Biomimetic iterative method for polyketide synthesis

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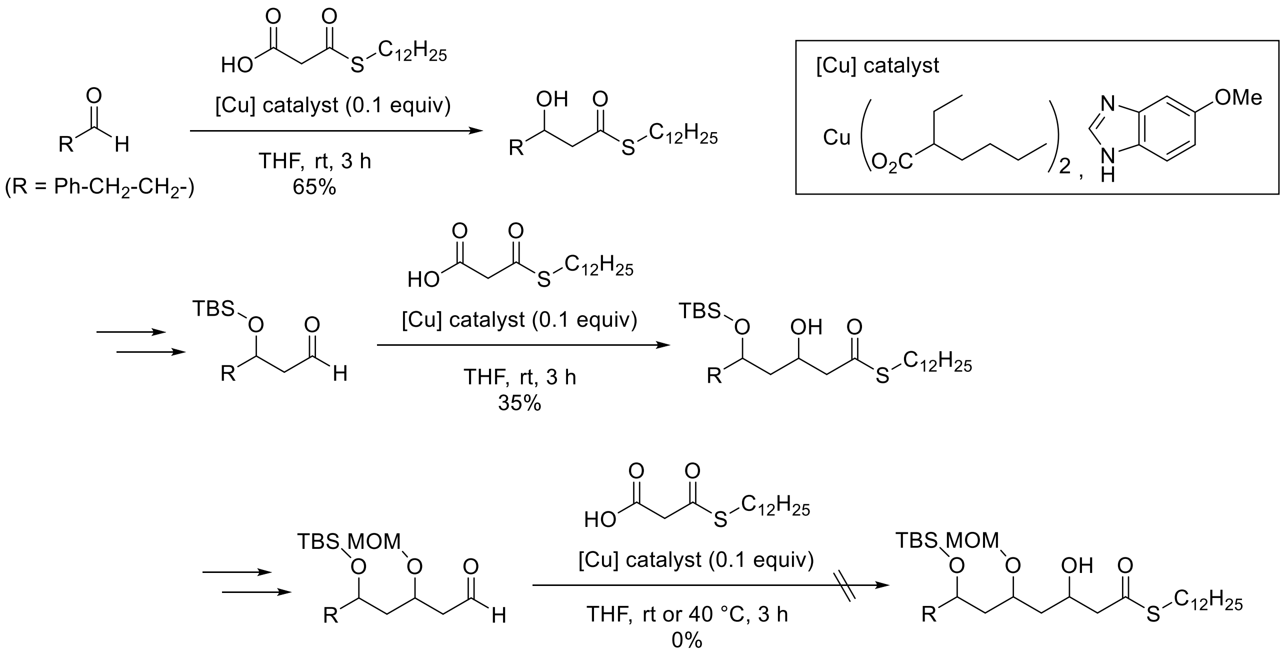


Scheme S1 Attempt for iterative elongation by the aldol reaction with MAHT.

General information.

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively on a JEOL JNM-LA400 spectrometer, and chemical shifts were referenced to internal tetramethylsilane (TMS, δ = 0.0 ppm) for ^{1}H and the central line of $CDCl_3$ (δ = 77.0 ppm) for ^{13}C. High-resolution FAB-MS measurements were performed on a JEOL JMS-600H mass spectrometer. Unless otherwise noted, the data were collected in a positive-ion mode with polyethylene glycol 400 as an internal mass calibrant.

Synthetic procedures and spectral data.

General procedure for the decarboxylative condensation of carboxylic acids with MAHT 1.

To a solution of a carboxylic acid (0.4 M) in DME, COMU (1 equiv.) and DIEA (1 equiv.) were added, and the mixture was stirred for 15 min. In another flask, to a solution of MAHT **1** (1.3 to 2 equiv.) in the same amount of DME used above, a THF solution (1 M) of isopropylmagnesium bromide (the same equiv. to **1**) was added at 0 °C. The solution was allowed to warm to room temperature and stirred for 3 min. The solution was added to the solution of the carboxylic acid, COMU, and DIEA. After stirring the solution for 2 to 3 h, a 10% aqueous solution of citric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography or preparative TLC on silica gel (eluent: hexanes/ethyl acetate) to afford a β-ketothioester.

General procedure for the hydrolysis of thioesters.

To a solution of a thioester in 1,4-dioxane/water, a 30% aqueous solution of hydrogen peroxide (10 equiv.) and an aqueous solution of cesium hydroxide (5 equiv.) were added. At this point, the concentration of the thioester was 0.05 M in 1,4-dioxane/water (4:1 v/v). The mixture was stirred for 20 min. When the starting thioester remained, a 30% aqueous solution of hydrogen peroxide (5 equiv.) was added, and the mixture was stirred for an additional 20 min. Diethyl ether was added, and the resulting mixture was extracted with water. In case that the layers did not segregate, brine was added to facilitate the phase separation. The aqueous layer was acidified with an aqueous solution of hydrochloric acid, and diethyl ether was added to extract the product. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The removal of the solvent under reduced pressure afforded a carboxylic acid. For the hydrolysis of a 1,3-dithiolane-protected thioester, the reaction was performed without the addition of hydrogen peroxide. In this case, the reaction time was 72 h at room temperature (ca. 20 °C) or 48 h at 30 °C.

General procedure for the reduction of β-ketothioesters to β-hydroxythioesters.

To the solution of a β-ketothioester (0.1 M) and ground cerium(III) chloride heptahydrate (1 equiv.) in THF/acetic acid (1:1 v/v), sodium cyanoborohydride (5 equiv.) was added in three portions. After stirring for 30 min, a saturated aqueous solution of sodium bicarbonate was carefully added with stirring until foaming ceased. The resulting mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate) to afford a β-hydroxythioester.

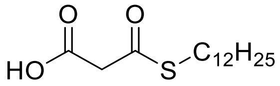
General procedure for the dehydration of β-hydroxythioesters to α,β-unsaturated thioesters.

To the solution of a β-hydroxythioester (0.1 M) in dichloromethane, Martin sulfurane (1.5 equiv.) was added. The mixture was stirred for 10 min. When the starting β-hydroxythioester remained, Martin sulfurane (0.5 equiv.) was added, and the mixture was stirred for an additional 10 min. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate) to afford an α,β-unsaturated thioester.

General procedure for the reduction of α,β-unsaturated thioesters to saturated thioesters.

To the solution of an α,β-unsaturated thioester (0.05 M) and polymethylhydrosiloxane (20 equiv.) in toluene, a 0.1 M THF solution of copper acetate monohydrate and 1,2-bis(diphenylphosphino) benzene (1:1 mixture, 0.05 equiv.) was added. After stirring the mixture for 6 h, the THF solution of the copper complex (0.05 equiv.) was added again. After stirring for an additional 6 h, a 10%

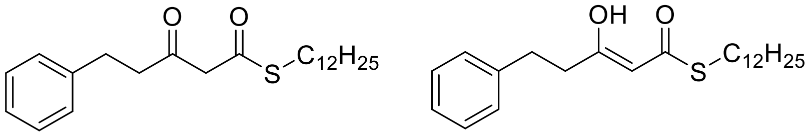
aqueous solution of citric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate) to afford a saturated thioester.



3-(Dodecylthio)-3-oxopropanoic acid (1)

To a suspension of malonic acid (10.45 g, 100.4 mmol) in toluene (100 mL), phosphoryl chloride (9.35 mL, 100 mmol), 1-dodecanethiol (23.0 mL, 96.6 mmol), *N,N*-dimethyl-4-aminopyridine (1.22 g, 9.99 mmol) were added. The mixture in an open flask was heated to 60 °C in a fume hood. After string for 12 h at this temperature, the reaction mixture was cooled to room temperature. A soluble part was transferred to a separation funnel with ethyl acetate. Water was added, and the layers were separated. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 9:1 → 3:7) to afford MAHT **1** (12.66 g, 45% yield) as a pale yellow solid.

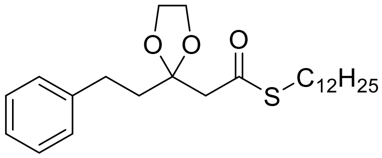
^{1}**H NMR** (400 MHz, CDCl$_3$) δ 3.63 (s, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.60 (quin, *J* = 6.9 Hz, 2H), 1.40-1.21 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 192.0, 170.4, 48.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 28.8, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m/z*: calculated for $C_{15}H_{29}O_3S$ $[M+H]^+$: 289.1837, found 289.1844.



S-Dodecyl 3-oxo-5-phenylpentanethioate, *S*-Dodecyl (*Z*)-3-hydroxy-5-phenylpent-2-enethioate (3)

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **2** (1.00 g, 6.67 mmol) was performed with 1.3 equiv. of MAHT **1** for 2 h. The purification by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 9:1) afforded β-ketothioester **3** (2.34 g, 93% yield) as a pale orange oil.

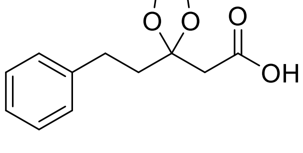
Keto/enol ratio = 80:20. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.32-7.15 (m, 5H), 5.14 (s, 0.2H), 3.64 (s, 1.6H), 2.94-9.85 (m, 5.6H), 2.46 (t, *J* = 8.0 Hz, 0.4H), 1.64-1.52 (m, 2H), 1.40-1.21 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 201.1, 194.8, 192.0, 174.9, 140.5, 140.4, 128.5, 128.3, 128.2, 126.3, 126.2, 99.7, 57.8, 44.6, 36.7, 32.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.8, 28.2, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m/z*: calculated for $C_{23}H_{37}O_2S$ $[M+H]^+$: 377.2514, found 377.2506.



S-Dodecyl 2-(2-phenethyl-1,3-dioxolan-2-yl)ethanethioate (4)

To a solution of β-ketothioester **3** (1.16 g, 3.07 mmol) and ethylenedioxybis(trimethylsilane) (3.76 mL, 5 equiv.) in dichloromethane (15 mL), trimethylsilyl trifluoromethanesulfonate (565 µL, 1 equiv.) was added at 0 °C. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm to room temperature. After stirring for additional 1 h, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 9:1) to afford thioester **4** (1.27 g, 98% yield) as a white solid.

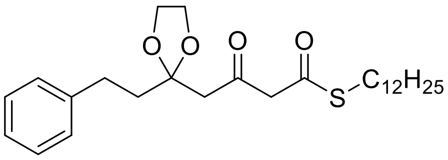
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 4.08-3.99 (m, 4H), 2.91 (s, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.75-2.70 (m, 2H), 2.13-2.07 (m, 2H), 1.55 (quin, *J* = 7.4 Hz, 2H), 1.40-1.21 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 141.7, 128.4, 128.4, 125.8, 108.9, 65.2, 51.2, 39.7, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 22.7, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{25}H_{41}O_3S$ $[M+H]^+$: 421.2776, found 421.2776.

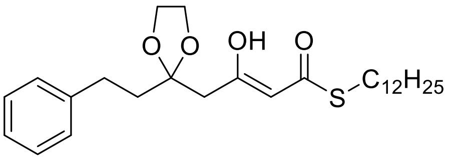


2-(2-Phenethyl-1,3-dioxolan-2-yl)acetic acid (5)

Synthesized according to the general procedure for hydrolysis of a thioester. After 20 min from starting the reaction, 5 equiv. of hydrogen peroxide was added, and the mixture was stirred for additional 20 min. The reaction of thioester **4** (209 mg, 0.496 mmol) afforded carboxylic **5** (115 mg, 98% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 4.10-4.01 (m, 4H), 2.76-2.70 (m, 2H), 2.75 (s, 2H), 2.18-2.13 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 141.5, 128.4, 128.3, 125.9, 108.8, 65.2, 42.5, 39.3, 29.6; **HRMS** (FAB, negative ion mode, matrix and internal calibrant: glycerol) *m*/*z*: calculated for $C_{13}H_{15}O_4$ [M–H]$^-$: 235.0971, found 235.0966.



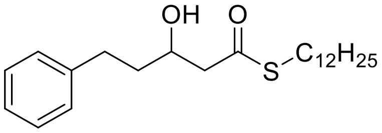


_S_-Dodecyl 3-oxo-4-(2-phenethyl-1,3-dioxolan-2-yl)butanethioate,

_S_-Dodecyl (_Z_)-3-hydroxy-4-(2-phenethyl-1,3-dioxolan-2-yl)but-2-enethioate (6)

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **5** (87.5 mg, 0.370 mmol) was performed with 1.8 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 4:1) afforded β-ketothioester **6** (155 mg, 91% yield) as a slightly yellow solid.

Keto/enol ratio = 45:55. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 5.52 (s, 0.55H), 4.07-3.98 (m, 4H), 3.78 (s, 0.9H), 2.92 (t, *J* = 7.6 Hz, 1.1H), 2.91 (t, *J* = 7.4 Hz, 0.9H), 2.91 (s, 0.9H), 2.76-2.66 (m, 2H), 2.51 (s, 1.1H), 2.09-1.98 (m, 2H), 1.64-1.53 (m, 2H), 1.40-1.21 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 199.4, 194.8, 192.3, 170.9, 141.8, 141.5, 128.4, 128.3, 125.9, 125.8, 109.7, 109.2, 102.2, 65.3, 65.1, 58.7, 50.0, 43.1, 39.7, 39.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.1, 29.1, 28.9, 28.8, 28.2, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{27}H_{43}O_4S$ [M+H]$^+$: 463.2882, found 463.2882.

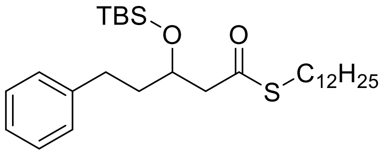


_S_-Dodecyl 3-hydroxy-5-phenylpentanethioate (7)

Synthesized according to the general procedure for reduction of a β-ketothioester. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 4:1). The reaction of β-ketothioester **3** (176 mg, 0.468 mmol) afforded β-hydroxythioester **7** (155 mg, 88% yield) as a colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.20-7.14 (m, 3H), 4.05 (oct, *J* = 4.0 Hz, 1H), 2.92 (broad s, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.84-2.63 (m, 4H), 1.86-1.68 (m, 2H), 1.56 (quin, *J* = 7.6 Hz, 2H), 1.38-1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 199.5, 141.5, 128.4, 128.3, 125.8, 67.8, 50.6, 38.1, 31.8, 31.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.0, 28.9, 28.7, 22.6, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{23}H_{39}O_2S$ [M+H]$^+$: 379.2671, found

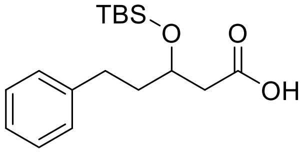
379.2673.



S-Dodecyl 3-[(*tert*-butyldimethylsilyl)oxy]-5-phenylpentanethioate (8)

To a solution of β-hydroxythioester **7** (520 mg, 1.37 mmol) in DMF (2.75 mL), imidazole (467 mg, 5 equiv.) and *tert*-butyldimethylchlorosilane (1.04 g, 5 equiv.) were added. After stirring the mixture for 1 h, an aqueous saturated solution of ammonium chloride was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 95:5) to afford thioester **8** (657 mg, 97% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20-7.14 (m, 3H), 4.24 (quin-like, J = 5.6 Hz, 1H), 2.86 (t, J = 7.2 Hz, 2H), 2.78 (dd, J = 14.4, 6.8 Hz, 1H), 2.73-2.58 (m, 3H), 1.89-1.73 (m, 2H), 1.56 (quin, J = 7.2 Hz, 2H), 1.39-1.19 (m, 18H), 0.89 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 0.07 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 142.1, 128.4, 128.3, 125.8, 69.2, 51.6, 39.3, 31.9, 31.3, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 25.8, 22.7, 18.0, 14.1, –4.6, –4.8; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{29}H_{53}O_2SSi$ $[M+H]^+$: 493.3535, found 493.3538.

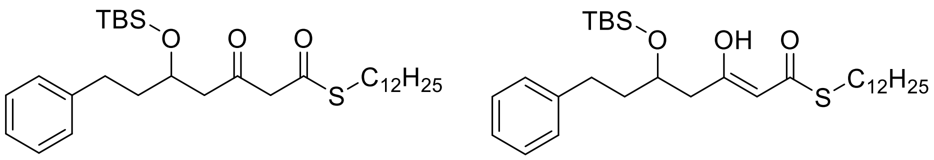


3-[(*tert*-Butyldimethylsilyl)oxy]-5-phenylpentanoic acid (9)

Synthesized according to the general procedure for hydrolysis of a thioester. After 20 min from starting the reaction, 5 equiv. of hydrogen peroxide was added, and the mixture was stirred for additional 20 min. The reaction of thioester **8** (330 mg, 0.670 mmol) afforded carboxylic **9** (202 mg, 98% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 4.19 (quin, J = 6.0 Hz, 1H), 2.73-2.60 (m, 2H), 2.57 (d, J = 5.6 Hz, 2H), 1.91-1.83 (m, 2H), 0.90 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 141.6, 128.4, 128.3, 125.9, 68.9, 41.8, 39.0, 31.4, 25.7, 18.0, –4.6, –4.8; **HRMS** (FAB, negative ion mode, matrix: glycerol) *m*/*z*: calculated for $C_{17}H_{27}O_3Si$ $[M-H]^-$:

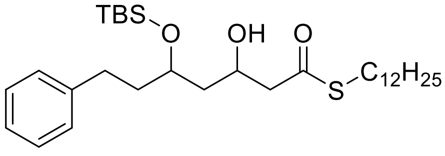
307.1730, found 307.1733.



***S*-Dodecyl 5-[(*tert*-butyldimethylsilyl)oxy]-3-oxo-7-phenylheptanethioate,**
***S*-Dodecyl (*Z*)-5-[(*tert*-butyldimethylsilyl)oxy]-3-hydroxy-7-phenylhept-2-enethioate (10)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **9** (202 mg, 0.654 mmol) was performed with 1.5 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **10** (314 mg, 90% yield) as a colorless oil.

Keto/enol ratio = 65:35. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.33-7.26 (m, 2H), 7.22-7.16 (m, 3H), 5.47 (s, 0.35H), 4.26 (quin, J = 6.0 Hz, 0.65H), 4.13 (quin, J = 6.0 Hz, 0.35H), 3.71 (d, J = 14.4 Hz, 0.65H), 3.66 (d, J = 14.4 Hz, 0.65H), 2.96-2.90 (m, 2H), 2.80 (dd, J = 16.0, 6.8 Hz, 0.65H), 2.73-2.62 (m, 2.65H), 2.35 (dd, J = 13.5, 5.8 Hz, 0.35H), 2.31 (dd, J = 13.5, 7.0 Hz, 0.35H), 1.91-1.73 (m, 2H), 1.62 (quin, J = 7.6 Hz, 0.7H), 1.60 (quin, J = 7.6 Hz, 1.3H), 1.42-1.23 (m, 18H), 0.91 (s, 9H), 0.91 (t, J = 6.8 Hz, 3H), 0.10 (s, 1.95H), 0.08 (s, 1.05H), 0.06 (s, 1.95H), 0.04 (s, 1.05H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 200.9, 194.6, 191.8, 173.0, 142.1, 141.9, 128.4, 128.3, 125.8, 101.6, 69.3, 68.2, 58.9, 50.1, 43.0, 39.4, 39.2, 31.9, 31.3, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 28.8, 28.1, 25.8, 25.8, 22.7, 18.0, 18.0, 14.1, –4.6, –4.7, –4.9; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for C$_{31}$H$_{55}$O$_3$SSi [M+H]$^+$: 535.3641, found 535.3647.

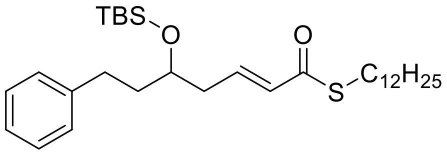


***S*-Dodecyl 5-[(*tert*-butyldimethylsilyl)oxy]-3-hydroxy-7-phenylheptanethioate (11)**

Synthesized according to the general procedure for reduction of a β-ketothioester. Sodium cyanoborohydride (2 equiv.) was added five times in every 5 min. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1). The reaction of β-ketothioester **10** (88.3 mg, 0.165 mmol) afforded β-hydroxythioester **11** (73.7 mg, 83% yield) as a colorless oil.

Diastereomeric ratio = 54:46. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.31-7.24 (m, 2H), 7.21-7.14 (m, 3H), 4.43-4.35 (m, 0.46H), 4.25-4.17 (m, 0.54H), 4.08-3.94 (m, 1H), 3.49 (d, J = 2.0 Hz, 0.46H), 3.30 (d, J =

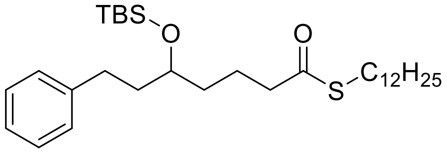
2.4 Hz, 0.54H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.80-2.58 (m, 4H), 1.92-1.61 (m, 4H), 1.57 (quin, *J* = 7.6 Hz, 2H), 1.39-1.17 (m, 18H), 0.91-0.90 (s×2, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.10-0.07 (s×4, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.7, 198.6, 142.1, 141.9, 128.4, 128.2, 125.8, 125.8, 71.1, 70.2, 67.3, 65.6, 51.5, 51.1, 42.5, 41.4, 39.2, 38.5, 31.9, 31.7, 31.1, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.8, 25.8, 22.7, 18.0, 14.1, –4.2, –4.5, –4.6, –4.7; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{31}H_{57}O_3SSi$ $[M+H]^+$: 537.3797, found 537.3801.



***S*-Dodecyl (*E*)-5-[(*tert*-butyldimethylsilyl)oxy]-7-phenylhept-2-enethioate (12)**

Synthesized according to the general procedure for dehydration of a β-hydroxythioester. After 10 min from starting the reaction, 0.5 equiv. of Martin sulfurane was added, and the mixture was stirred for additional 10 min. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1). The reaction of β-hydroxythioester **11** (72.9 mg, 0.136 mmol) afforded α,β-unsaturated thioester **12** (68.8 mg, 98% yield) as a colorless oil.

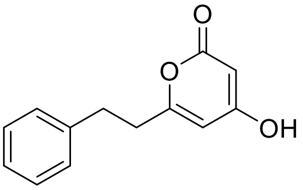
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20-7.14 (m, 3H), 6.89 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.12 (dt, *J* = 15.4, 1.4 Hz, 1H), 3.85 (quin, *J* = 5.8 Hz, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.74-2.55 (m, 2H), 2.44-2.31 (m, 2H), 1.77 (td, *J* = 8.0, 6.0 Hz, 2H), 1.59 (quin, *J* = 7.6 Hz, 2H), 1.41-1.20 (m, 18H), 0.91 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9, 142.0, 141.5, 130.8, 128.4, 128.3, 125.8, 70.8, 40.1, 39.1, 31.9, 31.7, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 28.7, 25.8, 22.7, 18.0, 14.1, –4.4, –4.5; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{31}H_{55}O_2SSi$ $[M+H]^+$: 519.3692, found 519.3703.



***S*-Dodecyl 5-[(*tert*-butyldimethylsilyl)oxy]-7-phenylheptanethioate (13)**

Synthesized according to the general procedure for reduction of an α,β-unsaturated thioester. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1). The reaction of α,β-unsaturated thioester **12** (18.4 mg, 35.5 μmol) afforded saturated thioester **13** (14.9 mg, 81% yield) as a colorless oil.

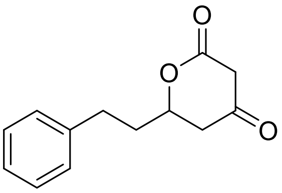
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20-7.14 (m, 3H), 3.72 (quin, *J* = 5.8 Hz, 1H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.71-2.56 (m, 2H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.80-1.62 (m, 4H), 1.61-1.48 (m, 4H), 1.40-1.19 (m, 18H), 0.91 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.05 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 142.5, 128.3, 128.3, 125.7, 71.4, 44.1, 38.9, 36.0, 31.9, 31.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.8, 28.8, 25.9, 22.7, 21.5, 18.1, 14.1, –4.4, –4.4; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{31}H_{57}O_2SSi$ $[M+H]^+$: 521.3848, found 521.3857.



4-Hydroxy-6-phenethyl-2-pyrone (14)

To a solution of β-ketothioester **6** (30.6 mg, 66.1 μmol) in dichloromethane (1.32 mL), ground iron(III) chloride hexahydrate (54 mg, 3 equiv.) was added. After stirring the mixture for 20 min, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (1.32 mL), and DBU (9.9 μL, 1 equiv.) was added. After stirring the mixture for 10 min, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: chloroform/methanol = 95:5) to afford pyrone **14** (12.6 mg, 88% yield) as a white solid.

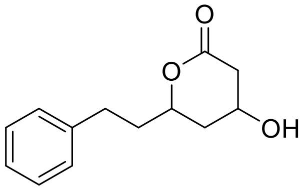
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.23-7.13 (m, 3H), 5.95 (s, 1H), 5.60 (s, 1H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 168.1, 165.9, 139.6, 128.6, 128.2, 126.5, 101.8, 90.0, 35.4, 32.8; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{13}H_{13}O_3$ $[M+H]^+$: 217.0864, found 217.0862.



6-Phenethyldihydro-2*H*-pyran-2,4(3*H*)-dione (15)

To a solution of ß-ketothioester **10** (25.7 mg, 48.0 µmol) in 1,4-dioxane (456 µL) and water (24 µL), *p*-toluenesulfonic acid monohydrate (45.6 mg, 5 equiv.) was added. After stirring the mixture for 6 h, a solution of potassium hydroxide (54 mg, 20 equiv.) in water (90 µL) was added. After stirring the mixture for additional 10 h, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: chloroform/methanol = 95:5) to afford dihydropyrane **15** (9.1 mg, 87% yield) as a white solid.

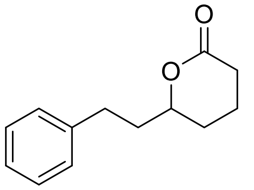
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.18 (m, 5H), 4.62-4.54 (m, 1H), 3.55 (d, *J* = 18.8 Hz, 1H), 3,43 (d, *J* = 18.8 Hz, 1H), 2.92 (ddd, *J* = 14.0, 9.0, 5.6 Hz, 1H), 2.82 (dt, *J* = 14.0, 8.4 Hz, 1H) , 2.68 (dd, *J* = 18.0, 2.6 Hz, 1H) , 2.50 (dd, *J* = 18.0, 11.6 Hz, 1H), 2.22-2.11 (m, 1H), 2.05-1.95 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.7, 167.1, 140.0, 128.7, 128.4, 126.5, 74.3, 47.1, 43.5, 36.1, 30.8; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{13}H_{15}O_3$ $[M+H]^+$: 219.1021, found 219.1021.



4-Hydroxy-6-phenethyltetrahydro-2*H*-pyran-2-one (16)

To a solution of ß-hydroxthioester **11** (52.9 mg, 98.5 µmol) in acetonitrile (1.97 mL), *p*-toluenesulfonic acid monohydrate (56.3 mg, 3 equiv.) was added. After stirring the mixture for 1 h, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate = 1:1 → 1:2) to afford tetrahydropyrane **16** (18.3 mg, 84% yield) as a colorless oil.

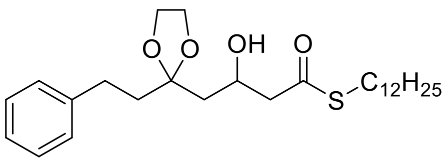
Diastereomeric ratio = 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 4.76-4.67 (m, 0.5H), 4.38 (broad s-like, 0.5H), 4.27-4.13 (m, 1H), 2.93-2.81 (m, 1.5H), 2.80-2.69 (m, 1.5H), 2.63 (ddd, *J* = 17.2, 3.6, 1.2 Hz, 0.5H), 2.47 (dd, *J* = 17.2, 7.6 Hz, 0.5H), 2.42 (broad s, 1H), 2.28-2.20 (m, 0.5H), 2,12-1.85 (m, 2.5H), 1.77 (ddd, *J* = 14.4, 11.2, 3.2 Hz, 0.5H), 1.62 (ddd, *J* = 14.0, 12.0, 9.2 Hz, 0.5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 170.7, 141.0, 140.7, 128.5, 128.5, 128.4, 128.4, 126.1, 126.1, 76.1, 75.1, 63.7, 62.6, 39.5, 38.6, 37.8, 37.3, 37.1, 35.9, 31.1, 31.0; **HRMS** (FAB, negative ion mode, matrix and internal calibrant: glycerol) *m*/*z*: calculated for $C_{13}H_{15}O_3$ $[M–H]^-$: 219.1021, found 219.1030.



6-Phenethyltetrahydro-2*H*-pyran-2-one (17)

To a solution of saturated thioester **13** (29.1 mg, 55.9 μmol) in acetonitrile (1.12 mL), *p*-toluenesulfonic acid monohydrate (32.4 mg, 3 equiv.) was added. After stirring the mixture for 30 min, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 1:1) to afford tetrahydropyrane **17** (10.9 mg, 96% yield) as a colorless oil.

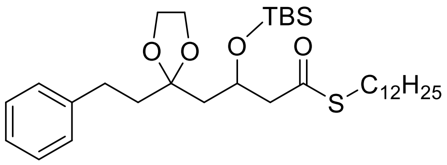
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 4.31-4.23 (m, 1H), 2.87 (ddd, *J* = 14.0, 9.6, 5.6 Hz, 1H), 2.75 (ddd, *J* = 14.0, 9.2, 7.2 Hz, 1H), 2.63-2.54 (m, 1H), 2.46 (ddd, *J* = 17.6, 8.8, 7.2 Hz, 1H), 2.08-1.98 (m, 1H), 1.96-1.78 (m, 4H), 1.62-1.52 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 141.1, 128.5, 126.0, 79.4, 37.5, 31.1, 29.4, 27.9, 18.4; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1228, found 205.1220.



S-Dodecyl 3-hydroxy-4-(2-phenethyl-1,3-dioxolan-2-yl)butanethioate (18)

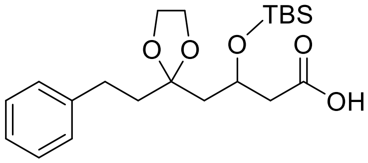
Synthesized according to the general procedure for reduction of a β-ketothioester. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 2:1). The reaction of β-ketothioester **6** (201 mg, 0.434 mmol) afforded β-hydroxythioester **18** (181 mg, 90% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.21-7.15 (m, 3H), 4.42-4.34 (m, 1H), 4.07-3.97 (m, 4H), 3.68 (s, 1H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.79 (dd, *J* = 15.0, 7.6 Hz, 1H), 2.68 (t, *J* = 8.8 Hz, 2H), 2.65 (dd, *J* = 15.0, 5.2 Hz, 1H), 2.05-1.83 (m, 4H), 1.57 (quin, *J* = 7.6 Hz, 2H), 1.39-1.20 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 141.6, 128.4, 128.3, 125.9, 111.2, 65.3, 65.0, 64.7, 51.1, 42.3, 39.1, 31.9, 30.0, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 29.0, 28.8, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{27}H_{45}O_4S$ $[M+H]^+$: 465.3038, found 465.3031.



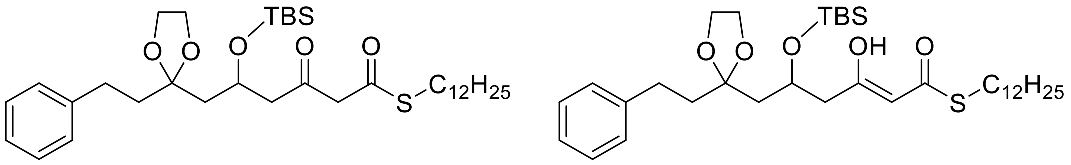
S-Dodecyl 3-[(*tert*-butyldimethylsilyl)oxy]-4-(2-phenethyl-1,3-dioxolan-2-yl)butanethioate (19)
To a solution of β-hydroxythioester **18** (140 mg, 0.301 mmol) in DMF (602 µL), imidazole (102 mg, 5 equiv.) and *tert*-butyldimethylchlorosilane (230 mg, 5 equiv.) were added. After stirring the mixture for 1 h, an aqueous saturated solution of ammonium chloride was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) to afford thioester **19** (171 mg, 98% yield) as a colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 4.40-4.33 (m, 1H), 4.01-3.91 (m, 4H), 2.96 (dd, J = 14.4, 3.6 Hz, 1H), 2.85 (t, J = 7.4 Hz, 2H), 2.70 (dd, J = 14.4, 8.4 Hz, 1H), 2.67 (t-like, J = 8.2 Hz, 2H), 1.99-1.89 (m, 4H), 1.56 (quin, J = 7.6 Hz, 2H), 1.39-1.20 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H), 0.84 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 198.1, 142.0, 128.4, 128.3, 125.8, 109.9, 66.3, 65.0, 64.7, 52.7, 44.5, 39.8, 31.9, 29.9, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 28.9, 25.8, 22.7, 17.9, 14.1, –4.5, –5.0; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{33}H_{59}O_4SSi$ $[M+H]^+$: 579.3903, found 579.3889.



3-[(*tert*-Butyldimethylsilyl)oxy]-4-(2-phenethyl-1,3-dioxolan-2-yl)butanoic acid (20)
Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 70 min without additional hydrogen peroxide. The reaction of thioester **19** (85.0 mg, 0.147 mmol) afforded carboxylic **20** (49.9 mg, 86% yield) as a colorless oil.

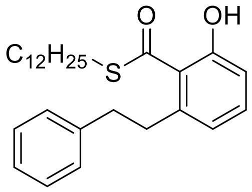
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 4.34-4.27 (m, 1H), 4.02-3.91 (m, 4H), 2.81 (dd, J = 15.4, 4.2 Hz, 1H), 2.71-2.65 (m, 2H), 2.55 (dd, J = 15.4, 6.8 Hz, 1H), 2.04-1.89 (m, 4H), 0.87 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 175.9, 141.8, 128.4, 128.3, 125.8, 109.7, 66.1, 64.9, 64.7, 44.0, 42.8, 39.6, 29.9, 25.7, 17.9, –4.6, –5.0; **HRMS** (FAB, negative ion mode, matrix: glycerol) *m/z*: calculated for $C_{21}H_{33}O_5Si$ $[M–H]^-$: 393.2098, found 393.2095.



S-Dodecyl 5-[(*tert*-butyldimethylsilyl)oxy]-3-oxo-6-(2-phenethyl-1,3-dioxolan-2-yl)hexanesthioate, *S*-Dodecyl (*Z*)-5-[(*tert*-butyldimethylsilyl)oxy]-3-hydroxy-6-(2-phenethyl-1,3-dioxolan-2-yl)hex-2-enethioate (21)

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **20** (49.4 mg, 0.125 mmol) was performed with 2 equiv. of MAHT **1** for 3 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **21** (70.1 mg, 90% yield) as a colorless oil.

Keto/enol ratio = 65:35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 5.46 (s, 0.35H), 4.41-4.34 (m, 0.65H), 4.25-4.17 (m, 0.35H), 4.01-3.89 (m, 4H), 3.69 (d, J = 14.6 Hz, 0.65H), 3.65 (d, J = 14.6 Hz, 0.65H), 2.98-2.84 (m, 2.65H), 2.76-2.62 (m, 3H), 2.15 (dd, J = 13.8, 8.6 Hz, 0.35H), 1.98-1.87 (m, 4H), 1.64-1.53 (m, 2H), 1.40-1.20 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H), 0.84 (s, 9H), 0.08 (s, 1.95H), 0.05 (s, 1.05H), 0.04 (s, 1.95H), 0.00 (s, 1.05H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 194.5, 191.9, 173.6, 142.0, 128.3, 128.3, 125.7, 110.0, 109.9, 101.7, 66.3, 65.3, 65.0, 64.9, 64.7, 64.7, 58.9, 51.2, 44.9, 44.2, 44.1, 39.9, 39.7, 31.9, 29.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.1, 29.1, 28.8, 28.7, 28.1, 25.8, 25.8, 22.7, 17.9, 17.9, 14.1, –4.6, –4.7, –4.9, –5.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{35}H_{81}O_5SSi$ $[M+H]^+$: 621.4009, found 621.4027.

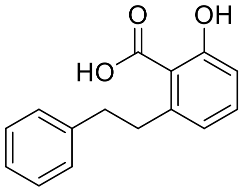


S-Dodecyl 2-hydroxy-6-phenethylbenzothioate (22)

By modifying the literature procedure,[1] silica-supported iron(III) chloride was prepared. To a solution of iron(III) chloride hexahydrate (135 mg) in acetone (0.6 mL), Wakogel® C-200 (1.1 g) was added. Until the mixture became slurry, acetone was added with stirring. The solvent was removed under reduced pressure, and the residue was transferred to an empty column with a filter at the bottom. The silica-supported reagent was washed by filtration with dichloromethane and chloroform, and dried under reduced pressure.

To a solution of β-ketothioester **21** (25.8 mg, 41.5 μmol) in chloroform (0.83 mL), silica-supported iron(III) chloride (40 mg) was added. After stirring the mixture for 50 min, the silica was filtered off with chloroform. Water was added, and the resulting mixture was extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (0.42 mL), and DBU (18.6 µL, 3 equiv.) was added. After stirring the mixture for 2 h, an aqueous saturated solution of ammonium chloride was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 4:1) to afford benzothioate **22** (13.5 mg, 76% yield) as a colorless oil.

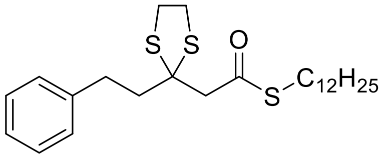
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.32-7.17 (m, 6H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.77 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.27-3.21 (m, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 2.98-2.91 (m, 2H), 1.71 (quin, *J* = 7.6 Hz, 2H), 1.43 (quin, *J* = 7.2 Hz, 2H), 1.37-1.22 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 156.2, 141.4, 141.3, 132.7, 128.4, 128.4, 126.1, 124.2, 122.6, 115.6, 38.2, 36.7, 31.9, 30.1, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 29.0, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{27}H_{39}O_2S$ $[M+H]^+$: 427.2671, found 427.2671.



6-Phenethylsalicylic acid (23)

To a solution of benzothioate **22** (13.5 mg, 31.6 µmol) in 1,4-dioxane (504 µL) and water (12 µL), an aqueous 30% solution of hydrogen peroxide (36 µL, 10 equiv.) and a solution of cesium hydroxide (23.6 mg, 5 equiv.) in water (78 µL) were added. An aqueous 30% solution of hydrogen peroxide (18 µL, 5 equiv.) was added twice in every 30 min, and the mixture was stirred for 2 h in total. Diethyl ether was added, and the resulting mixture was extracted with water. The aqueous layer was acidified with an aqueous 1 N solution of hydrochloric acid. Diethyl ether was added, and the layers were separated. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was washed with hexanes by decantation to afford substituted salicylic acid **23** (7.0 mg, 91%) as a white solid.

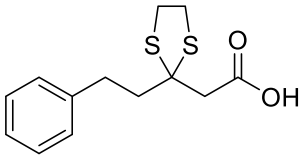
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (broad s, 1H), 7.39-7.16 (m, 6H), 6.91 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.75 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.34-3.27 (m, 2H), 2.96-2.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 163.7, 146.3, 141.7, 135.6, 128.4, 128.4, 126.0, 123.0, 116.3, 110.4, 38.5, 38.2; **HRMS** (FAB, negative ion mode, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{15}H_{13}O_3$ $[M-H]^-$: 241.0865, found 241.0862.



S-Dodecyl 2-(2-phenethyl-1,3-dithiolan-2-yl)ethanethioate (24)

To a solution of β-ketothioester **3** (932 mg, 2.47 mmol) in 1,2-dichloroethane (12.4 mL), 1,2-ethandithiol (218 μL, 1.05 equiv.) and trimethylsilyl trifluoromethanesulfonate (456 μL, 1 equiv.) were added. After stirring the mixture for 10 min, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 95:5) to afford thioester **24** (1.07 g, 95% yield) as a colorless oil.

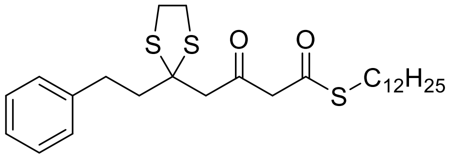
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 3.35 (s, 2H), 3.33 (s, 4H), 2.89 (t, J = 7.4 Hz, 2H), 2.89-2.82 (m, 2H), 2.39-2.32 (m, 2H), 1.57 (quin, J = 7.4 Hz, 2H), 1.40-1.20 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.0, 141.4, 128.5, 128.4, 125.9, 67.1, 56.6, 44.8, 39.8, 33.3, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) m/z: calculated for $C_{25}H_{40}OS_3$ $[M]^{+}$: 452.2241, found 452.2234.

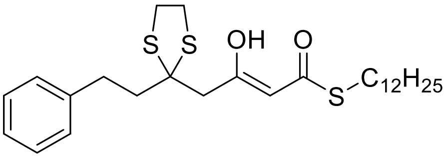


2-(2-Phenethyl-1,3-dithiolan-2-yl)acetic acid (25)

Synthesized according to the general procedure for hydrolysis of a thioester without hydrogen peroxide. The reaction of thioester **24** (326 mg, 0.719 mmol) afforded carboxylic **25** (192 mg, 99% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.23-7.15 (m, 3H), 3.36 (s, 4H), 3.17 (s, 2H), 2.91-2.84 (m, 2H), 2.45-2.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 141.3, 128.5, 128.4, 126.0, 66.4, 48.2, 44.3, 39.9, 33.3; **HRMS** (FAB, negative ion mode, matrix: 3-nitrobenzyl alcohol) m/z: calculated for $C_{13}H_{15}O_2S_2$ $[M–H]^{–}$: 267.0514, found 267.0515.

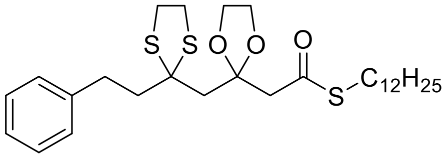




_S_-Dodecyl 3-oxo-4-(2-phenethyl-1,3-dithiolan-2-yl)butanethioate,
_S_-Dodecyl (_Z_)-3-hydroxy-4-(2-phenethyl-1,3-dithiolan-2-yl)but-2-enethioate (26)

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **25** (52.7 mg, 0.196 mmol) was performed with 1.6 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **26** (90.3 mg, 93% yield) as a pale orange solid.

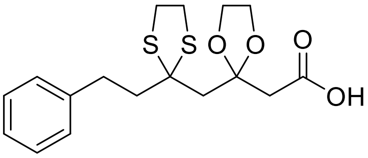
Keto/enol ratio = 20:80. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.30-7.14 (m, 5H), 5.61 (s, 0.8H), 3.64 (s, 0.4H), 3.35 (s, 0.4H), 3.33 (s, 3.2H), 3.31-3.26 (m, 0.8H), 2.95-2.86 (m, 5.2H), 2.82-2.76 (m, 0.4H), 2.38-2.33 (m, 0.4H), 2.32-2.25 (m, 1.6H), 1.65-1.52 (m, 2H), 1.42-1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 198.7, 194.9, 191.8, 171.1, 141.5, 141.4, 128.5, 128.3, 125.8, 102.4, 68.8, 66.1, 58.2, 55.8, 48.7, 45.2, 44.2, 39.9, 39.5, 33.3, 33.3, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.8, 28.3, 22.7, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for C$_{27}$H$_{42}$O$_2$S$_3$ [M]$^{+}$: 494.2347, found 494.2352.



_S_-Dodecyl 2-(2-[(2-phenethyl-1,3-dithiolan-2-yl)methyl]-1,3-dioxolan-2-yl)ethanethioate (27)

The reaction was performed under argon atmosphere. To a solution of β-ketothioester **26** (102 mg, 0.205 mmol) and ethylenedioxybis(trimethylsilane) (1.01 mL, 20 equiv.) in dichloromethane (4.1 mL), trimethylsilyl trifluoromethanesulfonate (38 μL, 1 equiv.) was added at 0 °C. After stirring the mixture for 96 h at this temperature, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) to afford thioester **27** (88.5 mg, 80% yield) as a colorless oil.

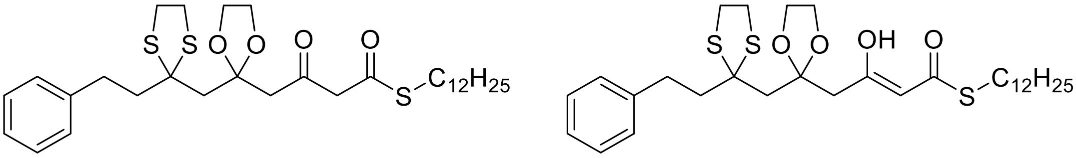
^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.29-7.13 (m, 5H), 4.08-4.00 (m, 4H), 3.34-3.23 (m, 4H), 2.97 (s, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.88-2.82 (m, 2H), 2.80 (s, 2H), 2.31-2.24 (m, 2H), 1.56 (quin, *J* = 7.2 Hz, 2H), 1.39-1.20 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 194.8, 142.2, 128.4, 128.2, 125.6, 108.5, 68.1, 64.4, 52.2, 47.7, 45.9, 38.9, 33.3, 31.8, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.0, 28.7, 22.6, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{29}H_{46}O_3S_3$ $[M]^+$: 538.2609, found 538.2610.



2-(2-[(2-Phenethyl-1,3-dithiolan-2-yl)methyl]-1,3-dioxolan-2-yl)acetic acid (28)

Synthesized according to the general procedure for hydrolysis of a thioester without hydrogen peroxide. The reaction of thioester **27** (218 mg, 0.404 mmol) afforded carboxylic **28** (138 mg, 97% yield) as a white solid.

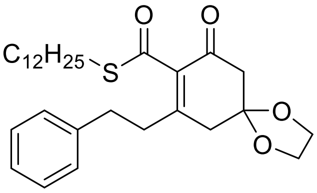
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.22-7.14 (m, 3H), 4.12-4.02 (m, 4H), 3.35-3.25 (m, 4H), 2.90-2.83 (m, 2H), 2.83 (s, 2H), 2.81 (s, 2H), 2.32-2.25 (m, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 173.8, 142.1, 128.5, 128.3, 125.7, 108.4, 68.1, 64.5, 47.6, 45.9, 43.5, 39.1, 33.4; **HRMS** (FAB, negative ion mode, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{17}H_{21}O_4S_2$ $[M–H]^-$: 353.0882, found 353.0886.



***S*-Dodecyl 3-oxo-4-(2-[(2-phenethyl-1,3-dithiolan-2-yl)methyl]-1,3-dioxolan-2-yl)butanethioate, *S*-Dodecyl (*Z*)-3-hydroxy-4-(2-[(2-phenethyl-1,3-dithiolan-2-yl)methyl]-1,3-dioxolan-2-yl)but-2-enethioate (29)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **28** (64.1 mg, 0.181 mmol) was performed with 1.9 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **29** (101 mg, 96% yield) as a pale orange solid.

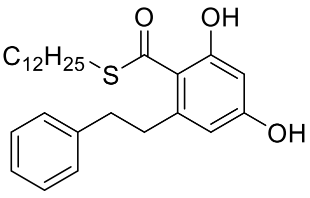
Keto/enol ratio = 70:30. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.14 (m, 3H), 5.55 (s, 0.3H), 4.09-3.98 (m, 4H), 3.78 (s, 1.4H), 3.34-3.25 (m, 4H), 3.00 (s, 1.4H), 2.94-2.81 (m, 4H), 2.73 (s, 0.6H), 2.67 (s, 1.4H), 2.54 (s, 0.6H), 2.31-2.24 (m, 2H), 1.65-1.52 (m, 2H), 1.44-1.20 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 198.8, 194.7, 192.1, 170.5, 142.2, 142.1, 128.4, 128.3, 125.7, 125.7, 109.4, 108.6, 102.3, 68.2, 68.1, 64.5, 64.4, 58.7, 50.9, 47.9, 47.6, 46.0, 45.6, 44.5, 39.0, 33.4, 33.3, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.8, 28.2, 22.6, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{31}H_{48}O_4S_3$ $[M]^{+}$: 580.2715, found 580.2718.



S-Dodecyl 9-oxo-7-phenethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-carbothioate (30)

To a solution of β-ketothioester **29** (30.5 mg, 51.0 µmol) in dichloromethane (832 µL), a DME solution (0.5 M) of orthoperiodic acid[2] (208 µL, 2 equiv.) was added at 0 °C. The reaction flask was allowed to warm to room temperature. After stirring the mixture for 10 min, an aqueous saturated solution of sodium thiosulfate was added. The resulting mixture was extracted with diethyl ether, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (1.04 mL), and triethylamine (36.0 µL, 5 equiv.) was added. After stirring the mixture for 30 min, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate = 3:1) to afford cyclic thioester **30** (17.2 mg, 68% yield) as a colorless oil.

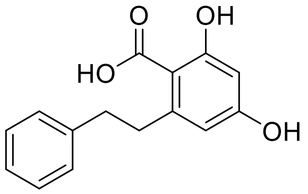
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.16 (m, 5H), 4.02-3.93 (m, 4H), 3.02 (t, J = 7.4 Hz, 2H), 2.88-2.82 (m, 2H), 2.72 (s, 2H), 2.68 (s, 2H), 2.64-2.58 (m, 2H), 1.63 (quin, J = 7.2 Hz, 2H), 1.42-1.21 (m, 18H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.3, 193.1, 158.6, 140.2, 137.6, 128.6, 128.2, 126.5, 107.4, 64.8, 47.7, 40.9, 37.4, 34.0, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.9, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{29}H_{43}O_4S$ $[M+H]^{+}$: 487.2882, found 487.2884.



S-Dodecyl 2,4-dihydroxy-6-phenethylbenzothioate (31)

Cyclic thioester **30** (12.1 mg, 24.9 µmol) was dissolved in formic acid (0.4 mL) and water (0.1 mL), and the mixture was stirred for 48 h. Diethyl ether and water were added, and the layers were separated. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: chloroform/methanol = 95:5) to afford benzothioate **31** (8.0 mg, 73% yield) as a colorless oil.

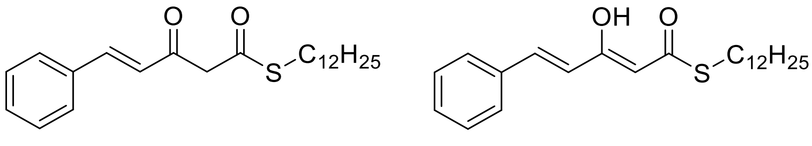
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (broad s, 1H), 7.33-7.18 (m, 5H), 6.28 (d, J = 2.6 Hz, 1H), 6.25 (d, J = 2.6 Hz, 1H), 5.36 (broad s, 1H), 3.36-3.29 (m, 2H), 3.09 (t, J = 7.4 Hz, 2H), 2.99-2.92 (m, 2H), 1.69 (quin, J = 7.2 Hz, 2H), 1.43 (quin, J = 7.2 Hz, 2H), 1.37-1.20 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 161.5, 159.6, 145.0, 141.3, 128.4, 128.4, 126.1, 116.3, 110.8, 101.9, 38.0, 37.6, 31.9, 30.1, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.0, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m/z*: calculated for $C_{27}H_{39}O_3S$ $[M+H]^{+}$: 443.2620, found 443.2621.



2,4-Dihydroxy-6-phenethylbenzoic acid (32)

To a solution of benzothioate **31** (13.4 mg, 30.3 μmol) in 1,4-dioxane (484 μL) and water (121 μL), *m*-chloroperoxybenzoic acid (containing ca. 30% water, 37.4 mg, 5 equiv.) was added. After stirring the mixture for 30 min, an aqueous saturated solution of sodium thiosulfate was added. Diethyl ether was added, and the layers were separated. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: chloroform/methanol = 97:3 → 3:1) to afford benzoic acid **32** (7.5 mg, 96% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (broad s, 1H), 7.33-7.17 (m, 5H), 6.33 (d, J = 2.2 Hz, 1H), 6.24 (d, J = 2.2 Hz, 1H), 3.28-3.19 (m, 2H), 2.95-2.87 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.4, 166.5, 161.2, 149.0, 141.6, 128.4, 126.0, 111.4, 103.7, 101.9, 38.7, 37.9; **HRMS** (FAB, negative ion mode, matrix: 3-nitrobenzyl alcohol) *m/z*: calculated for $C_{15}H_{13}O_4$ $[M-H]^{-}$: 257.0814, found 257.0813.

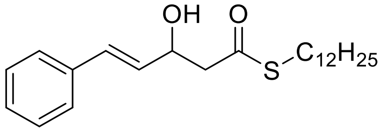


***S*-Dodecyl (*E*)-3-oxo-5-phenylpent-4-enethioate,**

***S*-Dodecyl (2*Z*,4*E*)-3-hydroxy-5-phenylpenta-2,4-dienethioate (34)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **33** (76.2 mg, 0.512 mmol) was performed with 1.5 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **34** (177 mg, 92% yield) as a pale yellow solid.

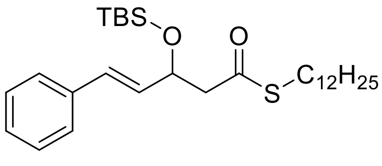
Keto/enol ratio = 17:83. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 0.17H), 7.58-7.53 (m, 0.34H), 7.52-7.46 (m, 2.49H), 7.42-7.30 (m, 3H), 6.82 (d, *J* = 16.0 Hz, 0.17H), 6.36 (d, *J* = 16.0 Hz, 0.83H), 5.58 (s, 0.83H), 3.91 (s, 0.34H), 2.96 (t, *J* = 7.6 Hz, 1.66H), 2.93 (t, *J* = 7.2 Hz, 0.34H), 1.63 (quin, *J* = 7.6 Hz, 1.66H), 1.59 (quin, *J* = 7.0 Hz, 0.34H), 1.44-1.19 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8, 192.2, 191.3, 166.3, 145.1, 138.4, 135.2, 134.1, 131.0, 129.6, 129.0, 128.8, 128.6, 127.6, 125.0, 121.4, 101.7, 56.2, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 28.9, 28.8, 28.4, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{23}H_{35}O_2S$ [M+H]$^+$: 375.2358, found 375.2356.



S-Dodecyl (E)-3-hydroxy-5-phenylpent-4-enethioate (35)

Synthesized according to the general procedure for reduction of a β-ketothioester. The reaction was performed for 3 h with 1.5 equiv. of cerium(III) chloride heptahydrate. The purification was performed by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 4:1). The reaction of β-ketothioester **38** (123 mg, 0.328 mmol) afforded β-hydroxythioester **35** (115 mg, 93% yield) as a pale yellow solid.

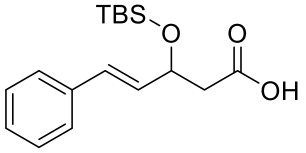
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 6.65 (dd, *J* = 16.0, 0.8 Hz, 1H), 6.20 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.77 (broad q-like, *J* = 6.7 Hz, 1H), 2.93-2.82 (m, 5H), 1.57 (quin, *J* = 7.6 Hz, 2H), 1.39-1.21 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.8, 136.4, 130.9, 129.7, 128.6, 127.8, 126.5, 69.5, 50.6, 31.9, 29.6, 29.5, 29.4, 29.4, 29.3, 29.1, 28.8, 22.7, 14.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{23}H_{36}O_2S$ [M]$^+$: 376.2436, found 376.2433.



S-Dodecyl (E)-3-[(*tert*-butyldimethylsilyl)oxy]-5-phenylpent-4-enethioate (36)

To a solution of β-hydroxythioester **35** (84.6 mg, 0.225 mmol) in DMF (450 μL), imidazole (77.1 mg, 5 equiv.) and *tert*-butyldimethylchlorosilane (170 mg, 5 equiv.) were added. After stirring the mixture for 30 min, an aqueous saturated solution of ammonium chloride was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) to afford thioester **36** (109 mg, 99% yield) as a colorless oil.

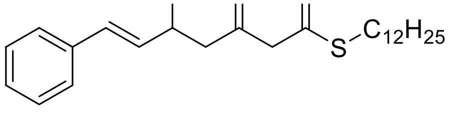
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.20 (m, 5H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 15.6, 6.6 Hz, 1H), 4.82-4.76 (m, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.86 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.70 (dd, *J* = 14.4, 5.2 Hz, 1H), 1.55 (quin, *J* = 7.4 Hz, 2H), 1.38-1.20 (m, 18H), 0.89 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.07 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 136.6, 131.4, 129.9, 128.5, 127.6, 126.5, 70.8, 52.7, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 29.1, 28.8, 25.8, 22.7, 18.2, 14.1, –4.3, –5.1; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m/z*: calculated for $C_{29}H_{50}O_2SSi$ $[M]^{+\cdot}$: 490.3301, found 490.3299.

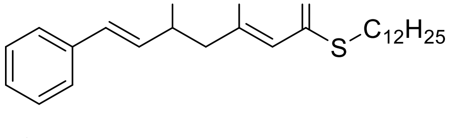


(*E*)-3-[(*tert*-Butyldimethylsilyl)oxy]-5-phenylpent-4-enoic acid (37)

Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 50 min without additional hydrogen peroxide. The reaction of thioester **36** (134 mg, 0.272 mmol) afforded carboxylic **37** as a slightly yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, 5H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.19 (dd, *J* = 15.6, 6.6 Hz, 1H), 4.80-4.73 (m, 1H), 2.67 (dd, *J* = 15.0, 7.6 Hz, 1H), 2.61 (dd, *J* = 15.0, 5.6 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 136.4, 130.8, 130.5, 128.6, 127.8, 126.5, 70.5, 43.4, 25.7, 18.1, –4.2, –5.1; **HRMS** (FAB, negative ion mode, matrix: glycerol) *m/z*: calculated for $C_{17}H_{25}O_3Si$ $[M-H]^-$: 305.1573, found 305.1570.

