Efficient Nazarov Cyclizations of 2-Alkoxy-1,4-pentadien-3-ones

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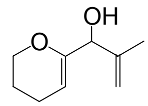
Supporting Information

General. Unless otherwise noted, infrared spectra (IR) were obtained on NaCl plates with a ATI Mattson Gemini FTIR spectrometer. Proton NMR spectra (^{1}H NMR) were recorded at 400 MHz in $CDCl_3$ and carbon NMR spectra (^{13}C NMR) were recorded at 100 MHz in $CDCl_3$ on Bruker AMX-400 spectrometer. High resolution mass spectra (HRMS) were obtained on VG ProSpec Mass Spectrometer using electron impact (EI) at 70 eV unless otherwise noted. Preparative HPLC was performed on a Varian preparative HPLC instrument with a dynamax Microsorb Si column (ID: 21.4 mm, particle size 8 µm, length: 25 cm, pore size: 60 Å) with a linear gradient of 8% EtOAc in hexanes to 25% EtOAc in hexanes over a course of 30 min with a flow rate of 21.6 mL/min. Enantioselectivities were measured on chiral analytical HPLC with a CHIRALPAK AD column (250 X 4.6 mm) with a linear gradient of 2% isopropanol in hexanes to 20% isopropanol in hexanes over a course of 18 min with a flow rate of 1.0 mL/min. The products of the Nazarov electrocyclizations were purified and confirmed by NMR spectra before enantioselectivities were measured. The peaks of two enantiomers were located based on the retention times derived from racemic mixture. Integration was done manually and the estimated error of e.e. is ±1%.

All reaction mixtures were magnetically stirred in oven-dried glassware under a blanket of nitrogen. External bath temperatures were used to record all reaction mixture temperatures. Analytical thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} TLC plates. TLC visualization was accomplished using 254 nm UV light or charring solutions of $KMnO_4$ Flash chromatography was performed on ICN siliTech 32-63 D 60 Å silica gel according to the procedure of Still.[1]

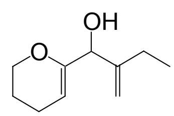
Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) were dried according to the procedure described by Bergman.[2] Benzene was distilled from CaH_2 immediately prior to use. Acetonitrile (MeCN) was distilled from P_2O_5 immediately prior to use. Extracts were dried over anhydrous Na_2SO_4 and solvents were removed with a rotary evaporator at aspirator pressure.

The preparation of compounds **8a**, **8b**, **8c**, **8e**, **8g**, **8h**, **8j**, **8k**, **8l**, **8m** and **8n** followed the same general procedure. A representative procedure was demonstrated below.



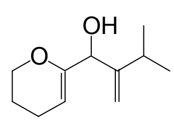
8a

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-prop-2-en-1-ol (8a) To 0.500 g (5.94 mmol) of dihydropyrone in 0.3 mL of THF was added 3.84 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC and treated with 0.2 mL of THF, the reaction mixture was cooled back to –78 ºC and was treated with 0.480g (6.53 mmol) of 2-methyl-propenal dropwise. The reaction mixture was allowed to warm to 0 ºC. Upon reaching 0 ºC, the reaction was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo.* The product was purified by column chromatography (EtOAc: hexanes = 1:6) to afford 0.503 g (55%) of **8a** as colorless oil. R_f 0.20 (EtOAc: hexanes = 1:6); IR 3427(br), 2928, 2873, 2849, 1675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.08 (s, 1 H), 4.94 (m, 1 H), 4.81 (t, 1 H, *J* = 3.8 Hz), 4.34 (d, 1 H, *J* = 5.9 Hz), 3.98 (m, 2 H), 2.22 (d, 1 H, *J* = 6.1 Hz), 2.03 (m, 2 H), 1.80 (m, 2 H), 1.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 152.87, 144.67, 111.46, 98.01, 76.00, 66.49, 22.28, 19.92, 18.80; HRMS calcd for $C_9H_{14}O_2$ $(M)^+$ 154.0994, found: 154.0990.



8b

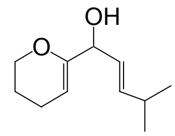
1-(5,6-Dihydro-4H-pyran-2-yl)-2-ethyl-prop-2-en-1-ol (8b) Yield: 83%; Colorless oil. R_f 0.14 (EtOAc: hexanes = 1:9); IR 3434(br), 2965, 2932, 2876, 2849, 1675, 1650cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.13 (s, 1 H), 4.92 (s, 1 H), 4.79 (t, 1 H, *J* = 3.7 Hz), 4.35 (d, 1 H, *J* = 6.0 Hz), 4.01 (m, 1 H), 3.93 (m, 1 H), 2.36 (d, 1 H, *J* = 6.0 Hz), 2.01 (m, 4 H), 1.76 (m, 2 H),1.03 (t, 3 H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 153.12, 150.34, 108.99, 98.02, 75.45, 66.41, 24.82, 22.25, 19.92, 12.12; HRMS calcd for $C_{10}H_{16}O_2$ $(M)^+$ 168.1150, found: 168.1153.



8c

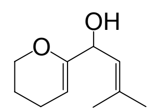
1-(5,6-Dihydro-4H-pyran-2-yl)-2-isopropyl-prop-2-en-1-ol (8c) Yield: 75%; Colorless oil; R_f 0.21 (EtOAc: hexanes = 1:9); IR 3433(br), 2959, 2930, 2871, 2850, 1675, 1649cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.10 (s, 1 H), 4.91 (s, 1 H), 4.76 (t, 1 H, *J* = 3.7 Hz), 4.34 (d, 1 H, *J* = 6.0 Hz), 3.95 (m, 1 H), 3.88 (m, 1 H), 2.47 (d, 1 H, *J* = 6.2 Hz), 2.22 (m, 1 H), 1.97 (m, 2 H), 1.72 (m, 2 H), 0.99 (d, 3 H, *J* = 6.8 Hz), 0.96 (d, 3 H, *J* = 6.8 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ_C 155.23, 153.40, 107.73, 98.04, 74.60, 66.29, 29.93, 22.92, 22.22, 19.93; HRMS calcd for $C_{11}H_{18}O_2$ $(M)^+$ 182.1307 found: 182.1305.



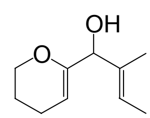
8e

1-(5,6-Dihydro-4H-pyran-2-yl)-4-methyl-pent-2-en-1-ol (8e) Yield: 91%; Colorless oil. R_f 0.21 (EtOAc: hexanes = 1:9); IR 3440(br), 2957, 2931, 2869, 2851, 1677cm^{-1}; ^1H NMR δ_H 5.67 (ddd, 1 H, J = 15.4, 6.4, 1.0 Hz), 5.48 (ddd, 1 H, J = 15.4, 6.4, 1.0 Hz), 4.73 (t, 1 H, J = 3.7 Hz), 4.36 (t, 1 H, J = 5.3 Hz), 4.00 (m, 2 H), 2.28 (m, 1 H), 2.18 (d, 1 H, J = 4.8 Hz), 2.00 (m, 2 H), 1.79 (m, 2 H), 0.97 (dd, 6 H, J = 6.8, 1.2 Hz); ^{13}C NMR δ_C 154.37, 140.30, 126.16, 96.87, 73.22, 66.41, 30.66, 22.34, 22.19, 22.13, 19.90; HRMS calcd for $C_{11}H_{18}O_2$ $(M)^+$ 182.1307, found: 182.1308



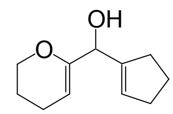
8g

1-(5,6-Dihydro-4H-pyran-2-yl)-3-methyl-but-2-en-1-ol (8g) Yield: 87%; Colorless oil. R_f 0.21 (EtOAc: hexanes = 1:6); IR 3412 (br), 2967, 2928, 2875, 2850, 1675 cm^{-1}; ^1H NMR δ_H 5.32 (dt, 1 H, J = 8.6, 1.3 Hz), 4.75 (t, 1 H, J = 3.8 Hz), 4.65 (q, 1 H, J = 4.3 Hz), 4.03 (t, 2 H, J = 5.1 Hz), 2.00 (m, 3 H), 1.80 (m, 2 H), 1.73 (d, 3 H, J = 1.0 Hz), 1.69 (d, 3 H, J = 1.0 Hz); ^{13}C NMR δ_C 154.45, 136.75, 124.17, 96.43, 69.24, 66.46, 25.88, 22.36, 19.90, 18.19; HRMS calcd for $C_{10}H_{16}O_2$ $(M)^+$ 168.1150, found: 168.1155



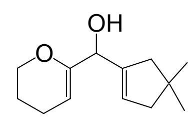
8h

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-but-2-en-1-ol (8h) Yield: 92%; Colorless oil. R_f 0.23 (EtOAc: hexanes = 1:6); IR 3435 (br), 2928, 2861, 1677 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.56 (q, 1 H, J = 6.7 Hz), 4.76 (t, 1 H, J = 3.7 Hz), 4.29 (d, 1 H, J = 4.7 Hz), 3.99 (m, 1 H), 3.94 (m, 1 H), 2.22 (d, 1 H, J = 5.2 Hz), 2.01 (m, 2 H), 1.77 (m, 2 H), 1.61 (d, 3 H, J = 6.8 Hz), 1.58 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 153.41, 135.18, 121.37, 96.99, 77.10, 66.34, 22.34, 19.88, 13.21, 12.08; HRMS calcd for $C_{10}H_{16}O_2$ $(M)^+$ 168.1150, found: 168.1149.



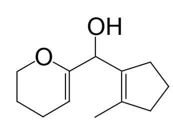
8j

Cyclopent-1-enyl-(5,6-dihydro-4H-pyran-2-yl)-methanol (8j) Yield: 90%; Colorless oil. R_f 0.10 (EtOAc: hexanes = 1:6); IR 3434(br), 2945, 2847 cm^{-1}; ^1H NMR (400 MHz, C_6H_6) δ_H 5.76 (m, 1 H), 4.75 (t, 1 H, J = 3.6 Hz), 4.63 (d, 1 H, J = 3.5 Hz), 3.67 (m, 2 H), 2.42 (m, 3 H), 2.28 (m, 2 H), 1.78 (m, 4 H), 1.40 (m, 2 H); ^{13}C NMR (100 MHz, C_6H_6) δ_C 154.73, 145.34, 126.19, 96.26, 72.22, 66.14, 32.69, 32.43, 23.75, 22.65, 20.17; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150, found: 180.1150.



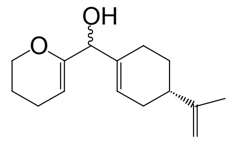
8k

(5,6-Dihydro-4H-pyran-2-yl)-(4,4-dimethyl-cyclopent-1-enyl)-methanol (8k) Yield: 85%; Colorless oil. R_f 0.27 (EtOAc: hexanes = 1:6); IR 3432 (br), 2947, 2864, 1675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.53 (s, 1 H), 4.73 (t, 1 H, J = 1.7 Hz), 4.42 (s, 1 H), 3.96 (m, 2 H), 2.32 (d, 1 H, J = 4.3 Hz), 2.13 (d, 2 H, J = 1.7 Hz), 2.07 (s, 2 H), 1.99 (m, 2 H), 1.76 (m, 2 H), 1.04 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 153.37, 142.79, 124.74, 97.18, 72.22, 66.28, 47.34, 47.09, 38.55, 29.69, 29.64, 22.34, 19.89; HRMS calcd for $C_{13}H_{20}O_2$ $(M)^+$ 208.1463, found: 208.1460.



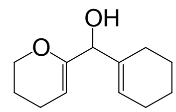
8l

(5,6-Dihydro-4H-pyran-2-yl)-(2-methyl-cyclopent-1-enyl)-methanol (8l) Yield: 85%; Colorless oil. R_f 0.32 (EtOAc: hexanes = 1:6); IR 3428 (br), 2944, 2928, 2847, 1678 cm^{-1}; ^1H NMR δ_H 4.83 (s, 1 H), 4.74 (t, 1 H, J = 3.7 Hz), 4.02 (m, 2 H), 2.47 (m, 1 H), 2.33 (m, 3 H), 2.14 (s, 1 H), 2.03 (m, 2 H), 1.80 (m, 4 H), 1.70 (s, 3 H); ^{13}C NMR δ_C 153.75, 136.61, 134.32, 95.66, 68.75, 66.33, 38.90, 31.79, 22.42, 21.58, 19.88, 13.96; HRMS calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found: 194.1311



8m

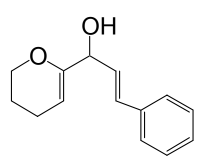
(5,6-Dihydro-4H-pyran-2-yl)-(4-isopropenyl-cyclohex-1-enyl)-methanol (8m) Yield: 88%; Colorless oil. R_f 0.27 (EtOAc: hexanes = 1:6); IR 3434(br), 2917, 1676, 1643cm^{-1}; ^{1}H NMR δ_H 5.83 (s, 1 H), 4.81 (q, 1 H, J = 3.5 Hz), 4.73 (s, 2 H), 4.35 (d, 1 H, J = 7.2 Hz), 4.02 (m, 2 H), 2.10 (m, 8 H), 1.84 (m, 3 H), 1.75 (s, 3 H), 1.46 (m, 1 H); ^{13}C NMR δ_C 153.38, 153.22, 149.89, 137.13, 136.83, 123.34, 122.57, 108.49, 97.48, 97.12, 75.90, 75.74, 66.36, 41.05, 30.48, 27.49, 25.29, 24.89, 22.35, 20.69, 19.91; HRMS calcd for $C_{15}H_{22}O_2$ (M)$^+$ 234.1620, found: 234.1618



8n

Cyclohex-1-enyl-(5,6-dihydro-4H-pyran-2-yl)-methanol (8n) Yield: 94%; Colorless oil. R_f 0.27 (EtOAc: hexanes = 1:6); IR 3425(br), 2927, 2854, 1677cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.76 (s, 1 H), 4.76 (t, 1 H, J = 3.4 Hz), 4.26 (d, 1 H, J = 4.8 Hz), 4.02 (m, 1 H), 3.95 (m, 1 H), 2.14 (d, 1 H, J = 5.5 Hz), 2.03 (m, 4 H), 1.93 (m, 2 H), 1.79 (m, 2 H), 1.57 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 153.35, 137.25, 123.50, 97.23, 76.15, 66.34, 24.97, 24.56, 22.57, 22.36, 19.91; HRMS calcd for $C_{12}H_{18}O_2$ (M)$^+$ 194.1307, found: 194.1305

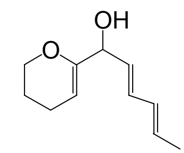
The preparation of compounds **8d**, **8f**, and **8i** followed the same general procedure. A representative procedure was demonstrated below.



8d

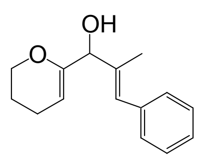
1-(5,6-Dihydro-4H-pyran-2-yl)-3-phenyl-prop-2-en-1-ol (8d) To 0.500 g (5.94 mmol) of dihydropyrone in 0.3 mL of THF was added 3.84 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC, it was treated with 0.862 g (6.53 mmol) of 3-phenyl-propenal in 1 mL of THF dropwise. The reaction mixture was kept at 0 ºC for 1 h before it was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo.* The product was purified by column chromatography (EtOAc:

hexanes = 1:6) to afford 0.770 g (60%) of **8d** as lightly yellow oil. R*f* 0.17 (EtOAc: hexanes = 1:6); IR 3432(br), 3081, 3057, 3026, 2930, 2876, 2848, 1674cm^{-1}; ^{1}H NMR δ_H 7.39 (d, 2 H, *J* = 7.3 Hz), 7.31 (t, 2 H, *J* = 7.3 Hz), 7.23 (t, 1 H, *J* = 7.3 Hz), 6.66 (d, 1 H, *J* = 6.0 Hz), 6.31 (dd, 1 H, *J* = 15.9, 6.3 Hz), 4.85 (t, 1 H, *J* = 3.7 Hz), 4.62 (t, 1 H, *J* = 5.4 Hz), 4.05 (m, 2 H), 2.30 (d, 1 H, *J* = 5.3 Hz), 2.04 (m, 2 H), 1.83 (m, 2 H); ^{13}C NMR δ_C 153.78, 136.62, 131.23, 128.78, 128.48, 127.63, 126.57, 97.47, 73.24, 66.51, 22.29, 19.89; HRMS calcd for $C_{14}H_{16}O_2$ (M)$^+$ 216.1150, found: 216.1153



8f

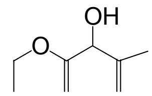
1-(5,6-Dihydro-4H-pyran-2-yl)-hexa-2,4-dien-1-ol (8f) Yield: 45%; Colorless oil. R*f* 0.19 (EtOAc: hexanes = 1:6); IR 3440(br), 3017, 2930, 2876, 2850, 1675cm^{-1}; ^{1}H NMR δ_H 6.25 (dd, 1 H, *J* = 15.2, 10.4 Hz), 6.07 (m, 1 H), 5.70 (m, 2 H), 4.79 (t, 1 H, *J* = 3.8 Hz), 4.46 (s, 1 H), 4.03 (m, 2 H), 2.21 (d, 1 H, *J* = 4.5 Hz), 2.03 (m, 2 H), 1.82 (m, 2 H), 1.76 (d, 3 H, *J* = 6.7 Hz); ^{13}C NMR δ_C 154.03, 131.86, 130.80, 130.24, 129.57, 97.13, 73.02, 66.47, 22.33, 19.91, 18.11; HRMS calcd for $C_{11}H_{16}O_2$ (M)$^+$ 180.1150 found: 180.1149



8i

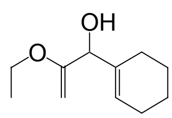
1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-3-phenyl-prop-2-en-1-ol (8i) Yield: 68%; Colorless oil. R*f* 0.24 (EtOAc: hexanes = 1:6); IR 3429(br), 3080, 3054, 3023, 2945, 2930, 2870, 2849, 1675 cm^{-1}; ^{1}H NMR δ_H 7.32 (m, 4 H), 7.21 (m, 1 H), 6.64 (s, 1 H), 4.88 (t, 1 H, *J* = 3.7 Hz), 4.51 (d, 1 H, *J* = 4.4 Hz), 4.03 (m, 2 H), 2.54 (d, 1 H, *J* = 5.2 Hz), 2.06 (m, 2 H), 1.88 (d, 3 H, *J* = 1.1 Hz), 1.82 (m, 2 H); ^{13}C NMR δ_C 153.16, 137.69, 137.40, 129.03, 128.00, 126.33, 126.23, 97.85, 66.47, 22.34, 19.99, 14.49; HRMS calcd for $C_{15}H_{18}O_2$ (M)$^+$ 230.1307, found: 230.1310

The preparation of compounds **8p**, **8r** and **8s** followed the same general procedure. A representative procedure was demonstrated below.



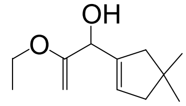
8p

2-Ethoxy-4-methyl-penta-1,4-dien-3-ol (8p) To 0.500 g (6.93 mmol) of ethyl vinyl ether in 0.4 mL of THF was added 3.71 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC and treated with 0.3 mL of THF, the reaction mixture was cooled back to –78 ºC and was treated with 0.400 g (5.73 mmol) of 2-methyl-propenal dropwise. The reaction mixture was allowed to warm to 0 ºC. Upon reaching 0 ºC, the reaction was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo.* The product was purified by column chromatography (EtOAc: hexanes = 1:15) to afford 0.400 g (49%) of **8p** as colorless oil. R_f 0.23 (EtOAc: hexanes = 1:9); IR 3436(br), 2979, 2917, 2882, 1658, 1625cm^{-1}; ^{1}H NMR δ_H 5.06 (s, 1 H), 4.92 (dd, 1 H, *J* = 2.5, 1.5 Hz), 4.43 (d, 1 H, *J* = 6.0 Hz), 4.16 (d, 1 H, *J* = 2.3 Hz), 4.01 (d, 1 H, *J* = 2.3 Hz), 3.74 (q, 2 H, *J* = 7.0 Hz), 2.33 (d, 1 H, *J* = 6.2 Hz) 1.71 (s, 3 H), 1.28 (t, 3 H, *J* = 7.0Hz); ^{13}C NMR δ_C 161.37, 144.71, 111.89, 82.33, 76.35, 63.09, 18.44, 14.21; HRMS calcd for $C_8H_{14}O_2$ (M)$^+$ 142.0994, found: 142.0997



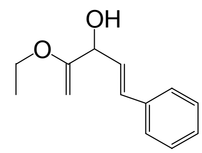
8r

1-Cyclohex-1-enyl-2-ethoxy-prop-2-en-1-ol (8r) Yield: 78%; Colorless oil. R_f 0.12 (EtOAc: hexanes = 1:20); IR 3410(br), 2978, 2927, 1657, 1623cm^{-1}; ^{1}H NMR δ_H 5.71 (s, 1 H), 4.33 (d, 1 H, *J* = 3.9 Hz), 4.11 (d, 1 H, *J* = 2.0 Hz), 3.96 (d, 1 H, *J* = 2.0 Hz), 3.71 (q, 2 H, *J* = 7.0 Hz), 2.36 (d, 1 H, *J* = 5.0 Hz), 1.93 (m, 4 H), 1.55 (m, 4 H), 1.25 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ_C 162.00, 137.36, 123.98, 81.77, 76.62, 62.99, 25.04, 24.26, 22.62, 22.41, 14.29; HRMS calcd for $C_{11}H_{18}O_2$ (M)$^+$ 182.1307, found: 182.1307



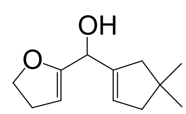
8s

1-(4,4-Dimethyl-cyclopent-1-enyl)-2-ethoxy-prop-2-en-1-ol (8s) Yield: 58%; Colorless oil. R_f 0.30 (EtOAc: hexanes = 1:9); IR 3441(br), 2952, 2925, 2901, 2866, 2840, 1717, 1650, 1622cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.56 (s, 1 H), 4.55 (d, 1 H, *J* = 6.0 Hz), 4.11 (d, 1 H, *J* = 1.8 Hz), 3.97 (d, 1 H, *J* = 1.8 Hz), 3.75 (q, 2 H, *J* = 7.0 Hz), 2.28 (d, 1 H, *J* = 6.4 Hz), 2.15 (s, 2 H), 2.10 (s, 2 H), 1.28 (t, 3 H, *J* = 7.0 Hz), 1.06 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 161.78, 142.74, 125.14, 81.74, 72.56, 62.97, 47.35, 46.79, 38.57, 29.63, 14.27; HRMS calcd for $C_{12}H_{20}O_2$ (M)$^+$ 196.1463, found: 196.1463



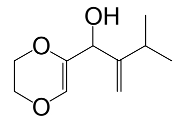
8q

4-Ethoxy-1-phenyl-penta-1,4-dien-3-ol (8q) To 0.500 g (6.93 mmol) of ethyl vinyl ether in 0.4 mL of THF was added 3.71 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC, it was treated with 0.757 g (5.73 mmol) of 3-phenyl-propenal in 1 mL of THF dropwise. The reaction mixture was kept at 0 ºC for 1 h before it was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:9) to afford 0.678 g (58%) of **8q** as colorless oil. R_f 0.26 (EtOAc: hexanes = 1:6); IR 3368(br), 3027, 2979, 2360, 2335, 1658, 1625cm^{-1}; ^{1}H NMR δ_H 7.43 (d, 2 H, *J* = 7.6 Hz), 7.34 (t, 2 H, *J* = 7.6 Hz), 7.27 (d, 1 H, *J* = 7.6 Hz), 6.70 (d, 1 H, *J* = 16.0 Hz), 6.35 (dd, 1 H, *J* = 16.0, 6.2 Hz), 4.74 (t, 1 H, *J* = 3.7 Hz), 4.25 (d, 1 H, *J* = 2.1 Hz), 4.06 (d, 1 H, *J* = 2.1 Hz), 3.83 (q, 2 H, *J* = 7.0 Hz), 2.42 (d, 1 H, *J* = 5.5 Hz), 1.36 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ_C 162.32, 136.71, 131.32, 129.17, 128.54, 127.71, 126.63, 81.99, 73.64, 63.27, 14.36; HRMS calcd for $C_{13}H_{16}O_2$ $(M)^+$ 204.1150, found: 204.1153



8o

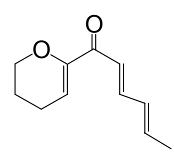
(4,5-Dihydro-furan-2-yl)-(4,4-dimethyl-cyclopent-1-enyl)-methanol (8o) To 0.500 g (7.13 mmol) of dihydrofuran in 0.3 mL of THF was added 4.62 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC and treated with 0.2 mL of THF, the reaction mixture was cooled back to –78 ºC and was treated with 0.974 g (7.84 mmol) of 4,4-dimethyl-cyclopent-1-enecarbaldehyde dropwise. The reaction mixture was allowed to warm to 0 ºC. Upon reaching 0 ºC, the reaction was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:6) to afford 1.18 g (85%) of **8o** as colorless oil; R_f 0.27 (EtOAc: hexanes = 1:6); IR 3460(br), 2951, 2929, 2892, 2865, 2840, 1714 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.61 (d, 1 H, *J* = 1.2 Hz), 4.86 (t, 1 H, *J* = 2.2 Hz), 4.76 (d, 1 H, *J* = 5.1 Hz), 4.36 (m, 2 H), 2.65 (m, 2 H), 2.18 (d, 2 H, *J* = 2.0 Hz), 2.15 (d, 2 H, *J* = 2.0 Hz), 2.02 (d, 1 H, *J* = 5.6 Hz), 1.08 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 157.80, 141.93, 125.76, 95.95, 70.34, 67.64, 47.32, 46.77, 38.58, 29.77, 29.69, 29.67; HRMS calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found: 194.1312



8t

1-(5,6-Dihydro-[1,4]dioxin-2-yl)-2-isopropyl-prop-2-en-1-ol (8t) To 0.500 g (5.81 mmol) of 2,3-dihydro-[1,4]dioxine in 0.3 mL of THF was added 3.76 mL of a 1.7 M solution of *t*-BuLi in pentane dropwise at –78 ºC. The reaction mixture was warmed to 0 ºC. After the reaction mixture was stirred for 30 min at 0 ºC and treated with 0.2 mL of THF, the reaction mixture was cooled back to –78 ºC and was treated with 0.627 g (6.39 mmol) of 2-isopropyl-propenal dropwise. The reaction mixture was allowed to warm to 0 ºC. Upon reaching 0 ºC, the reaction was quenched with water (50 mL) and diluted with EtOAc (100 mL). The two layers were separated and the aqueous layer was extracted with EtOAc (2 X 40 mL). The combined organic layers were washed with brine (80 mL), dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:6) to afford 0.696 g (65%) of **8t** as colorless oil; R_f 0.21 (EtOAc: hexanes = 1:4); IR 3428(br), 2961, 2931, 2874, 1680, 1649 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.10 (s, 1 H), 5.21 (s, 1 H), 5.02 (s, 1 H), 4.40 (d, 1 H, *J* = 4.2 Hz), 4.08 (s, 2 H), 3.98 (m, 2 H), 2.26 (m, 2 H), 1.06 (d, 3 H, *J* = 6.8 Hz), 1.03 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 154.43, 136.88, 125.18, 108.06, 72.16, 64.62, 64.07, 30.28, 22.97, 22.01; HRMS calcd for $C_{10}H_{16}O_3$ $(M)^+$ 184.1100, found: 184.1102

The oxidation of compounds **8** to **9** was carried out by either Dess-Martin oxidation or MnO_2. The representative procedures of both methods were demonstrated below.

