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Solvent Free Three Component Strecker Reaction of Ketones Using Highly Recyclable and hydrophobic Sulfonic Acid Based Nanoreactors

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Table of Contents

Experimental procedures, TEM, TGA, BET, BJH, and N_2 adsorption-desorption isotherm

1. Experimental Procedure:

1.1. Preparation of SBA-15-Pr-SH: The synthesis of SBA-15-Pr-SH has been achieved using known procedure described by Stucky and his co-workers (Margolese, D.; Melero, J. A.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2448). This procedure involved a synthetic strategy based on co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as structure directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h. TGA diagram for SBA-15-Pr-SH is shown in Figure 1.

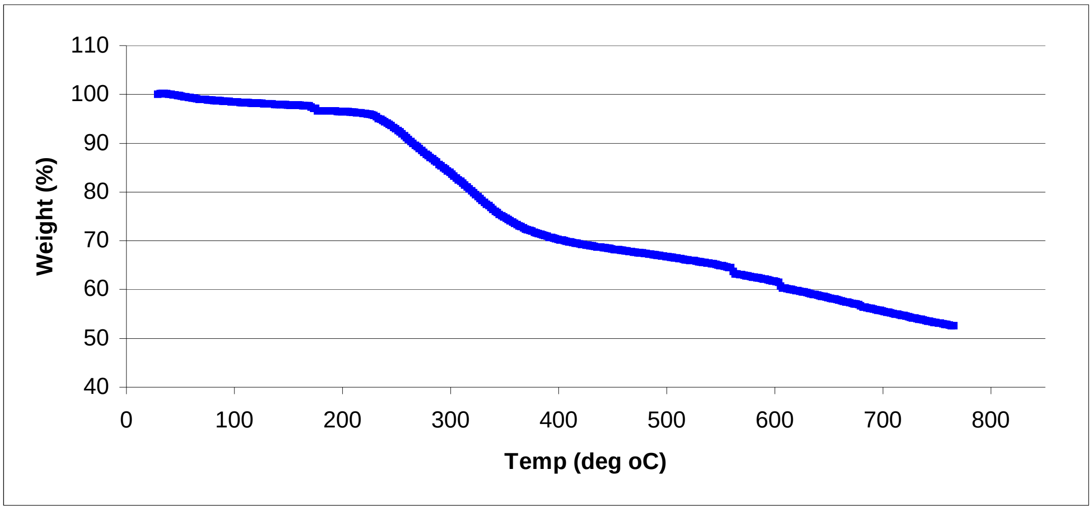


Figure 1. TGA diagram for SBA-15-Pr-SH

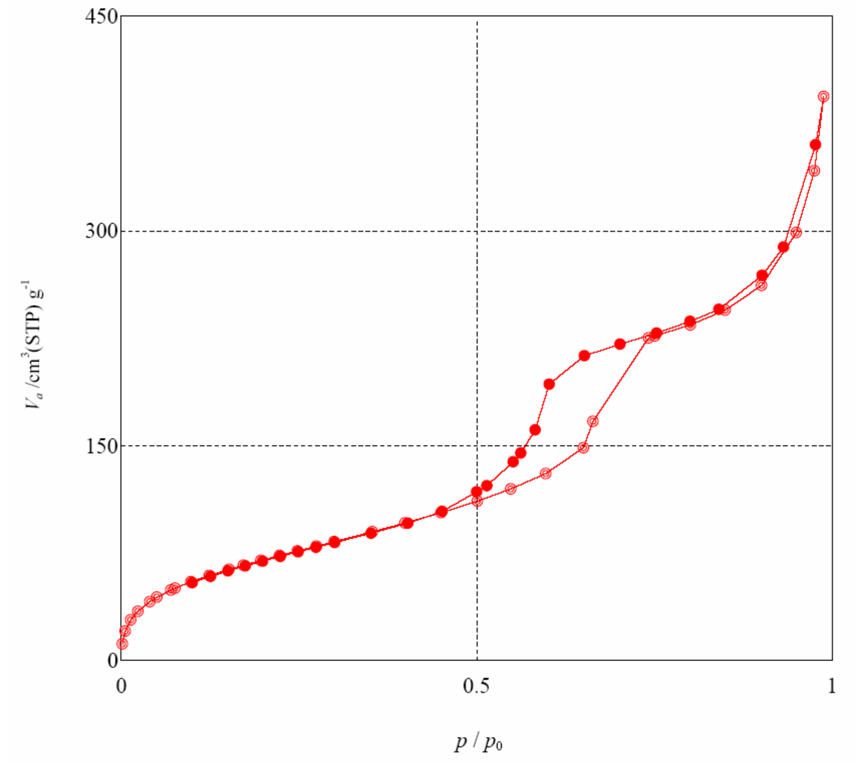


Figure 2. Nitrogen adsorption-desorption isotherm for SBA-15-Pr-SH

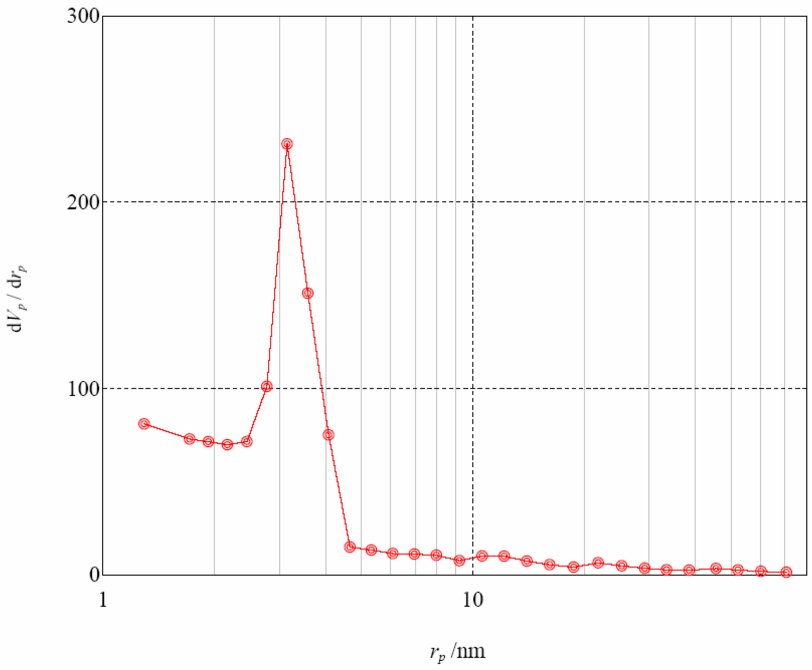


Figure 3. BJH average pore diameter diagram for SBA-15-Pr-SH

1.2. Preparation of SBA-15-Ph-Pr-SH:

To a suspension of SBA-15-Pr-SH (3 g) in dry toluene $PhSi(OEt)_3$ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24 h. The solid materials was filtered and successively washed with toluene, EtOH, and Et_2O and dried overnight at 120 °C to afford the corresponding SBA-15-Ph-Pr-SH.

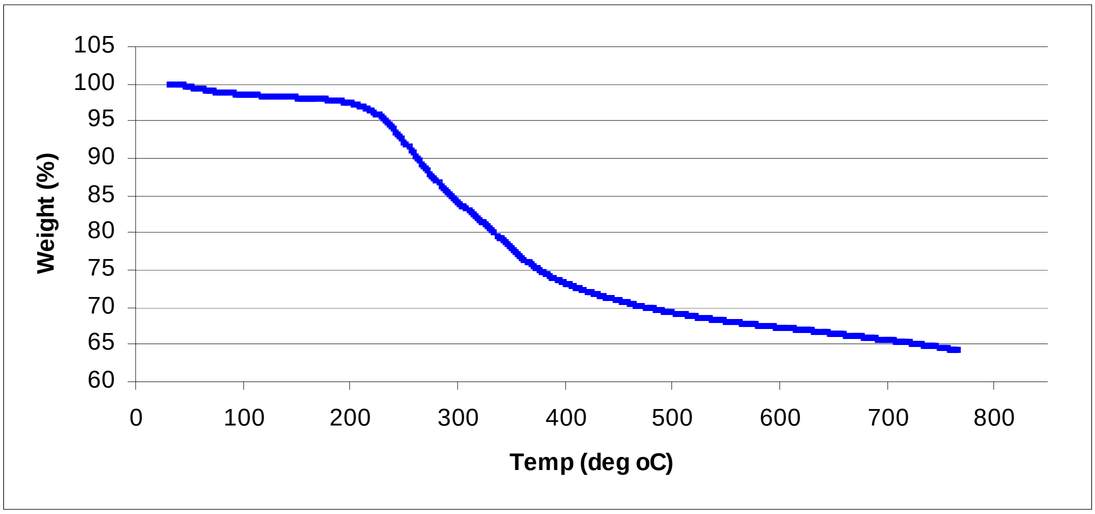


Figure 4. TGA diagram for SBA-15-Ph-Pr-SH

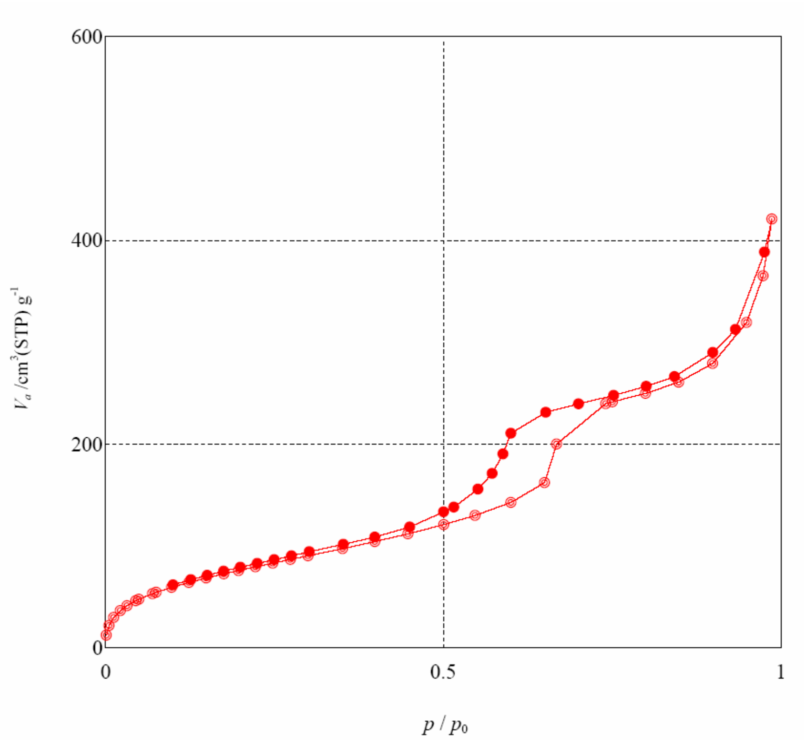


Figure 5. Nitrogen adsorption-desorption isotherm for SBA-15-Ph-Pr-SH

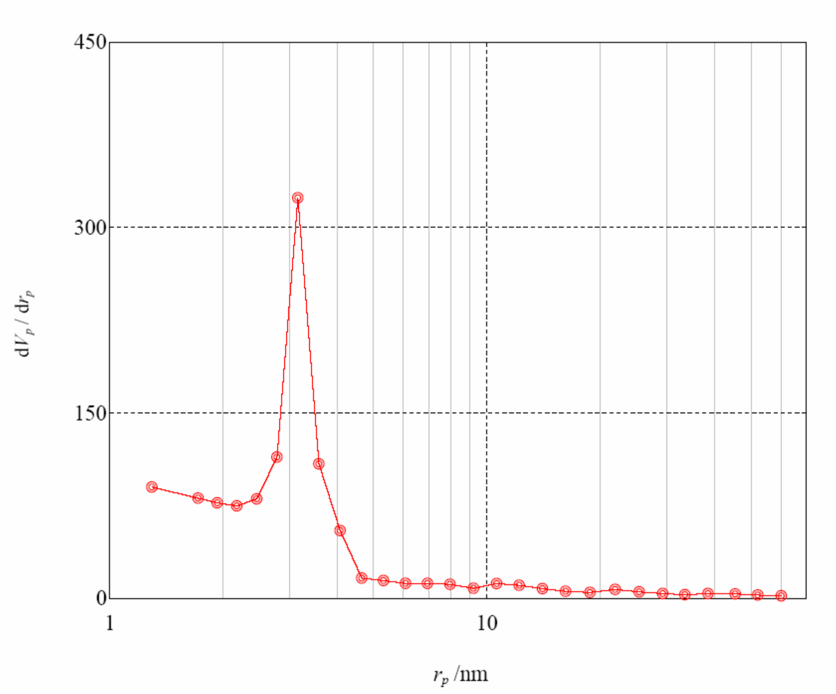


Figure 6. BJH average pore diameter diagram for SBA-15-Ph-Pr-SH

1.3. Preparation of SBA-15-Pr-SO$_3$H: Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2h and then was washed several times with deionized water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding nanoreactor SBA-15-Pr-SO_3H.

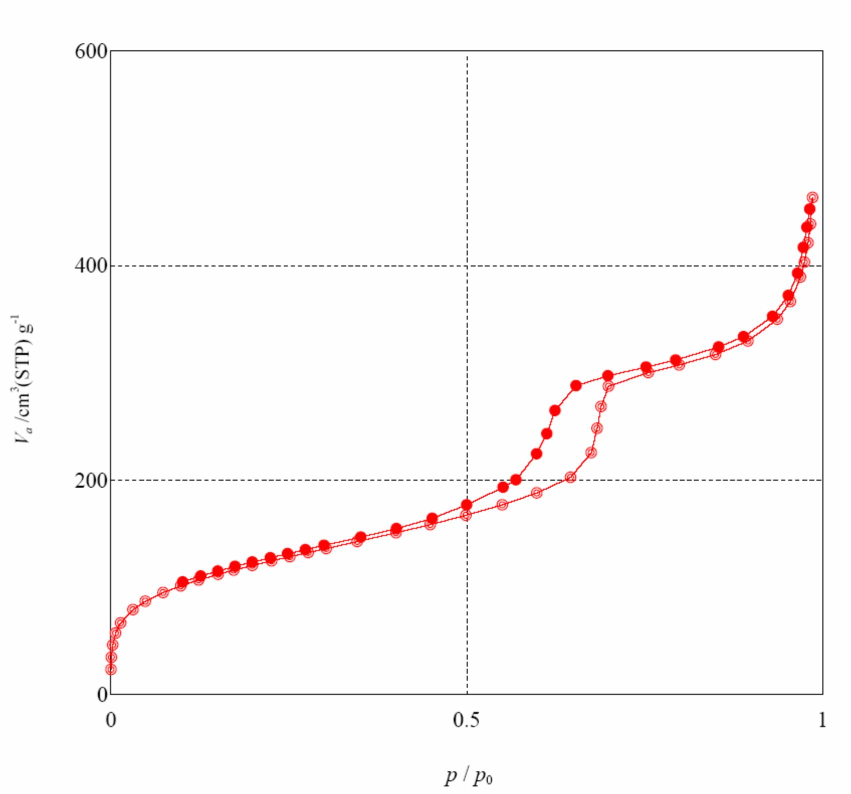


Figure 7. Nitrogen adsorption-desorption isotherm for SBA-15-Pr-SO_3H

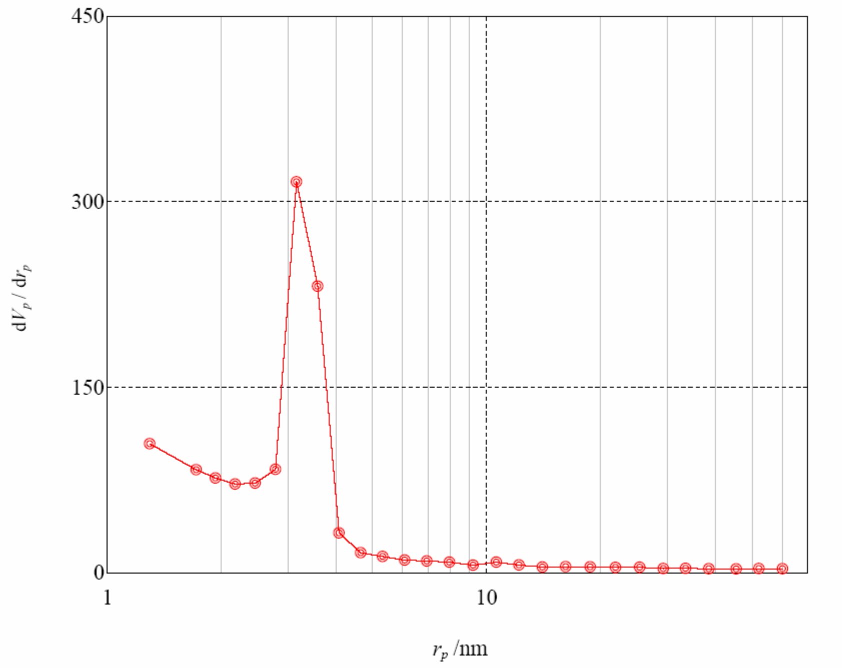


Figure 8. BJH average pore diameter diagram for SBA-15-Pr-SO_3H

1.4. Preparation of SBA-15-Ph-Pr-SO_3H:

Conversion of thiol groups of catalyst to sulfonic acid moiety was accomplished by hydrogen peroxide. Typically, 0.3 g of solid hodrophobic material was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2h and then was washed several times with water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding nanoreactor SBA-15-Ph-Pr-SO_3H.

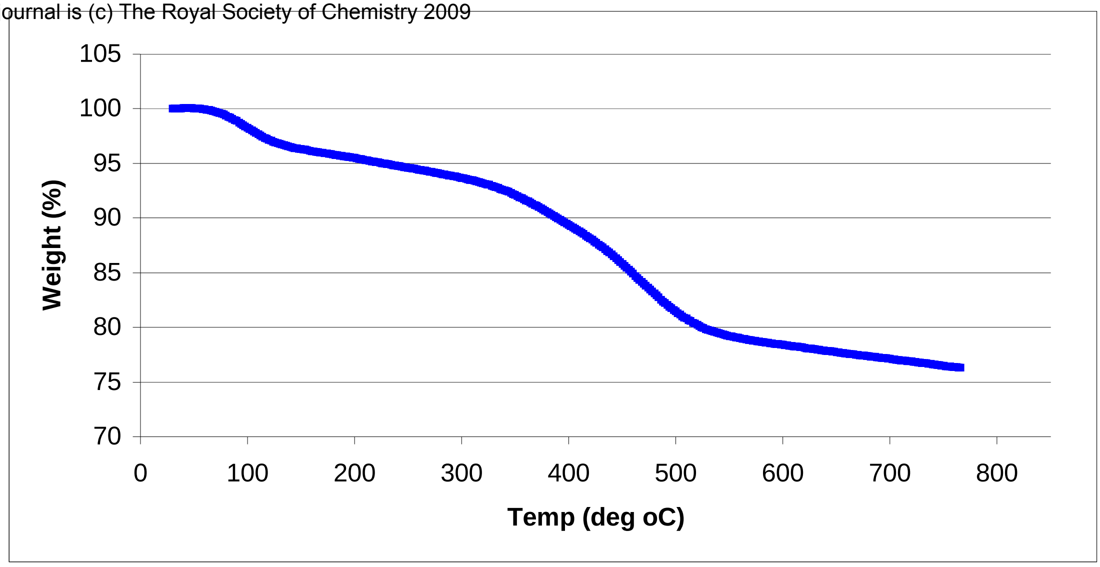


Figure 9. TGA diagram of SBA-15-Ph-Pr-SO_3H

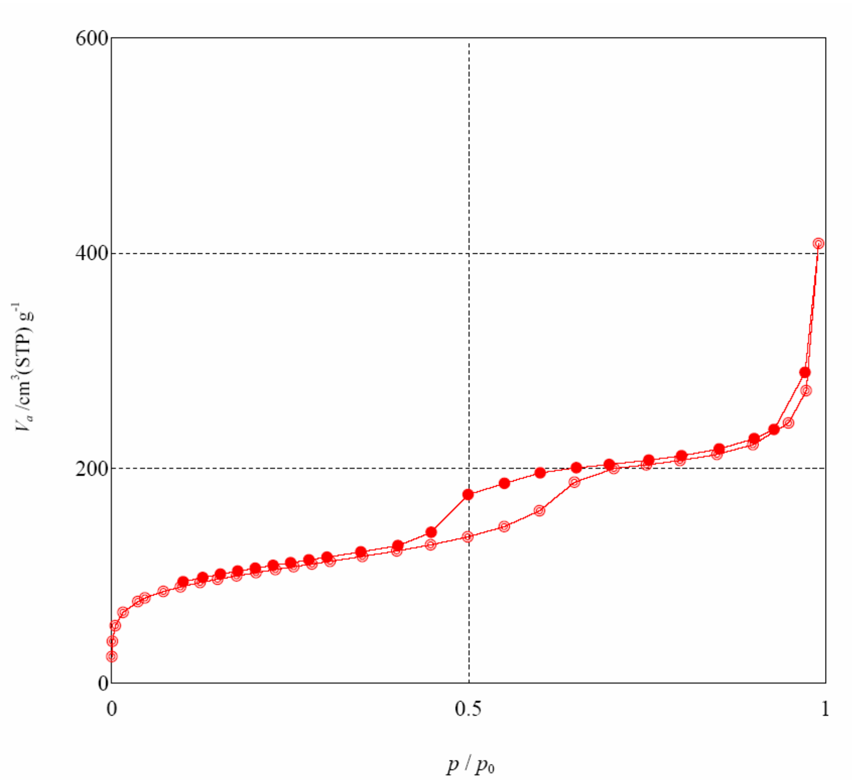


Figure 10. Nitrogen adsorption-desorption isotherm for SBA-15-Ph-Pr-SO_3H

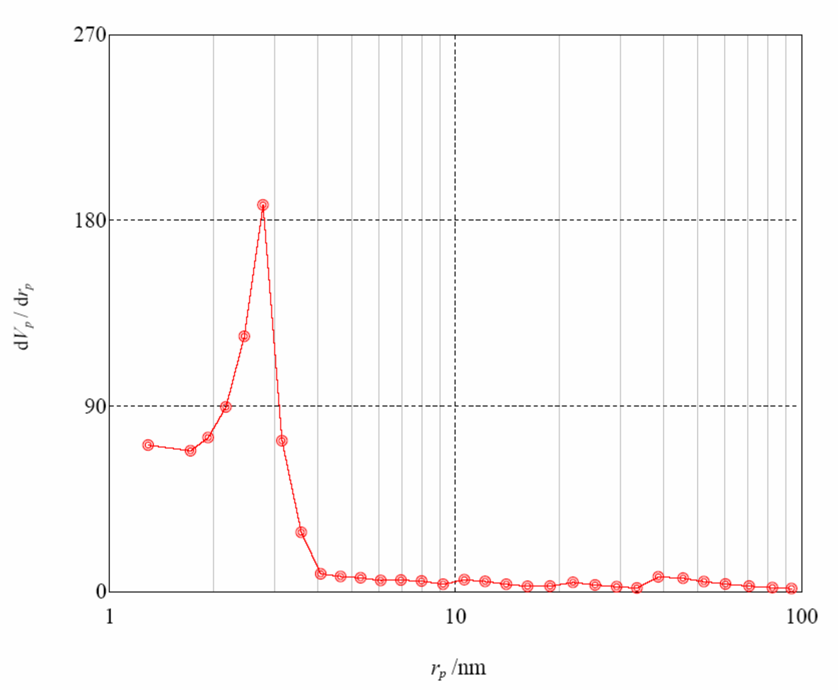


Figure 11. BJH average pore diameter diagram for SBA-15-Ph-Pr-SO_3H

1.5. General procedure for the Strecker reaction of aldehydes and ketones using SBA-15-Ph-Pr-SO_3H: To the mixture of aldehyde/ketone (3 mmol), amine (3 mmol), and catalyst **1** (93 mg; ~5mol% -SO_3H group) in sealed tube, trimethylsilyl cyanide (98%, Merck) (3.6 mmol) was added at 50 °C with constant stirring at the desired time as indicated in Table 2. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with dichloromethane and filtrated to obtain the crude product. In some cases the crude product was purified by column chromatography on silica gel and then recrystallized to afford the pure related α-amino nitrile in good to excellent yields (Table 2).

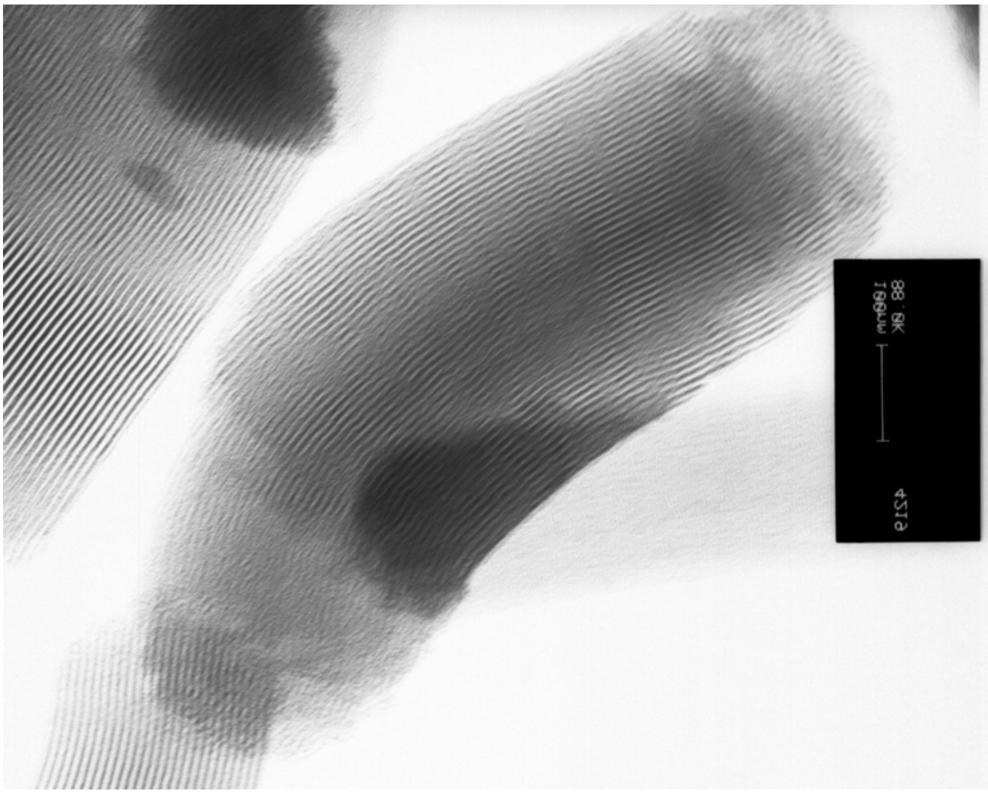


Figure 12: TEM image of SBA-15-Ph-Pr-SO_3H

1.6. Spectral data for Table 2:

Table 2 (Entry 1): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.45-7.60 (m, 5H), 7.29-7.33 (t, J=7.5 Hz, 2H), 6.89-6.95 (t, J=7.25 Hz, 1H), 6.78-6.81 (d, J=8.25 Hz, 2H), 5.43-5.46 (d, J=7.5 Hz, 1H), 4.04-4.08 (d, J=8.25 Hz 1H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 144.7, 133.9, 129.6, 129.5, 127.3, 120.3, 118.2, 114.2, 50.2; Mass: m/z: 208
Table 2 (Entry 2): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.40-7.63 (m, 5H), 6.75-6.88 (m, 4H), 5.34-5.38 (d, J=8.25 Hz, 1H), 3.78-3.81 (d, J=8.5 Hz, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 154.1, 138.5, 134.1, 129.5, 129.3, 127.3, 118.5, 116.3, 115.0, 55.7, 51.6; Mass: m/z: 238
Table 2 (Entry 3): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.62-7.65 (d, J=7.5 Hz 2H), 7.33-7.44 (m, 3H), 7.09-7.16 (t, J=7.25 Hz, 2H), 6.78-6.84 (t, J=6.75 Hz, 1H), 6.53-6.56 (d, J=8.25 Hz, 2H), 4.31 (bs, 1H), 1.95 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 143.4, 139.8, 129.2, 129.0, 128.6, 124.9, 120.7, 119.9, 115.7, 57.1, 33.4; Mass: m/z: 222
Table 2 (Entry 4): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 8.14-8.17 (d, J=7.75 Hz 2H), 7.77-7.96 (m, 3H), 7.20-7.24 (d, J=9 Hz, 2H), 7.04-7.08 (d, J=8.75 Hz, 2H), 4.51 (bs, 1H), 4.22 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 161.7, 154.2, 140.1, 137.2, 129.1, 128.6, 125.1, 118.4, 114.4, 58.2, 50.5, 32.9; Mass: m/z: 252
Table 2 (Entry 5): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.61-7.87 (m, 5H), 7.29-7.41 (m, 2H), 7.06-7.10 (d, J=8 Hz, 2H), 4.84 (bs, 1H), 4.32 (s, 3H), 2.45 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 160.3, 143.5, 141.7, 130.3, 129.0, 120.7, 119.9, 117.1, 115.7, 113.8, 110.7, 57.1, 55.3, 33.3; Mass: m/z: 252
Table 2 (Entry 6): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.70-7.87 (m, 3H), 7.39-7.42 (m, 2H), 7.20-7.24 (d, J=8.75 Hz, 2H), 7.05-7.09 (d, J=9 Hz, 2H), 4.54-4.60 (bs, 1H), 4.32 (s, 3H), 4.21 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 160.2, 154.0, 141.9, 137.3, 130.2, 120.9, 118.2, 117.3, 114.4, 113.8, 110.9, 58.1, 55.4, 55.3, 32.9; Mass: m/z: 282
Table 2 (Entry 7):): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 8.06-8.10 (d, J=8.5 Hz, 3H), 7.87-7.90 (d, J=8.5 Hz, 2H), 7.61-7.68 (t, J=8 Hz, 2H), 7.31-7.37 (d, J=7.5 Hz, 2H), 4.80 (bs, 1H), 2.44 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 146.4, 139.8, 134.5, 129.4, 129.1, 126.4, 120.3, 115.8, 112.7, 56.7, 33.2; Mass: m/z: 256
Table 2 (Entry 8): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 8.07-8.10 (d, J=8.5 Hz, 2H), 7.87-7.90 (d, J=8.5 Hz, 2H), 7.77 (s, 1H), 7.20-7.24 (d, J=8.75 Hz, 2H), 7.02-7.06 (d, J=8.75 Hz, 1H), 4.47-4.49 (bs, 1H), 4.22 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 32.9, 55.5, 57.7, 114.5, 118.5, 126.6, 129.3, 129.7, 134.5, 136.8, 138.7, 154.3: TMS): Mass: m/z: 286
Table 2 (Entry 9): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 7.22-7.28 (m, 2H), 6.87-6.93 (m, 3H), 3.60 (bs, 1H), 2.31-2.35 (m, 2H), 1.63-1.76 (m, 8H), 1.32 (bs, 1H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 143.6, 129.2, 121.2, 120.5, 117.5, 54.4, 36.6, 24.9, 22.2; Mass: m/z: 200
Table 2 (Entry 10): ^{1}H-NMR (250 MHz; CDCl$_3$; TMS): δ_H = 6.95-7.00 (m, 2H), 6.80-6.85 (m, 2H), 3.77 (s, 3H), 3.15 (bs, 1H), 2.17-2.19 (m, 2H), 1.58-1.82 (m, 7H), 1.26-1.30 (m, 1H); ^{13}C-NMR (62.9 MHz, CDCl$_3$; TMS): δ_C = 155.8, 136.1, 123.3, 121.6, 114.4, 56.6, 55.5, 36.4, 24.9, 22.3; Mass: m/z: 230

Table 2 (Entry 11): ^{1}H-NMR (250 MHz; $CDCl_3$; TMS): δ_H = 8.12-8.16 (m, 4H), 7.87-7.95 (m, 4H), 7.77 (m, 2H), 7.34-7.71 (m, 2H), 7.33-7.39 (m, 1H), 7.12-7.15 (m, 2H), 4.93-5.00 (s, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$; TMS): δ_C = 143.5, 139.6, 129.2, 128.96, 128.93, 126.3, 120.2, 119.8, 116.1, 65.4; Mass: m/z: 284

Table 2 (Entry 12): ^{1}H-NMR (250 MHz; $CDCl_3$; TMS): δ_H = 8.14-8.16 (m, 4H), 7.83-7.93 (m, 6H), 7.77 (m, 1H), 7.22-7.26 (d, J=8.75 Hz, 2H), 7.07-7.11 (d, J=9 Hz, 1H), 4.72 (s, 1H), 4.23 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$; TMS): δ_C = 153.9, 139.8, 137.4, 129.1, 128.7, 126.3, 120.1, 118.0, 114.4, 66.3, 55.5; Mass: m/z: 314

Table 2 (Entry 13): ^{1}H-NMR (250 MHz; $CDCl_3$; TMS): δ_H = 8.07-8.42 (m, 4H), 7.88-7.96 (m, 4H), 7.87 (m, 1H), 7.65-7.77 (m, 2H), 7.35-7.41 (m, 1H), 7.11-7.14 (m, 2H), 4.91 (s, 1H), ^{13}C-NMR (62.9 MHz, $CDCl_3$; TMS): δ_C = 64.9, 116.1, 119.4, 120.4, 126.2, 127.8, 129.1, 19.2, 129.37, 129.42, 135.0, 139.4, 143.3, 156.1: Mass: m/z: 318