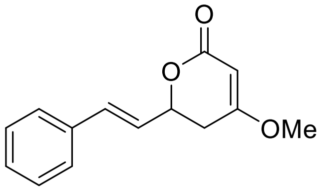




S-Dodecyl (*E*)-5-[(*tert*-butyldimethylsilyl)oxy]-3-oxo-7-phenylhept-6-enethioate,
S-Dodecyl (2*Z*,6*E*)-5-[(*tert*-butyldimethylsilyl)oxy]-3-hydroxy-7-phenylhepta-2,6-dienethioate (38)

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **37** (obtained from 0.272 mmol of **36**) was performed with 1.3 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **38** (115 mg, 80% yield from **36**) as a yellow solid.

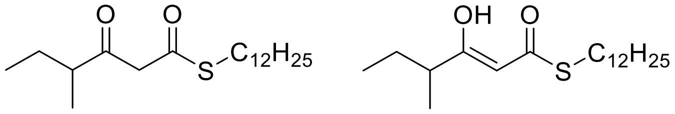
Keto/enol ratio = 55:45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 5H), 6.57 (d, *J* = 16.0 Hz, 0.45H), 6.56 (d, *J* = 16.0 Hz, 0.55H), 6.18 (dd, *J* = 16.0, 6.4 Hz, 0.45H), 6.16 (dd, *J* = 16.0, 6.6 Hz, 0.55H), 5.48 (s, 0.45H), 4.82-4.76 (m, 0.55H), 4.69-4.62 (m, 0.45H), 3.73 (d, *J* = 15.0 Hz, 0.55H), 3.69 (d, *J* = 15.0 Hz, 0.55H), 2.96-2.86 (m, 2.55H), 2.69 (dd, *J* = 15.6, 4.4 Hz, 0.55H), 2.40 (dd, *J* = 13.6, 4.6 Hz, 0.45H), 2.33 (dd, *J* = 13.6, 8.4 Hz, 0.45H), 1.64-1.52 (m, 2H), 1.41-1.21 (m, 18H), 0.89 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.08 (s, 1.65H), 0.06 (s, 1.65H), 0.04 (s, 1.35H), 0.03 (s, 1.35H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4, 194.7, 191.9, 172.2, 136.6, 136.5, 131.9, 131.4, 129.9, 129.7, 128.6, 127.7, 127.6, 126.5, 101.9, 70.7, 70.1, 59.0, 51.2, 44.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.5, 29.3, 29.2, 29.1, 29.1, 28.8, 28.1, 25.8, 25.8, 22.7, 18.2, 18.1, 14.1, –4.3, –4.5, –5.0, –5.2; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{31}H_{52}O_3SSi$ $[M]^{+}$: 532.3406, found 532.3402.



Kavain (40)

To a solution of β-ketothioester **38** (30.6 mg, 57.4 μmol) in 1,4-dioxane (1.09 mL) and water (57.4 μL), *p*-toluenesulfonic acid monohydrate (55.0 mg, 5 equiv.) was added. After stirring the mixture for 12 h, a solution of potassium hydroxide (67.9 mg, 20 equiv.) in water (215 μL) was added. After stirring the mixture for additional 5 h, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (1.15 mL), and DIEA (50.0 μL, 5 equiv.) was added. The solution was cool to –78 °C, and trimethyloxonium tetrafluoroborate (30 mg, 3 equiv.) was added. After stirring the mixture for 10 min at –78 °C, the reaction flask was allowed to warm to room temperature. After stirring for additional 20 min, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: chloroform/methanol = 97:3) to afford kavain (10.1 mg, 76% yield) as a white solid.

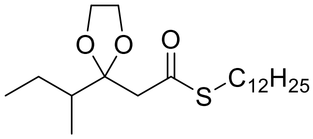
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.27 (m, 5H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 5.10-5.03 (m, 1H), 3.77 (s, 3H), 2.67 (ddd, *J* = 16.8, 11.2, 1.2 Hz, 1H), 2.55 (dd, *J* = 16.8, 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 172.3, 166.7, 135.7, 133.1, 128.7, 128.3, 126.7, 125.4, 90.5, 75.9, 56.1, 33.3; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for C$_{14}$H$_{15}$O$_3$ [M+H]$^+$: 231.1021, found 231.1021.



***S*-Dodecyl 4-methyl-3-oxohexanethioate, *S*-Dodecyl (*Z*)-3-hydroxy-4-methylhex-2-enethioate (42)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **41** (103 mg, 1.01 mmol) was performed with 1.5 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **42** (308 mg, 93% yield) as a pale orange oil.

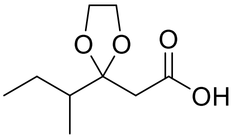
Keto/enol ratio = 65:35. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 5.42 (s, 0.35H), 3.69 (s, 1.3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.61 (sext, *J* = 6.8 Hz, 0.65H), 2.29 (sext, *J* = 6.8 Hz, 0.35H), 1.77-1.20 (m, 22H), 1.13 (d, *J* = 6.8 Hz, 1.05H), 1.10 (d, *J* = 7.6 Hz, 1.95H), 0.90 (t, *J* = 7.2 Hz, 1.05H) , 0.89 (t, *J* = 7.2 Hz, 1.95H) , 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 205.7, 194.7, 192.1, 180.1, 98.4, 56.0, 48.1, 40.9, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.7, 28.1, 27.1, 25.5, 22.7, 17.5, 15.4, 14.1, 11.7, 11.4; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for C$_{19}$H$_{37}$O$_2$S [M+H]$^+$: 329.2514, found 329.2514.



***S*-Dodecyl 2-[2-(*sec*-butyl)-1,3-dioxolan-2-yl]ethanethioate (43)**

To a solution of β-ketothioester **42** (94.8 mg, 0.289 mmol) and ethylenedioxybis(trimethylsilane) (354 μL, 5 equiv.) in dichloromethane (1.44 mL), trimethylsilyl trifluoromethanesulfonate (53.2 μL, 1 equiv.) was added at 0 °C. After stirring for 3 h at this temperature, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) to afford thioester **43** (90.5 mg, 84% yield) as a colorless oil.

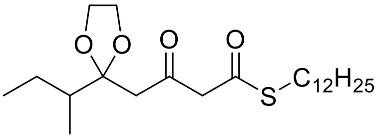
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.04-3.90 (m, 4H), 2.89 (s, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.79-1.65 (m, 2H), 1.56 (quin, *J* = 7.4 Hz, 2H), 1.40-1.20 (m, 18H), 1.12-1.01 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H) , 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 112.0, 65.4, 65.3, 48.5, 42.6, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 23.6, 22.7, 14.1, 13.3, 12.2; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{21}H_{41}O_3S$ $[M+H]^+$: 373.2776, found 373.2778.

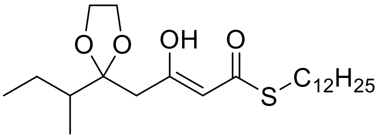


2-[2-(*sec*-Butyl)-1,3-dioxolan-2-yl]acetic acid (44)

Synthesized according to the general procedure for hydrolysis of a thioester. After 20 and 40 min from starting the reaction, 5 equiv. of hydrogen peroxide was added respectively. The mixture was stirred for 1 h in total. The reaction of thioester **43** (90.5 mg, 0.243 mmol) afforded carboxylic **44** (44.4 mg, 97% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09-3.94 (m, 4H), 2.74 (d, *J* = 14.2 Hz, 1H), 2.70 (d, *J* = 14.2 Hz, 1H), 1.84-1.63 (m, 2H), 1.15-1.01 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 111.8, 65.3, 65.2, 42.2, 39.6, 23.6, 13.3, 12.1; **HRMS** (FAB, negative ion mode, matrix: polyethylene glycol 400) *m/z*: calculated for $C_9H_{15}O_4$ $[M–H]^–$: 187.0971, found 187.0966.

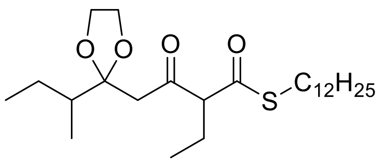




***S*-Dodecyl 4-[2-(*sec*-butyl)-1,3-dioxolan-2-yl]-3-oxobutanethioate,**
***S*-Dodecyl (*Z*)-4-[2-(*sec*-butyl)-1,3-dioxolan-2-yl]-3-hydroxybut-2-enethioate (45)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **44** (34.4 mg, 0.183 mmol) was performed with 1.5 equiv. of MAHT **1** for 2 h. The purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) afforded β-ketothioester **45** (59.1 mg, 78% yield) as a colorless oil.

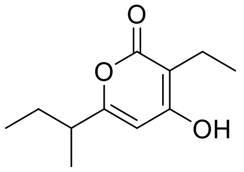
Keto/enol ratio = 70:30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.54 (s, 0.3H), 4.01-3.91 (m, 4H), 3.80 (s, 1.4H), 2.91 (t, *J* = 7.2 Hz, 0.6H), 2.91 (t, *J* = 7.2 Hz, 1.4H), 2.85 (s, 1.4H), 2.48 (s, 0.6H), 1.74-1.53 (m, 4H), 1.41-1.21 (m, 18H), 1.10-0.85 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.2, 194.6, 192.4, 171.9, 112.6, 112.4, 102.3, 65.5, 65.3, 65.0, 65.0, 58.8, 46.8, 42.7, 42.6, 40.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 28.8, 28.8, 28.1, 23.7, 22.7, 14.1, 13.5, 13.4, 12.2; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m/z*: calculated for $C_{23}H_{43}O_4S$ $[M+H]^+$: 415.2882, found 415.2882.



***S*-Dodecyl 4-[2-(*sec*-butyl)-1,3-dioxolan-2-yl]-2-ethyl-3-oxobutanethioate (46)**

To a solution of β-ketothioester **45** (80.4 mg, 0.194 mmol) in DMF (1.94 mL), ethyl iodide (46.6 μL, 3 equiv.) and DBU (29.0 μL, 1 equiv.) were added. After stirring the mixture for 8 h, an aqueous saturated solution of ammonium chloride was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 7:1) to afford α-ethylated β-ketothioester **46** (71.7 mg, 84% yield) as a colorless oil.

Diastereomeric ratio = 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.04-3.89 (m, 4H), 3.87 (t, *J* = 7.2 Hz, 0.5H), 3.87 (t, *J* = 7.2 Hz, 0.5H), 2.93 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.75 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.88 (quin, *J* = 7.2 Hz, 2H), 1.72-1.62 (m, 2H), 1.57 (quin, *J* = 7.2 Hz, 2H), 1.40-1.20 (m, 18H), 1.12-0.96 (m, 1H), 0.95-0.85 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 201.4, 195.8, 195.8, 112.5, 70.3, 65.1, 65.1, 65.0, 65.0, 45.6, 45.5, 42.5, 42.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 28.7, 23.8, 23.5, 22.7, 22.3, 22.3, 14.1, 13.6, 13.2, 12.2, 12.2, 11.8; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{25}H_{47}O_4S$ $[M+H]^+$: 443.3195, found 443.3190.



Germicidin A (47)

To a solution of α-ethylated β-ketothioester **46** (27.0 mg, 61.0 μmol) in dichloromethane (1.22 mL), ground iron(III) chloride hexahydrate (47 mg, 3 equiv.) was added. After stirring the mixture for 10 min, an aqueous saturated solution of sodium bicarbonate was added. The resulting mixture was extracted with diethyl ether. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (1.22 mL), and DBU (9.1 μL, 1 equiv.) was added. After stirring the mixture for 10 min, an aqueous 1 N solution of hydrochloric acid was added. The resulting mixture was extracted with chloroform, and the organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: chloroform/methanol = 95:5) to afford germicidin A (10.6 mg, 89% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (broad s, 1H), 6.18 (s, 1H), 2.49 (q, J = 7.2 Hz, 2H), 2.44 (sext, J = 6.8 Hz, 1H), 1.68 (d quin, J = 14.8, 7.2 Hz, 1H), 1.51 (d quin, J = 14.8, 7.2 Hz, 1H), 1.18 (d, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 167.1, 166.9, 104.6, 100.0, 39.7, 27.4, 17.7, 16.4, 12.5, 11.6; **HRMS** (FAB, matrix: 3-nitrobenzyl alcohol) *m*/*z*: calculated for $C_{11}H_{17}O_3$ $[M+H]^+$: 197.1177, found 197.1177.

Procedure for enantioselective reduction of β-ketothioester 34.

A flask containing β-ketothioester **34** (20.6 mg, 55.0 μmol), $[NH_2Me_2][\{RuCl((R)\text{-segphos})\}_2(\mu\text{-}Cl)_3]$ (purchased from TCI, 9.6 mg, 0.1 equiv.), THF (1.1 mL), and methanol (1.1 mL) was degassed, and filled with hydrogen. The mixture was stirred under hydrogen atmosphere at 50 °C for 3 h. The flask was cooled to room temperature, and hydrogen was replaced with air. After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 3:1) to afford β-hydroxythioester **35** (16.1 mg, 78% yield). Enantiomeric ratio was determined by HPLC analysis (Chiralcel OD-H, hexane/2-propanol = 95:5, 1.0 mL min^{-1}): t_R = 15.1 min (minor), 19.1 min (major).

Enantioenriched β-hydroxythioester **35** was converted to kavain. By comparing with the literature data,[3] the absolute configuration of the major enantiomer was determined.

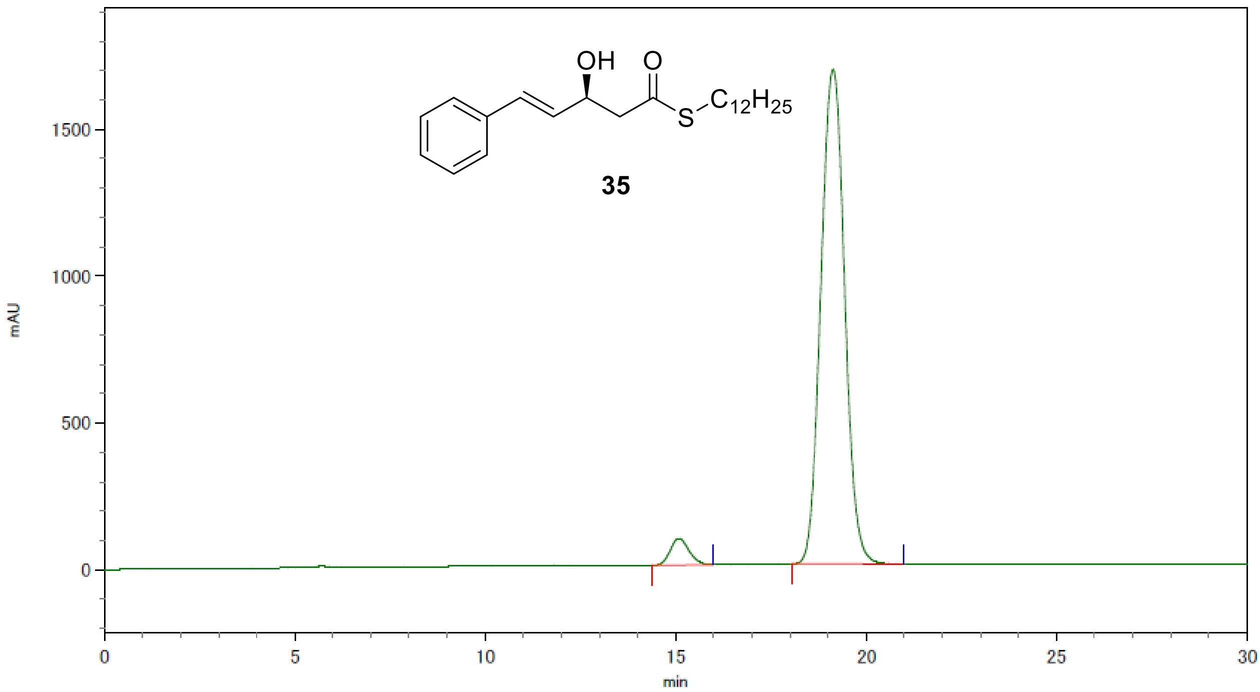
References.

1 K. S. Kim, Y. H. Song, B. H. Lee and C. S. Hahn, *J. Org. Chem.*, 1986, **51**, 404–407.

2 X.-X. Shi, S. P. Khanapure and J. Rokach, *Tetrahedron Lett.*, 1996, **37**, 4331–4334.

3 L. Lin, Z. Chen, X. Yang, X. Liu and X. Feng, *Org. Lett.*, 2008, **10**, 1311–1314.

Chiralcel OD-H column, hexane/2-propanol = 95:5, 1.0 mL min^{-1}



1: 254 nm, 8 nm

retention time	area	area %
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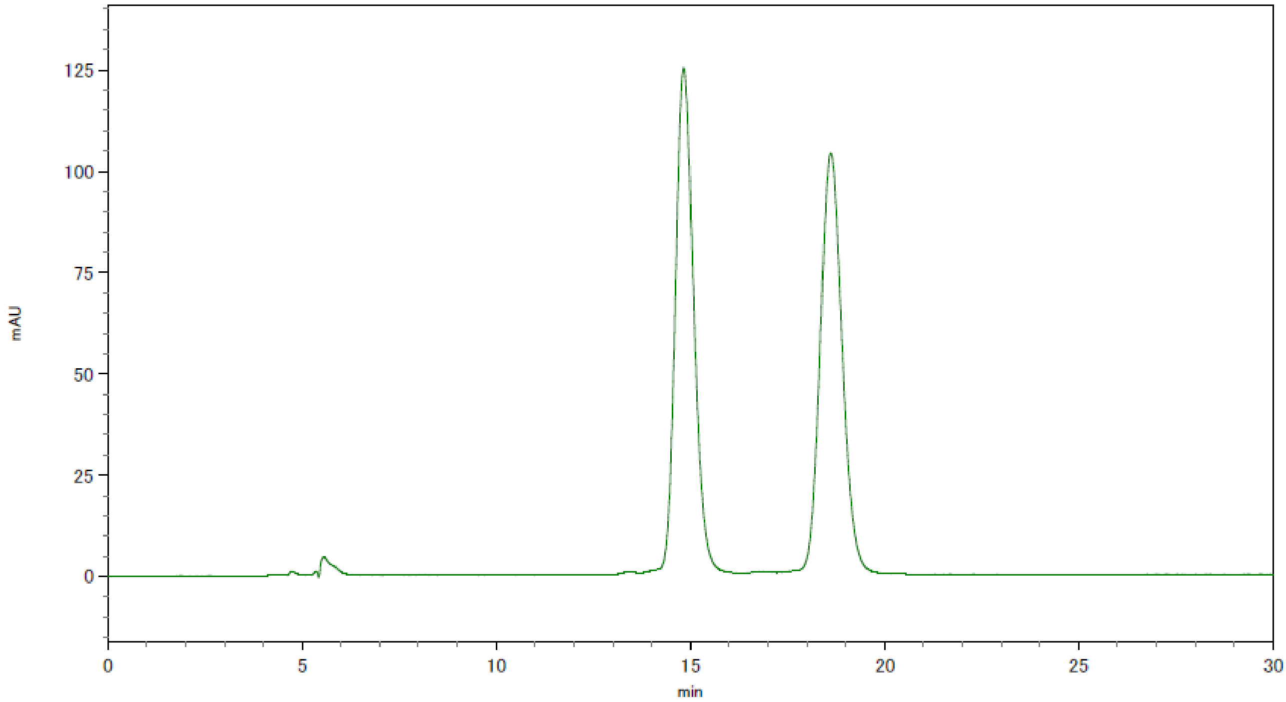
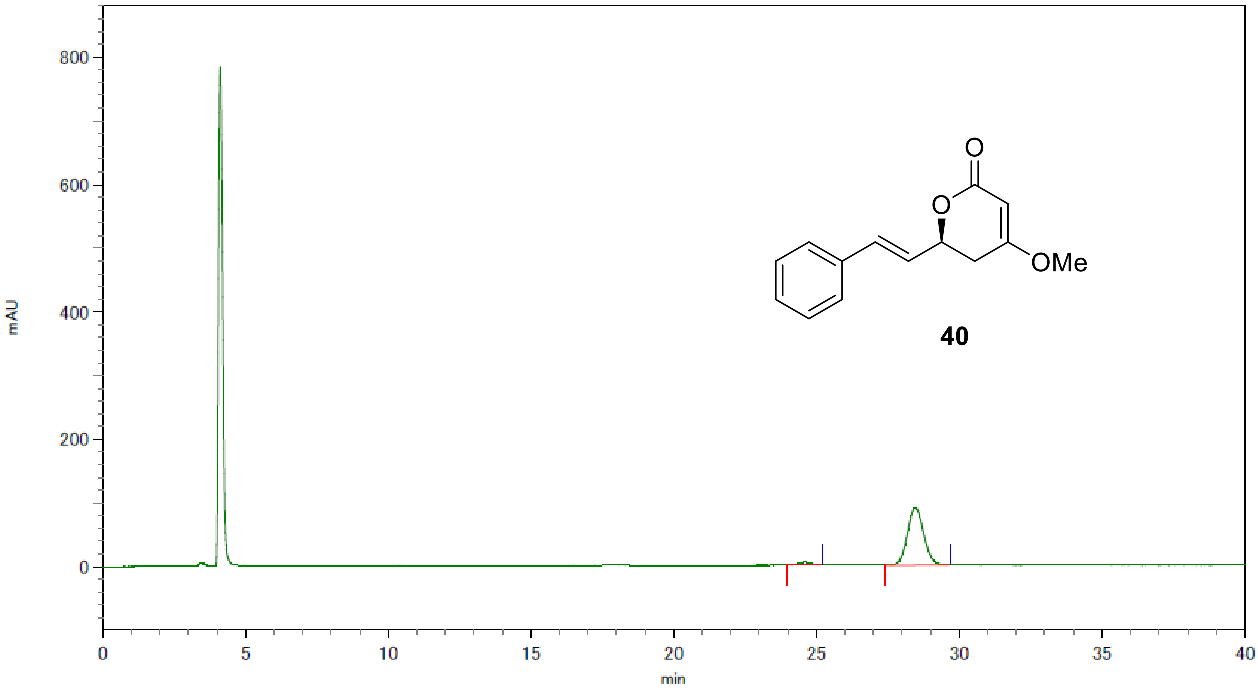
19.130	72711593	95.91
Total	75813064	100.00

racemic sample



Chiralpak AD-H column, hexane/2-propanol = 90:10, 1.0 mL min^{-1}



1: 210 nm, 8 nm

retention time	area	area %
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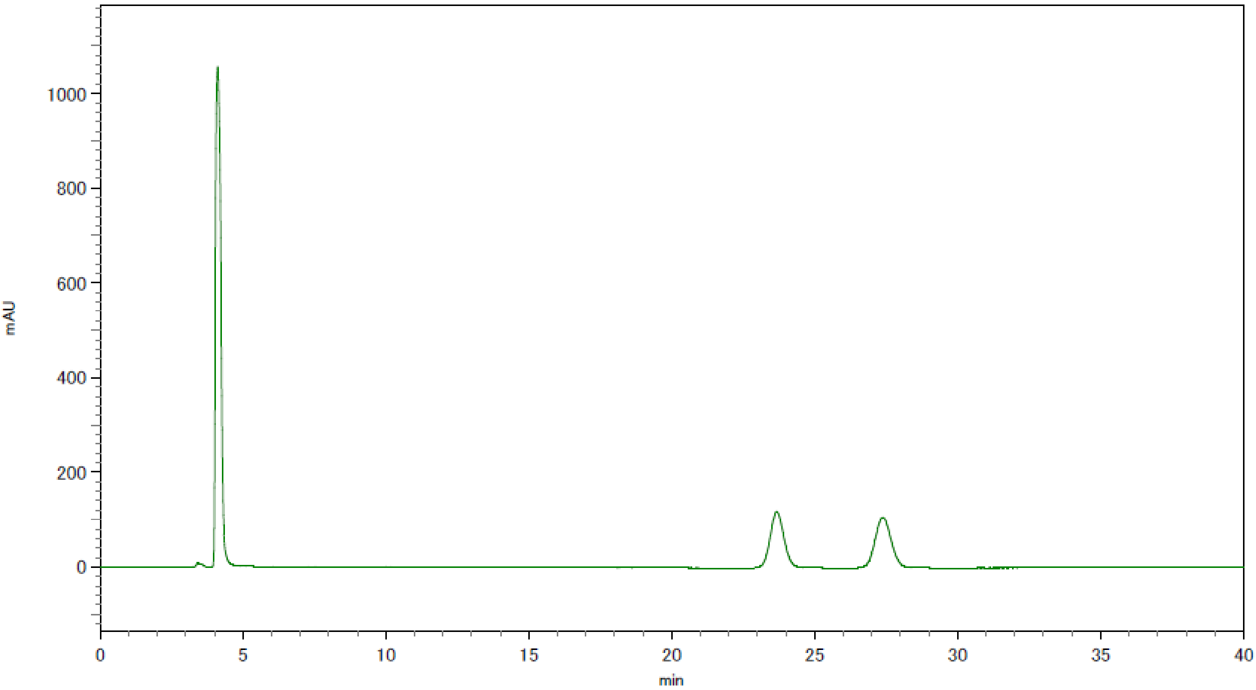
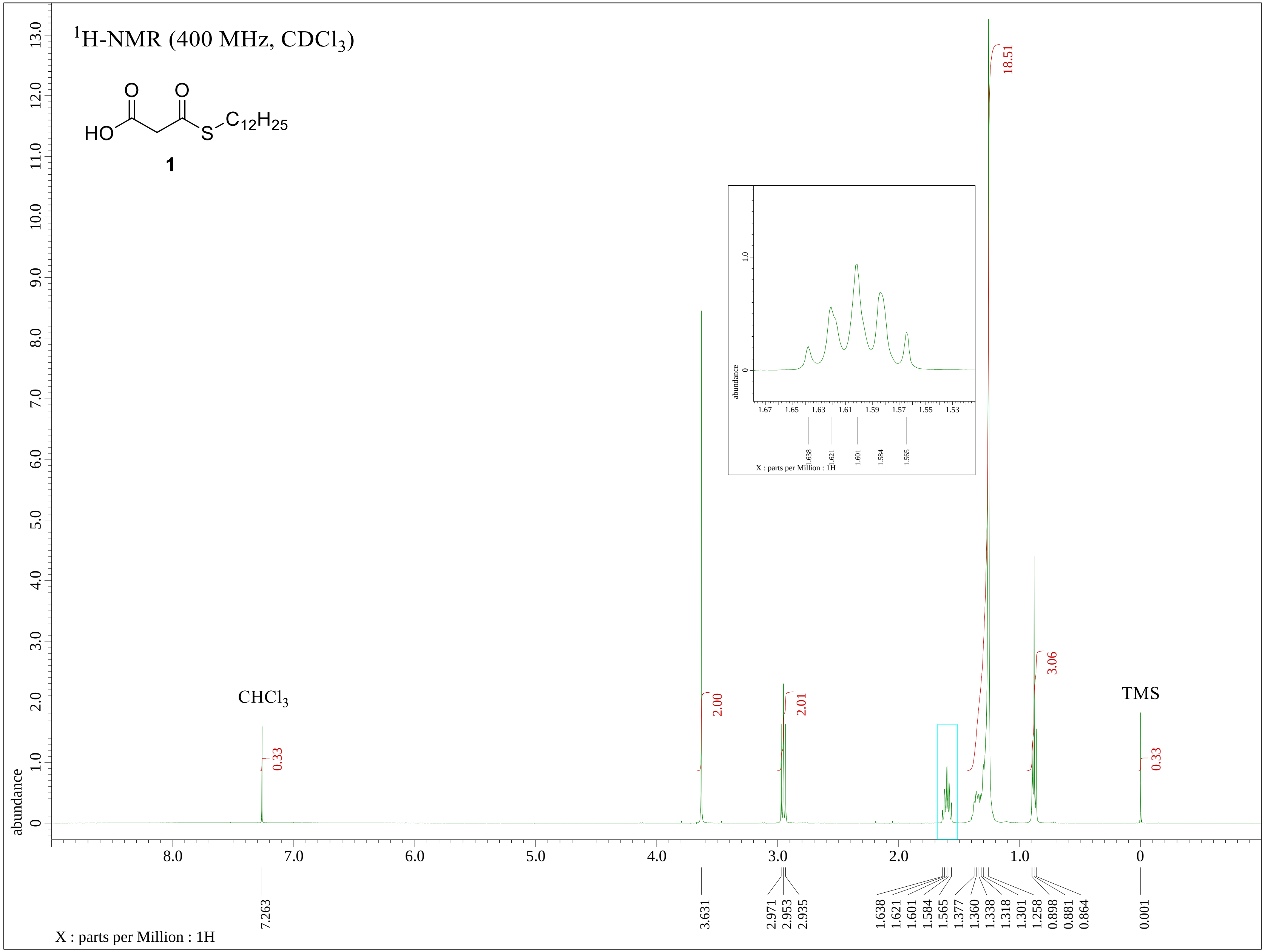
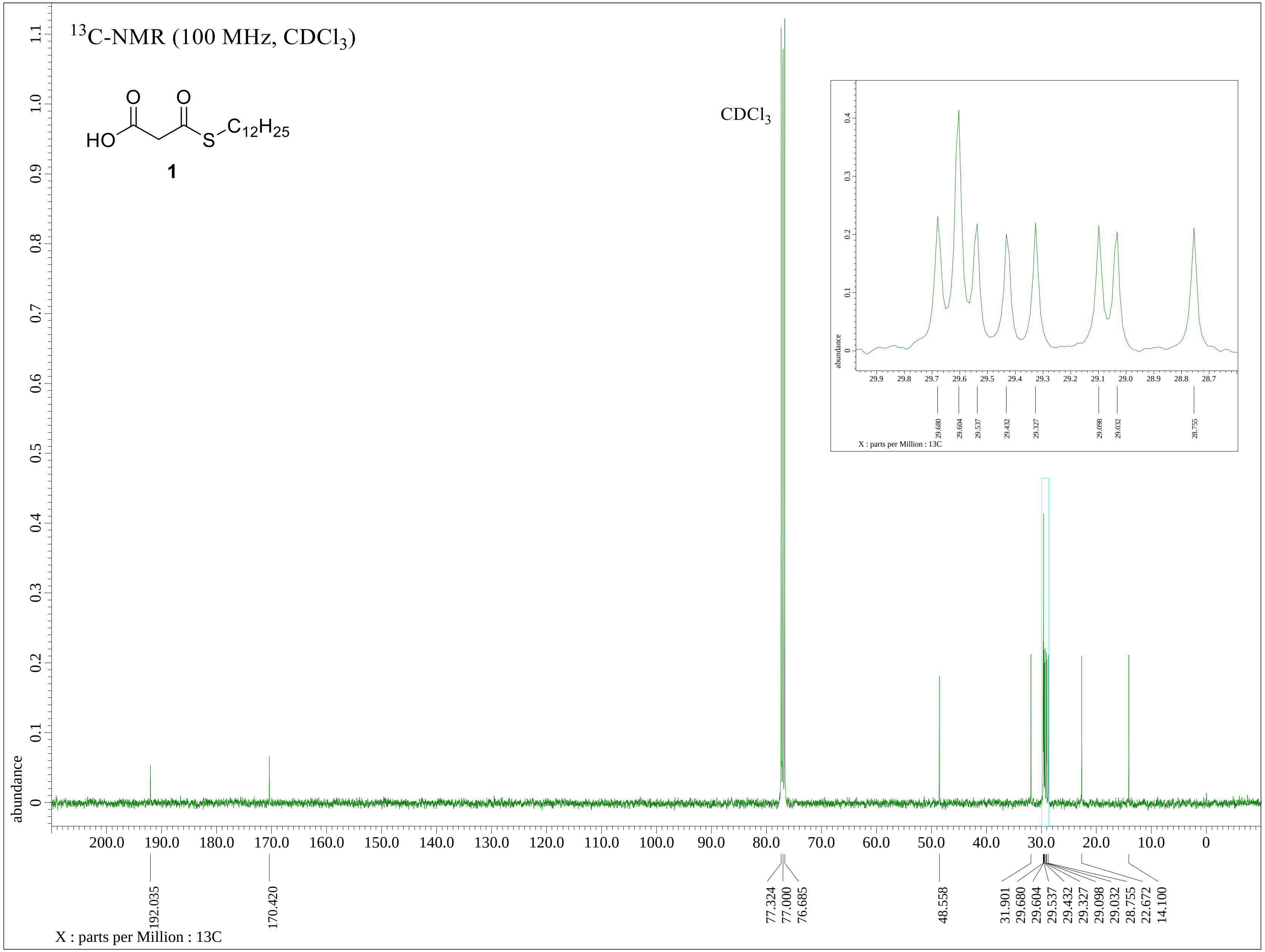
28.461	3596994	95.98
Total	3747700	100.00

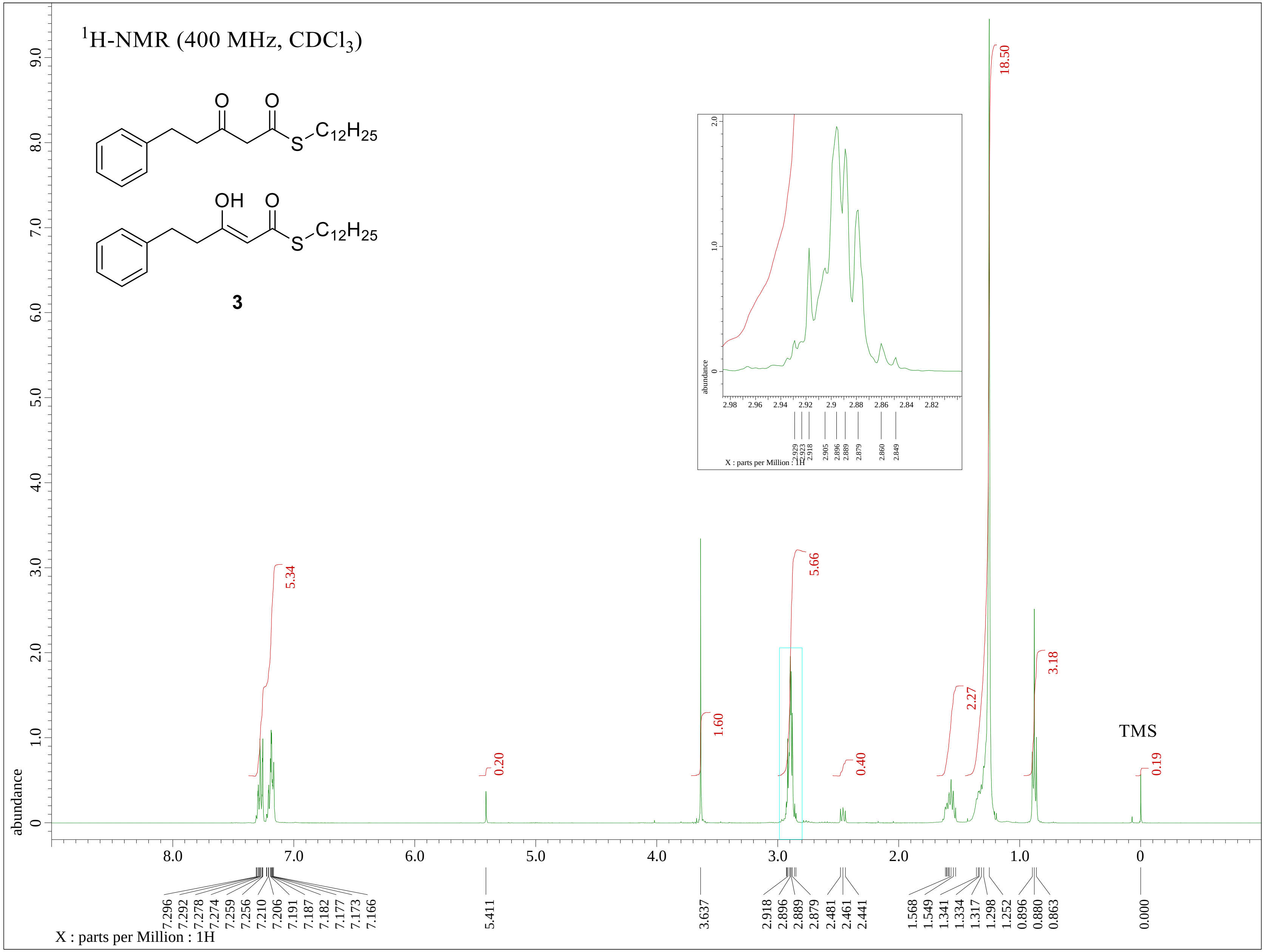
racemic sample

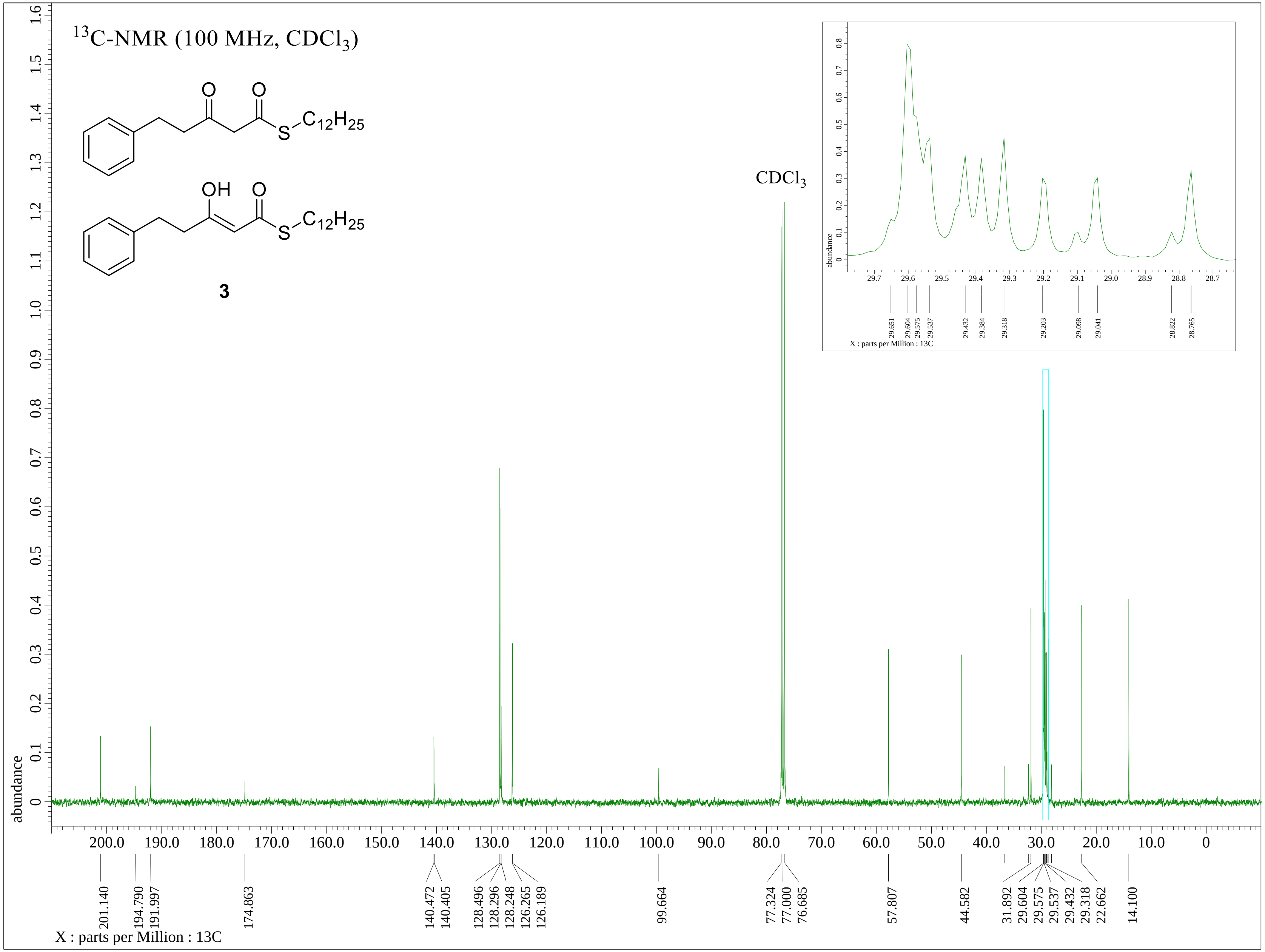




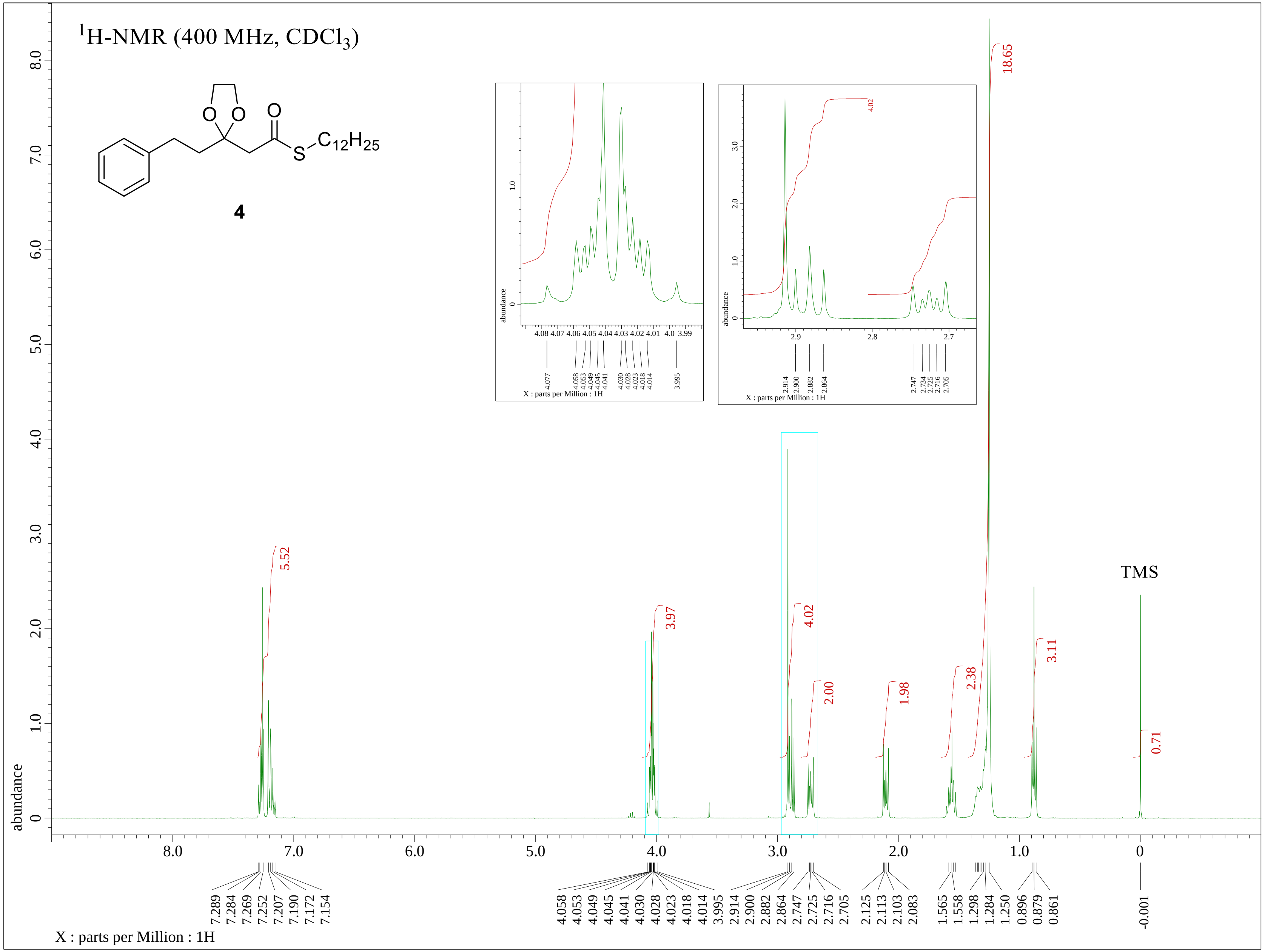
^{1}H-NMR (400 MHz, $CDCl_3$)
HO
O
O
S
$C_{12}H_{25}$
1
$CHCl_3$
TMS
0.33
2.00
2.01
18.51
3.06
0.33
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.263
3.631
2.971
2.953
2.935
1.638
1.621
1.601
1.584
1.565
1.377
1.360
1.338
1.318
1.301
1.258
0.898
0.881
0.864
0.001
X : parts per Million : 1H
abundance
0
1.0
1.67
1.65
1.63
1.61
1.59
1.57
1.55
1.53
1.638
1.621
1.601
1.584
1.565
X : parts per Million : 1H


^{13}C-NMR (100 MHz, CDCl$_3$)
HO
O
O
S
C$_{12}$H$_{25}$
1
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.035
170.420
77.324
77.000
76.685
48.558
31.901
29.680
29.604
29.537
29.432
29.327
29.098
29.032
28.755
22.672
14.100
X : parts per Million : 13C
29.9
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.680
29.604
29.537
29.432
29.327
29.098
29.032
28.755
X : parts per Million : 13C

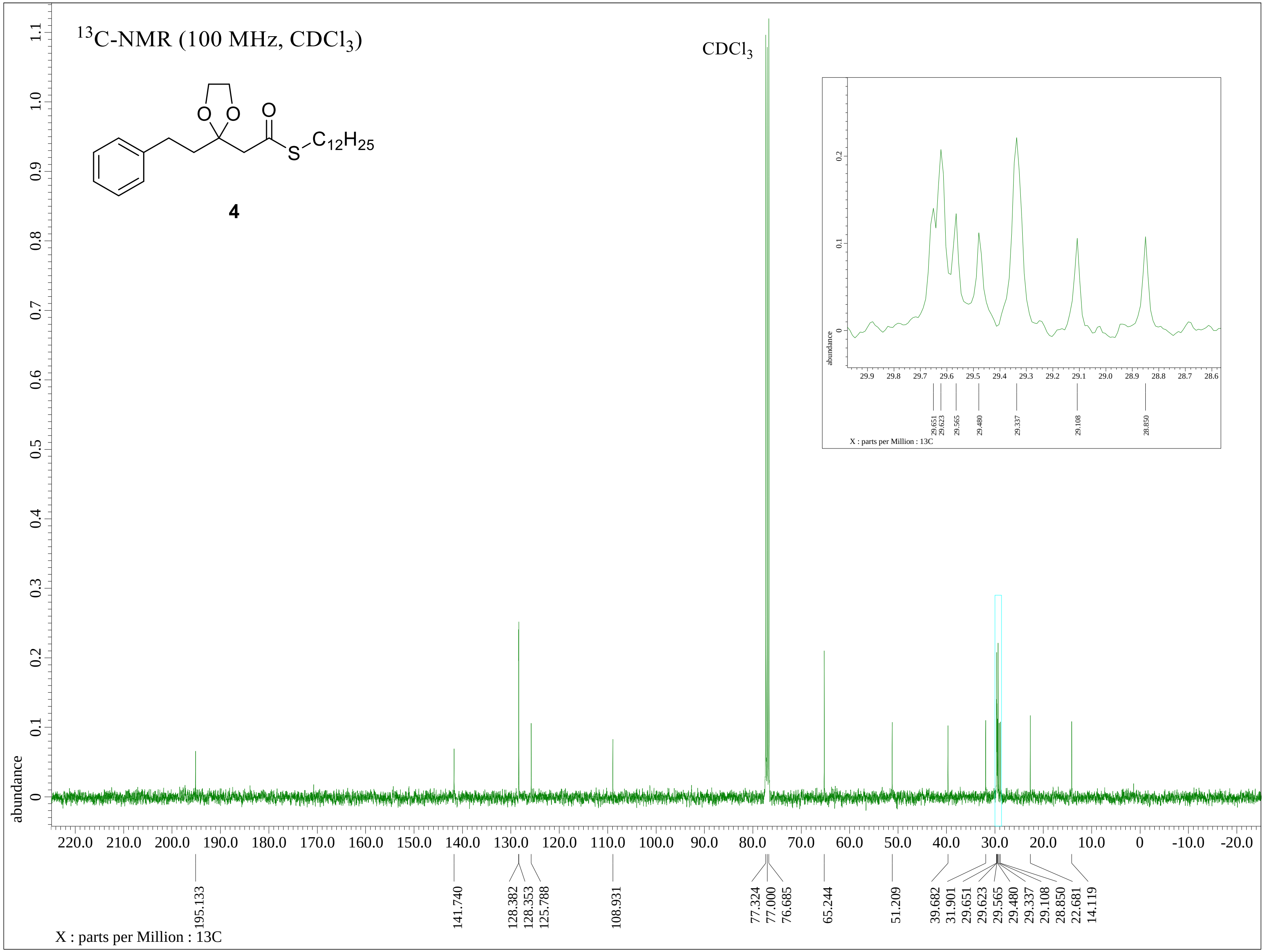

1H-NMR (400 MHz, CDCl3)
O
O
S
C12H25
OH
O
S
C12H25
3
TMS
5.34
0.20
1.60
5.66
0.40
2.27
18.50
3.18
0.19
7.296
7.292
7.278
7.274
7.259
7.256
7.210
7.206
7.191
7.187
7.182
7.177
7.173
7.166
5.411
3.637
2.918
2.896
2.889
2.879
2.481
2.461
2.441
1.568
1.549
1.341
1.334
1.317
1.298
1.252
0.896
0.880
0.863
0.000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
abundance
X : parts per Million : 1H
2.98
2.96
2.94
2.92
2.9
2.88
2.86
2.84
2.82
2.929
2.923
2.918
2.905
2.896
2.889
2.879
2.860
2.849
2.0
1.0
0



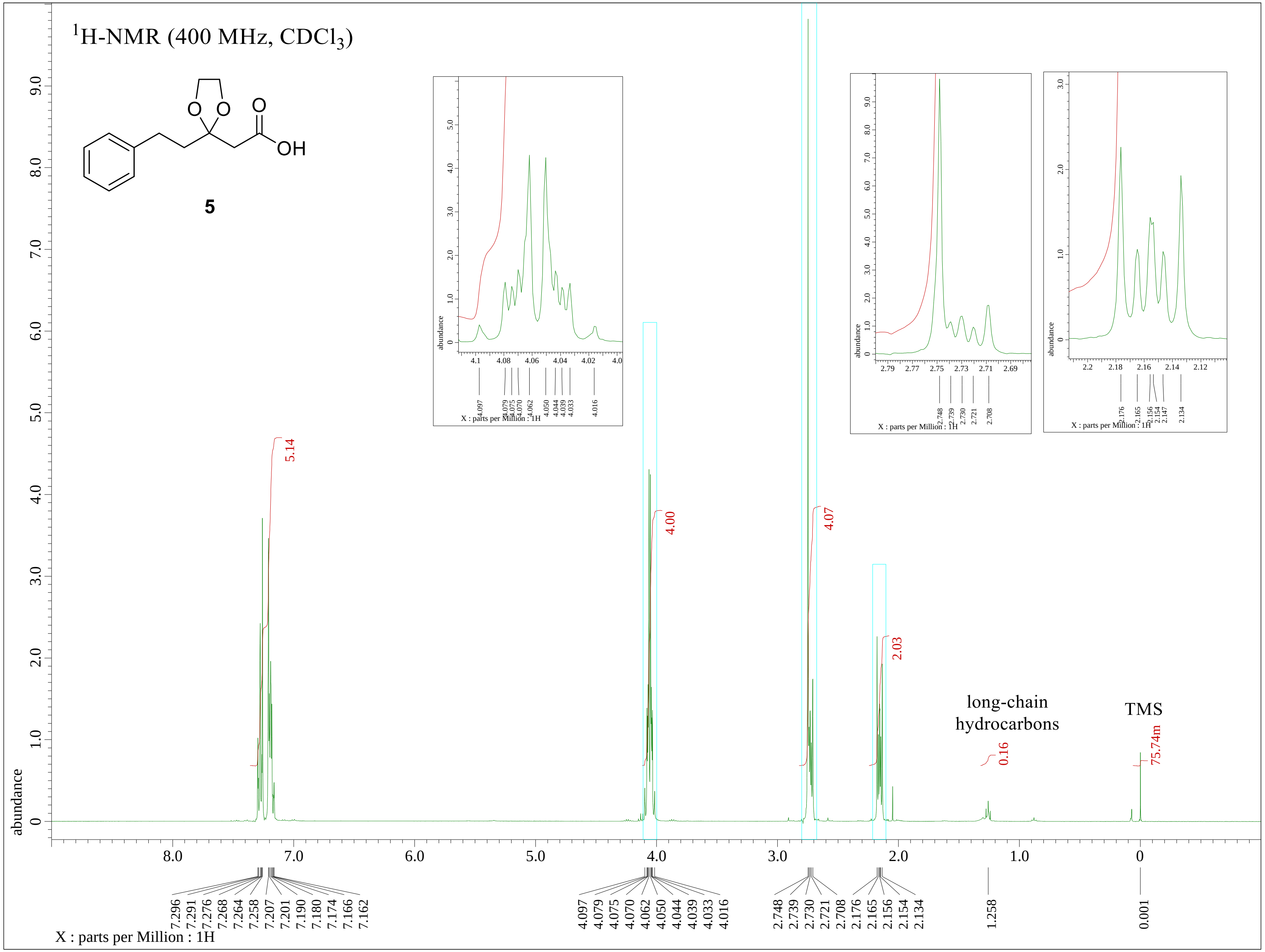
^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
S
C$_{12}$H$_{25}$
OH
O
S
C$_{12}$H$_{25}$
3
CDCl$_3$
abundance
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
201.140
194.790
191.997
174.863
140.472
140.405
128.496
128.296
128.248
126.265
126.189
99.664
77.324
77.000
76.685
57.807
44.582
31.892
29.604
29.575
29.537
29.432
29.318
22.662
14.100
X : parts per Million : 13C
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.651
29.604
29.575
29.537
29.432
29.384
29.318
29.203
29.098
29.041
28.822
28.765
X : parts per Million : 13C

