Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Data

A magnetic nanoparticle catalyzed eco-friendly synthesis of cyanohydrins in deep eutectic solvent

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Materials and Instrumentation

All starting materials, reagents and solvents are commercially available and were purchased and used without further purification. All products were confirmed by melting point or boiling point, FTIR spectroscopy, 1H NMR, spectroscopy and mass spectrometry. Water and other solvents were distilled before used. All the reactions are monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel with UV light as detecting agents. Melting points and boiling points were recorded in Buchi 535 melting point apparatus and are uncorrected. FT-IR spectra were determined on a BrukerVector-22 infrared spectrometer using KBr disks.1H NMR spectra were recorded at r.t. on a FT-NMR Bruker Ultra ShieldTM (500 MHz) instrument as CDCl3 as a solvent, chemical shifts have been expressed in (ppm) downfield from TMS. Flash column chromatography was performed with silica gel eluting with ethyl acetate-petroleum ether.

DES preparation: Choline chloride-urea deep eutectic solvent was prepared according to the literature.2 Urea (200 mmol) and choline chloride (100 mmol) were mixed, stirred and heated at 60 0C for 50 minutes until a clear liquid was appeared. The obtained deep eutectic solvent was used without any further purification. (Figure 1).

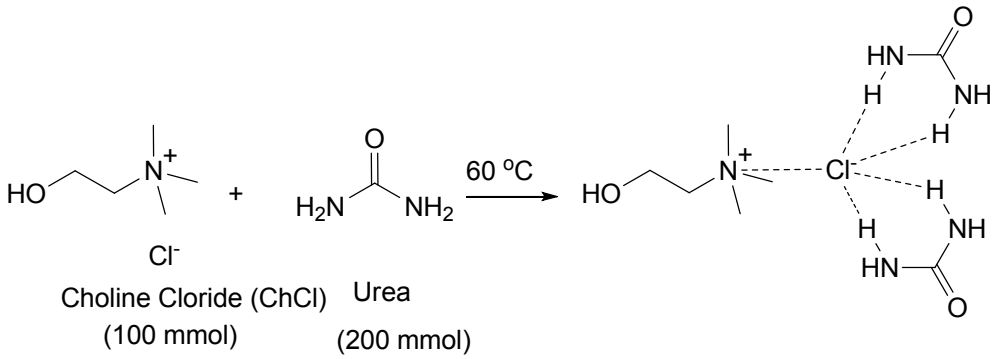


Fig. 1. Deep eutectic solvent preparation from urea and ChCl

Preparation of catalyst (Fe_3O_4)

The magnetic Fe3O4 nanoparticle were synthesized through solvothermal reaction according to the previously reported method. $FeCl_2.7H_2O$ (5 mmol) and $FeCl_3 \cdot 6H_2O$ (10 mmol) were dissolved in deionized water (50 mL) and stirred mechanically at 80 °C for 15 min under a nitrogen atmosphere. This was followed by drop wise addition (about 10 min) of NaOH (10 mmol) to the reaction mixture and was stirred for 2 h. Then the precipitate was collected by a strong permanent magnet and washed with deionized water to pH 7. The collected precipitate was washed twice with ethanol and dried under vacuum at 60 °C overnight to obtain the Fe_3O_4 nanoparticles.

General procedure

A dried test tube, equipped with a magnetic stir bar, was charged with DES (0.5 mL), carbonyl compounds or epoxides (1.0 mmol), TMSCN (1.2 mmol), and Fe_3O_4 (10 mg), and the mixture was heated at 60 °C until the reaction was complete. After this time, ethyl acetate was added, to extract the product from DES phase. After evaporation of ethyl acetate, the resulting solid or viscous liquid was treated with acidic water and was purified by flash column chromatography or recrystallization with ethanol or diethyl ether to give pure products.

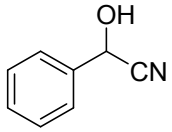


Table1, Entry1

2-hydroxy-2-phenylacetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.52 (s, 1H), 7.41 (m, 3H), 7.62 (d, ^3J = 7.39 Hz, 2H).

IR (KBr) (ν_{max}, cm^{-1}): 3012 (OH), 2253 (CN).

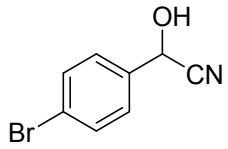


Table1, Entry4

2-(4-bromophenyl)-2-hydroxyacetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.49 (s, 1H), 7.37 (d, ^3J = 8.42 Hz, 2H), 7.55 (d, ^3J = 8.35, 2H).

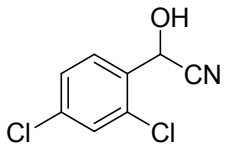


Table1, Entry5

2-(2,4-dichlorophenyl)-2-hydroxyacetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.75 (s, 1H), 7.33-7.35 (m, 1H), 7.40-7.41 (m, 1H), 7.67 (d, ^3J = 8.44 Hz, 1H).

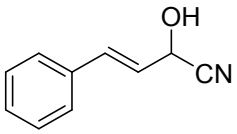


Table1, Entry7

(E)-2-hydroxy-4-phenylbut-3-enenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.11 (d, ^3J = 5.92 Hz, 1H), 6.17-6.21 (m, 1H), 6.81 (d, ^3J = 15.74 Hz, 1H), 7.31-7.42 (m, 5H).

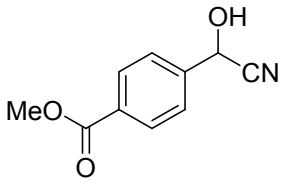


Table1, Entry8

methyl 4-(cyano(hydroxy)methyl)benzoate

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.79 (s, 3H, Me), 5.46 (s, 1H), 6.9-6.93 (m, 2H), 7.38-7.43 (m, 2H).

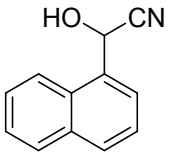


Table1, Entry9

2-hydroxy-2-(naphthalen-1-yl)acetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.46 (br.s, 1H, OH), 5.91 (s, 1H), 7.33-7.36 (m, 1H), 7.47-7.5 (m, 2H), 7.65-7.69 (m, 1H), 7.78-7.82 (m, 2H), 7.93-7.95 (m, 1H).

IR (KBr) (ν_{max}, cm^{-1}): 3401 (OH), 3060, 2253 (CN), 1688, 1396.

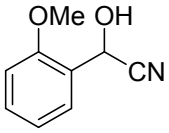


Table1, Entry11

2-hydroxy-2-(2-methoxyphenyl)acetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.82 (s, 3H, Me), 5.87 (s, 1H), 6.88-6.9 (m, 1H), 7.02 (m, 1H), 7.35 (m, 1H), 7.62-7.63 (m, 1H).

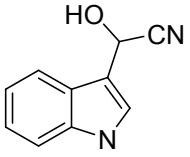


Table1, Entry14

2-(1λ^2-indol-3-yl)-2-hydroxyacetonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.84-5.88 (m, 1H), 7.23-7.37 (m, 4H), 7.78-7.81 (m, 1H), 8.63 (br.s, 1H, NH).

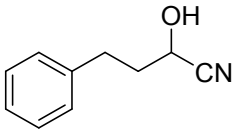


Table1, Entry15

2-hydroxy-4-phenylbutanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.15-2.17 (m, 2H), 2.84 (t, ^3J = 7.73 Hz, 2H), 4.39 (m, 1H), 7.22-7.25 (m, 3H), 7.32-7.35 (m, 2H).

IR (KBr) (ν_{max}, cm^{-1}): 3031 (OH), 2253 (CN), 1250, 1105, 725.

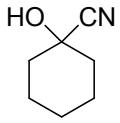


Table1, Entry16

1-hydroxycyclohexane-1-carbonitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.54-1.62 (m, 6H), 1.74 (m, 2H), 2.03 (m, 2H).

