Supporting Information

Iterative synthesis of nitrogen-containing polyketide *via* oxime intermediates

Yuta Takeuchi, Shun Kawasaki, Kengo Akagawa and Kazuaki Kudo*

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

**e-mail: kkudo@iis.u-tokyo.ac.jp*

Table of contents:

General information

NMR spectra were recorded on a JEOL JNM-LA400 (400 MHz for ^{1}H and 100 MHz for $^{13}C\{^{1}H\}$), or a JEOL JNM-ECZ600R (600 MHz for ^{1}H and 151 MHz for $^{13}C\{^{1}H\}$), 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) or CD_3OD (δ = 49.0 ppm) for $^{13}C\{^{1}H\}$. 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. High-resolution MALDI-TOFMS measurements were performed on a JMS-S3000 Spiral-TOF mass spectrometer. The data were collected in a spiral positive mode with polyethylene glycol 200 or 400 as an internal mass calibrant, and sodium iodide as a cationization agent. High-performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments with Chiralcel OJ-H column (Daicel, 4.6 × 250 mm). The synthetic procedures and spectral data for compounds **1**,[1] **3**,[1] **8**,[1] **9**,[1] **10**,[1] and **24**[2] were reported. The enantiomeric ratio of **23** was determined by HPLC analysis according to the literature.[3]

Synthetic procedures and spectral data

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

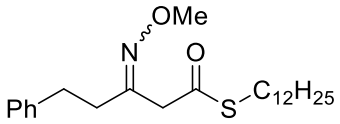
To a solution of a carboxylic acid (0.4 M) in DME, COMU (1 equiv.) and DIEA (1 equiv.) were added, and the mixture was stirred for 15 min. In another flask, to a solution of MAHT **1** (1.3 to 2 equiv.) in the same amount of DME used above, a THF solution (1 M) of isopropylmagnesium bromide (the same 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, 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 on silica gel or preparative TLC on silica gel plates (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 (determined by TLC), 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 separate, brine was added to facilitate the phase separation. The aqueous layer was acidified with a 1 N 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. Removal of the solvent under reduced pressure afforded the carboxylic acid.

General procedure for the *O*-methyloximation of β-ketothioesters

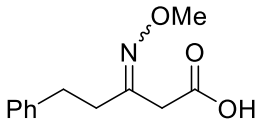
To a solution of β-ketothioester (0.1 to 0.2 M) in dichloromethane/pyridine (1:1 v/v), methoxyamine hydrochloride (3 equiv.) was added. After stirring the mixture for 2.5 to 6 h, a saturated aqueous solution of ammonium chloride was added. The resulting mixture was extracted with chloroform, and the 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 plates (eluent: hexanes/ethyl acetate) to afford a β-methoxyiminothioester.



***S*-Dodecyl 3-(methoxyimino)-5-phenylpentanethioate (4)**

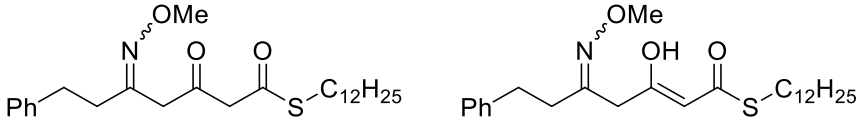
Synthesized according to the general procedure for *O*-methyloximation. The reaction of β-ketothioester **3** (126.5 mg, 0.3359 mmol, 0.1 M) was performed for 3 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-methoxyiminothioester **4** (128.6 mg, 94% yield) as a colorless oil.

Diastereomeric ratio = 62:38. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.23–7.16 (m, 3H), 3.88 (s, 1.13H), 3.86 (s, 1.87H), 3.57 (s, 1.24H), 3.30 (s, 0.76H), 2.92–2.75 (m, 4H), 2.70–2.63 (m, 0.76H), 2.61–2.54 (m, 1.24H), 1.56 (quin, J = 7.6 Hz, 2H), 1.41–1.12 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.4, 194.1, 154.2, 152.3, 141.0, 140.9, 128.4, 128.3, 128.2, 126.2, 126.1, 61.7, 61.5, 48.9, 43.2, 36.4, 32.5, 31.9, 31.5, 30.3, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 28.8, 22.7, 14.1; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{24}H_{39}NNaO_2S$ $[M+Na]^+$: 428.2594, found 428.2574.



3-(Methoxyimino)-5-phenylpentanoic acid (5)

Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 1 h without additional hydrogen peroxide. The reaction of thioester **4** (128.6 mg, 0.3170 mmol) afforded crude product (73.7 mg) containing carboxylic acid **5**, which was used for the next reaction without further purification.

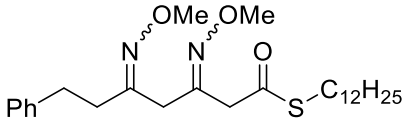


***S*-Dodecyl 5-(methoxyimino)-3-oxo-7-phenylheptanethioate,**

***S*-Dodecyl (2*Z*)-3-hydroxy-5-(methoxyimino)-7-phenylhept-2-enethioate (6)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **5** (obtained from 0.3170 mmol of **4**) was performed with 1.5 equiv. of MAHT **1** for 3 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-ketothioester **6** (98.1 mg, 69% yield from **4**) as a colorless oil.

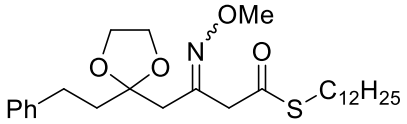
Keto/enol ratio = 81:19. Diastereomeric ratio = 58:42 (keto) and 55:45 (enol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.23–7.15 (m, 3H), 5.41 (s, 0.10H), 5.41 (s, 0.09H), 3.87 (s, 0.26H), 3.86 (s, 0.31H), 3.85 (s, 1.02H), 3,83 (s, 1.41H), 3.69 (s, 0.94H), 3.67 (s, 0.68H), 3.45 (s, 0.94H), 3.28 (s, 0.68H), 3.23 (s, 0.17H), 2.95–2.75 (m, 4H), 2.67–2.47 (m, 2H), 1.65–1.52 (m, 2H), 1.42–1.13 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.4, 196.7, 194.9, 192.0, 191.9, 170.9, 170.2, 155.2, 154.4, 153.3, 141.0, 140.9, 140.8, 140.8, 128.4, 128.3, 128.2, 126.2, 126.1, 100.8, 100.5, 61.6, 61.5, 61.4, 57.1, 56.8, 48.3, 43.1, 39.9, 36.8, 35.9, 34.0, 33.8, 32.6, 32.2, 31.9, 31.6, 31.3, 30.4, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.8, 28.3, 28.2, 24.6, 22.6, 14.1; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{26}H_{41}NNaO_3S$ $[M+Na]^+$: 470.2699, found 470.2681.



***S*-Dodecyl 3,5-bis(methoxyimino)-7-phenylheptanethioate (7)**

Synthesized according to the general procedure for *O*-methyloximation. The reaction of β-ketothioester **6** (98.1 mg, 0.219 mmol, 0.1 M) was performed for 3 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-methoxyiminothioester **7** (92.2 mg, 88% yield) as a colorless oil.

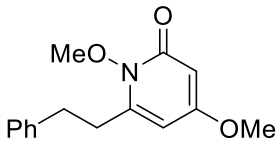
Diastereomeric ratio = 30:30:28:12. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.23–7.15 (m, 3H), 3.90 (s, 0.36H), 3.88 (s, 0.87H), 3.87 (s, 0.87H), 3.85 (s, 0.87H), 3.84 (s, 0.90H), 3.84 (s, 0.90H), 3.82 (s, 0.87H), 3.81 (s, 0.36H), 3.54 (s, 0.58H), 3.52 (s, 0.60H), 3.45 (s, 0.58H), 3.45 (s, 0.24H), 3.37 (s, 0.58H), 3.34 (s, 0.60H), 3.26 (s, 0.24H), 3.07 (s, 0.58H), 2.92–2.73 (m, 4H), 2.62–2.46 (m, 2H), 1.61–1.51 (m, 2H), 1.40–1.18 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.5, 195.2, 193.7, 193.6, 156.0, 155.5, 154.8, 154.6, 150.1, 149.7, 149.7, 149.1, 141.3, 141.2, 141.1, 141.1, 128.4, 128.4, 128.3, 126.1, 126.0, 126.0, 61.7, 61.7, 61.5, 61.5, 61.4, 61.3, 48.2, 47.7, 42.6, 42.4, 39.7, 36.4, 35.6, 33.5, 32.9, 32.7, 32.4, 31.9, 31.7, 31.4, 30.4, 30.0, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 29.1, 28.9, 28.8, 22.7, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{27}H_{44}N_2NaO_3S$ $[M+Na]^+$: 499.2965, found 499.2972.



***S*-Dodecyl 3-(methoxyimino)-4-(2-phenethyl-1,3-dioxolan-2-yl)butanethioate (11)**

Synthesized according to the general procedure for *O*-methyloximation. The reaction of β-ketothioester **10** (188 mg, 0.406 mmol, 0.2 M) was performed for 6 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 7:1) afforded β-methoxyiminothioester **11** (190 mg, 95% yield) as a colorless oil.

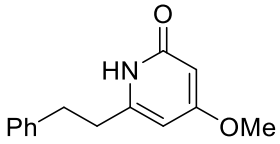
Diastereomeric ratio = 71:29. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 2H), 7.20–7.13 (m, 3H), 4.02–3.96 (m, 4H), 3.86 (s, 2.13H), 3.86 (s, 0.87H), 3.76 (s, 1.42H), 3.61 (s, 0.58H), 2.88 (t, *J* = 7.2 Hz, 0.58H), 2.87 (t, *J* = 7.2 Hz, 1.42H), 2.85 (s, 0.58H), 2.74-2.68 (m, 2H), 2.66 (s, 1.42H), 1.97–1.88 (m, 2H), 1.57 (quin, *J* = 7.6 Hz, 2H), 1.39–1.21 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 194.2, 151.0, 150.0, 142.1, 142.0, 128.3, 125.7, 125.7, 110.2, 110.1, 65.0, 64.9, 61.6, 61.6, 48.9, 43.2, 41.2, 39.4, 39.3, 34.6, 31.9, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 29.1, 28.8, 22.7, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{28}H_{46}NO_4S$ $[M+H]^+$: 492.3142, found 492.3145.



1,4-Dimethoxy-6-phenethylpyridin-2(1*H*)-one (12)

To a solution of β-ketothioester **6** (50.4 mg, 0.113 mmol) in dichloromethane (643 μL), DBU (16.86 μL, 0.113 mmol) was added. After stirring the reaction mixture for 9 h, DIEA (58.8 μL, 0.338 mmol) and dimethyl sulfate (53.4 μL, 0.563 mmol) were added. After stirring for additional 2 h, a 1 N aqueous 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 plates (eluent: chloroform/methanol = 9:1) to afford *N*-methoxy-2-pyridone **12** (19.3 mg, 66% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5H), 5.87 (d, *J* = 3.2 Hz, 1H), 5.65 (d, *J* = 2.8 Hz, 1H), 4.04 (s, 3H), 3.72 (s, 3H), 3.00–2.87 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 166.5, 160.6, 147.8, 140.0, 128.6, 128.3, 126.5, 98.5, 96.3, 64.0, 55.5, 34.1, 32.3; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1281, found 260.1283.

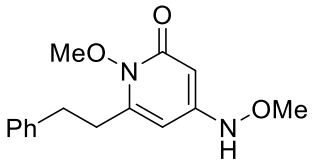


4-Methoxy-6-phenethylpyridin-2(1*H*)-one (13)

To *N*-methoxy-2-pyridone **12** (10.5 mg, 40.5 μmol), a 0.1 M THF solution of SmI_2 (1370 μL, 0.1370 mmol) was

added under argon atmosphere. At the points after 2 min and 40 min, the THF solution of SmI_2 (1370 μL, 0.1370 mmol) was added again. After stirring for 2 h in total, water was added to quench the reaction. The solvent was removed under reduced pressure, and the residue was purified by preparative TLC on silica gel plates (eluent: chloroform/methanol = 9:1) to afford 2-pyridone **13** (7.4 mg, 80% yield) as a white solid.

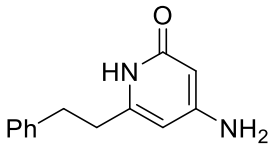
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (broad s, 1H), 7.32–7.17 (m, 5H), 5.77 (d, J = 2.4 Hz, 1H), 5.71 (d, J = 1.8 Hz, 1H), 3.75 (s, 3H), 3.00 (t, J = 7.9 Hz, 2H), 2.84 (t, J = 7.9 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.9, 167.4, 148.6, 140.2, 128.5, 128.5, 126.3, 99.4, 94.5, 55.4, 34.8, 34.5; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{14}H_{15}NNaO_2$ $[M+Na]^+$: 252.0995, found 252.0985.



1-Methoxy-4-(methoxyamino)-6-phenethylpyridin-2(1*H*)-one (14)

To a solution of β-methoxyiminothioester **7** (44.3 mg, 92.9 μmol) and ethyl 2-cyano-2-(hydroxyimino)acetate (264.0 mg, 1.858 mmol) in THF (1858 μL), silver trifluoroacetate (31.0 mg, 0.140 mmol) was added. After stirring for 24 h, the reaction mixture was passed through a column packed with basic activated alumina (eluent: chloroform/methanol = 95:5). After the removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel plates (eluent: chloroform/methanol = 9:1) to afford *N*-methoxy-2-pyridone **14** (18.8 mg, 74% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.35–7.15 (m, 5H), 5.96 (d, J = 2.8 Hz, 1H), 5.48 (d, J = 2.8 Hz, 1H), 4.03 (s, 3H), 3.68 (s, 3H), 2.98–2.86 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 160.3, 155.3, 148.1, 140.1, 128.6, 128.3, 126.5, 95.2, 93.7, 64.0, 63.4, 34.2, 32.6 ; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{15}H_{19}N_2O_3$ $[M+H]^+$: 275.1390, found 275.1384.

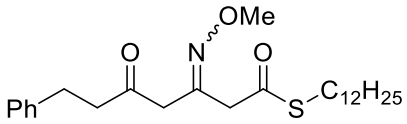


4-Amino-6-phenethylpyridin-2(1*H*)-one (15)

Raney nickel was prepared by the following procedure: To a 6 N aqueous solution of NaOH (10 mL), Ni-Al alloy (ca. 50% Ni, 1.0 g) was added portionwise at room temperature. The resulting suspension was heated to 50 °C and stirred for 1 h. The black precipitate was washed with water till neutral, and then water was added to prepare a slurry of 2 mL.

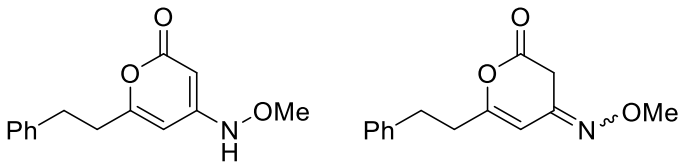
To a solution of *N*-methoxy-2-pyridone **14** (25.4 mg, 92.6 μmol) in MeOH (926 μL), the water slurry of Raney nickel (463 μL) was added, and filled with hydrogen. After stirring under hydrogen atmosphere for 3 h, the suspension was filtered through a pad of celite, and the catalyst was washed with MeOH. The solvent of filtrate was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: chloroform → chloroform/methanol = 4:1) to afford 4-amino-2-pyridone **15** (13.6 mg, 69%) as a white solid.

^{1}H NMR (600 MHz, CD_3OD) δ 7.28–7.23 (m, 2H), 7.28–7.23 (m, 3H), 5.67 (d, *J* = 2.1 Hz, 1H), 5.40 (d, *J* = 2.1 Hz, 1H), 2.90 (t, *J* = 7.9 Hz, 2H), 2.71 (t, *J* = 7.9 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, CD_3OD) δ 167.4, 161.3, 149.5, 141.7, 129.5, 127.3, 100.1, 92.2, 35.9, 35.8; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{13}H_{14}N_2NaO$ $[M+Na]^+$:237.0998, found 237.1000.



***S*-Dodecyl 3-(methoxyimino)-5-oxo-7-phenylheptanethioate (16)**

To a solution of thioester **11** (205.6 mg, 0.4181 mmol) in 1,4-dioxane (3.800 mL), concentrated hydrochloric acid (380 μL) was added. After stirring the solution for 29 h, water and diethyl ether were added. The organic layer was collected and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to afford crude product (172.9 mg) containing β-methoxyiminothioester **16**, which was used for the next reaction without further purification.



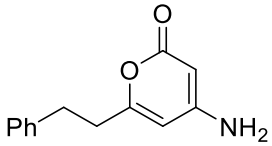
4-(Methoxyamino)-6-phenethyl-2*H*-pyran-2-one,

4-(Methoxyimino)-6-phenethyl-3,4-dihydro-2H-pyran-2-one (17)

To a solution of the crude product (32.8 mg) containing β-methoxyiminothioester **16** and ethyl 2-cyano-2-(hydroxyimino)acetate (9.3 mg, 65 μmol) in THF (700 μL), silver trifluoroacetate (19.4 mg, 87.8 μmol) was added. After stirring the mixture for 2.5 h, the solvent was removed under reduced pressure, and then ethyl acetate was added. The solid was filtered through cotton wool, and the solvent of filtrate was removed under reduced pressure. The residue was purified by preparative TLC on silica gel plates (eluent: dichloromethane/acetonitrile = 4:1) to afford 4-methoxyamino-2-pyrone **17** (13.6 mg, 70% yield from **11**) as a yellow oil.

N-Methoxyenamine/*N*-methoxyimine ratio = 66:34. Diastereomeric ratio (*N*-methoxyimine) = 88:12. **^{1}H NMR**

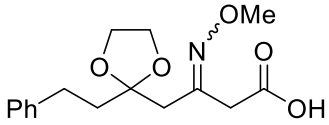
(400 MHz, $CDCl_3$) δ 7.88 and 7.83 (broad s, 0.66H in total), 7.34–7.12 (m, 5H), 6.12 (s, 0.04H), 5.62 (s, 0.30H), 5.52 (s, 0.66H), 5.47 (s, 0.66H), 3.89 (s, 0.90), 3.87 (s, 0.12), 3.72 (s, 1.98H), 3.67 (s, 0.60H), 3.55 (s, 0.08H), 2.96 (t, J = 7.3 Hz, 1.32H), 2.91 (t, J = 8.2 Hz, 0.68H), 2.71 (t, J = 7.8 Hz, 1.32H), 2.61 (t, J = 8.0 Hz, 0.68H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 165.2, 165.0, 164.9, 164.5, 159.5, 158.1, 157.4, 147.1, 144.2, 139.9, 139.9, 139.8, 128.6, 128.4, 128.3, 128.2, 126.5, 126.4, 99.7, 94.9, 94.6, 83.4, 63.6, 62.2, 62.0, 35.7, 35.3, 35.1, 33.8, 32.9, 32.3, 32.2, 30.0, 29.7; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{14}H_{15}NNaO_3$ $[M+Na]^+$: 268.0944, found 268.0947.



4-Amino-6-phenethyl-2*H*-pyran-2-one (18)

To a solution of 4-methoxyamino-2-pyrone **17** (18.8 mg, 76.7 μmol), a 0.1 M THF solution of SmI_2 (1.55 mL, 0.155 mmol) was added under argon atmosphere. After stirring the solution for 30 min, water (388 μL) was added. The resulting mixture was directly purified by preparative TLC on silica gel plates (eluent: chloroform/acetonitrile = 1:1) to afford 4-amino-2-pyrone **18** (10.2 mg, 62% yield) as a pale yellow oil.

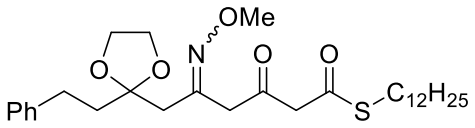
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 5.56 (d, *J* = 1.8 Hz, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 4.85 (s, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 165.3, 164.7, 158.4, 140.0, 128.5, 128.3, 126.4, 98.8, 84.3, 35.7, 32.9; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{13}H_{13}NNaO_2$ $[M+Na]^+$: 238.0838, found 238.0837.

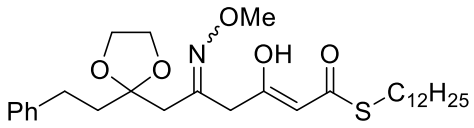


3-(Methoxyimino)-4-(2-phenethyl-1,3-dioxolan-2-yl)butanoic acid (19)

Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 20 min without additional hydrogen peroxide. The reaction of thioester **11** (90.8 mg, 0.185 mmol) afforded carboxylic **19** (56.6 mg, 99% yield).

Diastereomeric ratio = 65:35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.20-7.14 (m, 3H), 3.98 (s, 4H), 3.87 (s, 1.95H), 3.86 (s, 1.05H), 3.54 (s, 1.3H), 3.46 (s, 0.7H), 2.91 (s, 0.7H), 2.74-2.67 (m, 2H), 2.70 (s, 1.3H), 1.98-1.88 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 175.5, 174.8, 150.9, 149.9, 141.9, 128.3, 128.3, 125.8, 110.1, 65.0, 64.9, 61.7, 41.4, 39.6, 39.4, 39.3, 34.8, 34.3, 29.6, 29.6; **HRMS** (FAB, negative ion mode, matrix: glycerol) *m*/*z*: calculated for $C_{16}H_{20}NO_5$ $[M–H]^–$: 306.1347, found 306.1350.



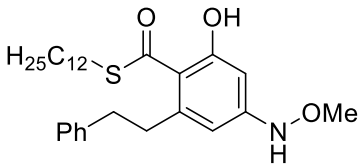


***S*-Dodecyl 5-(methoxyimino)-3-oxo-6-(2-phenethyl-1,3-dioxolan-2-yl)hexanethioate,**

***S*-Dodecyl (2*Z*)-3-hydroxy-5-(methoxyimino)-6-(2-phenethyl-1,3-dioxolan-2-yl)hex-2-enethioate (20)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **19** (56.6 mg, 0.184 mmol) was performed with 2 equiv. of MAHT **1** for 3 h. Purification by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 2:1) afforded β-ketothioester **20** (83.3 mg, 85% yield).

Keto/enol ratio = 87:13. Diastereomeric ratio = 70:30 (keto) and 56:44 (enol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 2H), 7.21-7.14 (m, 3H), 5.49 (s, 0.06H), 5.44 (s, 0.07H), 4.03-3.92 (m, 4H), 3.87 (s, 0.22H), 3.86 (s, 0.17H), 3.84 (s, 2.61H), 3.72 (s, 0.52H), 3.71 (s, 1.22H), 3.64 (s, 1.22H), 3.57 (s, 0.52H), 3.43 (s, 0.15H), 3.23 (s, 0.11H), 2.95-2.88 (m, 2H), 2.83 (s, 0.52H), 2.80 (s, 0.11H), 2.75-2.67 (m, 2H), 2.63 (s, 1.22H), 2.62 (s, 0.15H), 1.97-1.86 (m, 2H), 1.63-1.54 (m, 2H), 1.40-1.20 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.6, 196.8, 194.9, 191.9, 191.8, 171.6, 170.8, 152.0, 151.1, 150.9, 150.8, 142.0, 142.0, 141.9, 128.3, 125.7, 110.2, 110.1, 110.0, 100.9, 100.4, 64.9, 64.9, 64.8, 61.7, 61.6, 57.3, 57.0, 48.3, 43.0, 41.4, 40.8, 40.0, 39.4, 39.2, 34.7, 34.4, 33.7, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.8, 28.2, 28.2, 22.6, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for $C_{30}H_{48}NO_5S$ $[M+H]^+$: 534.3248, found 534.3255.

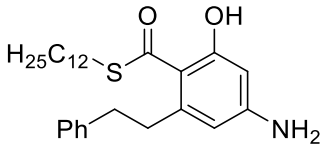


***S*-Dodecyl 2-hydroxy-4-(methoxyamino)-6-phenethylbenzothioate (21)**

To a solution of β-ketothioester **20** (15.3 mg, 28.7 μmol) in 1,4-dioxane (258 μL), an aqueous concentrated solution of hydrochloric acid (29 μL) was added. After stirring the mixture for 14 h, diethyl ether and water were added. The layers were separated, and the organic layer was dried under over anhydrous magnesium sulfate. After the removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane (287 μL), and triethylamine (19.9 μL, 0.143 mmol) was added. After stirring the mixture for 30 min, the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel (eluent: hexanes/ethyl acetate = 4:1) to afford benzothioate **21** (10.2 mg, 75% yield) as a pale orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.32-7.18 (m, 5H), 7.11 (s, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 3.73 (s, 3H), 3.36-3.30 (m, 2H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.99-2.92 (m, 2H), 1.69 (quin, *J* = 7.6 Hz, 2H), 1.43 (quin, *J* = 7.6 Hz, 2H), 1.37-1.21 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.6, 161.4, 152.8, 144.1, 141.4, 128.4, 126.1, 116.1, 107.6, 98.9, 63.5, 38.1, 37.9, 31.9, 30.0, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 22.7, 14.1; **HRMS** (FAB, matrix: 2-nitrophenyl octyl ether) *m*/*z*: calculated for

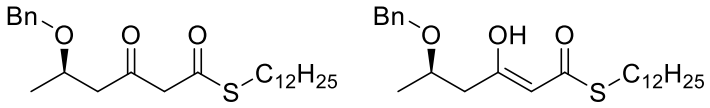
$C_{28}H_{42}NO_3S$ $[M+H]^+$: 472.2880, found 472.2880.



***S*-Dodecyl 4-amino-2-hydroxy-6-phenethylbenzothioate (22)**

To benzothioate **21** (7.1 mg, 15 μmol), a 0.1 M THF solution of SmI_2 (755 μL, 75.5 μmol) was added under argon atmosphere. After stirring the reaction solution for 15 min, the THF solution of SmI_2 (755 μL, 75.5 μmol) was added again. After stirring the reaction mixture for additional 15 min, water 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 plates (eluent: hexanes/ethyl acetate = 7:3) to afford benzothioate **22** (4.8 mg, 72% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 7.33–7.19 (m, 5H), 6.06 (d, *J* = 2.8 Hz, 1H), 6.03 (d, *J* = 2.3 Hz, 1H), 4.03 (broad s, 2H), 3.36–3.29 (m, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 3.00–2.93 (m, 2H), 1.69 (quin, *J* = 7.3 Hz, 2H), 1.47–1.38 (m, 2H), 1.37–1.18 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.1, 162.8, 151.4, 144.9, 141.6, 128.4, 126.0, 113.3, 110.2, 99.7, 38.1, 38.1, 31.9, 29.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 29.1, 22.7, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{27}H_{39}NNaO_2S$ $[M+Na]^+$: 464.2594, found 464.2594.



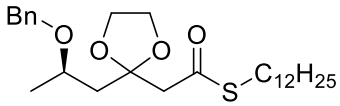
***S*-Dodecyl (*R*)-5-(benzyloxy)-3-oxohexanethioate,**

***S*-Dodecyl (*R*,*Z*)-5-(benzyloxy)-3-hydroxyhex-2-enethioate (25)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **24** (31.0 mg, 0.160 mmol) was performed with 1.5 equiv. of MAHT **1** for 2 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-ketothioester **25** (56.7 mg, 84% yield).

Keto/enol ratio = 73:27. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 5.49 (s, 0.27H), 4.57 (d, J = 11.9 Hz, 0.27H), 4.56 (d, J = 11.5 Hz, 0.73H), 4.49 (d, J = 11.9 Hz, 0.27H), 4.45 (d, J = 11.5 Hz, 0.73H), 4.09–4.00 (m, 0.73H), 3.90 (sext, J = 6.2 Hz, 0.27H), 3.67 (s, 1.46H), 2.95–2.83 (m, 2.73H), 2.61 (dd, J = 16.0, 5.0 Hz, 0.73H), 2.48 (dd, J = 13.7, 6.9 Hz, 0.27H), 2.24 (dd, J = 13.7, 5.5 Hz, 0.27H), 1.66–1.52 (m, 2H), 1.43–1.16 (m, 21H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.8, 194.8, 192.0, 172.9, 138.3, 138.3, 128.3, 127.7, 127.6, 127.6, 127.5, 101.1, 72.2, 71.3, 70.8, 70.8, 58.4, 50.1, 42.4, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2,

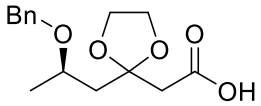
29.1, 29.0, 28.8, 28.8, 28.1, 22.7, 19.9, 19.7, 14.1; **HRMS** (MALDI-TOF, matrix: dithranol) *m*/*z*: calculated for $C_{25}H_{40}NaO_3S$ $[M+Na]^+$: 443.2590, found 443.2576.



