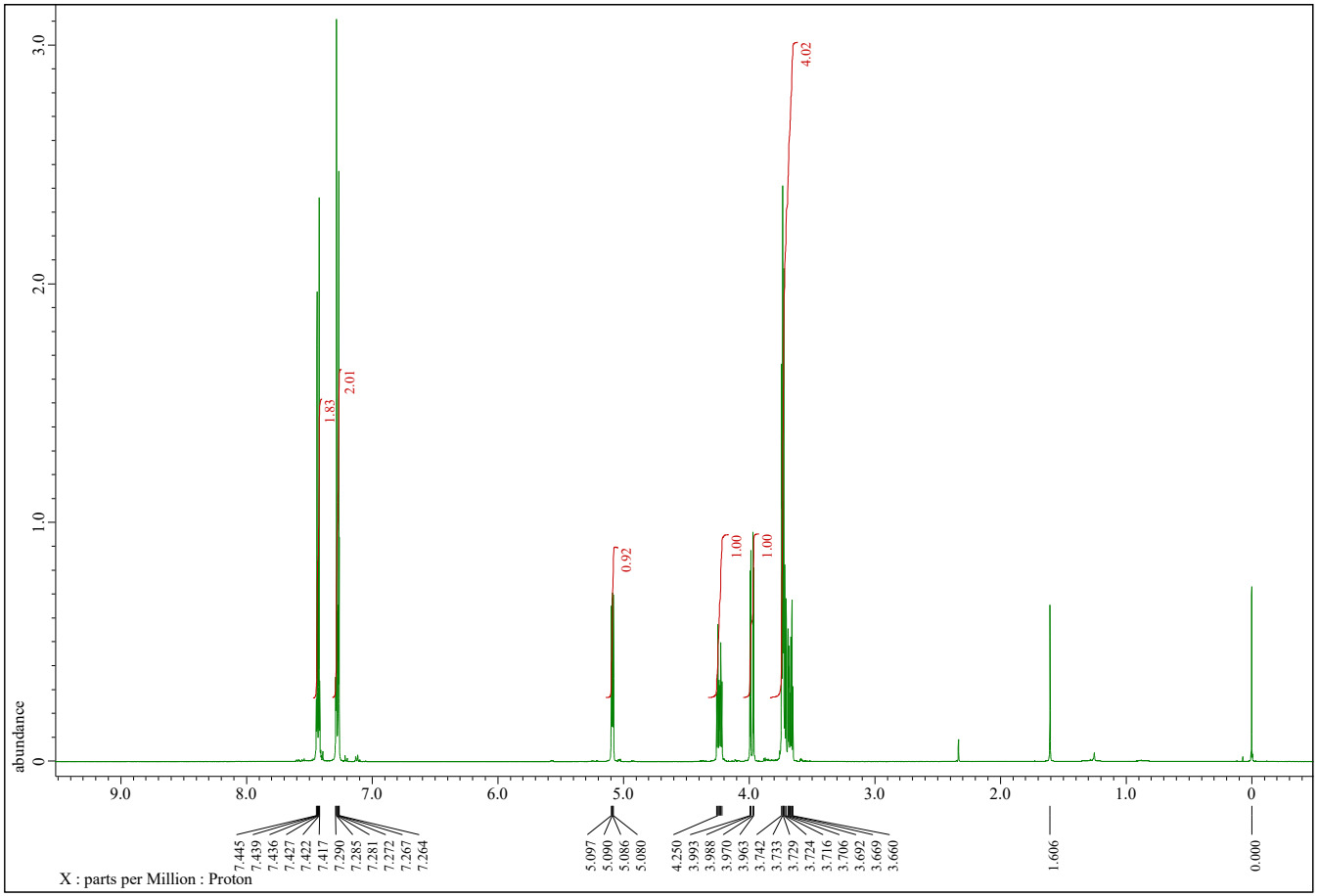
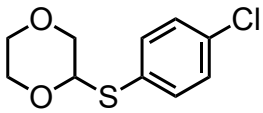


^{13}C NMR spectrum of the compound (3.18)



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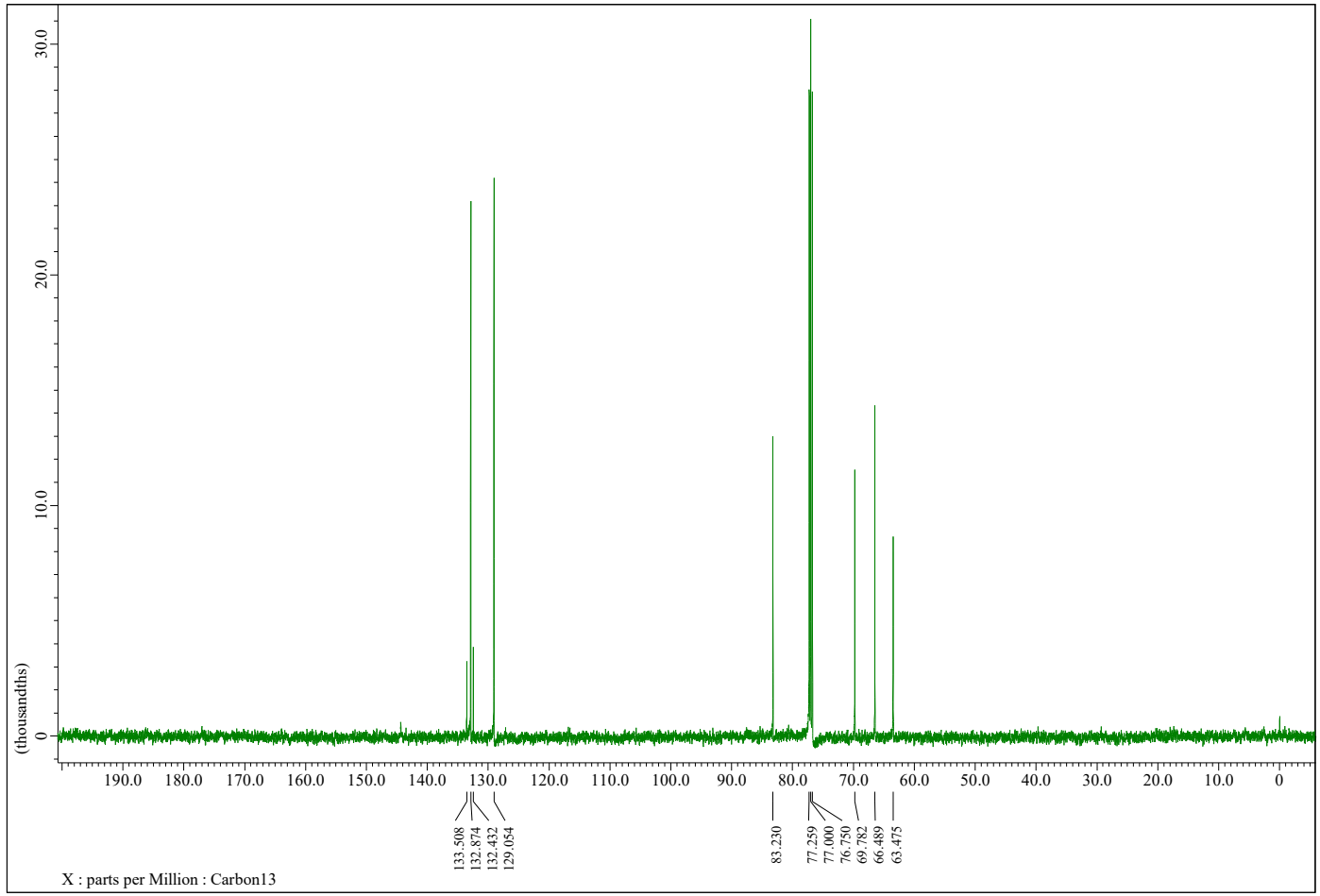
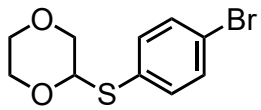


^{1}H NMR spectrum of the compound (3.19)



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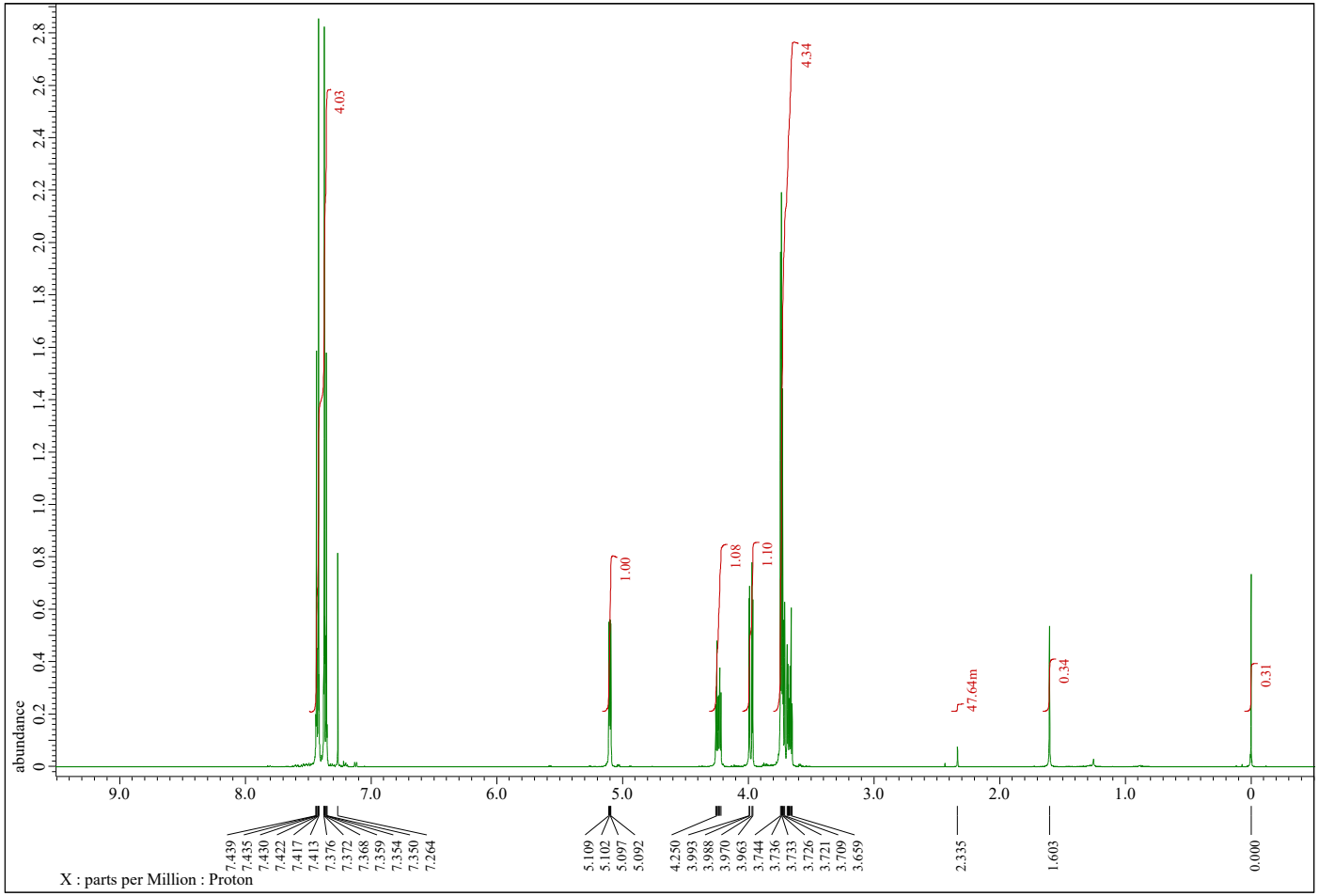
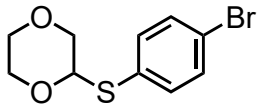


^{13}C NMR spectrum of the compound (3.19)



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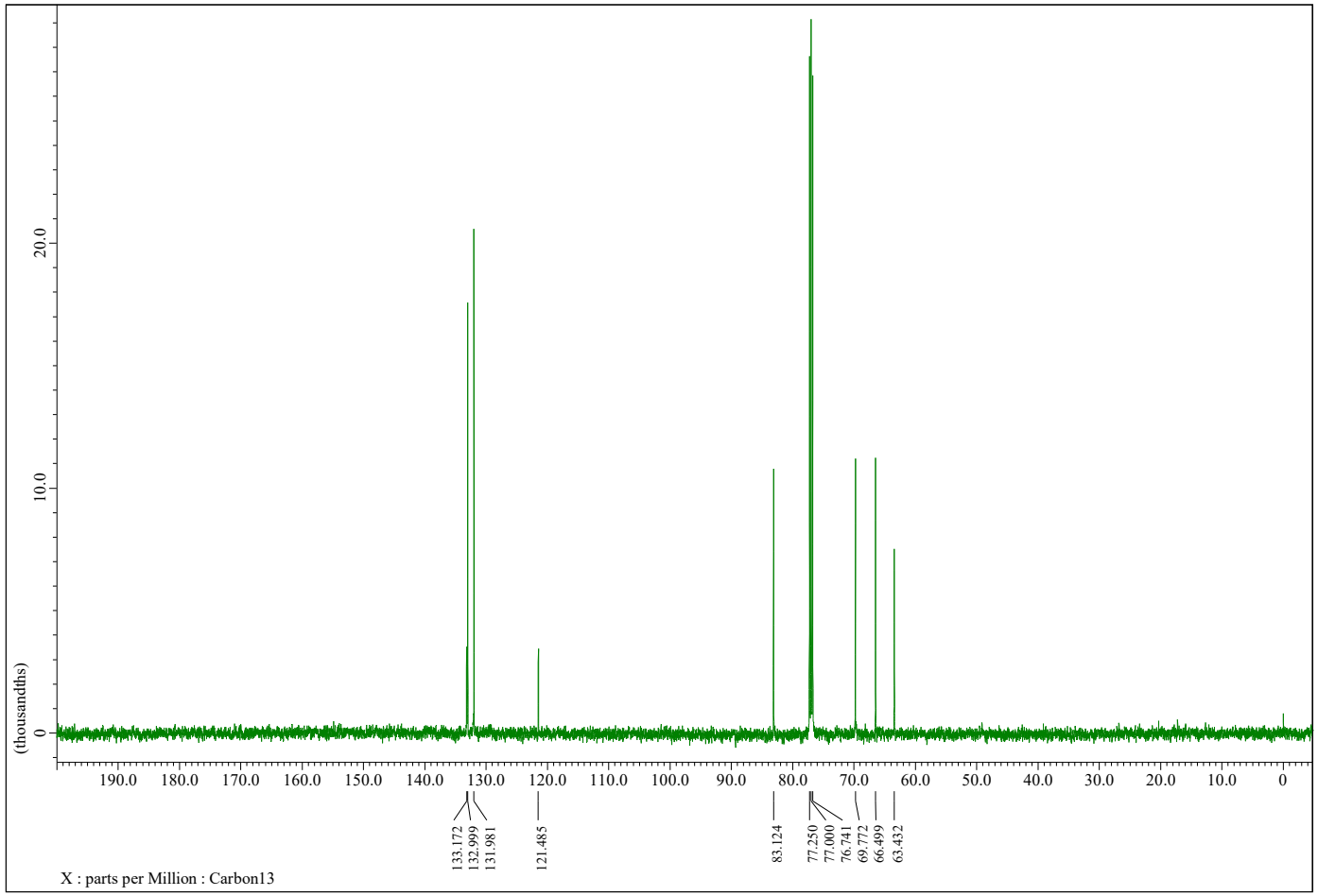
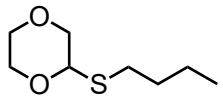


^{1}H NMR spectrum of the compound (3.20)



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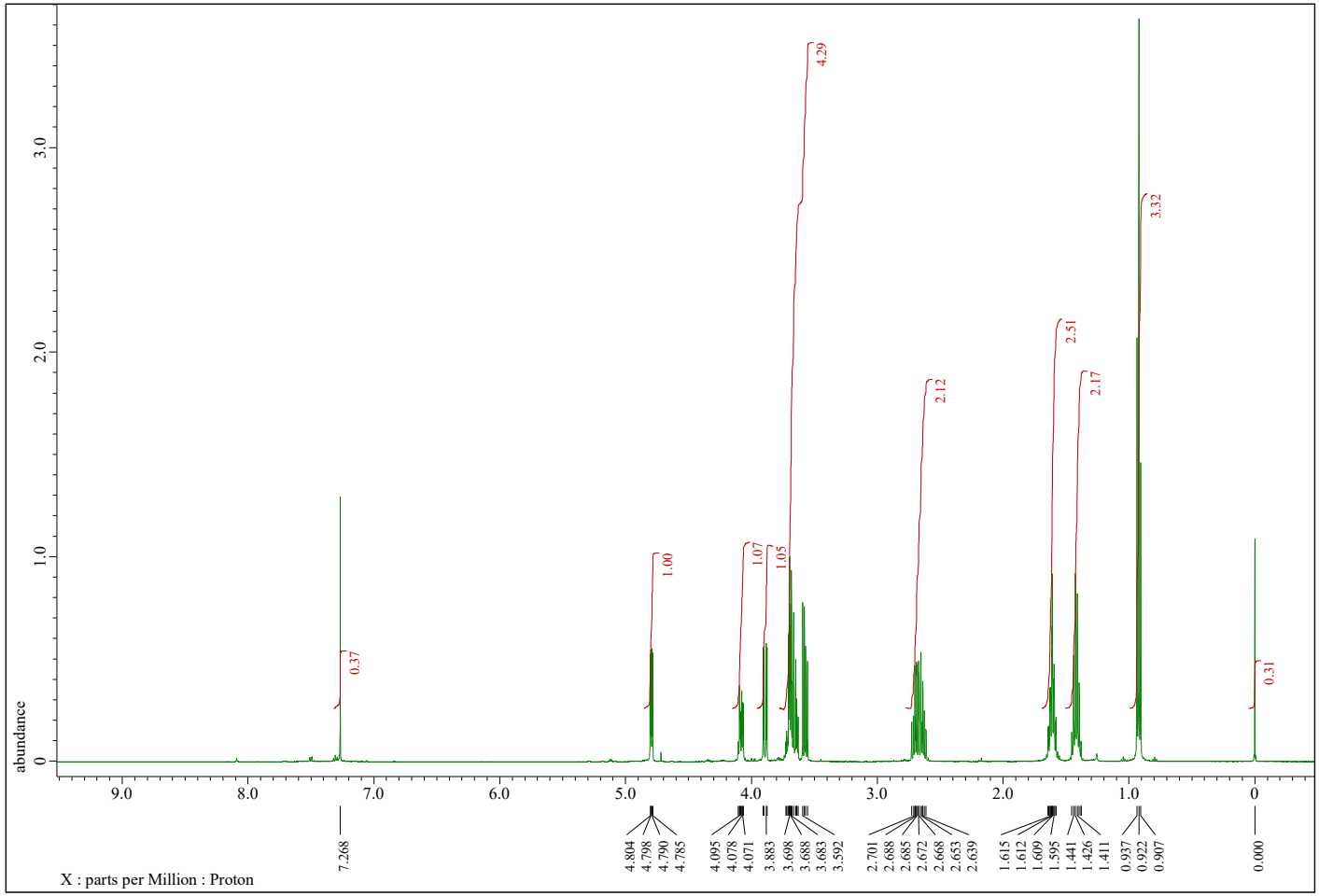
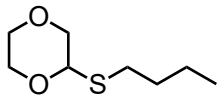


^{13}C NMR spectrum of the compound (3.20)



