

Supporting Information

Details on the purification and characterization data for compounds **1b-j** and **8a-c**; copies of ^1H NMR and ^{13}C NMR spectra for **1b-i** and **8a-c**.

(26 pages)

3-(Vinyloxy)-1,1'-biphenyl (1b): from column chromatography (CHCl₃/hexane 10:90), a colorless liquid: since this compound contains 12% of the 4-substituted isomer (coming from the commercially available starting material **3b**), its NMR and IR data are not described here; however copies of ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR spectra are provided below; HRMS (FAB) calcd for C₁₄H₁₃O (M + H)⁺ 197.0966, found 197.0966.

2-(Vinyloxy)-1,1'-biphenyl (1c): from column chromatography (CHCl₃/hexane 10:90), a colorless liquid: ¹H NMR (500 MHz, acetone-*d*₆) δ 4.34 (dd, *J* = 6.1, 1.5 Hz, 1H), 4.53 (dd, *J* = 13.7, 1.5 Hz, 1H), 6.70 (dd, *J* = 13.7, 6.1 Hz, 1H), 7.15 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.21 (dt, *J* = 1.1, 7.5 Hz, 1H), 7.32-7.43 (m, 5H), 7.50 (m, 2H); ¹³C NMR δ 94.5, 118.3, 124.0, 127.3, 128.2, 128.7, 129.4, 131.2, 132.6, 137.8, 149.2, 153.5; IR (neat) 3040, 3010, 1630, 1570, 1490, 1470, 1420, 1245, 1210, 1140, 945, 745, 725, 685 cm⁻¹; HRMS (FAB) calcd for C₁₄H₁₃O (M + H)⁺ 197.0966, found 197.0966.

1-(Hexyloxy)-4-(vinyloxy)benzene (1d): from column chromatography (CHCl₃/hexane 20:80), a colorless liquid: ¹H NMR (500 MHz, acetone-*d*₆) δ 0.89 (br t, 3H), 1.34 (m, 4H), 1.46 (m, 2H), 1.74 (m, 2H), 3.94 (t, *J* = 6.5, 2H), 4.30 (dd, *J* = 6.1, 1.2 Hz, 1H), 4.55 (dd, *J* = 13.7, 1.2 Hz, 1H), 6.69 (dd, *J* = 13.7, 6.1 Hz, 1H), 6.92 (m, 4H); ¹³C NMR δ 14.0, 22.6, 25.7, 29.3, 31.6, 68.4, 93.4, 115.2, 118.5, 149.5, 150.3, 155.2; IR (neat) 3030, 2940, 2910, 2840, 1630, 1495, 1460, 1375, 1210, 1140, 950, 820 cm⁻¹; HRMS (FAB) calcd for C₁₄H₂₁O₂ (M + H)⁺ 221.1543, found 221.1542.

1-Bromo-4-(vinyloxy)benzene (1e): from column chromatography (CHCl₃/hexane 5:95), a colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 4.50 (dd, *J* = 6.1, 1.8 Hz, 1H), 4.80 (dd, *J* = 13.7, 1.8 Hz, 1H), 6.61 (dd, *J* = 13.7, 6.1 Hz, 1H), 6.91 (m, 2H), 7.44 (m, 2H); ¹³C NMR δ 95.9, 115.6, 118.8, 132.5, 147.7, 155.8; IR (neat) 3050, 1635, 1575, 1475, 1230, 1160, 1140, 1060, 1000, 950, 815 cm⁻¹.

4-(Vinyloxy)benzonitrile (1f): from column chromatography (EtOAc/hexane 5:95), a colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 4.67 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.97 (dd, *J* =

13.6, 2.0 Hz, 1H), 6.66 (dd, $J = 13.6, 6.0$ Hz, 1H), 7.09 (m, 2H), 7.65 (m, 2H); ^{13}C NMR δ 98.5, 106.2, 117.0, 118.7, 134.1, 146.0, 159.9; IR (neat) 3080, 3050, 2200, 1635, 1590, 1490, 1300, 1290, 1235, 1160, 1125, 945, 825 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_9\text{H}_8\text{NO}$ ($\text{M} + \text{H}$) $^+$ 146.0606, found 146.0606.

1-Nitro-4-(vinylloxy)benzene (1g): from column chromatography ($\text{CHCl}_3/\text{hexane}$ 30:70 $\rightarrow$ 35:65 $\rightarrow$ 40:60), colorless crystals: ^1H NMR (400 MHz, CDCl_3) δ 4.72 (dd, $J = 6.0, 2.0$ Hz, 1H), 5.02 (dd, $J = 13.6, 2.0$ Hz, 1H), 6.70 (dd, $J = 13.6, 6.0$ Hz, 1H), 7.10 (m, 2H), 8.26 (m, 2H); ^{13}C NMR δ 99.1, 116.3, 125.8, 142.9, 145.8, 161.5; IR (KBr) 3090, 3060, 1640, 1600, 1580, 1500, 1480, 1330, 1230, 1160, 1125, 1100, 945, 935, 870, 850, 840, 740, 675, 625 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_8\text{H}_8\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 166.0504, found 166.0504.

Methyl 4-(vinylloxy)benzoate (1h): from column chromatography ($\text{EtOAc}/\text{hexane}$ 10:90), colorless crystals: ^1H NMR (500 MHz, $\text{acetone-}d_6$) δ 3.85 (s, 3H), 4.59 (dd, $J = 6.0, 1.6$ Hz, 1H), 4.86 (dd, $J = 13.5, 1.6$ Hz, 1H), 6.90 (dd, $J = 13.5, 6.0$ Hz, 1H), 7.14 (m, 2H), 8.01 (m, 2H); ^{13}C NMR δ 51.9, 97.2, 116.0, 124.6, 131.6, 146.6, 160.3, 166.4; IR (neat, melted crystals) 3100, 3050, 2980, 2940, 1710, 1635, 1595, 1495, 1425, 1300, 1270, 1235, 1155, 1135, 1100, 840, 755 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 179.0712, found 179.0708.

***N*-[4-(Vinylloxy)phenyl]acetamide (1i):** from column chromatography ($\text{EtOAc}/\text{hexane}$ 70:30), a white solid: ^1H NMR (400 MHz, CDCl_3) δ 2.19 (s, 3H), 4.43 (dd, $J = 6.1, 1.7$ Hz, 1H), 4.74 (dd, $J = 13.7, 1.7$ Hz, 1H), 6.62 (dd, $J = 13.7, 6.1$ Hz, 1H), 6.98 (m, 2H), 7.26 (br s, 1H), 7.46 (m, 2H); ^{13}C NMR δ 24.0, 94.8, 117.4, 122.0, 133.5, 148.4, 153.2, 169.3; IR (KBr) 3260, 3190, 3130, 3060, 1650, 1600, 1550, 1495, 1305, 1235, 1210, 1165, 1145, 960, 940, 830 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_{12}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 178.0868, found 178.0868.

Methyl *N*-(*tert*-butoxycarbonyl)-*O*-vinyl-*L*-tyrosinate (1j): from column chromatography ($\text{EtOAc}/\text{hexane}$ 15:85), a white solid: ^1H NMR (500 MHz, $\text{acetone-}d_6$) δ 1.34

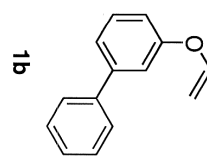
(s, 9H), 2.94 (dd, $J = 13.9, 8.9$ Hz, 1H), 3.09 (dd, $J = 13.9, 5.3$ Hz, 1H), 3.66 (s, 3H), 4.36 (m, 1H), 4.40 (dd, $J = 6.1, 1.3$ Hz, 1H), 4.67 (dd, $J = 13.6, 1.3$ Hz, 1H), 6.14 (br d, 1H), 6.76 (dd, $J = 13.6, 6.1$ Hz, 1H), 6.96 (d, $J = 8.4, 2H$), 7.24 (d, $J = 8.4, 2H$); ^{13}C NMR δ 28.2, 37.4, 52.1, 54.4, 79.7, 95.0, 117.0, 130.4, 130.7, 148.0, 155.0, 155.7, 172.2; IR (KBr) 3370, 3050, 3030, 2990, 2970, 2960, 2940, 2910, 1735, 1700, 1635, 1595, 1495, 1430, 1355, 1225, 1160, 1135, 1050, 1005, 955, 825 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_5$ ($\text{M} + \text{H}$) $^{+}$ 322.1654, found 322.1654. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.50; H, 7.58, N, 4.32.

1-Vinylpyridin-4(1H)-one (8a): from column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{NH}_4\text{OH}$ 90:10:1), a colorless liquid: ^1H NMR (400 MHz, CDCl_3) δ 4.97 (dd, $J = 8.8, 2.8$ Hz, 1H), 5.22 (dd, $J = 15.5, 2.8$ Hz, 1H), 6.40 (m, 2H), 6.66 (dd, $J = 15.5, 8.8$ Hz, 1H), 7.54 (m, 2H); ^{13}C NMR δ 101.7, 118.6, 135.4, 136.2, 179.5; IR (neat) 3370, 1625, 1550, 1395, 1355, 1215, 1180, 845 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_7\text{H}_8\text{NO}$ ($\text{M} + \text{H}$) $^{+}$ 122.0606, found 122.0606.