IR (KBr) (ν_{max}, cm^{-1}): 2942, 2863, 2232 (CN), 1452, 1254, 1160, 876.

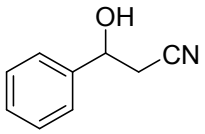


Table2, Entry1

3-hydroxy-2-phenylpropanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.69 (d, 2H), 3.71 (br.s, 1H), 5.03 (t, 1H), 7.35–7.46 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 142.6, 128.3, 128.6, 125.1, 118.3, 70.4, 23.7.

IR (KBr) (ν_{max}, cm^{-1}): 3072–3431 (br, OH), 2923, 2243 (CN), 1511, 1223, 1058.

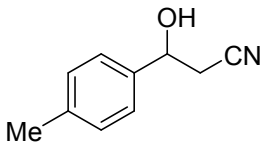


Table2, Entry2

3-hydroxy-2-(p-tolyl)propanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.29 (s, 3H), 2.58 (br.s, 1H, OH), 3.22 (m, 2H), 4.91-4.95(m, 1H), 7.21 (d, J=8.1 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 21.7, 28.1, 71.3, 116.4, 126.2, 130.6, 138.7, 139.3.

IR (KBr) (ν_{max}, cm^{-1}): 3023 (OH), 2251 (CN).

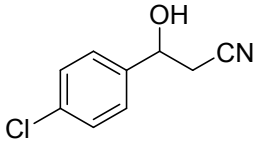


Table2, Entry3

2-(4-chlorophenyl)-3-hydroxypropanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.67 (m, 2H), 3.29 (br.s, 1H, OH), 4.91-5.03 (m, 1H), 7.07-7.21 (m, 2H), 7.31-7.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 27.8, 68.6, 115.2, 116.9, 126.7, 137.1, 161.8.

IR (KBr) (ν_{max}, cm^{-1}): 3151 (OH), 2239 (CN).

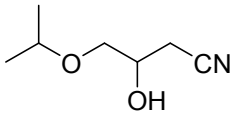


Table2, Entry4

3-hydroxy-4-isopropoxybutanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.18 (d, J = 6.8 Hz, 6H), 2.75 (d, J = 6.2 Hz, 2H), 3.3-3.8 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 22.8, 47.2, 69.5, 70.1, 72.4, 96.7.

IR (KBr) (ν_{max}, cm^{-1}): 3062 (OH), 2242 (CN)

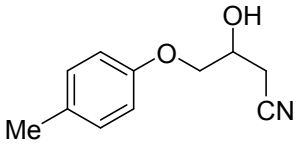


Table2, Entry5

3-hydroxy-4-(4-methylphenoxy)butanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.31 (s, 3H), 2.78-2.86 (m, 2H), 3.71-3.85 (m, 2H), 4.13 (m, 1H), 4.41 (br.s, 1H), 6.87 (m, 2H), 7.24 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 21.2, 23.1, 65.8, 71.2, 114.9, 117.8, 131.2, 132.4, 156.5.

IR (KBr) (ν_{max}, cm^{-1}): 3041–3427 (br, OH), 2923, 2248 (CN).

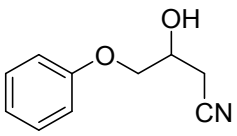


Table2, Entry6

3-hydroxy-4-phenoxybutanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.69-2.81 (m, 2H), 2.92 (m, 1H), 4.12-4.17 (m, 2H), 4.39 (br.s, 1H), 7.02-7.13 (m, 3H), 7.31-7.39 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 26.8, 28.7, 29.6, 31.2, 60.8, 116.1, 117.4, 119.2, 159.1.

IR (KBr) (ν_{max}, cm^{-1}): 3046–3391 (br, OH), 2915, 2264 (CN).

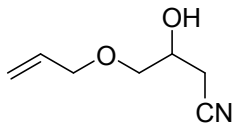


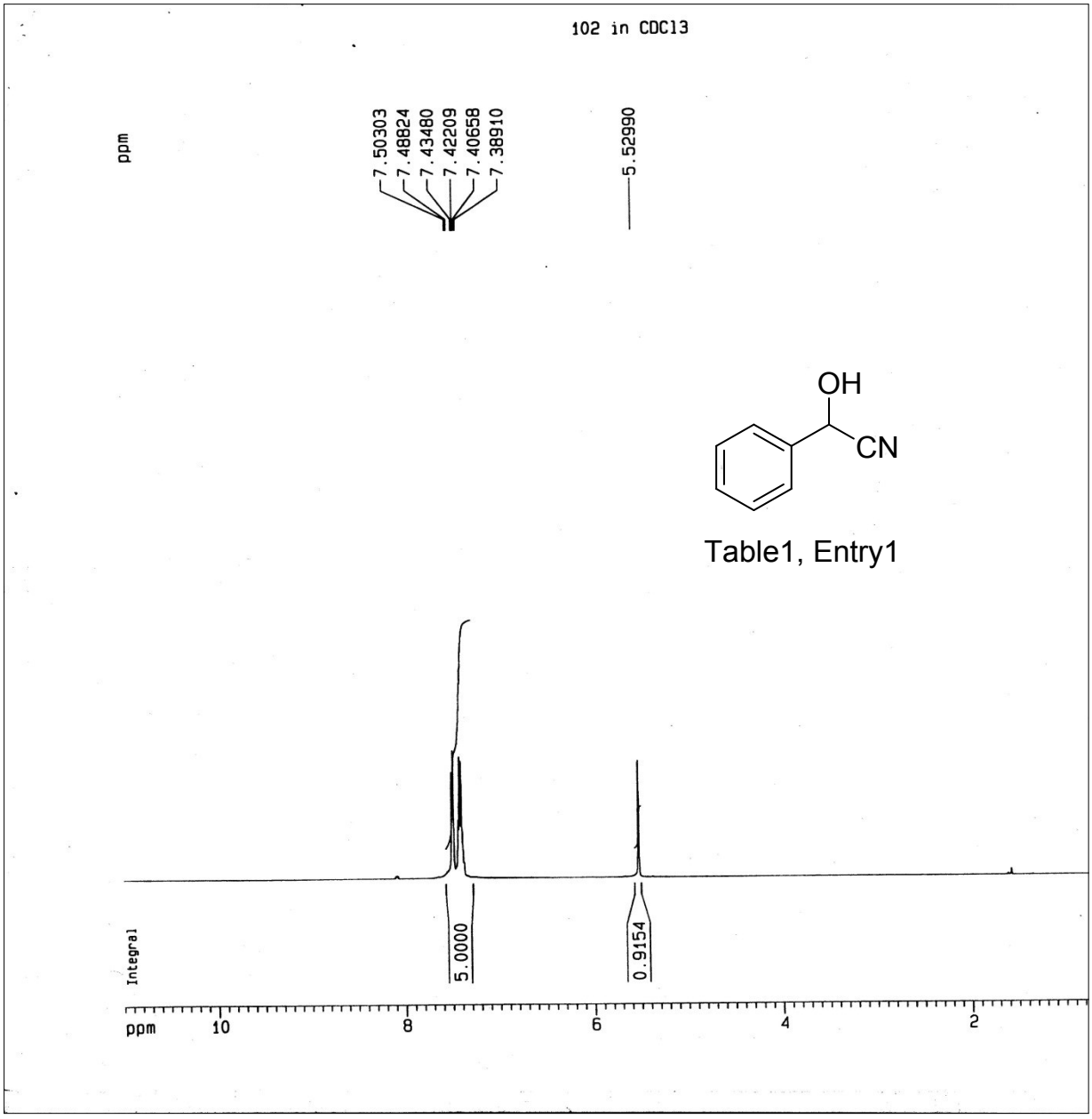
Table2, Entry7

4-(allyloxy)-3-hydroxybutanenitrile

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.72 (d, J = 6.2 Hz, 2H), 3.33-3.84 (m, 6H), 5.22-5.25 (m, 2H), 6.12-6.14 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 23.1, 65.8, 71.7, 72.2, 116.4, 117.8, 135.2.