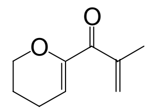


9f

1-(5,6-Dihydro-4H-pyran-2-yl)-hexa-2,4-dien-1-one (9f) Oxidation by Dess-Martin reagent: To 0.250 g (1.39 mmol) of **8f** and 1 mL pyridine in 25 mL of CH_2Cl_2 was added 0.718 g (1.46 mmol) of Dess-Martin reagent at 23 °C. After 20 min, the reaction was quenched with 20 mL 1:1 mixture of water and 6 N NaOH solution. The mixture was stirred vigorously for 10 min. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 15 mL). The combined organic layers were washed with brine (30 mL), dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:9) to afford 0.990 g (40%) of **9f** as colorless oil;

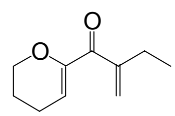
Oxidation by MnO_2: To a suspension of 7.80 g manganese (IV) oxide in 50 mL benzene was added 0.780 g (4.33 mmol) of **8f** dissolved in 50 mL benzene. After 5 min, the reaction mixture was filtered through Celite and washed with EtOAc (4 X 50 mL). The combined filtrate was concentrate *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:9) to afford 0.733 g (95%) of **9f** as colorless oil R_f

0.23 (EtOAc: hexanes = 1:6); IR 2991, 2950, 2934, 1671, 1620, 1580cm^{-1}; ^{1}H NMR δ_H 7.30 (m, 1 H), 6.32 (d, 1 H, *J* = 15.0 Hz), 6.20 (m, 2 H), 5.99 (t, 1 H, *J* = 4.2 Hz), 4.09 (t, 2 H, *J* = 5.1 Hz), 2.21 (dd, 2 H, *J* = 10.7, 6.3 Hz), 1.84 (m, 5 H); ^{13}C NMR δ_C 185.78, 151.94, 144.23, 140.68, 130.65, 121.84, 110.20, 66.31, 21.58, 20.86, 18.83; HRMS calcd for $C_{11}H_{14}O_2$ $(M)^+$ 178.0994, found: 178.0998



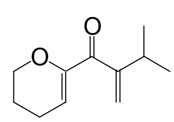
9a

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-propenone (9a) Dess-Martin oxidation afforded **9a** as colorless oil in 85% yield. R_f 0.33 (EtOAc: hexanes = 1:6); IR 2928, 2878, 1657, 1625 cm^{-1}; ^{1}H NMR (500 Hz, $CDCl_3$) δ_H 5.84 (t, 1 H, *J* = 4.1 Hz), 5.66 (s, 1 H), 5.64 (t, 1 H, *J* = 1.4 Hz), 4.11 (t, 2 H, *J* = 5.1 Hz), 2.22 (m, 2 H), 1.93 (t, 3 H, *J* = 1.1 Hz), 1.87 (m, 2 H); ^{13}C NMR (125 Hz, $CDCl_3$) δ_C 192.61, 150.89, 142.79, 123.83, 113.83, 66.28, 21.43, 20.82, 18.92; HRMS calcd for $C_9H_{12}O_2$ $(M)^+$ 152.0837, found: 152.0839



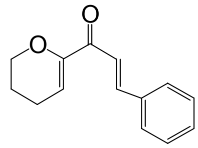
9b

1-(5,6-Dihydro-4H-pyran-2-yl)-2-ethyl-propenone (9b) Dess-Martin oxidation afforded **9b** as colorless oil in 82% yield. R_f 0.27 (EtOAc: hexanes = 1:6); IR 2967, 2934, 2876, 1656, 1625cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.72 (t, 1 H, *J* = 4.2 Hz), 5.43 (d, 1 H, *J* = 1.0 Hz), 5.39 (d, 1 H, *J* = 1.0 Hz), 3.96 (t, 2 H, *J* = 5.1 Hz), 2.19 (m, 2 H), 2.08 (m, 2 H), 1.71 (m, 2 H), 0.87 (t, 3 H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 192.80, 151.08, 148.56, 120.87, 114.67, 66.18, 25.39, 21.25, 20.74, 12.02; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0993



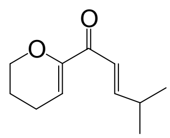
9c

1-(5,6-Dihydro-4H-pyran-2-yl)-2-isopropyl-propenone (9c) Dess-Martin oxidation afforded **9c** as a colorless oil in 88% yield. R_f 0.23 (EtOAc: hexanes = 1:9); IR 2961, 2932, 2873, 1660, 1625cm^{-1}; ^{1}H NMR δ_H 5.74 (t, 1 H, *J* = 4.2 Hz), 5.33 (d, 2 H, *J* = 4.4 Hz), 3.98 (t, 2 H, *J* = 5.1 Hz), 2.73 (m, 1 H), 2.10 (m, 2 H), 1.74 (m, 2 H), 0.9 (d, 6 H, *J* = 7.0 Hz); ^{13}C NMR δ_C 193.60, 153.34, 151.51, 118.34, 115.30, 66.29, 29.92, 21.32, 21.07, 20.89; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150 found: 181.1153



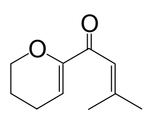
9d

1-(5,6-Dihydro-4H-pyran-2-yl)-3-phenyl-propenone (9d) Oxidation by MnO_2 afforded **9d** as lightly yellow oil in 80% yield. R_f 0.34 (EtOAc: hexanes = 1:6); IR 3059, 3026, 2950, 2932, 2874, 1664, 1628, 1599, 1575cm^{-1}; ^{1}H NMR δ_H 7.70 (d, 1 H, *J* = 5.8 Hz), 7.54 (m, 2 H), 7.32 (m, 4 H), 6.09 (t, 1 H, *J* = 4.2 Hz), 4.11 (t, 2 H, *J* = 5.0 Hz), 2.21 (dd, 2 H, *J* = 10.6, 6.2 Hz), 1.84 (m, 2 H); ^{13}C NMR δ_C 185.28, 151.83, 143.71, 134.88, 130.32, 128.80, 128.39, 120.5, 110.88, 66.34, 21.49, 20.87; HRMS calcd for $C_{14}H_{14}O_2$ $(M)^+$ 214.0994, found: 214.0989



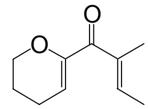
9e

1-(5,6-Dihydro-4H-pyran-2-yl)-4-methyl-pent-2-en-1-one (9e) Dess-Martin oxidation afforded **9e** as colorless oil in 55% yield. R_f 0.28 (EtOAc: hexanes = 1:15); IR 2961, 2933, 2871, 1683, 1671, 1634, 1614cm^{-1}; ^{1}H NMR δ_H 6.89 (dd, 1 H, *J* = 15.5, 6.7 Hz), 6.53 (d, 1 H, *J* = 15.5 Hz), 5.94 (t, 1 H, *J* = 4.2 Hz), 4.02 (t, 2 H, *J* = 5.0 Hz), 2.39 (m, 1 H), 2.14 (dd, 2 H, *J* = 10.8, 6.2 Hz), 1.78 (m, 2 H), 0.98 (d, 6 H, *J* = 6.8Hz); ^{13}C NMR δ_C 185.69, 154.74, 151.62, 121.0, 110.72, 66.20, 31.27, 21.43, 21.23, 20.75; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150, found: 180.1152



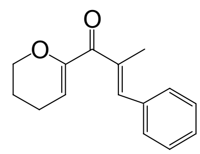
9g

1-(5,6-Dihydro-4H-pyran-2-yl)-3-methyl-but-2-en-1-one (9g) Oxidation by MnO_2 afforded **9g** as colorless oil in 91% yield. R_f 0.34 (EtOAc: hexanes = 1:9); IR 2972, 2934, 2875, 1663, 1631, 1611 cm^{-1}; ^{1}H NMR δ_H 6.43 (t, 1 H, *J* = 1 Hz), 5.88 (t, 1 H, *J* = 4.2 Hz), 4.02 (t, 2 H, *J* = 5.1 Hz), 2.12 (m, 2 H), 2.07 (s, 3 H), 1.85 (s, 3 H), 1.77 (m, 2 H); ^{13}C NMR δ_C 186.56, 156.56, 152.31, 119.50, 109.23, 66.23, 27.93, 21.56, 20.99, 20.74; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0989



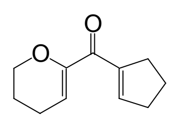
9h

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-but-2-en-1-one (9h) Dess-Martin oxidation afforded **9h** as colorless oil in 70% yield. R_f 0.26 (EtOAc: hexanes = 1:6); IR 2931, 2874, 1649 cm^{-1}; ^{1}H NMR δ_H 6.40 (m, 1 H), 5.55 (t, 1 H, *J* = 4.1 Hz), 4.00 (t, 2 H, *J* = 5.2 Hz), 2.10 (m, 2 H), 1.77 (m, 2 H), 1.72 (m, 6 H); ^{13}C NMR δ_C 193.07, 151.23, 137.73, 136.13, 111.86, 66.26, 21.53, 20.67, 14.37, 12.35; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0993.



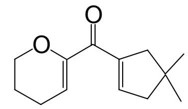
9i

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-3-phenyl-propenone (9i) Dess-Martin oxidation afforded **9i** as colorless oil in 83% yield. R_f 0.23 (EtOAc: hexanes = 1:9); IR 3055, 3024, 2954, 2929, 2873, 2841, 1654, 1626 cm^{-1}; ^{1}H NMR δ_H 7.35 (m, 4 H), 7.27 (m, 1 H), 7.21 (d, 1 H, *J* = 1.3 Hz), 5.79 (t, 1 H, *J* = 4.2 Hz), 4.12 (t, 2 H, *J* = 5.1 Hz), 2.21 (m, 2 H), 2.10 (d, 3 H, *J* = 1.4 Hz), 1.87 (m, 2 H); ^{13}C NMR δ_C 193.68, 151.18, 138.74, 135.77, 135.72, 129.54, 128.35, 128.24, 113.27, 66.37, 21.51, 20.84, 14.72; HRMS calcd for $C_{15}H_{16}O_2$ $(M)^+$ 228.1150, found: 228.1152



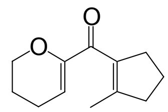
9j

Cyclopent-1-enyl-(5,6-dihydro-4H-pyran-2-yl)-methanone (9j) Dess-Martin oxidation afforded **9j** as colorless oil in 60% yield. R_f 0.26 (EtOAc: hexanes = 1:6); IR 2947, 2872, 1644, 1609 cm^{-1}; ^{1}H NMR δ_H 6.79, (m, 1 H), 5.84 (t, 1 H, *J* = 4.2 Hz), 4.10 (t, 2 H, *J* = 5.1 Hz), 2.61 (m, 2 H), 2.54 (m, 2 H), 2.19 (m, 2 H), 1.86 (m, 4 H); ^{13}C NMR δ_C 187.61, 152.02, 145.08, 142.97, 111.16, 66.24, 34.32, 32.15, 22.29, 21.58, 20.74; HRMS calcd for $C_{11}H_{14}O_2$ $(M)^+$ 178.0994, found: 178.0993.



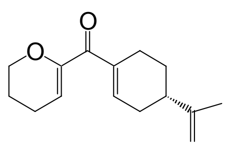
9k

(5,6-Dihydro-4H-pyran-2-yl)-(4,4-dimethyl-cyclopent-1-enyl)-methanone (9k) Dess-Martin oxidation afforded **9k** as colorless oil in 65% yield. R_f 0.32 (EtOAc: hexanes = 1:9); IR 2952, 2930, 2867, 2845,, 1646, 1610 cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 6.68 (s, 1 H), 5.82 (t, 1 H, *J* = 4.1 Hz), 4.09 (t, 2 H, *J* = 5.1 Hz), 2.43 (d, 2 H, *J* = 1.9 Hz), 2.35 (m, 2 H), 2.19 (dd, 2 H, *J* = 10.6, 6.3 Hz), 1.85 (m, 2 H), 1.08 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 187.52, 152.00, 143.79, 141.73, 110.99, 66.17, 48.99, 46.74, 37.67, 29.38, 21.55, 20.70; HRMS calcd for $C_{13}H_{18}O_2$ $(M)^+$ 206.1307, found: 206.1309.



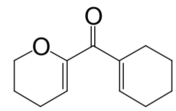
9l

(5,6-Dihydro-4H-pyran-2-yl)-(2-methyl-cyclopent-1-enyl)-methanone (9l) Dess-Martin oxidation afforded **9l** as colorless oil in 57% yield. R_f 0. 18 (EtOAc: hexanes = 1:9); IR 2932, 2869, 2623 cm^{-1}; ^{1}H NMR δ_H 5.84 (t, 1 H, *J* = 4.2 Hz), 4.11 (t, 2 H, *J* = 5.1 Hz), 2.67 (m, 2 H), 2.44 (dt, 2 H, *J* = 7.8, 1.0 Hz), 2.22 (m, 2 H), 1.86 (m, 7 H); ^{13}C NMR δ_C 191.80, 152.20, 148.85, 135.14, 112.74, 66.33, 30.96, 35.56, 22.25, 21.54, 20.90, 16.27; HRMS calcd for $C_{12}H_{16}O_2$ $(M)^+$ 192.1150, found: 192.1148



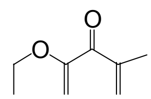
9m

(5,6-Dihydro-4H-pyran-2-yl)-(4-isopropenyl-cyclohex-1-enyl)-methanone (9m) Dess-Martin oxidation afforded **9m** as colorless oil in 78% yield. R_f 0.33 (EtOAc: hexanes = 1:6); IR 3079, 2915, 1642cm^{-1}; ^{1}H NMR δ_H 6.70 (m, 1 H), 5.67 (t, 1 H, *J* = 4.1 Hz), 4.71 (m, 2 H), 4.08 (t, 2 H, *J* = 6.0 Hz), 2.46 (m, 1 H), 2.33 (m, 1 H), 2.18 (m, 5 H), 1.85 (m, 3 H), 1.72 (s, 3 H), 1.43 (m, 1 H); ^{13}C NMR δ_C 191.95, 151.33, 148.83, 139.67, 137.09, 111.91, 109.13, 66.27, 40.16, 31.12, 26.88, 24.59, 21.53, 20.70, 20.65; HRMS calcd for $C_{15}H_{20}O_2$ $(M)^+$ 232.1463, found: 232.1459, $[\alpha]^{20}_D$ –82.3 (c 0.6, $CHCl_3$).



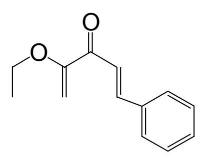
9n

Cyclohex-1-enyl-(5,6-dihydro-4H-pyran-2-yl)-methanone (9n) Dess-Martin oxidation afforded **9n** as colorless oil in 70% yield. R_f 0.22 (EtOAc: hexanes = 1:9); IR 2930, 2861, 1648, 1630cm^{-1}; ^{1}H NMR δ_H 6.66 (m, 1 H), 5.64 (t, 1 H, *J* = 4.1 Hz), 4.06 (t, 2 H, *J* = 5.0 Hz), 2.19 (m, 6 H), 1.83 (m, 2 H), 1.59 (m, 4 H); ^{13}C NMR δ_C 192.32, 151.29, 140.36, 137.42, 111.79, 66.24, 25.75, 24.09, 21.90, 21.53, 20.67; HRMS calcd for $C_{12}H_{16}O_2$ $(M)^+$ 192.1150, found: 192.1154



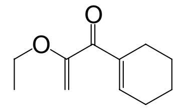
9p

2-Ethoxy-4-methyl-penta-1,4-dien-3-one (9p) Dess-Martin oxidation afforded **9p** as colorless oil in 75% yield. R_f 0.32 (EtOAc: hexanes = 1:30); IR 2982, 2928, 2882, 1667, 1601cm^{-1}; ^{1}H NMR δ_H 5.85 (t, 1 H, *J* = 1.0 Hz), 5.75 (m, 1 H), 4.85 (d, 1 H, *J* = 2.6 Hz), 4.57 (d, 1 H, *J* = 2.6 Hz), 3.80 (q, 2 H, *J* = 7.0 Hz), 1.91 (dd, 3 H, *J* = 1.4, 1.0 Hz), 1.34 (t, 3 H, *J* = 7.0Hz); ^{13}C NMR δ_C 191.13, 157.66, 142.71, 126.45, 93.44, 63.64, 18.36, 14.16; HRMS calcd for $C_8H_{12}O_2$ $(M)^+$ 140.0837 found: 142.0840



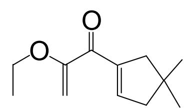
9q

4-Ethoxy-1-phenyl-penta-1,4-dien-3-one (9q) Oxidation by MnO_2 afforded **9q** as colorless oil in 93 % yield. R_f 0.28 (EtOAc: hexanes = 1:15); IR 3080, 3060, 3028, 2981, 1930, 2901, 1736, 1678, 1594cm^{-1}; ^{1}H NMR δ_H 7.75 (d, 1 H, *J* = 5.9 Hz), 7.58 (m, 2 H), 7.37 (m, 4 H), 5.29 (d, 1 H, *J* = 2.5 Hz), 4.51 (d, 1 H, *J* = 2.5 Hz), 3.84 (q, 2 H, *J* = 7.0 Hz), 1.41 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR δ_C 186.40, 158.17, 144.46, 134.84, 130.49, 128.83, 128.51, 120.56, 91.68, 63.81, 14.32; HRMS calcd for $C_{13}H_{14}O_2$ $(M)^+$ 202.0994, found: 202.0993



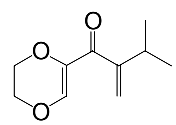
9r

1-Cyclohex-1-enyl-2-ethoxy-propenone (9r) Dess-Martin oxidation afforded **9r** as colorless oil in 85% yield. R_f 0.20 (EtOAc: hexanes = 1:30); IR 2980, 2932, 2992, 2868, 1657, 1632, 1607cm^{-1}; ^{1}H NMR δ_H 6.85 (m, 1 H), 4.63 (d, 1 H, J = 2.5 Hz), 4.45 (d, 1 H, J = 2.5 Hz), 3.77 (q, 2 H, J = 7.0 Hz), 2.19 (m, 4 H), 1.59 (m, 4 H), 1.31 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ_C 192.78, 158.36, 143.34, 137.57, 91.44, 63.53, 26.07, 23.59, 21.86, 21.52, 14.24; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150, found: 180.1153. This compound is previously reported. The analysis data matches those reported.[3]



9s

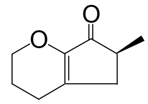
1-(4,4-Dimethyl-cyclopent-1-enyl)-2-ethoxy-propenone (9s) Dess-Martin oxidation afforded **9s** as colorless oil in 75% yield. R_f 0.25 (EtOAc: hexanes = 1:20); IR 2979, 2954, 2930, 2868, 2848, 2831, 1655, 1601 cm^{-1}; ^{1}H NMR δ_H 6.80 (s, 1 H), 4.91 (s, 1 H), 4.44 (s, 1 H), 3.79 (q, 2 H, J = 7.0 Hz), 2.41 (s, 2 H), 2.34 (s, 2 H), 1.34 (t, 3 H, J = 7.0 Hz) 1.06 (s, 6 H); ^{13}C NMR δ_C 187.94, 158.87, 145.63, 141.93, 91.72, 63.64, 49.17, 46.50, 37.73, 29.43, 14.29; HRMS calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found: 194.1308



9t

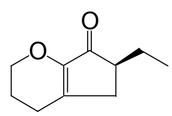
1-(5,6-Dihydro-[1,4]dioxin-2-yl)-2-isopropyl-propenone (9t) Dess-Martin oxidation afforded **9t** as colorless oil in 46% yield. R_f 0.21 (EtOAc: hexanes = 1:4); IR 3428(br), 2960, 2930, 2875, 1649, 1607 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.15 (s, 1 H), 5.36 (s, 1 H), 5.34 (s, 1 H), 4.18 (s, 4 H), 2.85 (m, 1 H), 1.04 (d, 6 H, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 191.83, 153.33, 142.36, 137.51, 116.81, 65.14, 63.47, 30.43, 21.05; HRMS calcd for $C_{10}H_{14}O_3$ $(M)^+$ 182.0943, found: 182.0941

The Nazarov cyclization of compounds **9** was carried out by the catalysis of 10 mol% $AlCl_3$ in either CH_2Cl_2 or MeCN. The amount of the substrates used in the cyclization was generally around 90-120 mg. The representative procedure was demonstrated below.



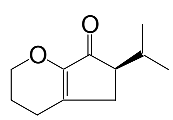
10a

6-Methyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10a) To 0.011 g (0.079 mmol) of $AlCl_3$ in 2 mL CH_2Cl_2 was added 0.120 g (0.788mmol) of **9a** in 2 mL CH_2Cl_2. The reaction mixture was stirred for 1 min before it was quenched water (4 mL). The mixture was further diluted with 10 mL CH_2Cl_2. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL). The combined organic layers were washed with brine (10 mL), dried, filtered and concentrated *in vacuo*. The product was purified by column chromatography (EtOAc: hexanes = 1:4) to afford 0.110 g (92%) **10a** as colorless oil. R_f 0.14 (EtOAc: hexanes = 1:4); IR 2962, 2928, 2872, 1707, 1648 cm^{-1}; ^{1}H NMR (500 Hz, $CDCl_3$) δ_H 4.10 (m, 2 H), 2.69 (m, 1 H), 2.38 (m, 1 H), 2.32 (t, 2 H, *J* = 6.2 Hz), 2.03 (dd, 1 H, *J* = 7.4, 1.8 Hz), 1.95 (m, 2 H), 1.18 (d, 3 H, *J* = 7.4 Hz); ^{13}C NMR (125 Hz, $CDCl_3$) δ_C 203.44, 150.13, 143.82, 66.71, 37.95, 34.80, 23.98, 21.57, 16.45; HRMS calcd for $C_9H_{12}O_2$ $(M)^+$ 152.0837, found: 152.0838



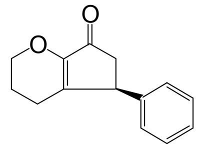
10b

6-Ethyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10b) Cyclization of **9b** in CH_2Cl_2 afforded **10b** as colorless oil in 91% yield. Reaction time: 1 min; R_f 0.20 (EtOAc: hexanes = 1:4); IR 2961, 2929, 2875, 1706, 1650cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 4.03 (m, 2 H), 2.55 (m, 1 H), 2.28 (t, 2 H, *J* = 6.2 Hz), 2.21 (m, 1 H), 2.06 (dd, 1 H, *J* = 17.5, 1.8 Hz), 1.91 (m, 2 H), 1.77 (m, 1 H), 1.34 (m, 1 H), 0.87 (t, 3 H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 202.84, 150.57, 144.38, 66.69, 44.66, 32.14, 24.31, 23.97, 21.54, 11.09; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0997



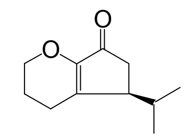
10c

6-Isopropyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10c) Cyclization of **9c** in CH_2Cl_2 afforded **10c** as colorless oil in 93% yield. Reaction time: 1 min; R_f 0.22 (EtOAc: hexanes = 1:4); IR 2956, 2930, 2872, 1706, 1650cm^{-1}; ^{1}H NMR δ_H 4.03 (m, 2 H), 2.37 (m, 1 H), 2.29 (m, 3 H), 2.17 (m, 2 H), 1.89 (m, 2 H), 0.92 (d, 3 H, *J* = 7.0 Hz), 0.71 (d, 3 H, *J* = 6.8 Hz); ^{13}C NMR δ_C 202.59, 151.27, 144.74, 66.75, 49.10, 28.55, 28.12, 24.02, 21.63, 20.39, 16.95; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150 found: 181.1151



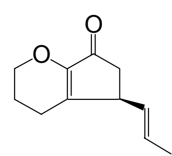
10d

5-Phenyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10d) Cyclization of **9d** in MeCN afforded **10d** as colorless oil in 86% yield. Reaction time: 10 min; R_f 0.26 (EtOAc: hexanes = 1:3); IR 2928, 1710, 1648cm^{-1}; ^{1}H NMR δ_H 7.33 (m, 2 H), 7.26 (m, 1 H), 7.14 (m, 2 H), 4.15 (m, 2 H), 3.85 (dd, 1 H, *J* = 6.6, 1.6 Hz), 2.91 (dd, 1 H, *J* = 19.0, 6.6 Hz), 2.32 (dt, 1 H, *J* = 19.0, 0.9 Hz), 2.12 (tq, 2 H, *J* = 19.0, 6.2 Hz), 1.92 (m, 2 H); ^{13}C NMR δ_C 200.08, 151.50, 147.39, 141.72, 129.00, 127.17, 127.10, 66.94, 43.66, 42.94, 22.20, 21.46; HRMS calcd for $C_{14}H_{14}O_2$ $(M)^+$ 214.0994, found: 214.0998



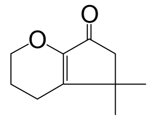
10e

5-Isopropyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10e) Cyclization of **9e** in MeCN afforded **10e** as colorless oil in 92% yield. Reaction time: 50 min; R_f 0.13 (EtOAc: hexanes = 1:6); IR 2955, 2930, 2872, 1709, 1645cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 4.13 (m, 1 H), 4.00 (m, 1 H), 2.69 (s, 1 H), 2.33 (dd, 1 H, *J* = 18.6, 6.8 Hz), 2.22 (m, 2 H), 2.03 (m, 2 H), 1.90 (m, 2 H), 0.93 (d, 3 H, *J* = 6.8 Hz), 0.66 (d, 3 H, *J* = 6.8Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 200.40, 151.34, 147.65, 66.74, 43.06, 33.96, 28.03, 22.61, 21.44, 20.66, 15.52; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150, found: 180.1151



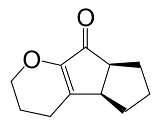
10f

5-Propenyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10f) Cyclization of **9f** in MeCN afforded **10f** as colorless oil in 90% yield. Reaction time:30 min; R_f 0.20 (EtOAc: hexanes = 1:4); IR 2933, 1710, 1645cm^{-1}; ^{1}H NMR δ_H 5.58 (m, 1 H), 5.14 (m, 1 H), 4.07 (m, 2 H), 3.20 (t, 1 H, *J* = 7.4 Hz), 2.62 (dd, 1 H, *J* = 18.8, 6.3 Hz), 2.34 (dt, 1 H, *J* = 18.8, 6.3 Hz), 2.14 (m, 2 H), 1.91 (m, 2 H), 1.67 (m, 3 H); ^{13}C NMR δ_C 199.87, 150.79, 147.39, 131.41, 127.59, 66.78, 41.11, 40.21, 22.19, 21.42, 17.72; HRMS calcd for $C_{11}H_{14}O_2$ $(M)^+$ 178.0994, found: 178.0996



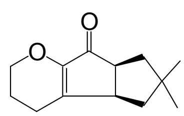
10g

5,5-Dimethyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (10g) Cyclization of **9g** in MeCN afforded **10g** as colorless oil in 85% yield. Reaction time: 12 h; R_f 0.15 (EtOAc: hexanes = 1:4); IR 2957, 2928, 2869, 1710, 1645 cm^{-1}; ^1H NMR (500 Hz, $CDCl_3$) δ_H 4.07 (t, 2 H, J = 5.2 Hz), 2.28 (t, 2 H, J = 6.2 Hz), 2.25 (s, 2 H), 1.94 (m, 2 H), 1.18 (s, 6 H); ^{13}C NMR (125 Hz, $CDCl_3$) δ_C 199.59, 152.70, 148.93, 66.50, 49.17, 36.78, 27.18, 21.41, 18.91; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0989



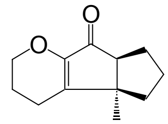
10j

2,3,3a,5,6,8a-Hexahydro-1H,4H-7-oxa-cyclopenta[α]inden-8-one (10j) Cyclization of **9j** in CH_2Cl_2 afforded **10j** as colorless oil in 88% yield. Reaction time: 40 min; R_f 0.19 (EtOAc: hexanes = 1:4); IR 2945, 2867, 1706, 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 4.01, (m, 2 H), 3.01 (m, 1 H), 2.65 (m, 1 H), 2.32 (m, 1 H), 2.20 (m, 1 H), 1.89 (m, 2 H), 1.79 (m, 1 H), 1.55 (m, 4 H), 1.20 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 203.78, 151.41, 147.70, 67.03, 48.74, 43.21, 28.93, 28.18, 24.03, 22.67, 21.84; HRMS calcd for $C_{11}H_{14}O_2$ $(M)^+$ 178.0994, found: 178.0987.



