

SUPPORTING INFORMATION

**Copper-Catalyzed Homo-dimerization of Nitronates
and Enolates under Oxygen Atmosphere**

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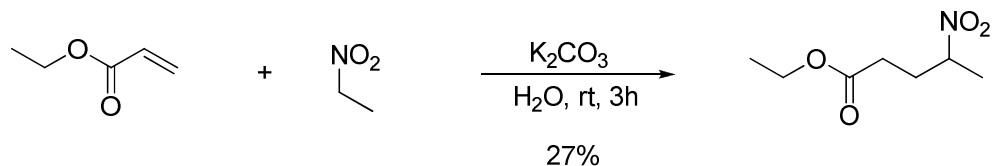
Experimental Section

General considerations. Reactions were performed in 1-dram vials using polypropylene screw caps with 13 mm hole and white silicone septa with white teflon face (SUPELCO). Flash chromatography was performed on 60Å silica gel (Sorbent Technologies). Purification by preparative HPLC was performed on a Shimadzu Prominence LC (LC-20AB) equipped with a SPD-20A UV-Vis detector and a Varian Dynamax (250 mm x 21.4 mm) column. GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). GC analyses were performed on a Shimadzu GC-2010 chromatograph equipped with a Restek column (Rtx®-5, 15m, 0.25 mm I.D.) The ^1H and ^{13}C NMR spectra were recorded on a JEOL ECX-400 spectrometer using residual solvent peak as a reference. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. IR spectra were obtained using ThermoNicolet Avatar 370 FT-IR instrument. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker. All compounds are racemic unless noted otherwise.

Materials. The following starting materials were obtained from commercial sources and were used without further purification: *t*-butyl acetate, zinc chloride (anhydrous, 99.99%), copper(II) chloride, and 4-pentenal were purchased from Alfa Aesar. Pinacolone, 2,4-dimethyl-3-pentanone, nitroethane, benzene (anhydrous), suberic acid, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, aluminum chloride, diisopropyl amine (redistilled), propiophenone, acrolein, ethyl acrylate, 2-nitropropane, nitrocyclohexane, sodium borohydride, 2-nitro-1-propanol, pentanal, butyllithium solution (2.5 M in hexanes), copper(II) acetylacetonate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and aluminum oxide (activated, basic, Brockmann I, standard grade) were obtained from Aldrich. *L*-Carvone was bought from SAFC. 2-Nitropropene was prepared from 2-nitro-1-propanol.¹

Synthesis of Starting Materials.

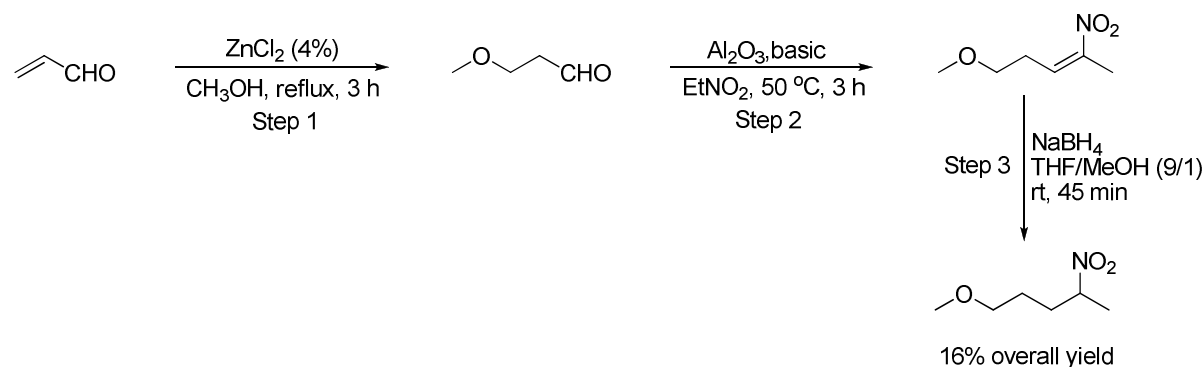
Ethyl 4-nitropentanoate



This compound was synthesized by following a literature procedure.² Nitroethane (3.75 g, 50 mmol) was added to an aqueous solution of K₂CO₃ (13.8 g in 75 mL of water). The resulting

mixture was stirred for 5 minutes at room temperature followed by addition of ethyl acrylate (5.0 g, 50 mmol). The reaction mixture was stirred for 3 hours, then extracted with ethyl acetate (3 x 100 mL). The organic layer was dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography (silica gel, hexanes/AcOEt 6/4) to give a colorless oil (2.36 g, 27%). This compound is known.³ ¹H NMR (400 MHz, CDCl₃) δ 1.26 (t, *J* = 7.2 Hz, 3H), 1.57 (d, *J* = 6.5 Hz, 3H), 2.02-2.15 (m, 1H), 2.21-2.47 (m, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.61-4.72 (m, 1H).

1-Methoxy-4-nitropentane



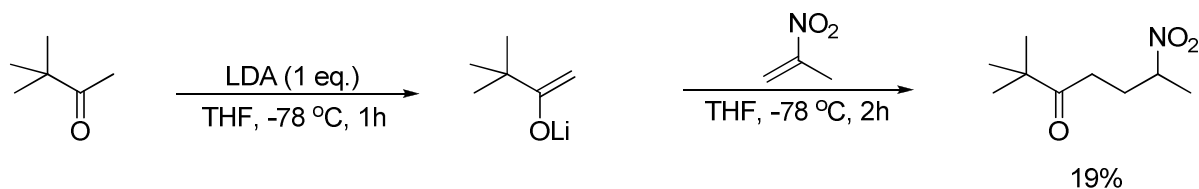
Step 1:⁴ A solution of acrolein (5.6 g, 100 mmol) and anhydrous zinc chloride (544 mg, 4.0 mmol) in methanol (30 mL) was refluxed for 3 h under argon. The resulting mixture was concentrated to about 5 mL and filtered through a silica gel column using ether eluent. Organic solvents of the filtrate were removed on a rotary evaporator to yield crude 3-methoxypropanal. This intermediate was subjected to the next step without further purification.

Step 2:⁵ A dried 200 mL Schlenk flask was charged with aluminum oxide (basic, activated, Brockmann I, 60 g) inside the glovebox. The flask was taken out of glovebox. Nitroethane (80 mL) and 3-methoxypropanal from Step 1 were added under argon atmosphere. The resulting mixture was stirred at 50 °C for 3 hours. The solid was filtered off and washed with ethyl acetate. Combined organic solvents were removed on a rotary evaporator to yield a residue. It was purified by column chromatography (hexane/ethyl acetate 6/4) to afford 5-methoxy-2-nitropent-2-ene that was directly used in Step 3.

Step 3:⁶ 5-Methoxy-2-nitropent-2-ene and THF/MeOH mixture (9/1, 100 mL total) were combined in a 250 mL Erlenmeyer flask. Sodium borohydride (950 mg, 25 mmol) was added in four portions. The reaction mixture was stirred at room temperature for 45 minutes and

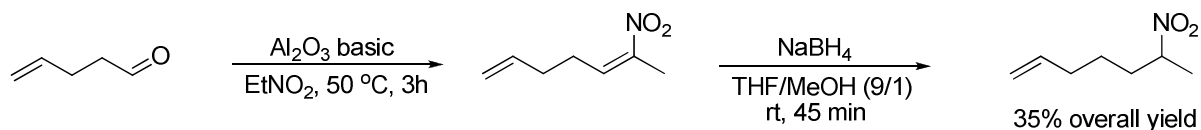
then quenched with water (70 mL). The organic solvents were removed on a rotary evaporator. The resulting aqueous solution was extracted with ether (3 x 100 mL). The combined ether layers were washed with brine and dried over magnesium sulfate. After filtration, solvent was removed and the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate 6/4) to afford the title compound as a colorless oil (2.4 g, 16 % overall yield). $R_f = 0.43$ (SiO₂, AcOEt/hexanes 3/7). ¹H NMR (400 MHz, CDCl₃) δ 1.50-1.65 (m, 5H), 1.79-1.91 (m, 1H), 1.98-2.13 (m, 1H), 3.30-3.47 (m, 5H), 4.50-4.65 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 19.3, 25.8, 32.0, 58.6, 71.5, 83.4. FT-IR (neat, cm⁻¹) ν 1549, 1451, 1391, 1360, 1117. Anal calcd for C₆H₁₃NO₃ (147.17 g/mol): C, 48.97; H, 8.90; N, 9.52; Found. C, 49.07; H, 8.67; N, 9.05.

2,2-Dimethyl-6-nitroheptan-3-one



This compound was prepared by following a literature procedure.⁷ A flame-dried 100 mL Schlenk flask was charged with a stir bar, dry THF (60 mL), and diisopropyl amine (7.0 mL) under argon atmosphere. The solution was cooled down to -78 °C followed by the addition of *n*-BuLi (18 mL, 2.5M in hexanes). After 5 minutes, pinacolone (4.5 g, 45 mmol) was added dropwise. The reaction was stirred at -78 °C for 1 hour. A solution of 2-nitropropene (2.43 g, 28 mmol) in THF (10 mL) was then added dropwise. Stirring was continued for another 2 hours. The reaction was warmed to -40 °C followed by addition of acetic acid (4.5 mL) at -40 °C. The cooling bath was then removed. The reaction mixture was poured into ice water (150 mL). The resulting mixture was extracted by CH₂Cl₂. The combined CH₂Cl₂ layers were washed with brine and dried over MgSO₄. The residue obtained after solvent removal was purified by column chromatography using hexanes/ether (8.5/1.5) as an eluent to afford 1.0 g of a light tan oil (19 %). $R_f = 0.48$ (SiO₂, AcOEt/hexanes 3/7). ¹H NMR (400 MHz, CDCl₃) δ 1.14 (s, 9H), 1.55 (d, $J = 6.5$ Hz, 3H), 2.06-2.16 (m, 2H), 2.53-2.59 (m, 2H), 4.55-4.65 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 19.6, 26.4, 29.0, 32.2, 44.1, 82.8, 214.2. FT-IR (neat, cm⁻¹) ν 1706, 1549, 1365. Anal calcd for C₉H₁₇NO₃ (187.24 g/mol): C, 57.73; H, 9.15; N, 7.48; Found. C, 58.14; H, 9.01; N, 7.4.

6-Nitrohept-1-ene



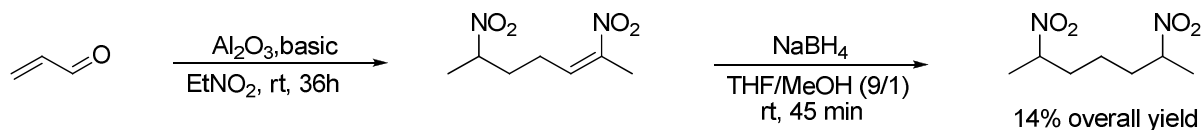
Step 1:⁵ A dried 100 mL Schlenk flask was charged with aluminum oxide (basic, activated, Brockmann I, 40 g) inside the glovebox. The flask was then taken out of glovebox. Nitroethane (60 mL) and 4-pentenal (4.2 g, 50 mmol) were added under argon atmosphere. The resulting mixture was stirred at 50 °C for 3 hours. The solid was filtered off and washed with ethyl acetate. Organic solvent of the combined filtrates was then removed on a rotary evaporator. The residue was purified by column chromatography (hexane/ethyl acetate 8/2) to yield 6-nitrohepta-1,5-diene.

Step 2:⁶ The intermediate 6-nitrohepta-1,5-diene from Step 1 was combined with THF/MeOH (9/1, 100 mL) in a 250 mL Erlenmeyer flask. Sodium borohydride (1.14 g, 30 mmol) was added in four portions. The reaction mixture was stirred at room temperature for 45 minutes and then quenched with water (50 mL). The volatile solvents were removed on a rotary evaporator. The resulting aqueous solution was extracted with ether (3 x 100 mL). The combined ether layers were washed with brine and dried over magnesium sulfate. After filtration, solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate 7/3) to afford the title compound as a light tan oil (2.5 g, 35 % overall yield). This compound is known.⁸ $R_f = 0.57$ (SiO_2 , AcOEt/hexanes 3/7). ^1H NMR (400 MHz, CDCl_3) δ 1.38-1.48 (m, 2H), 1.53 (d, $J = 6.8$ Hz, 3H), 1.67-1.78 (m, 1H), 1.95-2.13 (m, 3H), 4.51-4.62 (m, 1H), 4.95-5.07 (m, 2H), 5.69-5.82 (m, 1H).

2-Nitroheptane

This compound was synthesized from pentanal and nitroethane by using a procedure analogous to the synthesis of 6-nitrohept-1-ene. The product was obtained as light tan oil (2.2 g, 30% overall yield). This compound is known.⁹ $R_f = 0.60$ (SiO_2 , AcOEt/hexanes 3/7). ^1H NMR (400 MHz, CDCl_3) δ 0.85-0.91 (m, 3H), 1.23-1.38 (m, 6H), 1.52 (d, $J = 6.5$ Hz, 3H), 1.64-1.76 (m, 1H), 1.93-2.06 (m, 1H), 4.51-4.61 (m, 1H).

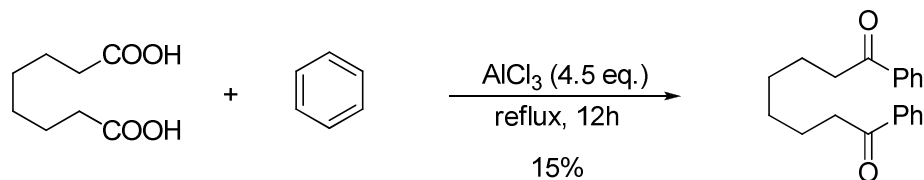
2,6-Dinitroheptane



Step 1:⁵ A flame-dried 100 mL Schlenk flask was charged with aluminum oxide (basic, activated, Brockmann I, 50 g) inside the glovebox. The flask was taken out of glovebox. Nitroethane (70 mL) was added under argon atmosphere. To this suspension was added dropwise acrolein (2.8 g, 50 mmol). The resulting mixture was stirred at room temperature for 36 hours. The solid was filtered off and washed with ethyl acetate. Organic solvent of the combined filtrates was then removed on a rotary evaporator. The residue was purified by column chromatography (hexanes/ethyl acetate 1/1) to afford 2,6-dinitrohept-2-ene.

Step 2:⁶ 2,6-dinitrohept-2-ene from step 1 was dissolved in a mixture of THF/MeOH (9/1, 50 mL) in a 250 mL Erlenmeyer flask. Sodium borohydride (0.46 g, 12 mmol) was added in four portions. The reaction mixture was stirred at room temperature for 45 minutes and then quenched with water (25 mL). The organic solvent was removed on a rotary evaporator. The resulting aqueous solution was extracted with ether (3 x 100 mL). The combined ether layers were washed with brine and dried over magnesium sulfate. After filtering off magnesium sulfate and solvent removal, the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate 7/3) to afford the title compound as a light tan oil (mixture of diastereomers, 1.33 g, 14 % overall yield). This compound is known.¹ $R_f = 0.37$ (SiO_2 , AcOEt/hexanes 3/7). ^1H NMR (400 MHz, CDCl_3) δ 1.33-1.43 (m, 2H), 1.54 (d, $J = 6.7$ Hz, 6H), 1.68-1.83 (m, 2H), 1.97-2.10 (m, 2H), 4.50-4.61 (m, 2H).

1,8-Diphenyloctane-1,8-dione



This compound was prepared by following a literature method with minor modifications.¹⁰ To a stirred benzene (30 mL) suspension of AlCl_3 (12.0 g, 90 mmol) was added a benzene (10 mL) solution of 1,6-hexanedicarboxylic acid (3.48 g, 20 mmol) at 0 °C under argon atmosphere. The mixture was stirred at room temperature for 30 minutes and then refluxed for 12 hours. The reaction mixture was poured into chilled hydrochloric acid (5 M) and

organic materials were extracted by CH_2Cl_2 . The combined extracts were washed with 1 M aqueous NaOH solution, water, and brine, and then dried over MgSO_4 . After filtering off magnesium sulfate and solvent removal, the residue was purified by column chromatography (silica gel, hexanes/ethyl acetate 8/2) to afford the title compound as a colorless solid (0.89 g, 15%). ^1H NMR (400 MHz, CDCl_3) δ 1.40-1.49 (m, 4H), 1.71-1.81 (m, 4H), 2.98 (t, $J = 7.0$ Hz, 4H), 7.42-7.59 (m, 6H), 7.93-7.99 (m, 4H).

Optimization of Reaction Conditions for The Dimerization of Nitrocyclohexane

The general procedure for dimerization of nitroalkanes (see below) was used for all optimization of reaction conditions.

For determination of GC yields, response factors for 1,1'-dinitrobi(cyclohexane), cyclohexanone and 2,2,7,7-tetramethyloctane-3,6-dione with respect to internal standard dodecane were determined.

Mixtures of dodecane (54 mg, 0.3 mmol) with different amount of 1,1'-dinitrobi(cyclohexane) (32 mg, 0.25 mmol; 64 mg, 0.5 mmol and 96 mg, 0.75 mmol) were prepared by using 4 mL of ethyl acetate as the solvent. These mixtures were analyzed by GC and three values of response factor were determined from the ratio of analyte and the internal standard peak areas. Three values of this response factor were found to be similar and the final response factor used was the average of these values.

Similarly, the response factor for cyclohexanone with internal standard dodecane was determined from the GC results of mixtures of dodecane (54 mg, 0.3 mmol) with different amounts of cyclohexanone (4.9 mg, 0.05 mmol; 7.3 mg, 0.075 mmol and 9.8 mg, 0.1 mmol) in ethyl acetate (4 mL).

The prepared mixtures of ethyl acetate (4 mL), dodecane (54 mg, 0.3 mmol) and 2,2,7,7-tetramethyloctane-3,6-dione (50 mg, 0.25 mmol; 74 mg, 0.5 mmol and 99 mg, 1.0 mmol) were used for determining the response factor for this product.

To the reaction mixtures was added dodecane (54 mg, 0.3 mmol) as the internal standard followed by dilution with ethyl acetate for GC analysis. The amounts of the products formed were calculated from the peak area of dodecane, products, and the response factor obtained previously. All GC yields are the average of at least two runs.

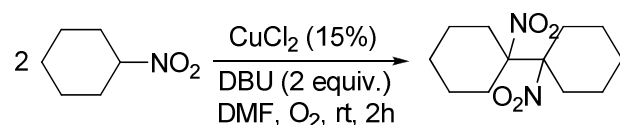


Table S1. Optimization of Reaction Solvent

Solvent	GC Yield
DMF	51%
THF	29%
Dioxane	38%
DCM	44%
Acetonitrile	22%
Methanol	21%

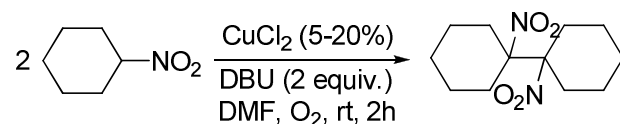
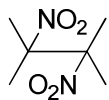


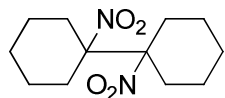
Table S2. Optimization of Catalyst Loading

Catalyst Loading	GC Yield
5%	38%
10%	45%
15%	53%
20%	57%

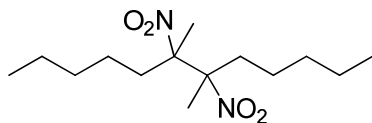
General procedure for dimerization of nitroalkanes. A 1-dram vial equipped with a magnetic stir bar was charged with anhydrous copper(II) chloride (10-15 mol %), substrate (1 mmol), DMF (0.8 mL), and DBU (2.0 equiv). The vial was capped with a septum fitted cap. Dry oxygen was introduced to the reaction via needle. The vial was flushed with dry oxygen for 30 seconds then stirred at room temperature under 1 atmosphere of oxygen for indicated time. The reaction mixture was directly subjected to column chromatography on silica gel (hexanes followed by appropriate solvent to elute the products). After concentrating the fractions containing the product, the residue was dried under reduced pressure.



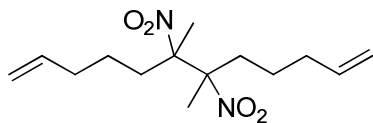
2,3-Dimethyl-2,3-dinitrobutane (Entry 1, Table 1): Copper(II) chloride (13.5 mg, 0.1 mmol), 2-nitropropane (89 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 1 hour. After column chromatography (hexanes, then 1/9 followed by 2/8 ethyl acetate/hexanes) 70 mg (80%) of a colorless solid was obtained. $R_f = 0.37$ (SiO₂, 3/7 ethyl acetate/hexanes). This compound is known.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 1.74 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 23.0, 91.4.



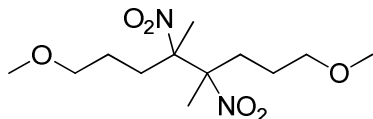
1,1'-Dinitrobi(cyclohexane) (Entry 2, Table 1): Copper(II) chloride (20.3 mg, 0.15 mmol), nitrocyclohexane (129 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 2 hours. After column chromatography (hexanes, then 1/9 followed by 2/8 ethyl acetate/hexanes) 70 mg (55%) of a light yellow solid was obtained. $R_f = 0.55$ (SiO₂, 3/7 ethyl acetate/hexanes). This compound is known.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 1.06-1.29 (m, 6H), 1.53-1.68 (m, 6H), 1.73-1.83 (m, 4H), 2.55-2.64 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 22.5, 24.0, 29.8, 96.2.



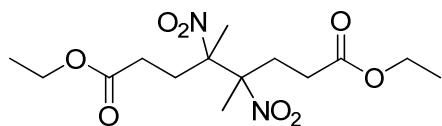
6,7-Dimethyl-6,7-dinitrododecane (Entry 3, Table 1): Copper(II) chloride (20.3 mg, 0.15 mmol), 2-nitroheptane (145 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 70 minutes. After column chromatography (hexanes, then 1/9 followed by 2/8 ethyl acetate/hexanes) 105 mg (73%) of a light tan oil (1:1 mixture of diastereomers by GC and NMR analysis) was obtained. $R_f = 0.62$ (SiO₂, 3/7 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃; mixture of diastereomers) δ 0.82-1.07 (m, 8H), 1.21-1.44 (m, 10H), 1.51-1.74 (m, 7H), 1.96-2.08 (m, 1H), 2.34-2.46 (m, 2H). ¹³C NMR (100 MHz, CDCl₃; mixture of diastereomers; 3 signals could not be located) δ 13.9, 18.5, 18.7, 22.31, 22.35, 23.9, 31.6, 34.0, 34.7, 95.6, 95.9. FT-IR (neat, cm⁻¹) ν 2958, 1544, 1388. Anal calcd for C₁₄H₂₈N₂O₄ (288.38 g/mol): C, 58.31; H, 9.79; N, 9.71; Found. C, 59.26; H, 9.75; N, 9.5.