***S*-Dodecyl (*R*)-2-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)ethanethioate (26)**

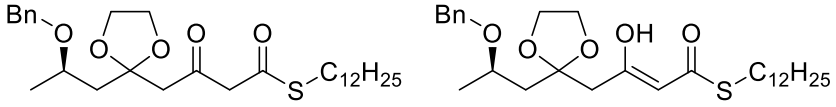
To a solution of β-ketothioester **25** (264.8 mg, 0.6295 mmol) and ethylenedioxybis(trimethylsilane) (773 μL, 3.15 mmol) in dichloromethane (3148 μL), *tert*-butyldimethylsilyl trifluoromethanesulfonate (145 μL, 0.631 mmol) was added at 0 °C. After stirring the solution for 4 h at this temperature, 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 plates (eluent: hexanes/ethyl acetate = 9:1) afforded thioester **26** (226.0 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.02–3.89 (m, 4H), 3.81–3.72 (m, 1H), 2.96 (s, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.24 (dd, *J* = 14.7, 6.4 Hz, 1H), 1.86 (dd, *J* = 14.7, 5.0 Hz, 1H) 1.55 (quin, *J* = 7.6 Hz, 2H), 1.39–1.14 (m, 18H), 1.25 (d, *J* = 6.0 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.3, 138.8, 128.3, 127.7, 127.3, 108.4, 71.3, 70.2, 64.9, 51.4, 44.5, 31.9 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 22.7, 20.8, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{27}H_{44}NaO_4S$ $[M+Na]^+$: 487.2853, found 487.2849.



(*R*)-2-(2-(2-(Benzyloxy)propyl)-1,3-dioxolan-2-yl)acetic acid (27)

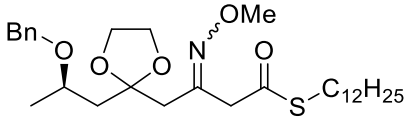
Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 30 min without additional hydrogen peroxide. The reaction of thioester **26** (275 mg, 0.592 mmol) afforded crude product (164.2 mg) containing carboxylic acid **27**, which was used for the next reaction without further purification.



***S*-Dodecyl (*R*)-4-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-3-oxobutanethioate,**
***S*-Dodecyl (*R*,*Z*)-4-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-3-hydroxybut-2-enethioate (28)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **27** (obtained from 0.592 mmol of **26**) was performed with 1.5 equiv. of MAHT **1** for 3 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-ketothioester **28**.

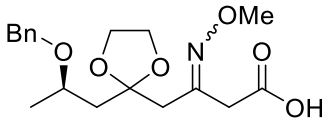
Keto/enol ratio = 68:32. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.21 (m, 5H), 5.49 (s, 0.32H), 4.59–4.39 (m, 2H), 4.04–3.82 (m, 4H), 3.82–3.70 (m, 1H), 3.62 (s, 1.36H), 2.98–2.83 (m, 3.32H), 2.56 (d, *J* = 14.2 Hz, 0.32H), 2.52 (d, *J* = 14.2 Hz, 0.32H), 2.17 (dd, *J* =14.7, 6.9 Hz, 0.32H), 2.14 (dd, *J* = 14.7, 7.3 Hz, 0.68H), 1.80 (dd, *J* = 14.7, 4.6 Hz, 0.32H), 1.76 (dd, *J* = 14.7, 4.1 Hz, 0.68H), 1.63–1.51 (m, 2H), 1.43–1.10 (m, 21H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 199.3, 194.7, 192.2, 171.2, 138.7, 138.7, 128.3, 128.2, 128.0, 127.7, 127.5, 127.4, 109.1, 108.6, 102.3, 71.5, 71.4, 70.3, 65.0, 64.9, 64.7, 64.6, 58.6, 50.2, 44.4, 44.2, 43.3, 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 29.1, 29.1, 28.9, 28.8, 28.2, 22.7, 20.8, 20.6, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{29}H_{46}NaO_5S$ $[M+Na]^+$: 529.2958, found 529.2961.



***S*-Dodecyl (*R*)-4-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-3-(methoxyimino)butanethioate (29)**

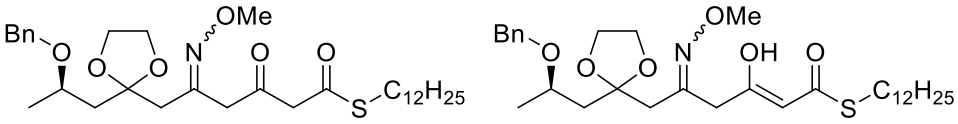
Synthesized according to the general procedure for *O*-methyloximation. The reaction of β-ketothioester **28** (obtained from 0.592 mmol of **26**) was performed for 2.5 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 4:1) afforded β-methoxyiminothioester **29** (227.7 mg, 72% yield from **26**).

Diastereomeric ratio = 70:30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 4.53 (d, *J* = 11.5 Hz, 0.70H), 4.52 (d, *J* = 11.5 Hz, 0.30H), 4.47 (d, *J* = 11.9 Hz, 0.70H), 4.47 (d, *J* = 11.9 Hz, 0.30H), 3.99–3.83 (m, 4H), 3.86 (s, 3H), 3.80–3.66 (m, 2.40H), 3.59 (s, 0.60H), 2.88 (d, *J* = 13.7 Hz, 0.30H), 2.86 (t, *J* = 7.3 Hz, 0.60H), 2.86 (t, *J* = 7.3 Hz, 1.40H), 2.81 (d, *J* = 13.7 Hz, 0.30H), 2.69 (d, *J* = 14.2Hz, 0.70H), 2.63 (d, *J* = 14.2 Hz, 0.70H), 2.10 (dd, *J* = 14.7, 5.5 Hz, 0.70H), 2.07 (dd, *J* = 15.1, 5.5 Hz, 0.30H), 1.77 (dd, *J* = 14.7, 5.5 Hz, 0.70H), 1.75 (dd, *J* = 15.1, 5.5 Hz, 0.30H), 1.55 (quin, *J* = 7.2 Hz, 2H), 1.39–1.14 (m, 18H), 1.23 (d, *J* = 6.4 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 195.9, 194.2, 151.0, 150.1, 138.9, 138.9, 128.3, 127.7, 127.3, 109.7, 109.5, 71.3, 71.2, 70.3, 70.2, 64.7, 64.6, 64.6, 64.5, 61.6, 61.6, 48.9, 44.0, 44.0, 43.3, 41.8, 31.9, 29.6, 29.6, 29.5, 29.3, 29.1, 29.1, 22.7, 21.2, 21.1, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{30}H_{49}NNaO_5S$ $[M+Na]^+$: 558.3224, found 558.3225.



(*R*)-4-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-3-(methoxyimino)butanoic acid (30)

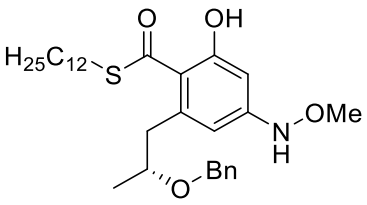
Synthesized according to the general procedure for hydrolysis of a thioester. The reaction was performed for 30 min without additional hydrogen peroxide. The reaction of thioester **29** (51.7 mg, 96.5 μmol) afforded crude product (50.9 mg) containing carboxylic acid **30**, which was used for the next reaction without further purification.



***S*-Dodecyl (*R*)-6-(2-(2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-5-(methoxyimino)-3-oxohexanethioate, *S*-Dodecyl (2*Z*)-6-(2-((*R*)-2-(benzyloxy)propyl)-1,3-dioxolan-2-yl)-3-hydroxy-5-(methoxyimino)hex-2-enethioate (31)**

Synthesized according to the general procedure for decarboxylative condensation. The reaction of carboxylic acid **30** (obtained from 96.5 μmol of **29**) was performed with 1.6 equiv. of MAHT **1** for 3 h. Purification by preparative TLC on silica gel plates (eluent: hexanes/ethyl acetate = 7:3) afforded β-ketothioester **31** (40.3 mg, 72% from **29**).

Keto/enol ratio = 88:12. Diastereomeric ratio = 70:30 (keto) and 55:45 (enol). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37–7.30 (m, 4H), 7.29–7.24 (m, 1H), 5.48 (s, 0.05H), 5.42 (s, 0.07H), 4.53 (d, *J* = 11.7 Hz, 0.7H), 4.52 (d, *J* = 11.0 Hz, 0.3H), 4.47 (d, *J* = 11.7 Hz, 0.7H), 4.46 (d, *J* = 11.7 Hz, 0.3H), 3.96–3.79 (m, 7H), 3.78–3.66 (m, 2.76H), 3.60 (s, 1.23H), 3.54 (s, 0.53H), 3.42 (d, *J* = 15.2 Hz, 0.07H), 3.38 (d, *J* = 15.2 Hz, 0.07H), 3.22 (d, J = 15.5 Hz, 0.05H), 3.19 (d, J = 15.2 Hz, 0.05H), 2.91 (t, J =7.2 Hz, 1.4H), 2.90 (t, J =7.6 Hz, 0.6H), 2.87–2.75 (m, 0.6H), 2.68–2.56 (m, 1.4H), 2.14–1.99 (m, 1H), 1.80–1.69 (m, 1H), 1.58 (quin, *J* = 7.6 Hz, 1.4H), 1.57 (quin, *J* = 7.6 Hz, 0.6H), 1.40–1.18 (m, 21H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 198.6, 196.8, 194.9, 192.0, 191.8, 171.7, 170.9, 152.0, 151.1, 150.9, 150.9, 138.8, 138.8, 128.8, 128.3, 128.2, 127.7, 127.3, 109.7, 109.5, 109.5, 100.8, 100.2, 71.4, 71.4, 71.3, 71.3, 71.2, 70.3, 70.2, 64.7, 64.7, 64.6, 64.5, 64.5, 64.4, 61.7, 61.5, 57.2, 57.0, 48.3, 44.2, 44.0, 43.8, 43.6, 43.3, 43.3, 42.0, 41.4, 40.1, 38.2, 35.1, 34.8, 34.0, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.0, 28.8, 28.2, 28.2, 22.6, 21.2, 21.1, 21.1, 21.0, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{32}H_{51}NNaO_6S$ $[M+Na]^+$: 600.3329, found 600.3329.

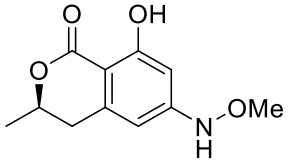


***S*-Dodecyl (*R*)-2-(2-(benzyloxy)propyl)-6-hydroxy-4-(methoxyamino)benzothioate (32)**

To a solution of β-ketothioester **31** (35.0 mg, 61.1 μmol) in acetone (1200 μL), *p*-toluenesulfonic acid monohydrate (35.6 mg, 0.187 mmol) was added. After stirring the mixture for 6 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 dissolved in dichloromethane (600 μL), and triethylamine (40 μL, 0.29 mmol) was added. After stirring the solution 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 preparative TLC on silica gel plates (eluent: chloroform/acetonitrile = 93:7) to afford benzothioate **32** (17.4 mg, 55% yield) as a colorless oil.

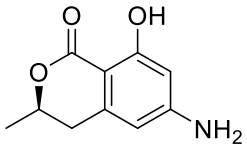
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.36–7.14 (m, 5H), 7.08 (s, 1H), 6.40 (d, J = 1.8 Hz, 1H), 6.26 (d, J = 2.3 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.34 (d, J = 11.9 Hz, 1H), 3.86–3.76 (m 1H), 3.73 (s, 3H), 3.28 (dd, J = 14.7, 5.5 Hz, 1H), 3.23 (dd, J = 14.7, 7.8 Hz, 1H), 3.02 (td, J = 7.1, 1.6 Hz, 2H), 1.64 (quin, J = 7.4 Hz, 2H), 1.47–1.14 (m, 18H), 1.22 (d, J = 6.0 Hz, 3H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 196.4, 161.2, 152.5, 141.2, 138.6, 128.2, 127.6, 127.4, 116.5, 109.3, 99.1, 75.9, 71.0, 63.5, 43.2, 31.9, 30.0, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 22.7, 19.9, 14.1; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{30}H_{45}NNaO_4S$ $[M+Na]^+$: 538.2962, found 538.2962.



(*R*)-8-Hydroxy-6-(methoxyamino)-3-methylisochroman-1-one (33)

To a solution of benzothioate **32** (17.2 mg, 33.3 μmol) in dichloromethane (670 μL), a 1 M dichloromethane solution of boron tribromide (100 μL, 0.100 mmol) was added at –78 °C. After stirring the solution for 1 h at this temperature, water was added to quench the reaction. 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 plates (eluent: chloroform/acetonitrile = 93:7) afforded lactone **33** (5.1 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.21 (s, 1H), 6.36 (d, J = 1.8 Hz, 1H), 6.17 (s, 1H), 4.67 (d quin, J = 9.2, 6.0 Hz, 1H), 3.76 (s, 3H), 2.91–2.80 (m, 2H), 1.51 (d, J = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.8, 163.9, 155.2, 141.0, 102.7, 101.8, 98.5, 75.5, 63.7, 34.9, 20.7; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{11}H_{13}NNaO_4$ $[M+Na]^+$: 246.0737, found 246.0742.



(*R*)-6-Amino-8-hydroxy-3-methylisochroman-1-one (34)

To a solution of lactone **33** (7.1 mg, 32 μmol) in THF (750 μL), a 0.1 M THF solution of SmI_2 (400 μL, 40.0 μmol) was added in three portion (100, 100, 200 μL) under argon atmosphere. After stirring the reaction solution for 40 min, the THF solution of SmI_2 (500 μL, 50.0 μmol) was added again. After stirring the reaction mixture for additional 1 h, water was added. The resulting mixture was extracted with ethyl acetate, 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 plates (eluent: hexanes/ethyl acetate = 2:3) to afford lactone **34** (4.3 mg, 70% yield) as a pale orange solid. The enantiomeric ratio was determined by HPLC analysis (Chiralcel OJ-H, hexane/2-propanol = 50:50, 0.8 mL min^{-1}): t_R = 34.1 min (minor) and 50.1 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.20 (s, 1H), 6.07 (d, *J* = 1.8 Hz, 1H), 5.95 (s, 1H), 4.68–4.58 (m, 1H), 4.19 (broad s, 2H), 2.81 (dd, *J* = 16.0, 10.1 Hz, 1H), 2.76 (dd, *J* = 16.0, 4.1 Hz, 1H), 1.49 (d, *J* = 6.0 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.9, 164.2, 153.6, 141.4, 104.9, 99.3, 75.2, 34.9, 20.8; **HRMS** (MALDI-TOF, matrix: 4-chloro-α-cyanocinnamic acid) *m*/*z*: calculated for $C_{10}H_{11}NNaO_3$ $[M+Na]^+$: 216.0631, found 216.0631.

References

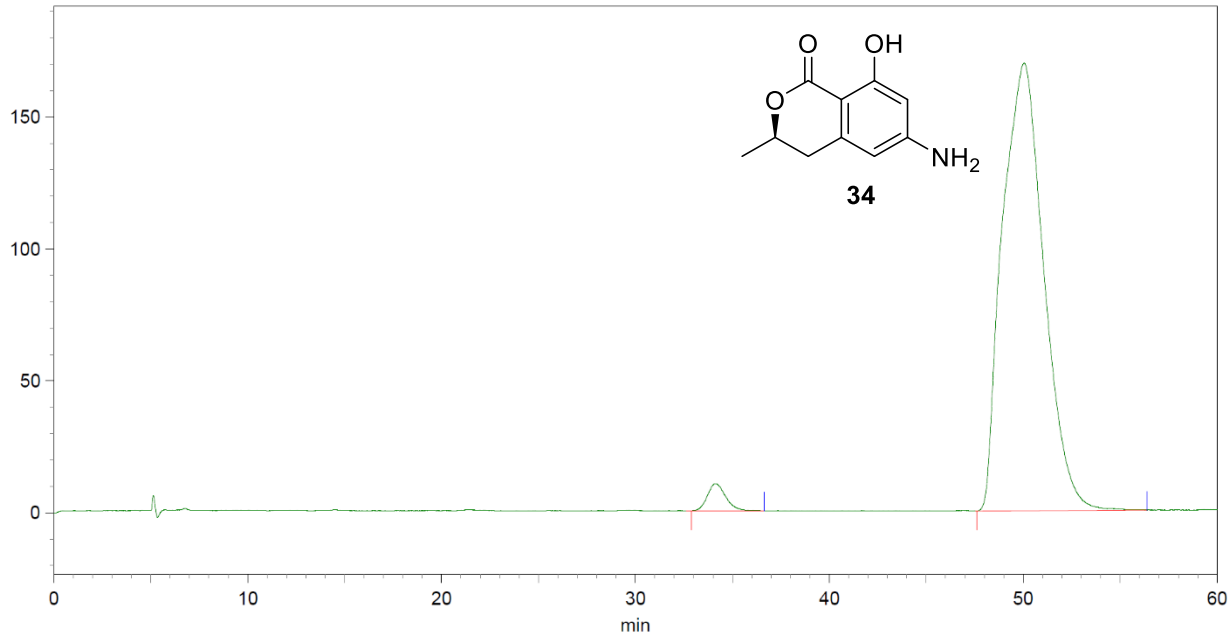
(1) K. Akagawa and K. Kudo, *Chem. Commun.*, 2017, **53**, 8645.

(2) H. Liu, Y. Zhang, R. Wei, G. Andolina and X. Li, *J. Am. Chem. Soc.*, 2017, **139**, 13420.

(3) H. C. Tseng, C. H. Martin, D. R. Nielsen and K. L. J. Prather, *Appl. Environ. Microbiol.*, 2009, **75**, 3137.

HPLC trace for 6-aminomellein **34**

Chiralcel OJ-H column, hexane/2-propanol = 50:50, 0.8 mL min^{-1}

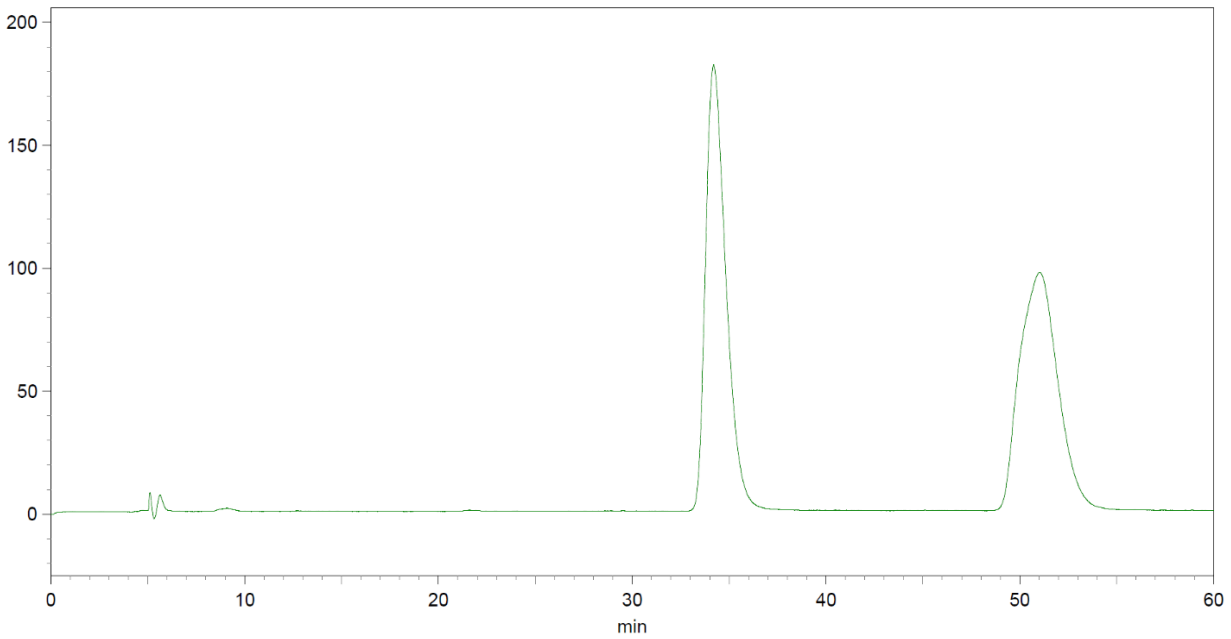


1: 320 nm, 8 nm

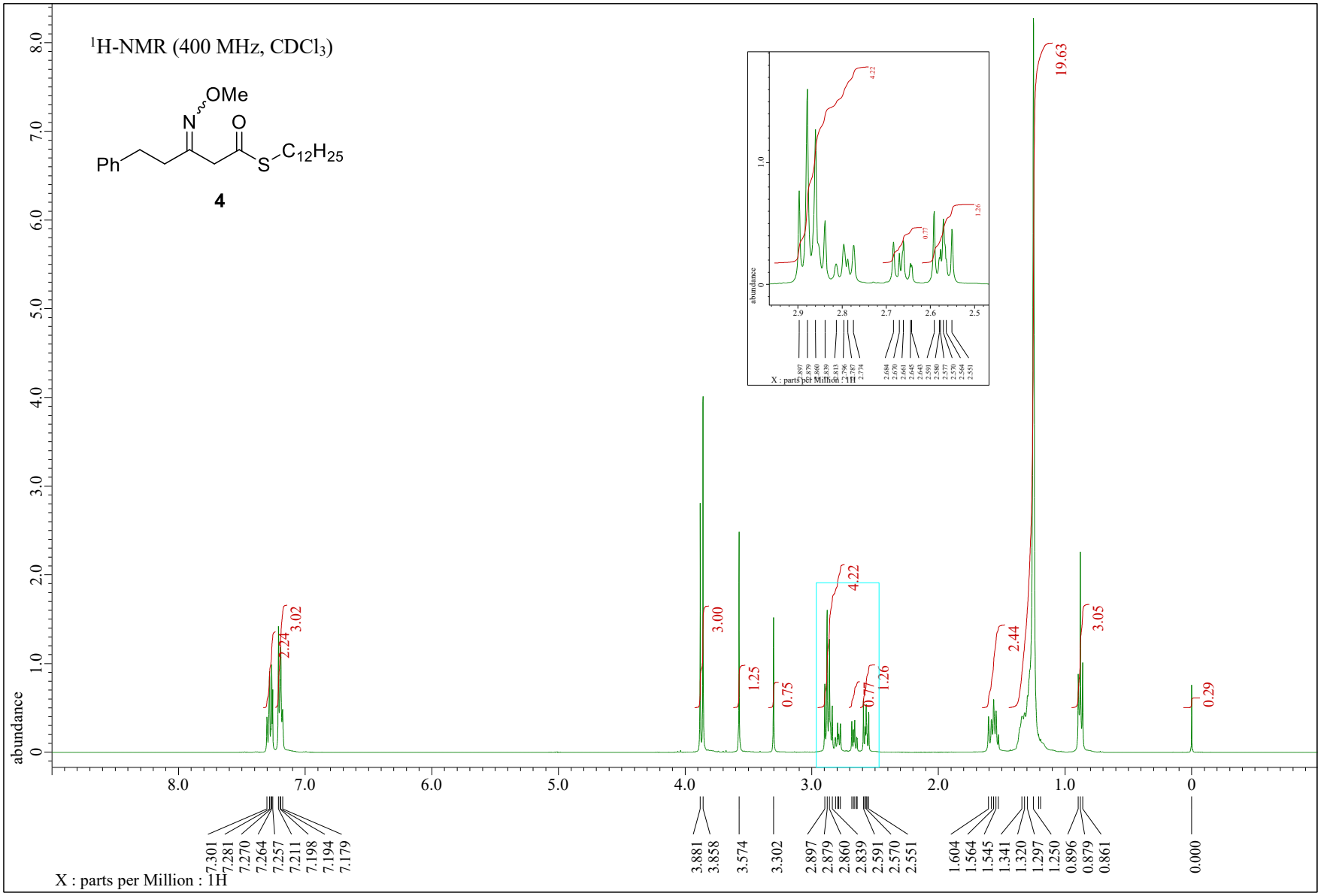
retention time	area	area%
34.147	673696	2.61
50.050	25171308	97.39

