Supporting Information for

Direct Alkylation of Amines with Alcohols Catalyzed by Base

Qiang-Qiang Li, Zu-Feng Xiao, Chuan-Zhi Yao, Hong-Xing Zheng, and Yan-Biao Kang*

Center of Advanced Nanocatalysis, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

E-mail: ybkang@ustc.edu.cn

Contents

1. General Information

Alcohols and bases were all purchased from comercial sources. All alcohols were dried on CaO and purified by fractional distillation at reduced pressure under argon. ICP-AES and elemental analysis were tested by the service at University of Science and Technology of China. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer; chemical shifts are reported in δ units relative to $CHCl_3$ [^{1}H δ = 7.26, ^{13}C δ = 77.36] or TMS [^{1}H δ = 0.00, ^{13}C δ = 0.00]. For the React-IR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem. Data manipulation was carried out using the IC IR software, version 4.2.

2. Experimental Procedures

2.1. Reaction Conditions (Scheme 2 in text)

2.1.1. Effect of Base

p-Toluenesulfonamide (1 mmol) and a base (150 mol %) [*t*-BuOK, KOH, NaOH, NaH (60% dispersion in mineral oil), Na_2CO_3, K_2CO_3, Cs_2CO_3 and $KHCO_3$] were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (1 mL) was added under argon flow. The reaction mixture was stirred (350 rpm) at 130 ℃ for 10 hours. After cooling to room temperature, the crude reaction mixture was examined on ^{1}H NMR spectrometer to determine the conversion using *tert*-butyl methyl ether and dimethylsulfoxide as internal standards.

2.1.2. Screening Reaction Conditions

p-Toluenesulfonamide salts (1 mmol) and bases (5-30 mol %) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (1 mL) was added under argon flow. The reaction mixture was stirred (350 rpm) at 130 ℃ for 25 hours. After cooling to room temperature, the crude reaction mixture was examined on ^{1}H NMR spectrometer to determine the conversion using *tert*-butyl methyl ether and dimethylsulfoxide as internal standards.

2.2. Control Experiments

2.2.1 Isotope Labelling Experiments

Potassium *p*-toluenesulfonamide (0.5 mmol) and potassium hydroxide (50 mol %) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, **1a**/**1a-D** (0.5 mL, 4.8 mmol) was added under

argon flow. The reaction mixture was stirred (350 rpm) at 130 ℃ for 1 hour. After cooling to room temperature, the crude reaction mixture was examined on ^{1}H NMR spectrometer to determine the conversion using 8-methylquinoline as internal standard. These two reactions were excuted parallelly and the k_H/k_D was determined to be 2.5:1.

p-Toluenesulfonamide (2 mmol) and potassium hydroxide (2.6 mmol, 130 mol %) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, **1a-D** (0.5 mL, 4.8 mmol) and 4-methylbenzyl alcohol (4.8 mmol) were added under argon flow. The reaction mixture was stirred (350 rpm) at 140 °C. After disppearing of the *p*-toluenesulfonamide on TLC, the reaction mixture was filtered through a thin pad of *Celite*, followed by washing with dichloromethane. The solvent was evaporated under reduced pressure and the solid residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product.

p-Toluenesulfonamide (2 mmol) and potassium hydroxide (2.6 mmol, 130 mol%) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, **1a-D** (0.5 mL, 4.8 mmol) and *p*-tolualdehyde (2 mmol) were added under argon flow. The reaction mixture was stirred (350 rpm) at 140 °C. After disppearing of the *p*-toluenesulfonamide on TLC, the reaction mixture was filtered through a thin pad of *Celite*, followed by washing with dichloromethane. The solvent was evaporated under reduced pressure and the solid residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product.

2.2.2 Effect of Oxygen

Potassium hydroxide (0.05 mmol, 5 mol %) was weighed into a 25 mL Schlenk tube and dried *in vacuo* for 15 min. Benzyl alcohol (1 mL) was first degassed by bubbling argon for 2 hours and then added into Schlenk tube under argon flow. Then the mixture was further degassed by freeze-pump-thaw method (in liquid nitrogen). Oxygen (0.02 mmol, 0.1 mmol) was added into the Schlenk *via* syringe. And the reaction mixture was stirred (350 rpm) at 130 ℃ for 13 hours. After cooling to room temperature, the crude reaction mixture was examined on GC to determine the conversion using 8-methylquinoline as internal standard.

2.3. ICP-AES Analysis of Reaction Mixture for Trace Transition Metals (Table S4)

The experiments was carried out on inductively coupled plasma atomic emission spectrometer (Optima 7300DV, Perkin Elmer Corporation) (N. D. refers to Not Detected).

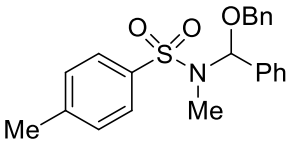
Table S4. ICP-AES Analysis

Metallic elements	Reaction mixture (ppm)	Metallic elements	Reaction mixture (ppm)
Pd	N. D.	Zn	N. D.
Ir	N. D.	Co	N. D.
Ru	N. D.	Sn	N. D.
Rh	N. D.	Pt	N. D.
Cu	N. D.	Pb	N. D.
Ni	N. D.		

3. Reaction Procedures

3.1. Preparation of 8a

N-benzylidene-4-methylbenzenesulfonamide (**5a**, 1 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (1 mL) was added under argon flow. Then the mixture was cooled to 0 ℃ and *t*-BuLi (1.2 mmol) was added slowly. After stirred at 0 ℃ for 5 minutes, the mixture was stirred at room temperature. After the imine disappeared, MeI (2 mmol) was added slowly. After completion of the reaction, the reaction mixture was filtrated through a thin pad of *Celite* and washed with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified on neutral aluminium oxide column with petroleum ether, dichloromethane and ethyl acetate to give the product.



***N*-((benzyloxy)(phenyl)methyl)-*N*,4-dimethylbenzenesulfonamide (7a)**

39%, 148.8 mg, Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.36-7.25 (m, 12 H), 6.37 (s, 1H), 4.59 (dd, *J* = 20.4, 11.6 Hz, 2 H), 2.58 (s, 3 H), 2.43 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 137.8, 137.7, 137.4, 130.0, 128.7, 128.6, 128.1, 128.0, 127.7, 127.0, 87.2, 70.4, 28.3, 21.9. **HRMS (ESI)** calcd. for $C_{22\,H23}NO_3S\,Na^+$ $[M+Na]^+$ 404.1293, found 404.1296.

3.2. Representative Procedure for Benzyl Alcohol Recovery

When the reaction of benzyl alcohol and potassium sulfonamide finished, the reaction mixture was filtrated through a thin pad of *Celite* and washed with dichloromethane. The solvent was evaporated under reduced pressure and the solid residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product and the unreacted alcohol. 80% (6.9 mmol) OF alcohol was recycled.

3.3. Procedure for ^{1}H NMR Monitoring Experiments.

3.3.1. ^{1}H NMR Monitoring Experiment

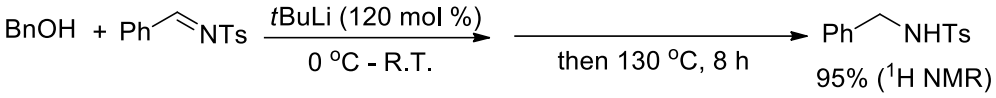
In an ice water bath *n*-BuLi (0.12 mmol) was added slowly into benzyl alcohol (0.12 mmol) in the vessel. The well-mixed solution was added into the solution of 4-methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (0.1 mmol) in DMSO-d_6 (0.5 mL) in NMR tube under argon flow. Shake the tube vigorously and take it for ^{1}H NMR test immediately. The operando ^{1}H NMR spectra was recorded over the course of the reaction.

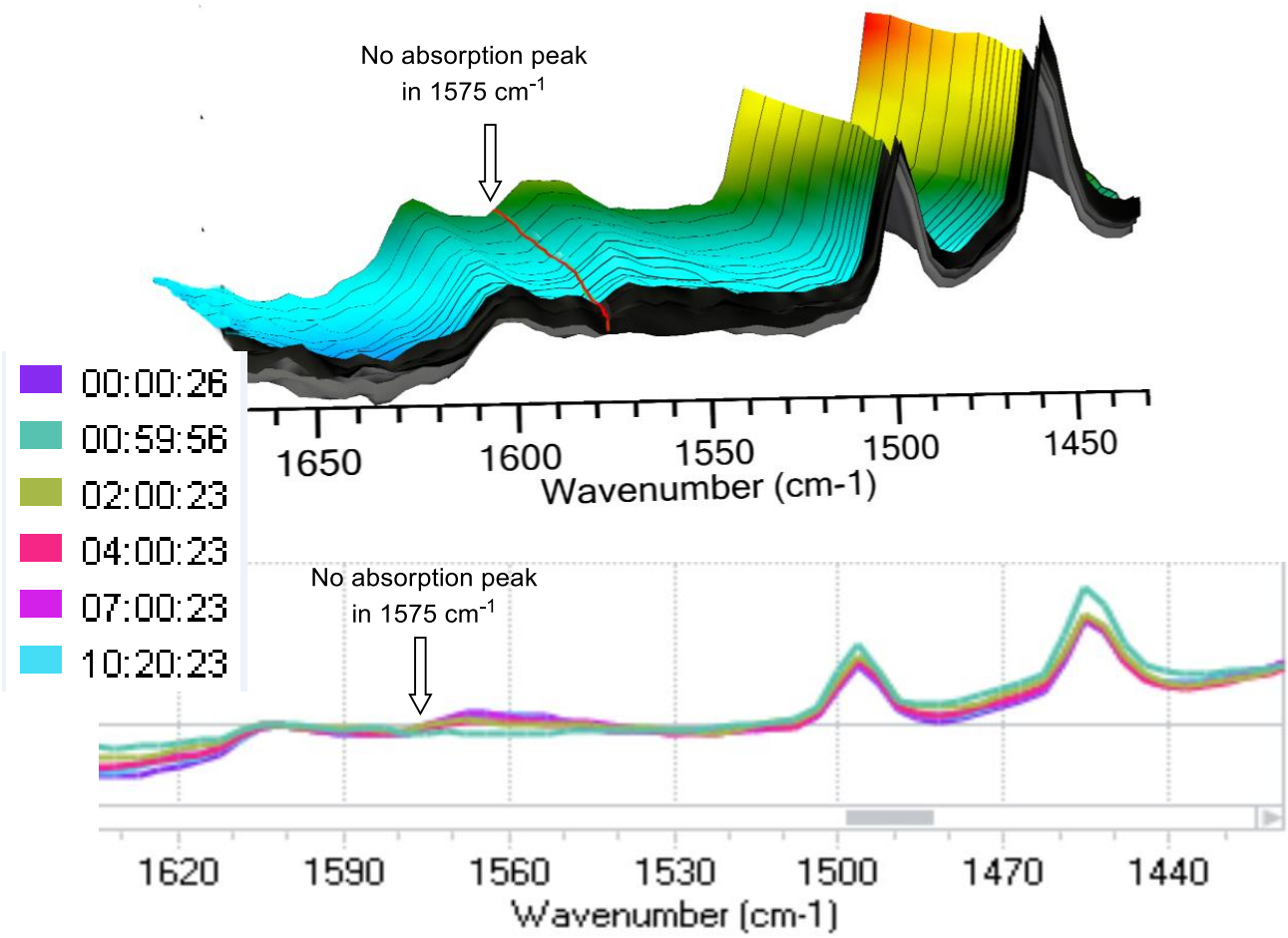
3.4. Procedure for React-IR Monitoring Experiments.

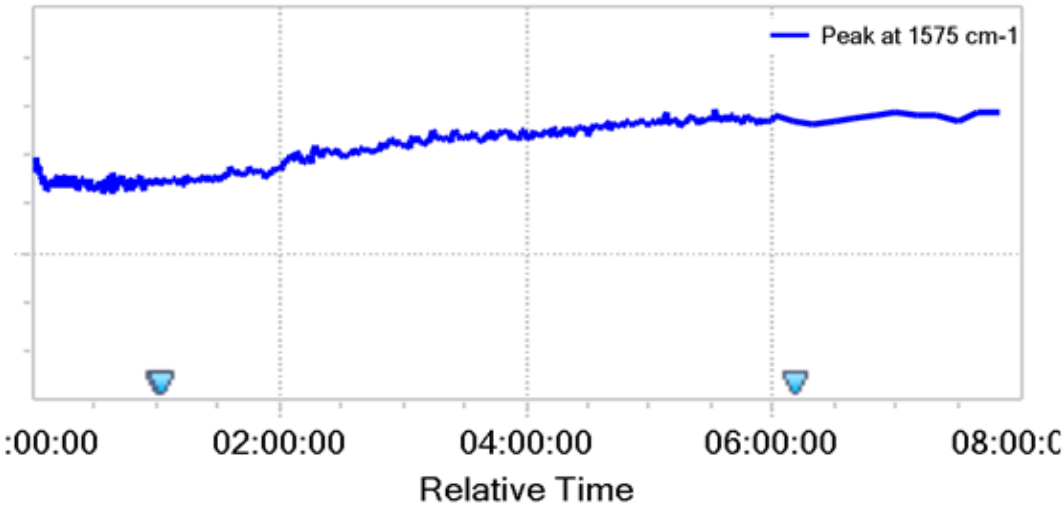
3.4.1. React-IR Monitoring the Reaction of Imine and Benzyl Alcohol

N-benzylidene-4-methylbenzenesulfonamide (2 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (3 mL) was added. Then the mixture was cooled to -78 ℃ and

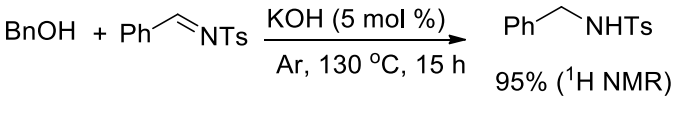
t-BuLi (2.4 mmol) was added slowly. The reaction mixture was stirred at 0 ℃ for a moment and *n*-pentane was removed by vacuumizing. The IR probe was inserted into the Schlenk tube through an adapter under argon flow. The reaction vessel was kept in 130 ℃ and operando IR spectra was recorded over the course of the reaction.

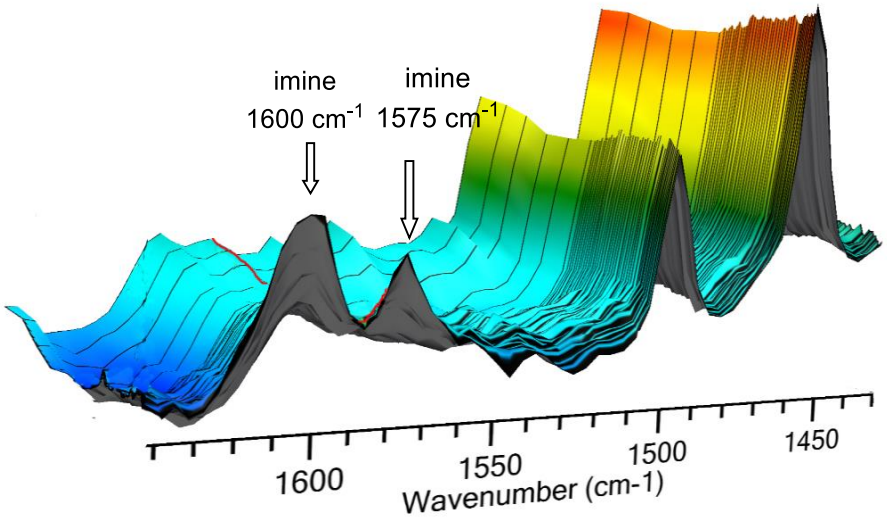


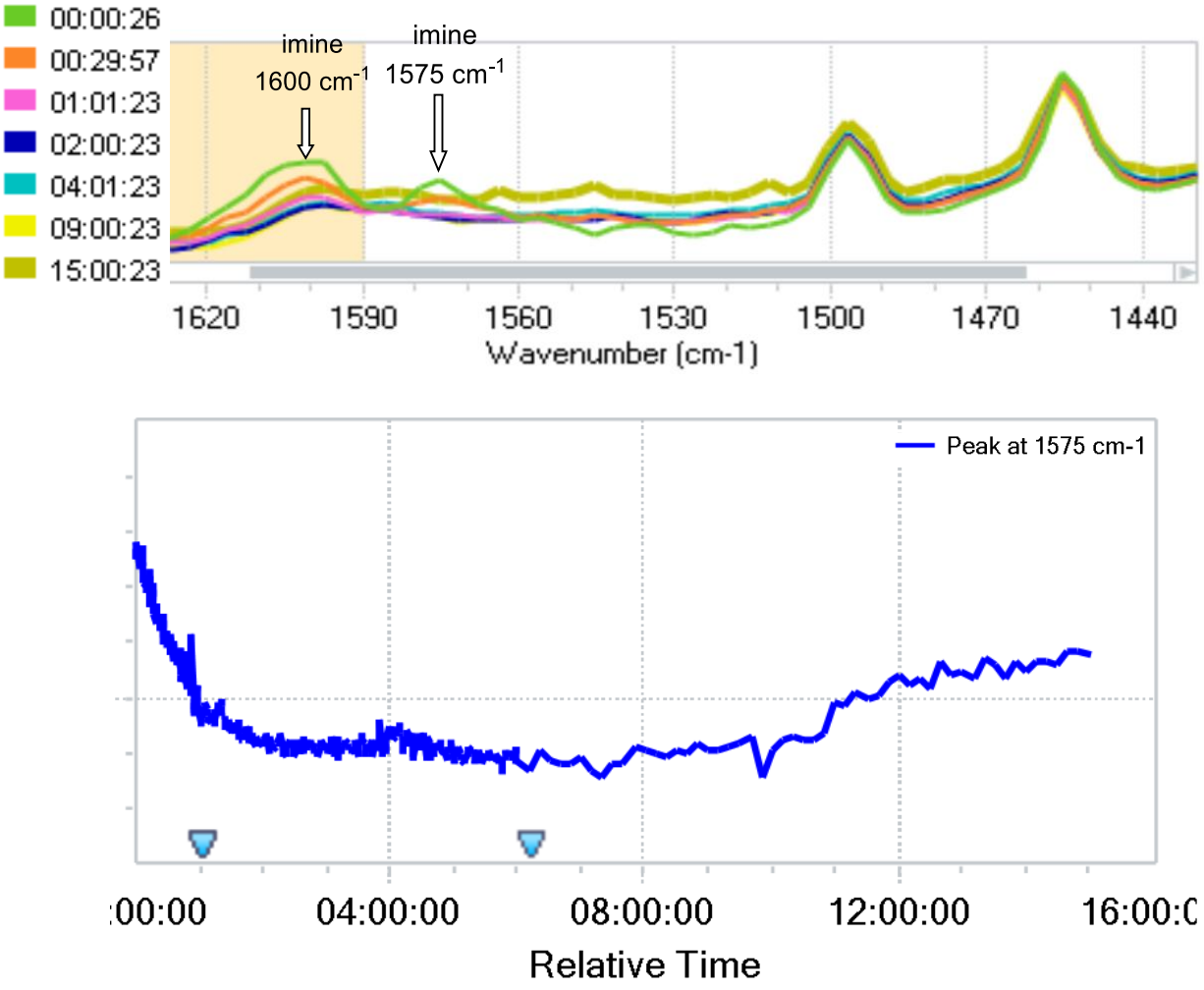




N-benzylidene-4-methylbenzenesulfonamide (2 mmol) and KOH (0.1 mmol) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (2 mL) was added. The IR probe was inserted into the Schlenk tube through an adapter under argon flow. The reaction vessel was kept in 130 ℃ and operando IR spectra was recorded over the course of the reaction (*Imine vanished soon after heating up to 130 °C*).

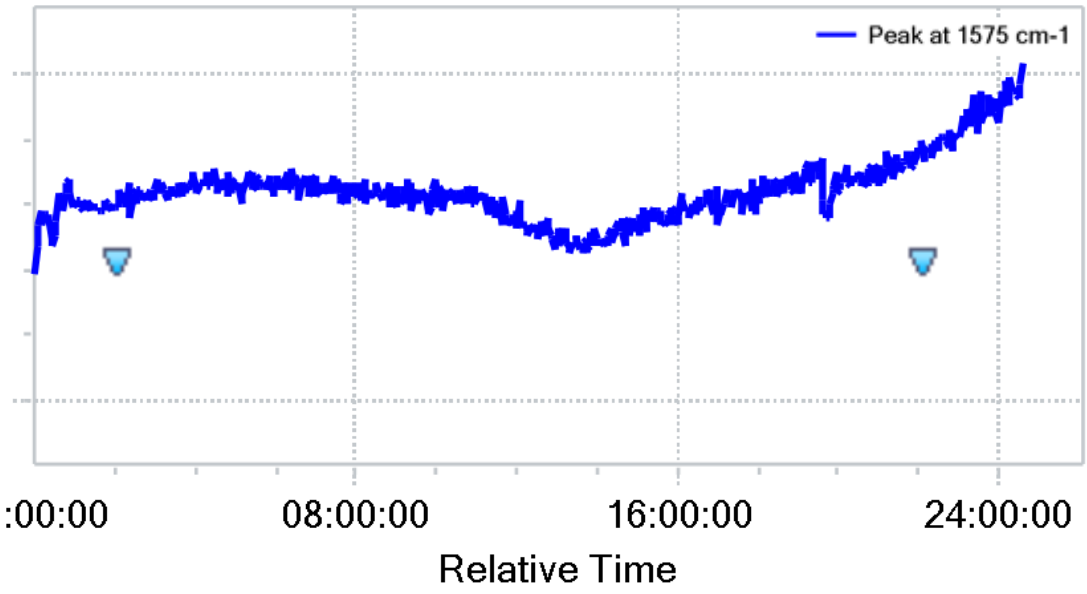






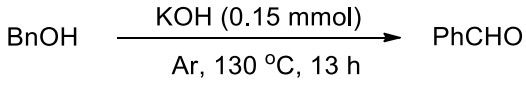
3.4.2. React-IR Monitoring the Reaction of Potassium Sulfonamide and Benzyl Alcohol

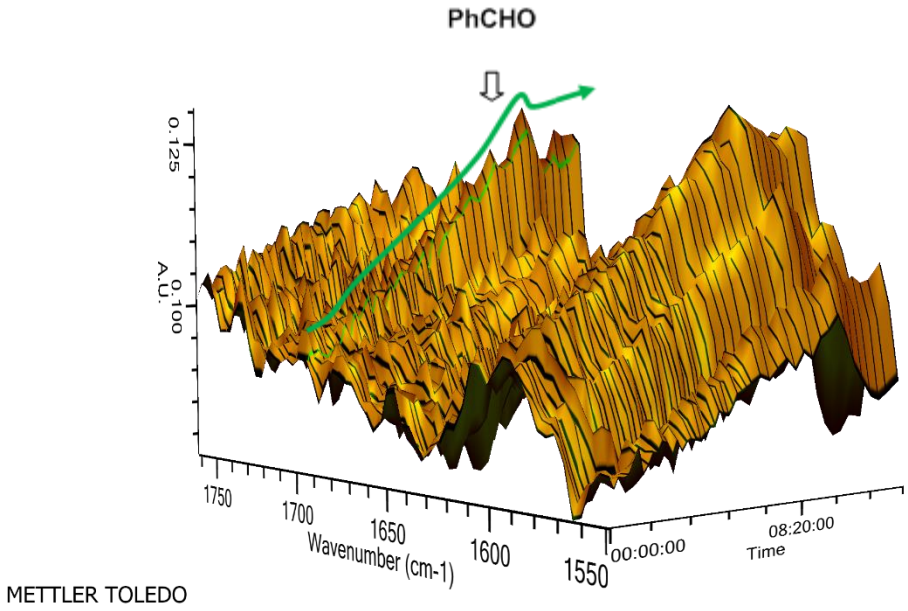
Potassium sulfonamide (2 mmol) and potassium hydroxide (0.1 mmol) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (3 mL) was added. The IR probe was inserted into the Schlenk tube through an adapter under argon flow. The reaction vessel was kept in 130 ℃ and operando IR spectra was recorded over the course of the reaction.