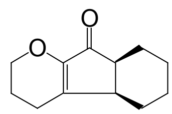
10k

2,2-Dimethyl-2,3,3a,5,6,8a-hexahydro-1H,4H-7-oxa-cyclopenta[a]inden-8-one (10k) Cyclization of **9k** in CH_2Cl_2 afforded **10k** as colorless oil in 92% yield. Reaction time: 30 min; R_f 0.29 (EtOAc: hexanes = 1:3); IR 2950, 2864, 1708, 1644 cm^{-1}; ^1H NMR δ_H 4.03 (m, 2 H), 3.13 (q, 1 H, J = 7.5 Hz), 2.87 (dd, 1 H, J = 16.6, 7.1 Hz), 2.24 (m, 2 H), 1.91 (m, 2 H), 1.73 (m, 2 H), 1.37 (dd, 1 H, J = 12.9, 7.6 Hz), 1.11 (dd, 1 H, J = 12.6, 7.4 Hz), 0.95 (d, 6 H, J = 4.7 Hz); ^{13}C NMR δ_C 203.45, 148.63, 148.44, 66.64, 48.89, 43.47, 43.43, 43.27, 41.23, 28.65, 27.81, 22.62, 21.55; HRMS calcd for $C_{13}H_{18}O_2$ $(M)^+$ 206.1302, found: 206.1309.



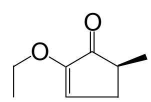
10l

3a-Methyl-2,3,3a,5,6,8a-hexahydro-1H,4H-7-oxa-cyclopenta[a]inden-8-one (10l) Cyclization of **9l** in CH_2Cl_2 afforded **10l** as colorless oil in 91% yield. Reaction time: 12 h; R_f 0. 27 (EtOAc: hexanes = 1:4); IR 2948, 2866, 1706, 1644 cm^{-1}; ^1H NMR δ_H 4.05 (m, 2 H), 2.28 (m, 3 H), 1.93 (m, 2 H), 1.75 (m, 3 H), 1.59 (m, 1 H), 1.25 (m, 5 H); ^{13}C NMR δ_C 202.95, 150.60, 150.03, 66.66, 56.27, 48.55, 35.68, 28.89, 25.01, 24.73, 21.57, 19.56; HRMS calcd for $C_{12}H_{16}O_2$ $(M)^+$ 192.1150, found: 192.1155



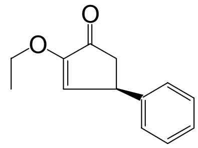
10n

3,4,4b,5,6,7,8,8a-Octahydro-2H-1-oxa-fluoren-9-one (G-037) Cyclization of **9n** in CH_2Cl_2 afforded **10n** as colorless oil in 88% yield. Reaction time: 20 min; Colorless oil. R_f 0.28 (EtOAc: hexanes = 1:4); IR 2931, 2863, 1707, 1644cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 4.09 (m, 1 H), 4.01 (m, 1 H), 2.69 (q, 1 H, J = 6.9 Hz), 2.35 (m, 2 H), 2.20 (dt, 1 H, J = 18.7, 5.8 Hz), 1.91 (m, 3 H), 1.79 (m, 1 H), 1.67 (m, 1 H), 1.46 (m, 2 H), 1.32 (m, 2 H), 1.15 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 202.74, 150.20, 148.31, 66.78, 43.64, 37.45, 26.60, 22.38, 21.91, 21.57, 20.44, 20.29; HRMS calcd for $C_{12}H_{16}O_2$ $(M)^+$ 192.1150, found: 192.1150



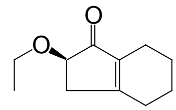
10p

2-Ethoxy-5-methyl-cyclopent-2-enone (10p) Cyclization of **9p** in CH_2Cl_2 afforded **10p** as colorless oil in 80% yield. Reaction time: 6 h; R_f 0.23 (EtOAc: hexanes = 1:6); IR 2978, 2929, 1712, 1623cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.28 (t, 1 H, J = 3.0 Hz), 3.90 (dq, 2 H, J = 7.0, 2.5 Hz), 4.85 (dq, 1 H, J = 17.6, 3.2 Hz), 2.39 (m, 1 H), 2.07 (dt, 1 H, J = 17.6, 2.5 Hz), 1.38 (t, 3 H, J = 7.0 Hz), 1.18 (d, 3 H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 205.46, 155.55, 125.66, 65.35, 38.49, 31.17, 16.42, 14.31; HRMS calcd for $C_8H_{12}O_2$ $(M)^+$ 140.0837 found: 142.0840; This compound is previously reported. The analysis data matches those reported.[4]



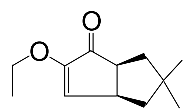
10q

2-Ethoxy-4-phenyl-cyclopent-2-enone (10q) Cyclization of **9q** in MeCN afforded **10q** as colorless oil in 40% yield. Reaction time: 30 h; R_f 0.20 (EtOAc: hexanes = 1:6); IR 3063, 3027, 2980, 2930, 2897, 1713, 1621, 1604cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.34 (t, 2 H, *J* = 7.2 Hz), 7.26 (m, 1 H), 7.18 (d, 2 H, *J* = 7.2 Hz), 6.37 (d, 1 H, *J* = 3.0 Hz), 3.99 (m, 3 H), 2.96 (dd, 1 H, *J* = 19.3, 6.7 Hz), 2.35 (dd, 1 H, *J* = 19.3, 2.1 Hz),1.43 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 202.30, 156.41, 143.03, 130.11, 128.86, 127.07, 126.89, 65.80, 43.08, 39.98, 14.31; HRMS calcd for $C_{13}H_{14}O_2$ $(M)^+$ 202.0994, found: 202.0997



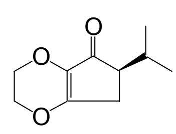
10r

2-Ethoxy-2,3,4,5,6,7-hexahydro-inden-1-one (10r) Cyclization of **9r** in MeCN afforded **10r** as colorless oil in 91% yield. Reaction time: 6 h; R_f 0.31 (EtOAc: hexanes = 1:6); IR 2973, 2930, 2864, 1707, 1644 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.96 (dd, 1 H, *J* = 6.3, 2.3 Hz), 3.88 (m, 1 H), 3.63 (m, 1 H), 2.79 (dd, 1 H, *J* = 7.6, 5.2 Hz), 2.39 (d, 1 H, *J* = 7.6 Hz), 2.24 (m, 2 H), 2.12 (m, 2 H), 1.73 (m, 2 H), 1.63 (m, 2 H), 1.24 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 205.70, 170.73, 137.12, 77.54, 65.79, 37.56, 28.46, 21.94, 21.49, 19.79, 15.28; HRMS calcd for $C_{11}H_{16}O_2$ $(M)^+$ 180.1150, found: 180.1148



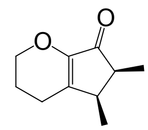
10s

2-Ethoxy-5,5-dimethyl-4,5,6,6a-tetrahydro-3aH-pentalen-1-one (10s) Cyclization of **9s** in refluxing MeCN afforded **10s** as colorless oil in 75% yield. Reaction time: 3 h; R_f 0.20 (EtOAc: hexanes = 1:9); IR 2952, 2933, 2902, 2864, 1711, 1618cm^{-1}; ^{1}H NMR δ_H 6.28 (d, 1 H, *J* = 3.2 Hz), 3.86 (q, 2 H, *J* = 7.0 Hz), 3.25 (m, 1 H), 2.91 (m, 1 H), 1.76 (m, 2 H), 1.43 (dd, 1 H, *J* = 12.9, 7.7 Hz), 1.35 (t, 3 H, *J* = 7.0 Hz), 1.13 (dd, 1 H, *J* = 12.6, 7.4 Hz), 0.95 (d, 6 H, *J* = 3.6 Hz); ^{13}C NMR δ_C 205.65, 154.16, 130.92, 65.35, 49.16, 45.09, 43.64, 41.87, 40.34, 28.72, 27.90, 14.30; HRMS calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found: 194.1311

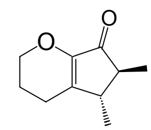


10t

6-Isopropyl-2,3,6,7-tetrahydro-cyclopenta[1,4]dioxin-5-one (10t) Cyclization of **9t** in CH_2Cl_2 afforded **10t** as colorless oil in 75% yield. Reaction time: 2 min; R_f 0.22 (EtOAc: hexanes = 1:2); IR 2957, 2930, 2873, 1707, 1641 cm^{-1}; ^1H NMR δ_H 4.30 (m, 2 H), 4.12 (t, 2 H, J = 4.0 Hz), 2.48 (dd, 1 H, J = 17.0, 6.6 Hz), 2.40 (m, 1H), 2.28 (m, 2 H), 0.95 (d, 3 H, J = 7.0 Hz), 0.76 (d, 3 H, J = 6.8 Hz); ^{13}C NMR δ_C 196.92, 165.08, 134.31, 66.88, 63.84, 47.66, 28.06, 24.78, 20.40, 16.54; HRMS calcd for $C_{10}H_{14}O_3$ $(M)^+$ 182.0943, found: 182.0944



11a

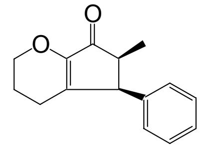


11b

Cyclization of **9h** in CH_2Cl_2 afforded **11a** and **11b** as colorless oil in 89% combined yield with a ratio of 3:2. Reaction time: 5 min; **11a** and **11b** were separated by HPLC.

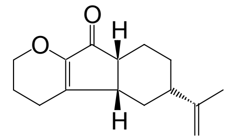
***Cis*-5,6-Dimethyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (11a)** R_f 0.20 (EtOAc: hexanes = 1:4); Retention time: 28.3 min, IR 2967, 1705, 1647 cm^{-1}; ^1H NMR δ_H 4.13, (m, 1 H), 4.01 (m, 1 H), 2.80 (m, 1 H), 2.48 (m, 1 H), 2.40 (m, 1 H), 2.20 (m, 1 H), 1.94 (m, 2 H), 1.08 (d, 3 H, J = 7.6 Hz), 1.03 (d, 3 H, J = 7.2 Hz); ^{13}C NMR δ_C 203.27, 149.70, 148.69, 66.81, 42.13, 36.06, 21.97, 21.66, 14.79, 11.22; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0994.

***Trans*-5,6-Dimethyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (11b)** R_f 0.20 (EtOAc: hexanes = 1:4); Retention time: 26.5 min, IR 2927, 1707, 1644 cm^{-1}; ^1H NMR δ_H 4.09, (m, 2 H), 2.40 (m, 1 H), 2.25 (m, 1 H), 2.18 (m, 1 H), 1.95 (m, 2 H), 1.22 (m, 1 H), 1.17 (d, 3 H, J = 7.4 Hz), 1.16 (d, 3 H, J = 7.1 Hz); ^{13}C NMR δ_C 202.63, 149.56, 147.43, 70.90, 66.64, 47.34, 41.31, 21.60, 17.84, 14.71; HRMS calcd for $C_{10}H_{14}O_2$ $(M)^+$ 166.0994, found: 166.0996.



12

6-Methyl-5-phenyl-3,4,5,6-tetrahydro-2H-cyclopenta[b]pyran-7-one (12) Cyclization of **9i** in CH_2Cl_2 afforded **12** as white solid in 88% yield. Reaction time: 5 min; R_f 0.22 (EtOAc: hexanes = 1:4); IR 3026, 2972, 2932, 2876, 1710, 1650 cm^{-1}; ^1H NMR δ_H 7.24 (m, 3 H), 7.00 (d, 2 H, J = 7.1 Hz), 4.16 (m, 2 H), 3.99 (d, 1 H, J = 6.6 Hz), 2.73 (m, 1 H), 2.16 (t, 2 H, J = 6.2 Hz), 1.93 (m, 2 H), 0.65 (d, 3 H, J = 7.6 Hz); ^{13}C NMR δ_C 202.97, 151.51, 144.91, 138.55, 128.81, 128.44, 127.08, 67.05, 48.78, 43.22, 22.46, 21.60, 12.27; HRMS calcd for $C_{15}H_{16}O_2$ $(M)^+$ 228.1150, found: 228.1148; m.p. 93.8-94.8 °C



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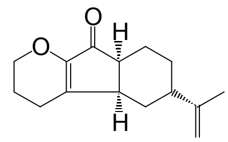


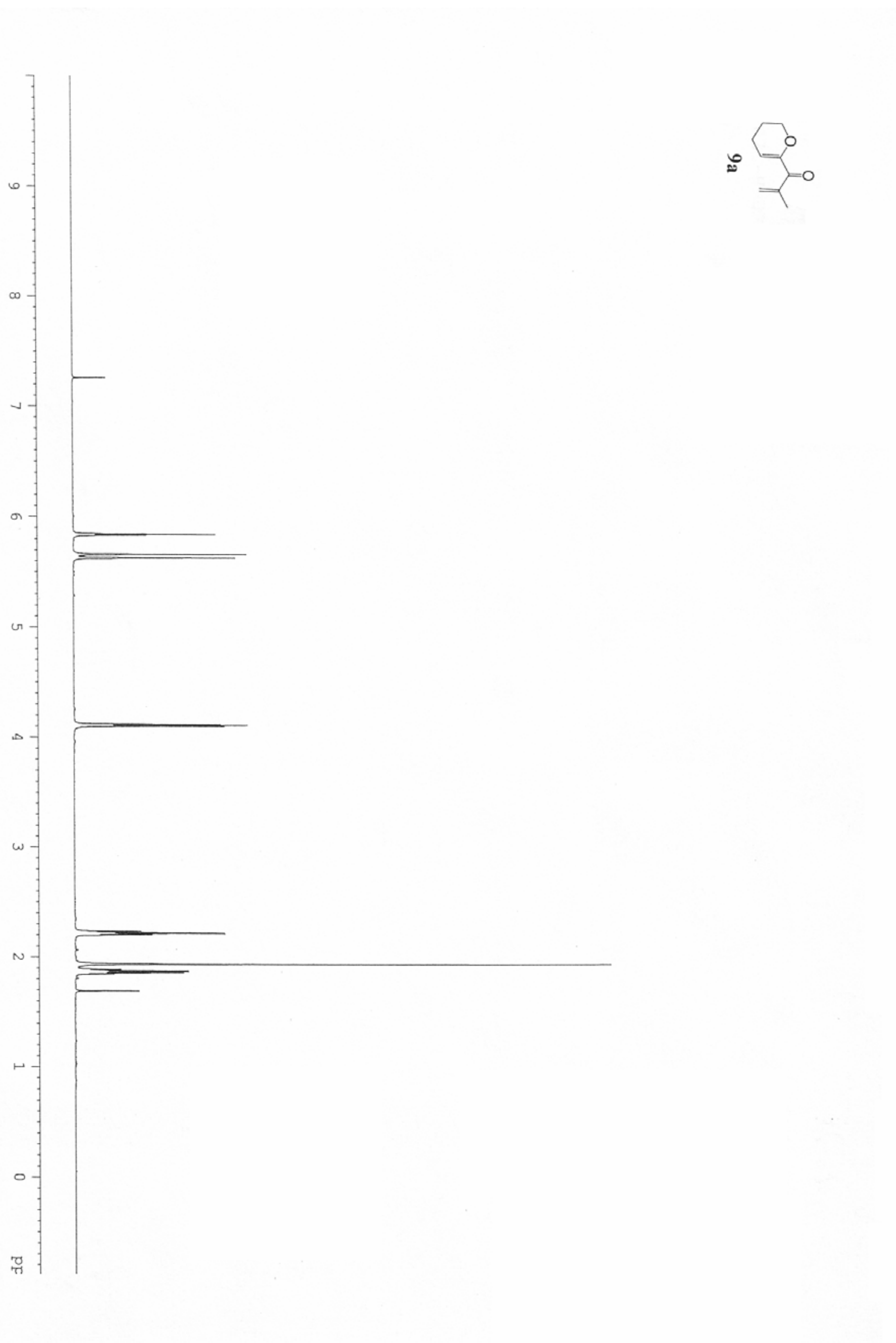
13b

Cyclization of **9m** in CH_2Cl_2 afforded **13a** and **13b** as colorless oil in 85% combined yield with 60% d.r.. Reaction time: 15 min; **13a** and **13b** were separated by HPLC.

6-Isopropenyl-3,4,4b,5,6,7,8,8a-octahydro-2H-1-oxa-fluoren-9-one (Major) R_f 0.21 (EtOAc: hexanes = 1:4); Retention time: 26.2 min; IR 2931, 2865, 1704, 1643cm^{-1}; ^{1}H NMR δ_H 4.65 (m, 2 H), 4.10 (m, 2 H), 2.96 (m, 1 H), 2.45 (q, 1 H, J = 6.2 Hz), 2.34 (dt, 1 H, J = 18.8, 6.6 Hz), 2.21 (dt, 1 H, J = 18.8, 5.8 Hz), 1.94 (m, 3 H), 1.77 (m, 8 H), 1.25 (m, 1 H); ^{13}C NMR δ_C 203.30, 150.83, 149.75, 146.87, 108.56, 66.81, 43.00, 36.86, 36.65, 28.20, 25.68, 22.89, 21.84, 21.55, 20.62; HRMS calcd for $C_{15}H_{20}O_2$ $(M)^+$ 232.1463, found: 232.1462, $[\alpha]^{20}_D$ 72.2 (c 0.9, $CHCl_3$).

6-Isopropenyl-3,4,4b,5,6,7,8,8a-octahydro-2H-1-oxa-fluoren-9-one (Minor) R_f 0.21 (EtOAc: hexanes = 1:4); Retention time: 23.1 min; IR 2924, 2857, 1706, 1634cm^{-1}; ^{1}H NMR δ_H 4.64 (m, 2 H), 4.13 (m, 1 H), 4.03 (m, 1 H), 2.75 (m, 1 H), 2.39 (m, 2 H), 2.25 (dt, 1 H, J = 18.8, 5.7 Hz), 1.98 (m, 5 H), 1.69 (m, 5 H), 1.14 (m, 1 H), 0.87 (m, 1 H); ^{13}C NMR δ_C 201.81, 149.88, 149.61, 148.39, 108.64, 66.85, 43.7, 42.14, 38.44, 35.35, 27.89, 22.58, 22.01, 21.67, 20.46; HRMS calcd for $C_{15}H_{20}O_2$ $(M)^+$ 232.1463, found: 232.1466, $[\alpha]^{20}_D$ –48.3 (c 0.4, $CHCl_3$).