6,7-Dimethyl-6,7-dinitrododeca-1,11-diene (Entry 4, Table 1): Copper(II) chloride (20.3 mg, 0.15 mmol), 6-nitrohept-1-ene (143 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 1 hour. After column chromatography (hexanes, then 1/9 followed by 2/8 ethyl acetate/hexanes) 85 mg (60%) of a yellow oil (1:1 mixture of diastereomers by GC and NMR) was obtained. R_f = 0.55 and 0.58 (SiO₂, 3/7 ethyl acetate/hexanes). This compound is known.⁸ ¹H NMR (400 MHz, CDCl₃; mixture of diastereomers) δ 1.02-1.20 (m, 2H), 1.40-1.76 (m, 9H), 1.98-2.16 (m, 5H), 2.34-2.48 (m, 2H), 4.96-5.08 (m, 4H), 5.67-5.81 (m, 2H). ¹³C NMR (100 MHz, CDCl₃; mixture of diastereomers; 2 signals could not be located) δ 18.5, 18.8, 23.4, 33.3, 33.5, 34.1, 95.4, 95.7, 115.68, 115.75, 137.14, 137.18.

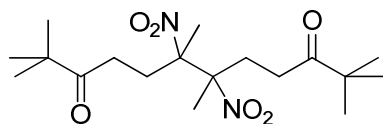


1,8-Dimethoxy-4,5-dimethyl-4,5-dinitrooctane (Entry 5, Table 1): Copper(II) chloride (13.5 mg, 0.1 mmol), 1-methoxy-4-nitropentane (147 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 1 hour. After column chromatography (hexanes, then 1/9 followed by 2/8, 3/7, 4/6 and 1/1 ethyl acetate/hexanes) 90 mg (62%) of a light tan oil (1:1 mixture of diastereomers by GC and NMR) was obtained. R_f = 0.29 (SiO₂, 3/7 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃; mixture of diastereomers) δ 1.20-1.33 (m, 2H), 1.55-1.73 (m, 8H), 1.84-1.94 (m, 1H), 2.08-2.18 (m, 1H), 2.40-2.54 (m, 2H), 3.29-3.47 (m, 10H). ¹³C NMR (100 MHz, CDCl₃; mixture of diastereomers; one signal could not be located) δ 18.5, 18.8, 24.5, 24.6, 31.3, 31.9, 58.62, 58.65, 71.6, 95.4, 95.9. FT-IR (neat, cm⁻¹) ν 1542, 1116. Anal calcd for C₁₂H₂₄N₂O₆ (292.33 g/mol): C, 49.30; H, 8.28; N, 9.58; Found. C, 49.99; H, 8.31; N, 9.23.

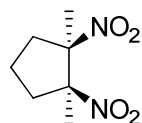


Diethyl 4,5-dimethyl-4,5-dinitrooctanedioate (Entry 6, Table 1): Copper(II) chloride (13.5 mg, 0.1 mmol), methyl 4-nitropentanoate (161 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 50 minutes. After column chromatography (hexanes, then 1/9

followed by 2/8, 3/7, and 4/6 ethyl acetate/hexanes) 110 mg (63 %) of a light tan oil (1:1 mixture of diastereomers by GC and NMR) was obtained. $R_f = 0.29$ (SiO₂, 3/7 ethyl acetate/hexanes). This compound is known.¹² ¹H NMR (400 MHz, CDCl₃; mixture of diastereomers) δ 1.21-1.30 (m, 6H), 1.59 (s, 3H), 1.65 (s, 3H), 2.10-2.47 (m, 6H), 2.75-2.90 (m, 2H), 4.10-4.20 (m, 4H). ¹³C NMR (100 MHz, CDCl₃; mixture of diastereomers; 3 signals could not be located) δ 14.1, 18.3, 18.6, 29.2, 29.4, 29.7, 61.1, 94.6, 94.9, 171.4, 171.5.



2,2,6,7,11,11-Hexamethyl-6,7-dinitrododecane-3,10-dione (Entry 7, Table 1): Copper(II) chloride (13.5 mg, 0.1 mmol), 2,2-dimethyl-6-nitroheptan-3-one (187 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol), 1 hour. After column chromatography (hexanes, then 1/9 followed by 2/8 ethyl acetate/hexanes) 85 mg (46 %) of a colorless solid (1:1 mixture of diastereomers by GC and NMR) was obtained. $R_f = 0.41$ (SiO₂, 3/7 ethyl acetate/hexanes), mp 125-130 °C (ether). ¹H NMR (400 MHz, CDCl₃; mixture of diastereomers) δ 1.12 (s, 9H), 1.13 (s, 9H), 1.61 (s, 3H), 1.62 (s, 3H), 2.12-2.47 (m, 6H), 2.60-2.70 (m, 2H). ¹³C NMR (100 MHz, CDCl₃; mixture of diastereomers; 3 signals could not be located) δ 18.6, 18.9, 26.3, 28.7, 28.8, 31.2, 31.3, 44.3, 95.2, 95.4, 213.1. FT-IR (neat, cm⁻¹) ν 1705, 1540. Anal calcd for C₁₈H₃₂N₂O₆ (372.46 g/mol): C, 58.05; H, 8.66; N, 7.52; Found. C, 58.05; H, 8.58; N, 7.57.



cis-1,2-Dimethyl-1,2-dinitrocyclopentane (Entry 8, Table 1): Copper(II) chloride (20.3 mg, 0.15 mmol), 2,6-dinitroheptane (190 mg, 1.0 mmol), DMF (1.0 mL), and DBU (608 mg, 4.0 mmol), 90 minutes. After column chromatography (hexanes, then 1/9 followed by 1.5/8.5 ether/hexanes) 100 mg (53 %) of a white solid was obtained as a single diastereomer by NMR and GC. $R_f = 0.48$ (SiO₂, 3/7 ethyl acetate/hexanes). This compound is known.¹ ¹H NMR (400 MHz, CDCl₃) δ 1.60 (s, 6H), 2.19-2.31 (m, 4H), 2.63-2.76 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 22.1, 37.6, 98.8.

Control Experiments for The Dimerization of Nitronates

The procedure of this experiment is the same with the general procedure for dimerization of nitroalkanes above, except that nitrogen atmosphere was used instead of oxygen atmosphere (entry 1 and 2) and/or catalyst CuCl_2 was not used (entries 1 and 3).

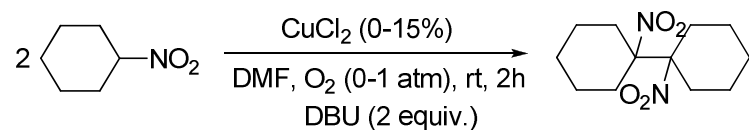


Table S3. Control Experiments

Catalyst Loading	Oxygen Pressure	GC Yield
0%	0 atm	Trace
15%	0 atm	9%
0%	1 atm	Trace
15%	1 atm	53%

Using Air as the Oxidant instead of Oxygen in The Dimerization of Nitronates

A 2-dram vial equipped with a magnetic stir bar was charged with anhydrous copper(II) chloride (20.3 mg, 0.15 mmol), nitrocyclohexane (129 mg, 1.0 mmol), DMF (0.8 mL), and DBU (304 mg, 2.0 mmol). The vials was opened in air and stirred at room temperature for indicated time. The reaction mixture was diluted by ethyl acetate and injected into GC for determining the GC yields.

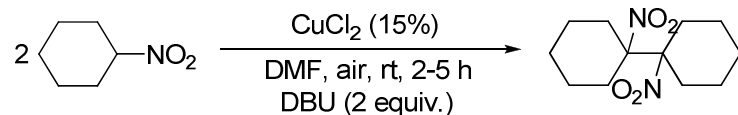
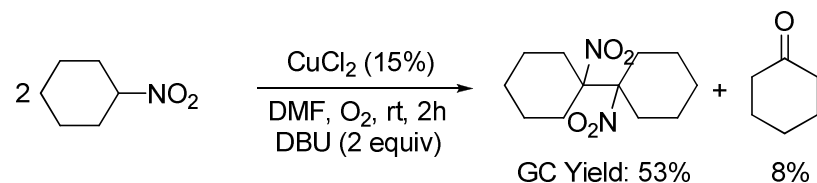


Table S4. Air as the Oxidant

Time	GC Yield
2h	37%
3h	45%
4h	51%
5h	52%

Determination of Nef reaction byproduct yield

The reaction mixture of entry 4, Table S3 was used in this part. The byproduct cyclohexanone, which was formed in the Nef reaction, was observed by GC in 8% yield.



General procedure for dimerization of enolates

Preparation of enolate solution. A flame-dried 10 mL Schlenk flask was charged with a stirrer, dry THF (4 mL), and diisopropyl amine (1 mL, 7.1 mmol) under argon atmosphere. The solution was cooled down to -78 °C followed by the addition of *n*-BuLi (2.2 mL, 2.5M in hexanes, 5.5 mmol). After 5 minutes, carbonyl compound (5.0 mmol) was added dropwise. The reaction was stirred at -78 °C for 30 minutes and then at room temperature for another 30 minutes. A solution of ZnCl₂ (0.3-0.5 equiv with respect to carbonyl compound) in dry THF (3 mL) was then added dropwise at room temperature. The resulting solution was stirred for 30 minutes. Solvent was partially evaporated under reduced pressure to afford 5 mL of a 1 M enolate solution. It is important to use recently purchased anhydrous ZnCl₂ for reproducible, optimal yields.

Oxidative dimerization reaction. A 1-dram vial equipped with a magnetic stir bar was charged with copper(II) acetylacetonate (10-20 mol %). The vial was flushed with argon and capped by a septum fitted cap. The 1 M enolate solution (1 mL, 1 mmol) prepared as described above was then added via syringe. Dry oxygen was introduced to the reaction via needle. The vial was flushed with dry oxygen for 15 seconds then stirred at room temperature under 1 atmosphere of oxygen for 10 minutes. The reaction mixture was directly subjected to column chromatography on silica gel (hexanes followed by appropriate solvent to elute the products). After concentrating the fractions containing the product, the residue was dried under reduced pressure.

Optimization of zinc amount for the dimerization of pinacolone

The general procedure for dimerization of enolates (see above) was used for all of the optimization reactions. GC yields were determined as described above.

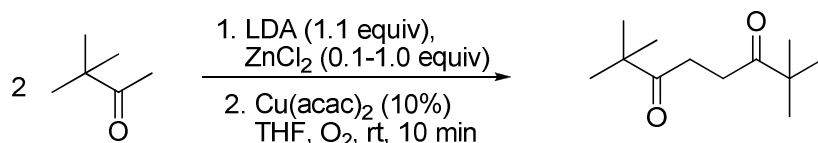
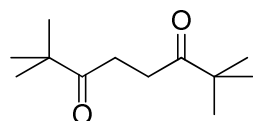


Table S5. Optimization of zinc amount

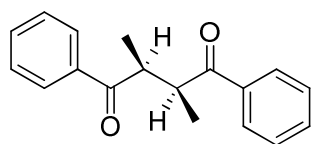
Equivalents of ZnCl ₂	GC Yield
0.1	22%
0.3	52%
0.5	67%
1.0	35%

Determination of alpha-peroxy carbonyl formation

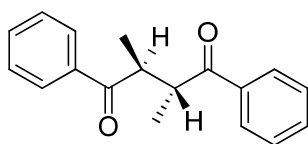
If the side product α -peroxy pinacolone would be formed in the reaction, it could be converted to α -hydroxy pinacolone by reduction with dimethyl sulfide.¹³ After the dimerization of enolate of pinacolone by standard procedure, excess dimethyl sulfide (0.2 mL, 2.7 mmol) was added to the reaction mixture. The mixture was stirred at 25 °C for 3 h and then diluted by ethyl acetate and analyzed by GC and GC-MS. α -Hydroxy pinacolone was not observed in the reaction mixture. Conclusion is that α -peroxy carbonyl compounds are not formed in enolate dimerizations in appreciable amounts.



2,2,7,7-Tetramethyloctane-3,6-dione (Entry 1, Table 2; pinacolone dimerization): Zinc chloride (0.5 equiv), copper(II) acetylacetonate (26.2 mg, 0.1 mmol). After column chromatography (hexanes, then 5/95 followed by 10/90, and 15/85 ethyl acetate/hexanes) 68 mg (69%) of a colorless oil was obtained. $R_f = 0.46$ (SiO₂, 1/9 ethyl acetate/hexanes). This compound is known.¹⁴ ¹H NMR (400 MHz, CDCl₃) δ 1.18 (s, 18H), 2.77 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 30.5, 44.0, 214.9.



Major diastereomer

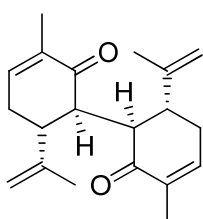


Minor diastereomer

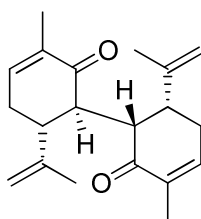
2,3-Dimethyl-1,4-diphenylbutane-1,4-dione (Entry 2, Table 2; propiophenone dimerization): Zinc chloride (0.3 equiv), copper(II) acetylacetonate (26.2 mg, 0.1 mmol). After column chromatography (hexanes, then 2/98 followed by 4/96, 6/94, 8/92, 10/90, 12/88, and 15/85 ether/hexanes) 18 mg of minor and 72 mg of major diastereomer (4:1, total yield 68%) were obtained. These compounds are known.¹⁵

- Major diastereomer: Colorless oil, $R_f = 0.24$ (SiO₂, 1/9 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 1.29 (d, $J = 6.5$ Hz, 6H), 3.92-4.03 (m, 2H), 7.43-7.49 (m, 4H), 7.52-7.58 (m, 2H), 7.97-8.02 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 15.5, 43.6, 128.5, 128.6, 132.9, 136.1, 204.3.

- Minor diastereomer: Colorless solid, $R_f = 0.28$ (SiO₂, 1/9 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 1.14 (d, $J = 6.5$ Hz, 6H), 4.01-4.11 (m, 2H), 7.48-7.54 (m, 4H), 7.58-7.63 (m, 2H), 8.04-8.09 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 17.5, 43.3, 128.5, 128.8, 133.4, 136.8, 203.8.



Major diastereomer

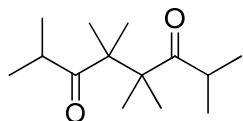


Minor diastereomer

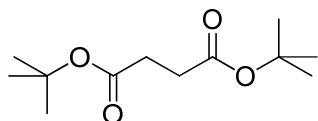
3,3'-Dimethyl-6,6'-di(prop-1-en-2-yl)-1,1'-bi(cyclohex-3-ene)-2,2'-dione (Entry 3, Table 2; (L)-carvone dimerization): Zinc chloride (0.3 equiv), copper(II) acetylacetonate (26.2 mg, 0.1 mmol). After column chromatography (hexanes, then 2/98 followed by 4/96, 6/94, 8/92, 10/90, 12/88, and 15/85 ether/hexanes) 62 mg of major and 33 mg of minor diastereomer (1.9:1, total yield 64 %) were obtained. These compounds are known.¹⁶

- Major diastereomer: Colorless solid, $R_f = 0.31$ (SiO₂, 1/9 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 1.64 (s, 6H), 1.75 (s, 6H), 2.22-2.42 (m, 4H), 2.50 (d, $J = 12.1$ Hz, 2H), 3.48 (dt, $J = 12.1$ Hz, 5.0 Hz, 2H), 4.82 (s, 2H), 4.86 (s, 2H), 6.66 (d, $J = 5.5$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.1, 19.1, 31.3, 48.2, 49.4, 114.4, 135.6, 142.8, 145.8, 200.4.

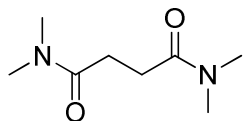
- Minor diastereomer: Colorless solid, $R_f = 0.23$ (SiO_2 , 1/9 ethyl acetate/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 1.63 (s, 3H), 1.66 (s, 3H), 1.69 (d, $J = 1.5$ Hz, 3H), 1.84 (d, $J = 1.5$ Hz, 3H), 2.33-2.71 (m, 4H), 2.74-3.08 (m, 4H), 4.64 (s, 1H), 4.73 (s, 1H), 4.78 (d, $J = 1.5$ Hz, 2H), 6.53 (br s, 1H), 6.73 (br s, 1H).



2,4,4,5,5,7-Hexamethyloctane-3,6-dione (Entry 4, Table 2; diisopropyl ketone dimerization): Zinc chloride (0.3 equiv), copper(II) acetylacetonate (39.3 mg, 0.15 mmol). After column chromatography (hexanes, then 2/98 followed by 3/97, 4/96, 5/95, 6/94, 7/93, and 8/92 ether/hexanes) 35 mg (31%) of a colorless oil was obtained. $R_f = 0.47$ (SiO_2 , 1/9 ethyl acetate/hexanes). This compound is known.¹⁴ ^1H NMR (400 MHz, CDCl_3) δ 1.05 (d, $J = 6.7$ Hz, 12H), 1.24 (s, 12H), 3.16 (septet, $J = 6.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 22.3, 35.6, 53.3, 219.8.

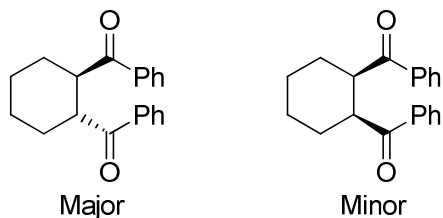


Di-tert-butyl succinate (Entry 5, Table 2; t-butyl acetate dimerization): *n*-BuLi (2.4 mL, 2.5M in hexanes, 6 mmol), zinc chloride (0.5 equiv), copper(II) acetylacetonate (26.2 mg, 0.1 mmol), 20 minutes. After column chromatography (hexanes, then 5/95 ethyl acetate/hexanes) 60 mg (52 %) of a colorless oil was obtained. $R_f = 0.23$ (SiO_2 , 1/9 ethyl acetate/hexanes). This compound is known.¹⁷ ^1H NMR (400 MHz, CDCl_3) δ 1.45 (s, 18H), 2.49 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 28.1, 30.6, 80.5, 171.7.



***N,N,N',N'*-Tetramethylsuccinamide (Entry 6, Table 2; dimethylacetamide dimerization):** Zinc chloride (0.5 equiv), copper(II) acetylacetonate (39.3 mg, 0.15 mmol). After column chromatography (a short column, eluent: hexanes, then 1/1 ethyl acetate/hexanes followed by ethyl acetate and 1/9, 2/8, 3/7 methanol/ethyl acetate) 50 mg (58 %) of a colorless solid was obtained. $R_f = 0.53$ (SiO_2 , 1/1 ethyl acetate/methanol). This

compound is known.¹⁸ ¹H NMR (400 MHz, CDCl₃) δ 2.67 (s, 4H), 2.95 (s, 6H), 3.06 (s, 6H).
¹³C NMR (100 MHz, CDCl₃) δ 28.1, 30.6, 80.5, 171.7.



1,2-Dibenzoylcyclohexane (Entry 7, Table 2): A flame-dried 10 mL Schlenk flask was charged with a stirrer, dry THF (4 mL), and diisopropyl amine (1 mL, 7.1 mmol) under argon atmosphere. The solution was cooled to -78 °C followed by the addition of BuLi (2.2 mL, 2.5M in hexanes, 5.5 mmol). After 5 minutes, a solution of 1,8-diphenyloctane-1,8-dione (2.5 mmol) in THF (2 mL) was added dropwise. The reaction was stirred at -78 °C for 30 minutes and then at room temperature for another 30 minutes. A solution of ZnCl₂ (204 mg, 1.5 mmol) in dry THF (3 mL) was then added dropwise at room temperature. The resulting solution was stirred for additional 30 minutes. Solvent was partly evaporated under reduced pressure to the volume of 5 mL yielding a 0.5 M dienolate solution. A 1-dram vial equipped with a magnetic stir bar was charged with copper(II) acetylacetonate (39.3 mg, 0.15 mmol). The vial was flushed with argon and capped by a septum fitted cap. The enolate solution (1 mL, 0.5 mmol of dienolate or 1 mmol of enolate) prepared above was then added. Dry oxygen was introduced to the reaction via needle. The vial was flushed by dry oxygen for 15 seconds then stirred at room temperature under 1 atmosphere of oxygen for 10 minutes. The reaction mixture was directly subjected to column chromatography on silica gel. After column chromatography (hexanes, then 2/98, 4/96, 6/94, 8/92, and 10/90 ethyl acetate/hexanes) and preparative HPLC (5/95 ethyl acetate/hexanes) 54 mg of a major and 26 mg of a minor diastereomer (2:1, total yield 55%) was obtained. These compounds are known.¹⁹

- The *trans*-isomer: Colorless solid, mp 114-116 °C (from ether, lit.¹⁹ 115-116 °C) R_f = 0.23 (SiO₂, 1/9 ethyl acetate/hexanes). ¹H NMR (400 MHz, CDCl₃) δ 1.33-1.54 (m, 4H), 1.85-1.96 (m, 2H), 2.11-2.20 (m, 2H), 3.87-3.97 (m, 2H), 7.43-7.49 (m, 4H), 7.52-7.58 (m, 2H), 7.98-8.03 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 25.9, 30.2, 47.1, 128.5, 128.6, 132.9, 136.1, 203.5.

- The *cis*-isomer: Colorless solid, $R_f = 0.20$ (SiO_2 , 1/9 ethyl acetate/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 1.47-1.57 (m, 2H), 1.68-1.79 (m, 2H), 1.88-1.98 (m, 2H), 2.21-2.32 (m, 2H), 3.74-3.81 (m, 2H), 7.40-7.46 (m, 4H), 7.48-7.54 (m, 2H), 7.82-7.87 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.5, 27.0, 45.3, 128.2, 128.5, 132.3, 137.1, 202.6.

Unsuccessful dimerizations. The dimerization of nitronates and enolates derived from the following compounds afforded either no product or low yields: (2-nitropropyl)benzene, 2-nitropropan-1-ol, 6-nitroheptanenitrile, diethylketone, acetophenone, and cyclohexanone.

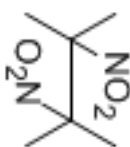
Control reactions for the dimerization of nitronates: If copper(II) chloride was omitted from the normal reaction conditions for the dimerization of 2-nitropropane, no product could be detected by GC.

