Synthetic and Mechanistic Aspects of the Regioselective Base-Mediated Reaction of Perfluoroalkyl- and Perfluoroarylsilanes with Heterocyclic *N*-Oxides

David E. Stephens, Gabriel Chavez, Martin Valdes, Monica Dovalina, Hadi Arman, and Oleg V. Larionov*

Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249, United States

General Procedures

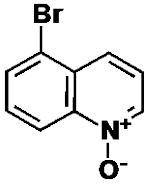
Materials and methods: Tetrahydrofuran was distilled from sodium benzophenone ketyl. Isoquinoline-*N*-oxide was purchased from Alfa Aesar, 4-phenylpyridine *N*-oxide, (pentafluorophenyl)trimethylsilane, and (pentafluoroethyl)trimethylsilane were purchased from TCI. (Trifluoromethyl)trimethylsilane was purchased from Matrix Scientific, and (difluoromethyl)trimethylsilane was purchased from Oakwood Chemicals. All other chemicals were used as commercially available (Sigma-Aldrich, Acros, Alfa Aesar, Combi-Blocks, Strem). All reactions were conducted with continuous magnetic stirring under an atmosphere of argon in oven-dried glassware. Low-temperature experiments were conducted using a Neslab Cryotrol CB-80 cryostat. Reactions were monitored by TLC until deemed complete using silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm).

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system with self-packed RediSep columns.

Characterization: ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded at 500 and 300 MHz (^{1}H), 125 and 75 MHz (^{13}C), and 282 MHz (^{19}F) on Varian Mercury VX 300 and Agilent Inova 500 instruments in $CDCl_3$ solutions. Chemical shifts (δ) are reported in parts per million (ppm) from the residual solvent peak and coupling constants (*J*) in Hz. Proton

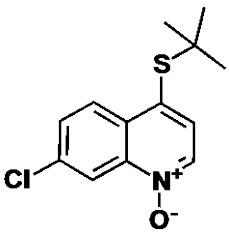
multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (quart.), quintet (quint.), septet (sept.), multiplet (m), broad (br).
Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module.

5-Bromoquinoline 1-oxide[1] (S1)



To a stirred solution of 5-bromoquinoline (400 mg, 1.94 mmol) in chloroform (10 mL) was added *meta*-chloroperoxybenzoic acid (620 mg, 2.52 mmol, 1.3 equiv., 70 % in H_2O). After 12 h the reaction was diluted with a saturated aqueous solution of sodium thiosulfate/sodium carbonate (20 mL, 1:1). After separating the layers the aqueous layer was extracted with dichloromethane (3 x 10 mL), the organic layers combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield **S1** (332 mg, 77 %) as tan solid. – m.p.: 65–67 °C. – ^{1}H NMR (500 MHz): 7.41 (1 H, dd, J = 6, 8 Hz), 7.61 (1 H, dd, *J* = 7.5, 8.5 Hz), 7.94 (1 H, dd, *J* = 1, 7.5 Hz), 8.12 (1 H, d, *J* = 8.5 Hz), 8.56 (1 H, dd, *J* = 0.5, 6 Hz), 8.77 (1 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 119.5, 121.8, 122.3, 125.9, 129.7, 130.5, 132.7, 136.2, 142.1 ppm. – IR: 1056, 1142, 1195, 1255, 1289, 1394, 1443, 1505, 1663, 2999, 3067, 3107 cm^{-1}.

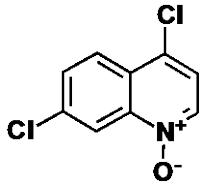
4-(*tert*-Butylthio)-7-chloroquinoline 1-oxide (S2)



To a stirred solution of **S3** (200 mg, 0.930 mmol) in ethanol (5 mL) was added sodium 2-methyl-2-propanethiolate (136 mg, 1.21 mmol, 1.3 equiv.) and the reaction heated to 50 °C for 12 h. The reaction was concentrated on Celite and purified by column chromatography [hexanes/EtOAc/Si_2O] to yield **S2** (151 mg, 61 %) as colorless solid. – m.p.: 125 – 127

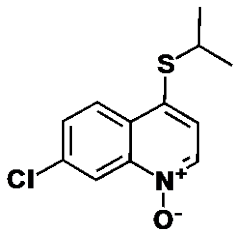
°C. – ^{1}H NMR (500 MHz): 1.32 (9 H, s), 7.52 (1 H, d, *J* = 7 Hz), 7.62 (1 H, dd, *J* = 2.5, 10 Hz), 8.46 (1 H, d, *J* = 6.5 Hz), 8.55 (1 H, d, *J* = 10 Hz), 8.75 (1 H, d, *J* = 2.5 Hz) ppm. – ^{13}C NMR (125 MHz): 31.2, 49.4, 119.4, 128.2, 129.5, 129.9, 130.4, 130.6, 132.0, 135.2, 137.2, 142.1 ppm. – IR: 1134, 1183, 1242, 1345, 1459, 2900, 2971, 3097 cm^{-1}. – MS (ESI): 267.9, HRMS: 268.0140, calcd: 268.0557 [M+H^{+}].

4,7-Dichloroquinoline 1-oxide[2] (S3)



S3 was prepared according to literature procedure. – m.p.: 164–165 °C[3] – ^{1}H NMR (500 MHz): 7.36 (1 H, d, *J* = 6.5 Hz), 7.68 (1 H, d, *J* = 9 Hz), 8.13 (1 H, d, *J* = 9 Hz), 8.43 (1 H, d, *J* = 6.5 Hz), 8.77 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 119.93, 121.22, 121.42, 125.60, 126.52, 126.75, 128.68, 129.85, 130.80, 135.96, 138.22, 142.33, 150.88 ppm. – IR: 829, 1091, 1291, 1367, 1412, 1555, 1609, 3025, 3094 cm^{-1}.

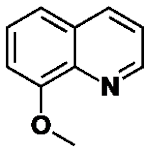
7-Chloro-4-(isopropylthio)quinoline 1-oxide (S4)



To a stirred solution of **S3** (200 mg, 0.930 mmol) in ethanol (5 mL) was added sodium 2-propanethiolate (118 mg, 1.21 mmol, 1.3 equiv.) and the reaction heated to 50 °C for 12 h. The reaction was concentrated on Celite and purified by column chromatography [hexanes/EtOAc/SiO_2] to yield **S4** (168 mg, 71 %) as yellow solid. – m.p.: 50–53 °C. – ^{1}H NMR (500 MHz): 1.41 (6 H, d, *J* = 6.5 Hz), 3.57 (1 H, sept., *J* = 6.5 Hz), 7.27 (1 H, s), 7.63 (1 H, dd, *J* = 2, 9 Hz), 8.26 (1 H, d, *J* = 9 Hz), 8.44 (1 H, d, *J* = 6.5 Hz), 8.81 (1 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (125 MHz): 22.8, 38.0, 119.7, 121.0, 127.0, 128.2,

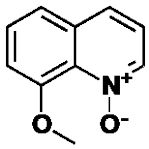
129.6, 134.8, 135.4, 137.3, 141.3 ppm. – IR: 1158, 1182, 1213, 1345, 1364, 1441, 1573, 2869, 2967, 3099 cm^{-1}. – MS (ESI): 253.9, HRMS: 253.8814, calcd: 254.0401 $[M+H^+]$.

8-Methoxyquinoline[4] (S5)



S5 was prepared according to literature procedure.[4] – ^{1}H NMR (300 MHz): 4.06 (3 H, s), 7.05 (1 H, td, *J* = 1, 7.5 Hz), 7.36–7.50 (3 H, m), 8.19 (1 H, td, *J* = 1, 7.5 Hz), 8.96 (1 H, td, *J* = 1, 7.5 Hz) ppm. – ^{13}H NMR (75 MHz): 56.03, 108.18, 119.52, 121.73, 127.25, 129.34, 137.24, 138.66, 148.45, 154.58 ppm. – IR: 1076, 1219, 1440, 1501, 1615, 2838, 2934, 3054 cm^{-1}.