IR (KBr) (ν_{max}, cm^{-1}): 3112 (OH), 2971, 2232 (CN).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4
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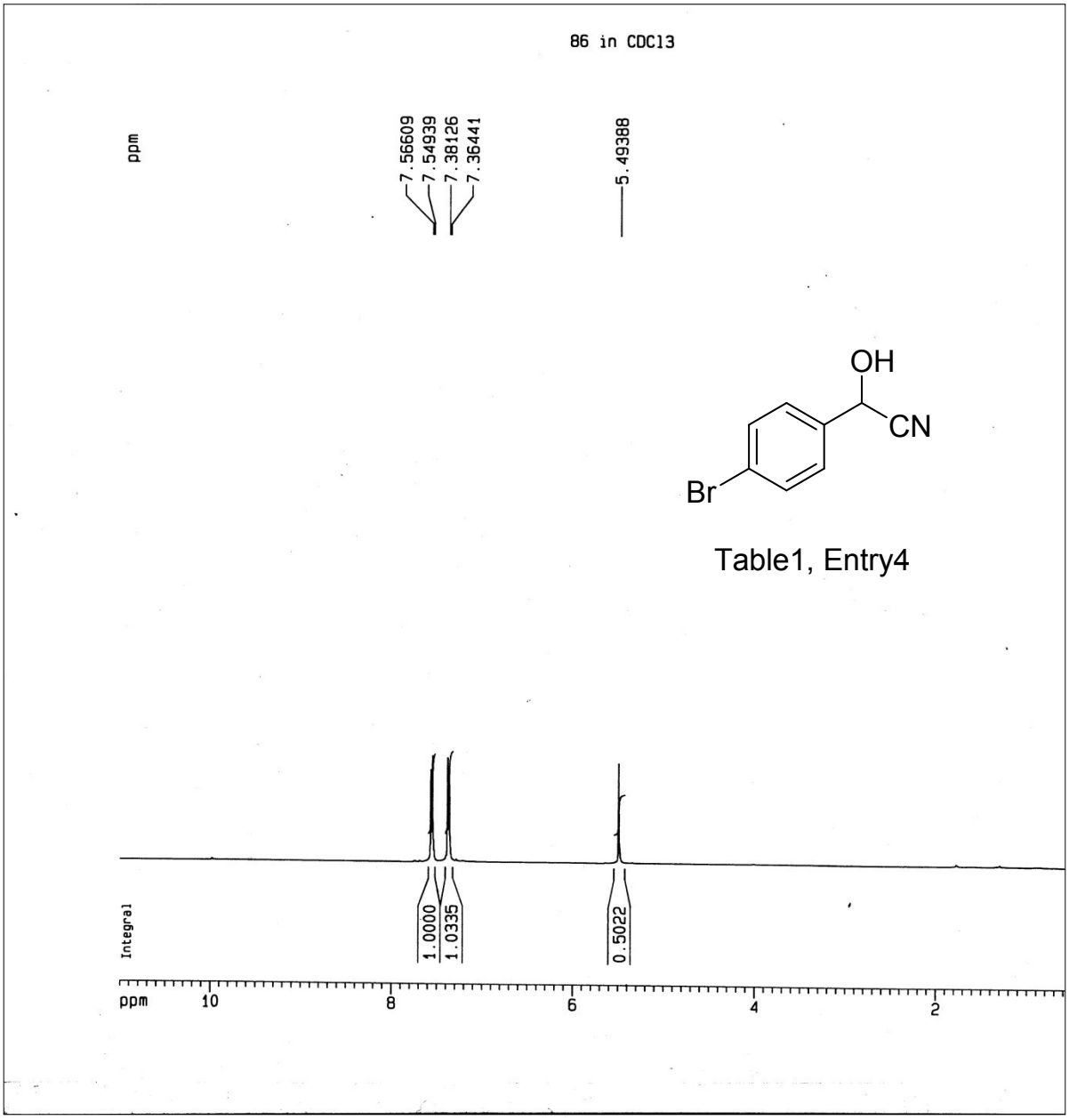

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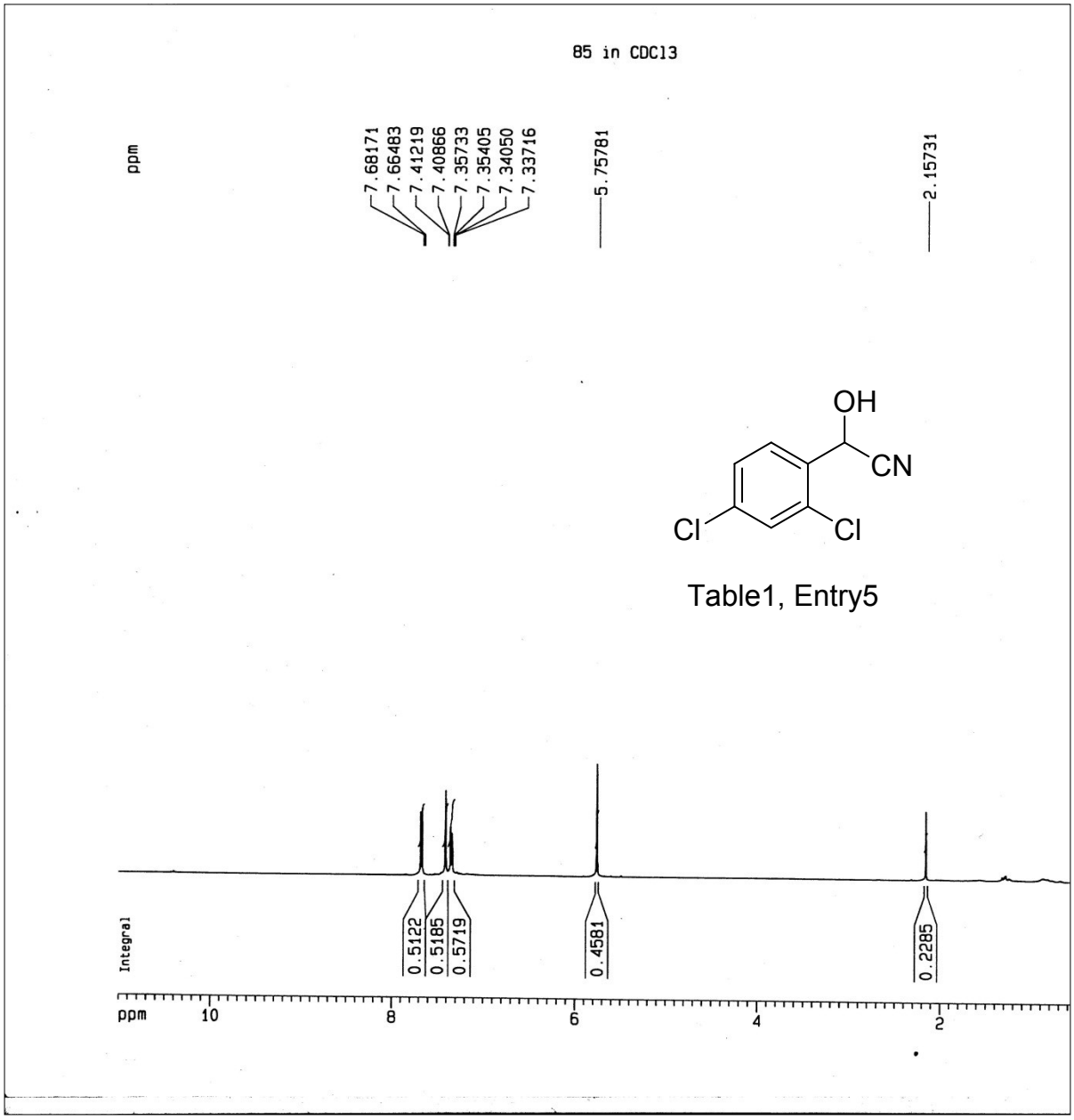