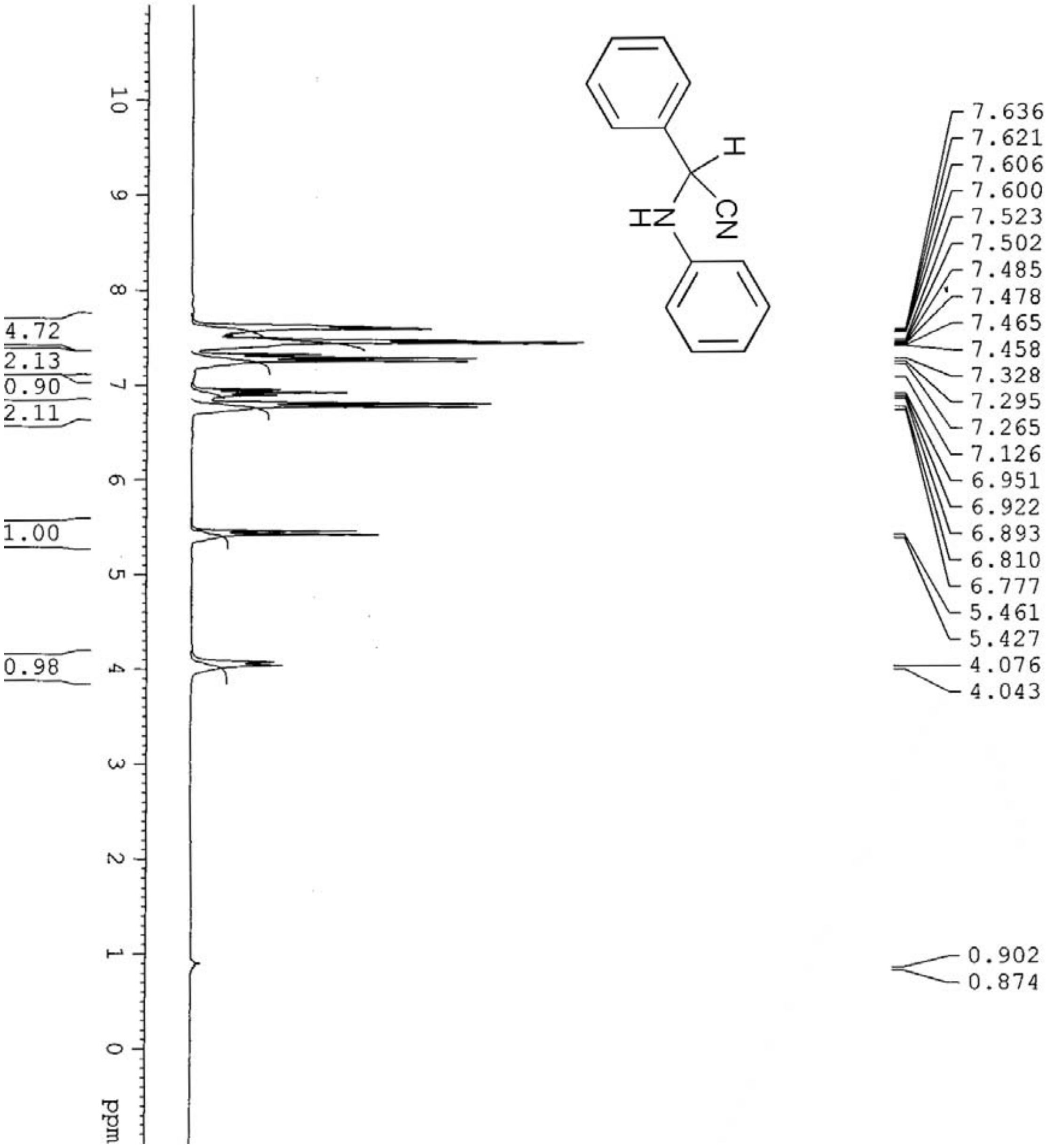
Table 2 (Entry 14): ^{1}H-NMR (250 MHz; $CDCl_3$; TMS): δ_H = 8.04-8.06 (d, J=6 Hz, 2H), 7.87-7.89 (d, J=6.75 Hz, 3H), 7.55-7.62 (t, J=8 Hz, 1H), 7.00-7.03 (d, J=8 Hz, 2H), 4.86 (s, 1H), 2.544 (m, 1H), 2.07-2.38 (m, 4H), 1.65-1.85 (m, 6H); ^{13}C-NMR (62.9 MHz, $CDCl_3$; TMS): δ_C = 145.1, 143.7, 128.9, 128.6, 128.4, , 126.4, 120.1, 119.6, 115.6, 65.5, 49.8, 28.0, 26.1, 25.8; Mass: m/z: 290

Table 2 (Entry 15): ^{1}H-NMR (250 MHz; $CDCl_3$; TMS): δ_H = 8.04-8.07 (d, J=7.25 Hz, 2H), 7.87-7.89 (d, J=7 Hz, 3H), 7.77 (s, 2H), 7.14-7.18 (d, J=8.75 Hz, 2H), 6.99-7.02 (d, J=8 Hz, 2H), 4.32 (s, 1H), 4.19 (s, 3H), 1.37-2.56 (m, 11H); ^{13}C-NMR (62.9 MHz, $CDCl_3$; TMS): δ_C = 25.8, 26.0, 29.7, 49.7, 60.0, 65.5, 115.7, 119.5, 120.2, 126.8, 128.58, 128.63, 128.91, 143.7, 145.1; Mass: m/z: 320

2. Copy of ^{1}H, ^{13}C-NMR and mass spectra of α-amino nitriles derivatives

Table 2 (Entries 1-15)

Solvent: $CDCl_3$ – Frequency: 250 MHz



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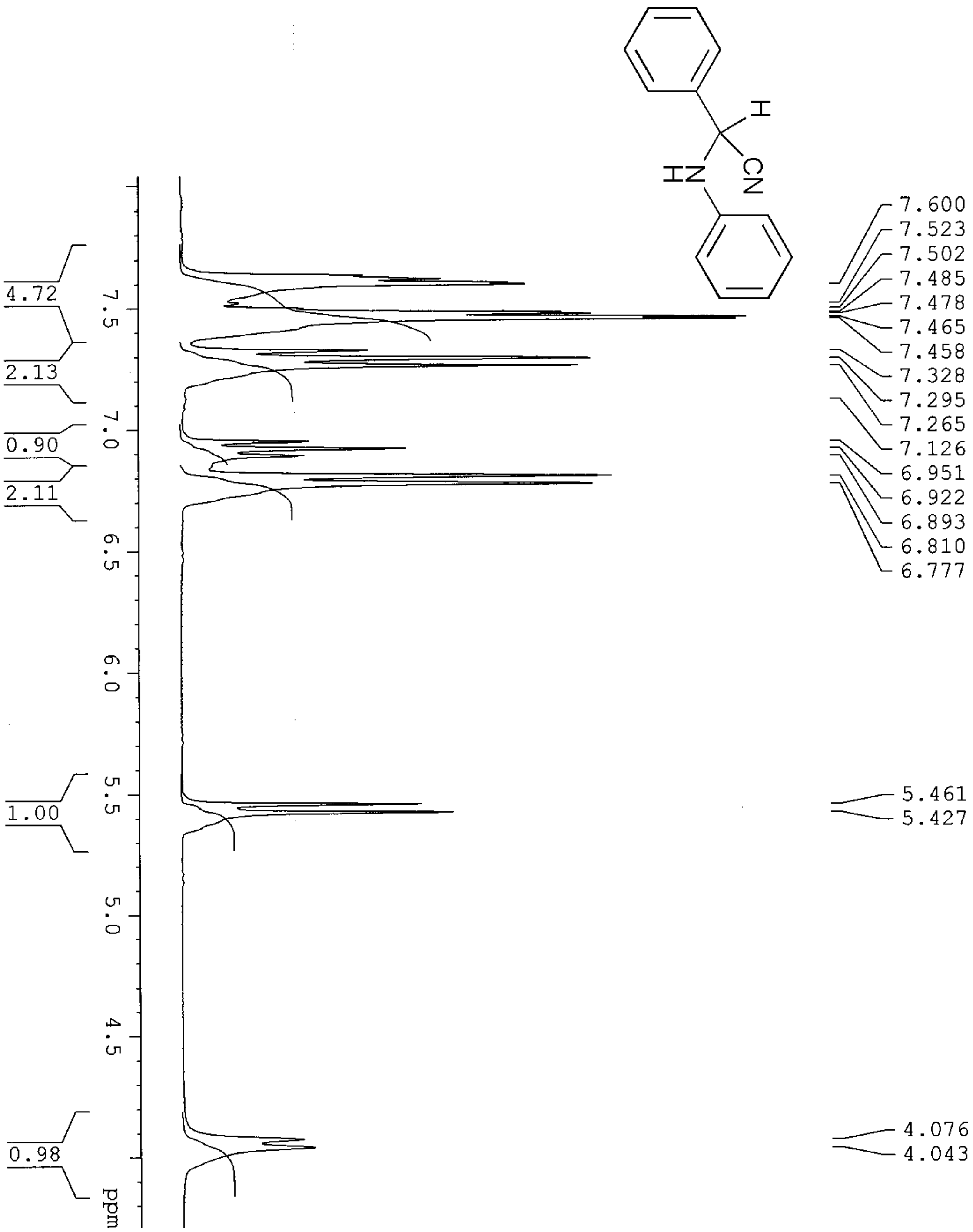

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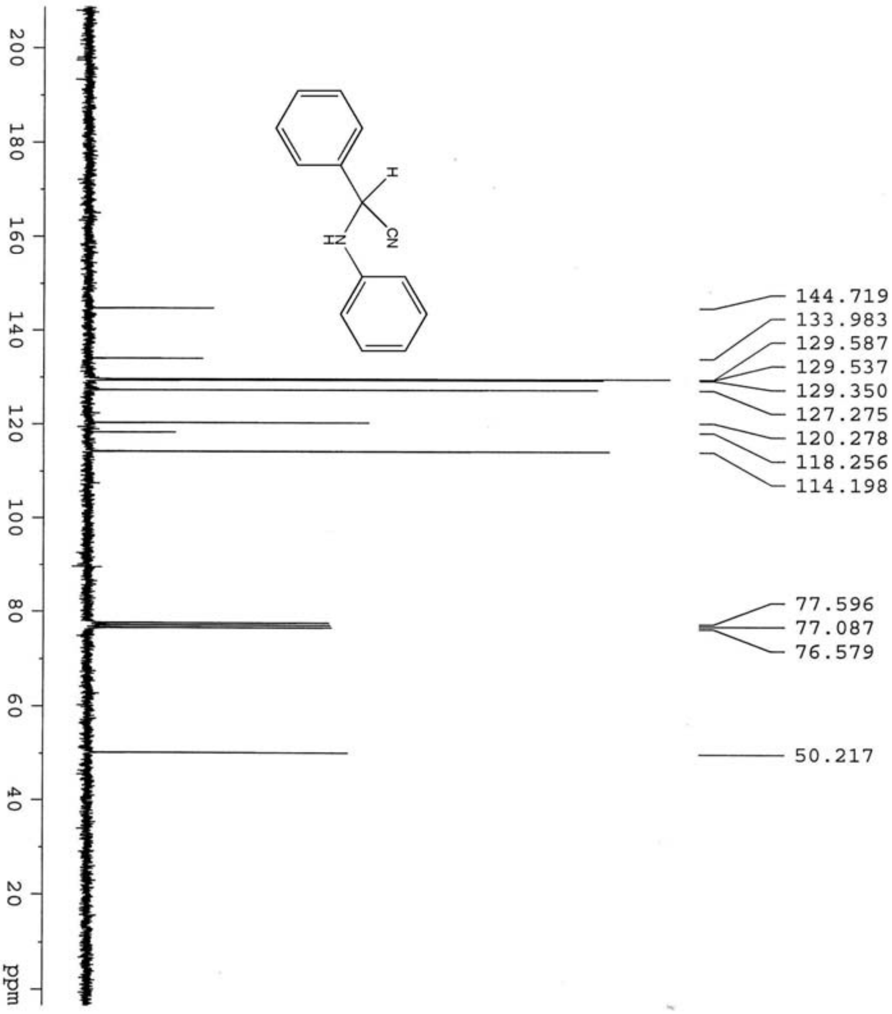

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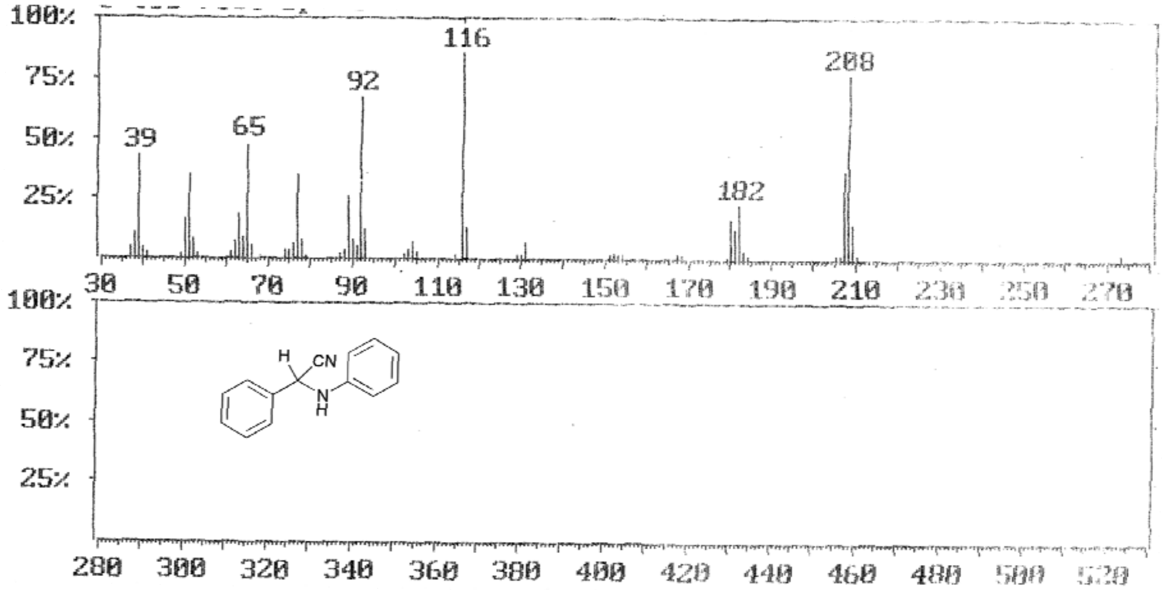

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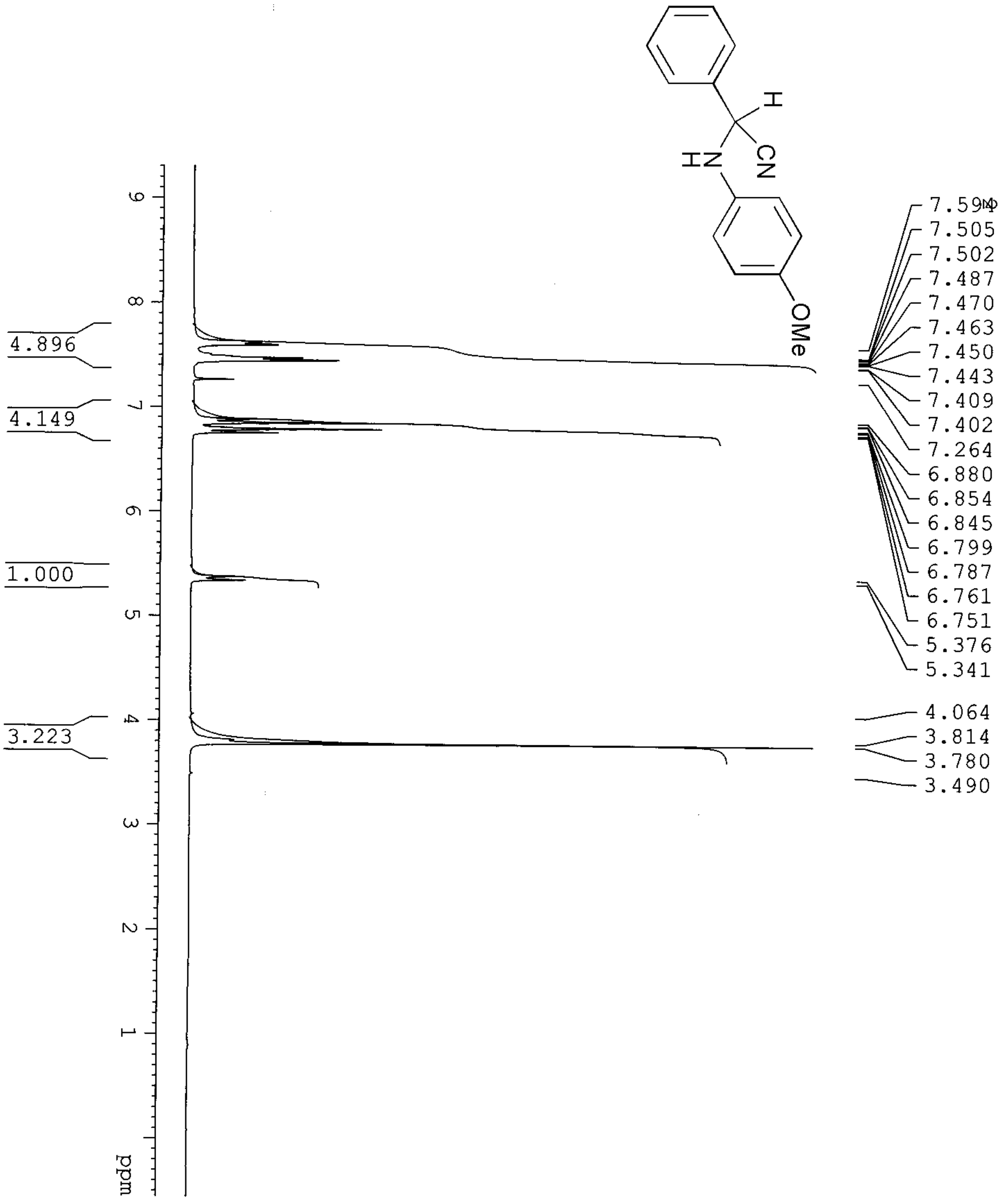

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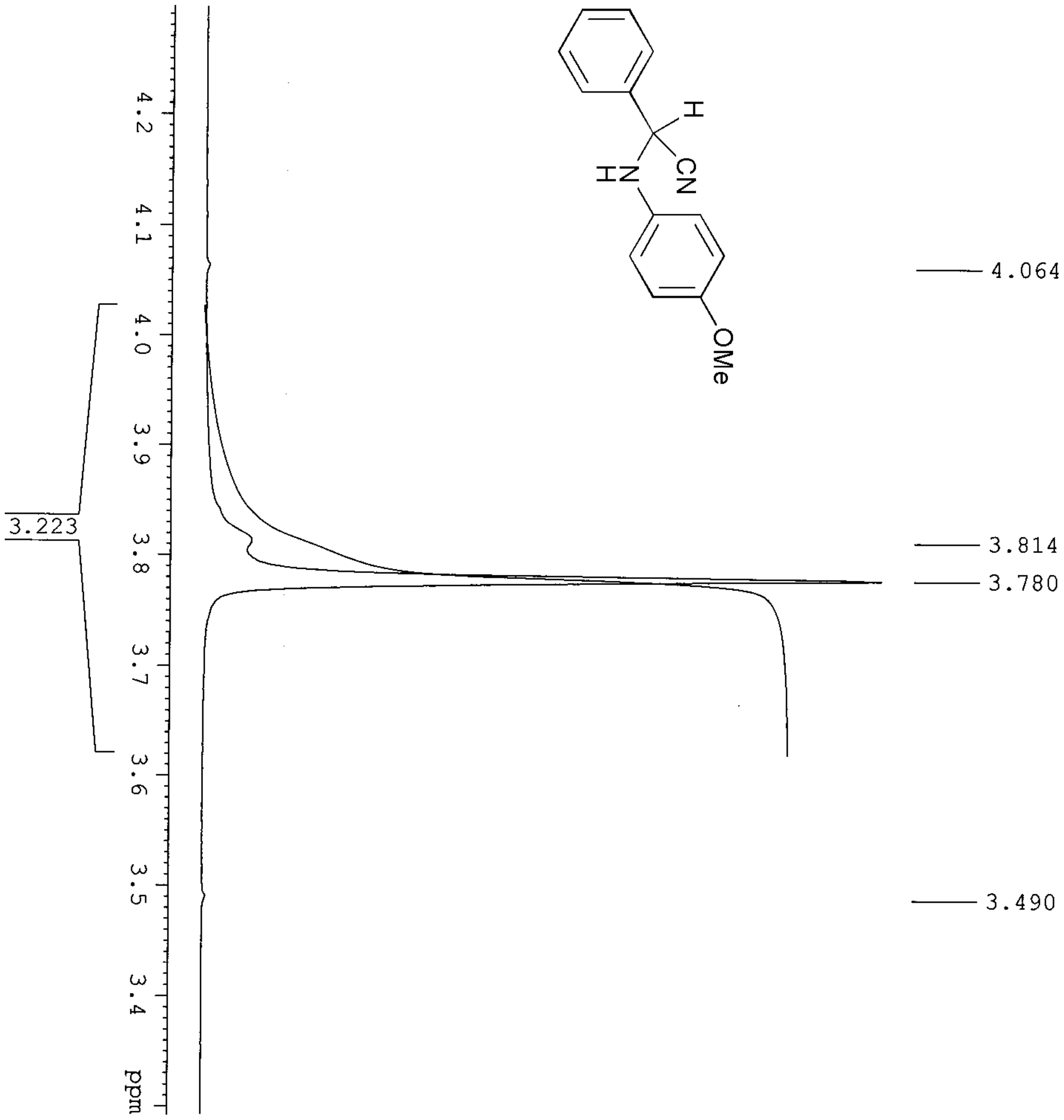

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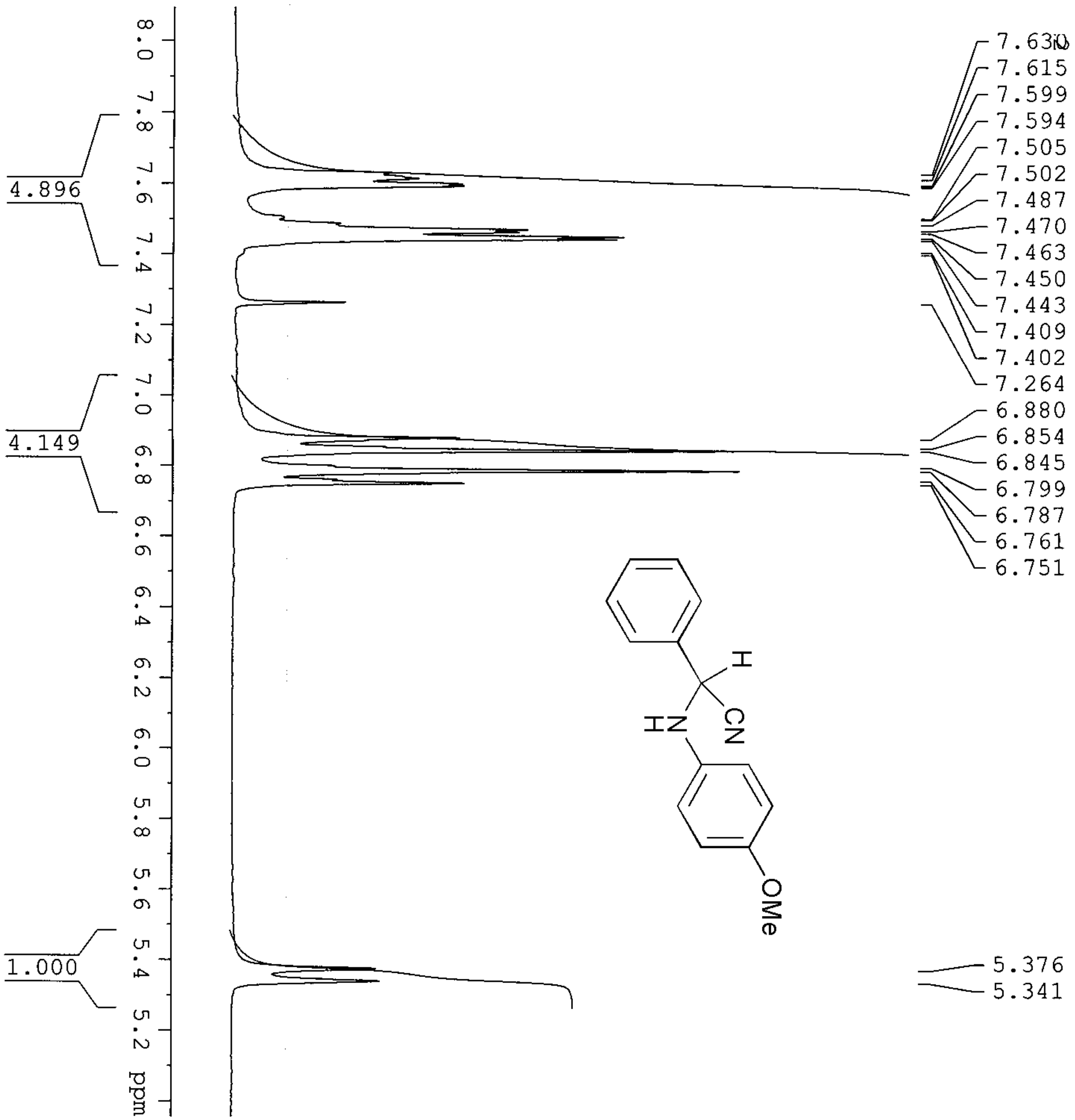

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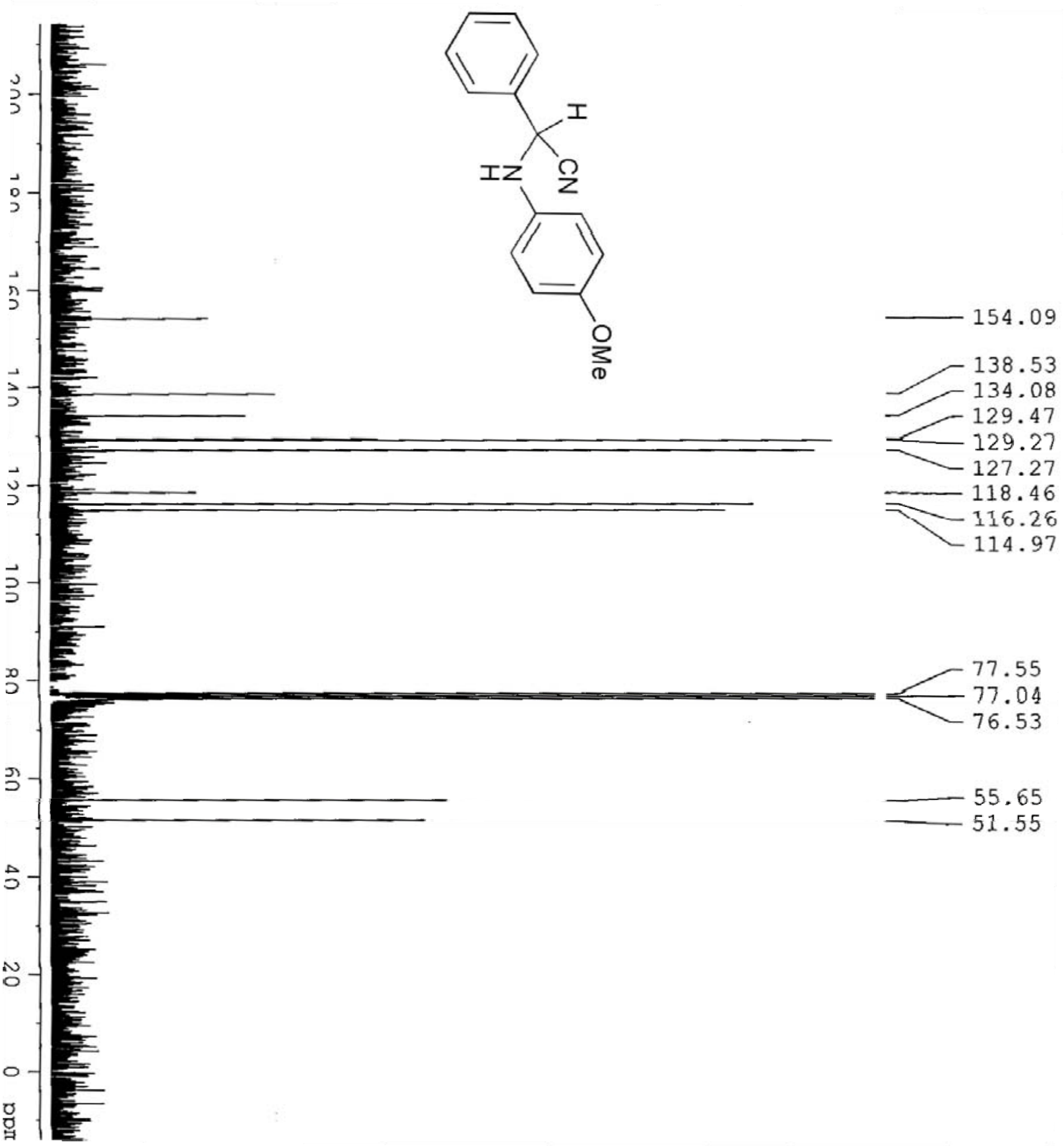

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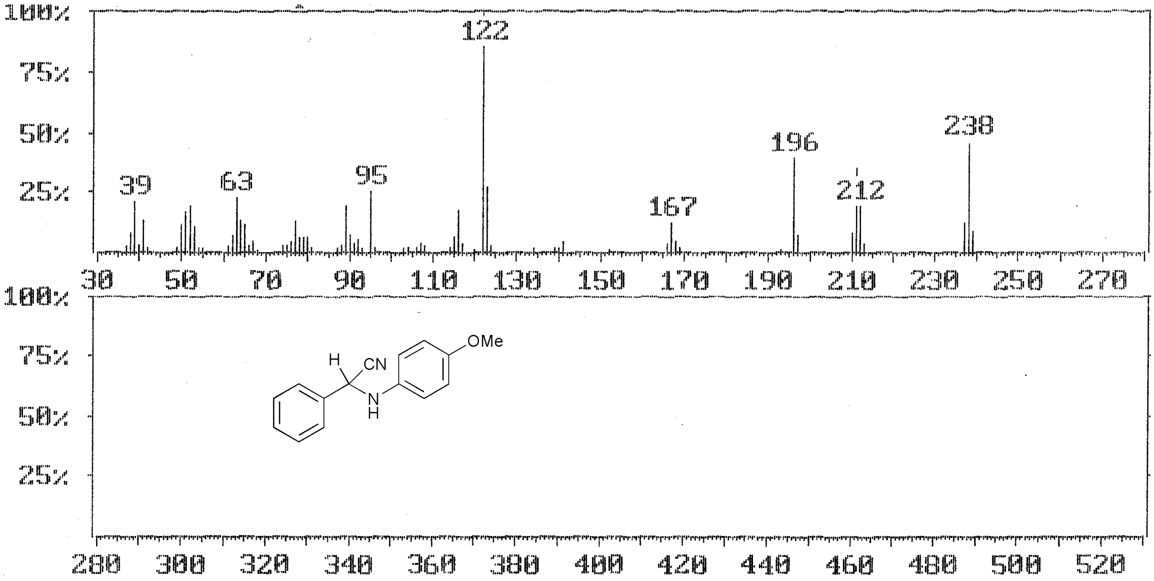

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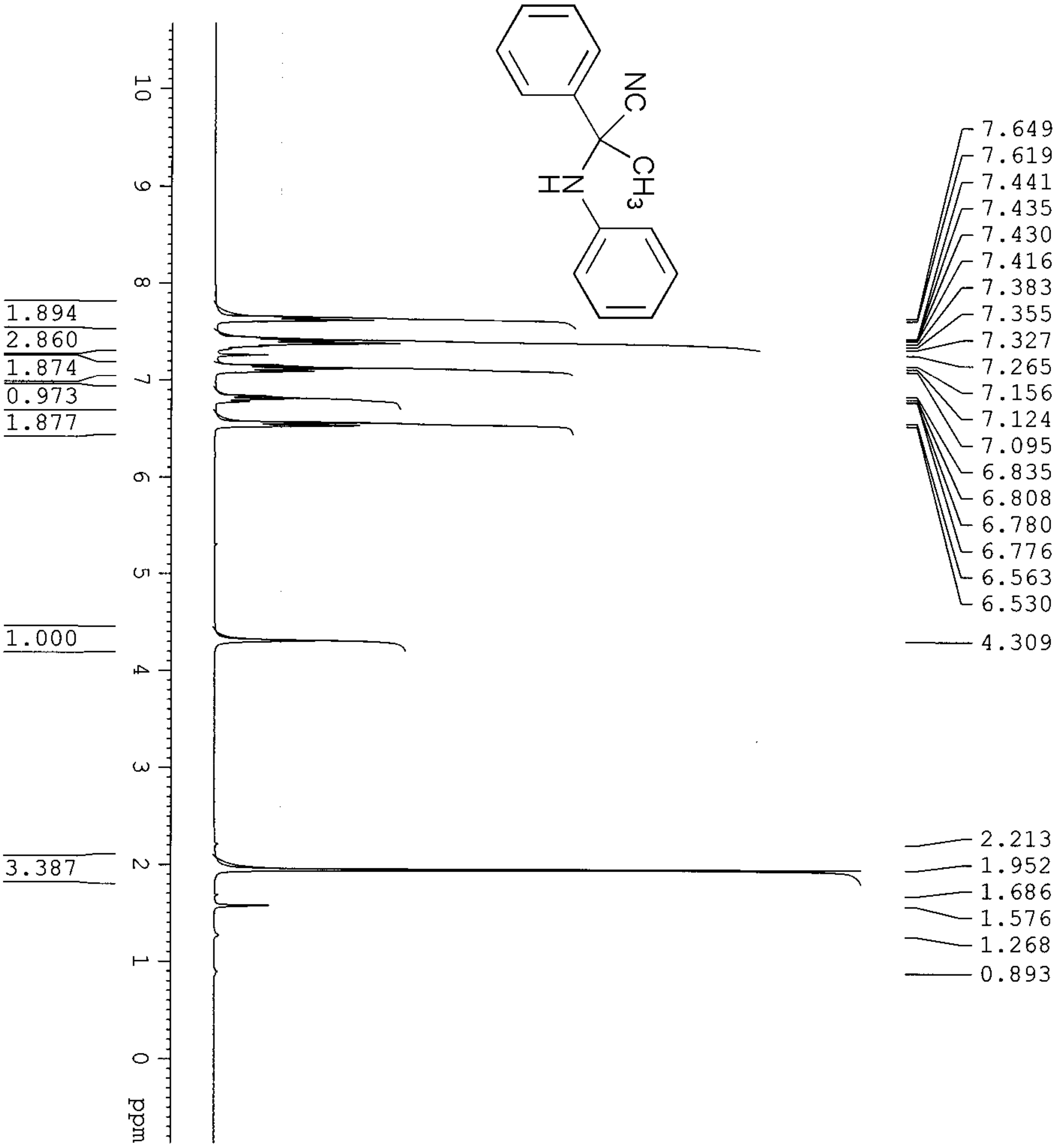

