Supporting Information

One-pot Cascade Michael-Michael-Aldol Condensation for Diastereoselective Synthesis of Nitro-Substituted Cyclohexanes

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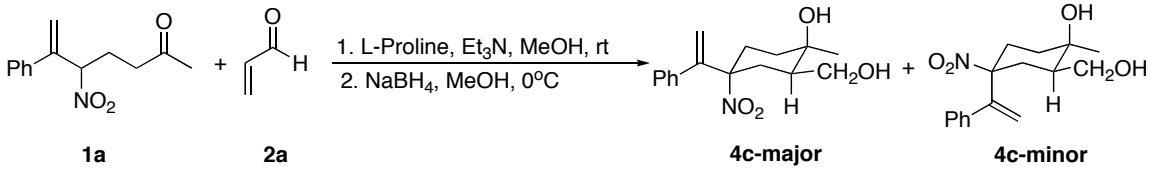
I. General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Joel 270 MHz and Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. HRMS were recorded on LTQ-FTUHRA spectrometer.

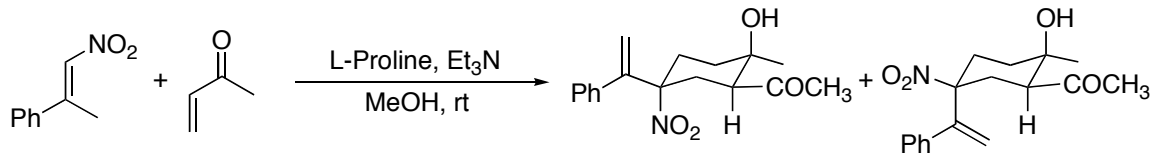
Allylic nitro compounds **1a-1e** were synthesized according to the literature:
X. Sun, S. Sengupta, J. L. Petersen, H. Wang, J. P. Lewis, X. Shi, *Org. Lett.* **2007**, *9*, 4495-4498.

Representative Procedure for Synthesis of cyclohexane derivatives



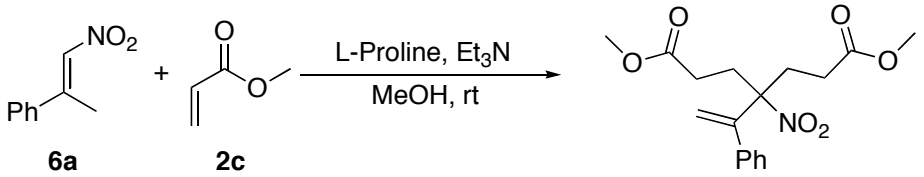
1a **2a** **4c-major** **4c-minor**

The allylic nitro compound **1a** (233 mg, 1 mmol) and L-Proline (23 mg, 0.2 mmol) was dissolved in MeOH (5 mL, 0.2 M). To this solution was added the Et_3N (101 mg, 1 mmol) and acrolein **2a** (117 mg, 90%, 1.5 mmol) at room temperature. The resulting mixture was then stirred and checked by TLC. After the reaction had completed, the mixture was diluted with MeOH (10 mL), the solution was passed through a short silica gel column and then treated with $NaBH_4$ (152 mg, 4 mmol) at 0℃. 15 min later, the solution was quenched with water, neutralized by dilute HCl solution and extracted with EtOAc (40 mL x 3). The combined organic layer was washed with brine and dried over with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a residue, the residue was the purified by flash silica gel chromatography to obtain two diasteroisomers **4c** as colorless oil, yield: 92%.



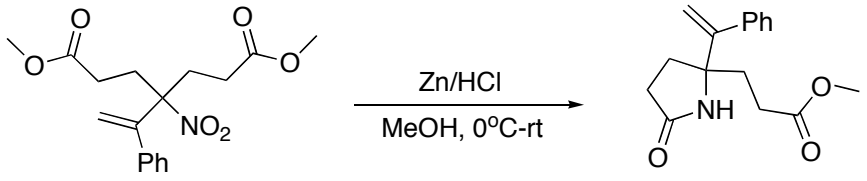
6a **2b** **7a-major** **7a-minor**

The nitroalkene **6a** (163 mg, 1 mmol) and L-Proline (23 mg, 0.2 mmol) was dissolved in MeOH (5 mL, 0.2 M). To this solution was added Et_3N (101 mg, 1 mmol) and MVK **2b** (280 mg, 4 mmol) at room temperature. The resulting mixture was then stirred at room temperature and checked by TLC. When the reaction had completed, the solvent was removed under reduced pressure to give a residue, the residue was then purified by flash silica gel chromatography to obtain two diasteroisomers **7a** as white solids, yield: 90%.



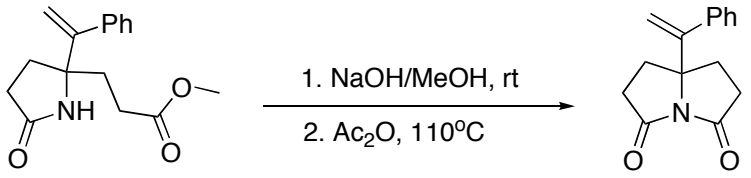
6a **2c** **3a**

The nitroalkene **6a** (163 mg, 1 mmol) and L-Proline (23 mg, 0.2 mmol) was dissolved in MeOH (5 mL, 0.2 M). To this solution was added the Et_3N (101 mg, 1 mmol) and methyl acrylate (344 mg, 4 mmol) at room temperature. The resulting mixture was then stirred and checked by TLC. After the reaction had completed, the solvent was removed under reduced pressure to give a residue, the residue was the purified by flash silica gel chromatography to obtain **3a** (298 mg, 0.89 mmol) as white solid, yield: 89%.



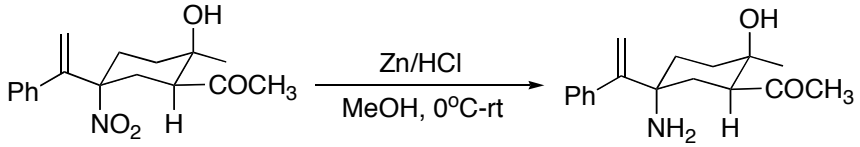
3a **8a**

To a solution of **3a** (200 mg, 0.6 mmol) in MeOH (40 mL), 1N HCl (6 mL, 6 mmol) and Zn powder (585 mg, 9 mmol) were added at 0 ℃. And the mixture was stirred at room temperature for 8 hr. To the mixture, was added $NaHCO_3$ (aq) until pH > 10, followed by the extraction with CH_2Cl_2 (30 mL x 5). The combined organic layer was washed with brine and then dried over with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by flash silica gel chromatography with EtOAc/Hexane (1:2, v/v) to get **8a** (140 mg, 0.51 mmol) as a white solid, yield: 85%.



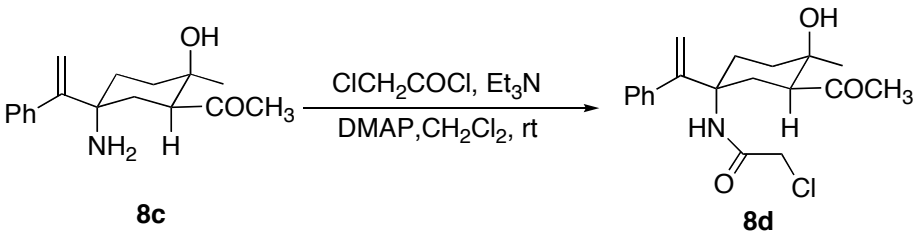
8a **8b**

To a solution of **8a** (100 mg, 0.37 mmol) in MeOH (5 mL) was added the NaOH (22 mg, 0.56 mmol) at room temperature. The mixture was stirred for an hour. To this mixture was added 2N HCl (0.5 mL) and then extract with EtOAc (20 mL x 3), the combined organic layer was washed with brine, dried over with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to get a colorless solid. To this solid was added Ac_2O (5 mL), the solution was stirred for 3 hr at 110 ℃. After returned to room temperature, the solution was poured into water (20 mL) and stirred for half an hour. Then neutralized by $NaHCO_3$ (aq), followed by extraction with EtOAc (20 mL x 3), the combined organic layer was washed with brine, dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to get a residue. The residue can purified by recrystallization (EtOAc/Hexane, 1:5, v/v) or flash silica gel chromatography with EtOAc/Hexane (1:3, v/v) to give **8b** (70 mg, 0.29 mmol) as colorless crystal, yield: 79%.



7a-major **8c**

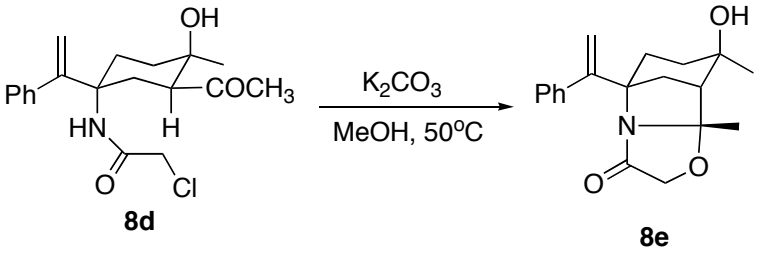
To a solution of **7a-major** (303 mg, 1 mmol) in MeOH (25 mL), 1N HCl (10 mL, 10 mmol) and Zn powder (975 mg, 15 mmol) were added at 0 ℃. And the mixture was stirred at room temperature for 4 hr. To the mixture was added $NaHCO_3$ (aq) until pH > 10, followed by the extraction with CH_2Cl_2 (20 mL x 5). The combined organic layer was washed with brine and dried over with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by flash silica gel chromatography with EtOAc/hexane (1:1, v/v) to give **8c** (240 mg, 0.88 mmol) as colorless oil, yield: 88%.



8c **8d**

To a solution of **8c** (273 mg, 1 mmol) DMAP (6 mg, 0.05 mmol) and Et_3N (150 mg, 1.5 mmol) in CH_2Cl_2 (10 mL), 2-chloroacetyl chloride (136 mg, 1.2 mmol) was added by

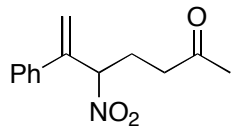
dropwise. The mixture solution was stirred at room temperature and monitored by TLC. The solution was diluted with EtOAc (20 mL), and poured into $NaHCO_3$ (aq), then extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine, dried over with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by flash silica gel chromatography with EtOAc/Hexane (1:5, v/v) to give **8d** (318 mg, 0.91 mmol) as white solid, yield: 91%.



8d **8e**

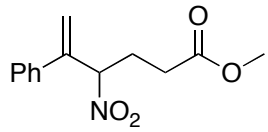
To a solution of **8d** (50 mg, 0.14 mmol) in MeOH (2 mL) was added the K_2CO_3 (29 mg, 0.21 mmol), the mixture solution was stirred at 50 ℃ and checked by TLC. The solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography with EtOAc/Hexane (1:2, v/v) to obtain **8e** (36 mg, 0.12 mmol) as colorless oil, yield: 83%.

II. Compound Characterization:



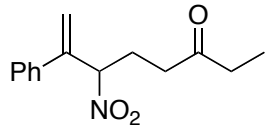
1a

5-nitro-6-phenylhept-6-en-2-one (**1a**). **1a** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 87%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.33-7.38(m, 5H), 5.59(s, 1H), 5.48-5.57(m, 2H), 2.21-2.58(m, 4H), 2.11(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 206.6, 143.4, 138.4, 128.8, 128.7, 126.7, 118.1, 88.9, 39.2, 30.1, 26.7. HRMS Calculated for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.09441, Found: 256.09446.



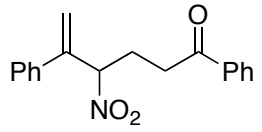
1b

Methyl 4-nitro-5-phenylhex-5-enoate (**1b**). **1b** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 82%. ^{1}H NMR (270 MHz, $CDCl_3$): 7.30-7.35(m, 5H), 5.50-5.67(m, 3H), 3.65(s, 3H), 2.01-2.62(m, 4H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 172.4, 143.3, 138.3, 128.8, 128.7, 126.7, 118.3, 88.9, 52.0, 30.1, 27.9. HRMS Calculated for $C_{13}H_{15}NO_4Na$ $[M+Na]^+$: 272.08933, Found: 272.08918.



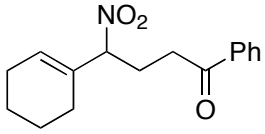
1c

6-nitro-7-phenyloct-7-en-3-one (**1c**). **1c** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 86% (combined all isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.39(m, 5H), 5.59(s, 1H), 5.51-5.59(m, 2H), 2.41-2.51(m, 3H), 2.27-2.40(m, 3H), 1.02(t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 209.2, 143.3, 138.3, 128.7, 128.5, 126.8, 117.8, 88.8, 37.7, 36.0, 26.6, 7.6. HRMS Calculated for $C_{14}H_{18}NO_3$ $[M+H]^+$: 248.12812, Found: 248.12815.



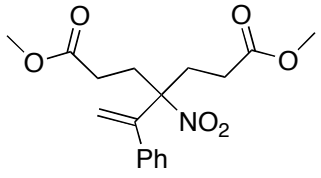
1d

4-nitro-1,5-diphenylhex-5-en-1-one and isomer (**1d**). **1d** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 83% (combined all isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97-7.99(m, 0.26H), 7.90-7.92(m, 2H), 7.55-7.61(m, 1.13H), 7.28-7.50(m, 7.65H), 7.15-7.17(m, 0.26H), 5.67(q, *J* = 4.8 Hz, 1H), 5.63(s, 1H), 5.61(s, 1H), 3.28-3.31(m, 0.26H), 3.03-3.15(m, 2.26H), 2.62-2.70(m, 1H), 2.48-2.54(m, 1H), 2.20(s, 0.39H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.9, 143.5, 138.3, 136.3, 133.4, 128.72, 128.66, 128.5, 127.9, 126.6, 118.1, 89.2, (35.9), 34.4, (31.6), 27.1, (24.6). HRMS Calculated for $C_{18}H_{18}NO_3$ $[M+H]^+$: 294.12812, Found: 294.12813.



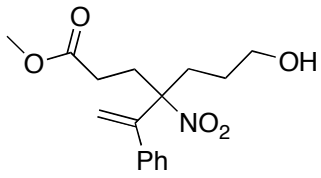
1e

4-cyclohexenyl-4-nitro-1-phenylbutan-1-one (**1e**). **1e** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, yield: 85%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.90-8.01(m, 2H), 7.51-7.63(m, 1H), 7.41-7.50(m, 2H), 5.96(s, 1H), 5.00(dd, *J* = 9.0 Hz, *J* = 6.0 Hz, 1H), 2.90-3.11(m, 2H), 2.50-2.62(m, 1H), 2.26-2.42(m, 1H), 1.93-2.18(m, 4H), 1.46-1.76(m, 4H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 198.0, 136.4, 131.9, 131.1, 128.7, 127.9, 92.8, 34.4, 25.3, 25.0, 24.1, 22.2, 21.7. HRMS Calculated for $C_{16}H_{19}NO_3Na$ $[M+Na]^+$: 296.12626, Found: 296.12555.



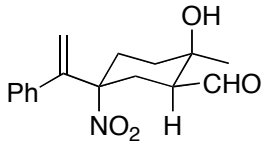
3a

Dimethyl 4-nitro-4-(1-phenylvinyl)heptanedioate (**3a**). **3a** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m. p: 85.5-86.6 ℃, yield: 89%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.30(m, 3H), 7.05-7.07(m, 2H), 5.59(s, 1H), 5.45(s, 1H), 3.65(s, 6H), 2.51-2.57(m, 2H), 2.31-2.40(m, 4H), 2.18-2.26(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.1, 146.1, 138.2, 128.3, 128.2, 128.1, 120.8, 95.3, 51.8, 28.8, 28.6. HRMS Calculated for $C_{17}H_{21}NO_6Na$ $[M+Na]^+$: 358.12411, Found: 358.12422.



3b

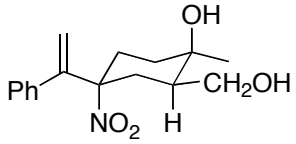
Methyl 7-hydroxy-4-nitro-4-(1-phenylvinyl)heptanoate (**3b**). **3b** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 2/1) as colorless oil, yield: 90%. ^{1}H NMR (600 MHz, $CDCl_3$): 7.28-7.50(m, 3H), 7.07-7.09(m, 2H), 5.63(s, 1H), 5.45(s, 1H), 3.68(s, 3H), 3.60-3.69(m, 2H), 2.57-2.63(m, 1H), 2.21-2.47(m, 4H), 2.04-2.09(m, 1H), 1.51-1.64(m, 2H), 1.35-1.43(m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.6, 146.7, 138.7, 128.4, 128.22, 128.15, 120.7, 95.9, 62.0, 52.0, 30.2, 29.0, 28.4, 27.0. HRMS Calculated for $C_{16}H_{21}NO_5Na$ $[M+Na]^+$: 330.13119, Found: 330.13128.



4a-major

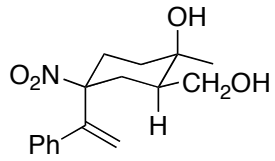
(1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(1-phenylvinyl)cyclohexanecarbaldehyde (**4a-major**). **4a-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) then was recrystallized from CH_2Cl_2/Hexane (1:5) to get a colorless crystal, m.p: 103.1-104.3 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.80(s, 1H), 7.29-7.35(m, 3H), 7.07-7.10(m, 2H), 5.66(s, 1H), 5.30(s, 1H), 2.75(dt, *J* = 14.4 Hz, *J* = 3.6 Hz, 1H), 2.52-2.60(m, 2H), 2.30(s, 1H), 2.21(td, *J* = 14.4 Hz, *J* = 4.2 Hz, 1H), 2.06(dd, *J* = 14.4 Hz, *J* = 13.2 Hz, 1H), 1.69(dt, *J* = 15.0 Hz, *J* = 3.6 Hz, 1H), 1.37-1.44(m, 1H), 1.36(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.8, 148.7, 138.4, 128.6, 128.2, 128.1, 118.8, 92.8, 68.6, 53.3, 35.9, 29.6, 29.0, 28.5. HRMS Calculated for $C_{16}H_{20}NO_4$ $[M+H]^+$: 290.13869, Found: 290.13879.

4a-major and **4a-minor** are unstable. At the same time, **4a-minor** is hard to be separated to obtain pure product, so in situ reduction the mixture of **4a** by treatment with $NaBH_4$ give stable **4c**.



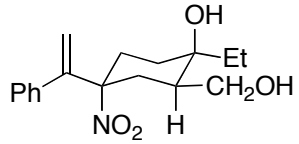
4c-major

(1R*,2R*,4R*)-2-(hydroxymethyl)-1-methyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4c-major**). **4c-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1-1/1) as colorless oil, yield: 92% (combined two isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29-7.32(m, 3H), 7.08-7.11(m, 2H), 5.66(s, 1H), 5.26(s, 1H), 4.21(dd, *J* = 12.0 Hz, *J* = 3.0 Hz, 1H), 3.61(dd, *J* = 10.8 Hz, *J* = 1.8 Hz, 1H), 2.39-2.58(m, 5H), 2.20(dt, *J* = 13.8 Hz, *J* = 3.6 Hz, 1H), 1.61-1.65(m, 1H), 1.40-1.47(m, 2H), 1.31(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.4, 138.6, 128.7, 128.0, 127.8, 118.3, 94.6, 70.9, 64.1, 41.5, 36.6, 32.9, 29.3, 28.3. HRMS Calculated for $C_{16}H_{22}NO_4$ $[M+H]^+$: 292.15434, Found: 292.15444.



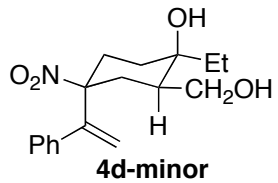
4c-minor

(1R*,2R*,4S*)-2-(hydroxymethyl)-1-methyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4c-minor**). **4c-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1-1/1) as colorless oil, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.32(m, 3H), 7.08-7.11(m, 2H), 5.84(s, 1H), 5.63(s, 1H), 4.11(dd, *J* = 11.4 Hz, *J* = 3.6 Hz, 1H), 3.48(dd, *J* = 10.8 Hz, *J* = 2.4 Hz, 1H), 2.69(t, *J* = 13.2 Hz, 1H), 2.38-2.50(m, 2H), 2.33(dt, *J* = 7.8 Hz, *J* = 3.0 Hz, 1H), 2.01(br, 2H), 1.61(dt, *J* = 6.6 Hz, *J* = 3.6 Hz, 1H), 1.40-1.50(m, 2H), 1.32(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 139.2, 128.3, 128.1, 128.0, 123.5, 92.4, 70.9, 64.1, 42.5, 37.1, 32.4, 29.0, 28.3. HRMS Calculated for $C_{16}H_{21}NO_4Na$ $[M+Na]^+$: 314.13628, Found: 314.13635.



4d-major

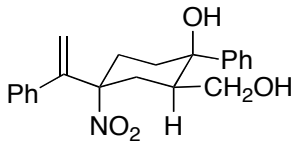
(1R*,2R*,4R*)-1-ethyl-2-(hydroxymethyl)-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4d-major**). **4d-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1-1/1) as colorless oil, yield: 85% (combined two isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.33(m, 3H), 7.09-7.12(m, 2H), 5.66(s, 1H), 5.26(s, 1H), 4.19(dd, *J* = 10.8 Hz; *J* = 2.4 Hz, 1H), 3.59(dd, *J* = 10.8 Hz, *J* = 2.4 Hz, 1H), 2.47-2.60(m, 1H), 2.43-2.46(m, 2H), 2.20(dt, *J* = 13.8 Hz, *J* = 4.2 Hz, 1H), 2.12 (br, 2H), 1.68-1.75(m, 1H), 1.57-1.64(m, 2H), 1.50-1.55(m, 1H), 1.40(dt, *J* = 13.8 Hz, *J* = 4.2 Hz, 1H), 0.86(t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.5, 138.9, 128.7, 128.0, 127.8, 118.3, 94.5, 73.1, 63.9, 39.3, 33.2, 33.0, 32.1, 29.1, 7.9. HRMS Calculated for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$: 328.15193, Found: 328.15215.



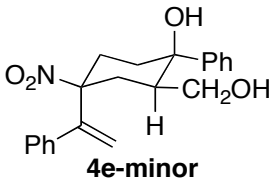
4d-minor

(1R*,2R*,4S*)-2-(hydroxymethyl)-4-nitro-1-phenyl-4-(1-phenylvinyl)cyclohexanol (**4d-minor**). **4d-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1-1/1) as colorless oil, hard to get purified product, NMR shows some major isomer included. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.32(m, 3H), 7.09-7.12(m, 2H), 5.85(s, 1H), 5.63(s, 1H), 4.07(dd, *J* = 10.8 Hz, *J* = 3.0 Hz, 1H), 3.43(dd, *J* = 11.4 Hz, *J* = 3.0 Hz, 1H), 2.74(t, *J* = 13.2 Hz, 1H), 2.32-2.50(m, 3H), 1.37-1.75(m, 7H), 0.88(t, *J* = 7.2 Hz,

3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.0, (139.3, 128.7, 128.3, 128.1, 128.03, 127.99, 127.8, 123.4, 118.3), 92.2, 73.1, (63.93), 63.89, 40.1, (39.4), (33.2), (33.0), 32.7, 32.4, (32.2), (29.2), 28.9, 8.0. HRMS Calculated for $C_{21}H_{23}NO_4Na$ $[M+Na]^+$: 376.15193, Found: 376.15185.

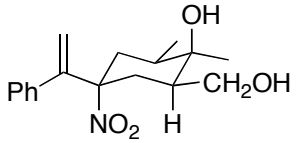


4e-major



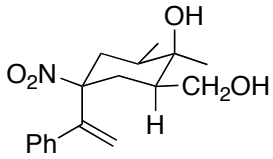
4e-minor

2-(hydroxymethyl)-4-nitro-1-phenyl-4-(1-phenylvinyl)cyclohexanol) (**4e**). **4e** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1-1/1) as colorless oil, yield: 84% (combined two isomers). Two disastereomers are hard to separated, NMR give dr = 3:1 isomers. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12-7.38(m, 13H), 5.95(s, 0.33H), 5.74(s, 0.33H), 5.70(s, 1H), 5.30(s, 1H), 3.57(dd, *J* = 10.2 Hz, *J* = 3.0 Hz, 1H), 3.45-3.48(m, 1.33H), 3.26(dd, *J* = 13.2 Hz, *J* = 3.0 Hz, 0.33H), 2.87(t, *J* = 13.2 Hz, 0.33H), 2.34-2.65(m, 5.32H), 1.66-2.00(m, 3.99H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.5, 146.6, 146.4, 145.1, 139.3, 138.9, 128.7, 128.44, 128.42, 128.1, 127.9, 127.0, 126.9, 124.6, 124.5, 123.7, 118.4, 94.5, (92.2), (75.7), 75.6, 64.4, (42.6), 41.7, (37.5), 36.9, 32.8, (32.3), 29.6, (29.4). HRMS Calculated for $C_{21}H_{23}NO_4Na$ $[M+Na]^+$: 376.15193, Found: 376.15212.



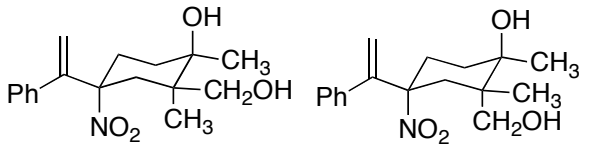
4f-major

(1R*,2R*,4R*,6S*)-2-(hydroxymethyl)-1,6-dimethyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4f-major**). **4f-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1-2/1) as colorless oil, yield: 78% (combined two isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.32(m, 3H), 7.07-7.10(m, 2H), 5.65(s, 1H), 5.24(s, 1H), 4.24(dd, *J* = 11.4 Hz, *J* = 3.0 Hz, 1H), 3.61(*J* = 11.4 Hz, *J* = 3.0 Hz, 1H), 2.59(s, 2H), 2.50(dt, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.40-2.46(m, 2H), 1.96(dd, *J* = 12.0 Hz, *J* = 14.4 Hz, 1H), 1.41-1.51(m, 2H), 1.29(s, 3H), 0.95(d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.4, 138.8, 128.7, 128.0, 127.8, 118.3, 94.4, 72.8, 64.3, 42.4, 37.6, 37.4, 33.0, 24.4, 14.3. HRMS Calculated for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$: 328.15193, Found: 328.15201.



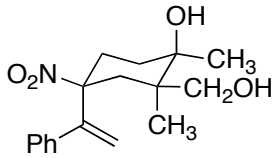
4f-minor

(1R*,2R*,4S*,6S*)-2-(hydroxymethyl)-1,6-dimethyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4f-minor**). **4f-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1-2/1) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.32(m, 3H), 7.06-7.10(m, 2H), 5.83(s, 1H), 5.61(s, 1H), 4.15(dd, *J* = 10.8 Hz, *J* = 3.0 Hz, 1H), 3.48(dd, *J* = 10.8 Hz, *J* = 3.0 Hz, 1H), 2.68(t, *J* = 13.2 Hz, 1H), 2.26-2.35(m, 2H), 2.35(t, *J* = 13.2 Hz, 1H), 2.06(s, 3H), 0.92(d, *J* = 5.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.2, 139.2, (128.7), 128.3, 128.1, 128.02, 127.96, 127.8, 123.2, (118.3), (94.4), 92.0, 72.8, 64.4, (64.3), 43.4, (42.4), 38.4, (37.6), (37.4), 37.1, (33.0), 32.4, 24.6, (22.4), 14.3. HRMS Calculated for $C_{17}H_{24}NO_4$ $[M+H]^+$: 306.16999, Found: 306.17019.



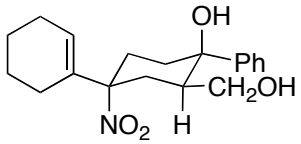
4g-isomer one **4g-isomer two**

2-(hydroxymethyl)-1,2-dimethyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4g**). **4g** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1-1/1) as colorless oil. NMR shows 1:1 ratio isomers (NMR show 2:2:1 ratio for three isomers), yield: 66% (combined two isomers). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.32(m, 5.7H), 7.06-7.10(m, 3.8H), 5.70(s, 1H), 5.68(s, 0.9H), 5.26(s, 0.9H), 5.23(s, 1H), 3.91(d, *J* = 11.4 Hz, 1H), 3.25(d, *J* = 11.4 Hz, 1H), 3.22(s, 1.8H), 2.89(d, *J* = 13.2 Hz, 1H), 2.69(dd, *J* = 15.6 Hz, *J* = 2.4 Hz, 1H), 1.82-2.62(m, 10.3H), 1.60-1.93(m, 1.9H), 1.57(dt, *J* = 14.4 Hz, *J* = 2.4 Hz, 1H), 1.23(s, 3H), 1.18(s, 2.7H), 1.12(s, 3H), 0.64(s, 2.7H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.3, (149.6), 138.9, (138.7), 128.8, 128.7, 128.2, 128.00, 127.96, 127.9, 127.8, (118.8), 118.3, (92.9), 92.1, 75.1, 71.0, 69.8, 65.4, 43.1, 40.2, 37.0, 36.0, 33.9, 32.9, (29.0), 28.8, 25.0, (24.8), 19.7, (19.3). HRMS Calculated for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$: 328.15193, Found: 328.15190.



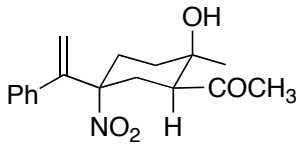
4g-isomer three

(1R*,2R*,4R*)-2-(hydroxymethyl)-1,2-dimethyl-4-nitro-4-(1-phenylvinyl)cyclohexanol (**4g-isomer three**). **4g-siomer three** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1-1/1) as colorless oil, yield: 16%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.33(m, 3H), 7.04-7.07(m, 2H), 5.76(s, 1H), 5.22(s, 1H), 3.65(d, *J* = 10.2 Hz, 1H), 3.12(d, *J* = 10.2 Hz, 1H), 2.73(dq, *J* = 15.0 Hz, *J* = 3.0 Hz, 1H), 2.54(dd, *J* = 3.0 Hz, *J* = 15.0 Hz, 1H), 2.40(br, 2H), 2.02(td, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 1.64-1.71(m, 2H), 1.45(dt, *J* = 13.8 Hz, *J* = 3.6 Hz, 1H), 1.28(s, 3H), 1.03(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.0, 138.7, 128.6, 128.1, 128.0, 118.4, 90.5, 73.9, 70.9, 41.0, 93.3, 33.4, 31.2, 23.1, 16.8. HRMS Calculated for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$: 328.15193, Found: 328.15215.



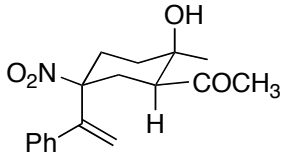
4h-major

(1R*,2R*,4R*)-4-cyclohexenyl-2-(hydroxymethyl)-4-nitro-1-phenylcyclohexanol (**4h-major**). **4h-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1) as colorless oil, yield: 83%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.41(m, 2H), 7.30-7.36(m, 2H), 7.23-7.26(m, 1H), 6.02-6.04(m, 1H), 3.62(dd, *J* = 10.8 Hz, *J* = 3.0 Hz, 1H), 3.52(dd, *J* = 10.8 Hz, *J* = 3.0 Hz, 1H), 2.64-2.68(m, 1H), 2.53(t, *J* = 14.4 Hz, 1H), 2.31(td, *J* = 13.2 Hz, *J* = 4.2 Hz, 1H), 2.10-2.14(m, 2H), 2.03-2.09(m, 2H), 1.98(dq, *J* = 12.6 Hz, *J* = 3.0 Hz, 1H), 1.82(td, *J* = 12.6 Hz, *J* = 4.2 Hz, 1H), 1.74(dq, *J* = 14.4 Hz, *J* = 2.4 Hz, 1H), 1.62-1.67(m, 2H), 1.54-1.60(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.7, 136.5, 128.4, 126.9, 125.9, 124.6, 95.6, 75.9, 64.7, 41.8, 37.1, 31.8, 28.4, 25.4, 23.8, 22.7, 21.7. HRMS Calculated for $C_{19}H_{25}NO_4Na$ $[M+Na]^+$: 354.16758, Found: 354.16756.



7a-major

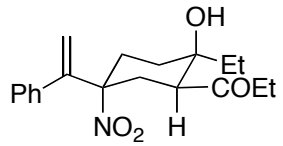
1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(1-phenylvinyl)cyclohexyl)ethanone (**7a-major or 4b-major**). **7a-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 98.2-98.9 ℃, yield: 66%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.22-7.36(m, 3H), 6.98-7.09(m, 2H), 5.60(s, 1H), 5.24(s, 1H), 3.40-3.90 (br, 1H), 2.47-2.67(m, 3H), 2.17-2.32(m, 4H), 2.08(t, *J* = 13.6 Hz, 1H), 1.69(dq, *J* = 14.6 Hz, *J* = 1.5 Hz, 1H), 1.19-1.33(m, 1H), 1.14(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.5, 148.5, 138.3, 128.6, 128.1, 128.0, 118.7, 93.1, 68.3, 52.3, 34.8, 32.1, 31.5, 29.0, 28.2. HRMS Calculated for $C_{17}H_{21}NO_4Na$ $[M+Na]^+$: 326.13683, Found: 326.13606.



7a-minor

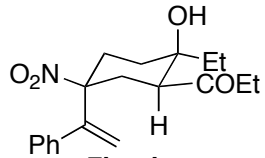
1-((1S*,2R*,5S*)-2-hydroxy-2-methyl-5-nitro-5-(1-phenylvinyl)cyclohexyl)ethanone (**7a-minor or 4b-minor**). **7a-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 75.6-77.1 ℃, yield: 24%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.32-7.43(m, 3H), 7.16-7.25(m, 2H), 5.92(s, 1H), 5.73(s, 1H), 3.88(d, *J* = 2.5 Hz, 1H), 2.24-2.62(m, 5H), 1.69-1.81(m, 4H), 1.37-1.53(m, 1H), 1.17(s, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 213.0, 144.0, 138.9, 128.5, 128.3, 128.1, 124.0, 90.7, 68.5,

52.7, 35.8, 31.0, 30.0, 29.6, 28.0. HRMS Calculated for $C_{17}H_{21}NO_4Na$ $[M+Na]^+$: 326.13683, Found: 326.13608.



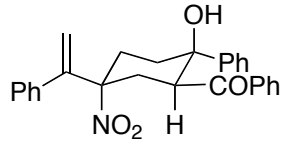
7b-major

1-((1S*,2R*,5R*)-2-ethyl-2-hydroxy-5-nitro-5-(1-phenylvinyl)cyclohexyl)propan-1-one (**7b-major**). **7b-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 78.7-80.3 ℃, yield: 61%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.18-7.42(m, 3H), 6.96-7.14(m, 2H), 5.61(s, 1H), 5.25(s, 1H), 3.79(d, *J* = 2.5 Hz, 1H), 2.06-2.76(m, 8H), 1.75(dt, *J* = 14.6 Hz, *J* = 3.7 Hz, 1H), 1.10-1.54(m, 3H), 1.05(t, *J* = 7.2 Hz, 3H), 0.74(t, *J* = 7.4 Hz, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 217.5, 148.7, 138.3, 128.6, 128.1, 127.9, 118.6, 93.2, 70.9, 50.7, 37.8, 33.6, 32.5, 30.6, 28.8, 7.7, 7.2. HRMS Calculated for $C_{19}H_{25}NO_4Na$ $[M+Na]^+$: 354.16813, Found: 354.16738.



7b-minor

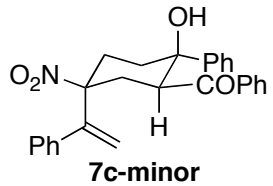
1-((1S*,2R*,5S*)-2-ethyl-2-hydroxy-5-nitro-5-(1-phenylvinyl)cyclohexyl)propan-1-one (**7b-minor**). **7b-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 20%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.30-7.44(m, 3H), 7.15-7.25(m, 2H), 5.92(s, 1H), 5.71(s, 1H), 3.89(d, *J* = 2.7 Hz, 1H), 2.28-2.65(m, 5H), 1.88-2.07(m, 2H), 1.75(dt, *J* = 14.1 Hz, *J* = 3.7 Hz, 1H), 1.23-1.55(m, 3H), 0.78-0.92(m, 6H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 216.1, 144.2, 139.0, 128.5, 128.24, 128.15, 124.0, 90.7, 71.1, 50.3, 36.4, 33.4, 31.7, 31.4, 29.5, 29.4, 7.9, 7.1. HRMS Calculated for $C_{19}H_{25}NO_4Na$ $[M+Na]^+$: 354.16813, Found: 354.16739.



7c-major

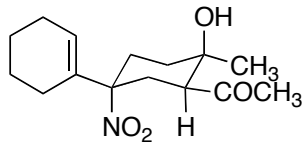
1-((1S*,2R*,5R*)-2-hydroxy-5-nitro-2-phenyl-5-(1-phenylvinyl)cyclohexyl)(phenyl) methanone (**7c-major**). **7c-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 163.2-164.8 ℃, yield: 72%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91-7.93(m, 2H), 7.55-7.59(m, 1H), 7.43-7.46(m, 2H), 7.30-7.36(m, 5H), 7.17-7.21(m, 2H), 7.09-7.13(m, 3H), 5.66(s, 1H), 5.30(s, 1H), 5.12(d, *J* = 3.0 Hz, 1H), 4.21(dd, *J* = 12.6 Hz, *J* = 3.0 Hz, 1H), 2.93(dt, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.71(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.47-2.58(m, 2H), 1.90(dq, *J* = 14.4 Hz, *J* = 3.0

Hz, 1H), 1.67-1.75(m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.6, 148.8, 146.3, 138.4, 135.5, 134.2, 129.0, 128.7, 128.4, 128.3, 128.2, 128.1, 127.0, 124.4, 118.8, 93.8, 73.2, 46.5, 36.9, 33.8, 29.9. HRMS Calculated for $C_{27}H_{25}NO_4Na$ $[M+Na]^+$: 450.16813, Found: 450.16712.



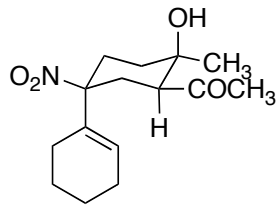
7c-minor

1-((1S*,2R*,5S*)-2-hydroxy-5-nitro-2-phenyl-5-(1-phenylvinyl)cyclohexyl)(phenyl) methanone (**7c-minor**). **7c-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1-3/1) as colorless oil, yield: 10%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.48(m, 6H), 7.33-7.35(m, 2H), 7.09-7.23(m, 7H), 6.08(s, 1H), 5.88(s, 1H), 5.40(s, 1H), 3.85(dd, *J* = 12.0 Hz, *J* = 4.2 Hz, 1H), 2.73-2.84(m, 4H), 1.88-1.92(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.4, 146.2, 144.6, 139.4, 135.4, 133.8, 129.0, 128.7, 128.6, 128.41, 128.35, 127.9, 127.0, 124.9, 124.4, 90.7, 73.4, 46.4, 37.8, 32.4, 30.6. HRMS Calculated for $C_{27}H_{25}NO_4Na$ $[M+Na]^+$: 450.16813, Found: 450.16723.



7d-major

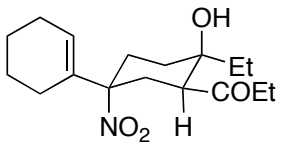
1-((1S*,2R*,5R*)-5-cyclohexenyl-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7d-major**). **7d-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 129.5-130.8 ℃, yield: 74%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.84(m, 1H), 3.81(d, *J* = 2.4Hz, 1H), 2.50-2.64(m, 2H), 2.43(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.20(s, 3H), 1.83-2.18(m, 6H), 1.37-1.35(m, 5H), 1.03-1.26(m, 1H), 1.09(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.4, 135.5, 125.9, 94.0, 68.3, 52.6, 31.2, 31.1, 27.6, 25.1, 23.5, 22.4, 21.3. HRMS Calculated for $C_{15}H_{23}NO_4Na$ $[M+Na]^+$: 304.15248, Found: 304.15180.



7d-minor

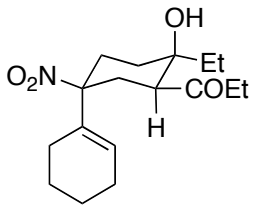
1-((1S*,2R*,5S*)-5-cyclohexenyl-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7d-minor**). **7d-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 54.2-55.1 ℃, yield: 14%. ^{1}H NMR (270 MHz, $CDCl_3$): δ

6.17(m, 1H), 3.85(d, J = 2.4 Hz, 1H), 2.15-2.60(m, 7H), 2.25(s, 3H), 1.94-2.05(m, 1H), 1.52-1.77(m, 5H), 1.22-1.38(m, 1H), 1.17(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 213.2, 131.3, 130.6, 92.2, 68.6, 53.5, 36.0, 30.9, 29.8, 27.4, 25.8, 24.1, 222.6, 21.4. HRMS Calculated for $C_{15}H_{23}NO_4Na$ $[M+Na]^+$: 304.15248, Found: 304.15177.



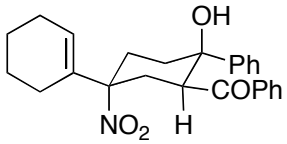
7e-major

1-((1S*,2R*,5R*)-5-cyclohexenyl-2-ethyl-2-hydroxy-5-nitrocyclohexyl)propan-1-one (**7e-major**). **7e-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 91.8-92.9 ℃, yield: 71%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.80(m, 1H), 3.70(d, J = 2.5 Hz, 1H), 2.29-2.67(m, 5H), 1.80-2.13(m, 6H), 1.61(dt, J = 13.6 Hz, J = 3.7 Hz, 1H), 1.14-1.54(m, 6H), 1.07(dt, J = 13.6 Hz, J = 3.5 Hz, 1H), 0.95(t, J = 7.2 Hz, 3H), 0.72(t, J = 8.6 Hz, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 217.2, 135.5, 125.7, 93.9, 70.8, 50.5, 37.4, 33.4, 31.4, 30.5, 27.4, 25.1, 23.4, 22.3, 21.3, 7.5, 6.9. HRMS Calculated for $C_{17}H_{27}NO_4Na$ $[M+Na]^+$: 332.18378, Found: 332.18303.



7e-minor

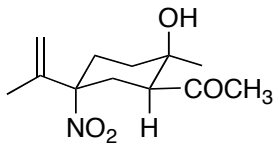
1-((1S*,2R*,5S*)-5-cyclohexenyl-2-ethyl-2-hydroxy-5-nitrocyclohexyl)propan-1-one (**7e-minor**). **7e-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 6/1) as colorless oil, yield: 13%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.14(t, J = 1.0 Hz, 1H), 3.82(d, J = 2.5 Hz, 1H), 2.10-2.69(m, 9H), 1.88-2.02(m, 2H), 1.08-1.78(m, 8H), 1.02(t, J = 7.2 Hz, 3H), 0.81(t, J = 7.4 Hz, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 216.3, 131.2, 130.6, 92.1, 71.0, 51.5, 37.2, 33.3, 31.7, 30.2, 27.1, 25.8, 24.0, 22.5, 21.4, 7.6, 7.1. HRMS Calculated for $C_{17}H_{27}NO_4Na$ $[M+Na]^+$: 332.18378, Found: 332.18305.



7f-major

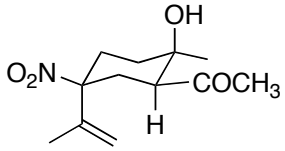
1-((1S*,2R*,5R*)-5-cyclohexenyl-2-hydroxy-5-nitro-2-phenylcyclohexyl)(phenyl)methanone (**7f-major**). **7f-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 6/1) as white solid, m.p: 133.1-134.6 ℃, yield: 82%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96-7.98(m, 2H), 7.56-7.60(m, 1H), 7.45-7.48(m, 2H), 7.35-7.38(m, 2H),

7.19-7.22(m, 2H), 7.09-7.13(m, 1H), 5.98(m, 1H), 5.17(d, J = 1.8 Hz, 1H), 4.20(dd, J = 12.6 Hz, J = 3.0 Hz, 1H), 2.96(dt, J = 14.4 Hz, J = 3.0 Hz, 1H), 2.70(dq, J = 14.4 Hz, J = 3.0 Hz, 1H), 2.48(td, J = 13.2 Hz, J = 4.2 Hz, 1H), 2.39(dd, J = 13.2 Hz, J = 12.6 Hz, 1H), 1.96-2.12(m, 4H), 1.89(dq, J = 13.0 Hz, J = 3.0 Hz, 1H), 1.51-1.71(m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.8, 146.5, 135.7, 135.5, 134.2, 129.0, 128.5, 128.3, 126.9, 126.5, 124.4, 94.7, 73.5, 46.6, 37.0, 32.9, 28.5, 25.4, 23.8, 22.6, 21.5. HRMS Calculated for $C_{25}H_{27}NO_4Na$ $[M+Na]^+$: 428.18378, Found: 428.18291.



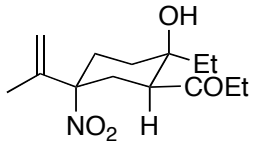
7g-major

1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(prop-1-en-2-yl)cyclohexyl)ethanone (**7g-major**). **7g-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 62.6-62.9 ℃, yield: 65%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.11(s, 1H), 5.06(q, J = 1.2 Hz, 1H), 3.85(d, J = 2.7 Hz, 1H), 2.56-2.69(m, 2H), 2.51(dq, J = 14.6 Hz, J = 3.0 Hz, 1H), 2.26(s, 3H), 1.99-2.24(m, 2H), 1.64-1.78(m, 4H), 1.17-32(m, 1H), 1.15(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.2, 142.5, 114.7, 93.7, 68.2, 52.5, 34.8, 31.2, 31.1, 28.1, 28.0, 27.9. HRMS Calculated for $C_{12}H_{19}NO_4Na$ $[M+Na]^+$: 264.12118, Found: 264.12043.



7g-minor

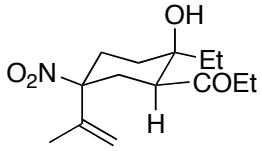
1-((1S*,2R*,5S*)-2-hydroxy-2-methyl-5-nitro-5-(prop-1-en-2-yl)cyclohexyl)ethanone (**7g-minor**). **7g-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as colorless oil, yield: 15%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.18(s, 1H), 5.12(q, J = 1.5 Hz, 1H), 2.69-2.86(m, 3H), 2.46(s, 1H), 2.32(s, 3H), 1.53-2.00(m, 8H), 1.18(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 210.6, 142.5, 115.2, 93.5, 71.1, 55.3, 38.4, 32.4, 32.2, 30.4, 21.5, 21.4, 18.7. HRMS Calculated for $C_{12}H_{19}NO_4Na$ $[M+Na]^+$: 264.12118, Found: 264.12051.



7h-major

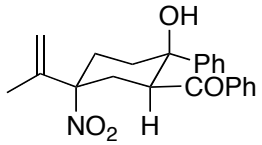
1-((1S*,2R*,5R*)-2-ethyl-2-hydroxy-5-nitro-5-(prop-1-en-2-yl)cyclohexyl)propan-1-one (**7h-major**). **7h-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 112.3-113.9 ℃, yield: 60%. ^{1}H NMR (600 MHz,

$CDCl_3$): δ 5.16(s, 1H), 5.10(q, *J* = 1.2 Hz, 1H), 2.70-2.82(m, 4H), 2.44-2.53(m, 1H), 2.17(br, 1H), 2.02(dd, *J* = 13.2 Hz, *J* = 15.0 Hz, 1H), 1.96(td, *J* = 3.6 Hz, *J* = 13.8 Hz, 1H), 1.77(d, *J* = 0.6 Hz, 3H), 1.66(dt, *J* = 4.2 Hz, *J* = 15.0 Hz, 1H), 1.55-1.63(m, 1H), 1.28-1.40(m, 2H), 1.03(t, *J* = 7.2 Hz, 3H), 0.87(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.9, 142.6, 115.2, 93.6, 72.8, 55.5, 37.8, 32.5, 32.3, 29.9, 24.4, 18.7, 7.4, 6.8. HRMS Calculated for $C_{14}H_{24}NO_4$ $[M+H]^+$: 270.16999, Found: 270.17004.



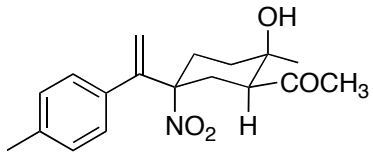
7h-minor

1-((1S*,2R*,5S*)-2-ethyl-2-hydroxy-5-nitro-5-(prop-1-en-2-yl)cyclohexyl)propan-1-one (**7h-minor**). **7h-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 77.6-78.9 ℃, yield: 12%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.34(s, 1H), 5.32(s, 1H), 2.68-2.74(m, 2H), 2.35-2.62(m, 4H), 2.05-2.23(m, 3H), 1.81(d, *J* = 0.6 Hz, 3H), 1.64-1.71(m, 1H), 1.42-1.52(m, 2H), 1.04(t, *J* = 7.2 Hz, 3H), 0.87(t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.1, 140.1, 118.5, 91.8, 72.8, 54.4, 36.4, 31.8, 31.0, 28.8, 27.1, 18.9, 7.5, 6.7. HRMS Calculated for $C_{14}H_{23}NO_4Na$ $[M+Na]^+$: 292.15193, Found: 292.15205.



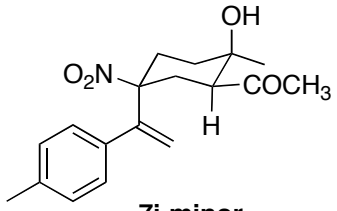
7i-major

1-((1S*,2R*,5R*)-2-hydroxy-5-nitro-2-phenyl-5-(prop-1-en-2-yl)cyclohexyl)phenyl-methanone (**7i-major**). **7i-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 141.8-142.7 ℃, yield: 77%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95-7.97(m, 2H), 7.58-7.61(m, 1H), 7.45-7.49(m, 2H), 7.35-7.38(m, 2H), 7.19-7.23(m, 2H), 7.10-7.14(m, 1H), 5.21(s, 1H), 5.17(d, *J* = 3.0 Hz, 1H), 5.13(q, *J* = 1.2 Hz, 1H), 2.95(dt, *J* = 14.4 Hz, *J* = 2.4 Hz, 1H), 2.72(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.54(td, *J* = 14.4 Hz, *J* = 4.2 Hz, 1H), 2.45(dd, *J* = 14.4 Hz, *J* = 13.2 Hz, 1H), 1.92(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 1.83(s, 3H), 1.67-1.74(m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.7, 146.4, 142.6, 135.4, 134.2, 129.0, 128.5, 128.4, 127.0, 124.4, 115.2, 94.4, 73.4, 46.4, 37.0, 32.9, 28.8, 18.7. HRMS Calculated for $C_{22}H_{23}NO_4Na$ $[M+Na]^+$: 388.15193, Found: 388.15213.



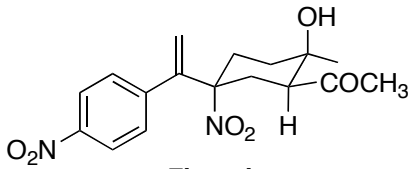
7j-major

1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(1-p-tolylvinyl)cyclohexyl)ethanone (**7j-major**). **7j-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 63%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.11(d, *J* = 8.0 Hz, 2H), 6.95(d, *J* = 8.0 Hz, 2H), 5.59(s, 1H), 5.24(s, 1H), 3.86(d, *J* = 2.7 Hz, 1H), 2.49-2.69(m, 3H), 2.04-2.36(m, 8H), 1.66-1.76(m, 1H), 1.20-1.35(m, 1H), 1.16(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.5, 148.5, 137.7, 135.4, 128.7, 128.4, 118.4, 93.3, 68.3, 52.6, 34.9, 32.1, 31.5, 29.0, 28.2, 21.1. HRMS Calculated for $C_{18}H_{23}NO_4Na$ $[M+Na]^+$: 340.15248, Found: 340.15170.



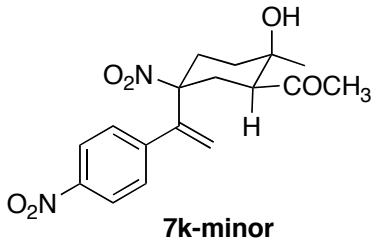
7j-minor

1-((1S*,2R*,5S*)-2-hydroxy-2-methyl-5-nitro-5-(1-p-tolylvinyl)cyclohexyl)ethanone (**7j-minor**). **7j-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 21%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.17(d, *J* = 8.2 Hz, 2H), 7.07(d, *J* = 8.2 Hz, 2H), 5.88(s, 1H), 5.69(s, 1H), 3.88(d, *J* = 2.5 Hz, 1H), 2.33-2.60(m, 8H), 1.81(s, 3H), 1.74(dt, *J* = 14.4 Hz, *J* = 3.8 Hz, 1H), 1.36-1.52(m, 1H), 1.17(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 213.1, 143.9, 138.2, 136.0, 129.1, 128.0, 123.6, 90.9, 68.5, 52.8, 35.9, 31.0, 30.2, 29.5, 28.1, 21.1. HRMS Calculated for $C_{18}H_{23}NO_4Na$ $[M+Na]^+$: 340.15248, Found: 40.15169.



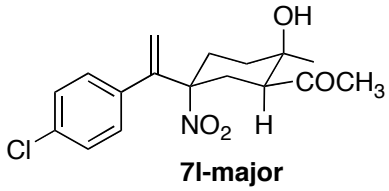
7k-major

1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(1-(4-nitrophenyl)vinyl)cyclohexyl) ethanone (**7k-major**). **7k-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 8/1) as white solid, m.p: 106.9-108.1 ℃, yield: 62%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16(d, *J* = 9.0 Hz, 2H), 7.24(d, *J* = 9.0 Hz, 2H), 5.74(s, 1H), 5.33(s, 1H), 3.69(br, 1H), 2.64(dd, *J* = 12.6 Hz, *J* = 3.0 Hz, 1H), 2.59(dt, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.52(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 2.22-2.28(m, 4H), 2.11(t, *J* = 13.2 Hz, 1H), 1.71(dt, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 1.28(td, *J* = 14.4 Hz, *J* = 3.6 Hz, 1H), 1.16(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 214.0, 147.7, 146.9, 145.0, 129.7, 123.4, 120.4, 92.6, 68.2, 52.5, 34.8, 32.1, 31.6, 29.1, 28.1. HRMS Calculated for $C_{17}H_{21}N_2O_6$ $[M+H]^+$: 349.13941, Found: 349.13966.



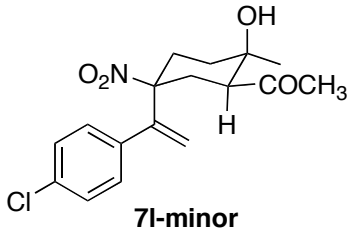
7k-minor

1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-nitro-5-(1-(4-nitrophenyl)vinyl)cyclohexyl) ethanone (**7k-minor**). **7k-minor** was purified by flash silica gel chromatography (CH_2Cl_2/MeOH, v/v, 50/1) as colorless oil, yield: 25%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24(d, *J* = 9.0 Hz, 2H), 7.40(d, *J* = 9.0 Hz, 2H), 6.03(s, 1H), 5.79(s, 1H), 3.79(br, 1H), 2.49-2.56(m, 2H), 2.44(dq, *J* = 13.8 Hz, *J* = 3.0 Hz, 1H), 2.33-2.40(m, 2H), 1.75(dt, *J* = 14.4 Hz, *J* = 3.6 Hz, 1H), 1.34(td, *J* = 12.6 Hz, *J* = 3.6 Hz, 1H), 1.19(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.1, 147.7, 145.5, 142.8, 129.3, 125.9, 123.8, 90.5, 68.4, 53.1, 35.8, 31.1, 30.5, 29.1, 28.1. HRMS Calculated for $C_{17}H_{21}N_2O_6Na$ $[M+Na]^+$: 371.12136, Found: 371.12125.



7l-major

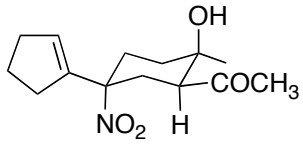
1-((1S*,2R*,5R*)-5-(1-(4-chlorophenyl)vinyl)-2-hydroxy-2-methyl-5-nitrocyclohex-yl)ethanone (**7l-major**). **7l-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as white solid, m.p: 78.6-79.9 ℃, yield: 65%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.29(d, *J* = 8.4 Hz, 2H), 7.00(d, *J* = 8.4 Hz, 2H), 5.65(s, 1H), 5.28(s, 1H), 3.85(d, *J* = 2.5 Hz, 1H), 2.48-2.71(m, 3H), 2.26(s, 3H), 2.00-2.34(m, 2H), 1.67-1.78(m, 1H), 1.20-1.35(m, 1H), 1.17(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.3, 147.5, 136.6, 134.1, 129.9, 128.3, 119.4, 92.9, 68.2, 52.6, 34.8, 32.0, 31.6, 29.0, 28.2. HRMS Calculated for $C_{17}H_{20}ClNO_4Na$ $[M+Na]^+$: 360.09786, Found: 360.09710.



7l-minor

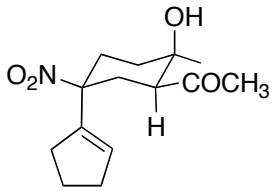
1-((1S*,2R*,5S*)-5-(1-(4-chlorophenyl)vinyl)-2-hydroxy-2-methyl-5-nitrocyclohexyl) ethanone (**7l-minor**). **7l-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 18%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.36(d, *J* = 8.4 Hz, 2H), 7.14(d, *J* = 8.4 Hz, 2H), 5.93(s, 1H), 5.72(s, 1H), 3.86(d, *J* = 2.5 Hz, 1H), 2.30-2.55(m, 5H), 1.88(s, 3H), 1.75(dt, *J* = 14.3 Hz, *J* = 3.5 Hz, 1H), 1.31-46(m, 1H), 1.18(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 212.7, 143.1, 137.3, 134.4, 129.5, 128.7,

124.6, 90.7, 68.5, 52.8, 35.8, 31.0, 30.3, 29.3, 28.0. HRMS Calculated for $C_{17}H_{20}ClNO_4Na$ $[M+Na]^+$: 360.09786, Found: 360.09715.



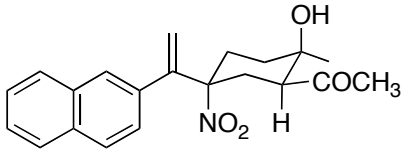
7m-major

1-((1S*,2R*,5R*)-5-cyclopentenyl-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7m-major**). **7m-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 61%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.73-5.79(m, 1H), 3.82(d, *J* = 2.7 Hz, 1H), 2.44-2.72(m, 3H), 1.95-2.36(m, 9H), 1.72-1.87(m, 2H), 1.62(dq, *J* = 14.6 Hz, *J* = 2.7 Hz, 1H), 1.09-1.25(m, 1H), 1.10(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.2, 142.1, 129.6, 91.1, 68.4, 52.5, 34.7, 32.3, 31.4, 31.2, 31.0, 28.2, 28.1, 22.7. HRMS Calculated for $C_{14}H_{21}NO_4Na$ $[M+Na]^+$: 290.13683, Found: 290.13612.



7m-minor

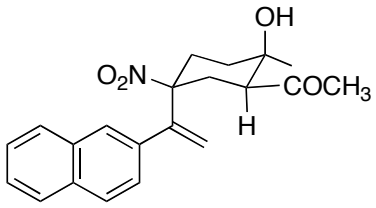
1-((1S*,2R*,5S*)-5-cyclopentenyl-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7m-minor**). **7m-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 5/1) as colorless oil, yield: 15%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.77-5.85(m, 1H), 2.57-2.89(m, 3H), 1.95-2.35(m, H), 1.71-1.89(m, 2H), 1.61(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 1.01-1.27(m, 1H), 1.12(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 210.7, 142.1, 130.1, 90.9, 71.2, 55.3, 38.3, 32.6, 32.5, 32.2, 31.2, 30.7, 22.8, 21.4. HRMS Calculated for $C_{14}H_{21}NO_4Na$ $[M+Na]^+$: 290.13683, Found: 290.13616.



7n-major

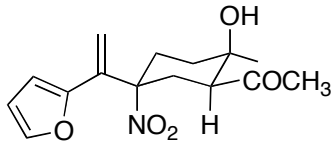
1-((1S*,2R*,5R*)-2-hydroxy-2-methyl-5-(1-(naphthalen-2-yl)vinyl)-5-nitrocyclohex-yl) ethanone (**7n-major**). **7n-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as white solid, m.p: 133.9-134.8 ℃, yield: 64%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77-7.85(m, 3H), 7.48-7.56(m, 3H), 7.21(d, *J* = 8.4 Hz, 1H), 5.72(s, 1H), 5.37(s, 1H), 3.81(br, 1H), 2.60-2.71(m, 3H), 2.36(td, *J* = 13.8 Hz, *J* = 4.2 Hz, 1H), 2.23(s, 3H), 2.19(t, *J* = 13.8 Hz, 1H), 1.73(dt, *J* = 14.4 Hz, *J* = 3.6 Hz, 1H), 1.31(td,

J = 13.8 Hz, J = 3.6 Hz, 1H), 1.17(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 214.3, 148.7, 135.9, 132.8, 132.7, 128.0, 127.73, 127.65, 127.5, 126.43, 126.38, 126.3, 119.1, 93.2, 68.3, 52.7, 34.9, 32.3, 31.5, 29.2, 28.2. HRMS Calculated for $C_{21}H_{23}NO_4Na$ $[M+Na]^+$: 376.15193, Found: 376.15208.



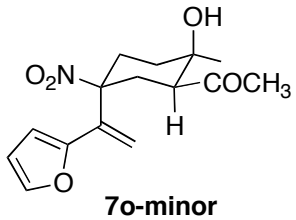
7n-minor

1-((1S*,2R*,5S*)-2-hydroxy-2-methyl-5-(1-(naphthalen-2-yl)vinyl)-5-nitrocyclohexyl)ethanone (**7n-minor**). **7n-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 10/1) as colorless oil, yield: 18%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81-7.86(m, 3H), 7.67(s, 1H), 7.50-7.54(m, 2H), 7.30(dd, J = 6.4 Hz, J = 1.8 Hz, 1H), 6.00(s, 1H), 5.82(s, 1H), 3.82(br, 1H), 2.40-2.61(m, 5H), 1.76(dt, J = 14.4 Hz, J = 3.6 Hz, 1H), 1.69(s, 3H), 1.49(td, J = 13.8 Hz, J = 4.2 Hz, 1H), 1.19(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.9, 144.2, 136.4, 133.0, 132.8, 128.2, 127.9, 127.6, 127.3, 126.8, 126.6, 125.9, 124.4, 91.0, 68.5, 52.9, 35.9, 31.2, 30.1, 29.6, 28.1. HRMS Calculated for $C_{21}H_{23}NO_4Na$ $[M+Na]^+$: 376.15193, Found: 376.15207.



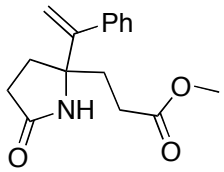
7o-major

1-((1S*,2R*,5R*)-5-(1-(furan-2-yl)vinyl)-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7o-major**). **7o-major** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 8/1) as light-yellow solid, m. p: > 70 ℃ decomp, yield: 56%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.29-7.38(m, 1H), 6.29-6.43(m, 2H), 5.77(s, 1H), 5.43(s, 1H), 3.91(d, J = 2.5 Hz, 1H), 2.81-2.91(m, 1H), 2.73(td, J = 2.7 Hz, J = 14.4 Hz, 1H), 2.41-2.58(m, 2H), 2.19-2.31(m 4H), 1.73(td, J = 3.8 Hz, J = 14.4 Hz, 1H), 1.34-1.68(m, 1H), 1.98(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 214.5, 150.3, 142.65, 142.56, 138.0, 115.6, 111.3, 108.7, 92.3, 68.7, 52.7, 34.8, 32.4, 31.7, 29.2, 28.5. HRMS Calculated for $C_{15}H_{19}NO_5Na$ $[M+Na]^+$: 316.11609, Found: 316.11538.



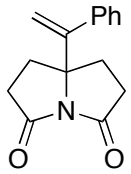
7o-minor

1-((1S*,2R*,5S*)-5-(1-(furan-2-yl)vinyl)-2-hydroxy-2-methyl-5-nitrocyclohexyl)ethanone (**7o-minor**). **7o-minor** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 8/1) as light-yellow oil, yield: 20%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.41(s, 1H), 6.40(d, *J* = 9.7 Hz, 2H), 6.11(s, 1H), 5.8(s, 1H), 3.88(d, *J* = 2.2 Hz, 1H), 2.40-2.76(m, 5H), 2.03(s, 3H), 1.80(td, *J* = 14.1 Hz, *J* = 3.5 Hz, 1H), 1.41-1.56(m, 1H), 1.19(s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 213.0, 150.8, 142.6, 142.5, 133.6, 121.8, 111.1, 109.0, 90.6, 68.7, 53.2, 36.1, 30.9, 30.5, 29.3, 28.0. HRMS Calculated for $C_{15}H_{19}NO_5Na$ $[M+Na]^+$: 316.11609, Found: 316.11537.