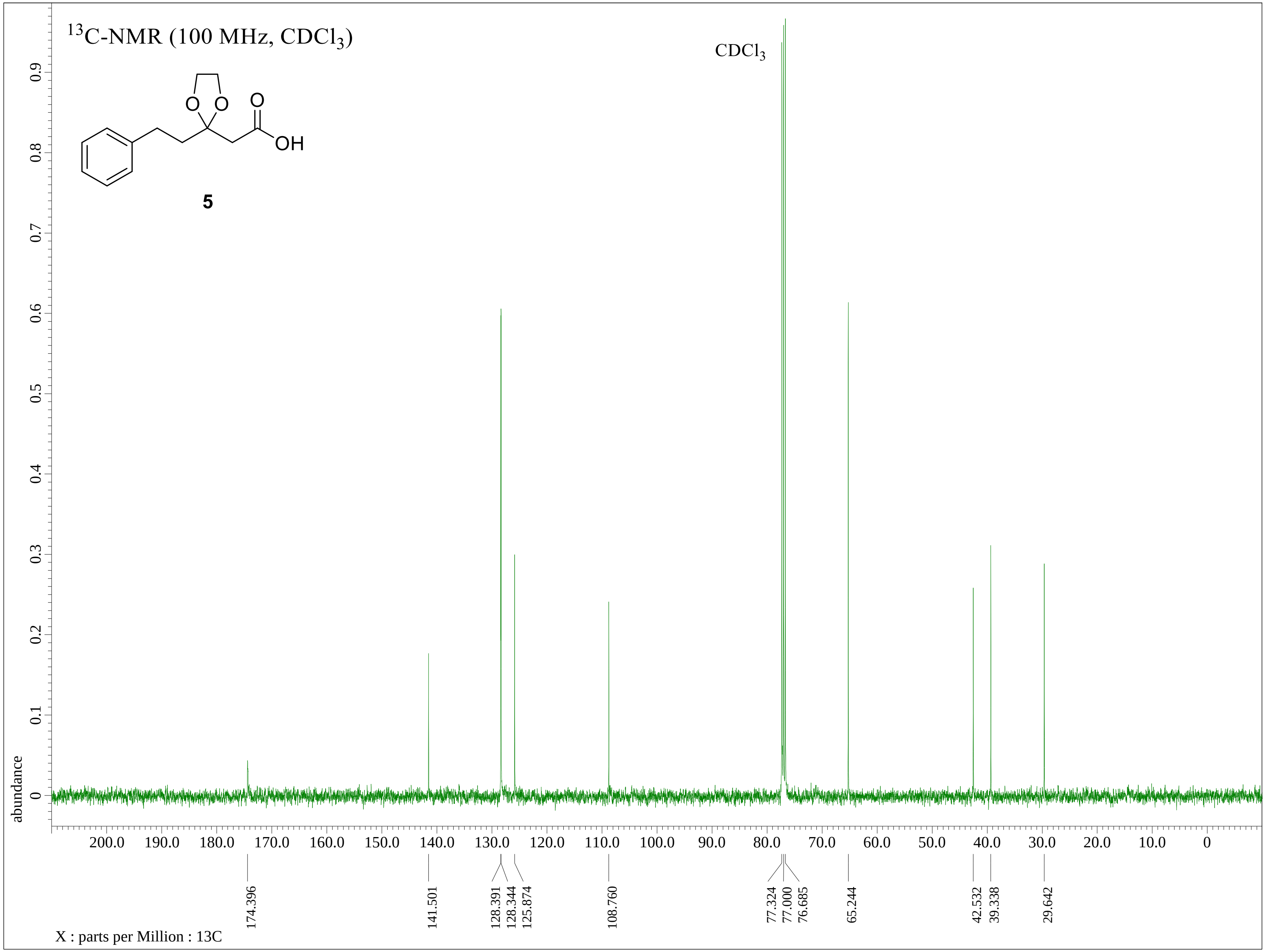


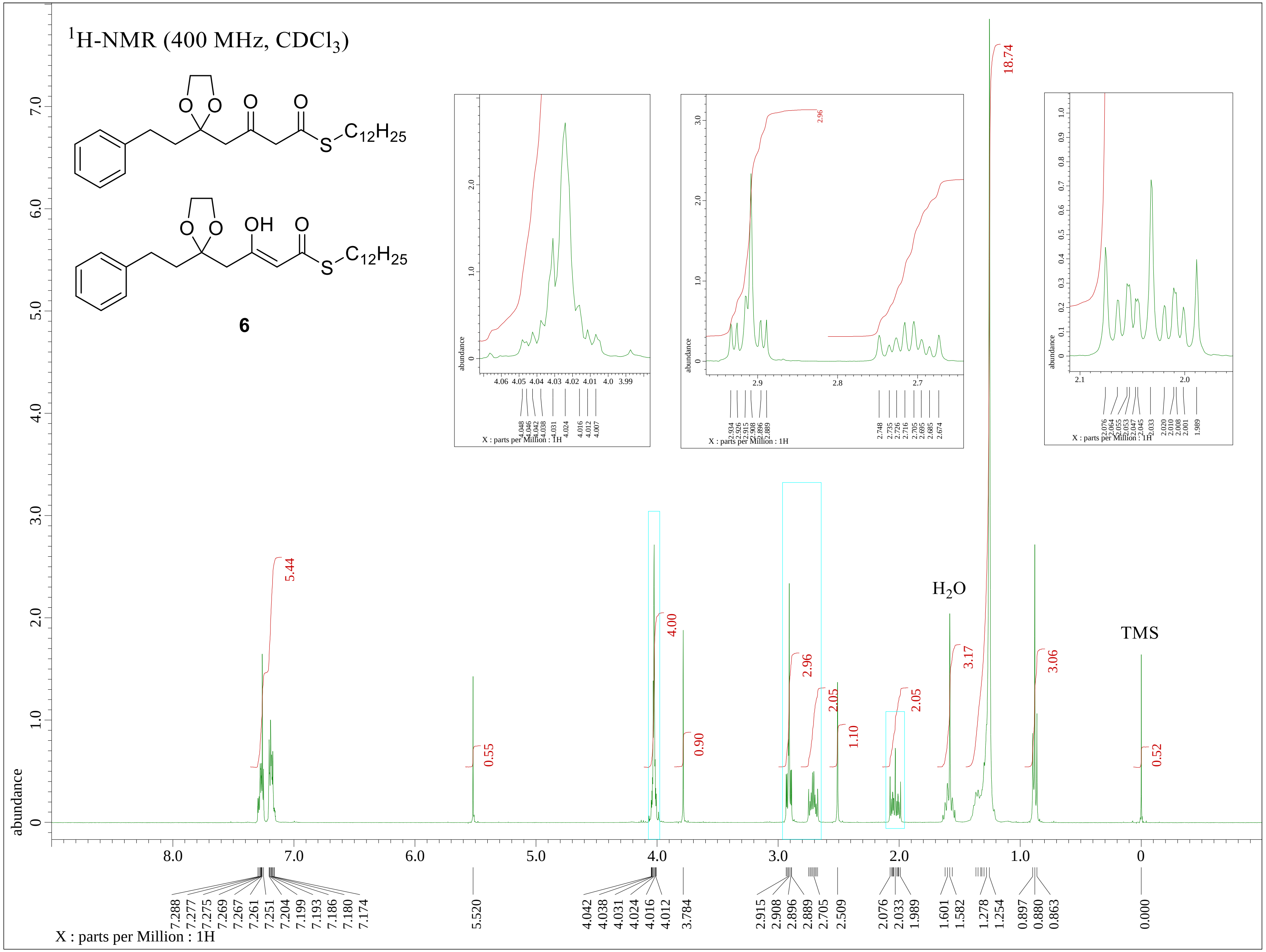
^{1}H-NMR (400 MHz, $CDCl_3$)
O
O O
S
$C_{12}H_{25}$
4
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.52
3.97
4.02
2.00
1.98
2.38
18.65
3.11
0.71
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.289
7.284
7.269
7.252
7.207
7.190
7.172
7.154
4.058
4.053
4.049
4.045
4.041
4.030
4.028
4.023
4.018
4.014
3.995
2.914
2.900
2.882
2.864
2.747
2.725
2.716
2.705
2.125
2.113
2.103
2.083
1.565
1.558
1.298
1.284
1.250
0.896
0.879
0.861
-0.001
X : parts per Million : 1H
abundance
0
1.0
4.08 4.07 4.06 4.05 4.04 4.03 4.02 4.01 4.0 3.99
4.077
4.058
4.053
4.049
4.045
4.041
4.030
4.028
4.023
4.018
4.014
3.995
X : parts per Million : 1H
abundance
0
1.0
2.0
3.0
4.02
2.9
2.8
2.7
2.914
2.900
2.882
2.864
2.747
2.734
2.725
2.716
2.705
X : parts per Million : 1H

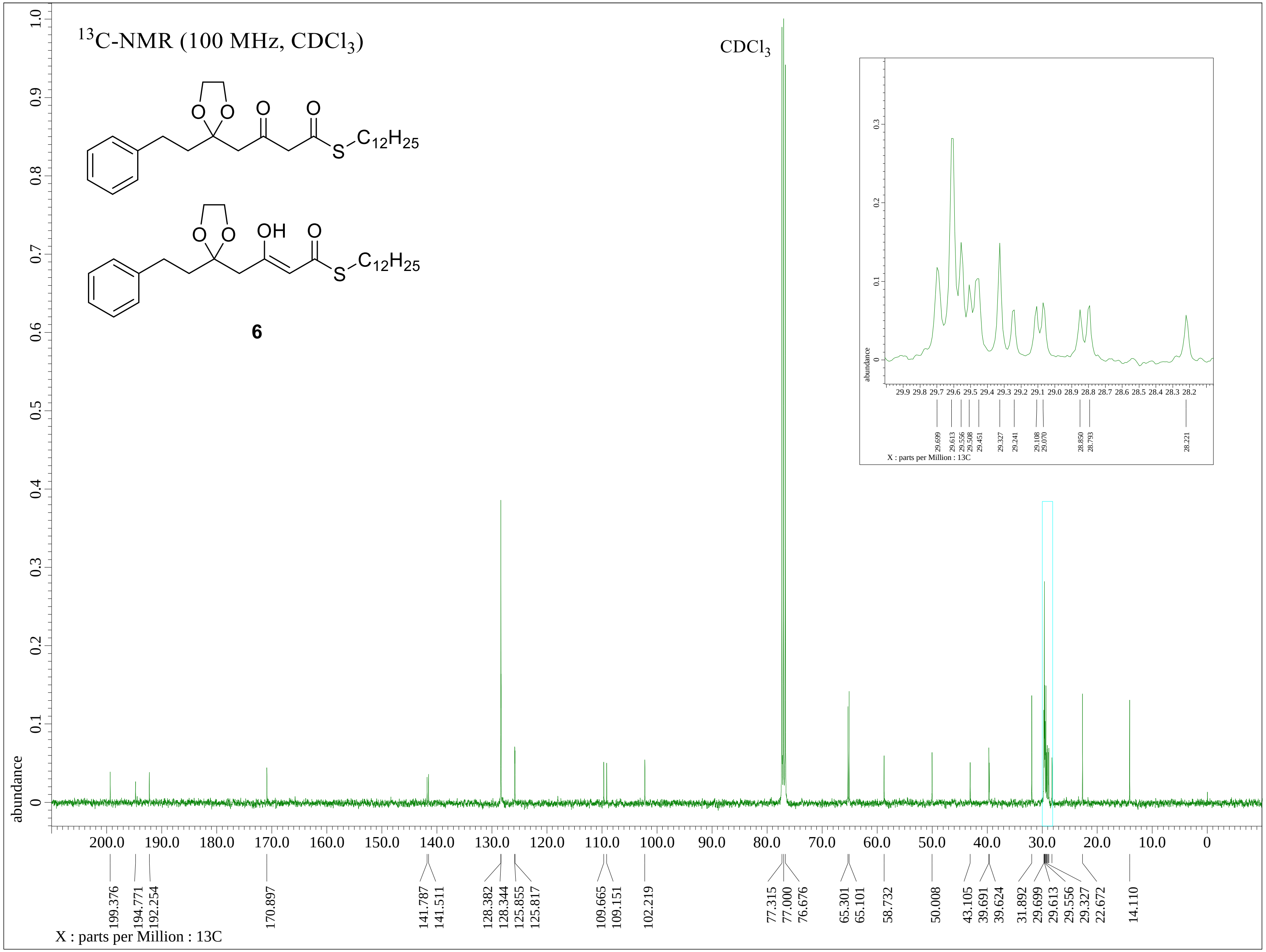


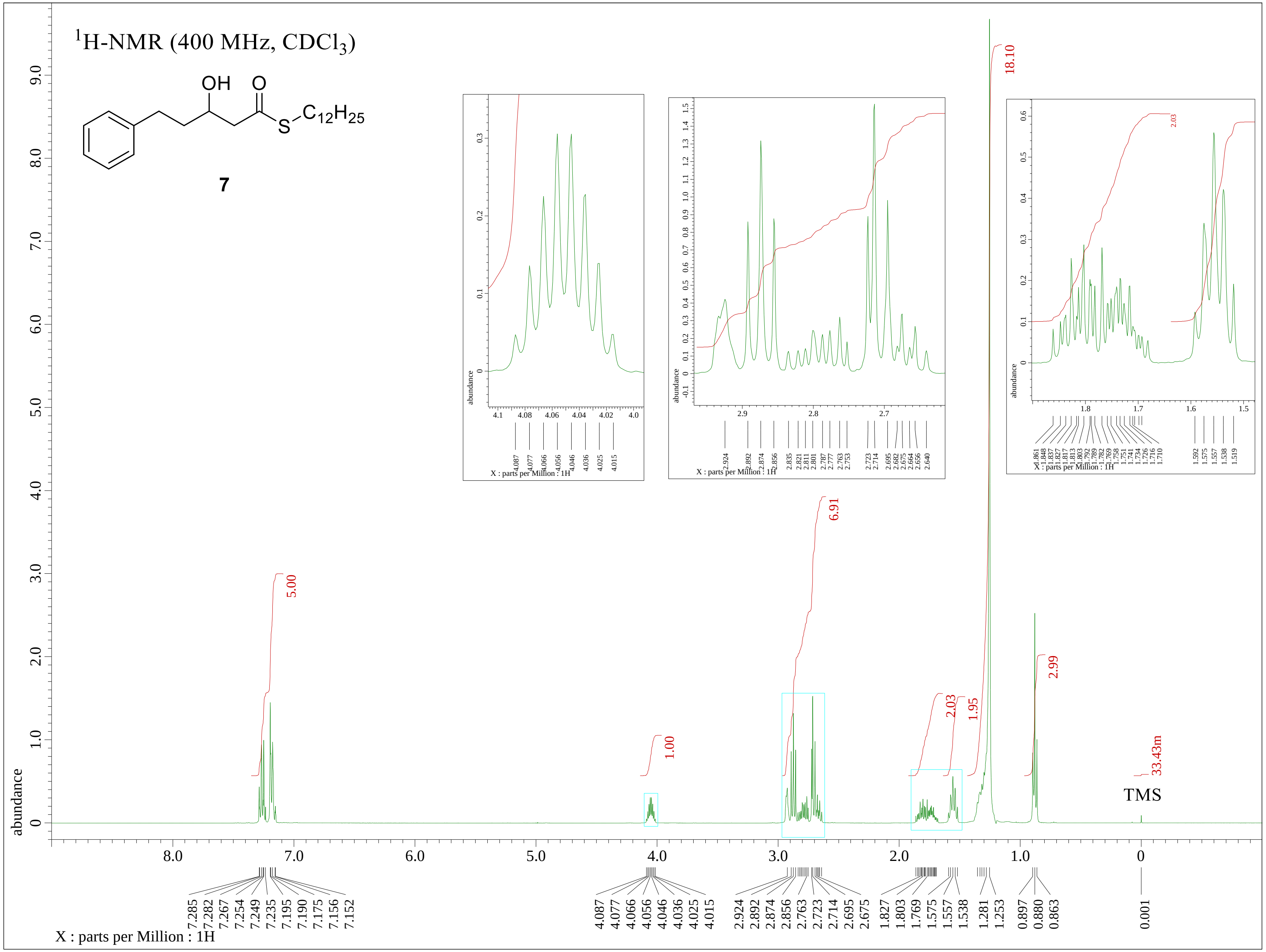
^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
O
S
C$_{12}$H$_{25}$
4
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
195.133
141.740
128.382
128.353
125.788
108.931
77.324
77.000
76.685
65.244
51.209
39.682
31.901
29.651
29.623
29.565
29.480
29.337
29.108
28.850
22.681
14.119
X : parts per Million : 13C
abundance
0
0.1
0.2
29.9
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
28.6
29.651
29.623
29.565
29.480
29.337
29.108
28.850
X : parts per Million : 13C


^{1}H-NMR (400 MHz, $CDCl_3$)
5
O
O
O
OH
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
5.14
4.00
4.07
2.03
0.16
75.74m
long-chain hydrocarbons
TMS
7.296
7.291
7.276
7.268
7.264
7.258
7.207
7.201
7.190
7.180
7.174
7.166
7.162
4.097
4.079
4.075
4.070
4.062
4.050
4.044
4.039
4.033
4.016
2.748
2.739
2.730
2.721
2.708
2.176
2.165
2.156
2.154
2.134
1.258
0.001
4.1
4.08
4.06
4.04
4.02
4.0
2.79
2.77
2.75
2.73
2.71
2.69
2.2
2.18
2.16
2.14
2.12

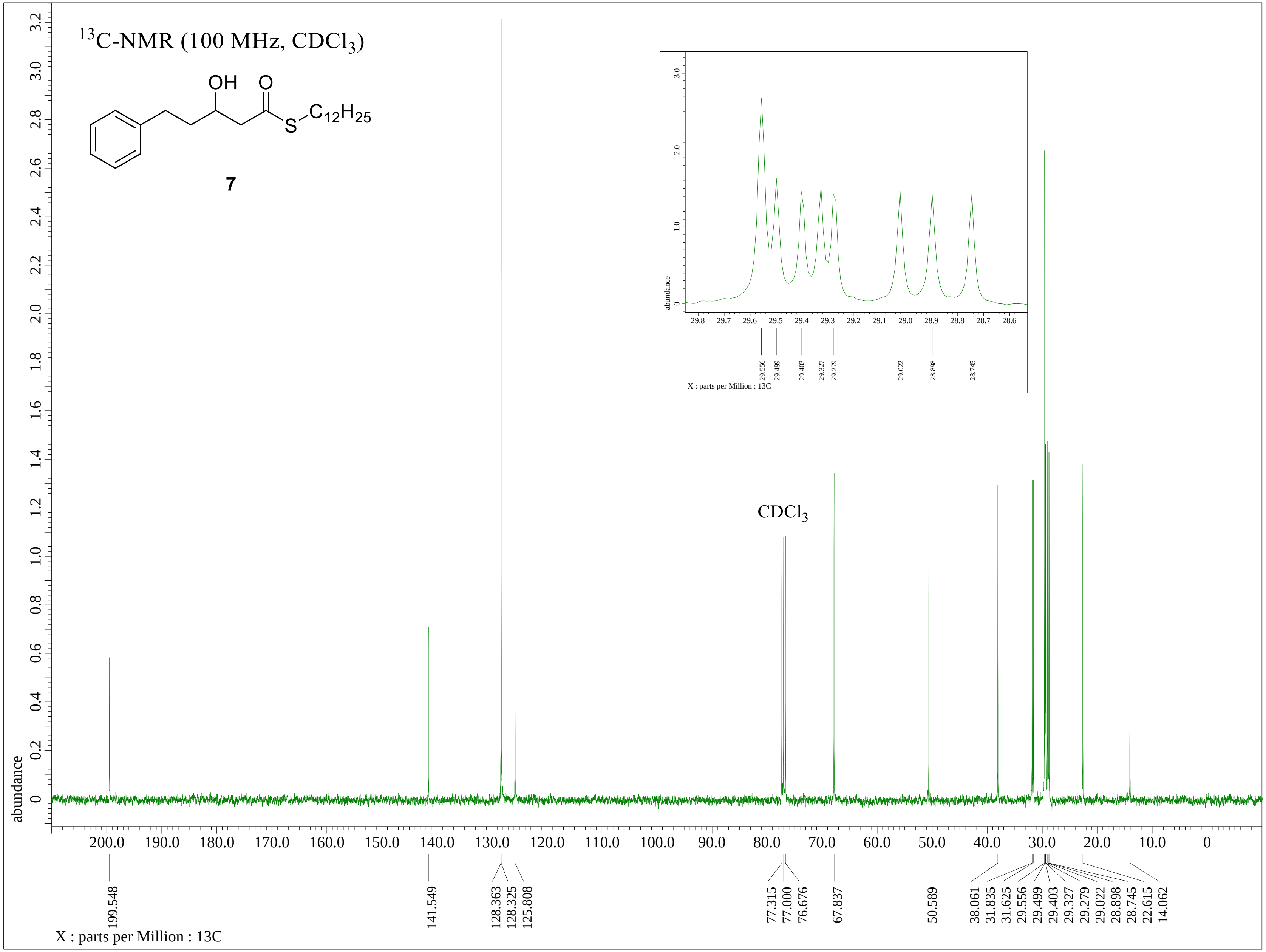

^{13}C-NMR (100 MHz, CDCl$_3$)
5
O
O
O
OH
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.396
141.501
128.391
128.344
125.874
108.760
77.324
77.000
76.685
65.244
42.532
39.338
29.642
X : parts per Million : 13C

^{1}H-NMR (400 MHz, CDCl$_3$)
O O O O S $C_{12}H_{25}$
O O OH O S $C_{12}H_{25}$
6
H$_2$O
TMS
5.44
0.55
4.00
0.90
2.96
2.05
1.10
2.05
3.17
18.74
3.06
0.52
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.288 7.277 7.275 7.269 7.267 7.261 7.251 7.204 7.199 7.193 7.186 7.180 7.174
5.520
4.042 4.038 4.031 4.024 4.016 4.012
3.784
2.915 2.908 2.896 2.889 2.705
2.509
2.076 2.033 1.989
1.601 1.582
1.278 1.254
0.897 0.880 0.863
0.000
X : parts per Million : 1H
4.06 4.05 4.04 4.03 4.02 4.01 4.0 3.99
4.048 4.046 4.042 4.038 4.031 4.024 4.016 4.012 4.007
2.9 2.8 2.7
2.934 2.926 2.915 2.908 2.896 2.889
2.748 2.735 2.726 2.716 2.705 2.695 2.685 2.674
2.96
2.1 2.0
2.076 2.064 2.055 2.053 2.047 2.045 2.033 2.020 2.010 2.008 2.001 1.989

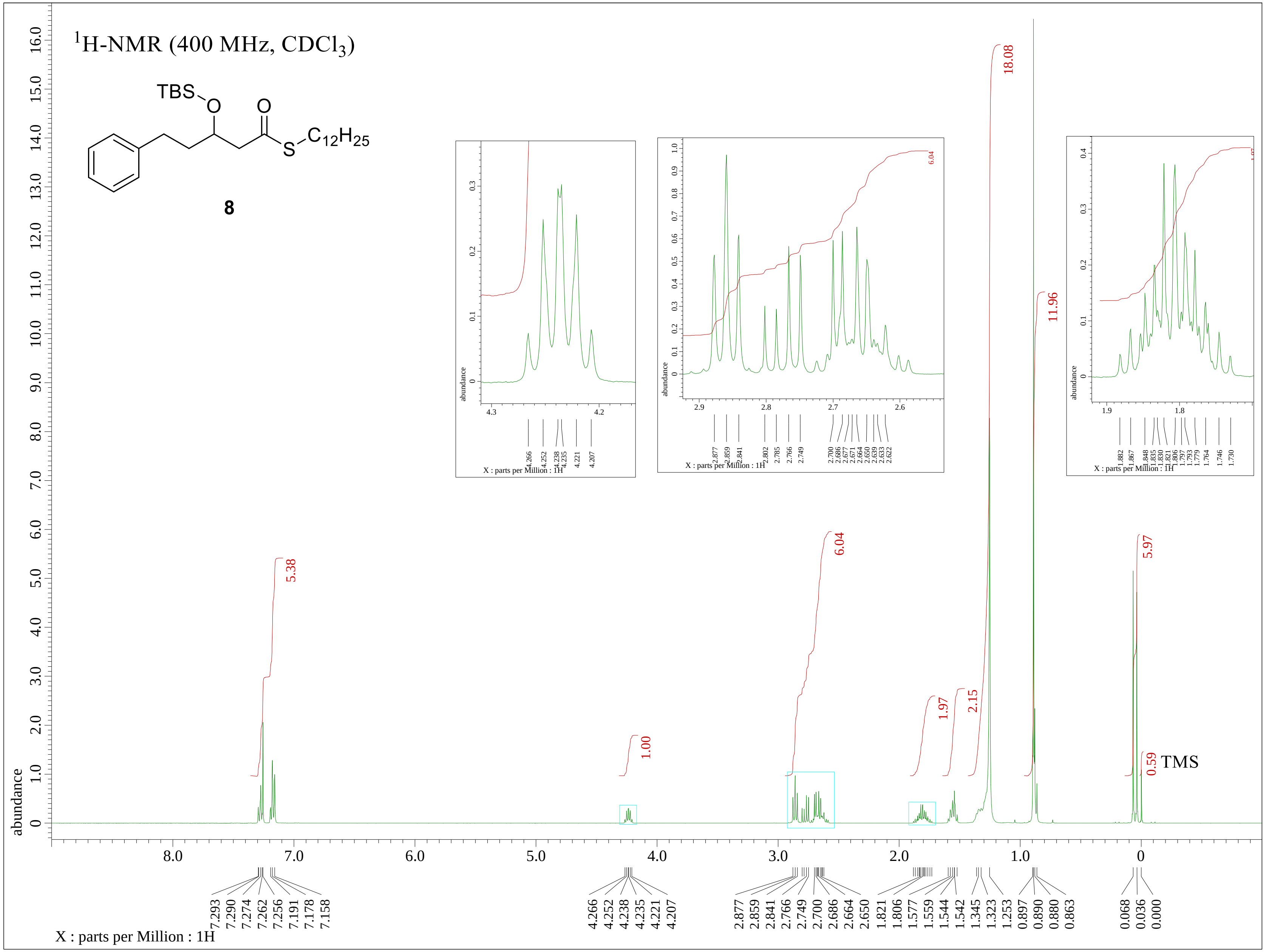

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
O
O
S
C$_{12}$H$_{25}$
O
O
OH
O
S
C$_{12}$H$_{25}$
6
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C
199.376
194.771
192.254
170.897
141.787
141.511
128.382
128.344
125.855
125.817
109.665
109.151
102.219
77.315
77.000
76.676
65.301
65.101
58.732
50.008
43.105
39.691
39.624
31.892
29.699
29.613
29.556
29.327
22.672
14.110
abundance
0
0.1
0.2
0.3
29.9
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
28.6
28.5
28.4
28.3
28.2
29.699
29.613
29.556
29.508
29.451
29.327
29.241
29.108
29.070
28.850
28.793
28.221
X : parts per Million : 13C



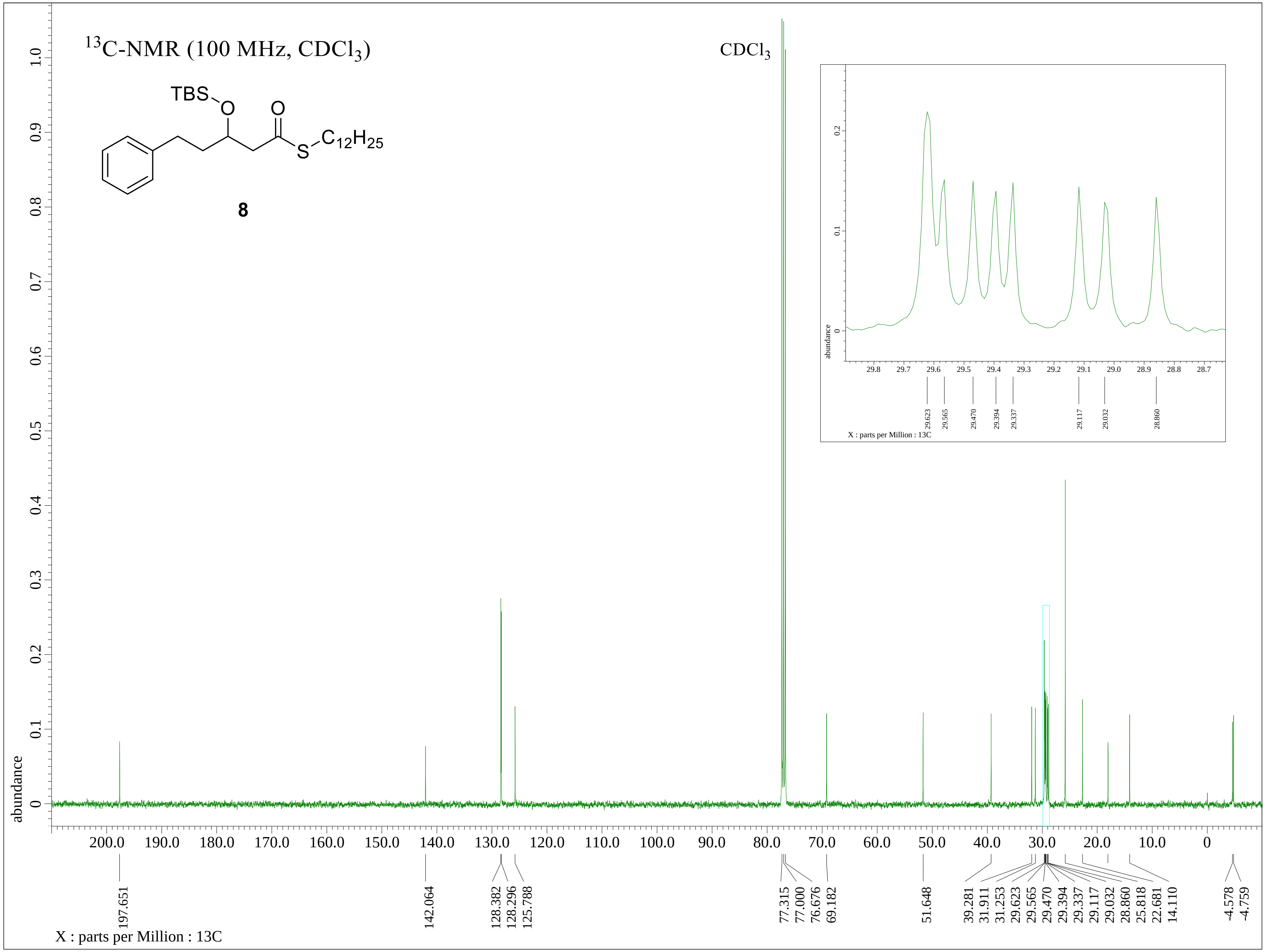
^{1}H-NMR (400 MHz, $CDCl_3$)
OH
O
S
$C_{12}H_{25}$
7
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
1.00
6.91
2.03
1.95
18.10
2.99
33.43m
TMS
7.285
7.282
7.267
7.254
7.249
7.235
7.195
7.190
7.175
7.156
7.152
4.087
4.077
4.066
4.056
4.046
4.036
4.025
4.015
2.924
2.892
2.874
2.856
2.763
2.723
2.714
2.695
2.675
1.827
1.803
1.769
1.575
1.557
1.538
1.281
1.253
0.897
0.880
0.863
0.001
2.835
2.821
2.811
2.801
2.787
2.777
2.753
2.682
2.664
2.656
2.640
1.861
1.848
1.837
1.817
1.813
1.792
1.789
1.782
1.758
1.751
1.741
1.734
1.726
1.716
1.710
1.592
1.519



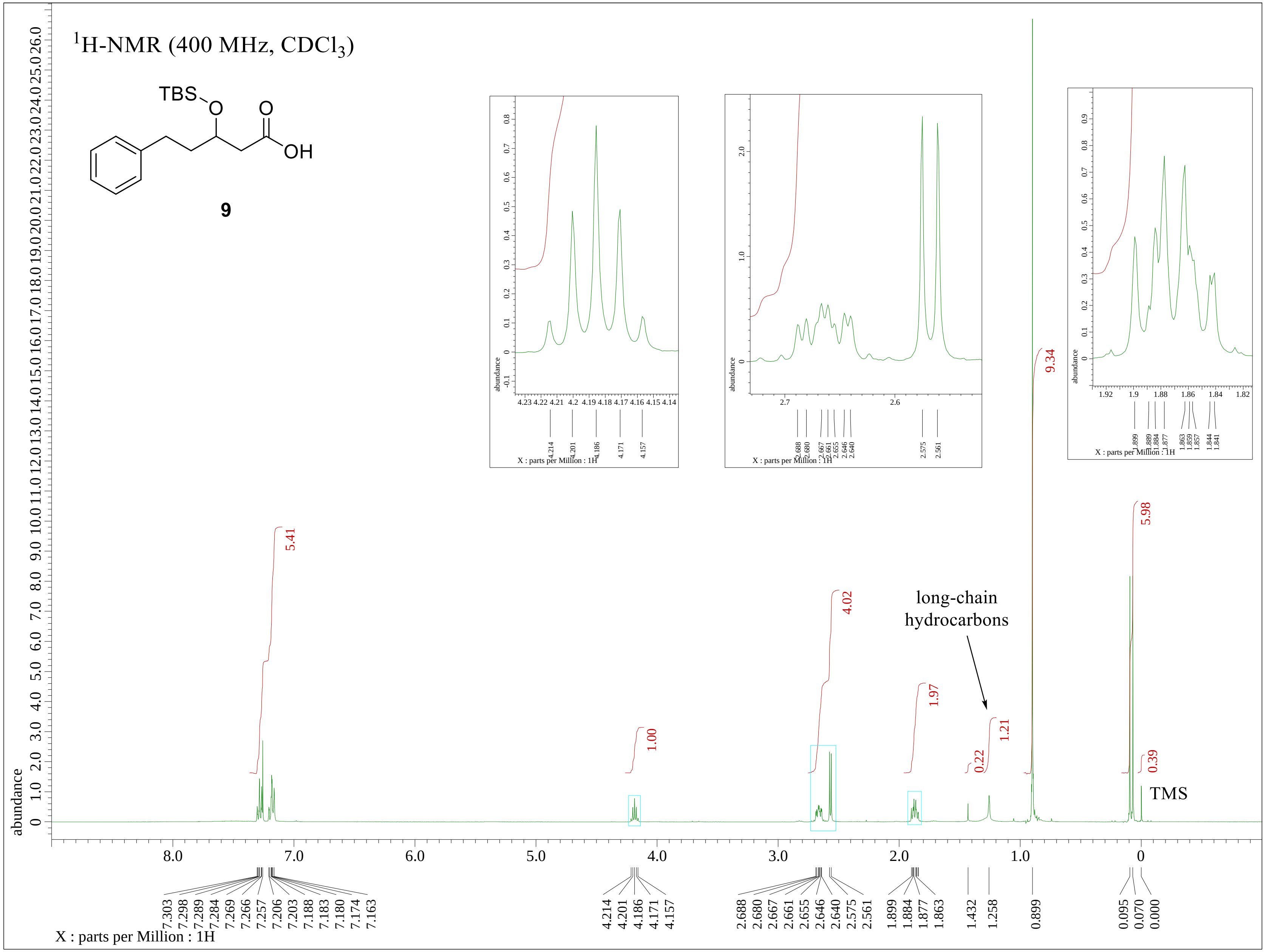
^{13}C-NMR (100 MHz, CDCl$_3$)
OH
O
S
C$_{12}$H$_{25}$
7
CDCl$_3$
abundance
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C
199.548
141.549
128.363
128.325
125.808
77.315
77.000
76.676
67.837
50.589
38.061
31.835
31.625
29.556
29.499
29.403
29.327
29.279
29.022
28.898
28.745
22.615
14.062
abundance
0
1.0
2.0
3.0
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
28.6
29.556
29.499
29.403
29.327
29.279
29.022
28.898
28.745
X : parts per Million : 13C

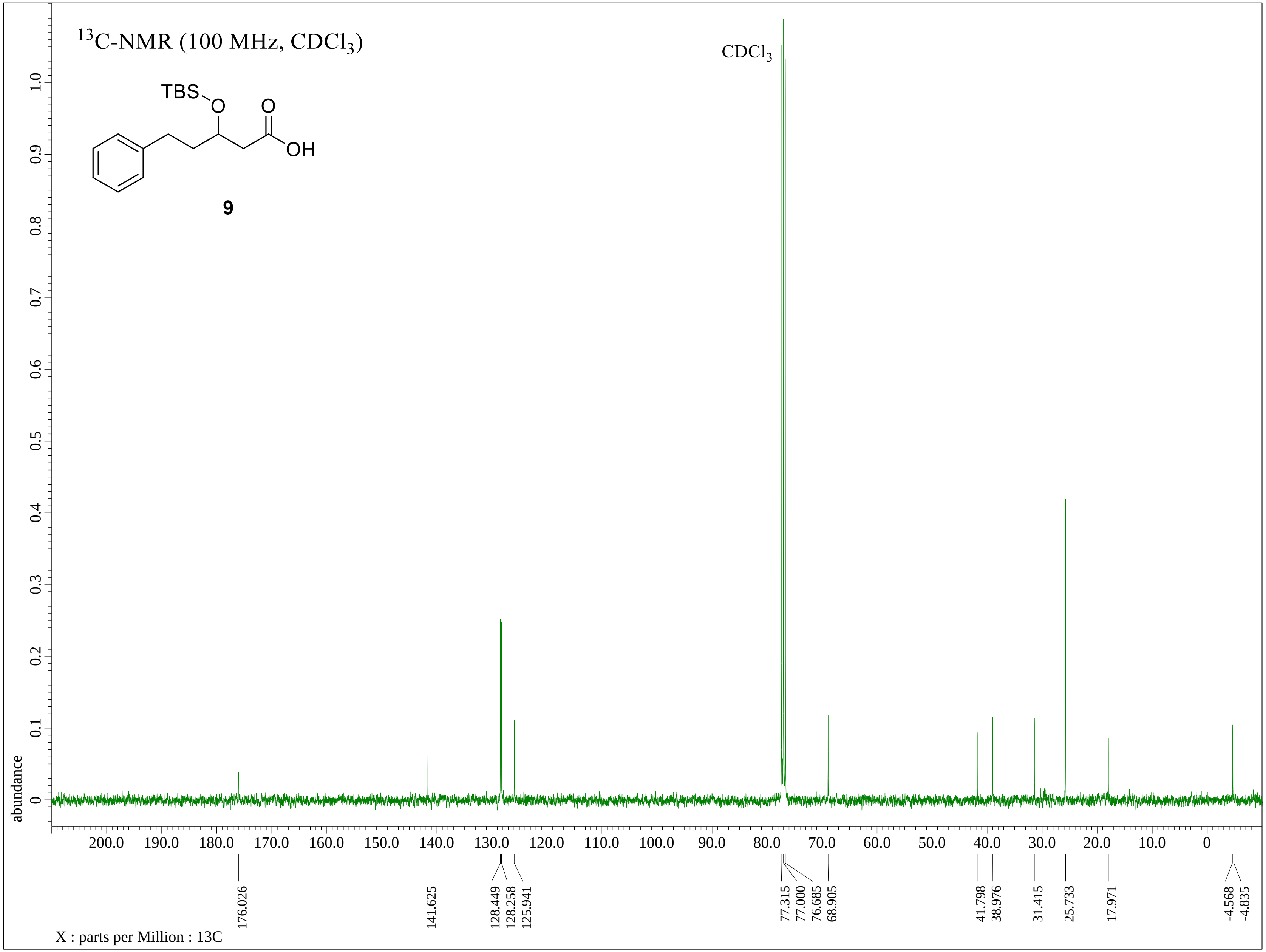


^{1}H-NMR (400 MHz, $CDCl_3$)
TBS
O
O
S
$C_{12}H_{25}$
8
abundance
X : parts per Million : 1H
TMS
5.38
1.00
6.04
1.97
2.15
18.08
11.96
5.97
0.59
7.293
7.290
7.274
7.262
7.256
7.191
7.178
7.158
4.266
4.252
4.238
4.235
4.221
4.207
2.877
2.859
2.841
2.766
2.749
2.700
2.686
2.664
2.650
1.821
1.806
1.577
1.559
1.544
1.542
1.345
1.323
1.253
0.897
0.890
0.880
0.863
0.068
0.036
0.000
2.802
2.785
2.677
2.671
2.639
2.633
2.622
1.882
1.867
1.848
1.835
1.830
1.797
1.793
1.779
1.764
1.746
1.730

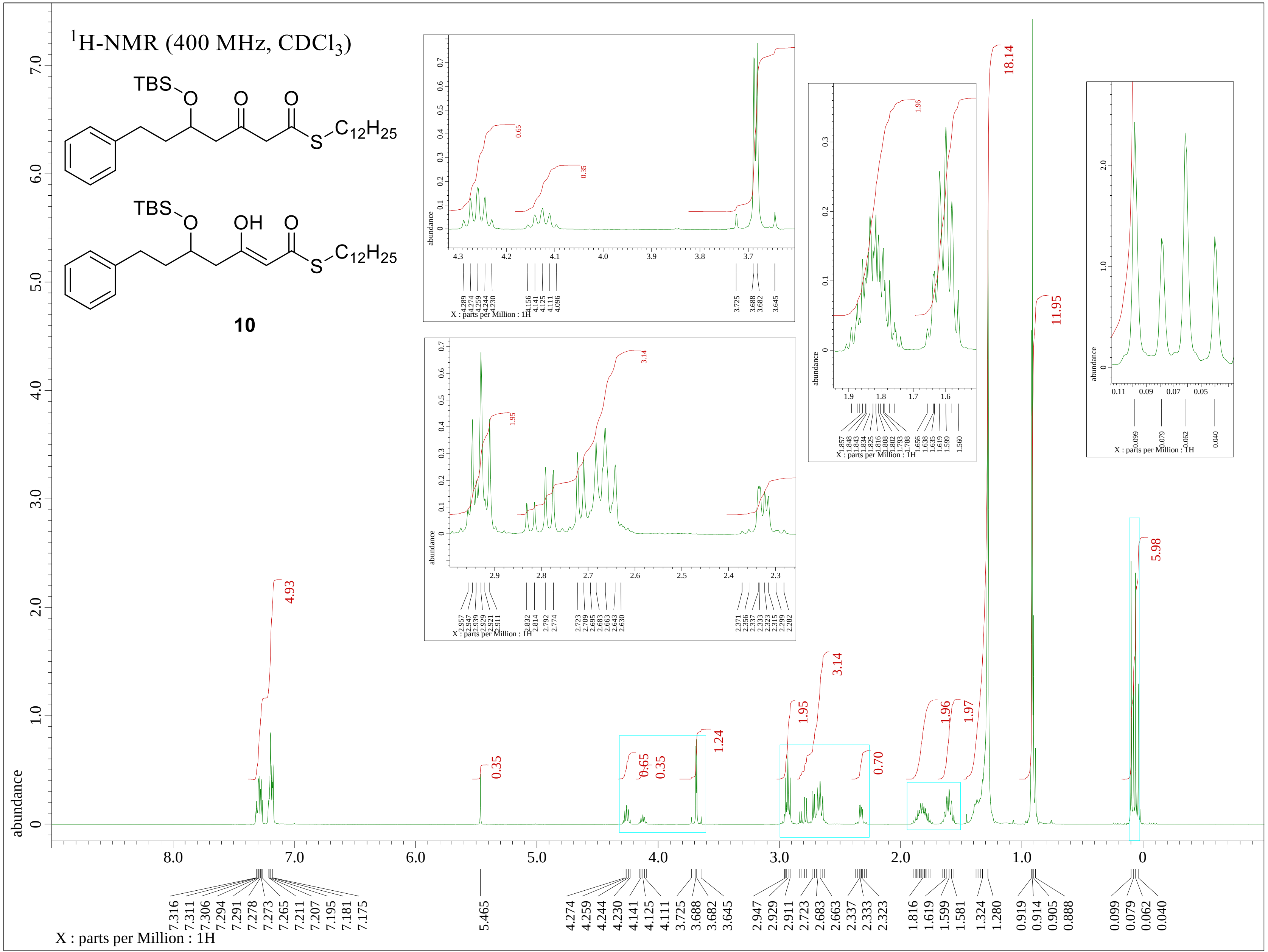


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
S
C$_{12}$H$_{25}$
8
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : 13C
197.651
142.064
128.382
128.296
125.788
77.315
77.000
76.676
69.182
51.648
39.281
31.911
31.253
29.623
29.565
29.470
29.394
29.337
29.117
29.032
28.860
25.818
22.681
14.110
-4.578
-4.759
abundance
0
0.1
0.2
29.8 29.7 29.6 29.5 29.4 29.3 29.2 29.1 29.0 28.9 28.8 28.7
29.623
29.565
29.470
29.394
29.337
29.117
29.032
28.860
X : parts per Million : 13C

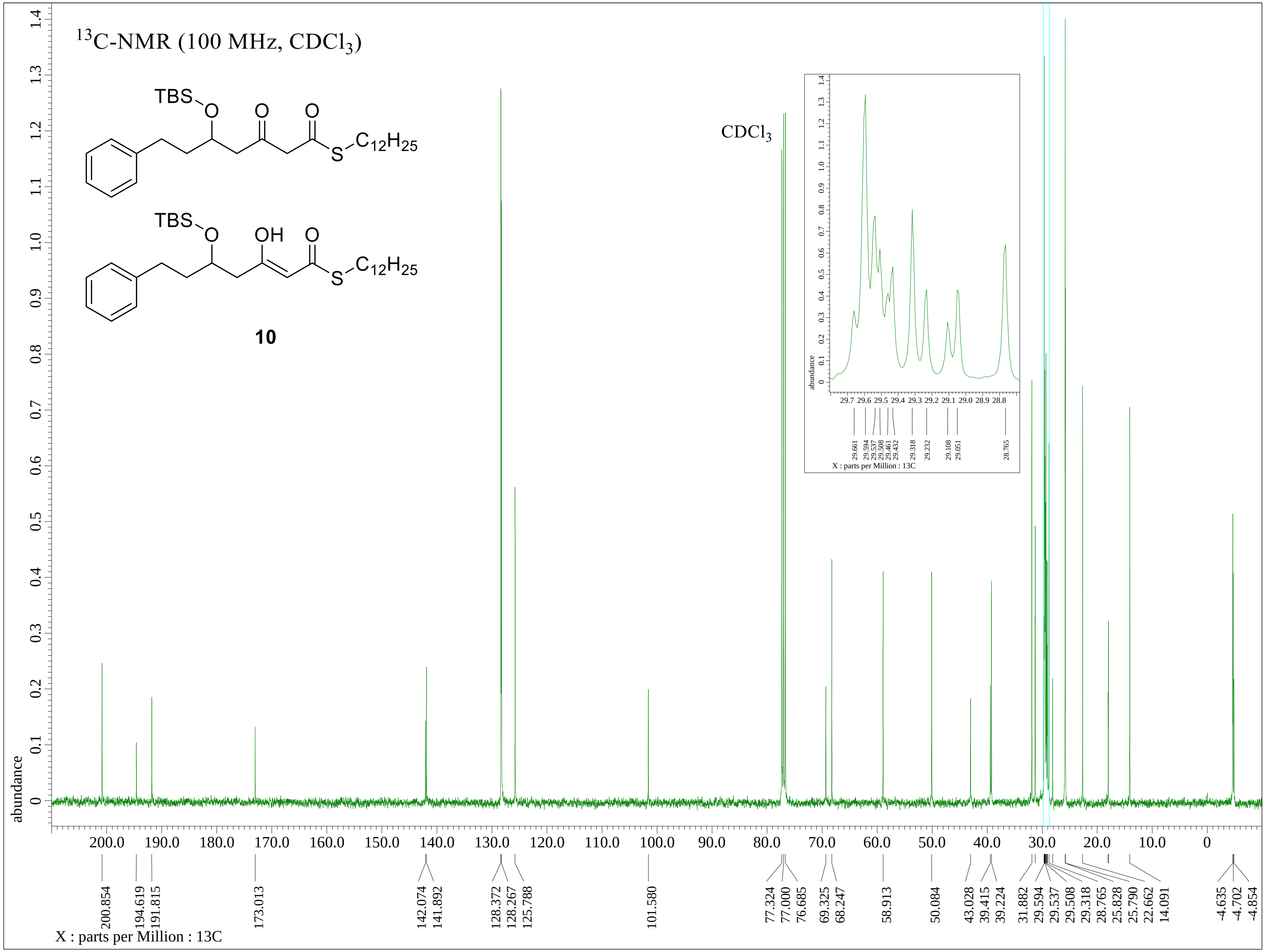

^{1}H-NMR (400 MHz, $CDCl_3$)
TBS
O
O
OH
9
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.41
1.00
4.02
1.97
0.22
1.21
9.34
5.98
0.39
long-chain hydrocarbons
TMS
7.303
7.298
7.289
7.284
7.269
7.266
7.257
7.206
7.203
7.188
7.183
7.180
7.174
7.163
4.214
4.201
4.186
4.171
4.157
2.688
2.680
2.667
2.661
2.655
2.646
2.640
2.575
2.561
1.899
1.884
1.877
1.863
1.432
1.258
0.899
0.095
0.070
0.000


13C-NMR (100 MHz, CDCl3)
TBS
O
O
OH
9
CDCl3
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
176.026
141.625
128.449
128.258
125.941
77.315
77.000
76.685
68.905
41.798
38.976
31.415
25.733
17.971
-4.568
-4.835
X : parts per Million : 13C

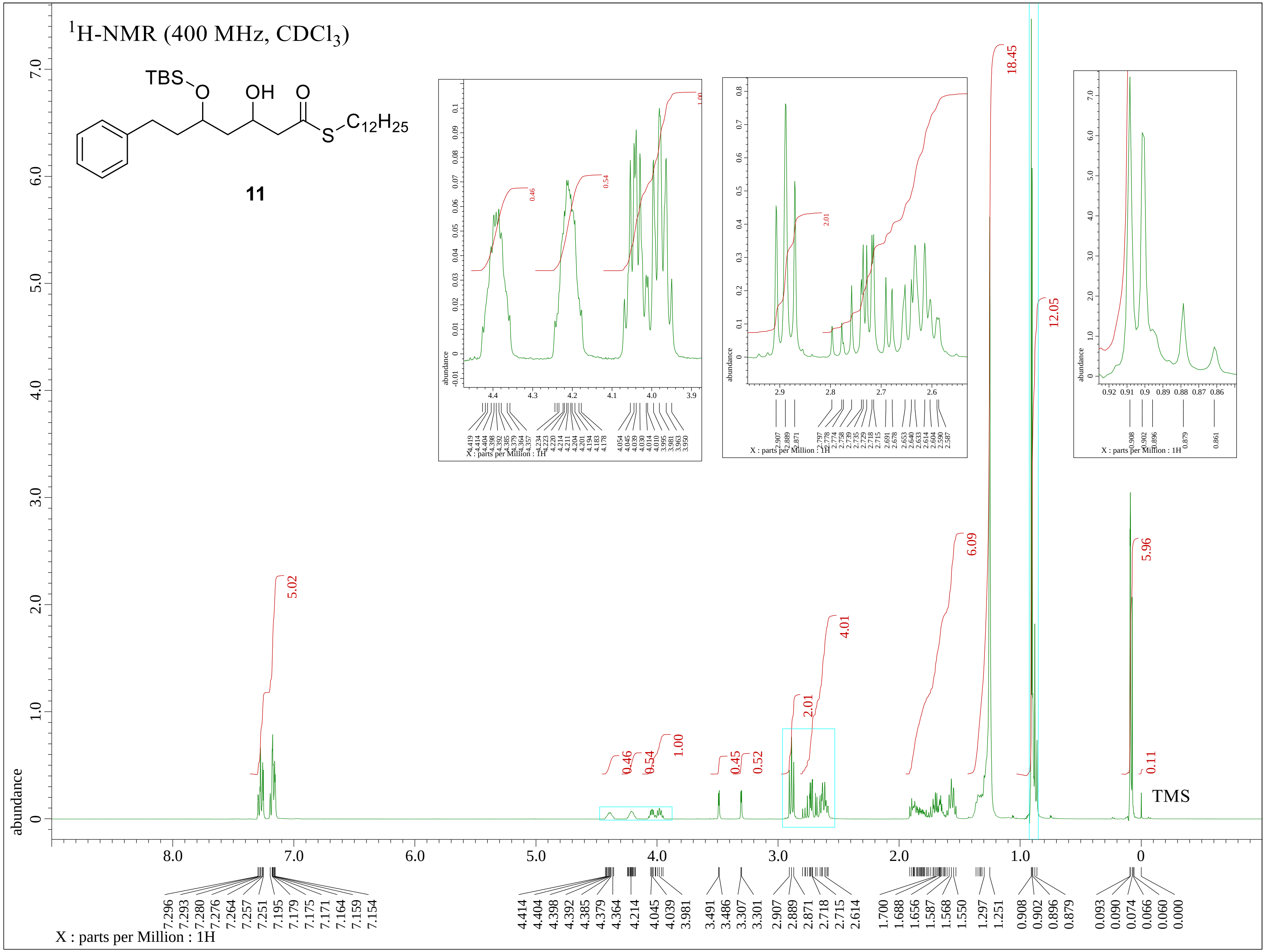
^{1}H-NMR (400 MHz, CDCl$_3$)



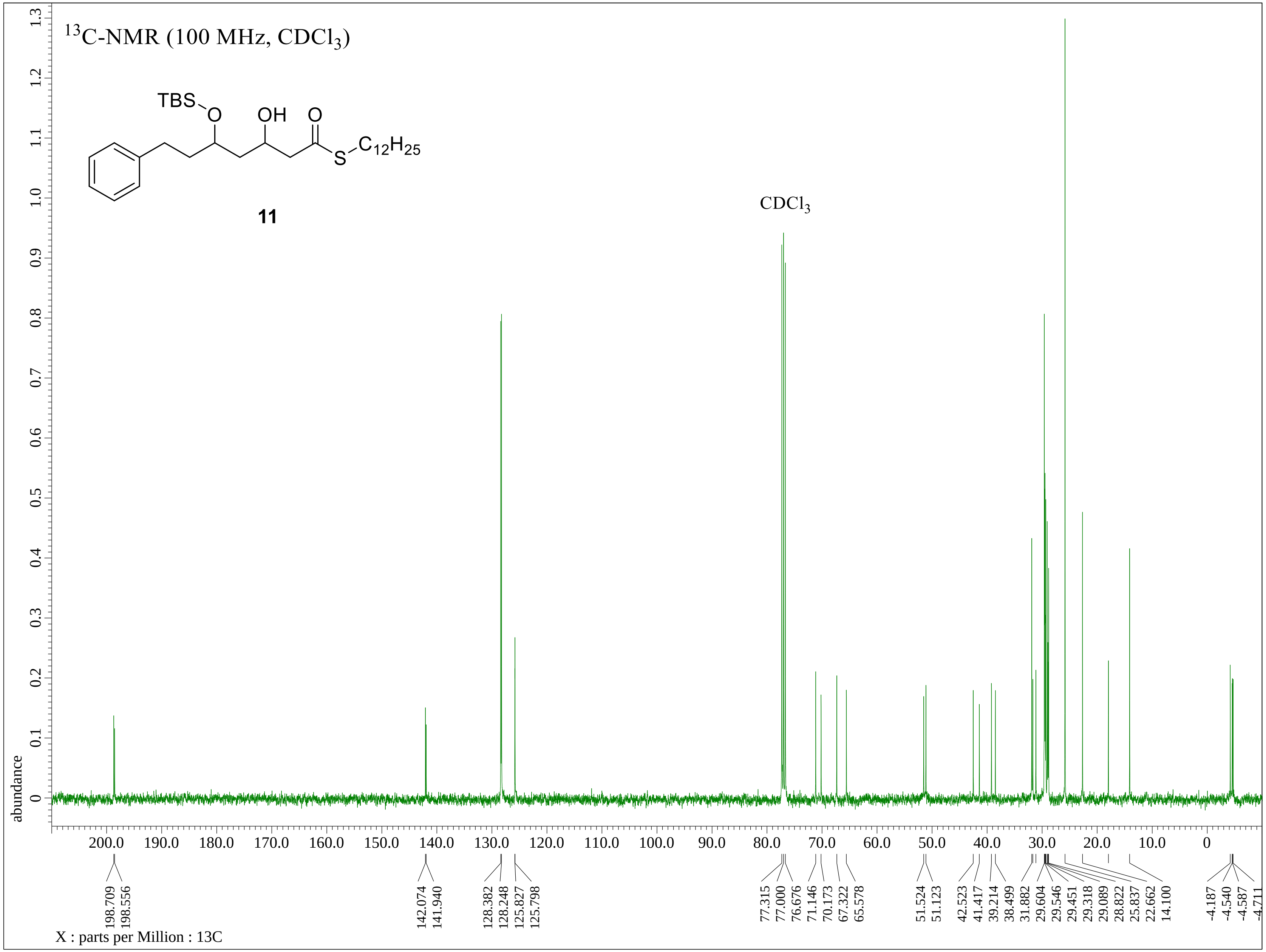
10



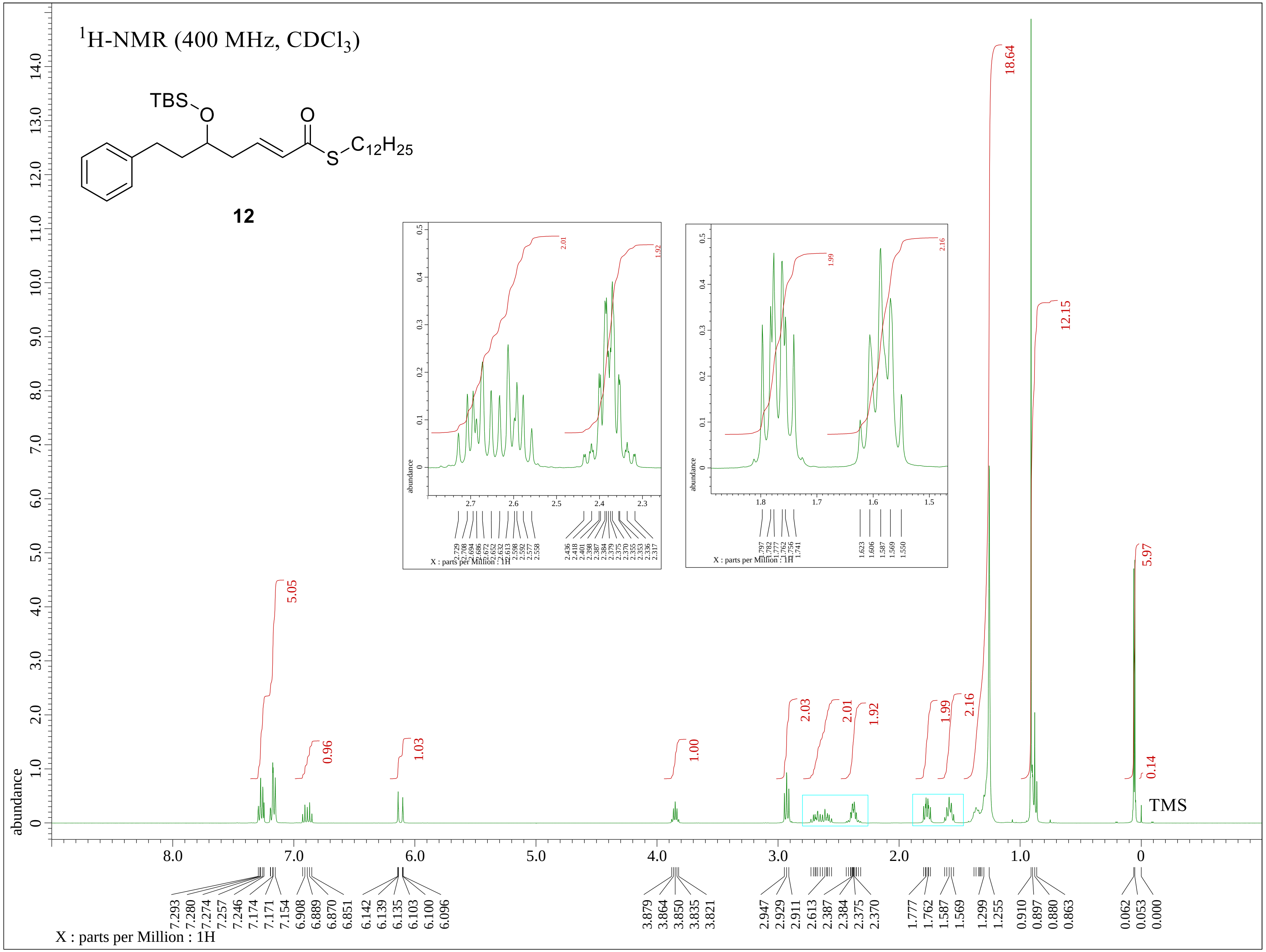
^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
O
S
C$_{12}$H$_{25}$
OH
10
CDCl$_3$
abundance
X : parts per Million : 13C
200.854
194.619
191.815
173.013
142.074
141.892
128.372
128.267
125.788
101.580
77.324
77.000
76.685
69.325
68.247
58.913
50.084
43.028
39.415
39.224
31.882
29.594
29.537
29.508
29.318
28.765
25.828
25.790
22.662
14.091
-4.635
-4.702
-4.854
29.661
29.594
29.537
29.508
29.461
29.432
29.318
29.232
29.108
29.051
28.765