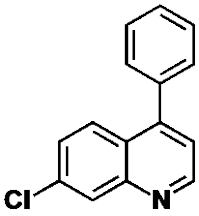
8-Methoxyquinoline 1-oxide[2] (S6)



To a stirred solution of **S5** (340 mg, 2.12 mmol) in acetonitrile (1 mL) was added hydrogen peroxide (313 μL, 3.18 mmol, 1.5 equiv., 30% in H_2O) and phosphomolybdic acid (197 μL, 0.21 mmol, 1 mol %, 20% in EtOH) followed by heating the reaction to 50 °C. After 12 h the reaction was diluted with a saturate aqueous solution of ammonium chloride (2 mL) and the aqueous layer extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to yield **S6** (260 mg, 71%) as brown solid. – m.p.: 38–41 °C – ^{1}H NMR (300 MHz): 3.92 (3 H, s), 6.88 (1 H, dd, *J* = 1.5, 8 Hz), 7.20–7.40 (3 H, m), 7.96 (1 H, dd, *J* = 1.5, 8 Hz), 8.78 (1 H, dd, *J* = 1.5, 4 Hz) ppm. – ^{13}C NMR (75 MHz): 55.84,

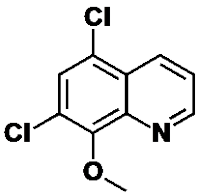
107.57, 119.42, 121.57, 126.72, 129.19, 136.07, 139.66, 148.89, 155.02 ppm. – IR: 910, 1090, 1232, 1378, 1467, 1504, 2858, 2954, 3037 cm^{-1}.

7-Chloro-4-phenylquinolinene[5] (S7)



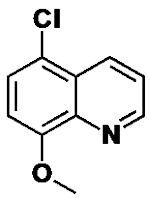
S7 was prepared according to a literature procedure.[5] – ^{1}H NMR (500 MHz): 7.30 (1 H, d, *J* = 4 Hz), 7.41 – 7.53 (6 H, m), 7.84 (1 H, d, *J* = 9 Hz), 8.19 (1 H, d, *J* = 1 Hz), 8.93 (1 H, d, *J* = 4 Hz) ppm. – ^{13}C NMR (125 MHz): 121.4, 125.0, 127.3, 127.4, 128.3, 128.7, 128.8, 129.4, 135.1, 137.4, 148.3, 149.1, 150.9 ppm. – IR: 1071, 1167, 1271, 1304, 1374, 1417, 1488, 1573, 2834, 2877, 3031 cm^{-1}.

5,7-Dichloro-8-methoxyquinoline[6] (S8)



S8 was prepared according to a literature procedure.[7] – m.p.: 84–86 °C. – ^{1}H NMR (500 MHz): 4.19 (3 H, s), 7.55 (1 H, dd, *J* = 4.5, 9 Hz), 7.67 (1 H, s), 8.54 (1 H, dd, *J* = 1, 9 Hz), 9.02 (1 H, dd, *J* = 1.5, 4.5 Hz) ppm. – ^{13}C NMR (125 MHz): 62.2, 121.9, 126.0, 126.1, 126.4, 127.6, 133.1, 143.4, 150.8, 151.4 ppm. – IR: 1112, 1190, 1246, 1353, 1385, 1402, 1488, 2848, 2942, 3068 cm^{-1}.

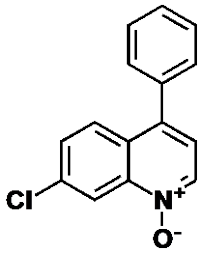
5-Chloro-8-methoxyquinoline[8] (S9)



S9 was prepared according to a literature procedure.[7] – ^{1}H NMR (500 MHz): 4.05 (3 H, s), 6.90 (1 H, d, *J* = 8.5 Hz), 7.46 (1 H, d, *J* = 8.5 Hz), 7.50 (1 H, dd, *J* = 4, 8.5 Hz), 8.46 (1 H, dd, *J* = 1, 8.5 Hz), 8.95 (1 H, dd, *J* = 1, 4

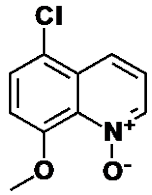
Hz) ppm. – ^{13}C NMR (125 MHz): 55.6, 106.9, 121.5, 125.9, 126.3, 127.9, 132.2, 140.0, 149.1, 154.1 ppm. – IR: 1100, 1159, 1252, 1269, 1307, 1385, 1440, 1502, 2841, 2956, 3035 cm^{-1}.

7-Chloro-4-phenylquinoline 1-oxide (S10)



To a stirred solution of **S7** (400 mg, 1.67 mmol) in dichloromethane (5 mL) was added *meta*-chloroperoxybenzoic acid (748 mg, 2.17 mmol, 1.3 equiv., 50 % solution in H_2O) at 0 °C. After 12 h the reaction was diluted with a saturated aqueous solution of sodium thiosulfate/sodium carbonate (30 mL, 1 : 1), and the aqueous layer extracted with dichloromethane (4 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to yield **S10** (472 mg, 85 %) as tan solid. – m.p.: 112 – 114 °C. – ^{1}H NMR (500 MHz): 7.23 (1 H, d, *J* = 6 Hz), 7.45 – 7.55 (6 H, m), 7.88 (1 H, d, *J* = 9 Hz), 8.55 (1 H, d, *J* = 6 Hz), 8.85 (1 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (125 MHz): 119.4, 121.5, 127.1, 128.2, 128.3, 128.8, 128.9, 129.4, 129.6, 135.6, 136.3, 136.8, 138.4, 141.6 ppm. – IR: 1001, 1083, 1152, 1208, 1301, 1373, 1442, 1551, 2992, 3032, 3103 cm^{-1}. – MS (ESI): 255.9, HRMS: 256.0550, calcd: 256.0524 [M+H^{+}].

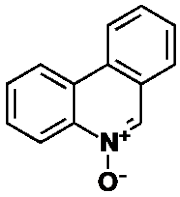
5-Chloro-8-methoxyquinoline 1-oxide (S11)



To a stirred solution of **S9** (500 mg, 2.59 mmol) in dichloromethane (5 mL) was added *meta*-chloroperoxybenzoic acid (1.16 g, 3.36 mmol, 1.3 equiv.,

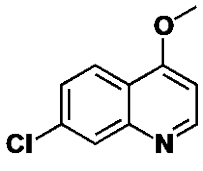
50 % solution in H_2O) at 0 °C. After 12 h the reaction was diluted with a saturated aqueous solution of sodium thiosulfate/sodium carbonate (30 mL, 1:1), and the aqueous layer extracted with dichloromethane (4 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to yield **S11** (501 mg, 92 %) as brown oil. – ^{1}H NMR (300 MHz): 3.98 (3 H, s), 6.95 (1 H, d, *J* = 5 Hz), 7.27–7.32 (1 H, m), 7.52 (1 H, d, *J* = 5 Hz), 8.00 (1 H, d, *J* = 9.5 Hz), 8.42 (1 H, d, *J* = 7 Hz) ppm. – ^{13}C NMR (125 MHz): 57.1, 110.5, 122.0, 122.2, 122.9, 128.7, 130.9, 134.8, 138.5, 152.8 ppm. – IR: 1092, 1160, 1264, 1342, 1397, 1464, 2838, 2887, 3015 cm^{-1}. – MS (ESI): 210.0, HRMS: 210.0376, calcd: 210.0316 [M+H$^+$].

Phenanthridine 5-oxide[2] (S12)



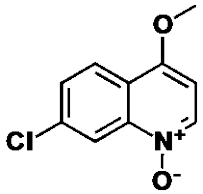
According to GP1, phenanthridine (50 mg, 0.279 mmol) was reacted with hydrogen peroxide (83 μL, 0.837 mmol, 3 equiv., 30% in H_2O) and phosphomolybdic acid (25 μL, 0.005 mmol, 2 mol%, 20% in EtOH) in acetonitrile (200 μL). The isolated product afforded **S12** (41 mg, 76%) as brown oil. – ^{1}H NMR (500 MHz): 7.25–8.09 (5 H, m), 8.53–8.63 (2 H, m), 8.97 (1 H, d, *J* = 2 Hz), 9.19 (1 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (125 MHz): 120.67, 122.13, 122.77, 127.06, 128.18, 128.99, 129.53, 129.71, 129.91, 130.15, 130.46, 133.83, 169.27 ppm. – IR: 1071, 1191, 1473, 1559, 1647, 3071 cm^{-1}.

7-Chloro-4-methoxyquinoline[9] (S13)



To a stirred solution of 4,7-dichloroquinoline (5 g, 25.51 mmol) in methanol (50 mL) was added sodium methoxide (6.88 g, 127.55 mmol, 5 equiv.). The reaction was heated at 95 °C for 12 h, then concentrated under reduced pressure, diluted with EtOAc (30 mL) and washed with H_2O (2 x 20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield **S13** (4.78 g, 97 %) as colorless solid. – m.p.: 145–148 °C[10] – ^{1}H NMR (300 MHz): 3.19 (3 H, s), 6.58 (1 H, d, *J* = 5.5 Hz), 7.32 (1 H, dd, *J* = 2, 9 Hz), 7.92 (1 H, d, *J* = 2 Hz), 7.98 (1 H, d, *J* = 9 Hz), 8.62 (1 H, d, *J* = 5 Hz) ppm. – ^{13}C NMR (75 MHz): 55.71, 100.26, 119.66, 123.36, 126.34, 127.64, 135.54, 149.45, 152.42, 162.16 ppm. – IR: 982, 1070, 1209, 1360, 1425, 1503, 1616, 2984, 3050 cm^{-1}.

