

A Novel NHC- Catalyzed Transformation of 2*H*-chromene-3-carboxaldehydes to 3-methyl-2*H*-chromen-2-ones

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General remarks

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 500 (1H) and 125 (13C) MHz respectively on a Bruker DPX-500 MHz NMR spectrometer. Chemical shifts (δ) are reported relative to TMS (1H) and CDCl₃ (13C) as the internal standards. Coupling constant (J) is reported in Hertz (Hz). Mass spectra were recorded under EI/HRMS or FAB using JEOL JMS 600H mass spectrometer. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrophotometer. Gravity column chromatography was performed using 100-200 mesh silica gel and mixtures of petroleum ether-ethyl acetate were used for elution.

General Procedure for the Synthesis of 3-methyl coumarins

DBU (20 mol %) was added to a suspension of the carbene precursor-1,3-dimesityl imidazolium chloride (SIMesCl) (15 mol %) and 2*H*-chromene-3-carboxaldehyde (0.50 mmol) in dry THF (5 mL) and the resulting solution was stirred for 8 h- 12 h. After the removal of the solvent by distillation in vacuum using a rotary evaporator, the residue was subjected to column chromatography

on a silica gel (100-200 mesh) column using 95:5 petroleum ether-ethyl acetate solvent mixtures to afford the 3-alkyl coumarin derivatives.

Characterization data for compounds

3-methyl-2H-chromen-2-one (5a): white solid, M.p: 90-92 °C, **IR** (film) 1709, 1638, 1447, 918 cm^{-1} . **^1H NMR** (CDCl_3 , 500 MHz): δ 7.42 (s, 1H) 7.39-7.35 (m, 1H) 7.32 (d, 1H, $J=8$ Hz) 7.2 (d, 1H, $J=8$ Hz) 7.17-7.14 (m, 1H) 2.14 (s, 3H). **^{13}C NMR** (CDCl_3 , 125 MHz): δ 161.9, 153.3, 139.0, 130.4, 126.8, 125.9, 124.1, 119.5, 116.4, 17.2 ppm. **LRMS-FAB** calcd. for $\text{C}_{10}\text{H}_8\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 161.06, found: 161.09.

6-bromo-3-methyl-2H-chromen-2-one (5b): Yellow solid, Mp: 152-153 °C, **IR** (film) 1726, 1599, 1478, 1248, 922, 815 cm^{-1} . **^1H NMR** (CDCl_3 , 500 MHz): δ 7.55-7.53 (m, 2H) 7.41 (s, 1H) 7.19 (d, 1H, $J=9.5$ Hz) 2.23 (s, 3H). **^{13}C NMR** (CDCl_3 , 125 MHz): δ 161.2, 152.1, 137.6, 133.2, 129.2, 127.3, 121.1, 118.2, 116.8, 17.3 ppm. **LRMS-FAB** calcd. for $\text{C}_{10}\text{H}_7\text{BrO}_2$ ($\text{M}+\text{H}$) $^+$: 238.97, found 239.11.

6-chloro-3-methyl-2H-chromen-2-one (5c): Yellow solid. Mp: 152-154 °C, **IR** (film) 1726, 1602, 1410, 1479, 925, 815 cm^{-1} . **^1H NMR** (CDCl_3 , 500 MHz): δ 7.43 (s, 1H) 7.41-7.38 (m, 2H) 7.25 (s, 1H) 2.23 (s, 3H). **^{13}C NMR** (CDCl_3 , 125 MHz): δ 161.2, 151.6, 137.7, 130.4, 129.5, 127.4, 126.1, 120.6, 117.9, 17.3 ppm. **LRMS-FAB** calcd. for $\text{C}_{10}\text{H}_7\text{ClO}_2$ ($\text{M}+\text{H}$) $^+$: 195.02, found:195.01.

6-isopropyl-3-methyl-2H-chromen-2-one (5d): colourless liquid, **IR** (film) 1724, 1619, 1428 cm^{-1} . **^1H NMR** (CDCl_3 , 500 MHz): δ 7.48 (s, 1H) 7.32-7.29 (m, 1H) 7.22-7.20 (m, 2H) 2.98-2.93 (m, 1H) 2.20 (s, 3H) 1.27 (d, 6H, $J=7$ Hz). **^{13}C NMR** (CDCl_3 , 125 MHz): δ 162.2, 151.5, 144.8, 139.2, 128.9, 125.5, 124.1, 119.3, 116.2, 33.5, 24.1, 17.2 ppm. **LRMS-FAB** calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 203.11, found 203.21.

3,7-dimethyl-2H-chromen-2-one (5e): white solid, M.p :104-106 °C, IR (film) 1710, 1623, 1437 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.69(s, 1H) 7.33(d, 1H, *J*=8 Hz) 7.15 (d, 1H, *J*=8 Hz) 7.11(s, 1H) 2.52 (s, 3H) 2.24 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 161.8, 153.8, 138.9, 135.9, 130.1, 126.5, 124.6, 117.1, 114.6, 21.7, 17.2 ppm. LRMS-FAB calcd. For C₁₁H₁₀O₂ (M+H)⁺: 175.07, found 175.20.

6-methoxy-3-methyl-2H-chromen-2-one (5f): white solid, M.p 114-116 °C, IR (film) 1704, 1630, 1538 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.45 (s, 1H) 7.23 (d, 1H, *J*=9 Hz) 7.03-7.00 (m, 1H) 6.82 (s, 1H) 3.83 (s, 3H) 2.21 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 162.0, 155.9, 147.7, 138.8, 126.3, 119.9, 117.8, 117.4, 109.2, 55.6, 17.3 ppm. LRMS-FAB calcd. for C₁₁H₁₀O₃ (M+H)⁺: 191.07, found 191.27.

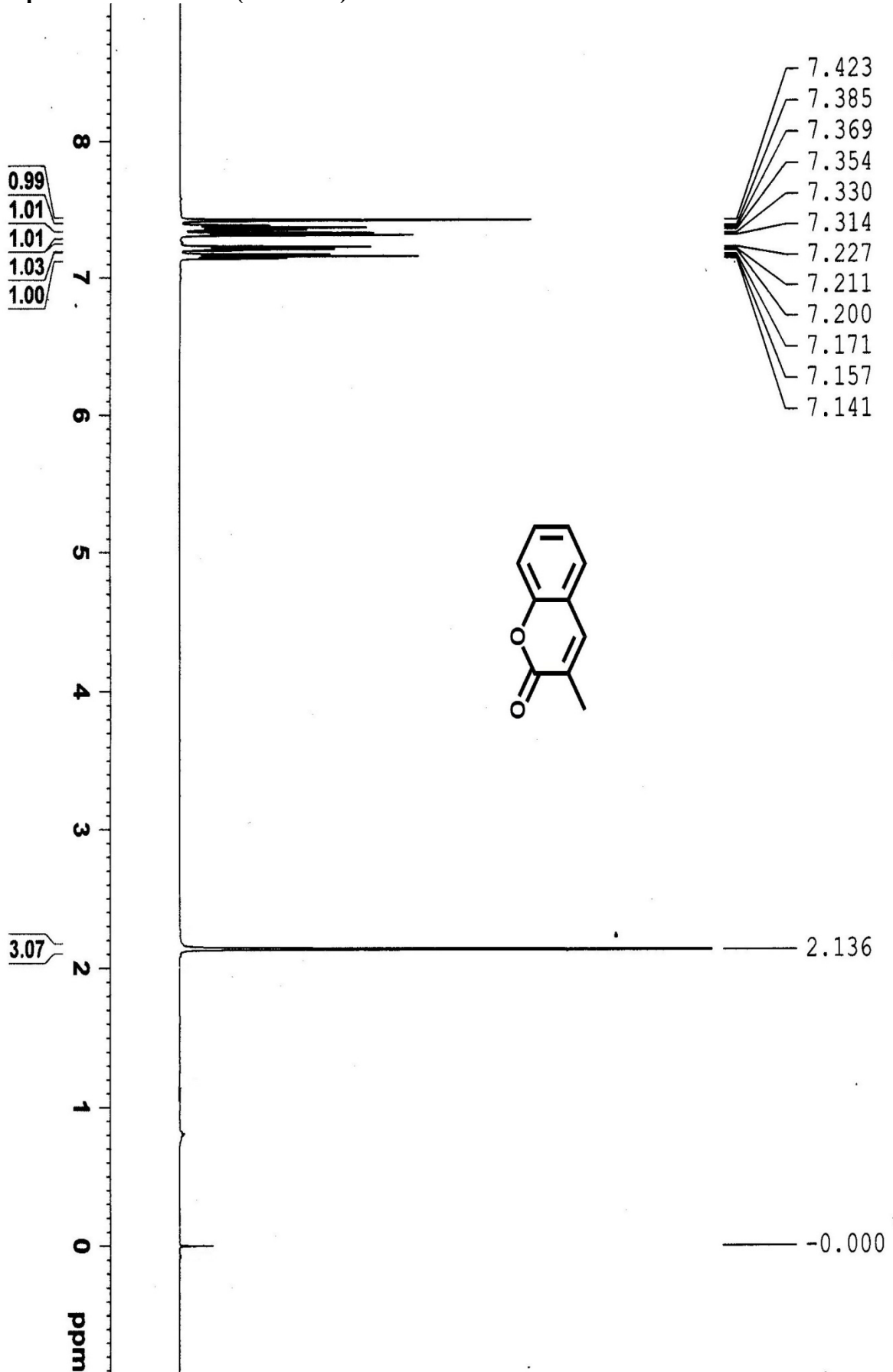
3,6-dimethyl-2H-chromen-2-one (5g): white solid, M.p :114-116 °C, IR (film) 1711, 1600 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.43 (s, 1H) 7.24-7.23 (m, 1H) 7.19-7.17 (m, 2H) 2.39 (s, 3H) 2.19 (s, 3H) ¹³C NMR (CDCl₃, 125 MHz): δ 162.1, 151.4, 138.9, 133.7, 131.3, 126.7, 125.7, 119.3, 116.2, 20.8, 17.2 ppm. LRMS-FAB calcd. For C₁₁H₁₀O₂ (M+H)⁺: 175.07, found 175.23.

