Supporting Information

Copper-Catalyzed Synthesis of Primary Arylamines via Cascade Reactions of Aryl Halides with Amidine Hydrochlorides

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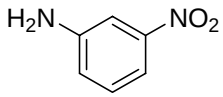
General experimental procedures

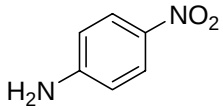
All reactions were performed under nitrogen atmosphere. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with tetramethylsilane or solvent resonance as the internal standard (^{1}H NMR: TMS at 0.00ppm, $CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO-d_6 at 40.0 ppm).

Characterization data for compounds 3



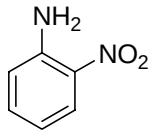
3a

3-Nitroaniline (3a).[1] Eluent: petroleum ether/ethyl acetate (10:1). Yield 127 mg (92%). Yellow solid. mp 113-114 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.20-7.35 (m, 4H), 5.76 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.62, 149.25, 130.39, 120.46, 110.28, 107.56. MS M^+ m/z 138.0.



3b

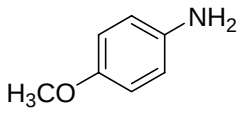
4-Nitroaniline (3b).[2] Eluent: petroleum ether/ethyl acetate (10:1). Yield 121 mg (88%). Yellow solid. mp 148-149 ^{o}C (lit.[2] 147-149 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.09-8.05 (m, 2H), 6.66-6.62 (m, 2H), 4.41 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.2, 136.2, 126.9, 112.9. MS M^+ m/z 138.1.



3c

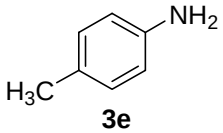
2-Nitroaniline (3c).[3] Eluent: petroleum ether/ethyl acetate (10:1). Yield 109 mg (79%).

Saffron solid. mp 79-80 ^{o}C (lit.[3] 71-72 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89-7.87 (d, 1H), δ 7.34-7.28 (t, 3H), 6.69-6.64 (d, 1H), δ6.55-6.50 (t, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.7, 136.1, 130.8, 126.1, 119.7, 115.9. MS M^+ m/z 138.1.



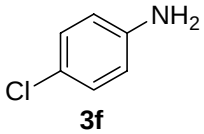
3d

***p*-Methoxyaniline (3d)**.[4] Eluent: petroleum ether/ethyl acetate (3:1). Yield 96 mg (78%). Colorless crystal. mp 63-65 ^{o}C (lit.[4] 57-60 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74-6.73 (d, 2H), 6.65-6.62 (d, 2H), 3.74 (s, 3H), 3.42 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 140.1, 116.5, 114.9, 55.8. MS M^+ m/z 122.9.



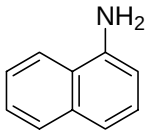
3e

***p*-Chloroaniline (3e)**.[5] Eluent: petroleum ether/ethyl acetate (5:1). Yield 77 mg (72%). Buff crystal. mp 42-43 ^{o}C (lit.[5] 40-44 ^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.79-6.76 (d, 2H), 6.44-6.42 (d, 2H), 4.74 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.6, 129.8, 124.5, 114.6, 20.65. MS M^+ m/z 107.1.



3f

***p*-Chloroaniline (3f)**.[6] Eluent: petroleum ether/ethyl acetate (5:1). Yield 92 mg (72%). Colorless solid. mp 84-85^{o}C (lit.[6] 71^{o}C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.03-6.98 (d, 2H), 6.95-6.53 (d, 2H), 5.18 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.2, 129.02,119.2, 115.7. MS M^+ m/z 126.9.



3g

1-Naphthylanine (3g).[7] Eluent: petroleum ether/ethyl acetate (3:1). Yield 96 mg (67%). Light red crystal. mp 55-56°C (lit.[7] 50-51°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.70 (m, 2H), δ 7.44-7.42 (m, 2H), δ 7.29 (m, 2H), 4.10 (s, 2H). ^{13}C NMR (75MHz, $CDCl_3$) δ 142.2, 134.5, 128.7, 126.4, 125.9, 125.0, 123.76, 120.9, 119.1, 109.8. MS M^+ m/z 143.2.

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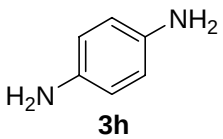
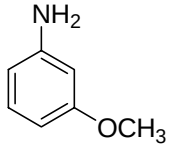


3h

***p*-Phenylenediamine (3h)**.[5] Eluent: petroleum ether/ethyl acetate (1:1). Yield 102 mg (94%). Brown solid. mp 143-145°C (lit.[5] 141°C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.34 (s, 4H), 4.16 (s, 4H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 139.4, 116.0. MS M^+ m/z 108.1.



3i

3- Methoxyaniline (3i). Eluent: petroleum ether/ethyl acetate (3:1). Brown oil. Yield 79 mg (64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07-7.02 (t, *J* = 7.89 Hz, 1H), 6.29-6.23 (m, 3H), 3.74 (s, 3H), δ 3.63, (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 147.9, 130.2, 108.0, 104.0, 101.2, 55.2. MS M^+ m/z 122.9.

References

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(4) Yasuhara, A.; Kasano, A.; Sakamoto, T. *J. Org. Chem.* **1999**, *64*, 2301.

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(6) Gowda,S.; Abiraj, K,; D. Gowda, C. *Tetrabedron* **2002**, *43*, 1329.