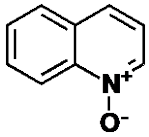
7-Chloro-4-methoxyquinoline 1-oxide[11] (S14)



To a stirred solution of **S13** (1.6 g, 5.54 mmol) in acetonitrile (2.5 mL) were added hydrogen peroxide (1.7 mL, 16.62 mmol, 3 equiv., 30% in H_2O) and phosphomolybdic acid (1 mL, 0.118 mmol, 2 mol%, 20% in EtOH) then heated to 50 °C. After 12 h the reaction was diluted with a saturated aqueous solution of ammonium chloride (10 mL), and the aqueous layer extracted with dichloromethane (4 x 15 mL). The organic layers were combined, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to yield **S14** (1.12 g, 97%) as colorless solid. – m.p.: 145–147 °C – ^{1}H NMR (500 MHz): 4.06 (3 H, s), 6.64 (1 H, d, *J* = 7 Hz), 7.59 (1 H, d, *J* = 2 Hz), 8.15 (1 H, d, *J* = 9 Hz), 8.46 (1 H, d, *J* = 7 Hz), 8.77 (1 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (125 MHz):

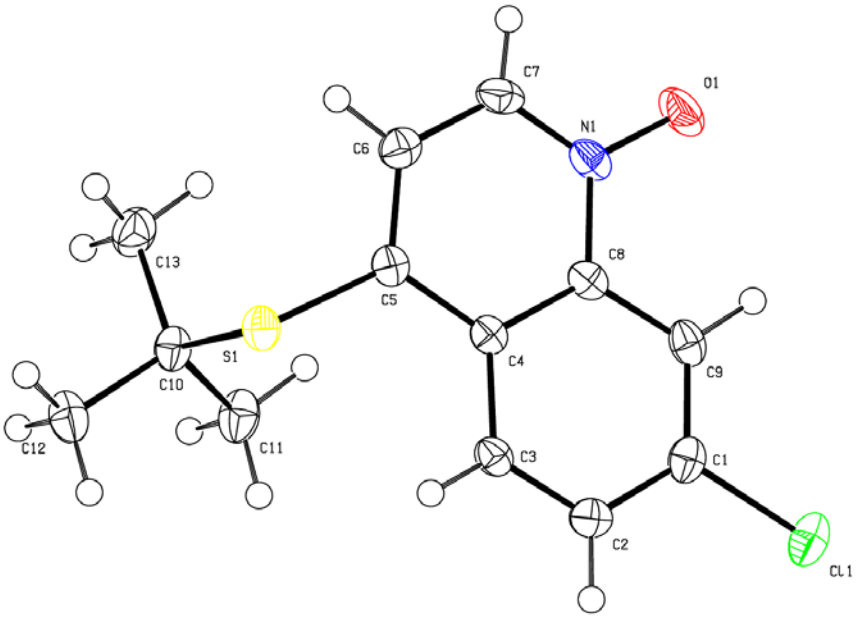
56.34, 99.84, 119.57, 120.99, 123.39, 124.28, 129.06, 136.99, 137.88, 154.26 ppm. – IR: 1110, 1243, 1325, 1445, 2988, 3025 cm^{-1}.

Quinoline 1-oxide[2] (2)



According to GP1, quinoline (5 g, 40.65 mmol) was reacted with hydrogen peroxide (6.1 mL, 60.97 mmol, 1.5 equiv., 30% in H_2O) and phosphomolybdic acid (3.7 mL, 0.406 mmol, 1 mol%, 20% in EtOH) in acetonitrile (20 mL). The crude product was purified by column chromatography to afford **2** (4.95 g, 88%) as brown solid. – m.p.: 60–62 °C[12] – ^{1}H NMR (300 MHz): 7.29 (1 H, dd, *J* = 6, 8 Hz), 7.64 (1 H, dt, *J* = 1, 7 Hz), 7.72–7.79 (2 H, m), 7.86 (1 H, dd, *J* = 1.5, 8 Hz), 8.52 (1 H, dd, *J* = 1, 6 Hz) ppm. – ^{13}C NMR: 119.81, 120.96, 125.87, 128.12, 128.76, 130.41, 130.50, 135.60 ppm. – IR: 1157, 1311, 1452, 1554, 2931, 2995, 3025 cm^{-1}.

Crystal Structure of 4-(*tert*-Butylthio)-7-chloroquinoline 1-oxide (S2)



Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=9.1435(17) b=6.0132(11) c=23.209(5)

alpha=90 beta=90.530(3) gamma=90

Temperature: 98 K

	Calculated	Reported
Volume	1276.0(4)	1276.0(4)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{13}H_{14}ClNOS$	$C_{13}H_{14}ClNOS$
Sum formula	$C_{13}H_{14}ClNOS$	$C_{13}H_{14}ClNOS$

Mr	267.77	267.76
Dx, g/cm^3	1.394	1.394
Z	4	4
Mu (mm^{-1})	0.445	0.445
F000	560.0	560.0
F000'	561.26	
h,k,l$_{max}$	11,7,28	11,7,28
N$_{ref}$	2521	2513
T$_{min}$,T$_{max}$	0.899,0.956	0.719,1.000
T$_{min}$'	0.837	

Correction method = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 26.000

R(reflections)= 0.0372(2348) wR2(reflections)= 0.1019(2513)