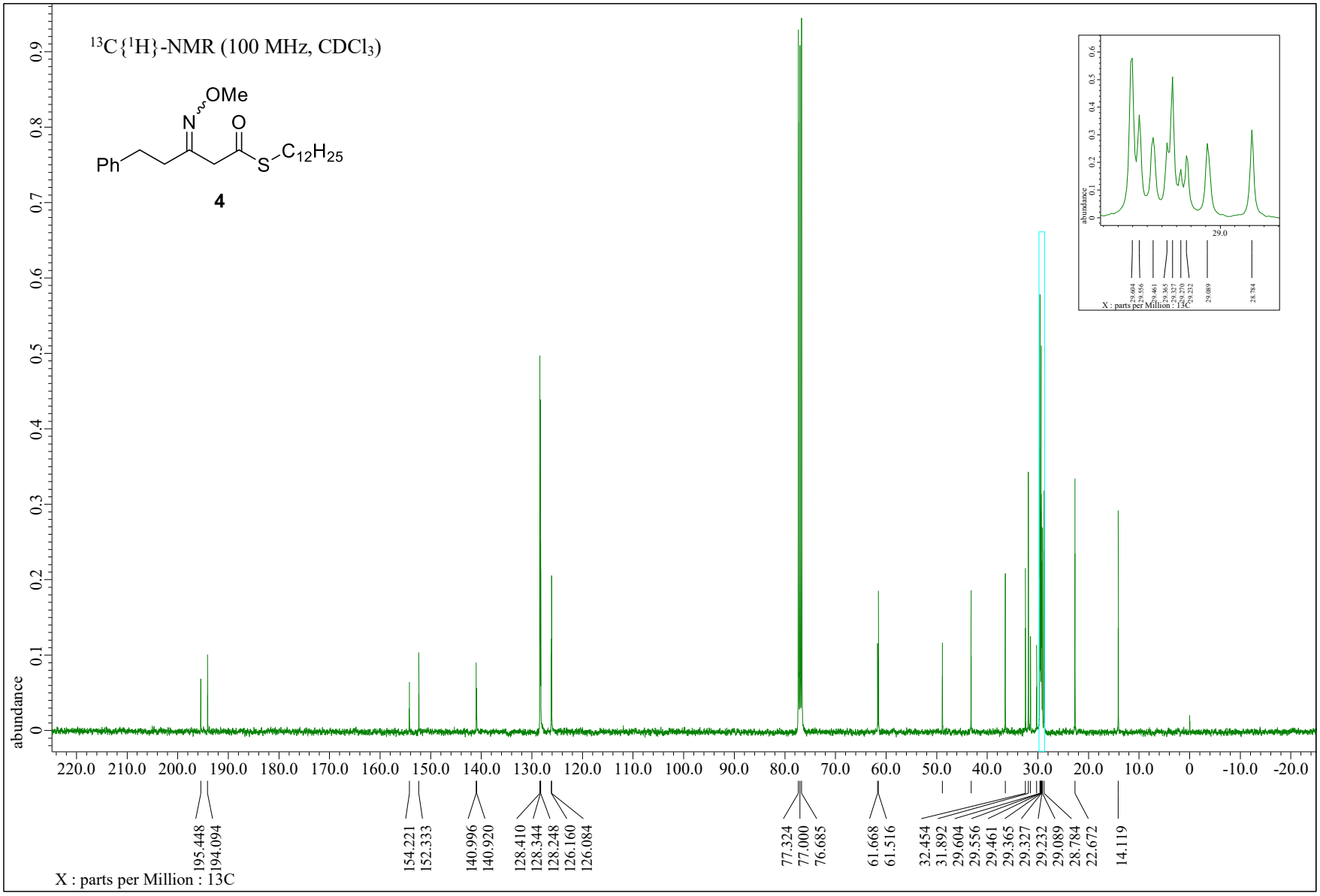
Total	25845004	100.00

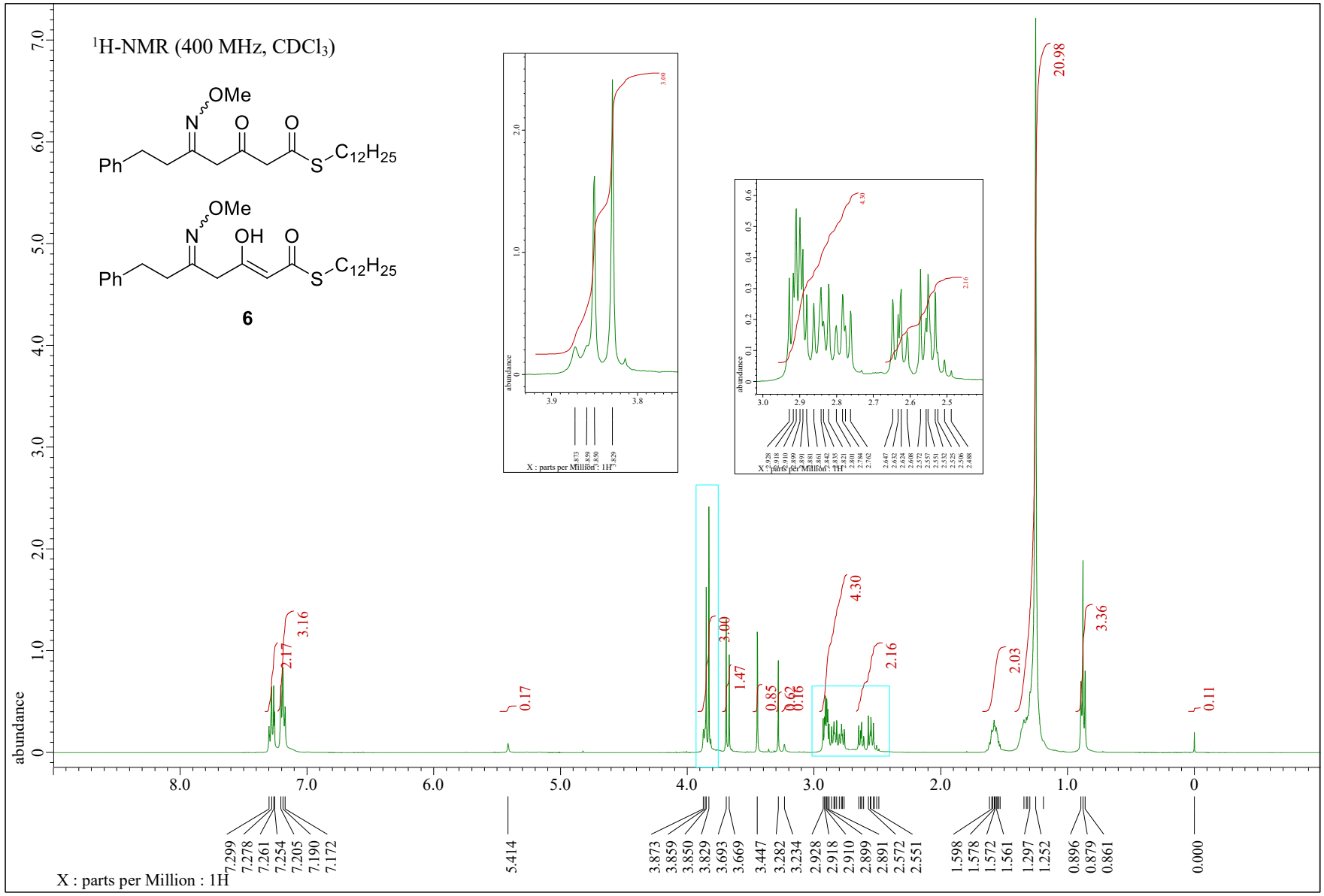
racemic sample

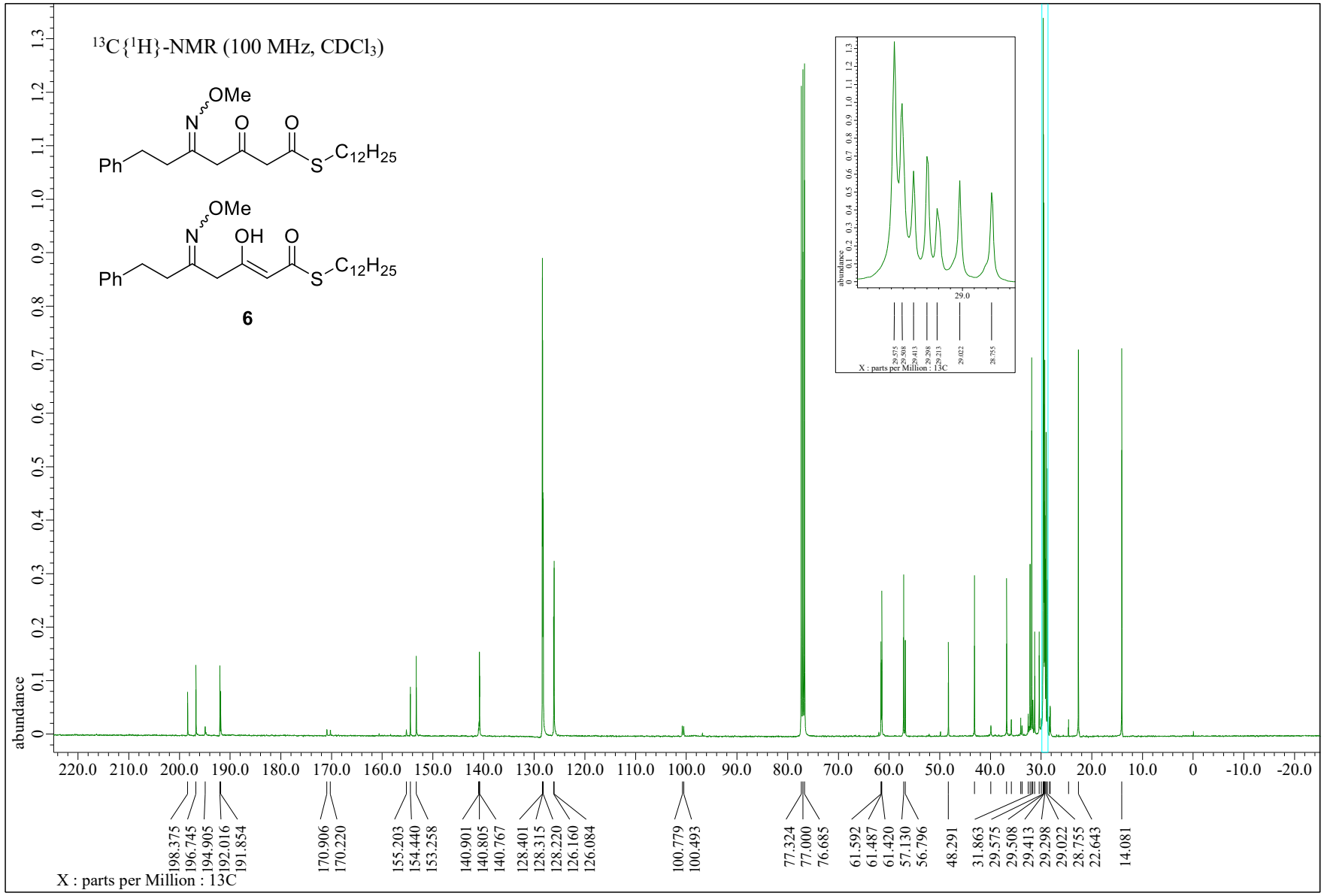


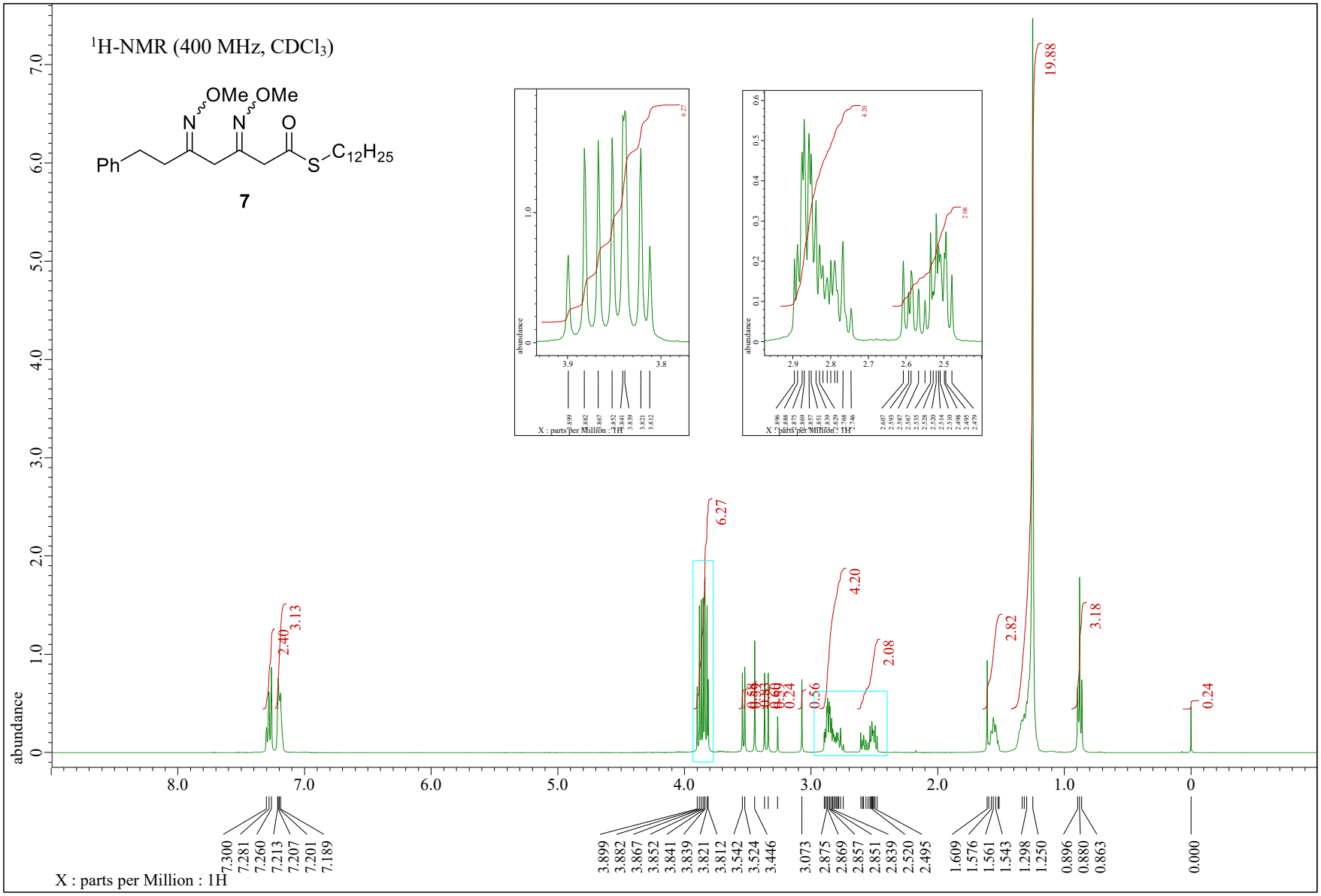
Copies of ^{1}H and ^{13}C NMR spectra

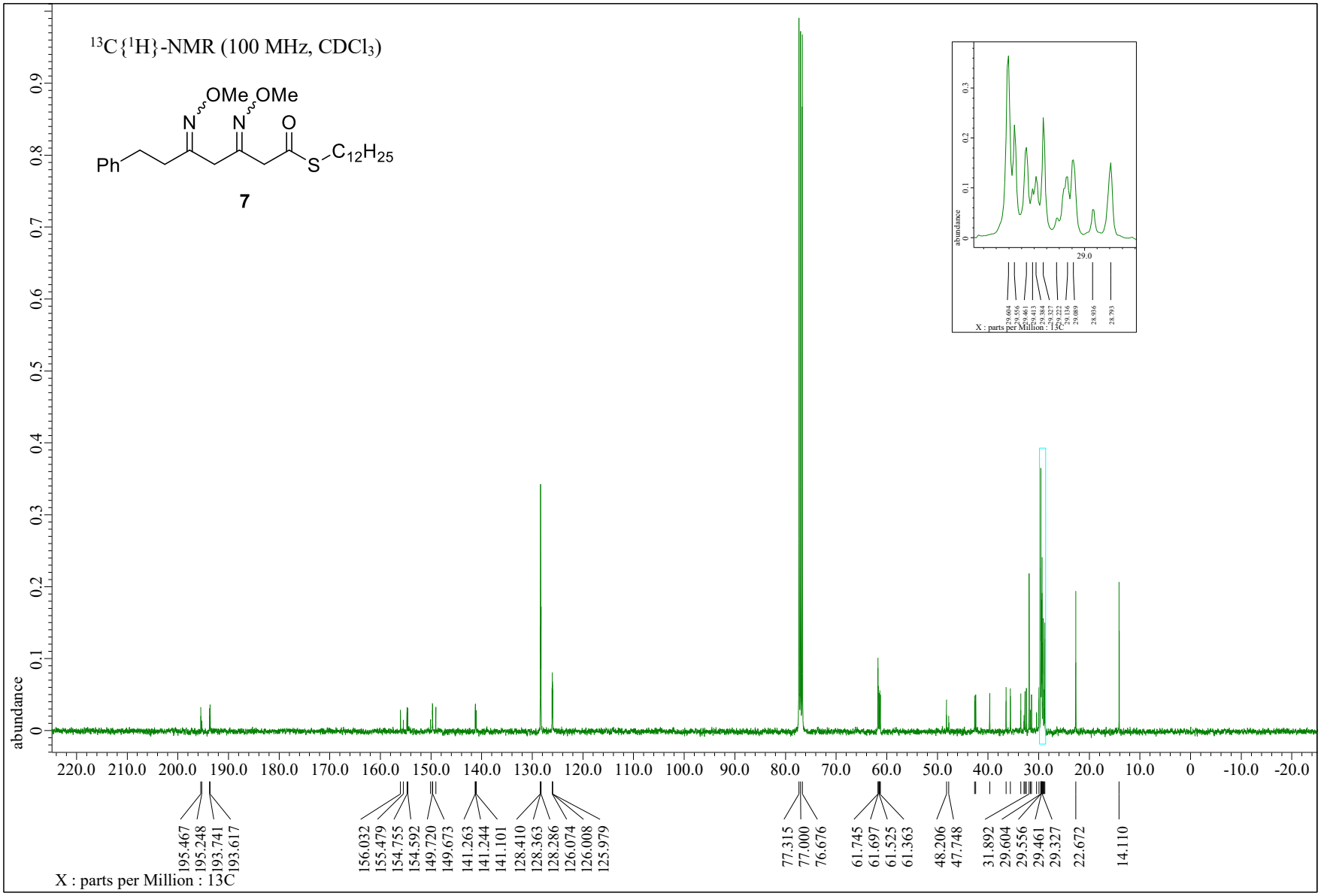


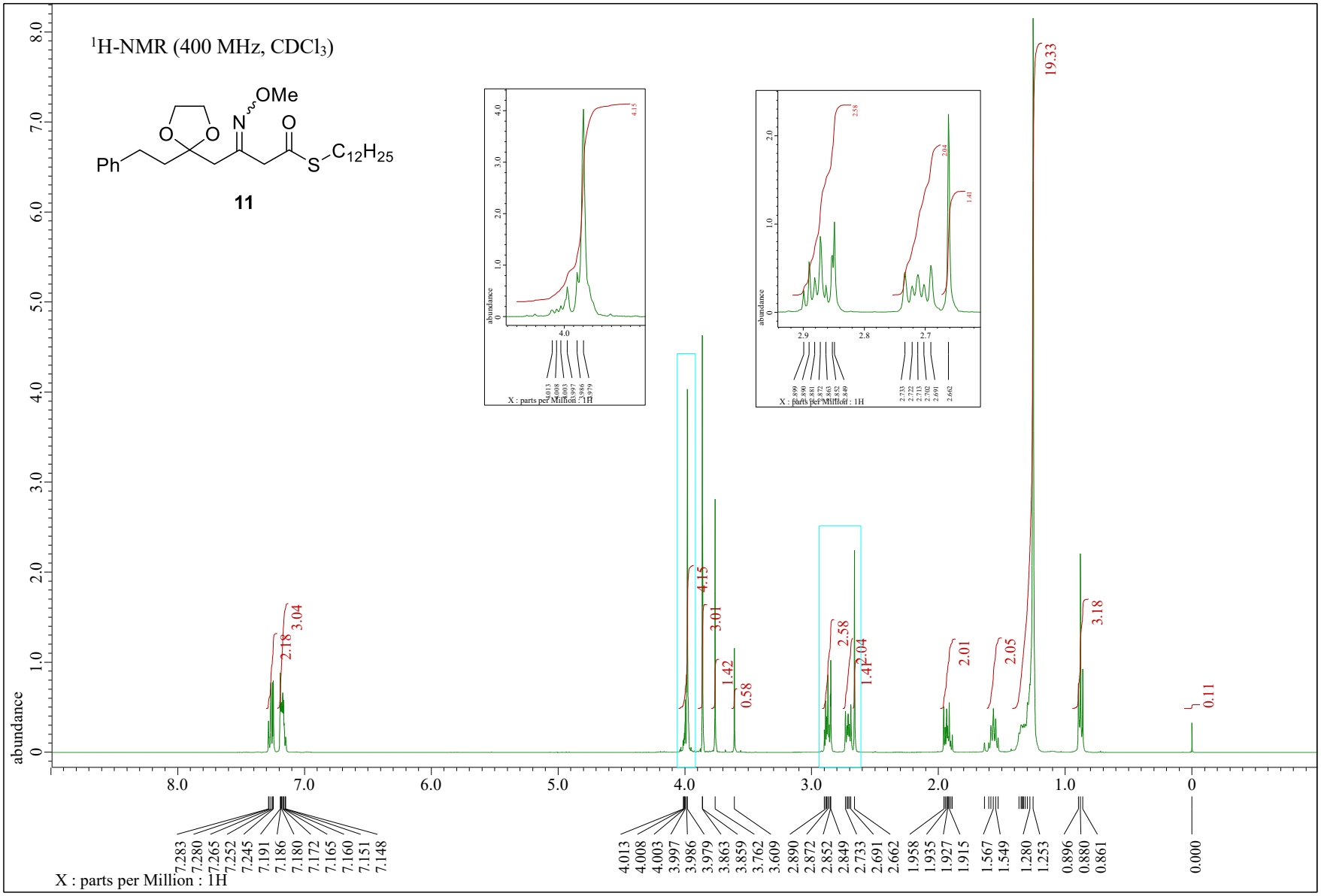

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe
N
O
Ph
S
$C_{12}H_{25}$
4
abundance
X : parts per Million : 13C
195.448
194.094
154.221
152.333
140.996
140.920
128.410
128.344
128.248
126.160
126.084
77.324
77.000
76.685
61.668
61.516
32.454
31.892
29.604
29.556
29.461
29.365
29.327
29.232
29.089
28.784
22.672
14.119

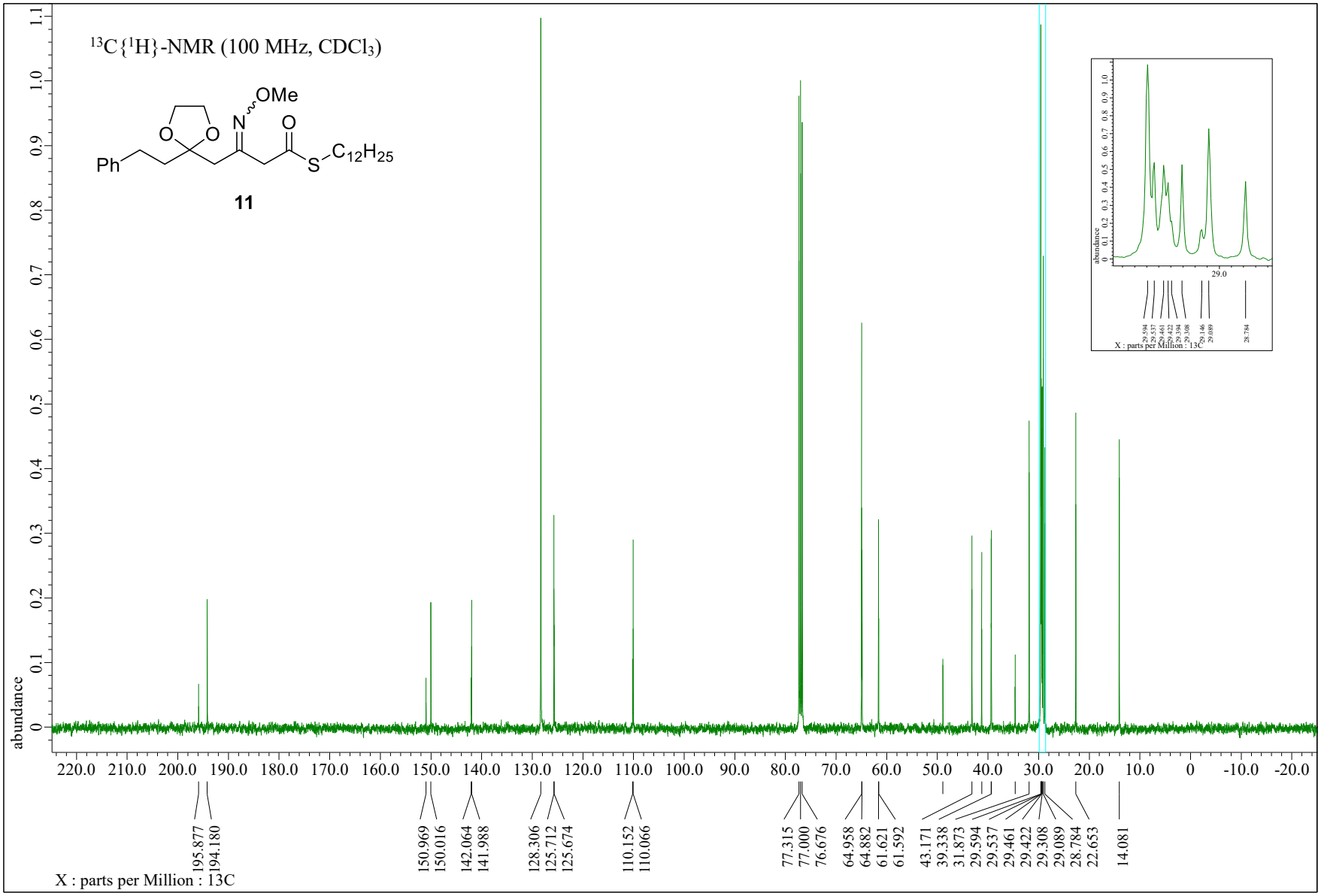

^{1}H-NMR (400 MHz, $CDCl_3$)
OMe
N
O
O
Ph
S
$C_{12}H_{25}$
OMe
N
OH
O
Ph
S
$C_{12}H_{25}$
6
abundance
X : parts per Million : 1H
20.98
4.30
3.36
3.16
3.00
2.17
2.16
2.03
1.47
0.85
0.62
0.17
0.11
7.299
7.278
7.261
7.254
7.205
7.190
7.172
5.414
3.873
3.859
3.850
3.829
3.693
3.669
3.447
3.282
3.234
2.928
2.918
2.910
2.899
2.891
2.572
2.551
1.598
1.578
1.572
1.561
1.297
1.252
0.896
0.879
0.861
0.000

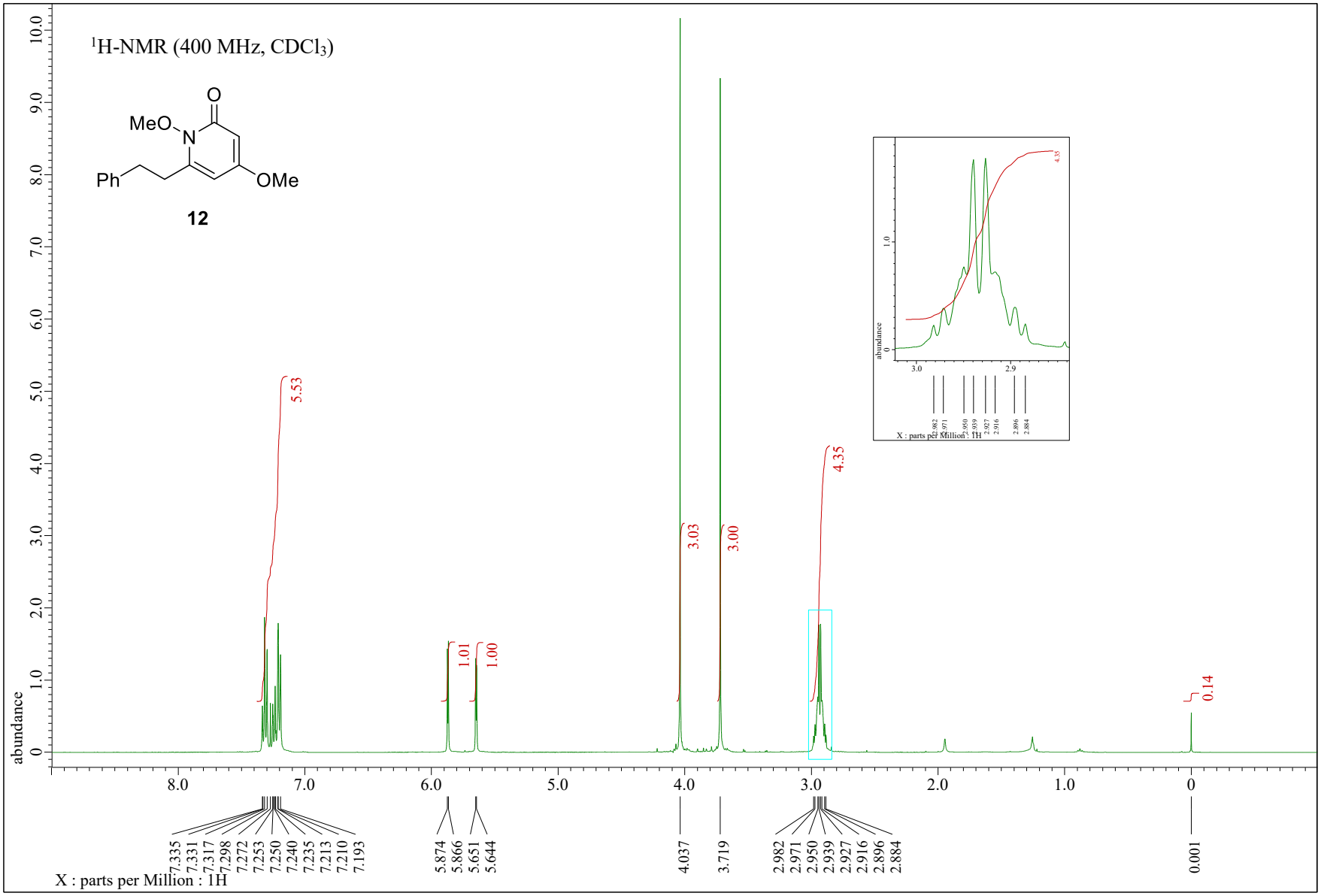

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe
N
O
O
Ph
S
$C_{12}H_{25}$
OMe
N
OH
O
Ph
S
$C_{12}H_{25}$
6
abundance
X : parts per Million : 13C
198.375
196.745
194.905
192.016
191.854
170.906
170.220
155.203
154.440
153.258
140.901
140.805
140.767
128.401
128.315
128.220
126.160
126.084
100.779
100.493
77.324
77.000
76.685
61.592
61.487
61.420
57.130
56.796
48.291
31.863
29.575
29.508
29.413
29.298
29.022
28.755
22.643
14.081

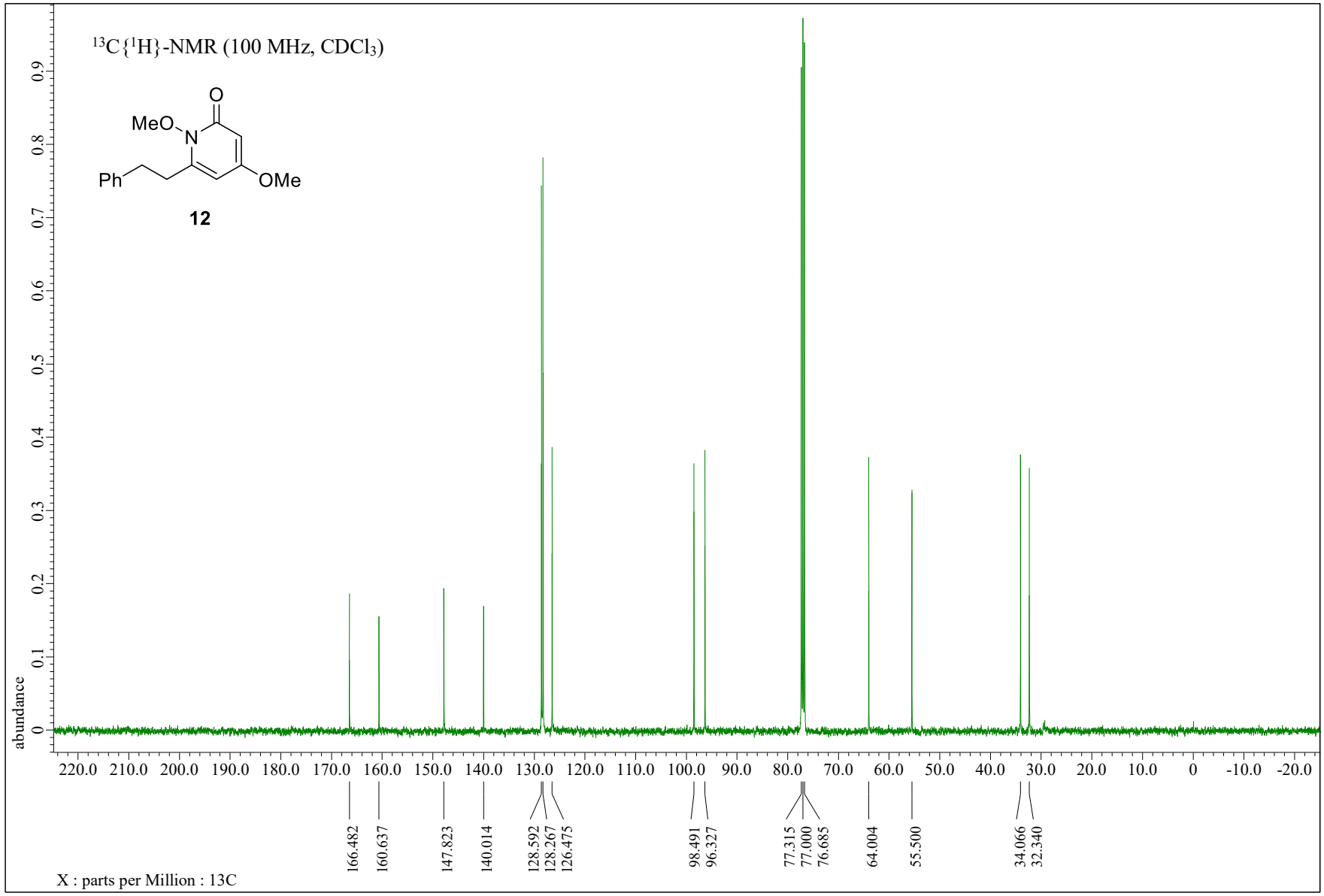

1H-NMR (400 MHz, CDCl3)
OMe OMe
N N O
Ph
S C12H25
7
abundance
X : parts per Million : 1H
19.88
6.27
4.20
3.13
2.40
2.08
2.82
3.18
0.56
0.24
0.24

