

Facile *N*-Arylation of Amines and Sulfonamides

Zhijian Liu and Richard C. Larock *

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Supporting Information

General. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported in the publication represent an average of at least two independent runs. CsF and acetonitrile were purchased from Sigma-aldrich Co.. The methoxy-substituted silylaryl triflate **1b** was prepared according to a previous literature procedure.¹

General procedure for the *N*-arylation of amines and sulfonamides.

Procedure A: To a solution of MeCN (4 mL), amine or sulfonamide (0.25 mmol) and silylaryl triflate (0.225 mmol) was added CsF (0.45 mmol). The reaction mixture was allowed to stir at room temperature for 1 d and the resulting solution was washed by brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Procedure B: To a solution of MeCN (4 mL), amine or sulfonamide (0.25 mmol) and silylaryl triflate (0.6 mmol) was added CsF (1.2 mmol). The reaction mixture was allowed to stir at room temperature for 3 d for *N*-arylated amines and 1 d for *N*-arylated sulfonamides. The resulting solution was washed with brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Diphenylamine (entry 1, Table 1). Using procedure A, silylaryl triflate **1a** (0.225 mmol, 67 mg), aniline (0.25 mmol, 24 mg) and CsF (0.45 mmol, 69 mg) afforded the indicated compound (31 mg) in an 81 % yield as a white solid: mp 49-50 °C (lit.² mp 50-52 °C). The ¹H and ¹³C NMR spectra match the literature data.³ ¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, *J* = 8.0, 1.2 Hz, 4H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 4H), 6.93 (td, *J* = 8.0, 1.2 Hz, 2H), 5.61 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.6 (2C), 129.8 (4C), 121.4 (2C), 118.3 (4C).

***N*-Phenyl-3-methoxyaniline (entry 2, Table 1).** Using procedure A, silylaryl triflate **1b** (0.225 mmol, 74 mg), aniline (0.25 mmol, 24 mg) and CsF (0.45 mmol, 69 mg) afforded the indicated compound (38 mg) in an 84 % yield as a colorless oil. The ¹H and ¹³C NMR spectra match the literature data.⁴ ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.10 (m, 5H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.69-6.67 (m, 2H), 6.51 (dd, *J* = 7.4, 1.9 Hz, 1H), 5.74 (s, 1H), 3.80 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 160.8 (1C), 144.7 (1C), 142.9 (1C), 130.2 (1C), 129.5 (1C), 121.4 (1C), 118.5 (1C), 110.4 (1C), 106.3 (1C), 103.4 (1C), 55.4 (1C).

Triphenylamine (entry 3, Table 1). Using procedure B, aniline (0.25 mmol, 24 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (60 mg) in a 98 % yield as a white solid: mp 123-124 °C (lit.⁵ mp 125-126 °C). The ¹H and ¹³C NMR spectra match the literature data.⁶ ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.29 (m, 6H), 7.18-7.15 (m, 6H), 7.11-7.04 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.2 (3C), 129.5 (6C), 124.5 (6C), 123.0 (3C).

***N,N*-bis(3-Methoxyphenyl)aniline (entry 4, Table 1).** Using procedure B, aniline (0.25 mmol, 24 mg), silylaryl triflate **1b** (0.6 mmol, 196 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (72 mg) in a 94 % yield as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.26-7.21 (m, 2H), 7.16-7.08 (m, 4H), 7.03-6.98 (m, 1H), 6.68-6.62 (m, 4H), 6.57-6.54 (dd, *J* = 8.1, 0.9 Hz, 2H), 3.71 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 160.6 (2C), 149.2 (2C), 147.8 (1C), 129.9 (2C), 129.4 (2C), 124.8 (2C), 123.2 (1C), 116.9 (2C), 110.2 (2C), 108.4 (2C), 55.4 (2C). IR (CDCl₃) 3000, 2953 cm⁻¹; HRMS *m/z* 305.1428 (calcd C₂₀H₁₉NO₂, 305.1415).

***N*-Phenyl-2-iodoaniline (entry 5, Table 1).** Using procedure A, silylaryl triflate **1a** (0.225 mmol, 67 mg), *o*-iodoaniline (0.25 mmol, 55 mg) and CsF (0.45 mmol, 69 mg) afforded the indicated compound (55 mg) in an 83 % yield as a light yellow oil. ¹H NMR

(300 MHz, CDCl₃) δ 7.78-7.75 (m, 1H), 7.34-7.28 (m, 2H), 7.20-7.18 (m, 2H), 7.14-7.10 (m, 2H), 7.05-7.00 (m, 1H), 6.64-6.58 (m, 1H), 5.90 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 144.2 (1C), 142.2 (1C), 139.7 (1C), 129.7 (1C), 129.3 (1C), 122.8 (1C), 122.1 (1C), 120.2 (1C), 116.1 (1C), 89.0 (1C). IR (CDCl₃) 3379, 3041 cm⁻¹; HRMS m/z 294.9865 (calcd C₁₂H₁₀N, 294.9858).

***N*-Propargylaniline (entry 6, Table 1).** Using procedure A, silylaryl triflate **1a** (0.225 mmol, 67 mg), propargyl amine (0.25 mmol, 14 mg) and CsF (0.45 mmol, 69 mg) afforded the indicated compound (19 mg) in a 62 % yield as a light yellow oil. The ¹H NMR spectrum matches the literature data.⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.25-7.18 (m, 2H), 6.81-6.72 (m, 1H), 6.70-6.67 (m, 2H), 3.94 (m, 3H), 2.12 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 147.1 (1C), 129.4 (2C), 118.9 (1C), 113.7 (2C), 81.2 (1C), 71.5 (1C), 33.9 (1C).

***N*-Phenyl-*N*-propargylaniline (entry 7, Table 1).** Using procedure B, propargyl amine (0.25 mmol, 14 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (40 mg) in a 78 % yield as a light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.23 (m, 4H), 7.10-6.98 (m, 6H), 4.41 (d, *J* = 2.4 Hz, 2H), 2.22 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 147.6 (2C), 129.5 (2C), 122.4 (2C), 121.4 (2C), 80.1 (1C), 72.5 (1C), 42.3 (1C). IR (CDCl₃) 3289, 3063, 2918 cm⁻¹; HRMS m/z 207.1051 (calcd C₁₅H₁₃N, 207.1048).

***N*-(2-Cyclohex-1-en-1-ylethyl)-*N,N*-diphenylamine (entry 8, Table 1).** Using procedure B, 2-(cyclohex-1-enyl)ethyl amine (0.25 mmol, 31 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (69 mg) in a 99 % yield as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.28-7.21 (m, 4H), 7.00-6.89 (m, 6H), 5.44 (s, 1H), 3.80-3.75 (m, 2H), 2.31-2.25 (t, *J* = 1.2 Hz, 2H), 1.97-1.92 (m, 4H), 1.60-1.51 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 148.1 (2C), 135.5 (1C), 129.4 (2C), 123.0 (1C), 121.2 (2C), 121.1 (2C), 51.4 (1C), 35.8 (1C), 28.8 (1C), 25.5 (1C), 23.1 (1C), 22.6 (1C). IR (CDCl₃) 3057, 3034, 2925 cm⁻¹; HRMS m/z 277.1835 (calcd C₂₀H₂₃N, 277.1830).

3-Diphenylamino-1-propanol (entry 9, Table 1). Using procedure B, 3-amino-1-propanol (0.25 mmol, 19 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (47 mg) in an 83 % yield as a colorless

oil. ^1H NMR (300 MHz, CDCl_3) δ 7.27-7.20 (m, 4H), 7.02-6.89 (m, 6H), 3.31 (t, $J = 7.2$ Hz, 2H), 3.68 (t, $J = 6.0$ Hz, 2H), 1.92-1.83 (m, 2H), 1.73 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3 (2C), 129.5 (2C), 121.6 (1C), 121.3 (2C), 60.8 (1C), 49.3 (1C), 30.6 (1C). IR (CDCl_3) 3351, 3041, 2943 cm^{-1} ; HRMS m/z 227.1316 (calcd $\text{C}_{15}\text{H}_{17}\text{NO}$, 227.1310).

***N-tert-Butyl-N-phenylaniline* (entry 10, Table 1).** Using procedure B, *tert*-butylamine (0.25 mmol, 18.5 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (55 mg) in a 97 % yield as a colorless oil. The ^1H and ^{13}C NMR spectra match the literature data.⁸ ^1H NMR (300 MHz, CDCl_3) δ 7.20-6.94 (m, 10H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.9 (2C), 128.9 (2C), 127.1 (2C), 122.5 (2C), 56.0 (1C), 30.5 (3C).

***N-Methyl-N-phenylaniline* (entry 11, Table 1).** Using procedure B, *N*-methylaniline (0.25 mmol, 27 mg), silylaryl triflate **1a** (0.3 mmol, 90 mg) and CsF (0.6 mmol, 91 mg) afforded the indicated compound (66 mg) in a 93 % yield as a colorless oil. The ^1H and ^{13}C NMR spectra match the literature data.⁹ ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.23 (m, 4H), 7.08-6.94 (m, 6H), 3.34 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.0 (2C), 129.2 (2C), 121.2 (2C), 120.4 (2C), 40.2 (1C).

***N,N*-Diphenylmethanesulfonamide** (entry 12, Table 1). Using procedure B, methanesulfonamide (0.25 mmol, 24 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (50 mg) in an 80 % yield as a white solid: mp 115-117 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.35 (m, 8H), 7.31-7.25 (m, 2H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5 (2C), 129.7 (2C), 127.8 (2C), 127.5 (2C), 40.3 (1C). IR (CDCl_3) 3071, 2983, 1343 cm^{-1} ; HRMS m/z 247.0672 (calcd $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$, 247.0667).