S = 1.003 Npar= Npar = 196

References

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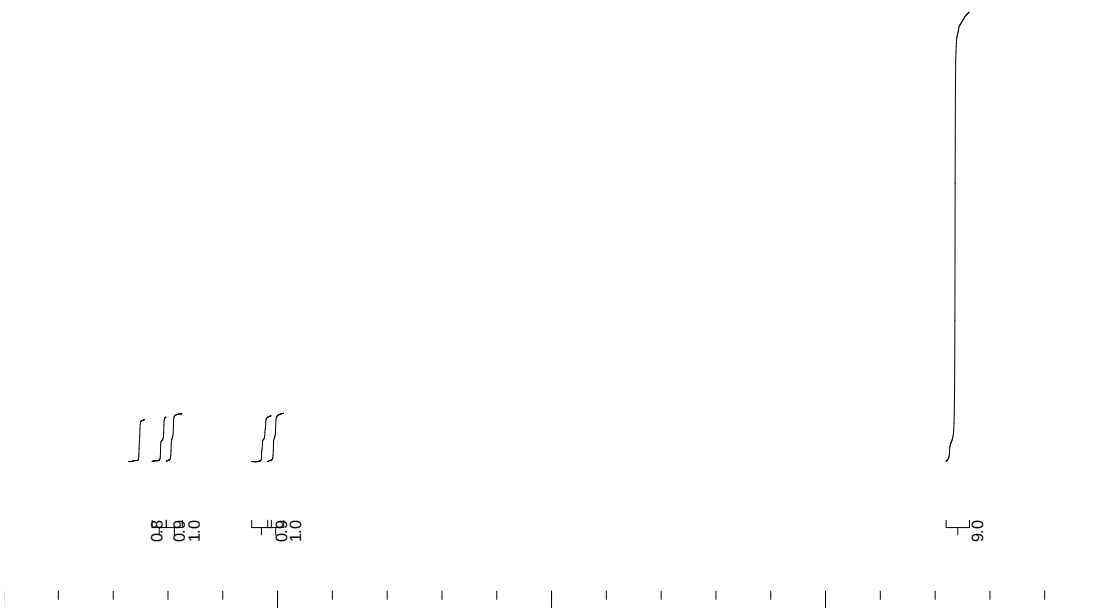
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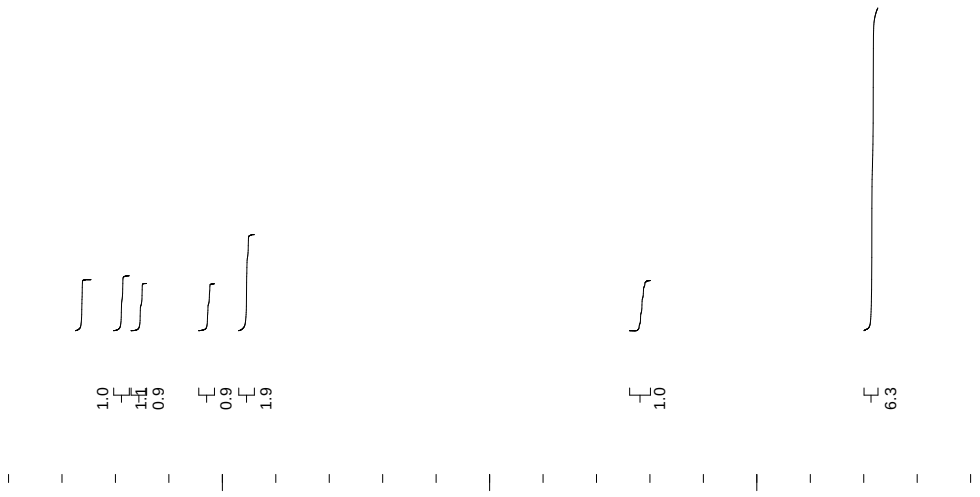
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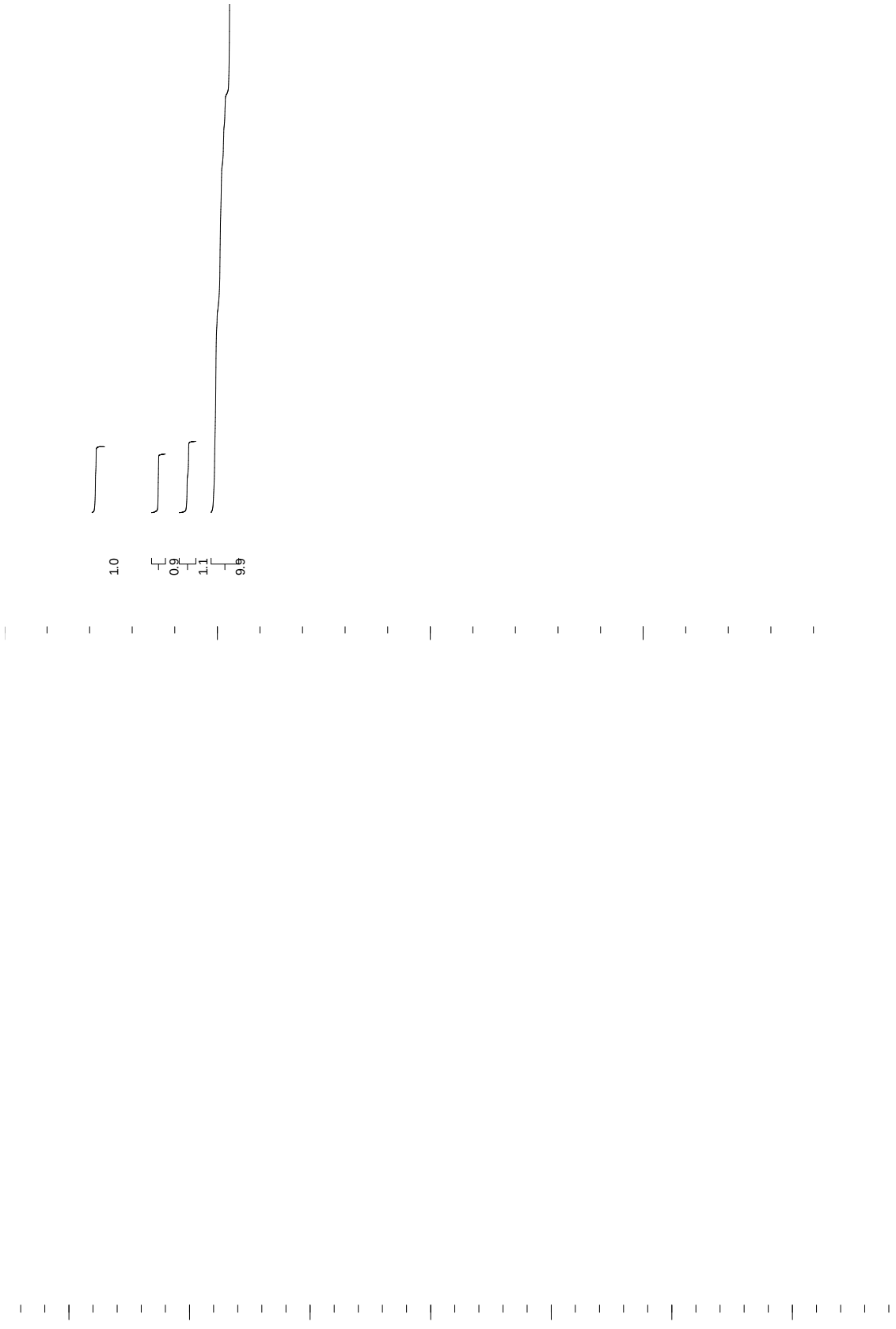