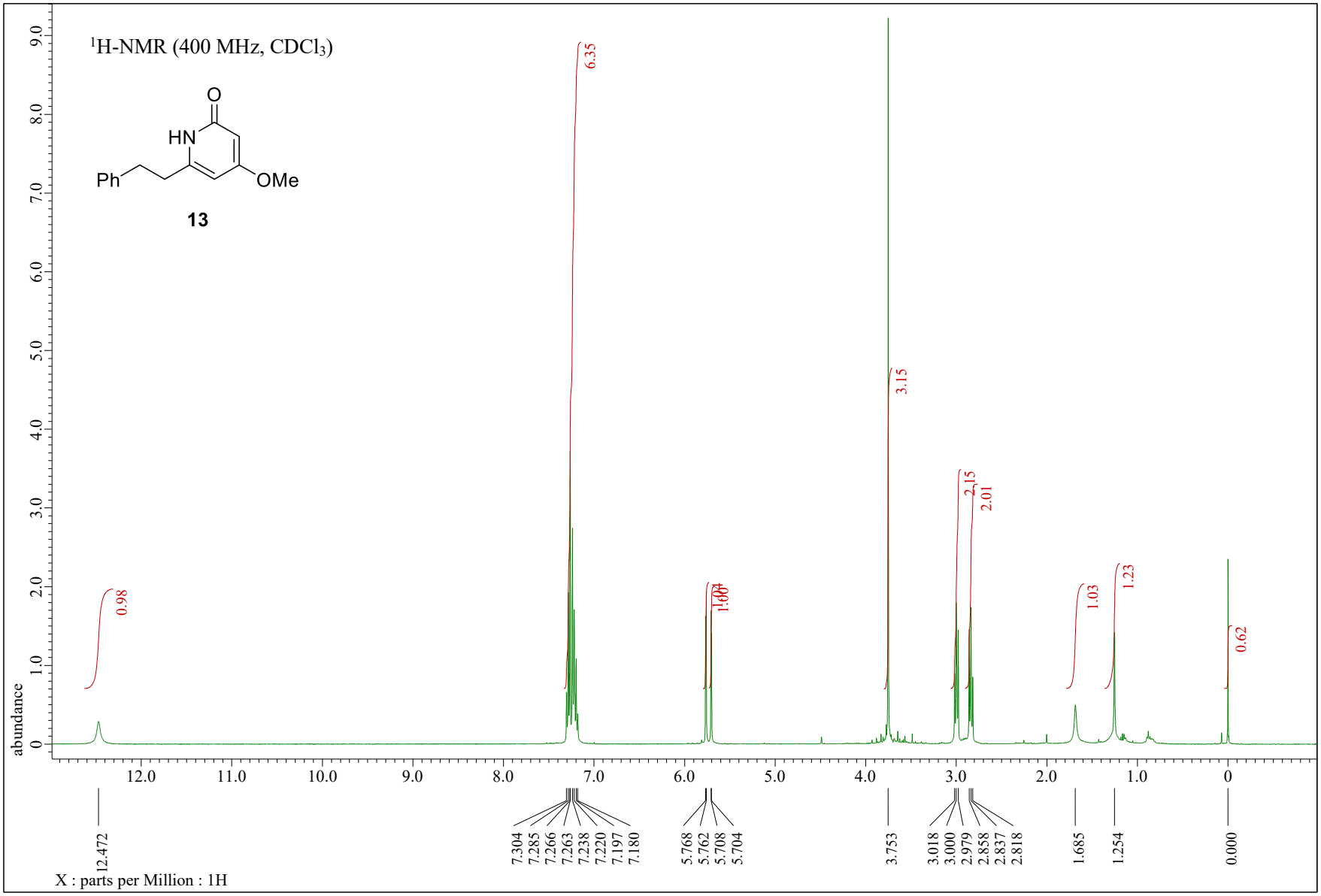

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe OMe
N N O
Ph
S $C_{12}H_{25}$
7
abundance
X : parts per Million : 13C
195.467 195.248 193.741 193.617
156.032 155.479 154.755 154.592 149.720 149.673 141.263 141.244 141.101 128.410 128.363 128.286 126.074 126.008 125.979
77.315 77.000 76.676 61.745 61.697 61.525 61.363 48.206 47.748 31.892 29.604 29.556 29.461 29.327 22.672 14.110

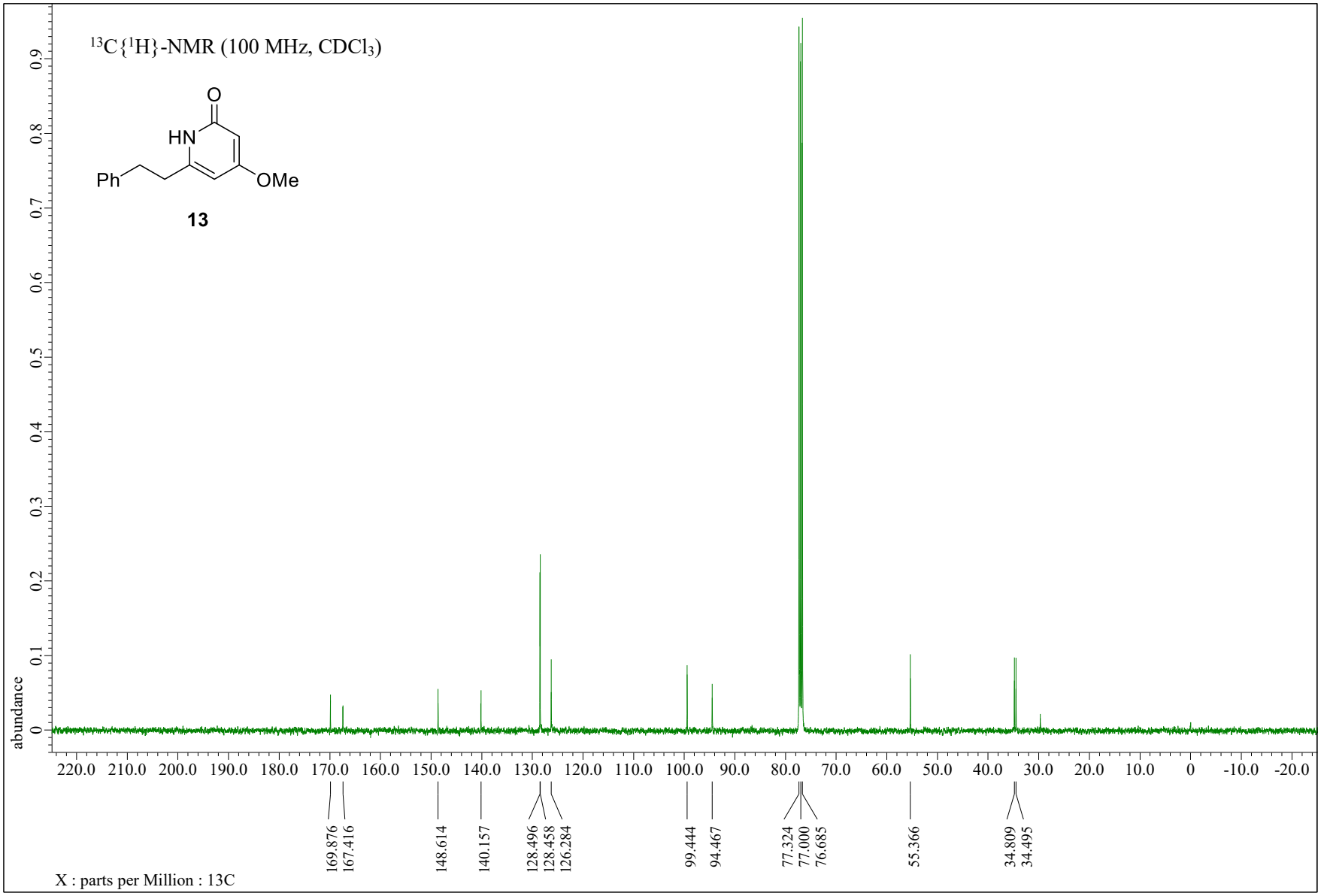

^{1}H-NMR (400 MHz, $CDCl_3$)
OMe
N
O
O
O
S
$C_{12}H_{25}$
Ph
11
abundance
X : parts per Million : 1H
19.33
4.15
3.04
3.01
3.18
2.58
2.18
2.04
2.01
2.05
1.42
1.41
0.58
0.11

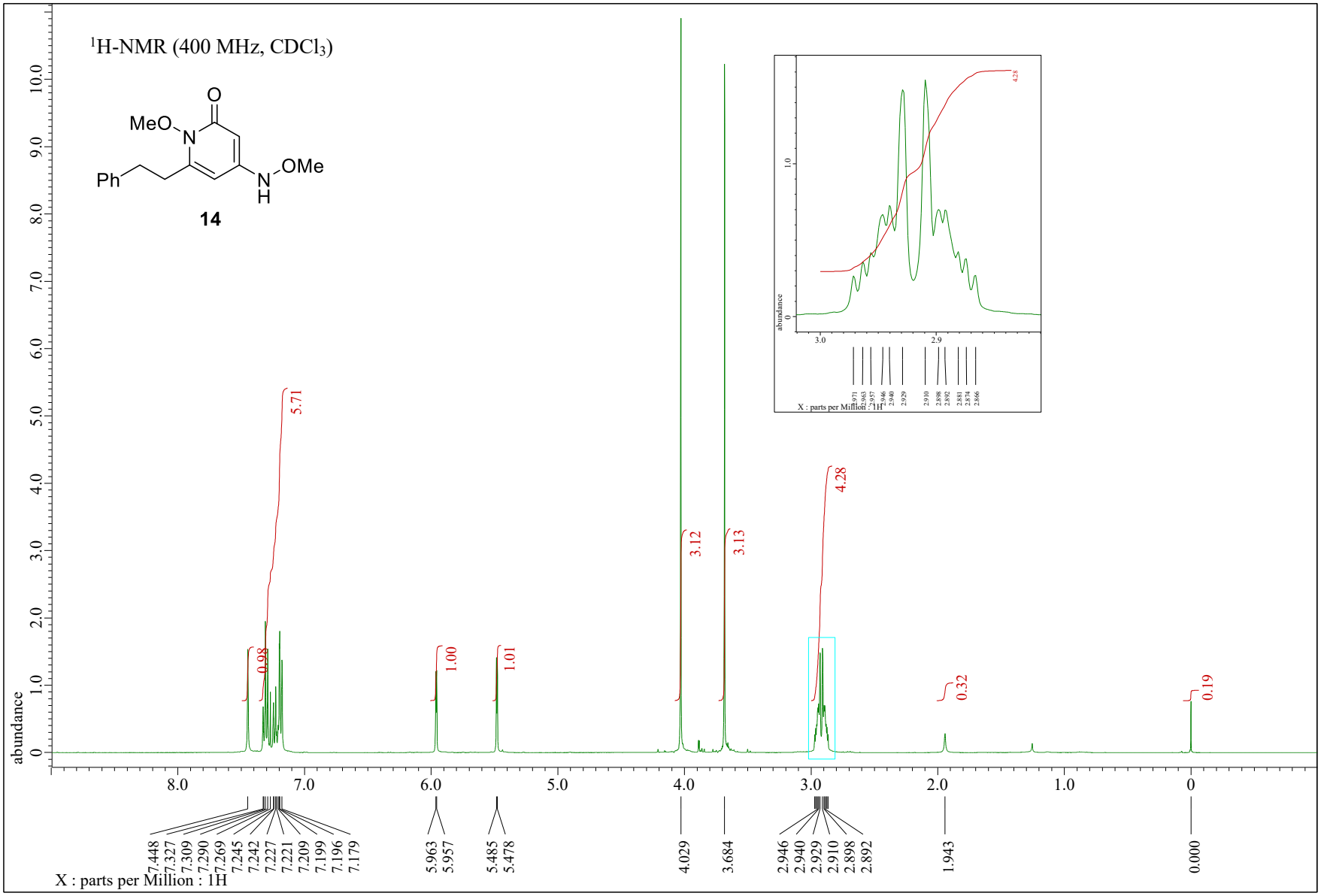

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe
N
O
O
O
Ph
S
$C_{12}H_{25}$
11
abundance
X : parts per Million : 13C
195.877
194.180
150.969
150.016
142.064
141.988
128.306
125.712
125.674
110.152
110.066
77.315
77.000
76.676
64.958
64.882
61.621
61.592
43.171
39.338
31.873
29.594
29.537
29.461
29.422
29.308
29.089
28.784
22.653
14.081

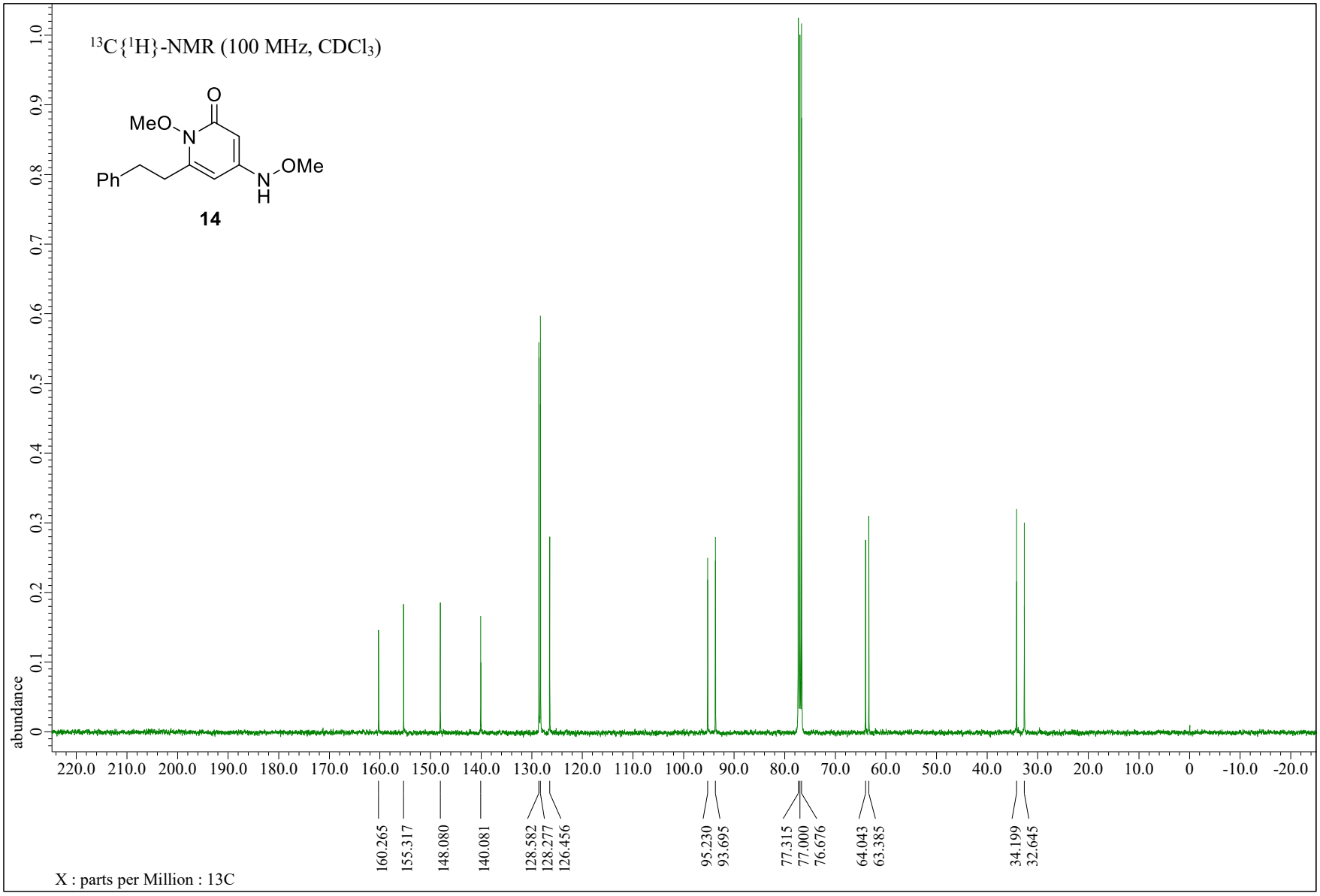

^{1}H-NMR (400 MHz, $CDCl_3$)
MeO
N
O
Ph
OMe
12
abundance
X : parts per Million : 1H
5.53
1.01
1.00
3.03
3.00
4.35
0.14
7.335
7.331
7.317
7.298
7.272
7.253
7.250
7.240
7.235
7.213
7.210
7.193
5.874
5.866
5.651
5.644
4.037
3.719
2.982
2.971
2.950
2.939
2.927
2.916
2.896
2.884
0.001

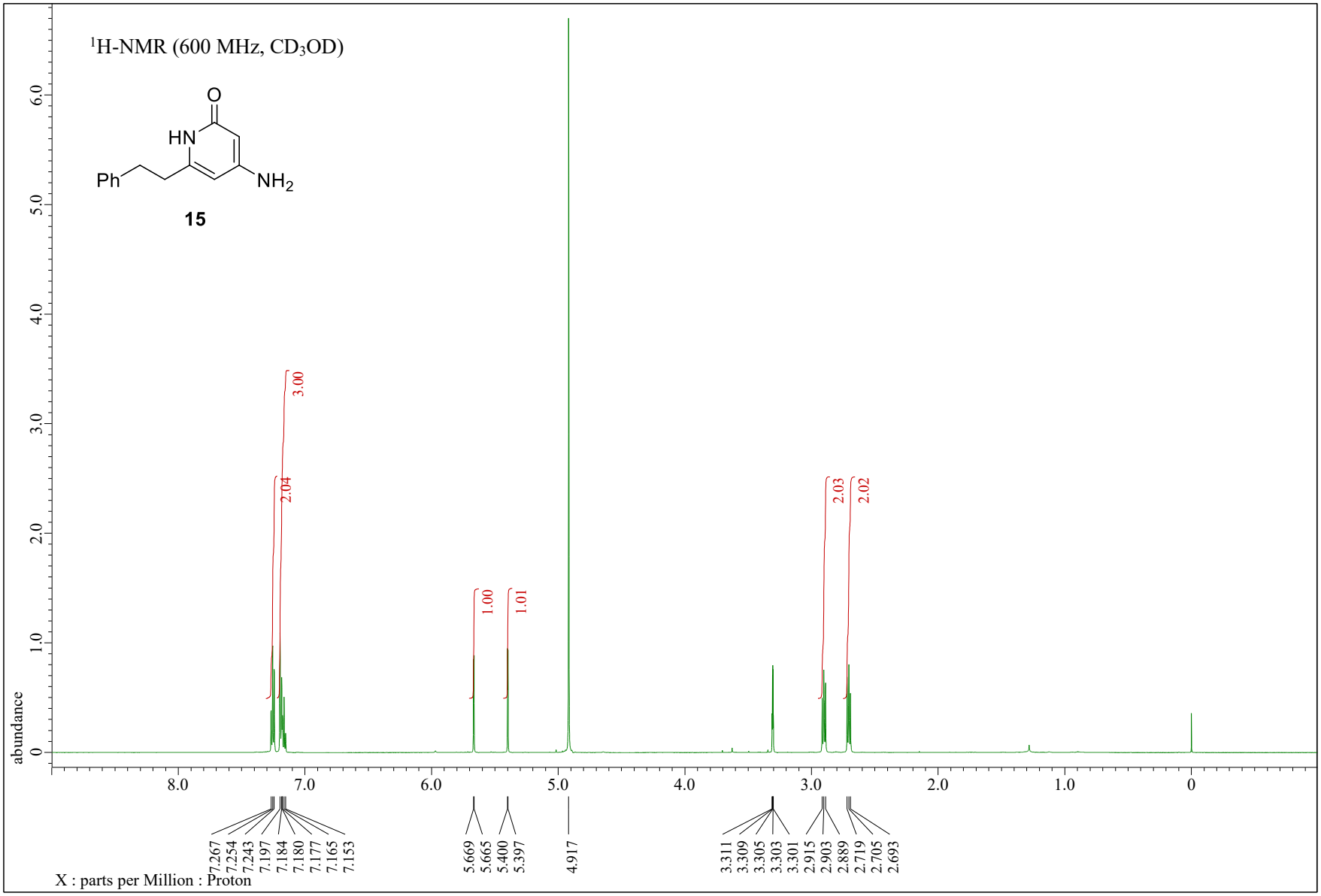

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
MeO
N
O
Ph
OMe
12
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
166.482
160.637
147.823
140.014
128.592
128.267
126.475
98.491
96.327
77.315
77.000
76.685
64.004
55.500
34.066
32.340
X : parts per Million : 13C

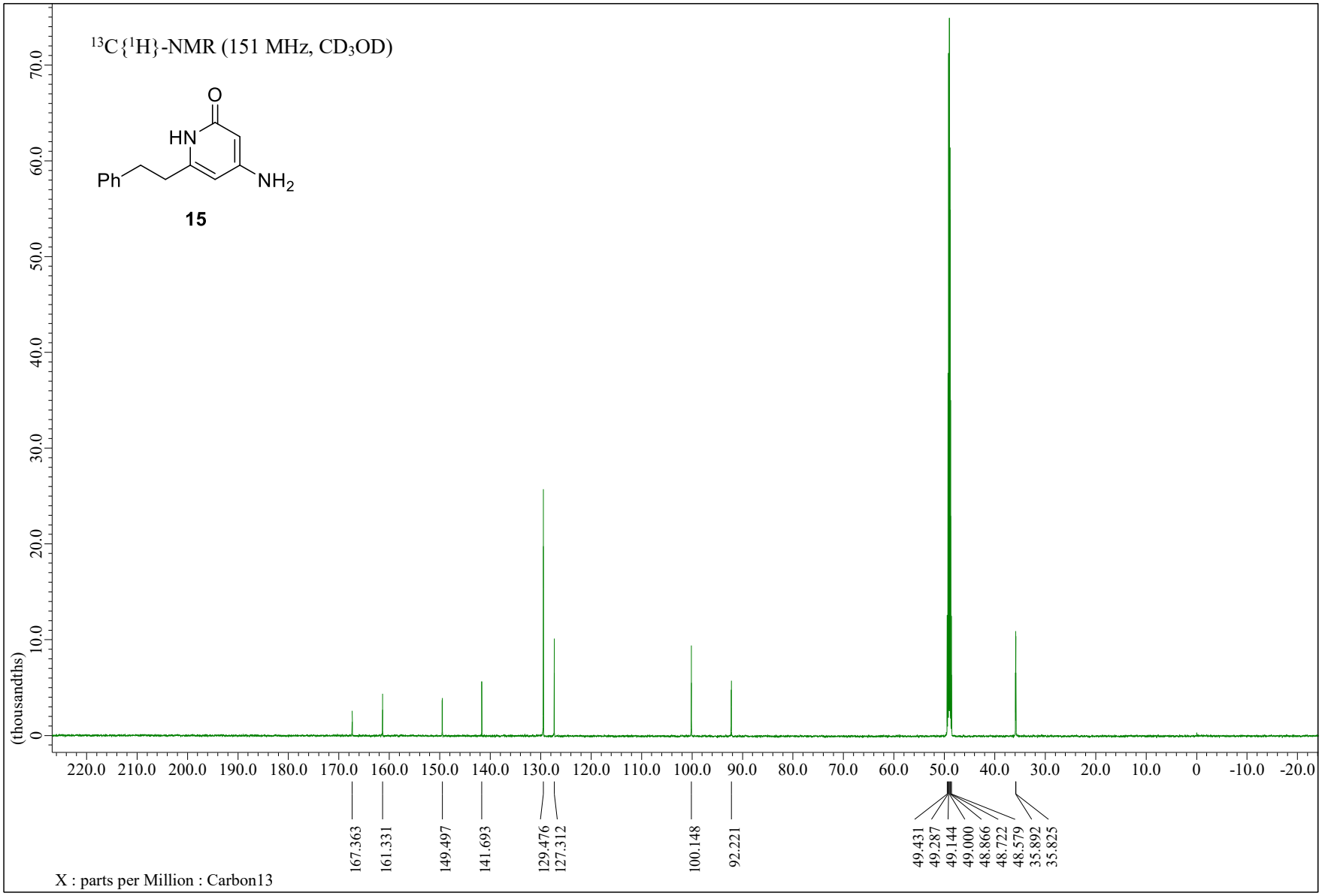

^{1}H-NMR (400 MHz, $CDCl_3$)
O
HN
Ph
OMe
13
abundance
X : parts per Million : 1H
6.35
3.15
2.15
2.01
1.03
1.23
0.98
1.00
0.62
12.472
7.304
7.285
7.266
7.263
7.238
7.220
7.197
7.180
5.768
5.762
5.708
5.704
3.753
3.018
3.000
2.979
2.858
2.837
2.818
1.685
1.254
0.000

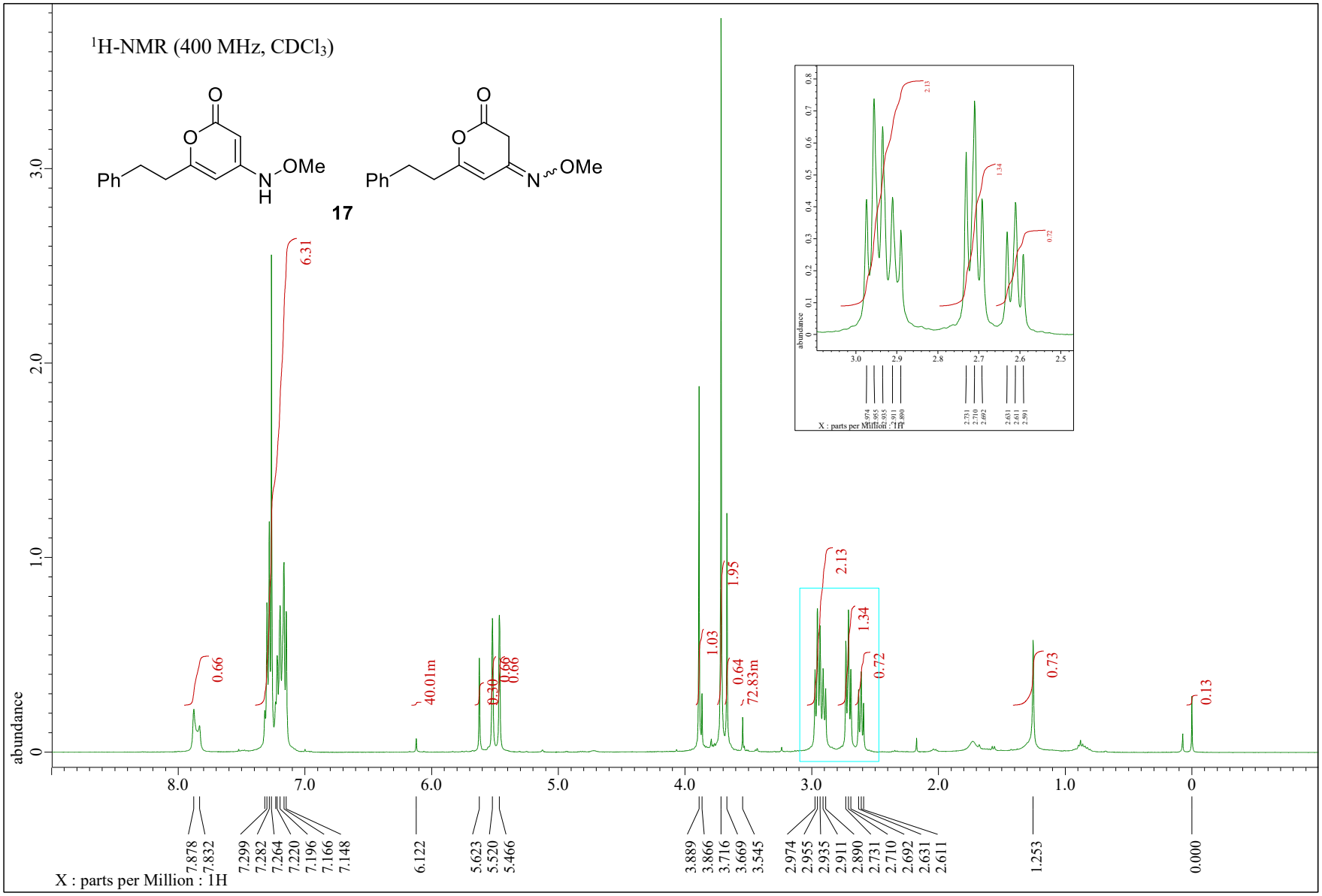

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
O
HN
Ph
OMe
13
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
169.876
167.416
148.614
140.157
128.496
128.458
126.284
99.444
94.467
77.324
77.000
76.685
55.366
34.809
34.495
X : parts per Million : 13C