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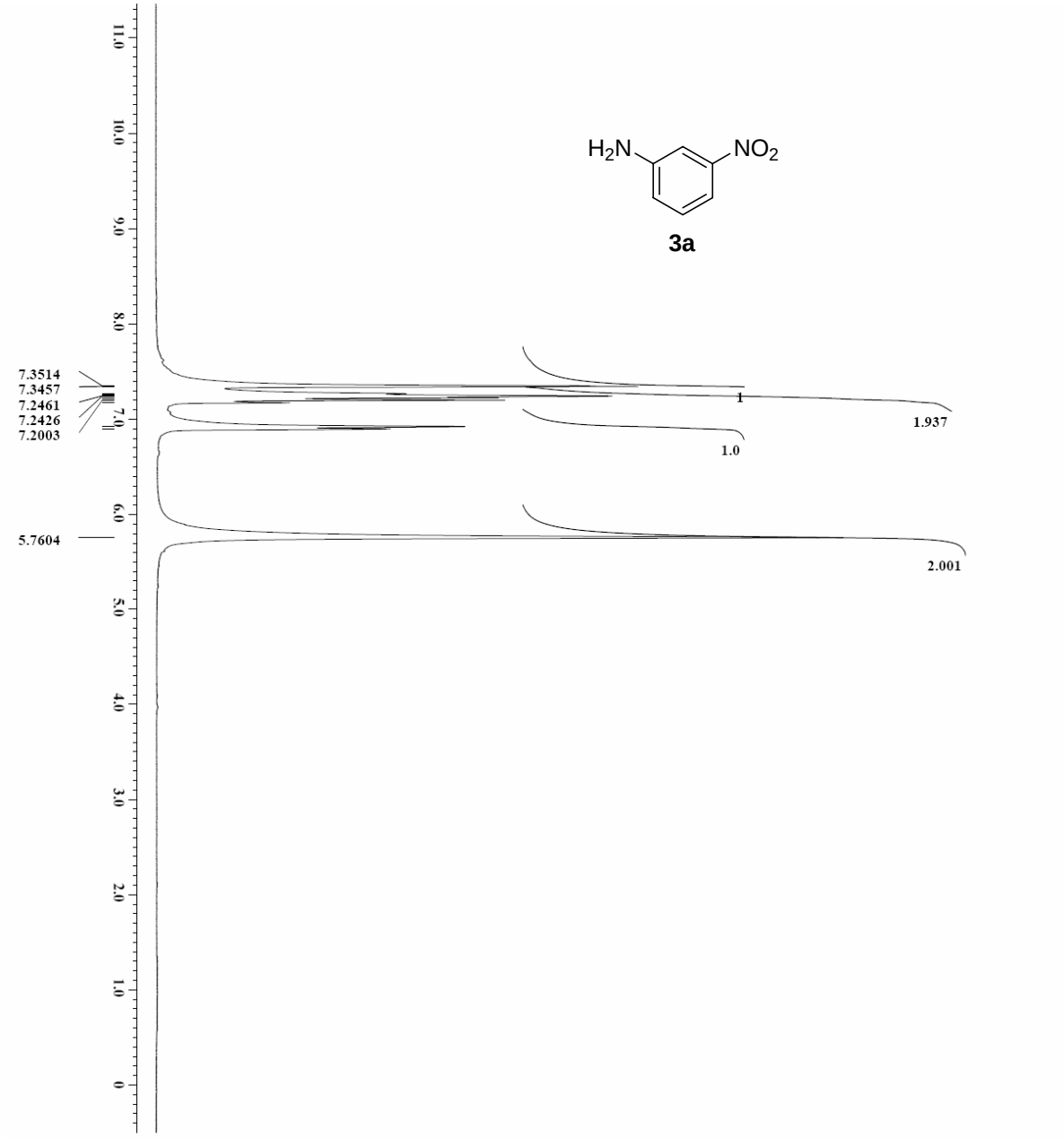
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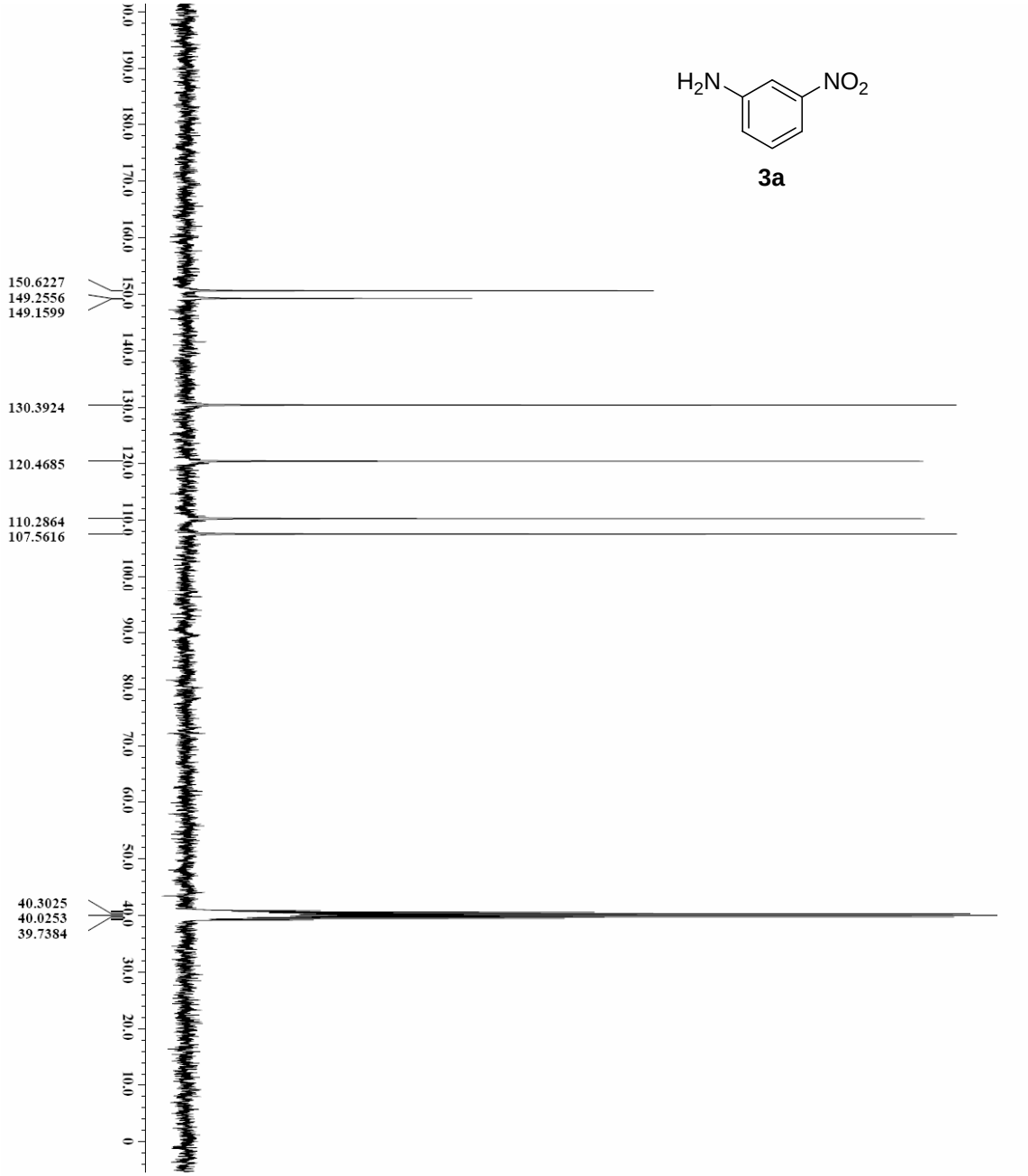
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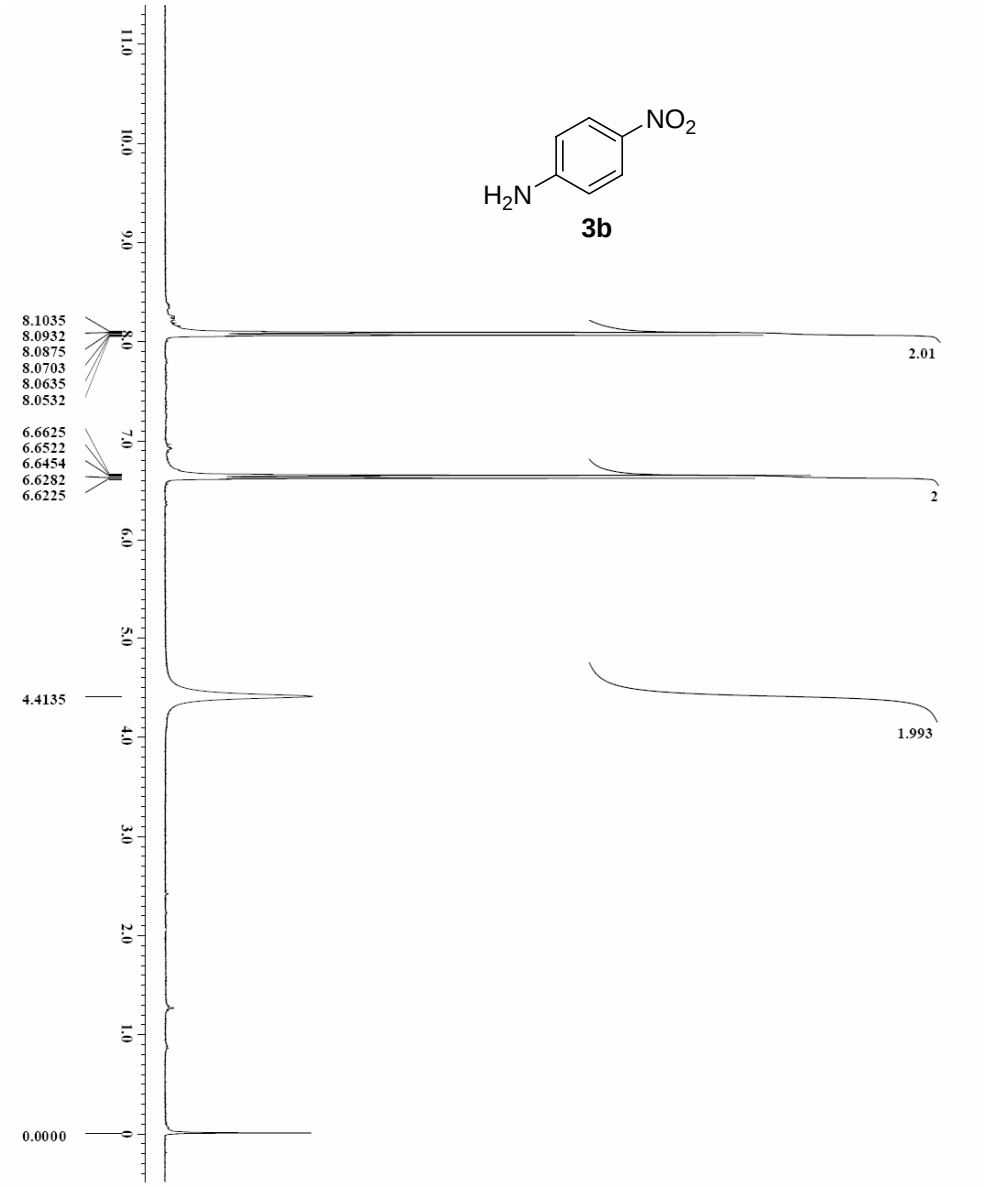