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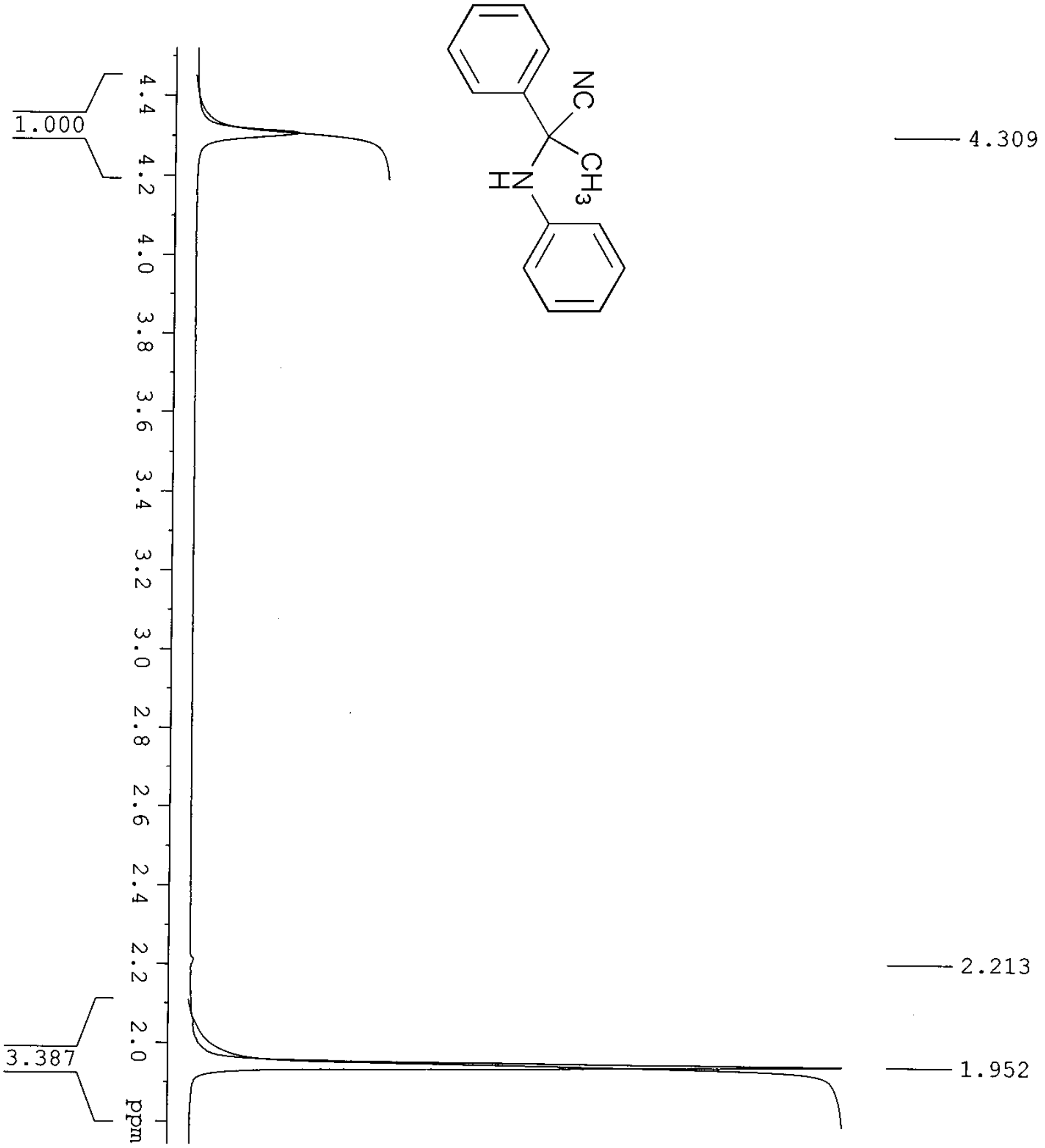

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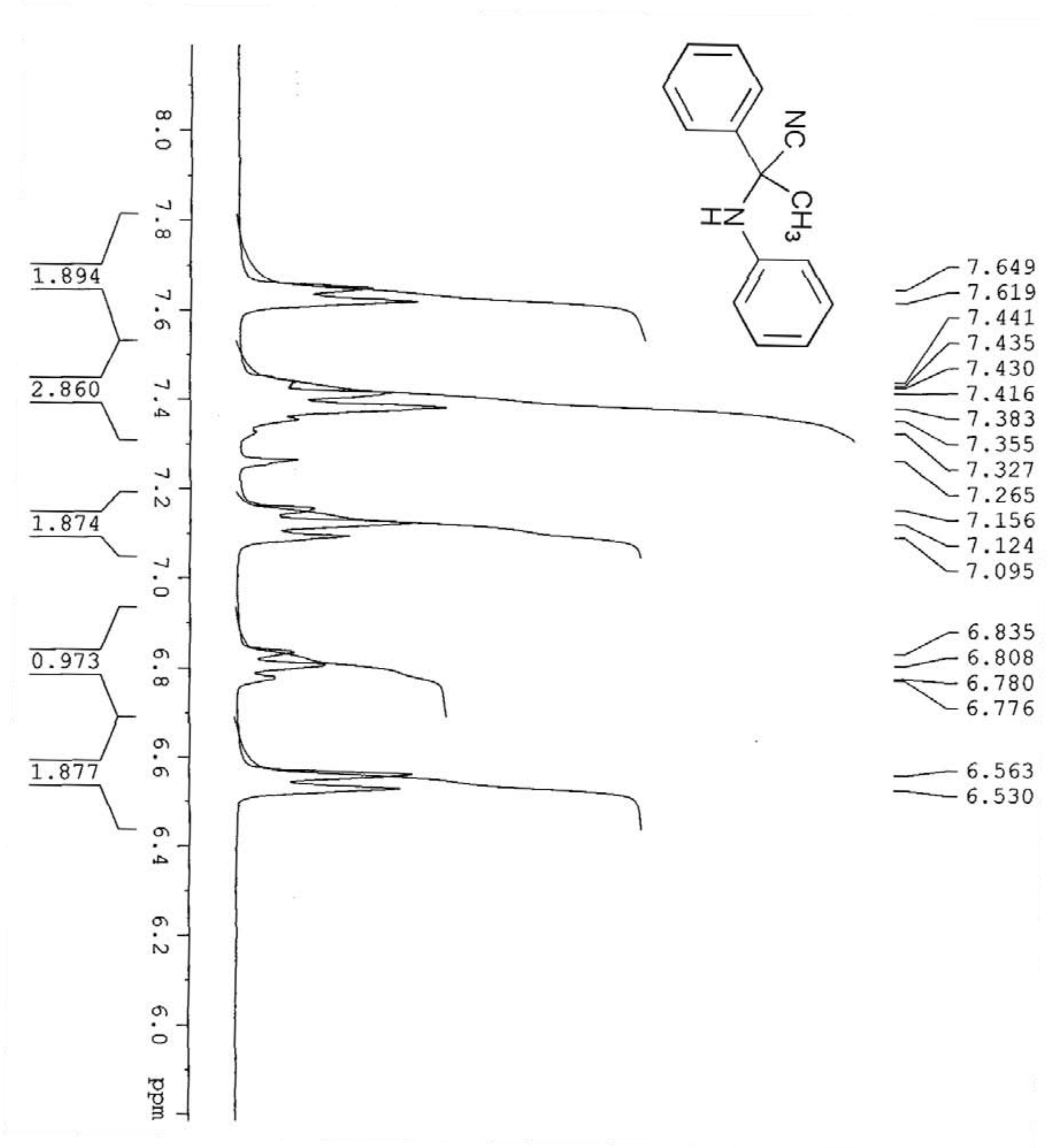

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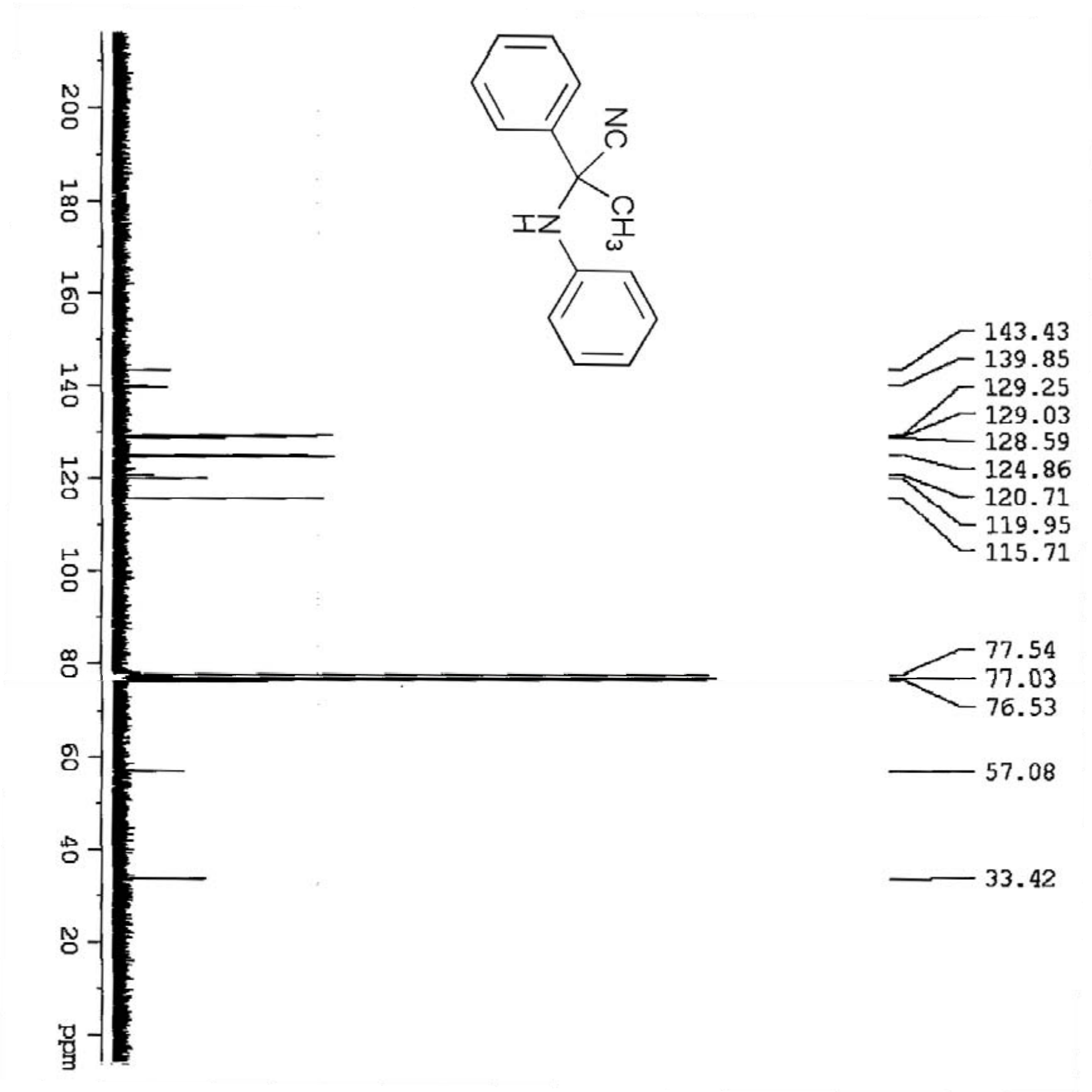

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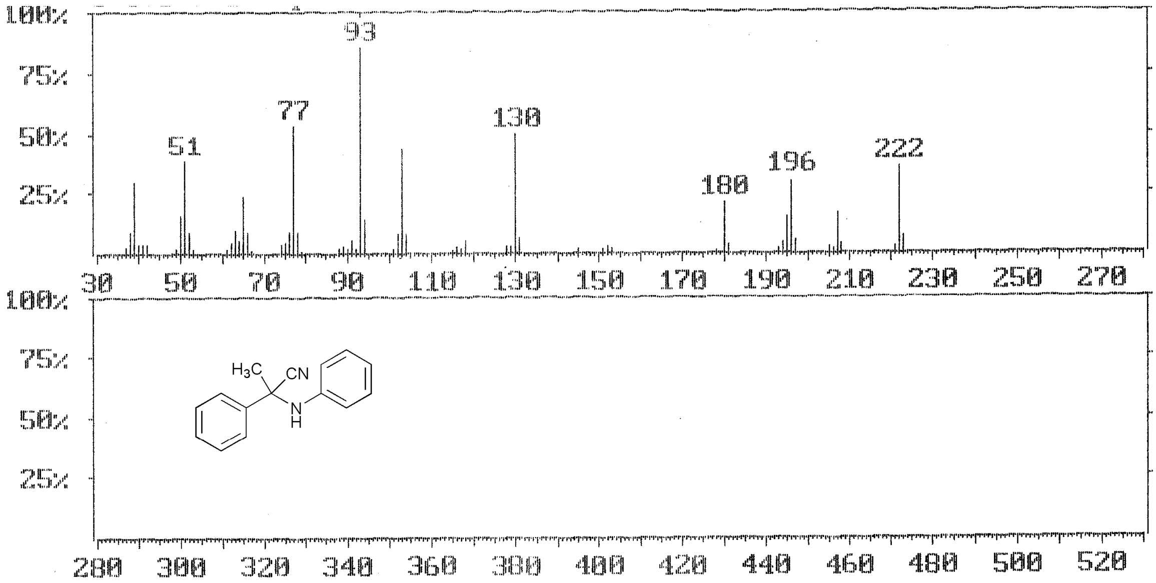

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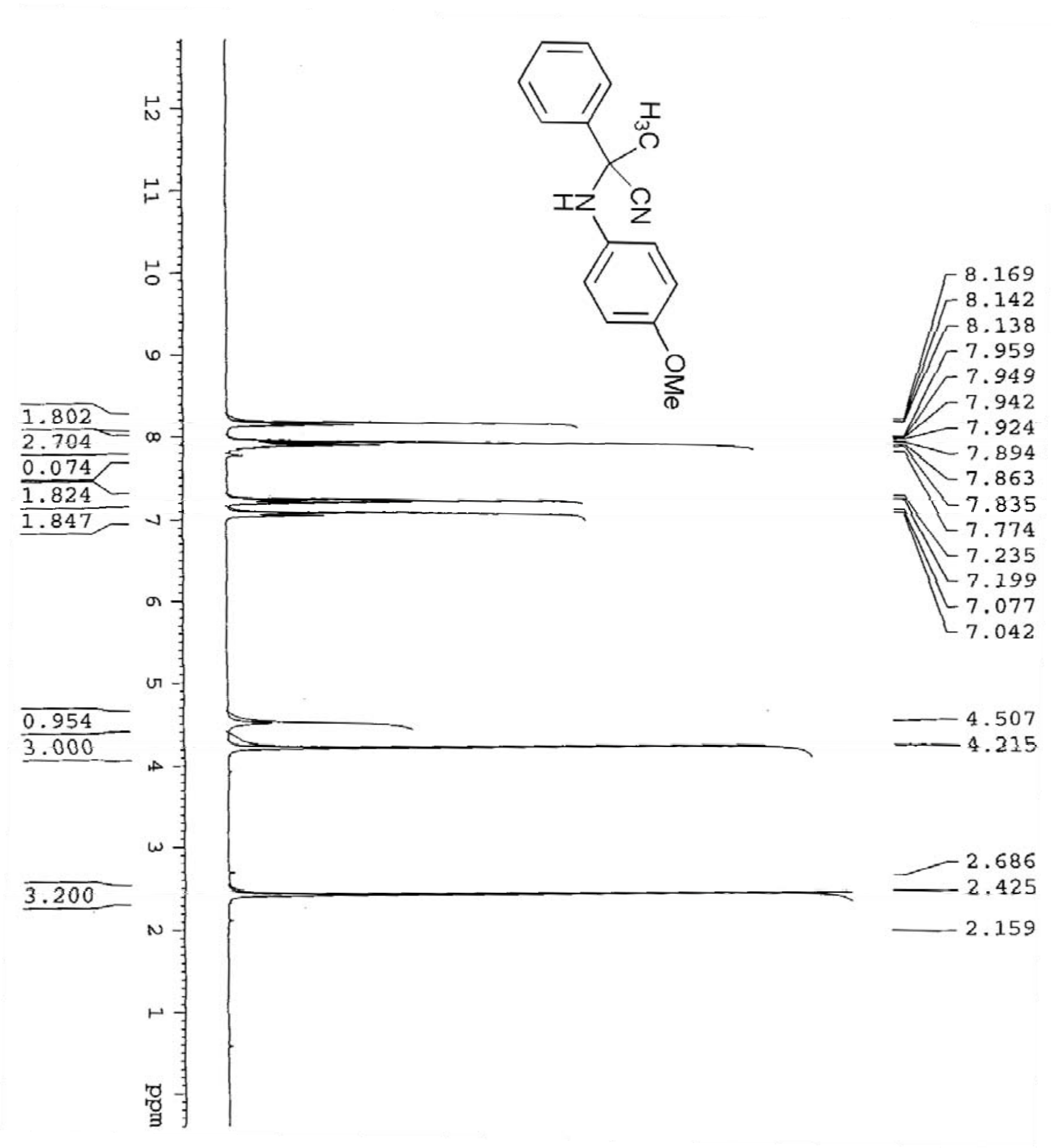

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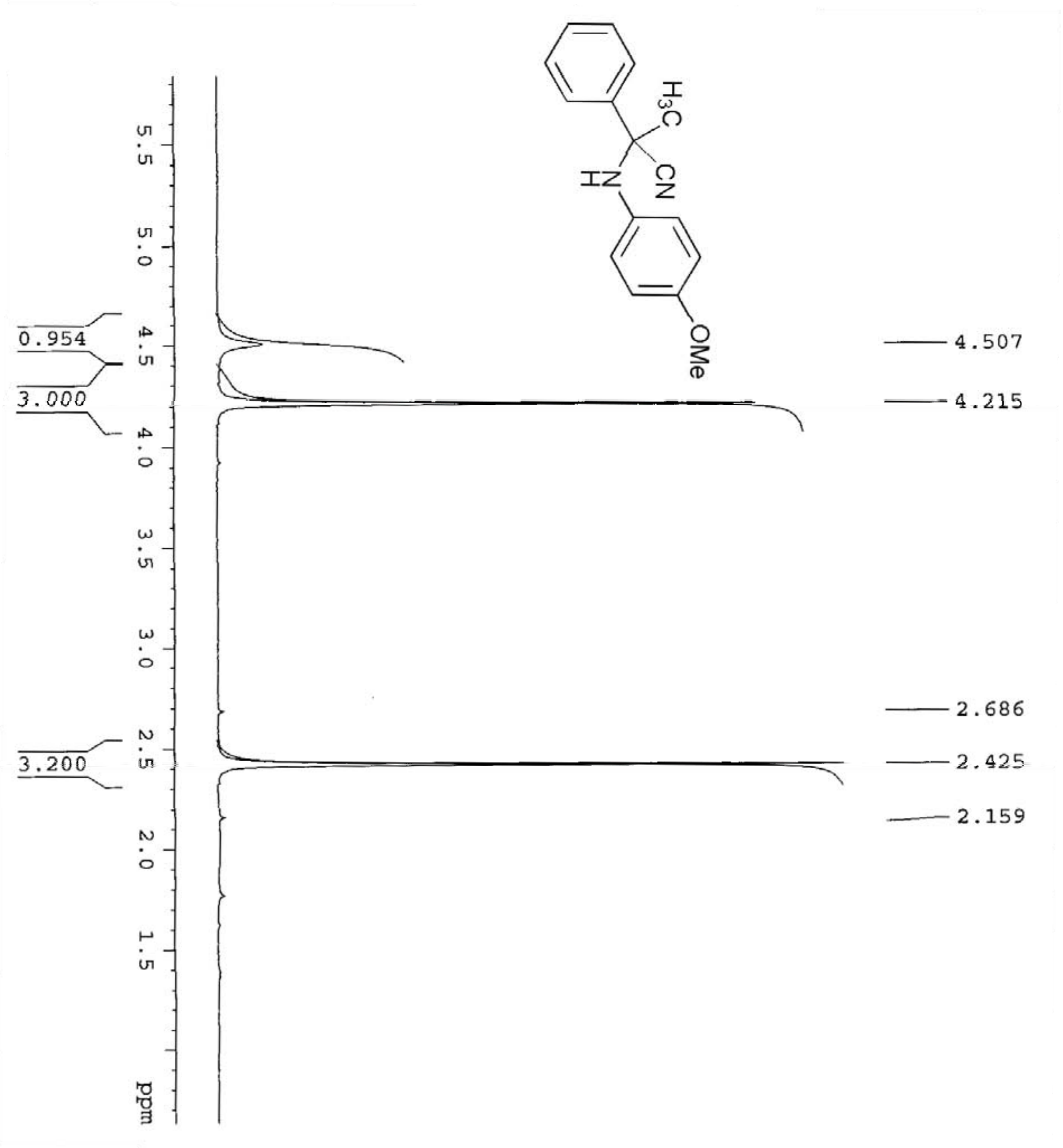

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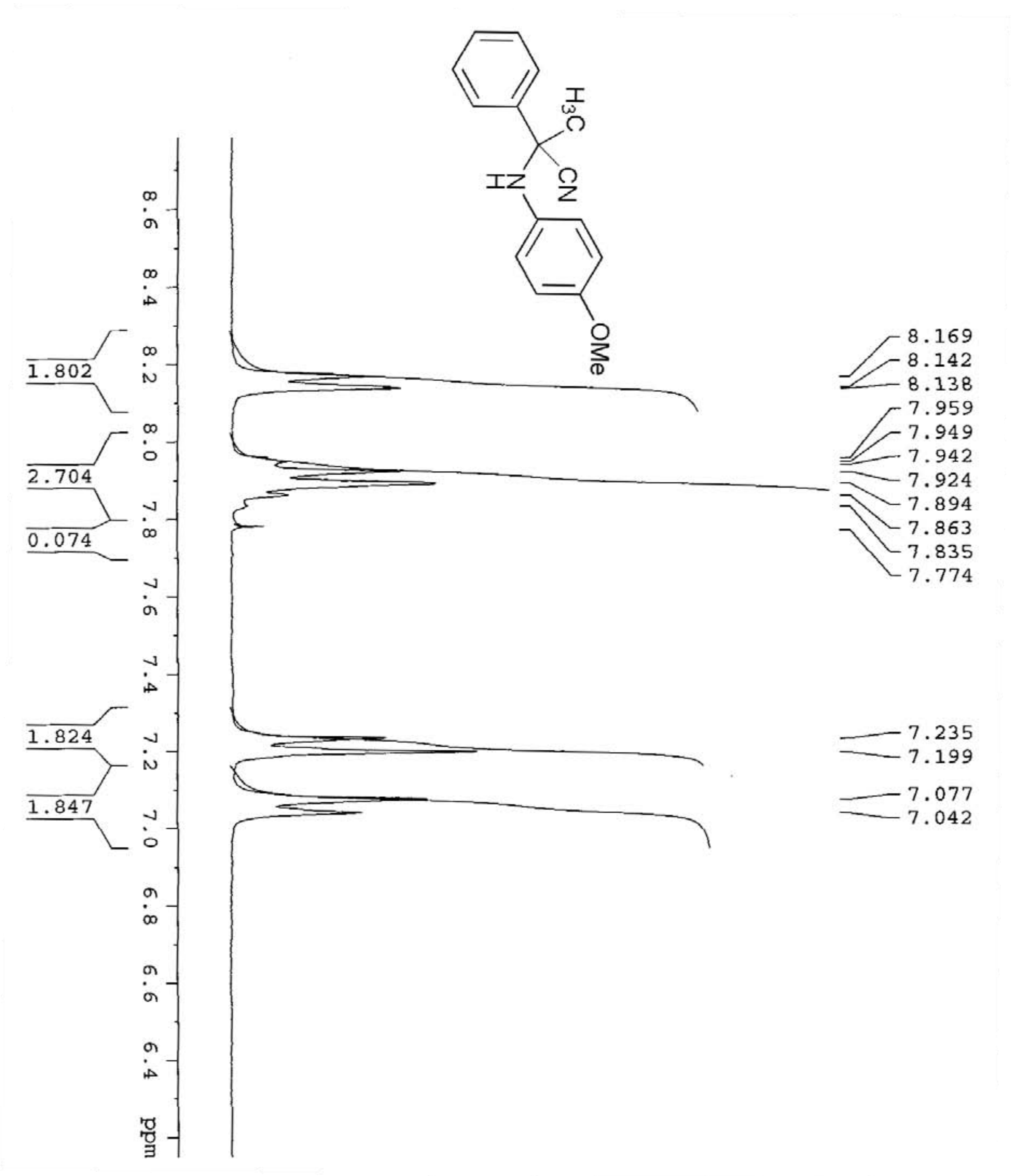

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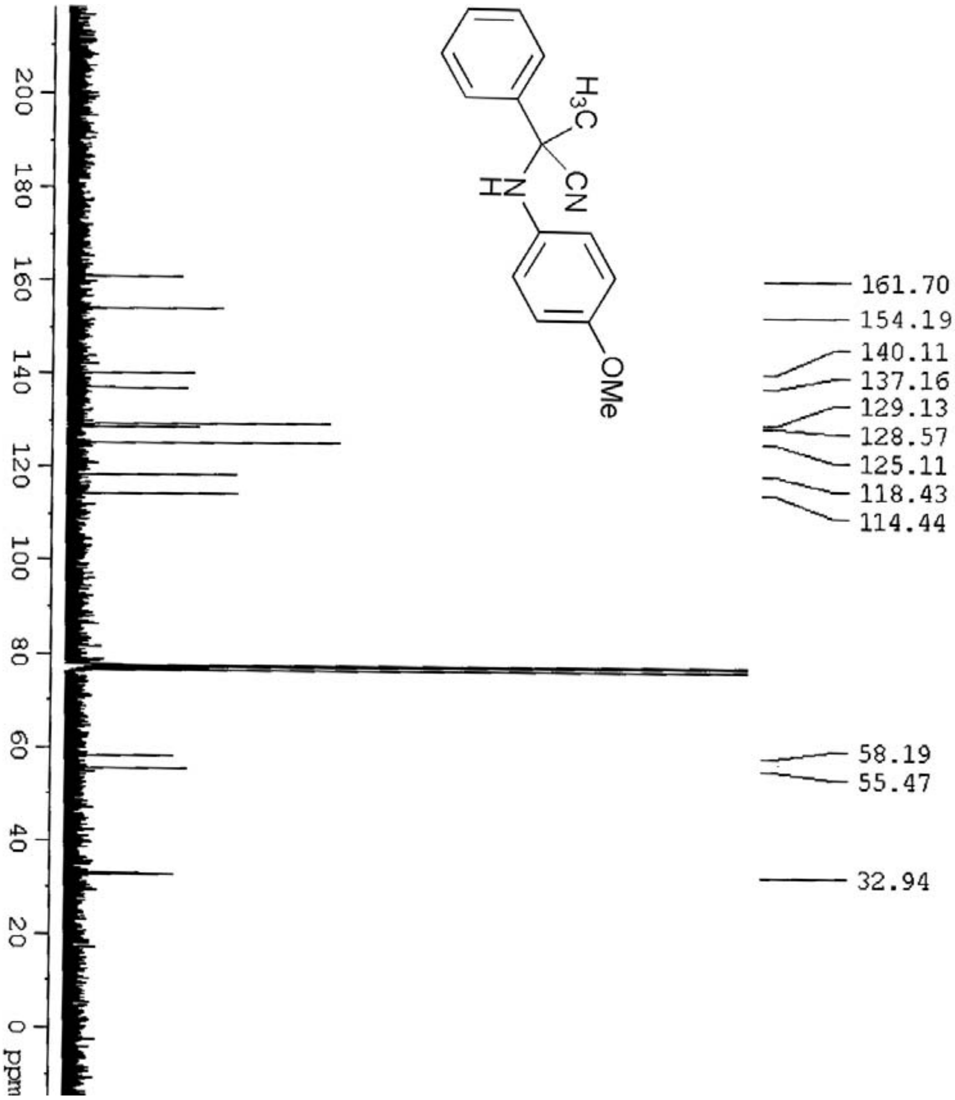

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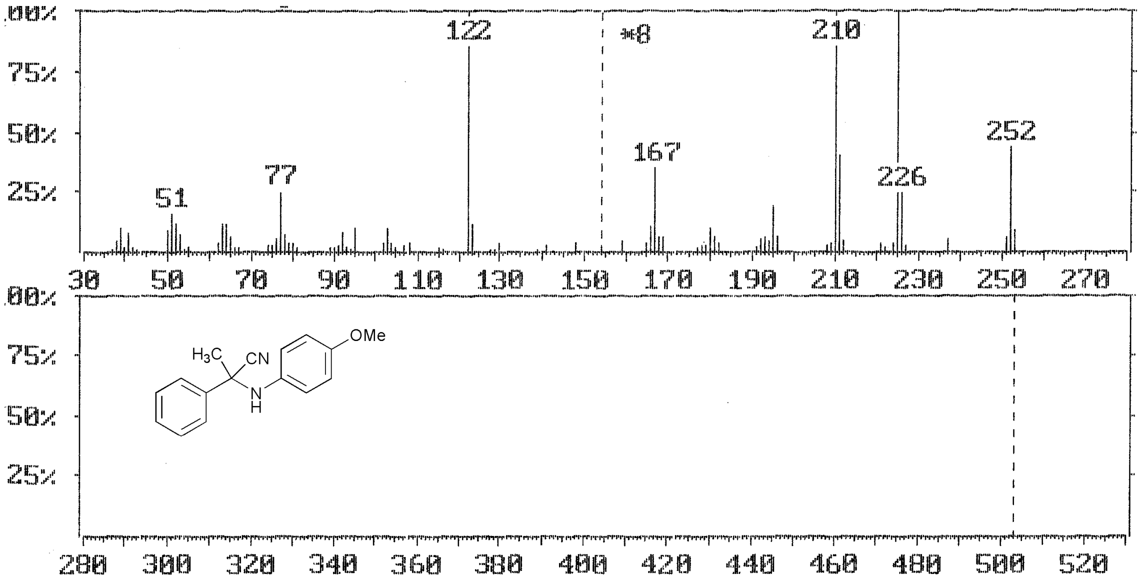

Table 2 (Entry 4)

Solvent: $CDCl_3$ – Frequency: 250 MHz

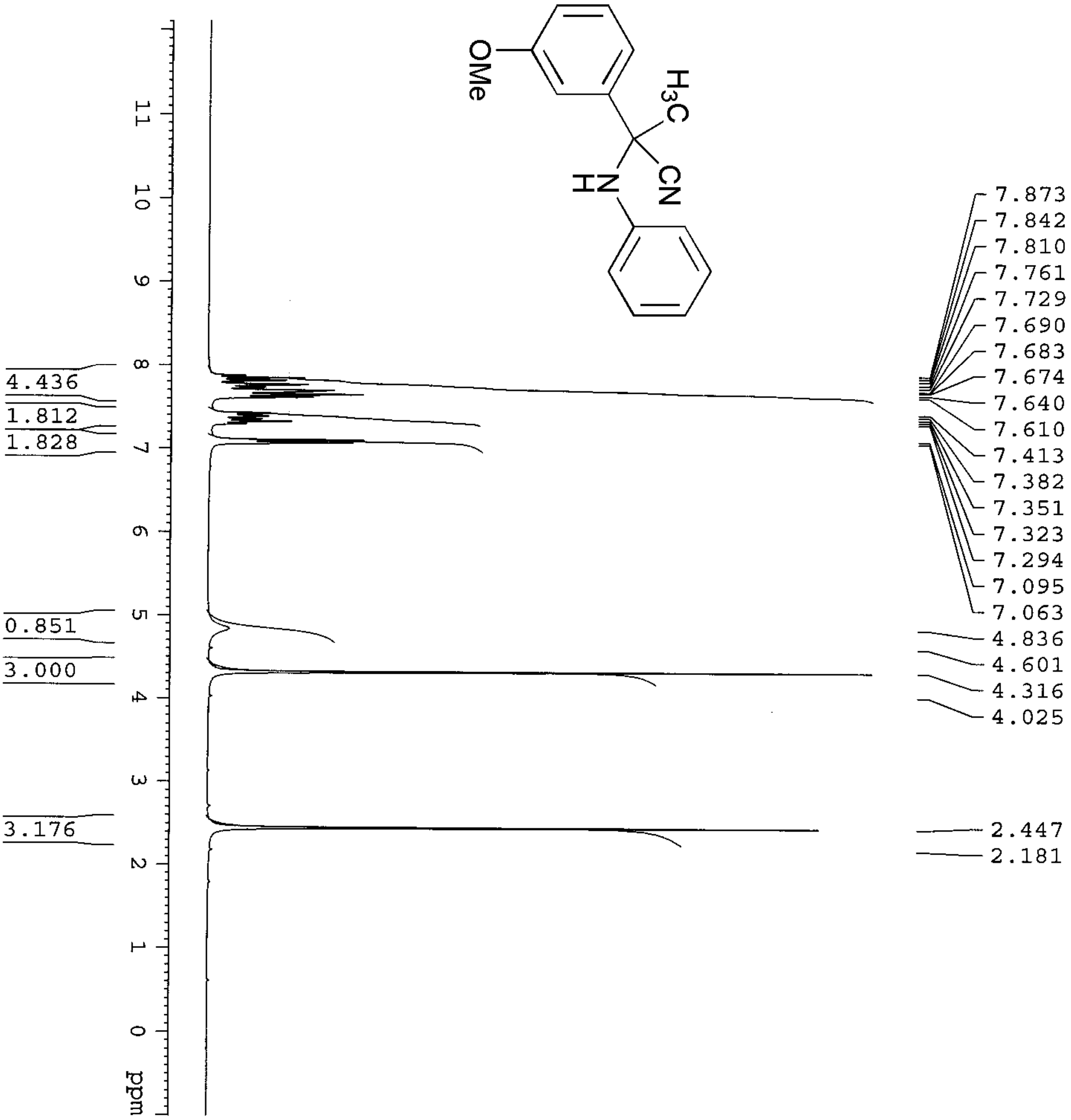

Table 2 (Entry 5)

