Electronic Supplementary Information

Copper(II)-Catalyzed Oxidative *N*-Nitrosation of Secondary and Tertiary Amines with Nitromethane Under an Oxygen Atmosphere

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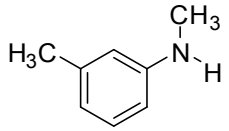
1. General Information

Nitromethane was distilled over $CaCl_2$ prior to use. All copper salts, metal catalysts, and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) were commercially available, and were used without further purification. Reactions were monitored via the TLC analysis of reaction aliquots. Thin-layer chromatography (TLC) was performed on silica gel 60 F254, and the components were located by observation under UV light. Column chromatography was also performed using silica gel. ^{1}H NMR spectra were measured at 500 (or 300) MHz using tetramethylsilane as an internal standard (0.00 ppm). ^{13}C NMR spectra were measured at 125 (or 75) MHz using the center peak of chloroform (77.0 ppm). High-resolution mass spectra were measured using NBA (3-nitrobenzylalchol) as a matrix.

2. Synthesis of *N*-methylaniline derivatives

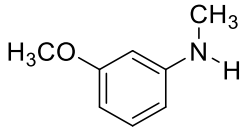
General procedure for the preparation of *N*-methylaniline derivatives (method A): To a screw-capped tube (30 mL) under air was successively added, a magnetic stirrer bar, an aryl halide (4 mmol), methylamine (1.7 mL, 20 mmol, a 40% aqueous solution), and copper(0) powder (12.7 mg, 0.200 mmol). The reaction mixture was stirred and heated at 100 ˚C. After the reaction, the reaction mixture was cooled to room temperature and ethyl acetate (20 mL) was added. The organic layer was separated and the aqueous layer was extracted by ethyl acetate (10 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane / ethyl acetate) to give the corresponding *N*-methylaniline derivative.[1)]

N-Methyl-*m*-toluidine [2)]



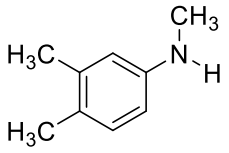
A yellow oil (628.2 mg, 52%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.81 (s, 3H), 3.54 (brs, 1H), 6.36-6.46 (m, 2H), 6.49-6.59 (m, 1H), 7.00-7.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 30.7, 109.6, 113.1, 118.2, 129.0, 138.9, 149.4; MS (EI) *m/z* 121 (M^+, 86), 120 (M^+−H, 100).

N-Methyl -*m*-anisidine [3)]



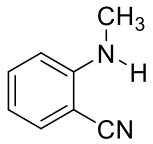
A yellow oil (508.6 mg, 74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.79 (s, 3H), 3.71 (brs, 1H), 3.76 (s, 3H), 6.15 (t, *J* = 2.4 Hz, 1H), 6.22 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.27 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 55.0, 98.2, 102.2, 105.6, 129.8, 150.7, 160.8; MS (EI) *m/z* 137 (M^+, 100).

***N*-Methyl-3,4-trimethylaniline** [4)]



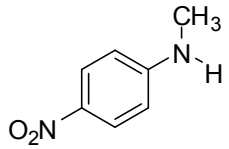
A yellow oil (830.2 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.20 (s, 3H), 2.78 (s, 3H), 3.40 (brs, 1H), 6.38 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 18.6, 20.0, 31.0, 109.8, 114.3, 125.2, 130.2, 137.2, 147.5; MS (FAB) *m/z* 135 (M^+, 36).

2-(Methylamino)benzonitrile [5)]



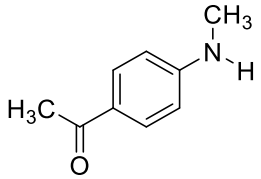
A white solid (602.7 mg, 46%): mp 69−70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (s, 3H), 4.66 (brs, 1H), 6.61-6.70 (m, 2H), 7.35-7.44 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 29.9, 95.4, 110.0, 117.9, 132.6, 134.3, 151.1; MS (FAB) *m/z* 132 (M^+, 18).

***N*-Methyl-*p*-nitroaniline** [2)]



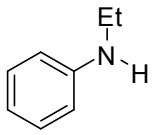
A yellow solid (180.7 mg, 30%): mp 149−150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.94 (d, *J* = 5.3 Hz, 3H), 4.66 (brs, 1H), 6.51-6.55 (m, 2H), 8.07-8.12 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.1, 110.7, 126.4, 137.8, 154.2; MS (FAB) *m/z* 153 (M^++H, 24).

***N*-Methyl-*p*-aminoacetophenone** [2)]



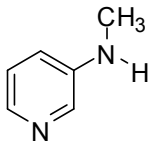
A white solid (345.4 mg, 58%): mp 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (s, 3H), 2.89 (d, *J* = 5.3 Hz, 3H), 4.42 (brs, 1H), 6.53-6.60 (m, 2H), 7.81-7.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 30.0, 110.9, 126.4, 130.7, 153.1, 196.4; MS (FAB) *m/z* 150 (M^++H, 100), 149 (M^+, 69).

_N_-Ethylaniline [6)]



A yellow oil (998.5 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H), 3.13 (q, J = 7.2 Hz, 2H), 3.36-3.59 (brs, 1H), 6.55-6.62 (m, 2H), 6.65-6.71 (m, 1H), 7.13-7.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 38.4, 112.7, 117.1, 129.2, 148.4; MS (EI) *m/z* 121 (M^+, 76), 106 (M^+−15, 100).

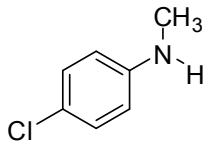
3-(Methylamino)pyridine [7)]



A yellow oil (925.8 mg, 86%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.85 (s, 3H), 3.86 (brs, 1H), 6.84-6.89 (m, 1H), 7.07-7.12 (m, 1H), 7.94-7.98 (m, 1H), 8.01-8.04 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.0, 117.8, 123.5, 135.5, 138.2, 145.1; MS (EI) *m/z* 108 (M^+, 100).

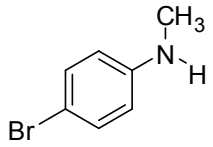
General procedure for the preparation of _N_-methylaniline derivatives (method B): An aniline derivative (4.06 mmol) was added to a suspension of NaOMe (1.09 g, 20.3mmol) in MeOH (6 mL). The resulting solution was poured into the suspension of paraformaldehyde (170 mg, 5.70 mmol) in MeOH (4 mL). The reaction mixture was stirred for 5 h at room temperature, and $NaBH_4$ (153 mg, 4.06 mmol) was then added. The solution was refluxed for 1.75 h. After the removal of the solvent under reduced pressure, the reaction mixture was treated with 1 M of KOH aqueous solution (20 mL). After extraction with Et_2O (20 mL x 2), the combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane /ethyl acetate) to give the corresponding *N*-methylaniline derivative.[8)]

_N_-Methyl-_p_-chloroaniline [3)]



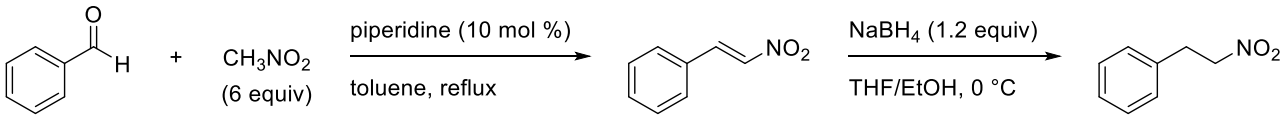
A yellow oil (350.6 mg, 61%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.78 (s, 3H), 3.68 (brs, 1H), 6.50 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 113.3, 121.6, 128.9, 147.8; MS (EI) *m/z* 140 (M^+−H, 100), 141 (M^+, 96), 143 (M^++2, 32).

***N*-Methyl-*p*-bromoaniline** [3)]



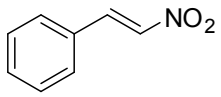
A yellow oil (415.6 mg, 45%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.76 (s, 3H), 3.70 (brs, 1H), 6.45 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 108.6, 113.8, 131.7, 148.2; MS (EI) *m/z* 185 (M^+, 100), 106 (M^++2, 96).

3. General procedure for the preparation of 1-phenyl-2-nitroethane



To a round-bottomed flask (300 mL) was successively added, a magnetic stirrer bar, benzaldehyde (6.36 g, 60.0 mmol), nitromethane (22.0 g, 360 mmol), piperidine (510 mg, 6.00 mmol), toluene (10 mL), and anhydrous $FeCl_3$ (584 mg, 6.00 mmol). The reaction mixture was refluxed for 4 h. After completion of the reaction, the mixture was cooled to room temperature. The excess solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: hexane /ethyl acetate) to afford (*E*)-*β*-nitrostyrene.[9)]

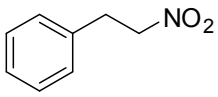
(*E*)-*β*-Nitrostyrene [9)]



A yellow solid (5.8 g, 64%): mp 58−59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.65 (m, 7H), 7.95-8.07 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 129.1, 129.4, 130.0, 132.1, 137.1, 139.0; MS (EI) *m/z* 149 (M^+, 78), 77 (M^+−72, 100).

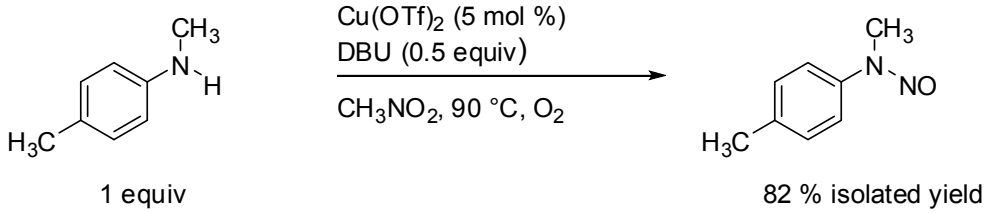
To a flame-dried round-bottomed flask (300 mL) was successively added, a magnetic stirrer bar, $NaBH_4$ (1.8 g, 48 mmol) and THF/EtOH (60 mL: v/v = 3/1). Then, THF solution (60 mL) containing (*E*)-*β*-nitrostyrene (6.0 g, 40 mmol) produced by the above procedure was added dropwise over 20 min at 0 ˚C. The solution was then stirred at 0 °C for a further 12 h. After the reaction, the reaction mixture was quenched with a saturated NH_4Cl solution and extracted with CH_2Cl_2 (20 mL x 3). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (eluent: hexane / ethyl acetate) to give 1-phenyl-2-nitroethane.[10)]

1-Phenyl-2-nitroethane [10)]



A colorless oil (2.9 g, 48%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.22 (t, 2H, *J* = 7.4 Hz), 4.51 (t, 2H, *J* = 7.4 Hz), 7.02-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4, 76.2, 127.4, 128.5, 128.9, 135.6. MS (EI) *m/z* 151 (M^+, 10).

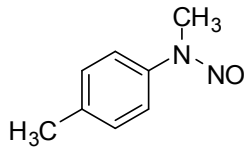
4. General procedure for the nitrosation of secondary or tertiary amines



1 equiv — 82 % isolated yield

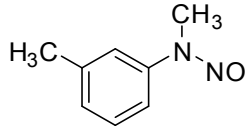
To a freshly distilled nitromethane solution (0.6 ml) in a sealed tube under an O_2 atmosphere were successively added a magnetic stirrer bar, $Cu(OTf)_2$ (0.0500 mmol, 10.9 mg), and DBU (0.300 mmol, 44.9 μL). After the addition of DBU, the color of the reaction mixture turned from green to brown. An amine (0.6 mmol) was then added. During the stirring of the reaction mixture under the conditions shown in the text, the reaction was monitored by TLC. After the reaction time shown in Schemes 1-3, the reaction mixture was directly subjected to a silica gel slurry filled in a column tube without a common work-up. The crude product was purified by a common silica gel chromatography (eluent: a mixture of hexane / ethyl acetate) to afford the nitrosamine product.

***N*-Methyl-*N*-*p*-tolylnitrosamine (1a)** [11)]



A yellow oil (73.9 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.44 (s, 3H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 31.7, 119.2, 129.9, 137.3, 139.9; MS (FAB) *m/z* 151 (M^++H, 100), 121 (M^+−29, 50).