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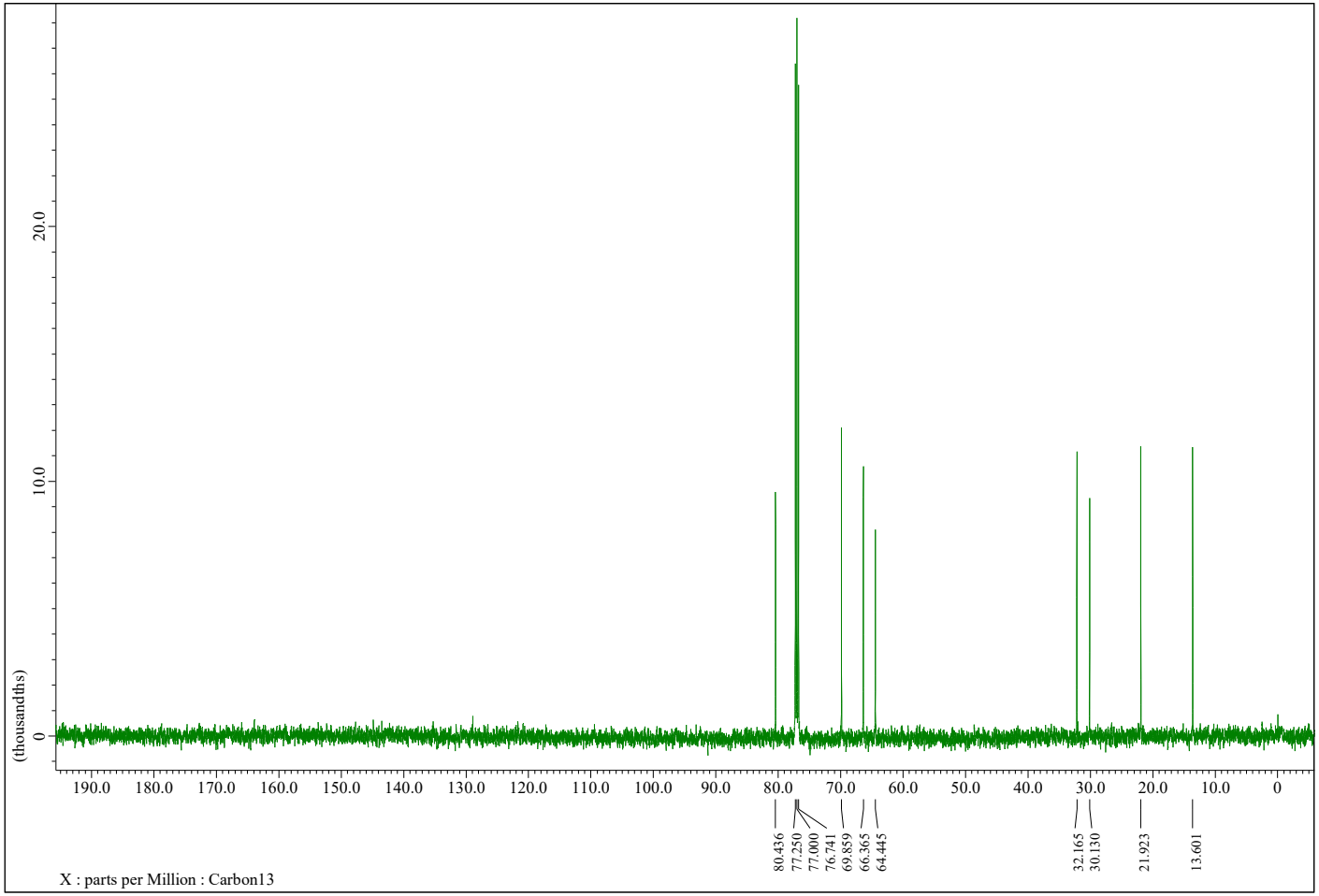
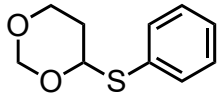


^{1}H NMR spectrum of the compound (3.21)



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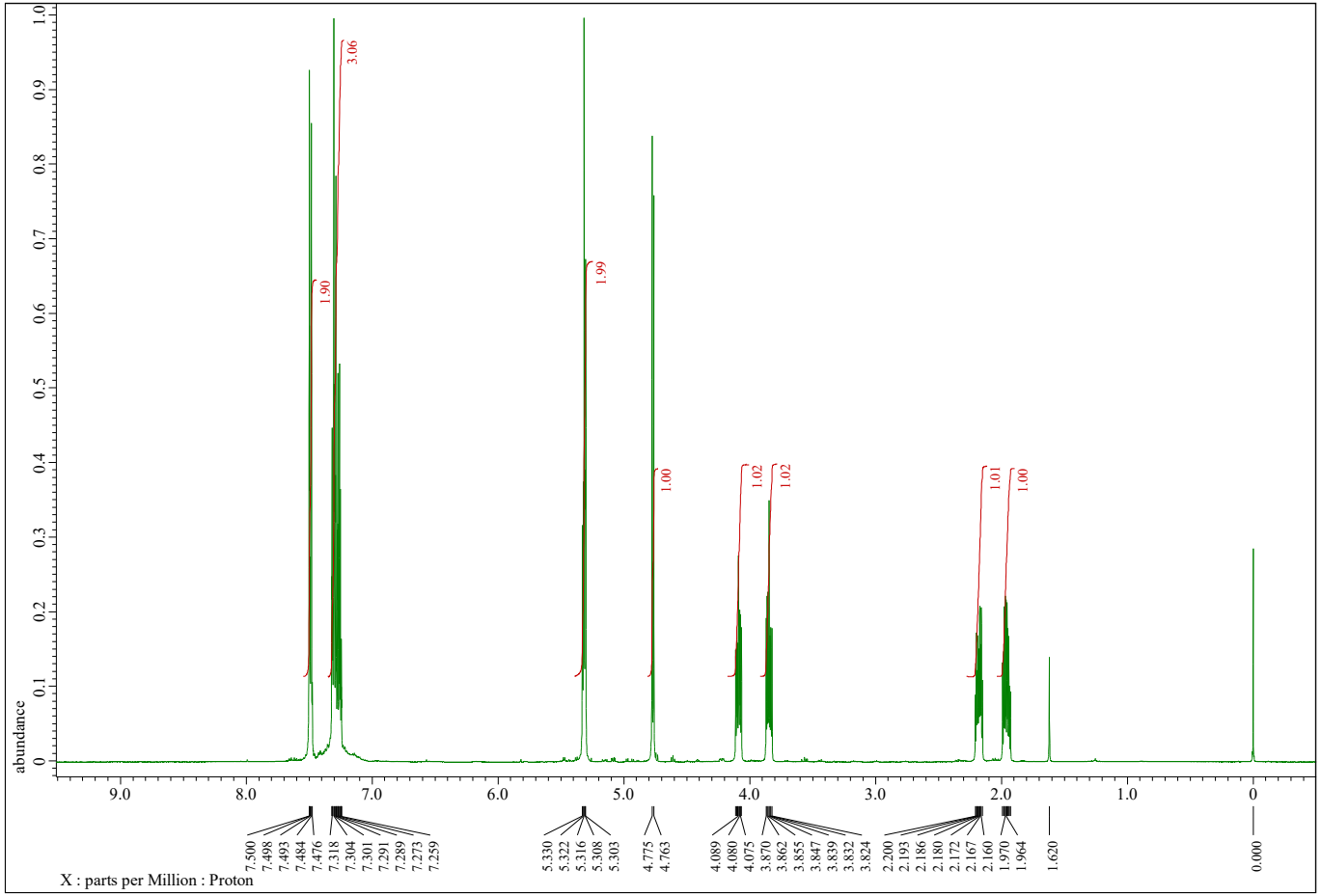
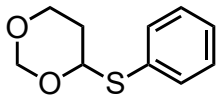


^{13}C NMR spectrum of the compound (3.21)



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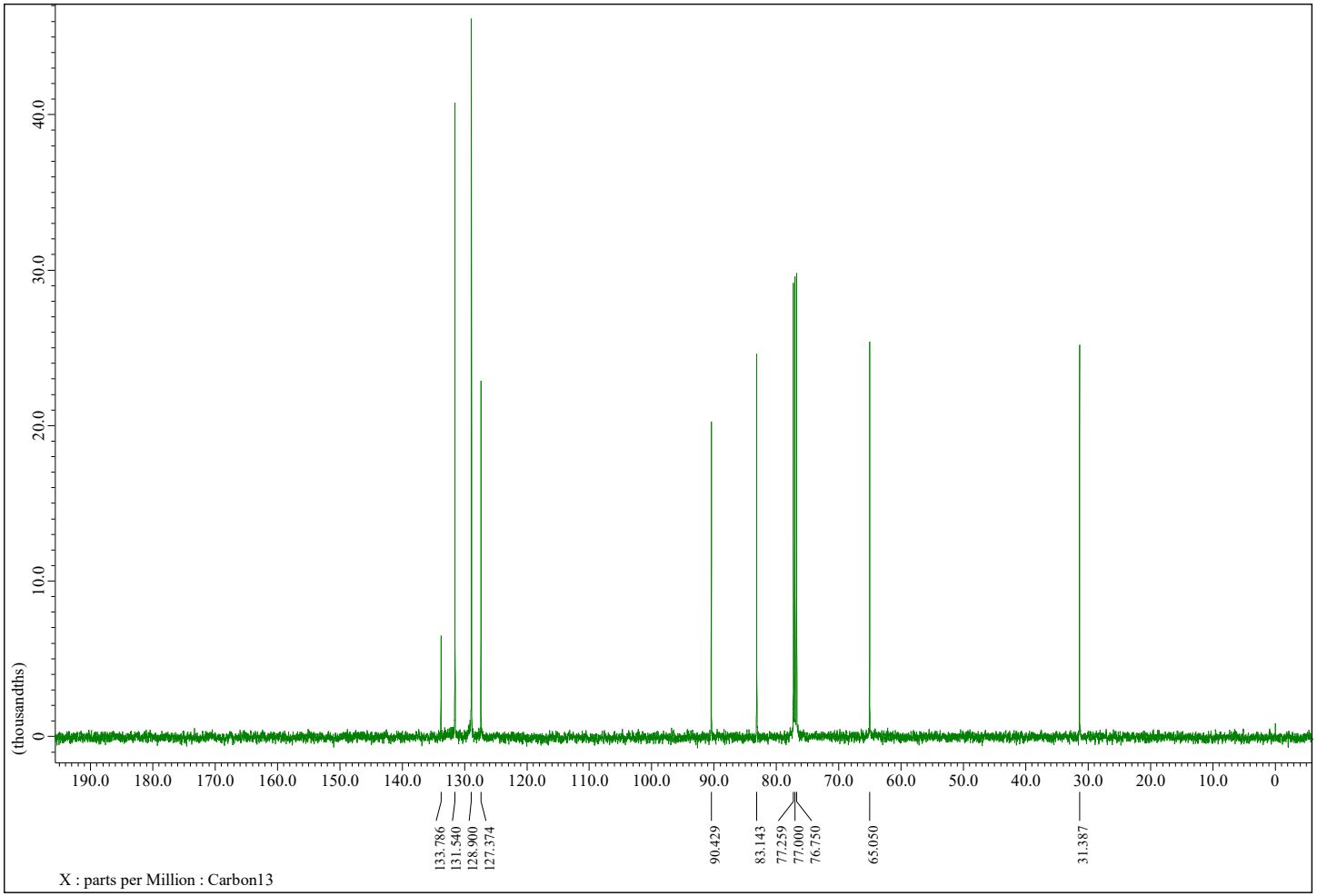

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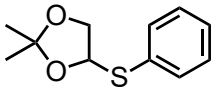

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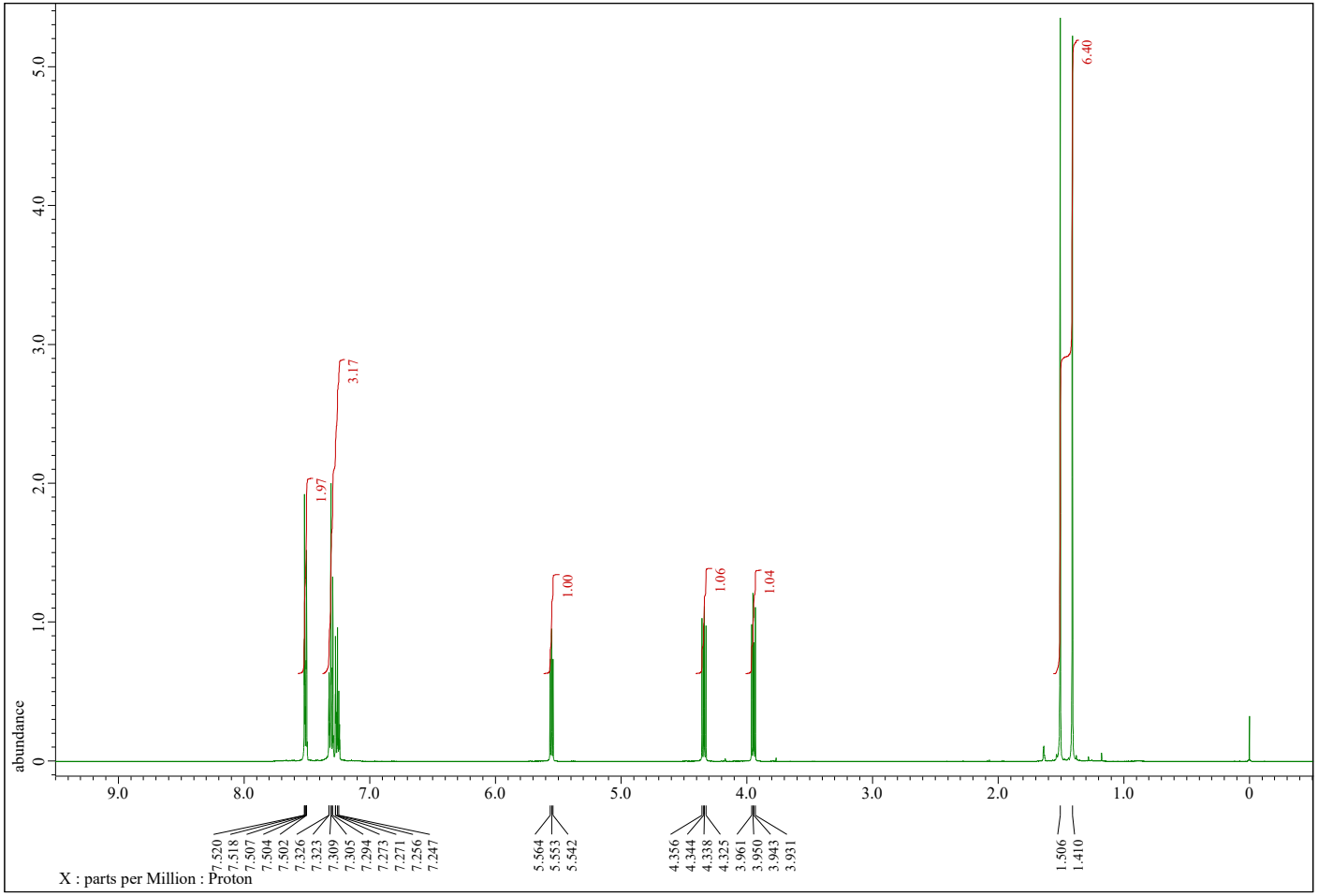
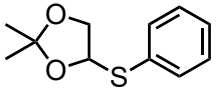


^{13}C NMR spectrum of the compound (3.22)



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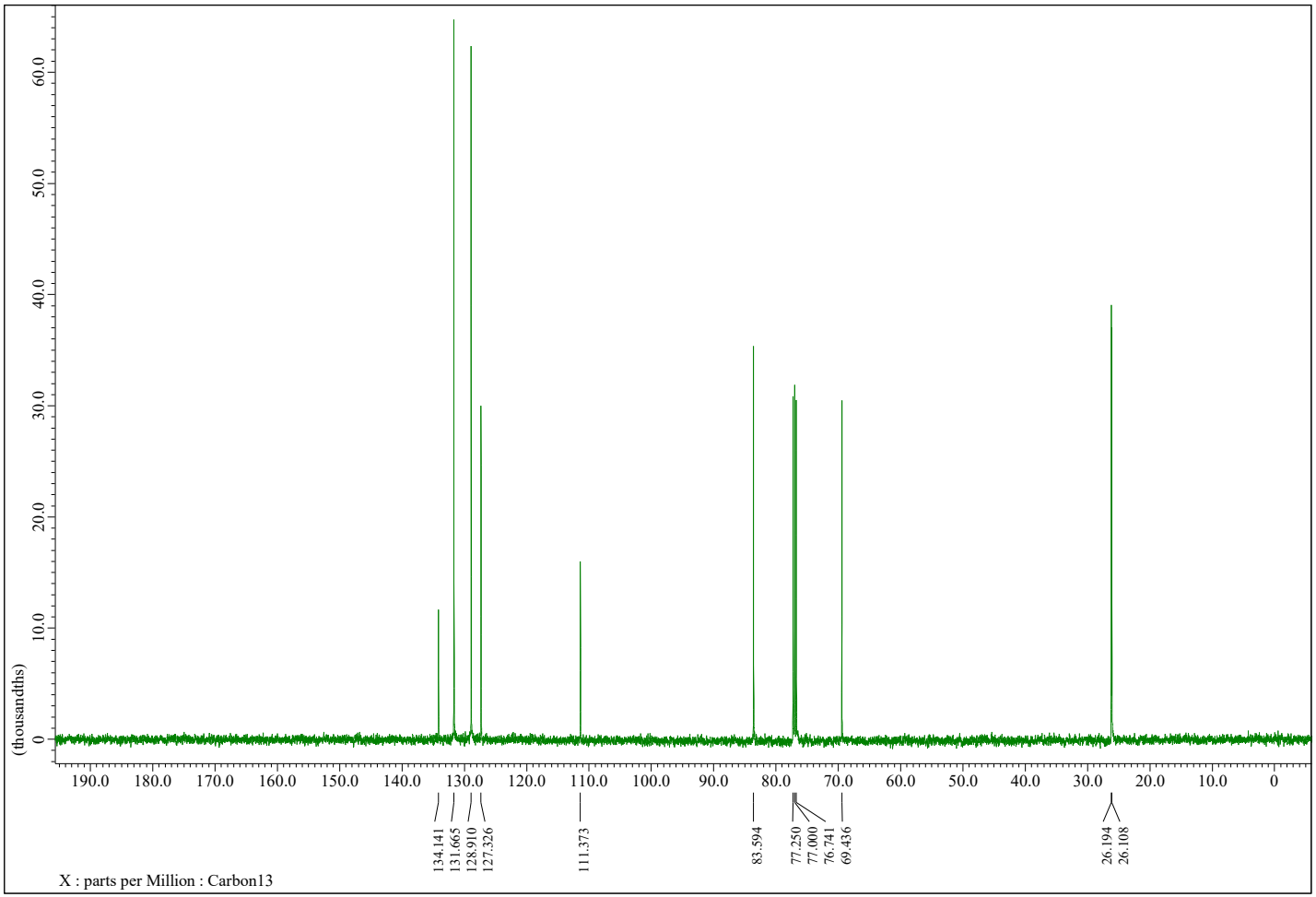

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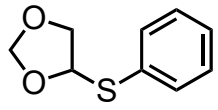

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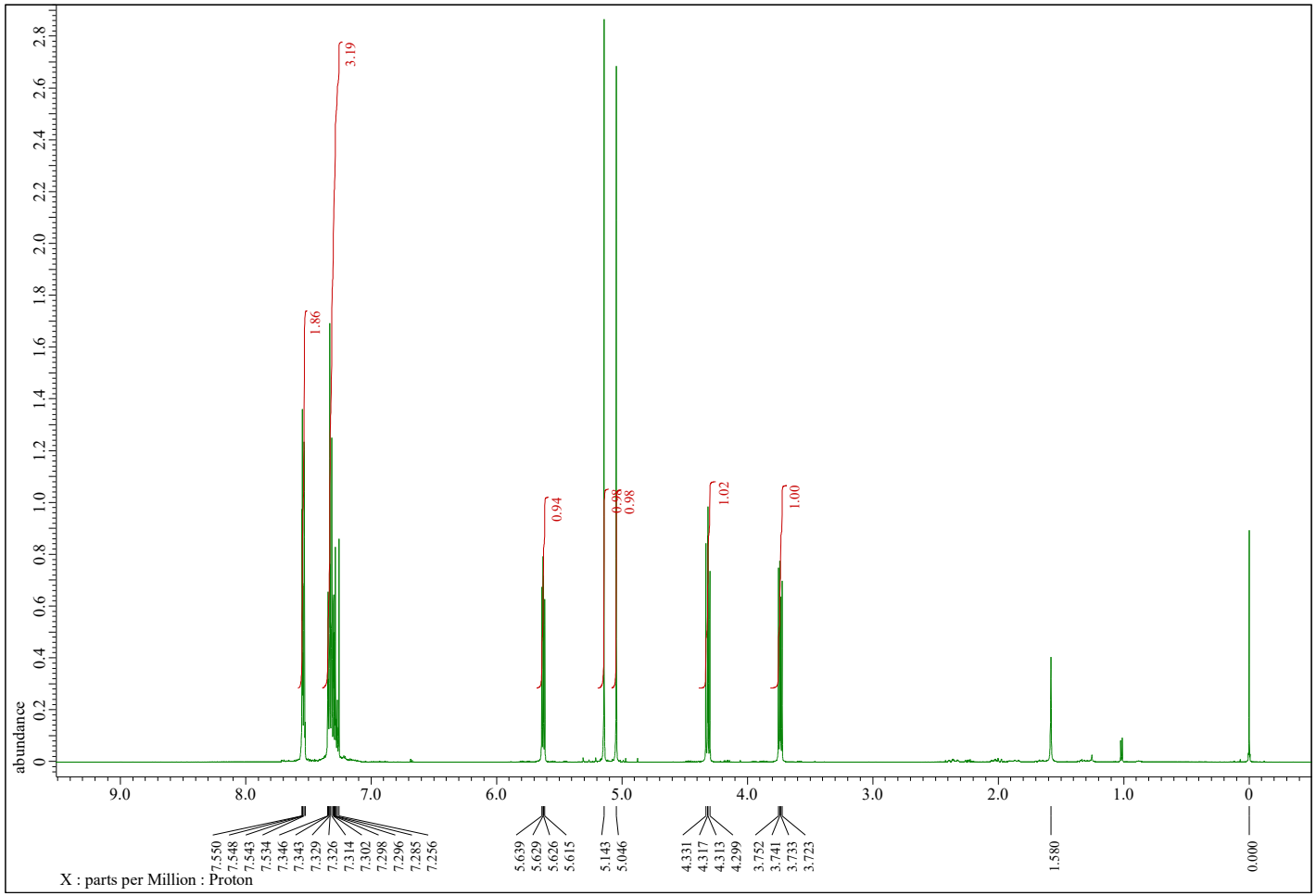
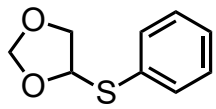