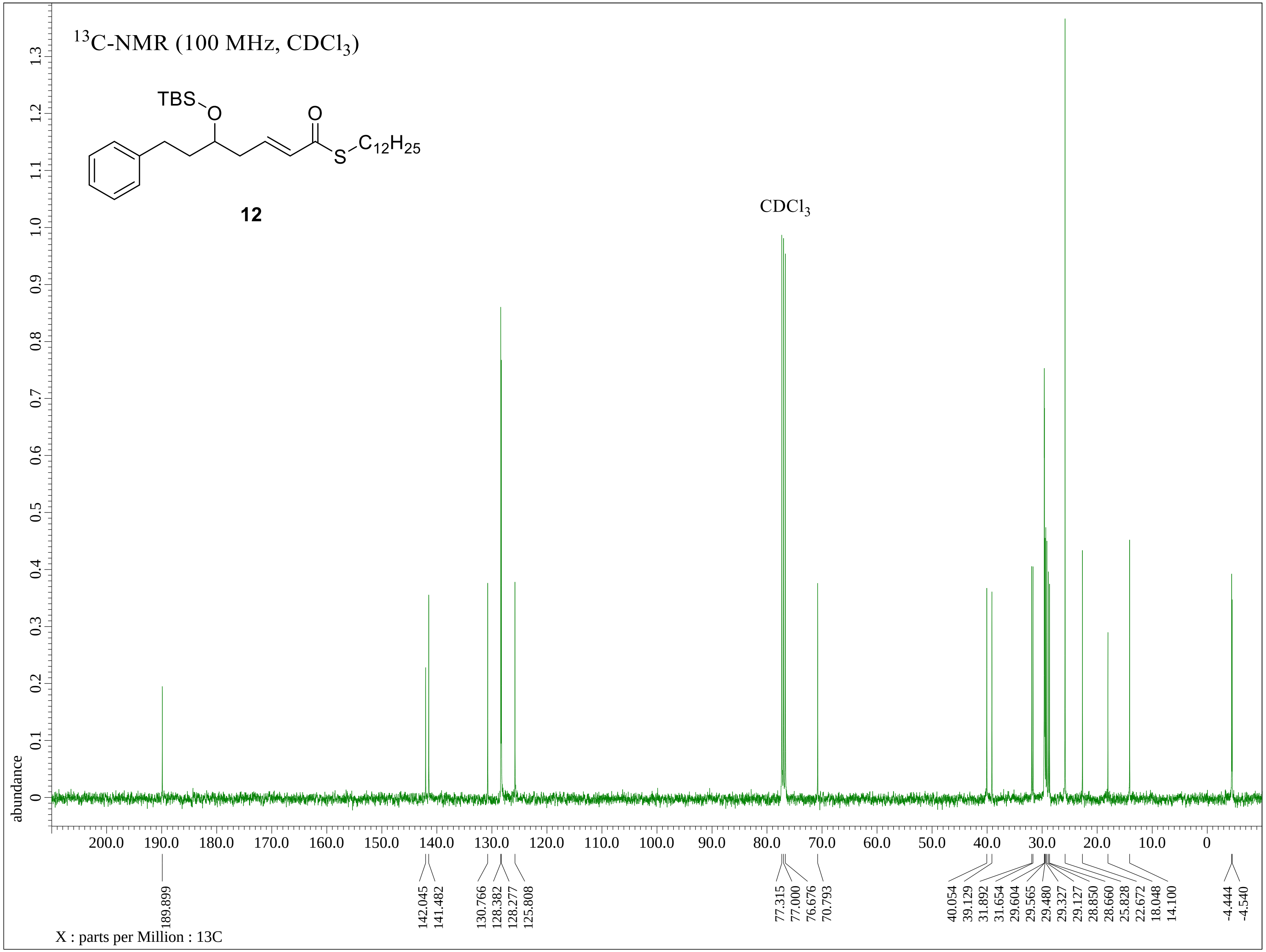


^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
O
OH
O
S
C$_{12}$H$_{25}$
11
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.02
0.46
0.54
1.00
0.45
0.52
2.01
4.01
6.09
18.45
12.05
5.96
0.11
TMS
7.296
7.293
7.280
7.276
7.264
7.257
7.251
7.195
7.179
7.175
7.171
7.164
7.159
7.154
4.414
4.404
4.398
4.392
4.385
4.379
4.364
4.214
4.045
4.039
3.981
3.491
3.486
3.307
3.301
2.907
2.889
2.871
2.718
2.715
2.614
1.700
1.688
1.656
1.587
1.568
1.550
1.297
1.251
0.908
0.902
0.896
0.879
0.093
0.090
0.074
0.066
0.060
0.000
4.419
4.414
4.404
4.398
4.392
4.385
4.379
4.364
4.357
4.234
4.223
4.220
4.214
4.211
4.204
4.201
4.194
4.183
4.178
4.054
4.045
4.039
4.030
4.014
4.010
3.995
3.981
3.963
3.950
2.907
2.889
2.871
2.797
2.778
2.774
2.758
2.739
2.735
2.729
2.718
2.715
2.691
2.678
2.653
2.640
2.633
2.614
2.604
2.590
2.587
0.908
0.902
0.896
0.879
0.861

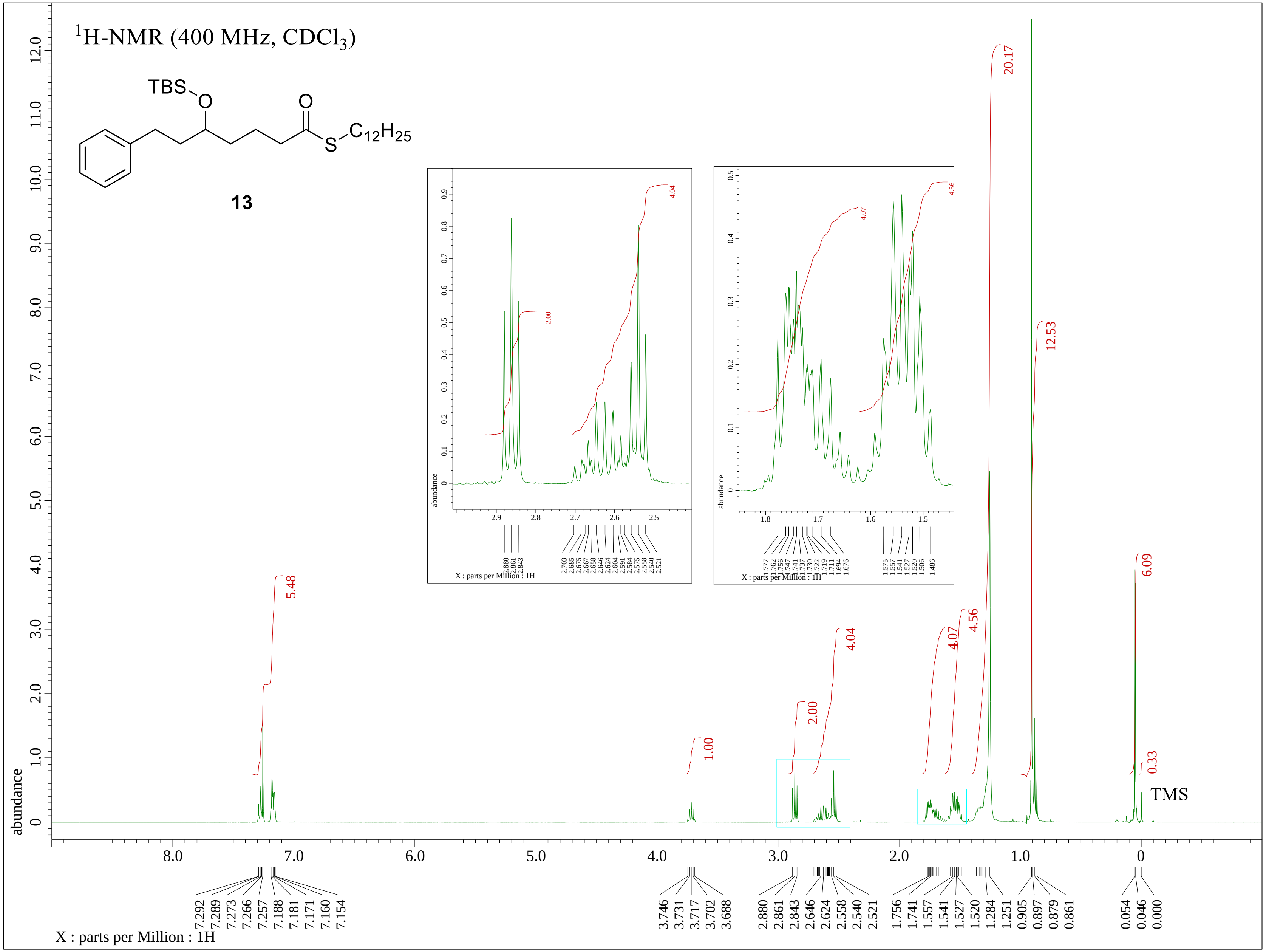


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
OH
O
S
C12H25
11
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
198.709
198.556
142.074
141.940
128.382
128.248
125.827
125.798
77.315
77.000
76.676
71.146
70.173
67.322
65.578
51.524
51.123
42.523
41.417
39.214
38.499
31.882
29.604
29.546
29.451
29.318
29.089
28.822
25.837
22.662
14.100
-4.187
-4.540
-4.587
-4.711
X : parts per Million : 13C

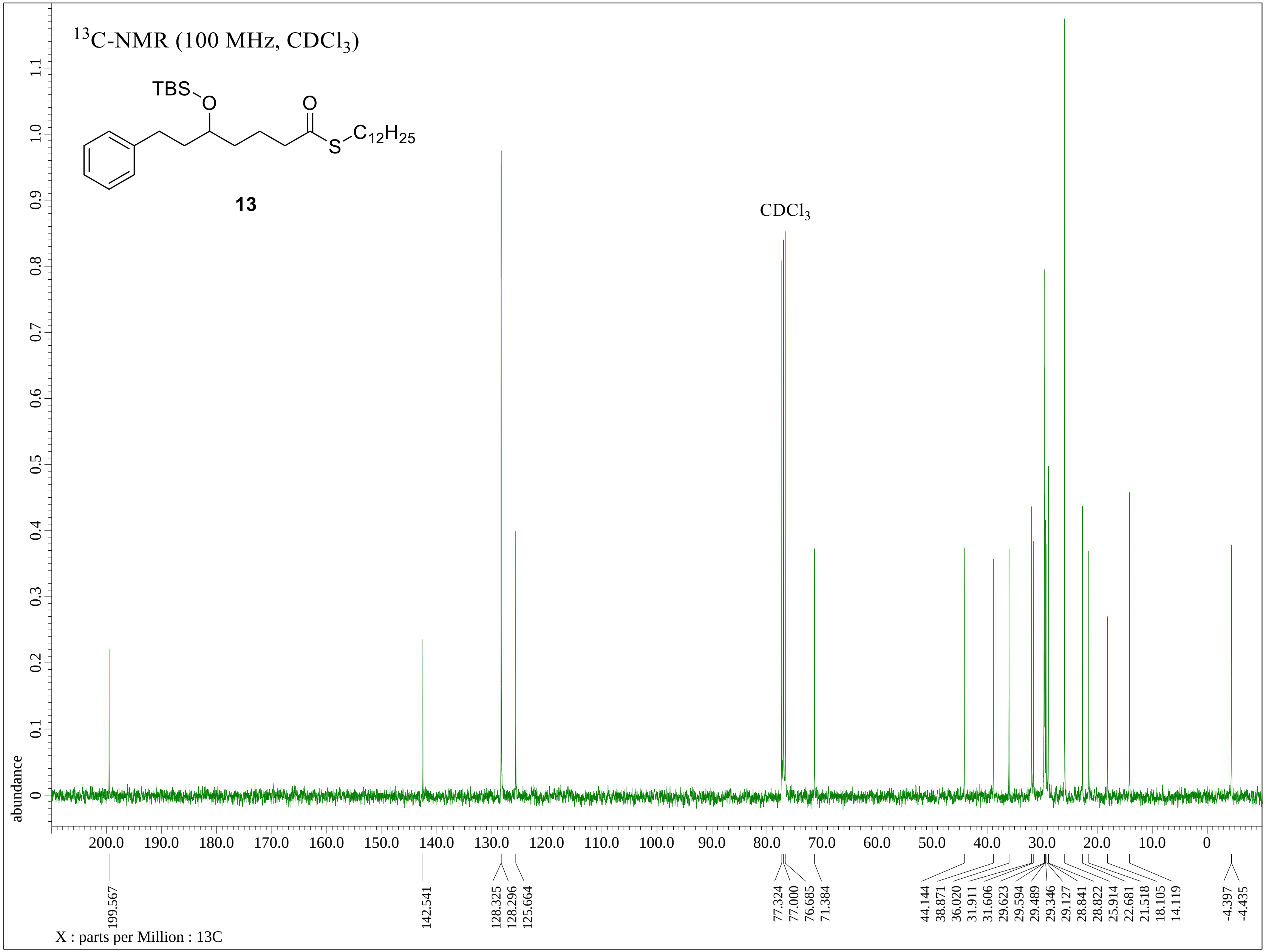

^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
O
O
S
C$_{12}$H$_{25}$
12
abundance
X : parts per Million : 1H
TMS
5.05
0.96
1.03
1.00
2.03
2.01
1.92
1.99
2.16
18.64
12.15
5.97
0.14
7.293
7.280
7.274
7.257
7.246
7.174
7.171
7.154
6.908
6.889
6.870
6.851
6.142
6.139
6.135
6.103
6.100
6.096
3.879
3.864
3.850
3.835
3.821
2.947
2.929
2.911
2.613
2.387
2.384
2.375
2.370
1.777
1.762
1.587
1.569
1.299
1.255
0.910
0.897
0.880
0.863
0.062
0.053
0.000
2.729
2.708
2.694
2.686
2.672
2.652
2.632
2.613
2.598
2.592
2.577
2.558
2.436
2.418
2.401
2.398
2.387
2.384
2.379
2.375
2.370
2.355
2.353
2.336
2.317
1.797
1.782
1.777
1.762
1.756
1.741
1.623
1.606
1.587
1.569
1.550

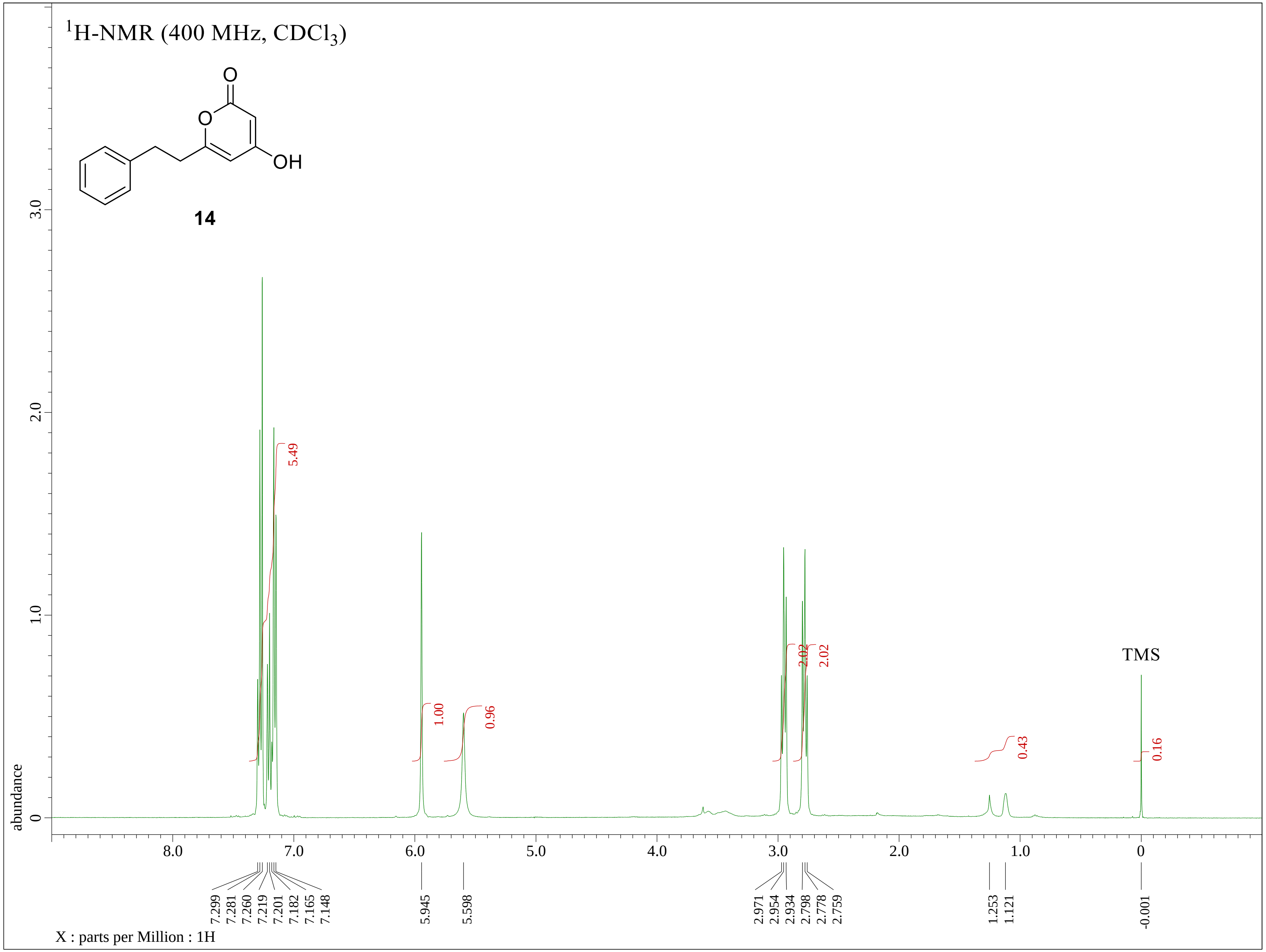


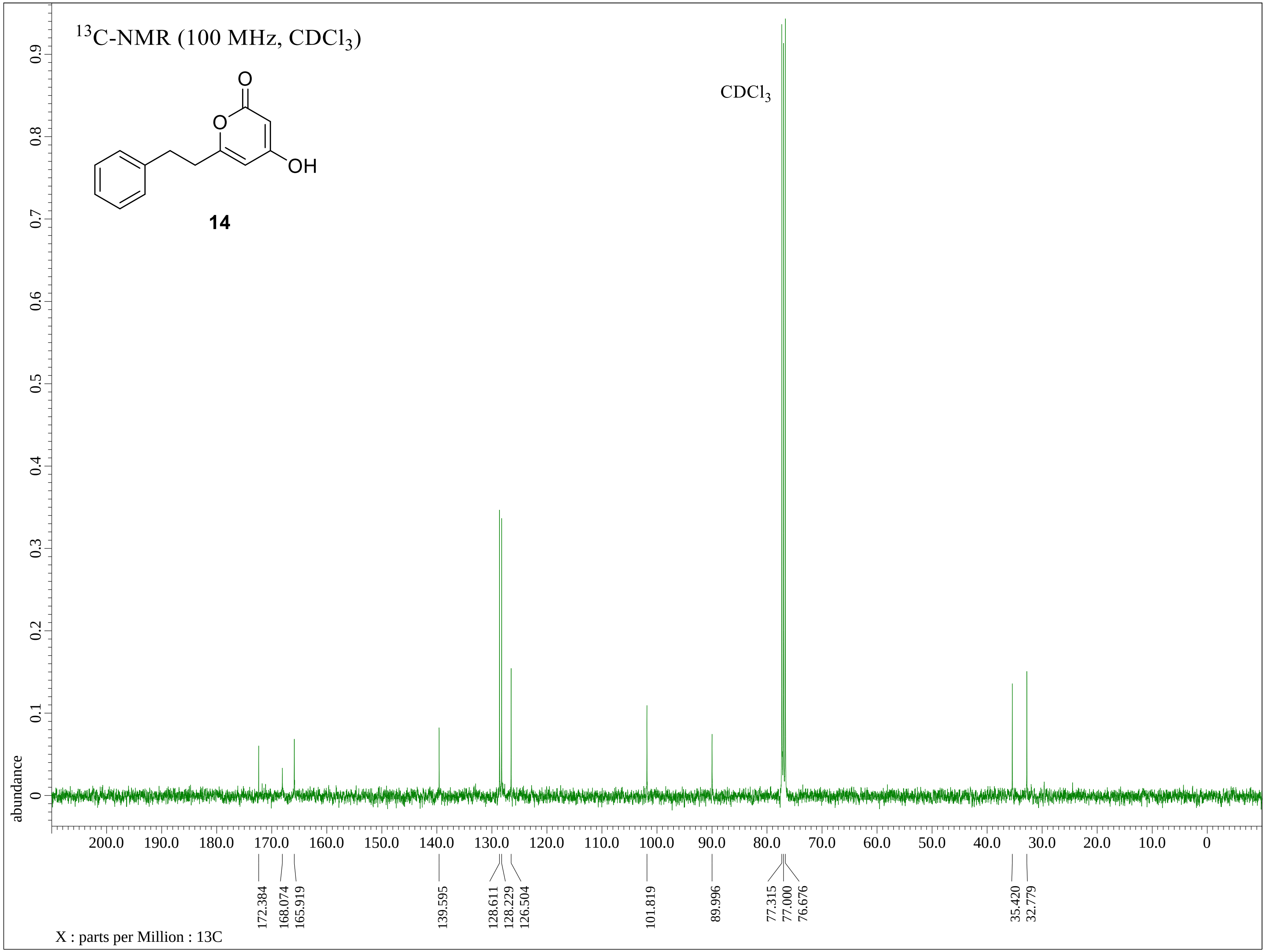
^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
S
C$_{12}$H$_{25}$
12
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
189.899
142.045
141.482
130.766
128.382
128.277
125.808
77.315
77.000
76.676
70.793
40.054
39.129
31.892
31.654
29.604
29.565
29.480
29.327
29.127
28.850
28.660
25.828
22.672
18.048
14.100
-4.444
-4.540
X : parts per Million : 13C

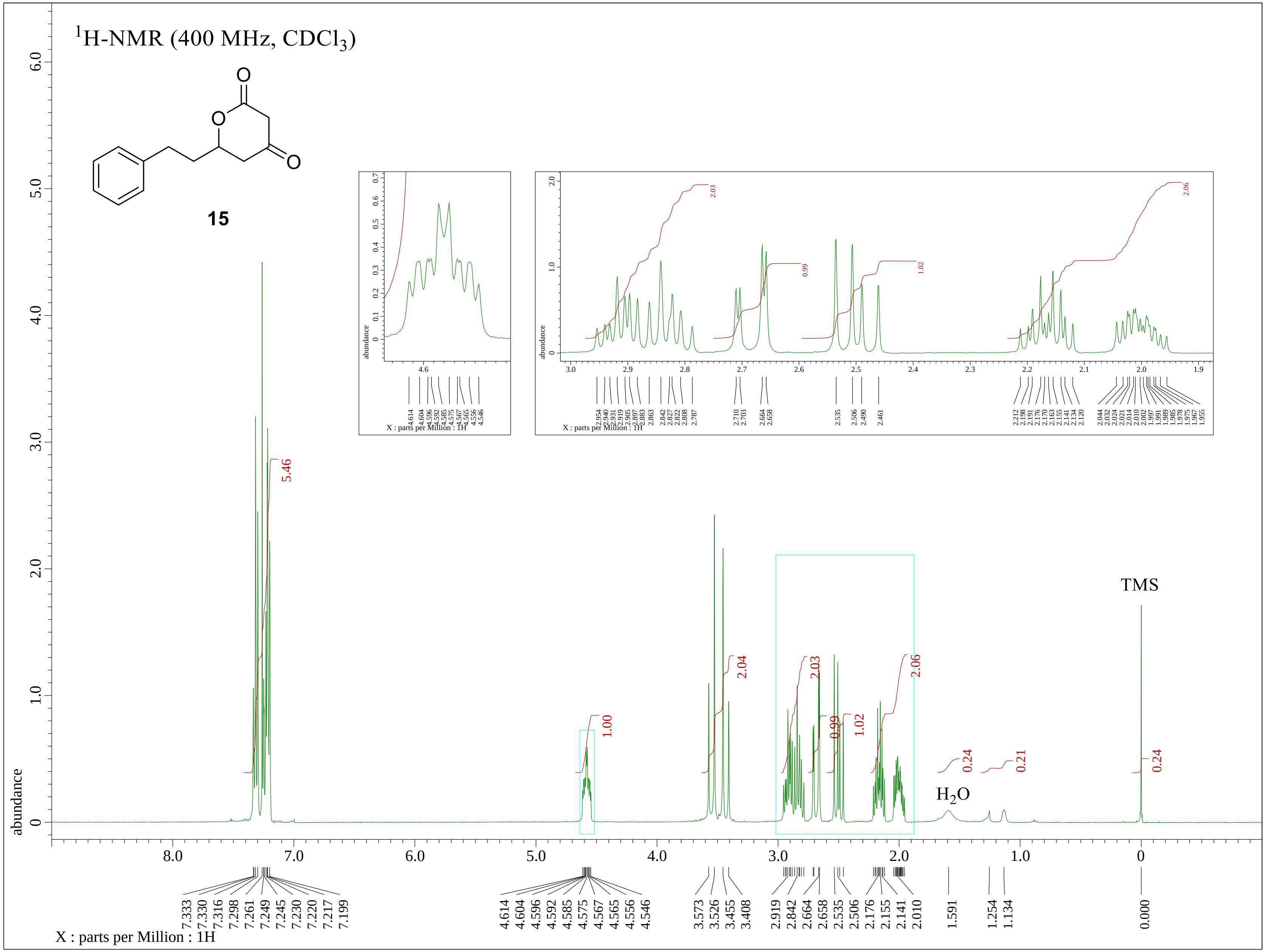


1H-NMR (400 MHz, CDCl3)
TBS
O
O
S
C12H25
13
abundance
X : parts per Million : 1H
5.48
1.00
2.00
4.04
4.07
4.56
20.17
12.53
6.09
0.33
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
7.292 7.289 7.273 7.266 7.257 7.188 7.181 7.171 7.160 7.154
3.746 3.731 3.717 3.702 3.688
2.880 2.861 2.843 2.646 2.624 2.558 2.540 2.521
1.756 1.741 1.557 1.541 1.527 1.520 1.284 1.251
0.905 0.897 0.879 0.861
0.054 0.046 0.000
2.880 2.861 2.843
2.703 2.685 2.675 2.667 2.658 2.646 2.624 2.604 2.591 2.584 2.575 2.558 2.540 2.521
1.777 1.762 1.756 1.747 1.741 1.737 1.730 1.722 1.719 1.711 1.694 1.676
1.575 1.557 1.541 1.527 1.520 1.506 1.486

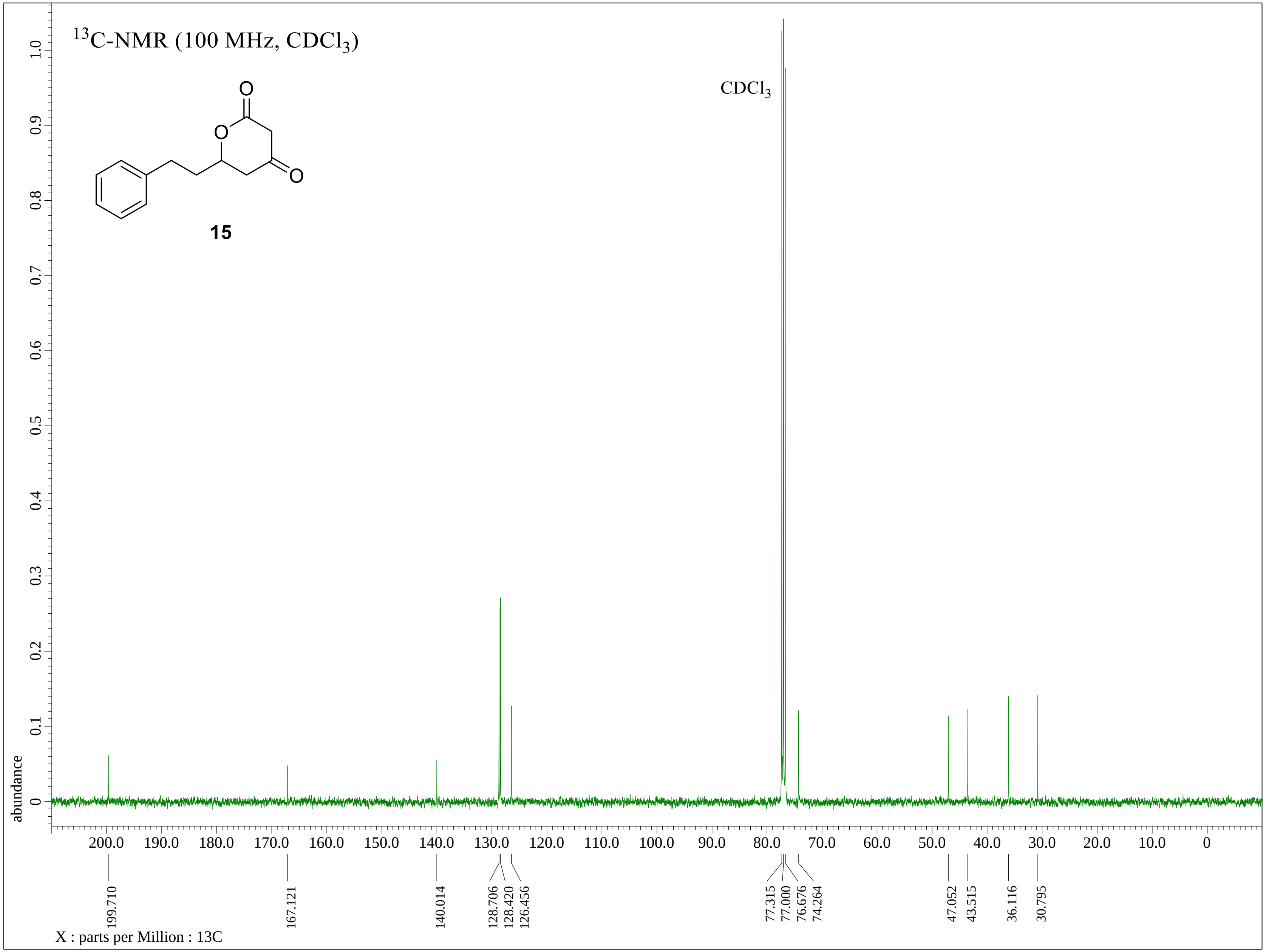

^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
S
C$_{12}$H$_{25}$
13
CDCl$_3$
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
199.567
142.541
128.325
128.296
125.664
77.324
77.000
76.685
71.384
44.144
38.871
36.020
31.911
31.606
29.623
29.594
29.489
29.346
29.127
28.841
28.822
25.914
22.681
21.518
18.105
14.119
-4.397
-4.435
X : parts per Million : 13C

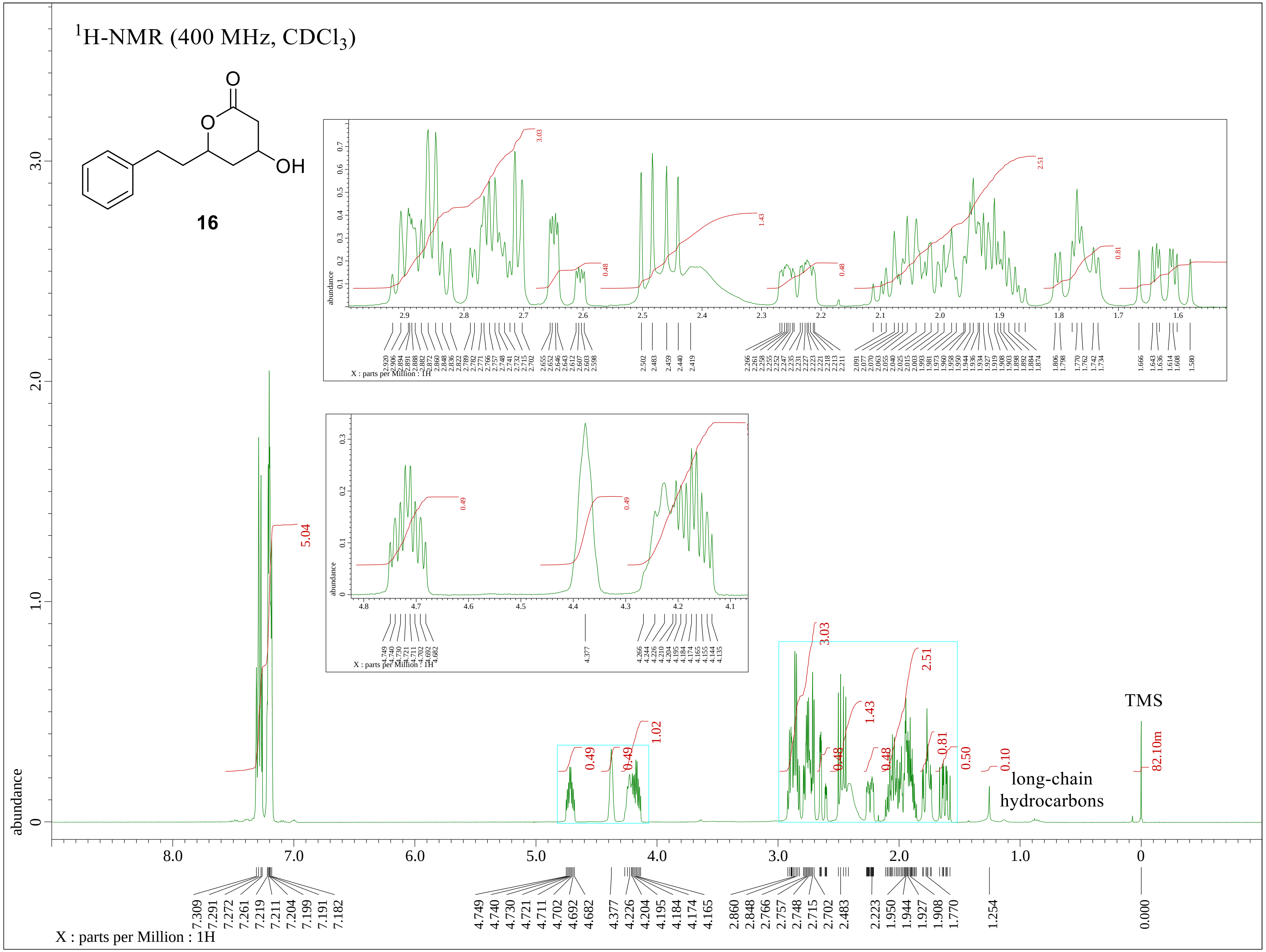

^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
OH
14
abundance
0
1.0
2.0
3.0
5.49
1.00
0.96
2.02
2.02
0.43
0.16
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.299
7.281
7.260
7.219
7.201
7.182
7.165
7.148
5.945
5.598
2.971
2.954
2.934
2.798
2.778
2.759
1.253
1.121
-0.001
X : parts per Million : 1H


^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
OH
14
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.384
168.074
165.919
139.595
128.611
128.229
126.504
101.819
89.996
77.315
77.000
76.676
35.420
32.779
X : parts per Million : 13C

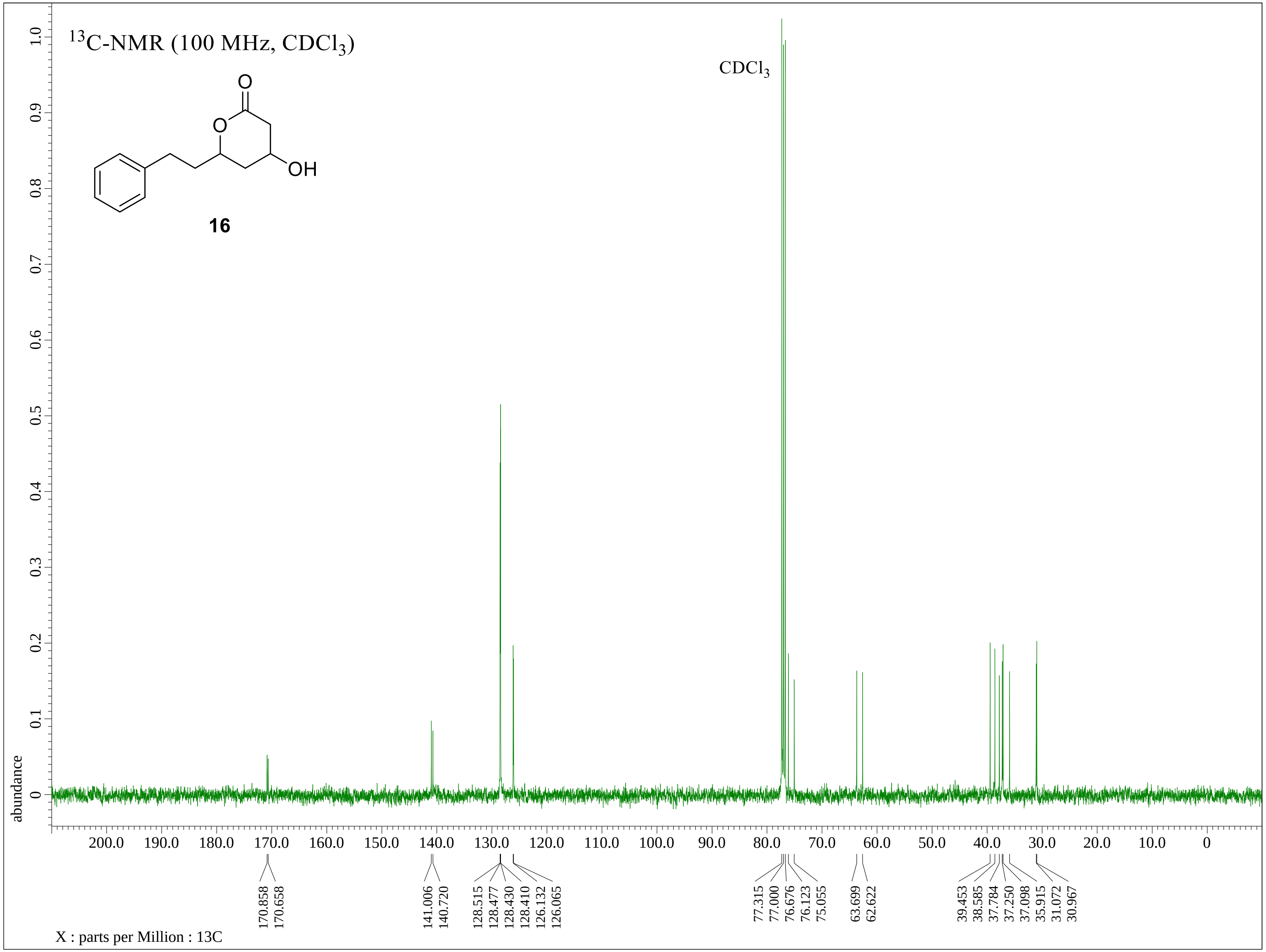


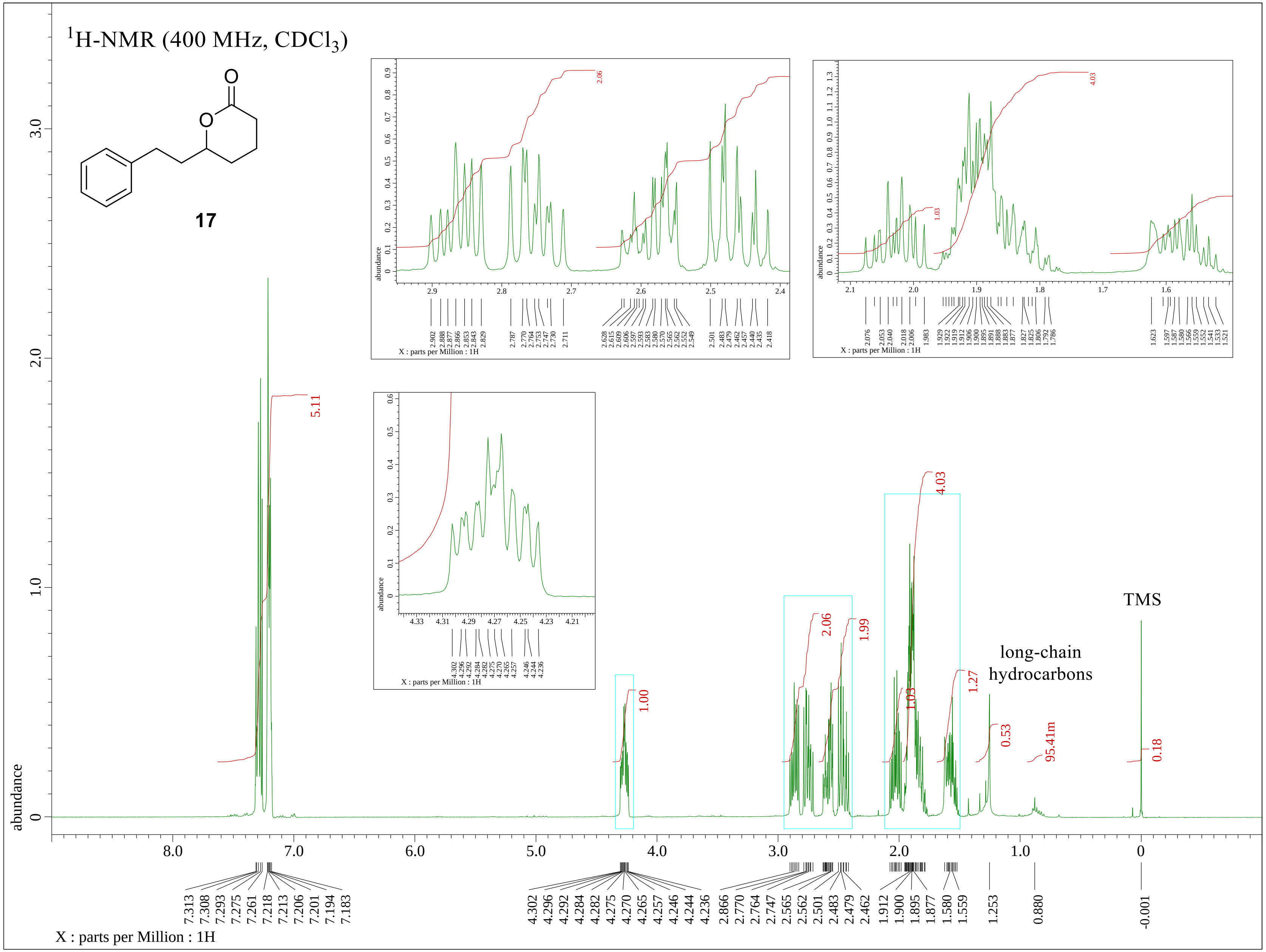
^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
O
15
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
5.46
1.00
2.04
2.03
0.99
1.02
2.06
0.24
0.21
0.24
H$_2$O
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.333
7.330
7.316
7.298
7.261
7.249
7.245
7.230
7.220
7.217
7.199
4.614
4.604
4.596
4.592
4.585
4.575
4.567
4.565
4.556
4.546
3.573
3.526
3.455
3.408
2.919
2.842
2.664
2.658
2.535
2.506
2.176
2.155
2.141
2.010
1.591
1.254
1.134
0.000
X : parts per Million : 1H

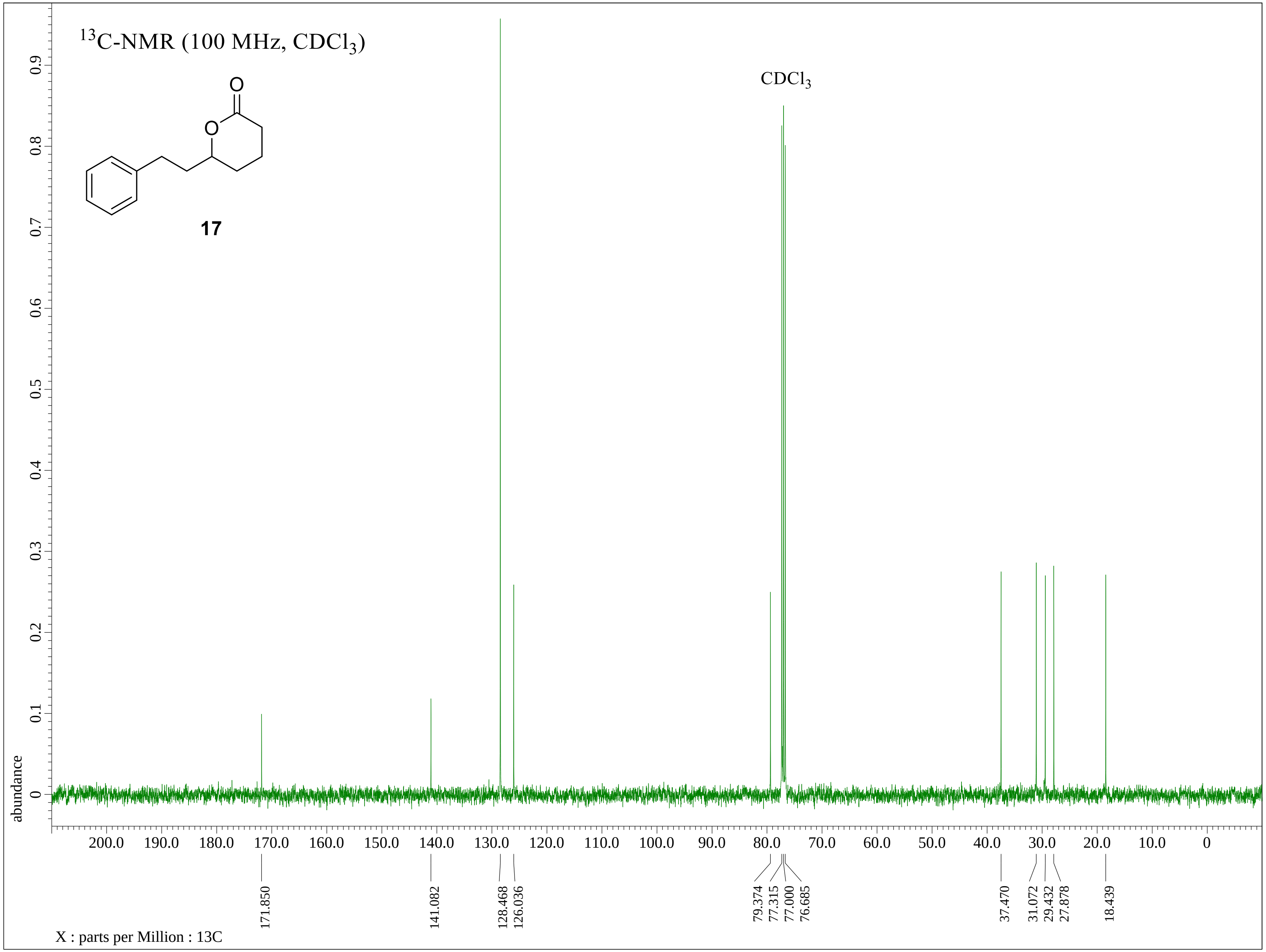

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
O
15
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
199.710
167.121
140.014
128.706
128.420
126.456
77.315
77.000
76.676
74.264
47.052
43.515
36.116
30.795
X : parts per Million : 13C

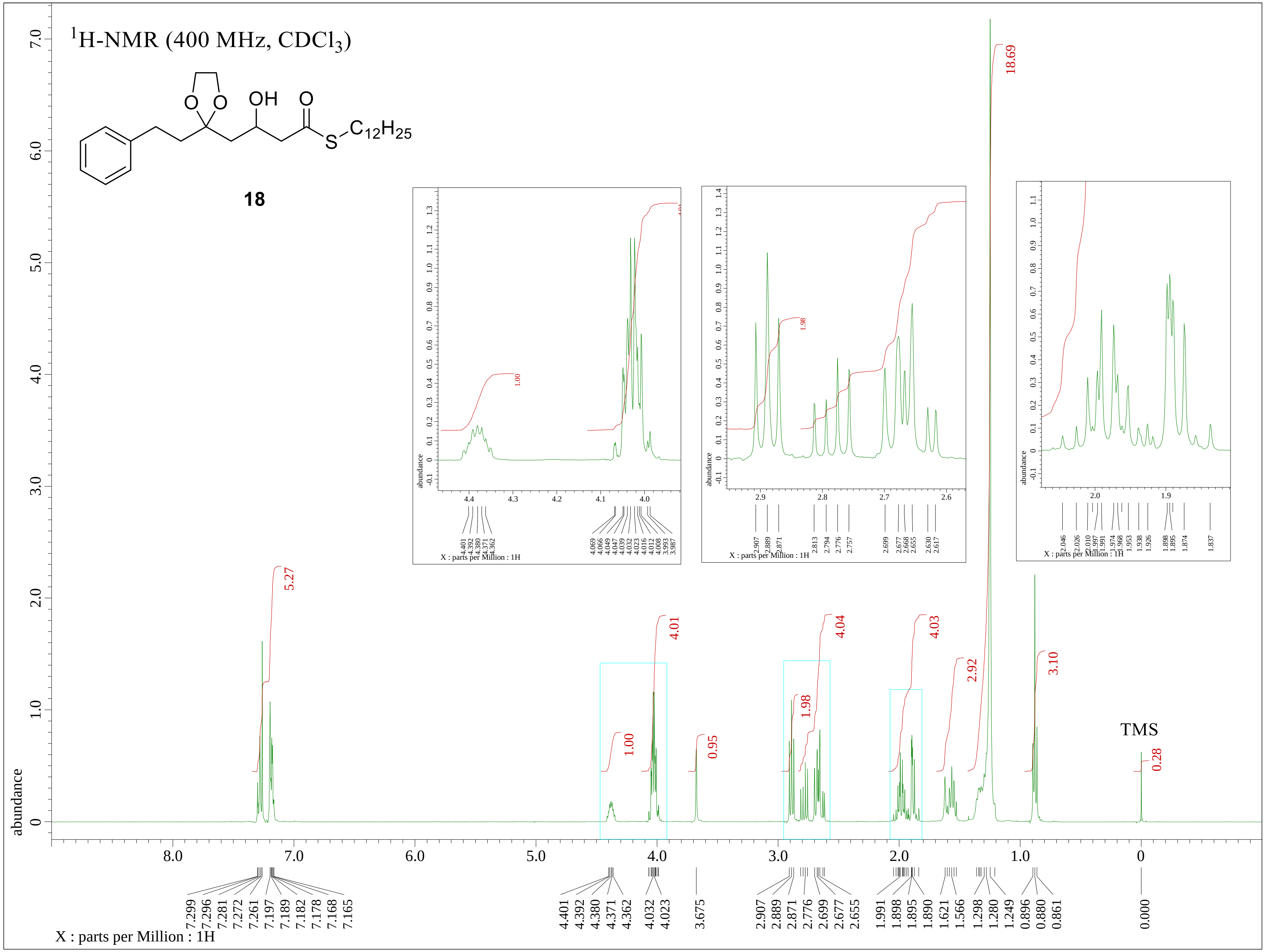


^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
OH
16
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
0
5.04
0.49
0.49
1.02
3.03
0.48
1.43
0.48
2.51
0.81
0.50
0.10
82.10m
TMS
long-chain
hydrocarbons
7.309
7.291
7.272
7.261
7.219
7.211
7.204
7.199
7.191
7.182
4.749
4.740
4.730
4.721
4.711
4.702
4.692
4.682
4.377
4.226
4.204
4.195
4.184
4.174
4.165
2.860
2.848
2.766
2.757
2.748
2.715
2.702
2.483
2.223
1.950
1.944
1.927
1.908
1.770
1.254
0.000

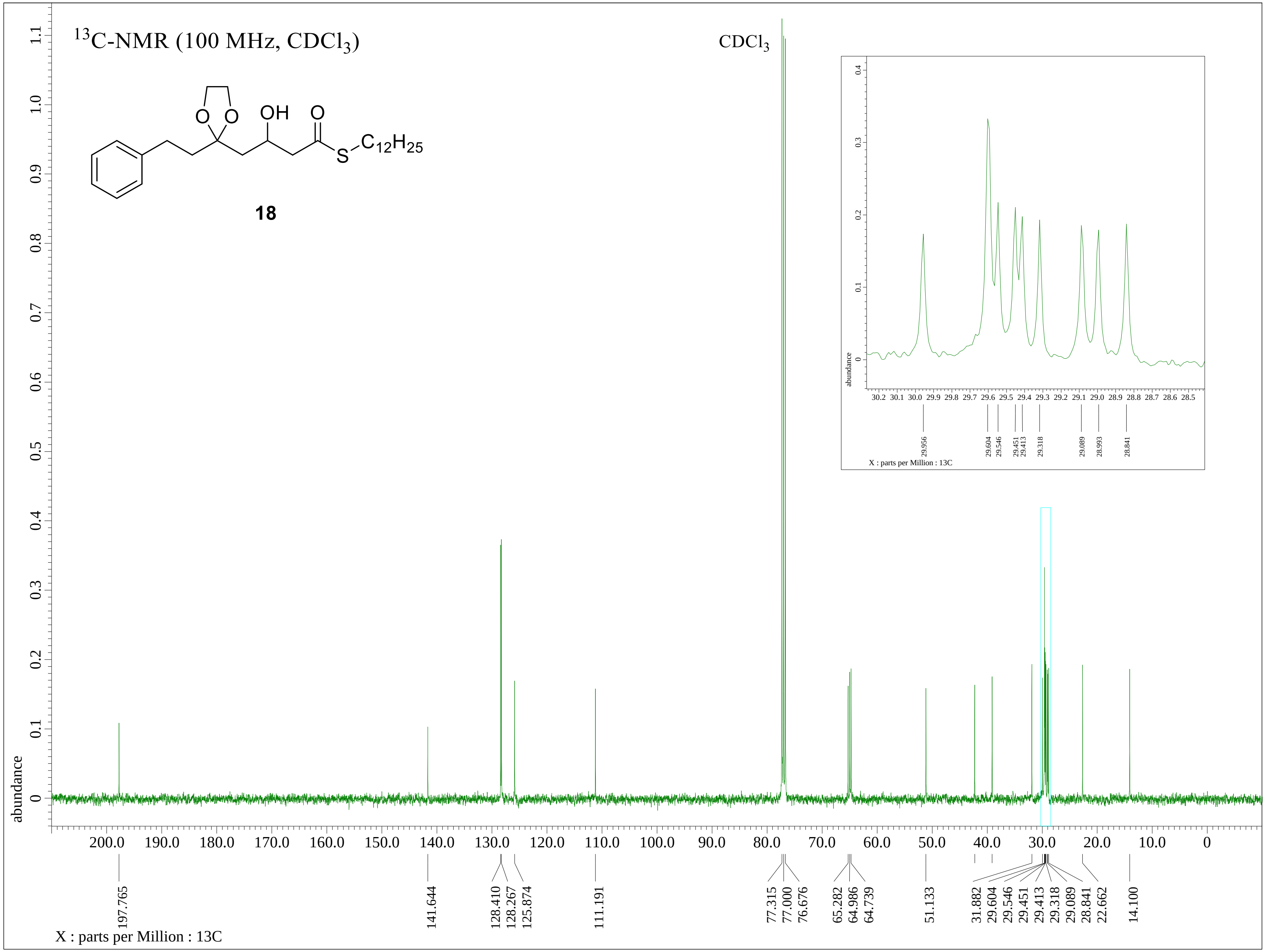

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
OH
16
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.858
170.658
141.006
140.720
128.515
128.477
128.430
128.410
126.132
126.065
77.315
77.000
76.676
76.123
75.055
63.699
62.622
39.453
38.585
37.784
37.250
37.098
35.915
31.072
30.967
X : parts per Million : 13C