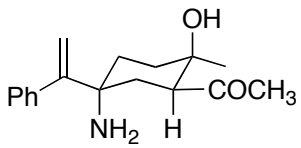
8a

Methyl 3-(5-oxo-2-(1-phenylvinyl)pyrrolidin-2-yl)propanoate (**8a**). **8a** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 3/1) as white solid, yield: 91%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46(s, 1H), 7.29-7.34(m, 3H), 7.21-7.23(m, 2H), 5.38(s, 1H), 5.16(m, 1H), 3.63(s, 3H), 2.31-2.44(m, 5H), 2.07-2.14(m, 2H), 1.93-1.99(m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.6, 173.5, 152.1, 140.2, 128.2, 128.1, 127.6, 1115.4, 65.4, 51.7, 34.1, 33.2, 30.0, 29.1. HRMS Calculated for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.14377, Found: 274.14383.



8b

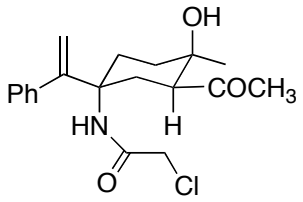
Tetrahydro-7a-(1-phenylvinyl)-6*H*-pyrrolizine-3,5-dione (**8b**). **8b** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 2/1) as white solid, m.p: 141.2-143.0 ℃, yield: 83%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.39(m, 5H), 5.52(s, 1H), 5.40(s, 1H), 2.68-2.76(m, 2H), 2.55-2.61(m, 4H), 2.13-2.18(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 148.0, 138.2, 128.6, 128.2, 127.6, 115.4, 72.0, 34.5, 31.1. HRMS Calculated for $C_{15}H_{15}NO_2Na$ $[M+Na]^+$: 264.09950, Found: 264.09953.



8c

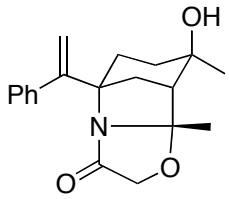
1-((1S*,2R*,5R*)-5-amino-2-hydroxy-2-methyl-5-(1-phenylvinyl)cyclohexyl)ethanone (**8c**). **8c** was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 2/1) as

colorless oil, yiled: 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22-7.29(m, 3H), 7.11-7.14(m, 2H), 5.28(s, 1H), 4.84(s, 1H), 3.86(br, 1H), 3.09(dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H), 2.15(s, 3H), 2.09(td, *J* = 13.2 Hz, *J* = 4.2 Hz, 1H), 1.98(t, *J* = 13.2 Hz, 1H), 1.67(td, *J* = 10.2 Hz, *J* = 4.2 Hz, 1H), 1.44-1.50(m, 2H), 1.28-1.33(m, 1H), 1.17(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 216.4, 159.2, 141.4, 129.0, 127.6, 126.7, 111.9, 69.1, 53.7, 52.3, 35.0, 34.0, 31.4, 31.1, 28.6. HRMS Calculated for $C_{17}H_{24}NO_2$ $[M+H]^+$: 274.18016, Found: 274.18012.



8d

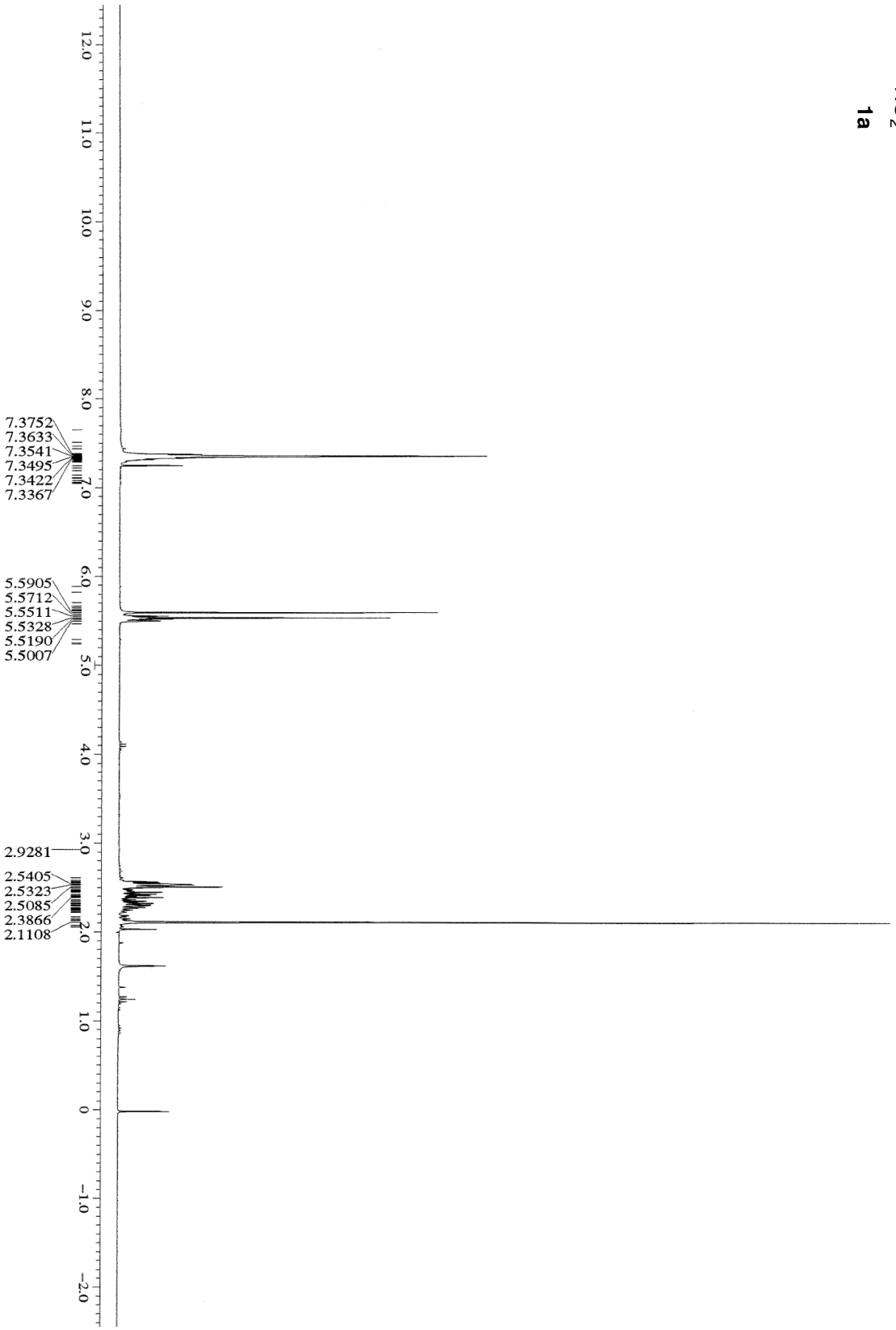
8d was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 1/1) as white solid, m.p: 154.2-155.9 ℃, yield: 91%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24-7.28(m, 3H), 7.08-7.11(m, 2H), 6.24(s, 1H), 5.36(s, 1H), 5.04(s, 1H), 3.95(d, *J* = 2.4 Hz, 1H), 3.94(d, *J* = 15.0 Hz, 1H), 3.87(d, *J* = 15.0 Hz, 1H), 2.90(dt, *J* = 13.2 Hz, *J* = 3.0 Hz, 1H), 2.56(dd, *J* = 13.2 Hz, *J* = 3.0 Hz, 1H), 2.18(s, 3H), 2.09(td, *J* = 13.8 Hz, *J* = 4.2 Hz, 1H), 1.98(t, *J* = 13.8Hz, 1H), 1.71(dq, *J* = 13.8 Hz, *J* = 3.0 Hz, 1H), 1.60(dq, *J* = 14.4 Hz, *J* = 3.0 Hz, 1H), 1.37(tt, *J* = 13.8 Hz, *J* = 3.0 Hz, 1H), 1.18(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 215.2, 165.3, 152.5, 140.6, 128.7, 127.7, 127.1, 114.9, 68.4, 58.9, 52.8, 42.9, 34.4, 32.2, 30.8, 29.8, 28.5. HRMS Calculated for $C_{19}H_{25}ClNO_3$ $[M+H]^+$: 350.15175, Found: 350.15174.

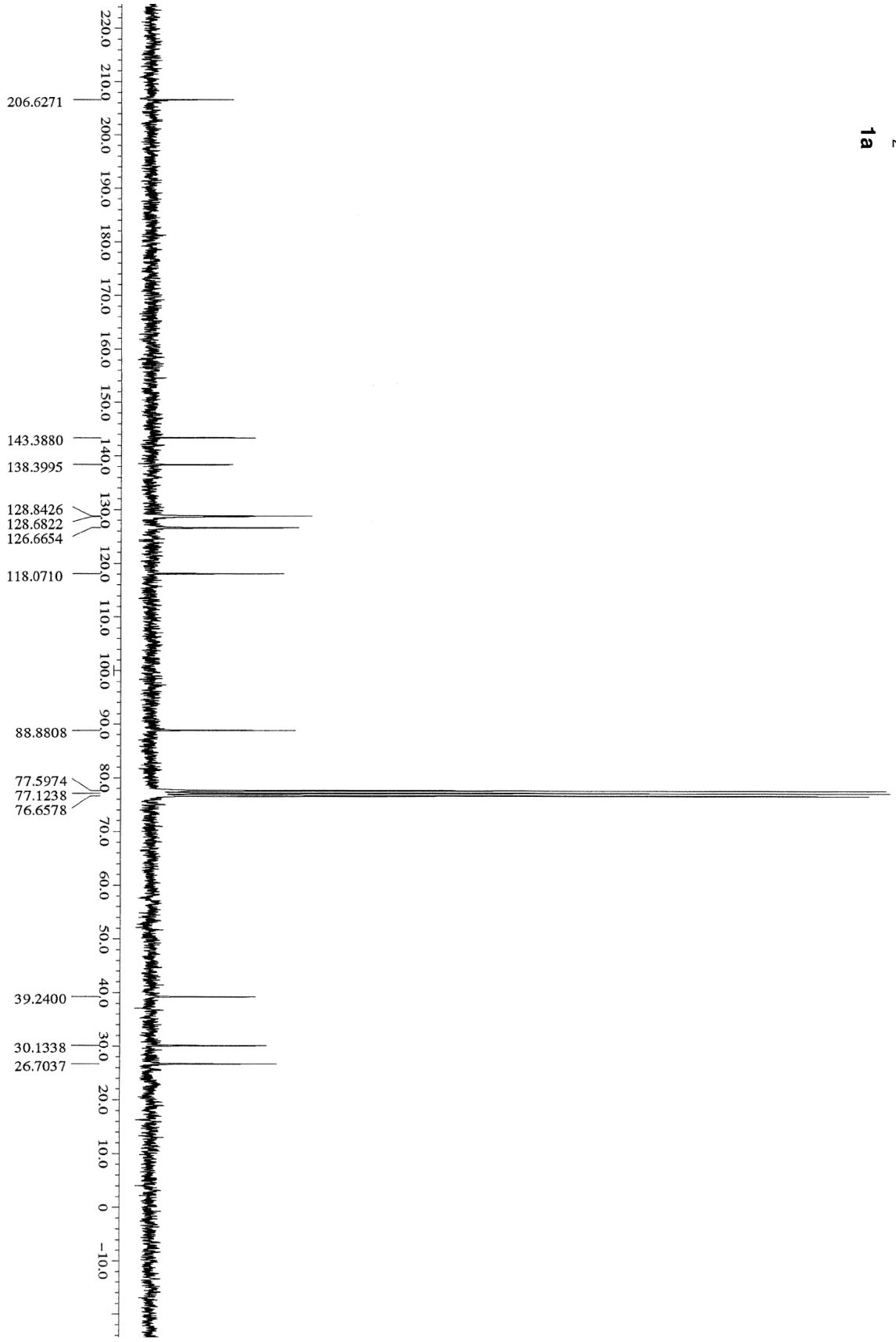


8e

8e was purified by flash silica gel chromatography (Hexane-EtOAc, v/v, 2/1) as colorless oil, yield: 83%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.32(m, 3H), 7.17-7.23(m, 2H), 5.44(s, 1H), 5.10(s, 1H), 4.65(d, *J* = 14.4 Hz, 1H), 4.98(d, *J* = 14.4 Hz, 1H), 4.04(s, 1H), 2.53-2.58(m, 1H), 2.28(ddd, *J* = 13.2 Hz, *J* = 4.8 Hz, *J* = 3.6 Hz, 1H), 1.98(d, *J* = 4.8 Hz, 1H), 1.86-1.94(m, 2H), 1.74-1.81(m, 1H), 1.57-1.64(m, 1H), 1.28(s, 3H), 1.25(s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.2, 150.2, 140.2, 129.1, 127.7, 127.3, 115.1, 106.7, 71.9, 71.4, 67.2, 51.4, 42.8, 35.8, 29.3, 27.3, 25.5. HRMS Calculated for $C_{19}H_{24}NO_3Na$ $[M+H]^+$: 314.17507, Found: 314.17518.

III. NMR spectra data

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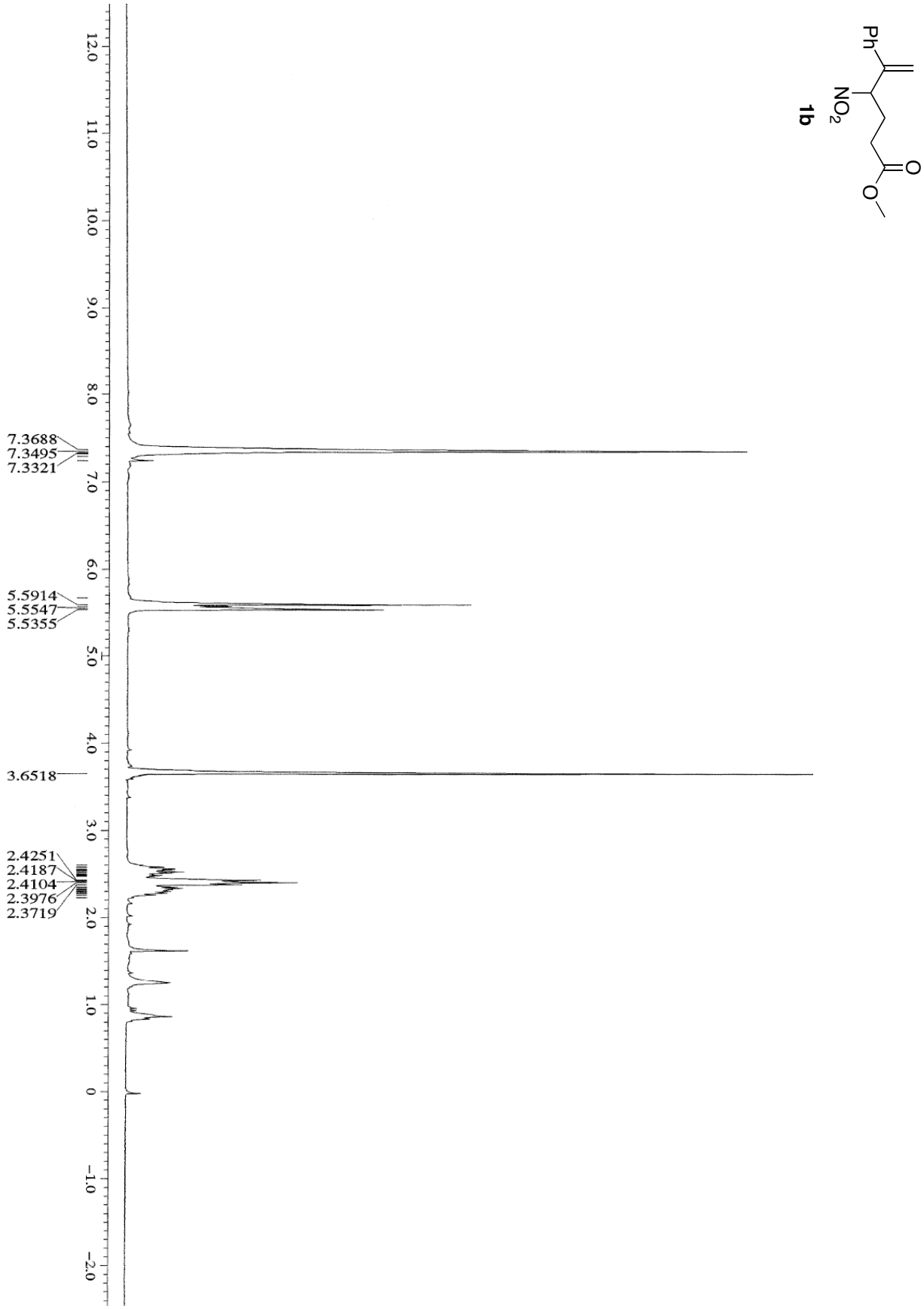
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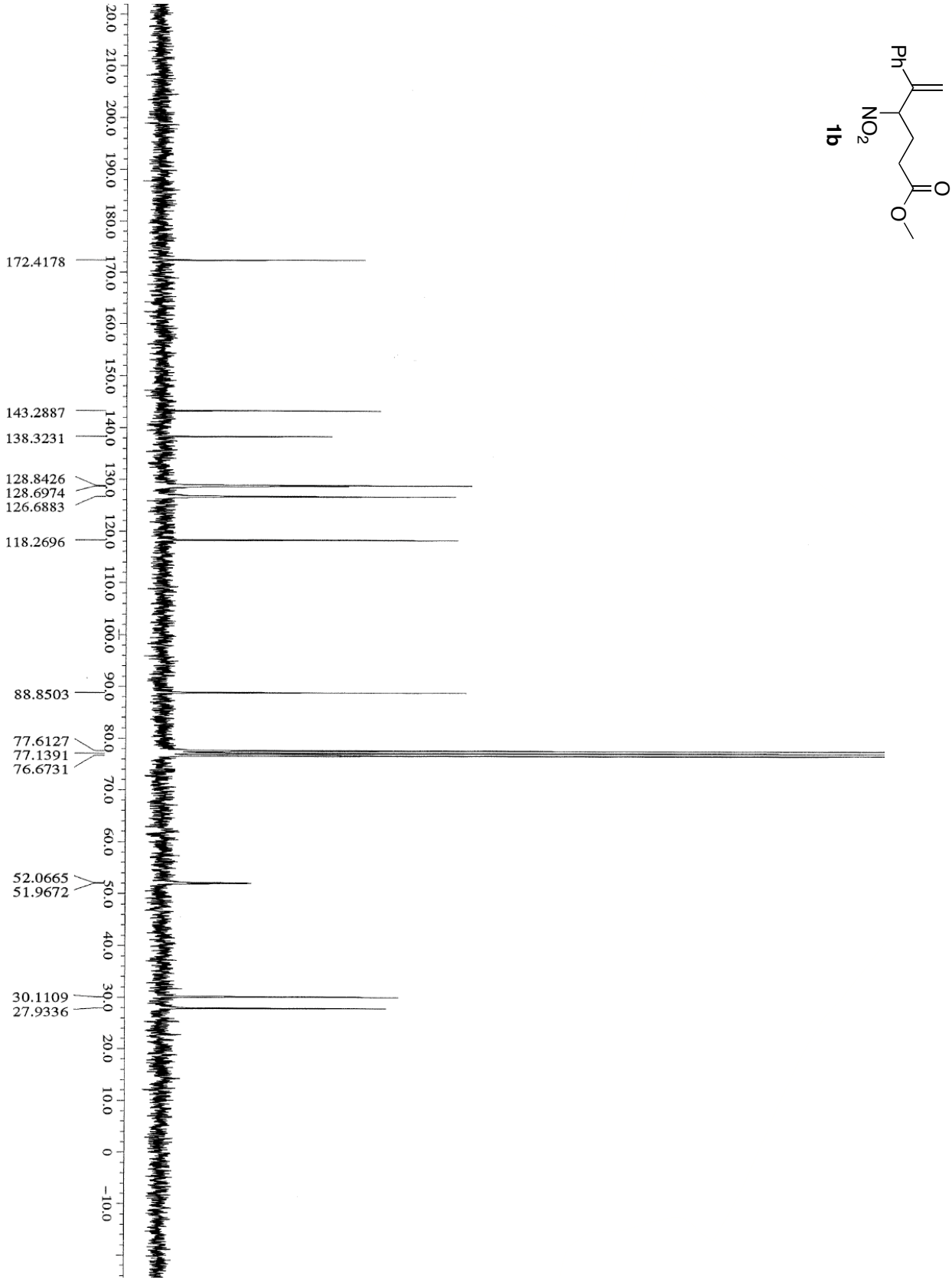
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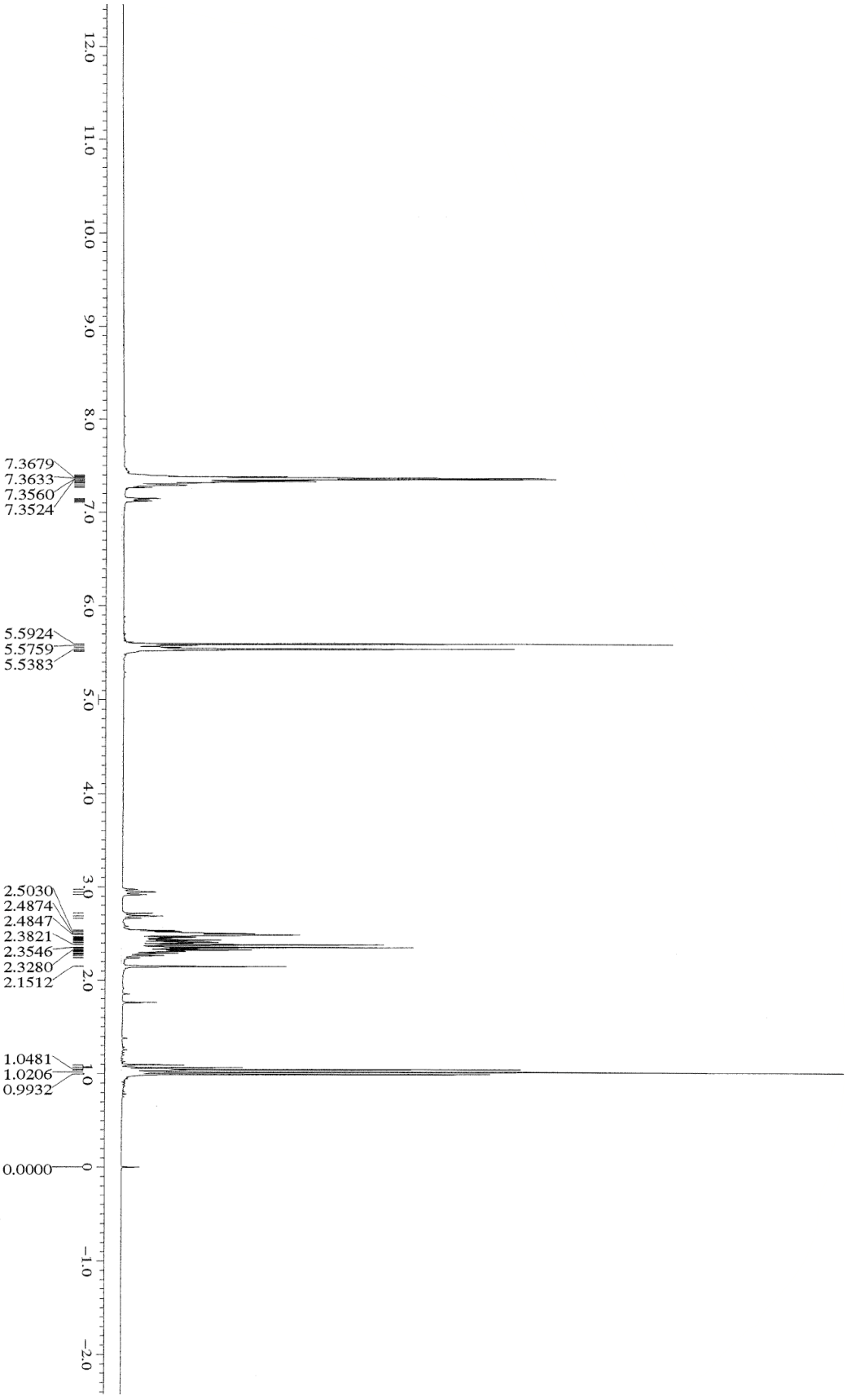
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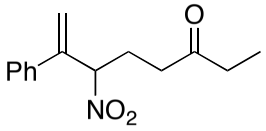

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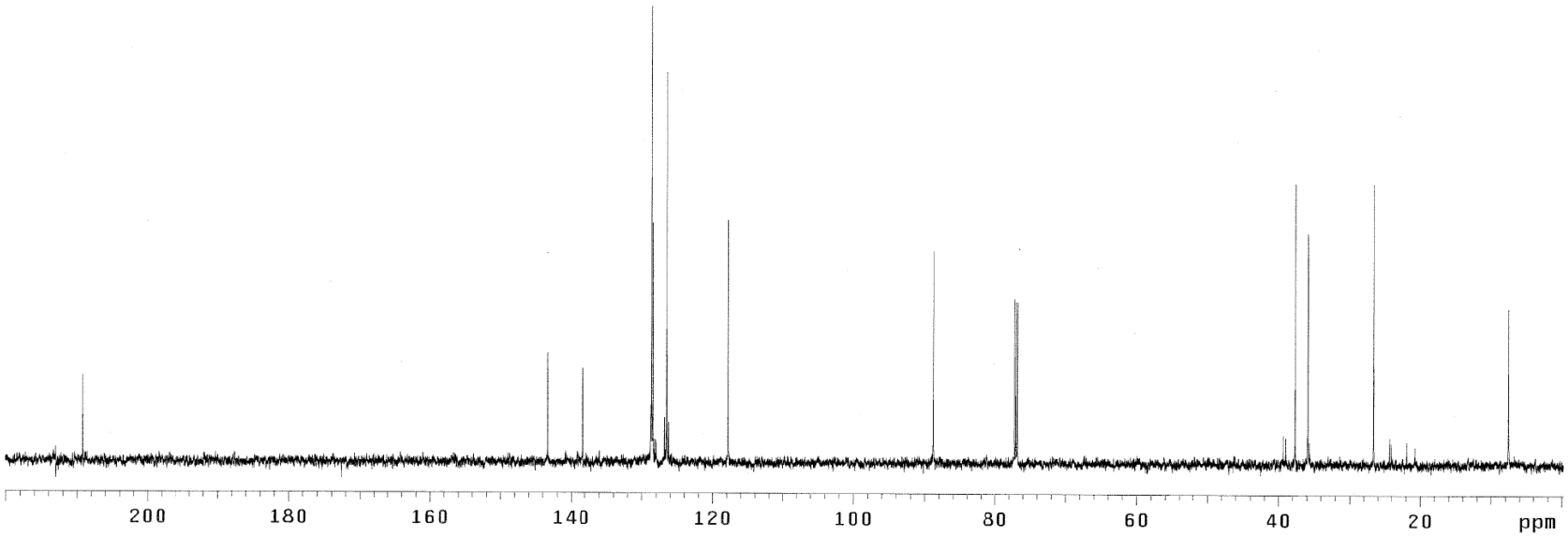

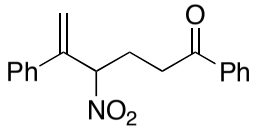

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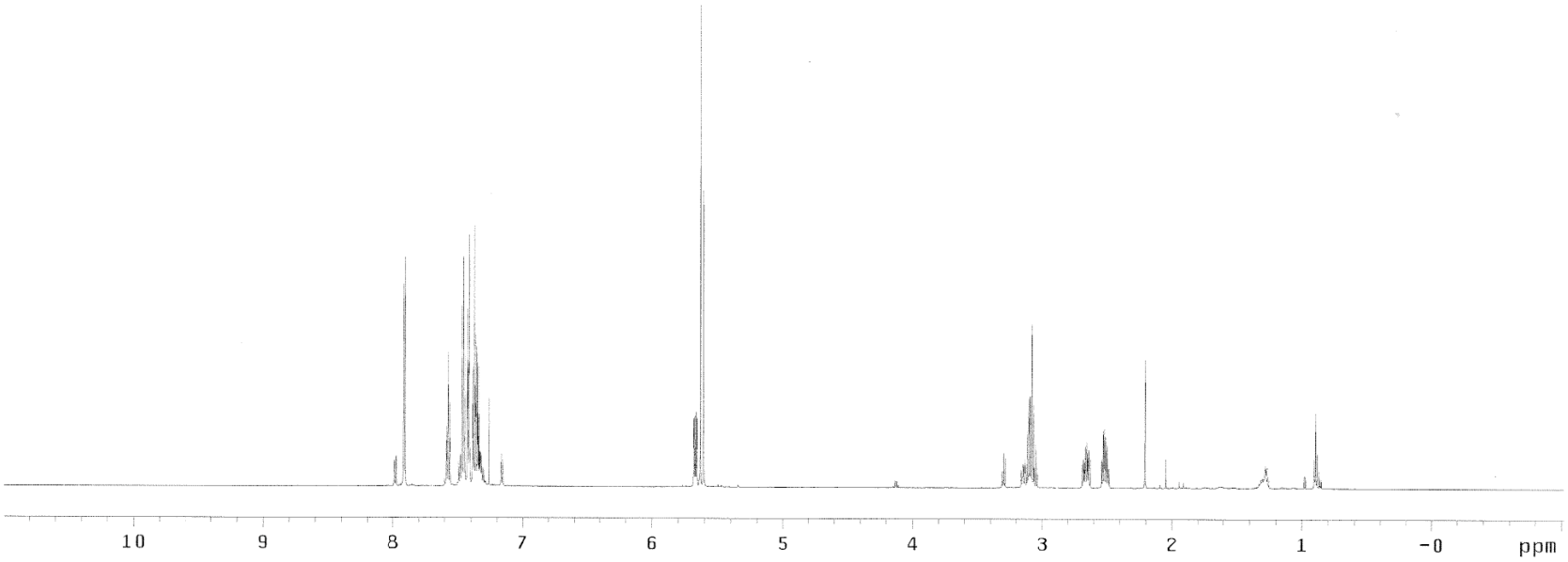

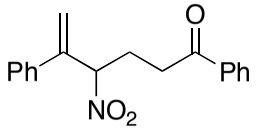

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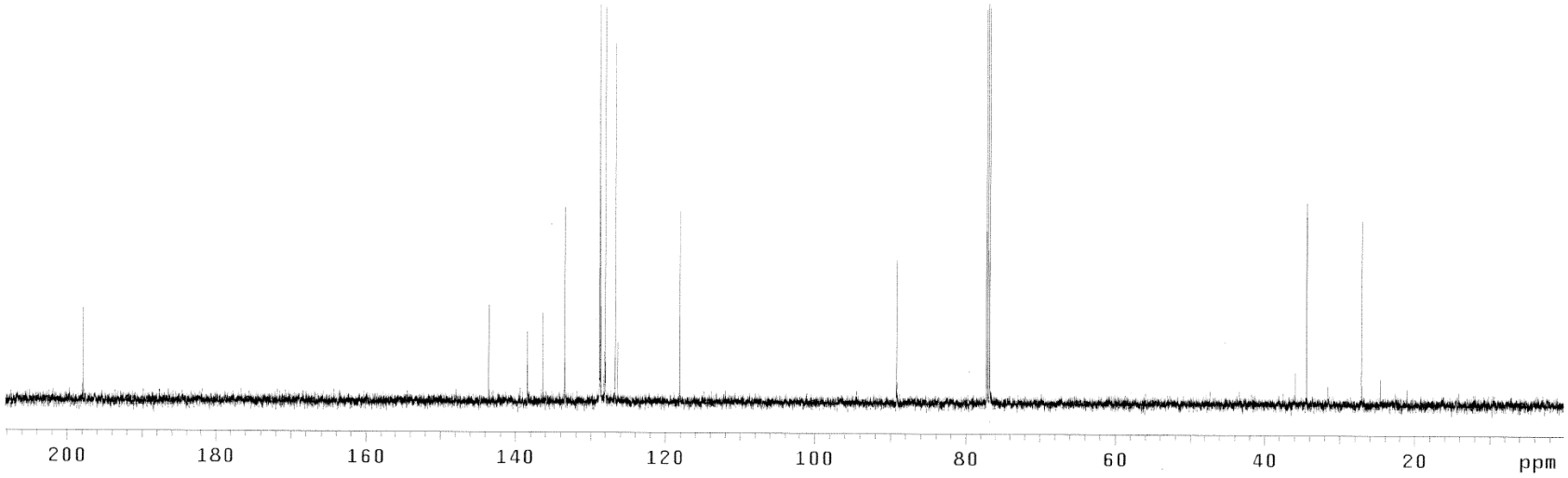

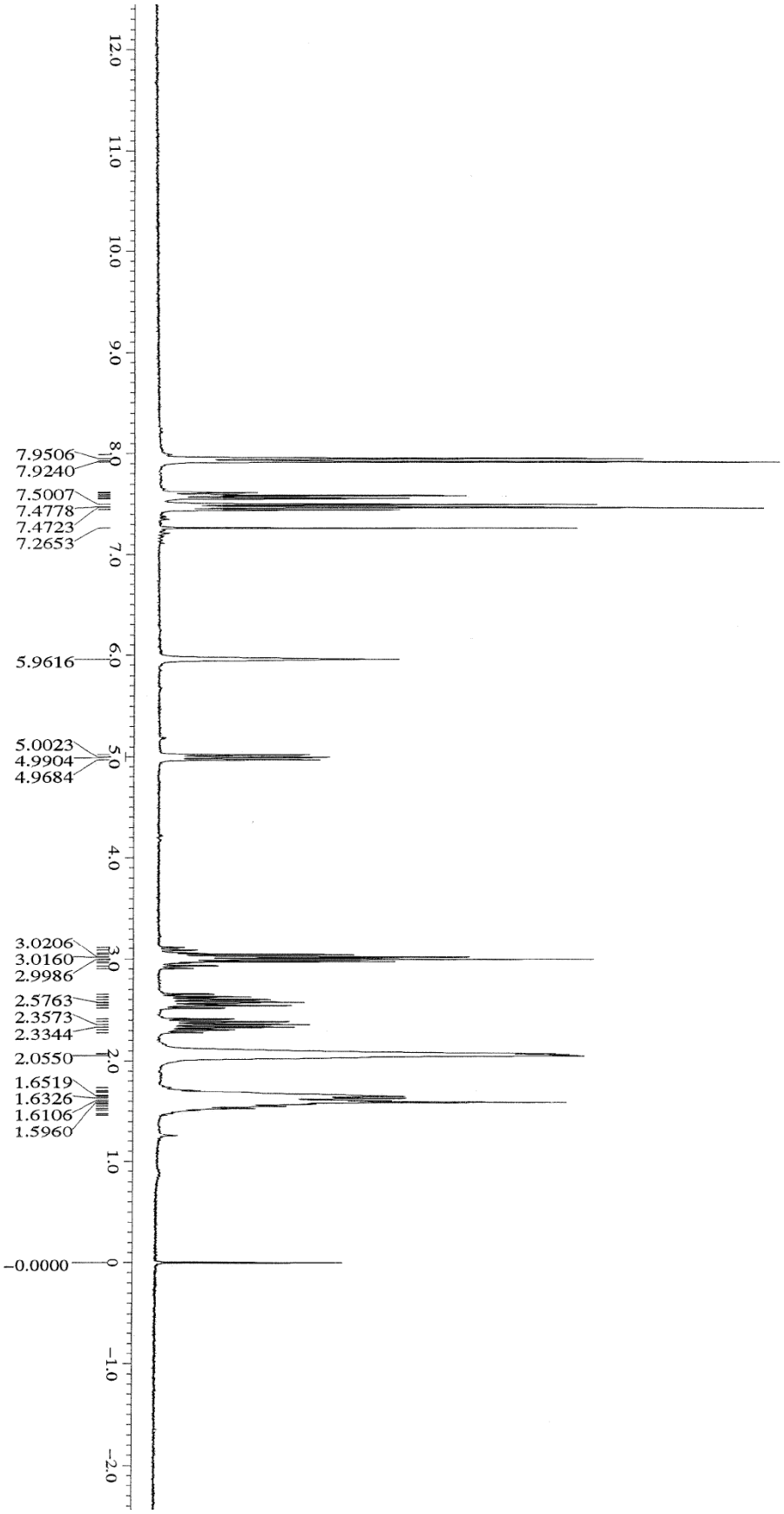
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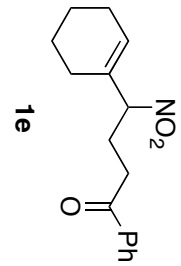
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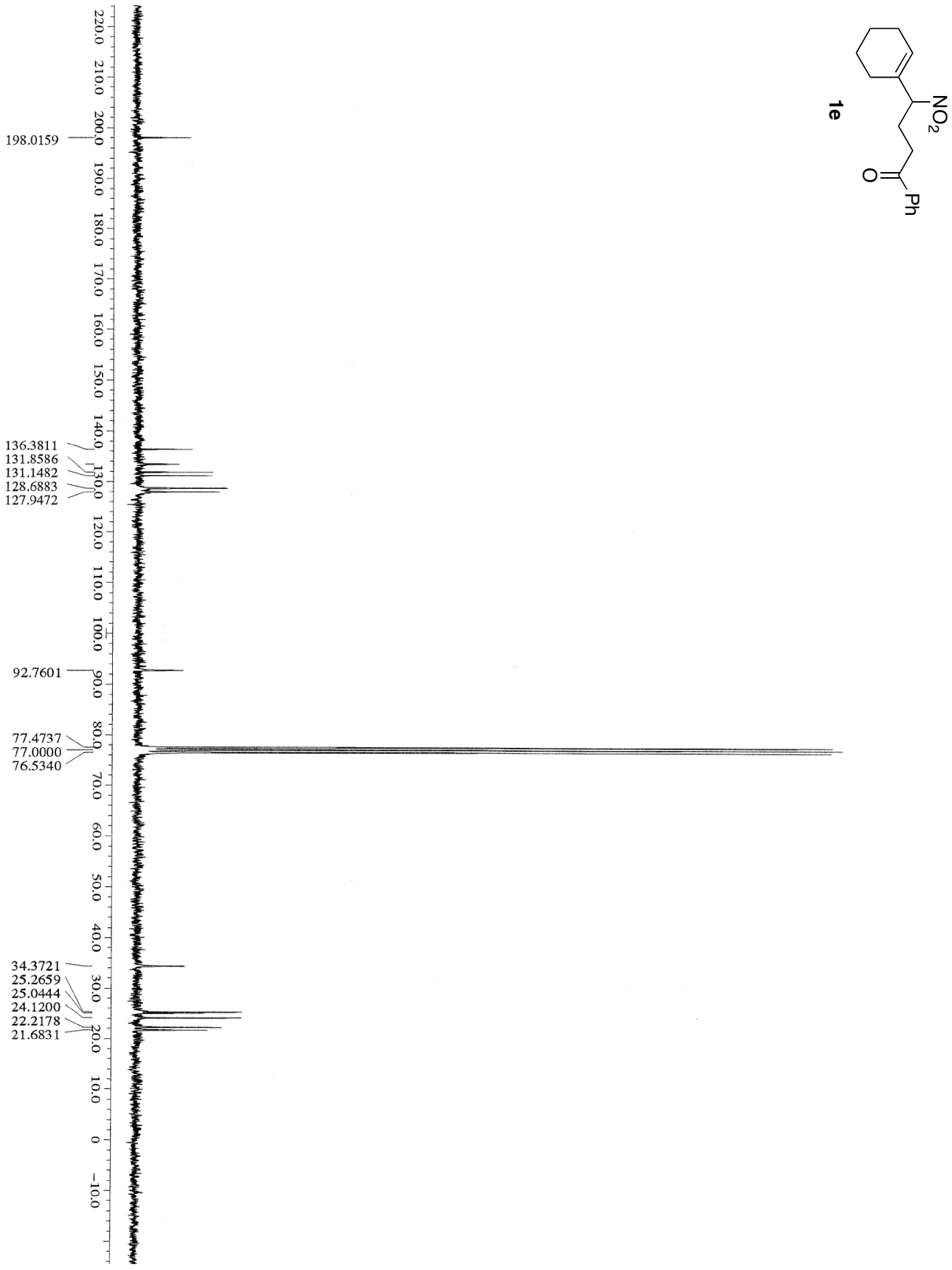
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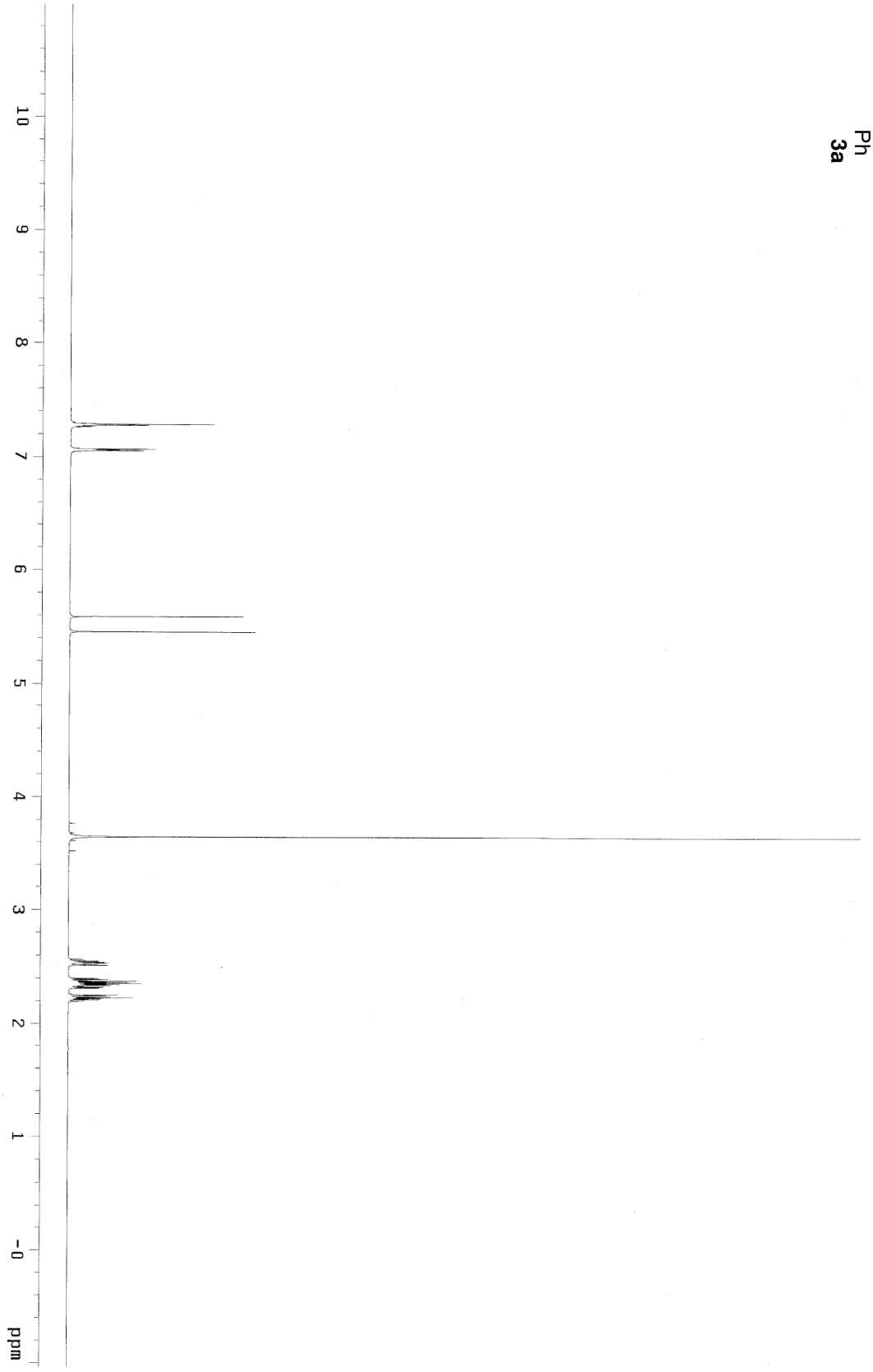
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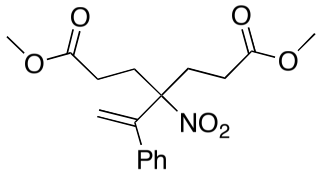

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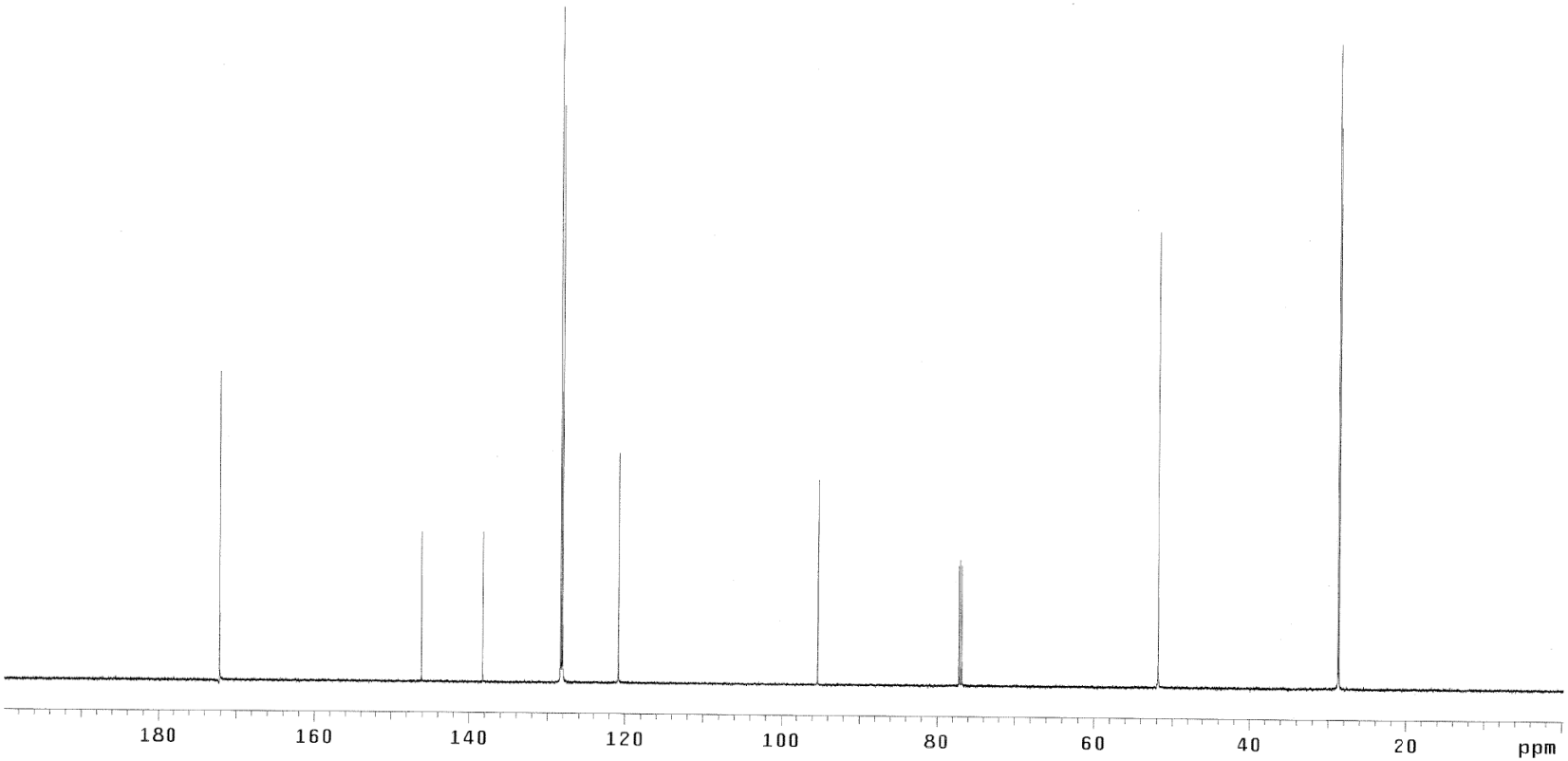

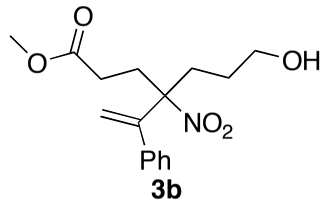

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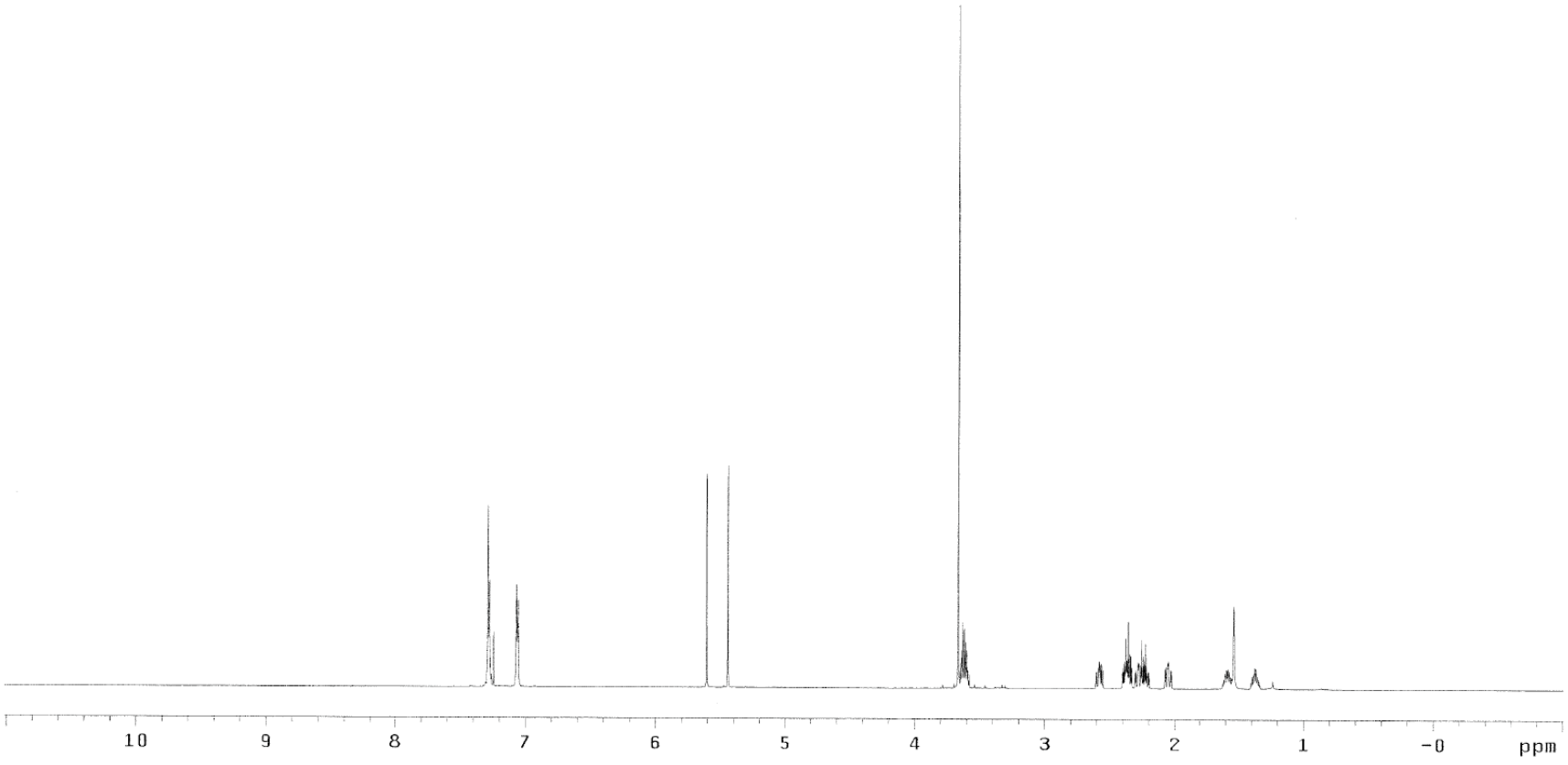

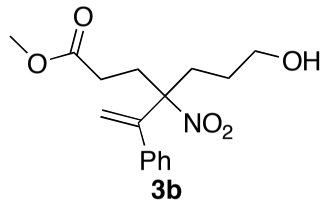

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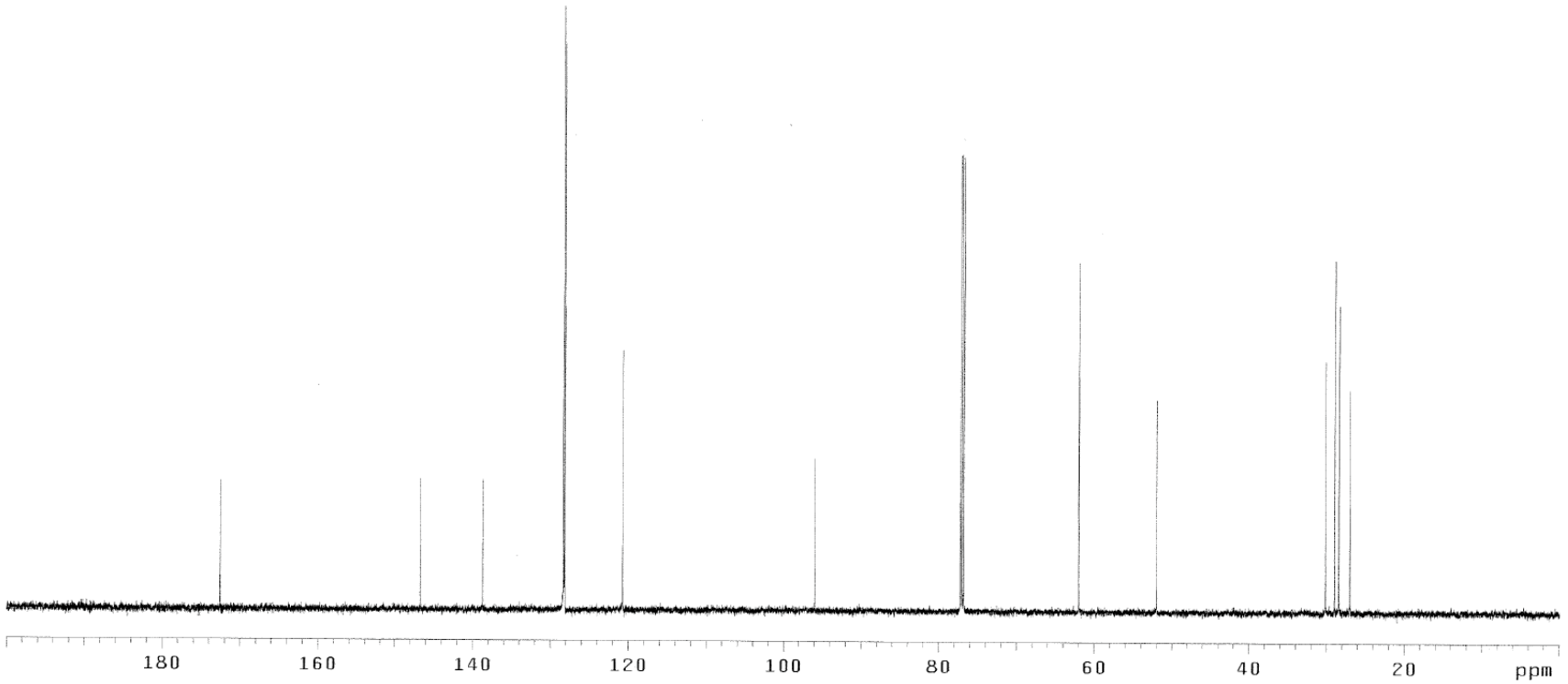

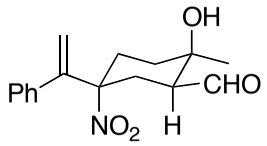

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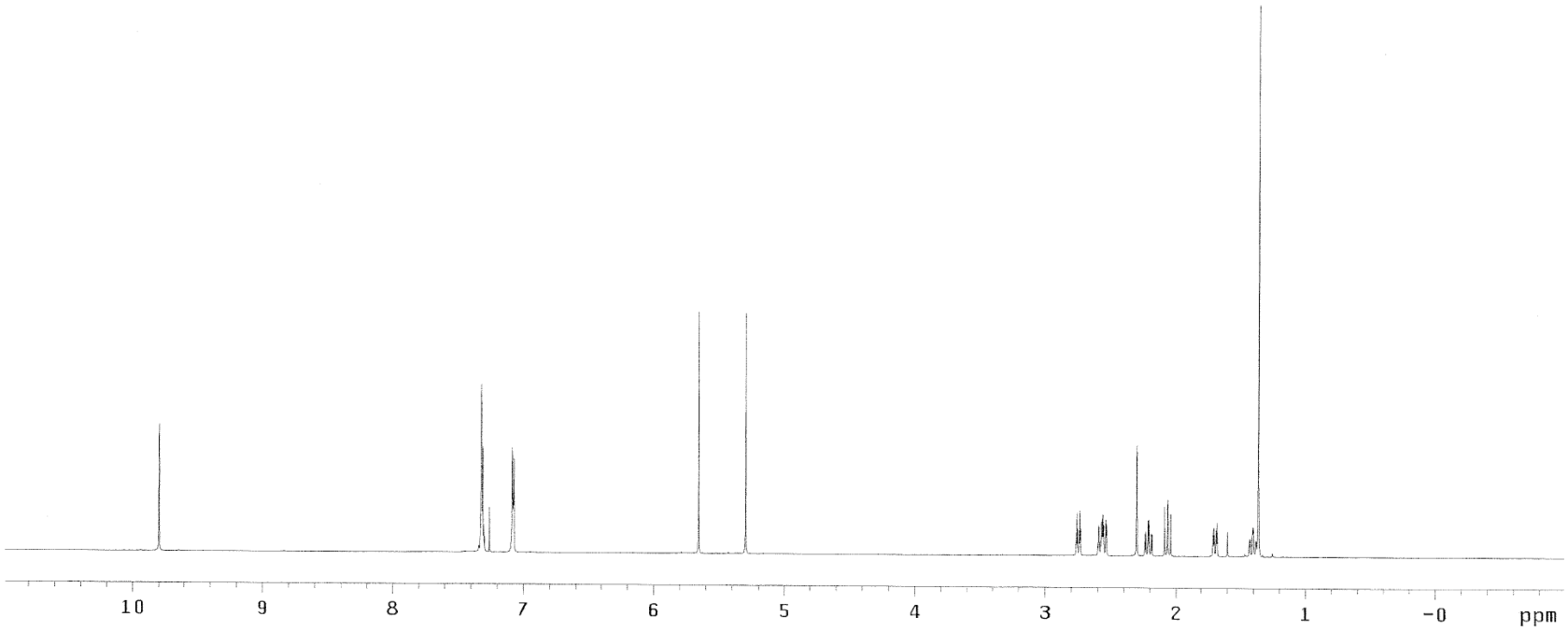

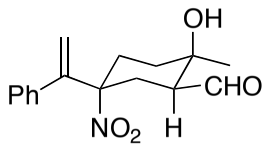

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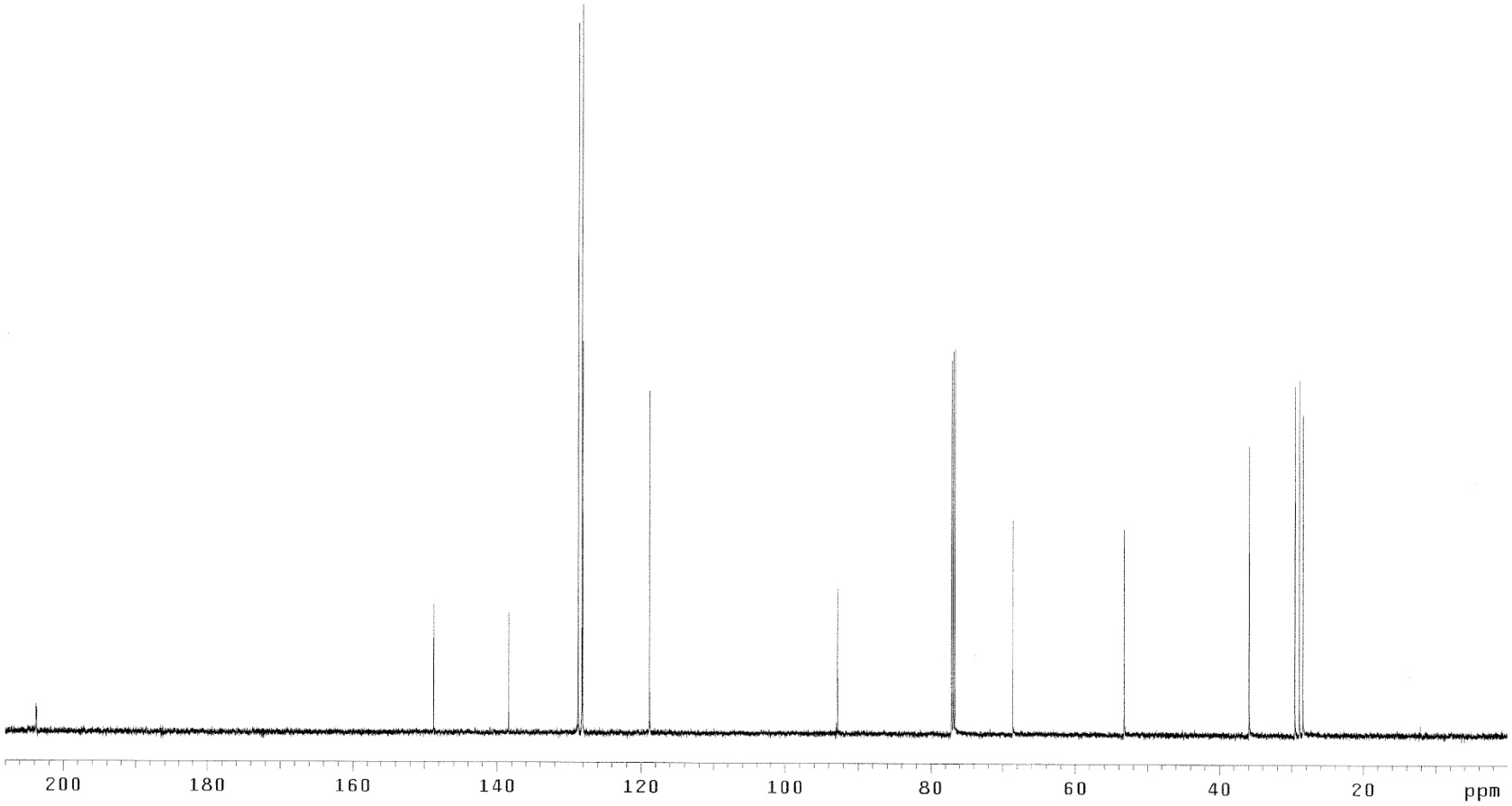

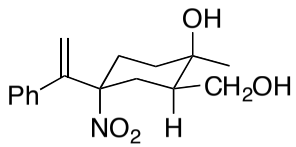

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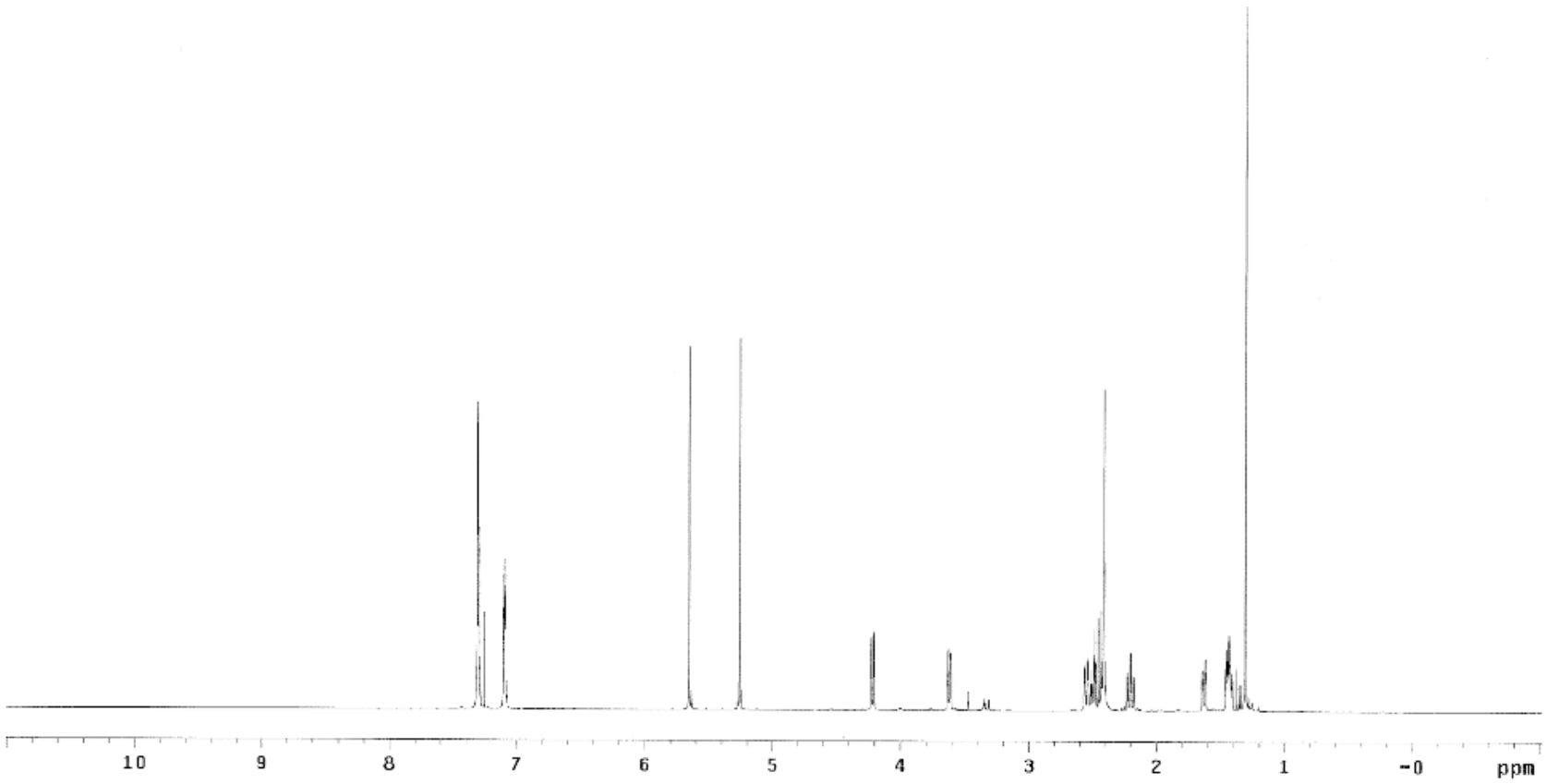

