Modified Palladium-Catalyzed Sonogashira Cross-Coupling Reaction under Copper-, Amine- and Solvent-Free Conditions

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Supporting Information

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(A) Typical Experimental Procedure

Typical experimental procedure for the Sonogashira cross-coupling reaction. A mixture of aryl halide **1** (0.5 mmol), alkyne **2** (0.6 mmol), $PdCl_2(PPh_3)_2$ (3 mol%), and TBAF·$3H_2O$ (3 equiv) was stirred under N_2 at 80 ^oC for the desired time until complete consumption of starting material as monitored by TLC. After the mixture was washed by water, extracted with ether and evaporated, the residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the corresponding coupled products **3-15**.

(B) Analytical data for 3─15

1-Methoxy-4-(2-phenylethynyl)benzene (3)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.51 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.34–7.32 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

1-(Dec-1-ynyl)-4-methoxybenzene (4)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.61–1.57 (m, 2H), 1.45–1.40 (m, 2H), 1.31–1.24 (m, 8H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:158.9, 132.8, 116.1, 113.7, 88.8, 80.1, 55.2, 31.8, 29.2, 29.1, 28.9, 28.8, 22.7, 19.4, 14.1.

3-(4-Methoxyphenyl)prop-2-yn-1-ol (5)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 2H), 3.80 (s, 3H), 1.97 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 133.2, 114.6, 114.0, 85.9, 85.6, 55.3, 51.7.

1-(2-(4-Nitrophenyl)ethynyl)benzene (6)[4]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.58─7.54 (m, 2H), 7.40─7.38 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.3, 132.6, 132.2, 130.6, 129.6, 128.8, 124.0, 122.5, 95.0, 87.9.

1-(Dec-1-ynyl)-4-nitrobenzene (7)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.74–1.59 (m, 2H), 1.47–1.43 (m, 2H), 1.31–1.26 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.6, 131.6, 123.8, 118.5, 97.2, 79.6, 32.2, 29.5, 29.4, 29.3, 28.7, 23.0, 19.9, 14.4.

3-(4-nitrophenyl)prop-2-yn-1-ol (8)[3]: ^{1}H NMR (300 MHz) δ: 8.19 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 4.54 (s, 2H); ^{13}C NMR (100 MHz) δ: 147.3, 132.4, 129.4, 123.6, 92.5, 83.8, 51.5.

1-(2-(4-Methoxyphenyl)ethynyl)-4-nitrobenzene (9): Yellow solid, m.p. 119-121 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.4, 146.7, 134.0, 133.4, 132.0, 123.6, 114.2, 114.1, 95.1, 86.6, 55.3; LRMS (EI, 20 eV) *m/z* (%): 253 (M^+, 100); HRMS (EI) for $C_{15}H_{11}NO_3$ (M^+): calcd. 253.0738, found 253.0710.

1-Fluoro-4-(2-(4-nitrophenyl)ethynyl)benzene (10): Pale yellow solid, m.p. 111-113 ^{o}C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.57─7.54 (m, 2H), 7.10 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 161.8, 146.9, 133.8, 132.2, 130.0, 123.7, 116.0 (d, J = 22 Hz, 1C),

93.6, 87.3; LRMS (EI, 20 eV) *m/z* (%): 241 (M^+, 100); HRMS (EI) for $C_{14}H_8FNO_2$ (M^+): 241.0539 found 241.0539.

1-(4-(2-Phenylethynyl)phenyl)ethanone (11)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.57─7.54 (m, 2H), 7.38─7.36 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.3, 136.2, 131.8, 131.7, 128.9, 128.5, 128.3, 128.2, 122.7, 92.8, 88.7, 26.6.

1,2-Diphenylethyne (12)[4]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60─7.51 (m, 4H), 7.39─7.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 132.0, 128.7, 128.6, 123.7, 89.7.

1-(2-*p*-Tolylethynyl)benzene (13)[1]: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54–7.50 (m, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35–7.31 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 132.9, 131.9, 129.6, 129.5, 128.8, 128.7, 128.4, 89.1, 83.4, 21.9.

1,3-Dimethyl-5-(2-phenylethynyl)benzene (14)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.50 (m, 2H), 7.34–7.32 (m, 3H), 7.17 (d, 2H), 6.96 (s, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:137.9, 131.6, 130.2, 129.3, 128.3, 128.1, 123.5, 122.9, 89.8, 88.7, 21.2.

1-(2-*o*-Tolylethynyl)benzene (15)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.52 (m, 3H), 7.35–7.33 (m, 4H), 7.23–7.22 (m, 2H) 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.2, 132.6, 131.9, 131.6, 129.5, 129.2, 128.4, 128.3, 128.2, 125.6, 88.4, 81.7, 20.7.

(C) References

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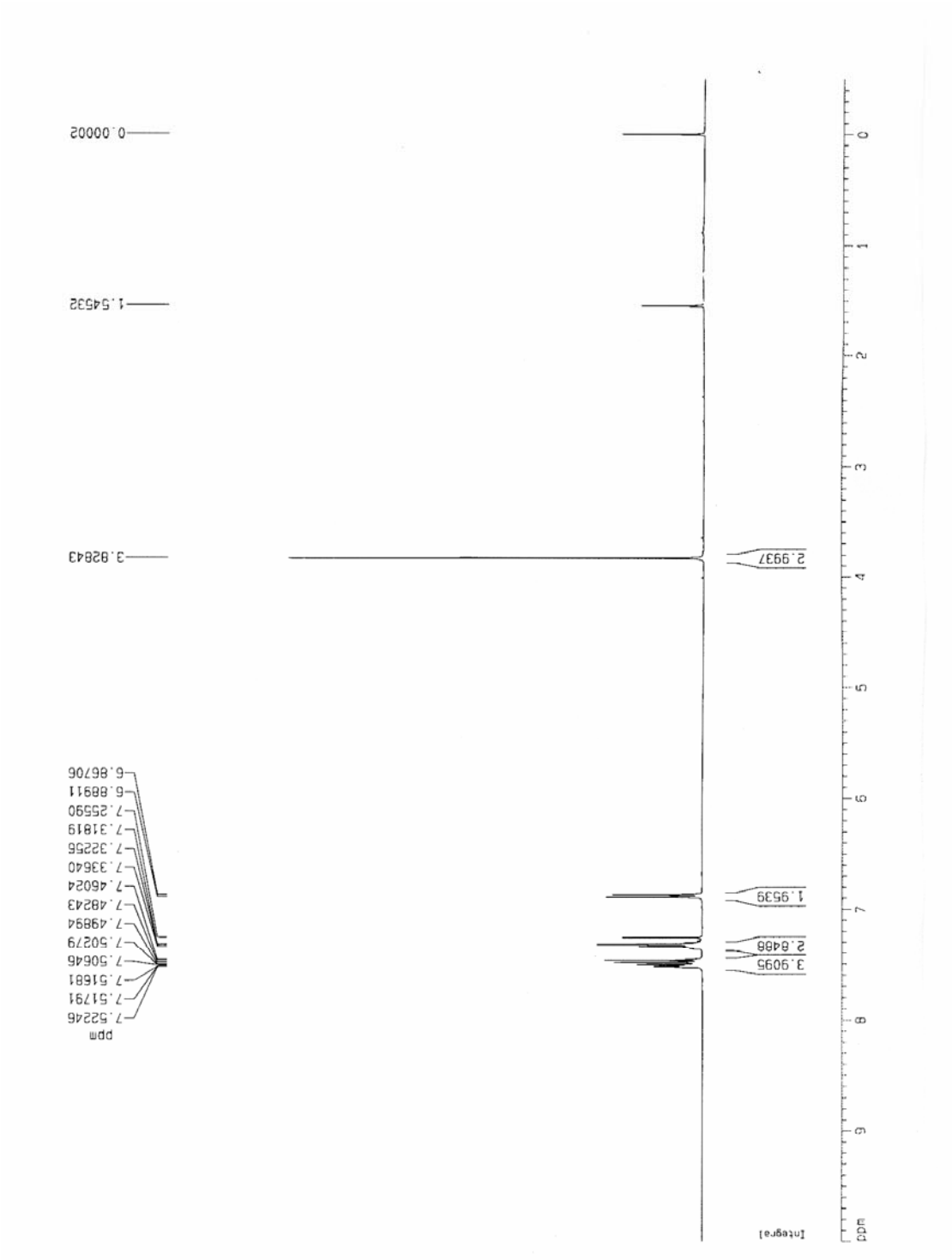
(D) Spectra

1-Methoxy-4-(2-phenylethynyl)benzene (3)



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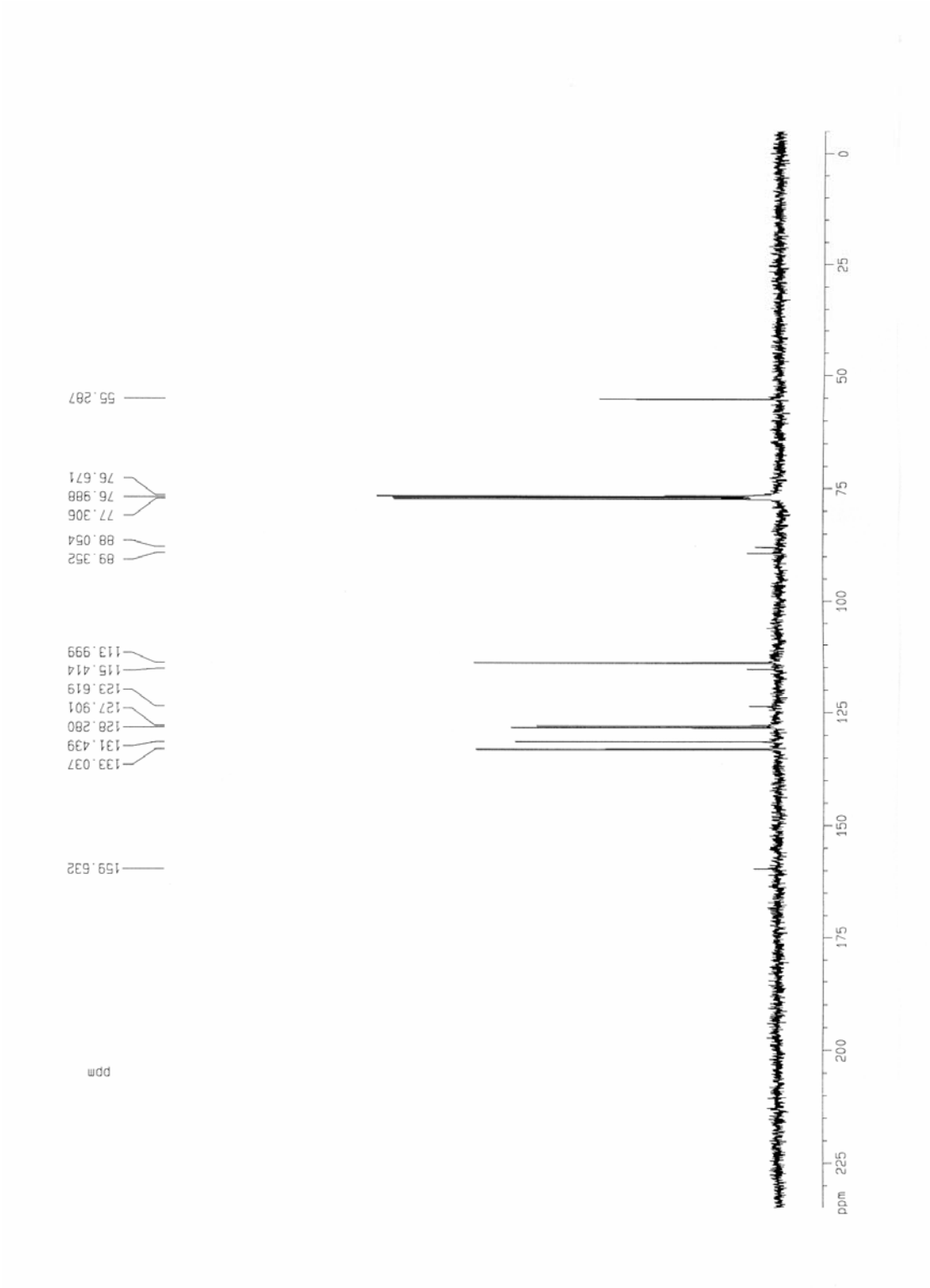