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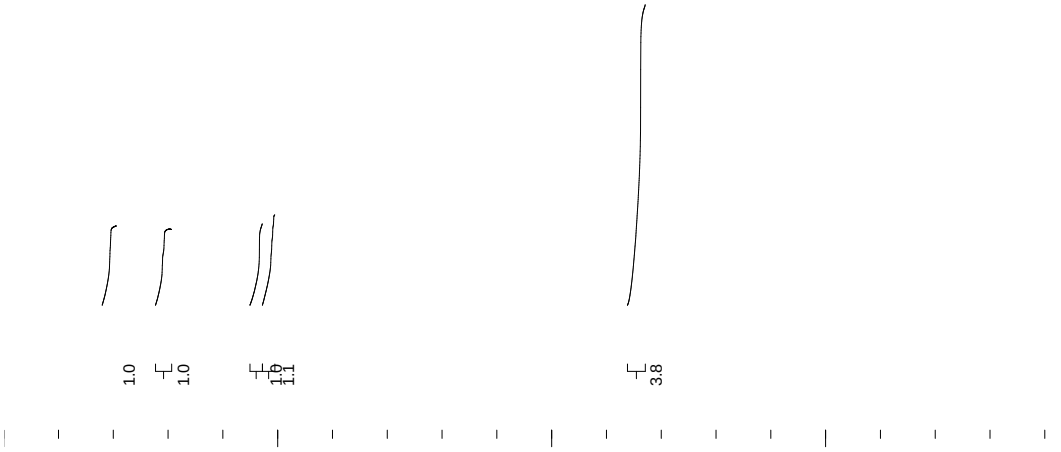
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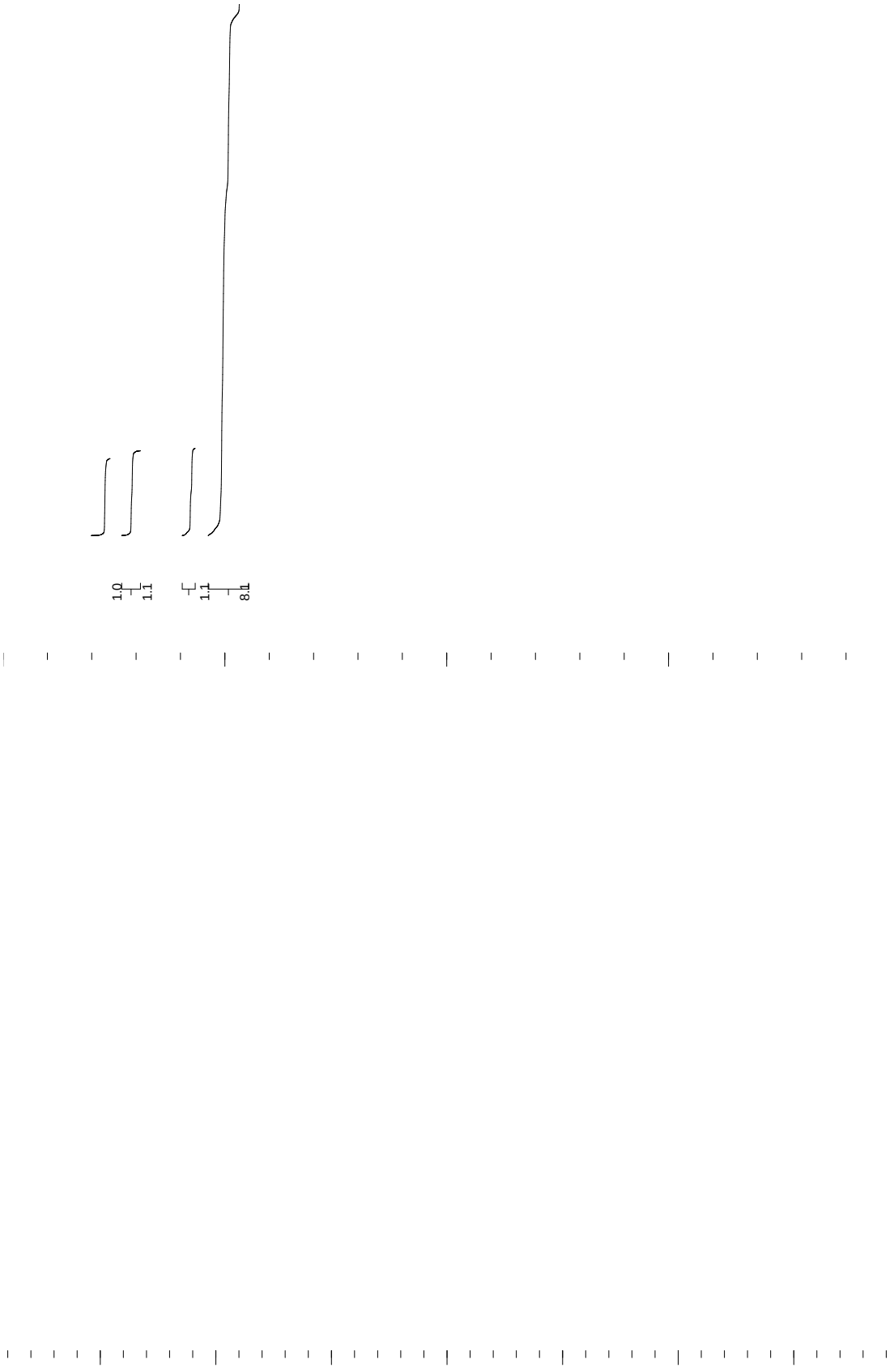
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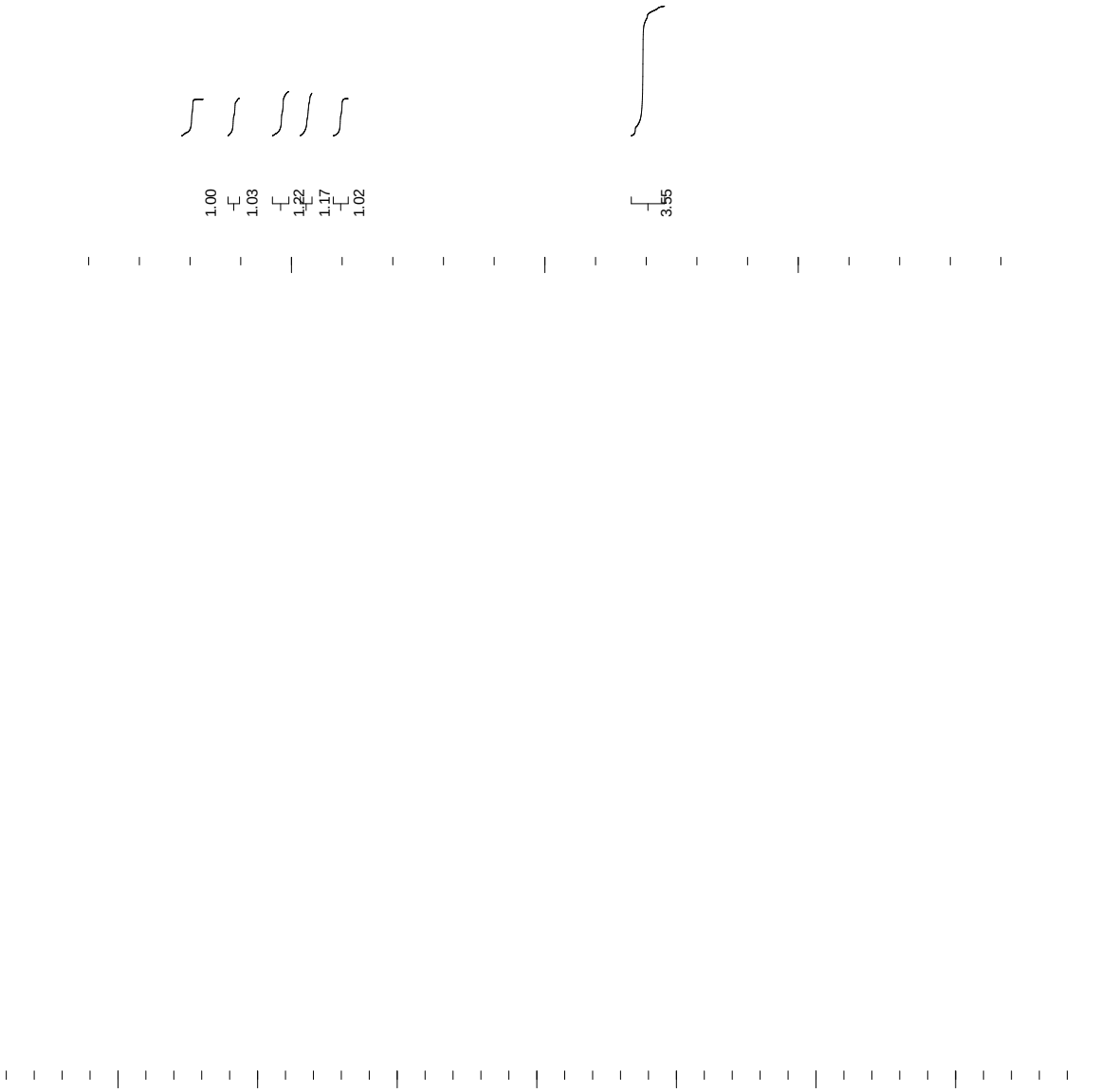