^{13}C NMR spectrum of the compound (3.23)



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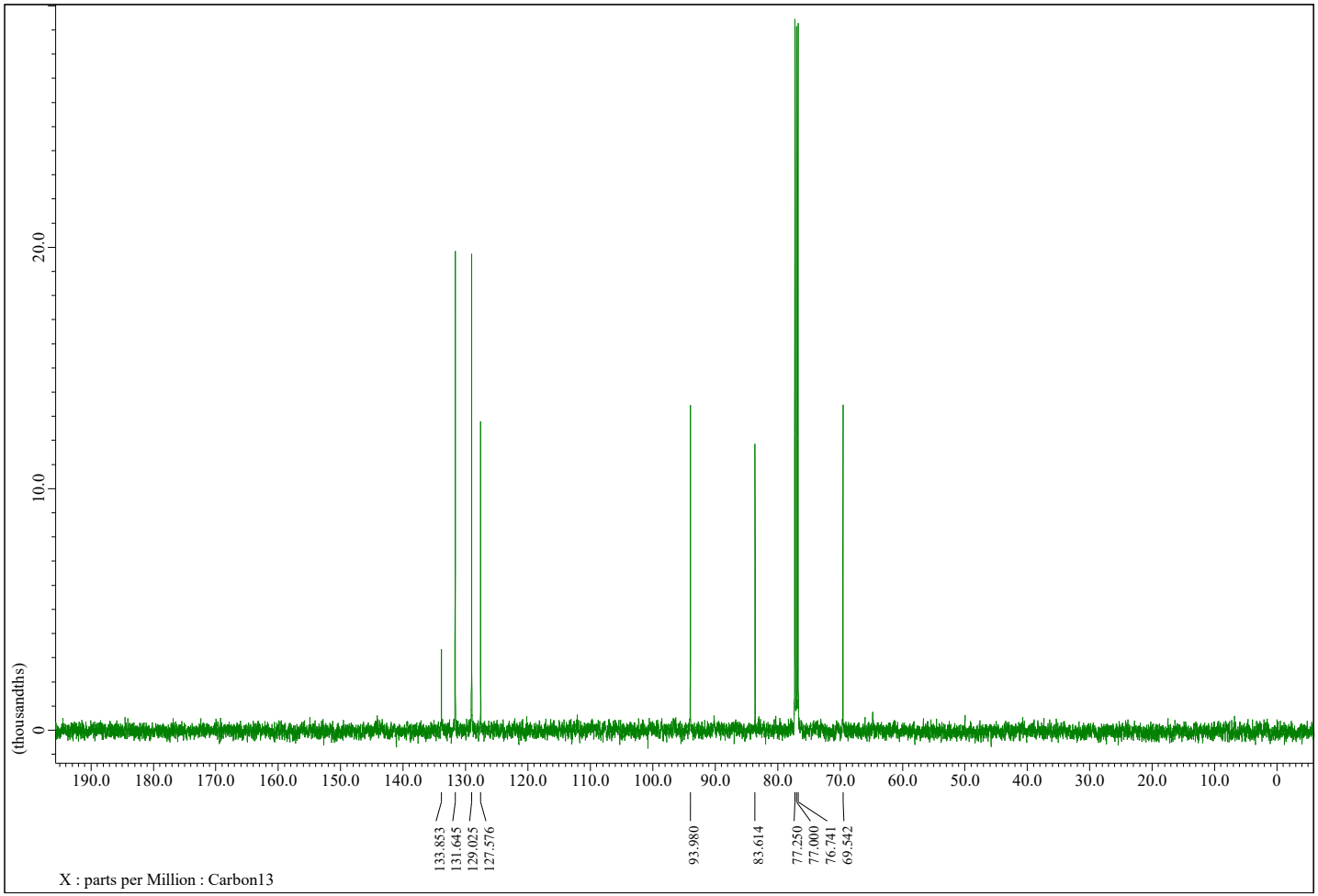
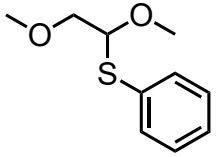


^{1}H NMR spectrum of the compound (3.24)



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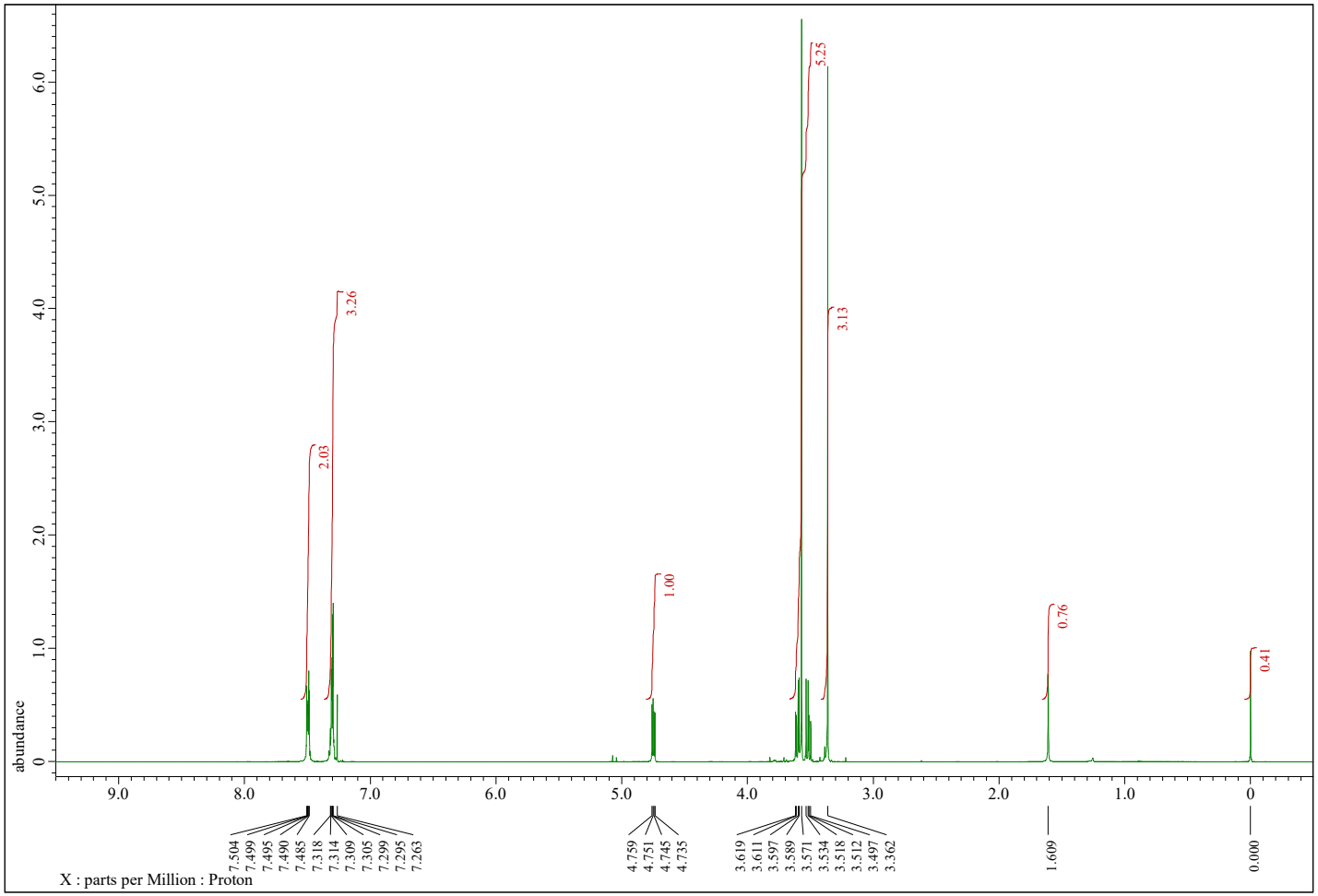
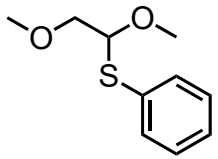


^{13}C NMR spectrum of the compound (3.24)



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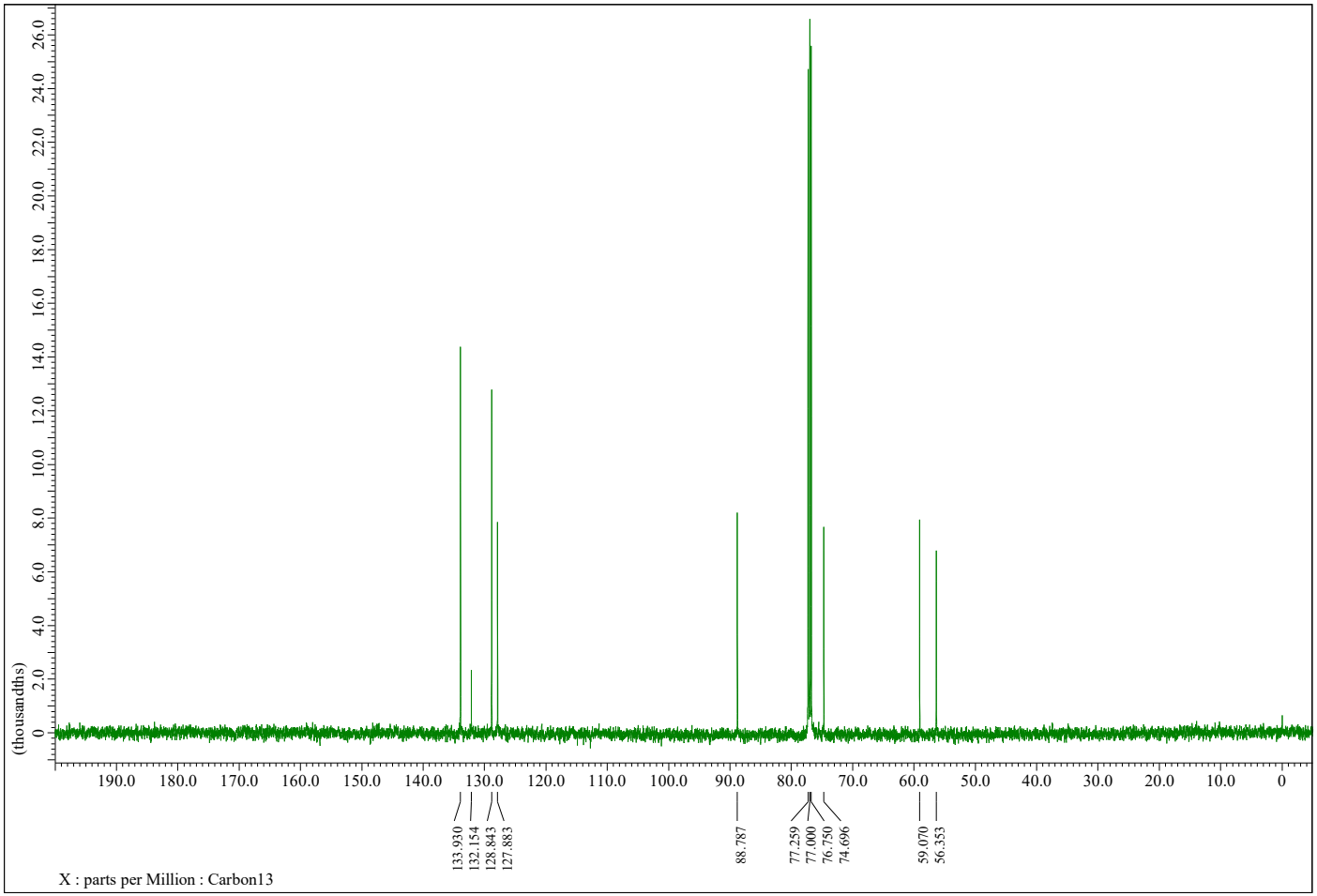
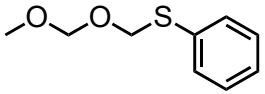


^{1}H NMR spectrum of the compound (3.25)



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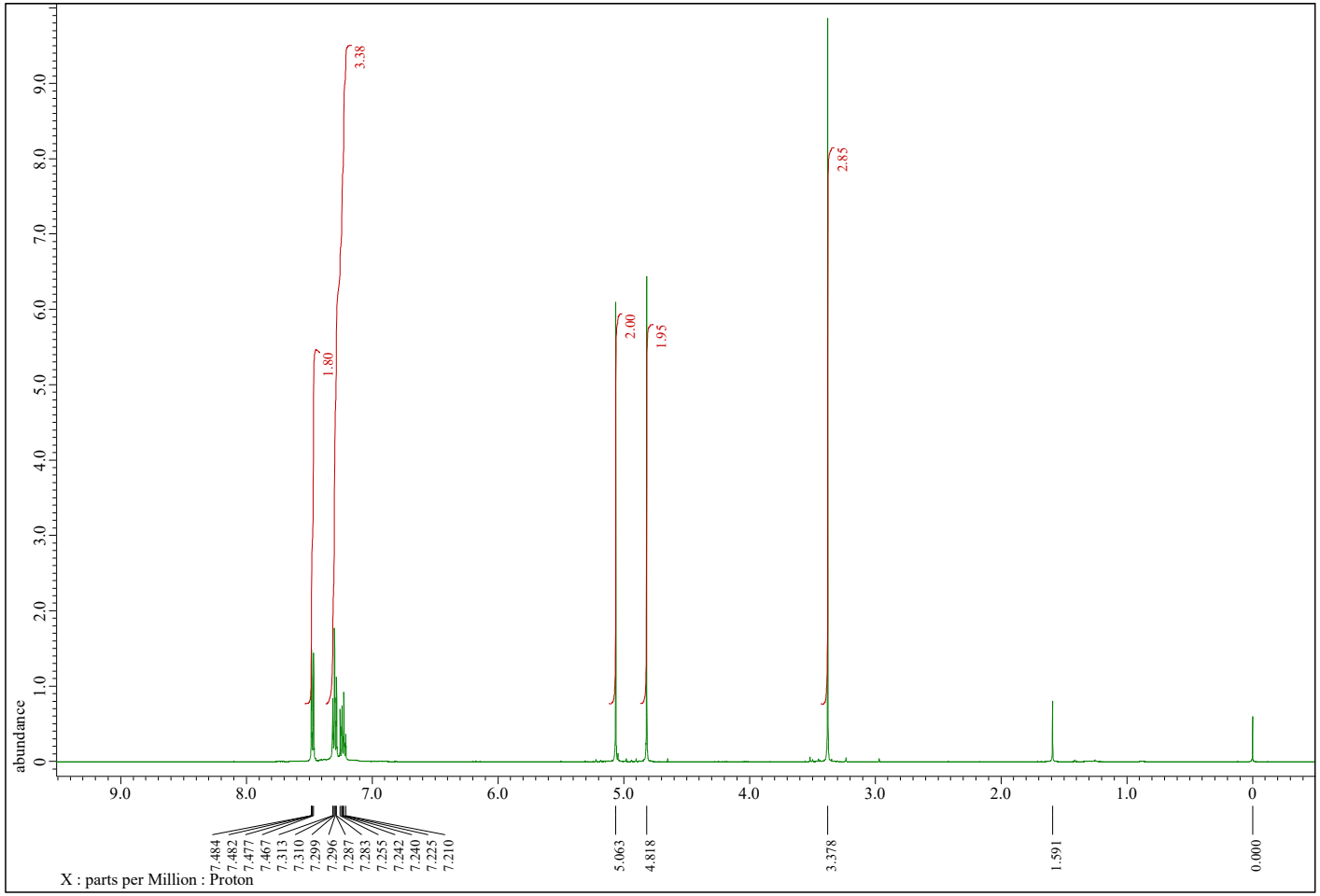
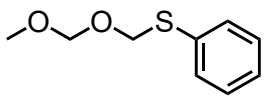


^{13}C NMR spectrum of the compound (3.25)



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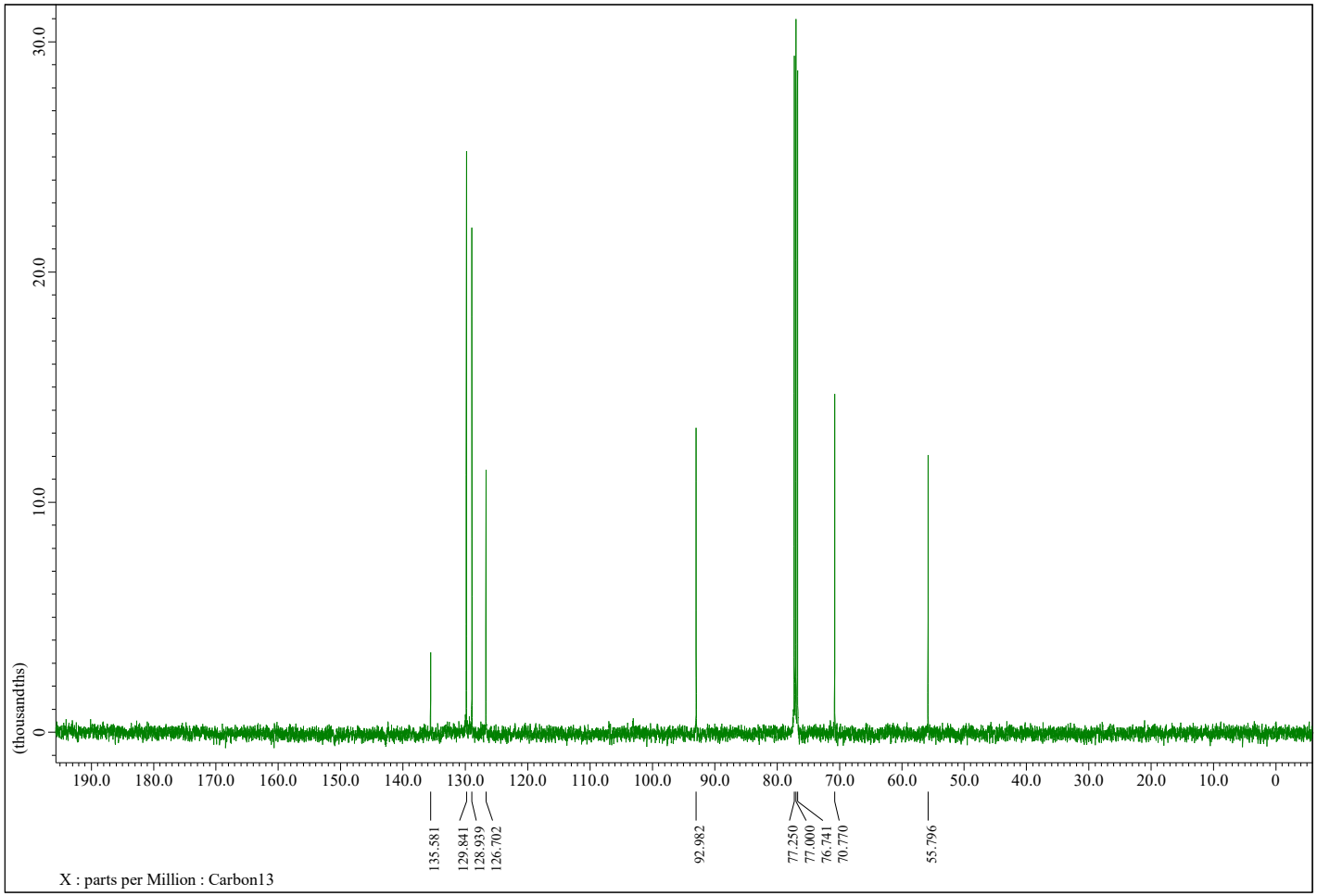
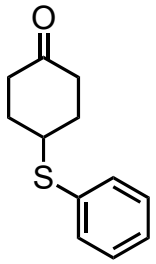


^{1}H NMR spectrum of the compound (3.26)