7-isopropyl-3-methyl-2H-chromen-2-one (5h): colourless liquid IR (film) 1706, 1627, 1533 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.47 (s, 1H) 7.30 (d, 1H, *J*=8 Hz) 7.17-7.15 (m, 1H) 7.11-7.09 (m, 1H,) 3.02-2.94 (m, 1H) 2.20 (s, 3H) 1.28 (d, 6H, *J*= 7 Hz) ¹³C NMR (CDCl₃, 125 MHz): δ 162.3, 152.3, 138.9, 135.3, 130.4, 126.6, 125.1, 117.5, 114.1, 34.2, 23.7, 23.6, 17.2 ppm. LRMS-FAB calcd. For C₁₃H₁₄O₂ (M+H)⁺: 203.11, found 203.13.

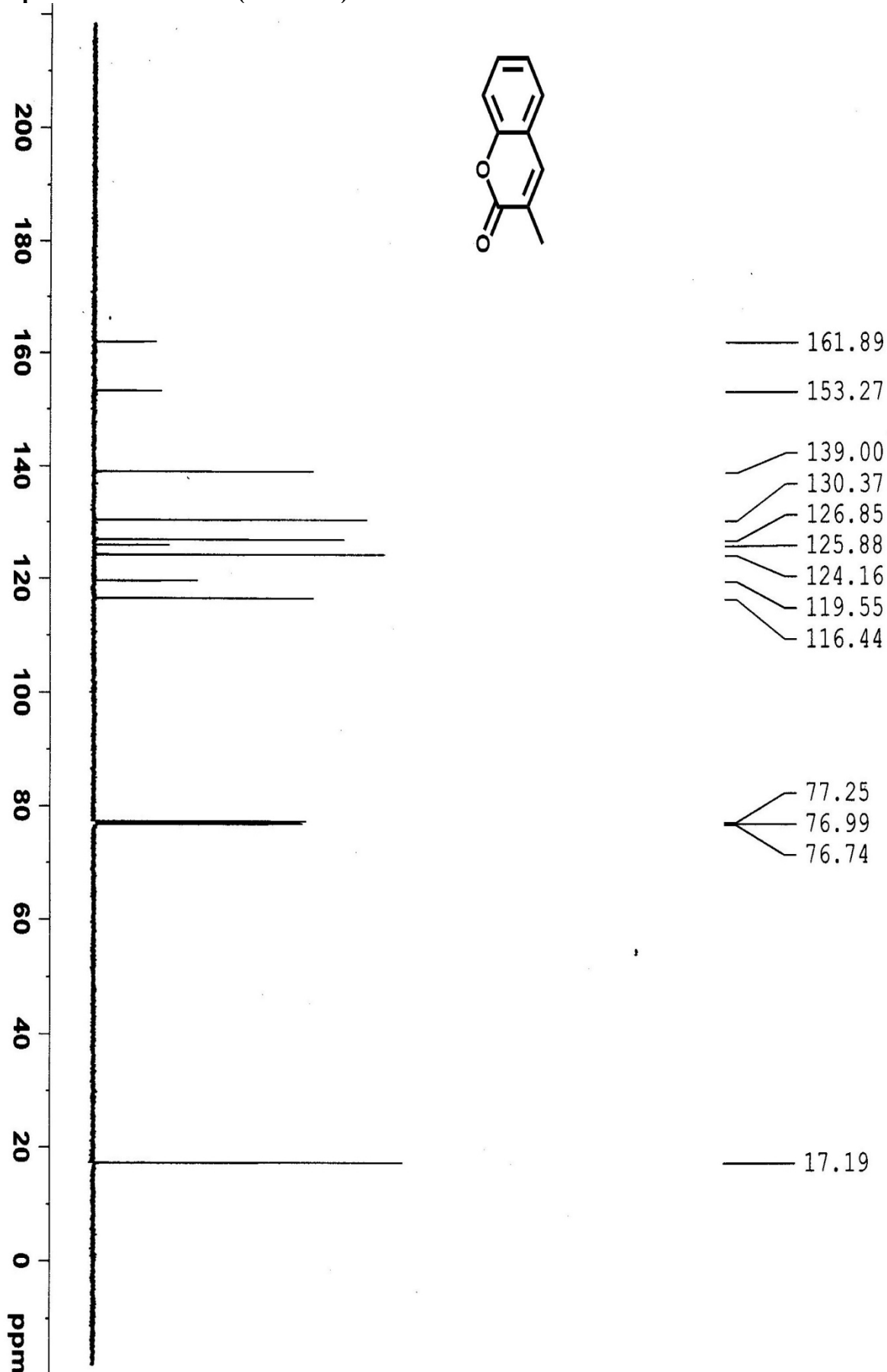
6-bromo-3-ethyl-2H-chromen-2-one (7): white solid, M.p: 110-112 °C, IR (film) 1719, 1628, 1599 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 7.50 (d, 1H, *J*=2 Hz) 7.48-7.46 (m, 1H) 7.31 (s, 1H) 7.13 (d, 1H, *J*=8.5 Hz) 2.57-2.52 (m, 2H) 1.19 (t, 3H, *J*=7Hz) ¹³C NMR (CDCl₃, 125 MHz): δ 159.7, 150.9, 134.8, 132.1,

131.7, 128.4, 120.1, 117.1, 115.7, 22.9, 11.1 ppm. **LRMS-FAB** calcd. For $C_{11}H_9BrO_2$ (M+H)⁺: 252.99, found 253.28.

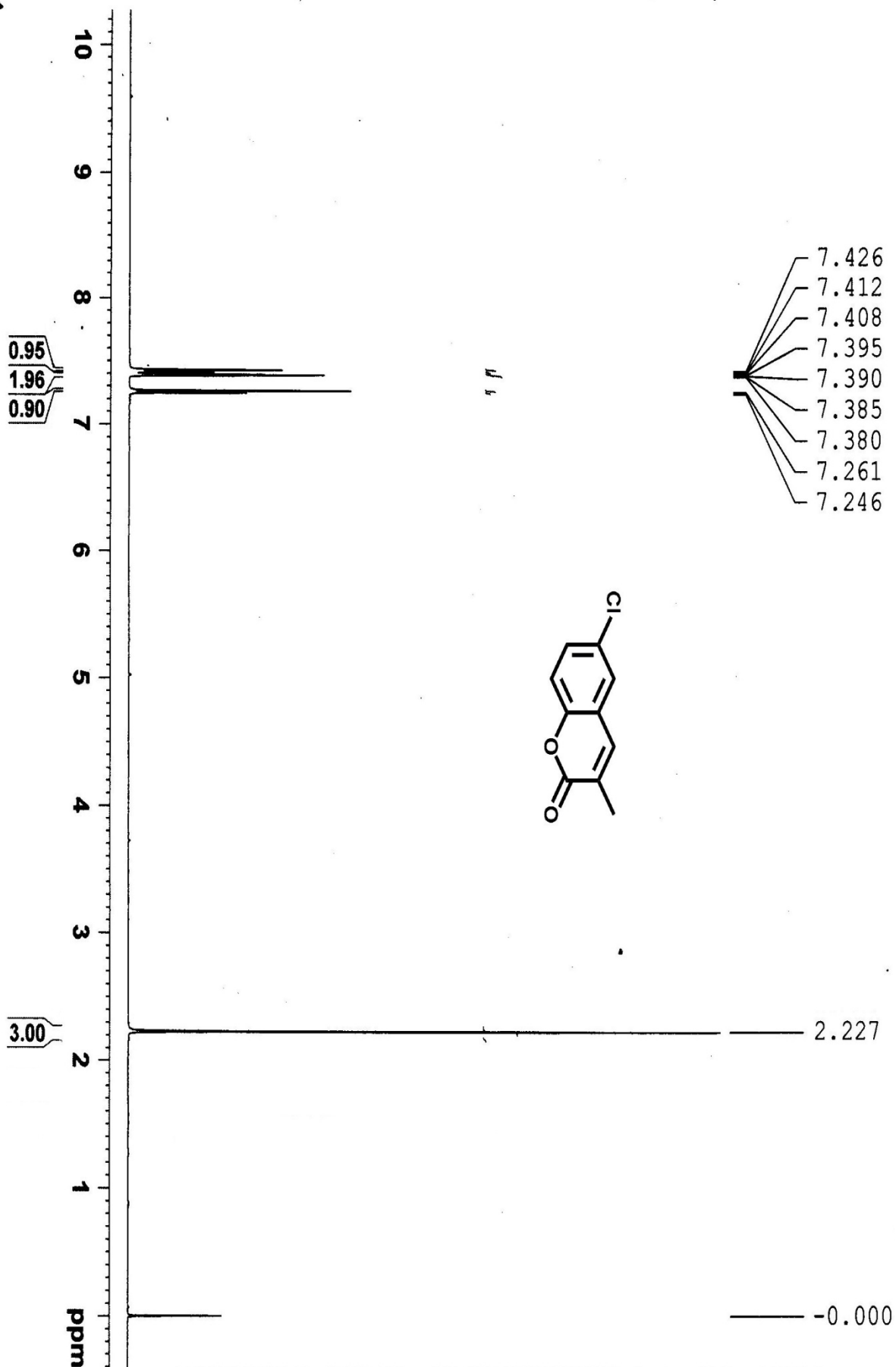
Compound -5a ¹H NMR (500 MHz)