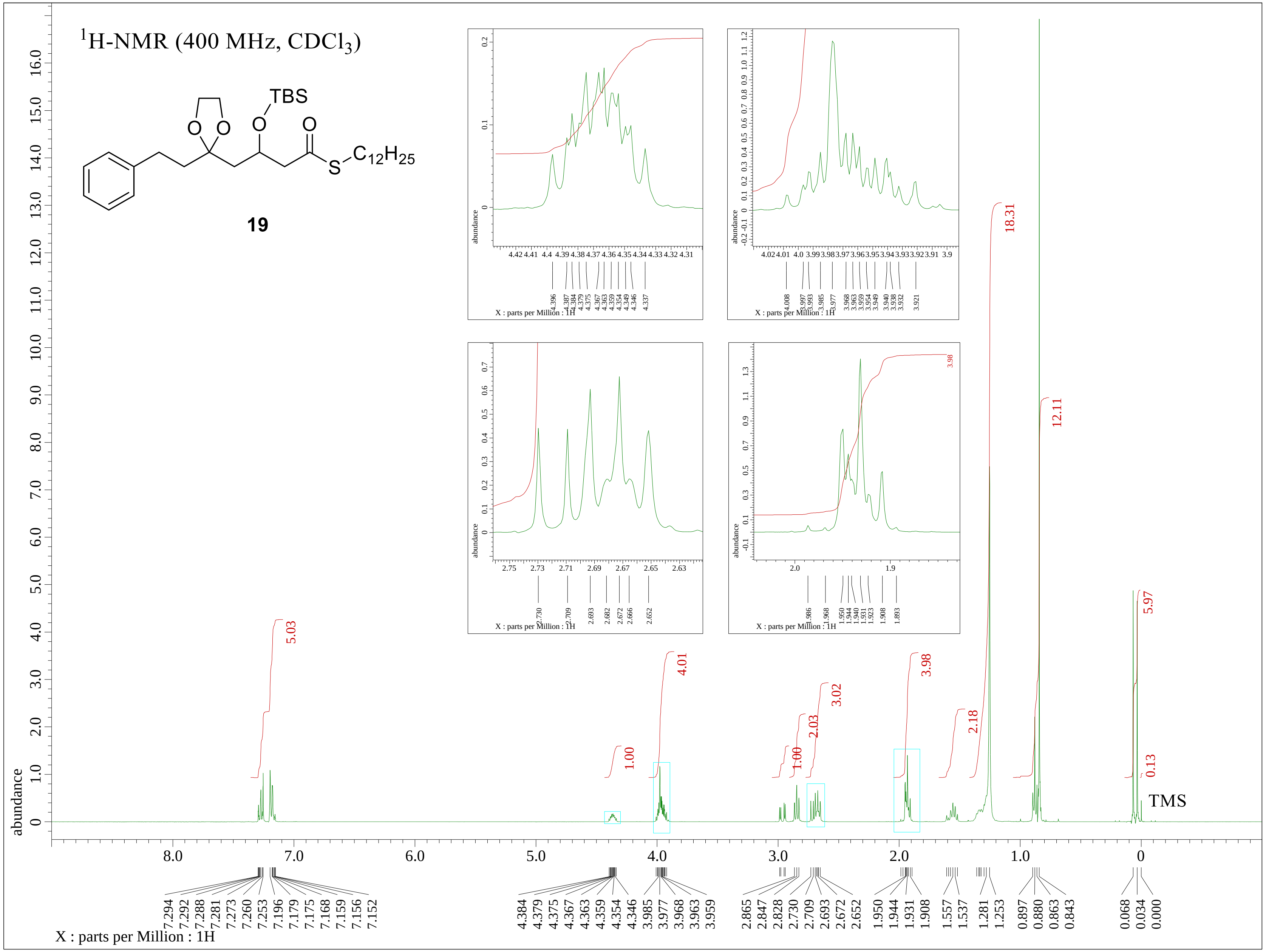

^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
17
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
5.11
1.00
2.06
1.99
1.03
4.03
1.27
0.53
95.41m
0.18
long-chain
hydrocarbons
TMS
7.313
7.308
7.293
7.275
7.261
7.218
7.213
7.206
7.201
7.194
7.183
4.302
4.296
4.292
4.284
4.282
4.275
4.270
4.265
4.257
4.246
4.244
4.236
2.866
2.770
2.764
2.747
2.565
2.562
2.501
2.483
2.479
2.462
1.912
1.900
1.895
1.877
1.580
1.559
1.253
0.880
-0.001

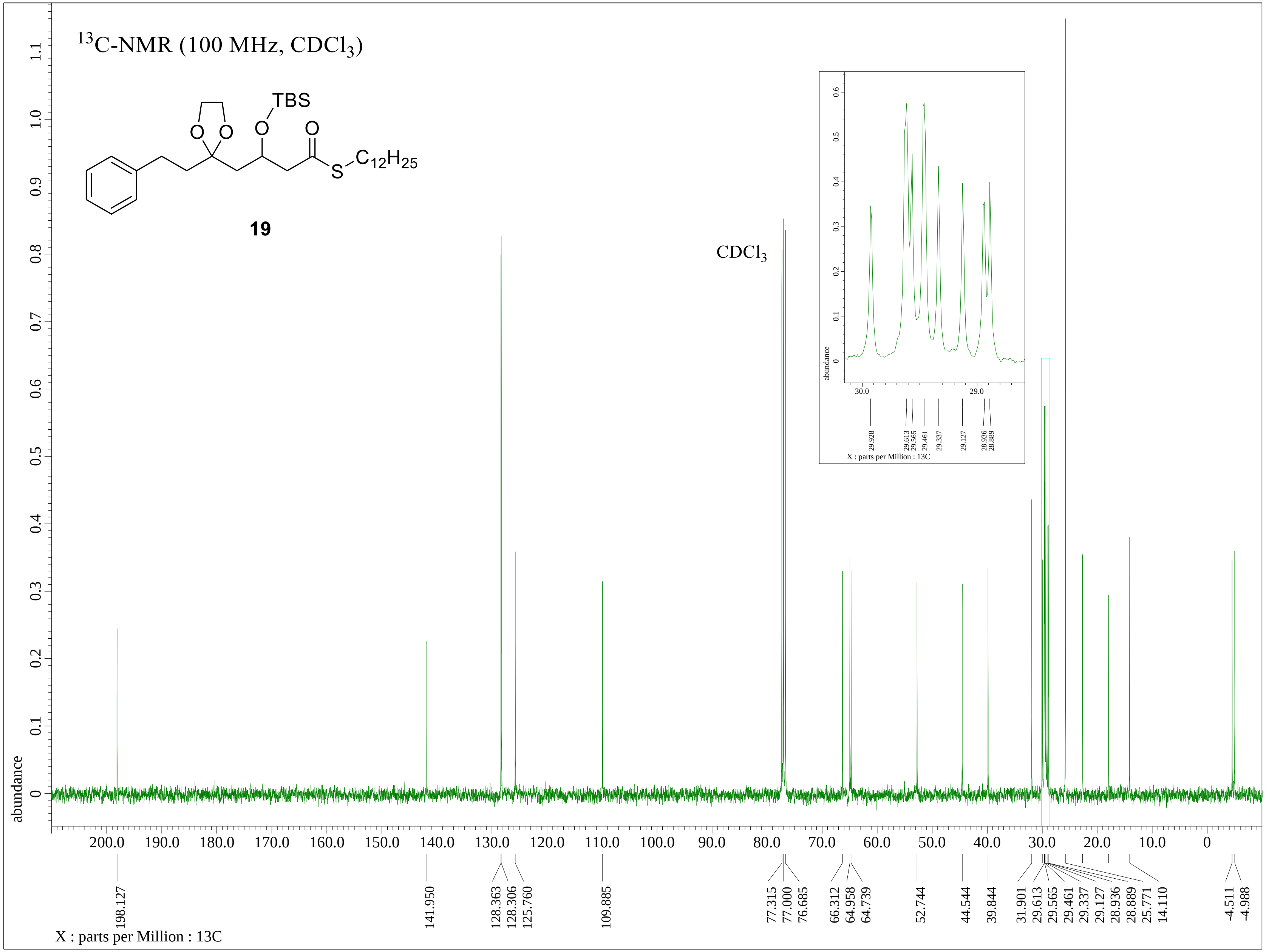

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
17
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.850
141.082
128.468
126.036
79.374
77.315
77.000
76.685
37.470
31.072
29.432
27.878
18.439
X : parts per Million : 13C

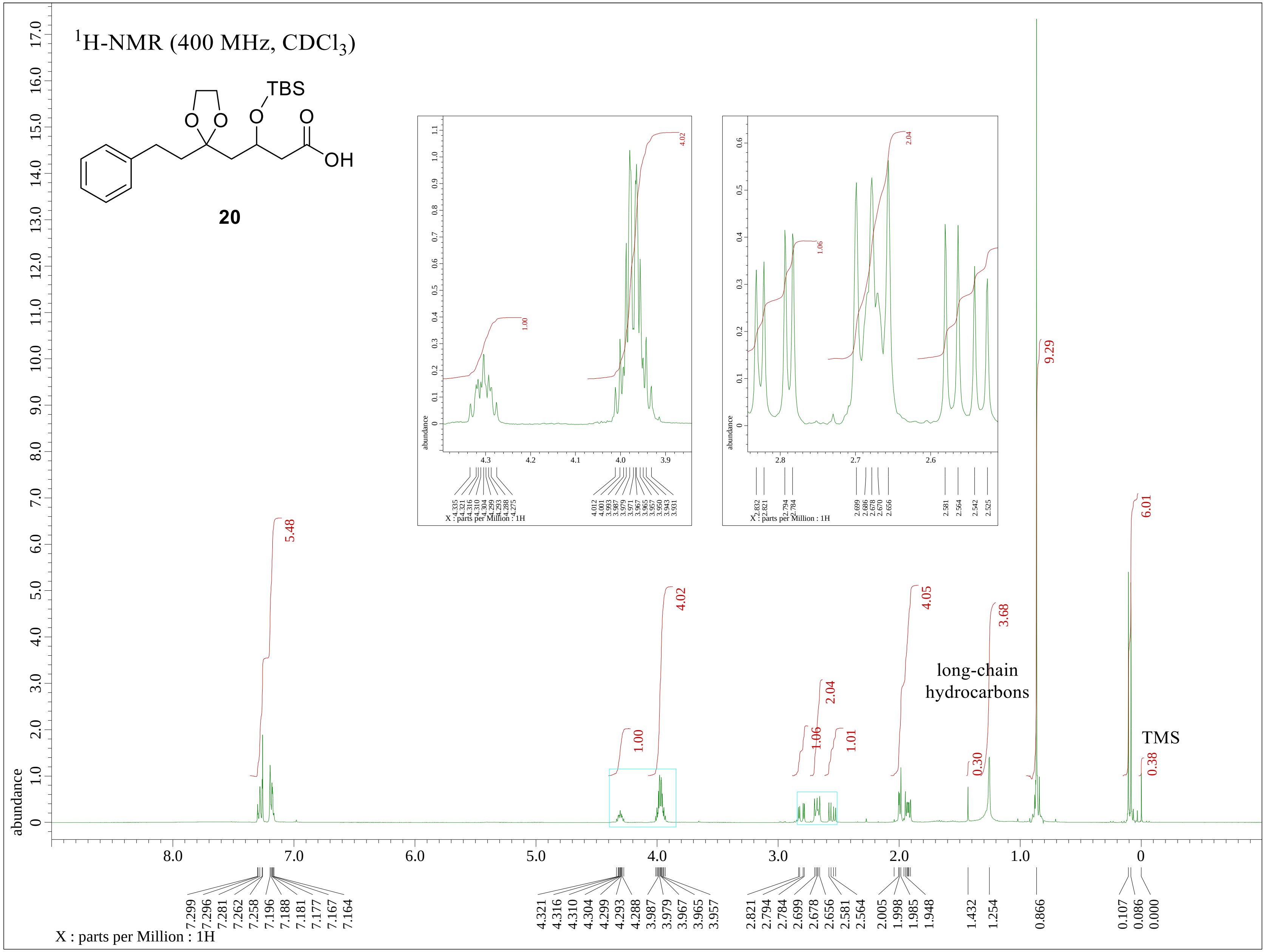


^{1}H-NMR (400 MHz, $CDCl_3$)
OH
O
O O
S
$C_{12}H_{25}$
18
abundance
X : parts per Million : 1H
TMS
5.27
1.00
4.01
0.95
1.98
4.04
4.03
2.92
18.69
3.10
0.28
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.299
7.296
7.281
7.272
7.261
7.197
7.189
7.182
7.178
7.168
7.165
4.401
4.392
4.380
4.371
4.362
4.032
4.023
3.675
2.907
2.889
2.871
2.776
2.699
2.677
2.655
1.991
1.898
1.895
1.890
1.621
1.566
1.298
1.280
1.249
0.896
0.880
0.861
0.000

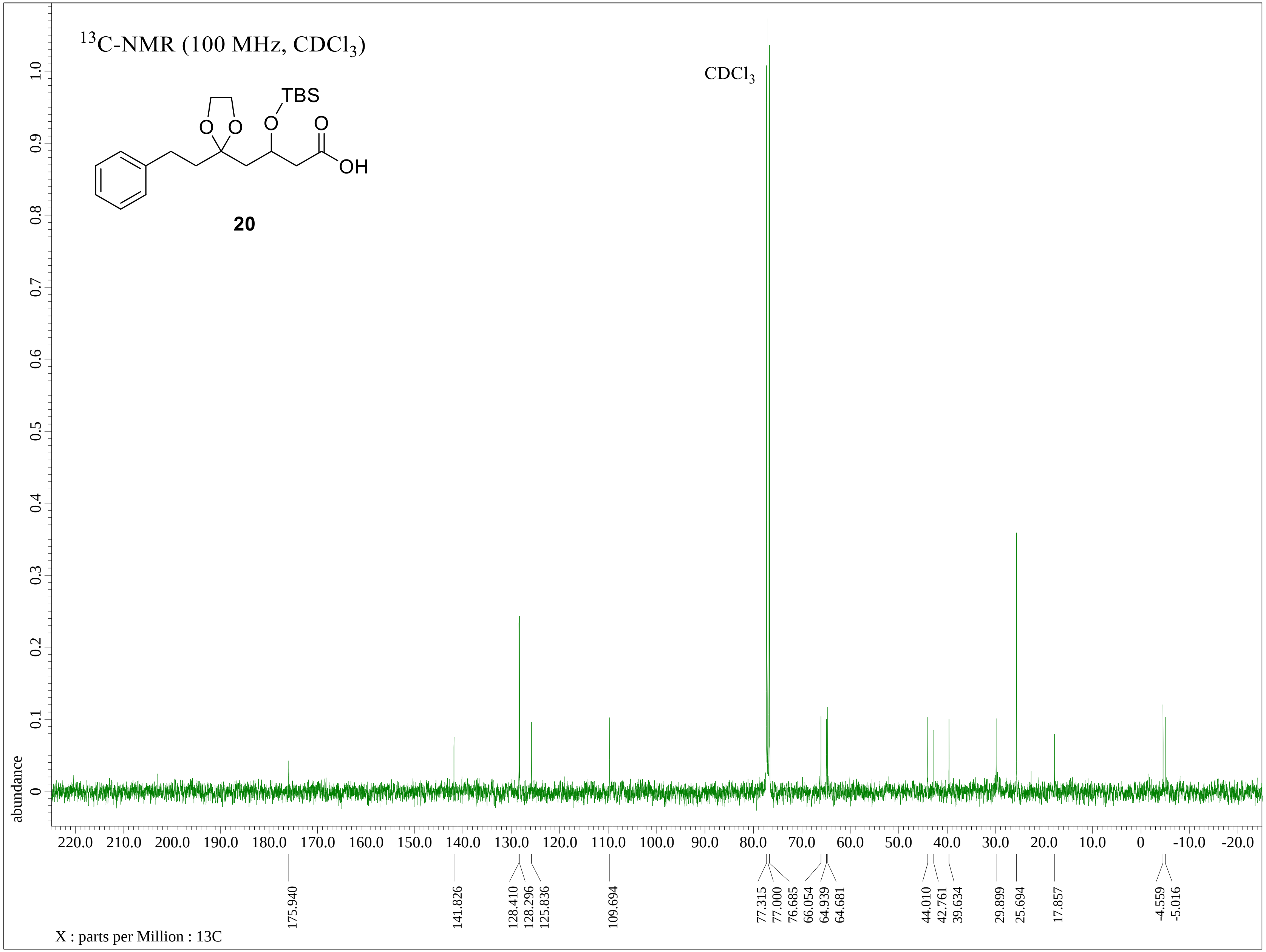

^{13}C-NMR (100 MHz, CDCl$_3$)
18
OH
O
S
C$_{12}$H$_{25}$
CDCl$_3$
abundance
X : parts per Million : 13C
197.765
141.644
128.410
128.267
125.874
111.191
77.315
77.000
76.676
65.282
64.986
64.739
51.133
31.882
29.604
29.546
29.451
29.413
29.318
29.089
28.841
22.662
14.100
29.956
28.993

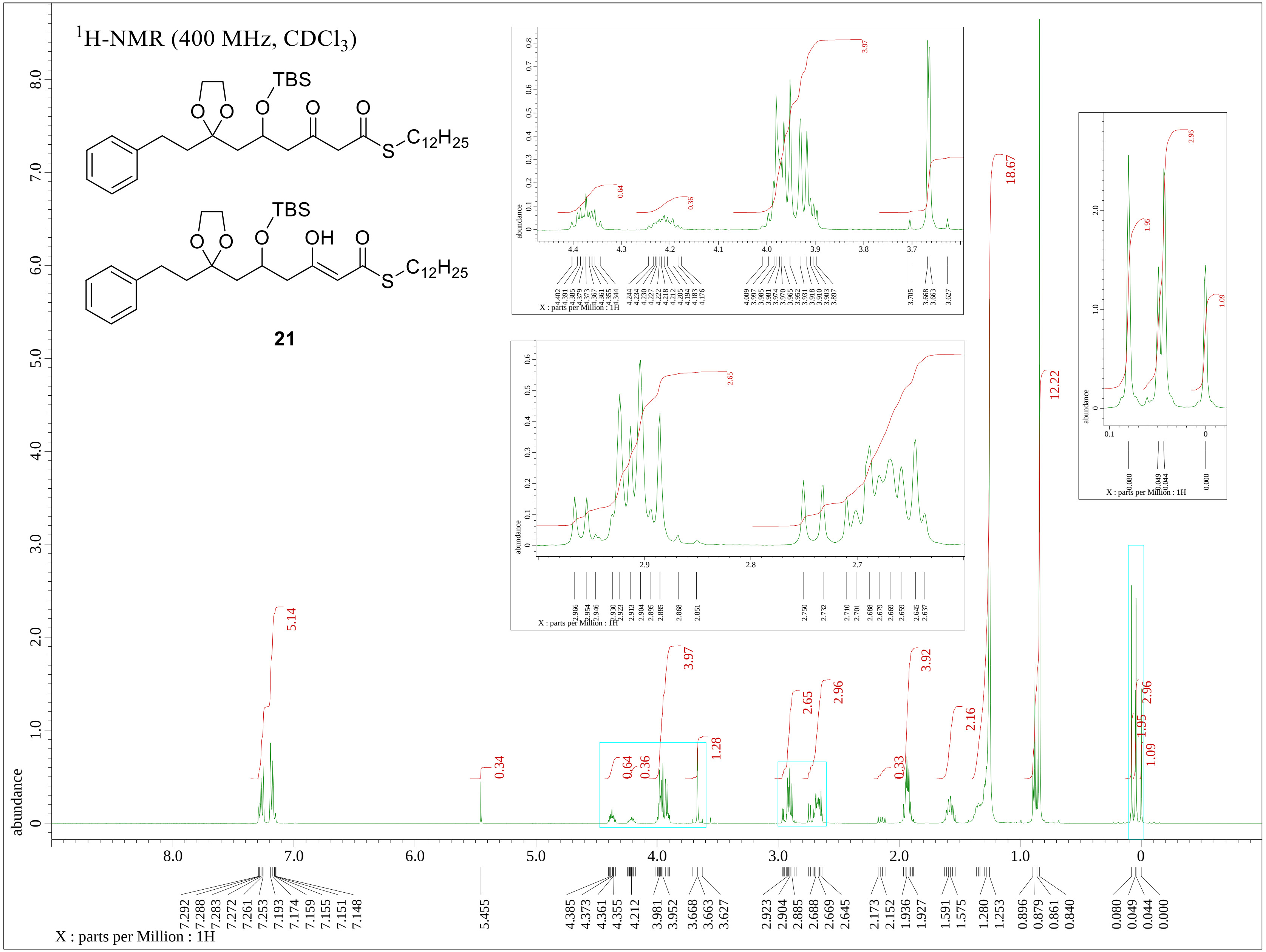

^{1}H-NMR (400 MHz, $CDCl_3$)
TBS
O
O
O
O
S
$C_{12}H_{25}$
19
abundance
X : parts per Million : 1H
TMS
5.03
1.00
4.01
1.00
2.03
3.02
3.98
2.18
18.31
12.11
5.97
0.13
7.294
7.292
7.288
7.281
7.273
7.260
7.253
7.196
7.179
7.175
7.168
7.159
7.156
7.152
4.384
4.379
4.375
4.367
4.363
4.359
4.354
4.346
3.985
3.977
3.968
3.963
3.959
2.865
2.847
2.828
2.730
2.709
2.693
2.672
2.652
1.950
1.944
1.931
1.908
1.557
1.537
1.281
1.253
0.897
0.880
0.863
0.843
0.068
0.034
0.000


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O O
O
S
C$_{12}$H$_{25}$
19
CDCl$_3$
abundance
X : parts per Million : 13C
198.127
141.950
128.363
128.306
125.760
109.885
77.315
77.000
76.685
66.312
64.958
64.739
52.744
44.544
39.844
31.901
29.613
29.565
29.461
29.337
29.127
28.936
28.889
25.771
14.110
-4.511
-4.988
29.928
30.0
29.0

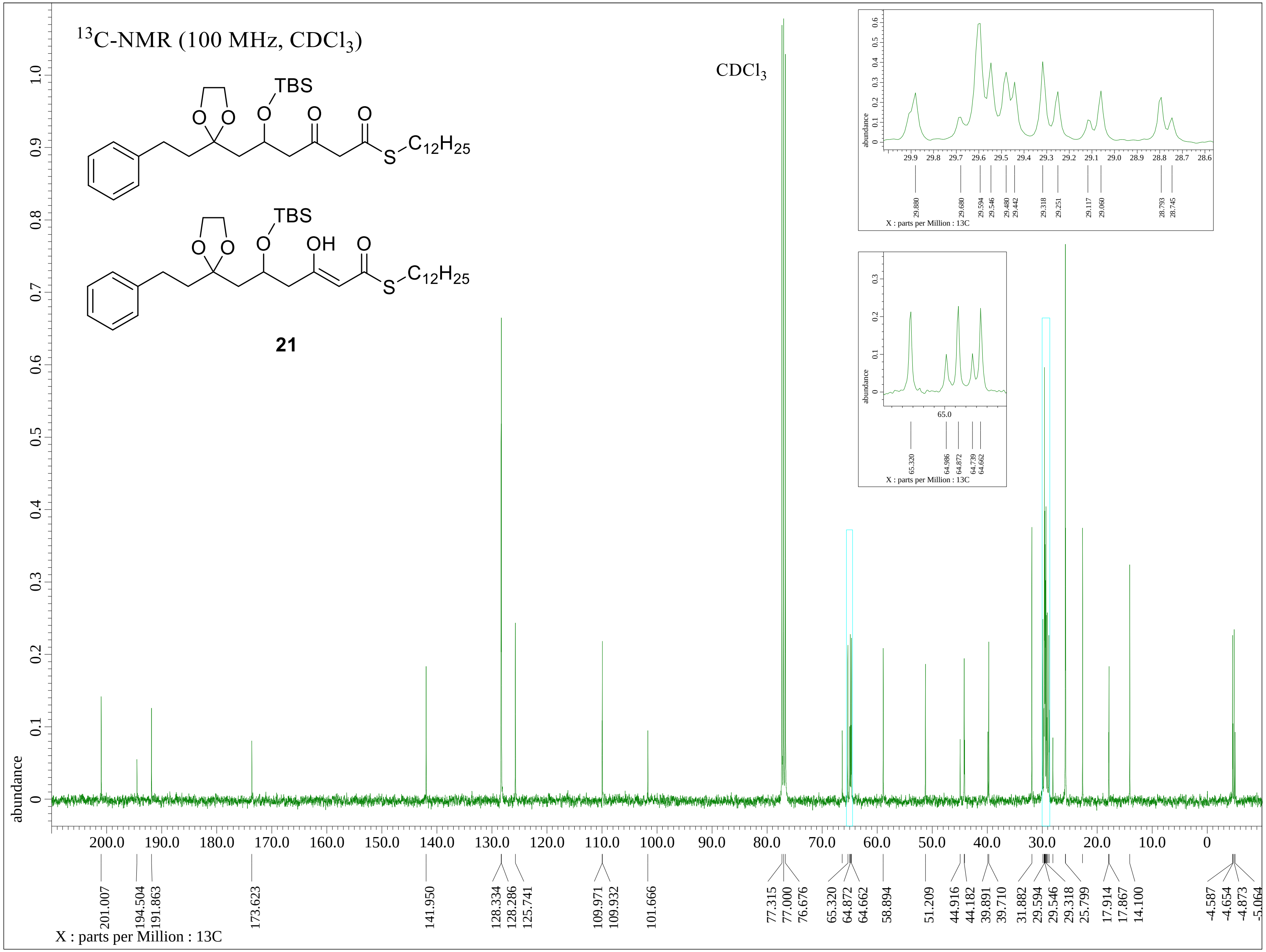


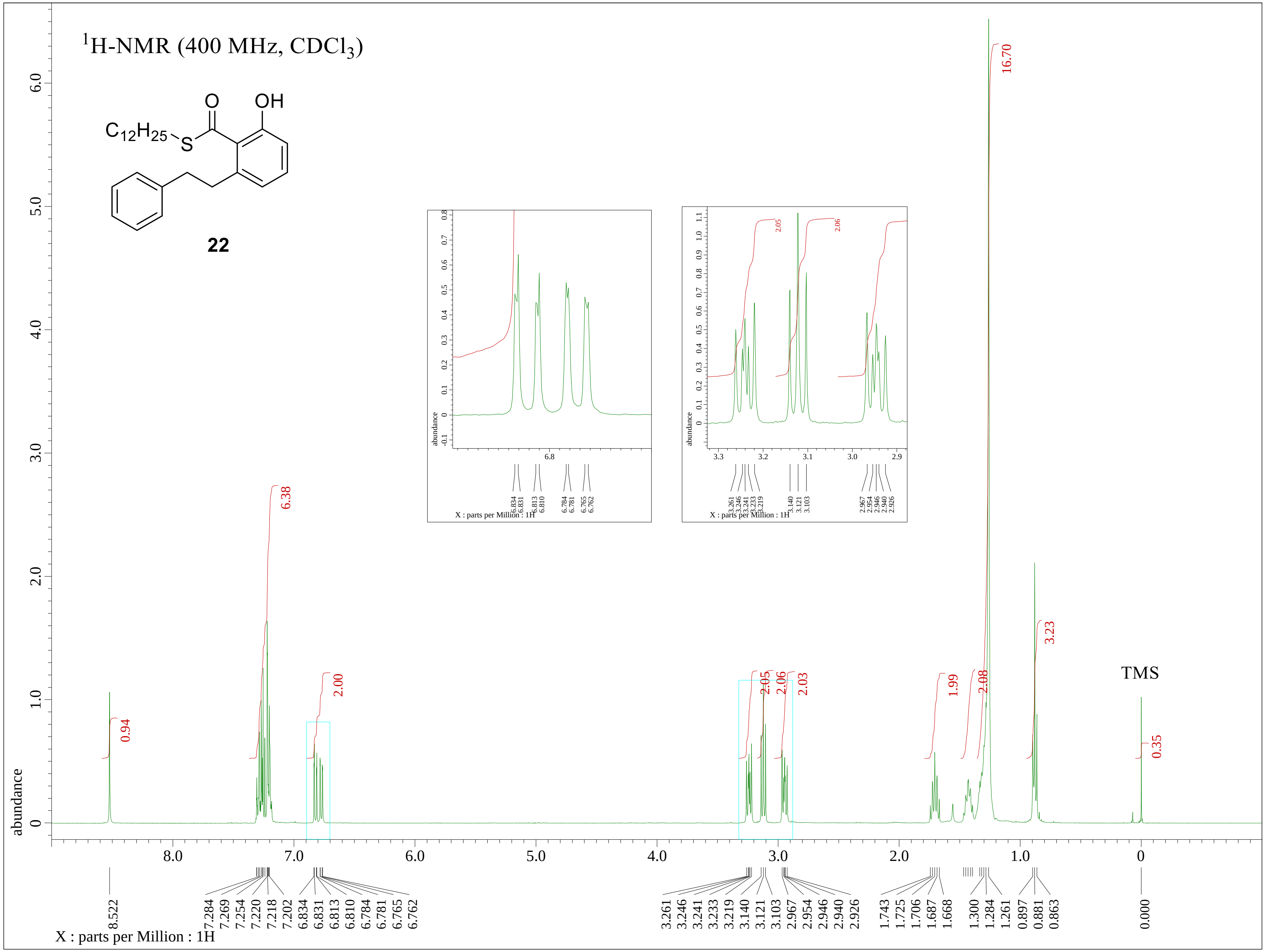
¹H-NMR (400 MHz, CDCl₃)
TBS
O
O
O
O
OH
20
abundance
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.48
4.02
1.00
1.06
2.04
1.01
4.05
0.30
3.68
9.29
6.01
0.38
long-chain
hydrocarbons
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.299
7.296
7.281
7.262
7.258
7.196
7.188
7.181
7.177
7.167
7.164
4.321
4.316
4.310
4.304
4.299
4.293
4.288
3.987
3.979
3.967
3.965
3.957
2.821
2.794
2.784
2.699
2.678
2.656
2.581
2.564
2.005
1.998
1.985
1.948
1.432
1.254
0.866
0.107
0.086
0.000
X : parts per Million : 1H
abundance
1.00
4.02
4.3
4.2
4.1
4.0
3.9
4.335
4.321
4.316
4.310
4.304
4.299
4.293
4.288
4.275
4.012
4.001
3.993
3.987
3.979
3.971
3.967
3.965
3.957
3.950
3.943
3.931
X : parts per Million : 1H
abundance
1.06
2.04
2.8
2.7
2.6
2.832
2.821
2.794
2.784
2.699
2.686
2.678
2.670
2.656
2.581
2.564
2.542
2.525
X : parts per Million : 1H


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O O
O
OH
20
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
175.940
141.826
128.410
128.296
125.836
109.694
77.315
77.000
76.685
66.054
64.939
64.681
44.010
42.761
39.634
29.899
25.694
17.857
-4.559
-5.016
X : parts per Million : 13C

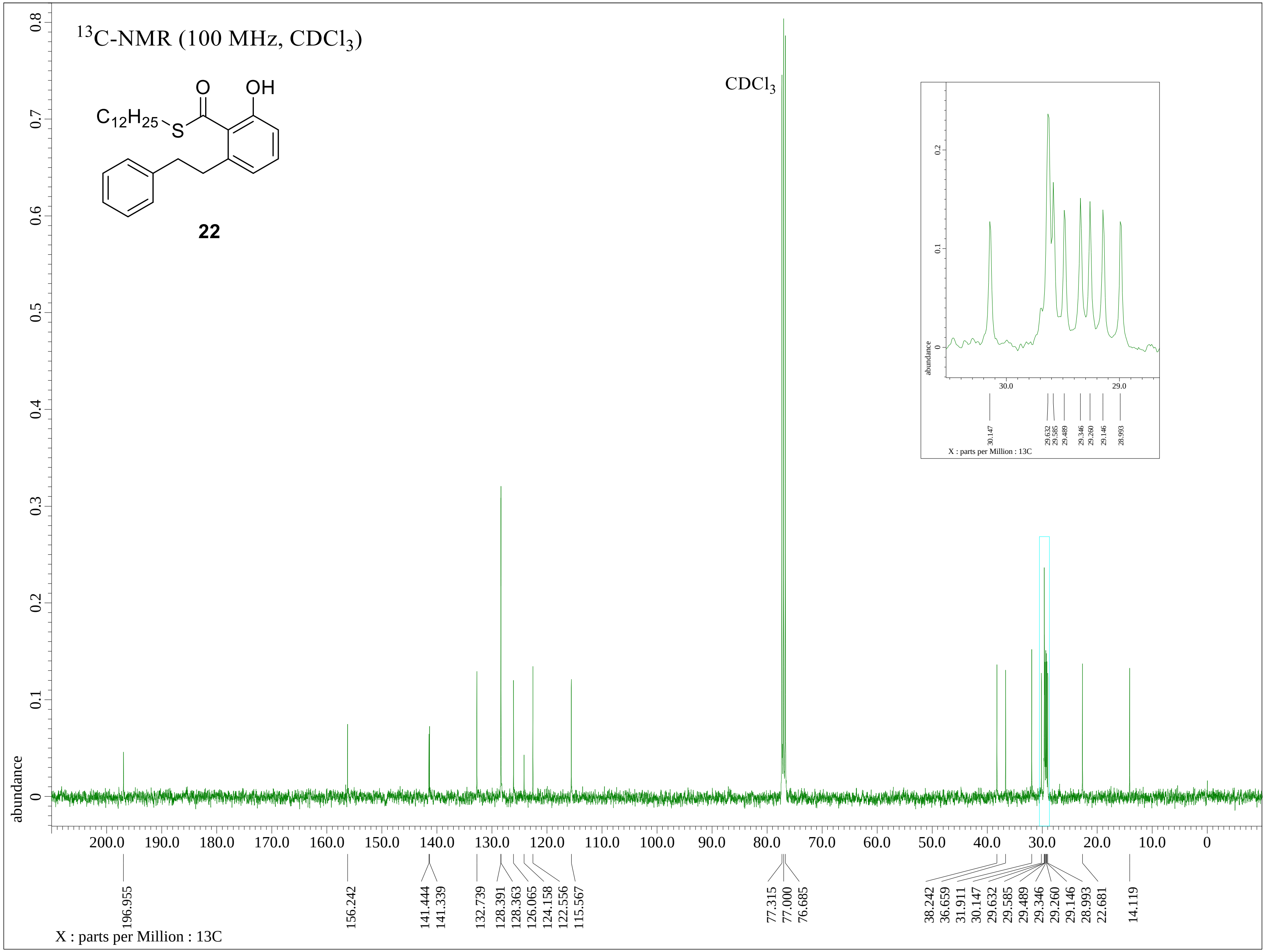


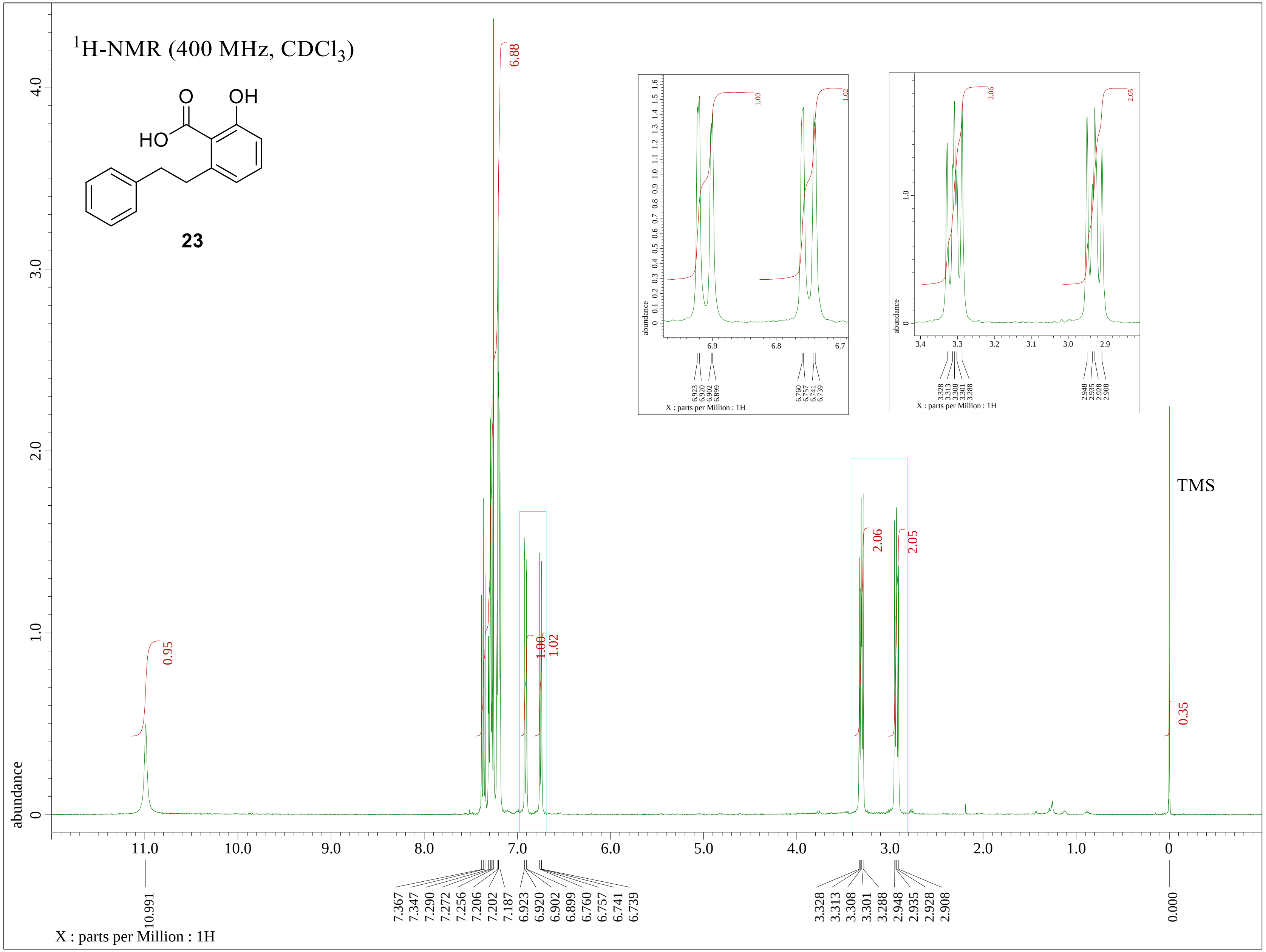
^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
OH
S
C$_{12}$H$_{25}$
21
5.14
0.34
0.64
0.36
3.97
1.28
2.65
2.96
0.33
3.92
2.16
18.67
12.22
1.95
2.96
1.09
7.292 7.288 7.283 7.272 7.261 7.253 7.193 7.174 7.159 7.155 7.151 7.148
5.455
4.385 4.373 4.361 4.355 4.212 3.981 3.952 3.668 3.663 3.627
2.923 2.904 2.885 2.688 2.669 2.645
2.173 2.152 1.936 1.927
1.591 1.575 1.280 1.253
0.896 0.879 0.861 0.840
0.080 0.049 0.044 0.000
abundance
X : parts per Million : 1H

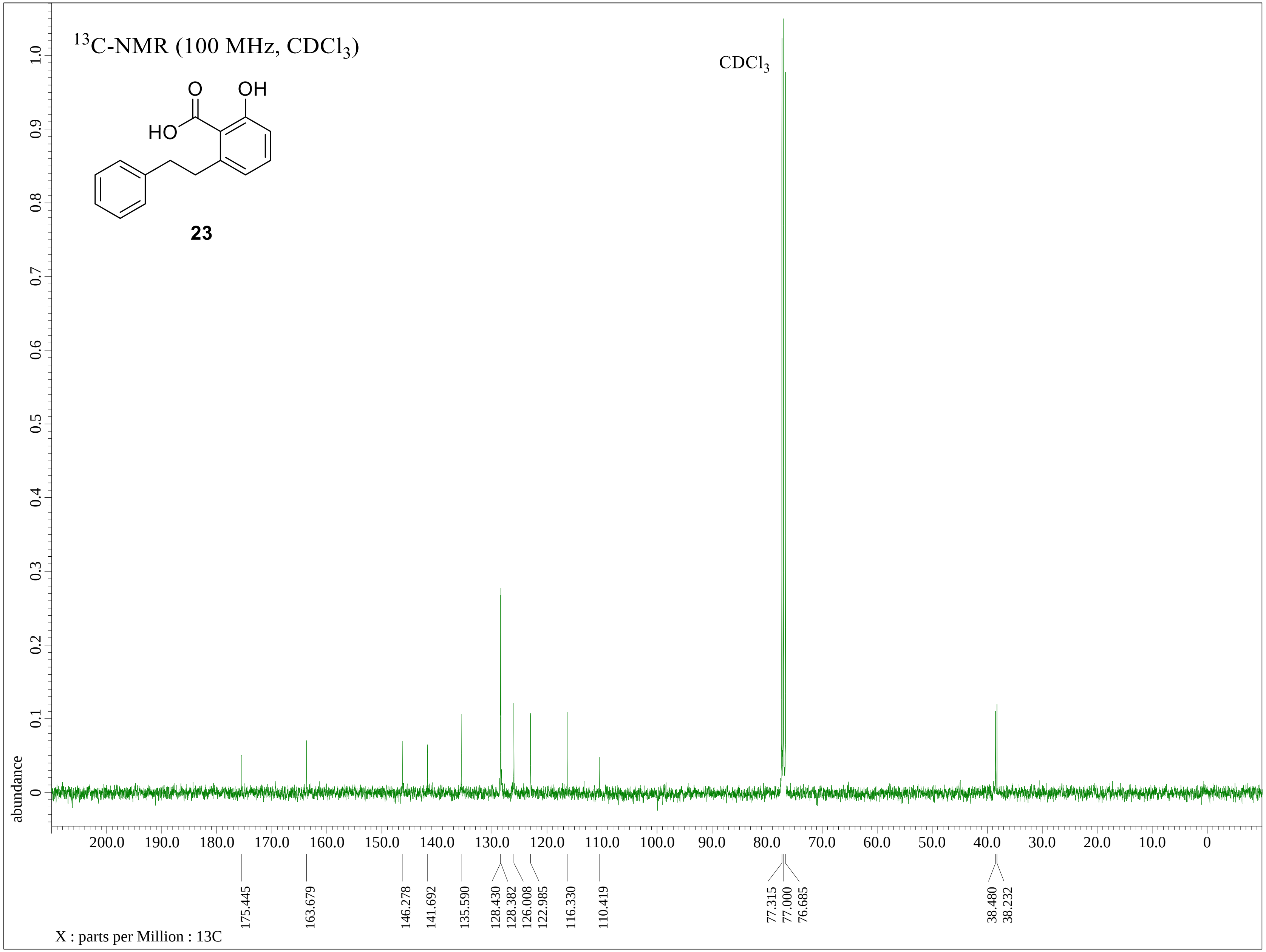

^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O O
O O
S
C$_{12}$H$_{25}$
OH
21
CDCl$_3$
abundance
X : parts per Million : 13C
201.007
194.504
191.863
173.623
141.950
128.334
128.286
125.741
109.971
109.932
101.666
77.315
77.000
76.676
65.320
64.872
64.662
58.894
51.209
44.916
44.182
39.891
39.710
31.882
29.594
29.546
29.318
25.799
17.914
17.867
14.100
-4.587
-4.654
-4.873
-5.064
29.880
29.680
29.594
29.546
29.480
29.442
29.318
29.251
29.117
29.060
28.793
28.745
65.320
64.986
64.872
64.739
64.662



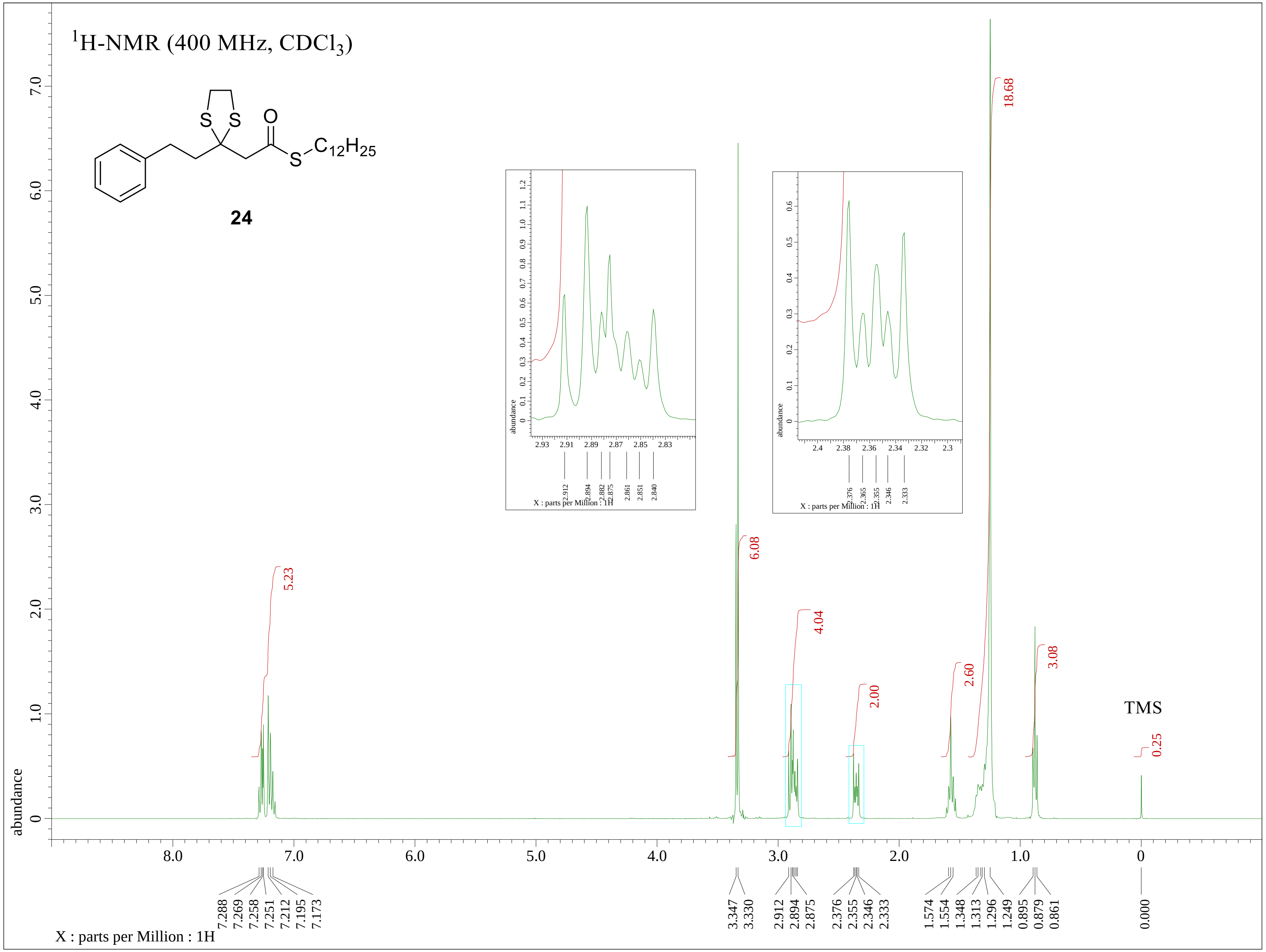
^{1}H-NMR (400 MHz, CDCl$_3$)
O
OH
C$_{12}$H$_{25}$
S
22
TMS
abundance
X : parts per Million : 1H
0.94
6.38
2.00
2.05
2.06
2.03
1.99
2.08
16.70
3.23
0.35
8.522
7.284
7.269
7.254
7.220
7.218
7.202
6.834
6.831
6.813
6.810
6.784
6.781
6.765
6.762
3.261
3.246
3.241
3.233
3.219
3.140
3.121
3.103
2.967
2.954
2.946
2.940
2.926
1.743
1.725
1.706
1.687
1.668
1.300
1.284
1.261
0.897
0.881
0.863
0.000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

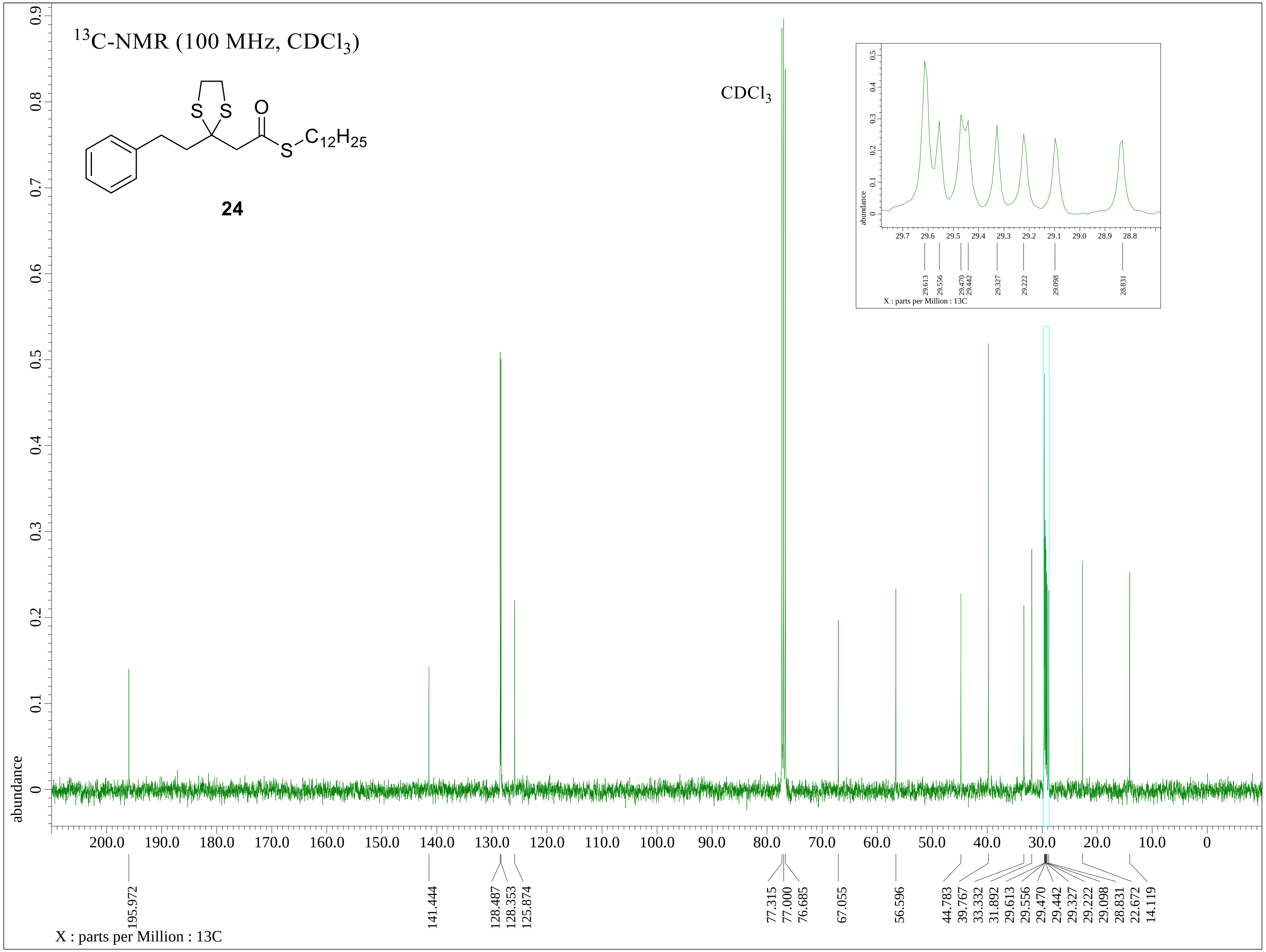

13C-NMR (100 MHz, CDCl3)
C12H25
S
O
OH
22
CDCl3
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : 13C
196.955
156.242
141.444
141.339
132.739
128.391
128.363
126.065
124.158
122.556
115.567
77.315
77.000
76.685
38.242
36.659
31.911
30.147
29.632
29.585
29.489
29.346
29.260
29.146
28.993
22.681
14.119
30.0
29.0
30.147
29.632
29.585
29.489
29.346
29.260
29.146
28.993
X : parts per Million : 13C

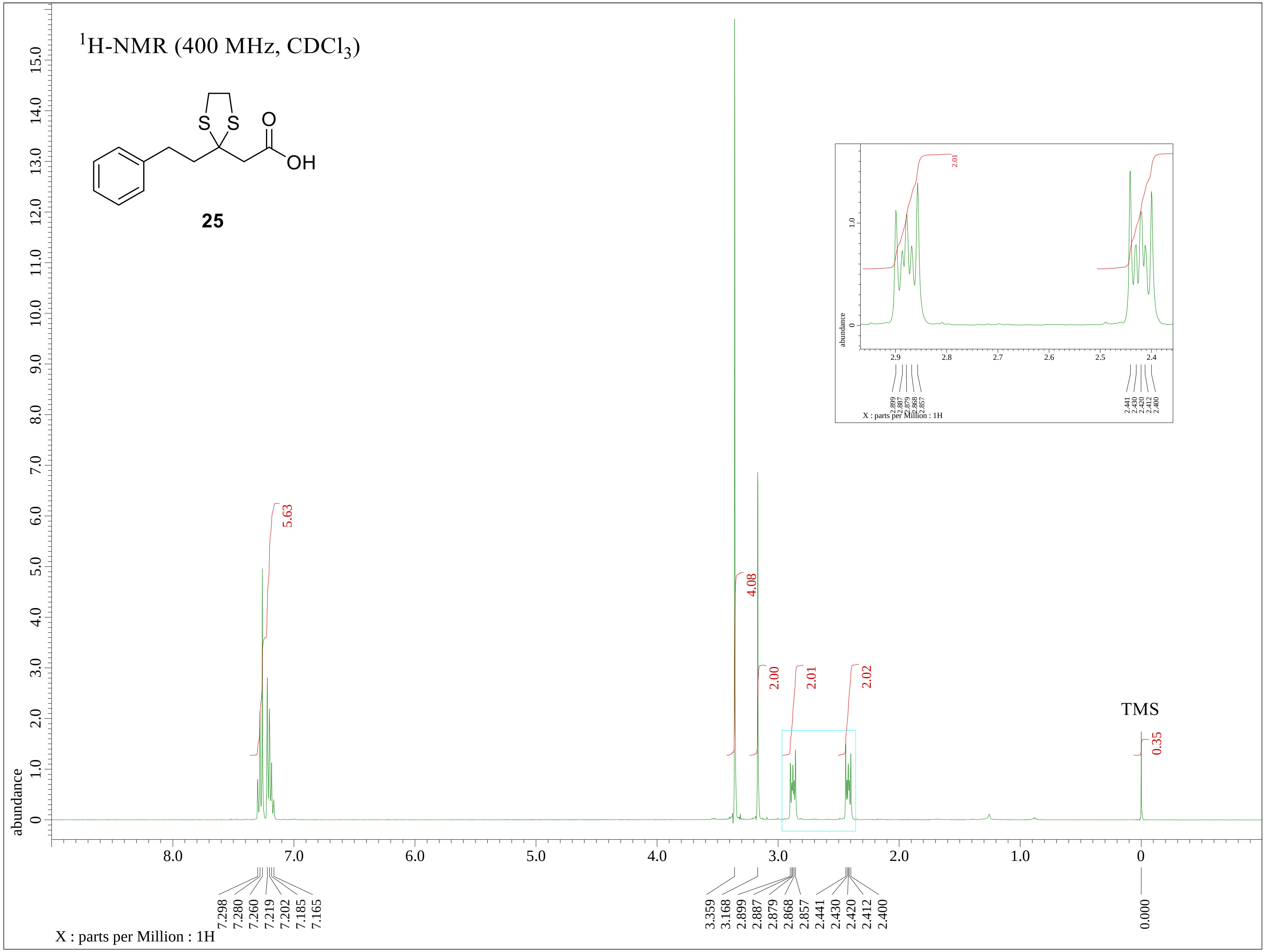

^{1}H-NMR (400 MHz, CDCl$_3$)
O
OH
HO
23
6.88
0.95
1.00
1.02
2.06
2.05
0.35
TMS
abundance
0
1.0
2.0
3.0
4.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.991
7.367
7.347
7.290
7.272
7.256
7.206
7.202
7.187
6.923
6.920
6.902
6.899
6.760
6.757
6.741
6.739
3.328
3.313
3.308
3.301
3.288
2.948
2.935
2.928
2.908
0.000
X : parts per Million : 1H
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
6.9
6.8
6.7
1.00
1.02
6.923
6.920
6.902
6.899
6.760
6.757
6.741
6.739
X : parts per Million : 1H
abundance
0
1.0
3.4
3.3
3.2
3.1
3.0
2.9
2.06
2.05
3.328
3.313
3.308
3.301
3.288
2.948
2.935
2.928
2.908
X : parts per Million : 1H