Solvent: $CDCl_3$ – Frequency: 250 MHz

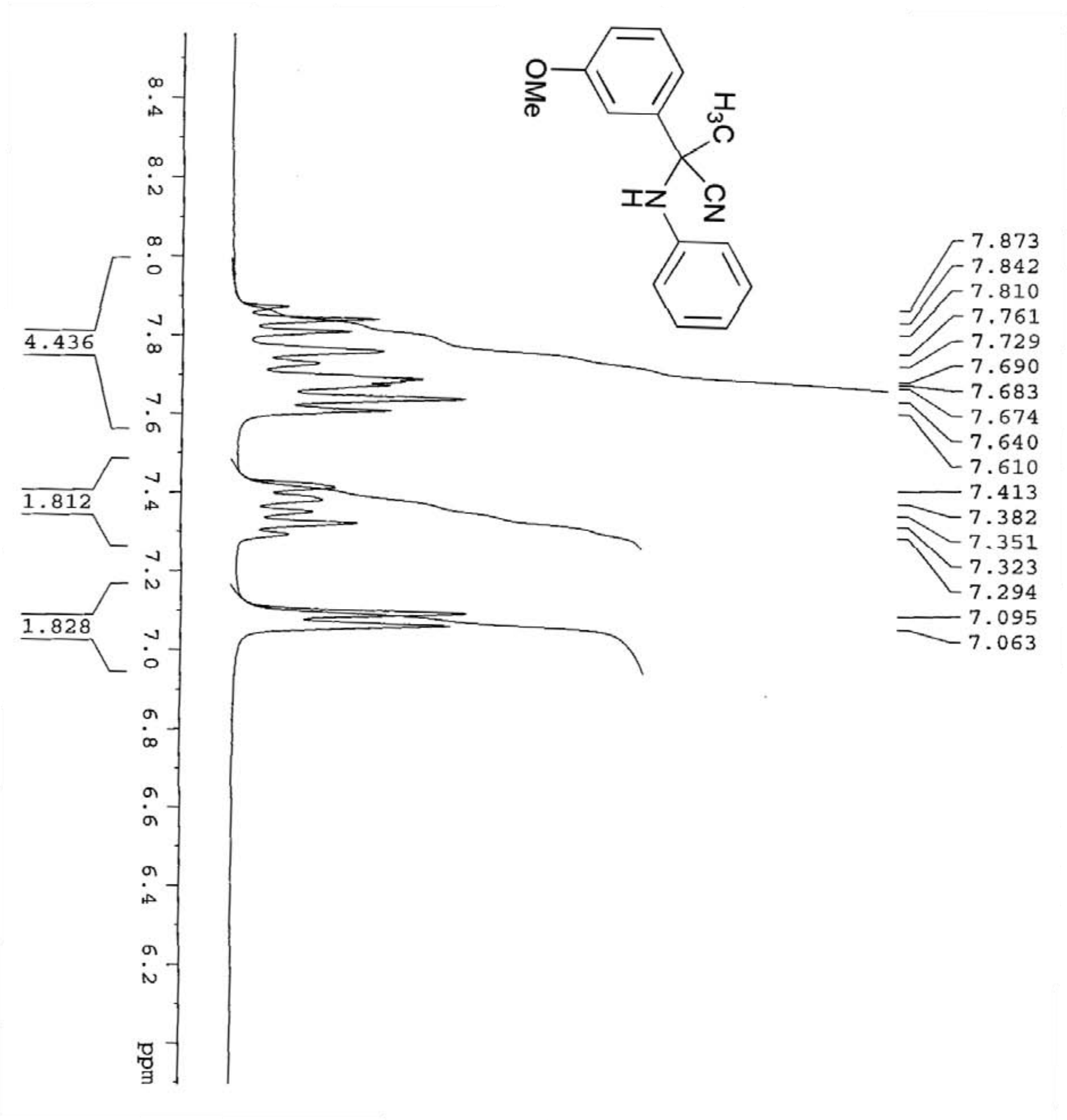

Table 2 (Entry 5)

Solvent: $CDCl_3$ – Frequency: 250 MHz

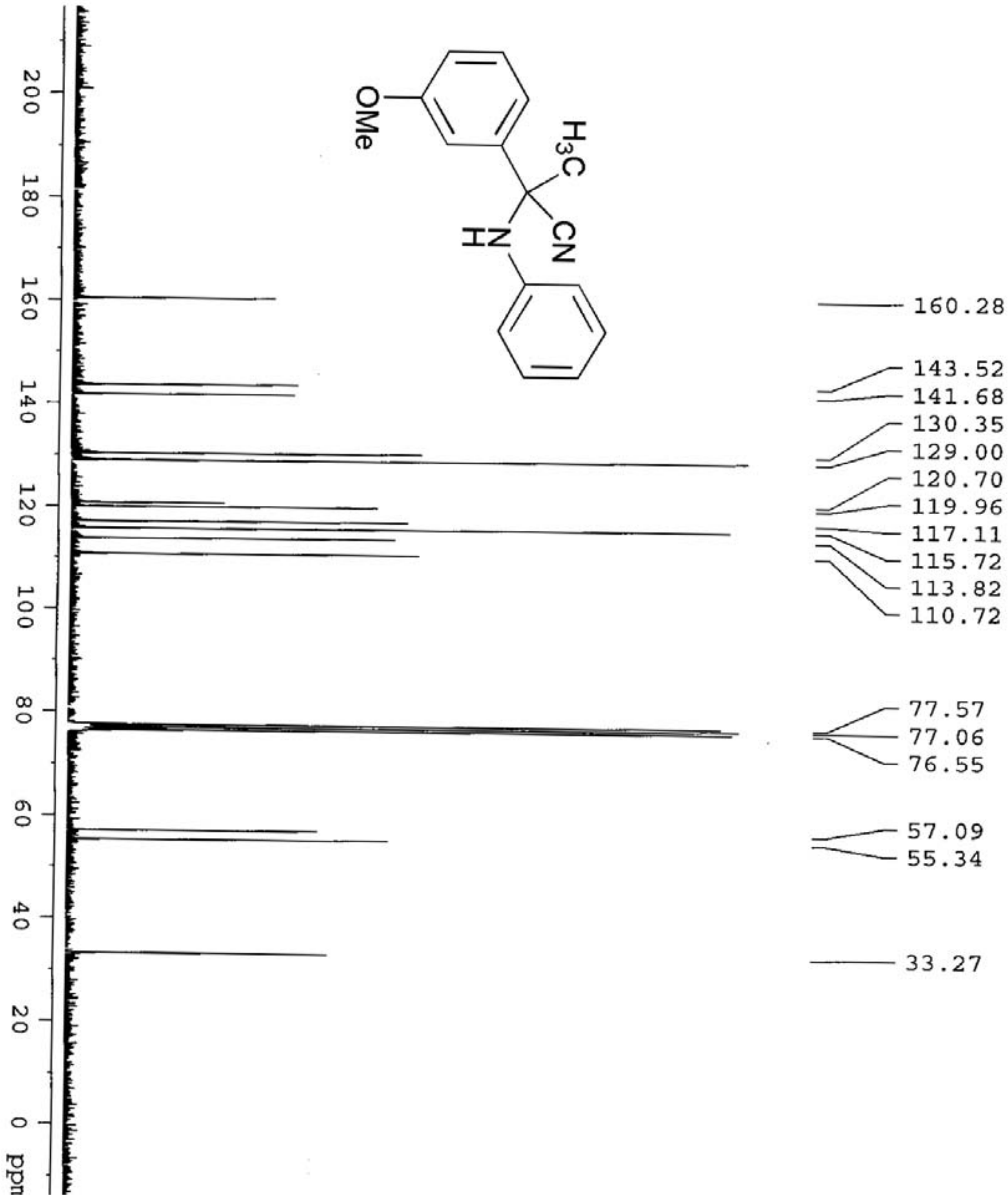

Table 2 (Entry 5)

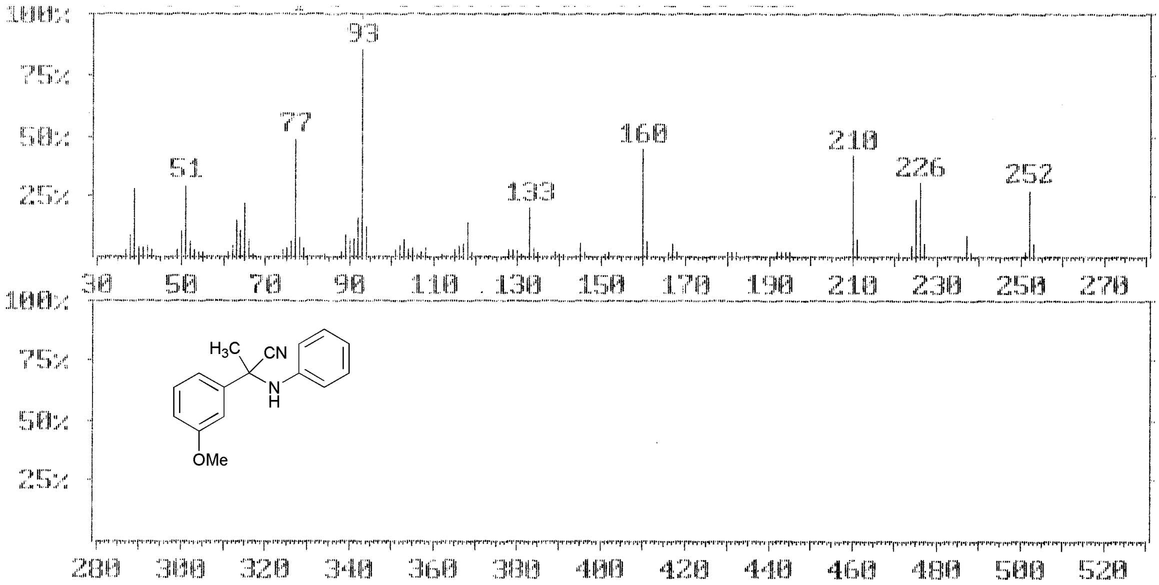

Table 2 (Entry 5)

Solvent: $CDCl_3$ – Frequency: 250 MHz

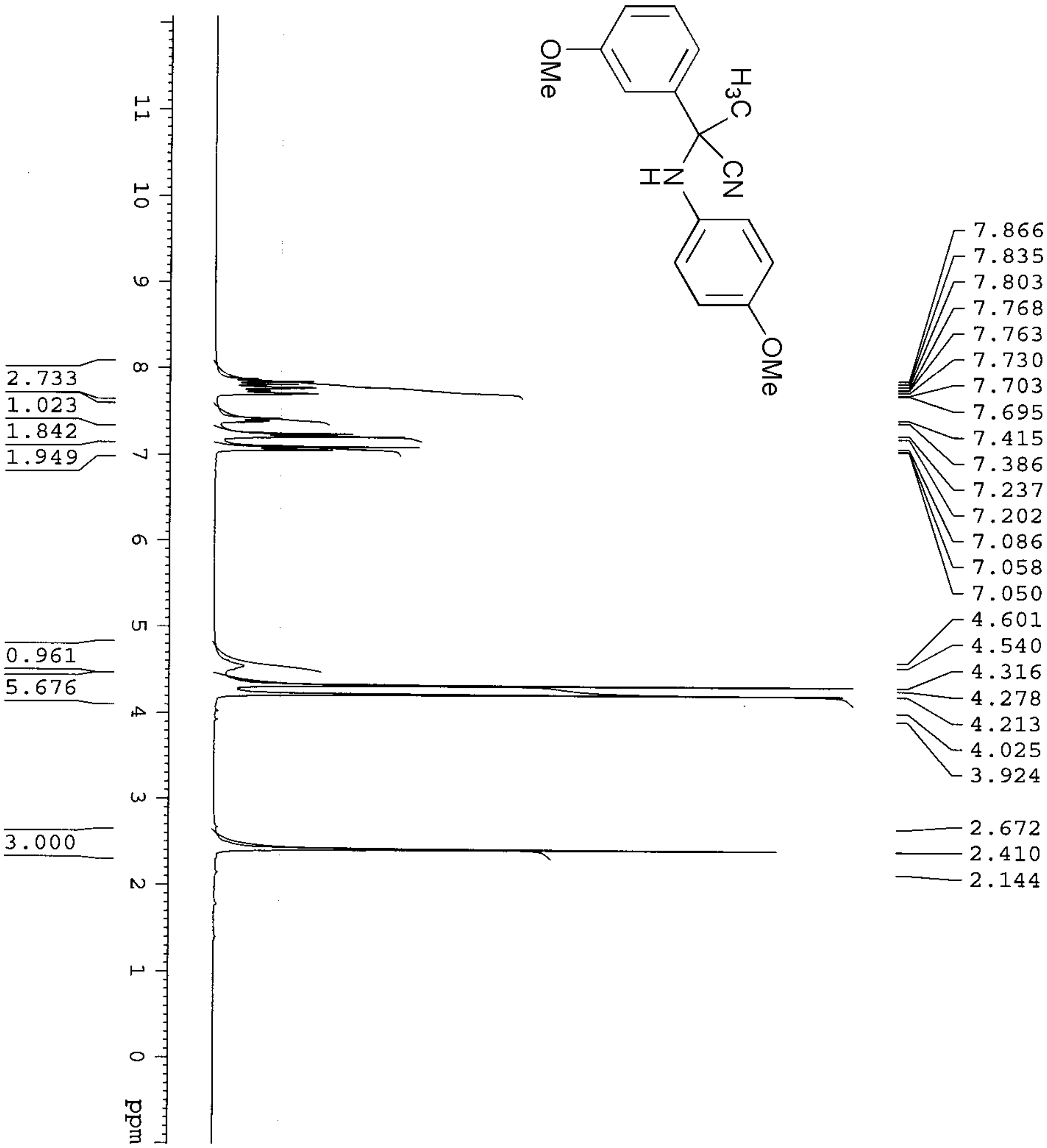

Table 2 (Entry 6)

Solvent: $CDCl_3$ – Frequency: 250 MHz

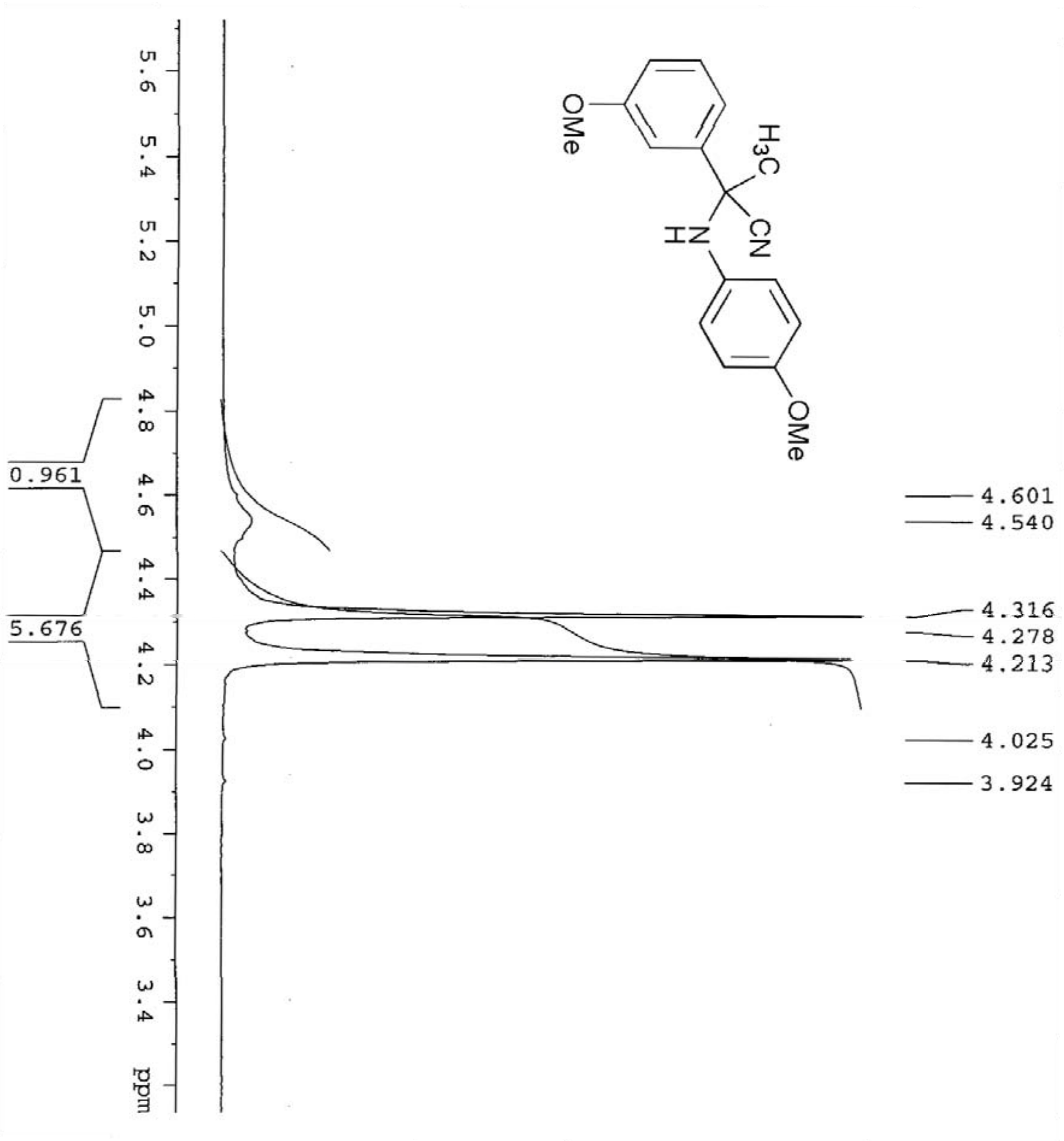

Table 2 (Entry 6)

Solvent: $CDCl_3$ – Frequency: 250 MHz

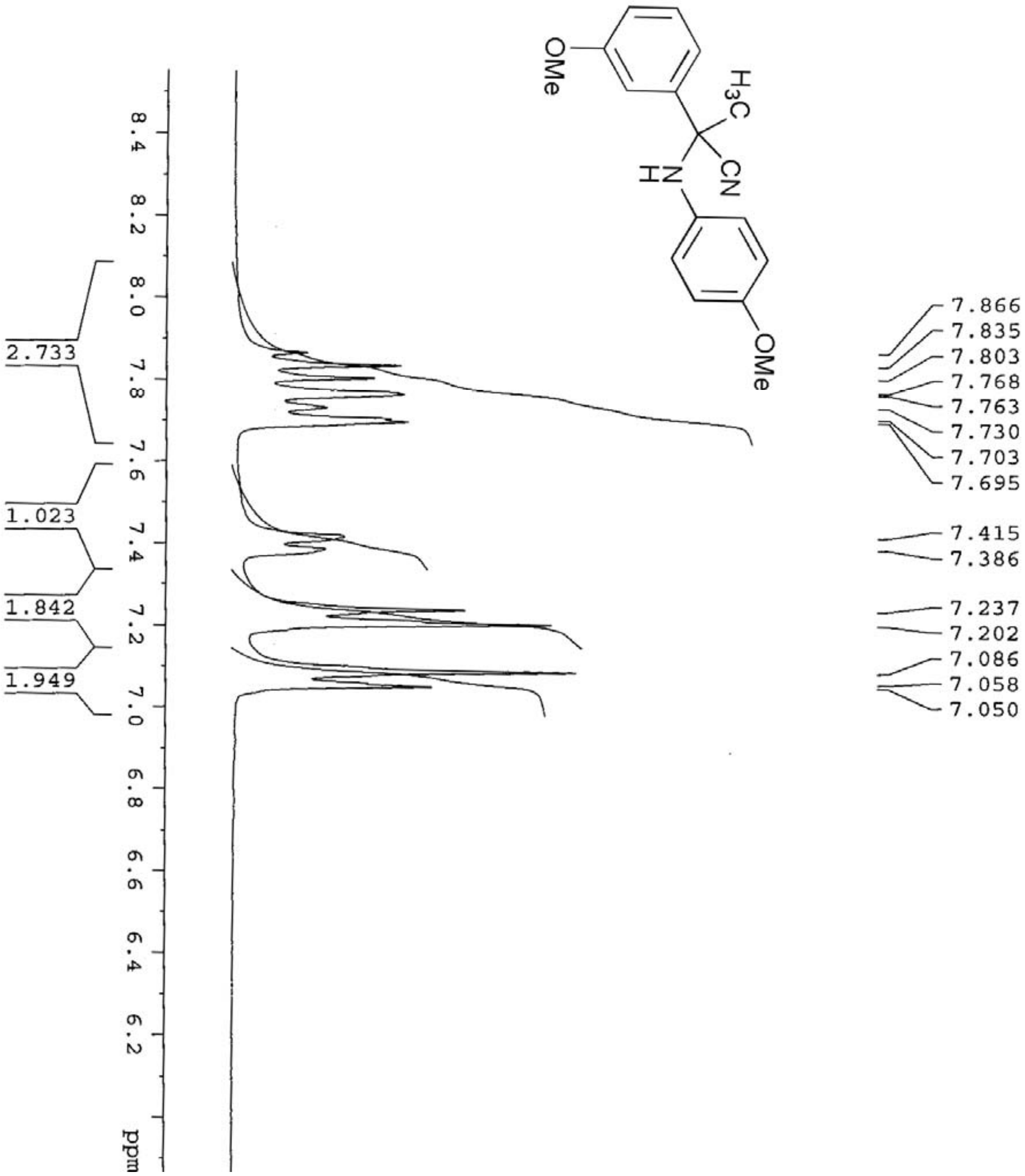

Table 2 (Entry 6)

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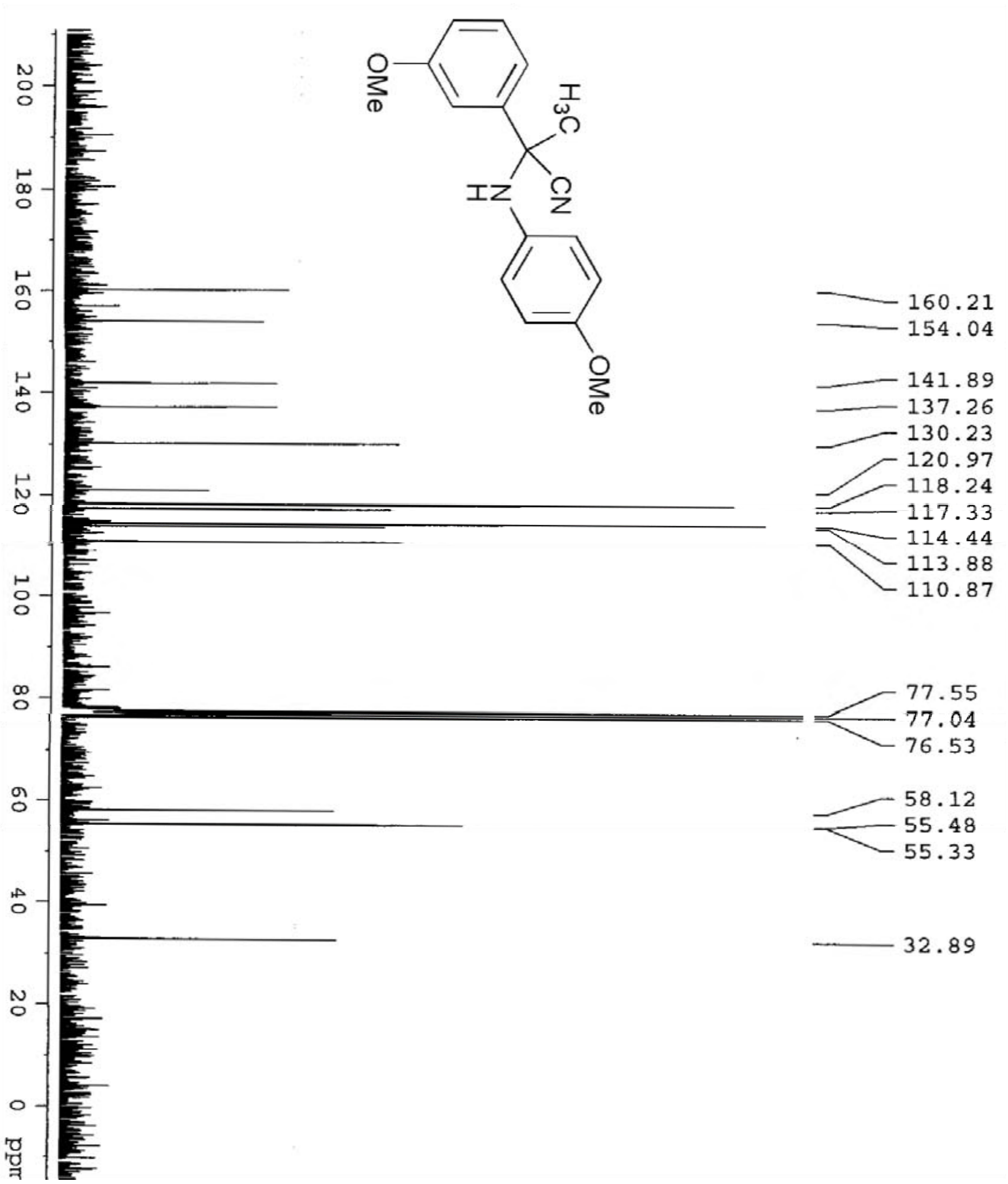

Table 2 (Entry 6)

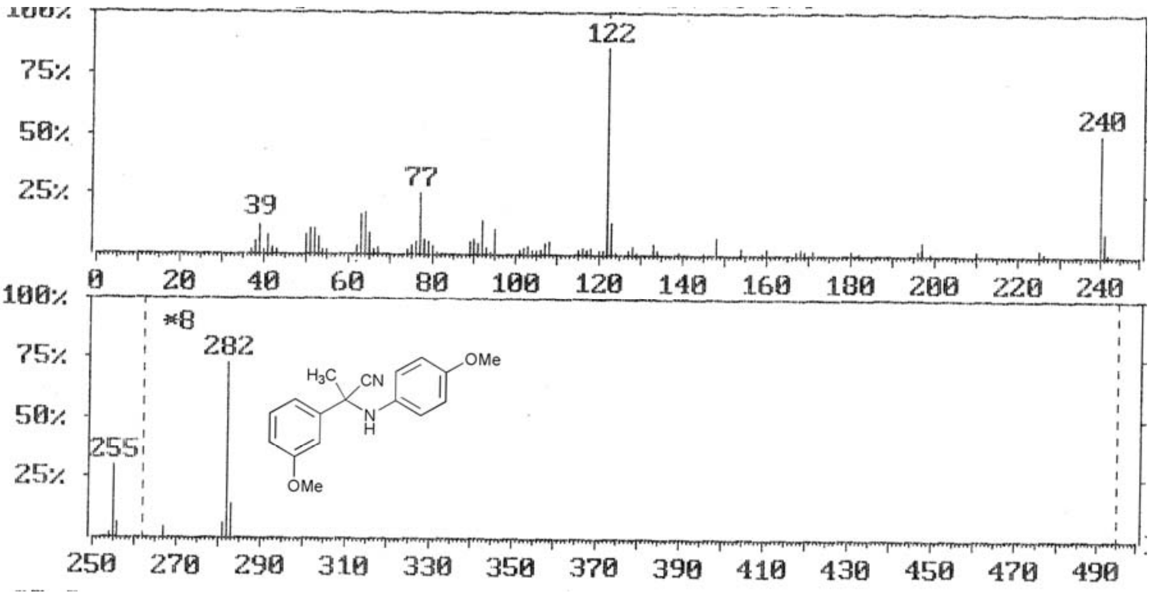

Table 2 (Entry 6)

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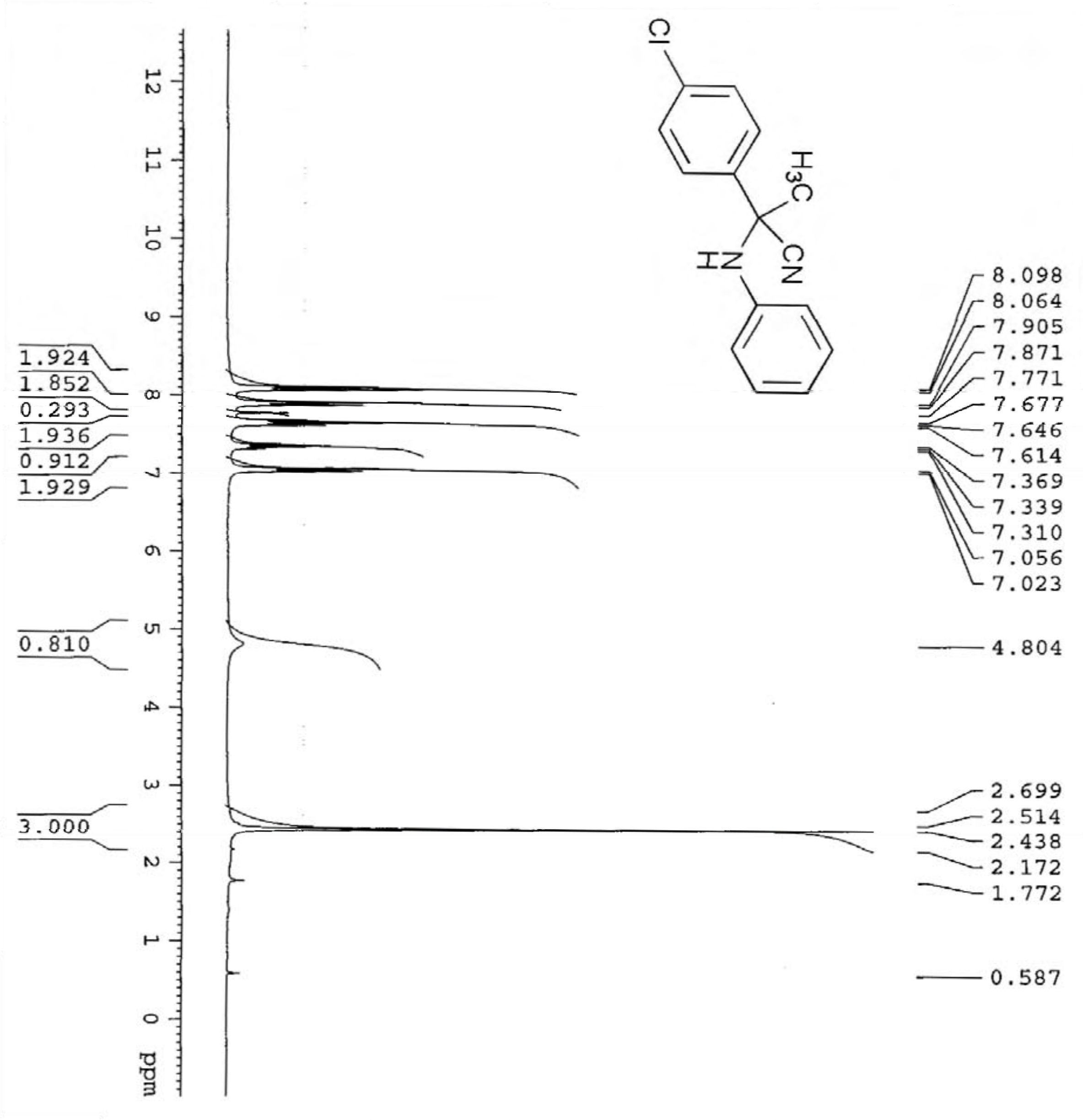

Table 2 (Entry 7)

Solvent: $CDCl_3$ – Frequency: 250 MHz

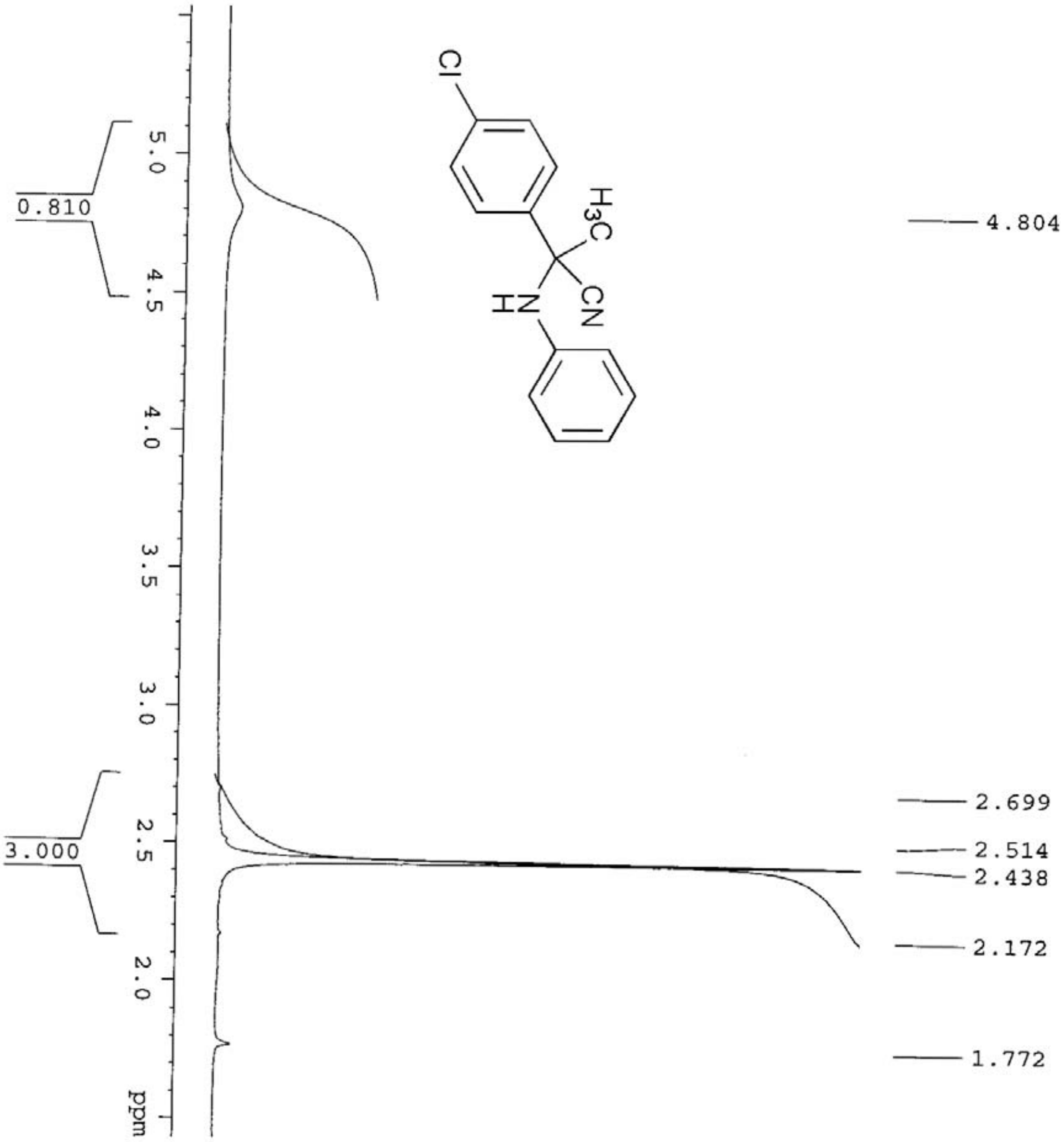

Table 2 (Entry 7)