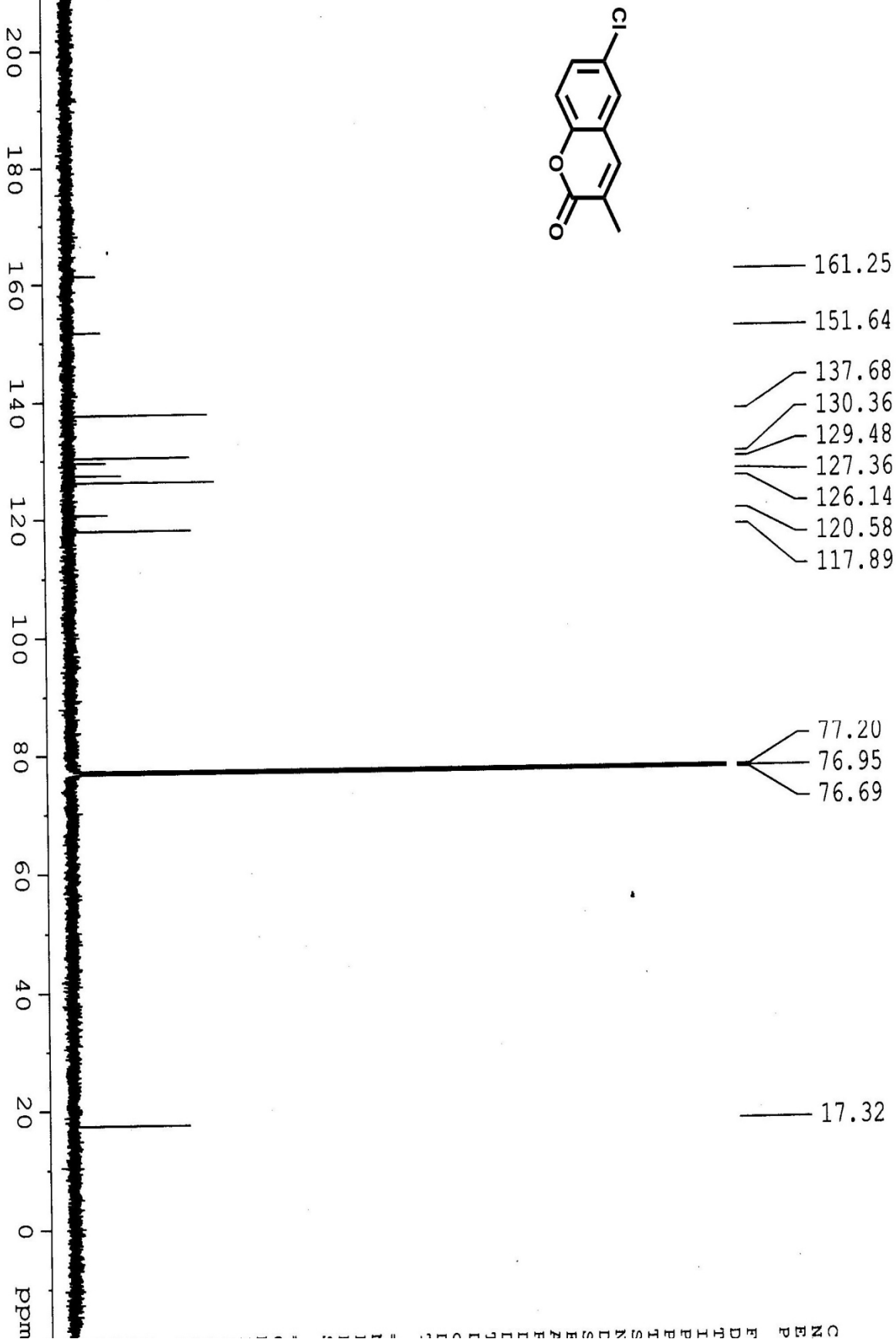
Compound -5a ^{13}C NMR (125 MHz)