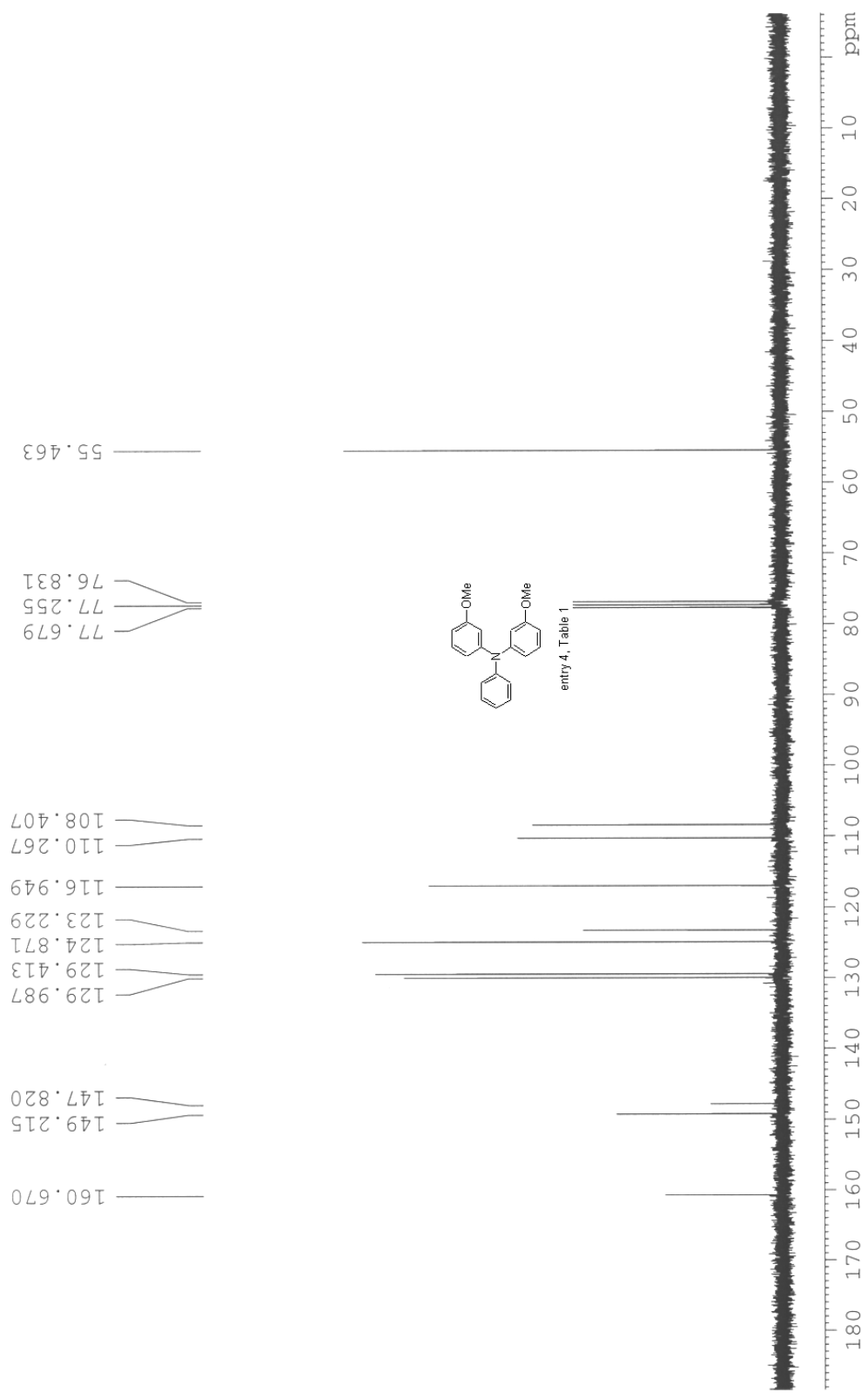
***N,N*-Diphenylbenzenesulfonamide** (entry 13, Table 1). Using procedure B, benzenesulfonamide (0.25 mmol, 39 mg), silylaryl triflate **1a** (0.6 mmol, 179 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (77 mg) in a 99 % yield as a white solid: mp 120-121 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.73-7.70 (m, 2H), 7.62-7.45 (m, 3H), 7.34-7.23 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.6 (2C), 140.7 (1C), 133.0 (1C), 129.5 (4C), 129.1 (2C), 128.5 (4C), 127.9 (2C), 127.7 (2C). IR (CDCl_3) 3061, 1353 cm^{-1} ; HRMS m/z 309.0829 (calcd $\text{C}_{18}\text{H}_{15}\text{NO}_2\text{S}$, 309.0823).

***N,N*-bis(3-Methoxyphenyl)-4-methylbenzenesulfonamide (entry 14, Table 1).** Using procedure B, *p*-toluenesulfonamide (0.25 mmol, 43 mg), silylaryl triflate **1b** (0.6 mmol, 197 mg) and CsF (1.2 mmol, 182 mg) afforded the indicated compound (88 mg) in a 92 % yield as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.22-7.16 (m, 2H), 6.84-6.77 (m, 6H), 3.73 (s, 6H), 2.41 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 160.3 (2C), 143.9 (1C), 142.7 (2C), 137.8 (1C), 129.9 (2C), 129.7 (2C), 128.0 (2C), 120.5 (2C), 114.4 (2C), 113.2 (2C), 55.6 (2C), 21.8 (1C). IR (CDCl₃) 3052, 2958, 1354 cm⁻¹; HRMS *m/z* 383.1199 (calcd C₂₁H₂₁NO₄S, 383.1191).

***N*-Methyl-*N*-phenyl-*p*-toluenesulfonamide (entry 15, Table 1).** Using procedure B, *N*-methyl-*p*-toluenesulfonamide (0.25 mmol, 47 mg), silylaryl triflate **1a** (0.3 mmol, 89 mg) and CsF (0.5 mmol, 76 mg) afforded the indicated compound (57 mg) in an 87 % yield as a white solid: mp 92-93 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.40 (m, 2H), 7.32-7.21 (m, 5H), 7.11-7.07 (m, 2H), 3.15 (s, 3H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 143.8 (1C), 141.8 (1C), 133.7 (1C), 129.5 (2C), 129.0 (2C), 128.1 (2C), 127.4 (1C), 126.8 (2C), 38.3 (1C), 21.7 (1C). IR (CDCl₃) 3018, 2918, 1344 cm⁻¹; HRMS *m/z* 261.0828 (calcd C₁₄H₁₅NO₂S, 261.0823).