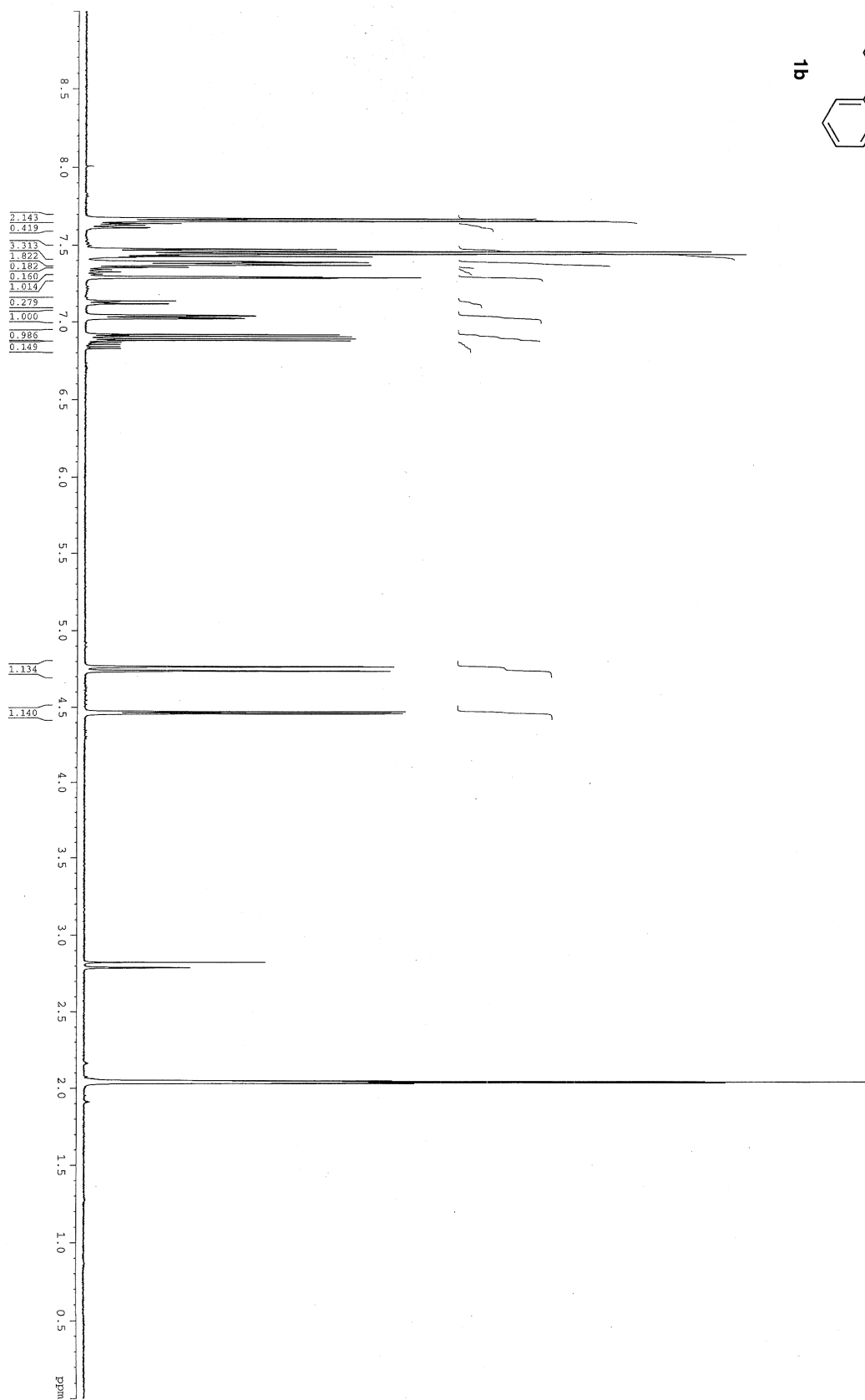
1-Vinylquinolin-2(1H)-one (8b): from column chromatography (EtOAc/hexane 70:30), a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 5.64 (d, $J = 15.9$ Hz, 1H), 5.82 (d, $J = 8.3$ Hz, 1H), 6.72 (d, $J = 9.5$ Hz, 1H), 6.75 (dd, $J = 15.9, 8.3$ Hz, 1H), 7.25 (m, 1H), 7.52 (m, 1H), 7.58 (m, 2H), ; 7.72 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR δ 115.4, 118.5, 120.4, 121.6, 122.5, 128.6, 130.3, 130.6, 139.1, 139.6, 161.7; IR (neat) 3460, 3050, 3040, 3020, 1645, 1580, 1550, 1480, 1440, 1390, 1285, 1235, 1210, 1155, 1130, 820, 740 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{10}\text{NO}$ ($\text{M} + \text{H}$) $^{+}$ 172.0762, found 172.0762.

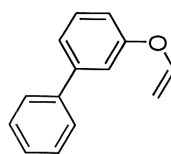
6-(Vinyloxy)quinoline (8c): from column chromatography (EtOAc/hexane 50:50), a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 4.58 (dd, $J = 6.0, 1.7$ Hz, 1H), 4.91 (dd, $J = 13.7, 1.7$ Hz, 1H), 6.77 (dd, $J = 13.7, 6.0$ Hz, 1H), 7.27 (d, $J = 2.7$ Hz, 1H), 7.38 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.46 (dd, $J = 9.2, 2.7$ Hz, 1H), 8.05-8.09 (m, 2H), 8.83 (m, 1H); ^{13}C NMR δ 96.6, 110.7, 121.5, 122.3, 128.9, 131.2, 135.1, 145.0, 147.4, 148.9, 154.7; IR (neat) 3360, 3060,

3040, 3010, 1630, 1605, 1585, 1560, 1490, 1450, 1365, 1315, 1245, 1210, 1155, 1130, 1100, 970, 930, 840, 820 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{10}\text{NO}$ ($\text{M} + \text{H}$)⁺ 172.0762, found 172.0762.



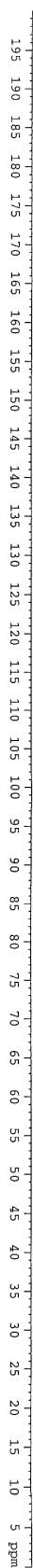
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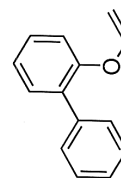




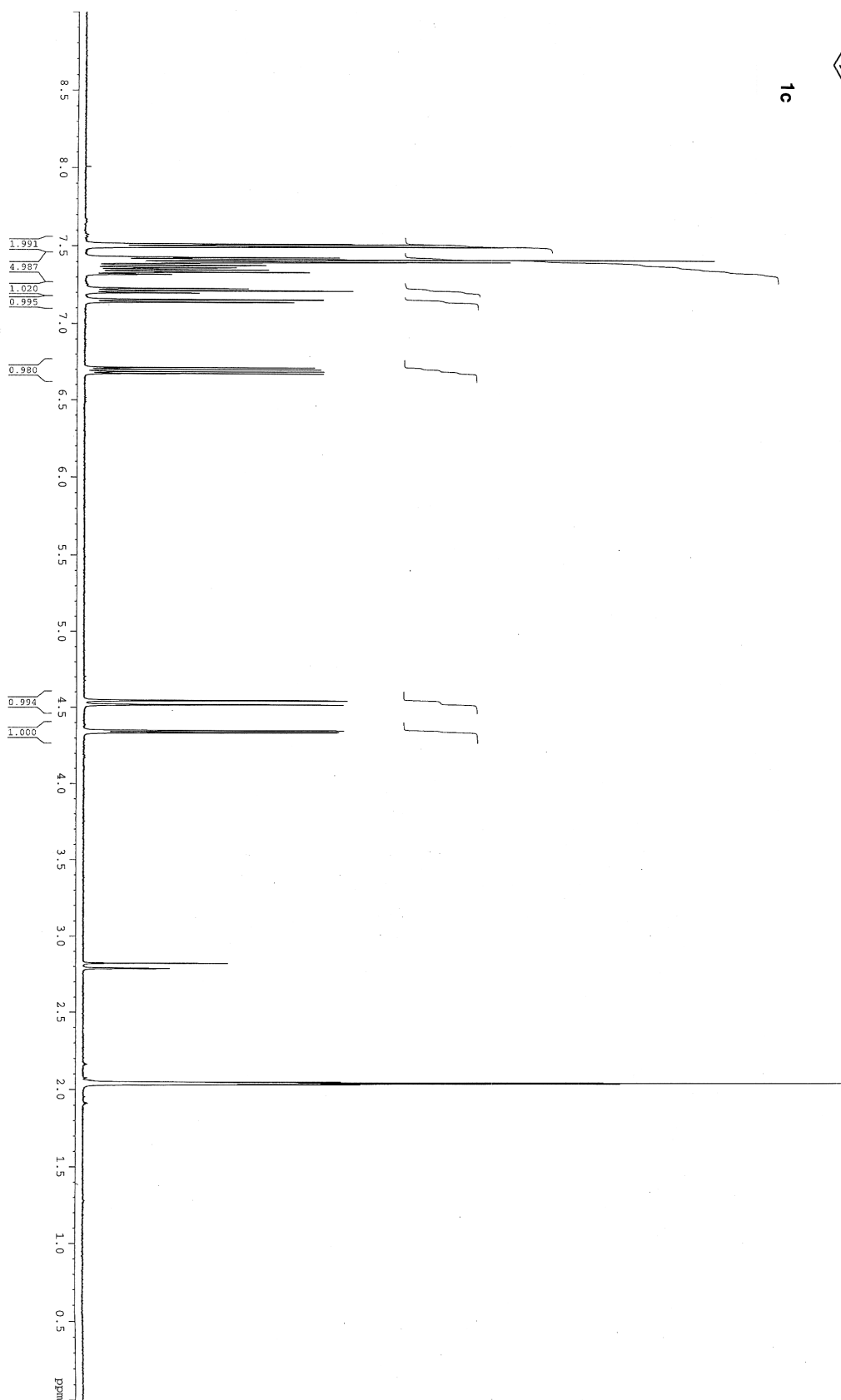
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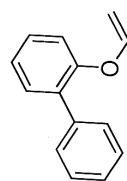
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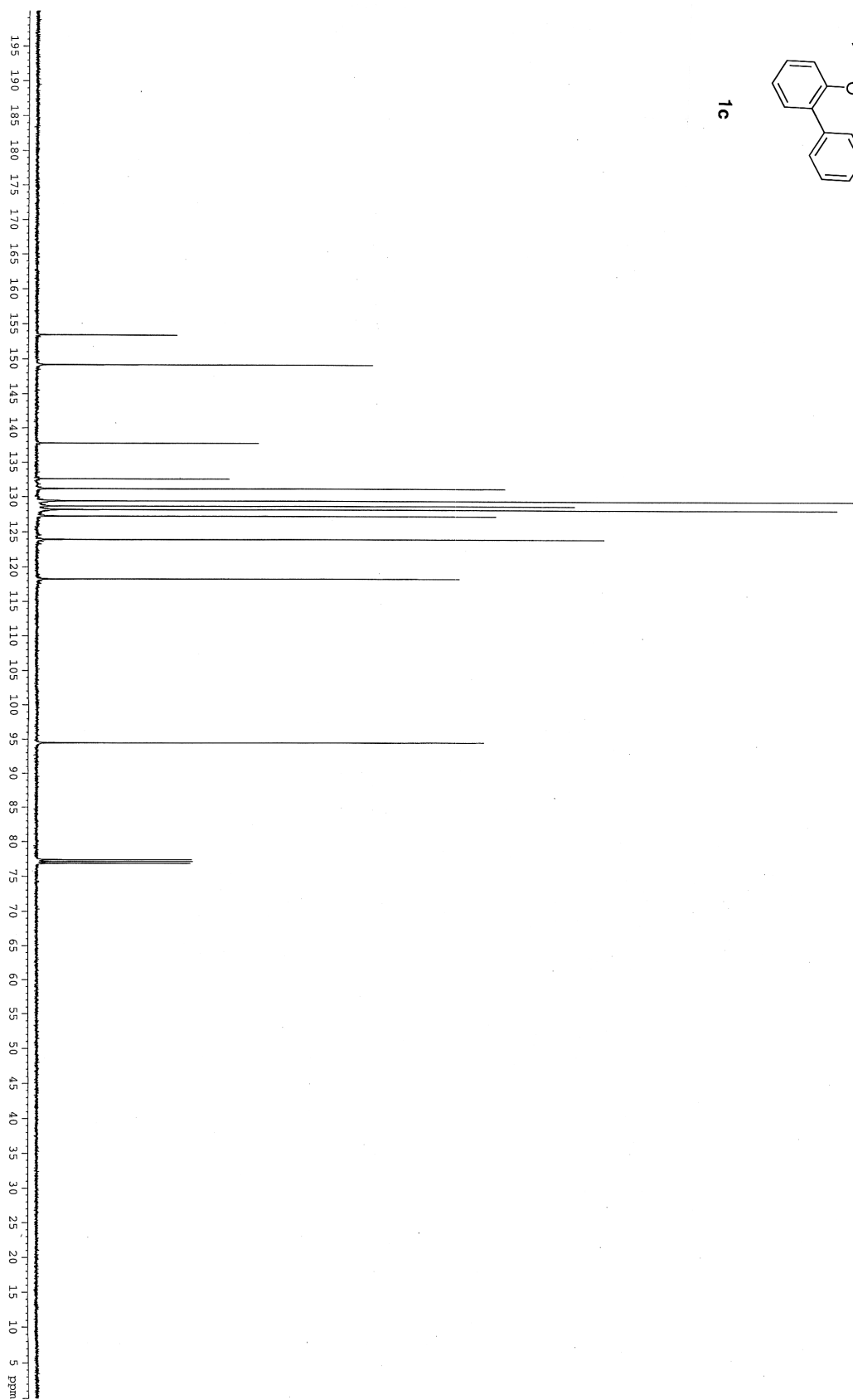