Solvent: $CDCl_3$ – Frequency: 250 MHz

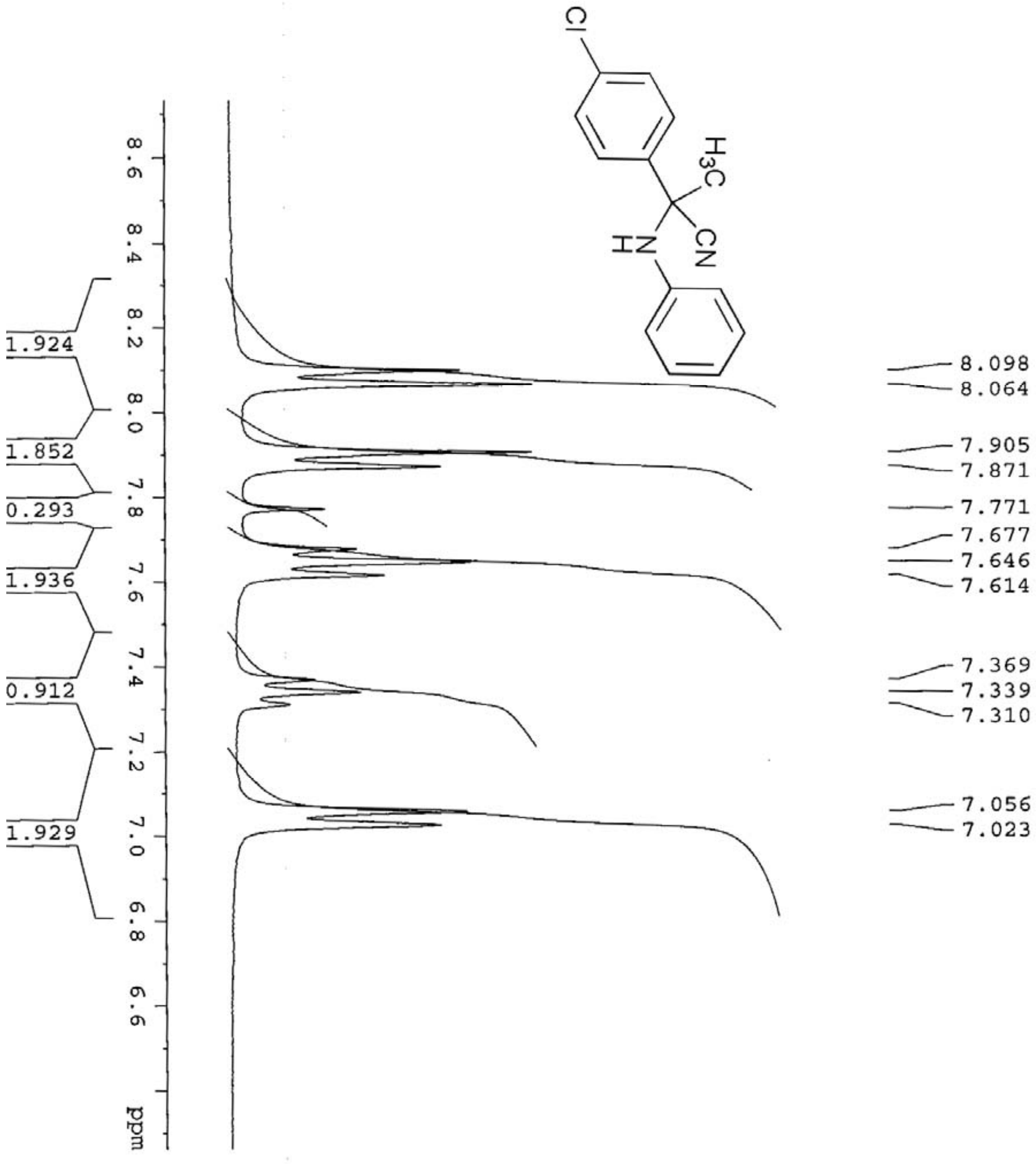

Table 2 (Entry 7)

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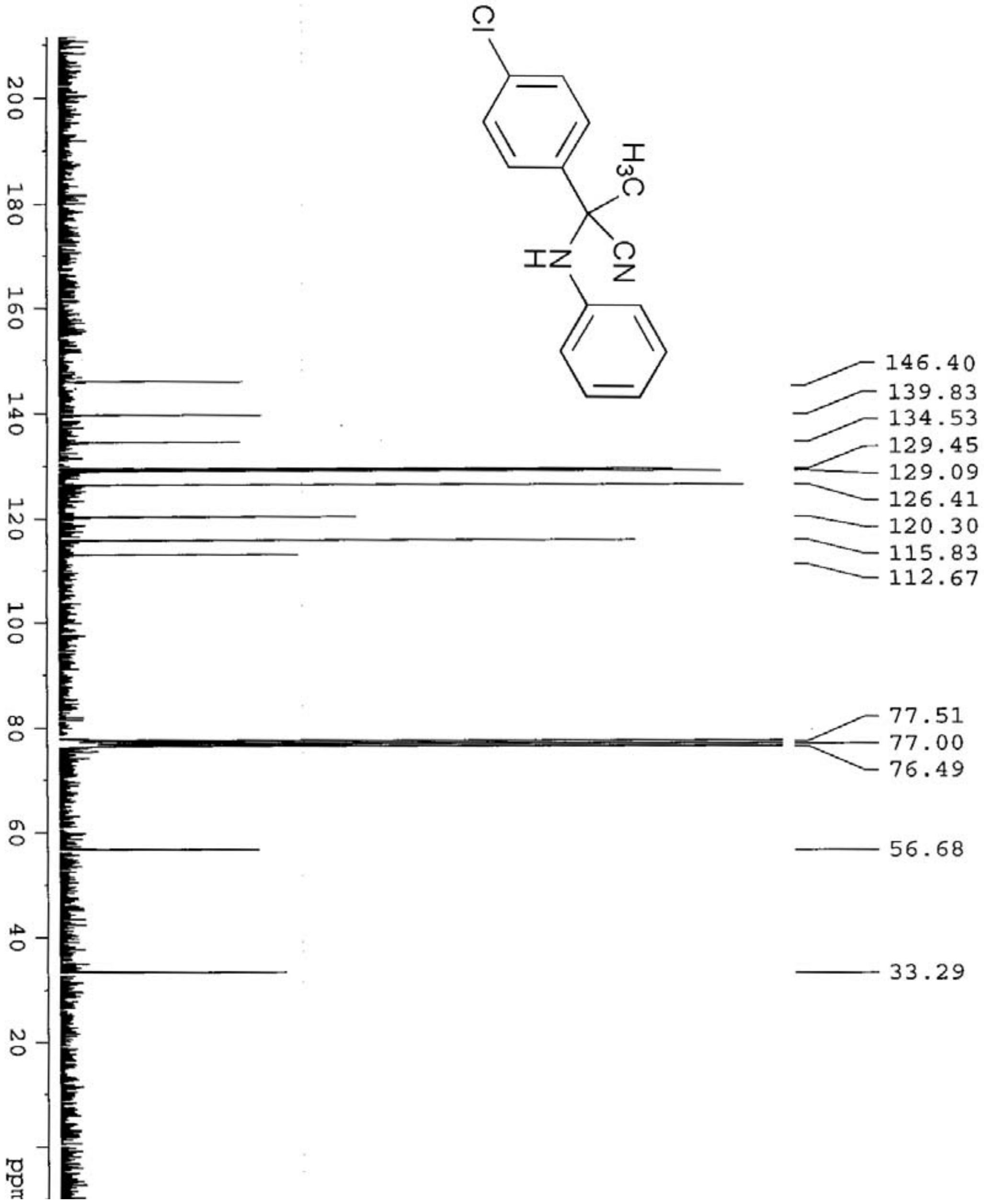
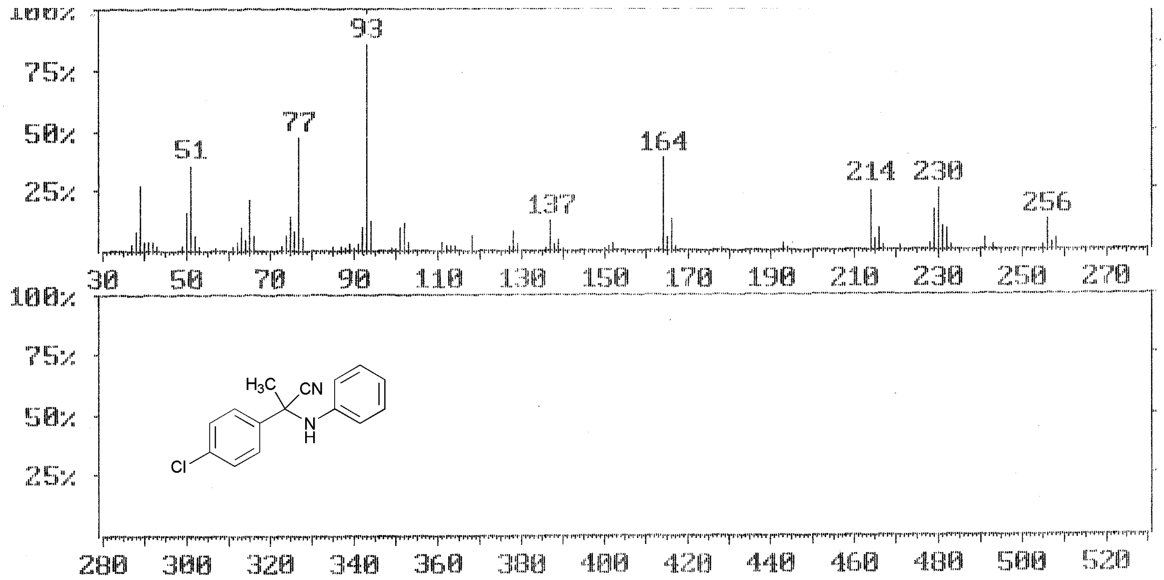


Table 2 (Entry 7)



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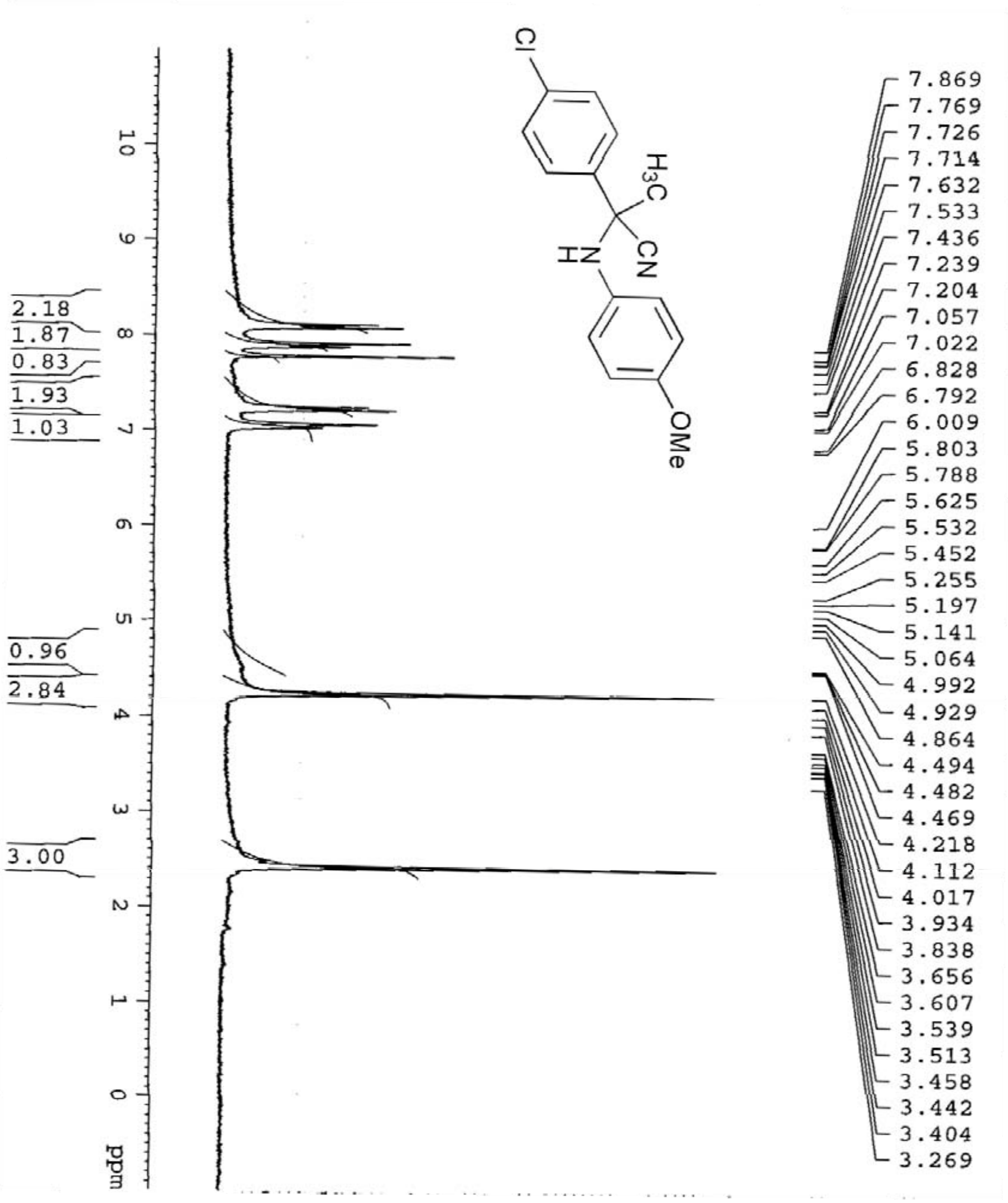

Table 2 (Entry 8)

Solvent: $CDCl_3$ – Frequency: 250 MHz

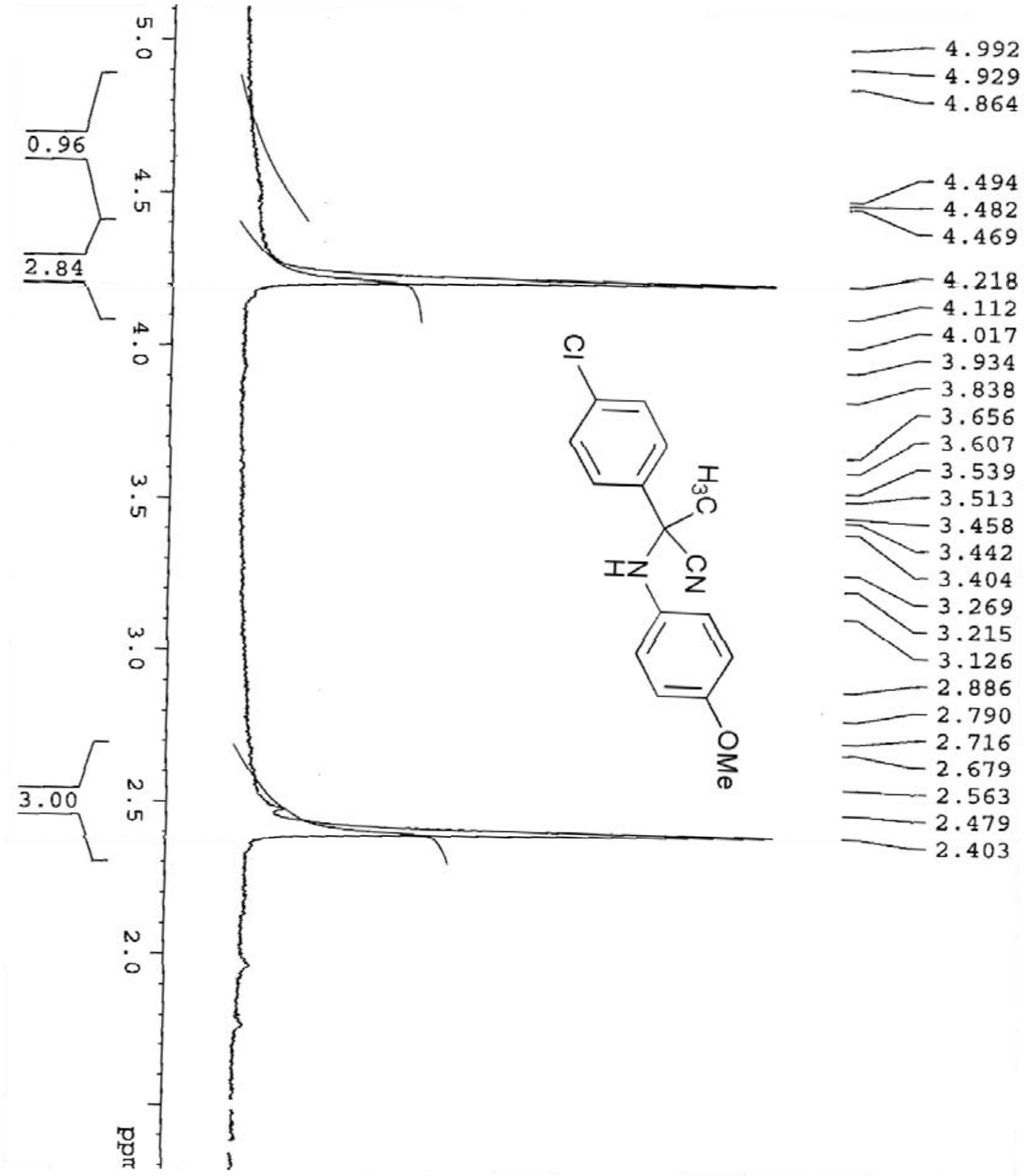

Table 2 (Entry 8)

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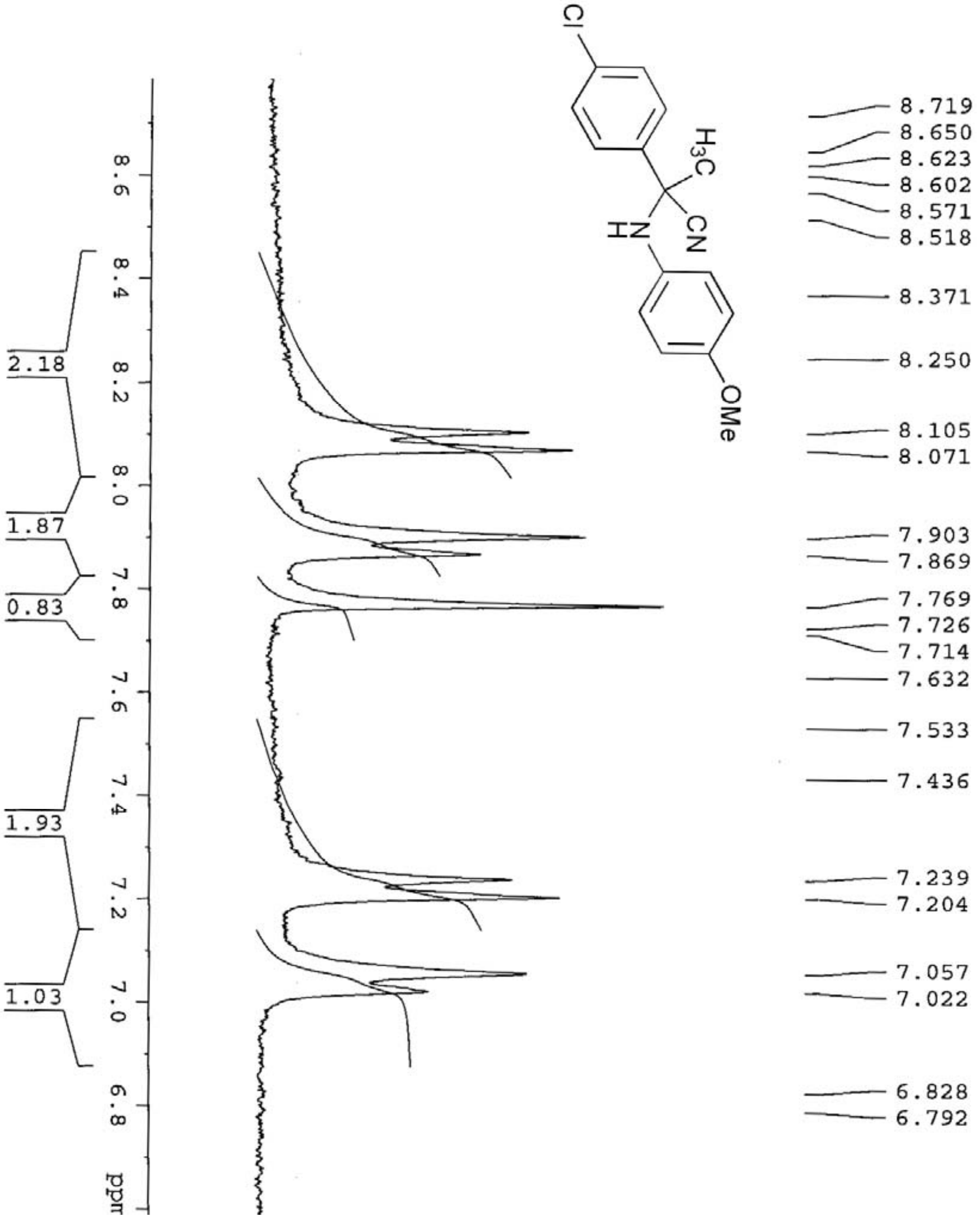

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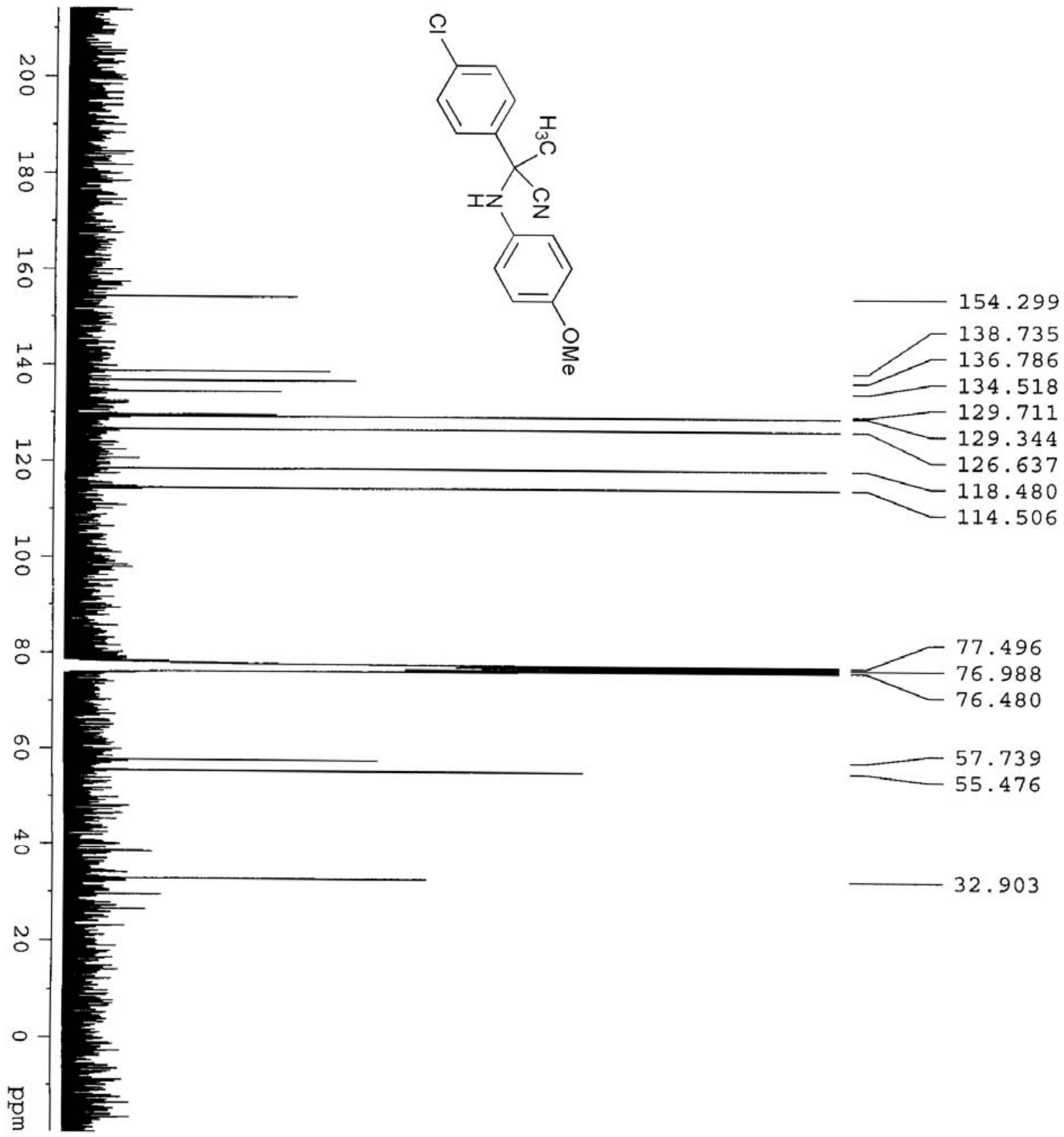

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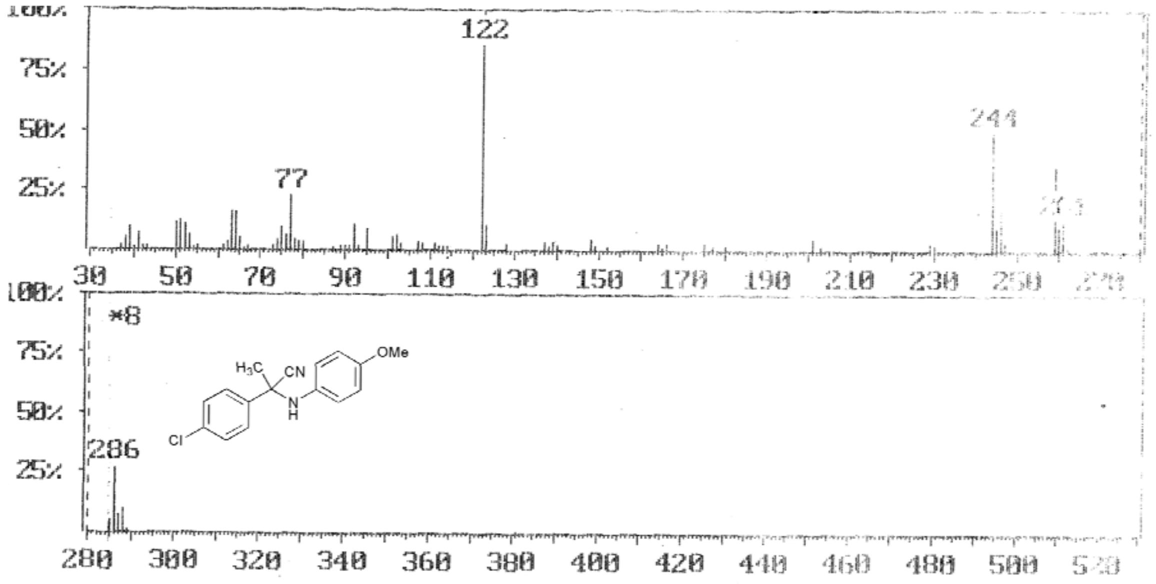

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Solvent: $CDCl_3$ – Frequency: 250 MHz

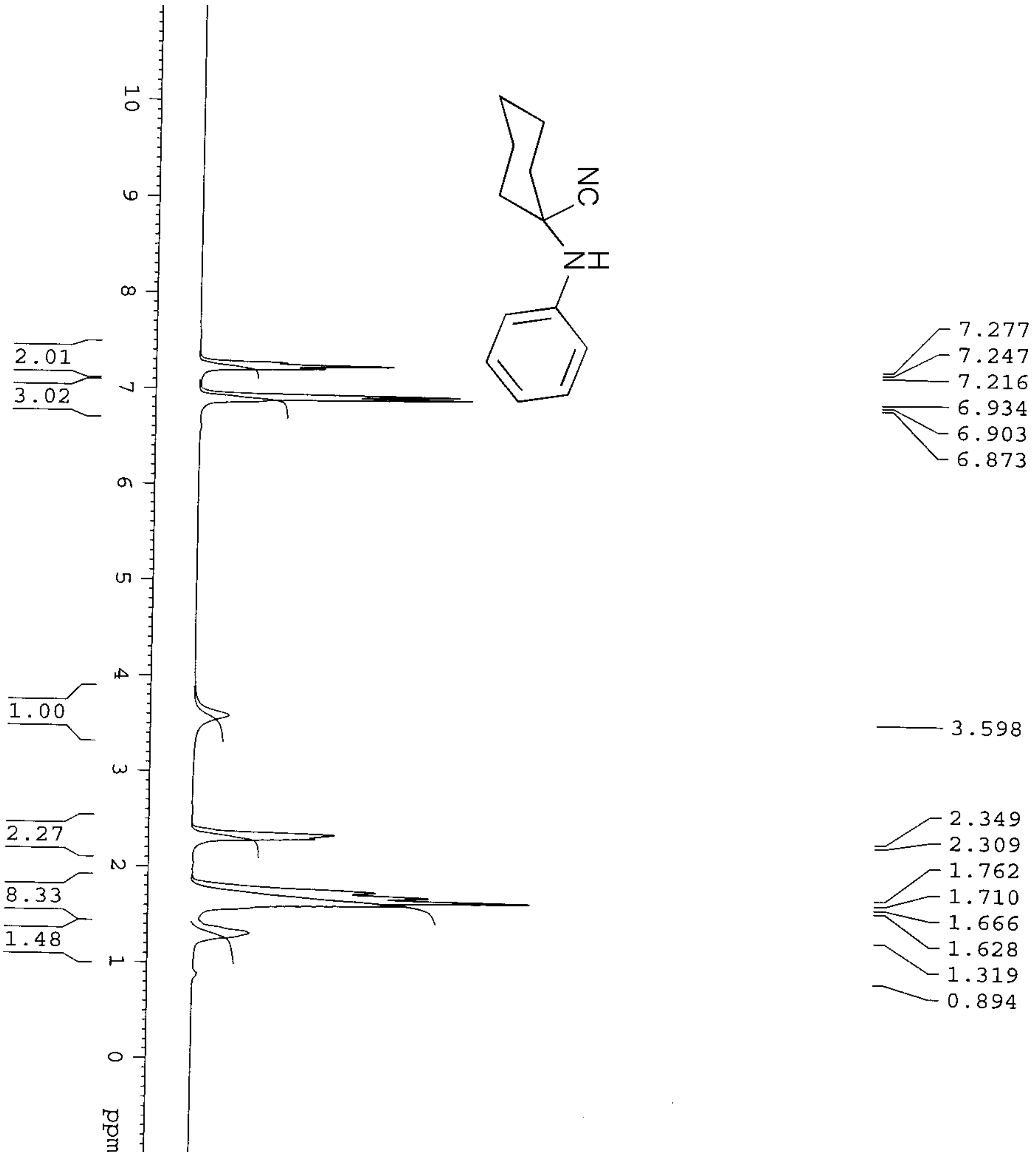


Table 2 (Entry 9)