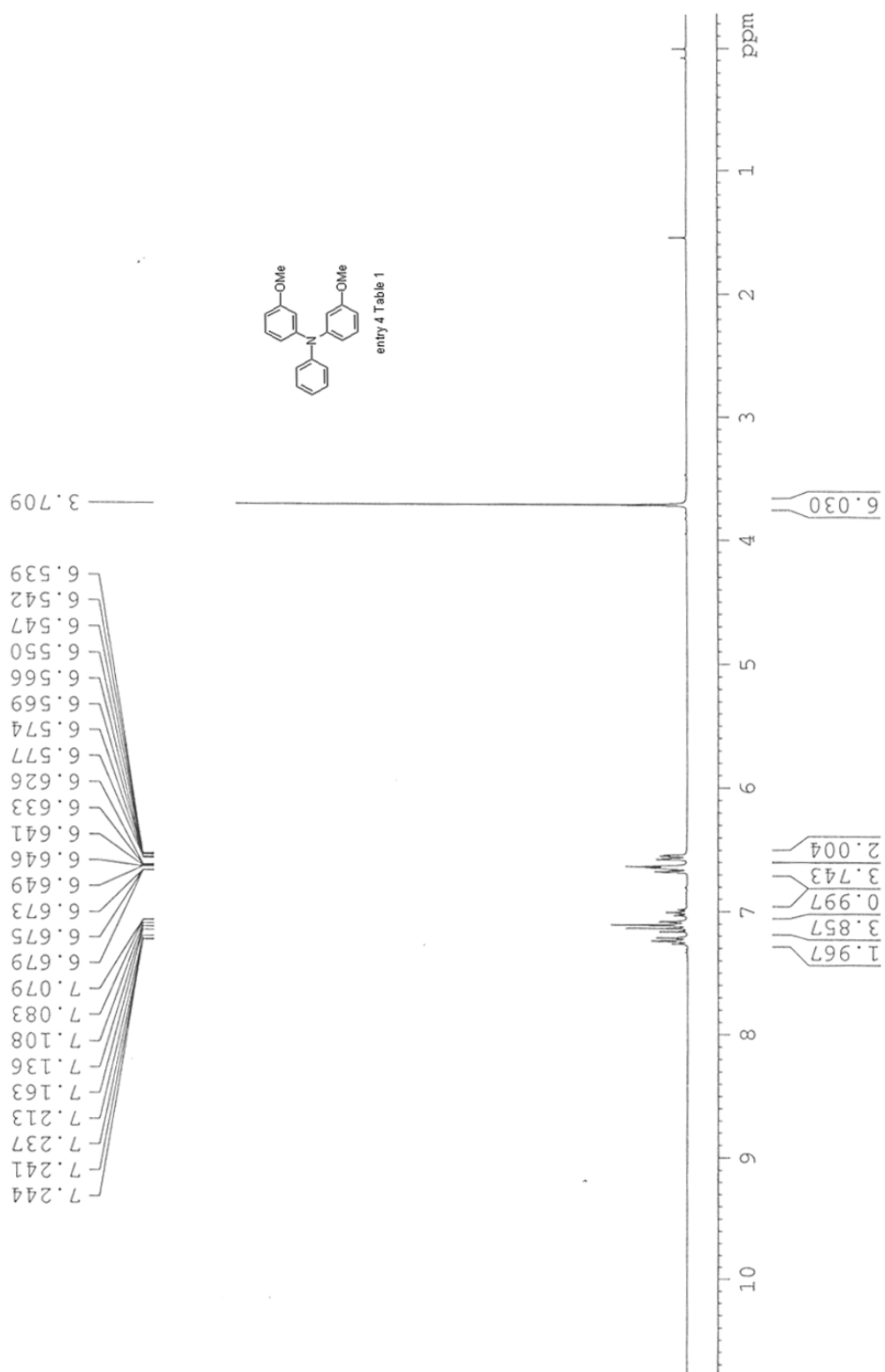
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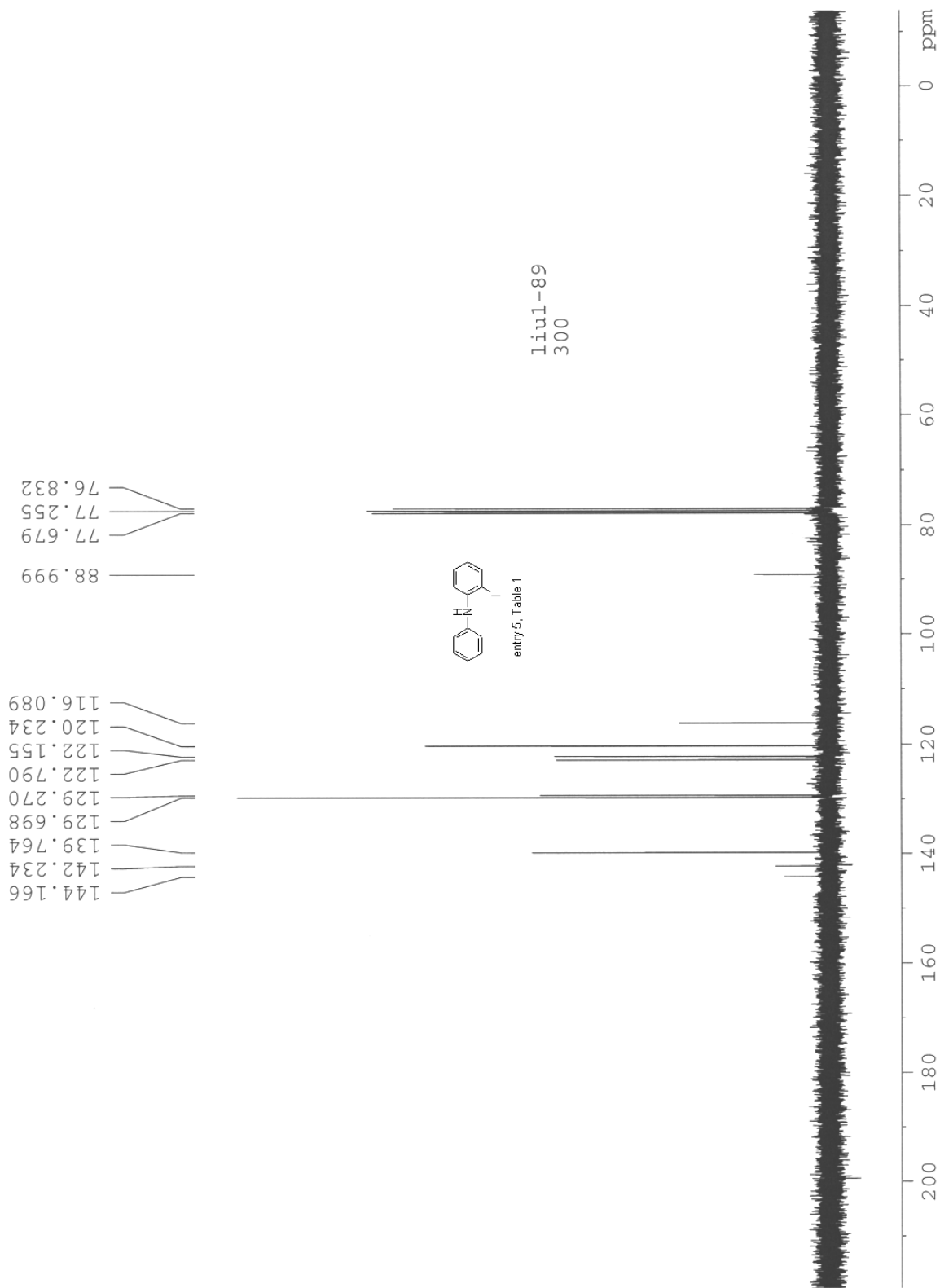
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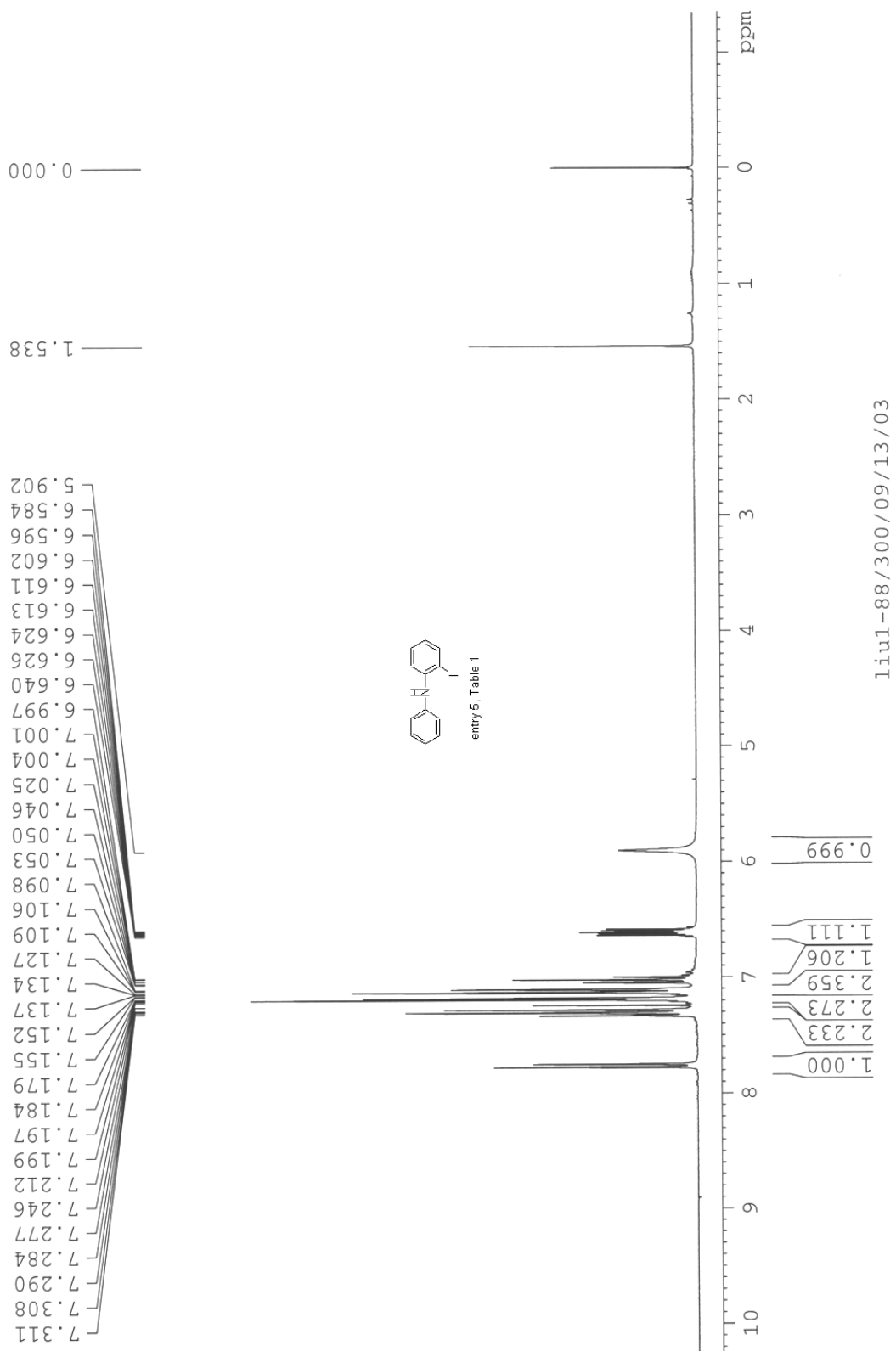