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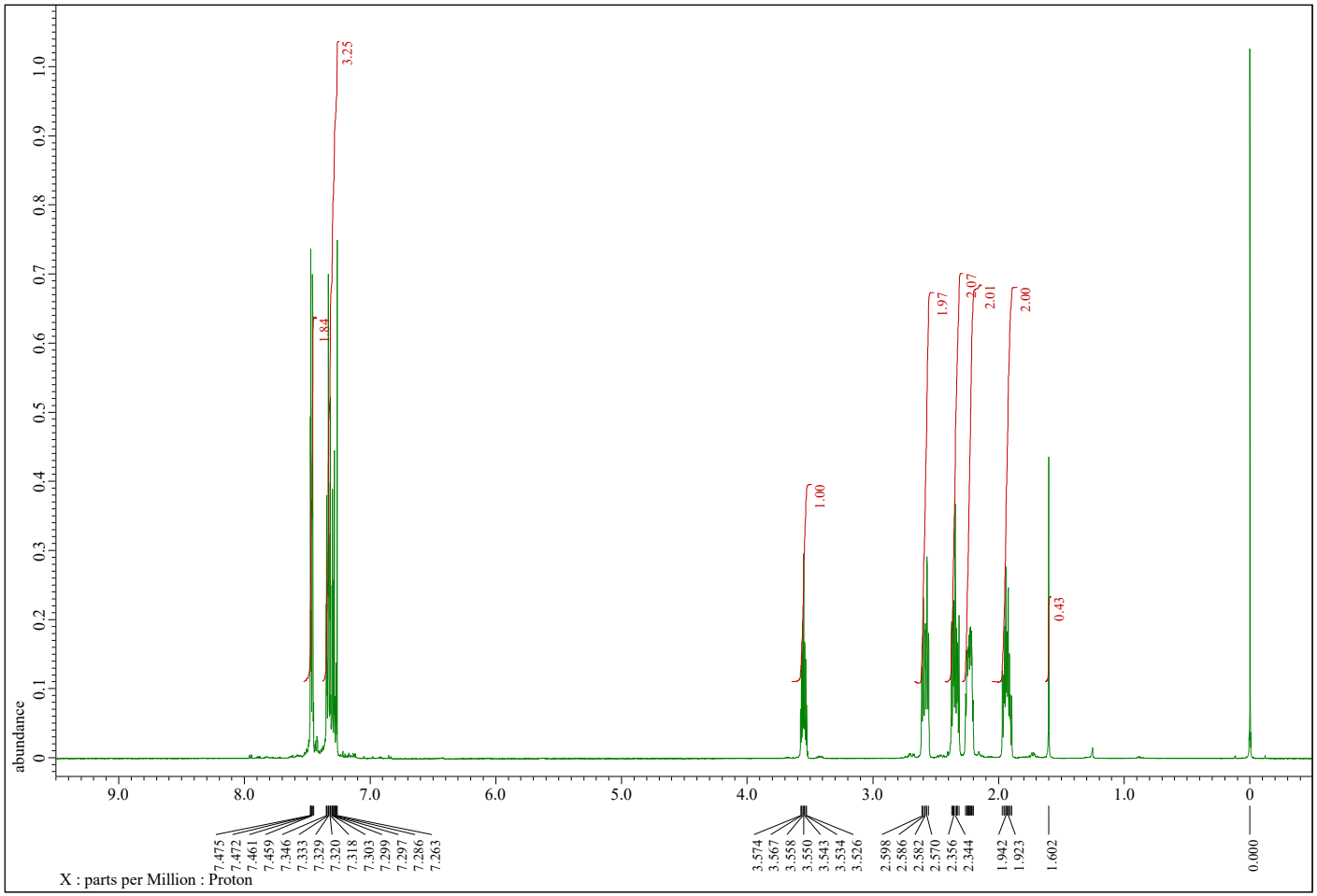
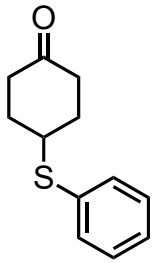


^{13}C NMR spectrum of the compound (3.26)



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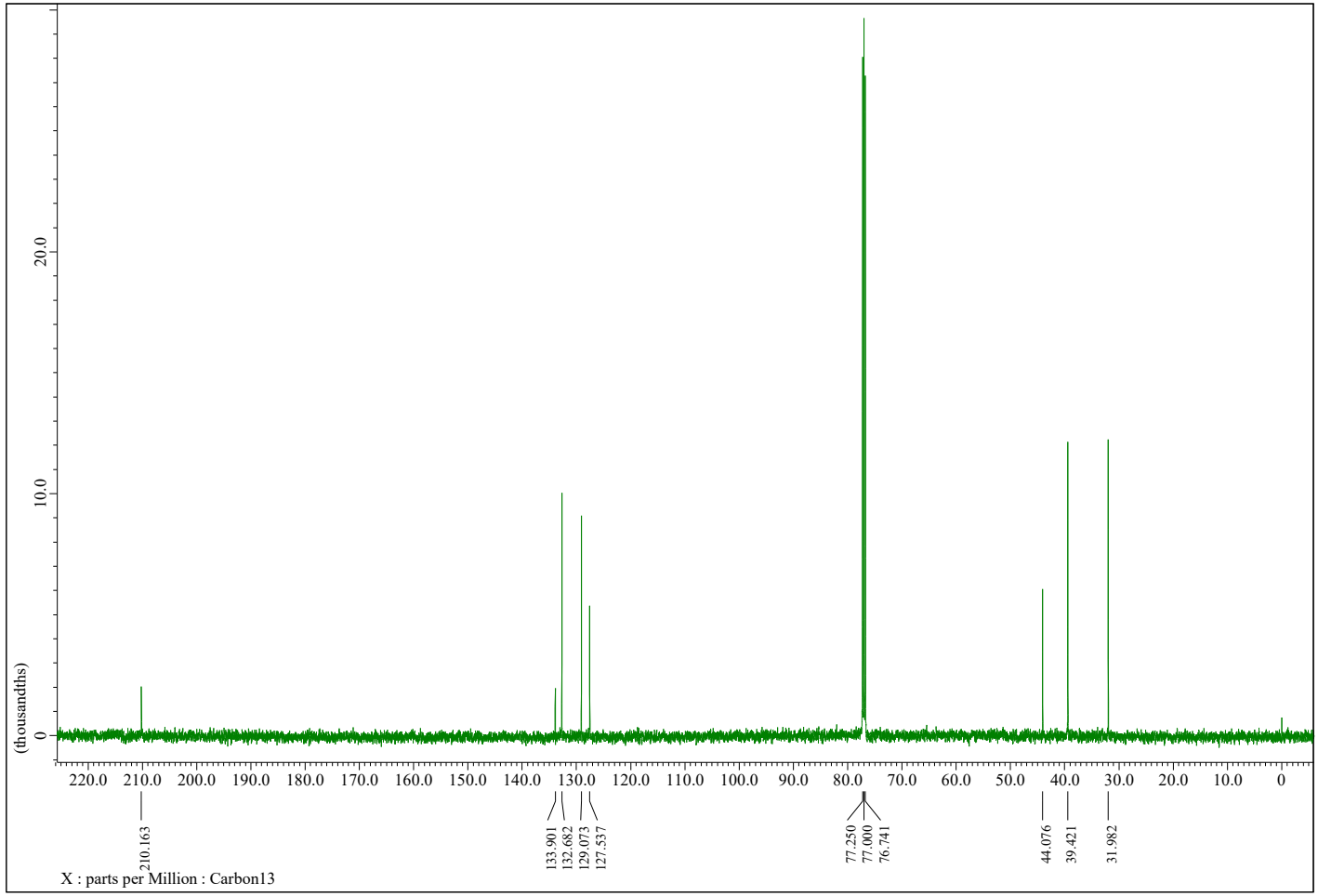
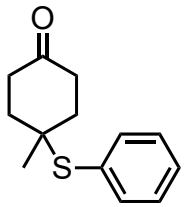


^{1}H NMR spectrum of the compound (3.27)



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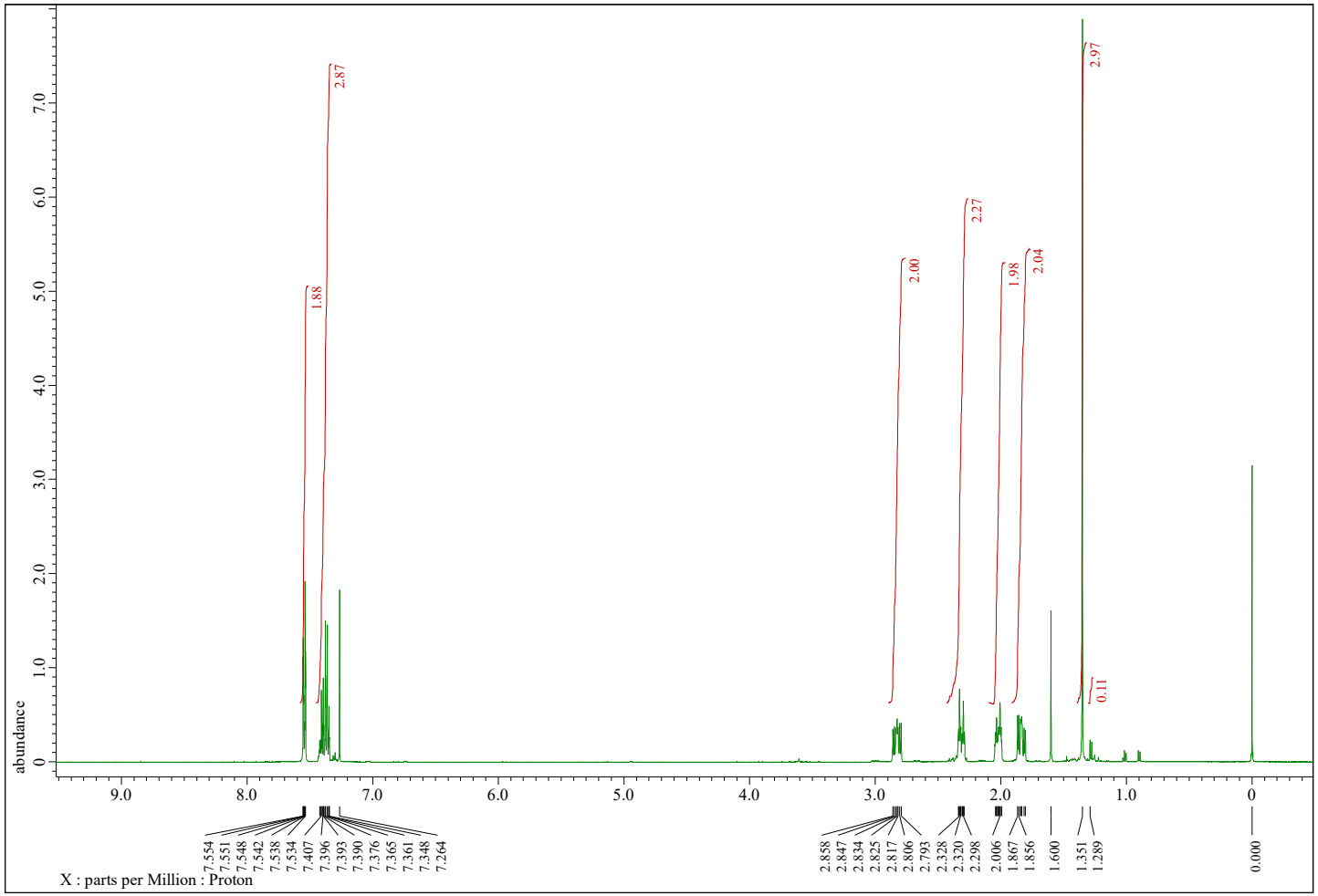
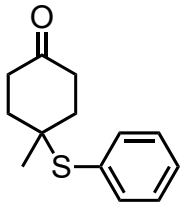


^{13}C NMR spectrum of the compound (3.27)



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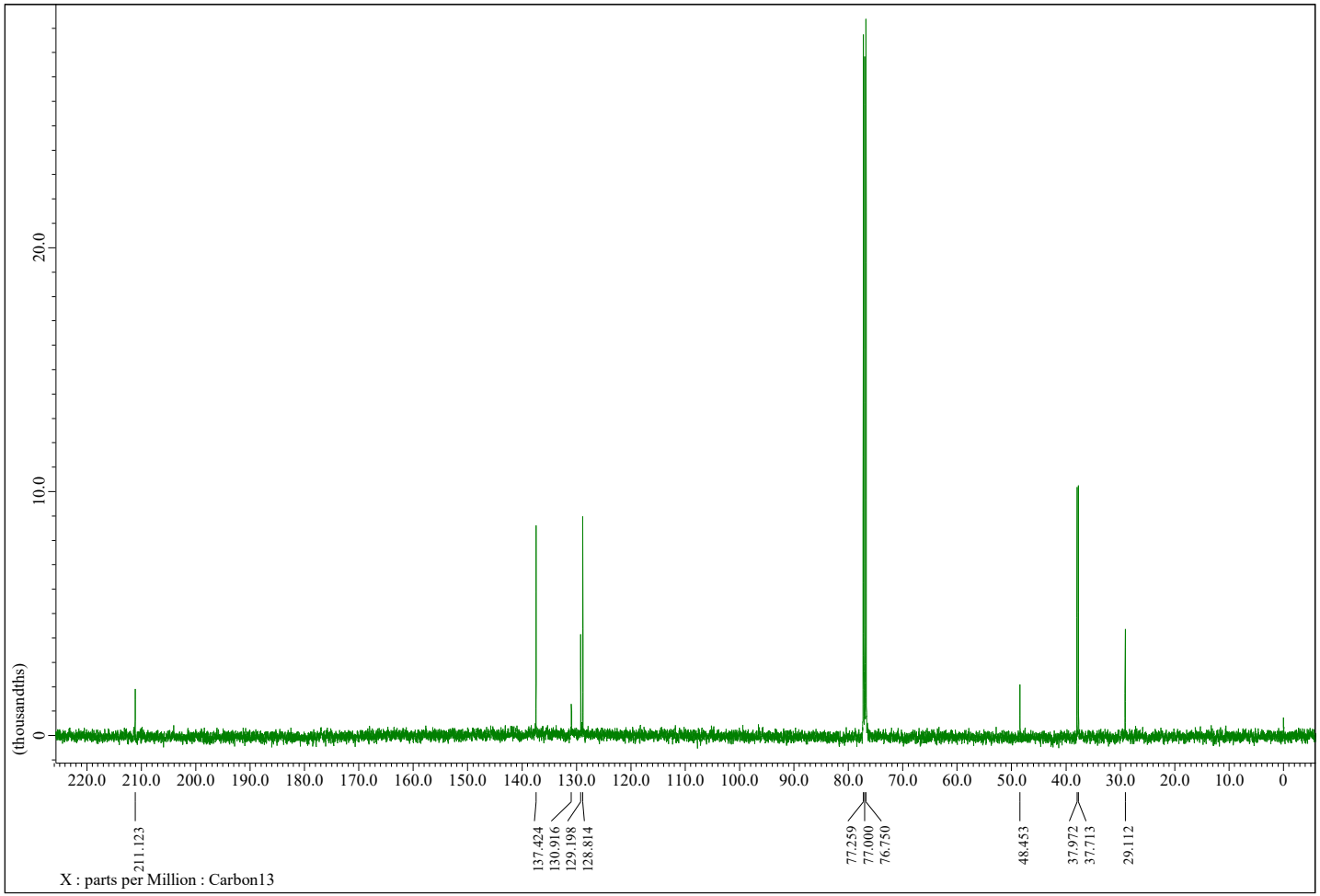
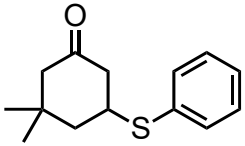


^{1}H NMR spectrum of the compound (3.28)



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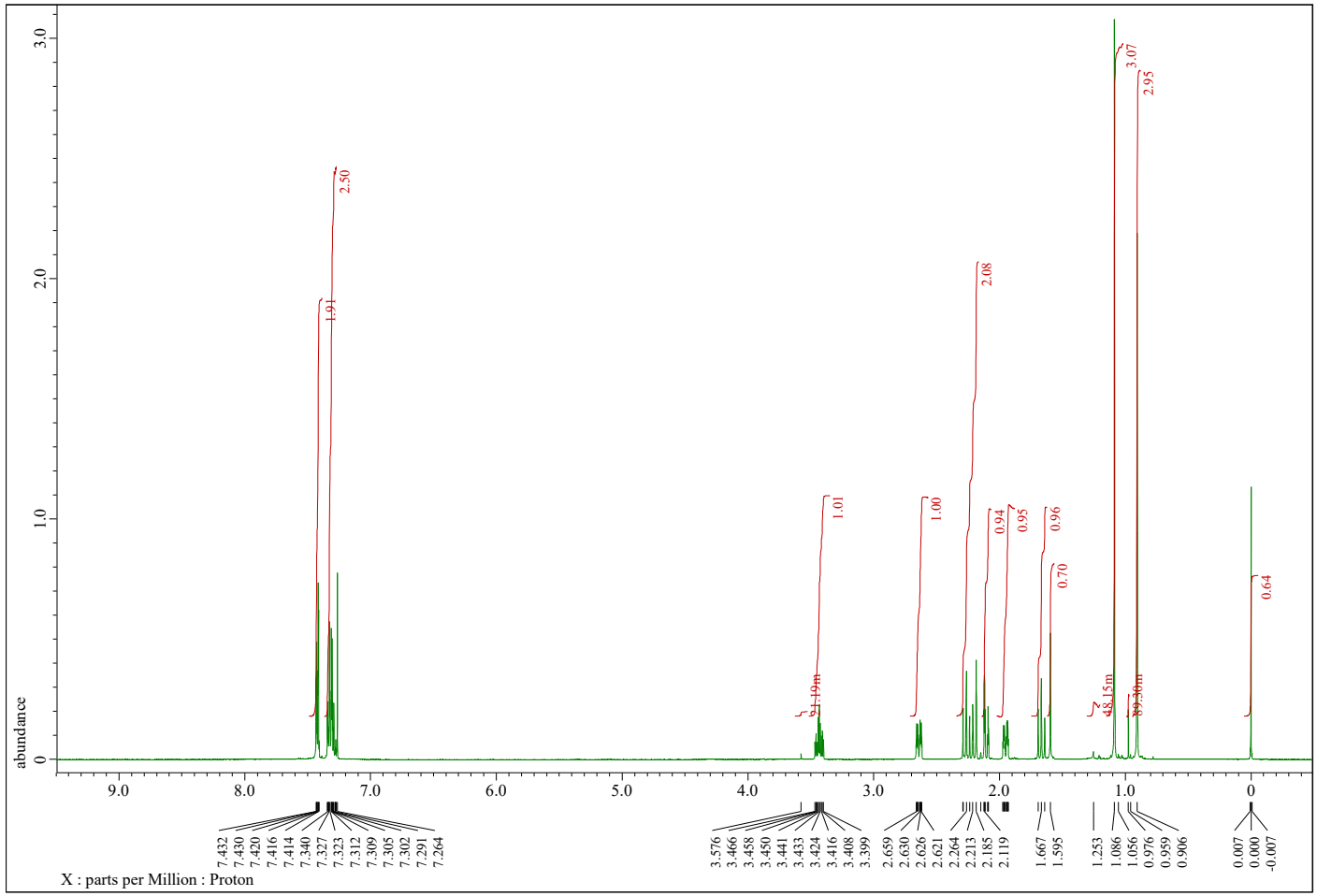
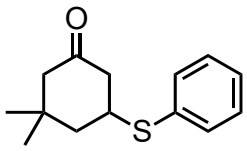


^{13}C NMR spectrum of the compound (3.28)