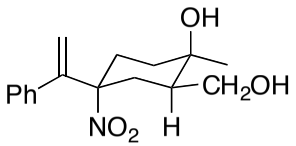

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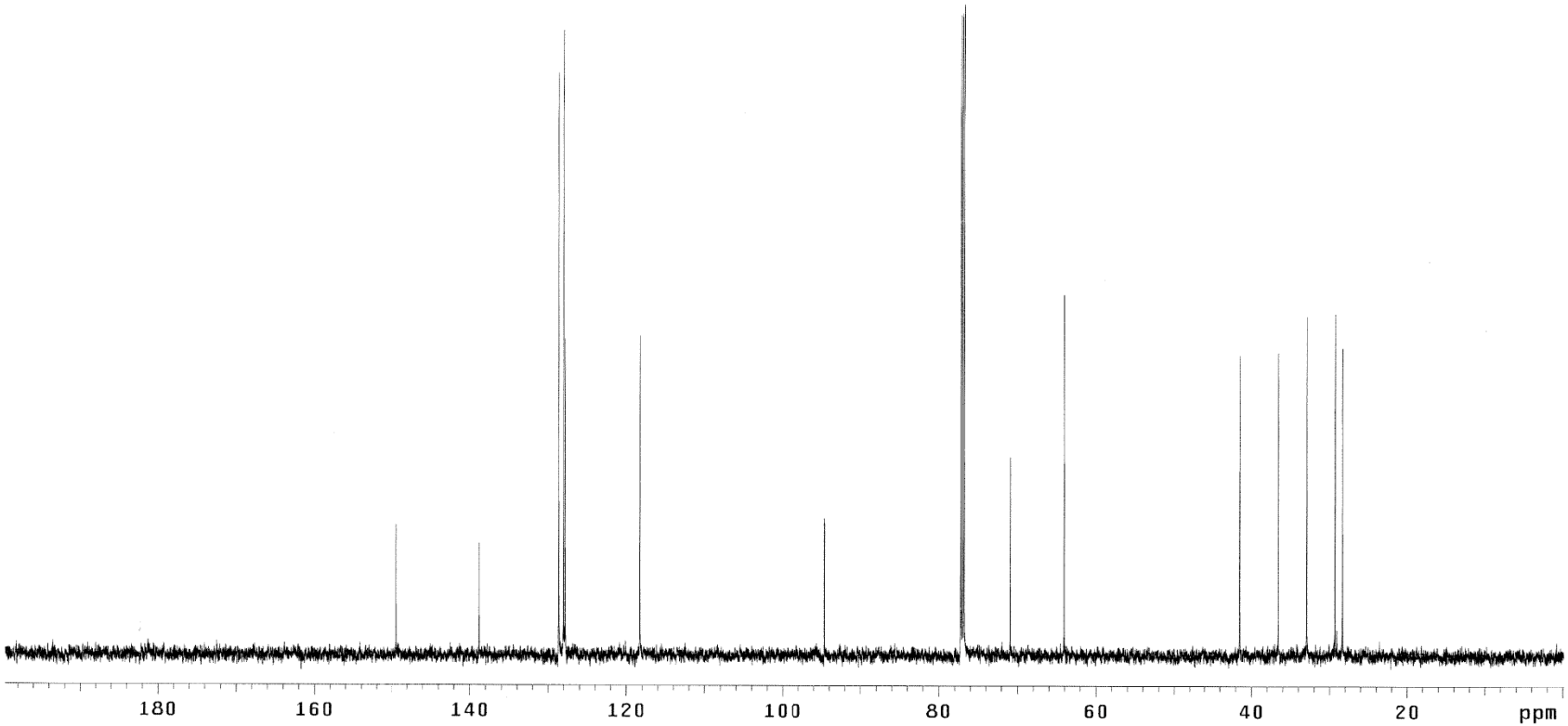

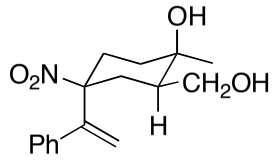

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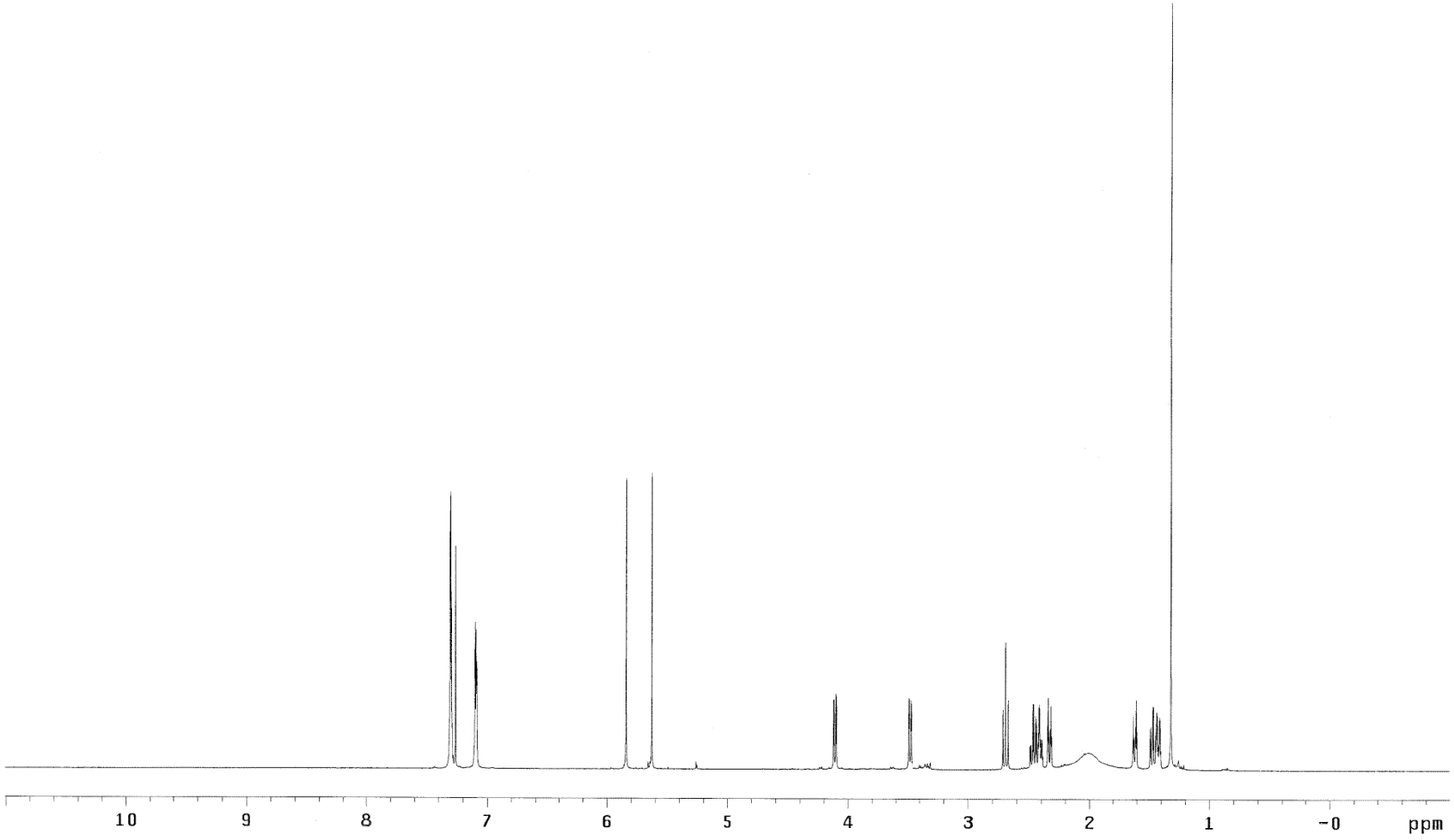

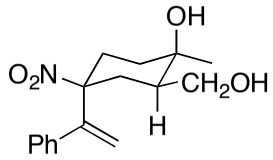

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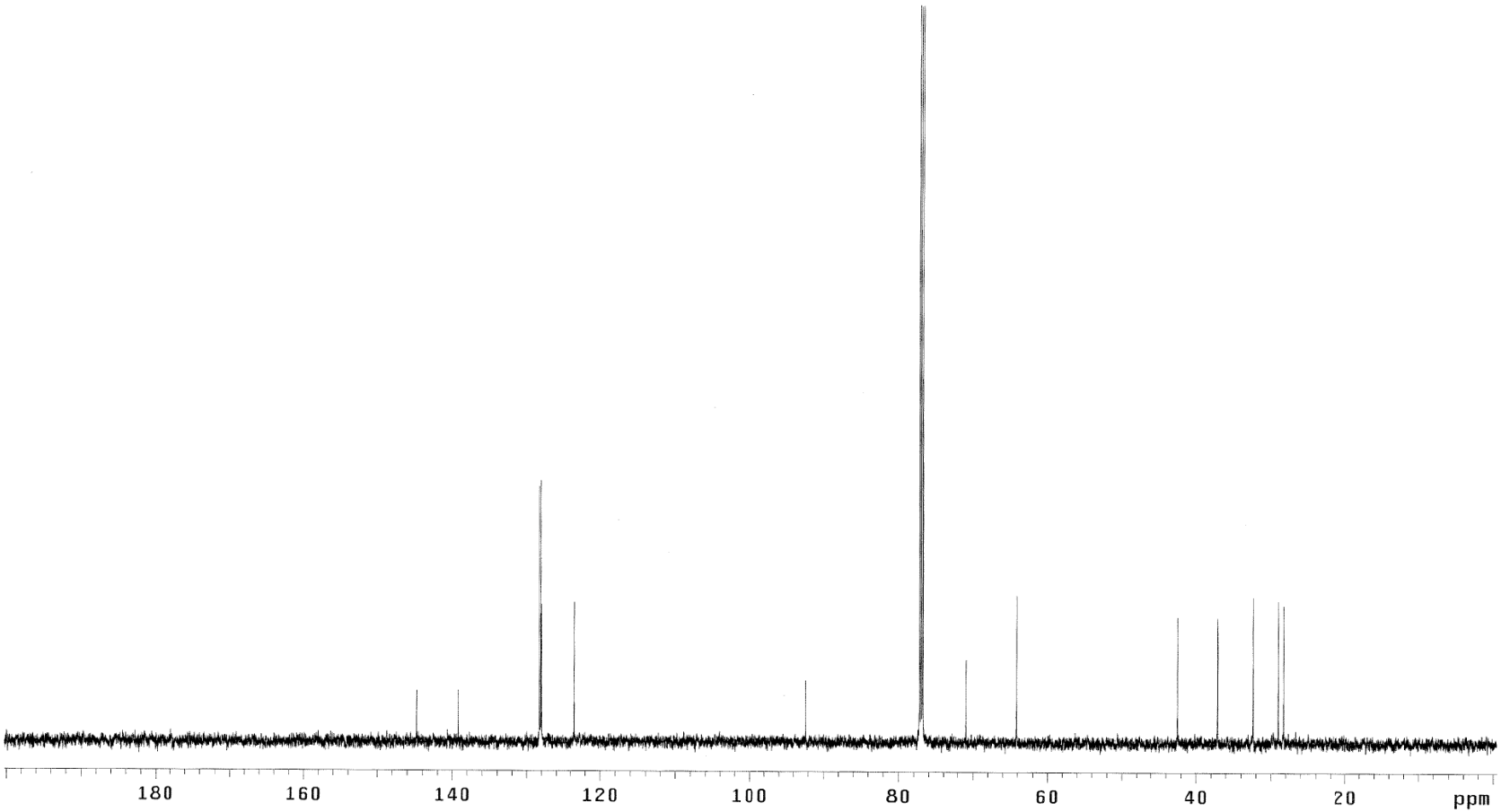

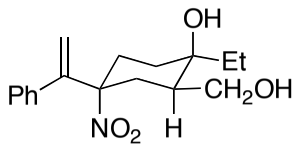

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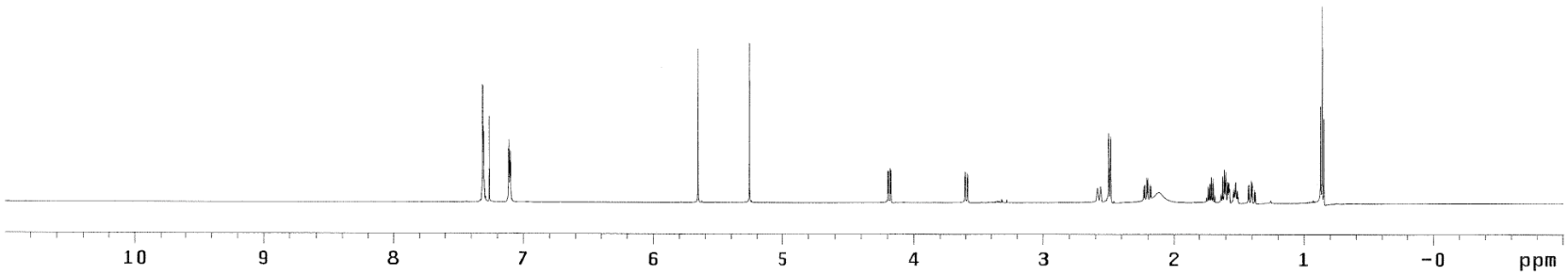

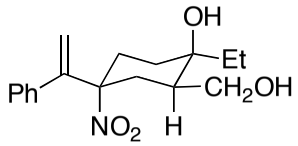

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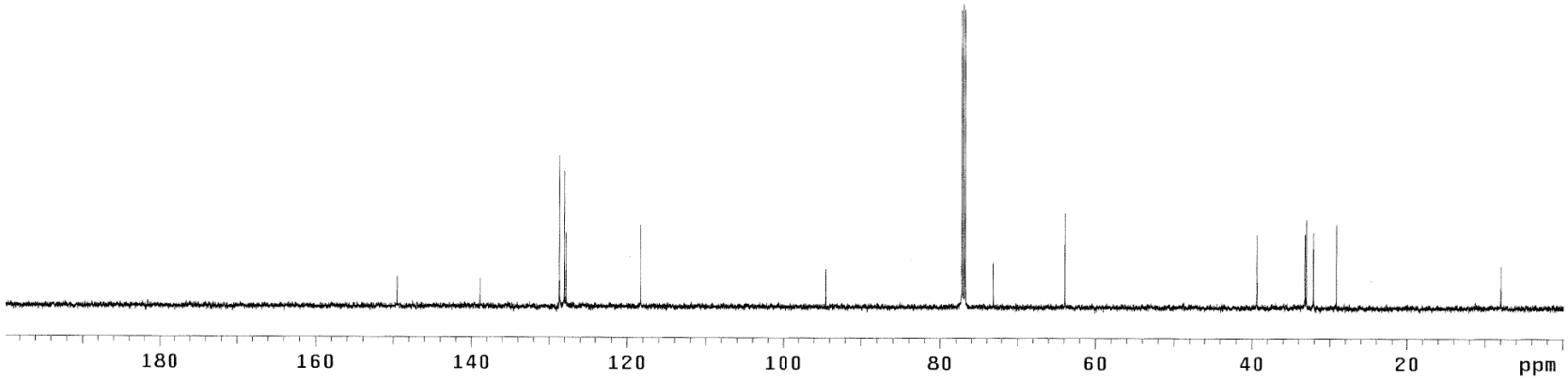

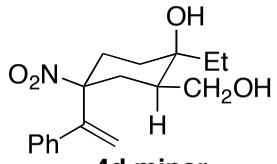

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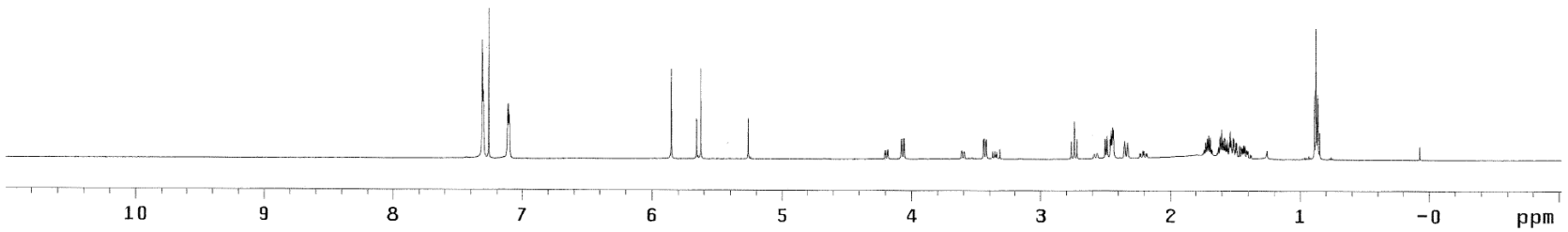

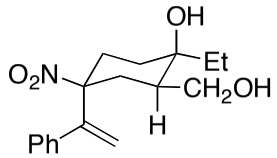

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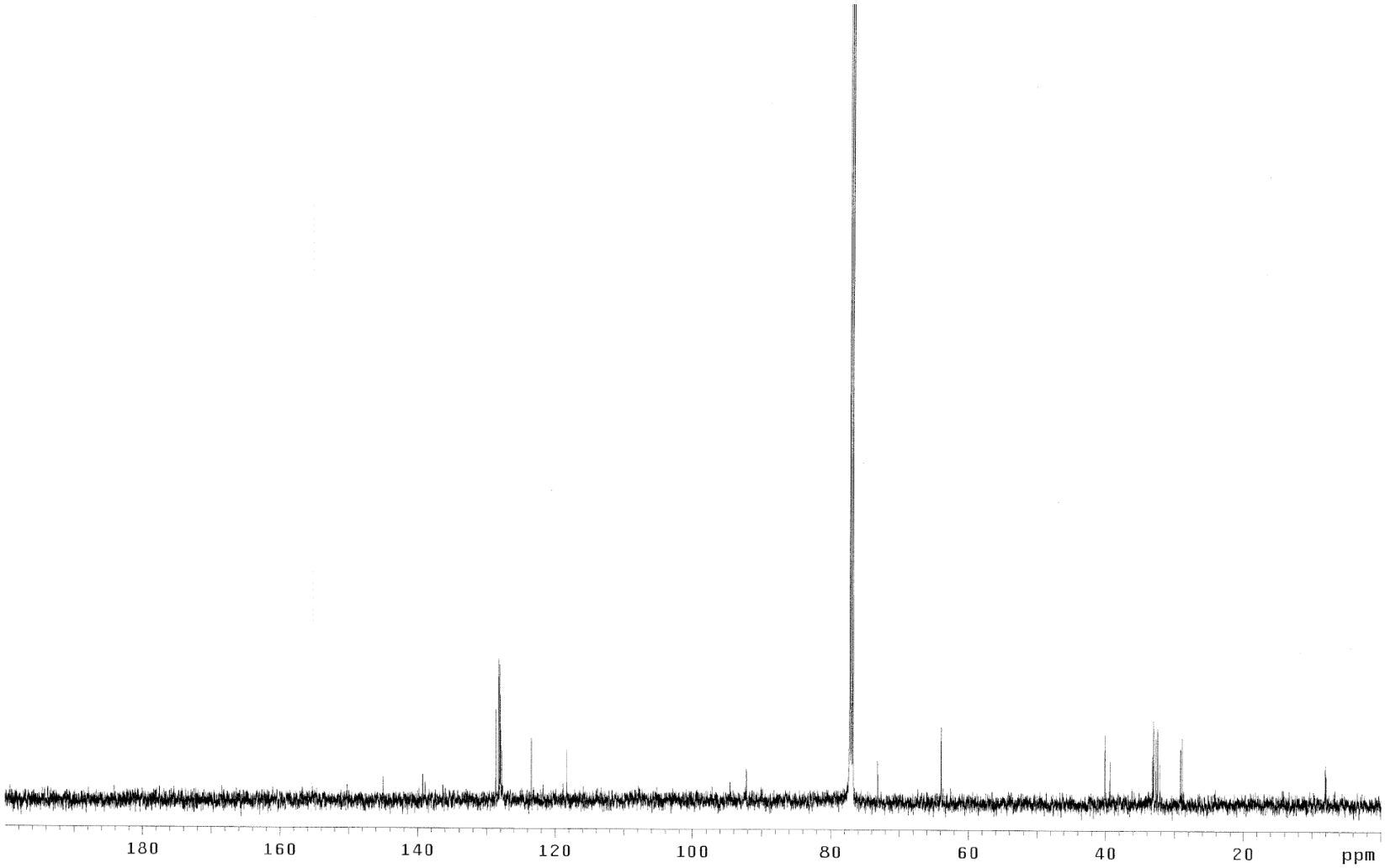

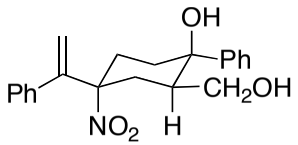

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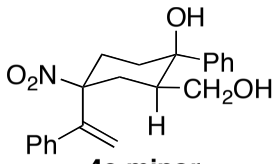

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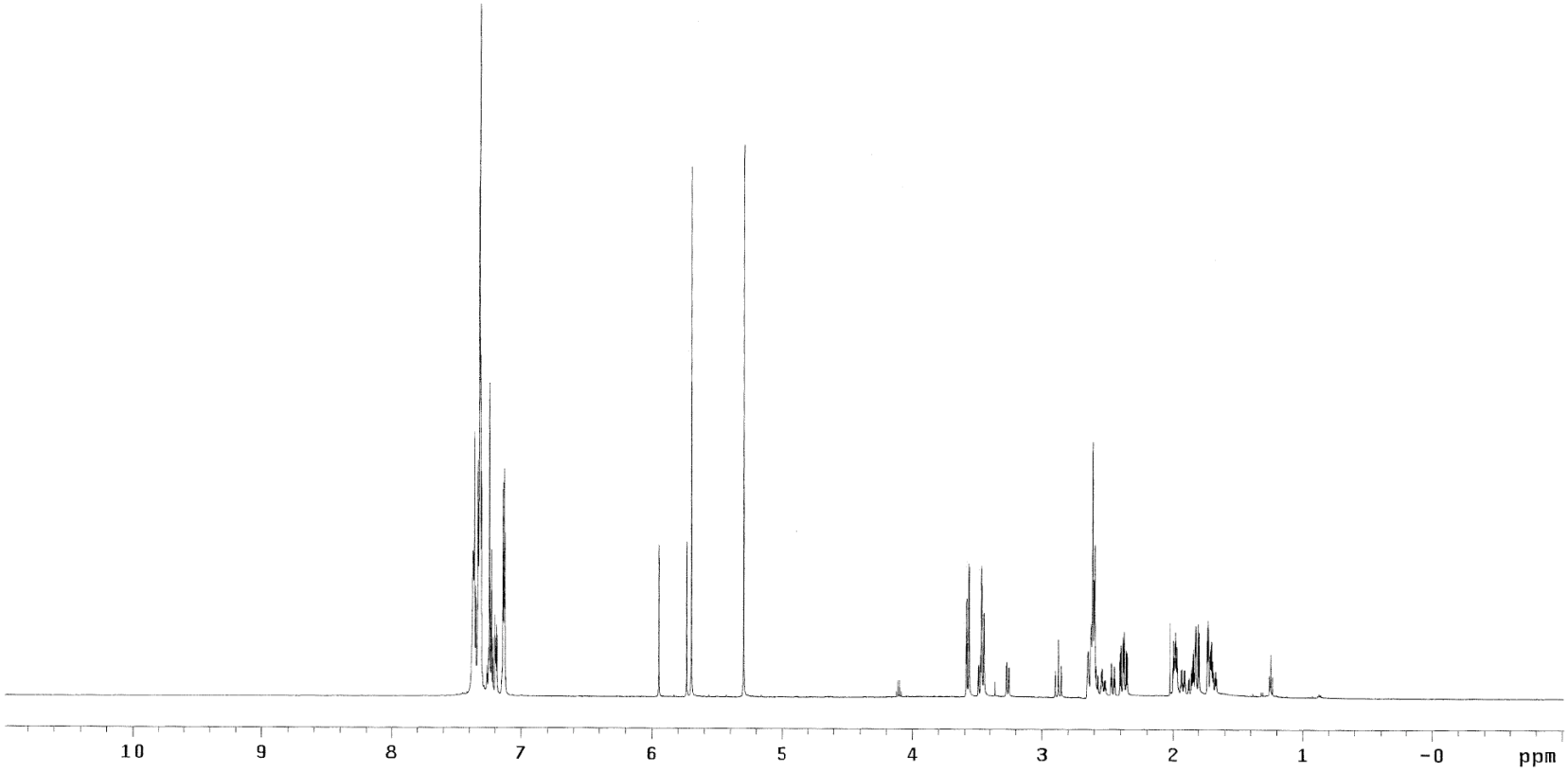

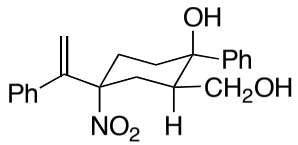

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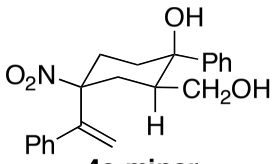

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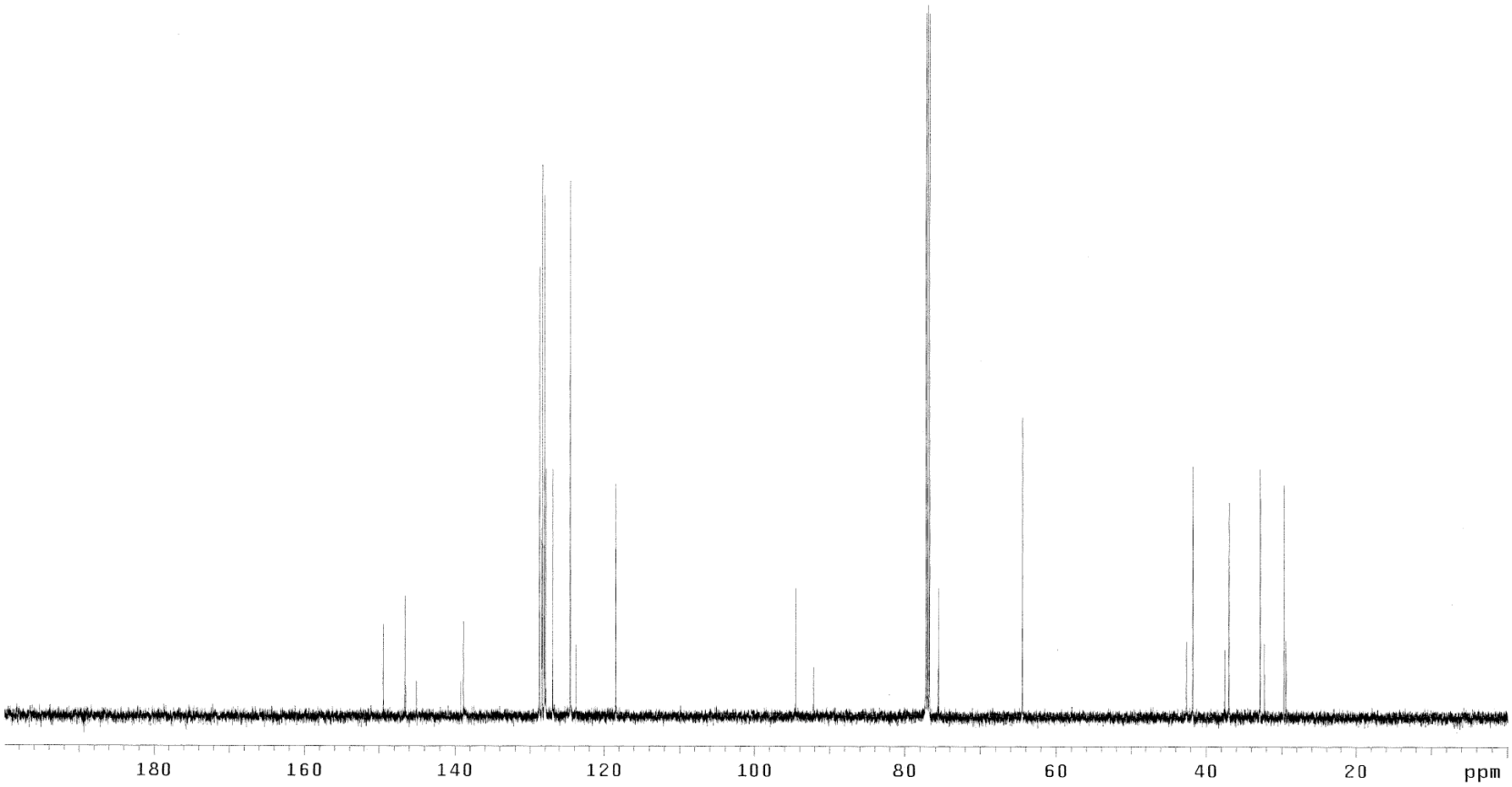

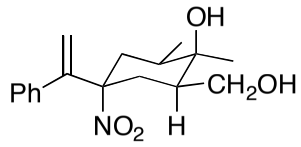

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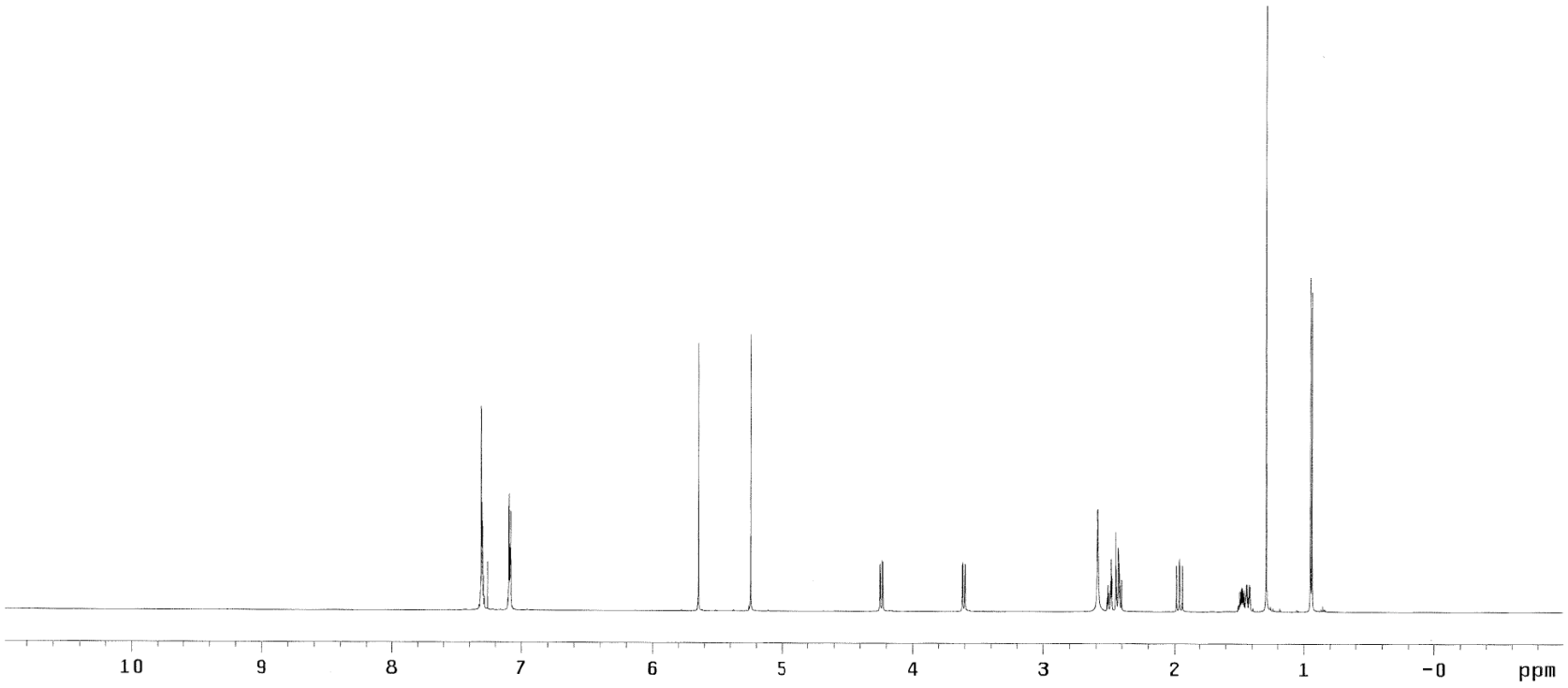

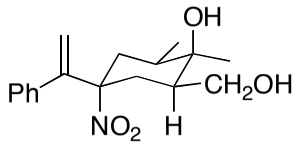

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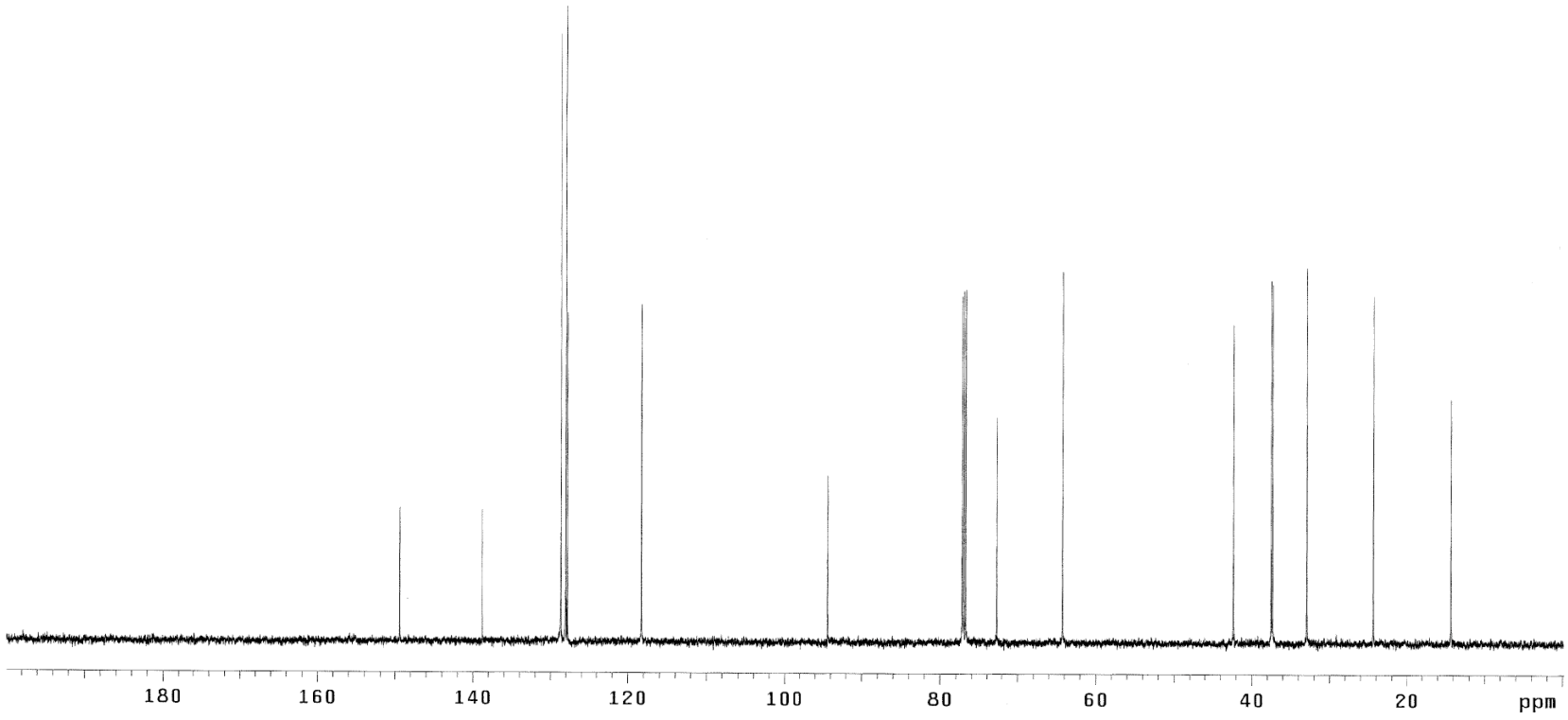

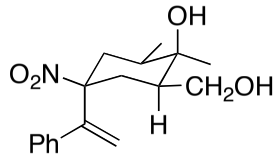

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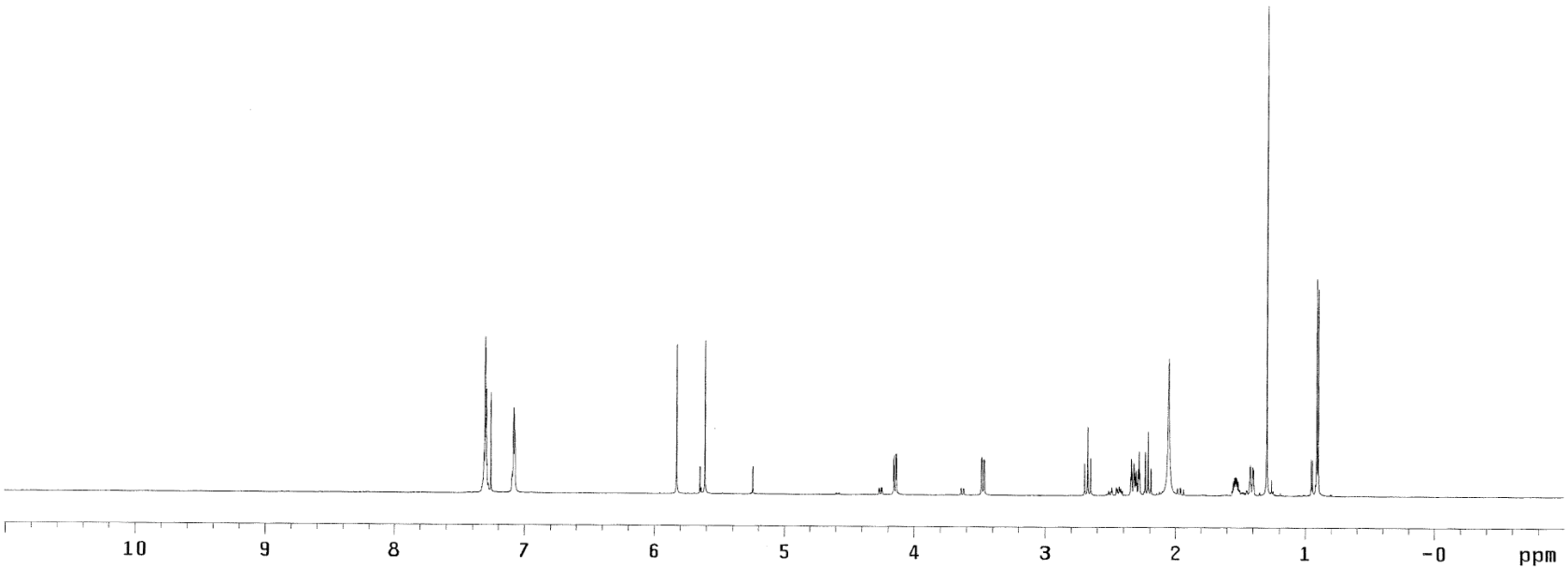

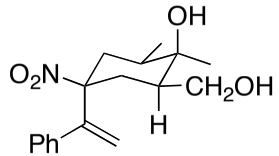

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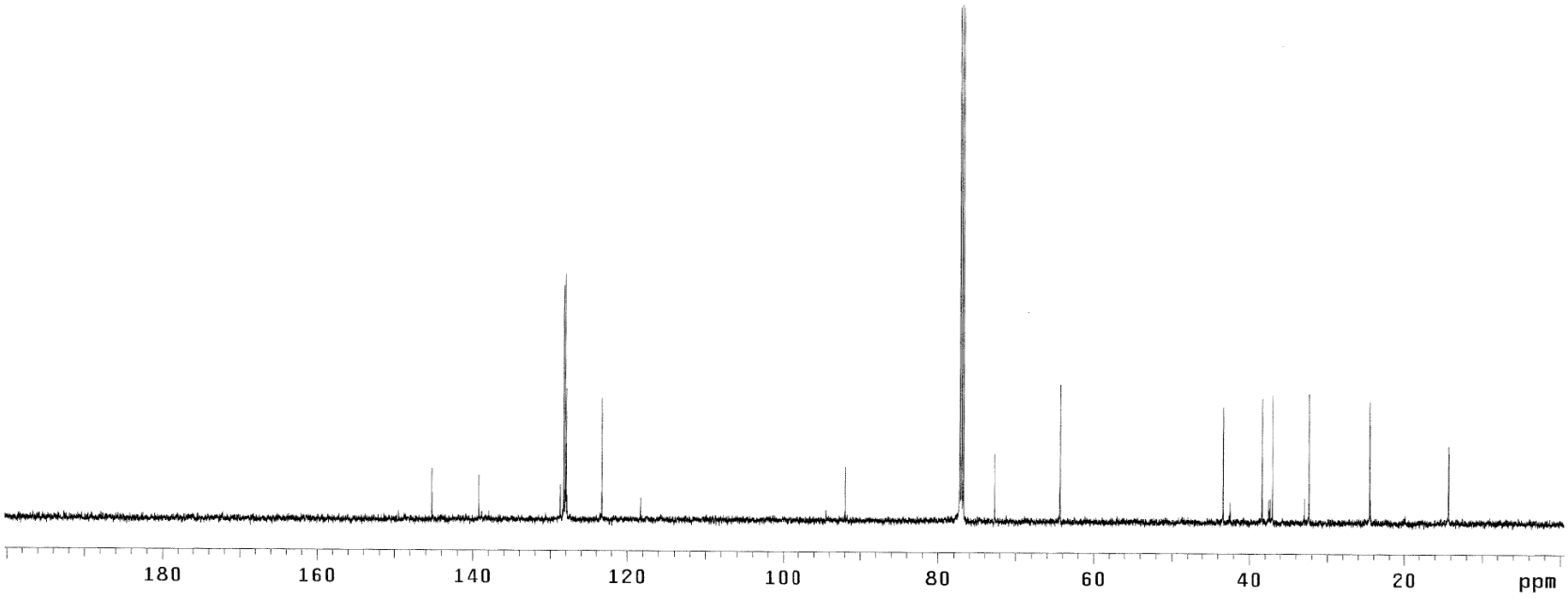

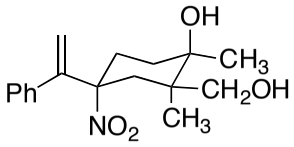

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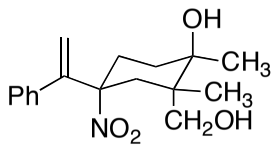
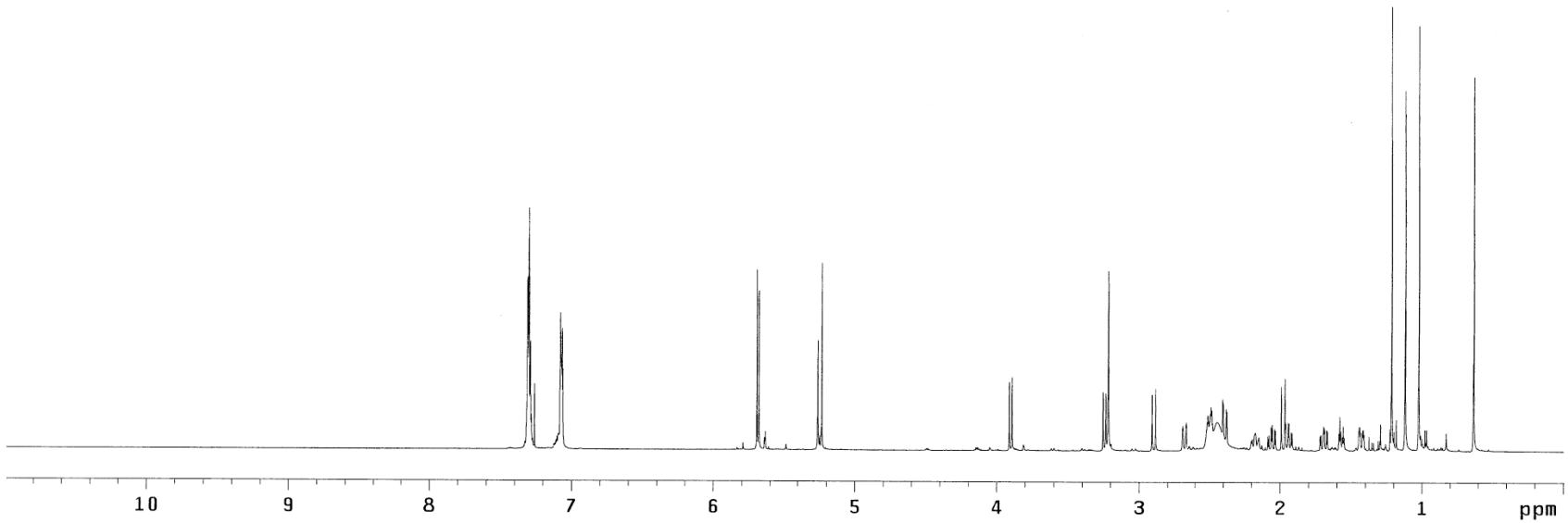
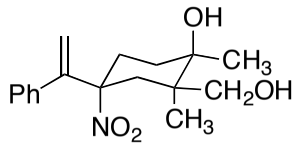


4g-isomer two





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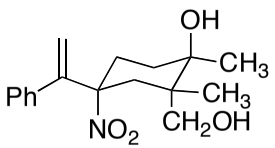

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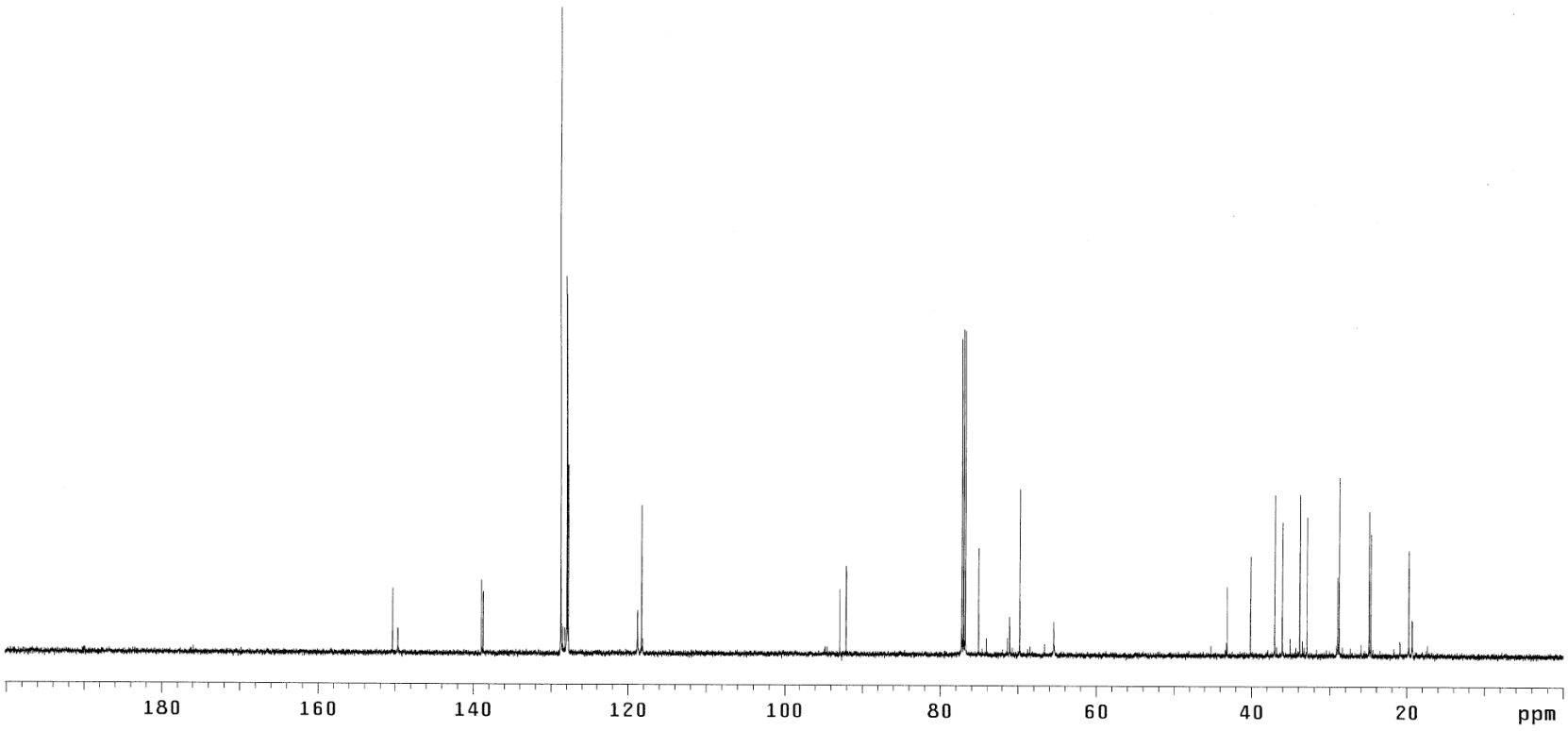

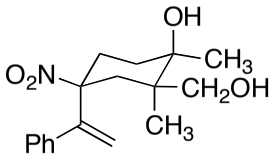

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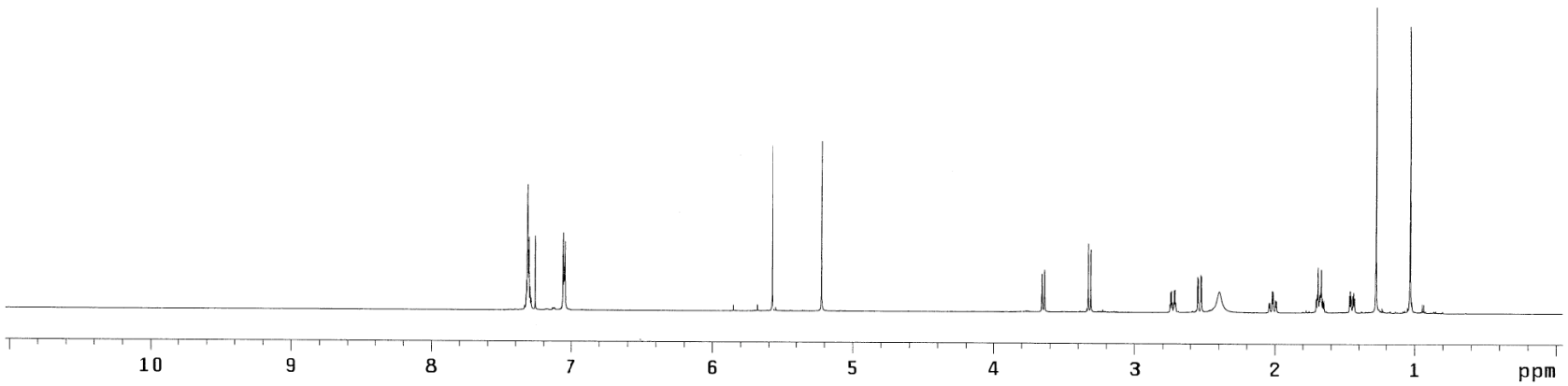
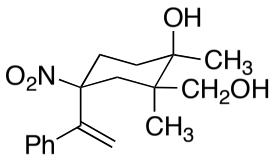
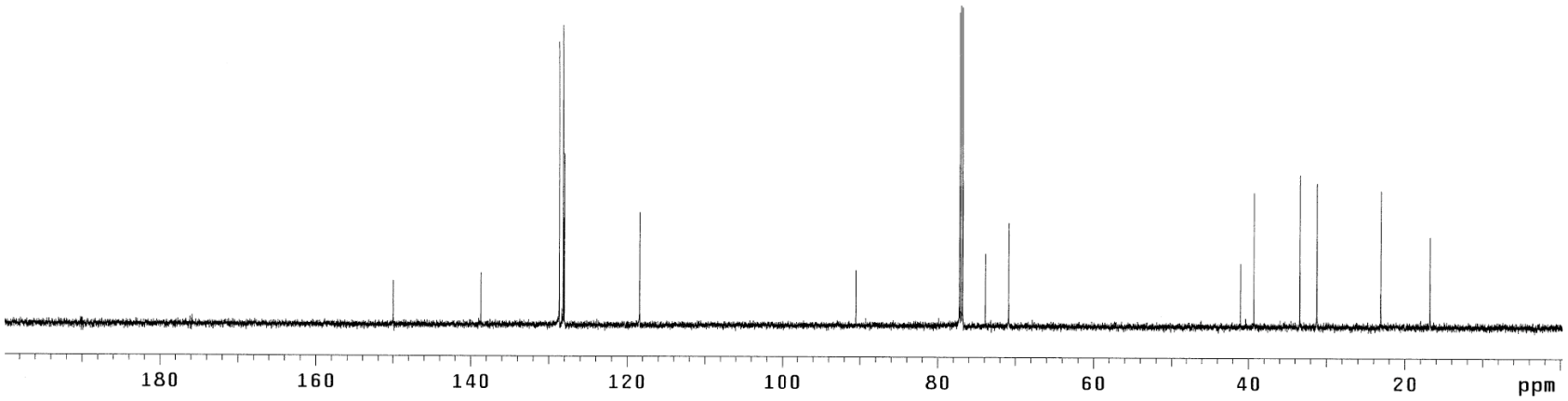
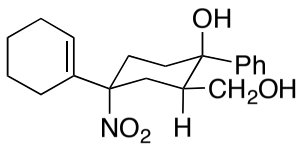


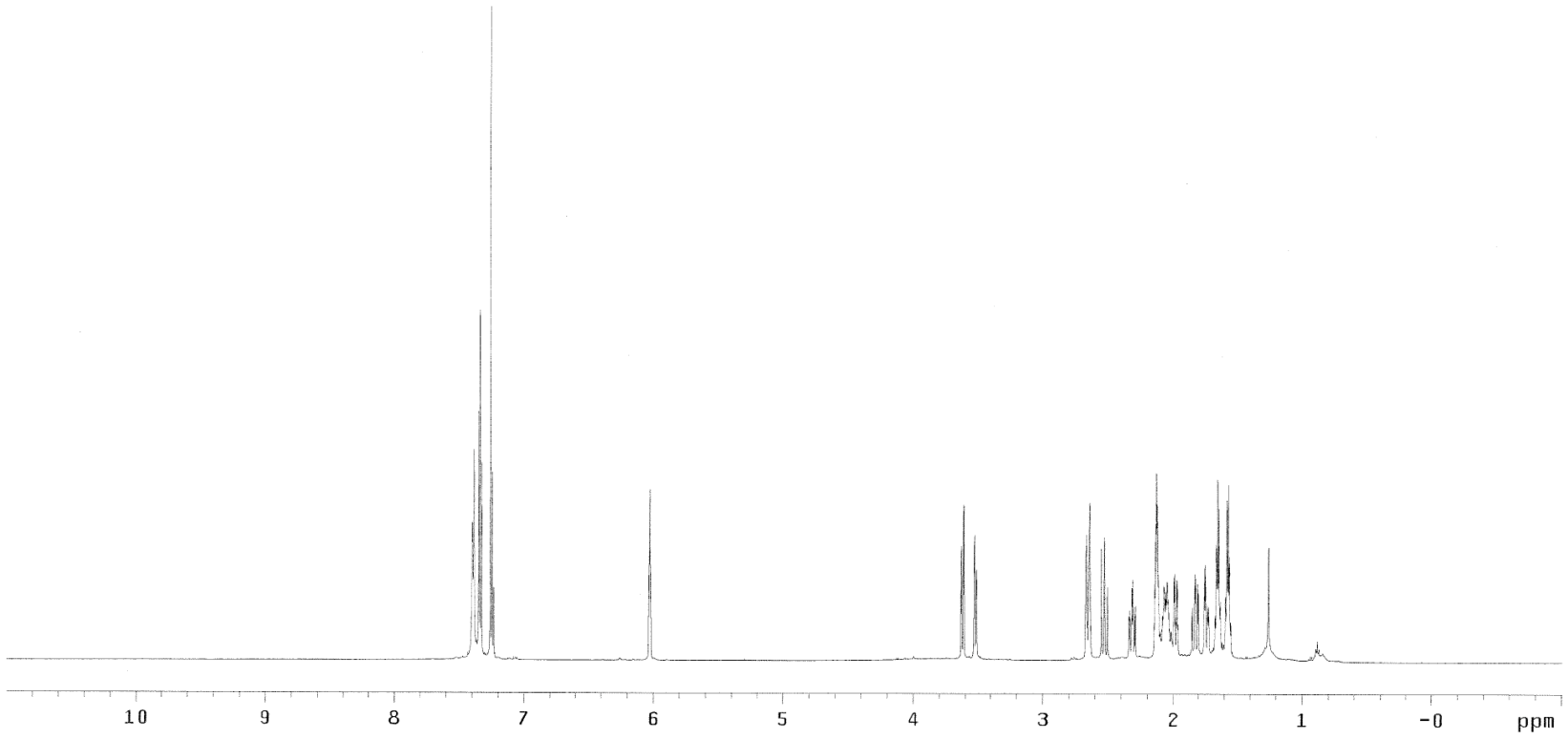


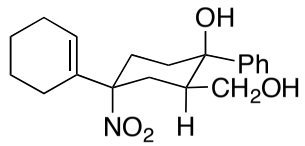
4g-isomer three





4h-major





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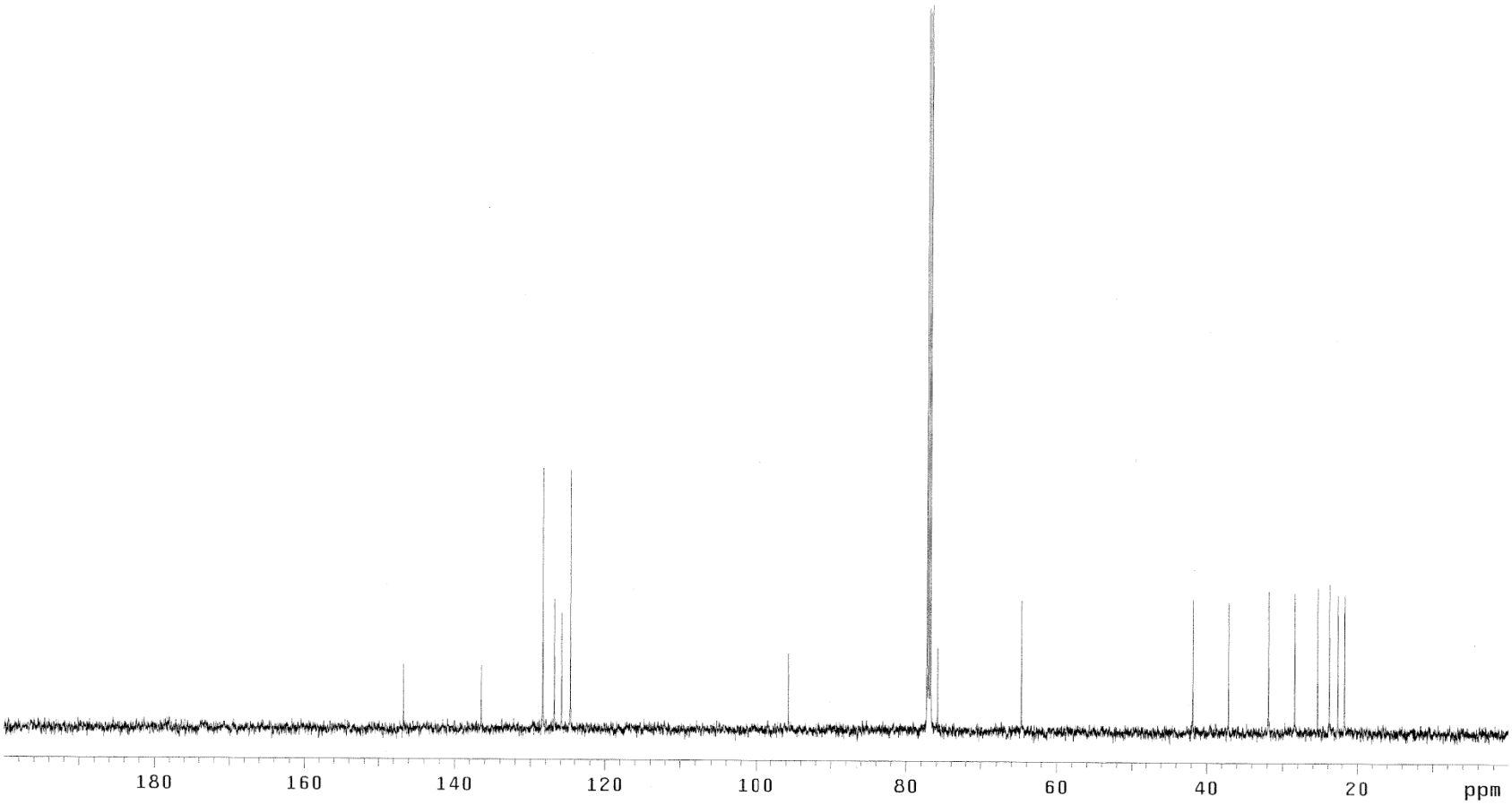