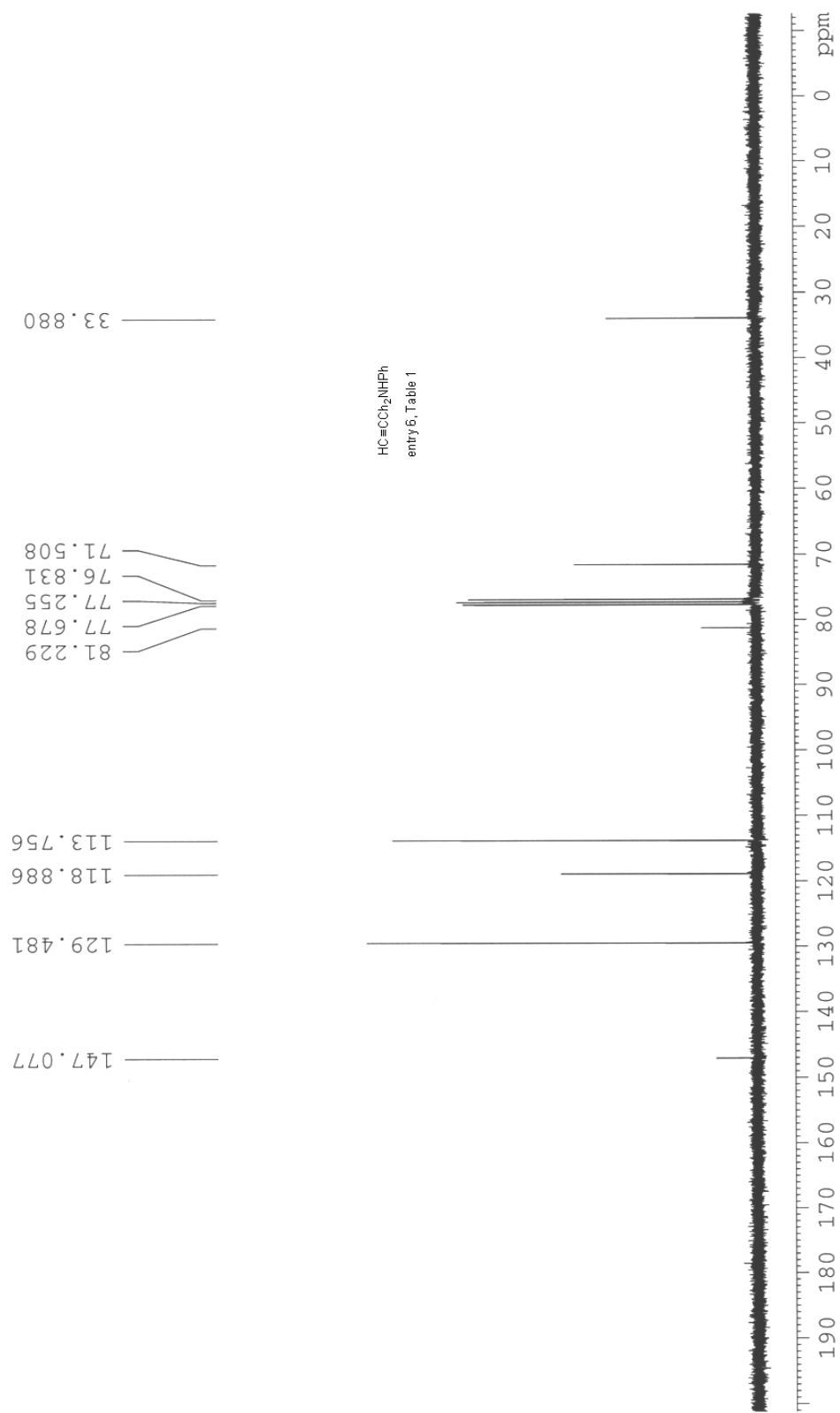
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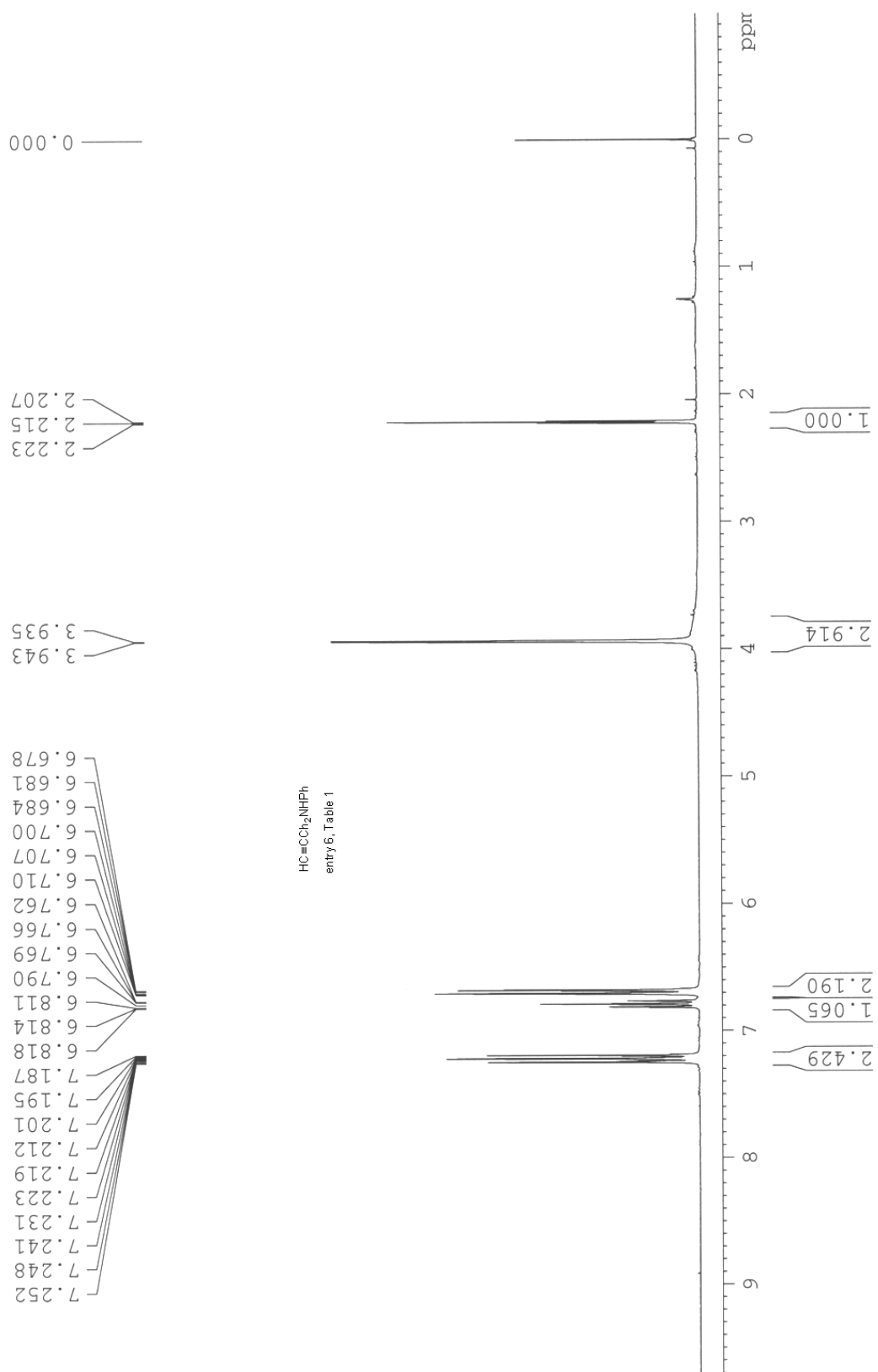