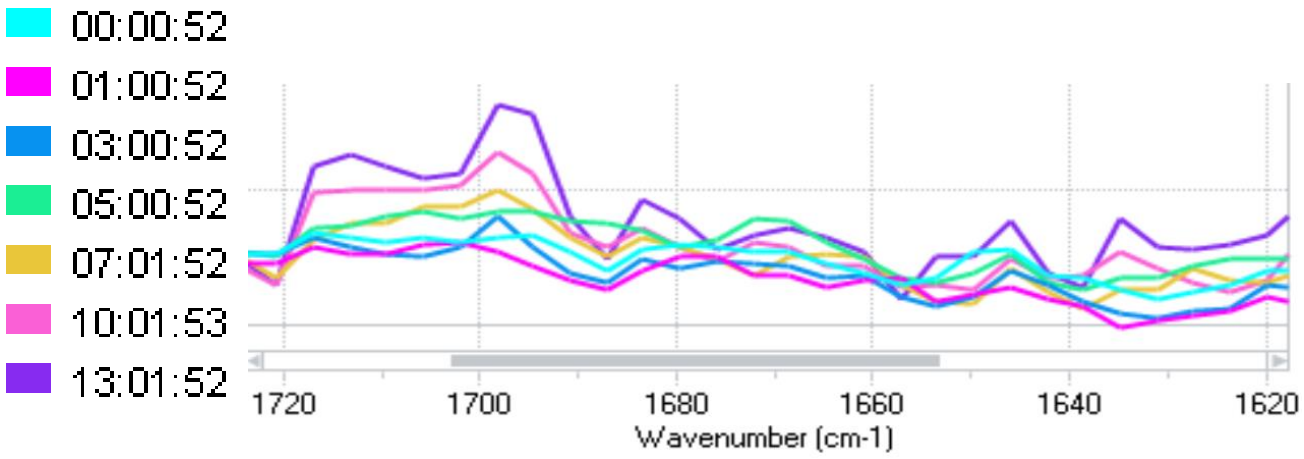


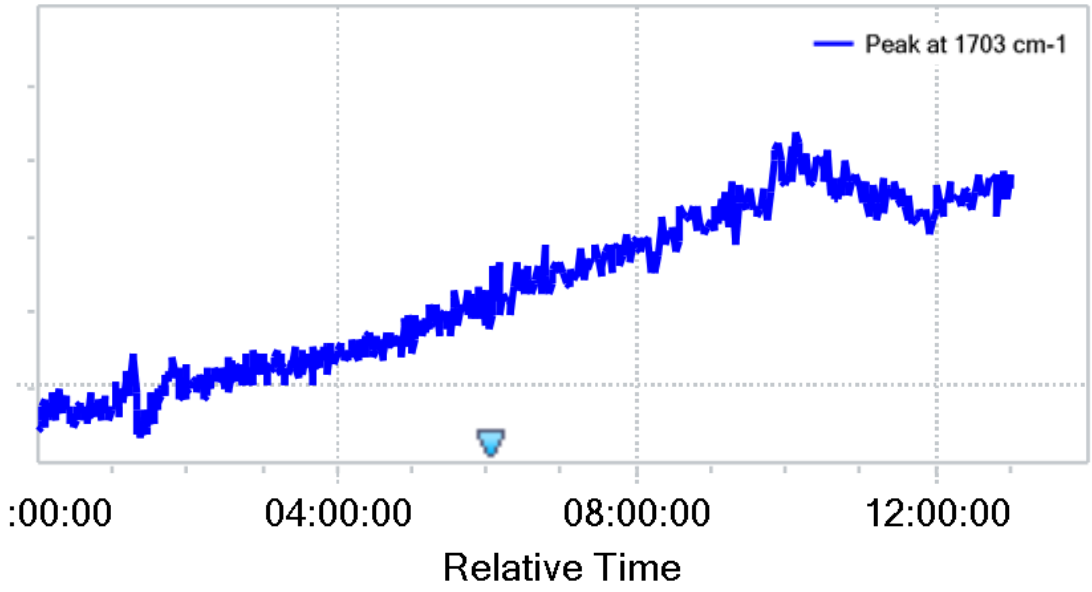
3.4.3. React-IR Monitoring the Oxidation of BnOH in Different Atmosphere

Potassium hydroxide (0.15 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (3 mL) was added. The IR probe was inserted into the Schlenk tube through an adapter under argon flow. The reaction vessel was kept in 130 ℃ and operando IR spectra was recorded over the course of the reaction.

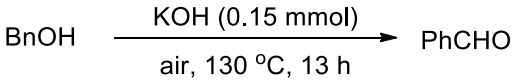


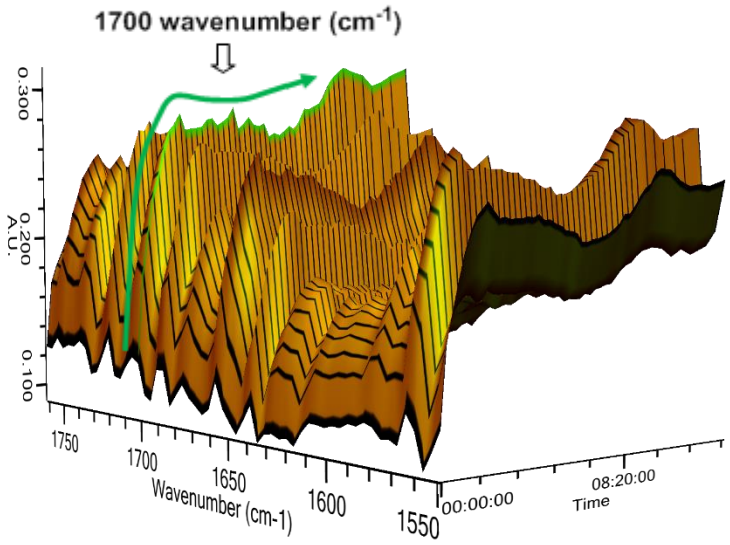




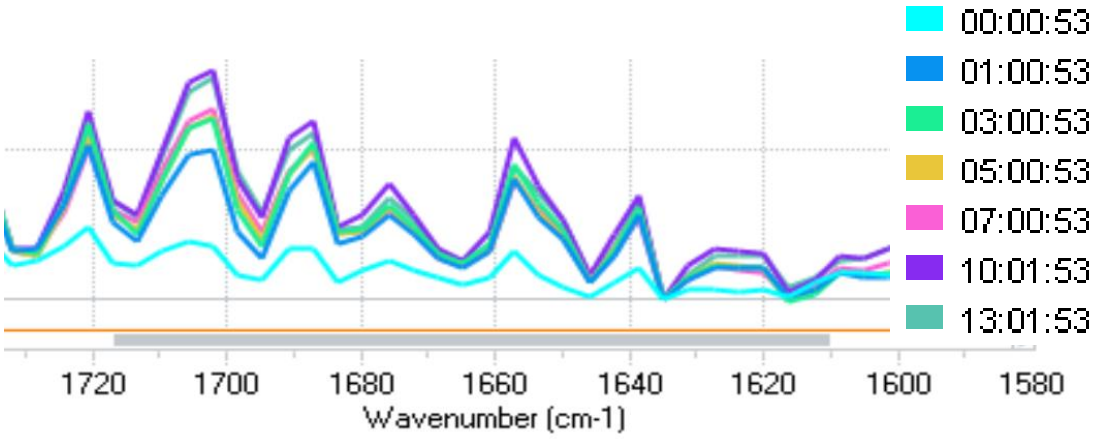


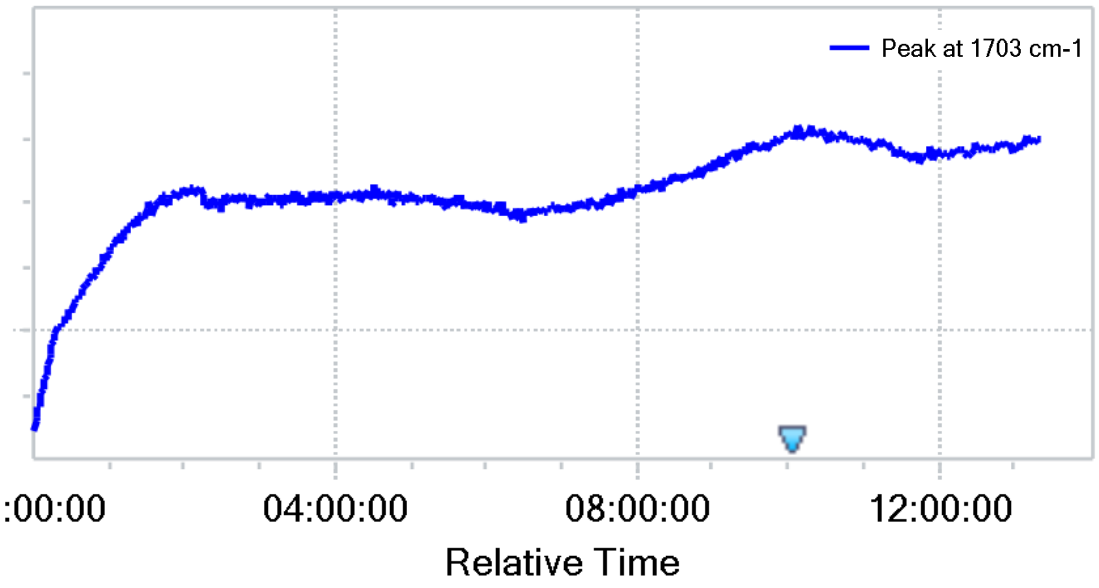
Potassium hydroxide (0.15 mmol) was weighed into a 25 mL Schlenk tube. Then benzyl alcohol (3 mL) was added. The IR probe was inserted through an adapter into the Schlenk tube. Then air balloon was connected to the branch of Schlenk tube.The reaction vessel was kept in 130 ℃ and operando IR spectra was recorded over the course of the reaction.





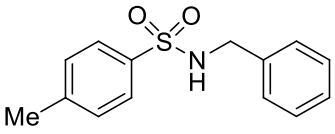
METTLER TOLEDO





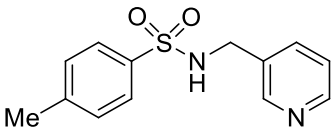
3.5. General Procedure for Direct Sulfonamidation of Alcohols

Potassium sulfonamide (1 mmol) and potassium hydroxide (0.05mmol) were weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, an alcohol (1 mL) was added under argon flow. The reaction mixture was stirred at 130 ℃. After disappearing of the potassium sulfonamide on TLC, the reaction mixture was filtrated through a thin pad of *Celite* and washed with dichloromethane. The solvent was evaporated under reduced pressure and the solid residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product.



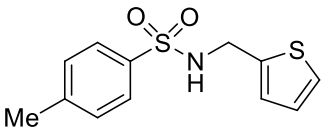
***N*-benzyl-4-methylbenzenesulfonamide (3a)[1]**

White solid, 25 h, 240 mg, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H), 7.32-7.18 (m, 7 H), 4.67 (t, *J* = 5.6 Hz, 1 H), 4.12 (d, *J* = 6.4 Hz, 2 H), 2.44 (s, 3 H).



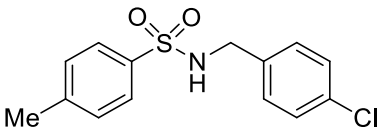
4-methyl-*N*-(pyridin-3-ylmethyl)benzenesulfonamide (3b)[3]

White solid, 25 h, 219.9 mg, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.8, 1.2 Hz, 1 H), 8.39 (d, *J* = 2.0 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.63-7.60 (m, 1 H), 7.32 - 7.30 (m, 2 H), 7.24-7.20 (m, 1 H), 5.09 (br s, 1 H), 4.15 (d, *J* = 6.4 Hz, 2 H), 2.44 (s, 3 H).



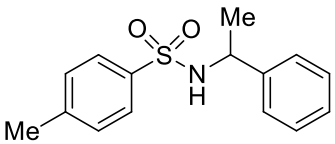
4-methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide (3c)[3]

White solid, 25 h, 262.0 mg, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.19 (dd, *J* = 5.2, 1.2 Hz, 1 H), 6.89-6.84 (m, 2 H), 4.84 (br s, 1H), 4.33 (d, *J* = 5.2 Hz, 2 H), 2.44 (s, 3 H).



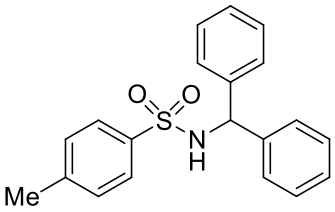
***N*-(4-chlorobenzyl)-4-methylbenzenesulfonamide (3d)[3]**

White solid, 25 h, 289.4 mg, 97%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.8 Hz, 2 H), 7.13 (d, *J* = 8.8 Hz, 2 H), 4.80 (t, *J* = 6.0 Hz, 1 H), 4.09 (d, *J* = 6.0 Hz, 2 H), 2.44 (s, 3 H).



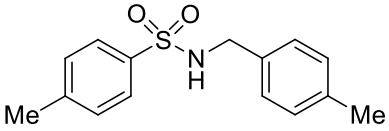
4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (3e)[8]

White solid, 21 h, 272.6 mg, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2 H), 7.20-7.16 (m, 5 H), 7.11-7.09 (m, 2 H), 5.14 (d, *J* = 6.8 Hz, 1 H), 4.45 (quintet, *J* = 6.8 Hz, 1 H), 2.38 (s, 3 H), 1.41 (d, *J* = 6.8 Hz, 3 H).



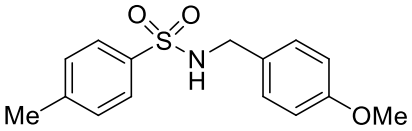
***N*-benzhydryl-4-methylbenzenesulfonamide (3f)[9]**

White solid, 19 h, 334.1 mg, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2 H), 7.22-7.19 (m, 6 H), 7.13-7.09 (m, 6 H), 5.57 (d, *J* = 7.2 Hz, 1 H), 5.38 (d, *J* = 7.2 Hz, 1 H), 2.37 (s, 3 H).



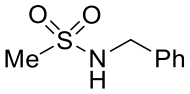
4-methyl-*N*-(4-methylbenzyl)benzenesulfonamide (3g)[1]

White solid, 25 h, 246.5 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.07 (s, 4 H), 4.79 (br s, 1 H), 4.06 (d, *J* = 6.0 Hz, 2 H), 2.44 (s, 3 H), 2.30 (s, 3 H).



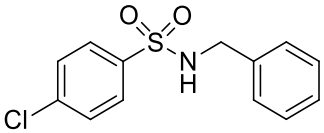
***N*-(4-methoxybenzyl)-4-methylbenzenesulfonamide (3 H)[1]**

White solid, 25 h, 273.8 mg, 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 4.54 (br s, 1 H), 4.05 (d, *J* = 6.0 Hz, 2 H), 3.78 (s, 3 H), 2.44 (s ,3 H).



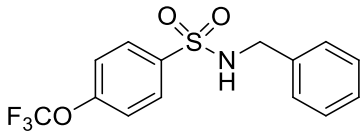
***N*-benzylmethanesulfonamide (3i)[3]**

White solid, 25 h, 153.5 mg, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5 H), 4.70 (br s, 1 H), 4.33 (d, *J* = 6.0 Hz, 2 H), 2.87 (s, 3 H).



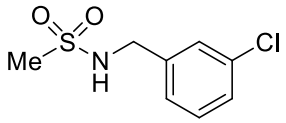
***N*-benzyl-4-chlorobenzenesulfonamide (3j)[2]**

White solid, 25 h, 249.6 mg, 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.32 - 7.27 (m, 3 H), 7.20 - 7.17 (m, 2 H), 4.70 (br s, 1 H), 4.17 (d, *J* = 6.0 Hz, 2 H).



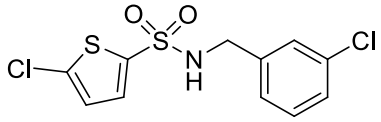
***N*-benzyl-4-(trifluoromethoxy)benzenesulfonamide (3k)[3]**

White solid, 25 h, 307.4 mg, 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2 H), 7.32-7.25 (m, 5 H), 7.18-7.16 (m, 2 H), 4.77 (t, *J* = 6.0 Hz, 1 H), 4.19 (d, *J* = 6.0 Hz, 2 H).



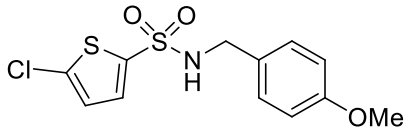
***N*-(3-chlorobenzyl)methanesulfonamide (3l)**

White solid, 30 h, 207.4 mg, 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (s, 1 H), 7.31-7.23 (m, 3 H), 5.00 (t, *J* = 6.0 Hz, 1 H), 4.29 (d, *J* = 6.0 Hz, 2 H), 2.89 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 134.8, 130.3, 128.3, 128.0, 126.1, 46.6, 41.2. **HRMS (ESI)** calcd. for $C_8H_{10}ClNO_2SNa^+$ $[M+Na]^+$ 242.0013, found 242.0009.



5-chloro-*N*-(3-chlorobenzyl)thiophene-2-sulfonamide (3m)

White solid, 30 h, 319.0 mg, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.0 Hz, 1 H), 7.29-7.27 (m, 2 H), 7.23 (s, 1 H), 7.16-7.14 (m, 1 H), 6.92 (d, *J* = 4.0 Hz, 1 H), 5.00 (br s, 1 H), 4.22 (d. *J* = 6.0 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 137.9 (2 peaks), 134.8, 132.0, 130.2, 128.5, 128.1, 126.9, 126.1, 47.0. **HRMS (ESI)** calcd. for $C_{11}H_{10}Cl_2NO_2S_2$ $[M+H]^+$ 321.9530, found 321.9524.

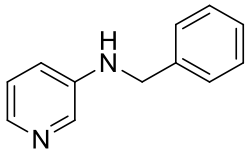


5-chloro-*N*-(4-methoxybenzyl)thiophene-2-sulfonamide (3n)

White solid, 30 h, 279.7 mg, 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.0 Hz, 1 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 4.0 Hz, 1 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 4.75 (br s, 1 H), 4.16 (d, *J* = 5.6 Hz, 2 H), 3.79 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 139.1, 137.5, 131.8, 129.5, 127.8, 126.9, 114.3, 55.5, 47.2. **HRMS (ESI)** calcd. for $C_{12\ H12}ClNO_3S_2Na^+$ $[M+Na]^+$ 339.9839, found 339.9841.

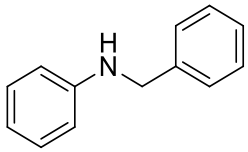
3.6. General procedure for direct aryl amination of aromatic alcohols.

Potassium hydroxide (3 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, an amine (1 mmol) and an alcohol (1 mL) was added under argon flow. The reaction mixture was stirred at 130 ℃. After disappearing of the amine on TLC, the reaction mixture was filtrated through a thin pad of *Celite* and washed with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product.



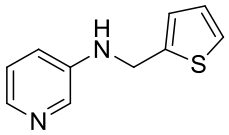
***N*-benzylpyridin-3-amine (3o)[2]**

Yellow solid, 25 h, 176.4 mg, 96%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.8 Hz, 1 H), 7.96 (dd, *J* = 4.4, 1.0 Hz, 1 H), 7.36-7.26 (m, 5 H), 7.06 (dd, *J* = 8.0, 4.4 Hz, 1 H), 6.86 (ddd, *J* = 8.0, 2.8, 1.0 Hz, 1 H), 4.33 (d, *J* = 5.2 Hz, 2 H), 4.20 (br s, 1 H).



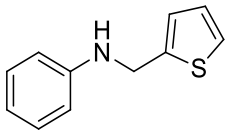
***N*-benzylaniline (3p)[2]**

Colorless oil, 48 h, 164.7 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.34 (m, 5 H), 7.29 (m, 2 H), 6.83-6.77 (m, 1 H), 6.73 - 6.69 (m, 2 H), 4.40 (d, *J* = 5.2 Hz, 2 H), 4.09 (br s, 1 H).



