Supporting information for:

Self-Assembled Organic-Inorganic Hybrid Silica with Ionic Liquid Framework: A Novel Support for the Catalytic Enantioselective Strecker Reaction of Imines Using Yb(OTf)$_3$-pybox Catalyst

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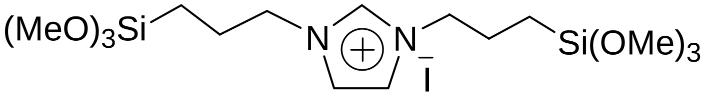
1. Experimental Procedure:

1-1. General: ^{1}H NMR spectra were recorded on commercial instruments (250 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: $\delta = 7.26$). Spectra are reported as follows: chemical shift (= ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constants (Hz), integration. ^{13}C NMR spectra were collected on commerical instruments (62.90 MHz) with complete proton decoupling. The solid state silicon spectra were obtained using a Varian Unity Inova spectrometer operating at 59.56 MHz and the solid state carbon spectra were obtained using a Varian VNMRS spectrometer at 100.56 MHz. The enantiomeric excesses were determined by HPLC analysis on CHIRALPAK AD. Optical rotations were measured on a commerical polarimeter and reported as follows: $[\alpha]_D^T$ (c = g/100 mL, solvent). Reagents obtained from commercial sources were used without further purification. Thermal treatments were conducted from room temperature to 800 ^{o}C in air flow using a Pheometric Scientific analyzer.

1-2. Preparation of 1,3-bis(3-trimethoxysilylpropyl) imidazolium iodide (BTMSPI) 1:

IL **1** was synthesized via a modification of a literature procedure[1]. In a well-dried two necked 200 mL Schlenk flask, 3-iodopropyl-trimethoxysilane (20.0 mmol) was added to a solution of sodium imidazolide (20.0 mmol) in absolute THF (120 mL) and stirred at 65 °C for 12h under an argon atmosphere. The reaction solution was then allowed to reach ambient temperature, after removal of the solvent under vacuum, the resulted mixture was added to another flask containing 20 mmol of 3-iodoropropyl-trimethoxysilane in absolute toluene (100 mL) and refluxed for

36h with exclusion of light. The final solution was first washed with toluene (5×30 mL) and then absolute dichloromethane (30 mL) was added to precipitate of NaCl from the mixture. The supernatant solution was transferred to a well-dried flask and a yellow viscose ionic liquid was obtained after removing of solvent under reduced pressure. The spectral data for IL **1** is as follows: ^{1}H-NMR (250 MHz, $CDCl_3$, 25 ºC, TMS): δ = 10.00 (s, 1H, NCHN), 7.46 (d, 2H, *J* = 1.7 Hz CHCH), 4.32 (t, 4H, *J* = 7.1 Hz, NCH_2), 3.6 (s, 18H, 6 OCH_3), 2.00 (m, 4H, $CH_2CH_2CH_2$), 0.62 (t, 4H, *J* = 8.1 Hz $SiCH_2$). ^{13}C-NMR (63 MHz, $CDCl_3$, 25 ºC, TMS): δ= 136.08 (NCHN), 122.20 (CHCH), 51.76 (NCH_2), 50.77 (OMe), 24.12 ($CH_2CH_2CH_2$), 5.81 ($SiCH_2$).



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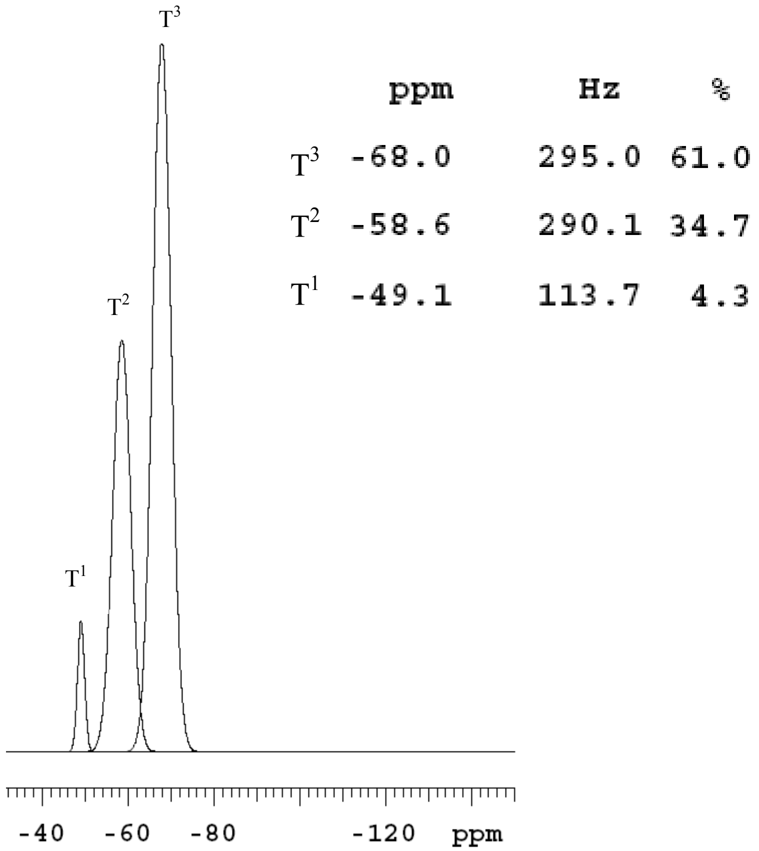
1-3. Synthesis of self-assembled ionic liquid (SAILP) under acidic condition

Typically, 40 mmol of 1,3-bis(3-trimethoxysilylpropyl) imidazolium iodide ionic liquid was added in 20 g of deionized water and 90 g of 2.0 M HCl solution with stirring at 40 °C for 24h under an argon atmosphere. The resulted mixture was then transferred into a Teflon-lined autoclave and heated at 100 ^{o}C for 72h under static conditions. The obtained mixture was first thoroughly washed with deionized water/ethanol solvent and then a yellow powder was obtained after drying of final material at room temperature.

The solid-state ^{29}Si and ^{13}C NMR spectroscopy of the SAILP material was investigated to demonstrate the presence of alkyl imidazolium group in the material framework. The ^{29}Si spectra of the SAIL exhibits three peaks at -49.5, -58.5, -67.5 ppm corresponding, respectively, to T^1 [C-Si-(OSi)$(OH)_2$], T^2 [C-Si-$(Osi)_2(OH)$], and T^3 [C-Si-$(Osi)_3$] sites for Si species which are covalently bonded to carbon atoms. Interestingly, the absence of any Q-type bonds in the Si spectrum significantly confirms the high stability of C-Si bands during the synthesis and washing conditions. Moreover, the higher intensity of T^3 band than T^2 and T^1 bands shows the high cross linking condensation and incorporation of ionic liquid moieties under applied conditions.



	ppm	Hz	%
T^3	-68.0	295.0	61.0
T^2	-58.6	290.1	34.7
T^1	-49.1	113.7	4.3

Figure1. Solid state ^{29}Si-NMR of the SSIL

The ^{13}C CP/MAS NMR spectrum of SAILP was also determined to clarify the characteristic signals of the IL bridging moiety. Fig. X illustrates the solid state ^{13}C NMR spectrum of this material, which can be assigned to the C species as follows: δ (ppm) = 10.5 ($SiCH_2$), 24.7 ($CH_2CH_2CH_2$), 52.8 (CH_2N), 123.6 (CHCH), and 136.7 (NCHN). This ^{13}C-solid state NMR spectrum goodly demonstrates that the ionic liquid groups were indeed well incorporated intact into the material network. In addition, the absence of any further carbon peak confirms that almost all Si-C bonds survived intact under the acidic polycondensation.

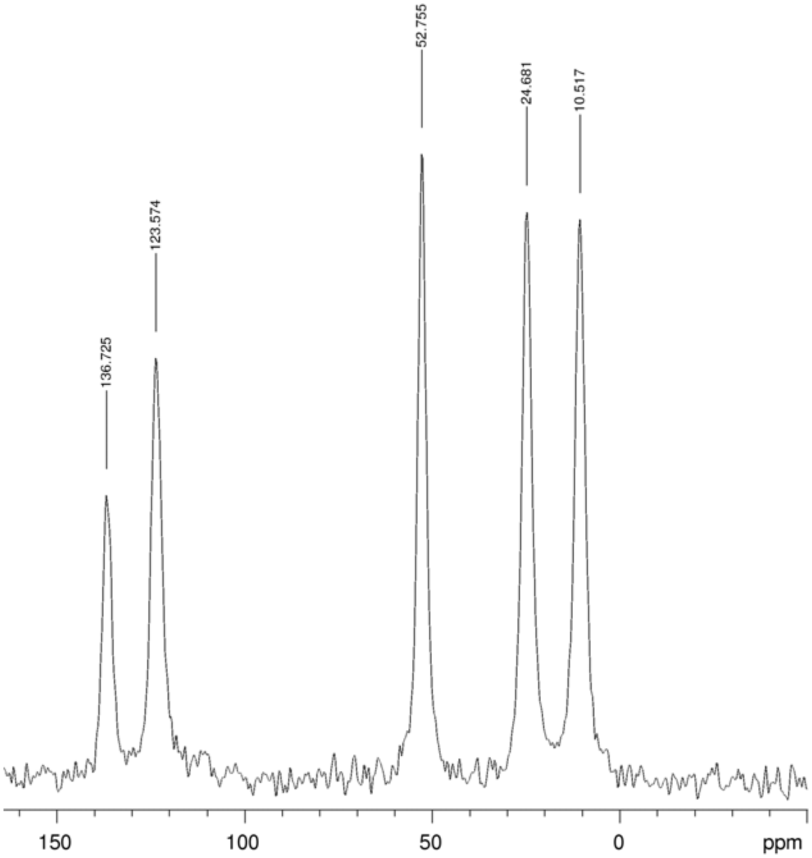
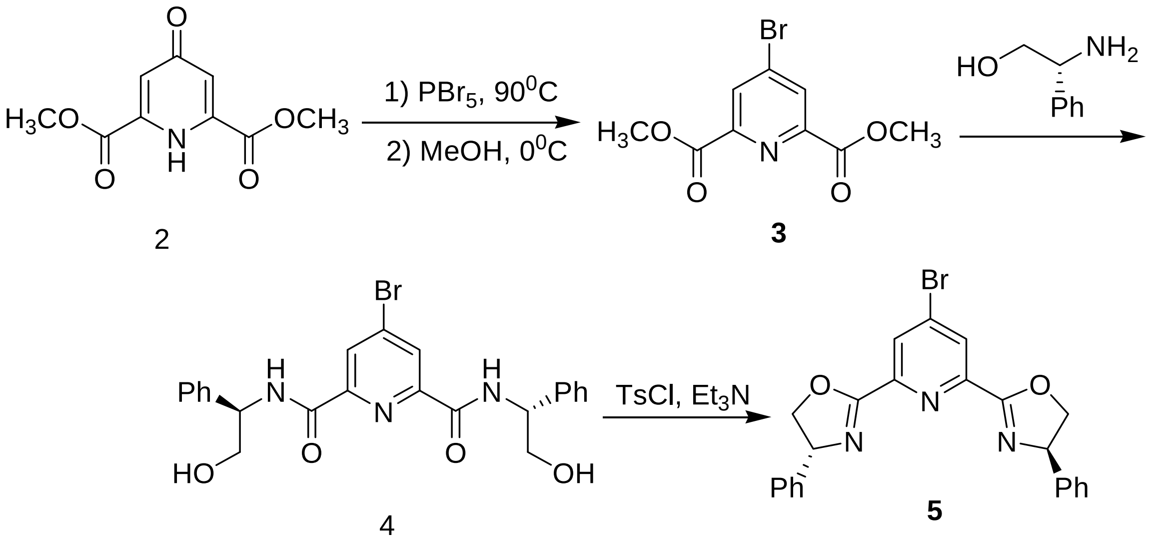


Figure 2. Solid state ^{13}C-NMR of the SSIL

1-4. Preparation of the Chiral Ligand[2]



The preparation of chiral 4-bromopyridine-2,6-bis(oxazoline) ligand (**5**) was achieved according to a known procedure reported by Moberg *et al.* almost without any modification. The reaction sequences were demonstrated in the above reaction scheme.

Compound 1: m.p. 155-156 °C; ^{1}H NMR (250 MHz, CDCl3): δ = 8.40 (s, 2H), 3.97 (s, 6H); ^{13}C NMR (62.90 MHz, CDCl3): δ =163.97, 149.05, 135.7, 131.27, 53.45.

Compound 2: m.p. 83-85 °C; ^{1}H NMR (250 MHz, CDCl3): δ = 8.50 (d, *J* = 7.5, 2H), 8.36 (s, 2H), 7.27 (m, 10H), 5.16 (m, 2H), 3.92 (d, *J* = 5.0 Hz, 4H), 2.94 (br s, 2H); ^{13}C NMR (62.90 MHz, CDCl3): δ =162.5, 149.8, 138.7, 136.3, 128.8, 128.4, 127.9, 126.6, 66.9, 56.9.

Compound 3: m.p. 195-196 °C; ^{1}H NMR (250 MHz, CDCl3): δ =8.51 (s, 2H), 7.29 (m, 10H), 5.44 (t, *J* = 7.5 Hz, 2H), 4.92 (t, *J* = 7.5 Hz, 2H), 4.42 (t, *J* = 10 Hz, 2H); ^{13}C NMR (62.90 MHz, CDCl3): δ =162.5, 147.6, 141.3, 134.0, 129.4, 128.9, 127.9, 126.8, 75.7, 70.3.

1-5. General Procedure for the Preparation of Imine Substrate: the aldehyde (20 mmol) and diphenylmethylamine (20 mmol) and Na_2SO_4 (0.5 gr) in dichloromethane (5 mL) were stirred in rt at 22 ^{o}C. The solution was filtrated and solvent was removed by vacuo. Products could be purified by recrystalyzation (Hexane-ethylacetate).

1-6. General Procedure for the Preparation of Yb(OTf)$_3$-pybox Complex: A 2-dram oven-dried vial was charged with a stirbar, Yb(OTf)$_3$ (30 mg, 0.048 mmol), and the corresponding pybox ligand (44 mg , 0.098 mmol) in a dry box. The vial was capped with a septum and removed from the dry box. Dichloromethane (1.0 mL) was added to the vial under an atmosphere of dry Ar. The resulting mixture was stirred vigorously at room temperature for 1 h until the reaction becomes homogeneous.

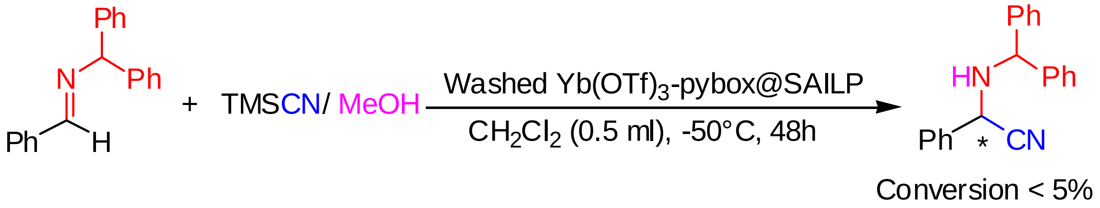
1-7. Immobilization of Yb(OTf)$_3$-pybox Complex onto SAILP: To the resulting complex solution in **1-6** were added 600 mg of the SAIL and 3cc other dichloromethane under argon and the resulting mixture was stirred for 12 h at rt. Then, dichloromethane was slowly removed under reduced pressure and the resulting free flowing yellow powder was then dried at 60 ^{o}C for overnight. Due to evaporation method almost all parts of catalysts were necessarily immobilize over the support. For further clarity, the amount of Yb was further determined by atomic absorption spectroscopy (AAS). AAS illustrated that the amount of Yb loaded onto the matrix was essentially the same with the amount of Yb(OTf)$_3$ that was used in the initial reaction mixture.

1-8. General Catalytic Strecker Reaction Using Yb(OTf)$_3$-pybox@SAILP: To the obtained powder were added 1 mmol of corresponding imine and 0.5cc dichloromethane under argon and then resulting solution was cooled to the desired temperature. After 20 min TMSCN (2 mmol) and methanol (2 mmol) were added to the flask in one portion. The reaction was maintained at the desired temperature until consumption of imine was monitored by thin layer chromatography. After completion of the reaction 20cc *n*-hexane was added to the reaction mixture at the same temperature and then the products were separated from the heterogeneous catalyst by filtration and were purified by flash chromatography on silica gel by THF/Hexane as eluent**.**

1-9. Recycling Experiment: the recycling experiment was performed according to the representative procedure described above. After separation of the catalyst and washing with 30 mL ***n***-hexane, the catalyst was then dried in vacuum oven at 60 ^{o}C for overnight**.** The recycled catalyst was used directly for the next cycle.

1-10. Note for elucidating nature of Yb(OTf)$_3$-pybox@SAILP

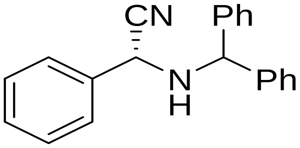
At the moment, we believe that our catalyst is physically adsorbed over SAILP. While the precise mechanism for this reaction is unclear at this stage; however, it seems reasonable that SAIL might function as both ionic support and also as ionic liquid supported reaction media. To elucidate whether the Yb(OTf)$_3$-pybox-complex is chemically or physically adsorbed into solid support, the Yb(OTf)$_3$-pybox@SAILP was thoroughly washed with MeOH. The resulting washed solid was then tested in the asymmetric Strecker reaction of *N*-benzylidenediphenylmethanamine under standard reaction conditions (Scheme 1).



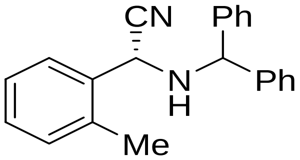
Scheme 1

Interestingly, the result demonstrated that only 5% conversion was observed after 48 h at -50 °C confirming that almost all Yb(OTf)$_3$-pybox-complex is removed through washing process with polar solvents such as MeOH. This study clearly proves the nature of physical immobilization of Yb(OTf)$_3$-pybox on the SAILP material. On the other hand, in a separate experiment Yb(OTf)$_3$-pybox@SAILP was washed with CH_2Cl_2 at -50 °C. The resulting washed solid was then tested in the asymmetric Strecker reaction of *N*-benzylidenediphenylmethanamine under standard reaction conditions. Interestingly, using this catalyst reaction went to completion within 36 h under our described conditions and the corresponding α-aminonitriles was isolated in 94% yield and 76% ee. The above-mentione results together may clearly show that while the catalyst is physically adsorbed, under the described reaction condition, the catalyst acts in a heterogeneous pathway.

1-11. Characterizations of Products:

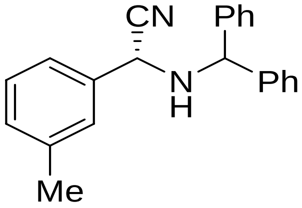


(Benzhydryl-amino)- phenyl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 95% yield as a white solid. The chromatographed material was determined to be of 80% ee by chiral HPLC analysis [Chiralpak AD, 90-10 *n*-hexane/*i*PrOH, 1.0 mL/min]; m.p. 94-96 ^{o}C; [α]$_D^{20}$ = 54.16 (c = 0.12 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.61-7.075 (m, 15 H), 5.27 (s, 1 H), 4.62 (s, 1 H), 2.16 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ =159.74, 142.73, 141.09, 134.92, 129.02, 128.80, 127.95, 127.73, 127.46, 127.26, 127.12, 118.78, 65.60, 52.39 ppm.

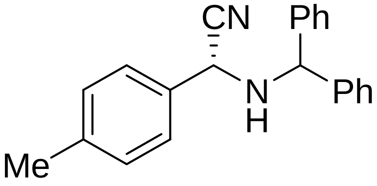


(Benzhydryl-amino)-*o*-tolyl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 94% yield as a white solid. The chromatographed material was determined to be of 79% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min]; m.p. 106-108 ^{o}C, [α]$_D^{20}$ = 128.57 (c = 0.28 in $CHCl_3$).

^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.61-7.22(m, 14 H), 5.31 (s, 1 H), 4.64 (s, 1 H), 2.30 (s, 3 H), 2.02 (s, 1 H; NH) ppm. ^{13}C NMR (62.90 MHz, CDCl$_3$): δ = 142.80, 141.04, 136.48, 133.21, 131.16, 129.23, 128.92, 128.76, 128.09, 127.89, 127.67, 127.49, 127.00, 126.71, 118.80, 65.81, 50.35, 18.93 ppm.

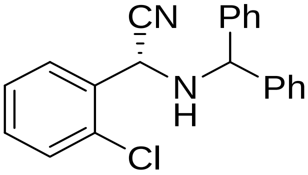


(Benzhydryl-amino)-*m*-tolyl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 93% yield as a white solid. The chromatographed material was determined to be of 71% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 69-71 °C; $[\alpha]_D^{20}$ = 27.85 (c = 0.70 in CHCl$_3$). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.58-7.24 (m, 14 H), 5.28 (s, 1 H), 4.58 (s, 1 H), 2.41 (s, 3 H), 2.15 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, CDCl$_3$): δ = 142.81, 141.17, 138.90, 134.90, 129.82, 129.04, 128.93, 128.80, 127.93, 127.72, 127.50, 127.18, 124.39, 118.92, 65.64, 52.41, 21.45ppm.

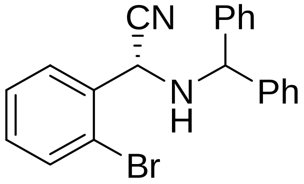


(Benzhydryl-amino)-*p*-tolyl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 86% yield as a white solid. The chromatographed material was determined to be of 77% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90: 10, 1.0 mL/min], m.p. 104-106 °C. $[\alpha]_D^{20}$ = 65.27 (c = 0.16 in CHCl$_3$). ^{1}H

NMR (250 MHz, $CDCl_3$): δ = 7.63-7.24 (m, 14 H), 5.29 (s, 1 H), 4.60 (s, 1 H), 2.41 (s, 3 H), 2.16 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.85, 141.27, 139.02, 132.09, 129.70, 129.06, 128.82, 127.94, 127.73, 127.50, 127.21, 127.18, 118.99, 65.60, 52.17, 21.23 ppm.

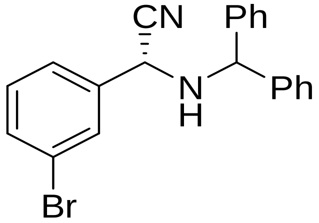


(Benzhydryl-amino)-(2-chloro-phenyl)-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 58% yield as a white solid. The chromatographed material was deter-mined to be of 71% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 95:5, 1.0 mL/min]; m.p. 98-100 °C, $[\alpha]_D^{20}$ = 78.57 (c = 0.14 in $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.59-7.02 (m, 14H), 5.25(s, 1 H), 4.91 (s, 1 H), 2.19 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.60, 140.73, 133.49,132.79, 130.58, 130.42, 129.26, 128.84, 128.78, 128.00, 127.74, 127.70, 127.60, 127.17, 118.17, 65.66, 50.23 ppm.

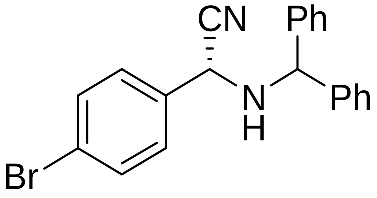


(Benzhydryl-amino)-(2-bromo-phenyl)-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 81% yield as a white solid. The chromatographed material was deter-mined to be of 86% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min]; m.p. 101-103 °C, $[\alpha]_D^{22}$ = 34.61 (c = 0.13 in

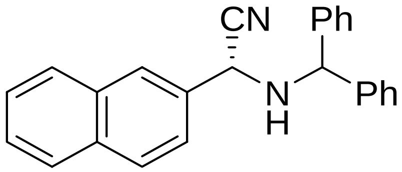
$CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.90-7.24(m, 14H), 5.23(s, 1 H), 4.89 (s, 1 H), 2.12 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.55, 140.67, 134.51,133.76, 130.77, 129.42, 128.77, 128.24, 128.01, 127.88, 127.73, 127.18, 123.42, 118.21, 65.63, 52.51ppm.



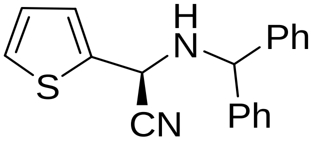
(Benzhydryl-amino)-(3-bromo-phenyl)-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 71% yield as a white solid. The chromatographed material was determined to be of 53% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 95:5, 1.0 mL/min]; m.p. 102-104 °C, $[\alpha]_D^{20}$ = 215 (c = 0.21 in $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.72-7.25 (m, 14 H), 5.25(s, 1 H), 4.58 (s, 1 H), 2.17 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.48, 140.78, 137.02, 132.27, 130.54, 130.36, 129.14, 128.86, 128.10, 127.85, 127.47, 127.12, 125.93, 123.02, 118.20, 65.66, 51.83 ppm



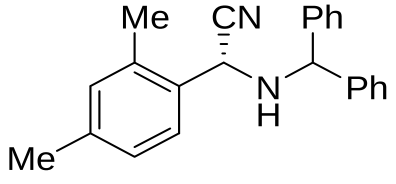
(Benzhydryl-amino)-(4-bromo-phenyl)-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 88% yield as a white solid. The chromatographed material was determined to be of 71% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 99-101 °C, $[\alpha]_D^{20}$ = 13.17 (c = 0.41 in $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.76-7.22 (m, 14 H), 5.25 (s, 1 H), 4.57 (s, 1 H), 2.17 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.52, 140.87, 133.93, 132.16, 129.12, 128.95, 128.86, 128.07, 127.83, 127.44, 127.07,123.21, 118.34, 65.62, 51.85 ppm.



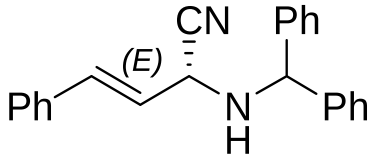
(Benzhydryl-amino)-naphthalen-2-yl-acetonitrile : The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 92% yield as a white solid. The chromatographed material was determined to be of 74% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min]; m.p. 119-121 °C, $[\alpha]_D^{20}$ = 20.62 (c = 0.16 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.94-7.04 (m, 17 H), 5.36 (s, 1 H), 4.79 (s, 1 H), 2.28(s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ =142.80, 141.23, 133.40, 133.10, 132.26, 129.15, 129.03, 128.87, 128.22, 128.05, 127.80, 127.59, 127.20, 126.91, 126.82, 126.35, 124.91, 118.87, 65.76, 52.60 ppm.



(Benzhydryl-amino)-thiophen- 2-yl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 55% yield as a white solid. The chromatographed material was determined to be of 82% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 83-85 °C, $[\alpha]_D^{24}$ = 30.00 (c = 0.12 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.63-7.00 (m, 13 H), 5.27 (s, 1 H), 4.80 (s, 1 H), 2.41 (s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.54, 140.84, 138.30, 129.14, 128.89, 128.08, 127.86, 127.36, 127.14, 126.95, 126.70, 126.09, 118.17, 65.41, 48.19 ppm.

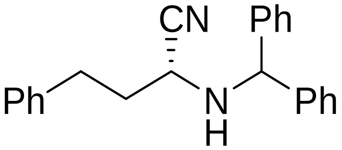


(Benzhydryl-amino)-(2,4-dimethyl-phenyl)-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 81% yield as a white solid. The chromatographed material was determined to be of 72% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 123-125 °C, $[\alpha]_D^{20}$ = 360 (c = 0.21 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.61-7.06 (m, 13 H), 5.29 (s, 1 H), 4.60 (d, *J* = 10 Hz, 1 H), 2.35 (s, 3H), 2.27 (s, 3H), 2.01 (d, *J* = 12.5 Hz, 1 H), ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.87, 141.13, 139.12, 136.24, 131.95, 130.36, 128.89, 128.74, 128.04, 127.86, 127.63, 127.47, 127.29, 126.99, 118.94, 65.78, 50.09, 21.08, 18.85 ppm.

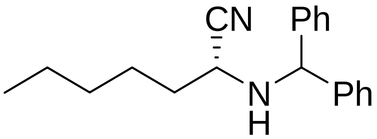


2-(Benzhydryl-amino)-4-phenyl-but-3-enenitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 97% yield as a white solid. The chromatographed material was determined to be of 90% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 90-92 °C, $[\alpha]_D^{20}$ = 27.89 (c = 0.19 in

$CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.64-7.03 (m, 15 H), 6.91 (d, *J* = 17.5 Hz, 1 H), 6.23 (dd, ^1J = 17.5 ^2J =5 Hz, 1 H), 5.22 (s, 1 H), 4.24 (s, 1 H), 1.01 (d, *J* = 12.5 Hz, 1 H) , ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 142.77, 141.02, 135.28, 133.81, 128.98, 128.81, 128.75, 128.61, 127.90, 127.73, 127.42, 127.11, 126.82, 122.35, 118.31, 65.37, 50.10 ppm.

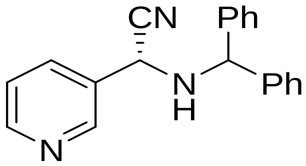


2-(Benzhydryl-amino)-4-phenyl-butyronitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:50) to afford the product in 91% yield as a white solid. The chromatographed material was determined to be of 44% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 98:2, 1.0 mL/min], m.p. 79-80 °C, $[\alpha]_D^{20}$ = 39.56 (c = 0.44 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.55-7.21 (m, 15 H), 5.23 (s, 1 H), 3.47 (s, 1 H), 2.90 (t, *J* = 7.5 Hz, 2 H), 2.15 (q, *J* = 7.5 Hz, 2 H), 1.91(s, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 143.29, 141.31, 140.17, 128.95, 128.86, 128.71, 128.47, 127.85, 127.75, 127.56, 127.18, 126.49, 120.22, 65.63, 47.96, 35.40, 31.88 ppm.

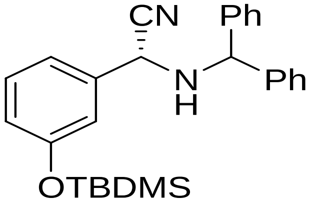


2-(Benzhydryl-amino)-heptanenitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:60) to afford the product in 85% yield as oil. The chromatographed material was determined to be of 45% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 95:5, 1.0 mL/min], m.p. 99-101 °C, $[\alpha]_D^{20}$ = 45.96 (c = 0.5 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.55-7.27 (m, 10 H), 5.21 (s, 1 H), 3.41 (s, 1 H), 1.81

(m, 3 H), 1.55 (m, 2 H), 1.33(m, 4 H), 0.97(m, 3 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 143.59, 141.78, 128.99, 128.84, 127.85, 127.69, 127.60, 127.28, 120.45, 65.66, 48.53, 33.73, 31.34, 25.43, 22.59, 14.20 ppm.



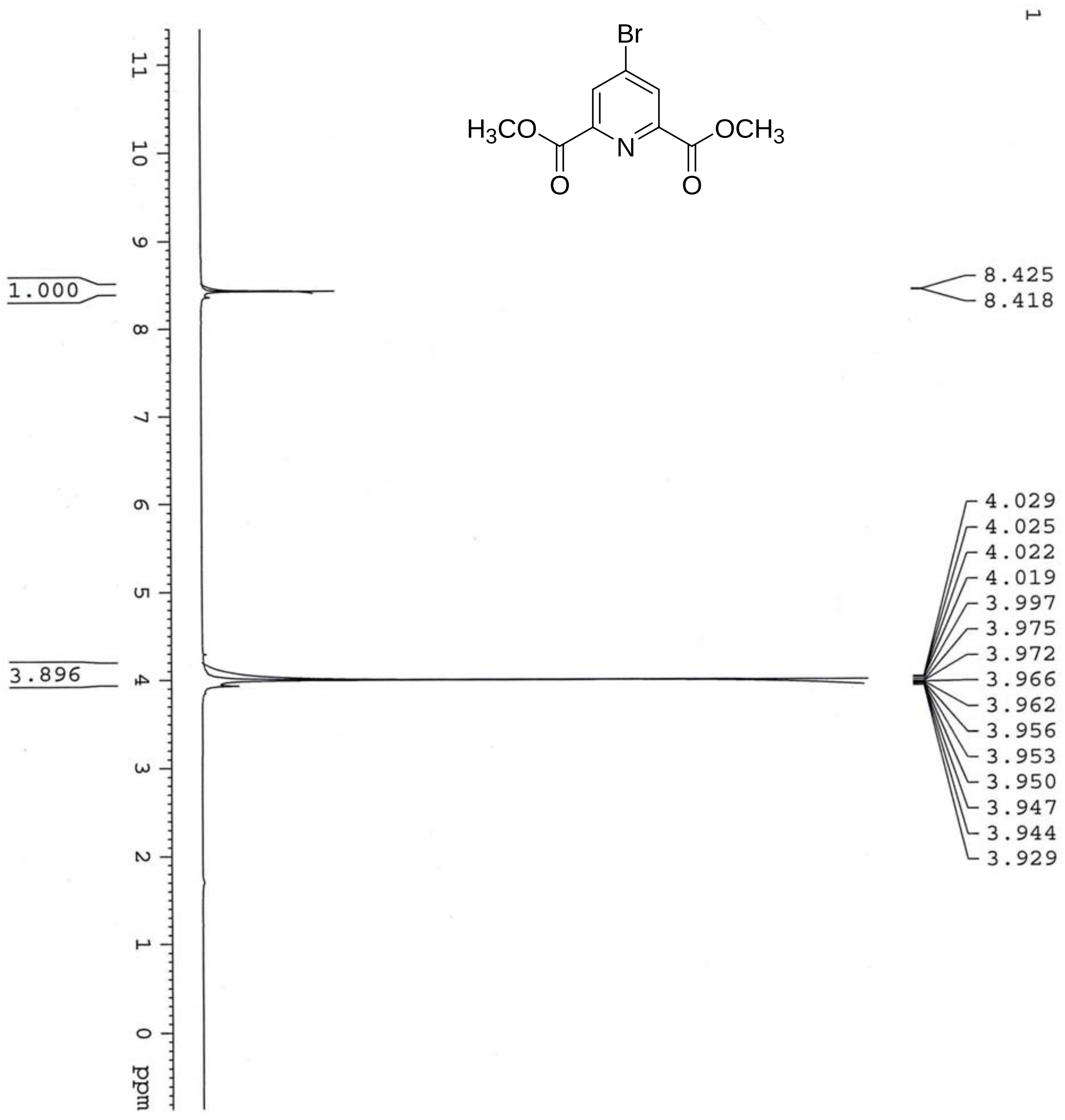
(Benzhydryl-amino)-pyridin- 3-yl-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:30) to afford the product in 95% yield as a yellow solid. The chromatographed material was determined to be of 71% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 90:10, 1.0 mL/min], m.p. 115-117 °C, $[\alpha]_D^{20}$ = 49.05 (c = 0.21 in $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.76 (s,1H), 8.58 (d, *J* = 5 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 7.5 Hz, 2 H), 7.45-7.21 (m, 8H), 4.63 (d, *J* = 10 Hz, 1 H), 2.31 (d, *J* = 10 Hz, 1 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 150.26, 148.78, 142.38, 140.73, 134.81, 130.85, 129.16, 128.86, 128.14, 127.85, 127.44, 127.05, 123.65, 117.81, 65.70, 50.30 ppm.

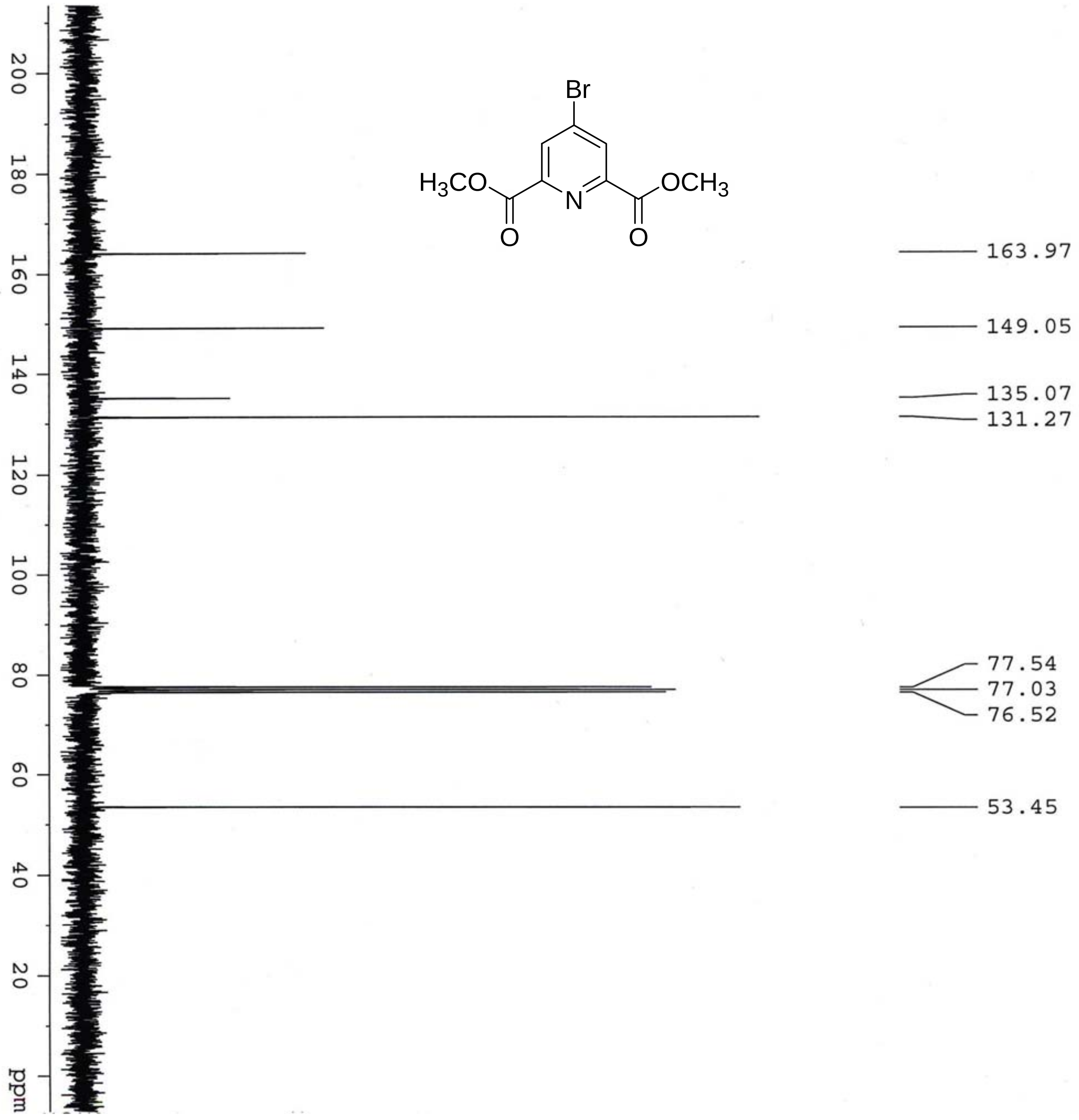


(Benzhydryl-amino)-[3-(tert-butyl-dimethyl-silanyloxy)-phenyl]-acetonitrile: The crude material was purified by flash chromatography on silica gel (THF/Hexane, 1:40) to afford the product in 89% yield as a white solid. The chromatographed material was determined to be of 60% ee by chiral HPLC analysis [Chiralpak AD, *n*-hexane/*i*PrOH, 98:2, 1.0 mL/min], m.p. 89-91

°C, $[\alpha]_D^{20}$ = 350.43 (c = 0.13 in $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.58-6.84 (m, 14 H), 5.23 (s, 1 H), 4.55 (s, 1 H), 2.18 (s, 1 H), 1.01 (s, 9 H), 0.24(s, 6 H) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 156.19, 142.74, 141.18, 136.35, 130.01, 129.01, 128.80, 127.93, 127.71, 127.45, 127.11, 120.65, 120.01, 119.00, 118.76, 65.54, 52.11, 25.70, 18.26, -4.34 ppm.