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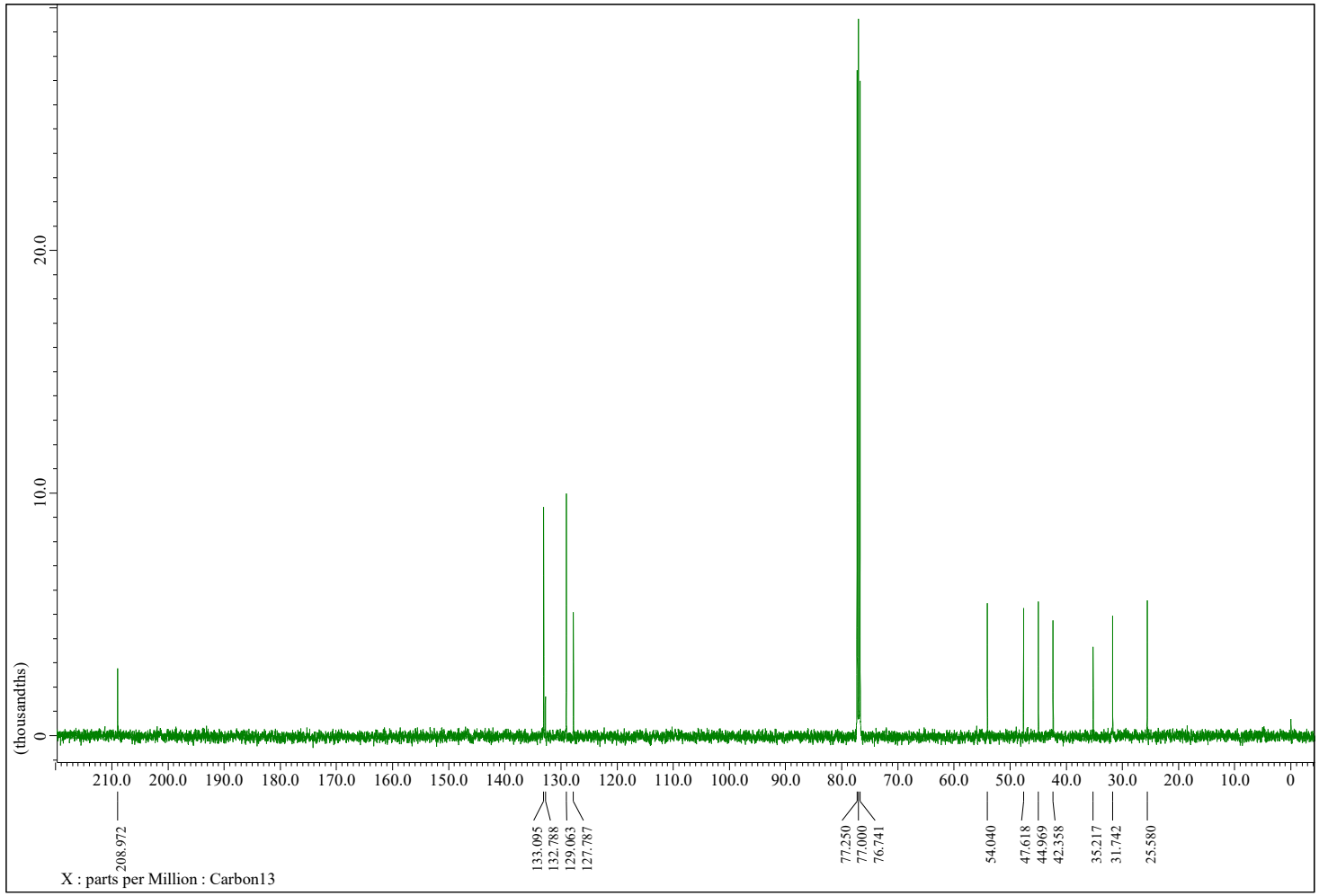
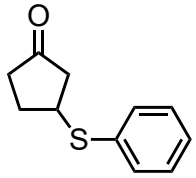
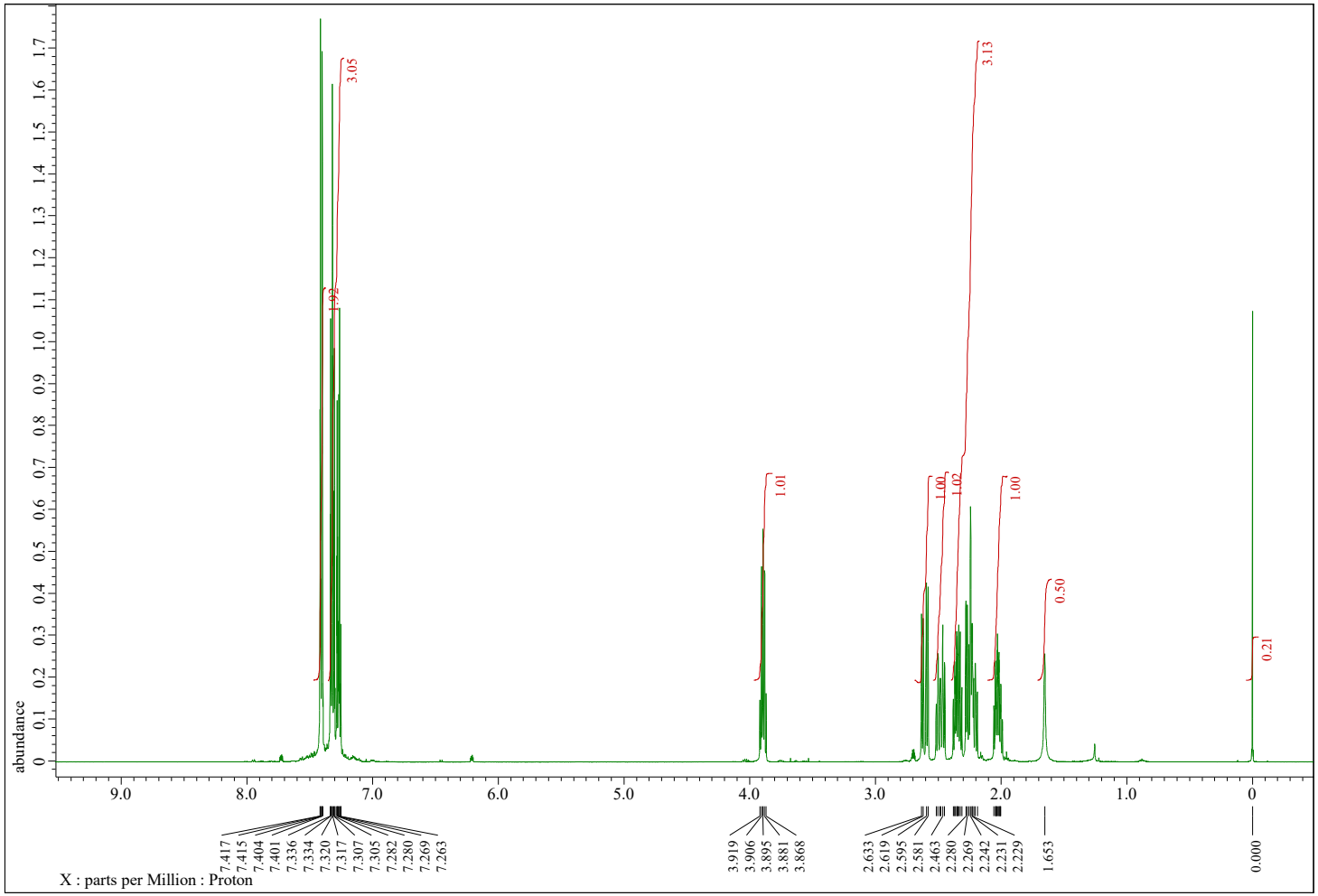


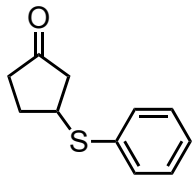
^{1}H NMR spectrum of the compound (3.29)



3.29



^{13}C NMR spectrum of the compound (3.29)



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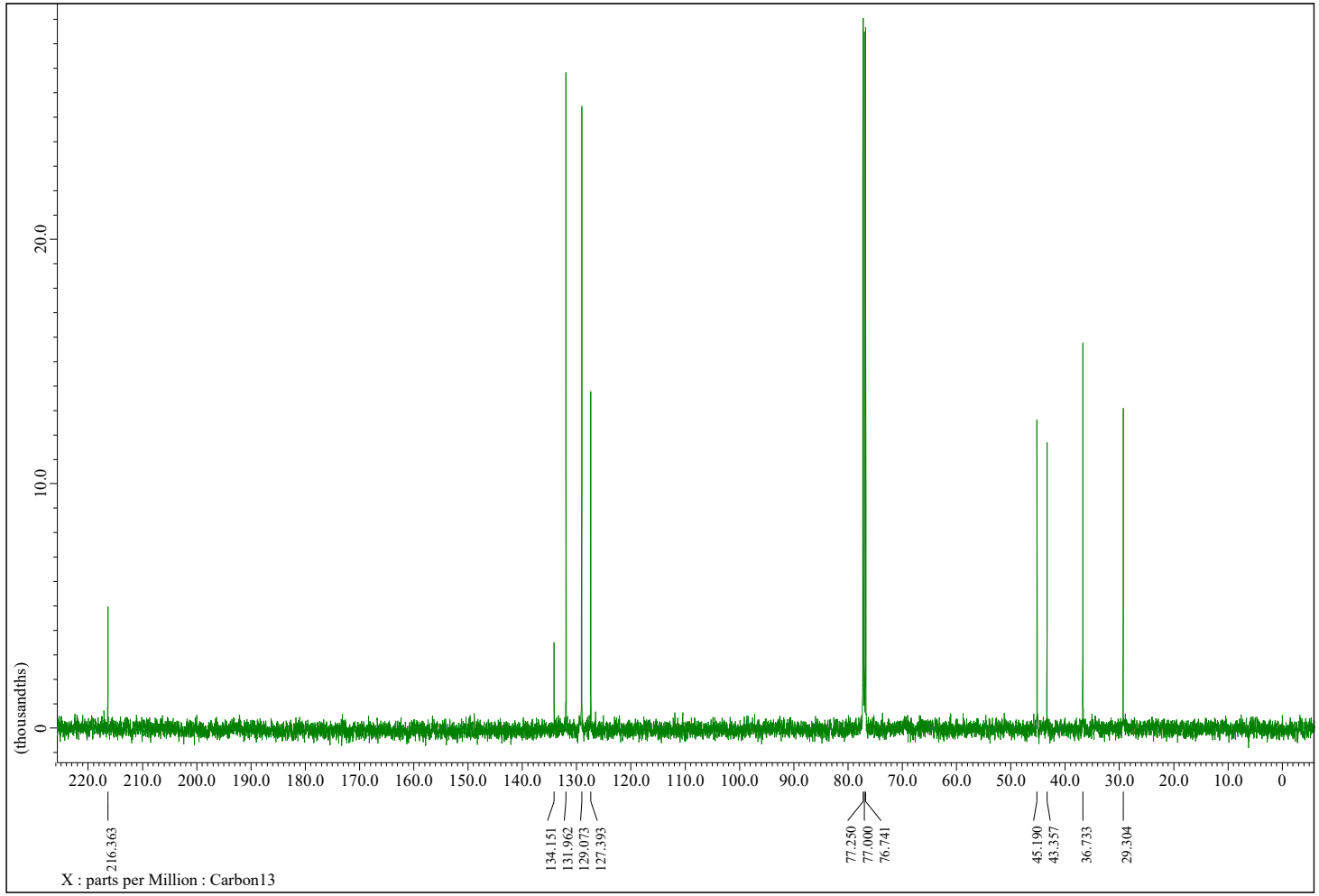
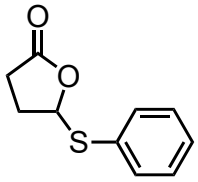


^{1}H NMR spectrum of the compound (3.30)



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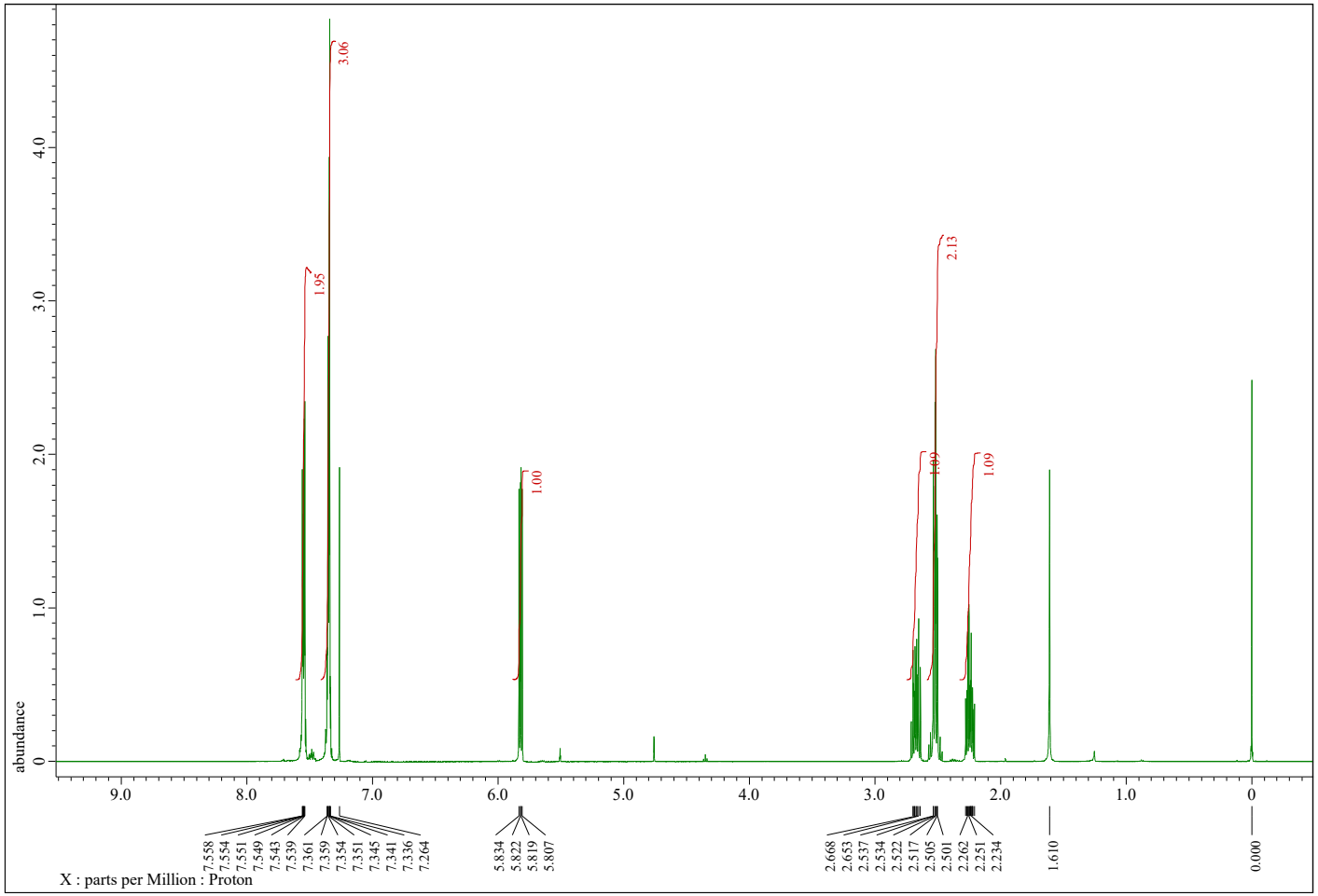
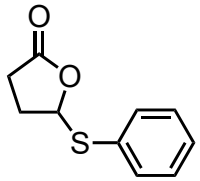


^{13}C NMR spectrum of the compound (3.30)



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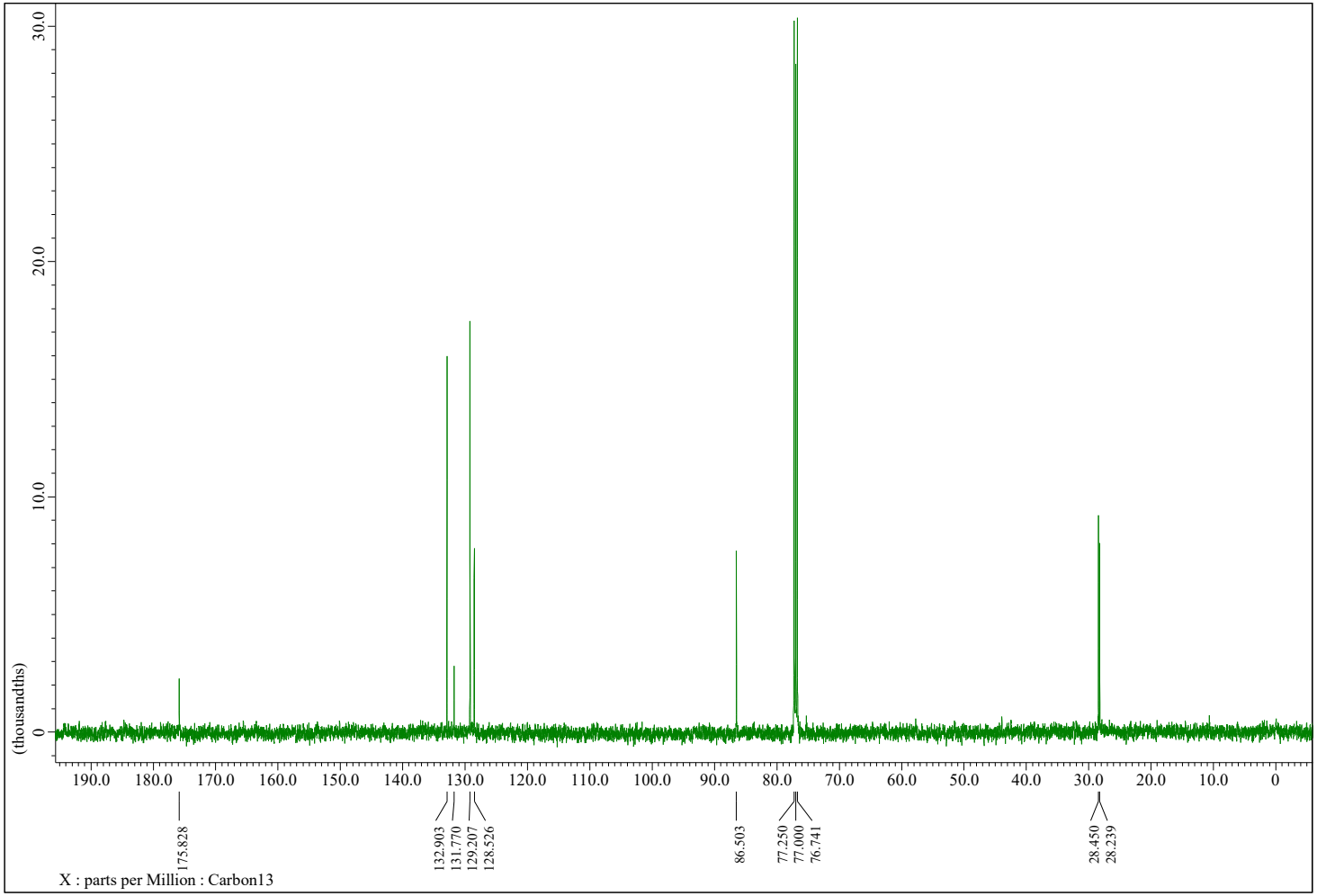
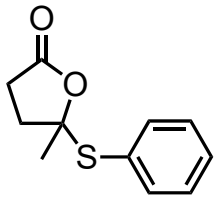


^{1}H NMR spectrum of the compound (3.31)



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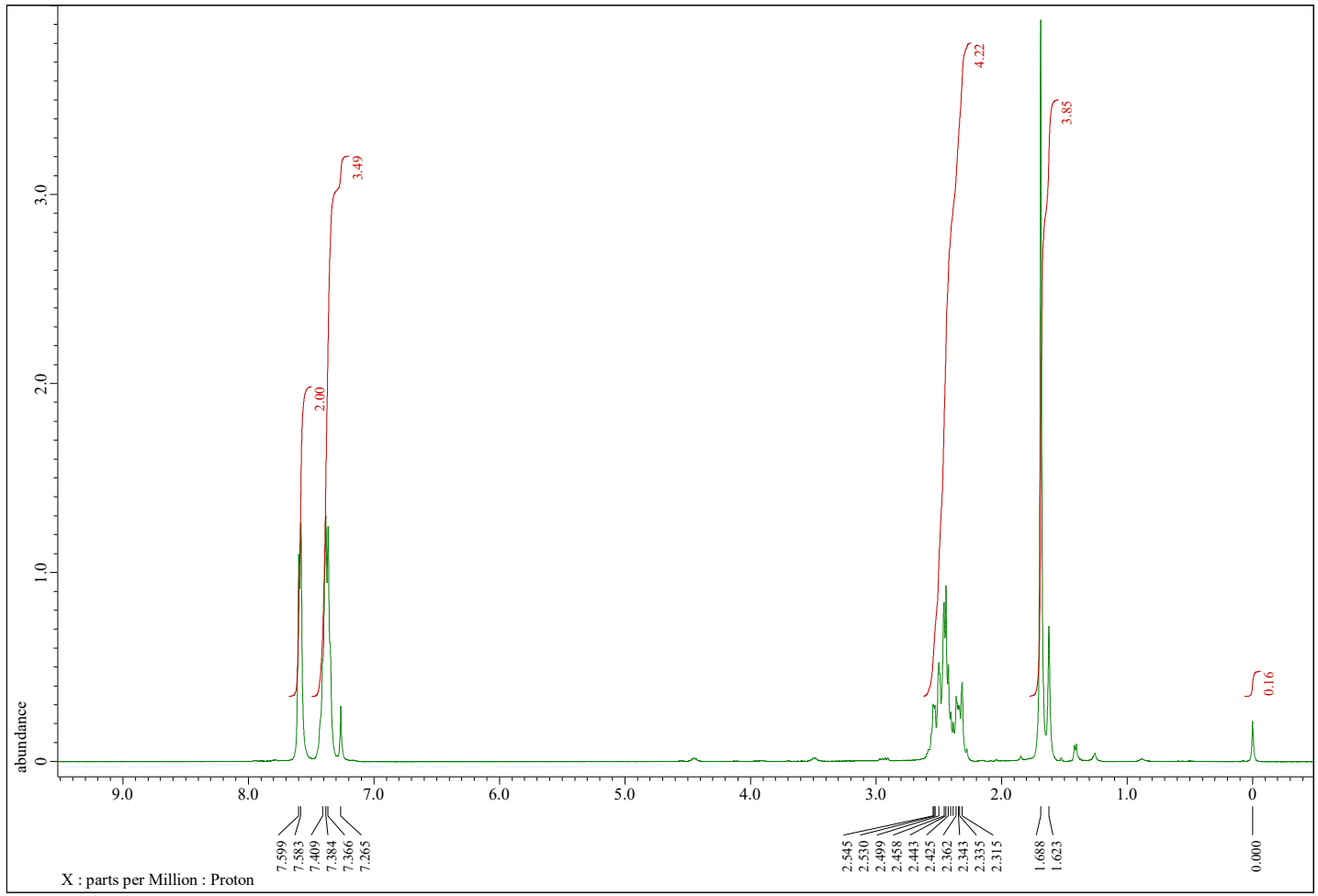
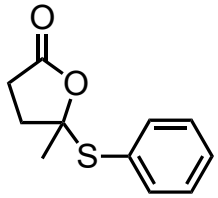