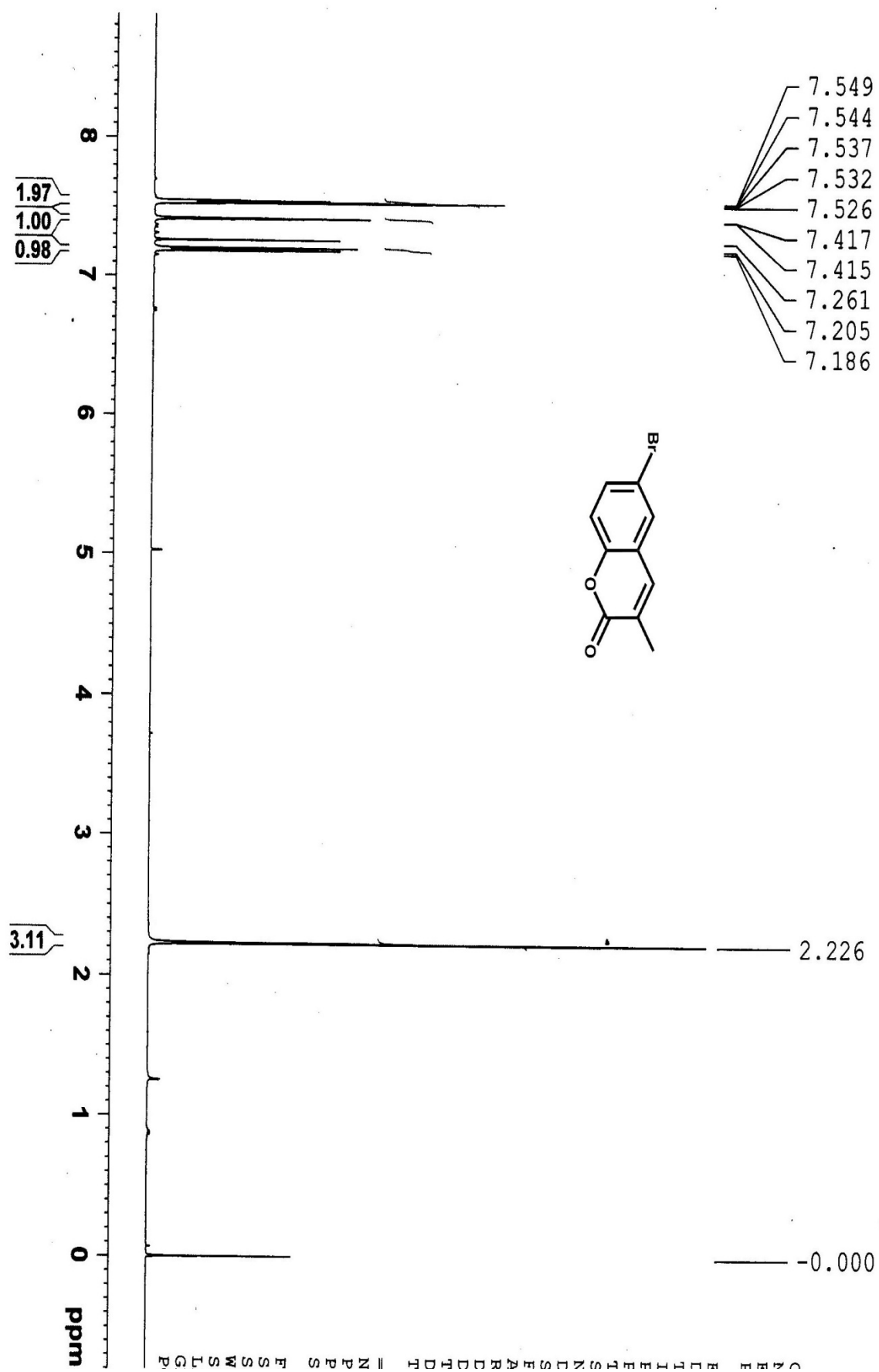
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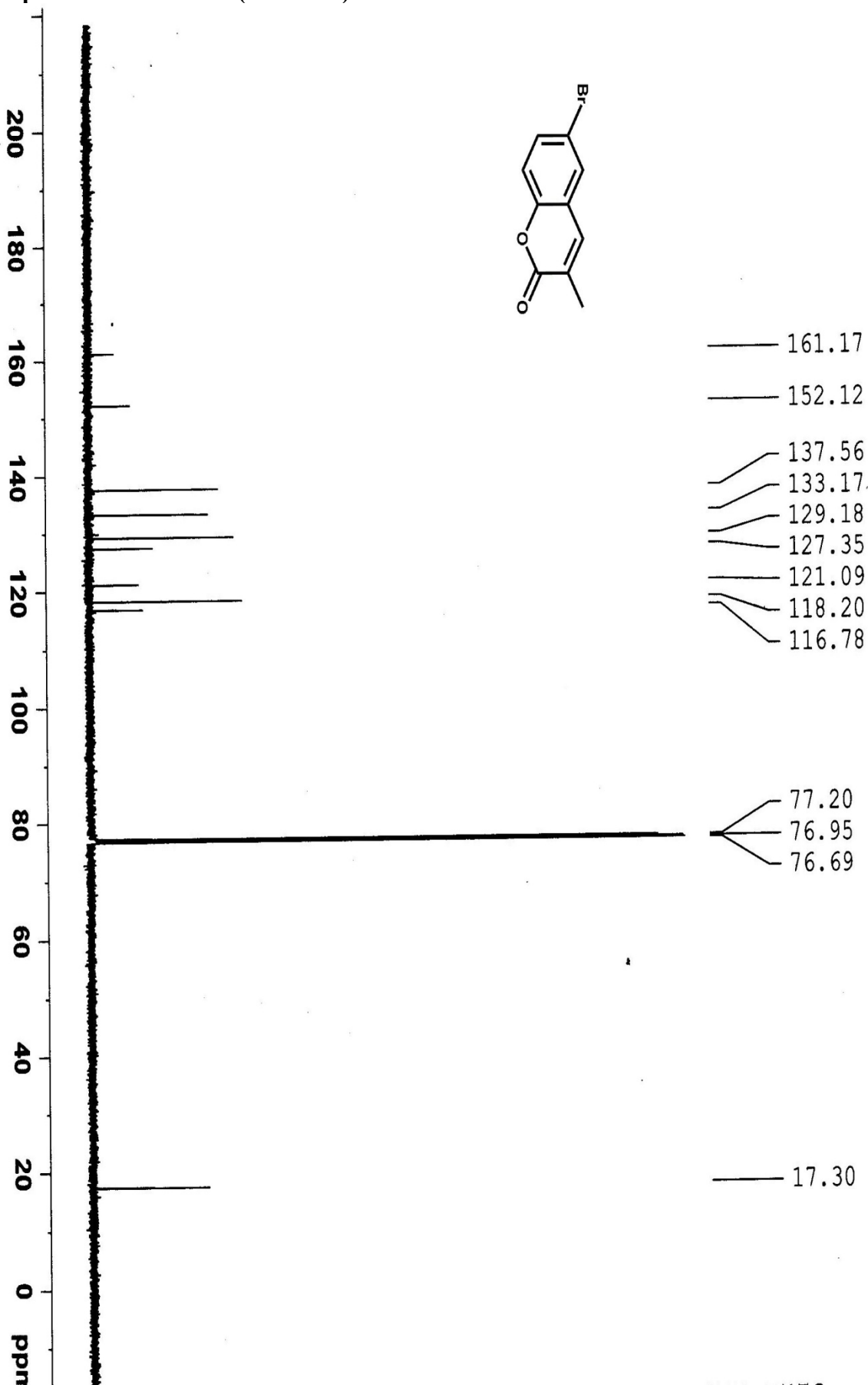
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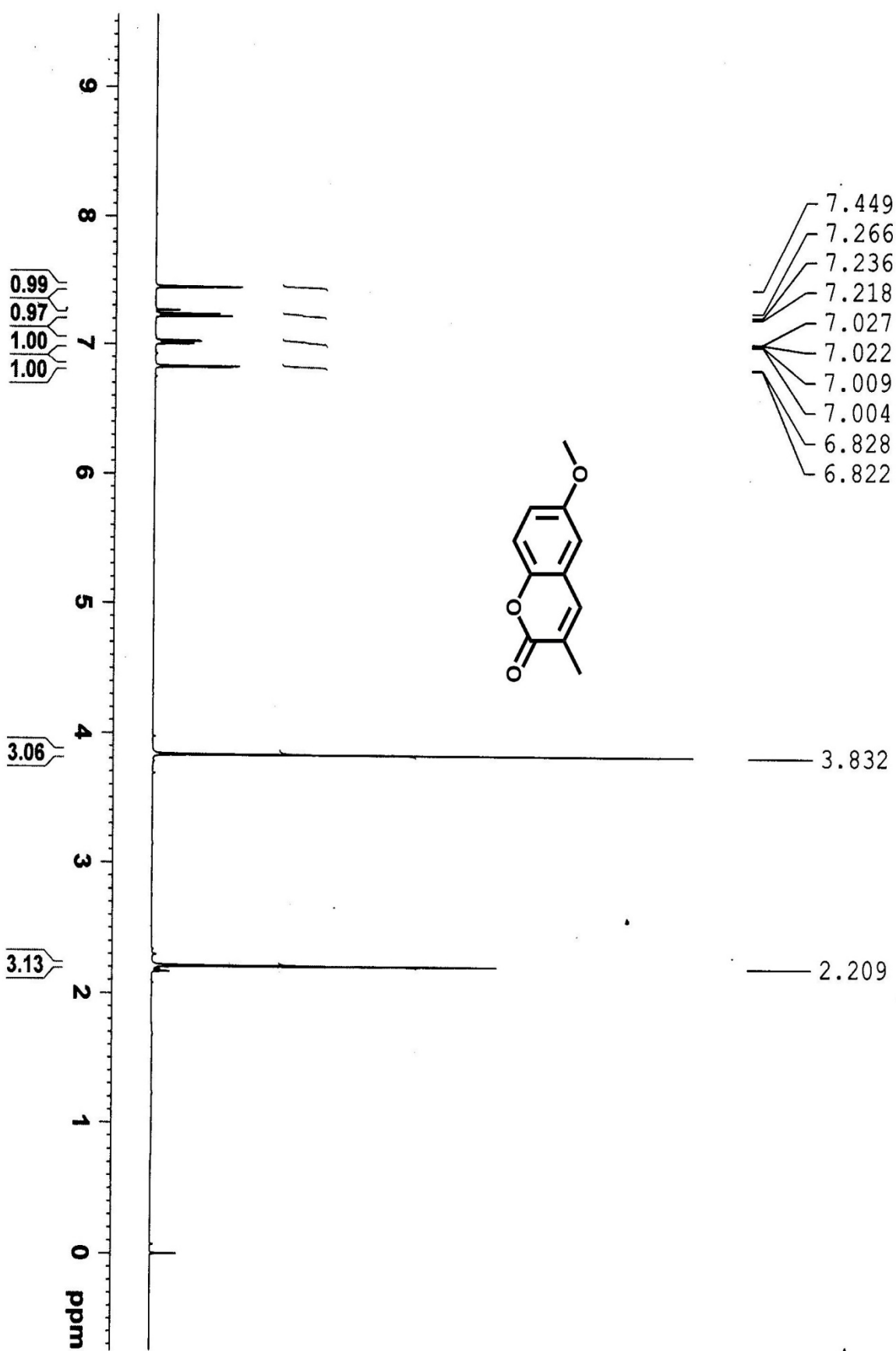