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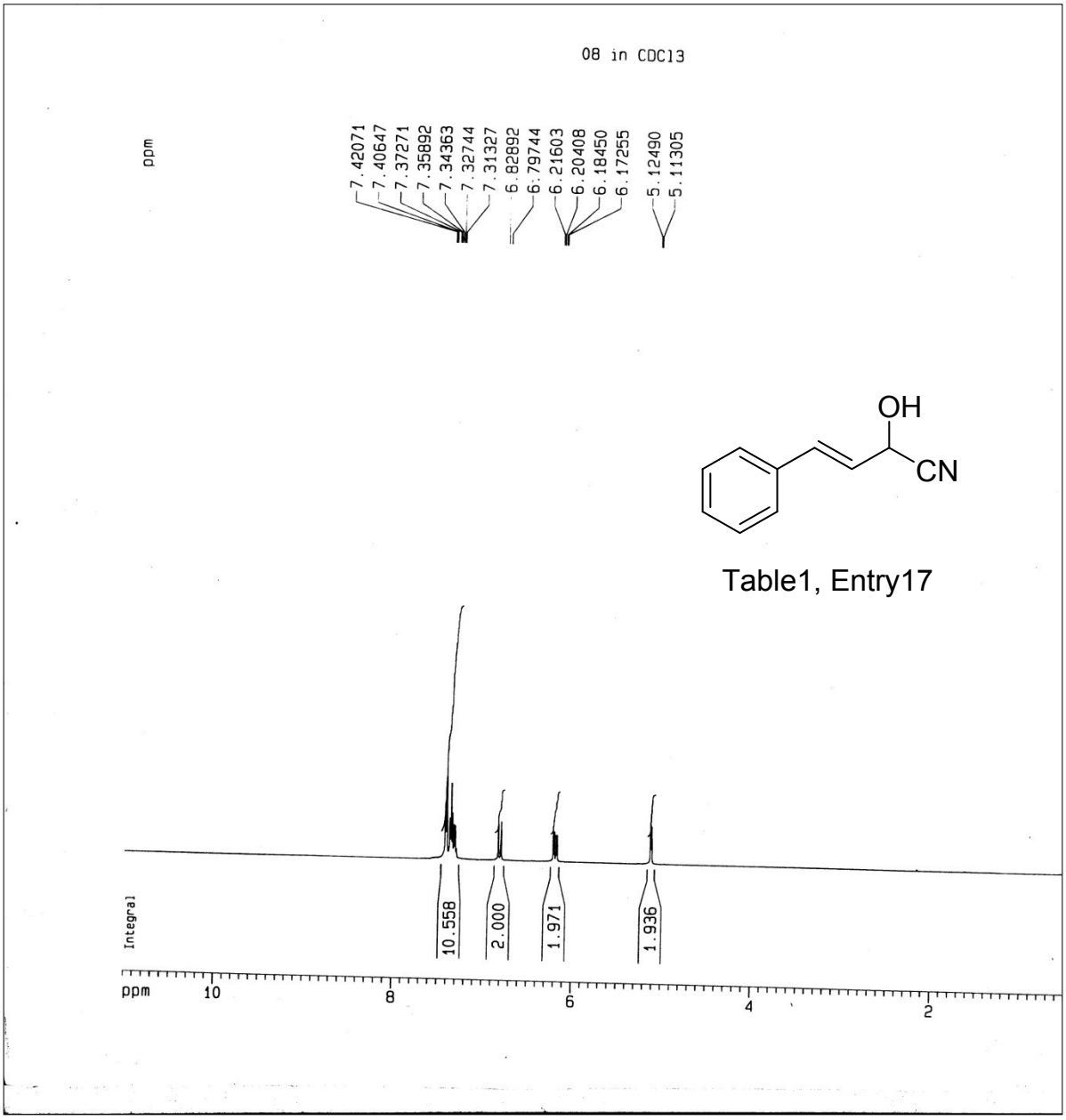
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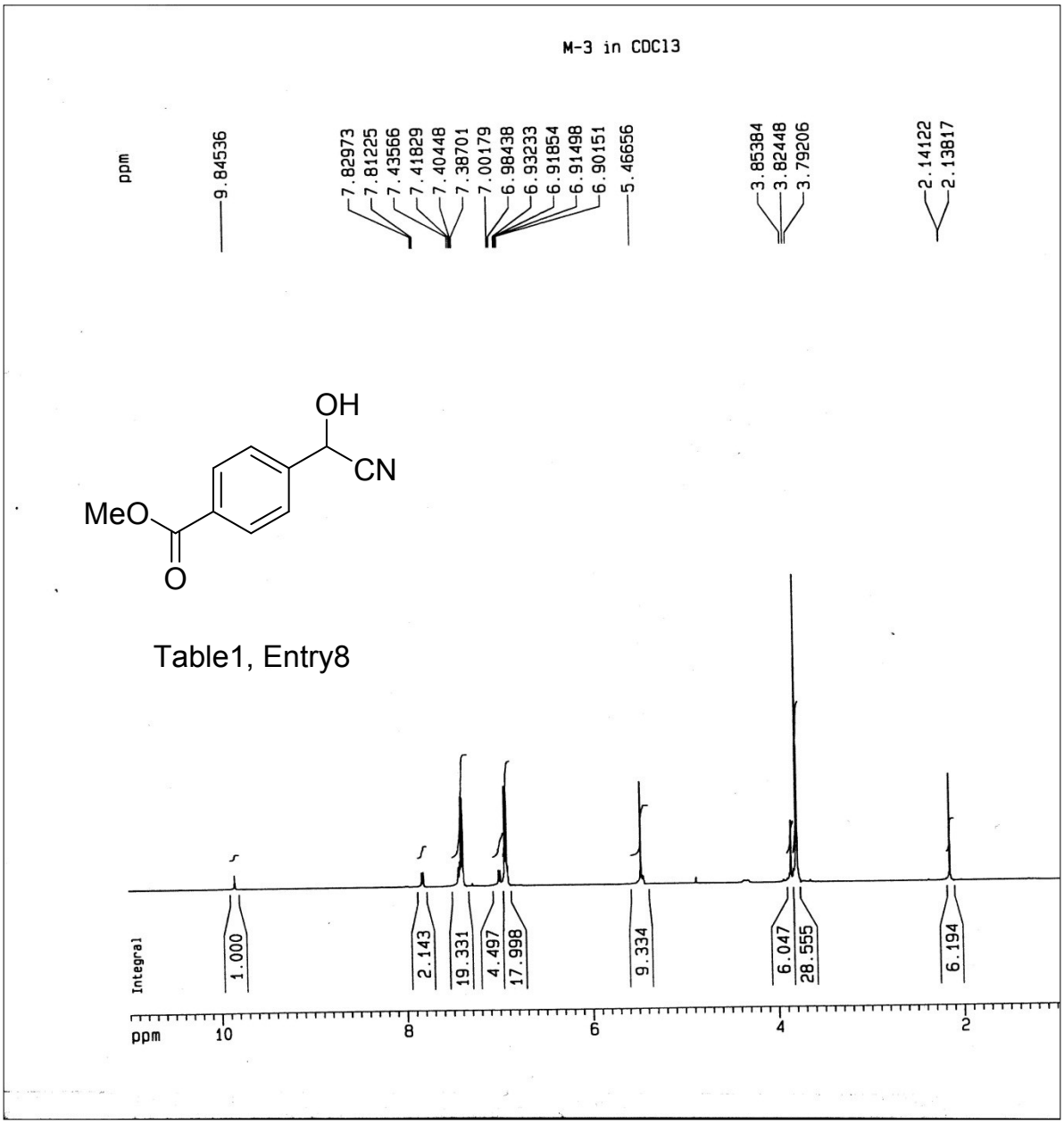
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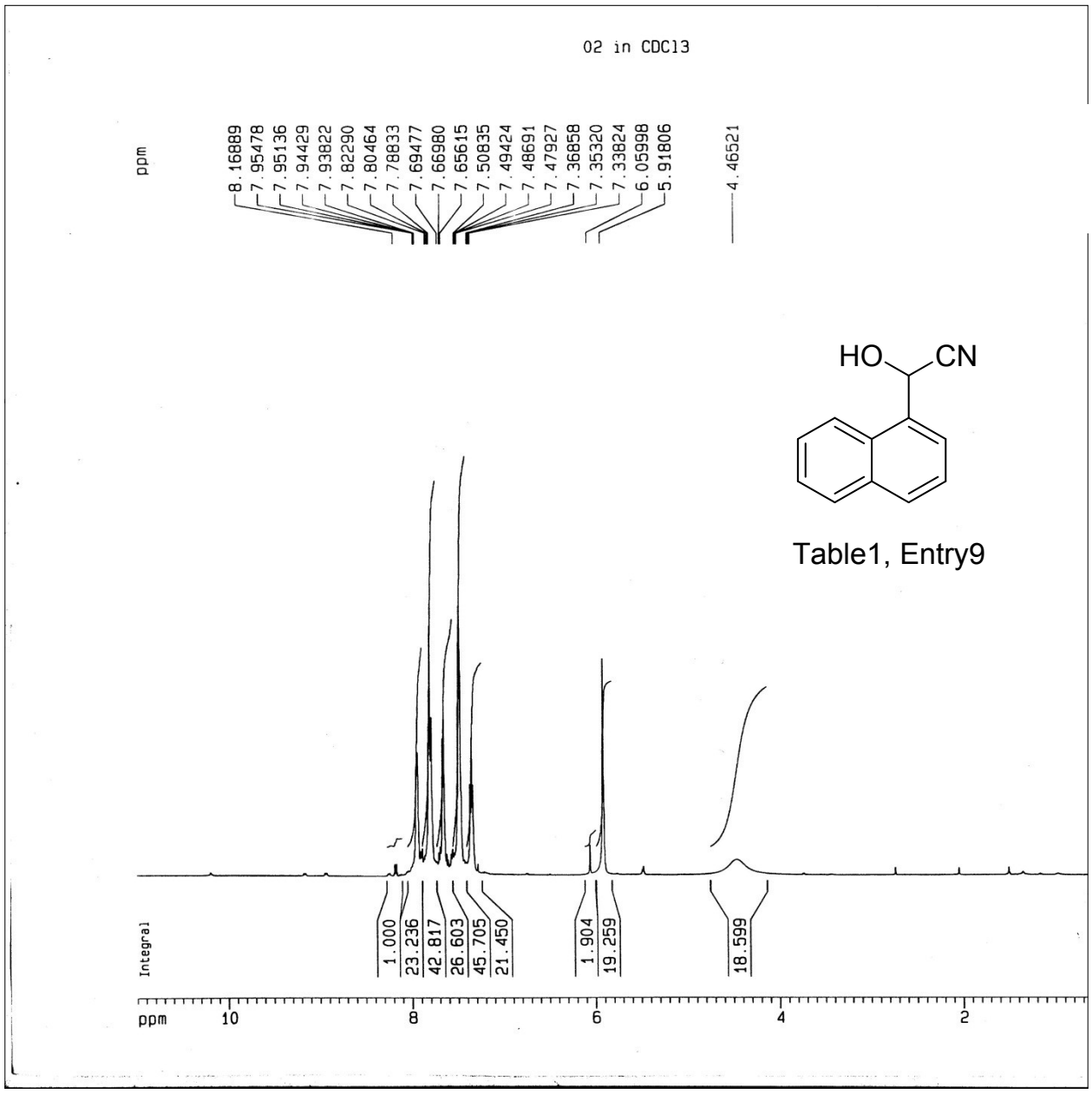