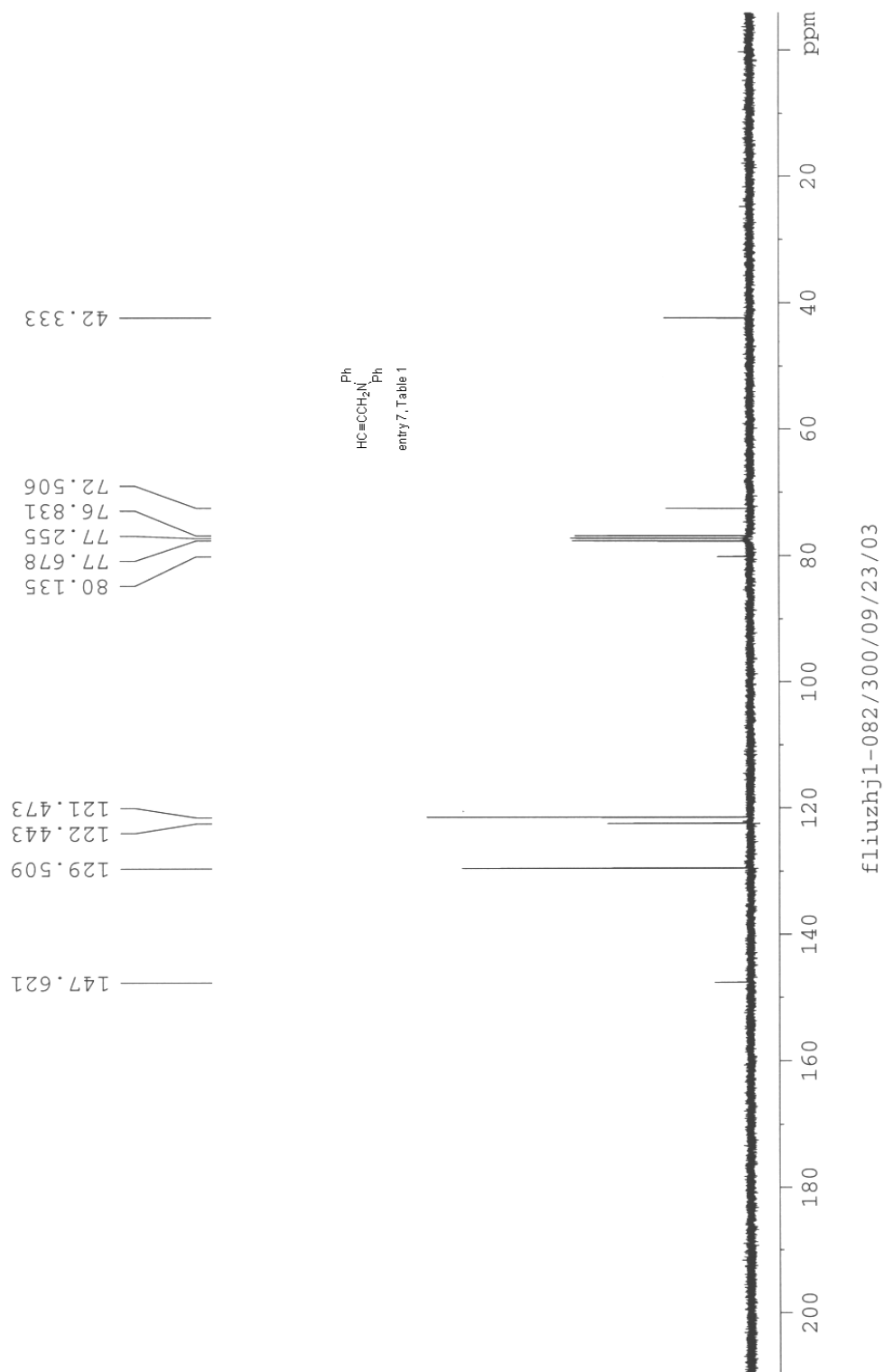




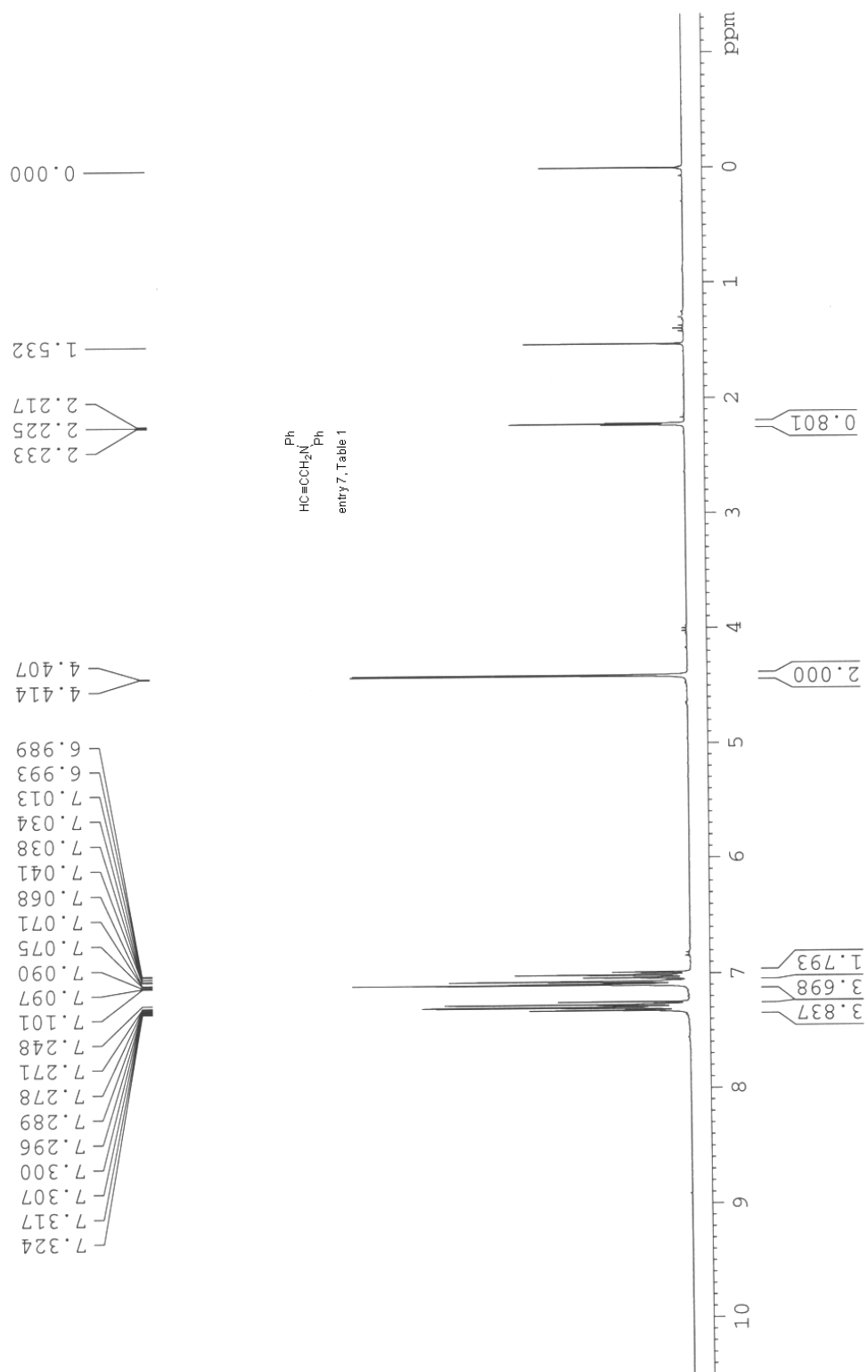
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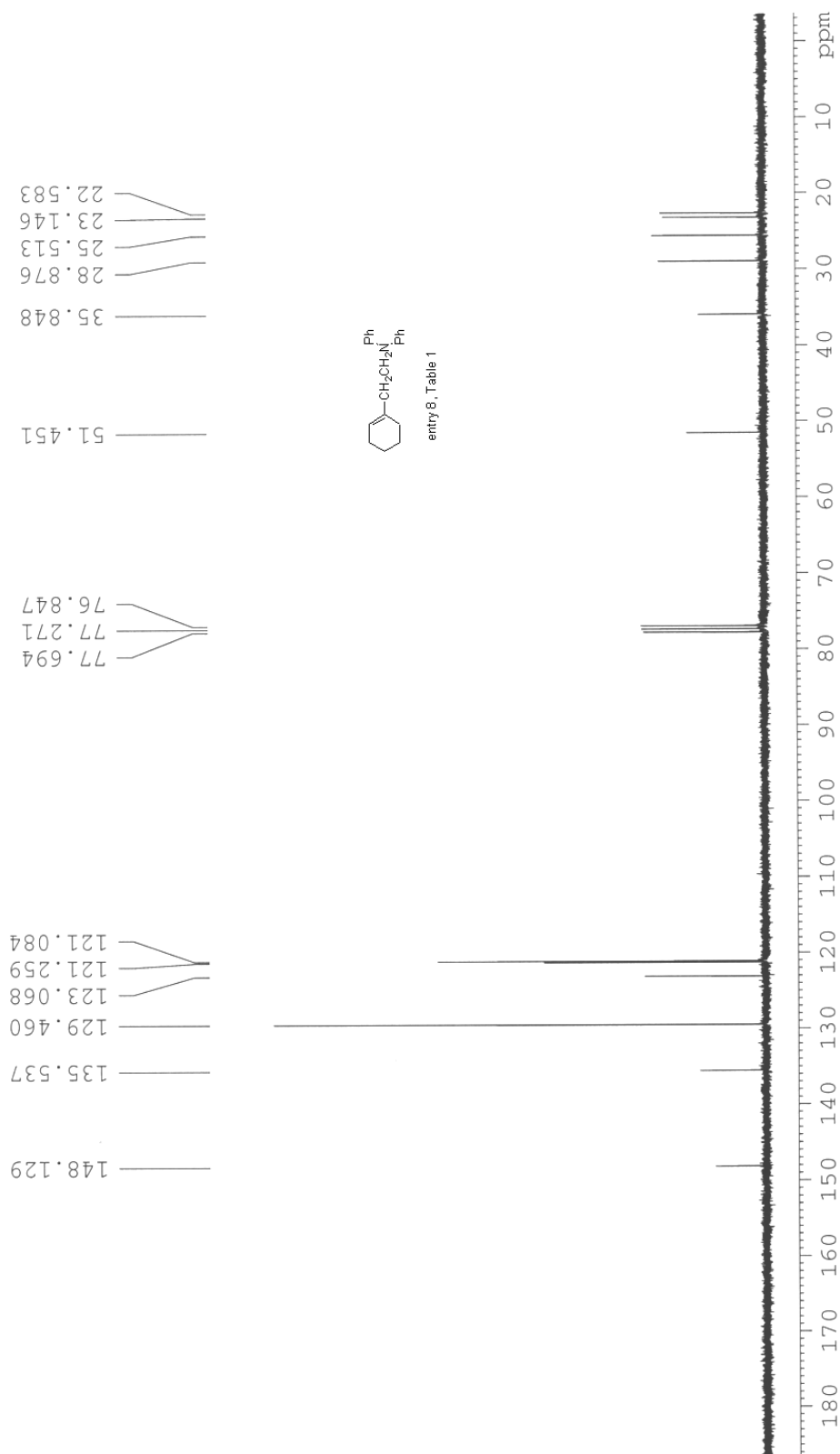
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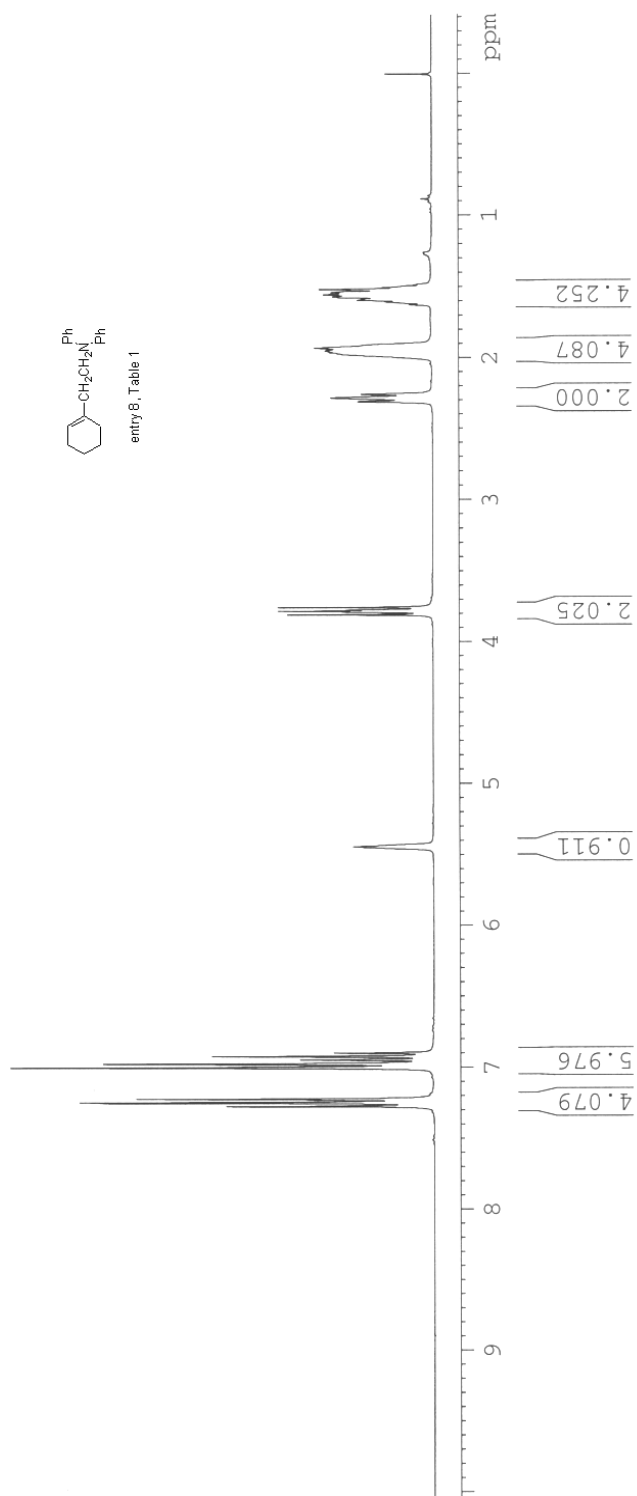


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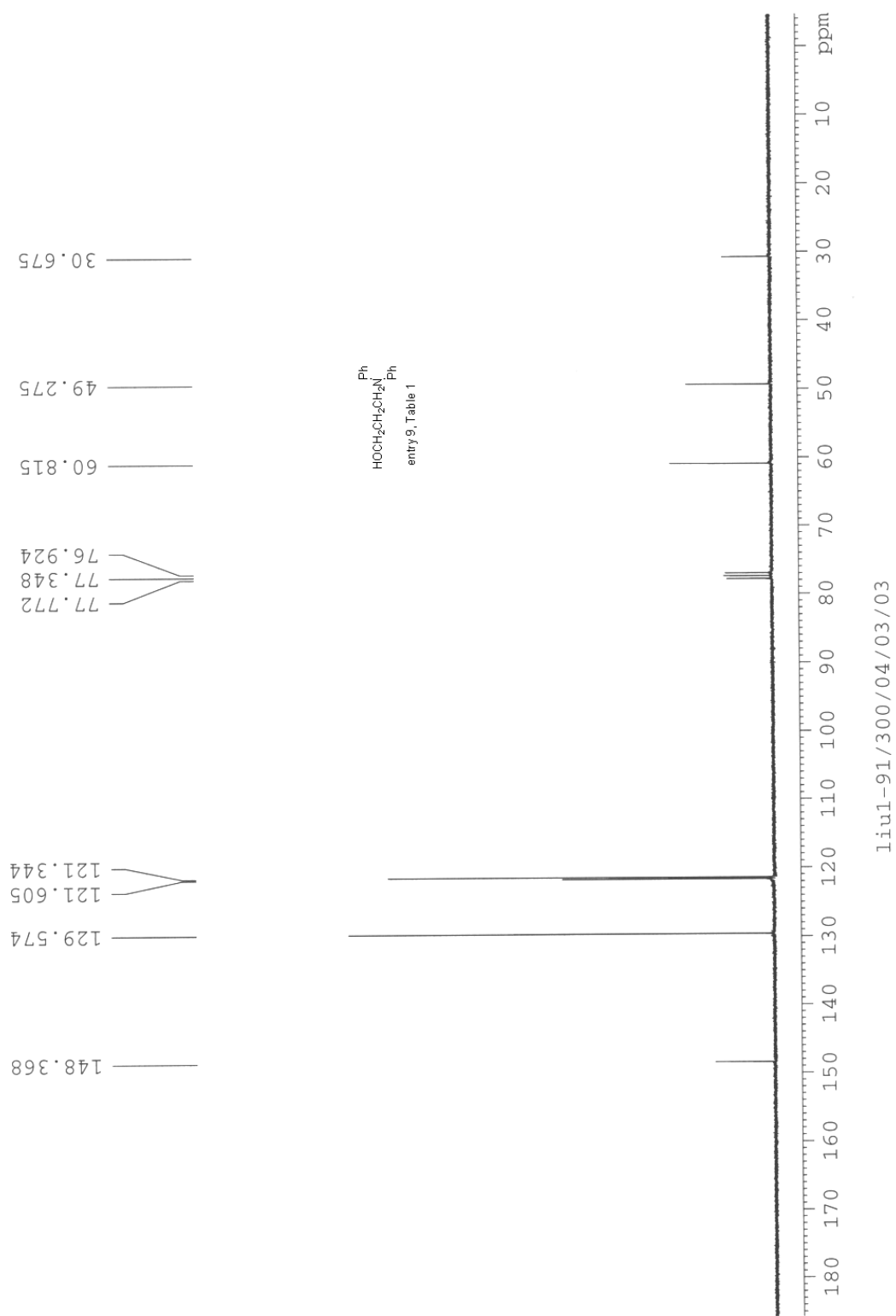