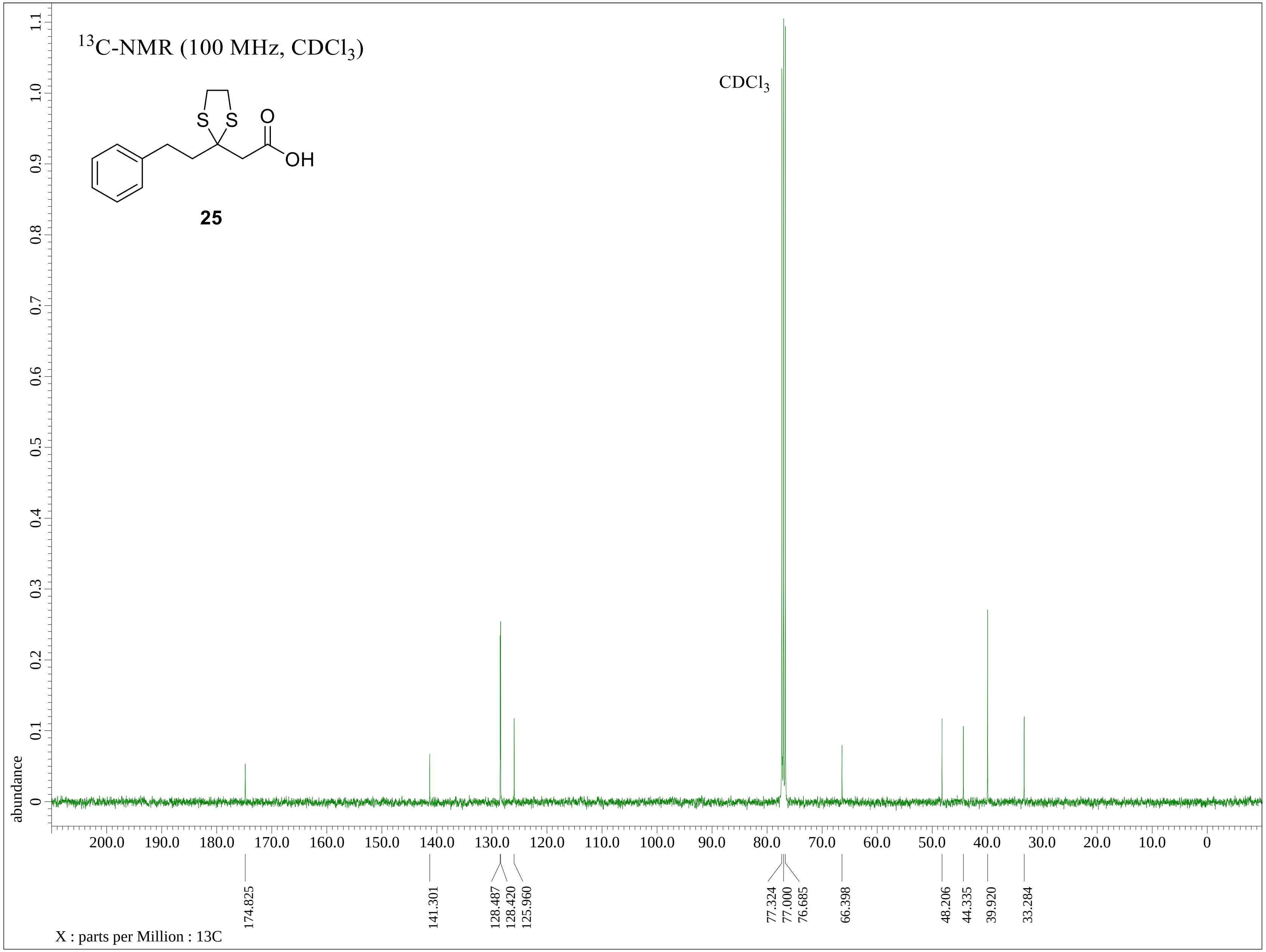


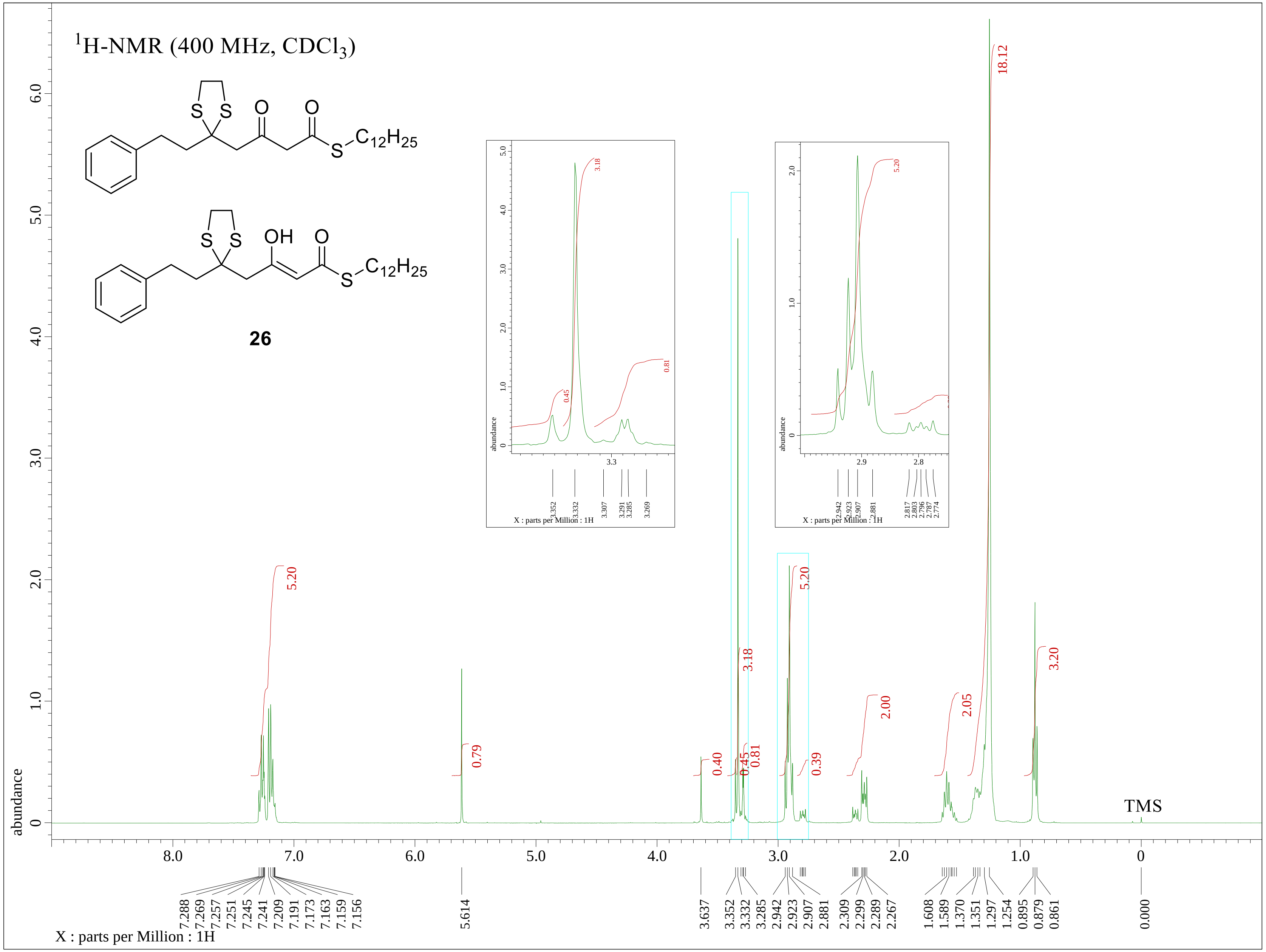
13C-NMR (100 MHz, CDCl3)
O
OH
HO
23
CDCl3
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
175.445
163.679
146.278
141.692
135.590
128.430
128.382
126.008
122.985
116.330
110.419
77.315
77.000
76.685
38.480
38.232
X : parts per Million : 13C

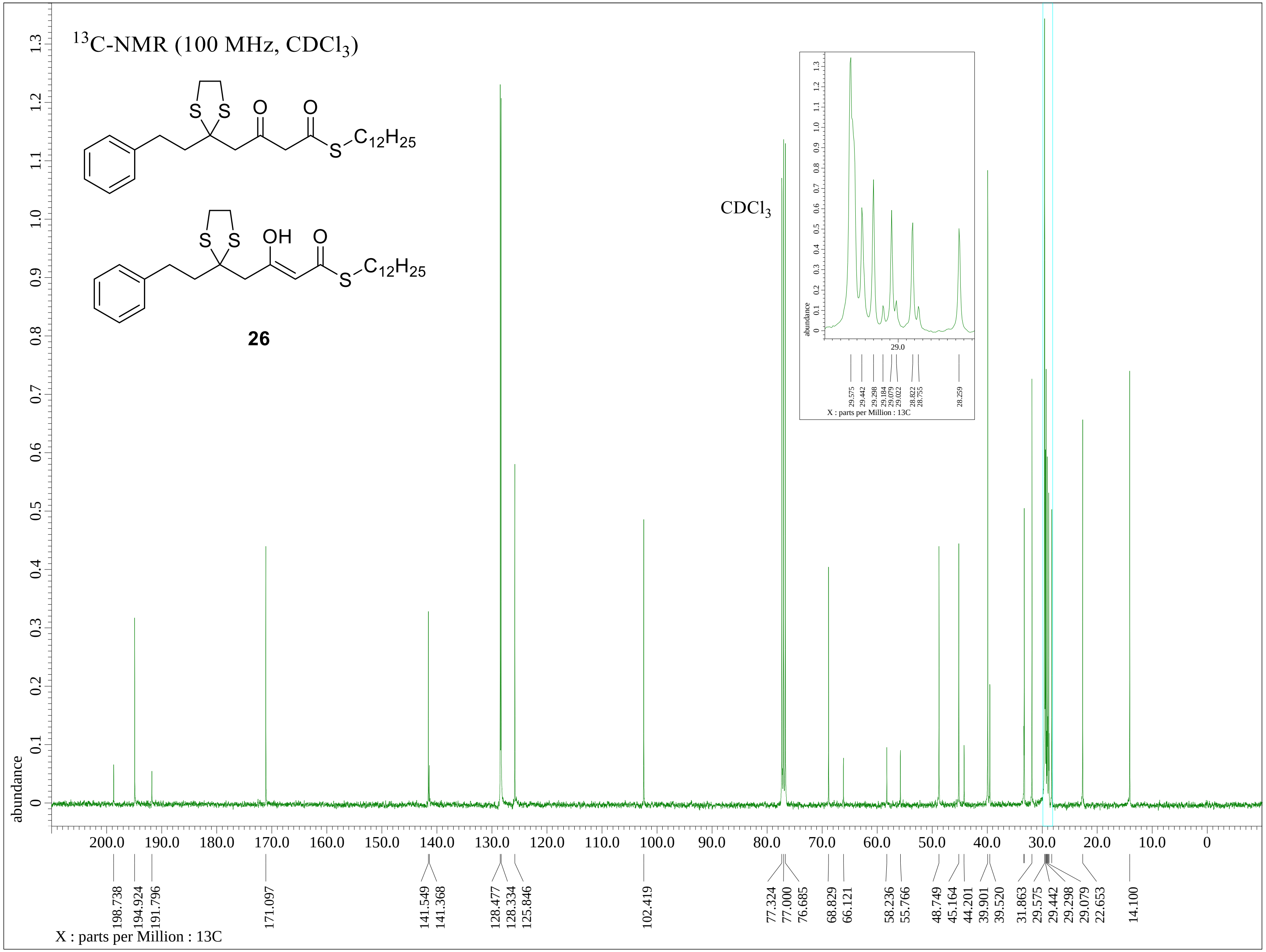

^{1}H-NMR (400 MHz, CDCl$_3$)
S
S
O
S
C$_{12}$H$_{25}$
24
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
5.23
6.08
4.04
2.00
2.60
18.68
3.08
0.25
TMS
7.288
7.269
7.258
7.251
7.212
7.195
7.173
3.347
3.330
2.912
2.894
2.875
2.376
2.355
2.346
2.333
1.574
1.554
1.348
1.313
1.296
1.249
0.895
0.879
0.861
0.000
2.93
2.91
2.89
2.87
2.85
2.83
2.912
2.894
2.882
2.875
2.861
2.851
2.840
2.4
2.38
2.36
2.34
2.32
2.3
2.376
2.365
2.355
2.346
2.333

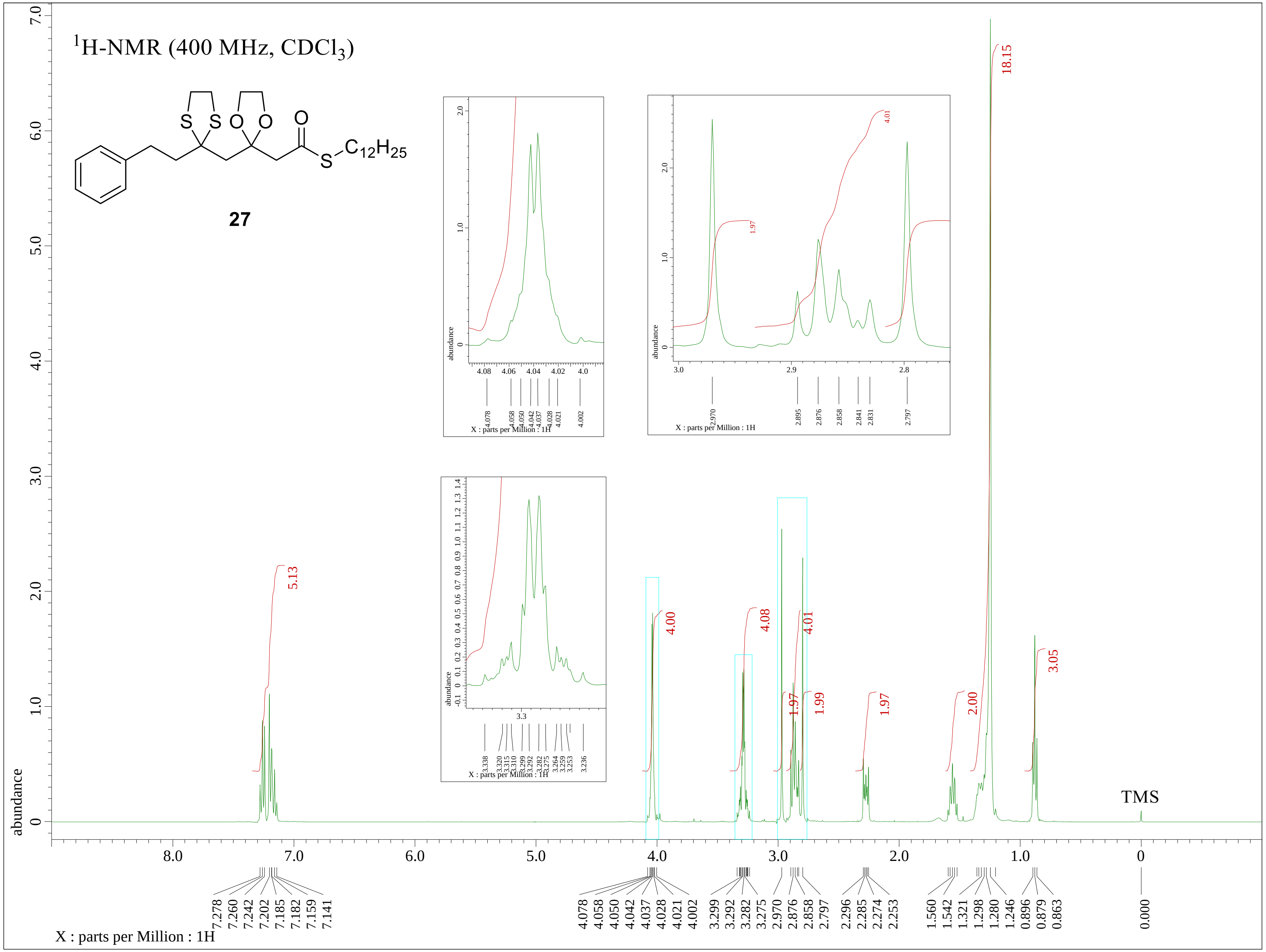

^{13}C-NMR (100 MHz, CDCl$_3$)
S
S
O
S
C$_{12}$H$_{25}$
24
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
195.972
141.444
128.487
128.353
125.874
77.315
77.000
76.685
67.055
56.596
44.783
39.767
33.332
31.892
29.613
29.556
29.470
29.442
29.327
29.222
29.098
28.831
22.672
14.119
X : parts per Million : 13C
abundance
0
0.1
0.2
0.3
0.4
0.5
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
29.613
29.556
29.470
29.442
29.327
29.222
29.098
28.831
X : parts per Million : 13C

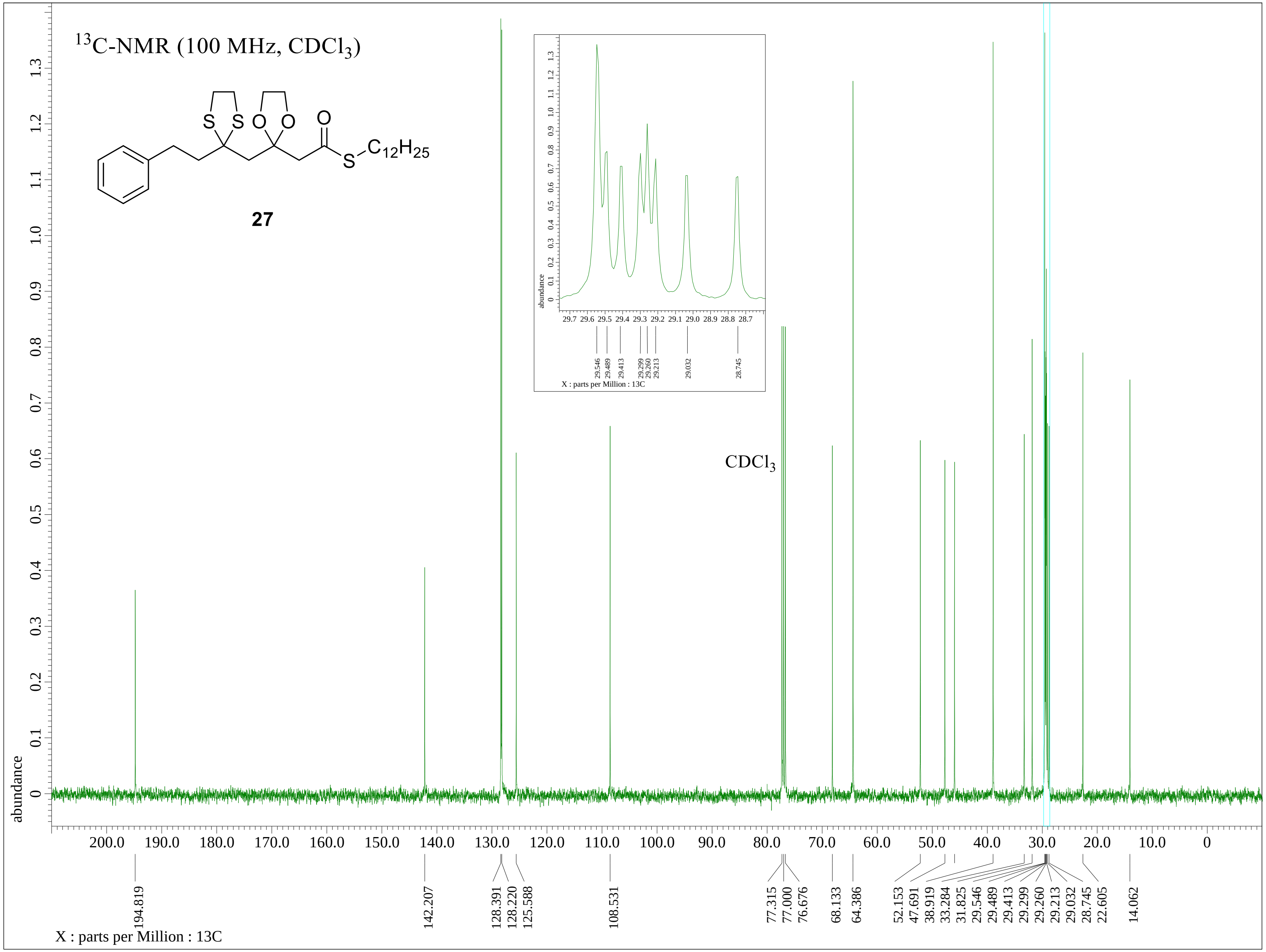

^{1}H-NMR (400 MHz, CDCl$_3$)
S
S
O
OH
25
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
5.63
4.08
2.00
2.01
2.02
0.35
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.298
7.280
7.260
7.219
7.202
7.185
7.165
3.359
3.168
2.899
2.887
2.879
2.868
2.857
2.441
2.430
2.420
2.412
2.400
0.000
X : parts per Million : 1H
2.01
1.0
0
abundance
2.9
2.8
2.7
2.6
2.5
2.4
2.899
2.887
2.879
2.868
2.857
2.441
2.430
2.420
2.412
2.400
X : parts per Million : 1H

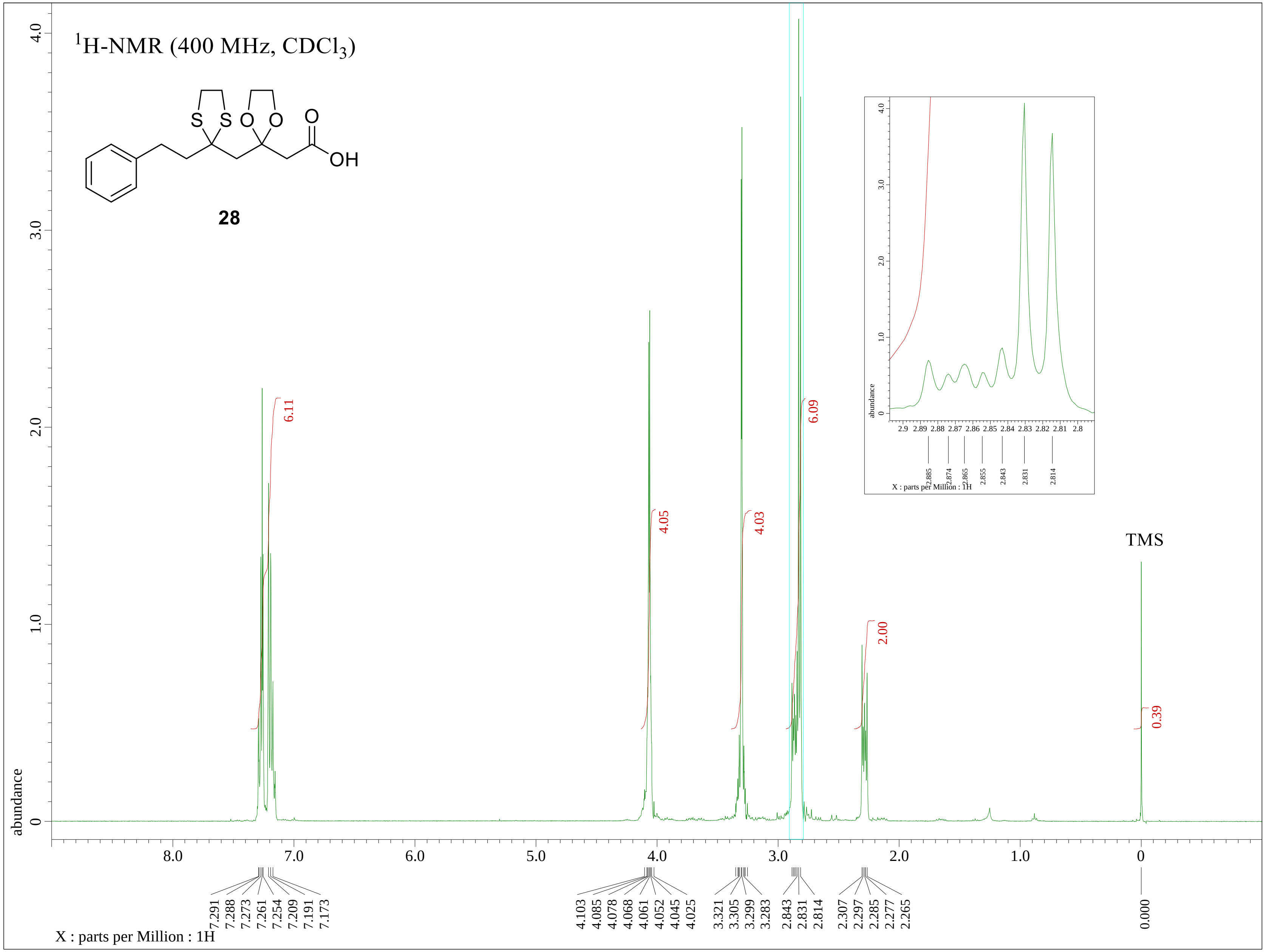

^{13}C-NMR (100 MHz, CDCl$_3$)
25
S
S
O
OH
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.825
141.301
128.487
128.420
125.960
77.324
77.000
76.685
66.398
48.206
44.335
39.920
33.284
X : parts per Million : 13C


^{1}H-NMR (400 MHz, CDCl$_3$)
S
S
O
O
S
C$_{12}$H$_{25}$
OH
26
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
TMS
5.20
0.79
0.40
0.45
3.18
0.81
5.20
0.39
2.00
2.05
18.12
3.20
7.288
7.269
7.257
7.251
7.245
7.241
7.209
7.191
7.173
7.163
7.159
7.156
5.614
3.637
3.352
3.332
3.285
2.942
2.923
2.907
2.881
2.309
2.299
2.289
2.267
1.608
1.589
1.370
1.351
1.297
1.254
0.895
0.879
0.861
0.000
3.3
3.307
3.291
3.269
2.9
2.8
2.817
2.803
2.796
2.787
2.774

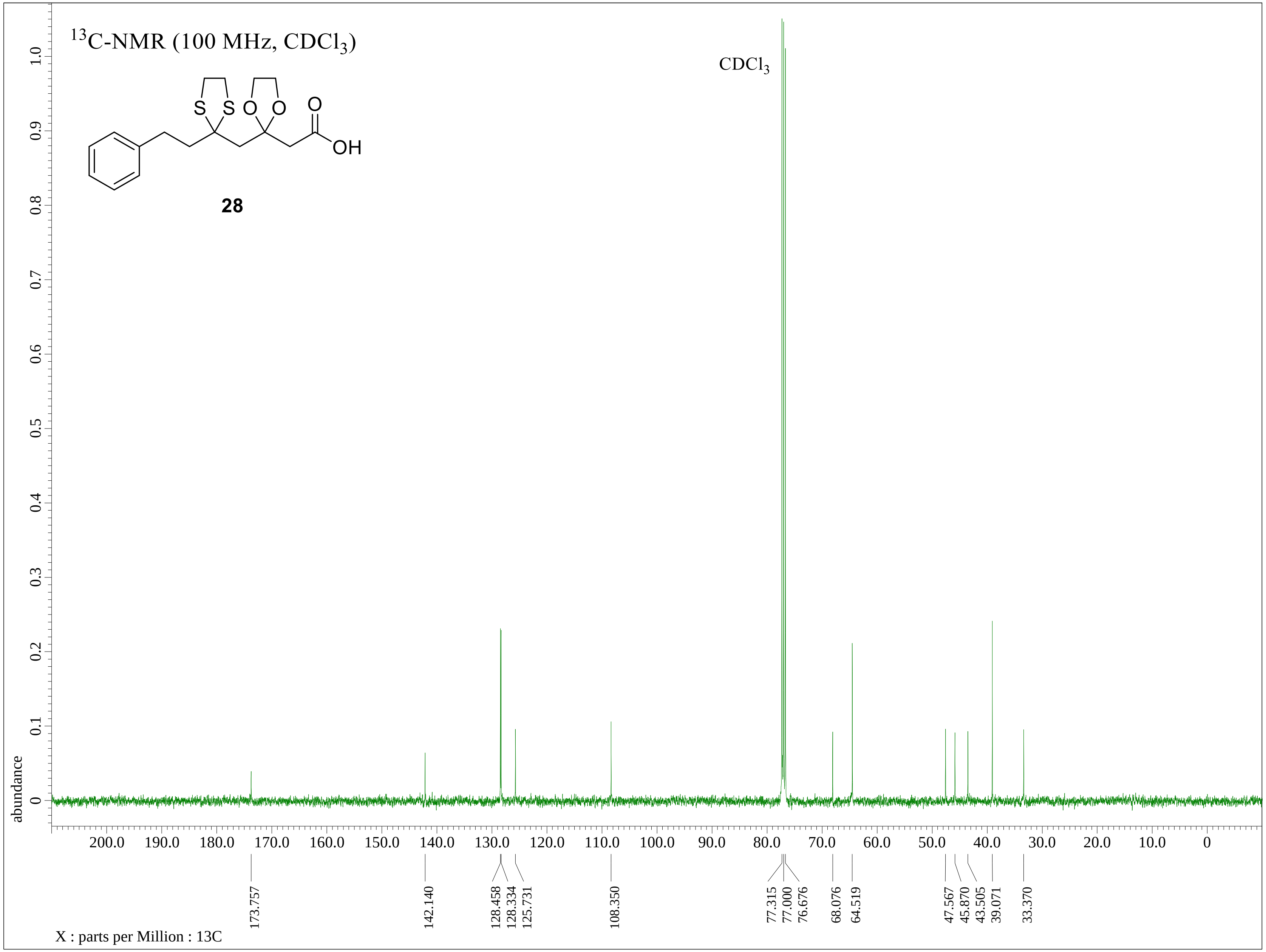

^{13}C-NMR (100 MHz, CDCl$_3$)
S S O O
S C12H25
S S OH O
S C12H25
26
CDCl3
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
198.738
194.924
191.796
171.097
141.549
141.368
128.477
128.334
125.846
102.419
77.324
77.000
76.685
68.829
66.121
58.236
55.766
48.749
45.164
44.201
39.901
39.520
31.863
29.575
29.442
29.298
29.079
22.653
14.100
X : parts per Million : 13C
29.0
29.575
29.442
29.298
29.184
29.079
29.022
28.822
28.755
28.259
X : parts per Million : 13C

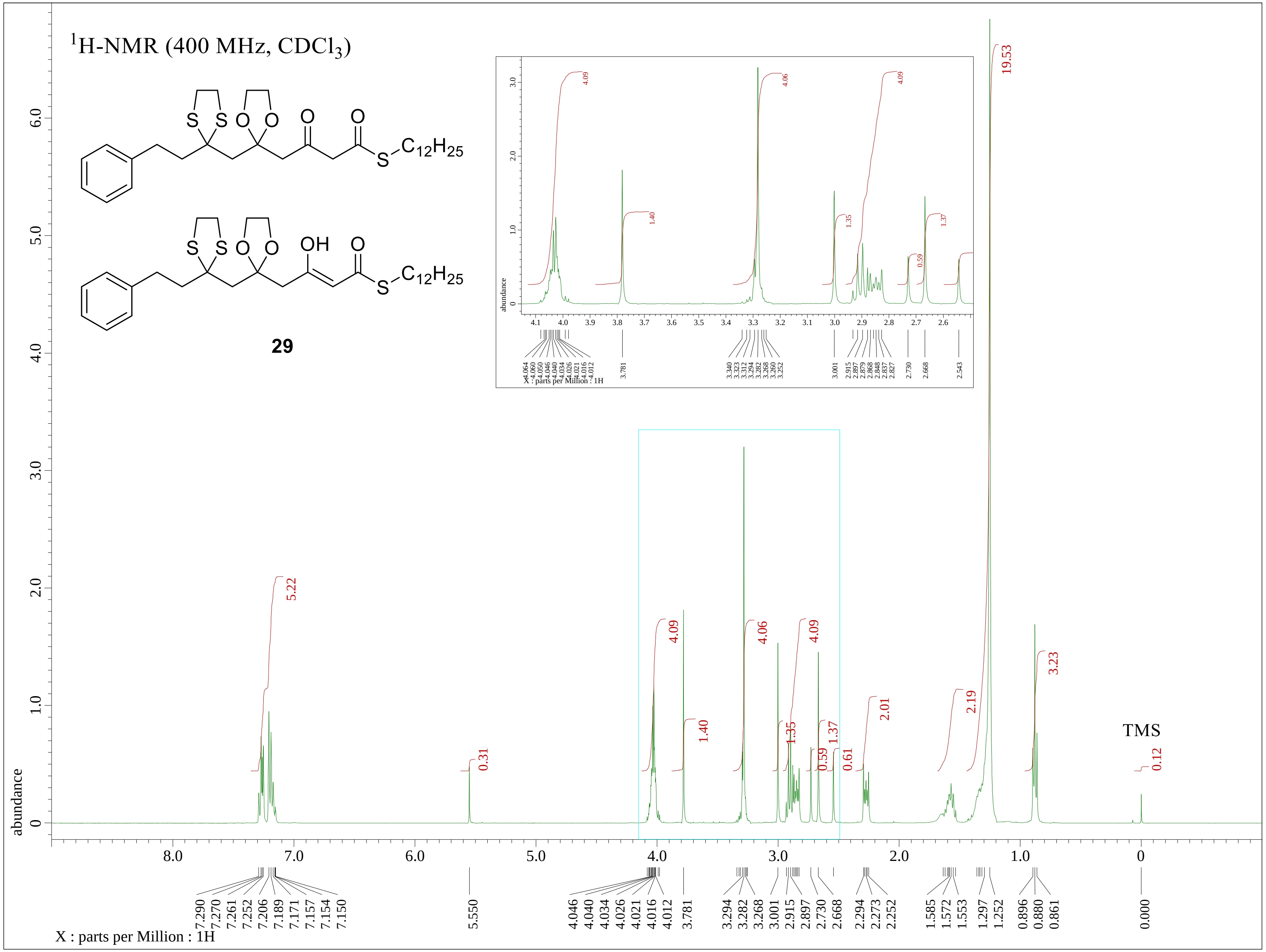

^{1}H-NMR (400 MHz, $CDCl_3$)
$C_{12}H_{25}$
S
S
O
O
O
S
27
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
TMS
5.13
4.00
4.08
4.01
1.97
1.99
1.97
2.00
18.15
3.05
7.278
7.260
7.242
7.202
7.185
7.182
7.159
7.141
4.078
4.058
4.050
4.042
4.037
4.028
4.021
4.002
3.299
3.292
3.282
3.275
2.970
2.876
2.858
2.797
2.296
2.285
2.274
2.253
1.560
1.542
1.321
1.298
1.280
1.246
0.896
0.879
0.863
0.000
3.338
3.320
3.315
3.310
3.299
3.292
3.282
3.275
3.264
3.259
3.253
3.236
2.970
2.895
2.876
2.858
2.841
2.831
2.797
1.97
4.01


^{13}C-NMR (100 MHz, $CDCl_3$)
S
S
O
O
O
S
$C_{12}H_{25}$
27
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
X : parts per Million : 13C
194.819
142.207
128.391
128.220
125.588
108.531
77.315
77.000
76.676
68.133
64.386
52.153
47.691
38.919
33.284
31.825
29.546
29.489
29.413
29.299
29.260
29.213
29.032
28.745
22.605
14.062
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.546
29.489
29.413
29.299
29.260
29.213
29.032
28.745

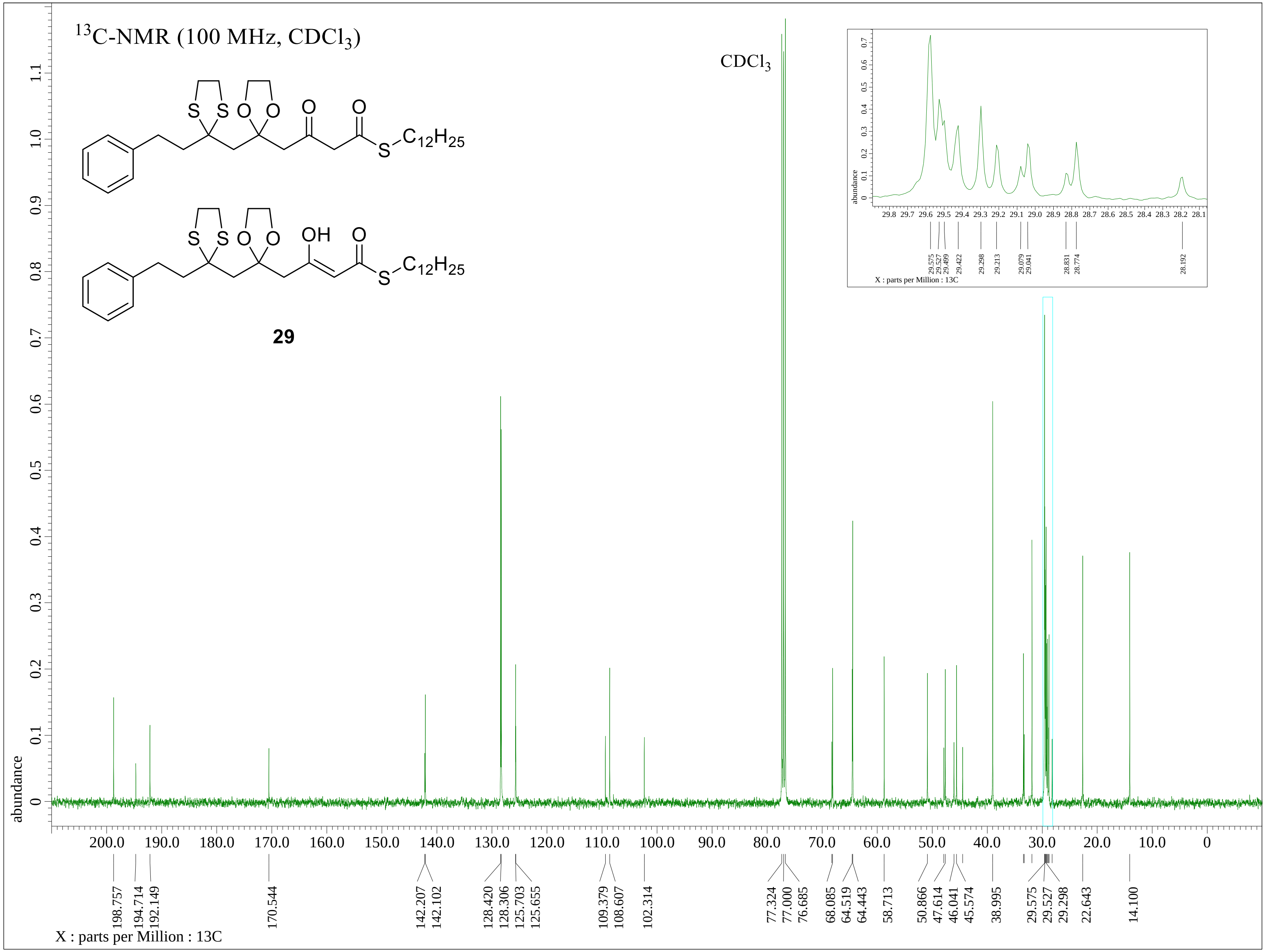


^{1}H-NMR (400 MHz, CDCl$_3$)
28
S
S
O
O
O
OH
TMS
6.11
4.05
4.03
6.09
2.00
0.39
abundance
0
1.0
2.0
3.0
4.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.291
7.288
7.273
7.261
7.254
7.209
7.191
7.173
4.103
4.085
4.078
4.068
4.061
4.052
4.045
4.025
3.321
3.305
3.299
3.283
2.843
2.831
2.814
2.307
2.297
2.285
2.277
2.265
0.000
X : parts per Million : 1H
2.9
2.89
2.88
2.87
2.86
2.85
2.84
2.83
2.82
2.81
2.8
2.885
2.874
2.865
2.855
2.843
2.831
2.814
X : parts per Million : 1H

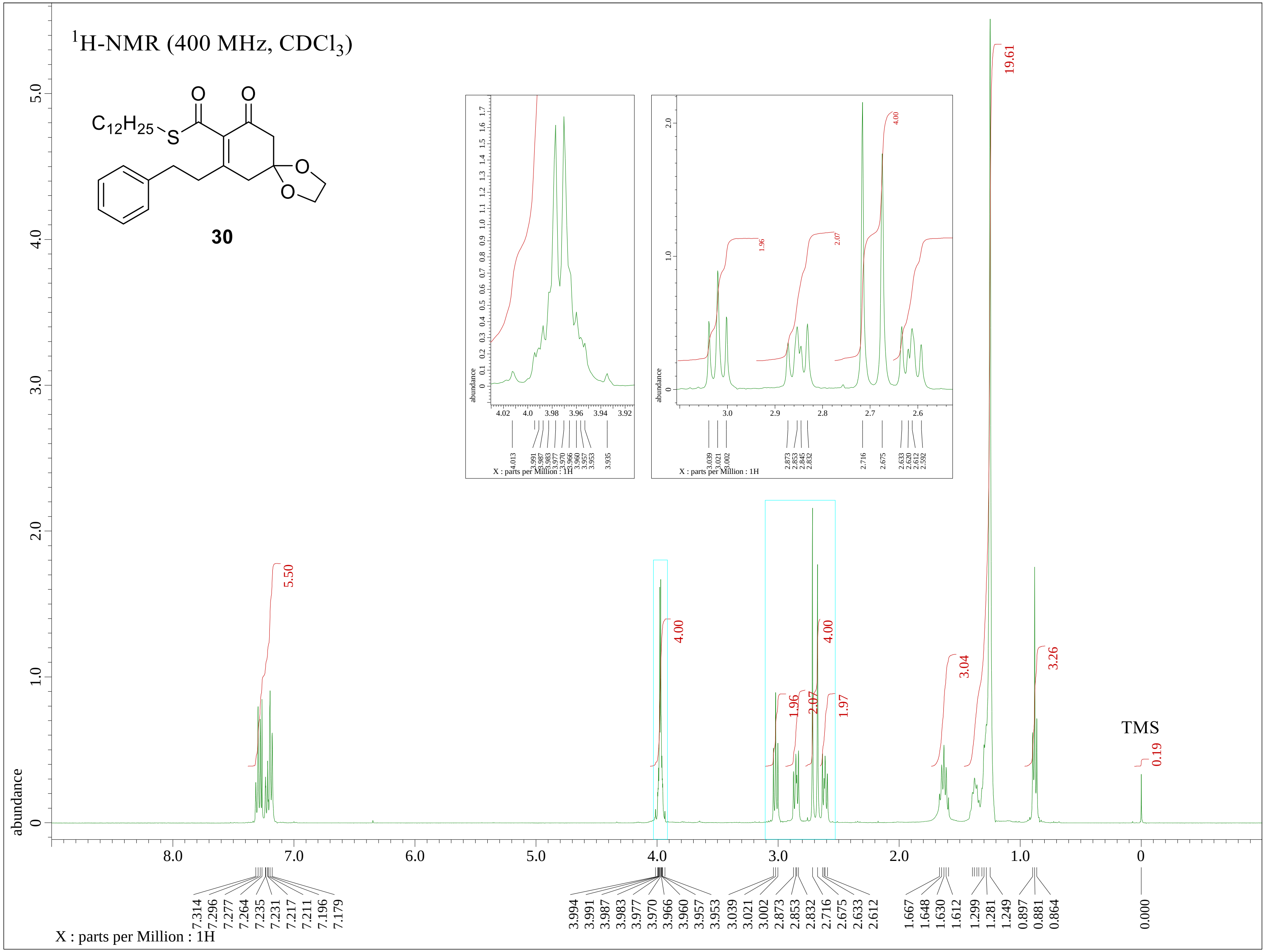

^{13}C-NMR (100 MHz, CDCl$_3$)
S
S
O
O
O
OH
28
CDCl$_3$
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.757
142.140
128.458
128.334
125.731
108.350
77.315
77.000
76.676
68.076
64.519
47.567
45.870
43.505
39.071
33.370
X : parts per Million : 13C



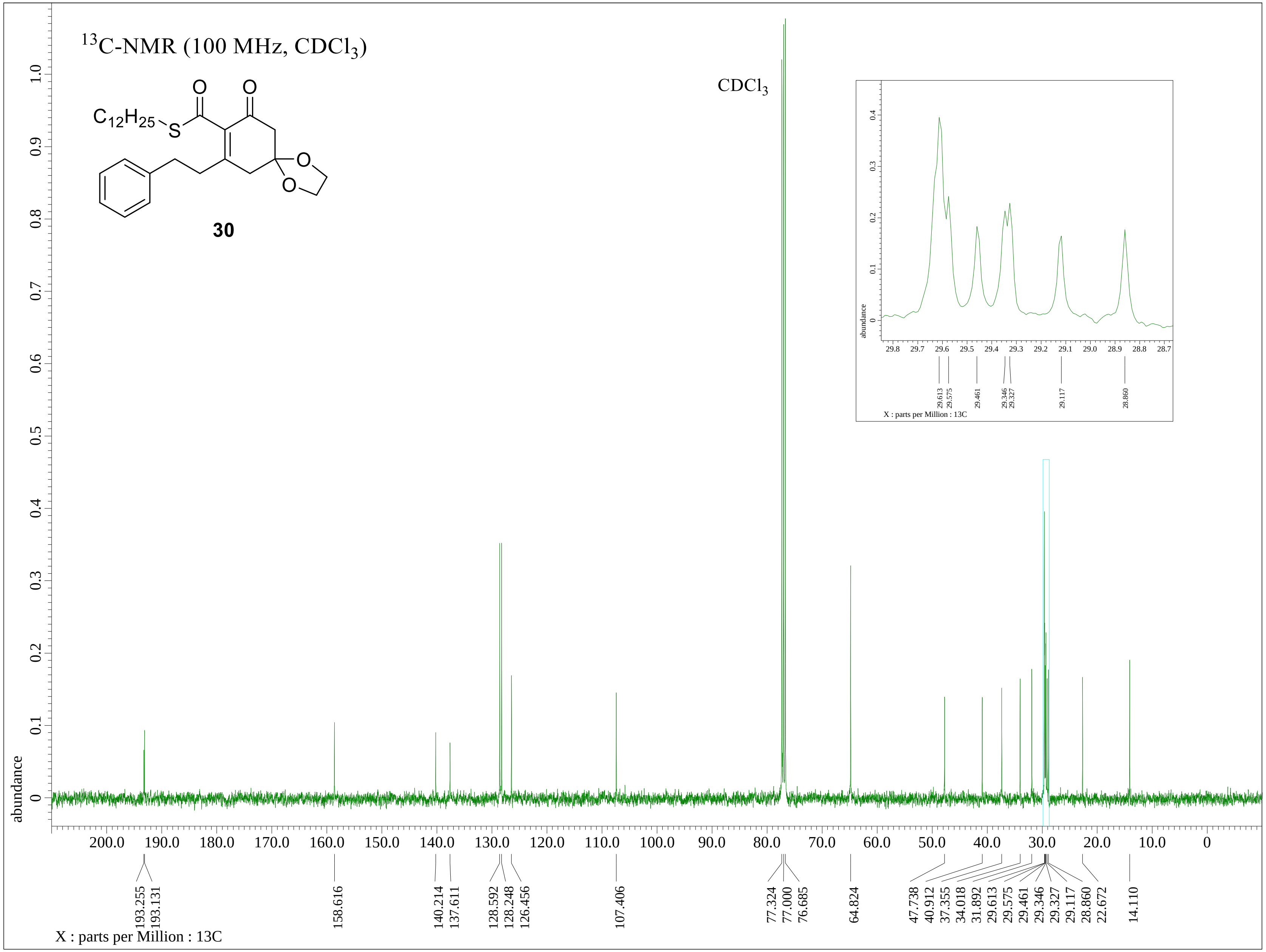
^{1}H-NMR (400 MHz, CDCl$_3$)
29
abundance
X : parts per Million : 1H
TMS
5.22
0.31
4.09
1.40
4.06
1.35
4.09
0.59
1.37
0.61
2.01
2.19
19.53
3.23
0.12
7.290
7.270
7.261
7.252
7.206
7.189
7.171
7.157
7.154
7.150
5.550
4.046
4.040
4.034
4.026
4.021
4.016
4.012
3.781
3.294
3.282
3.268
3.001
2.915
2.897
2.730
2.668
2.294
2.273
2.252
1.585
1.572
1.553
1.297
1.252
0.896
0.880
0.861
0.000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

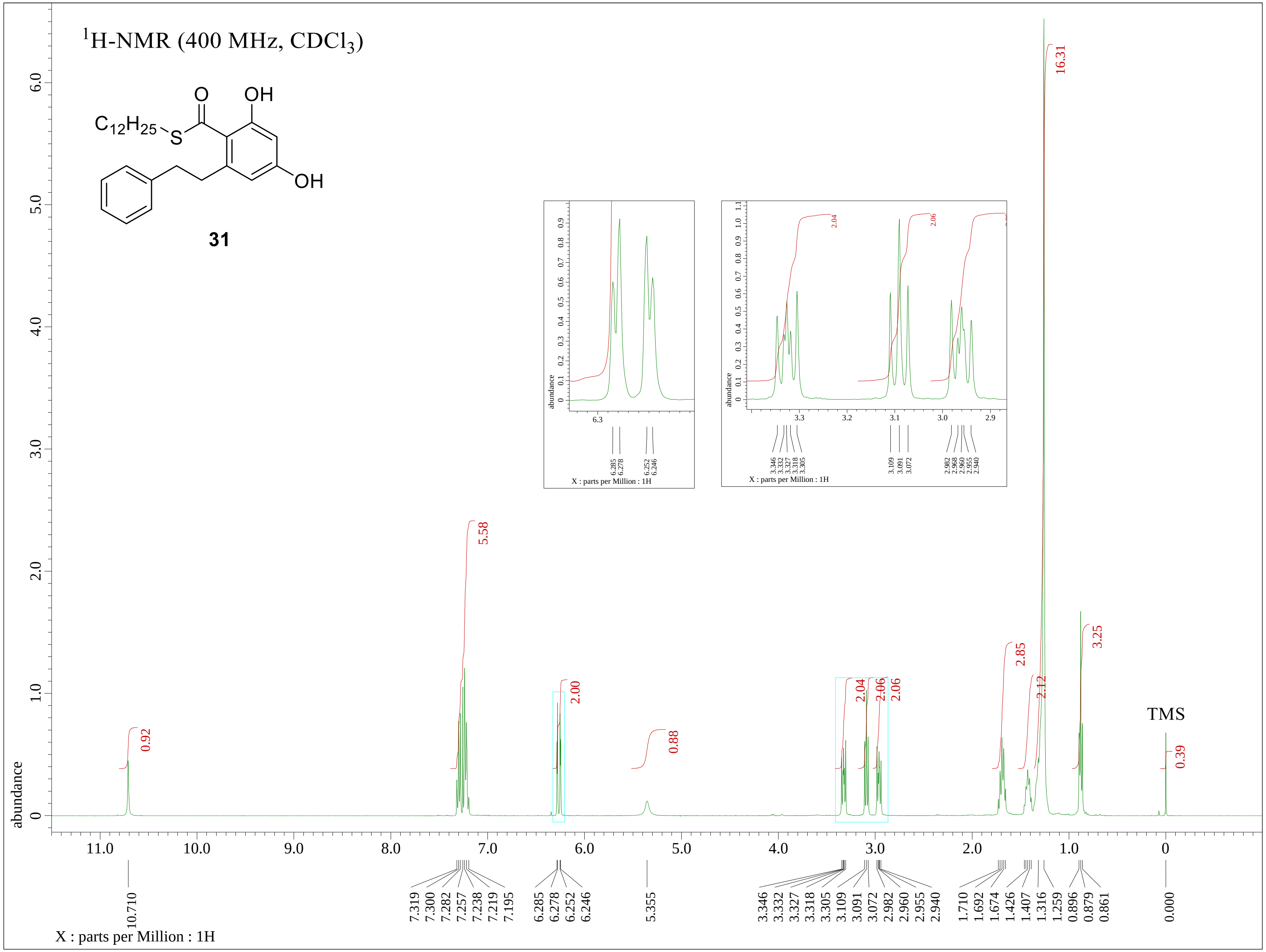


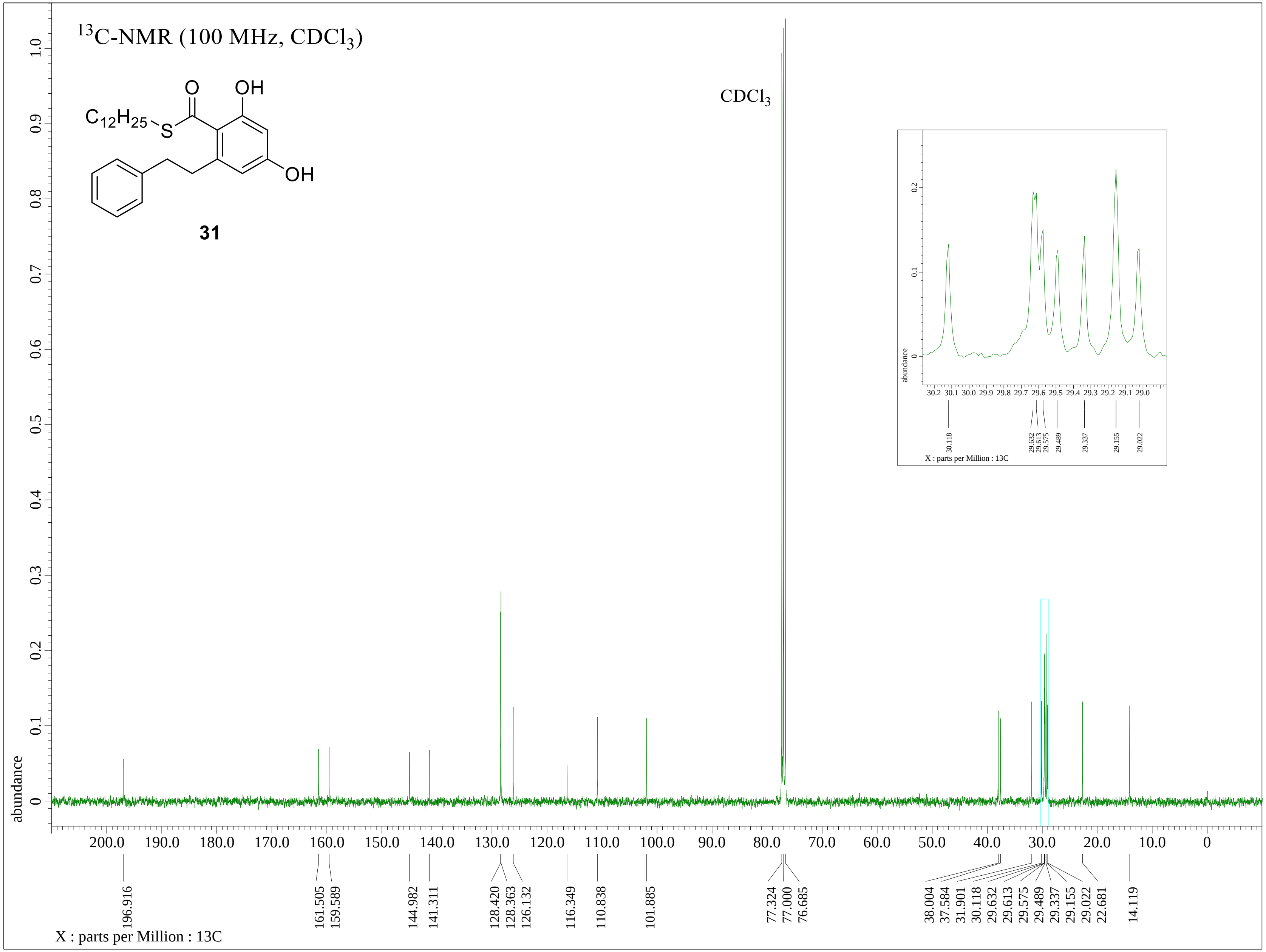
^{13}C-NMR (100 MHz, CDCl$_3$)
CDCl$_3$
S S O O O O
S C$_{12}$H$_{25}$
S S O O OH O
S C$_{12}$H$_{25}$
29
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
198.757
194.714
192.149
170.544
142.207
142.102
128.420
128.306
125.703
125.655
109.379
108.607
102.314
77.324
77.000
76.685
68.085
64.519
64.443
58.713
50.866
47.614
46.041
45.574
38.995
29.575
29.527
29.298
22.643
14.100
X : parts per Million : 13C
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
28.6
28.5
28.4
28.3
28.2
28.1
29.575
29.527
29.499
29.422
29.298
29.213
29.079
29.041
28.831
28.774
28.192
X : parts per Million : 13C