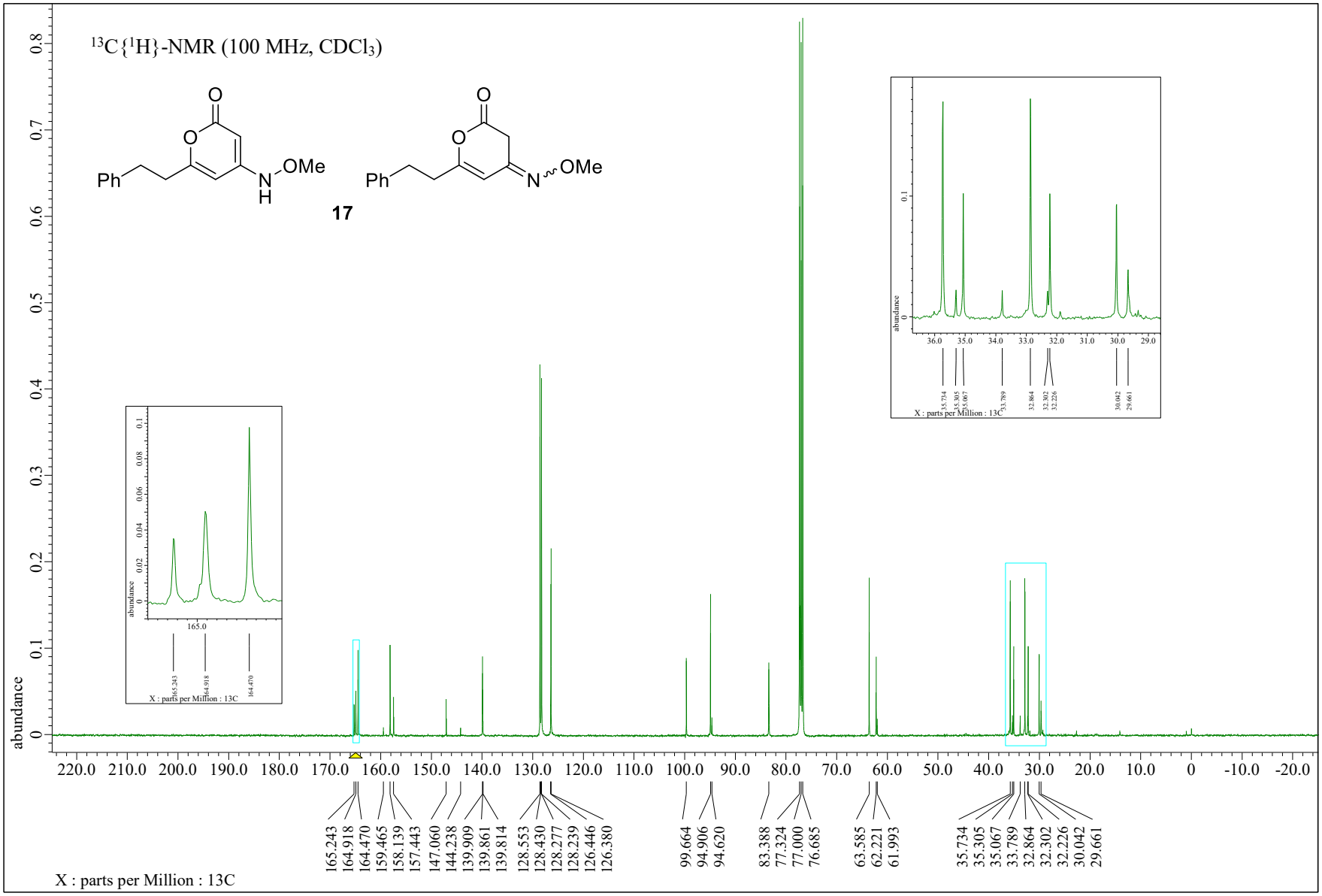

^{1}H-NMR (400 MHz, $CDCl_3$)
MeO
N
O
Ph
N
H
OMe
14
abundance
X : parts per Million : 1H
5.71
0.98
1.00
1.01
3.12
3.13
4.28
0.32
0.19
7.448
7.327
7.309
7.290
7.269
7.245
7.242
7.227
7.221
7.209
7.199
7.196
7.179
5.963
5.957
5.485
5.478
4.029
3.684
2.946
2.940
2.929
2.910
2.898
2.892
1.943
0.000

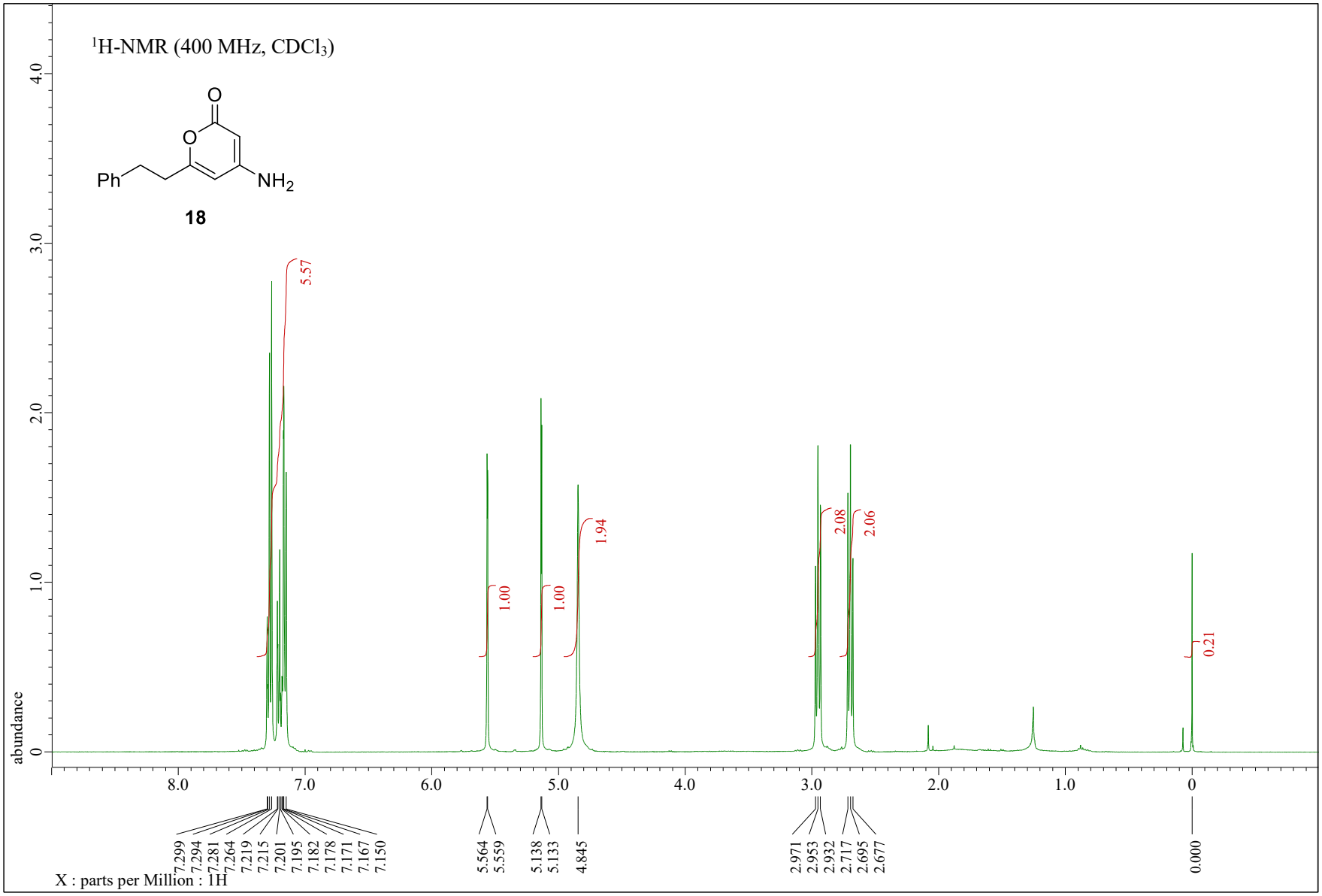

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
MeO
N
O
Ph
N
H
OMe
14
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
160.265
155.317
148.080
140.081
128.582
128.277
126.456
95.230
93.695
77.315
77.000
76.676
64.043
63.385
34.199
32.645
X : parts per Million : 13C

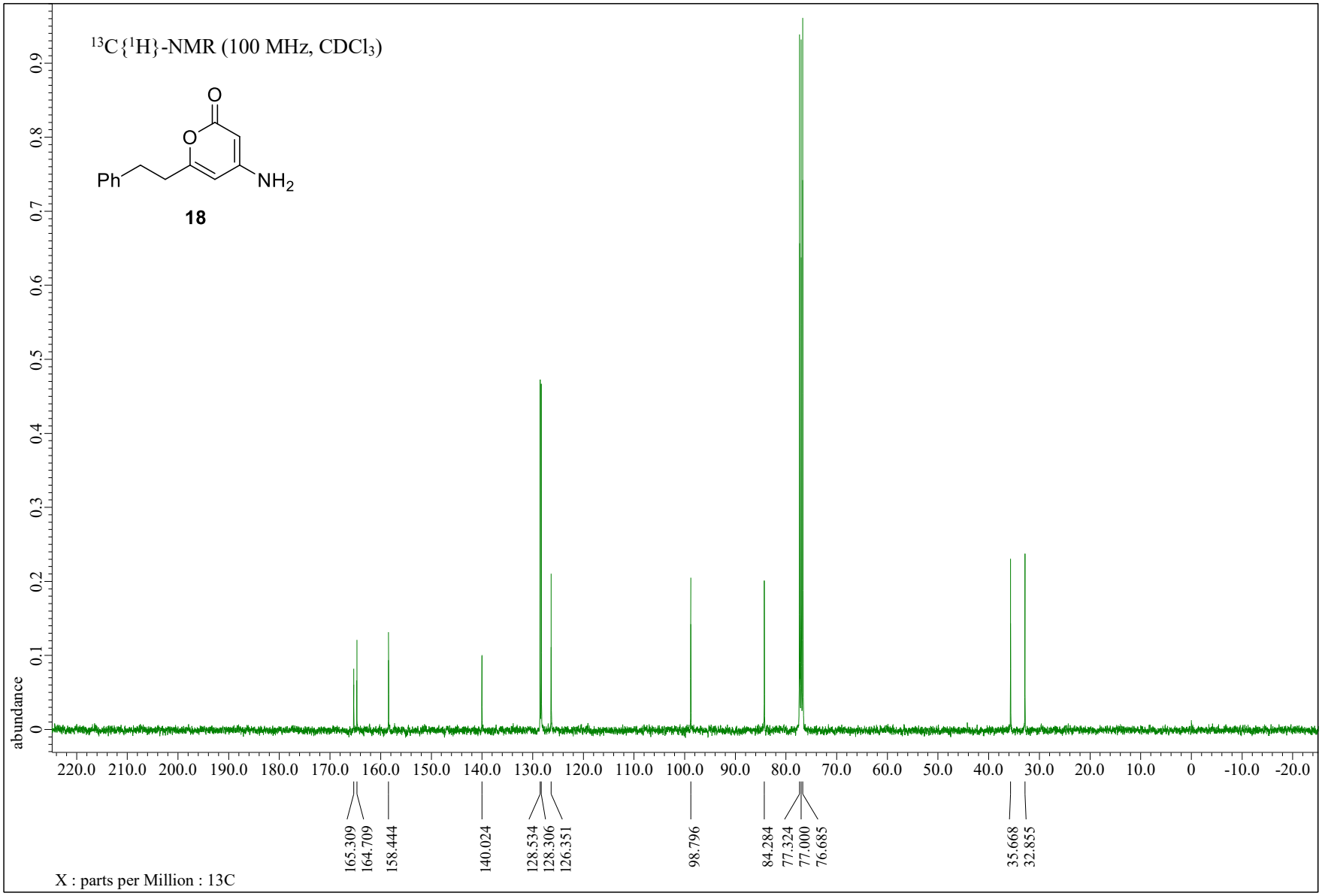

^{1}H-NMR (600 MHz, CD_3OD)
O
HN
Ph
NH_2
15
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
3.00
2.04
1.00
1.01
2.03
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.267
7.254
7.243
7.197
7.184
7.180
7.177
7.165
7.153
5.669
5.665
5.400
5.397
4.917
3.311
3.309
3.305
3.303
3.301
2.915
2.903
2.889
2.719
2.705
2.693
X : parts per Million : Proton

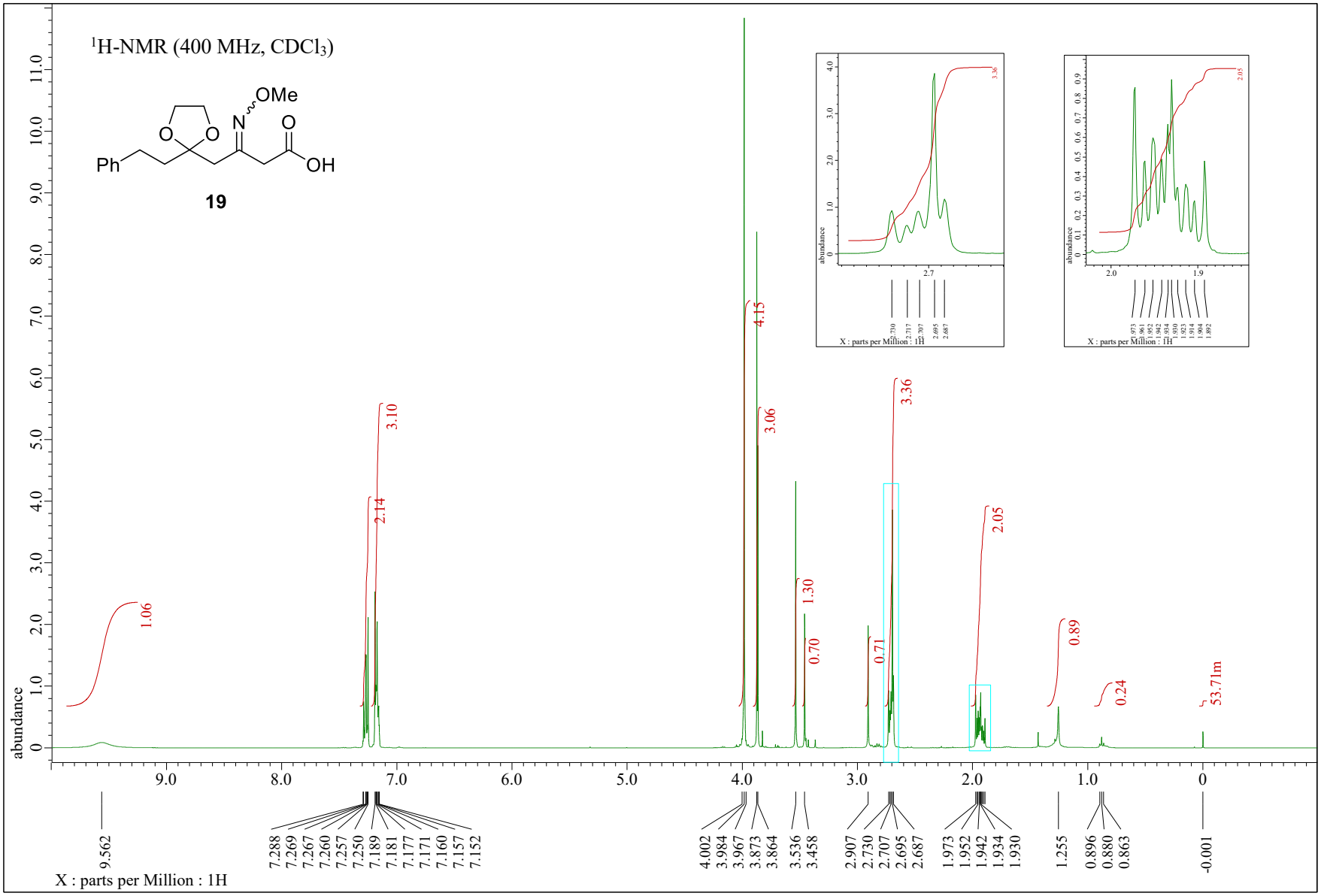

$^{13}C\{^{1}H\}$-NMR (151 MHz, CD_3OD)
O
HN
Ph
NH_2
15
(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.363
161.331
149.497
141.693
129.476
127.312
100.148
92.221
49.431
49.287
49.144
49.000
48.866
48.722
48.579
35.892
35.825
X : parts per Million : Carbon13

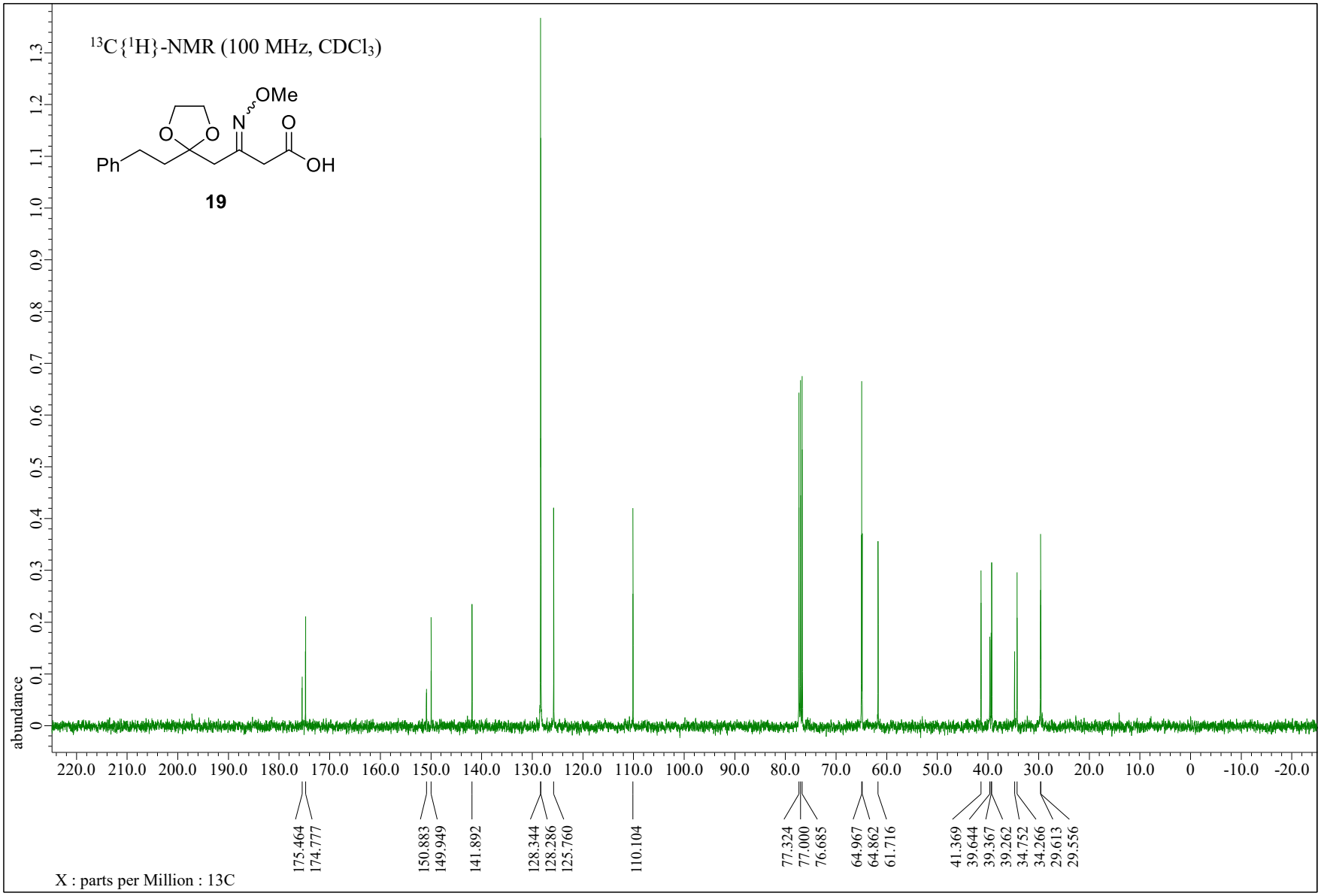

1H-NMR (400 MHz, CDCl3)
Ph
O
O
N
OMe
H
17
abundance
X : parts per Million : 1H
6.31
0.66
40.01m
1.03
1.95
0.64
72.83m
2.13
1.34
0.72
0.73
0.13
7.878
7.832
7.299
7.282
7.264
7.220
7.196
7.166
7.148
6.122
5.623
5.520
5.466
3.889
3.866
3.716
3.669
3.545
2.974
2.955
2.935
2.911
2.890
2.731
2.710
2.692
2.631
2.611
1.253
0.000

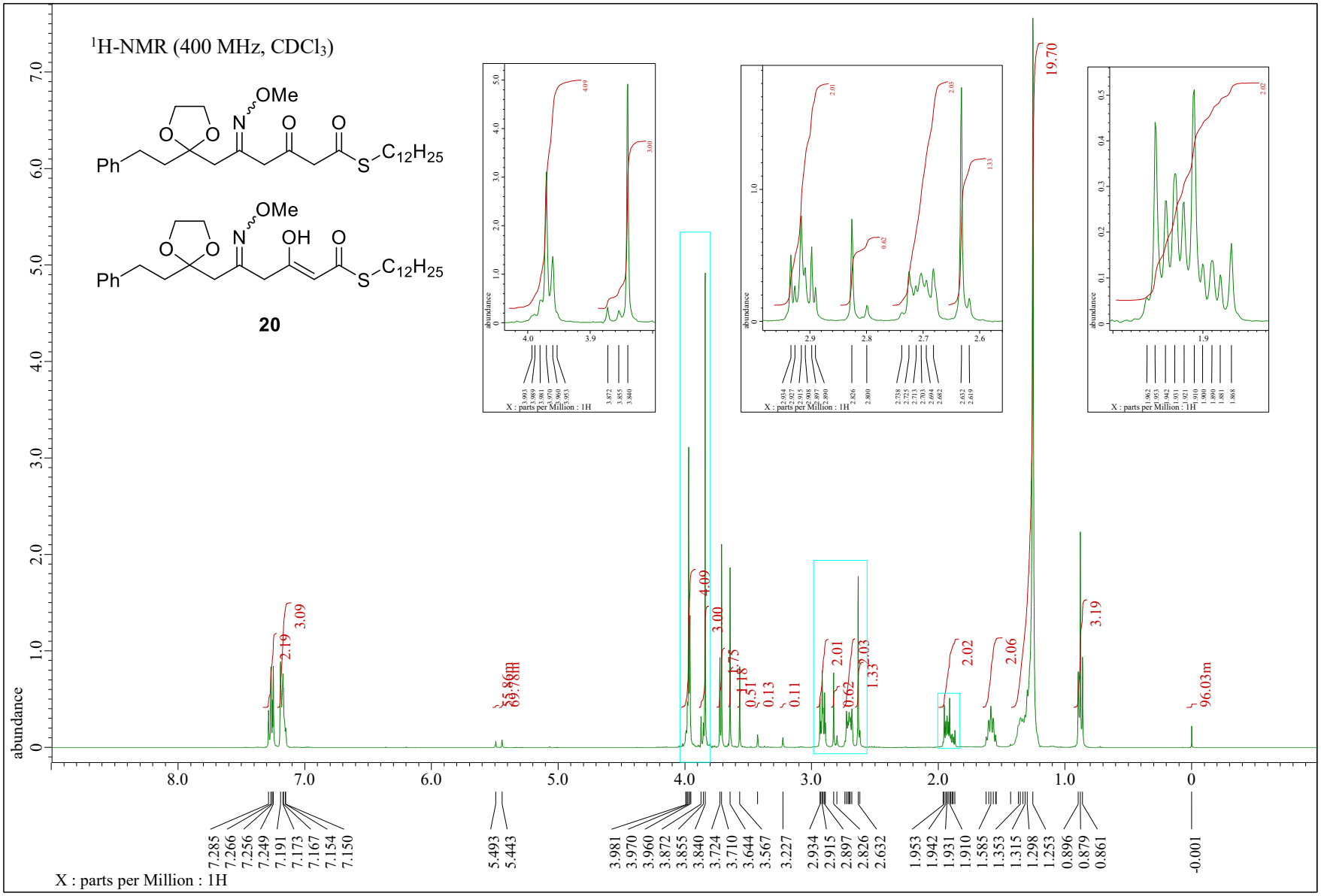

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
17
abundance
X : parts per Million : 13C
165.243
164.918
164.470
159.465
158.139
157.443
147.060
144.238
139.909
139.861
139.814
128.553
128.430
128.277
128.239
126.446
126.380
99.664
94.906
94.620
83.388
77.324
77.000
76.685
63.585
62.221
61.993
35.734
35.305
35.067
33.789
32.864
32.302
32.226
30.042
29.661

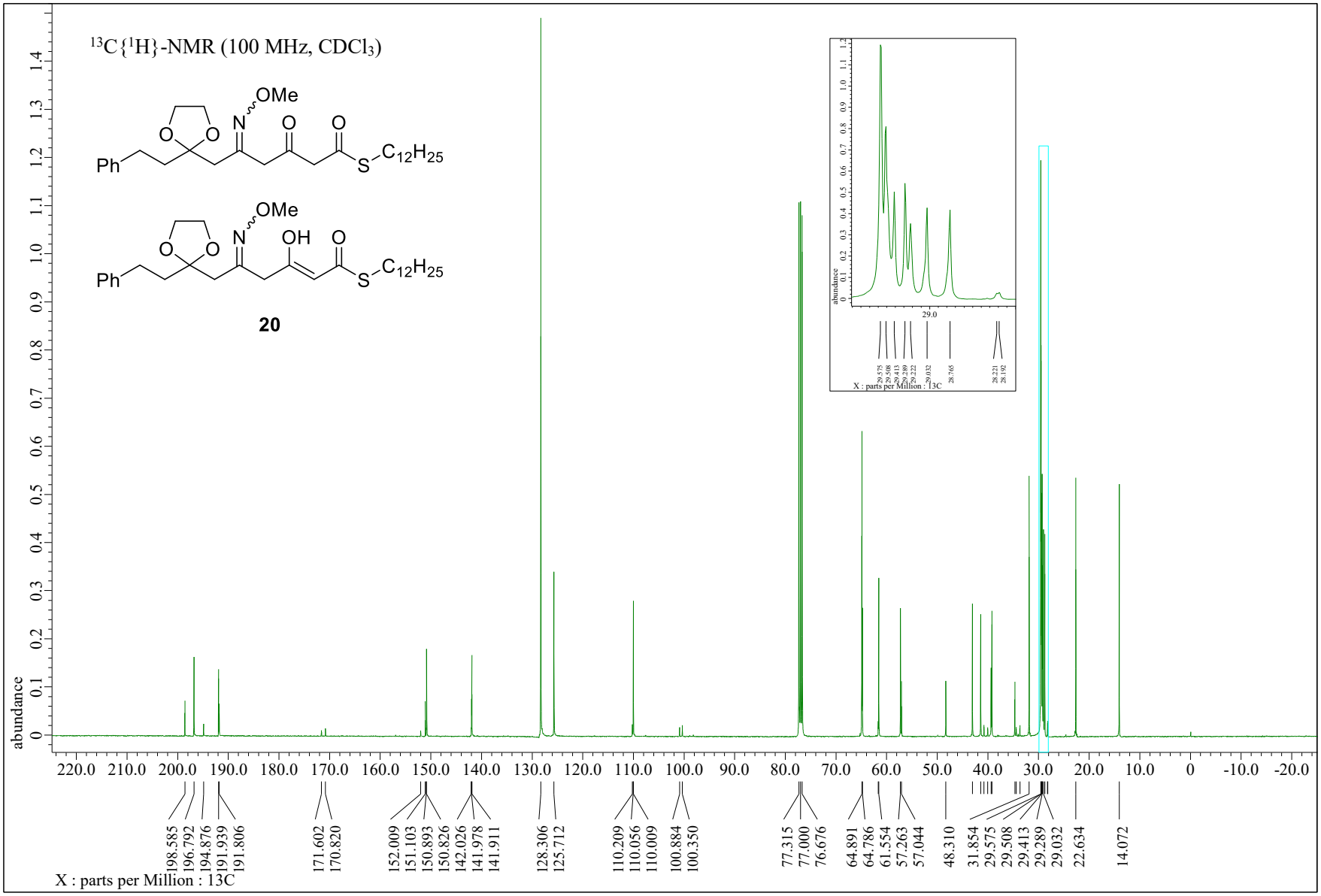

^{1}H-NMR (400 MHz, $CDCl_3$)
O
O
Ph
NH_2
18
abundance
4.0
3.0
2.0
1.0
0
5.57
1.00
1.00
1.94
2.08
2.06
0.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.299
7.294
7.281
7.264
7.219
7.215
7.201
7.195
7.182
7.178
7.171
7.167
7.150
5.564
5.559
5.138
5.133
4.845
2.971
2.953
2.932
2.717
2.695
2.677
0.000
X : parts per Million : 1H