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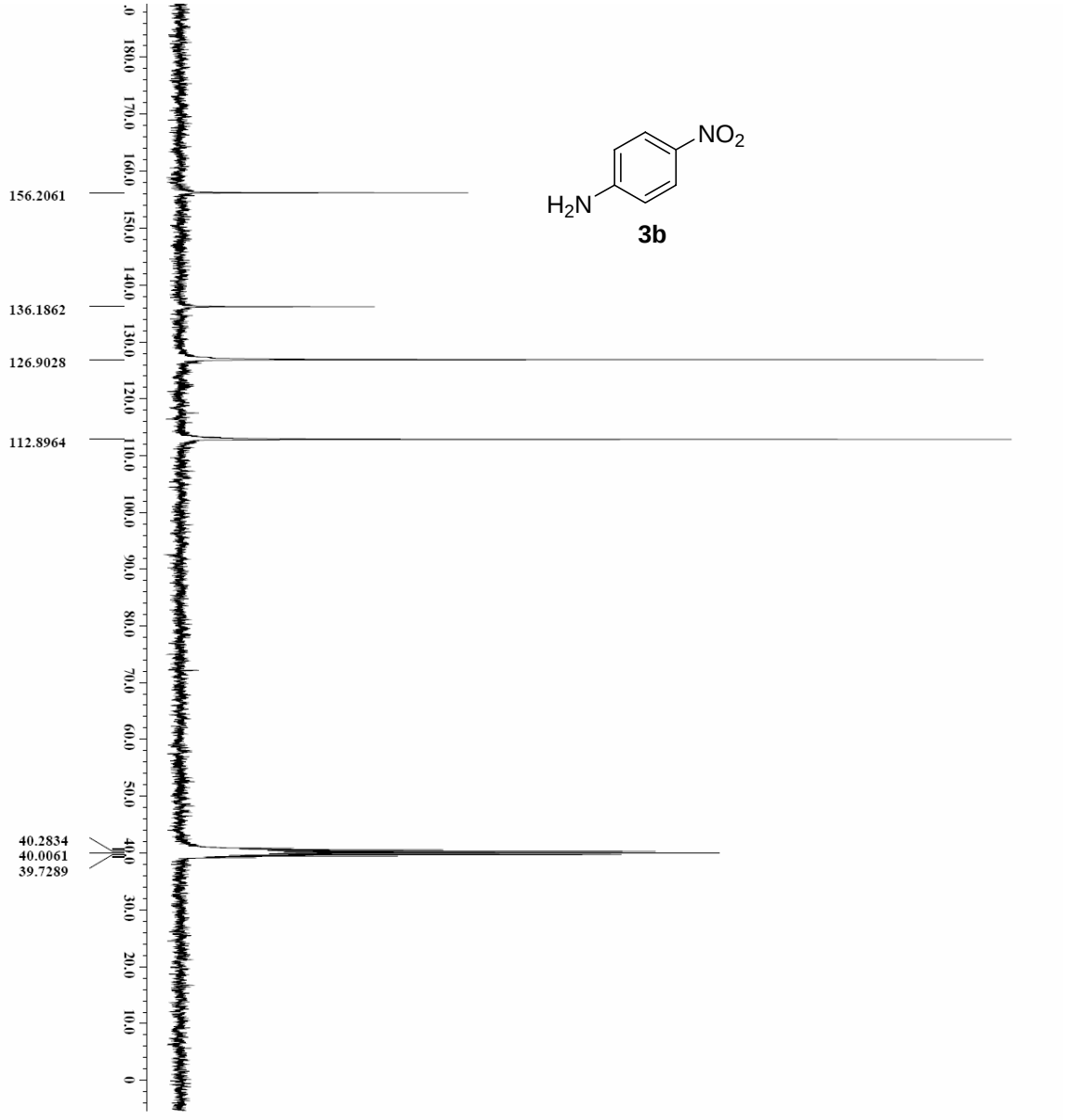
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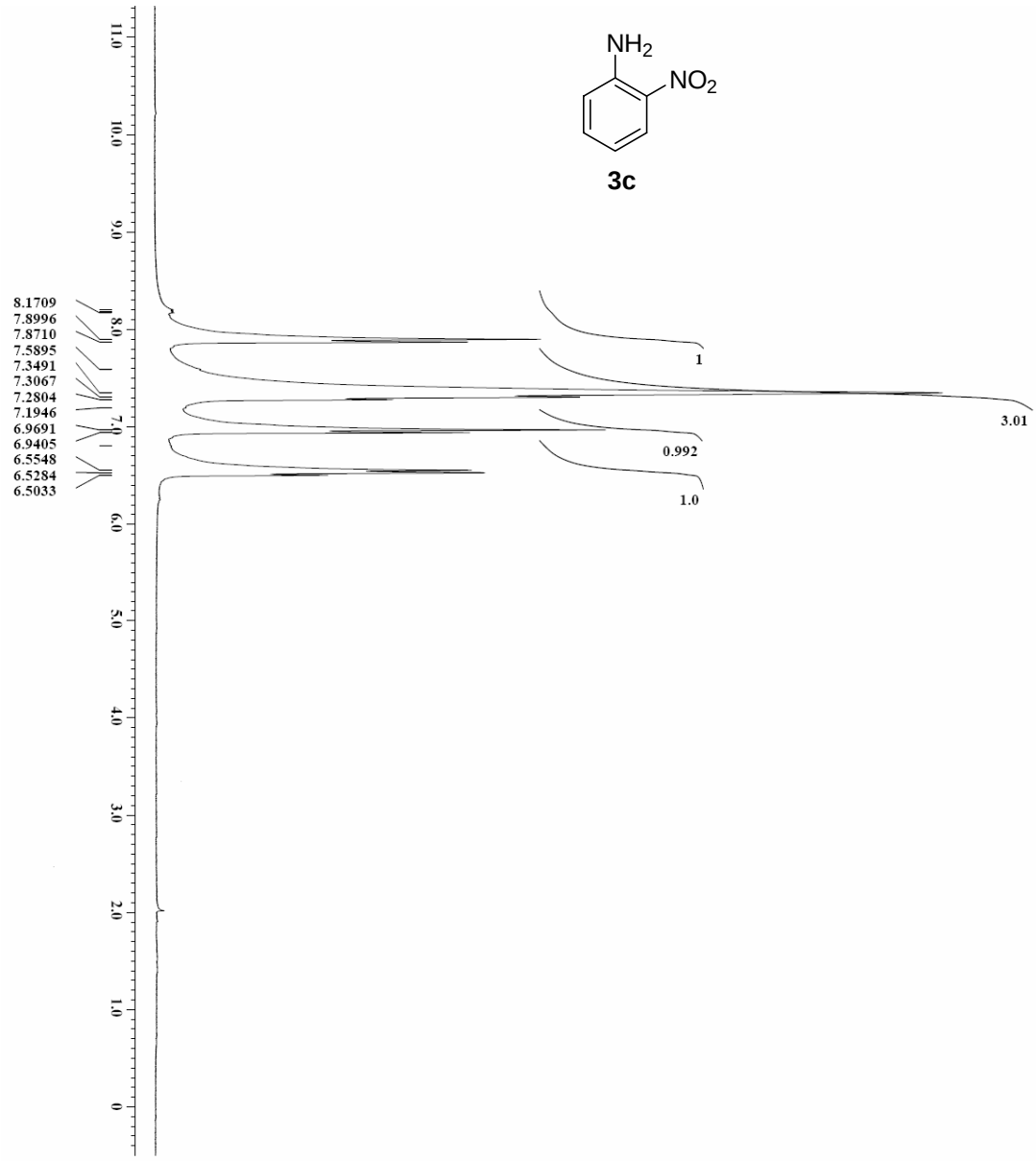