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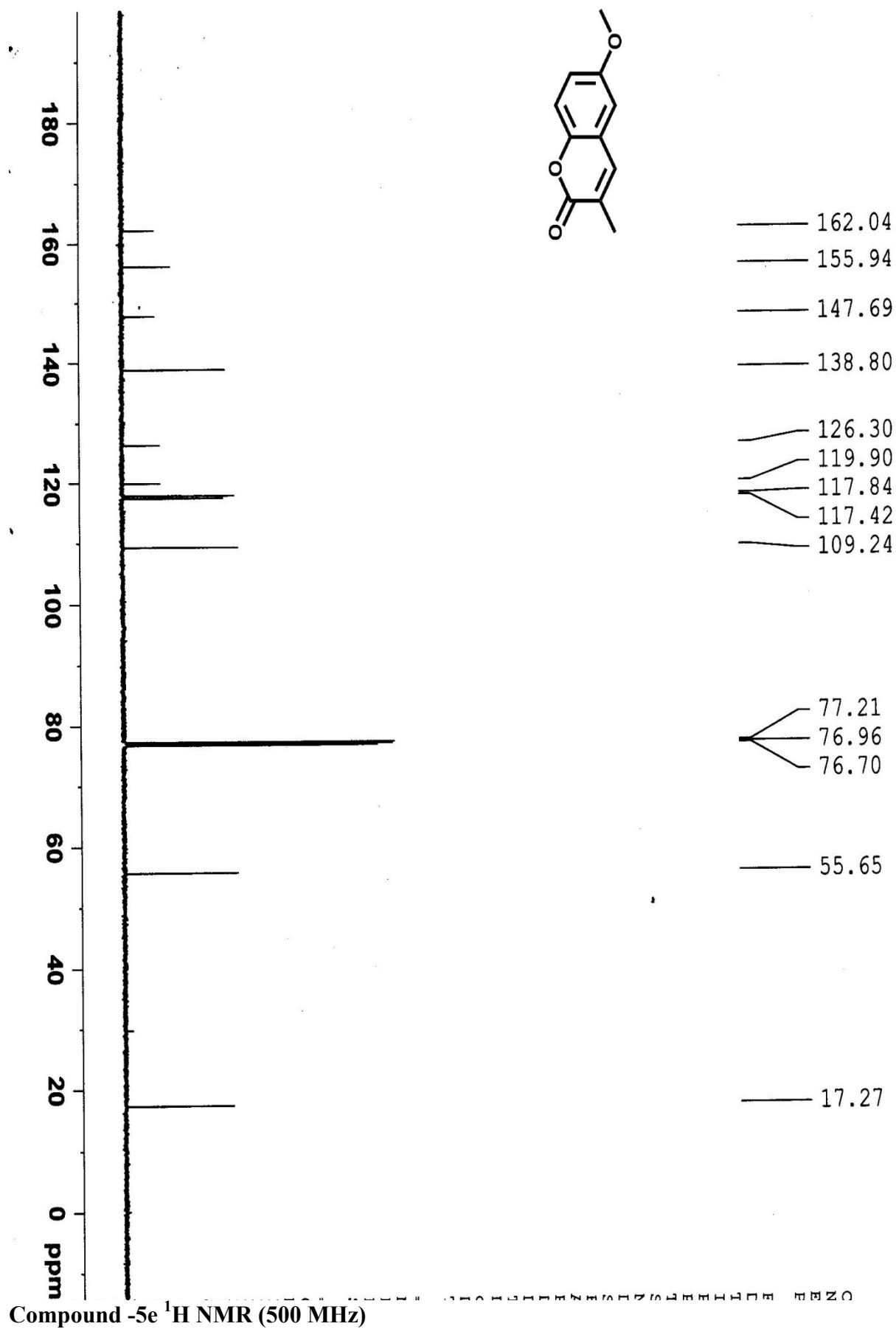
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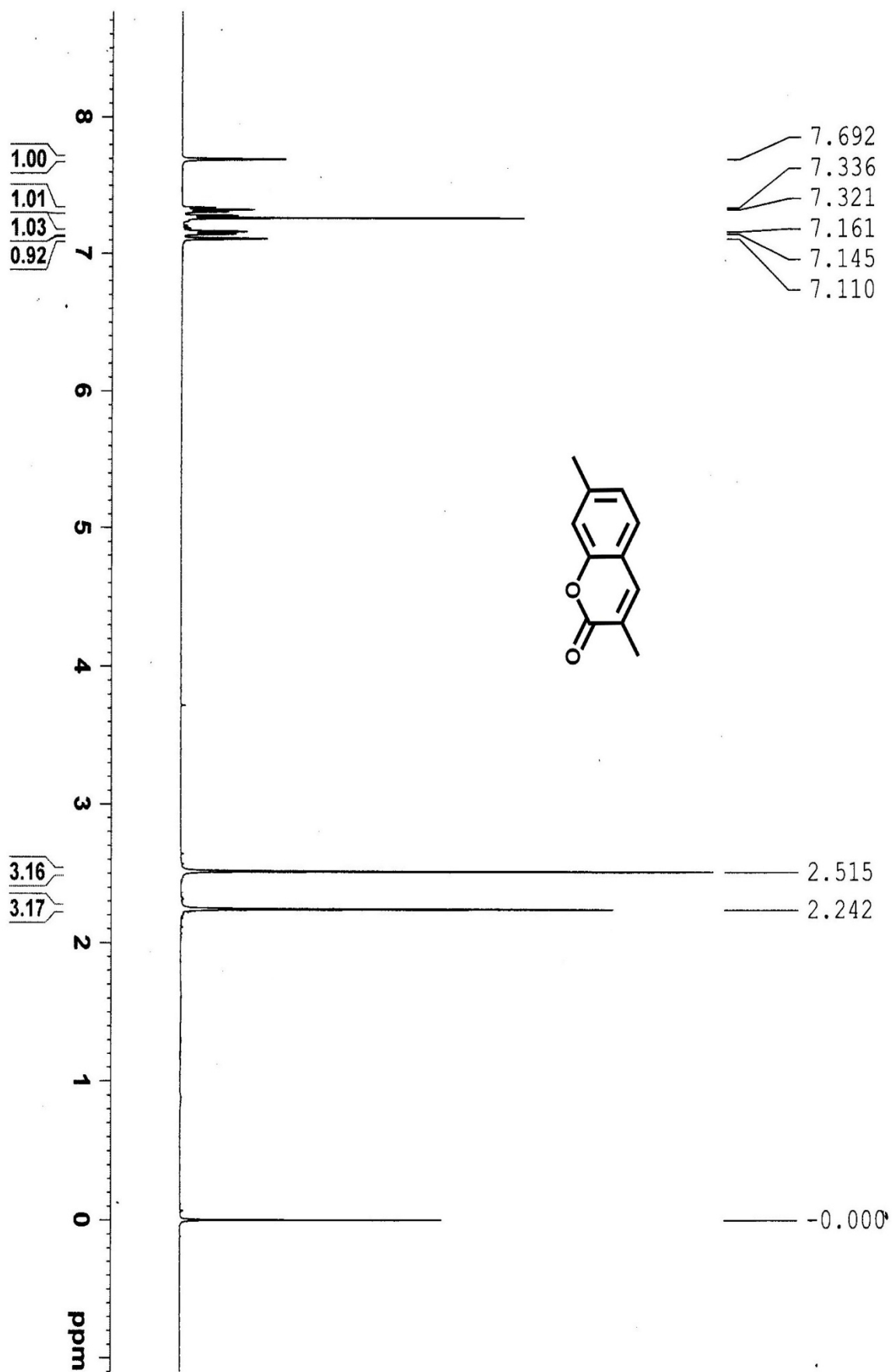