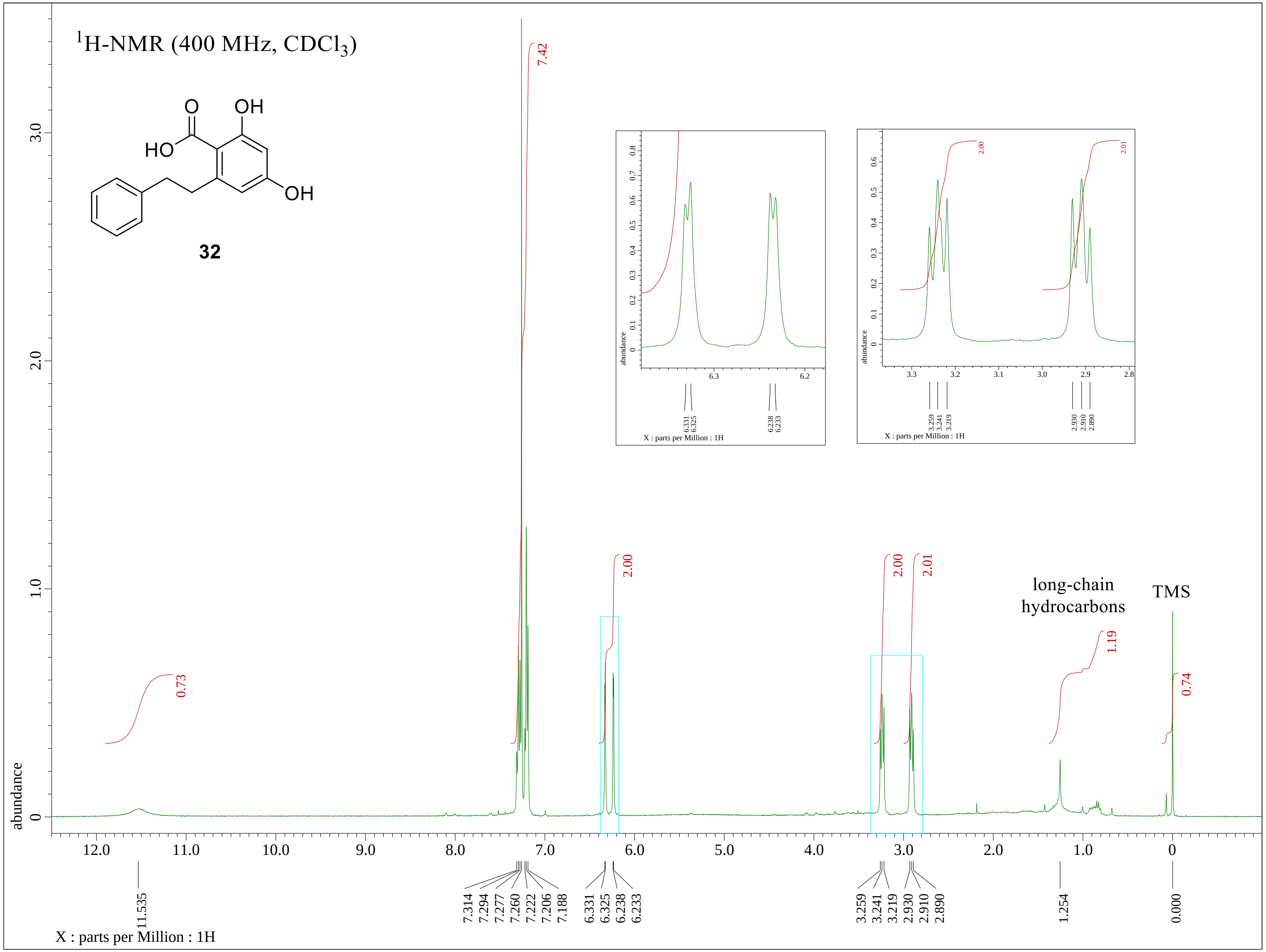


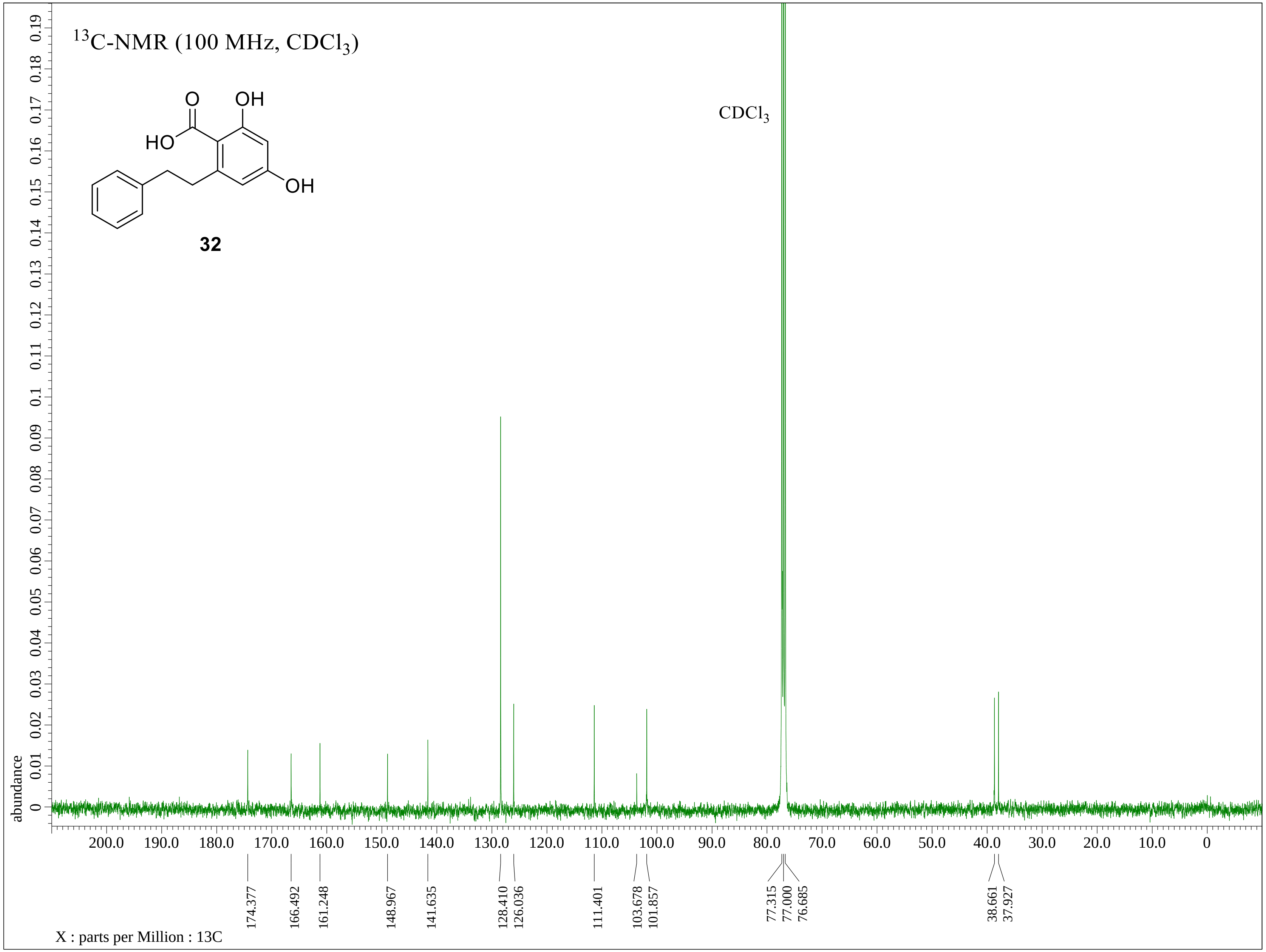
^{1}H-NMR (400 MHz, CDCl$_3$)
$C_{12}H_{25}$
S
O
O
O
O
30
abundance
0
1.0
2.0
3.0
4.0
5.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
5.50
4.00
1.96
2.07
4.00
1.97
3.04
19.61
3.26
0.19
TMS
7.314
7.296
7.277
7.264
7.235
7.231
7.217
7.211
7.196
7.179
3.994
3.991
3.987
3.983
3.977
3.970
3.966
3.960
3.957
3.953
3.039
3.021
3.002
2.873
2.853
2.832
2.716
2.675
2.633
2.612
1.667
1.648
1.630
1.612
1.299
1.281
1.249
0.897
0.881
0.864
0.000
4.013
3.991
3.987
3.983
3.977
3.970
3.966
3.960
3.957
3.953
3.935
3.039
3.021
3.002
2.873
2.853
2.845
2.832
2.716
2.675
2.633
2.620
2.612
2.592

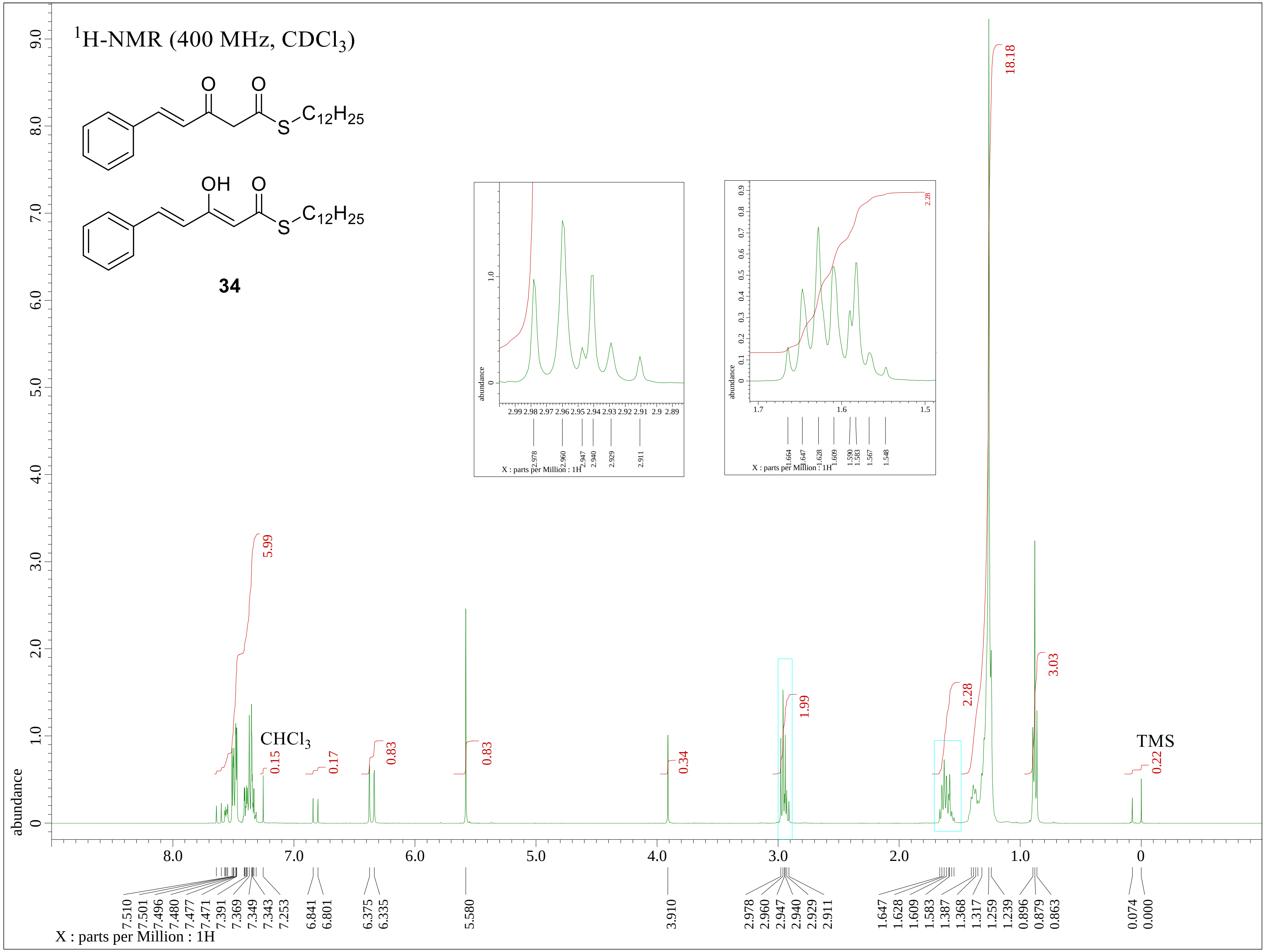

^{13}C-NMR (100 MHz, CDCl$_3$)
$C_{12}H_{25}$
S
O
O
O
O
30
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
193.255
193.131
158.616
140.214
137.611
128.592
128.248
126.456
107.406
77.324
77.000
76.685
64.824
47.738
40.912
37.355
34.018
31.892
29.613
29.575
29.461
29.346
29.327
29.117
28.860
22.672
14.110
X : parts per Million : 13C
abundance
0
0.1
0.2
0.3
0.4
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.613
29.575
29.461
29.346
29.327
29.117
28.860
X : parts per Million : 13C

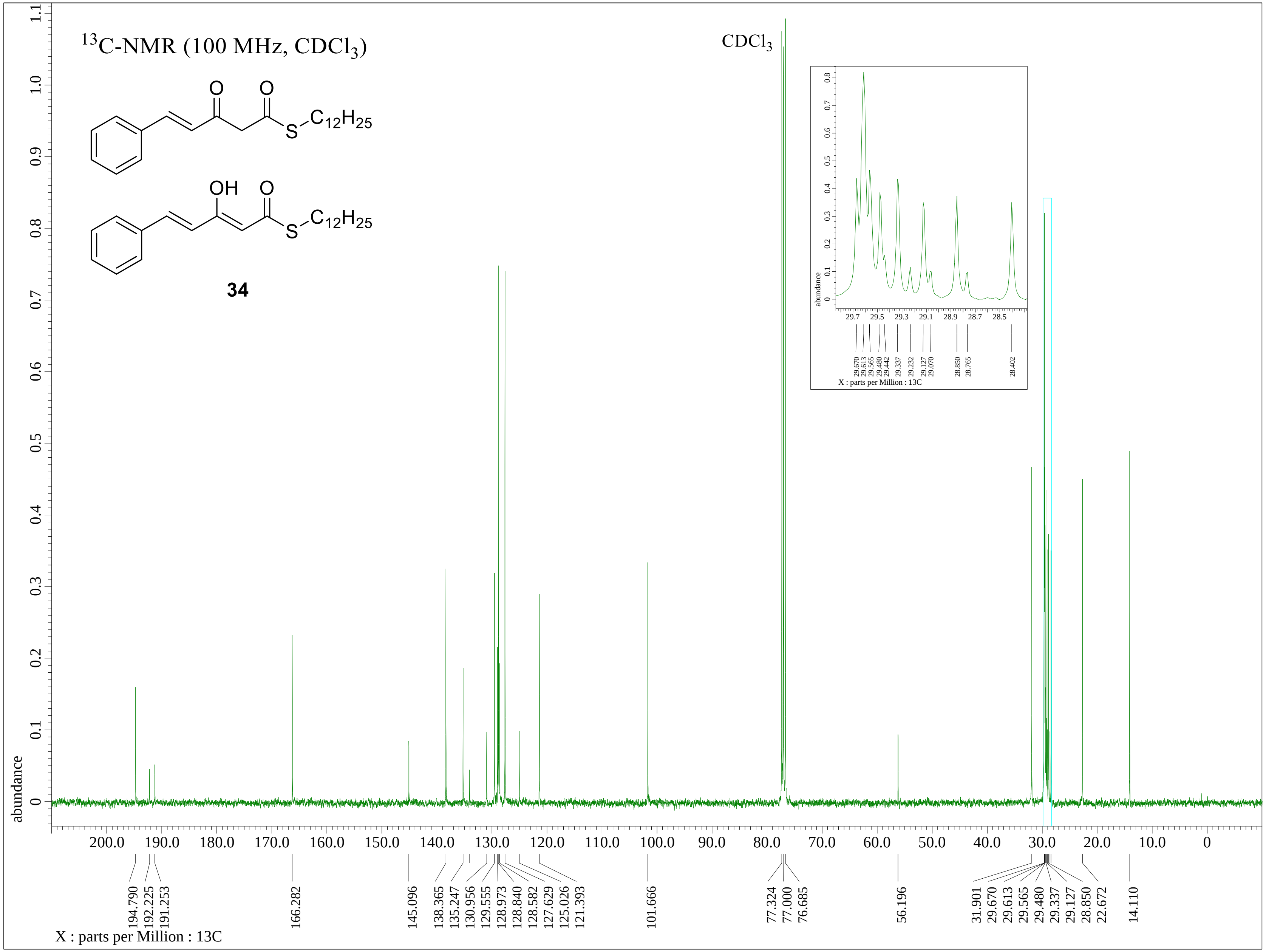

^{1}H-NMR (400 MHz, CDCl$_3$)
31
$C_{12}H_{25}$
S
O
OH
OH
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
0.92
5.58
2.00
0.88
2.04
2.06
2.06
2.85
2.12
16.31
3.25
0.39
TMS
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.710
7.319
7.300
7.282
7.257
7.238
7.219
7.195
6.285
6.278
6.252
6.246
5.355
3.346
3.332
3.327
3.318
3.305
3.109
3.091
3.072
2.982
2.960
2.955
2.940
1.710
1.692
1.674
1.426
1.407
1.316
1.259
0.896
0.879
0.861
0.000
X : parts per Million : 1H
6.3
2.968
3.3
3.2
3.1
3.0
2.9
X : parts per Million : 1H

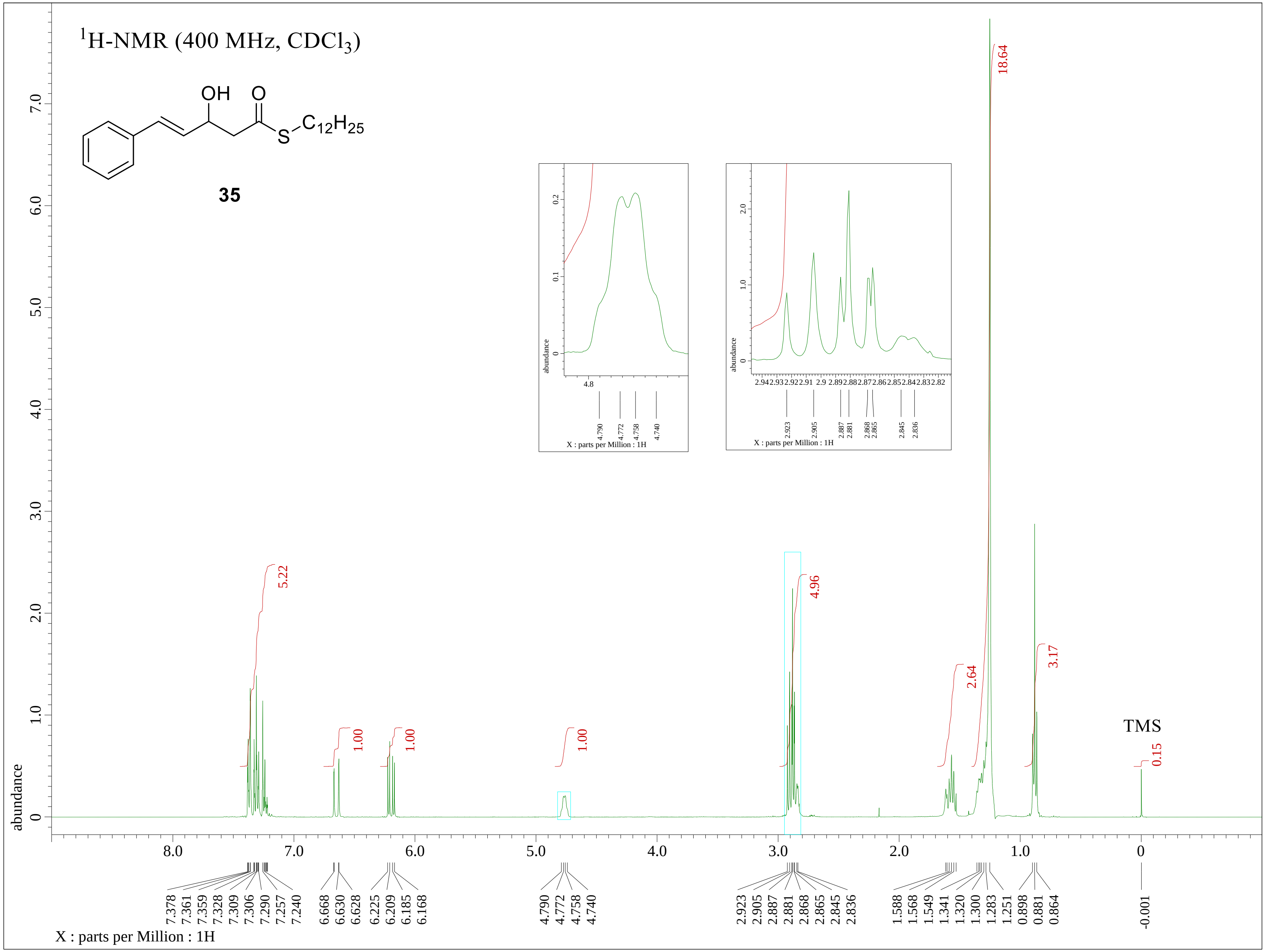
^{13}C-NMR (100 MHz, CDCl$_3$)
$C_{12}H_{25}$
S
O
OH
OH
31
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
196.916
161.505
159.589
144.982
141.311
128.420
128.363
126.132
116.349
110.838
101.885
77.324
77.000
76.685
38.004
37.584
31.901
30.118
29.632
29.613
29.575
29.489
29.337
29.155
29.022
22.681
14.119
X : parts per Million : 13C
abundance
0
0.1
0.2
30.2 30.1 30.0 29.9 29.8 29.7 29.6 29.5 29.4 29.3 29.2 29.1 29.0
30.118
29.632
29.613
29.575
29.489
29.337
29.155
29.022
X : parts per Million : 13C

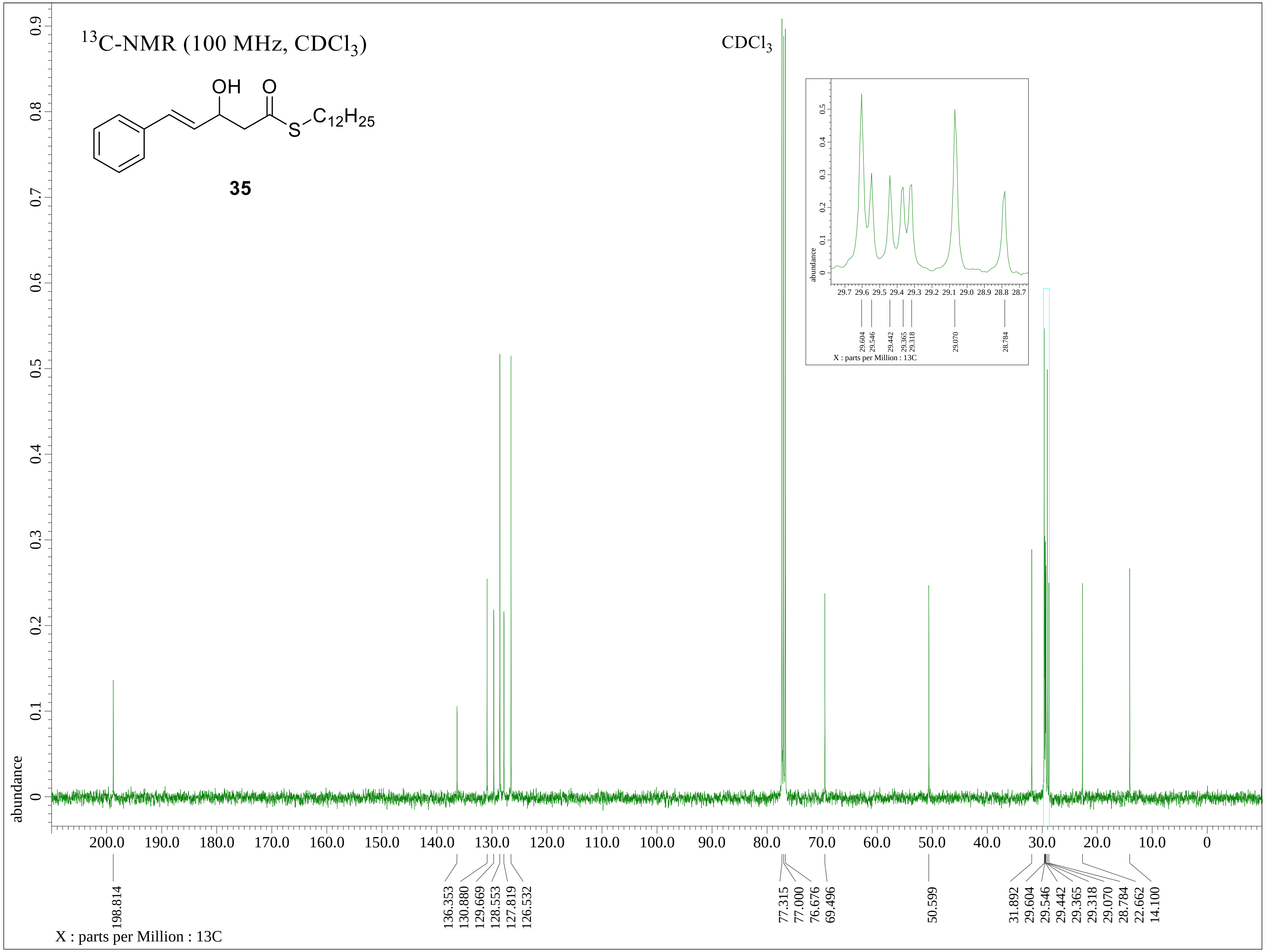

^{1}H-NMR (400 MHz, CDCl$_3$)
O
OH
HO
OH
32
7.42
2.00
2.00
2.01
0.73
1.19
0.74
long-chain hydrocarbons
TMS
abundance
0
1.0
2.0
3.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
11.535
7.314
7.294
7.277
7.260
7.222
7.206
7.188
6.331
6.325
6.238
6.233
3.259
3.241
3.219
2.930
2.910
2.890
1.254
0.000
X : parts per Million : 1H
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
6.3
6.2
6.331
6.325
6.238
6.233
X : parts per Million : 1H
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
2.00
2.01
3.3
3.2
3.1
3.0
2.9
2.8
3.259
3.241
3.219
2.930
2.910
2.890
X : parts per Million : 1H

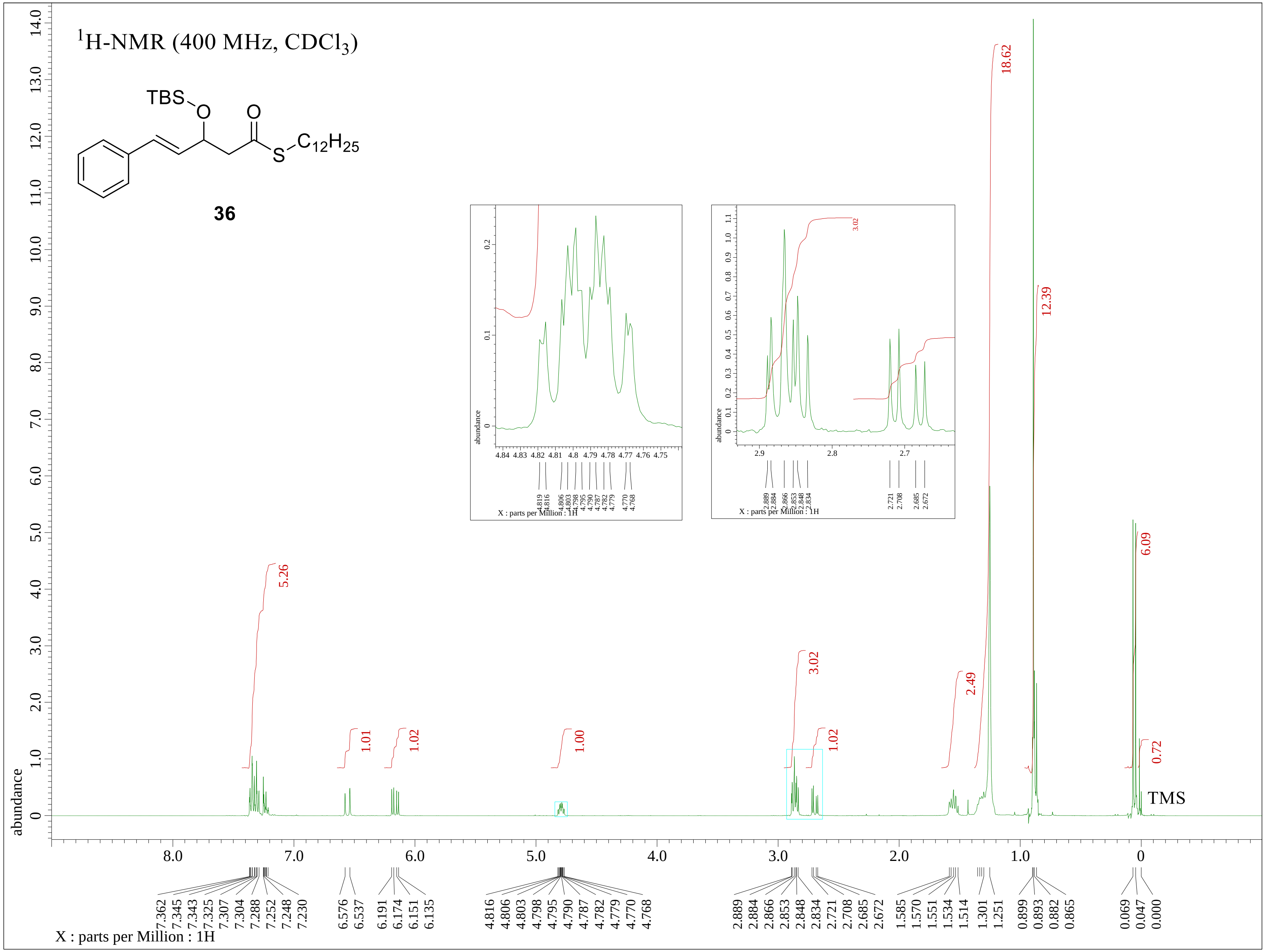

^{13}C-NMR (100 MHz, CDCl$_3$)
O
OH
HO
OH
32
CDCl$_3$
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.377
166.492
161.248
148.967
141.635
128.410
126.036
111.401
103.678
101.857
77.315
77.000
76.685
38.661
37.927
X : parts per Million : 13C

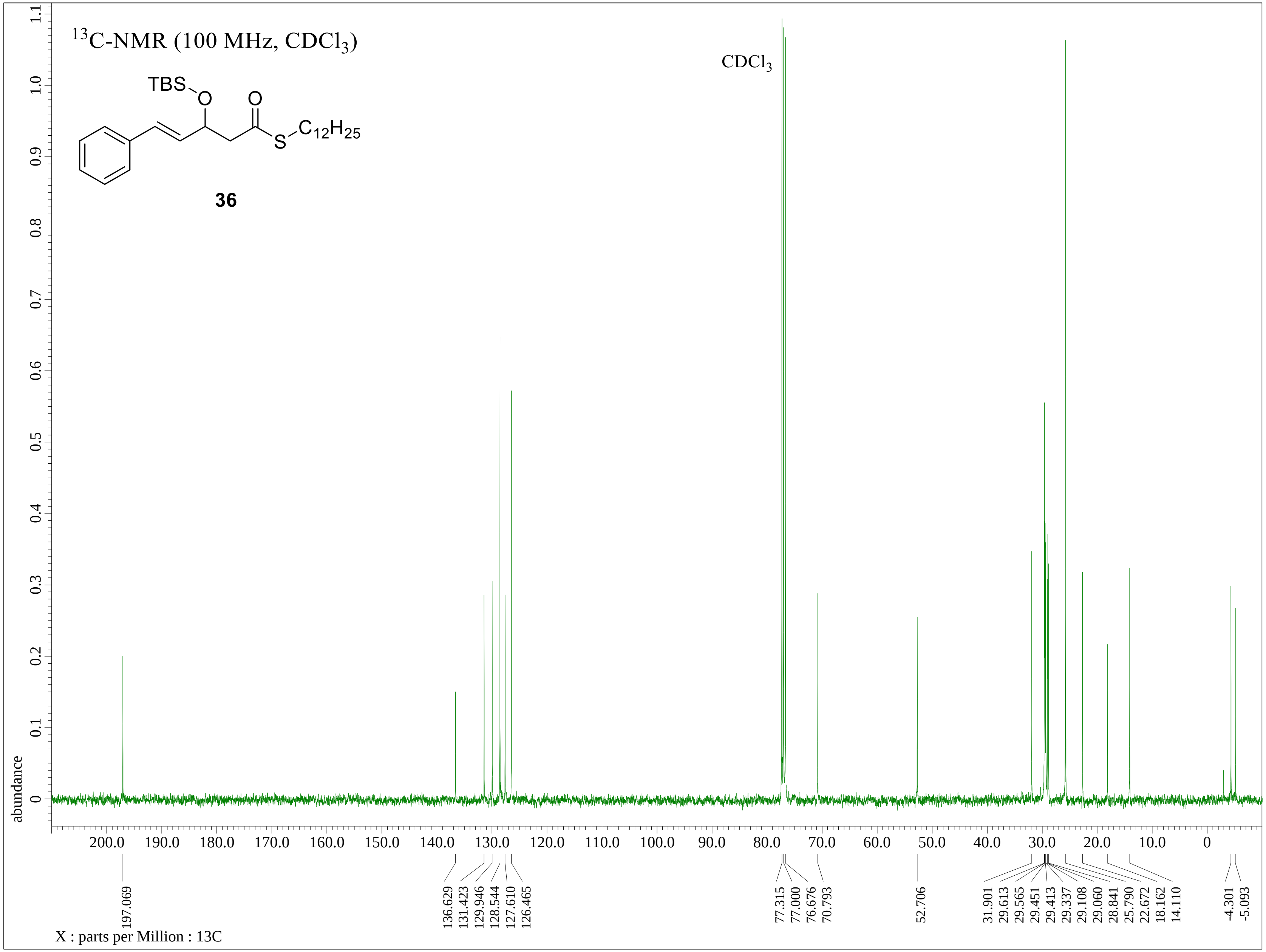

^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
S
C$_{12}$H$_{25}$
OH
O
S
C$_{12}$H$_{25}$
34
CHCl$_3$
TMS
5.99
0.15
0.17
0.83
0.83
0.34
1.99
2.28
18.18
3.03
0.22
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0
7.510
7.501
7.496
7.480
7.477
7.471
7.391
7.369
7.349
7.343
7.253
6.841
6.801
6.375
6.335
5.580
3.910
2.978
2.960
2.947
2.940
2.929
2.911
1.647
1.628
1.609
1.583
1.387
1.368
1.317
1.259
1.239
0.896
0.879
0.863
0.074
0.000
2.99
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.91
2.9
2.89
1.664
1.647
1.628
1.609
1.590
1.583
1.567
1.548
1.7
1.6
1.5
2.28

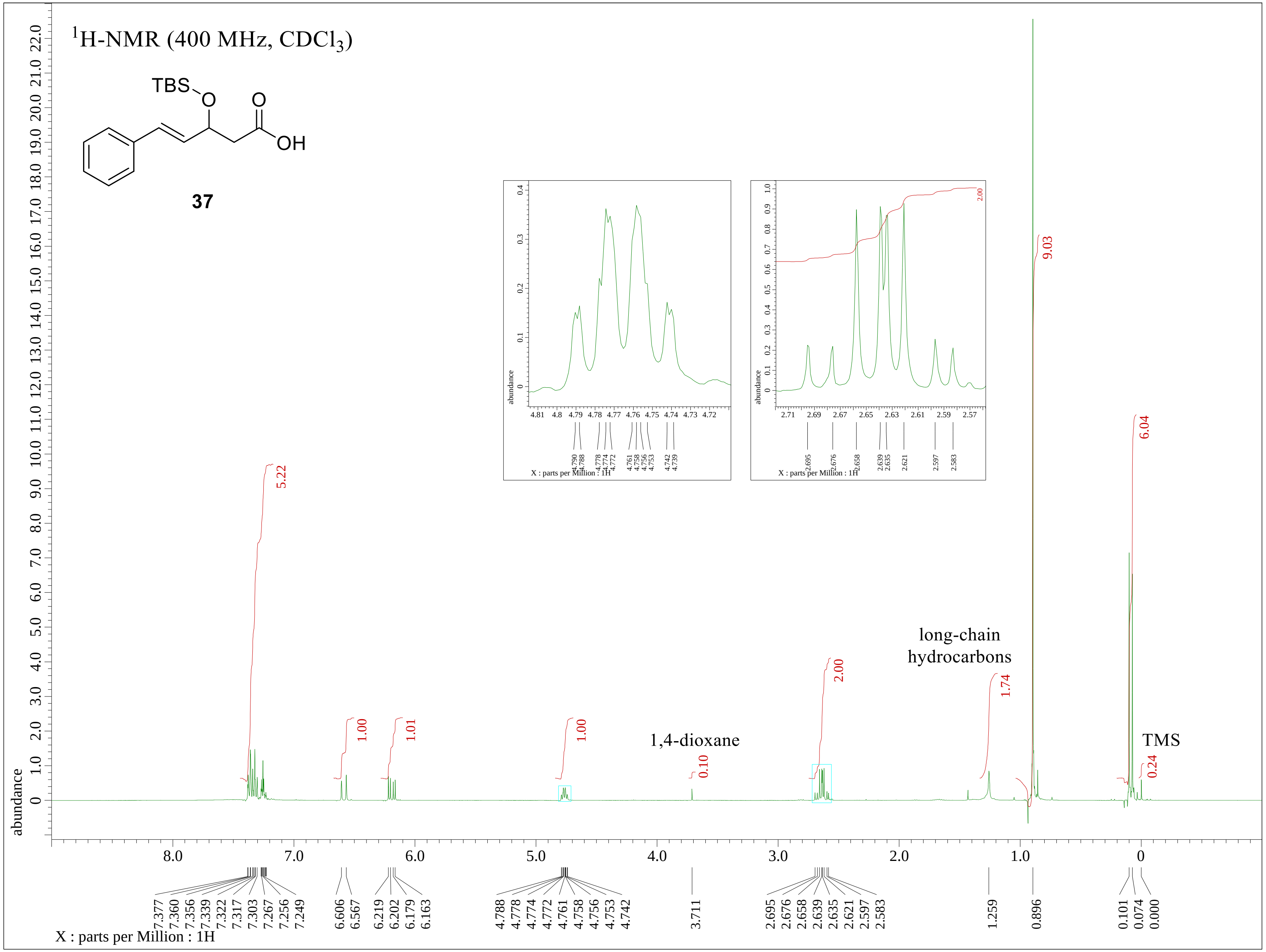

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
S
C$_{12}$H$_{25}$
OH
O
S
C$_{12}$H$_{25}$
34
CDCl$_3$
abundance
X : parts per Million : 13C
194.790
192.225
191.253
166.282
145.096
138.365
135.247
130.956
129.555
128.973
128.840
128.582
127.629
125.026
121.393
101.666
77.324
77.000
76.685
56.196
31.901
29.670
29.613
29.565
29.480
29.337
29.127
28.850
22.672
14.110
29.670
29.613
29.565
29.480
29.442
29.337
29.232
29.127
29.070
28.850
28.765
28.402

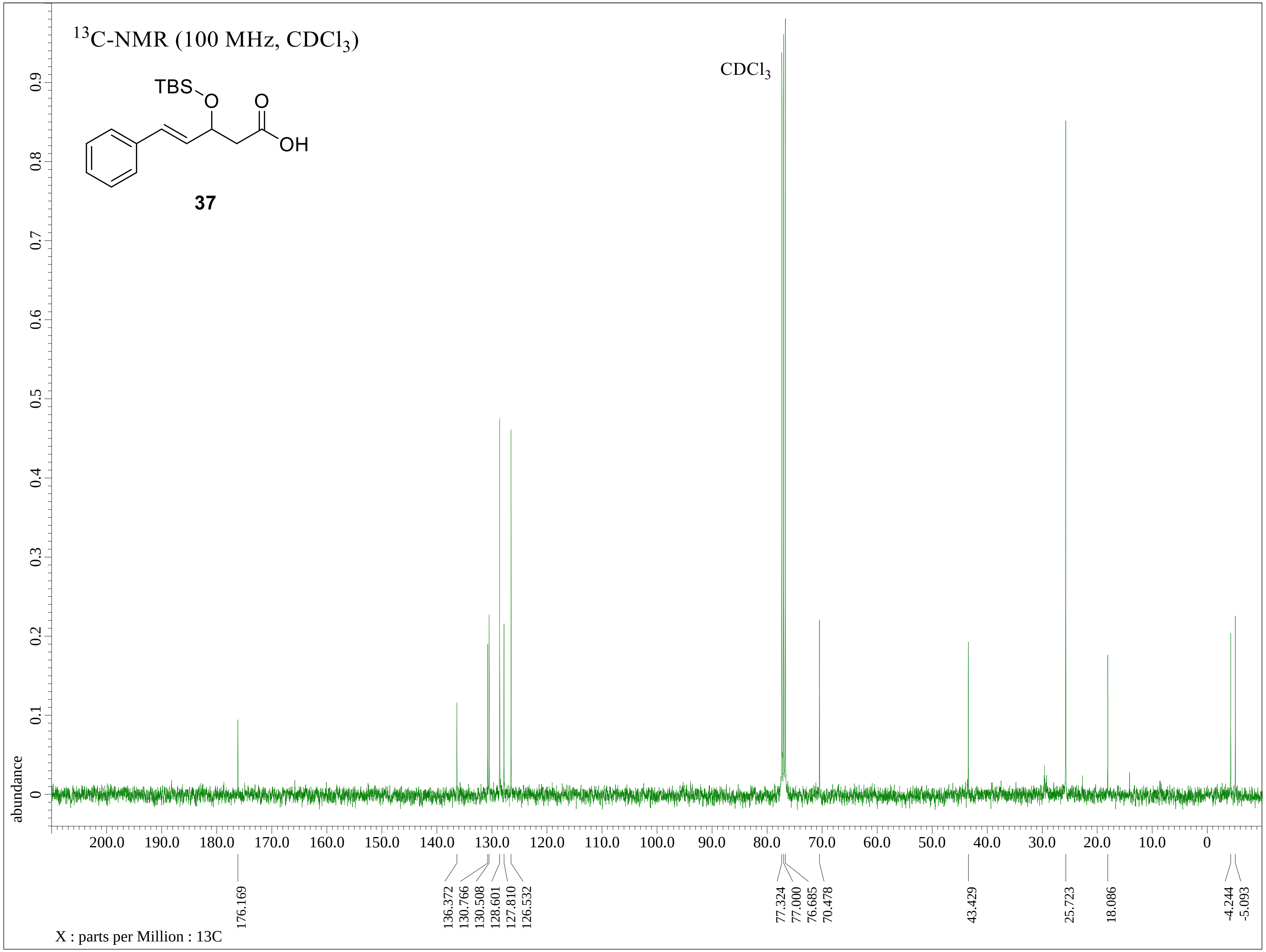

1H-NMR (400 MHz, CDCl3)
OH
O
S
C12H25
35
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
5.22
1.00
1.00
1.00
4.96
2.64
18.64
3.17
0.15
TMS
7.378
7.361
7.359
7.328
7.309
7.306
7.290
7.257
7.240
6.668
6.630
6.628
6.225
6.209
6.185
6.168
4.790
4.772
4.758
4.740
2.923
2.905
2.887
2.881
2.868
2.865
2.845
2.836
1.588
1.568
1.549
1.341
1.320
1.300
1.283
1.251
0.898
0.881
0.864
-0.001
0.2
0.1
4.8
X : parts per Million : 1H
2.0
1.0
2.94
2.93
2.92
2.91
2.9
2.89
2.88
2.87
2.86
2.85
2.84
2.83
2.82
X : parts per Million : 1H


^{13}C-NMR (100 MHz, CDCl$_3$)
OH
O
S
C$_{12}$H$_{25}$
35
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
198.814
136.353
130.880
129.669
128.553
127.819
126.532
77.315
77.000
76.676
69.496
50.599
31.892
29.604
29.546
29.442
29.365
29.318
29.070
28.784
22.662
14.100
X : parts per Million : 13C
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.604
29.546
29.442
29.365
29.318
29.070
28.784
X : parts per Million : 13C

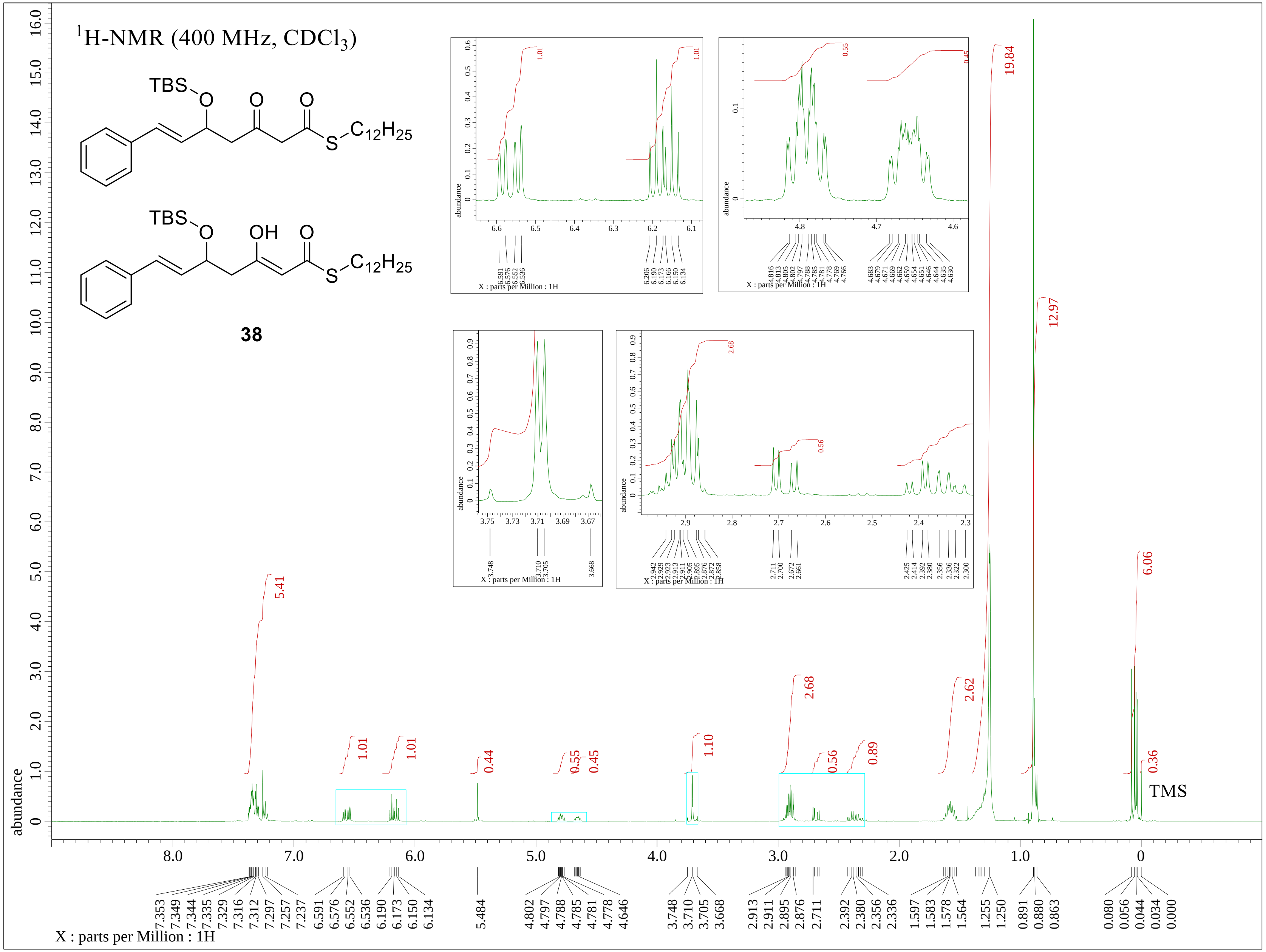

^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
O
O
S
$C_{12}H_{25}$
36
abundance
X : parts per Million : 1H
TMS
5.26
1.01
1.02
1.00
3.02
1.02
2.49
18.62
12.39
6.09
0.72
7.362 7.345 7.343 7.325 7.307 7.304 7.288 7.252 7.248 7.230
6.576 6.537
6.191 6.174 6.151 6.135
4.816 4.806 4.803 4.798 4.795 4.790 4.787 4.782 4.779 4.770 4.768
2.889 2.884 2.866 2.853 2.848 2.834 2.721 2.708 2.685 2.672
1.585 1.570 1.551 1.534 1.514
1.301 1.251
0.899 0.893 0.882 0.865
0.069 0.047 0.000
4.819 4.816 4.806 4.803 4.798 4.795 4.790 4.787 4.782 4.779 4.770 4.768
3.02
2.889 2.884 2.866 2.853 2.848 2.834 2.721 2.708 2.685 2.672


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
S
C$_{12}$H$_{25}$
36
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
197.069
136.629
131.423
129.946
128.544
127.610
126.465
77.315
77.000
76.676
70.793
52.706
31.901
29.613
29.565
29.451
29.413
29.337
29.108
29.060
28.841
25.790
22.672
18.162
14.110
-4.301
-5.093
X : parts per Million : 13C

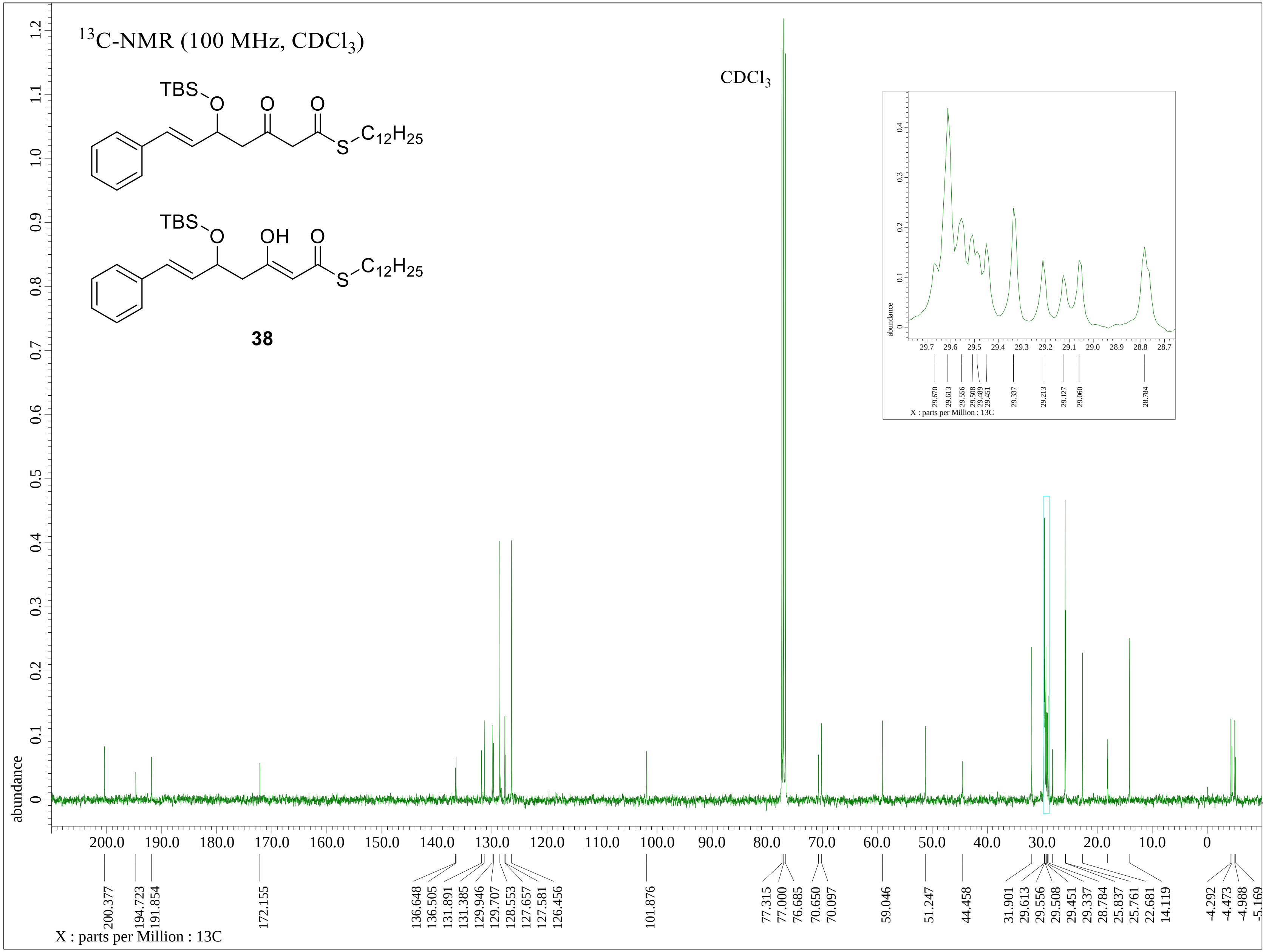
^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
O
O
OH
37
abundance
X : parts per Million : 1H
5.22
1.00
1.01
1.00
0.10
2.00
1.74
9.03
6.04
0.24
1,4-dioxane
long-chain hydrocarbons
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.377
7.360
7.356
7.339
7.322
7.317
7.303
7.267
7.256
7.249
6.606
6.567
6.219
6.202
6.179
6.163
4.788
4.778
4.774
4.772
4.761
4.758
4.756
4.753
4.742
3.711
2.695
2.676
2.658
2.639
2.635
2.621
2.597
2.583
1.259
0.896
0.101
0.074
0.000
4.790
4.788
4.778
4.774
4.772
4.761
4.758
4.756
4.753
4.742
4.739
2.695
2.676
2.658
2.639
2.635
2.621
2.597
2.583
2.00

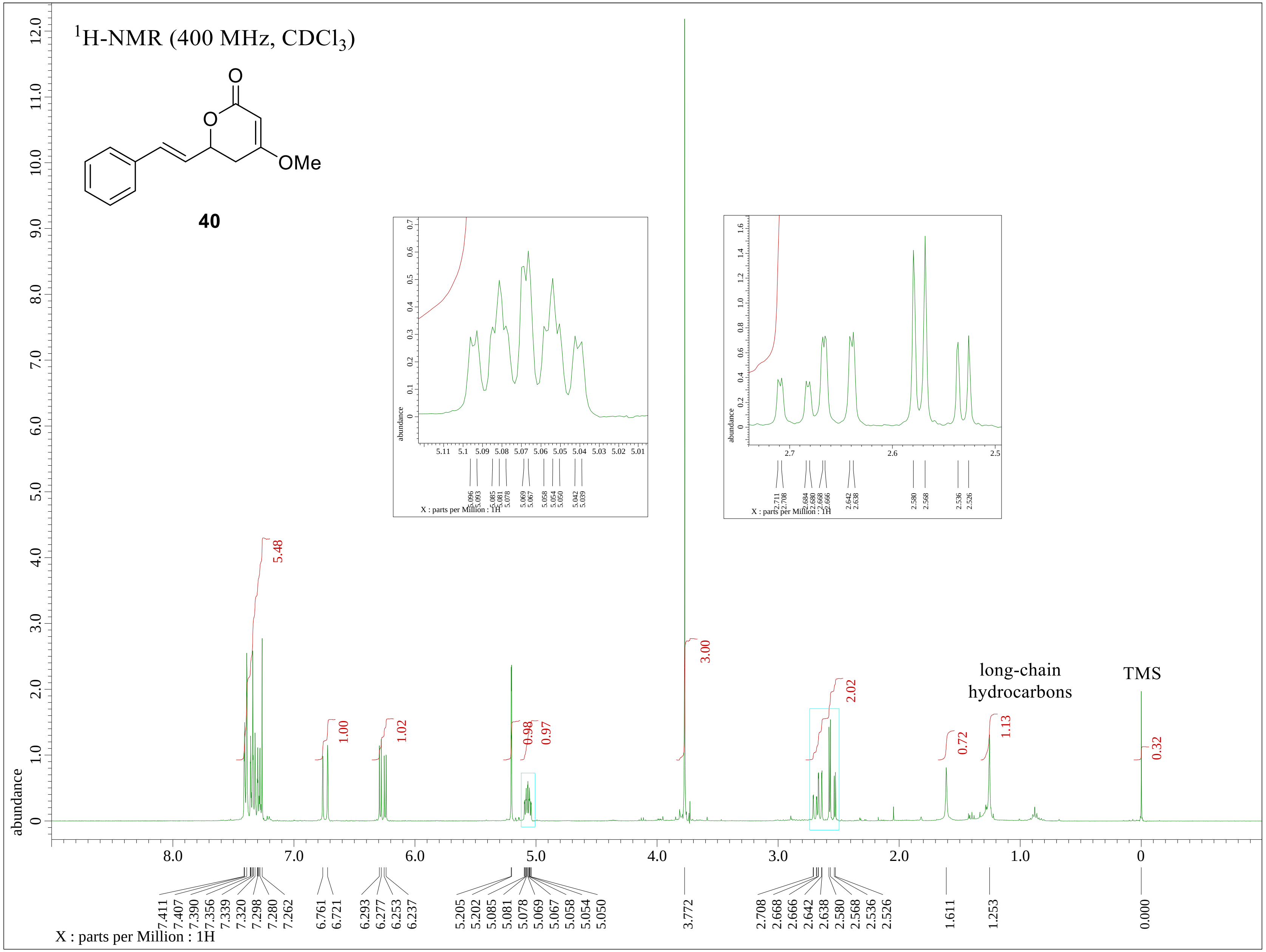


^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
OH
37
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
176.169
136.372
130.766
130.508
128.601
127.810
126.532
77.324
77.000
76.685
70.478
43.429
25.723
18.086
-4.244
-5.093
X : parts per Million : 13C