Control reactions for the dimerization of enolates: If copper(II) acetylacetonate was omitted from the normal reaction condition for the dimerization of pinacolone, about 7% of the dimerization product was observed.

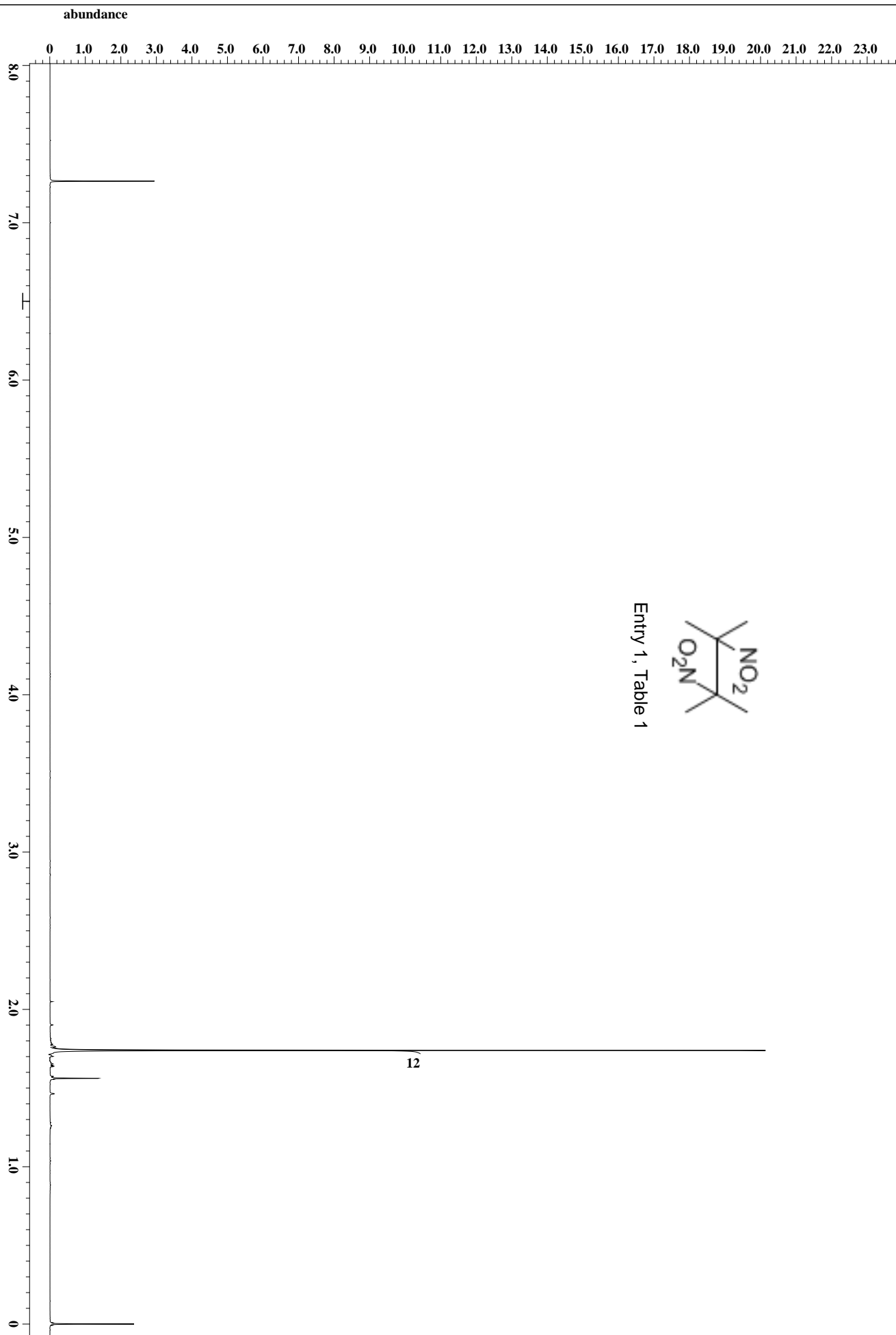
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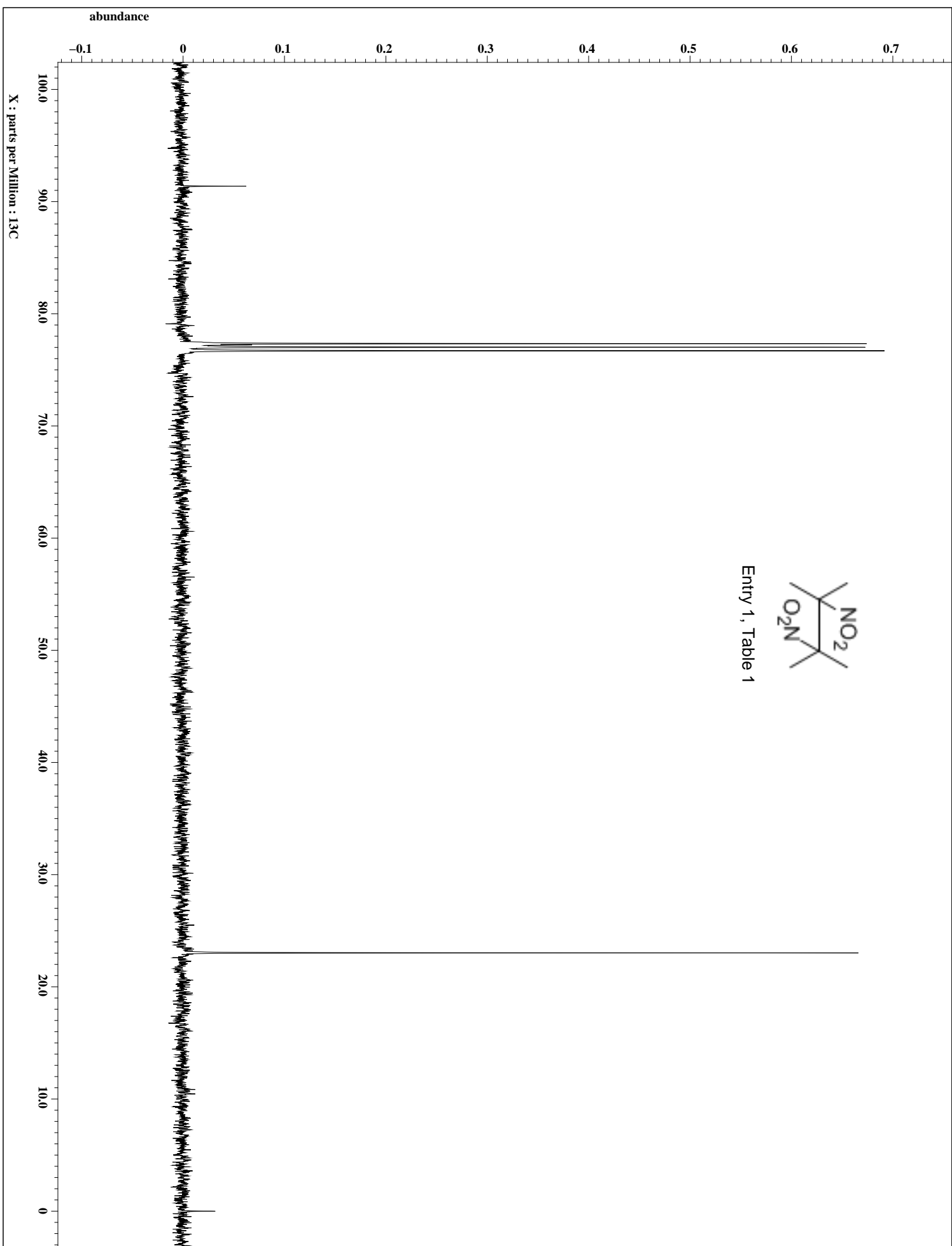
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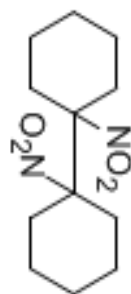


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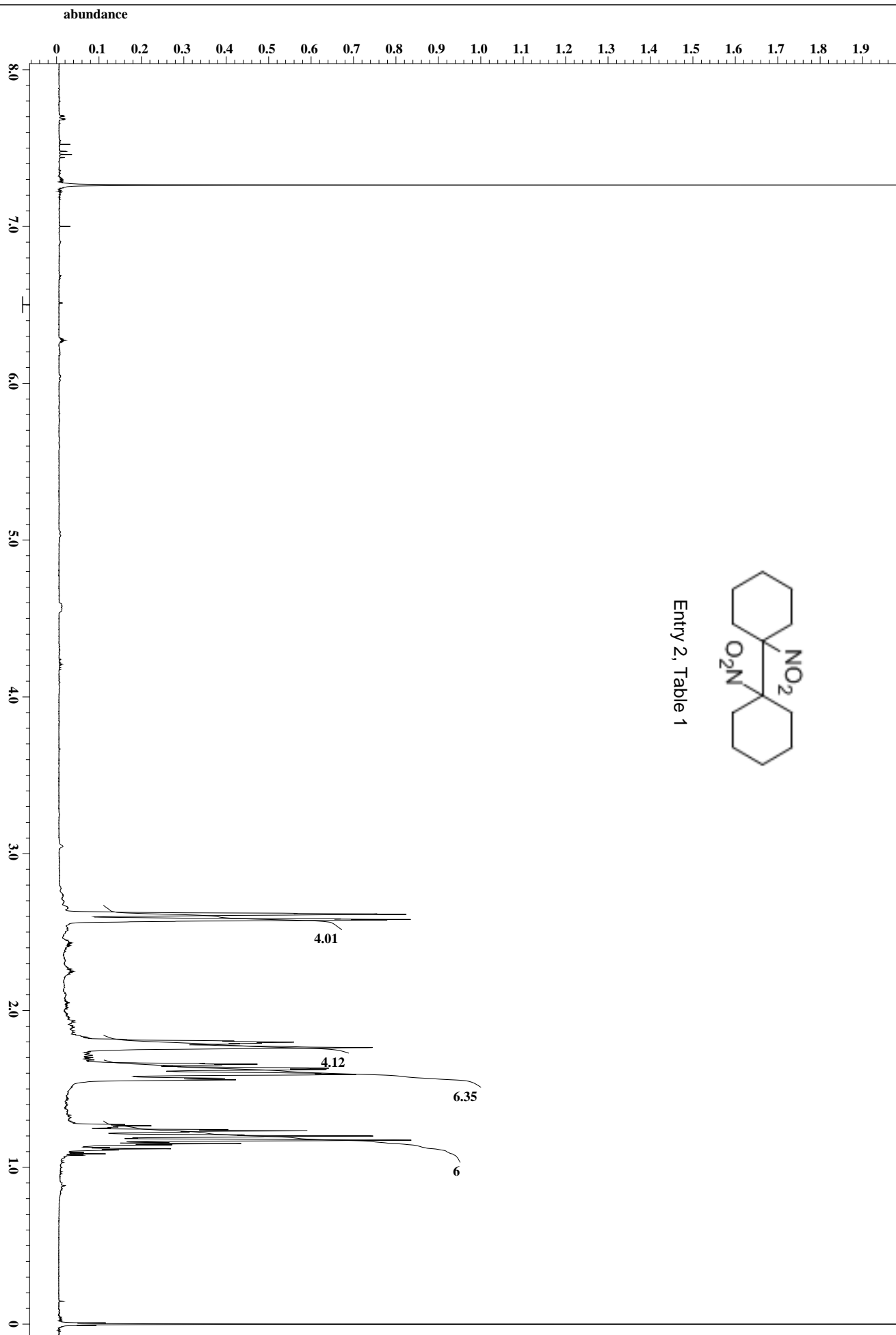


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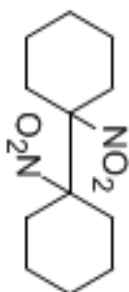




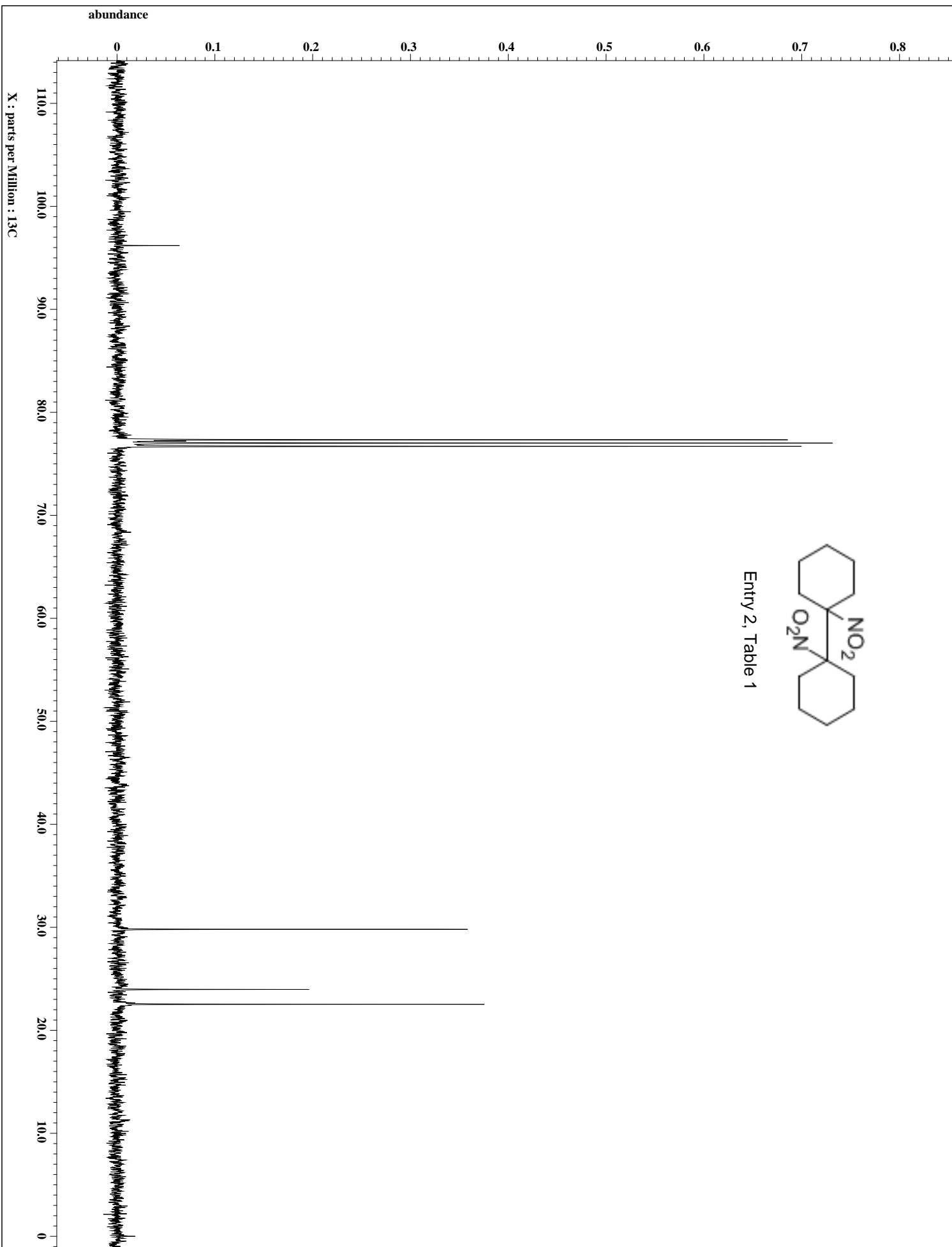
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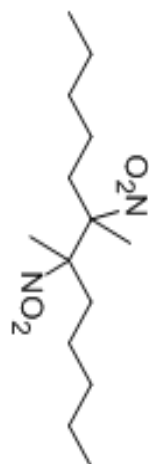


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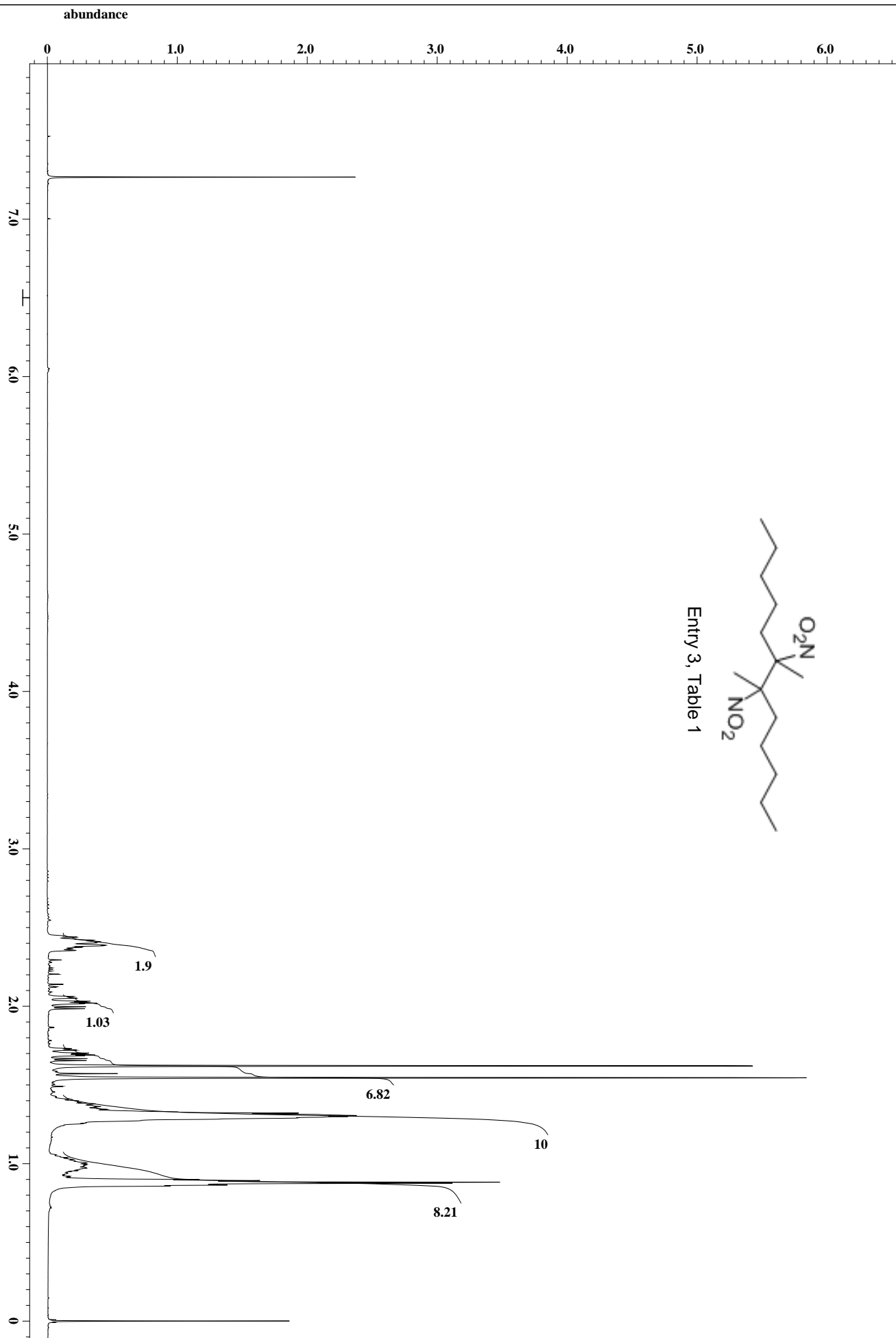


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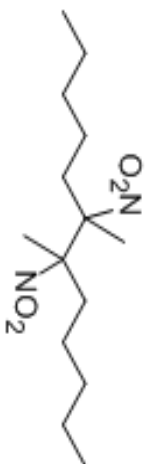




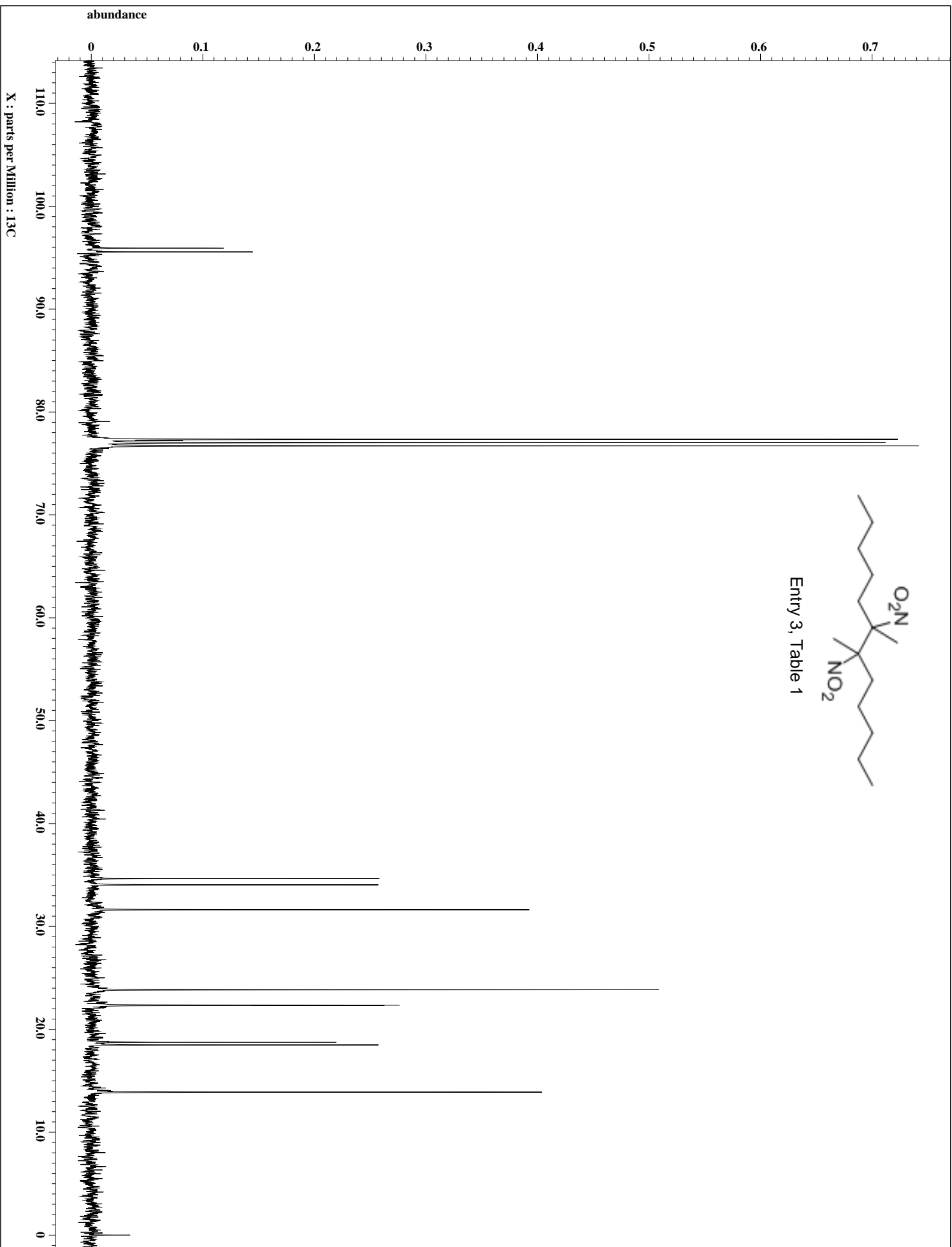
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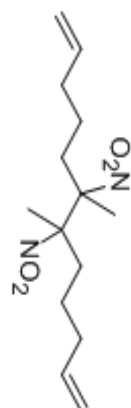