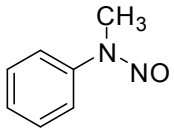
***N*-Methyl-*N*-*m*-tolylnitrosamine (2a)** [11)]



A yellow oil (57.7 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.44 (s, 3H), 7.18 (d, *J* =

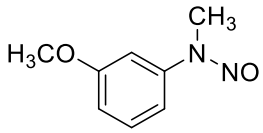
7.1 Hz, 1H), 7.29-7.44 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 31.5, 116.3, 119.9, 128.0, 129.2, 139.5, 142.2; MS (FAB) *m/z* 151 (M^++H, 100), 120 (M^+−30, 98).

_N_-Methyl- _N_-nitrosaniline (3a) [12)]



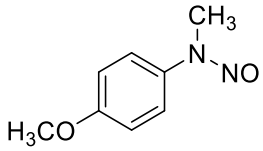
A yellow oil (63.1 mg, 77%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46 (d, *J* = 1.6 Hz, 3H), 7.34-7.39 (m, 1H), 7.45-7.51 (m, 2H), 7.52-7.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.4, 119.1, 127.2, 129.4, 142.2; MS (FAB) *m/z* 106 (M^+−30, 20).

_N_-Methyl-_m_-methoxy-_N_-nitrosaniline (4a) [11)]



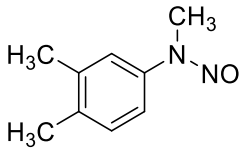
A brown oil (77.7 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 3.86 (s, 3H), 6.88-6.92 (m, 1H), 7.07-7.11 (m, 1H), 7.14-7.18 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 31.5, 116.3, 119.9, 128.0, 129.2, 139.5, 142.2; MS (EI) *m/z* 167 (M^++1, 18), 136 (M^+−30, 60).

_N_-Methyl-_p_-methoxy-_N_-nitrosaniline (5a) [11)]



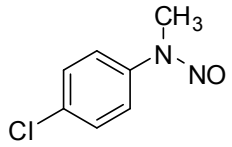
A brown solid (69.1 mg, 70%): mp 41−42 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 3.85 (s, 3H), 6.99 (d, *J* = 9.2 Hz, 2H), 7.44 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.2, 55.5, 114.5, 121.1, 135.6, 158.9; MS (FAB) *m/z* 167 (M^++H, 50), 136 (M^+−30, 100).

_N_-(3,4-dimethylphenyl)-_N_-methylnitrous amide (6a)



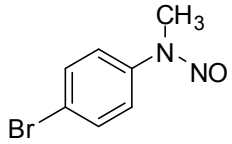
A yellow oil (90.0 mg, 91%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.33 (s, 3H), 3.44 (s, 3H), 7.19-7.26 (m, 2H), 7.33 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 19.3, 20.0, 31.8, 116.7, 120.6, 130.3, 136.0, 137.9, 140.1; MS (FAB) *m/z* 165 (M^++H, 100); HRMS (FAB-Magnetic Sector): Calcd for $C_9H_{13}N_2O$ (M^++H): 165.1028, Found: 165.1020.

***N*-Methyl-*p*-chloro-*N*-nitrosaniline (7a)** [13)]



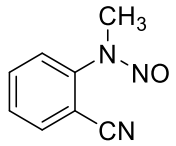
A yellow solid (89.9 mg, 90%): mp 44−45 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 7.45 (d, *J* = 9.2 Hz, 2H), 7.50 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 120.1, 129.6, 132.9, 142.2; MS (FAB) *m/z* 185 (M^+−34, 18).

***N*-Methyl-*p*-bromo-*N*-nitrosaniline (8a)** [13)]



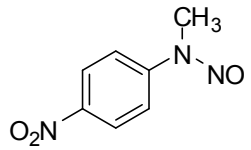
A yellow solid (121.2 mg, 91%): mp 69−70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 120.3, 120.7, 132.5, 141.3; MS (FAB) *m/z* 215 (M^++H, 28), 217 (M^++3, 26).

***N*-Methyl-*o*-cyano-*N*-nitrosaniline (9a)**



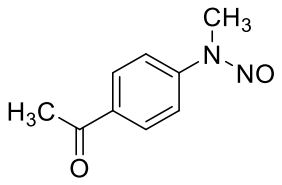
A yellow solid (24.1 mg, 34%): mp 52−53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.53 (d, *J* = 0.9 Hz, 3H), 7.52-7.57 (m, 2H), 7.74-7.79 (m, 1H), 7.83-7.86 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 34.4, 107.3, 116.3, 124.3, 128.5, 134.2, 144.5; MS (FAB) *m/z* 162 (M^++H, 45), 136 (M^+−25, 70); HRMS (FAB-Magnetic Sector): Calcd for $C_8H_8N_3O$ (M^++H): 162.0667, Found: 162.0654.

***N*-Methyl-*p*-nitro-*N*-nitrosaniline (10a)** [11)]



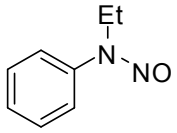
A yellow solid (35.0 mg, 33%) mp 94−95 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41 (s, 3H), 7.70 (d, *J* = 9.2 Hz, 2H), 8.29 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.0, 117.8, 125.2, 145.8, 147.0; (EI) *m/z* 151 (M^+−30, 100), 105 (M^+−64).

***N*-Methyl-*p*-acetyl-*N*-nitrosaniline (11a)** [12)]



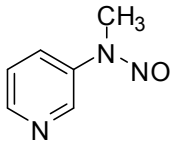
A yellow solid (69.6 mg, 66%): mp 104−105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.47 (s, 3H), 7.68 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 30.4, 117.9, 129.8, 135.3, 145.6, 196.7; MS (FAB) *m/z* 179 (M^++H, 18).

***N*-Ethyl-*N*-phenylnitrosamine (12a)** [11)]



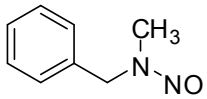
A yellow oil (70.8 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (t, 3H, *J* = 6.6 Hz), 4.08 (q, 2H, *J* = 6.6 Hz), 7.37 (t, 1H, *J* = 7.6 Hz), 7.48 (t, 2H, *J* = 7.6 Hz), 7.54 (d, 2H, *J* = 7.6 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) δ 11.7, 39.2, 119.5, 127.3, 129.5, 141.4; MS (FAB) *m/z* 151 (M^++H, 19), 120 (M^+−31, 20).

4-(*N*-Methyl-*N*-nitrosamino)pyridine (13a)



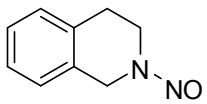
brown oil (55.4 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 (s, 3H), 7.43-7.48 (m, 1H), 7.92-7.98 (m, 1H), 8.60-8.66 (m, 1H), 8.83-8.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 123.9, 126.0, 138.6, 140.0, 148.3; MS (FAB) *m/z* 138 (M^++H, 100), 108 (M^+−30, 90); HRMS (FAB-Magnetic Sector): Calcd for $C_6H_8N_3O$ (M^++H): 138.0667, Found: 138.0686.

***N*-Benzyl-*N*-methylnitrosamine (14a)** [14)]



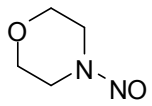
A brown liquid (53.0 mg, 56%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.95 (s, 2.31H), 3.69 (s, 1H), 4.81 (s, 1H), 5.31 (s, 1.58H), 7.24-7.43 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9, 38.4, 47.7, 57.6, 127.9, 128.0, 128.3, 128.5, 128.9, 129.0, 133.7, 134.4; MS (FAB) *m/z* 151 (M^++H, 38), 91 (M^+−59, 100).

2-Nitroso-1,2,3,4-tetrahydroisoquinoline (15a) [14)]



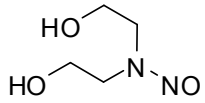
A yellow solid (40.6 mg, 40%): mp 48−49 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (t, *J* = 6.5 Hz, 1H), 3.12 (t, *J* = 6.0 Hz, 1.42H), 3.90 (t, *J* = 6.5 Hz, 1H), 4.55 (t, *J* = 6.0 Hz, 1.43H), 4.85 (s, 1.40H), 5.41 (s, 0.60H), 7.15-7.31 (m, 5.03H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 29.7, 40.7, 44.4, 47.6, 51.2, 126.1, 127.1, 127.2, 127.2, 127.9, 128.0, 128.6, 129.9, 132.3, 133.8, 134.9; MS (FAB) *m/z* 163 (M^++H, 163), 132 (M^+−30, 25).

4-Nitrosomorpholine (16a) [14)]



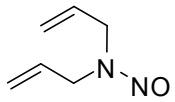
A yellow oil (40.7 mg, 57%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (t, *J* = 5.0 Hz, 2H), 3.80-3.94 (m, 4H), 4.30 (t, *J* = 5.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.3, 49.9, 65.8, 67.2; MS (FAB) *m/z* 117 (M^++H, 21).

***N*,*N*-Bis(2-hydroxyethyl)nitrosamine (17a)** [14)]



A brown oil (27.9 mg, 36%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.57 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.84 (t, *J* = 5.5 Hz, 2H), 3.30 (t, *J* = 5.5 Hz, 2H), 4.01 (s, 1H), 4.07 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 46.6, 55.2, 56.9, 58.8; MS (FAB) *m/z* 135 (M^++H, 8).

***N*,*N*-Diallylnitrosamine (18a)** [14)]



A brown oil (12.6 mg, 18%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12-4.23 (m, 1H), 4.67-4.77 (m, 1H), 5.05-5.14 (m, 2H), 5.15-5.23 (m, 1H), 5.28-5.39 (m, 1H), 5.55-5.69 (m, 2H), 5.85-5.98 (m, 2H); ^{13}C NMR 125 MHz, $CDCl_3$) δ 45.1, 54.1, 119.1, 120.2, 129.1, 131.8; MS (EI) *m/z* 126 (M^+, 48).