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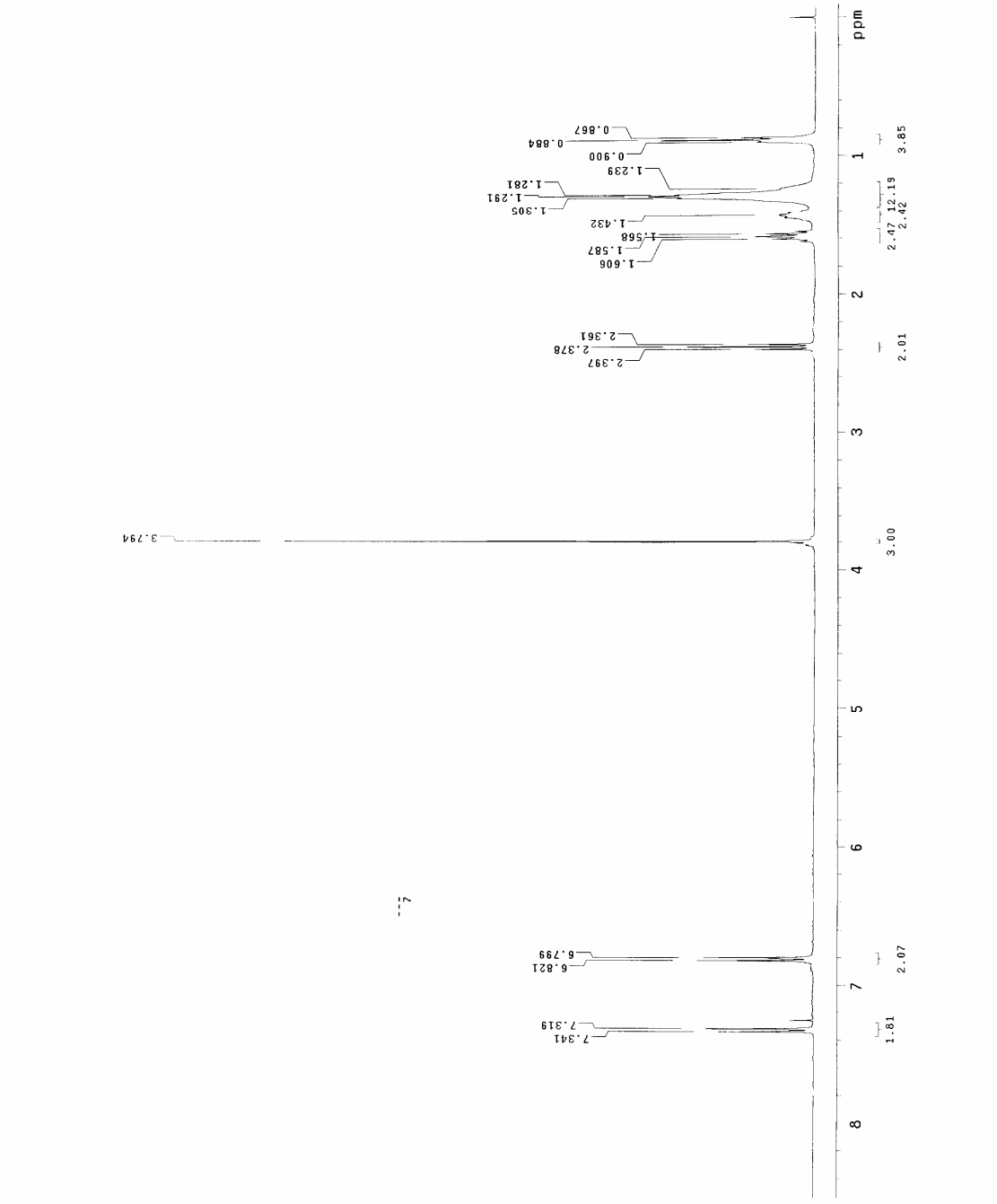

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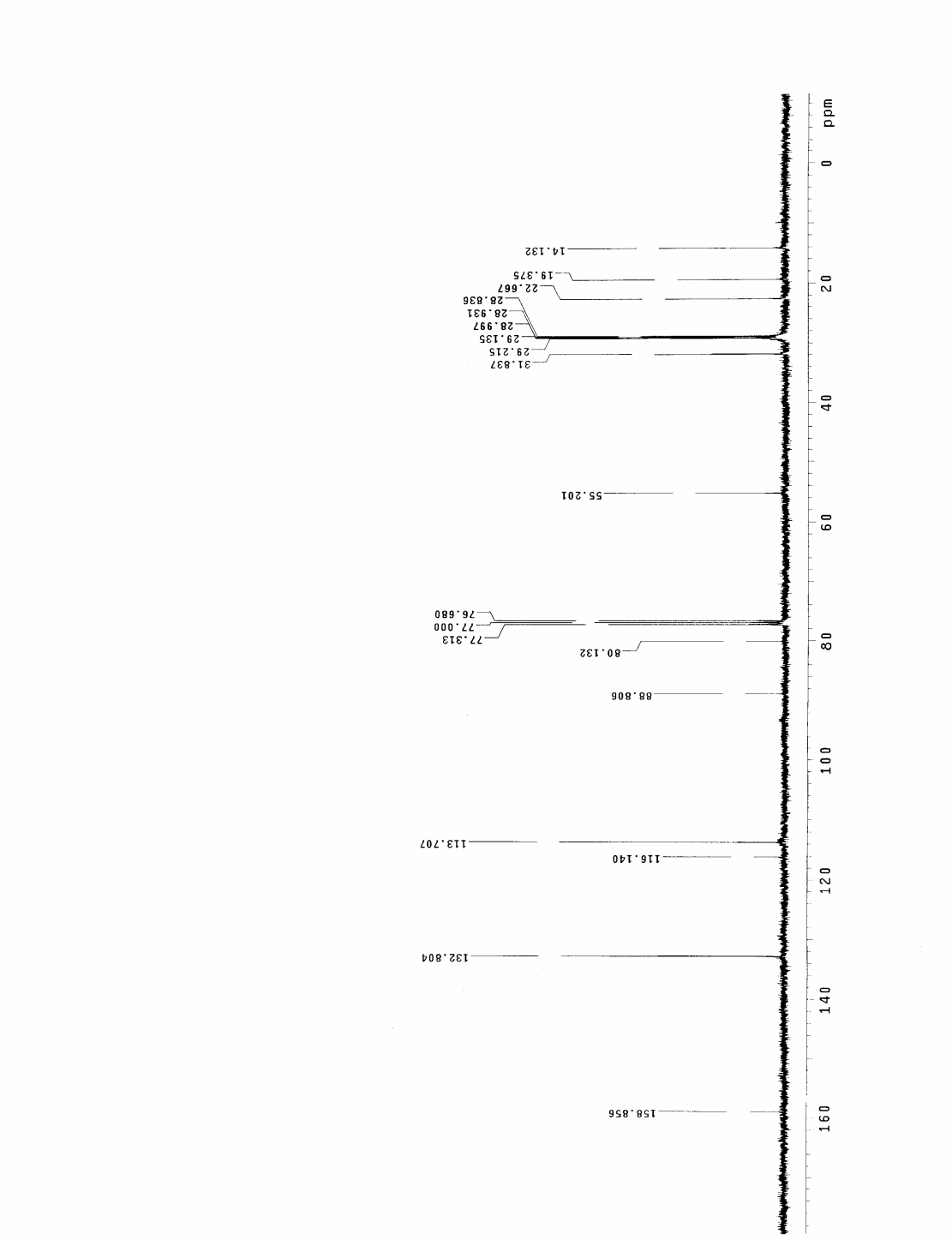

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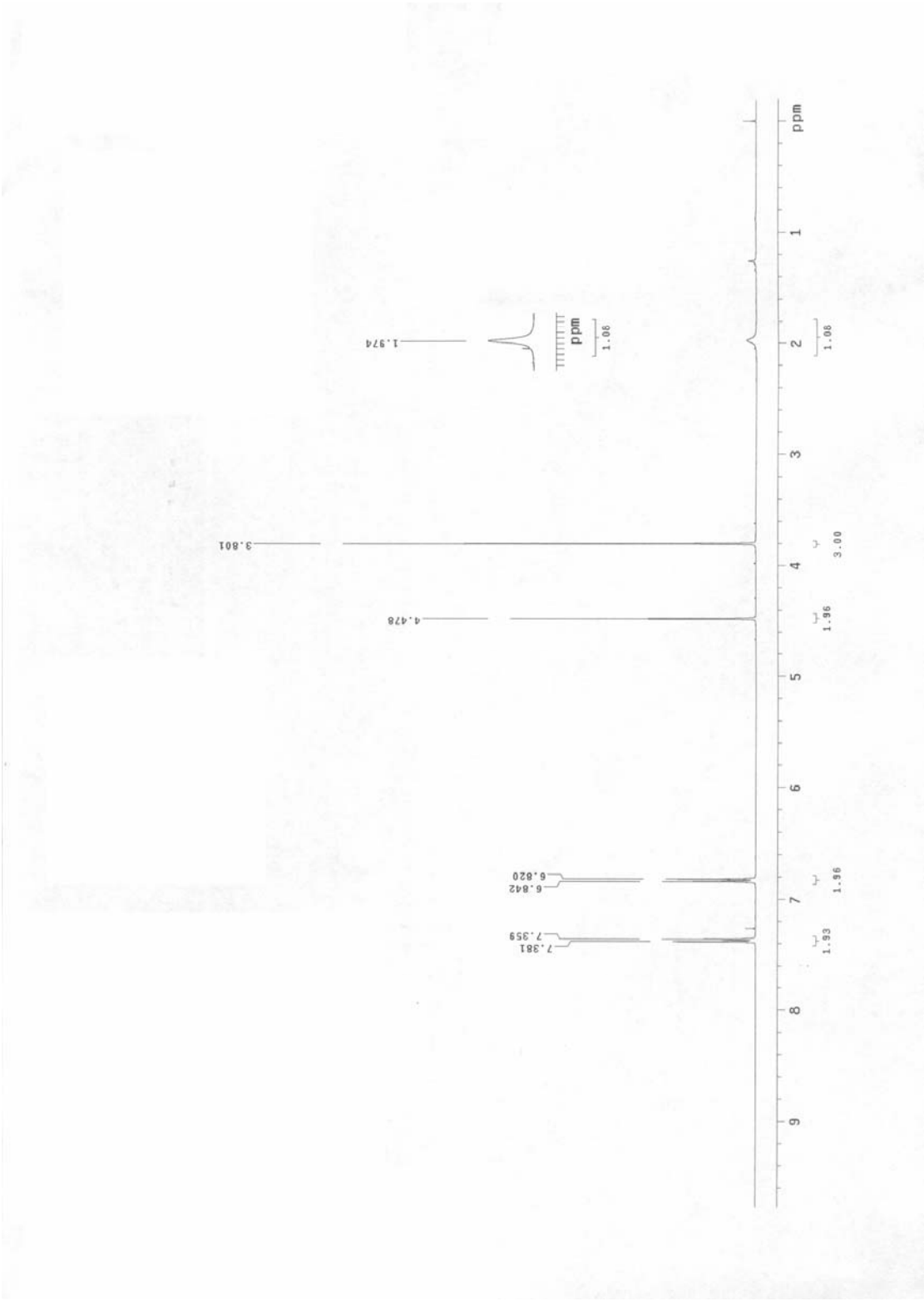

