

A novel water-soluble NHC-Pd polymer: an efficient and recyclable catalyst for the Suzuki coupling of aryl chlorides in water at room temperature

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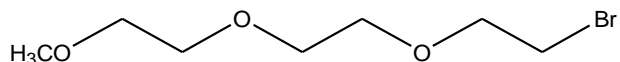
1. General information:

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Liquid NMR was obtained on a DMX-250 and DMX-400 MHz Bruker Avance instrument using CDCl_3 and DMSO-d_6 as solvent and TMS as internal standard. Thermogravimetric analysis was conducted from room temperature to 600 °C in an air flow using a Pheometric Scientific analyzer.

2. General procedure for the Synthesis of 1-(2-(2-methoxyethoxy)ethoxy)-2-bromoethane (TEG-Br):

The bromo compound **TEG-Br** was synthesized via a modification of a literature procedure.^[1] In a typical experiment, triethylene glycol monomethyl ether (2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethanol)(1.6 g, 10 mmol) was added in a well dried flask containing dry CH_2Cl_2 (50 mL) under an argon atmosphere. Carbon tetrabromide (4 g, 12 mmol) was added to this solution. After cooling the reaction mixture to 0°C, triphenyl phosphine (3.9 g, 15 mmol) in dichloromethane (10 ml) was added drop-wise to it. After stirring for 5 h the solvent from reaction mixture was evaporated out. 25 ml Ether was added to the reaction mixture, kept for 5 min and filtered. The same process (addition of ether, filtration) was repeated thrice. The residue was subjected to flash column chromatography to obtain the pure product.

The spectral data for **TEG-Br** is as follows: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 25 °C, TMS): δ = 3.29 (s, 3H), 3.34 (t, 2H, J = 6 Hz), 3.39 (t, 2H, J = 2.25 Hz), 3.47-3.51 (m, 6H), 3.64 (t, 2H, J = 6 Hz); $^{13}\text{C-NMR}$ (250 MHz, CDCl_3 , 25 °C, TMS): δ = 30.25, 58.83, 70.35, 70.42, 70.45, 71.03, 71.77. ($\text{C}_7\text{H}_{15}\text{BrO}_3$)



1-(2-(2-methoxyethoxy)ethoxy)-2-bromoethane

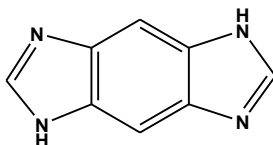
TEG-Br

3. Procedure for formation of Benzo-bis(imidazole) 2²:

1,2,4,5-Benzenetetraamine tetrahydrochloride (284 mg, 1.00 mmol) was poured into a round bottom flask was charged with a magnetic stir bar. Formic acid (88-99%) was added and the flask was fitted with an air-jacketed condenser. The reaction carried out in

an oil bath at 100 °C for 36 h. The reaction mixture was then allowed to cool, decanted into ice-cold water (equal volume to formic acid) and neutralized with K₂CO₃. Neutralization caused precipitation of the product which was collected via vacuum filtration, washed with cold water, and dried under vacuum over P₂O₅.

The desired product as a light brown solid;; ¹H NMR (250 MHz, DMSO-*d*₆, D₂O) δ 7.651 (s, 2H), 8.156 (s, 2H); ¹³C NMR (250 MHz, DMSO-*d*₆) δ 99.67, 135.38, 143.01.

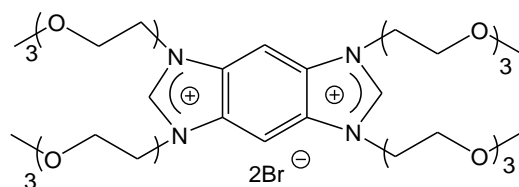


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4. General procedure for the synthesis of Tetra(triethylene glycol) benzo-bis(imidazolium) bromide **3**³:

In a well-dried two necked 50ml Schlenk flask, bis(imidazole) (320 mg, 2.00 mmol) was added to a solution of NaH (80 mg, 60 wt %, 4.00 mmol) in PhCH₃ (25 mL) under argon atmosphere. The resulting solution was heated to 110 °C for 1 h, after cooling the solution to room temperature, compound **TEG-Br** (3200mg, 14.00 mmol) was added via syringe. The suspension was placed in an oil bath at 110 °C for 4 h, then dry DMF (5 mL) was added via syringe and the reaction was maintained at 110 °C. After 6h, dry dioxane (10 ml) was added and stirred at the same temperature for 6h, then 75 °C for 10 h. Upon completion, the reaction mixture was concentrated. The residue was taken up in 1:1 CH₂Cl₂/EtOH and the insoluble NaBr was removed via filtration. To the filtrate was added 1:10 n-hexane/EtOAc until precipitation of the product occurred. The solids were collected via vacuum filtration and dried under vacuum to provide 1.15 g (60%) of the product as a brown powder. The final material was denoted as IM-TEG.

The spectral data for **3** is as follows: : Melting point: 245-250 °C (dec); ¹H-NMR (400 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 3.16 (s, 12H), 3.38-3.42 (m, 16H), 3.45 (t, 8H, *J* = 4.00 Hz), 3.56 (t, 8H, *J* = 4.00 Hz), 3.97 (t, 8H, *J* = 4.8 Hz), 4.89 (t, 8H, *J* = 4.8 Hz); ¹³C-NMR (400 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 58.5, 67.6, 69.9, 70.0, 70.1, 71.6, 100.3, 130.4, 146.7.; elemental analysis data found: C: 47.1%, H: 6.3%, N: 7.1%, Br: 17.2%, Calcd: C: 48%, H:6.9%, N:6.2%, Br: 17.7%.



3

5. Typical procedure for preparation of organometallic polymer **1b**:

Compound **3** (1.0 mmol) was dissolved in DMSO (5ml, ca. 0.2 M) and either Pd(OAc)₂ (1.0 eqv), was added in one portion. The solution was placed in a preheated oil bath at 110 °C and stirred open-air for 12 h. The reaction mixtures typically darkened in color (to green) as the reaction progressed. The cooled reaction mixture was added to CH₂Cl₂. The result precipitated polymer were collected via vacuum filtration and dried under vacuum.

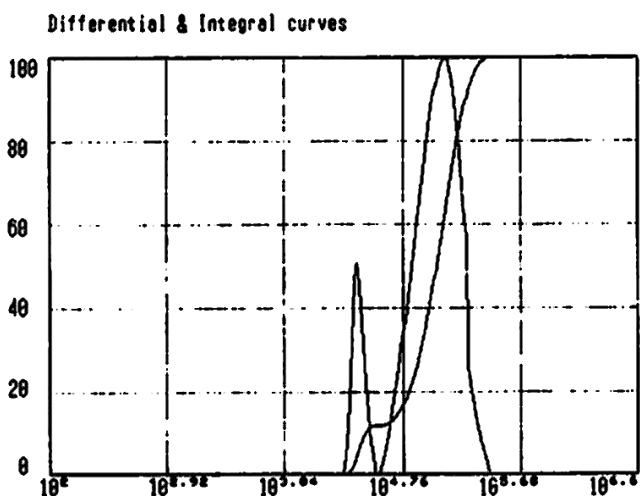


Figure 1S. Molecular weight of the organometallic polymer **1b**:

The molecular weight of **1b** has been measured using a Gel-Permeation Chromatography (GPC) technique (Column Waters, 10000 Å-DVB, a refractive index detector and, H₂O as eluent). The value for the fresh catalyst was found to be MWA ~ 107398 Da.

6. General procedure for the Suzuki coupling reaction using Pd-TEG as catalyst:

In 10-mL round-bottomed flask, aryl halide (1 mmol), arylboronic acid (1-1.2 mmol), K₂CO₃ (3 mmol), **1b** (0.005-0.1 mol %) and water (3 mL) were charged and stirred at room temperature under argon atmosphere. The reaction was monitored by GC. After

completion of the reaction, the product was extracted with *n*-hexane or ethyl acetate. The same product extraction was repeated thrice. The organic layer was dried with Na₂SO₄ and concentrated to get the crude product. The crude product was purified by column chromatography on silica using *n*-hexane and ethyl acetate mixture as eluent. All the products were characterized by ¹H NMR and ¹³C NMR.

7. Procedure for Reusability Test of **1b** as catalyst.

The **1b** (0.05 mol % Pd) and a mixture of 4-chlorobenzaldehyde (140 mg, 1 mmol), phenylboronic acid (110 mg, 1.1 mmol), and K₂CO₃ (415 mg, 3 mmol) in distilled water (3 mL) under argon atmosphere were placed in an oil bath at 60°C. After the reaction was finished, the product was extracted with hexane and the aqueous phase containing the Pd-TEG was loaded with the reactants and base. The catalyst in water could be reused without any obvious loss of the activity 17 runs.

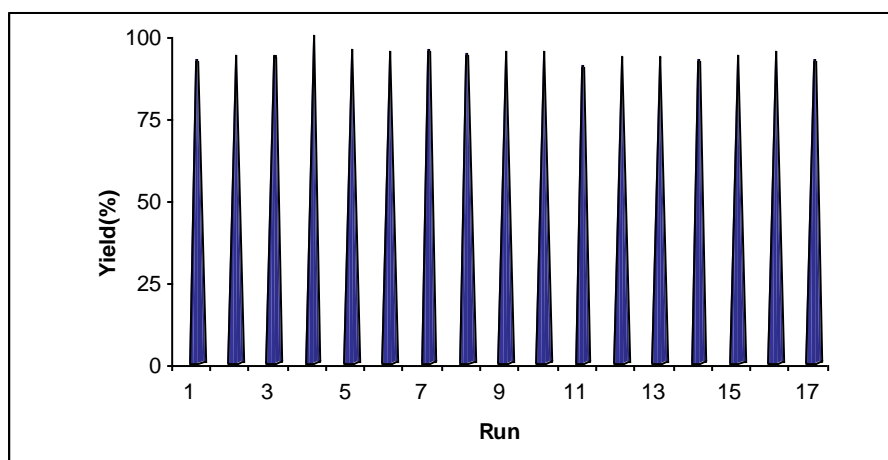


Figure 2S. Recyclability of catalyst **1b** for the Suzuki reaction of 4-chlorobenzaldehyde.

8. Procedure for Dialysis recovery of **1b:** In order to separate **1b** from other water-soluble species in the reaction mixture such as the excess of K₂CO₃, and boronic acid salts, a dialysis technique was performed. A 5 cm length of the dialysis tubing ((molecular weight cut-off = 10 kDa.) was washed with distilled water, and one end tied shut. On completion of the reaction, the reaction mixture was transferred into the dialysis

tubing and the open end of the tubing was tied. This dialysis bag was placed in a beaker containing 400 ml deionized water and allowed to equilibrate for 48h. To ensure a perfect separation, the used dialysate was changed every 8h.

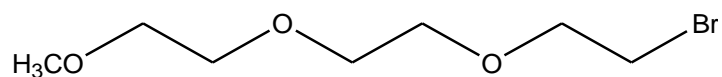


Figure 3S. Recyclability of catalyst **1b** from aqueous reaction residue using a simple dialysis technique.

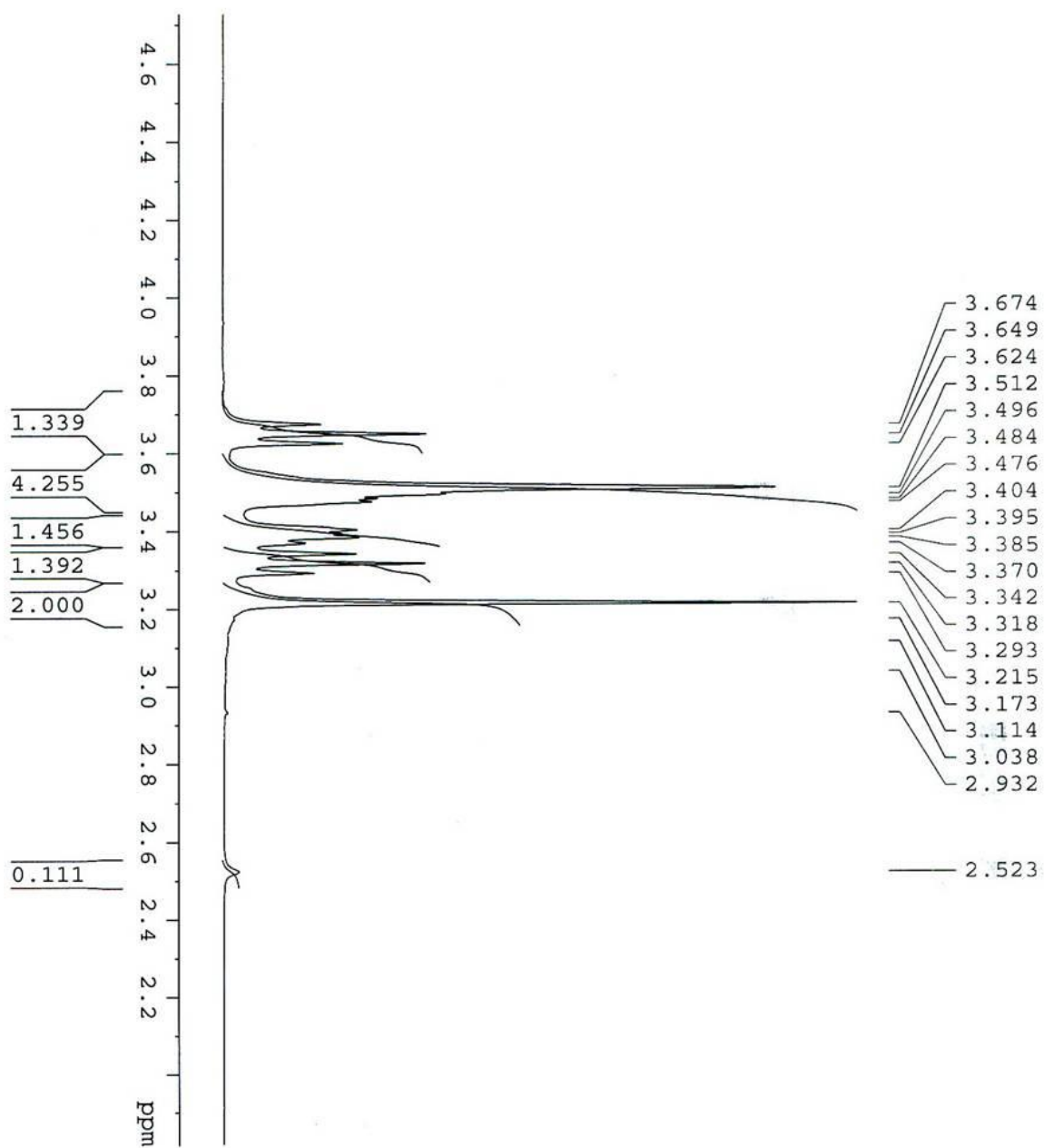
9. General procedure for the study of the effects of Hg(0) on 1b reactivity:

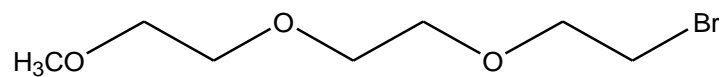
In a typical Suzuki reaction, Cen-Pd as catalyst (0.005 mol%), 3-bromoacetophenone (5.0 mmol), phenylboronic acid (6.0 mmol) K_2CO_3 (15 mmol), and poisoning agent (400 equivalent to total palladium content) were mixed in 10 ml H_2O in a three-neck round-bottom flask equipped with a condenser and rubber septum. The reaction assembly was then connected to the manifold of a Schlenk line and was gently purged with argon for 10 min. The reaction mixture was then allowed to heat in an oil bath at 60 °C with constant stirring. Aliquots were taken from the reaction mixture periodically, extracted with n-Hexane or Ether, and conversion was determined by GC chromatography.

10. ^1H and ^{13}C -NMR spectra data.

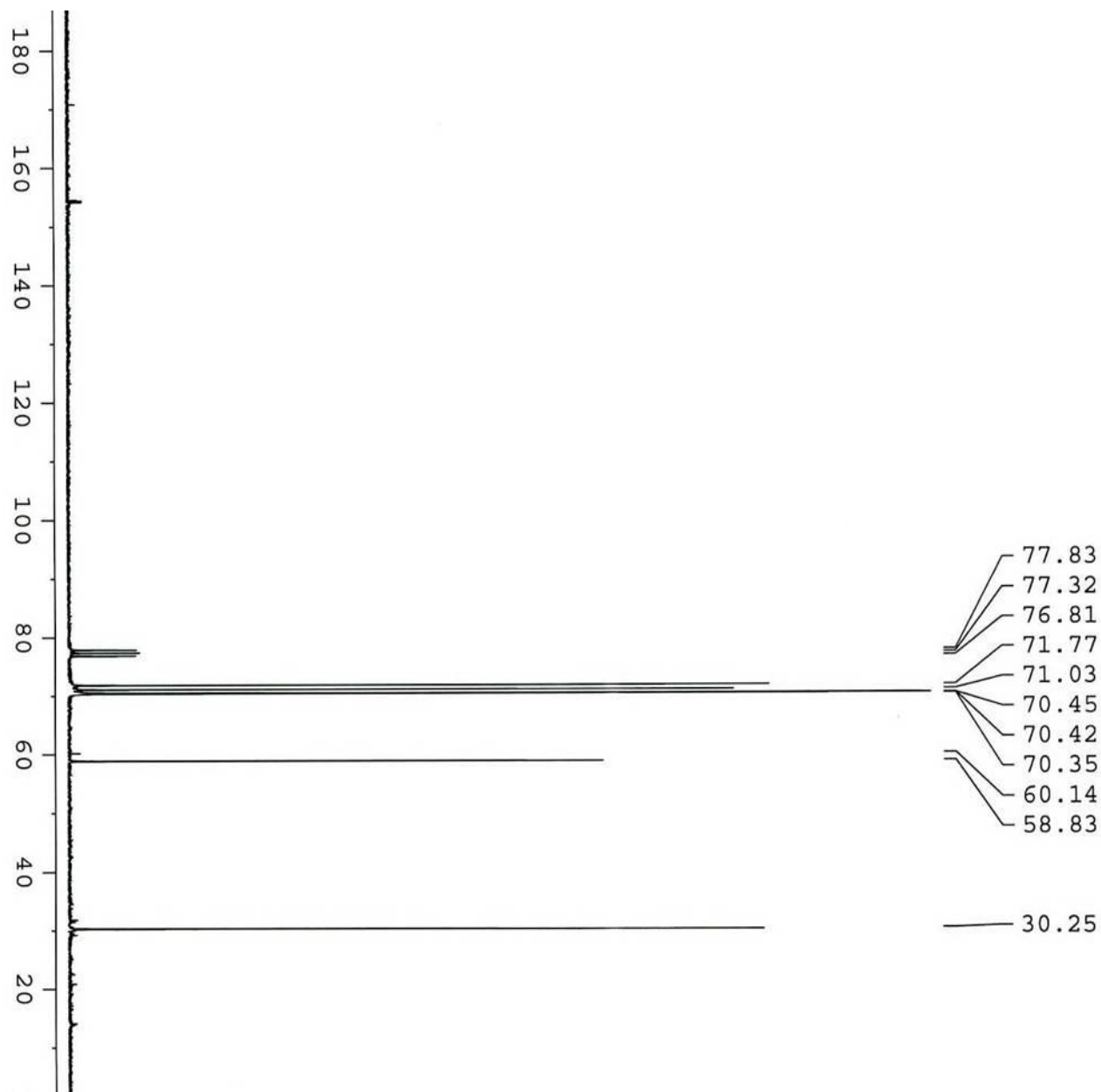


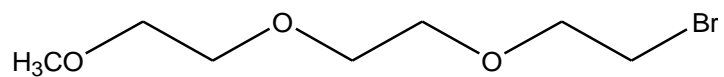
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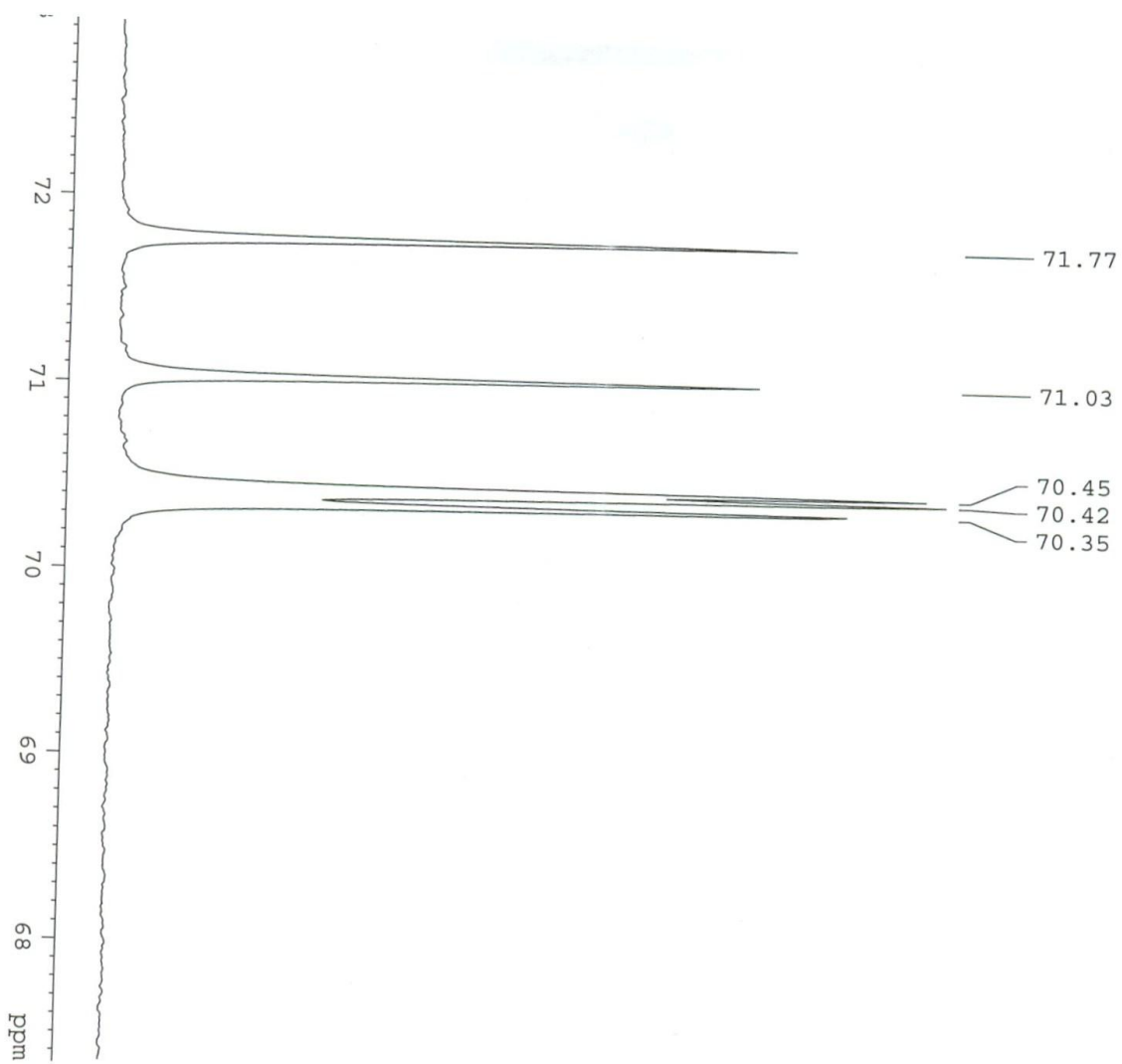


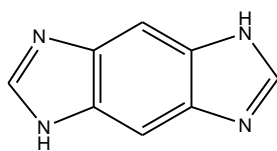
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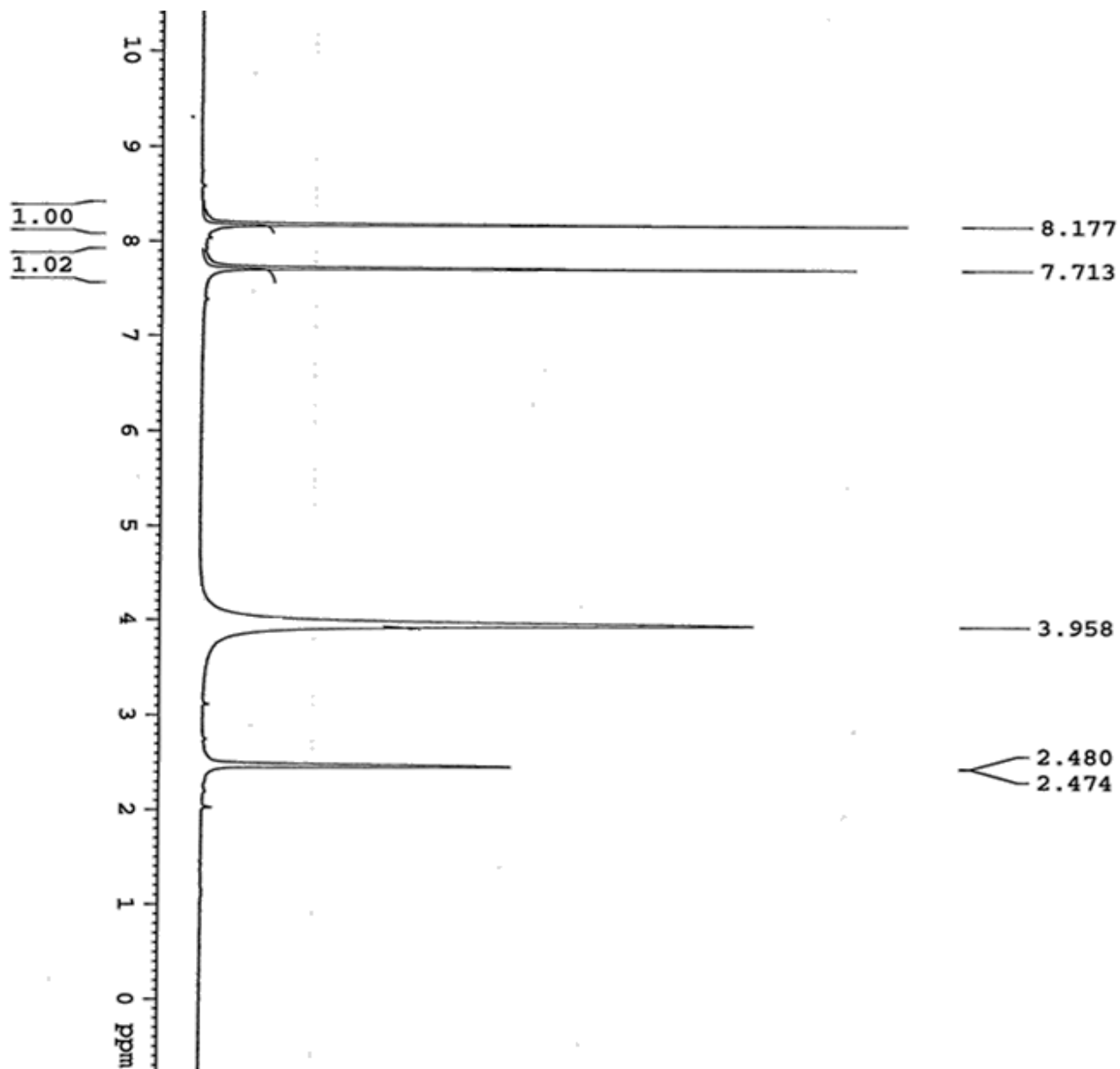


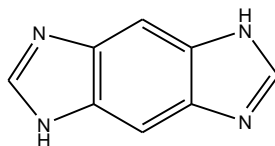
1-(2-(2-methoxyethoxy)ethoxy)-2-bromoethane (in CDCl₃)



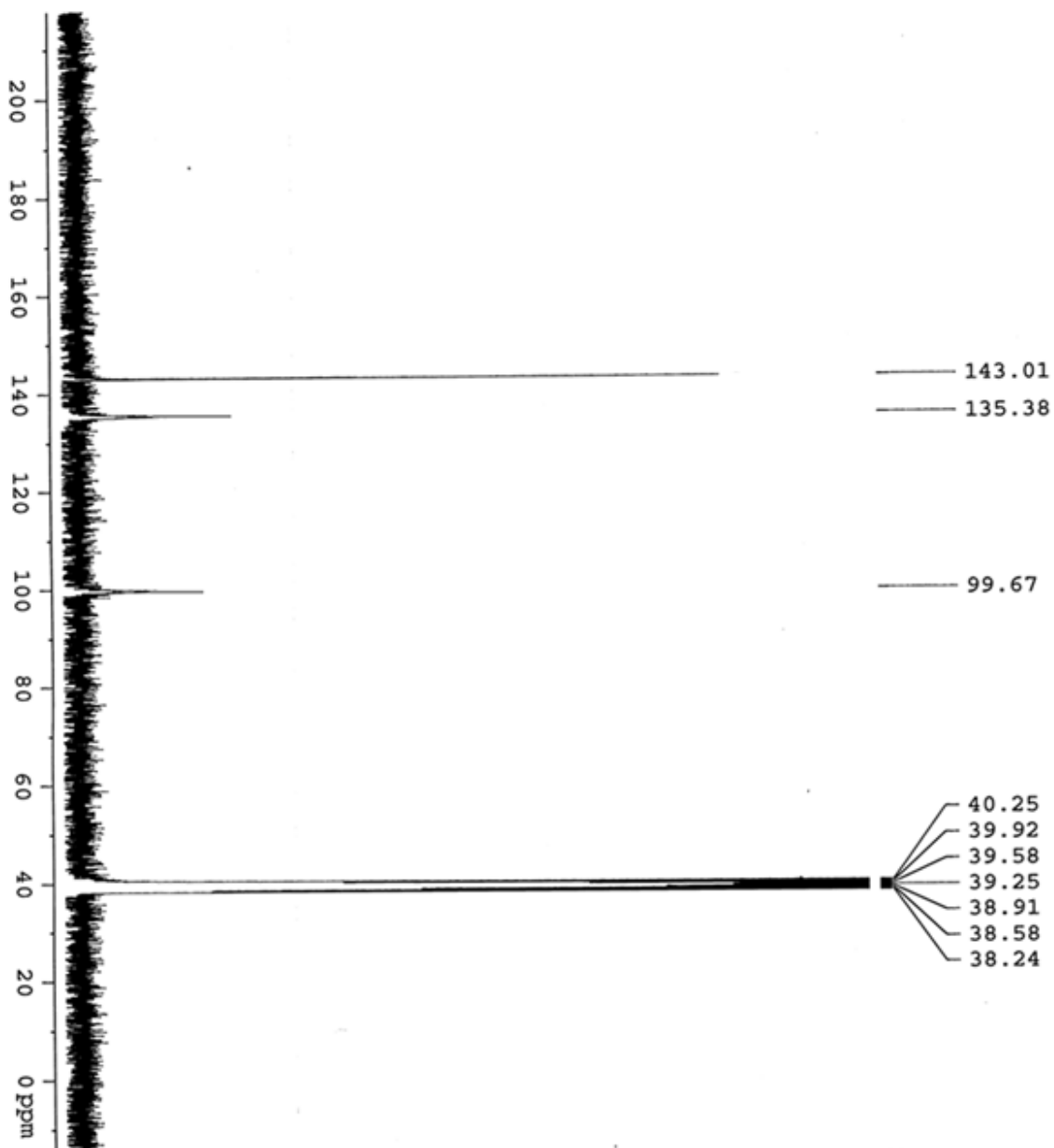


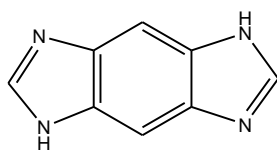
Benzo-bis(imidazole)(in DMSO-*d*₆, D₂O)



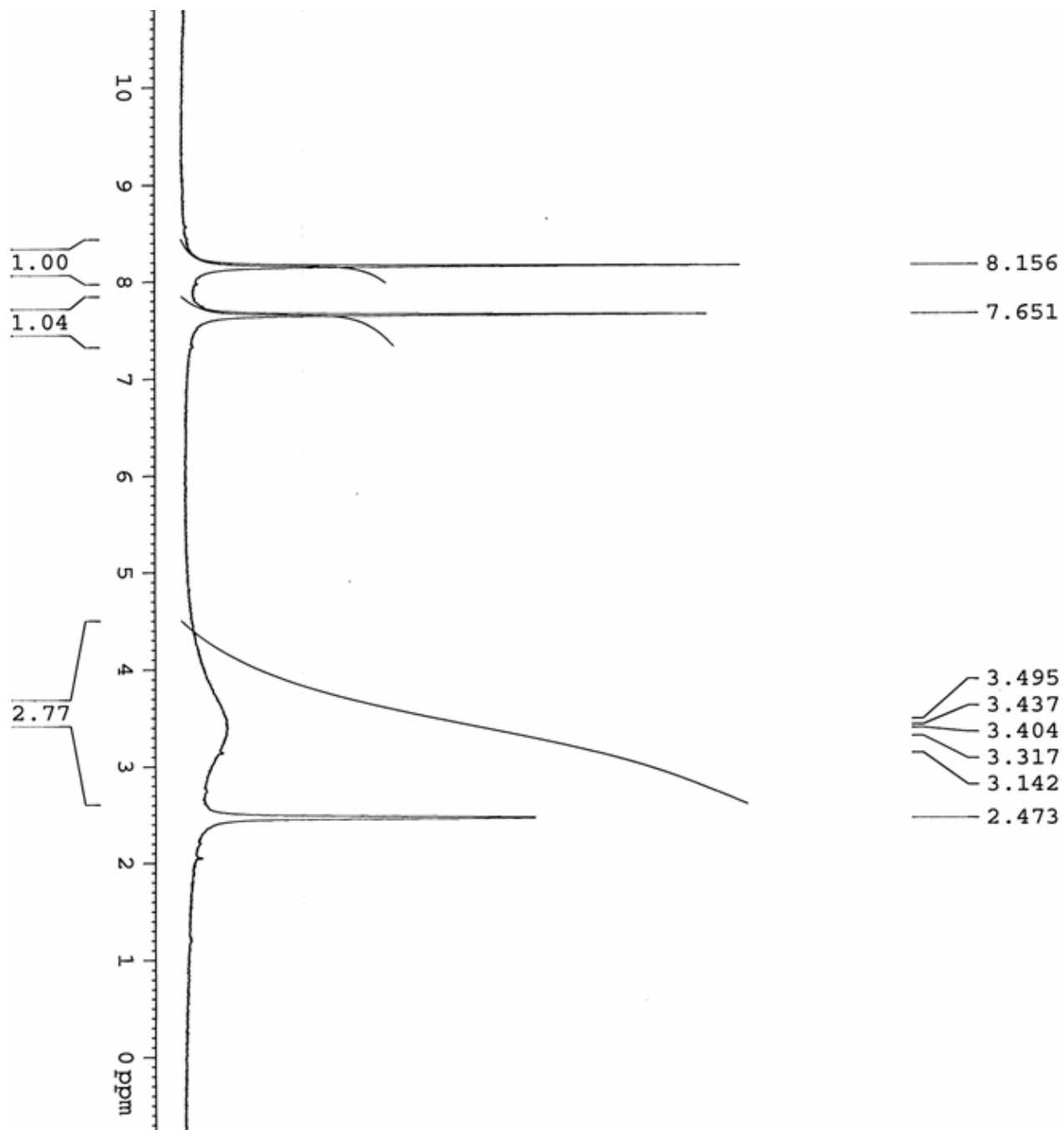


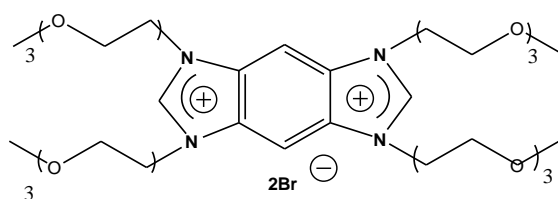
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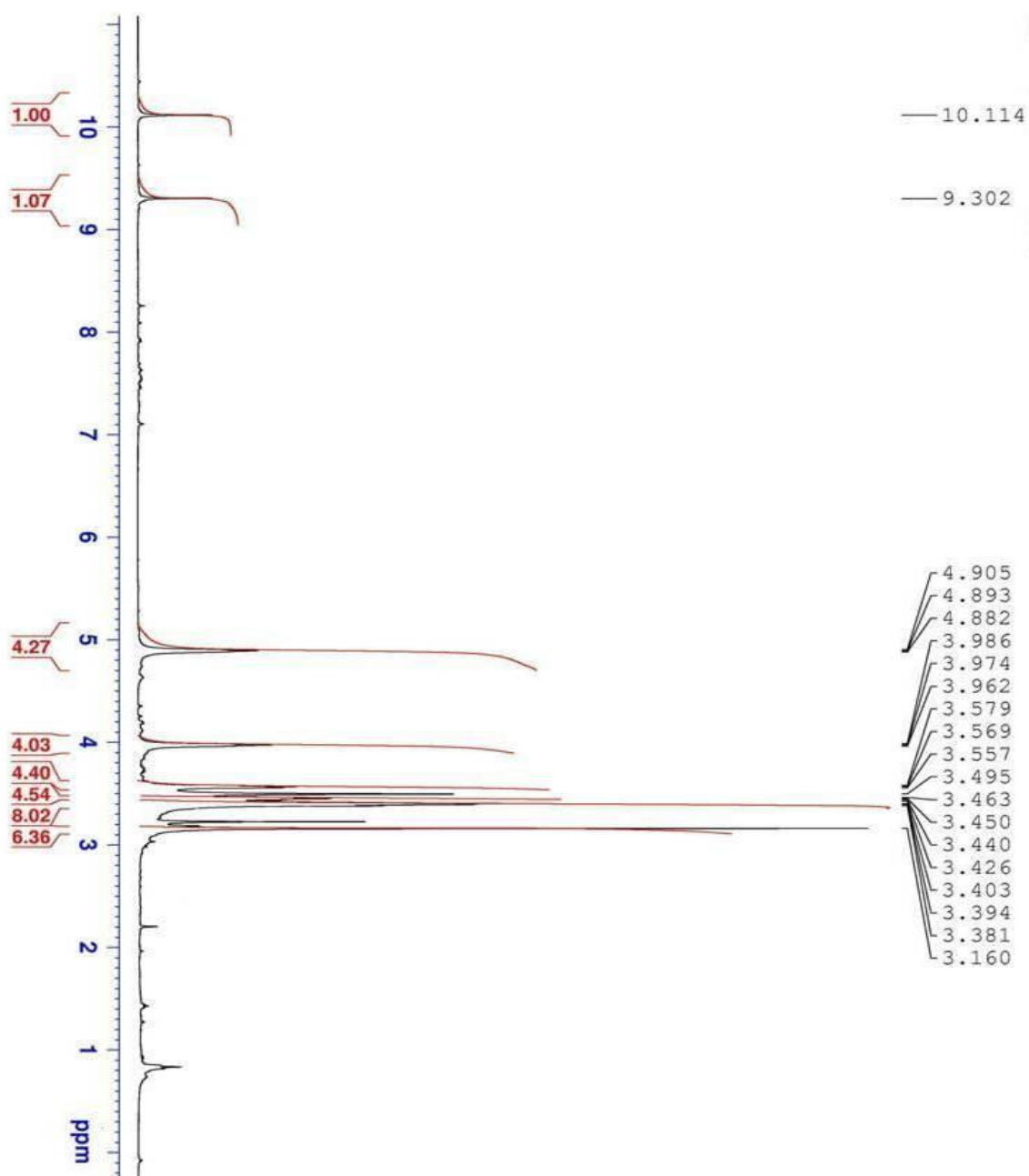