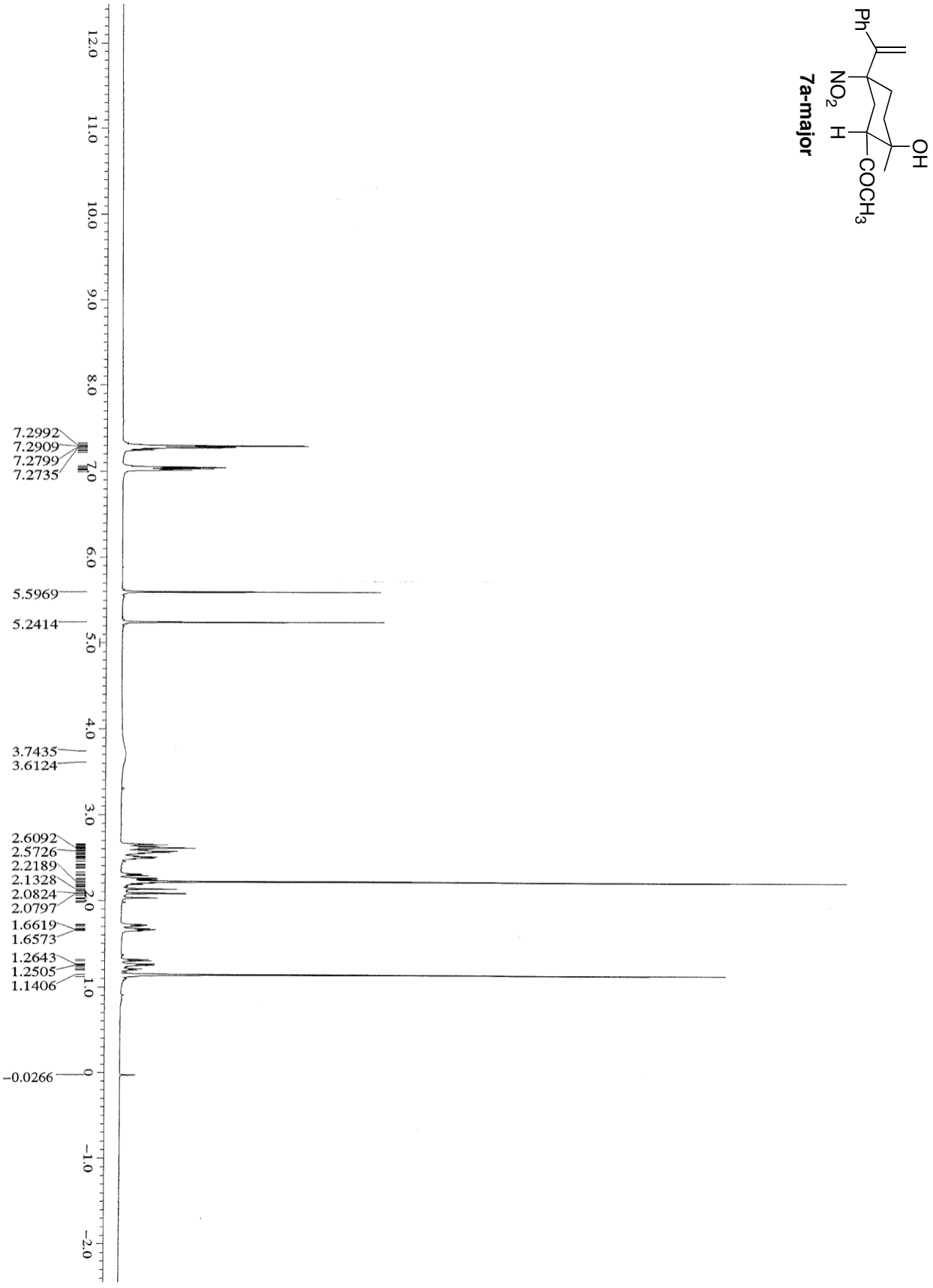
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NO2 H
OH
COCH3
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4.0
3.0
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1.0
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-2.0
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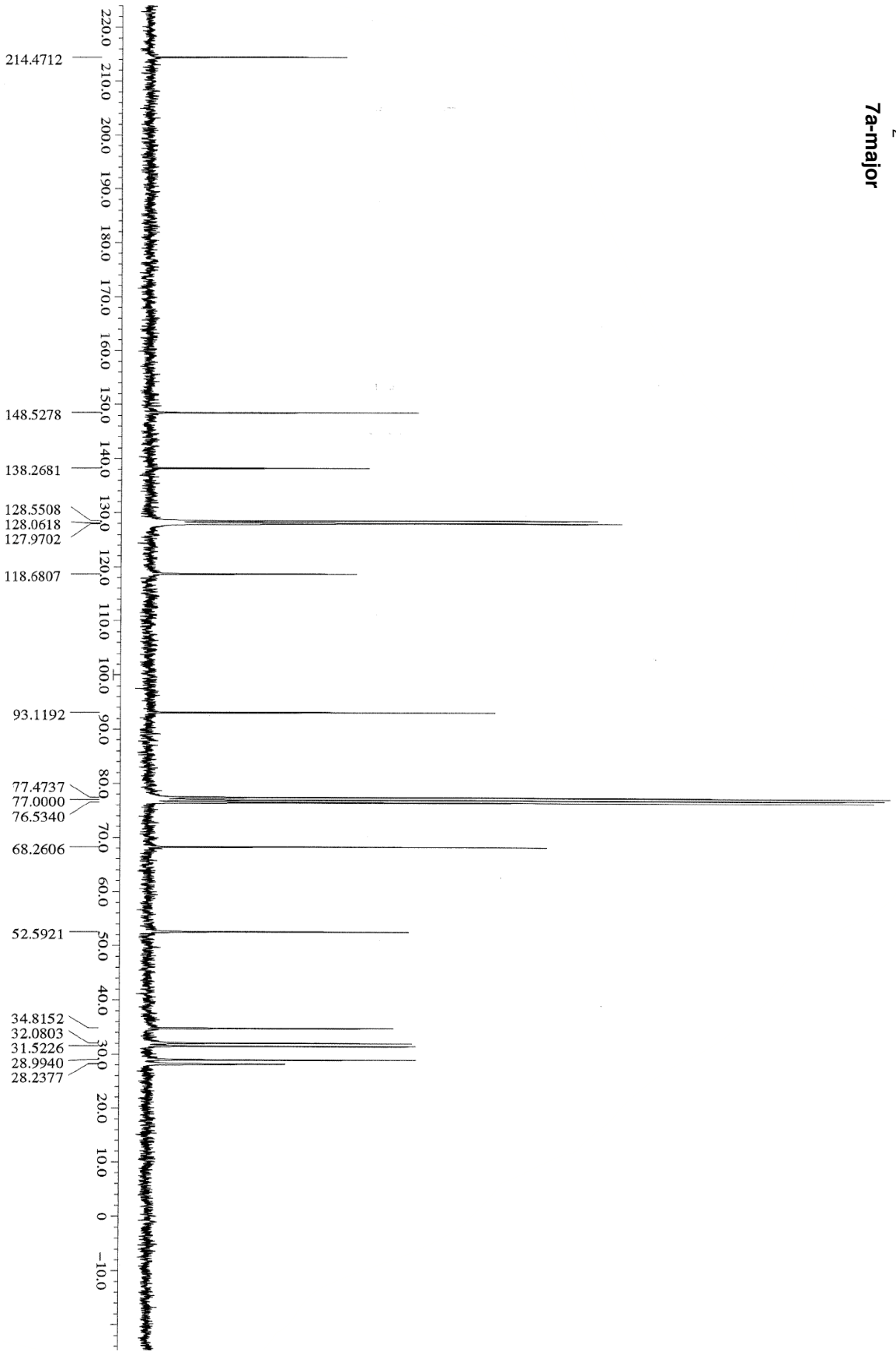
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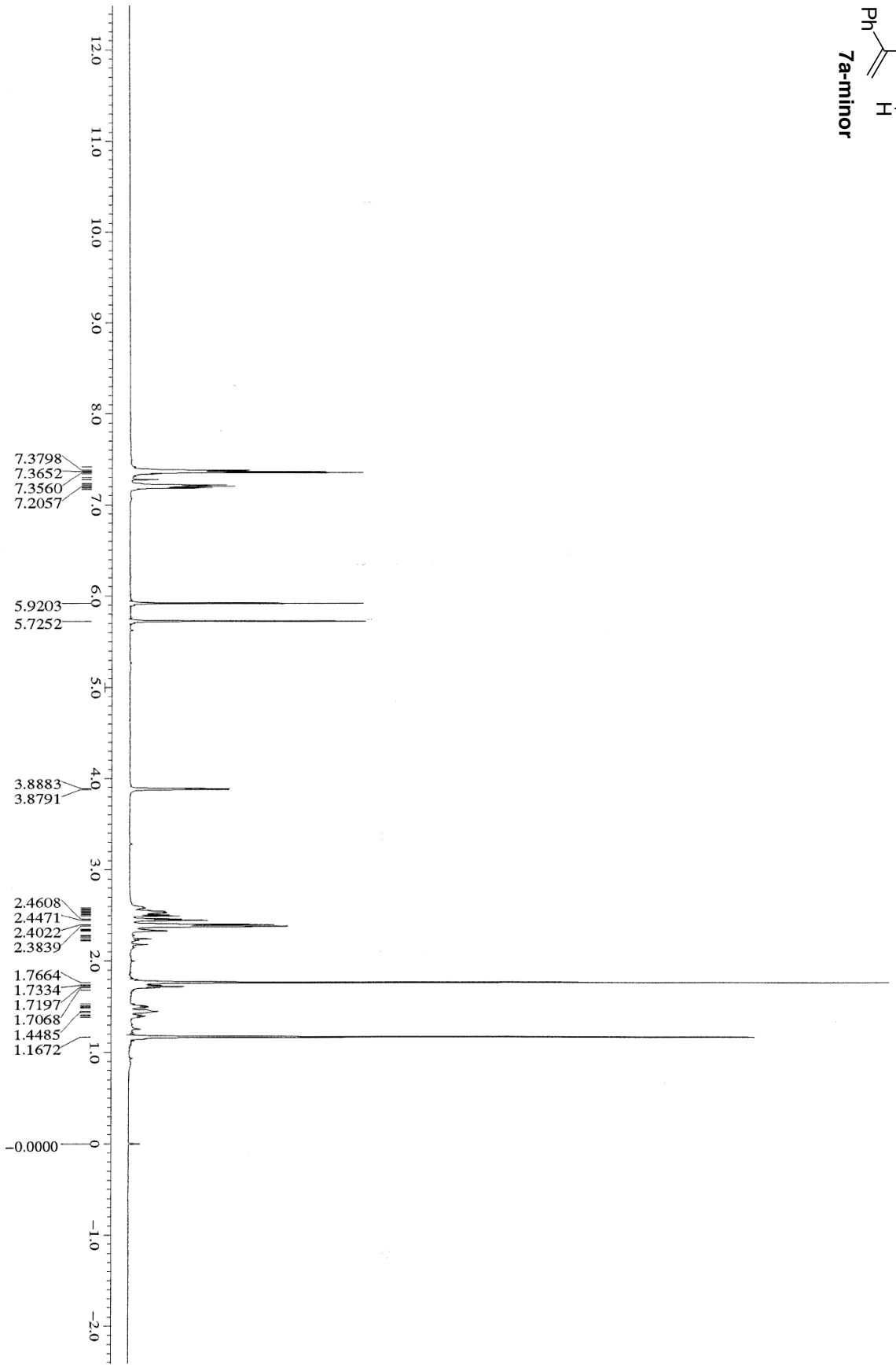
118.6807
93.1192
77.4737
77.0000
76.5340
68.2606
52.5921
34.8152
32.0803
31.5226
28.9940
28.2377
Ph
NO2
H
OH
COCH3
7a-major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3.8791
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2.4022
2.3839
1.7664
1.7334
1.7197
1.7068
1.4485
1.1672
−0.0000
12.0
11.0
10.0
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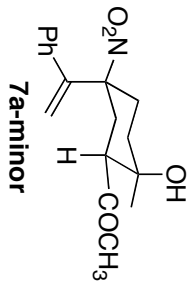
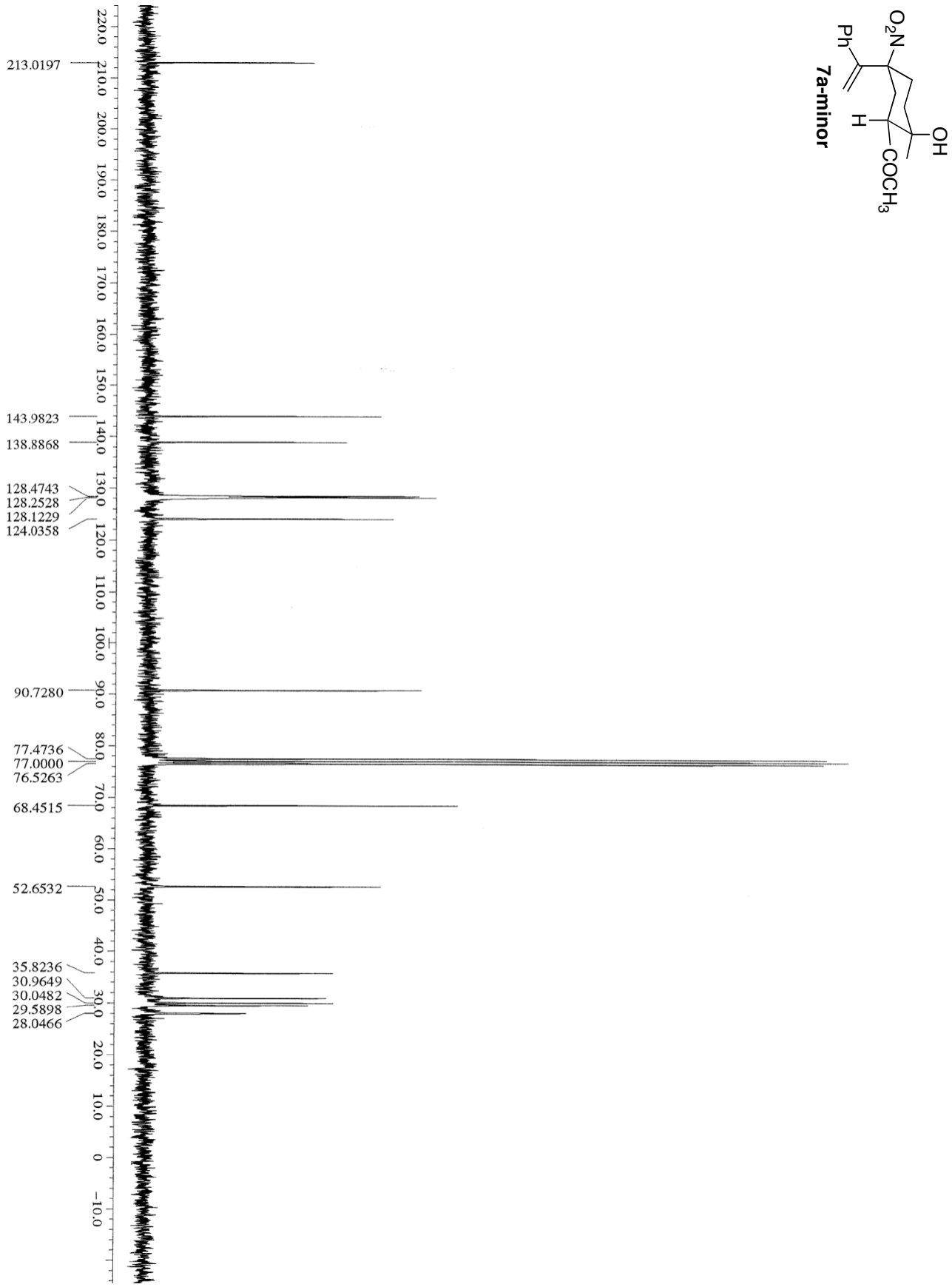
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0


O2N
Ph
H
OH
COCH3

7a-minor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30.0482
29.5898
28.0466
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180.0
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120.0
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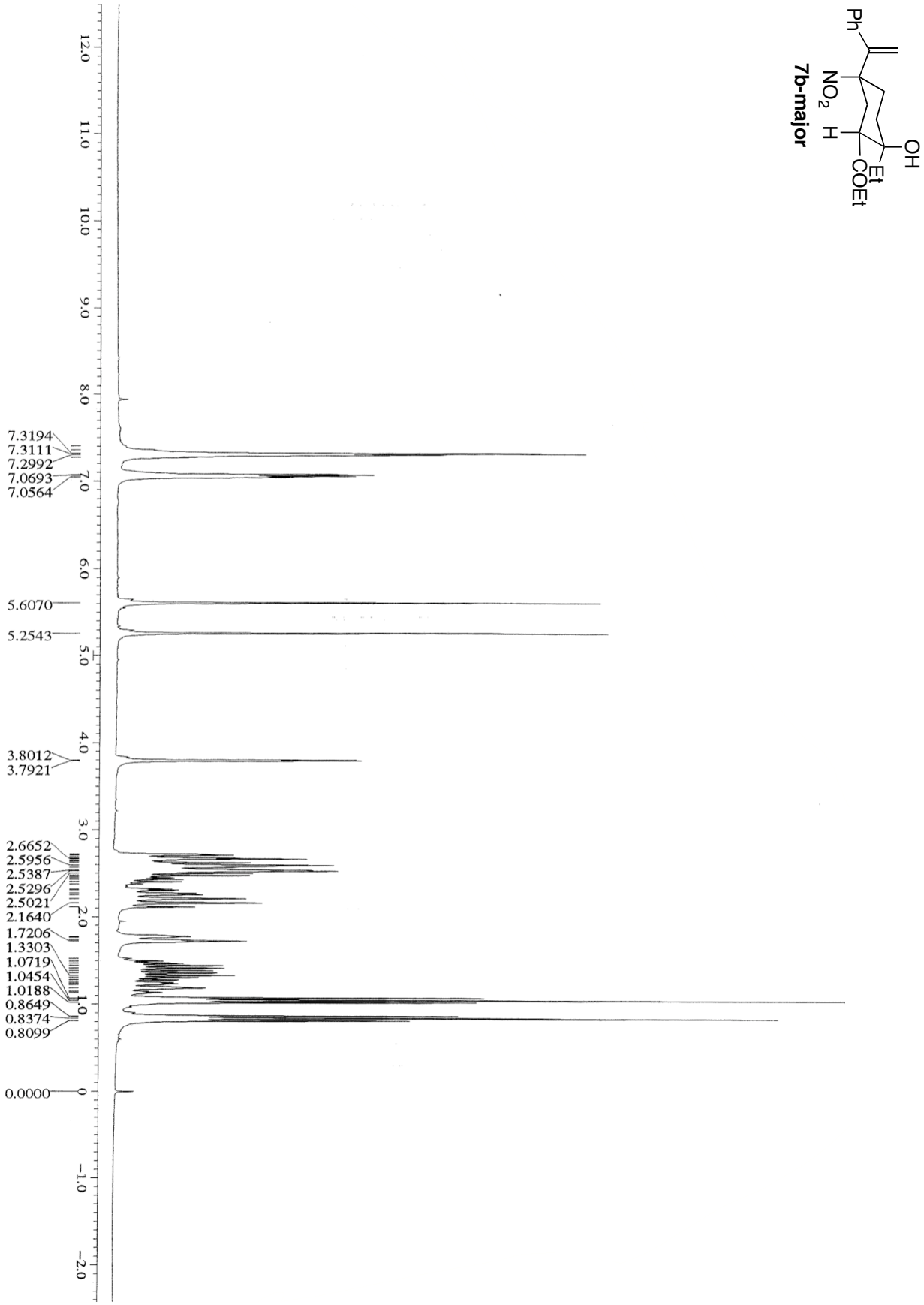
Ph
O2N
H
OH
COCH3
7a-minor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H
OH
Et
COEt
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7.0564
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5.2543
3.8012
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2.6652
2.5956
2.5387
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2.5021
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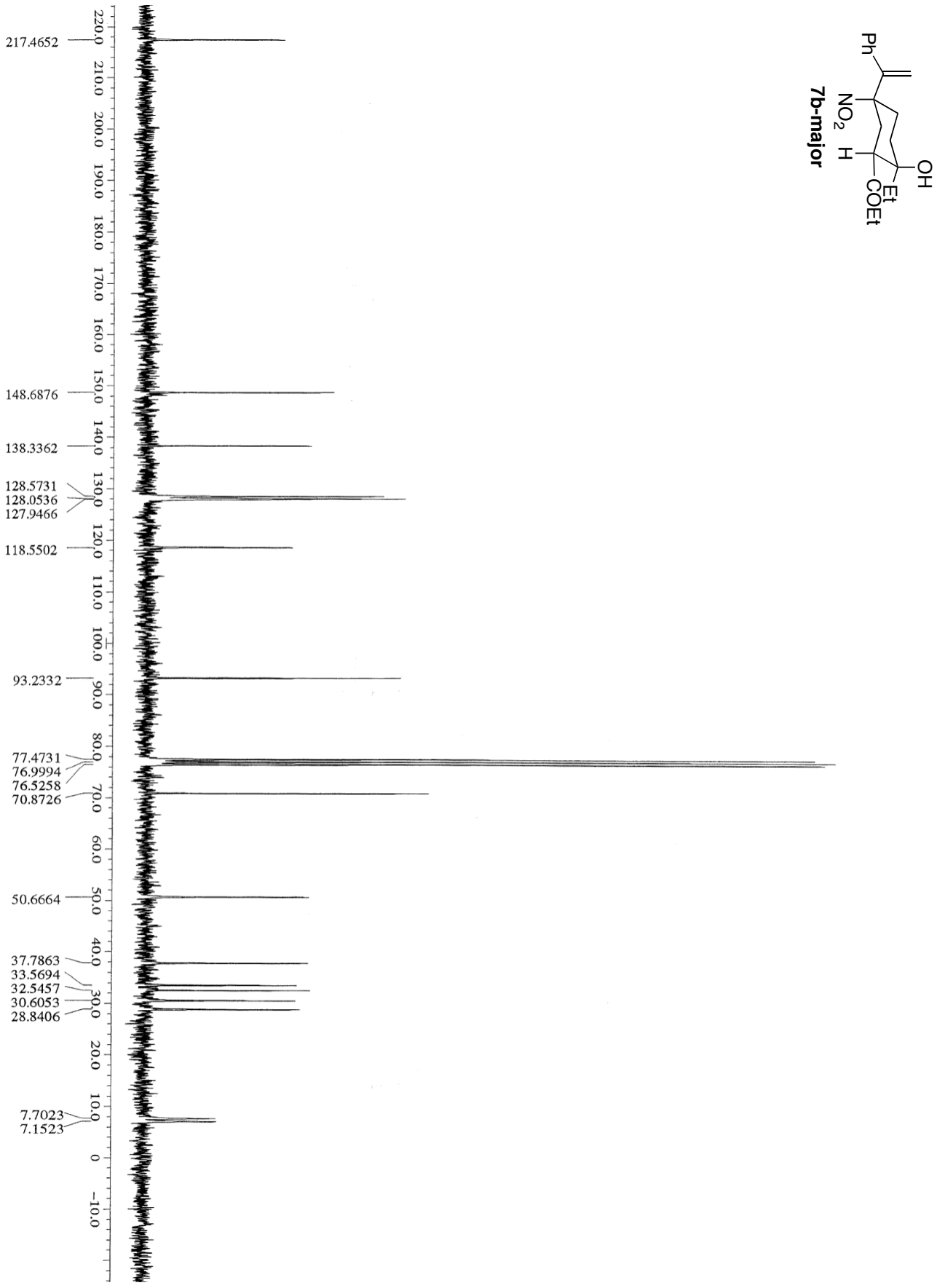
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70.8726
50.6664
37.7863
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30.6053
28.8406
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
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0
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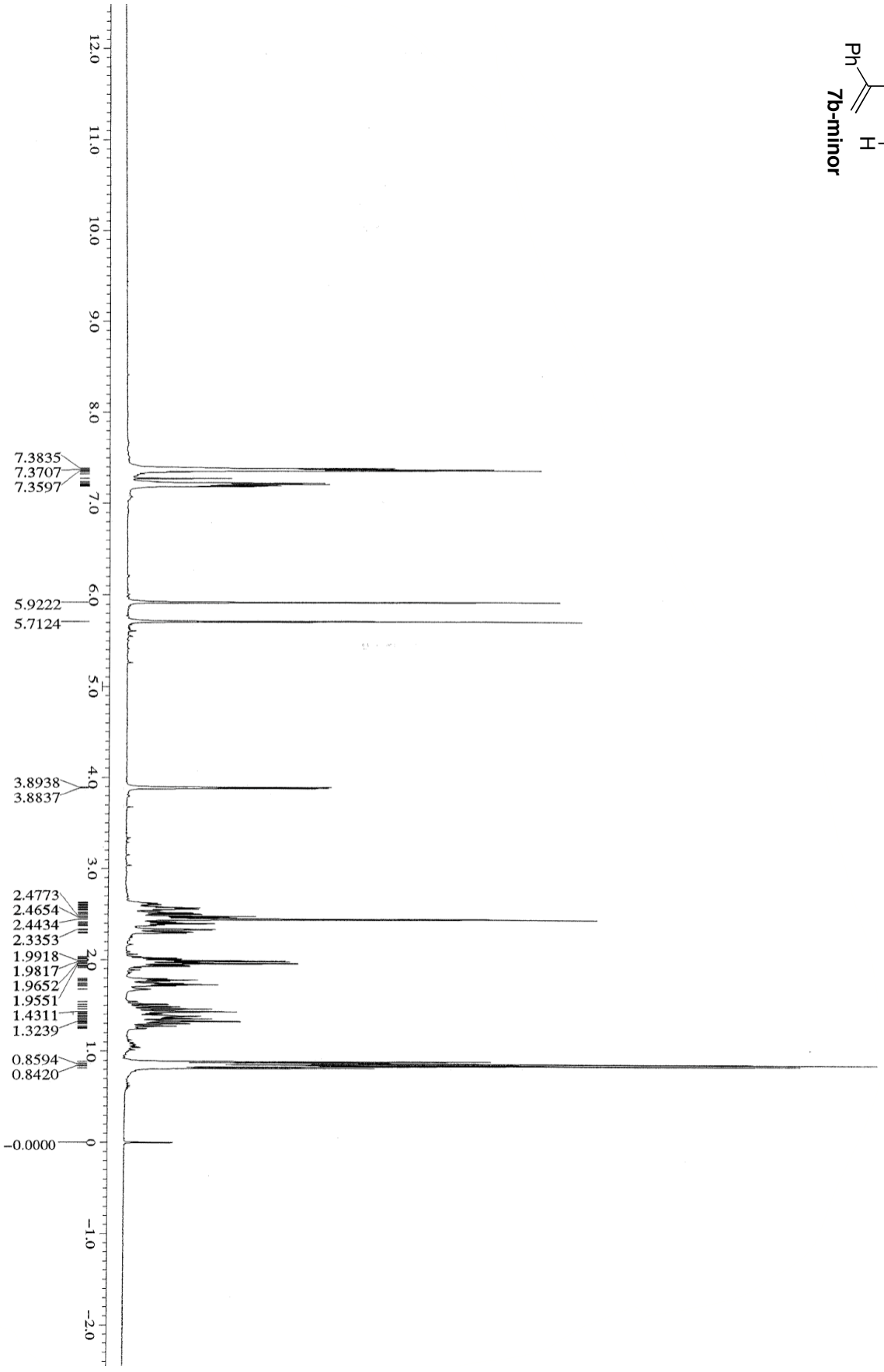
Ph
NO2
H
OH
Et
COEt
7b-major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1.9652
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−0.0000
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11.0
10.0
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2.0
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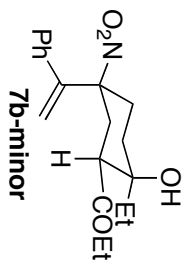
−2.0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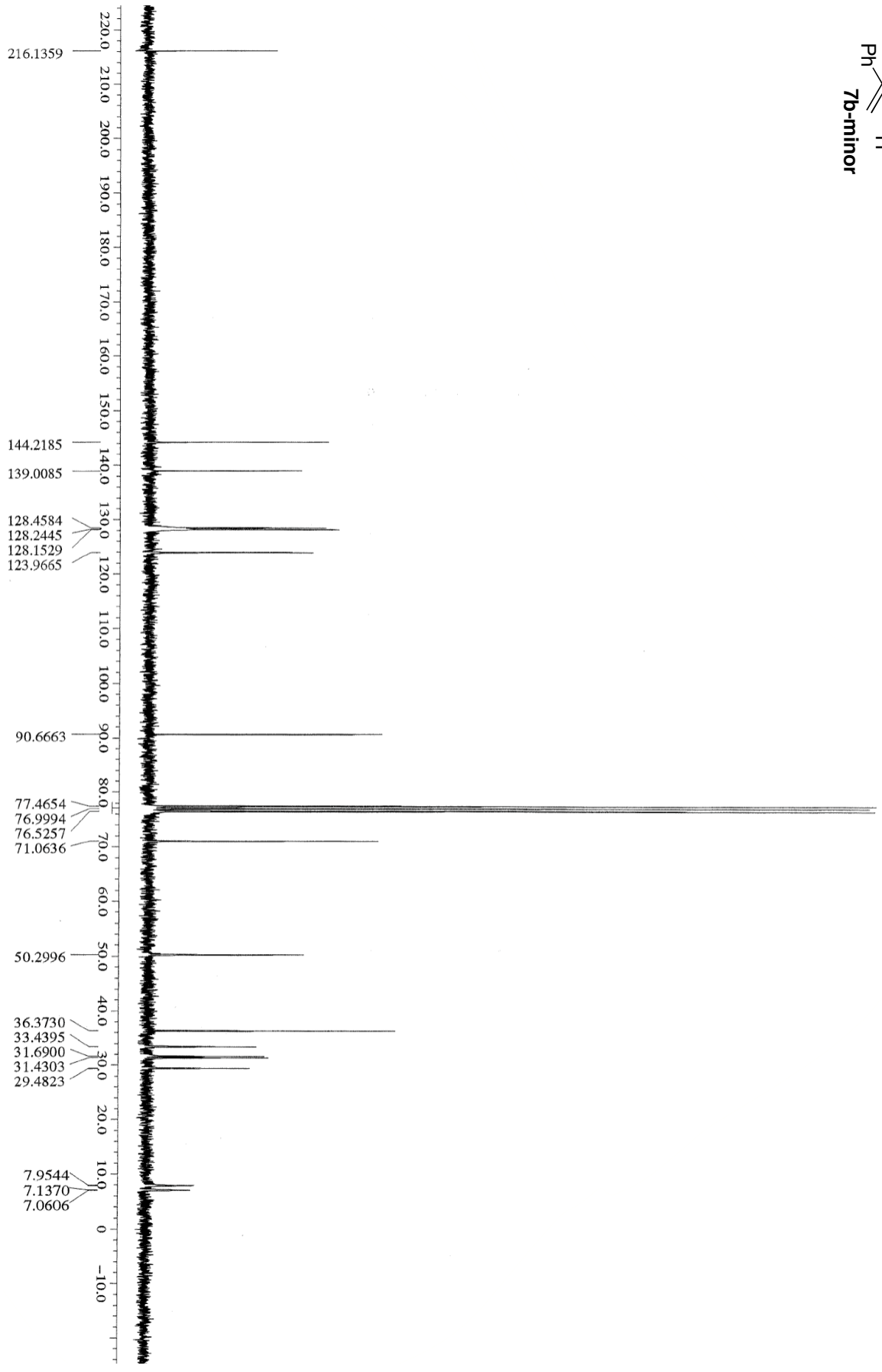
Ph
H
OH
Et
COEt

7b-minor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71.0636
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36.3730
33.4395
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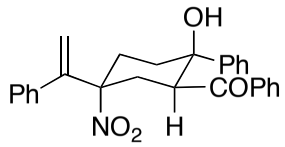
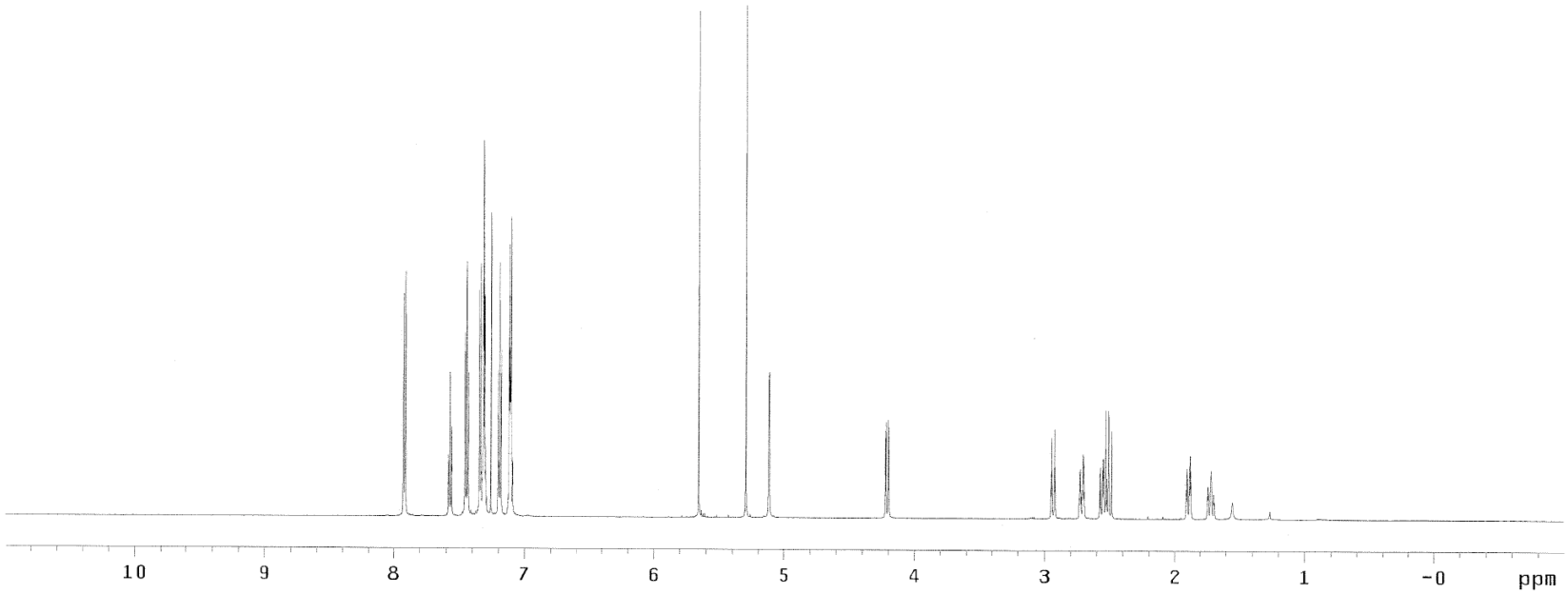
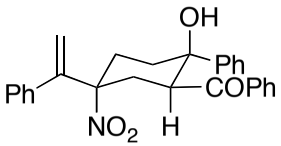
29.4823
7.9544
7.1370
7.0606
Ph
O2N
H
OH
Et
COEt
7b-minor

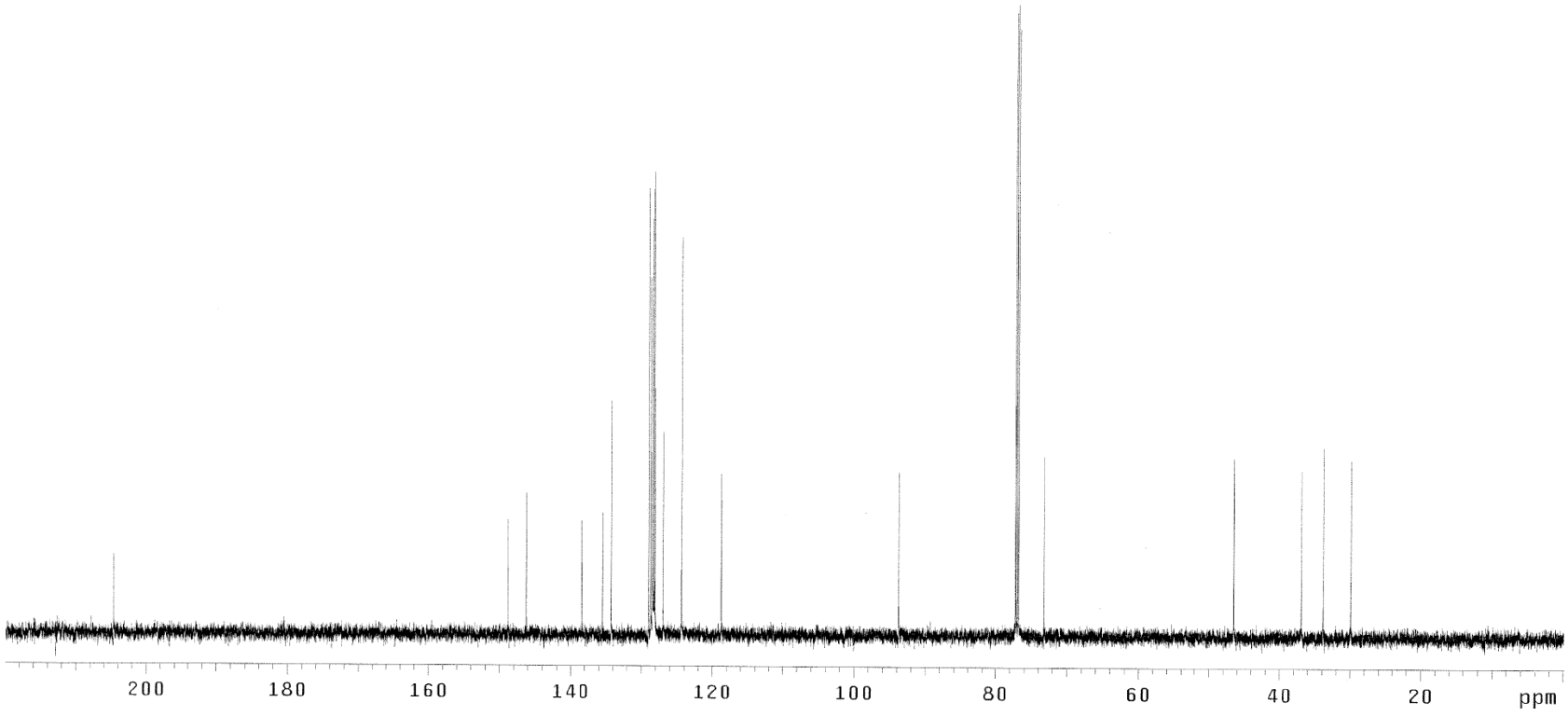


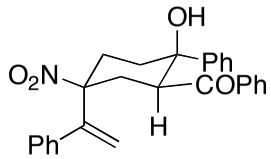
7c-major





7c-major





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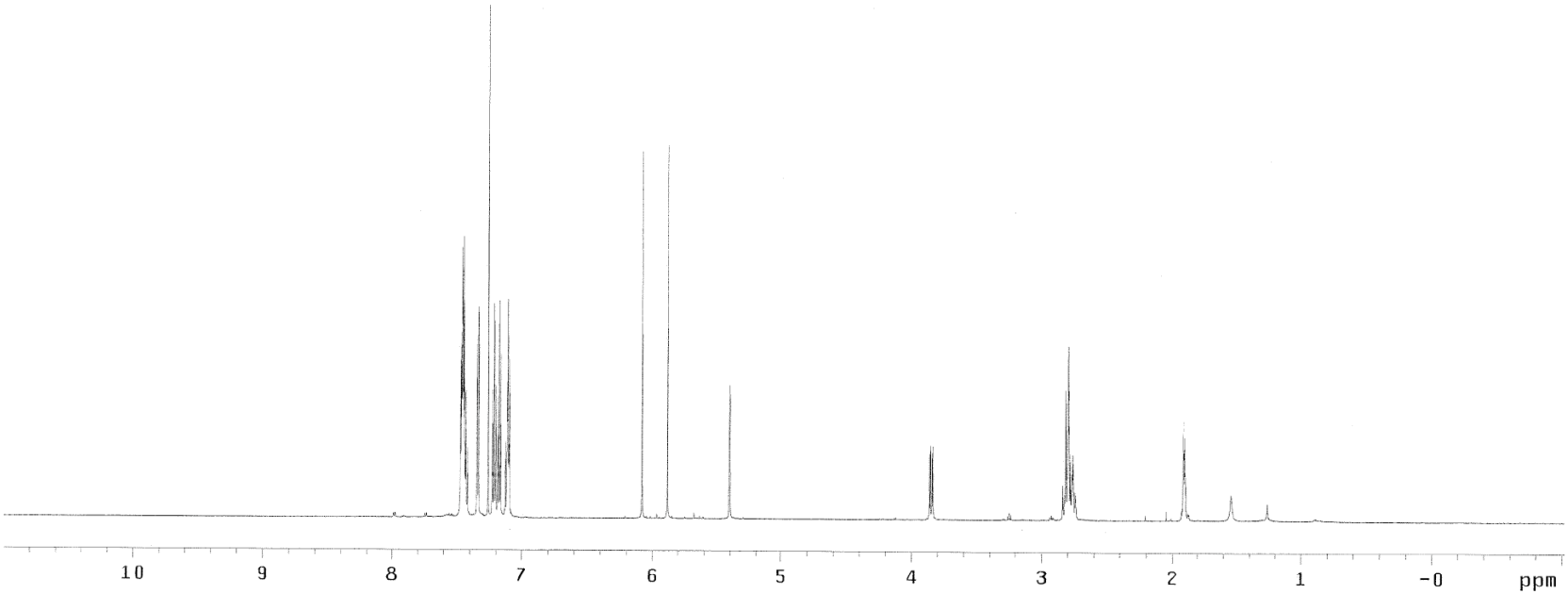

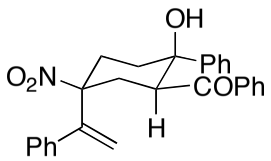

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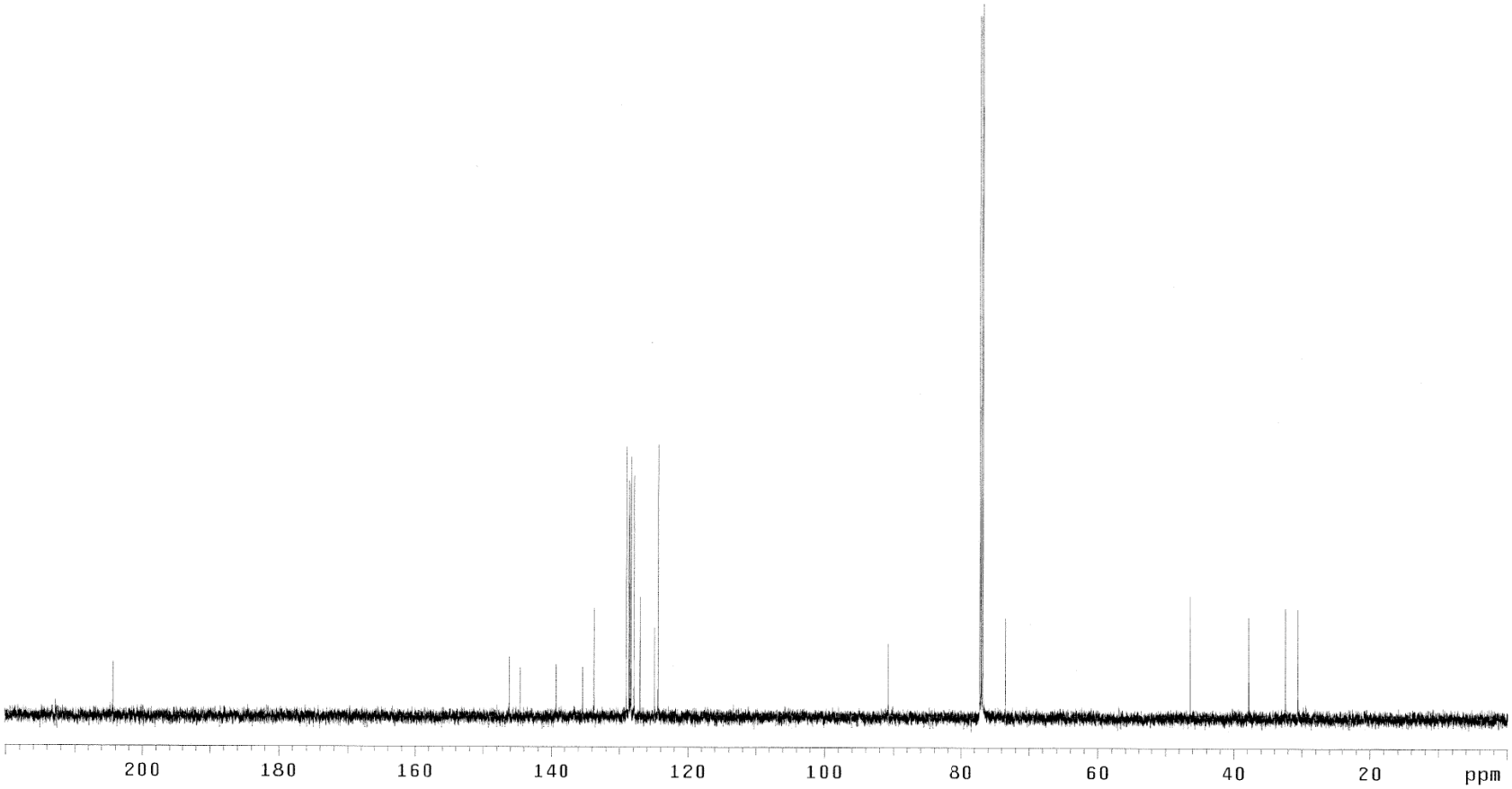

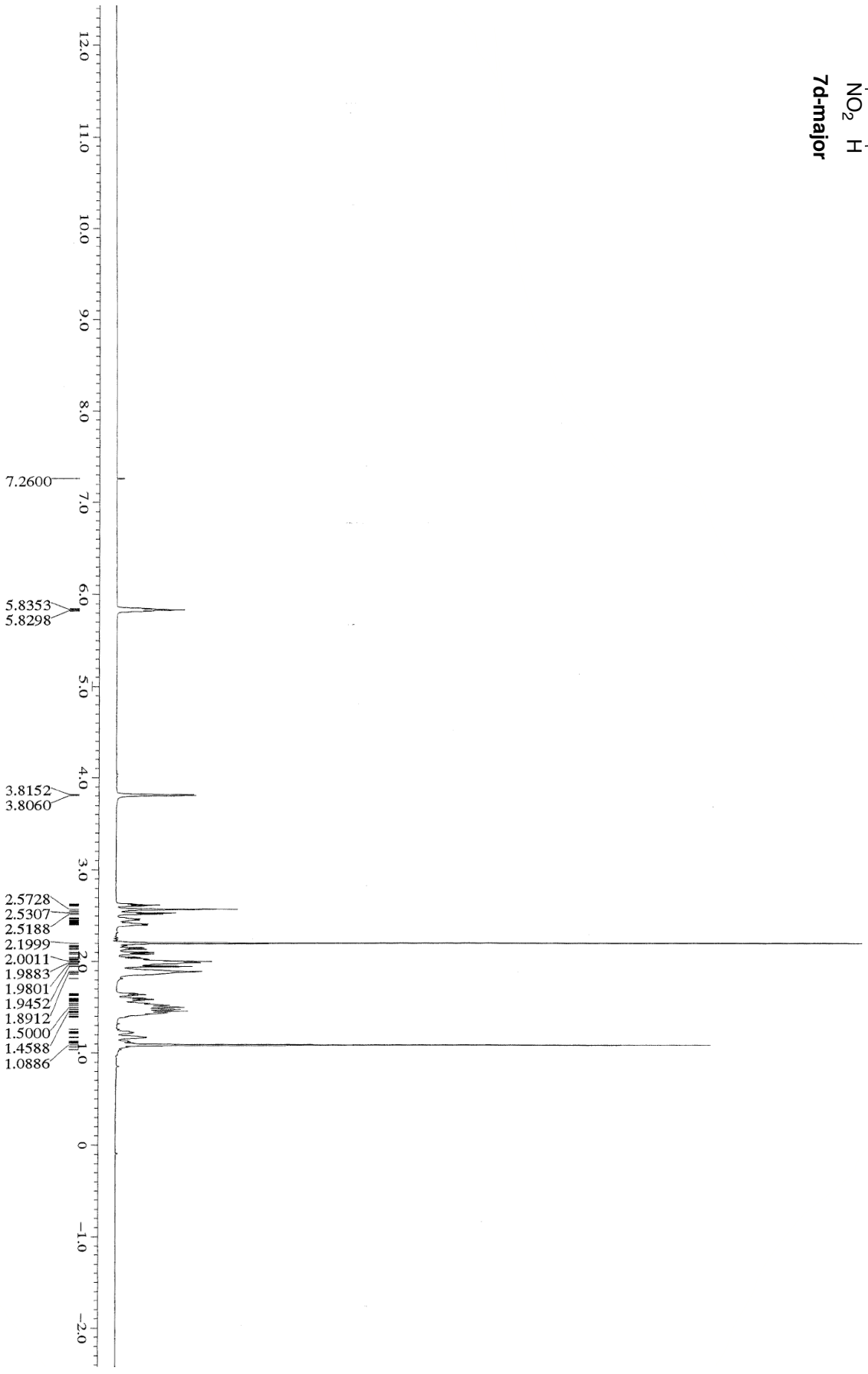
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4.0
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2.0
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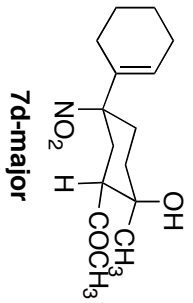
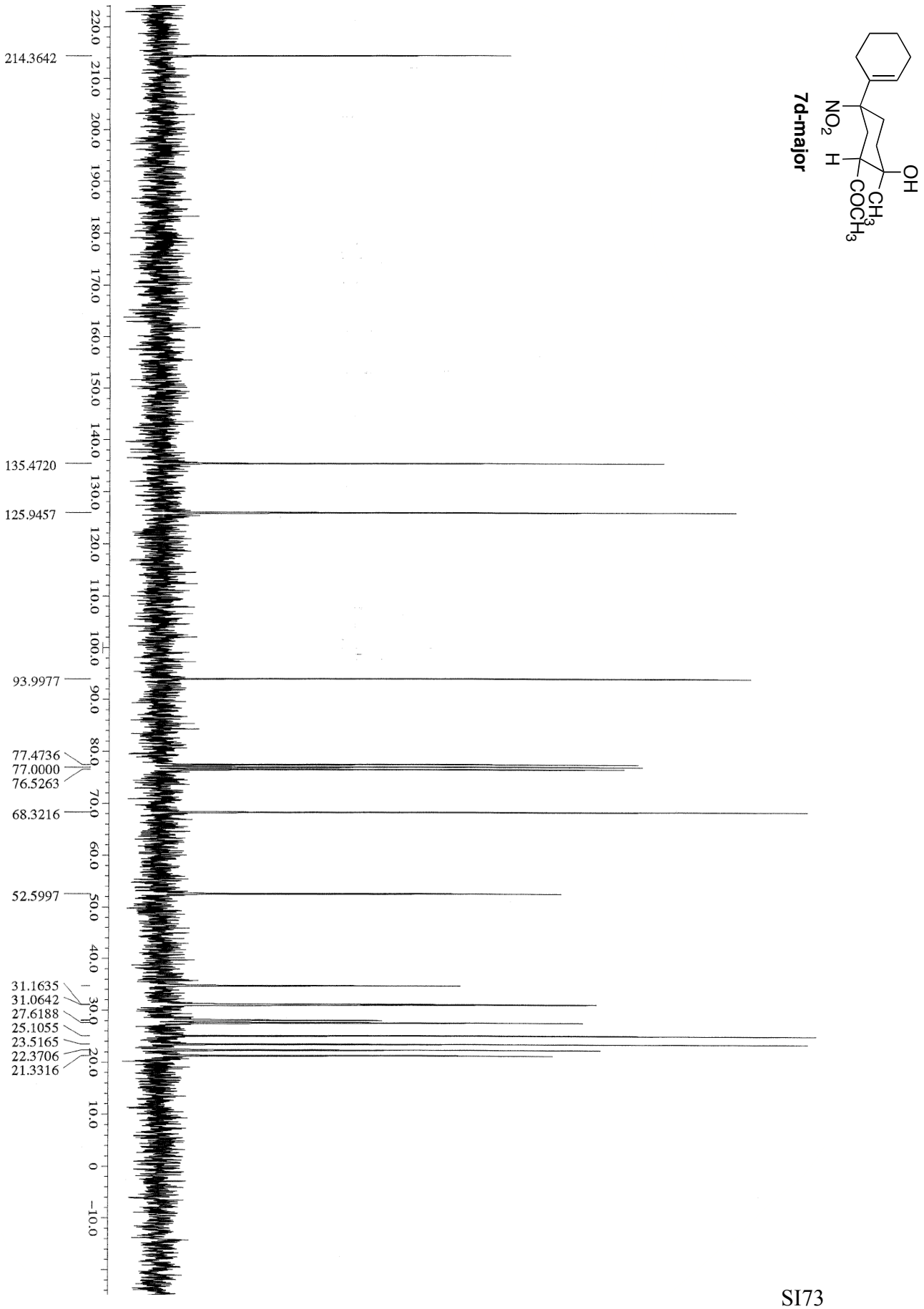
−1.0
−2.0


NO2
H
OH
CH3
COCH3

7d-major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180.0
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120.0
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100.0
90.0
80.0
70.0
60.0
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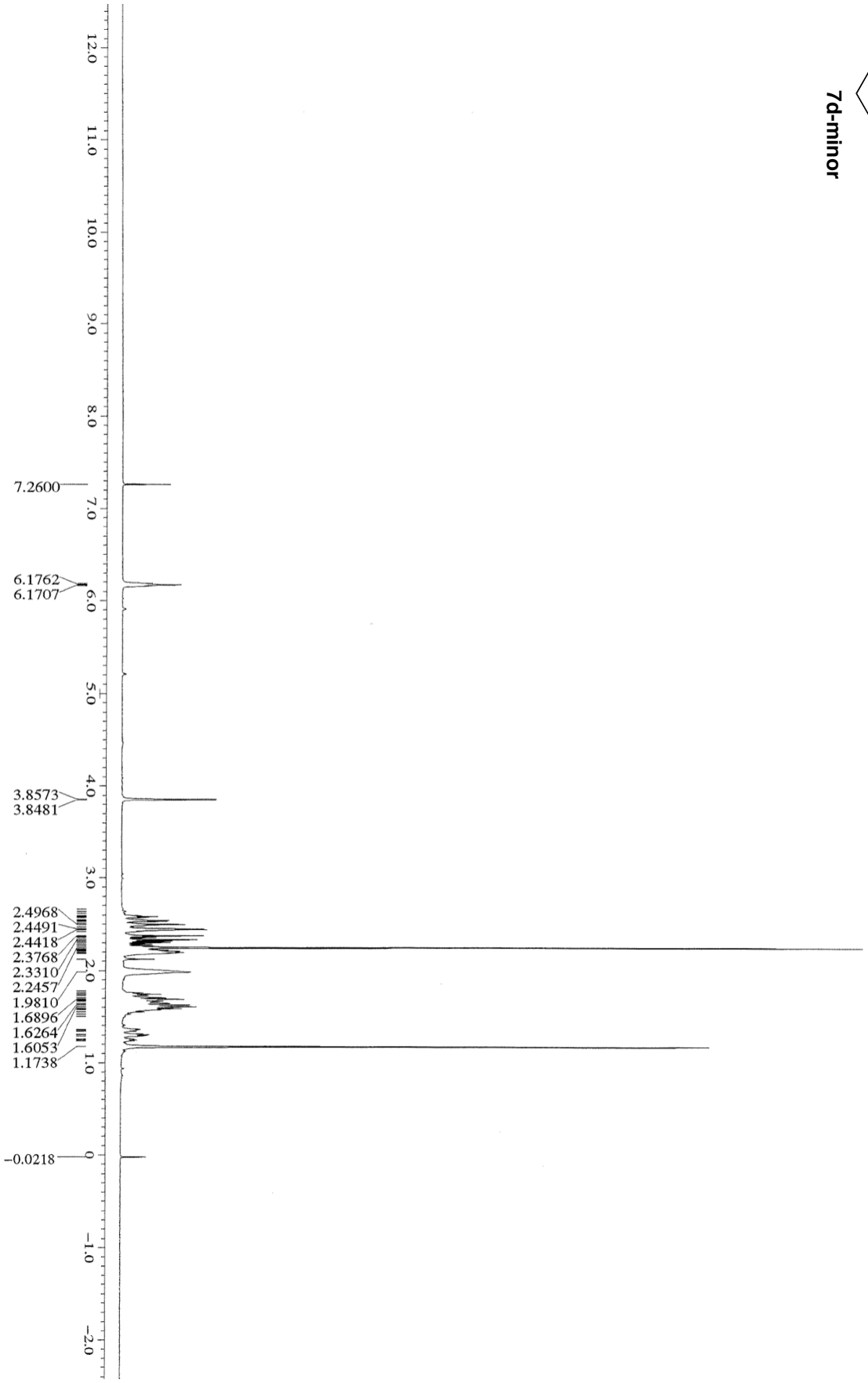
30.0
20.0
10.0
0
−10.0
NO2
H
OH
CH3
COCH3
7d-major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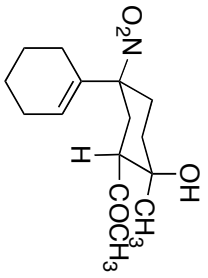
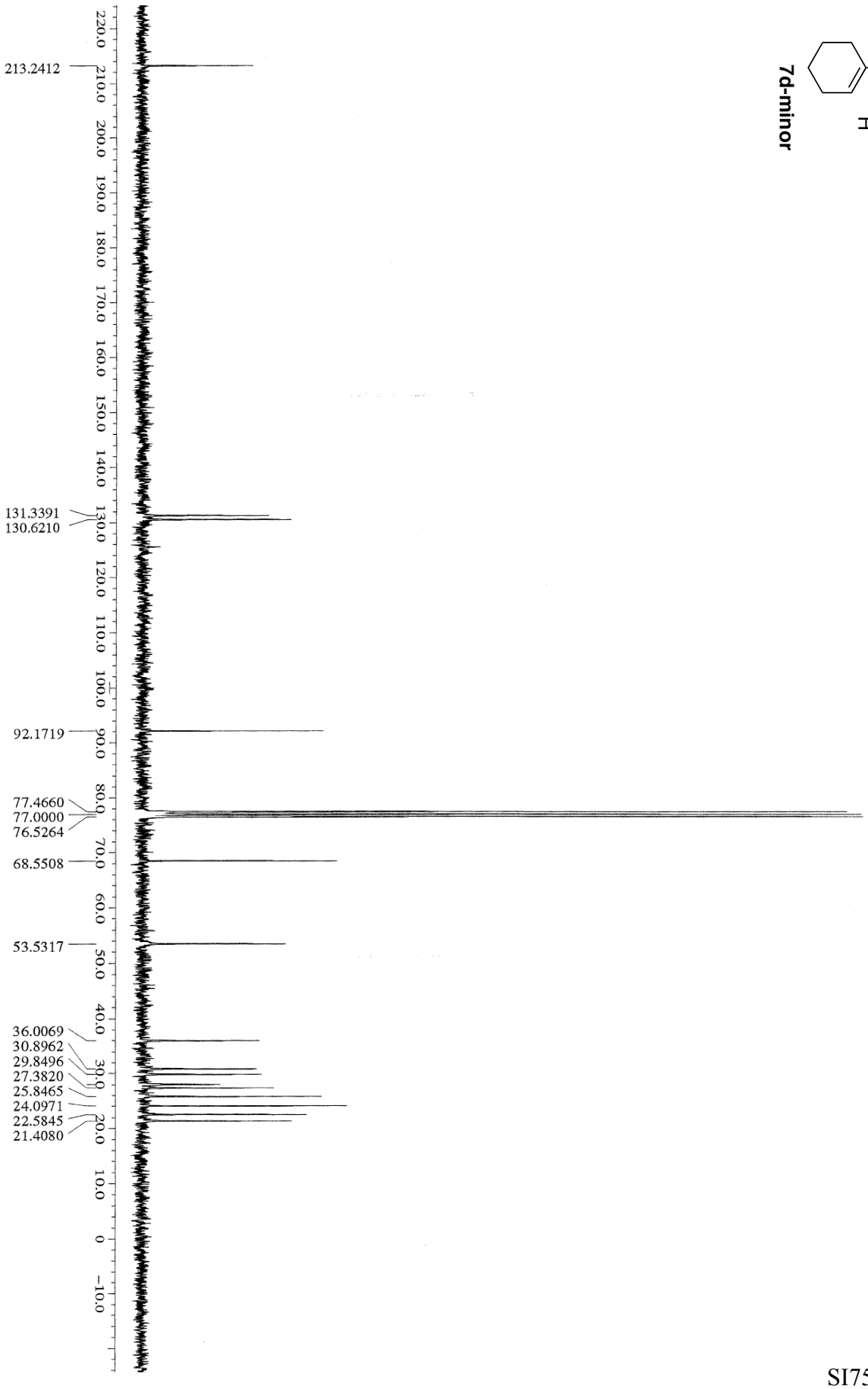

O2N
OH
H
CH3
COCH3

7d-minor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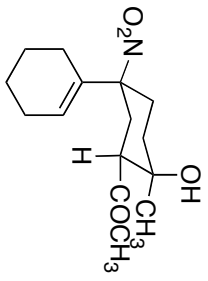
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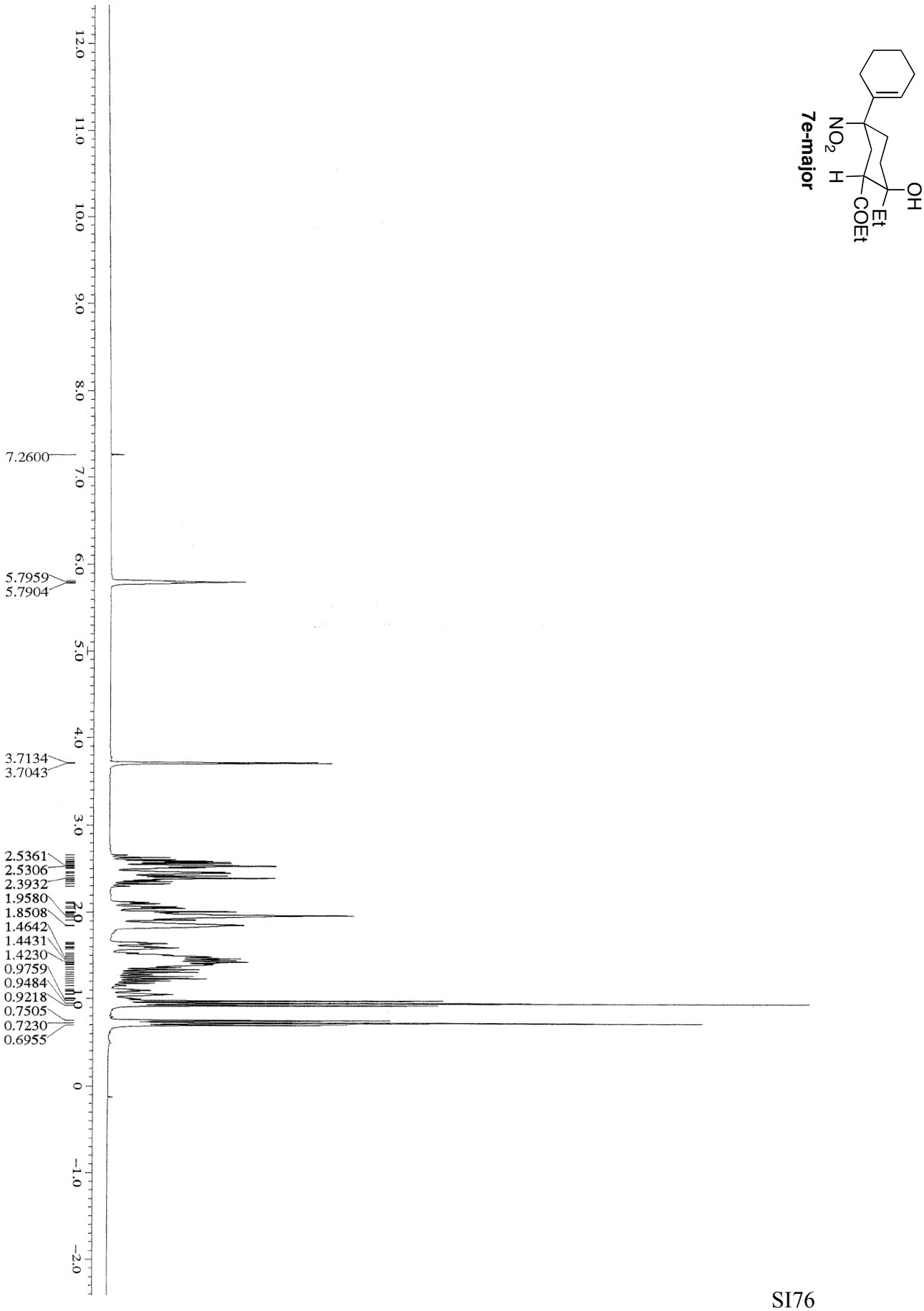
CH3
COCH3