5. References

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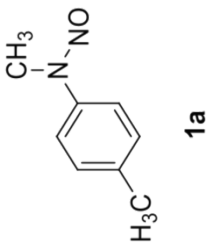
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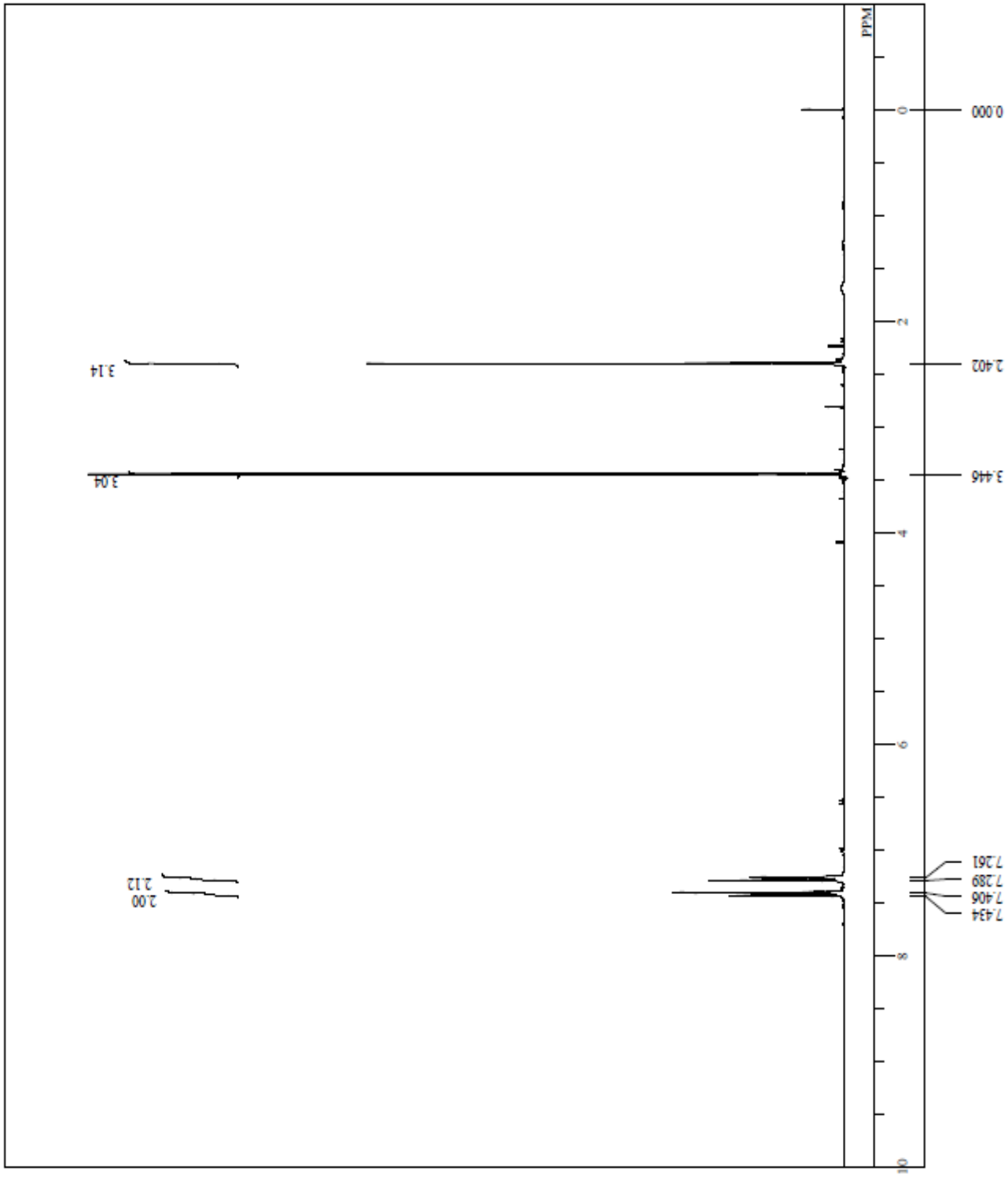
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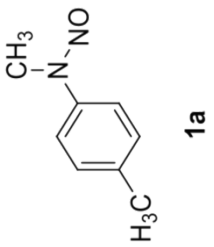
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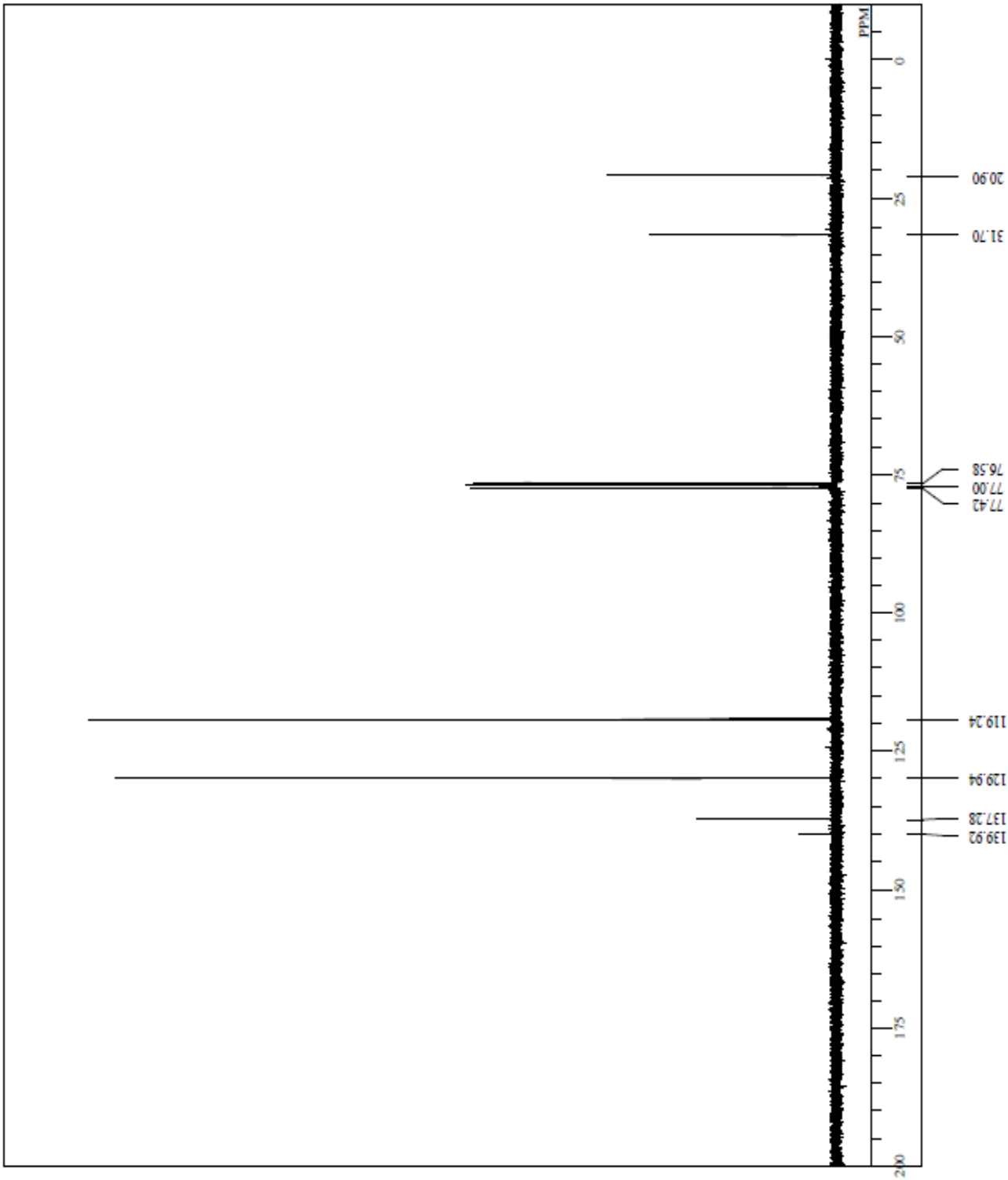
NO
H3C

1a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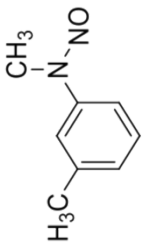
139.92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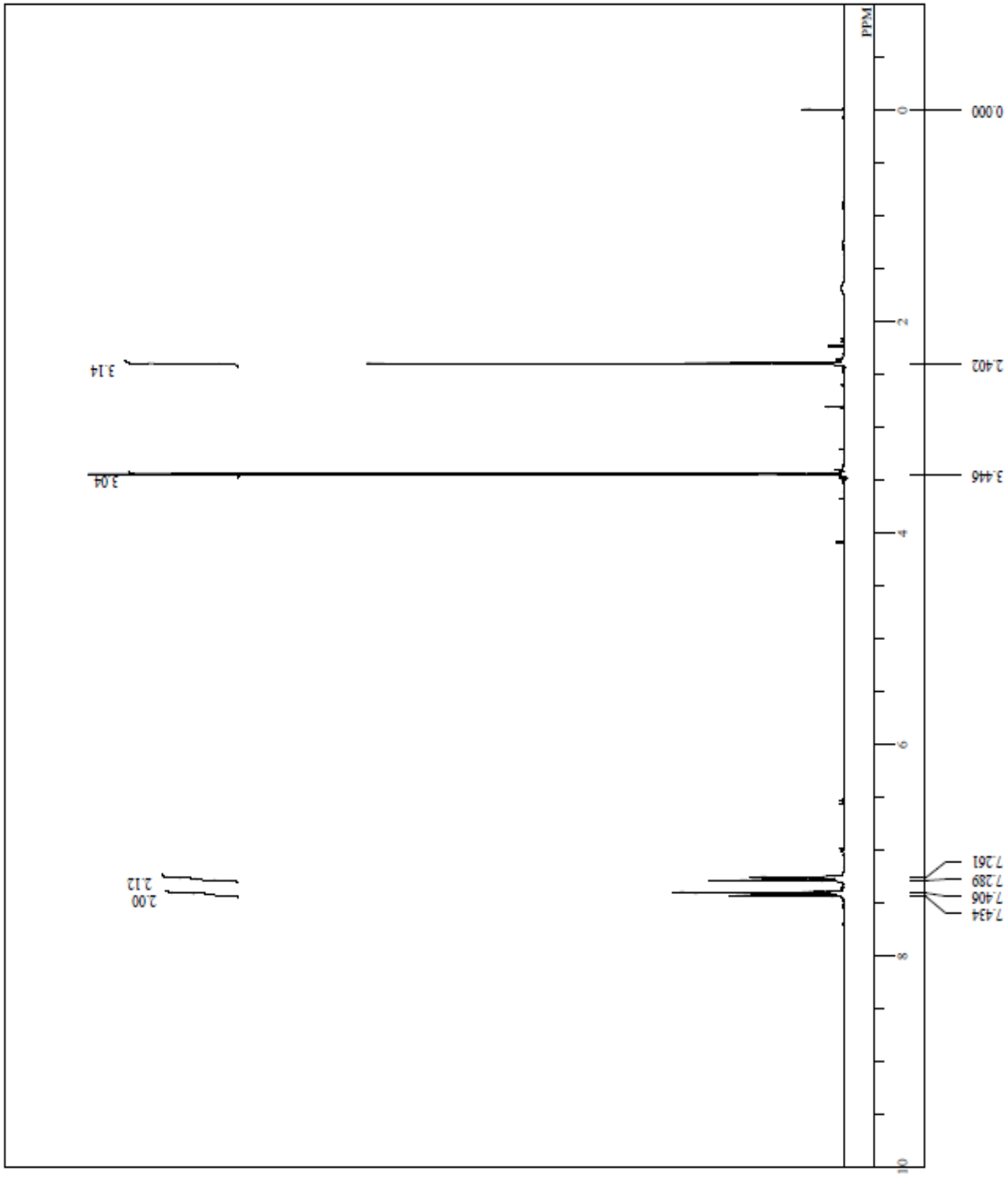
H3C

2a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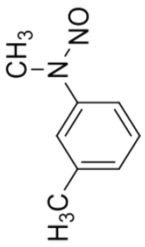
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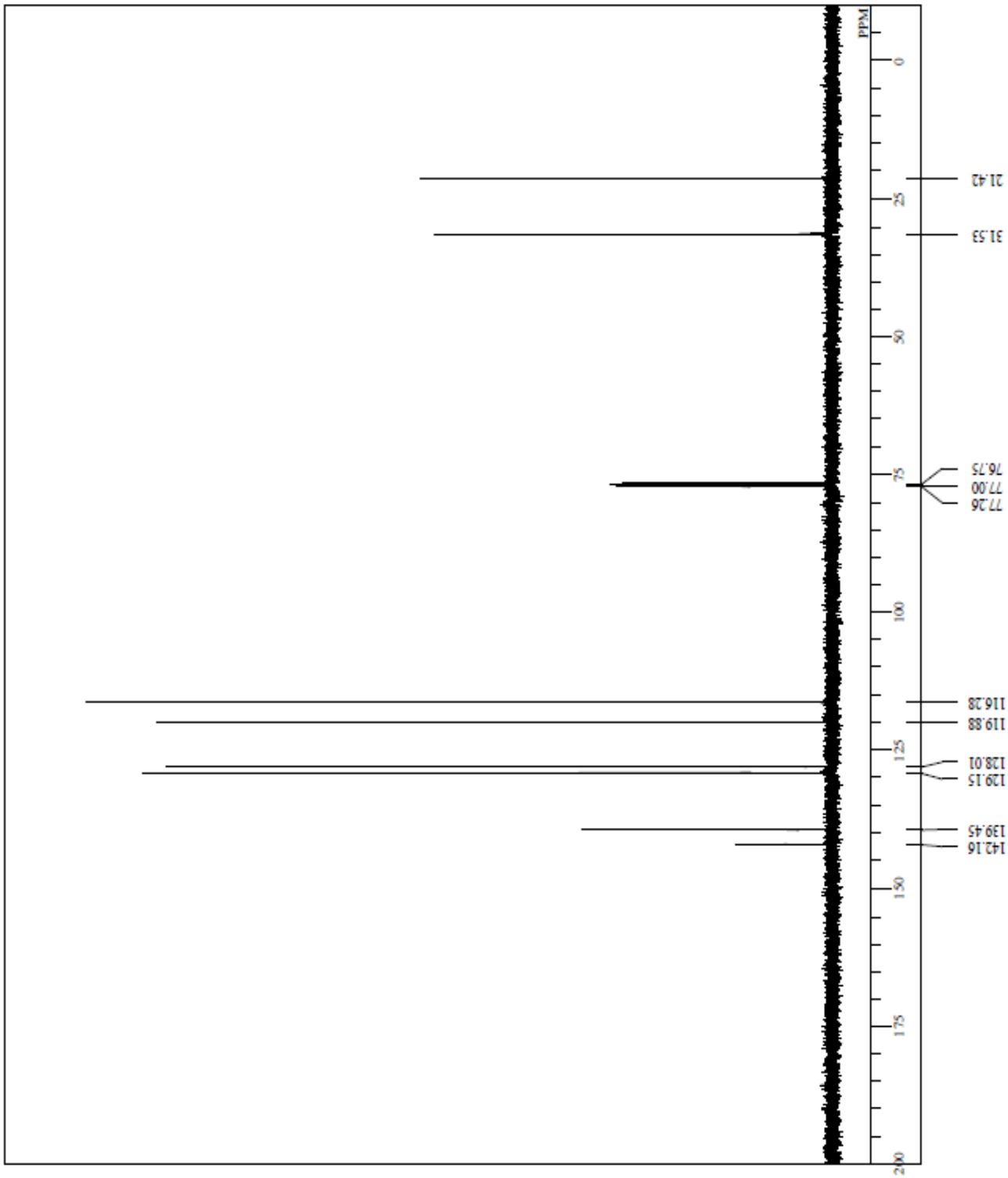
H3C