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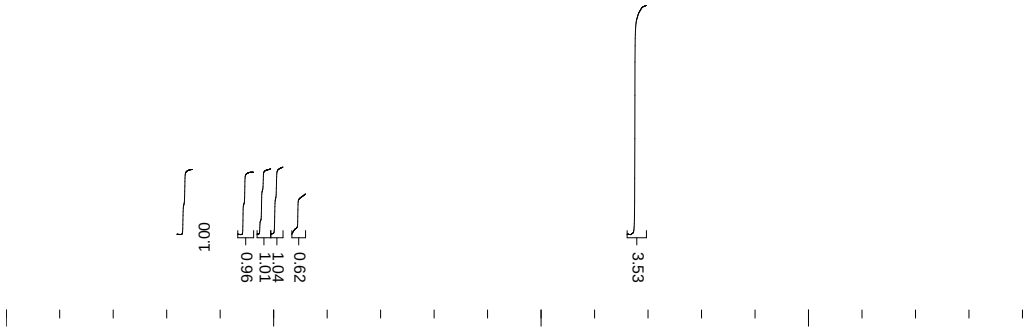
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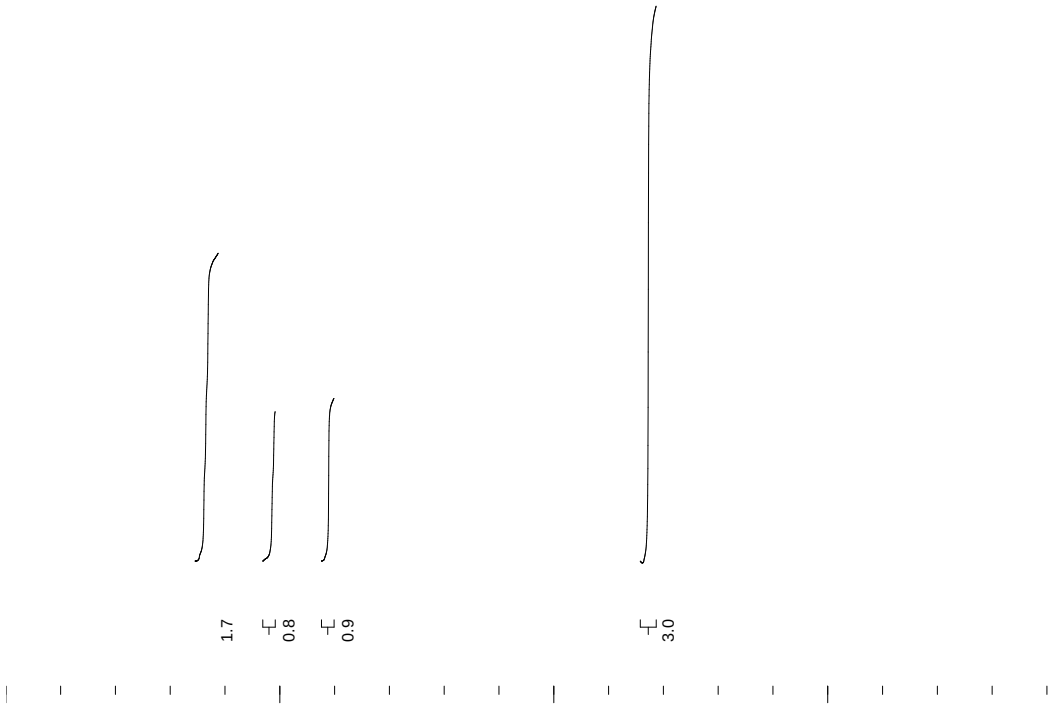
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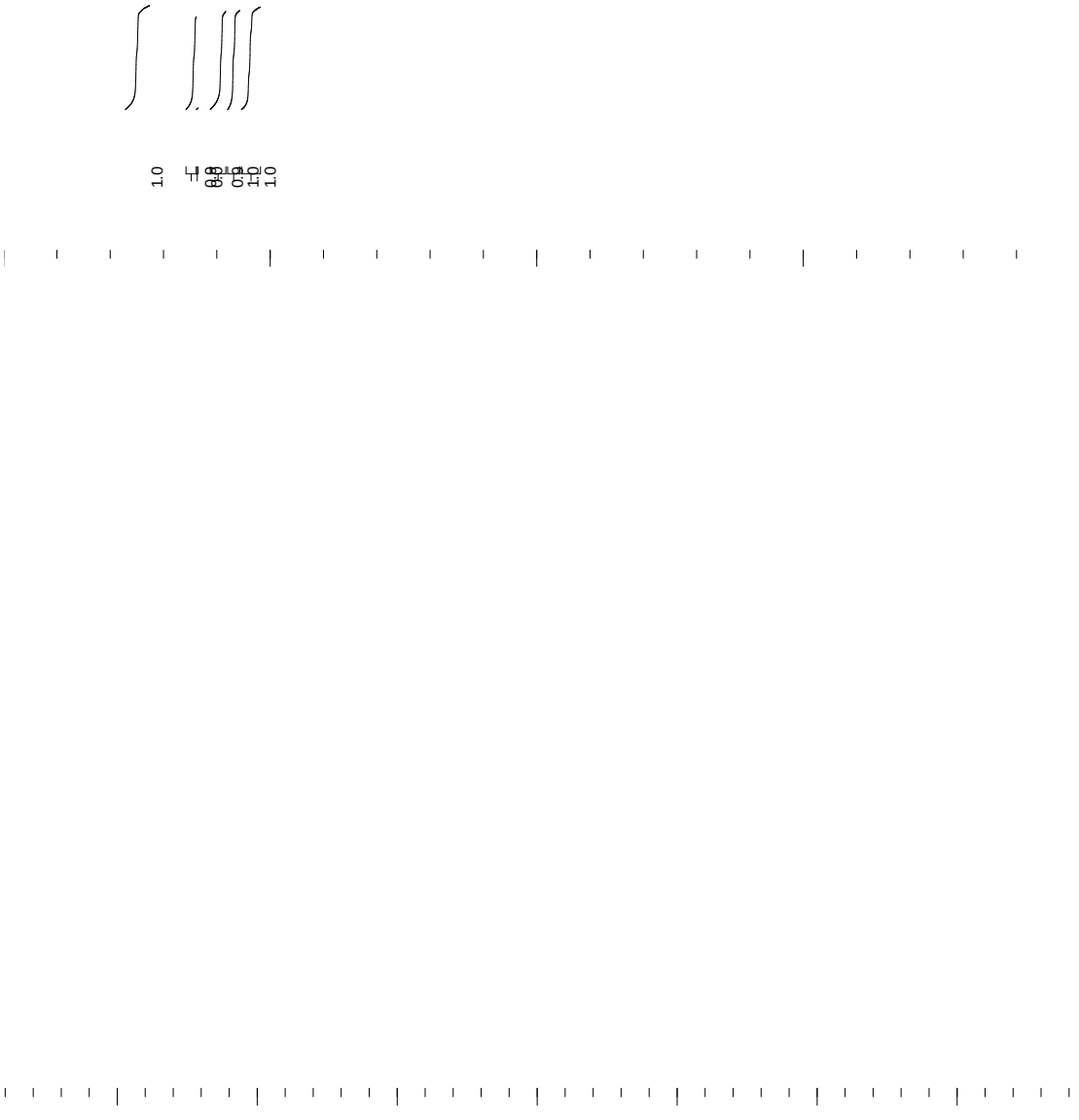