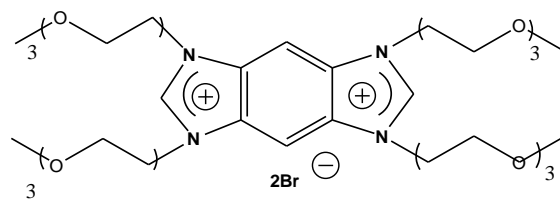
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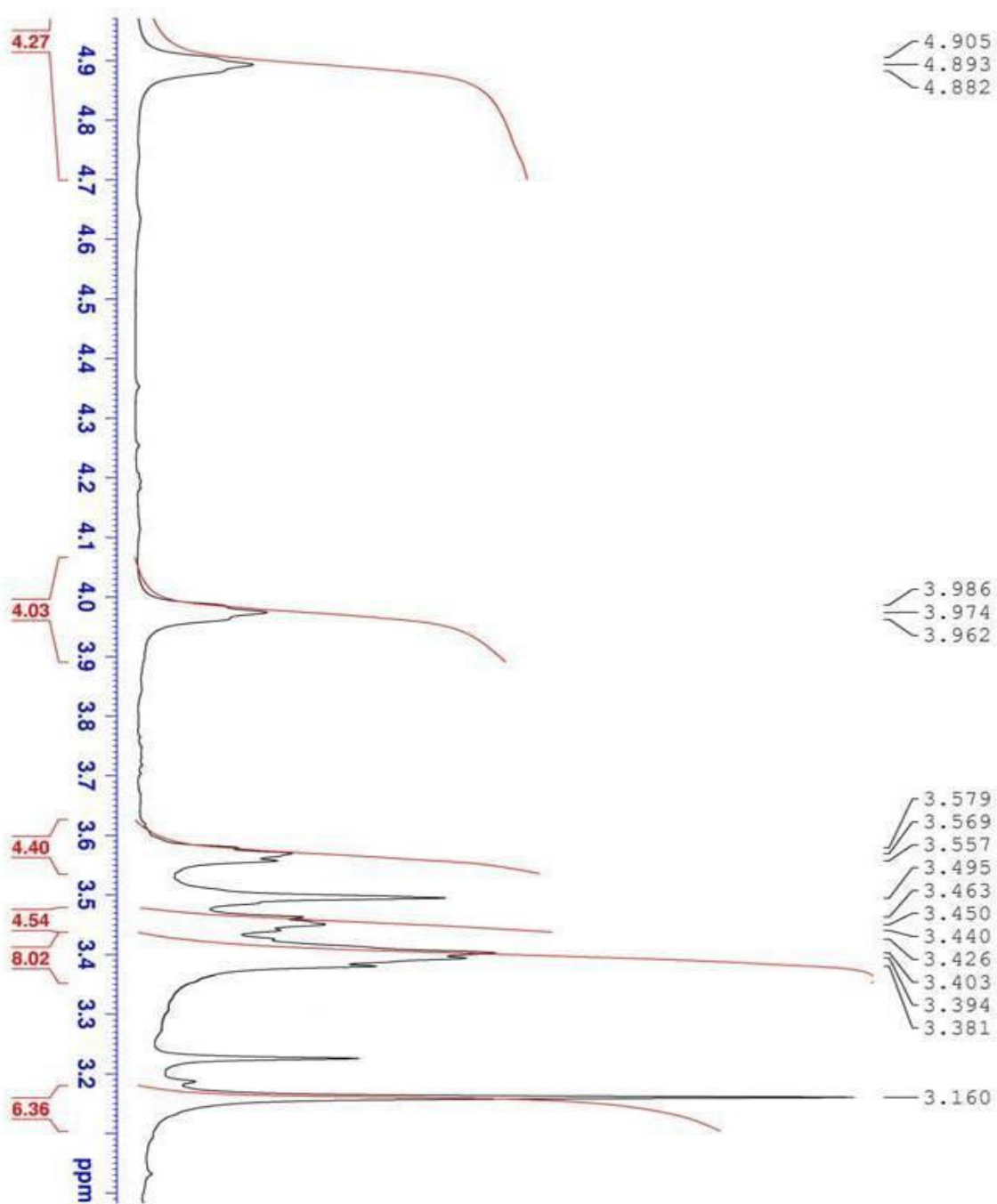


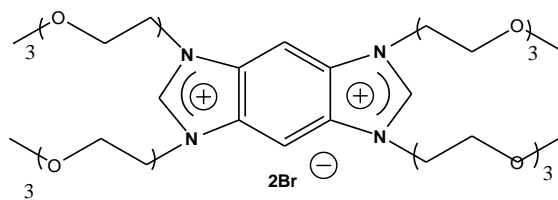
Tetra(triethylene glycol) benzo-bis(imidazolium) bromide (in DMSO-d₆)



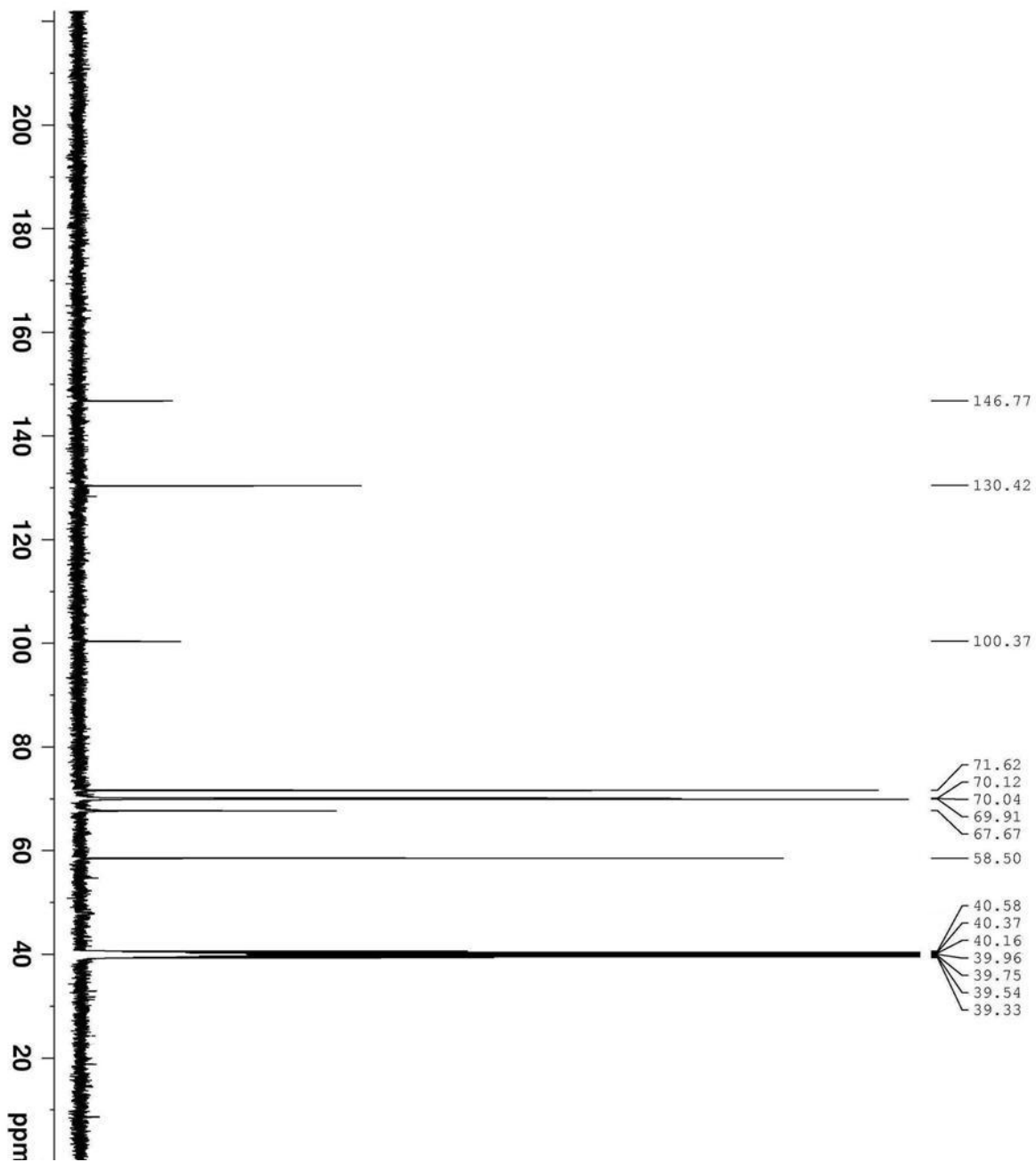


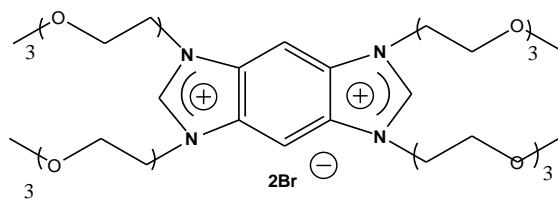
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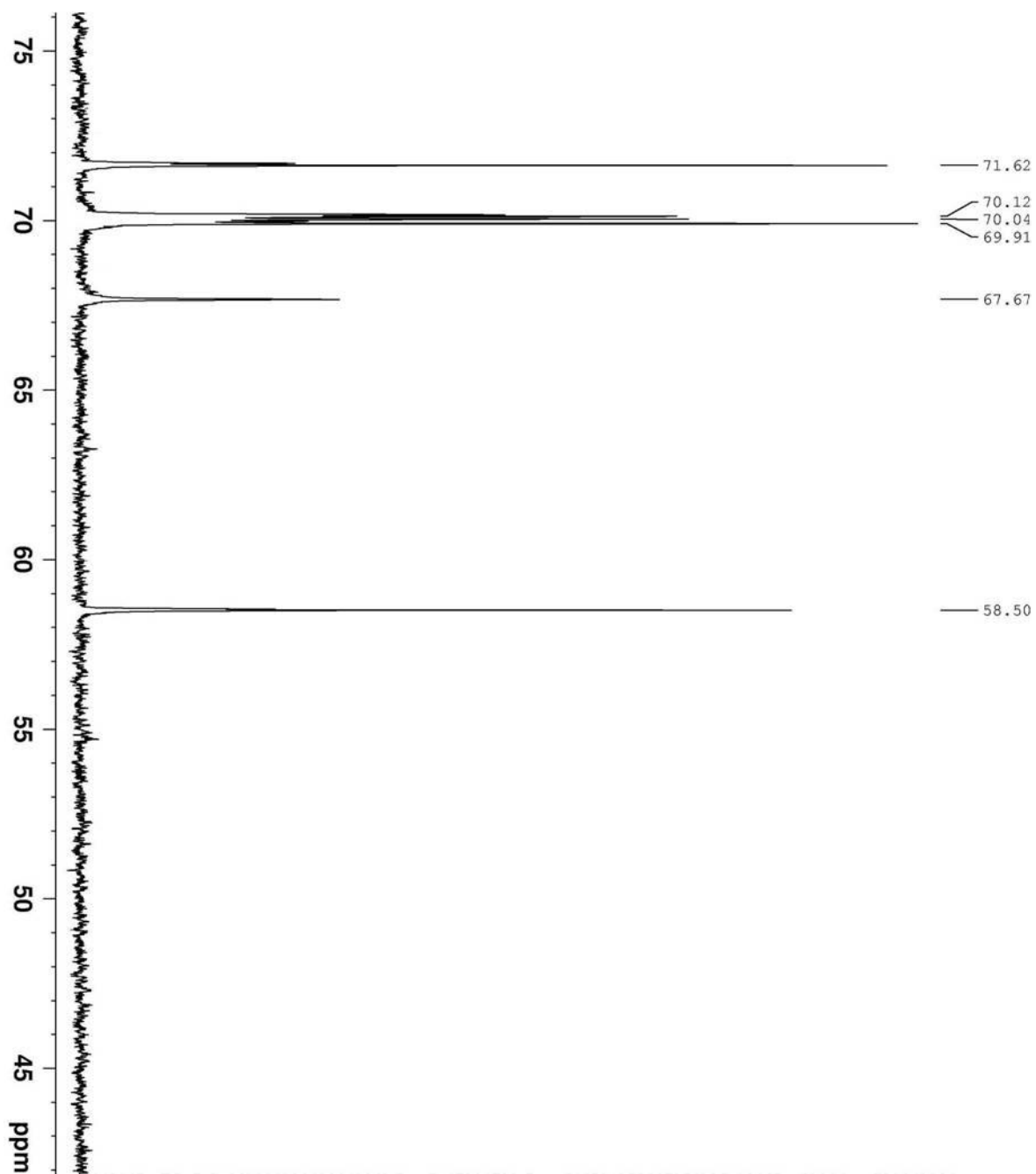


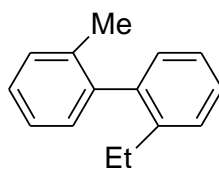
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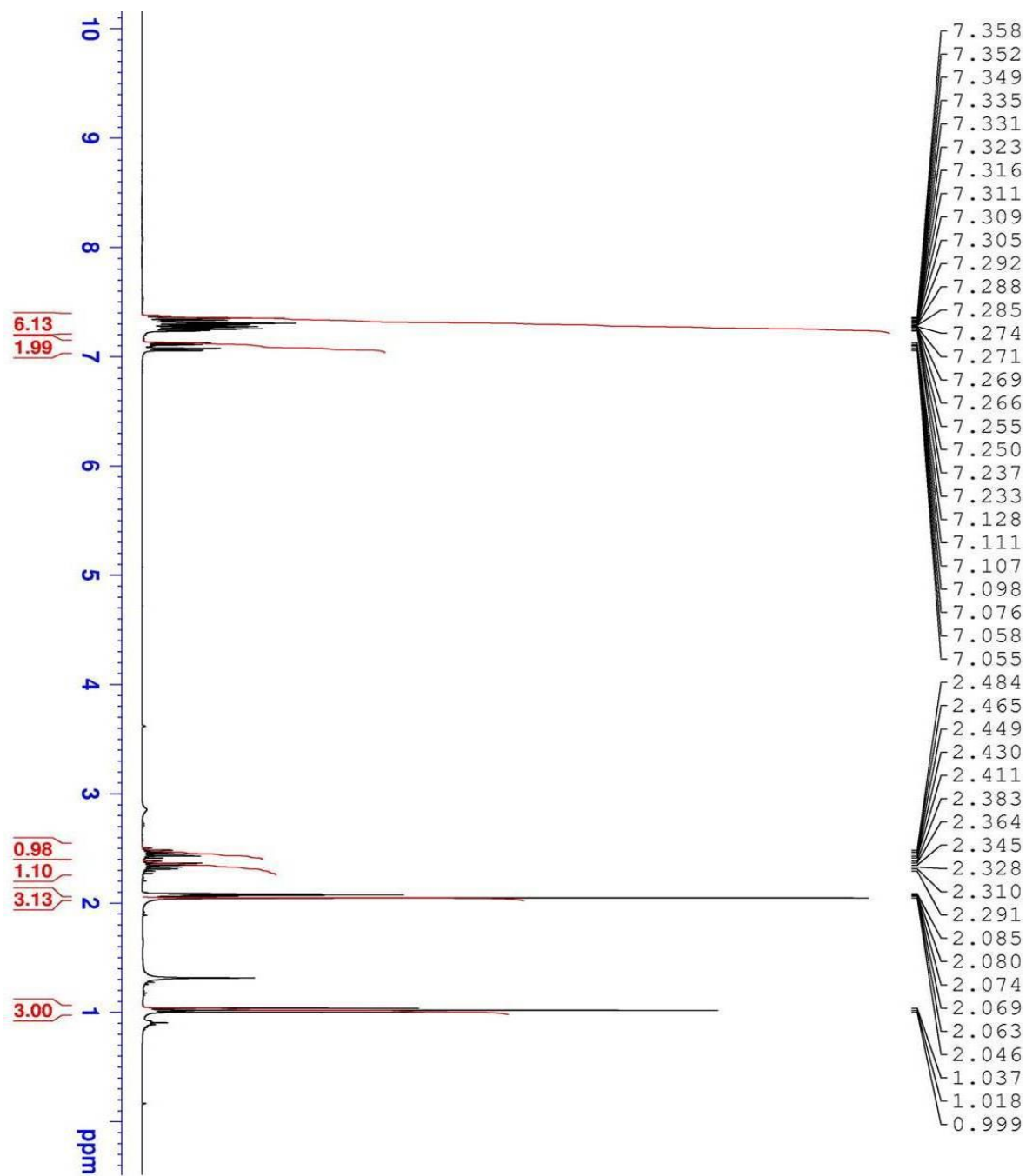


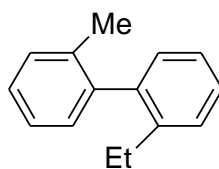
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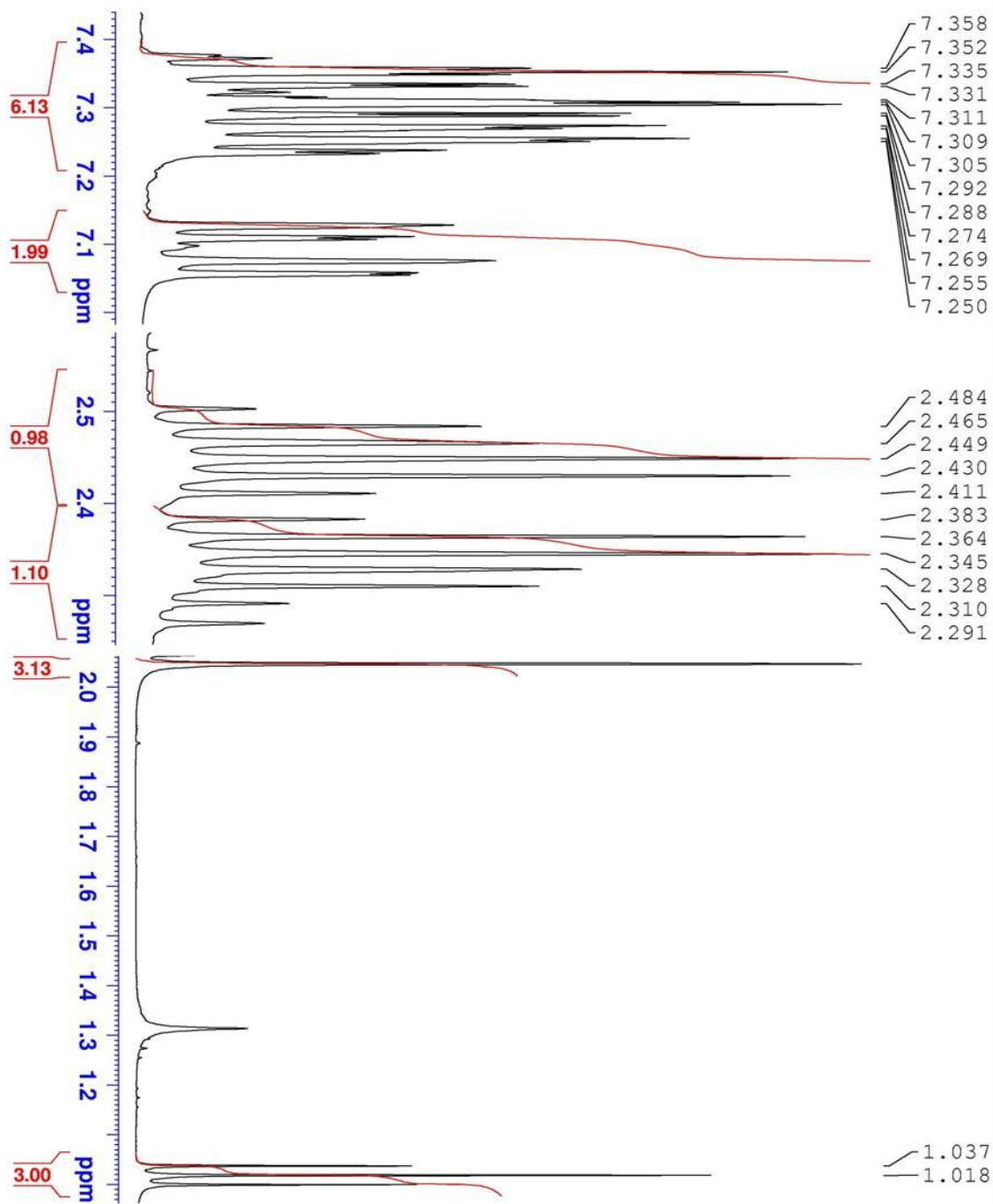


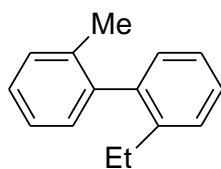
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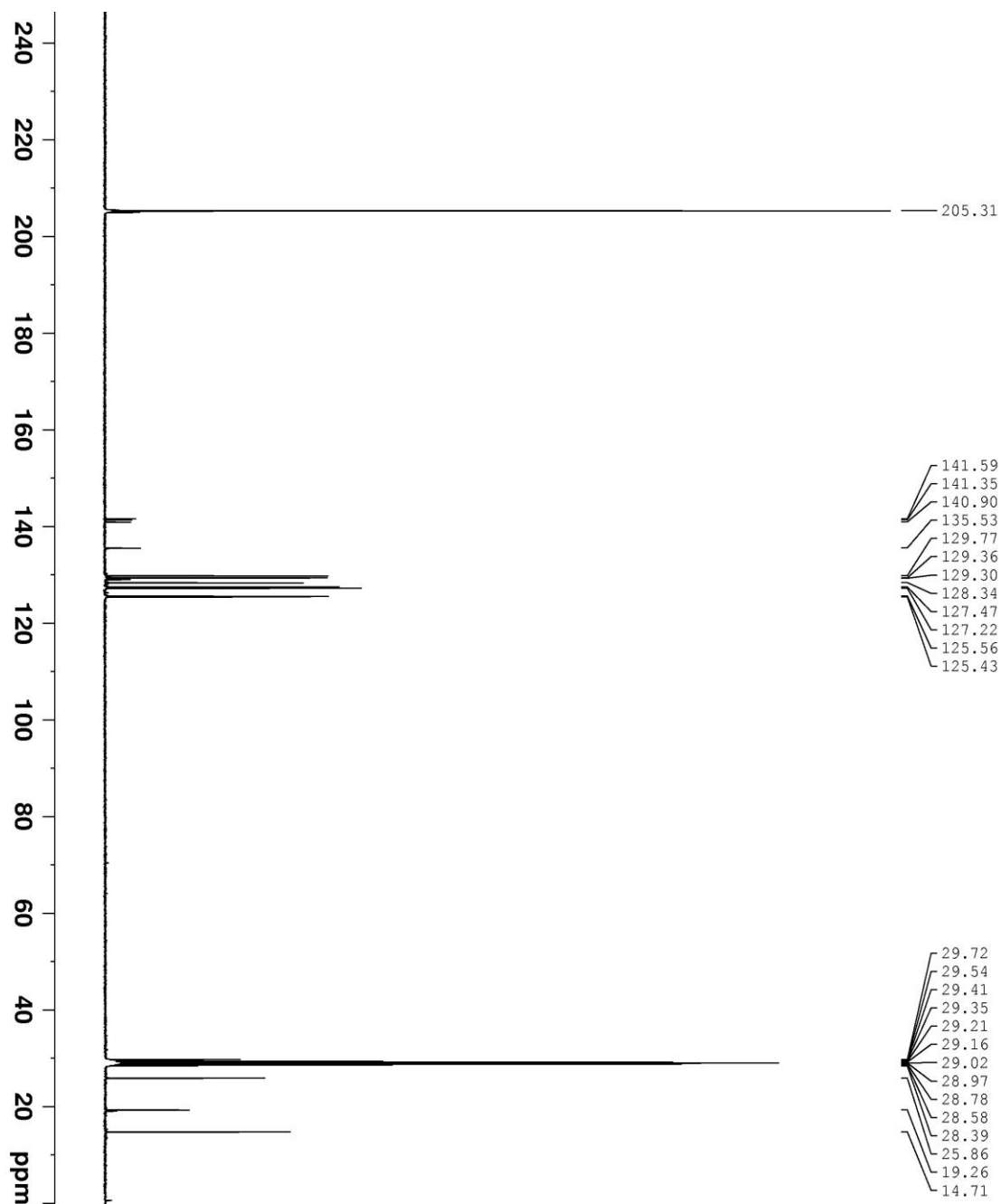


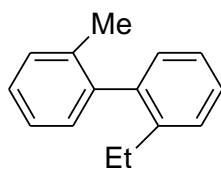
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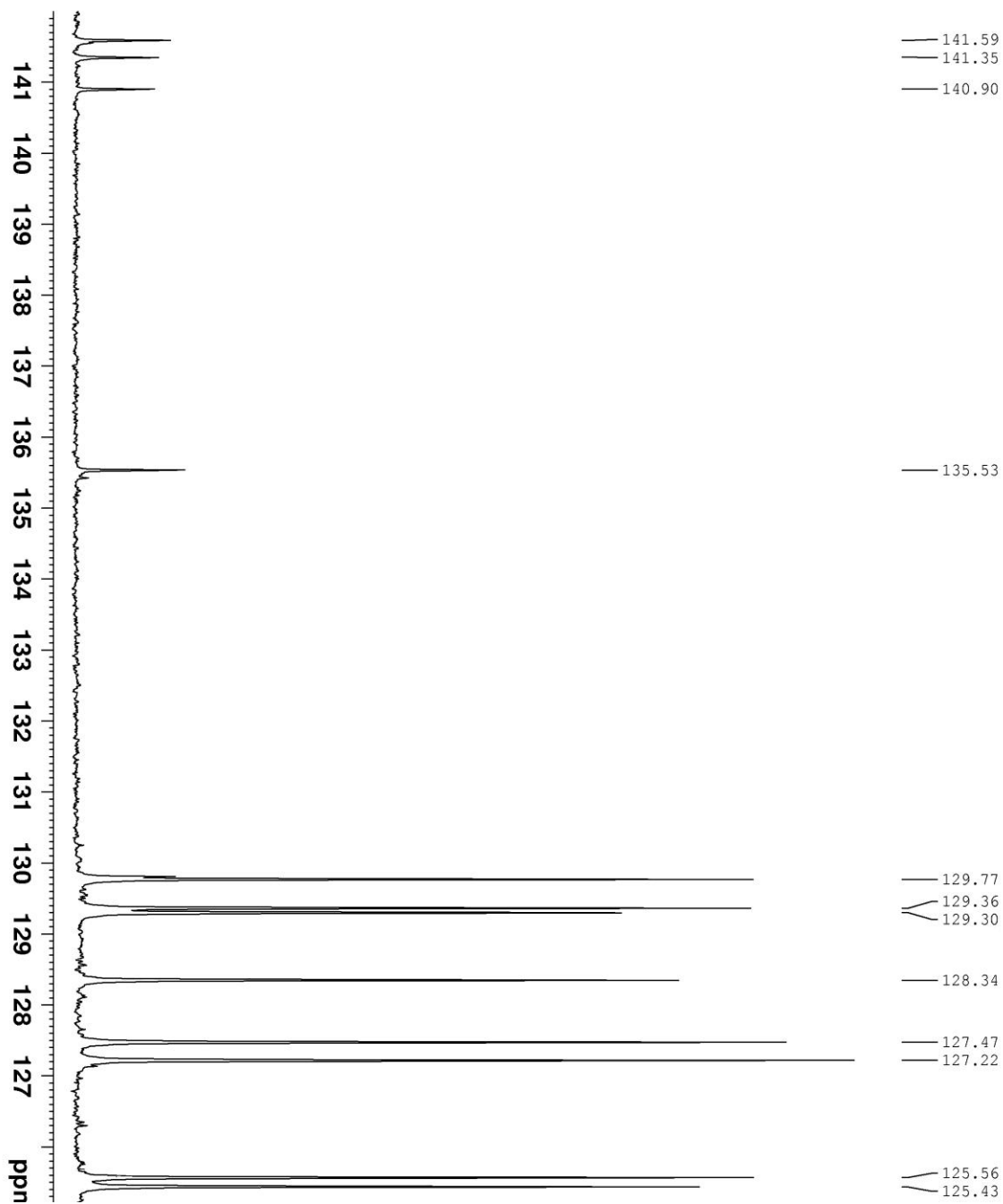


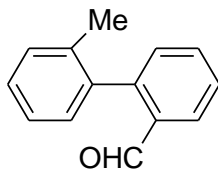
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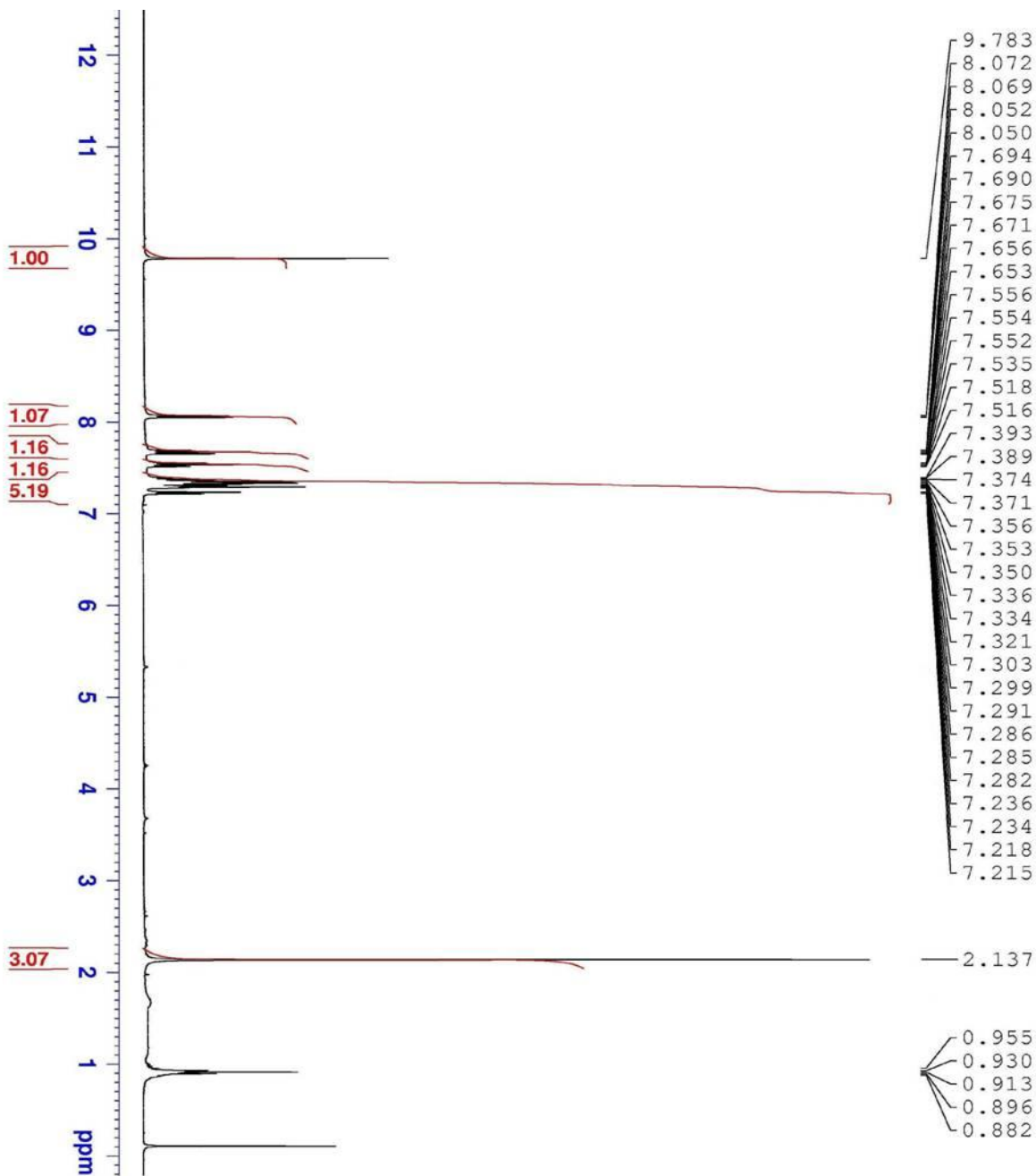


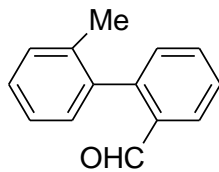
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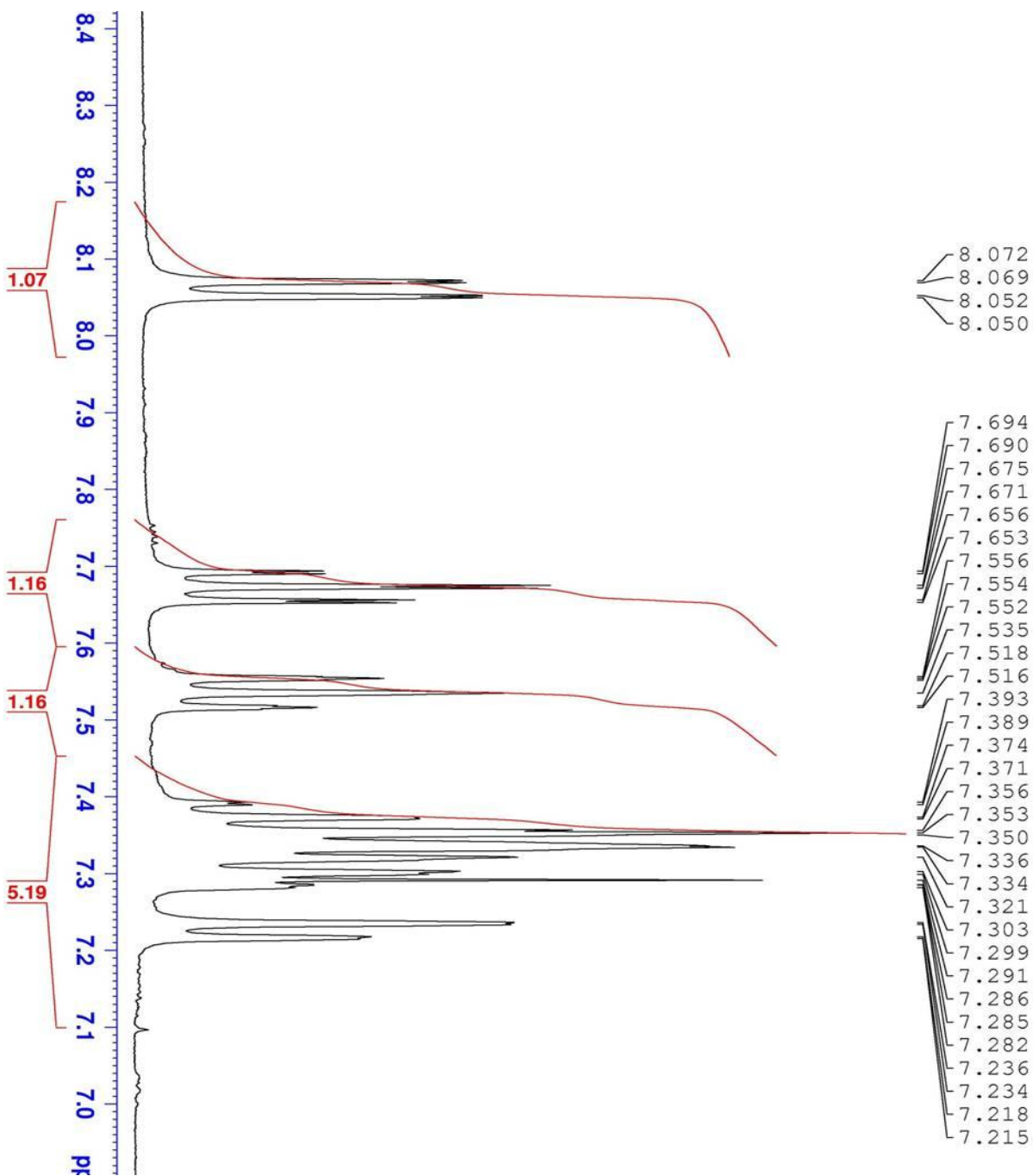


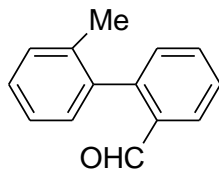
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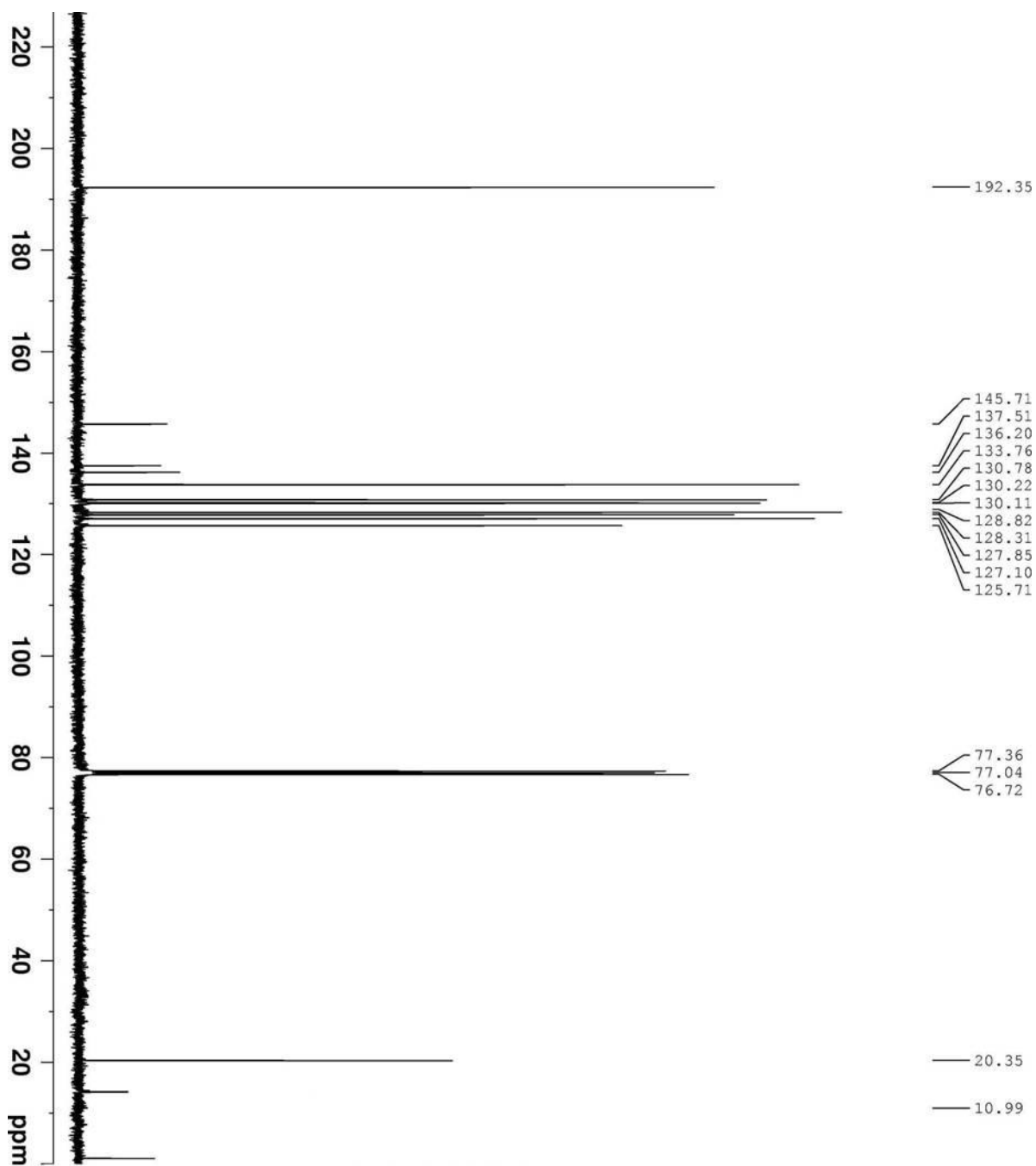