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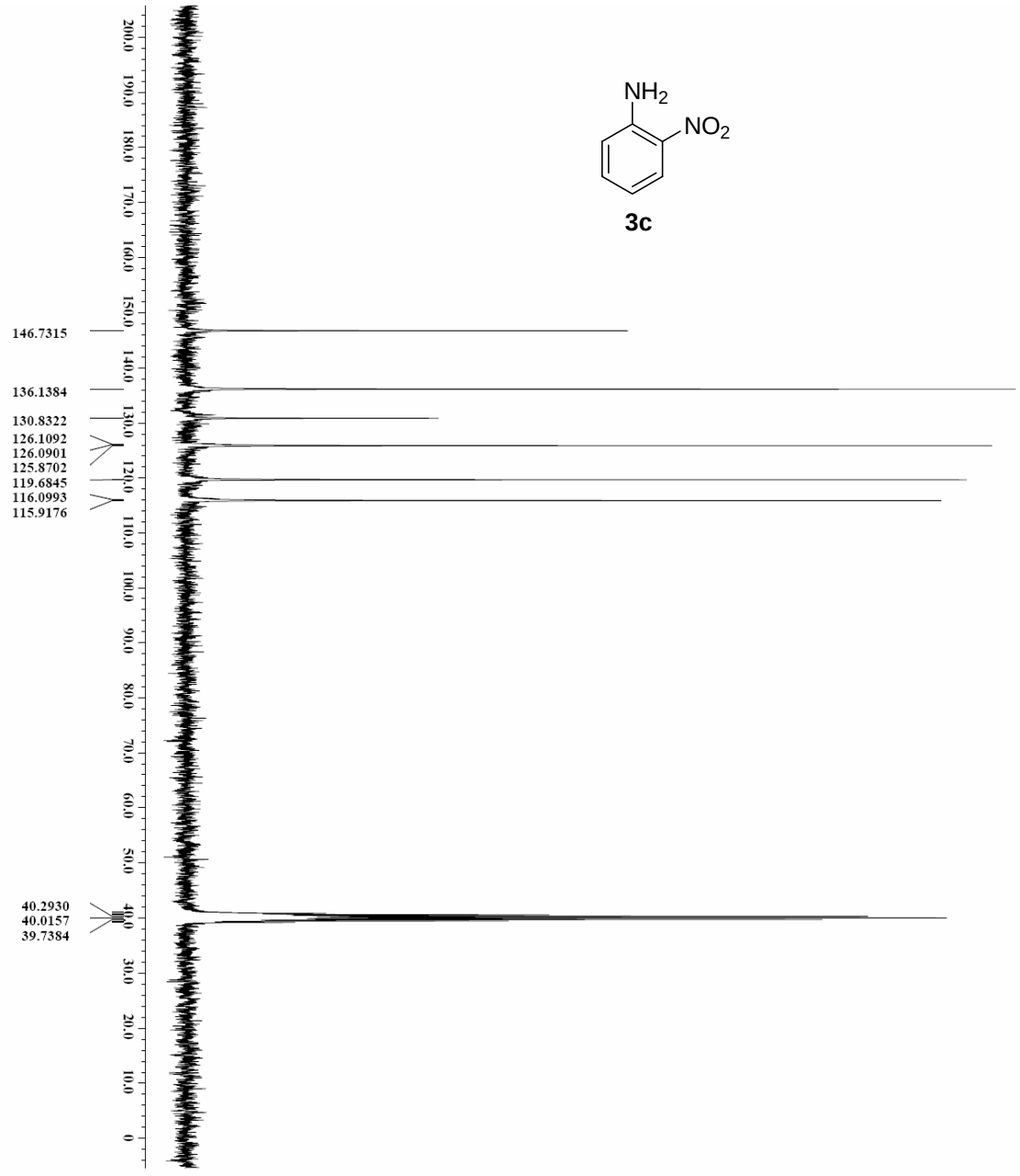
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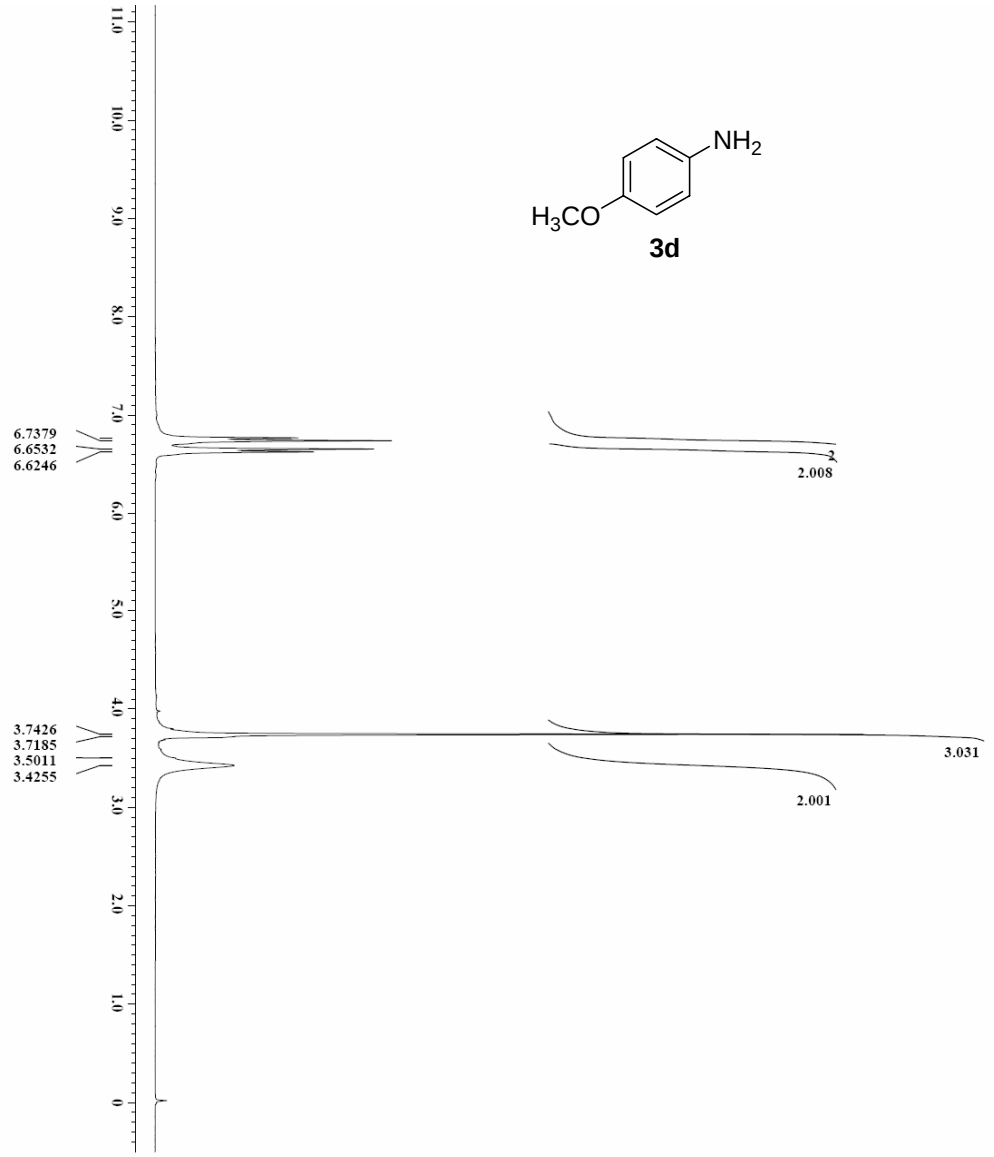
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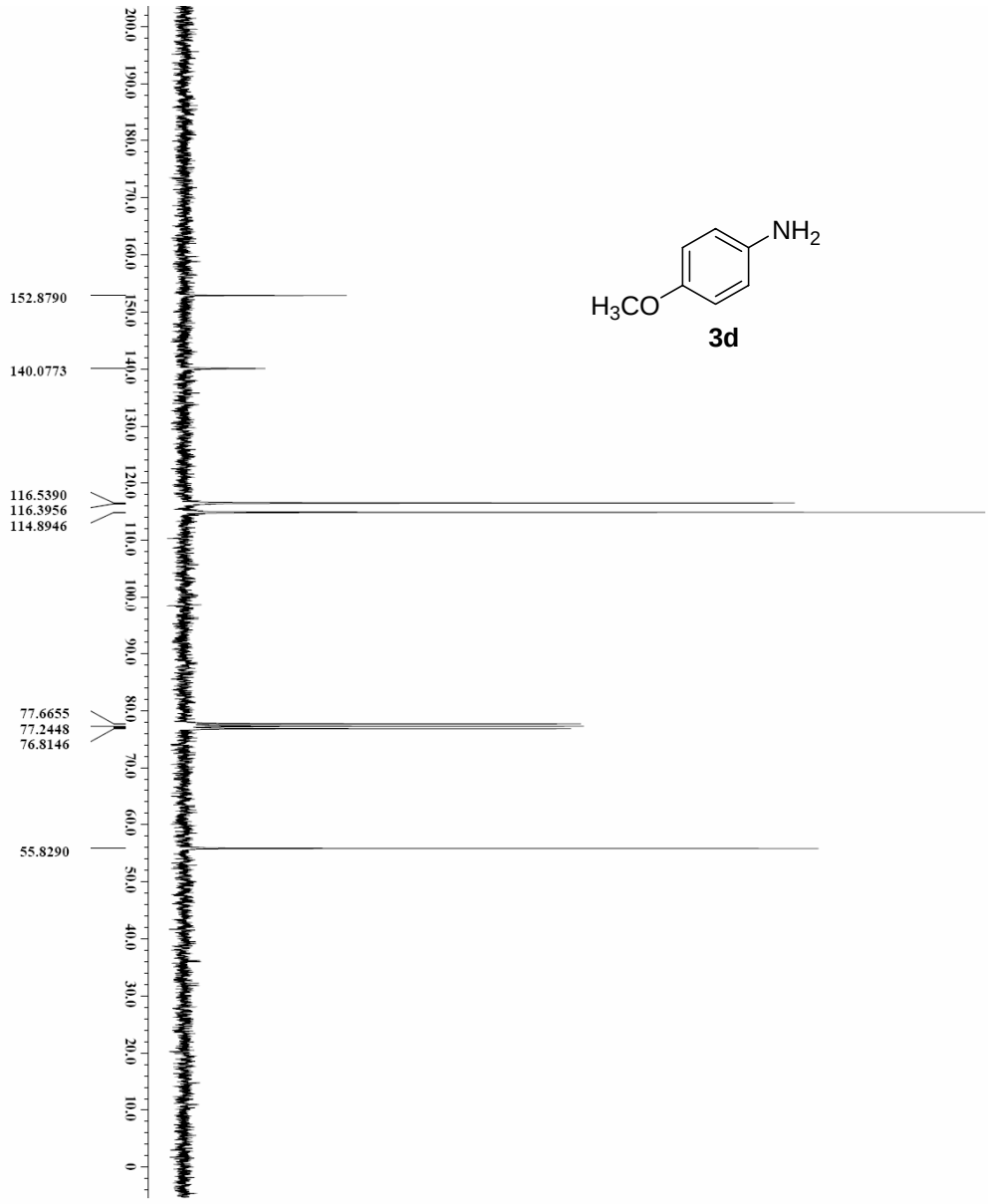