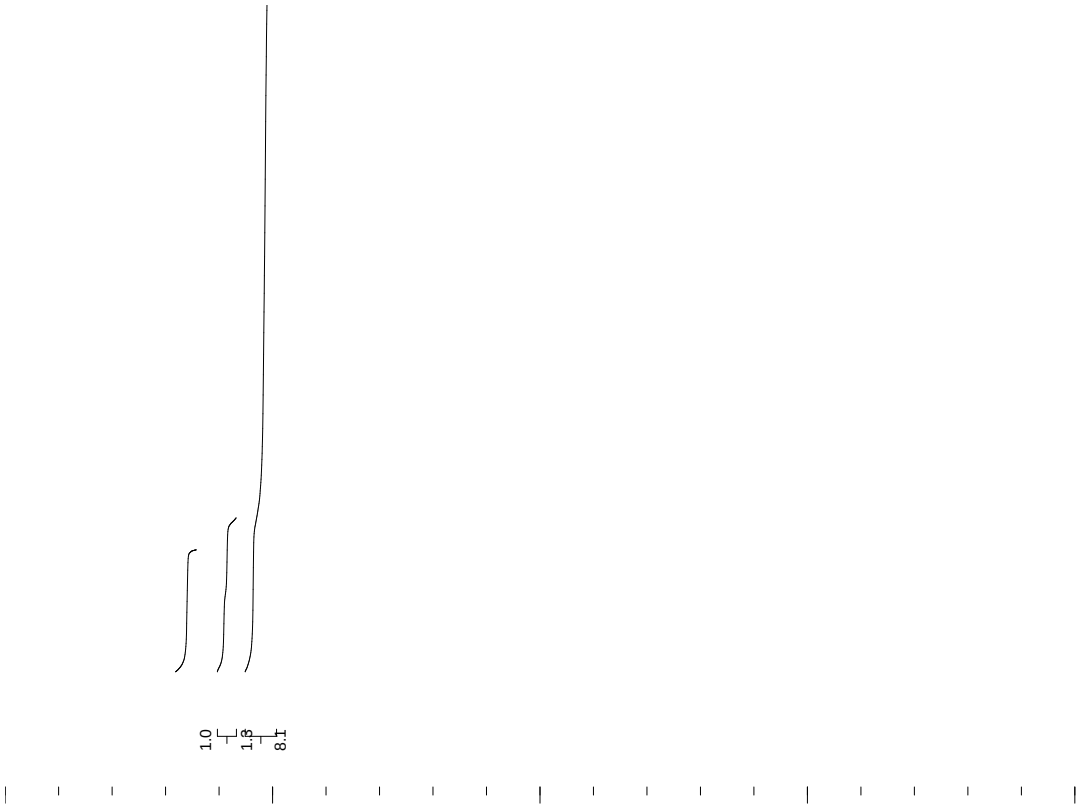
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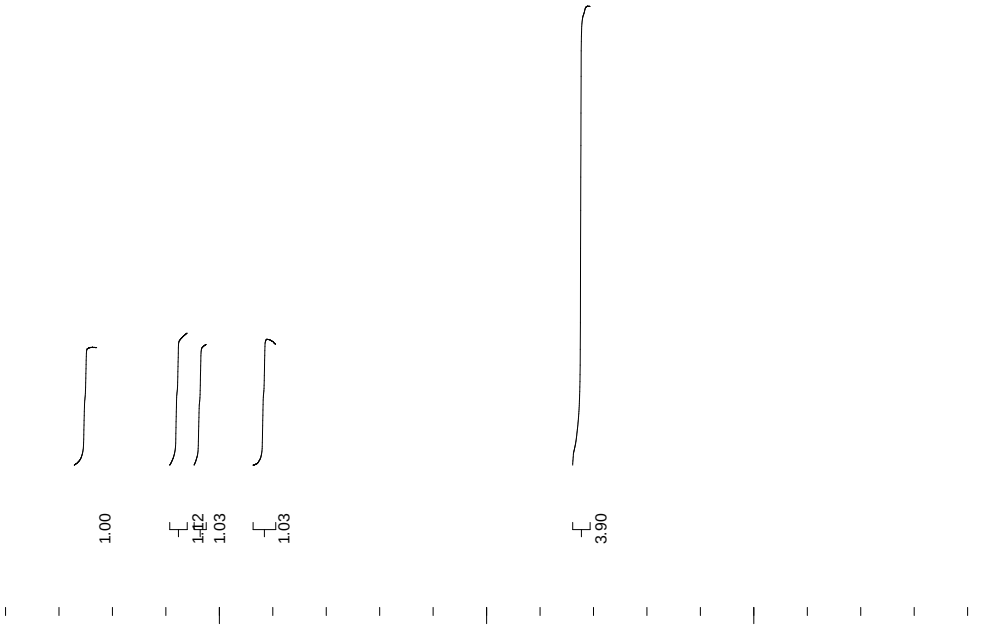
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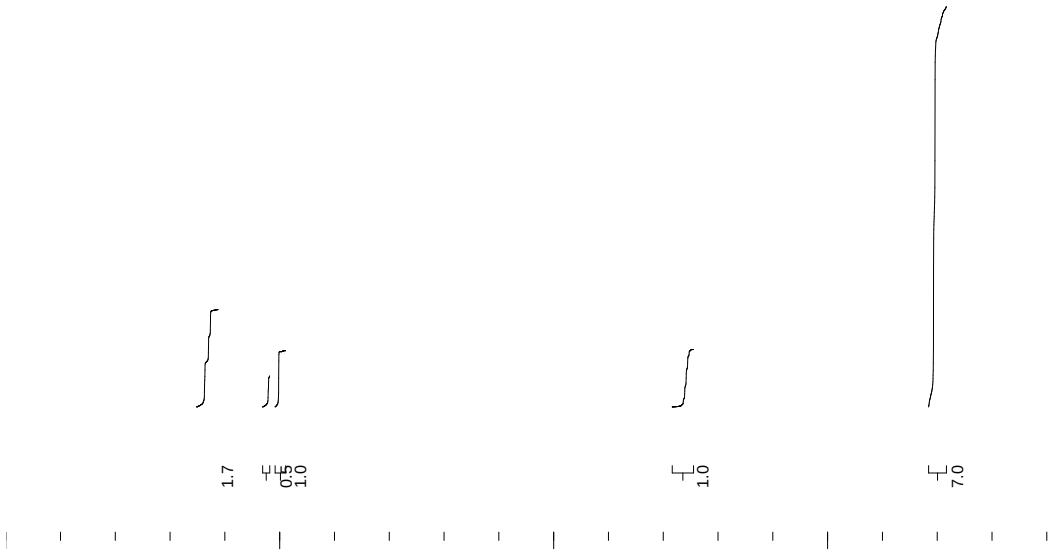
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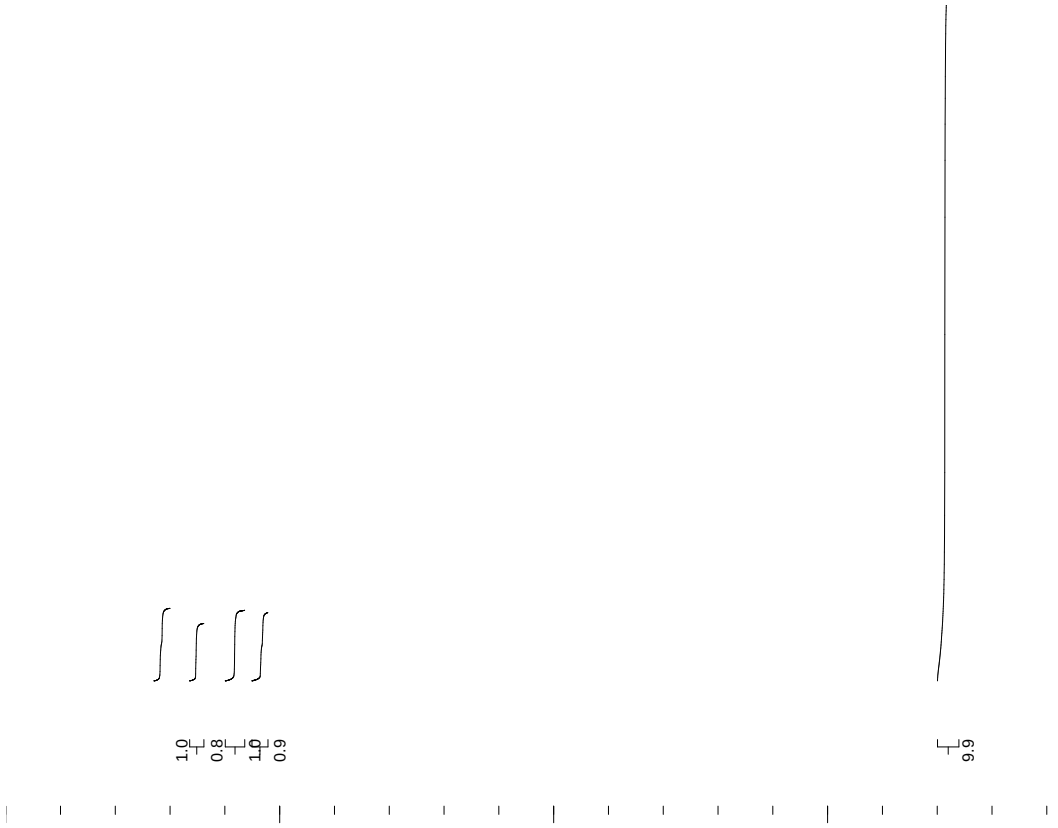
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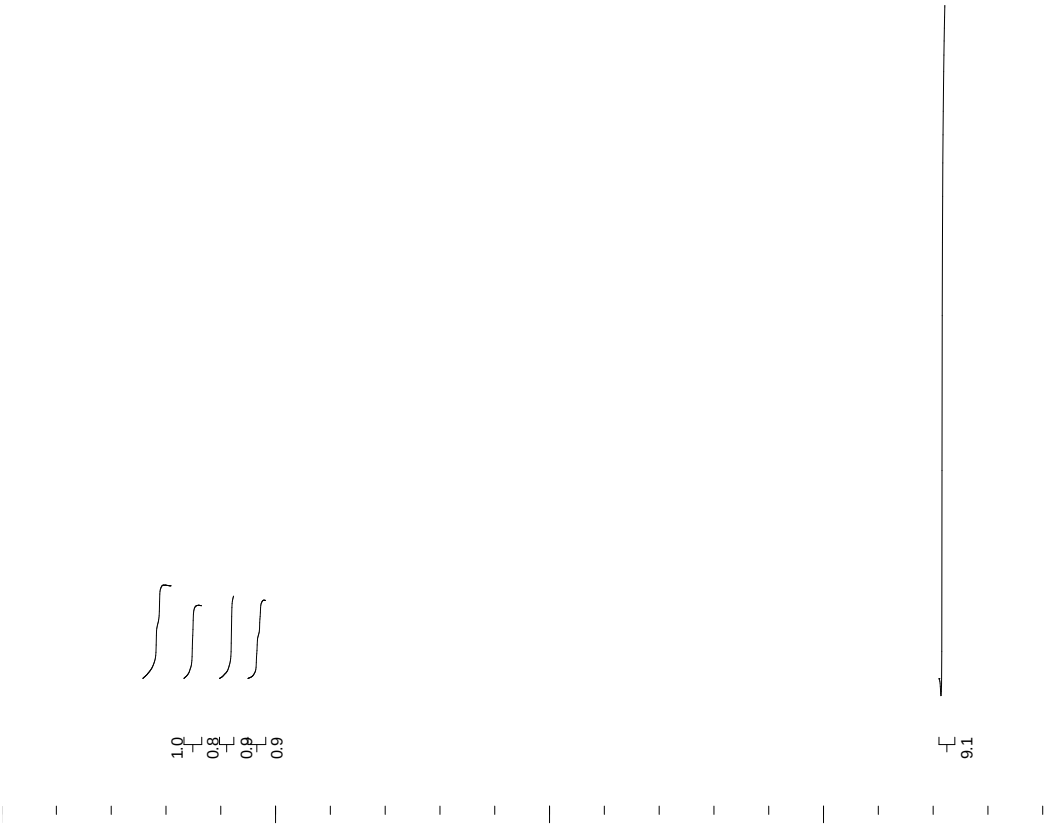
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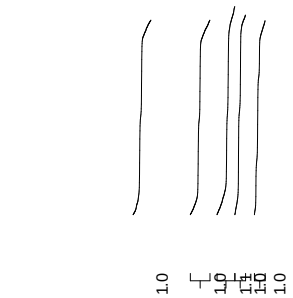