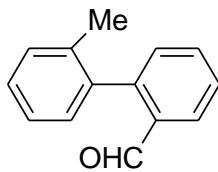
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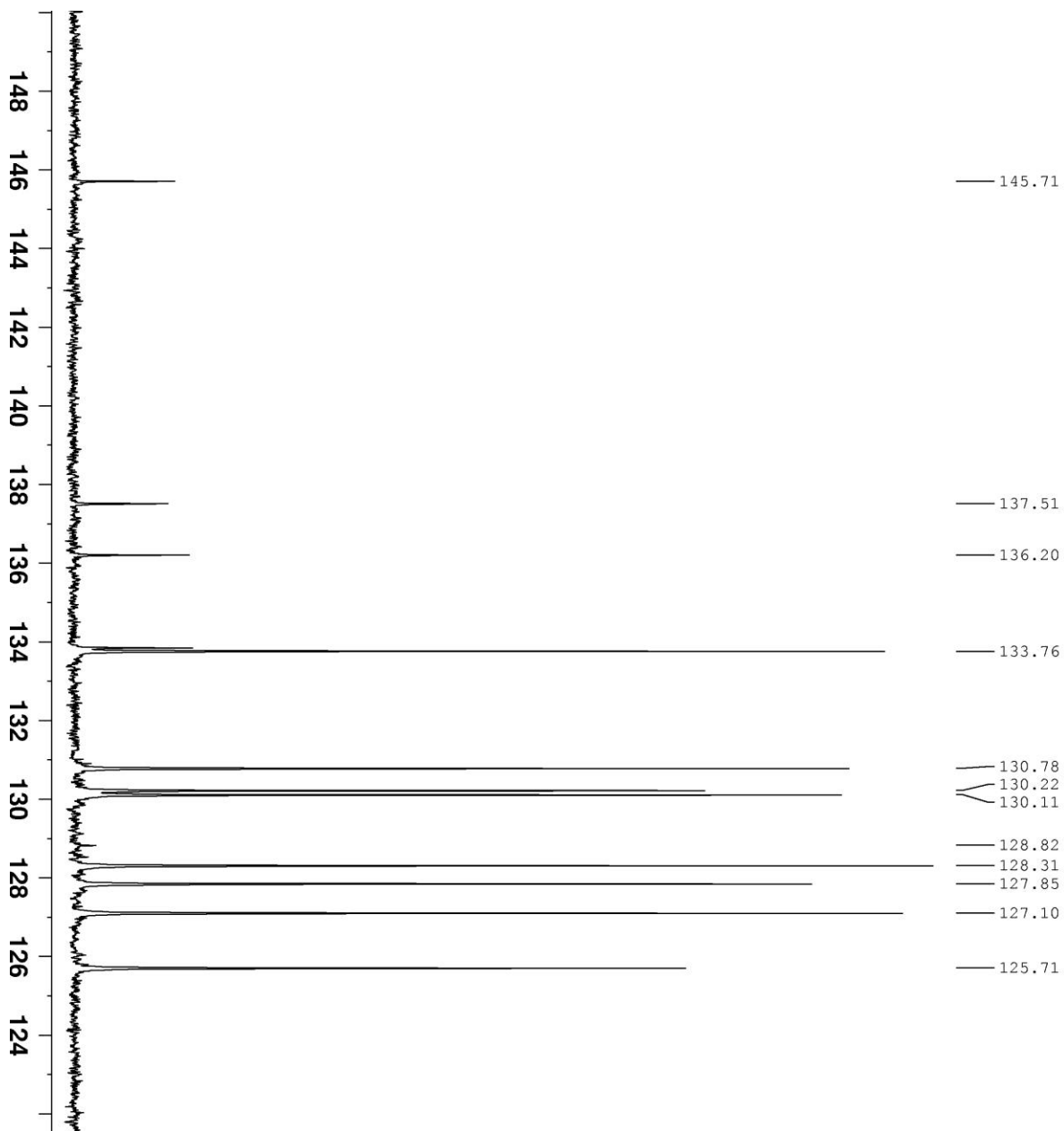


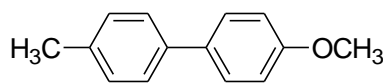
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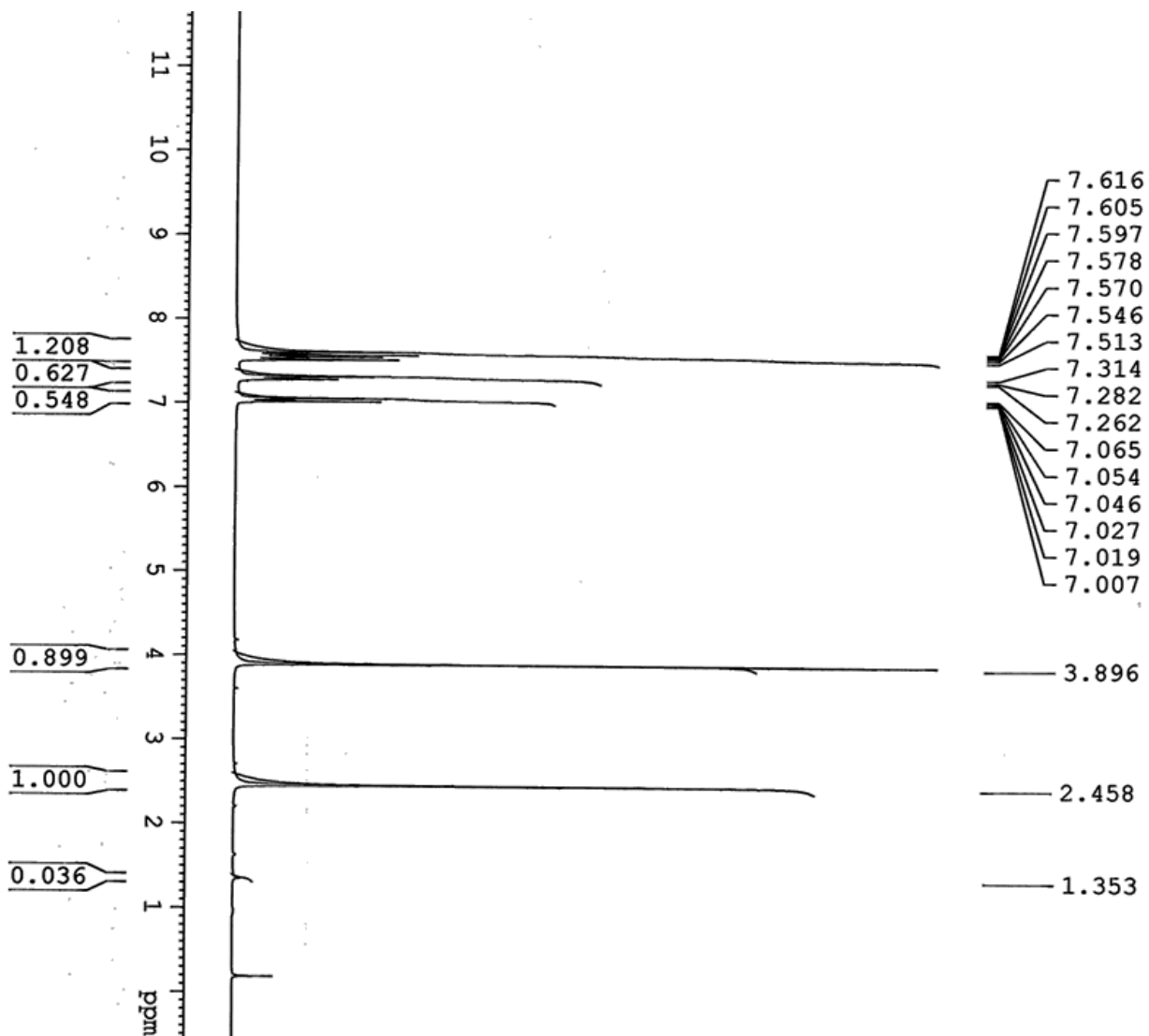


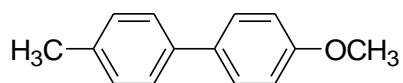
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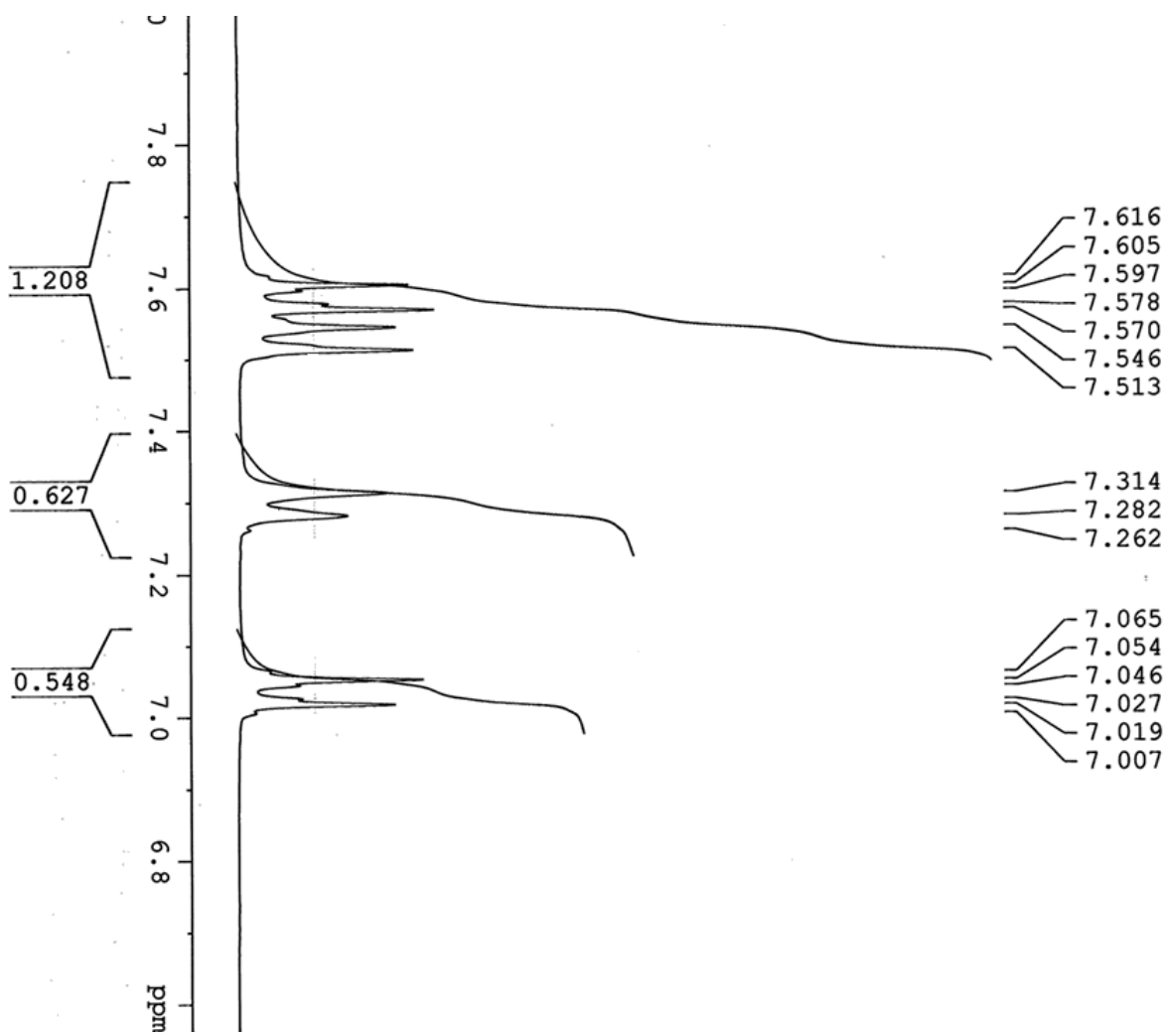


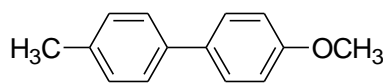
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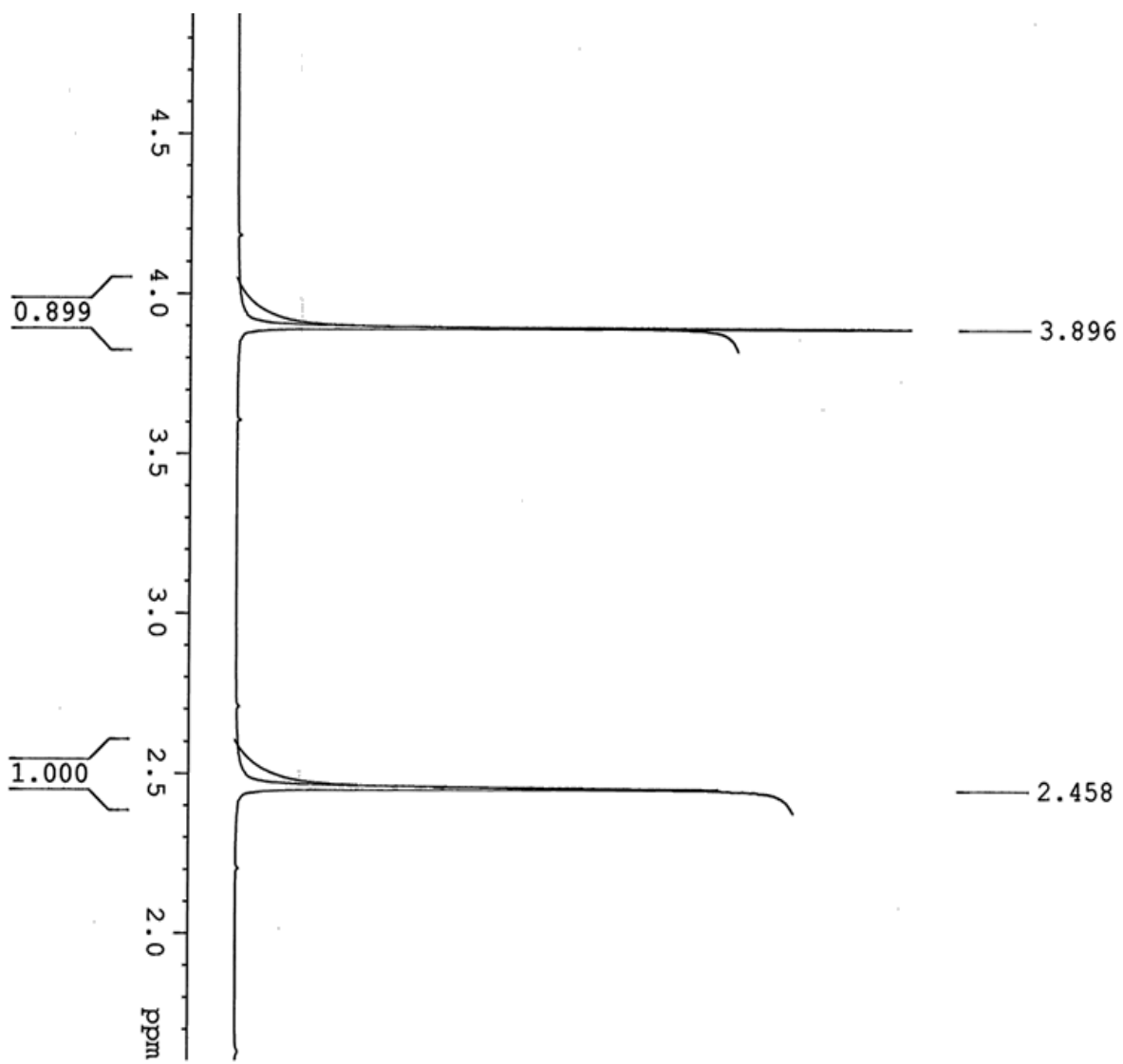


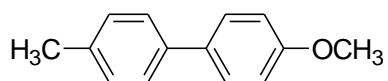
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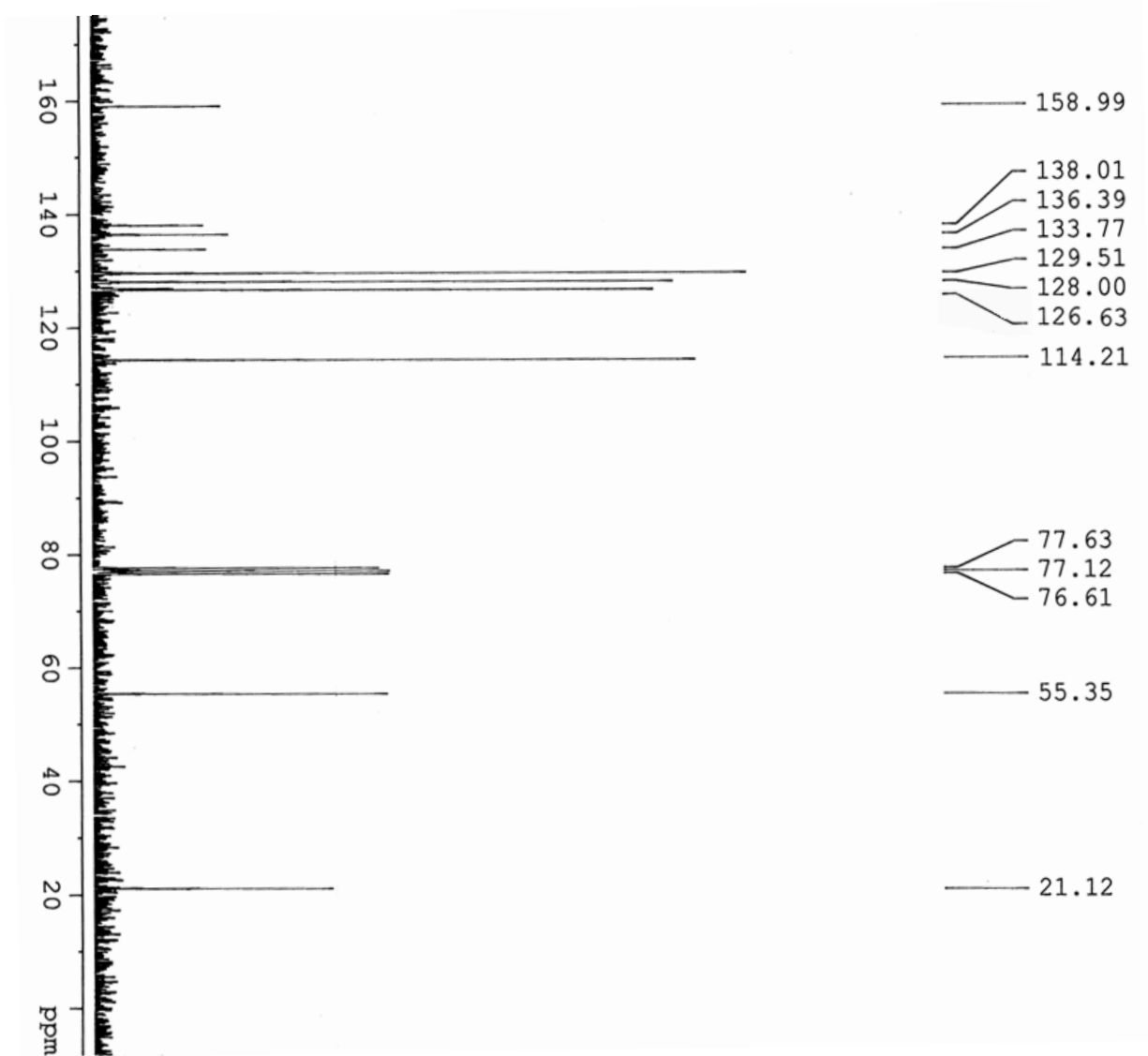


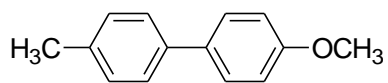
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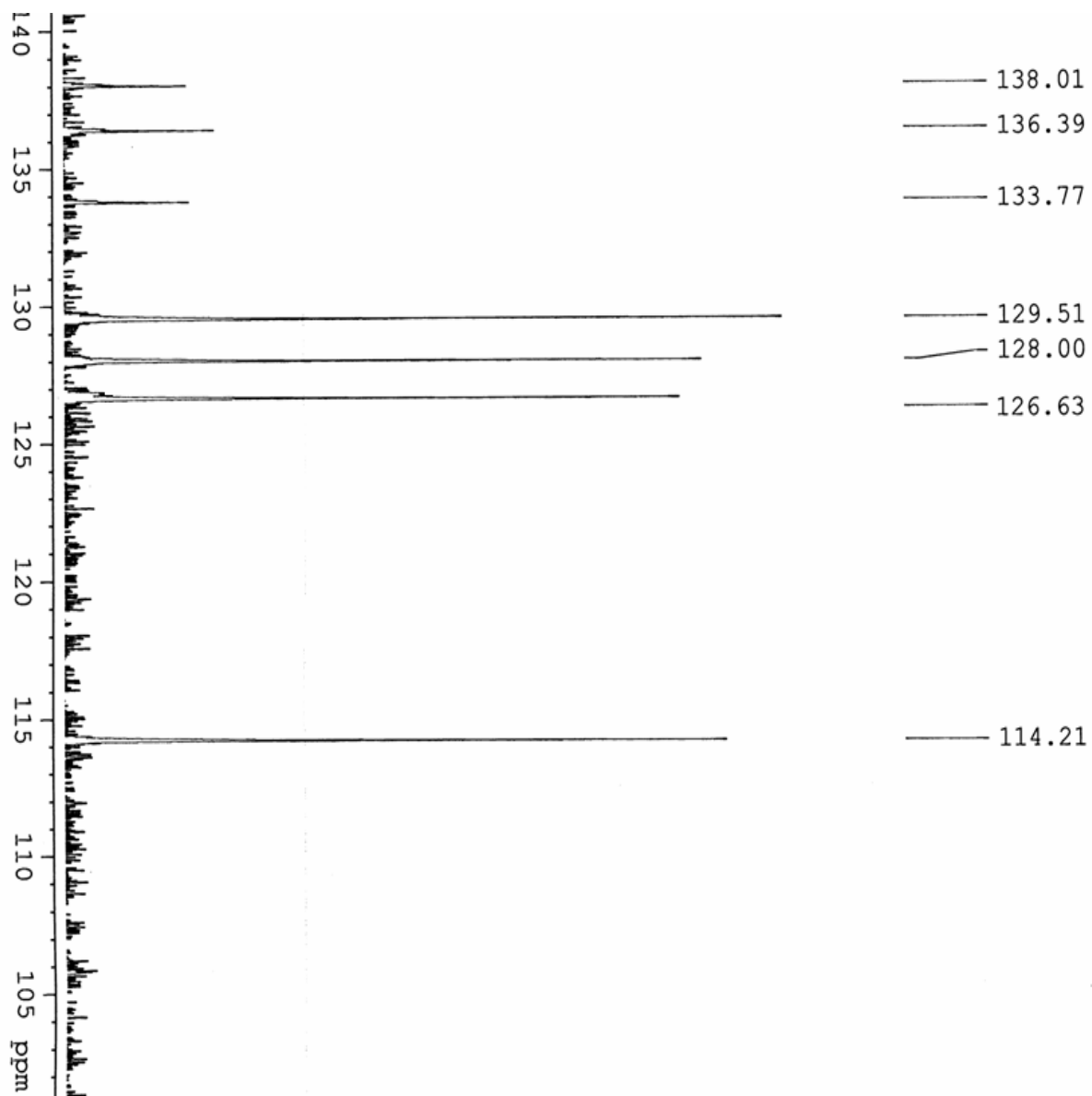


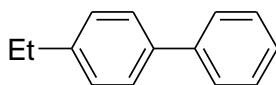
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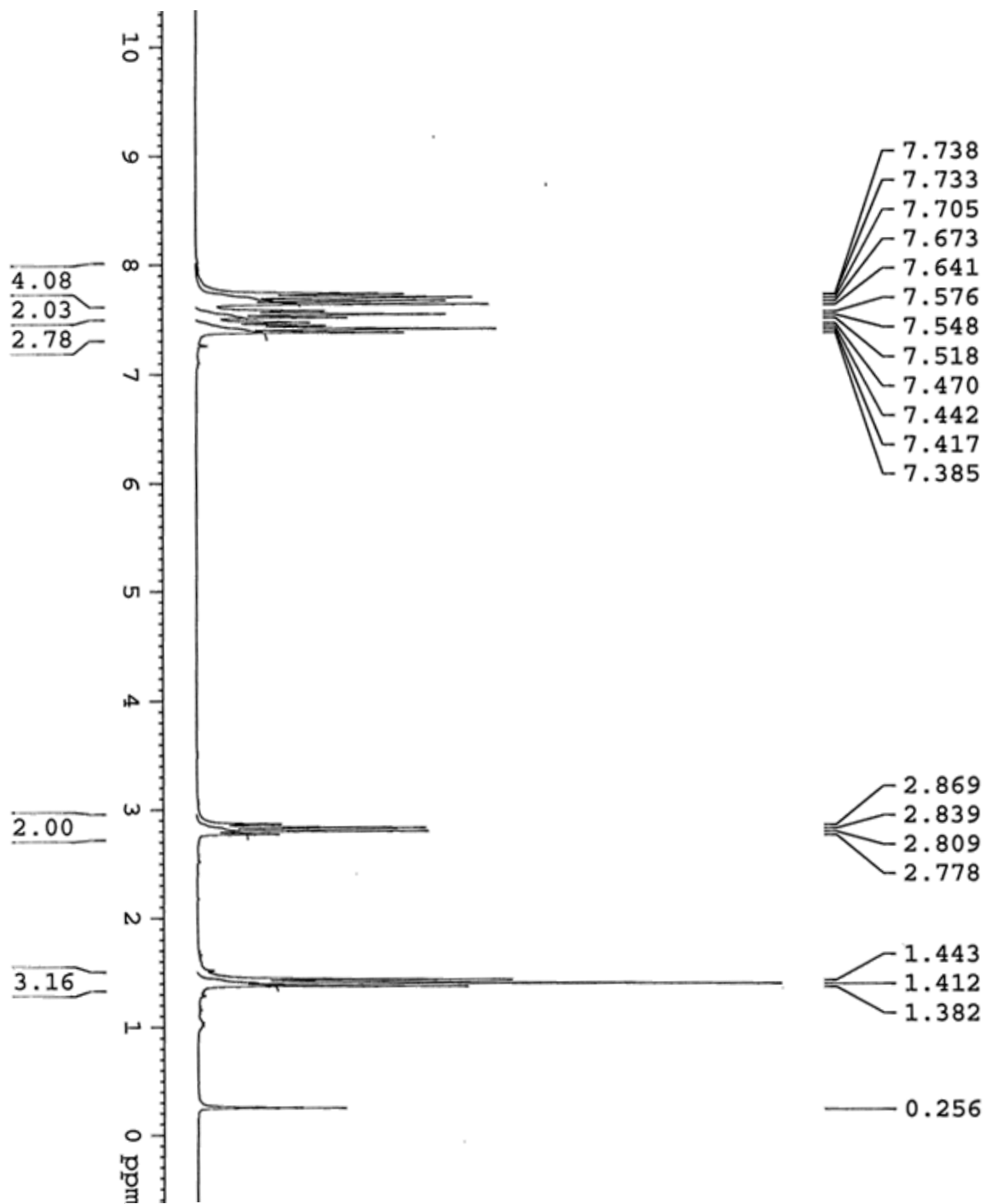


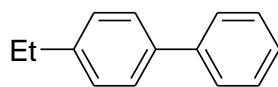
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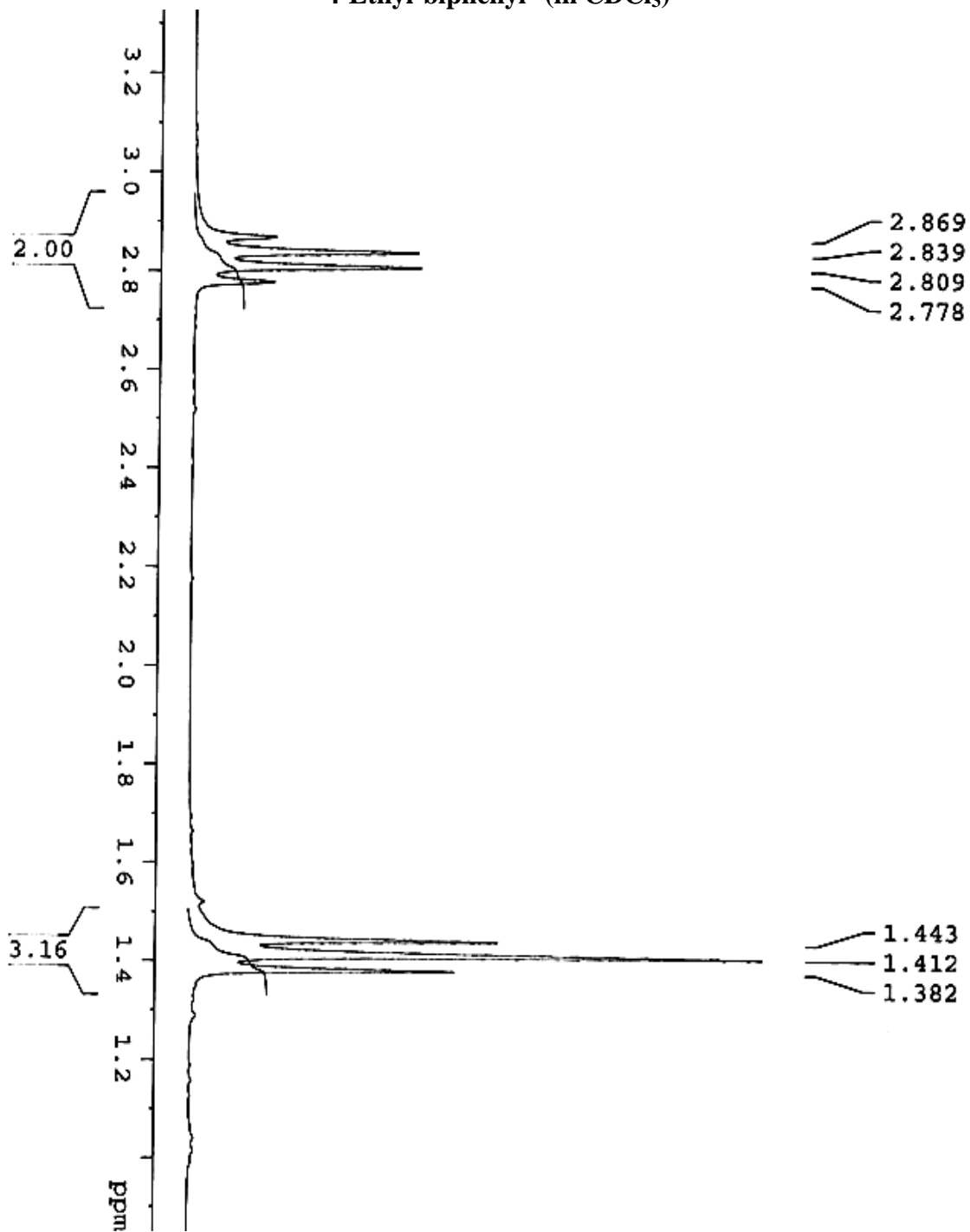


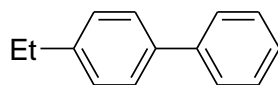
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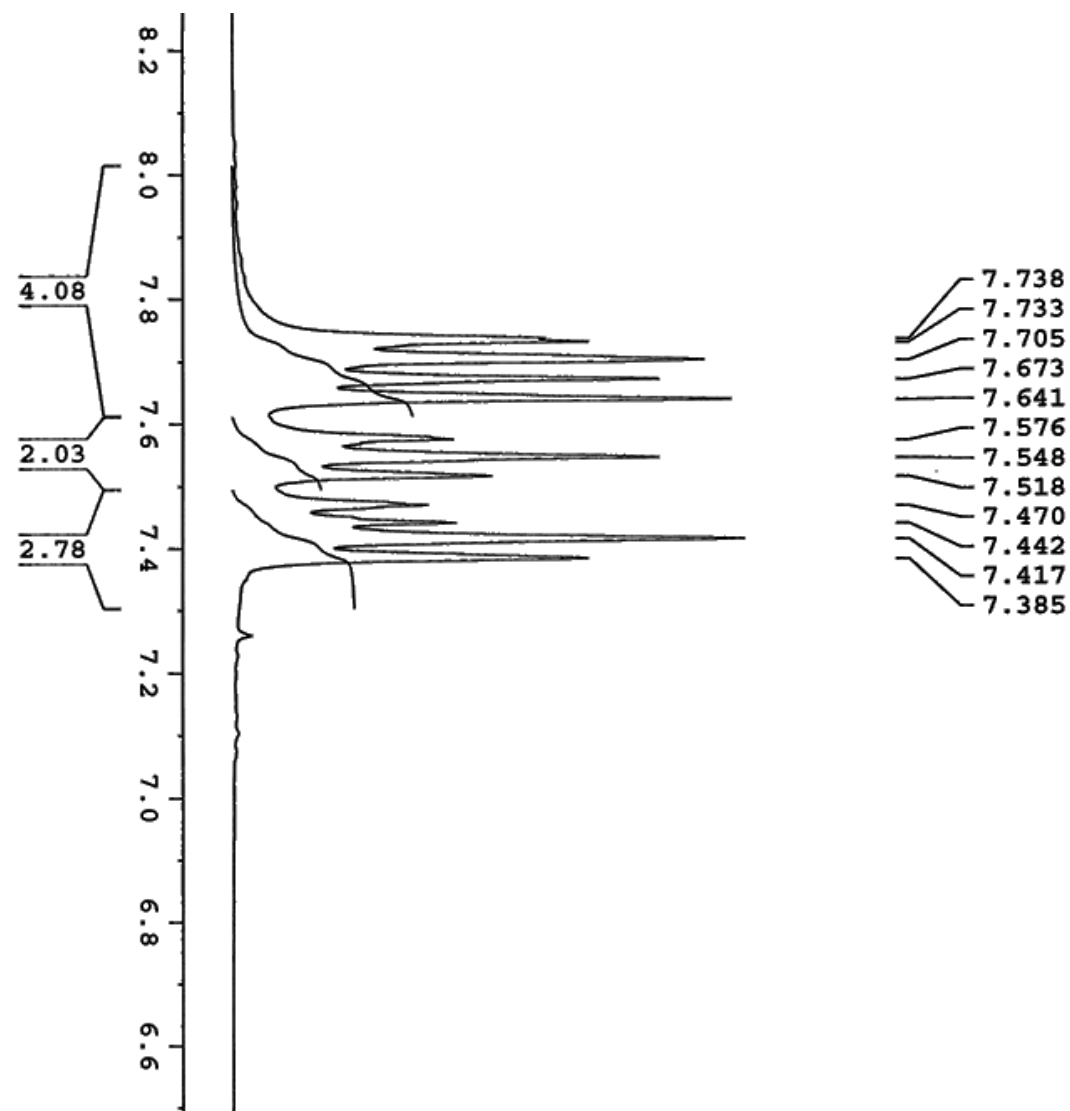


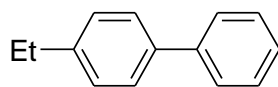
4-Ethyl-biphenyl (in CDCl₃)



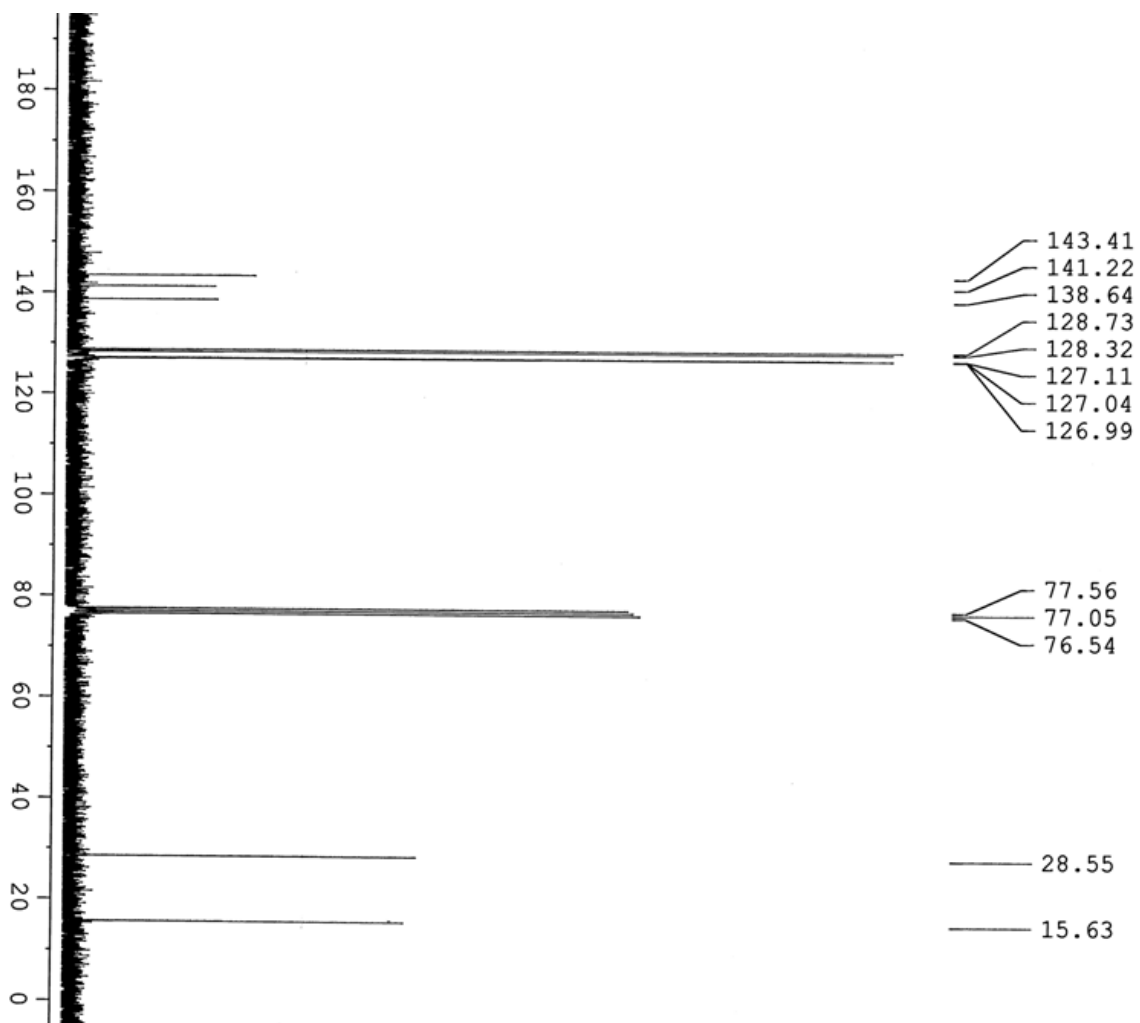


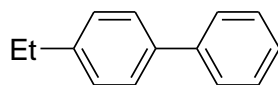
4-Ethyl-biphenyl (in CDCl₃)



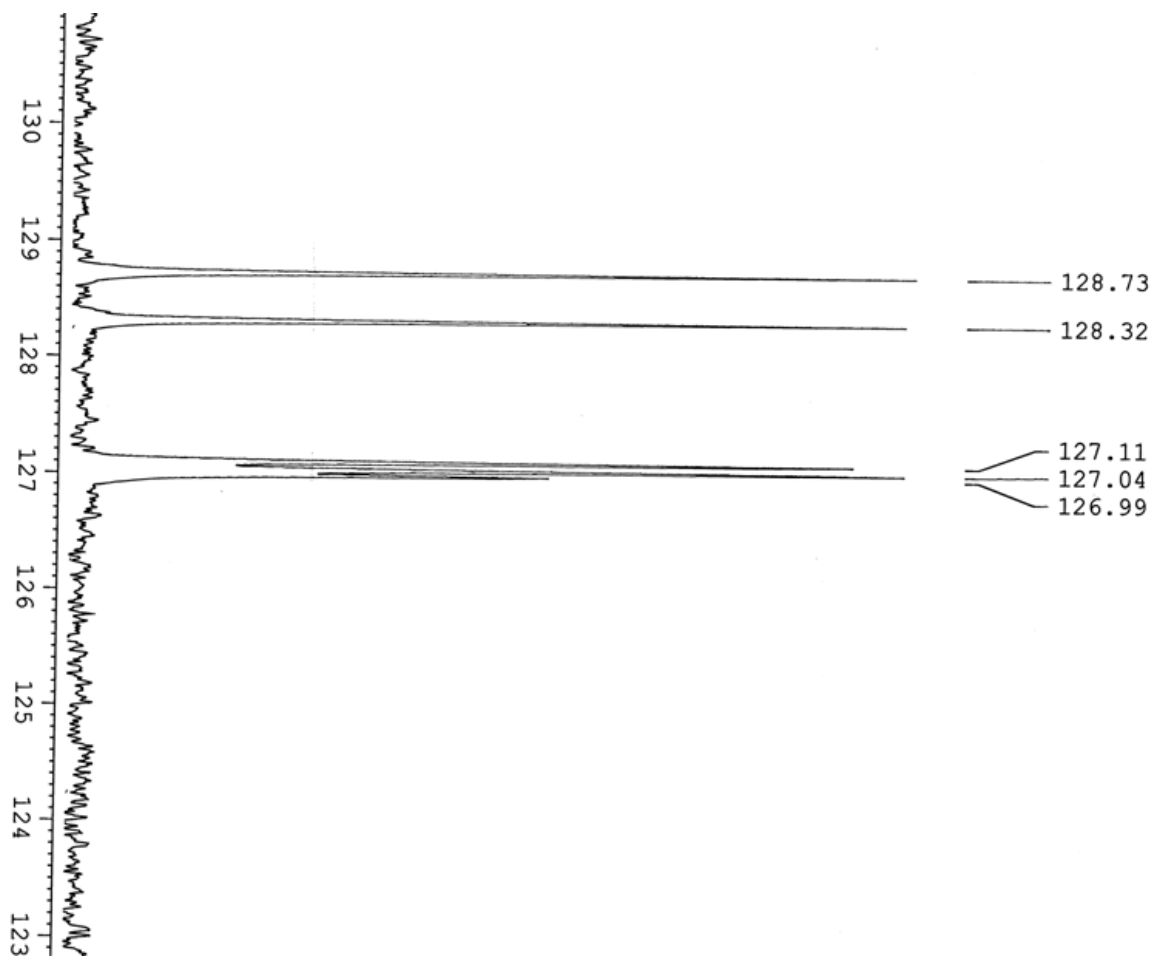


4-Ethyl-biphenyl (in CDCl₃)