2a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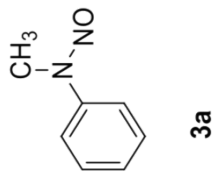

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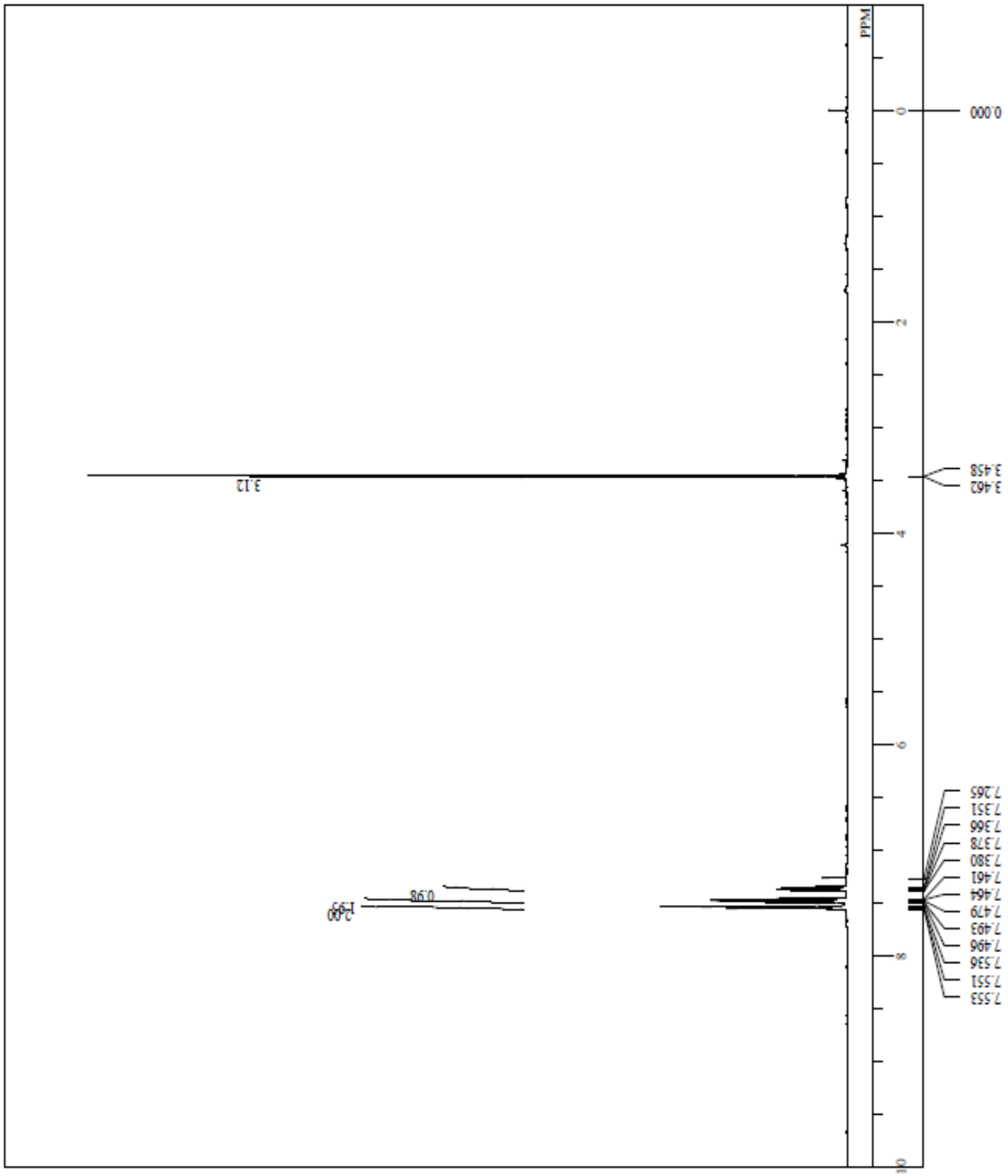
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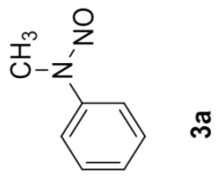