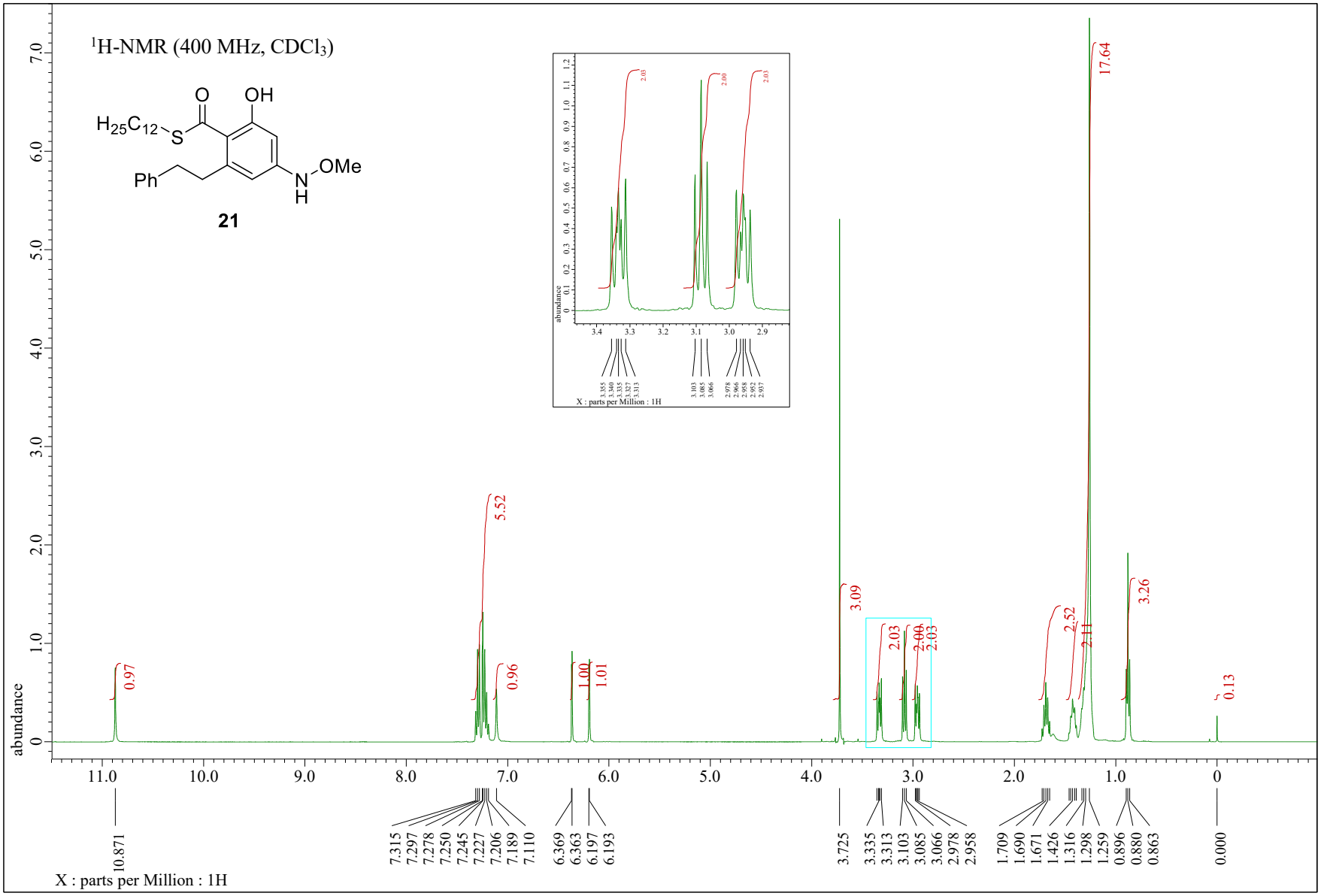

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
O
O
Ph
NH_2
18
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.309
164.709
158.444
140.024
128.534
128.306
126.351
98.796
84.284
77.324
77.000
76.685
35.668
32.855
X : parts per Million : 13C

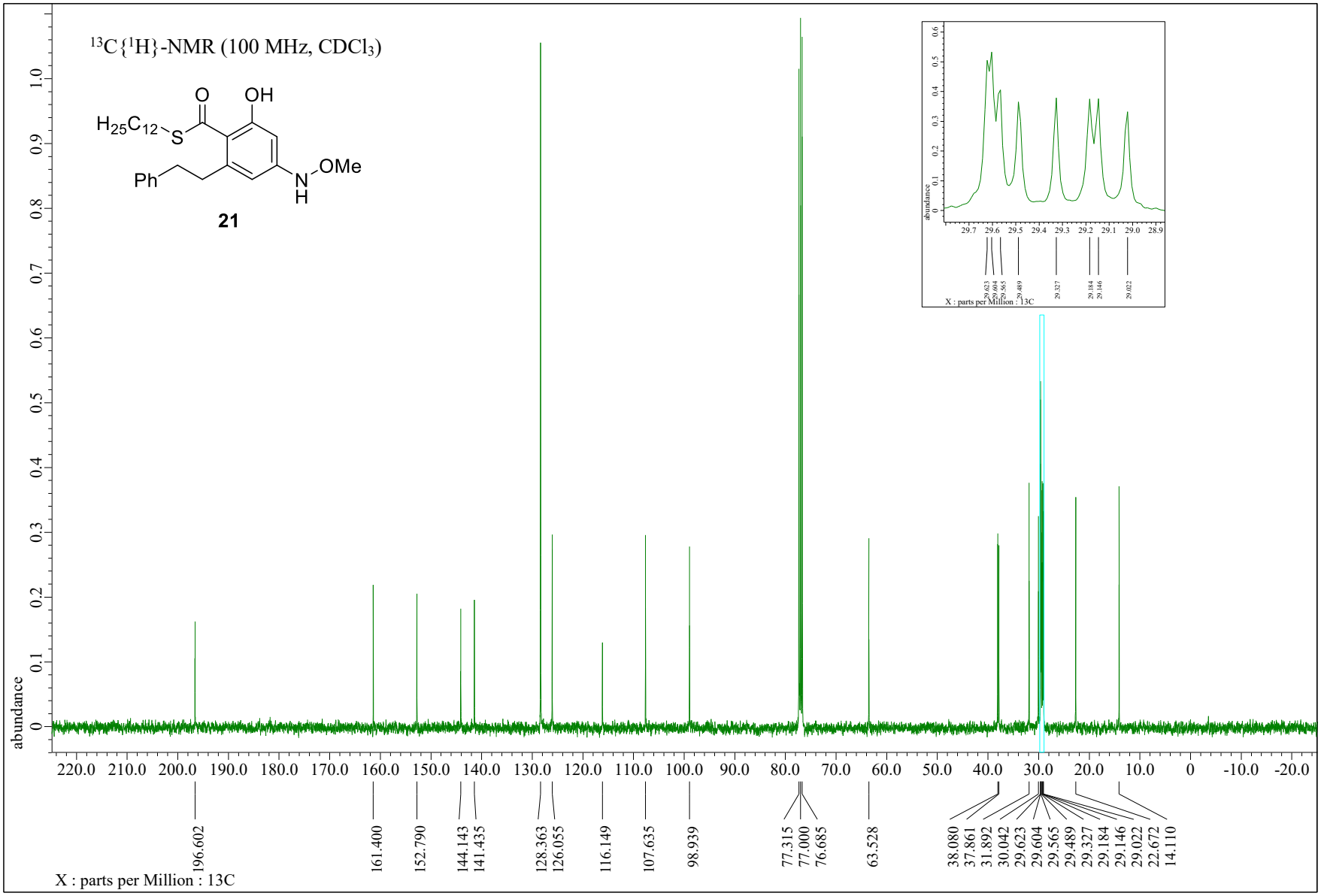

1H-NMR (400 MHz, CDCl3)
OMe
N
O
O
O
Ph
OH
19
abundance
X : parts per Million : 1H
1.06
2.14
3.10
4.15
3.06
1.30
0.70
0.71
3.36
2.05
0.89
0.24
53.71m
9.562
7.288
7.269
7.267
7.260
7.257
7.250
7.189
7.181
7.177
7.171
7.160
7.157
7.152
4.002
3.984
3.967
3.873
3.864
3.536
3.458
2.907
2.730
2.707
2.695
2.687
1.973
1.952
1.942
1.934
1.930
1.255
0.896
0.880
0.863
-0.001

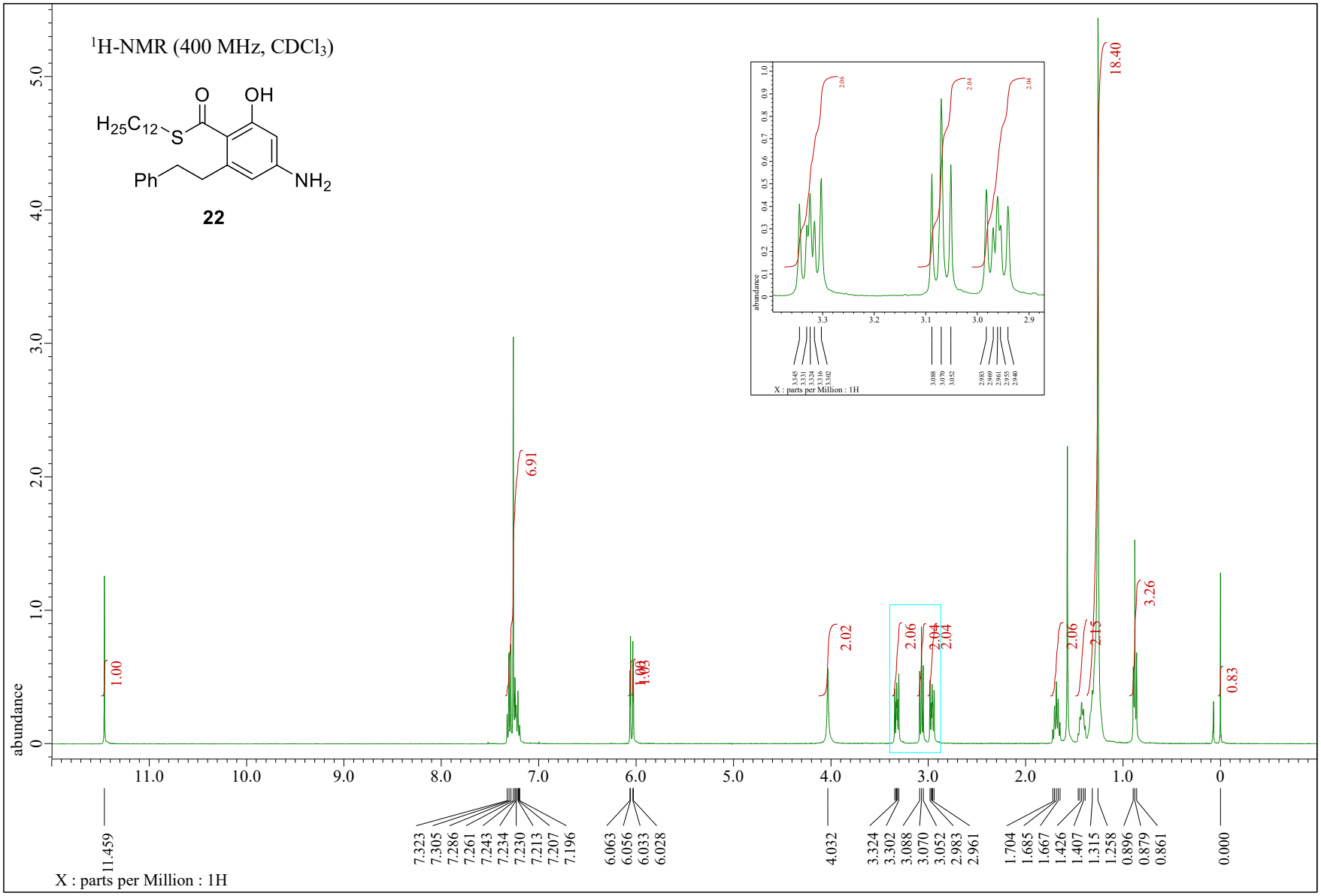

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe
N
O
O
O
Ph
OH
19
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
175.464
174.777
150.883
149.949
141.892
128.344
128.286
125.760
110.104
77.324
77.000
76.685
64.967
64.862
61.716
41.369
39.644
39.367
39.262
34.752
34.266
29.613
29.556
X : parts per Million : 13C

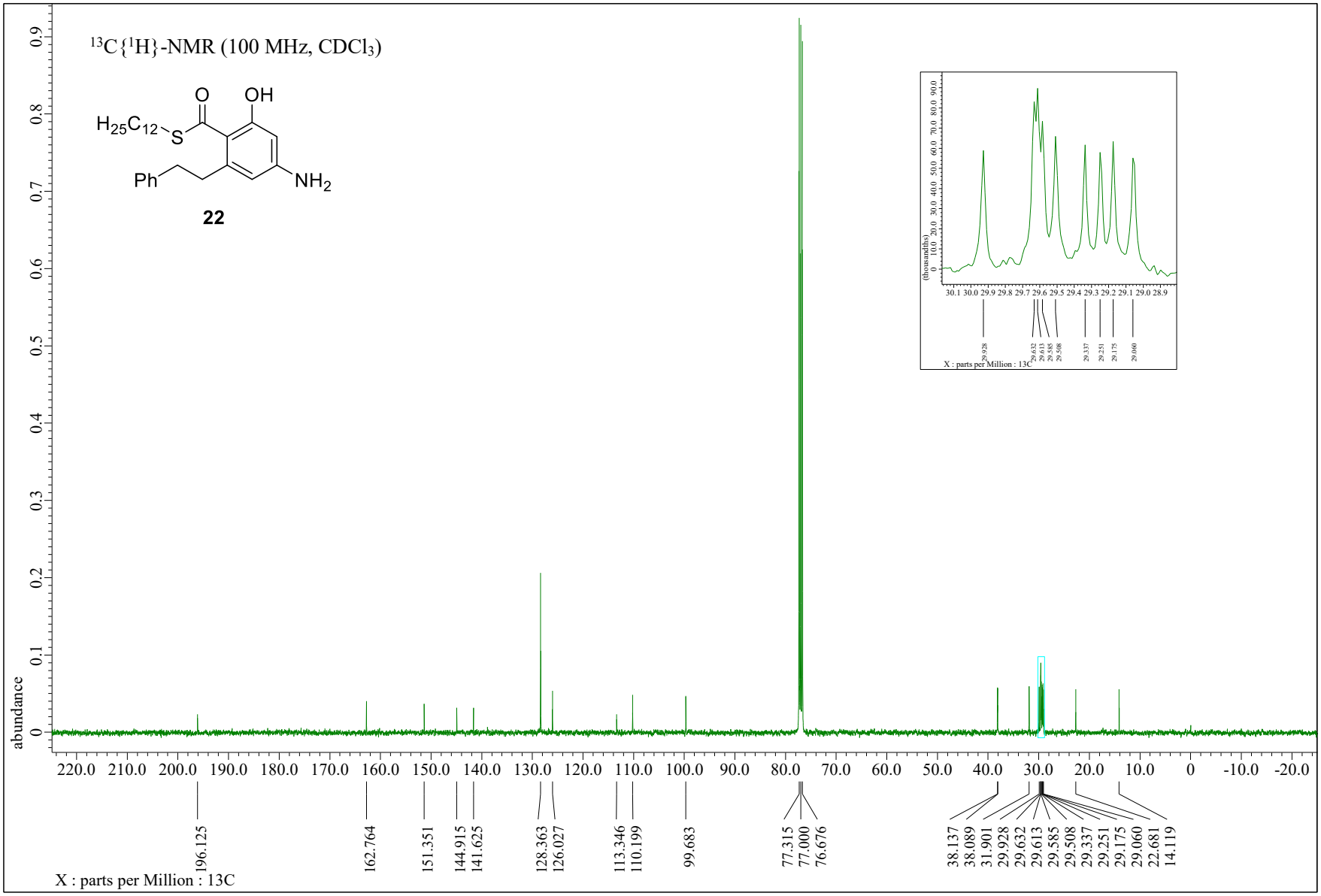

^{1}H-NMR (400 MHz, $CDCl_3$)
OMe
N
O
O
Ph
S
$C_{12}H_{25}$
OMe
N
OH
O
Ph
S
$C_{12}H_{25}$
20
abundance
X : parts per Million : 1H
19.70
3.09
2.19
4.09
3.00
1.75
1.18
0.51
0.13
0.11
2.01
0.62
2.03
1.33
2.02
2.06
3.19
96.03m
7.285
7.266
7.256
7.249
7.191
7.173
7.167
7.154
7.150
5.493
5.443
3.981
3.970
3.960
3.872
3.855
3.840
3.724
3.710
3.644
3.567
3.227
2.934
2.915
2.897
2.826
2.632
1.953
1.942
1.931
1.910
1.585
1.353
1.315
1.298
1.253
0.896
0.879
0.861
-0.001

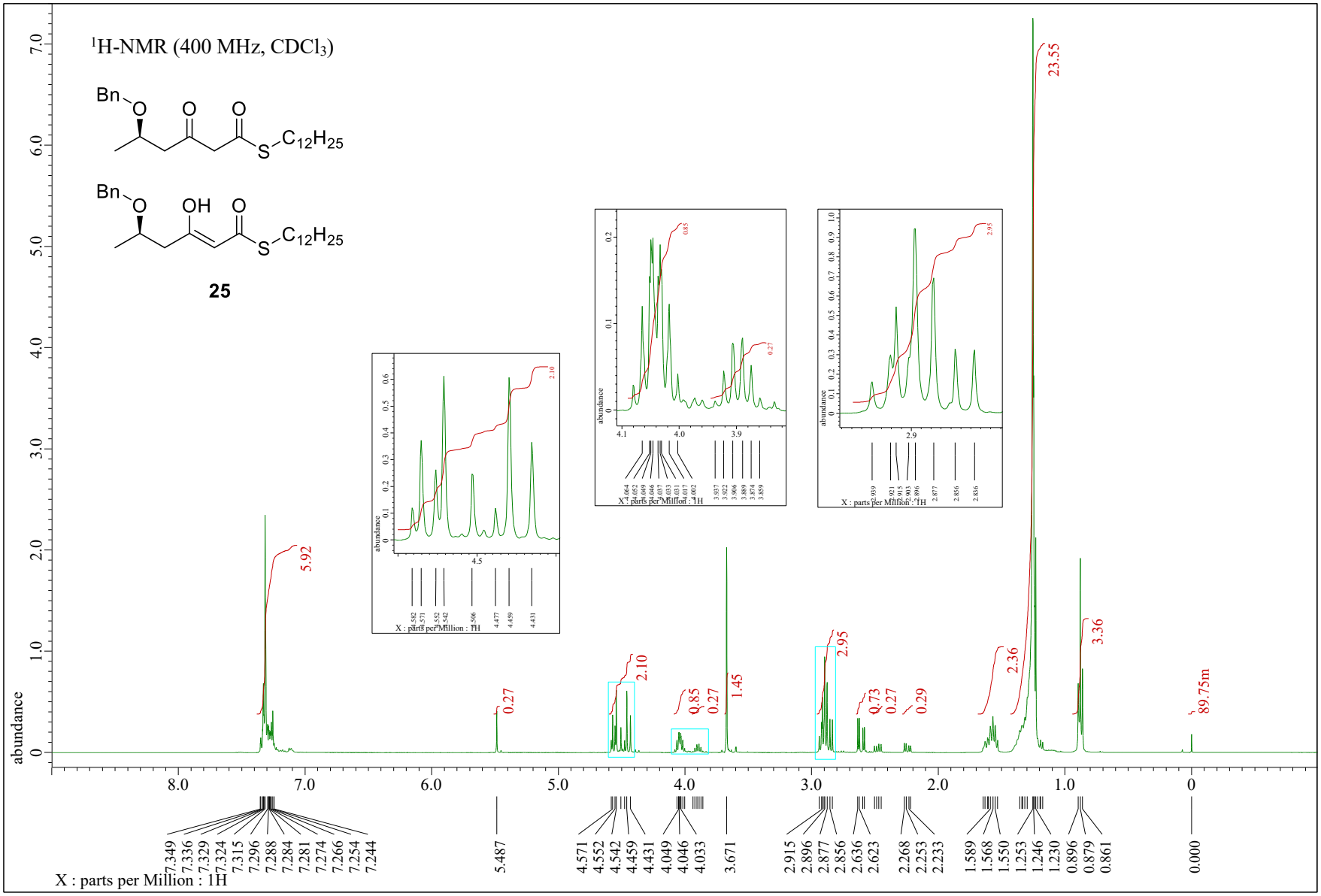

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
OMe
N
O
O
Ph
S
$C_{12}H_{25}$
OH
20
abundance
X : parts per Million : 13C
198.585
196.792
194.876
191.939
191.806
171.602
170.820
152.009
151.103
150.893
150.826
142.026
141.978
141.911
128.306
125.712
110.209
110.056
110.009
100.884
100.350
77.315
77.000
76.676
64.891
64.786
61.554
57.263
57.044
48.310
31.854
29.575
29.508
29.413
29.289
29.032
22.634
14.072

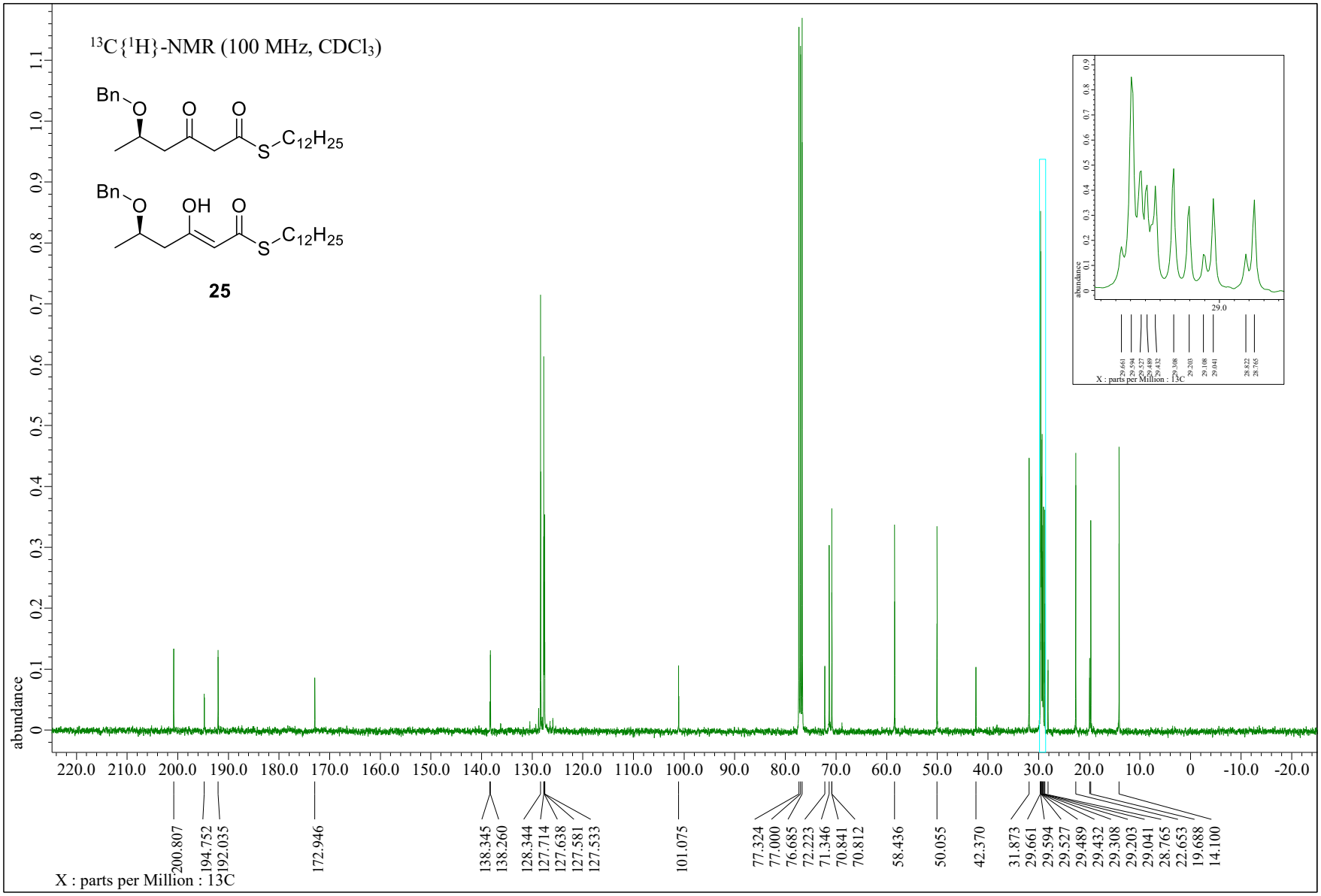

^{1}H-NMR (400 MHz, $CDCl_3$)
21
abundance
X : parts per Million : 1H
10.871
7.315
7.297
7.278
7.250
7.245
7.227
7.206
7.189
7.110
6.369
6.363
6.197
6.193
3.725
3.335
3.313
3.103
3.085
3.066
2.978
2.958
1.709
1.690
1.671
1.426
1.316
1.298
1.259
0.896
0.880
0.863
0.000
0.97
5.52
0.96
1.00
1.01
3.09
2.03
2.00
2.03
2.52
2.11
17.64
3.26
0.13

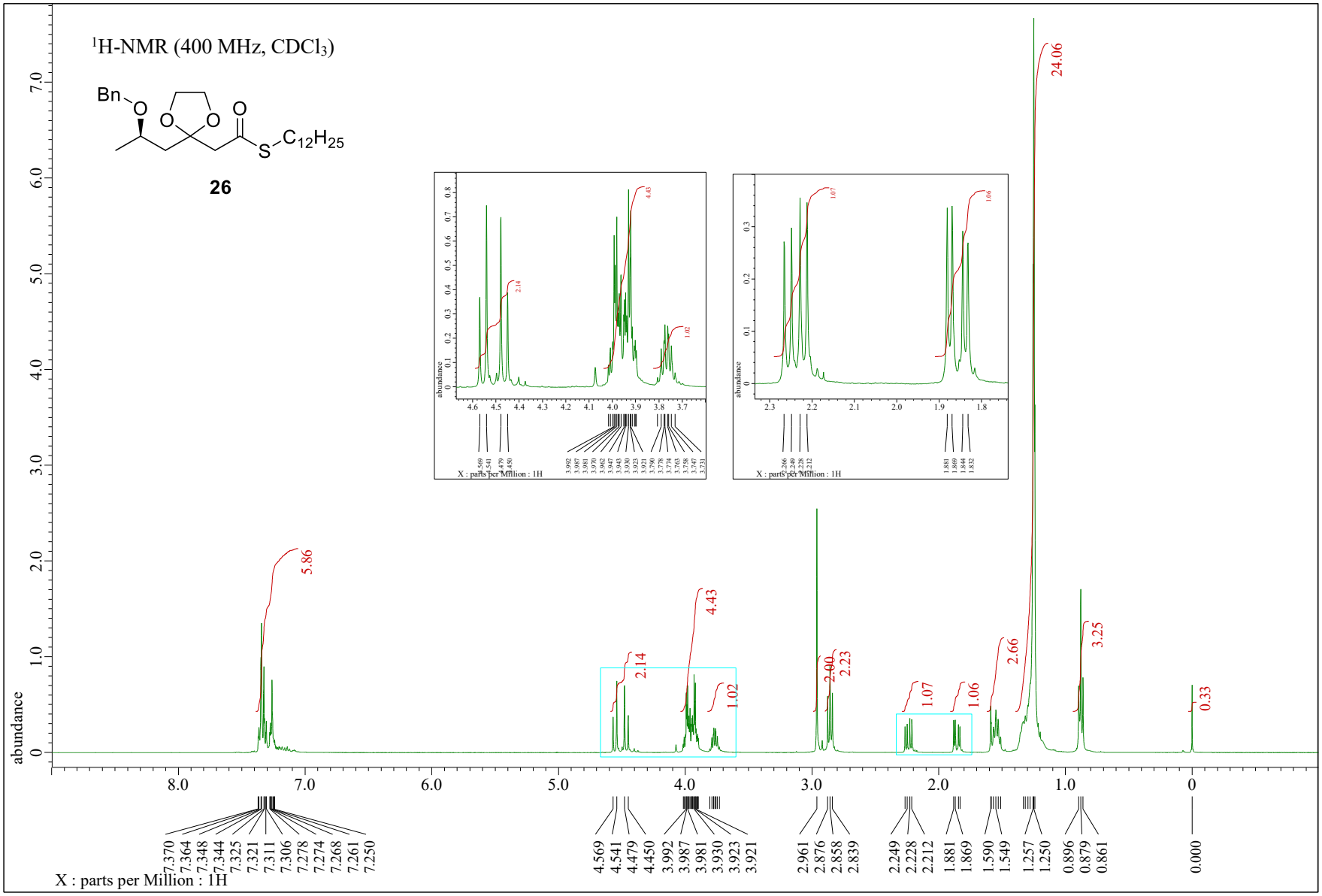

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
21
abundance
X : parts per Million : 13C
196.602
161.400
152.790
144.143
141.435
128.363
126.055
116.149
107.635
98.939
77.315
77.000
76.685
63.528
38.080
37.861
31.892
30.042
29.623
29.604
29.565
29.489
29.327
29.184
29.146
29.022
22.672
14.110