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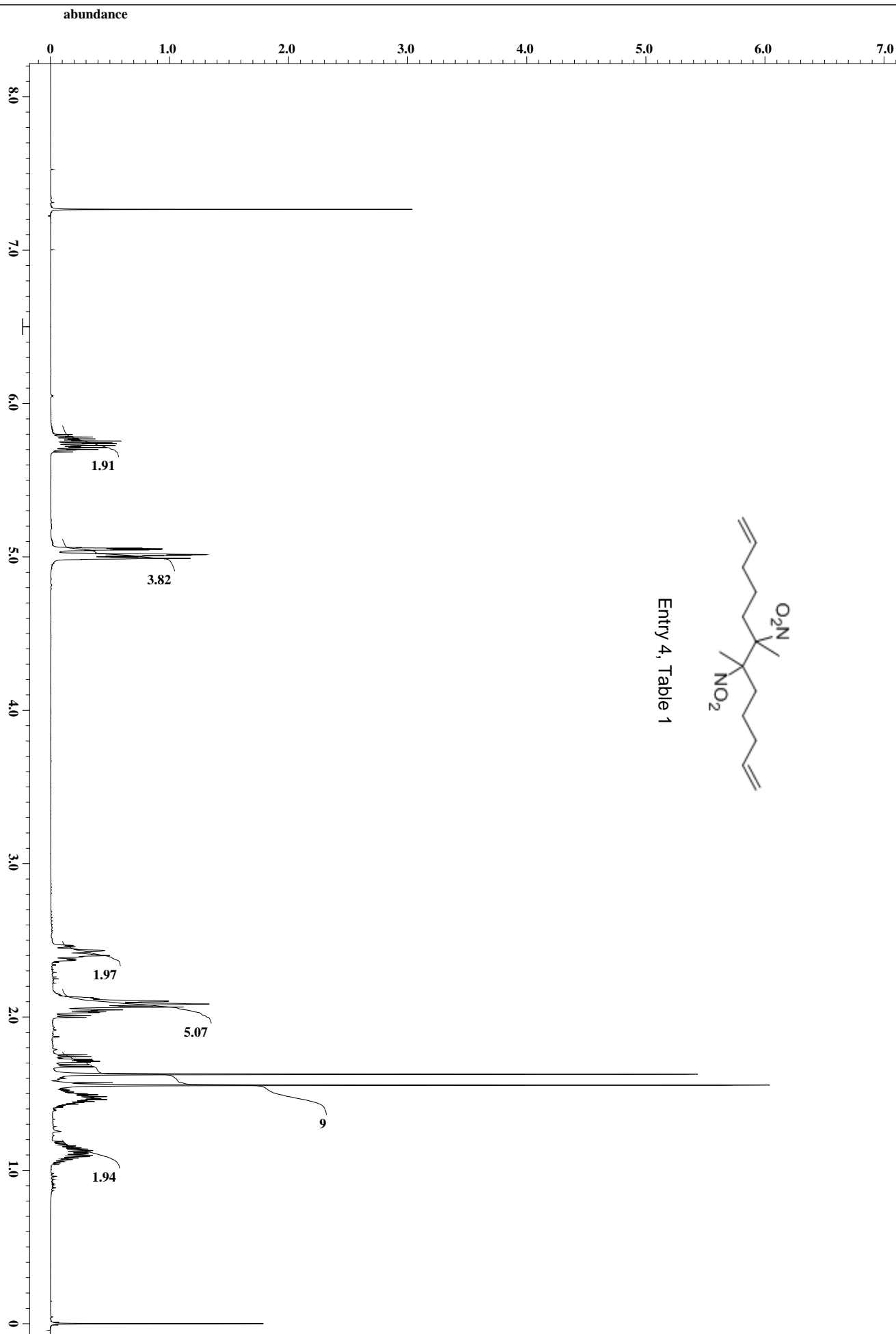


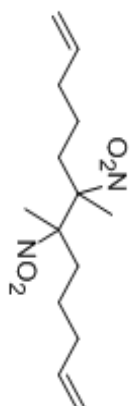
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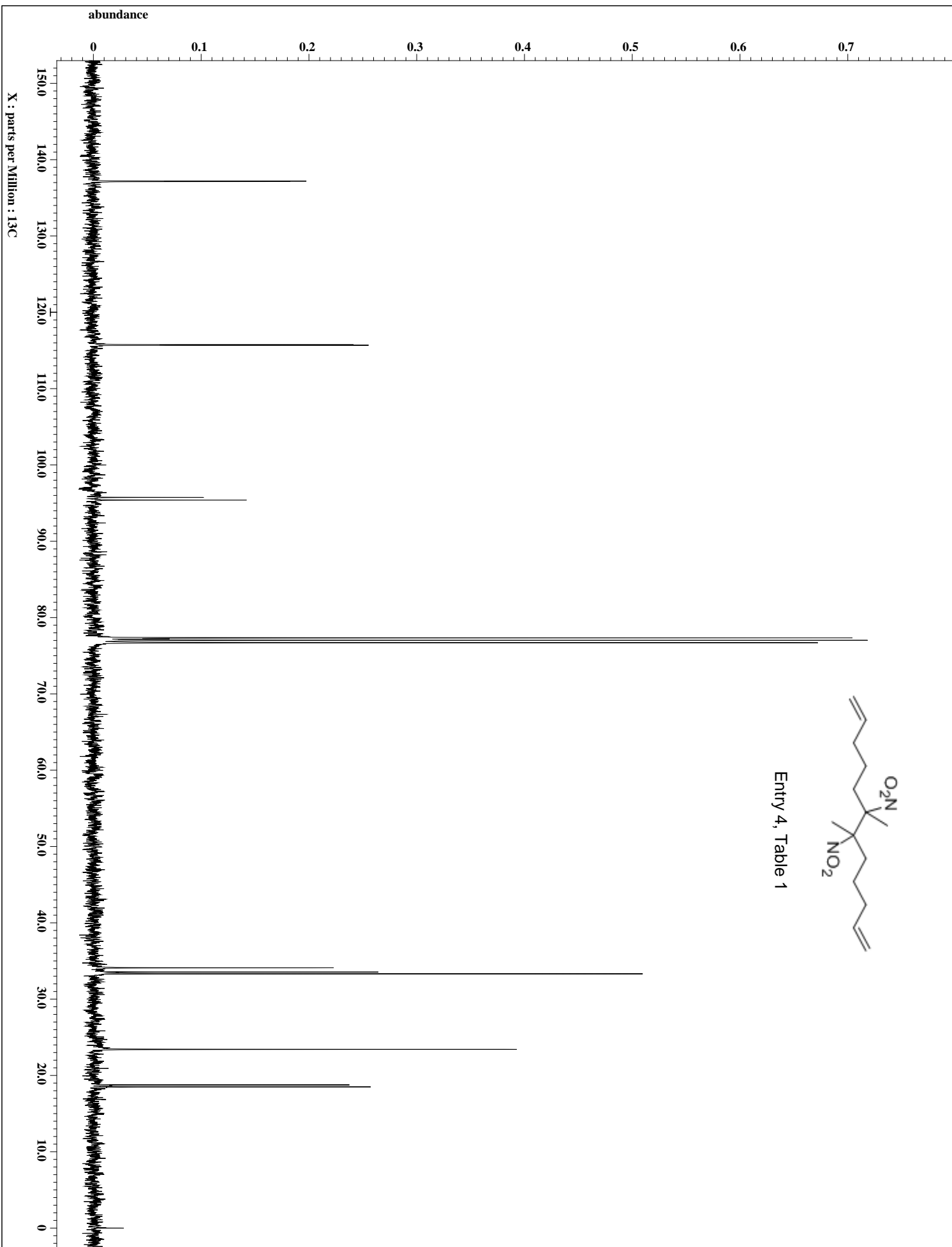