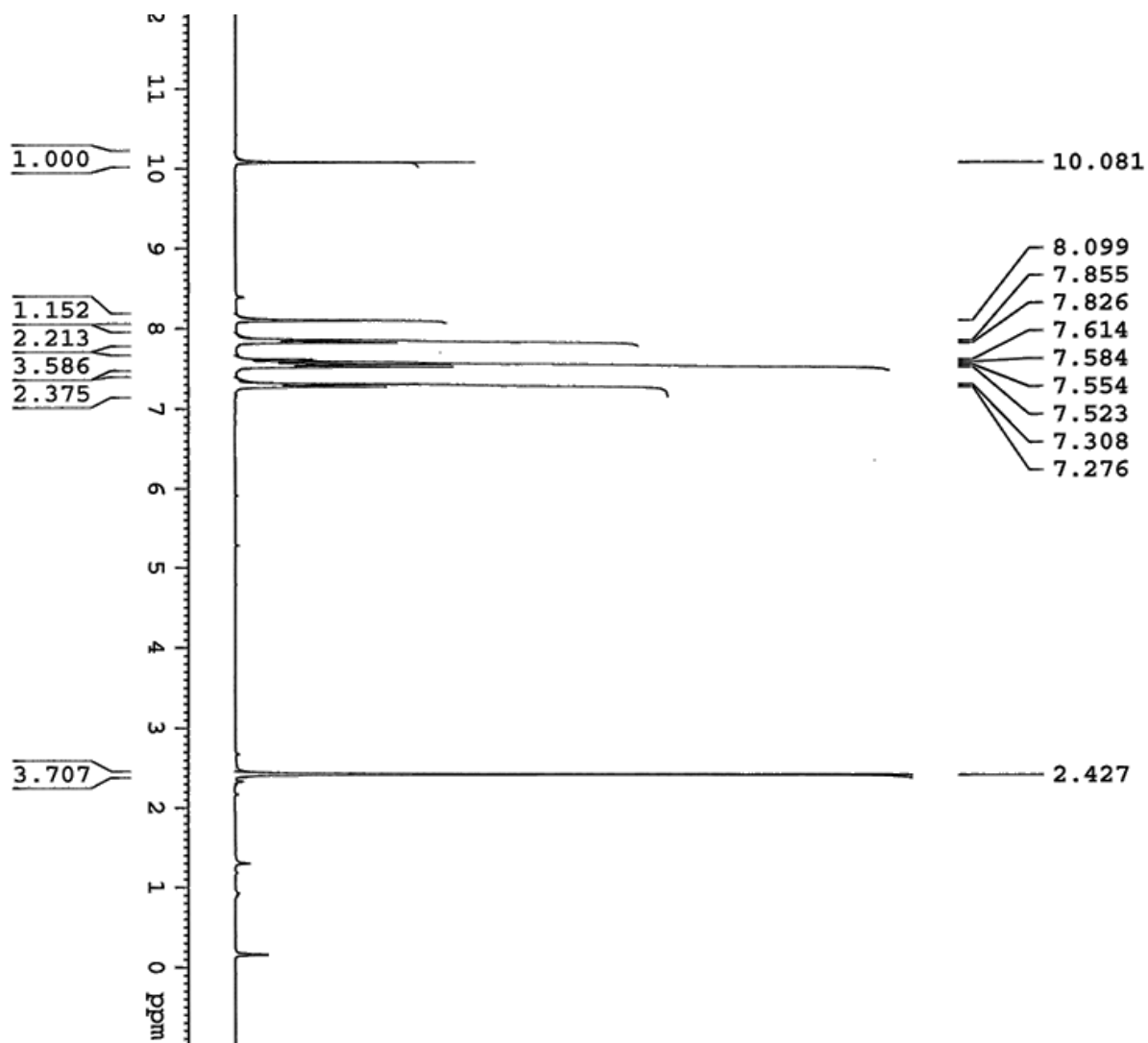




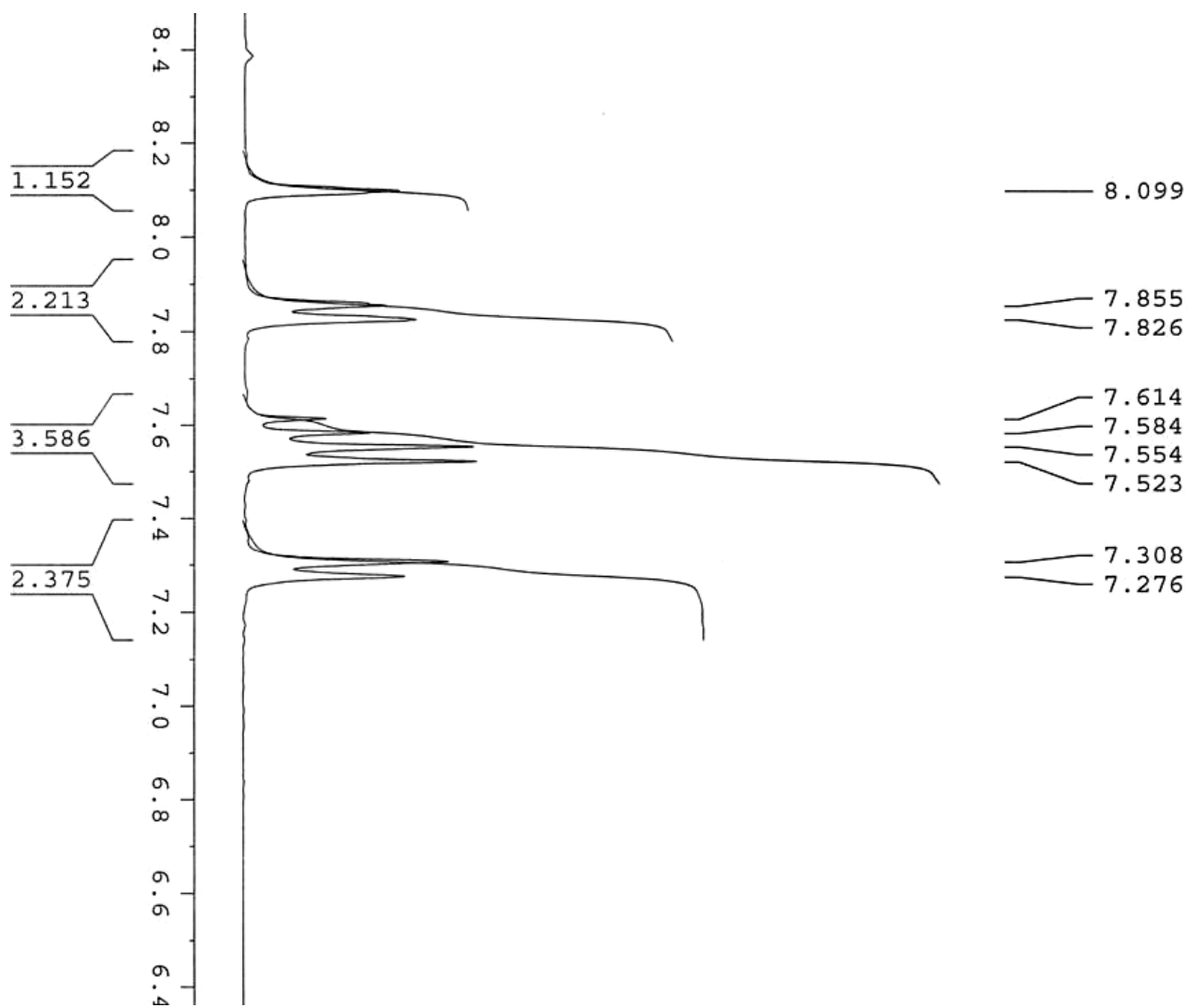
4-Ethyl-biphenyl (in CDCl₃)

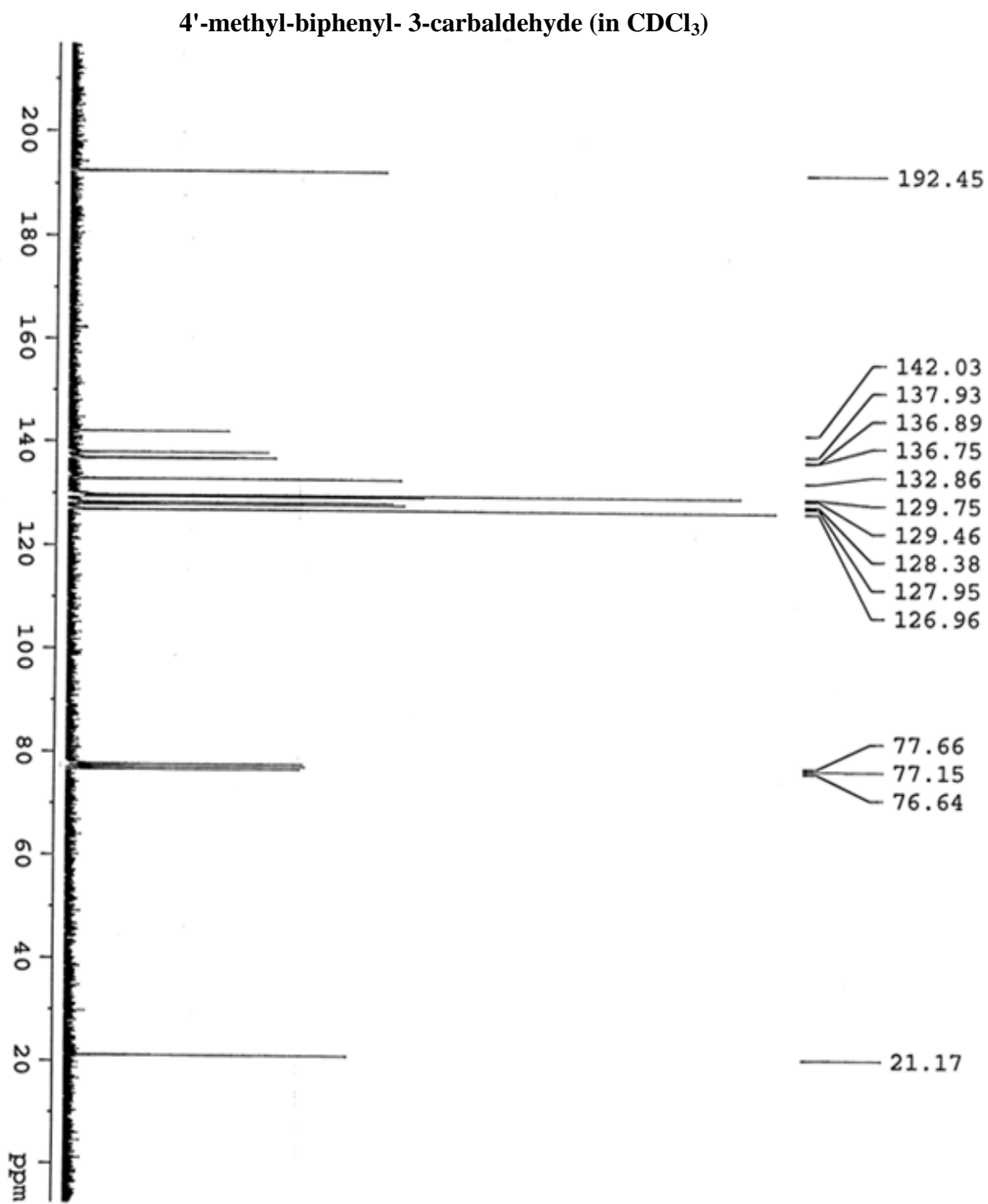


4'-methyl-biphenyl- 3-carbaldehyde (in CDCl₃)

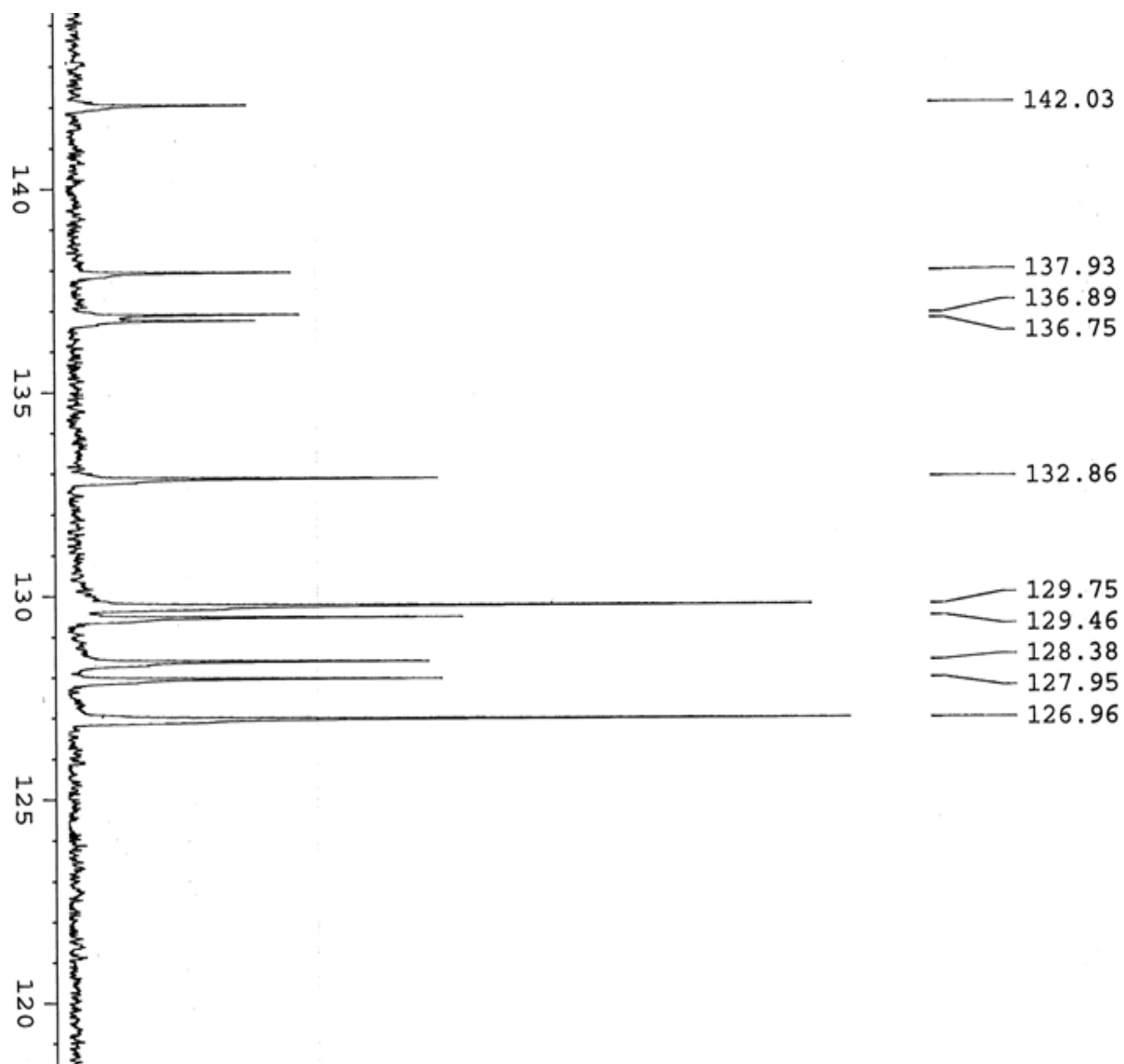


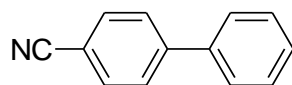
4'-methyl-biphenyl- 3-carbaldehyde (in CDCl₃)



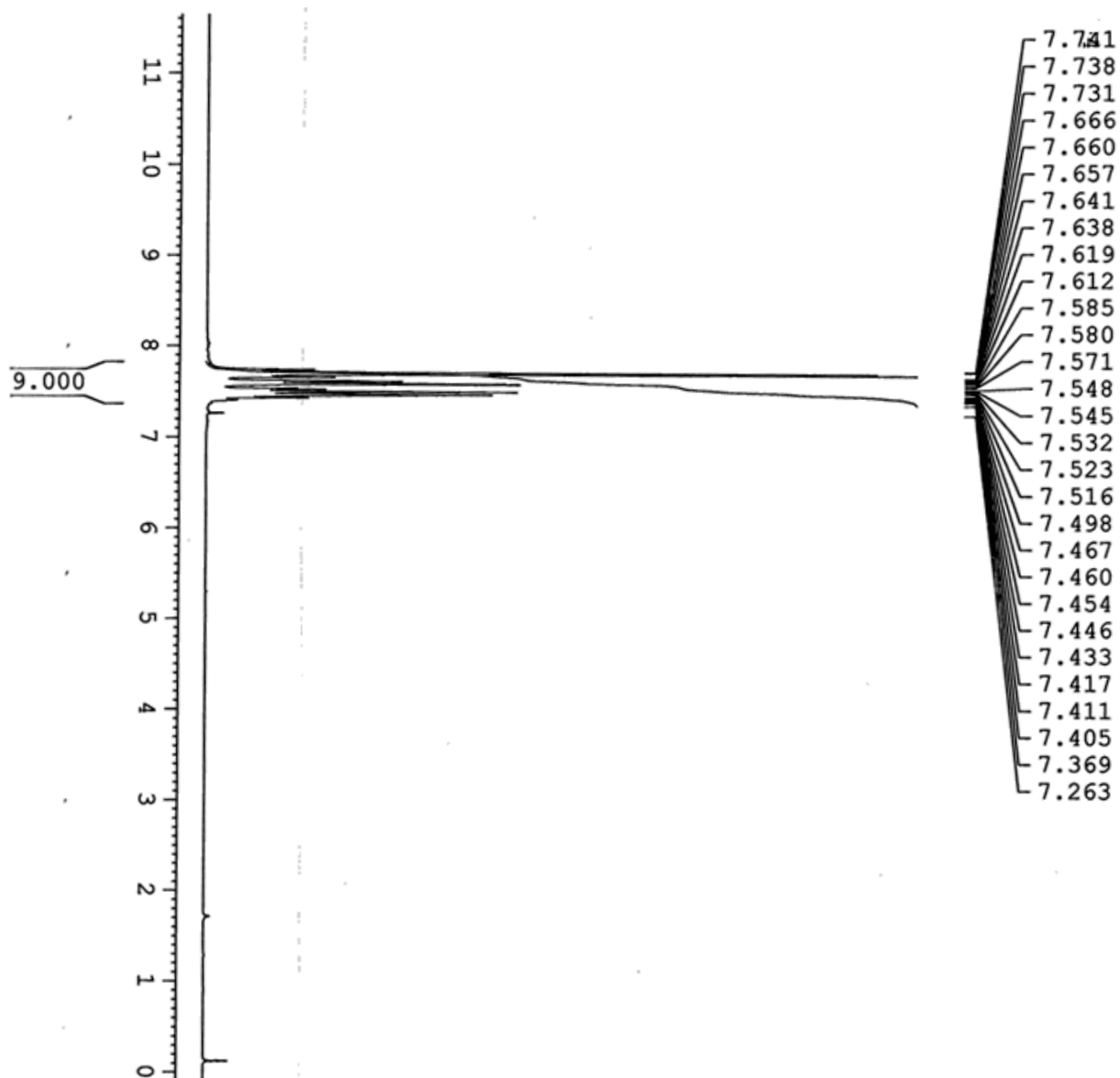


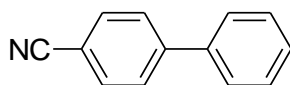
4'-methyl-biphenyl- 3-carbaldehyde (in CDCl₃)



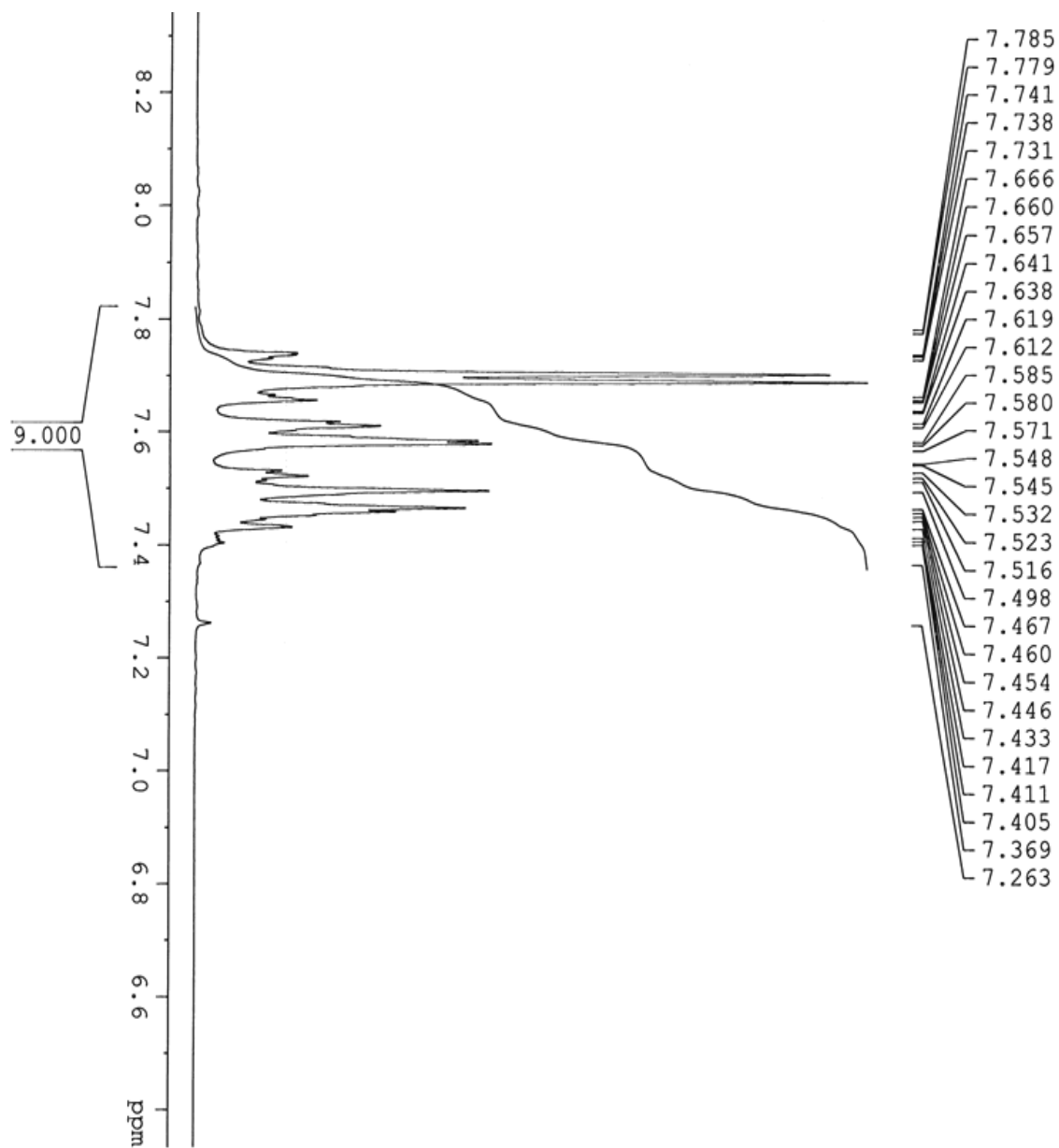


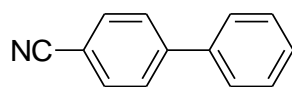
Biphenyl-4-carbonitrile (in CDCl₃)



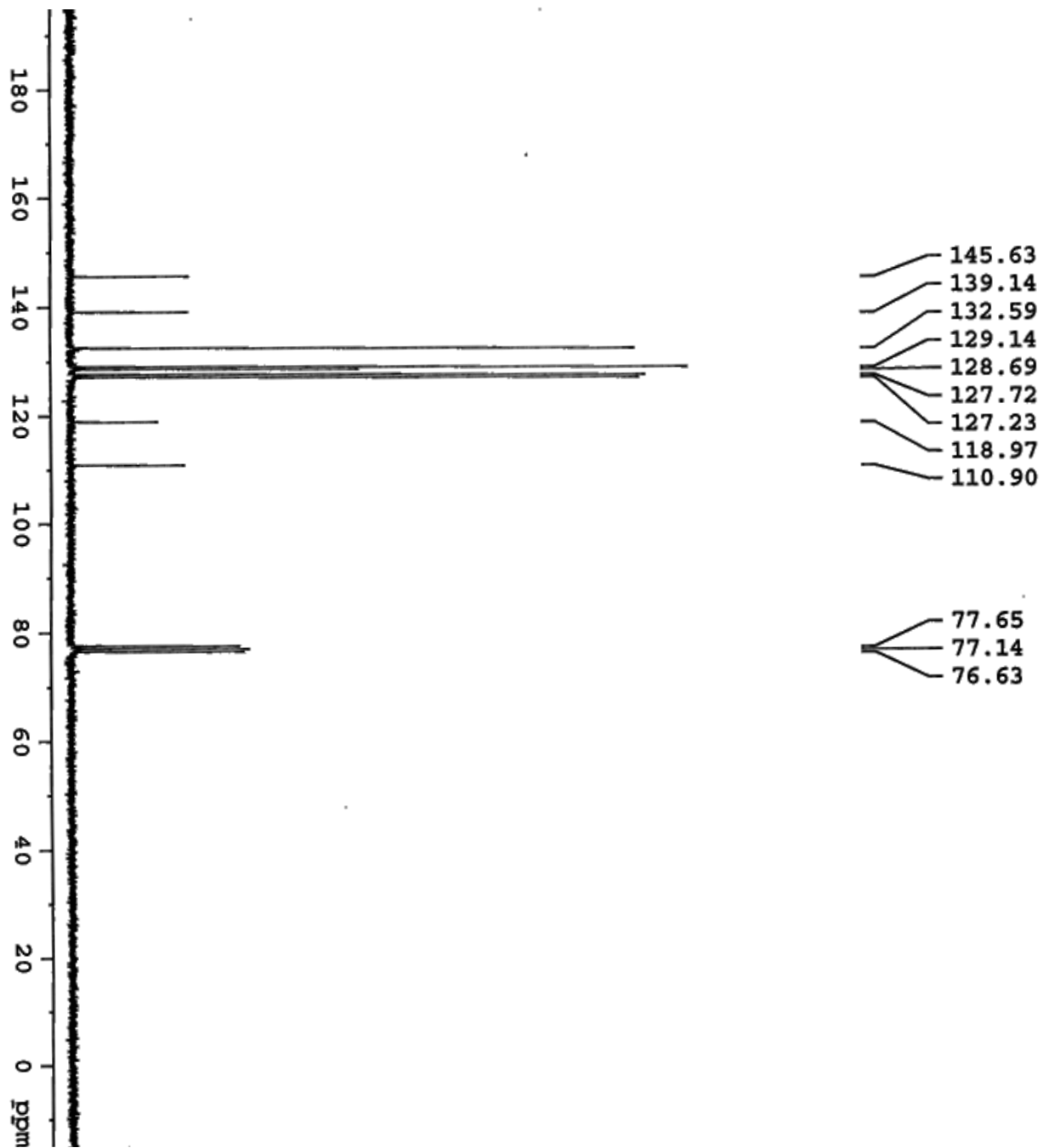


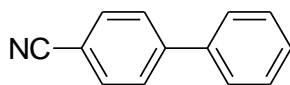
Biphenyl-4-carbonitrile (in CDCl₃)



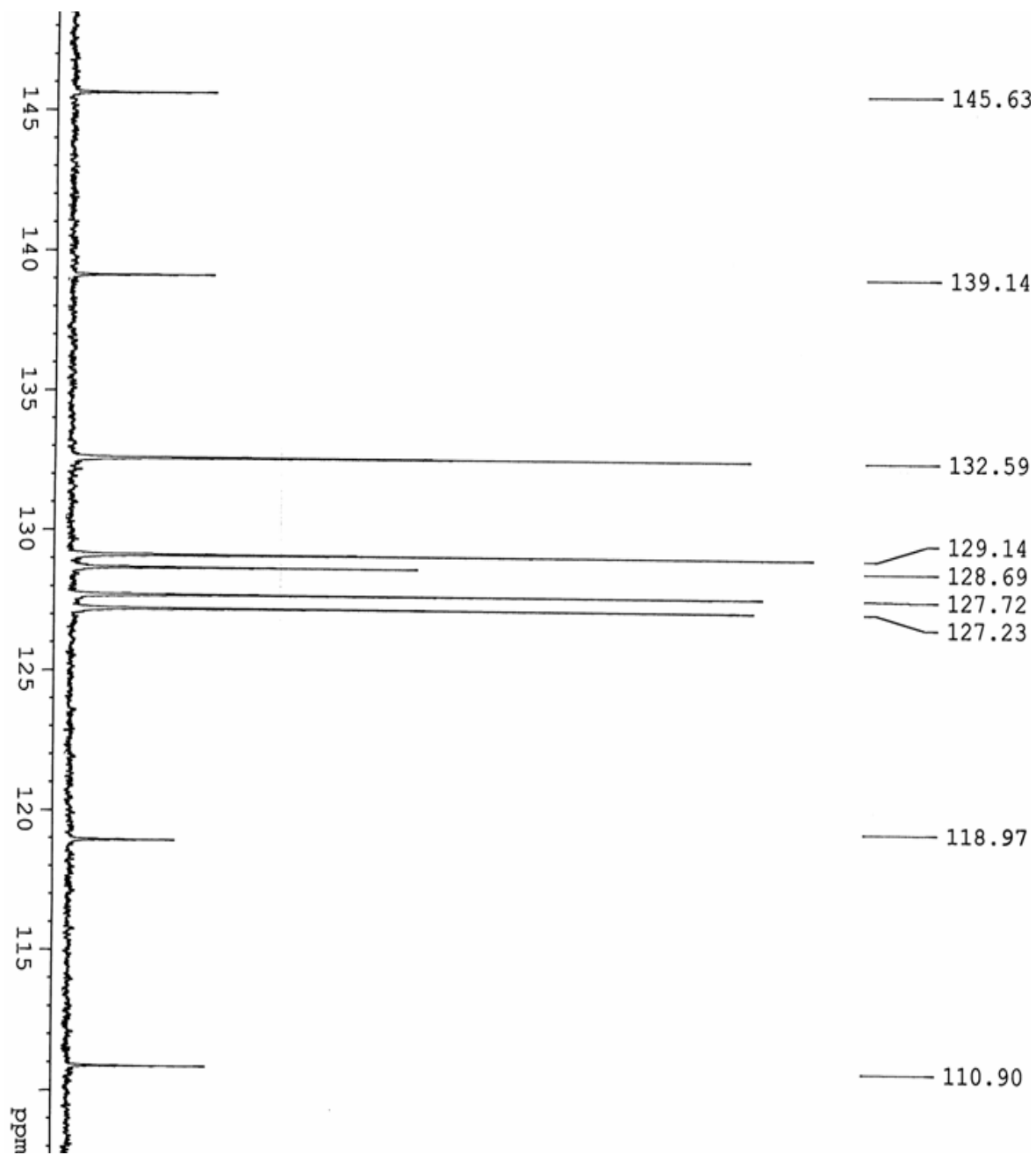


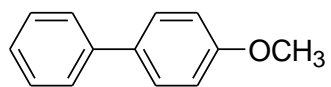
Biphenyl-4-carbonitrile (in CDCl₃)



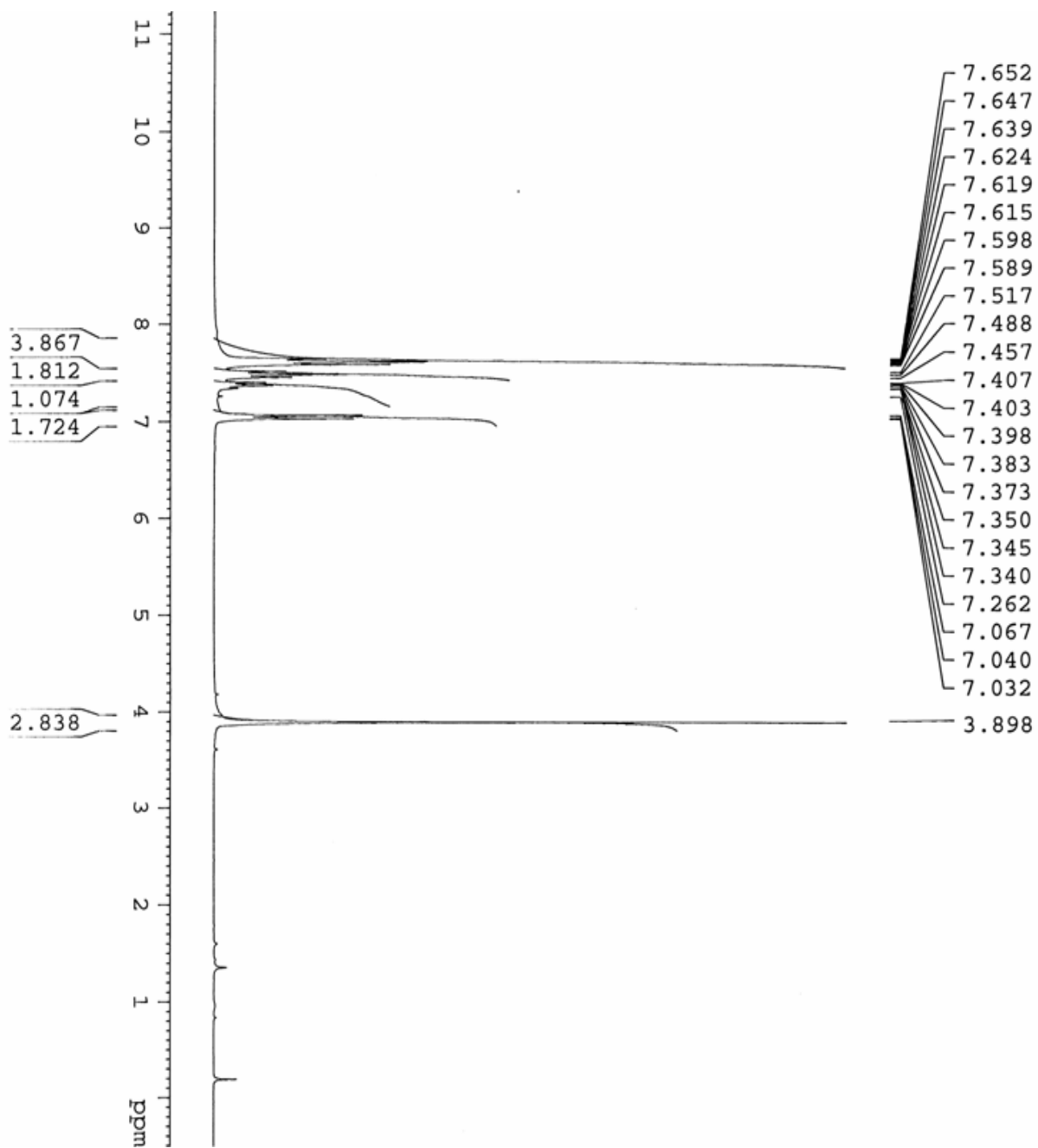


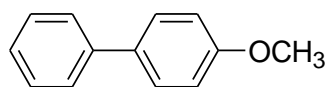
Biphenyl-4-carbonitrile (in CDCl₃)



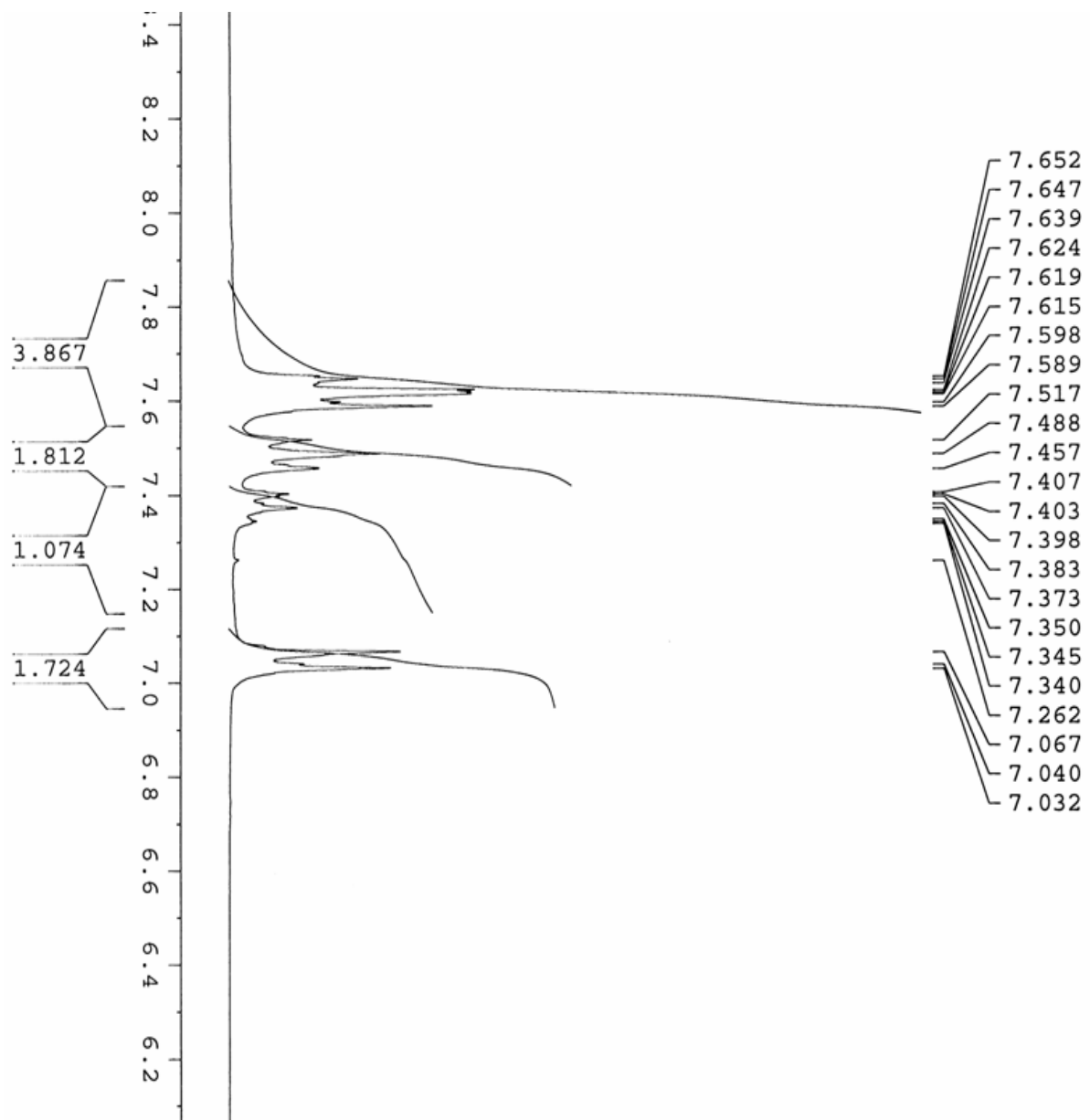


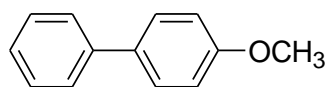
4-Methoxy-biphenyl (in CDCl₃)