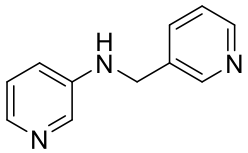
***N*-(thiophen-2-ylmethyl)pyridin-3-amine (3q)[4]**

Yellow solid, 25 h, 172.7 mg, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.8 Hz, 1 H), 7.99 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.08 (dd, *J* = 8.4, 4.8 Hz, 1 H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 4.8, 2.8 Hz, 1 H), 6.94 - 6.91 (m, 1 H), 4.52 (s, 2 H), 4.26 (br s, 1 H).



***N*-(thiophen-2-ylmethyl)aniline (3r)[5]**

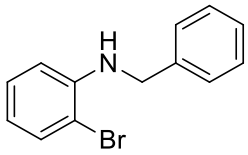
Yellow oil, 25 h, 153.9 mg, 81%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 - 7.16 (m, 3 H), 7.01-7.00 (m, 1 H), 6.96 (dd, *J* = 4.8, 3.2 Hz, 1 H), 6.74 (tt, *J* = 7.2, 1.2 Hz, 1 H), 6.68 - 6.65 (m, 2 H), 4.50 (d, *J* = 3.2 Hz, 2 H), 4.03 (br s, 1 H).



***N*-(pyridin-3-ylmethyl)pyridin-3-amine (3s)**

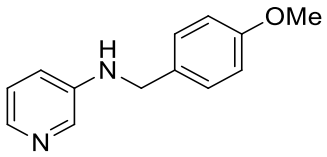
Brown oil, 25 h, 183.4 mg, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 2.4, 2.0 Hz, 1 H), 8.55 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.08 (dd, *J* = 2.8, 0.4 Hz, 1 H), 8.00 (dd, *J* = 4.8, 1.2 Hz, 1 H), 7.71 - 7.68 (m, 1 H),

7.29 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1 H), 7.08 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 6.88 (ddd, *J* = 8.4, 3.0, 1.4 Hz, 1 H), 4.39 (d, *J* = 3.6 Hz, 2 H), 4.25 (br s, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 149.1, 143.7, 139.3, 136.2, 135.1, 134.1, 123.9, 123.7, 118.8, 45.4. **HRMS (ESI)** calcd. for $C_{11}H_{12}N_3$ $[M+H]^+$ 186.1026, found 186.1034.



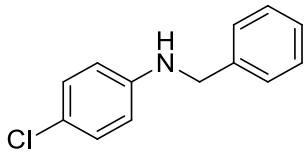
***N*-benzyl-2-bromoaniline (3t)[6]**

Yellow oil, 48 h, 235.9 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 1 H), 7.42-7.37 (m, 4 H), 7.36-7.7.32 (m, 1 H), 7.20-7.16 (m, 1H), 6.66-6.61 (m, 2 H), 4.82 (br s, 1H), 4.44 (d, *J* = 5.2 Hz, 2 H).



***N*-(4-methoxybenzyl)pyridin-3-amine (3u)[7]**

White solid, 25 h, 212.1 mg, 99%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.0 Hz, 1 H), 7.97 (dd, *J* = 4.8, 1.0 Hz, 1 H), 7.29-7.26 (m, 2 H), 7.07 (dd, *J* = 8.0, 4.8 Hz, 1 H), 6.91-6.86 (m, 3 H), 4.27 (d, *J* = 5.6 Hz, 2 H), 4.04 (br s, 1 H), 3.81 (s, 3 H).



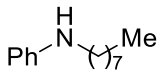
***N*-benzyl-4-chloroaniline (3v)[6]**

White solid, 48 h, 206.9 mg, 95%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 5 H), 7.12-7.08 (m, 2 H), 6.56-6.52 (m, 2 H), 4.29 (d, *J* = 4.8 Hz, 2 H), 4.05 (br s, 1 H).

3.7. General Procedure for Direct Aryl Amination of Aliphatic Alcohols.

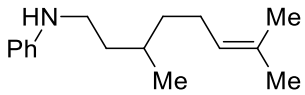
An alcohol (2 mL) was added into a 25 mL Schlenk tube after dried for 15 min. NaH (60% dispersion in mineral oil, 120 mg, 1.5 equiv) was added into the solution under argon flow and stirred for 5 min. Then an amine (2 mmol, 1 equiv) was added into the mixture and stirred at 160 ℃. After disappearing of

the amine on TLC, the reaction mixture was filtrated through a thin pad of *Celite* and washed with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified on silica gel column with petroleum ether, dichloromethane and ethyl acetate to give the product.



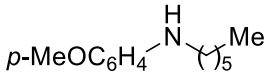
***N*-octylaniline (3w)[11]**

NaH (2.0 equiv), yellow oil, 46 h, 182.9 mg, 45%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.4, 7.2 Hz, 2 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 7.2 Hz, 2 H), 3.59 (s, 1 H), 3.11 (t, *J* = 7.2 Hz, 2 H), 1.66-1.59 (m, 2 H), 1.44-1.29 (m, 10 H), 0.90 (t, *J* = 6.8 Hz, 3 H).



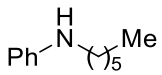
***N*-(3,7-dimethyloct-6-en-1-yl)aniline (3x)[10]**

NaH (1.5 equiv), yellow oil, 28 h, 232.3 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 2 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.6 Hz, 2 H), 5.10 (t, *J* = 6.8 Hz, 1 H), 3.54 (br s, 1 H), 3.16-3.09 (m, 2 H), 2.06-1.92 (m, 2 H), 1.70 (s, 3 H), 1.61 (s, 3 H), 1.47-1.17 (m, 5 H), 0.95 (d, *J* = 6.4 Hz, 3 H).



***N*-hexyl-4-methoxyaniline (3y)[12]**

NaH (2.5 equiv), yellow oil, 46 h, 239.8 mg, 58%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.8 Hz, 2 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H), 3.33 (br s, 1 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 1.64-1.57 (m, 2 H), 1.43-1.30 (m, 6 H), 0.90 (t, *J* = 7.2 Hz, 3 H).



***N*-hexylaniline (3z)[6]**

NaH (1.5 equiv), yellow oil, 40 h, 144.1 mg, 41%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.6 Hz, 2 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.6 Hz, 2 H), 3.60 (br s, 1 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 1.65-1.57 (m, 2 H), 1.44-1.30 (m, 6 H), 0.90 (t, *J* = 6.4 Hz, 3 H).

4. References

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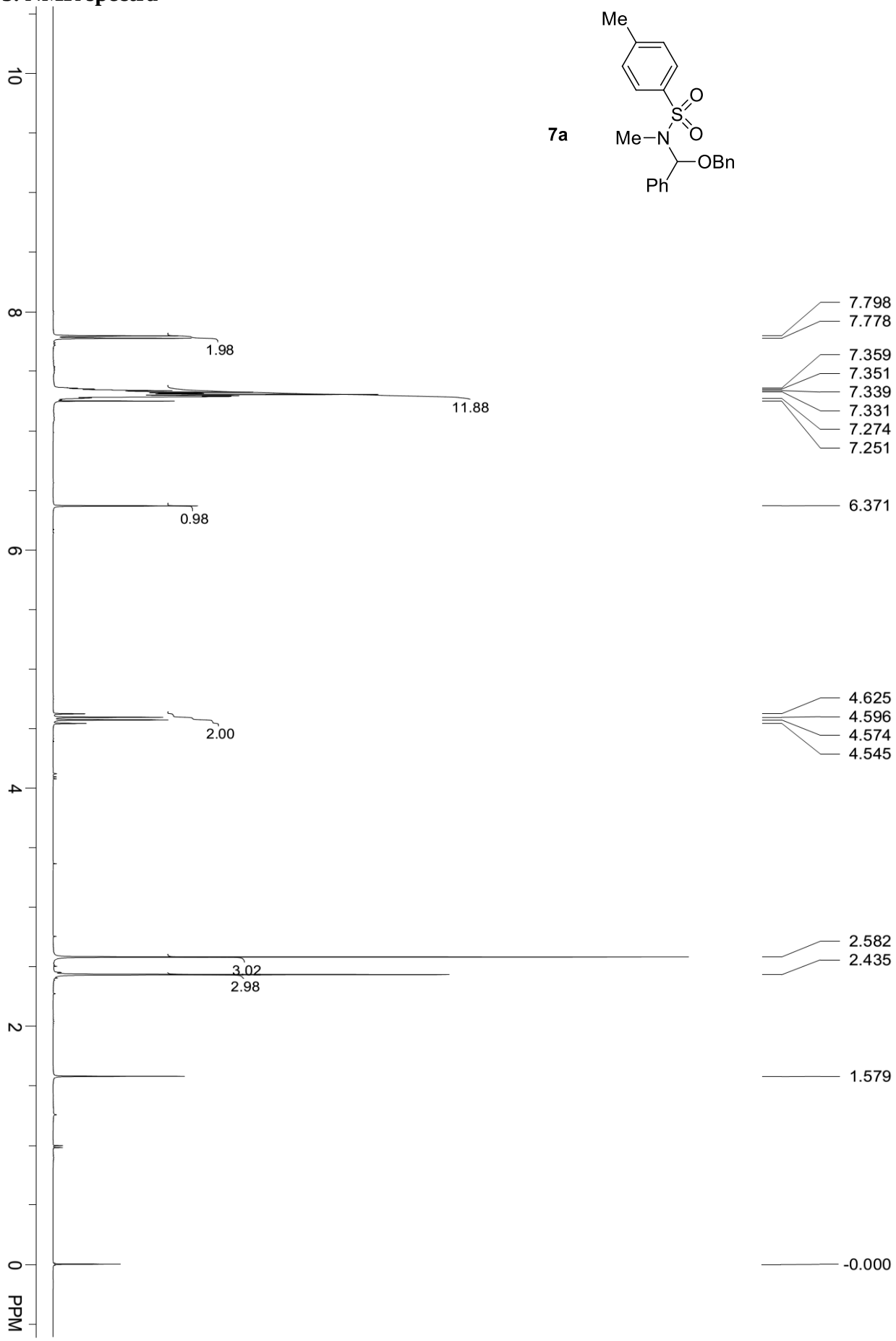
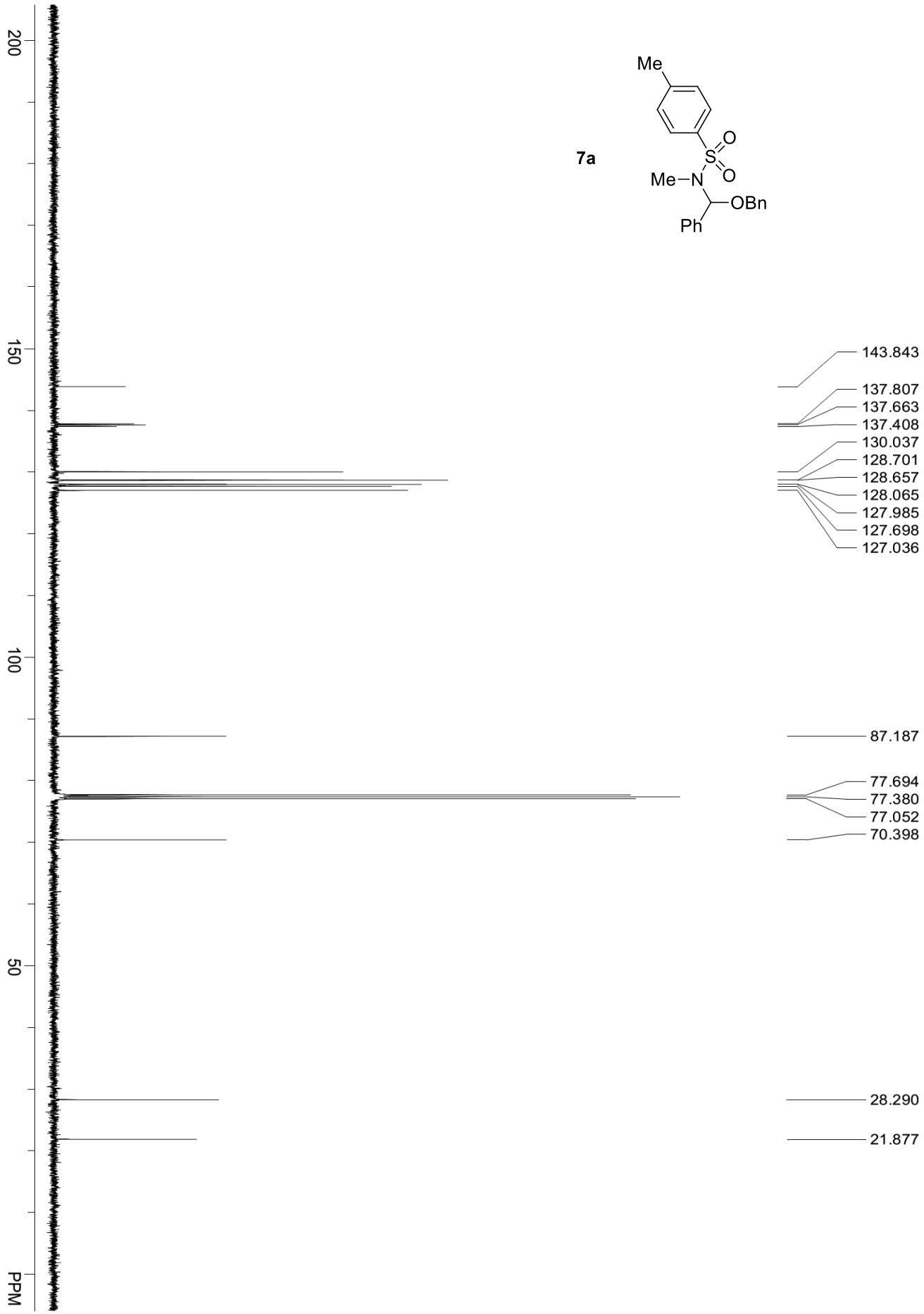
5. NMR spectra