7d-minor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−2.0
NO2
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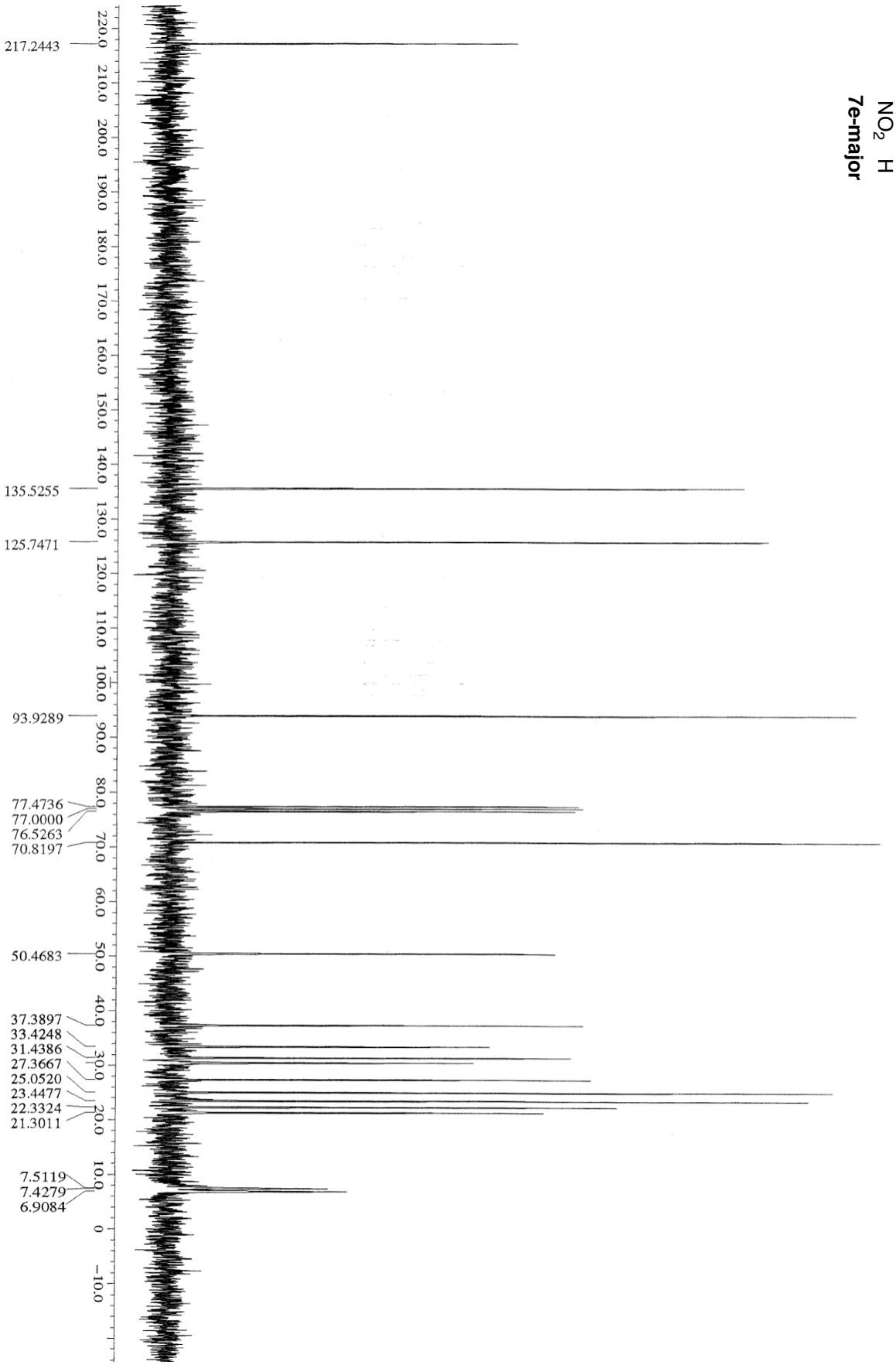
OH
Et
COEt
7e-major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90.0
80.0
70.0
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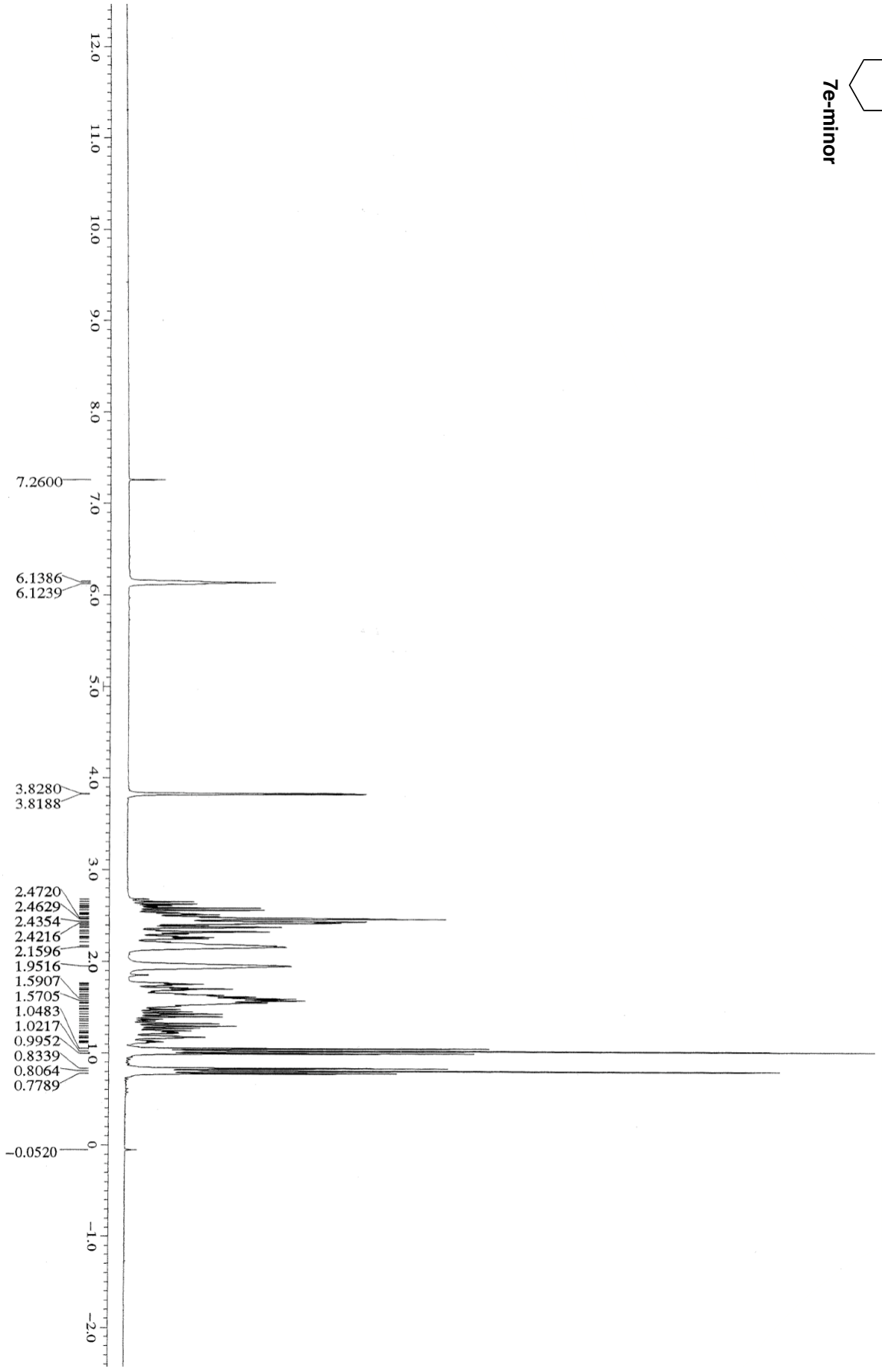
NO2
H
OH
Et
COEt
7e-major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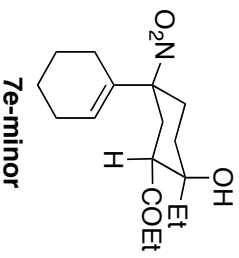
−2.0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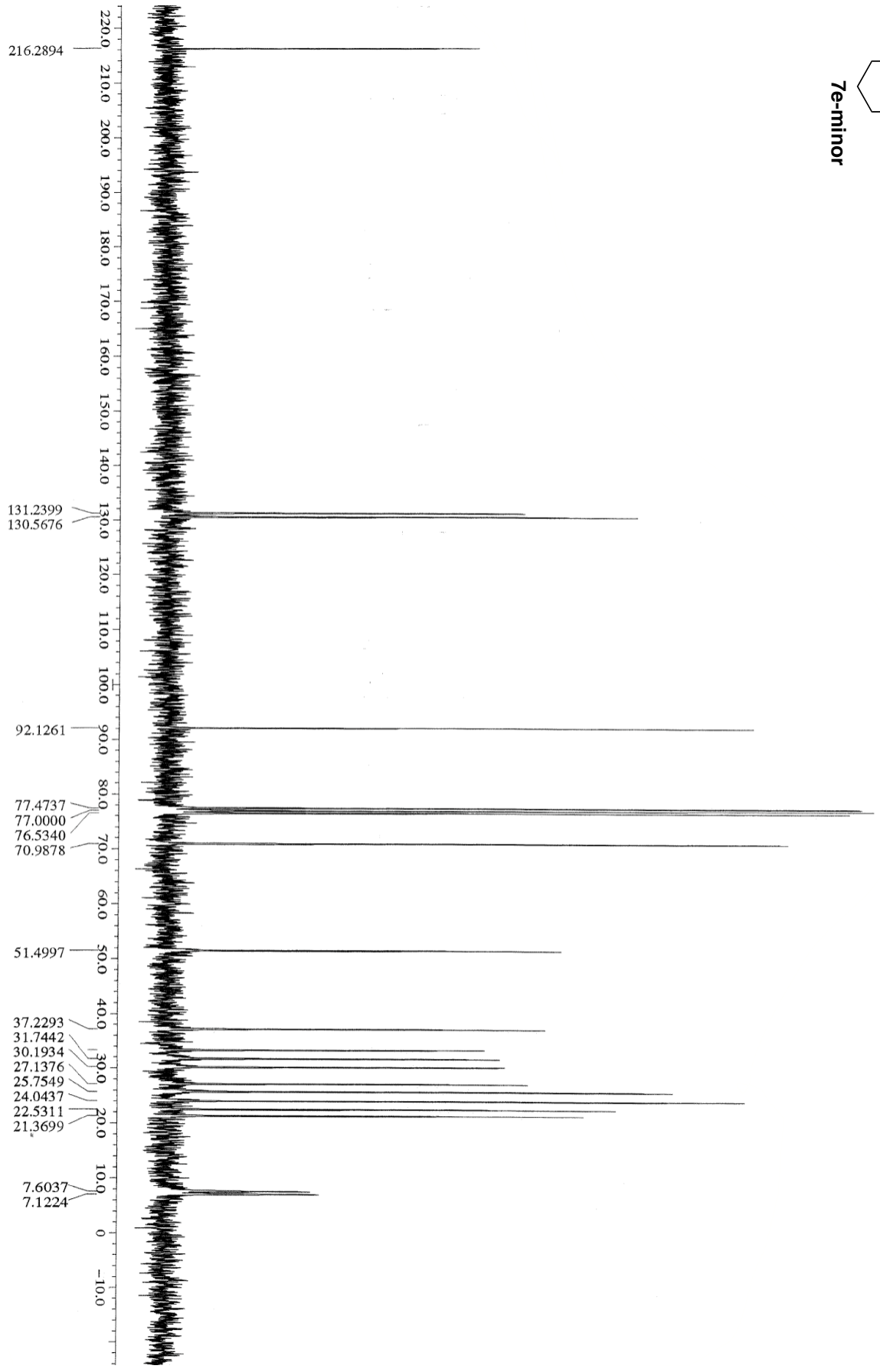
OH
H
Et
COEt

7e-minor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180.0
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150.0
140.0
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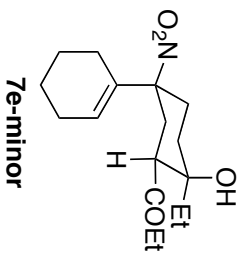
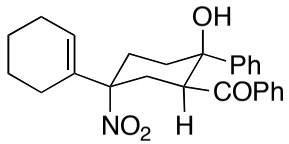
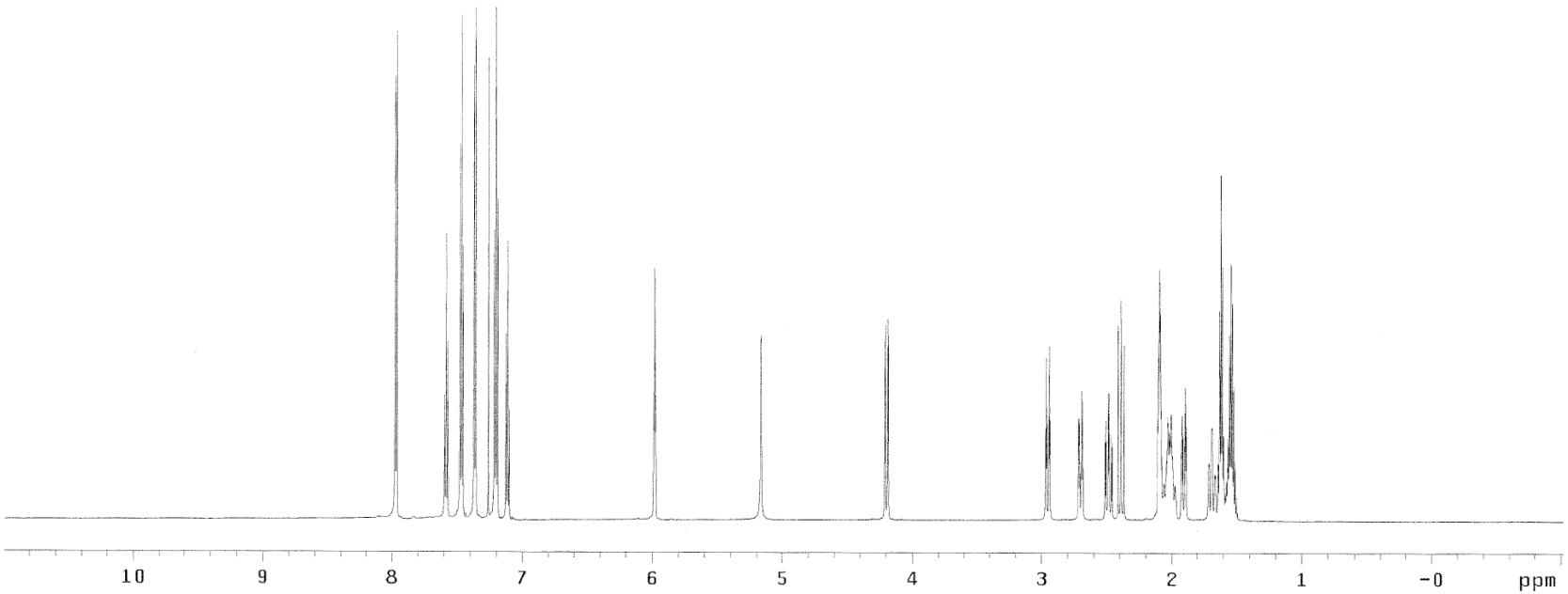
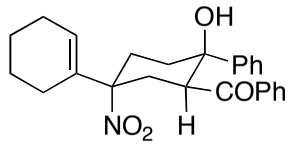

O2N
OH
H
Et
COEt

7e-minor

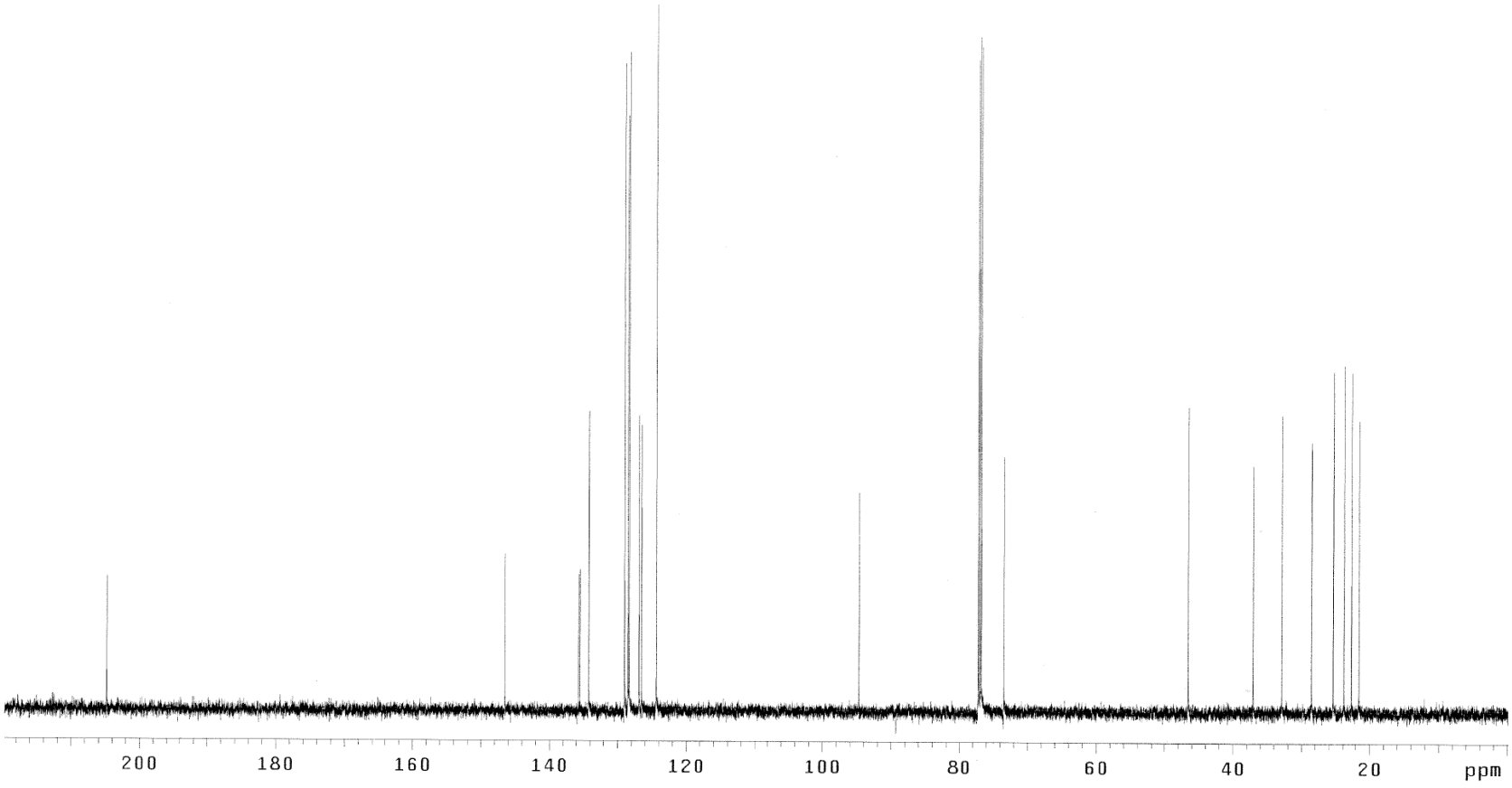


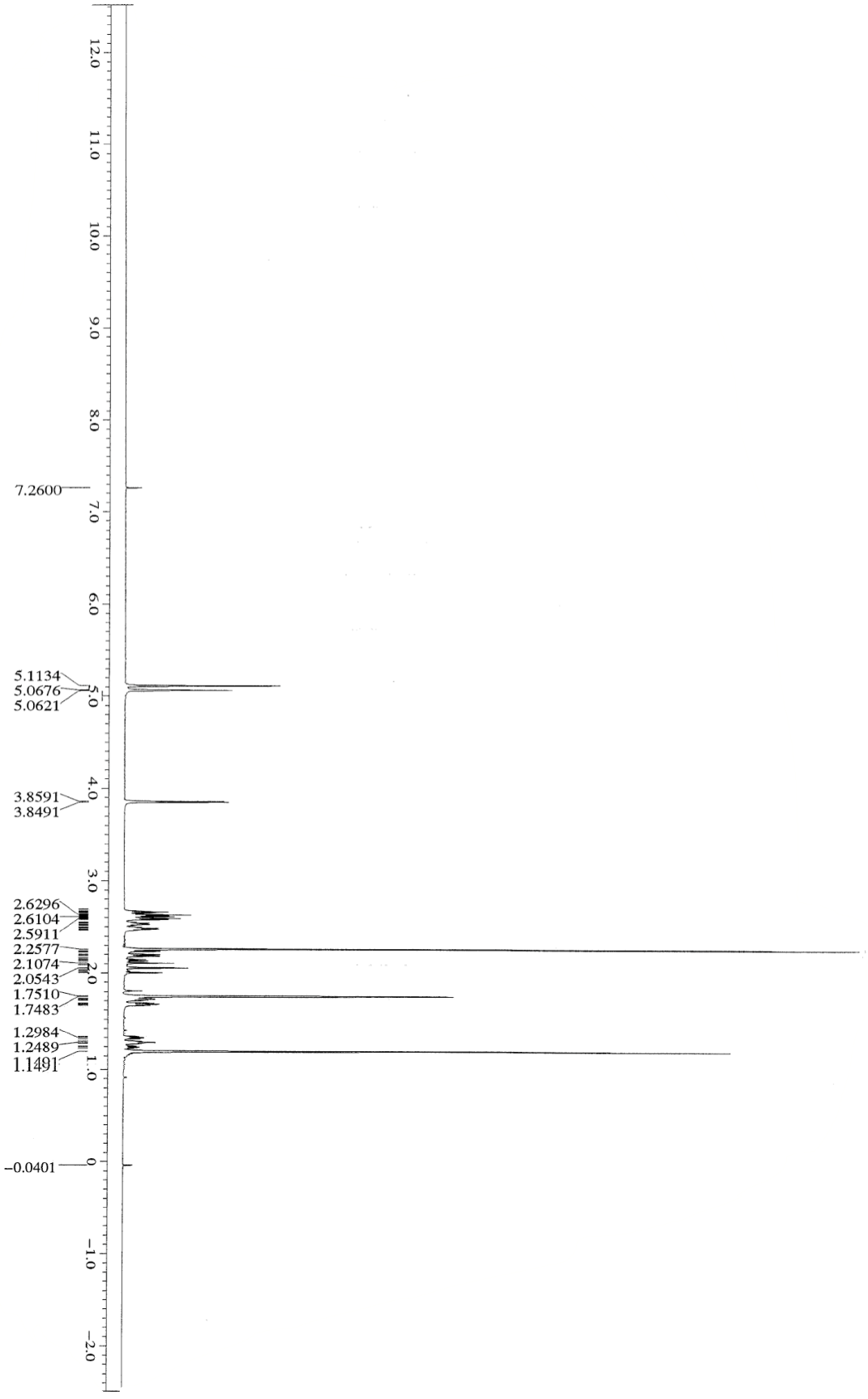
7f-major





7f-major

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2.6296
2.6104
2.5911
2.2577
2.1074
2.0543
1.7510
1.7483
1.2984
1.2489
1.1491
−0.0401
12.0
11.0
10.0
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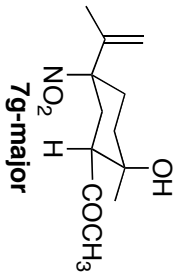
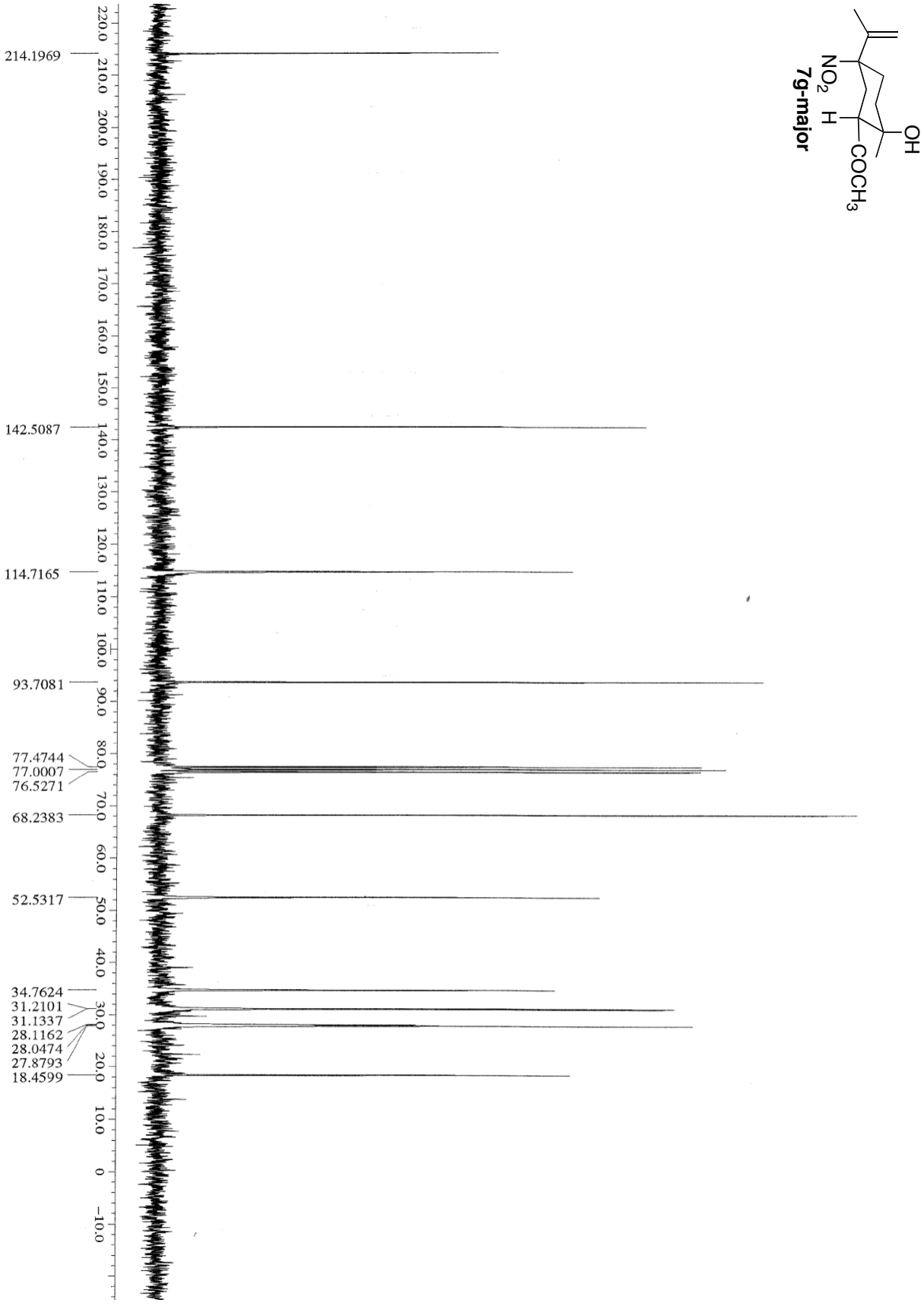
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0


OH
COCH3
NO2 H

7g-major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77.0007
76.5271
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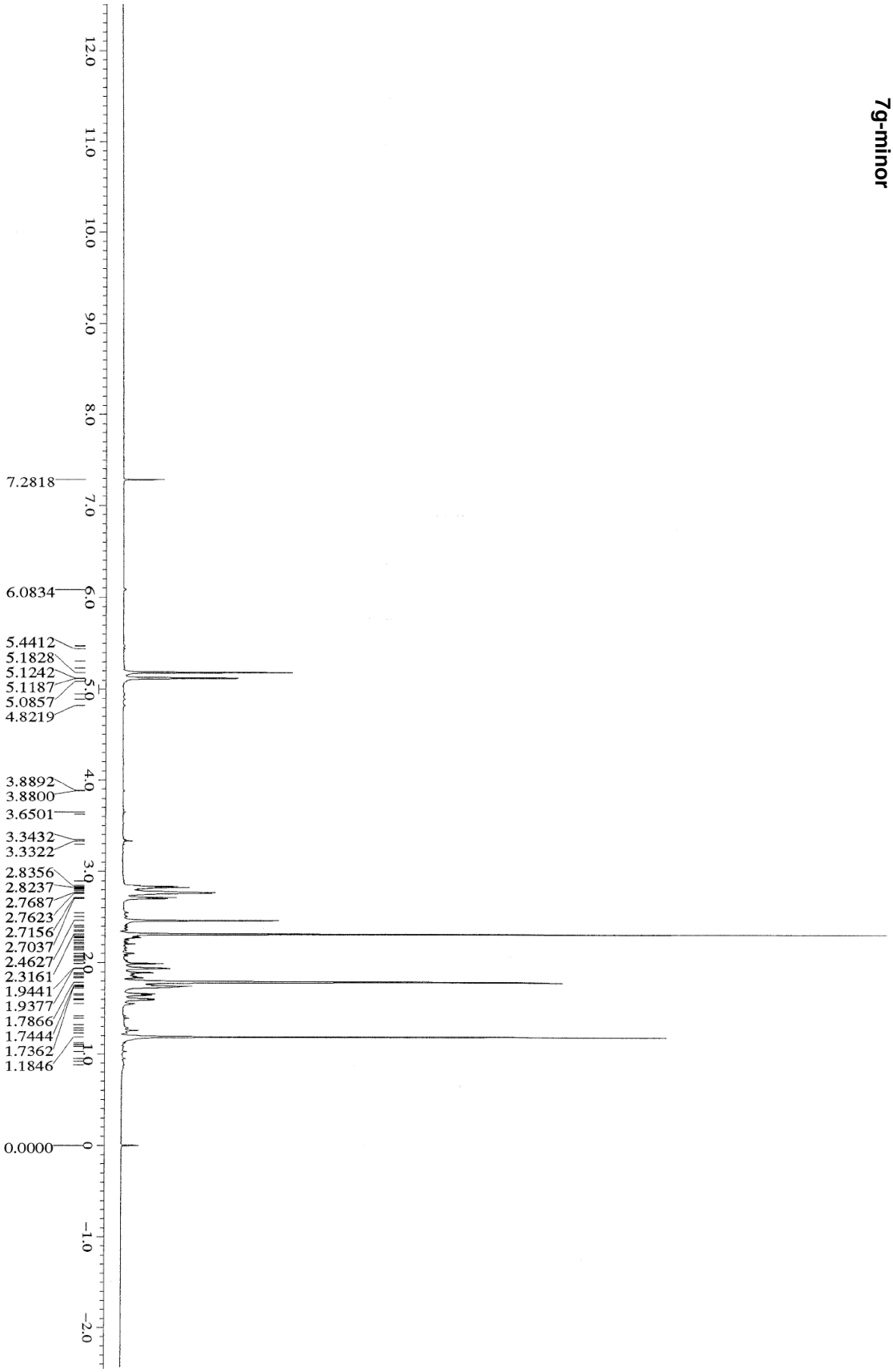
52.5317
34.7624
31.2101
31.1337
28.1162
28.0474
27.8793
18.4599
NO2
H
COCH3
OH
7g-major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5.0857
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3.3432
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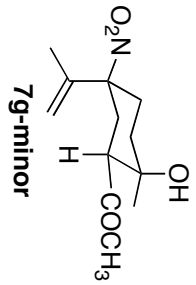
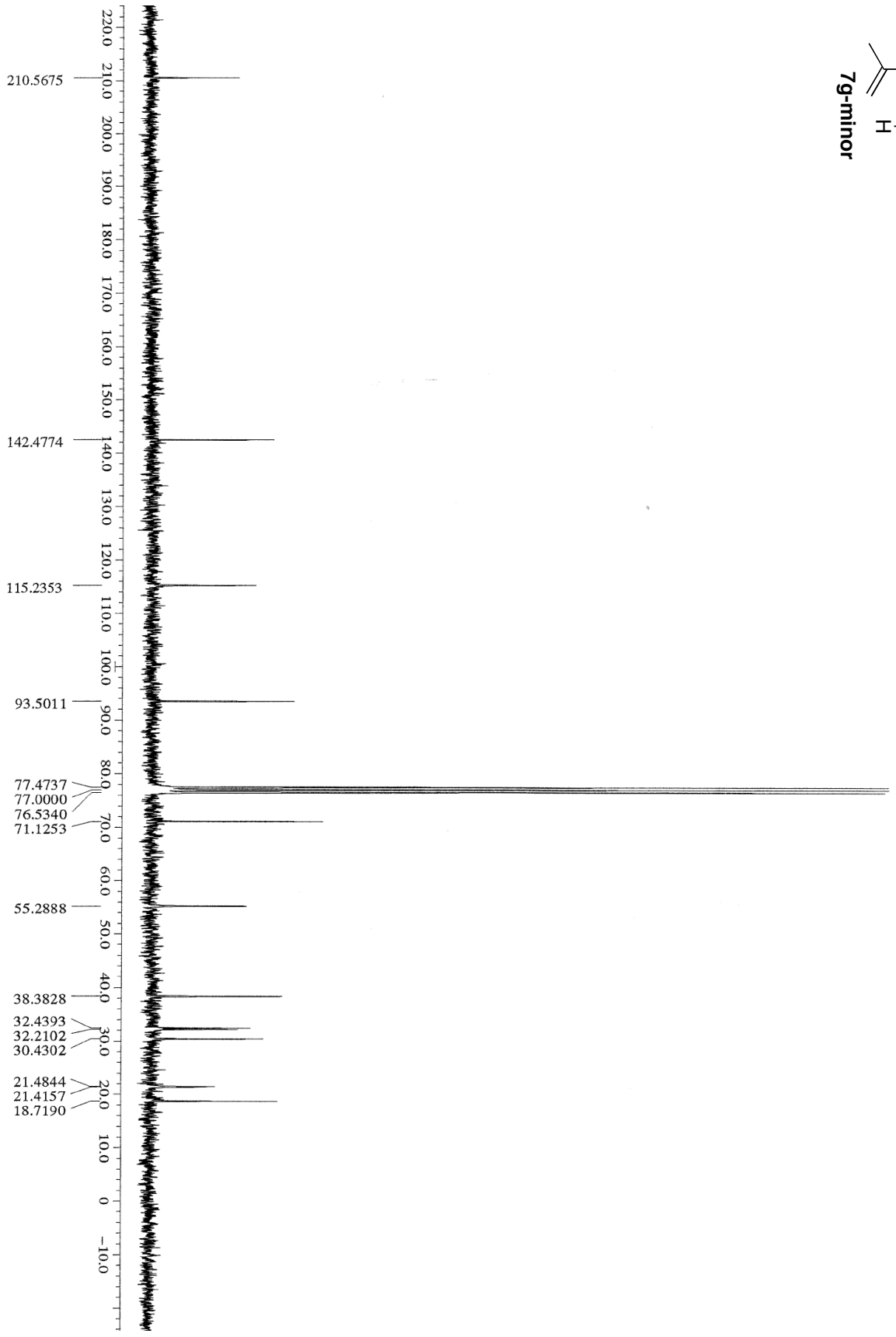
−1.0
−2.0


O2N
OH
H
COCH3

7g-minor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21.4157
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120.0
110.0
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30.0
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10.0
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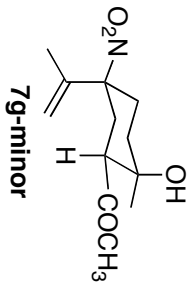
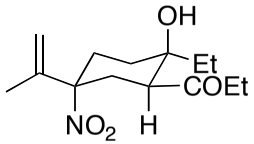
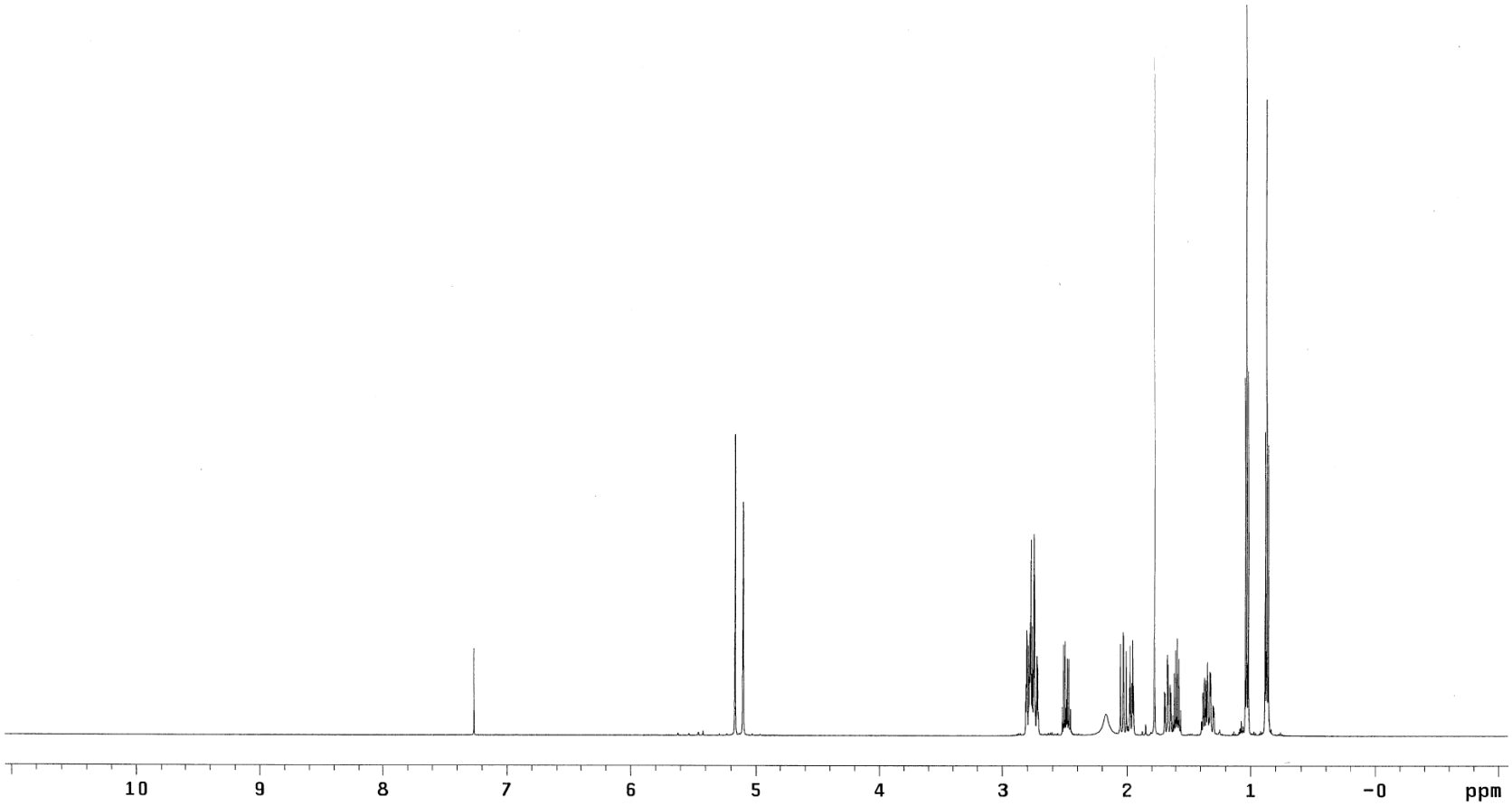
−10.0

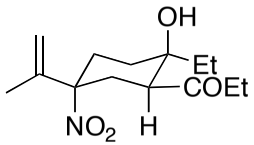

O2N
OH
H
COCH3

7g-minor



7h-major





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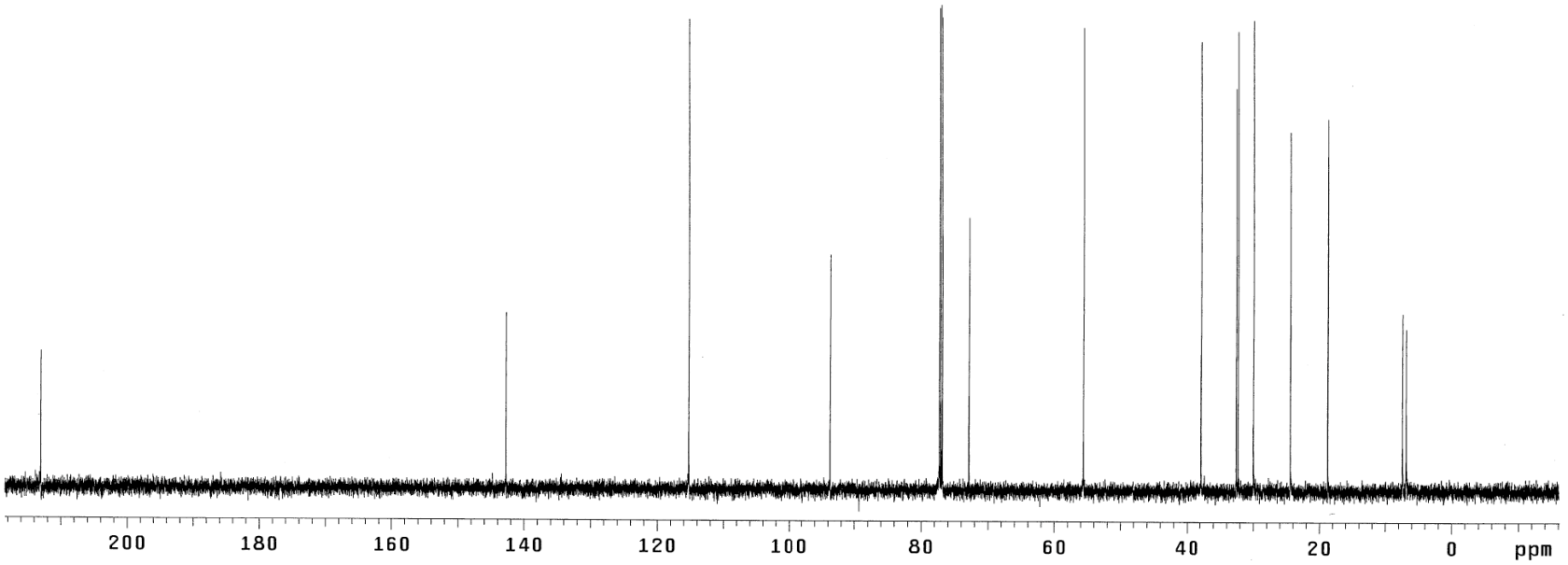
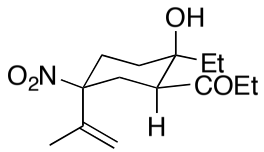
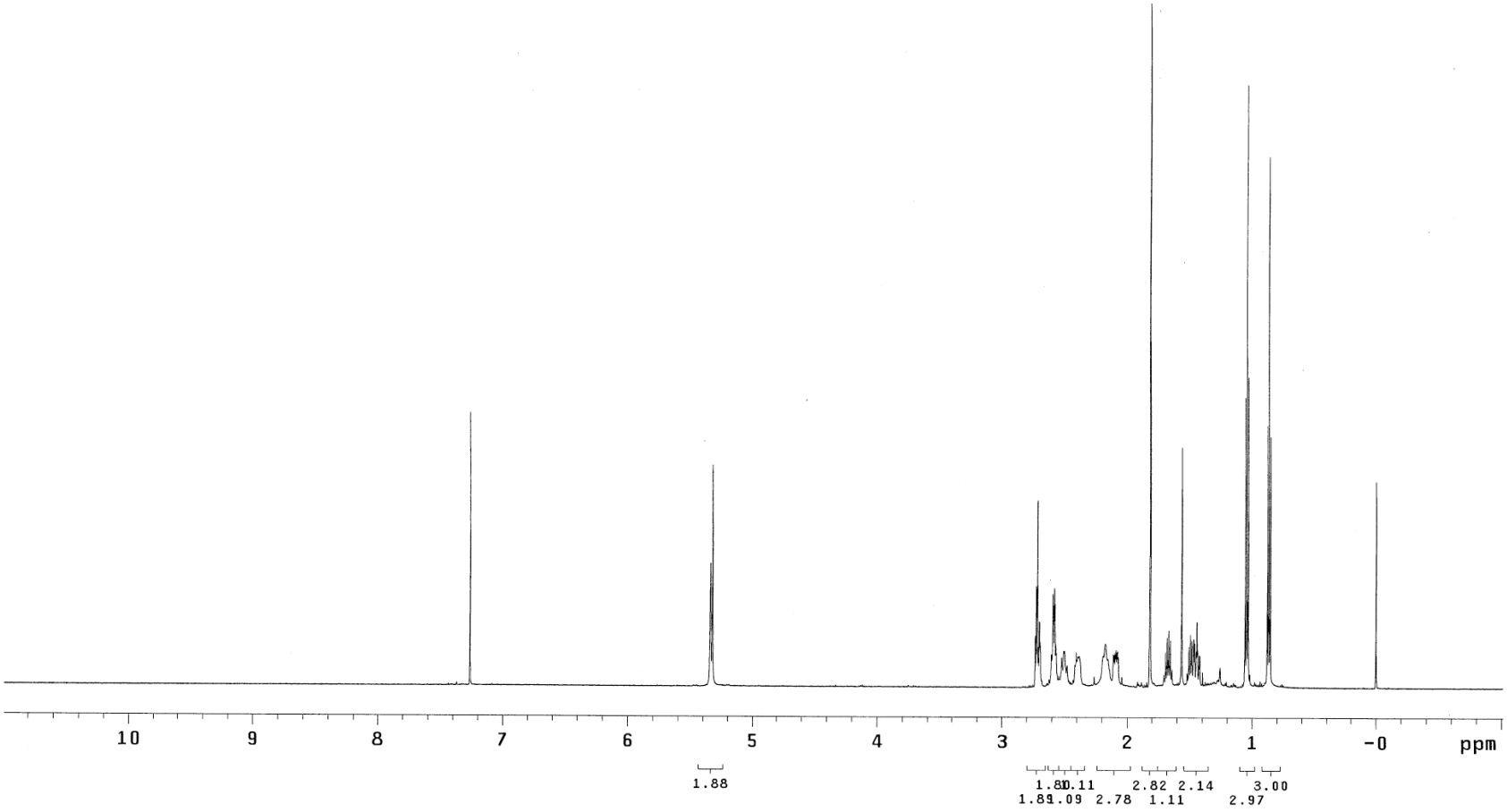



OH
Et
O_2N
COEt
H

7h-minor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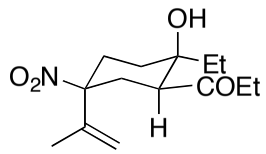
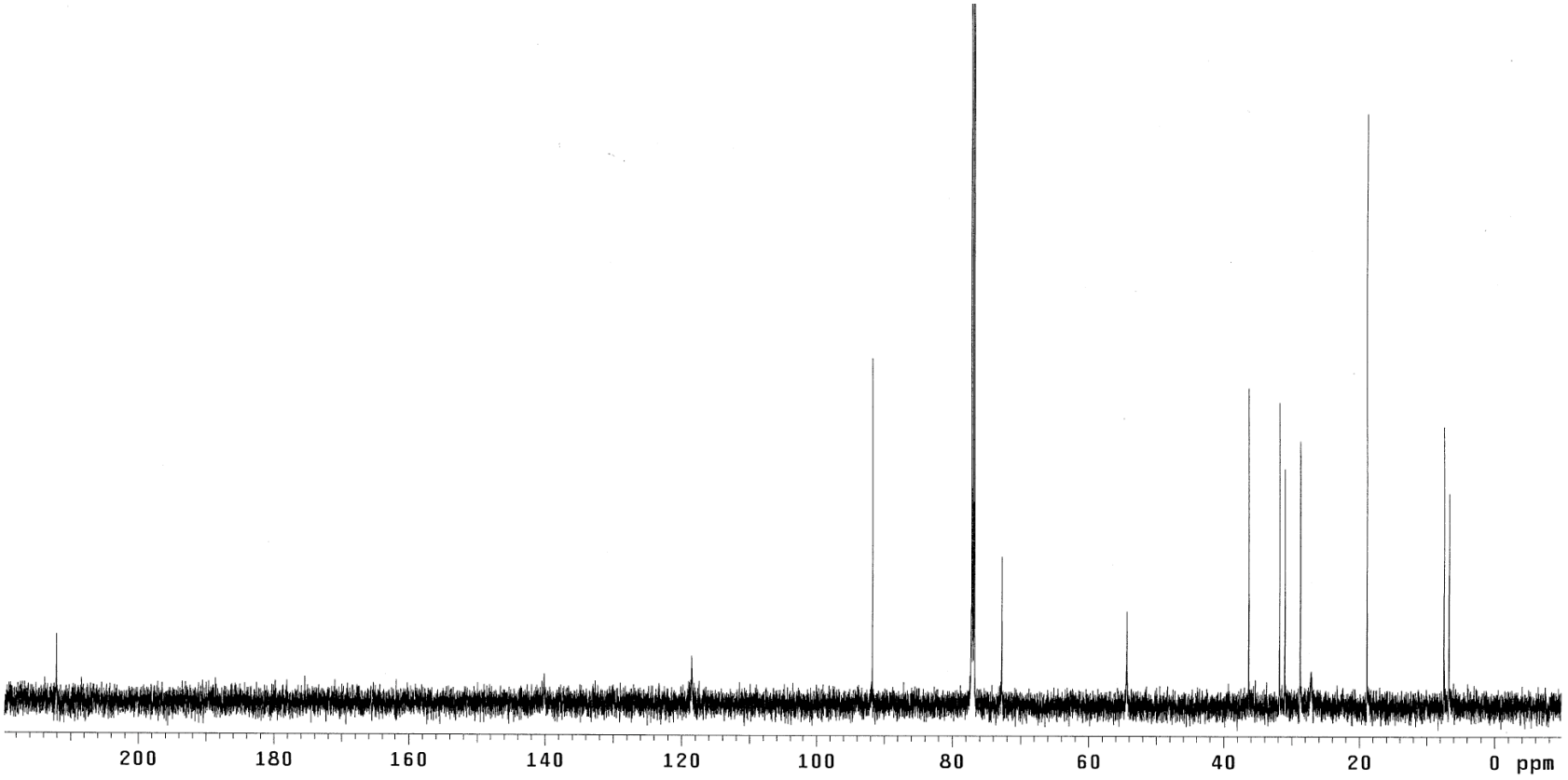
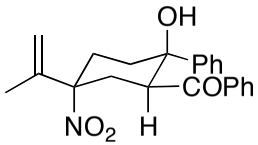
1.89
1.80
1.09
0.11
2.78
2.82
1.11
2.14
2.97
3.00

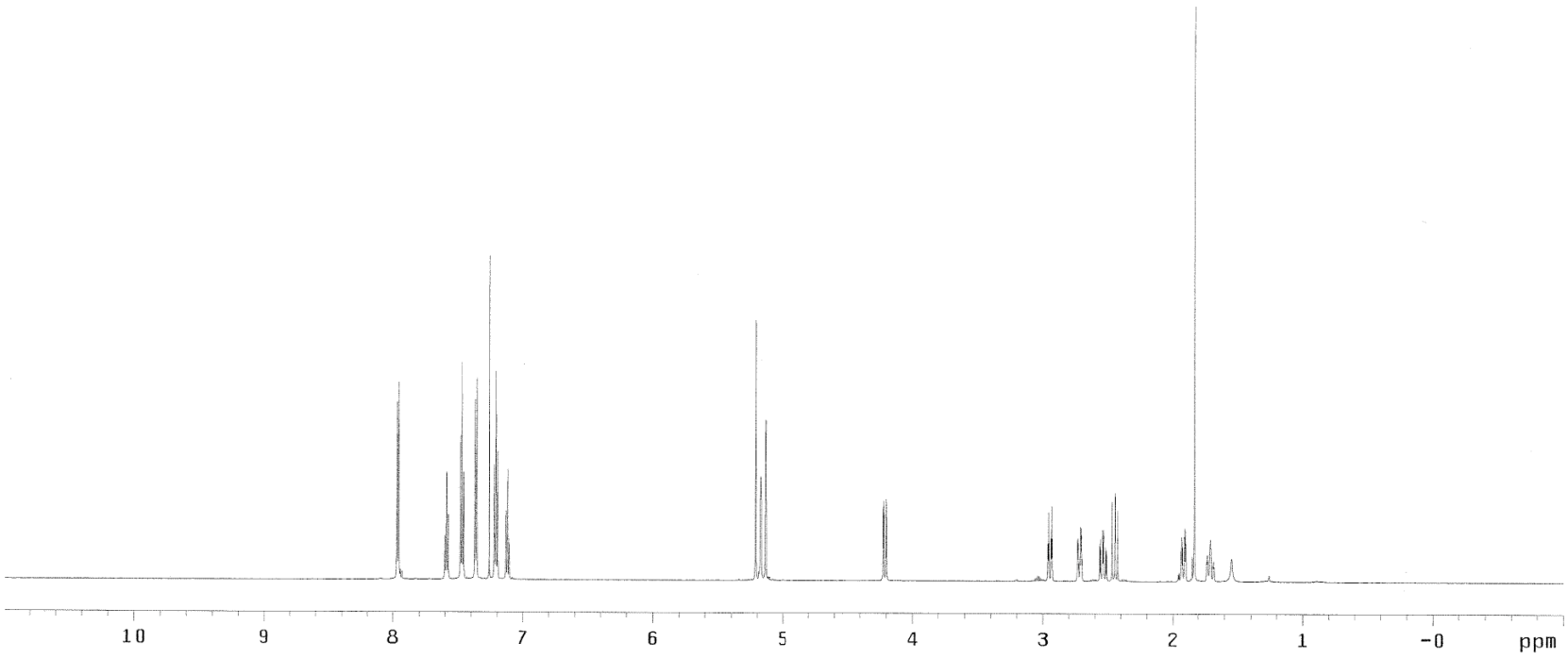


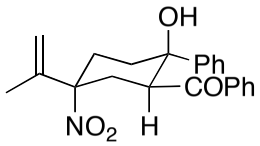
7h-minor



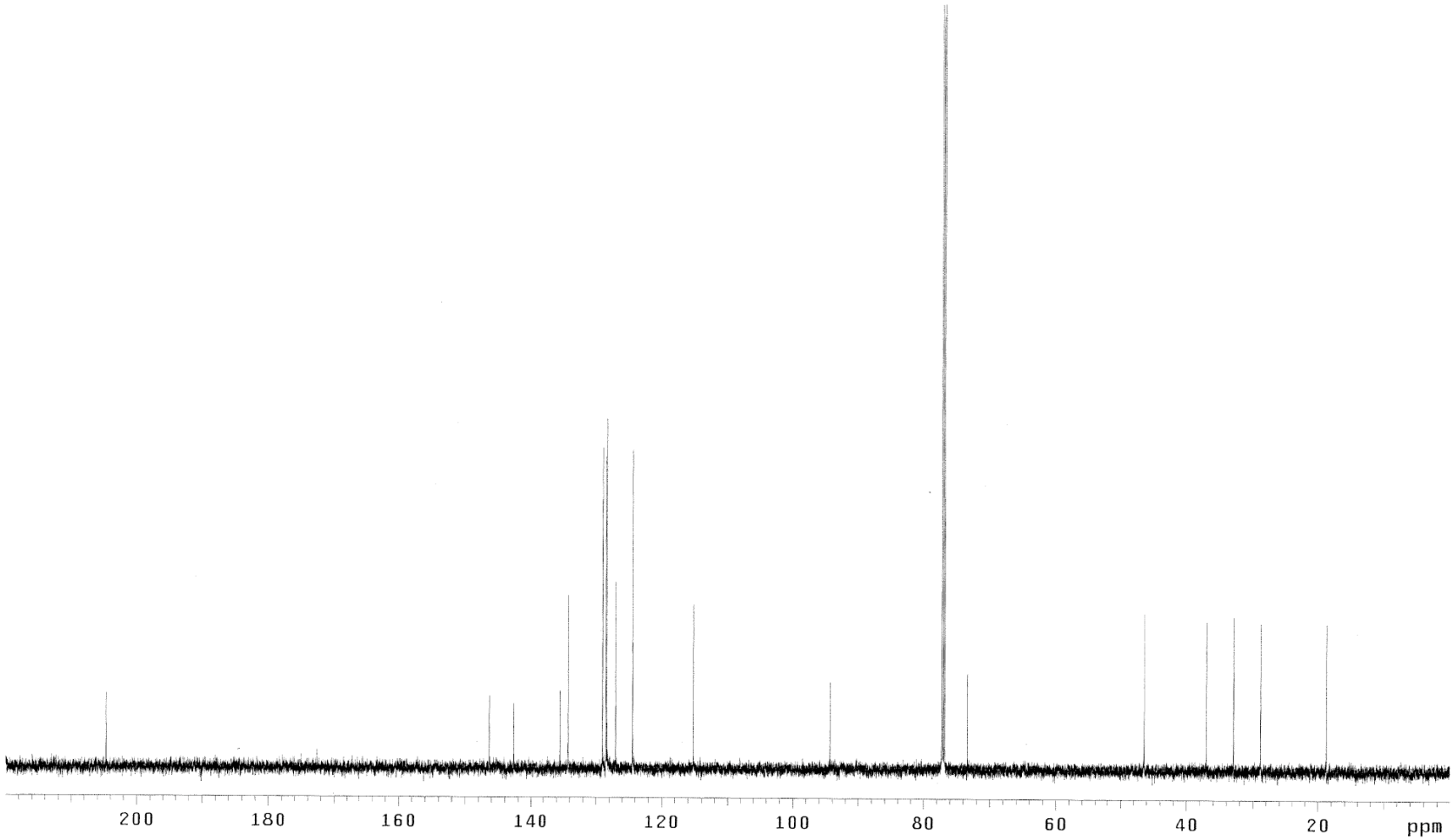


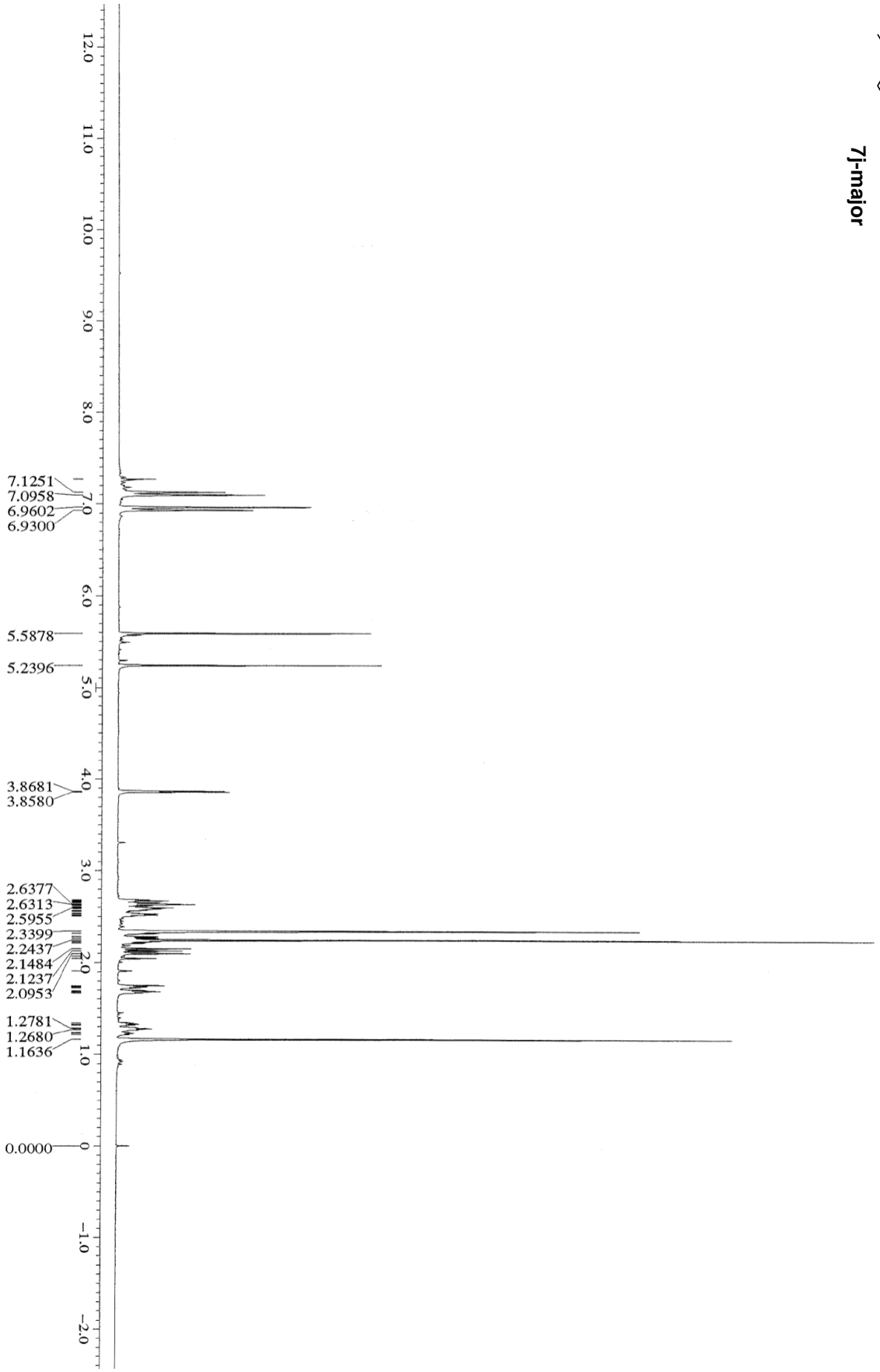
7i-major





7i-major

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2.2437
2.1484
2.1237
2.0953
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1.1636
0.0000
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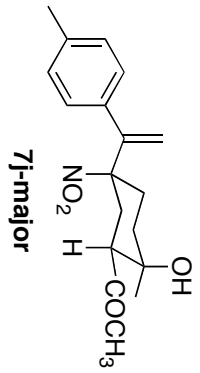
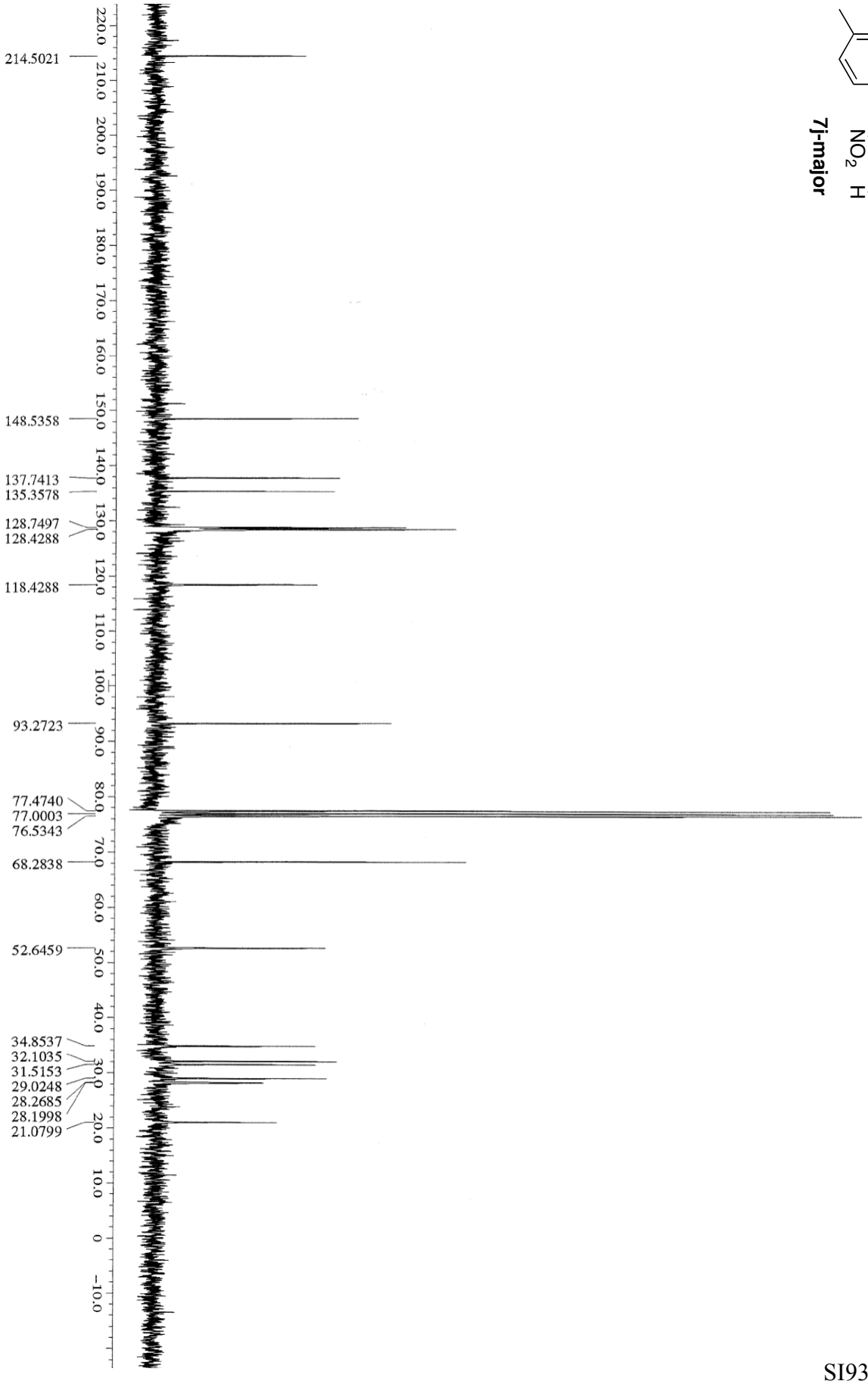
-2.0