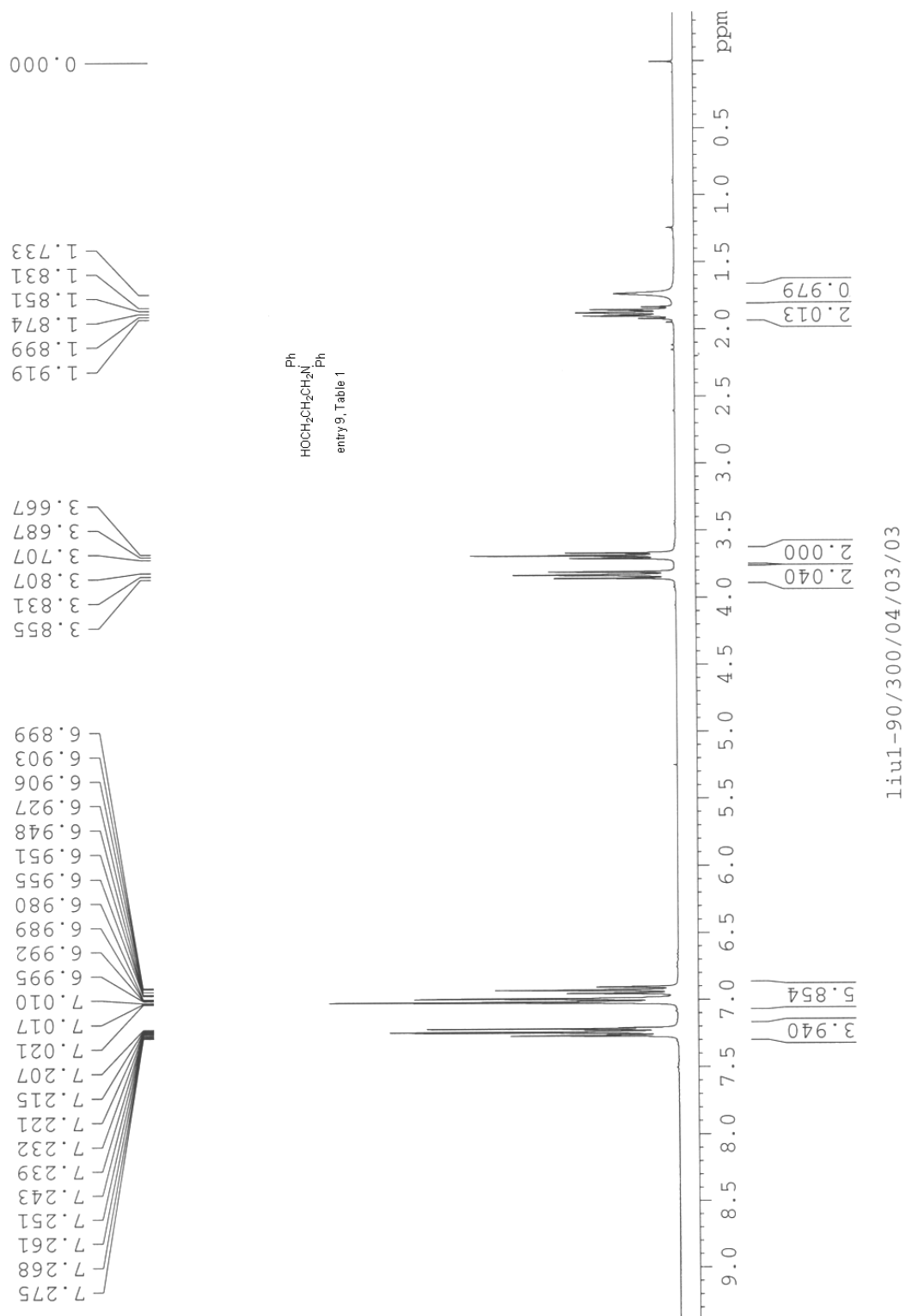
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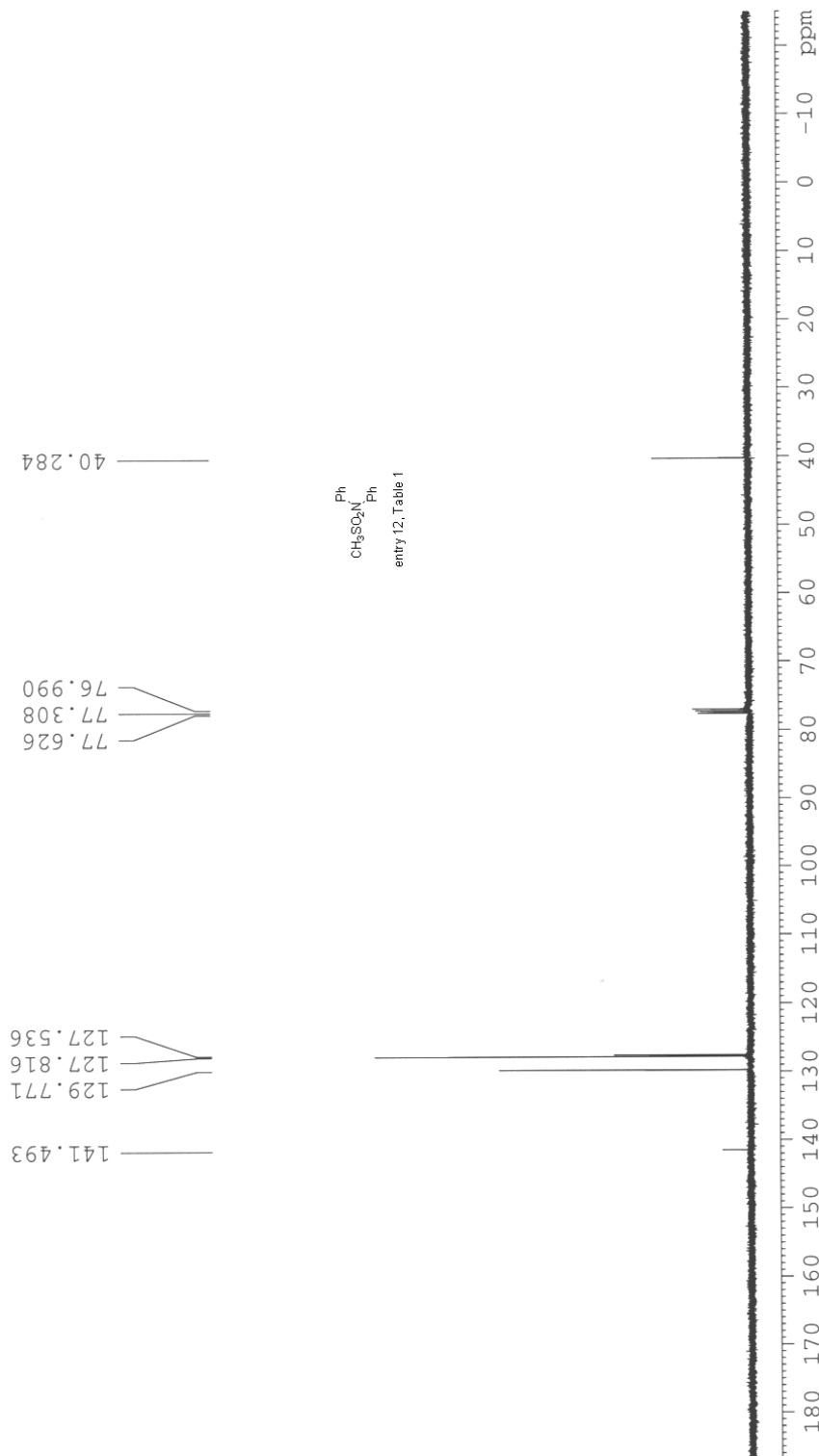