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
[2] Alaimo, P. J.; Peters, D. W.;Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, *78*, 64.
[3] Stille, J. K., Kwon, H. B., McKee, B. H.; *J. Org. Chem.* **1990**,*55*, 3114-3118
[4] Katritzky, A. R., Zhang, G., Jiang, J.; *J. Org. Chem.* **1995**, *60*, 7605-7611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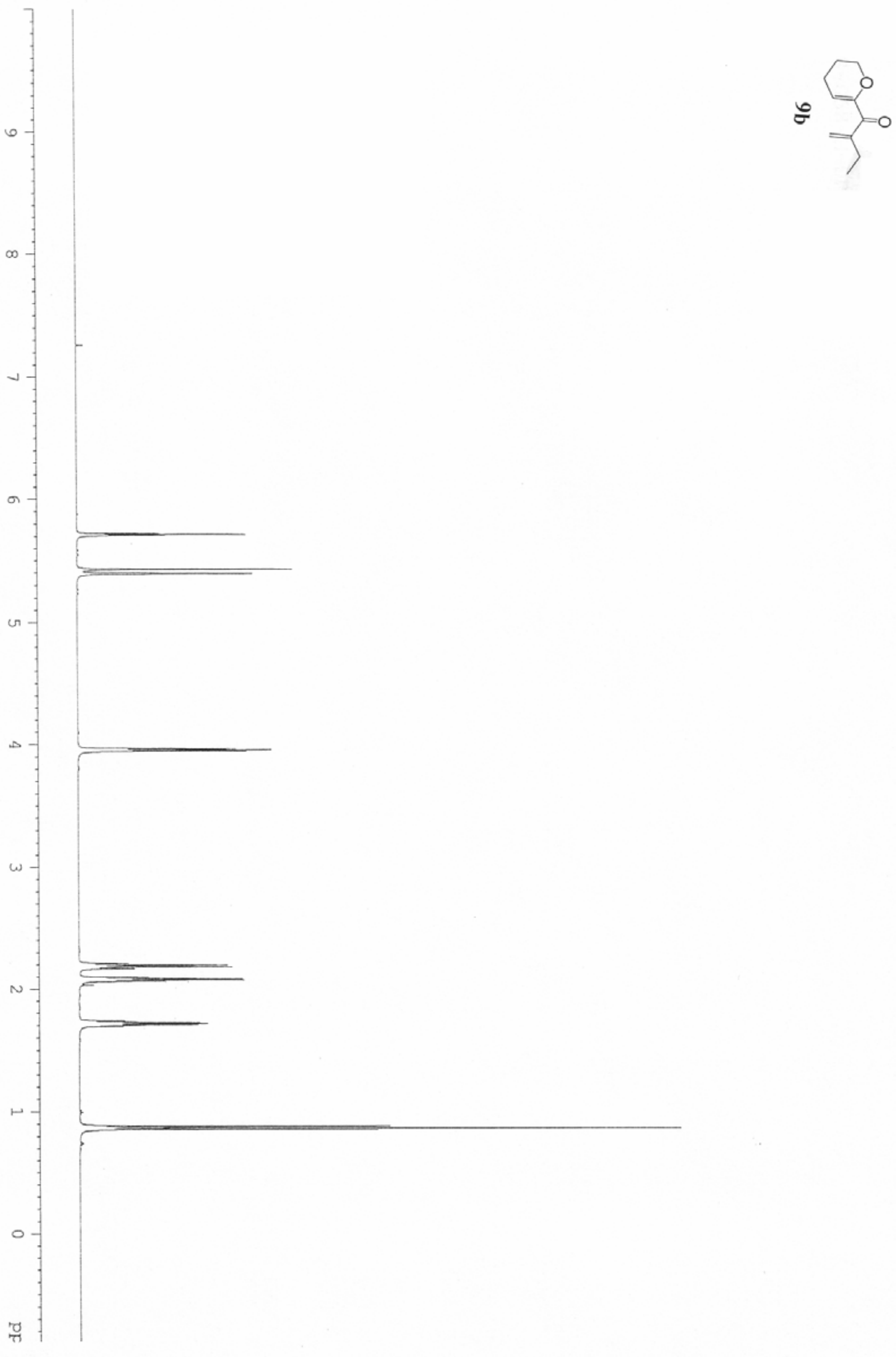
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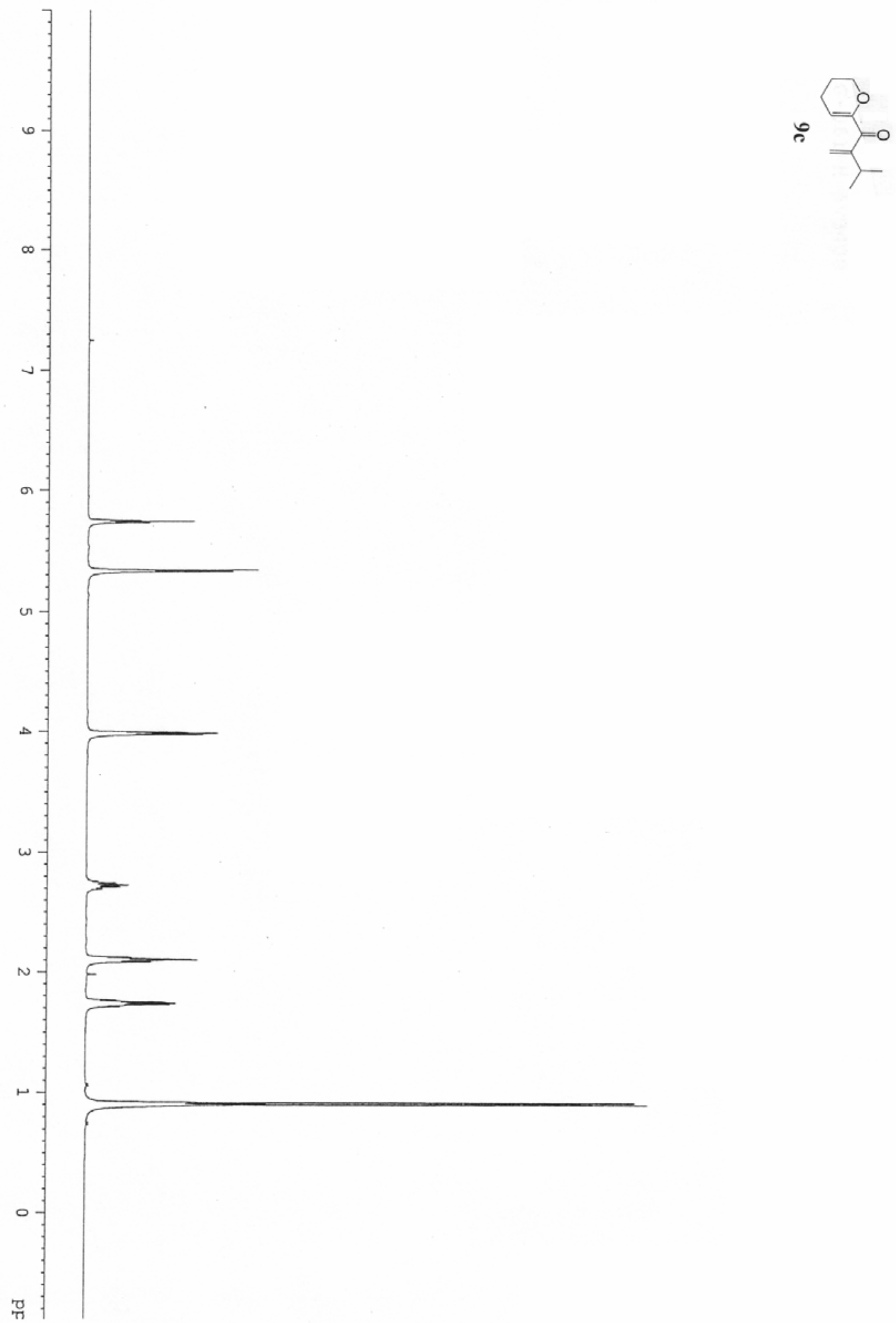
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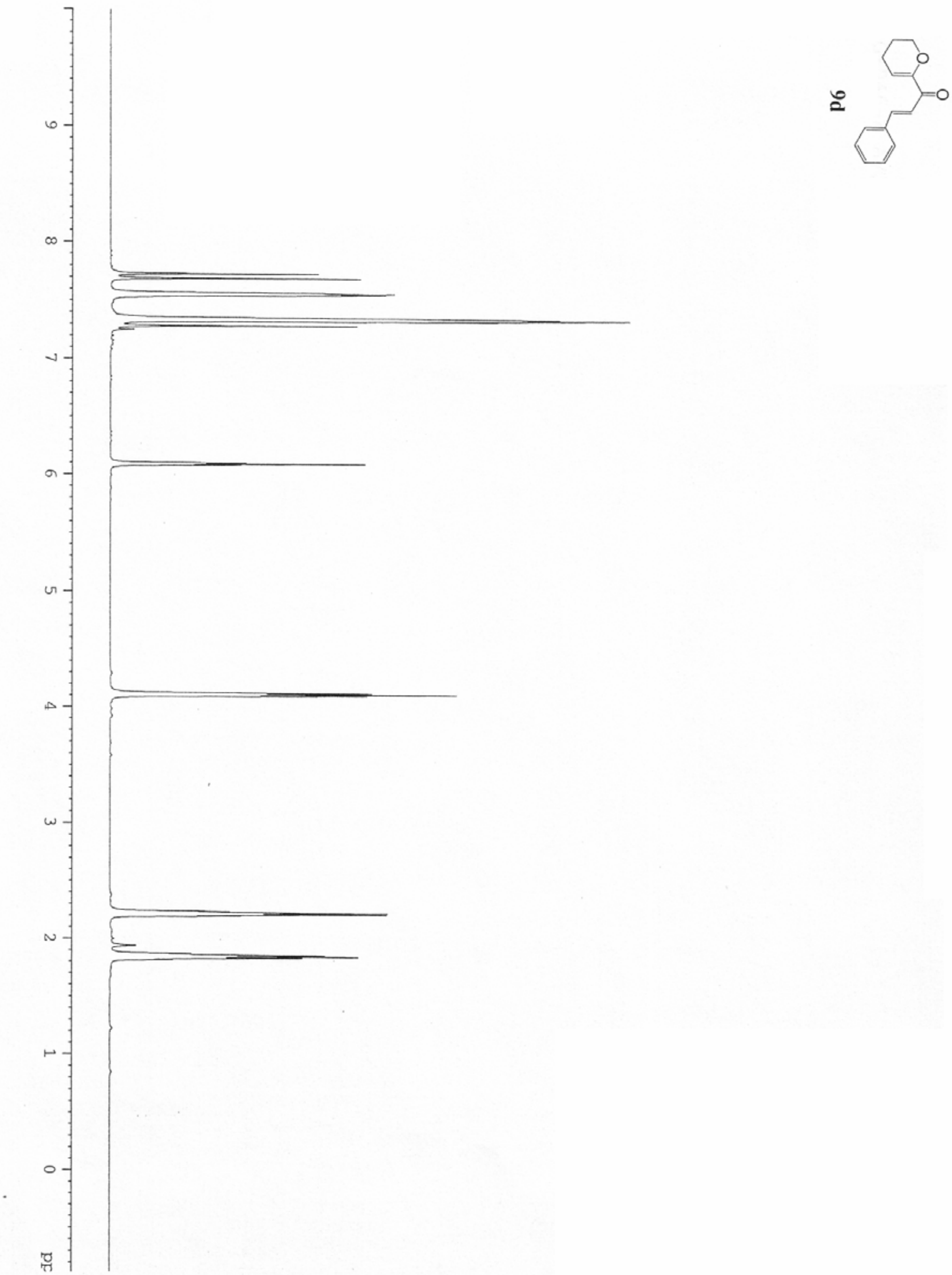
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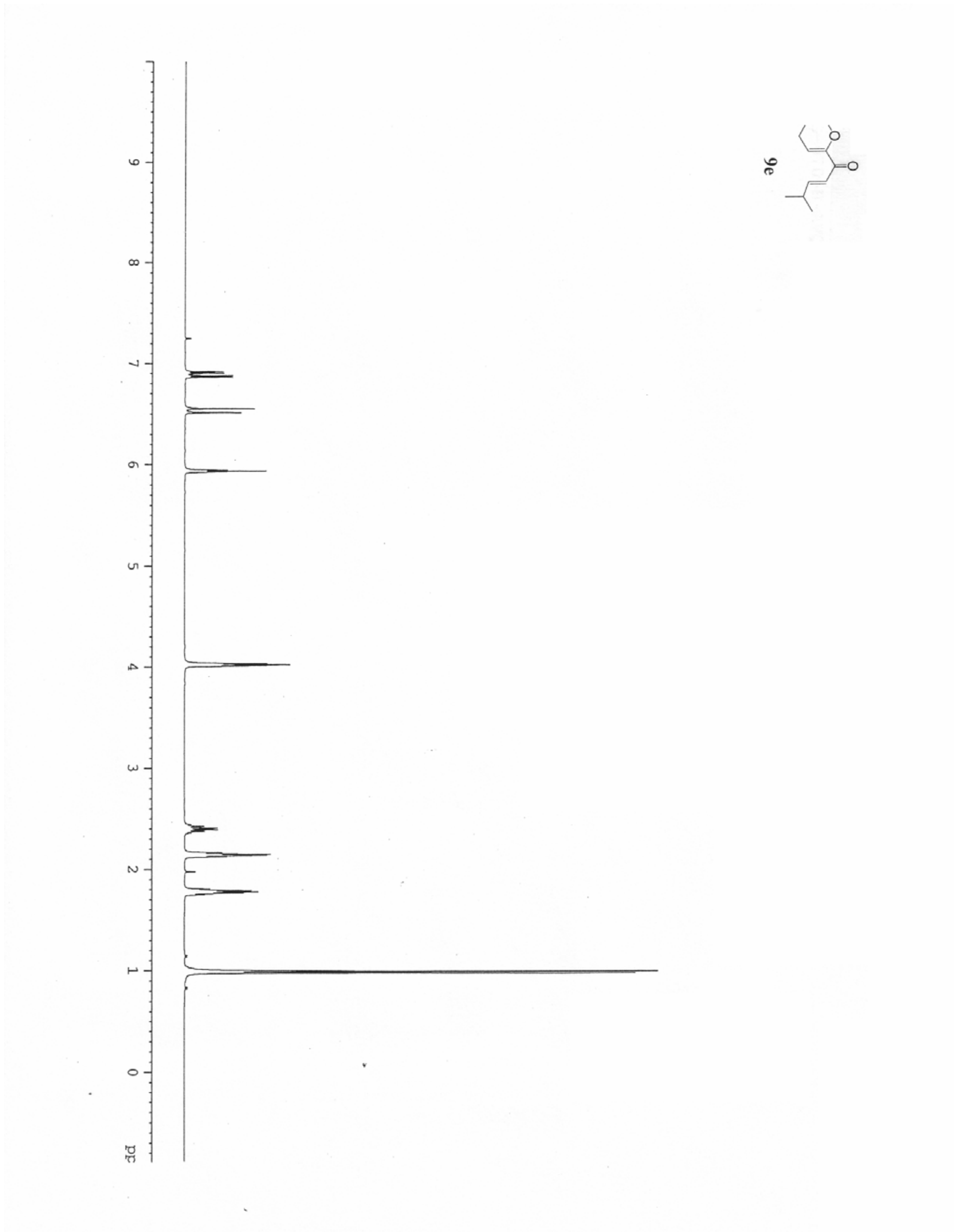
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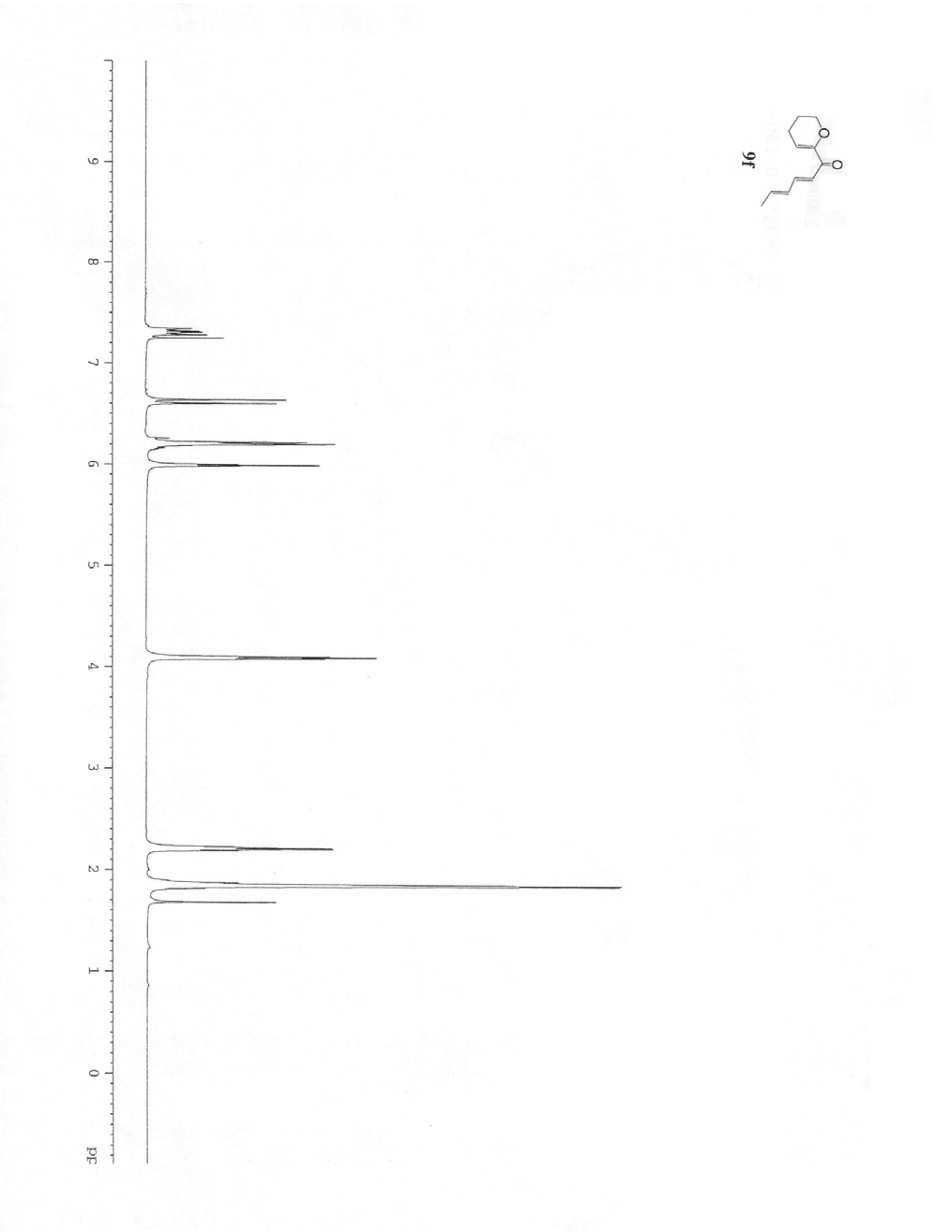
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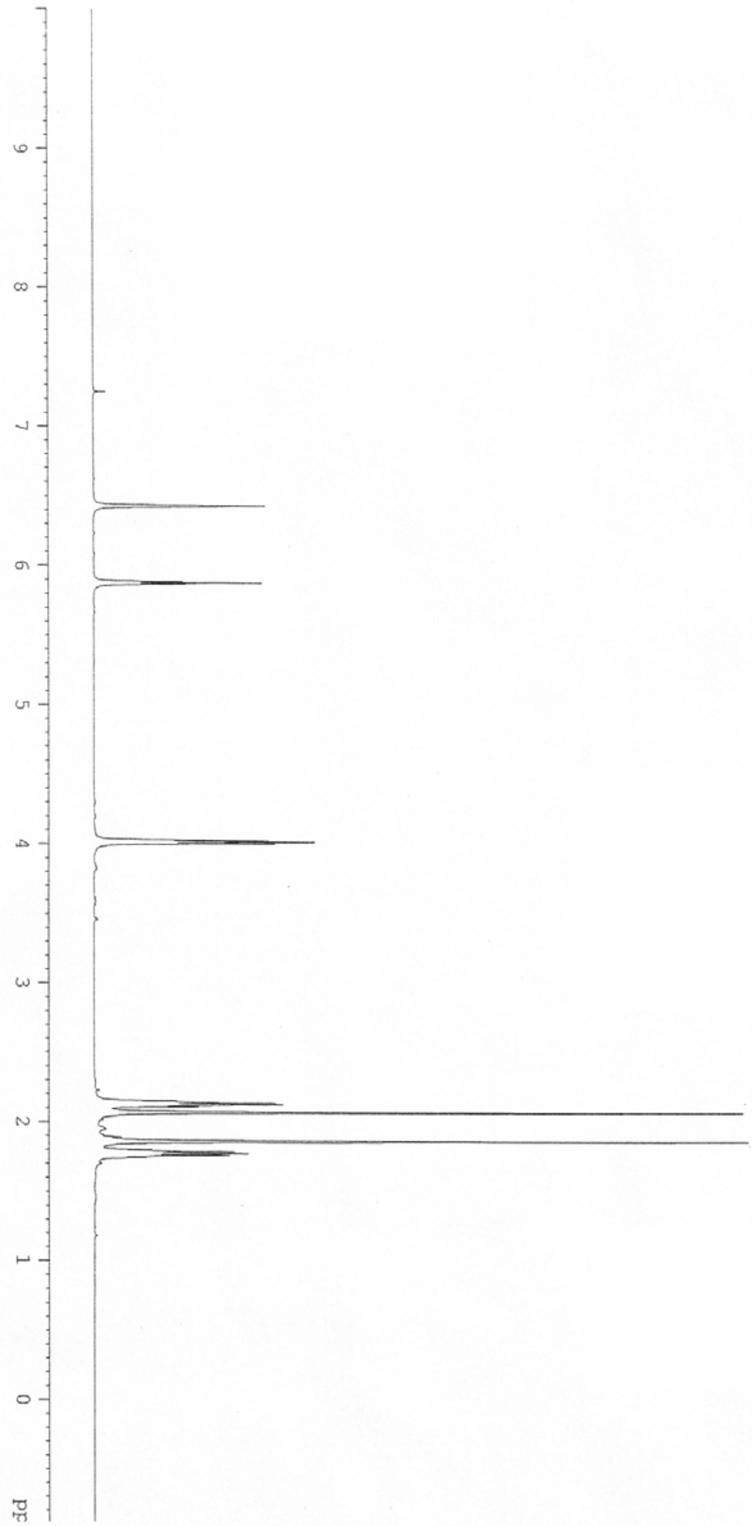

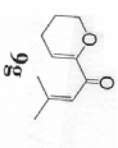

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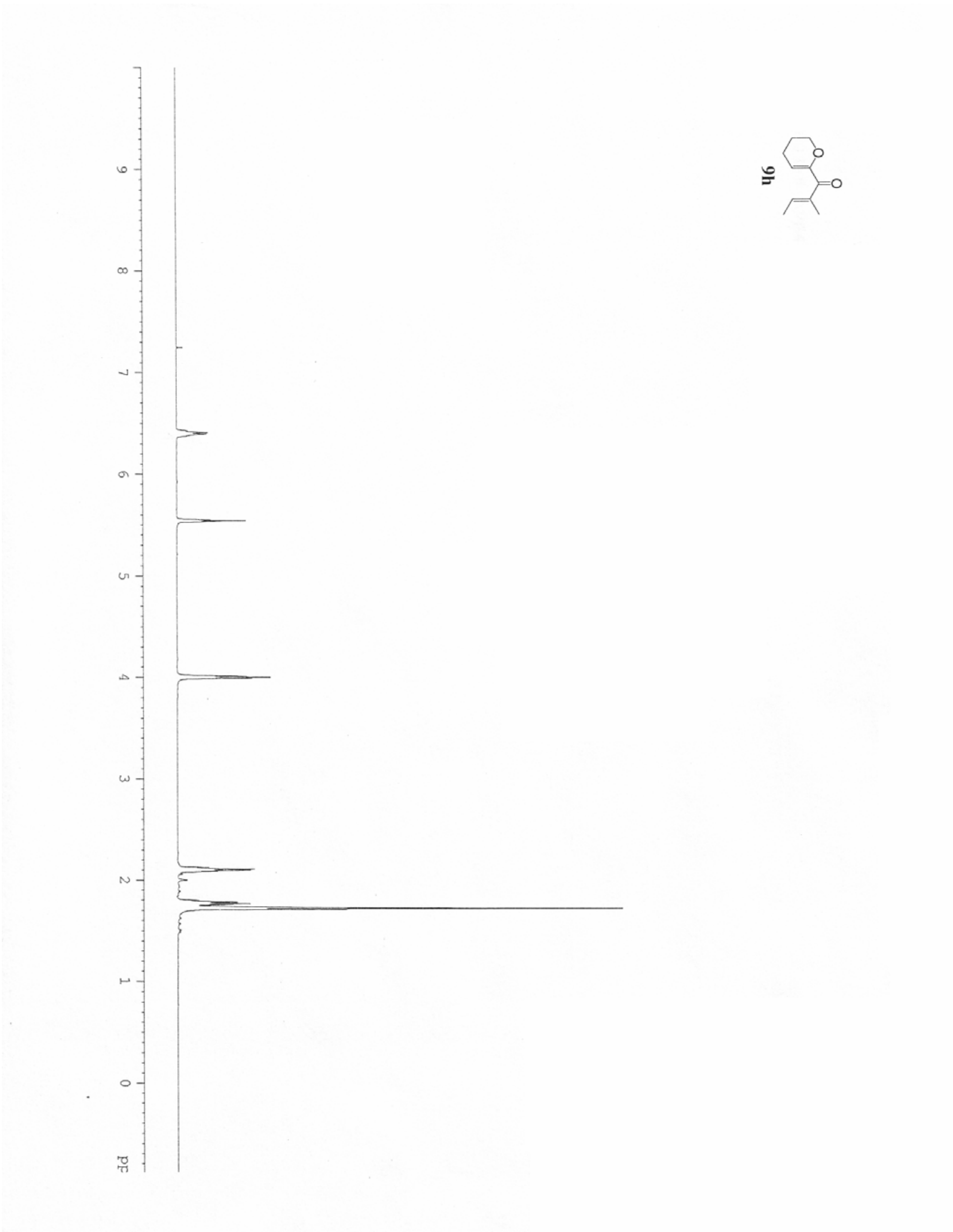
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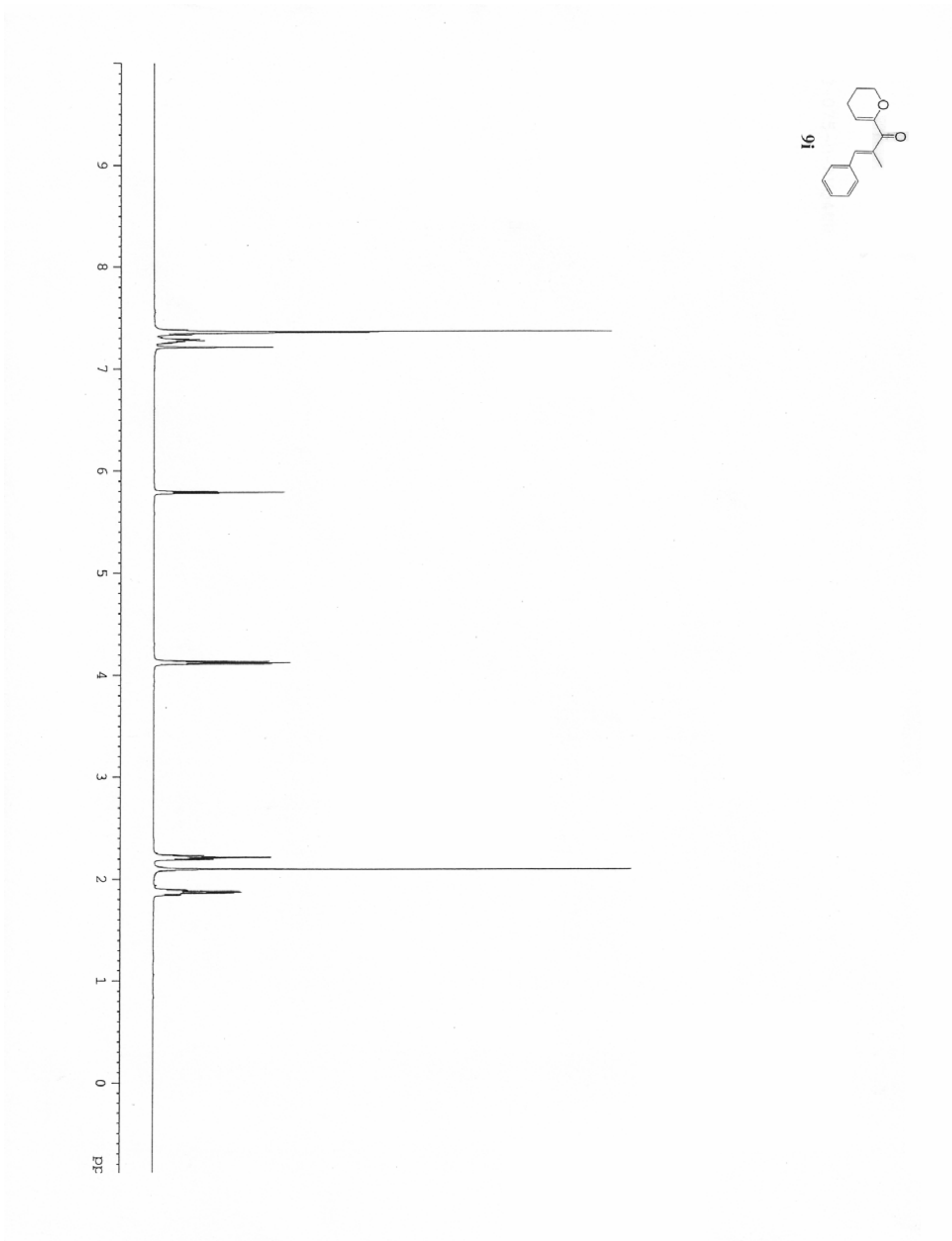
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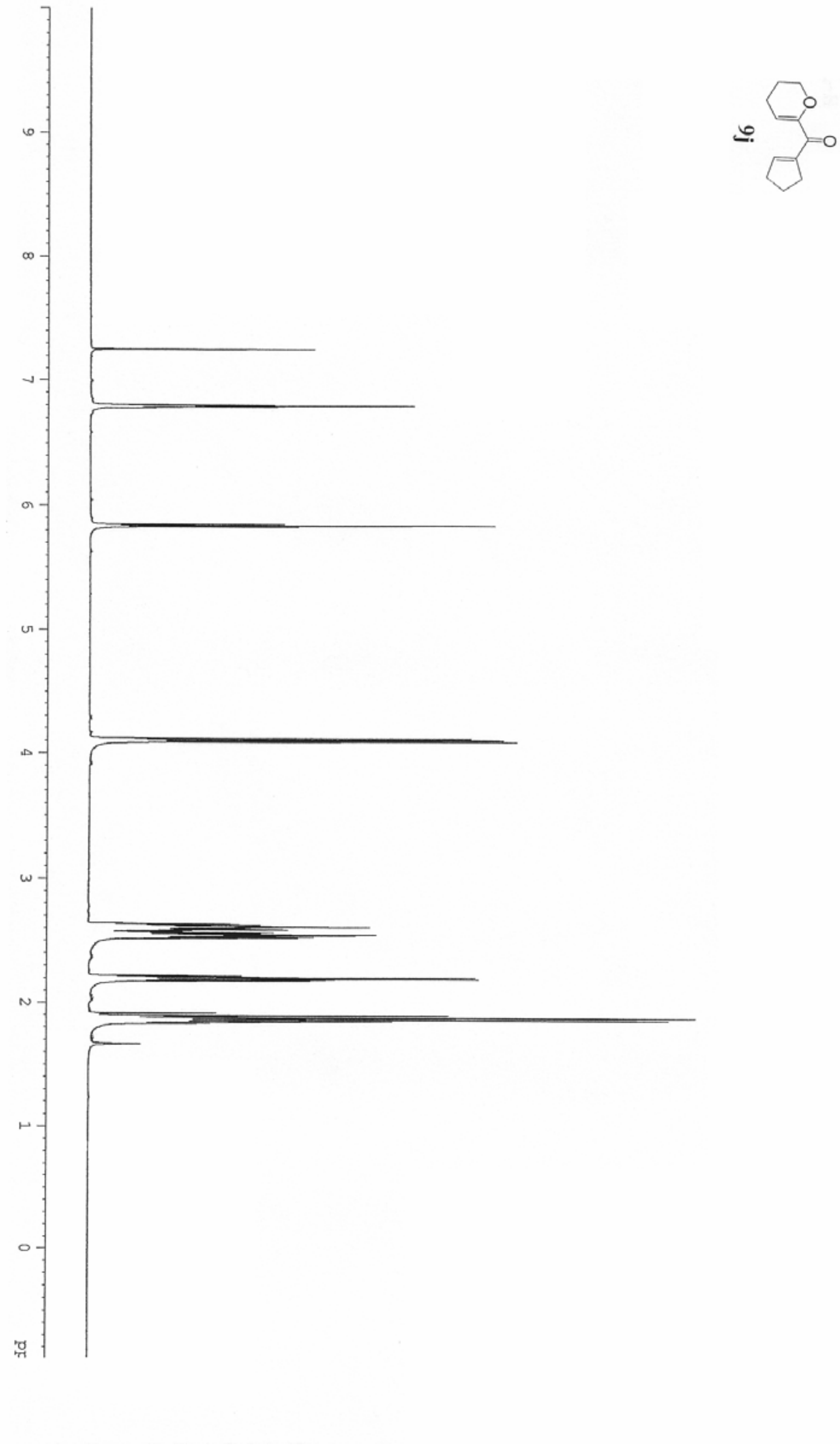
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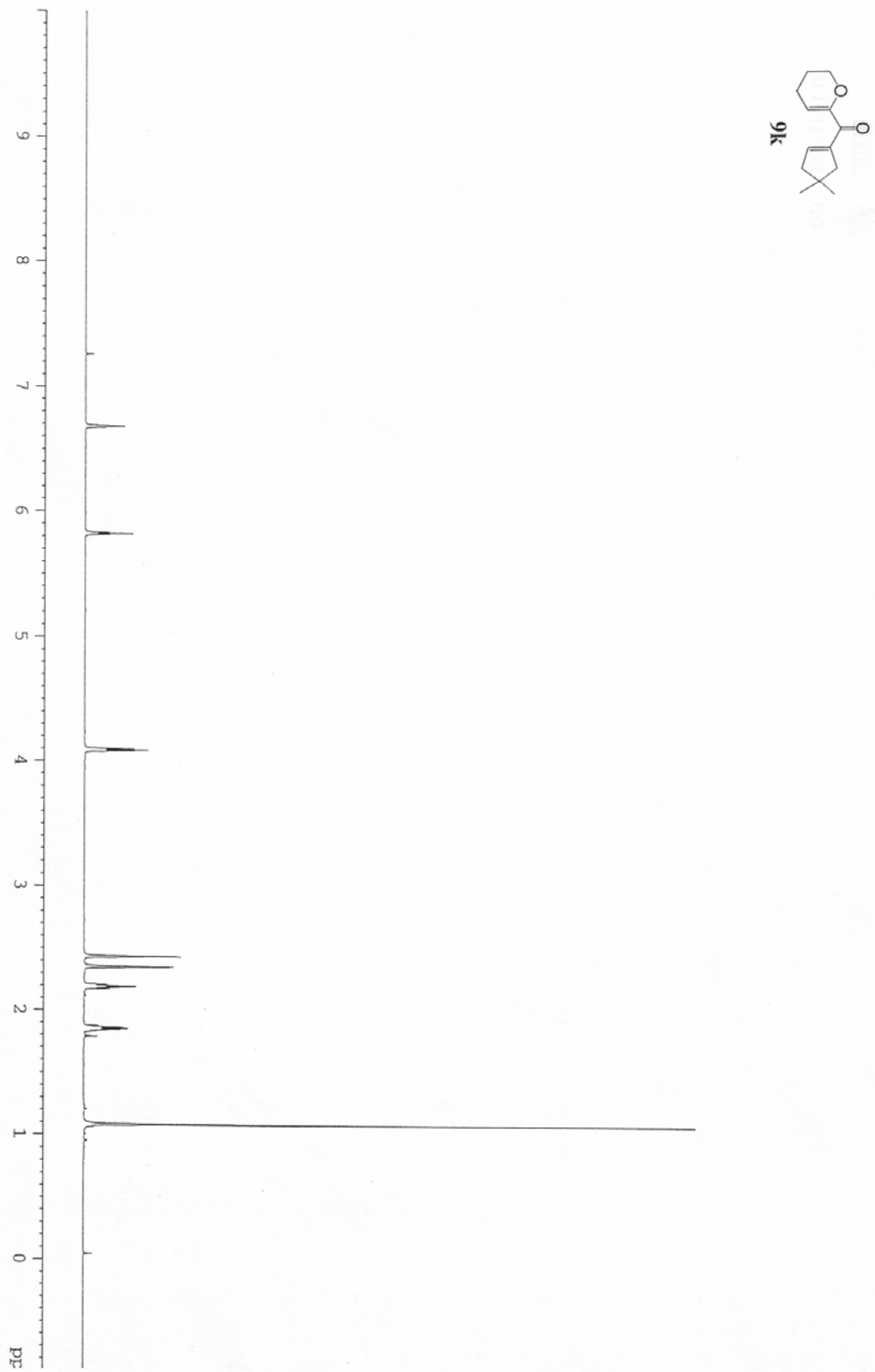