NO2
H
OH
COCH3

7j-major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120.0
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100.0
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80.0
70.0
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30.0
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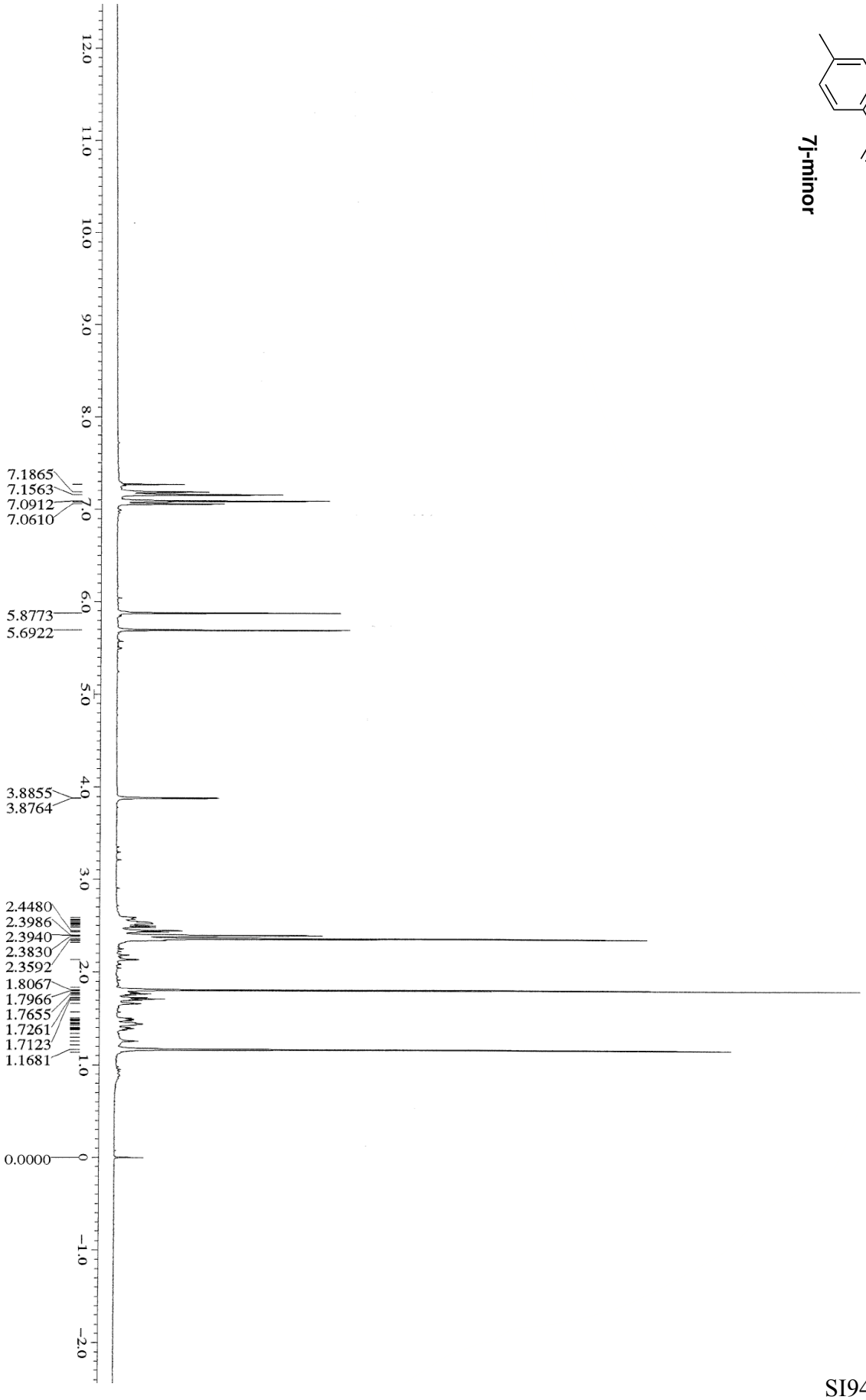
10.0
0
-10.0
NO2
H
OH
COCH3
7j-major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1.1681
0.0000
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8.0
7.0
6.0
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2.0
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0
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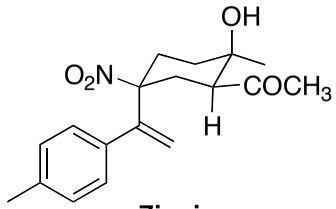
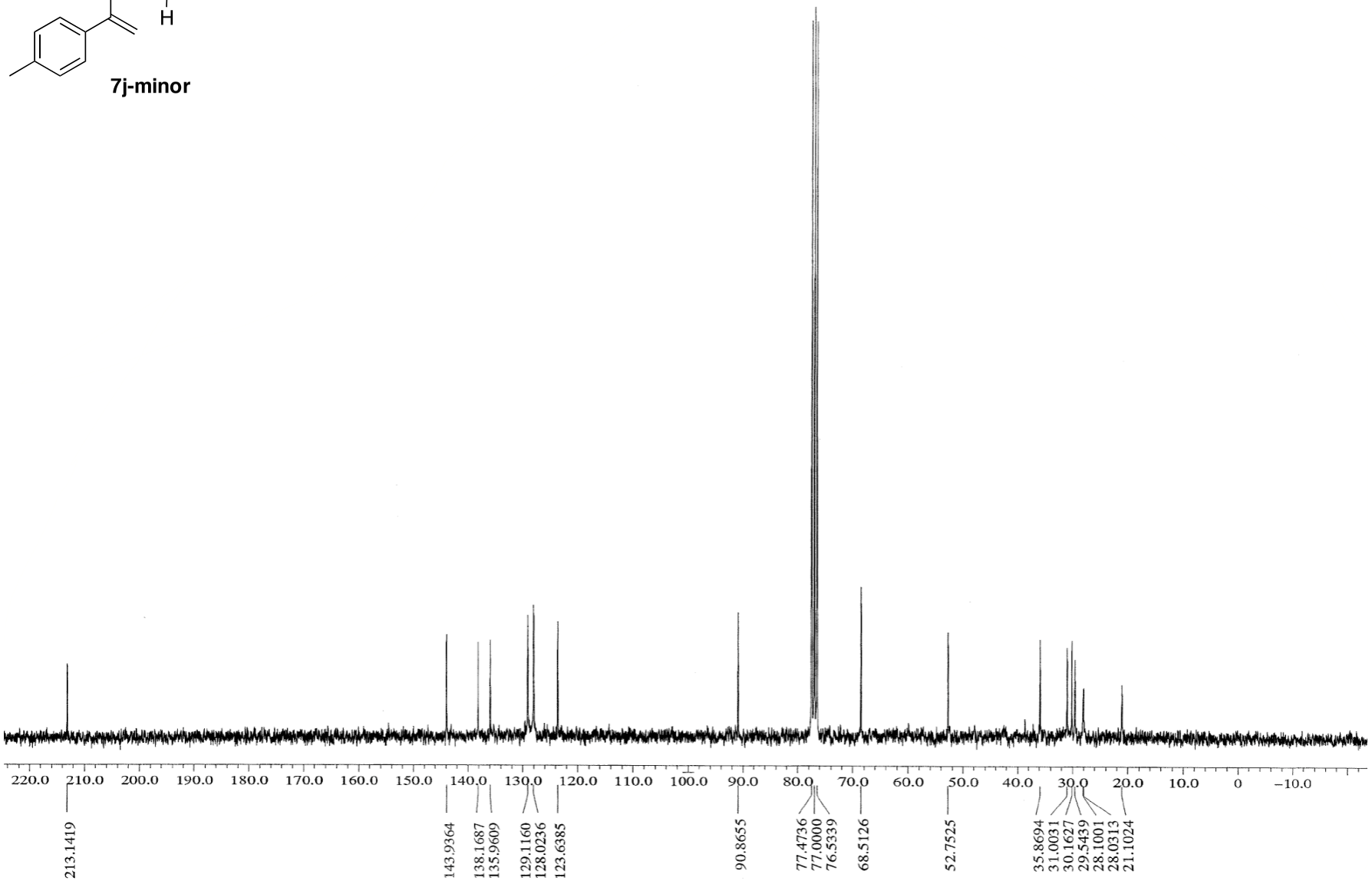
−2.0
O2N
OH
H
COCH3
7j-minor


OH
O_2N
$COCH_3$
H

7j-minor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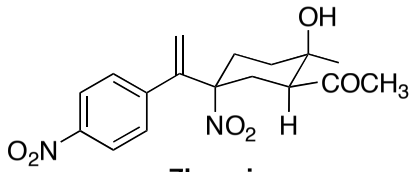
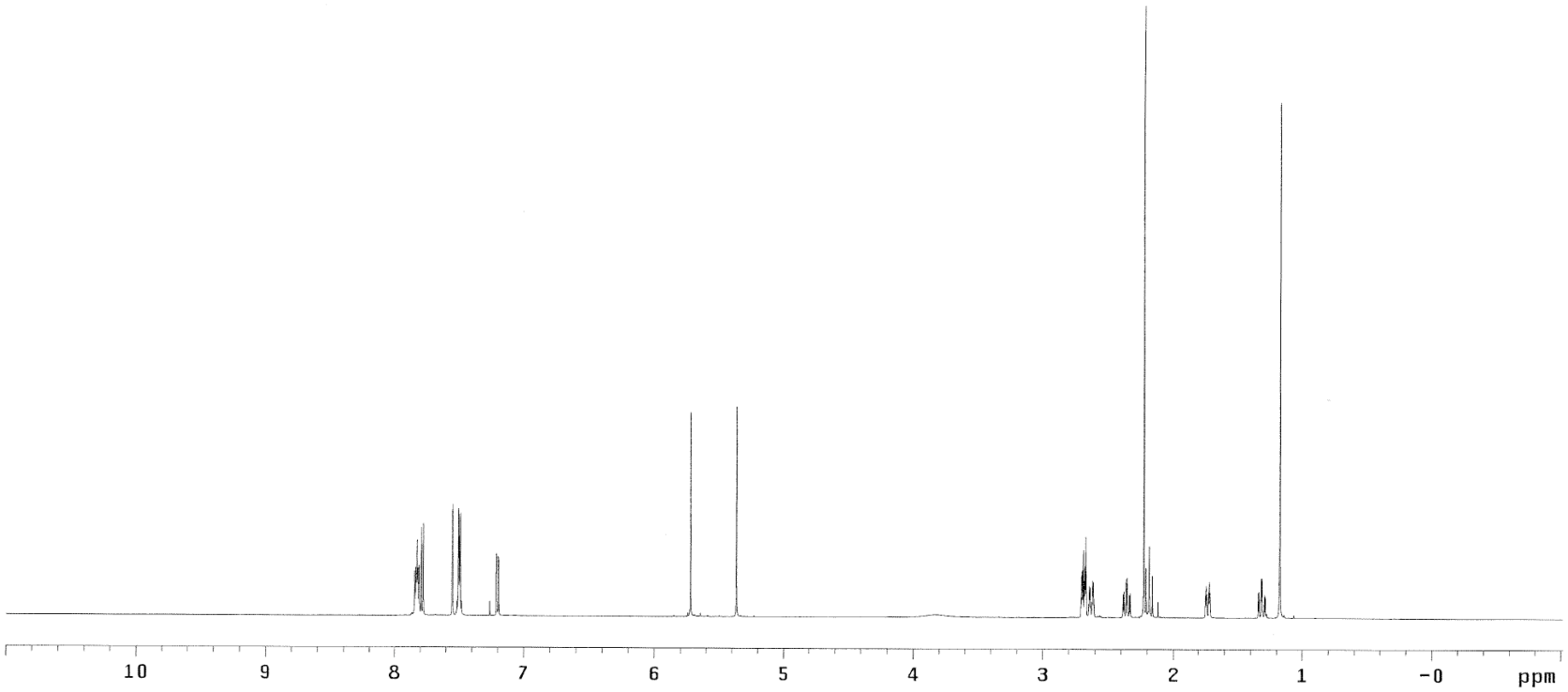
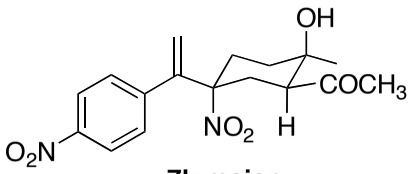
21.1024

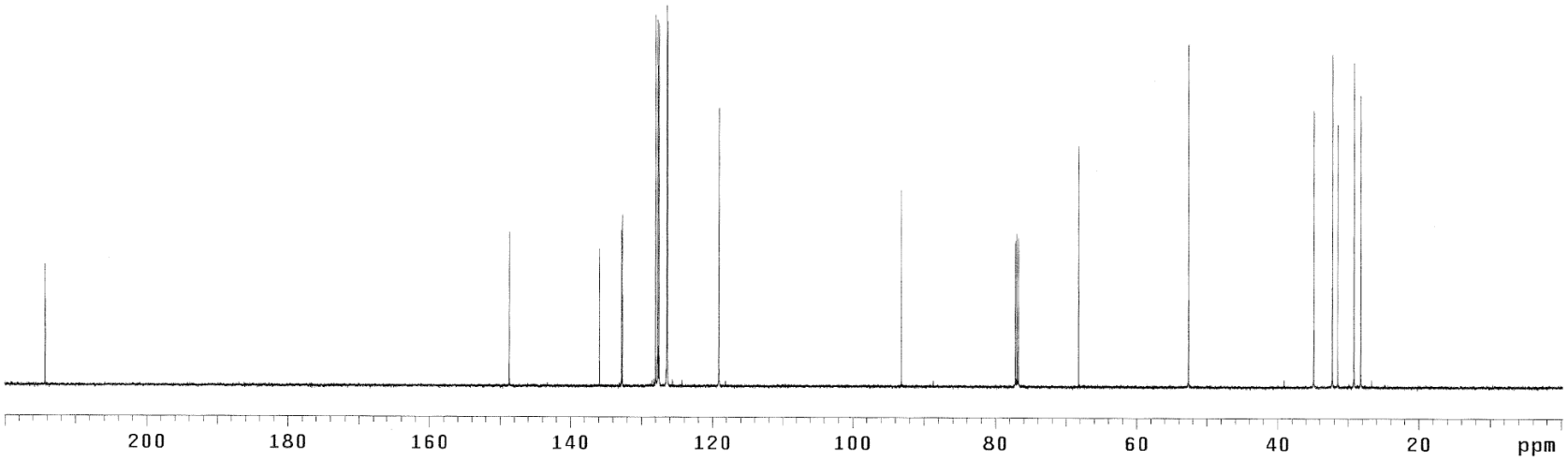


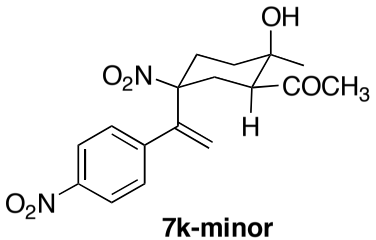
7k-major



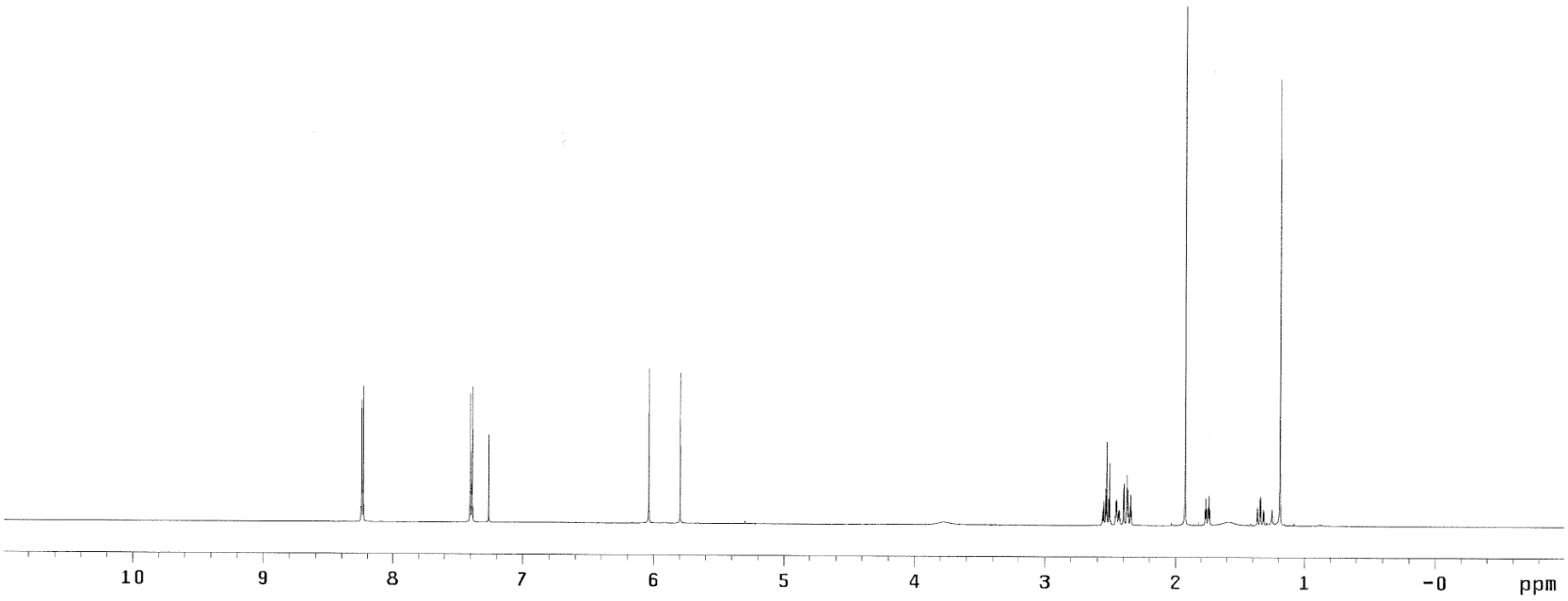


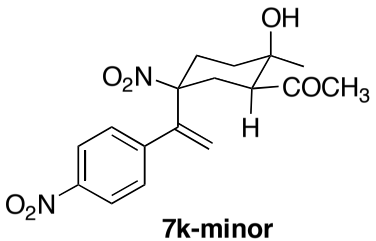
7k-major





7k-minor





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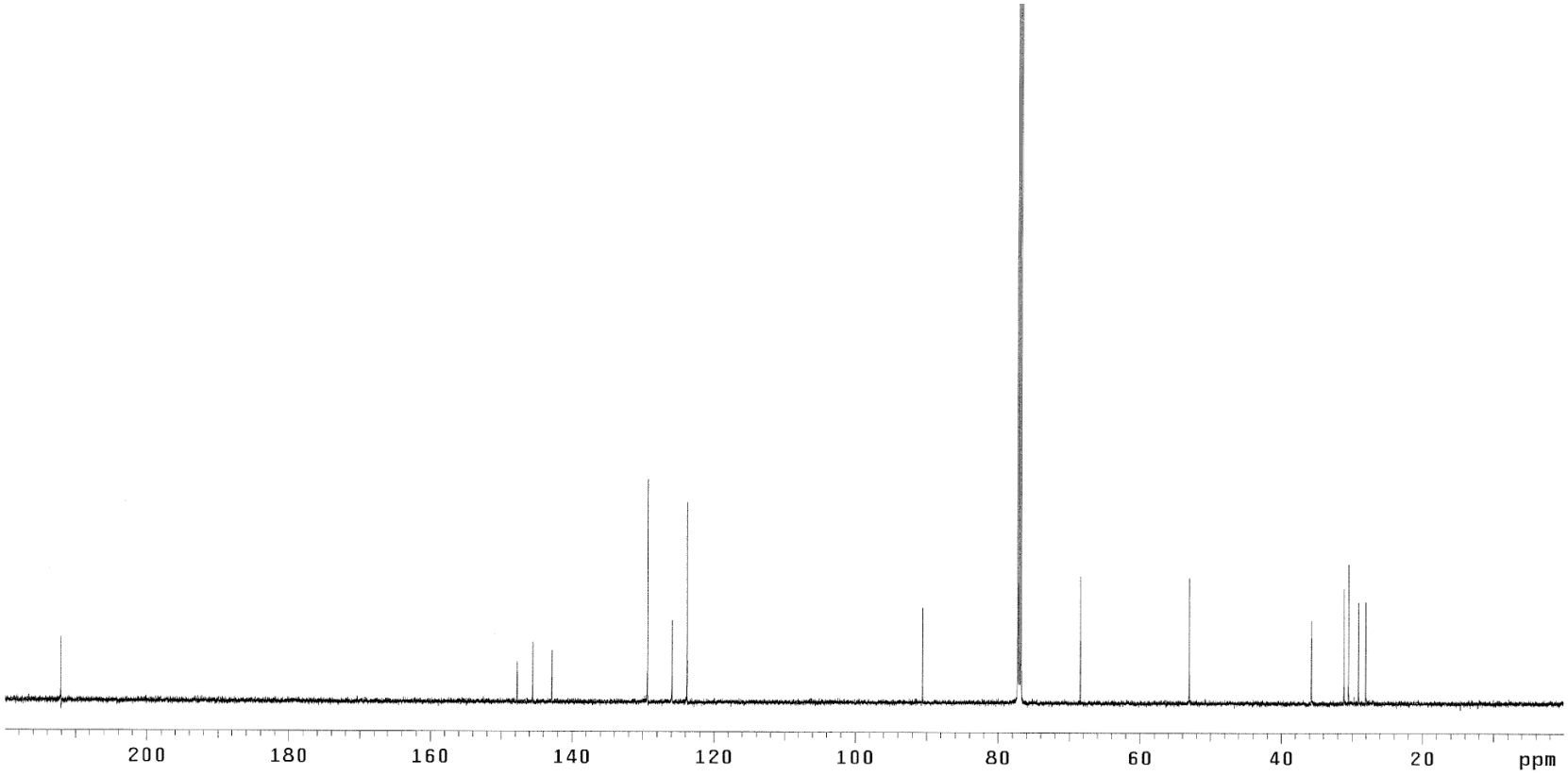

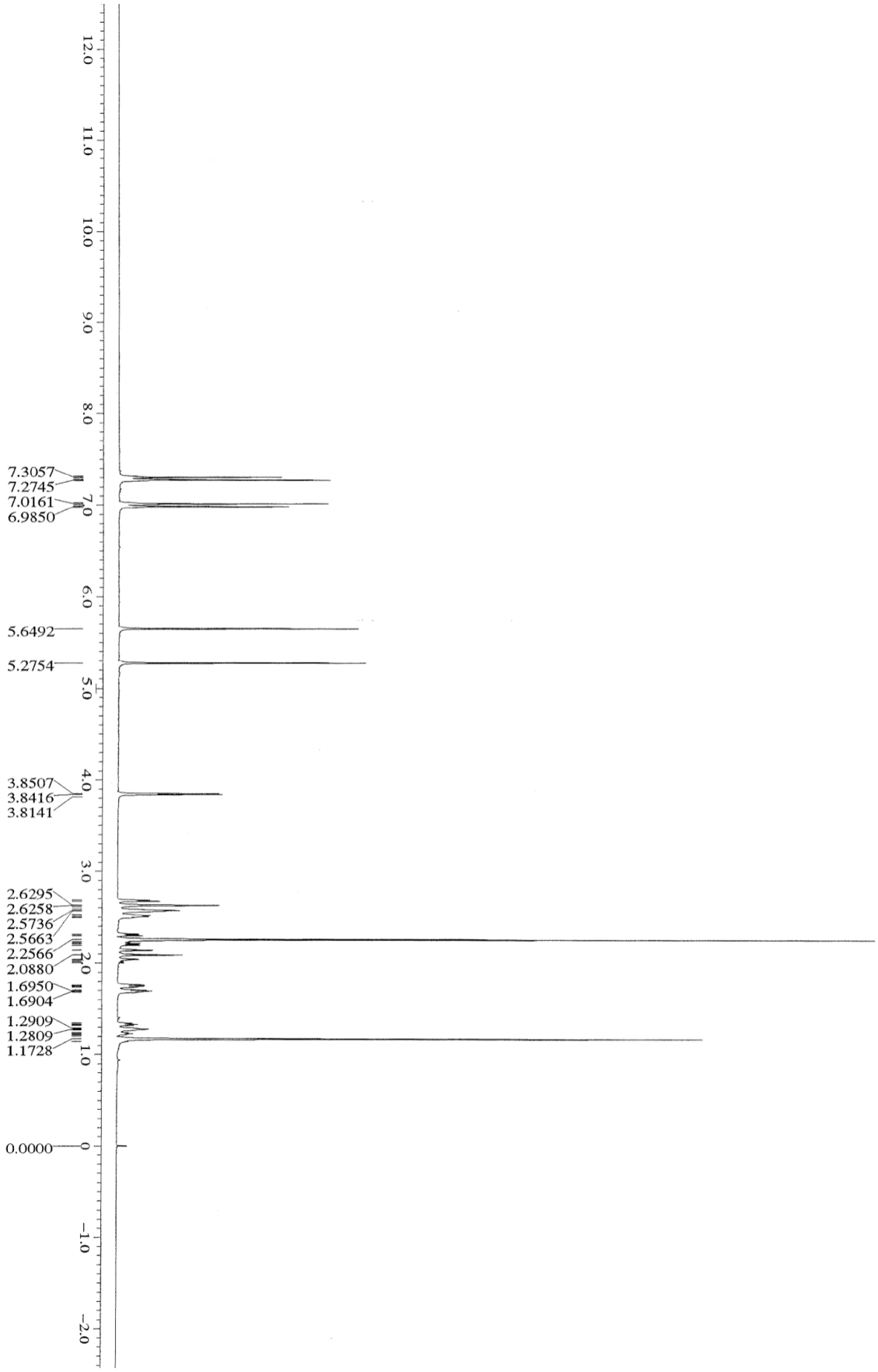
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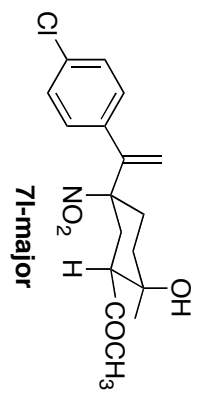
Cl
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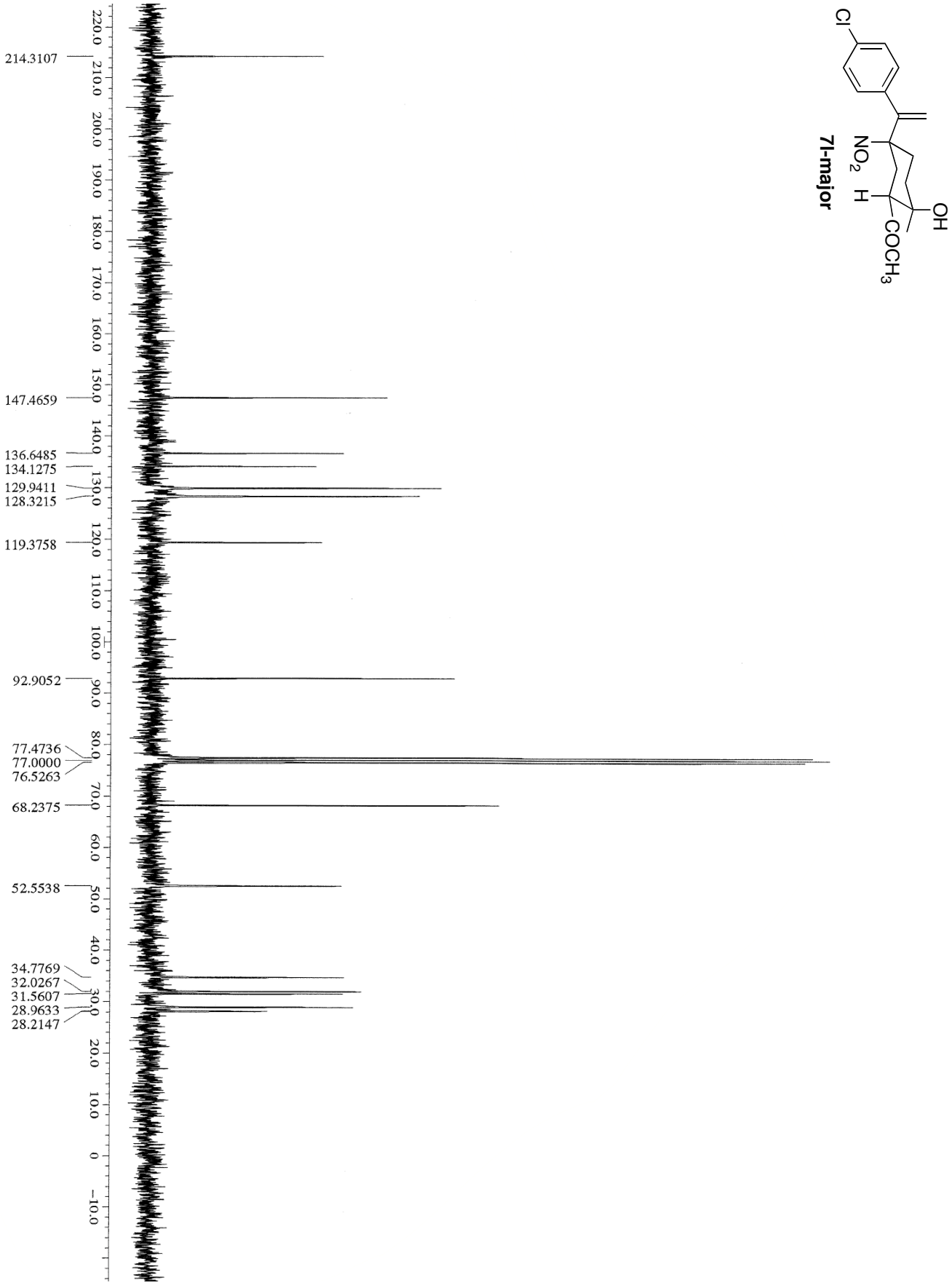
H
OH
COCH3

7l-major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68.2375
52.5538
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31.5607
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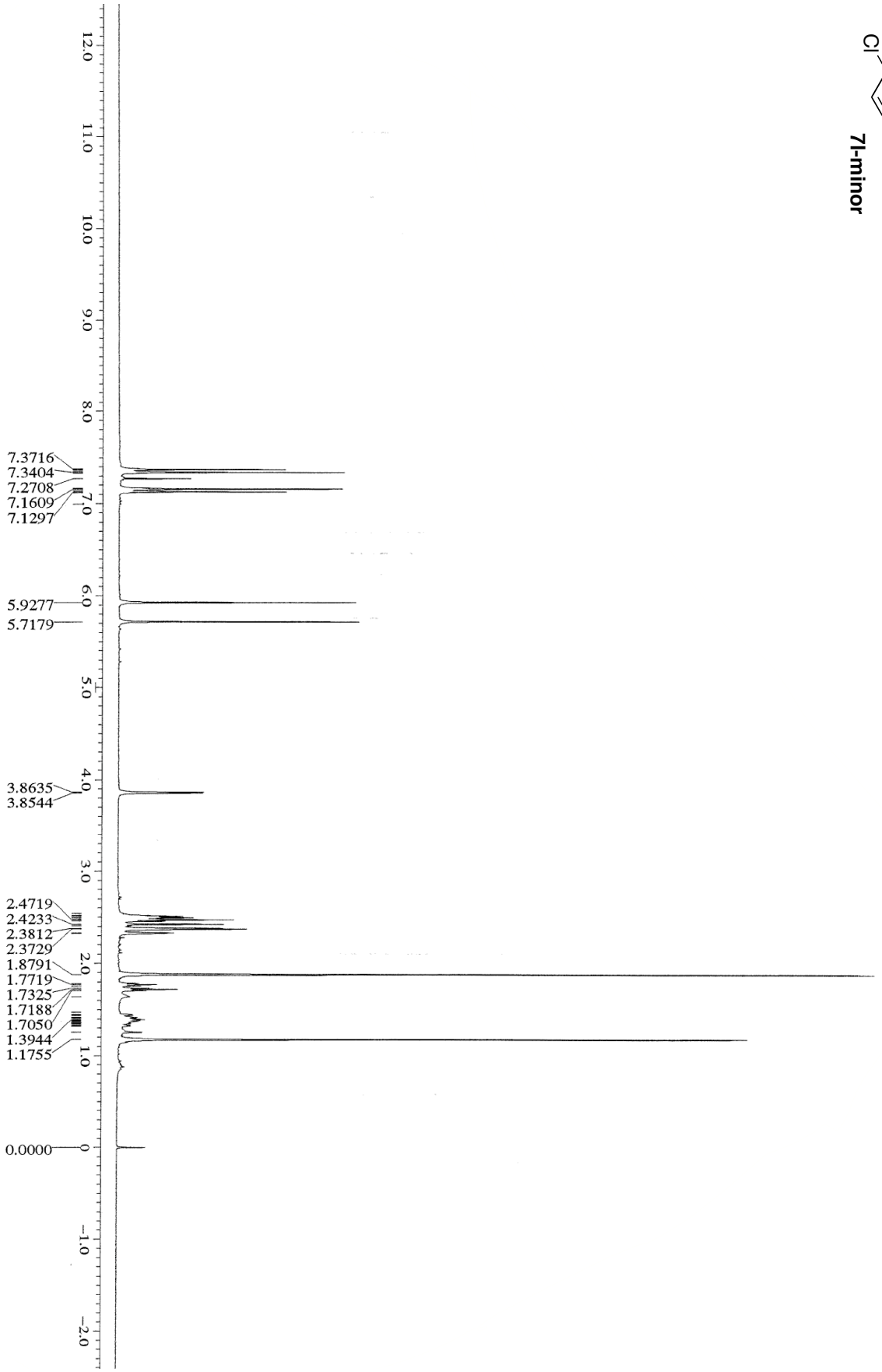
28.2147
Cl
NO2
H
OH
COCH3
7l-major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3.8544
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2.3812
2.3729
1.8791
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10.0
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6.0
5.0
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3.0
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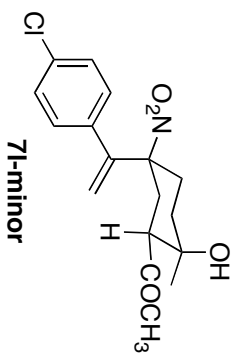
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O2N
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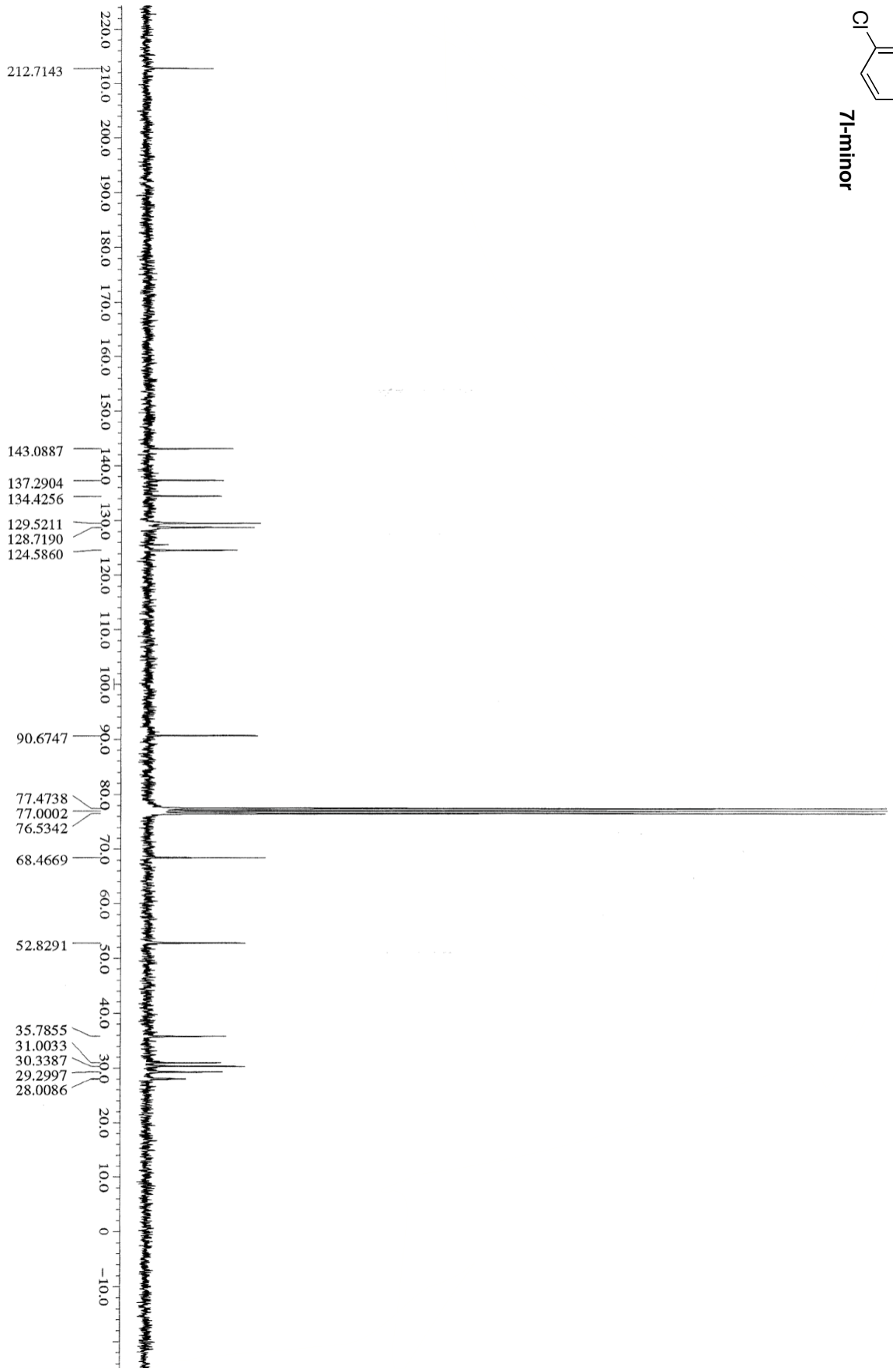
H
COCH3

7l-minor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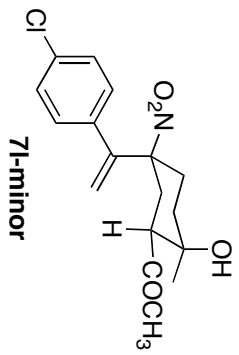
Cl
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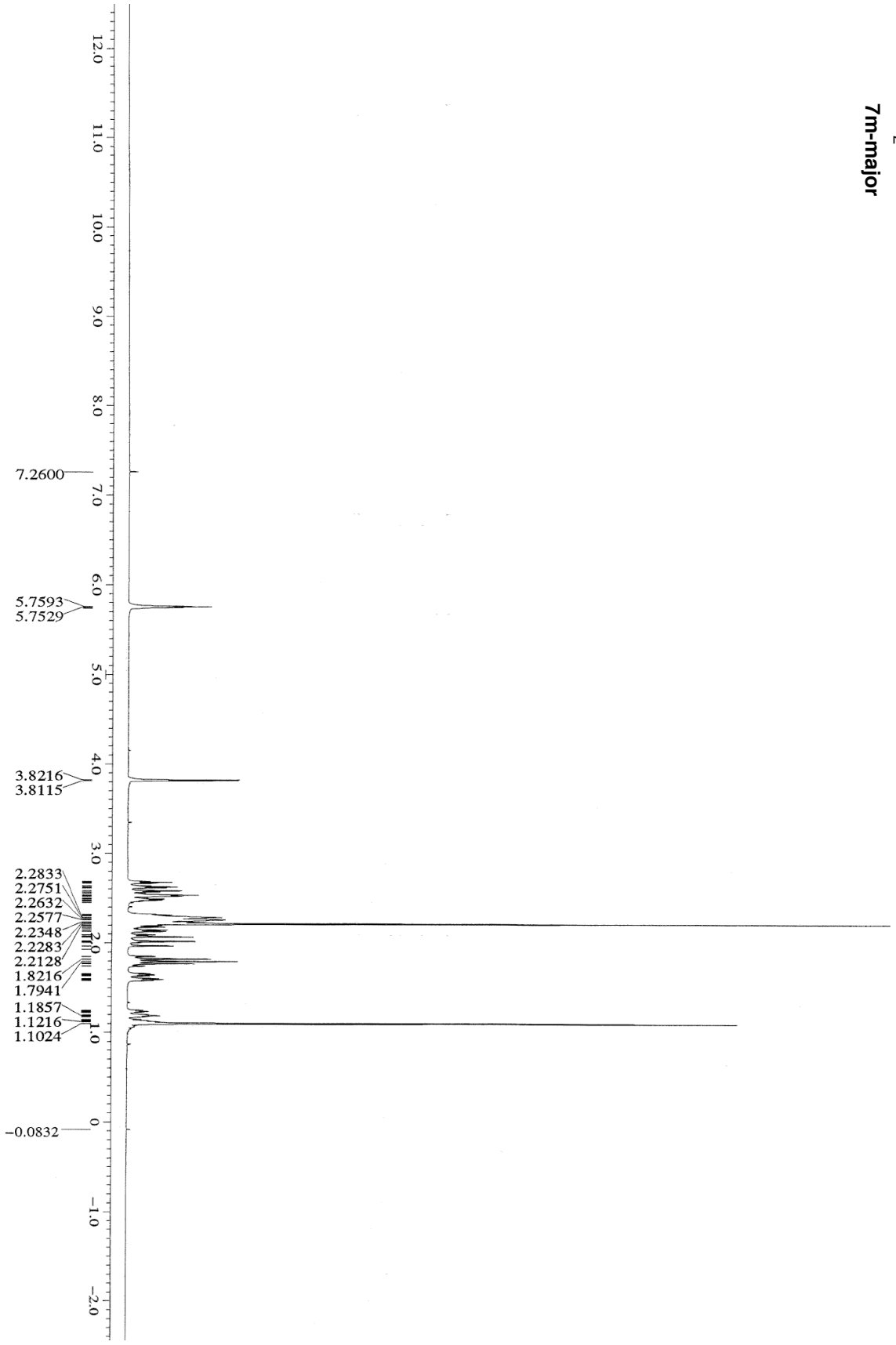
H
OH
COCH3

7l-minor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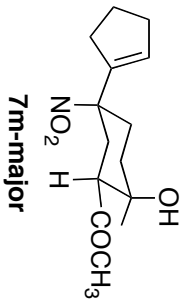
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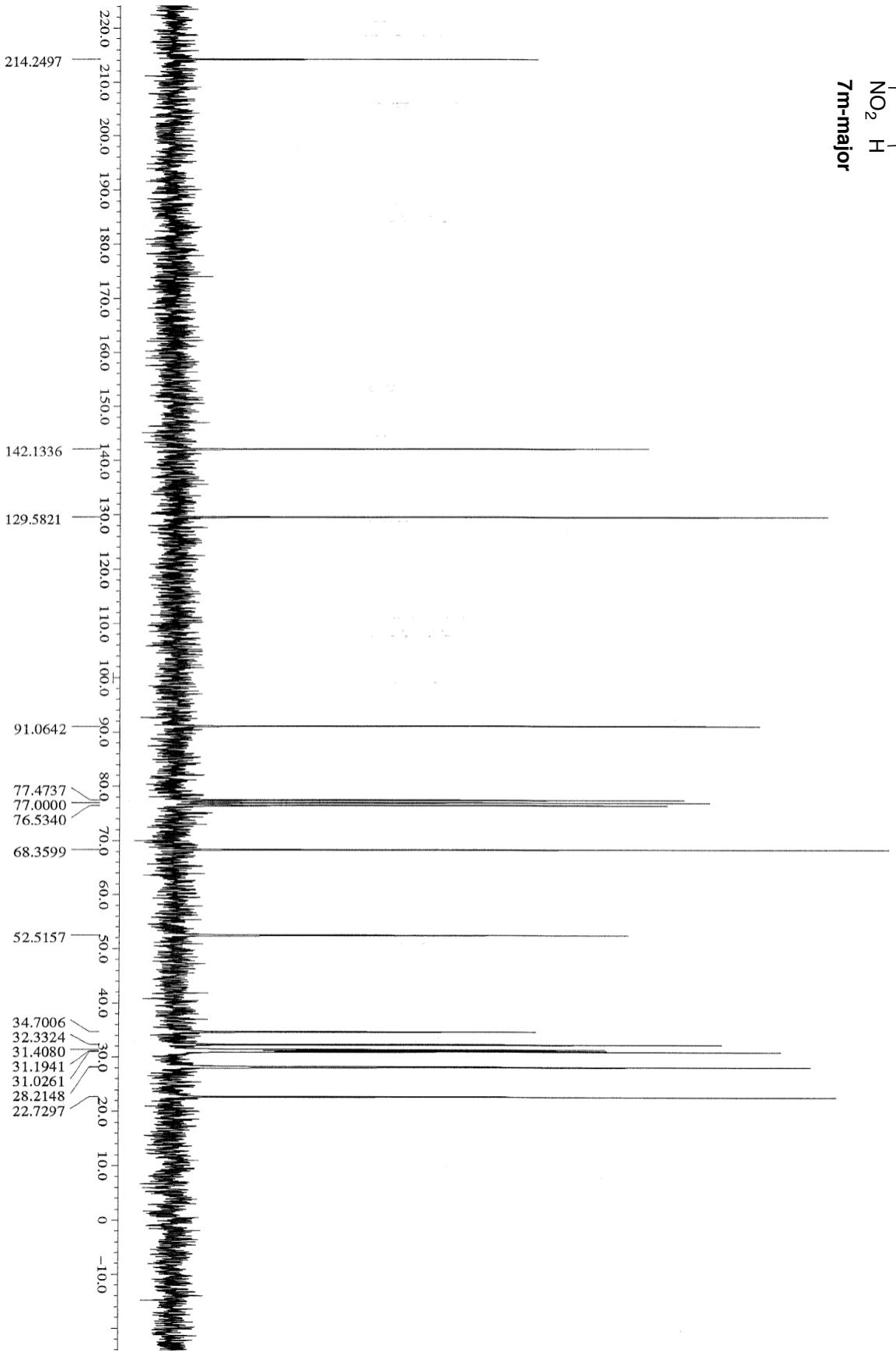
H
OH
COCH3

7m-major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130.0
120.0
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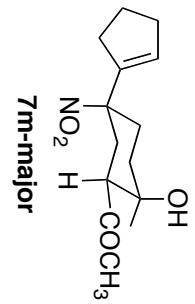
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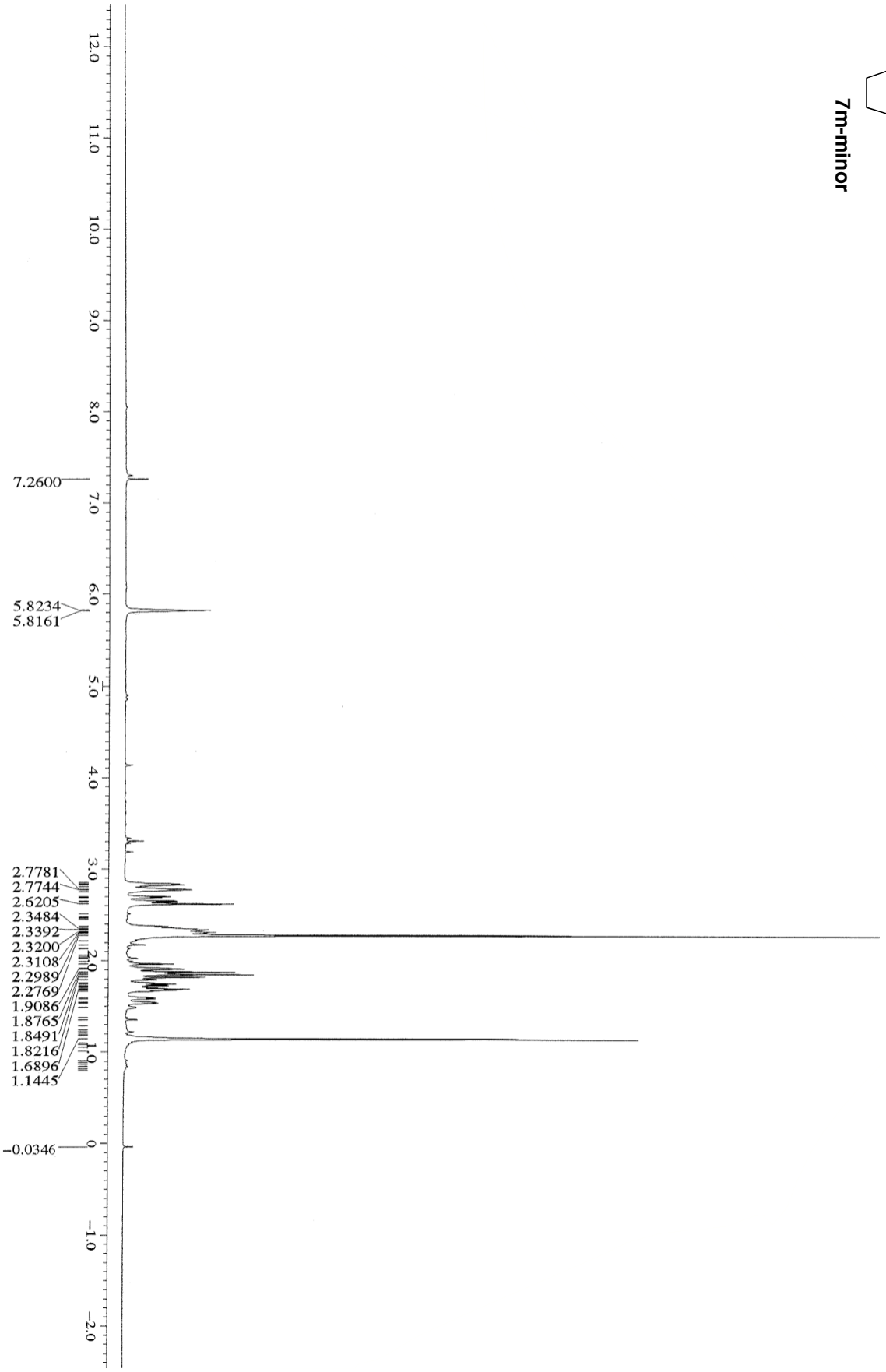
OH
COCH3

7m-major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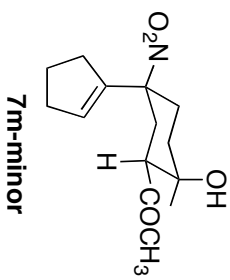
O2N
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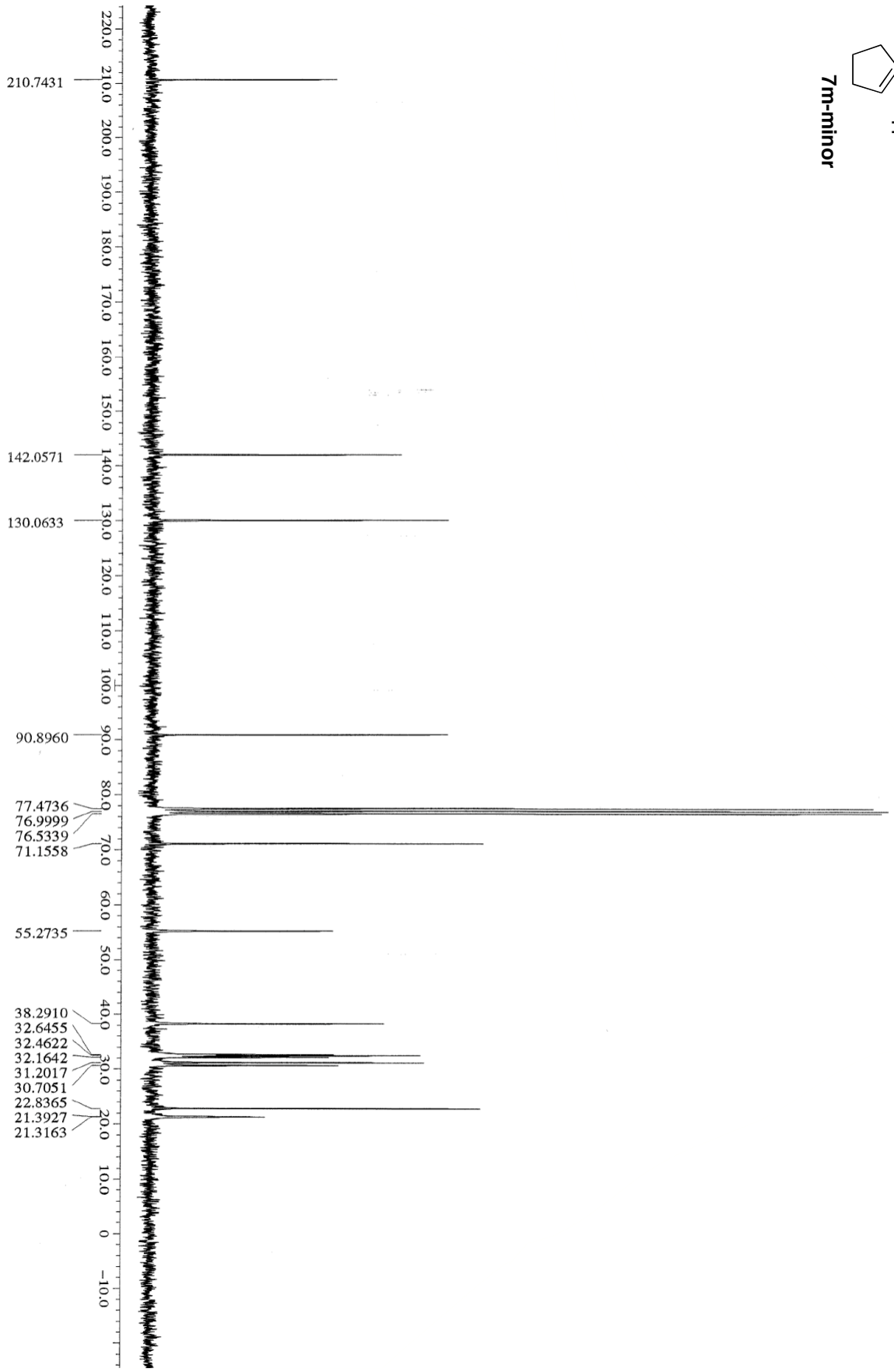
COCH3

7m-minor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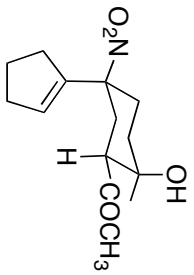
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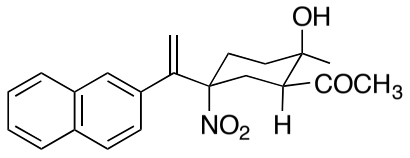
OH
COCH3

7m-minor



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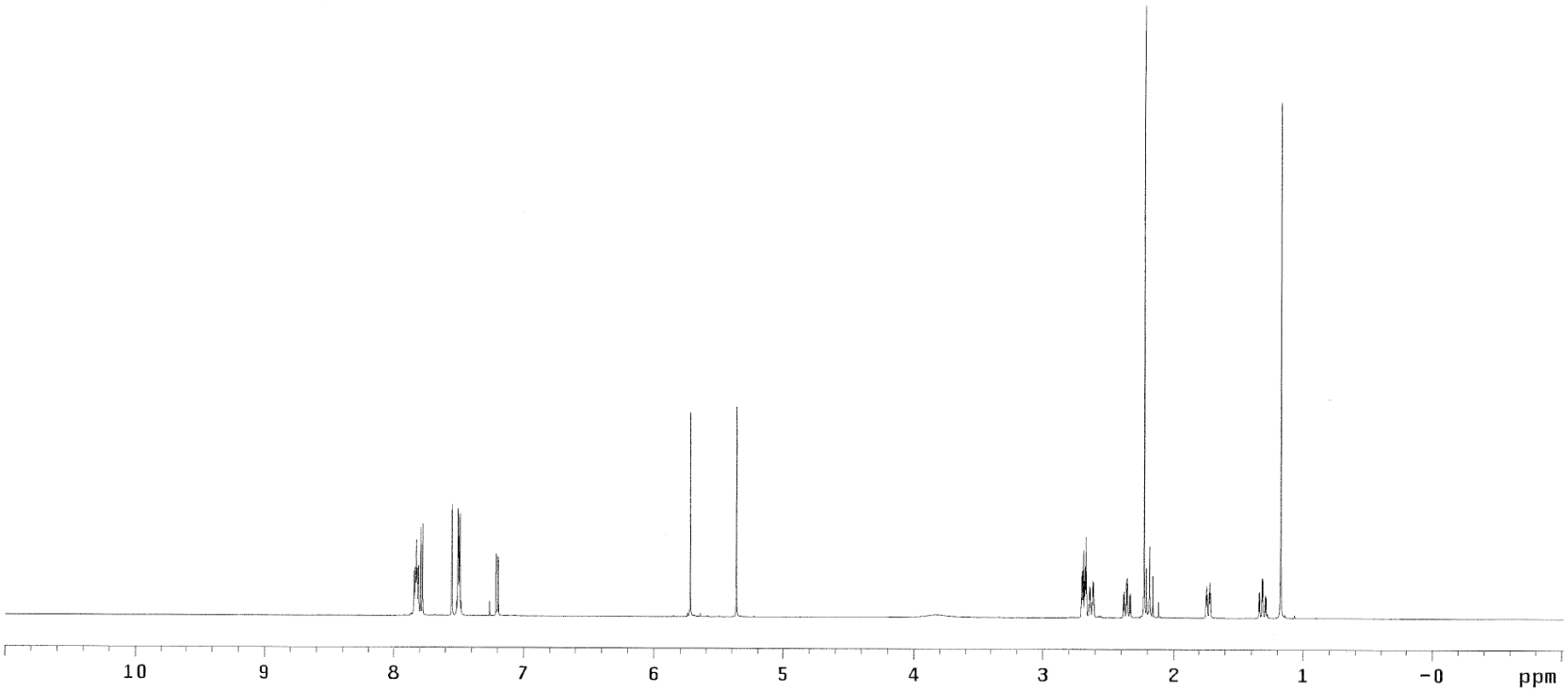

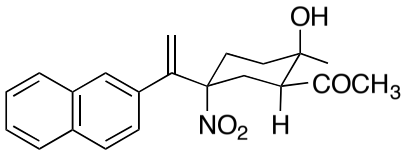

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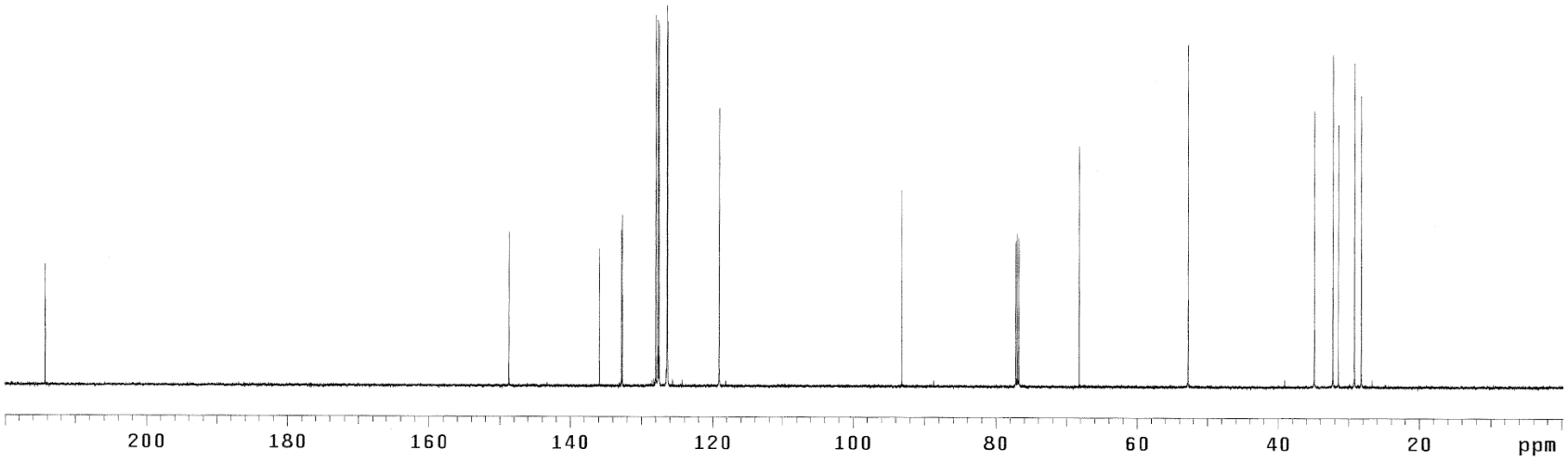

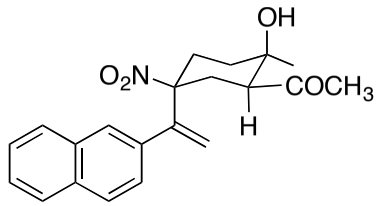

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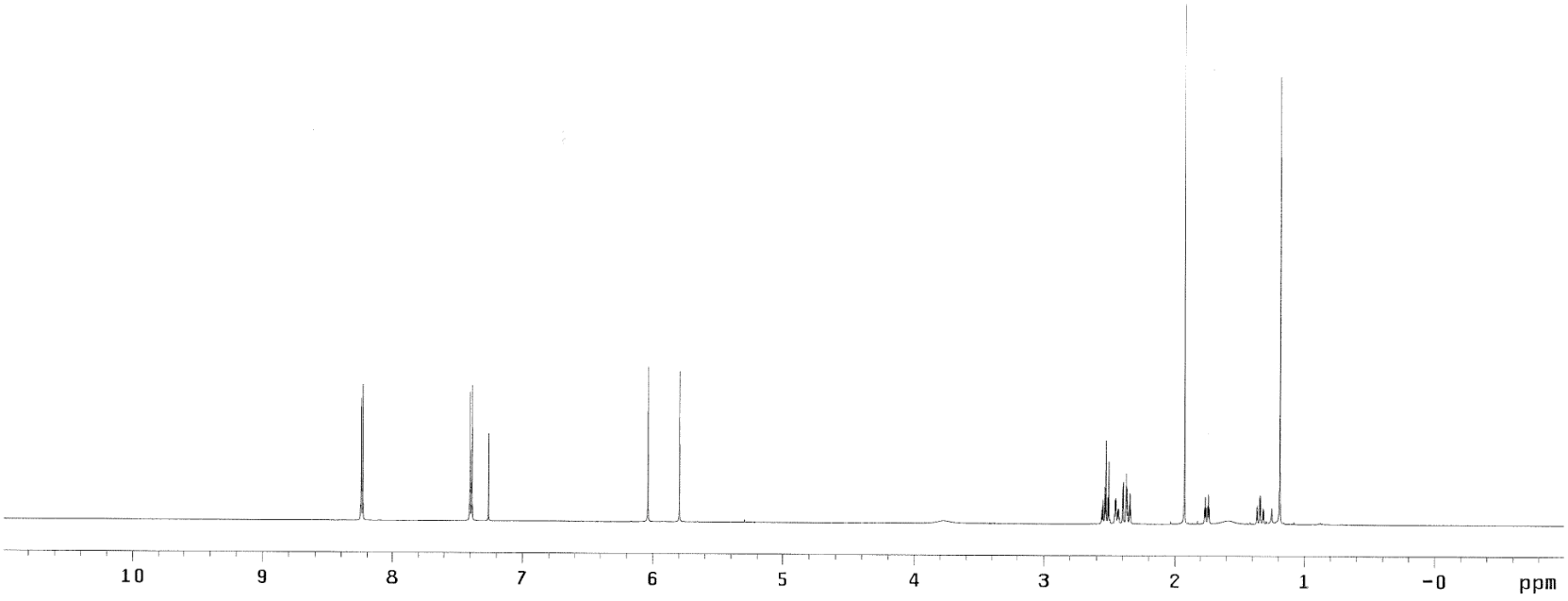

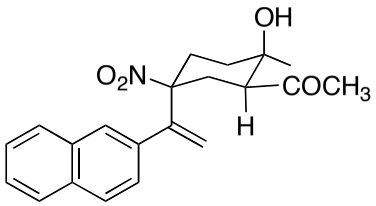

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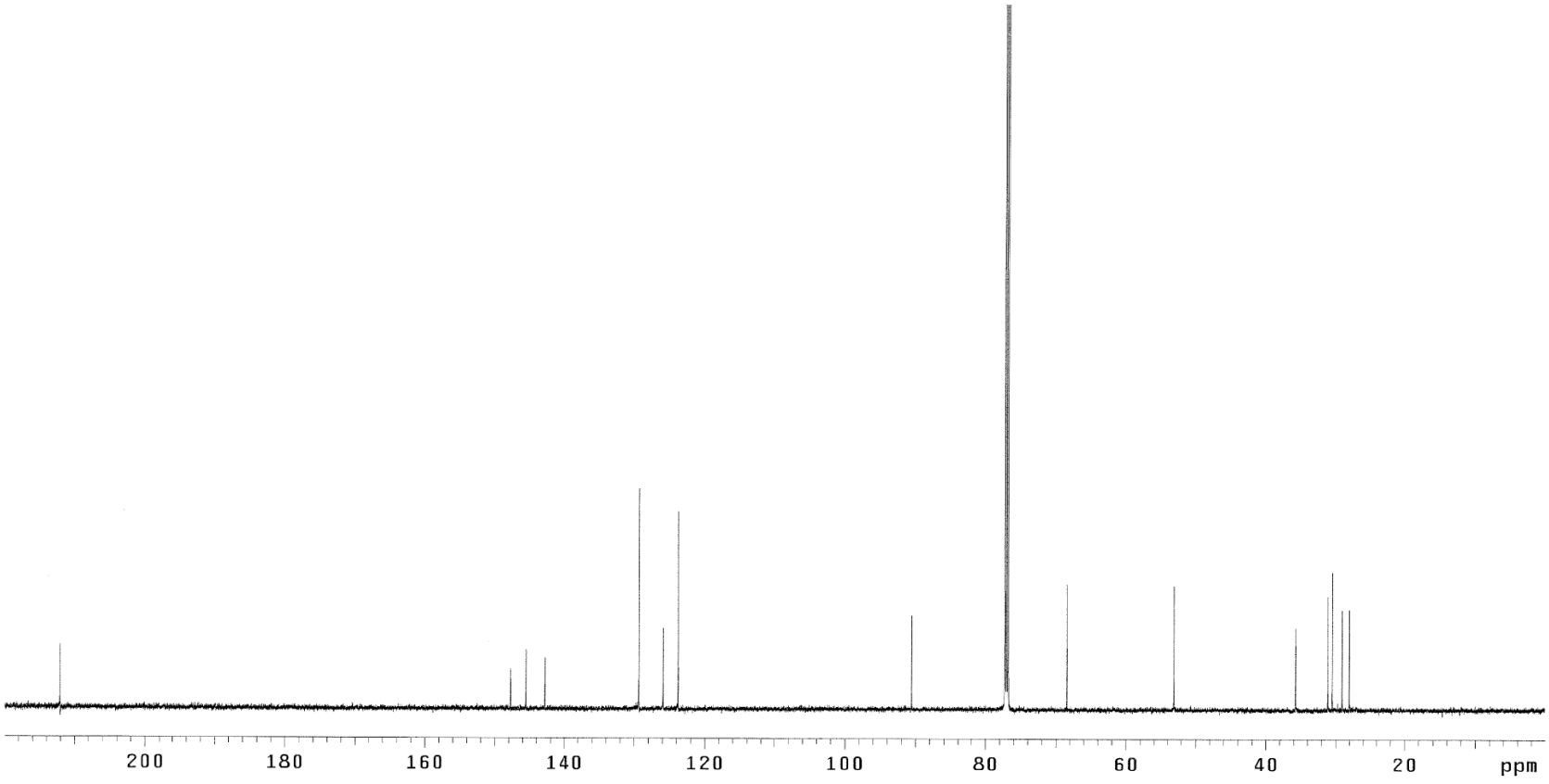