entry 8, Table 1



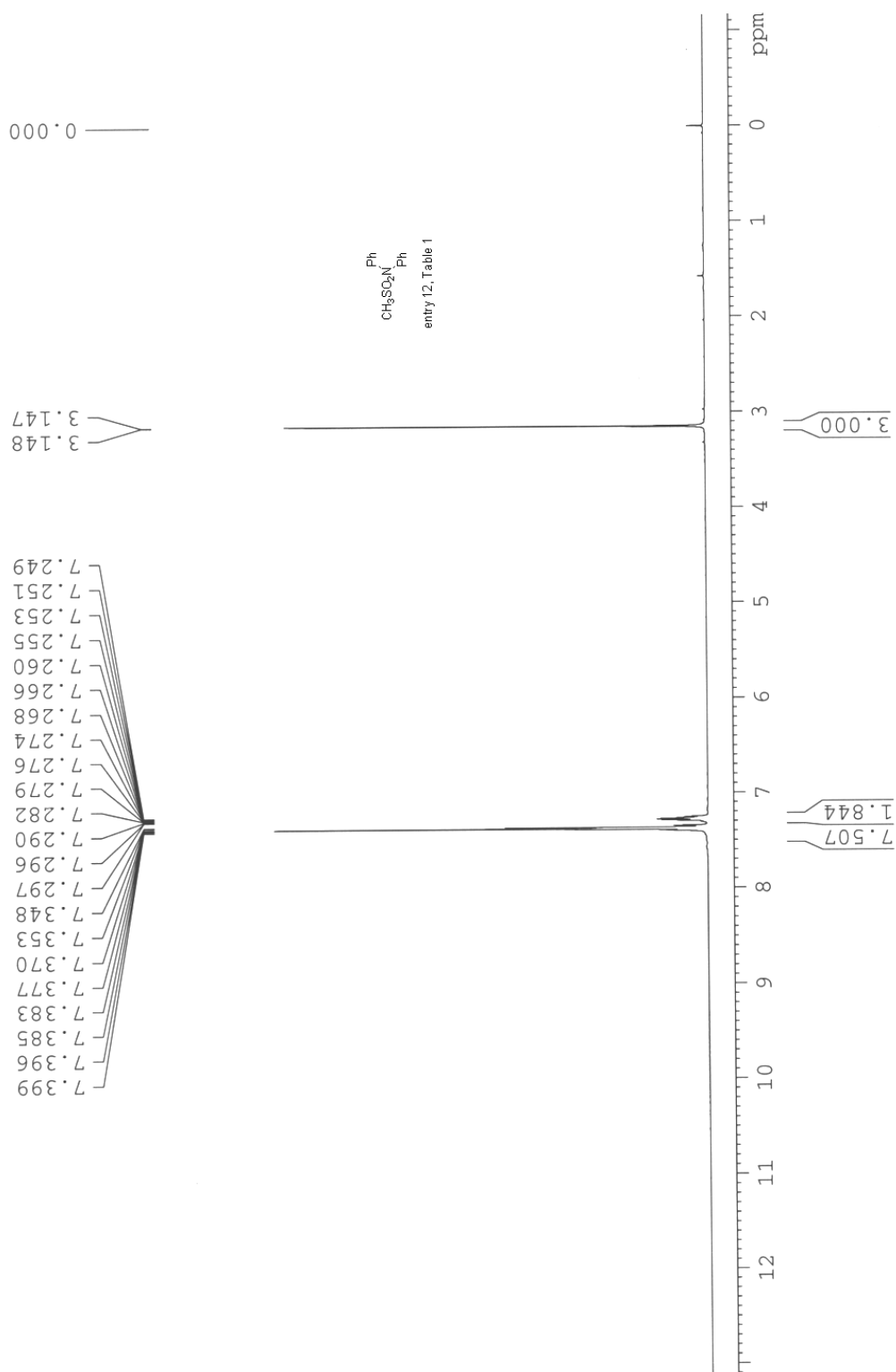


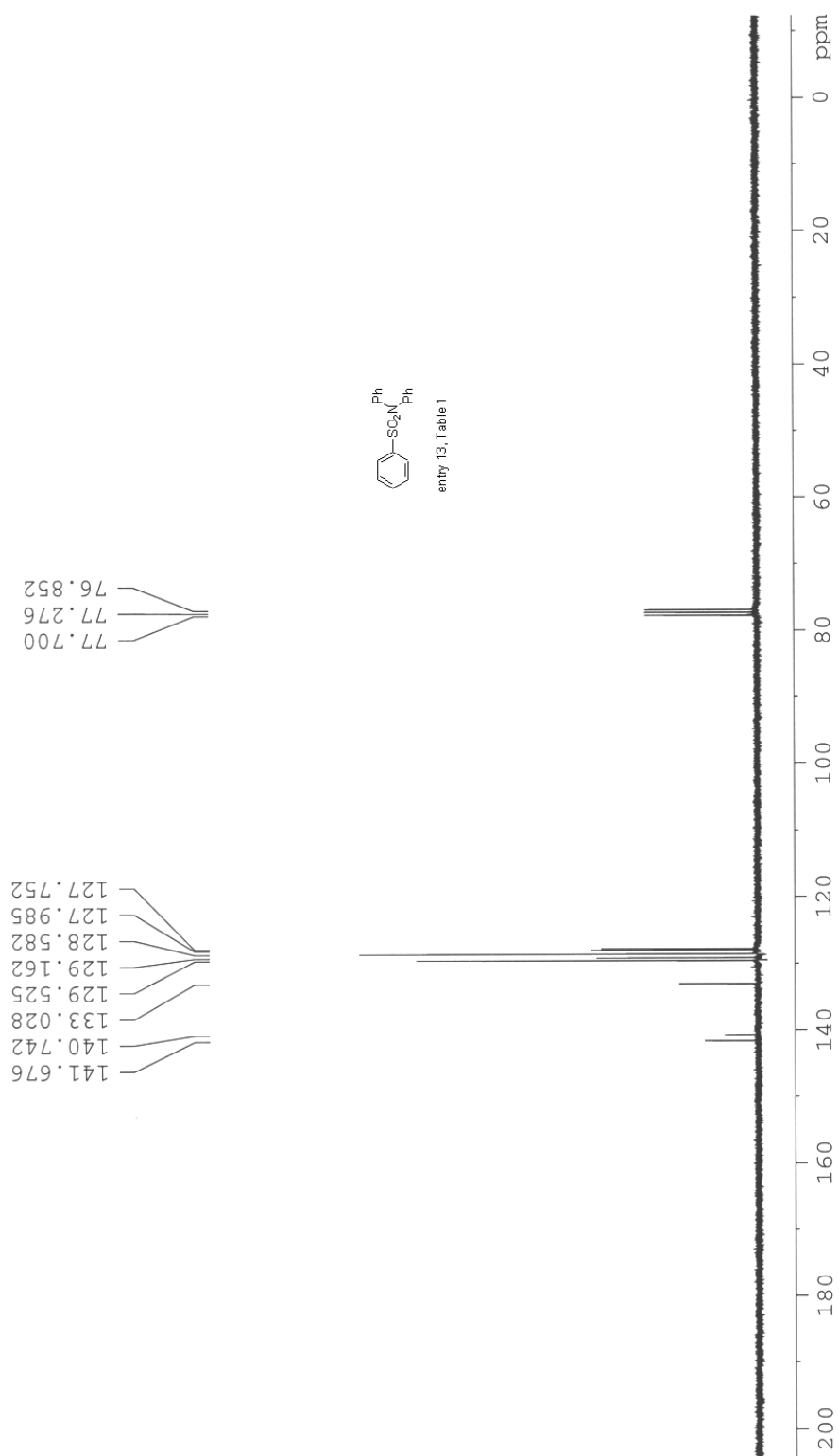




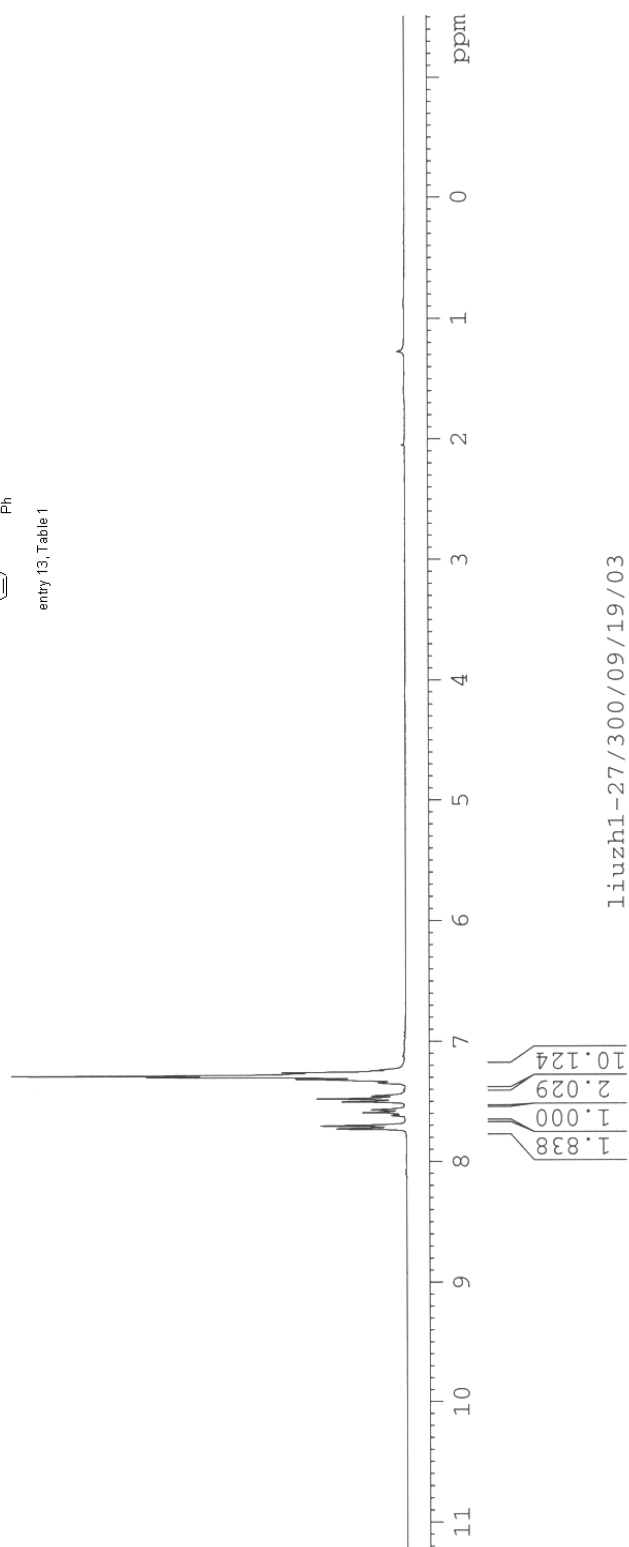
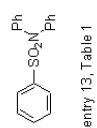
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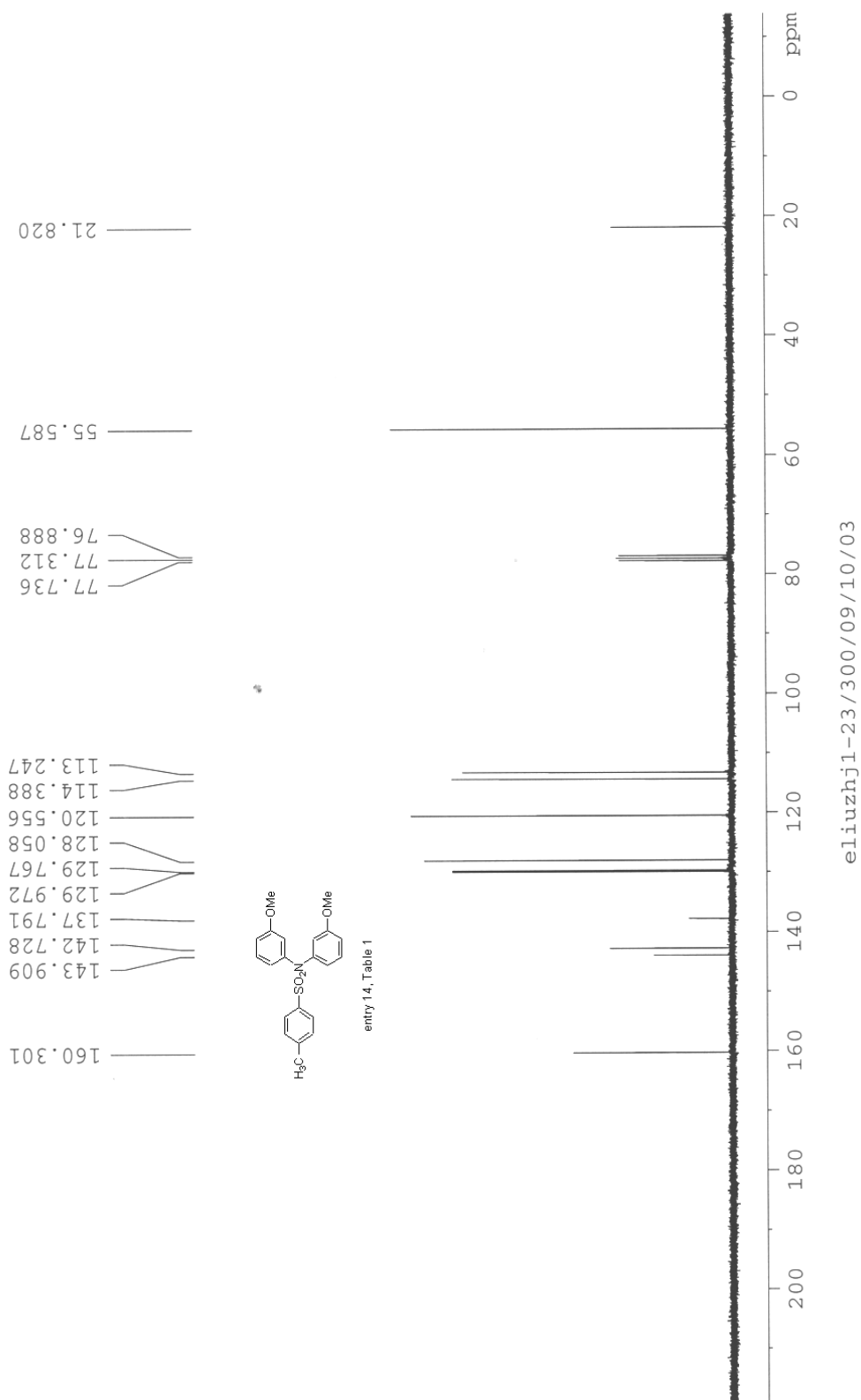