1-11. Copy of, ^{1}H , ^{13}C-NMR, HPLC and FT-IR spectra of α- amino nitril derivatives

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OCH_3
O
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149.05
135.07
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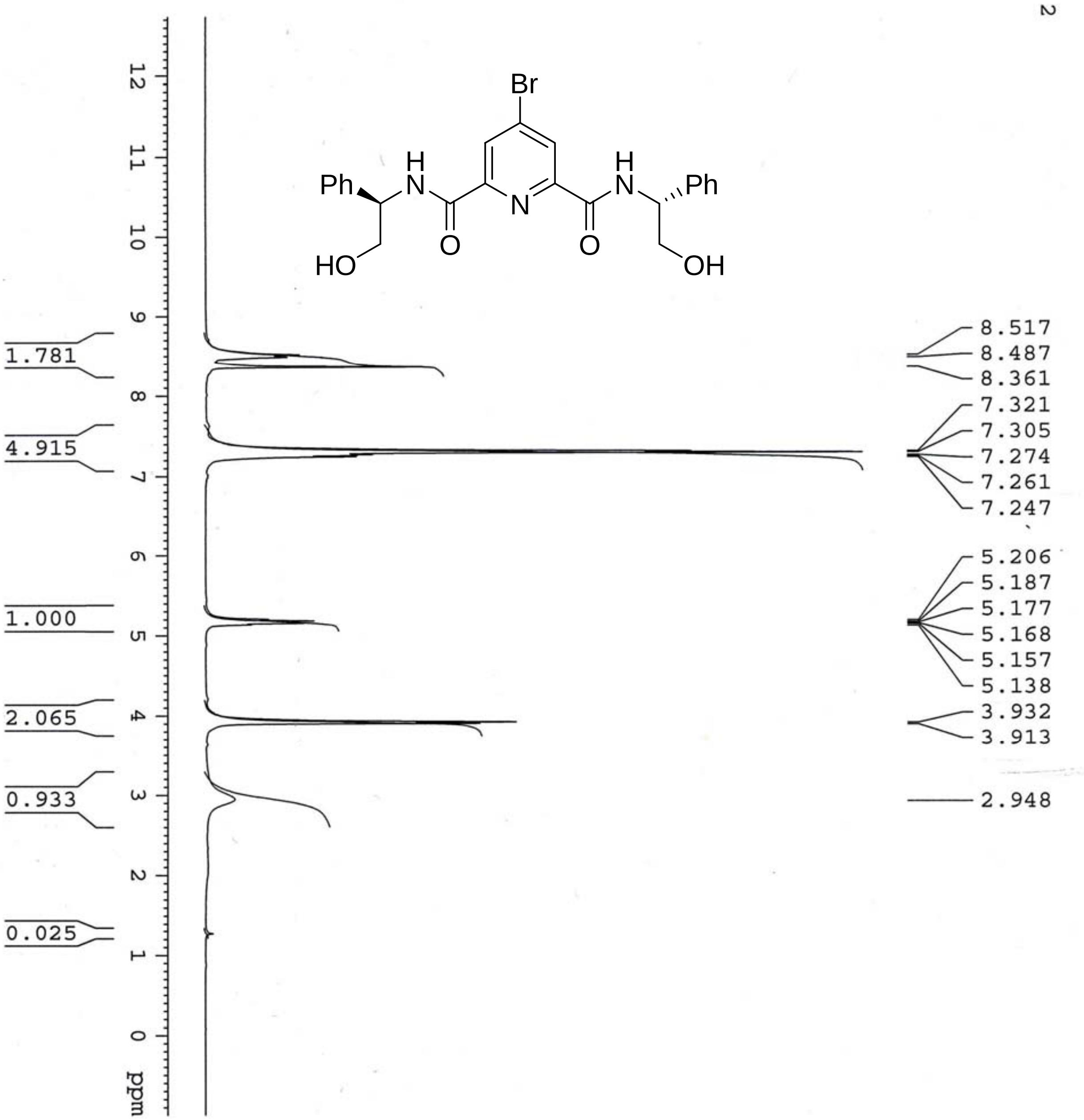
77.03
76.52
53.45
200
180
160
140
120
100
80
60
40
20
ppm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Ph
N
N
N
Ph
O
O
HO
OH
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11
10
9
8
7
6
5
4
3
2
1
0
ppm
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4.915
1.000
2.065
0.933
0.025
8.517
8.487
8.361
7.321
7.305
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5.206
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5.177
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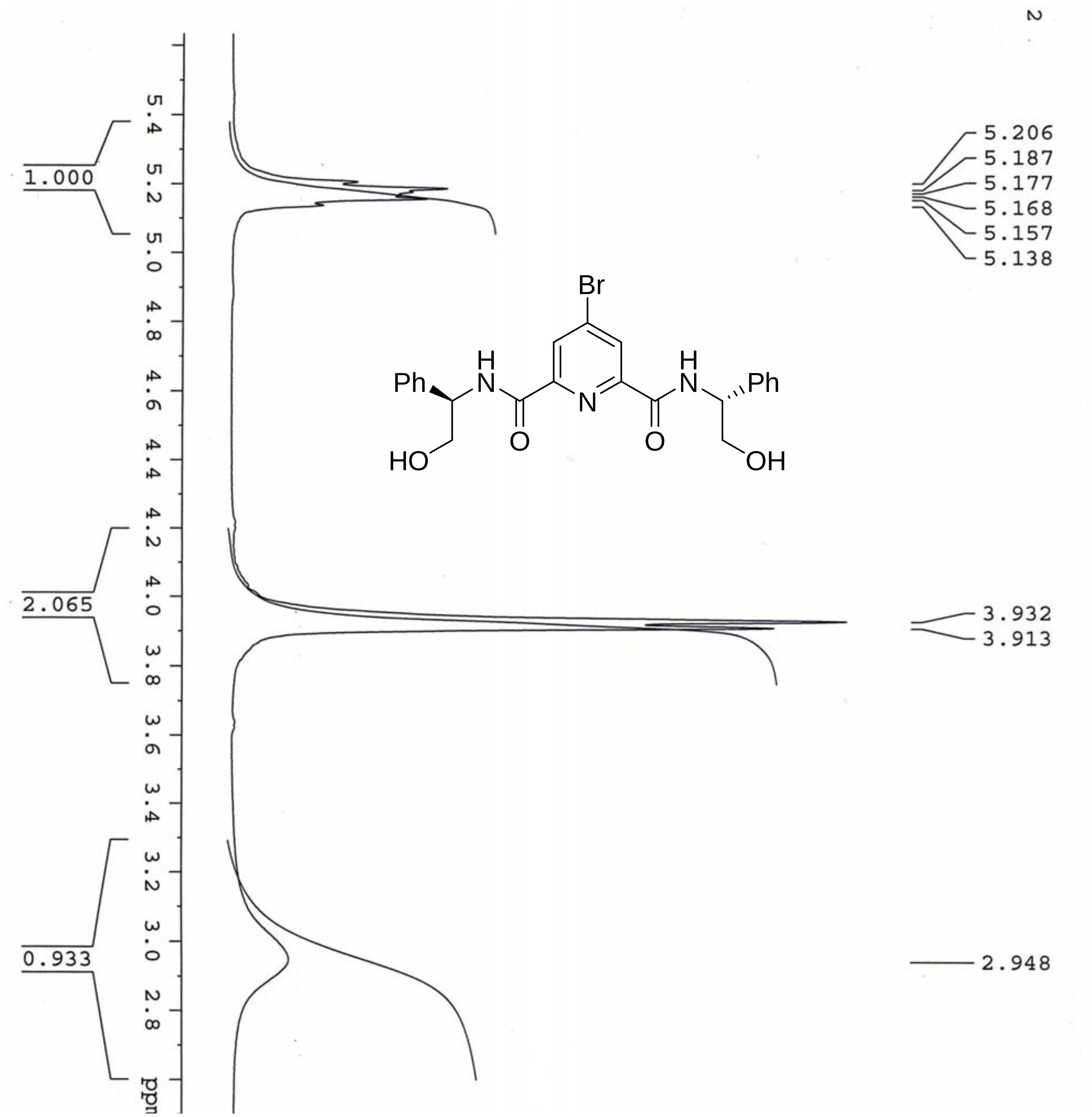
3.913
2.948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5.157
5.138
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3.913
2.948
1.000
2.065
0.933
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
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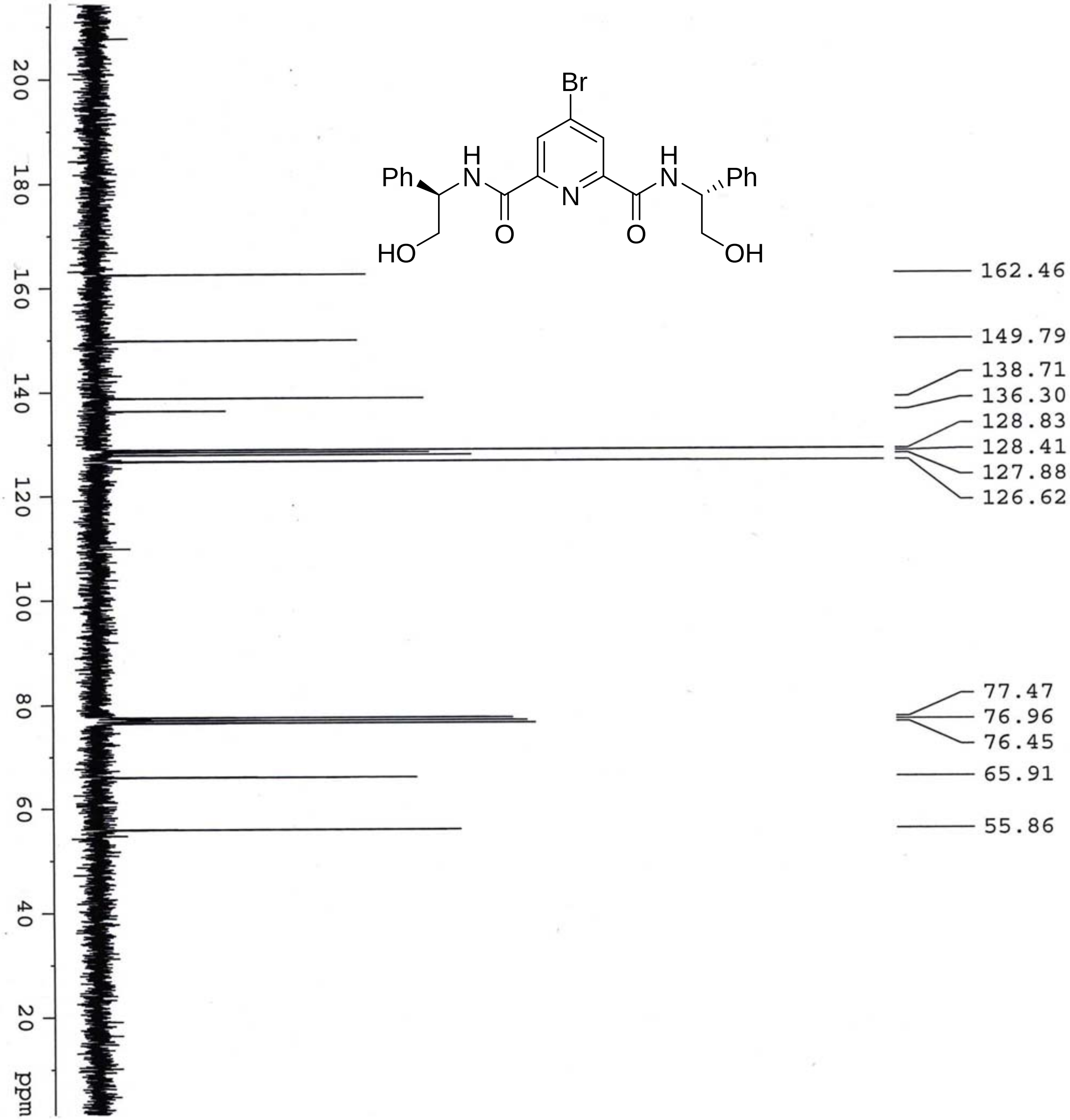
Ph
H
N
N
O
HO
OH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Ph
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N
N
H
N
Ph
HO
O
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OH
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138.71
136.30
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128.41
127.88
126.62
77.47
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76.45
65.91
55.86
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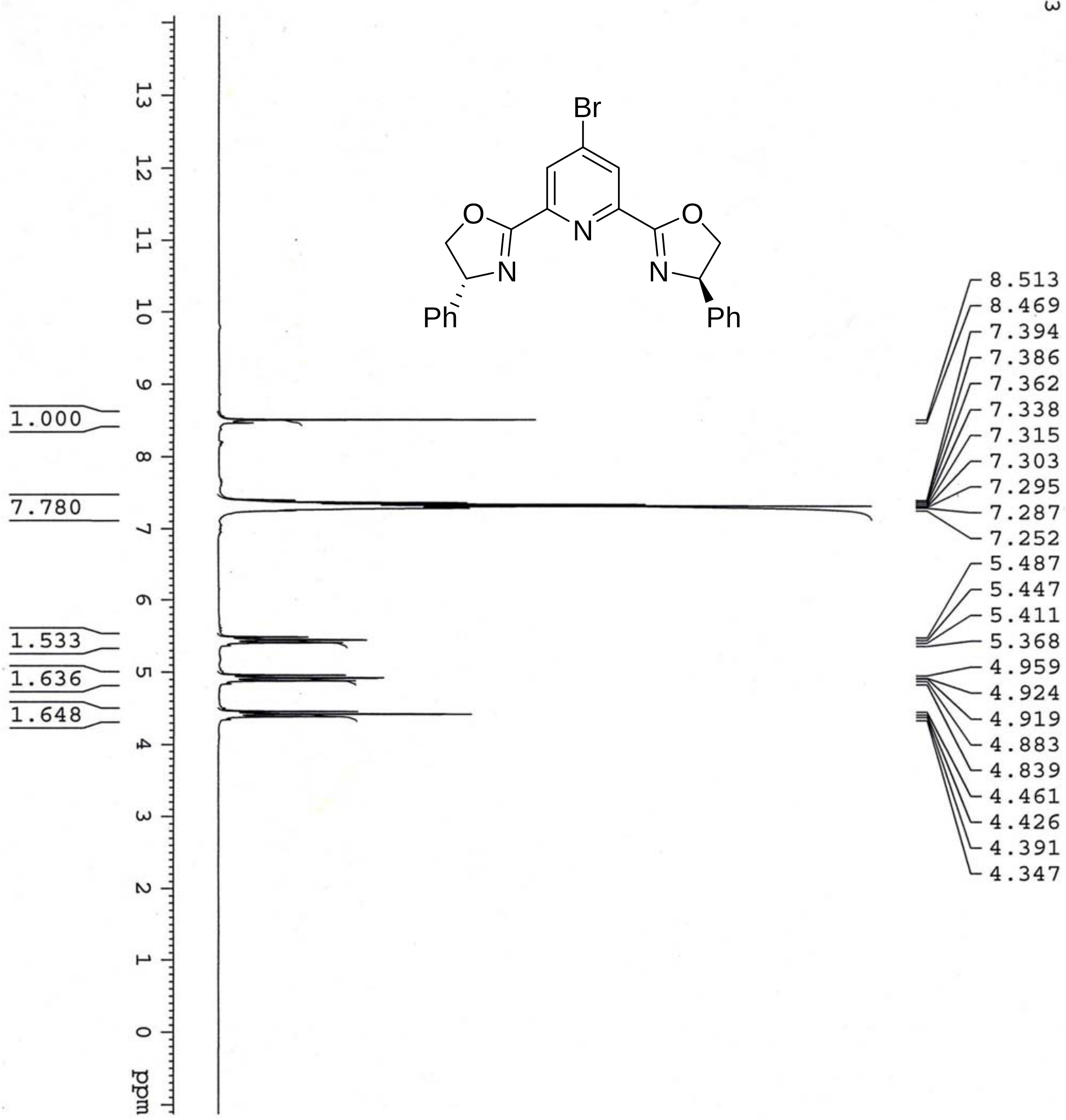
140
120
100
80
60
40
20
ppm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N
O
N
O
Ph
Ph
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1.636
1.648
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
8.513
8.469
7.394
7.386
7.362
7.338
7.315
7.303
7.295
7.287
7.252
5.487
5.447
5.411
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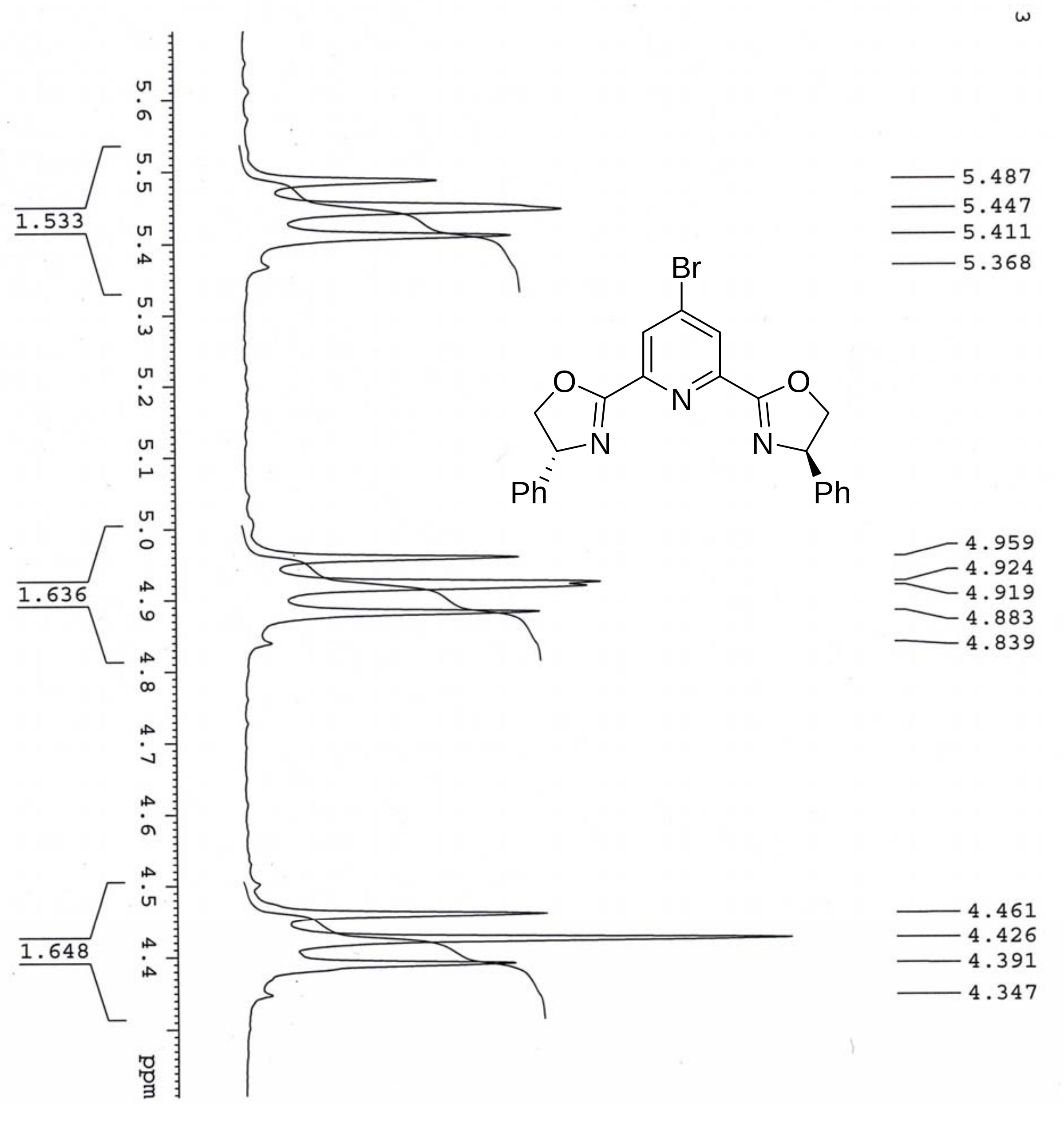
4.959
4.924
4.919
4.883
4.839
4.461
4.426
4.391
4.347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4.8
4.7
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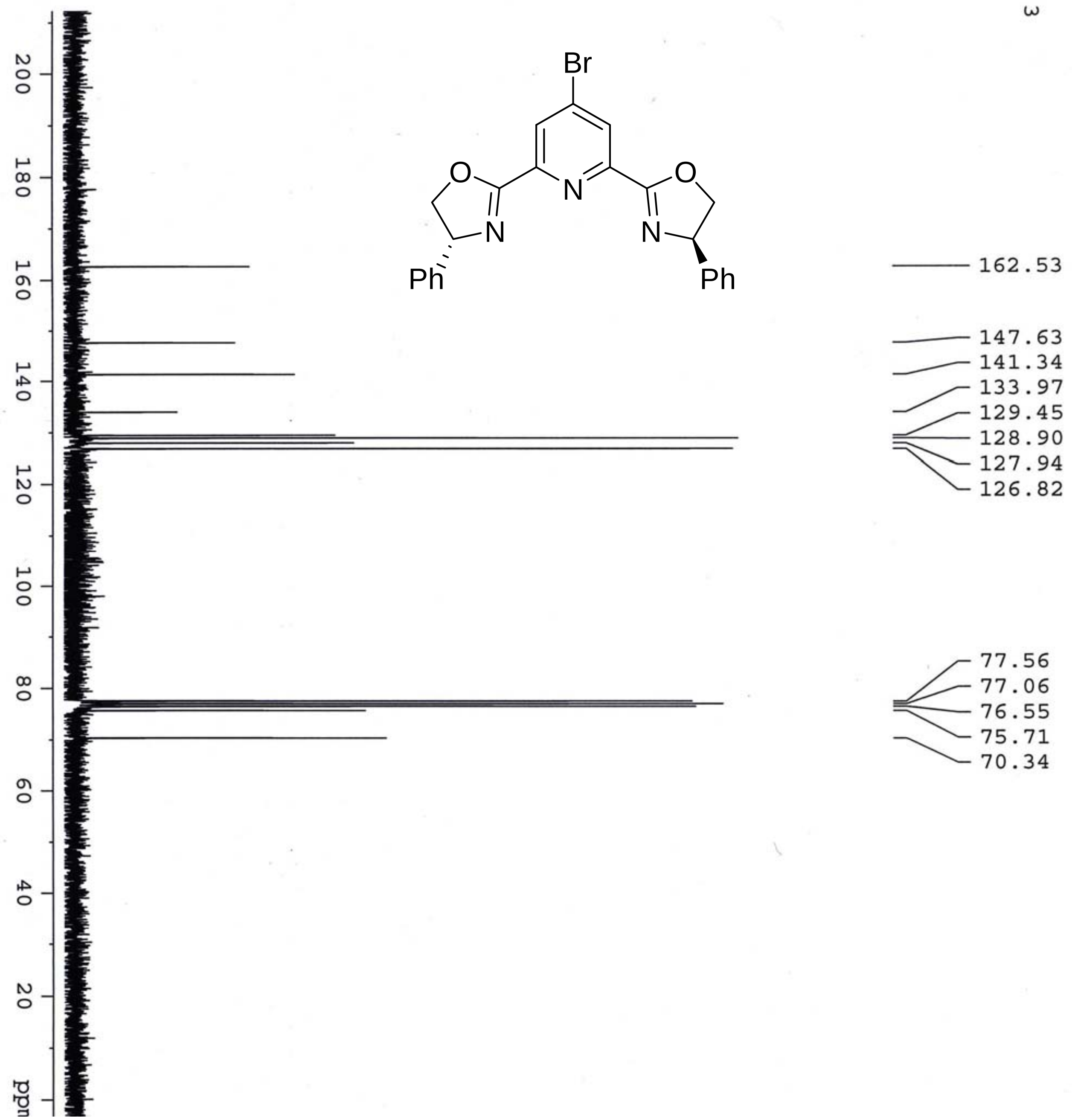
O
N
N
Ph
Ph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Br
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N
N
O
N
Ph
Ph
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147.63
141.34
133.97
129.45
128.90
127.94
126.82
77.56
77.06
76.55
75.71
70.34
200
180
160
140
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100
80
60
40
20
ppm

Table2, entry 1

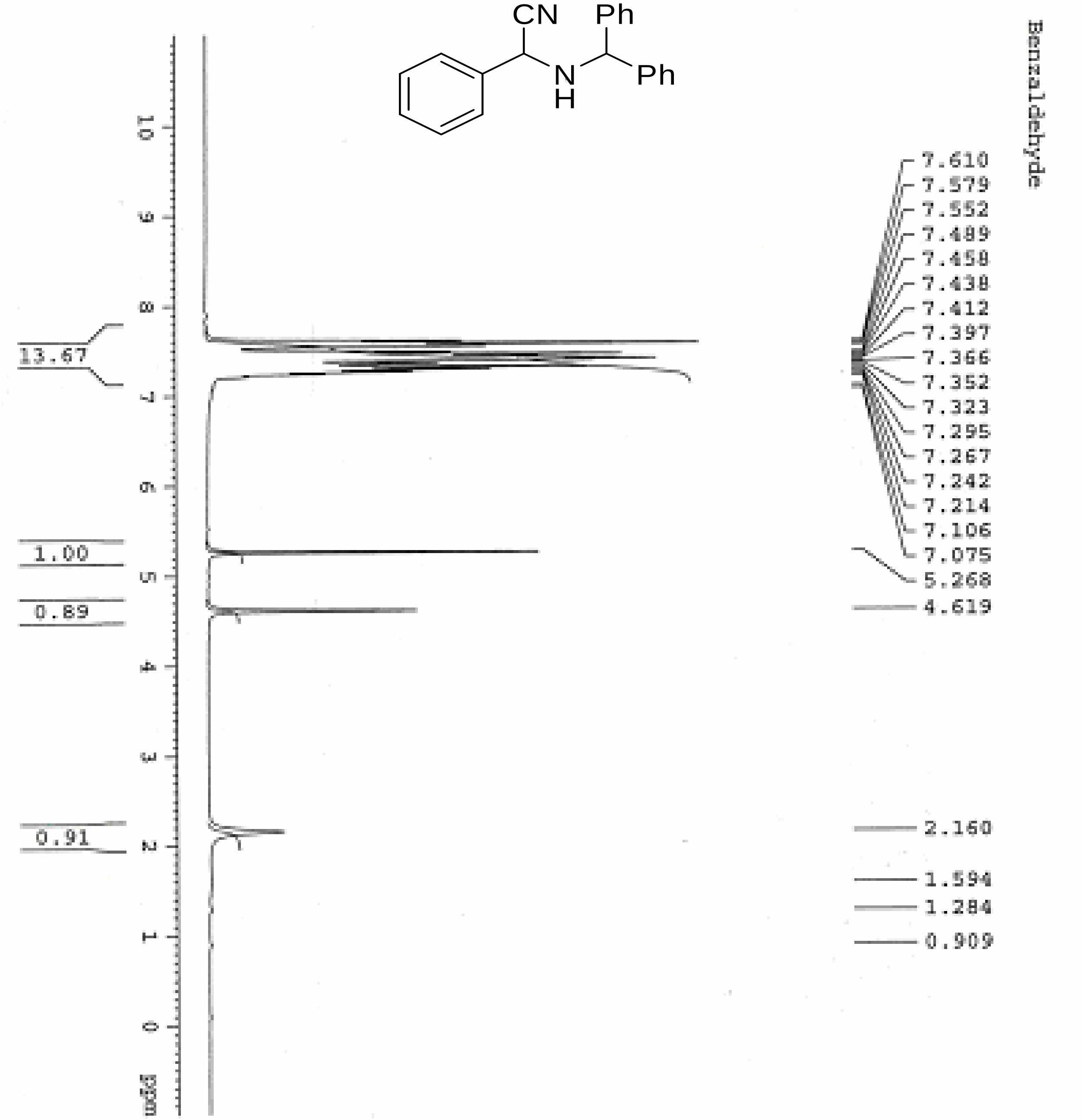


Table2, entry 1

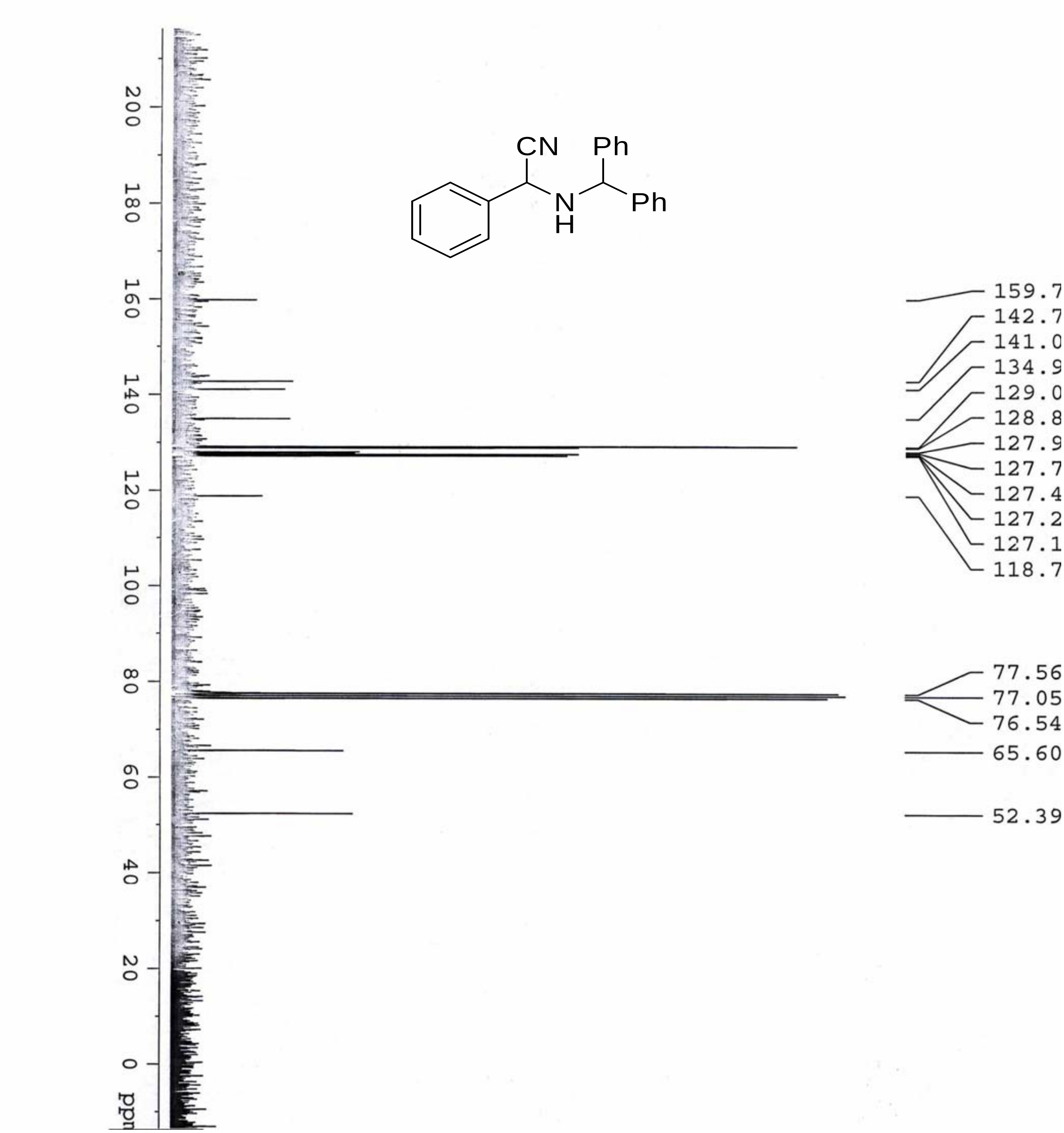
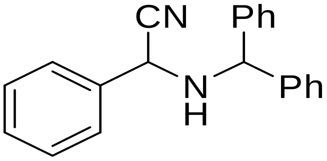
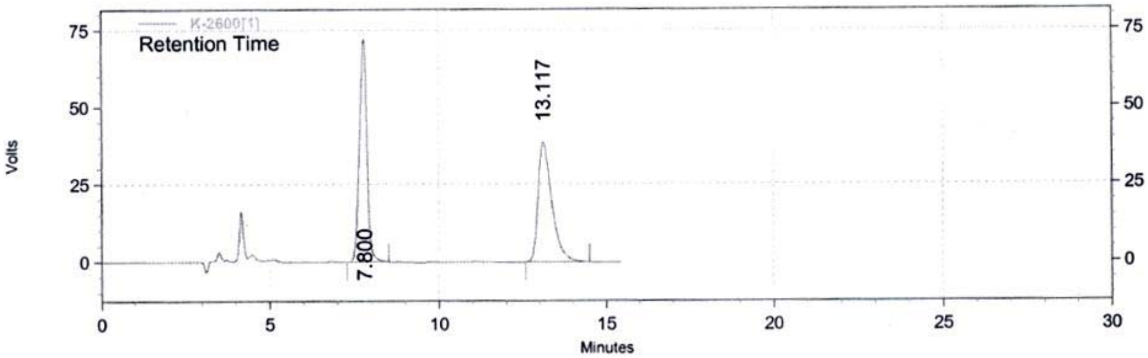


Table2, entry 1





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
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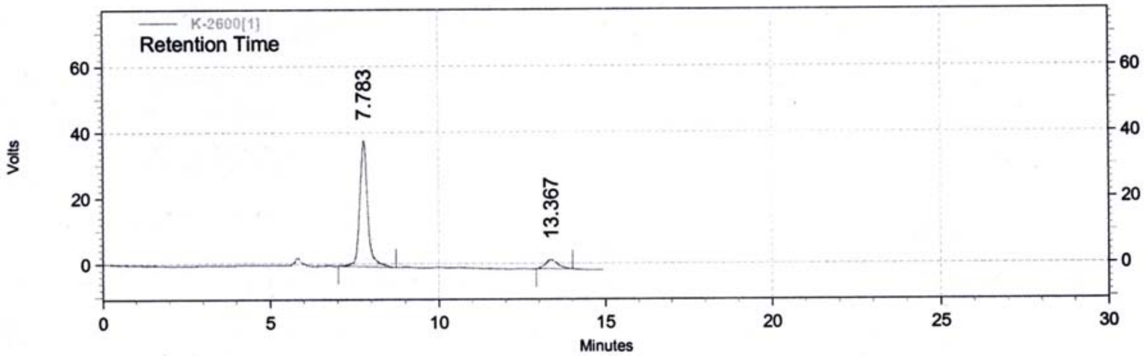


K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
7.783	628061	89.86	38267	93.49
13.367	70877	10.14	2663	6.51

Table2, entry 1

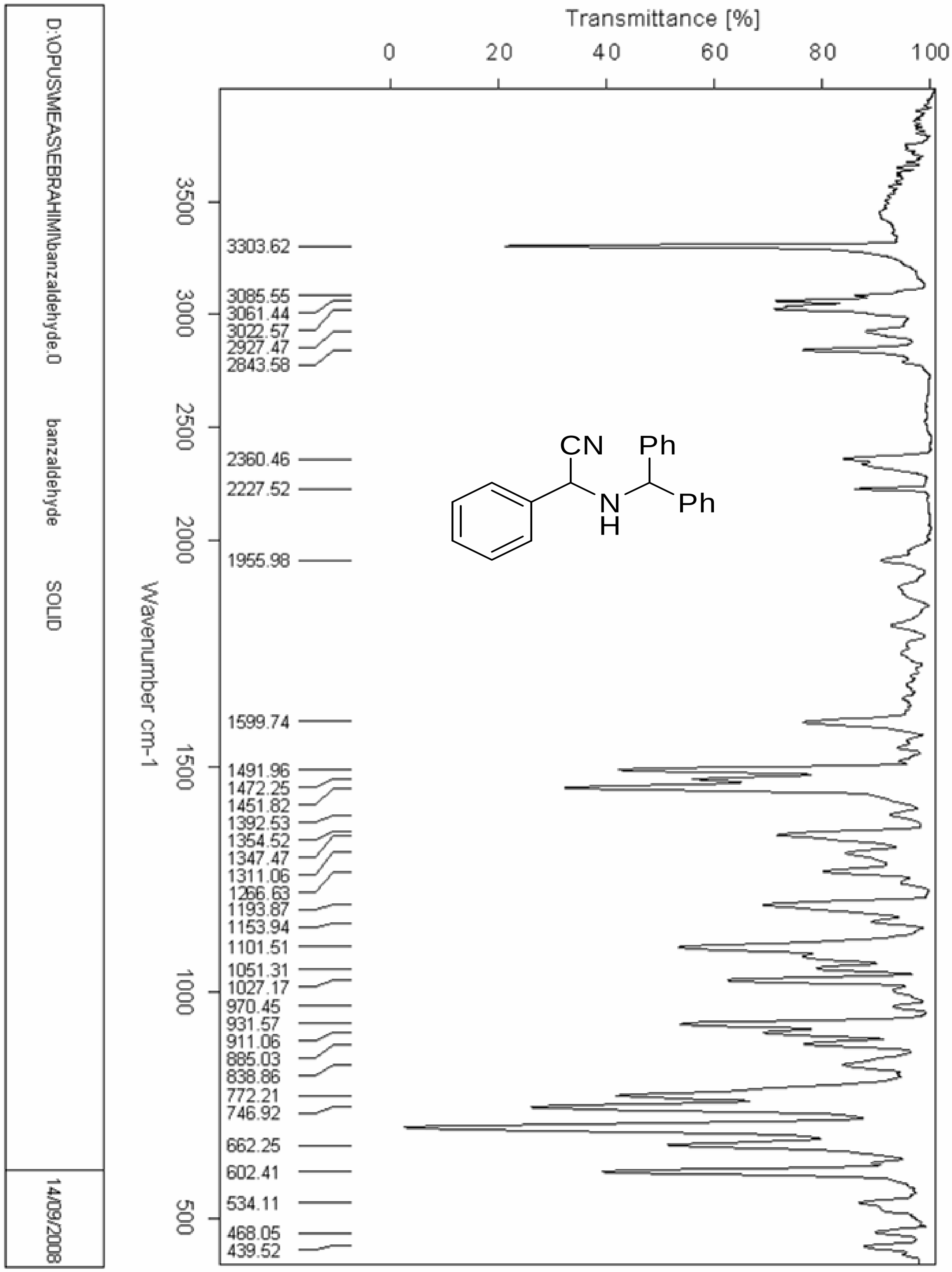


Table2, entry 2

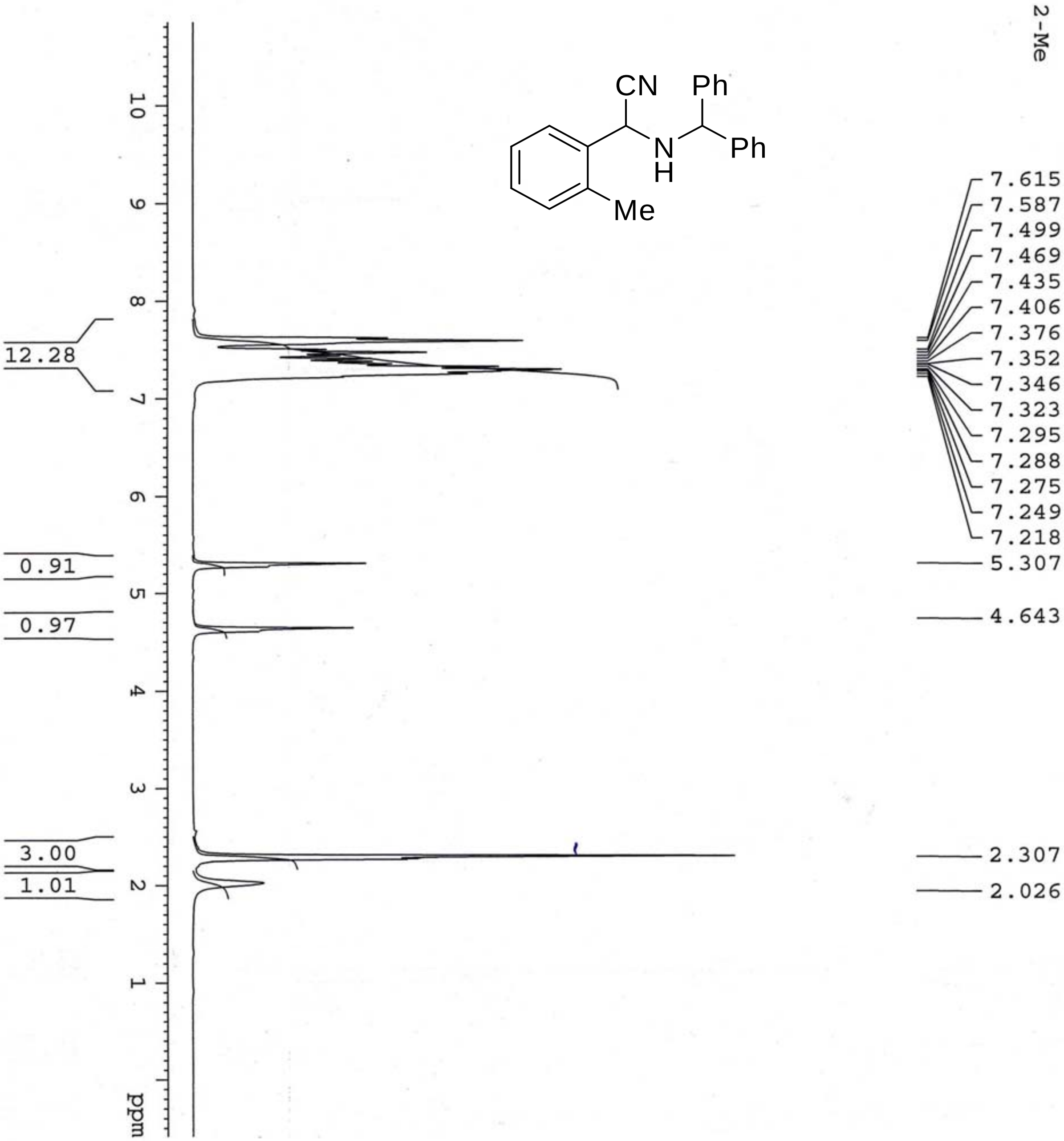
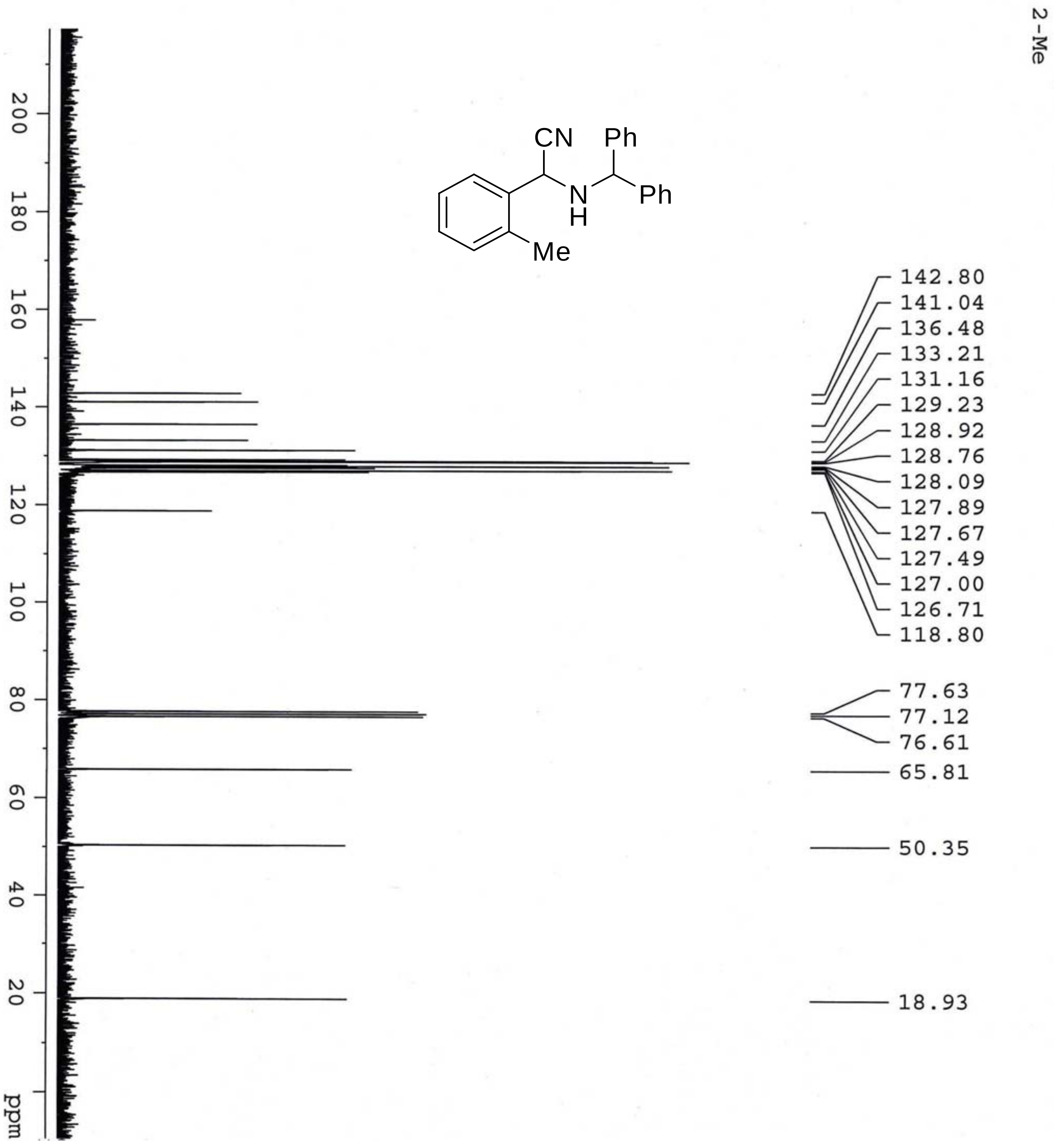