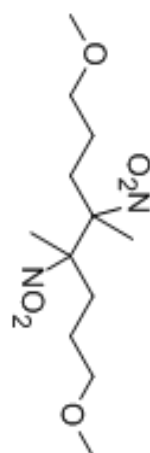
Entry 4, Table 1



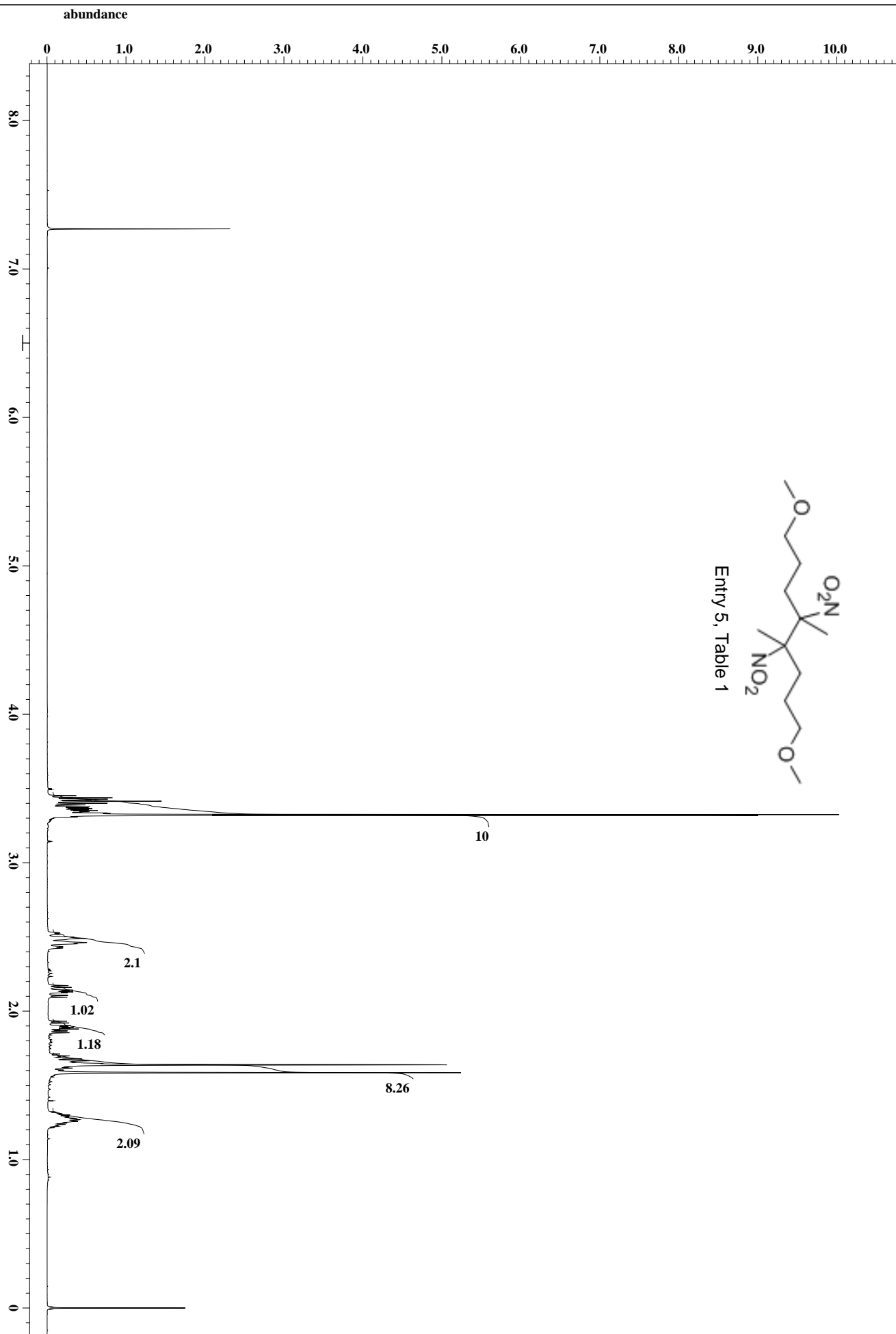


Entry 4, Table 1

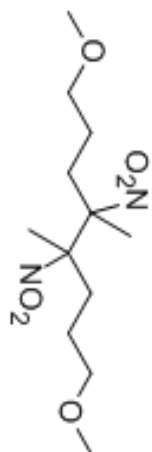




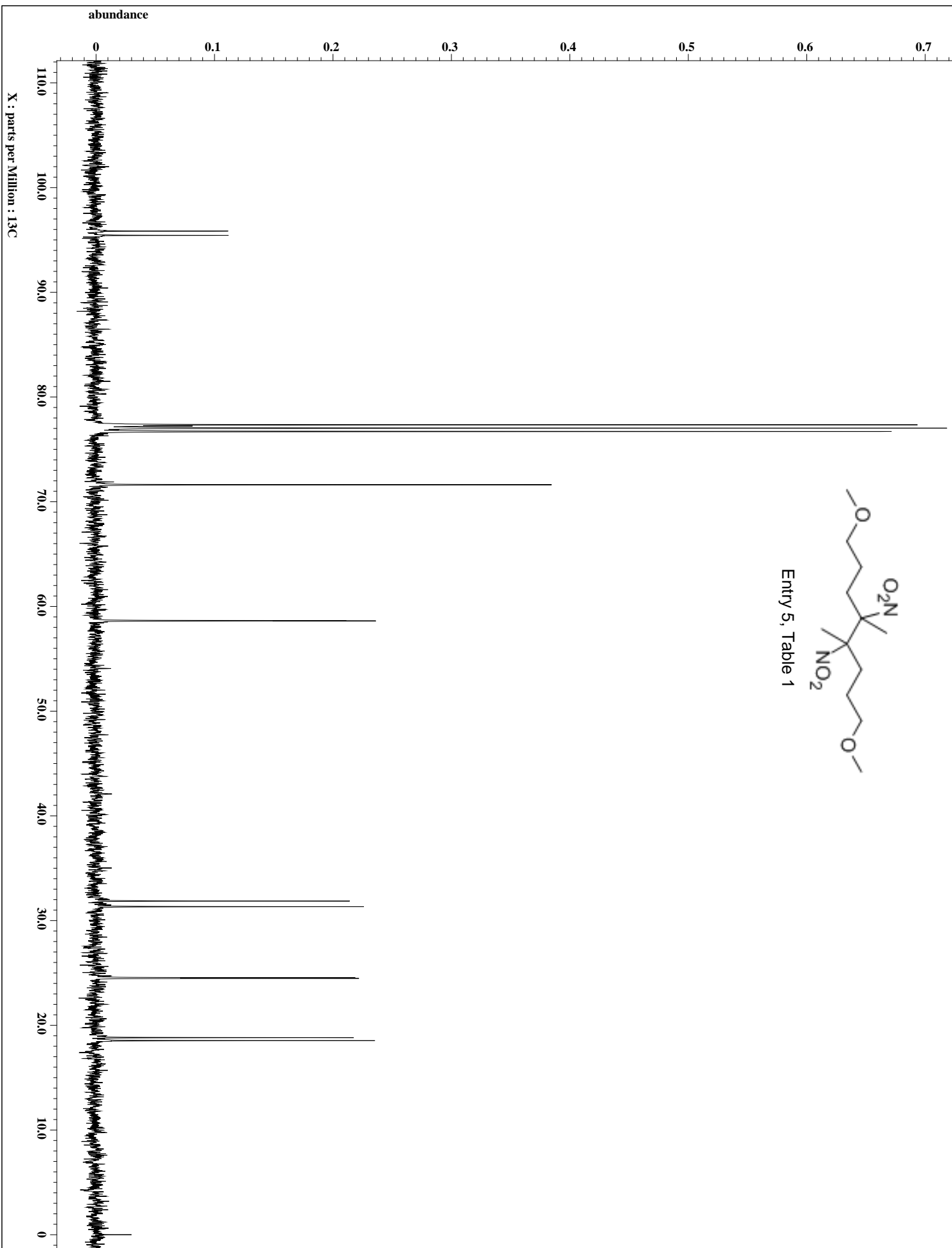
Entry 5, Table 1

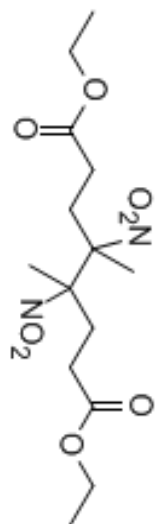


X : parts per Million : 1H

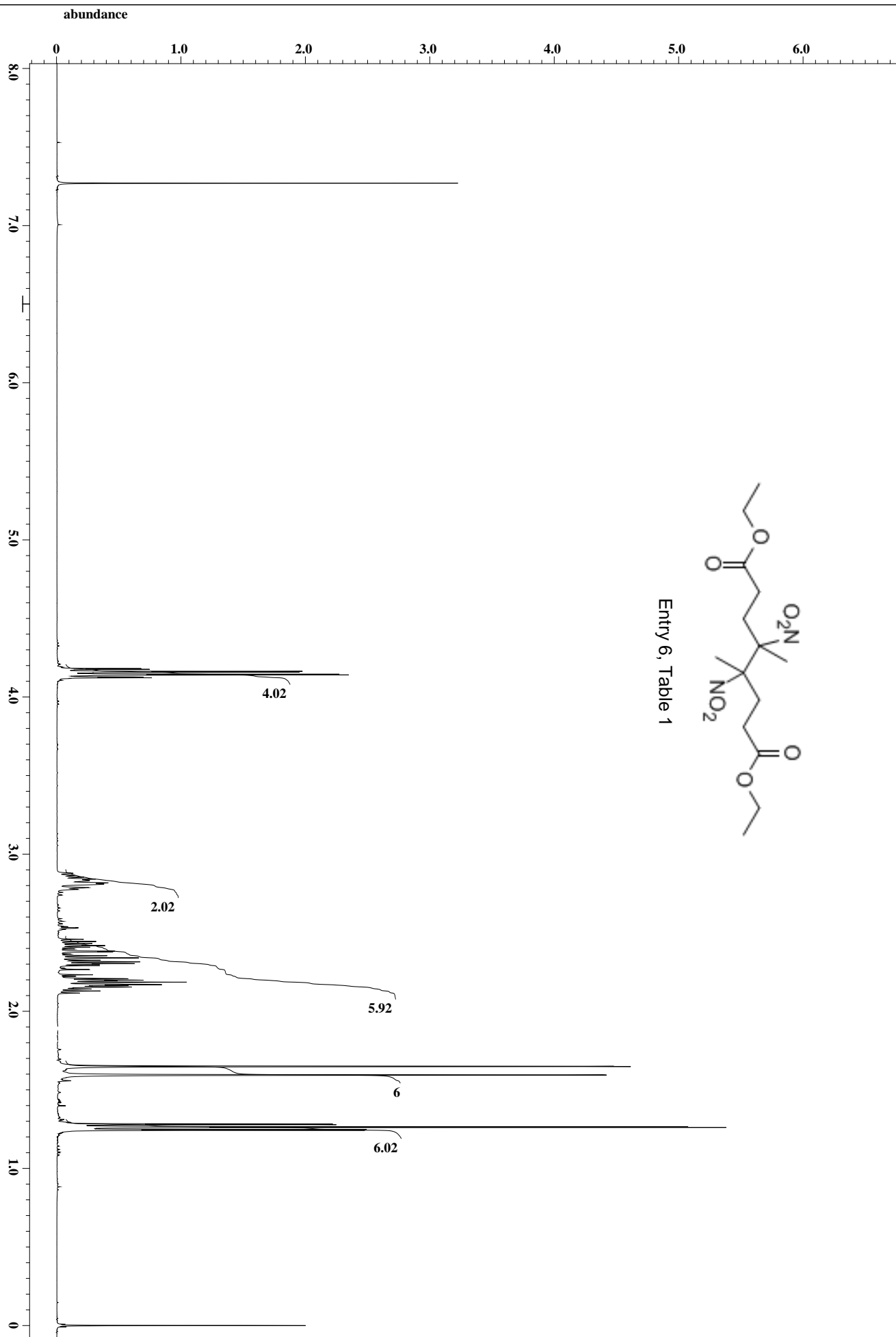


Entry 5, Table 1

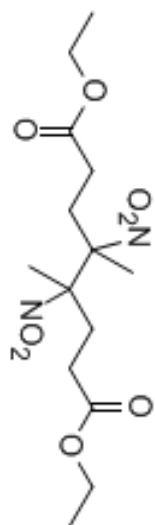




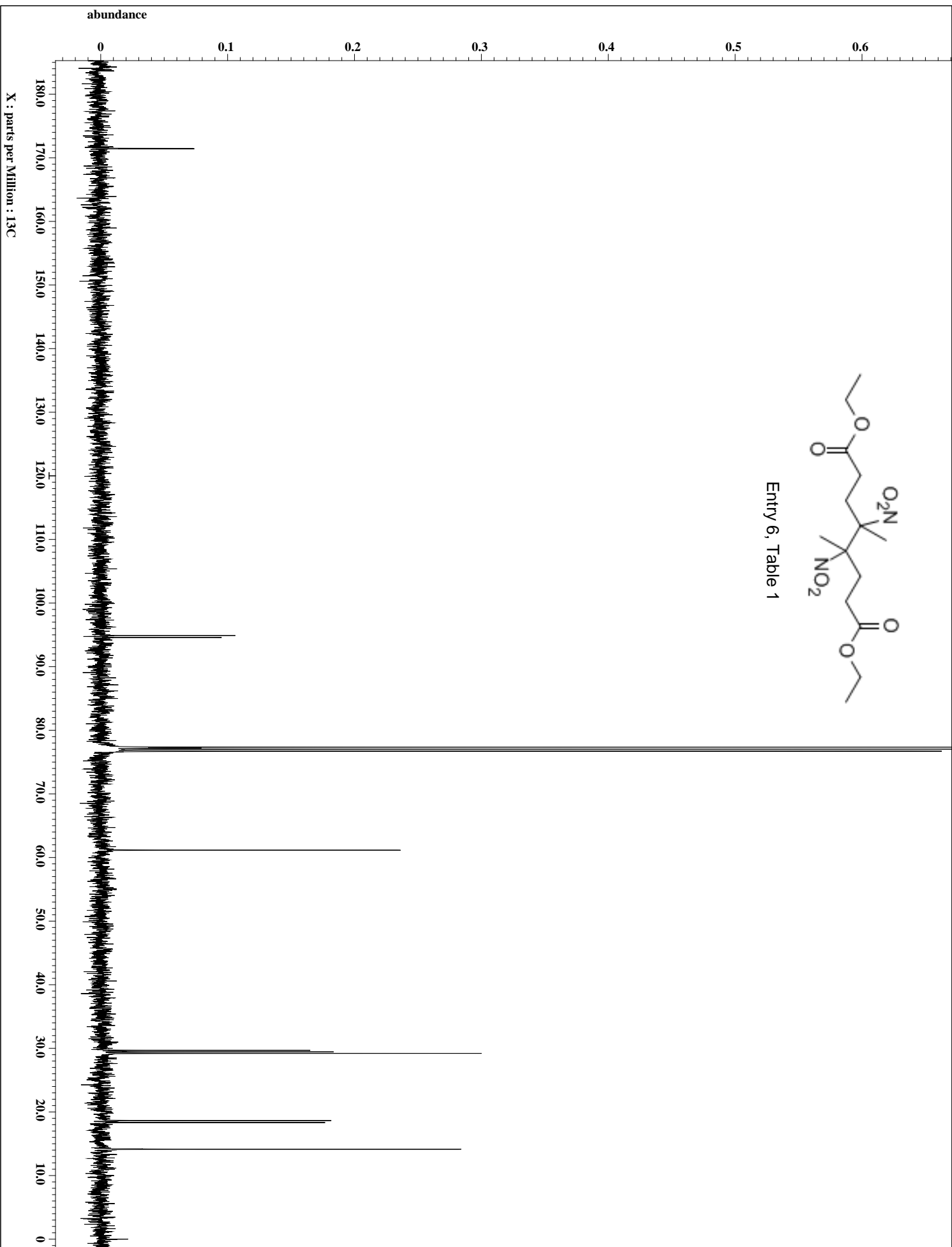
Entry 6, Table 1

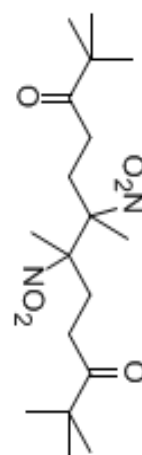


X : parts per Million : 1H

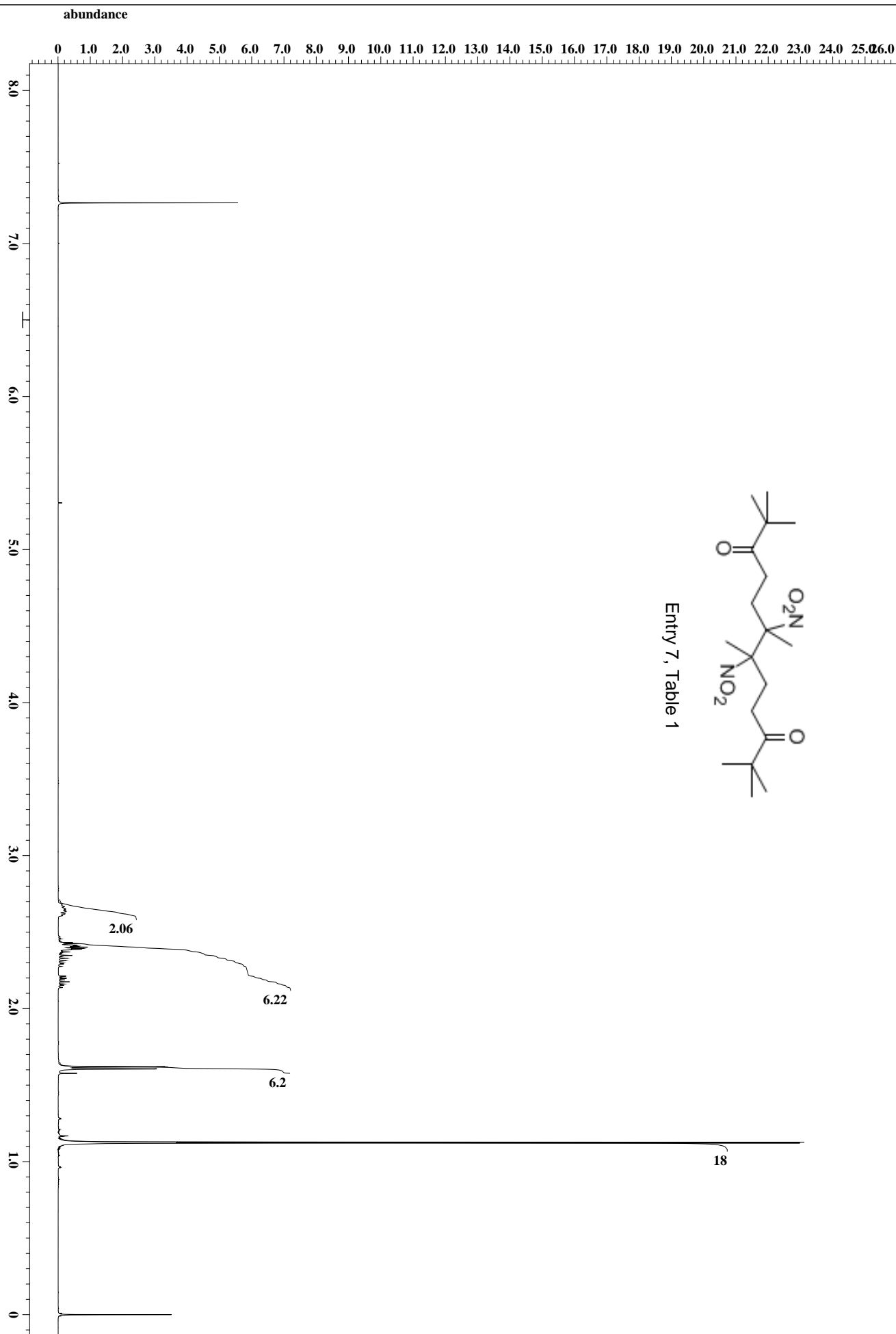


Entry 6, Table 1

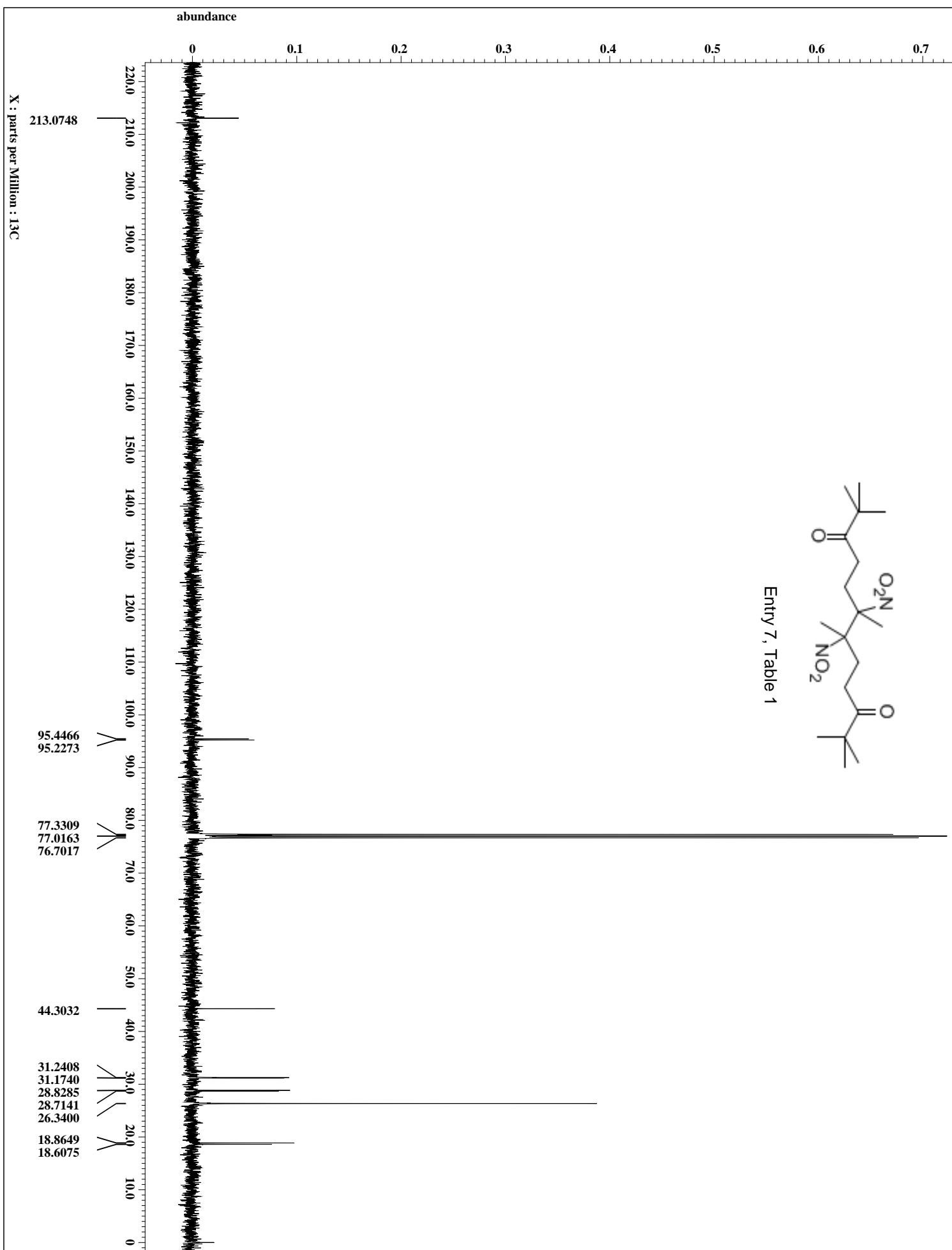


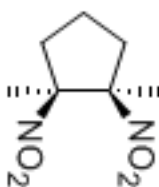


Entry 7, Table 1

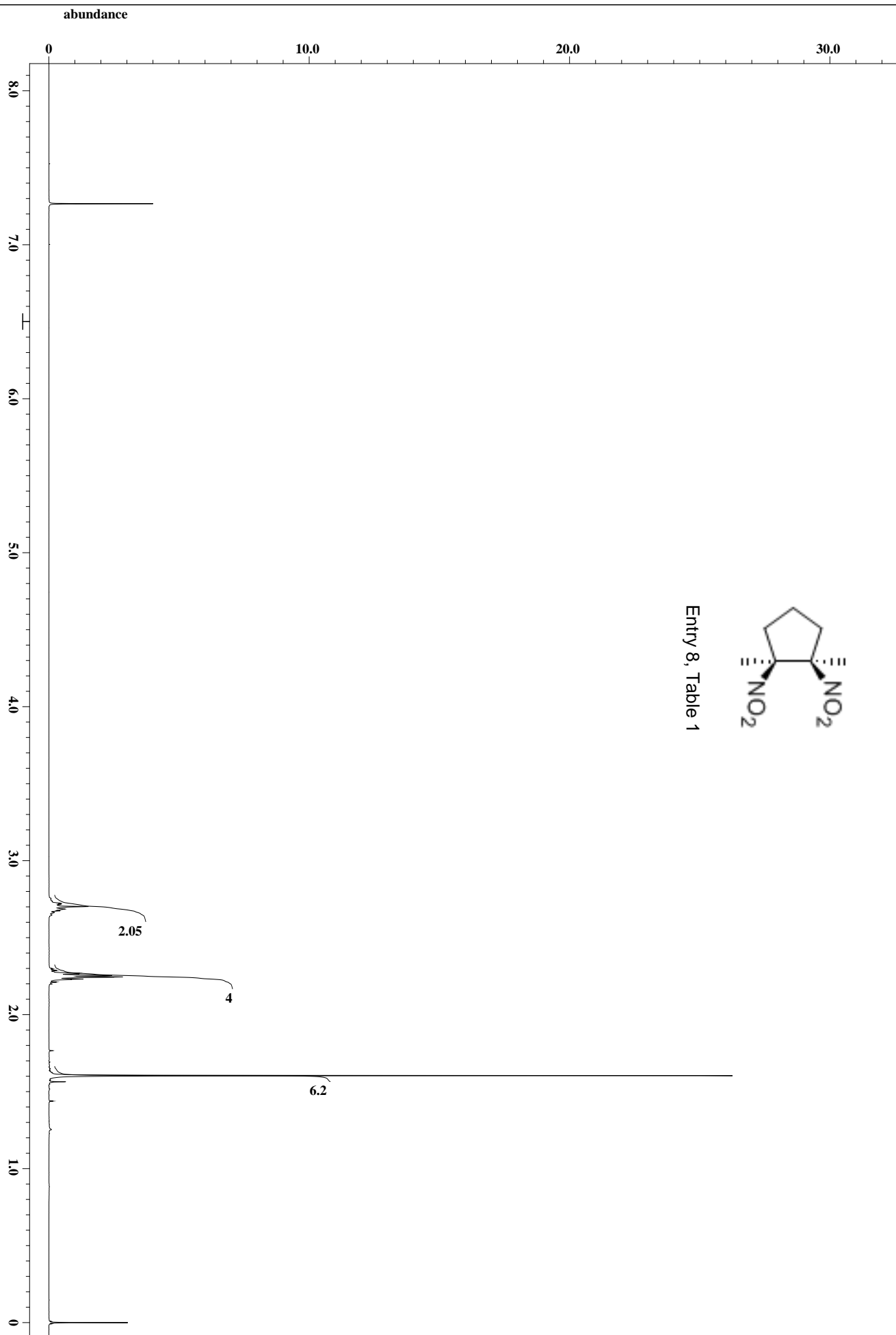


X : parts per Million : 1H

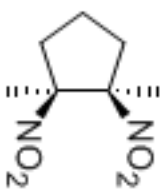




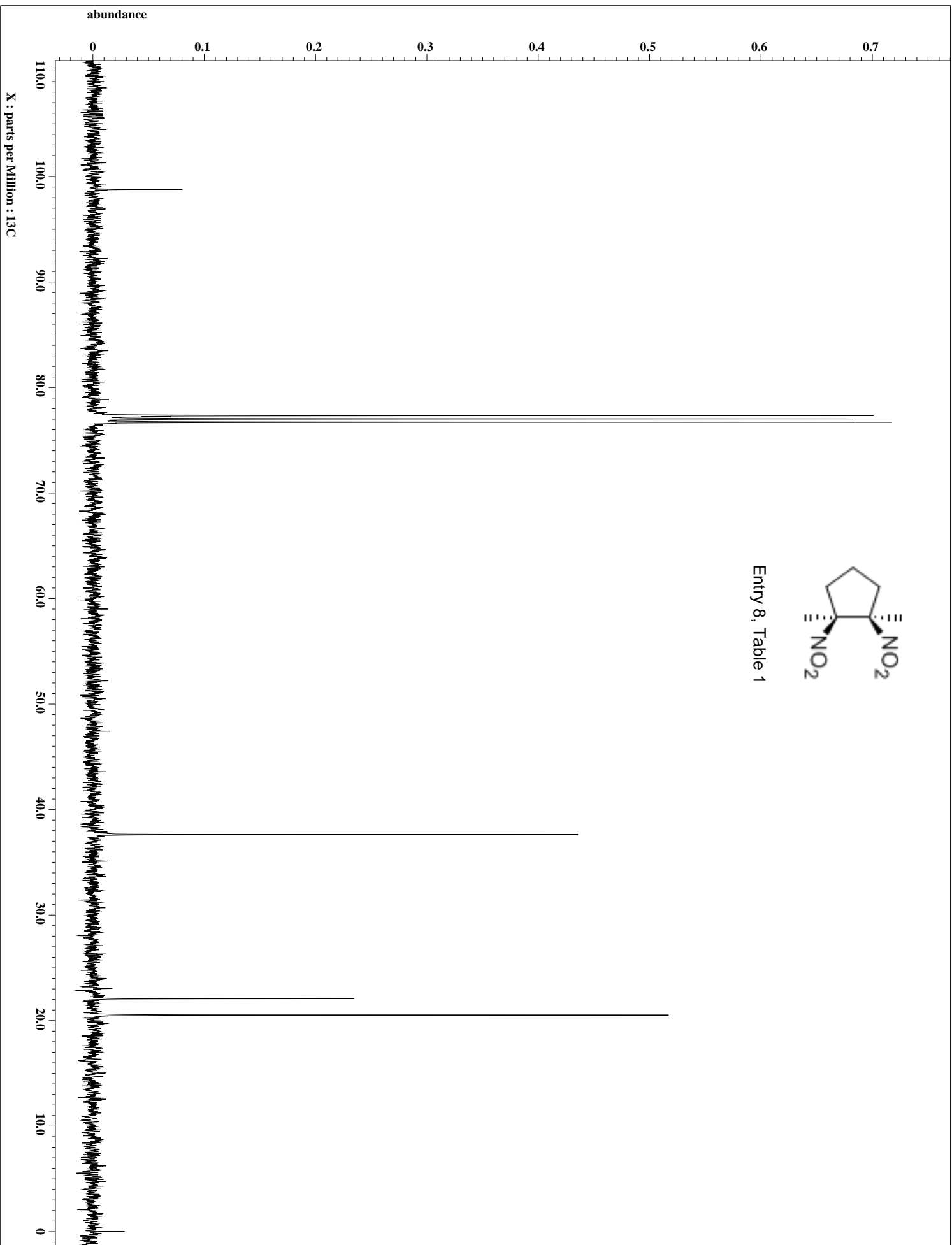