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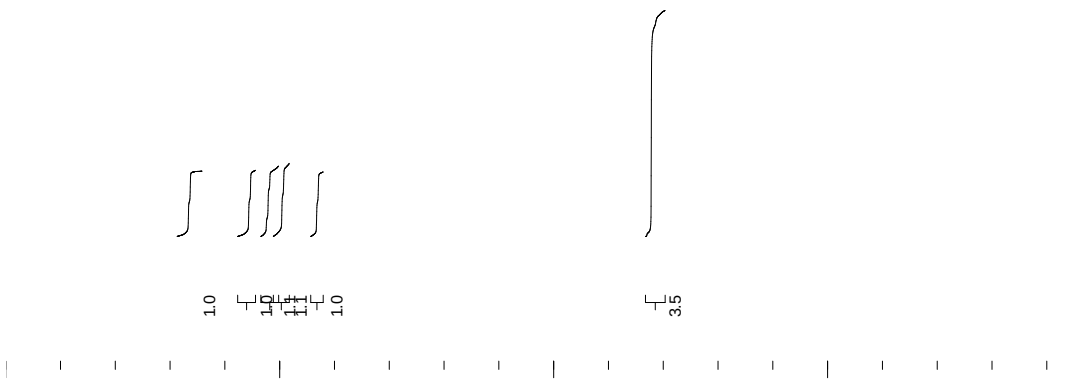
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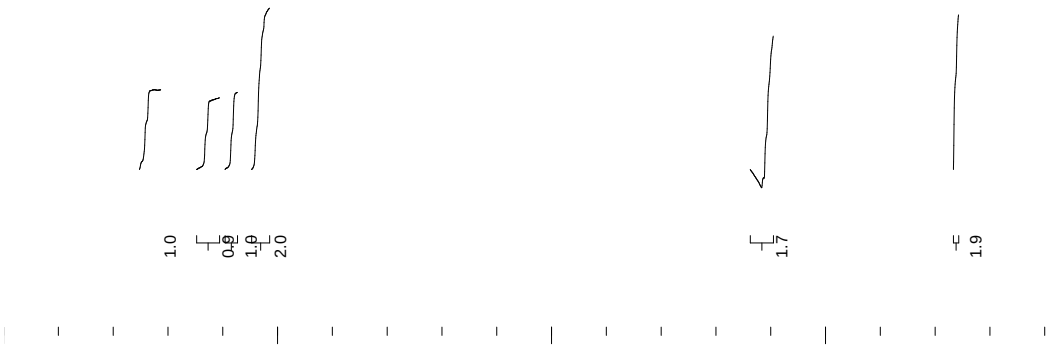
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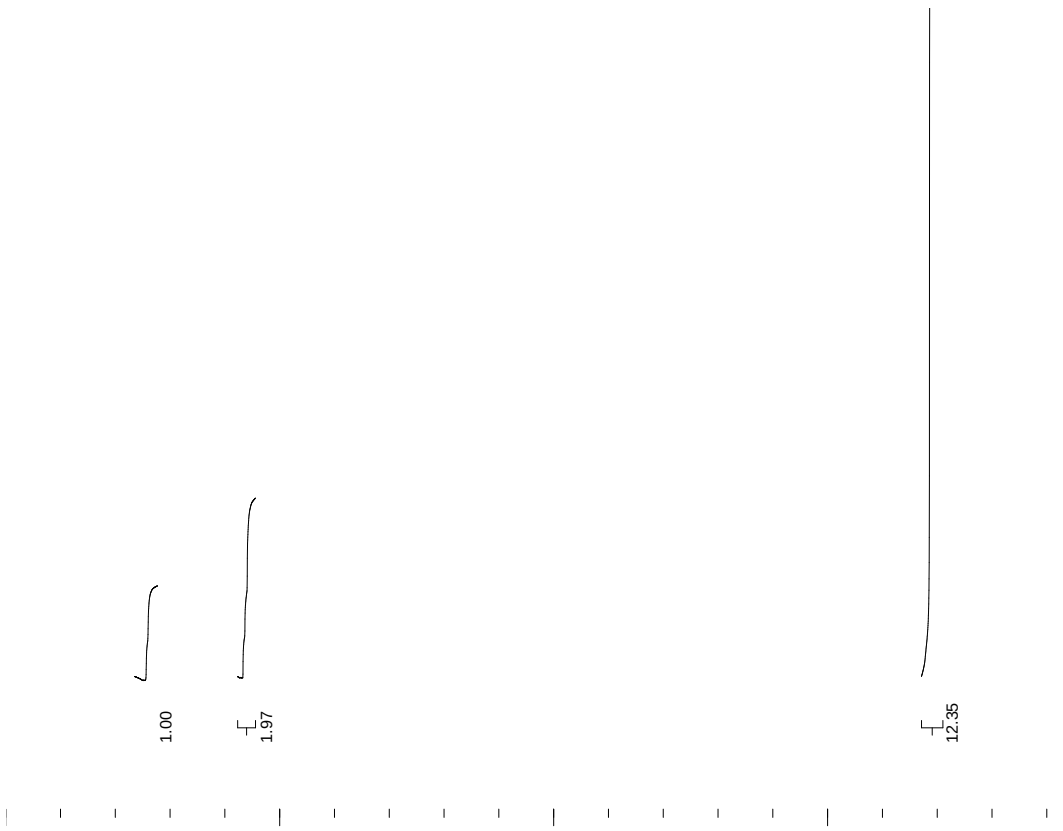
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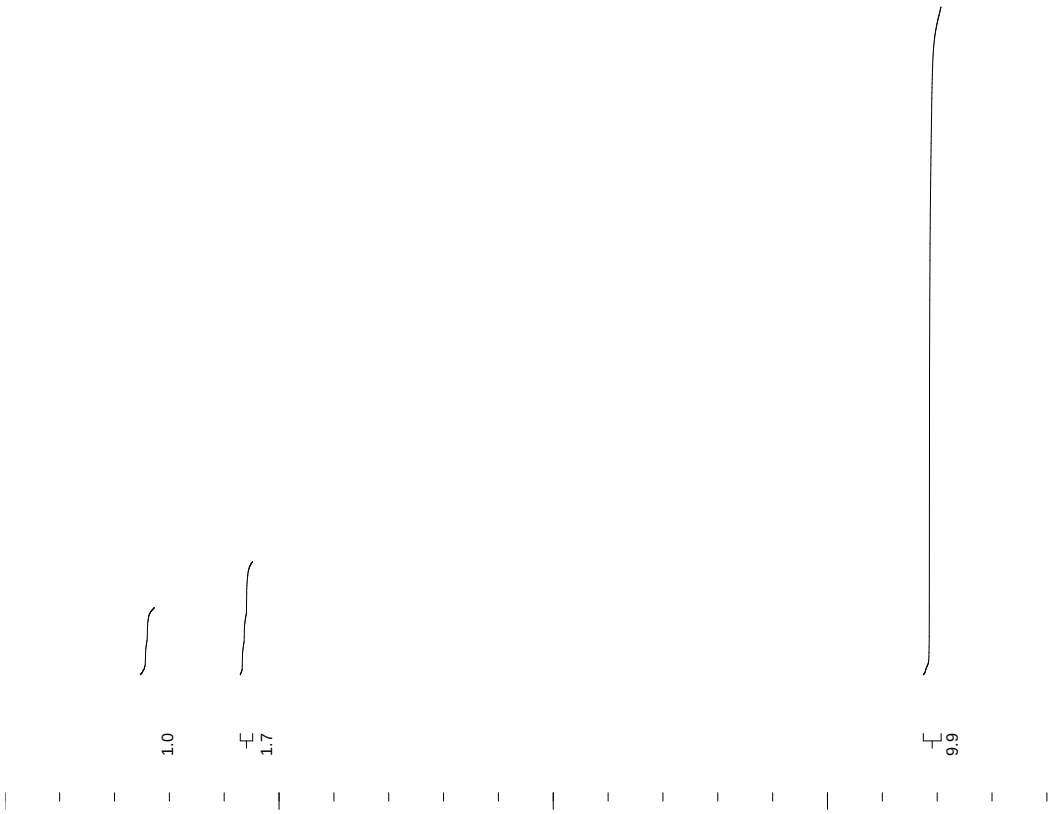
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