Table2, entry 2



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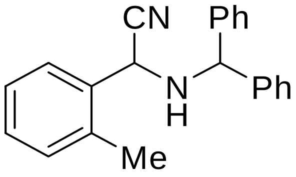
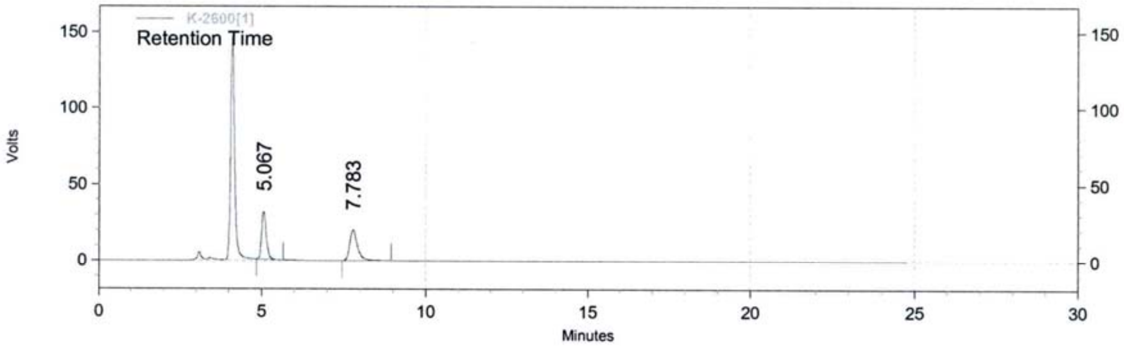
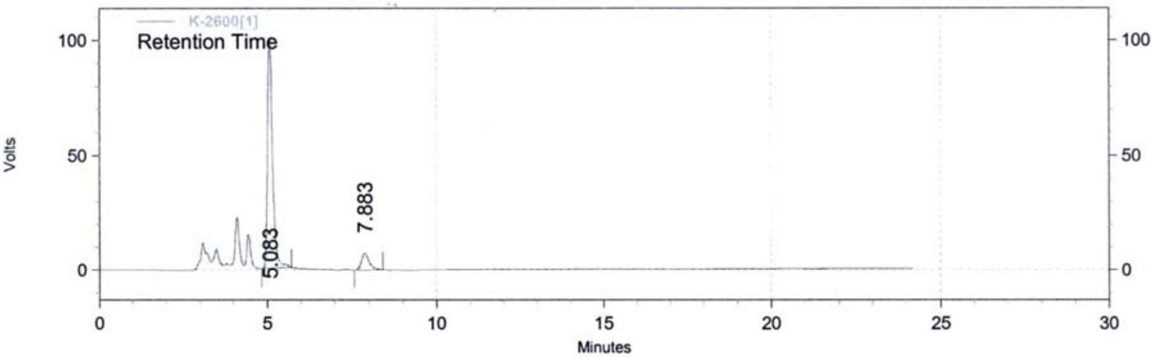




K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.067	308844	49.20	31368	61.06
7.783	318885	50.80	20008	38.94



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.083	1022565	89.40	100503	93.18
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Table2, entry 2

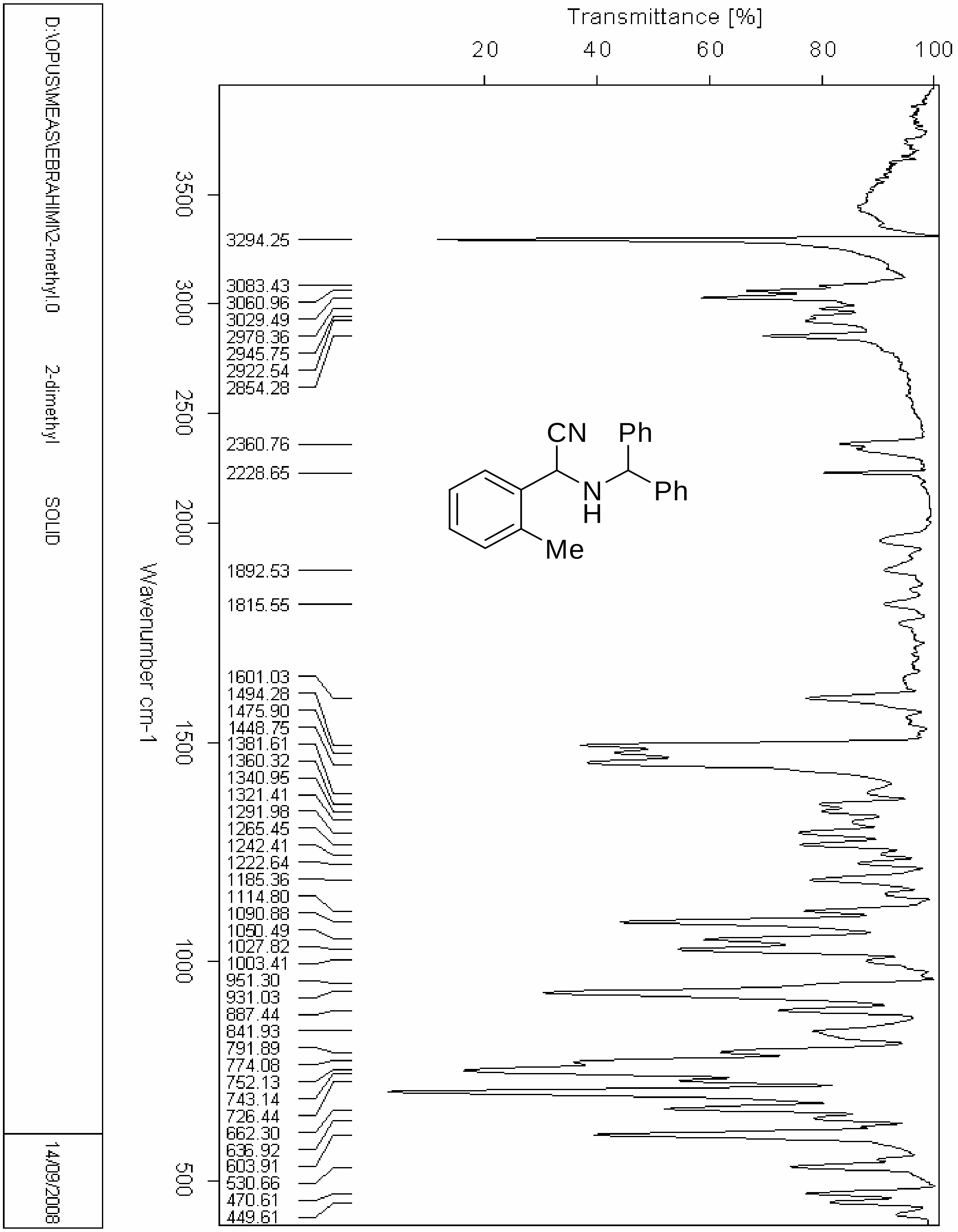
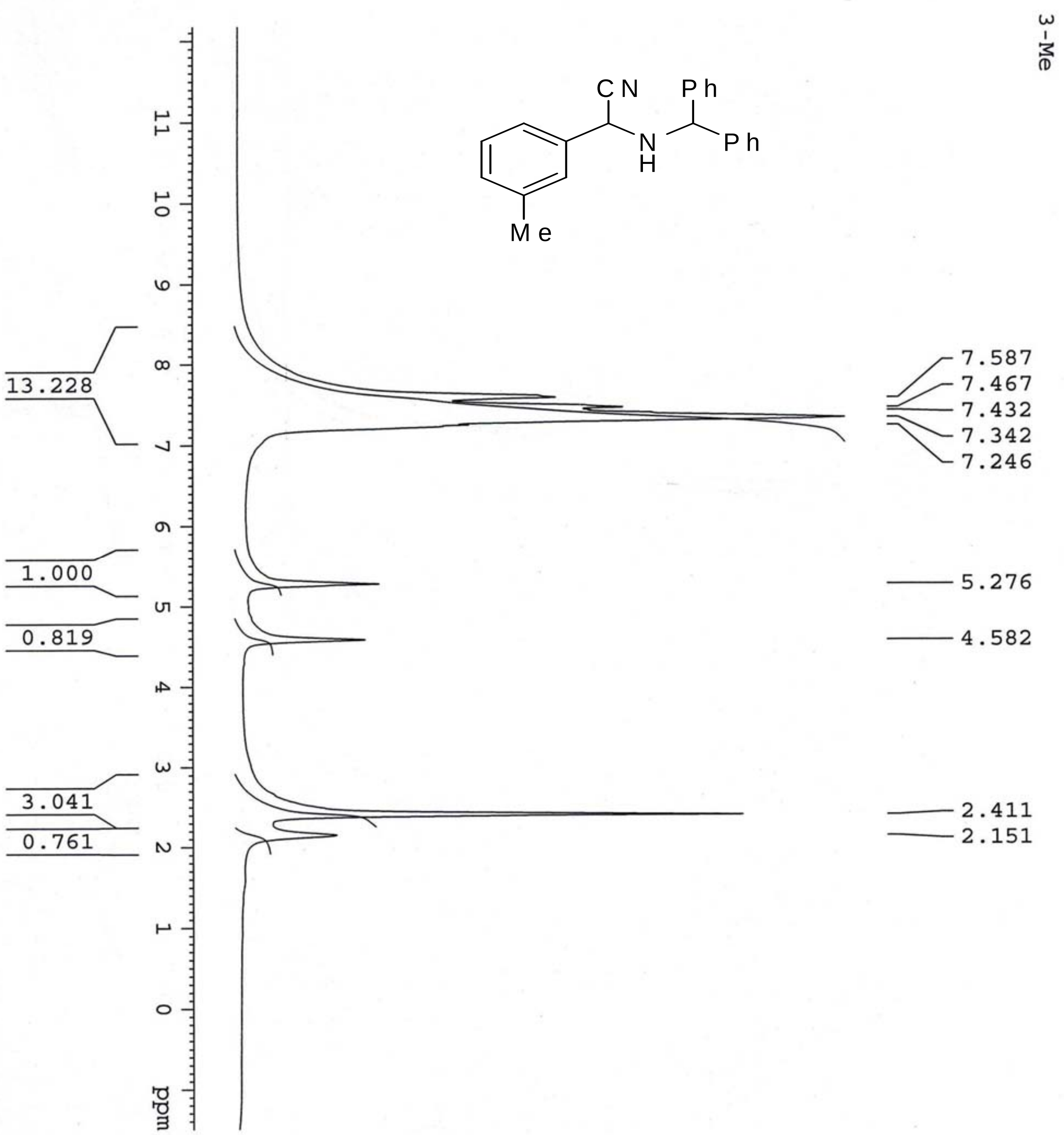


Table2, entry 3



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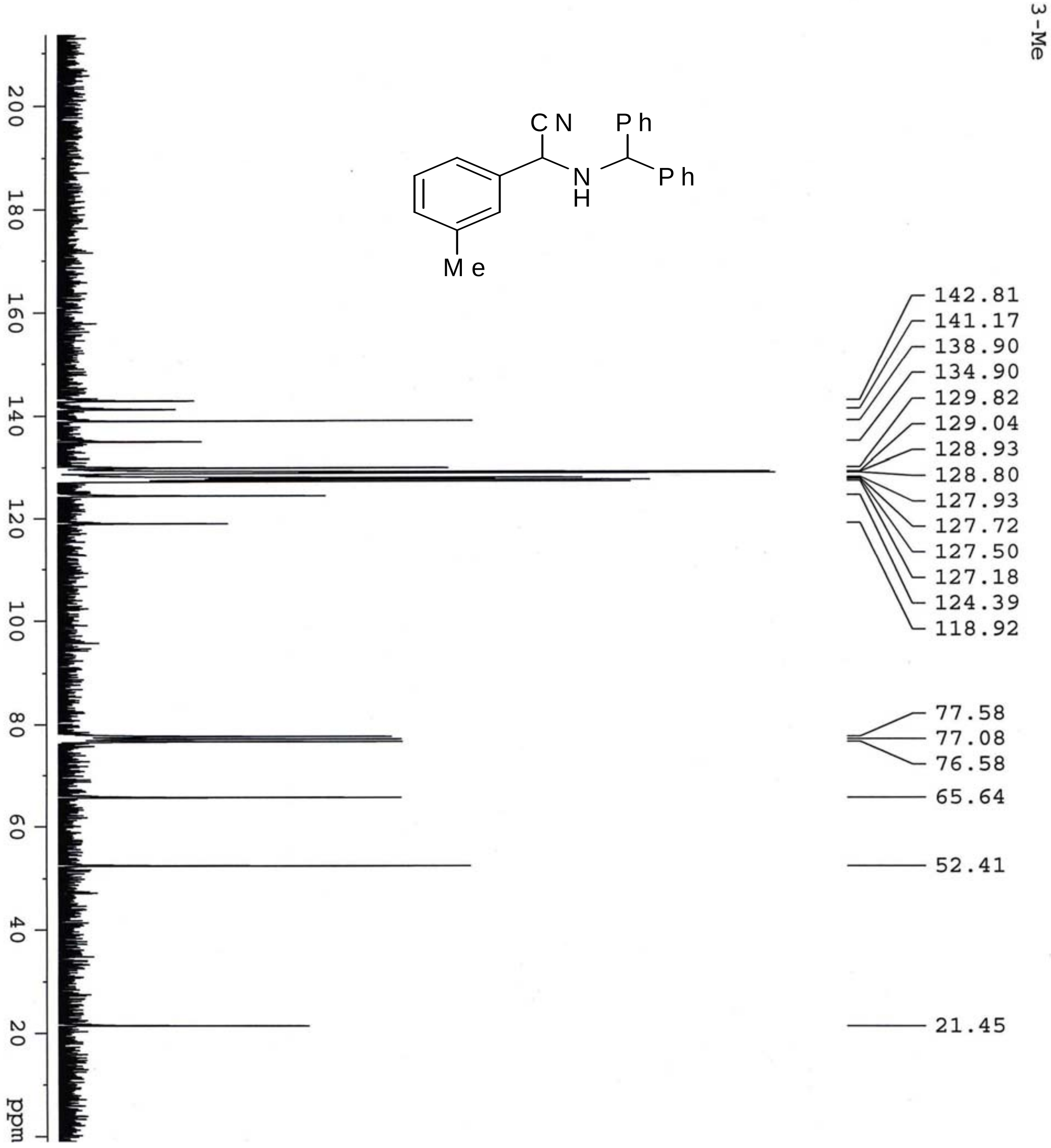

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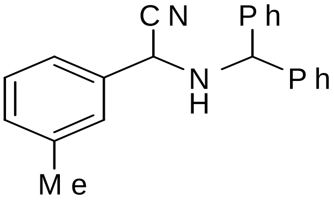

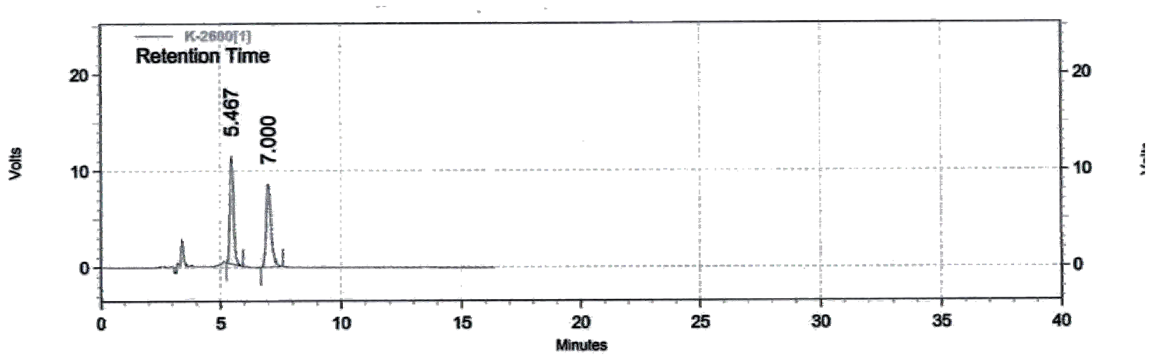

K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
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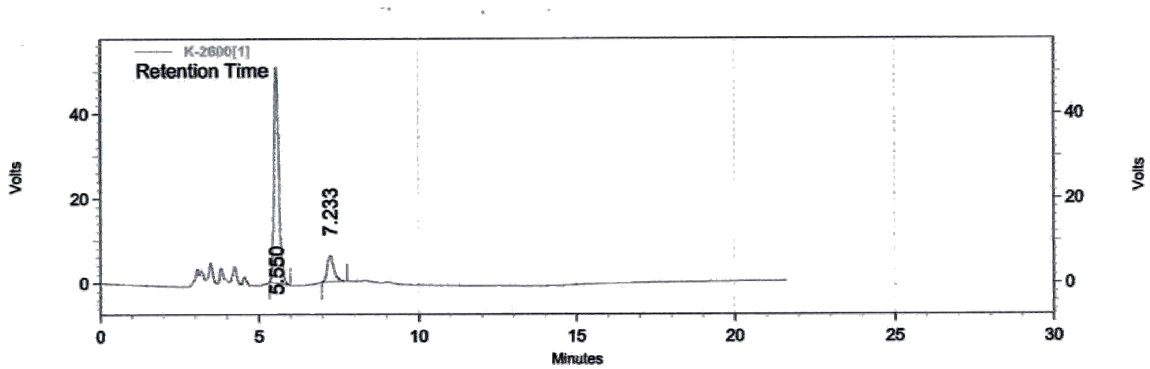

K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.550	533046	85.71	51134	89.27
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Table2, entry 3

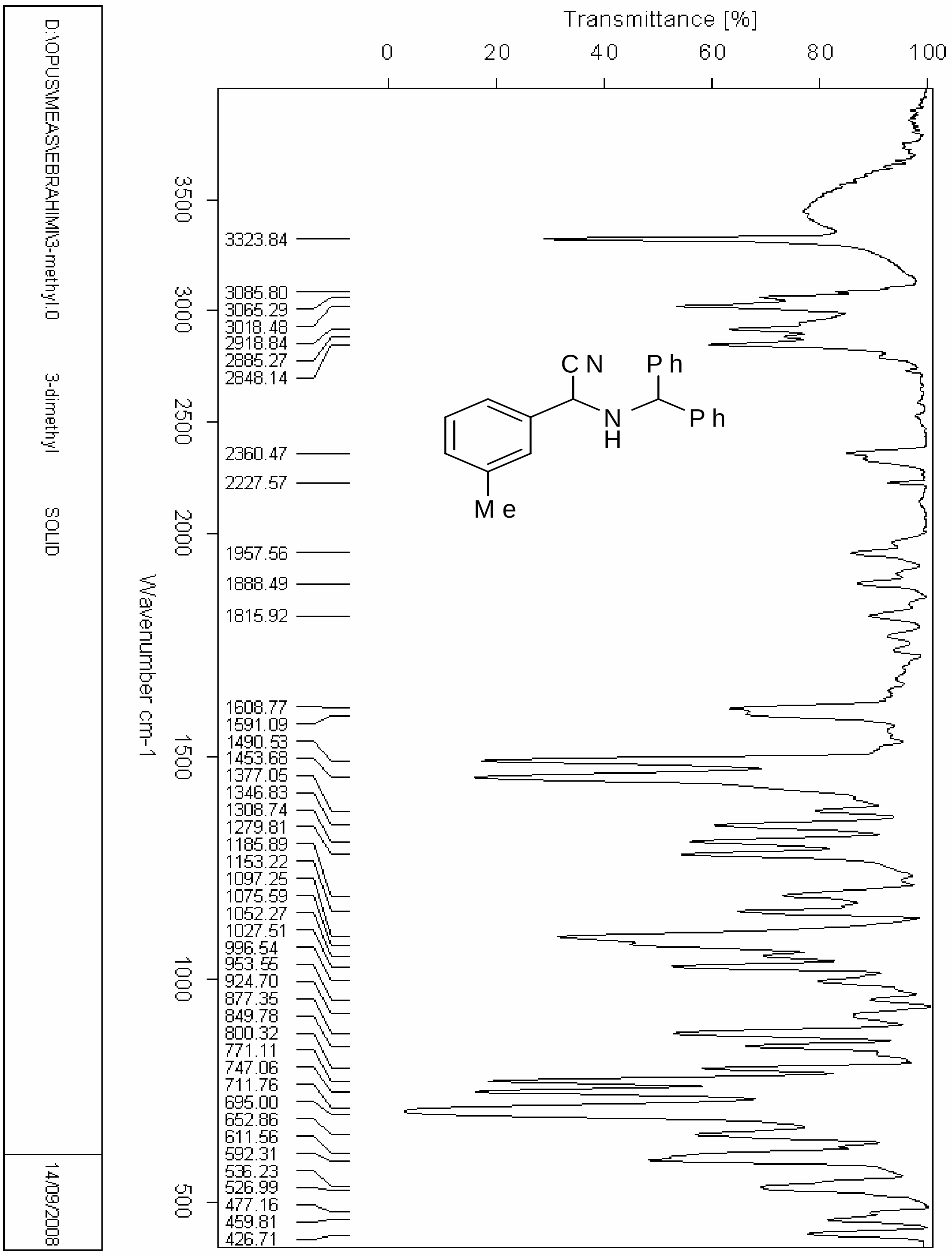
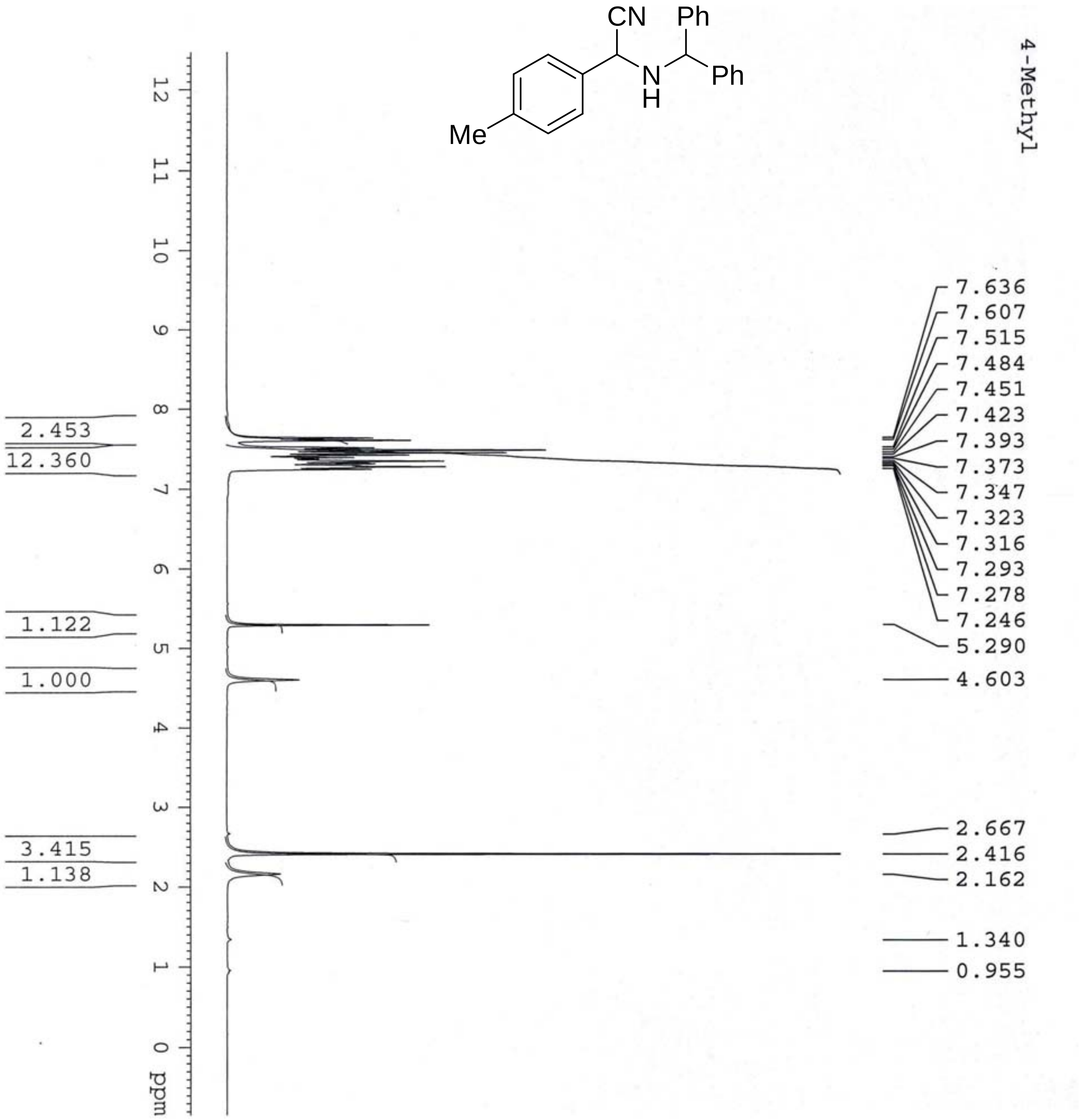


Table2, entry 4



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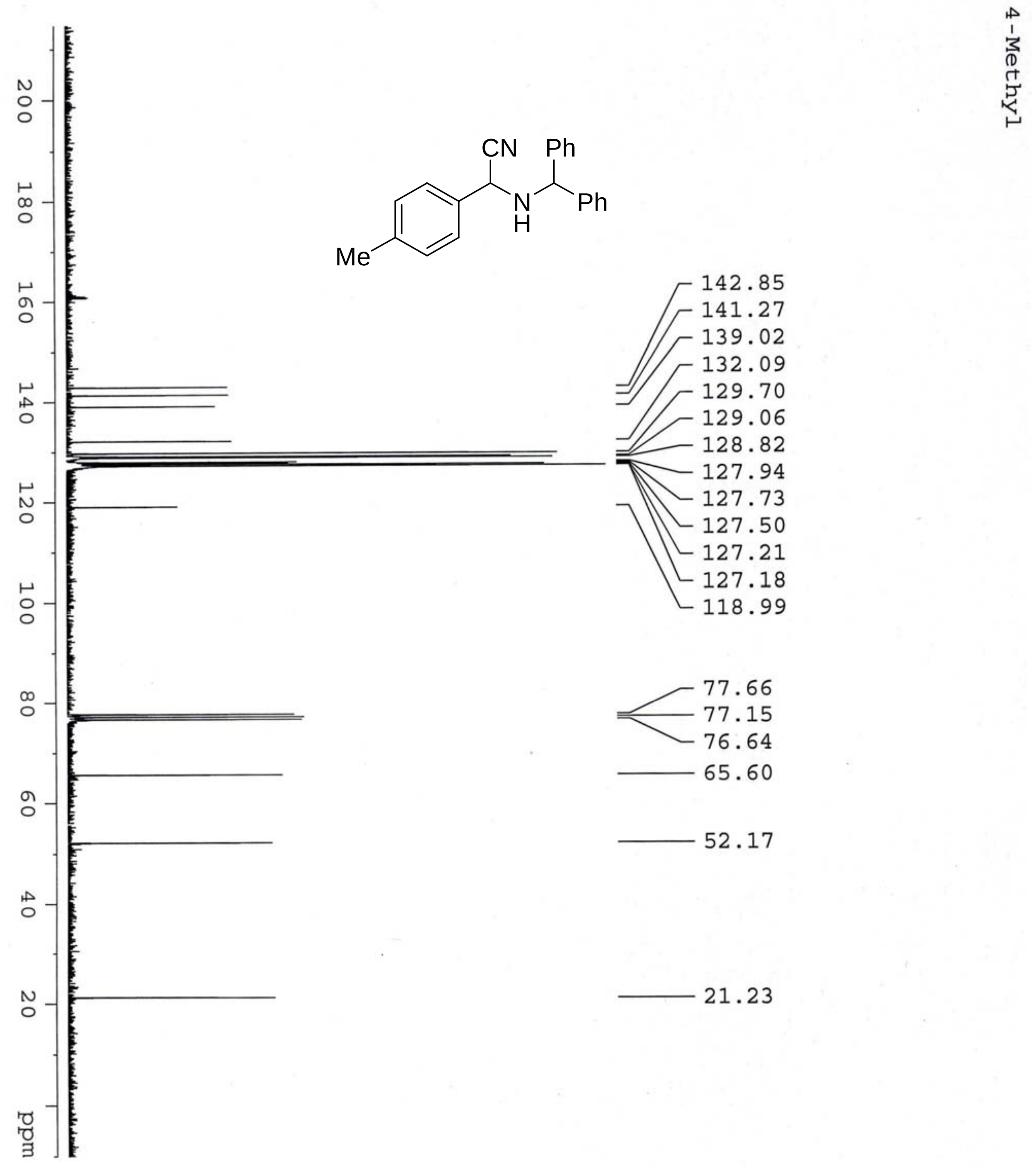
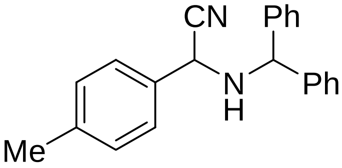
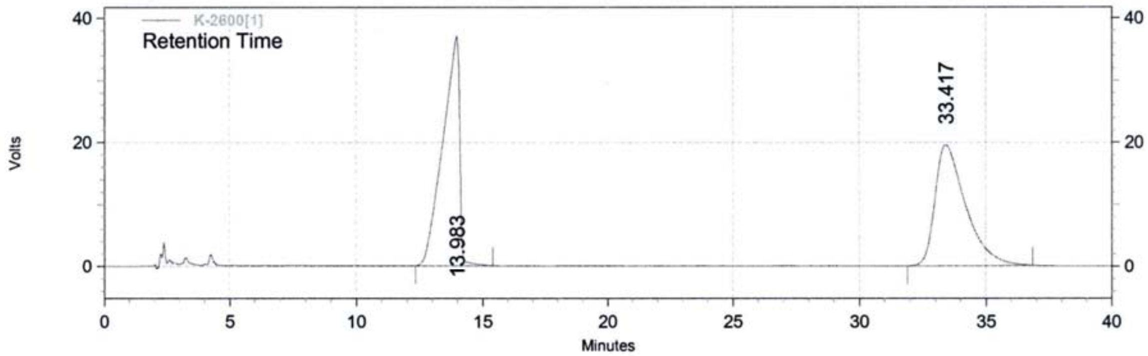


Table2, entry 4





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
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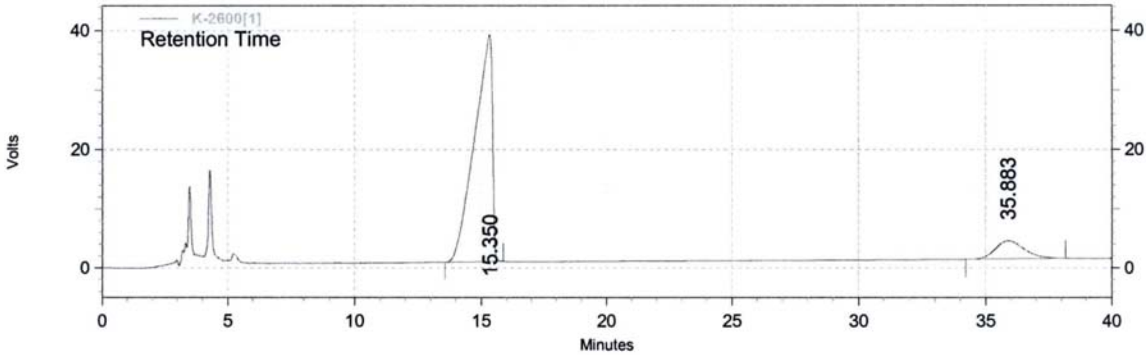
33.417	1636272	49.82	19443	34.49



K-2600[1] Results

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Table2, entry 4

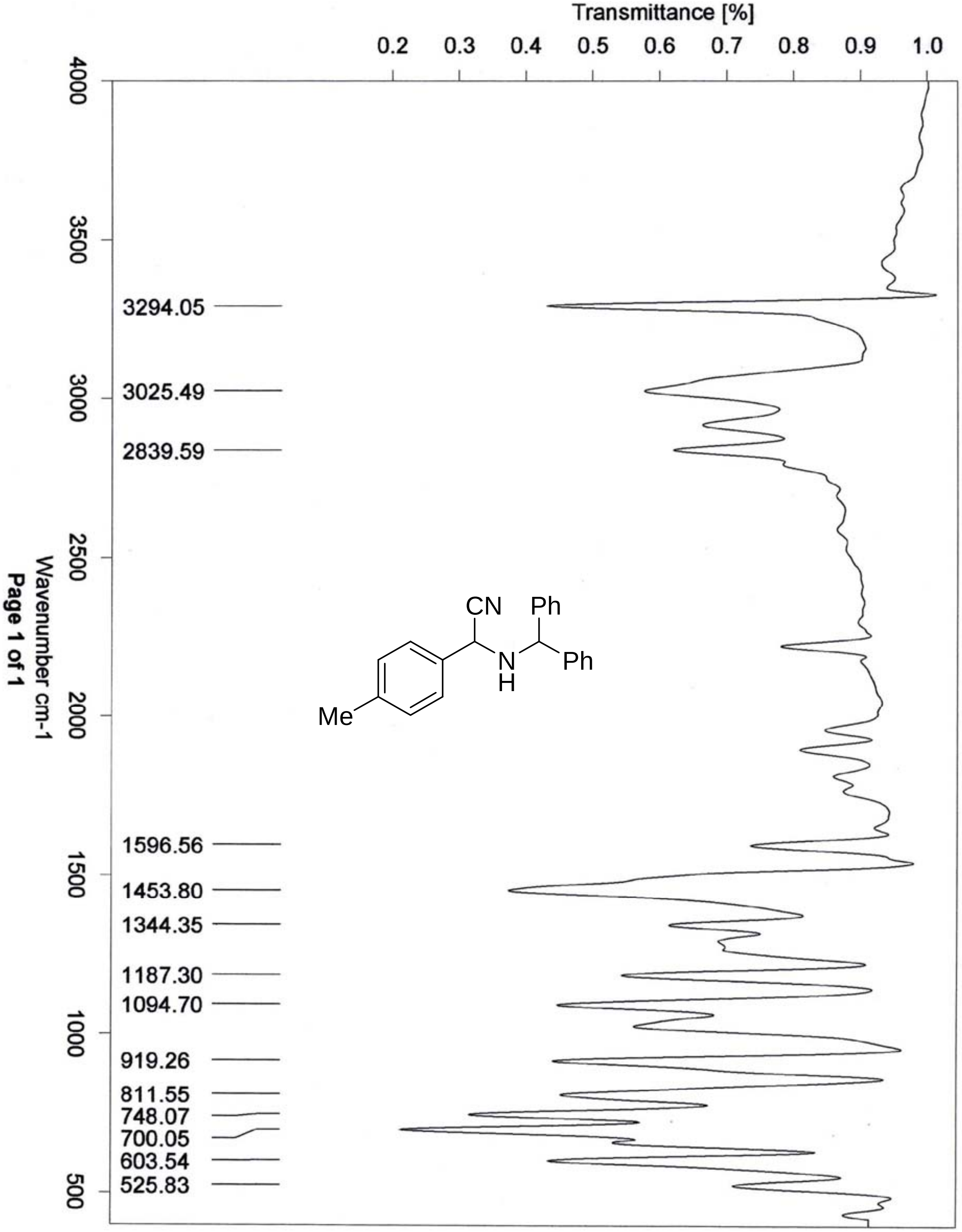
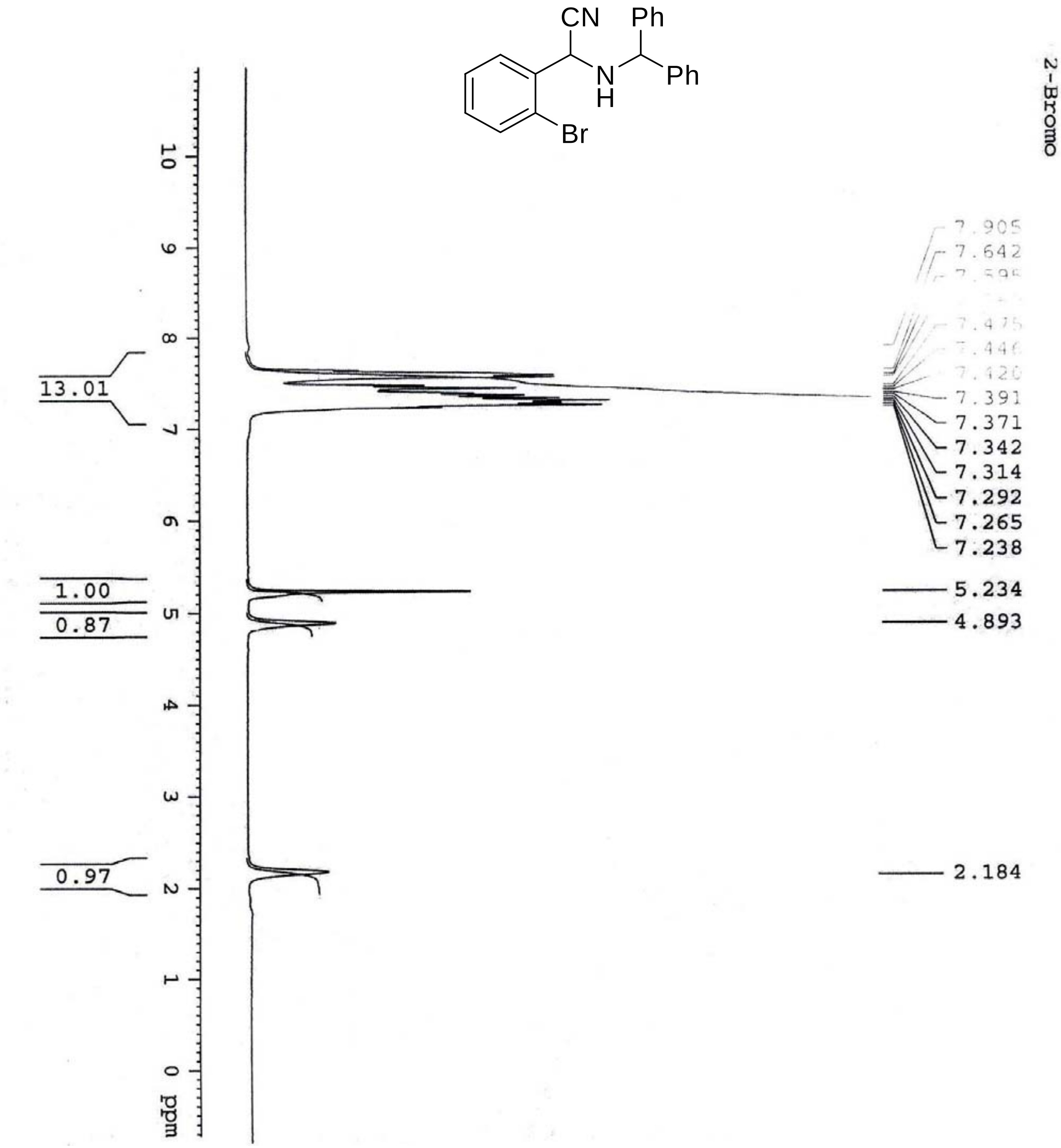


Table2, entry 5



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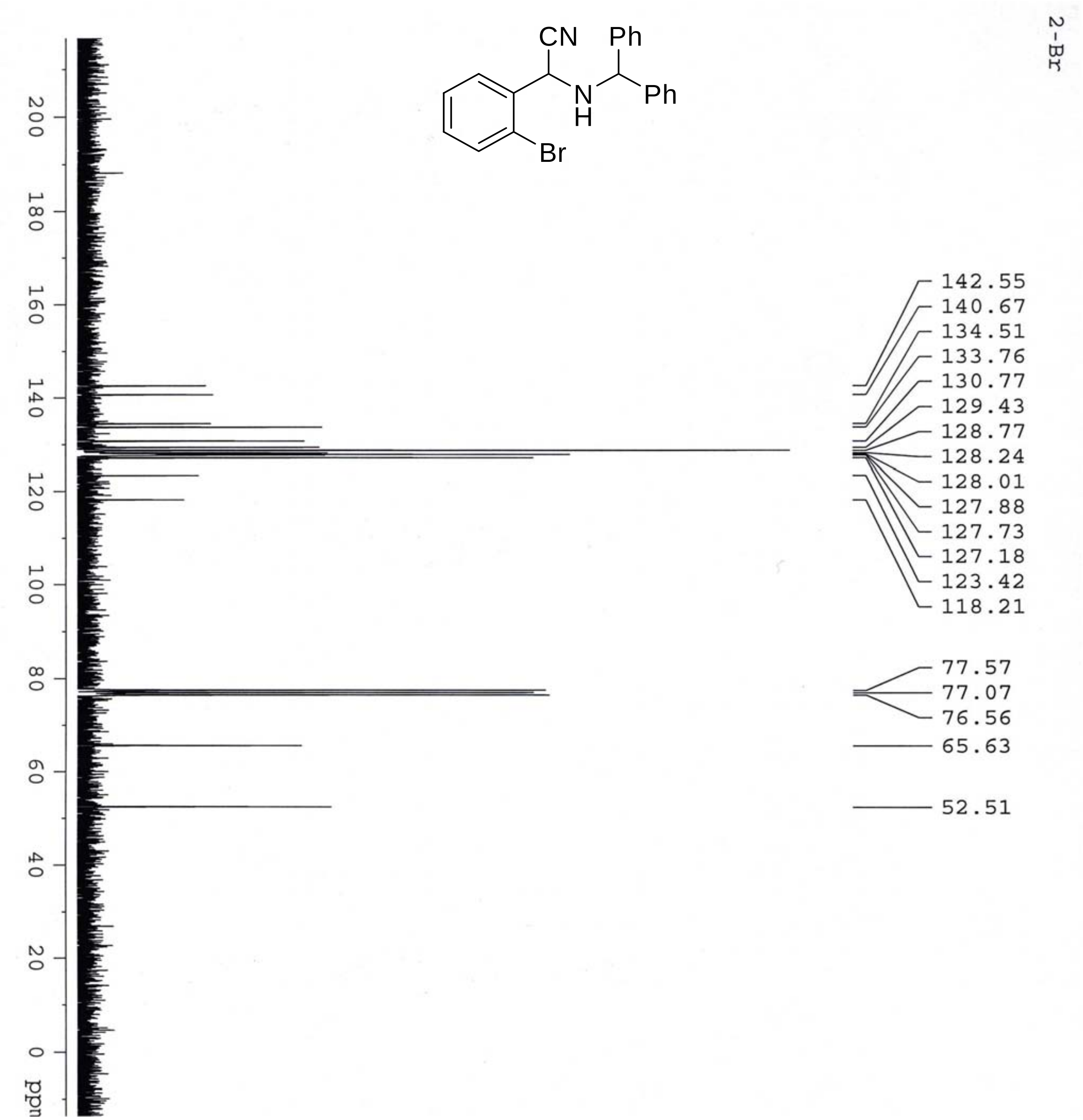
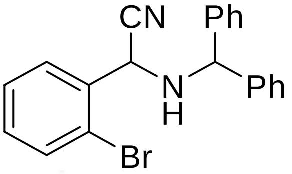
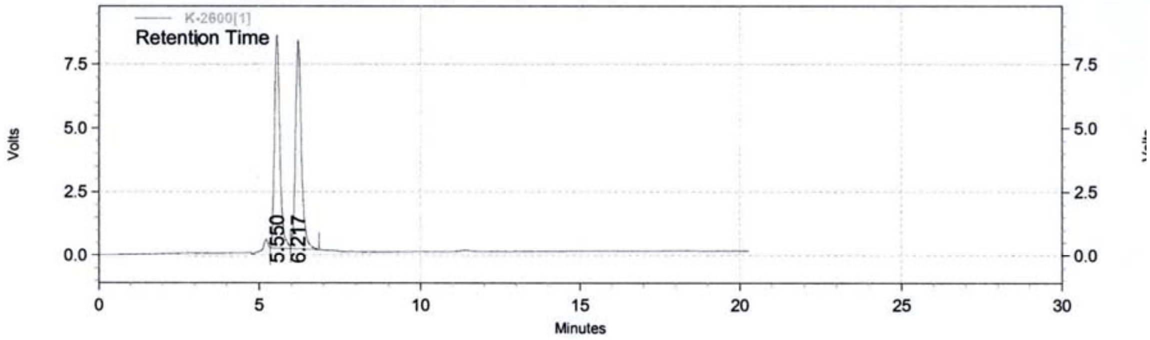