Entry 8, Table 1

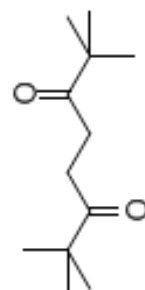


X : parts per Million : 1H

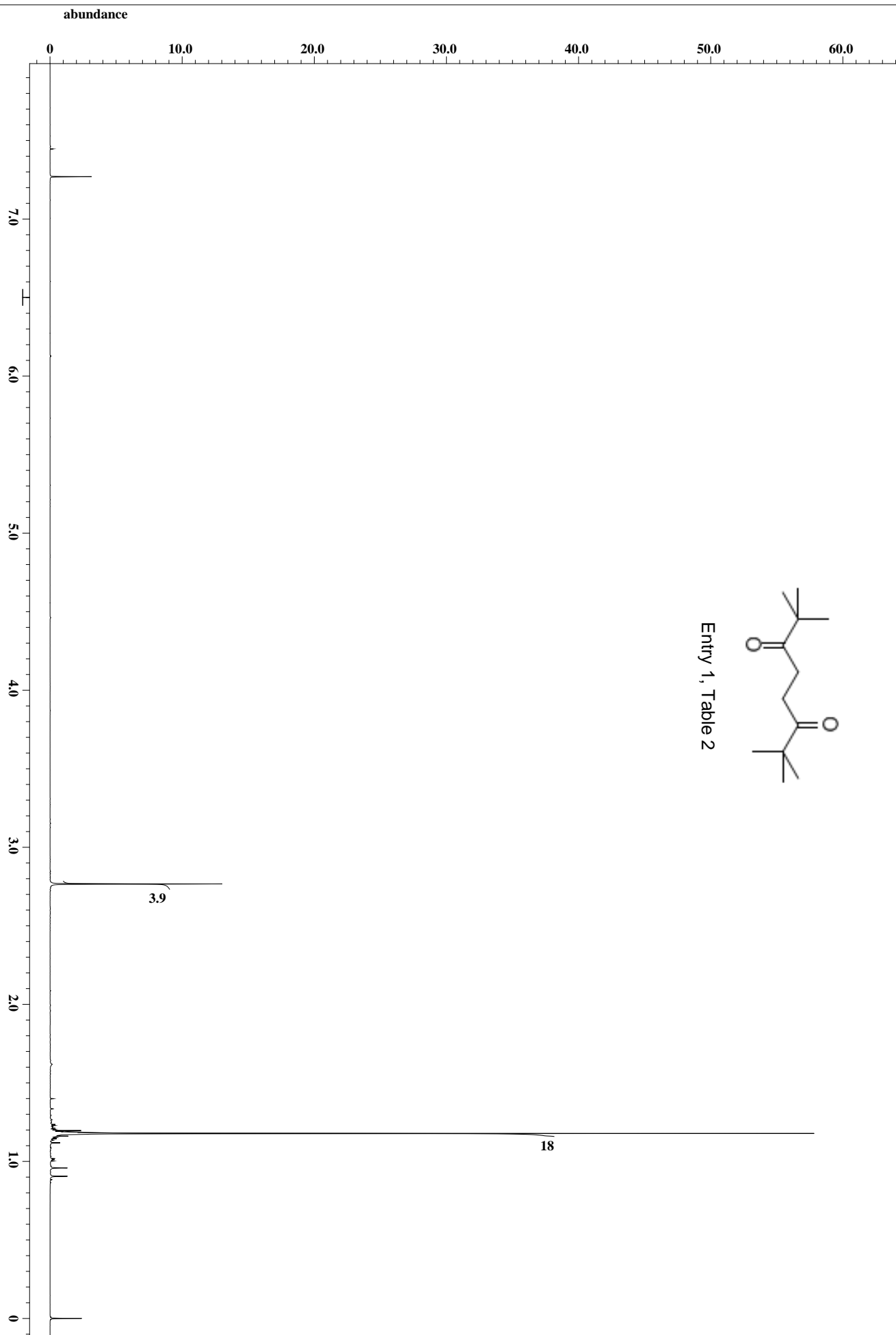


Entry 8, Table 1

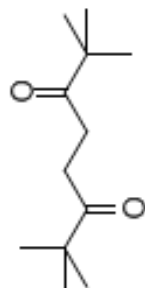




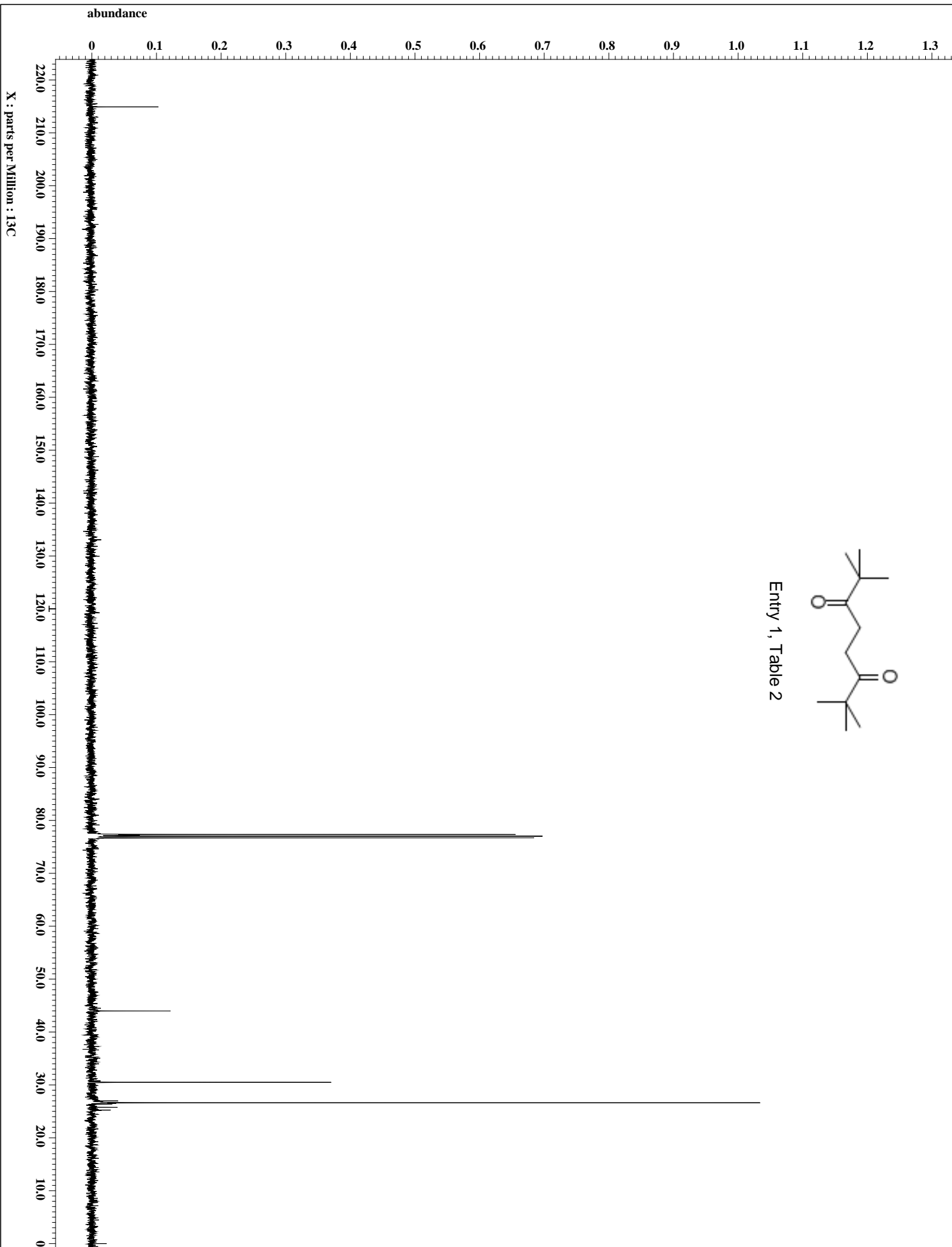
Entry 1, Table 2

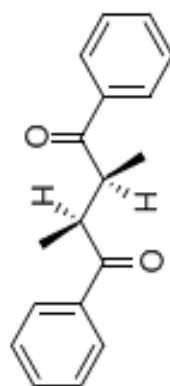


X : parts per Million : 1H

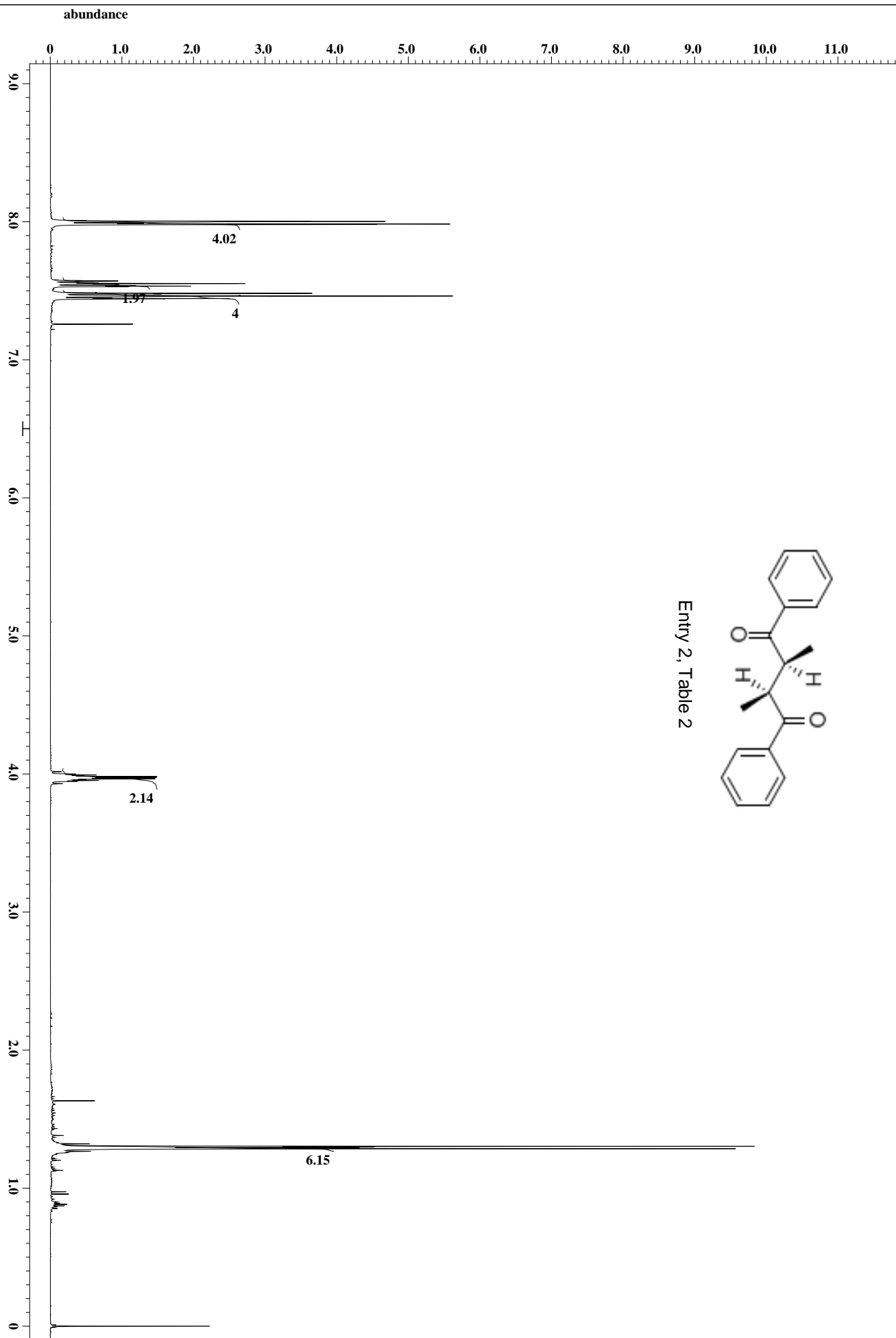


Entry 1, Table 2

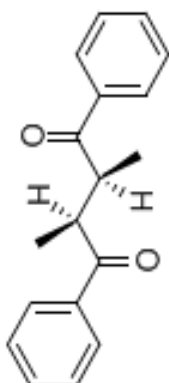




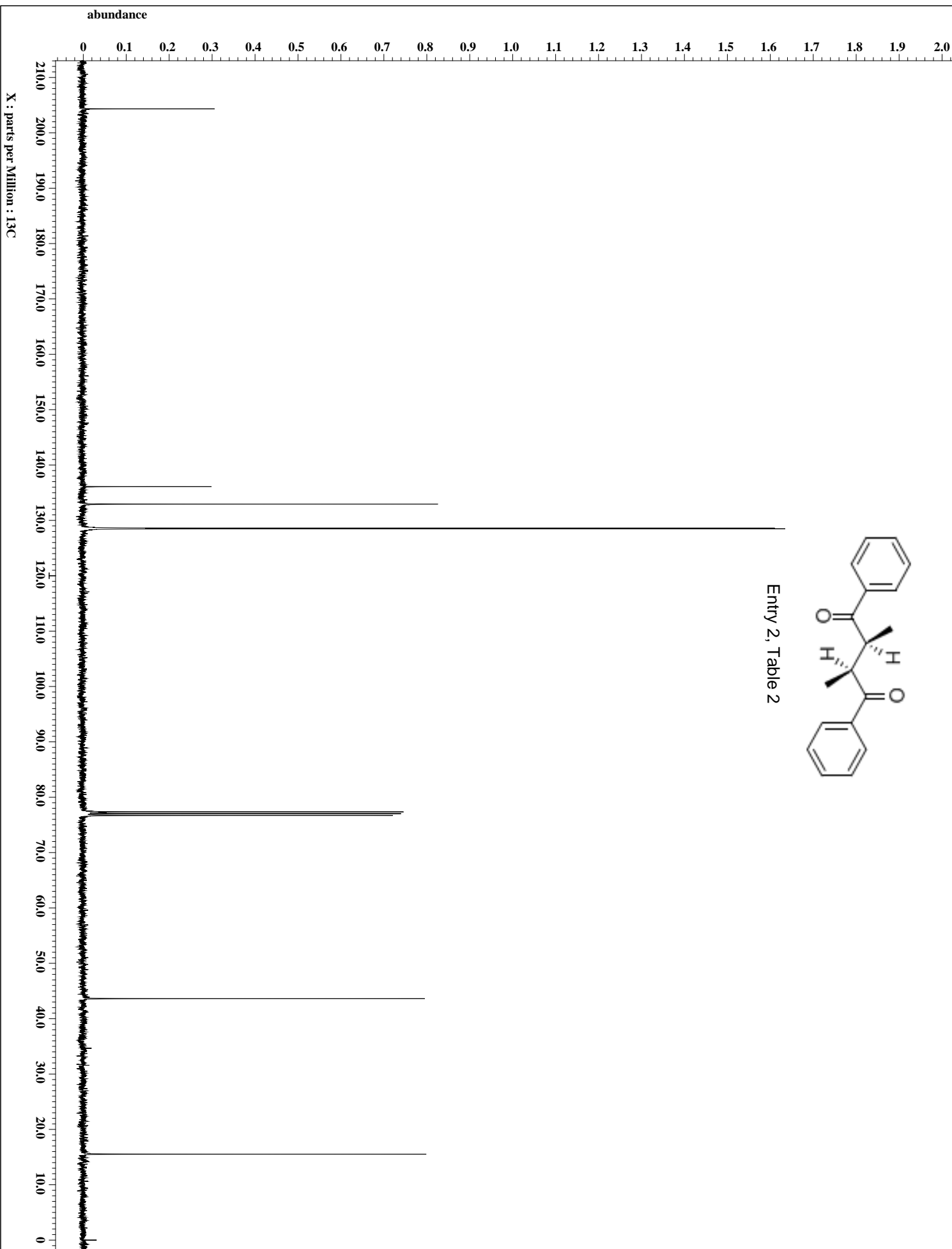
Entry 2, Table 2

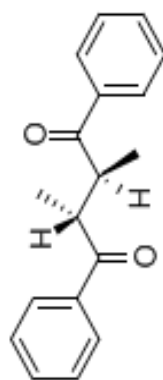


X : parts per Million : 1H

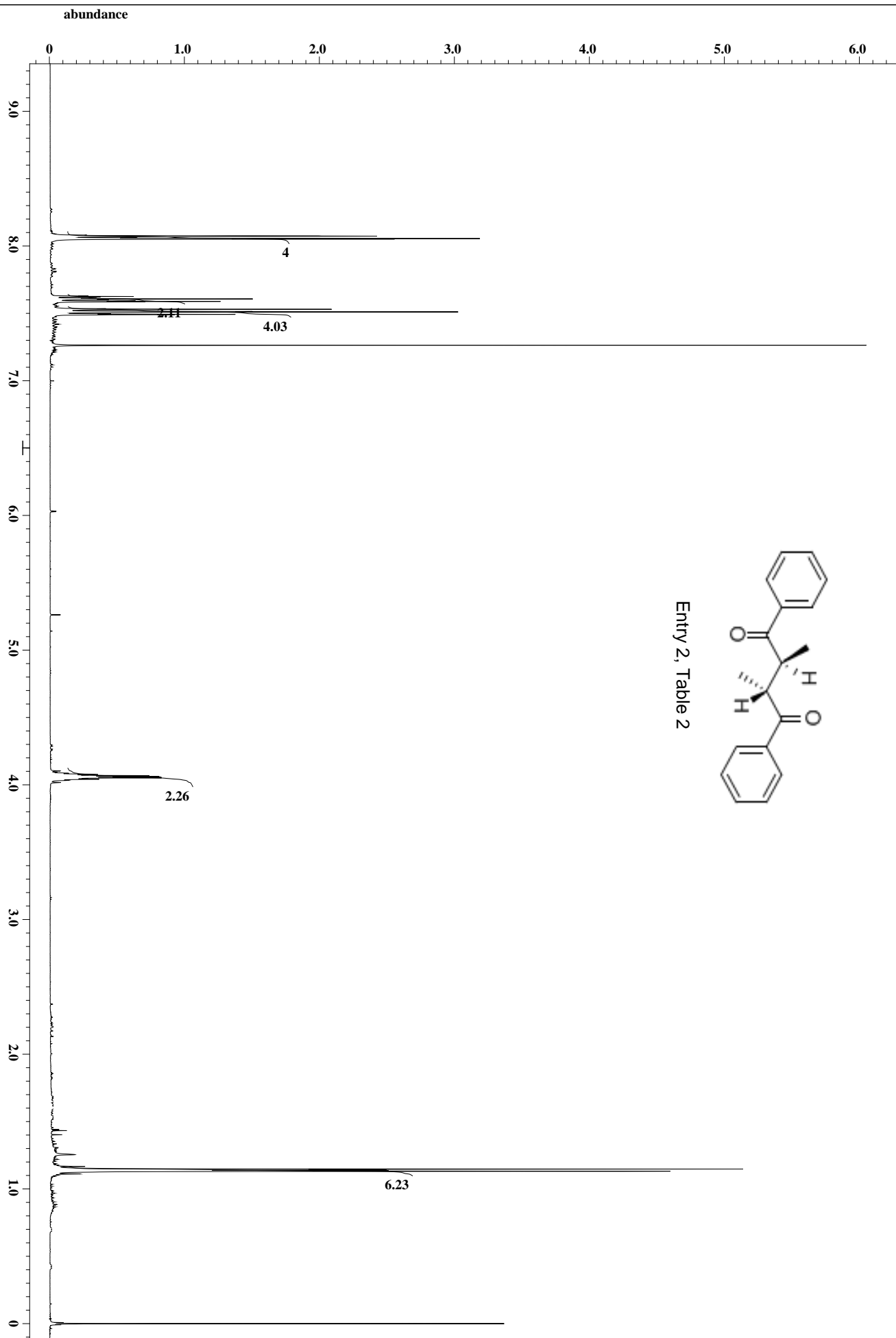


Entry 2, Table 2

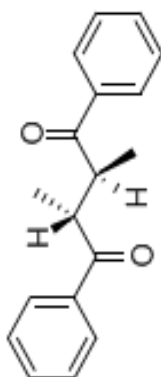




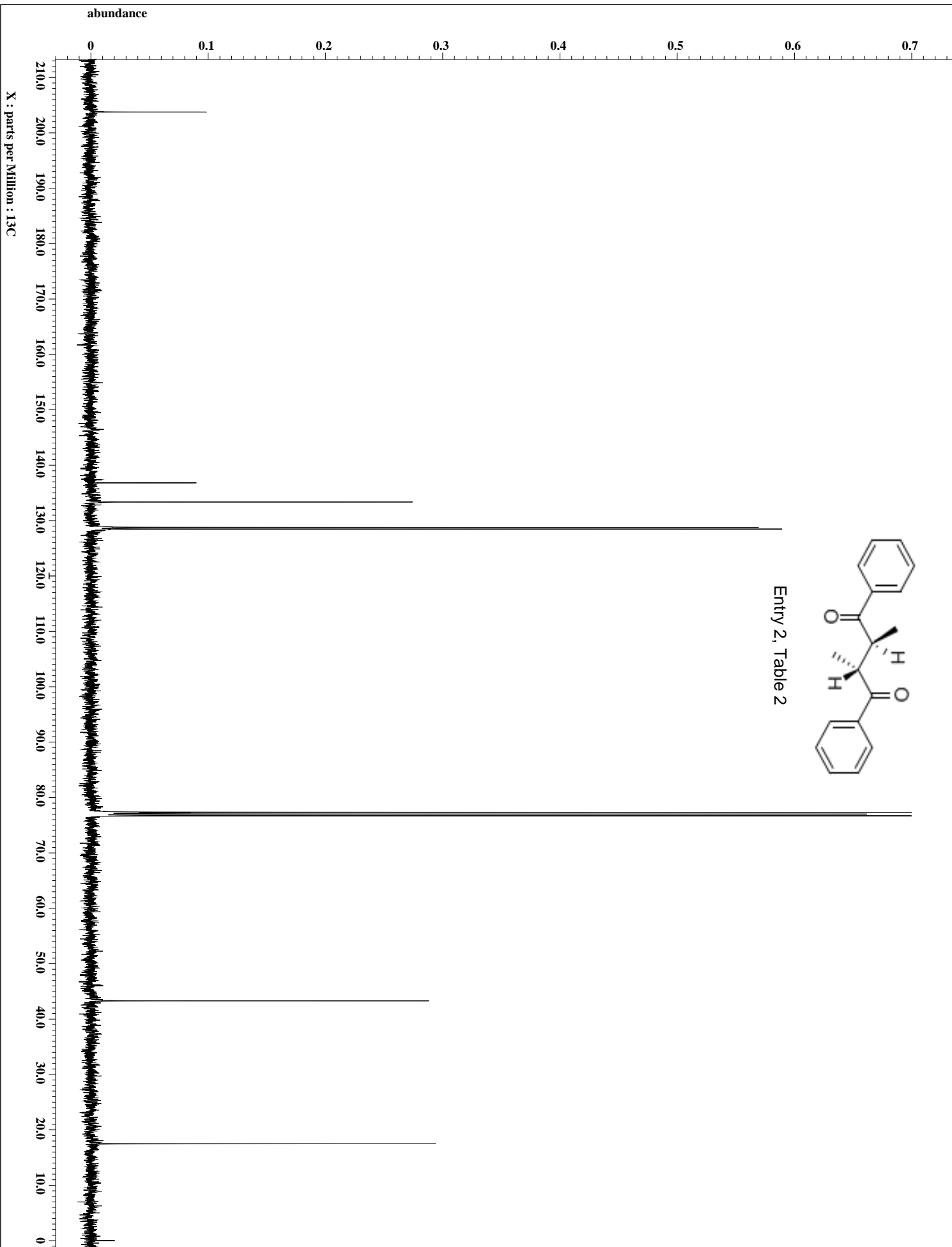
Entry 2, Table 2

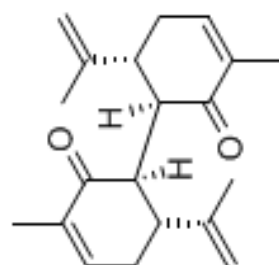


X : parts per Million : 1H

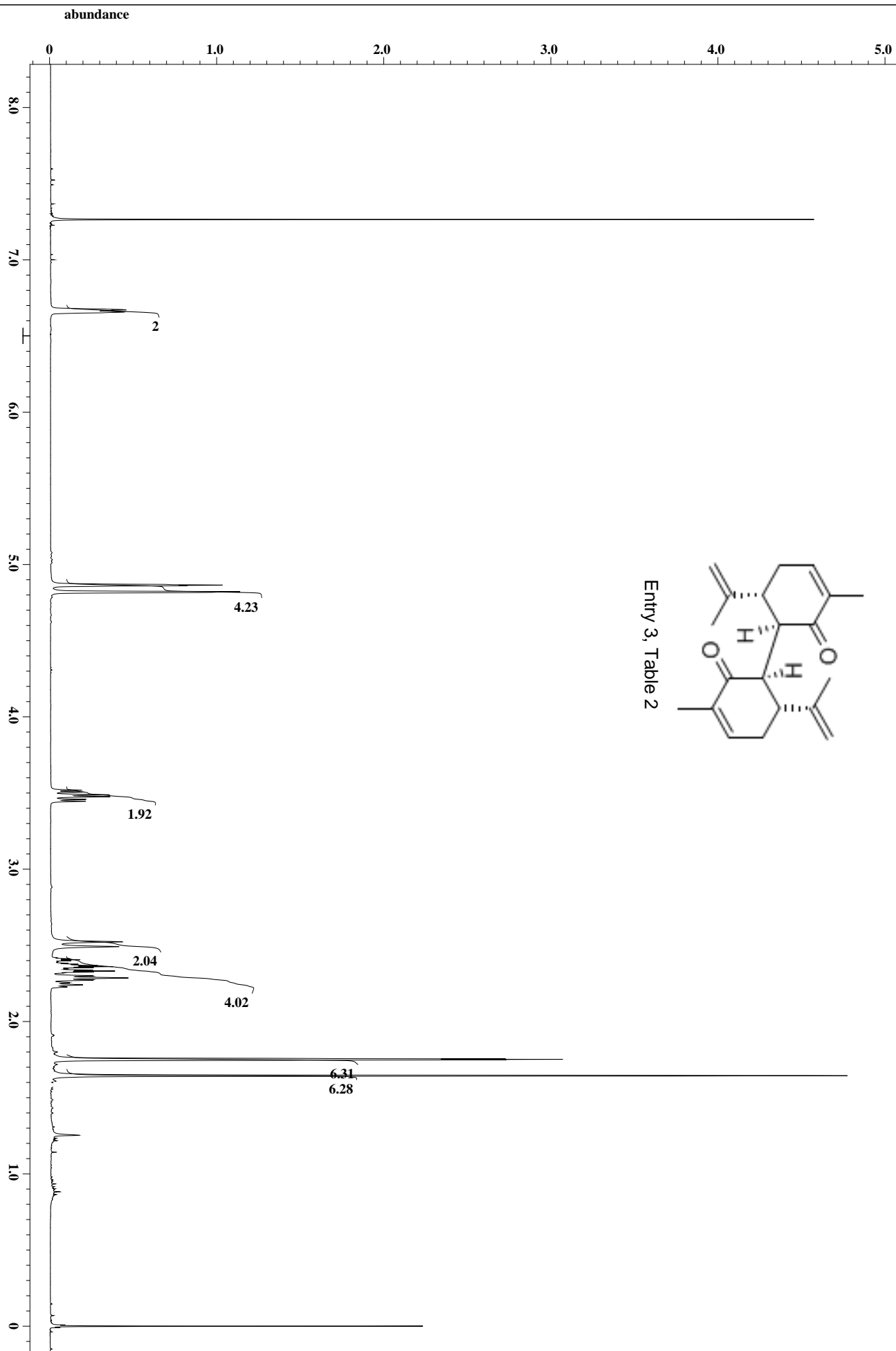