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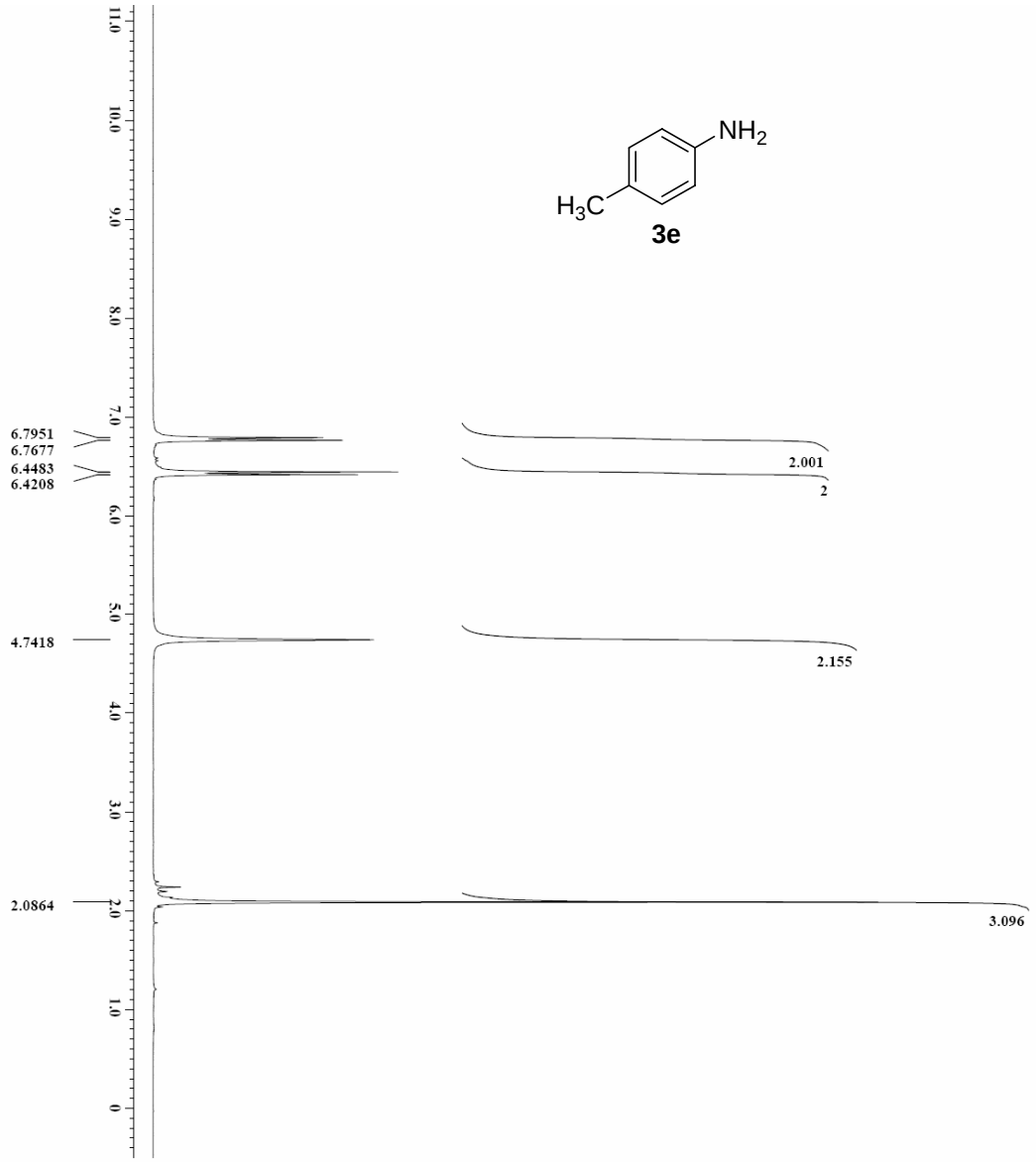
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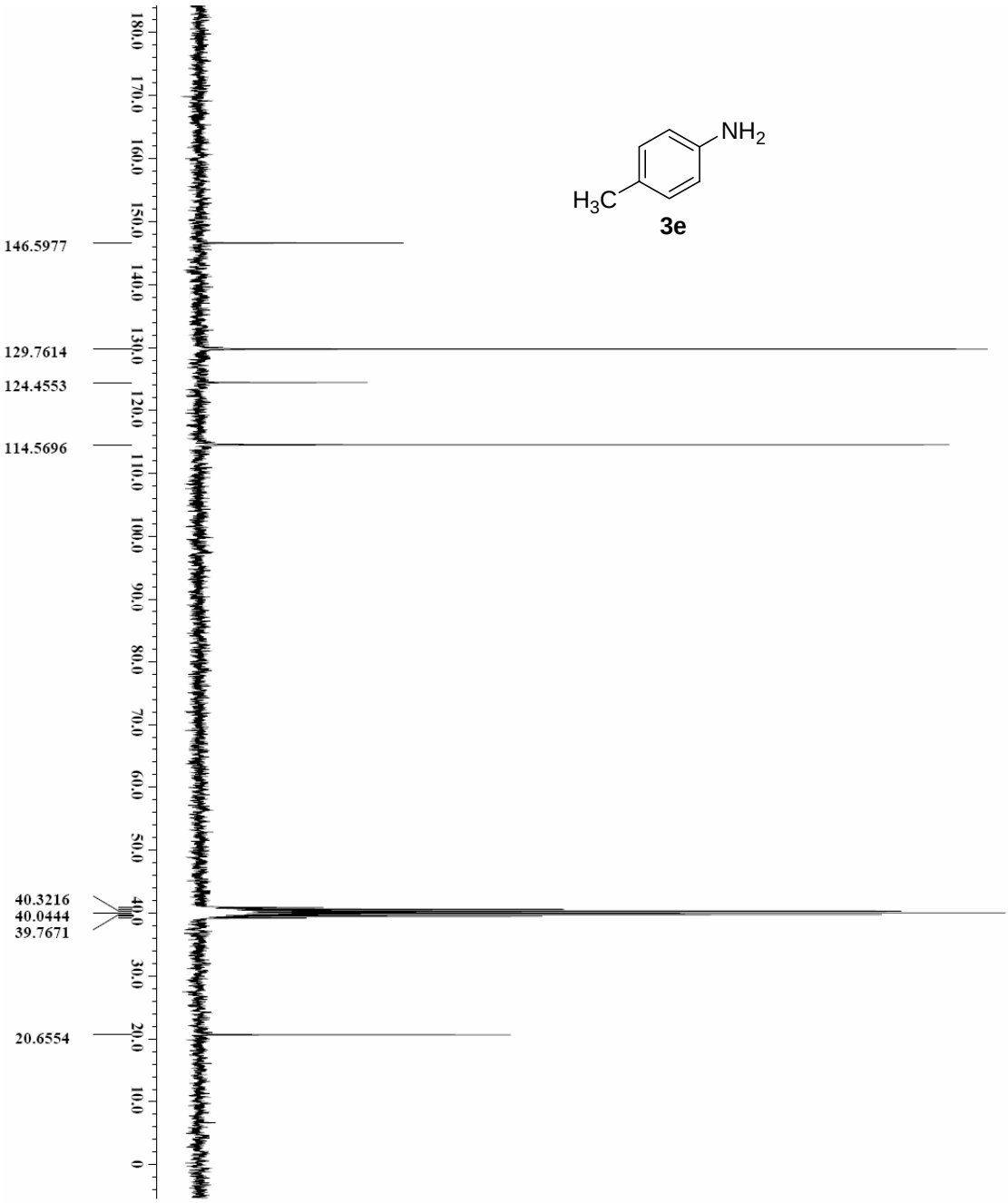
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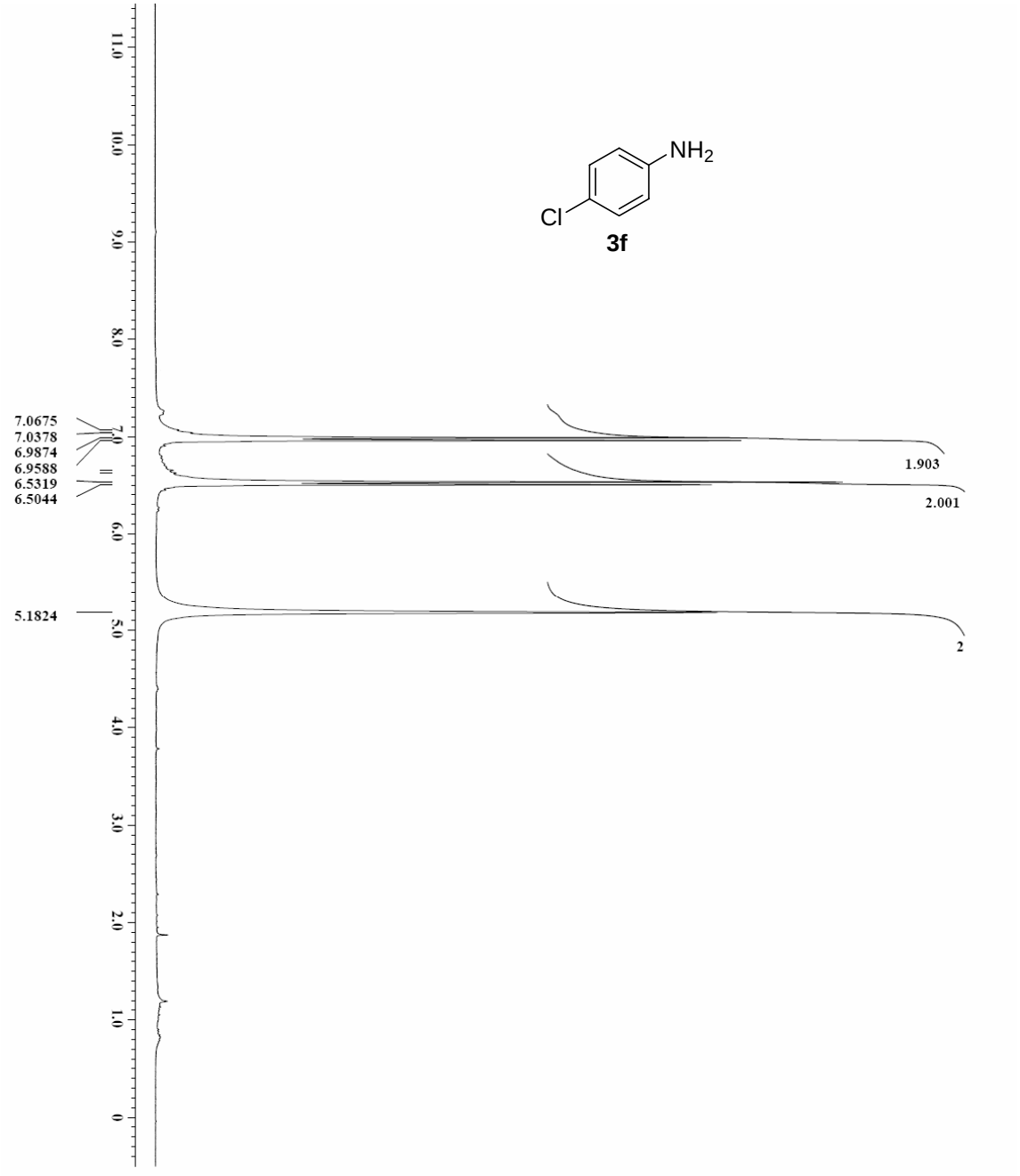