Solvent: $CDCl_3$ – Frequency: 250 MHz

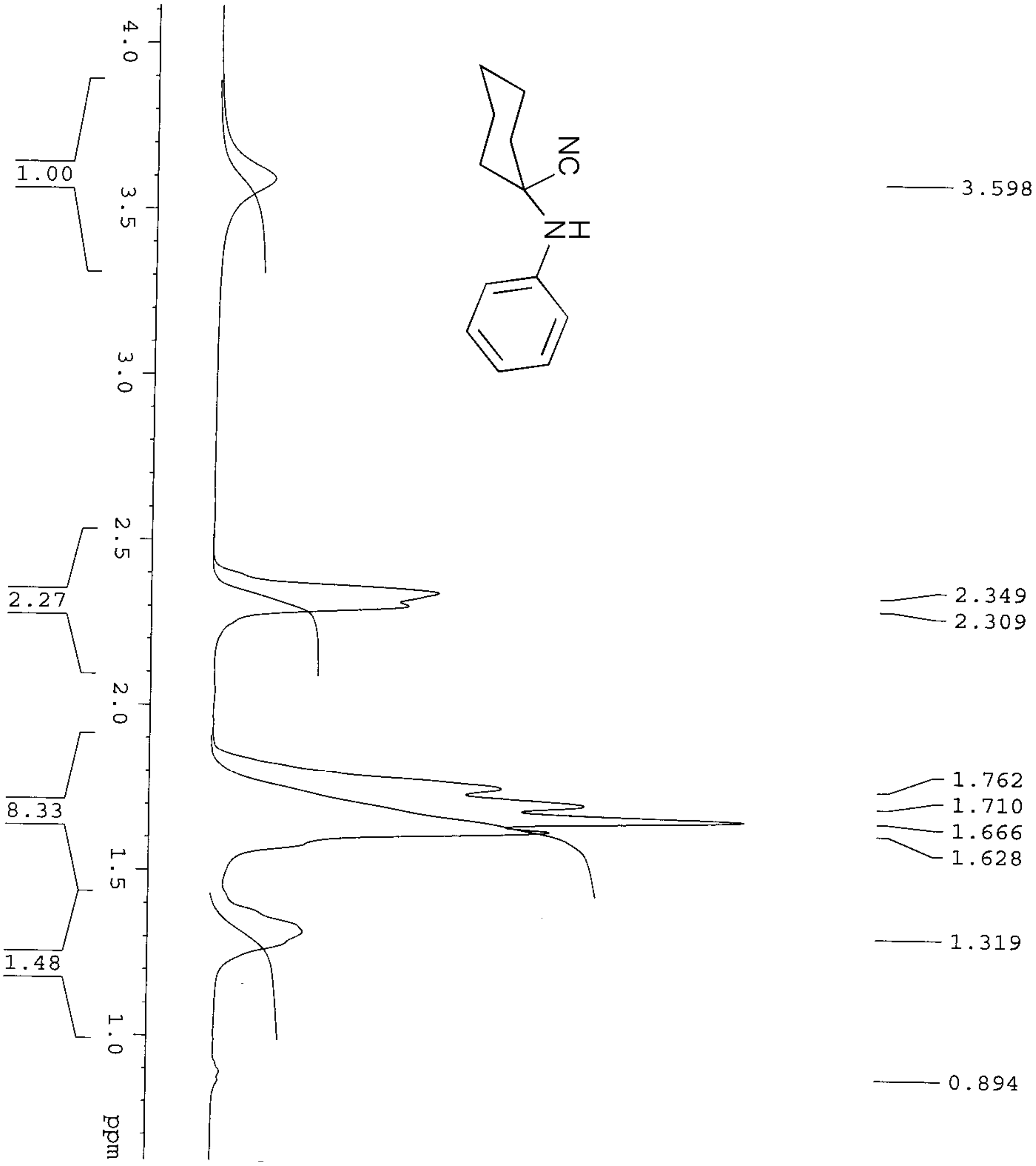
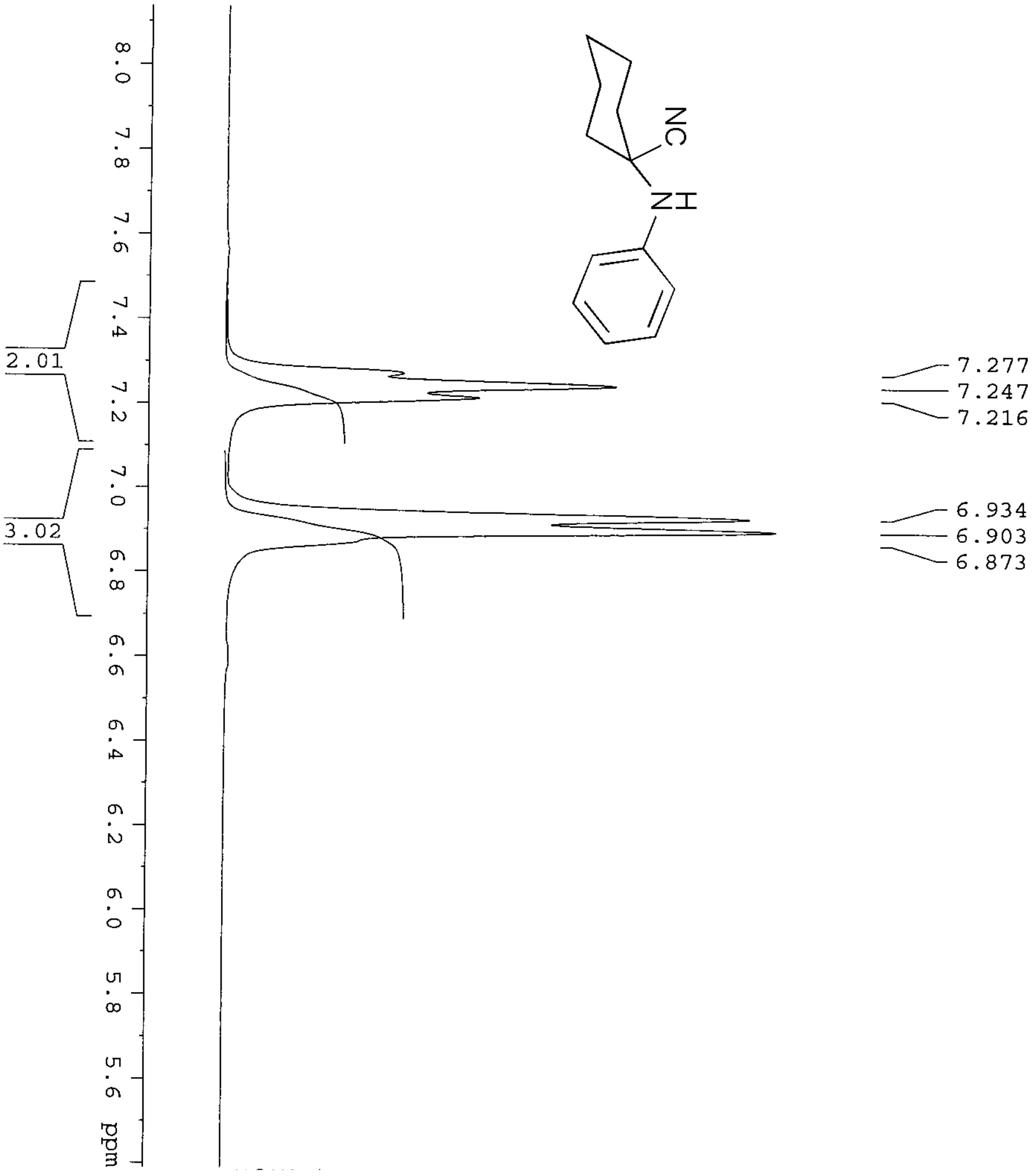


Table 2 (Entry 9)

Solvent: $CDCl_3$ – Frequency: 250 MHz



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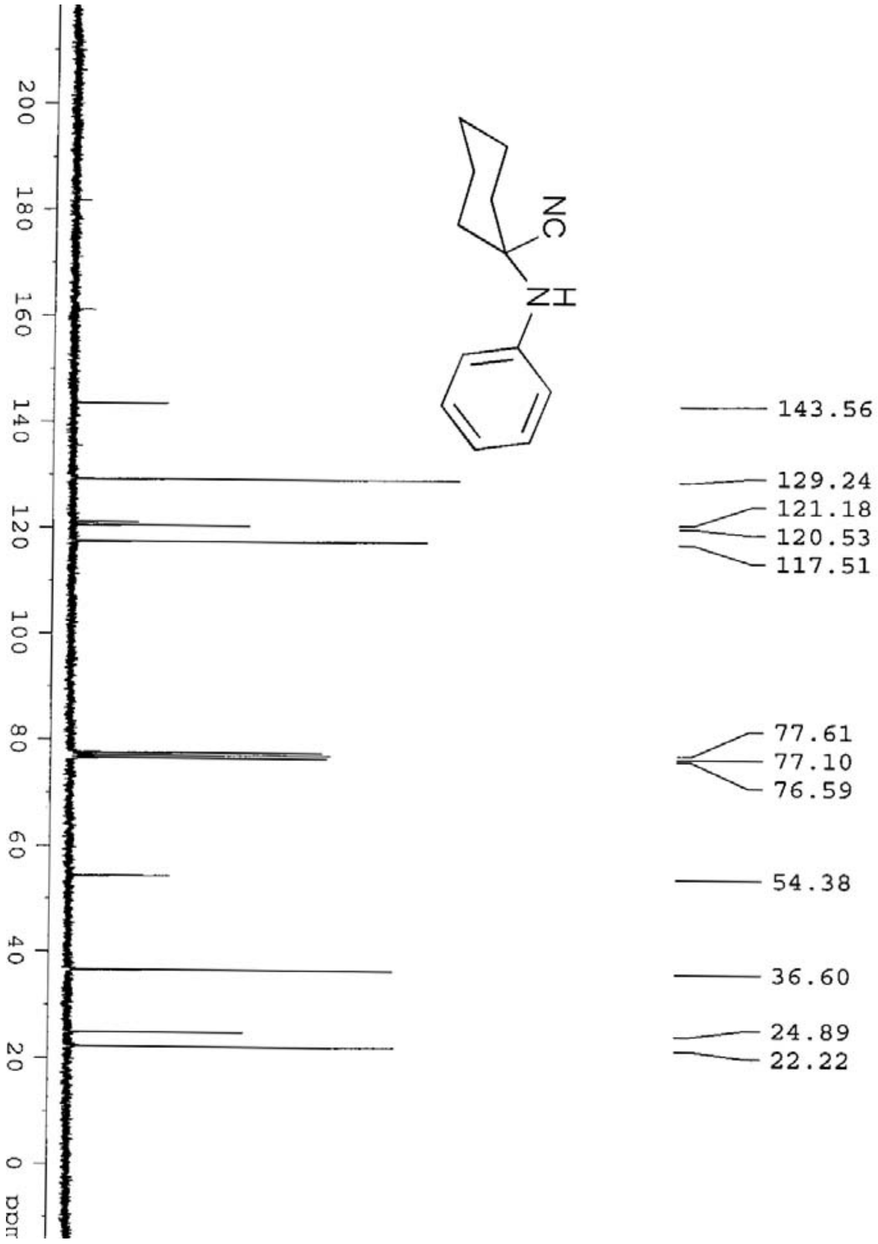

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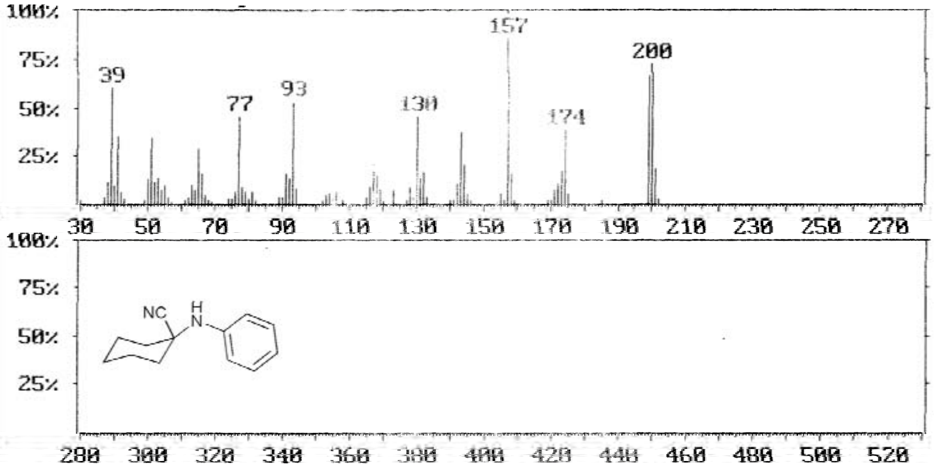

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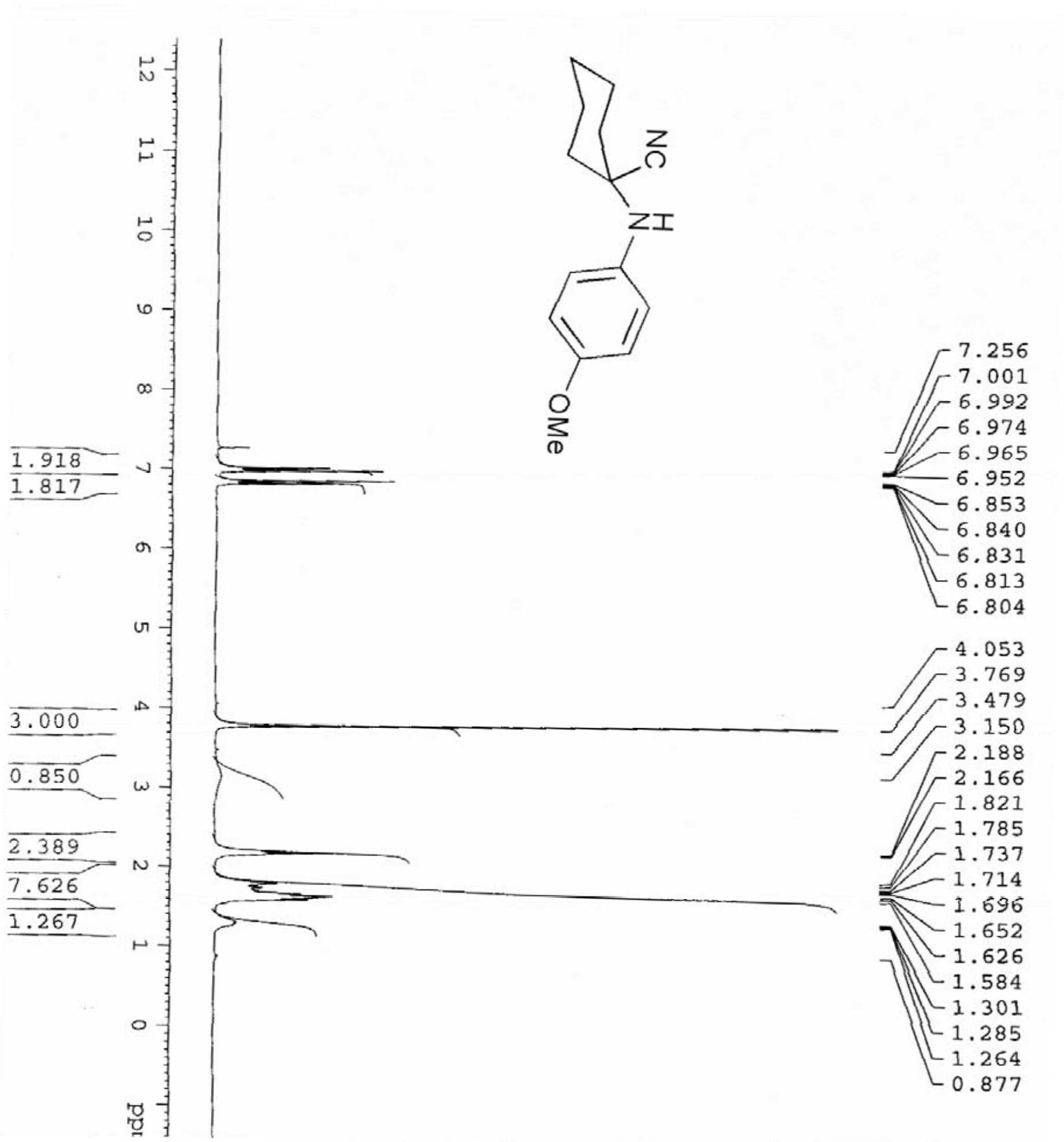
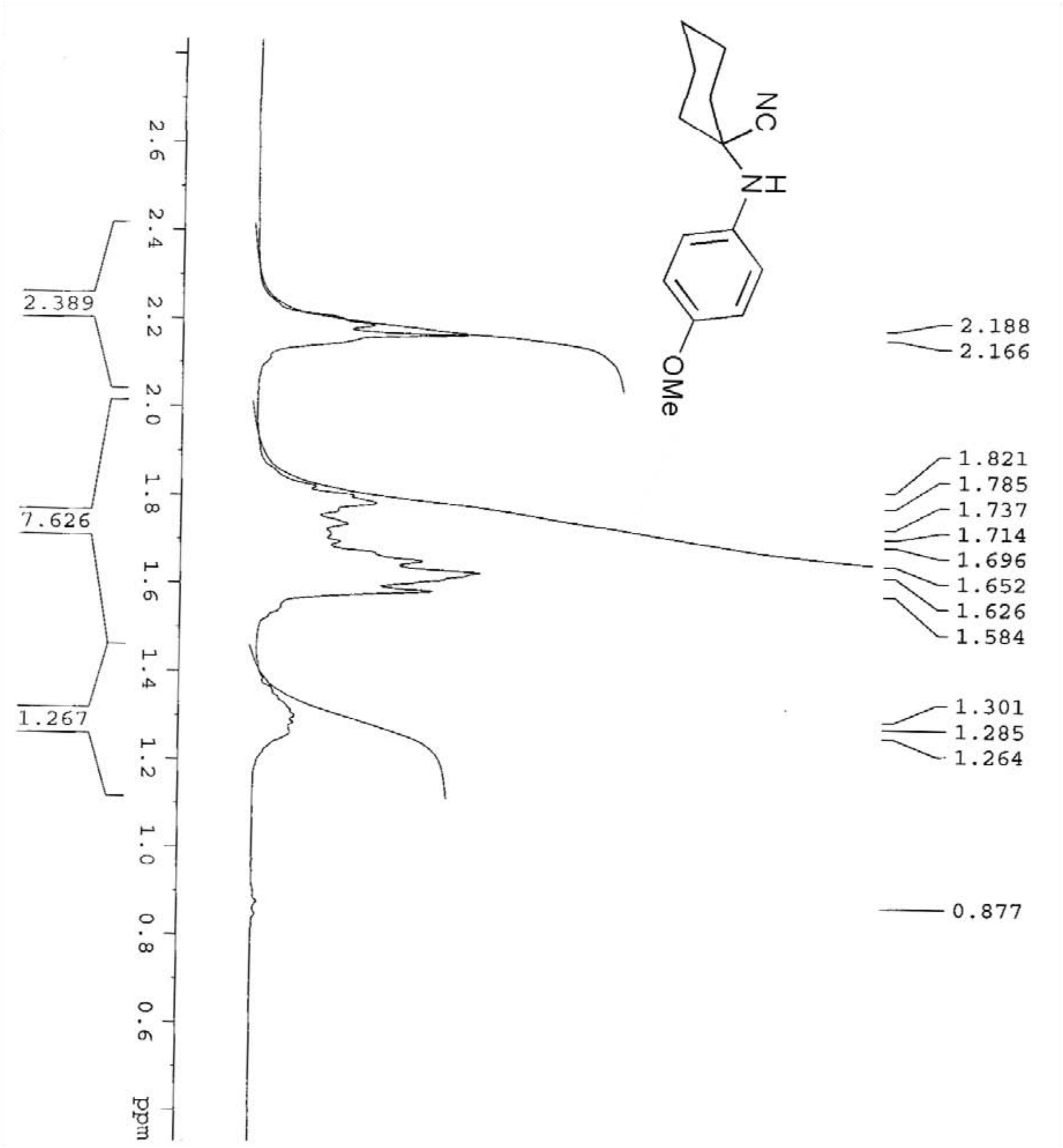


Table 2 (Entry 10)

Solvent: $CDCl_3$ – Frequency: 250 MHz



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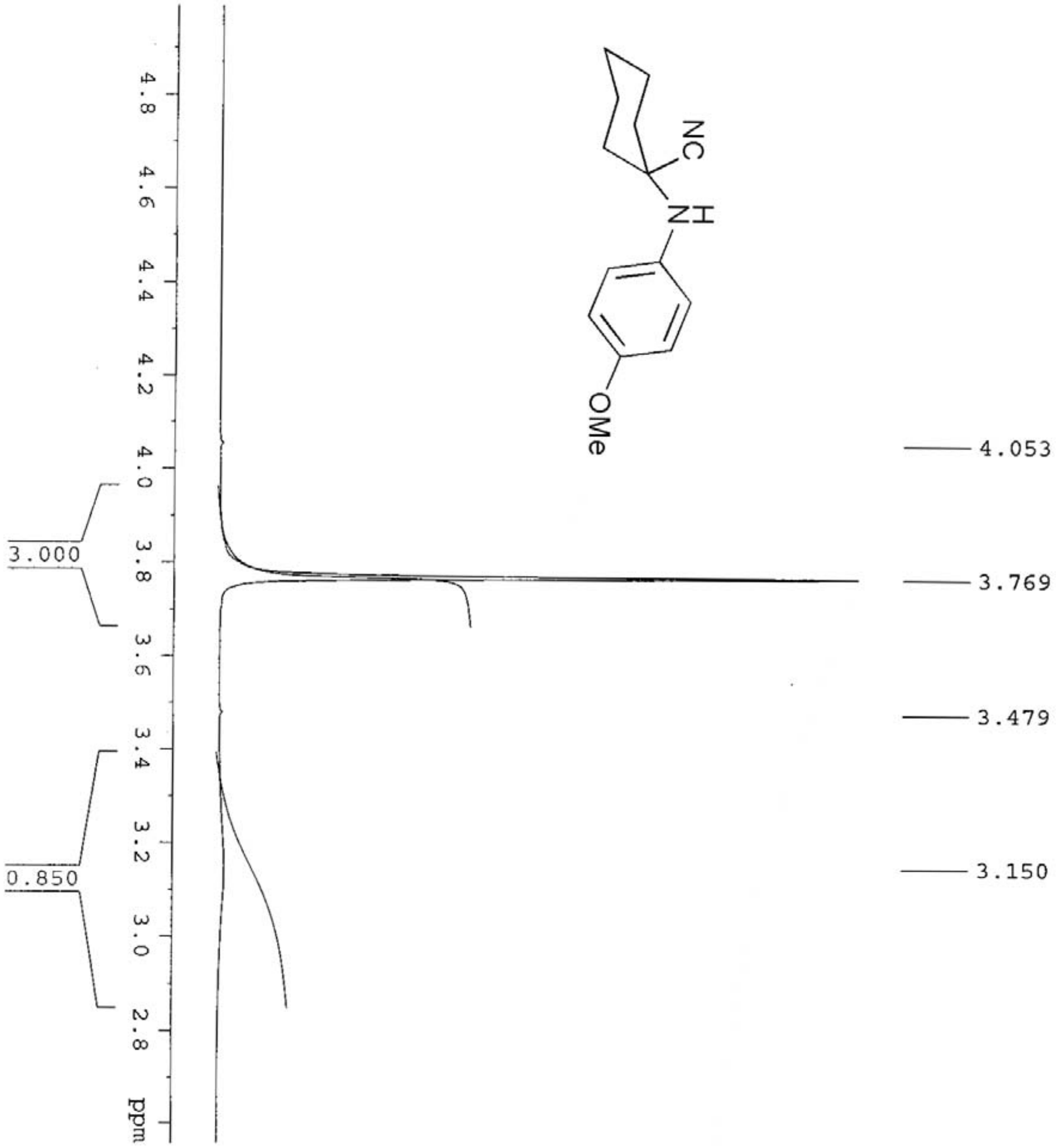

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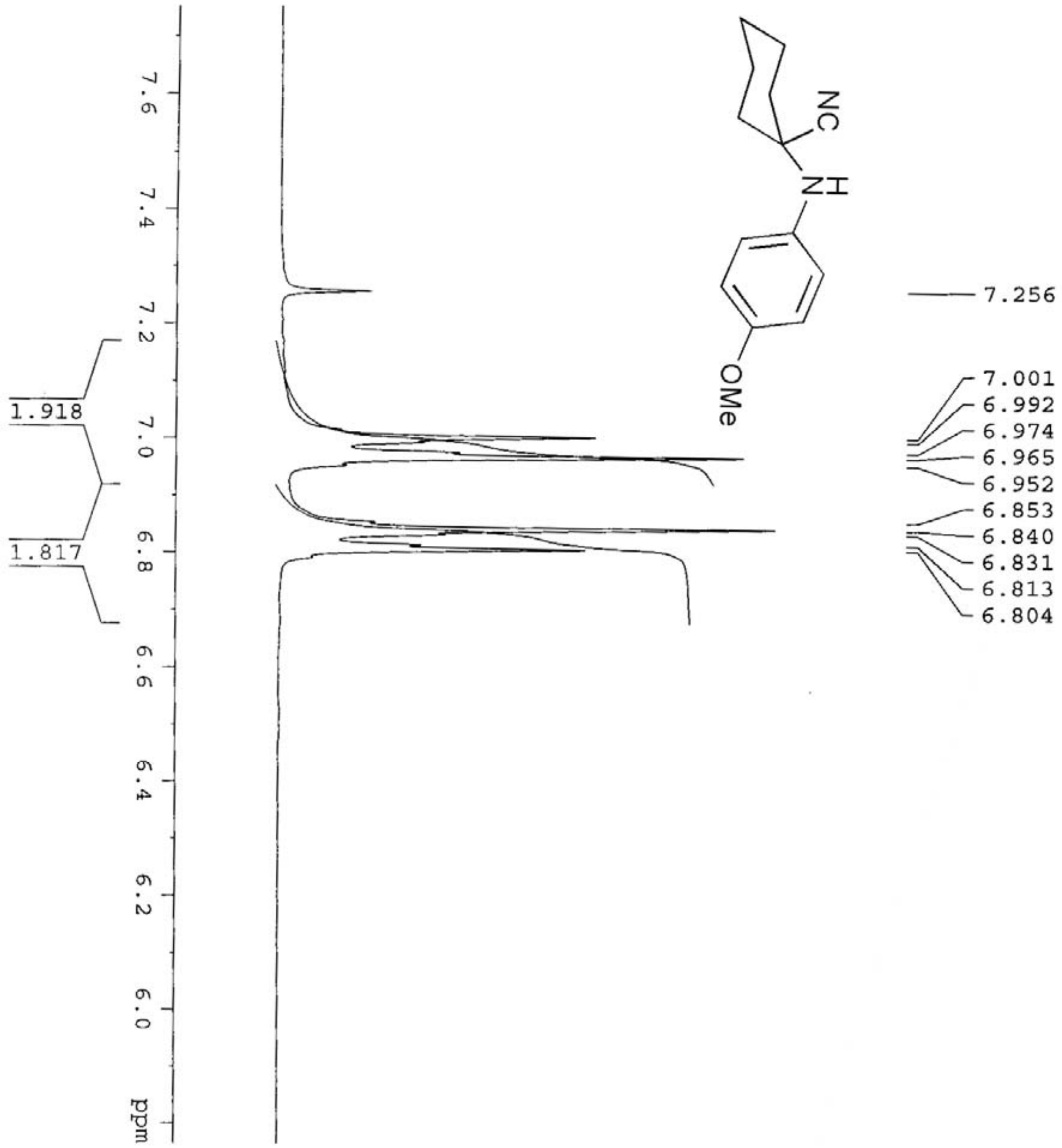

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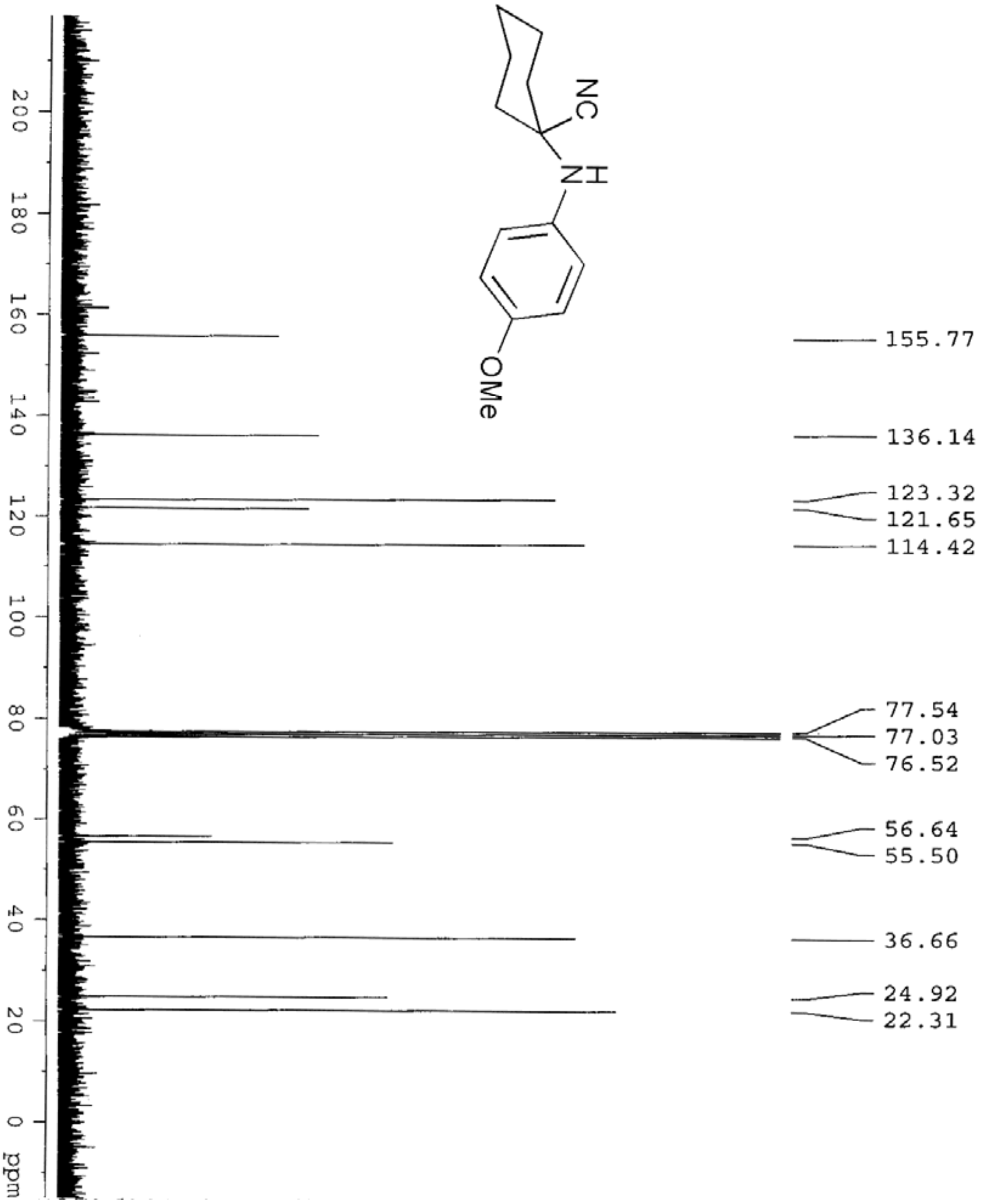

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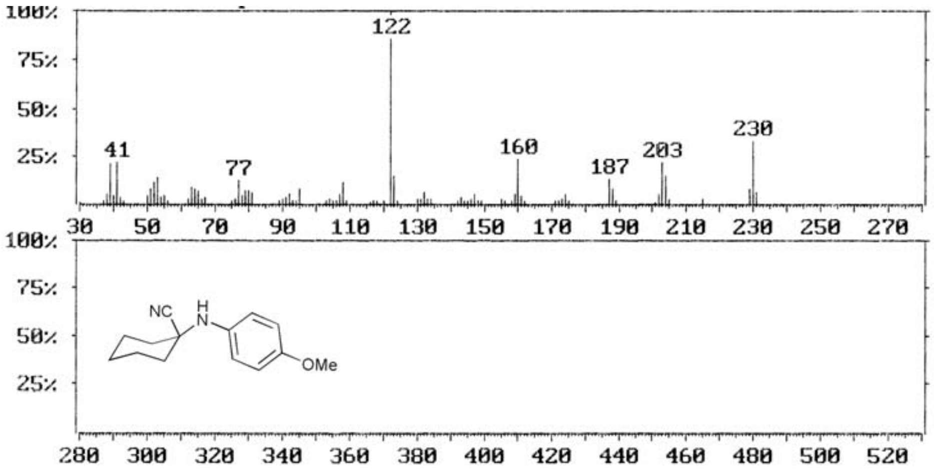

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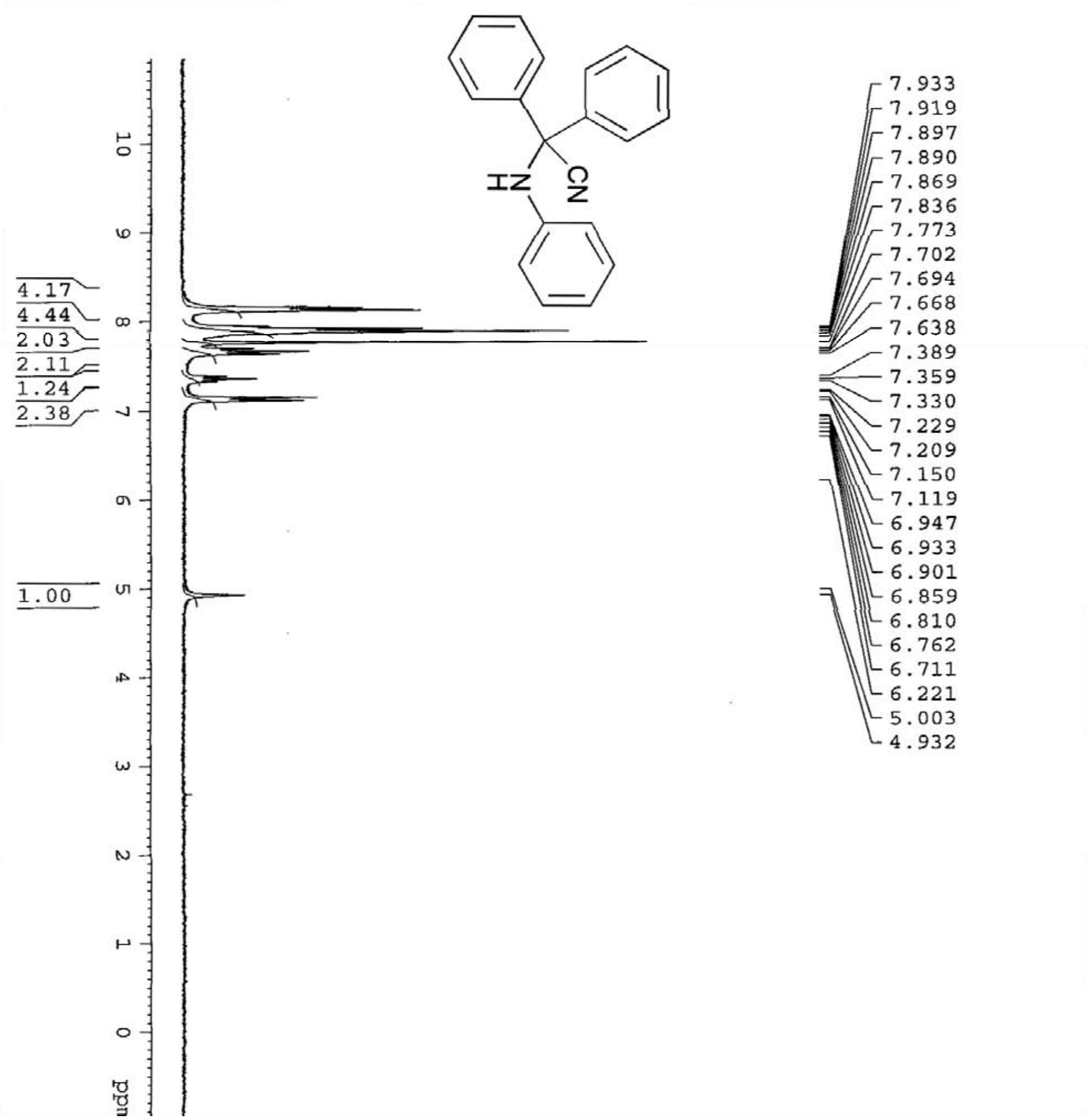
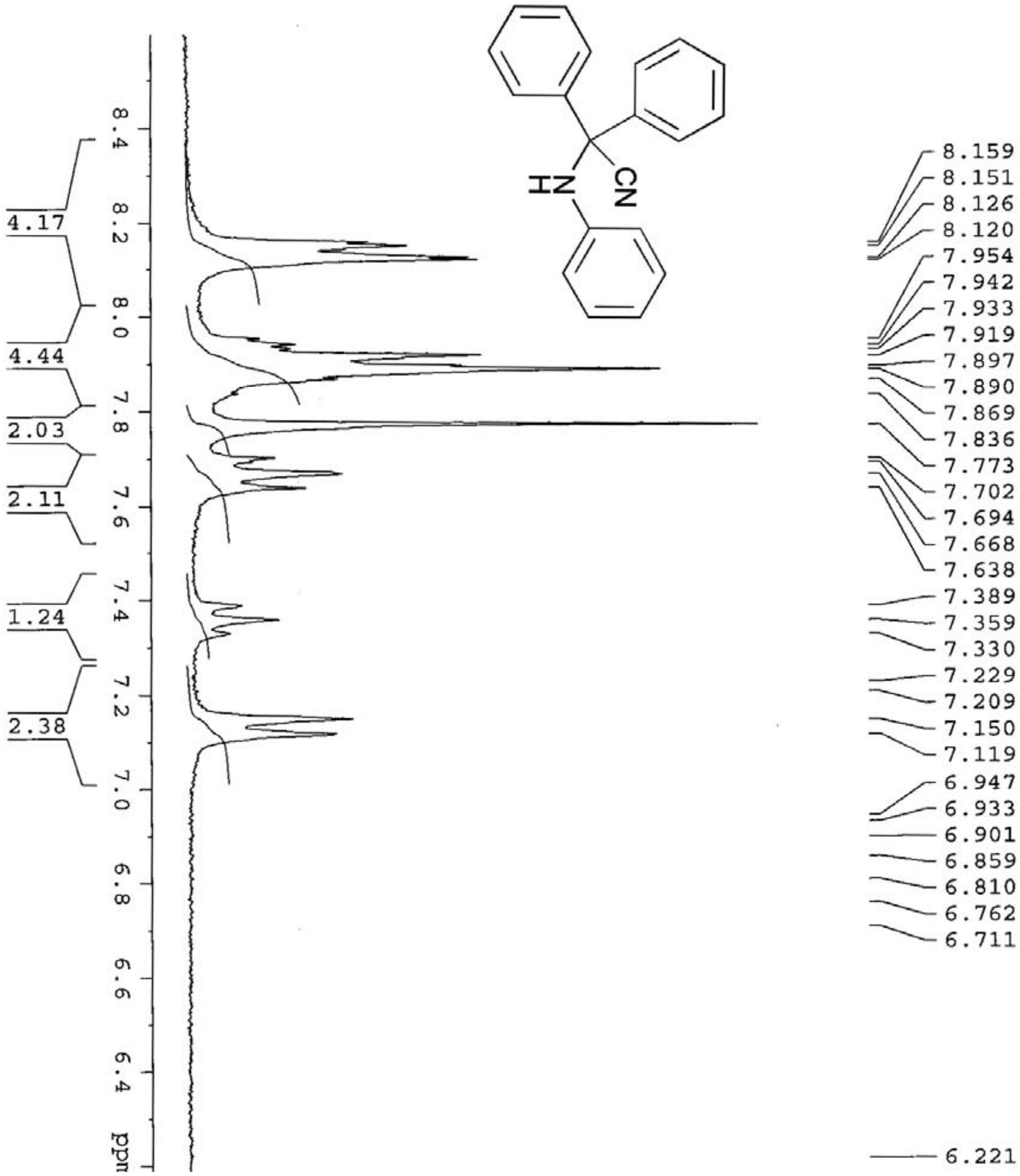