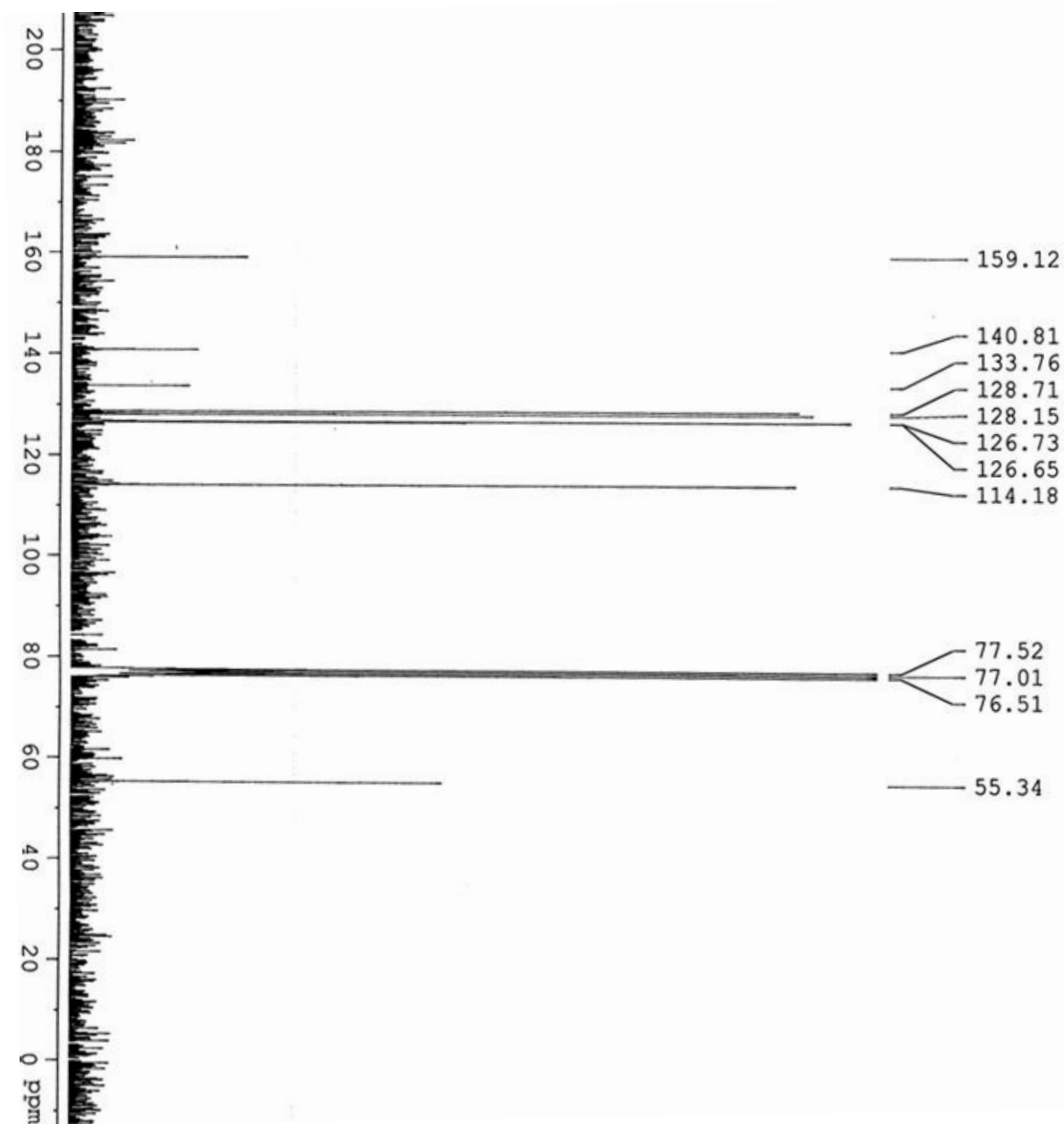


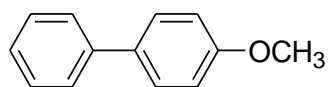
4-Methoxy-biphenyl (in CDCl₃)



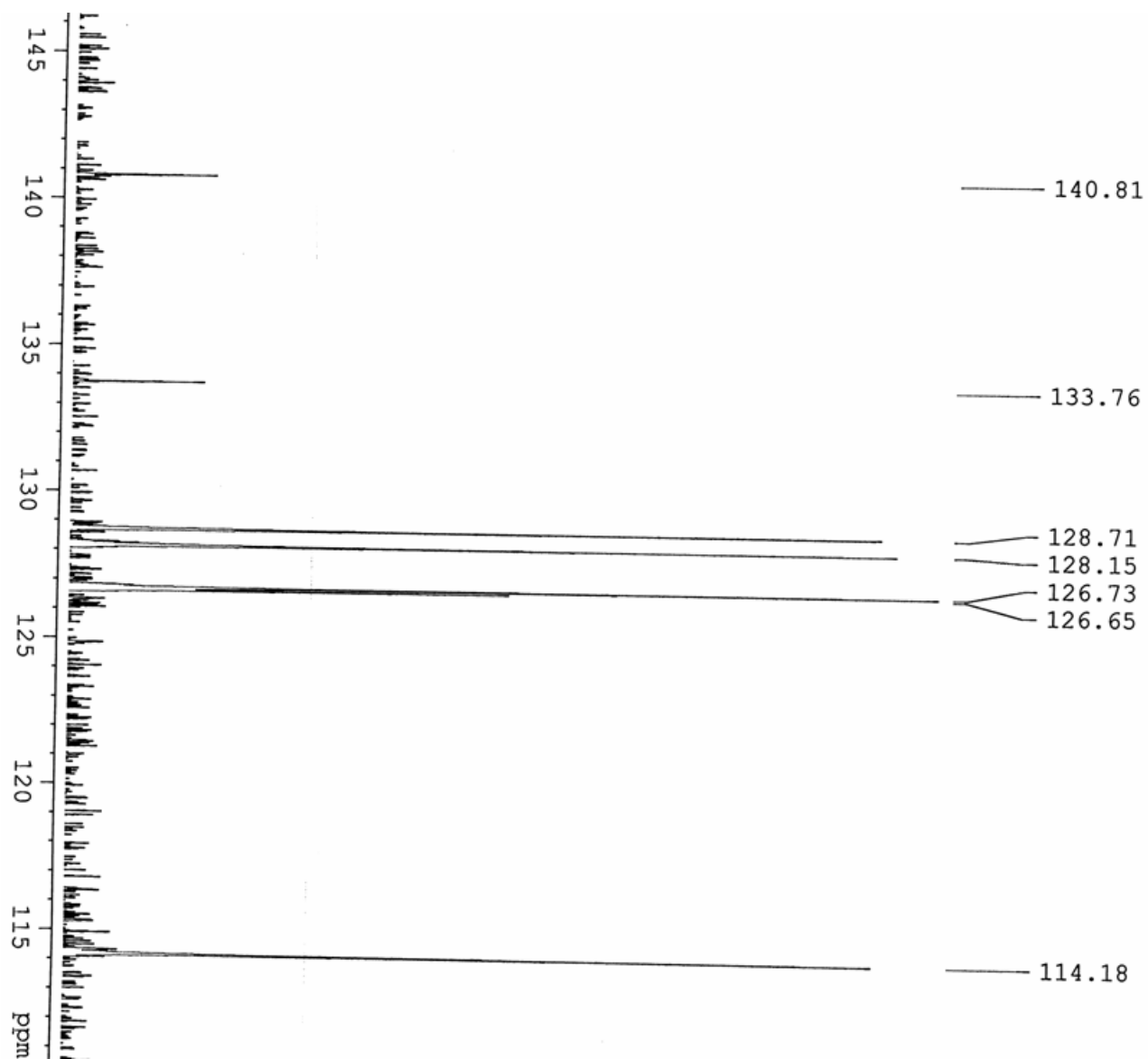


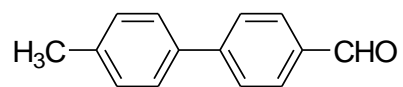
4-Methoxy-biphenyl (in CDCl₃)



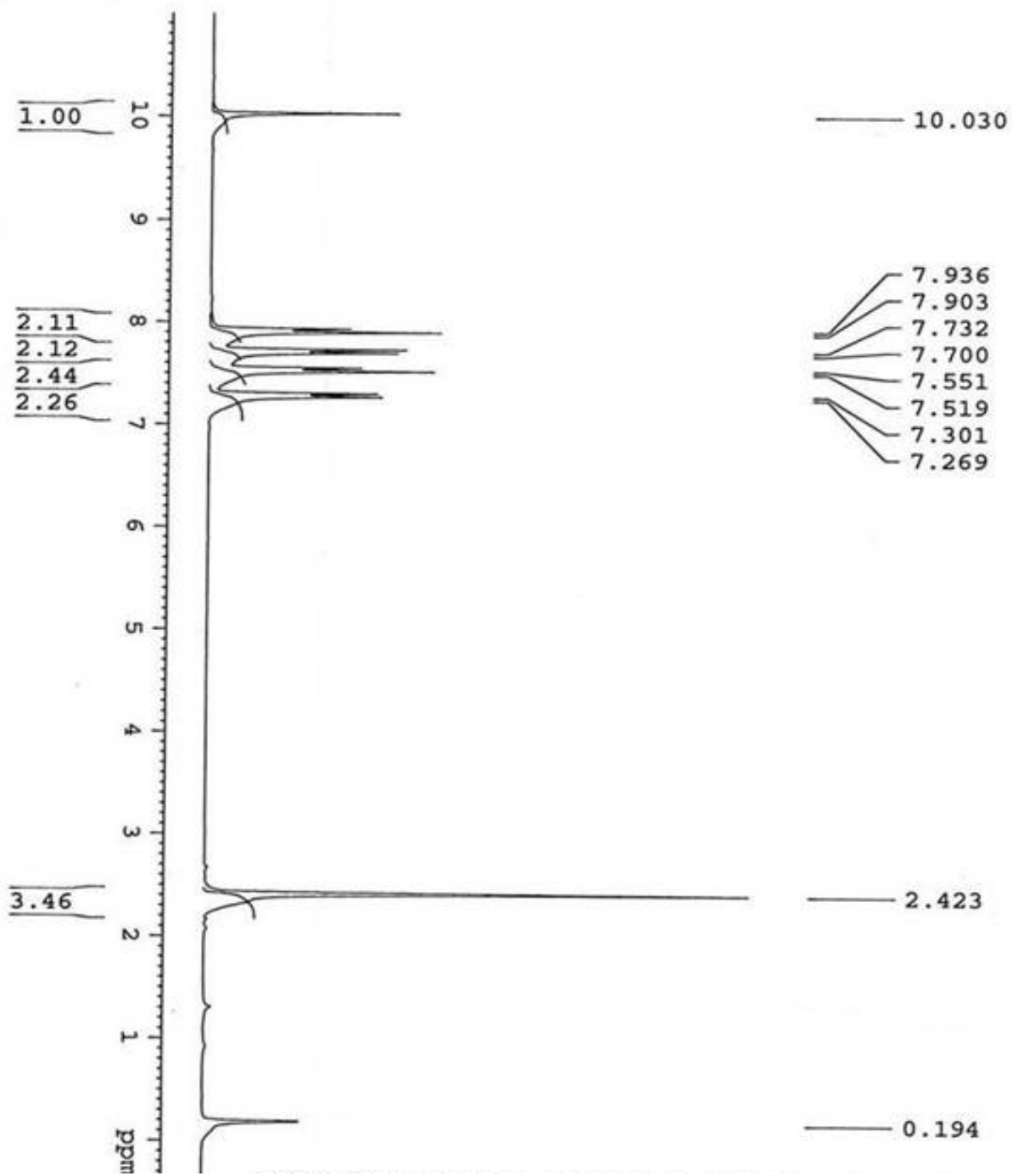


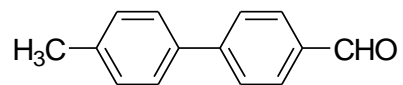
4-Methoxy-biphenyl (in CDCl₃)



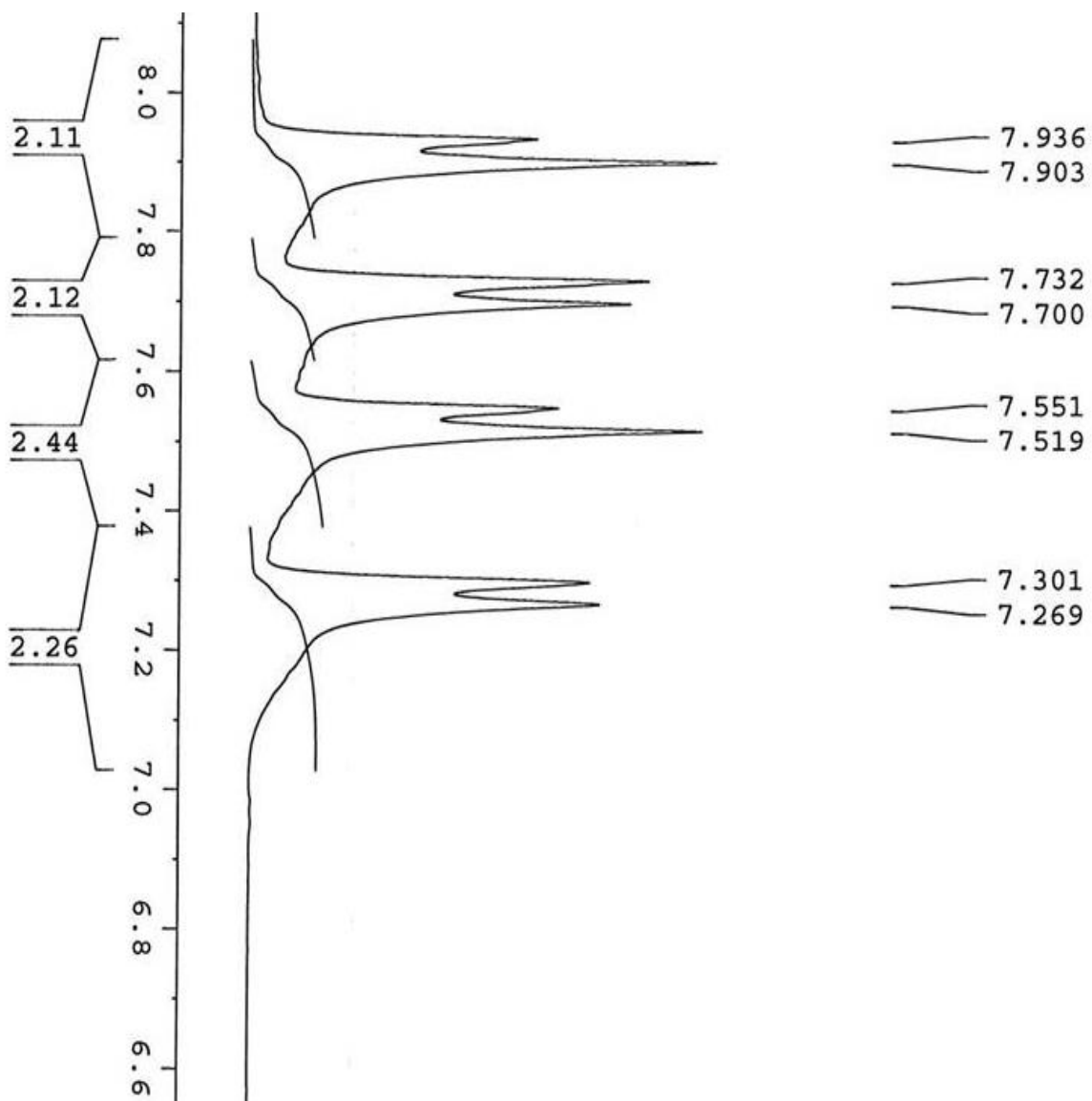


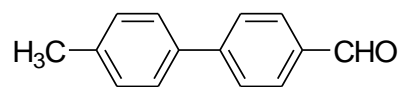
4'-methyl-biphenyl-4- carbaldehyde (in CDCl₃)



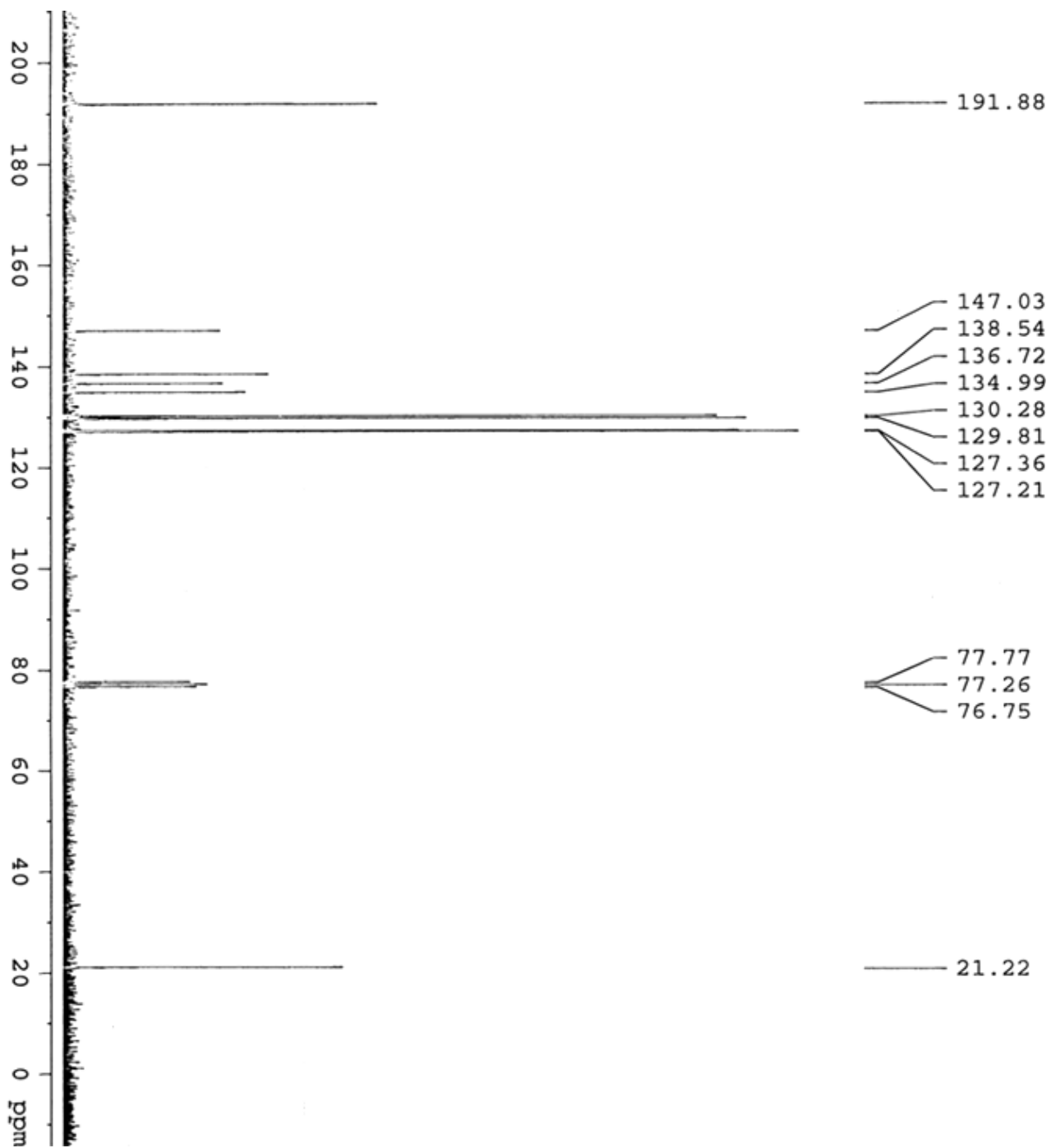


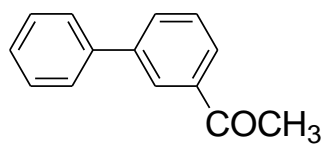
4'-methyl-biphenyl-4- carbaldehyde (in CDCl₃)



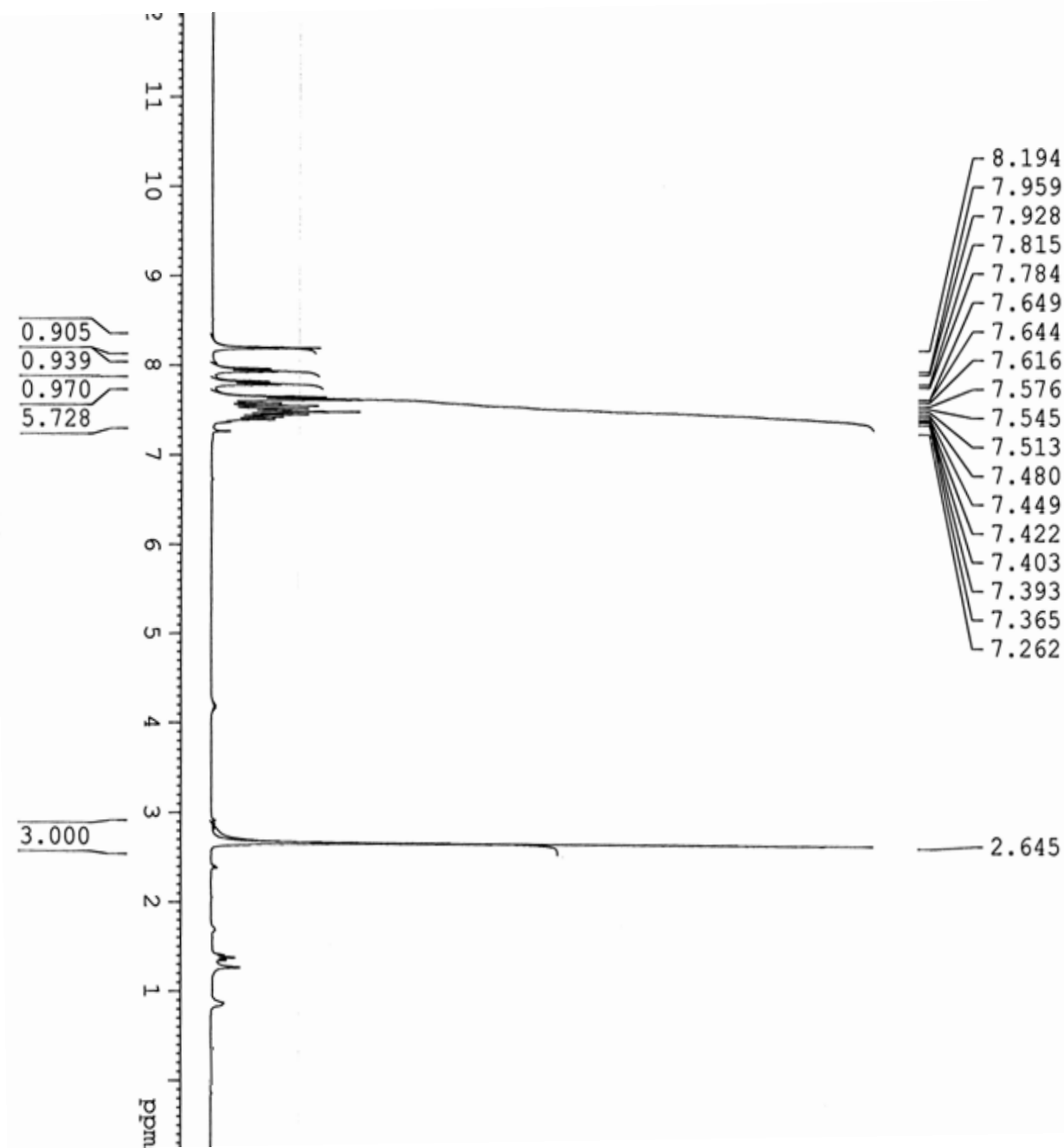


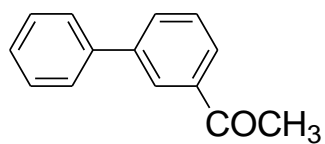
4'-methyl-biphenyl-4- carbaldehyde (in CDCl₃)



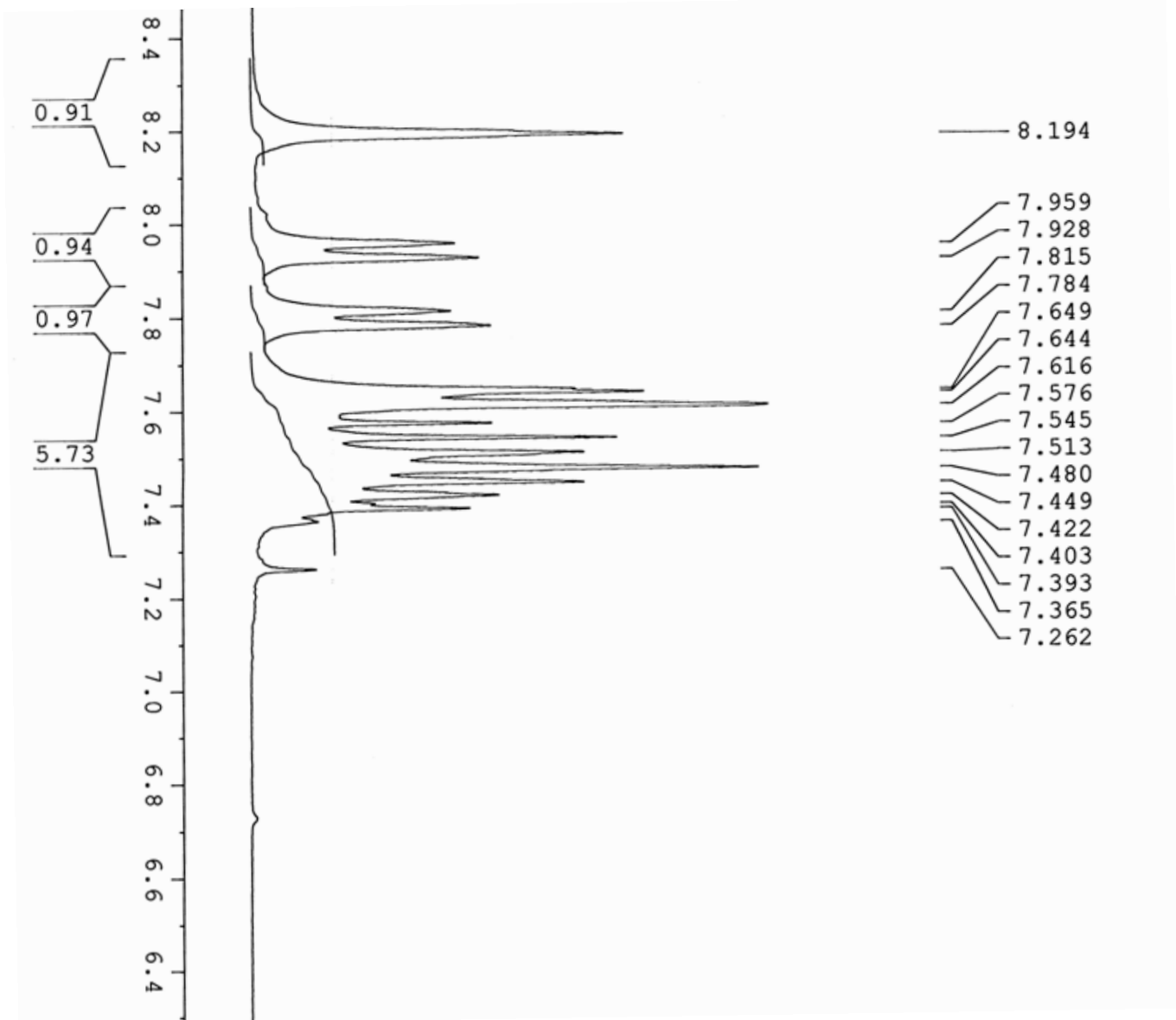


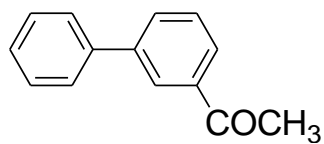
1-Biphenyl-3-yl-ethanone (in CDCl₃)



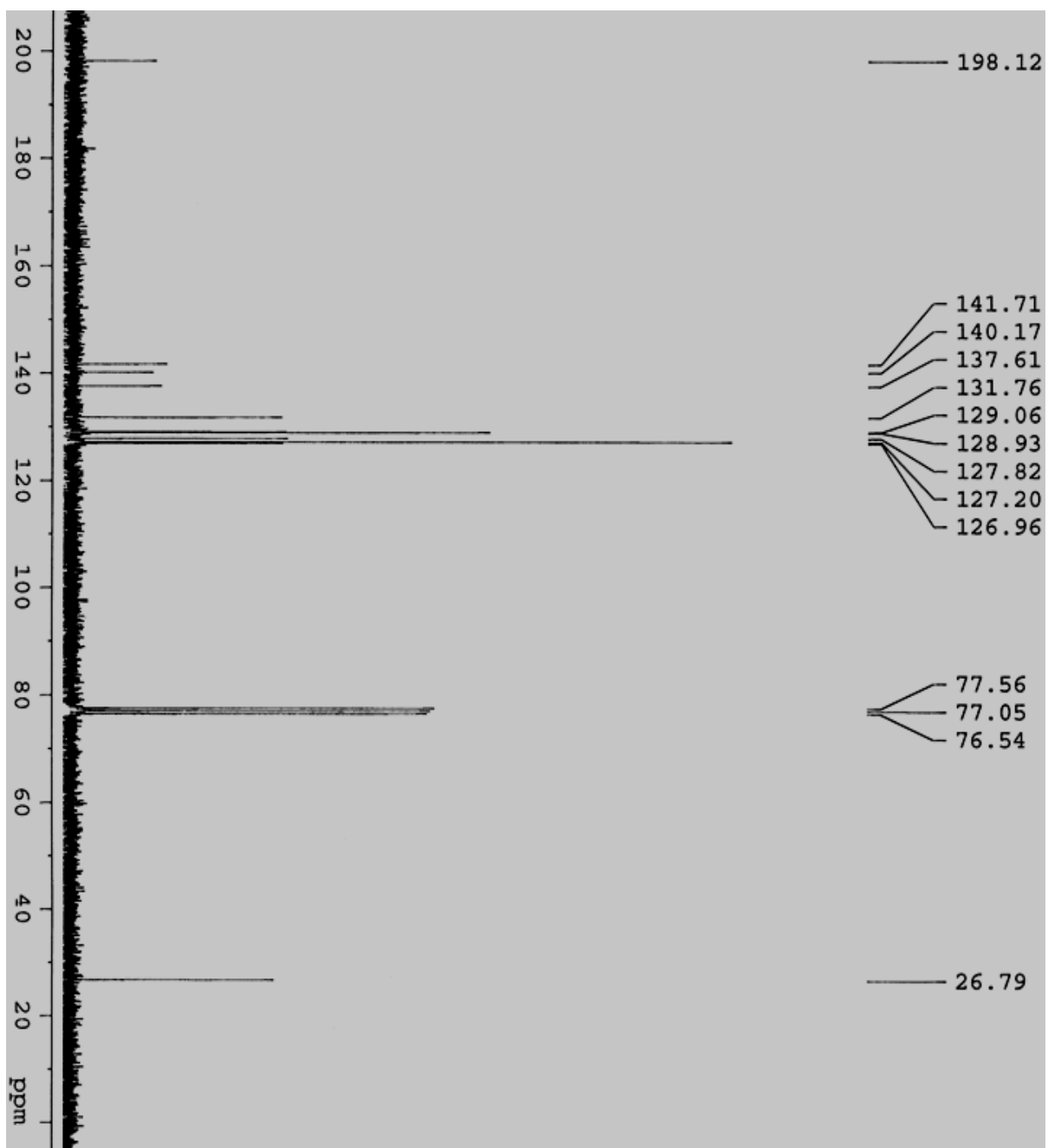


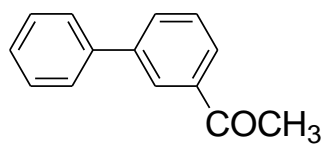
1-Biphenyl-3-yl-ethanone (in CDCl₃)



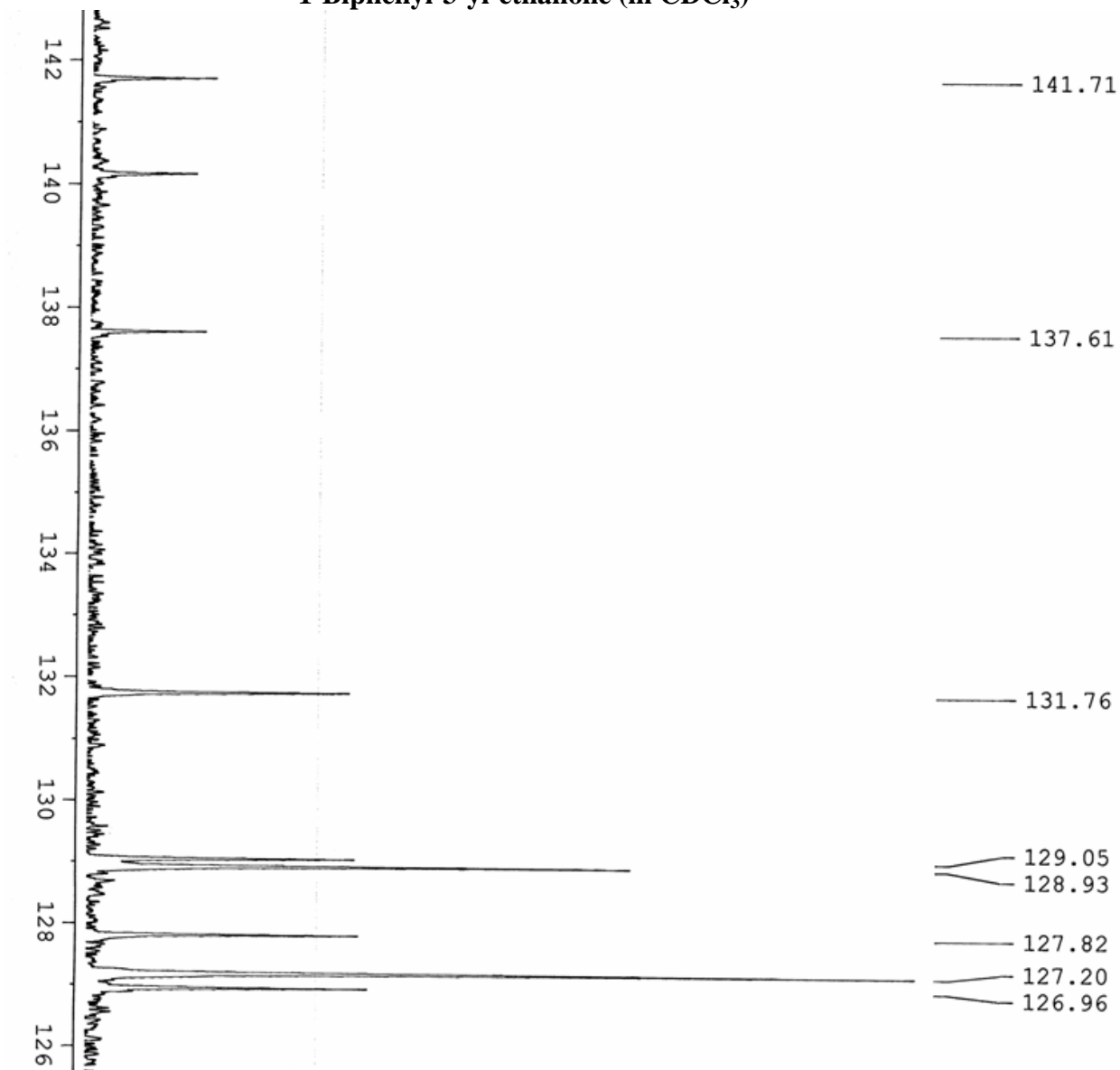


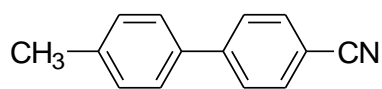
1-Biphenyl-3-yl-ethanone (in CDCl₃)



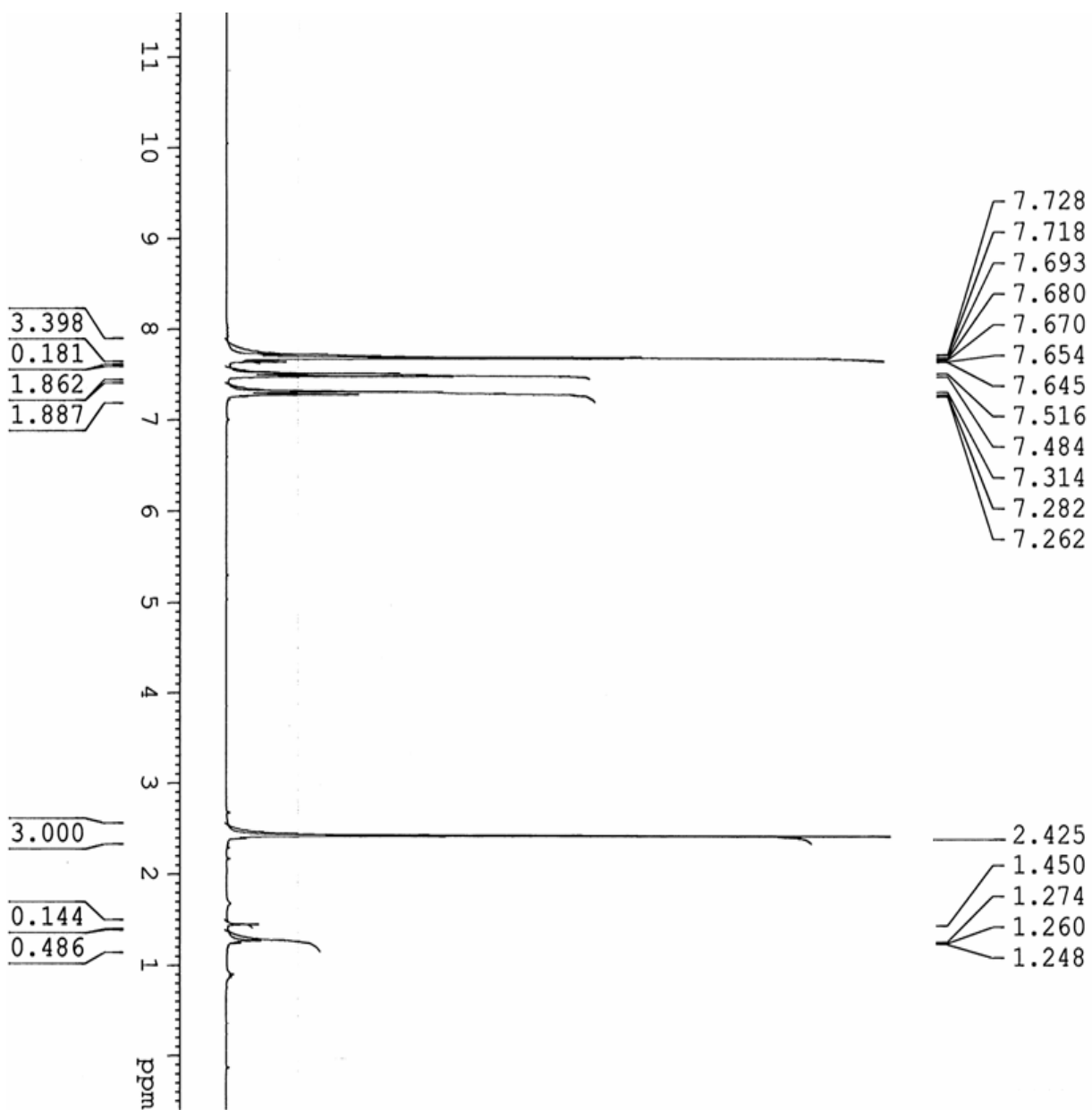


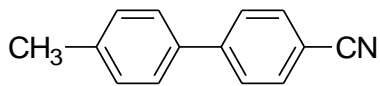
1-Biphenyl-3-yl-ethanone (in CDCl₃)