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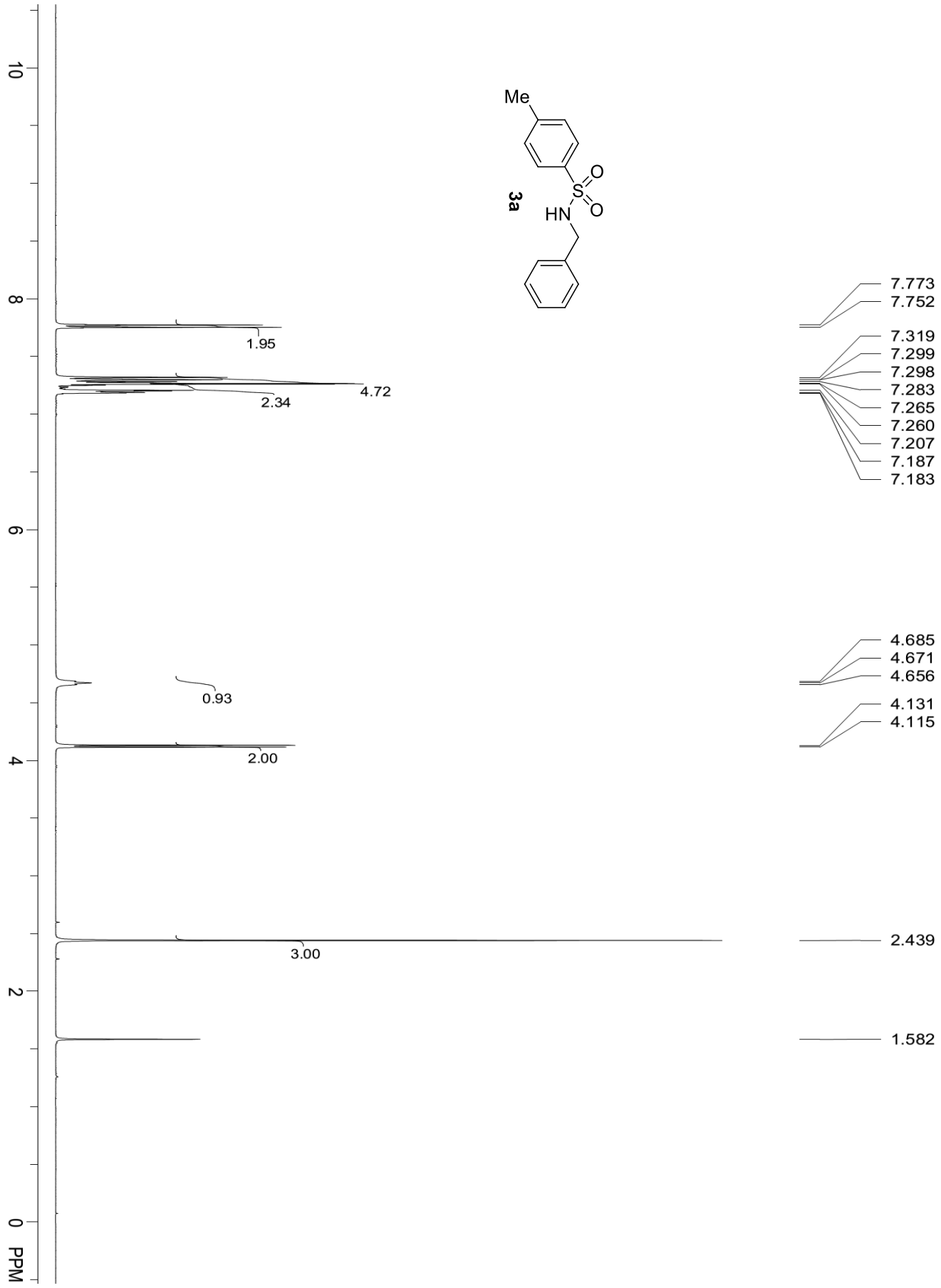
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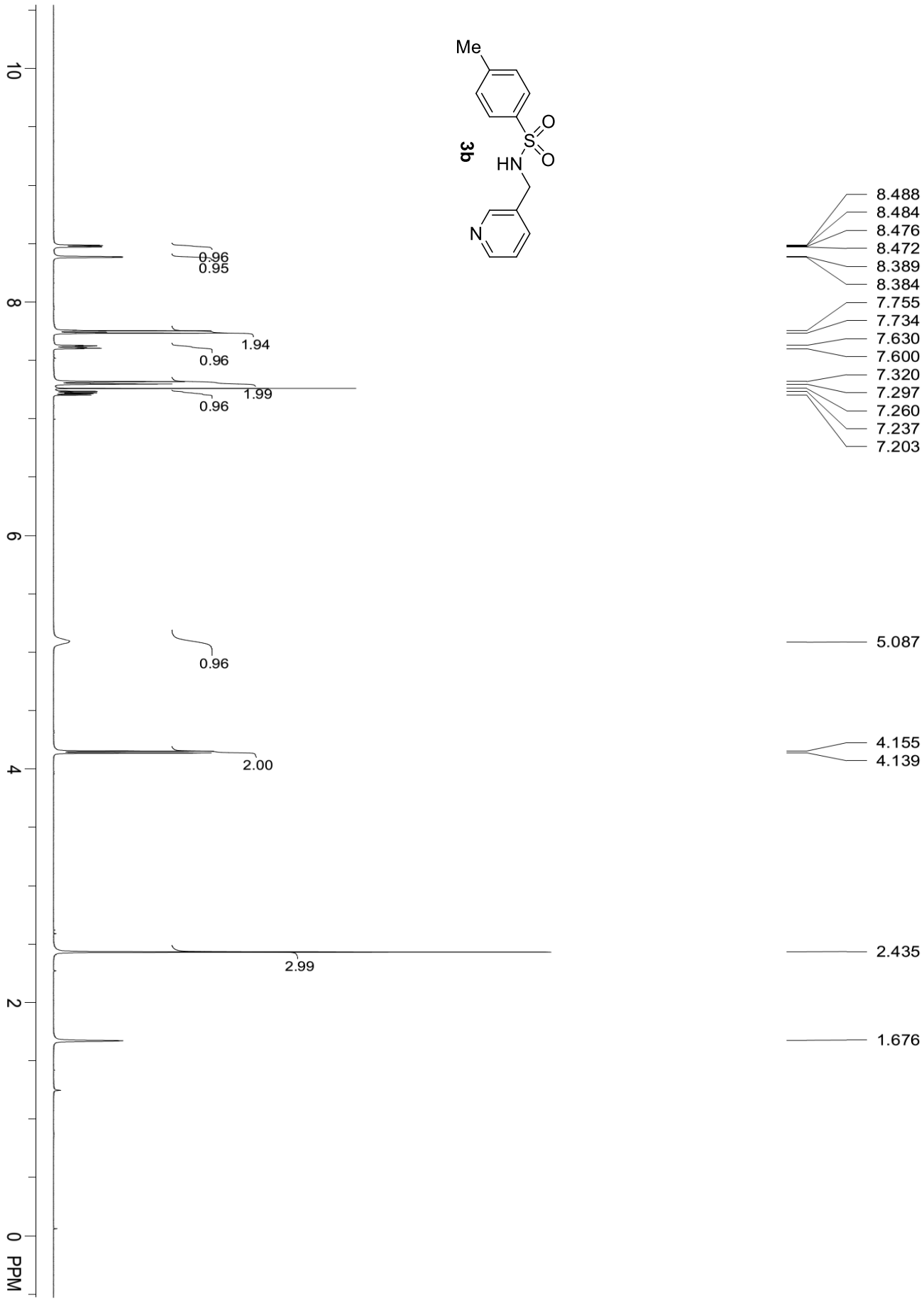
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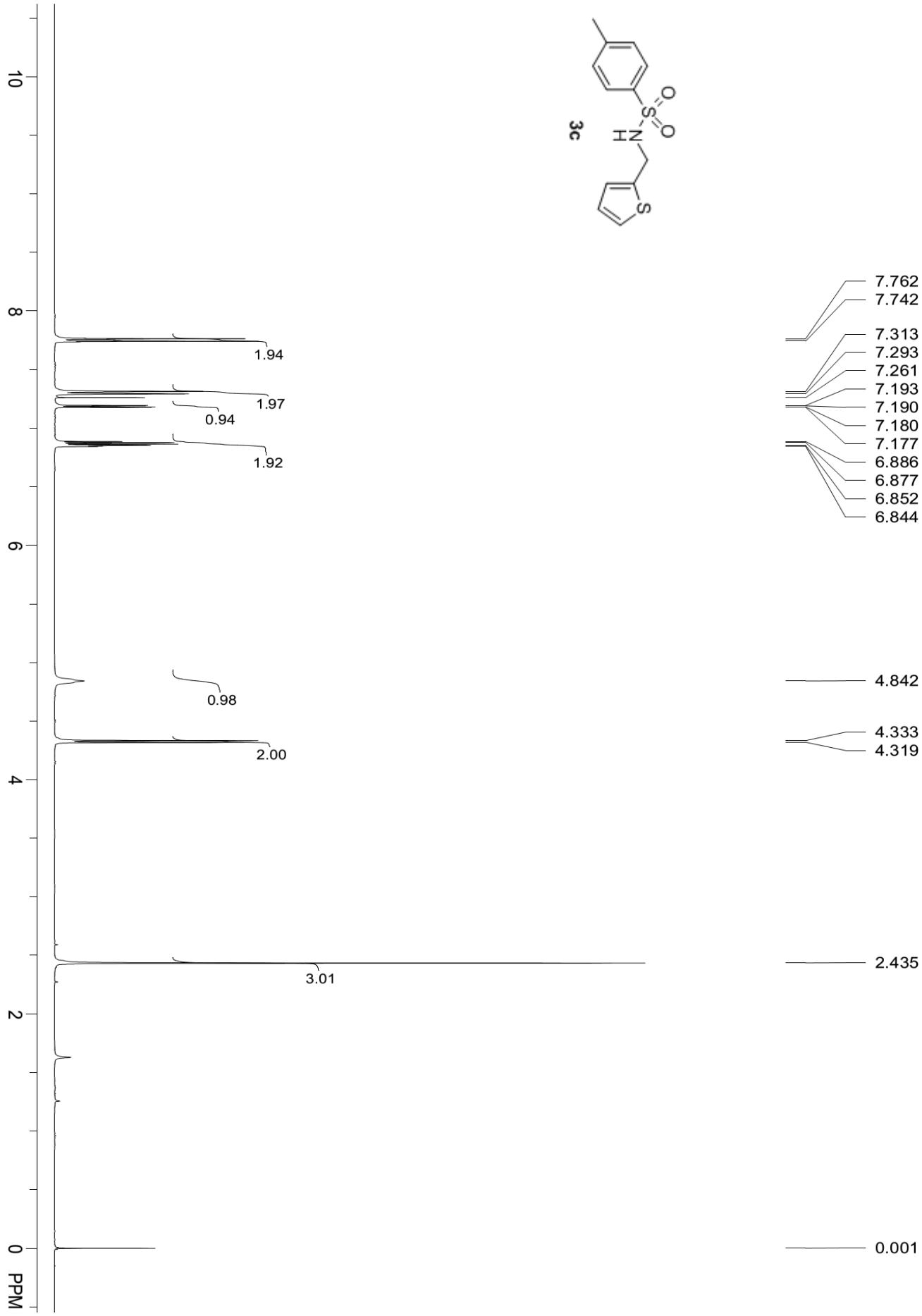
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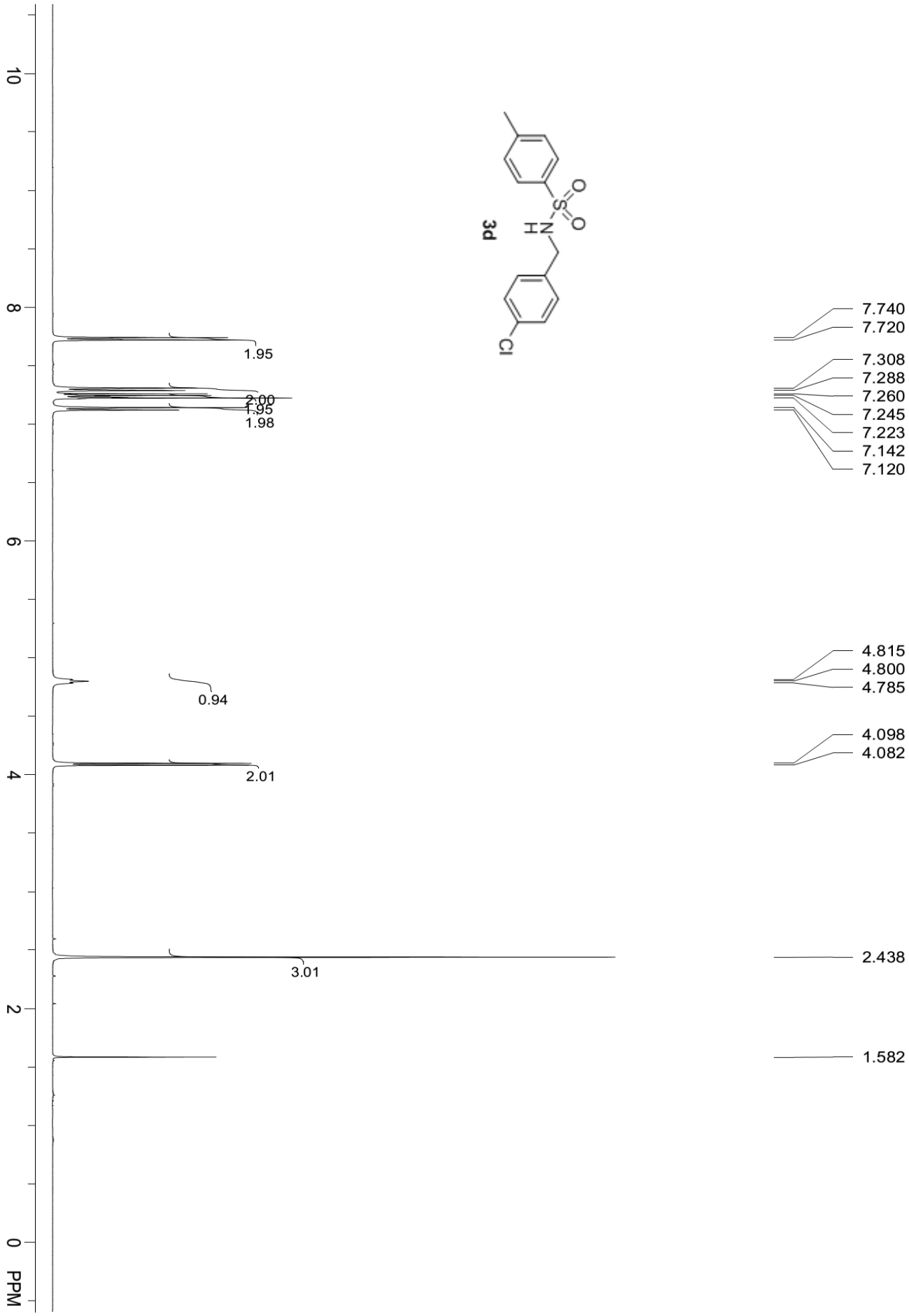
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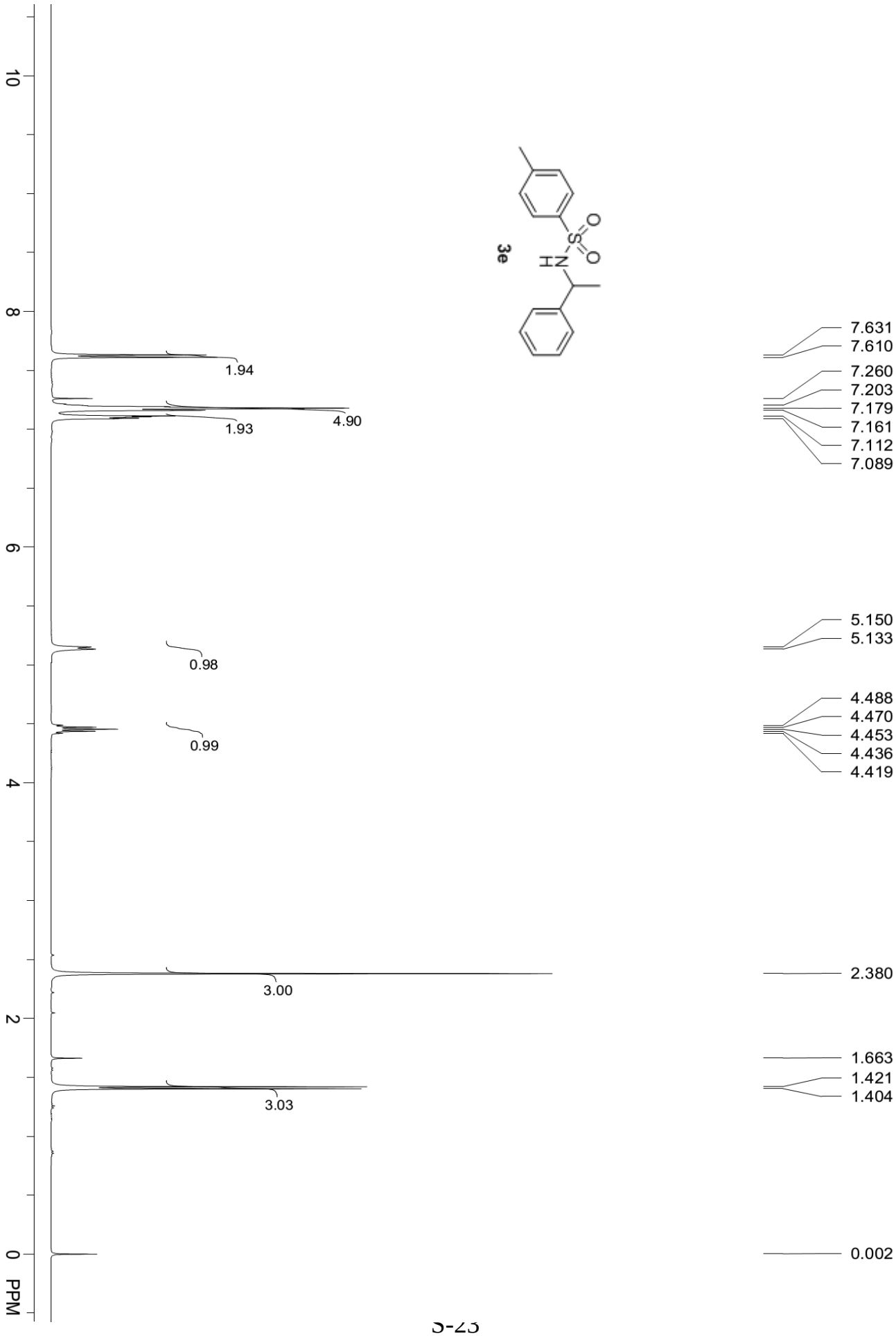
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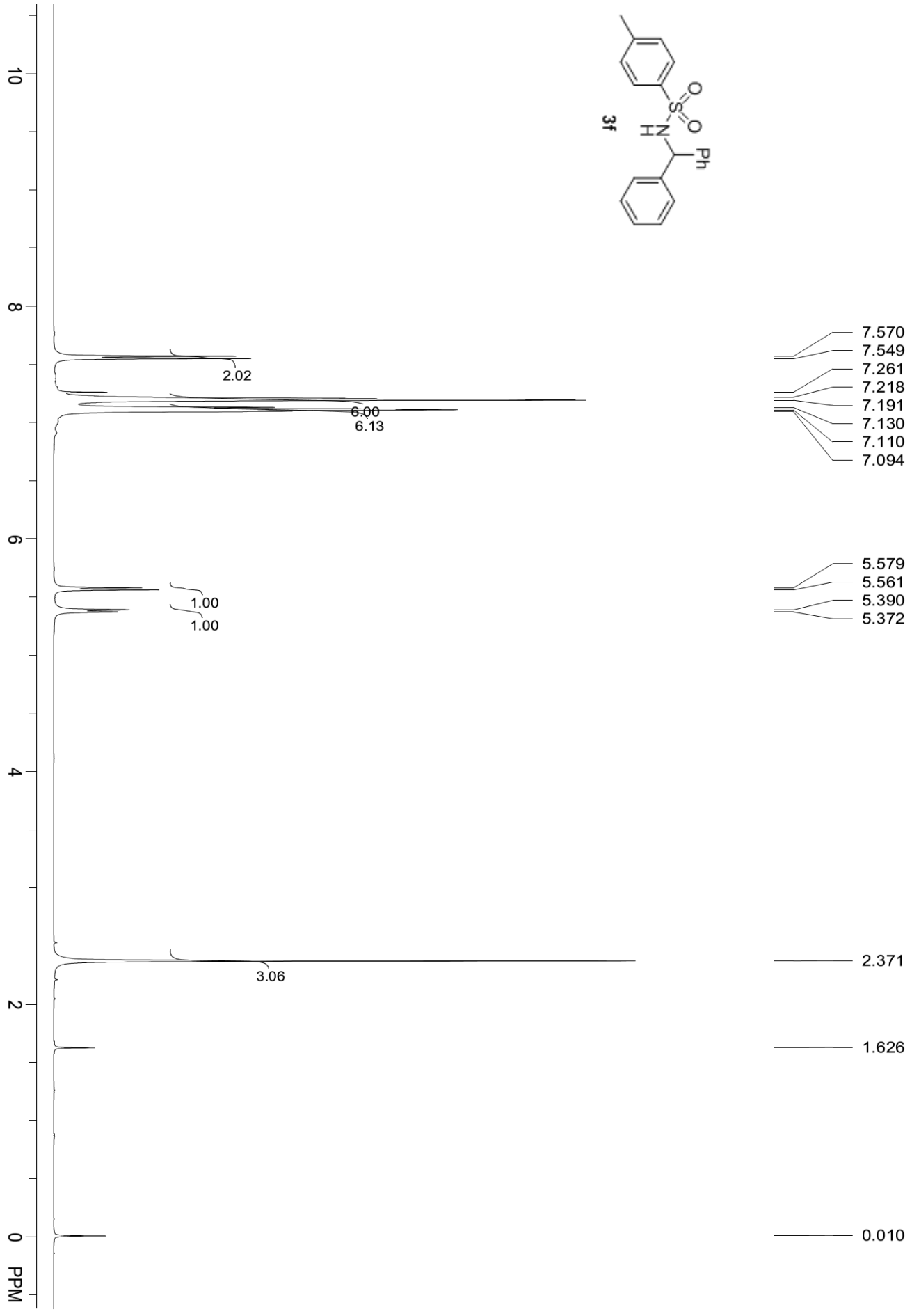
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O
S
O
N
H
Ph
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6.13
1.00
1.00
3.06
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7.549
7.261
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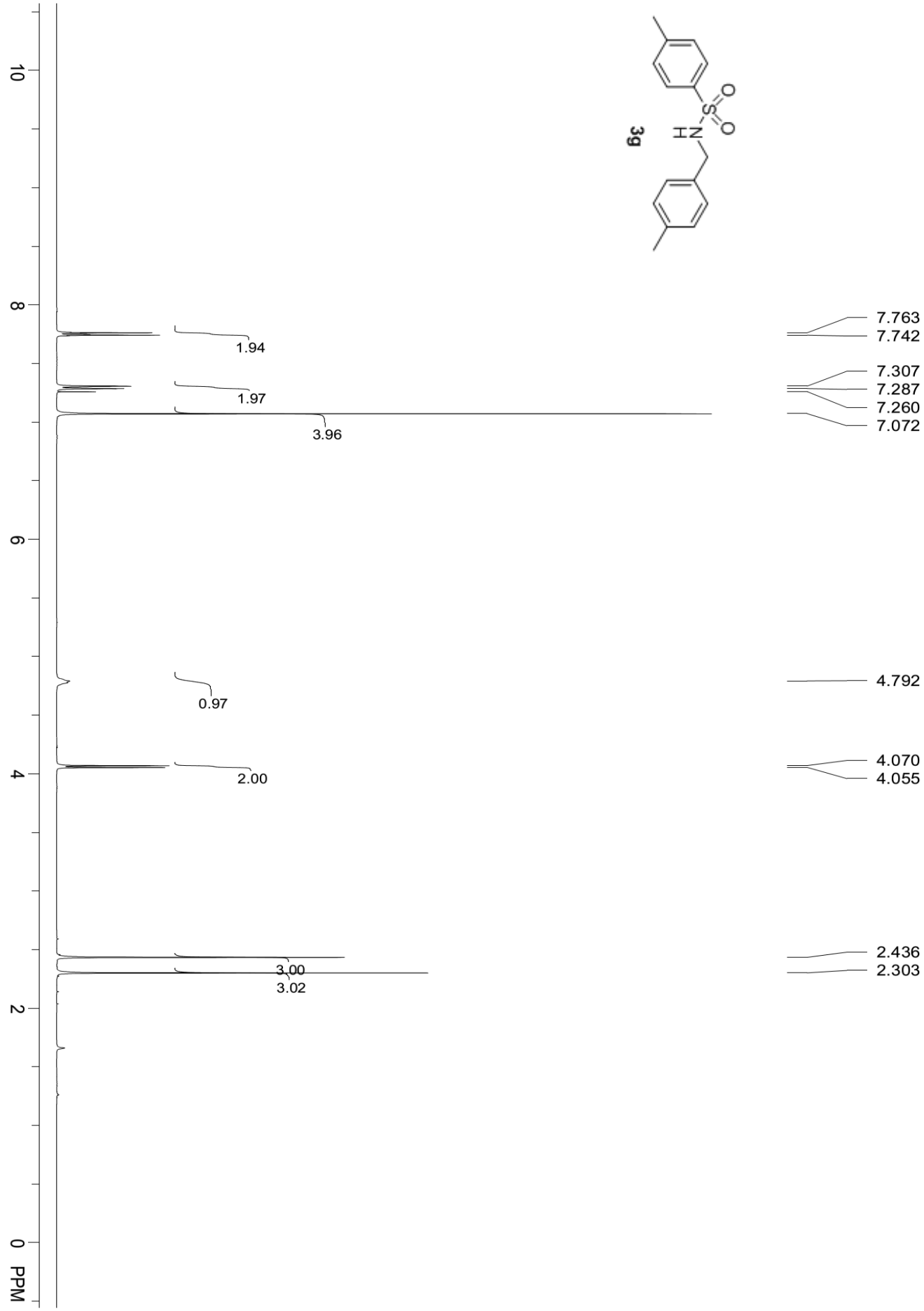
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4.792
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2.436
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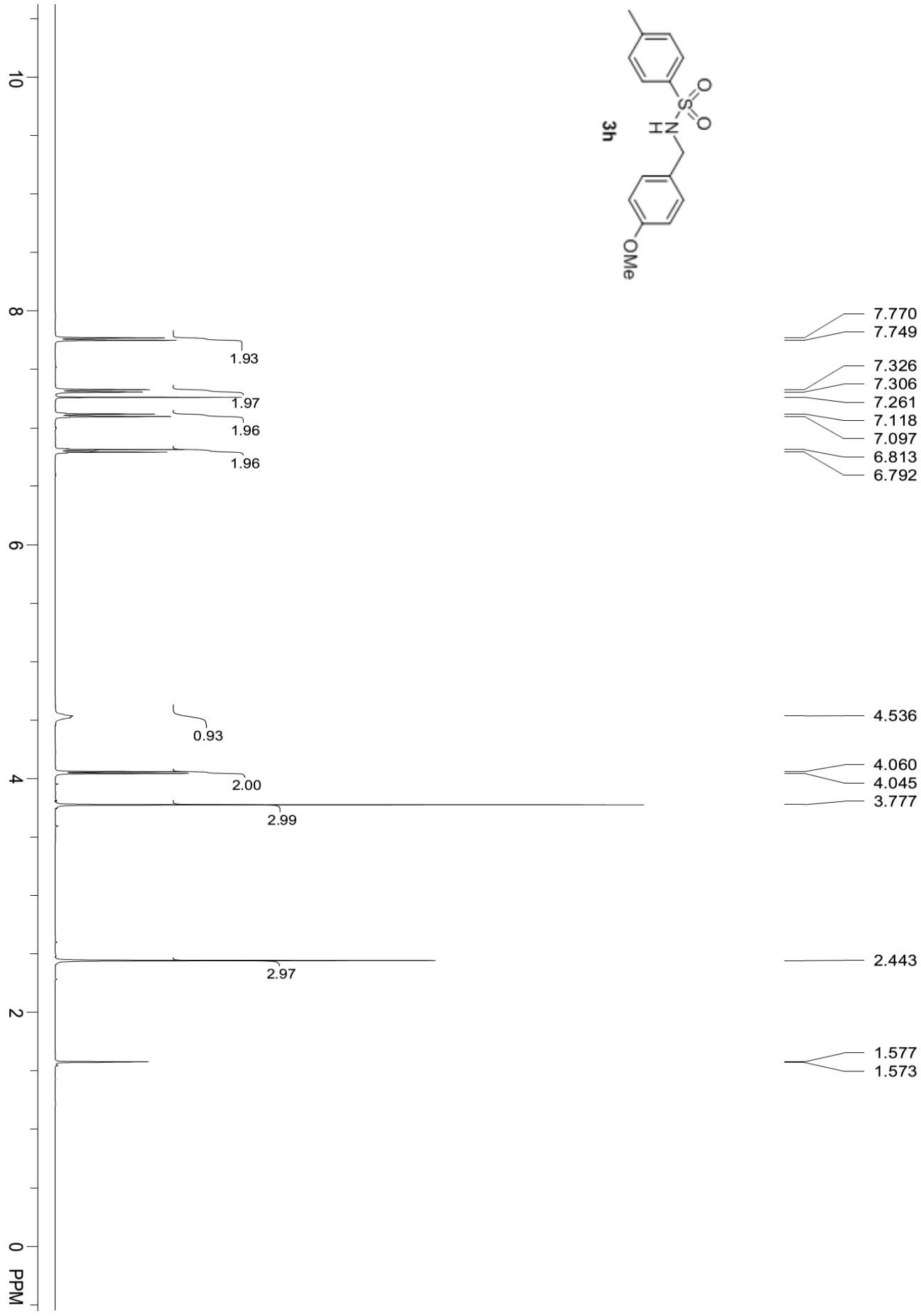
PPM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OMe
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PPM
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1.97
1.96
1.96
0.93
2.00
2.99
2.97
7.770
7.749
7.326
7.306
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4.045
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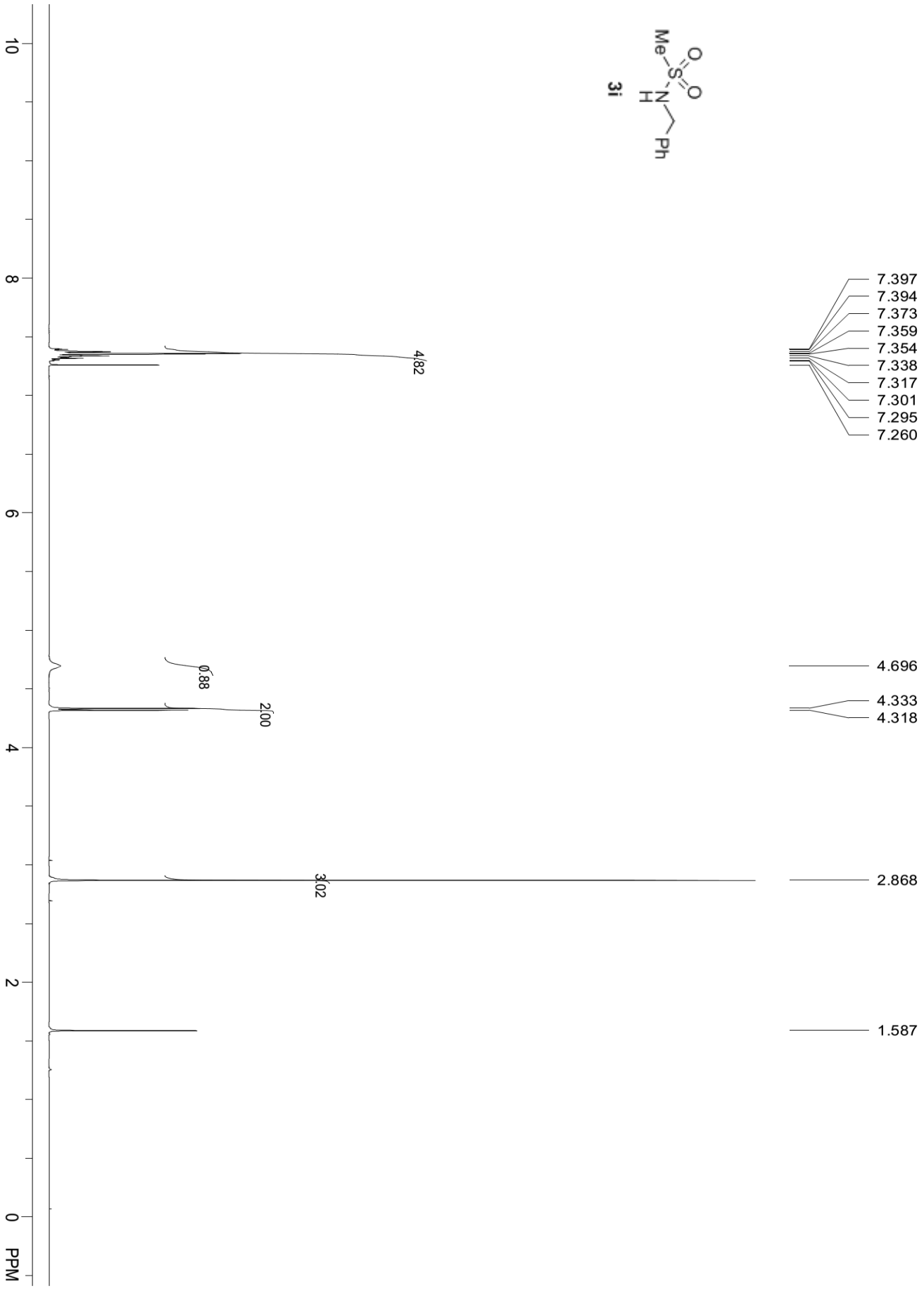
1.573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Me
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H
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7.301
7.295
7.260
4.696
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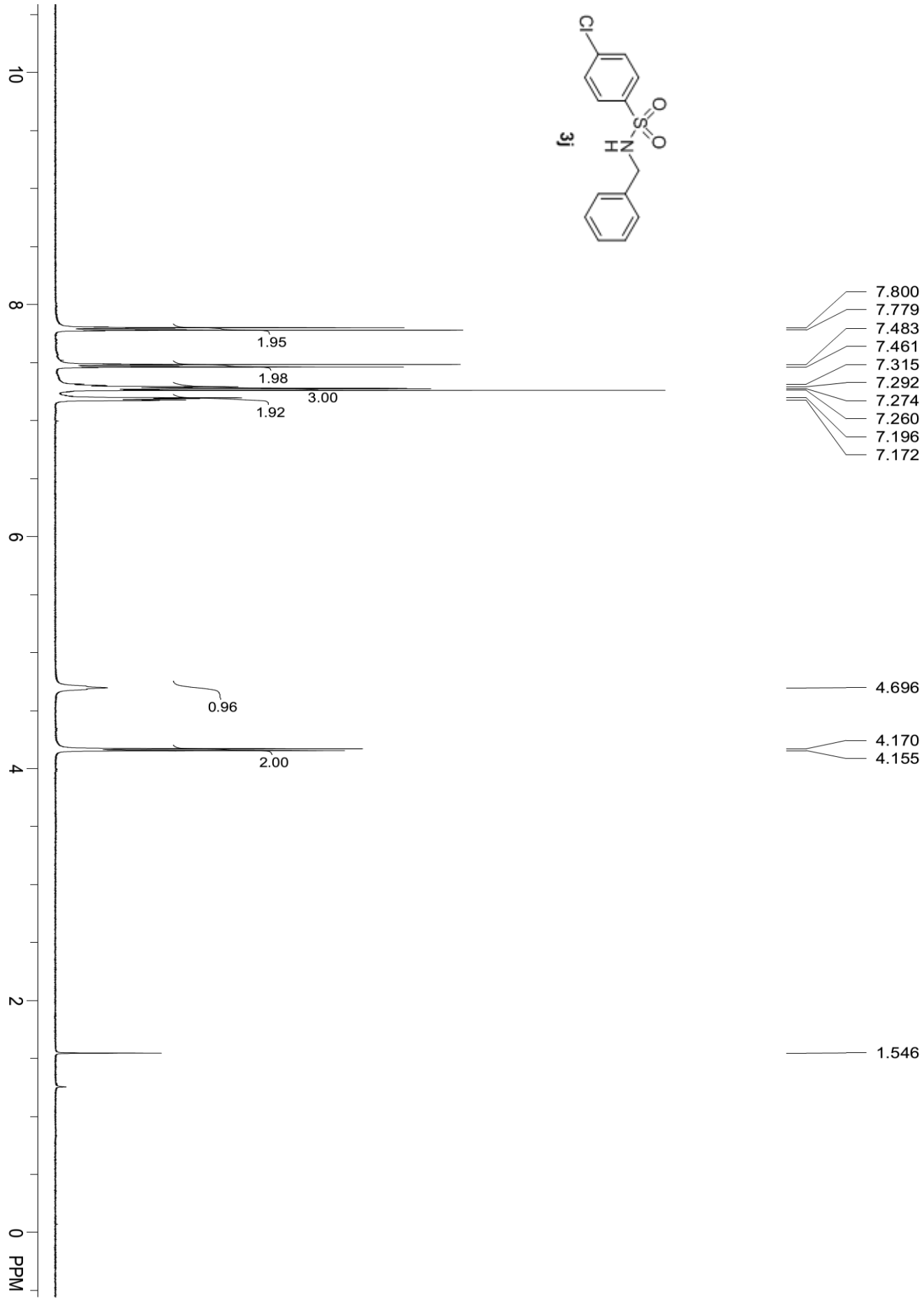
10
8
6
4
2
0
PPM