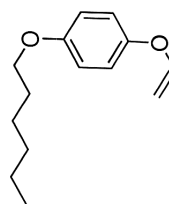
1c



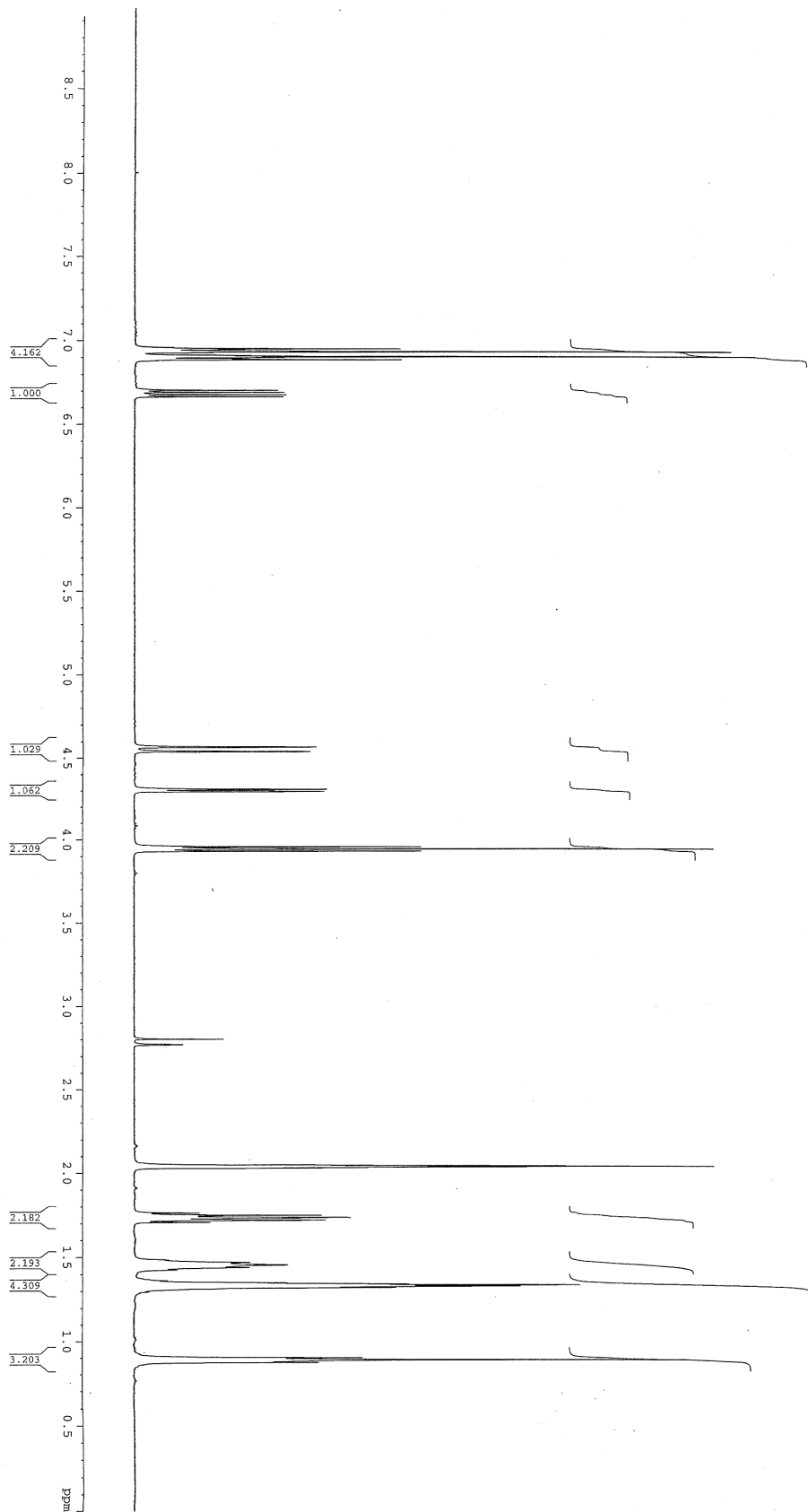


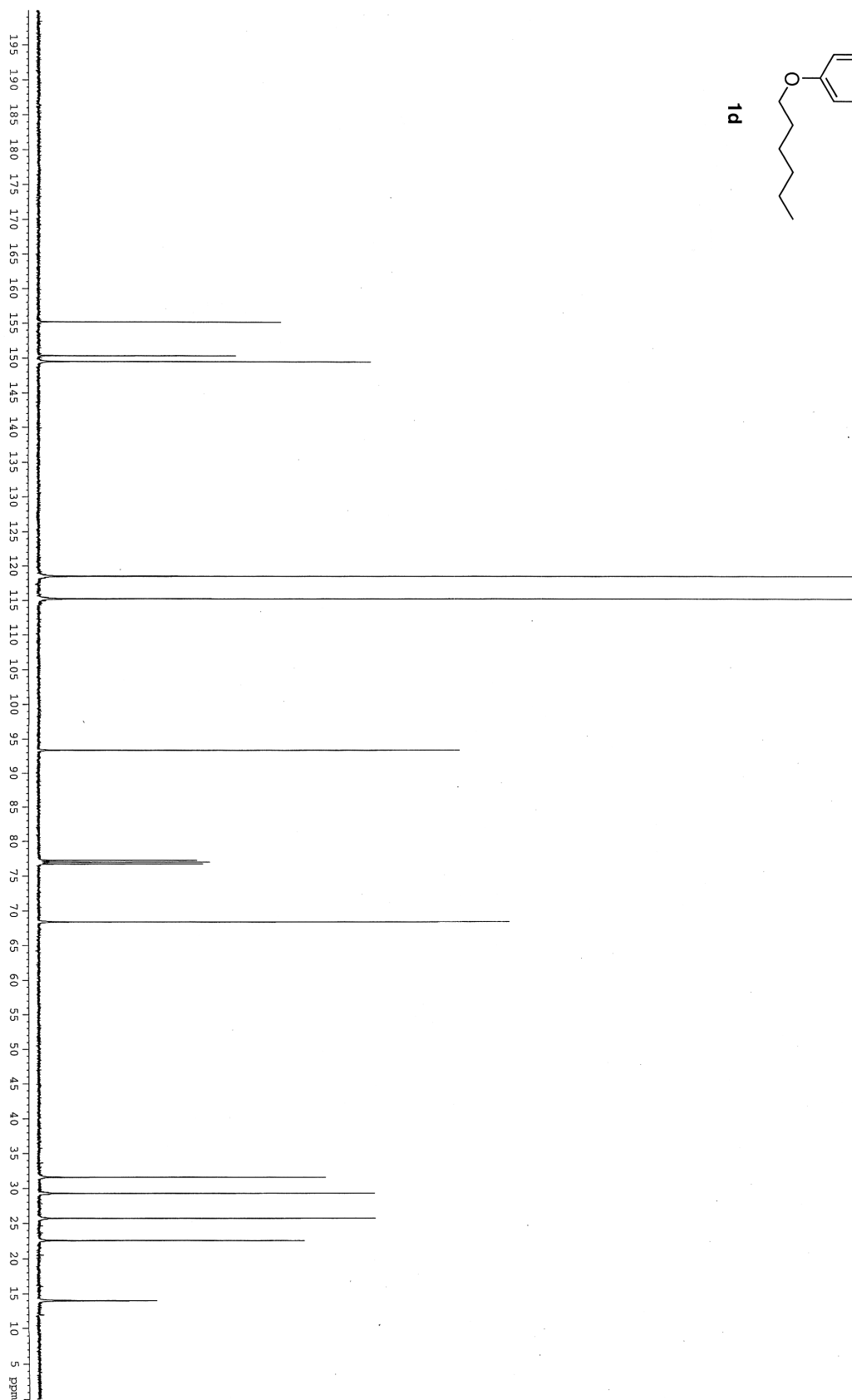
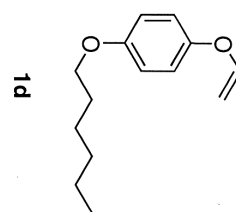
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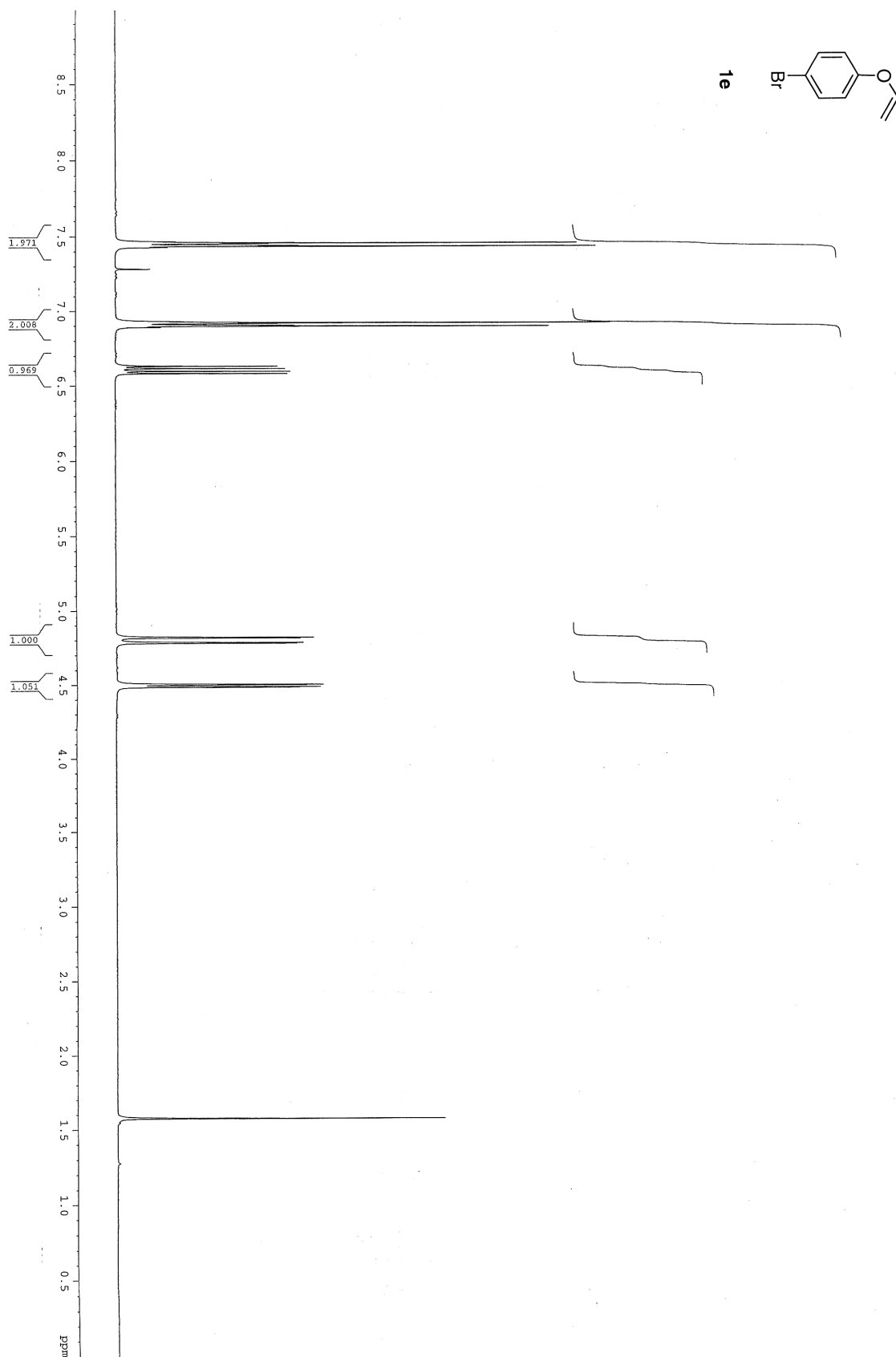