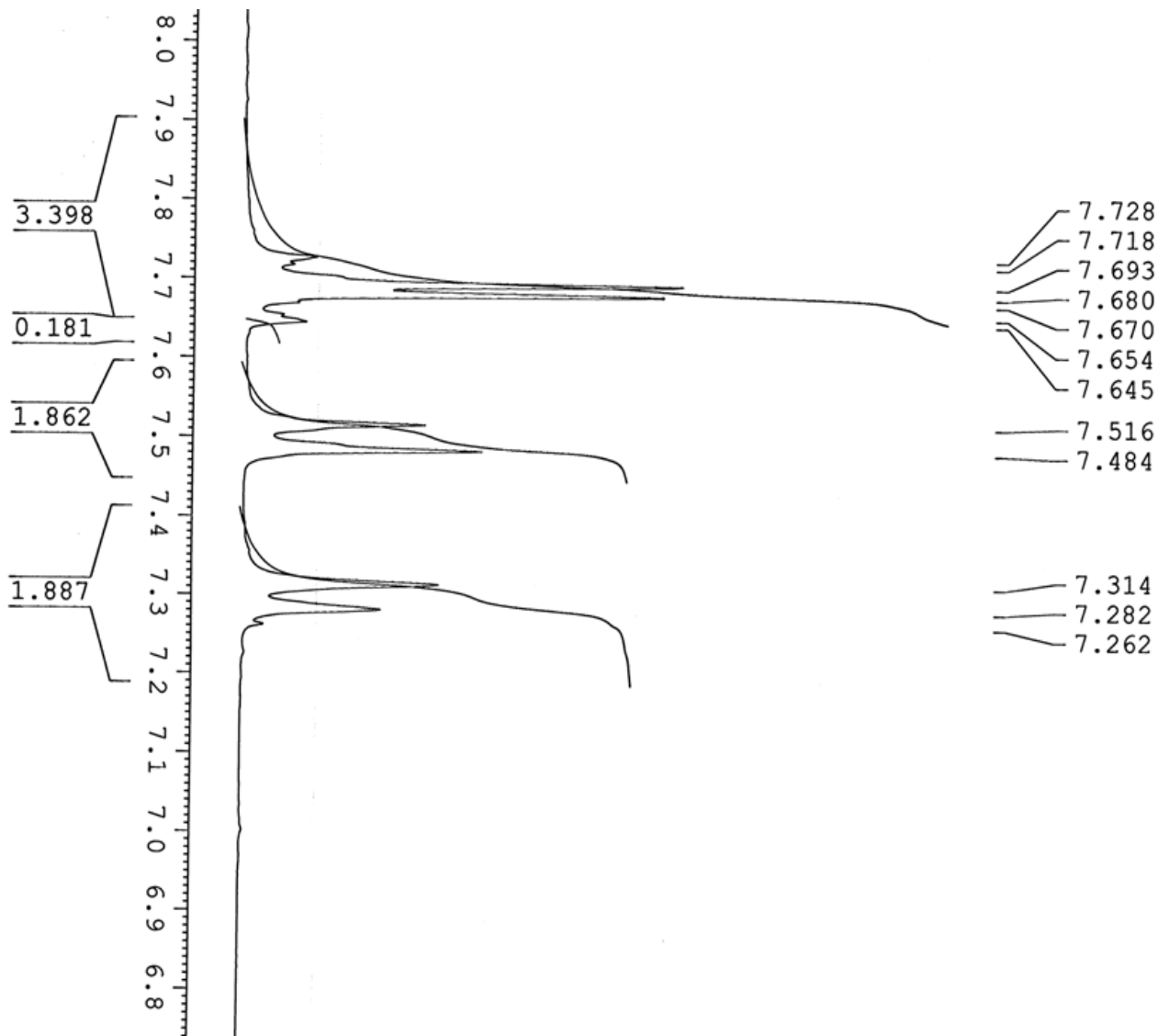


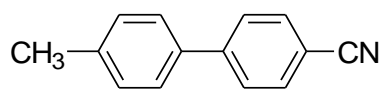
4'-Methyl-biphenyl-4-carbonitrile (in CDCl₃)



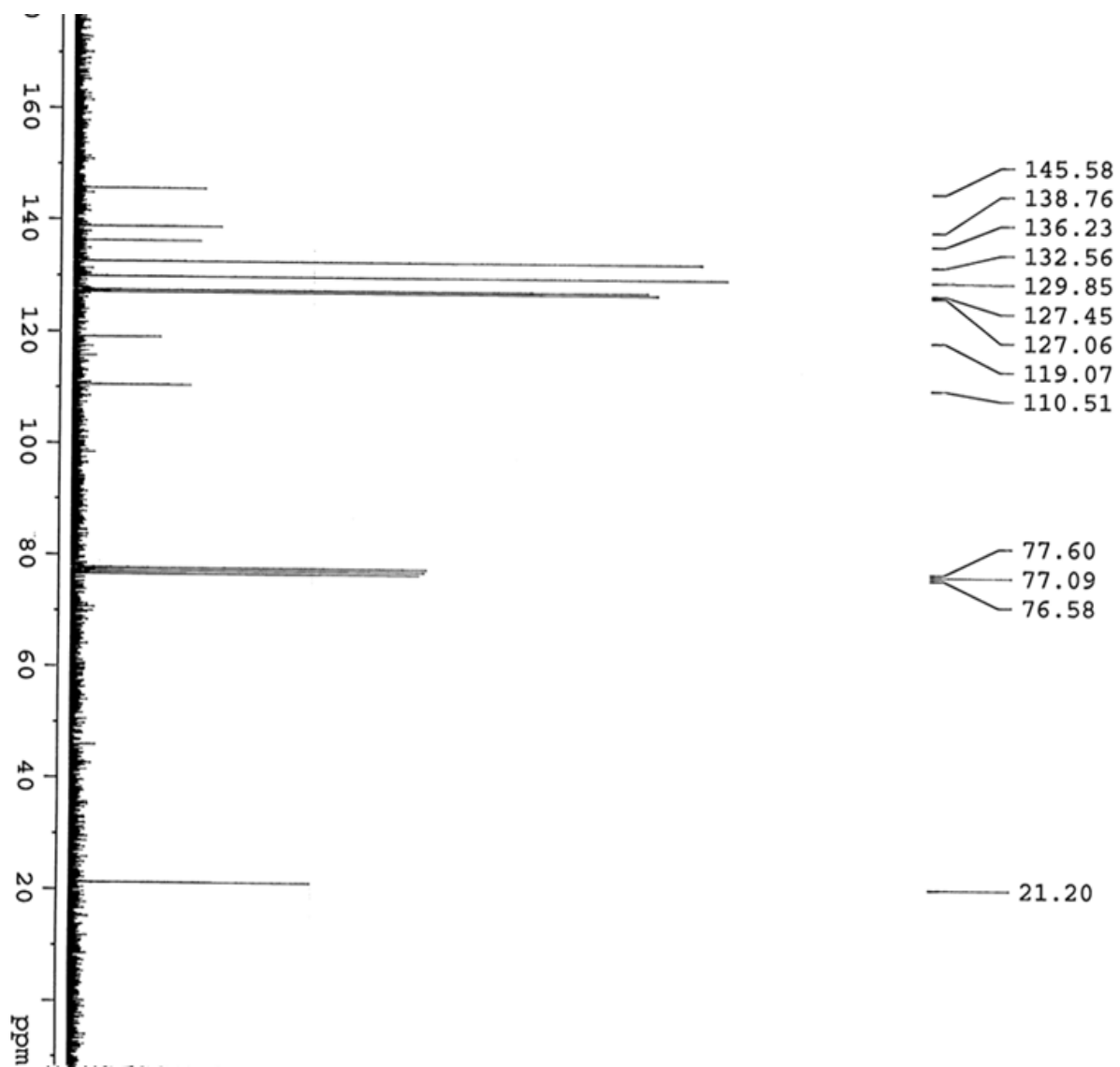


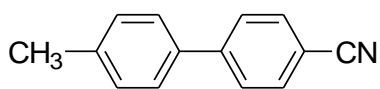
4'-Methyl-biphenyl-4-carbonitrile (in CDCl₃)



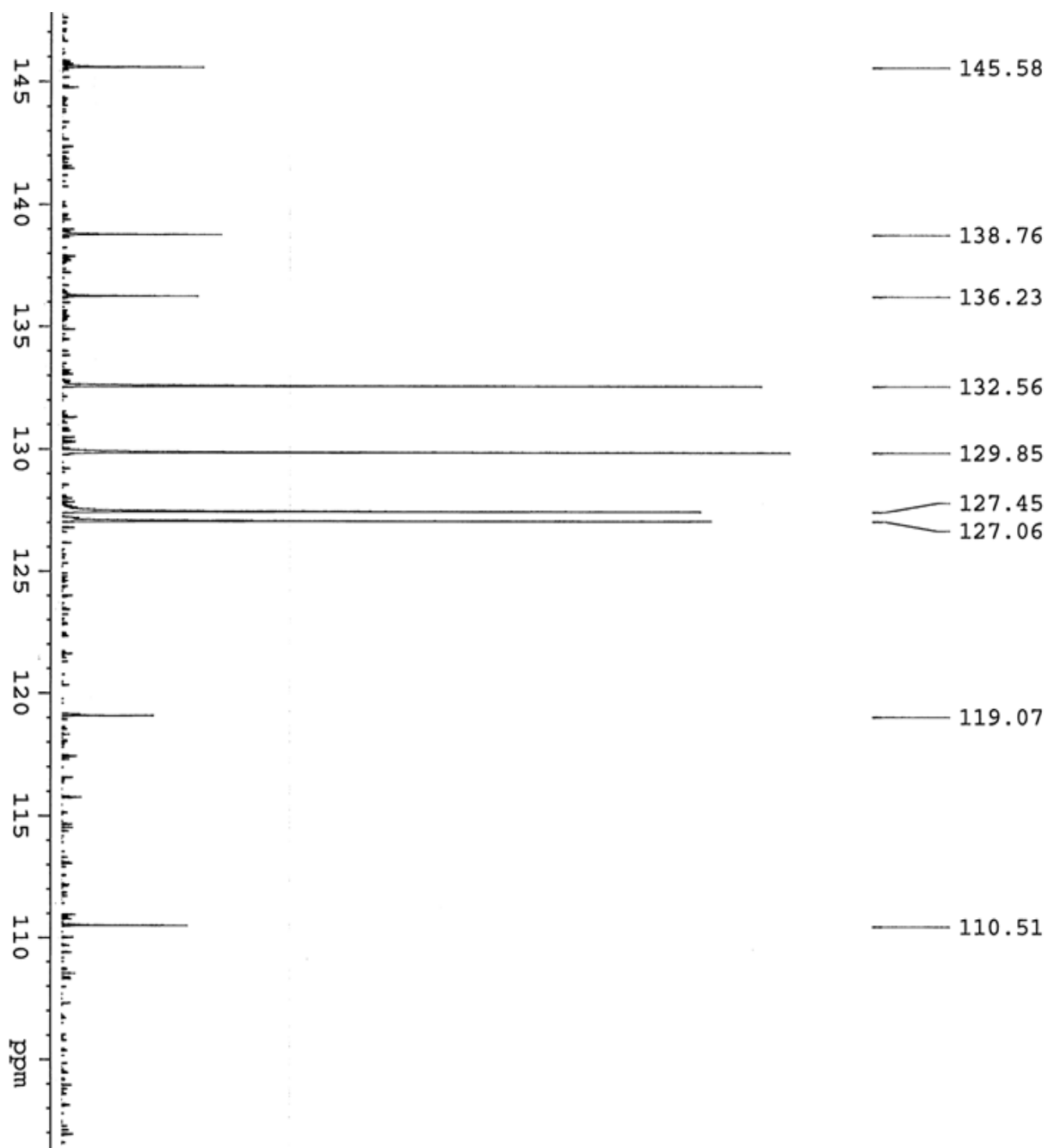


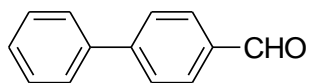
4'-Methyl-biphenyl-4-carbonitrile (in CDCl₃)



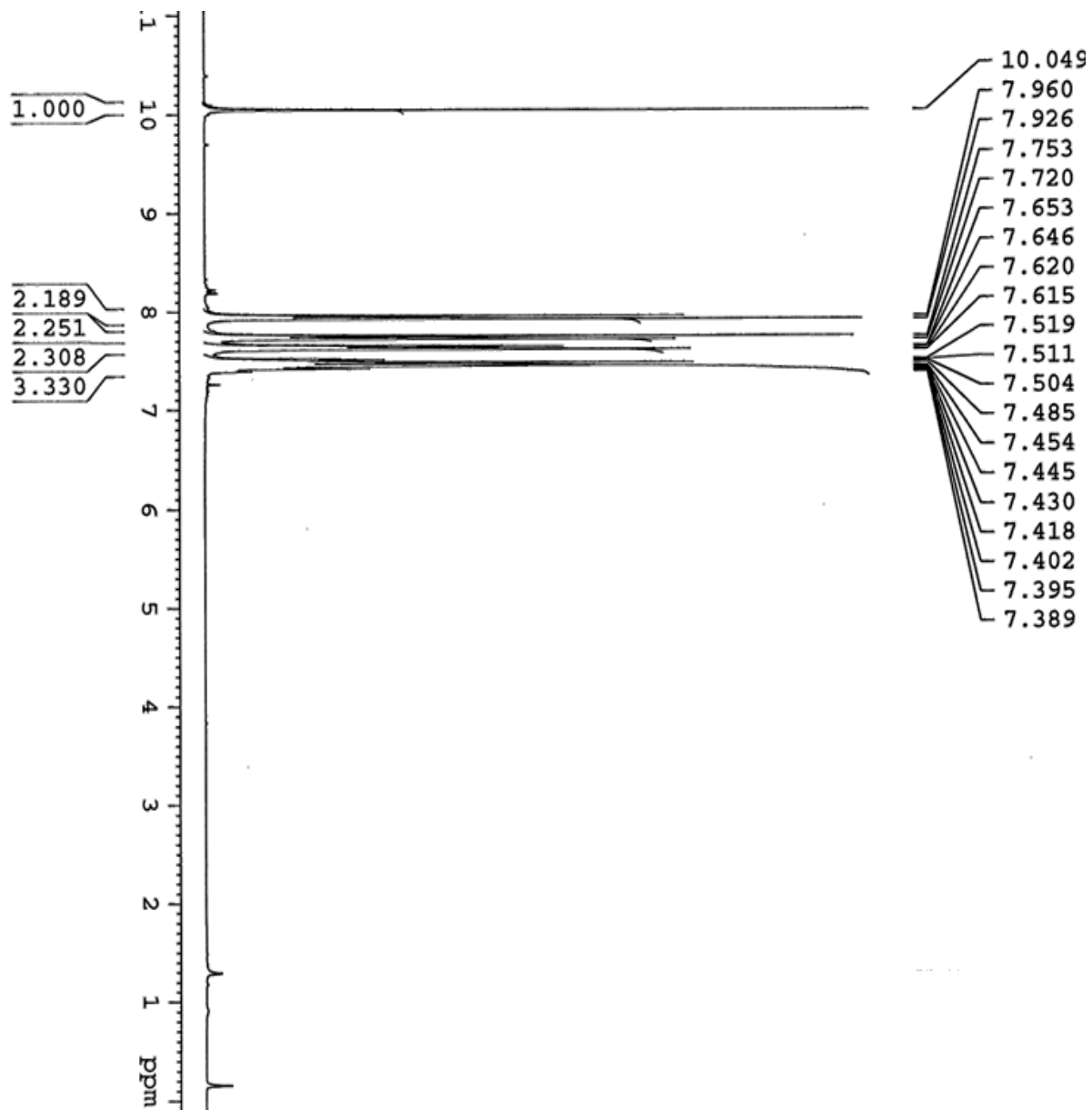


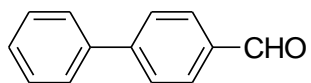
4'-Methyl-biphenyl-4-carbonitrile (in CDCl₃)



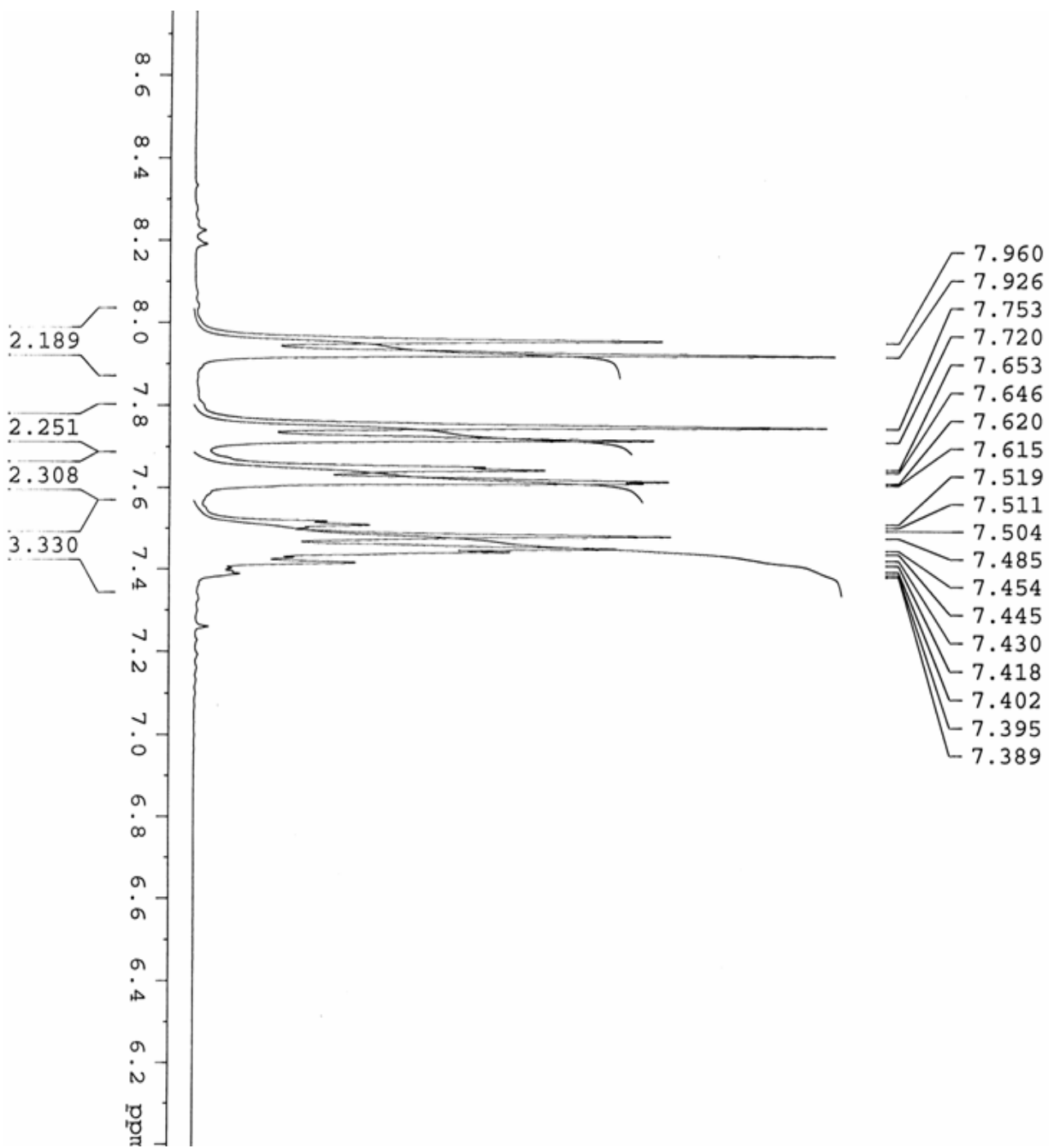


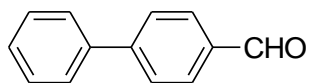
Phenyl- 4-carbaldehyde (in CDCl₃)



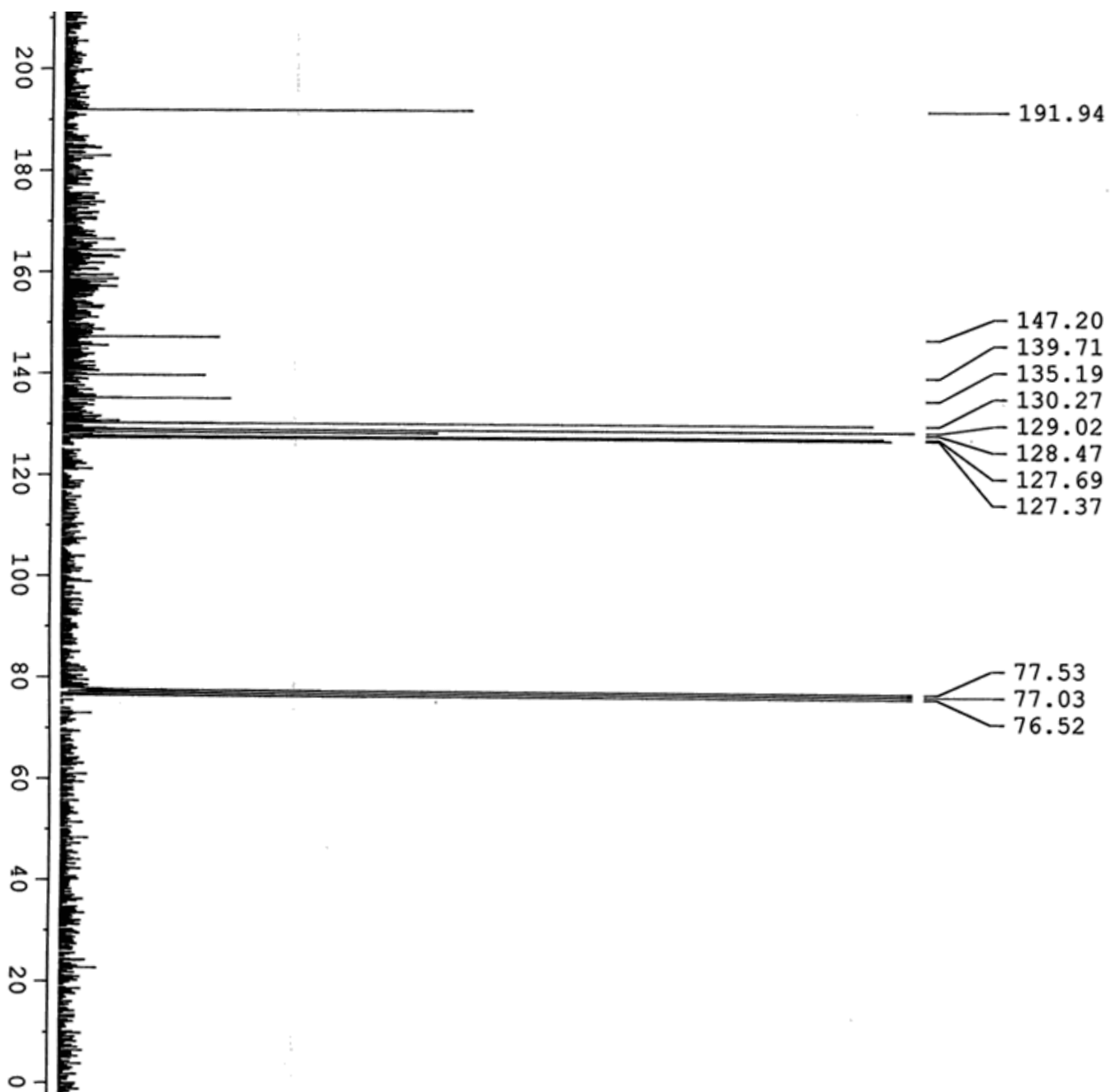


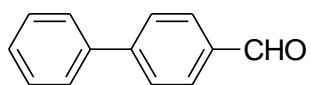
Phenyl- 4-carbaldehyde (in CDCl₃)



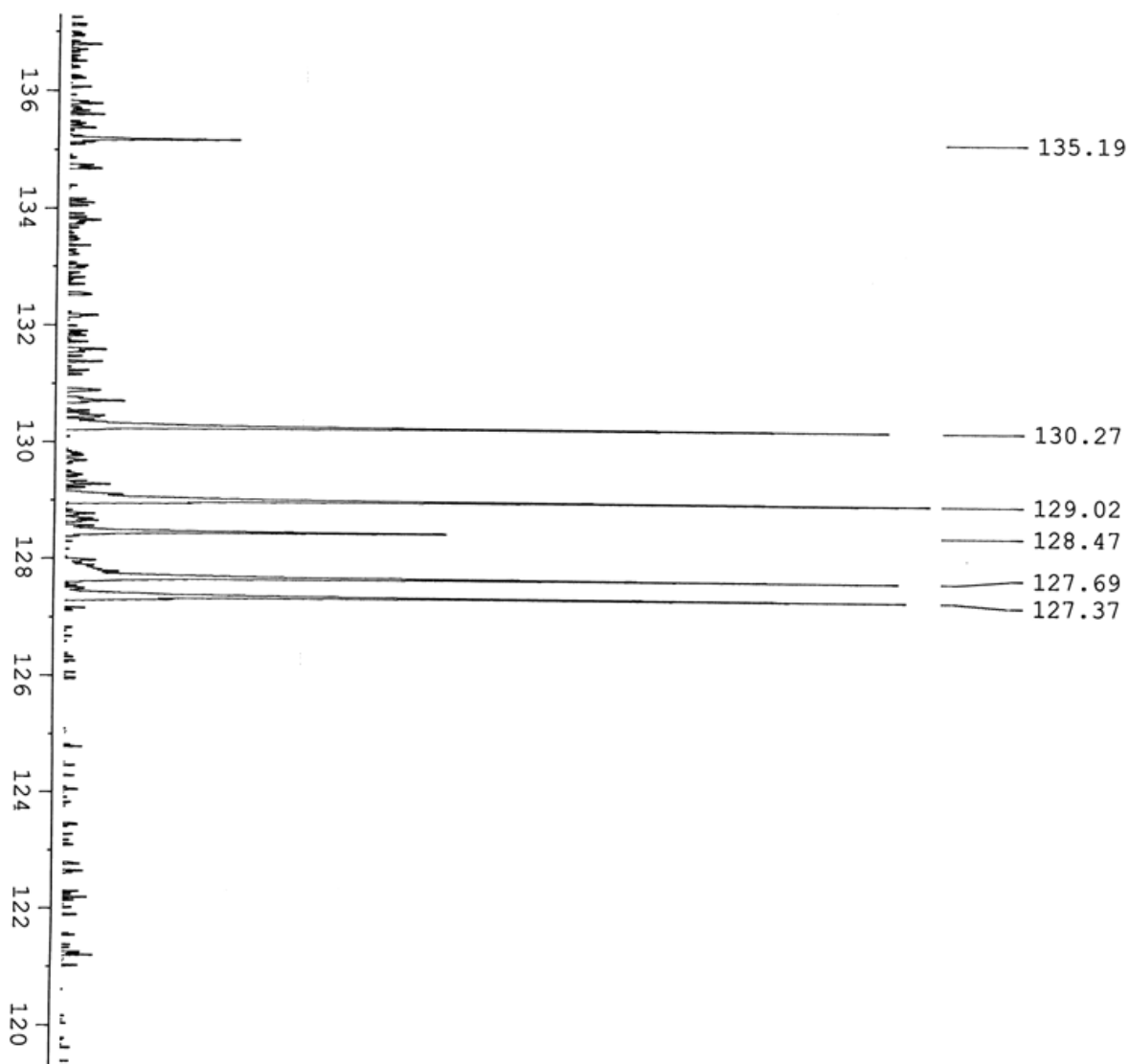


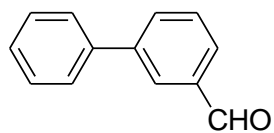
Phenyl- 4-carbaldehyde (in CDCl₃)



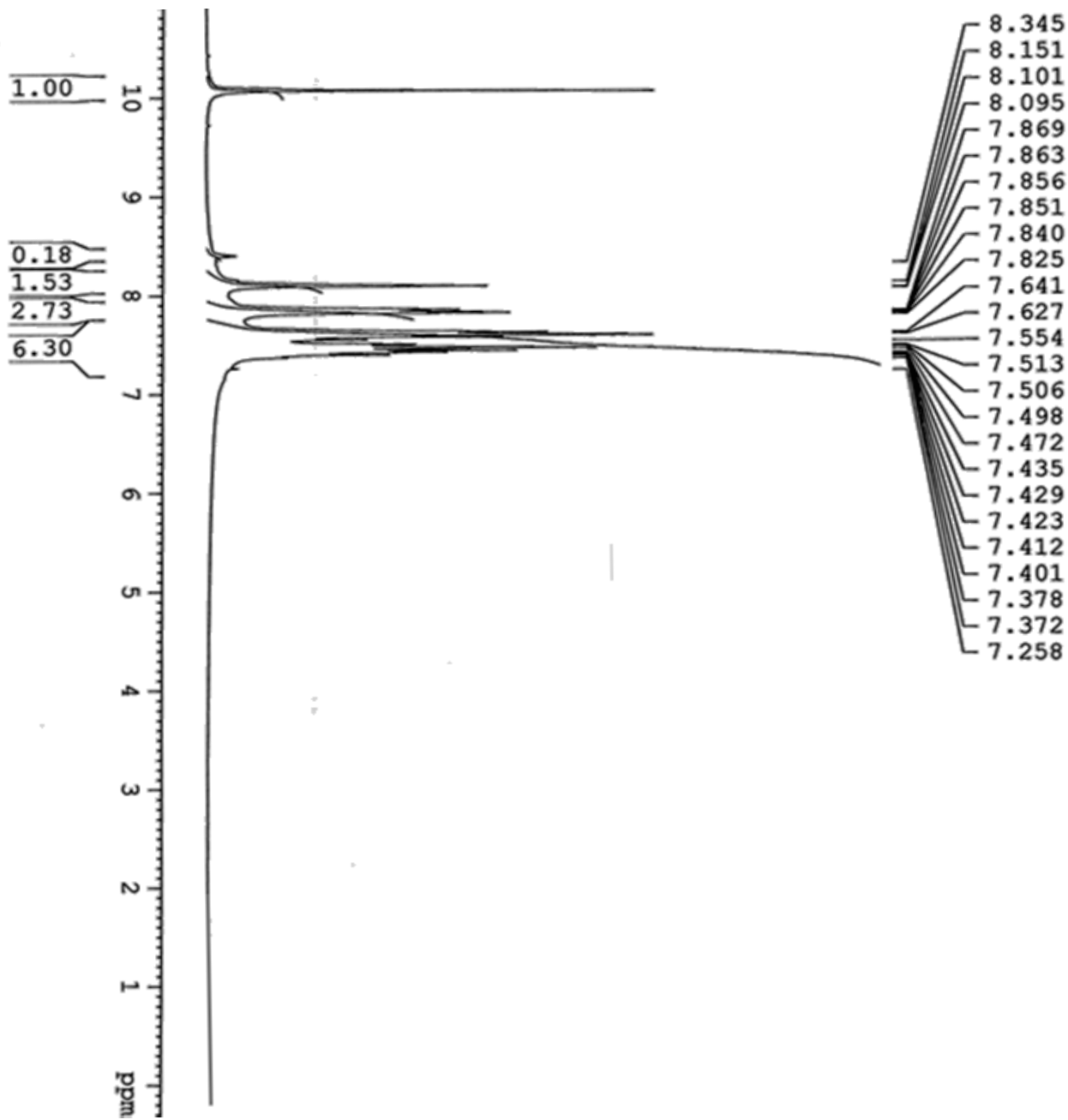


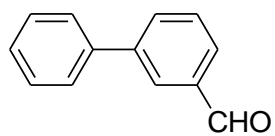
Phenyl- 4-carbaldehyde (in CDCl₃)



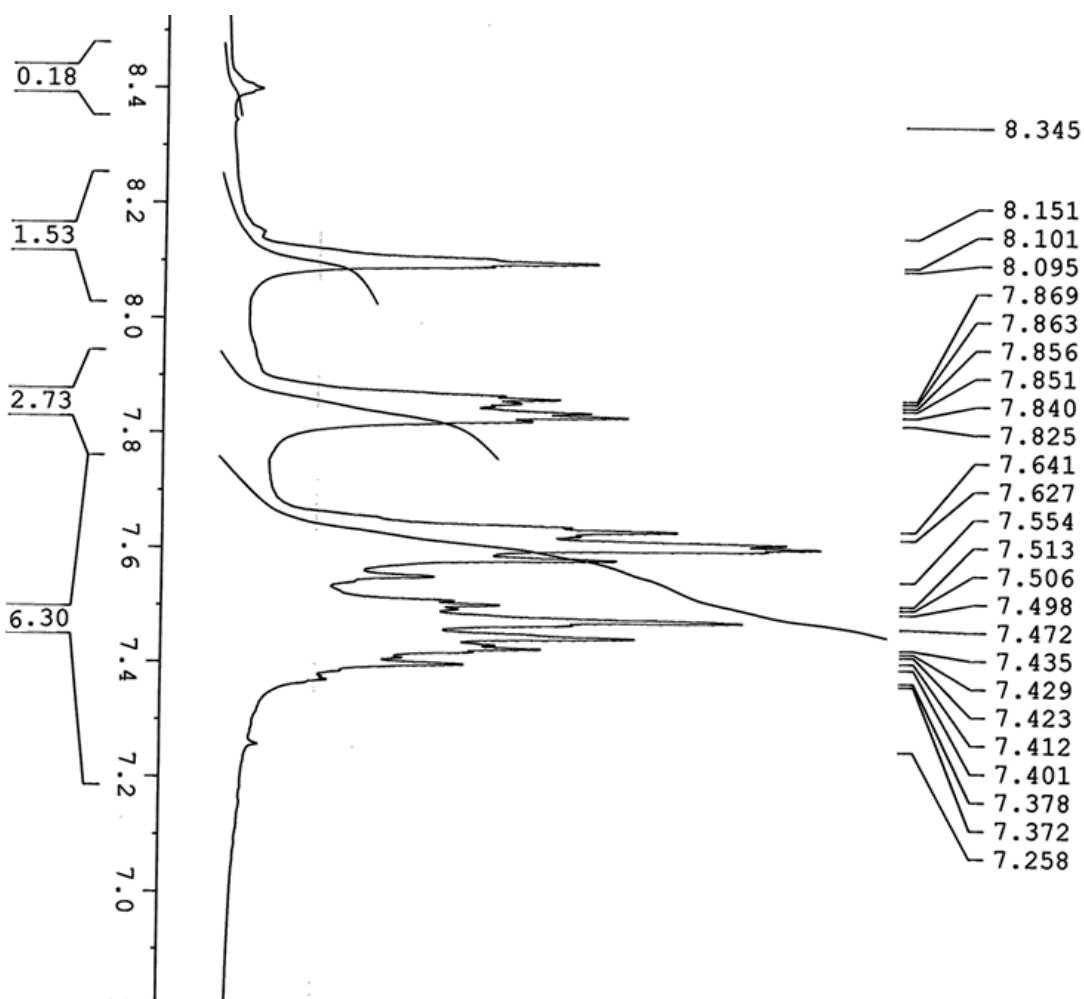


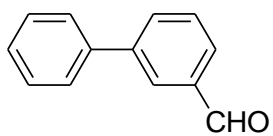
Phenyl- 4-carbaldehyde (in CDCl₃)



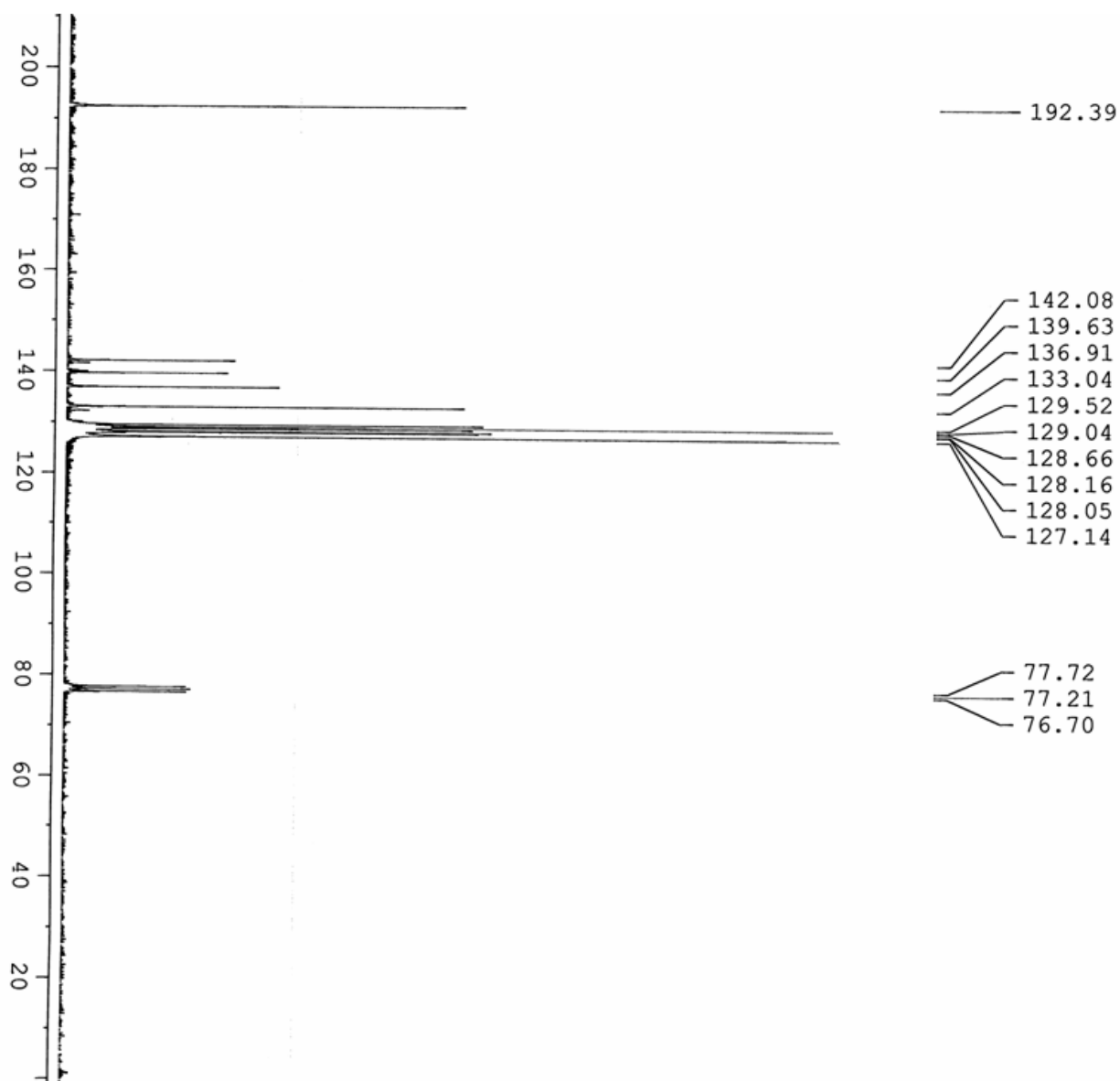


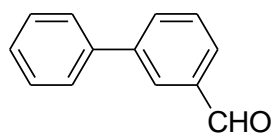
Phenyl- 4-carbaldehyde (in CDCl₃)