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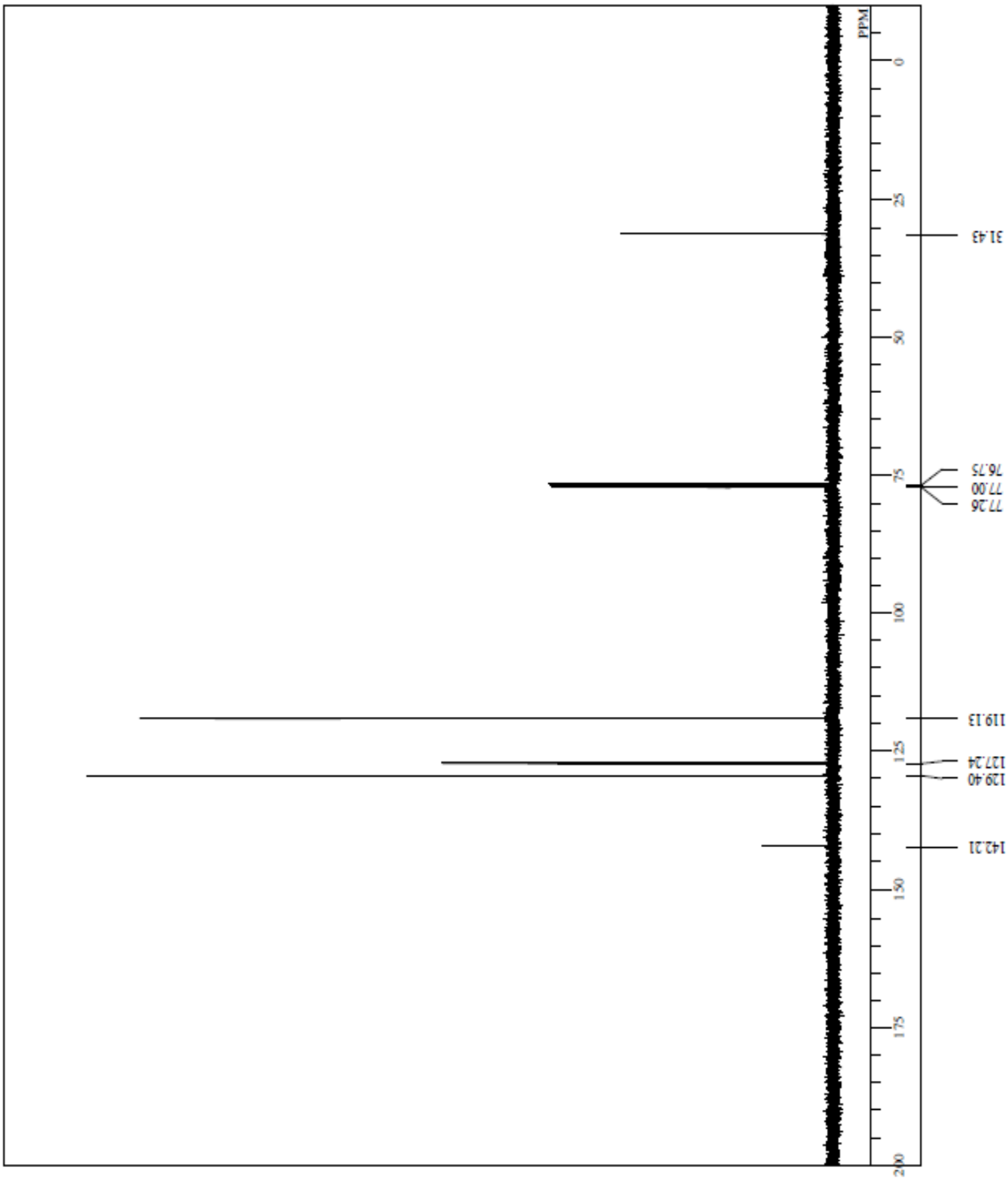
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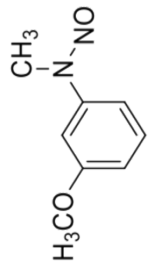
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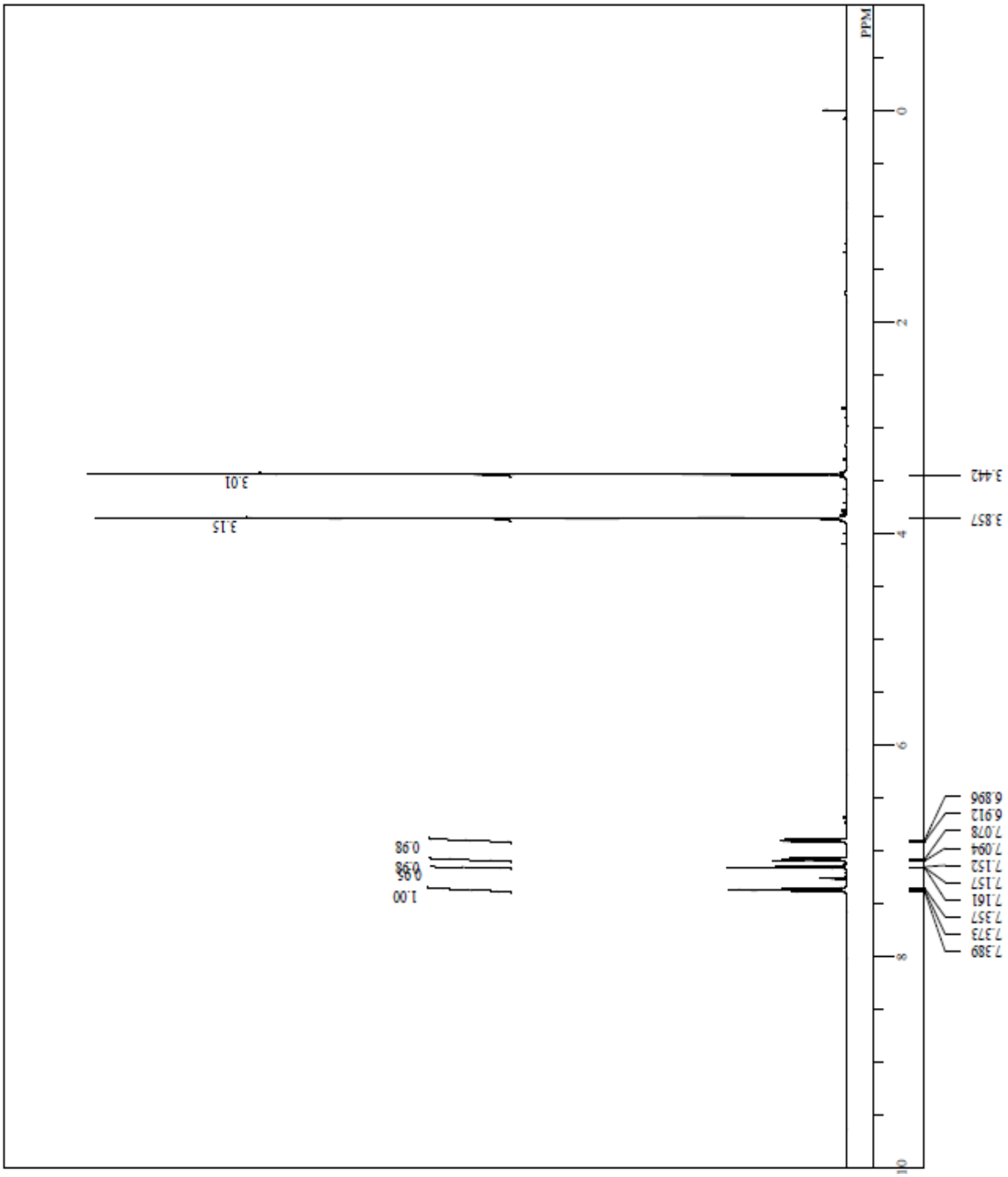
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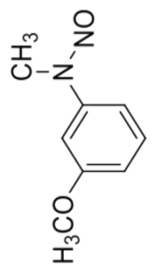
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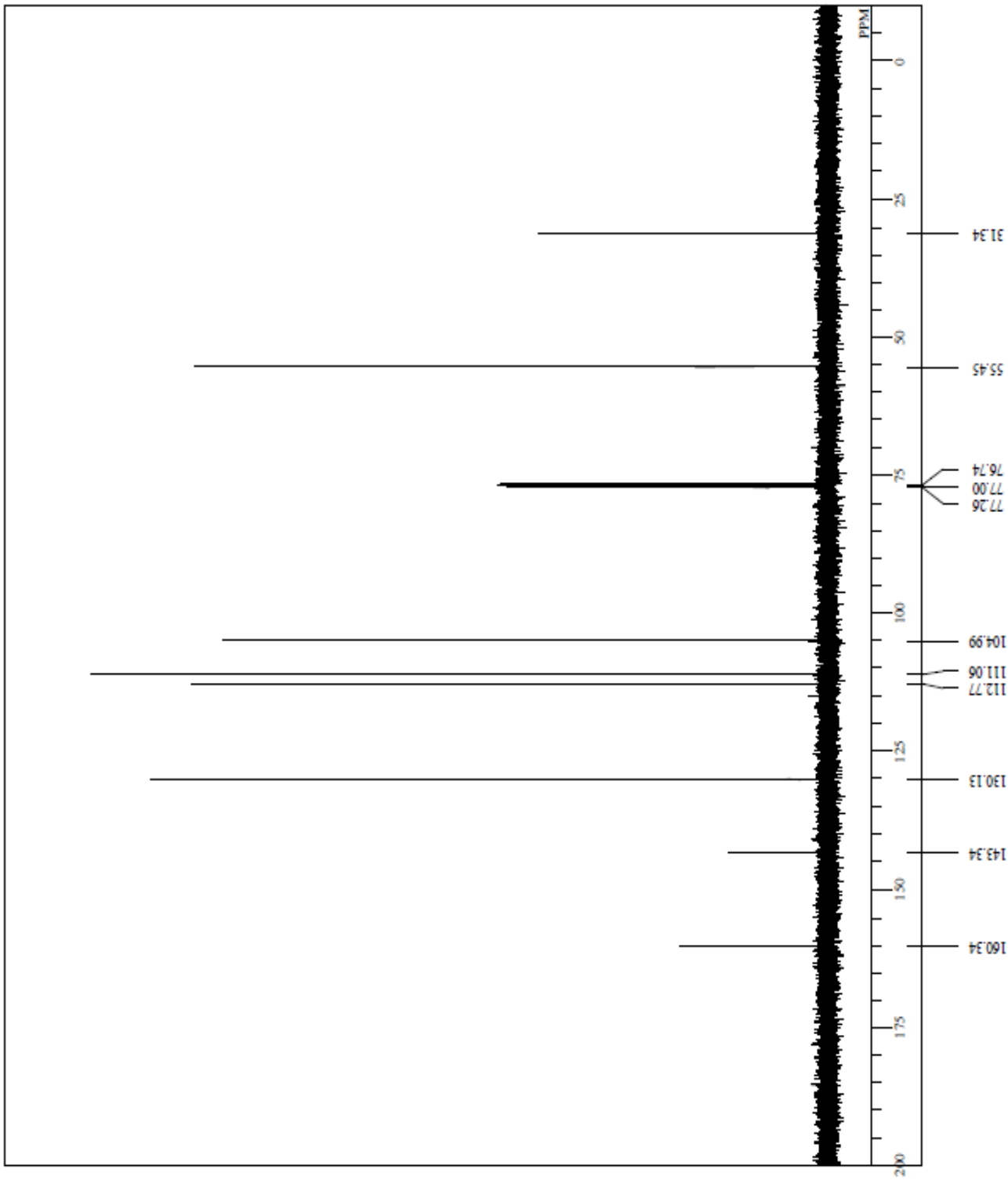
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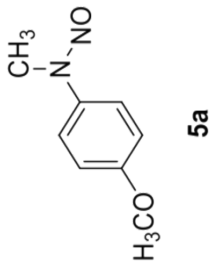
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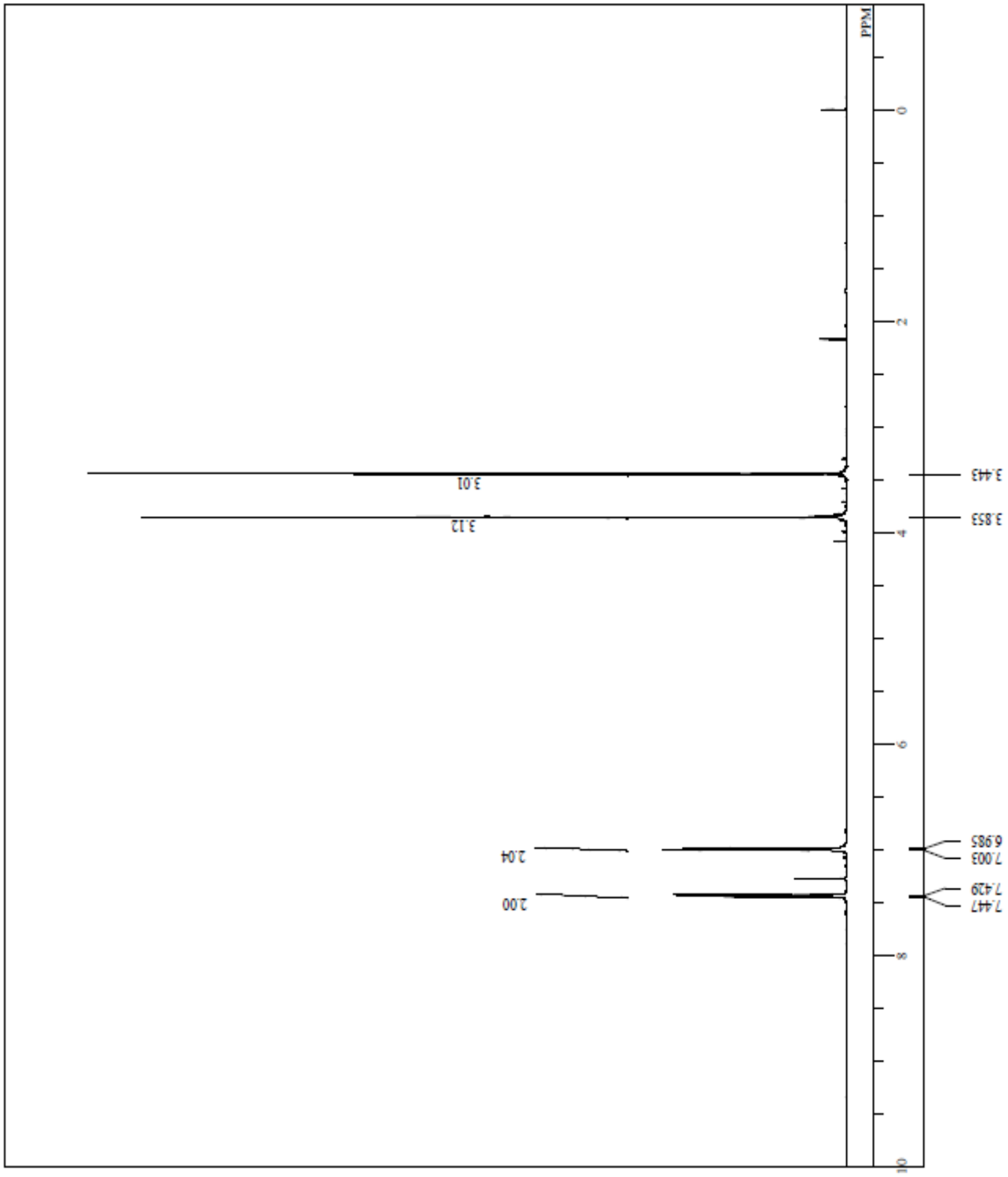
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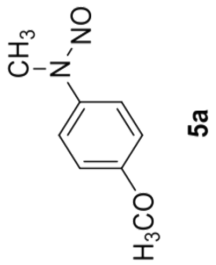
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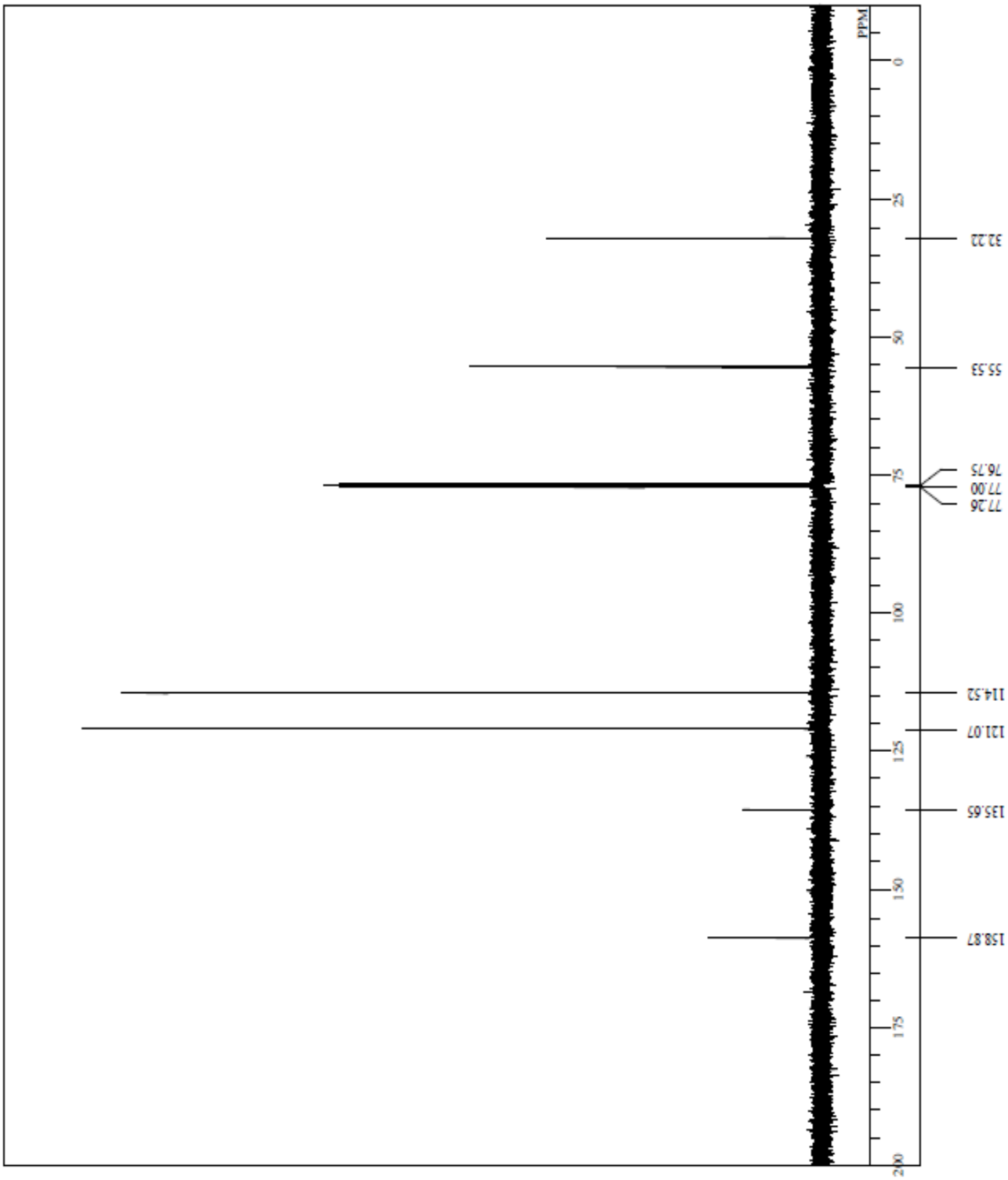
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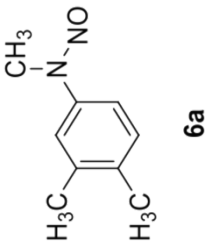
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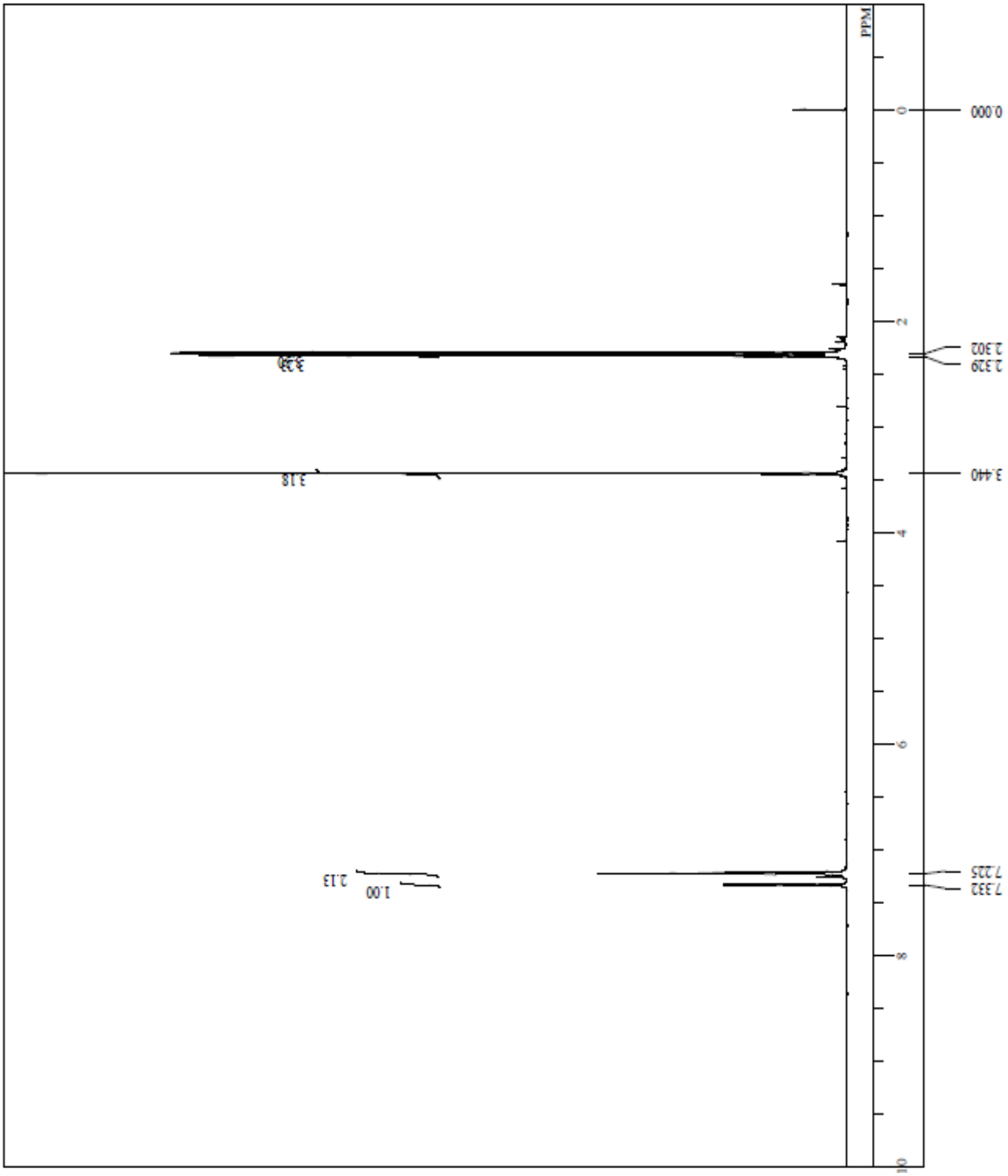
H3C