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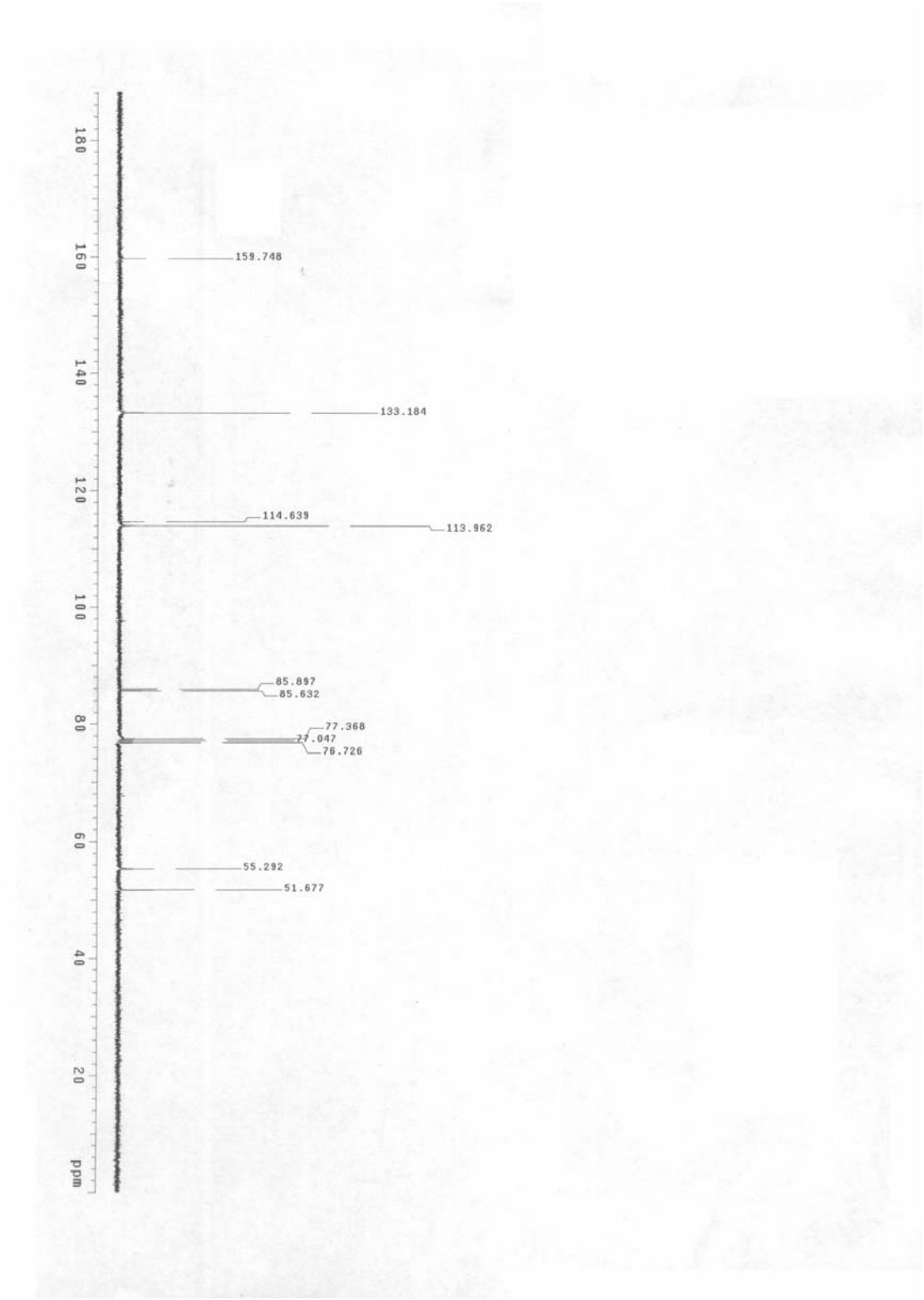

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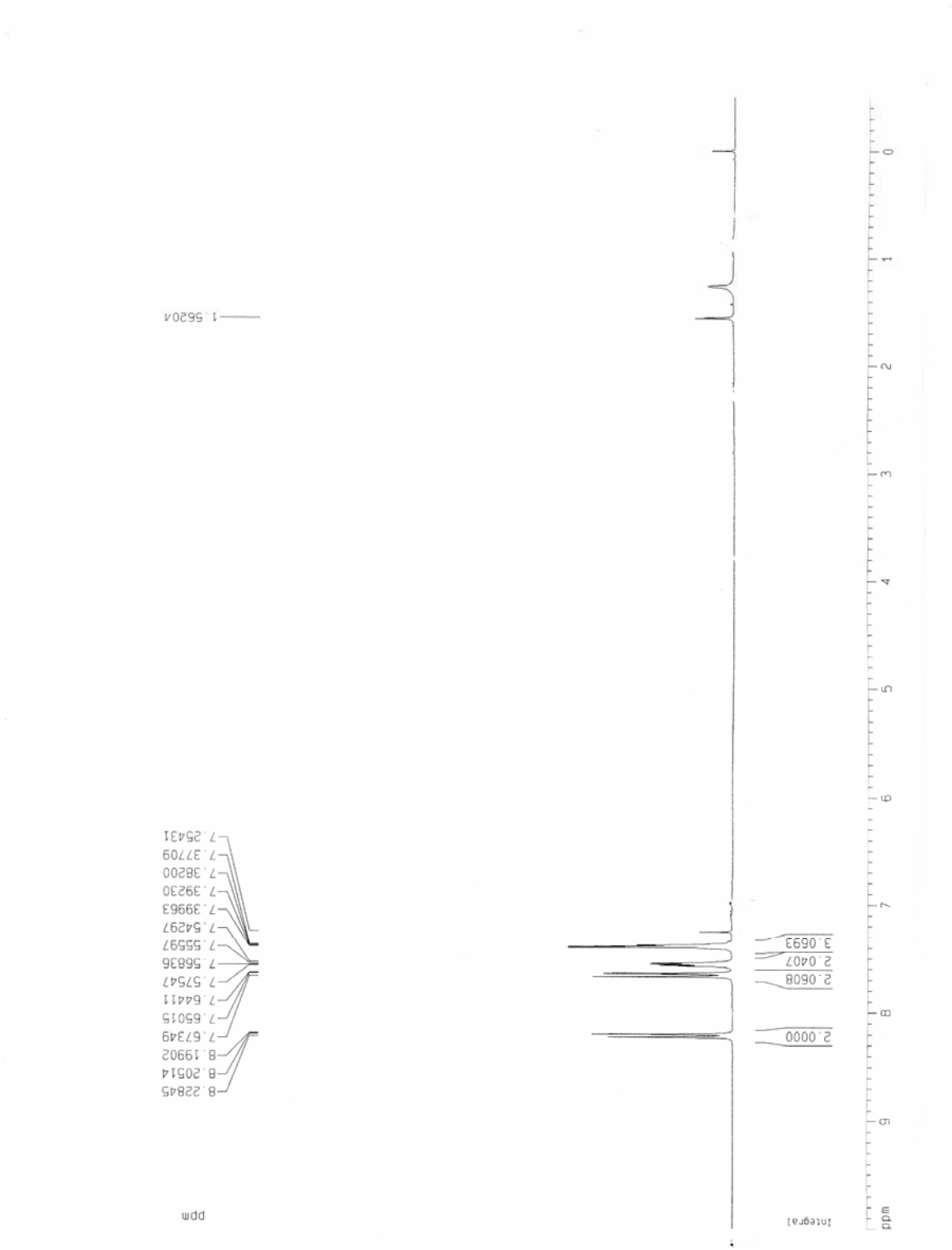

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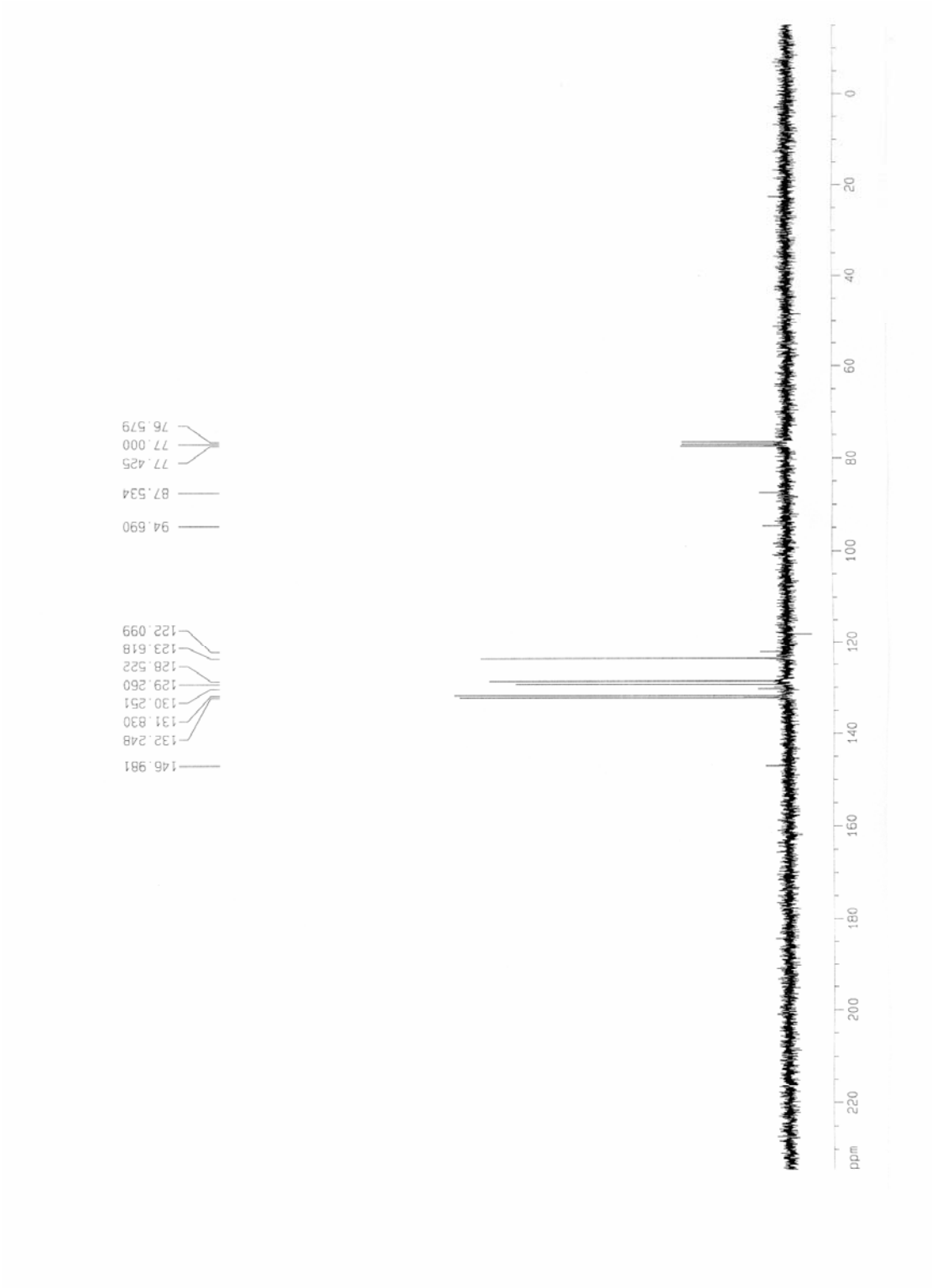

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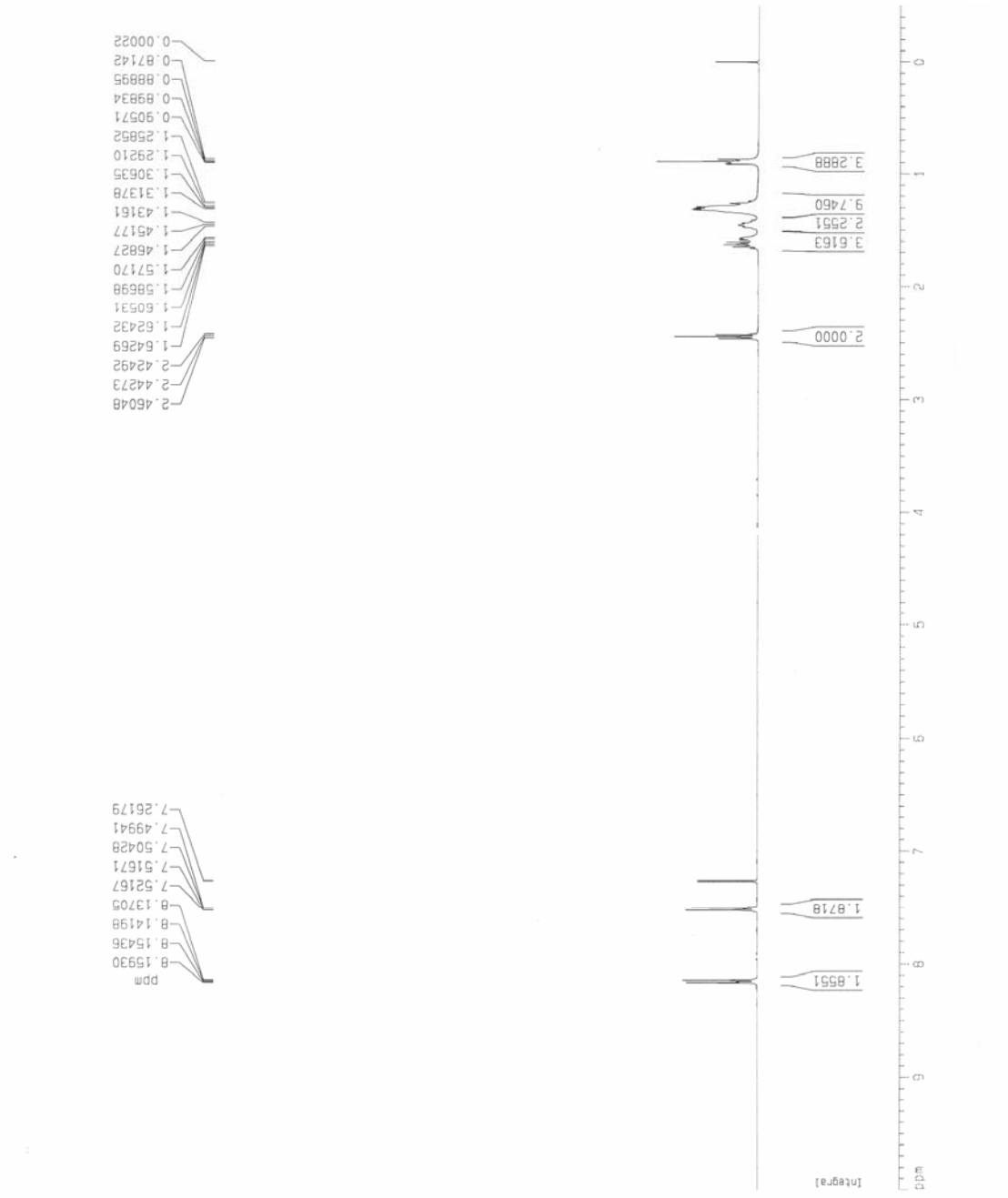