**Compound -5d ¹H NMR (500
MHz)**

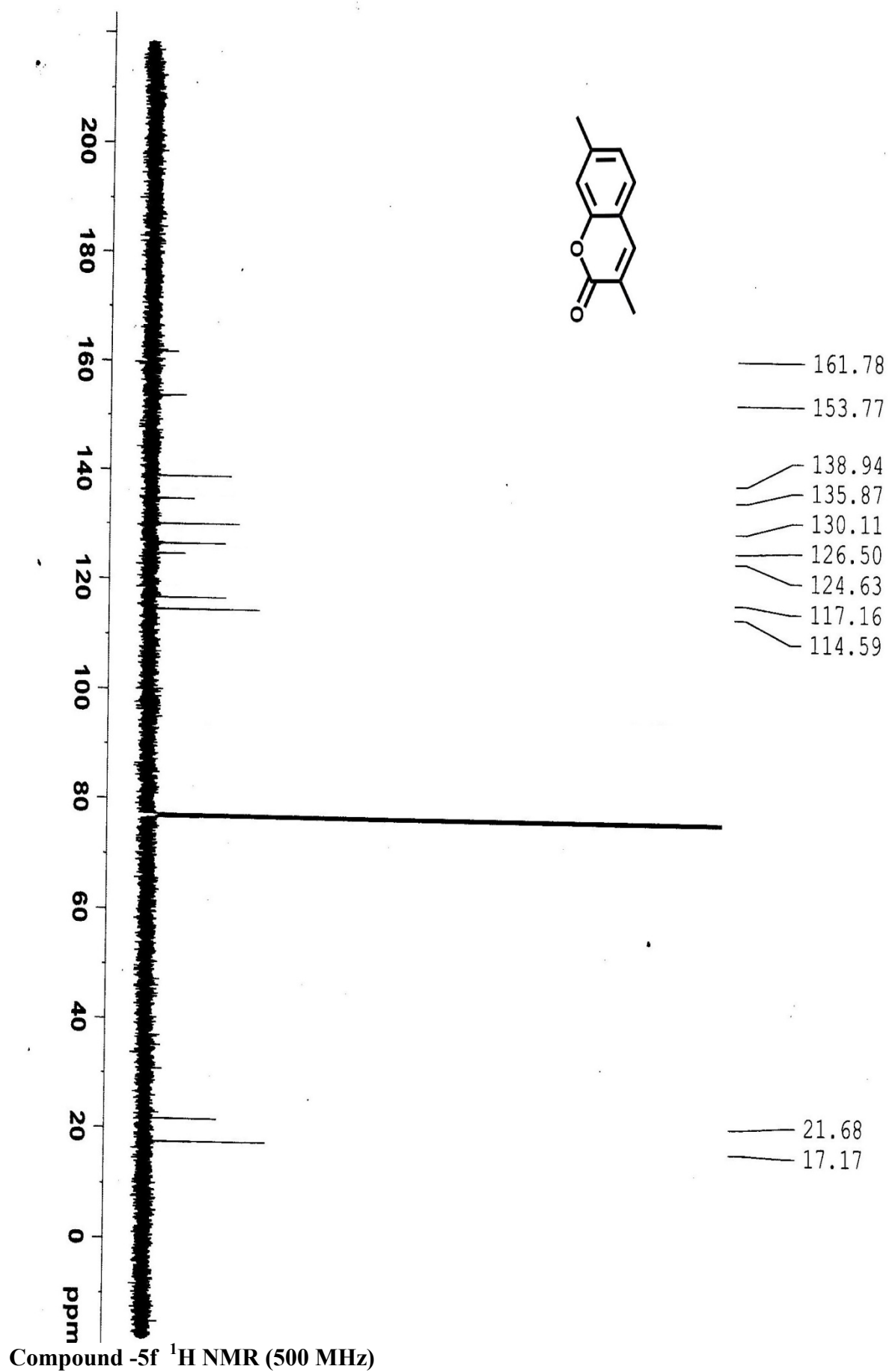


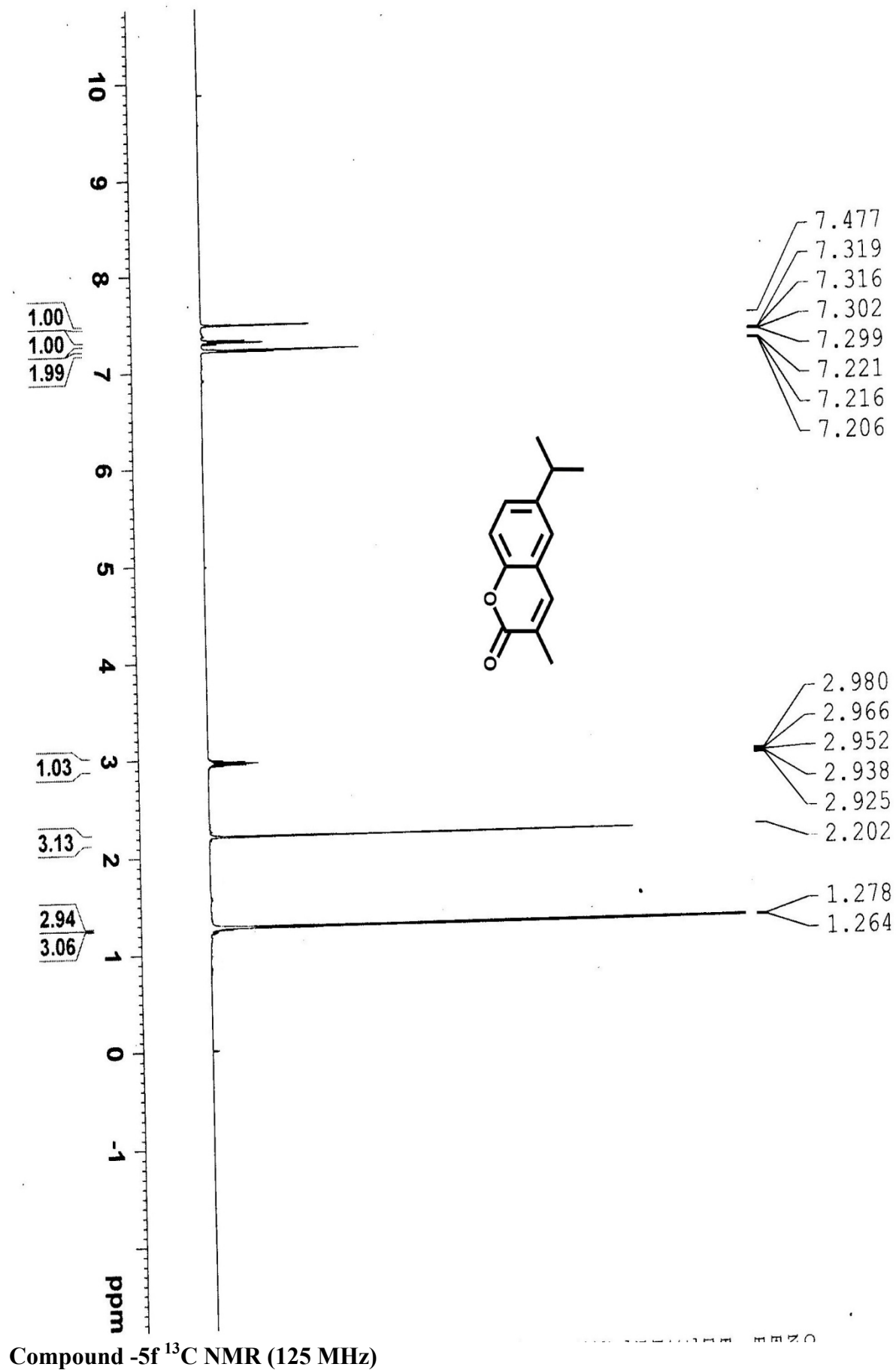
Compound -5d ^{13}C NMR (125 MHz)