Table 2 (Entry 11)

Solvent: $CDCl_3$ – Frequency: 250 MHz



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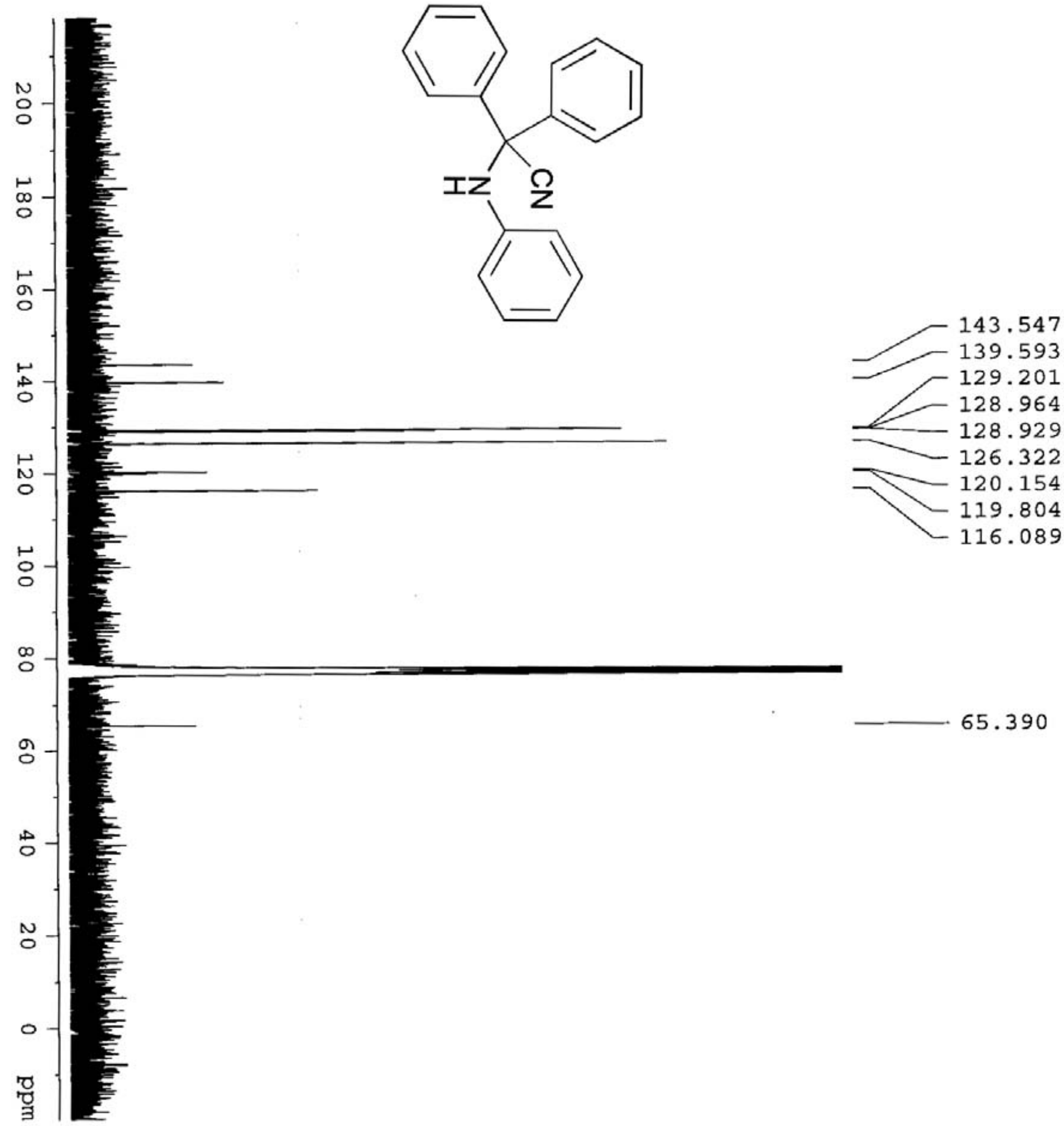

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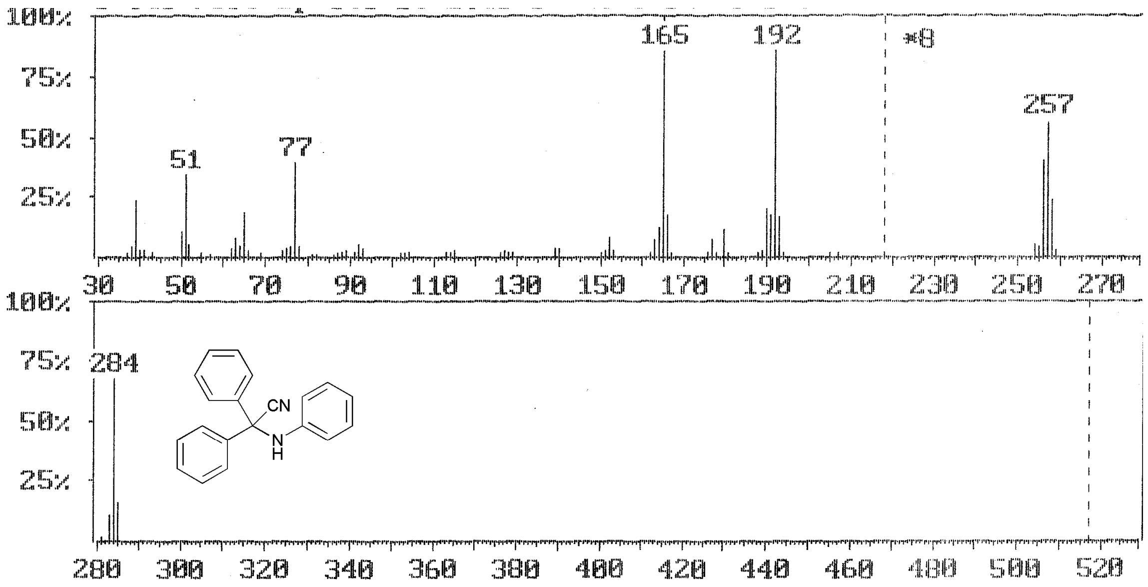

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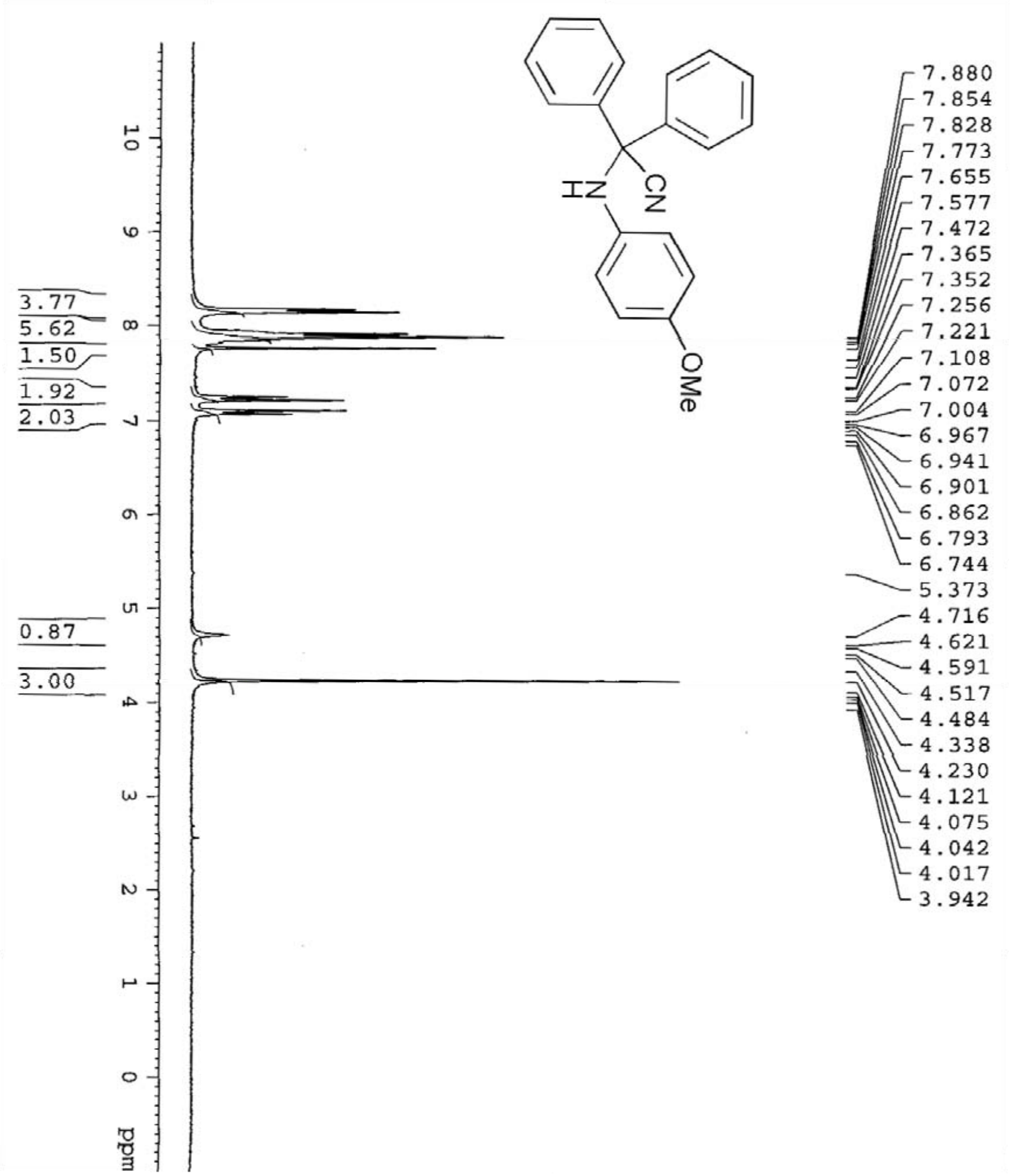

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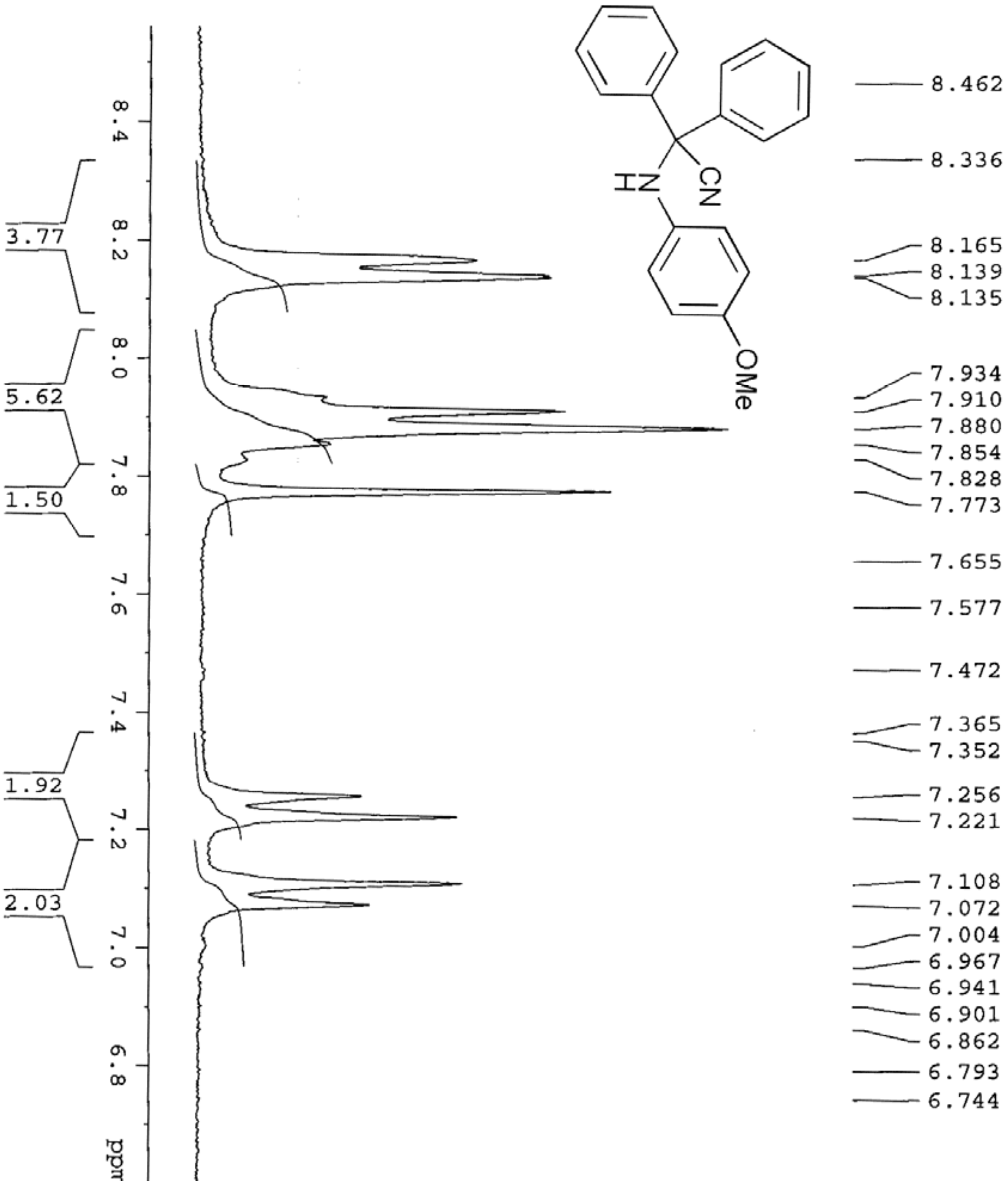

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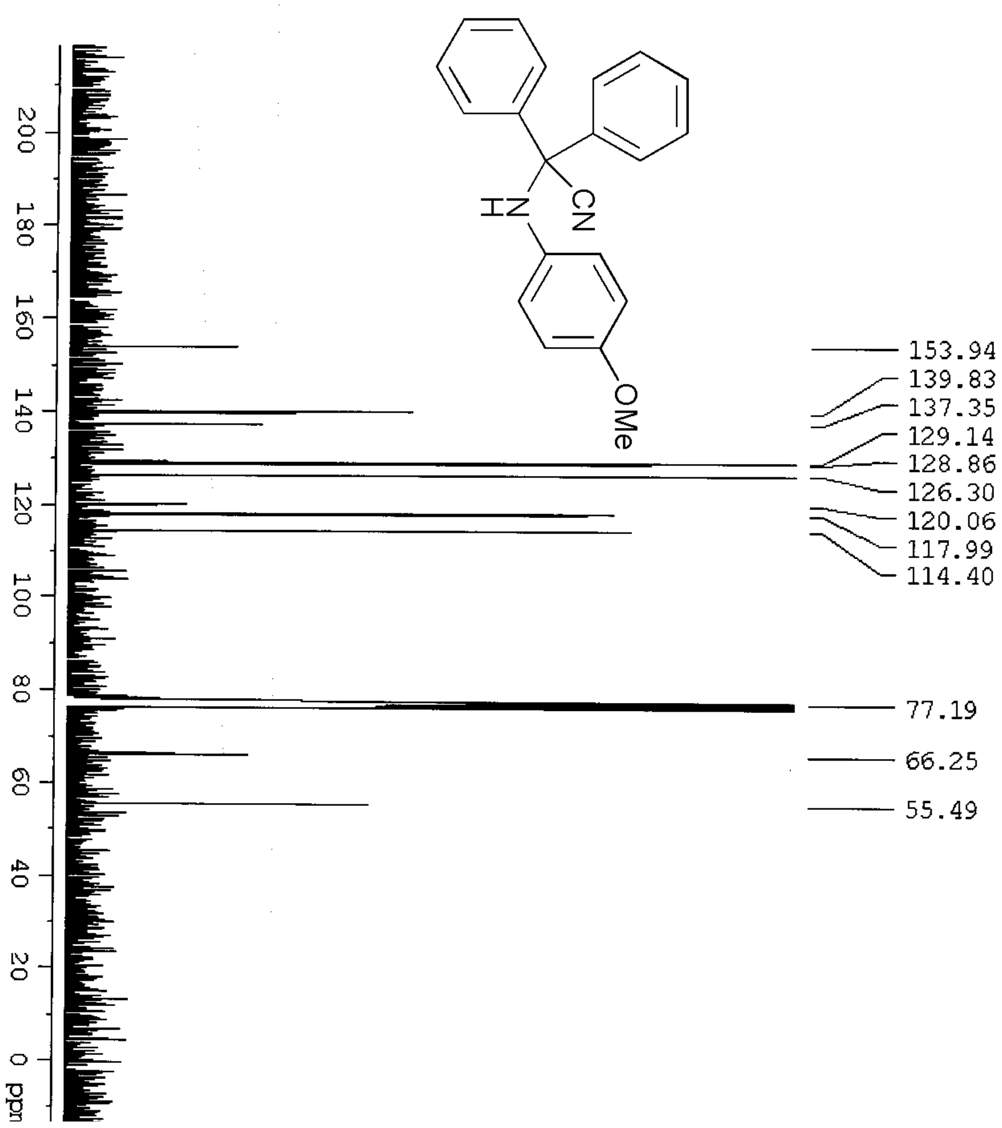

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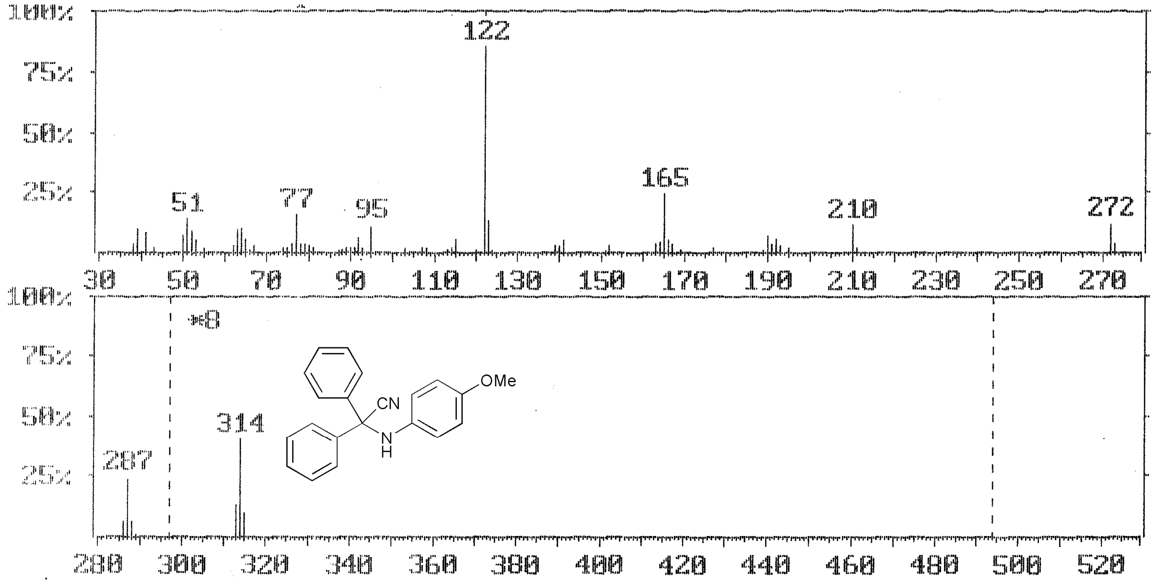

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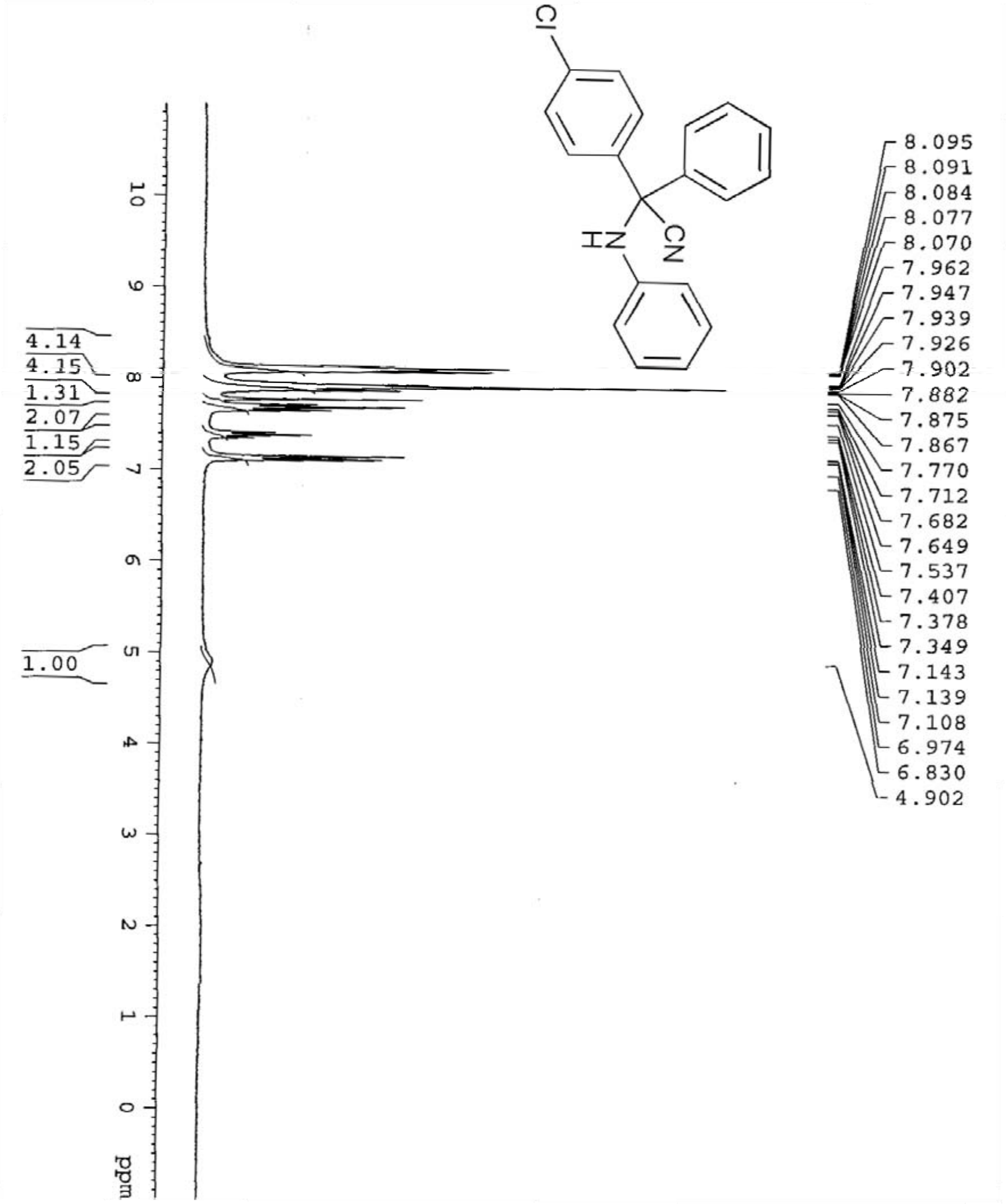

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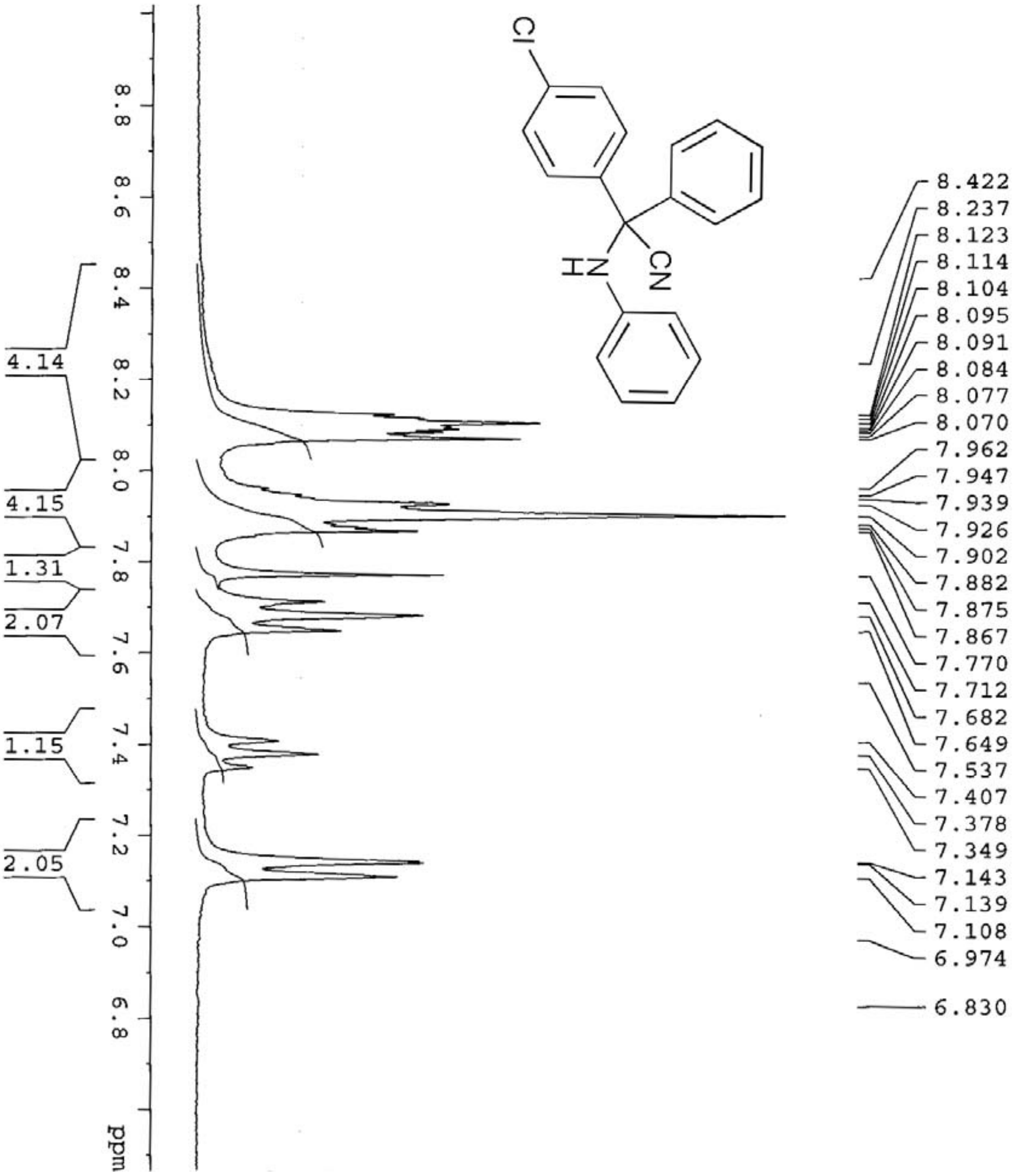

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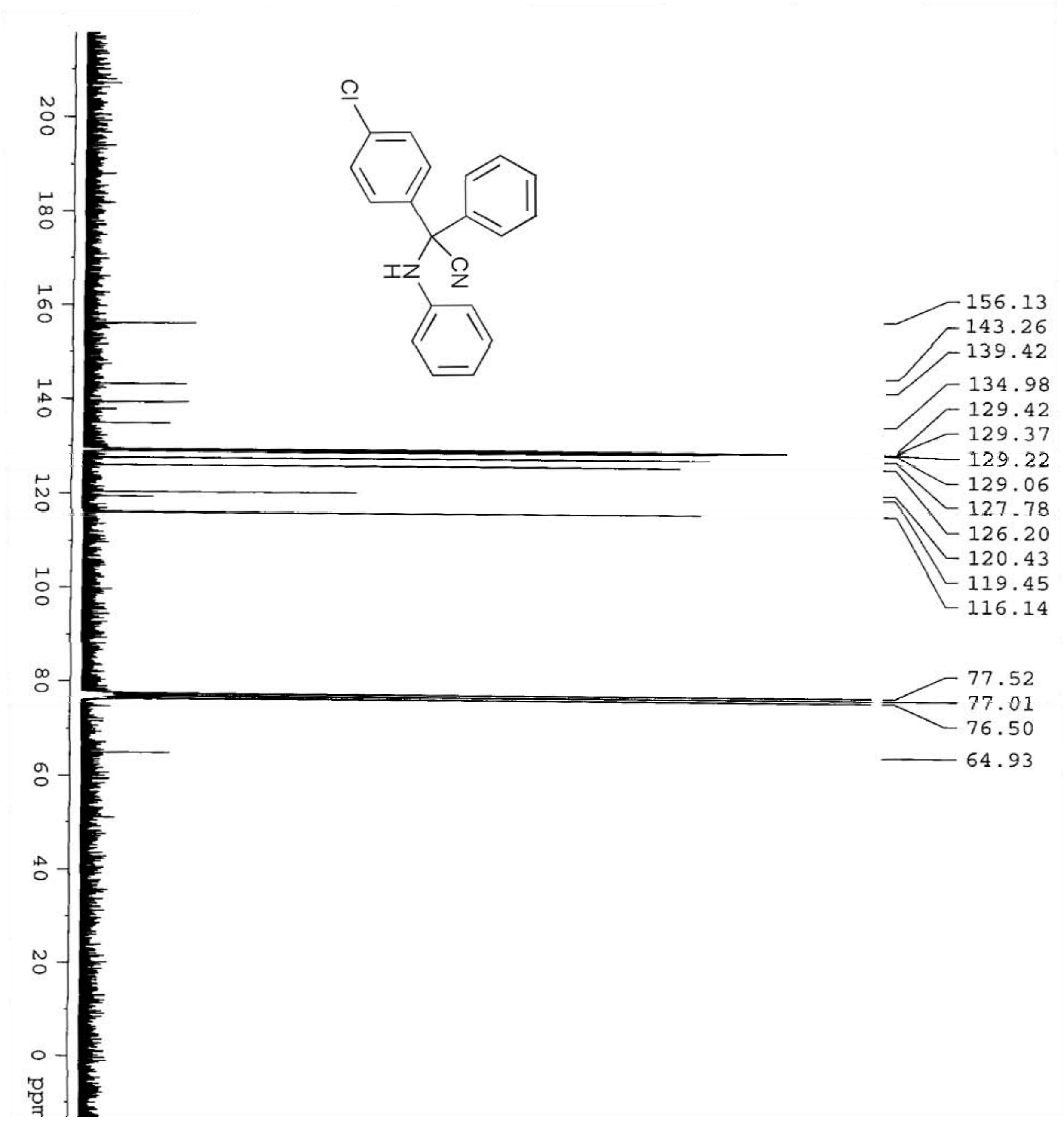

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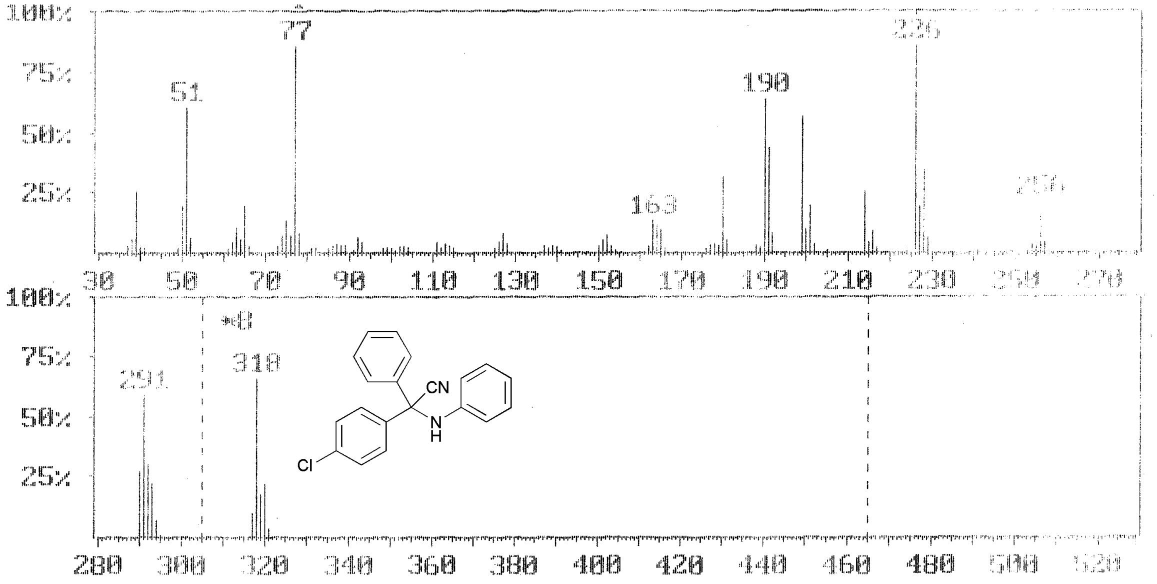