^{13}C NMR spectrum of the compound (3.31)



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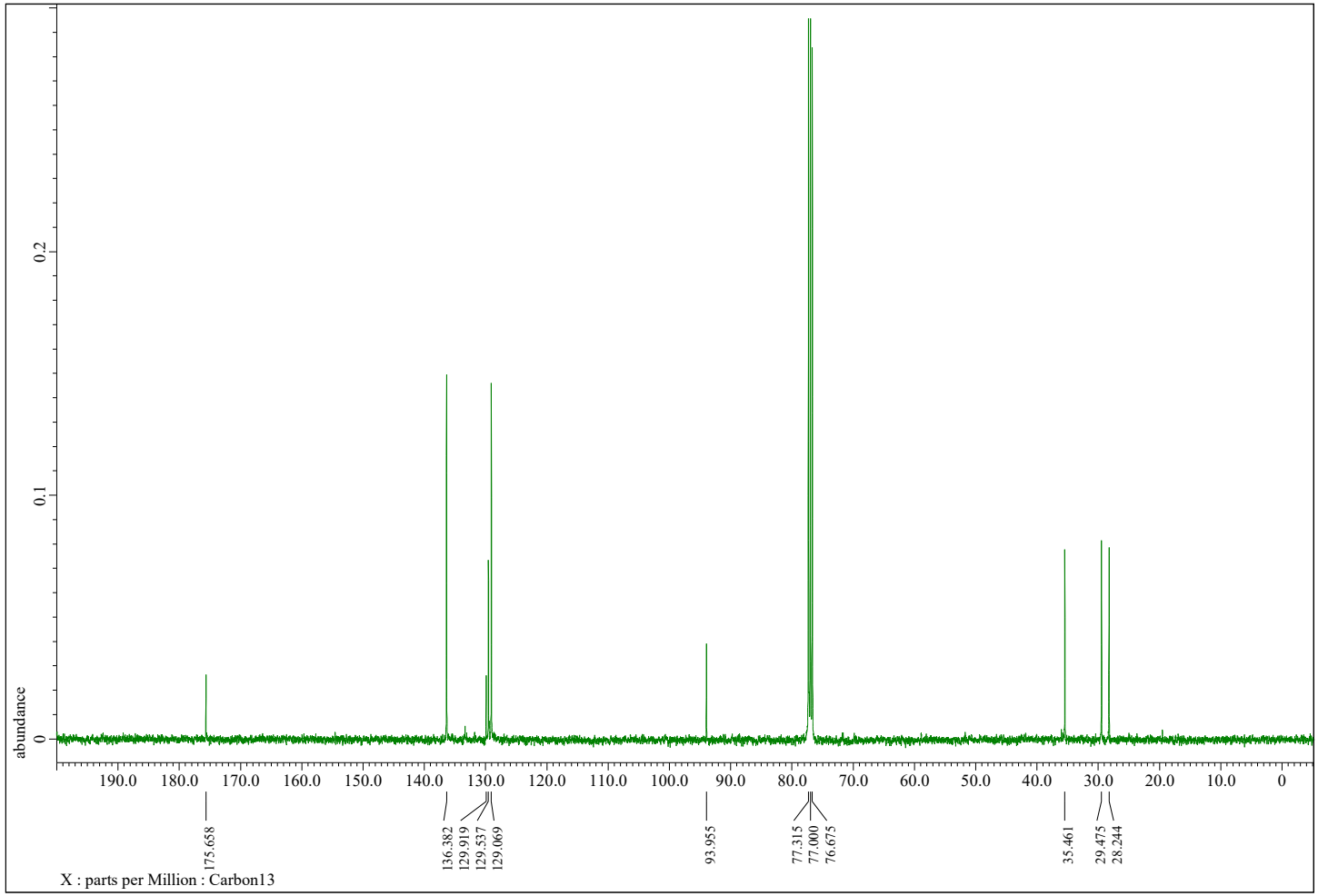
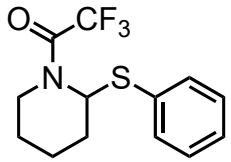


^{1}H NMR spectrum of the compound (3.32)



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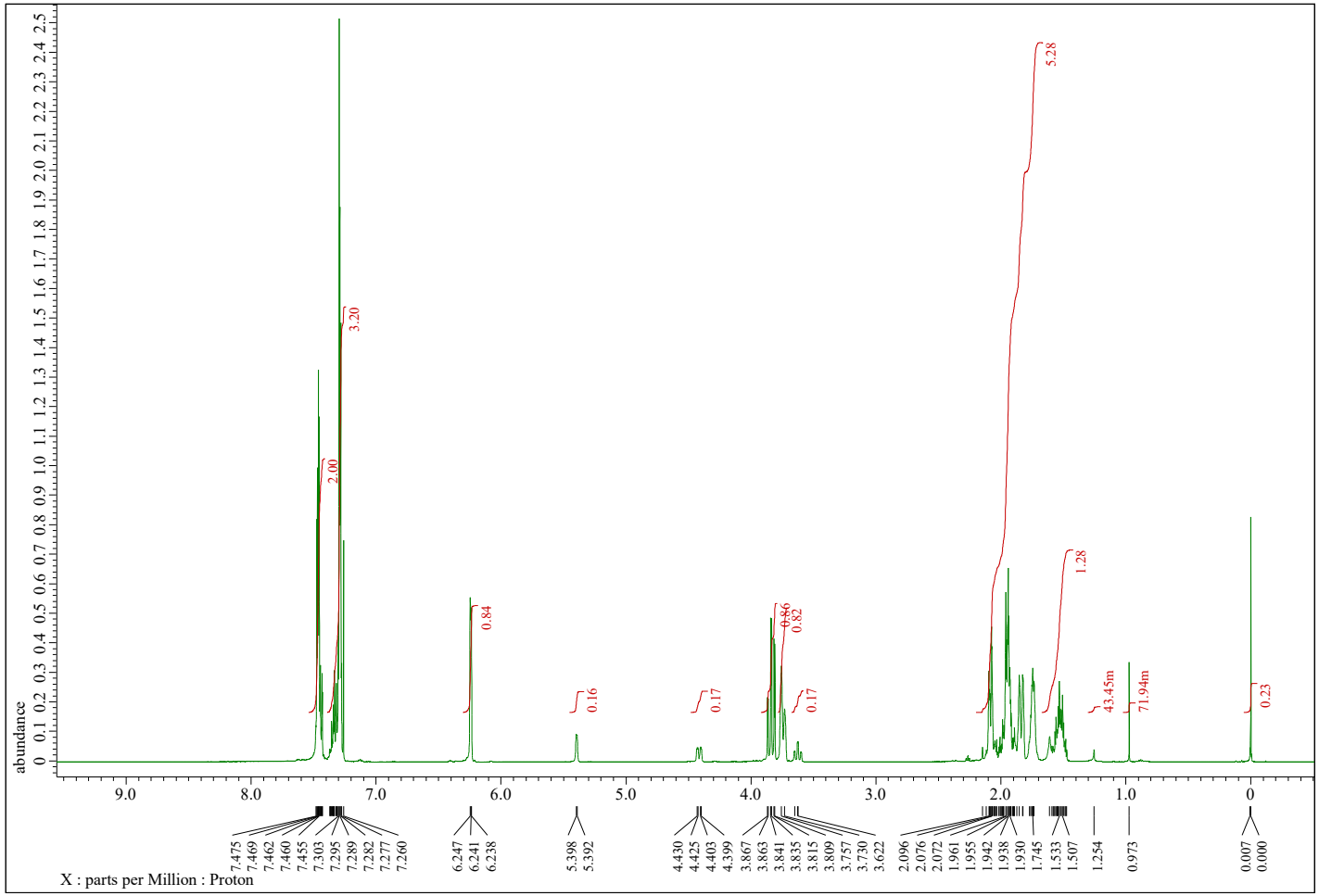
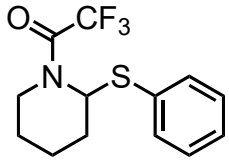


^{13}C NMR spectrum of the compound (3.32)



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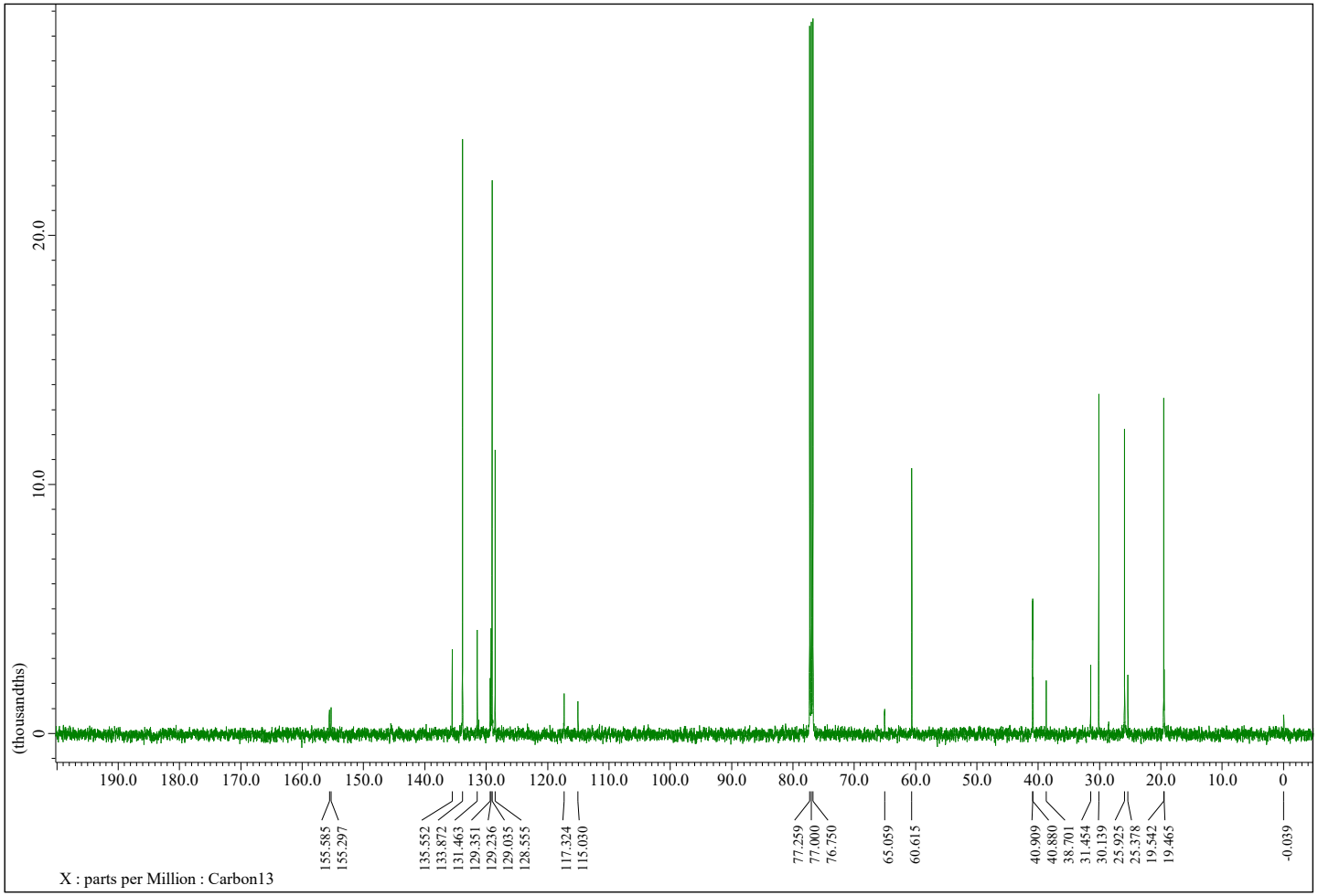
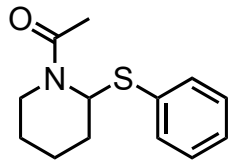


^{1}H NMR spectrum of the compound (3.33)



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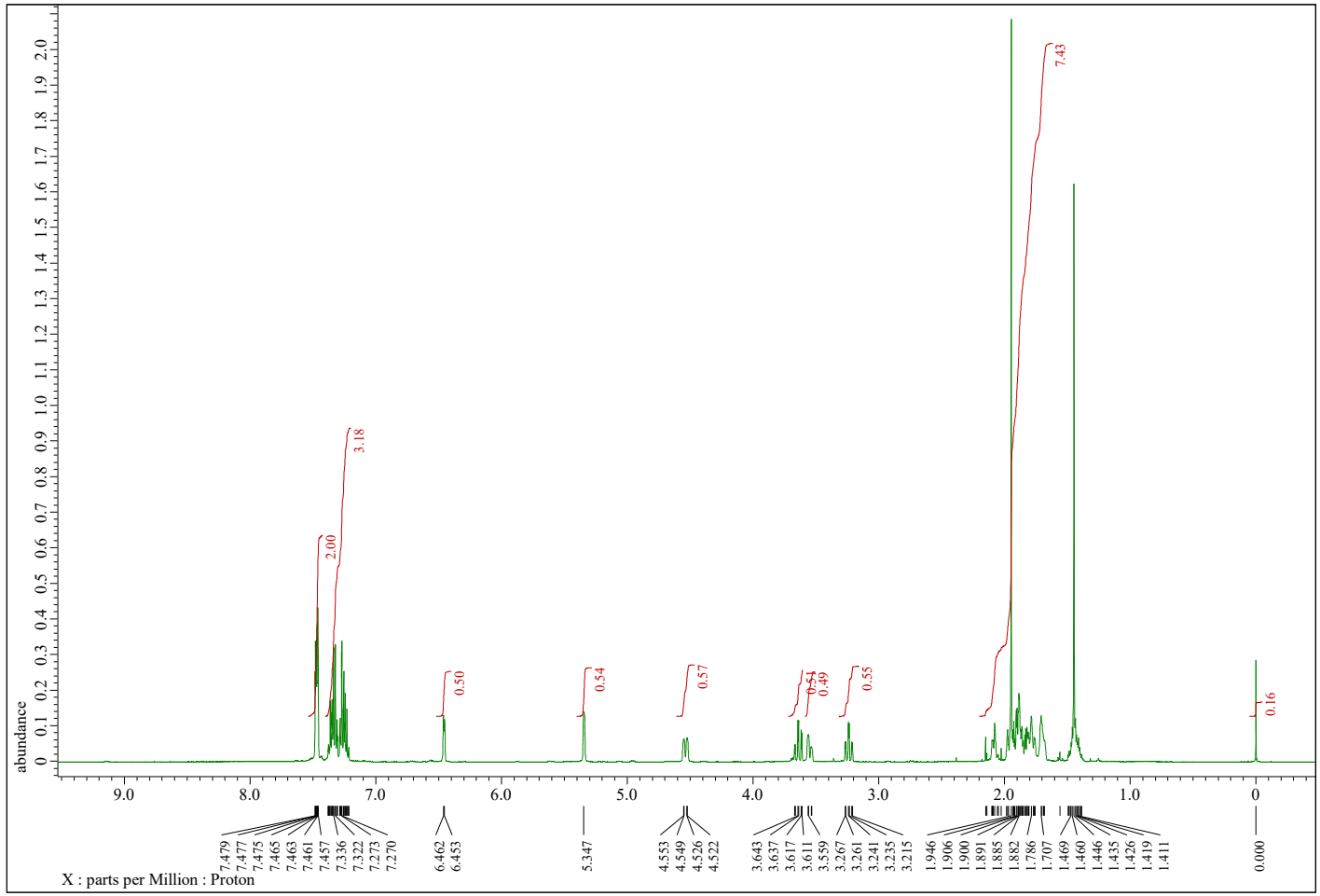
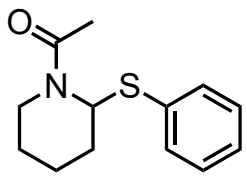


^{13}C NMR spectrum of the compound (3.33)



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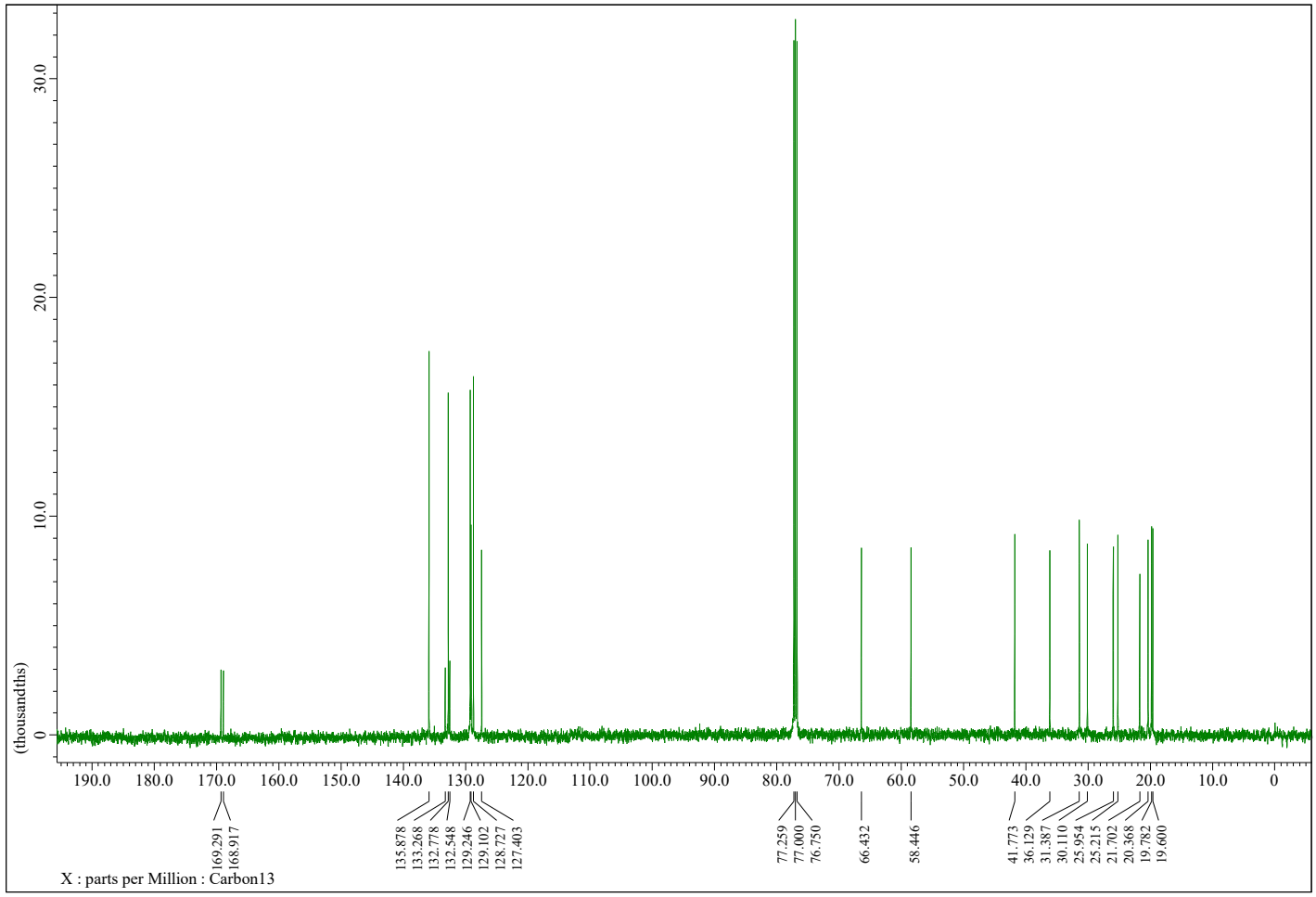
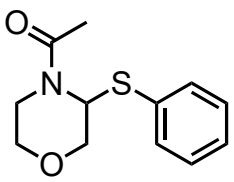


^{1}H NMR spectrum of the compound (3.34)