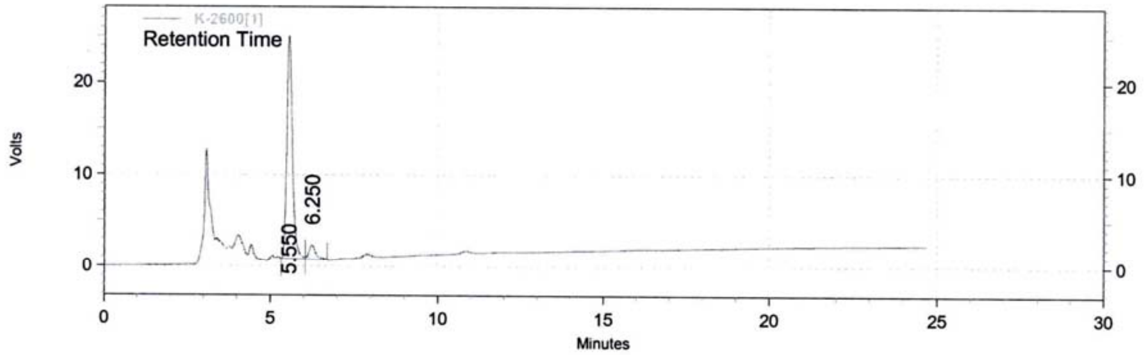
Table2, entry 5





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.550	100900	49.46	8372	50.52
6.217	103104	50.54	8199	49.48



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.550	286250	92.80	24295	93.95
6.250	22213	7.20	1565	6.05

Table2, entry 5

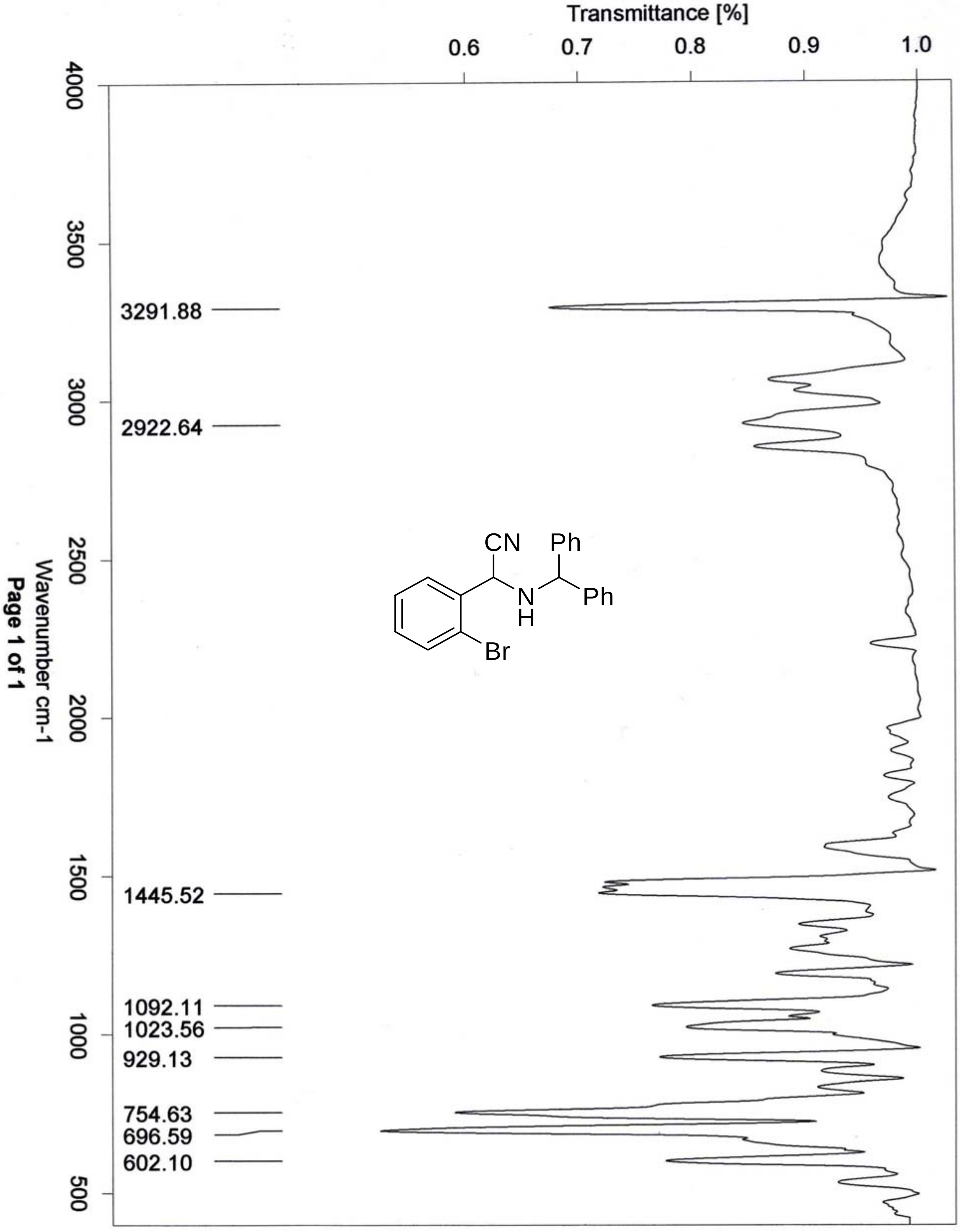


Table2, entry 6

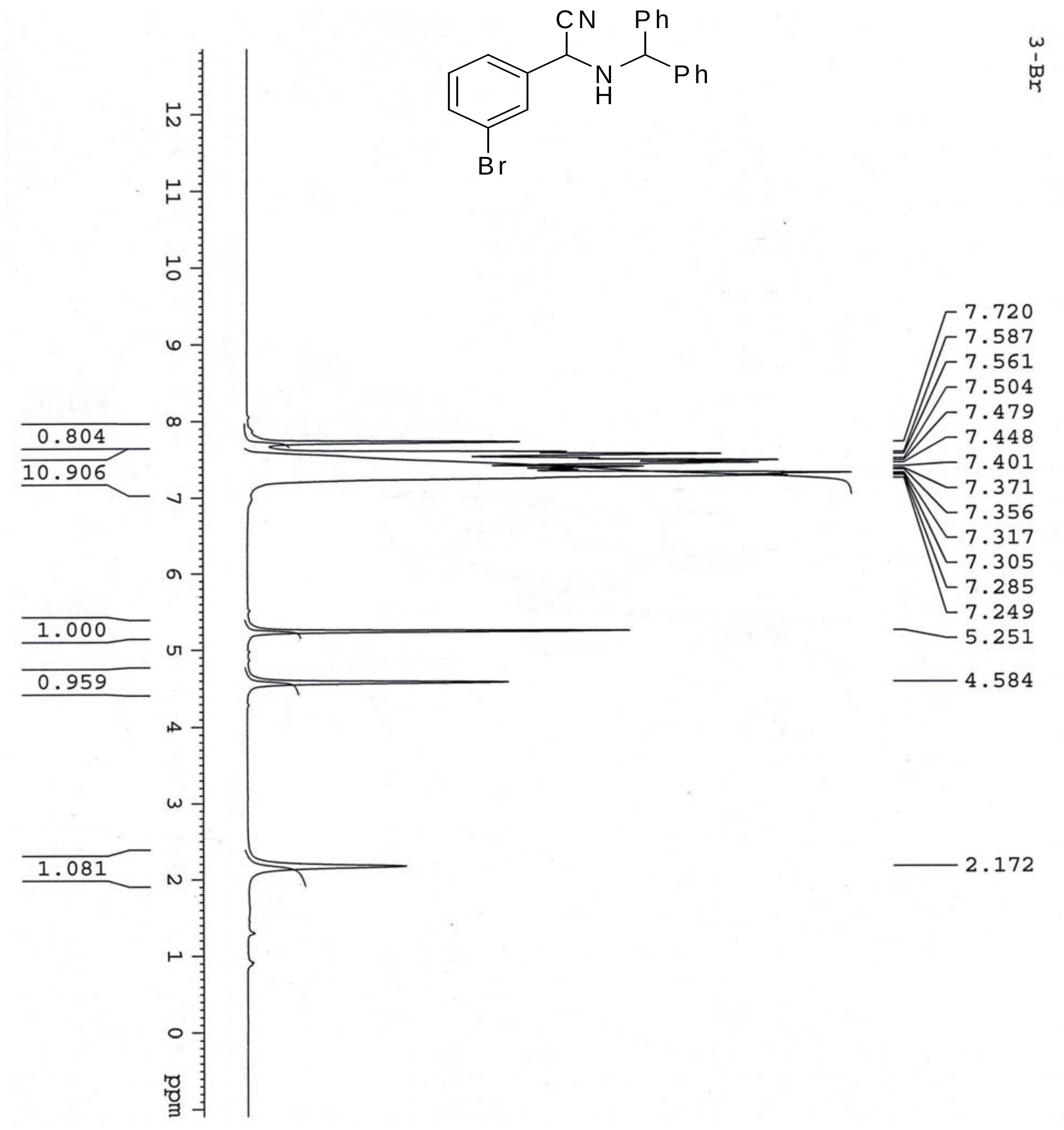


Table2, entry 6

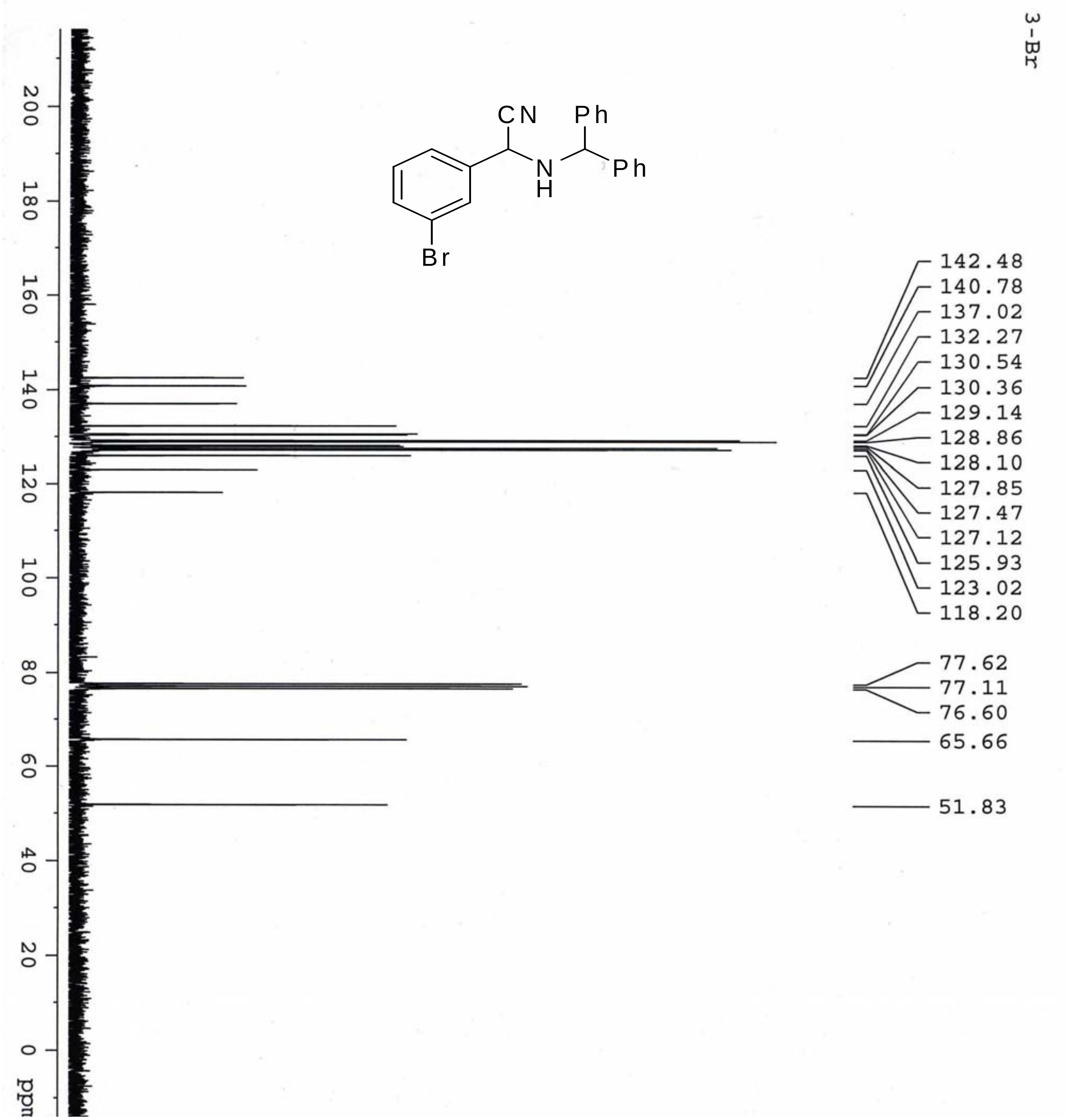
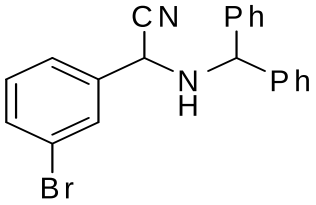
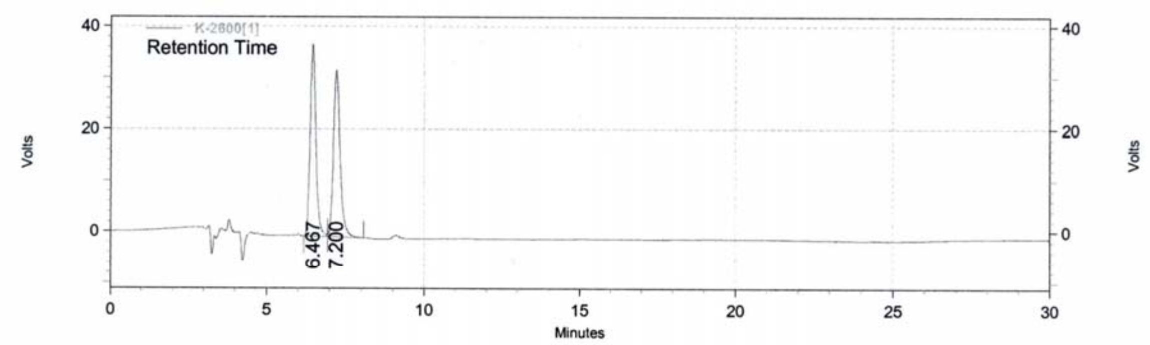


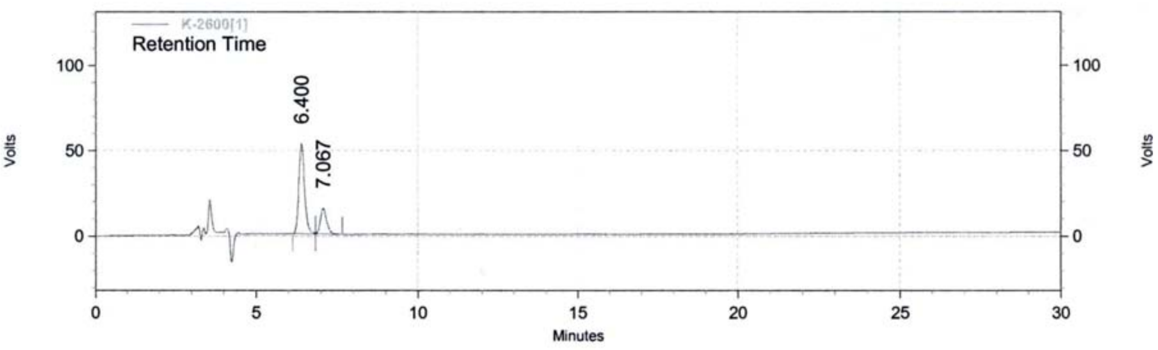
Table2, entry 6





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
6.467	478831	49.76	37539	53.58
7.200	483388	50.24	32518	46.42



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
6.400	652022	76.26	52641	77.76
7.067	202924	23.74	15053	22.24

Table2, entry 6

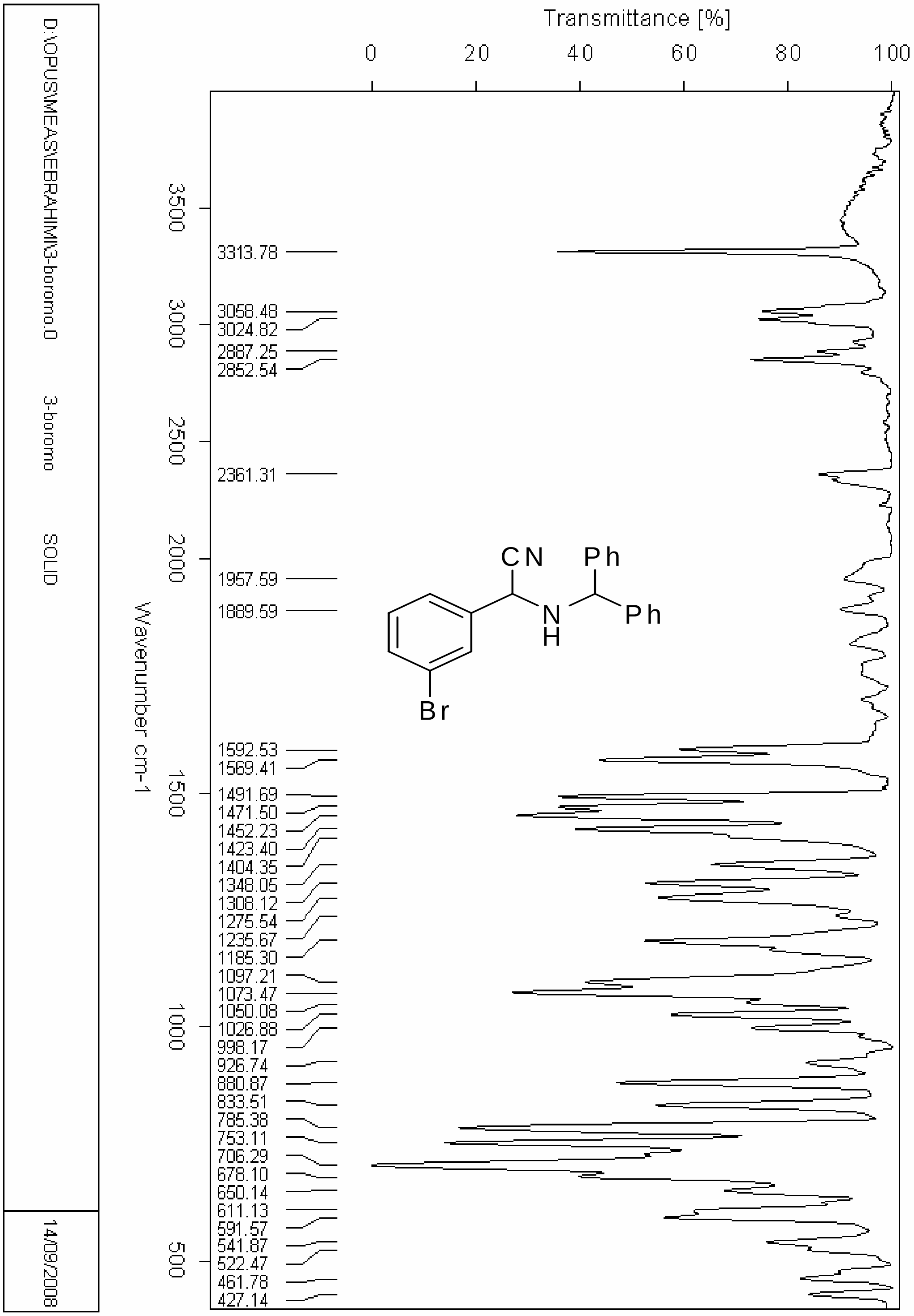


Table2, entry 7

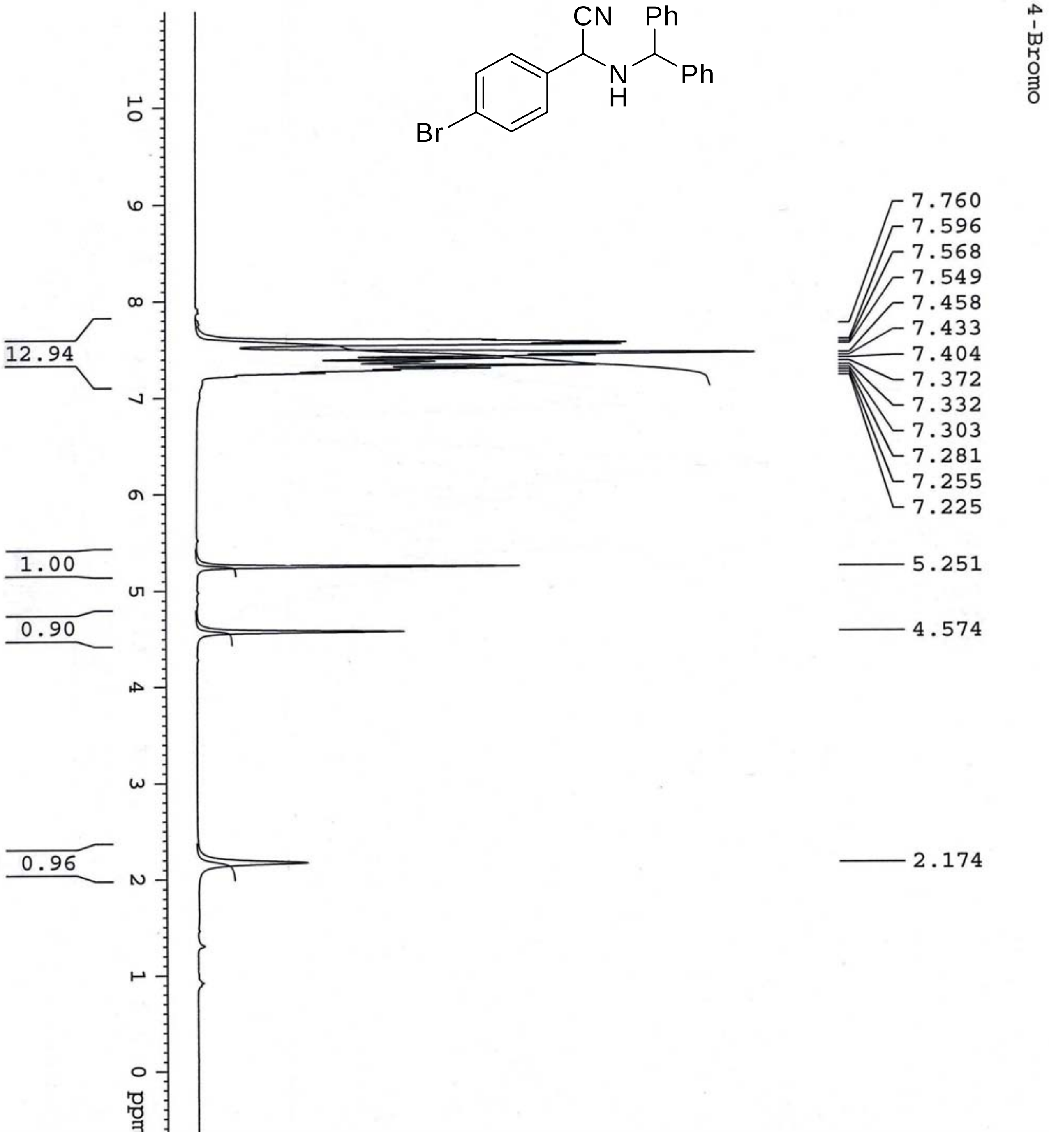


Table2, entry 7

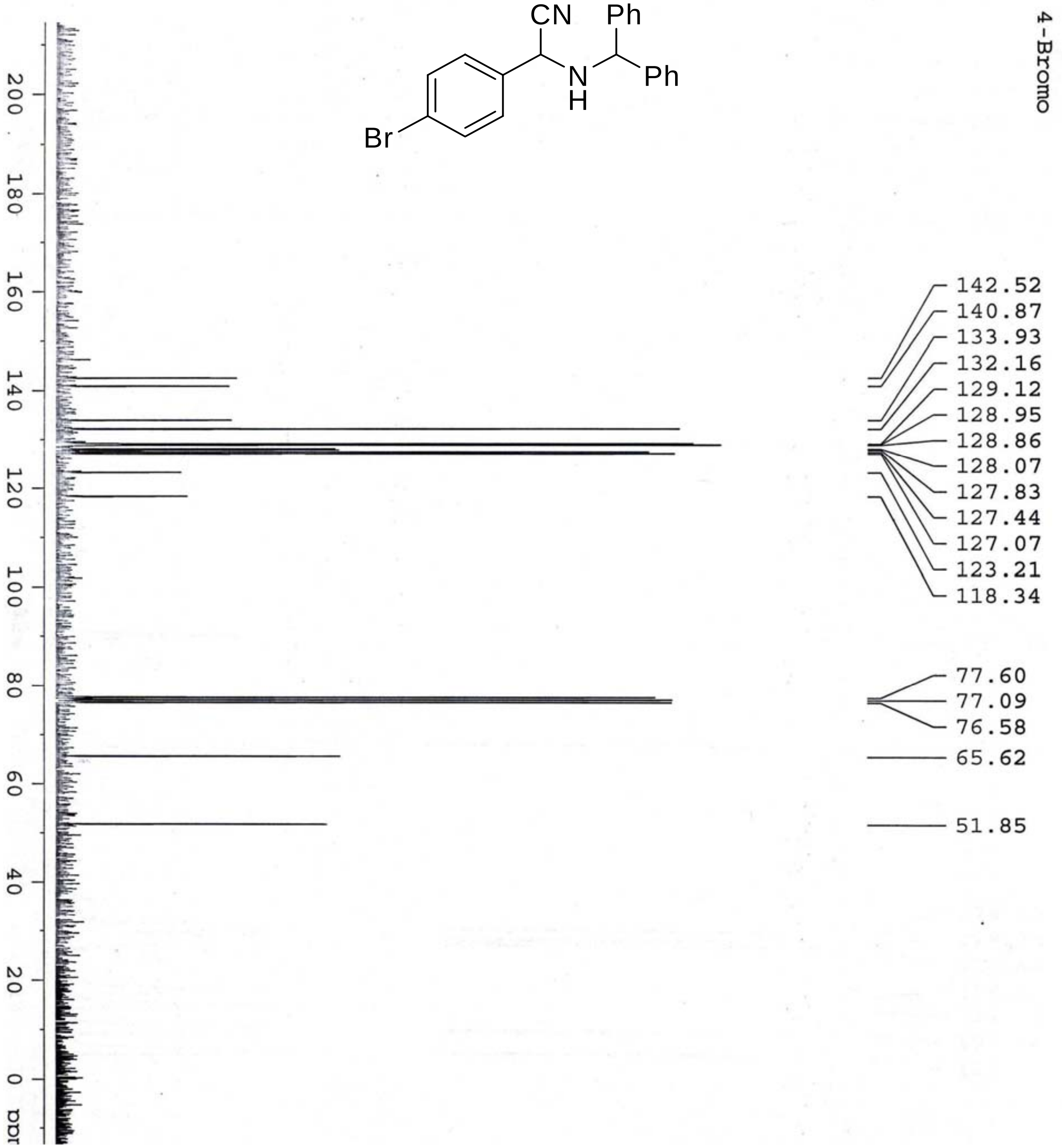
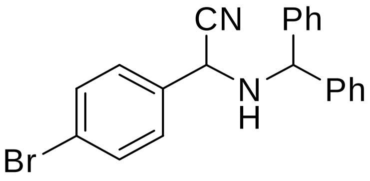
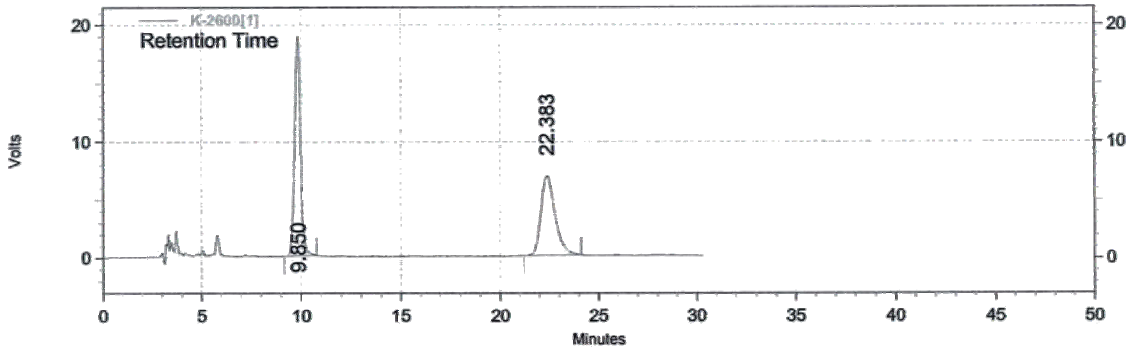


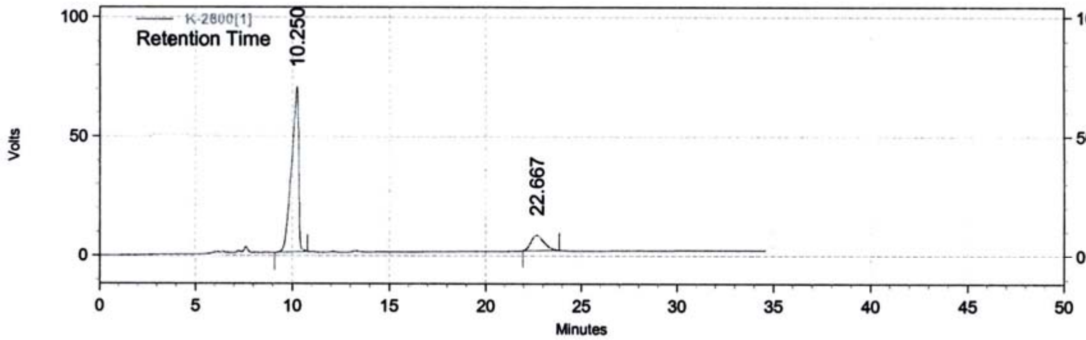
Table 2, entry 7





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
9.850	342685	50.07	18866	73.43
22.383	341727	49.93	6825	26.57



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
10.250	1745526	85.32	69255	91.60
22.667	300270	14.68	6351	8.40

Table 2, entry 7

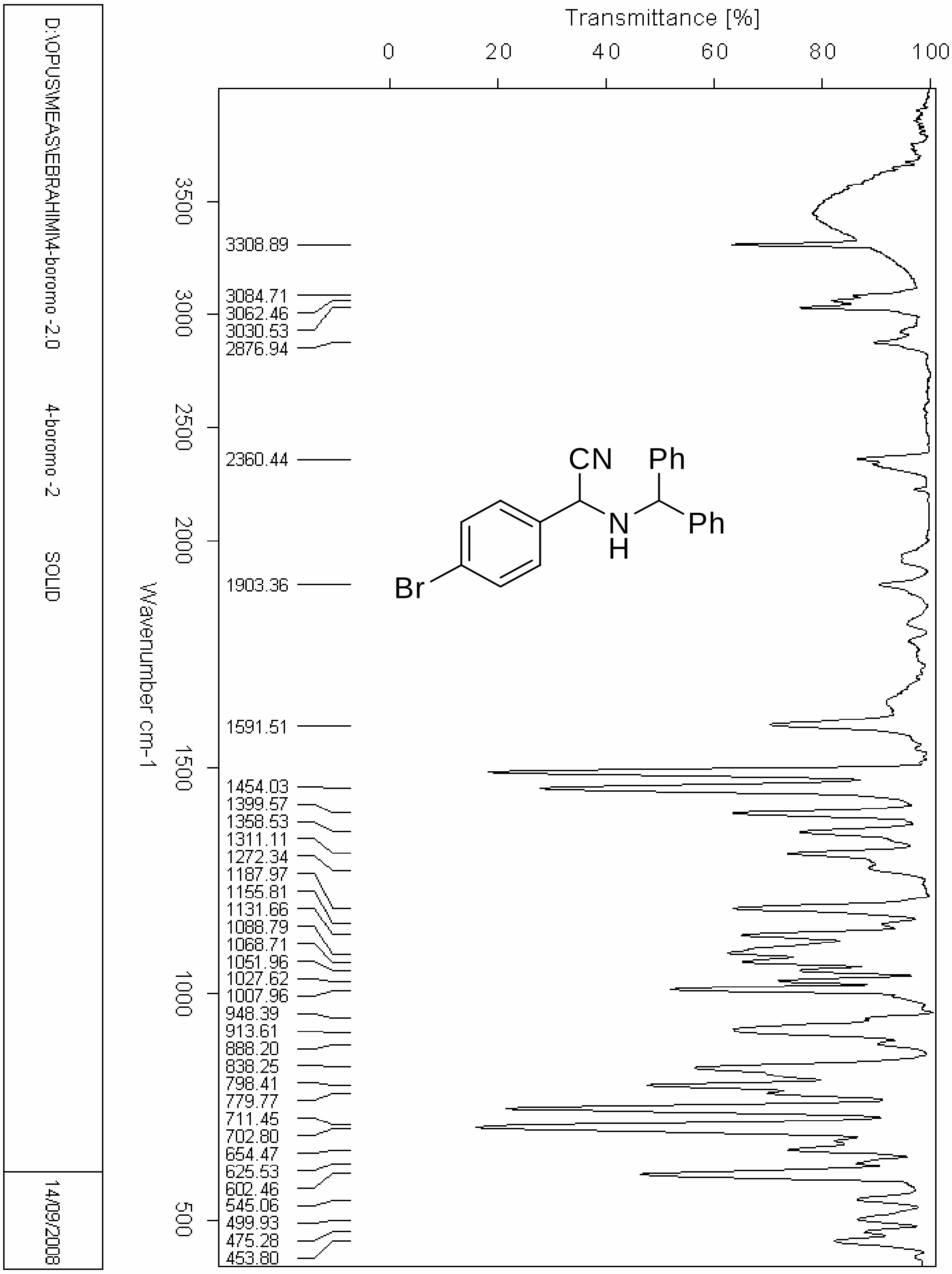


Table 2, entry 8

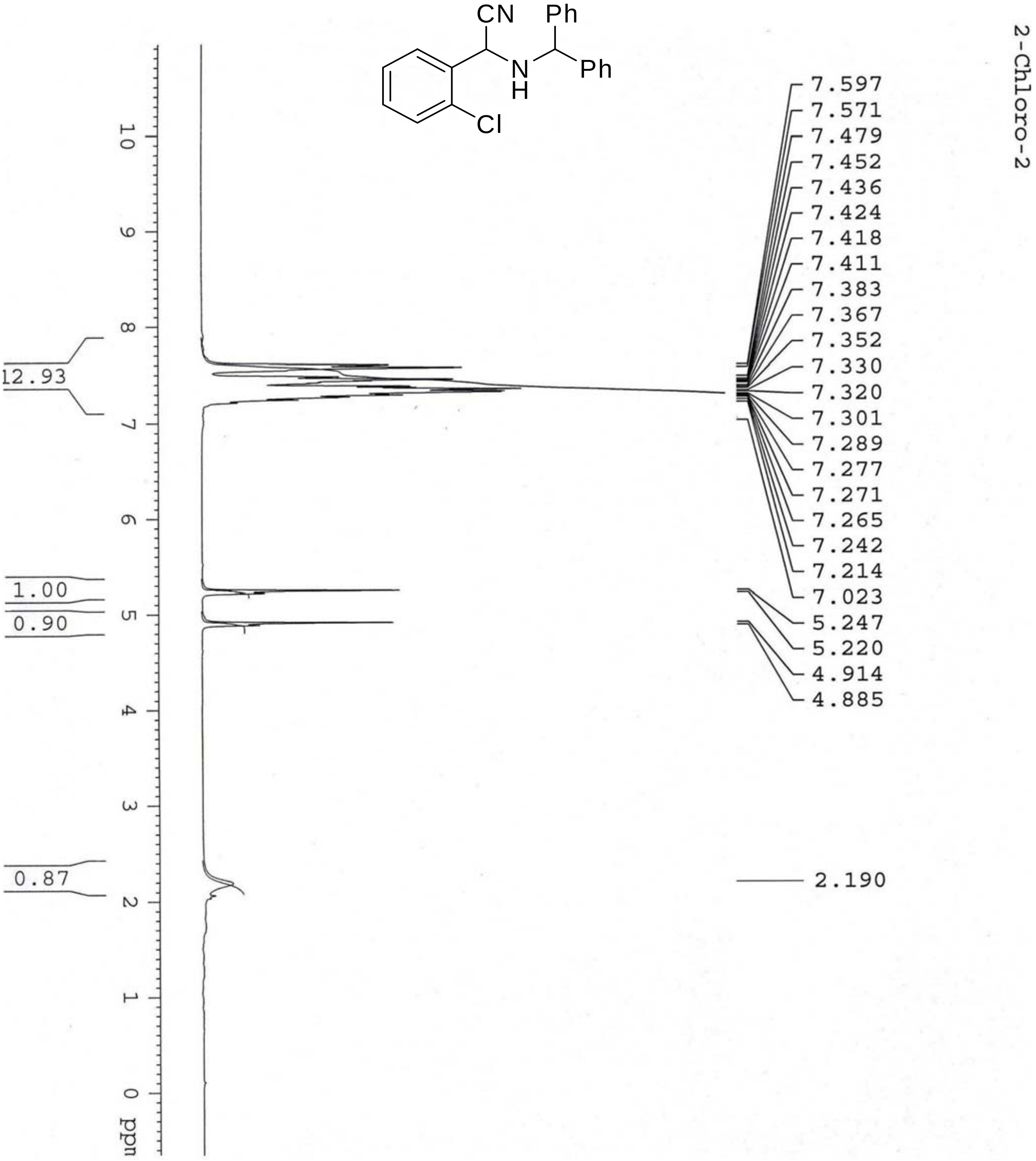


Table 2, entry 8

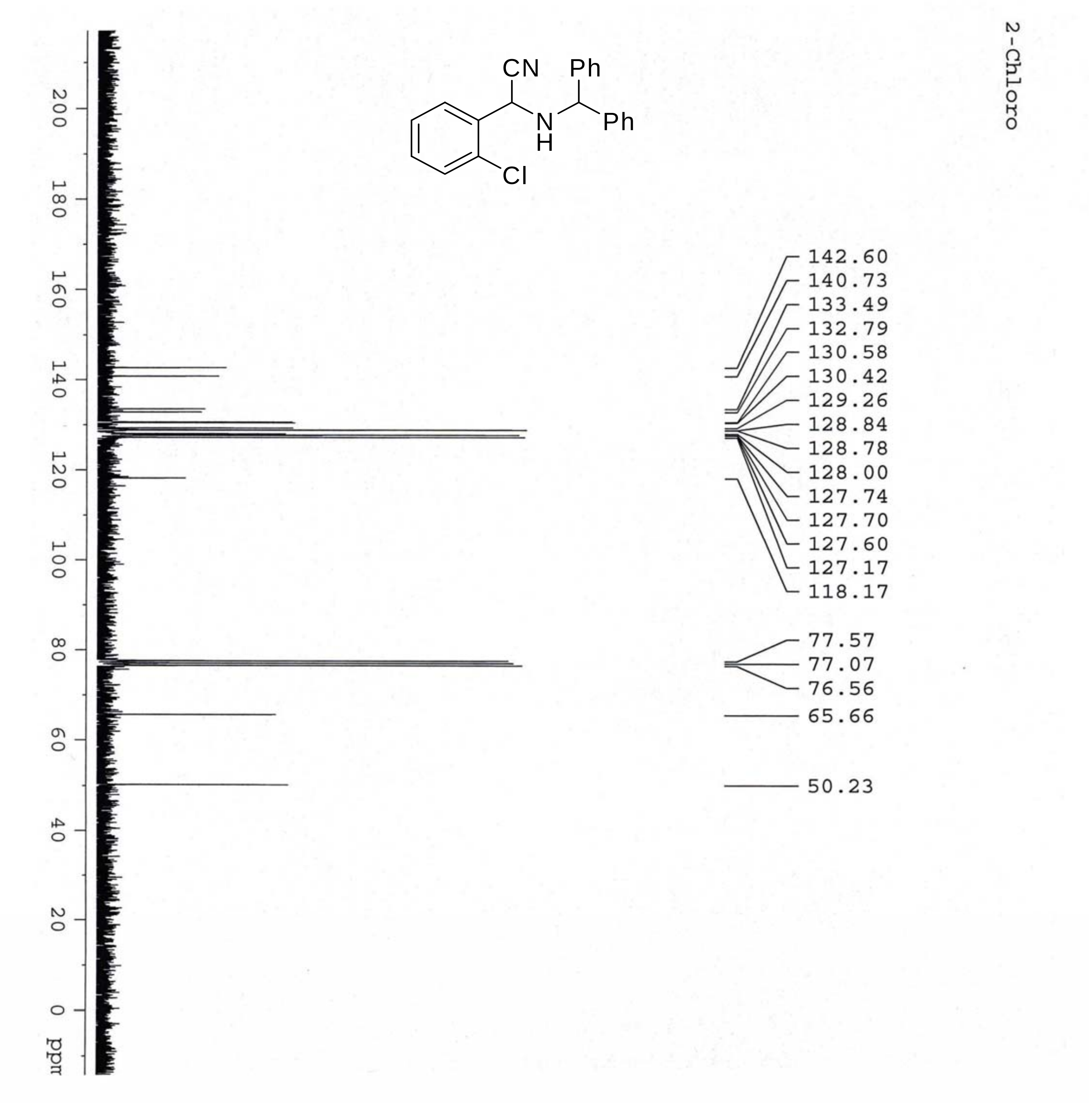
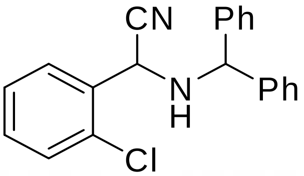
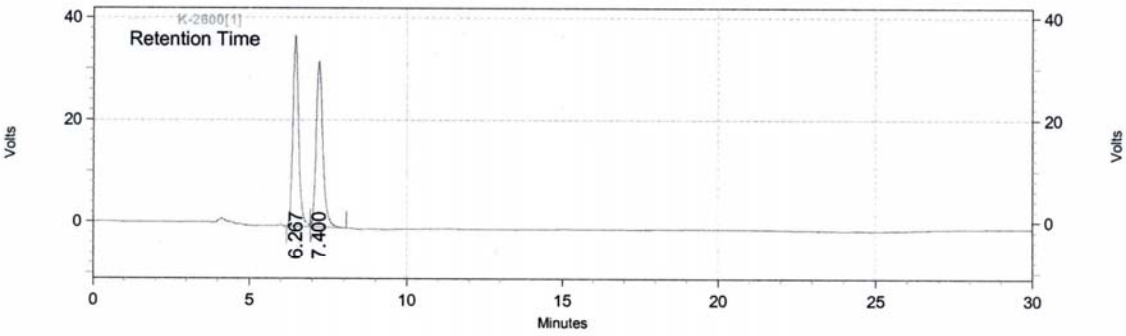