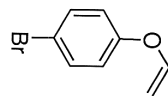


1d

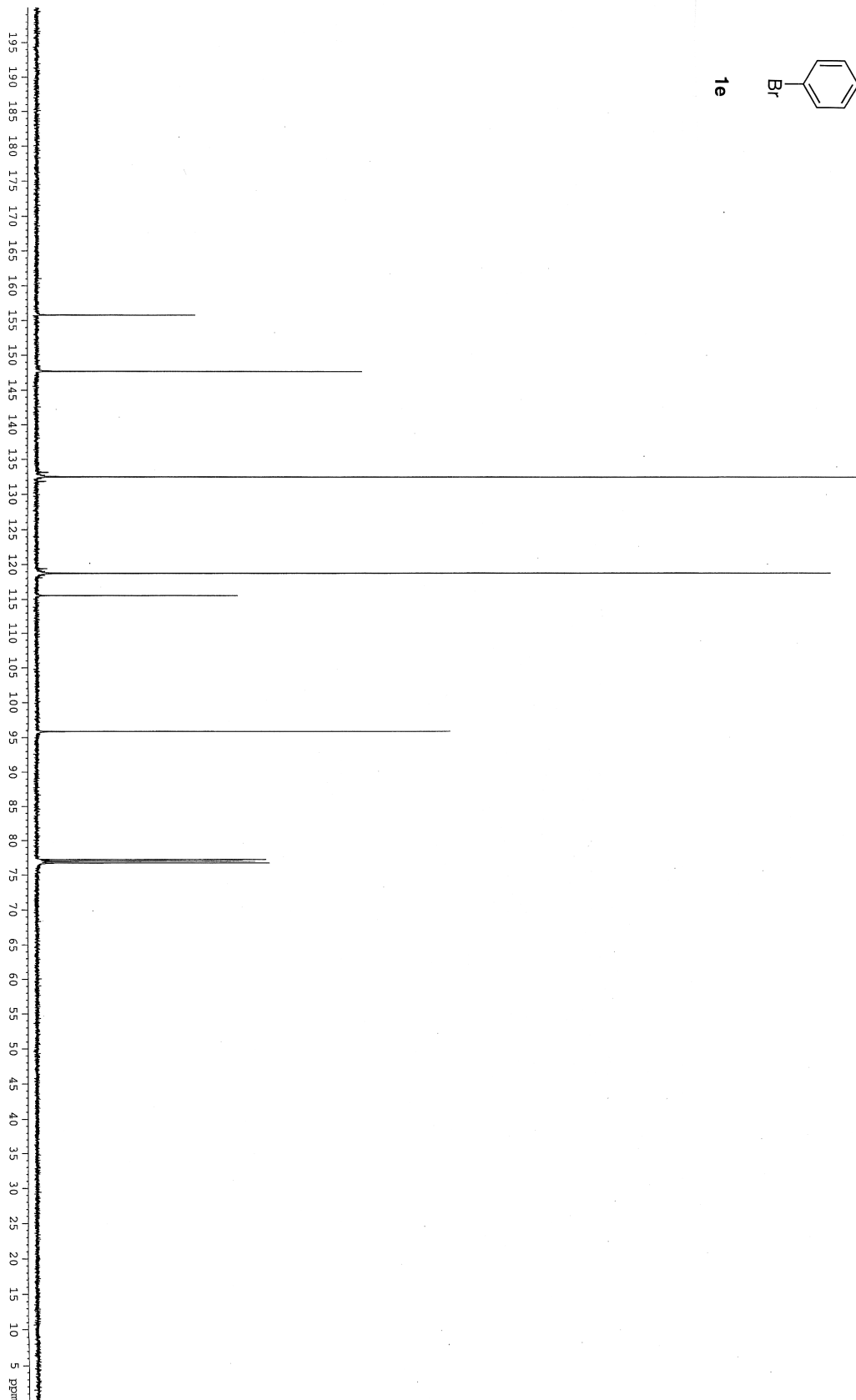


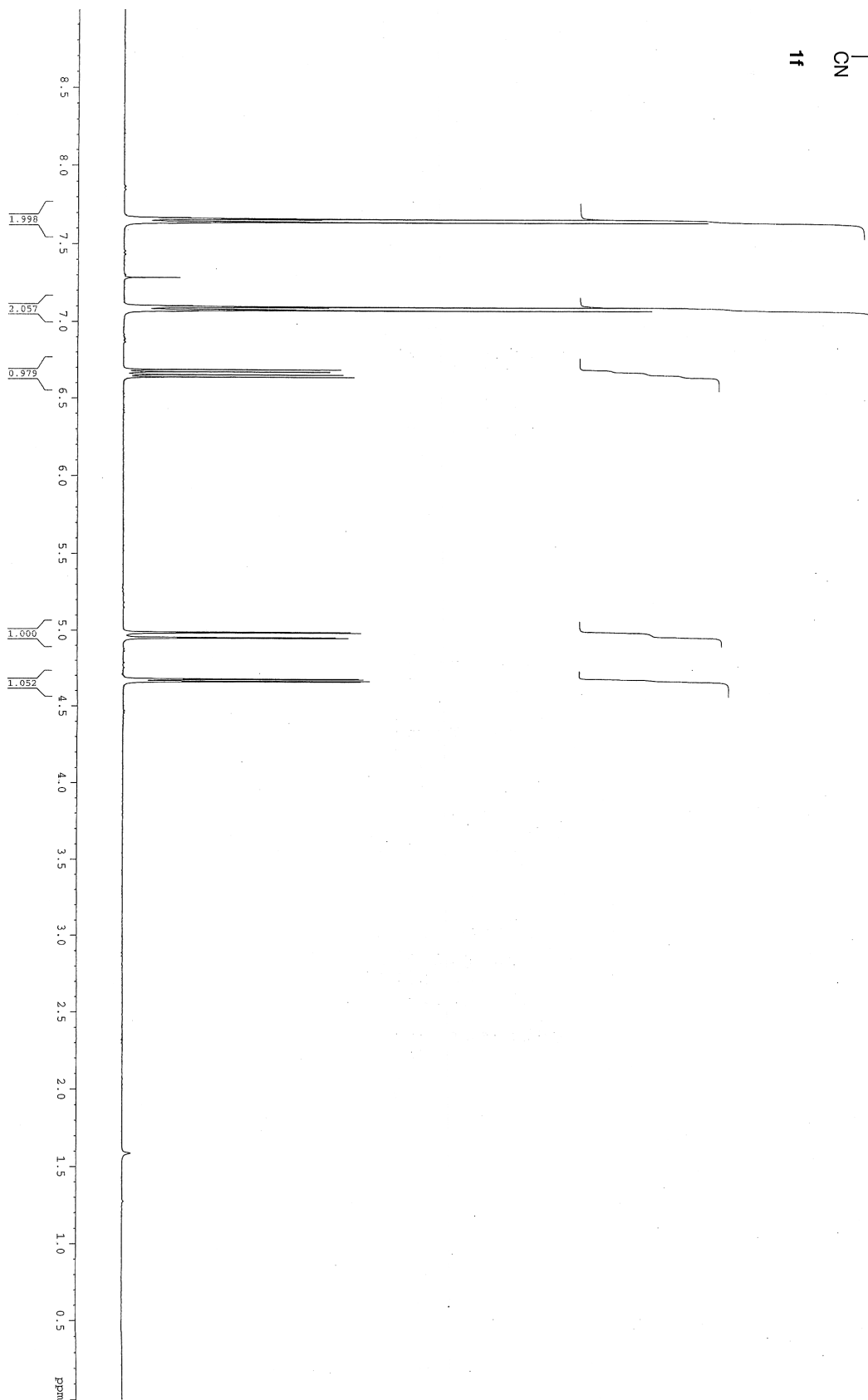
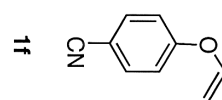


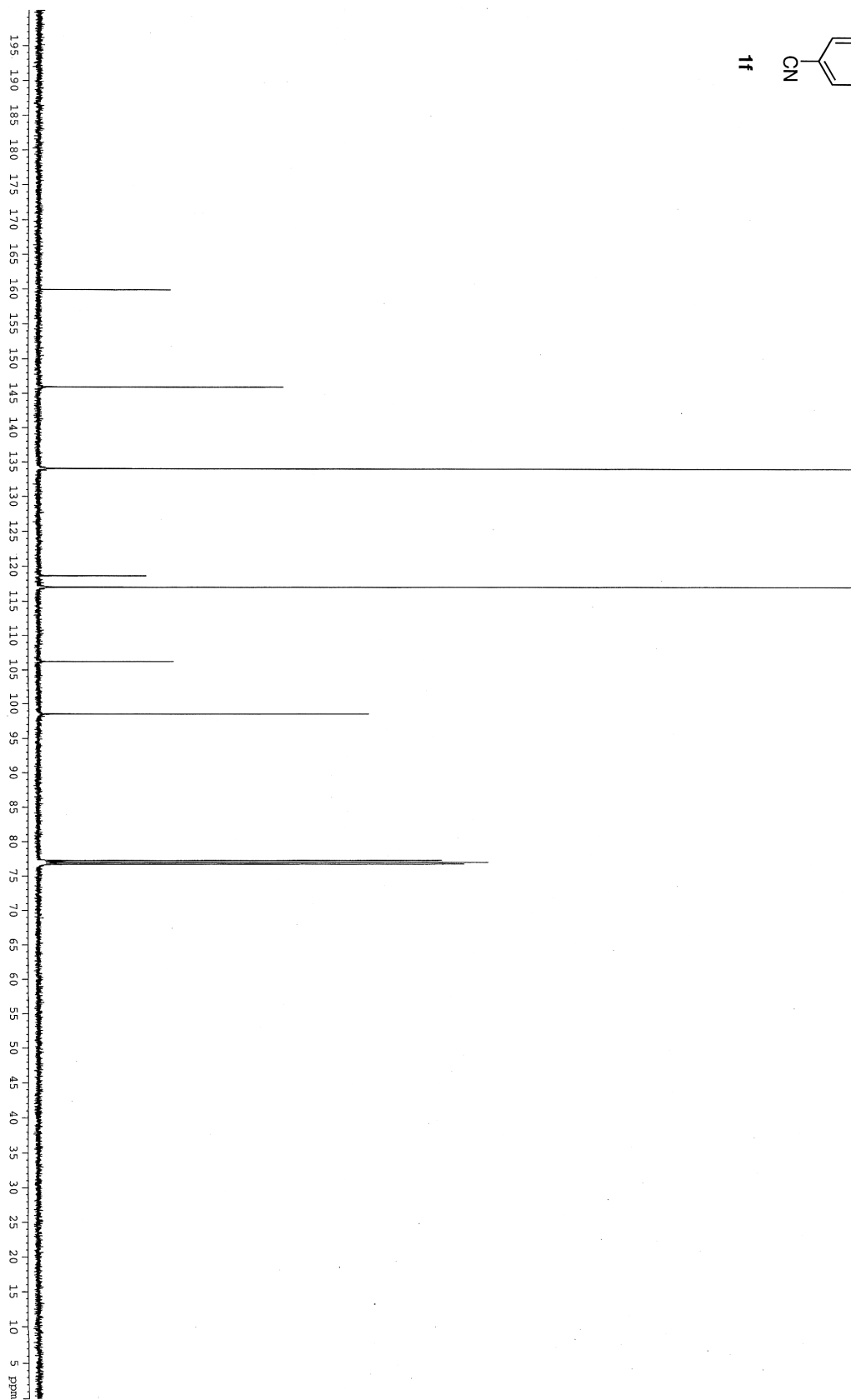
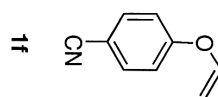