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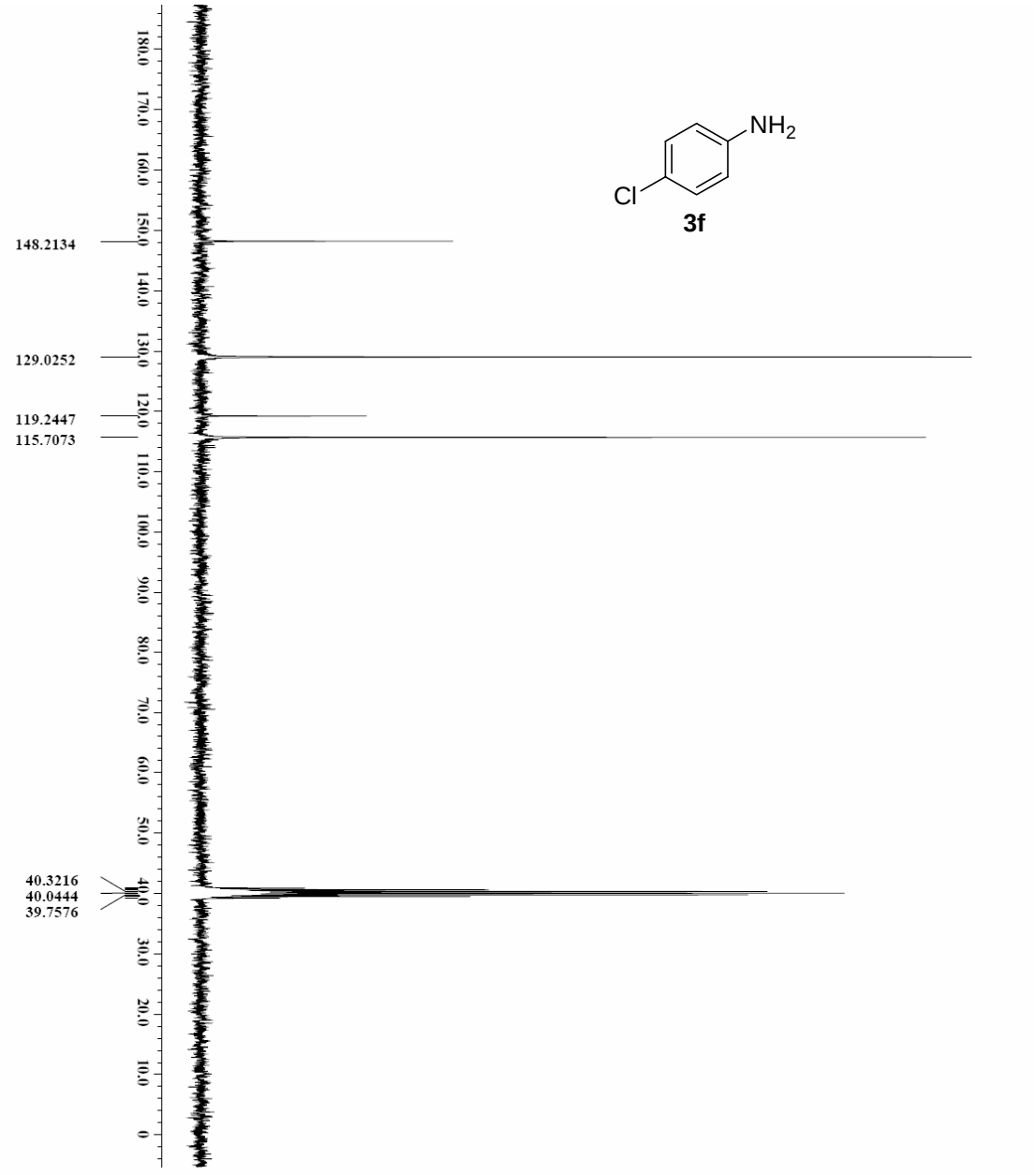
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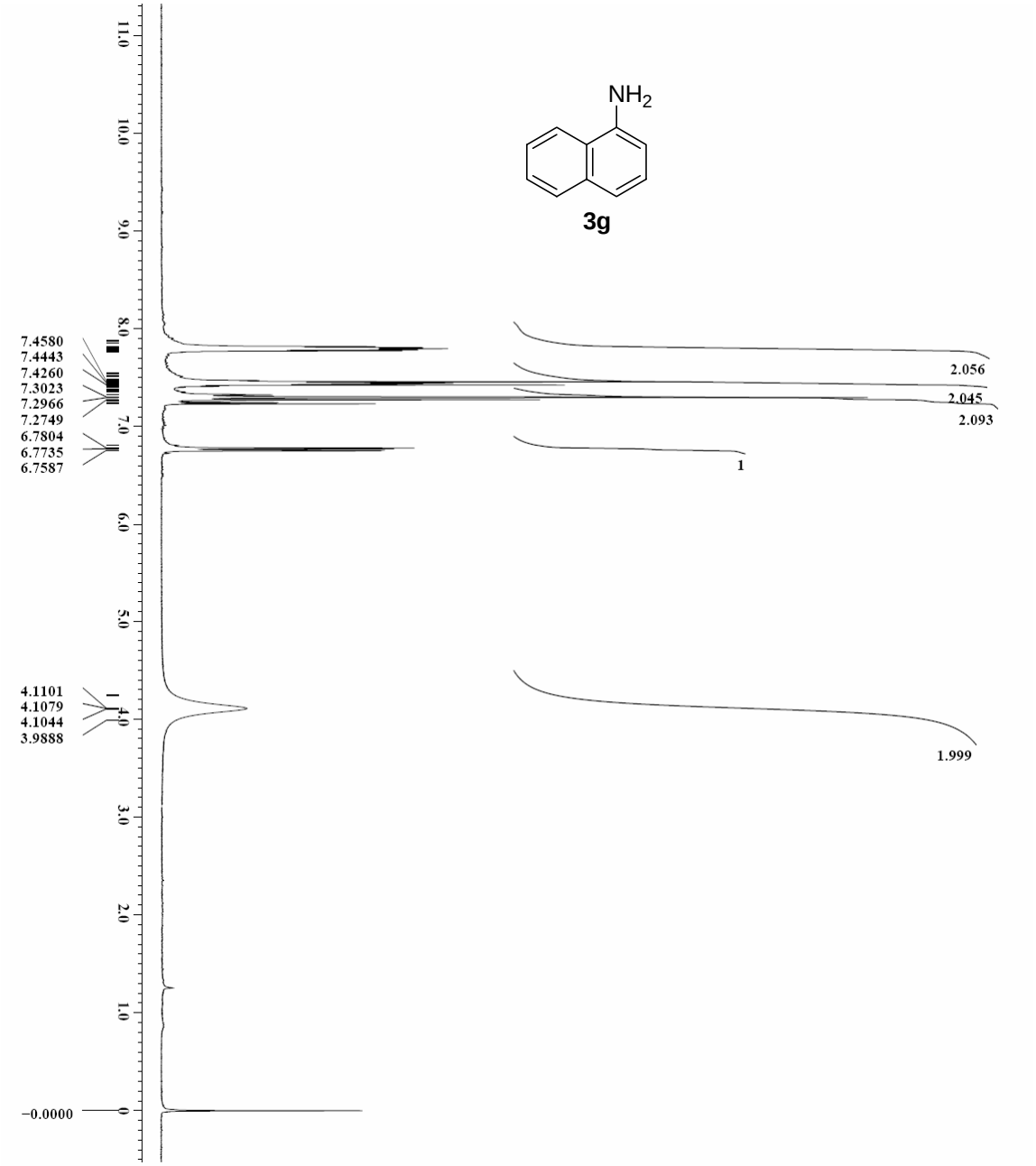