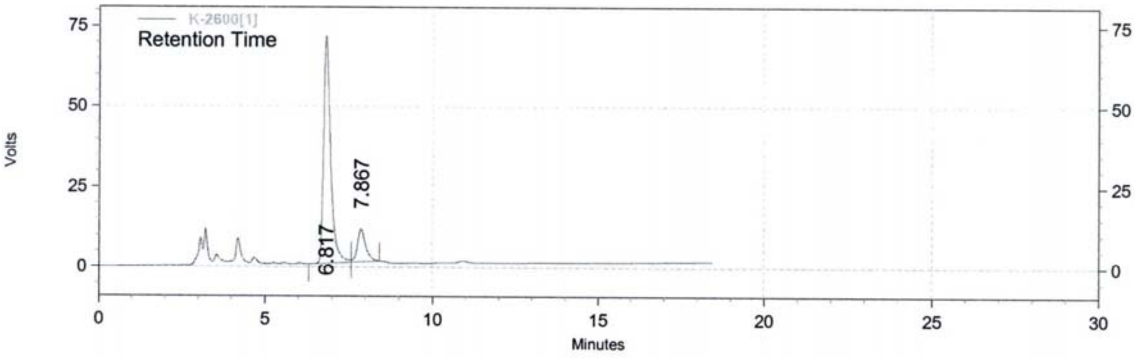
Table 2, entry 8





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
6.267	4657745	49.71	289406	58.34
7.400	4604059	50.29	206662	41.66



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
6.817	1034880	85.65	70828	87.48
7.867	173435	14.35	10138	12.52

Table 2, entry 8

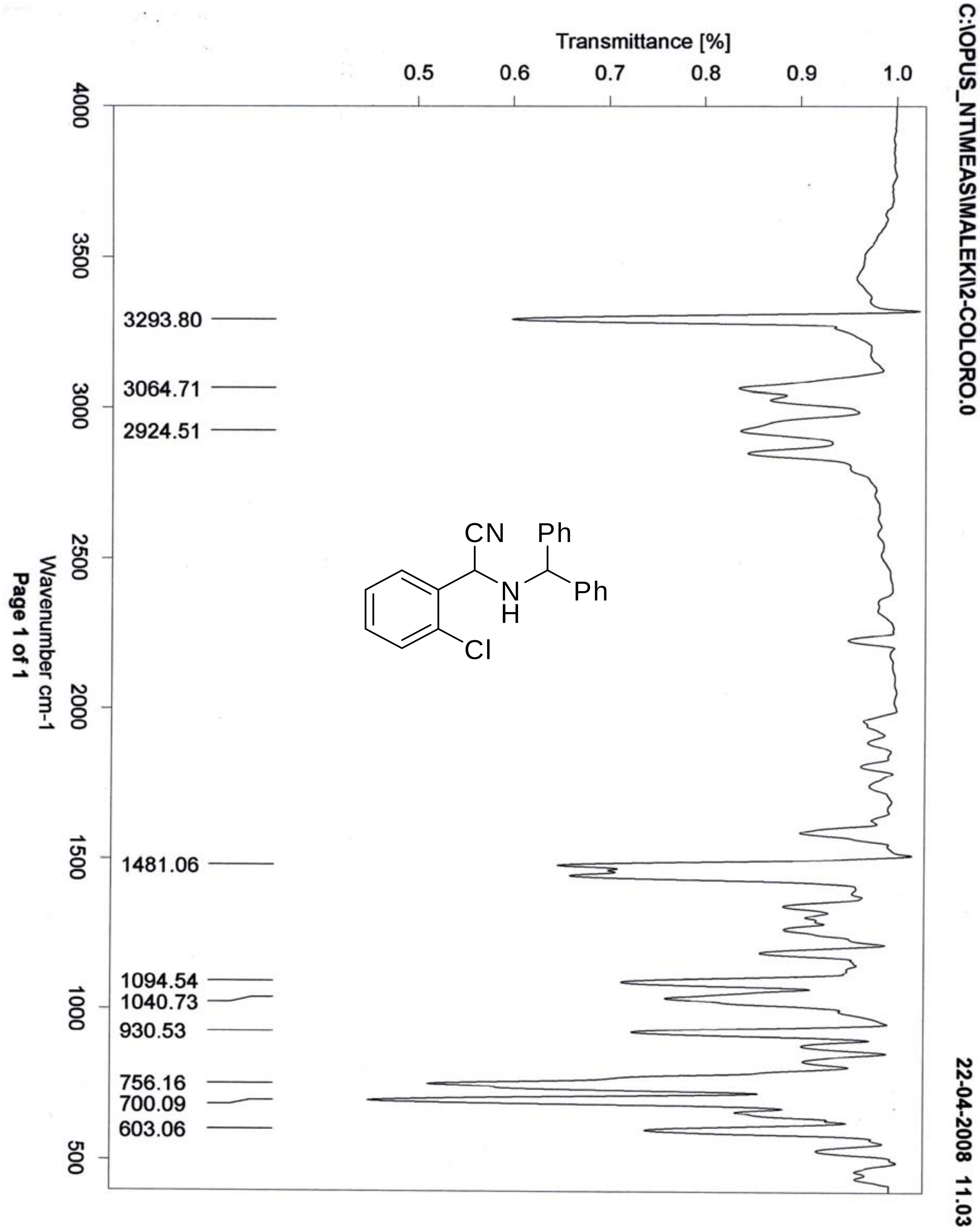


Table 2, entry 9

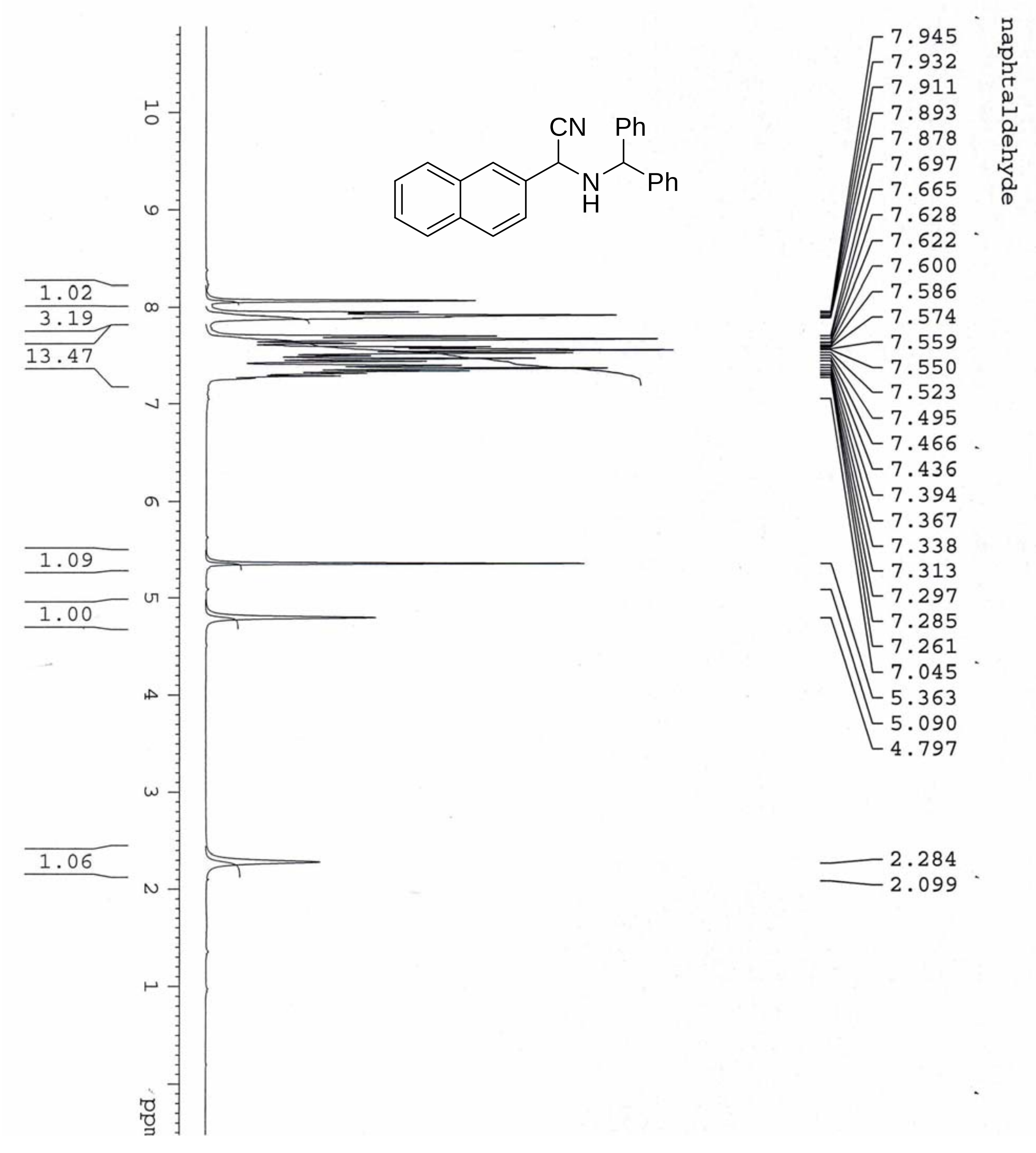


Table 2, entry 9

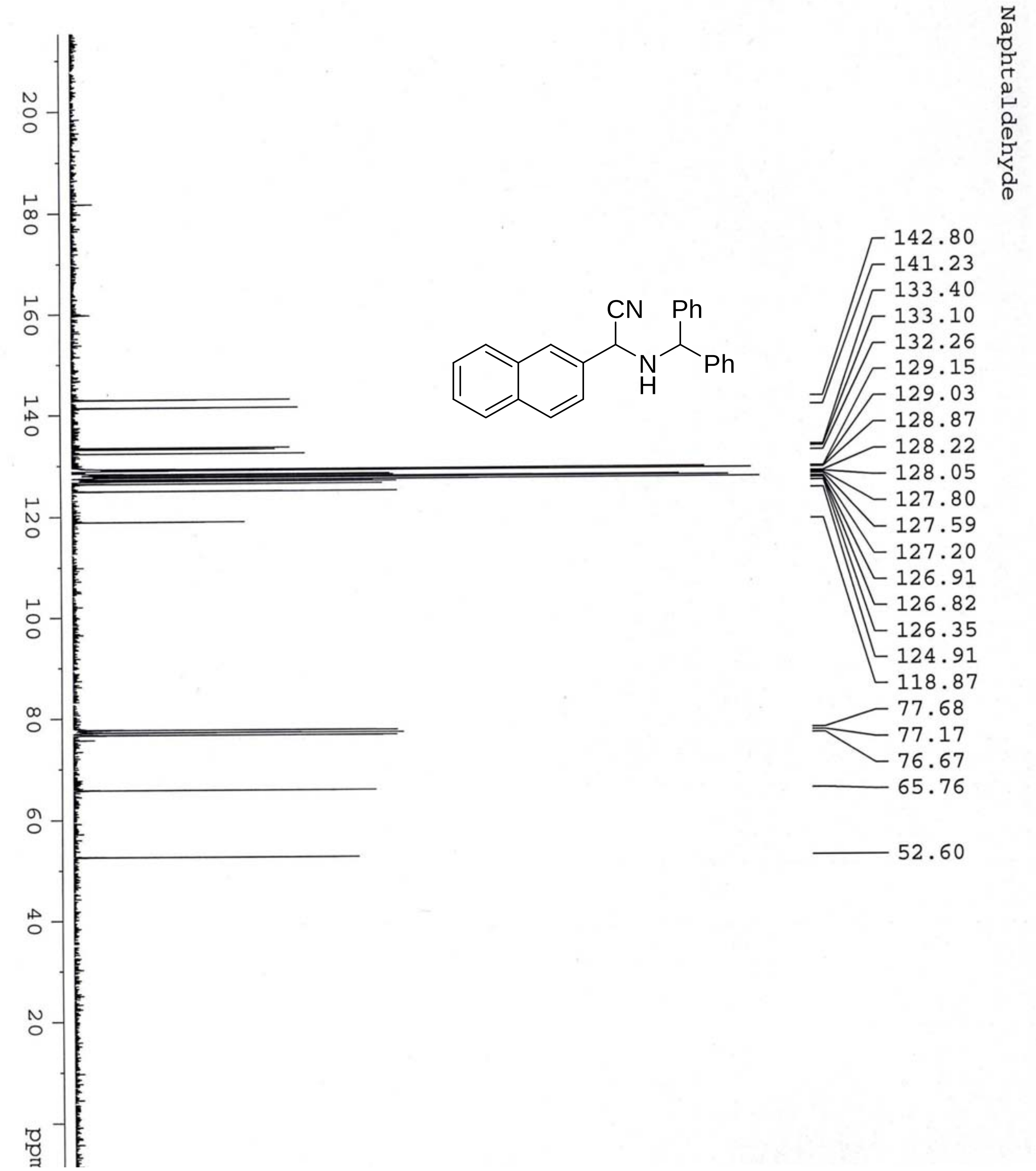
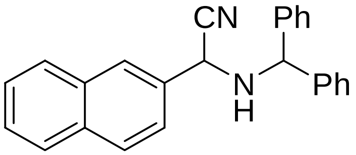
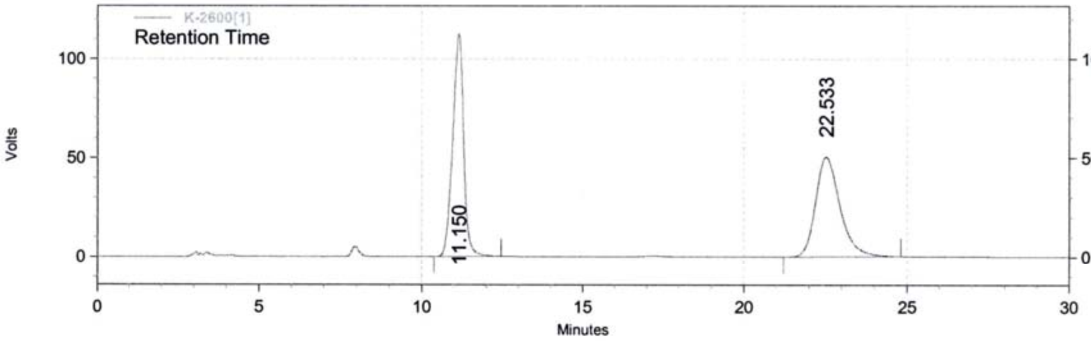


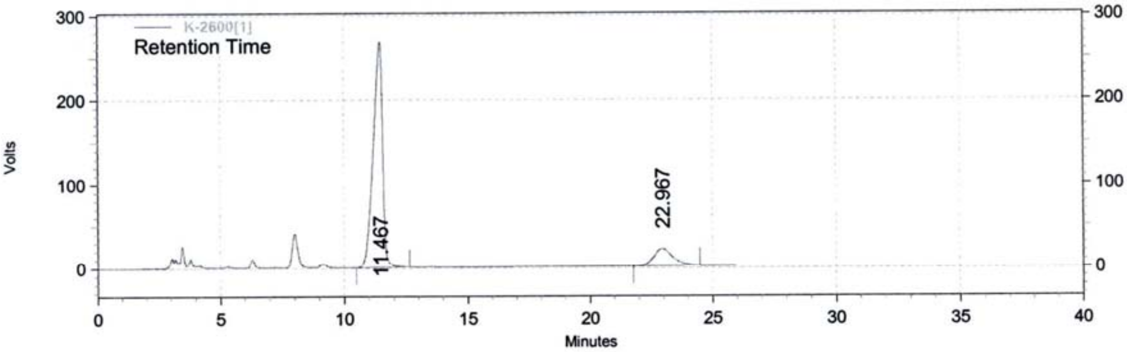
Table 2, entry 9





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
11.150	2648054	50.25	112474	69.08
22.533	2622141	49.75	50334	30.92



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
11.467	6974077	86.87	267763	93.00
22.967	1054496	13.13	20149	7.00

Table 2, entry 9

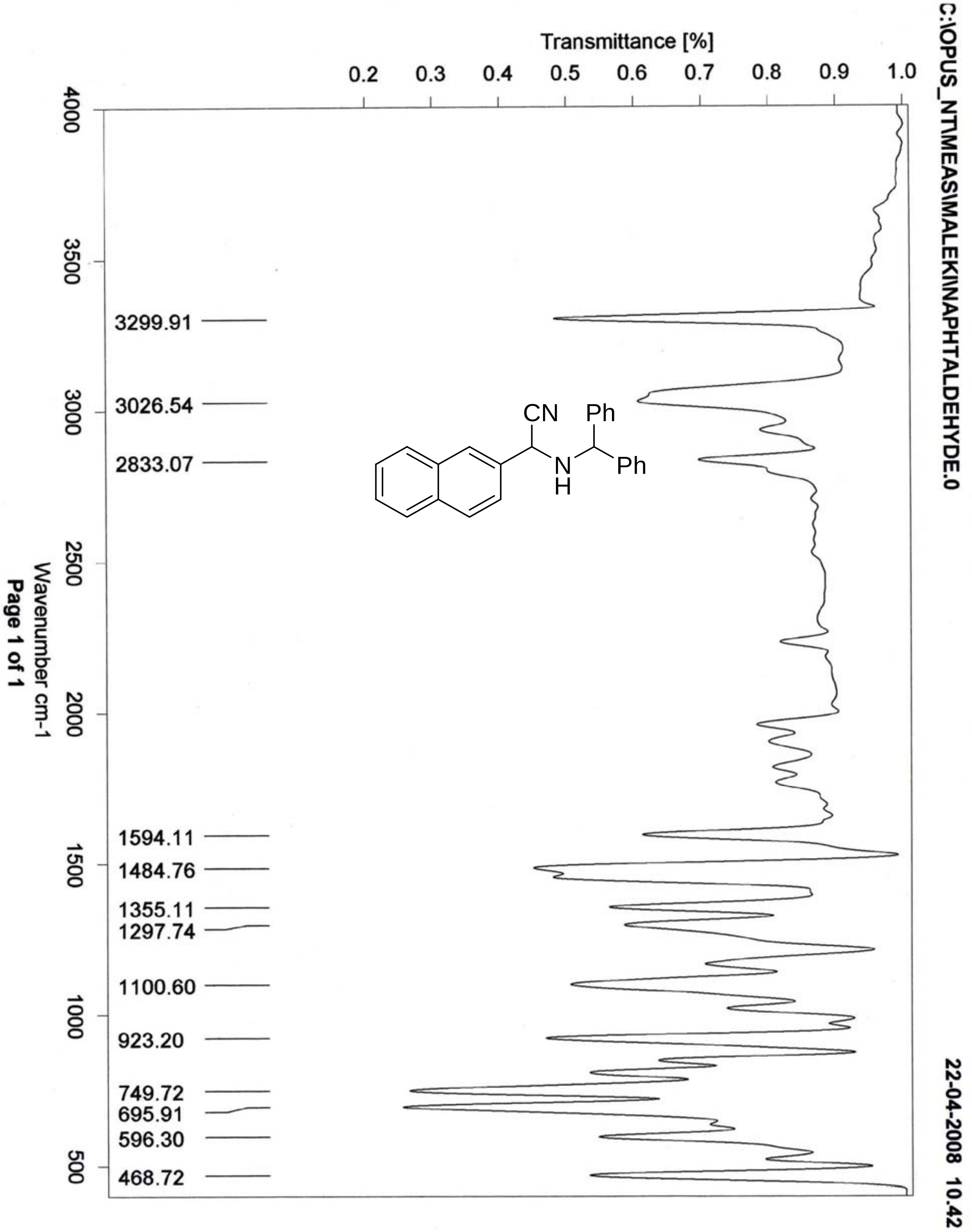


Table 2, entry 10

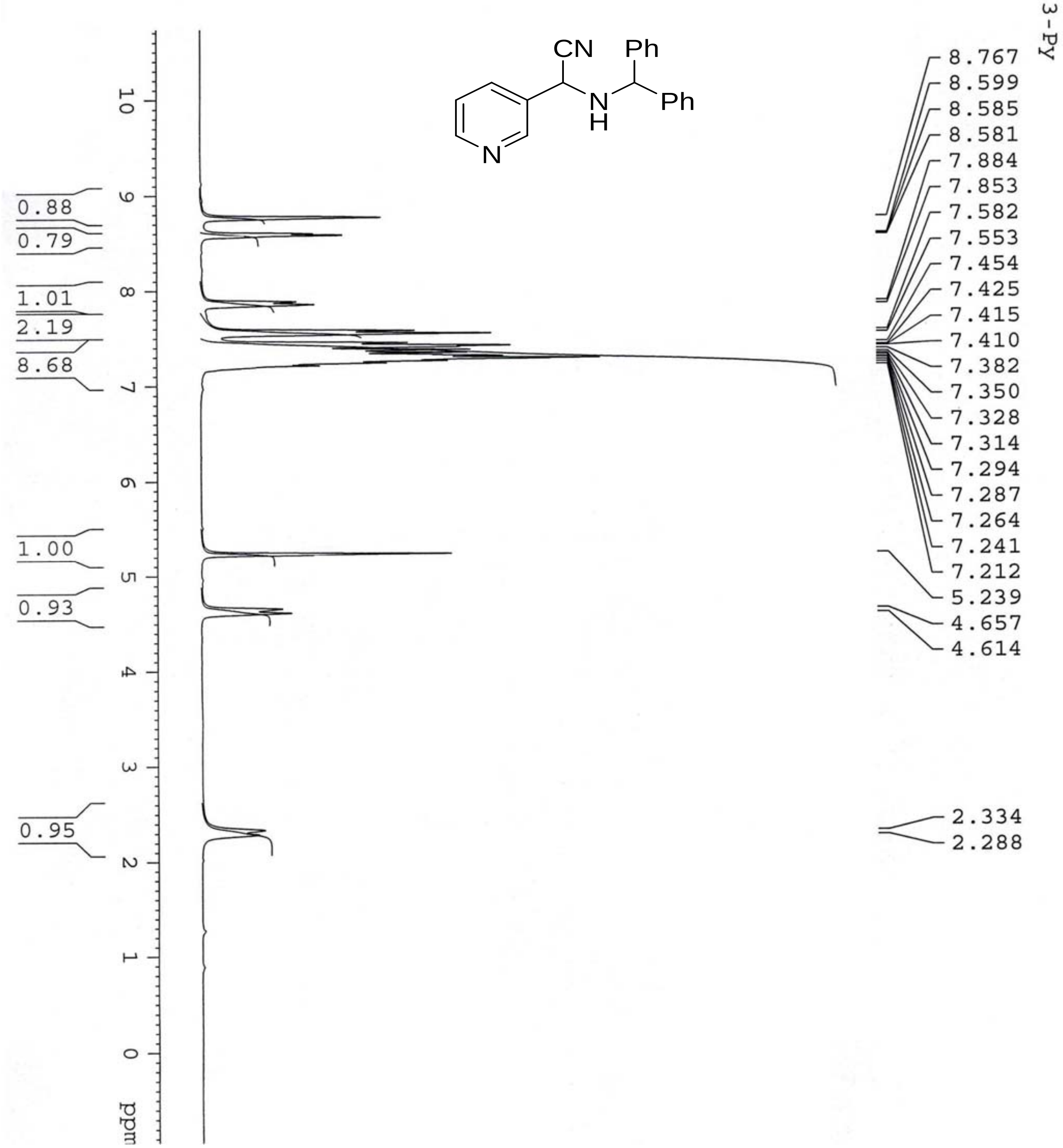


Table 2, entry 10

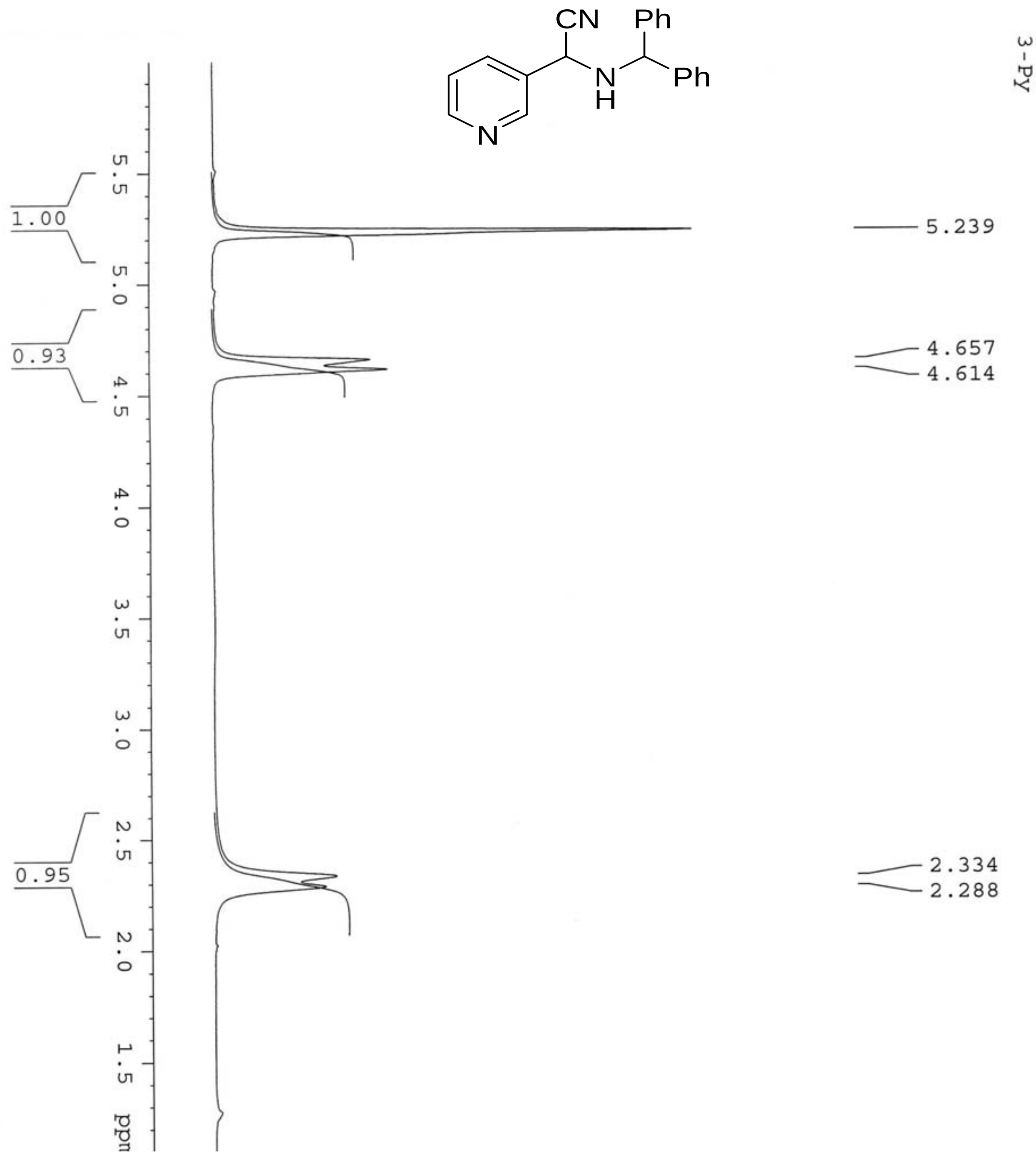


Table 2, entry 10

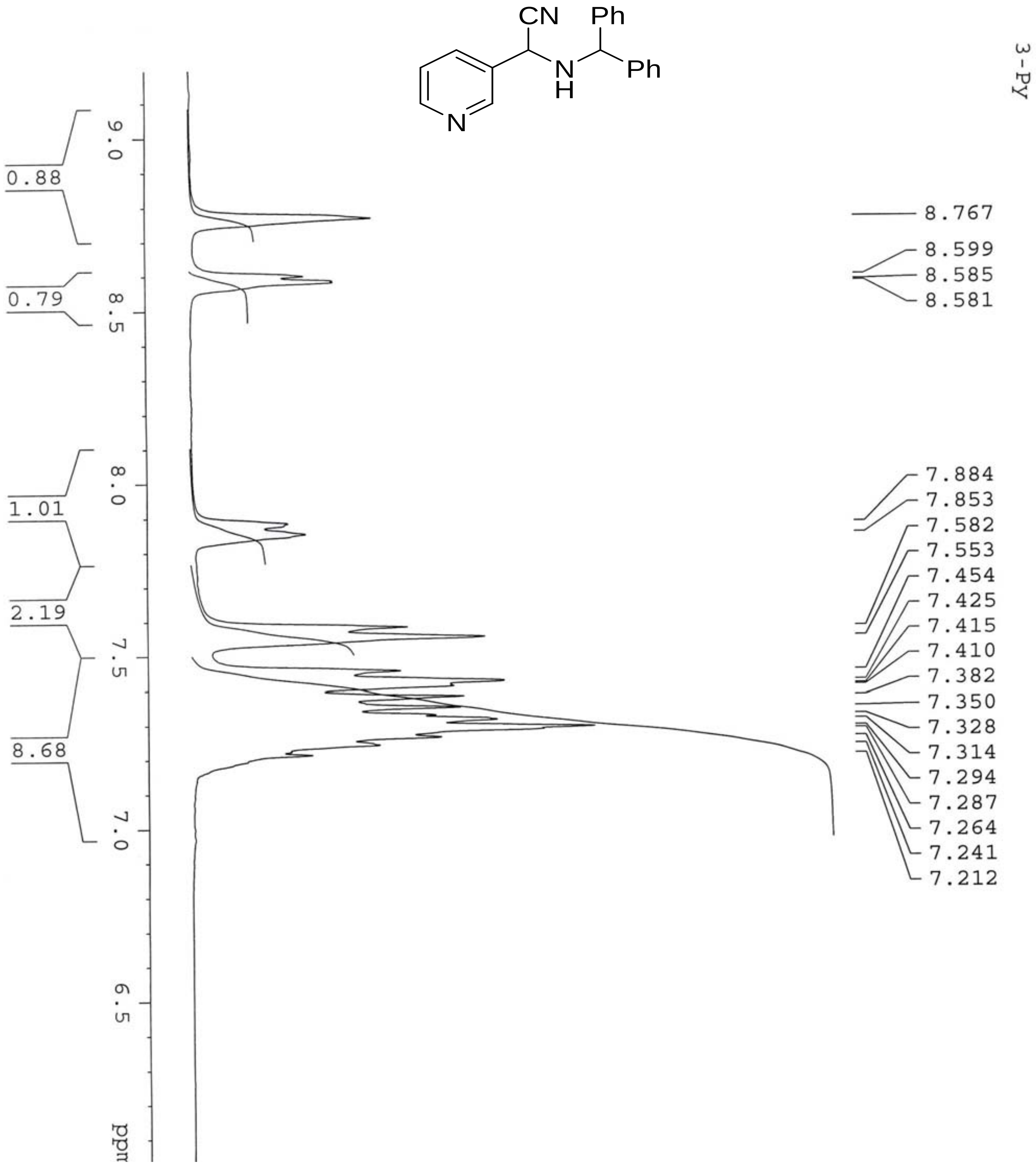


Table 2, entry 10

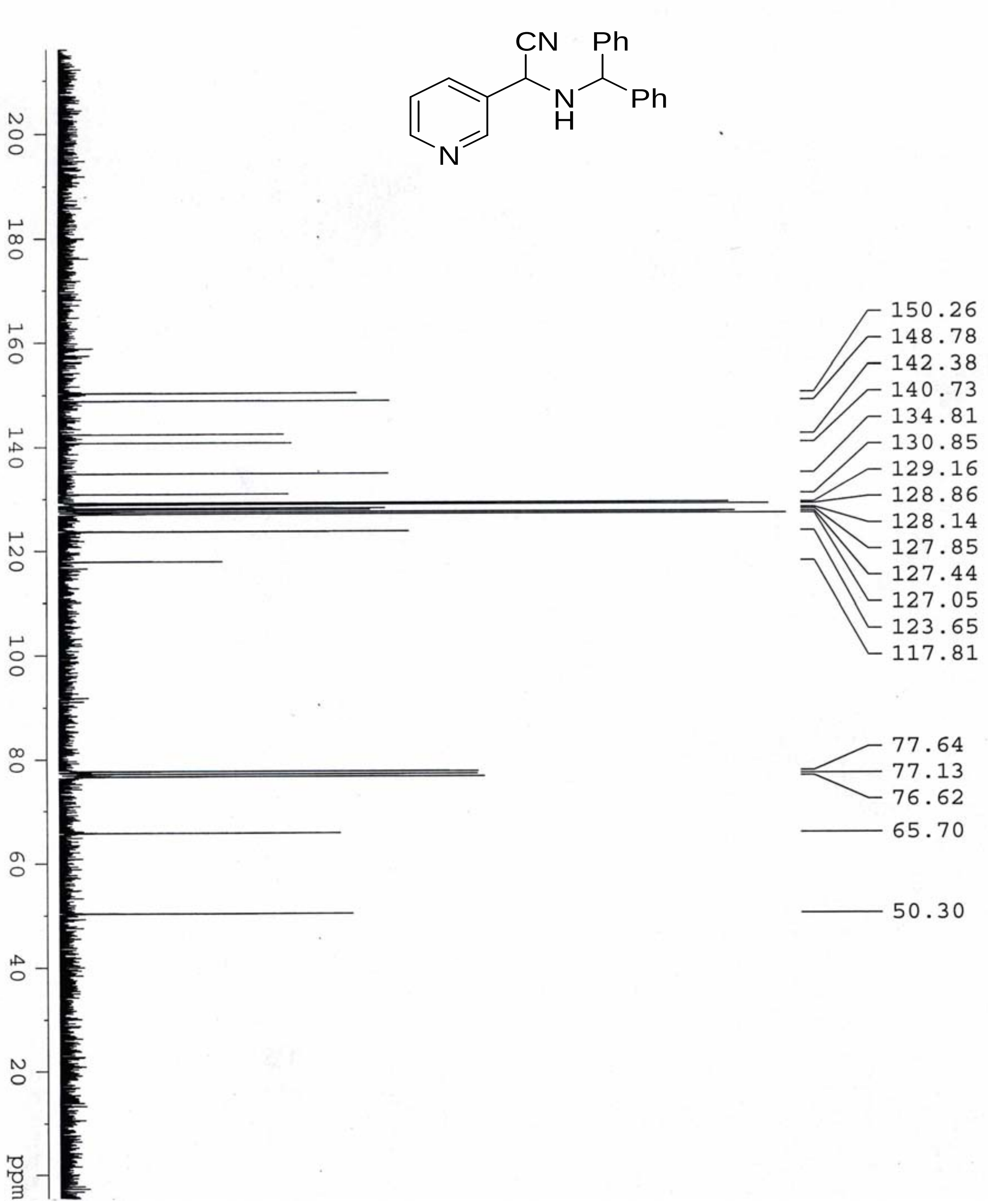
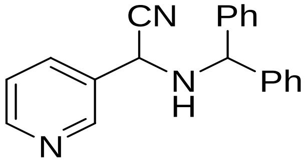
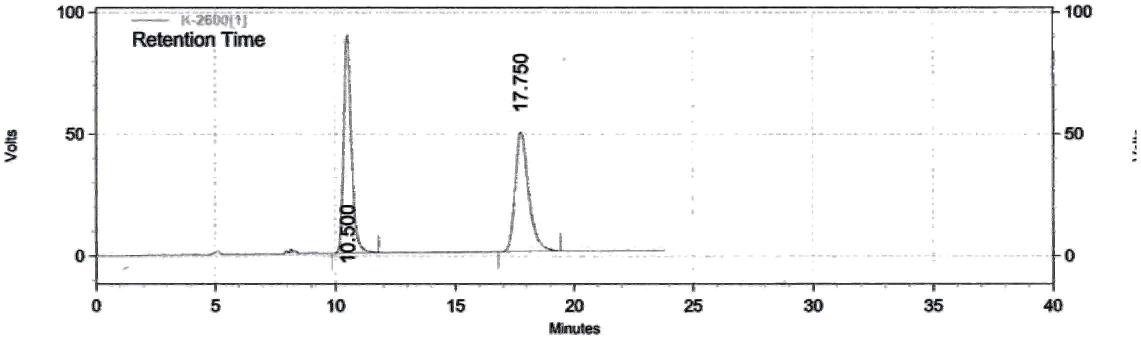


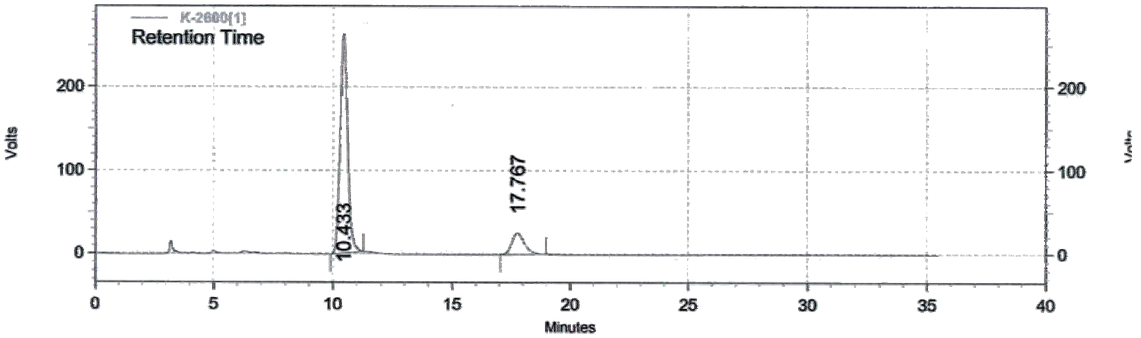
Table 2, entry 10





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
10.500	1986564	50.85	89324	64.66
17.750	1920132	49.15	48824	35.34



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
10.433	5698977	85.34	263652	91.17
17.767	979255	14.66	25524	8.83

Table 2, entry 10

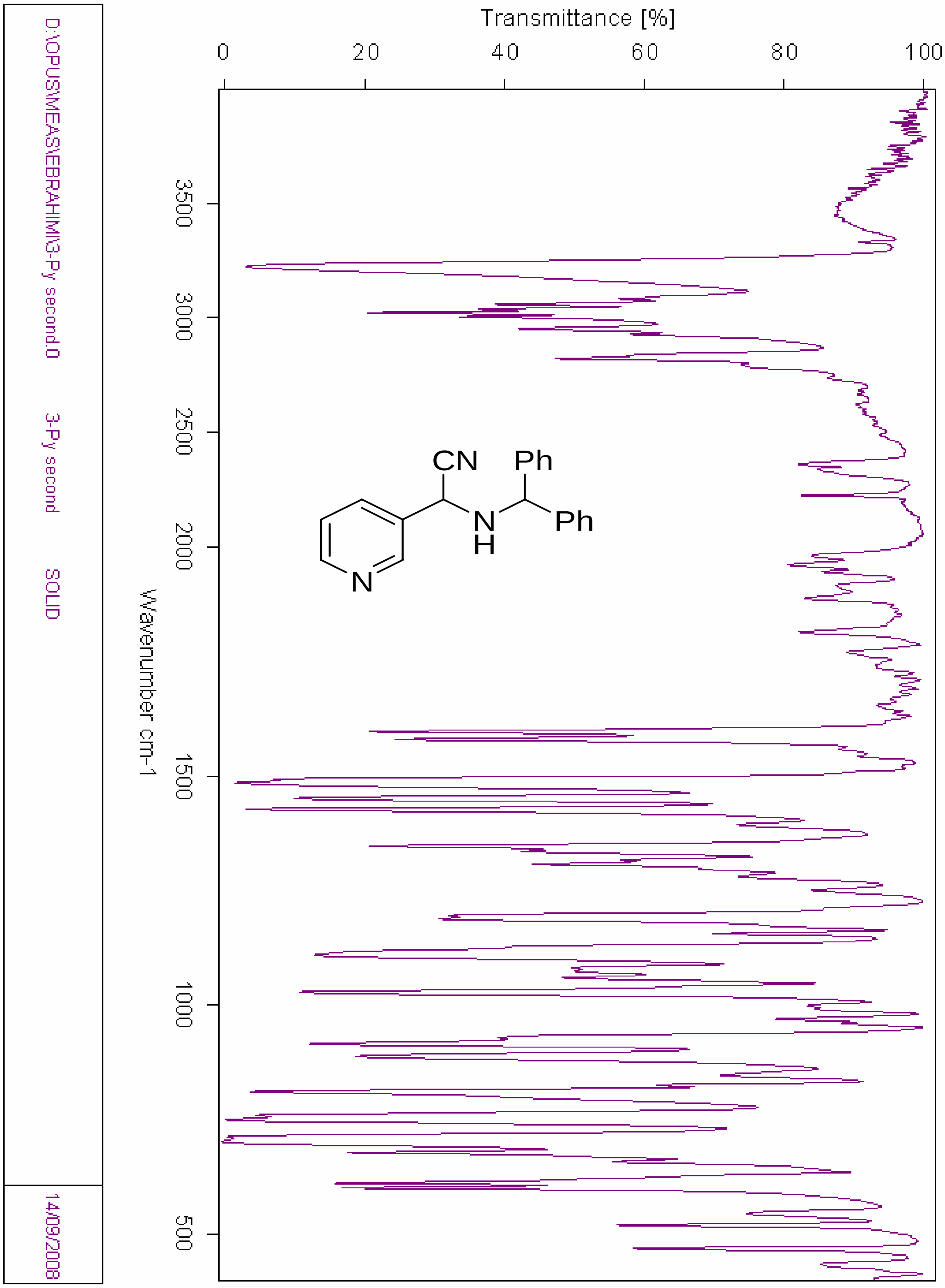
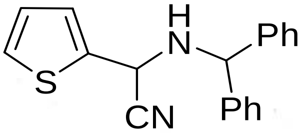