Cl
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S
O
N
H
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7.292
7.274
7.260
7.196
7.172
4.696
4.170
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1.98
3.00
1.92
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10
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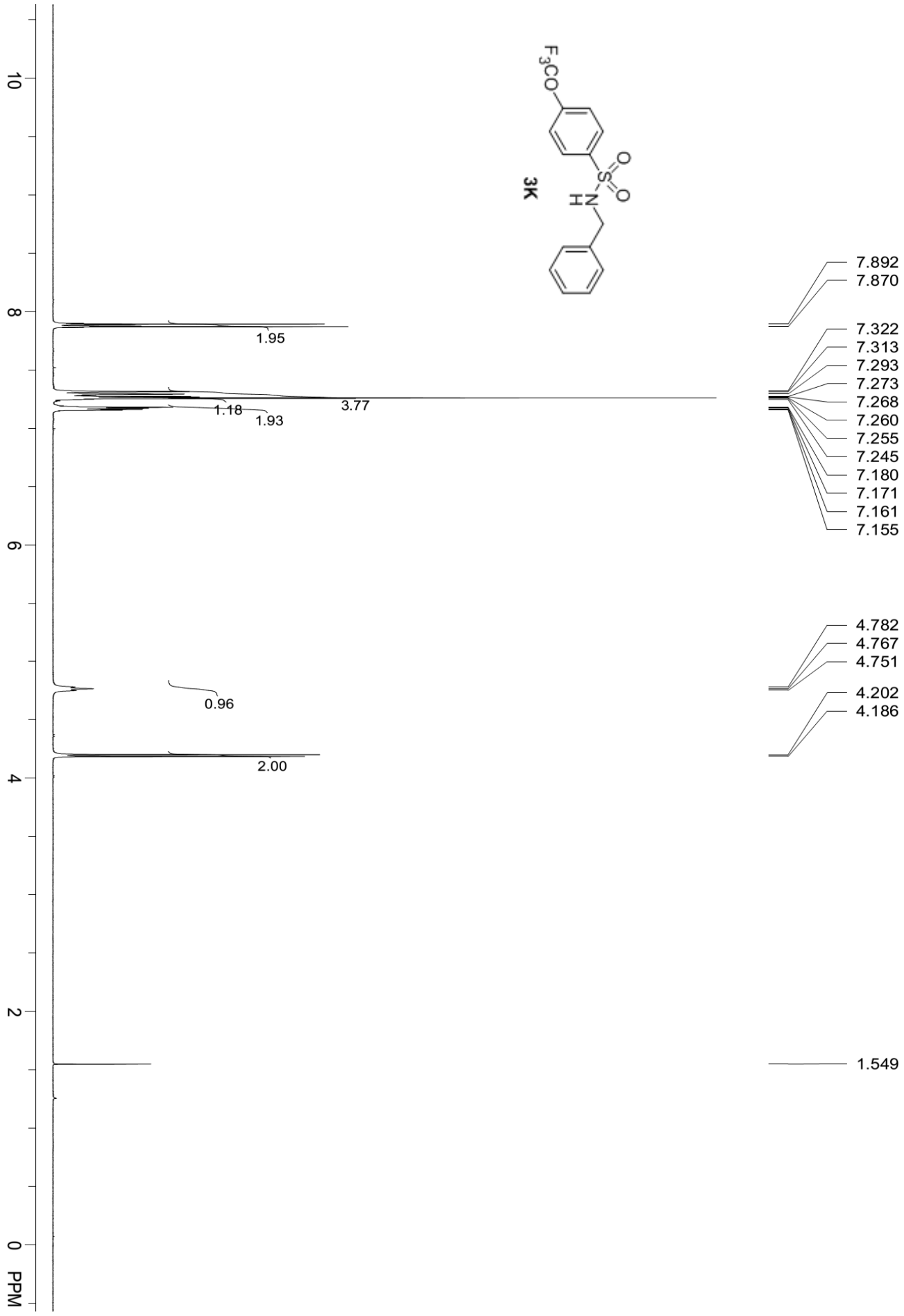
4
2
0
PPM


F3CO
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S
O
N
H
3K
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7.293
7.273
7.268
7.260
7.255
7.245
7.180
7.171
7.161
7.155
4.782
4.767
4.751
4.202
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1.18
1.93
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10
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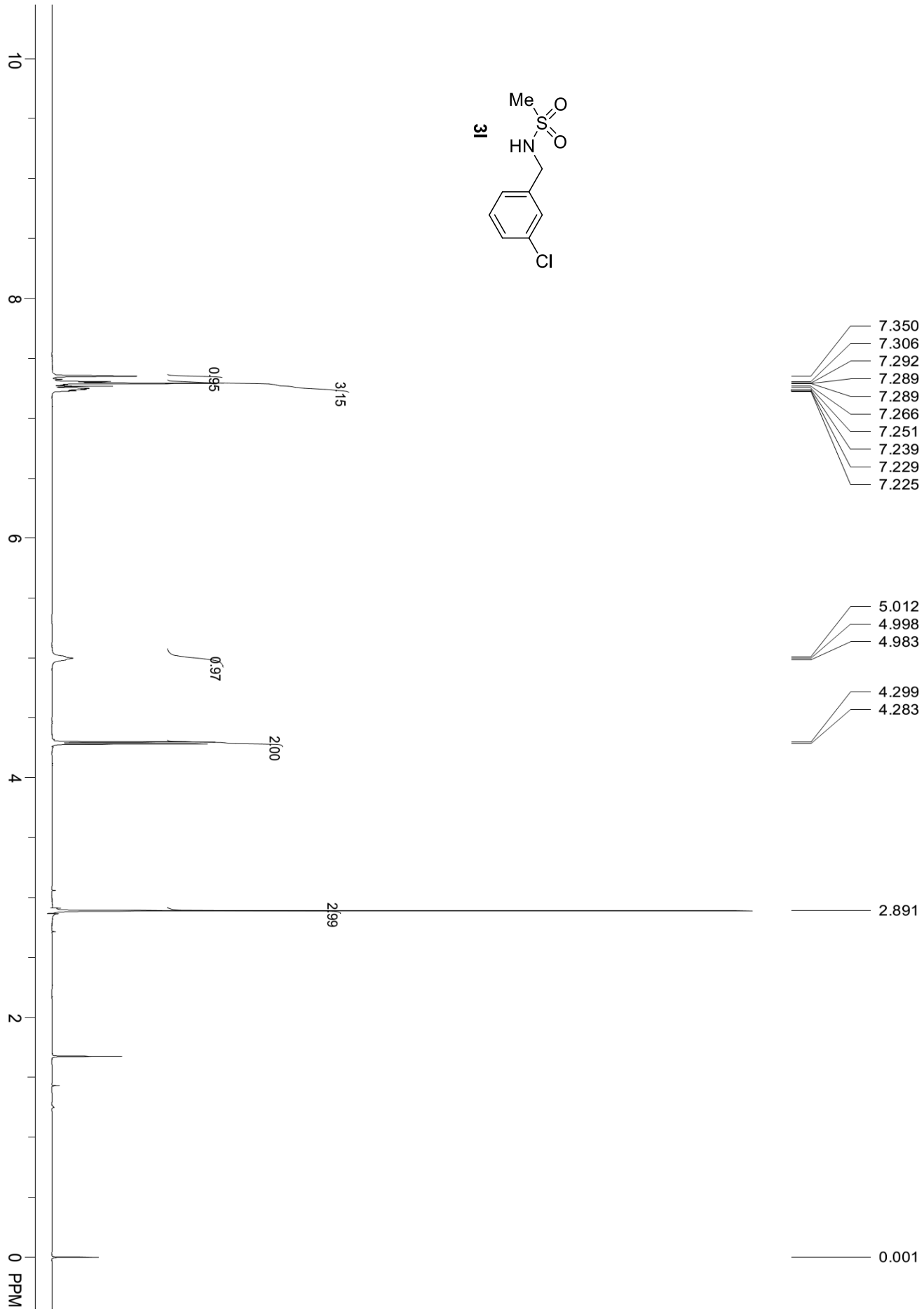
6
4
2
0
PPM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Me
S
O
O
HN
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7.289
7.266
7.251
7.239
7.229
7.225
5.012
4.998
4.983
4.299
4.283
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3.15
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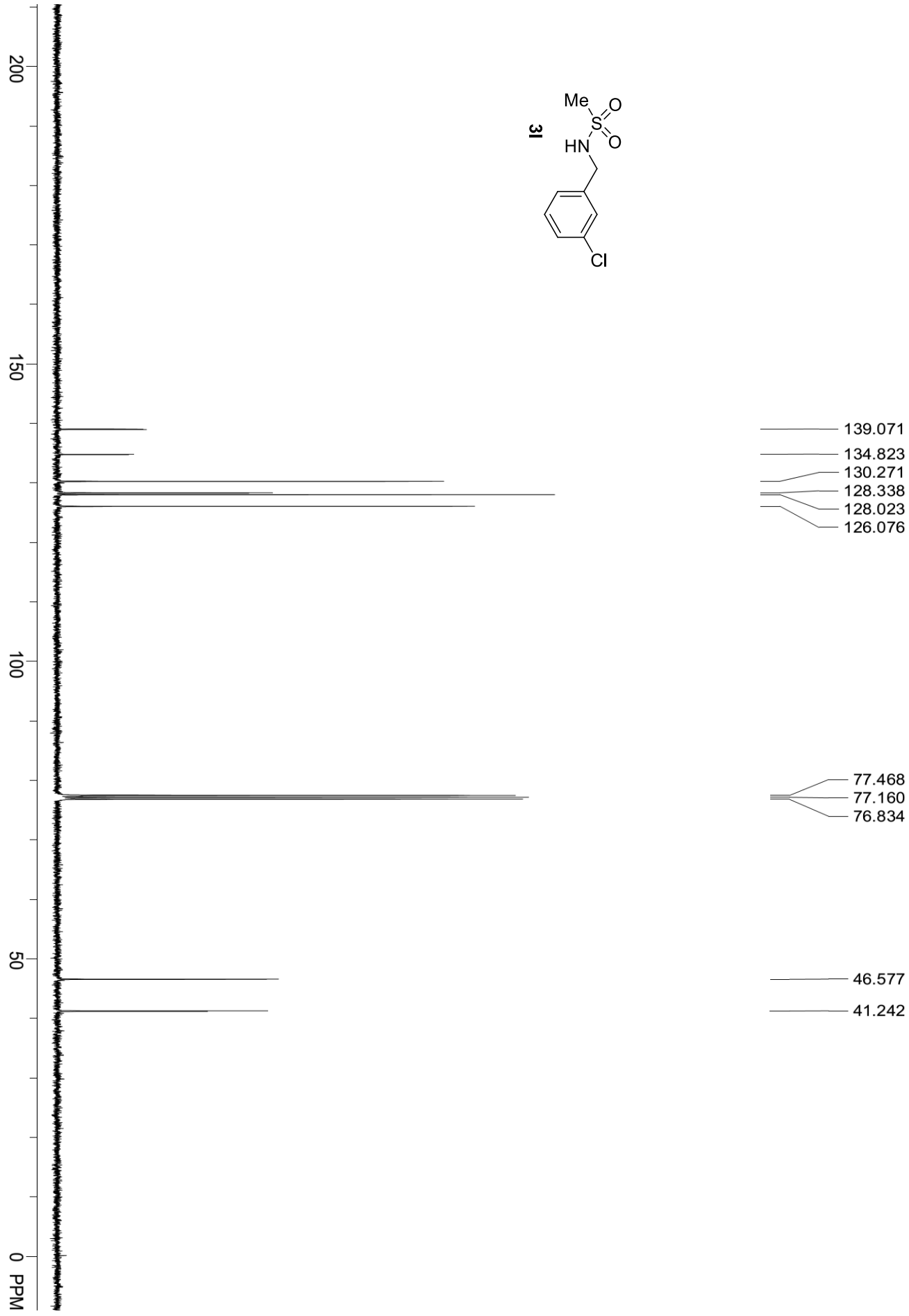
0.97
2.00
2.99
10
8
6
4
2
0 PPM