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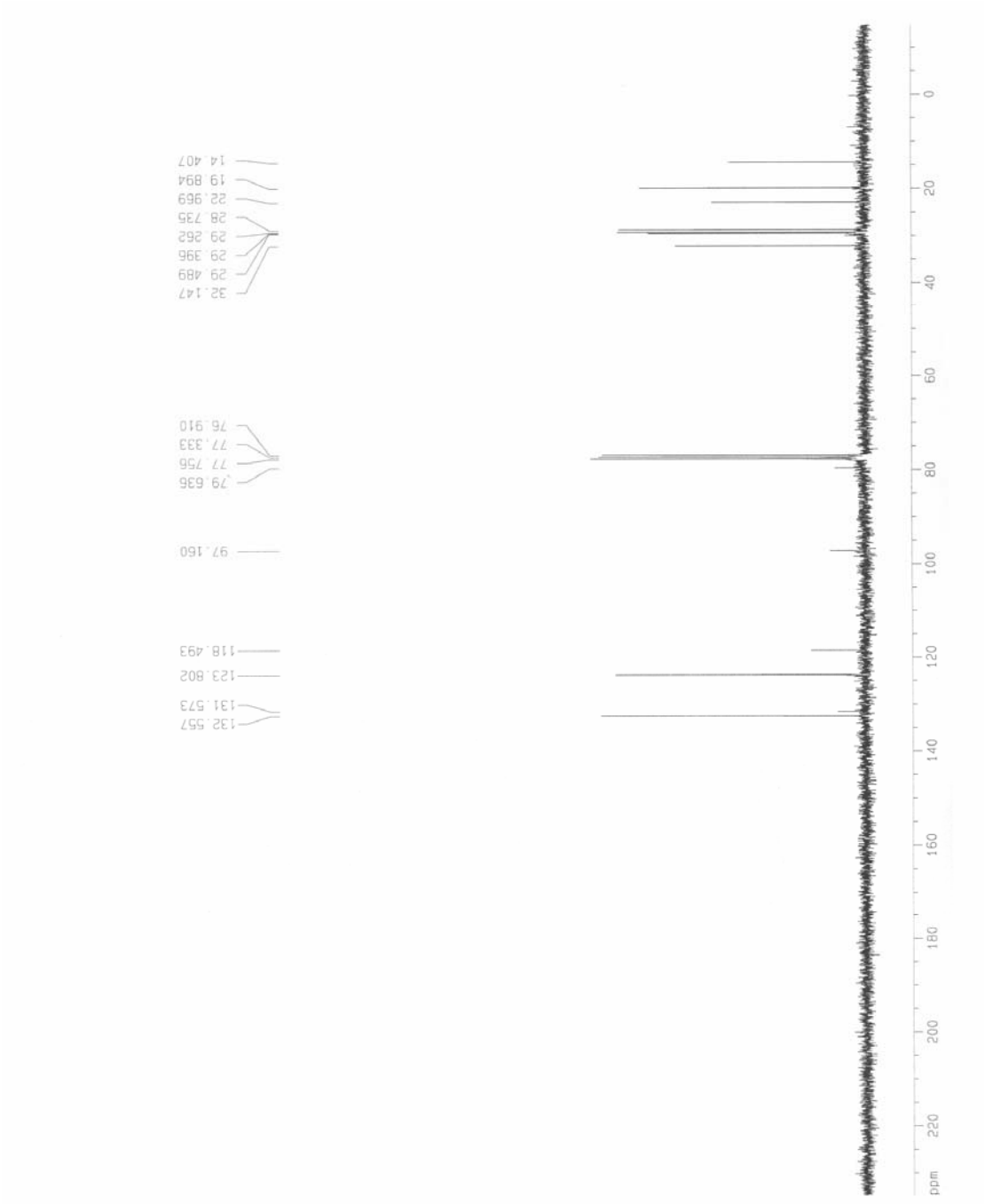

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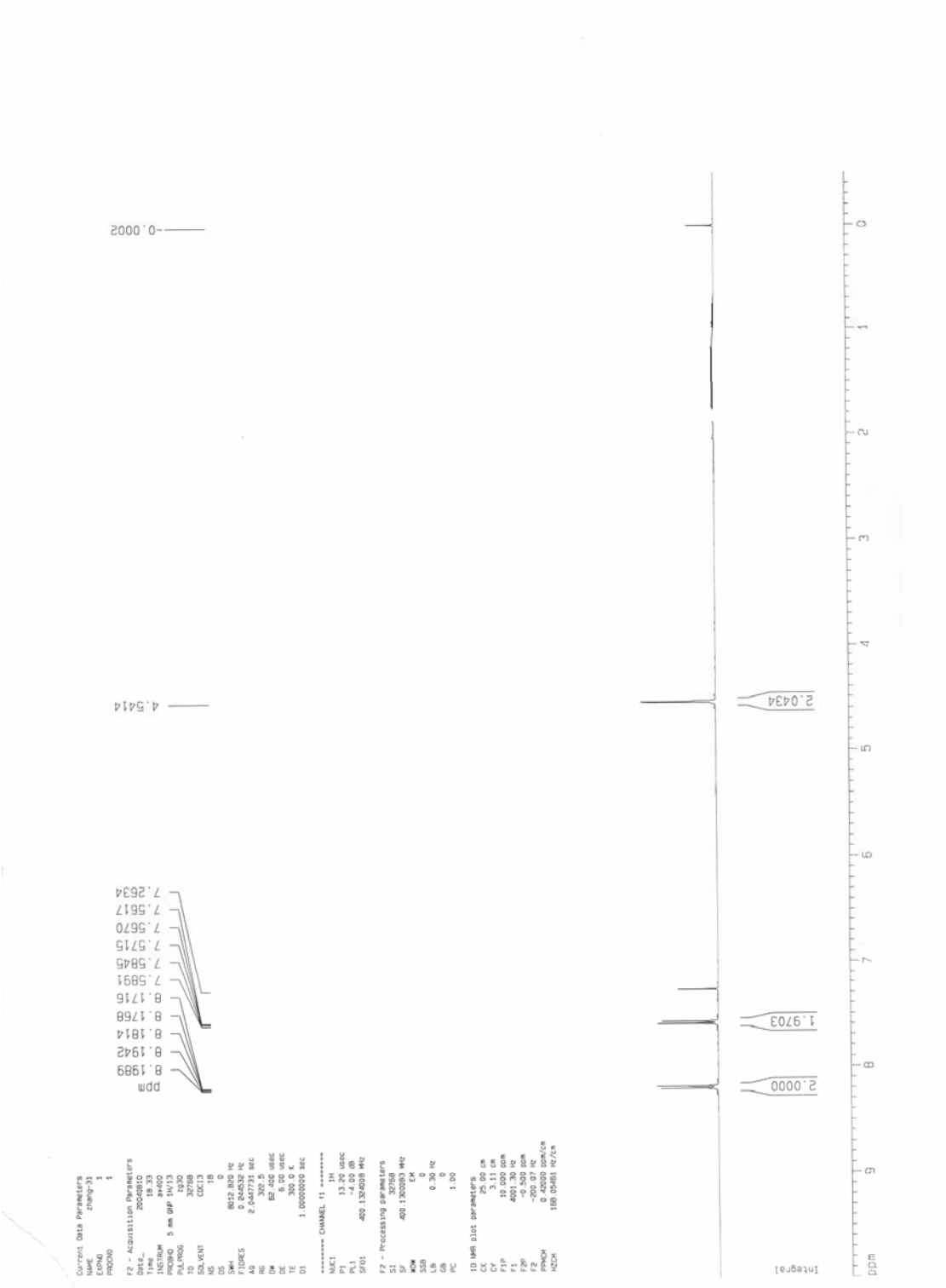