Table 2, entry 11



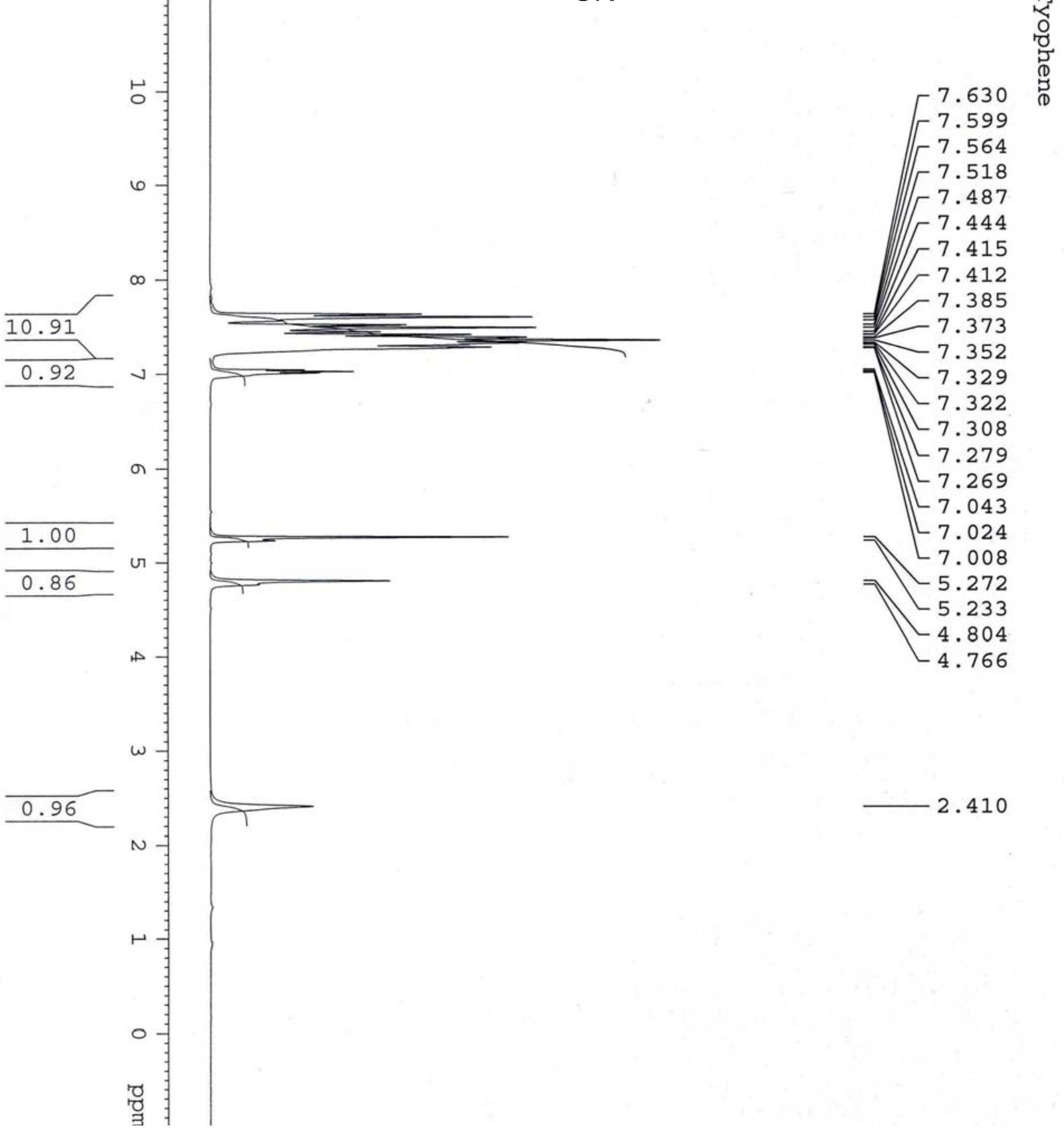
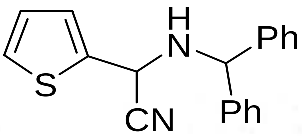


Table 2, entry 11



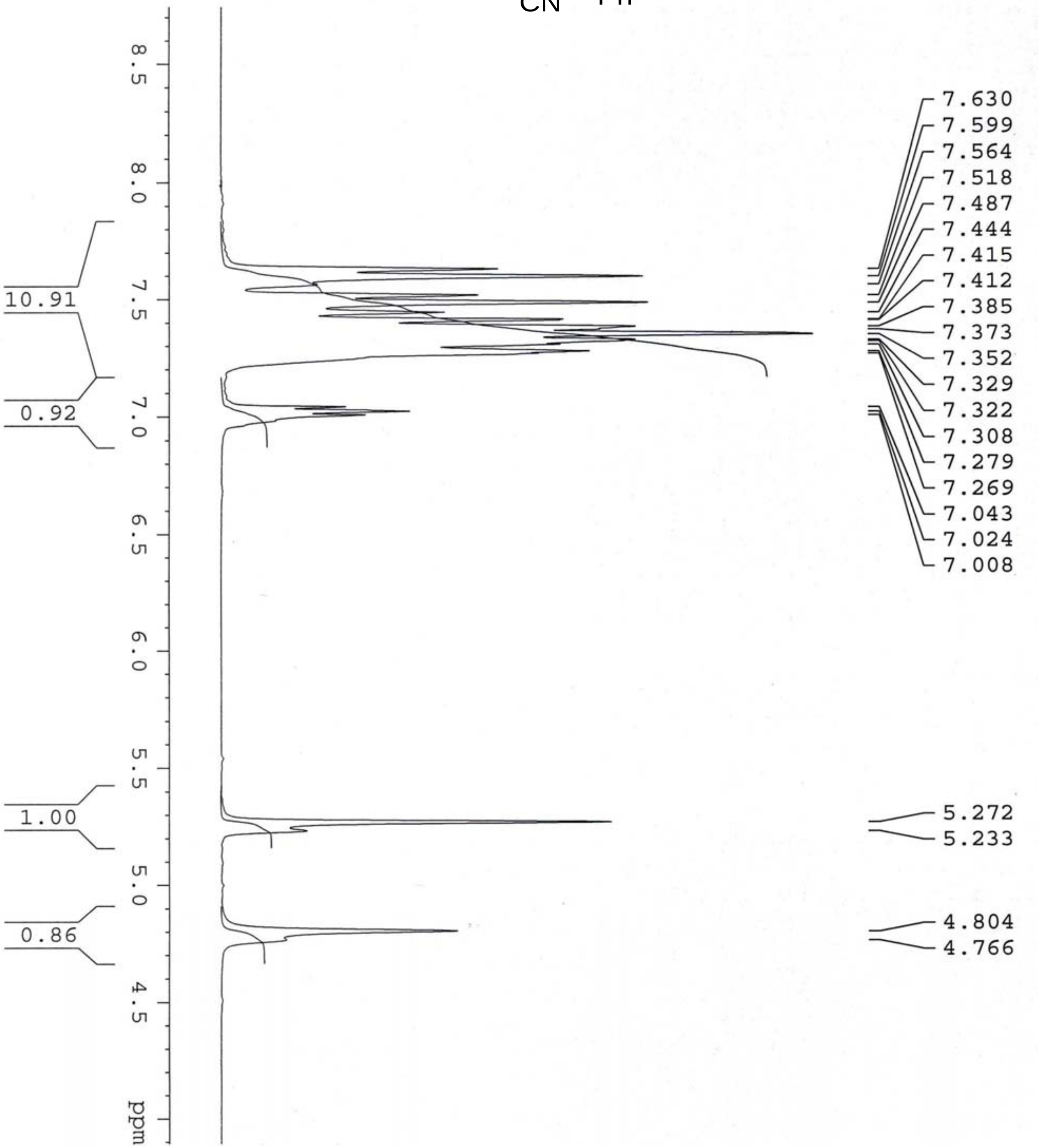


Table 2, entry 11

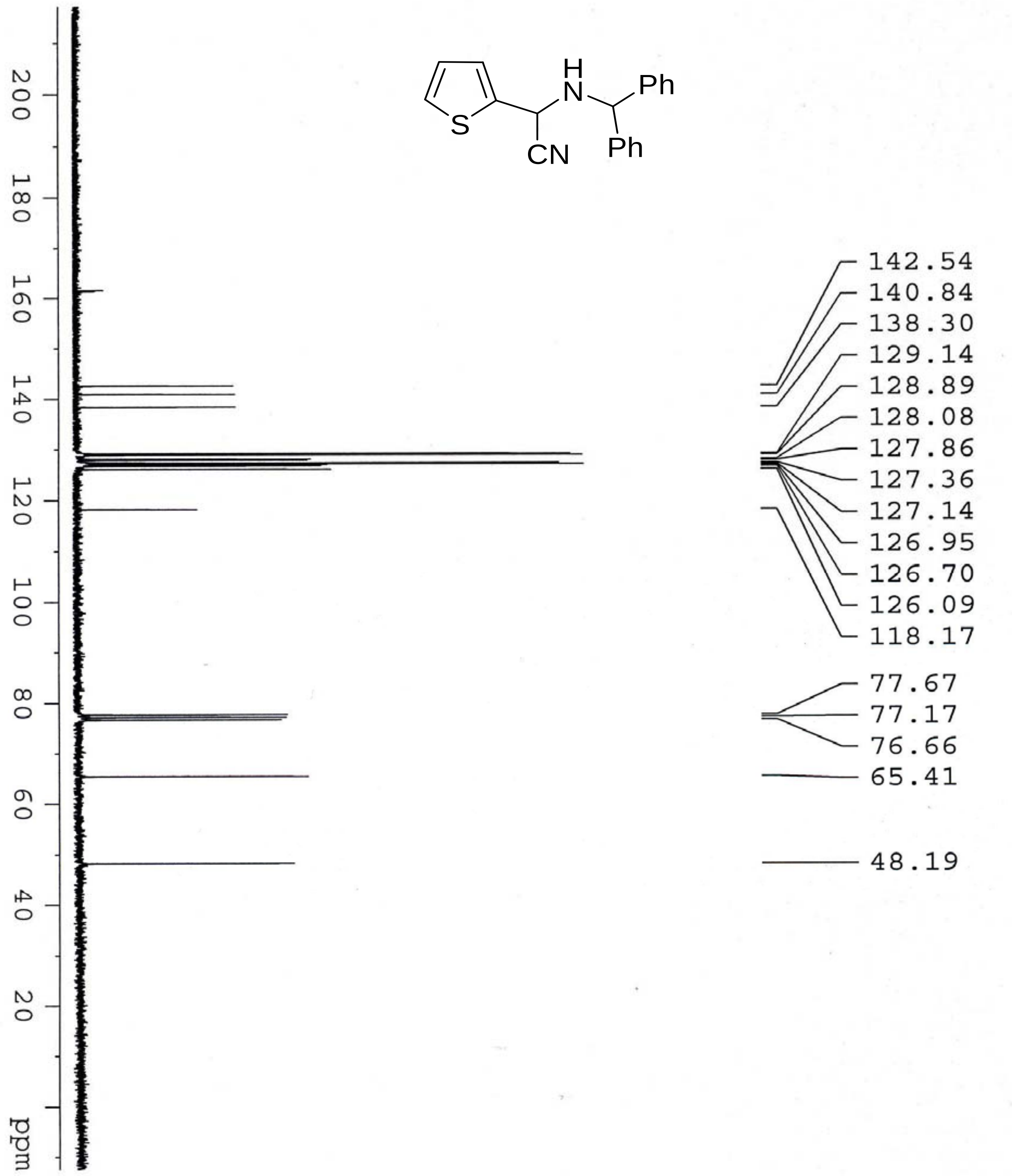


Table 2, entry 11

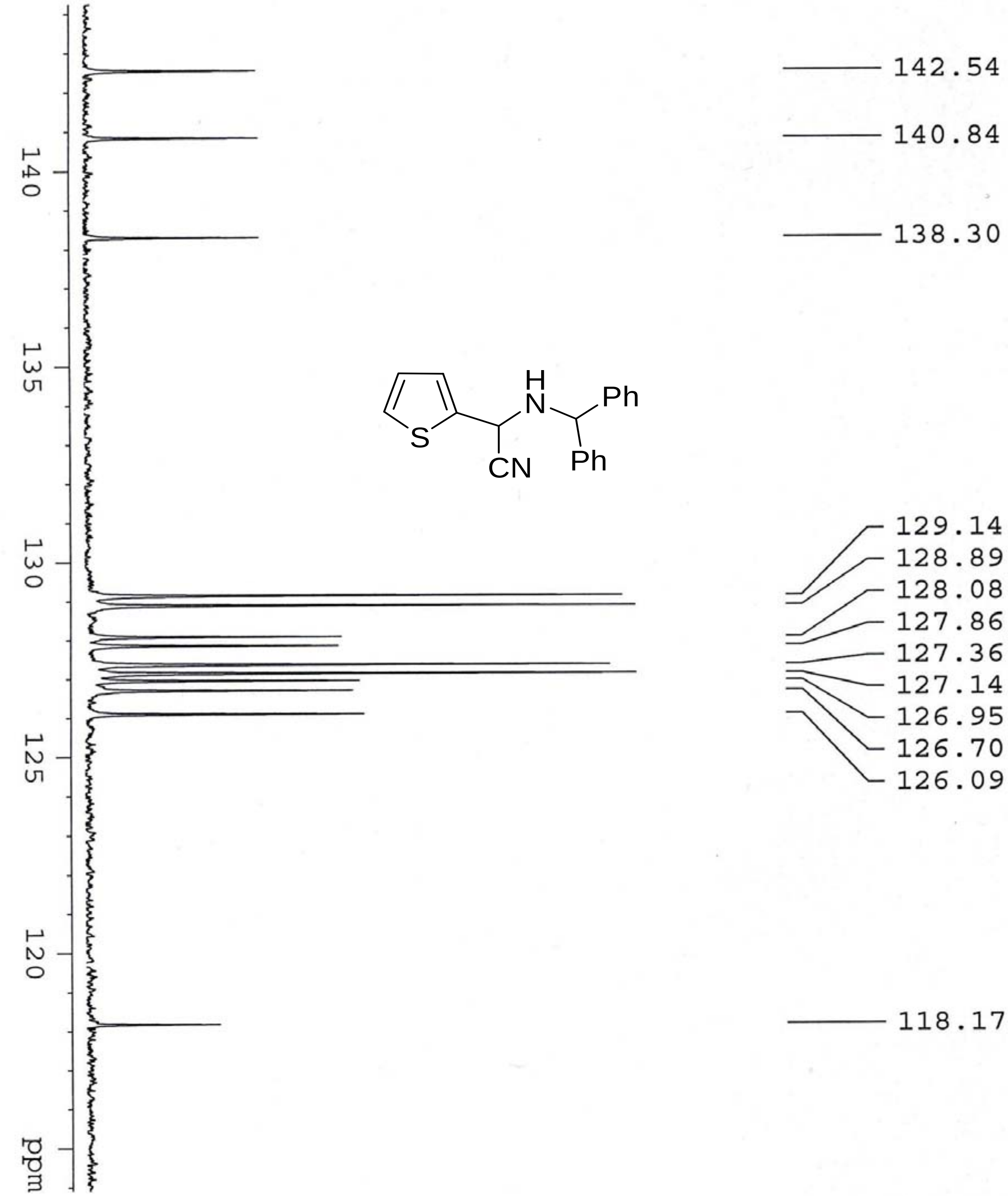
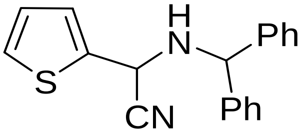
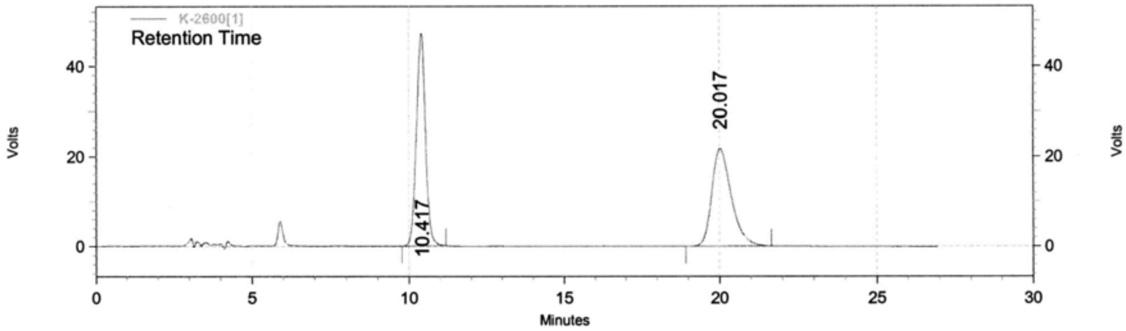


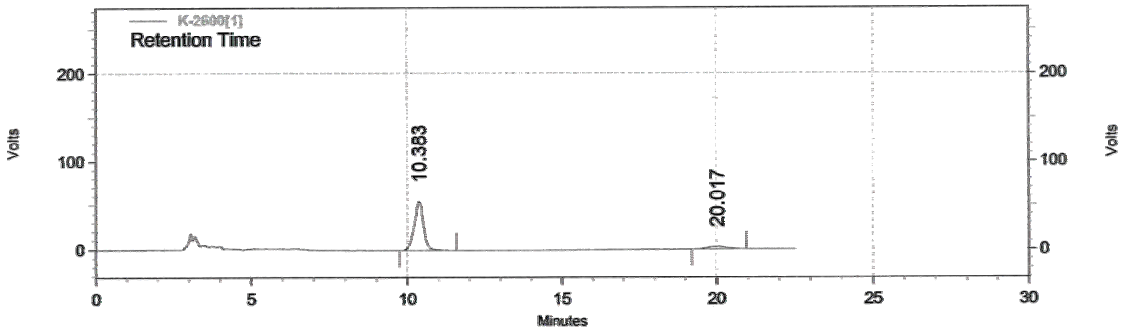
Table 2, entry 11





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
10.417	953695	50.42	47119	68.46
20.017	937706	49.58	21711	31.54



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
10.383	1131489	90.96	54828	95.21
20.017	112486	9.04	2761	4.79

Table 2, entry 11

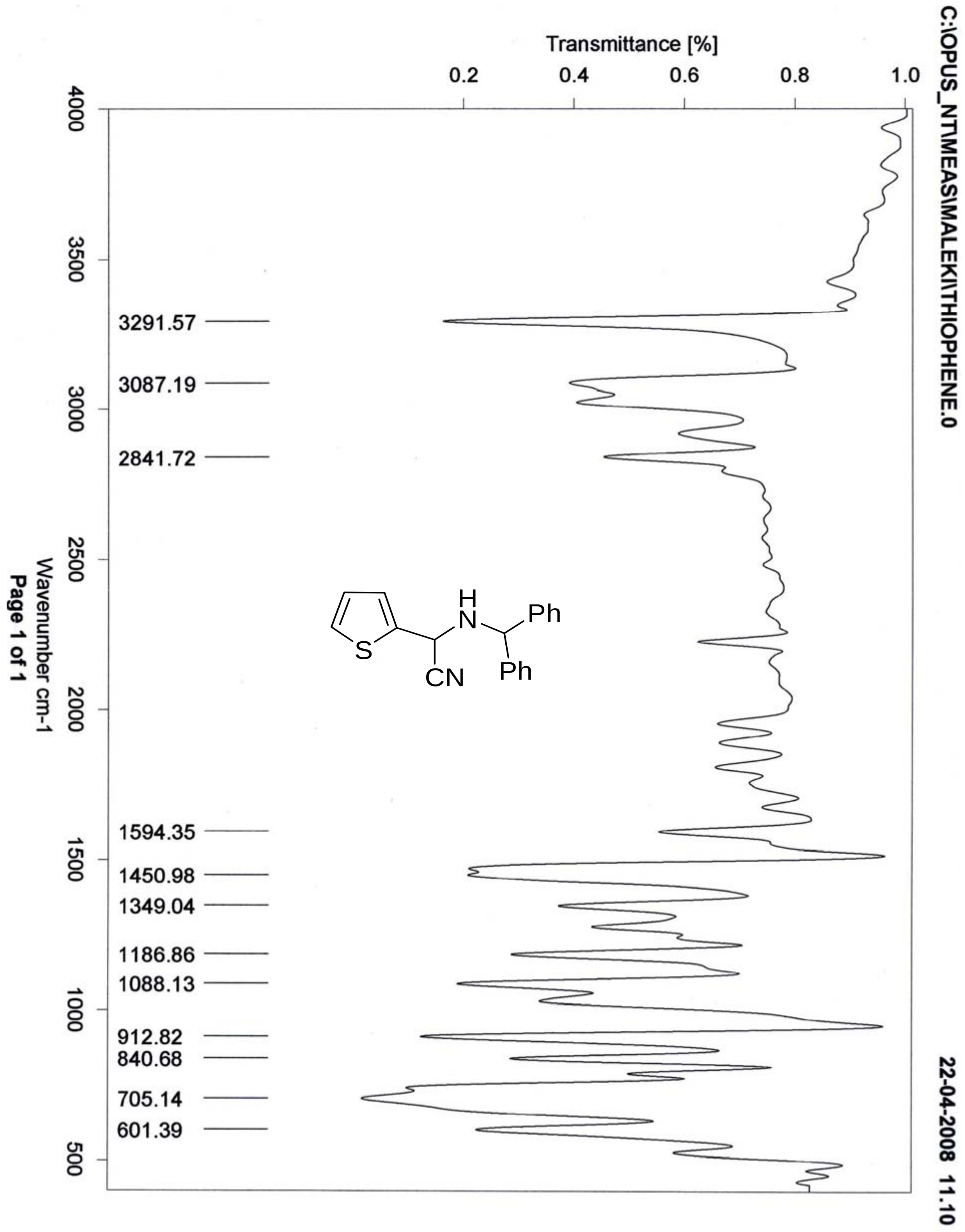


Table 2, entry 12

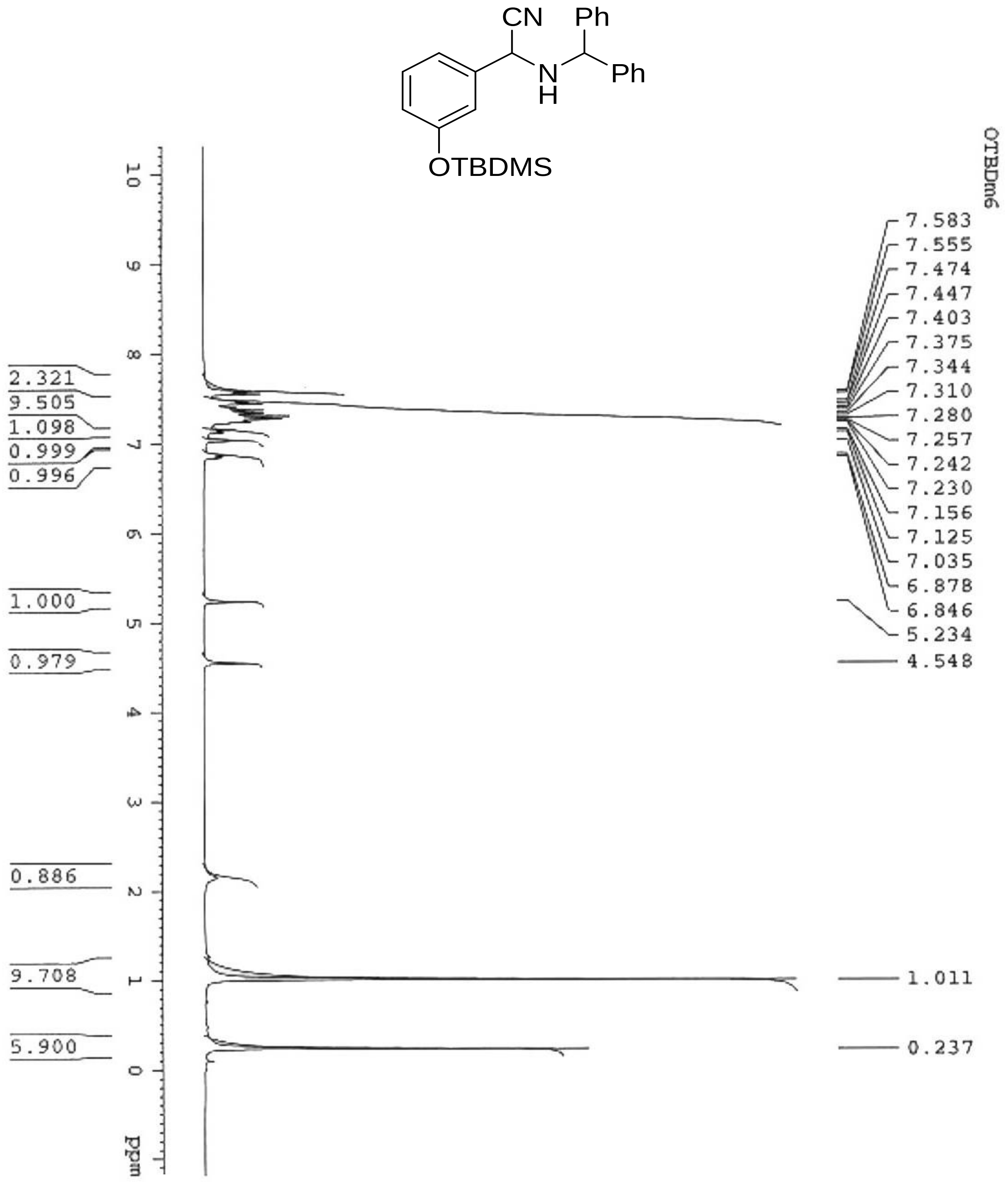


Table 2, entry 12

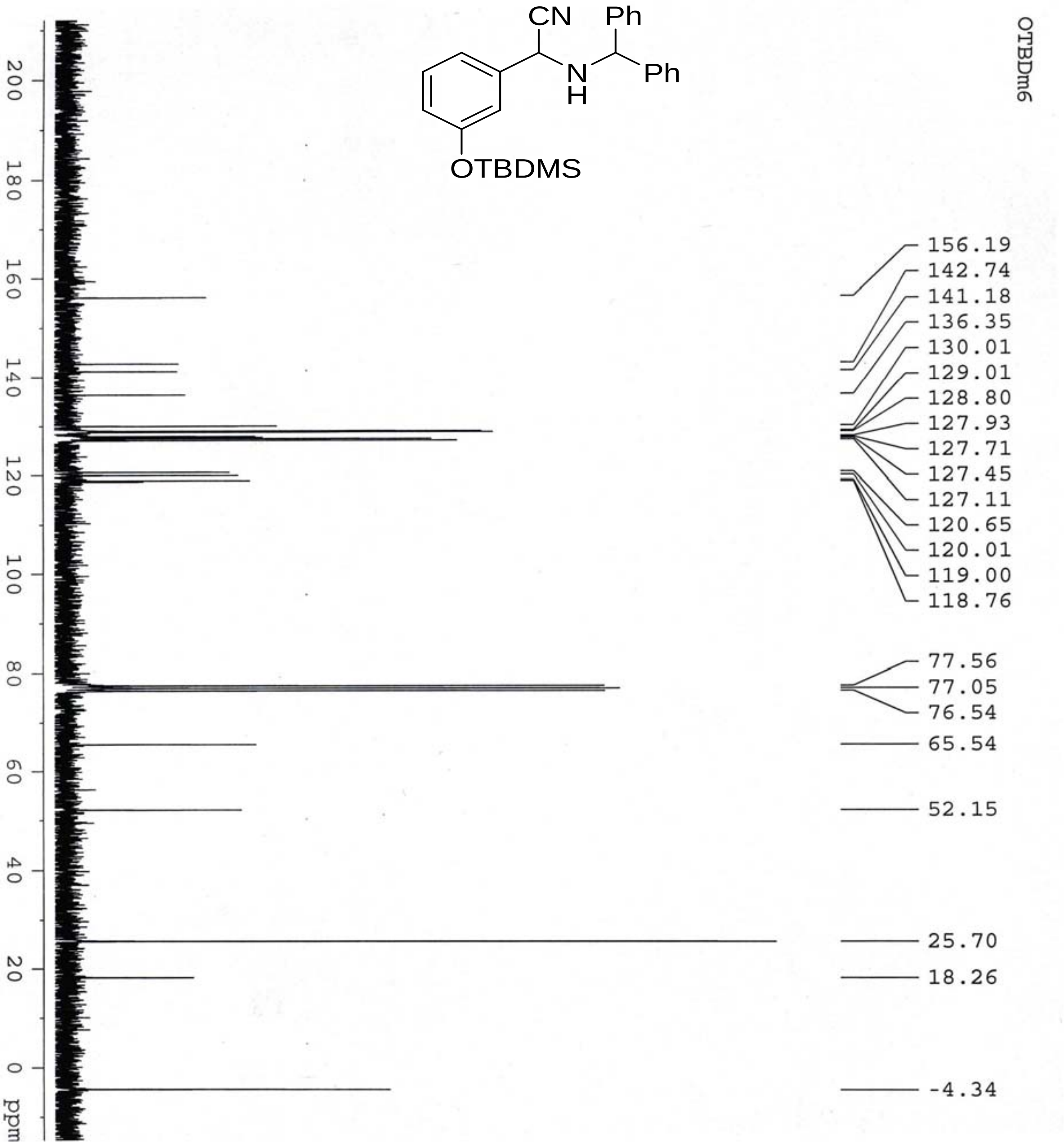


Table 2, entry 12

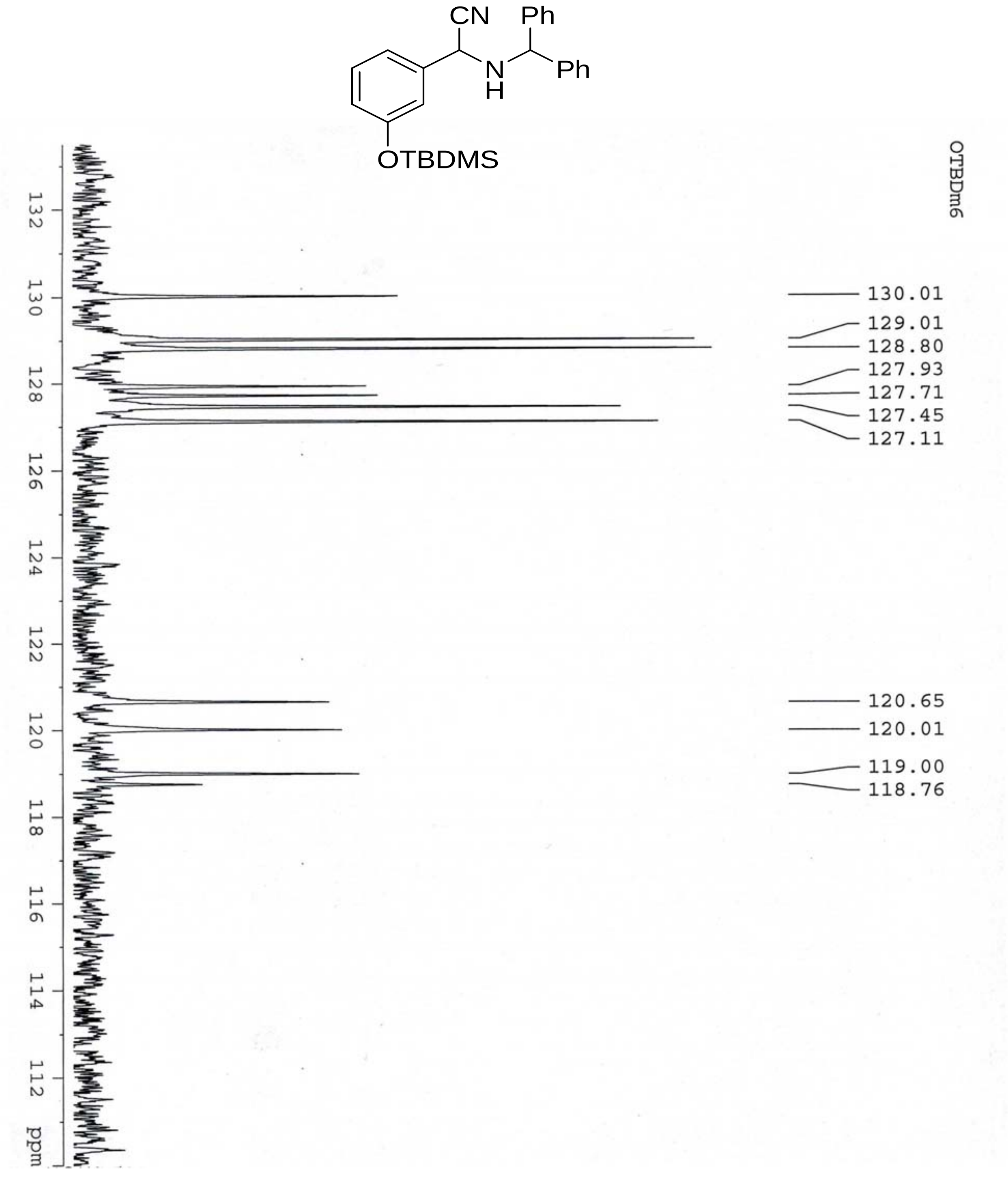
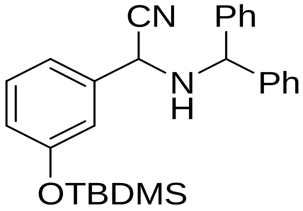
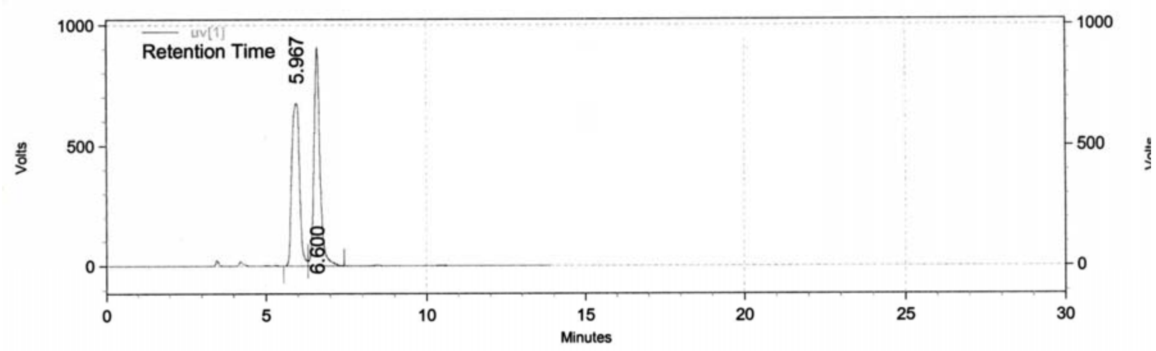


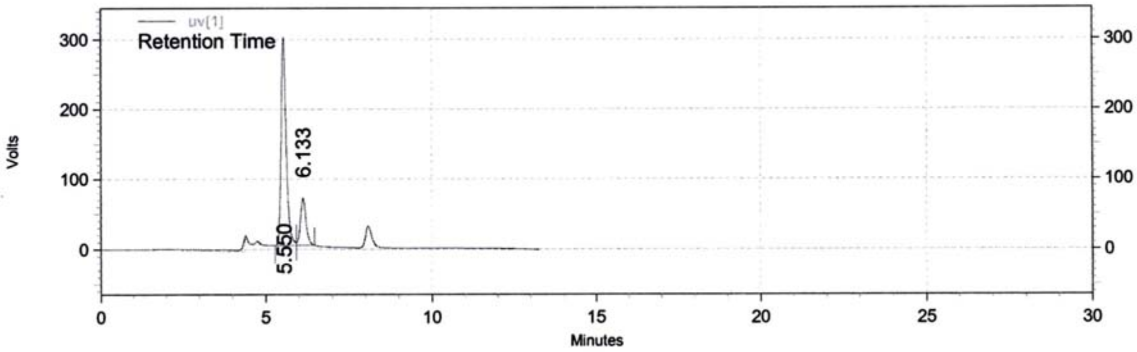
Table 2, entry 12





uv[1] Results

Retention Time	Area	Area %	Height	Height %
5.967	11315805	49.35	674347	42.60
6.600	11613978	50.65	908739	57.40



uv[1] Results

Retention Time	Area	Area %	Height	Height %
5.550	3155739	80.26	298471	81.58
6.133	776370	19.74	67384	18.42

Table 2, entry 12

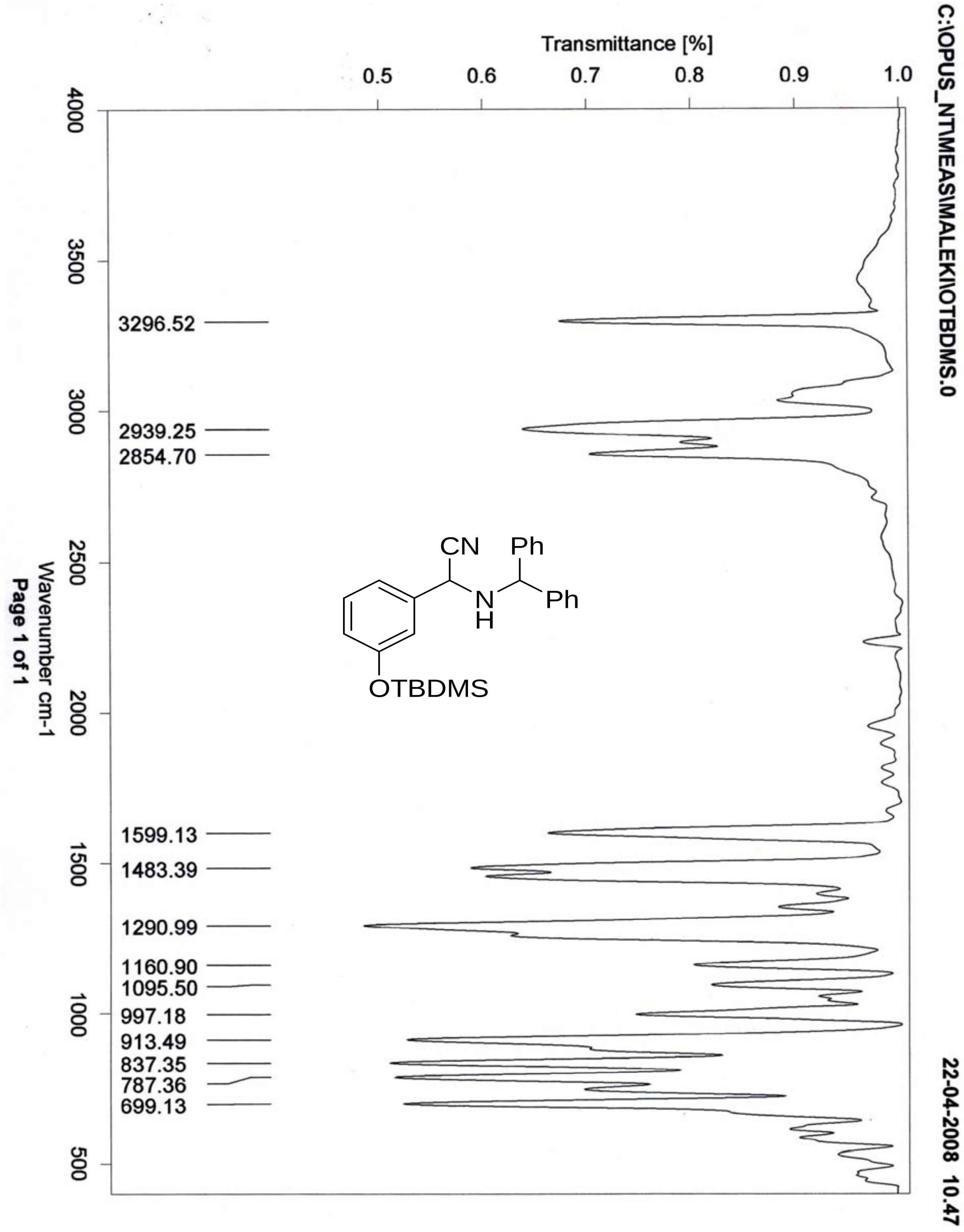


Table 2, entry 13

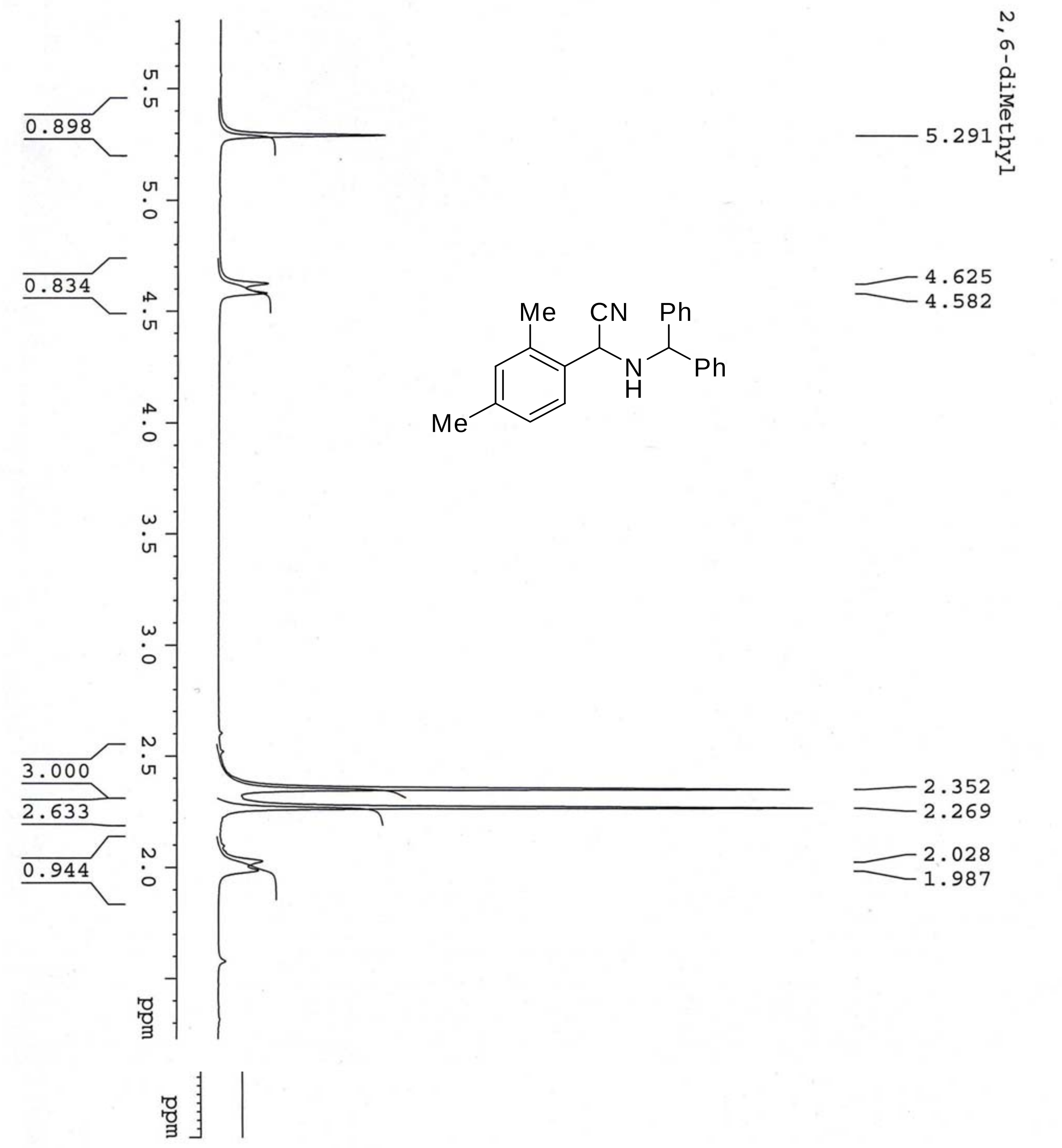


Table 2, entry 13

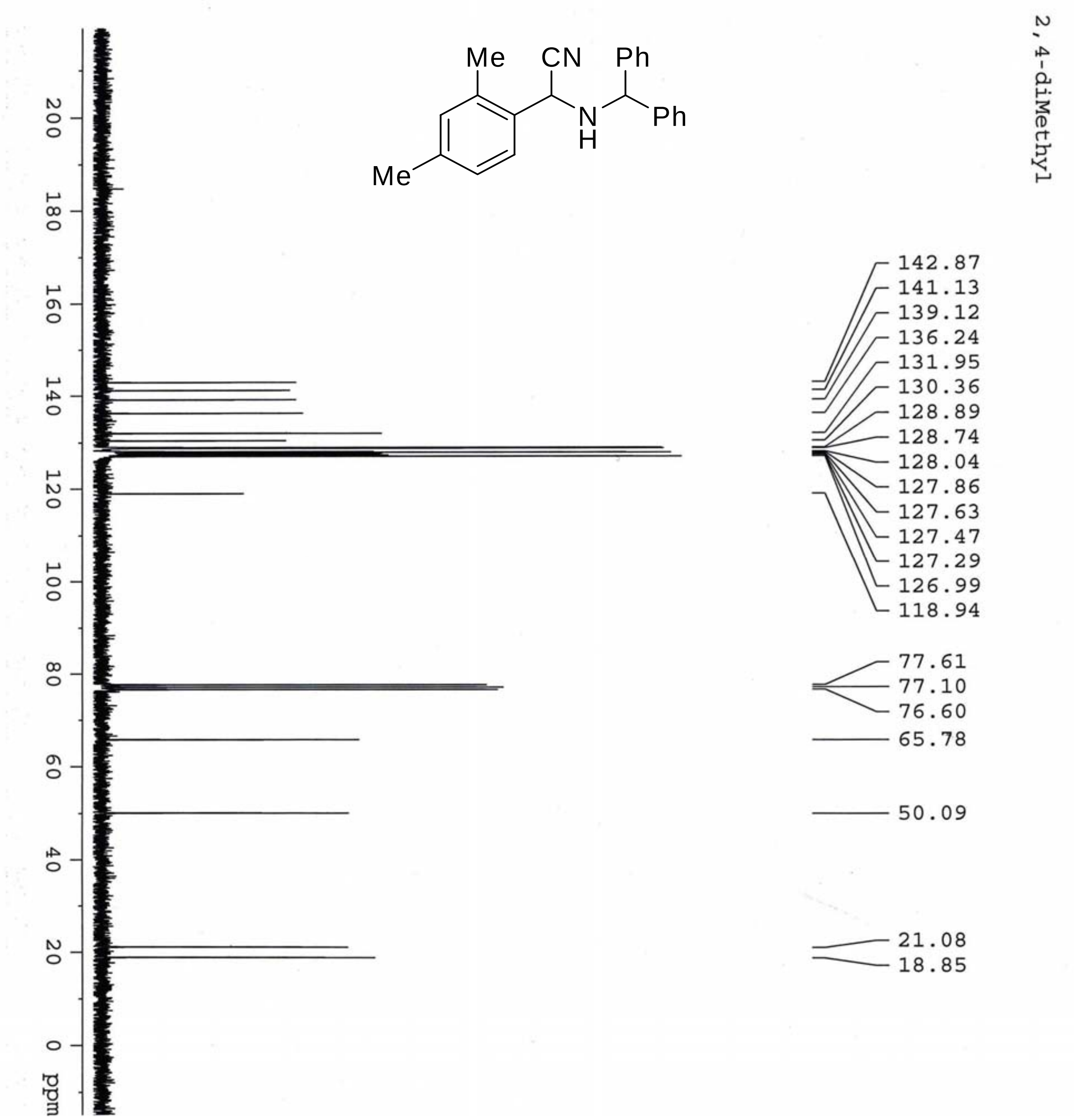
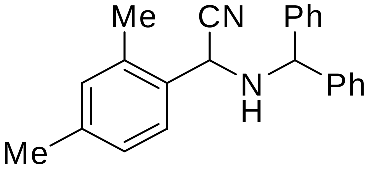
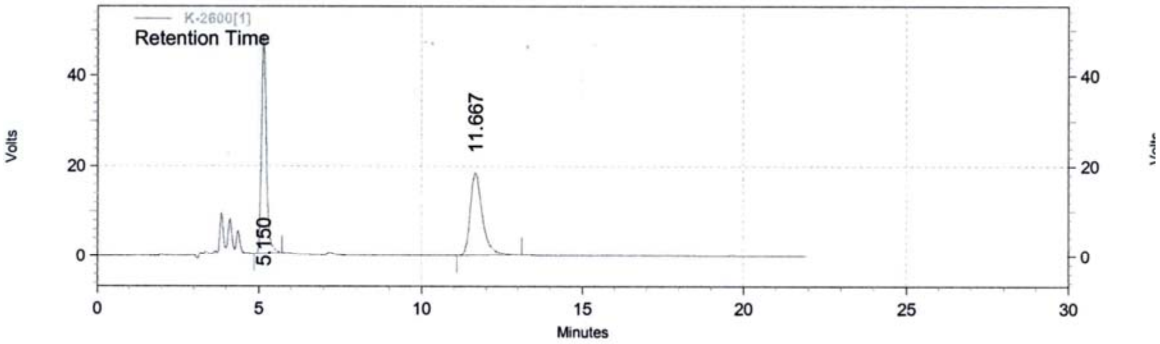