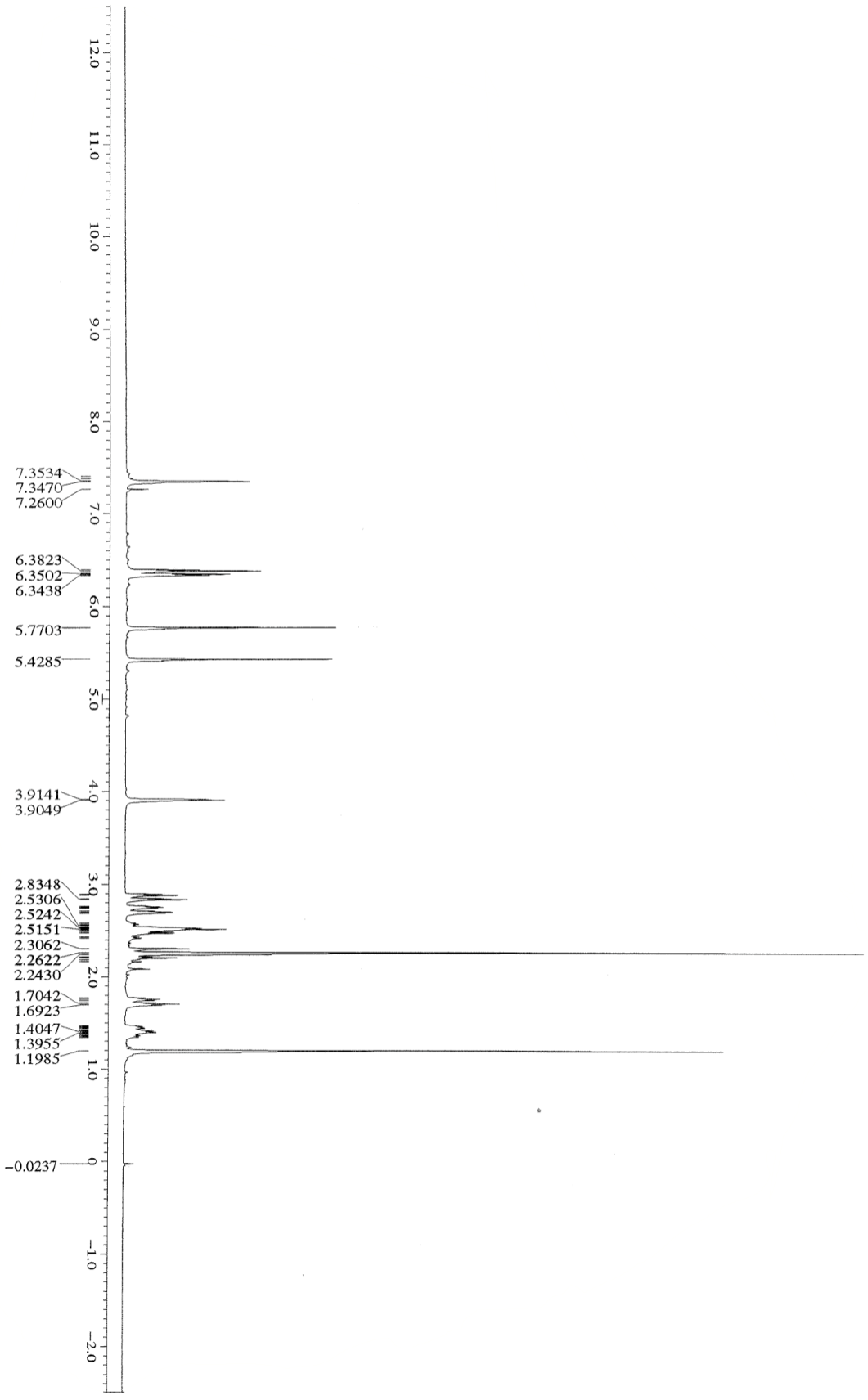
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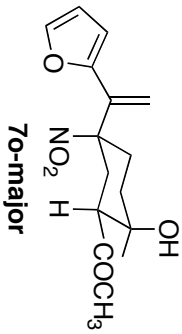
−2.0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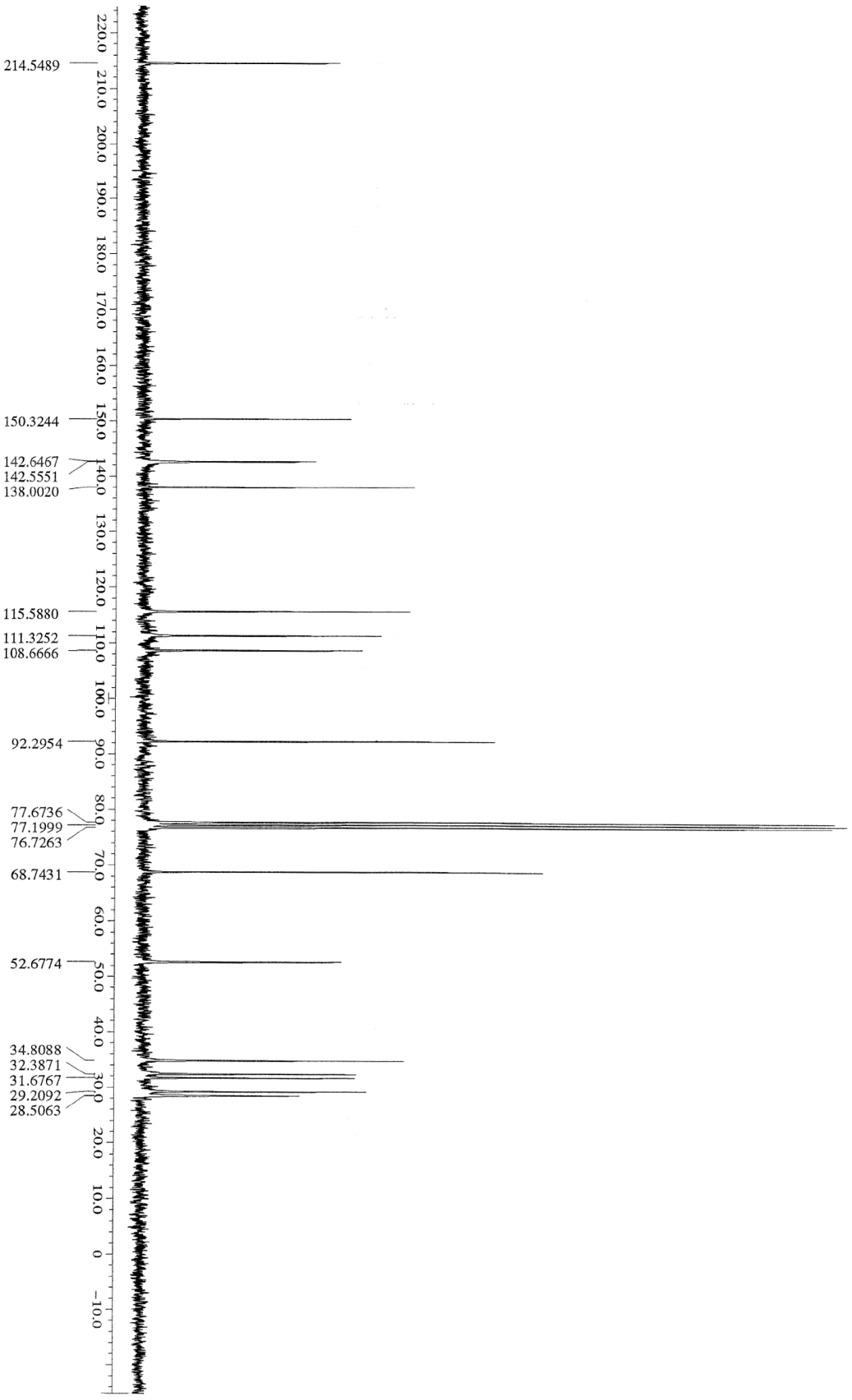
COCH3

7o-major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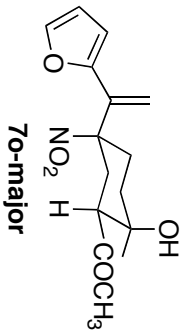
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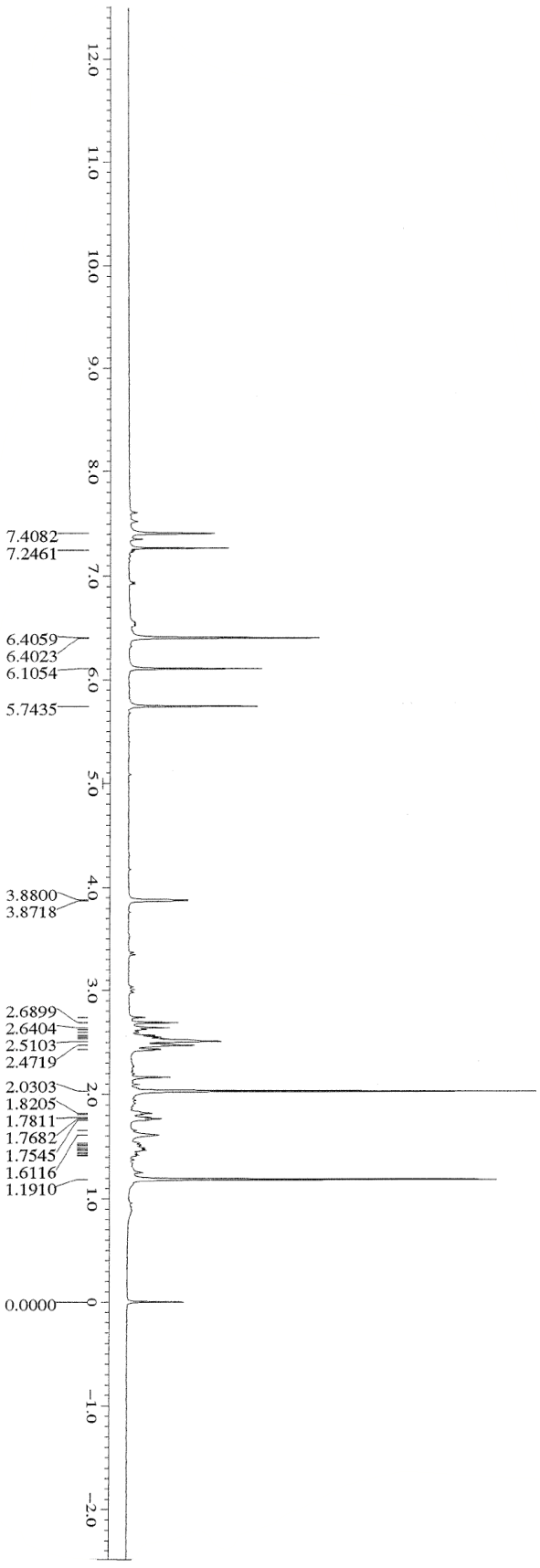
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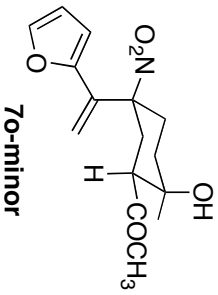
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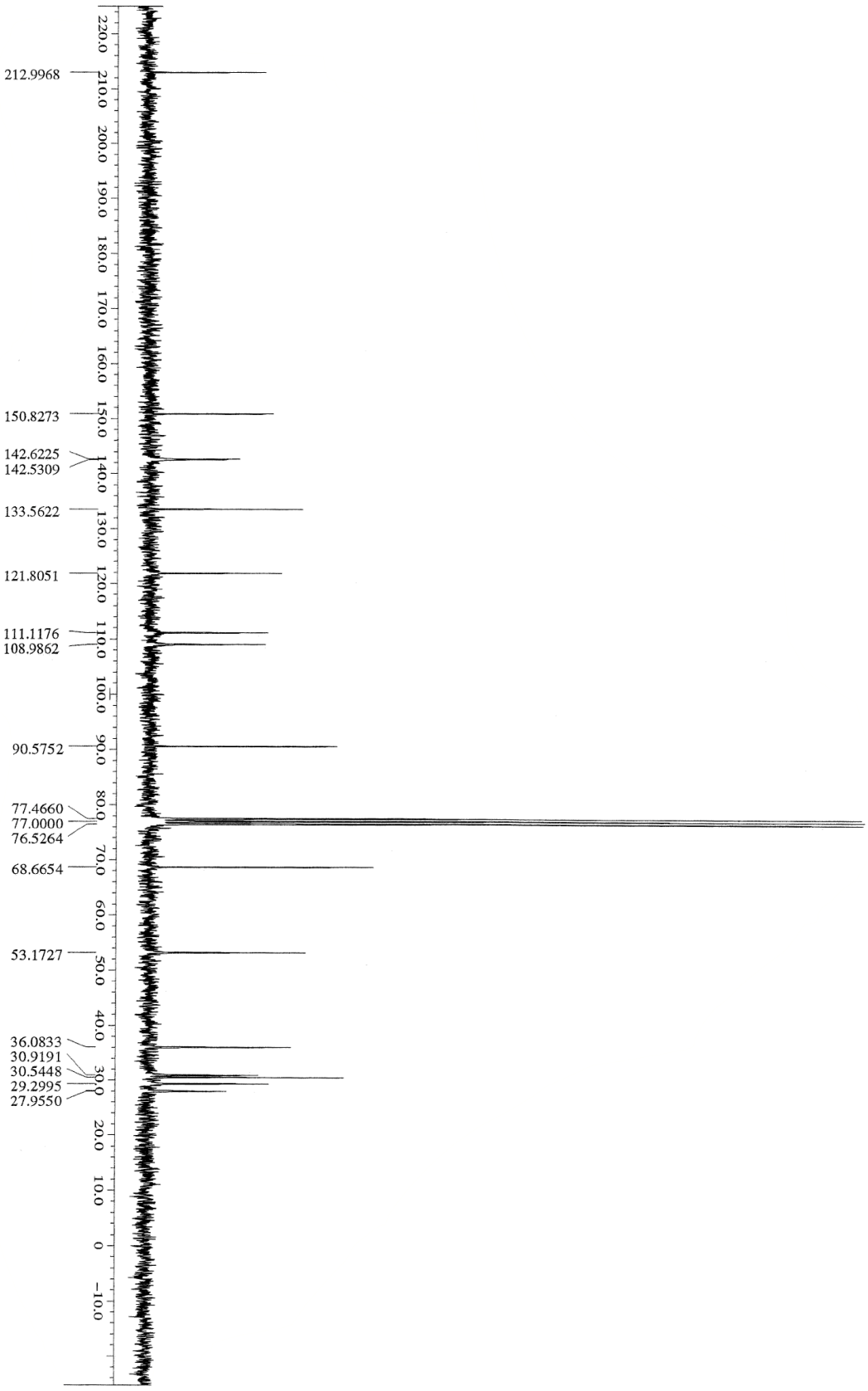
7o-minor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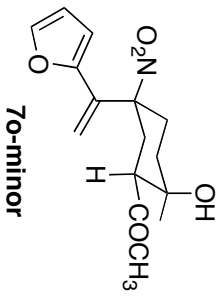
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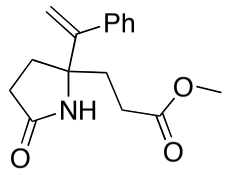
COCH3

7o-minor



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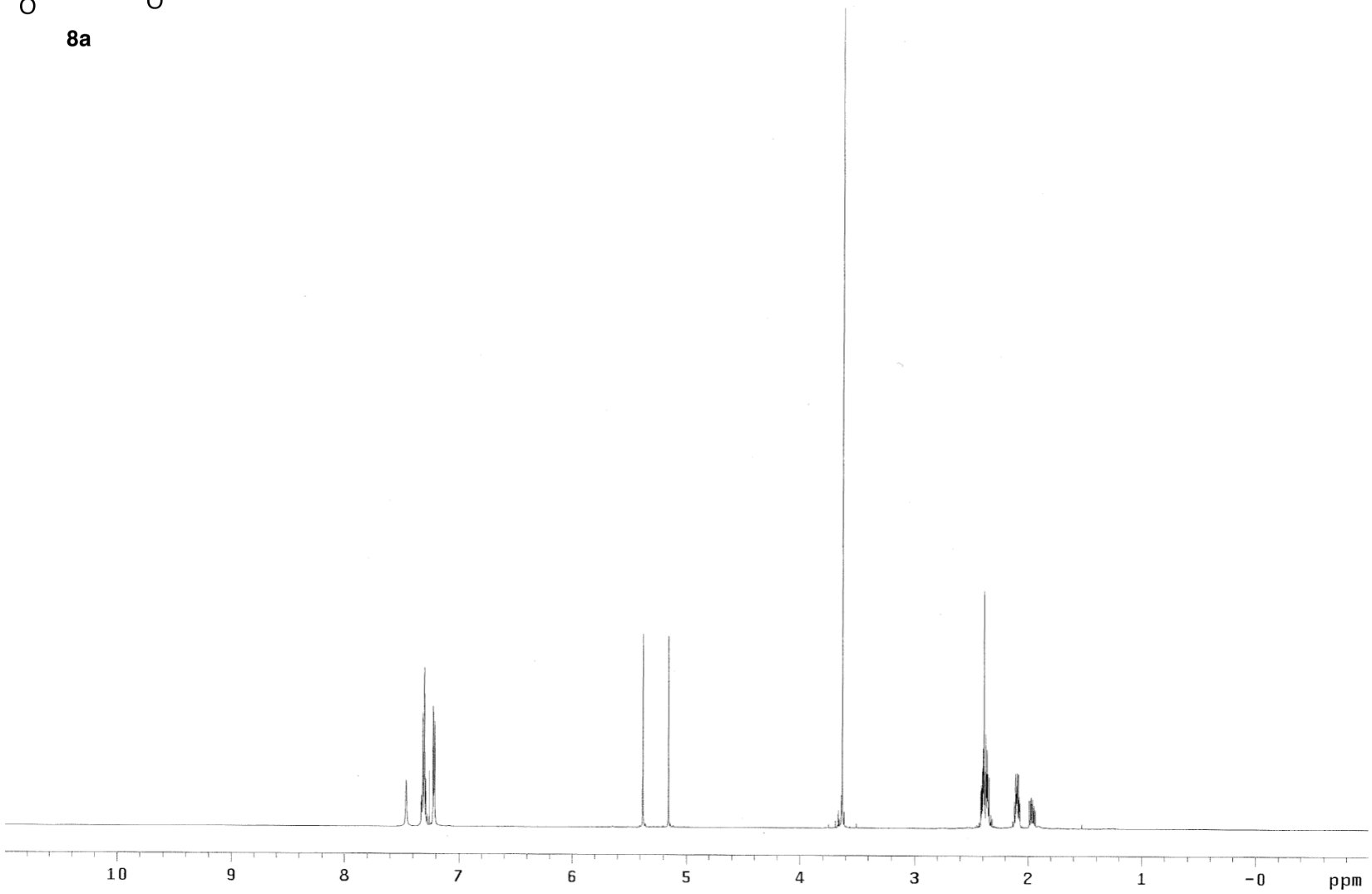

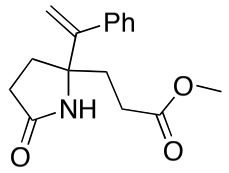

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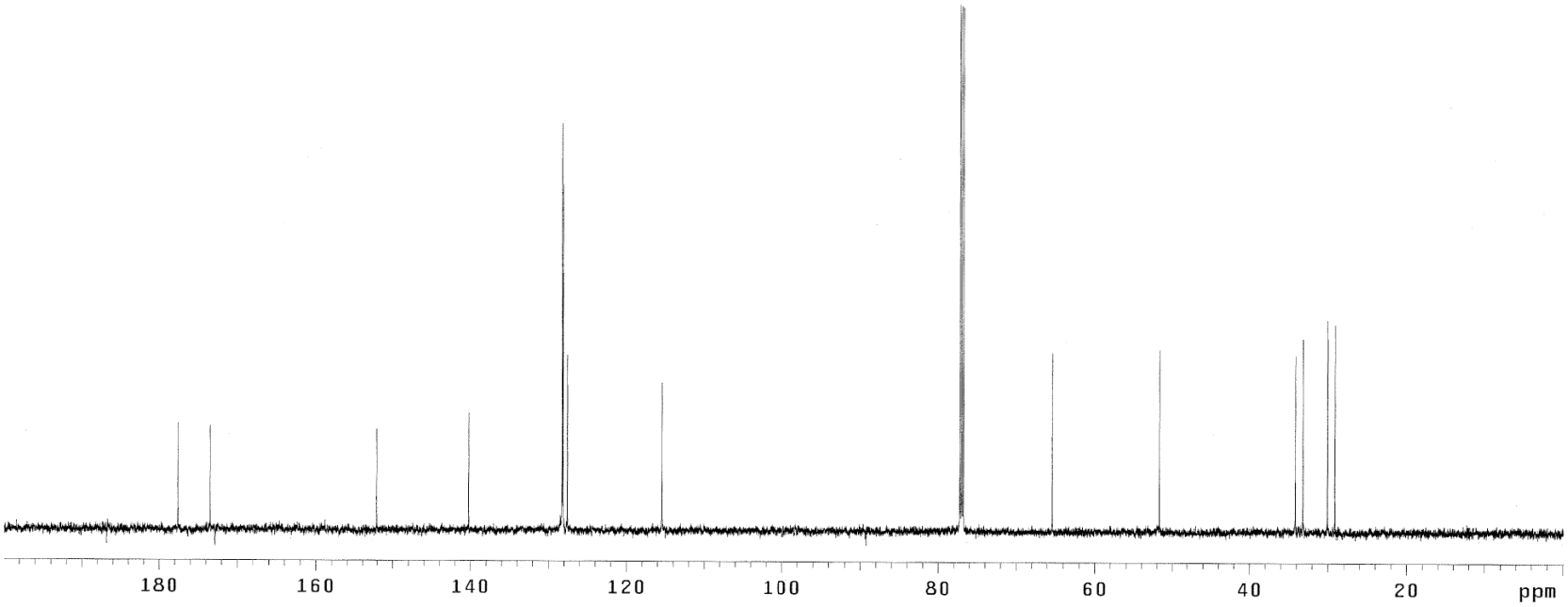

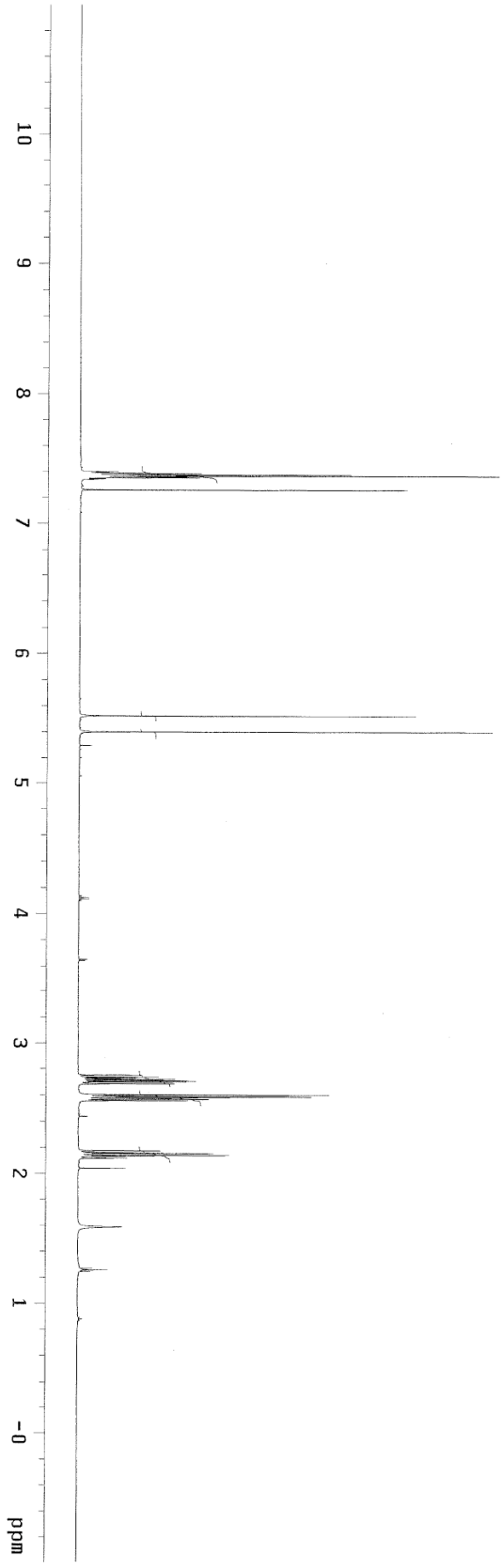

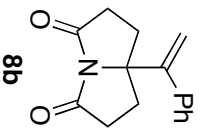

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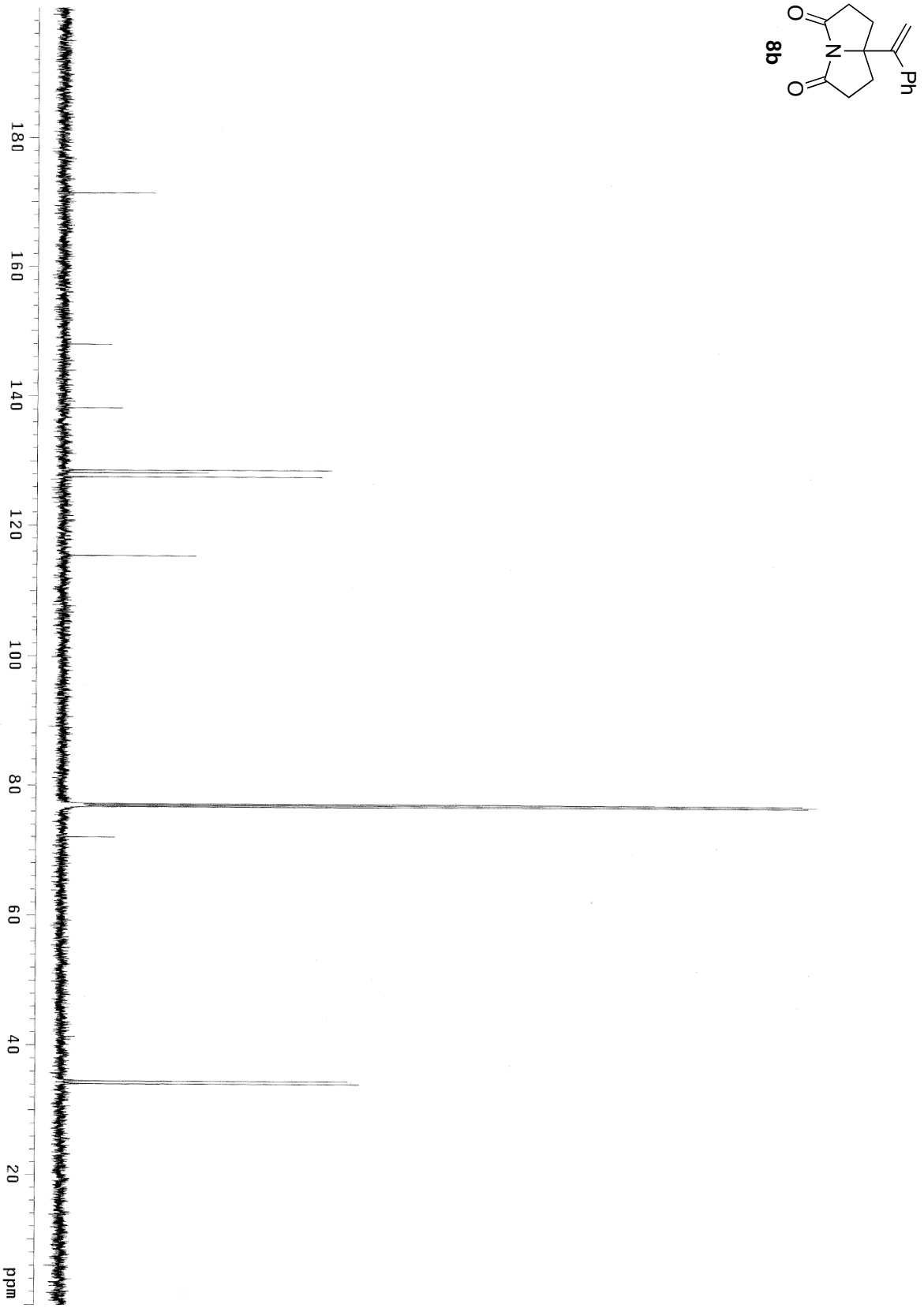
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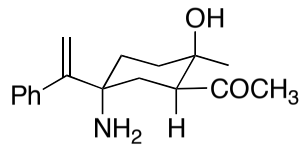

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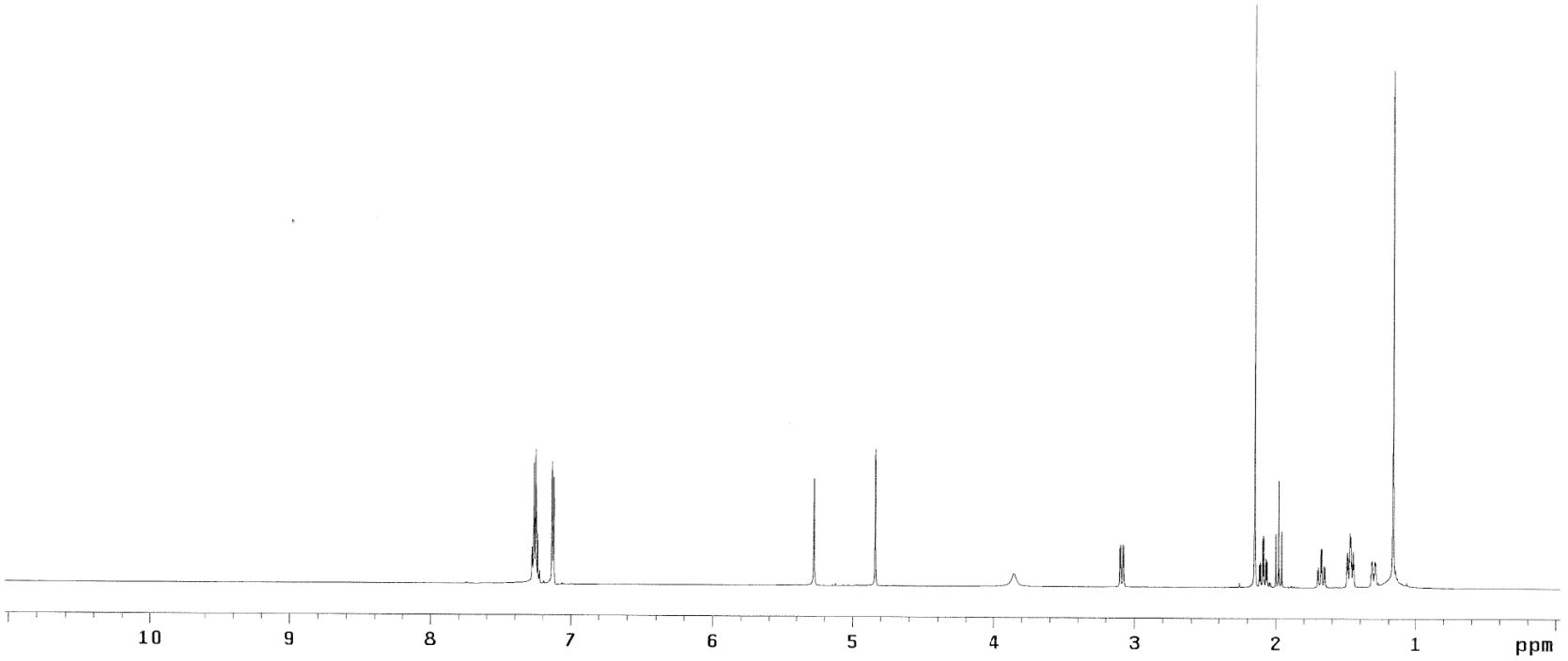

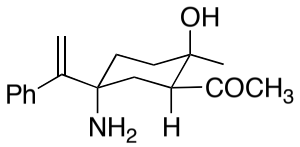

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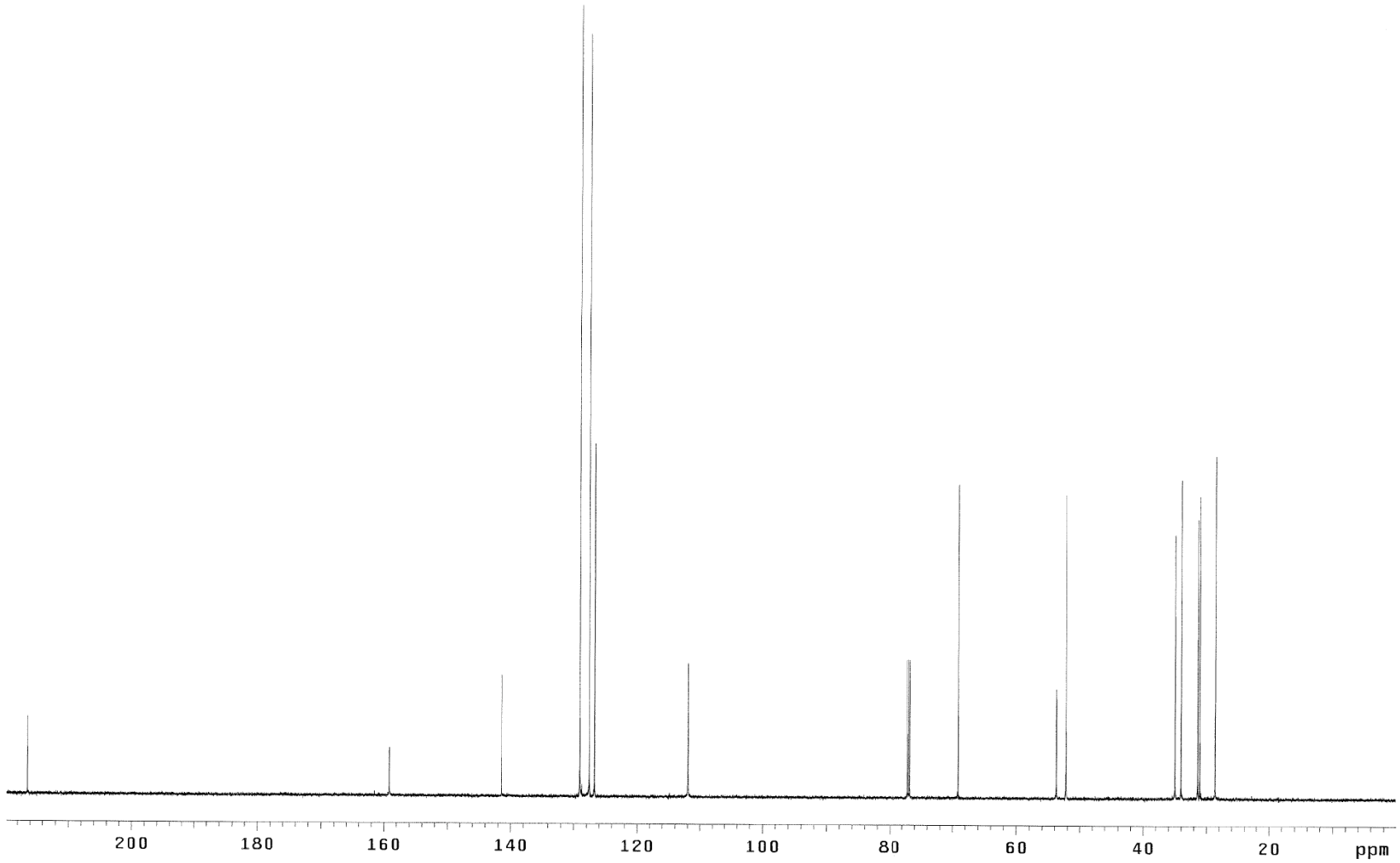

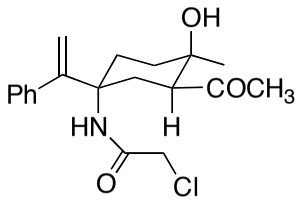

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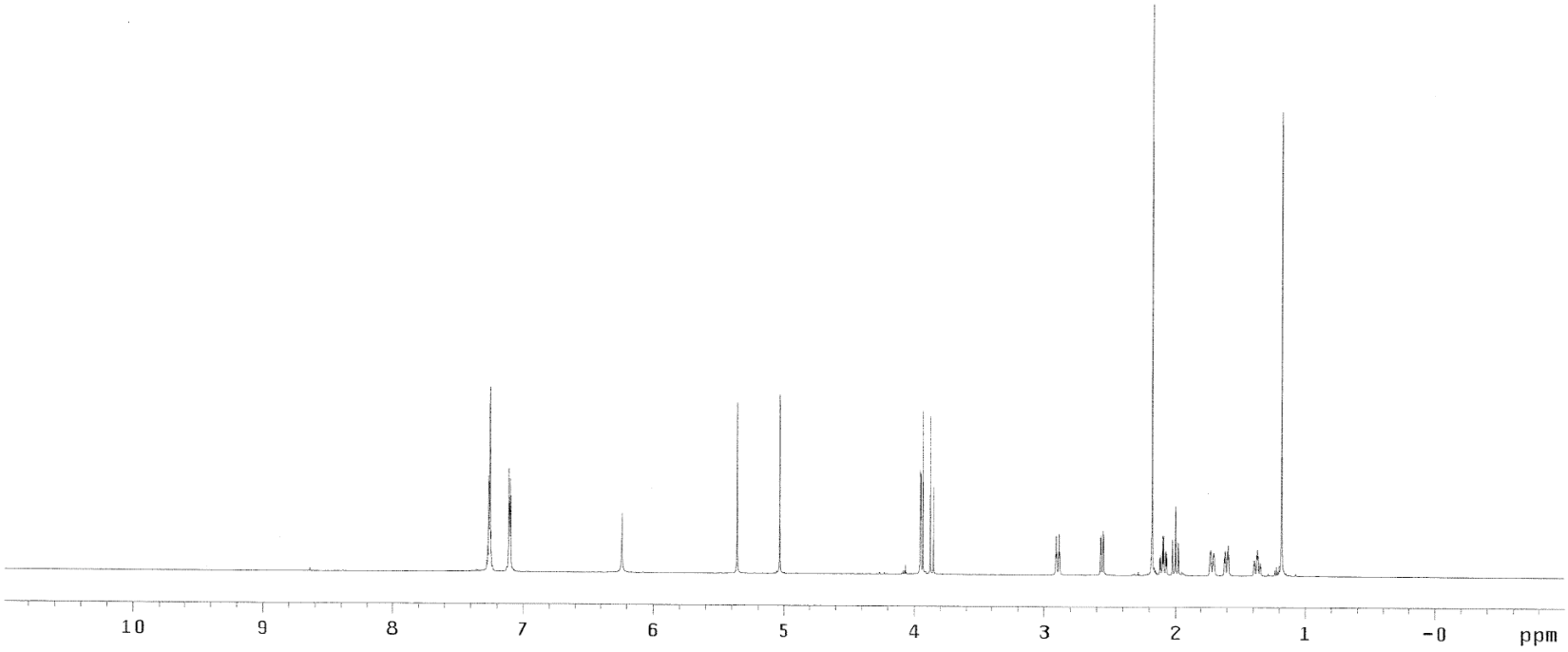

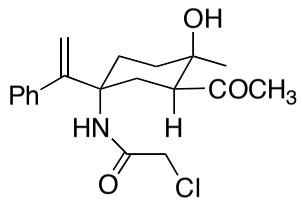

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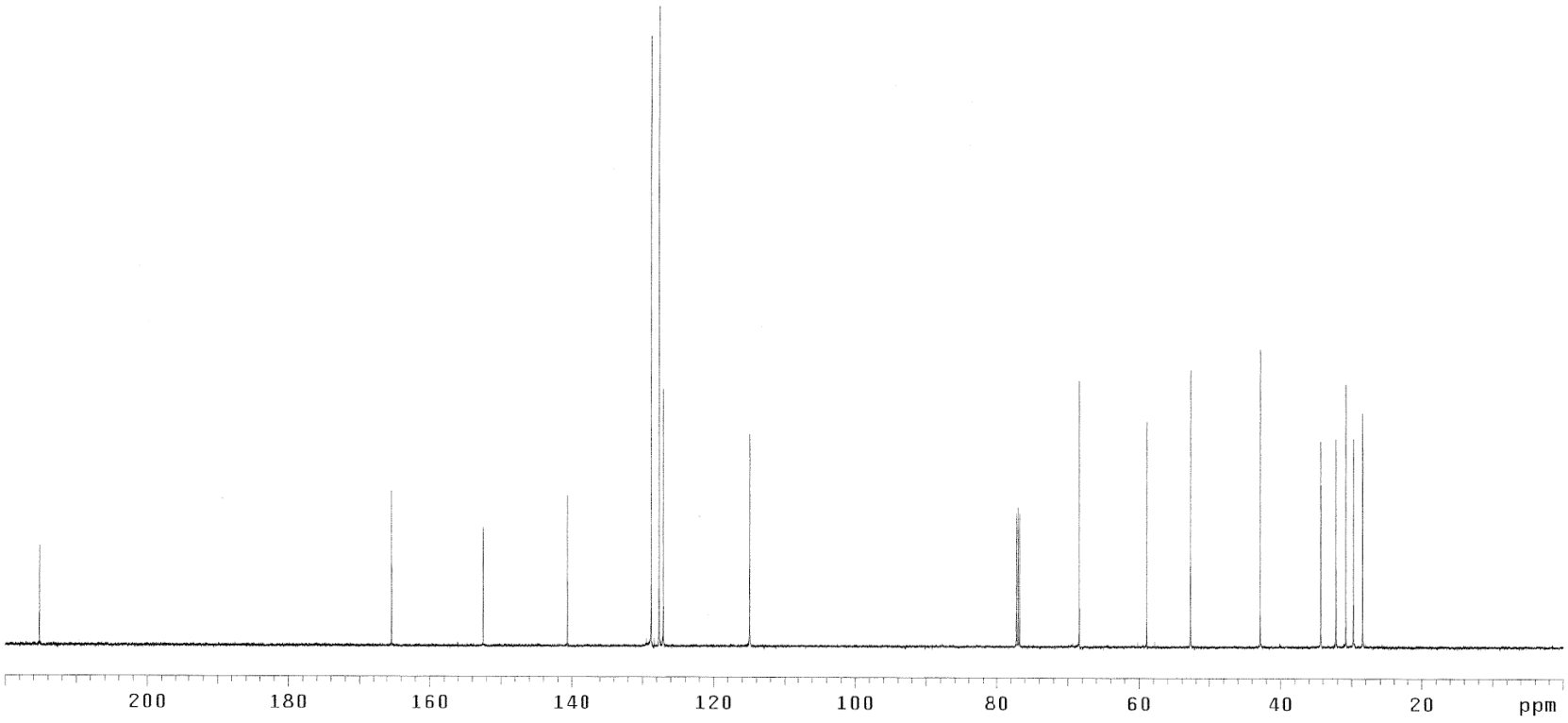
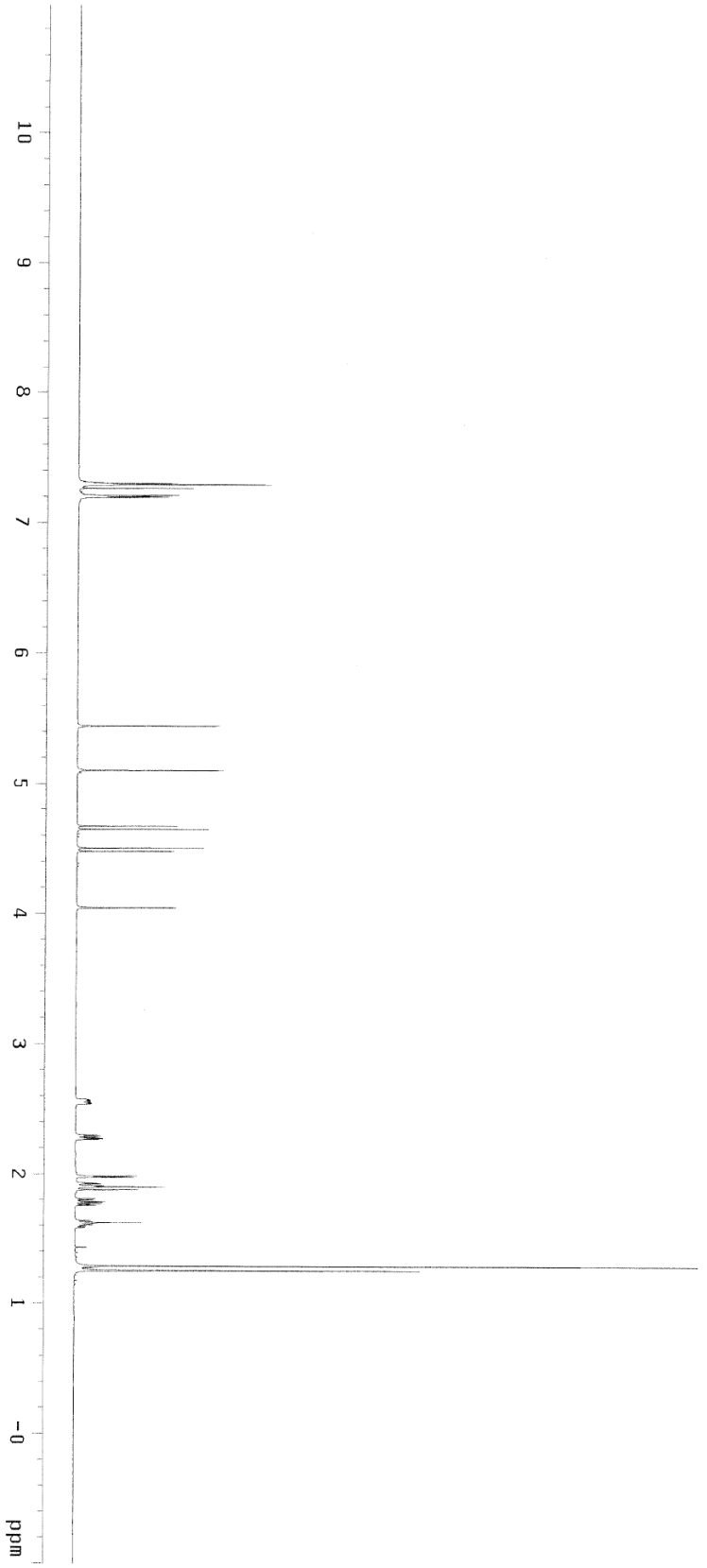
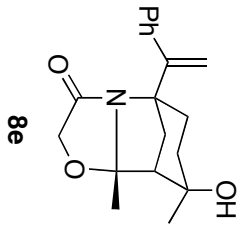
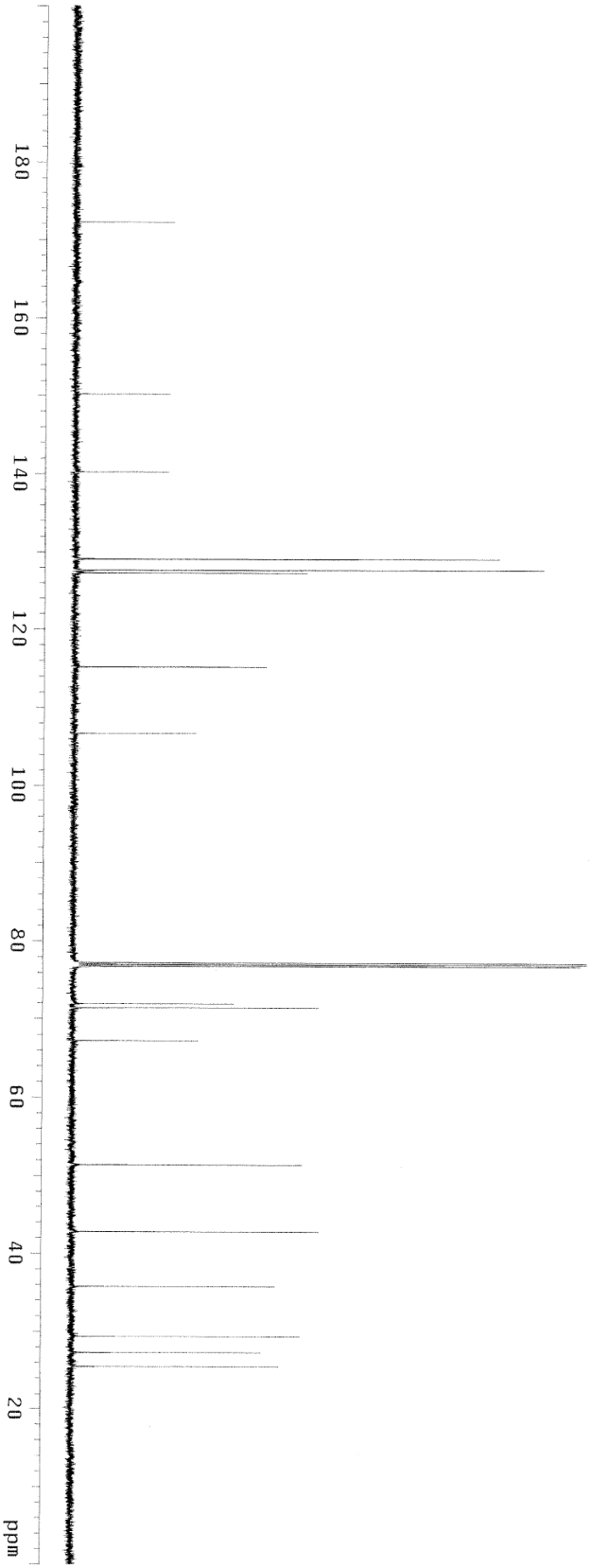
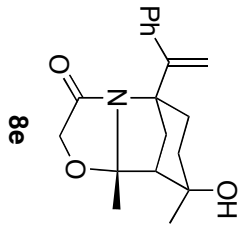






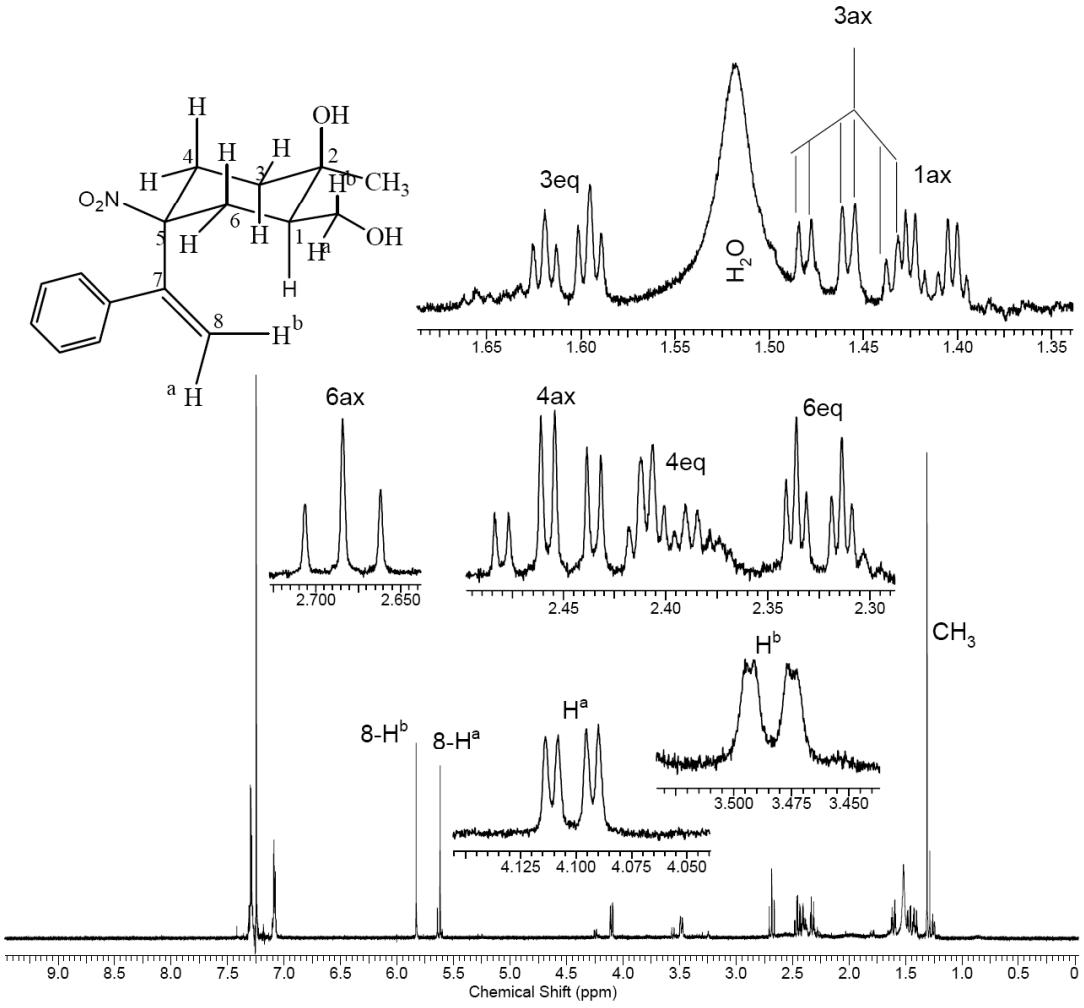
8e

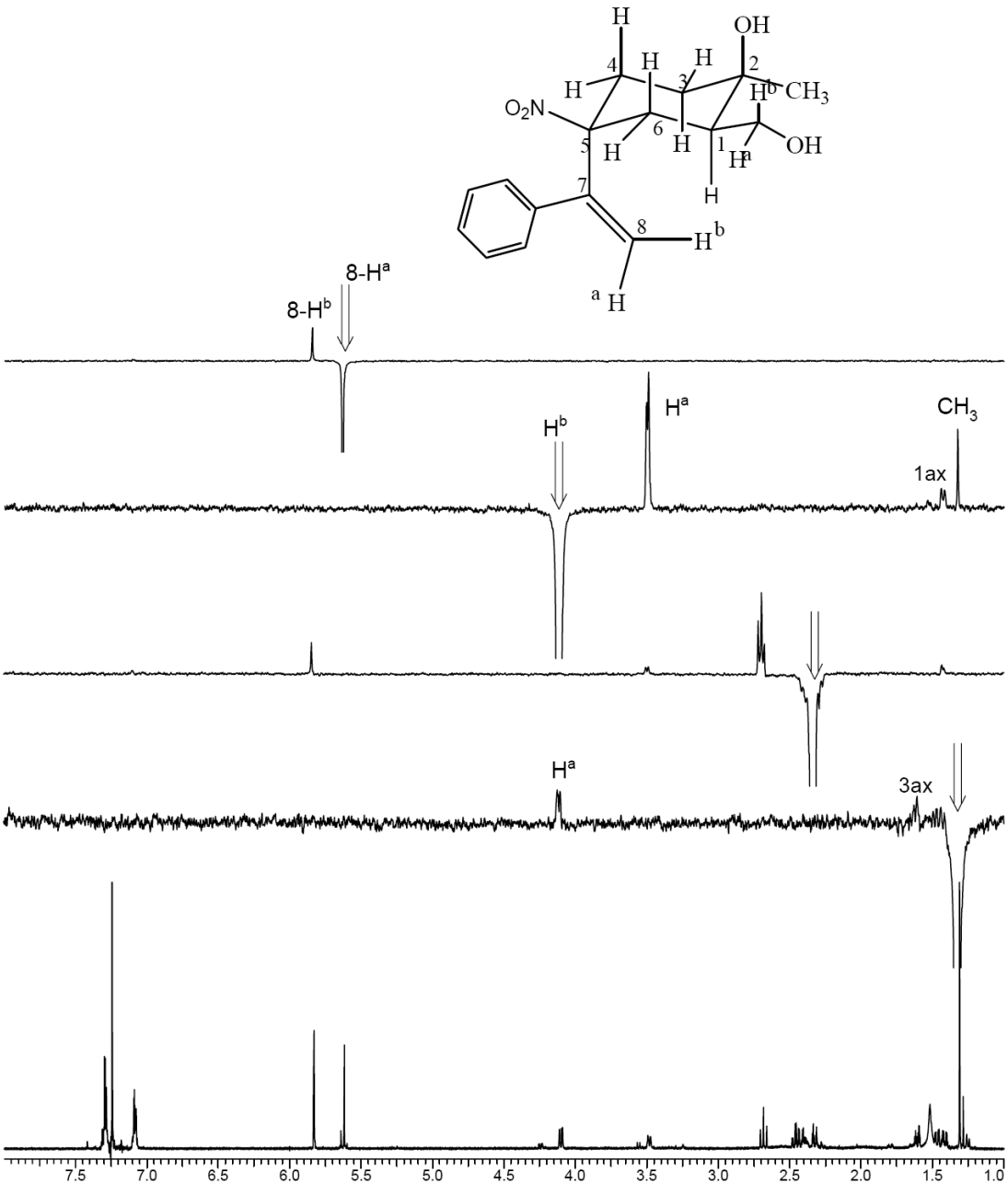




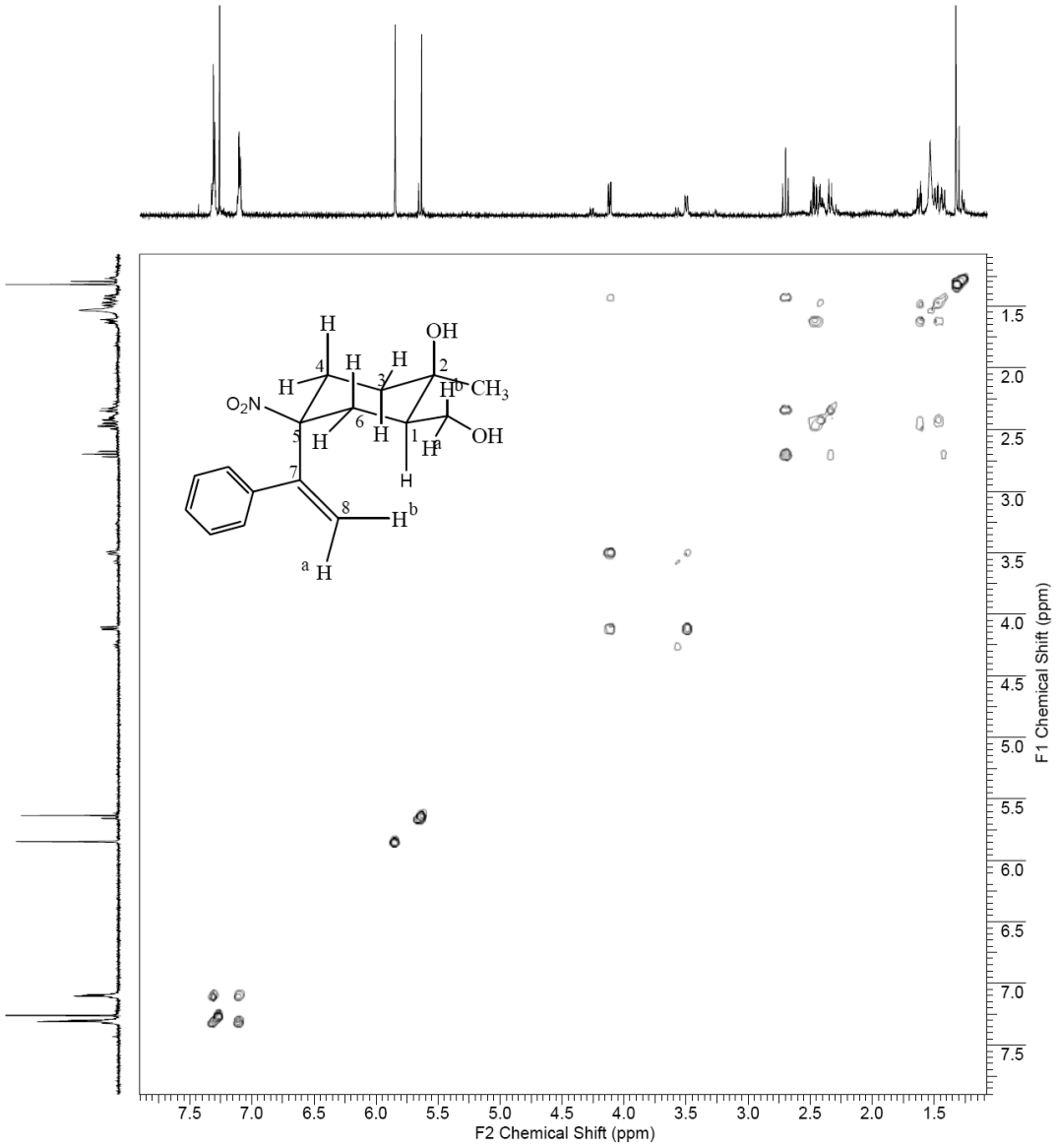
8e

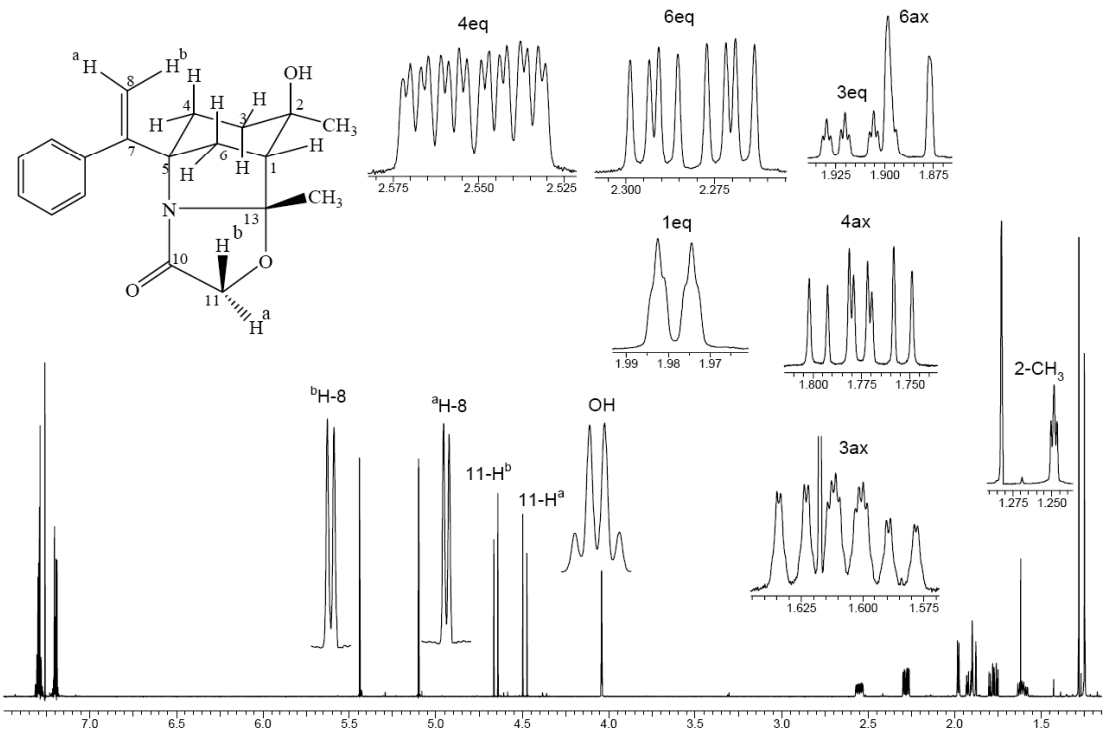
IV 1D and 2D NMR spectra data for **4c-minor** and **8e**.