Entry 2, Table 2

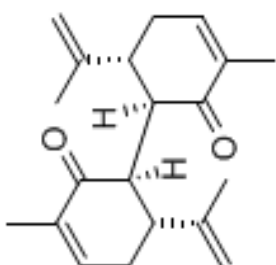




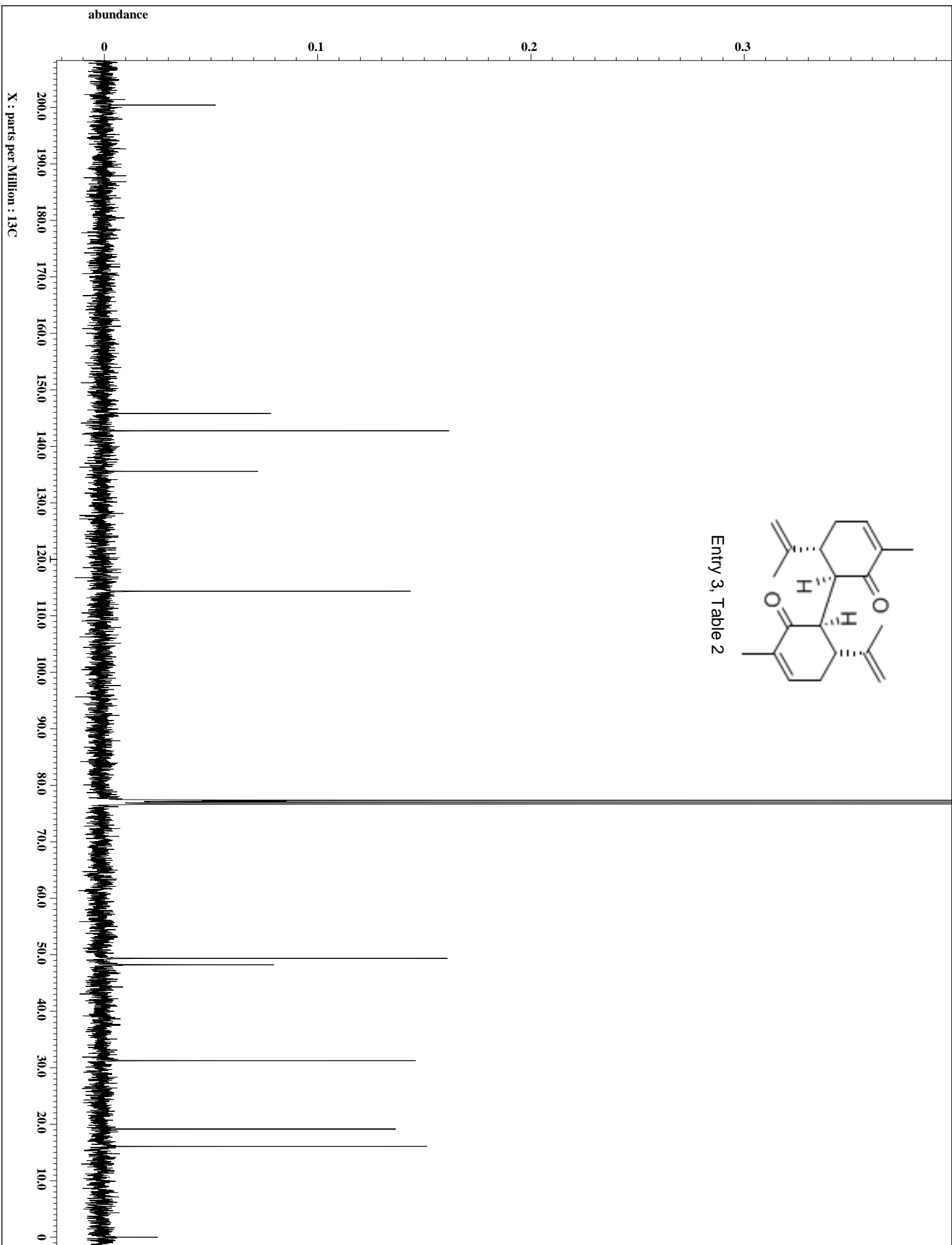
Entry 3, Table 2

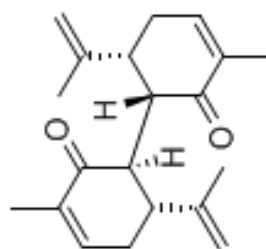


X : parts per Million : 1H

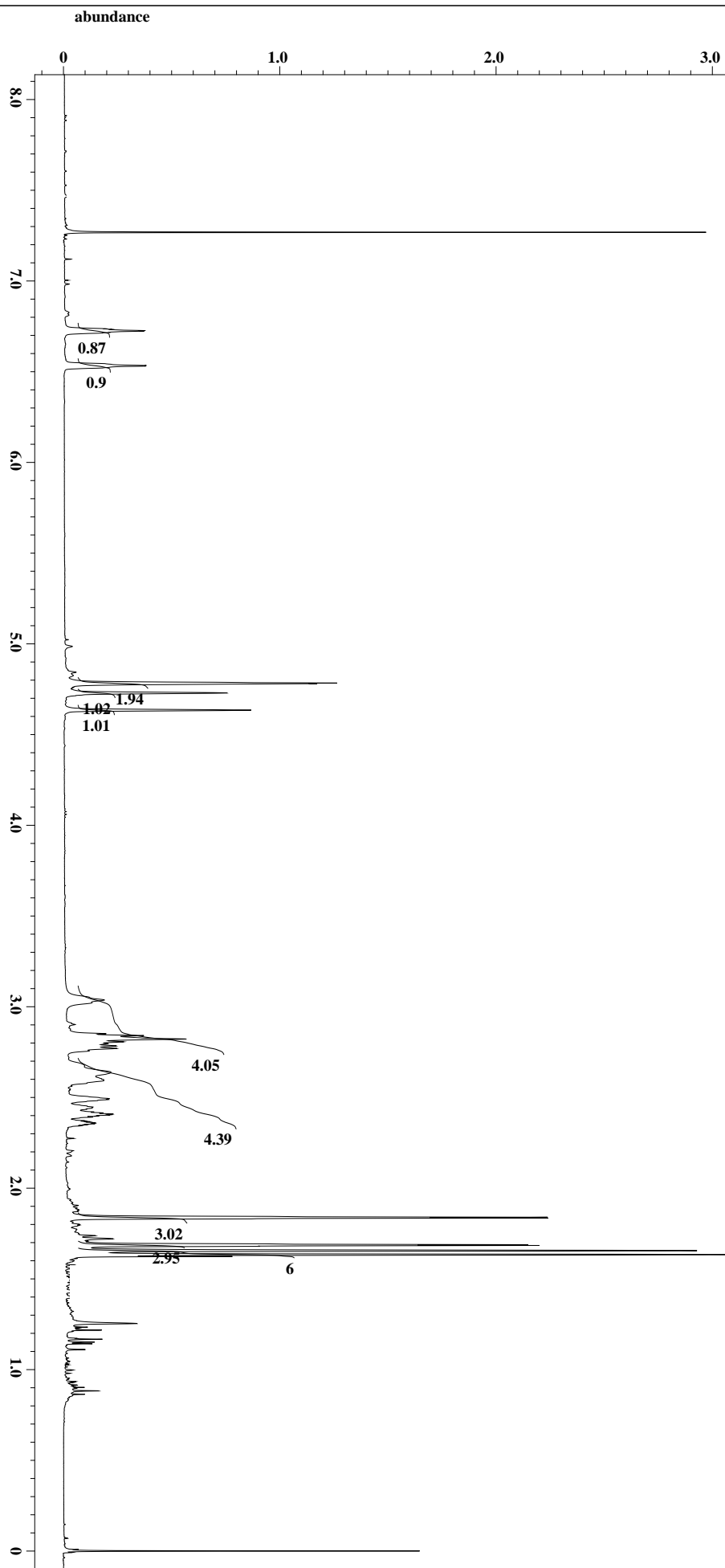


Entry 3, Table 2

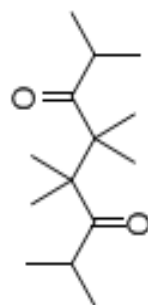




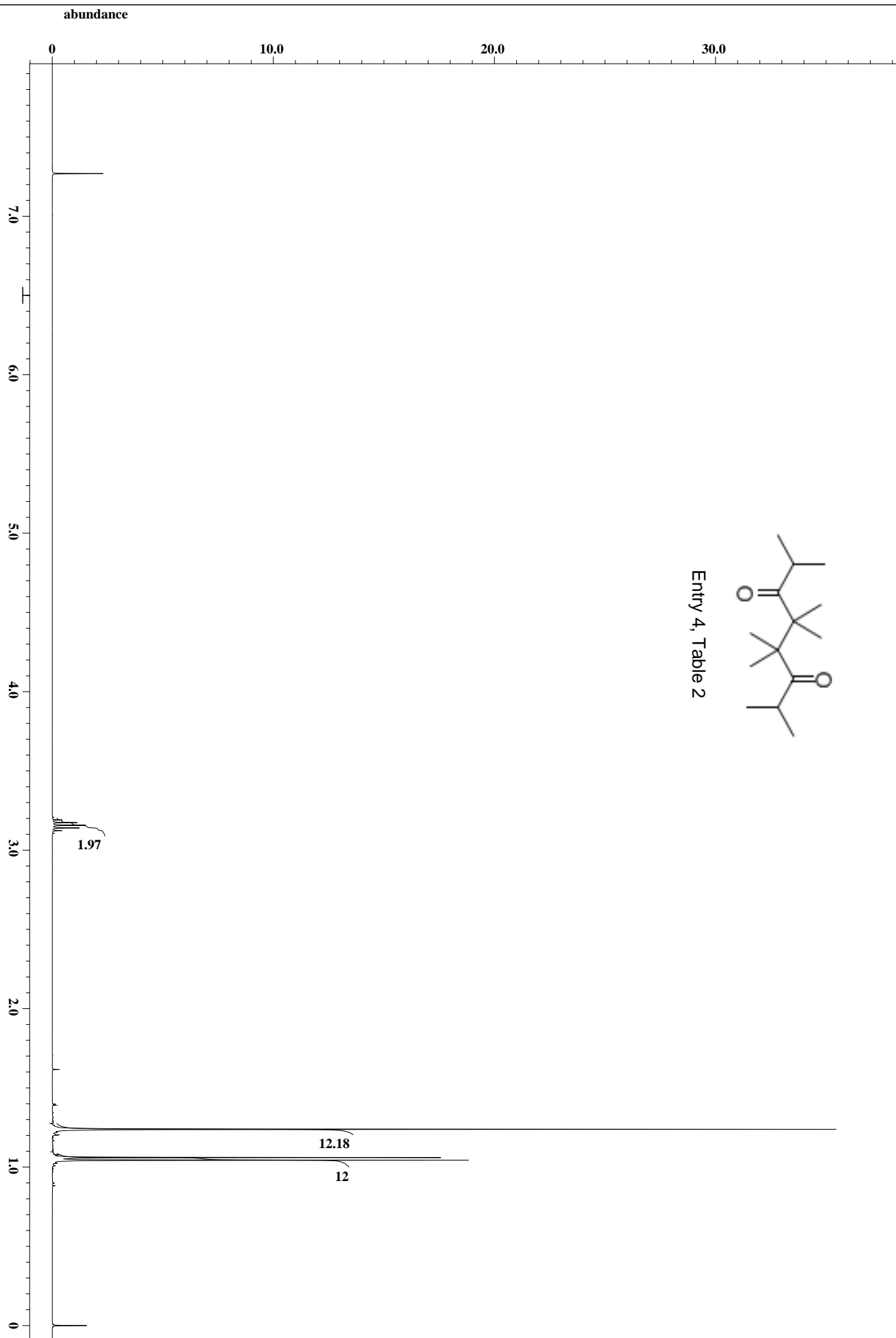
Entry 3, Table 2



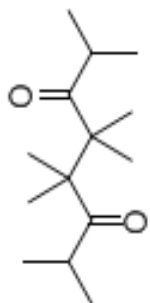
X : parts per Million : 1H



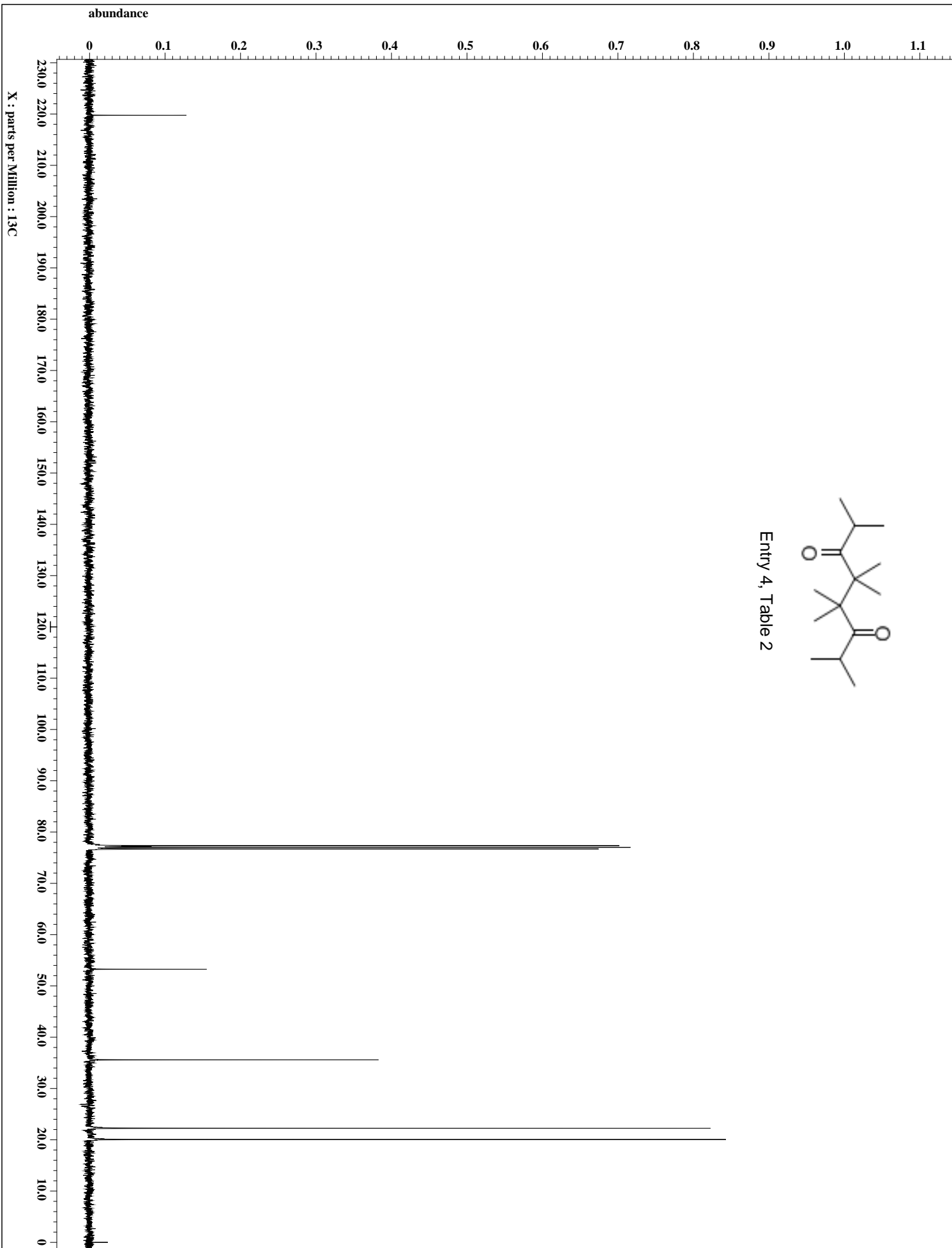
Entry 4, Table 2

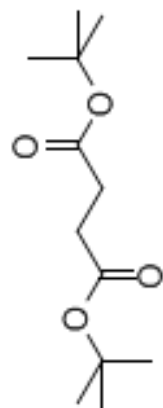


X : parts per Million : 1H

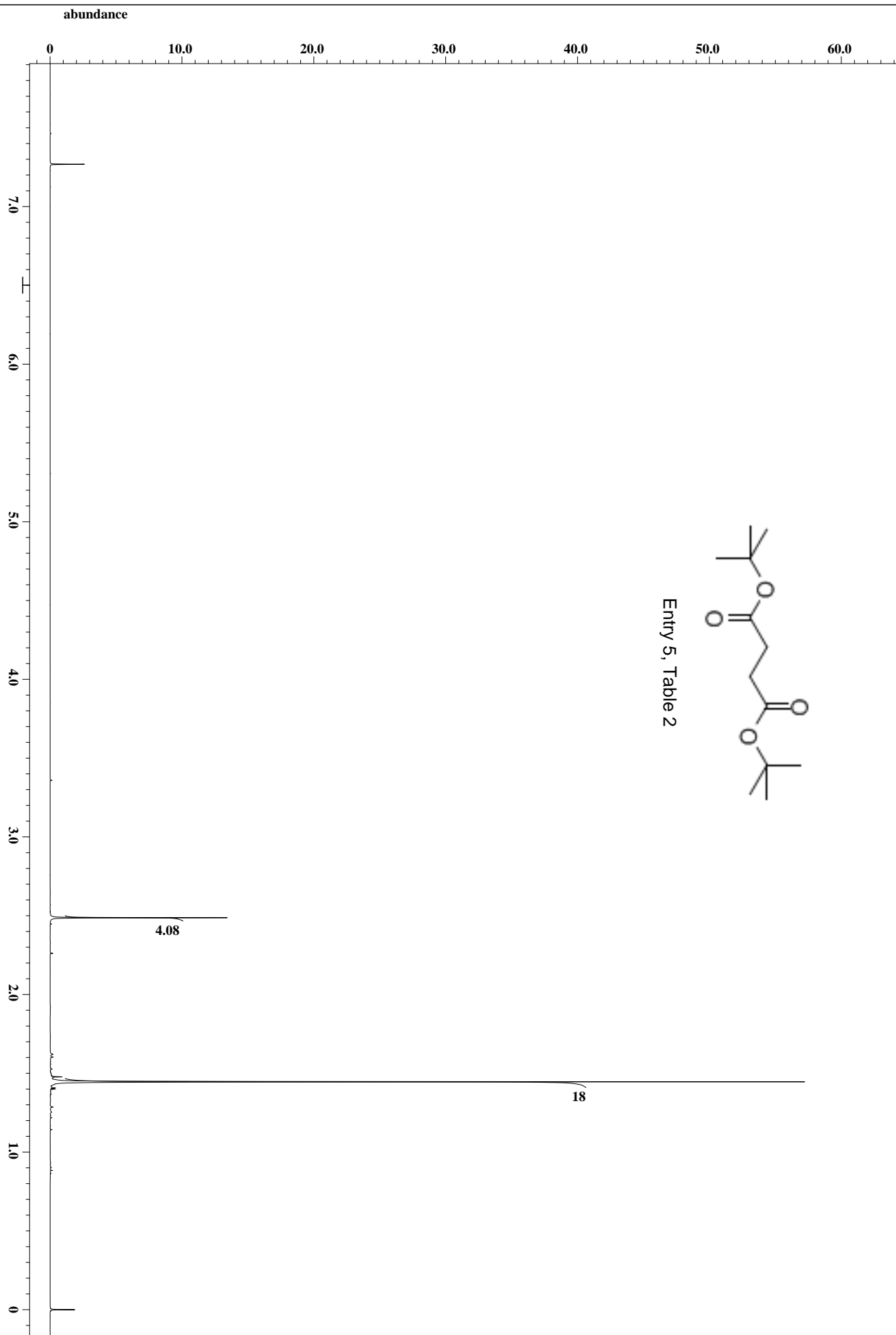


Entry 4, Table 2

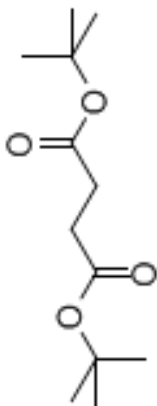




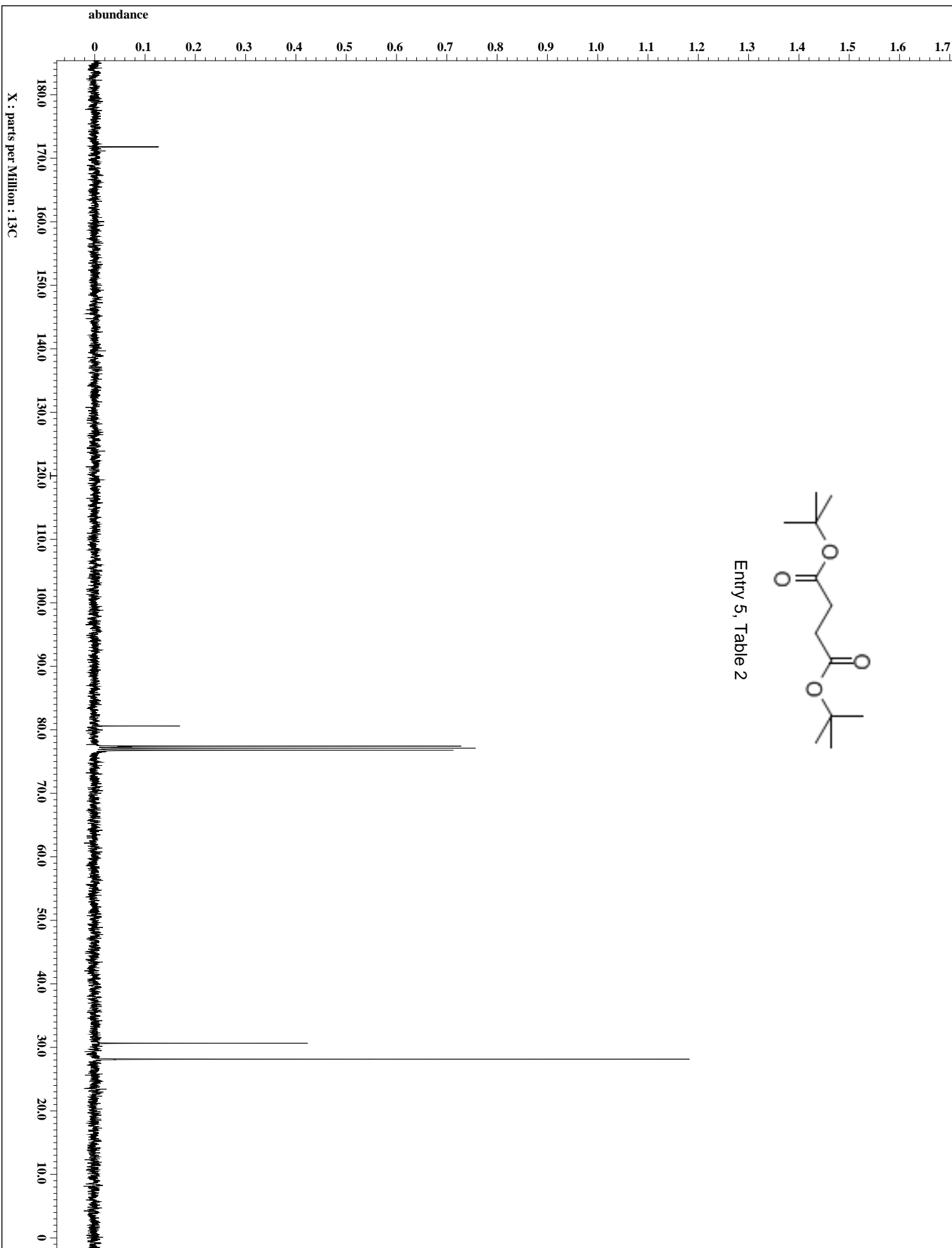
Entry 5, Table 2

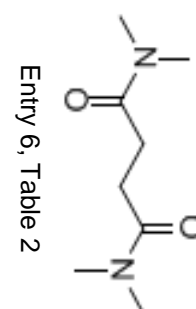
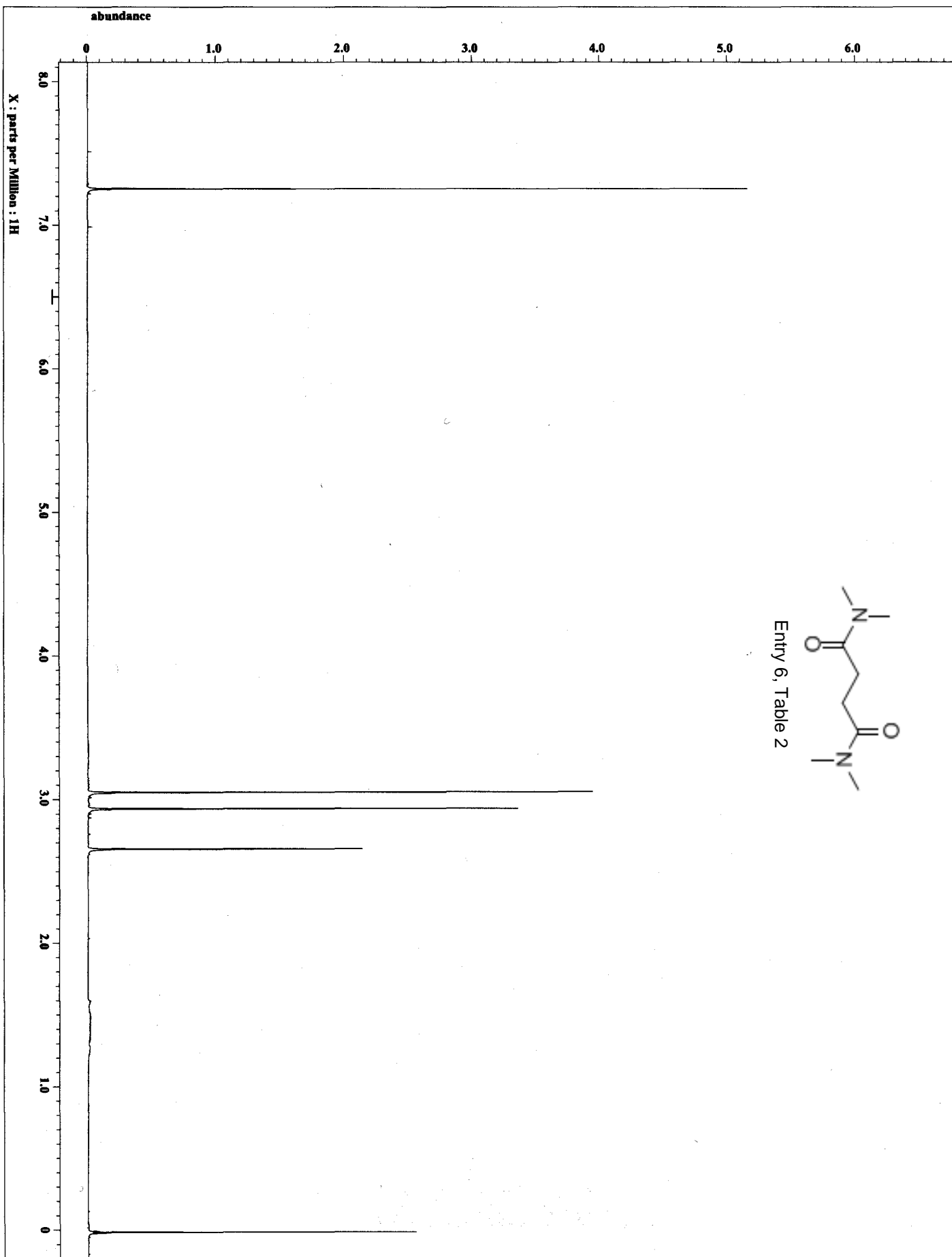


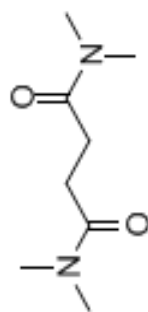