3l
Me
S
O
O
HN
Cl
200
150
100
50
0 PPM
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130.271
128.338
128.023
126.076
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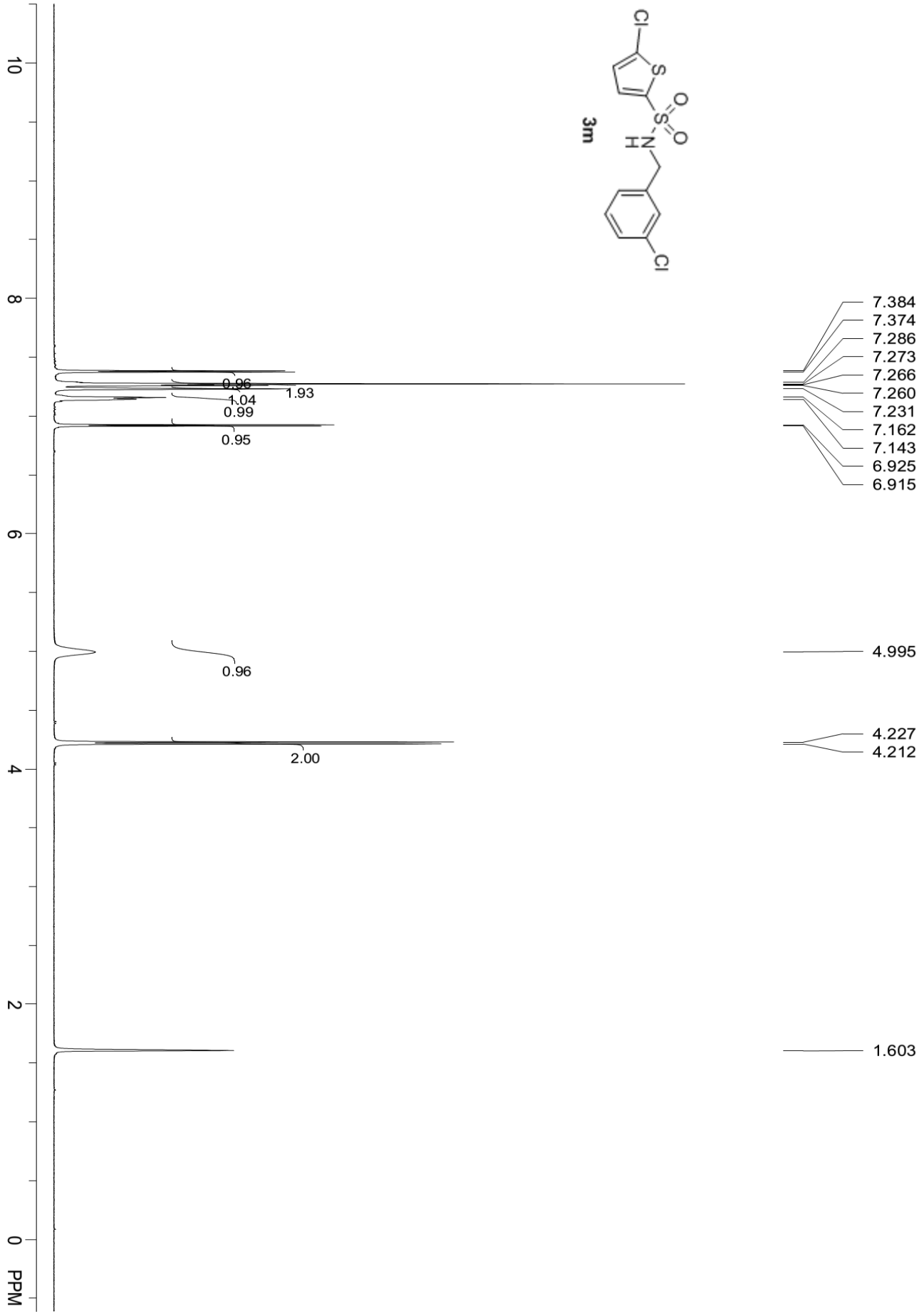
77.160
76.834
46.577
41.242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7.374
7.286
7.273
7.266
7.260
7.231
7.162
7.143
6.925
6.915
4.995
4.227
4.212
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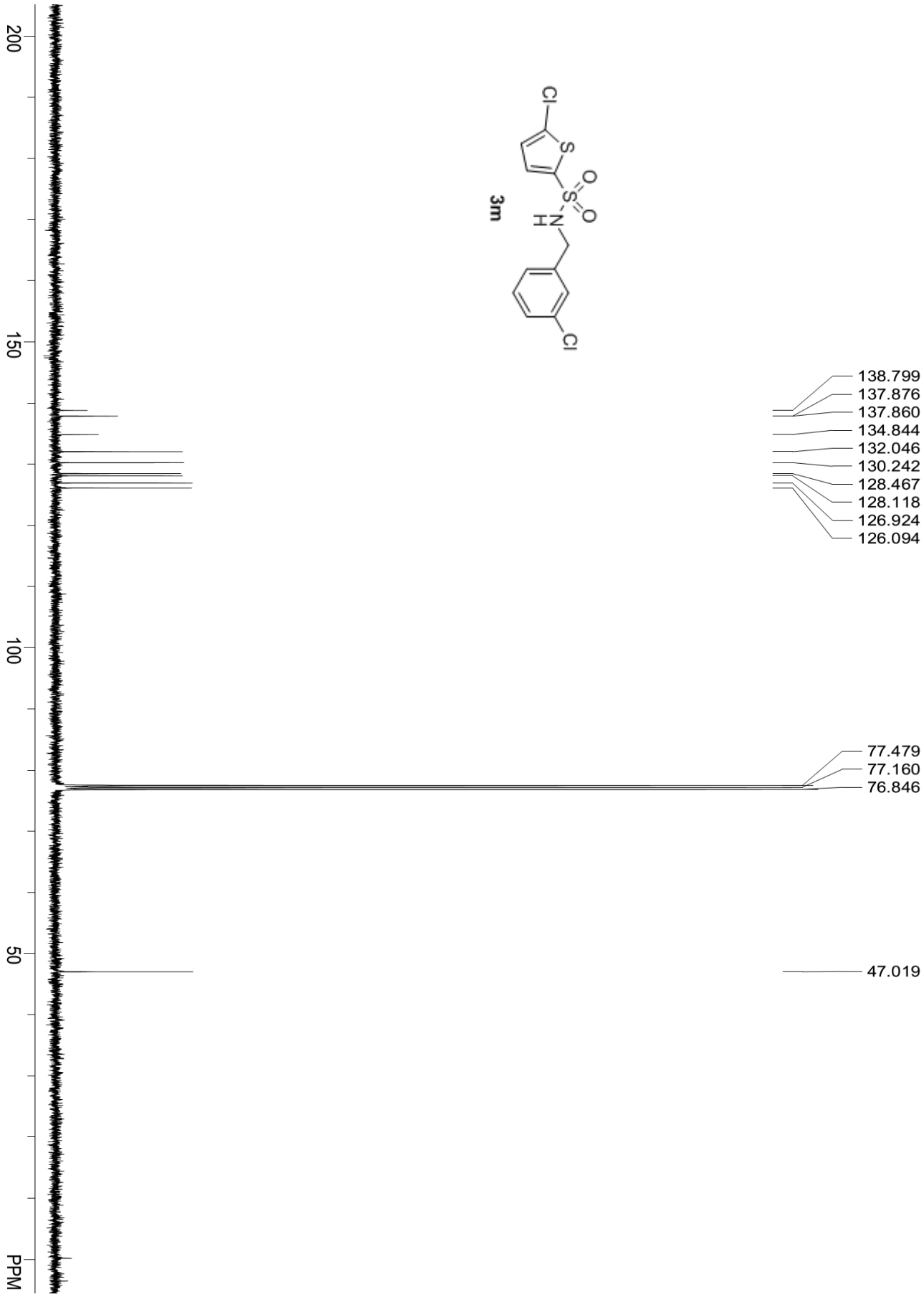
1.93
0.99
0.95
0.96
2.00
10
8
6
4
2
0
PPM


200
150
100
50
PPM
Cl
S
O
S
O
N
H
Cl
3m
138.799
137.876
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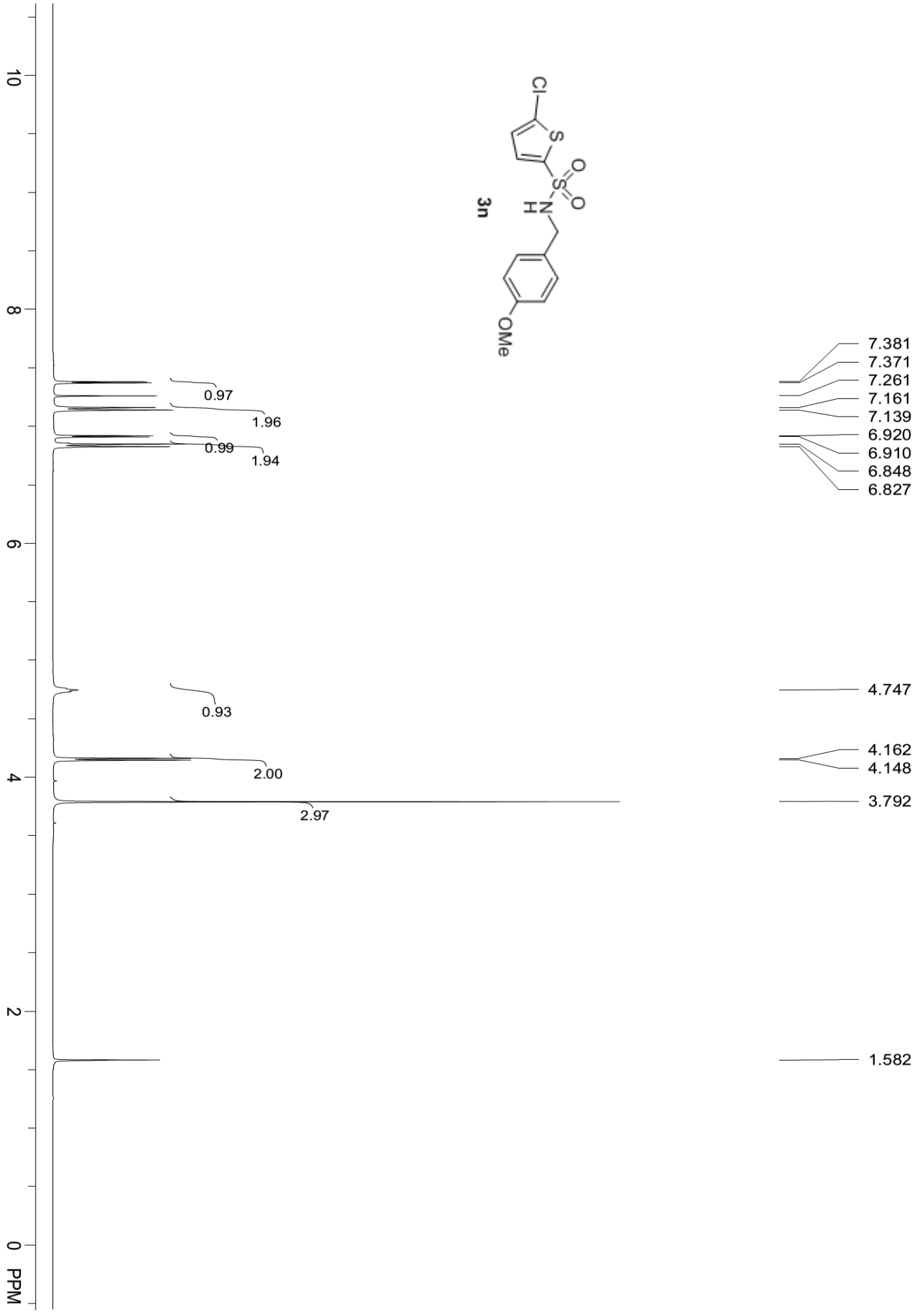
130.242
128.467
128.118
126.924
126.094
77.479
77.160
76.846
47.019


Cl
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O
S
O
N
H
3n
OMe
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7.261
7.161
7.139
6.920
6.910
6.848
6.827
4.747
4.162
4.148
3.792
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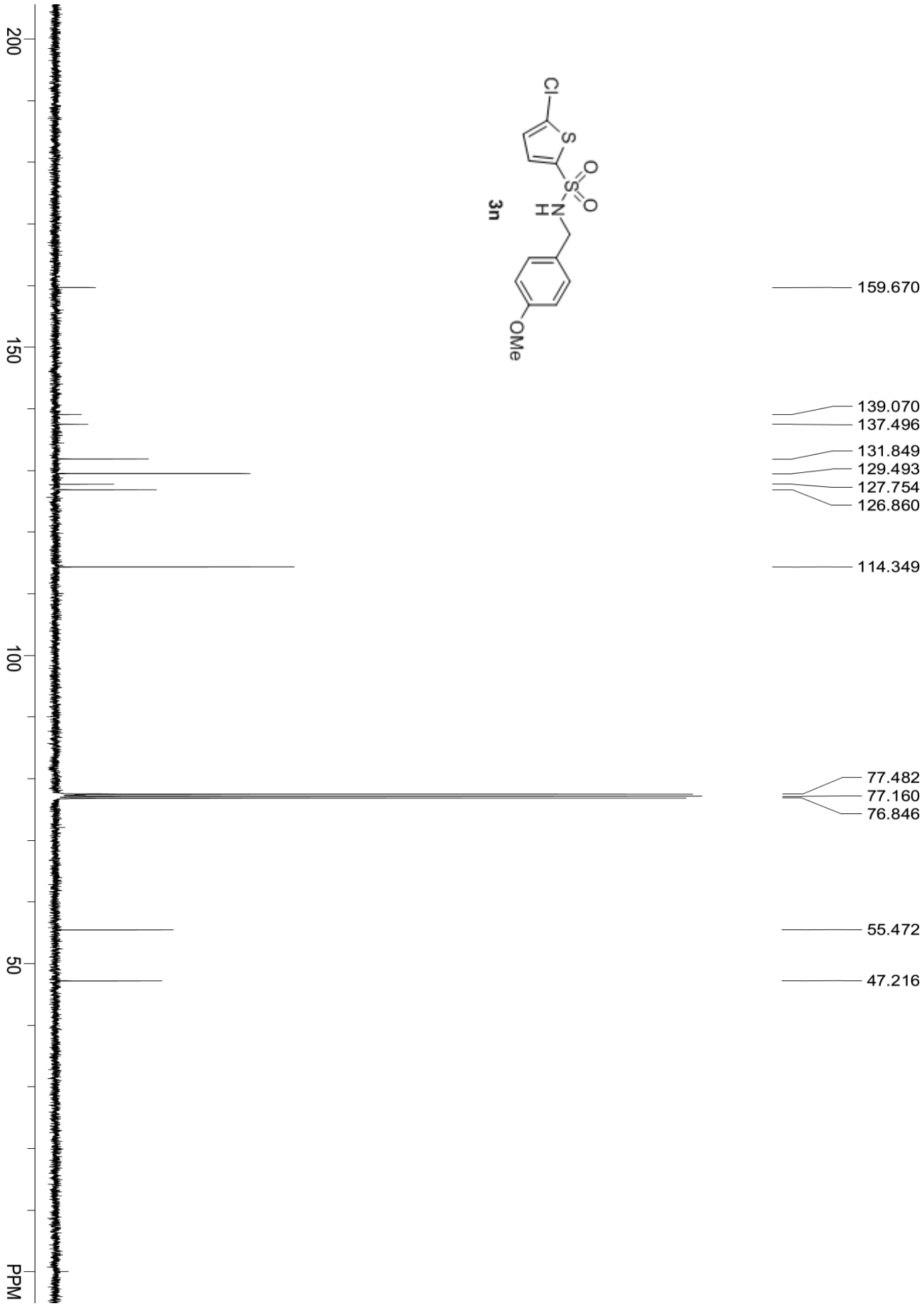
0.99
1.94
0.93
2.00
2.97
10
8
6
4
2
0
PPM


200
150
100
50
PPM
Cl
S
O
S
O
N
H
OMe
3n
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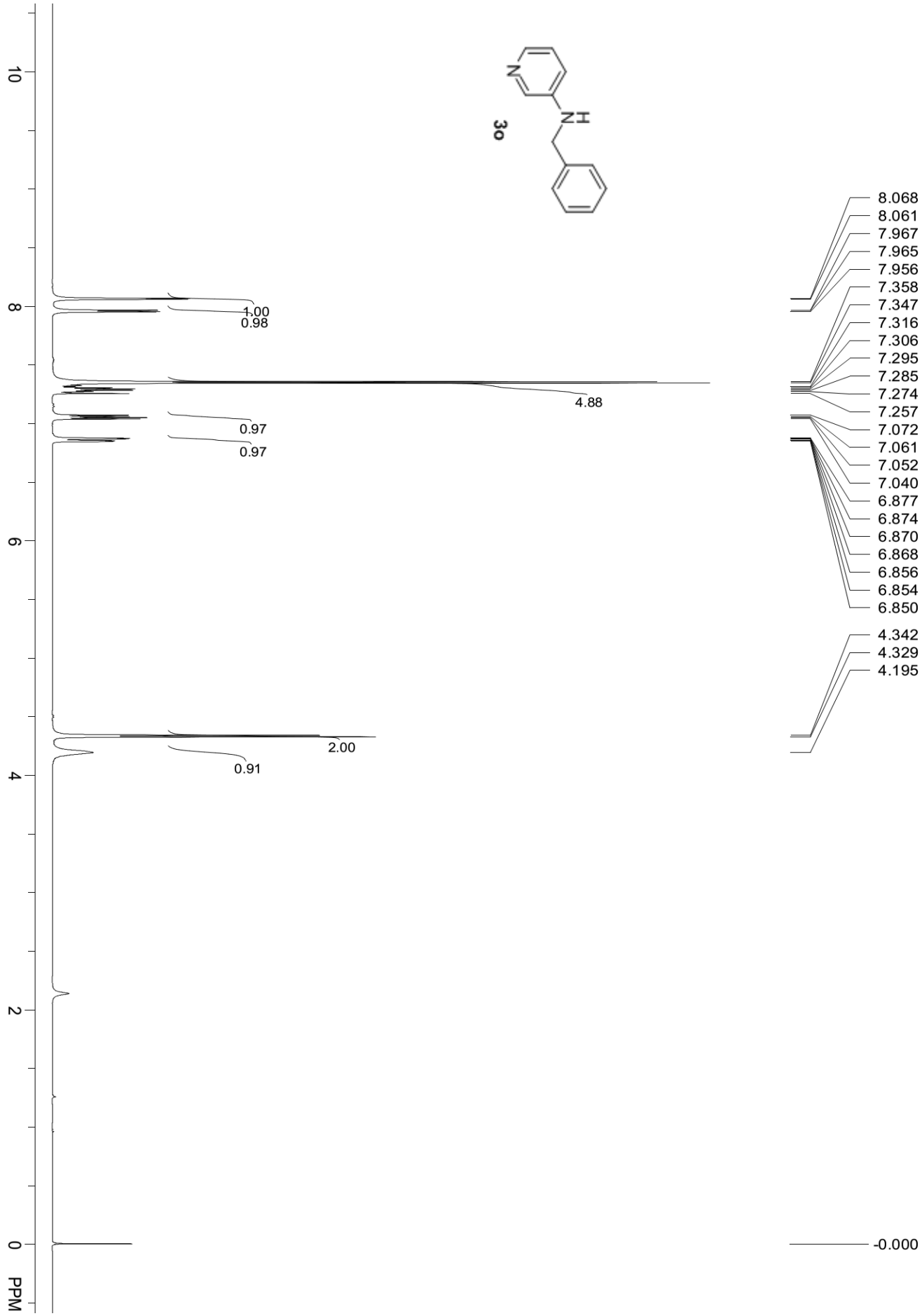
114.349
77.482
77.160
76.846
55.472
47.216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7.967
7.965
7.956
7.358
7.347
7.316
7.306
7.295
7.285
7.274
7.257
7.072
7.061
7.052
7.040
6.877
6.874
6.870
6.868
6.856
6.854
6.850
4.342
4.329
4.195
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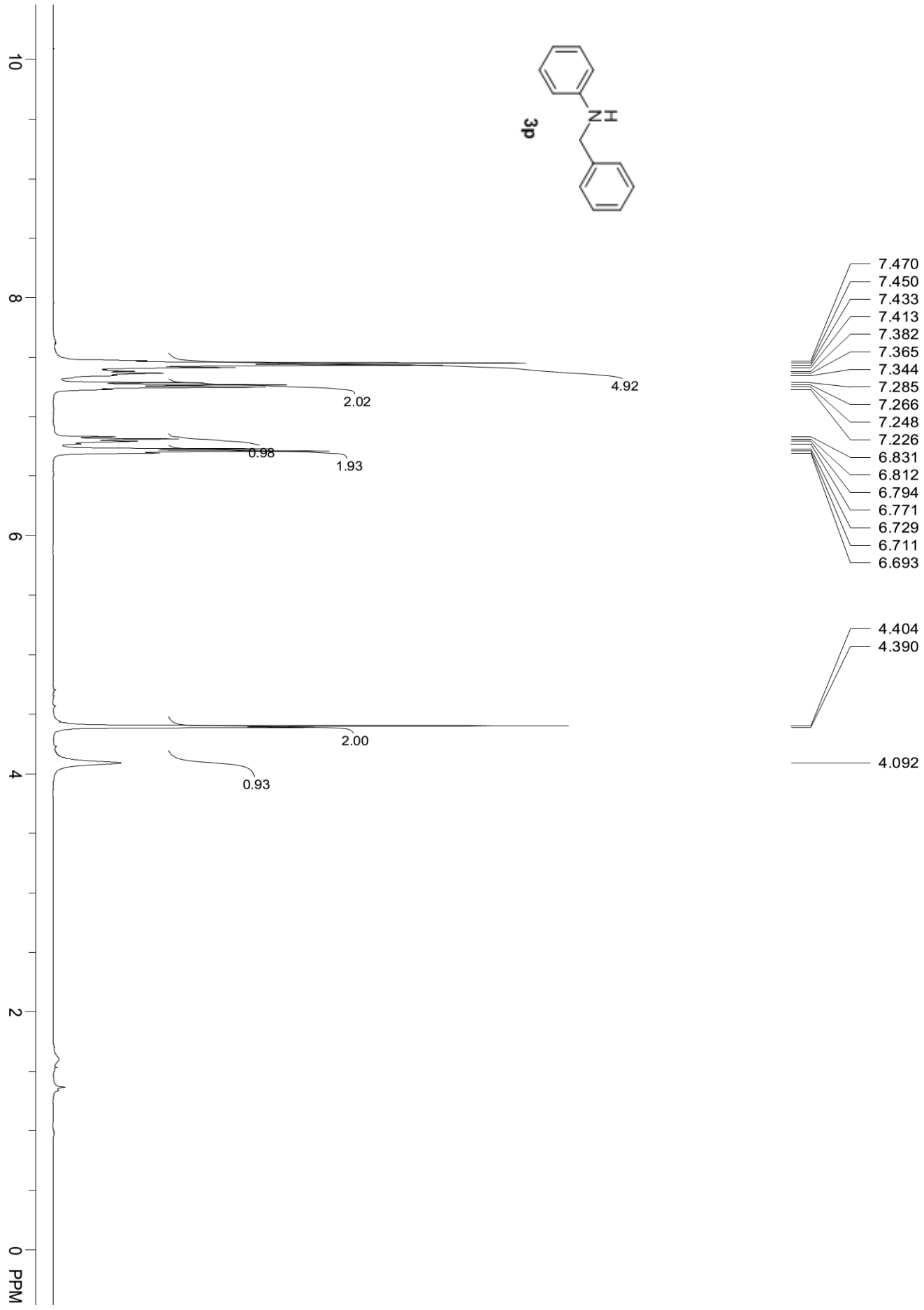
4.88
0.97
0.97
2.00
0.91
10
8
6
4
2
0
PPM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7.382
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7.285
7.266
7.248
7.226
6.831
6.812
6.794
6.771
6.729
6.711
6.693
4.404
4.390
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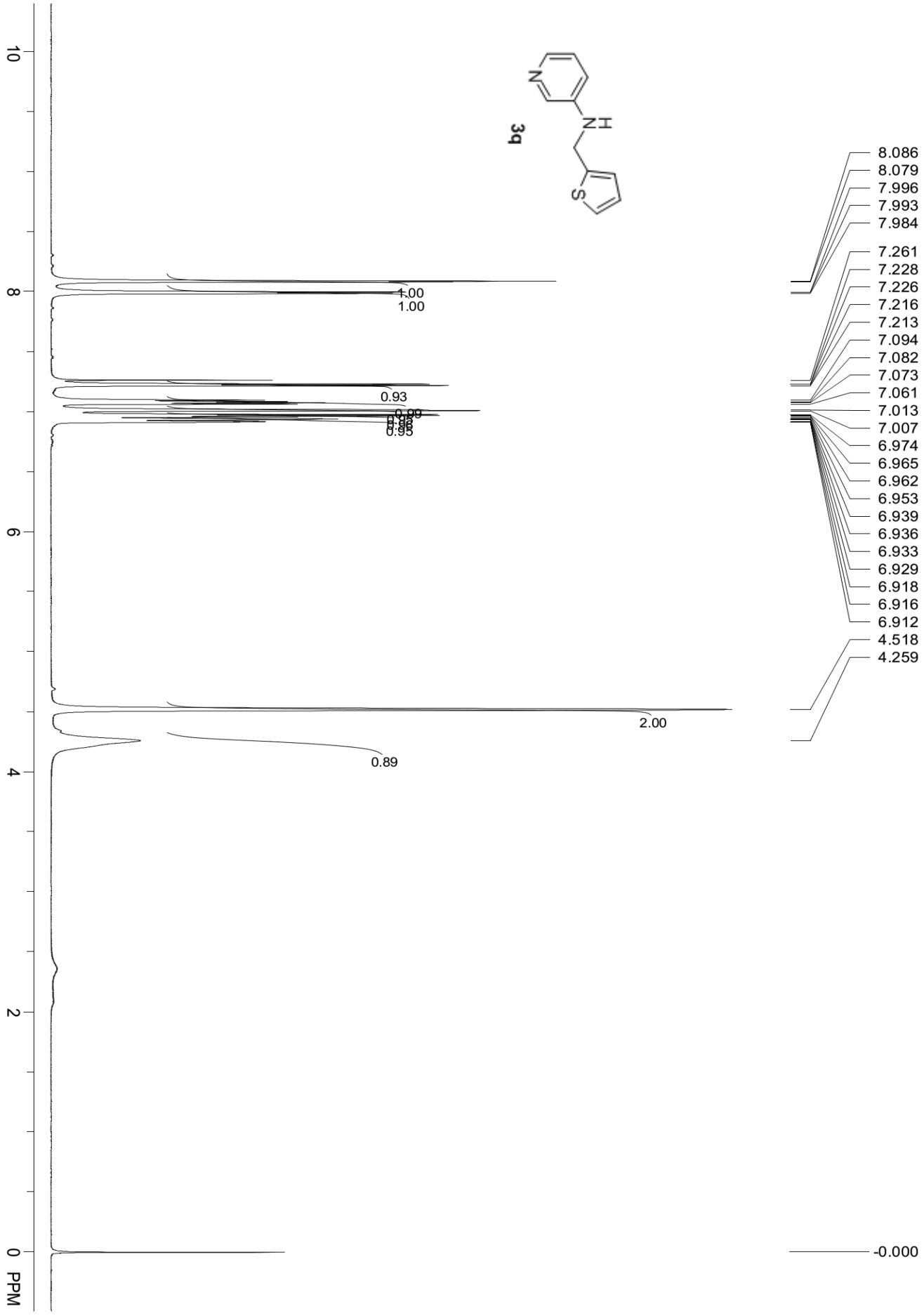
4.92
2.02
0.98
1.93
2.00
0.93
10
8
6
4
2
0
PPM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7.993
7.984
7.261
7.228
7.226
7.216
7.213
7.094
7.082
7.073
7.061
7.013
7.007
6.974
6.965
6.962
6.953
6.939
6.936
6.933
6.929
6.918
6.916
6.912
4.518
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1.00
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0.99
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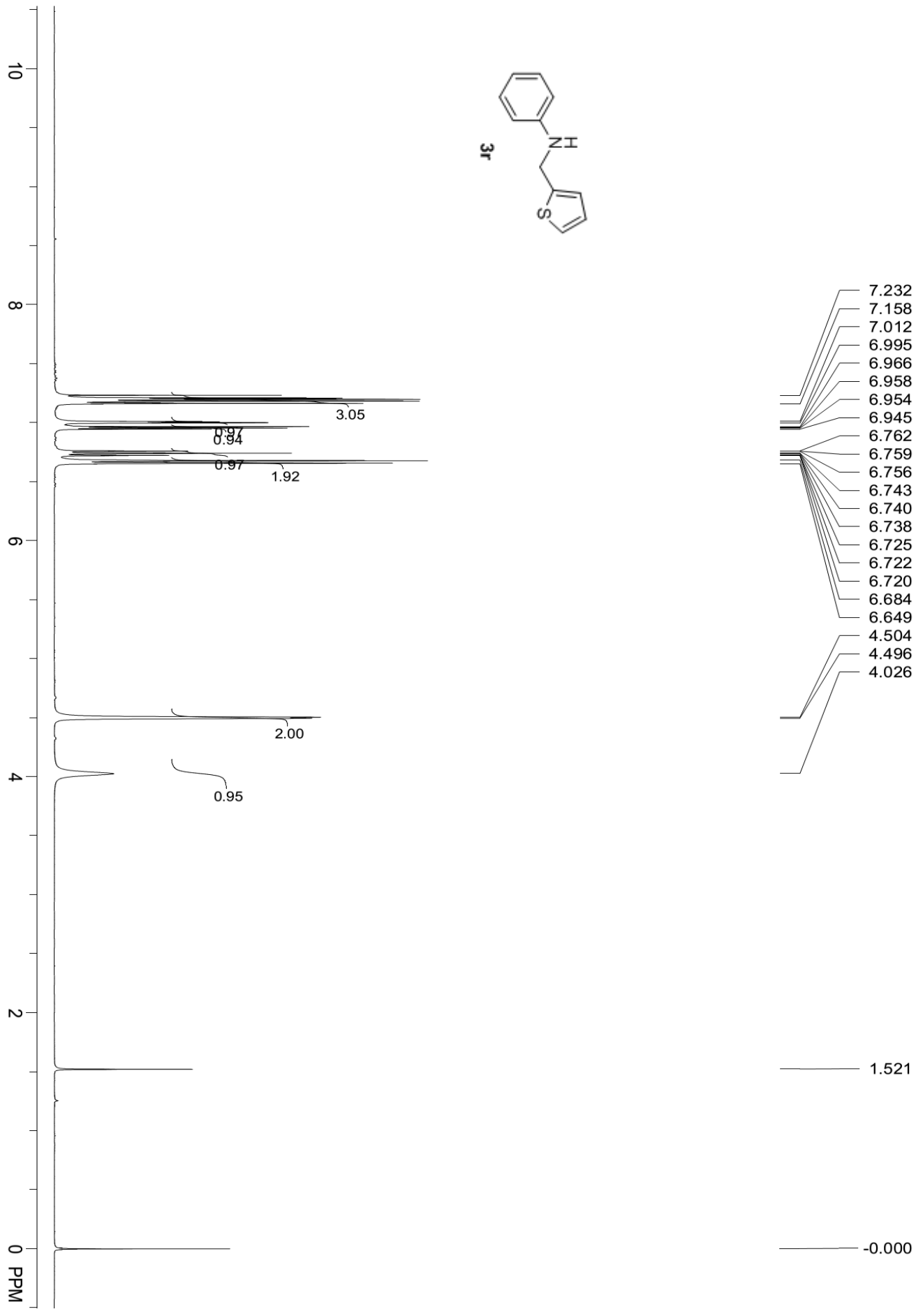
4
2
0
PPM