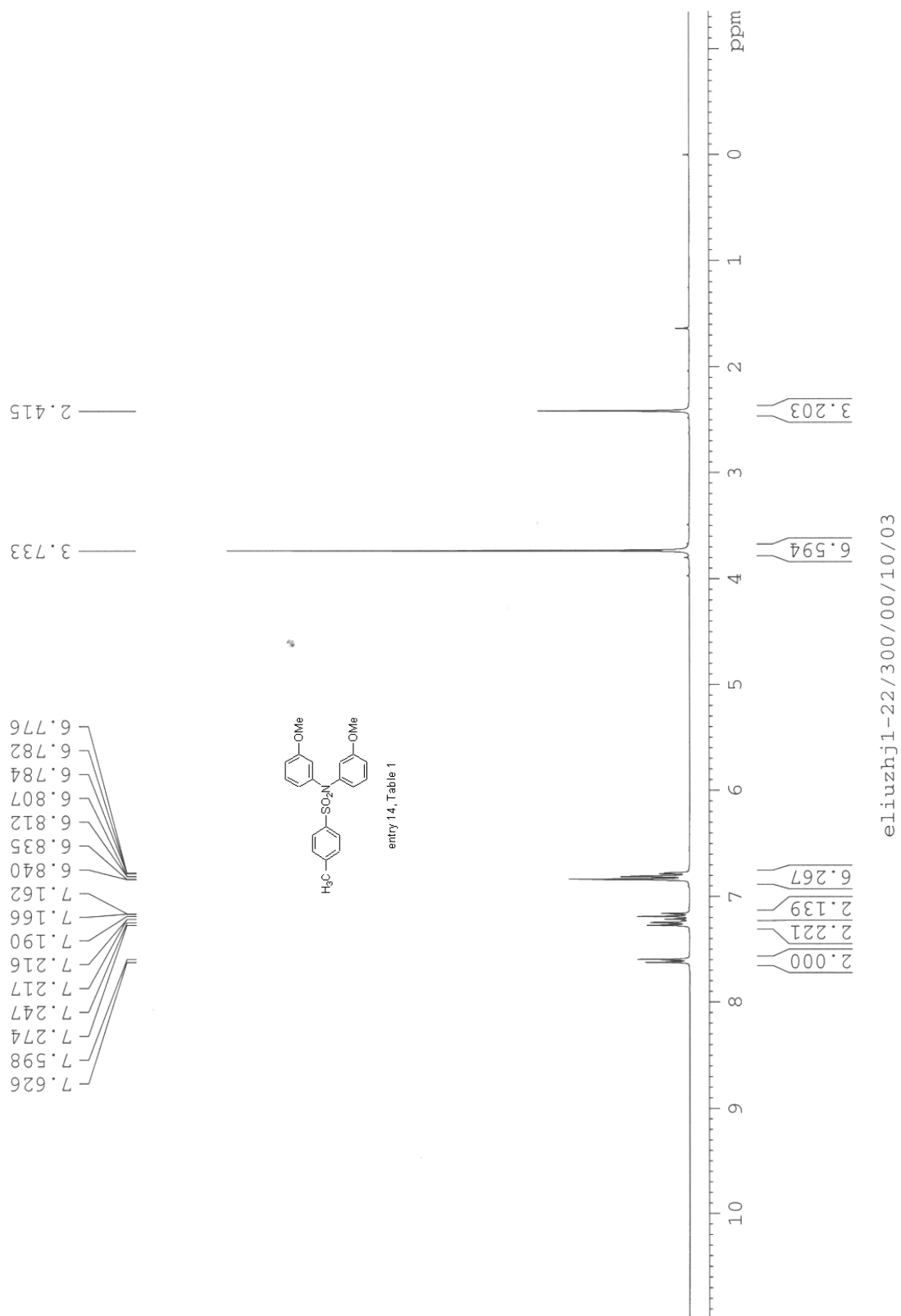


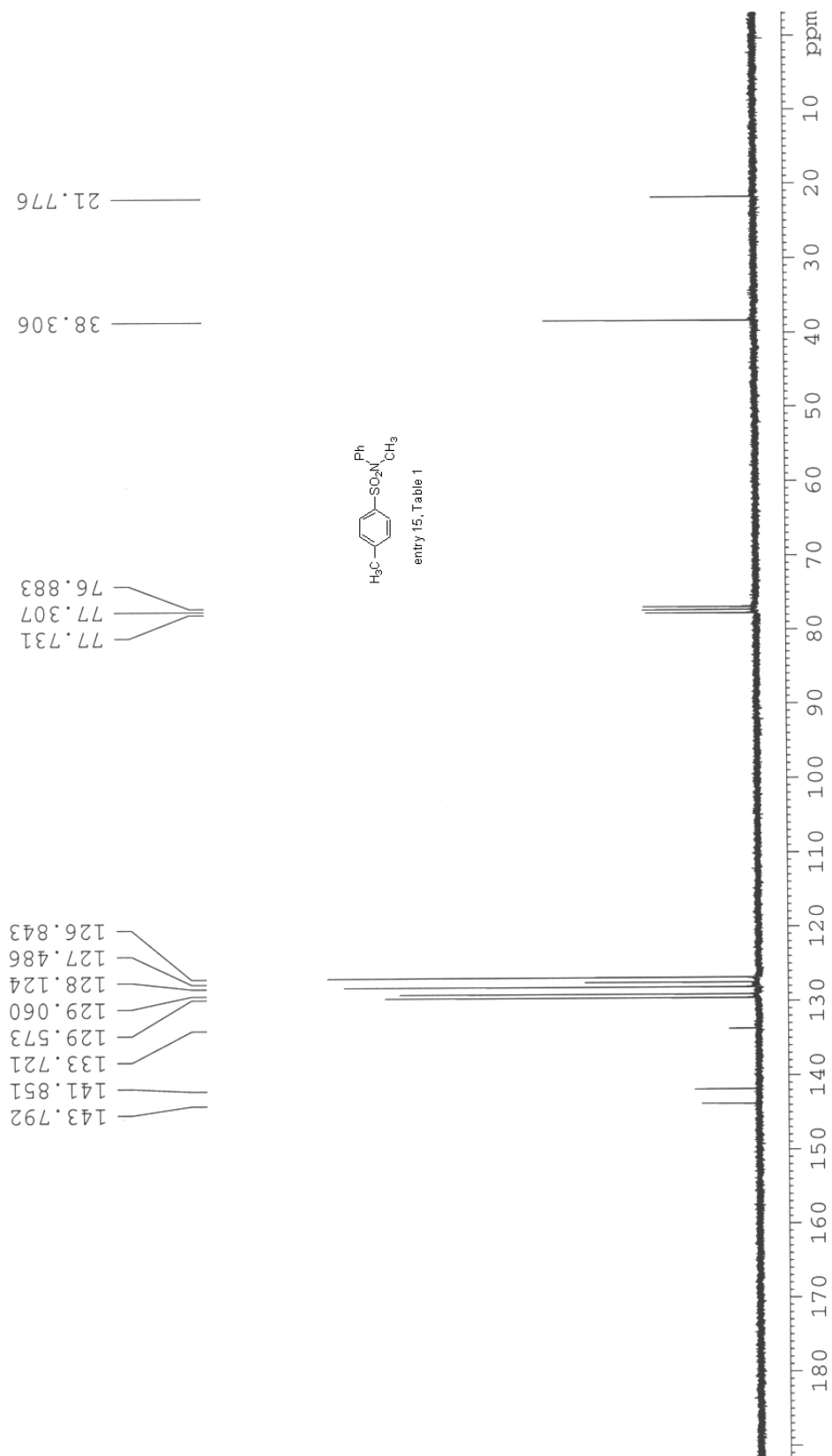
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