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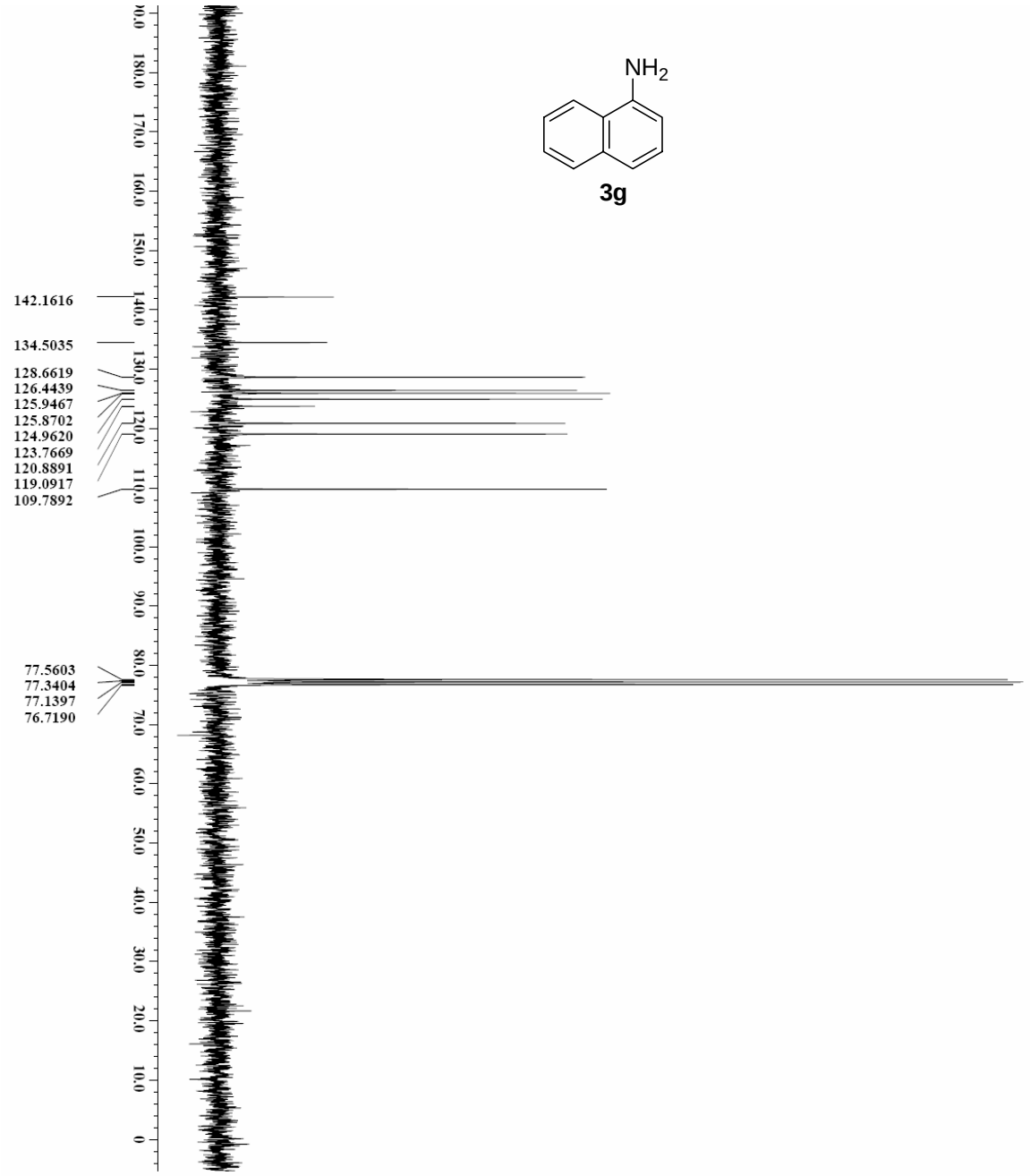
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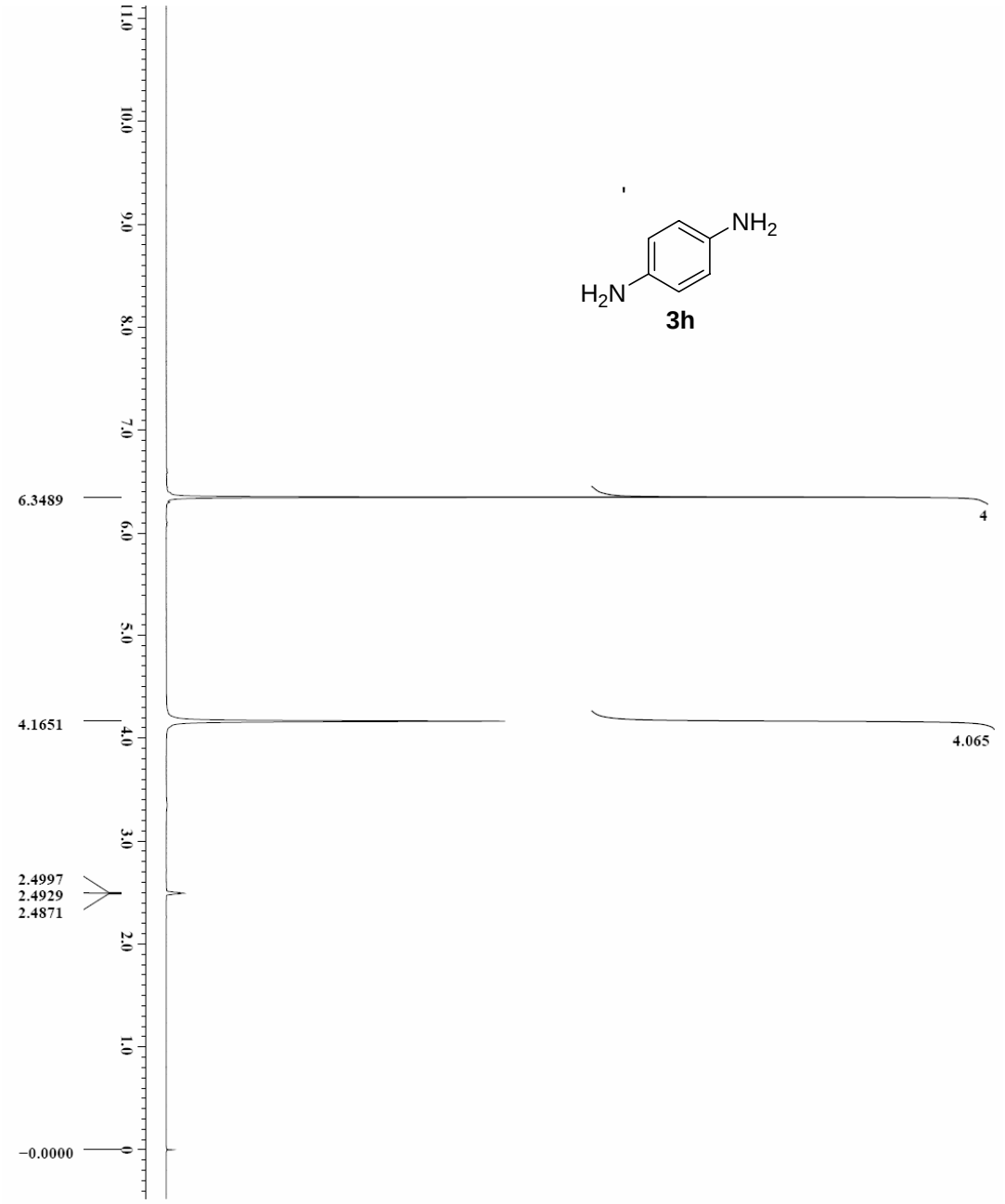
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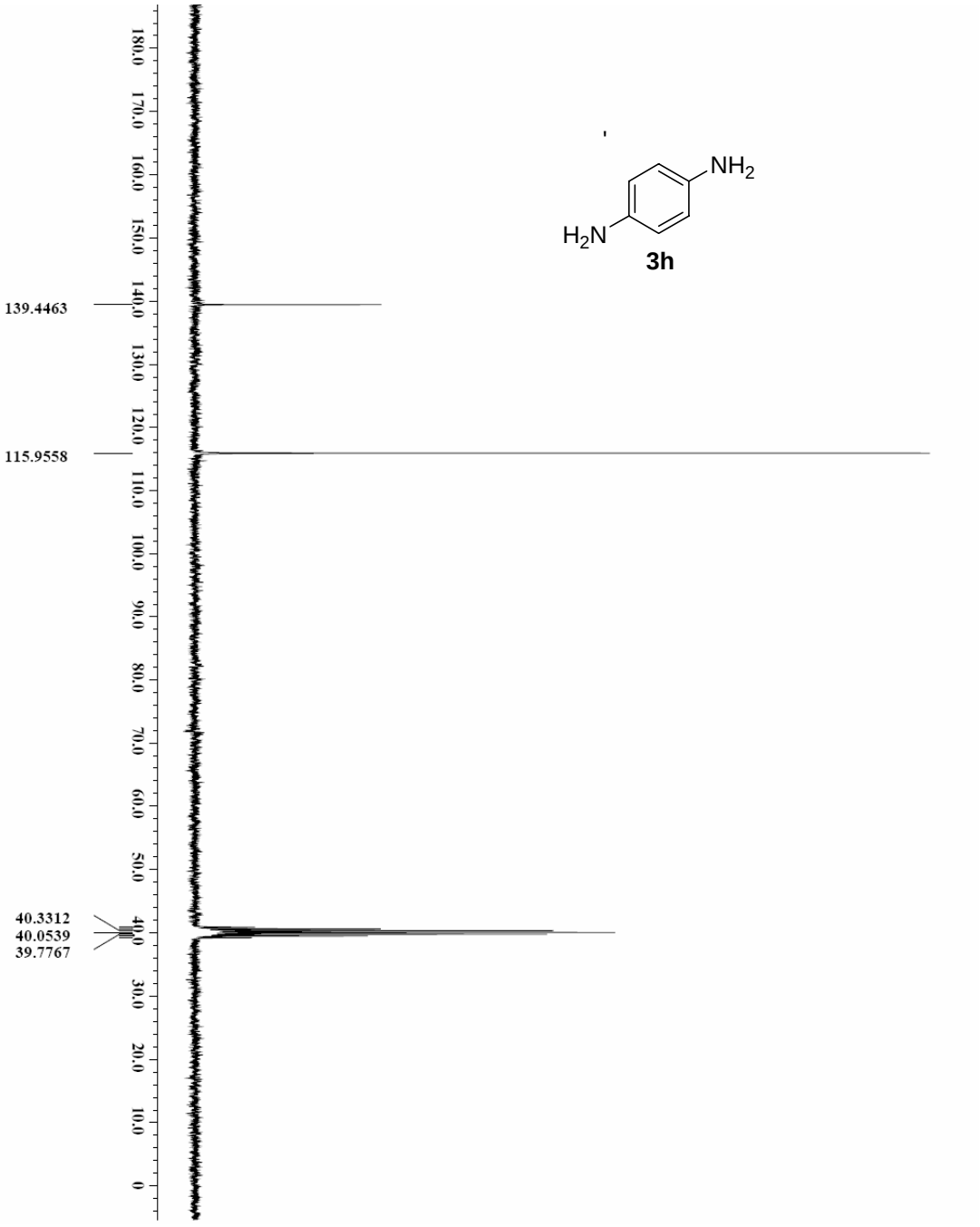