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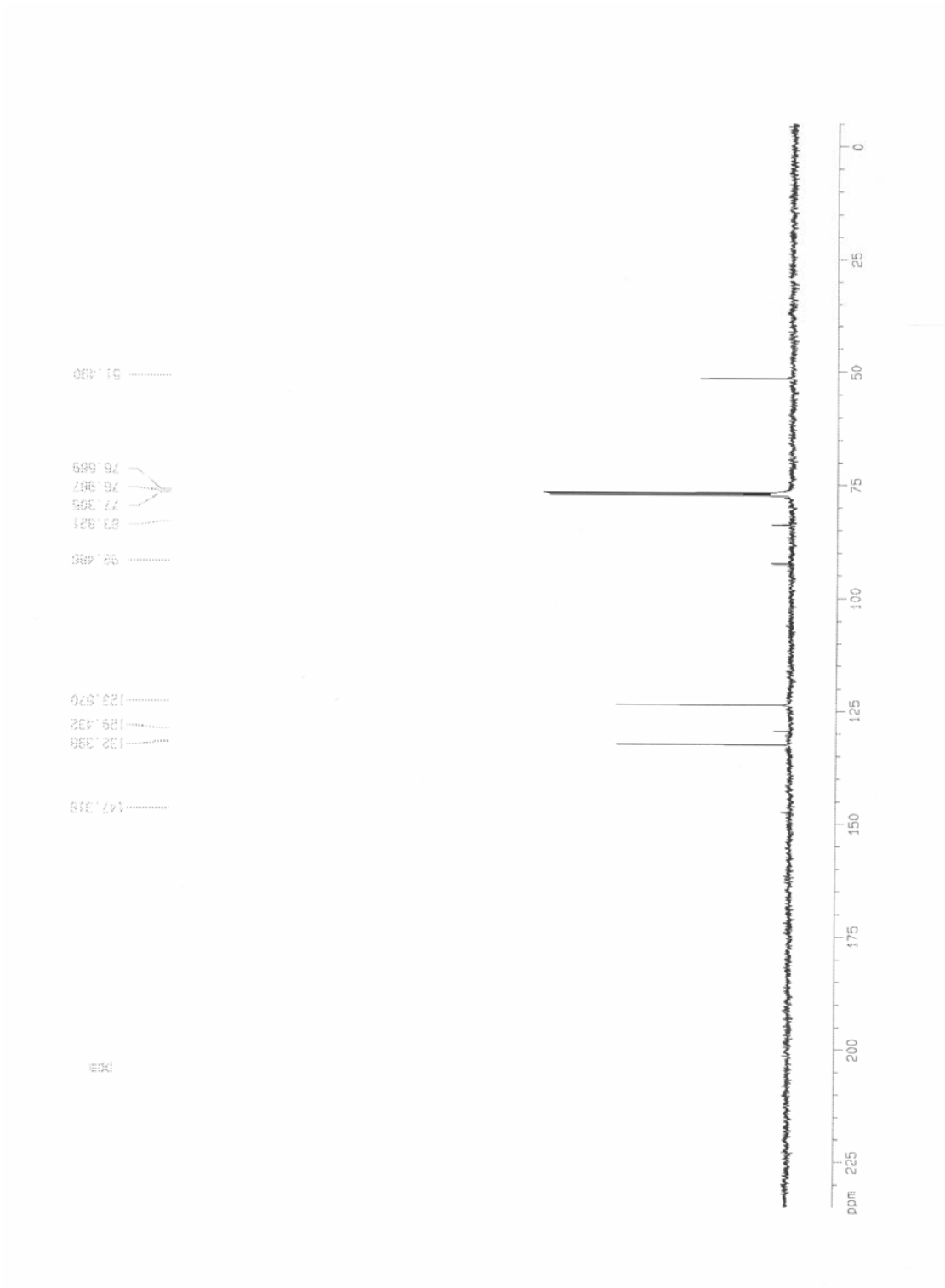
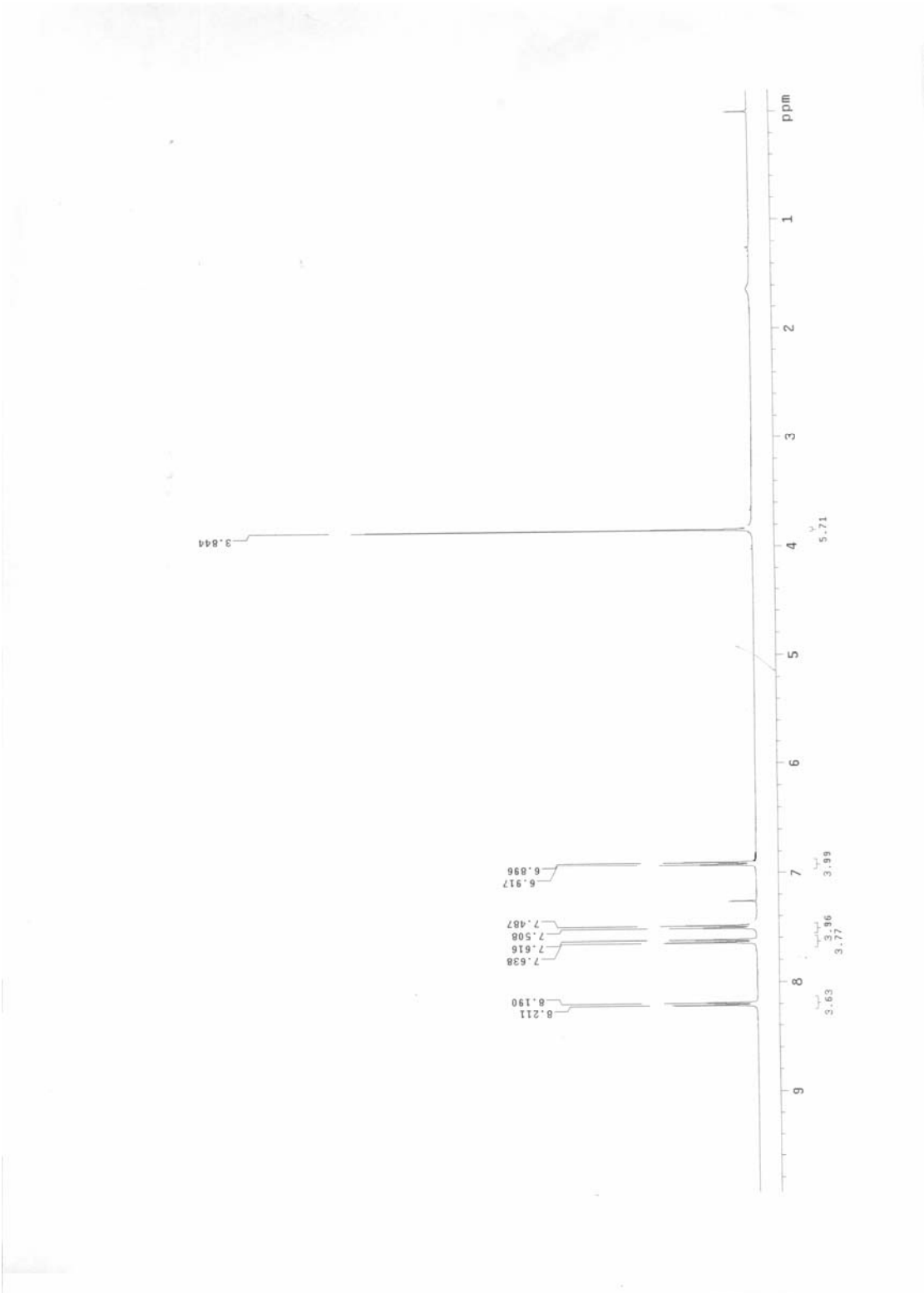


1-(2-(4-Methoxyphenyl)ethynyl)-4-nitrobenzene (9)



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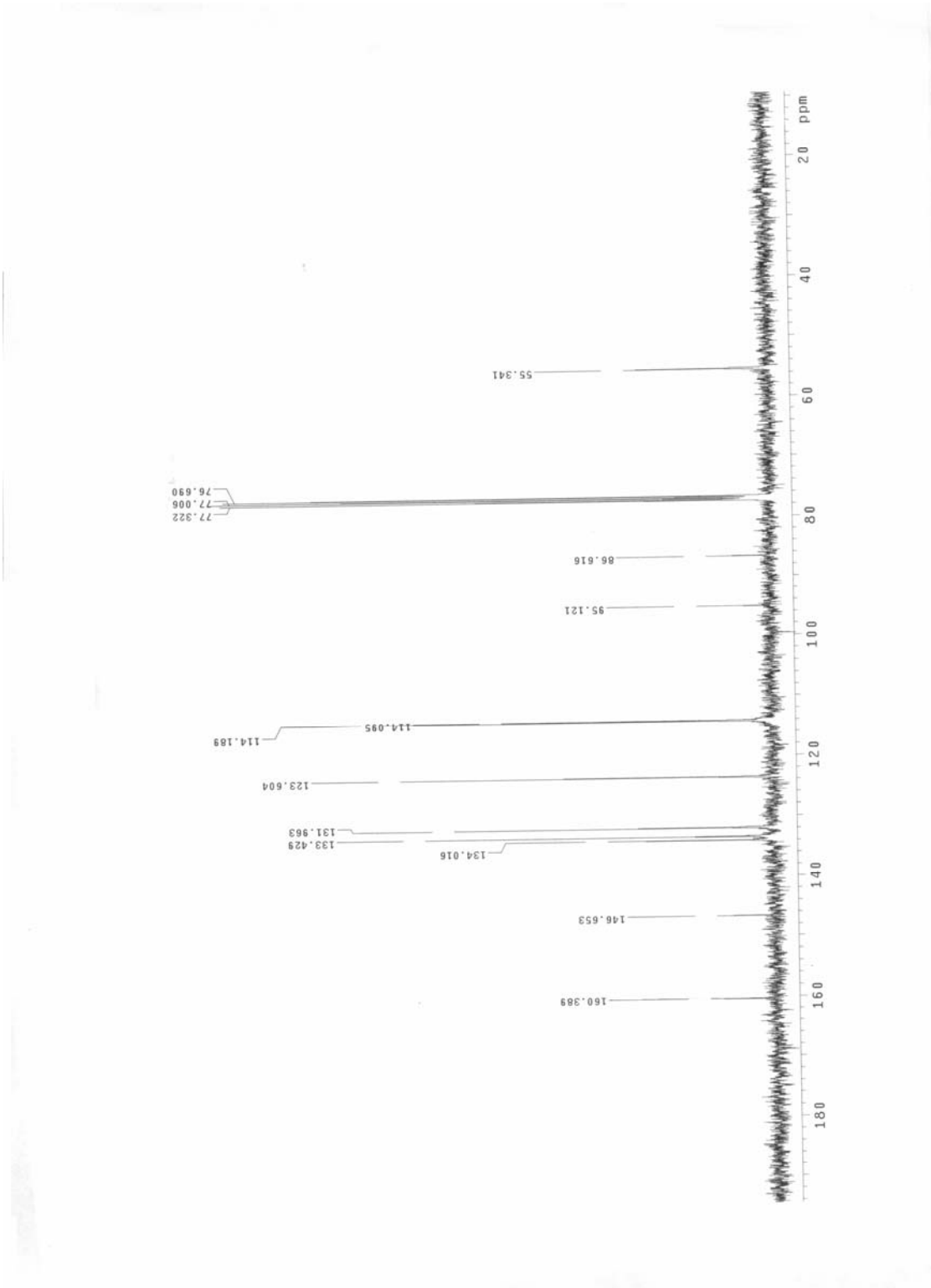

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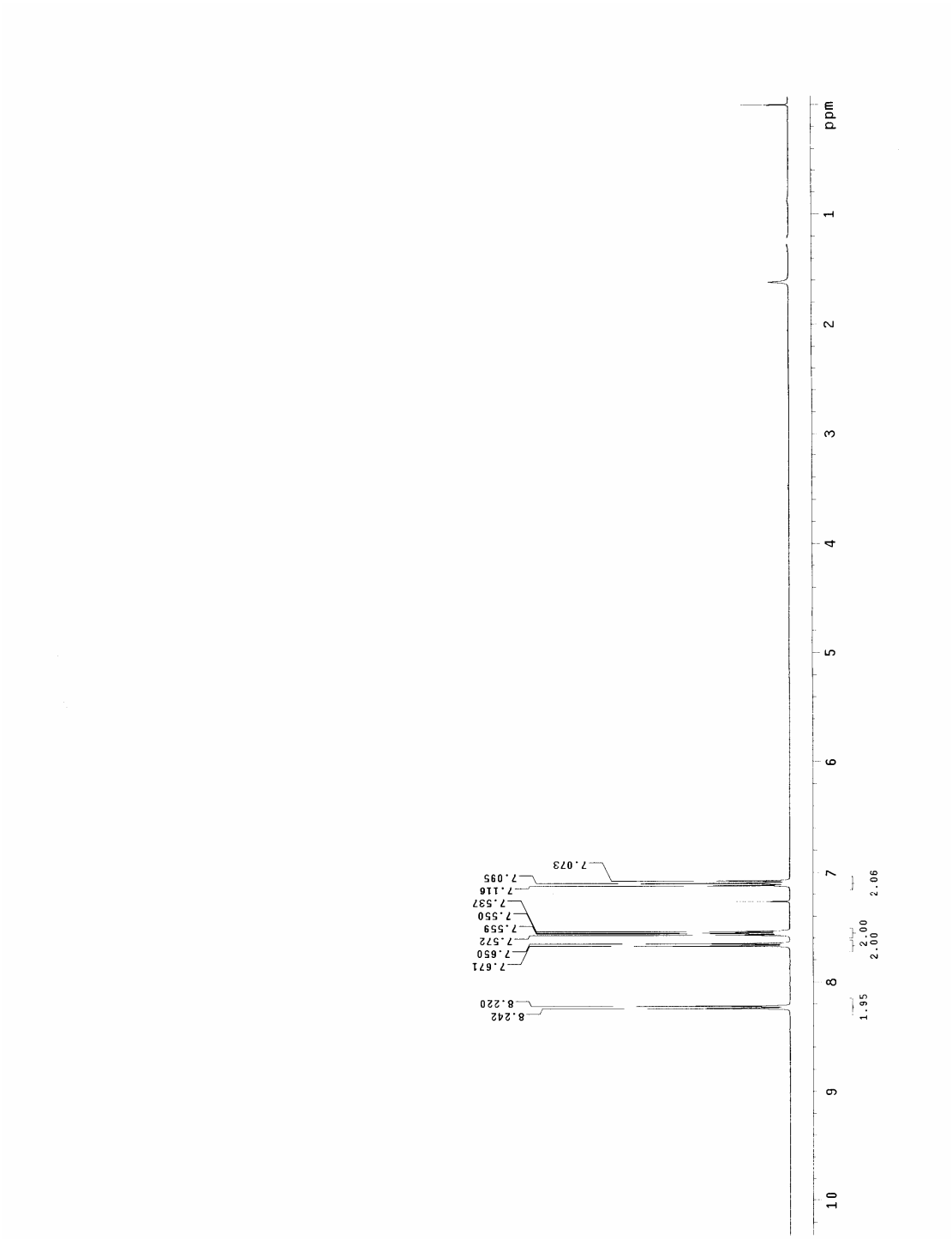