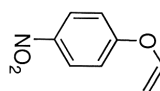


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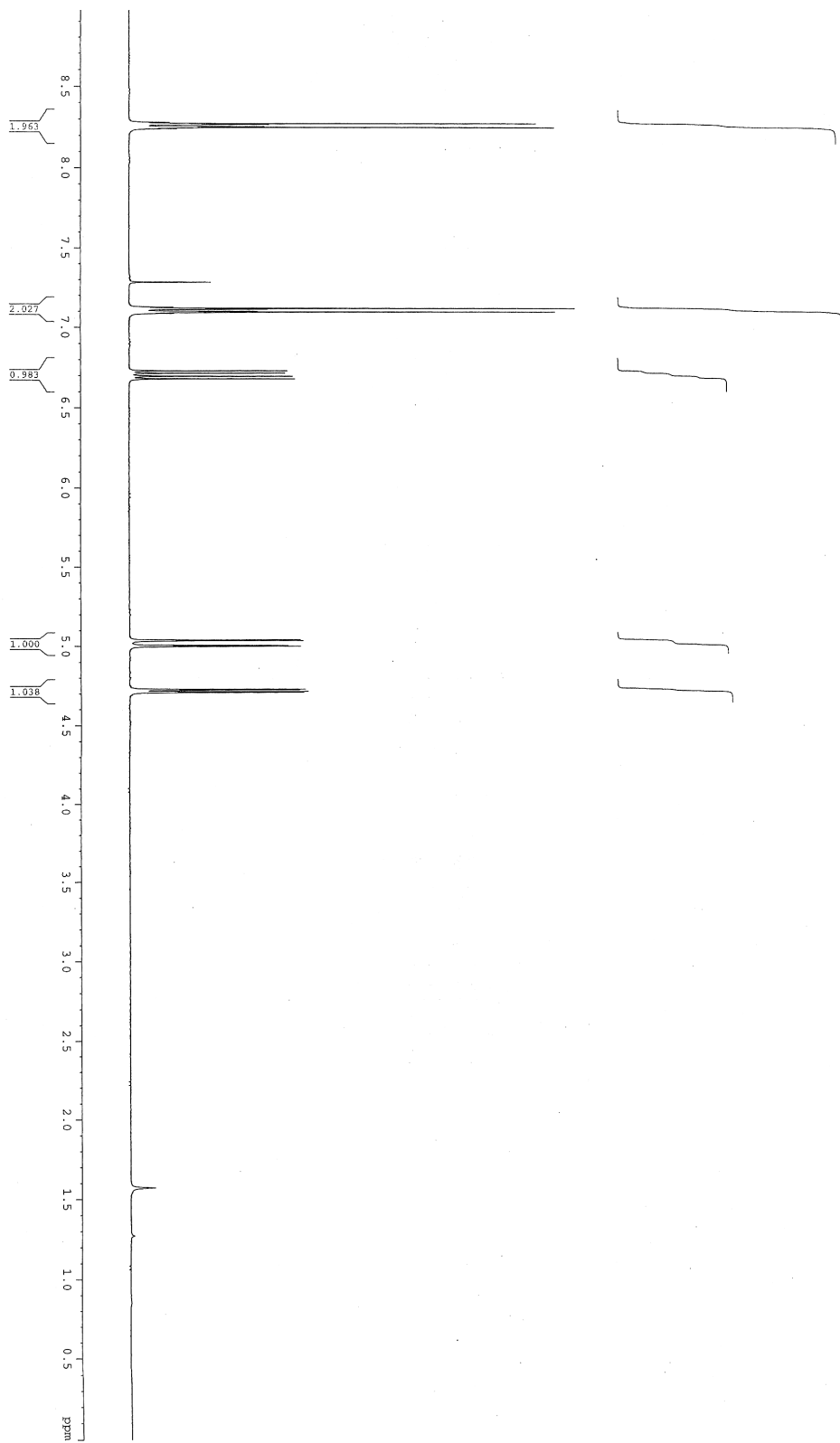