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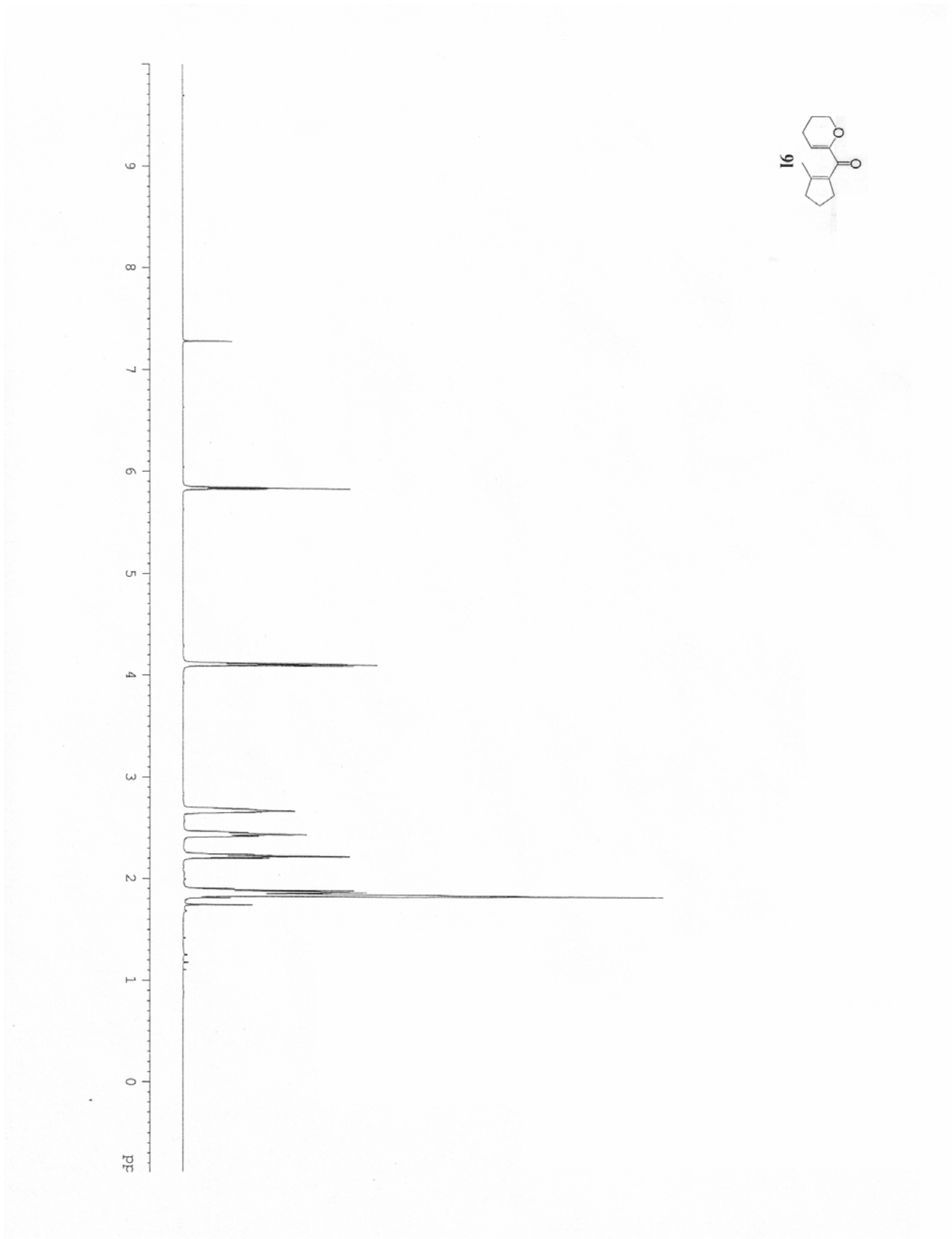
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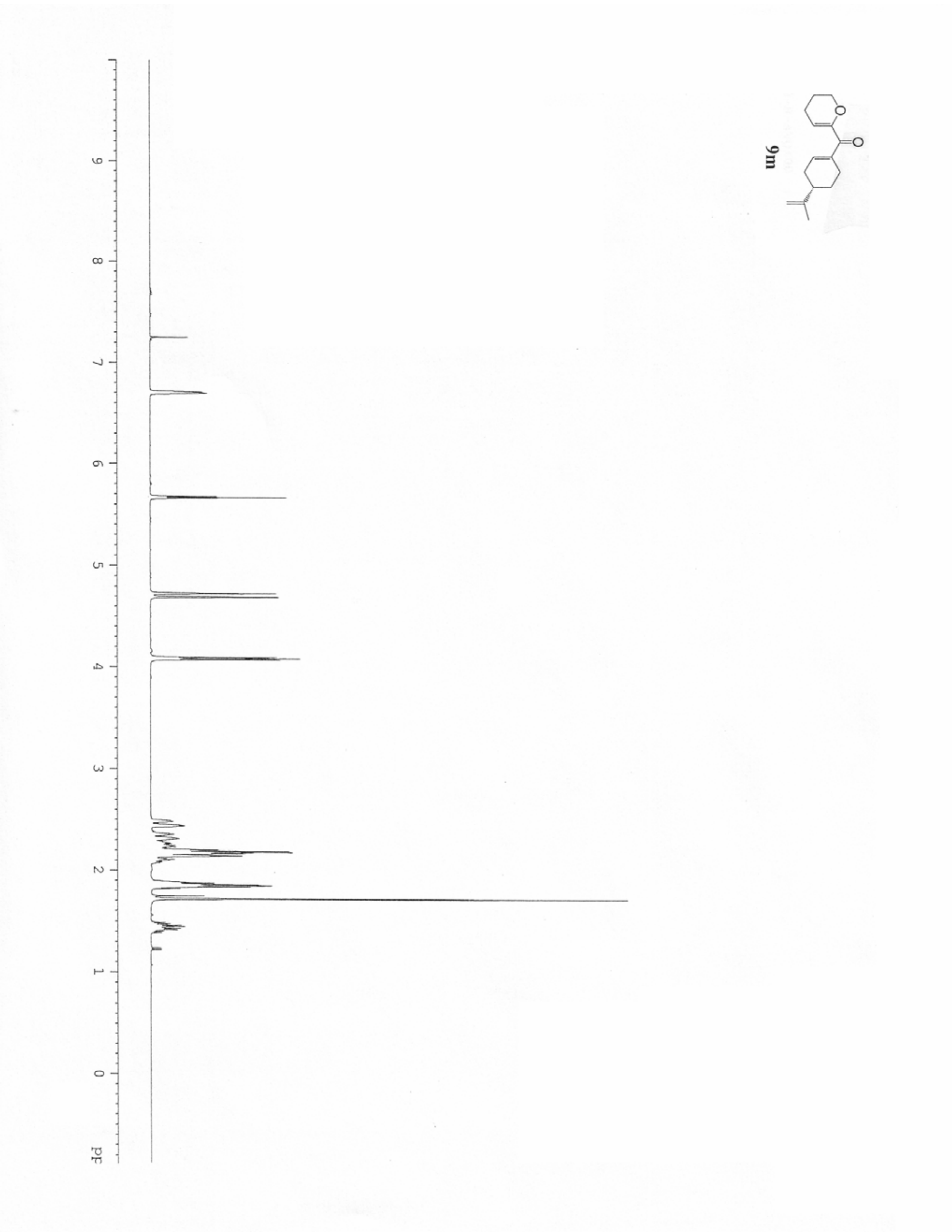

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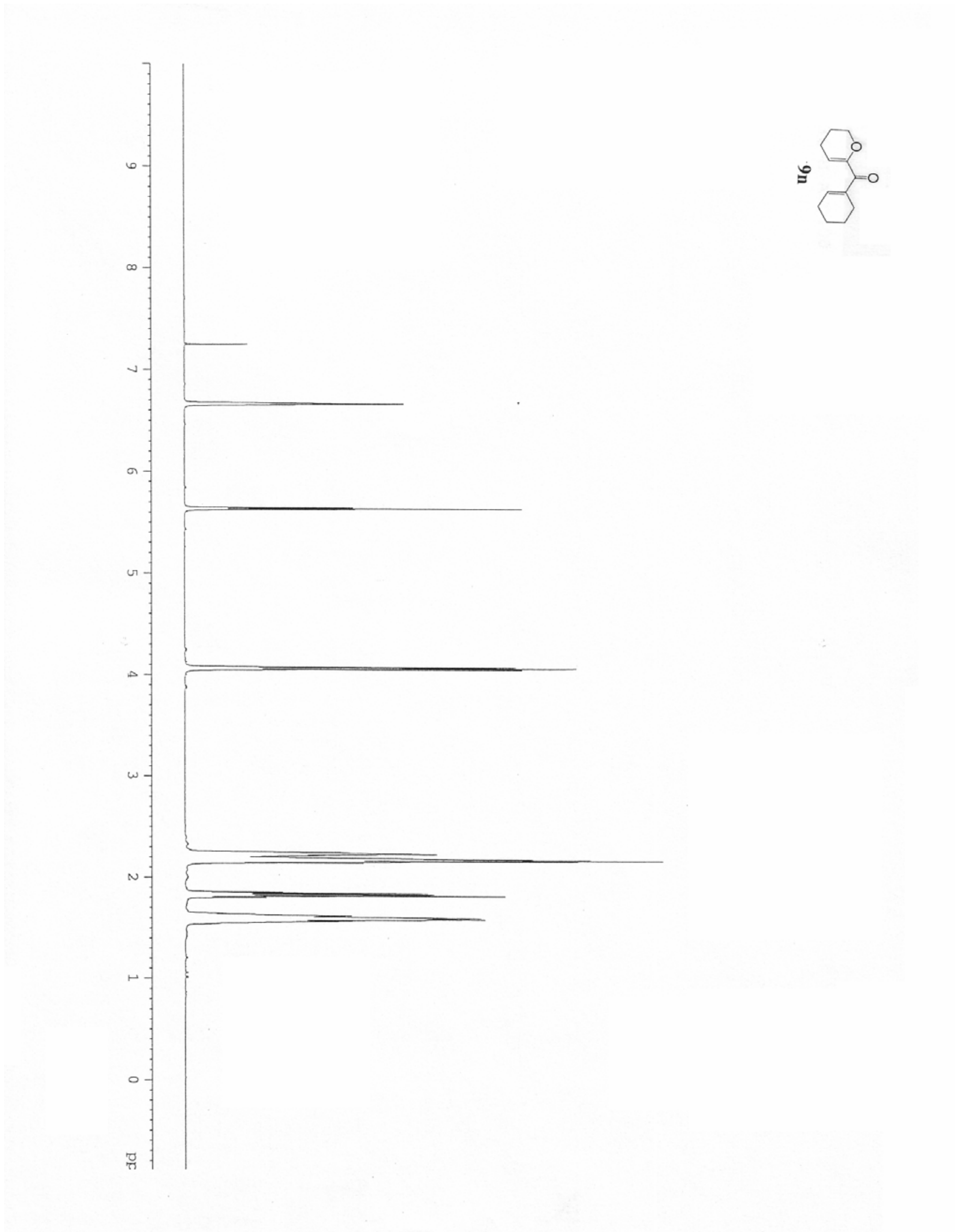
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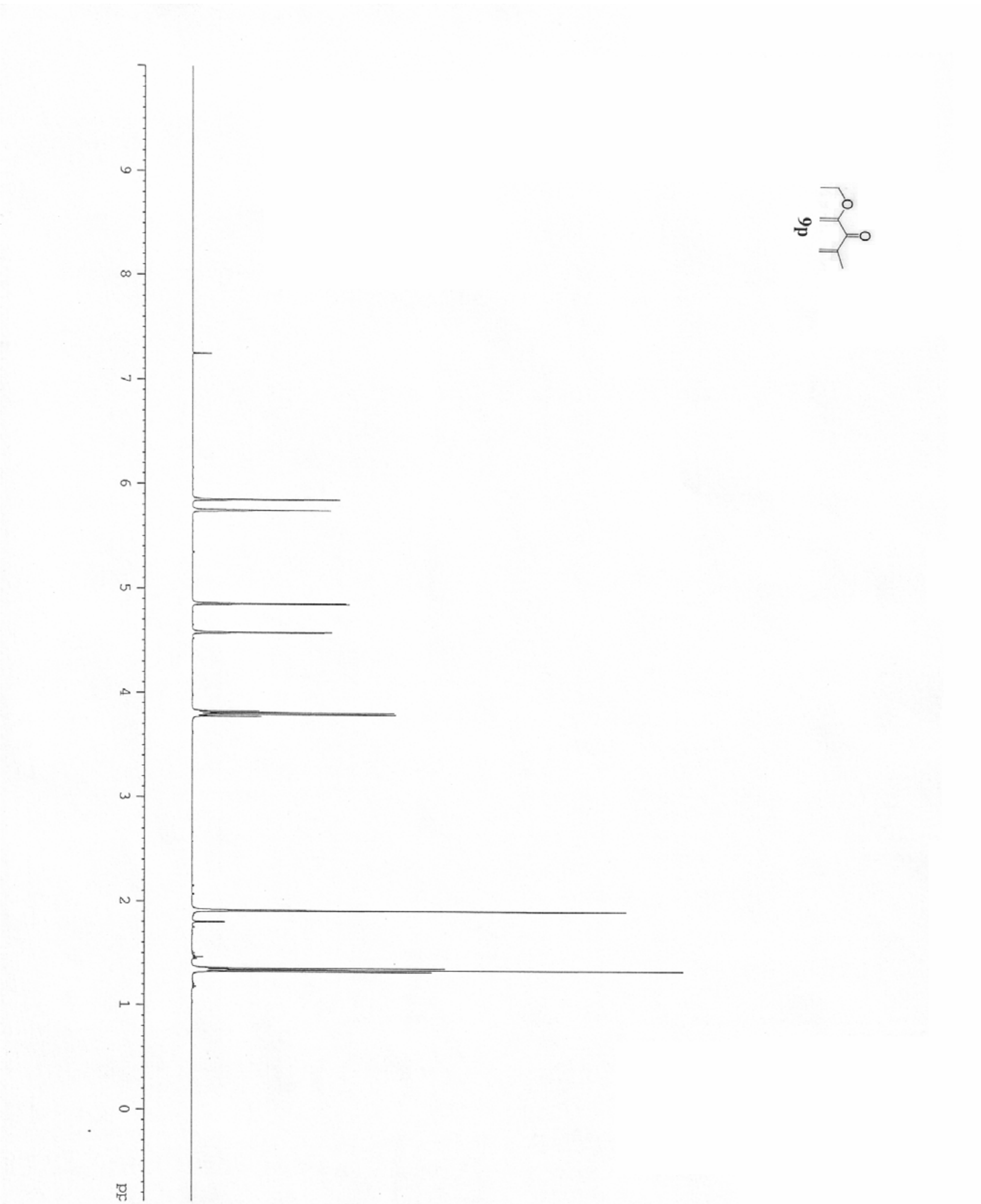
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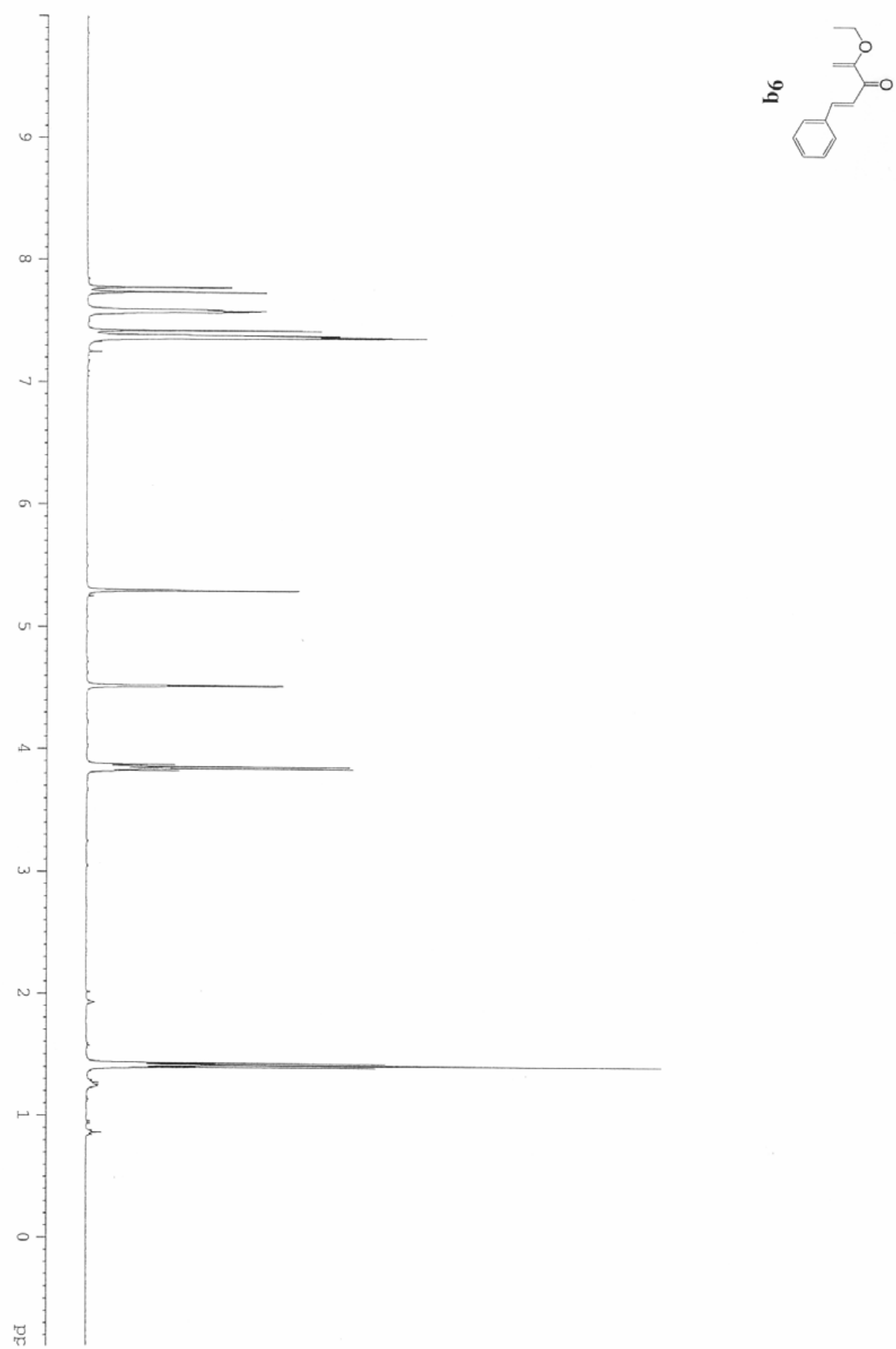
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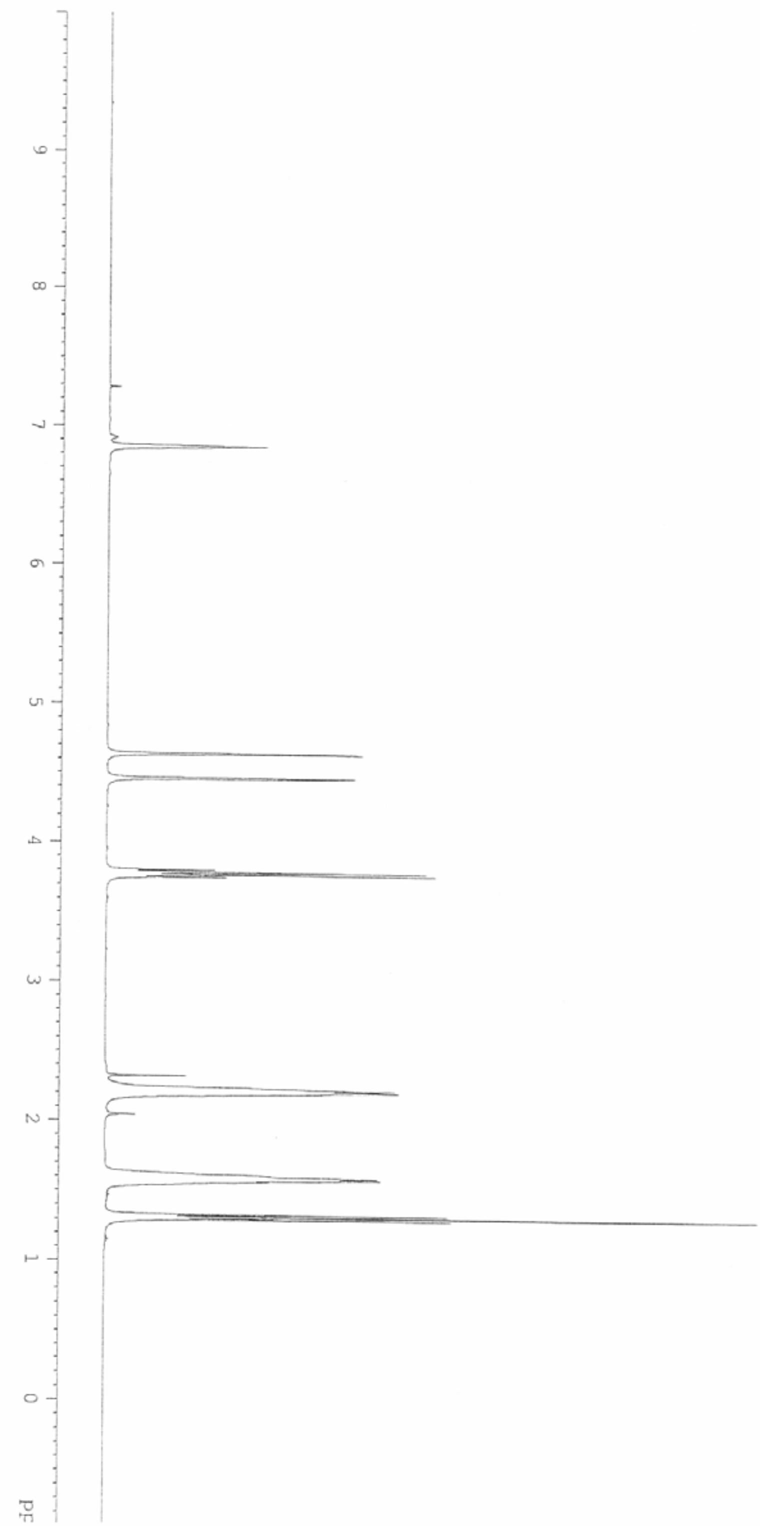

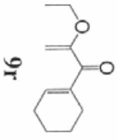

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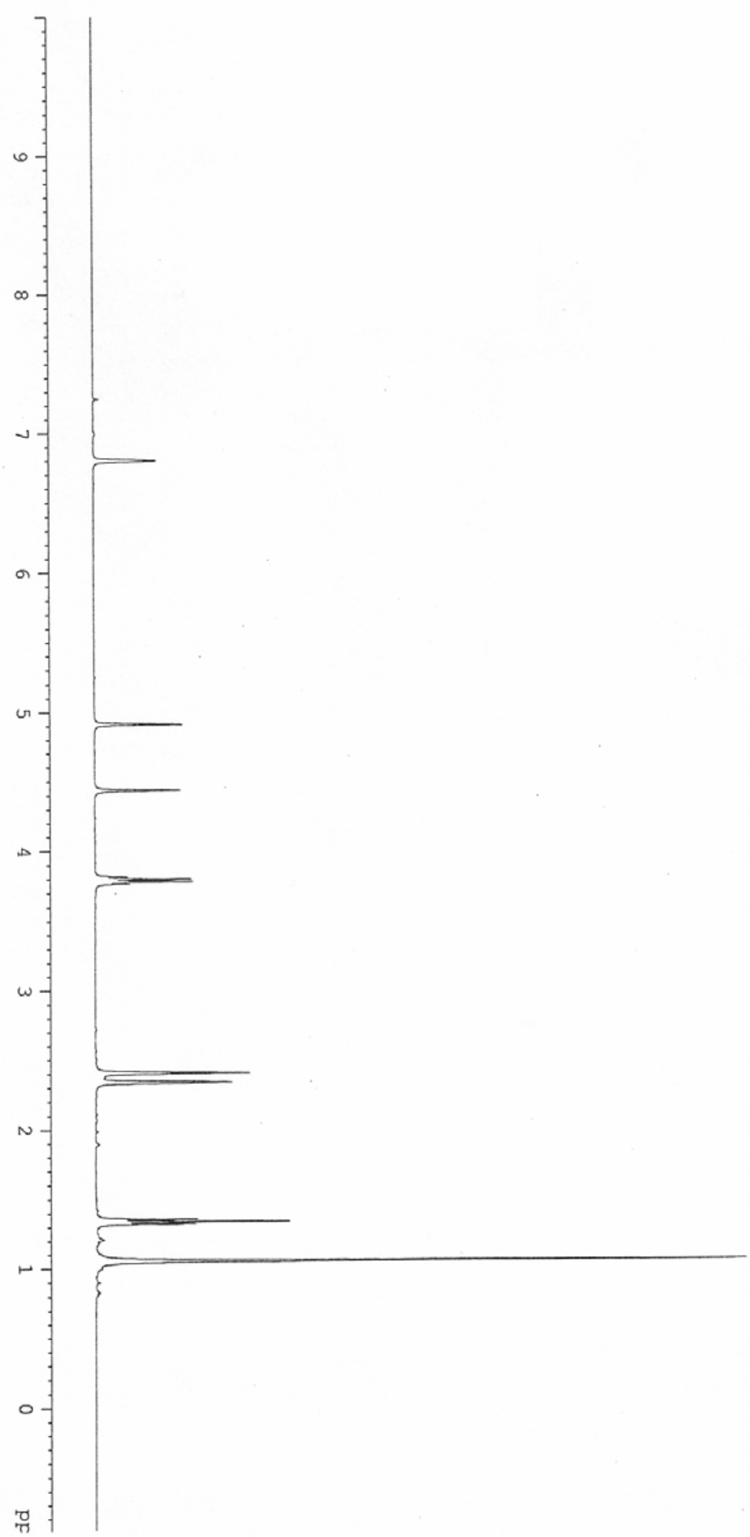

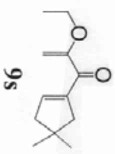

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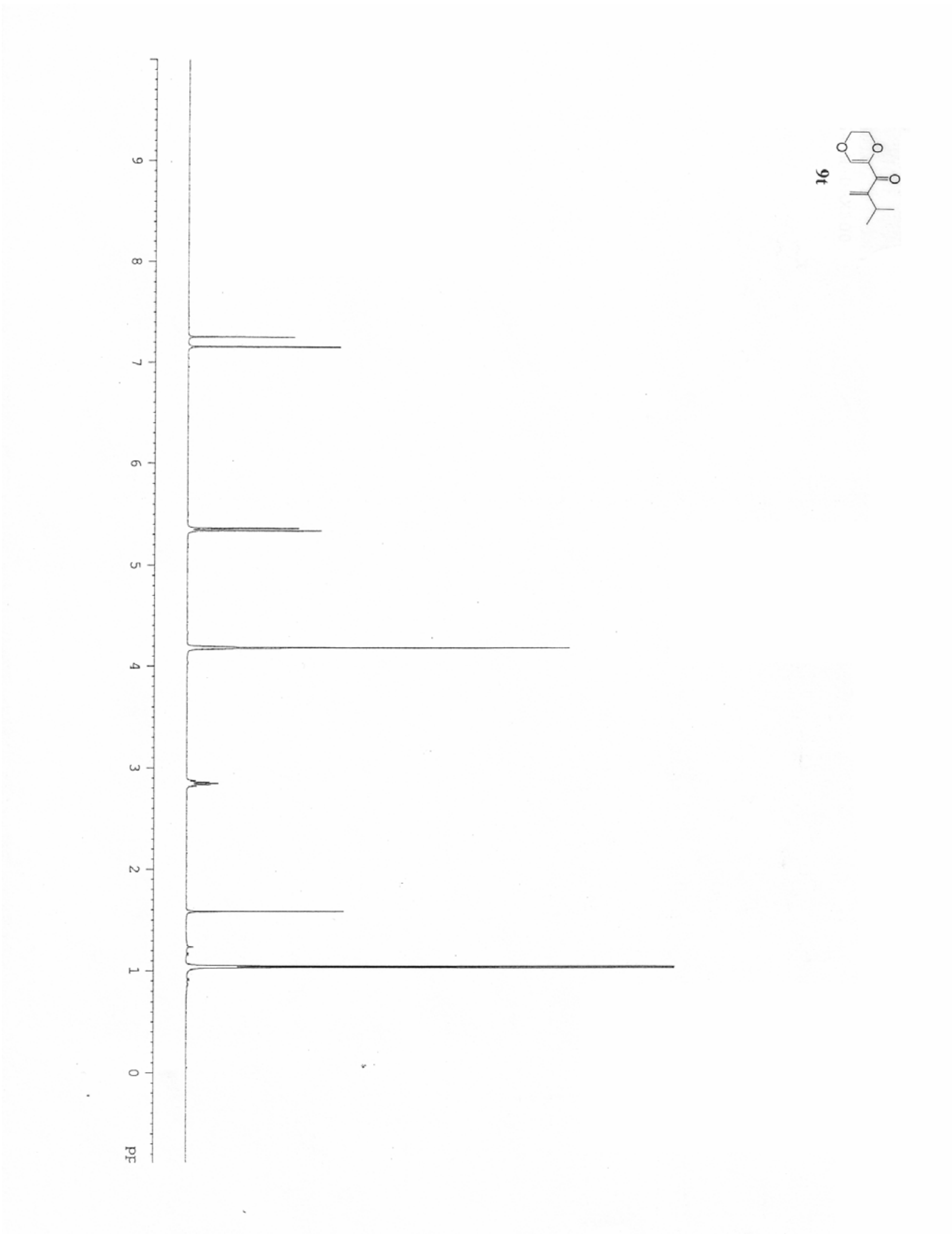
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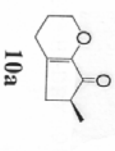