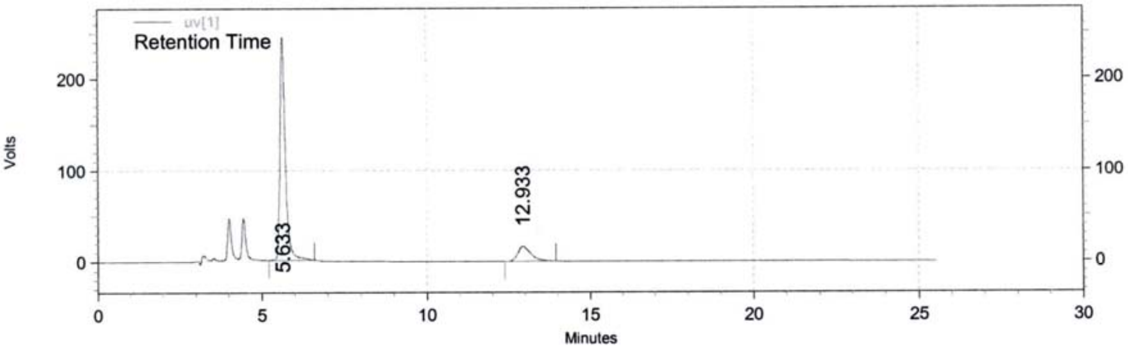
Table 2, entry 13





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
5.150	481459	50.06	48589	72.53
11.667	480305	49.94	18403	27.47



uv[1] Results

Retention Time	Area	Area %	Height	Height %
5.633	2768516	86.04	244005	93.78
12.933	449065	13.96	16195	6.22

Table 2, entry 13

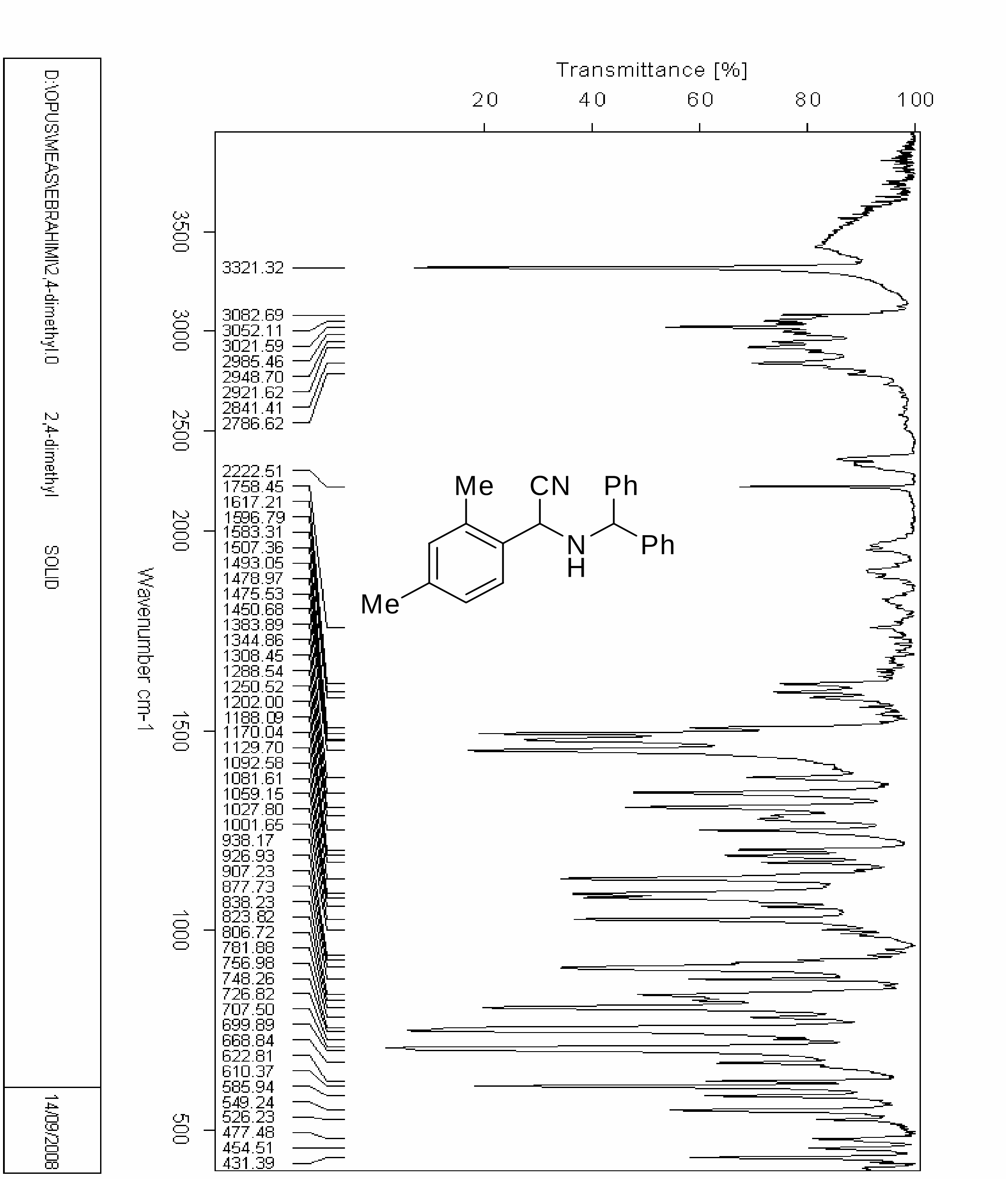


Table 2, entry 14

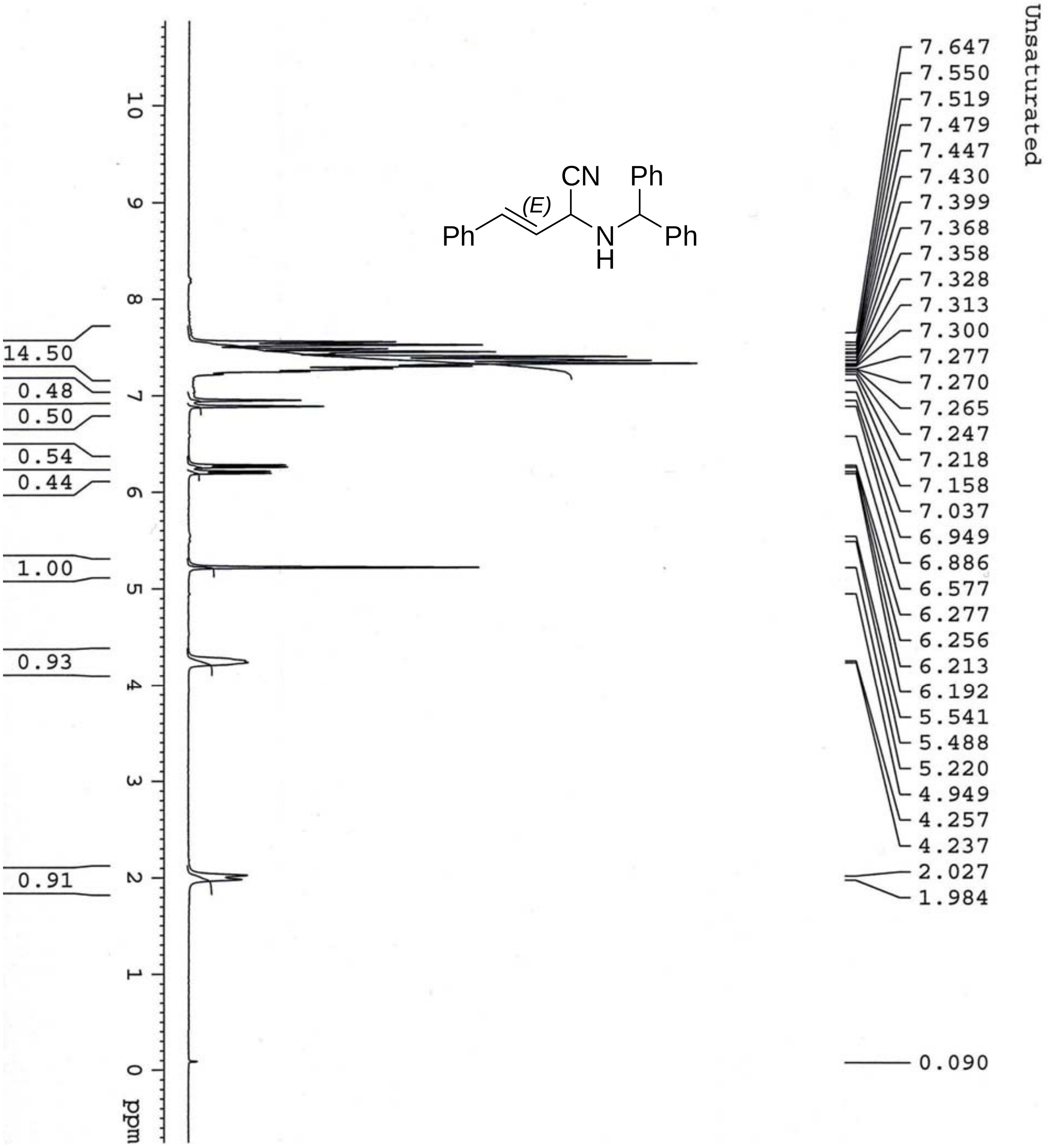


Table 2, entry 14

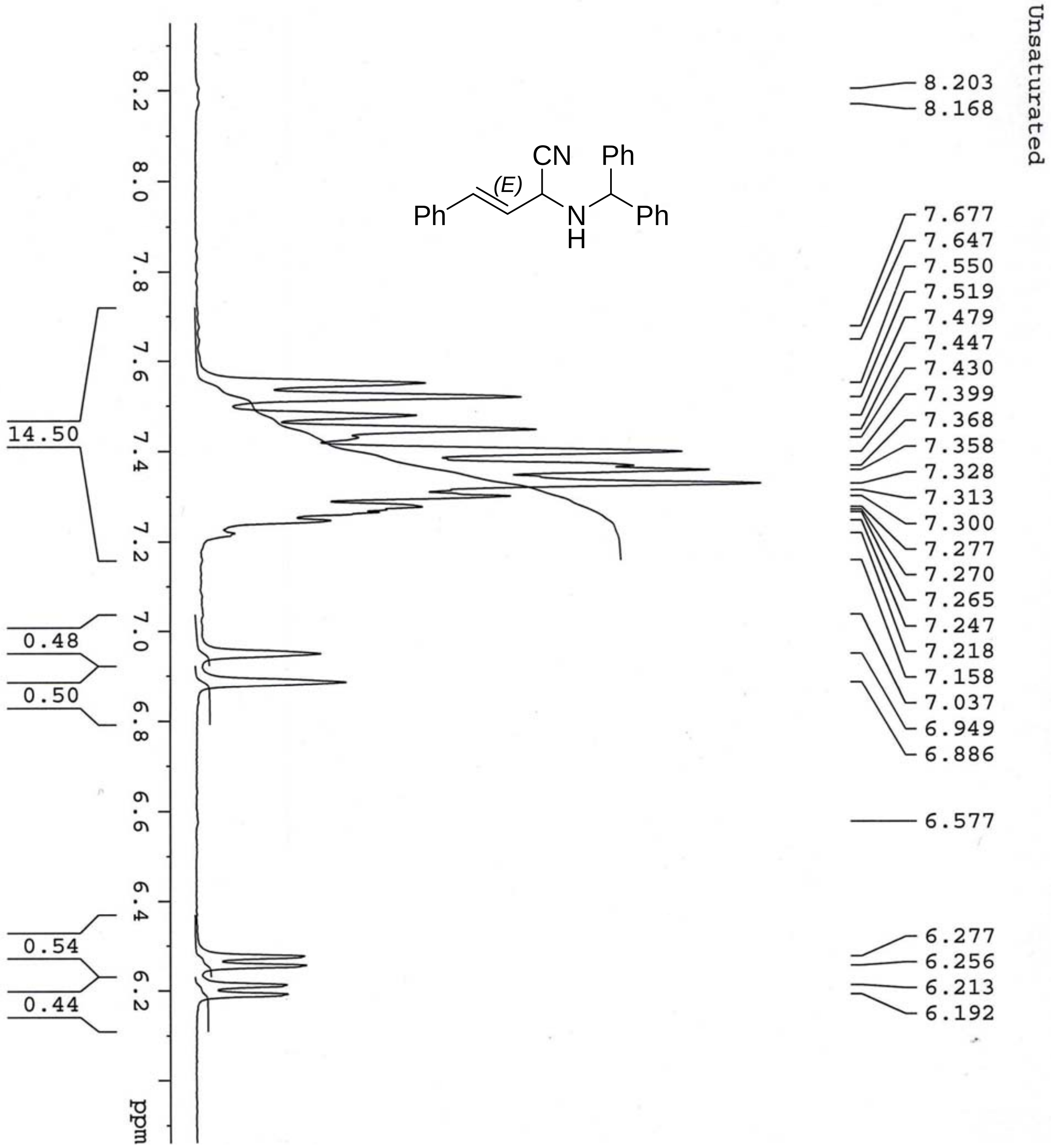
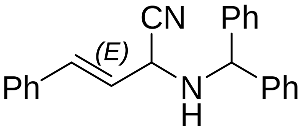
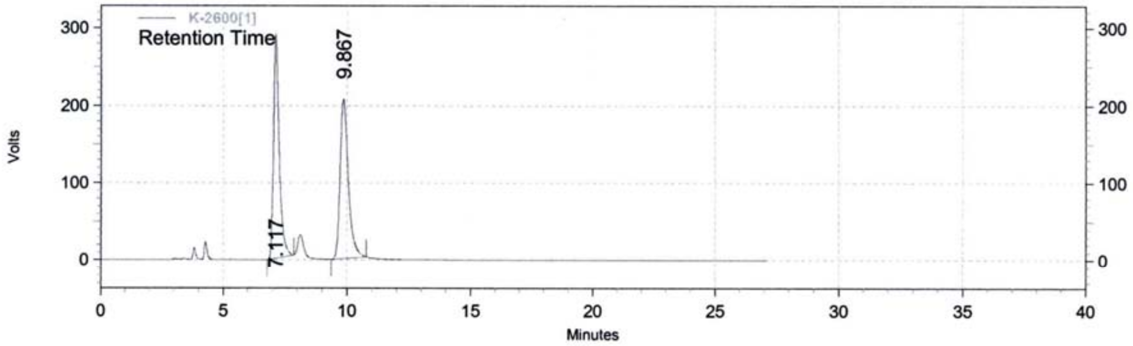


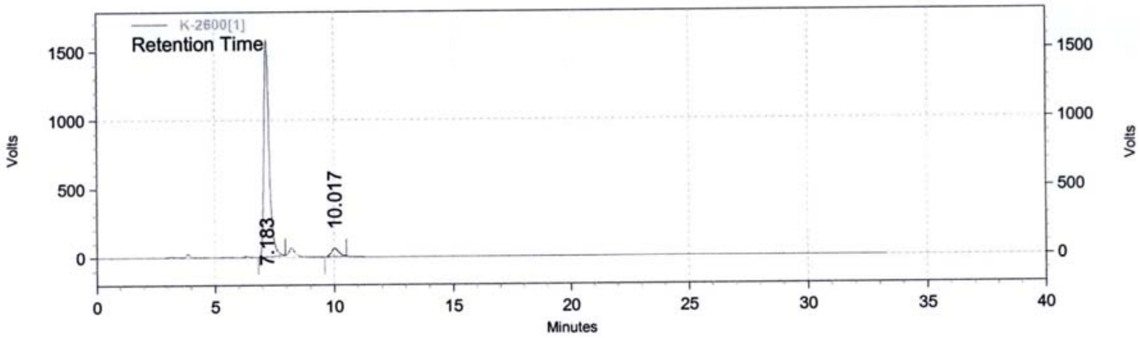
Table2, entry 14





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
7.117	4657745	49.29	289974	58.39
9.867	4791434	50.71	206662	41.61



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
7.183	23940527	94.89	1578720	96.37
10.017	1290172	5.11	59427	3.63

Table2, entry 14

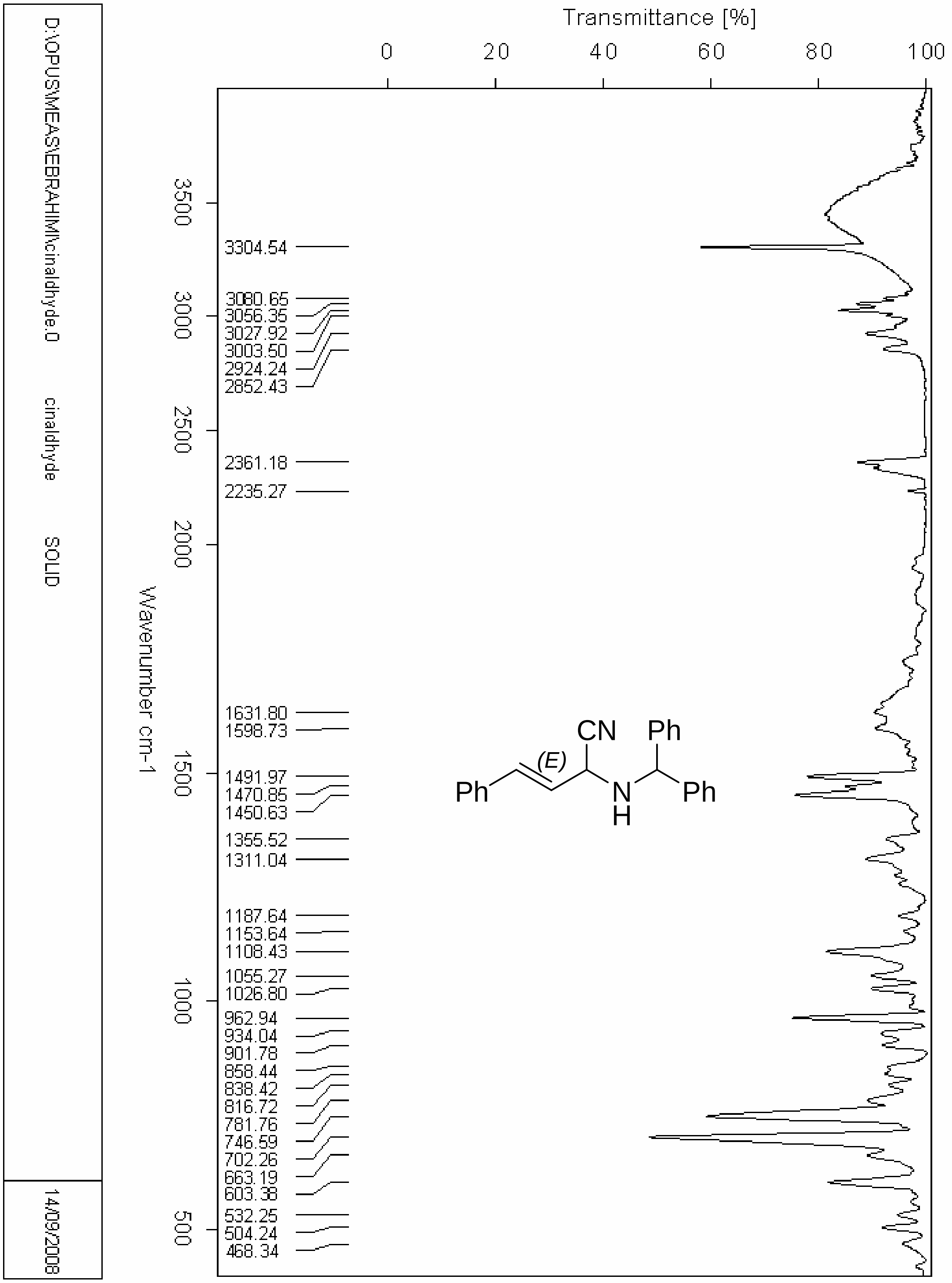


Table 2, entry 15

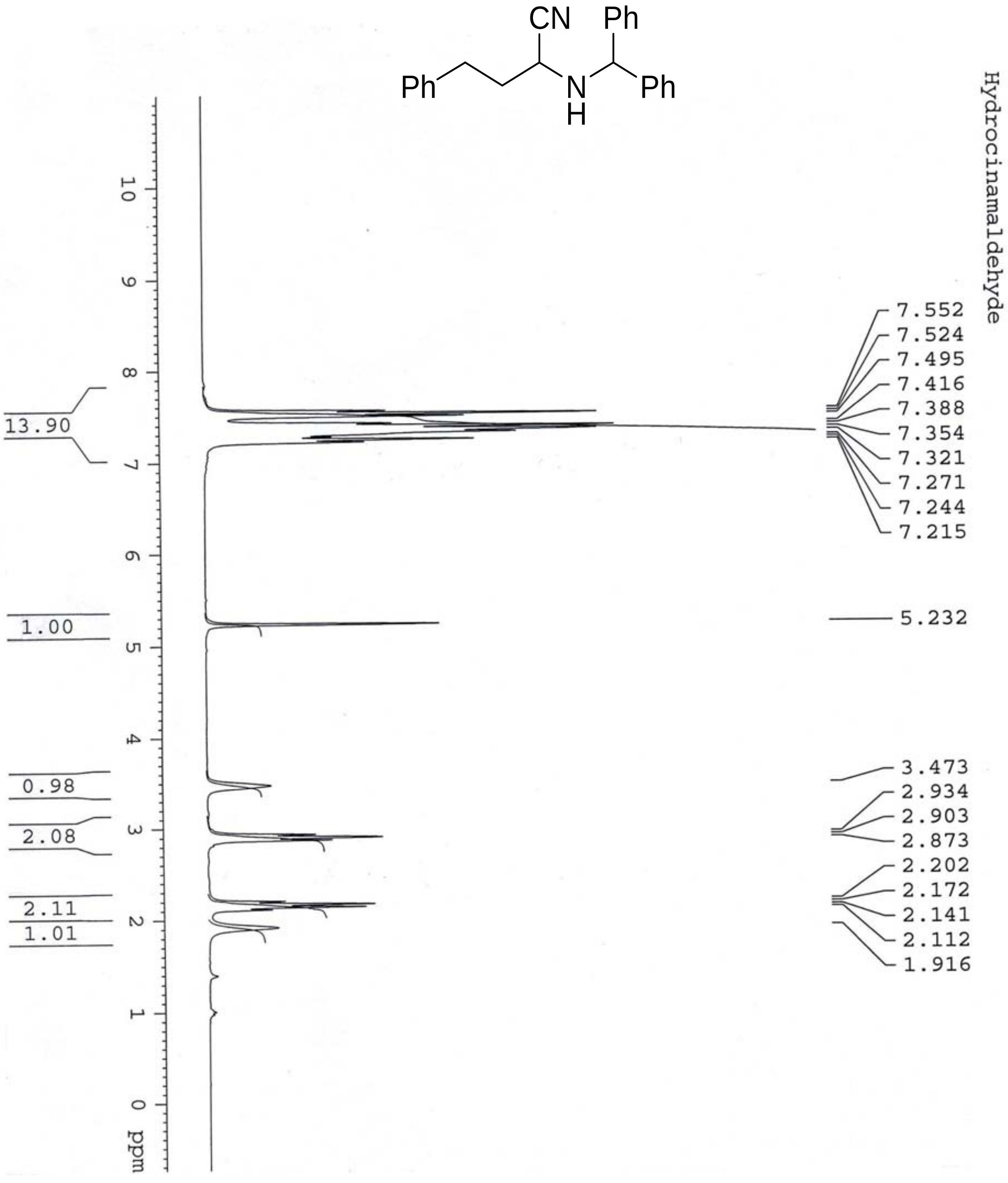


Table 2, entry 15

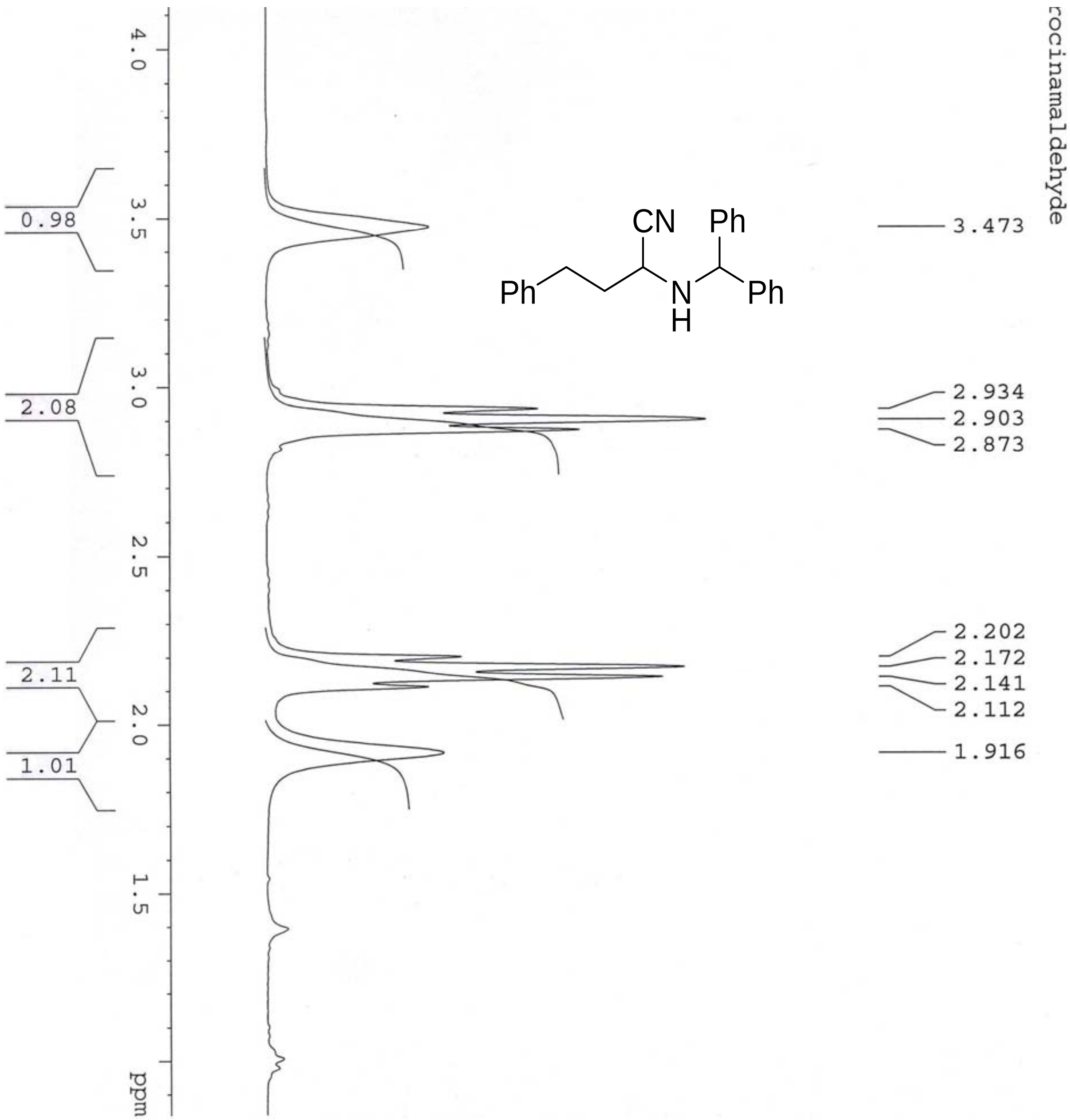


Table 2, entry 15

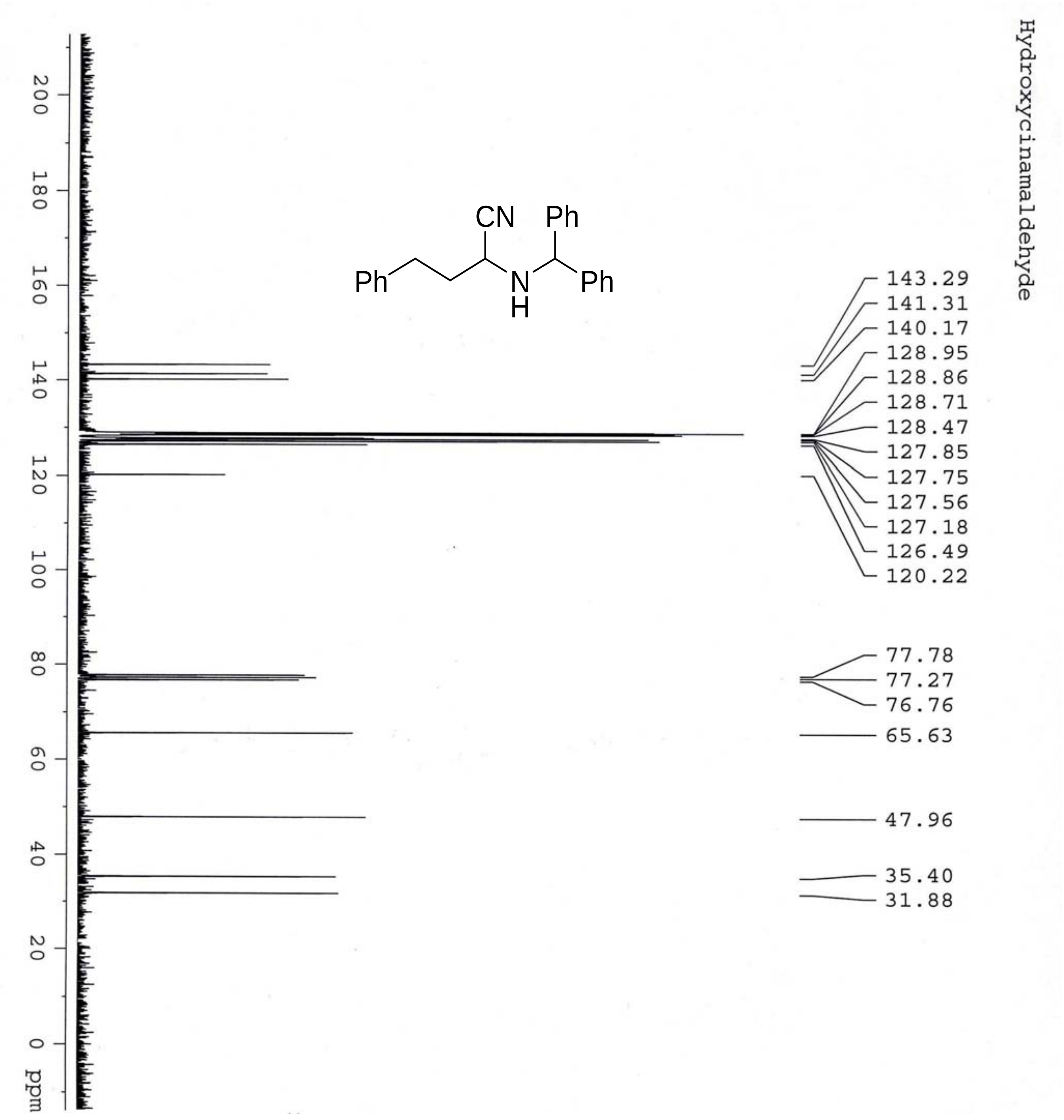


Table 2, entry 15

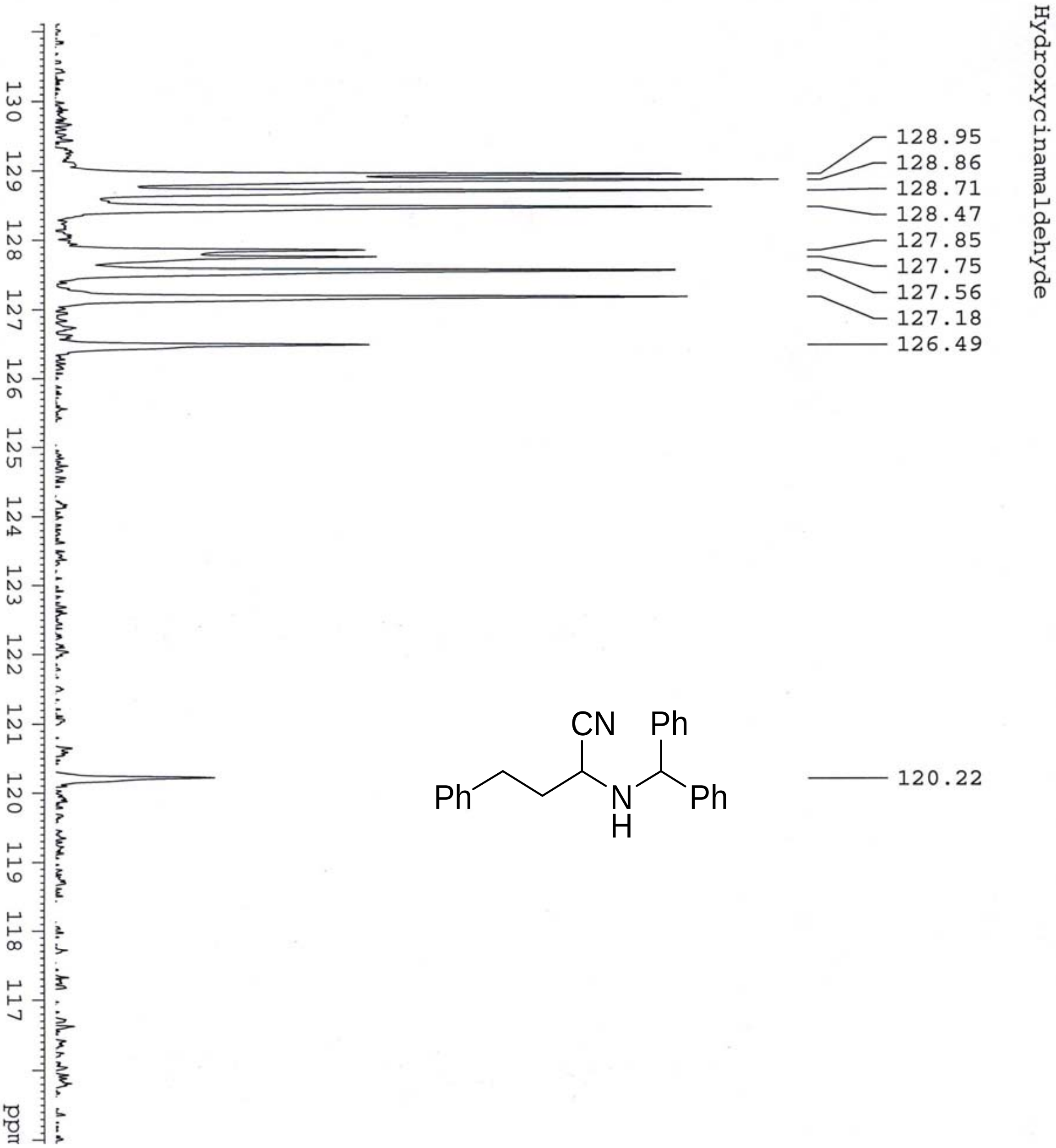
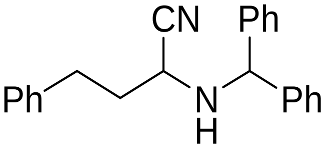
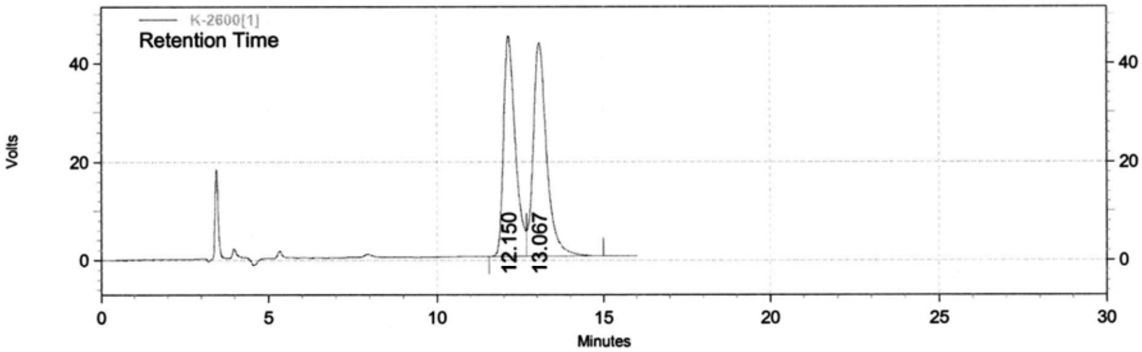


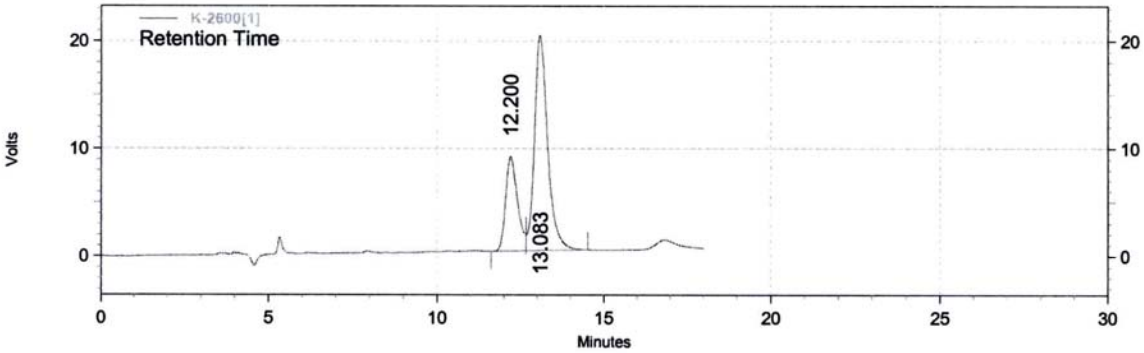
Table 2, entry 15





K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
12.150	1096697	47.35	44898	50.86
13.067	1219420	52.65	43374	49.14



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
12.200	216685	28.26	8771	30.43
13.083	550047	71.74	20053	69.57