6a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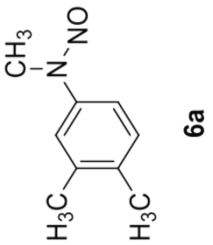
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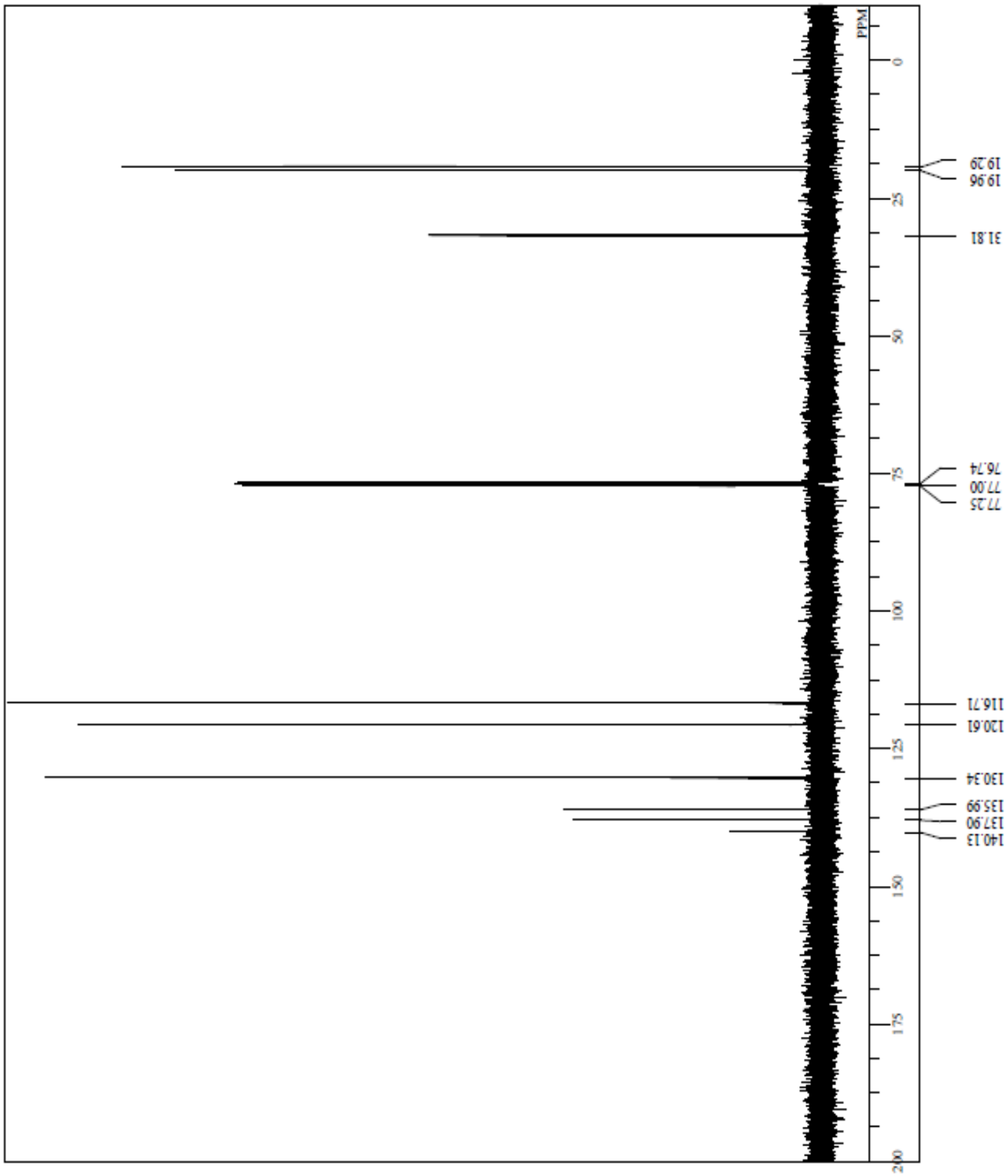
6a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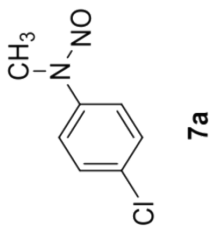
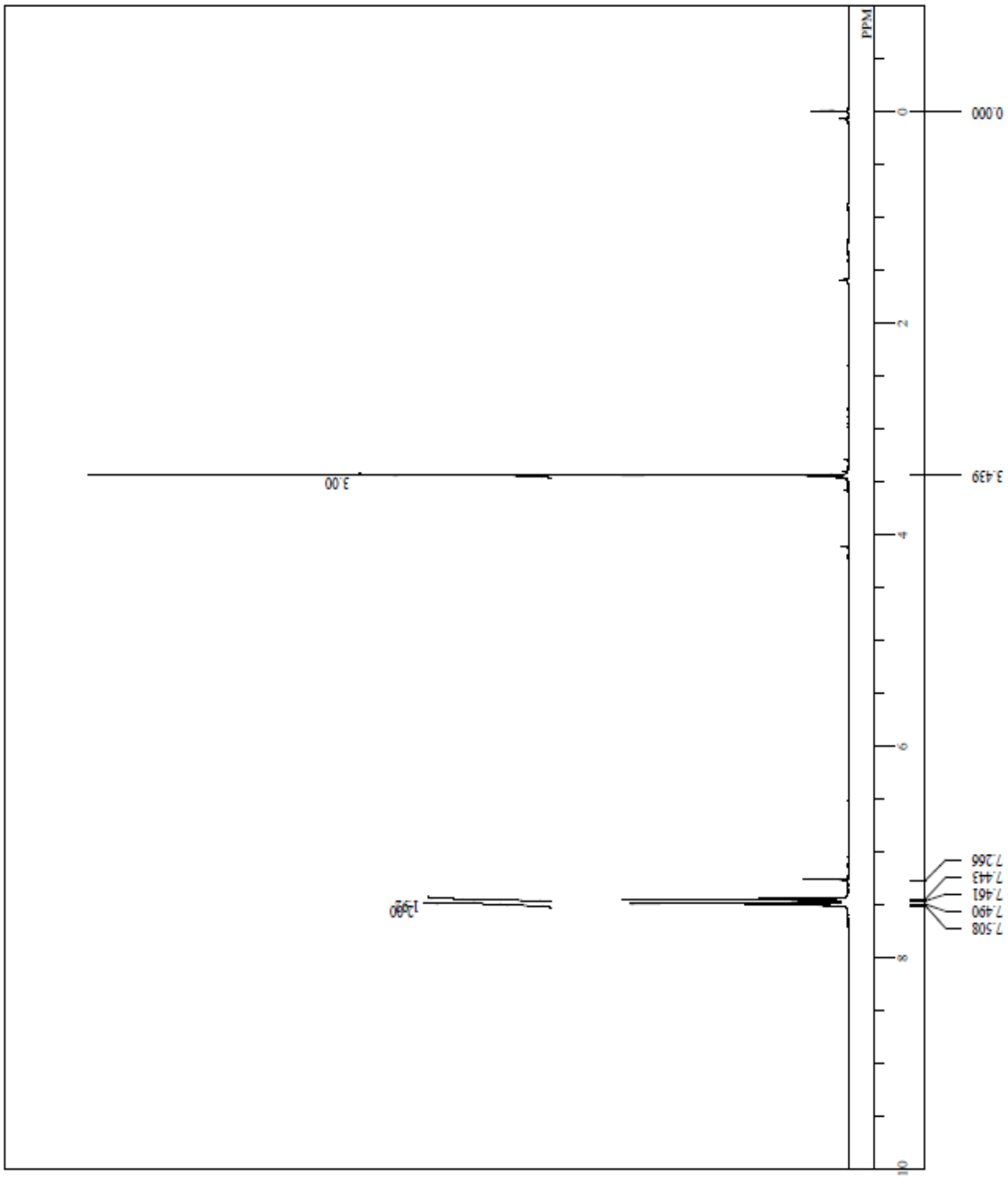
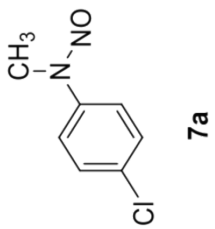
135.99
137.90
140.13