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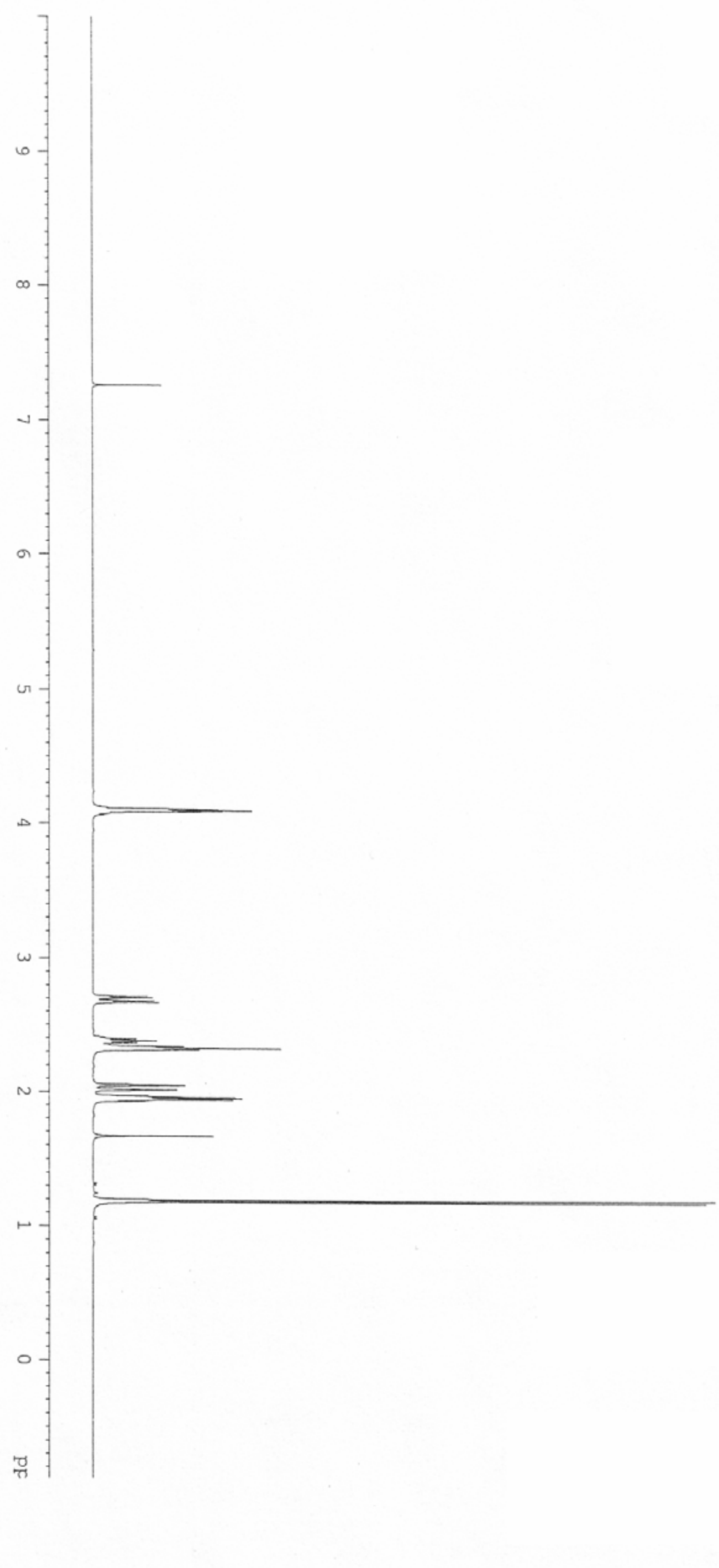

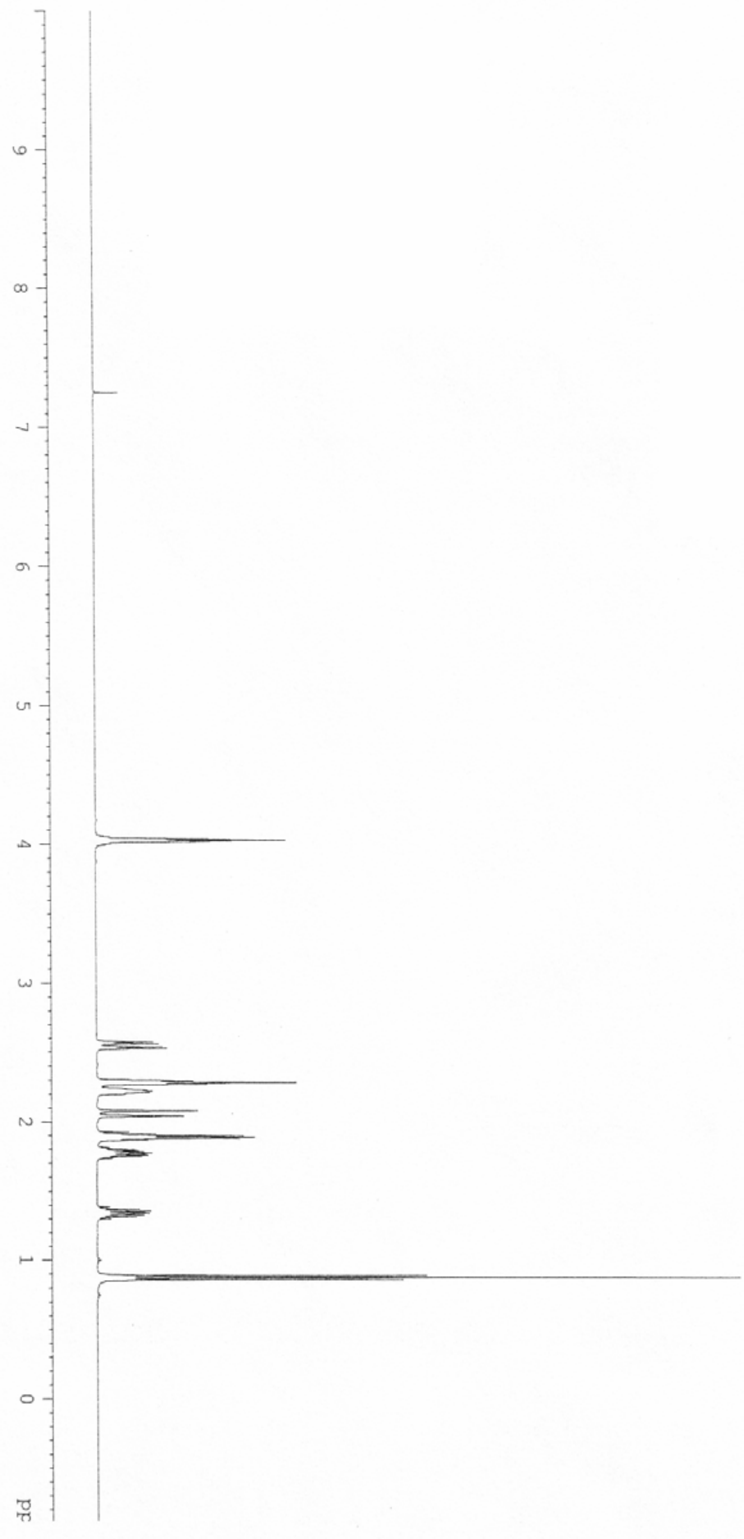

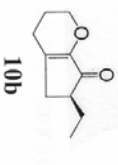

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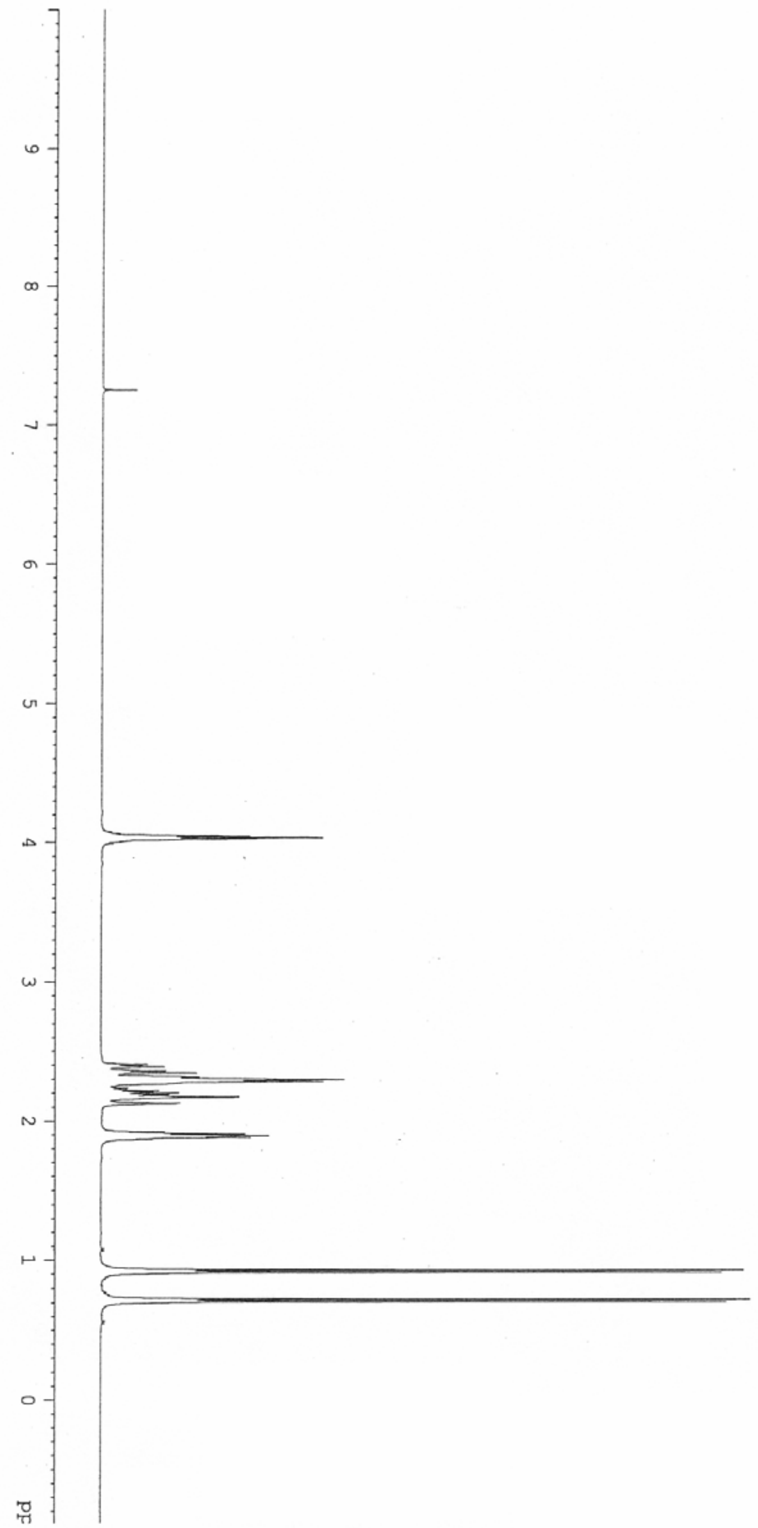

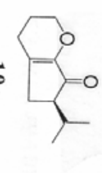

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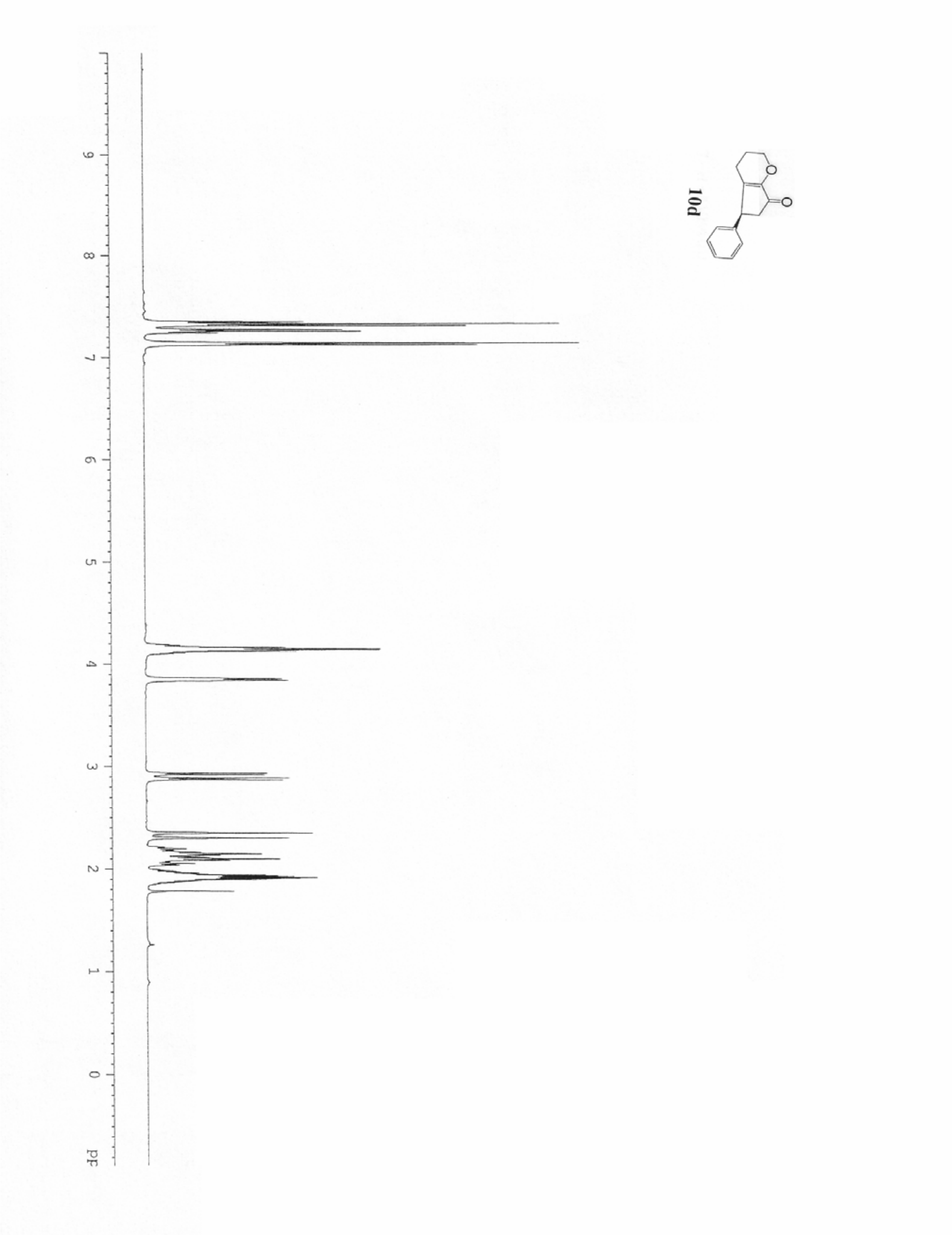
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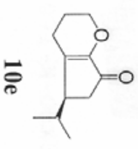

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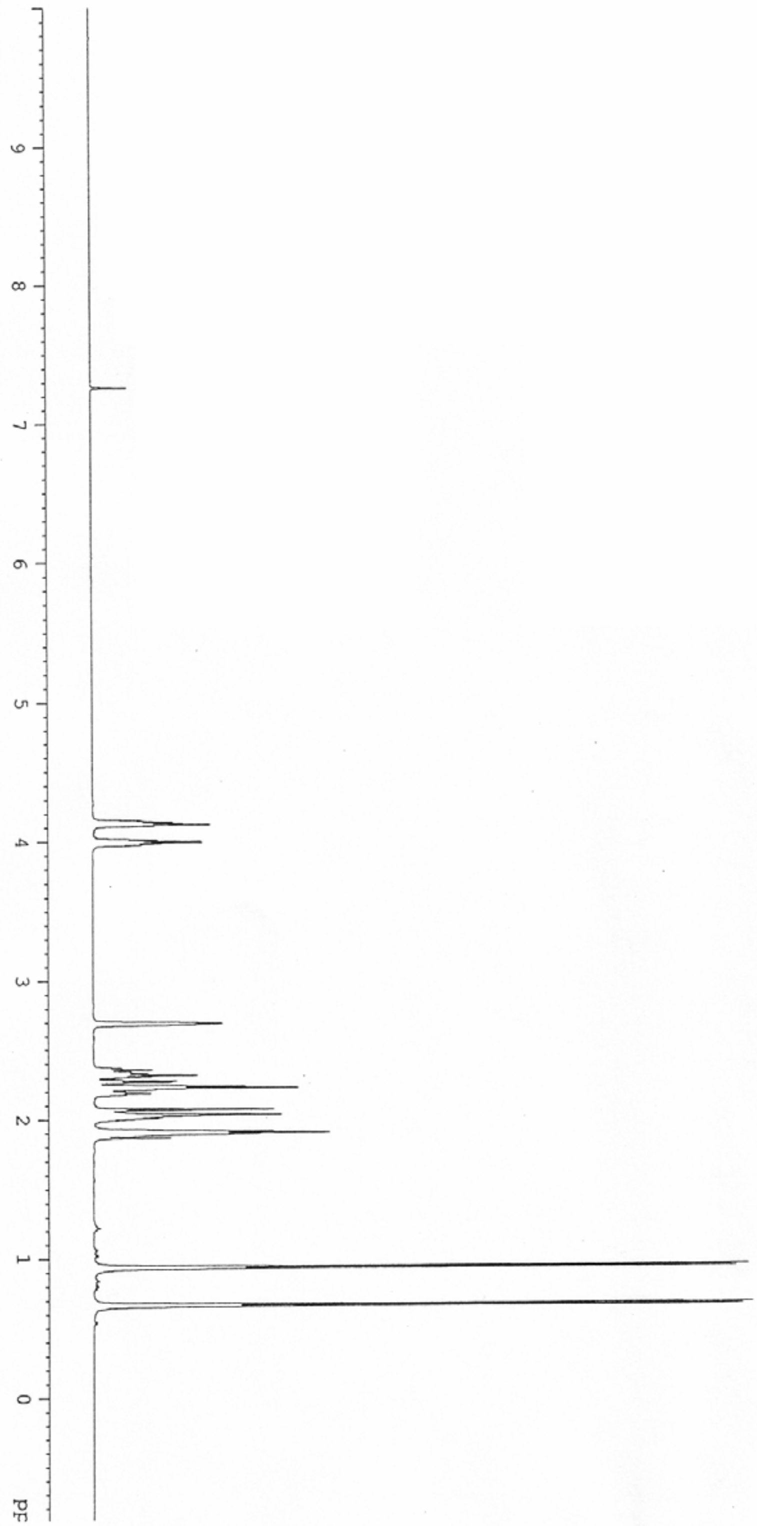

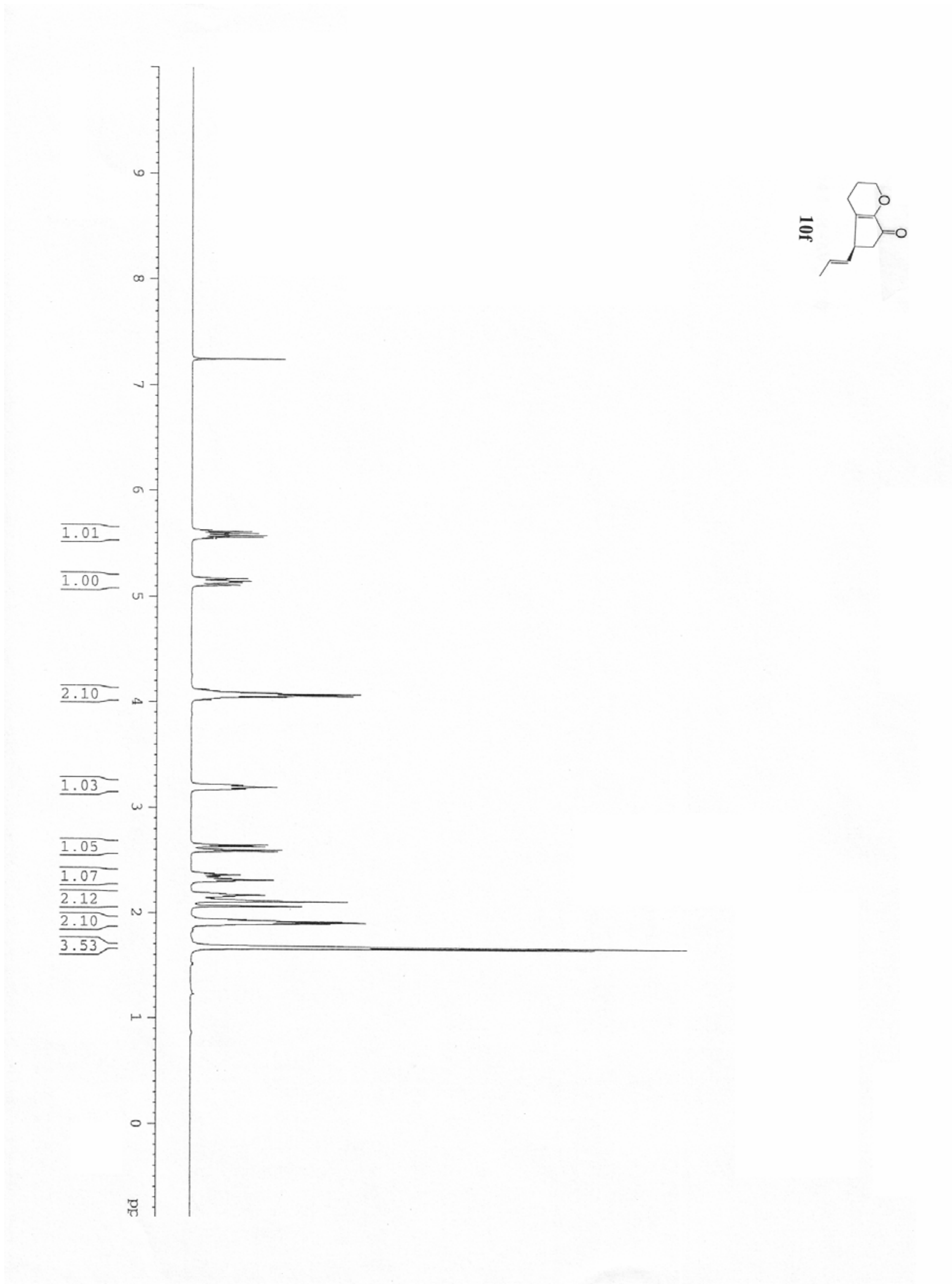
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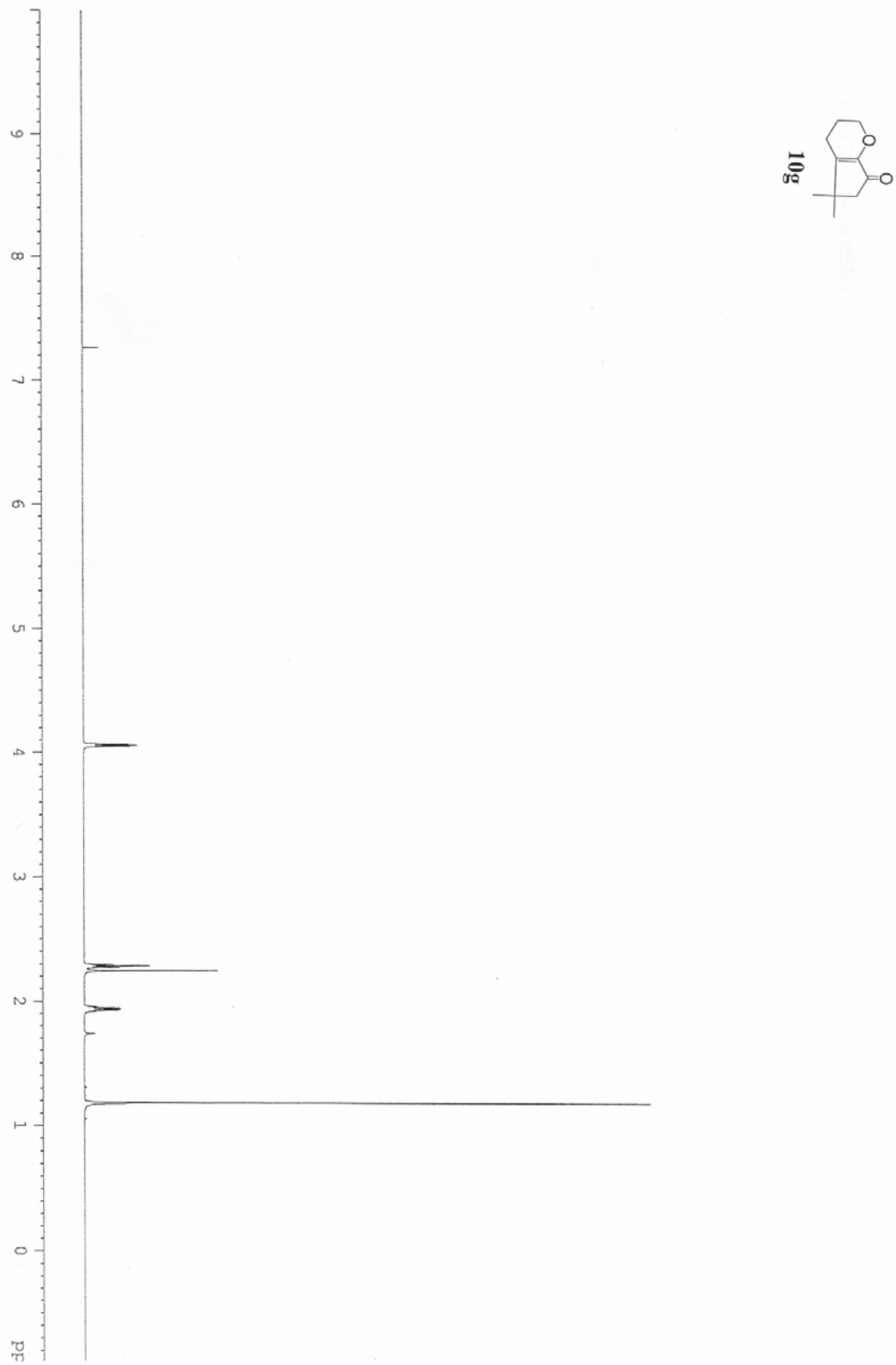
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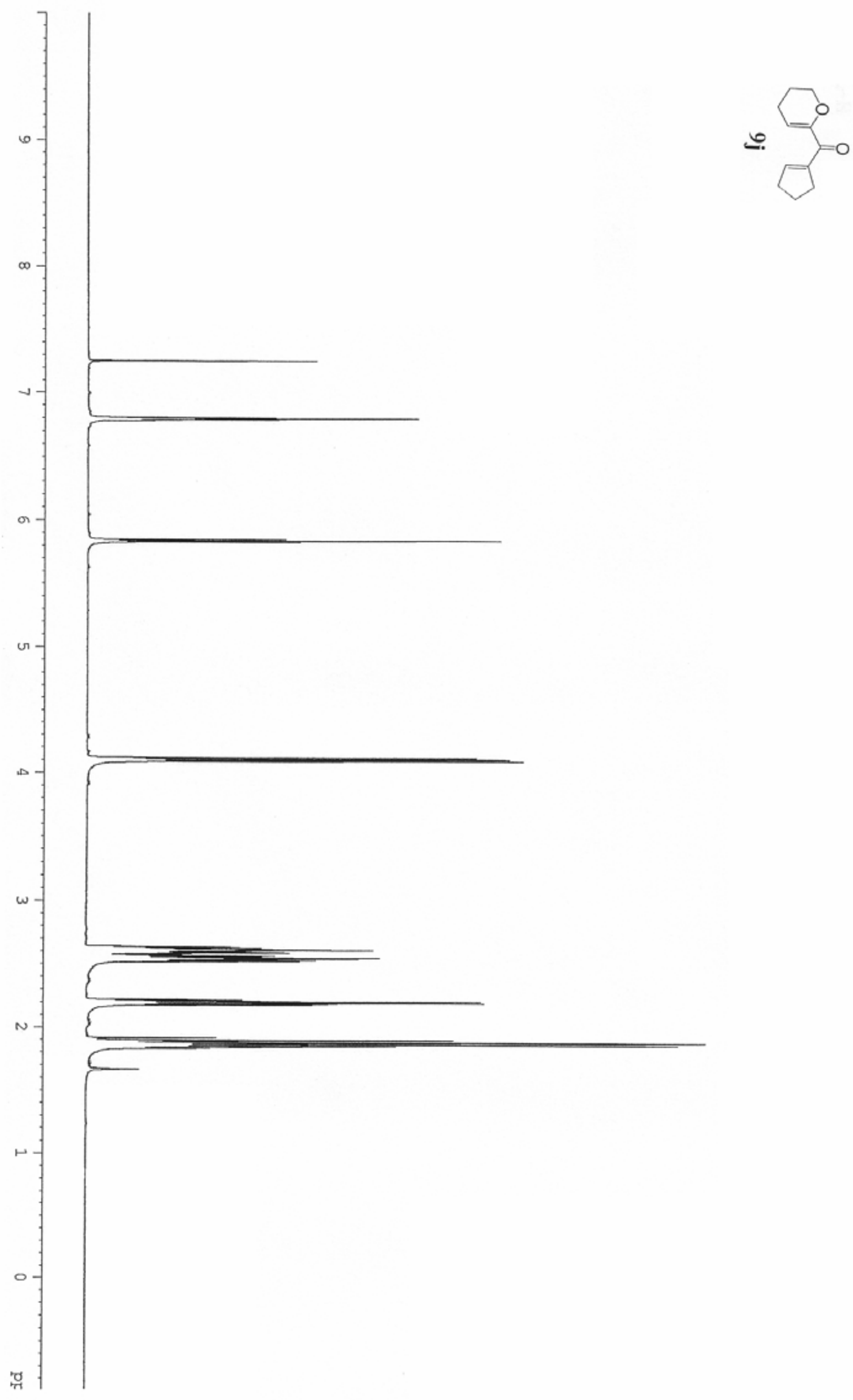
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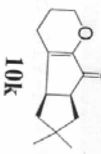