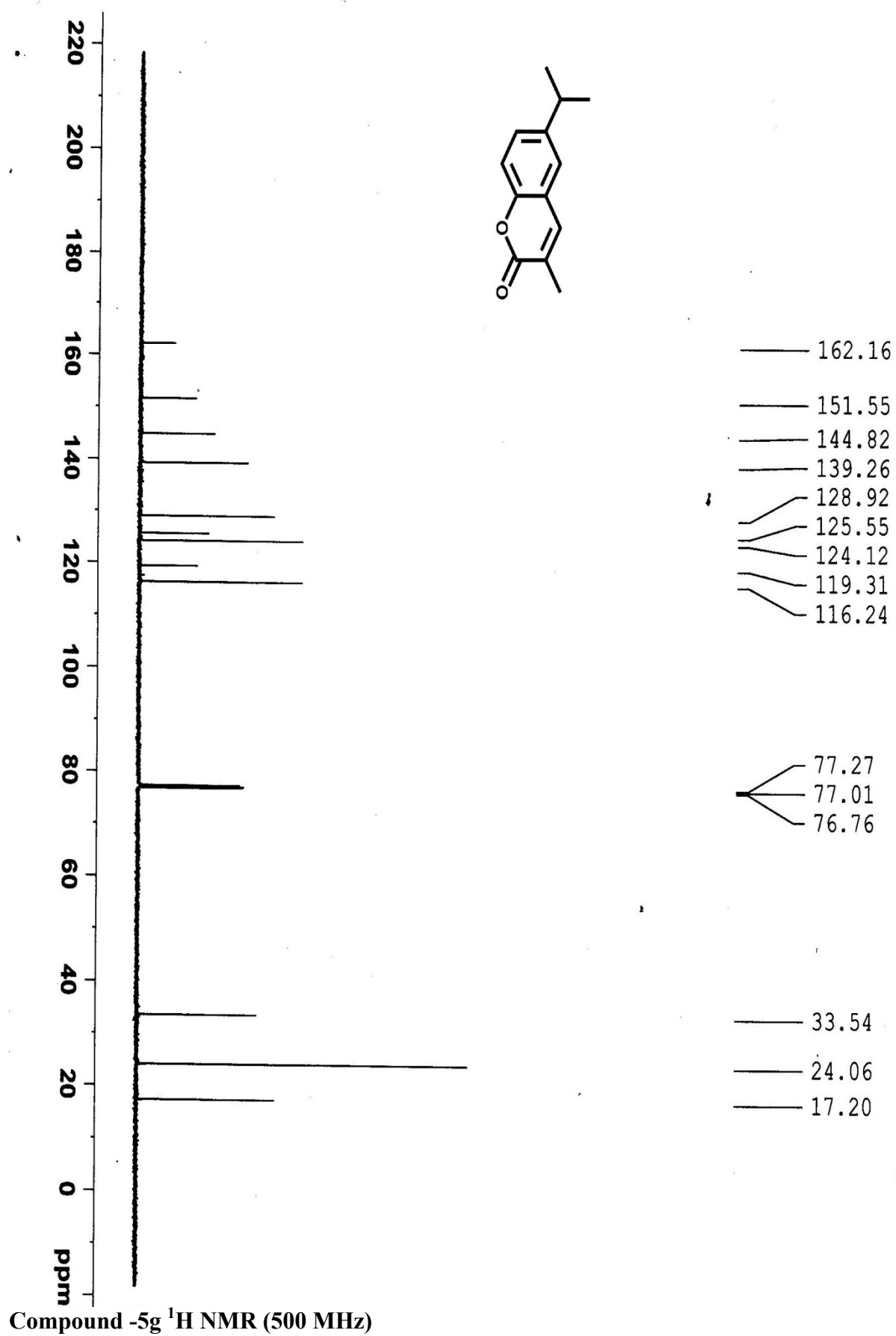


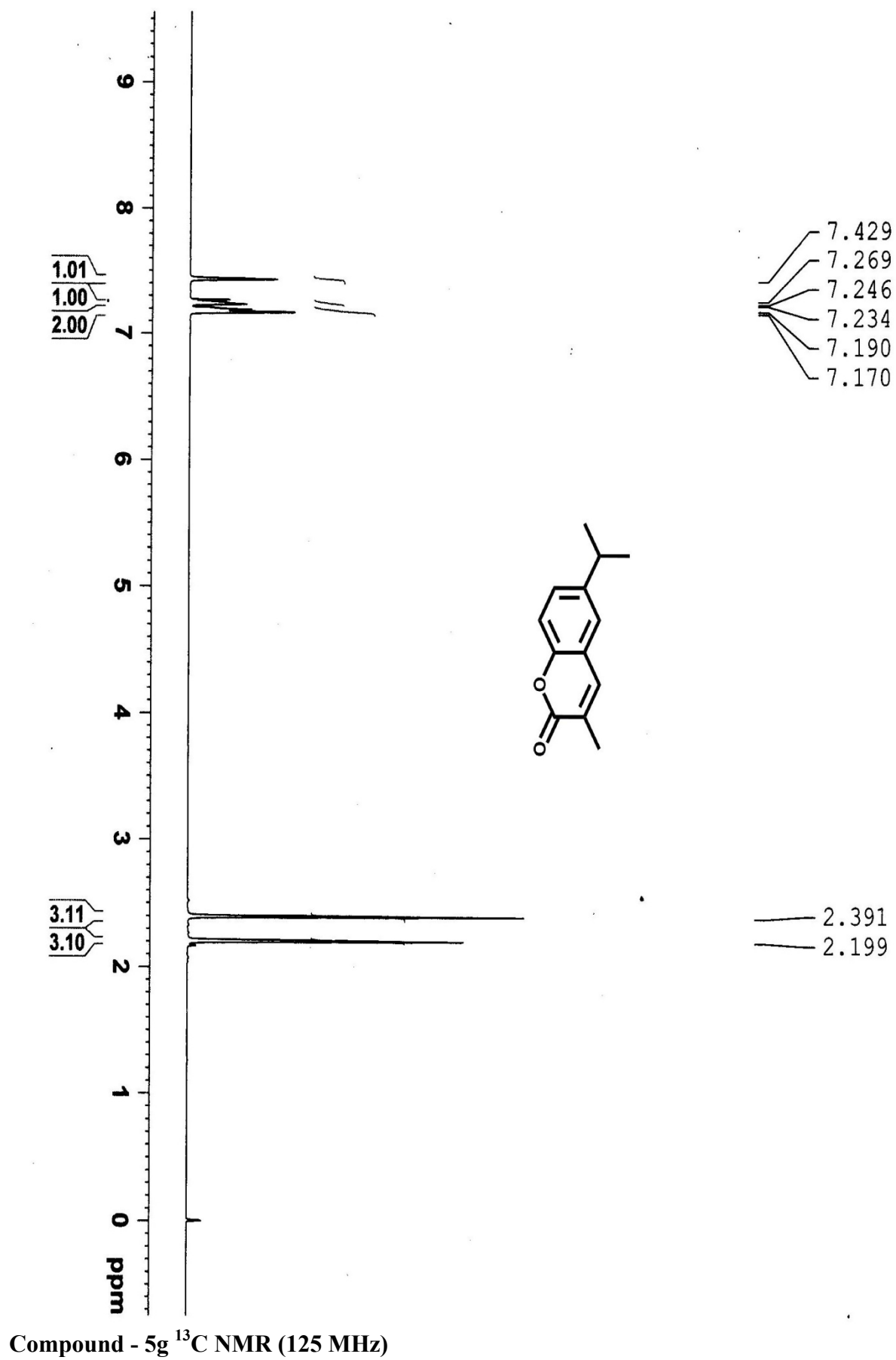


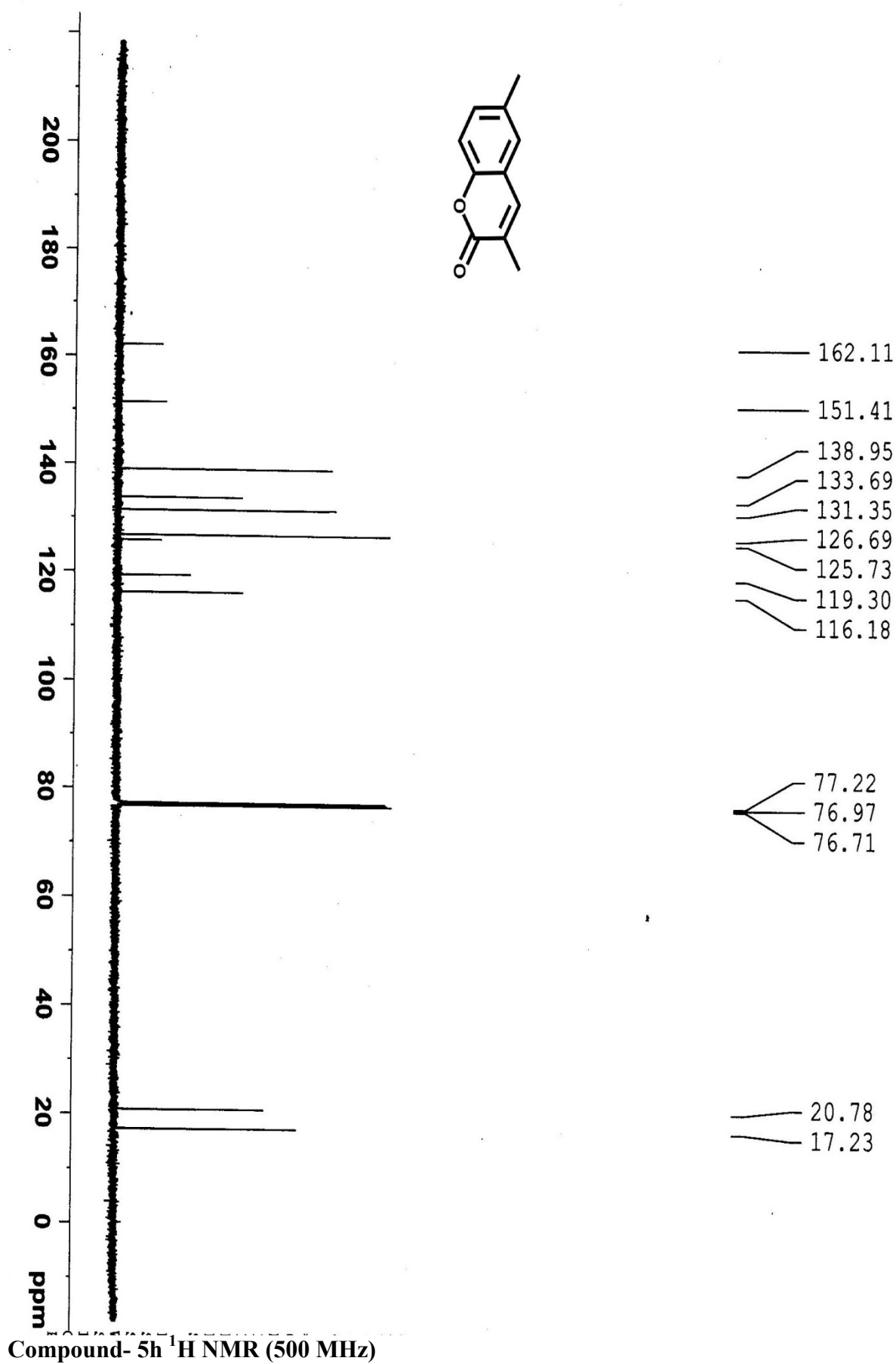
Compound -5e ^{13}C NMR (125 MHz)