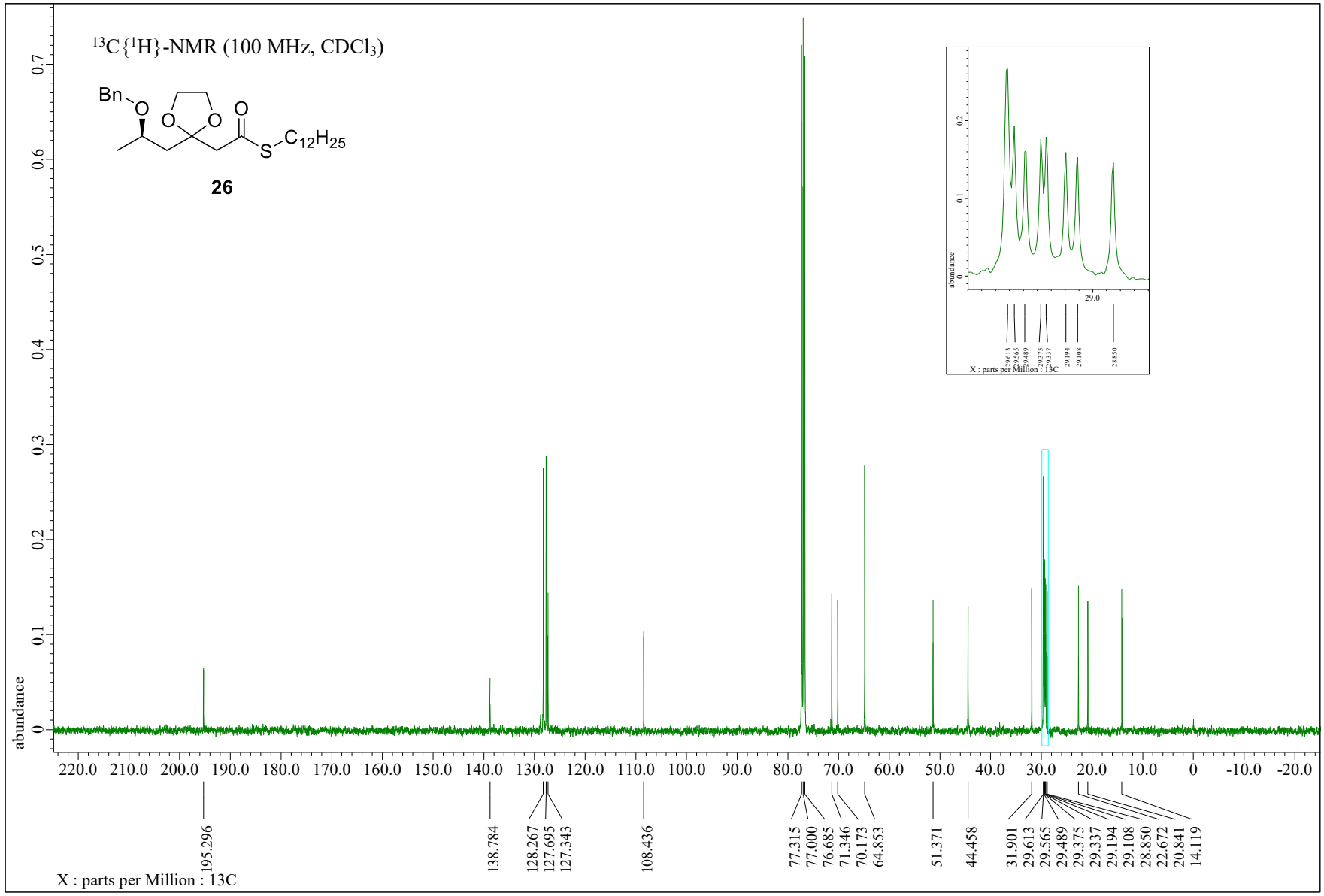

1H-NMR (400 MHz, CDCl3)
O
OH
H25C12
S
Ph
NH2
22
abundance
X : parts per Million : 1H
1.00
6.91
2.02
2.06
2.15
3.26
0.83
18.40
11.459
7.323
7.305
7.286
7.261
7.243
7.234
7.230
7.213
7.207
7.196
6.063
6.056
6.033
6.028
4.032
3.324
3.302
3.088
3.070
3.052
2.983
2.961
1.704
1.685
1.667
1.426
1.407
1.315
1.258
0.896
0.879
0.861
0.000

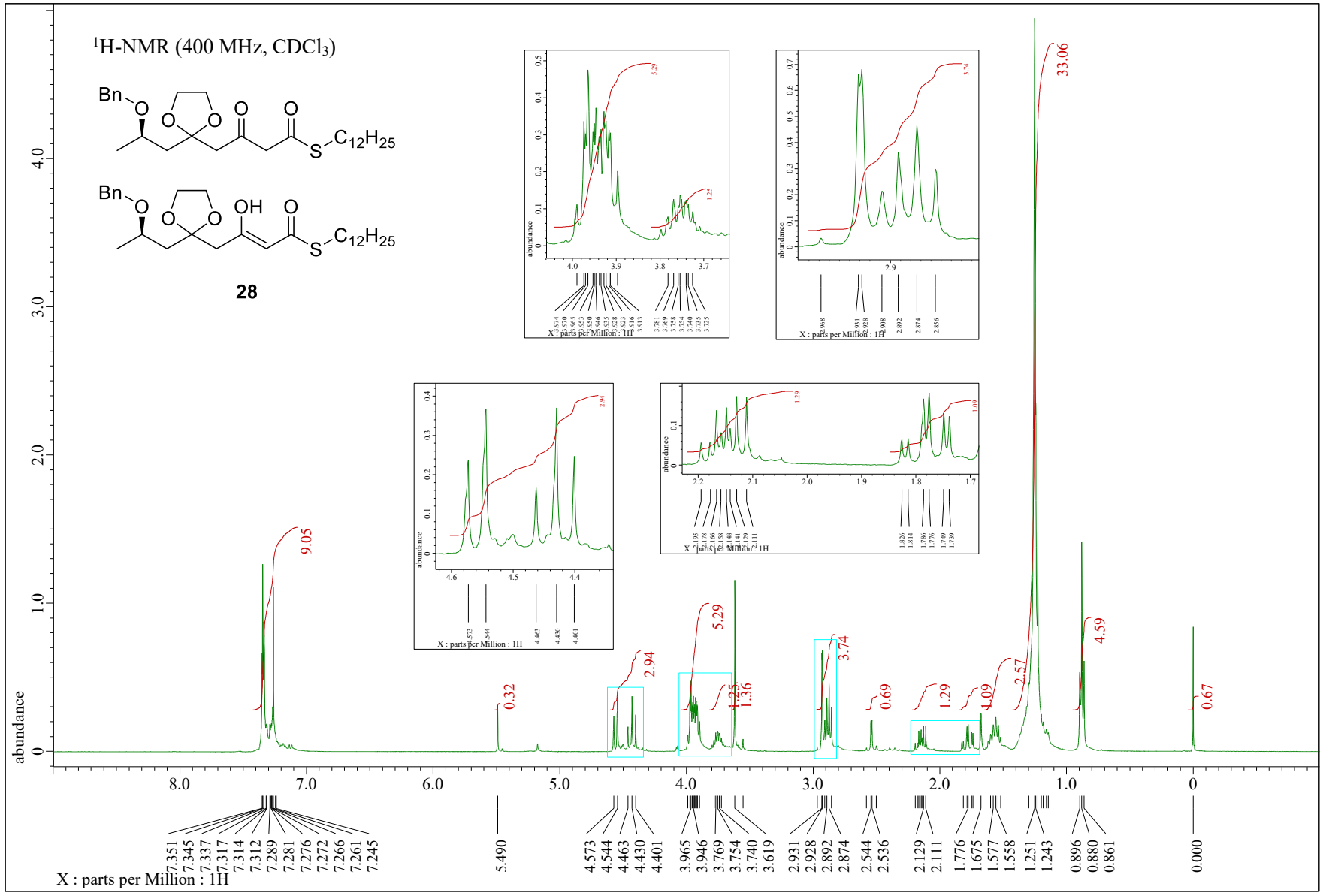

13C{1H}-NMR (100 MHz, CDCl3)
O
OH
H25C12
S
Ph
NH2
22
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
196.125
162.764
151.351
144.915
141.625
128.363
126.027
113.346
110.199
99.683
77.315
77.000
76.676
38.137
38.089
31.901
29.928
29.632
29.613
29.585
29.508
29.337
29.251
29.175
29.060
22.681
14.119
X : parts per Million : 13C
(thousandths)
30.1 30.0 29.9 29.8 29.7 29.6 29.5 29.4 29.3 29.2 29.1 29.0 28.9
29.928
29.632
29.613
29.585
29.508
29.337
29.251
29.175
29.060
X : parts per Million : 13C

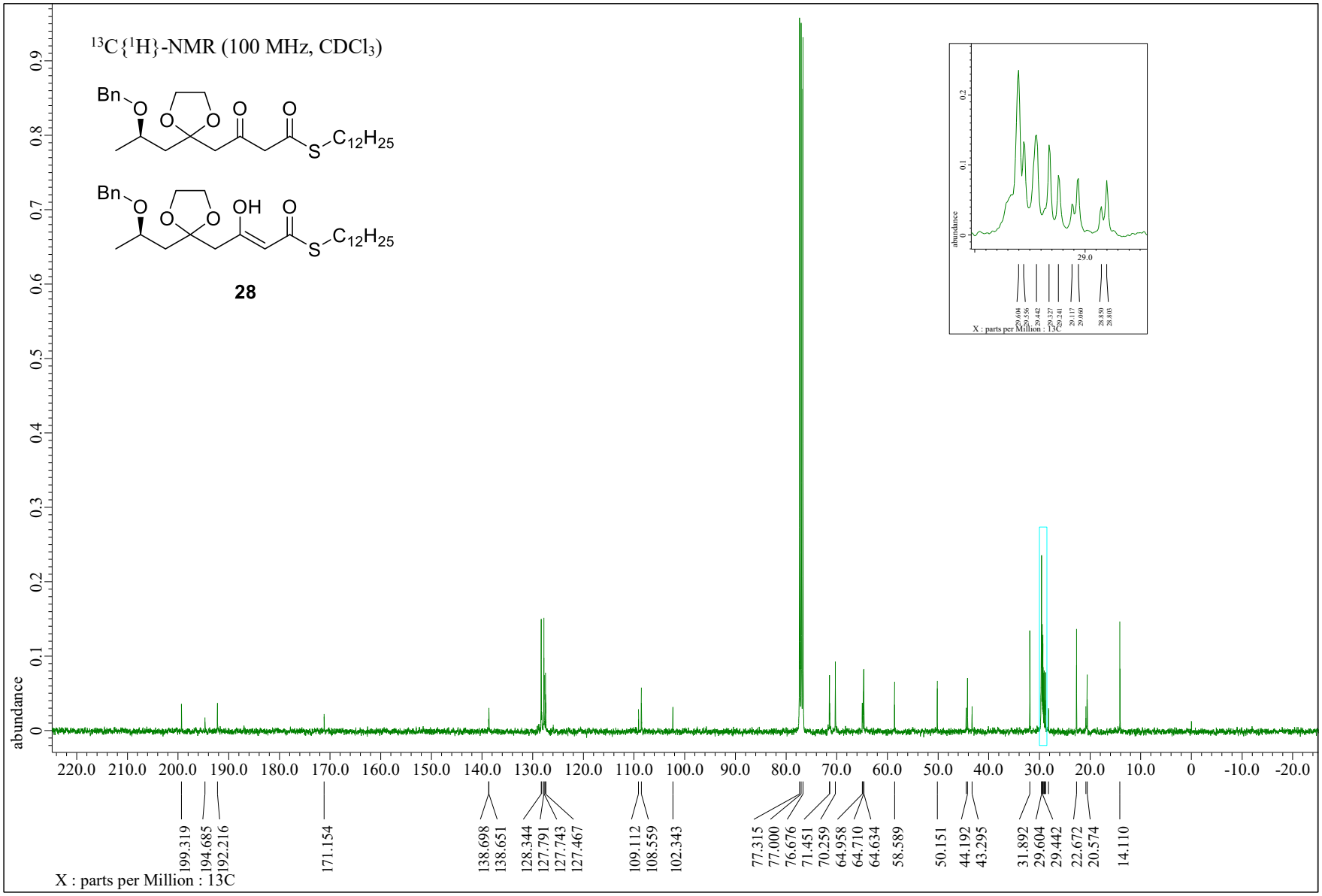

1H-NMR (400 MHz, CDCl3)
Bn
O
O
O
S
C12H25
Bn
O
OH
O
S
C12H25
25
abundance
X : parts per Million : 1H
5.92
0.27
2.10
0.85
0.27
1.45
2.95
0.73
0.27
0.29
2.36
3.36
89.75m
23.55

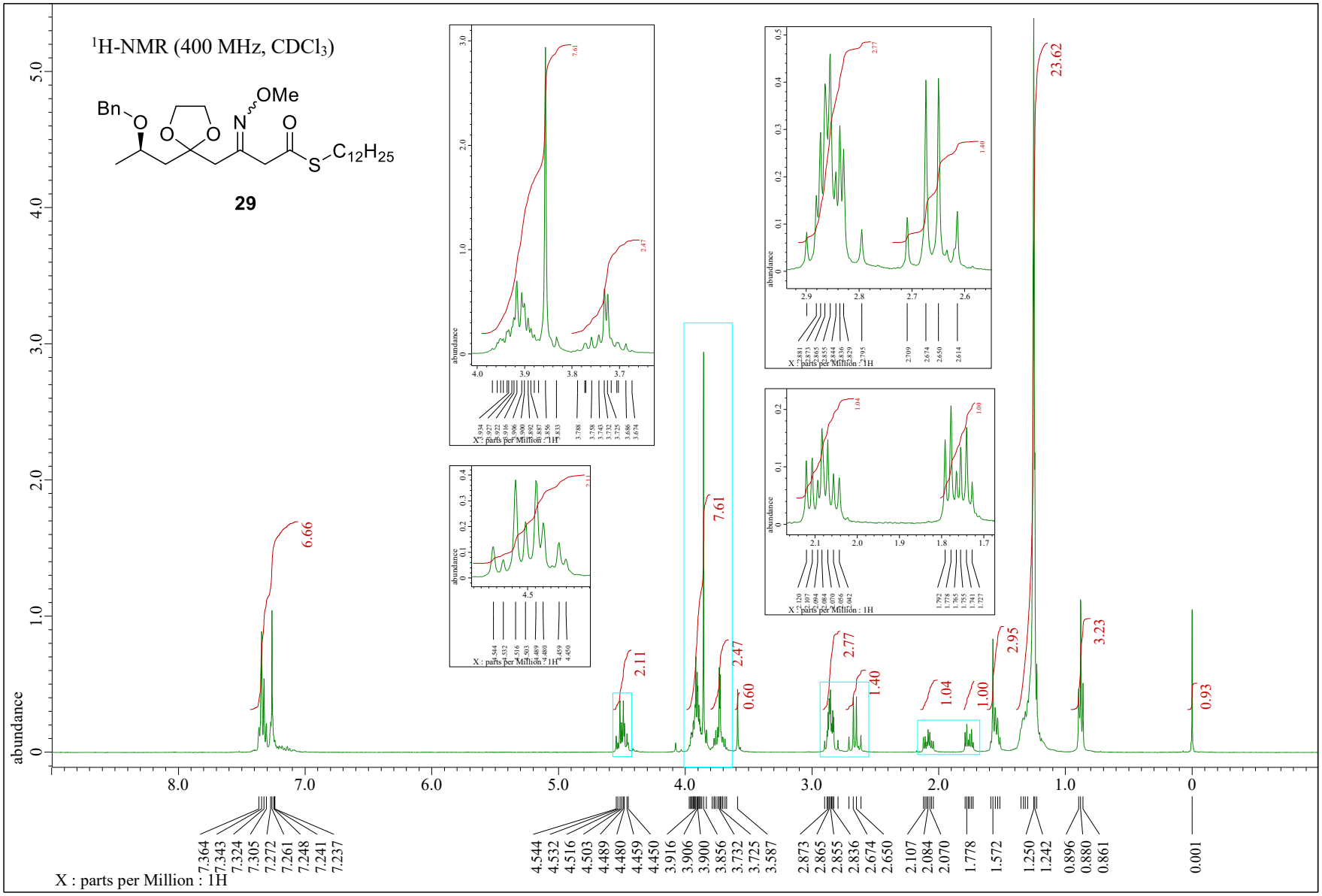

13C{1H}-NMR (100 MHz, CDCl3)
Bn
O
O
O
S
C12H25
Bn
O
OH
O
S
C12H25
25
abundance
X : parts per Million : 13C
200.807
194.752
192.035
172.946
138.345
138.260
128.344
127.714
127.638
127.581
127.533
101.075
77.324
77.000
76.685
72.223
71.346
70.841
70.812
58.436
50.055
42.370
31.873
29.661
29.594
29.527
29.489
29.432
29.308
29.203
29.041
28.765
22.653
19.688
14.100

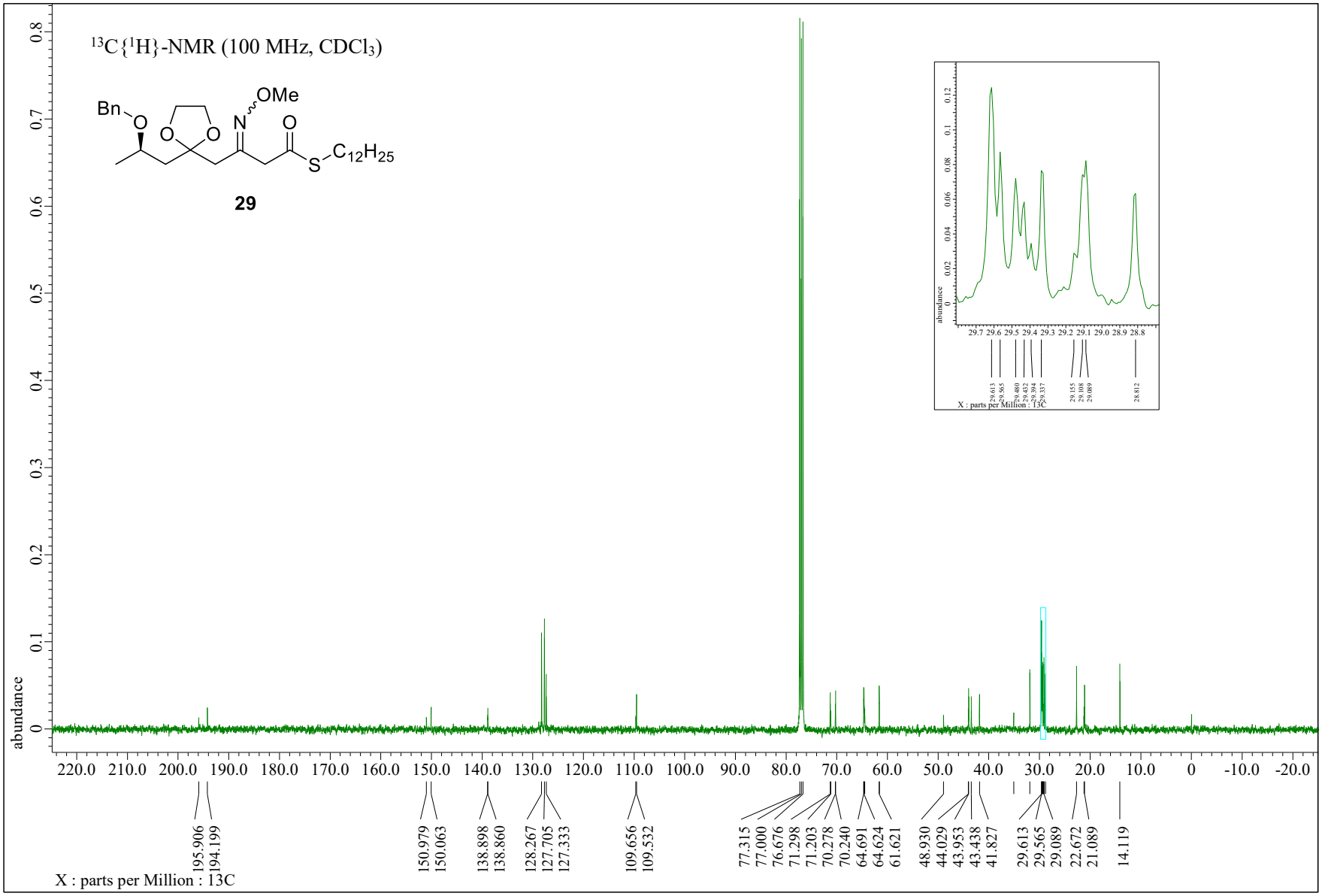

^{1}H-NMR (400 MHz, $CDCl_3$)
Bn
O
O
O
O
S
$C_{12}H_{25}$
26
abundance
X : parts per Million : 1H
5.86
2.14
4.43
1.02
2.00
2.23
1.07
1.06
2.66
3.25
24.06
0.33

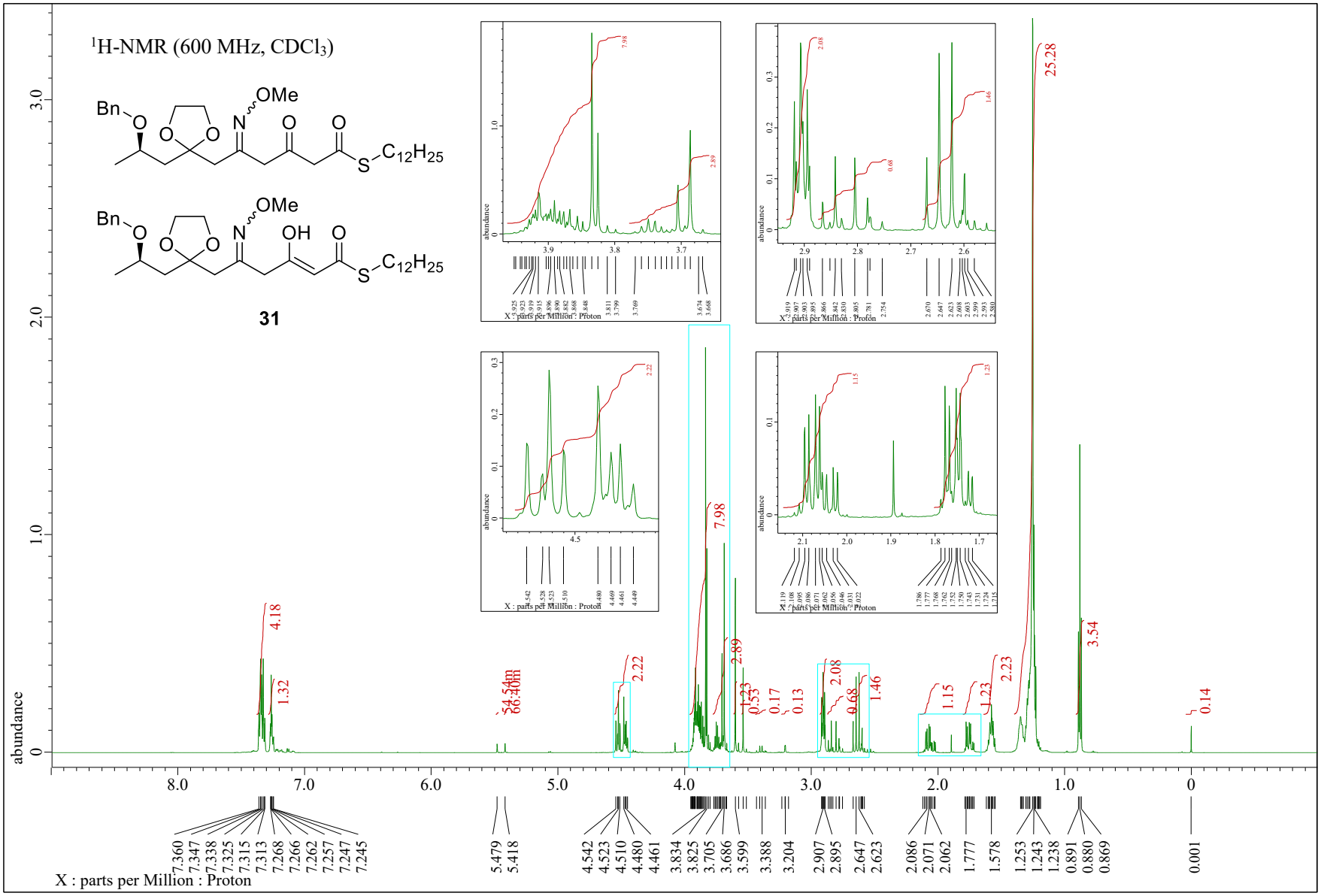

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
Bn
O
O
O
O
S
$C_{12}H_{25}$
26
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
195.296
138.784
128.267
127.695
127.343
108.436
77.315
77.000
76.685
71.346
70.173
64.853
51.371
44.458
31.901
29.613
29.565
29.489
29.375
29.337
29.194
29.108
28.850
22.672
20.841
14.119
X : parts per Million : 13C
abundance
0
0.1
0.2
29.0
29.613
29.565
29.489
29.375
29.337
29.194
29.108
28.850
X : parts per Million : 13C

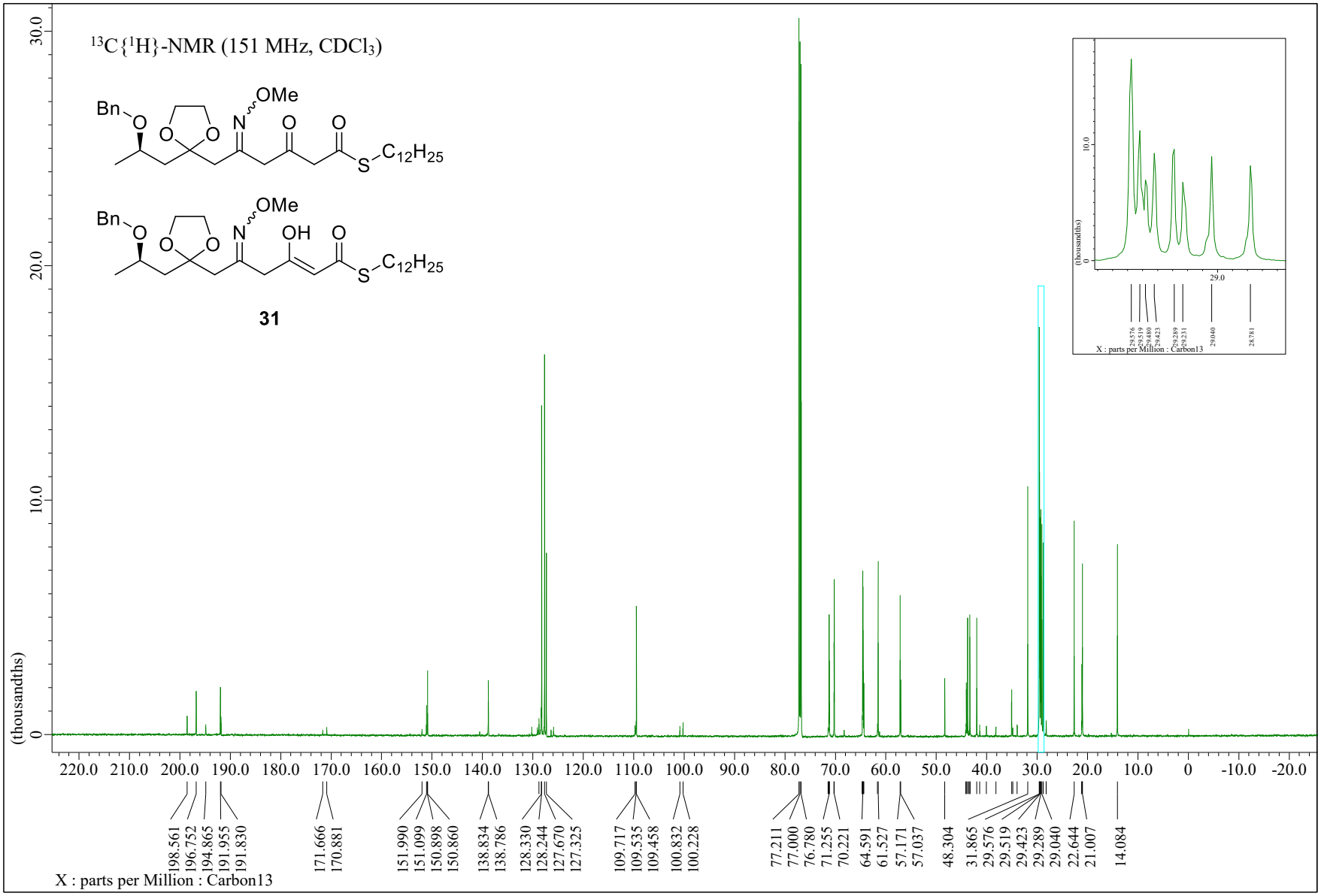

1H-NMR (400 MHz, CDCl3)
Bn
O
O
O
O
S
C12H25
Bn
O
O
OH
O
S
C12H25
28
abundance
X : parts per Million : 1H
9.05
0.32
2.94
5.29
1.25
1.36
3.74
0.69
1.29
1.09
2.57
33.06
4.59
0.67
7.351
7.345
7.337
7.317
7.314
7.312
7.289
7.281
7.276
7.272
7.266
7.261
7.245
5.490
4.573
4.544
4.463
4.430
4.401
3.965
3.946
3.769
3.754
3.740
3.619
2.931
2.928
2.892
2.874
2.544
2.536
2.129
2.111
1.776
1.675
1.577
1.558
1.251
1.243
0.896
0.880
0.861
0.000