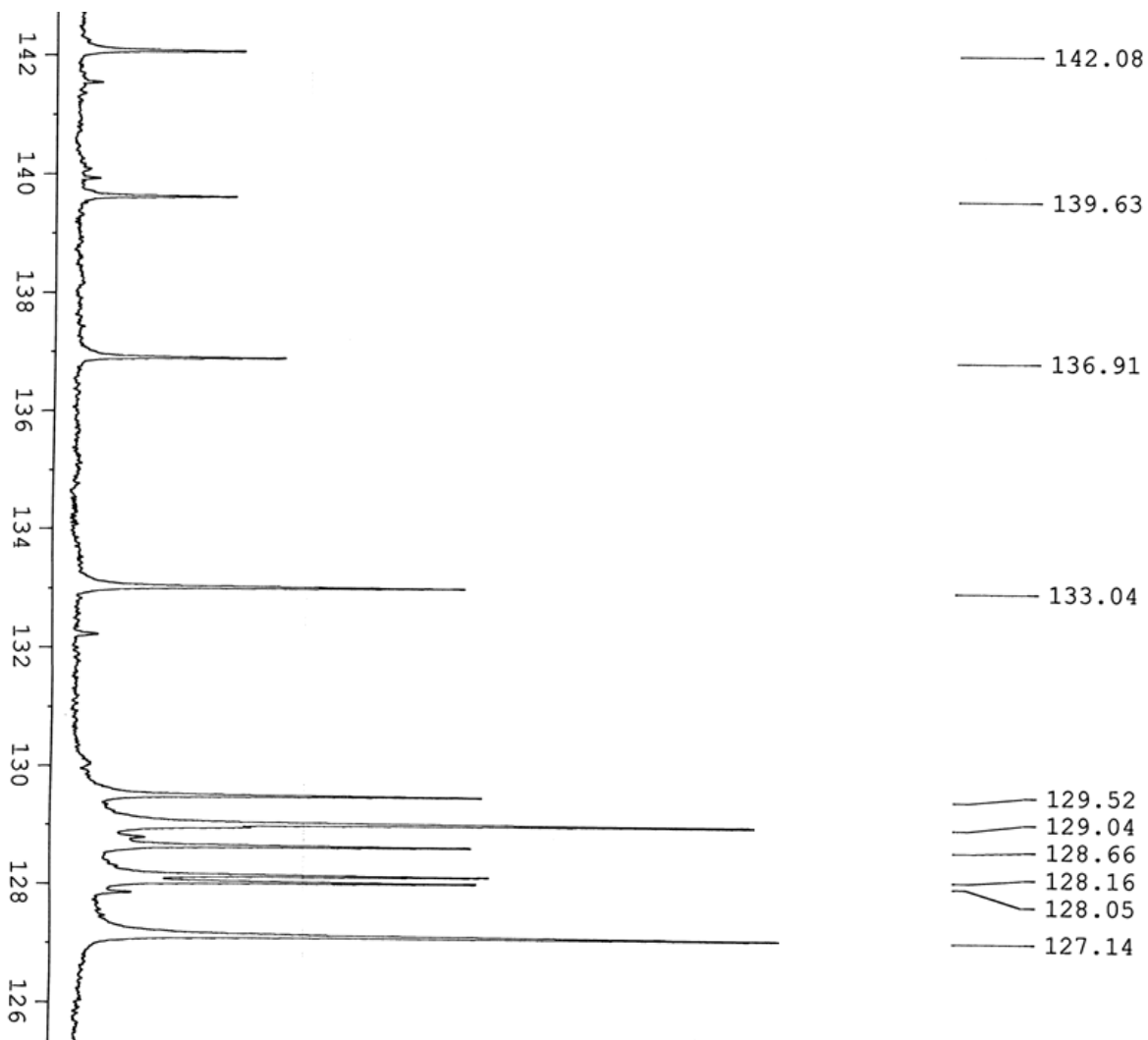


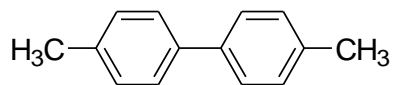
Phenyl- 4-carbaldehyde (in CDCl₃)



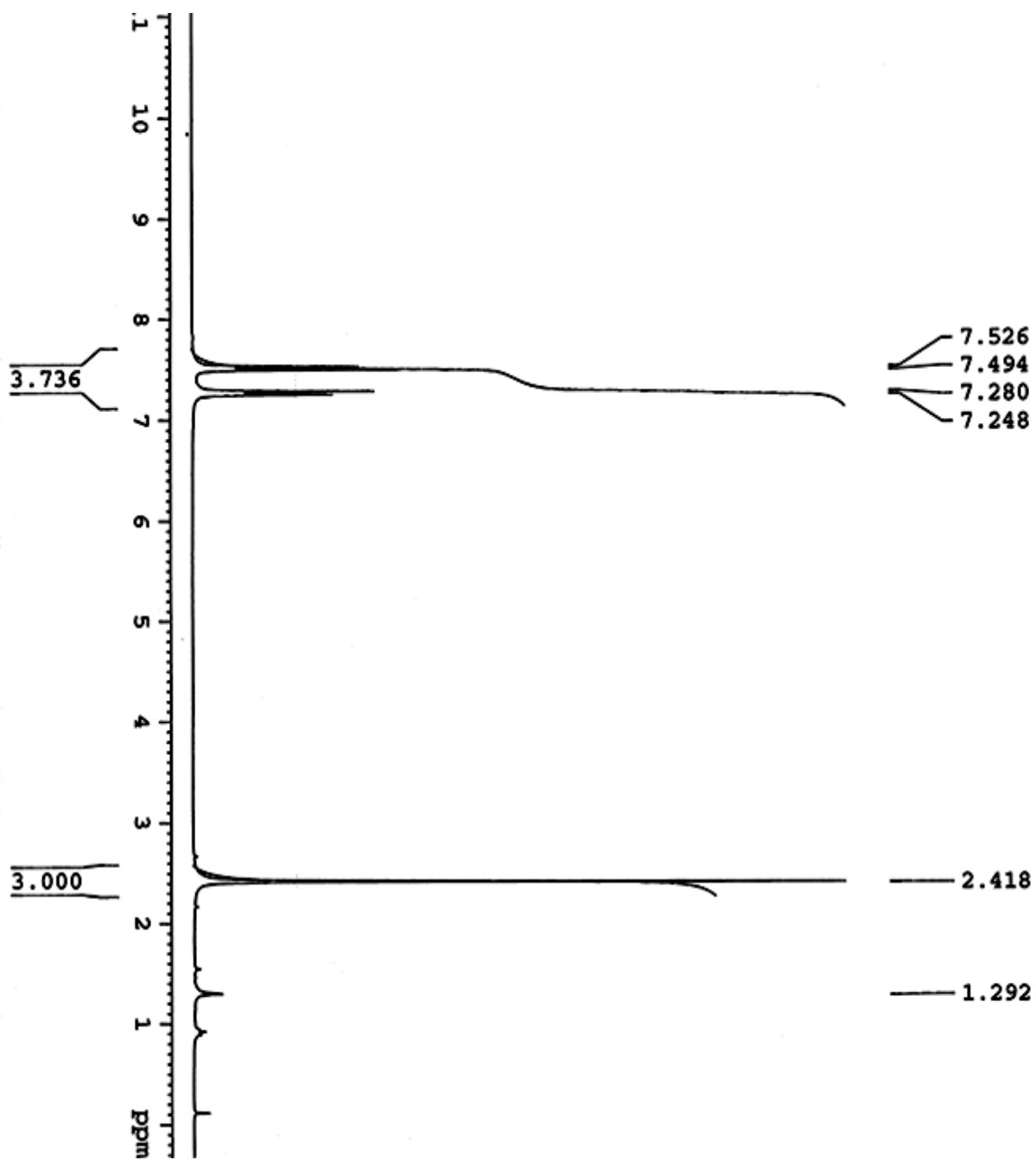


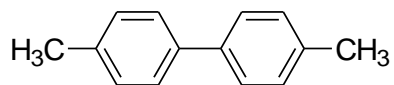
Phenyl- 4-carbaldehyde (in CDCl₃)



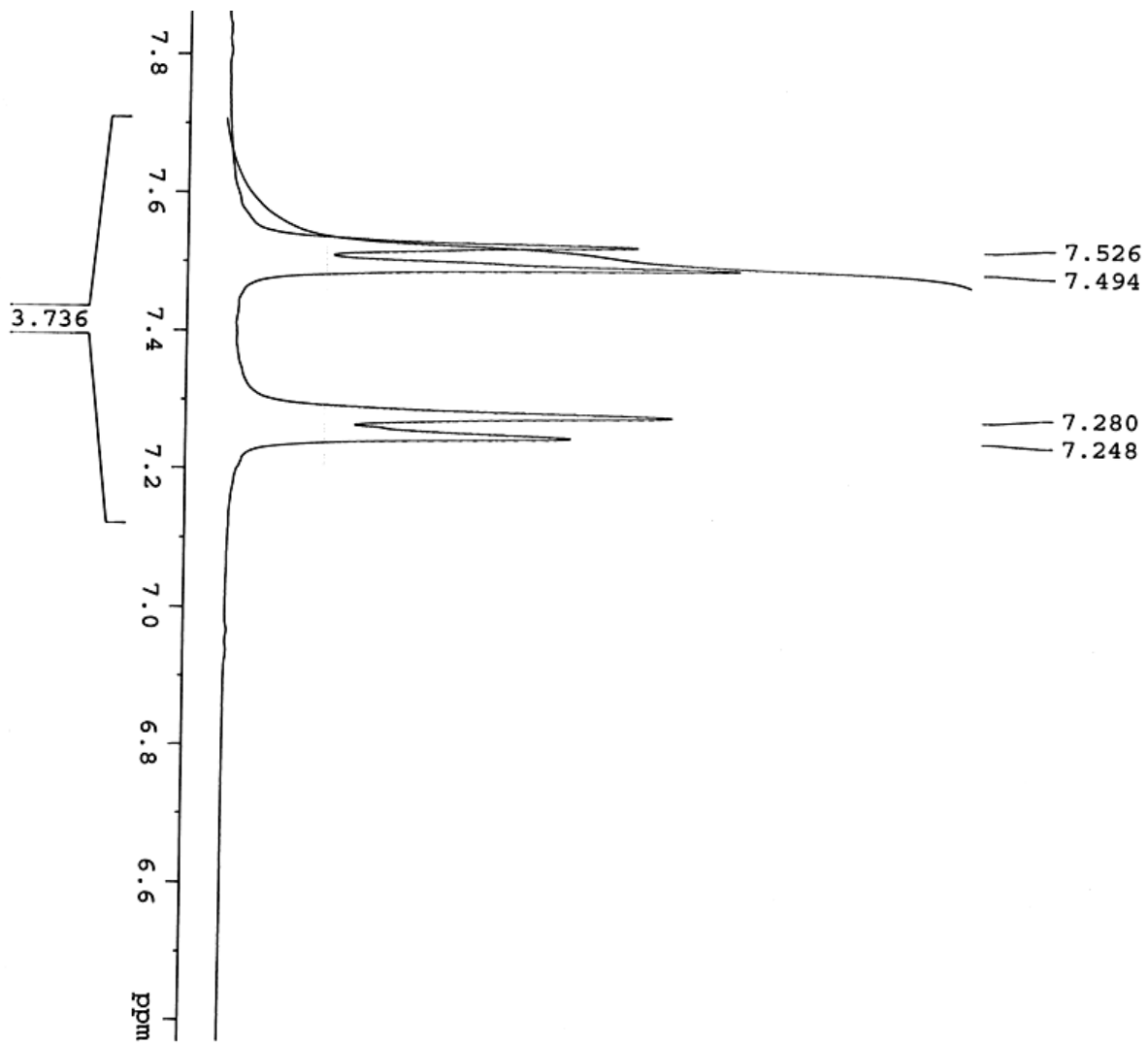


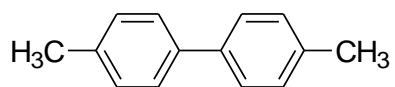
4, 4'-Dimethyl-biphenyl (in CDCl₃)



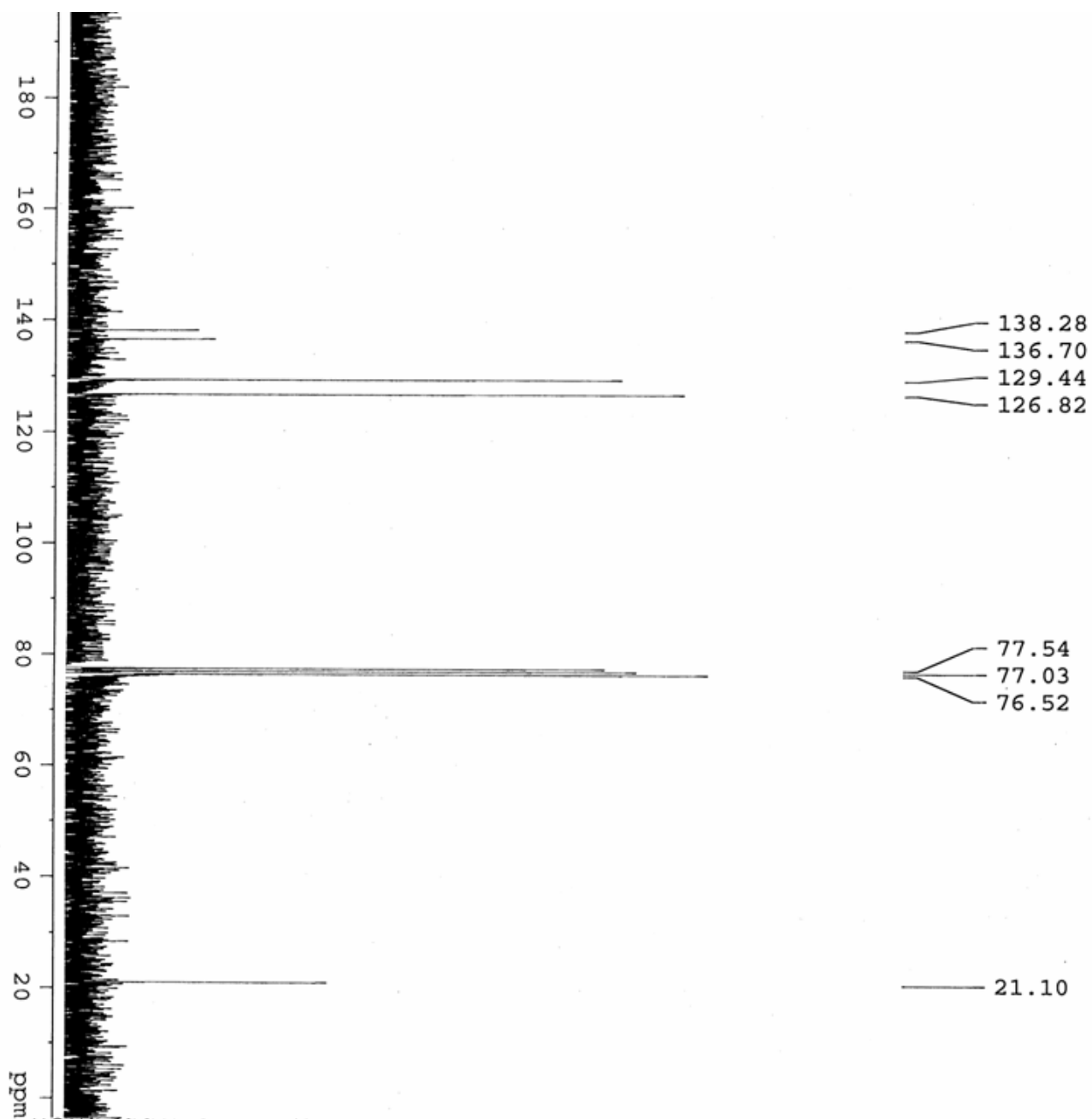


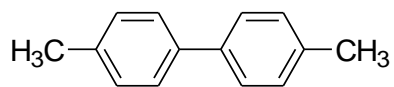
4, 4'-Dimethyl-biphenyl (in CDCl₃)



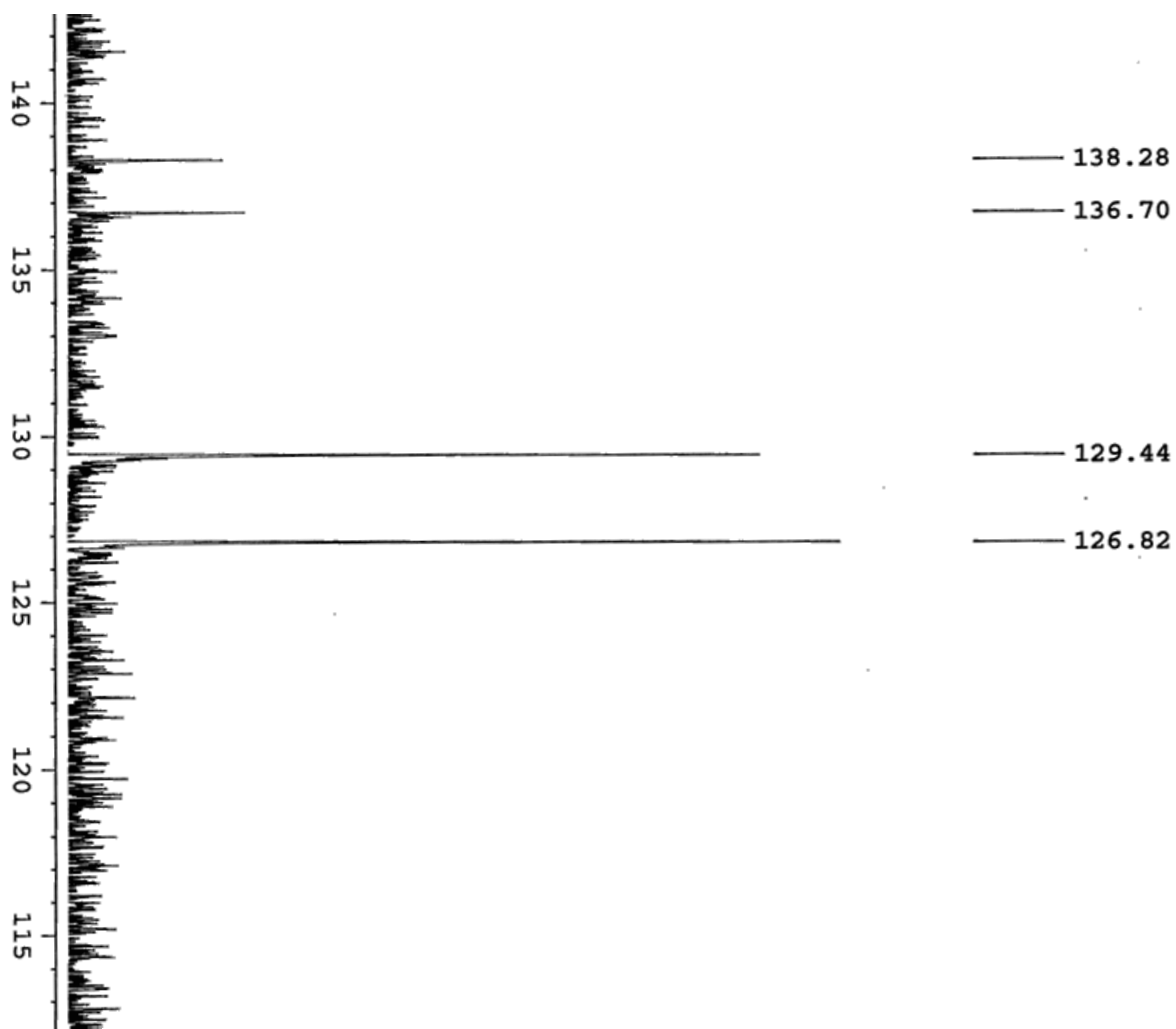


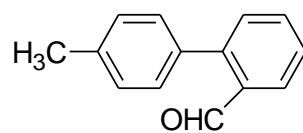
4, 4'-Dimethyl-biphenyl (in CDCl₃)



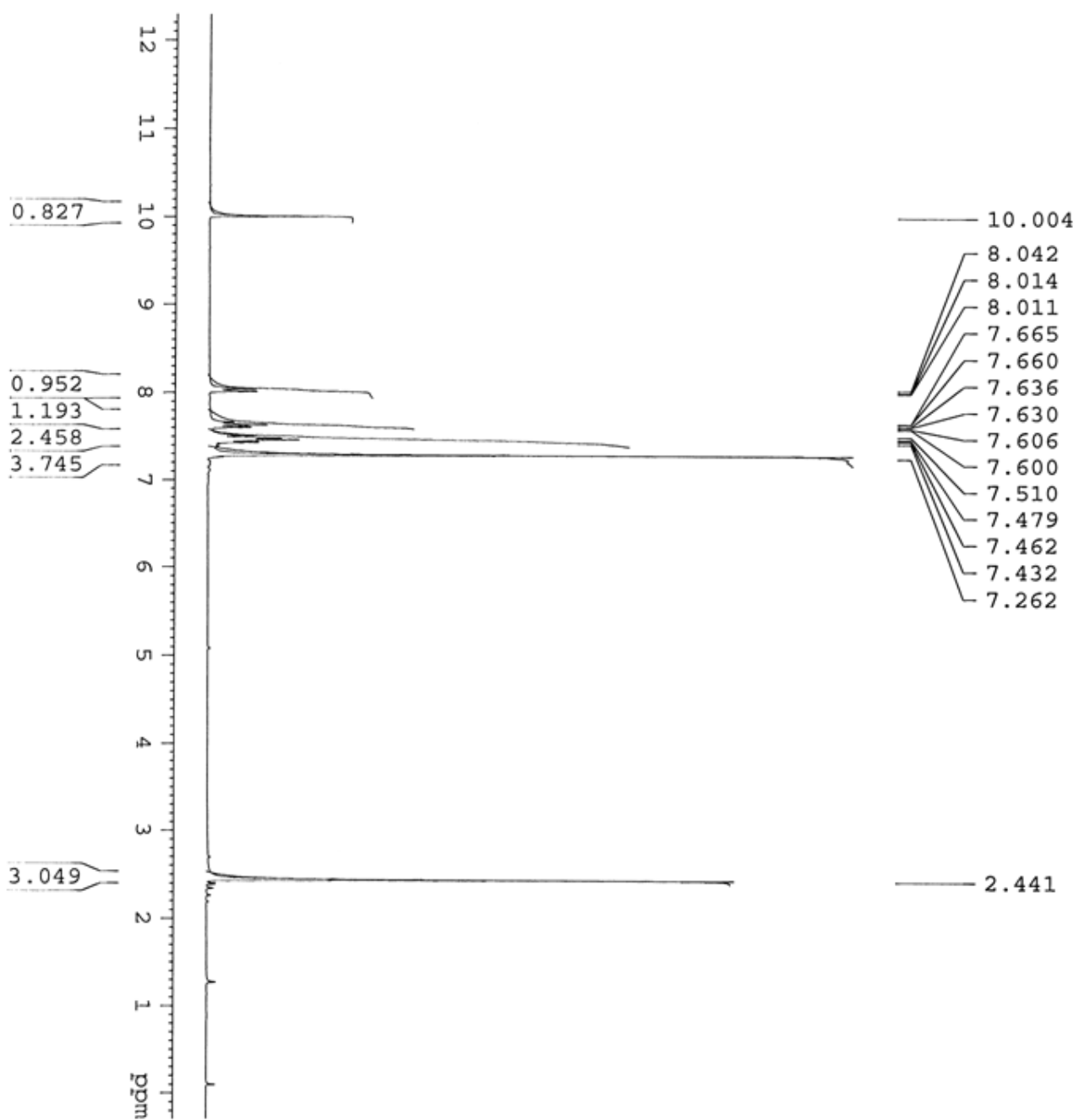


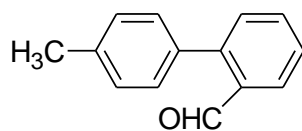
4, 4'-Dimethyl-biphenyl (in CDCl₃)



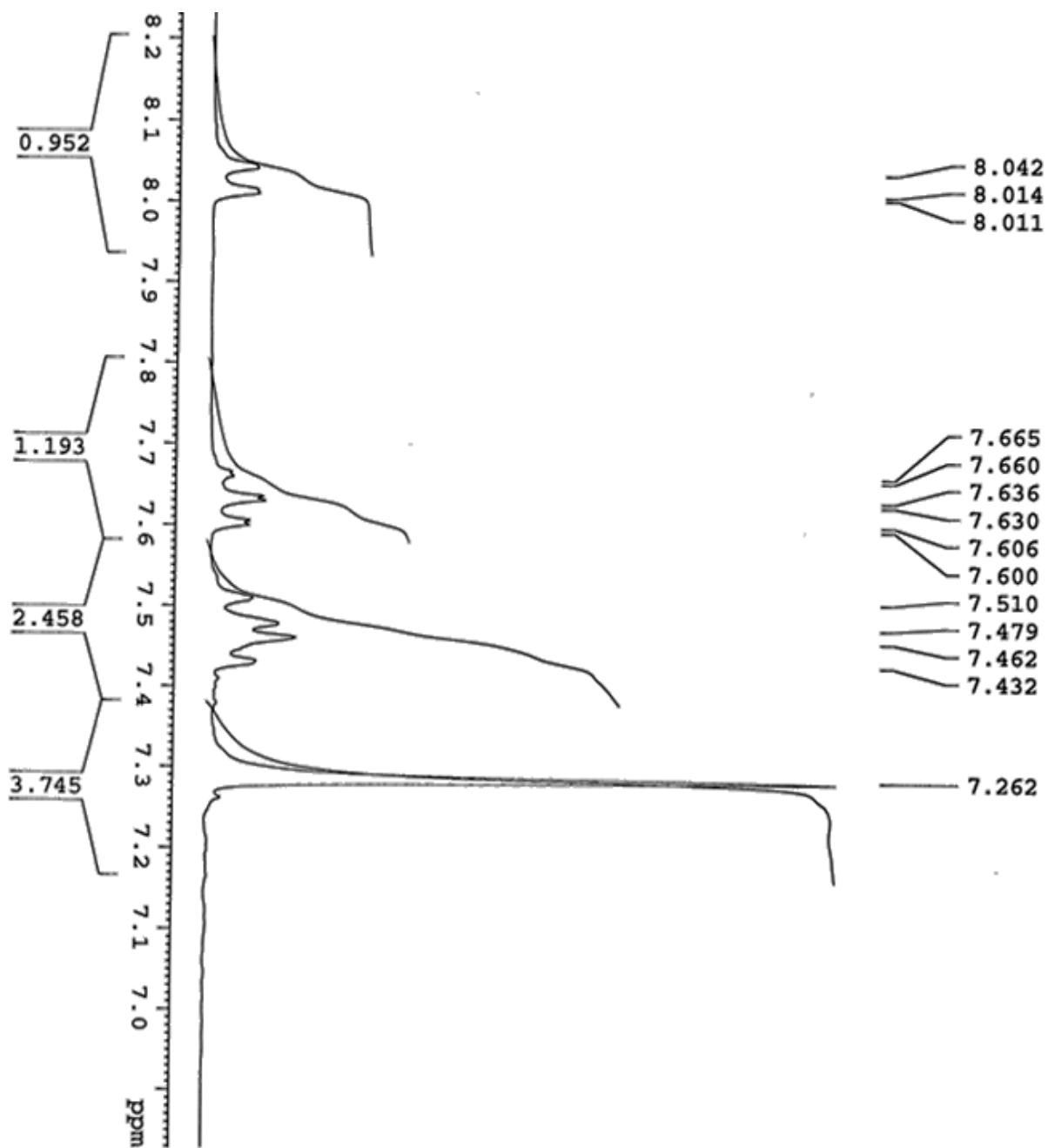


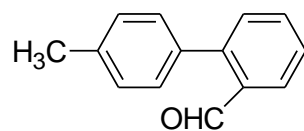
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl₃)



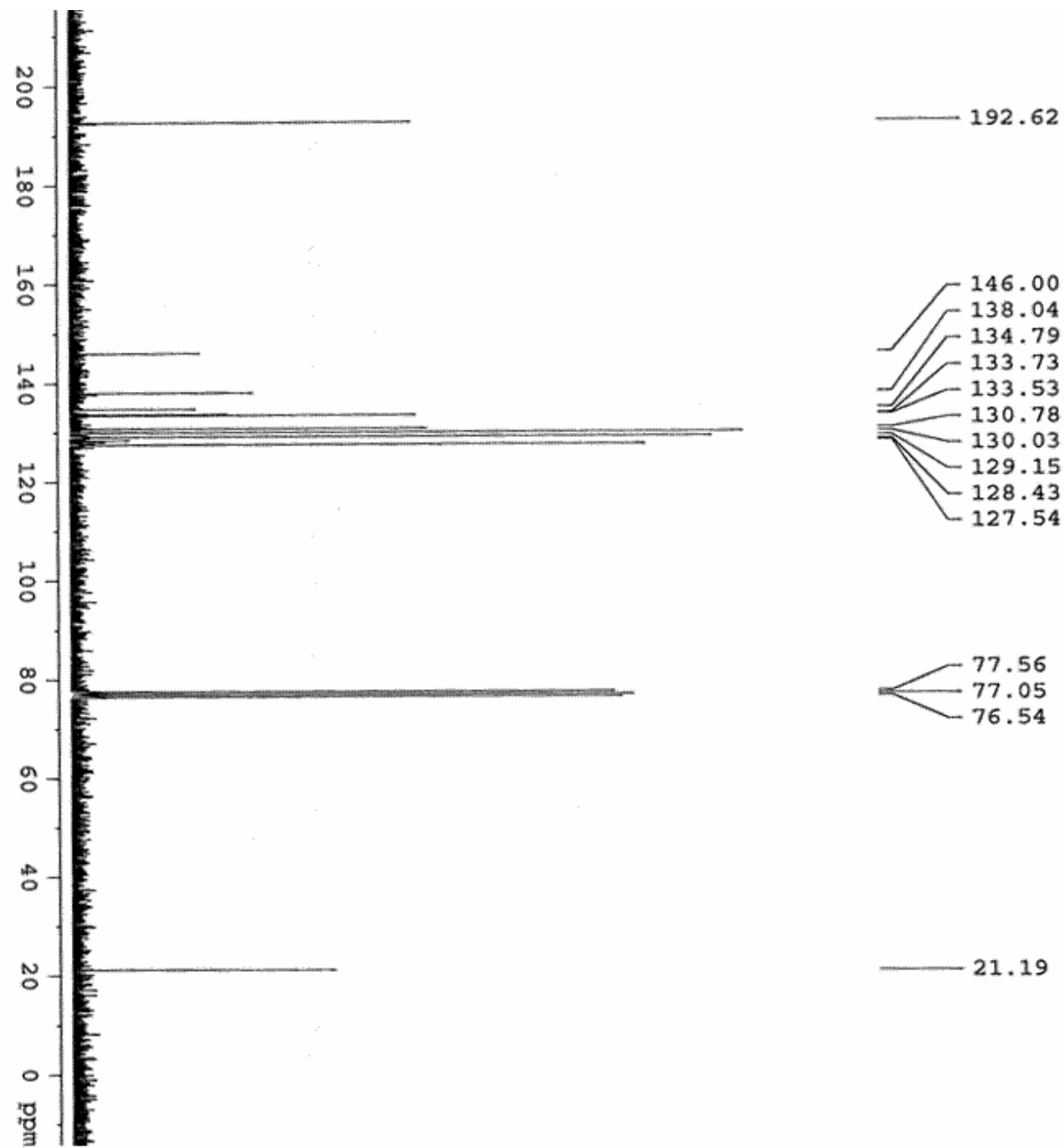


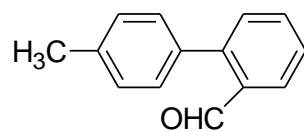
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl₃)



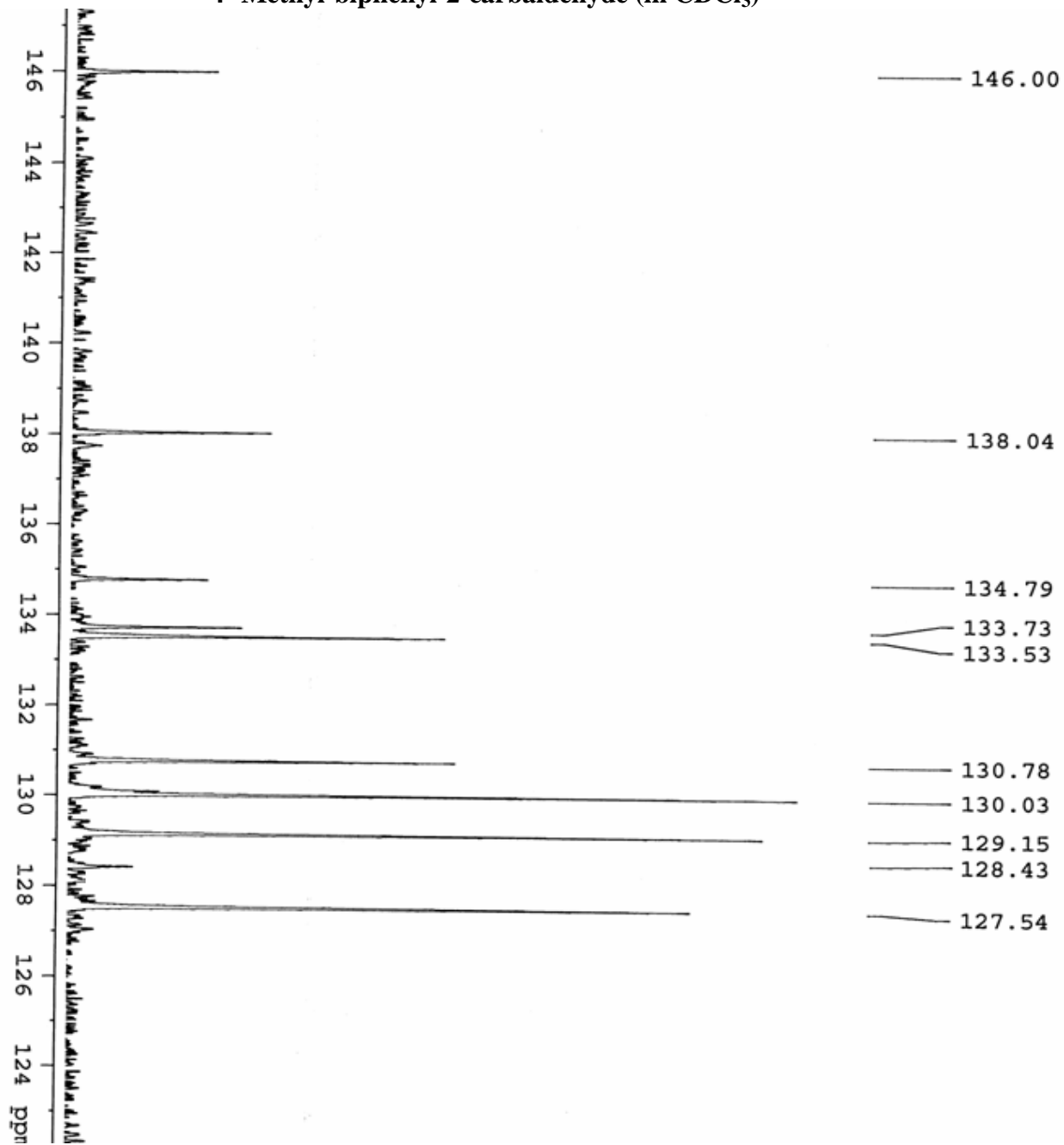


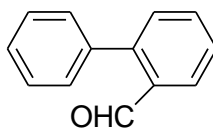
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl₃)



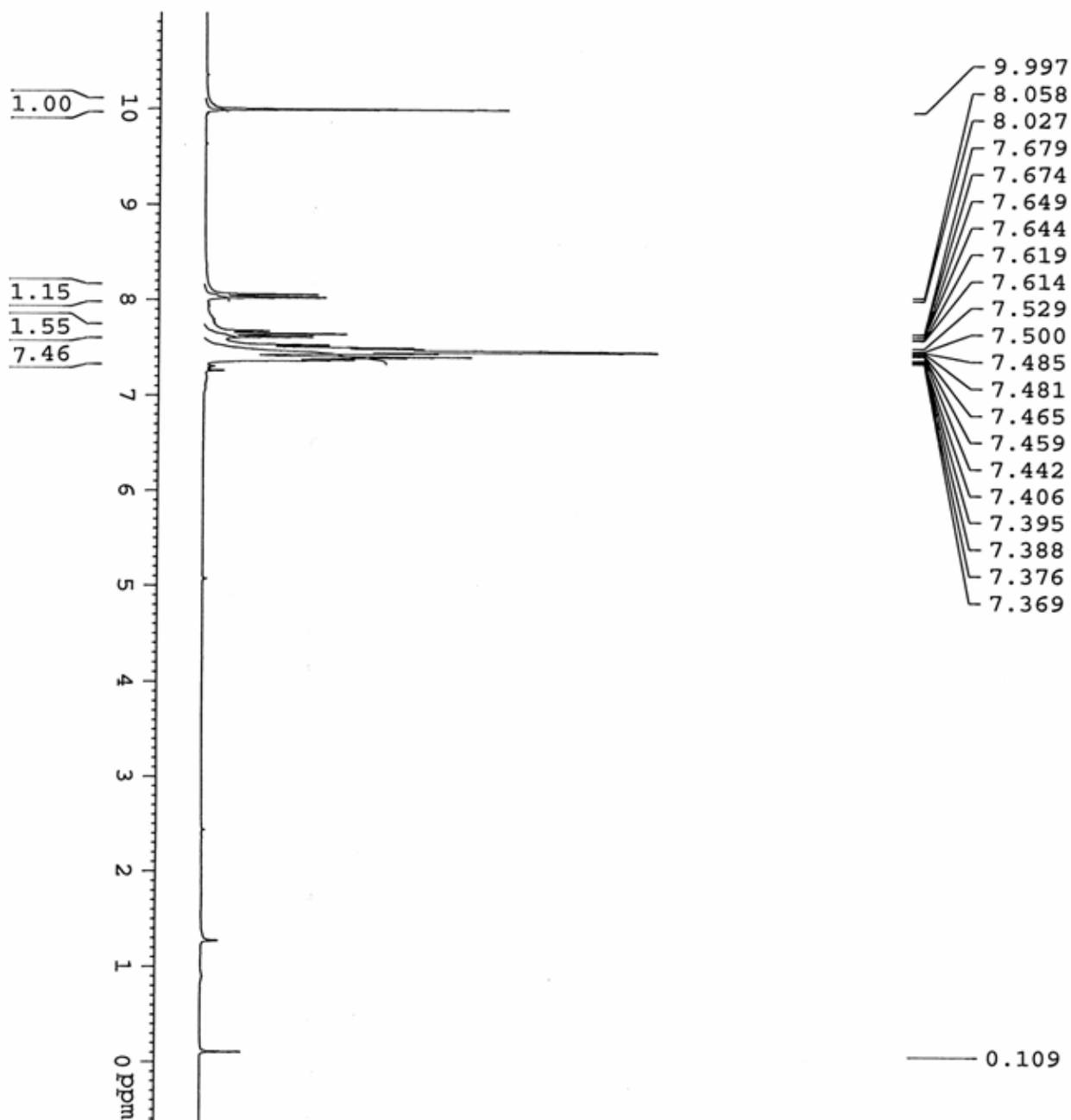


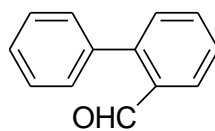
4'-Methyl-biphenyl-2-carbaldehyde (in CDCl₃)



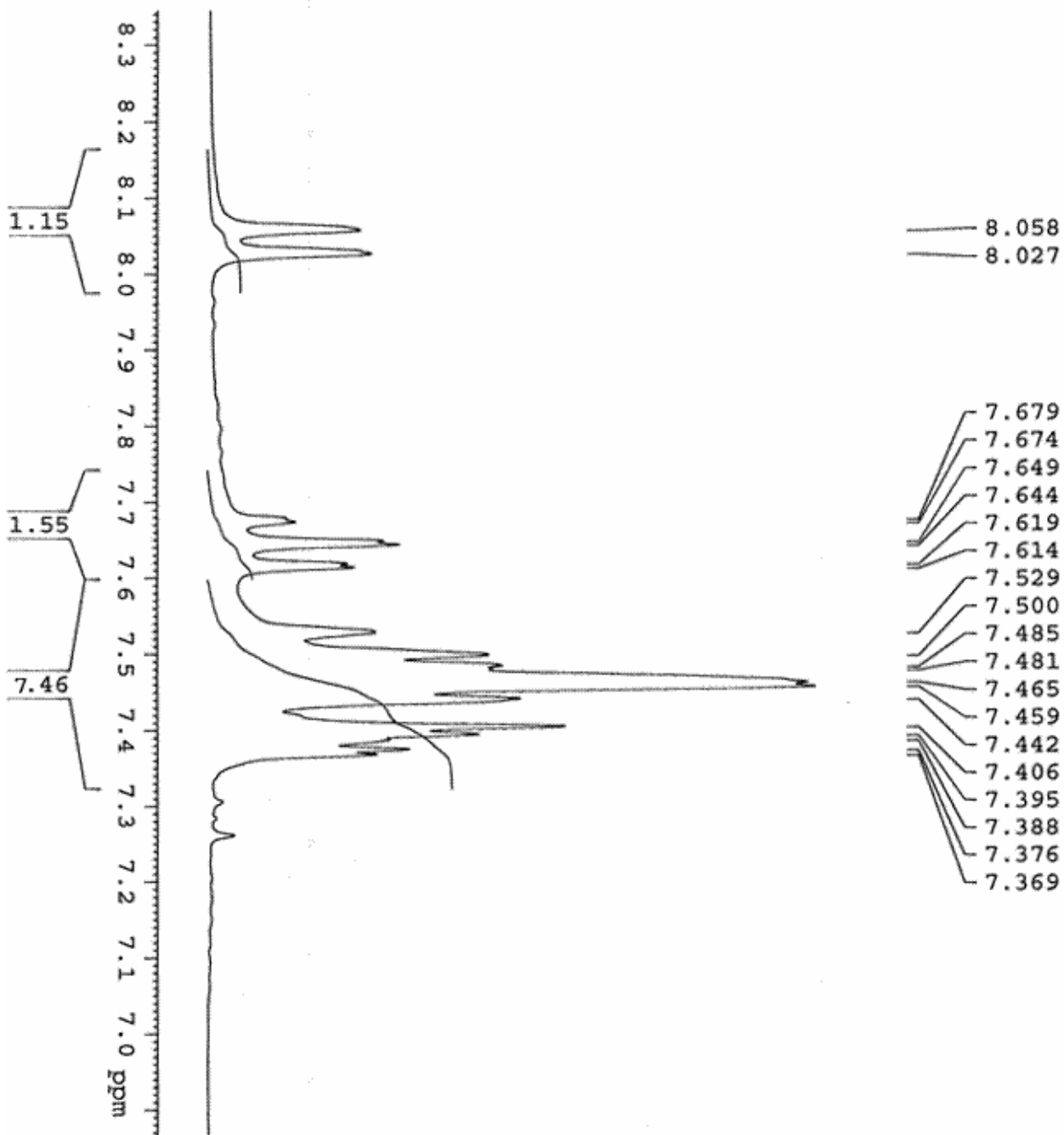


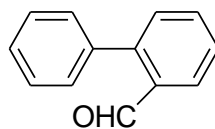
Biphenyl-2-carbaldehyde (in CDCl₃)