Table 2, entry 15

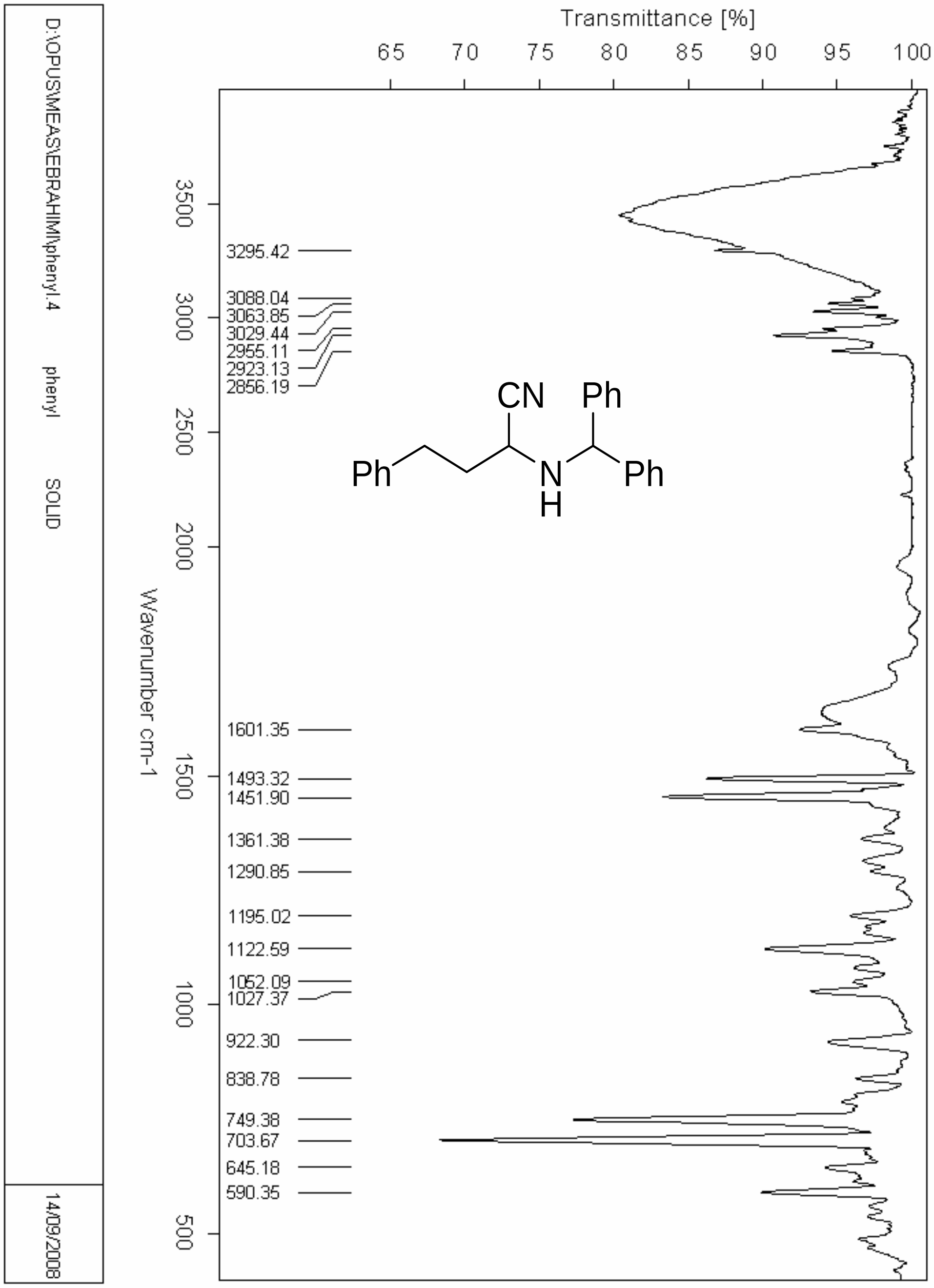


Table 2, entry 16

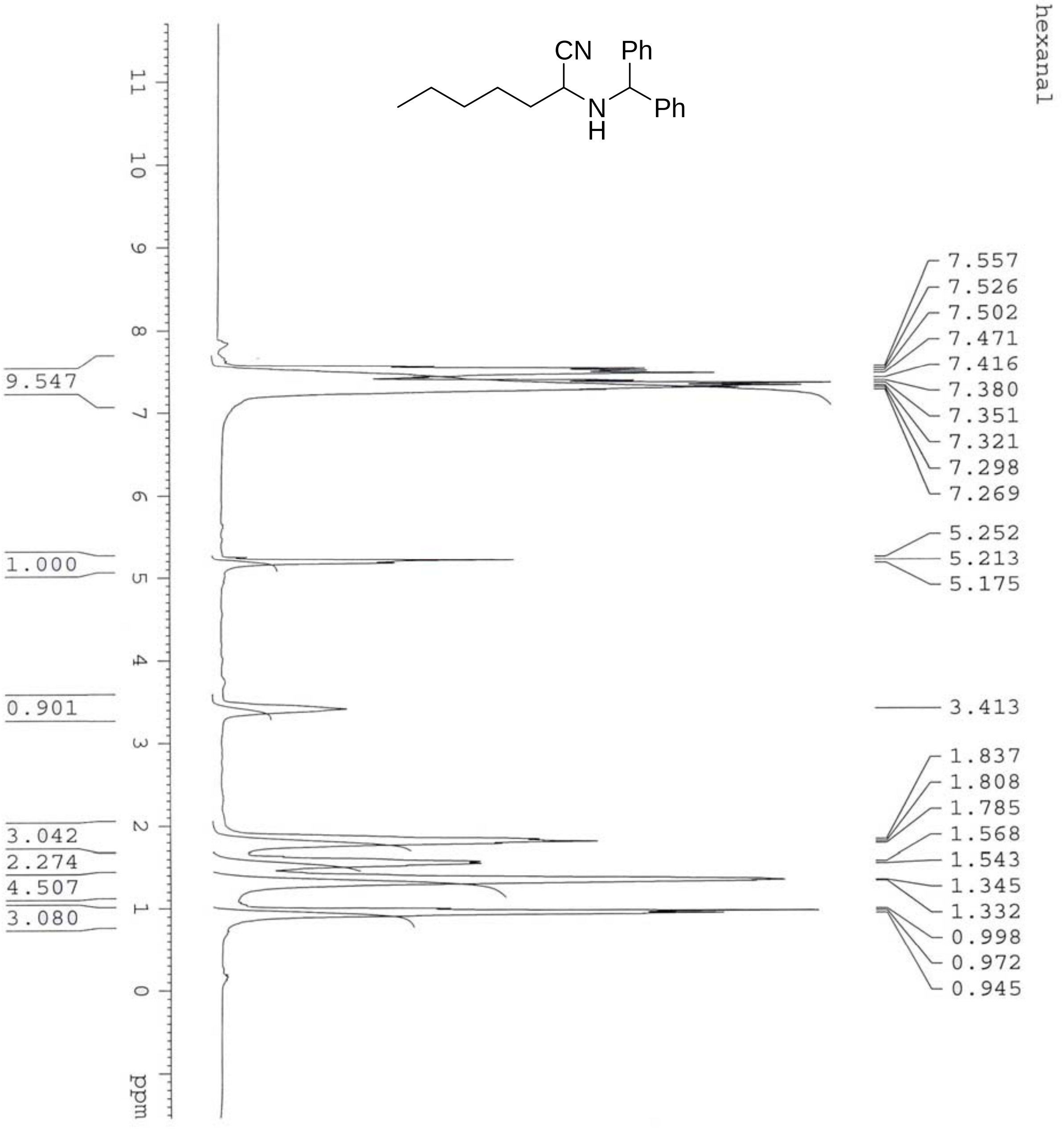


Table 2, entry 16

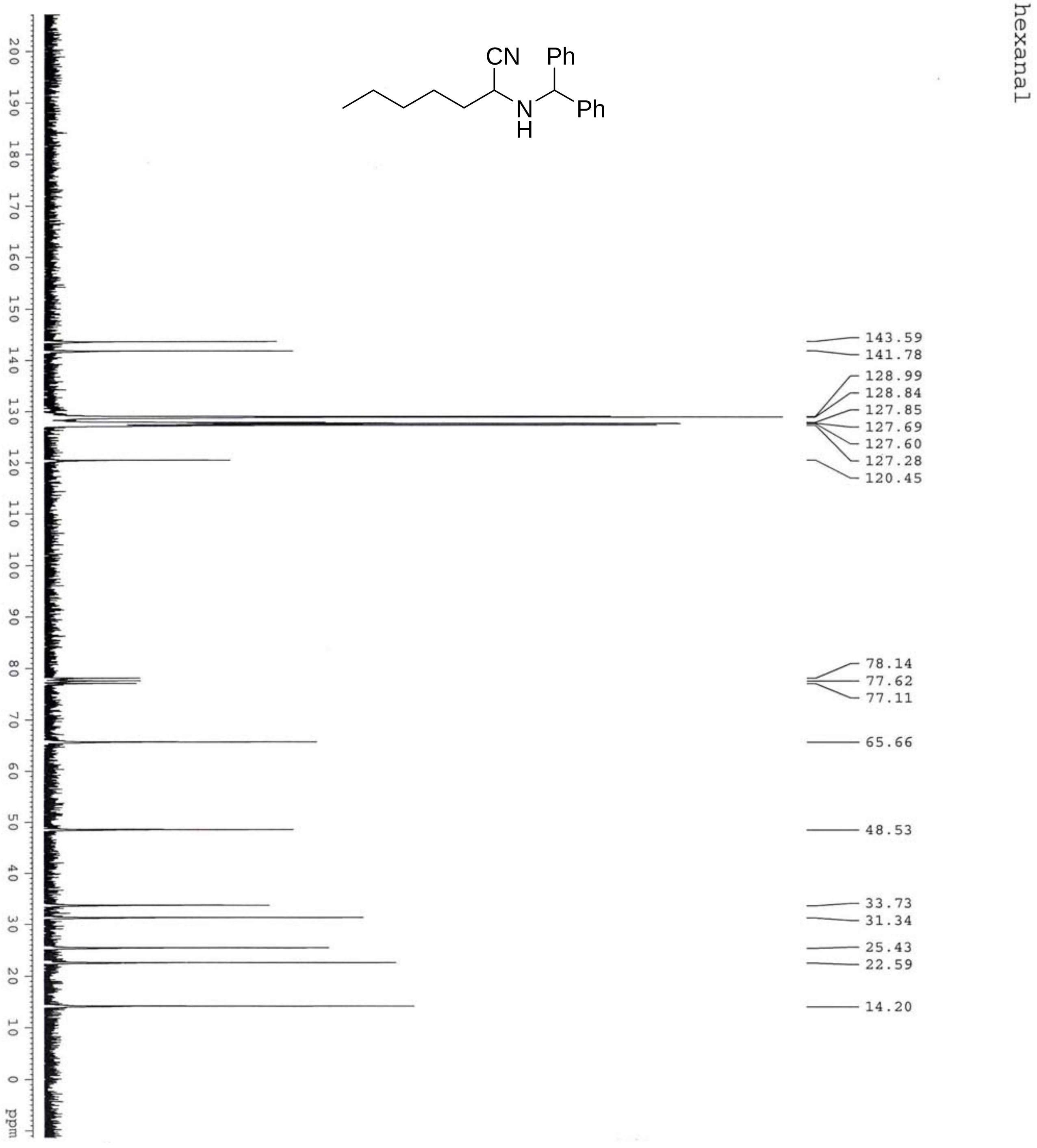


Table 2, entry 16

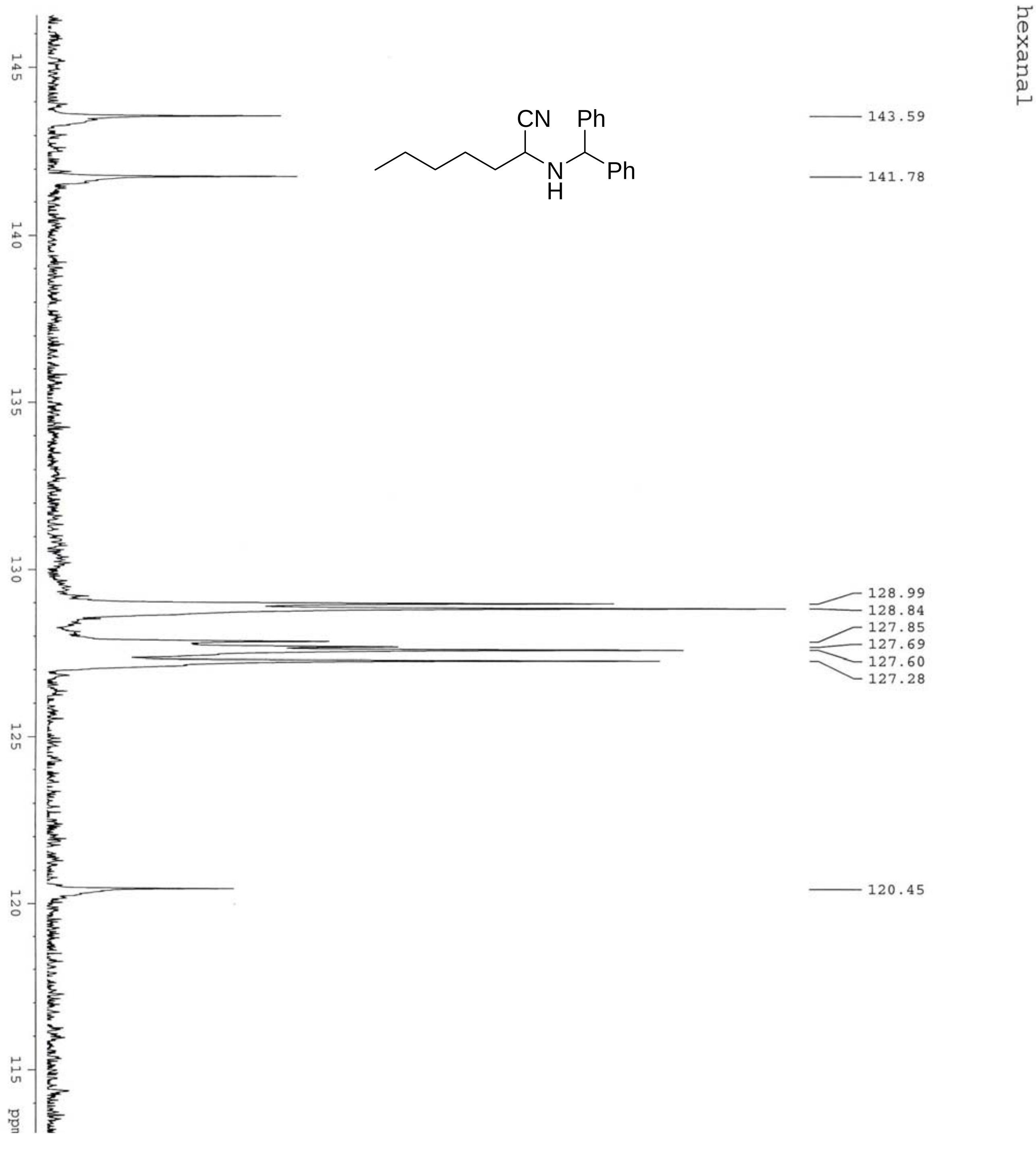
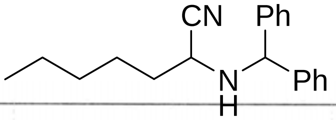
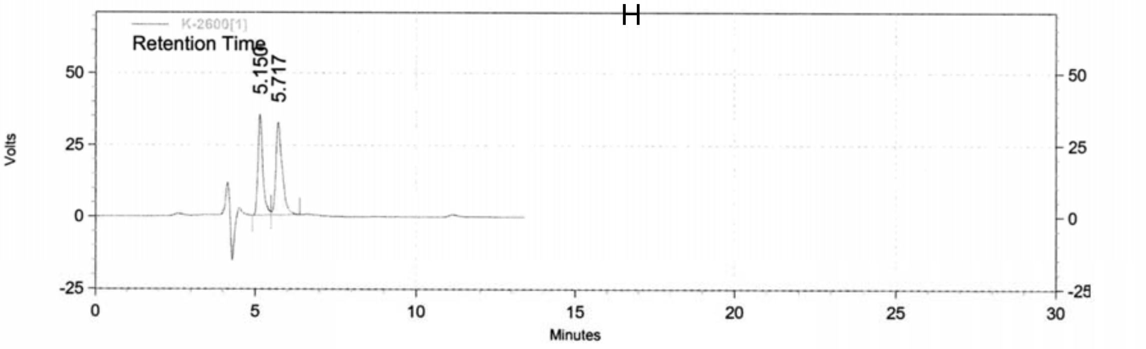


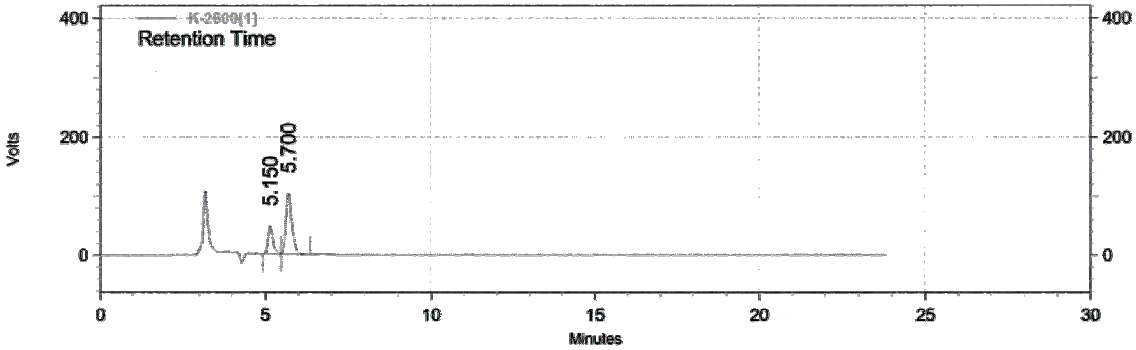
Table 2, entry 16





K-2600[1] Results

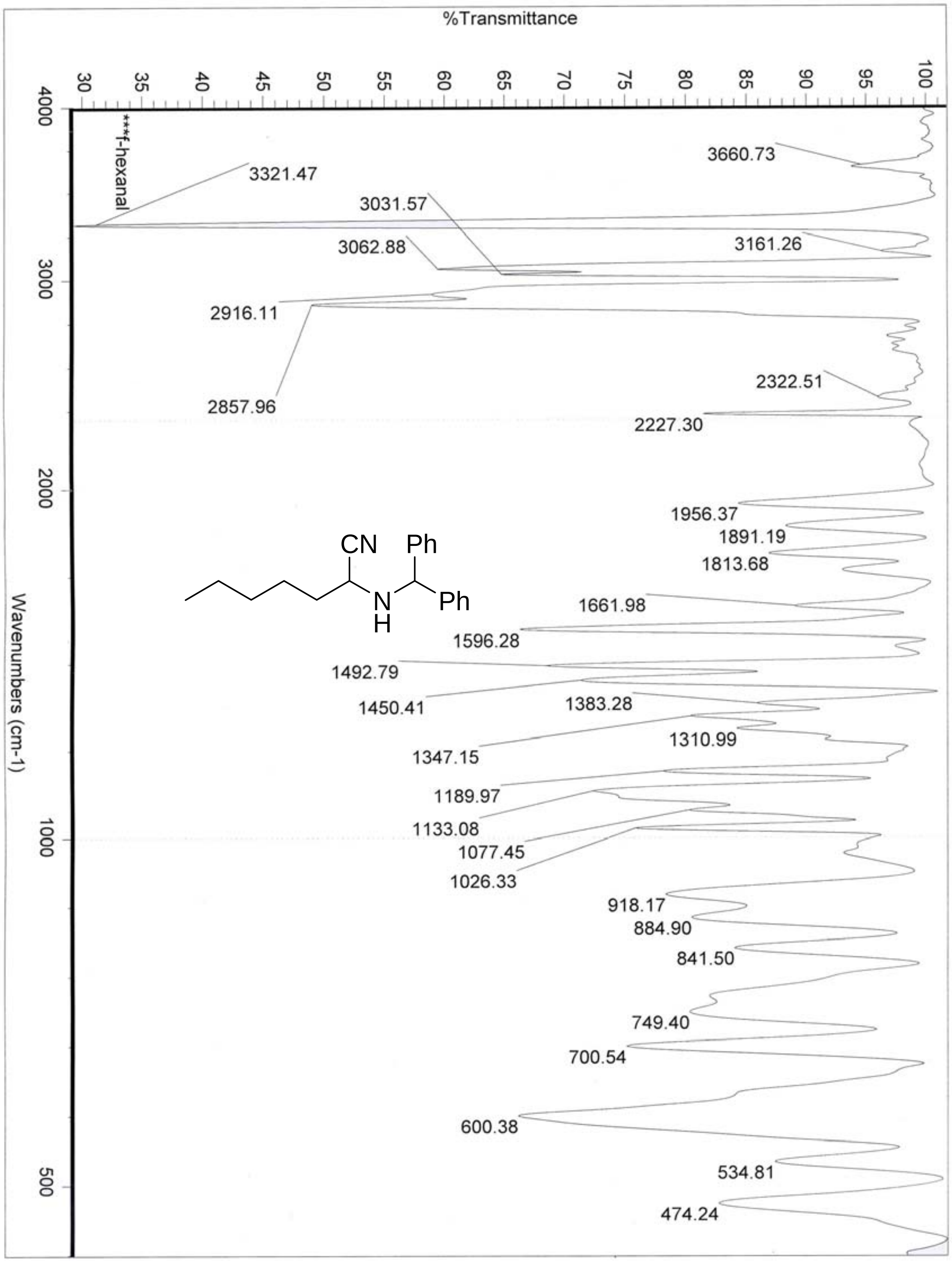
Retention Time	Area	Area %	Height	Height %
5.150	366141	49.38	35068	52.21
5.717	375335	50.62	32098	47.79



K-2600[1] Results

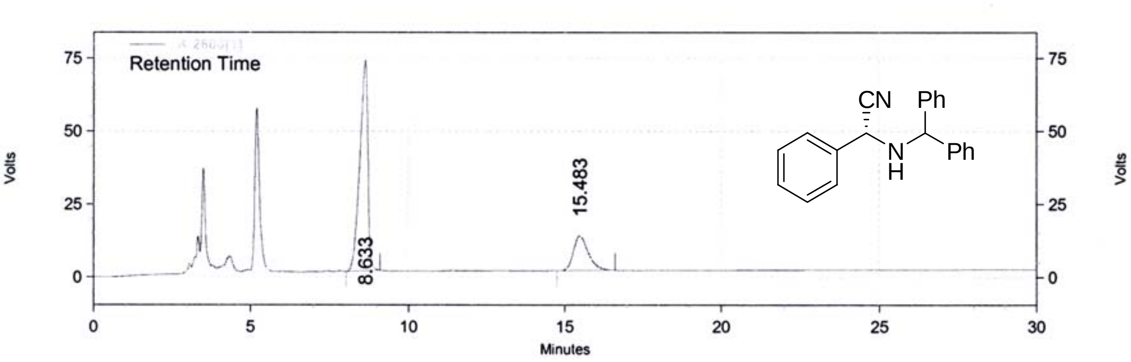
Retention Time	Area	Area %	Height	Height %
5.150	495062	27.65	47255	31.34
5.700	1295078	72.35	103550	68.66

Table 2, entry 16



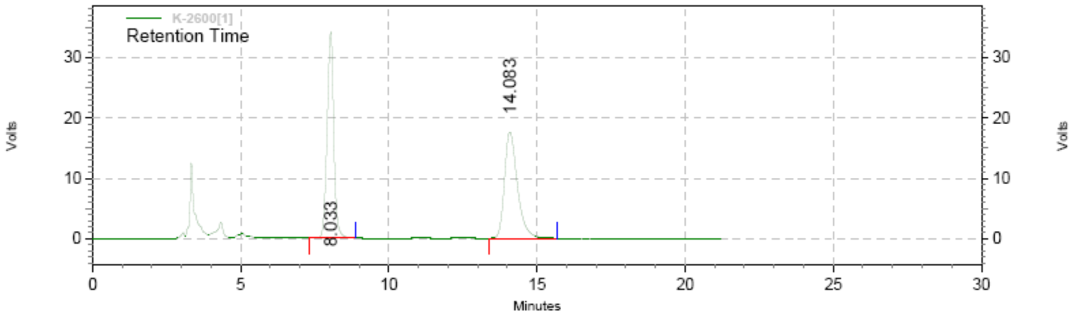
HPLC Chromatograms for Catalytic Enantioselective Strecker Reaction Using yb(OTf)$_3$-pybox system under Homogeneous Conditions at -50 °C

Table 2, entry 17



K-2600[1] Results

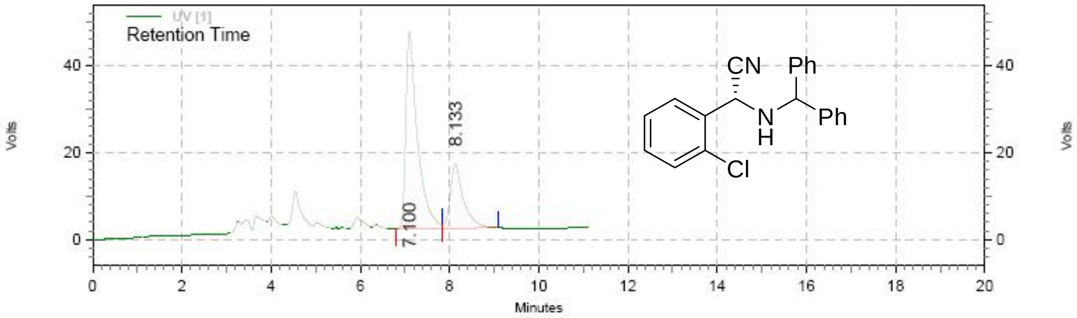
Retention Time	Area	Area %	Height	Height %
8.633	1274549	76.58	72270	85.93
15.483	389798	23.42	11829	14.07



K-2600[1] Results

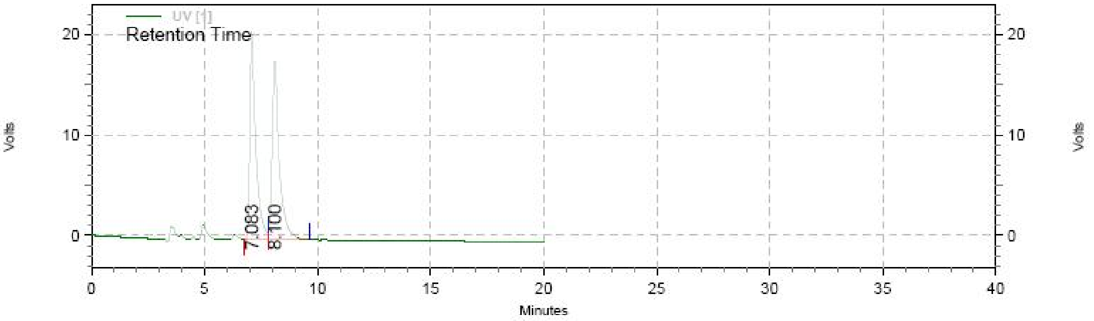
Retention Time	Area	Area %	Height	Height %
8.033	530333	49.79	34090	65.95
14.083	534790	50.21	17597	34.05

Table 2, Entry 18



UV [1] Results

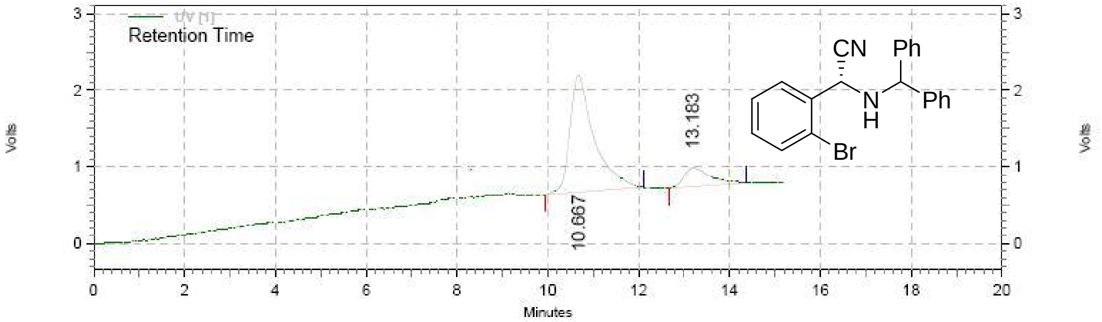
Retention Time	Area	Area %	Height	Height %
7.100	816799	73.10	45340	75.59
8.133	300535	26.90	14638	24.41



UV [1] Results

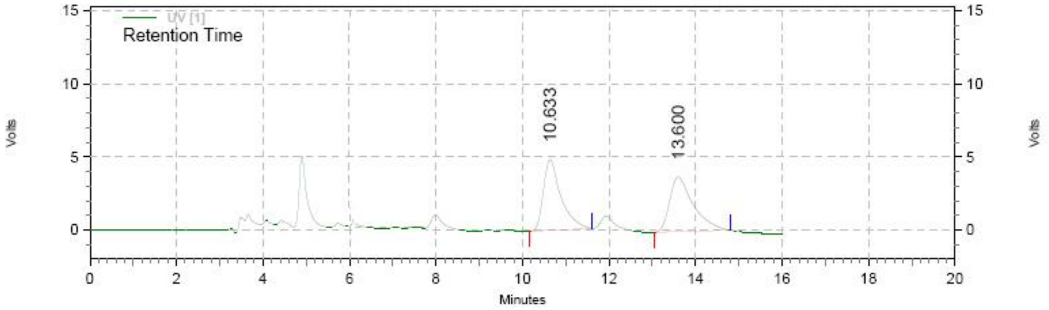
Retention Time	Area	Area %	Height	Height %
7.083	378151	49.71	20675	53.80
8.100	382634	50.29	17753	46.20

Table 2, Entry 19



UV [1] Results

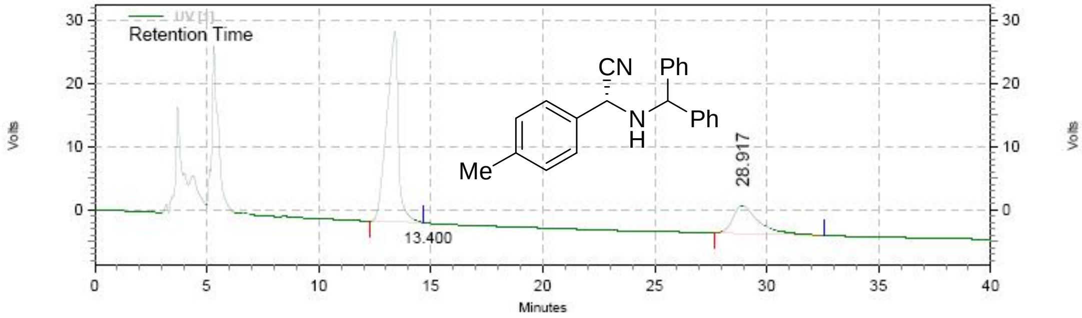
Retention Time	Area	Area %	Height	Height %
10.667	56920	85.31	1529	86.19
13.183	9800	14.69	245	13.81



UV [1] Results

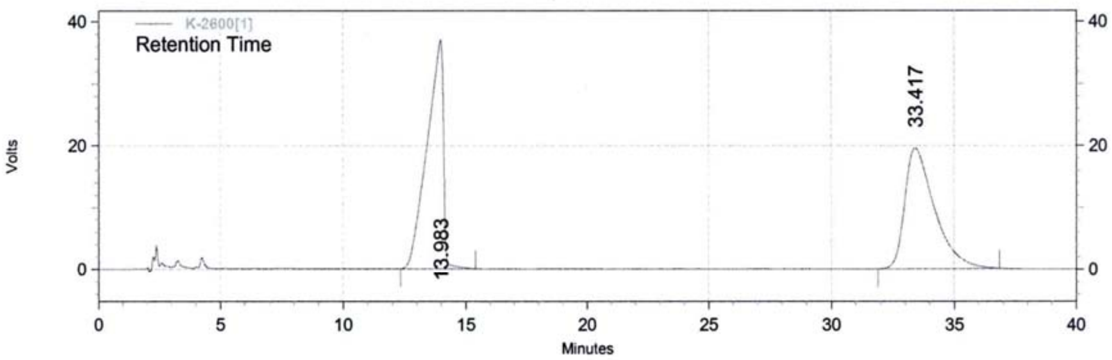
Retention Time	Area	Area %	Height	Height %
10.633	136975	49.14	4848	56.50
13.600	141747	50.86	3732	43.50

Table 2, Entry 20



UV [1] Results

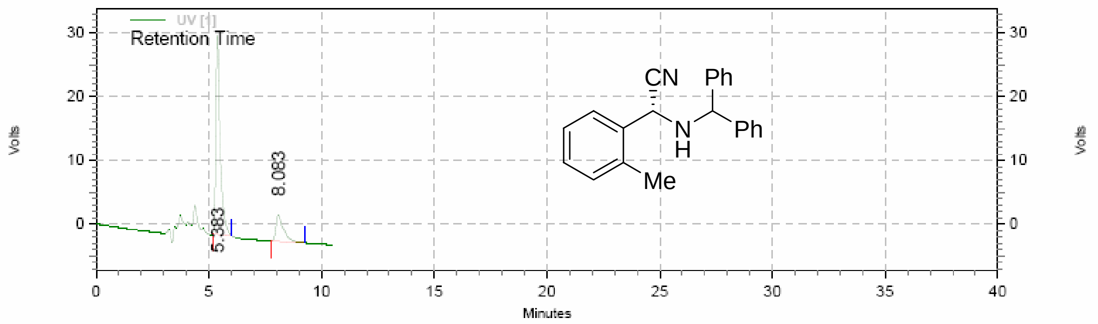
Retention Time	Area	Area %	Height	Height %
13.400	1074147	75.26	30104	87.11
28.917	353174	24.74	4453	12.89



K-2600[1] Results

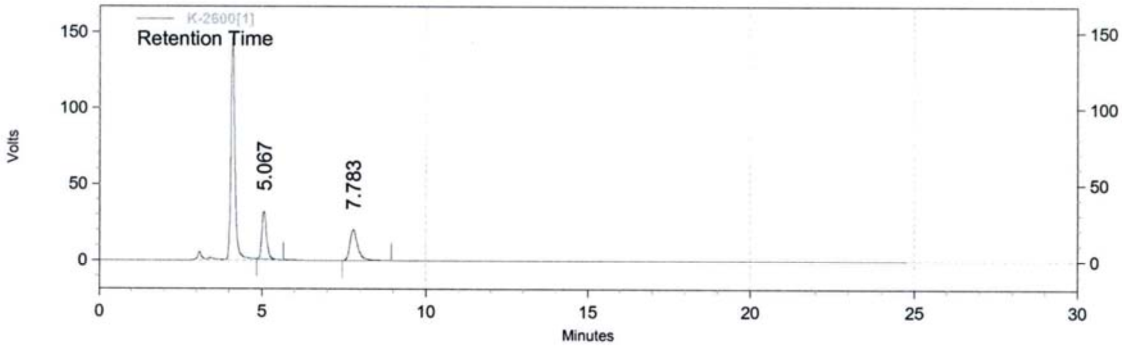
Retention Time	Area	Area %	Height	Height %
13.9 3	1648095	50.18	36935	65.51
33.417	1636272	49.82	19443	34.49

Table 2, Entry 21



UV [1] Results

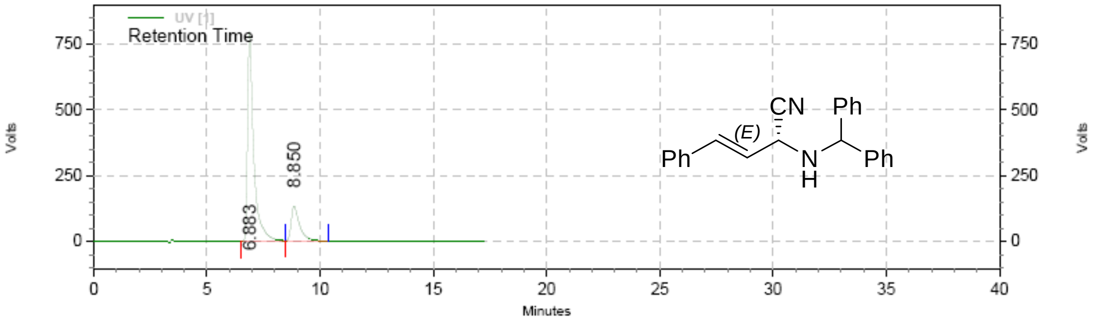
Retention Time	Area	Area %	Height	Height %
5.383	402930	80.62	31209	88.18
8.083	96887	19.38	4183	11.82



K-2600[1] Results

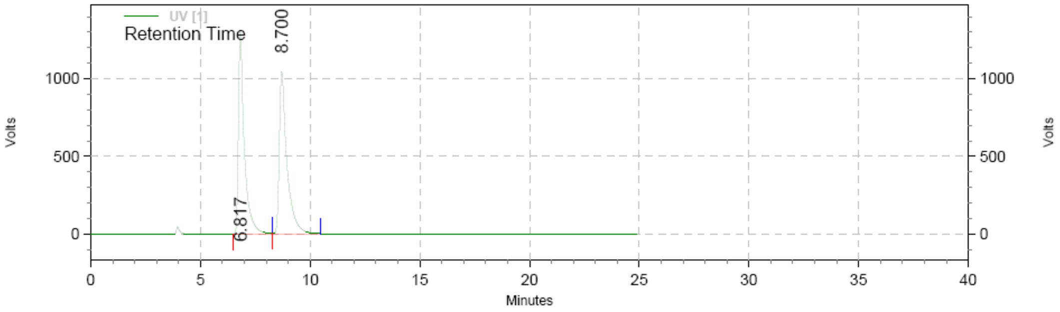
Retention Time	Area	Area %	Height	Height %
5.067	308844	49.20	31368	61.06
7.783	318885	50.80	20008	38.94

Table 2, entry 22



UV [1] Results

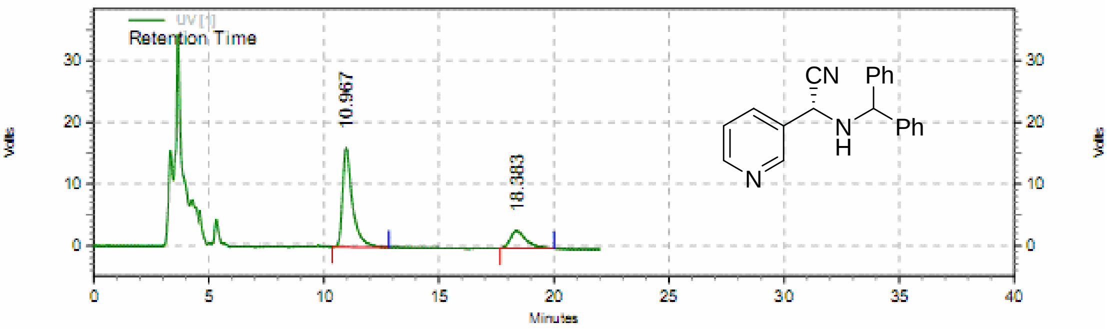
Retention Time	Area	Area %	Height	Height %
6.883	15086873	81.14	794568	85.60
8.850	3506026	18.86	133644	14.40



UV [1] Results

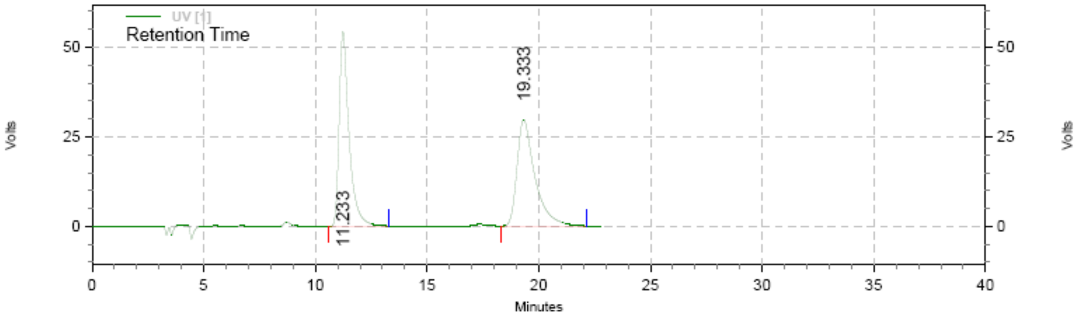
Retention Time	Area	Area %	Height	Height %
6.817	24454699	49.25	1308675	55.63
8.700	25202198	50.75	1043807	44.37

Table 2, entry 23



UV [1] Results

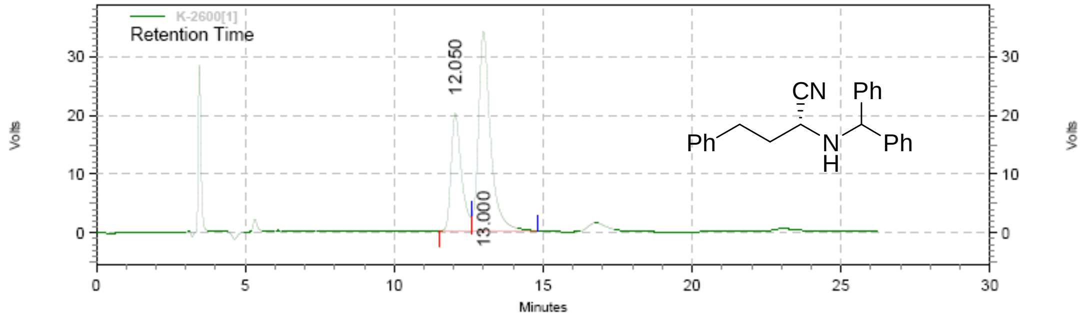
Retention Time	Area	Area %	Height	Height %
10.967	477345	78.19	16063	85.12
18.383	133177	21.81	2809	14.88



UV [1] Results

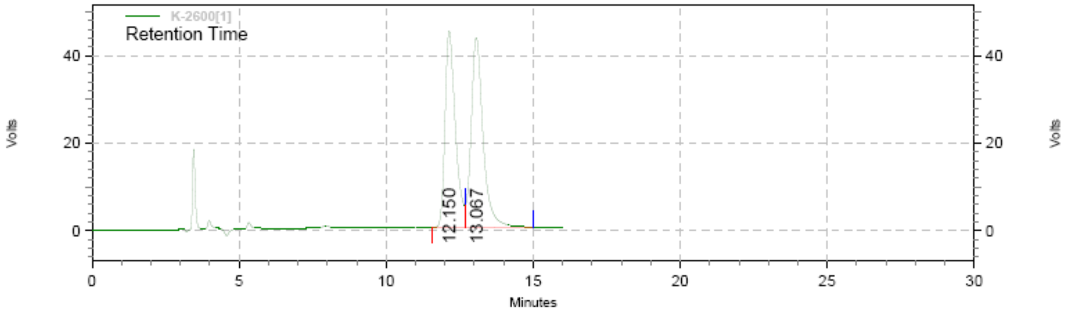
Retention Time	Area	Area %	Height	Height %
11.233	1681989	50.27	54388	64.67
19.333	1663894	49.73	29718	35.33

Table 2, entry 24



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
12.050	479903	33.33	19998	37.06
13.000	960152	66.67	33963	62.94



K-2600[1] Results

Retention Time	Area	Area %	Height	Height %
12.150	1096697	47.35	44898	50.86
13.067	1219420	52.65	43374	49.14

1-12. References:

(1) C. S. J. Cazin, M. Veith, P. Braunstein, R. B Bedford, *Synthesis*, **2005**, 622.

(2) Lundgren, S.; Lutsenko, S.; Jonsson, C.; Moberg, C. *Org. Lett.* **2003**, *5*, 3663**.**