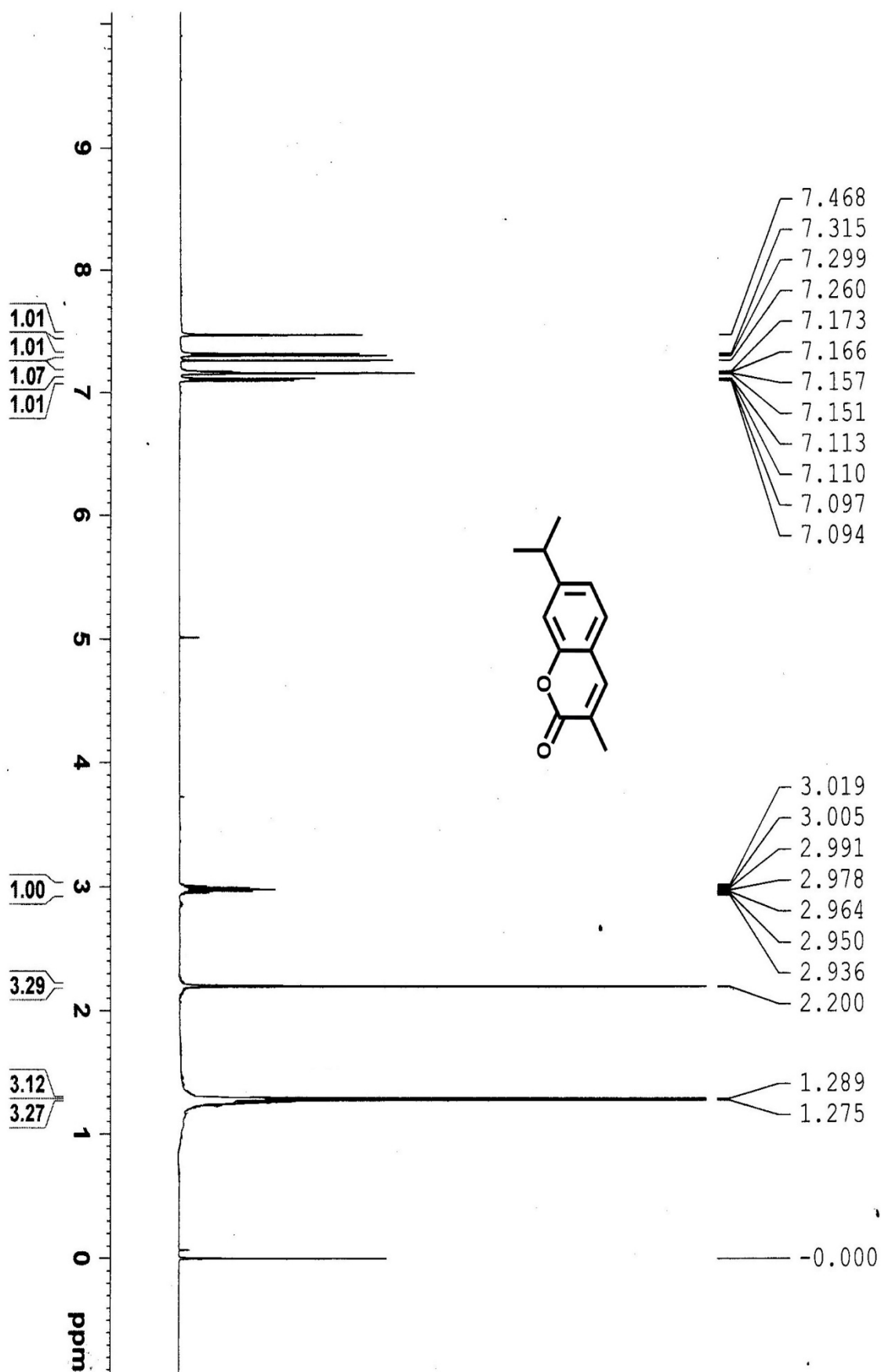




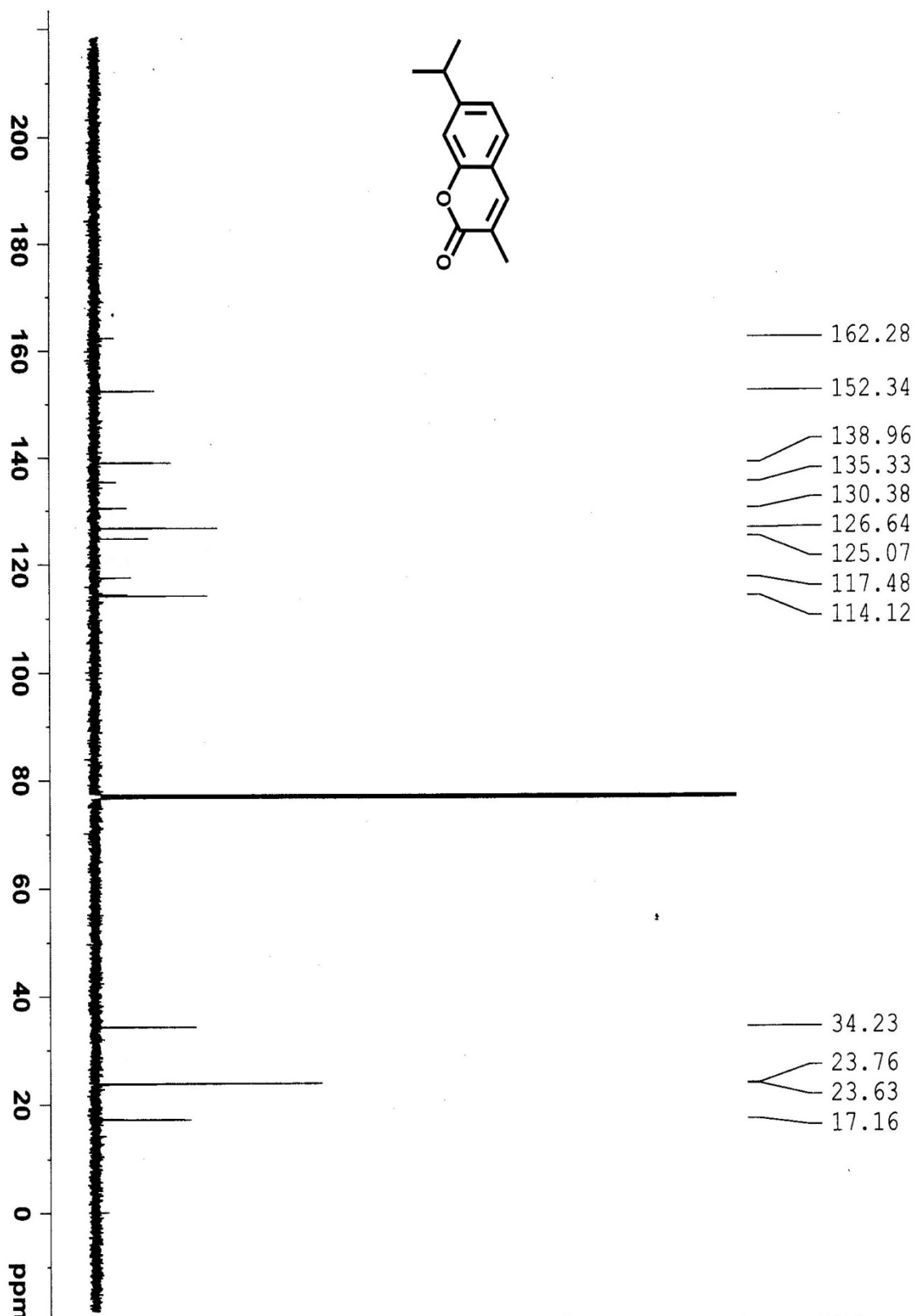




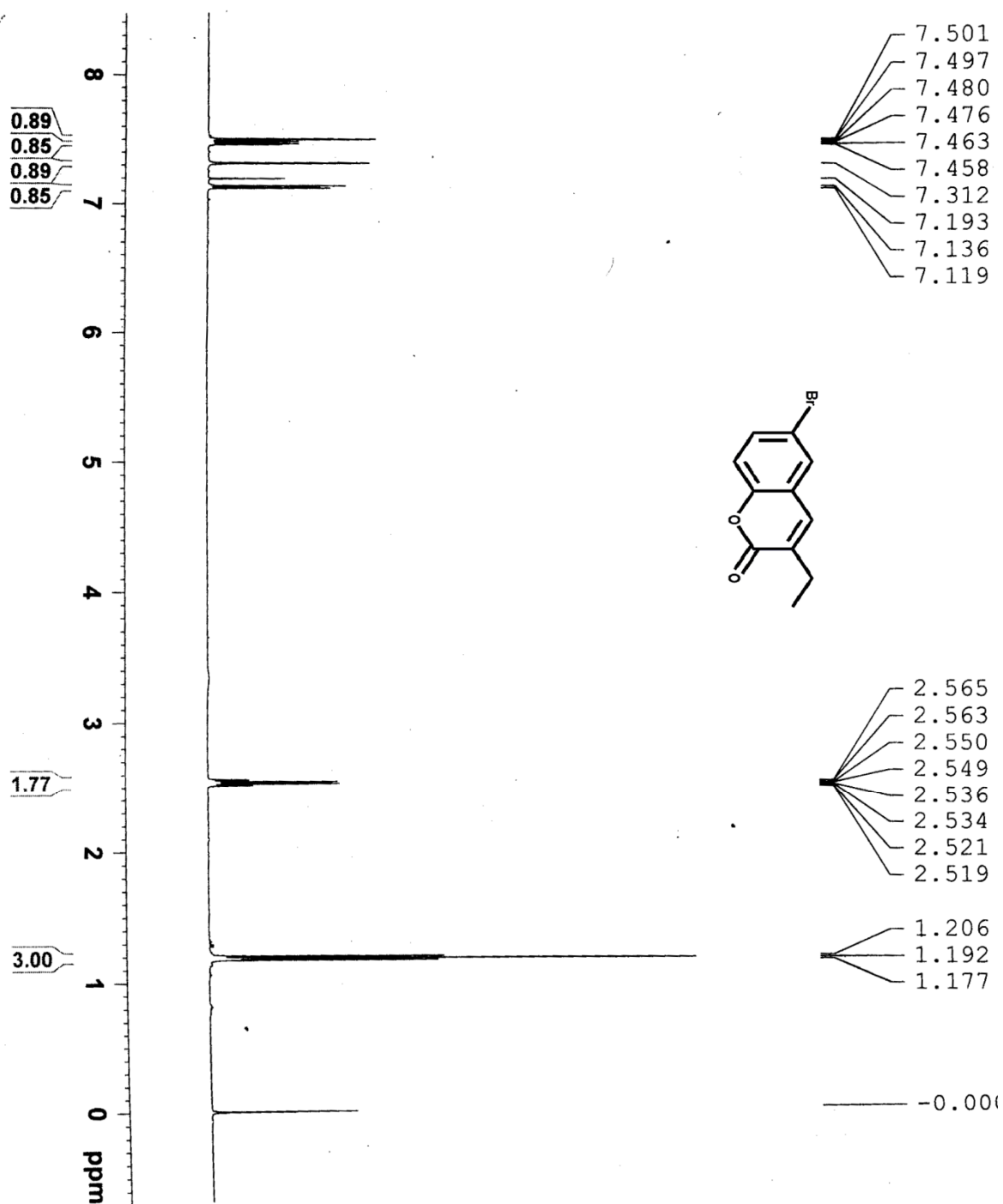




Compound-5h ^{13}C NMR (125 MHz)



Compound-7 ^1H NMR (500 MHz)



Compound-7 ^{13}C NMR (125 MHz)