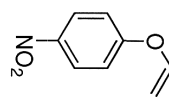




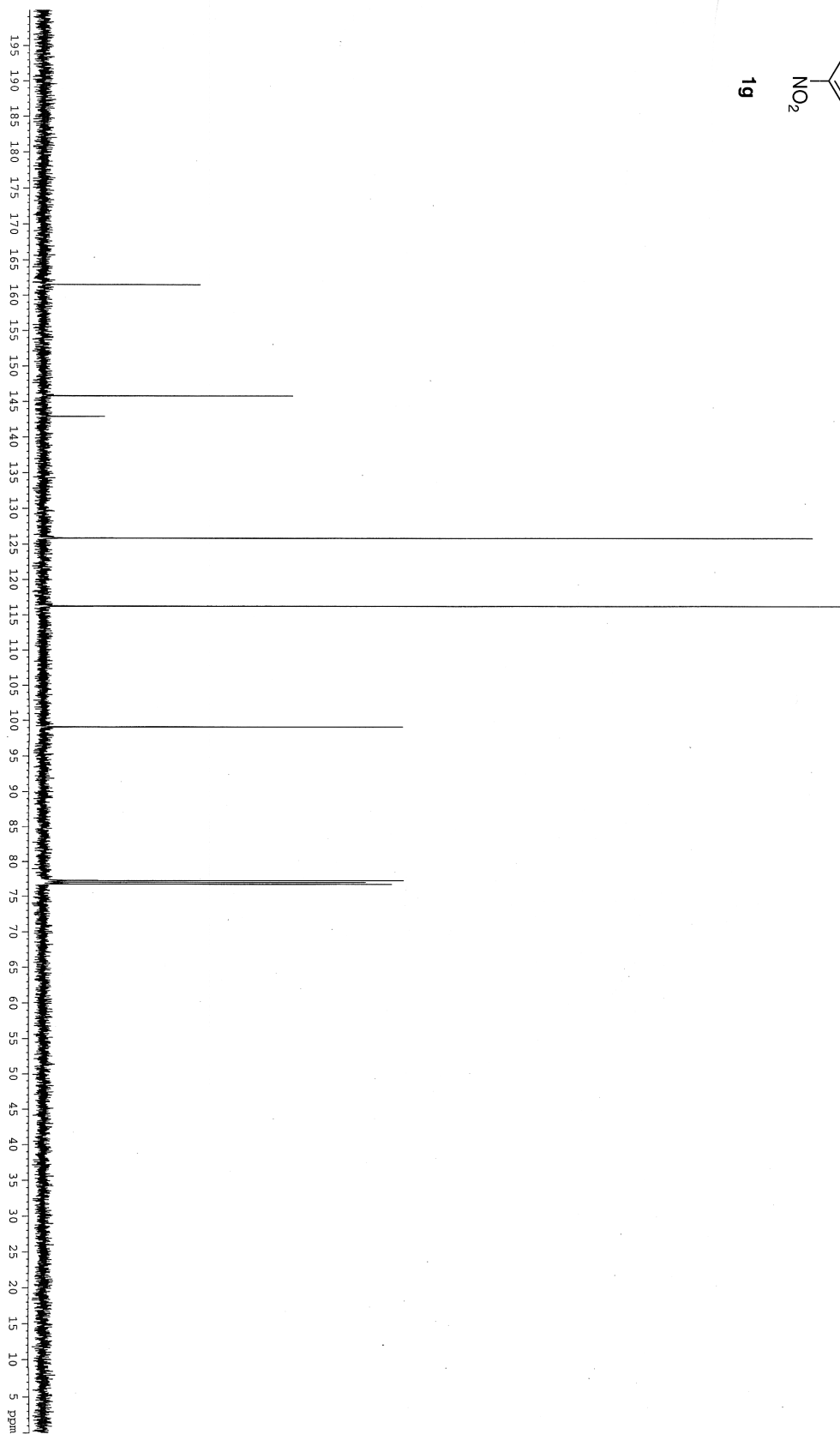


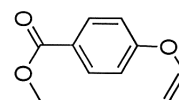
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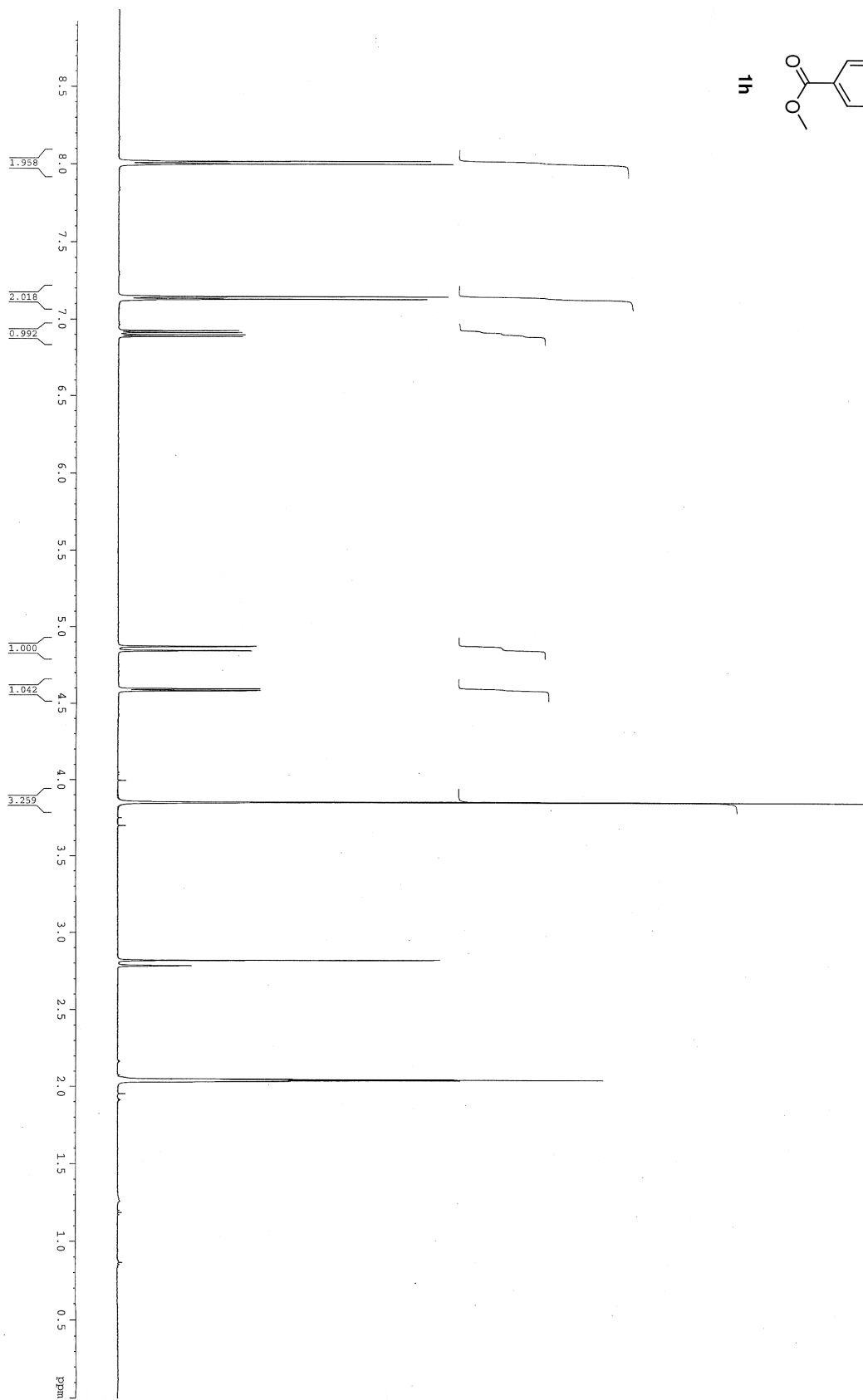


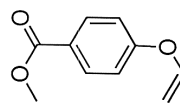
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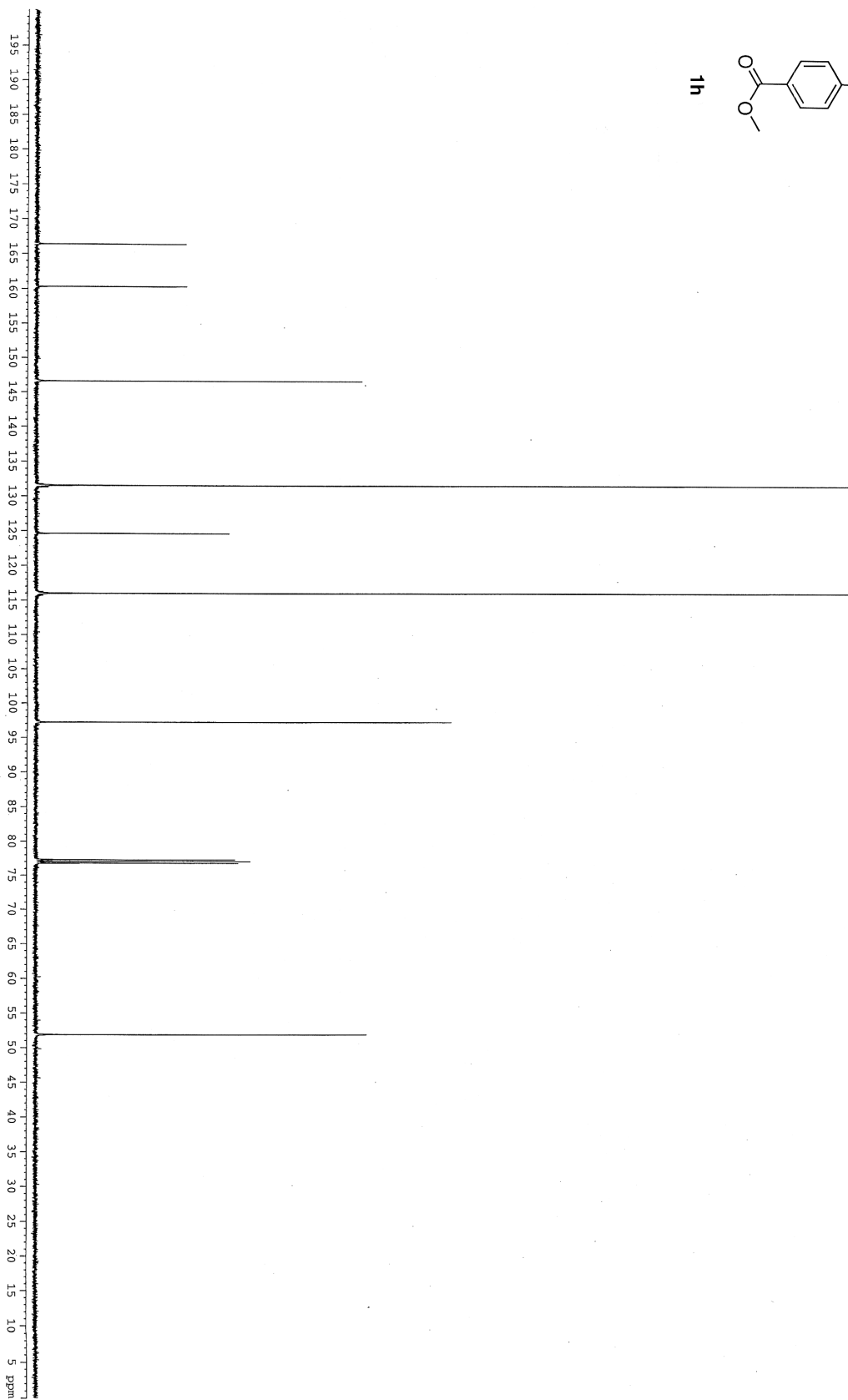


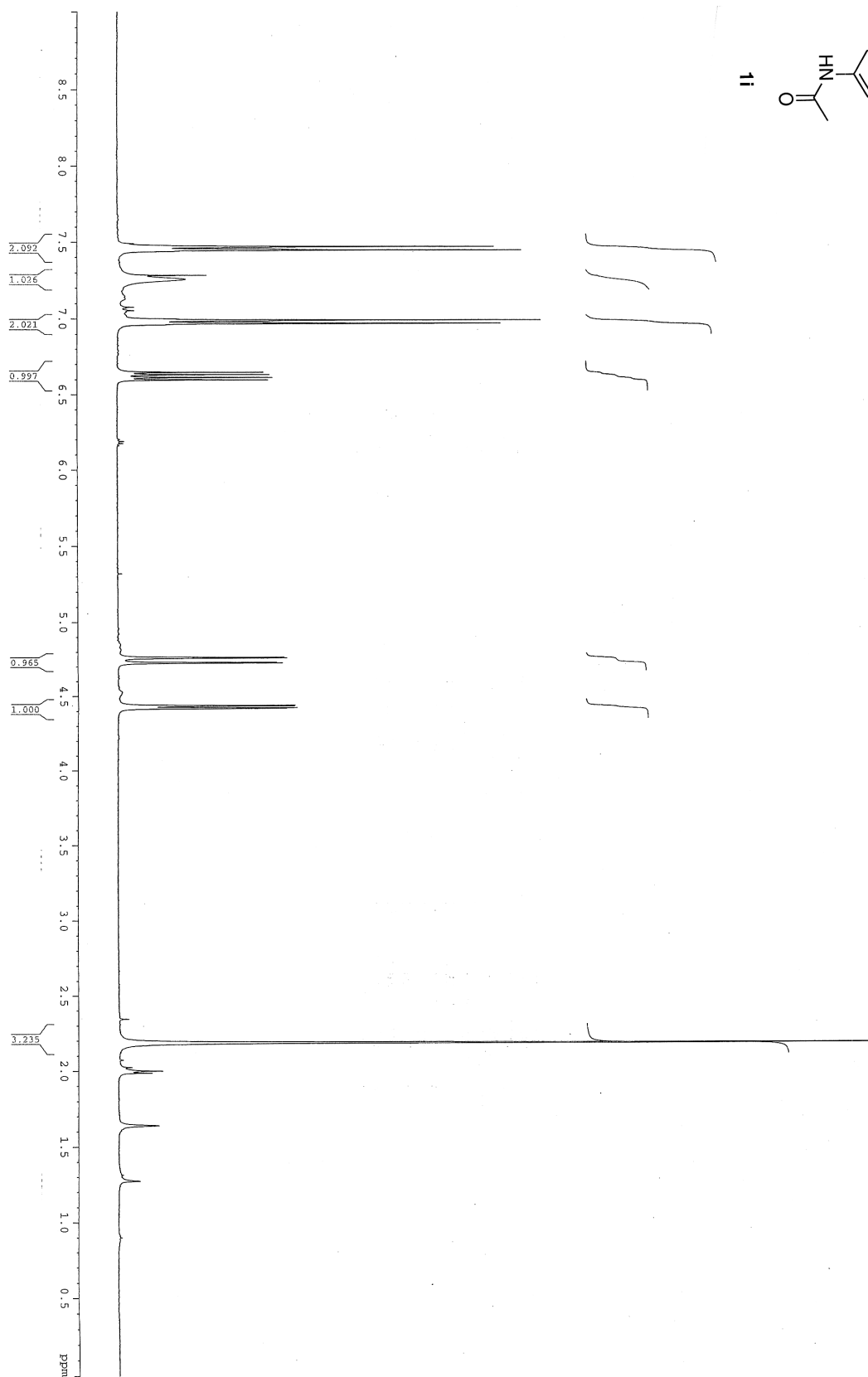
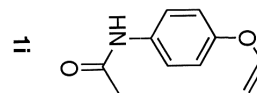
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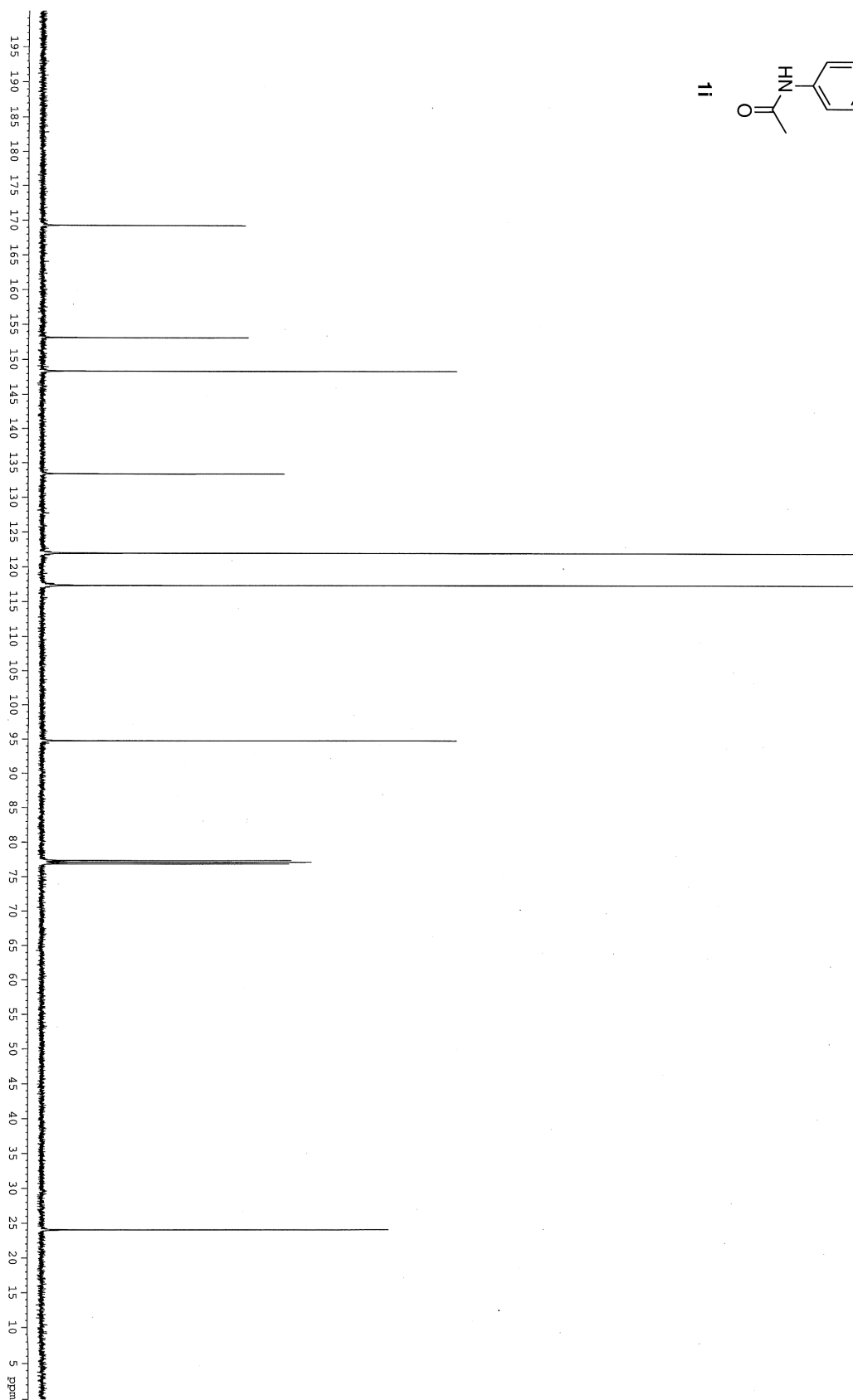
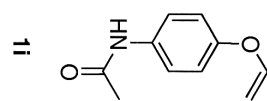