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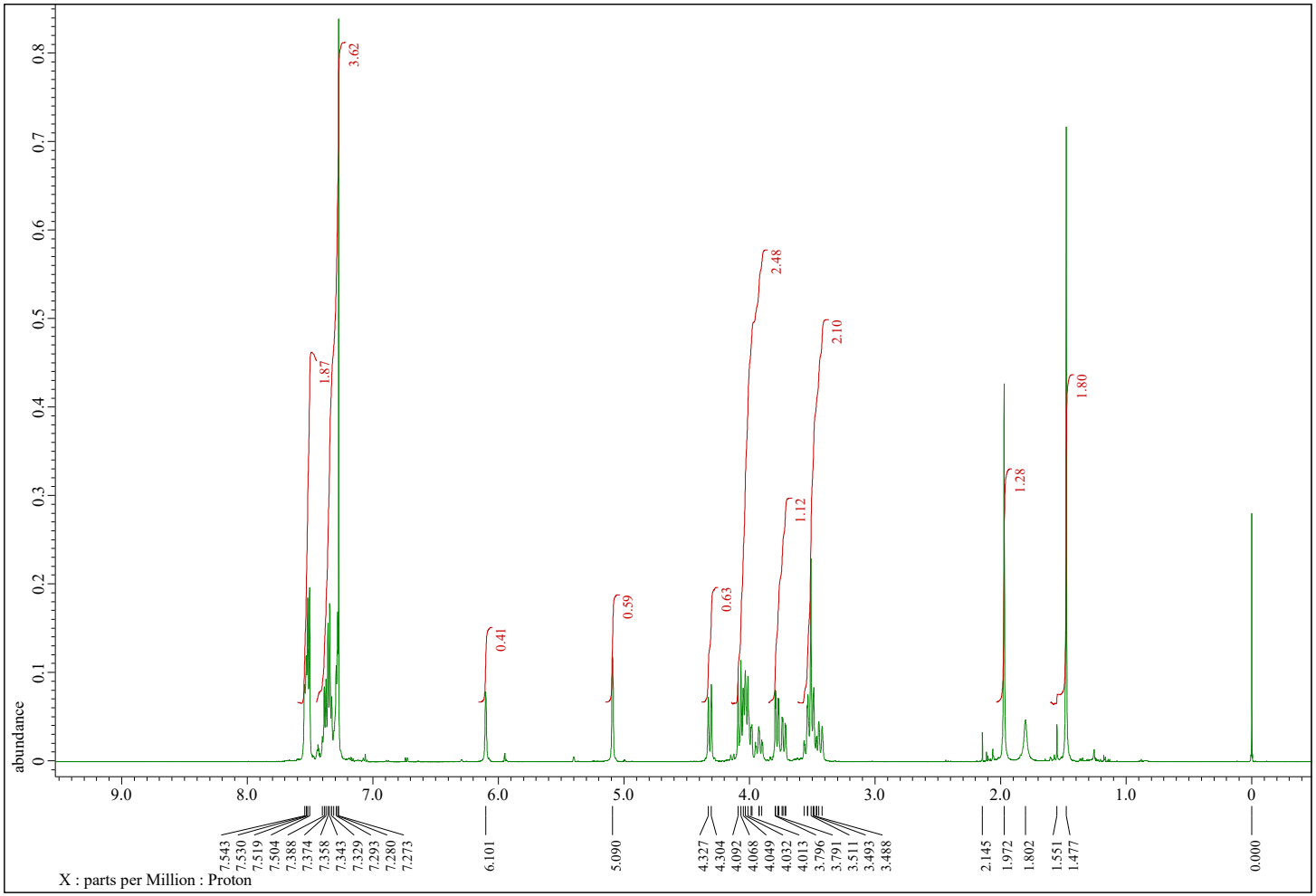
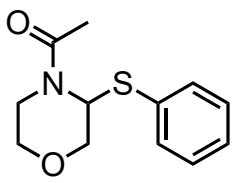


^{13}C NMR spectrum of the compound (3.34)



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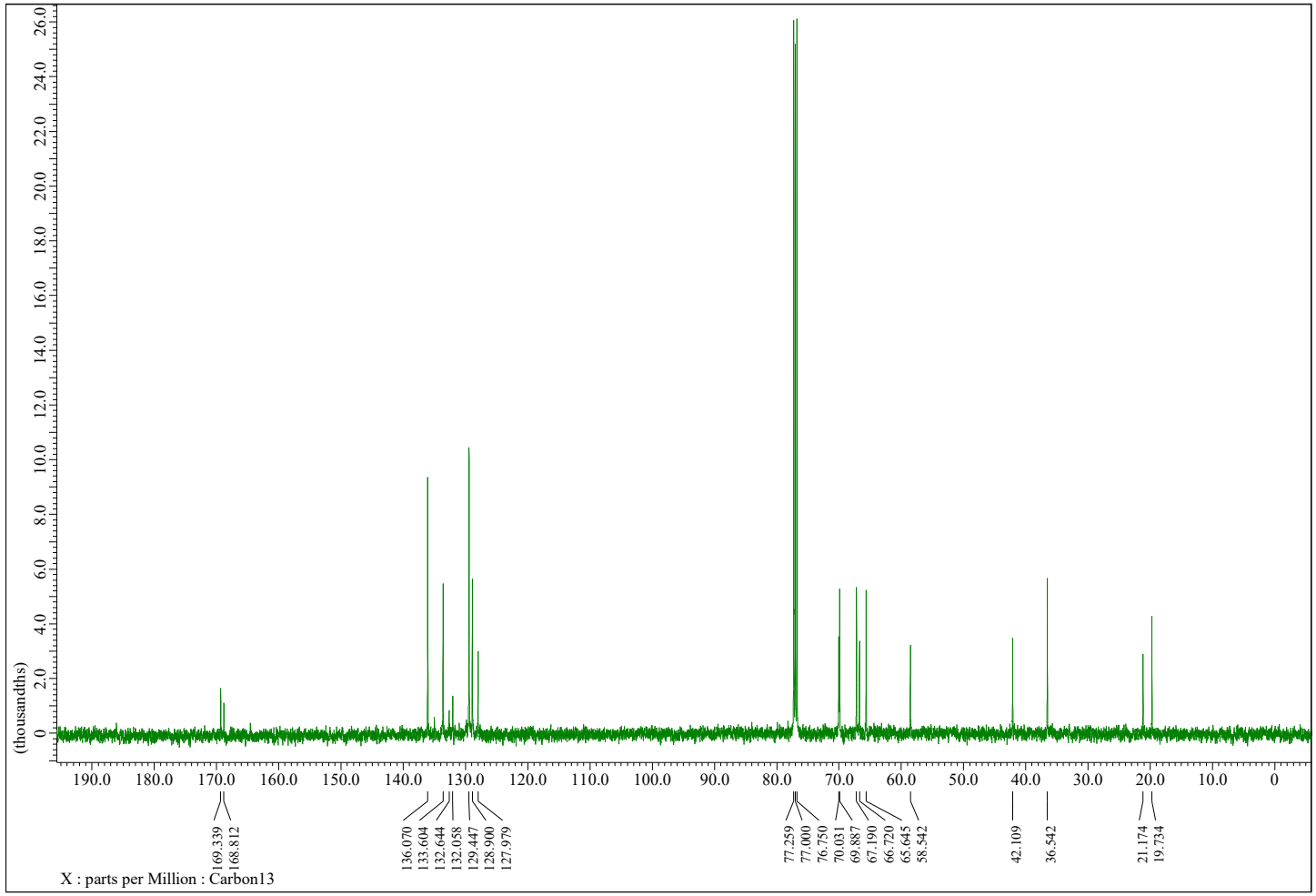
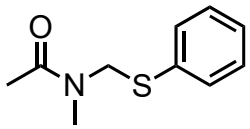


^{1}H NMR spectrum of the compound (3.35)



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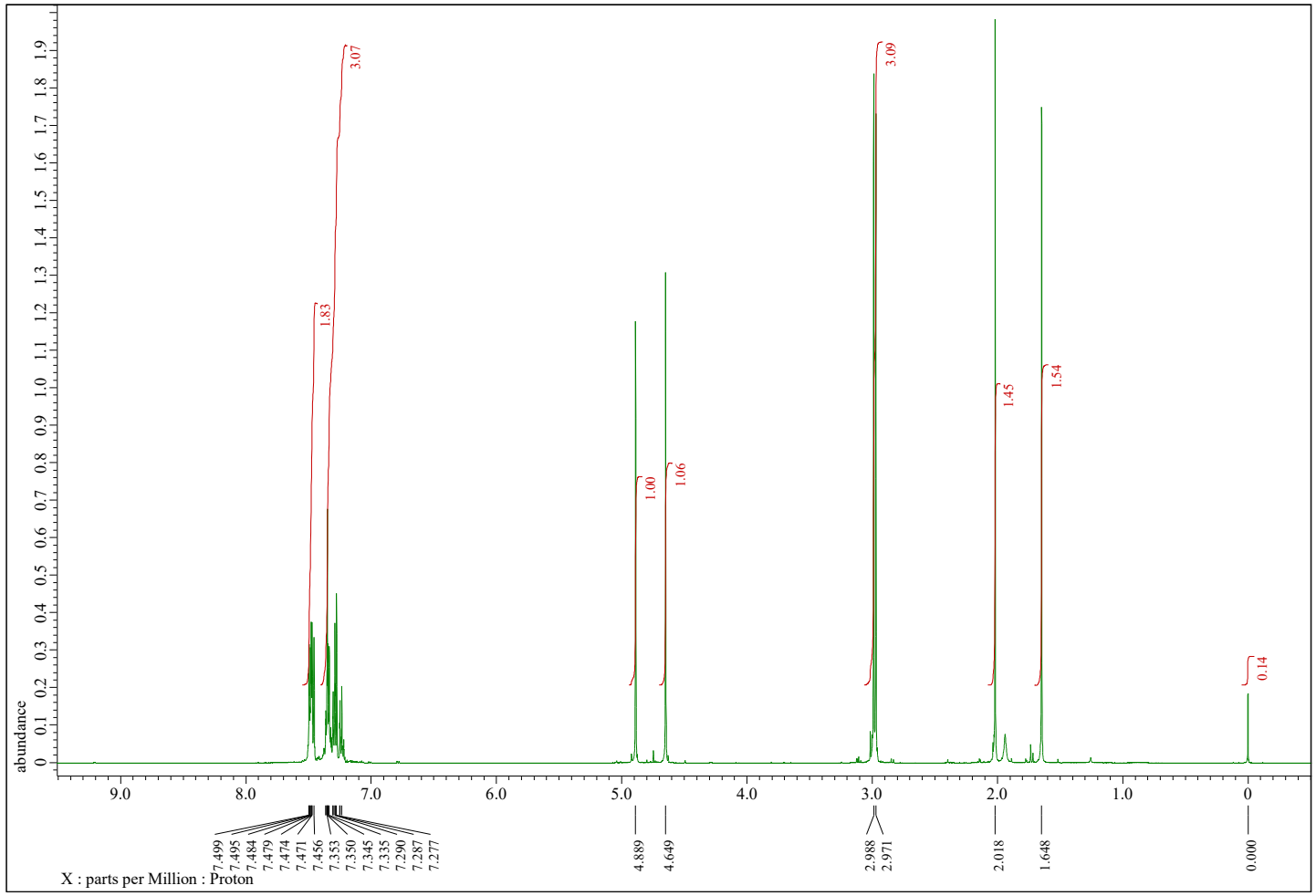
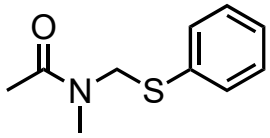


^{13}C NMR spectrum of the compound (3.35)



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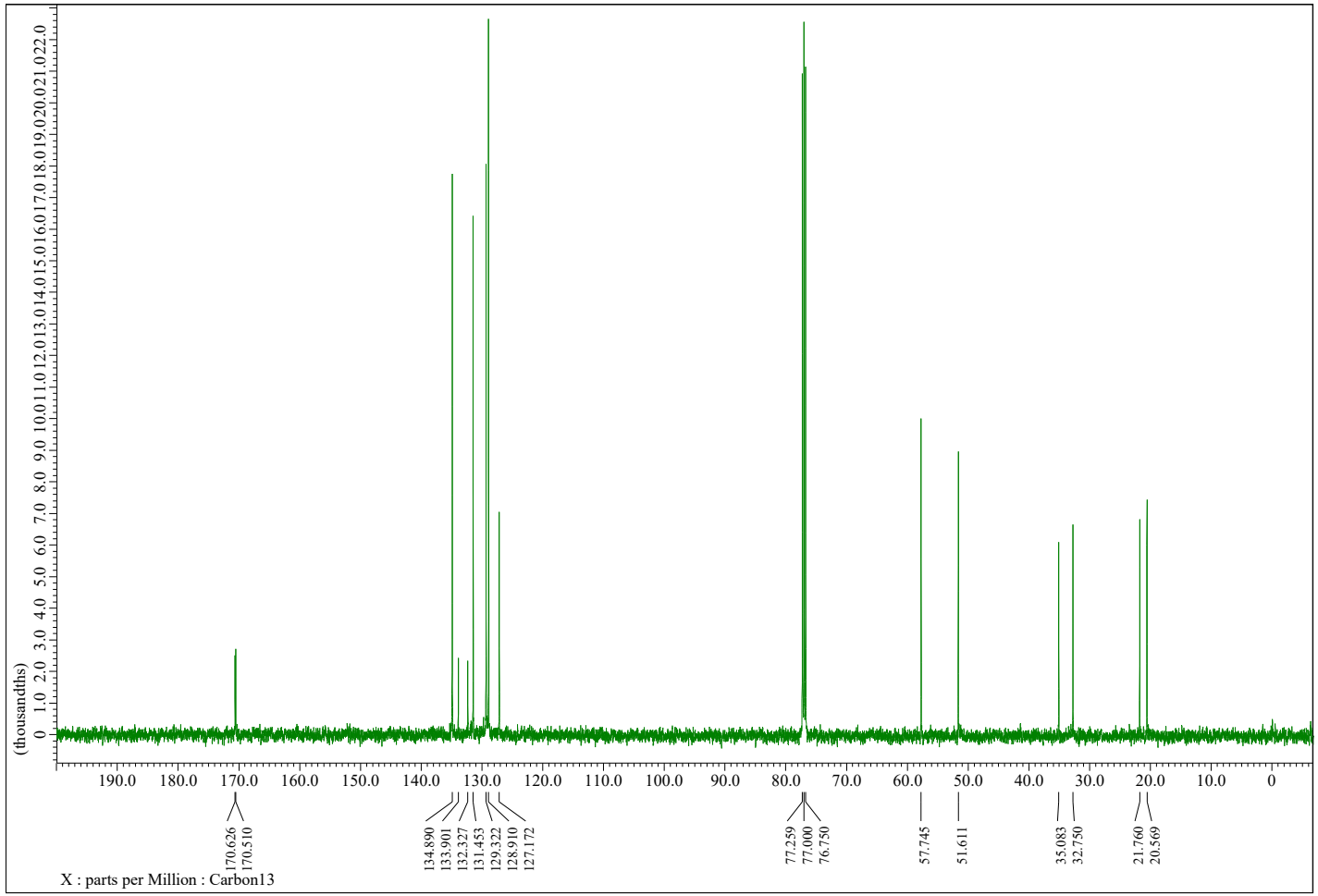
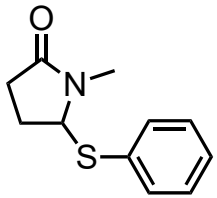


^{1}H NMR spectrum of the compound (3.36)



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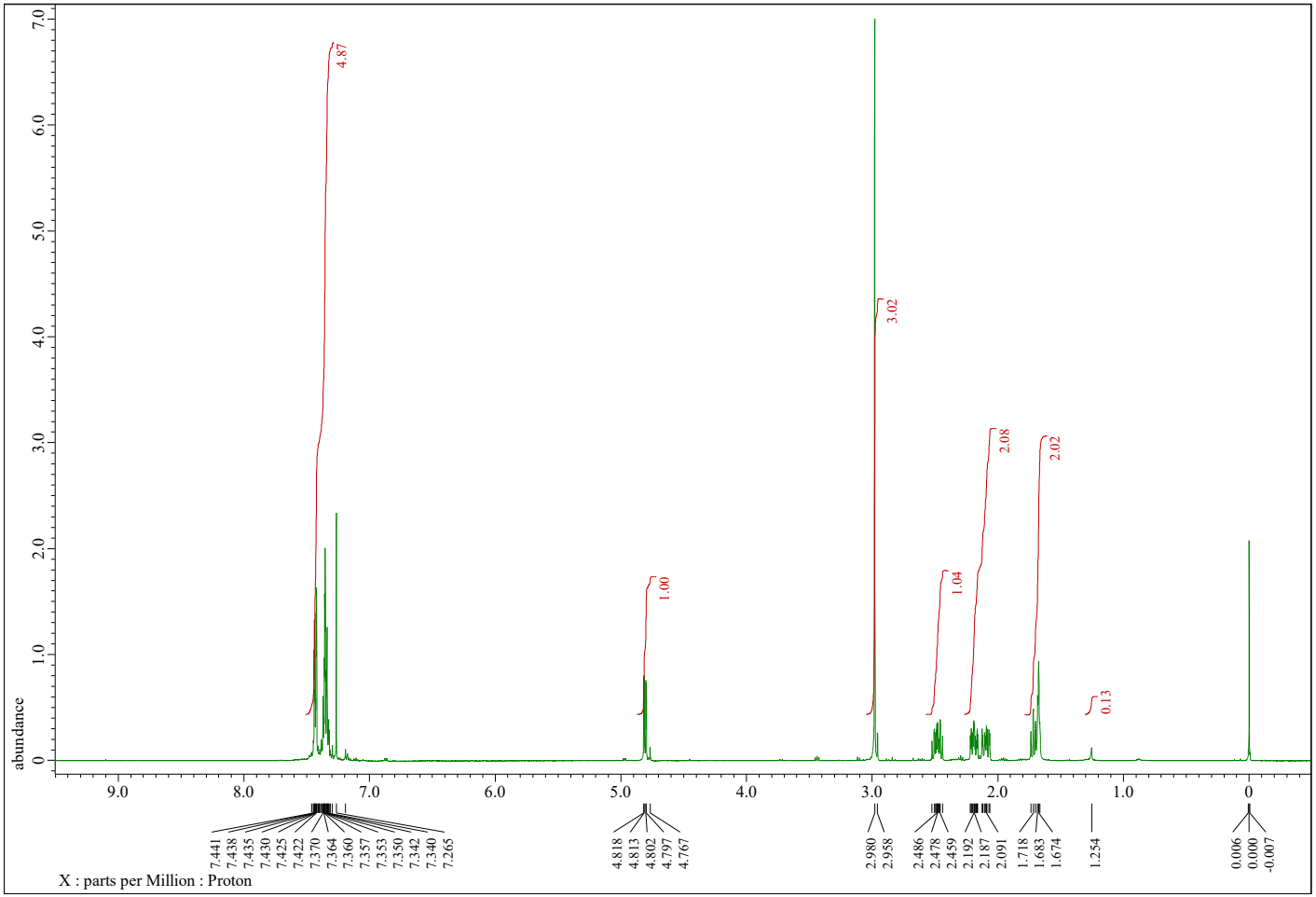
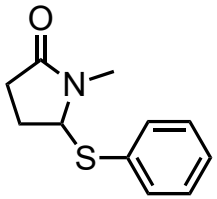


^{13}C NMR spectrum of the compound (3.36)



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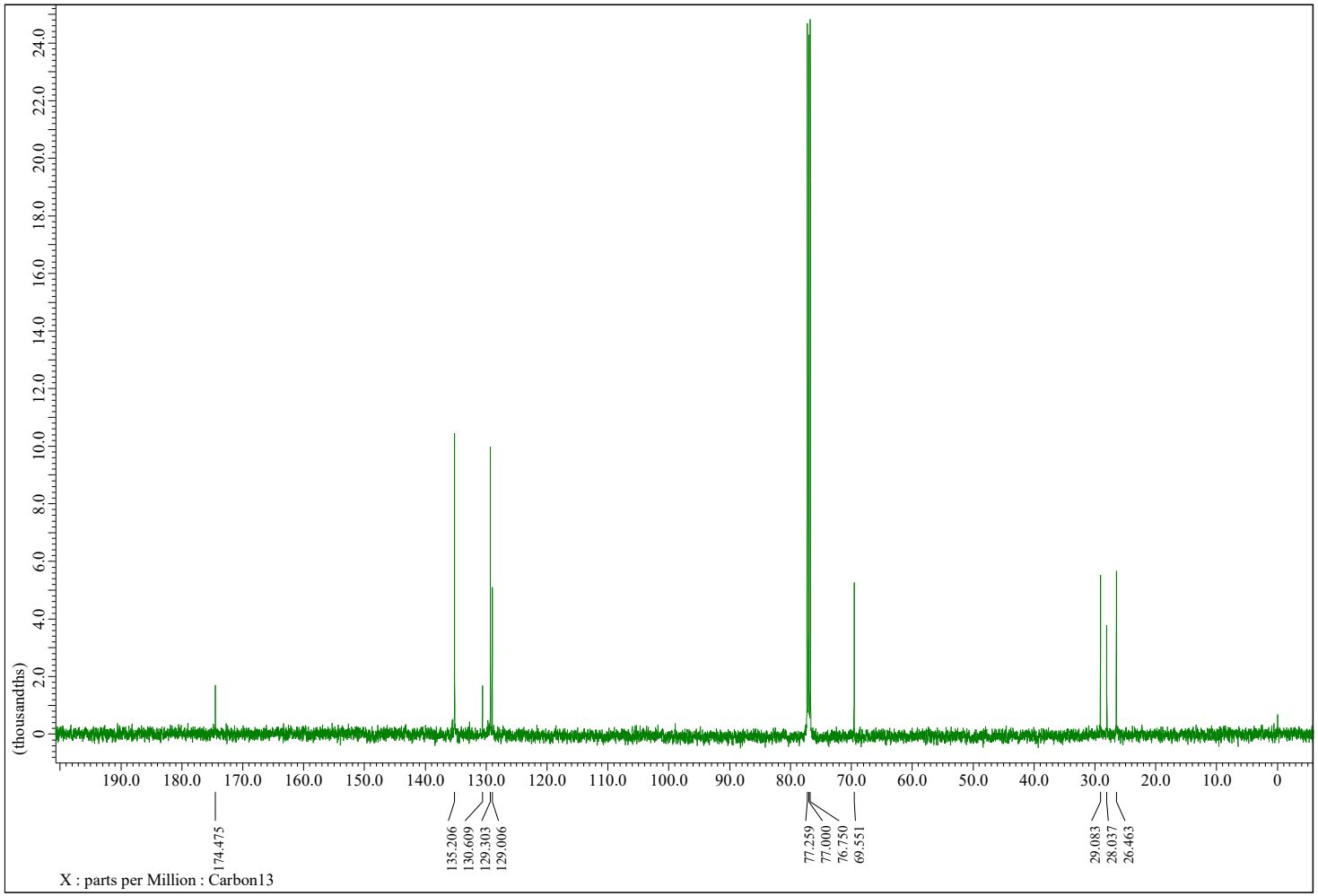
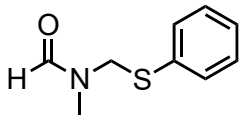