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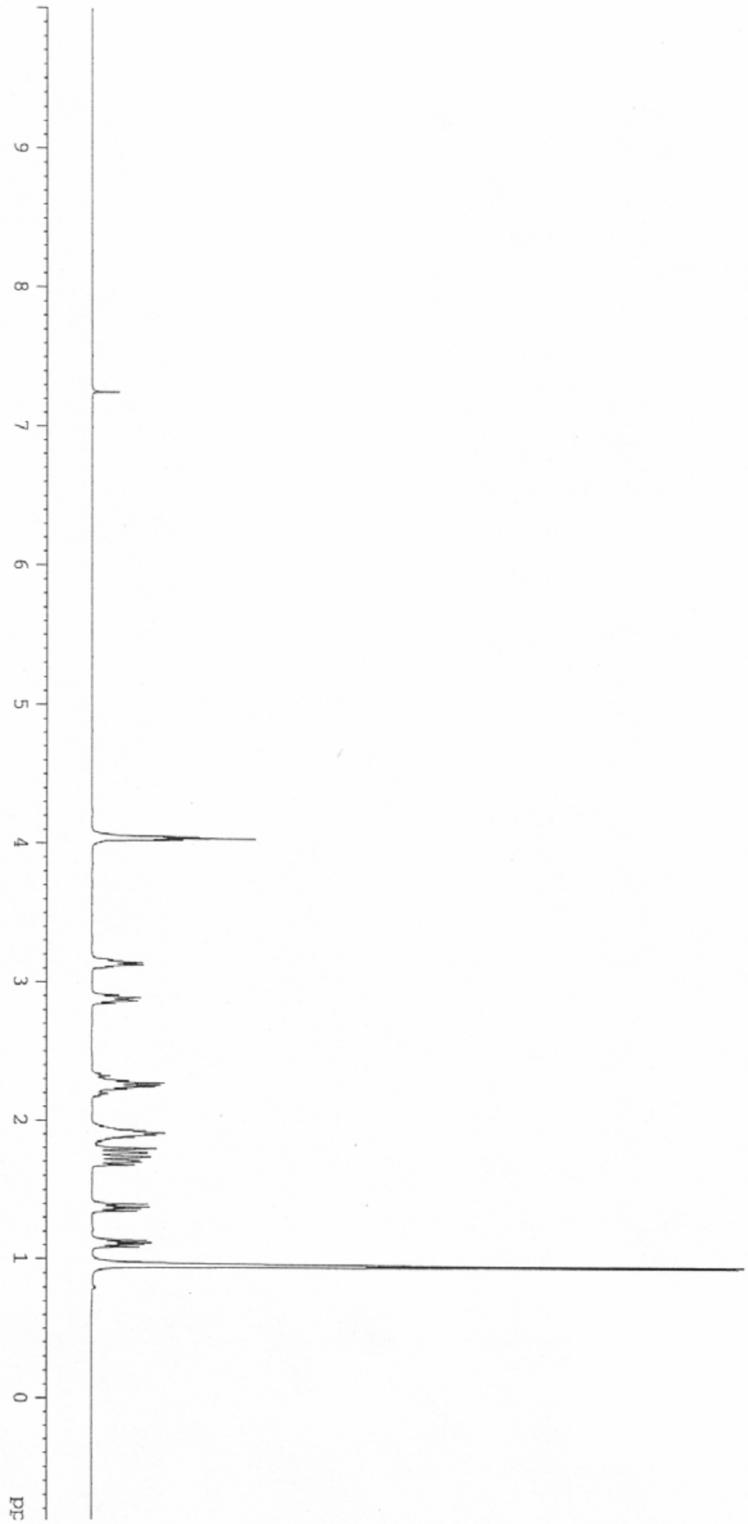

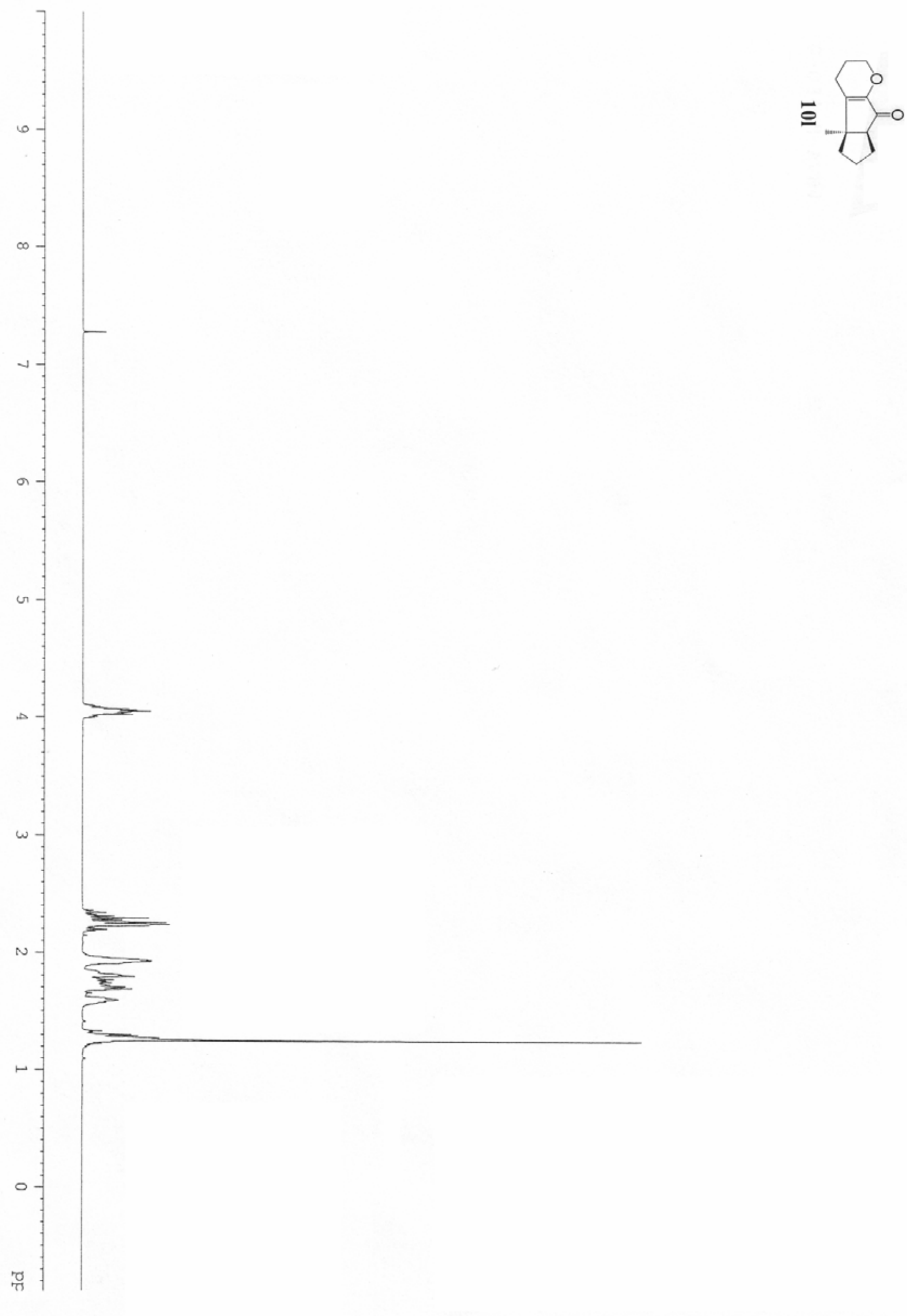
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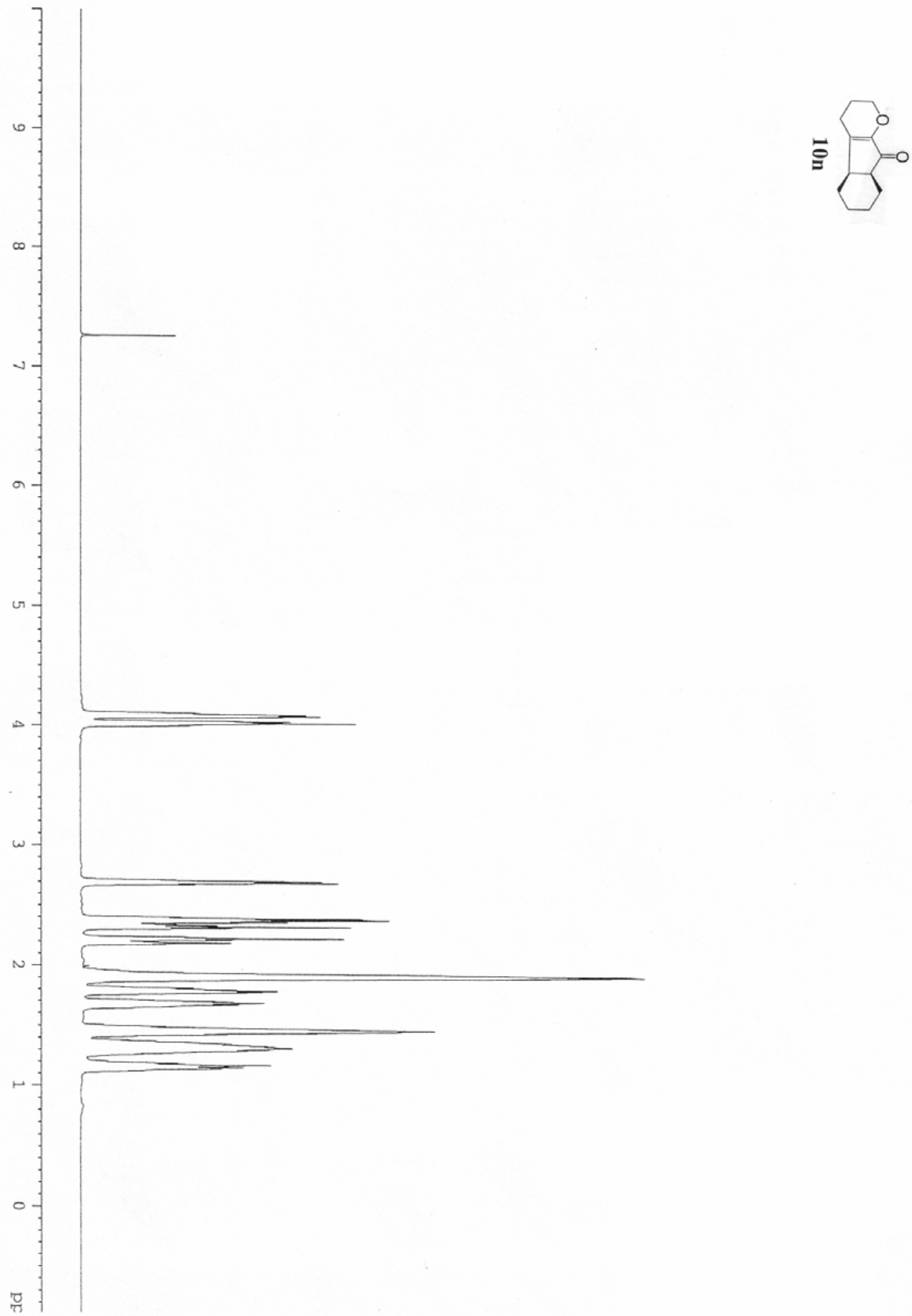

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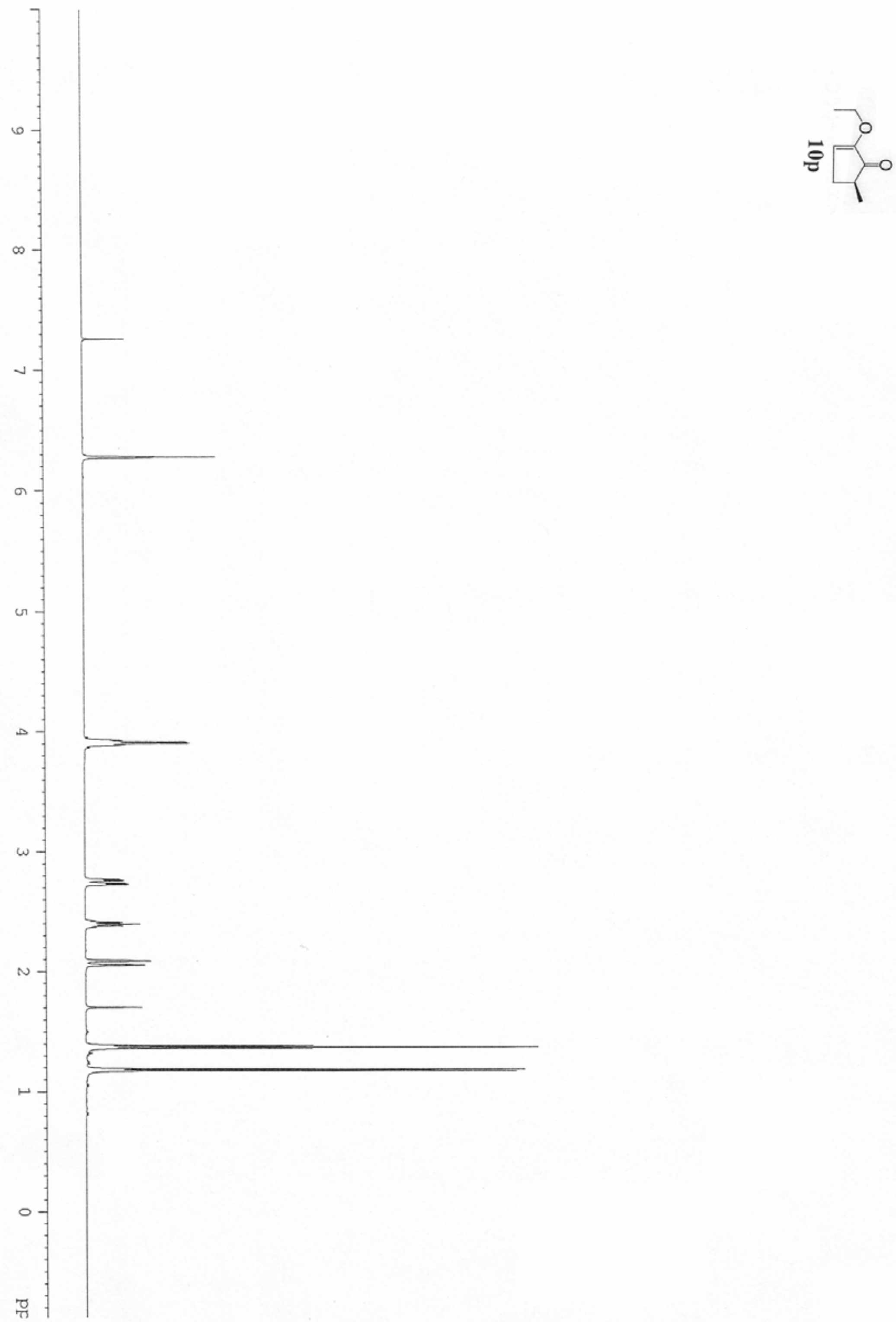
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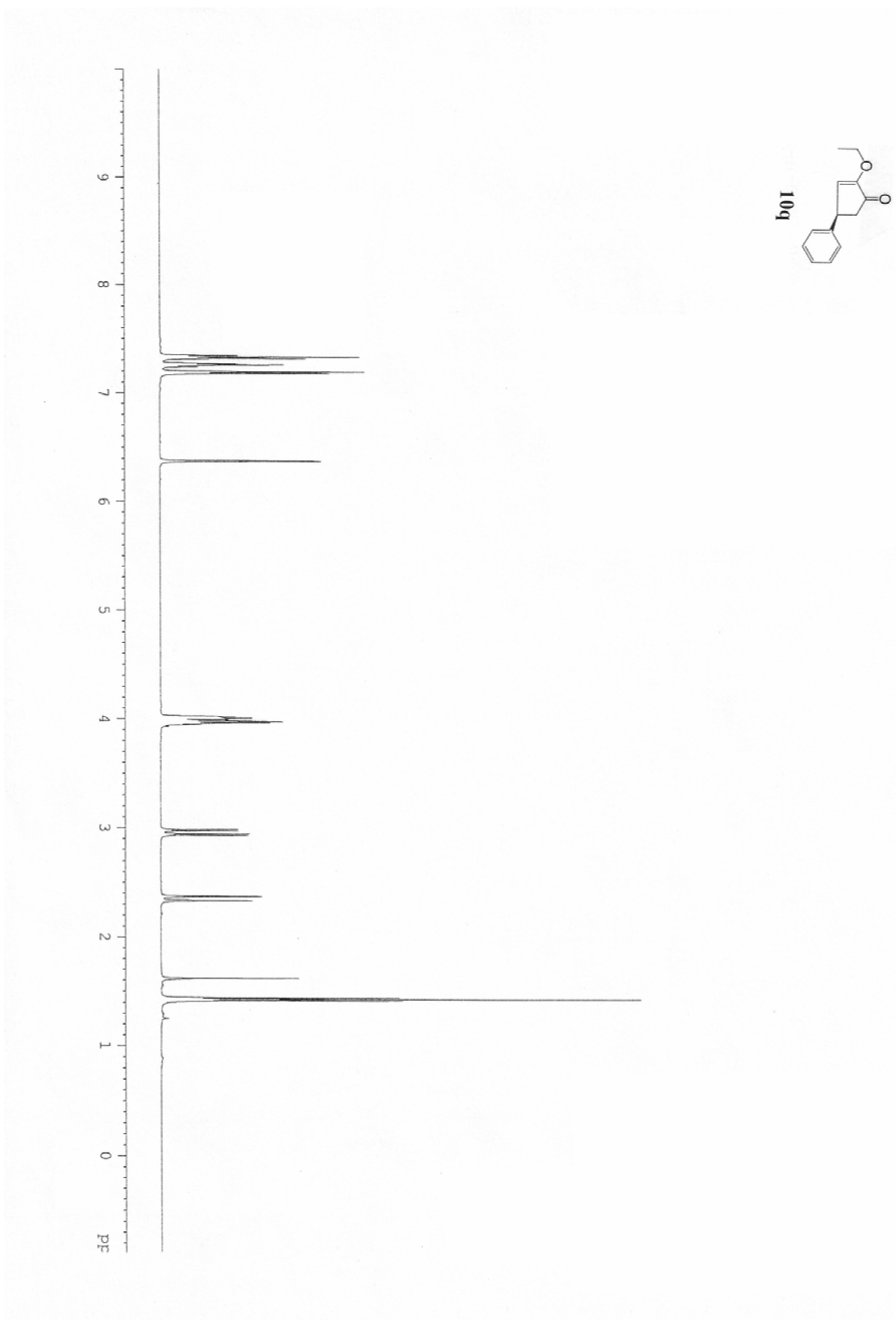
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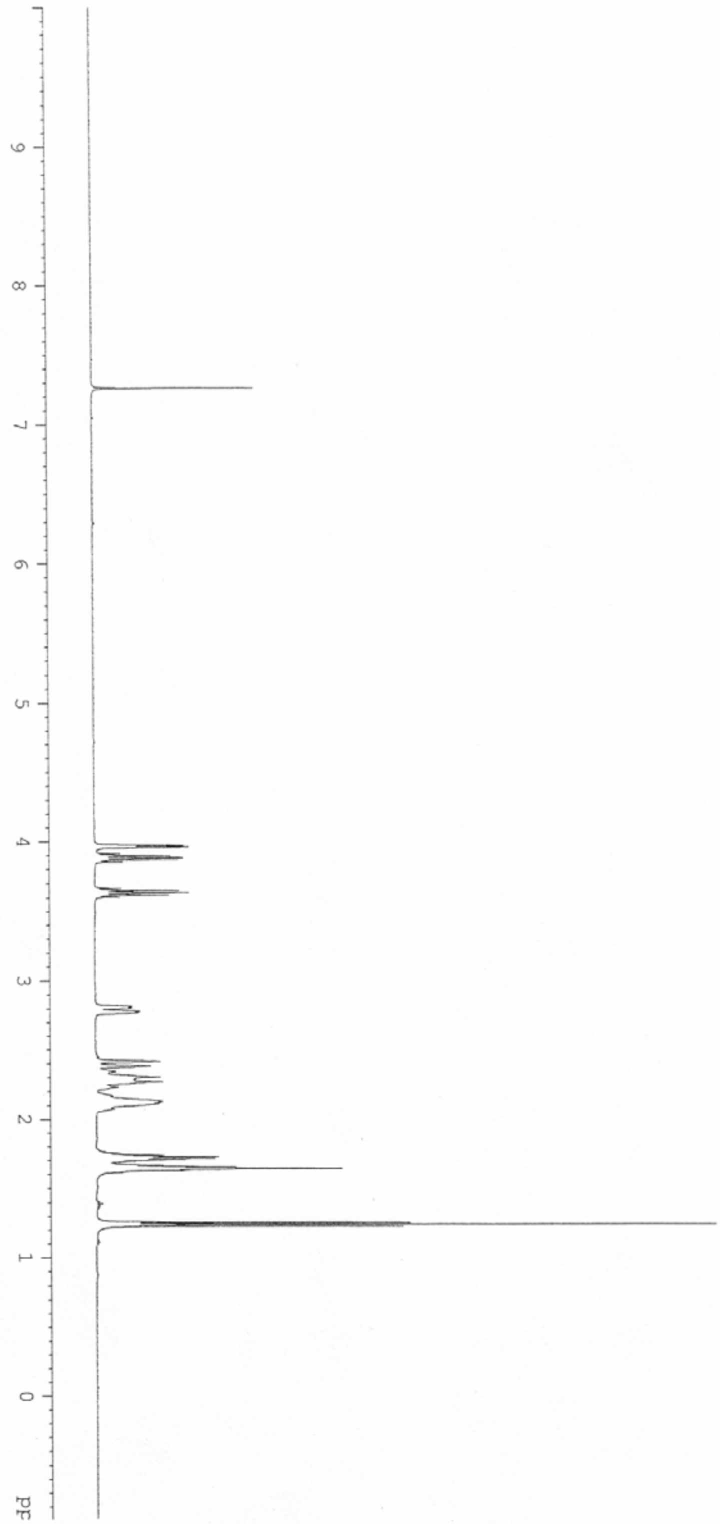