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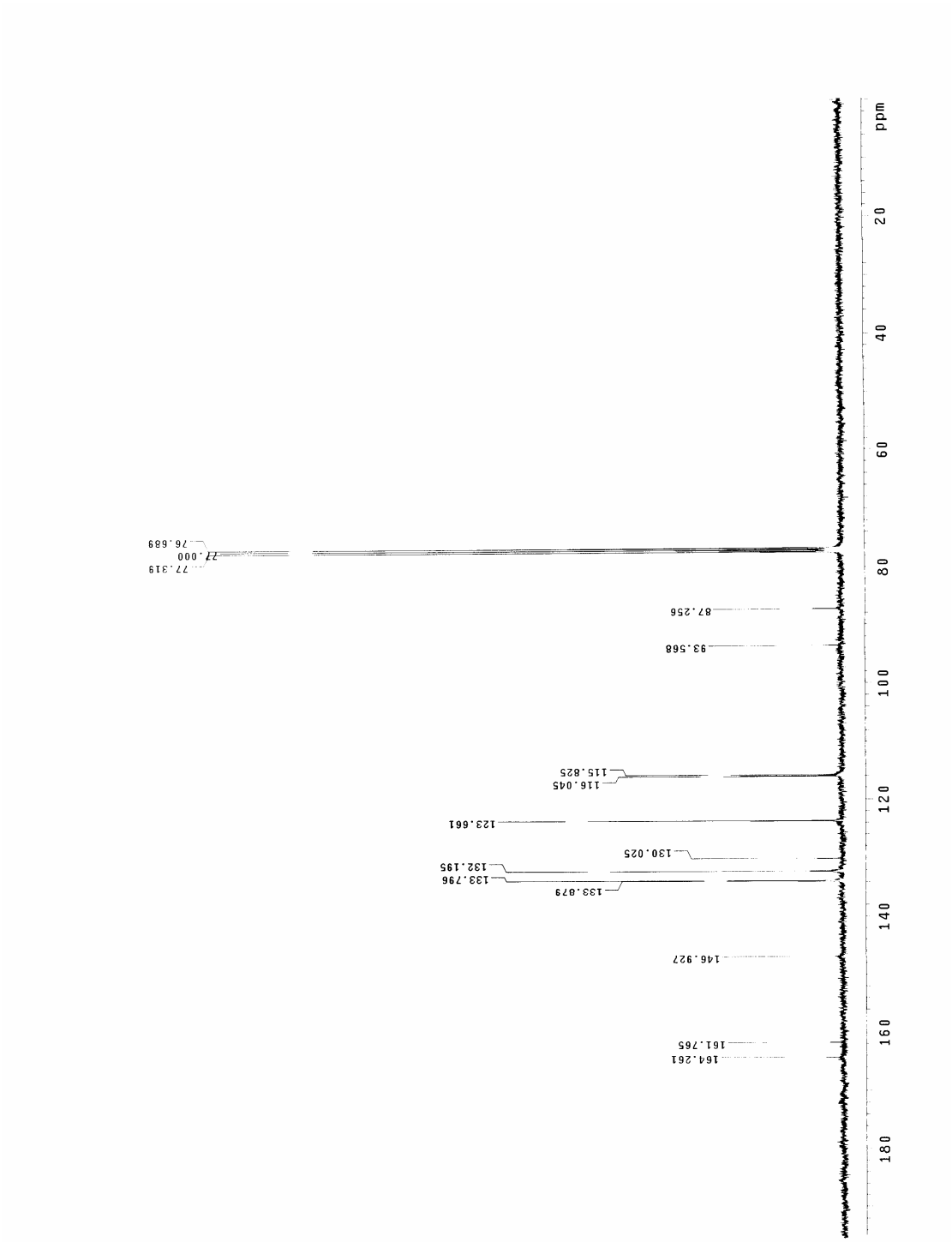
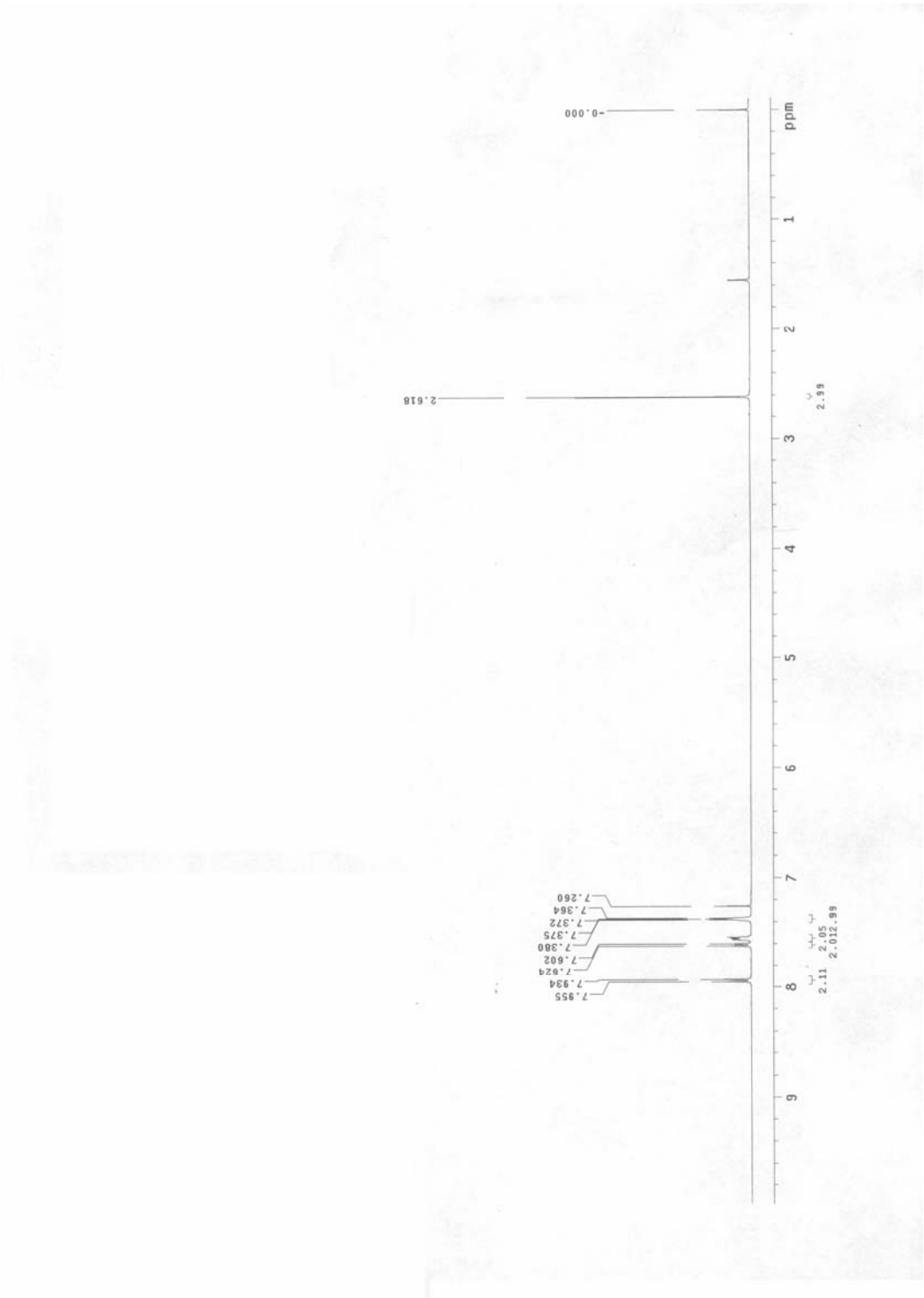


1-(4-(2-Phenylethynyl)phenyl)ethanone (11)



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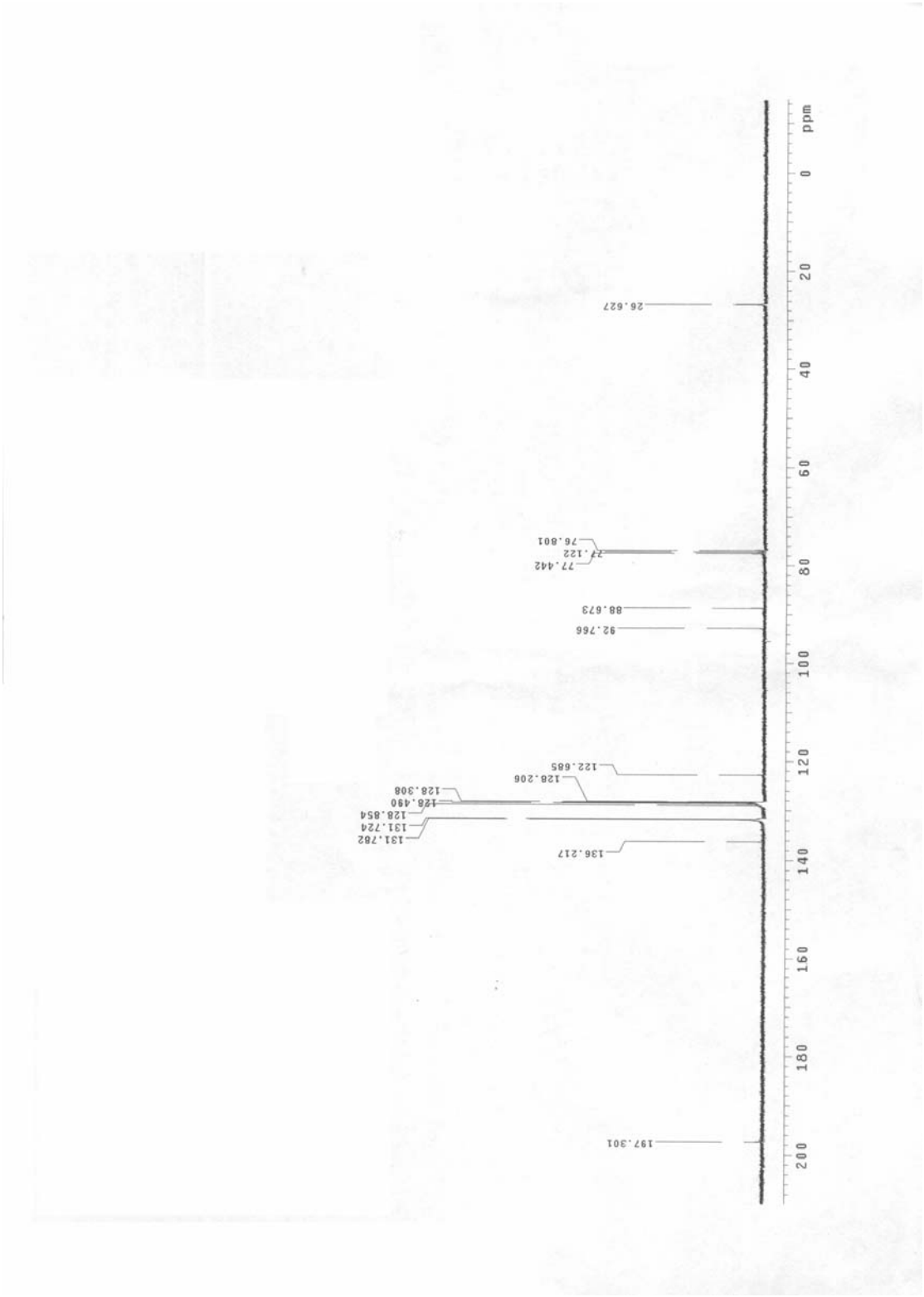