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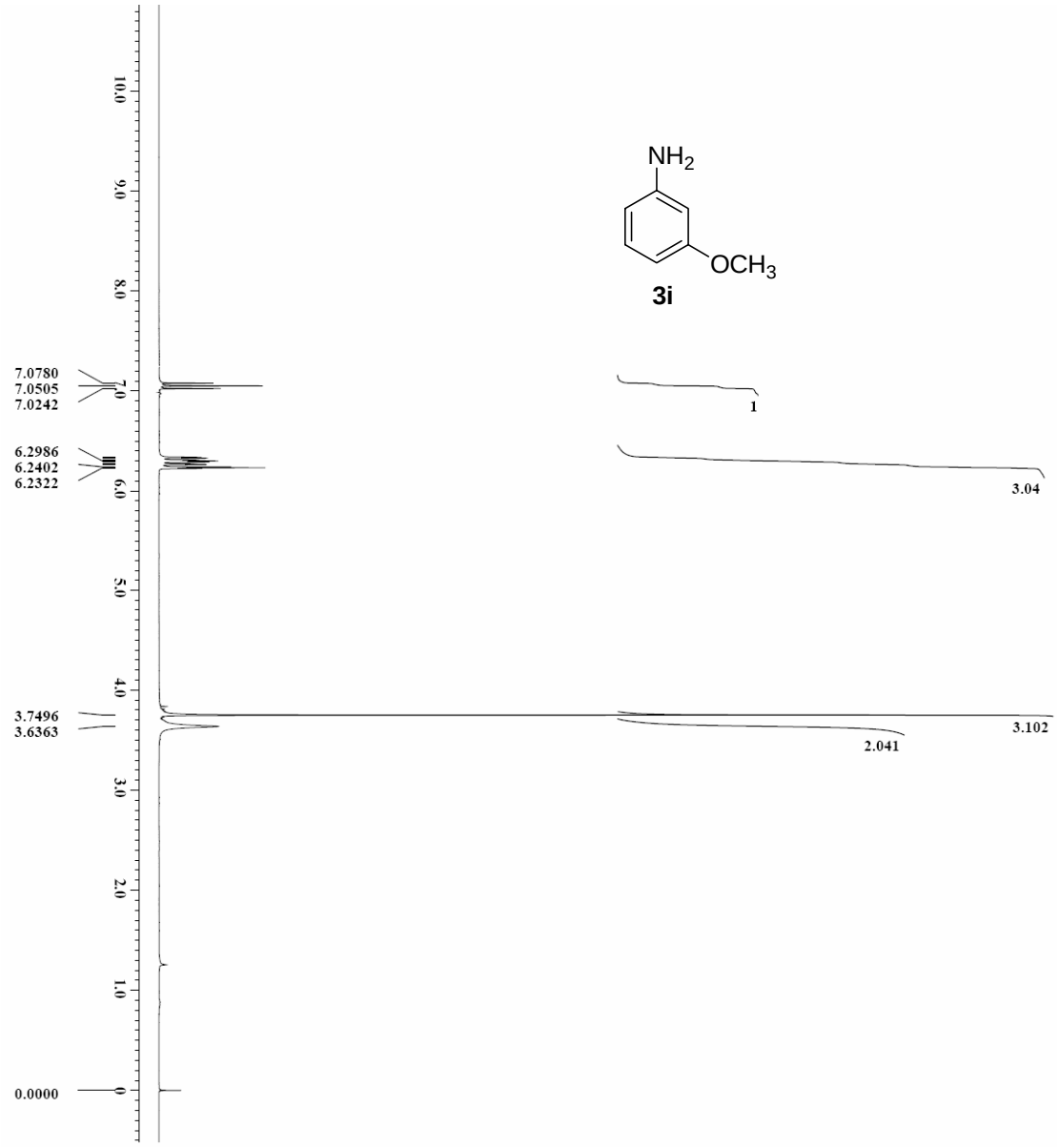
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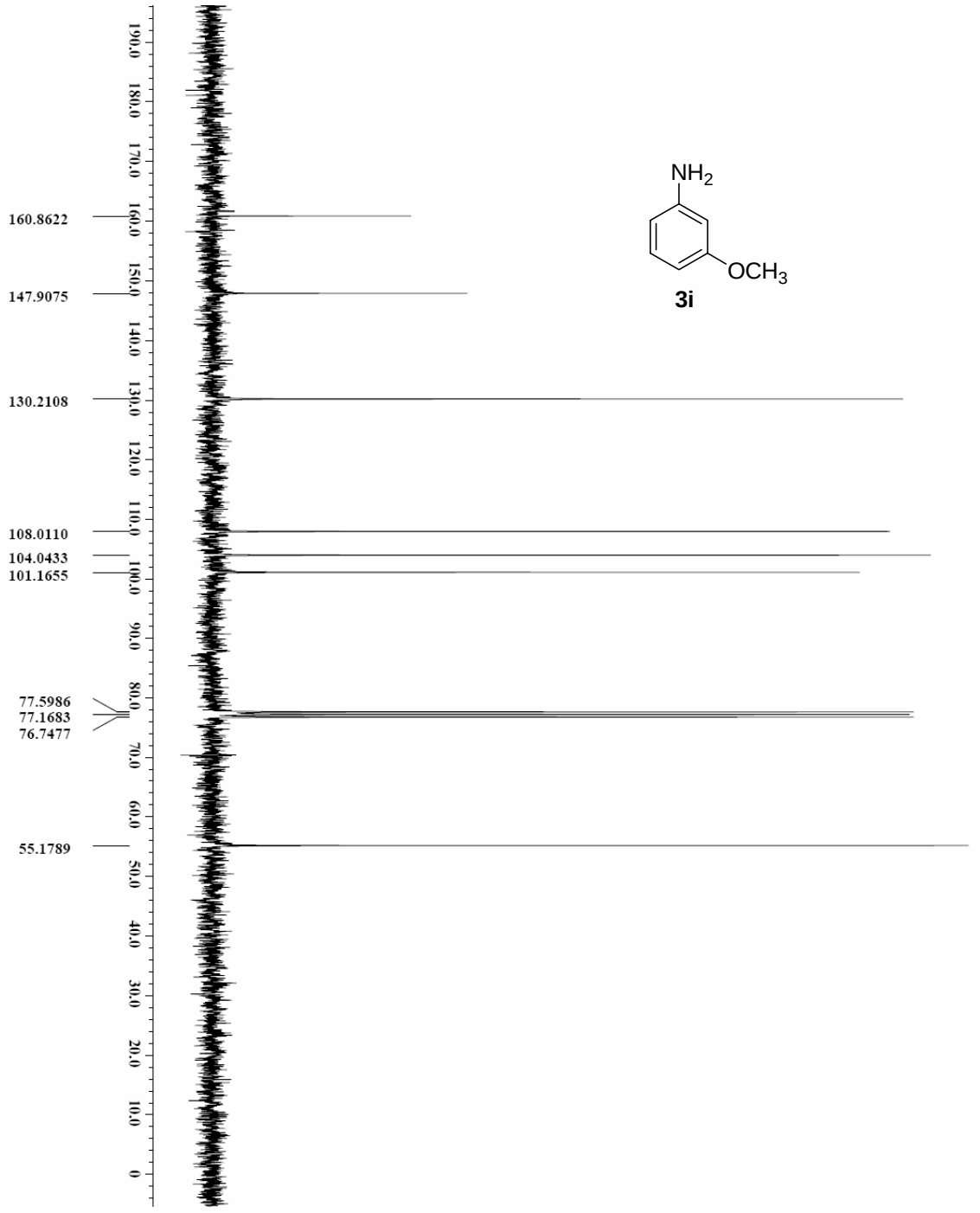
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