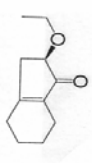

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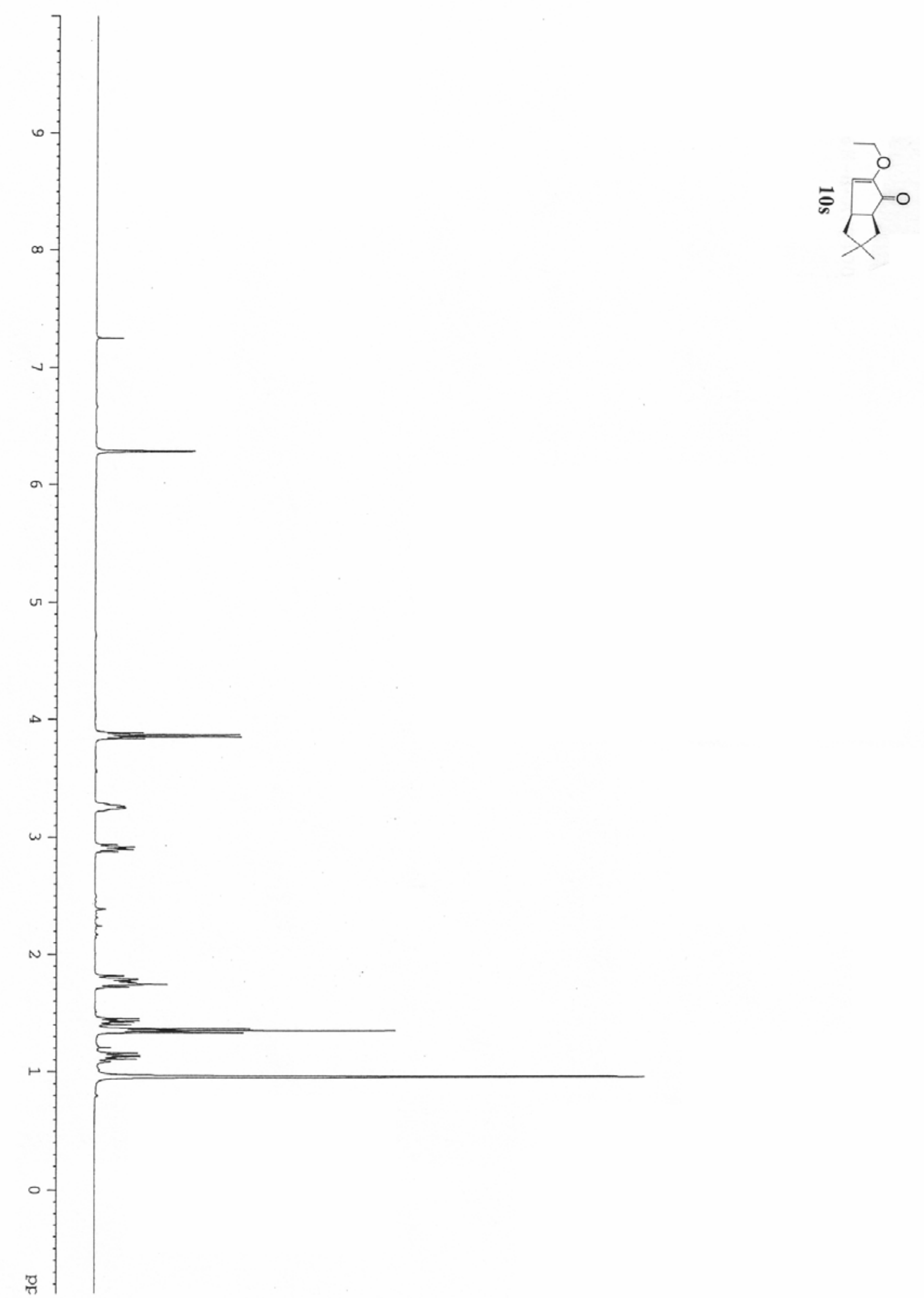
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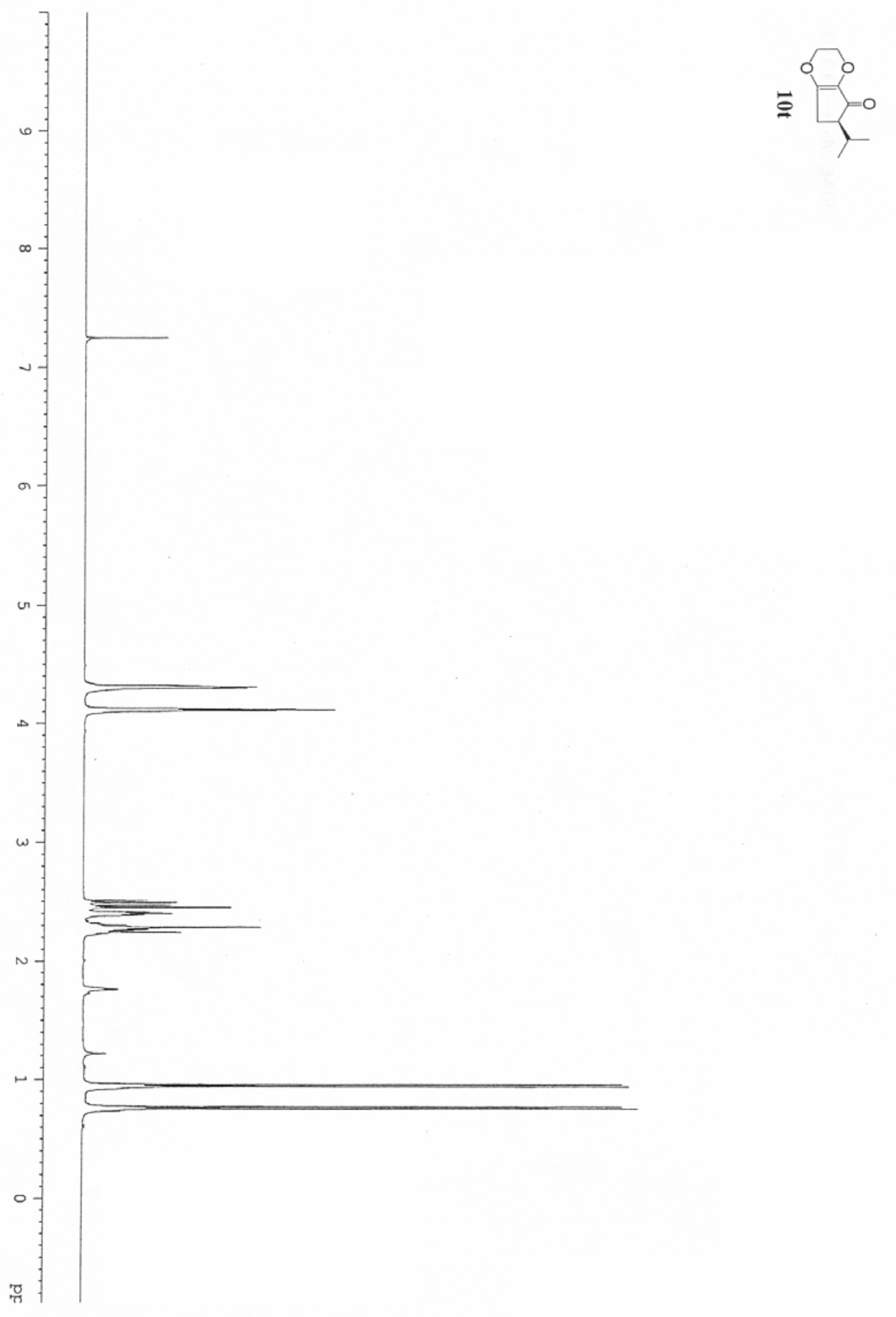
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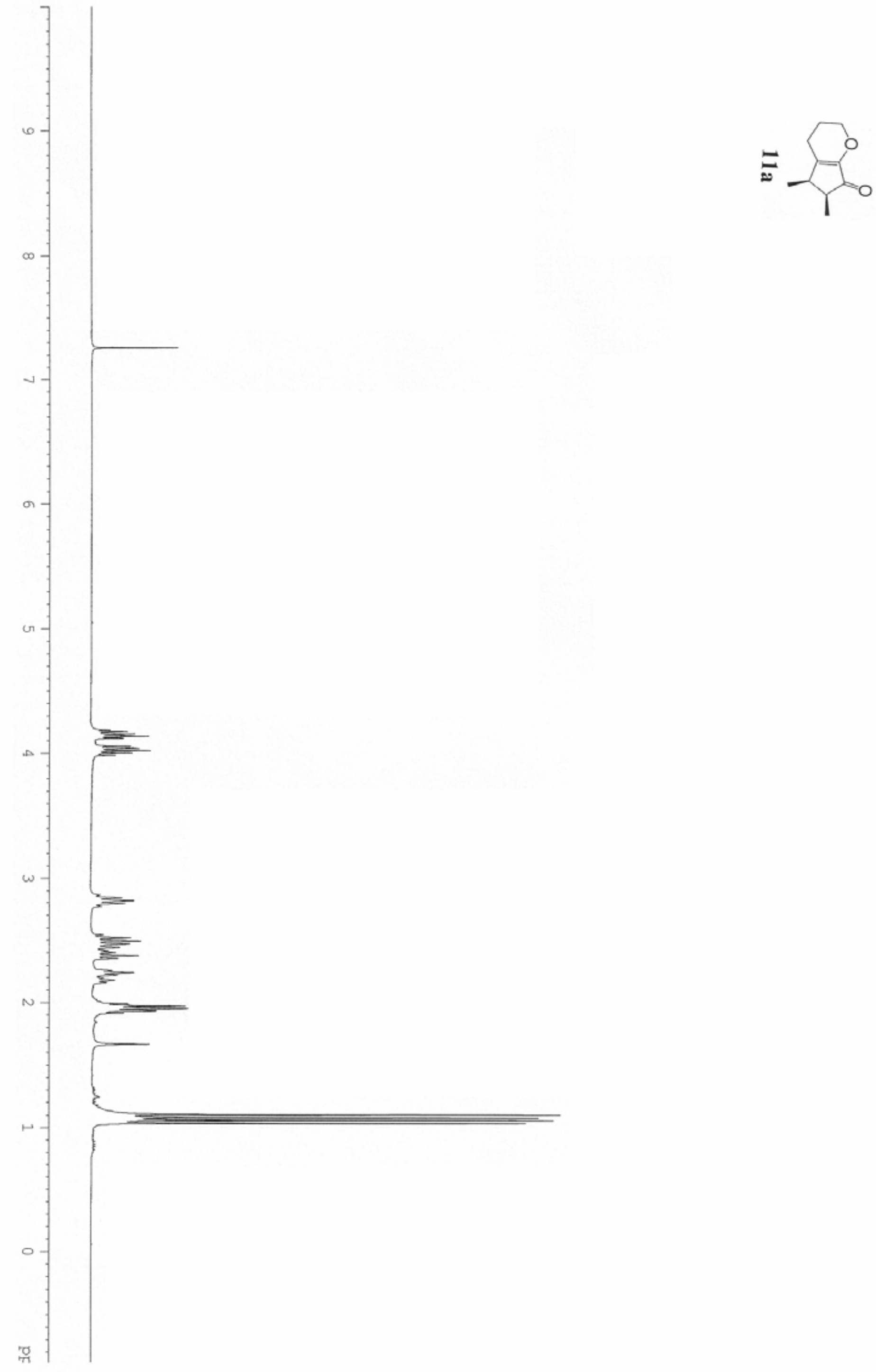
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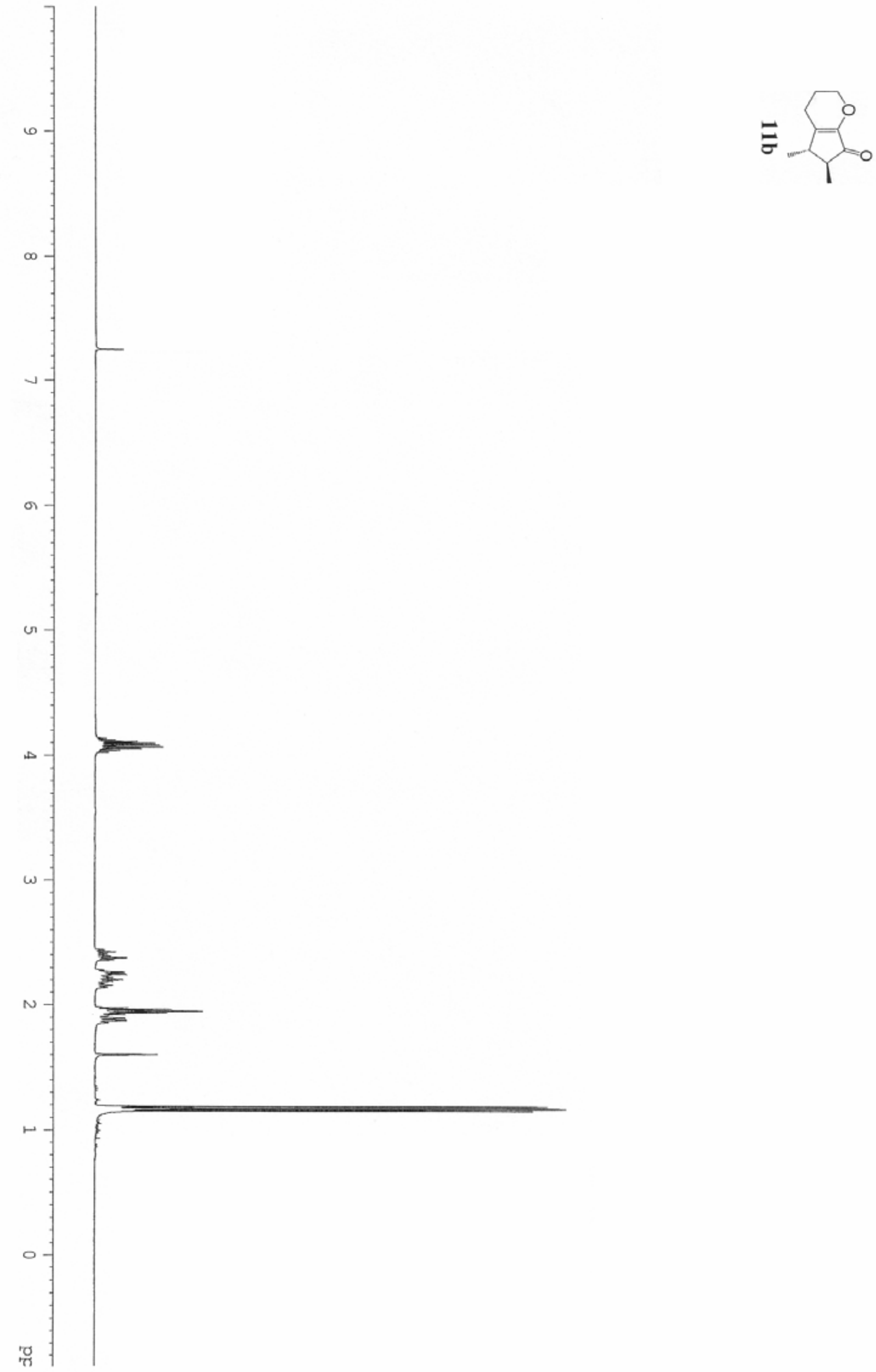
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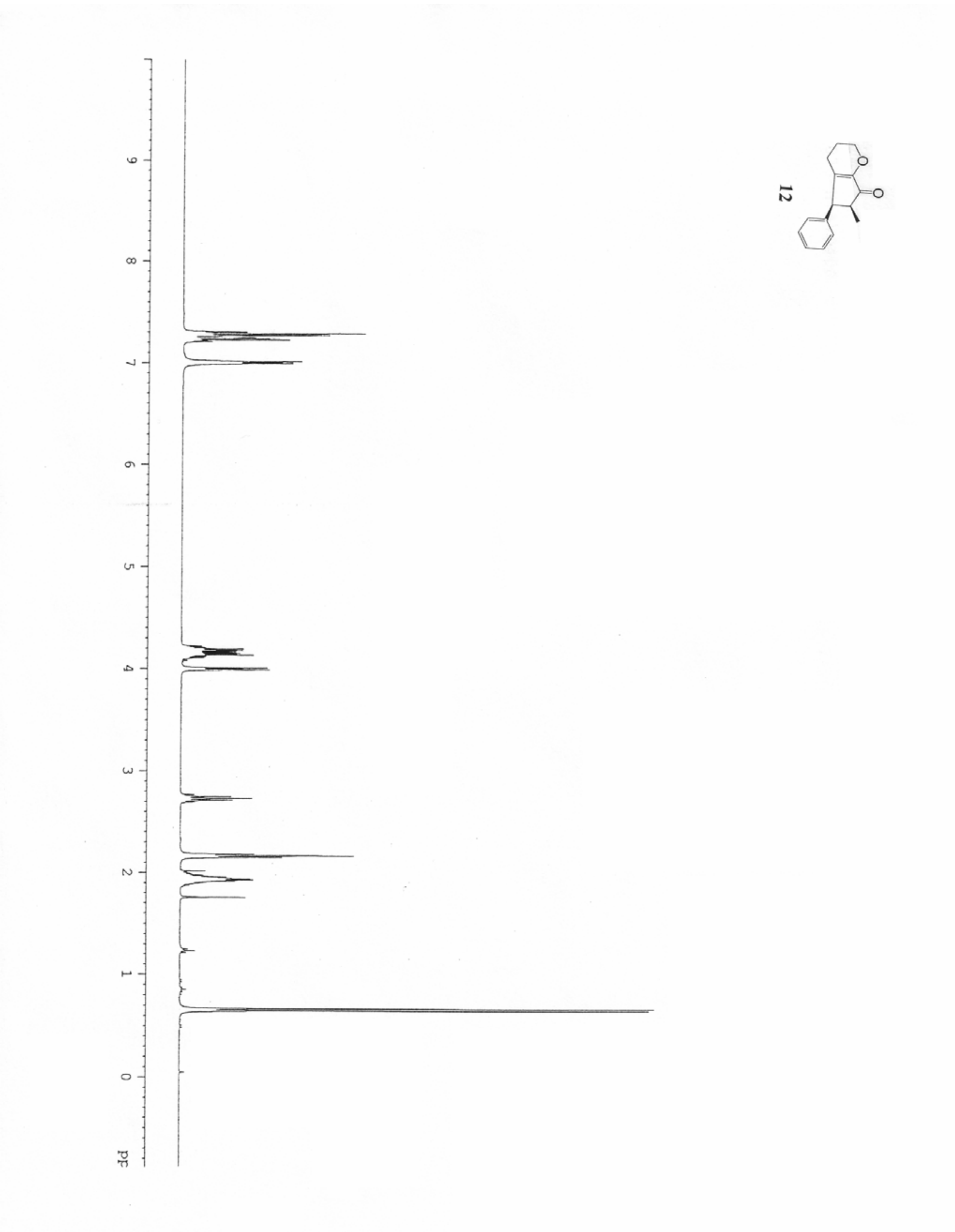
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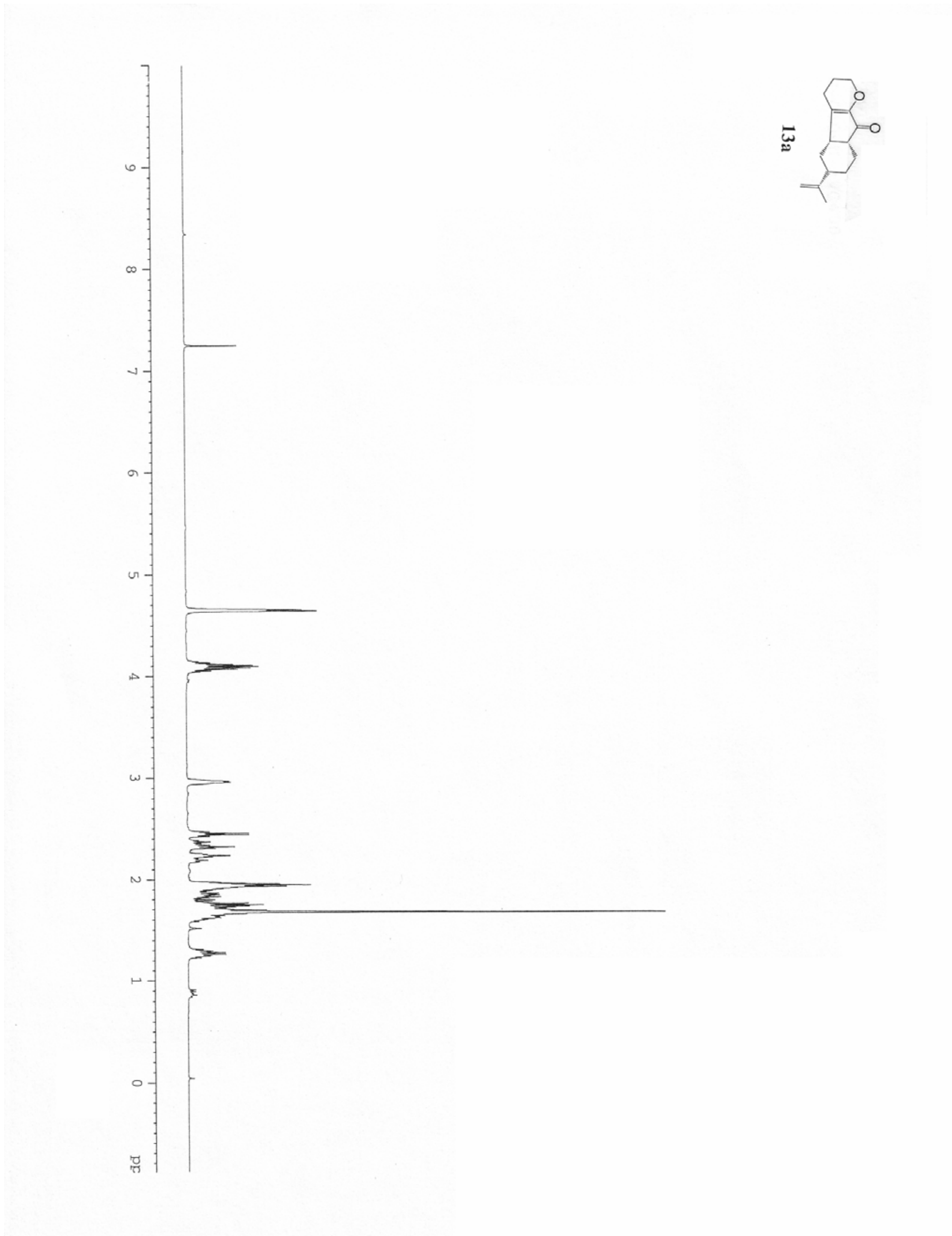
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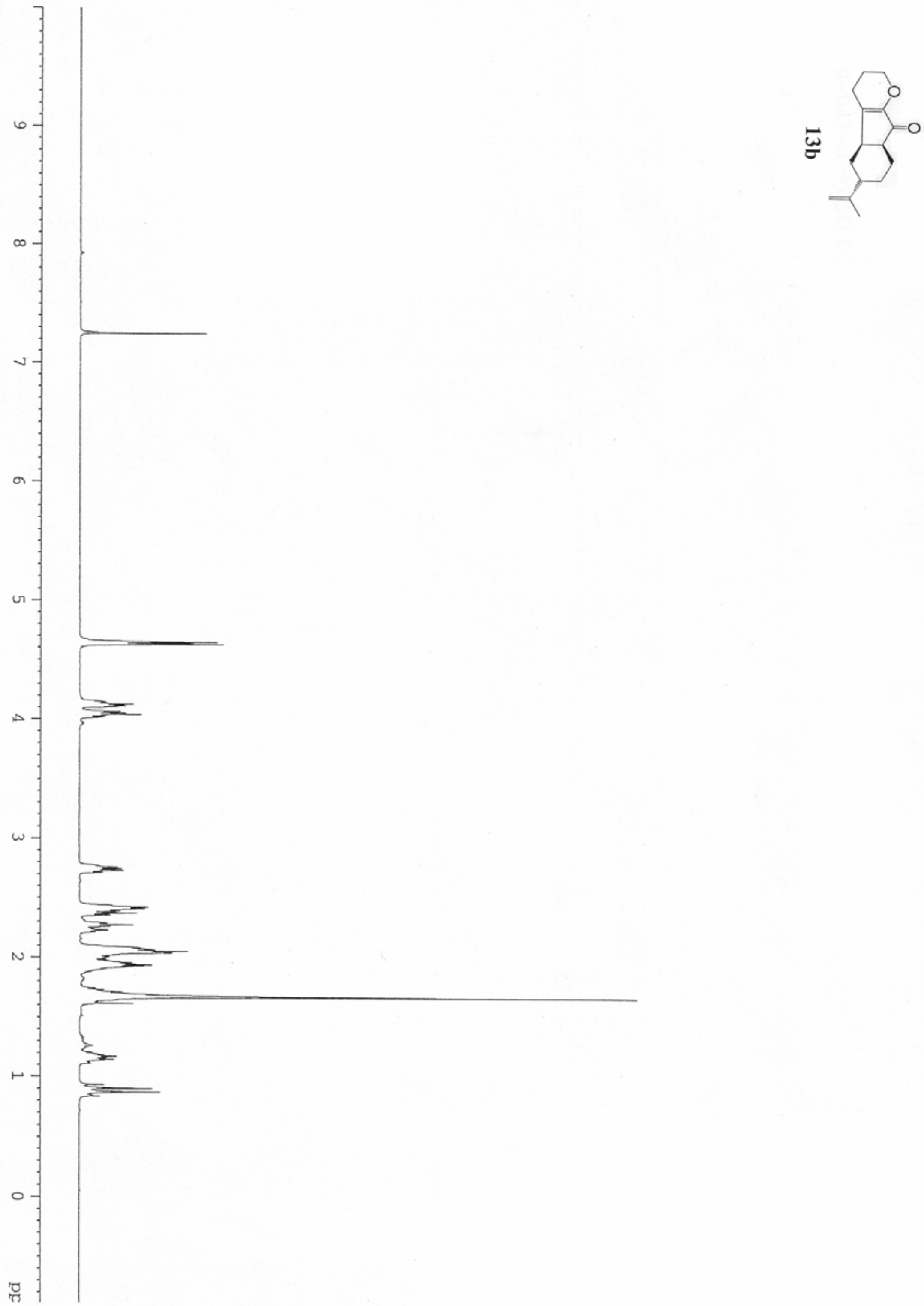
13b
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6
5
4
3
2
1
0
ppm

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$O_2C_{15}H_{16}$
Formula Weight	228.29
Crystal Color, Habit	colorless, blade
Crystal Dimensions	0.43 X 0.22 X 0.08 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 6.4685(7)Å b = 11.794(1) Å c = 15.938(2) Å β = 100.876(2)° V = 1194.1(2) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.270 g/cm^3
F_{000}	488.00
μ(MoKα)	0.83 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker SMART CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
$2\theta_{max}$	49.4°
No. of Reflections Measured	Total: 5115 Unique: 2090 (R_{int} = 0.041)
Corrections	Lorentz-polarization Absorption (Tmax = 0.98 Tmin = 0.52)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms

No. Observations (I>3.00σ(I))	1350
No. Variables	154
Reflection/Parameter Ratio	8.77
Residuals: R; Rw; Rall	0.050 ; 0.057; 0.079
Goodness of Fit Indicator	1.80
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.21 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.27 $e^-/Å^3$

Data File C:\HPCHEM\1\DATA\G\NAZ00026.D   Sample Name: 2-Sc-py-THF-rt

```
=====================================================================
Injection Date  : 4/7/03 11:50:50 AM            Seq. Line :   1
Sample Name     : 2-Sc-py-THF-rt                     Vial :  51
Acq. Operator   : G(Trauner)                          Inj :   1
Acq. Instrument : analytical HPLC             Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\1\METHODS\ST160.M
Last changed    : 3/11/03 4:11:47 PM by G(Trauner)
Analysis Method : C:\HPCHEM\1\METHODS\GRAD150S.M
Last changed    : 2/10/03 2:10:08 PM by Stefan
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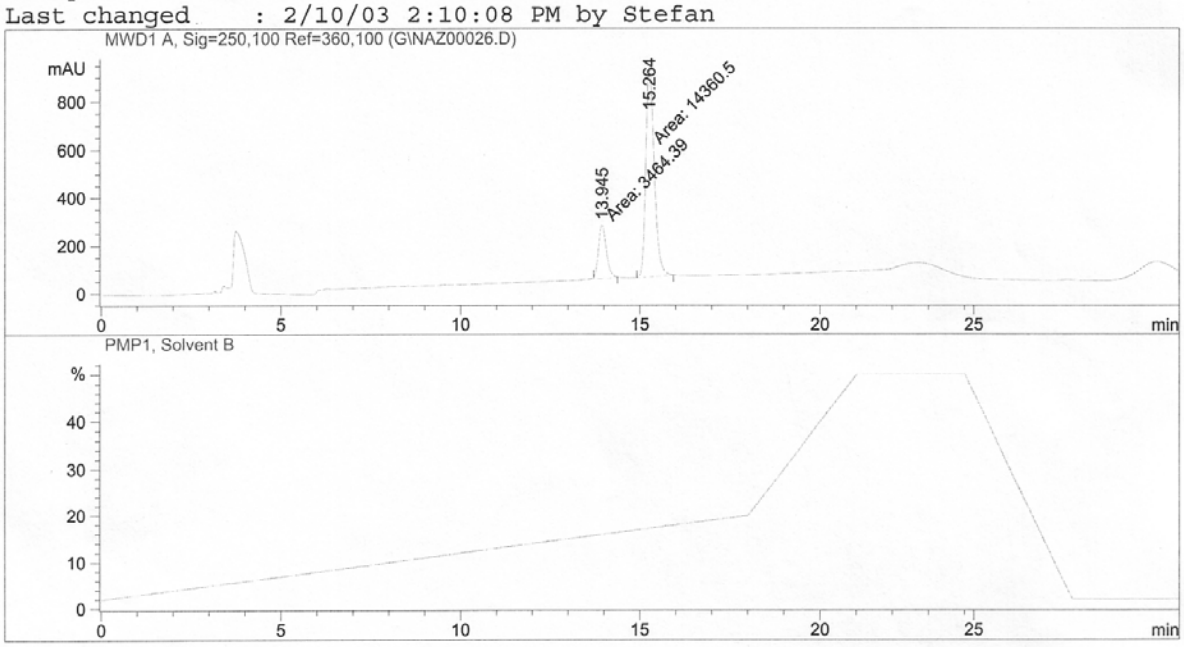


```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By           :      Signal
Multiplier          :      1.0000
Dilution            :      1.0000


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  13.945 MM T  0.2554 3464.39429  226.11496  19.4357
   2  15.264 MM T  0.2763 1.43605e4   866.36719  80.5643

Totals :                  1.78249e4  1092.48215
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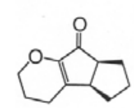

61% e.e.

```
 Results obtained with enhanced integrator!
=====================================================================
                       *** End of Report ***
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