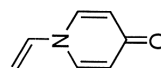


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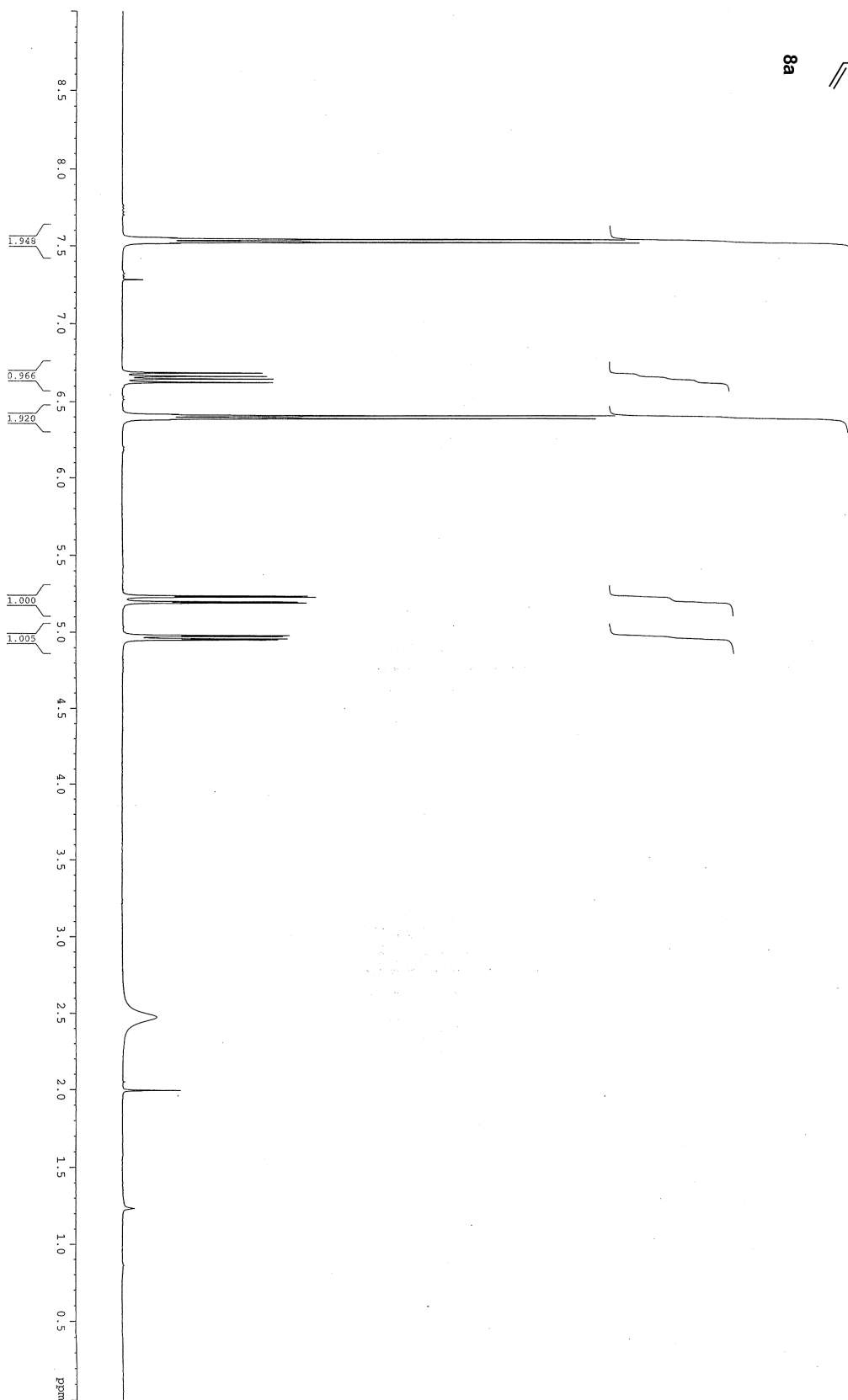