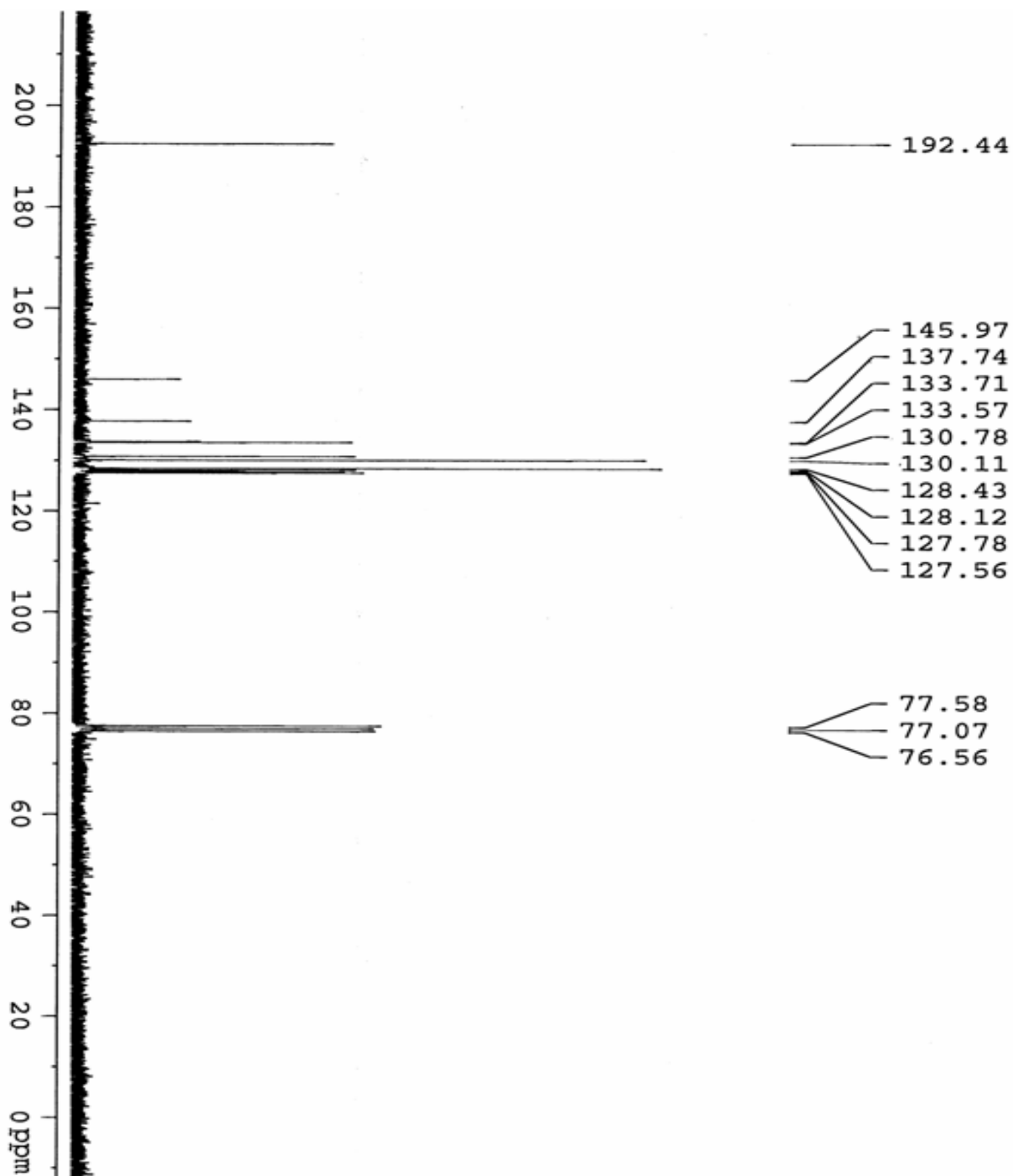


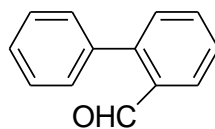
Biphenyl-2-carbaldehyde (in CDCl₃)



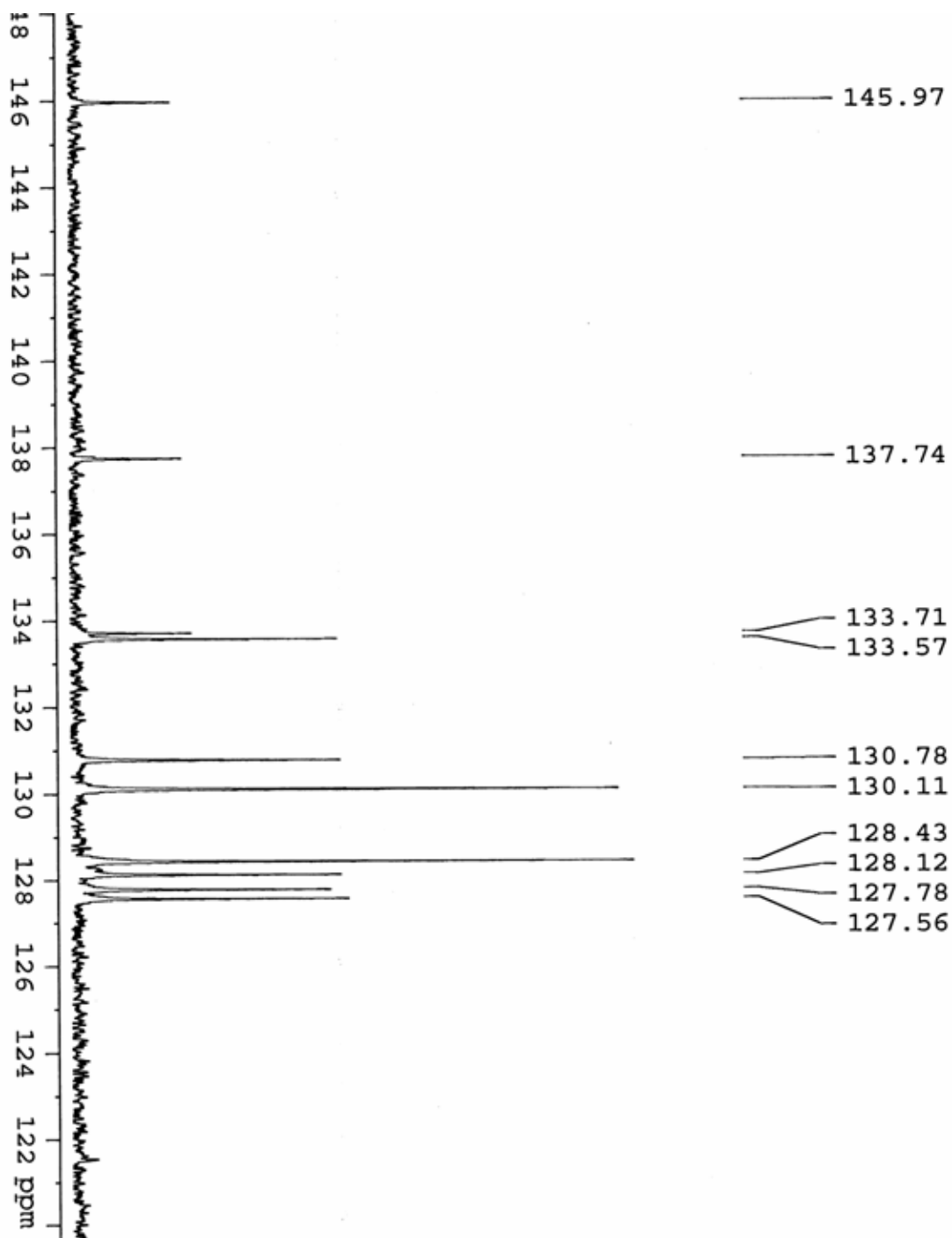


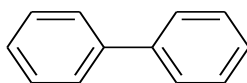
Biphenyl-2-carbaldehyde (in CDCl₃)



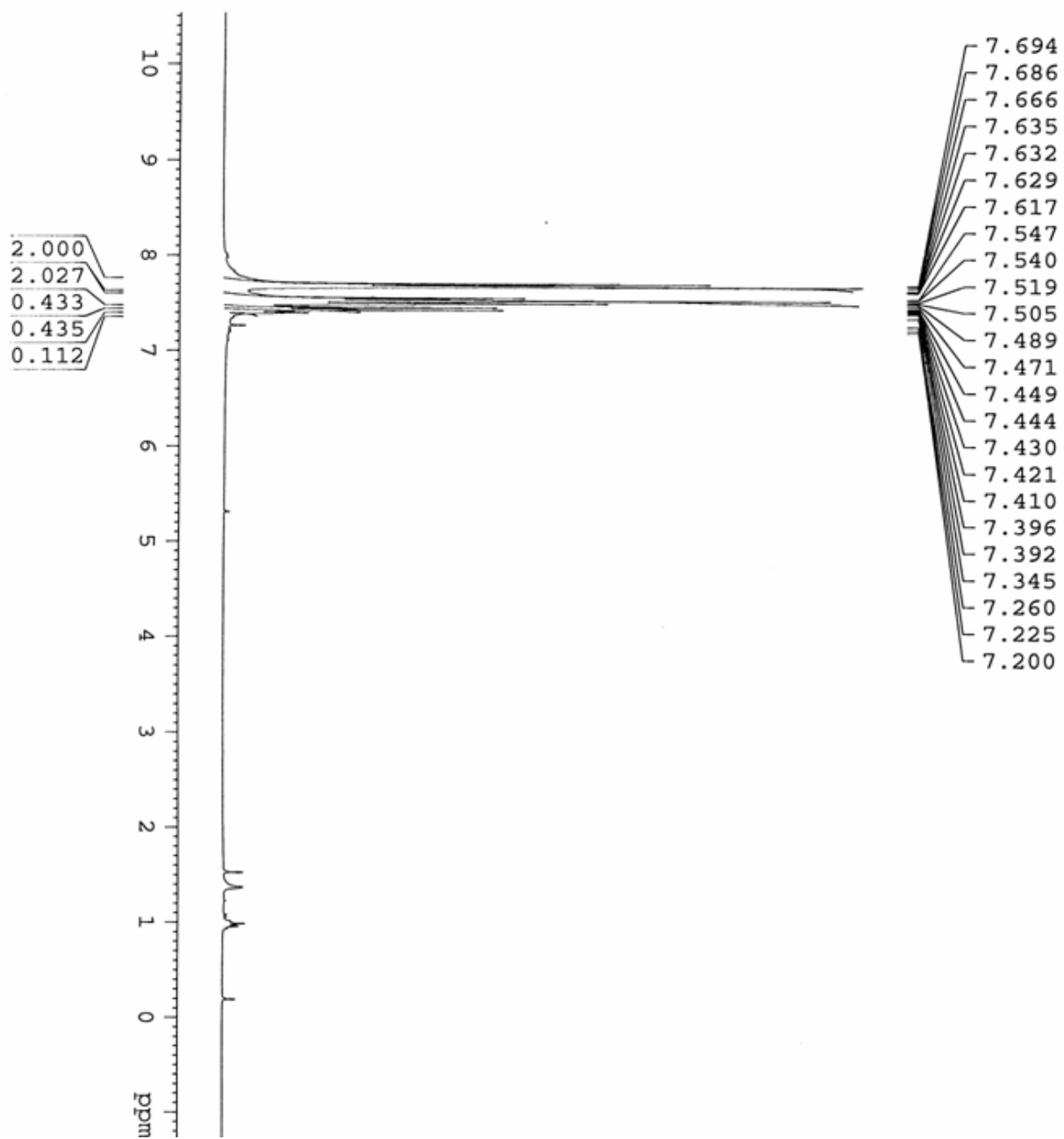


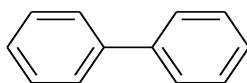
Biphenyl-2-carbaldehyde (in CDCl₃)



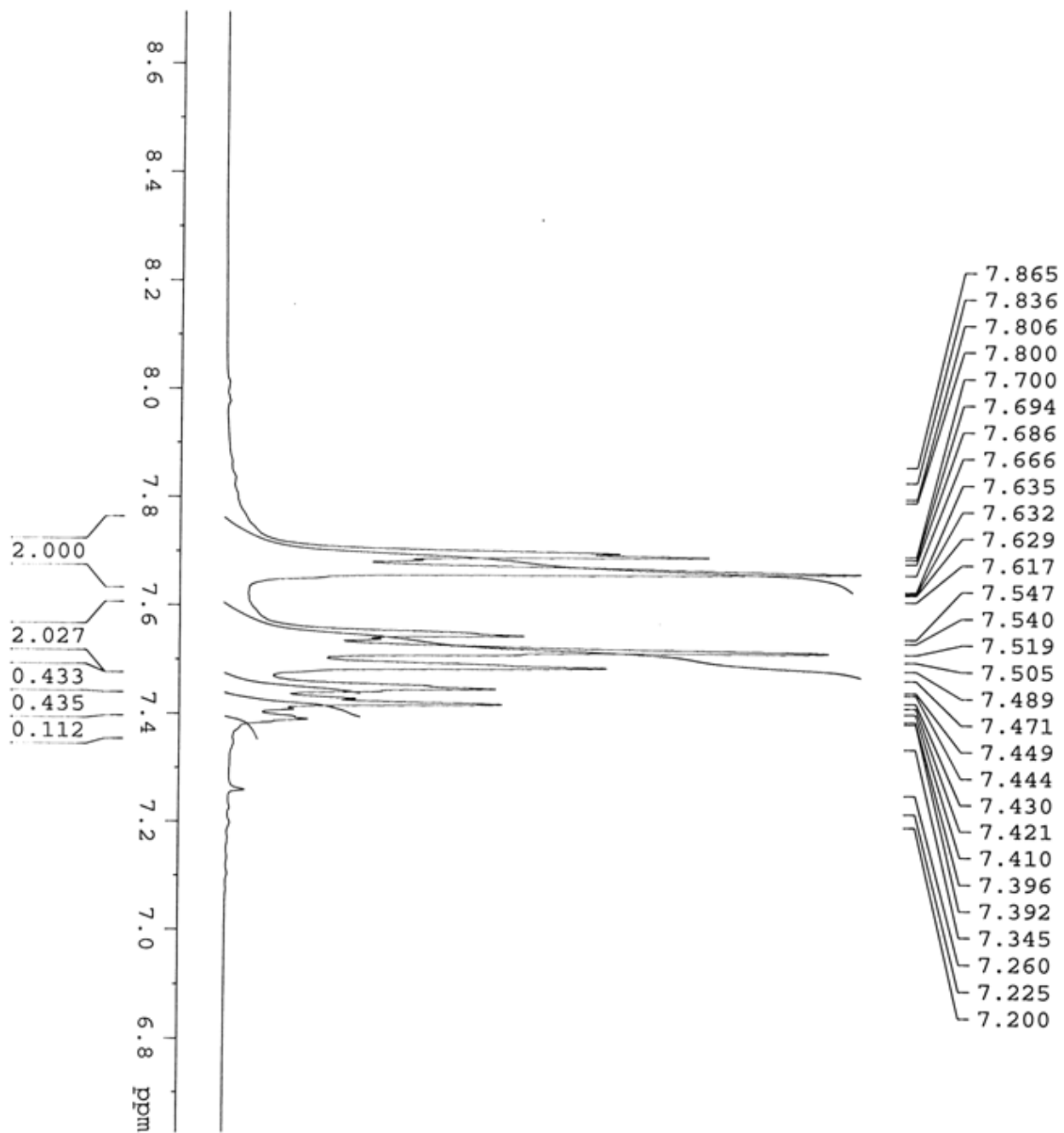


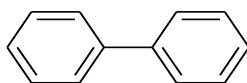
Biphenyl (in CDCl₃)



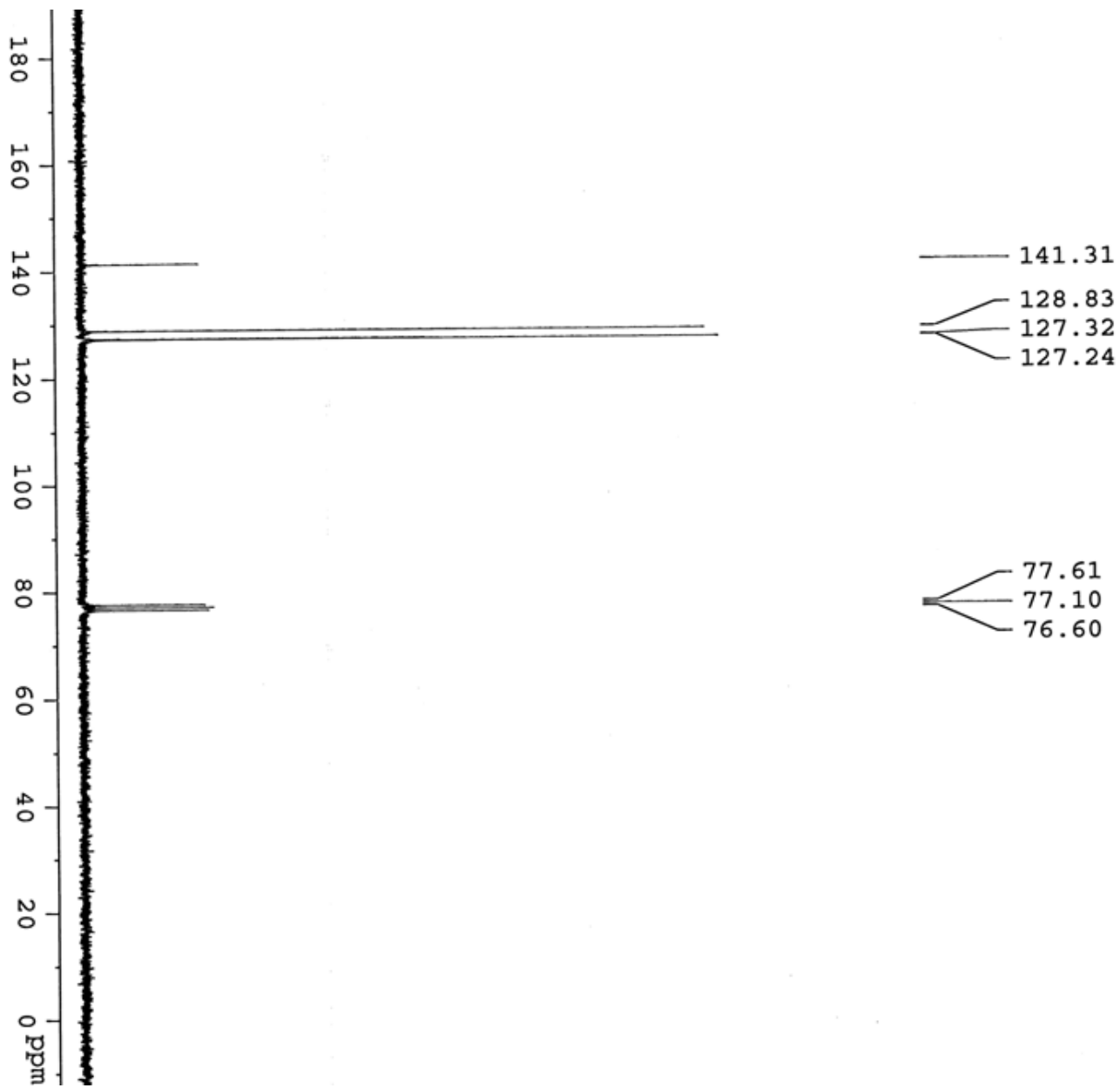


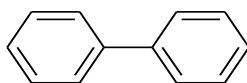
Biphenyl (in CDCl₃)



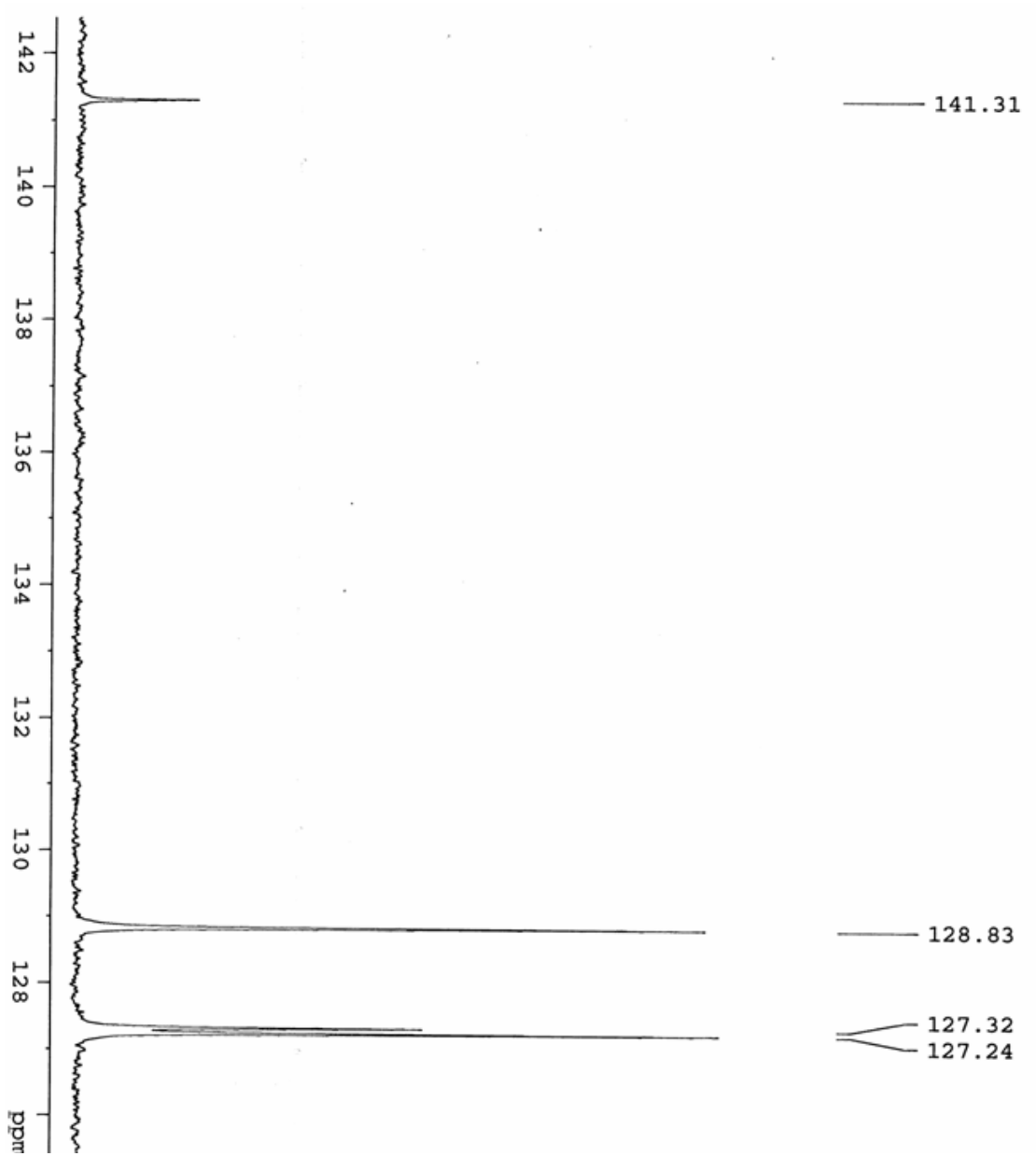


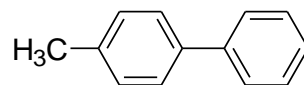
Biphenyl (in CDCl₃)



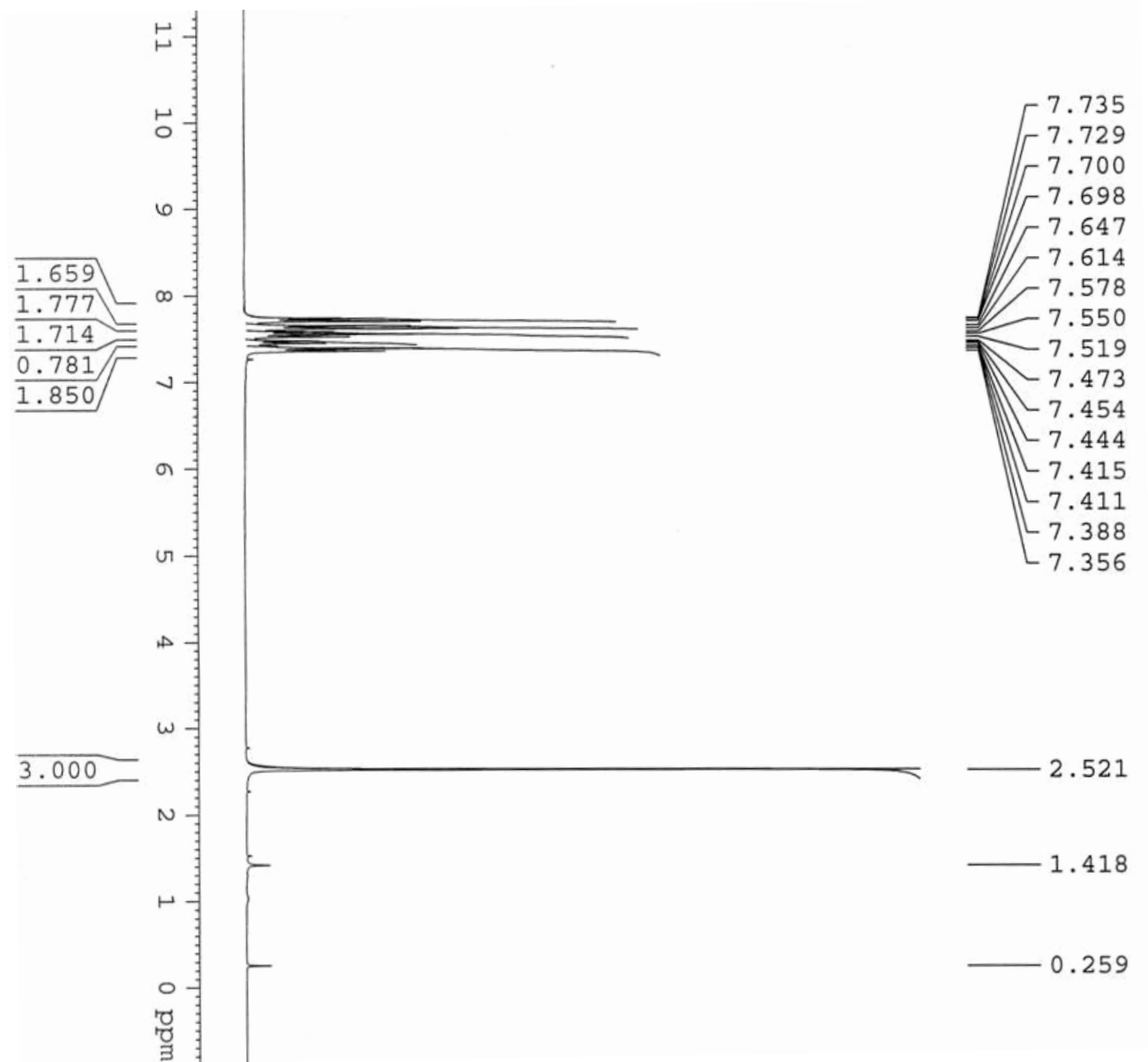


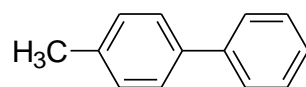
Biphenyl (in CDCl₃)



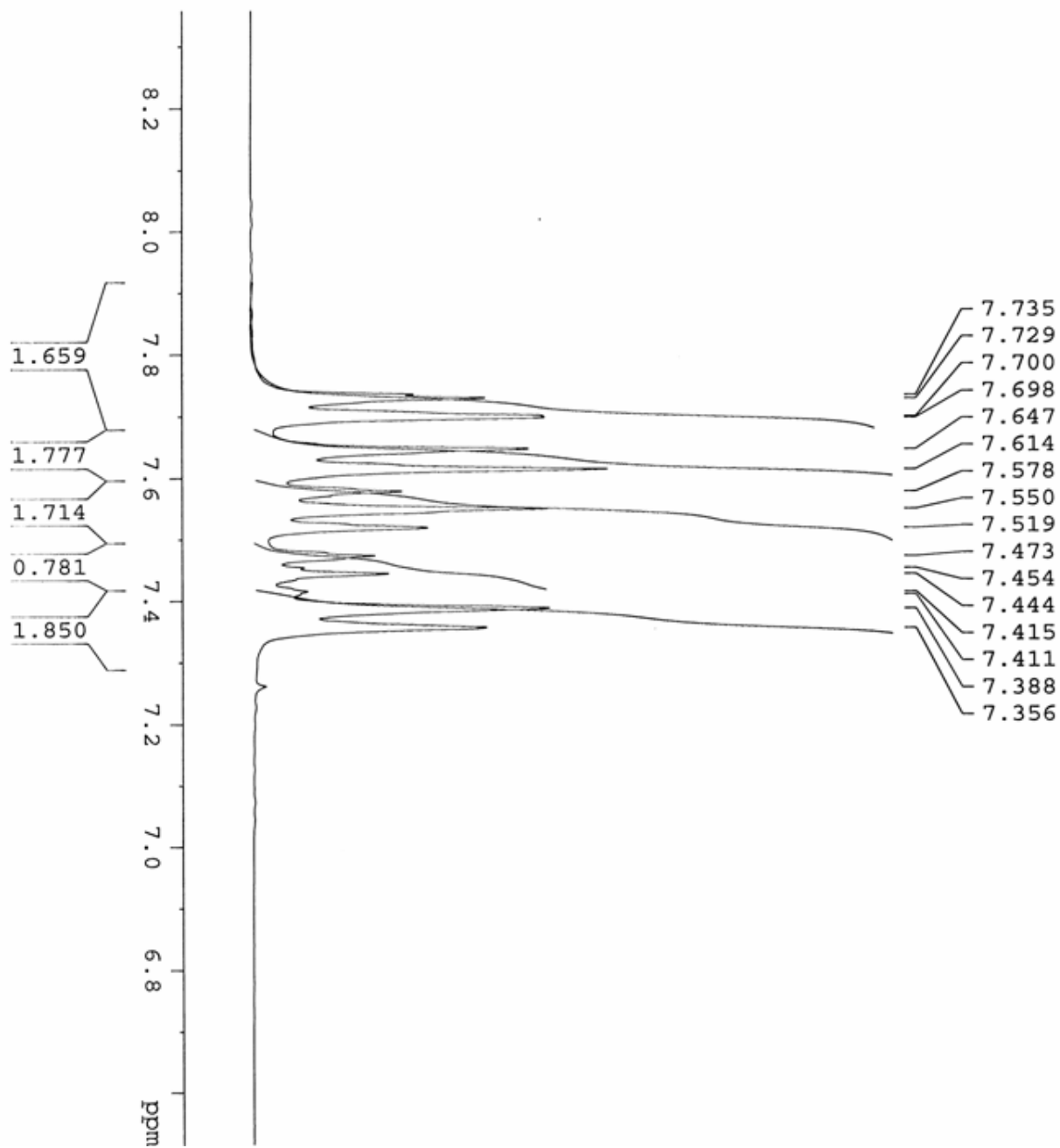


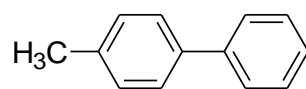
4-Methyl-biphenyl (in CDCl₃)



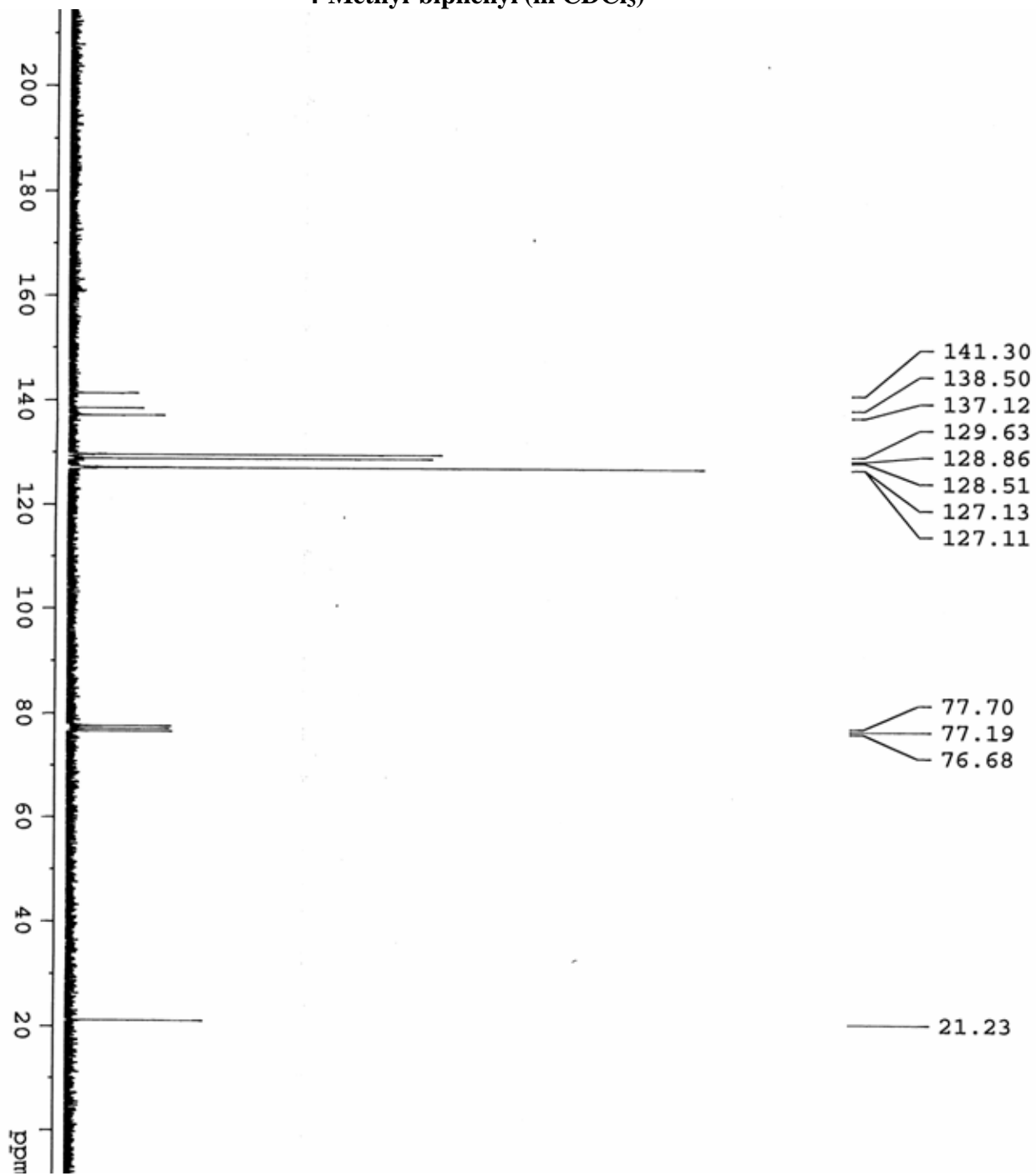


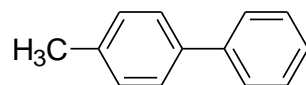
4-Methyl-biphenyl (in CDCl₃)



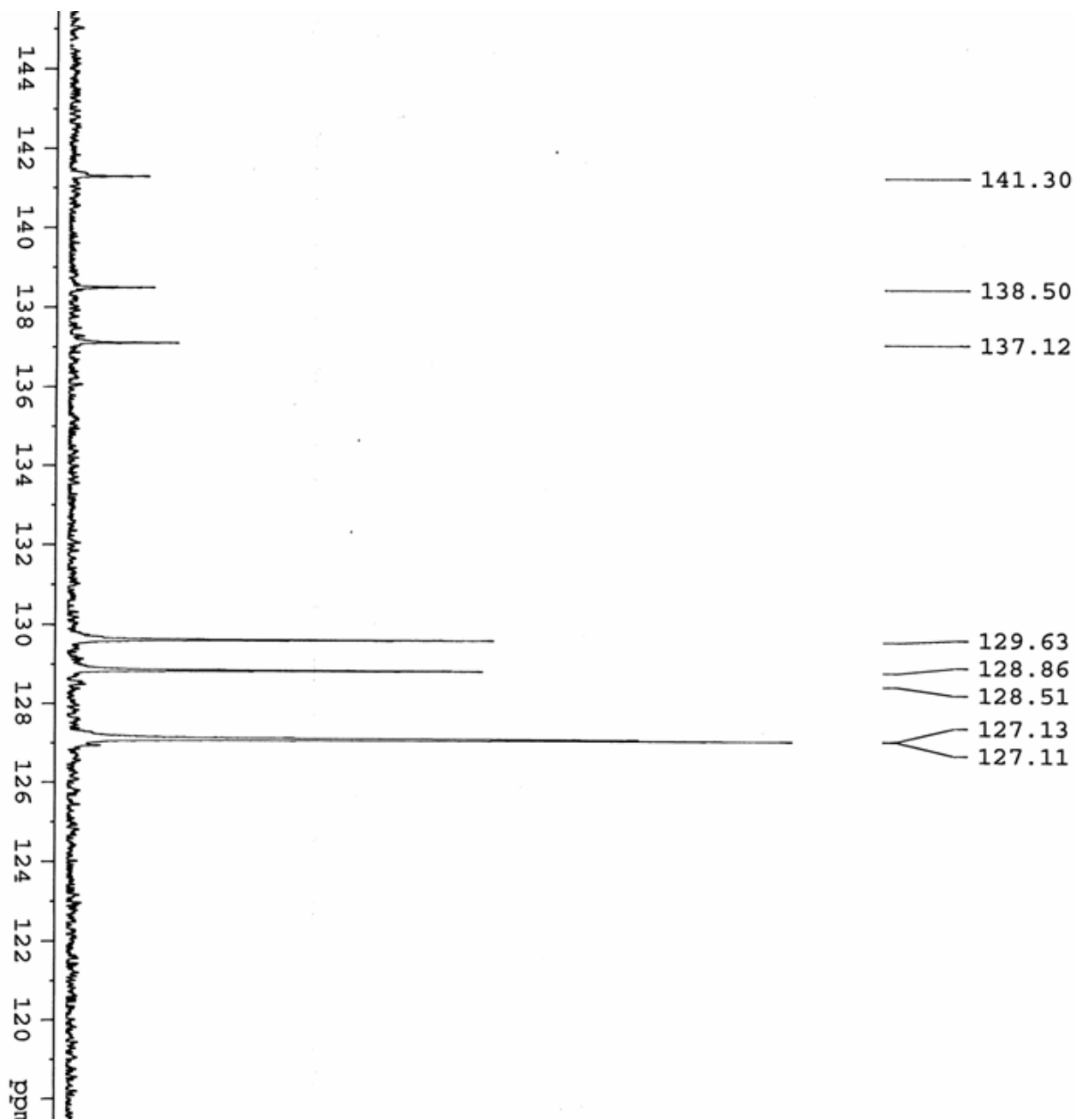


4-Methyl-biphenyl (in CDCl₃)





4-Methyl-biphenyl (in CDCl₃)



References:

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