^{1}H NMR spectrum of the compound (3.37)



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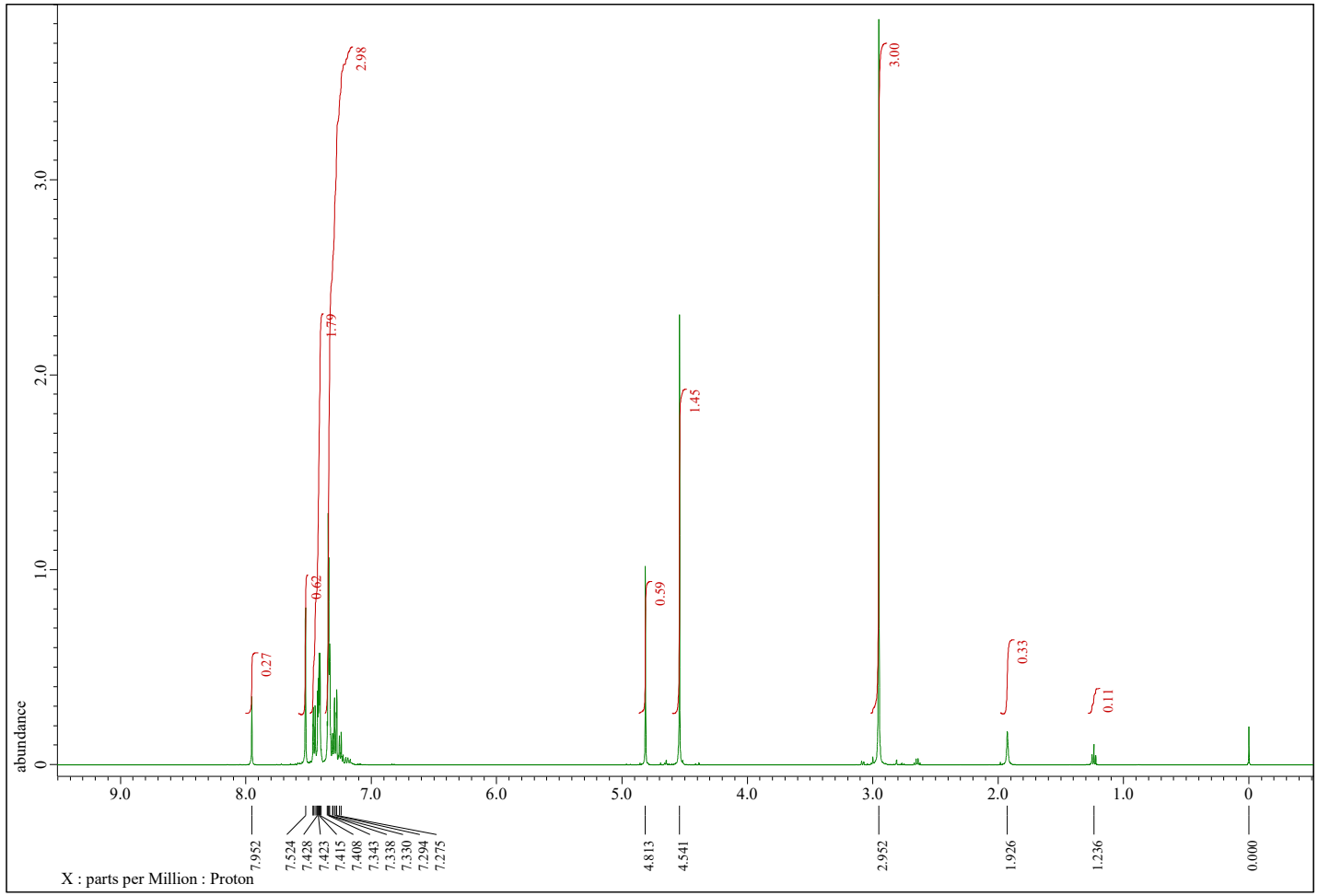
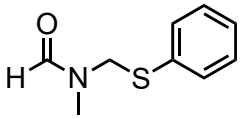


^{13}C NMR spectrum of the compound (3.37)



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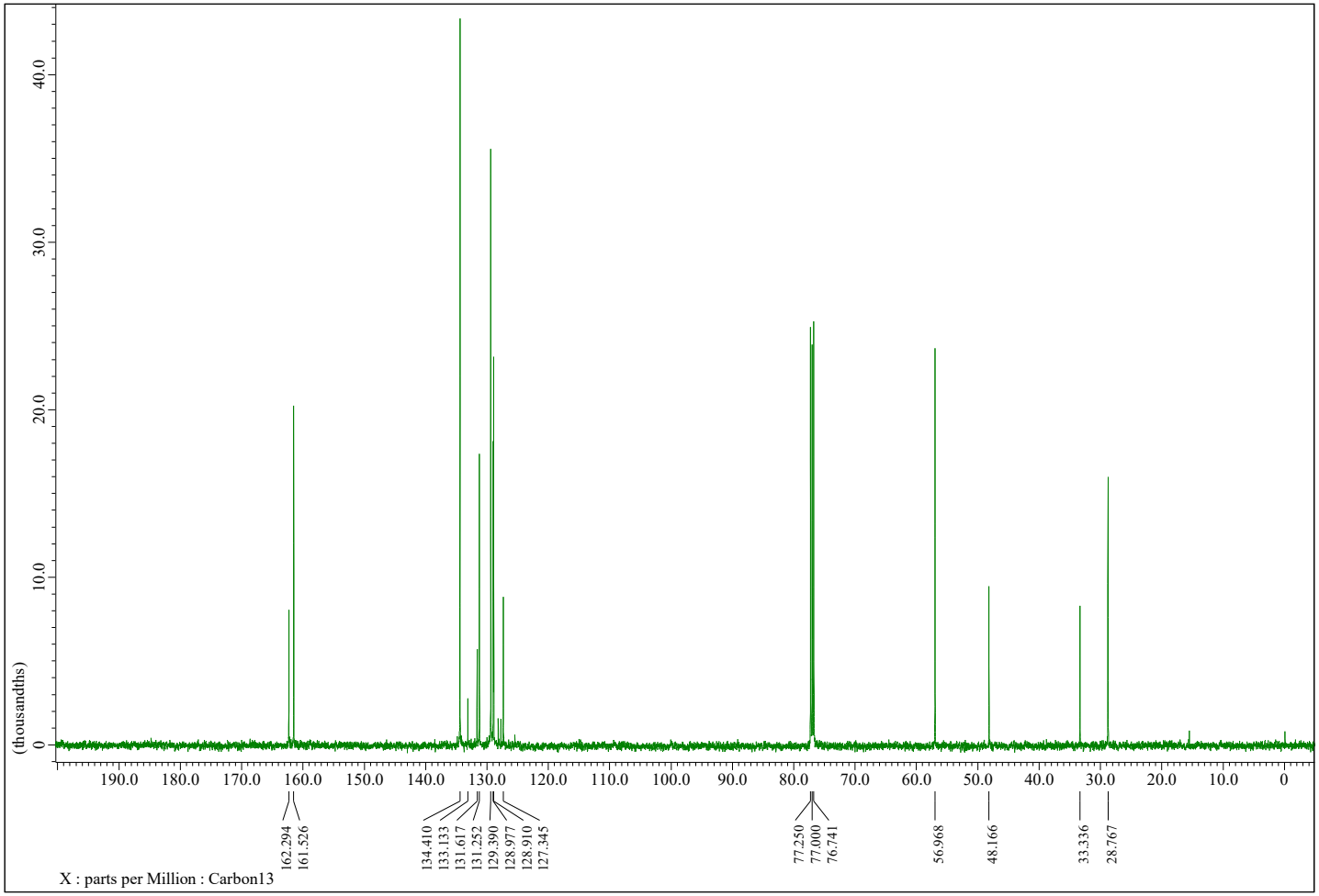
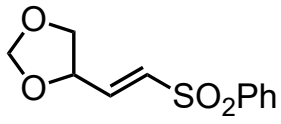


^{1}H NMR spectrum of the compound (5)



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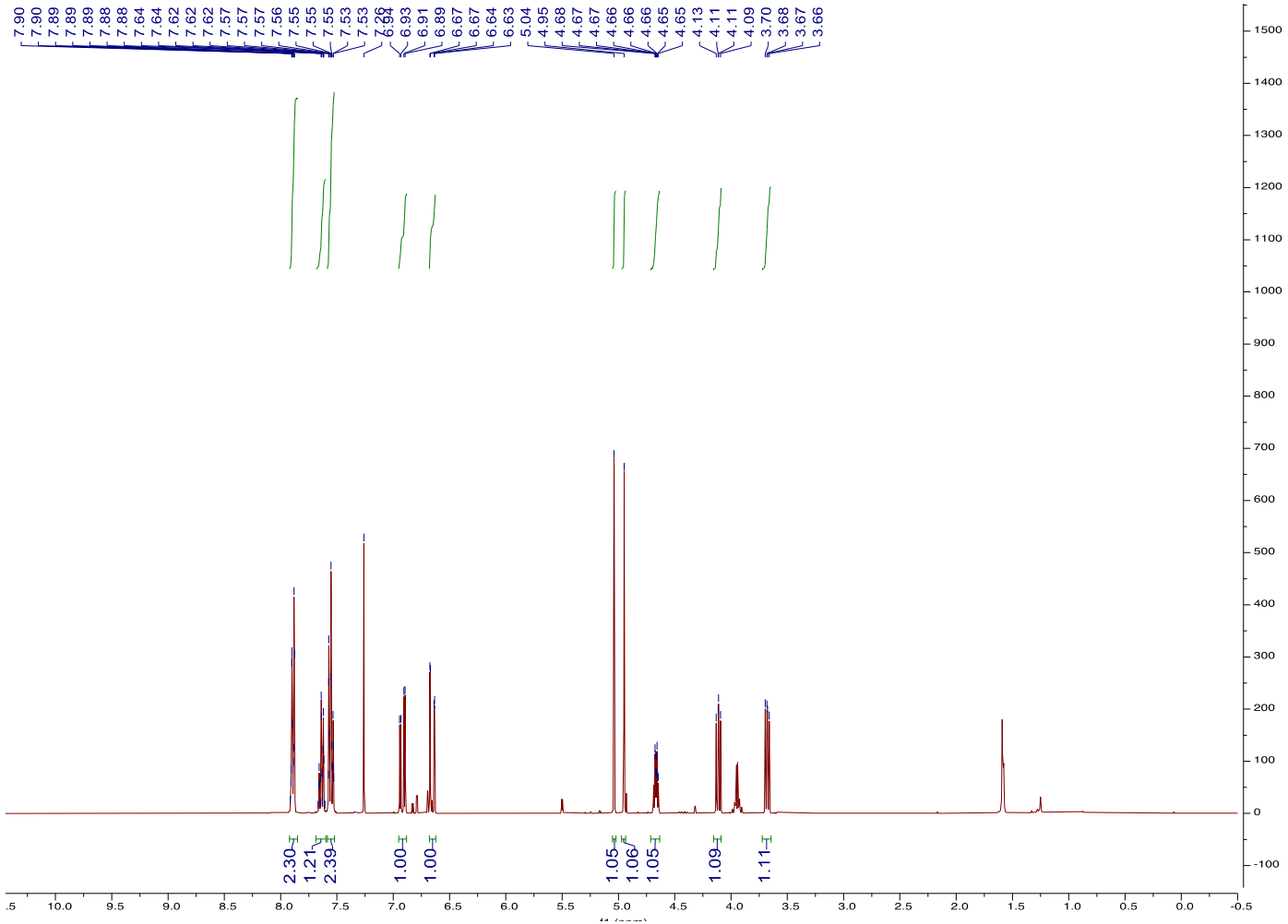
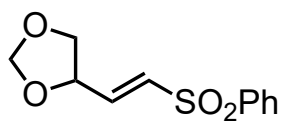


^{13}C NMR spectrum of the compound (5)



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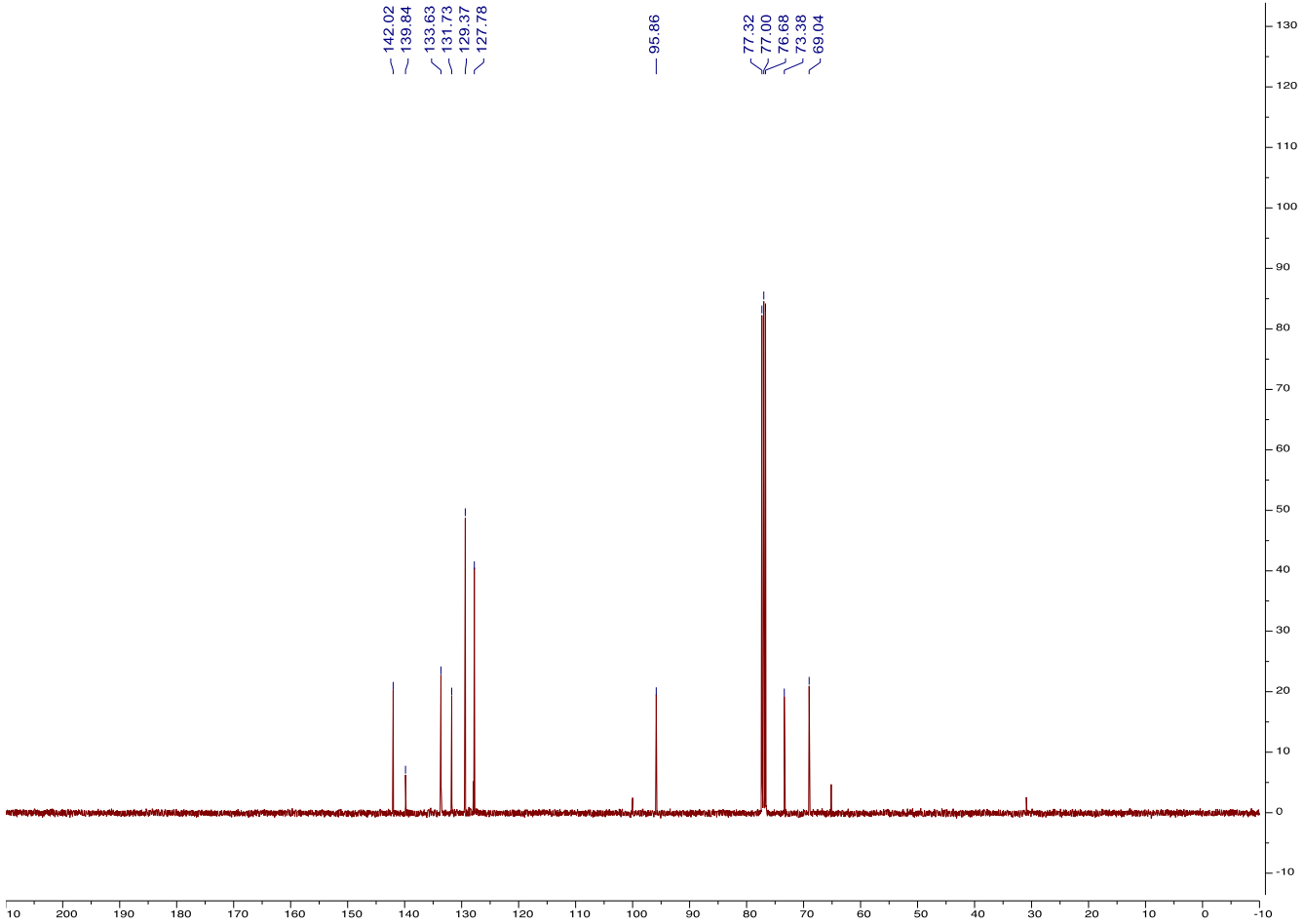
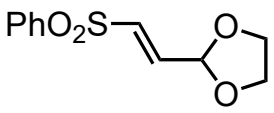
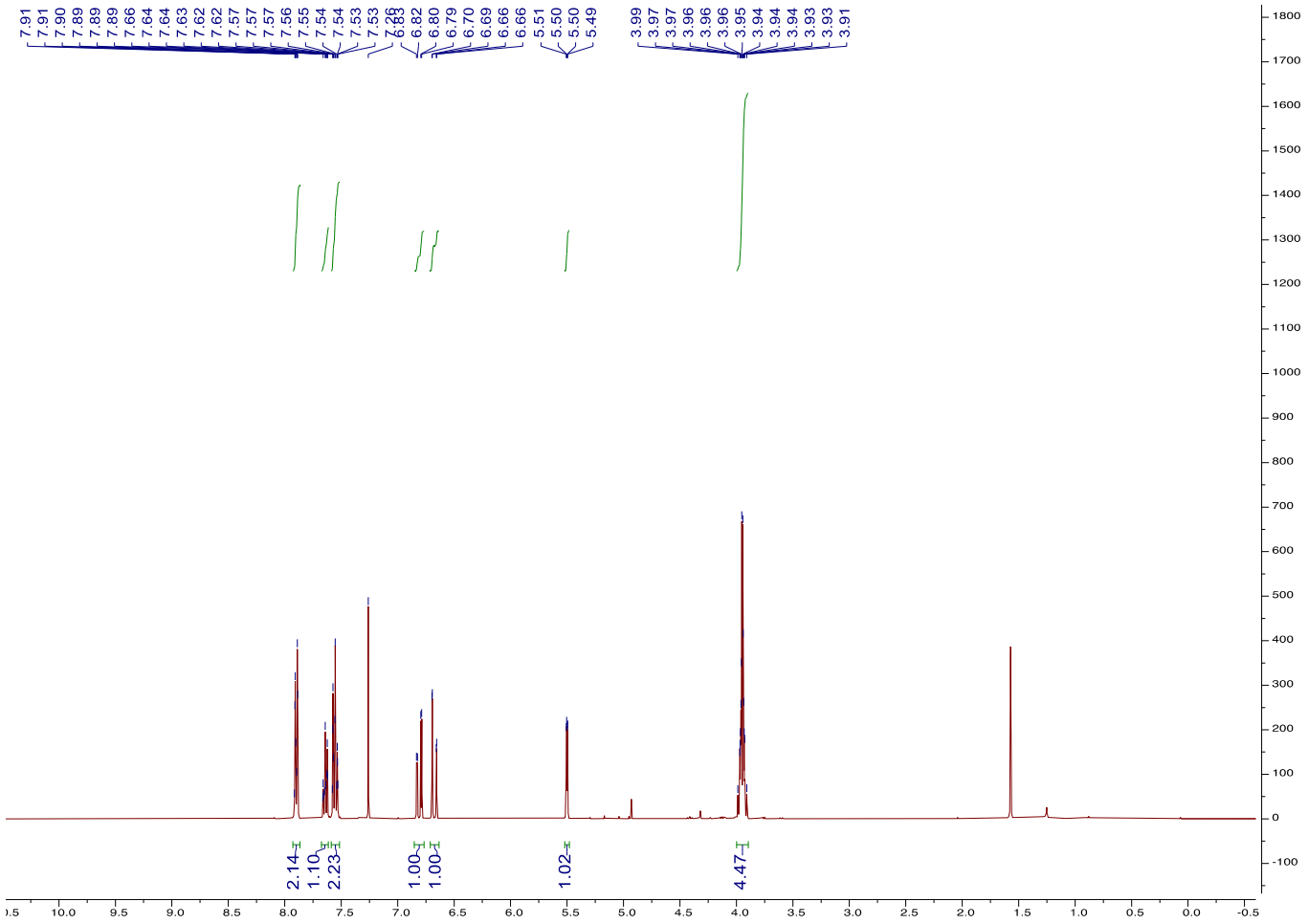


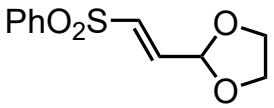
^{1}H NMR spectrum of the compound (5')



5'



^{13}C NMR spectrum of the compound (5')



5'