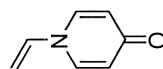




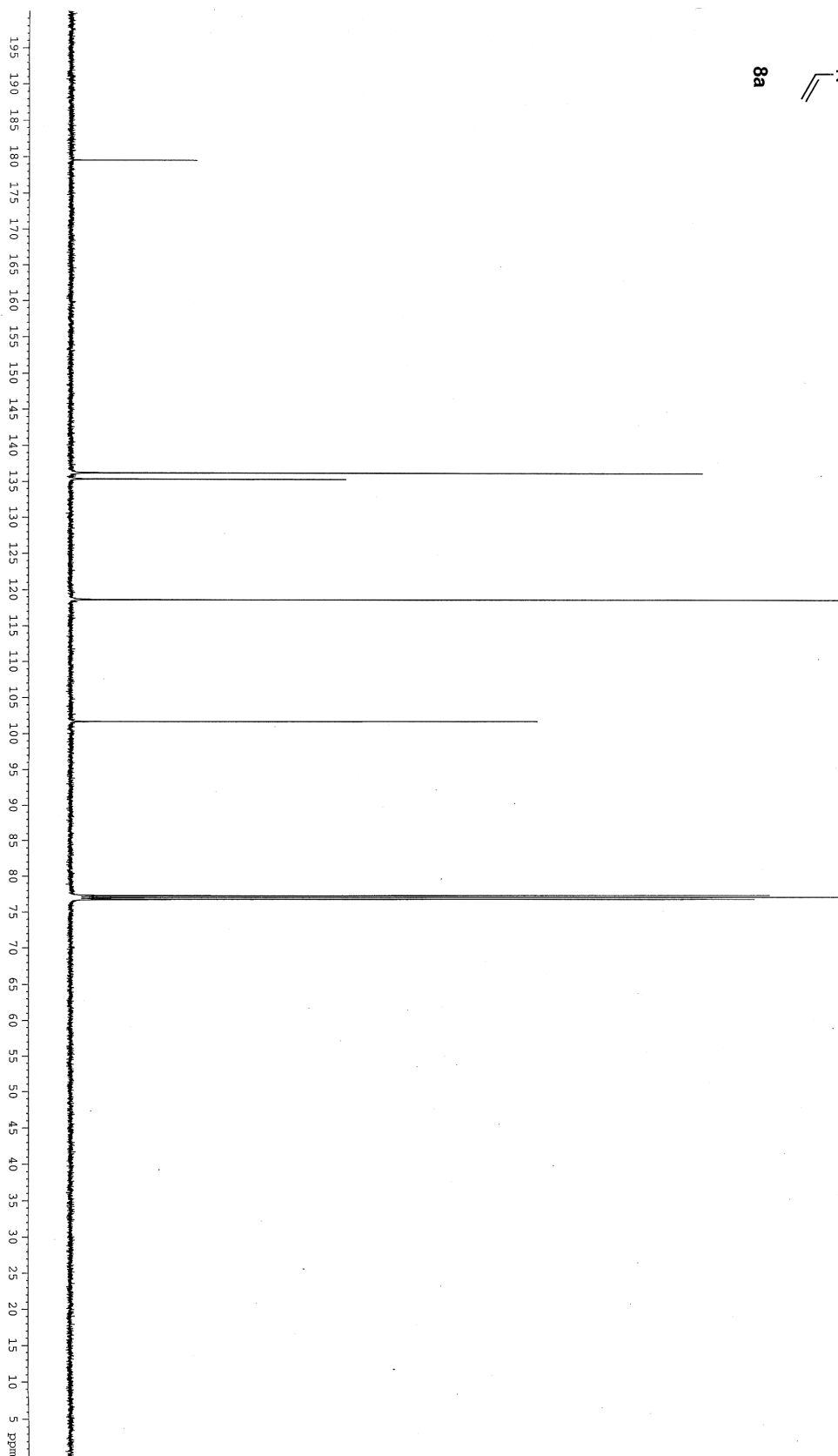


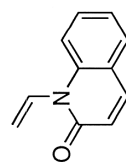
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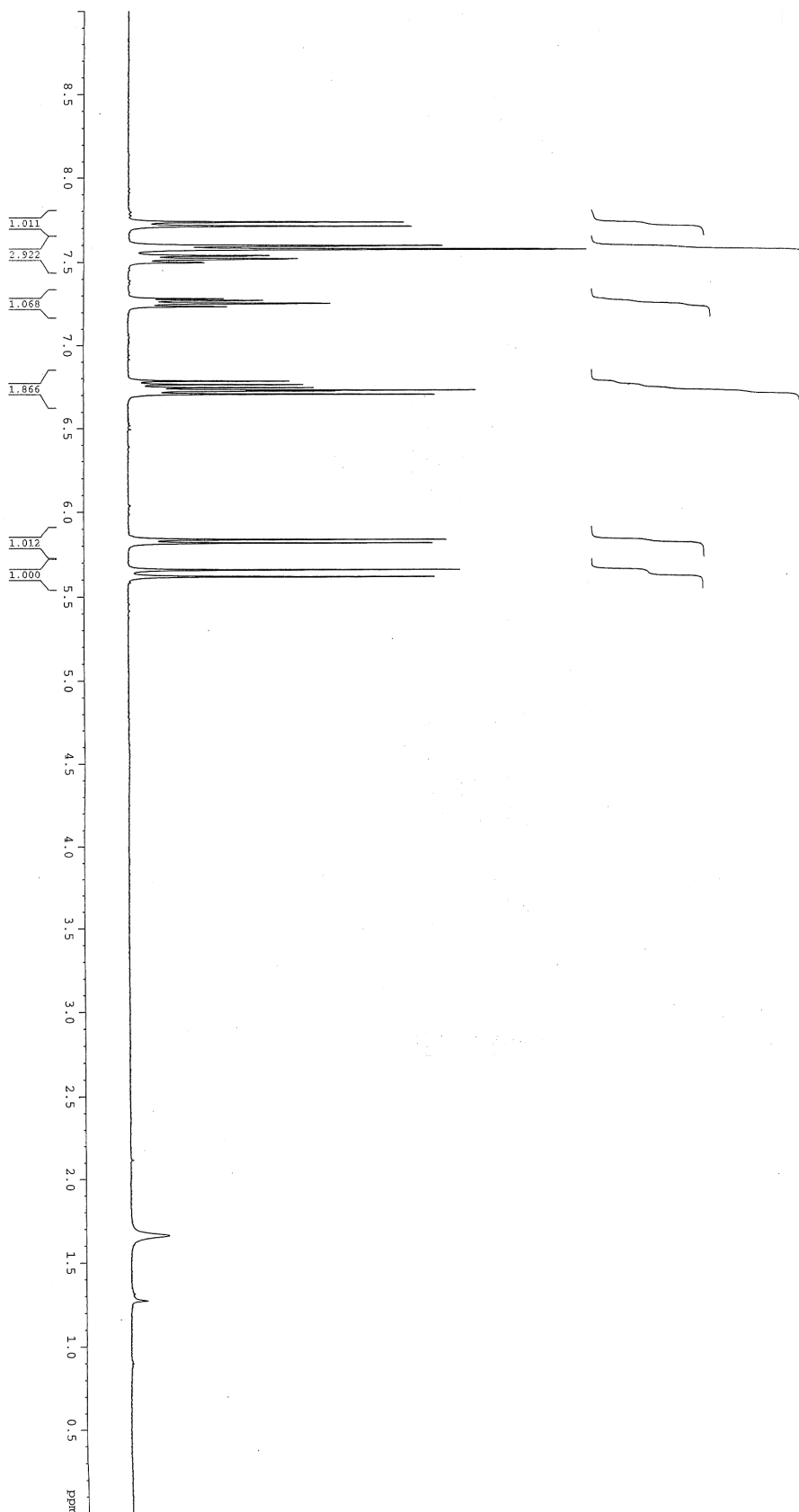


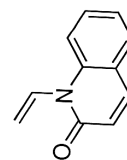
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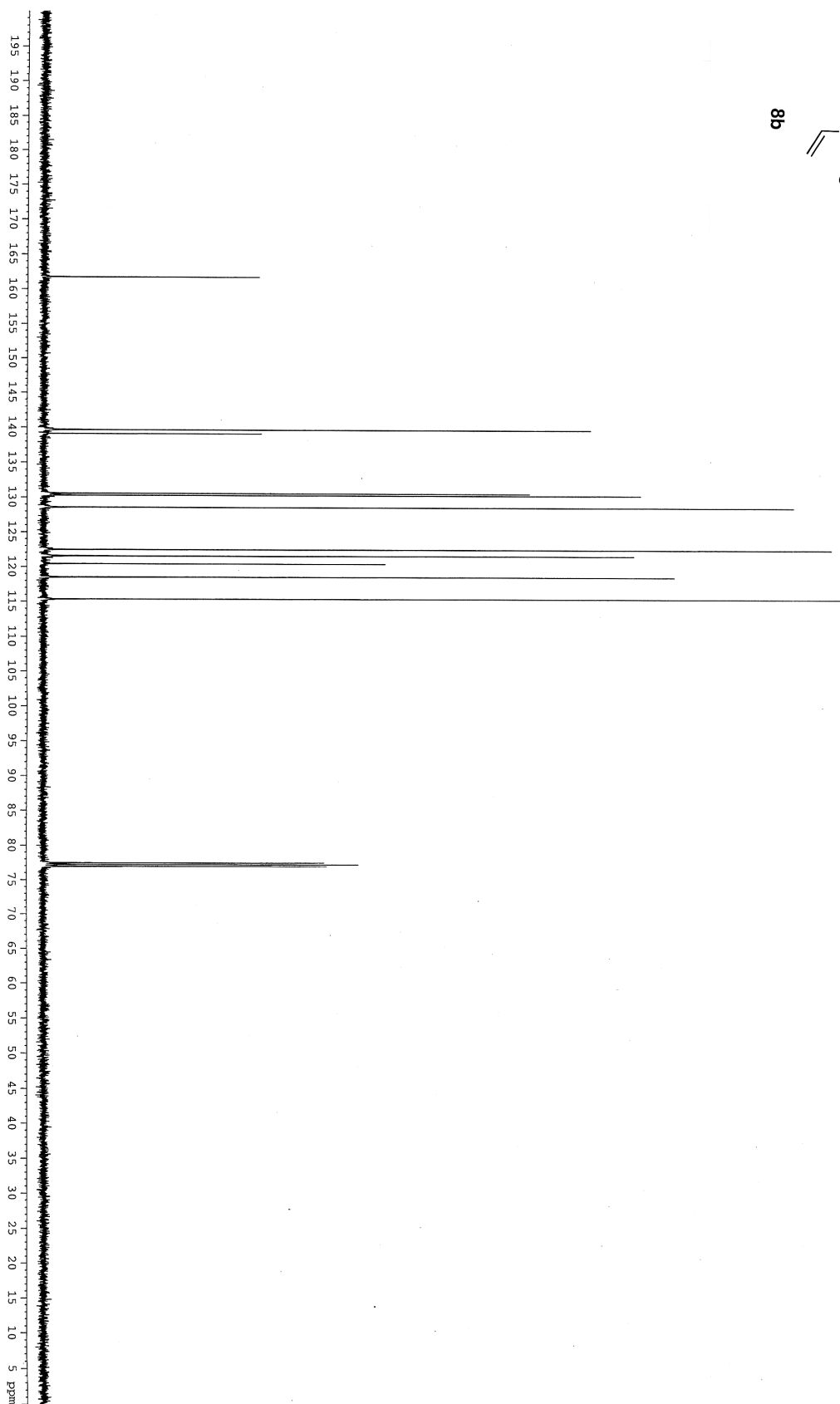


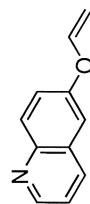
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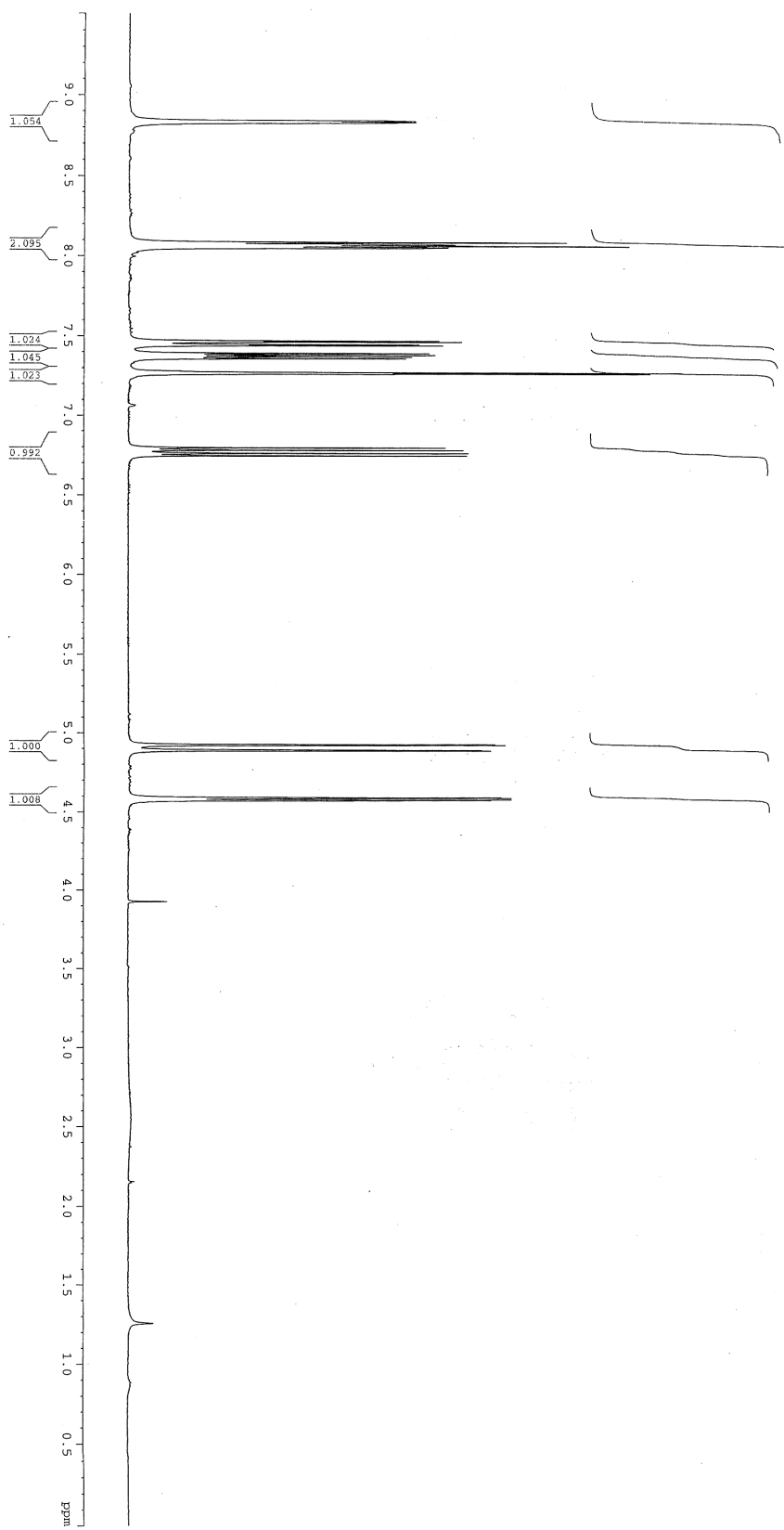


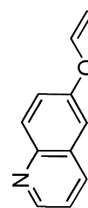
8b





8c





8c