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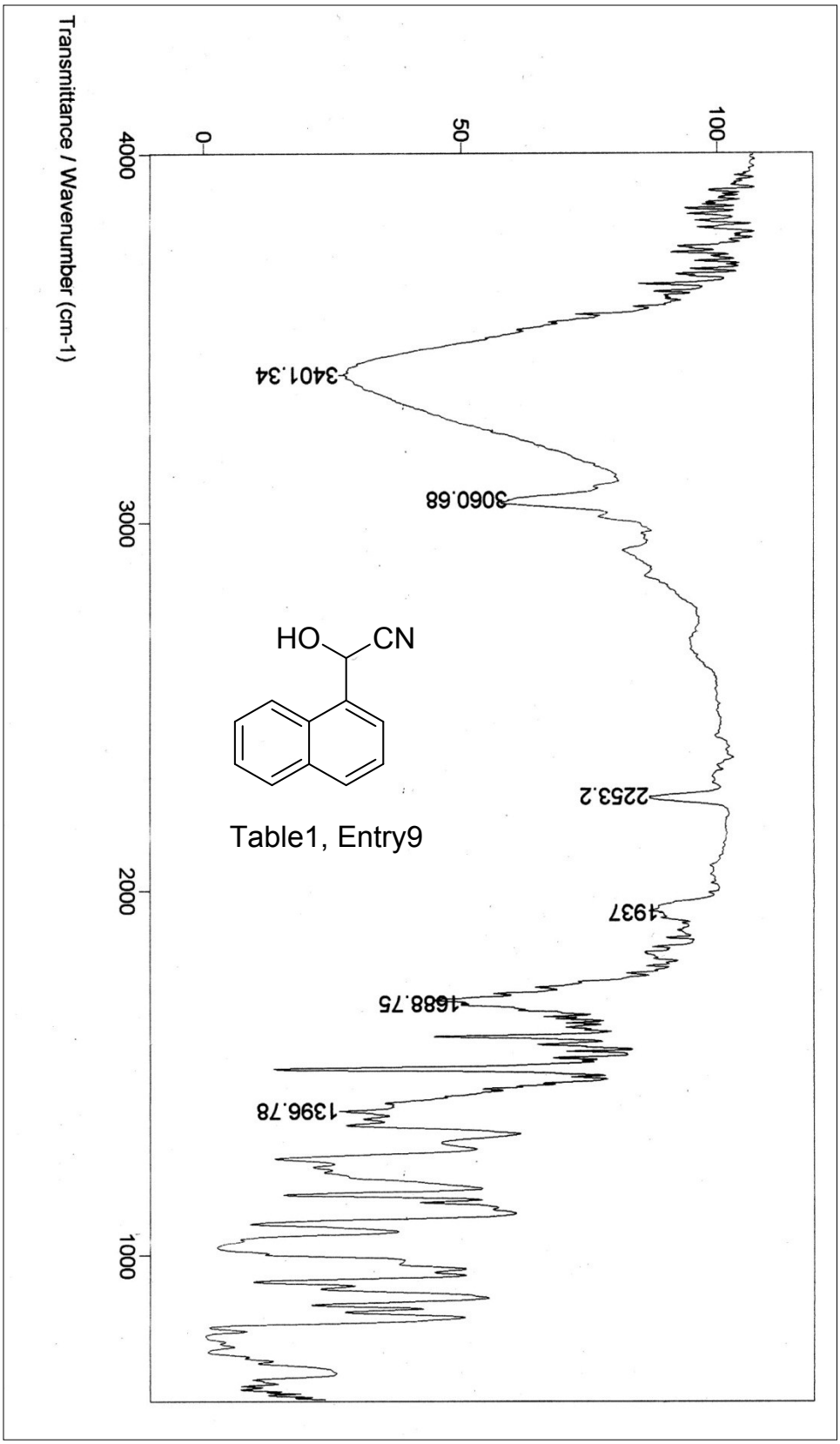