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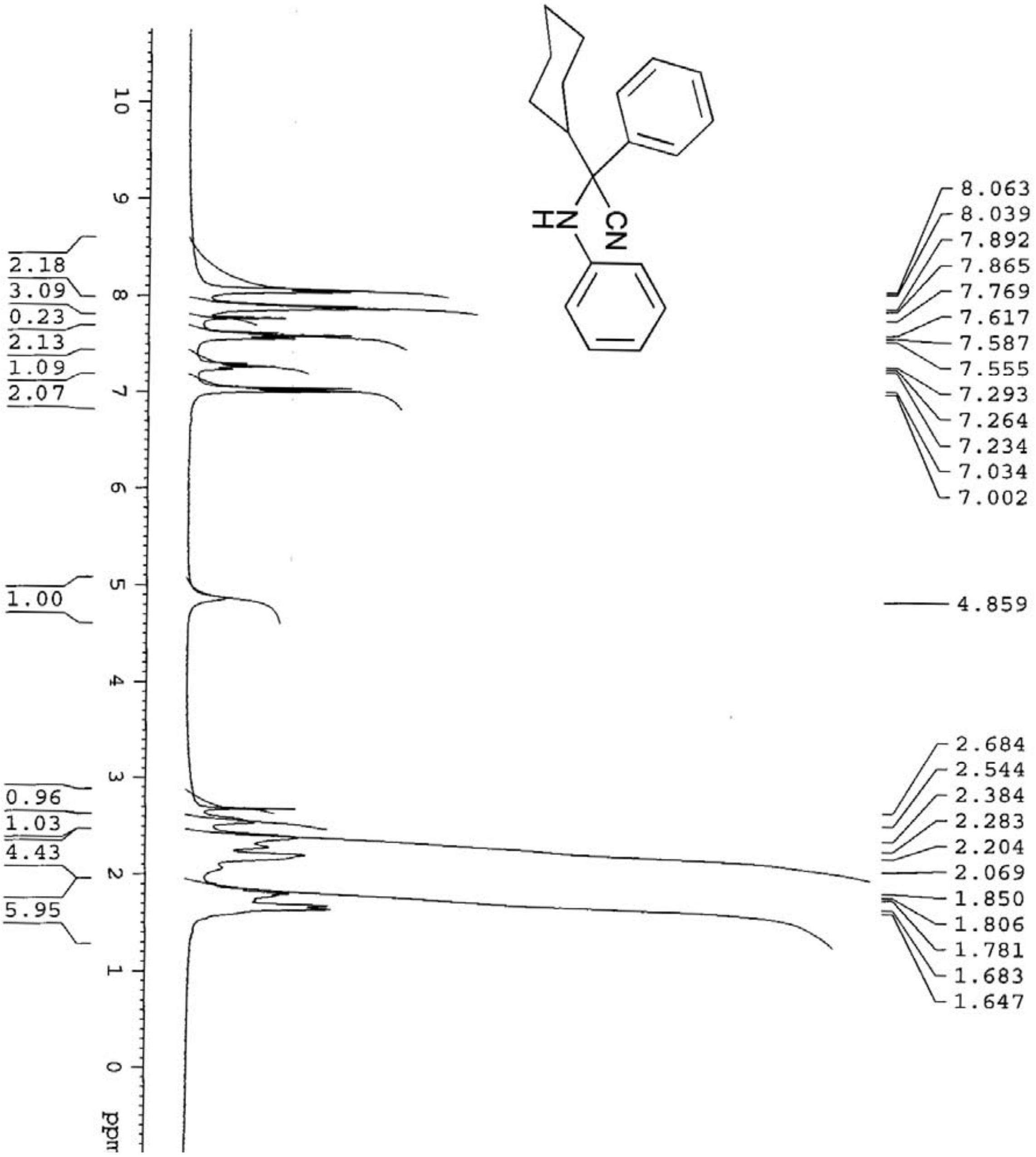

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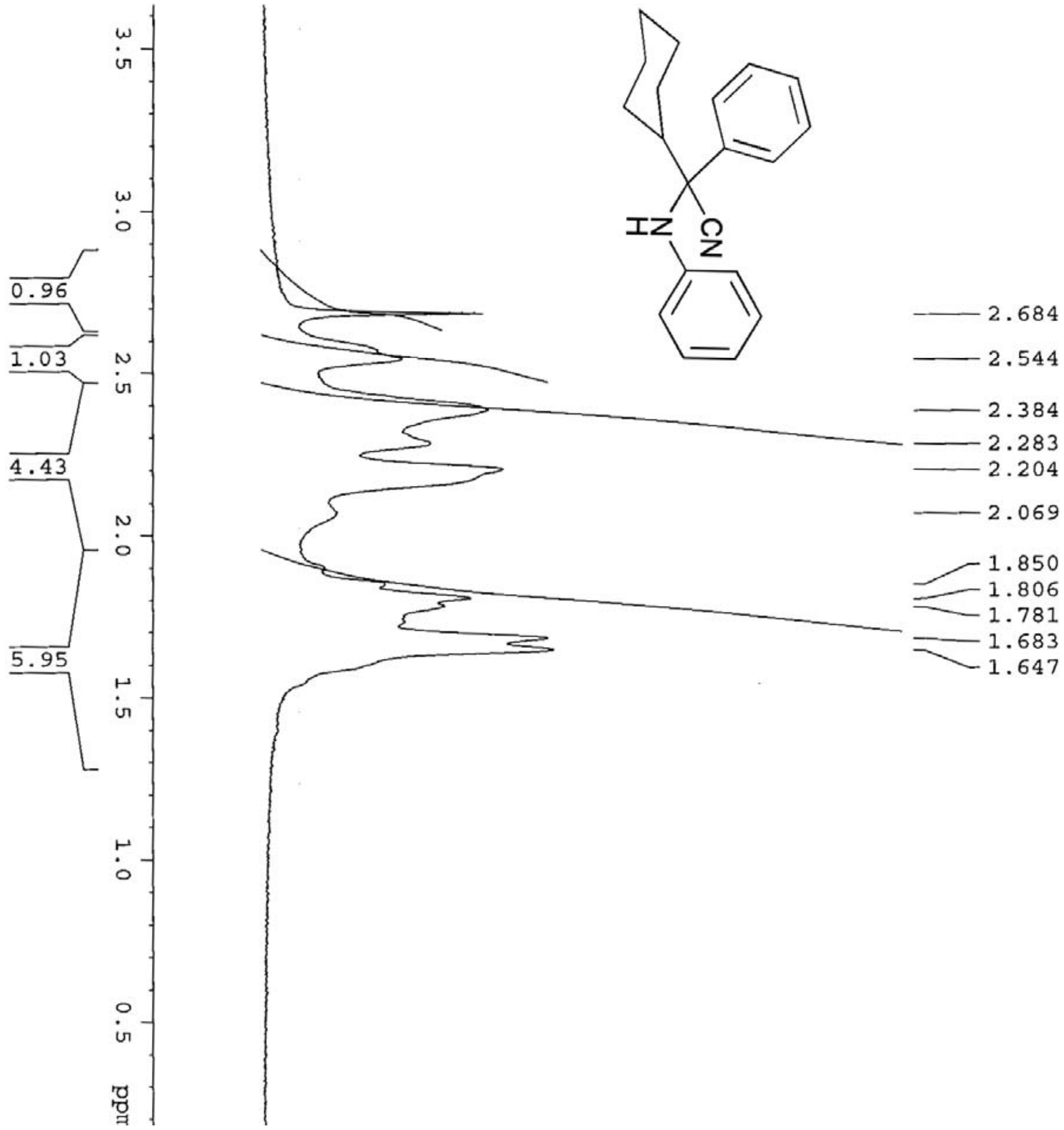
Solvent: $CDCl_3$ – Frequency: 250 MHz



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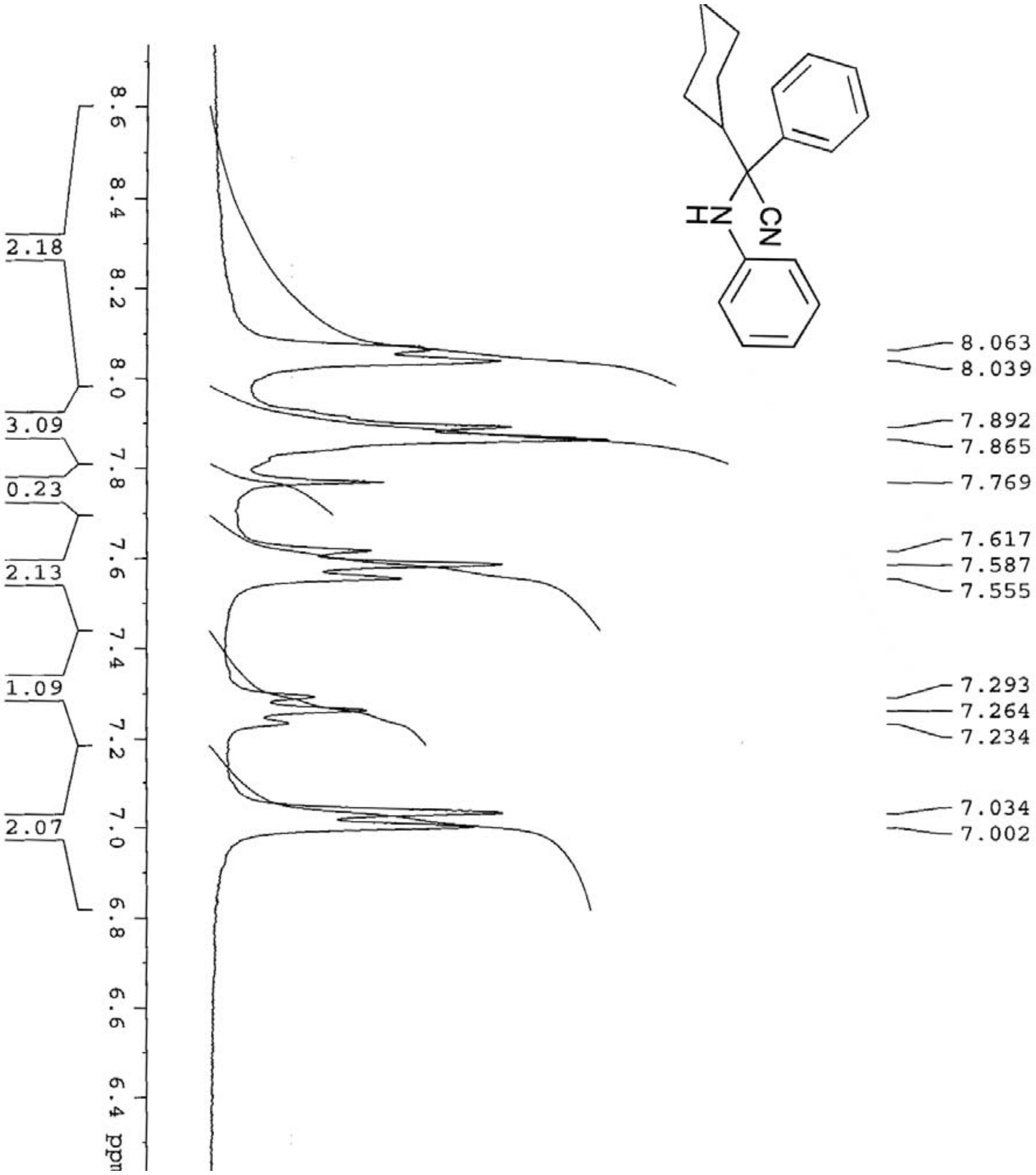

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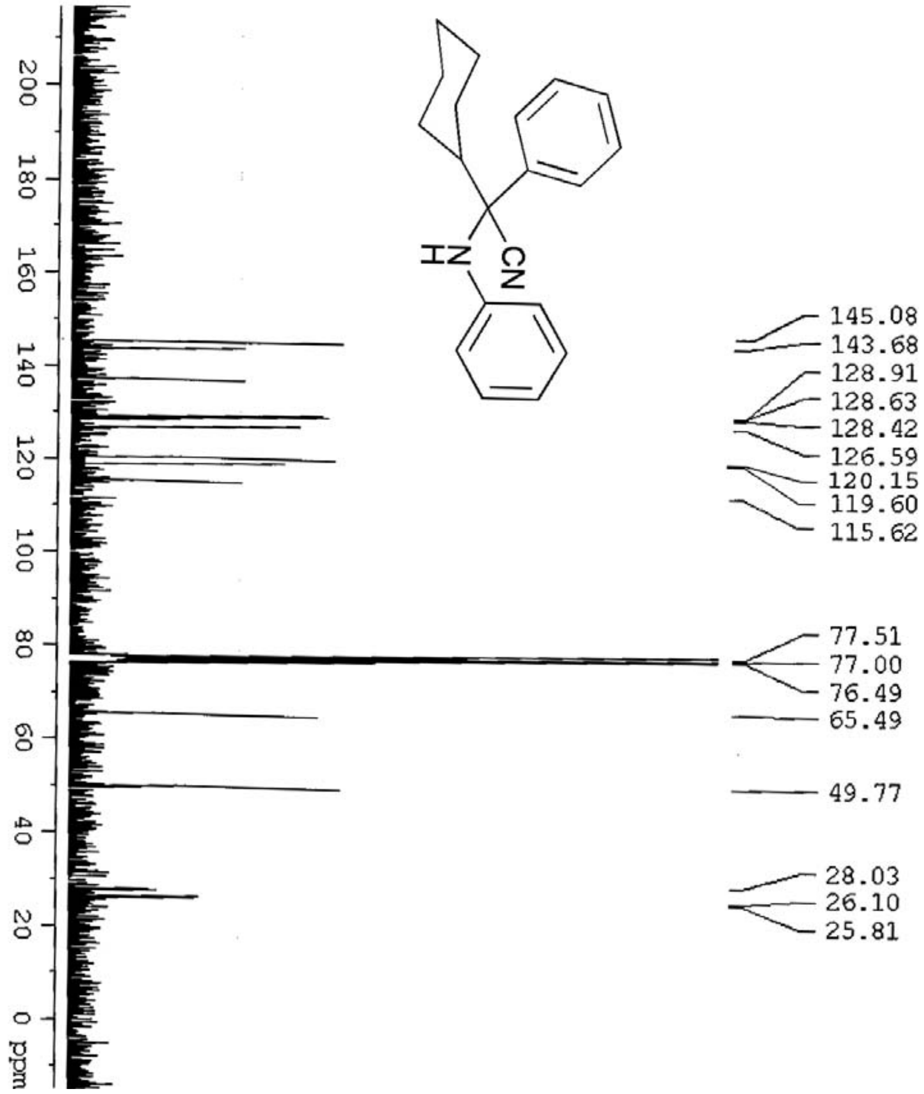

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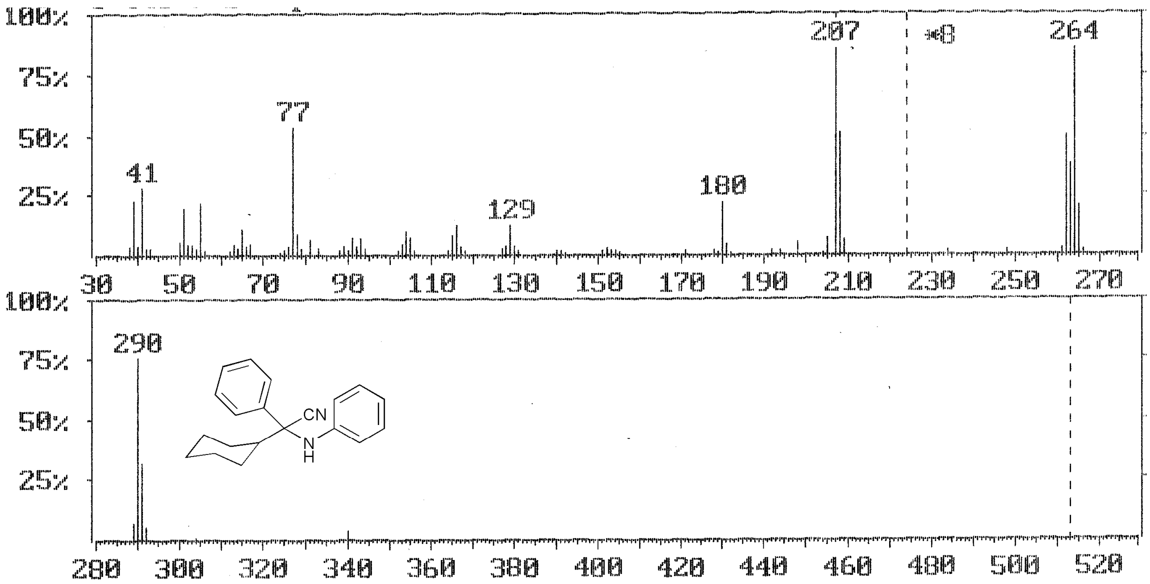

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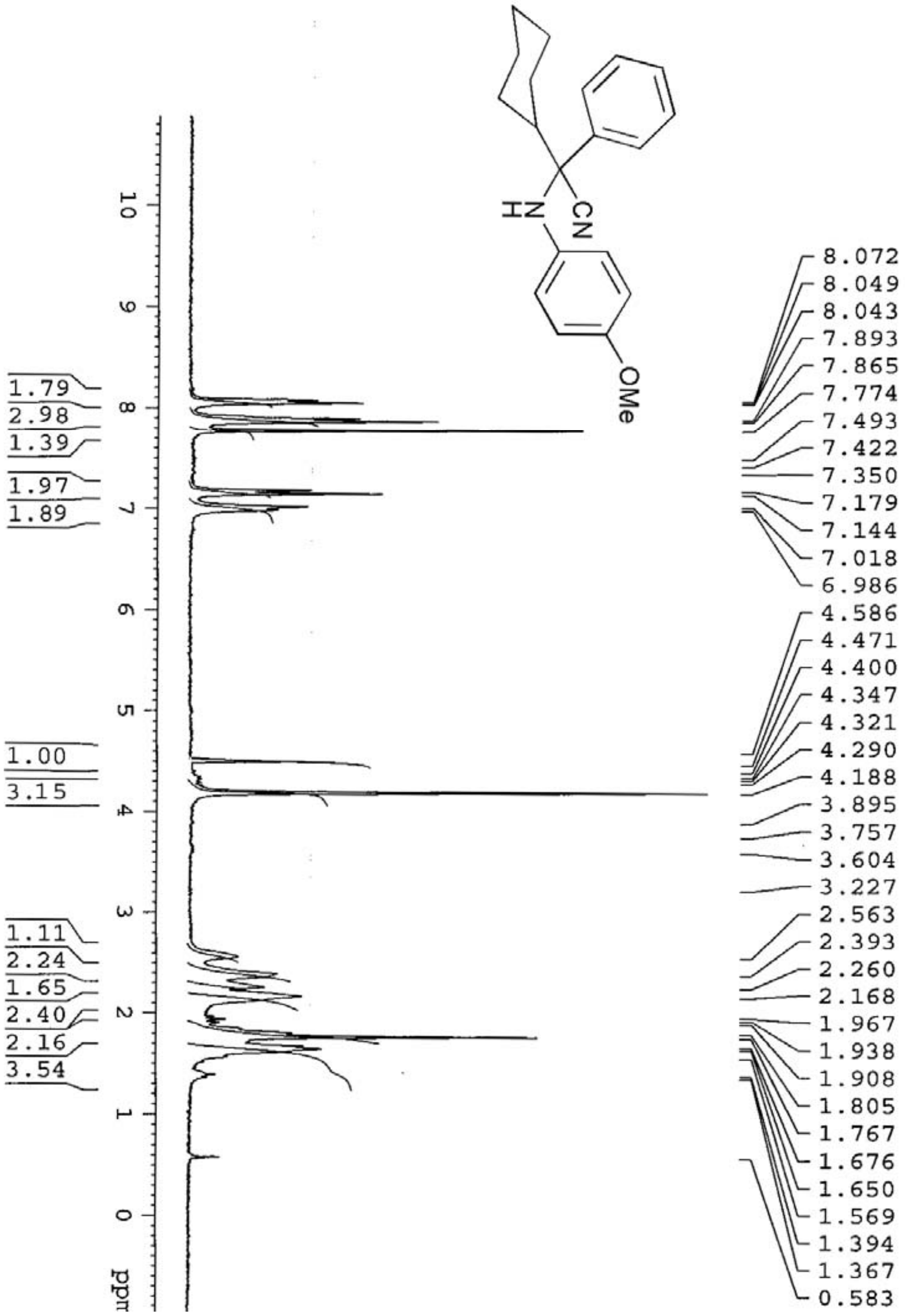

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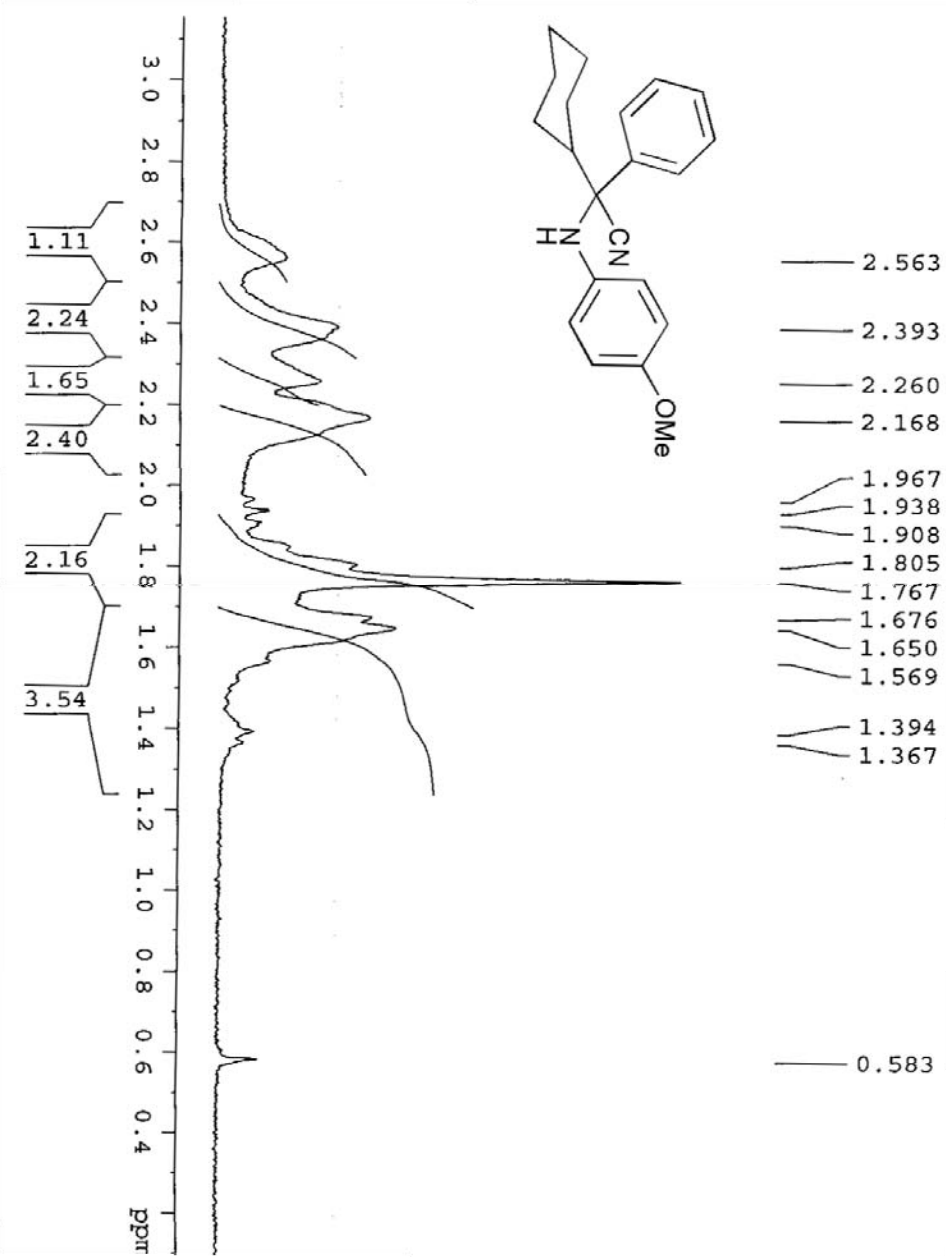

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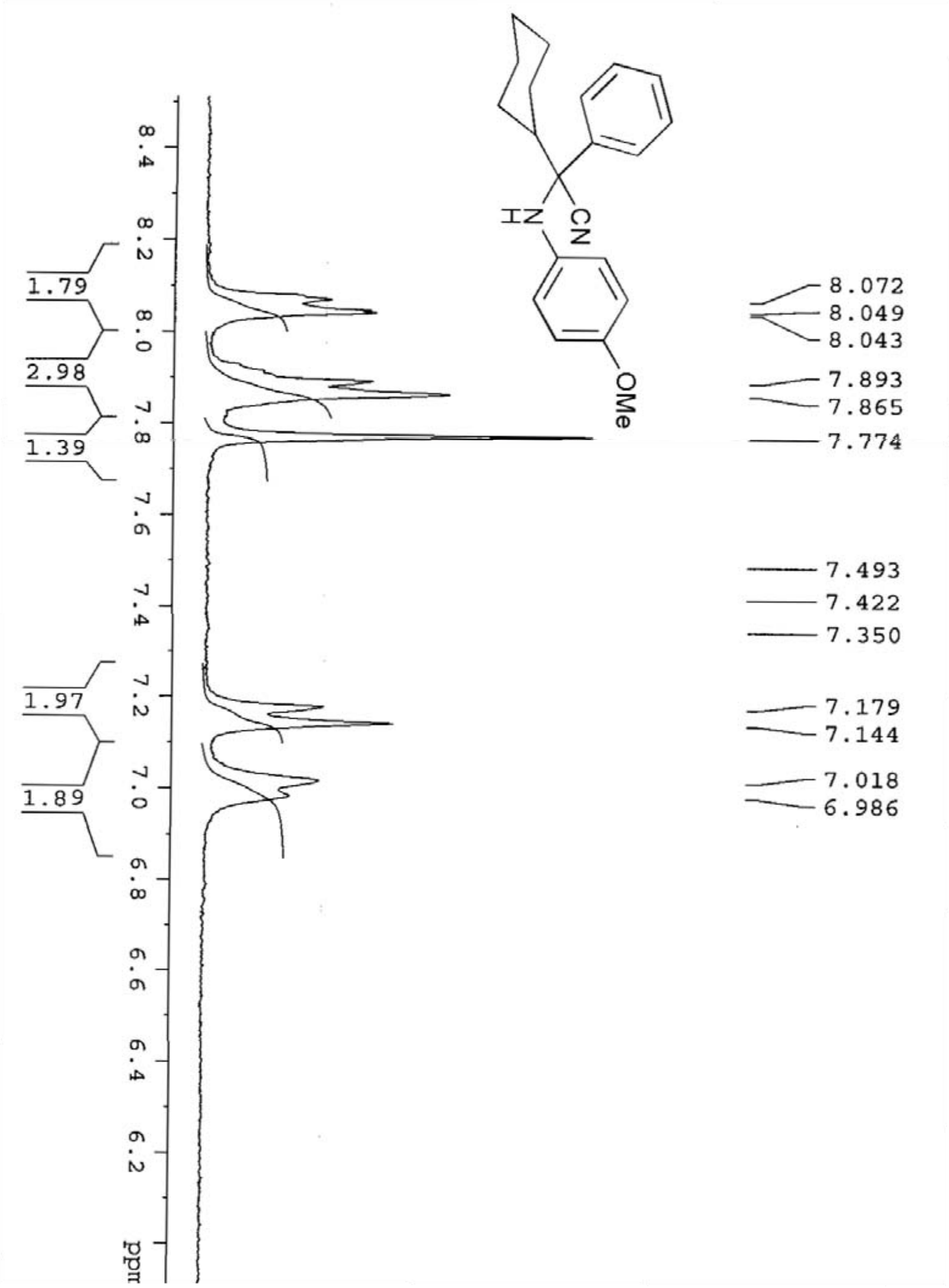
Solvent: $CDCl_3$ – Frequency: 250 MHz



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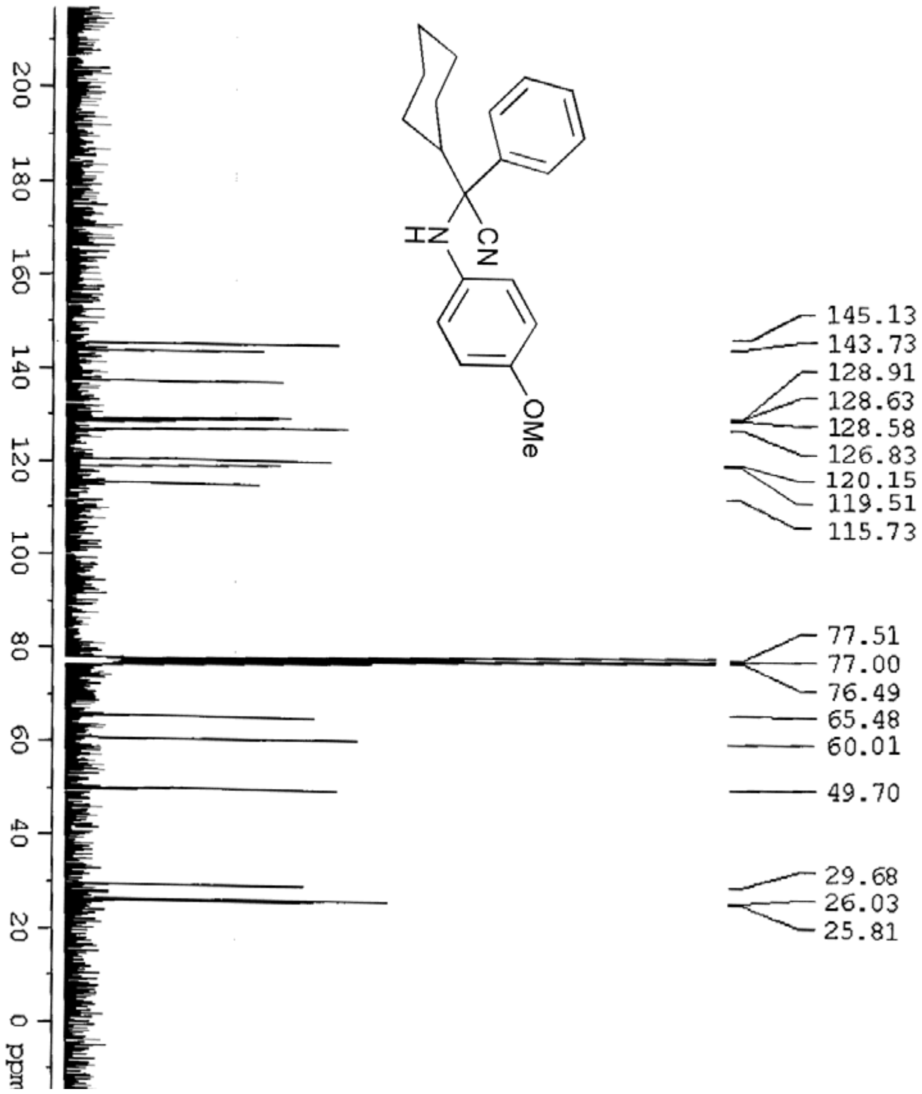

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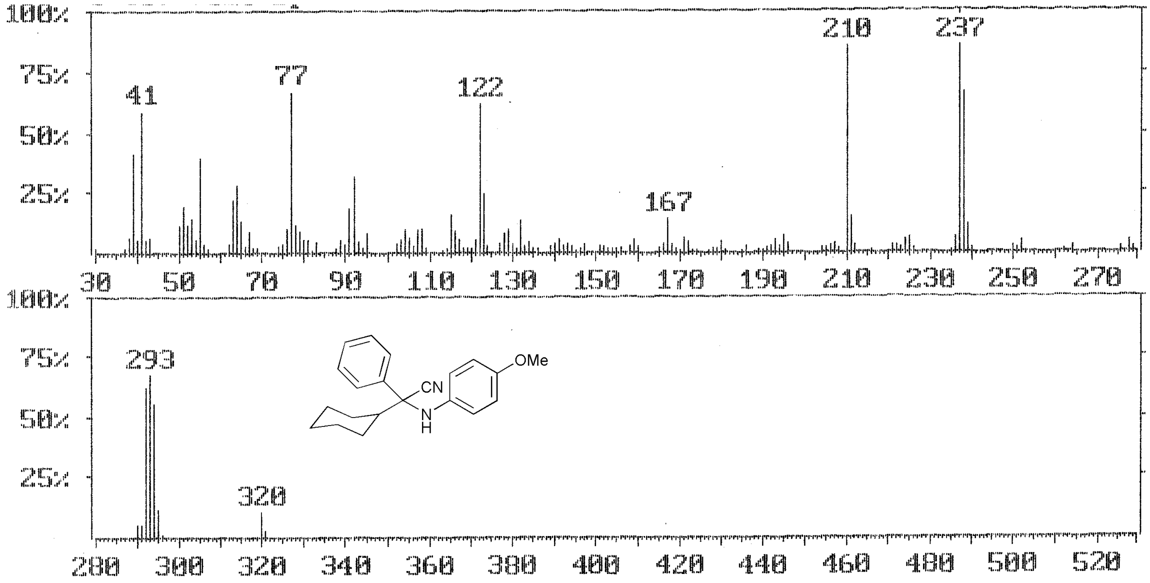

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