7a




CH3
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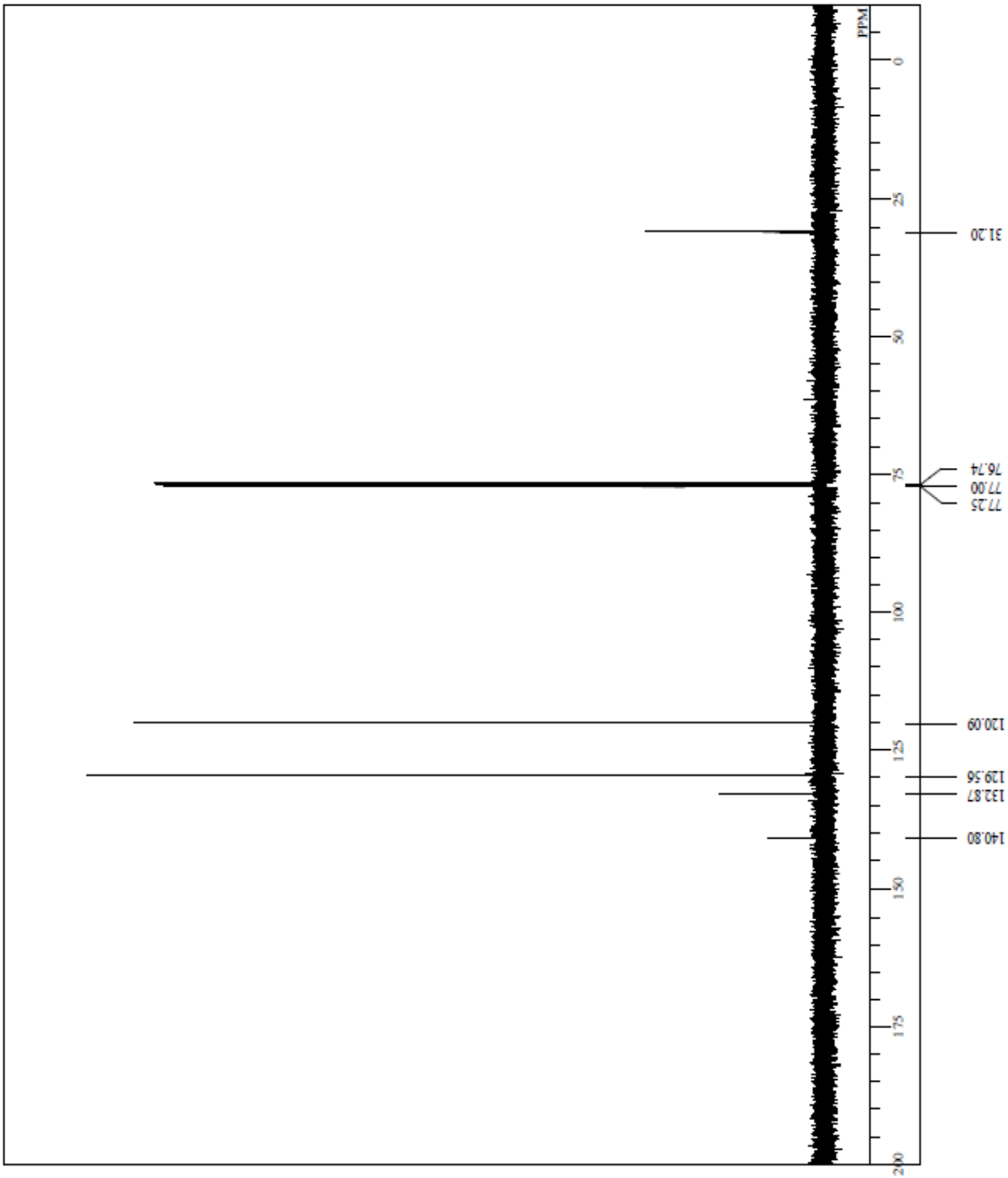
NO
Cl

7a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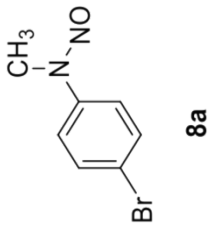
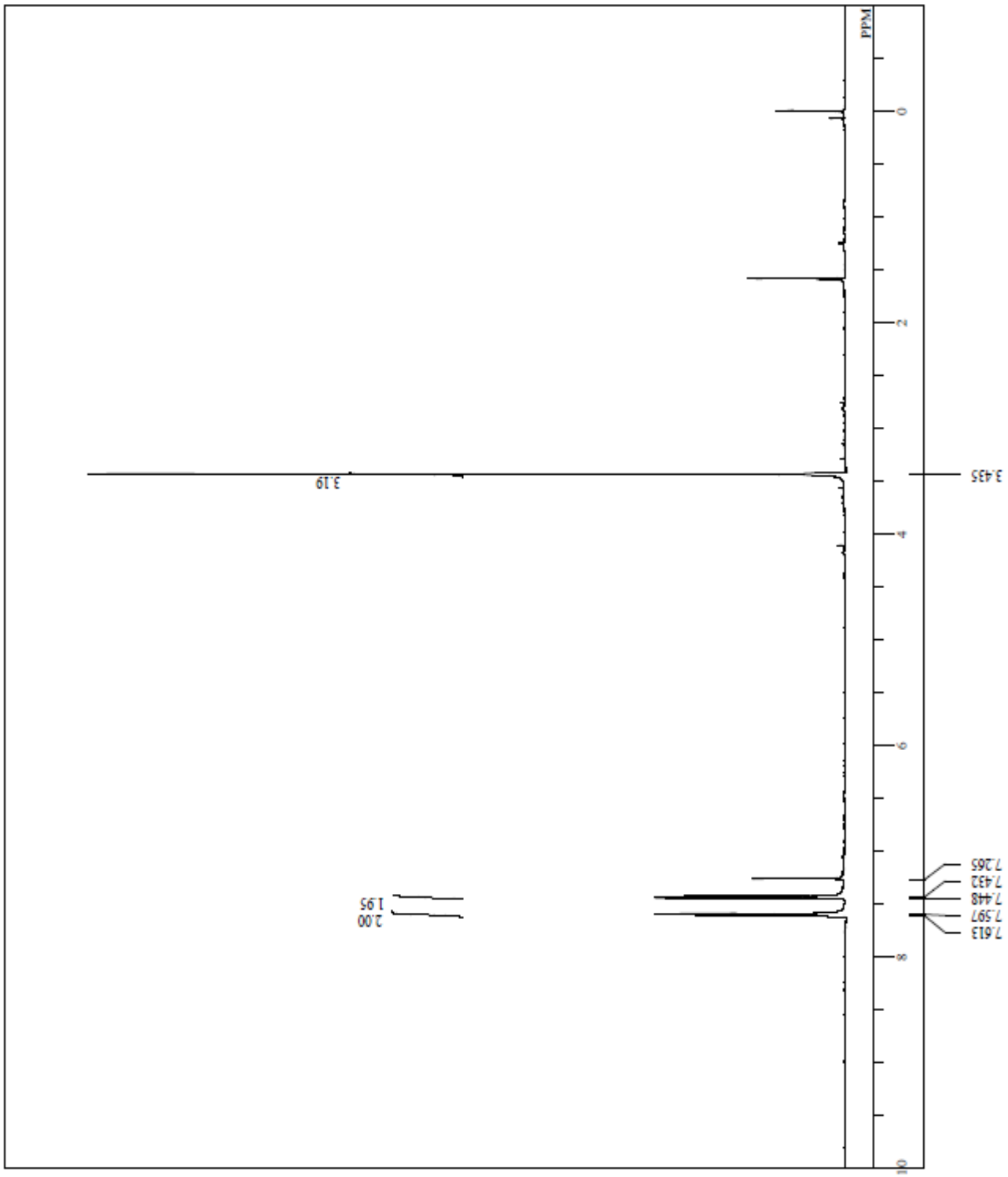
100
125
150
175
200
31.20
76.74
77.00
77.25
120.09
129.56
132.87
140.80


CH3
N
NO
Br

8a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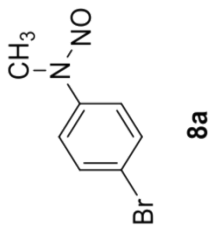
2.00
1.95
7.613
7.597
7.448
7.432
7.265


CH3
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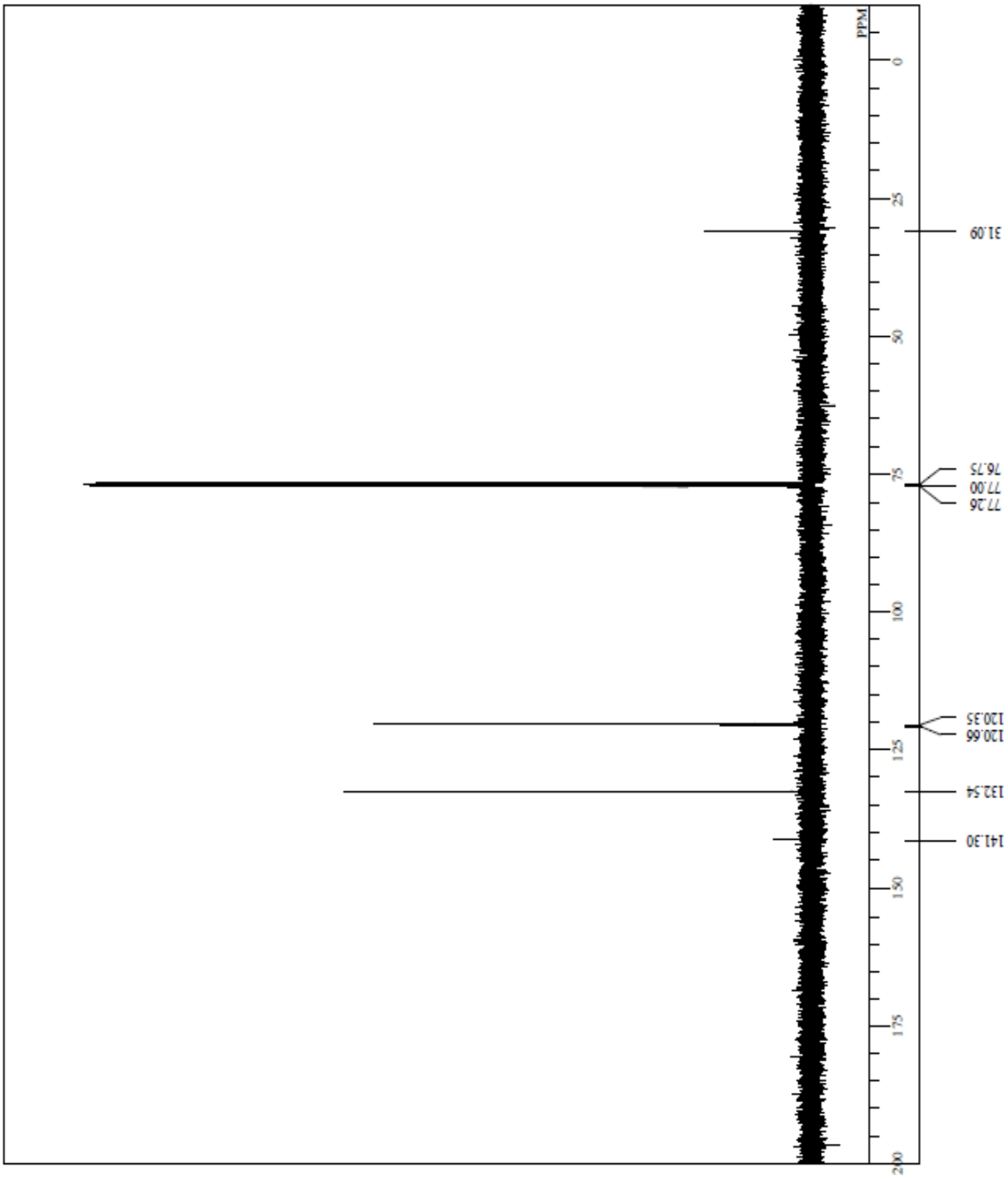
NO
Br