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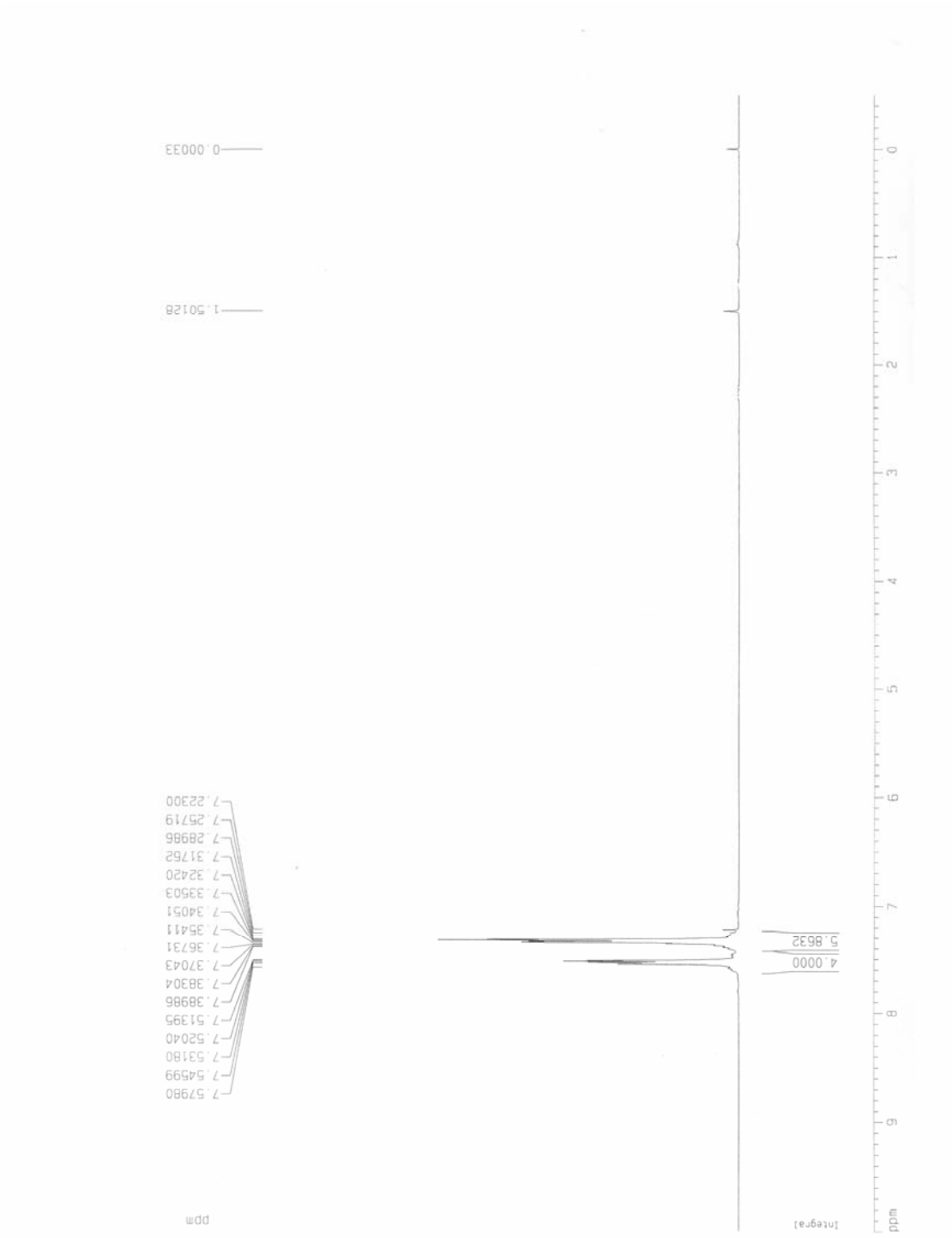

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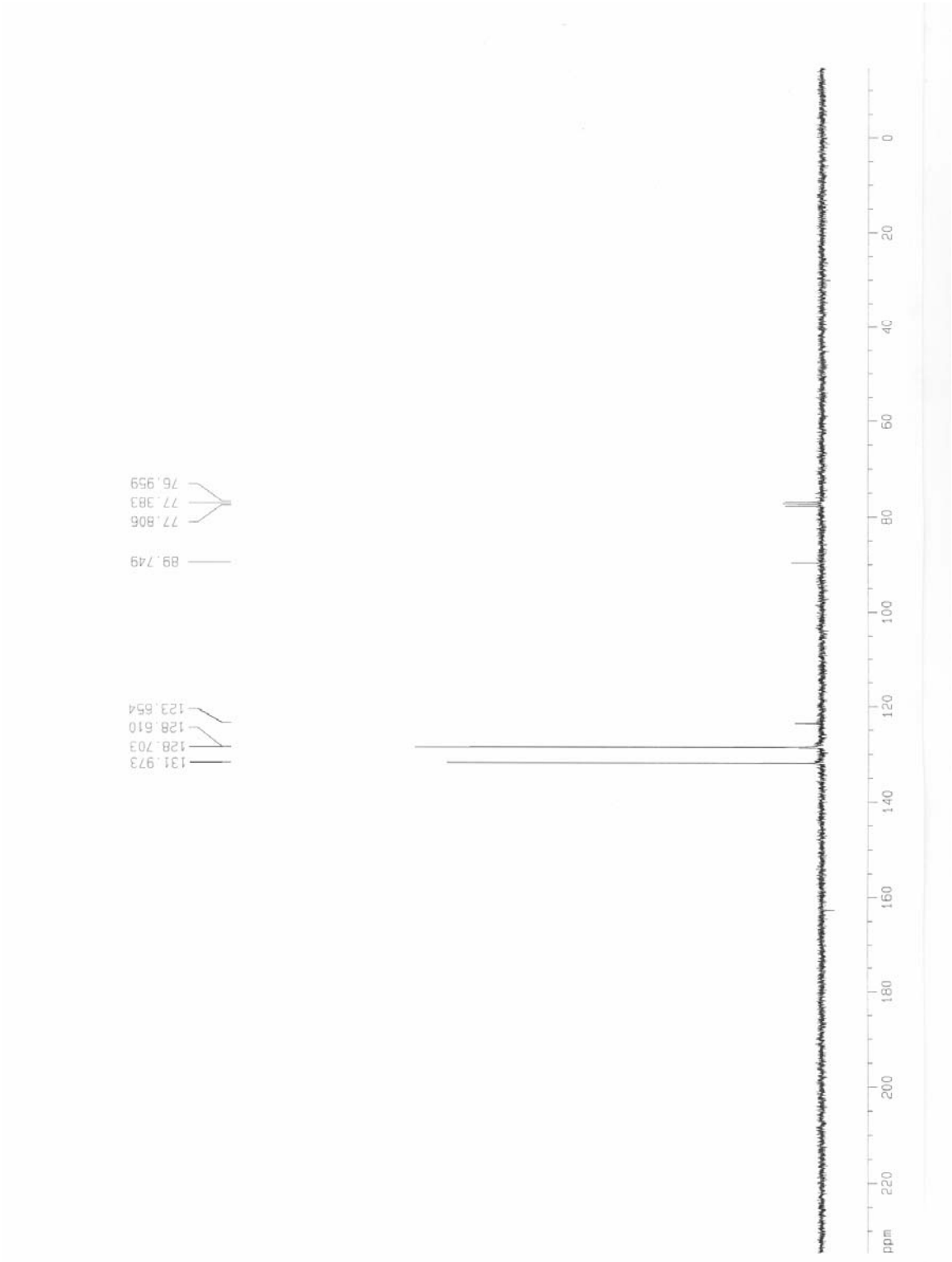
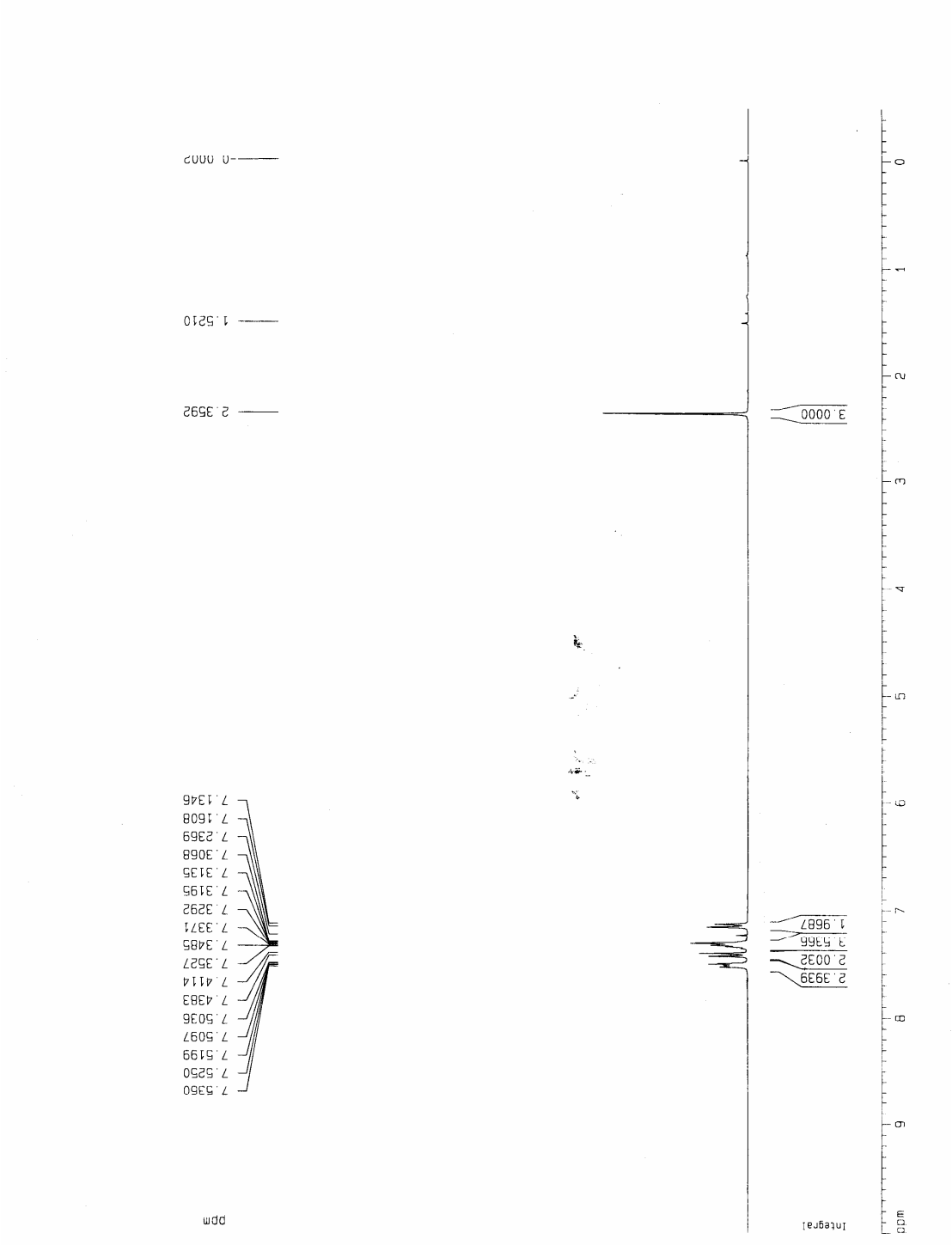


1-(2-*p*-Tolylethynyl)benzene (13)



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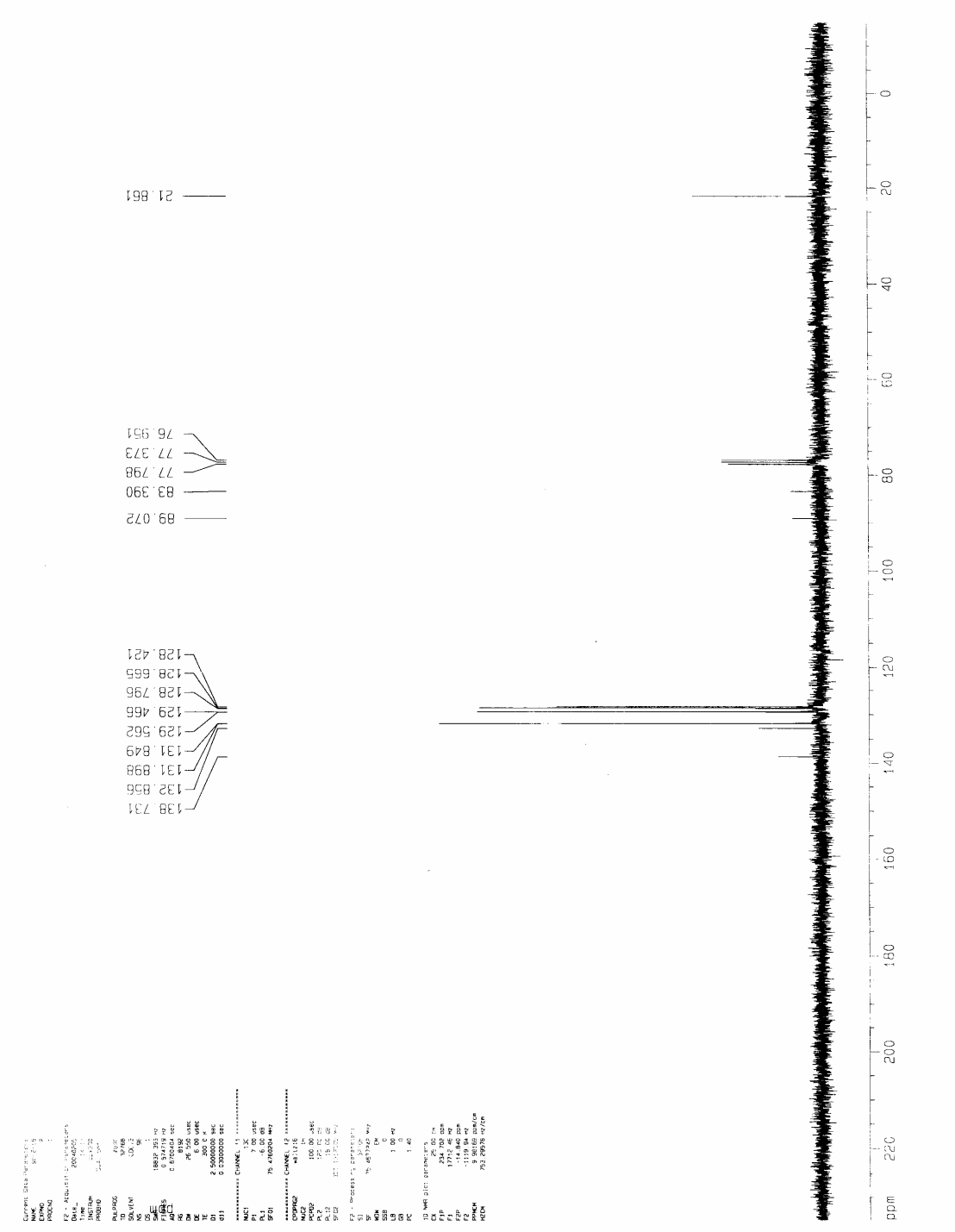