3r
NH
S
10
8
6
4
2
0
PPM
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0.97
0.94
0.97
1.92
2.00
0.95
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7.158
7.012
6.995
6.966
6.958
6.954
6.945
6.762
6.759
6.756
6.743
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6.738
6.725
6.722
6.720
6.684
6.649
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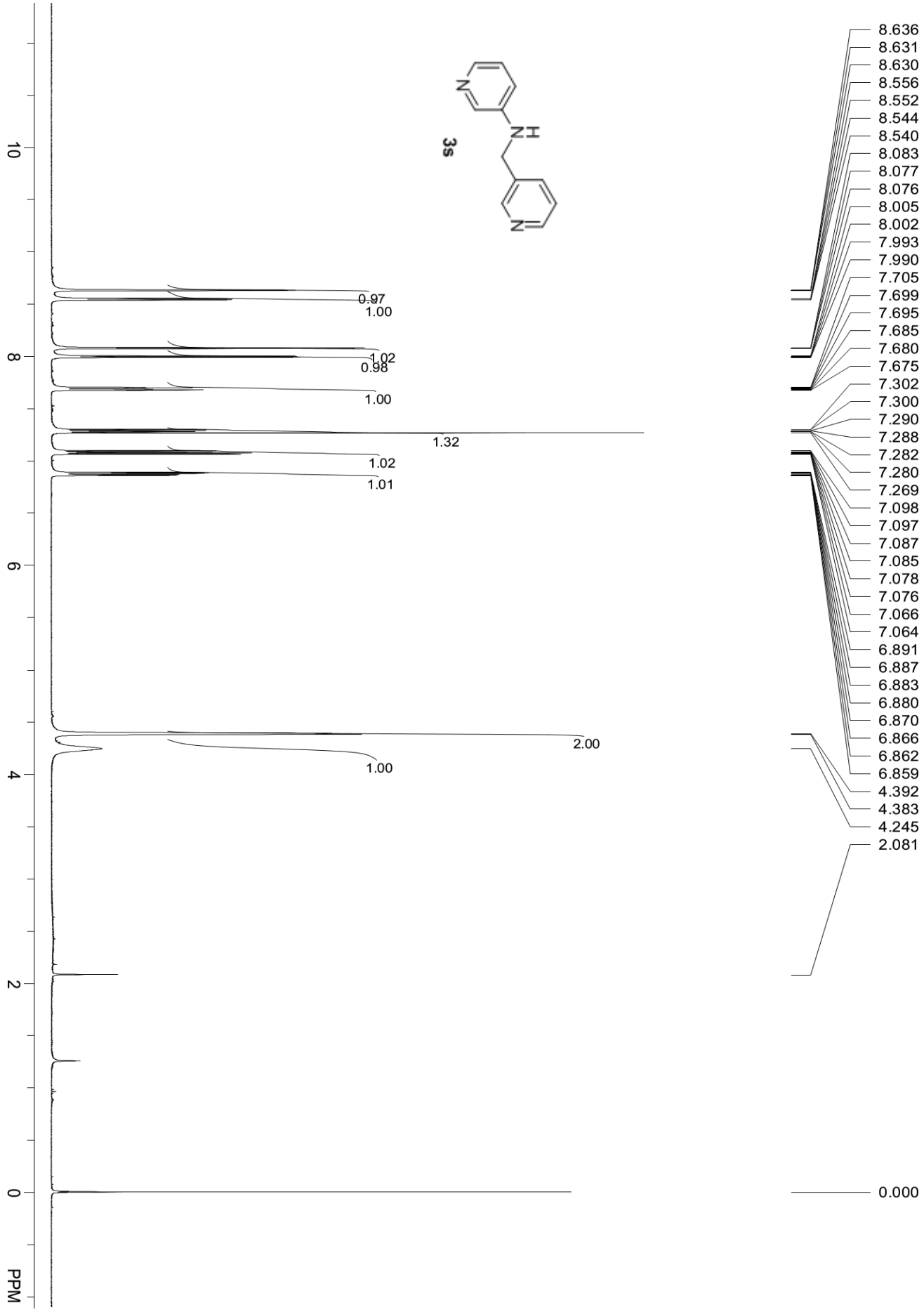
4.496
4.026
1.521
-0.000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8.552
8.544
8.540
8.083
8.077
8.076
8.005
8.002
7.993
7.990
7.705
7.699
7.695
7.685
7.680
7.675
7.302
7.300
7.290
7.288
7.282
7.280
7.269
7.098
7.097
7.087
7.085
7.078
7.076
7.066
7.064
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6.887
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6.880
6.870
6.866
6.862
6.859
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4.383
4.245
2.081
0.000
0.97
1.00
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1.01
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10
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4
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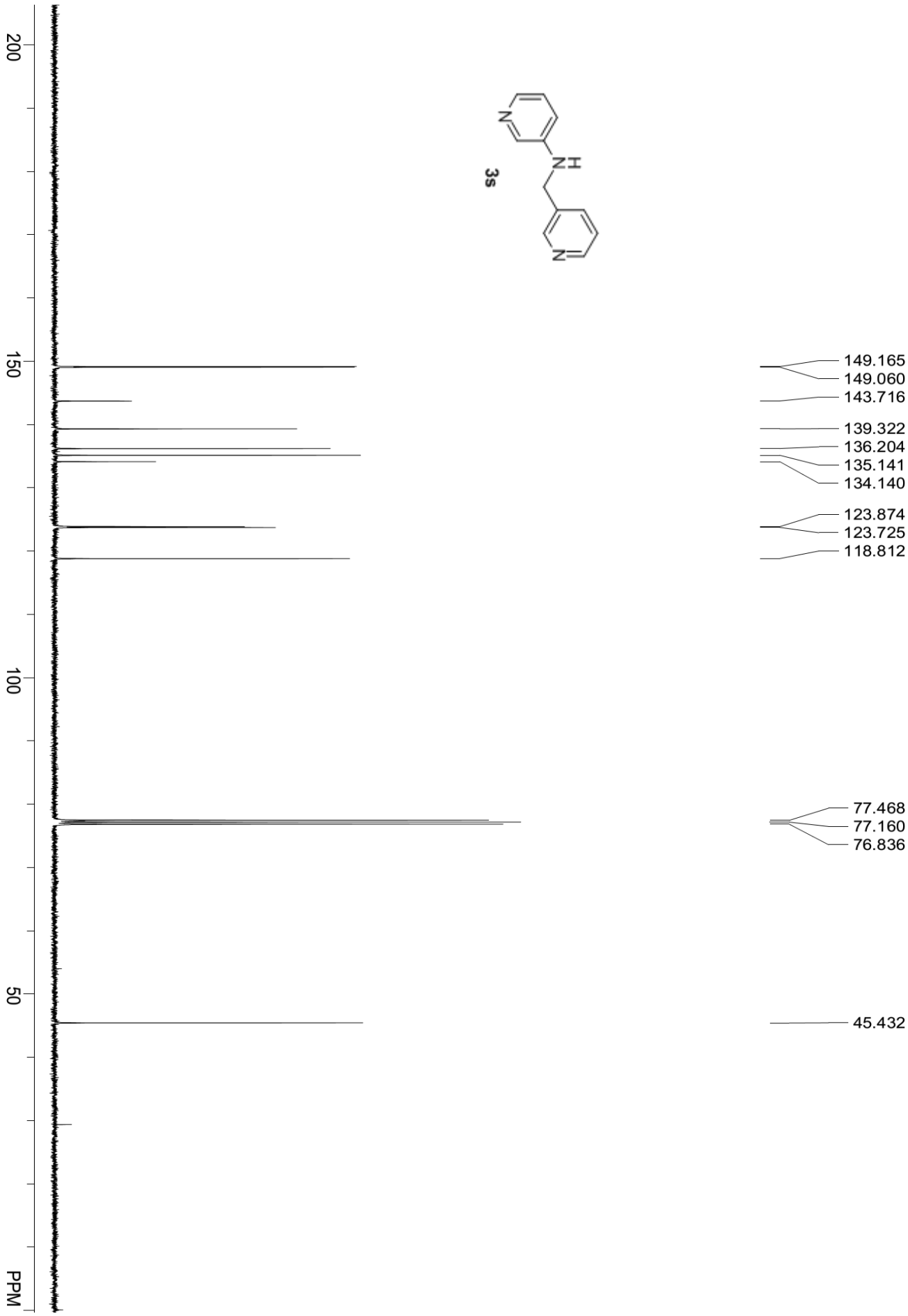
0
PPM


200
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PPM
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123.725
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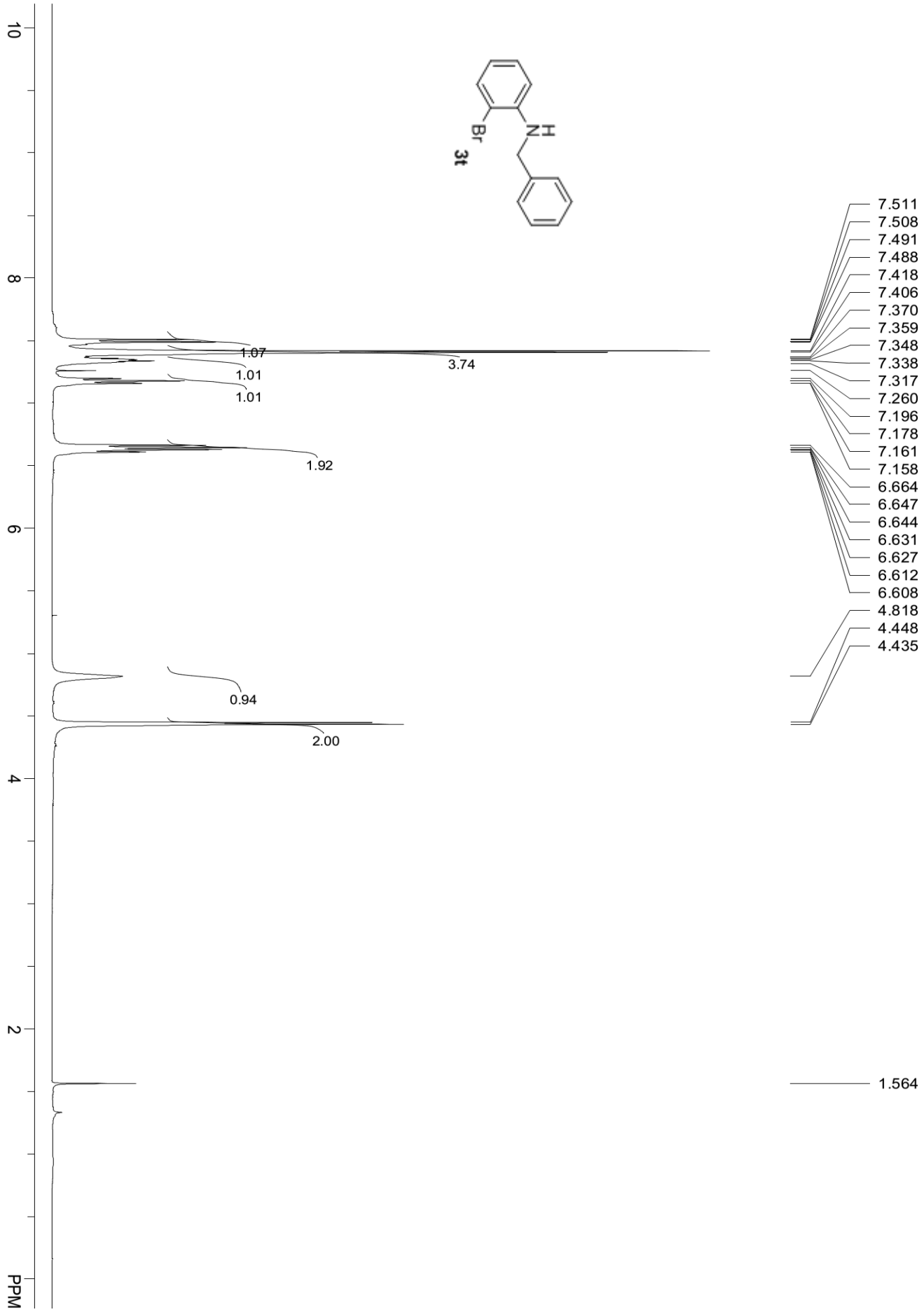
45.432


10
8
6
4
2
PPM
Br
H
N
3t
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1.01
1.01
3.74
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2.00
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7.508
7.491
7.488
7.418
7.406
7.370
7.359
7.348
7.338
7.317
7.260
7.196
7.178
7.161
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6.608
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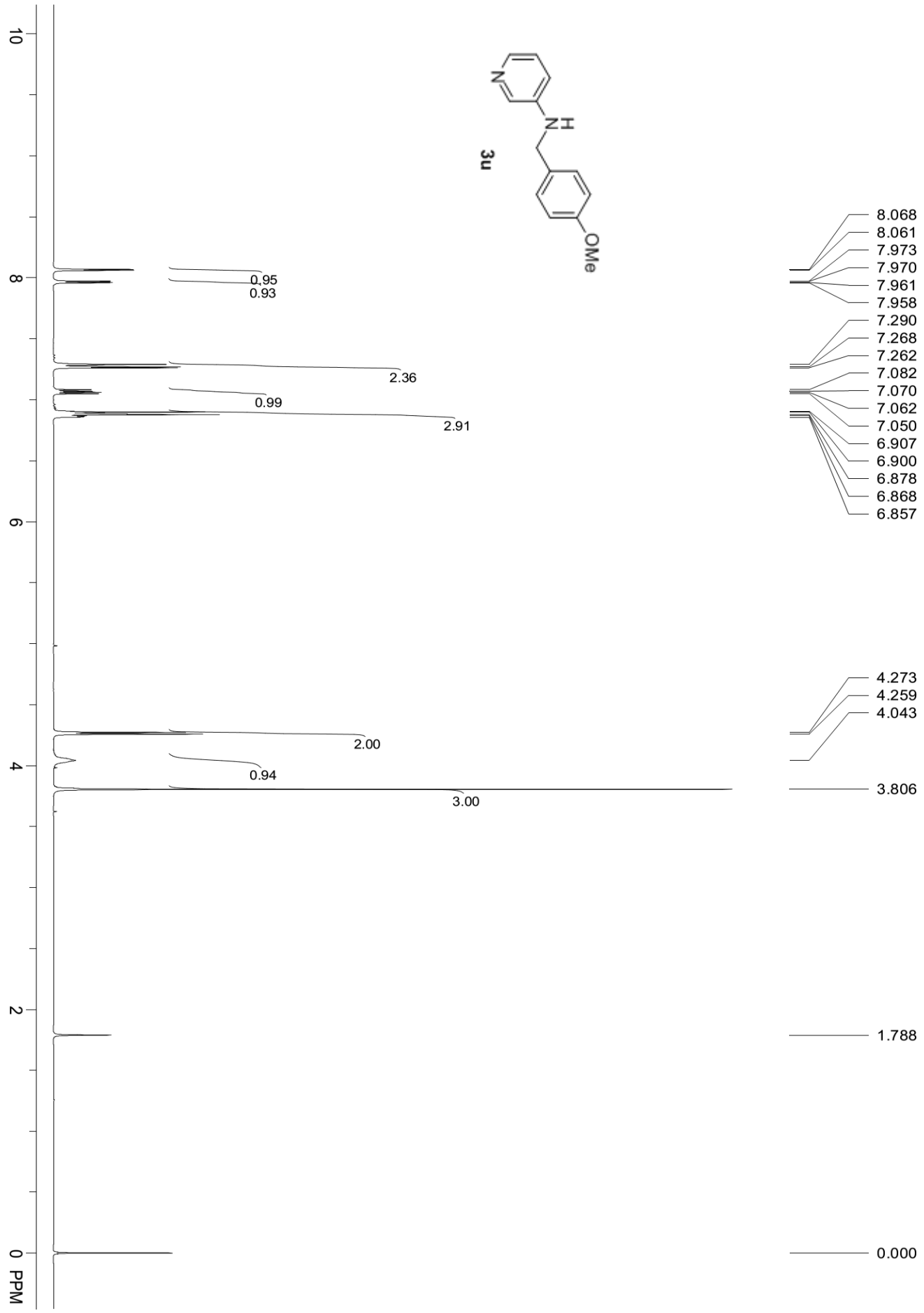
4.435
1.564