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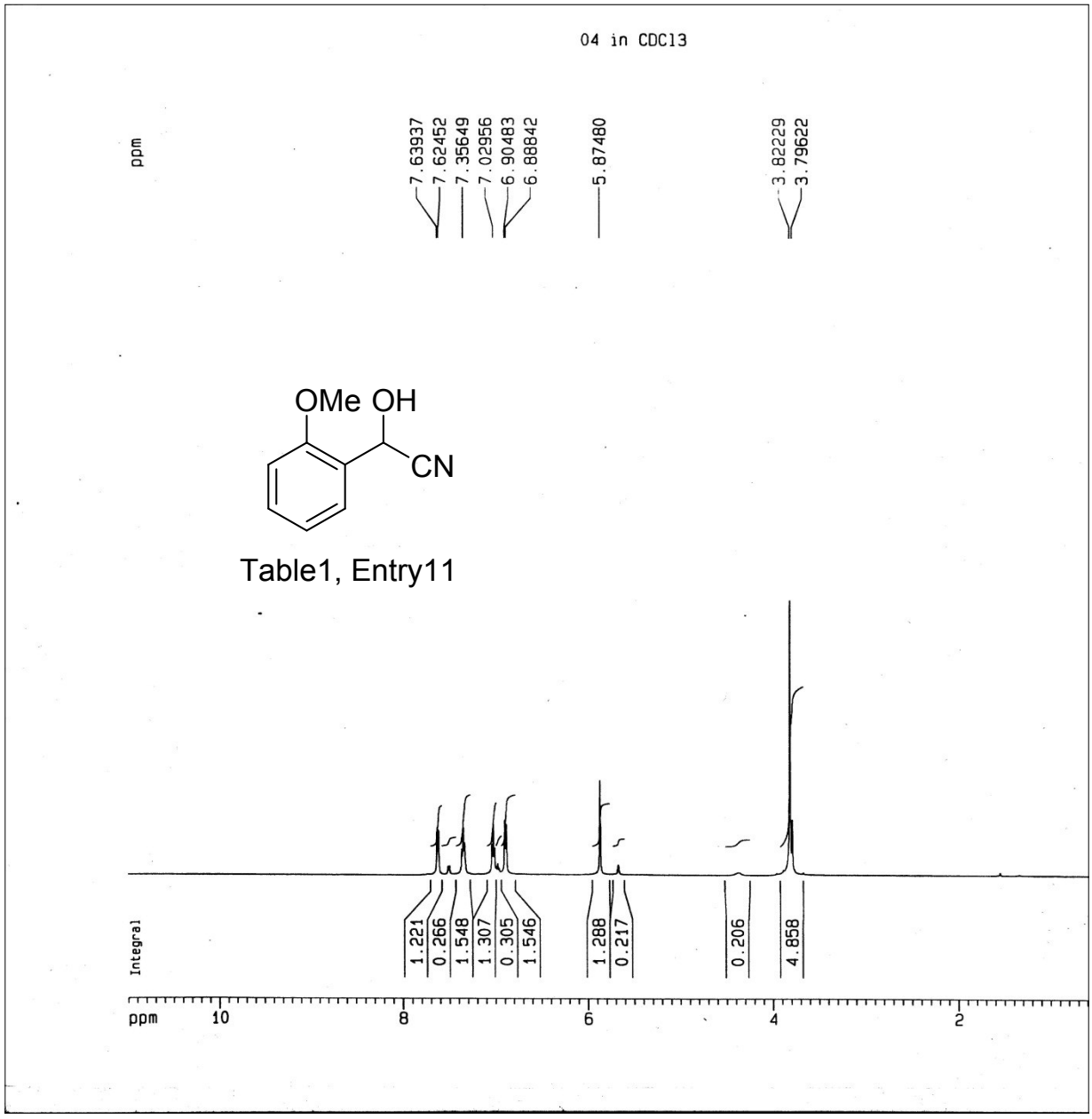
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CN
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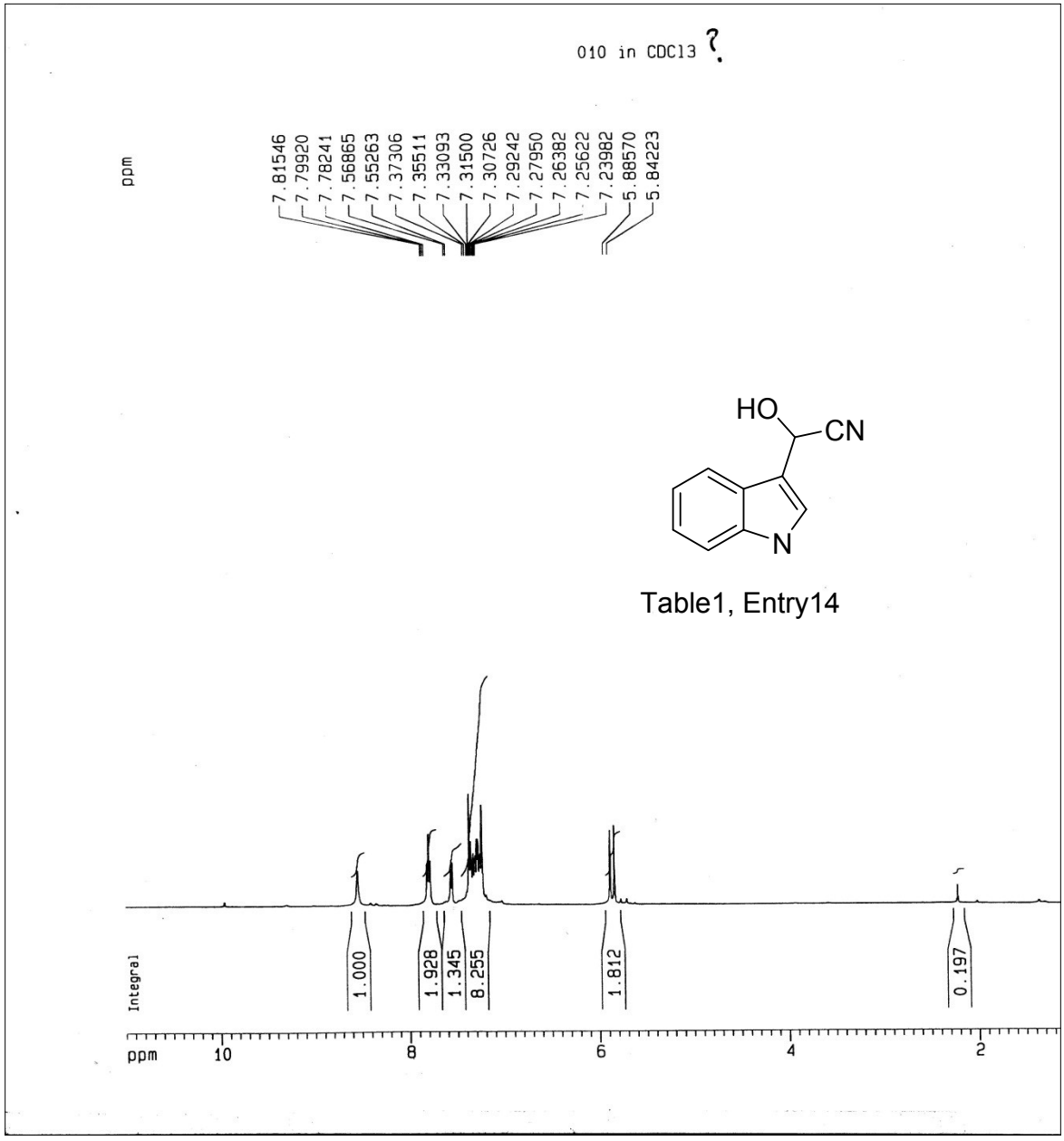