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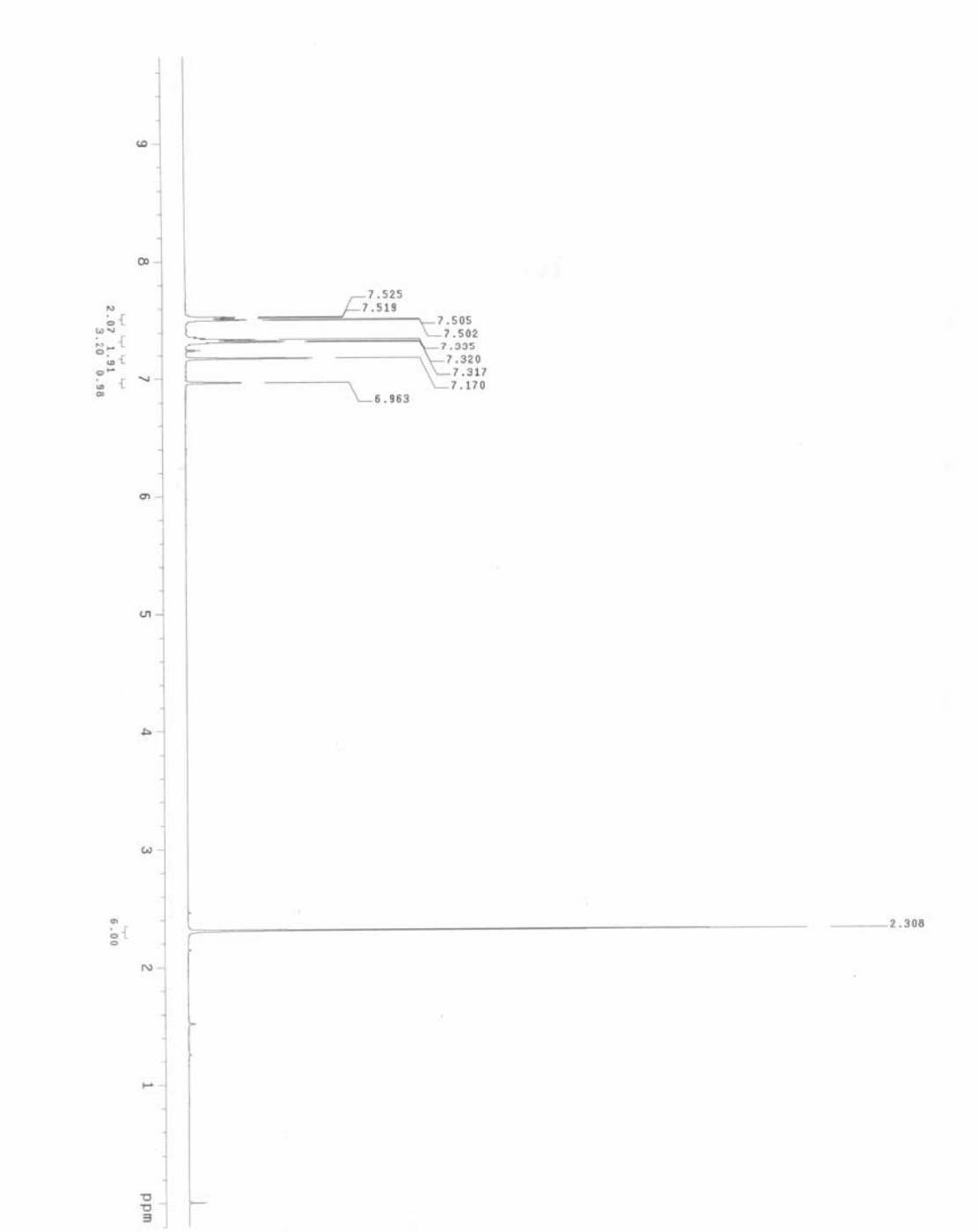

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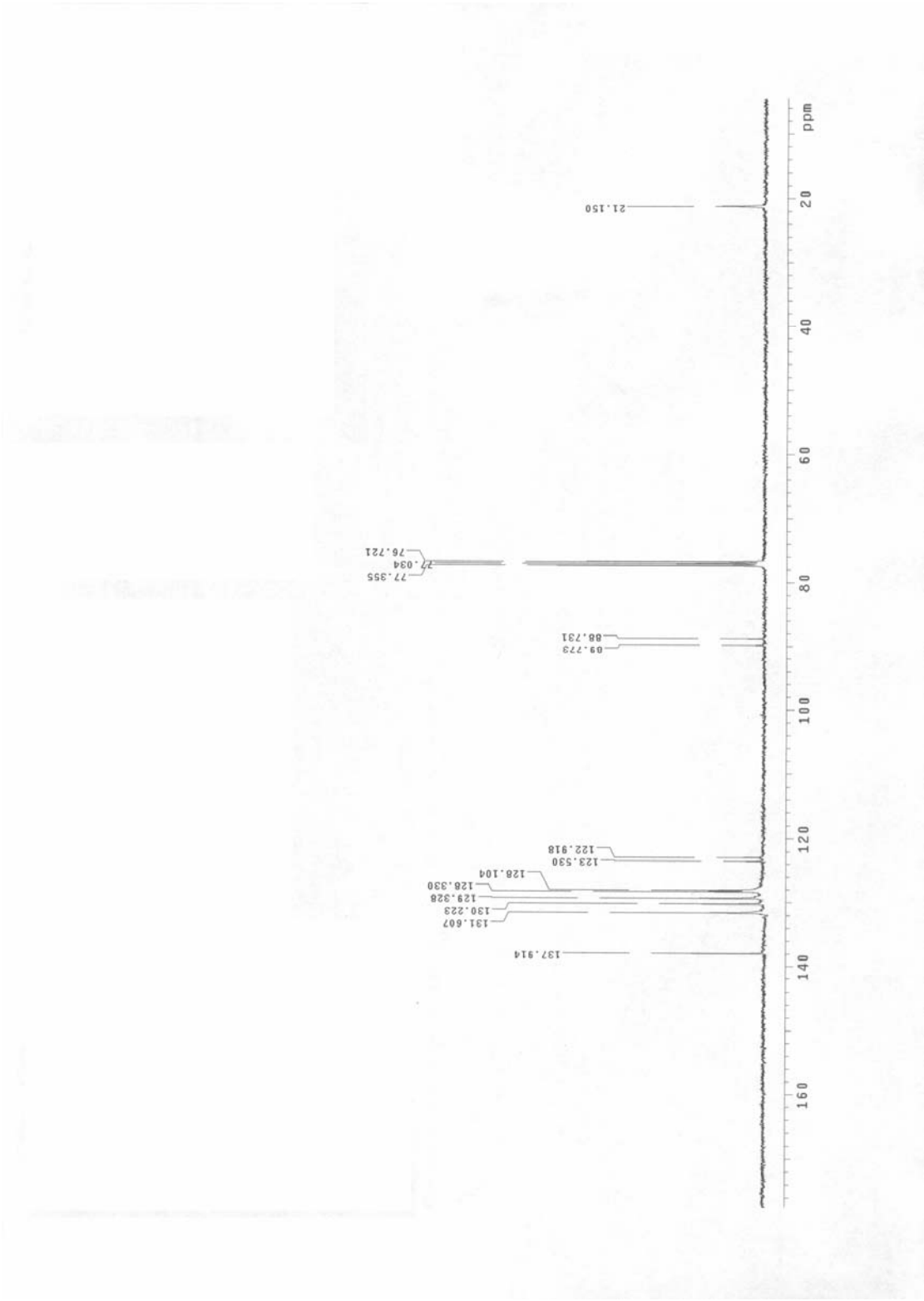

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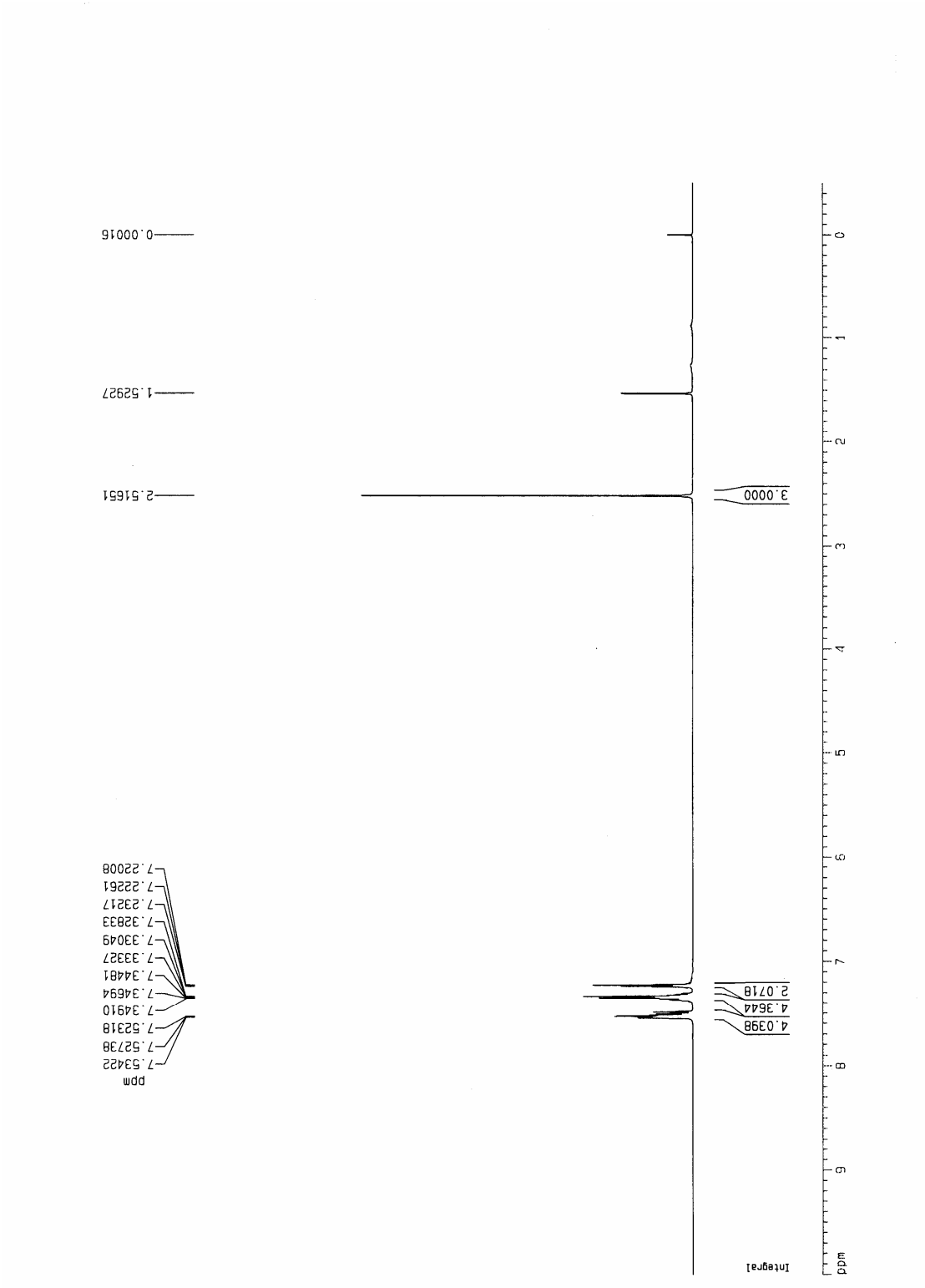

1-(2-*o*-tolylethynyl)benzene (15)