3u
N
H
N
OMe
10
8
6
4
2
0
PPM
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0.93
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2.91
2.00
0.94
3.00
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7.970
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7.958
7.290
7.268
7.262
7.082
7.070
7.062
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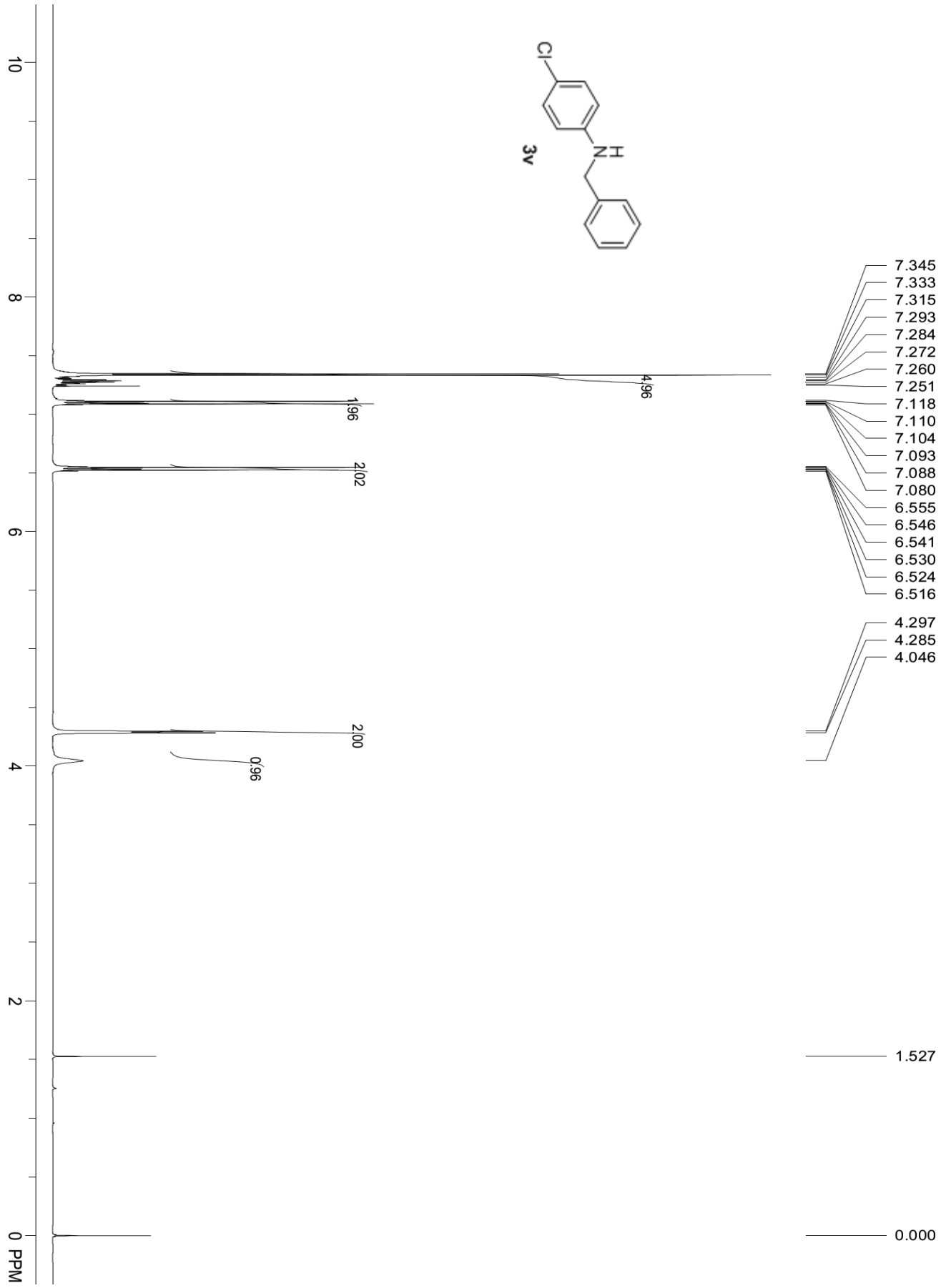
Cl
N
H
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7.272
7.260
7.251
7.118
7.110
7.104
7.093
7.088
7.080
6.555
6.546
6.541
6.530
6.524
6.516
4.297
4.285
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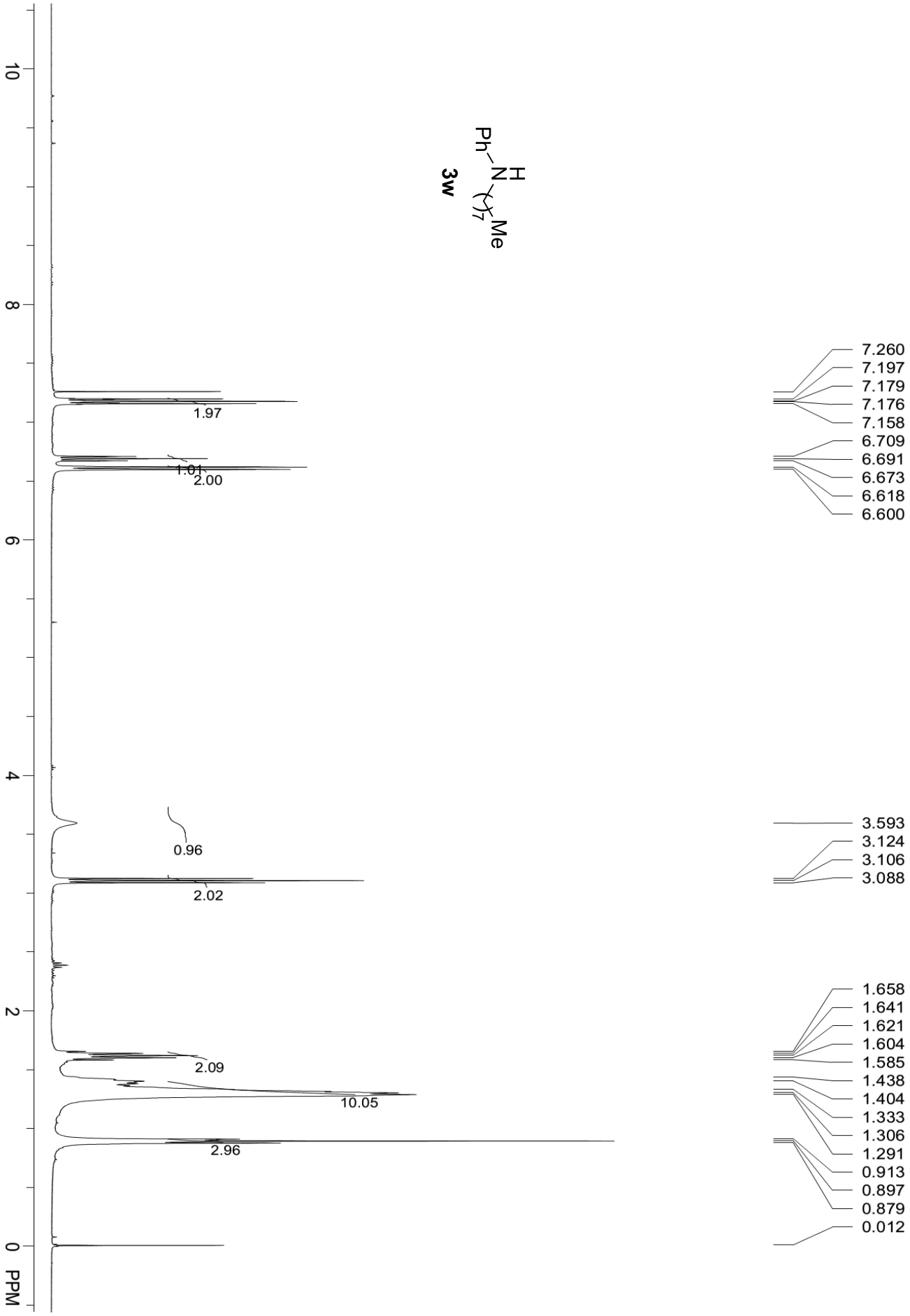
1.96
2.02
2.00
0.96
10
8
6
4
2
0 PPM


Ph
N
H
Me
7
3w
10
8
6
4
2
0
PPM
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1.01
2.00
0.96
2.02
2.09
10.05
2.96
7.260
7.197
7.179
7.176
7.158
6.709
6.691
6.673
6.618
6.600
3.593
3.124
3.106
3.088
1.658
1.641
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1.306
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0.913
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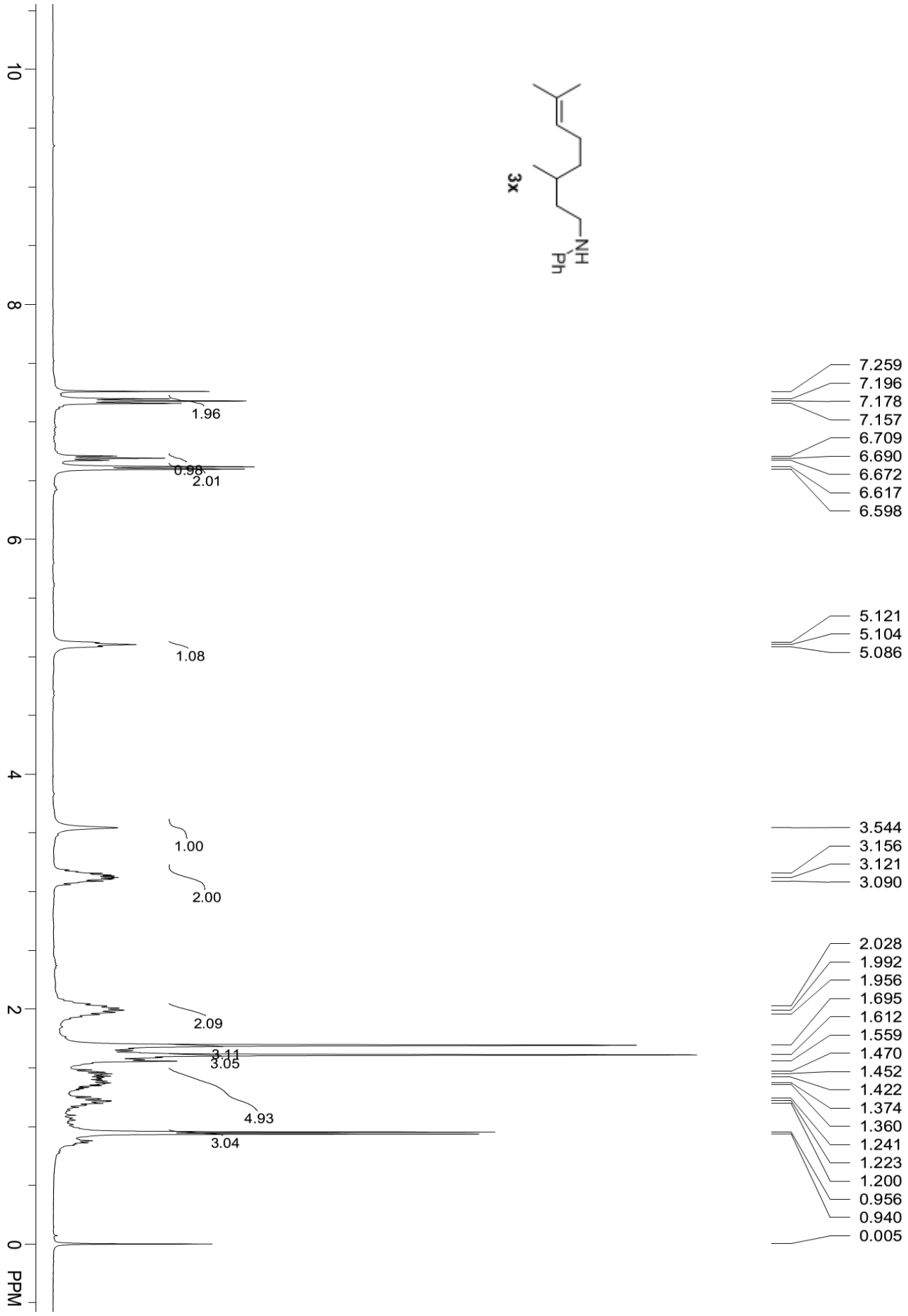
0.879
0.012


3x
NH
Ph
10
8
6
4
2
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PPM
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1.08
1.00
2.00
2.09
3.11
3.05
4.93
3.04
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7.196
7.178
7.157
6.709
6.690
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6.617
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3.156
3.121
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1.956
1.695
1.612
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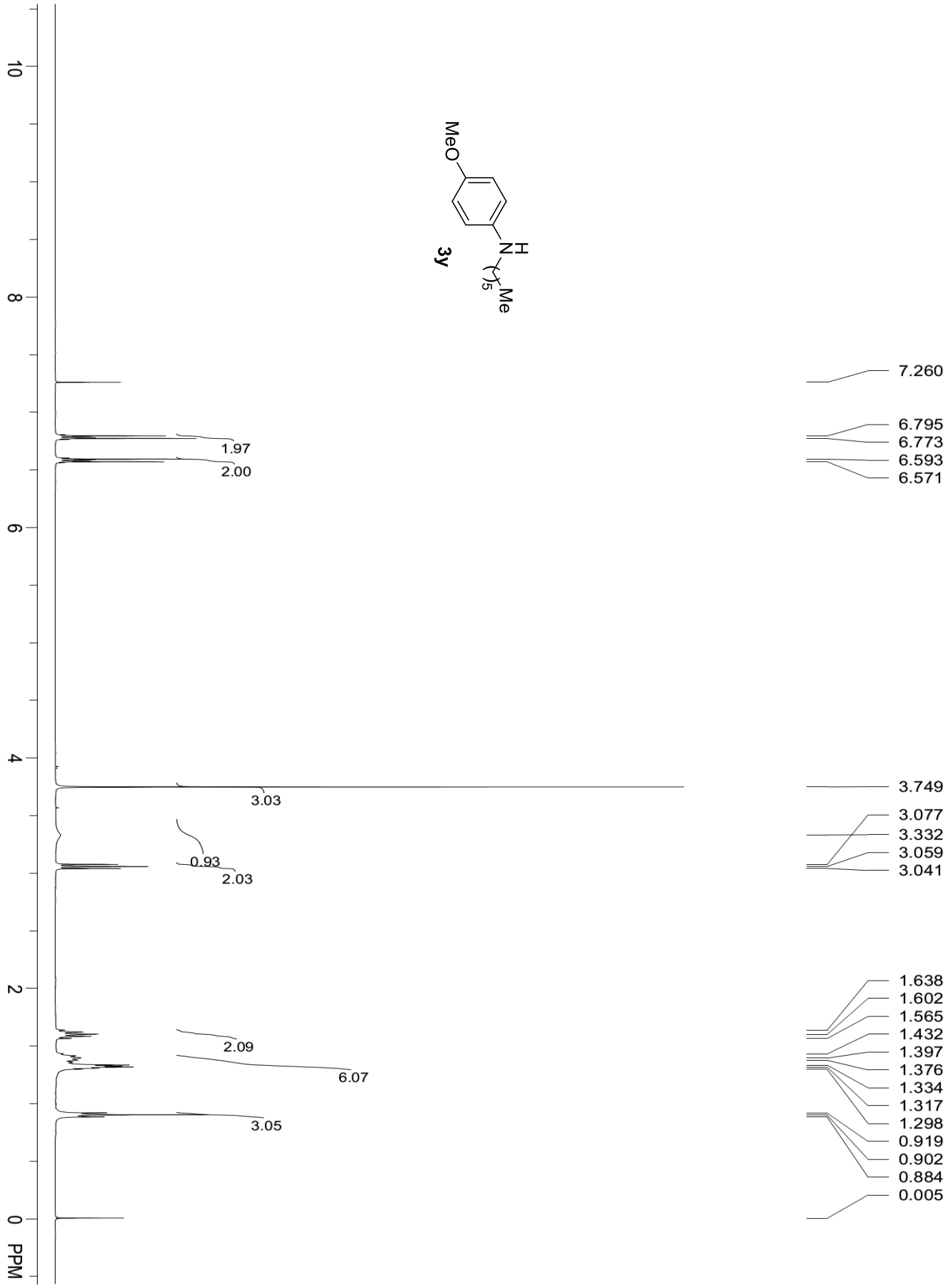
MeO
N
H
Me
5
3y
10
8
6
4
2
0
PPM
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2.00
3.03
0.93
2.03
2.09
6.07
3.05
7.260
6.795
6.773
6.593
6.571
3.749
3.077
3.332
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3.041
1.638
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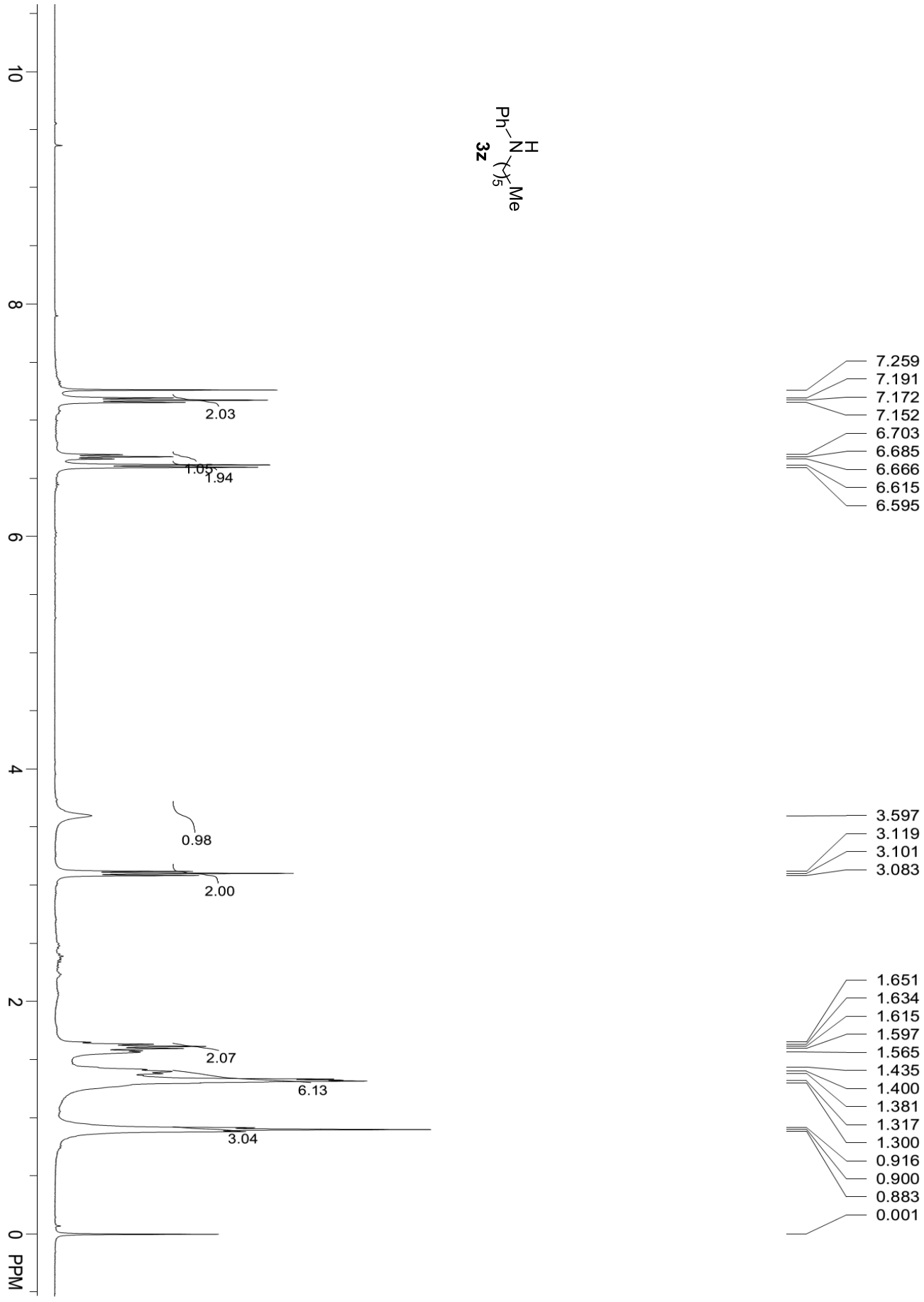
0.884
0.005


3z
Ph
N
H
Me
10
8
6
4
2
0
PPM
2.03
1.05
1.94
0.98
2.00
2.07
6.13
3.04
7.259
7.191
7.172
7.152
6.703
6.685
6.666
6.615
6.595
3.597
3.119
3.101
3.083
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1.634
1.615
1.597
1.565
1.435
1.400
1.381
1.317
1.300
0.916
0.900
0.883
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