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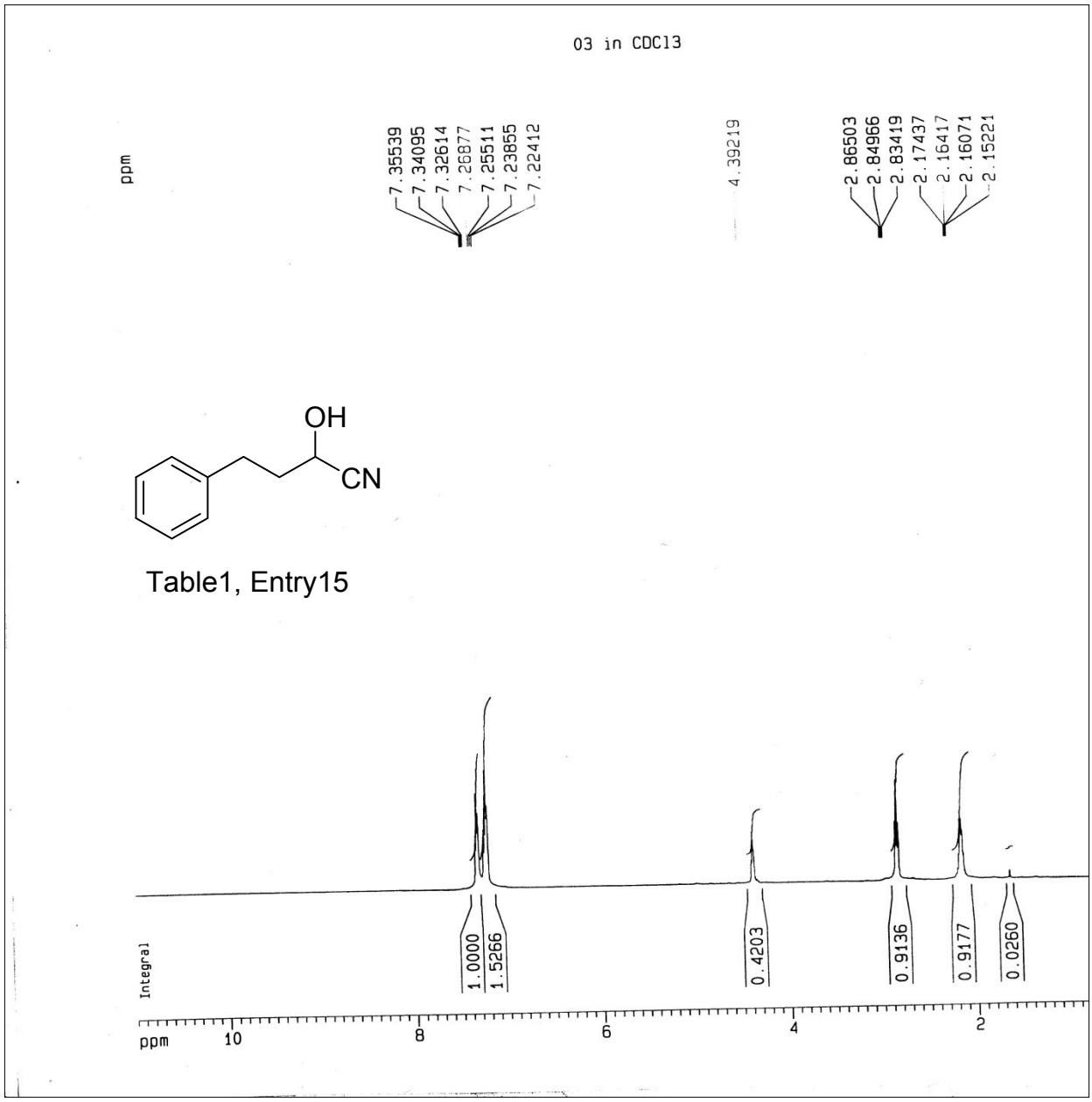
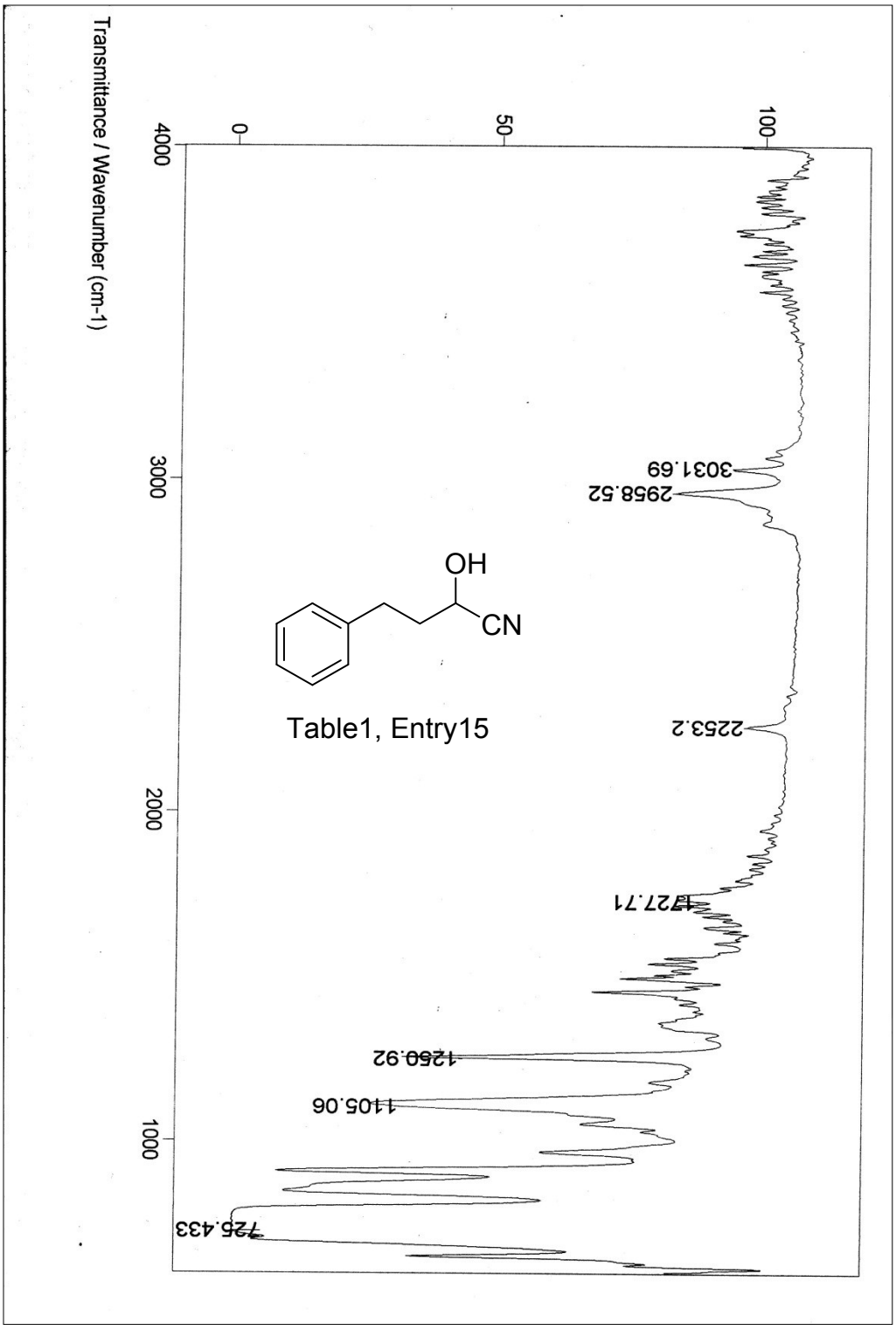