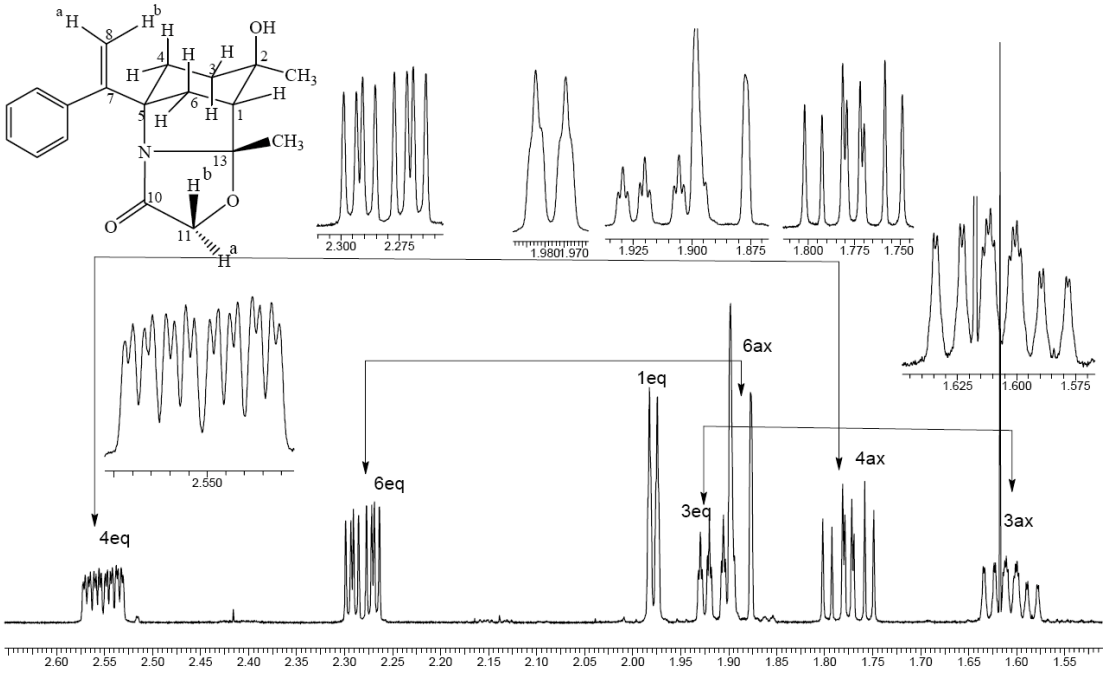


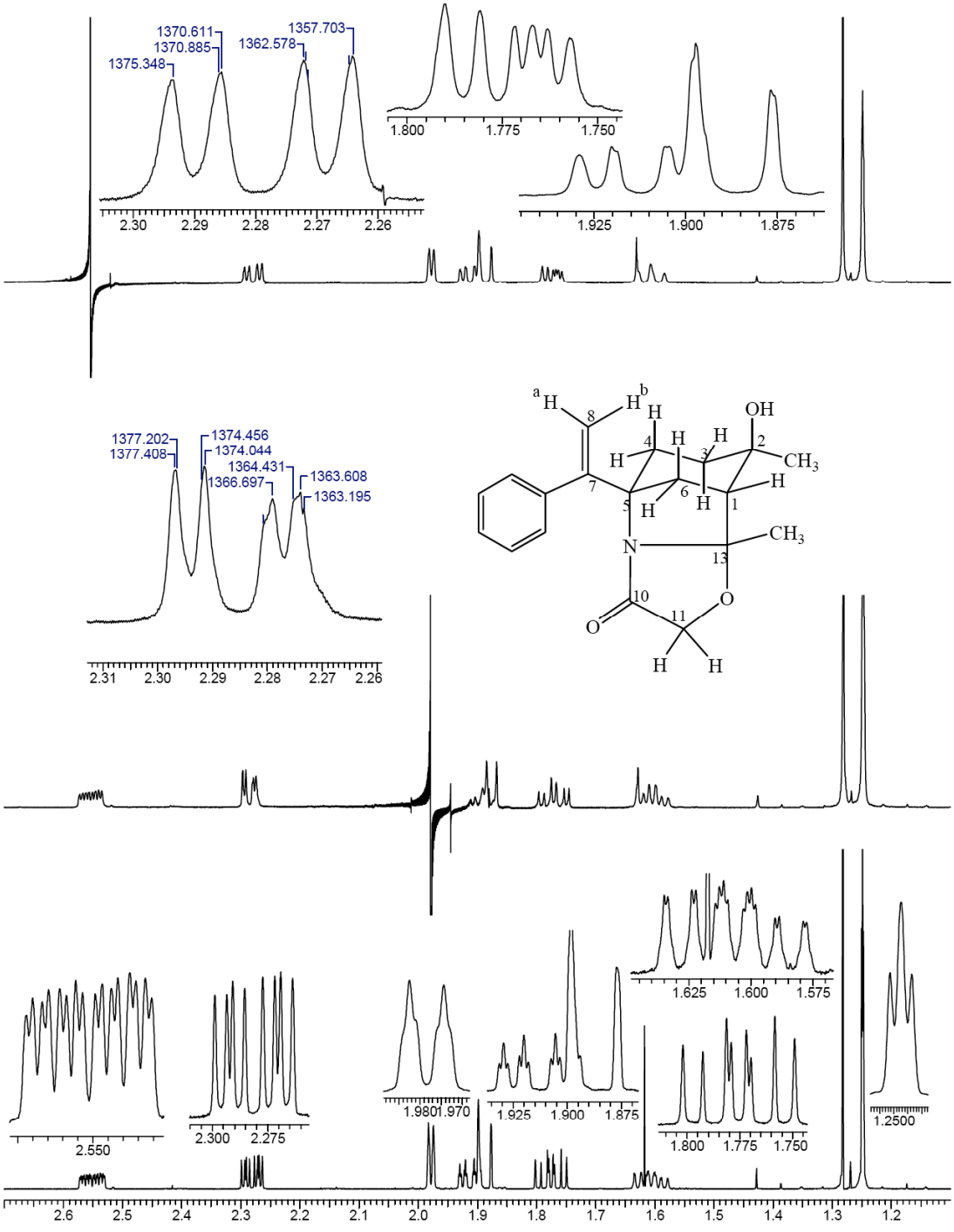

H
OH
4
H
H
2
3
H
H
O_2N
H^b
CH_3
6
5
H
H
1
H^a
OH
7
H
8
H^b
a H
8-H^a
8-H^b
H^a
H^b
CH_3
1ax
H^a
3ax
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

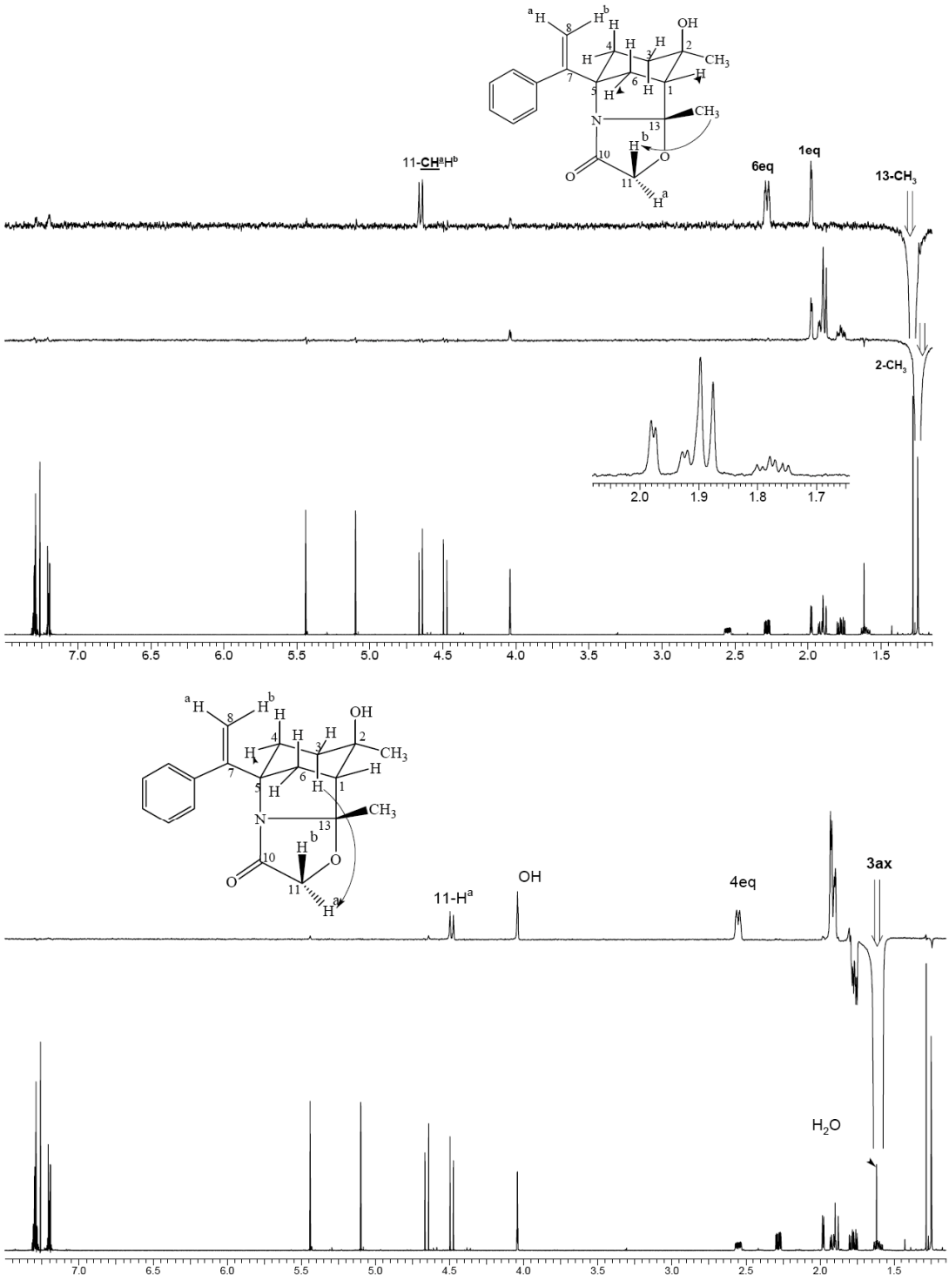

H
OH
4
H
H
2
H
3
H
b
CH3
O2N
6
5
H
H
1
H
a
OH
7
H
8
H
b
a
H
6ax
4ax
4eq
6eq
3eq
3ax
1ax
a
b
1.5
2.0
2.5
3.0
3.5
4.0
F1 Chemical Shift (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
F2 Chemical Shift (ppm)

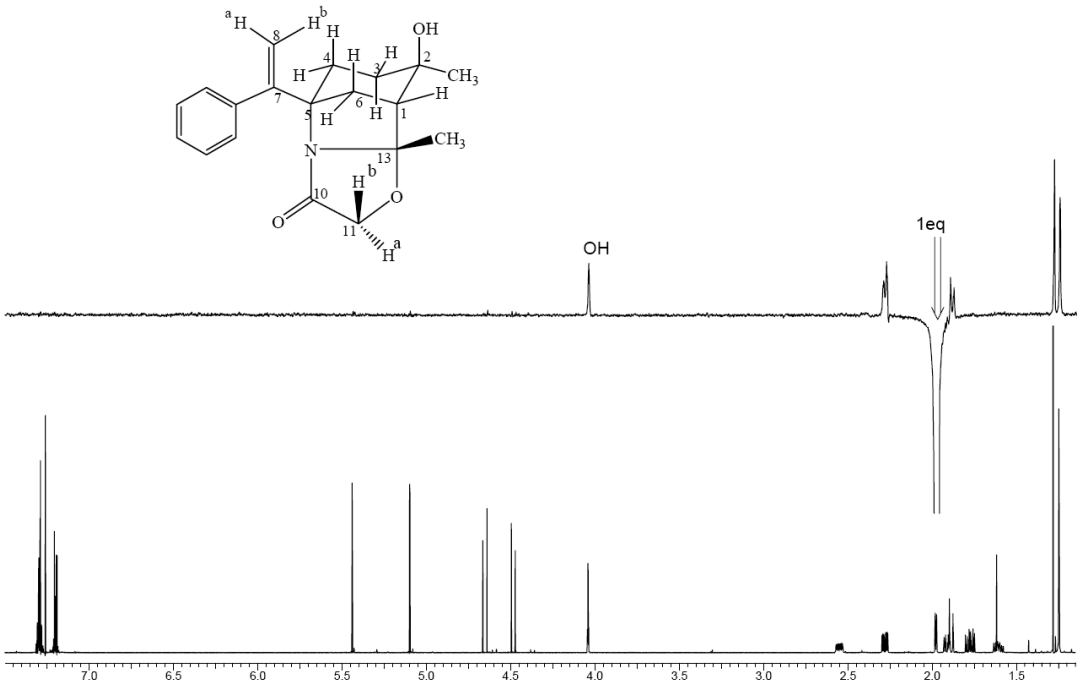

F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
OH
O_2N
CH_3
OH

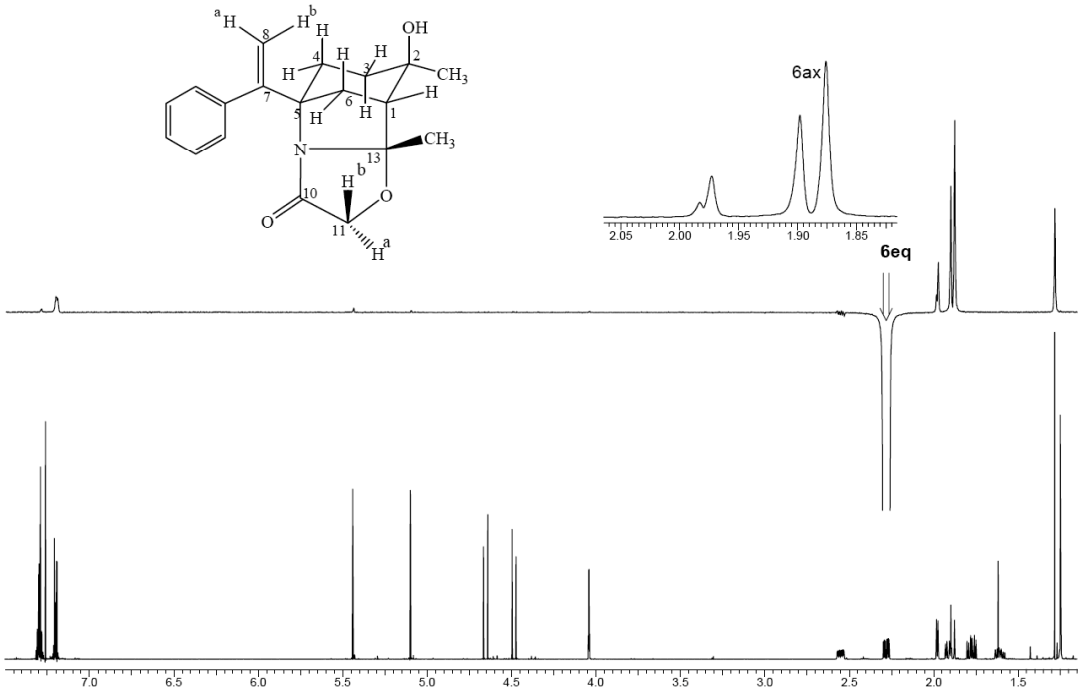

4eq
6eq
6ax
3eq
1eq
4ax
2-CH3
bH-8
aH-8
11-Hb
11-Ha
OH
3ax

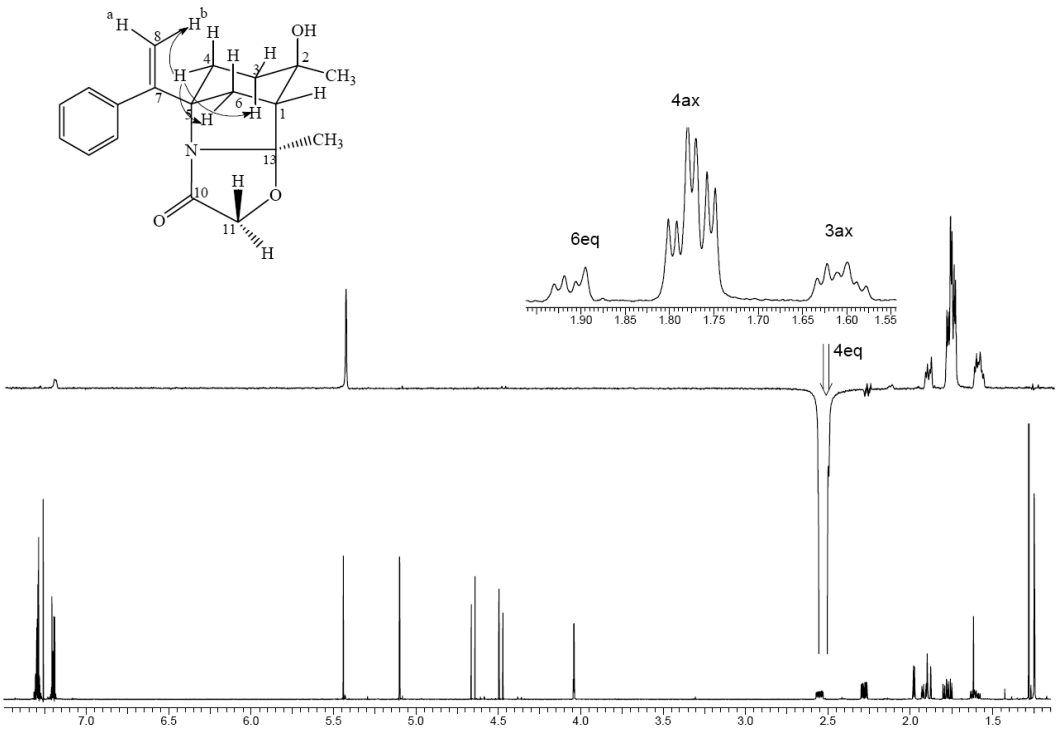

6ax
1eq
6eq
4ax
3eq
3ax
4eq

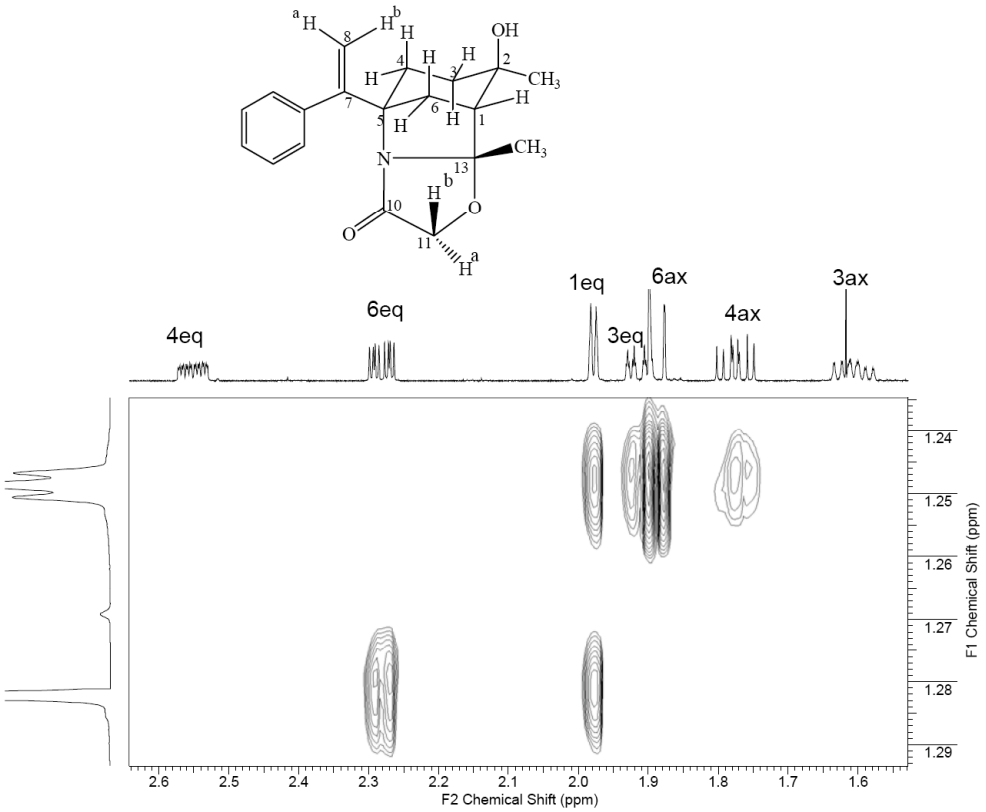

1370.611
1370.885
1375.348
1362.578
1357.703
1377.202
1377.408
1374.456
1374.044
1364.431
1366.697
1363.608
1363.195
OH
CH3
CH3
N
O
O
H
H
a
b

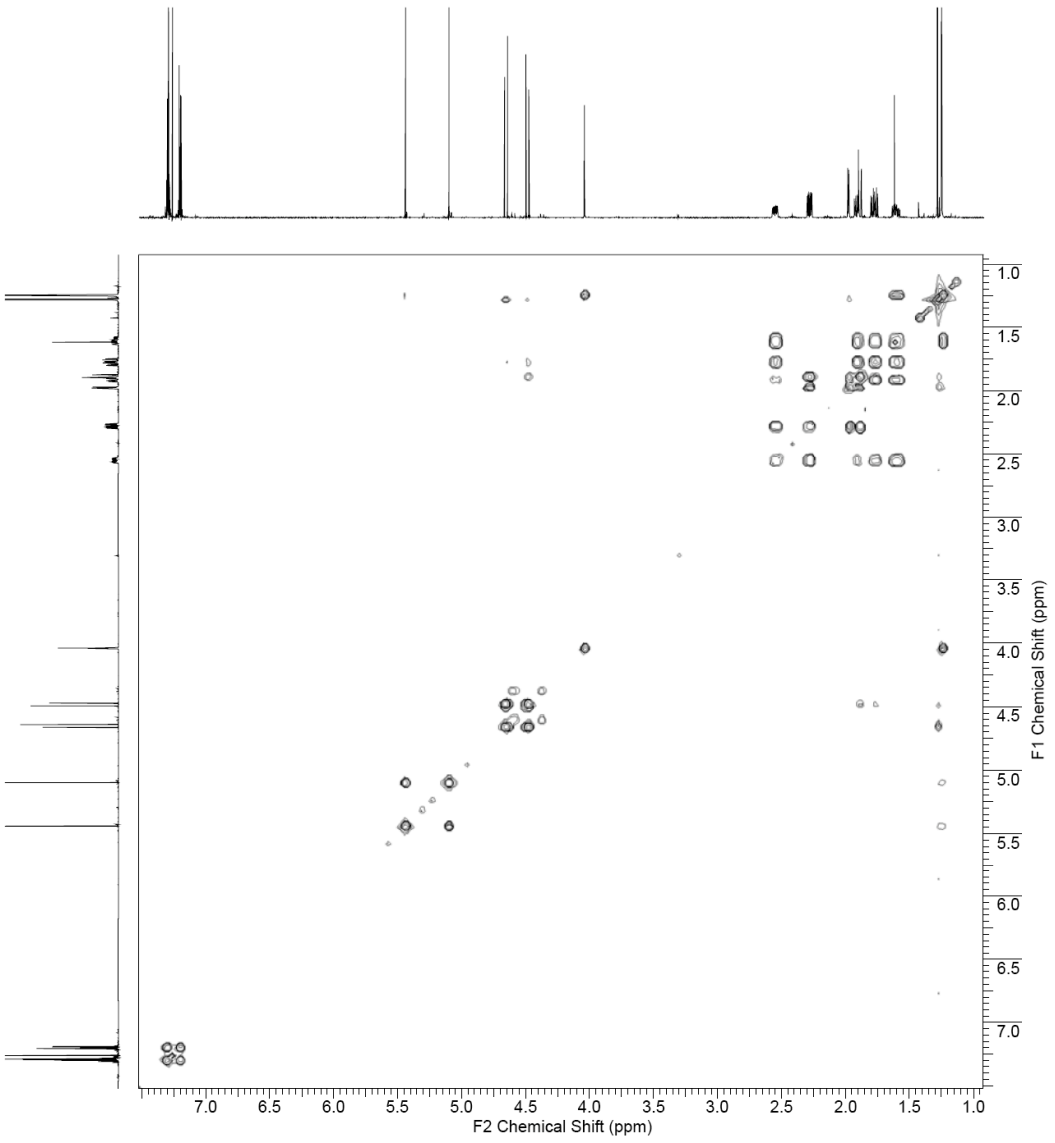

11-CHaHb
6eq
1eq
13-CH3
2-CH3
11-Ha
OH
4eq
3ax
H2O

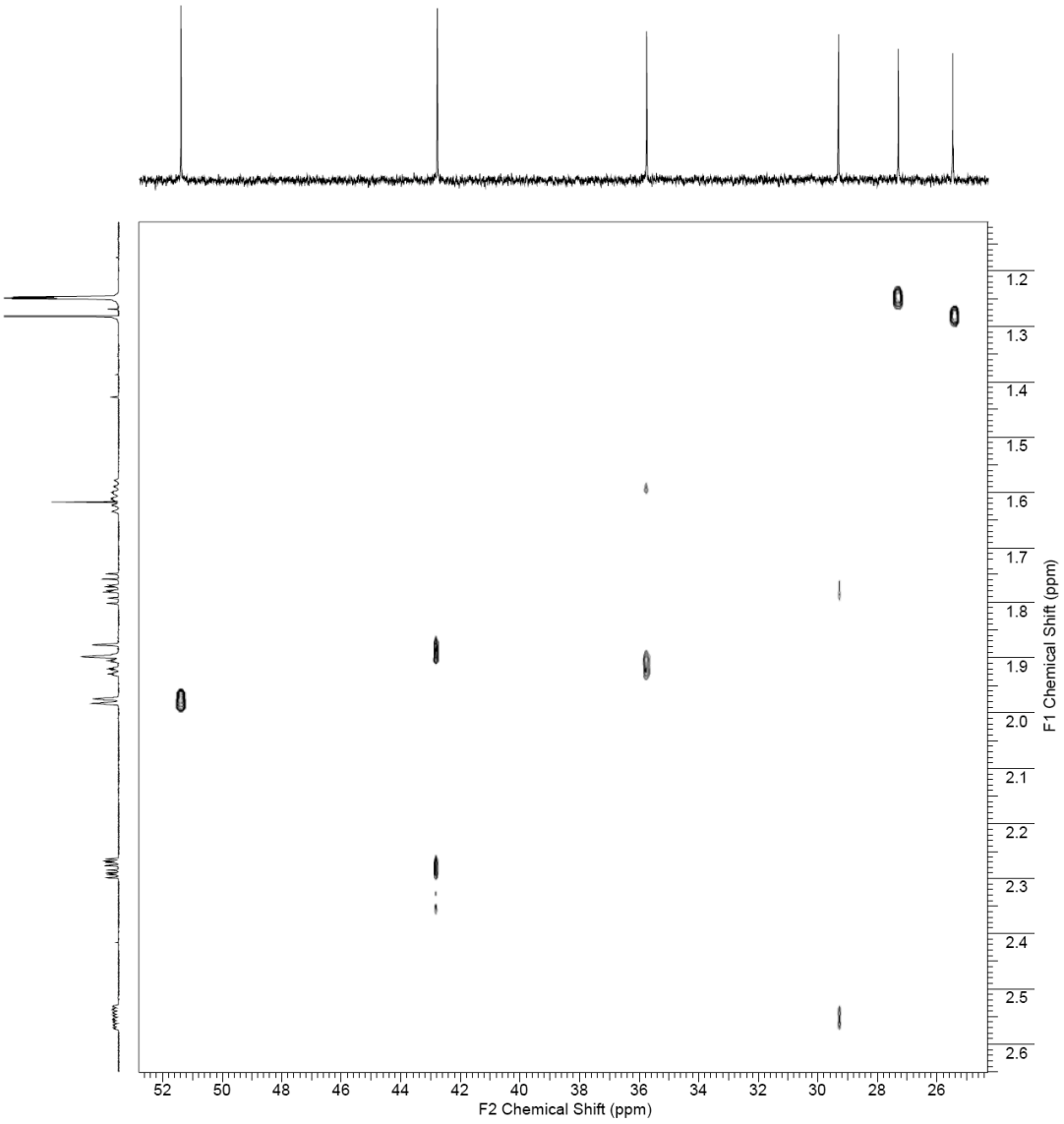

OH
1eq
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

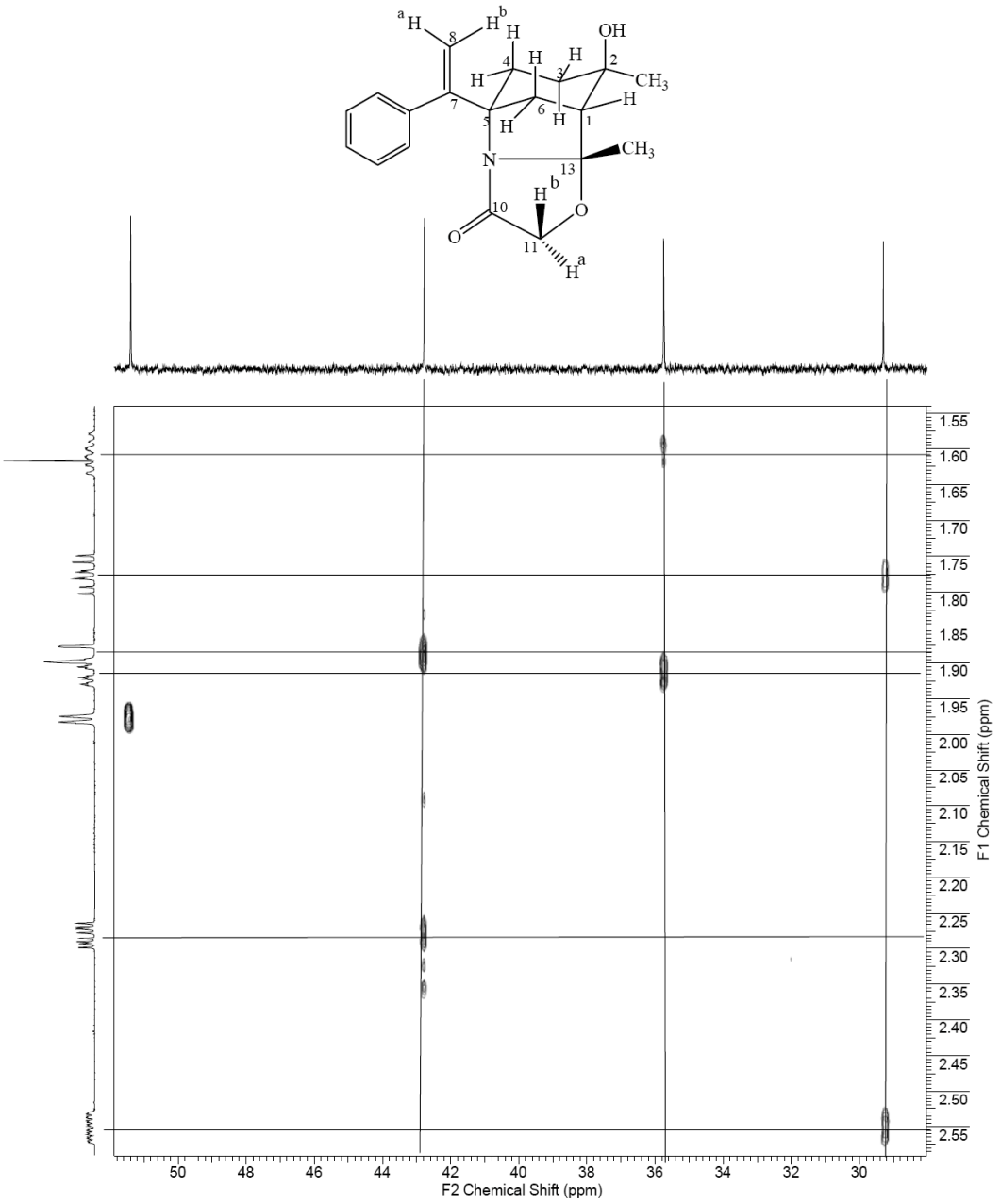

6ax
2.05
2.00
1.95
1.90
1.85
6eq
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

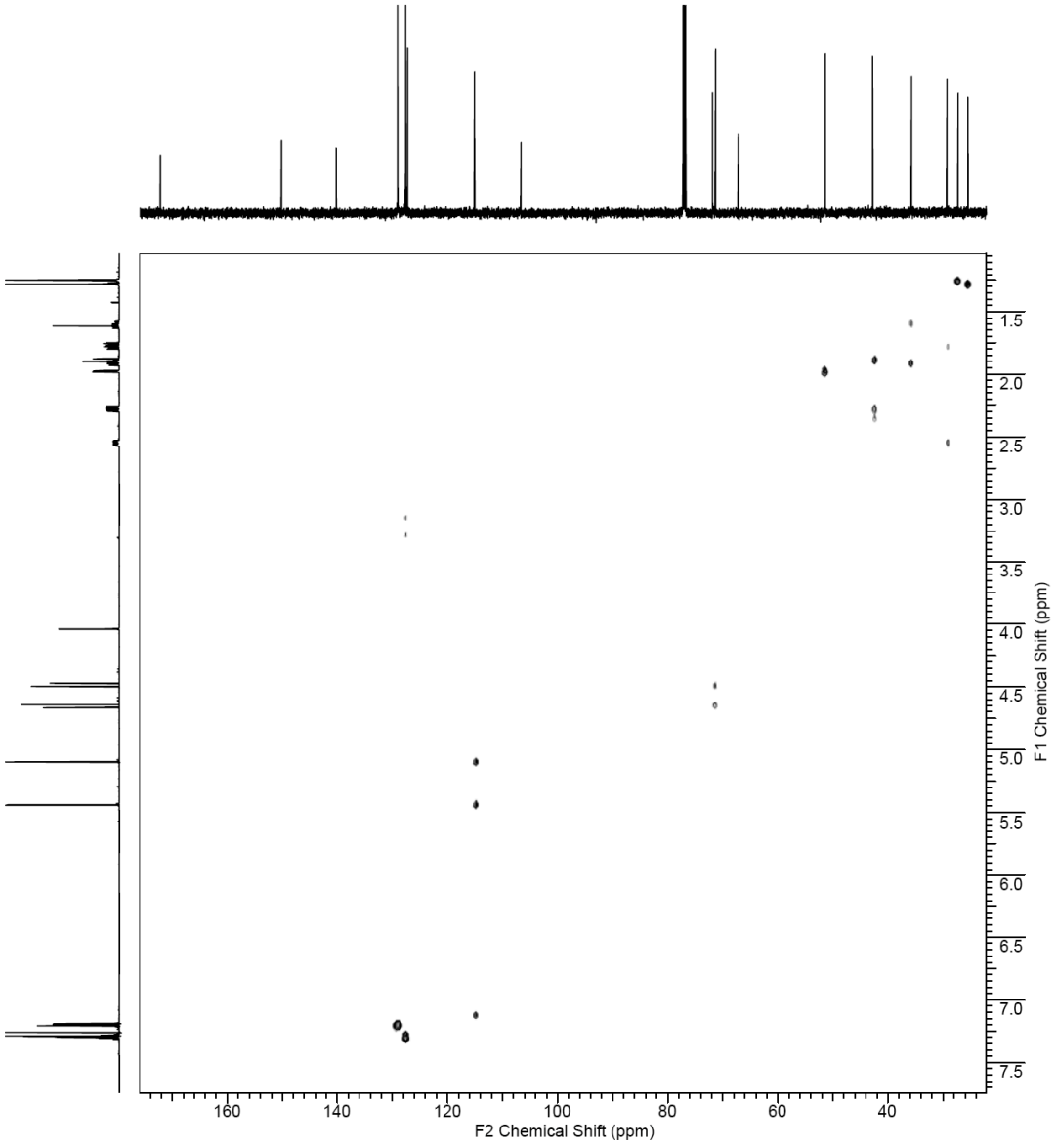

4ax
6eq
3ax
4eq

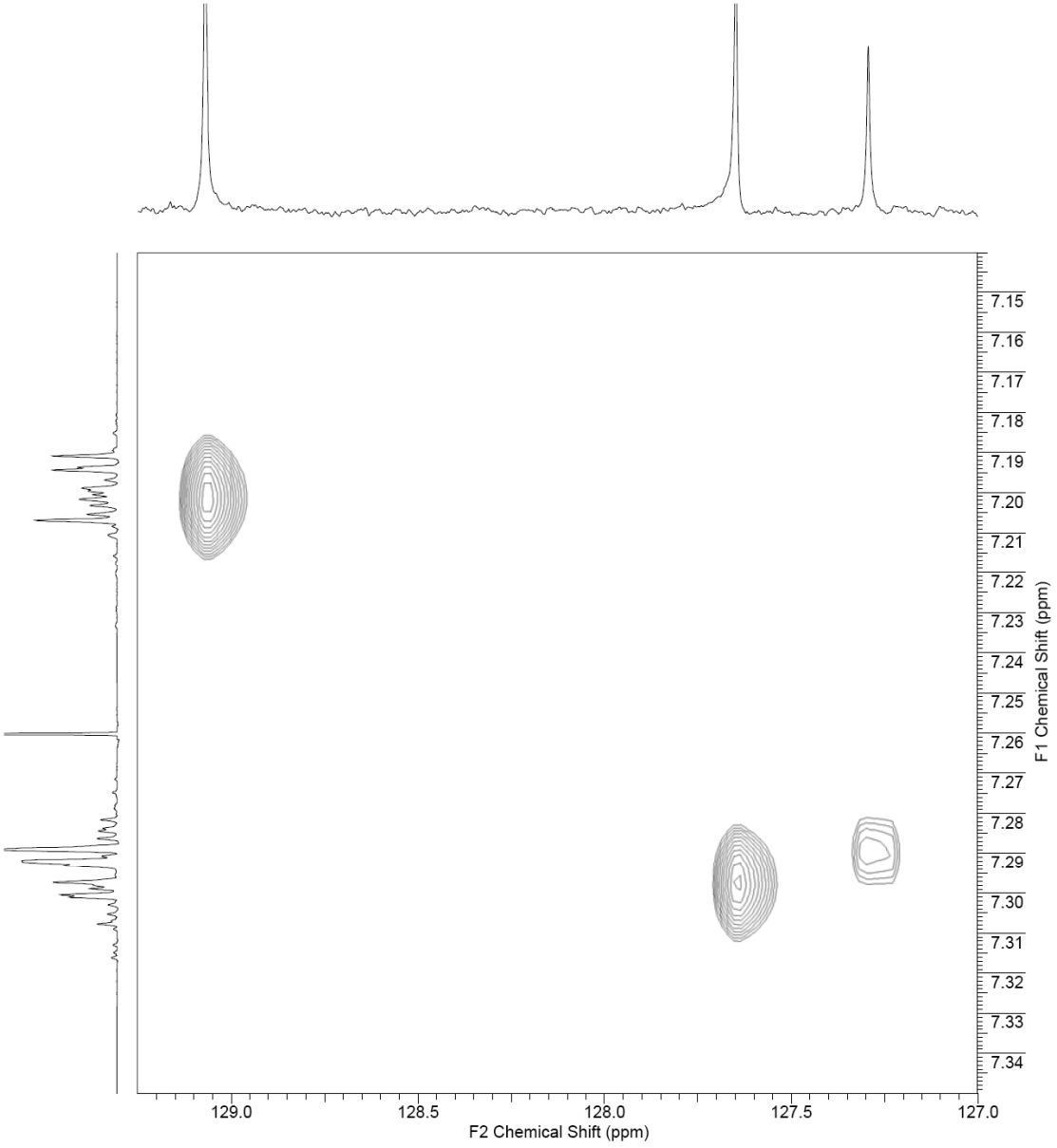

4eq
6eq
1eq
3eq
6ax
4ax
3ax
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

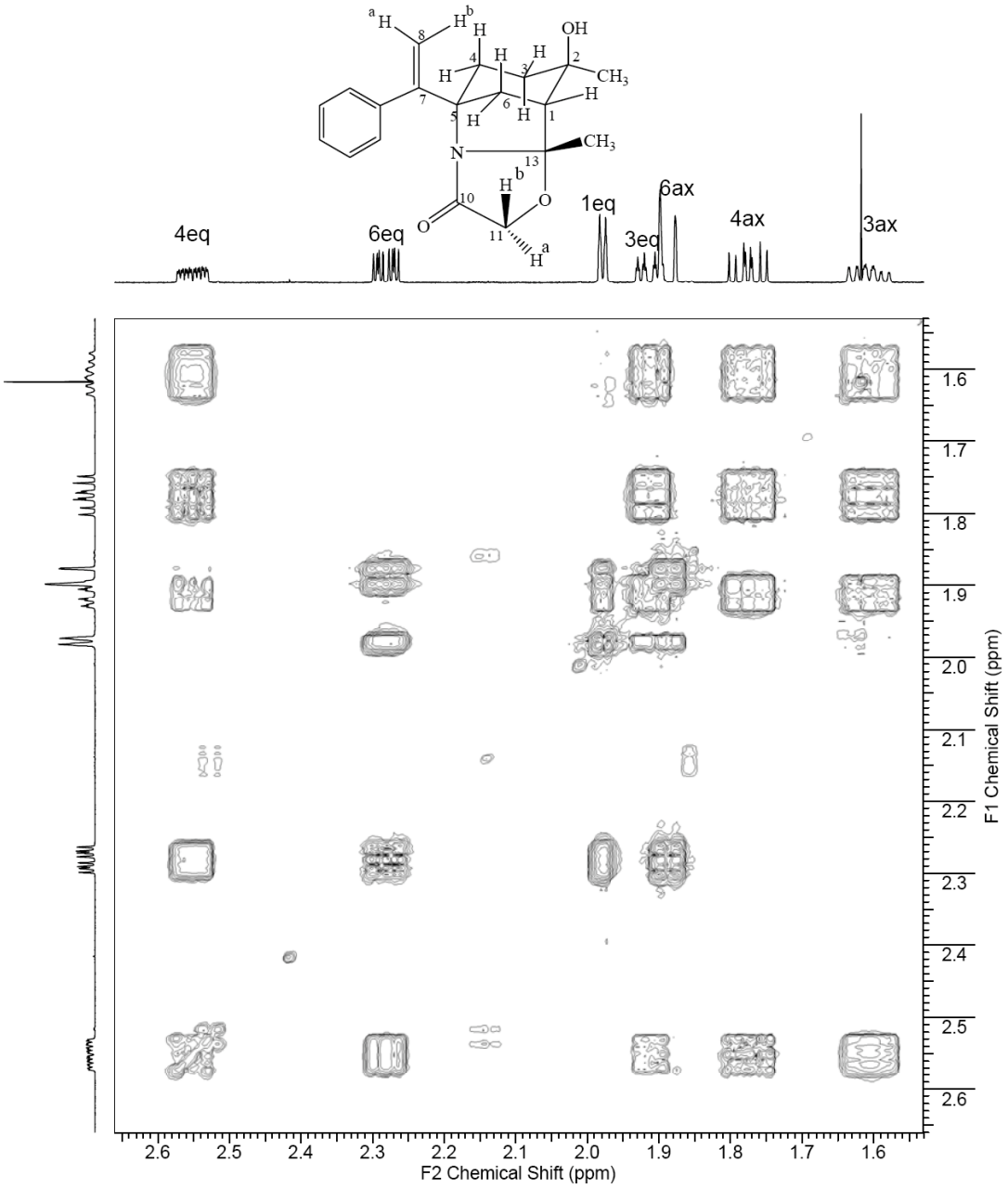

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
F1 Chemical Shift (ppm)

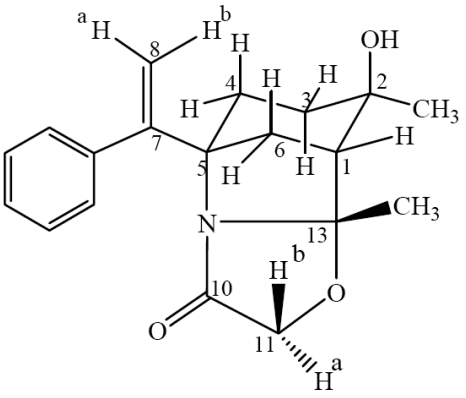

F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

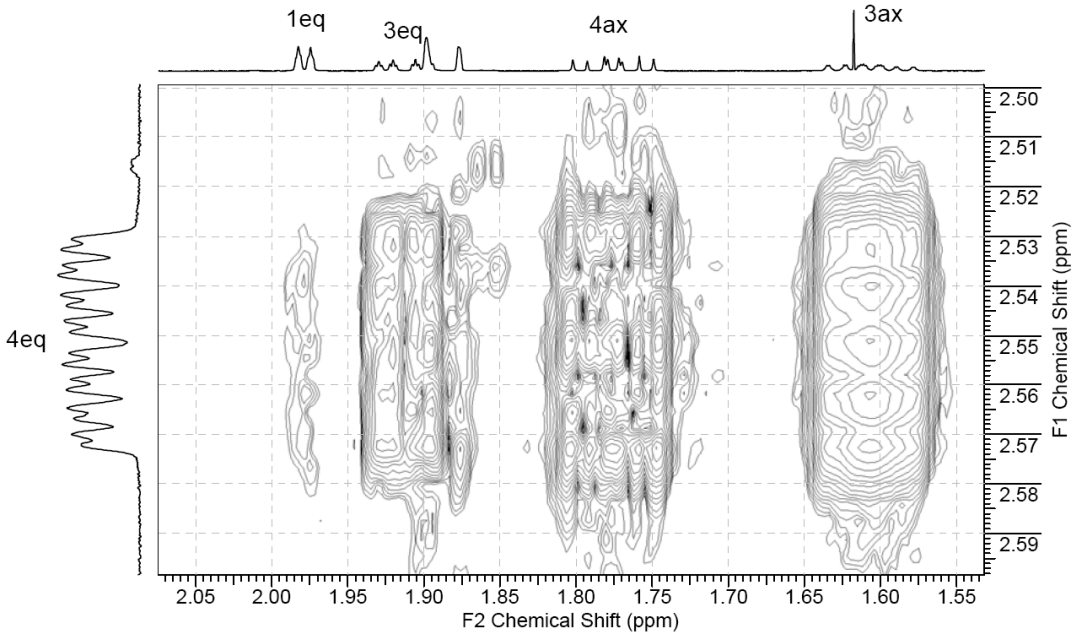

F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

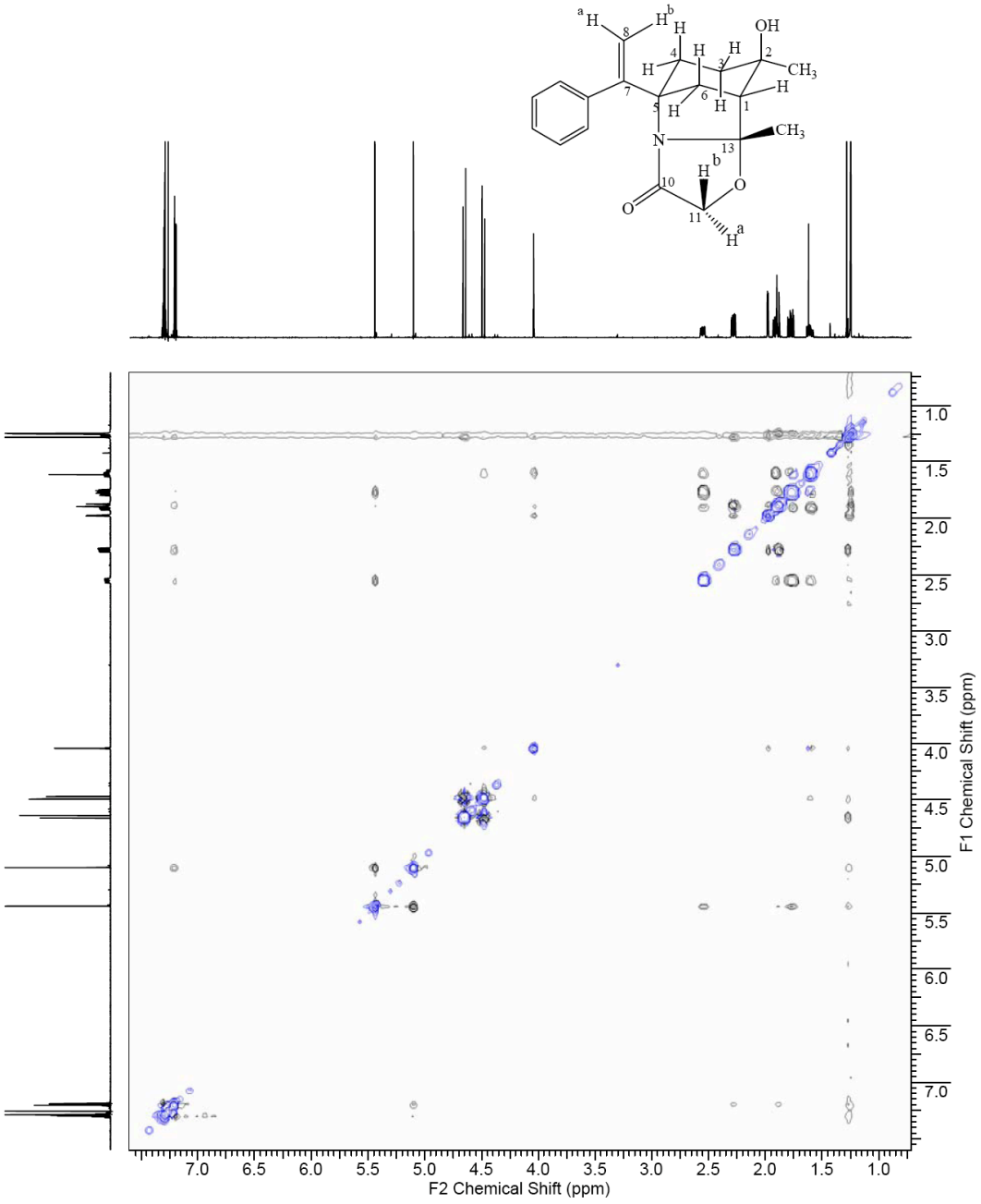

160
140
120
100
80
60
40
F2 Chemical Shift (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
F1 Chemical Shift (ppm)

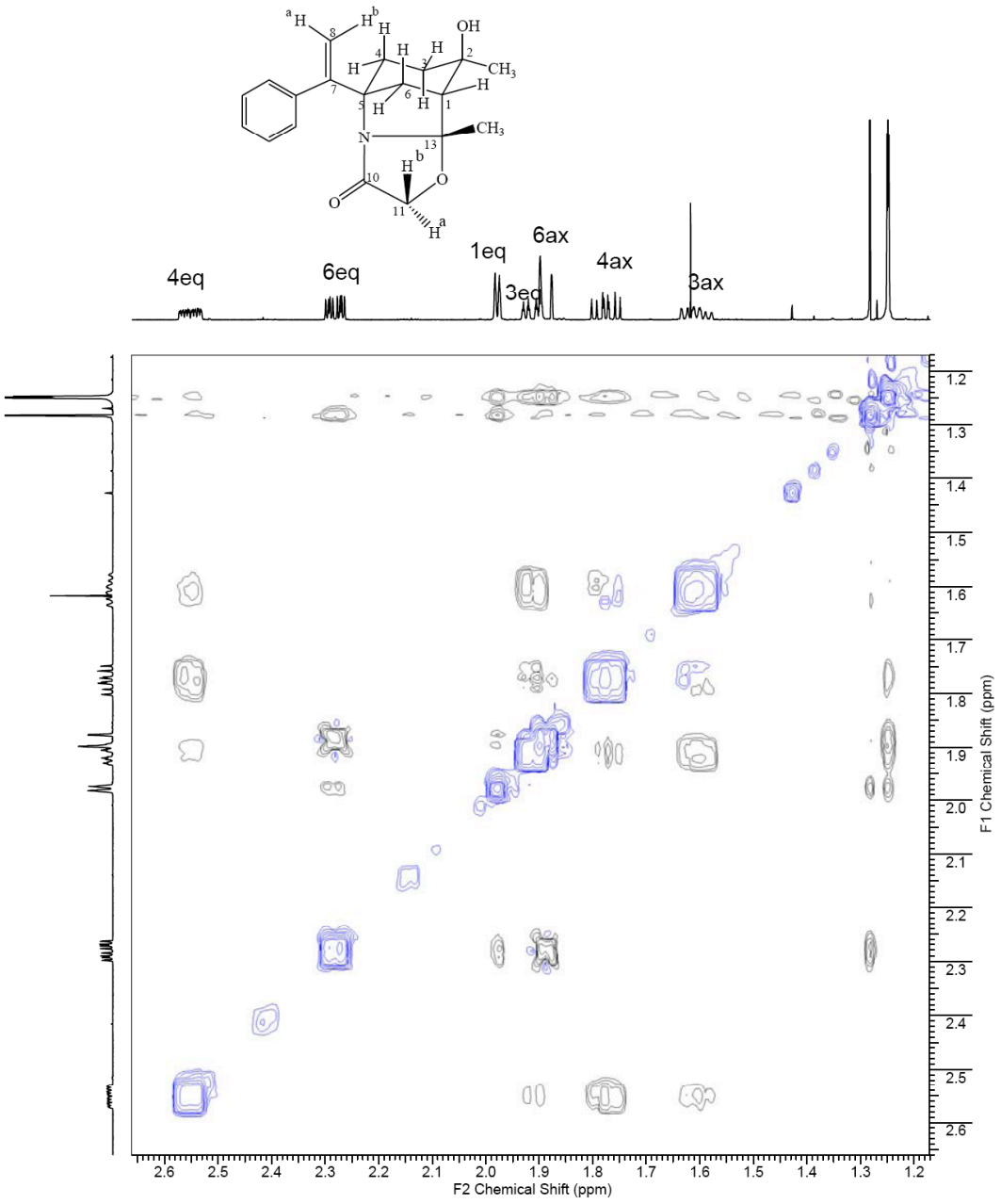

7.15
7.16
7.17
7.18
7.19
7.20
7.21
7.22
7.23
7.24
7.25
7.26
7.27
7.28
7.29
7.30
7.31
7.32
7.33
7.34
F1 Chemical Shift (ppm)
129.0
128.5
128.0
127.5
127.0
F2 Chemical Shift (ppm)

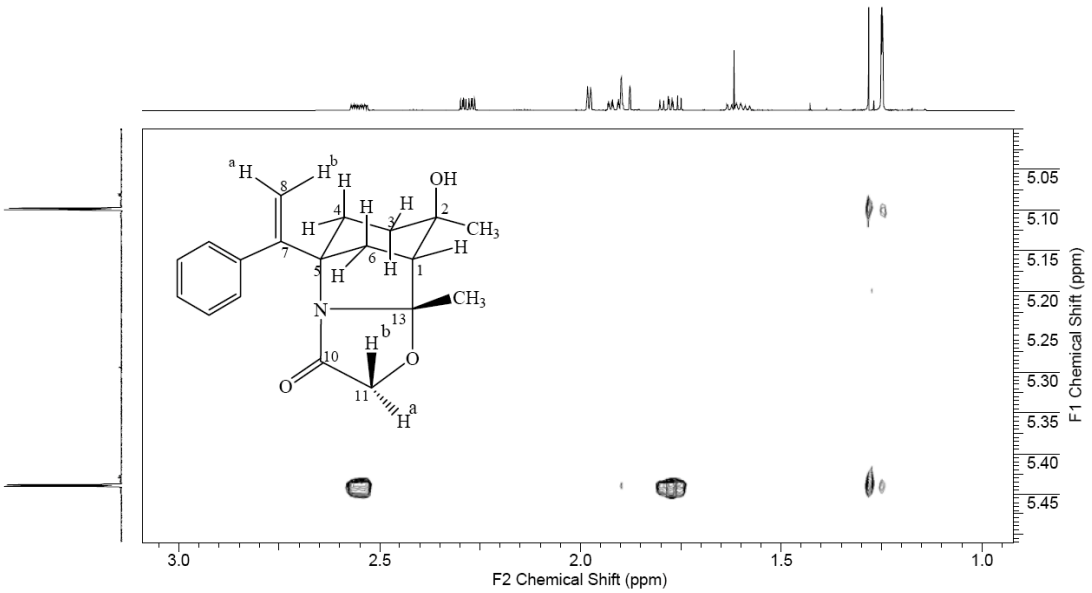

4eq
6eq
1eq
3eq
6ax
4ax
3ax
OH
CH3
CH3
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

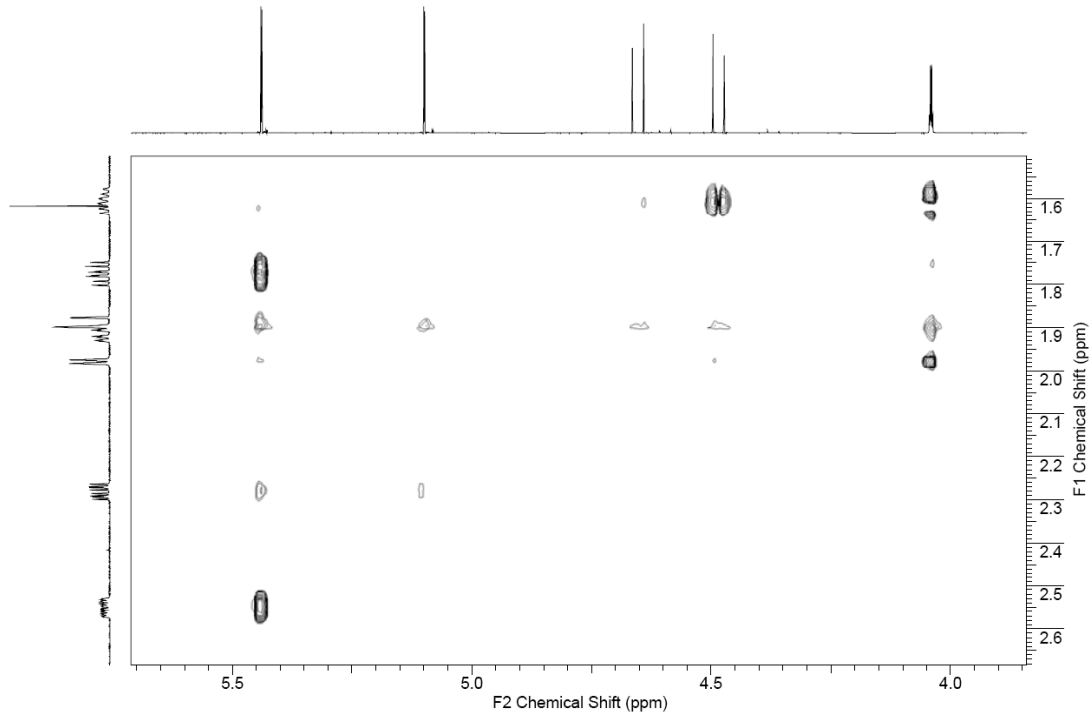

a
H
H
b
8
H
OH
4
H
H
2
H
3
CH3
7
6
H
H
5
H
H
1
CH3
N
13
H
b
10
O
O
11
H
a


1eq
3eq
4ax
3ax
4eq
2.50
2.51
2.52
2.53
2.54
2.55
2.56
2.57
2.58
2.59
F1 Chemical Shift (ppm)
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
F2 Chemical Shift (ppm)


F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


4eq
6eq
1eq
3eq
6ax
4ax
3ax
F1 Chemical Shift (ppm)
F2 Chemical Shift (ppm)


F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

V.ORTEP Drawing of the crystal structures

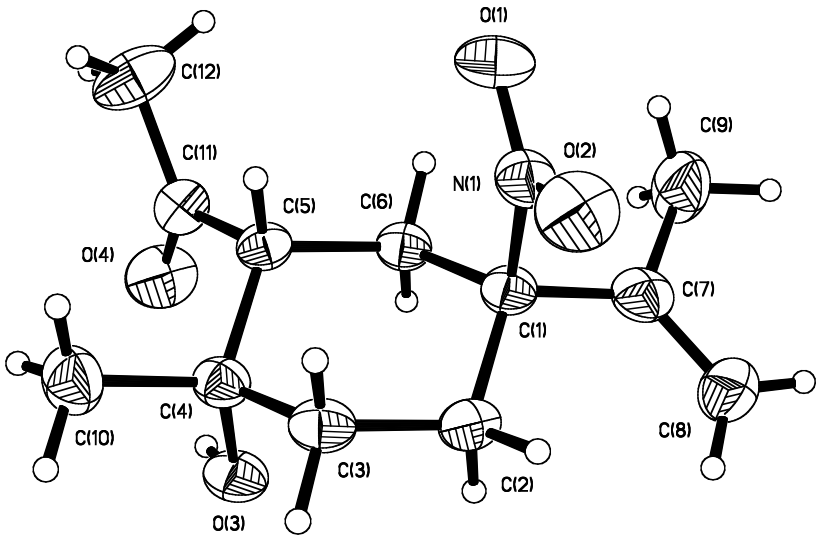


Figure 1. Perspective view of the molecular structure of **7g-major** with the atom labeling scheme. The CMe=CH_2 substituent containing carbons C(7)-C(9) exhibits a two-site rotational disorder. The thermal ellipsoids are scaled to enclose 30% probability.

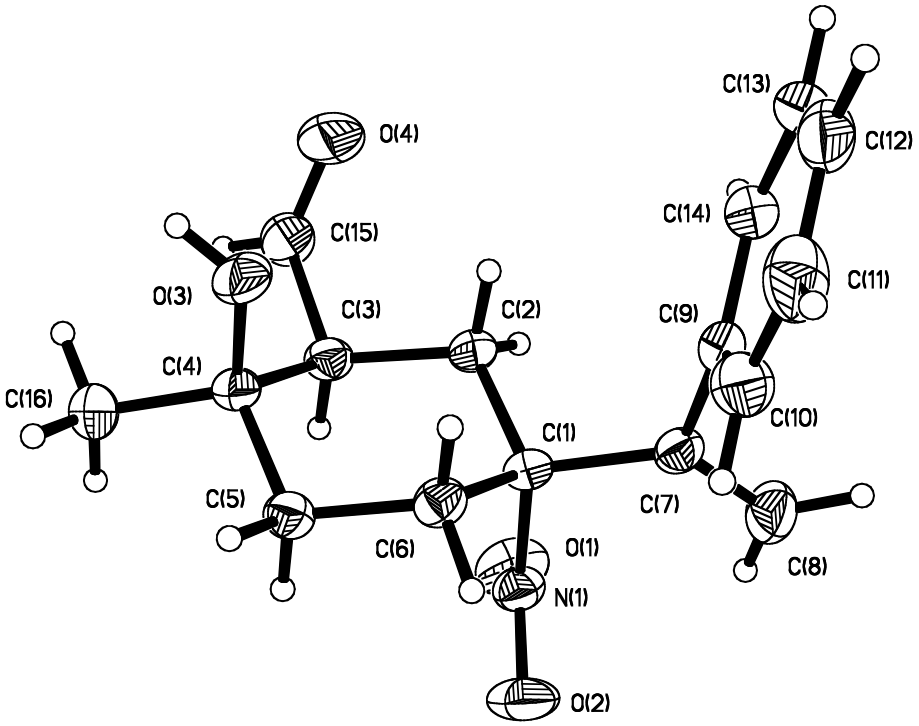


Figure 2. Perspective view of the molecular structure of **4a-major** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

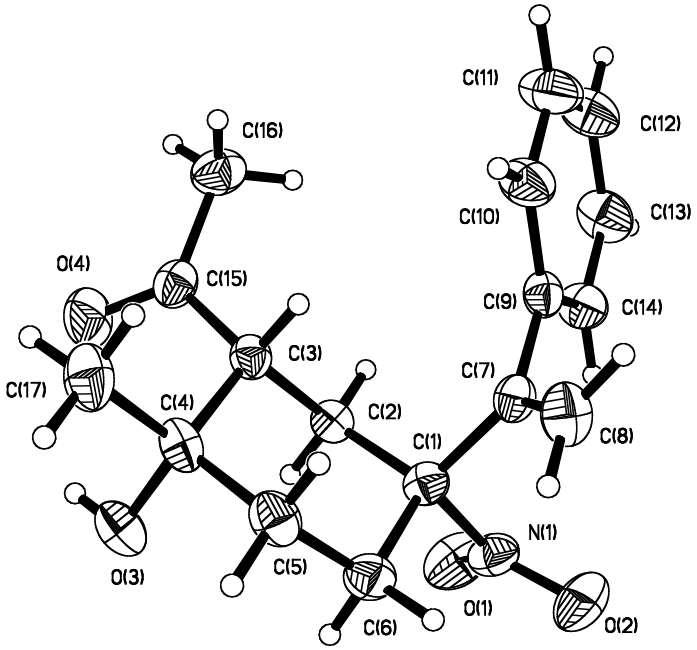


Figure 3. Perspective view of the molecular structure of **7a-minor** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

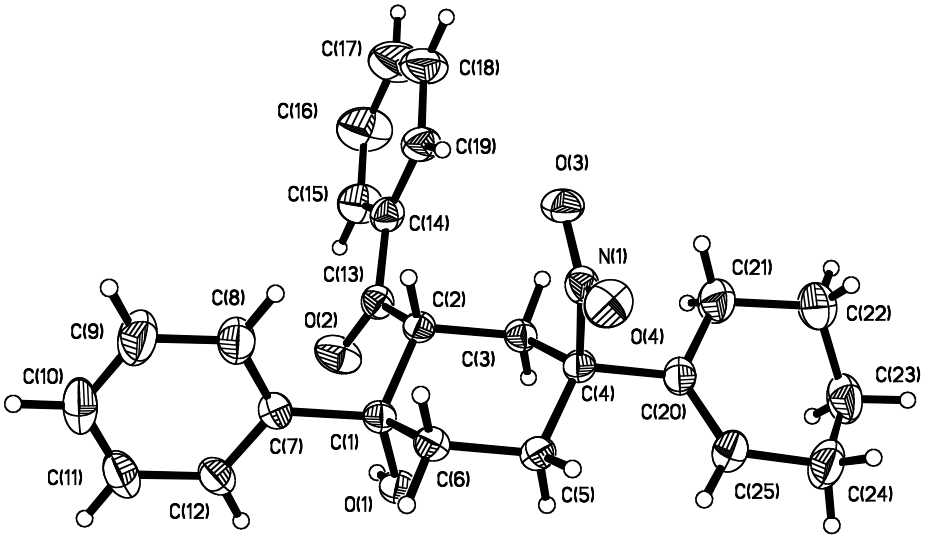


Figure 4. Perspective view of the molecular structure of **7f-major** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

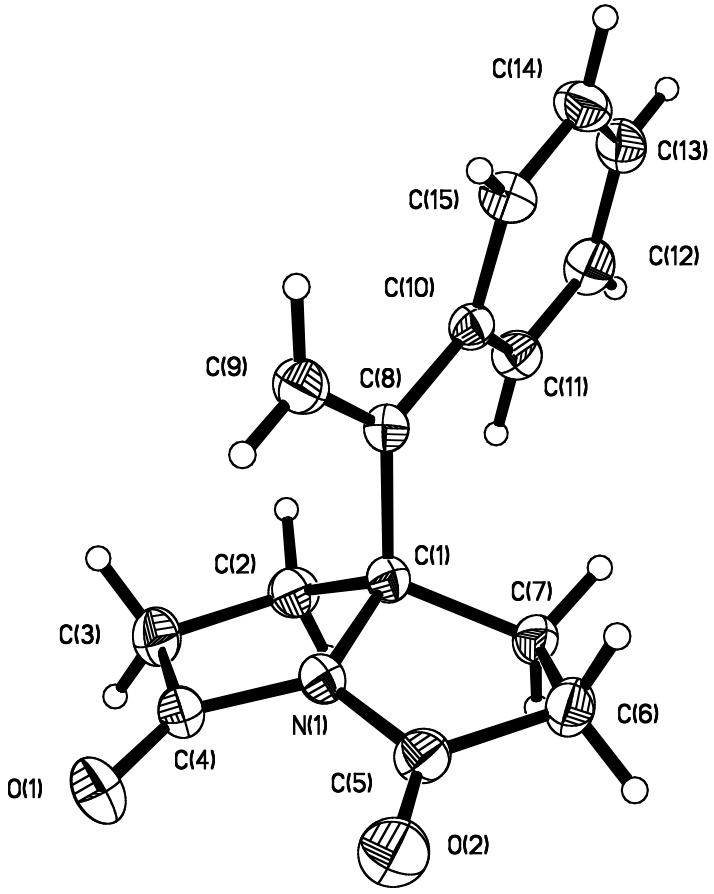


Figure 5. Perspective view of the molecular structure of **8b** with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.