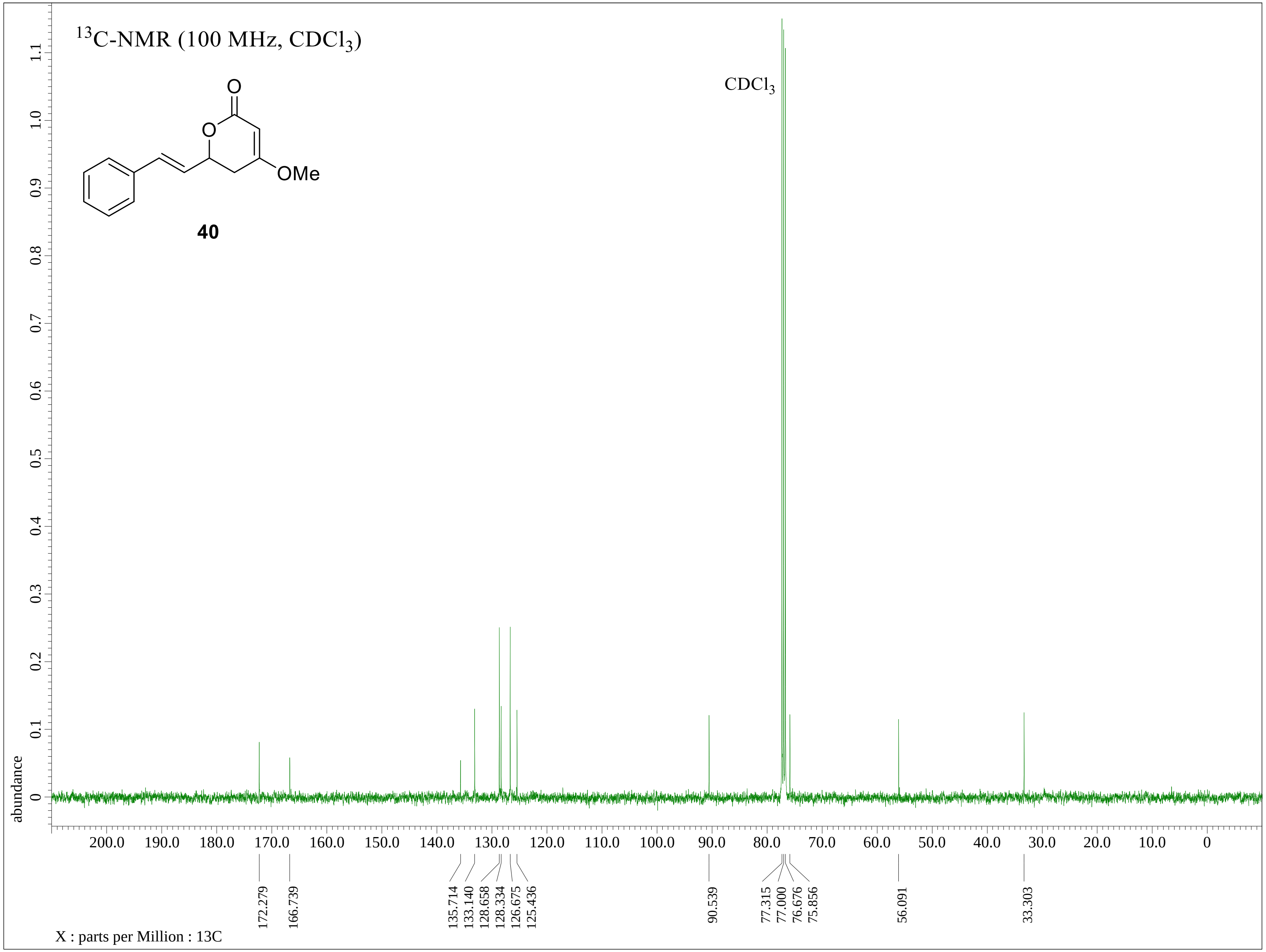
^{1}H-NMR (400 MHz, CDCl$_3$)
TBS
O
O
O
S
C$_{12}$H$_{25}$
TBS
O
OH
O
S
C$_{12}$H$_{25}$
38
abundance
X : parts per Million : 1H
TMS
5.41
1.01
1.01
0.44
0.55
0.45
1.10
2.68
0.56
0.89
2.62
19.84
12.97
6.06
0.36
7.353 7.349 7.344 7.335 7.329 7.316 7.312 7.297 7.257 7.237
6.591 6.576 6.552 6.536 6.190 6.173 6.150 6.134
5.484
4.802 4.797 4.788 4.785 4.781 4.778 4.646
3.748 3.710 3.705 3.668
2.913 2.911 2.895 2.876 2.711
2.392 2.380 2.356 2.336
1.597 1.583 1.578 1.564
1.255 1.250
0.891 0.880 0.863
0.080 0.056 0.044 0.034 0.000
6.206 6.190 6.173 6.166 6.150 6.134
4.816 4.813 4.805 4.802 4.797 4.788 4.785 4.781 4.778 4.769 4.766
4.683 4.679 4.671 4.669 4.662 4.659 4.654 4.651 4.646 4.644 4.635 4.630
2.942 2.929 2.923 2.913 2.911 2.905 2.895 2.876 2.872 2.858
2.711 2.700 2.672 2.661
2.425 2.414 2.392 2.380 2.356 2.336 2.322 2.300

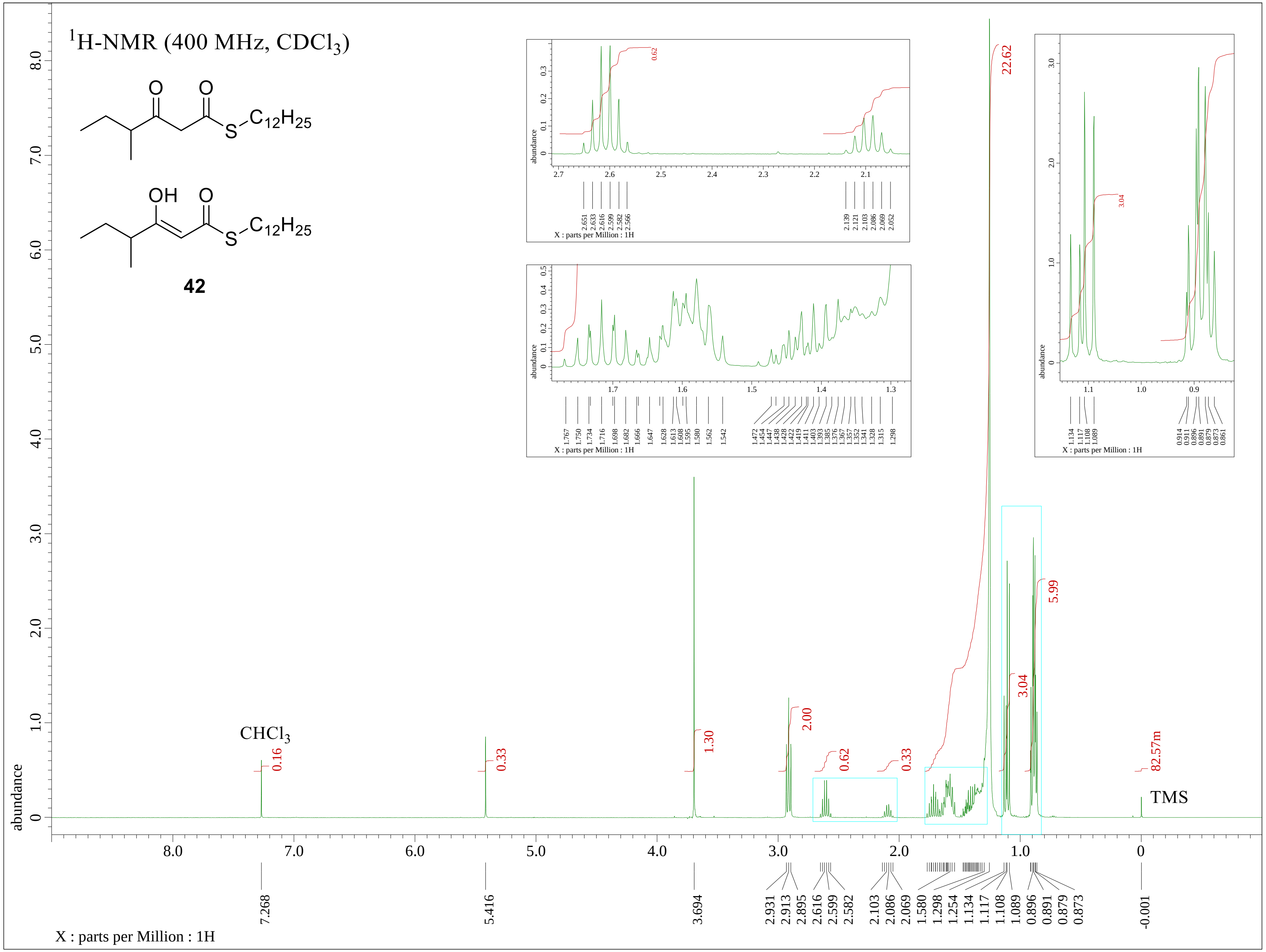

^{13}C-NMR (100 MHz, CDCl$_3$)
TBS
O
O
O
S
C12H25
OH
38
CDCl3
abundance
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.377
194.723
191.854
172.155
136.648
136.505
131.891
131.385
129.946
129.707
128.553
127.657
127.581
126.456
101.876
77.315
77.000
76.685
70.650
70.097
59.046
51.247
44.458
31.901
29.613
29.556
29.508
29.451
29.337
28.784
25.837
25.761
22.681
14.119
-4.292
-4.473
-4.988
-5.169
29.670
29.613
29.556
29.508
29.489
29.451
29.337
29.213
29.127
29.060
28.784



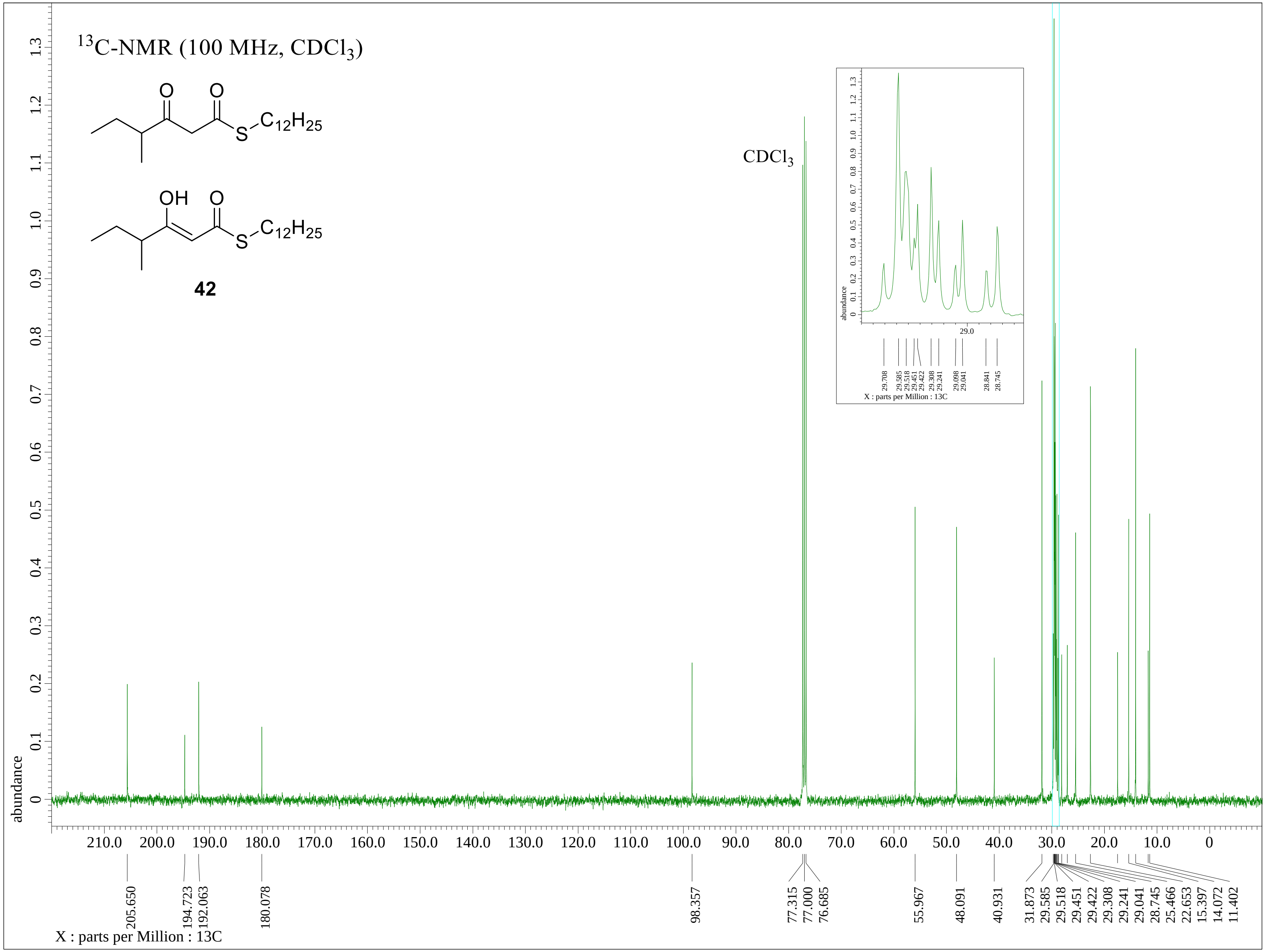
40

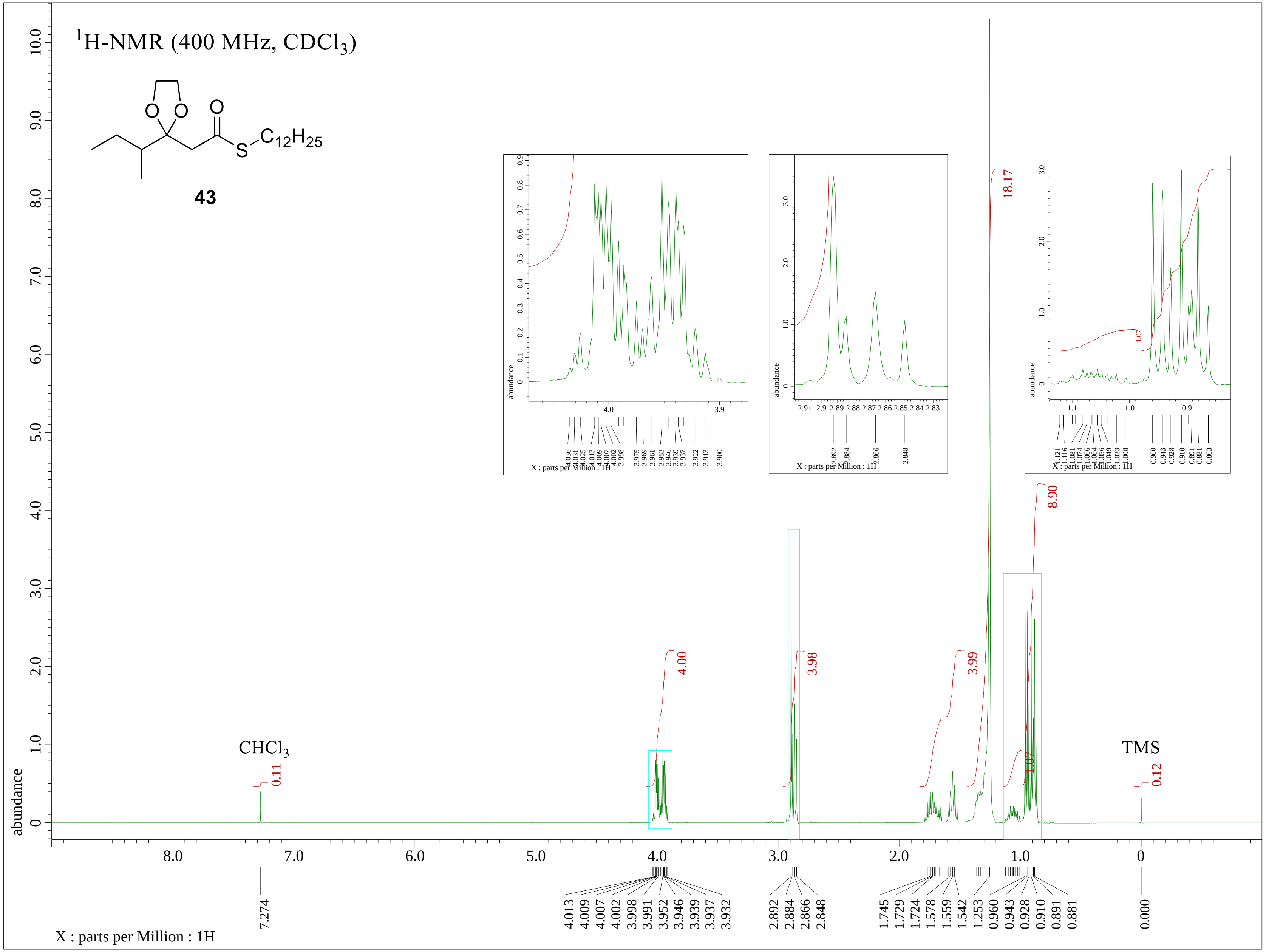
^{1}H-NMR (400 MHz, CDCl$_3$)
O
O
OMe
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
5.48
1.00
1.02
0.98
0.97
3.00
2.02
0.72
1.13
0.32
long-chain hydrocarbons
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.411
7.407
7.390
7.356
7.339
7.320
7.298
7.280
7.262
6.761
6.721
6.293
6.277
6.253
6.237
5.205
5.202
5.085
5.081
5.078
5.069
5.067
5.058
5.054
5.050
3.772
2.708
2.668
2.666
2.642
2.638
2.580
2.568
2.536
2.526
1.611
1.253
0.000
X : parts per Million : 1H
5.096
5.093
5.085
5.081
5.078
5.069
5.067
5.058
5.054
5.050
5.042
5.039
X : parts per Million : 1H
2.711
2.708
2.684
2.680
2.668
2.666
2.642
2.638
2.580
2.568
2.536
2.526
X : parts per Million : 1H

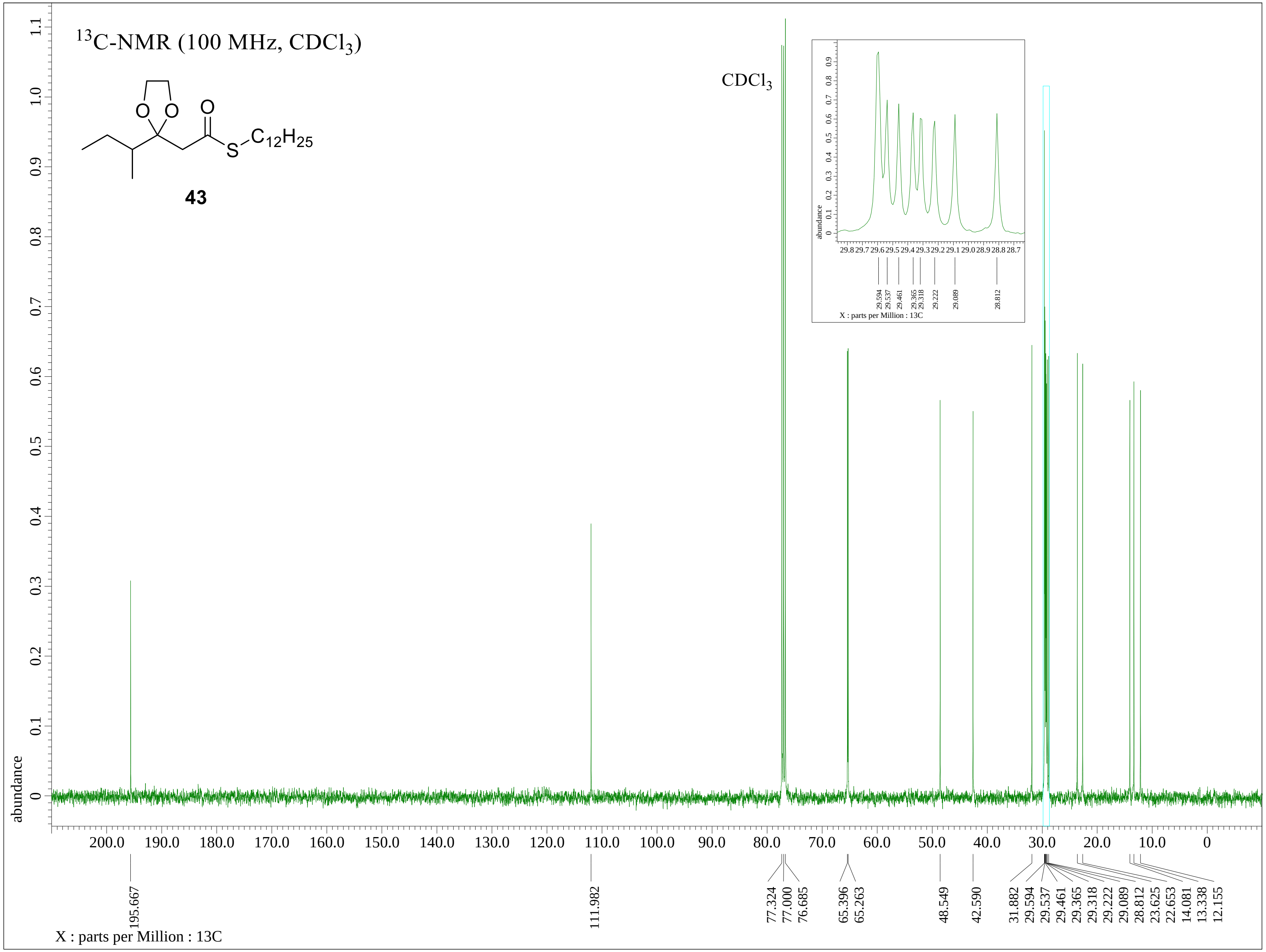

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
OMe
40
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.279
166.739
135.714
133.140
128.658
128.334
126.675
125.436
90.539
77.315
77.000
76.676
75.856
56.091
33.303
X : parts per Million : 13C

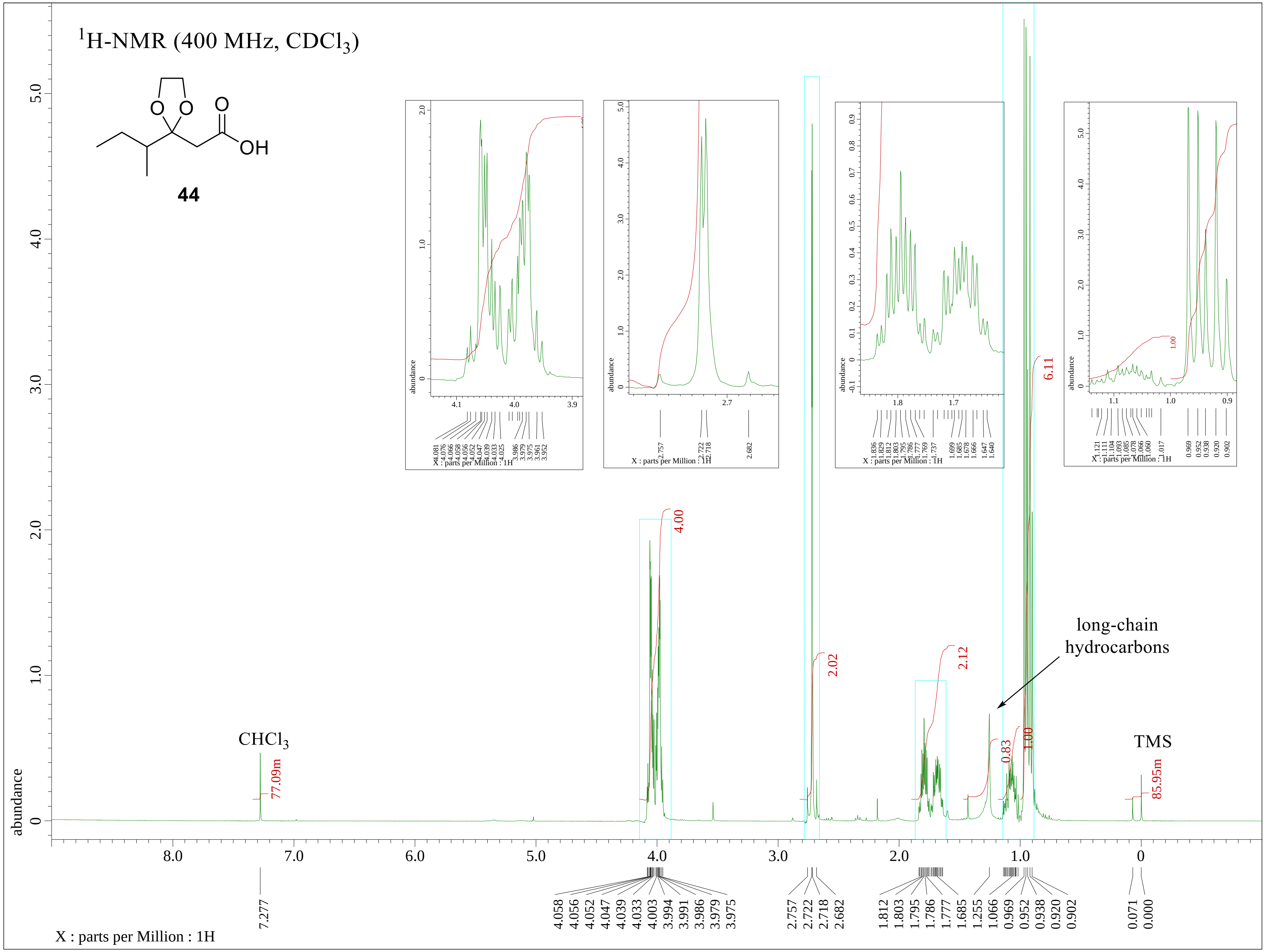


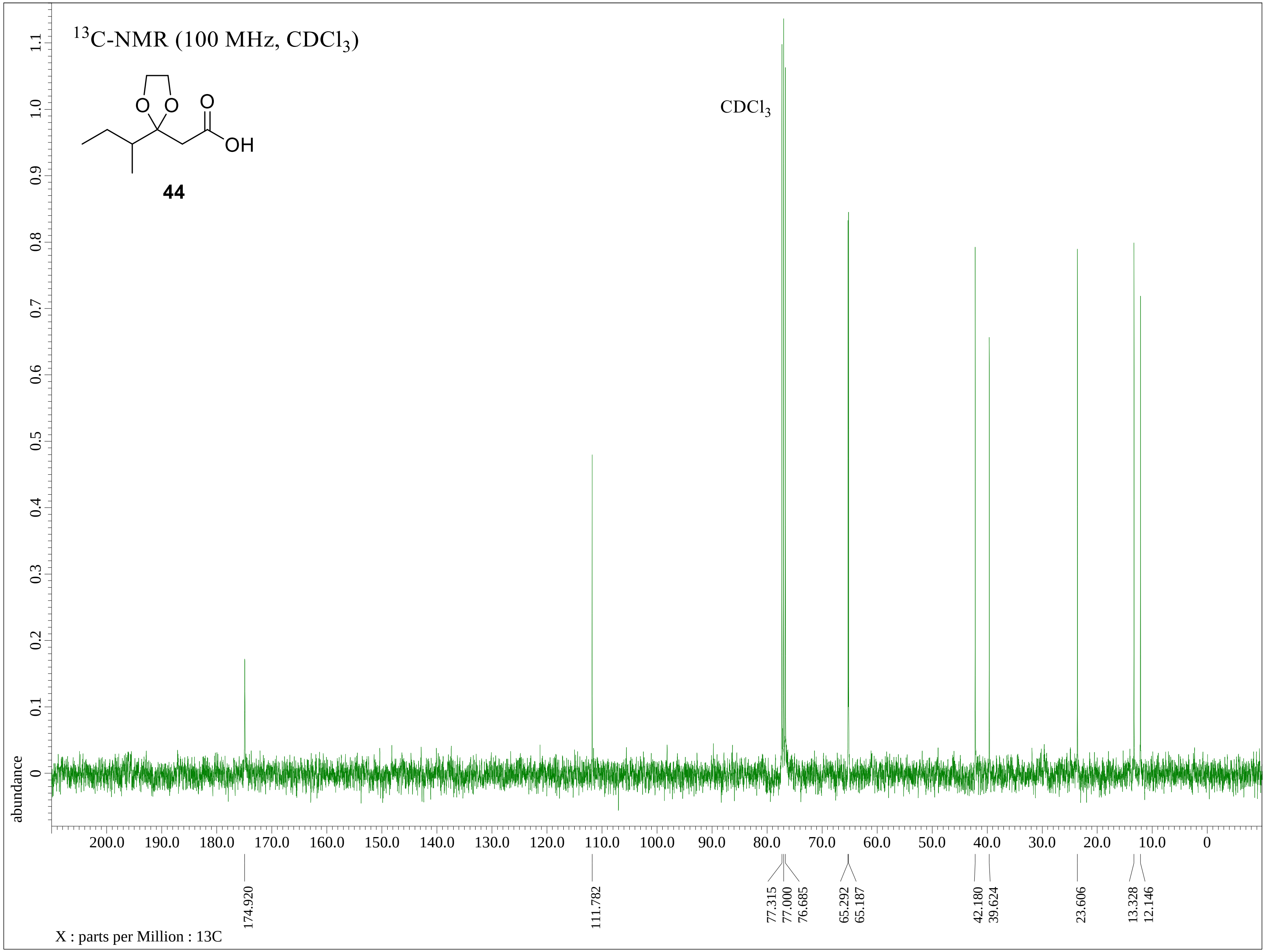
1H-NMR (400 MHz, CDCl3)
O
O
S
C12H25
OH
O
S
C12H25
42
CHCl3
TMS
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.16
0.33
1.30
2.00
0.62
0.33
22.62
3.04
5.99
82.57m
7.268
5.416
3.694
2.931
2.913
2.895
2.616
2.599
2.582
2.103
2.086
2.069
1.580
1.298
1.254
1.134
1.117
1.108
1.089
0.896
0.891
0.879
0.873
-0.001
2.651
2.633
2.616
2.599
2.582
2.566
2.139
2.121
2.103
2.086
2.069
2.052
0.62
1.767
1.750
1.734
1.716
1.698
1.682
1.666
1.647
1.628
1.613
1.608
1.595
1.580
1.562
1.542
1.472
1.454
1.447
1.438
1.428
1.422
1.419
1.411
1.403
1.393
1.385
1.376
1.367
1.357
1.352
1.341
1.328
1.315
1.298
1.134
1.117
1.108
1.089
0.914
0.911
0.896
0.891
0.879
0.873
0.861
3.04

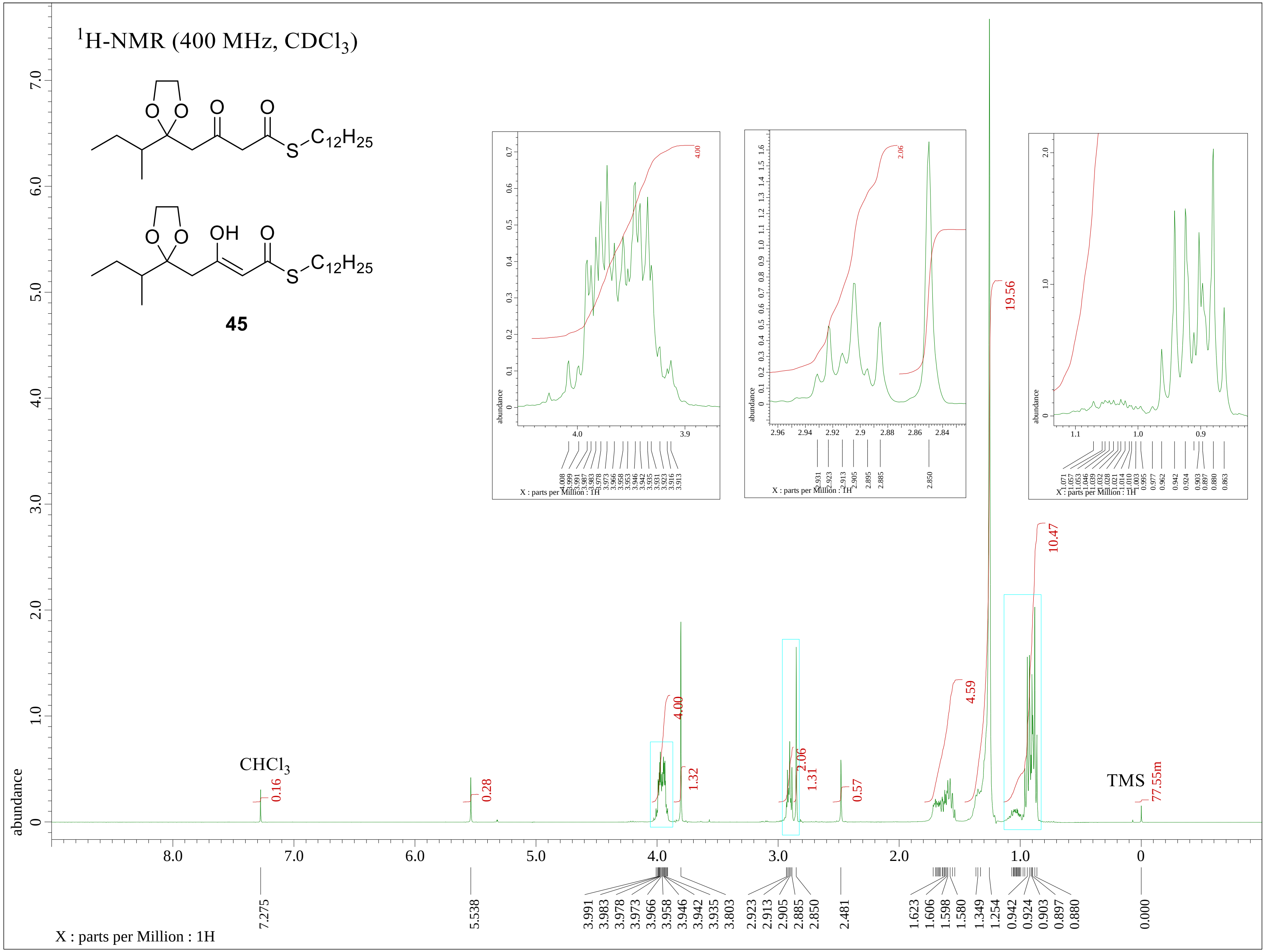

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
S
C$_{12}$H$_{25}$
OH
O
S
C$_{12}$H$_{25}$
42
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
205.650
194.723
192.063
180.078
98.357
77.315
77.000
76.685
55.967
48.091
40.931
31.873
29.585
29.518
29.451
29.422
29.308
29.241
29.041
28.745
25.466
22.653
15.397
14.072
11.402
X : parts per Million : 13C
29.0
29.708
29.585
29.518
29.451
29.422
29.308
29.241
29.098
29.041
28.841
28.745
X : parts per Million : 13C

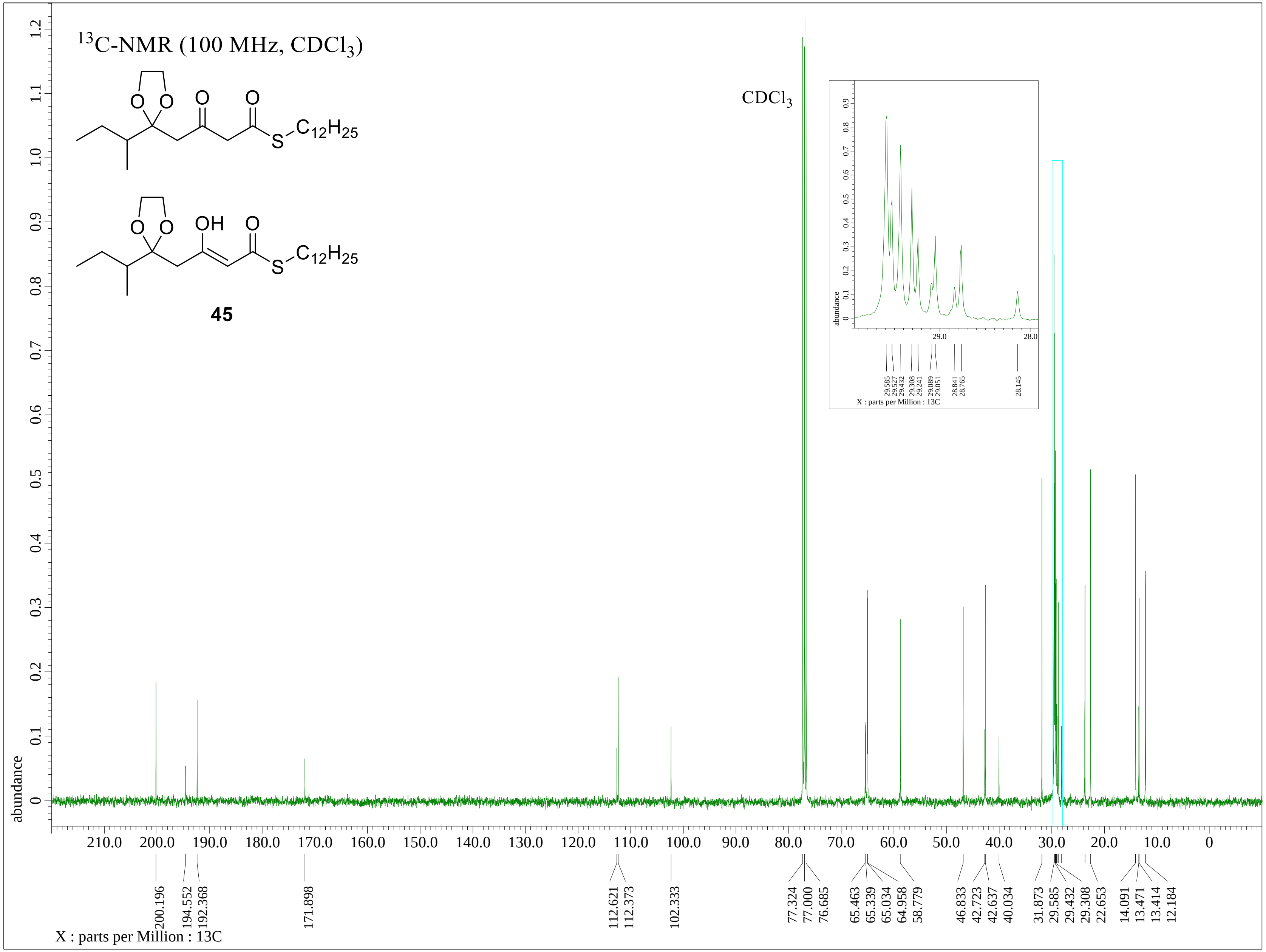

^{1}H-NMR (400 MHz, $CDCl_3$)
O
O
O
S
$C_{12}H_{25}$
43
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
CHCl$_3$
0.11
4.00
3.98
3.99
18.17
8.90
1.07
TMS
0.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.274
4.013
4.009
4.007
4.002
3.998
3.991
3.952
3.946
3.939
3.937
3.932
2.892
2.884
2.866
2.848
1.745
1.729
1.724
1.578
1.559
1.542
1.253
0.960
0.943
0.928
0.910
0.891
0.881
0.000
X : parts per Million : 1H

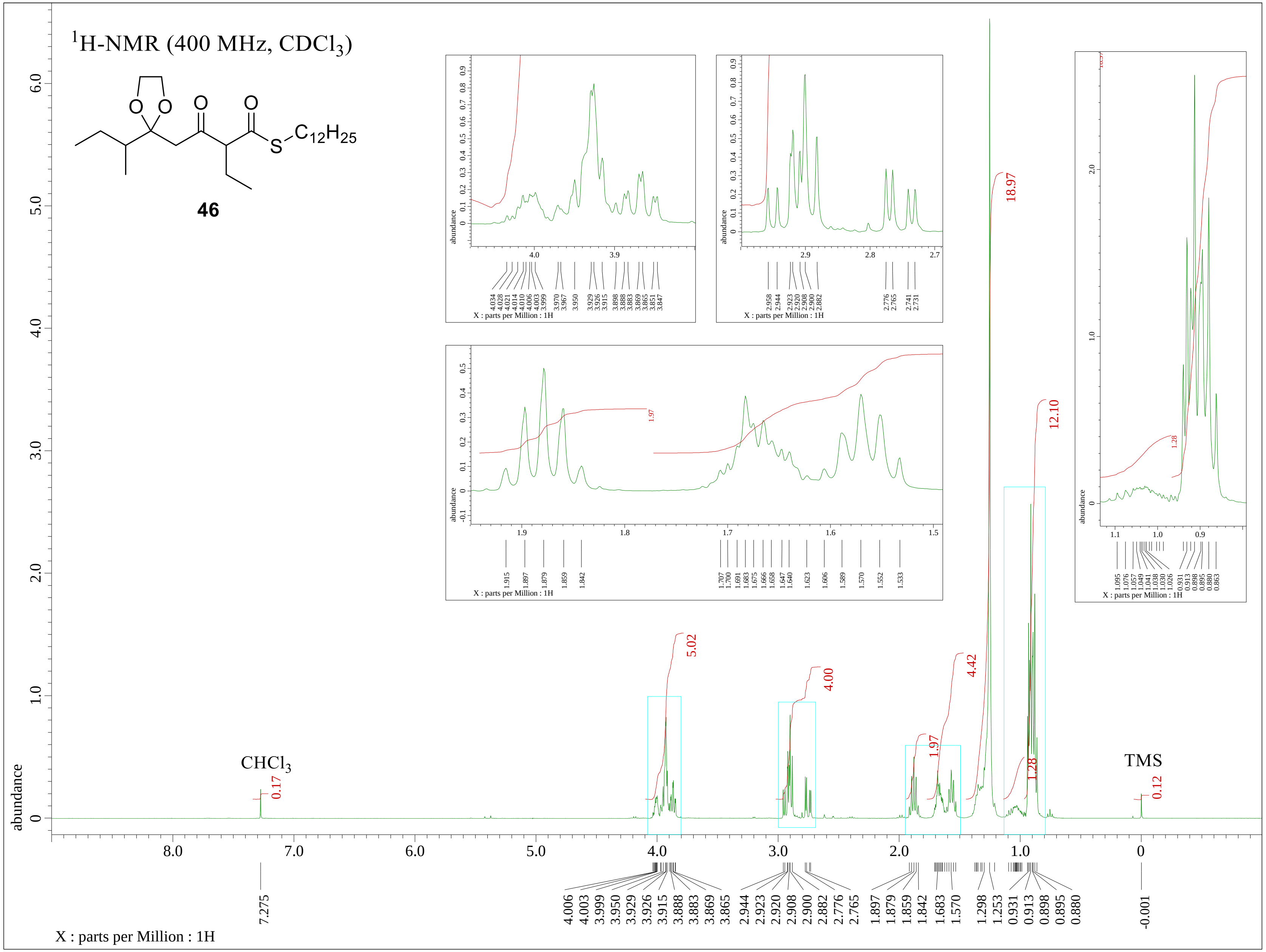

^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
O
S
C$_{12}$H$_{25}$
43
CDCl$_3$
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
195.667
111.982
77.324
77.000
76.685
65.396
65.263
48.549
42.590
31.882
29.594
29.537
29.461
29.365
29.318
29.222
29.089
28.812
23.625
22.653
14.081
13.338
12.155
X : parts per Million : 13C
abundance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
29.8
29.7
29.6
29.5
29.4
29.3
29.2
29.1
29.0
28.9
28.8
28.7
29.594
29.537
29.461
29.365
29.318
29.222
29.089
28.812
X : parts per Million : 13C

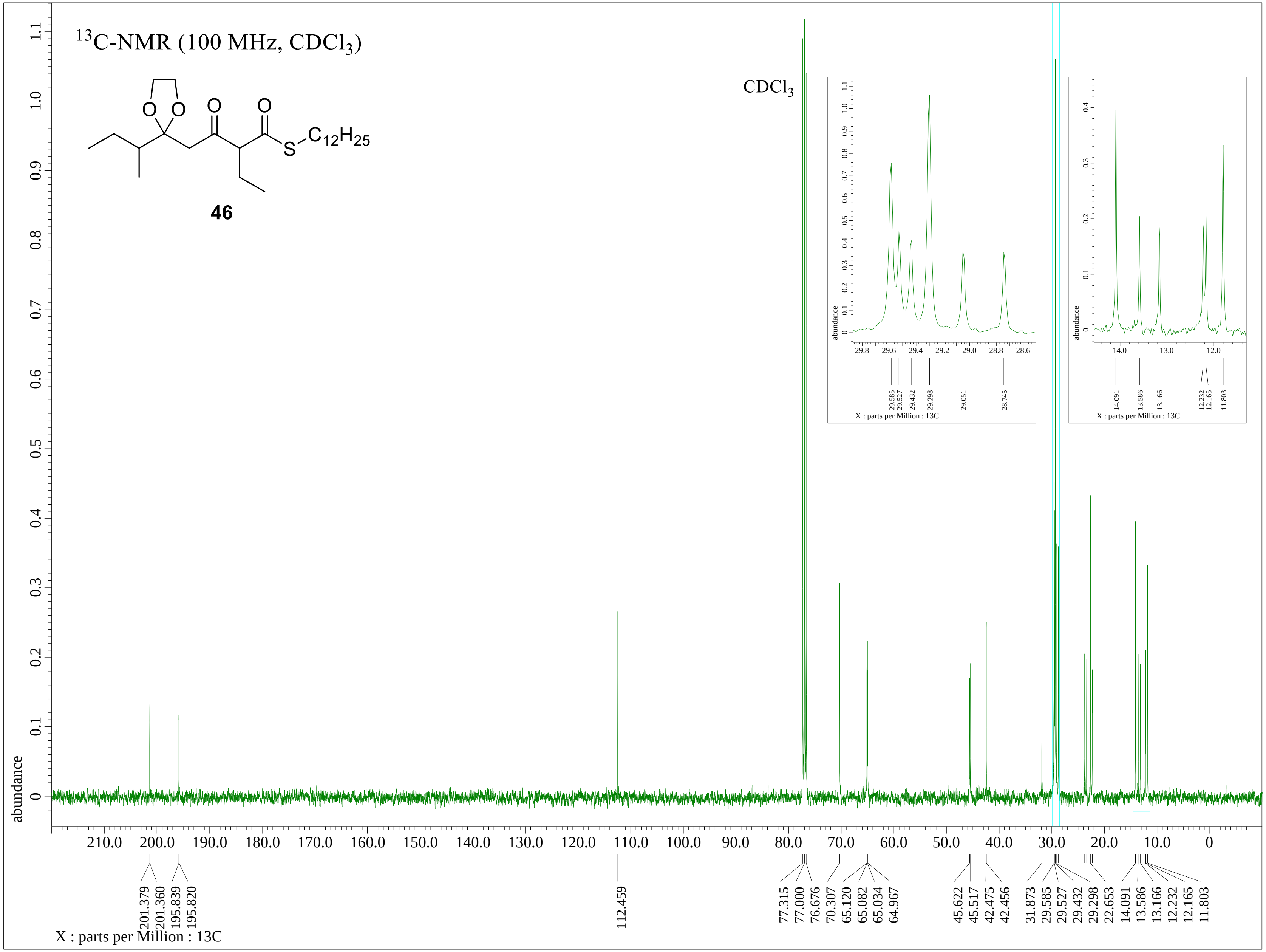

^{1}H-NMR (400 MHz, $CDCl_3$)
44
$CHCl_3$
77.09m
4.00
2.02
2.12
0.83
1.00
6.11
85.95m
long-chain hydrocarbons
TMS
abundance
X : parts per Million : 1H
7.277
4.058 4.056 4.052 4.047 4.039 4.033 4.003 3.994 3.991 3.986 3.979 3.975
2.757 2.722 2.718 2.682
1.812 1.803 1.795 1.786 1.777 1.685 1.255 1.066 0.969 0.952 0.938 0.920 0.902
0.071 0.000


^{13}C-NMR (100 MHz, CDCl$_3$)
44
O
O
O
OH
CDCl$_3$
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.920
111.782
77.315
77.000
76.685
65.292
65.187
42.180
39.624
23.606
13.328
12.146
X : parts per Million : 13C

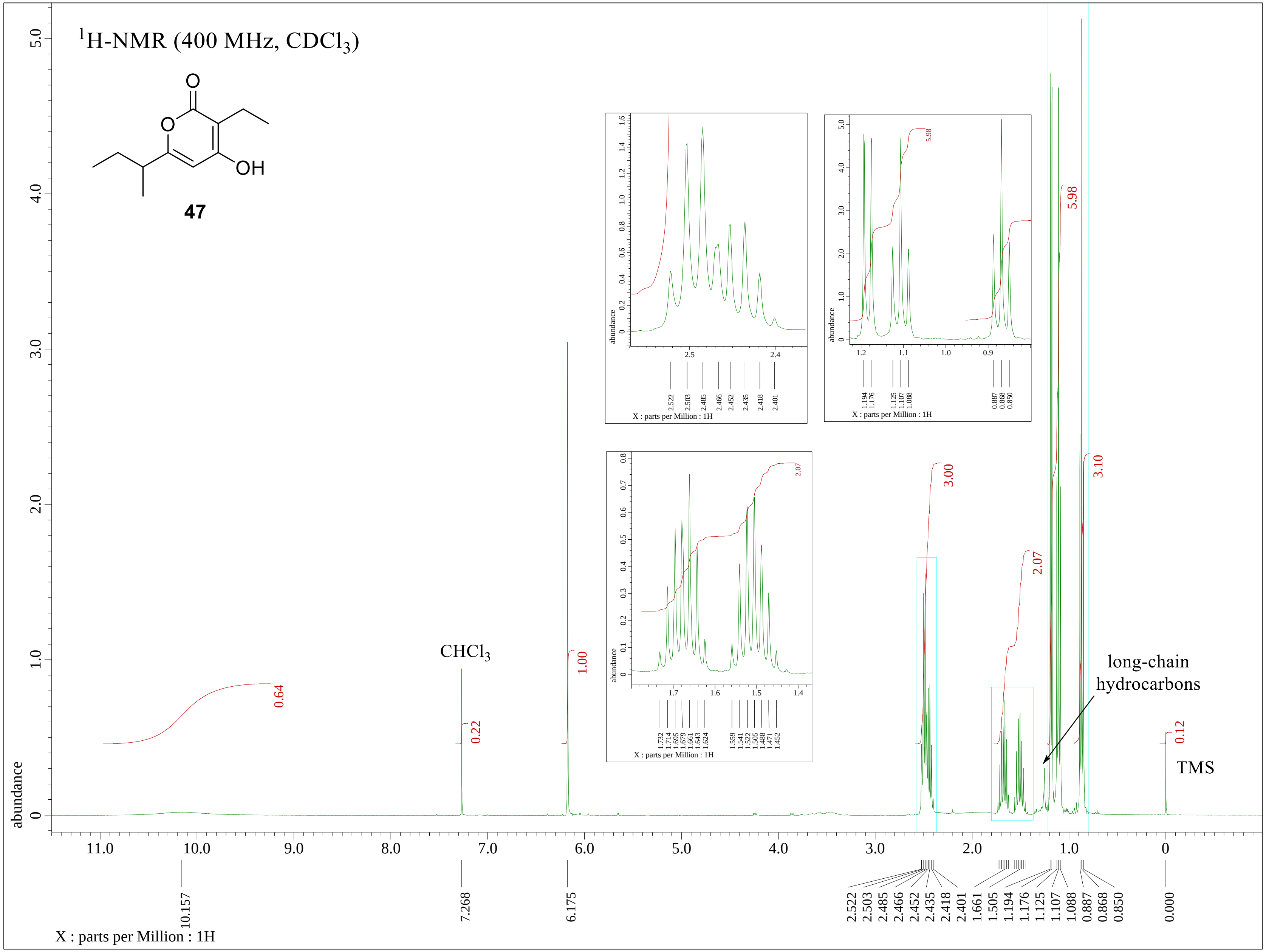

^{1}H-NMR (400 MHz, CDCl$_3$)
45
CHCl$_3$
TMS
0.16
0.28
4.00
1.32
2.06
1.31
0.57
4.59
19.56
10.47
77.55m
7.275
5.538
3.991
3.983
3.978
3.973
3.966
3.958
3.946
3.942
3.935
3.803
2.923
2.913
2.905
2.885
2.850
2.481
1.623
1.606
1.598
1.580
1.349
1.254
0.942
0.924
0.903
0.897
0.880
0.000
abundance
X : parts per Million : 1H

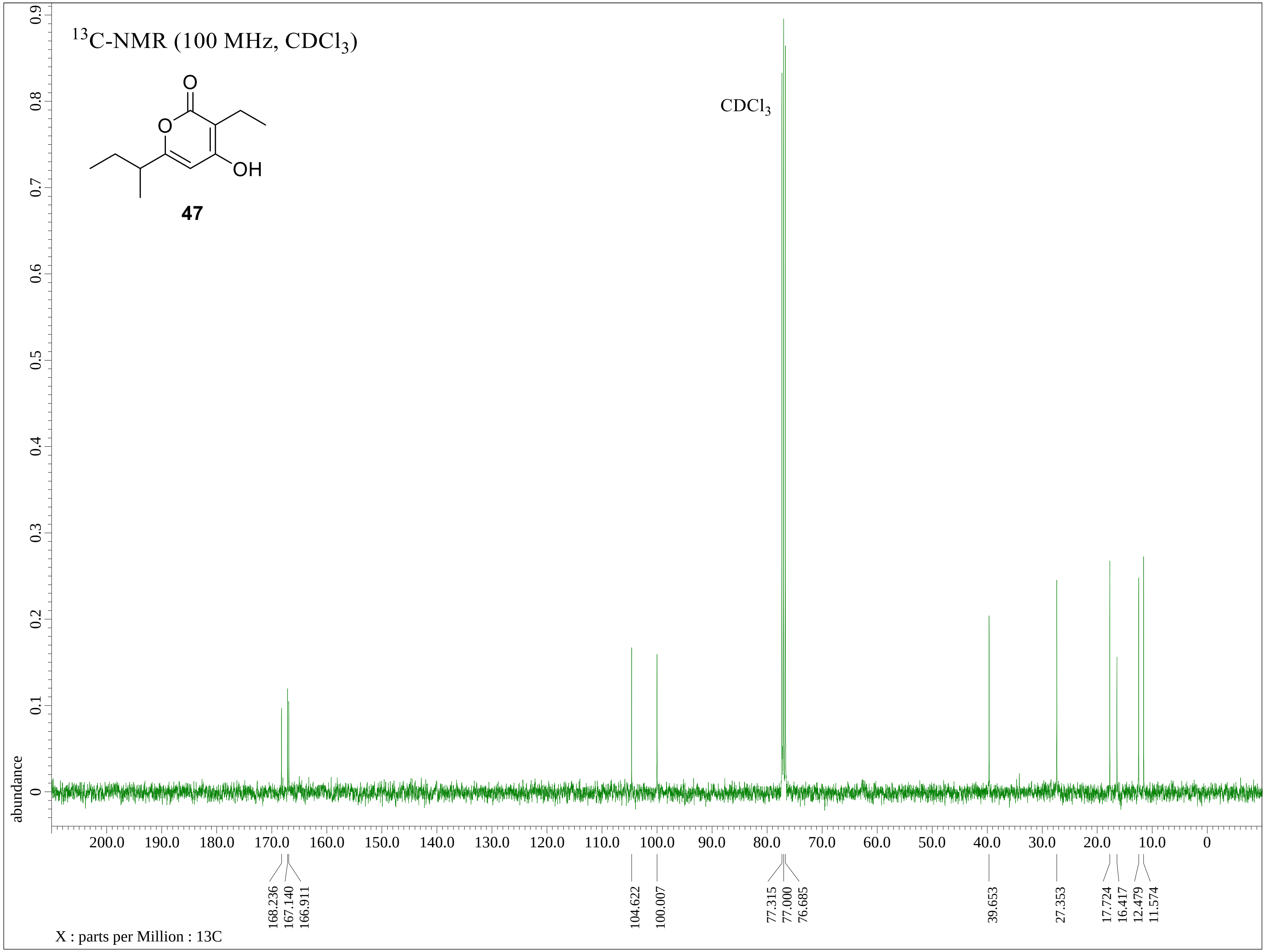

^{13}C-NMR (100 MHz, CDCl$_3$)
O O O O
S C$_{12}$H$_{25}$
O O OH O
S C$_{12}$H$_{25}$
45
CDCl$_3$
abundance
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
200.196
194.552
192.368
171.898
112.621
112.373
102.333
77.324
77.000
76.685
65.463
65.339
65.034
64.958
58.779
46.833
42.723
42.637
40.034
31.873
29.585
29.432
29.308
22.653
14.091
13.471
13.414
12.184
X : parts per Million : 13C
abundance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
29.0
28.0
29.585
29.527
29.432
29.308
29.241
29.089
29.051
28.841
28.765
28.145
X : parts per Million : 13C


^{1}H-NMR (400 MHz, $CDCl_3$)
46
$C_{12}H_{25}$
S
O
O O
$CHCl_3$
TMS
0.17
5.02
4.00
1.97
4.42
18.97
1.28
12.10
0.12
abundance
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.275
4.006
4.003
3.999
3.950
3.929
3.926
3.915
3.888
3.883
3.869
3.865
2.944
2.923
2.920
2.908
2.900
2.882
2.776
2.765
1.897
1.879
1.859
1.842
1.683
1.570
1.298
1.253
0.931
0.913
0.898
0.895
0.880
-0.001
4.034
4.028
4.021
4.014
4.010
4.006
4.003
3.999
3.970
3.967
3.950
3.929
3.926
3.915
3.898
3.888
3.883
3.869
3.865
3.851
3.847
2.958
2.944
2.923
2.920
2.908
2.900
2.882
2.776
2.765
2.741
2.731
1.915
1.897
1.879
1.859
1.842
1.707
1.700
1.691
1.683
1.675
1.666
1.658
1.647
1.640
1.623
1.606
1.589
1.570
1.552
1.533
1.095
1.076
1.057
1.049
1.041
1.038
1.030
1.026
0.931
0.913
0.898
0.895
0.880
0.863



^{13}C-NMR (100 MHz, CDCl$_3$)
O O O O
S C$_{12}$H$_{25}$
46
CDCl$_3$
abundance
X : parts per Million : 13C
201.379
201.360
195.839
195.820
112.459
77.315
77.000
76.676
70.307
65.120
65.082
65.034
64.967
45.622
45.517
42.475
42.456
31.873
29.585
29.527
29.432
29.298
22.653
14.091
13.586
13.166
12.232
12.165
11.803
29.585
29.527
29.432
29.298
29.051
28.745
14.091
13.586
13.166
12.232
12.165
11.803


^{1}H-NMR (400 MHz, $CDCl_3$)
OH
O
O
47
$CHCl_3$
long-chain hydrocarbons
TMS
abundance
X : parts per Million : 1H
0.64
0.22
1.00
3.00
2.07
5.98
3.10
0.12
10.157
7.268
6.175
2.522
2.503
2.485
2.466
2.452
2.435
2.418
2.401
1.661
1.505
1.194
1.176
1.125
1.107
1.088
0.887
0.868
0.850
0.000
1.732
1.714
1.695
1.679
1.661
1.643
1.624
1.559
1.541
1.522
1.505
1.488
1.471
1.452
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.0
4.0
3.0
2.0
1.0
0


^{13}C-NMR (100 MHz, CDCl$_3$)
47
CDCl$_3$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.236
167.140
166.911
104.622
100.007
77.315
77.000
76.685
39.653
27.353
17.724
16.417
12.479
11.574
X : parts per Million : 13C