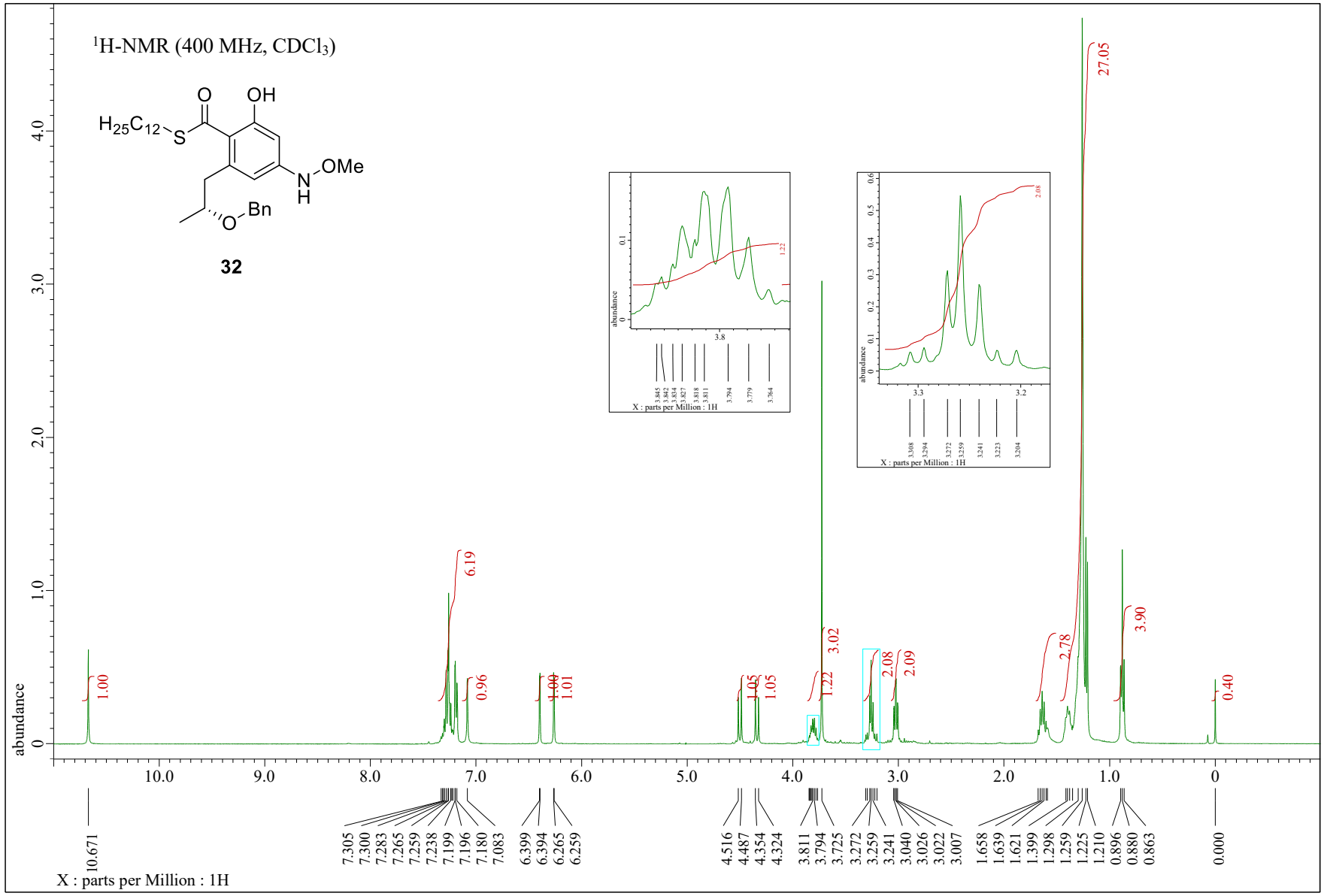

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
Bn
O
O
O
O
O
S
$C_{12}H_{25}$
Bn
O
O
O
OH
O
S
$C_{12}H_{25}$
28
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
199.319
194.685
192.216
171.154
138.698
138.651
128.344
127.791
127.743
127.467
109.112
108.559
102.343
77.315
77.000
76.676
71.451
70.259
64.958
64.710
64.634
58.589
50.151
44.192
43.295
31.892
29.604
29.442
22.672
20.574
14.110
X : parts per Million : 13C
abundance
0
0.1
0.2
29.0
29.604
29.556
29.442
29.337
29.241
29.117
29.060
28.850
28.805
X : parts per Million : 13C

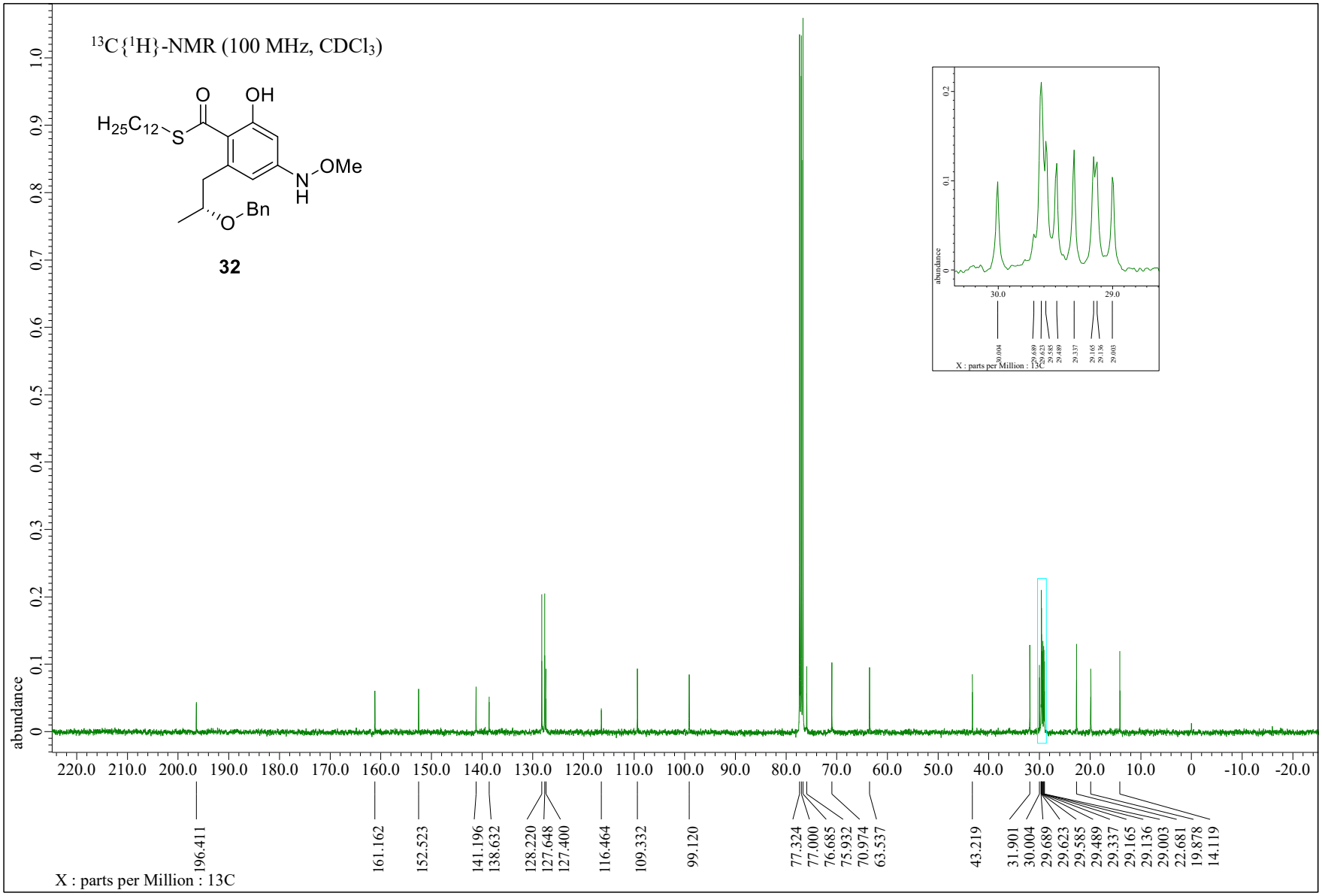

1H-NMR (400 MHz, CDCl3)
Bn
O
O
O
N
OMe
O
S
C12H25
29
abundance
X : parts per Million : 1H
6.66
2.11
7.61
2.47
0.60
2.77
1.40
1.04
1.00
2.95
3.23
23.62
0.93

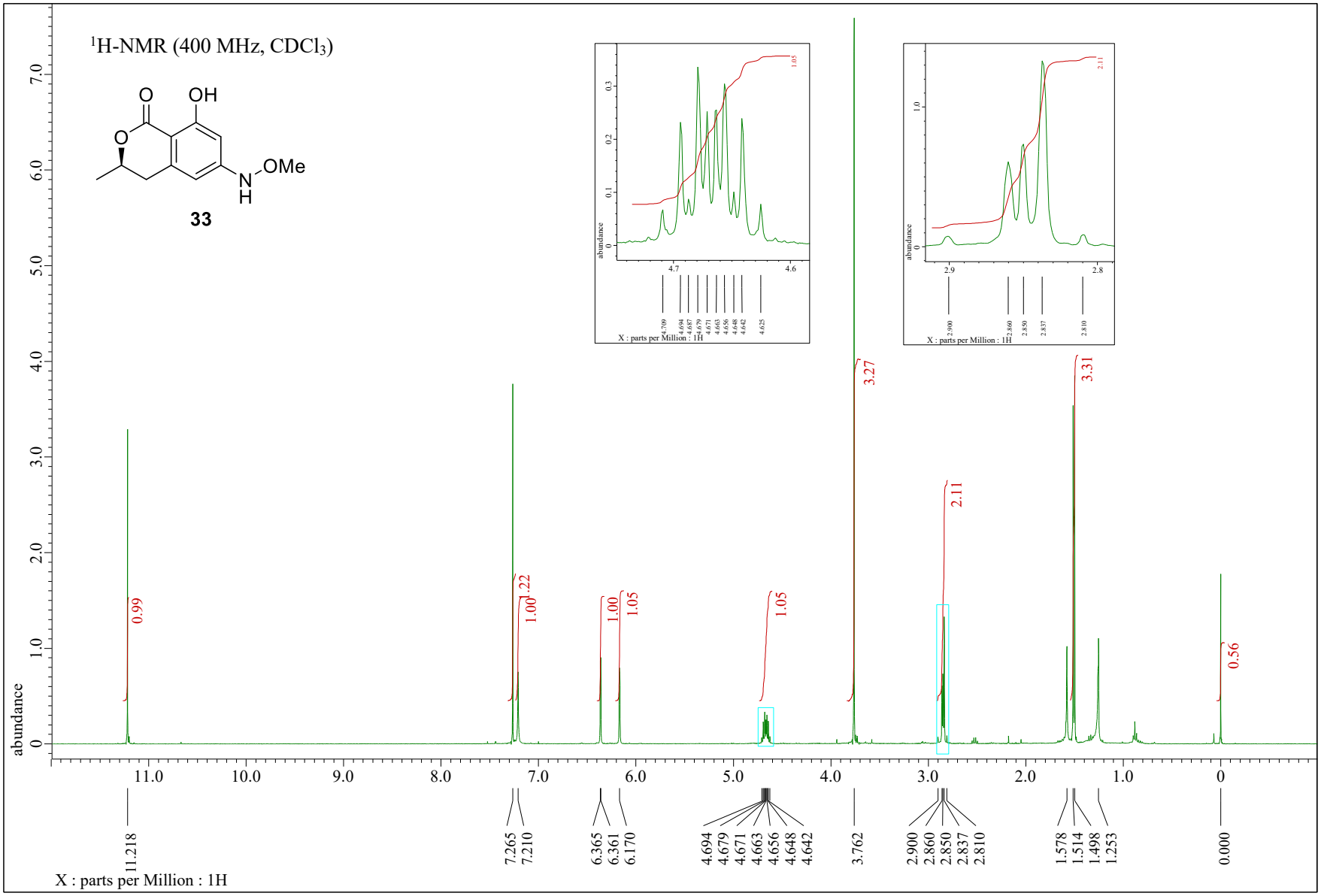

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
Bn
O
O
O
N
OMe
O
S
$C_{12}H_{25}$
29
abundance
X : parts per Million : 13C
195.906
194.199
150.979
150.063
138.898
138.860
128.267
127.705
127.333
109.656
109.532
77.315
77.000
76.676
71.298
71.203
70.278
70.240
64.691
64.624
61.621
48.930
44.029
43.953
43.438
41.827
29.613
29.565
29.089
22.672
21.089
14.119

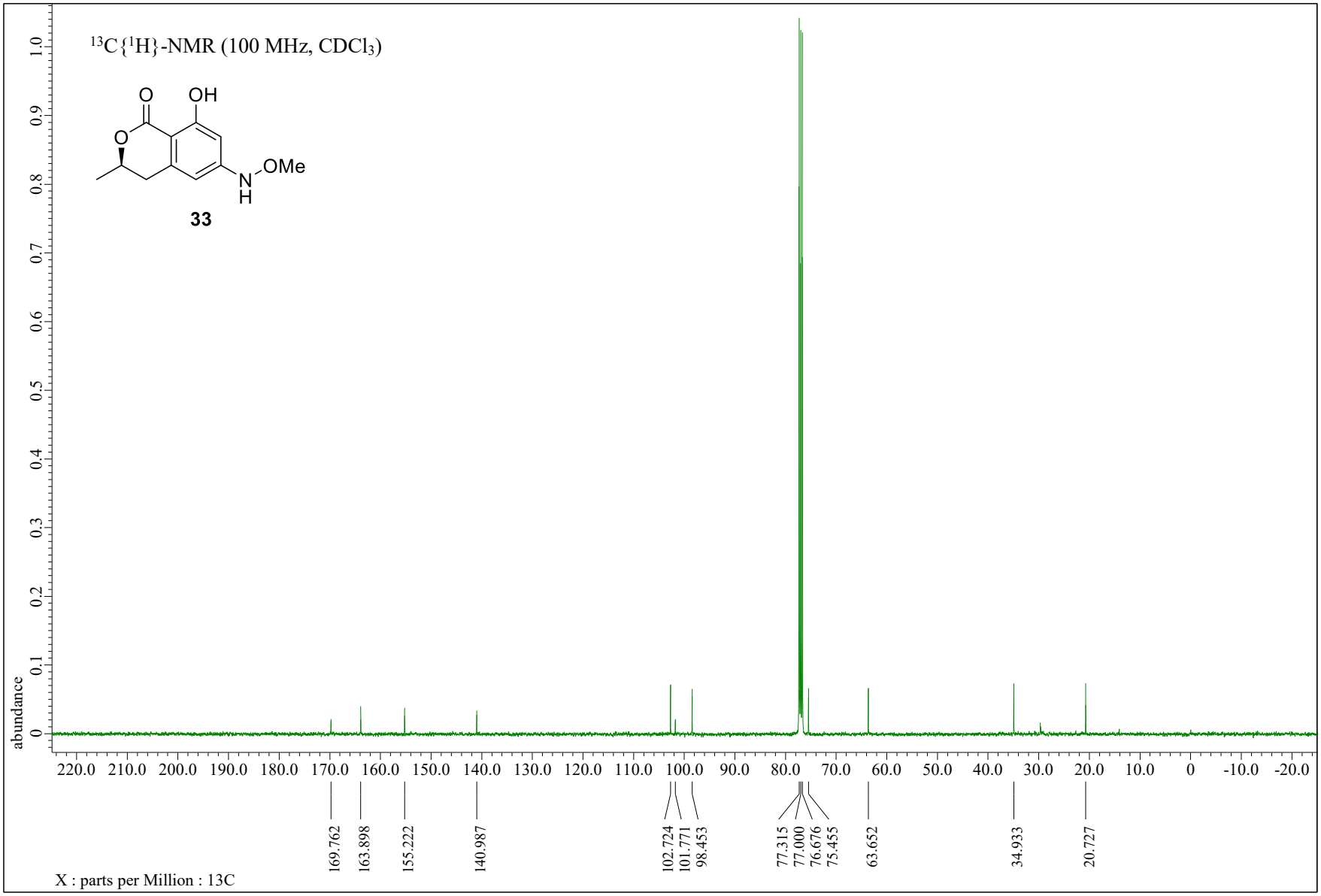

1H-NMR (600 MHz, CDCl3)
Bn
OMe
N
O
O
S
C12H25
OH
31
abundance
X : parts per Million : Proton
4.18
1.32
2.22
7.98
2.89
1.23
0.53
0.17
0.13
2.08
0.68
1.46
1.15
1.23
2.23
25.28
3.54
0.14

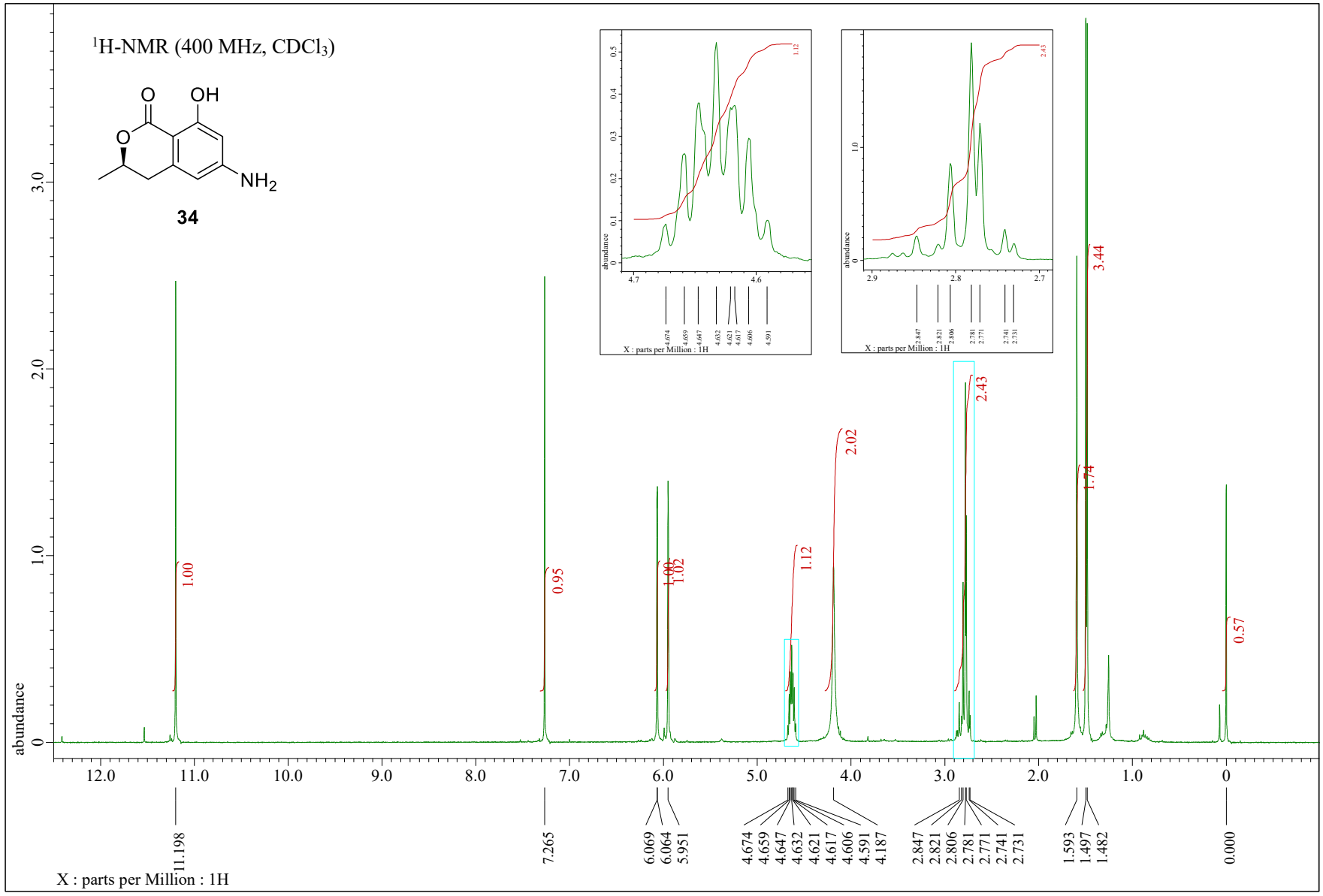

$^{13}C\{^{1}H\}$-NMR (151 MHz, $CDCl_3$)
Bn
OMe
N
O
O
O
O
S
$C_{12}H_{25}$
OH
31
(thousandths)
X : parts per Million : Carbon13
198.561
196.752
194.865
191.955
191.830
171.666
170.881
151.990
151.099
150.898
150.860
138.834
138.786
128.330
128.244
127.670
127.325
109.717
109.535
109.458
100.832
100.228
77.211
77.000
76.780
71.255
70.221
64.591
61.527
57.171
57.037
48.304
31.865
29.576
29.519
29.423
29.289
29.040
22.644
21.007
14.084

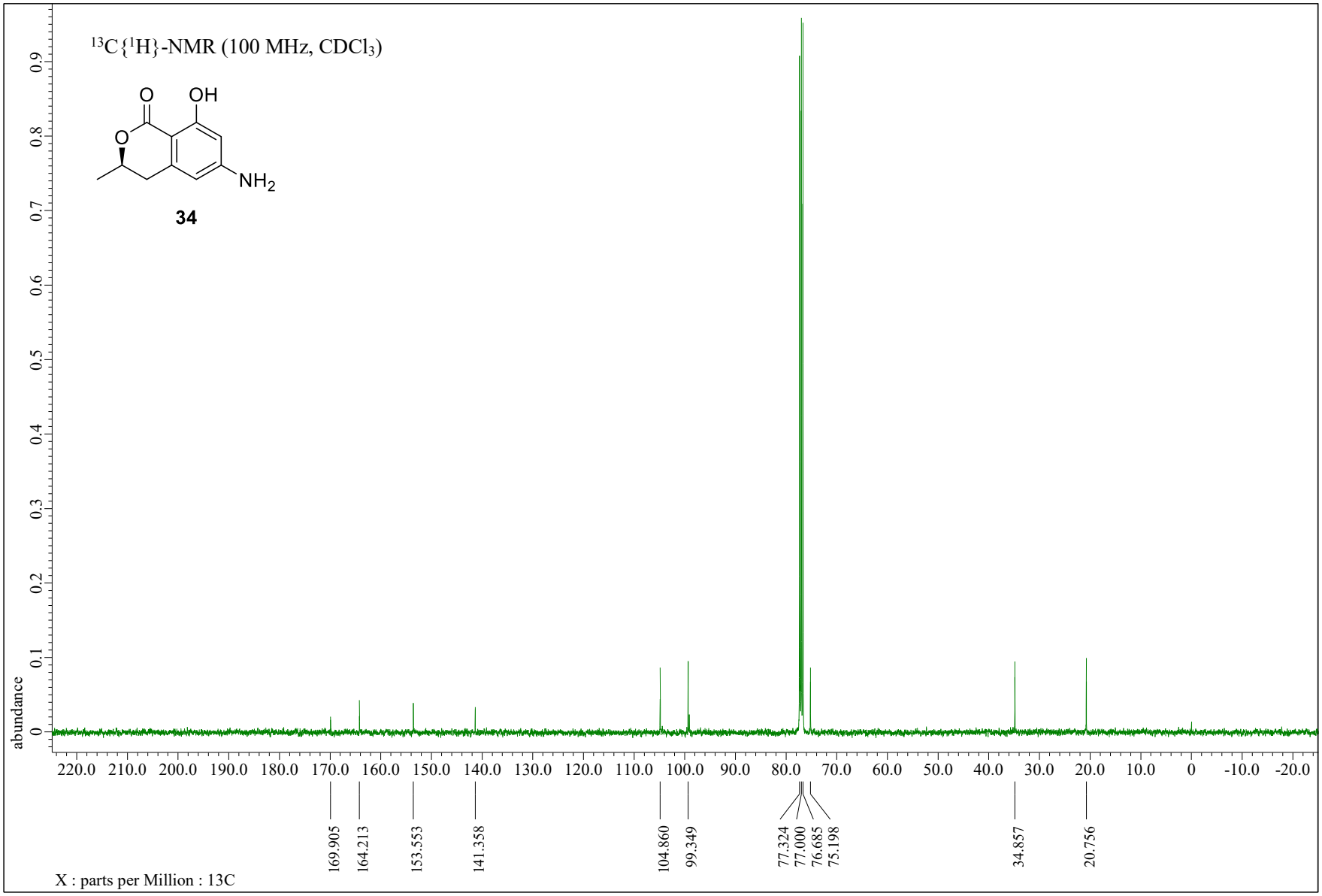

^{1}H-NMR (400 MHz, $CDCl_3$)
$H_{25}C_{12}$
S
O
OH
N
H
OMe
O
Bn
32
abundance
X : parts per Million : 1H
10.671
7.305
7.300
7.283
7.265
7.259
7.238
7.199
7.196
7.180
7.083
6.399
6.394
6.265
6.259
4.516
4.487
4.354
4.324
3.811
3.794
3.725
3.272
3.259
3.241
3.040
3.026
3.022
3.007
1.658
1.639
1.621
1.399
1.298
1.259
1.225
1.210
0.896
0.880
0.863
0.000
1.00
6.19
0.96
1.00
1.01
1.05
1.05
1.22
3.02
2.08
2.09
2.78
27.05
3.90
0.40


$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
32
abundance
X : parts per Million : 13C
196.411
161.162
152.523
141.196
138.632
128.220
127.648
127.400
116.464
109.332
99.120
77.324
77.000
76.685
75.932
70.974
63.537
43.219
31.901
30.004
29.689
29.623
29.585
29.489
29.337
29.165
29.136
29.003
22.681
19.878
14.119


^{1}H-NMR (400 MHz, $CDCl_3$)
O
OH
O
N
H
OMe
33
abundance
X : parts per Million : 1H
0.99
1.00
1.22
1.00
1.05
1.05
3.27
2.11
3.31
0.56
11.218
7.265
7.210
6.365
6.361
6.170
4.694
4.679
4.671
4.663
4.656
4.648
4.642
3.762
2.900
2.860
2.850
2.837
2.810
1.578
1.514
1.498
1.253
0.000


$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
O
OH
O
N
H
OMe
33
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
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
169.762
163.898
155.222
140.987
102.724
101.771
98.453
77.315
77.000
76.676
75.455
63.652
34.933
20.727
X : parts per Million : 13C


1H-NMR (400 MHz, CDCl3)
O
OH
O
NH2
34
abundance
X : parts per Million : 1H
11.198
7.265
6.069
6.064
5.951
4.674
4.659
4.647
4.632
4.621
4.617
4.606
4.591
4.187
2.847
2.821
2.806
2.781
2.771
2.741
2.731
1.593
1.497
1.482
0.000
1.00
0.95
1.00
1.02
1.12
2.02
2.43
1.74
3.44
0.57


$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)
O
OH
O
NH_2
34
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
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
169.905
164.213
153.553
141.358
104.860
99.349
77.324
77.000
76.685
75.198
34.857
20.756
X : parts per Million : 13C