X : parts per Million : 1H



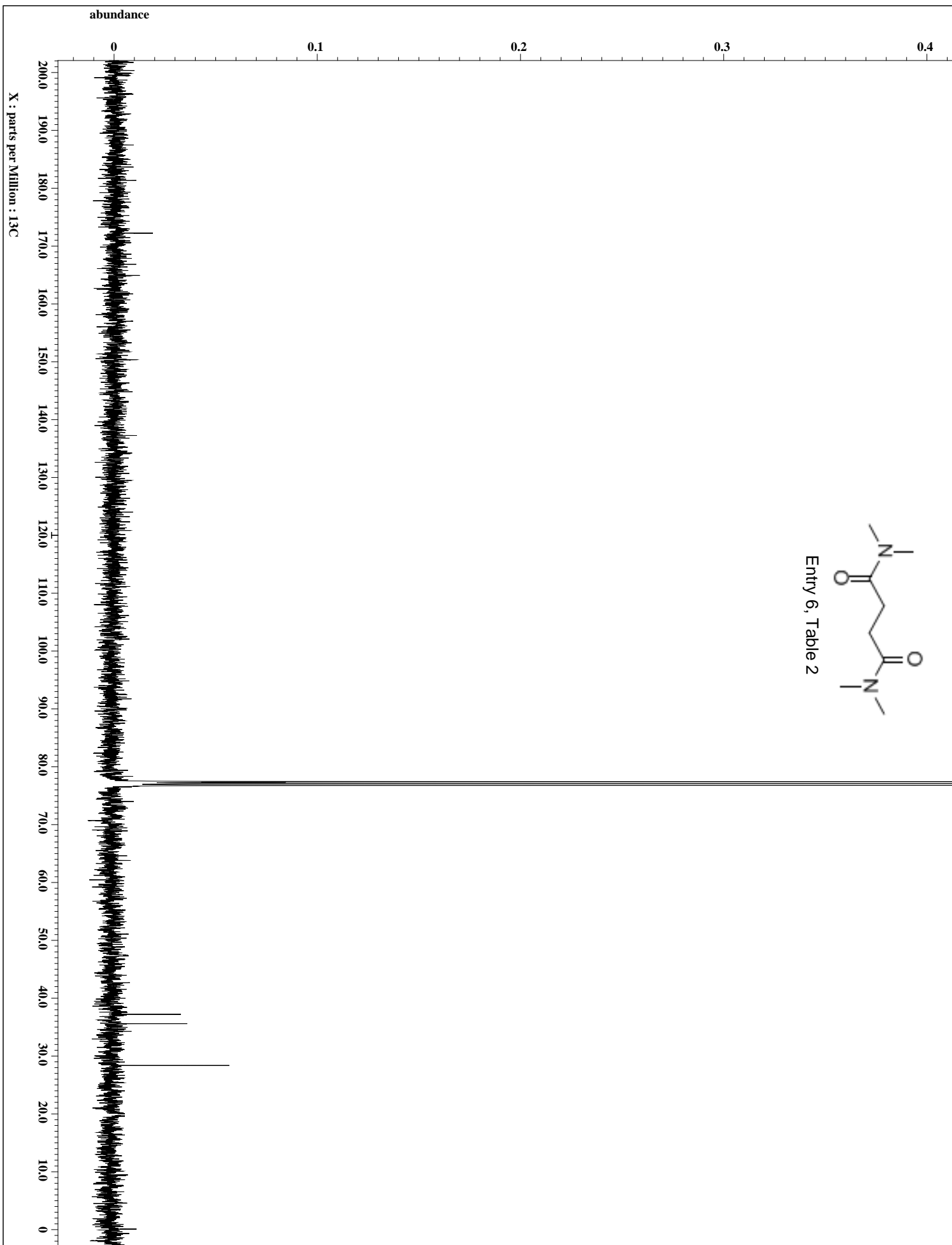
Entry 5, Table 2







Entry 6, Table 2



X : parts per Million : 1H

8.0124
7.9953
7.9907

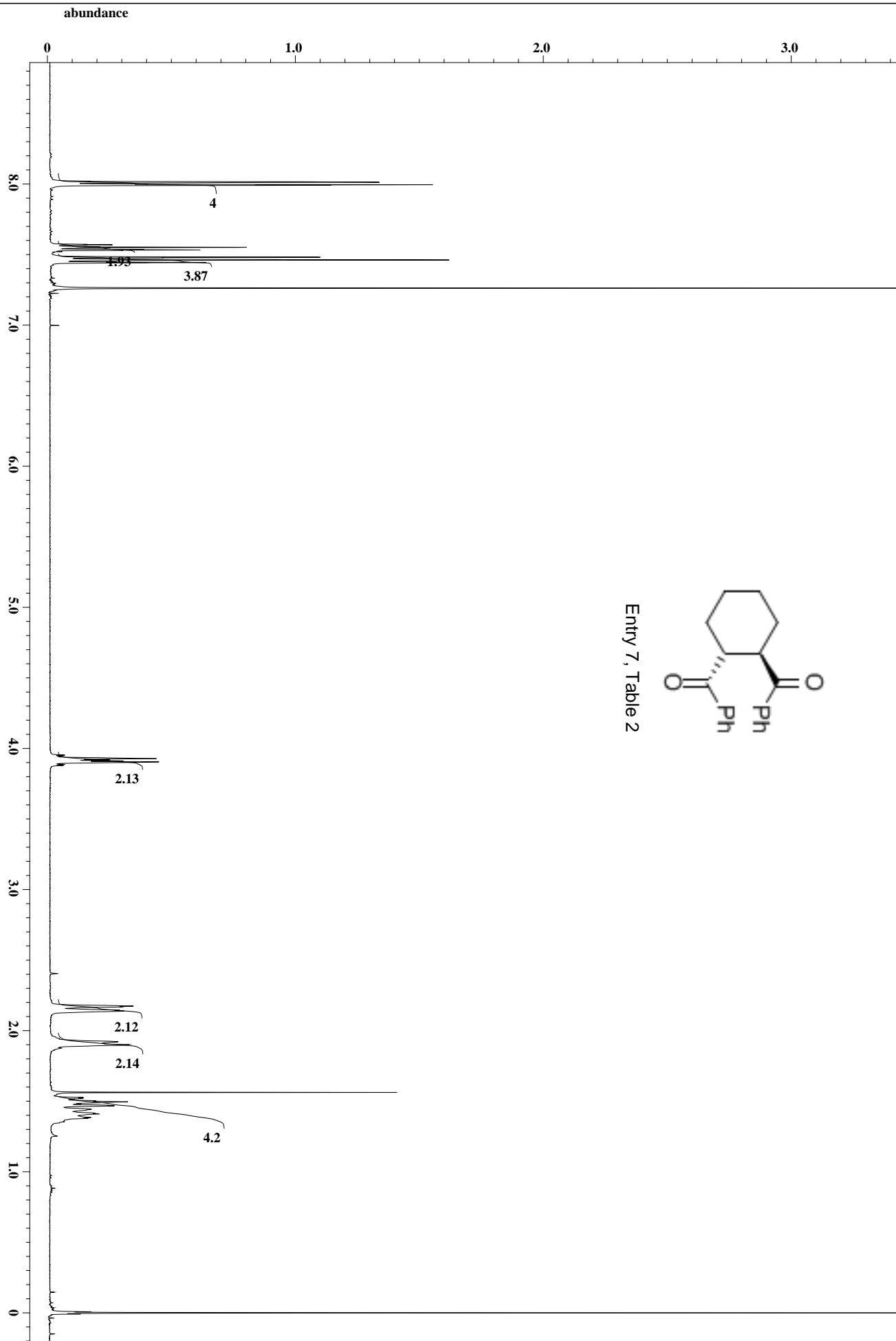
7.5520
7.4809
7.4615
7.2621
7.2255

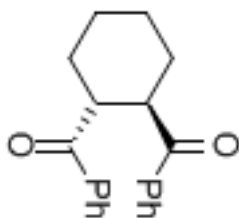
6.9975

3.9276
3.9121
3.9047

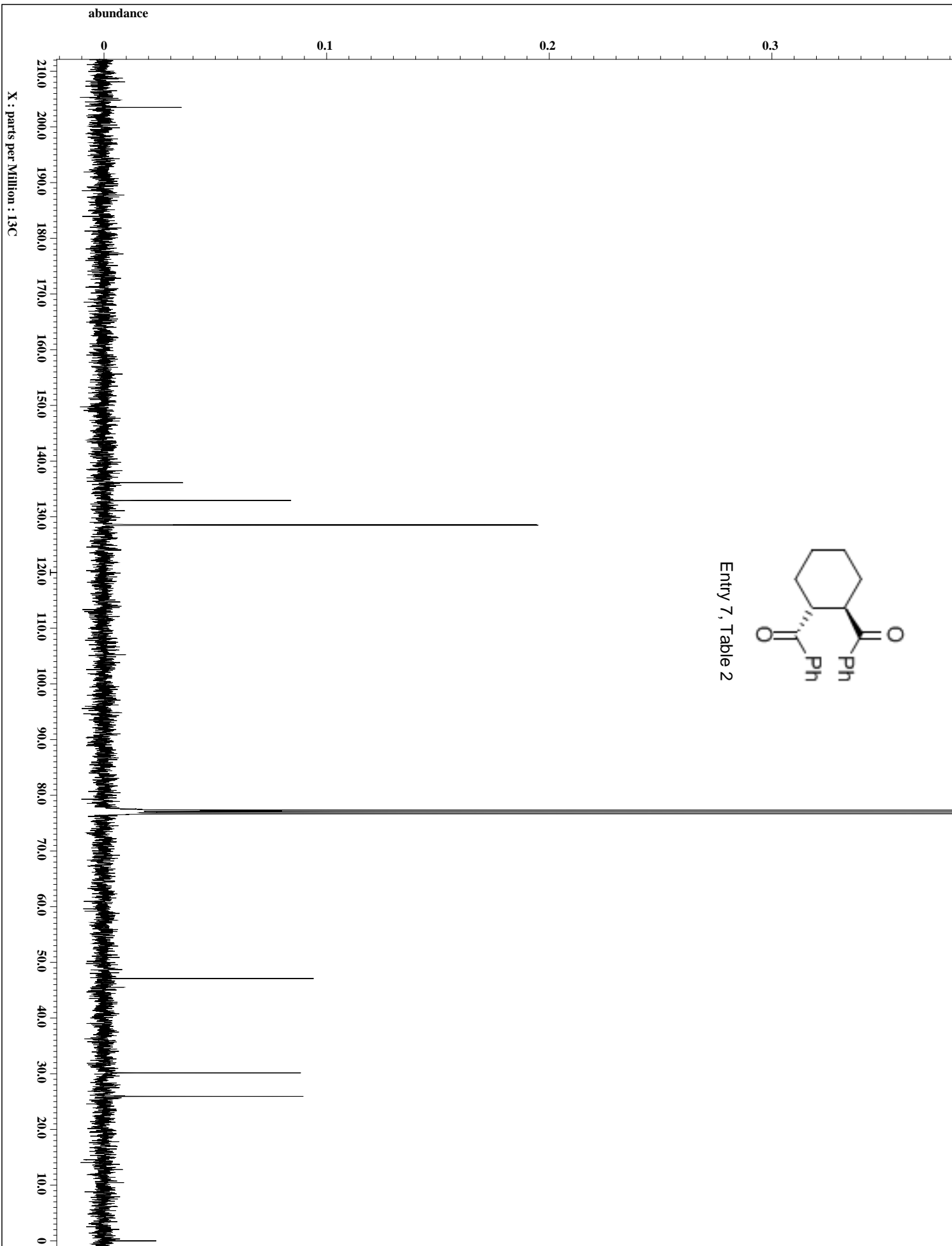
2.1739
2.1395
1.9219
1.9012
1.8978
1.5622
1.4957
1.4671
1.4098

0.0077
-0.0003
-0.0083





Entry 7, Table 2



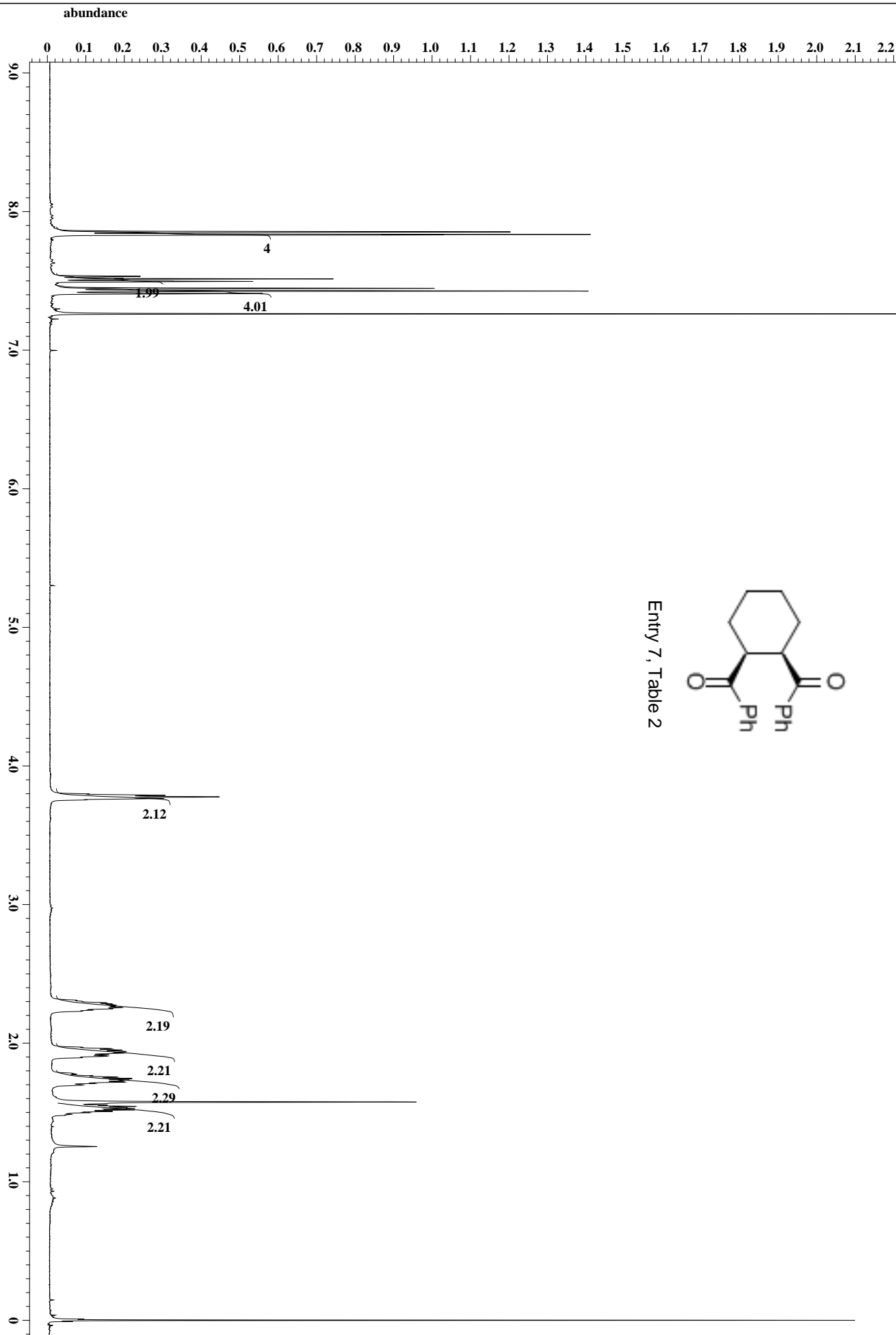
X : parts per Million : 1H

7.8536
7.8352
7.8318
7.5145
7.4469
7.4263
7.4091
7.2625
6.9979

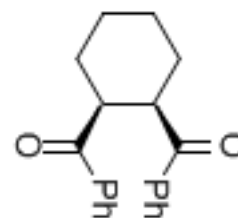
3.7882
3.7768
3.7653

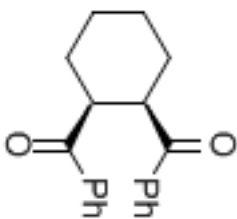
2.2739
2.2659
2.2567
1.7447
1.7344
1.5751
1.5442
1.5327
1.5293
1.5190
1.2532

0.0081
0.0001



Entry 7, Table 2





Entry 7, Table 2