Table1, Entry15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CN
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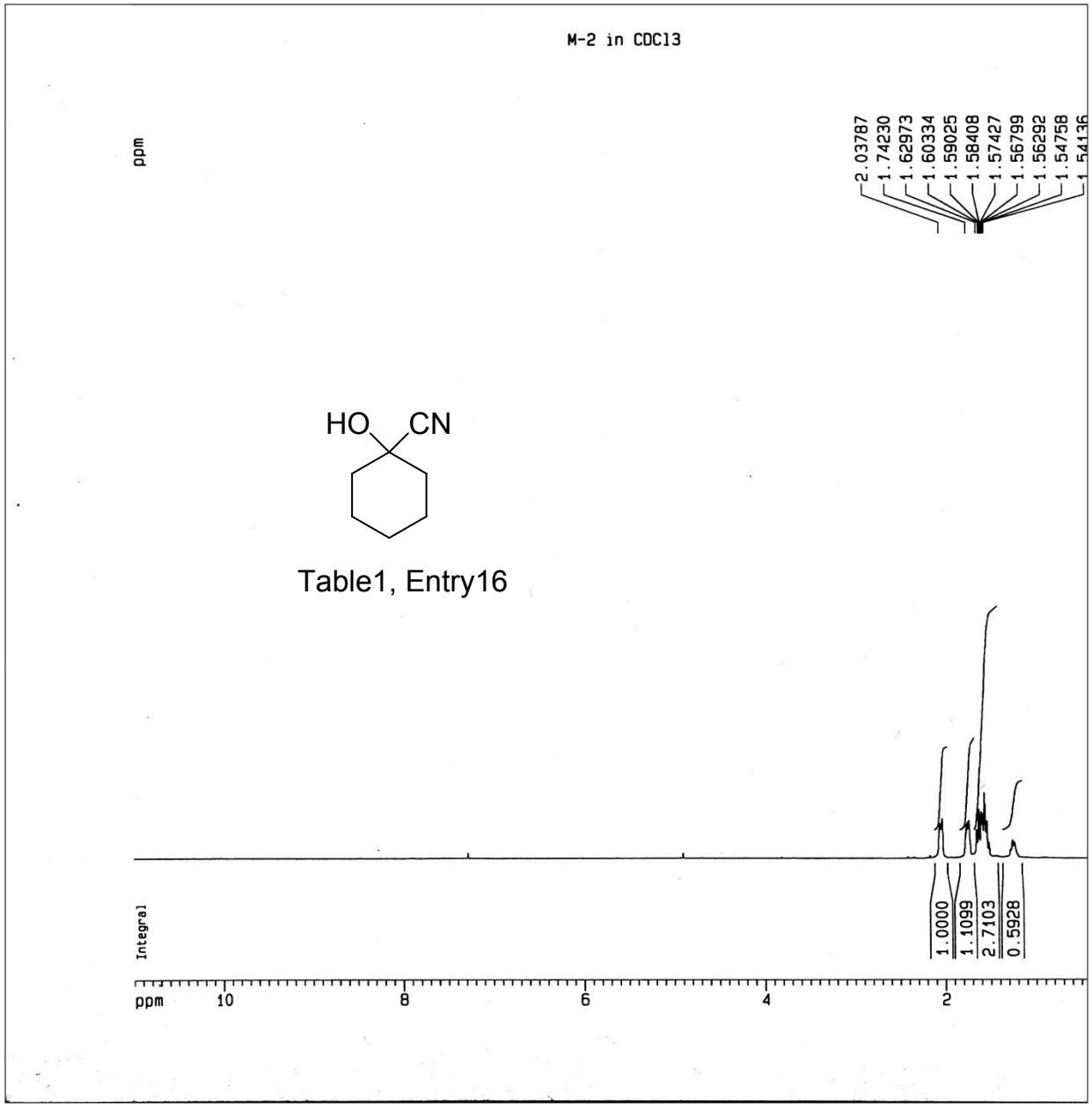

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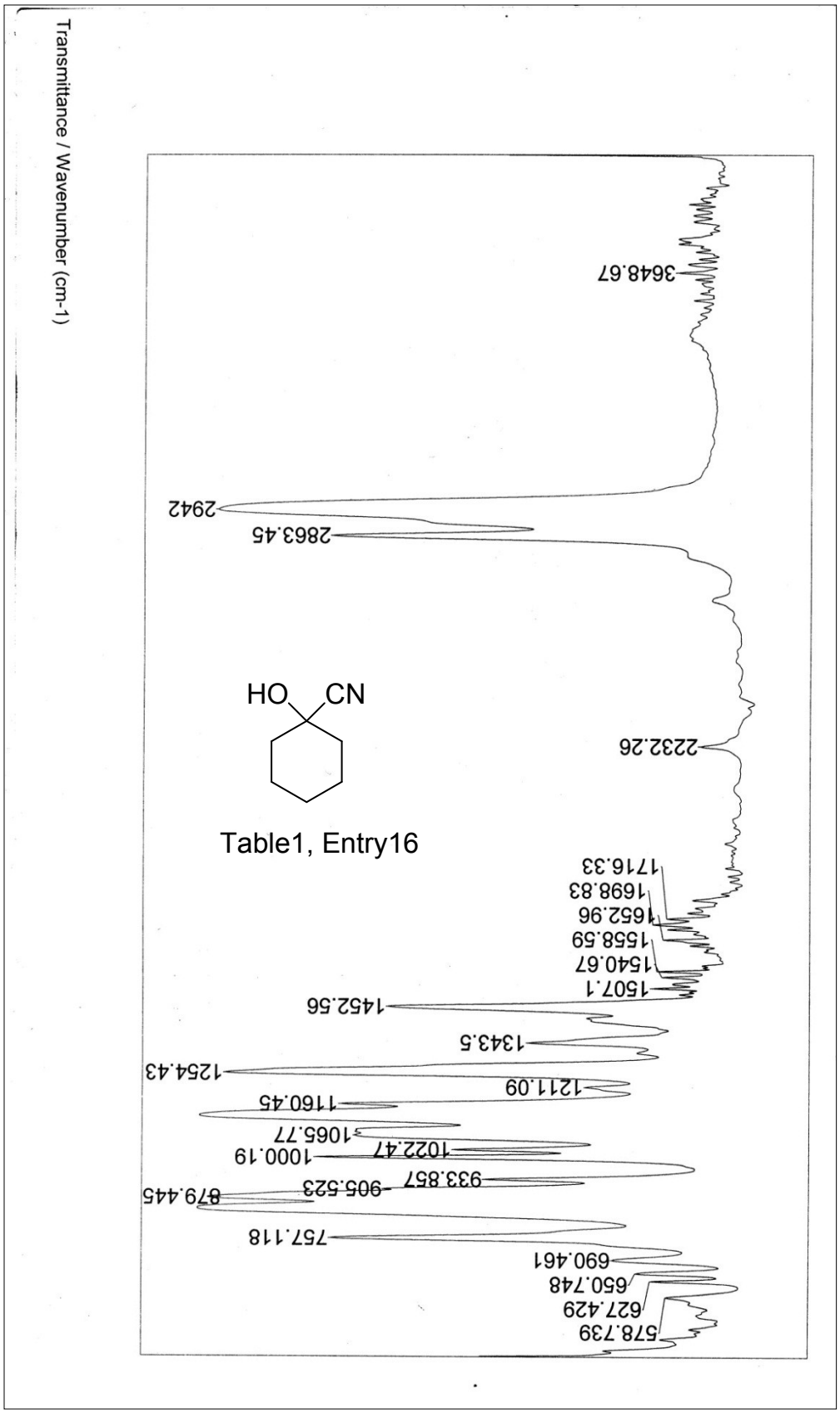

Table1, Entry16