8a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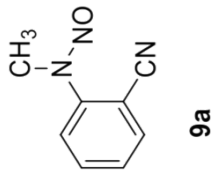
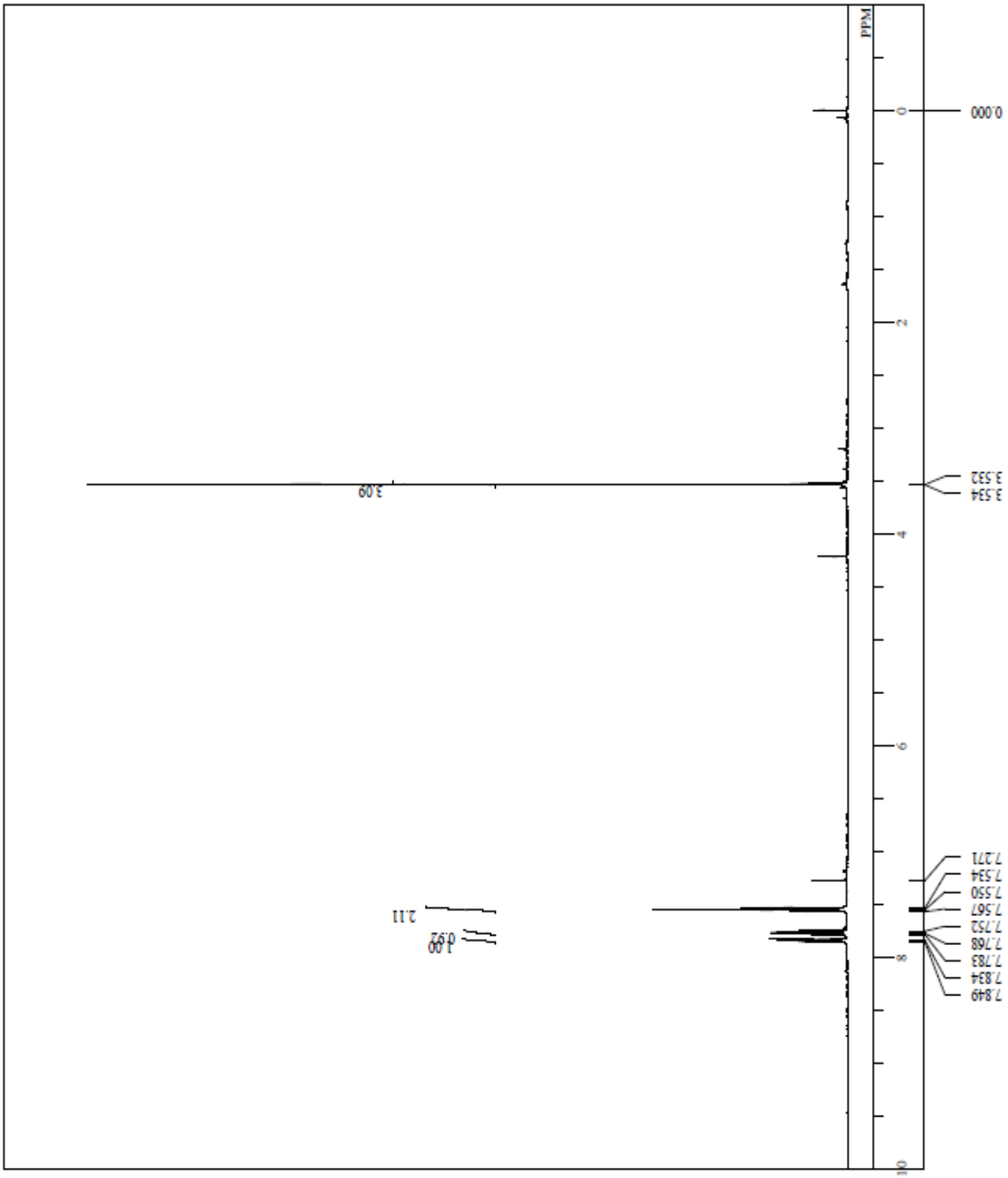
75
100
125
150
175
200
31.09
76.75
77.00
77.26
120.35
120.66
132.54
141.30



9a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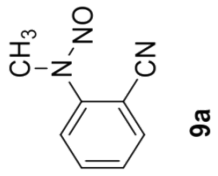
7.271
7.534
7.550
7.567
7.752
7.768
7.783
7.834
7.849
1.00
0.92
2.11
3.09


CH3
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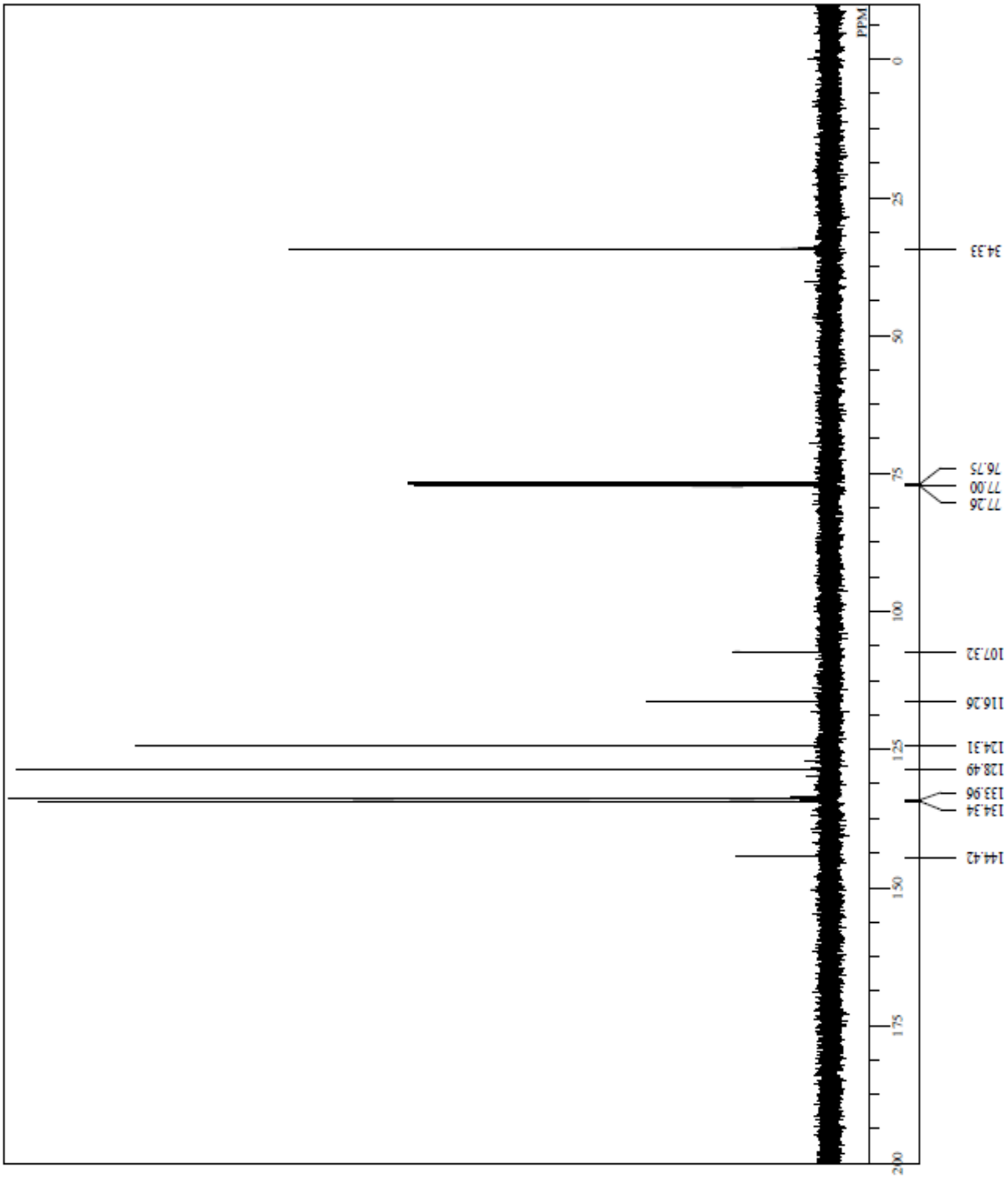
NO
CN

9a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50
75
100
125
150
175
200
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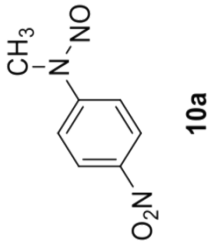
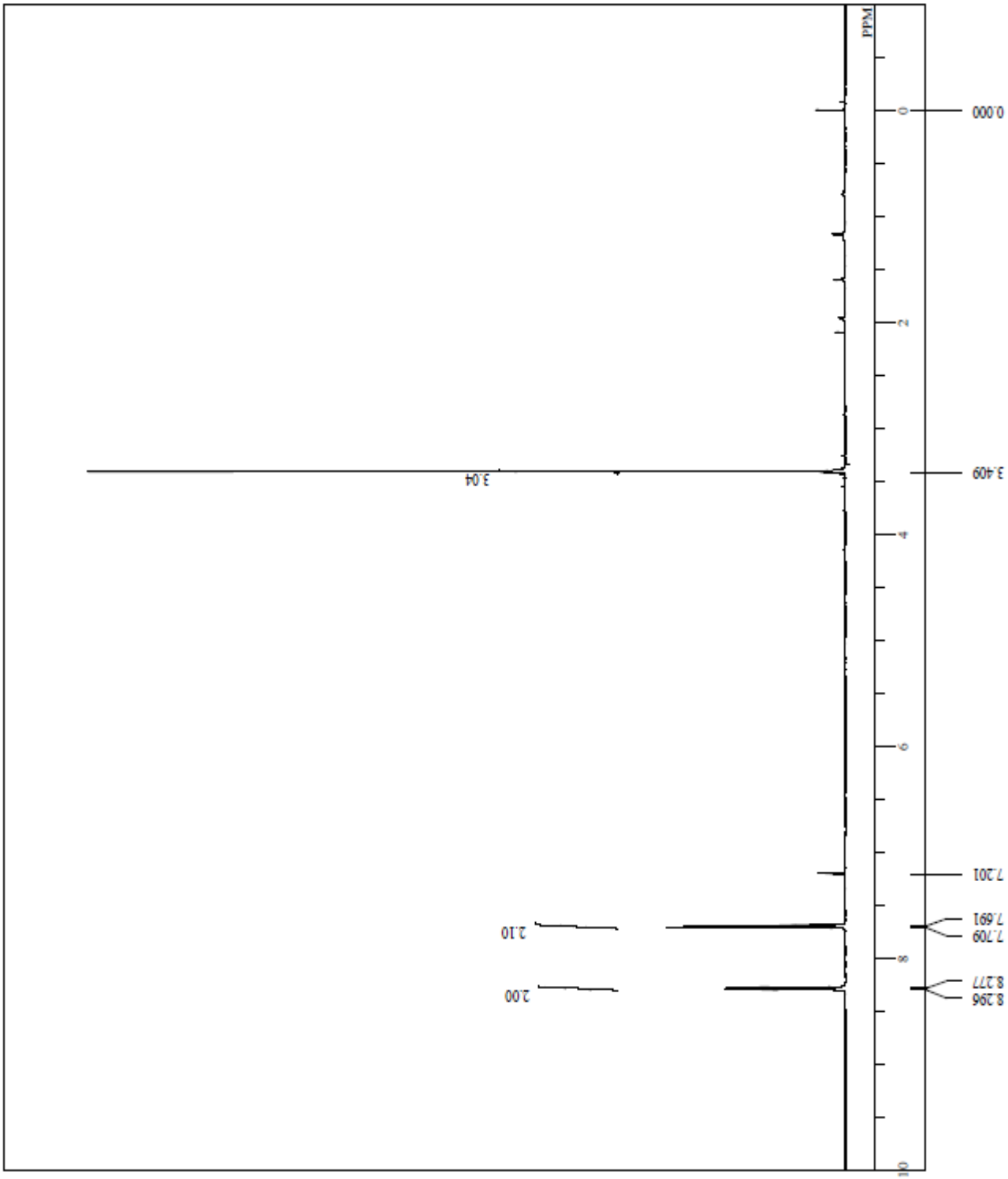
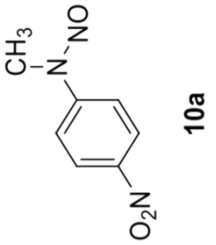
76.75
77.00
77.26
107.32
116.26
124.31
128.49
133.96
134.34
144.42



10a




CH3
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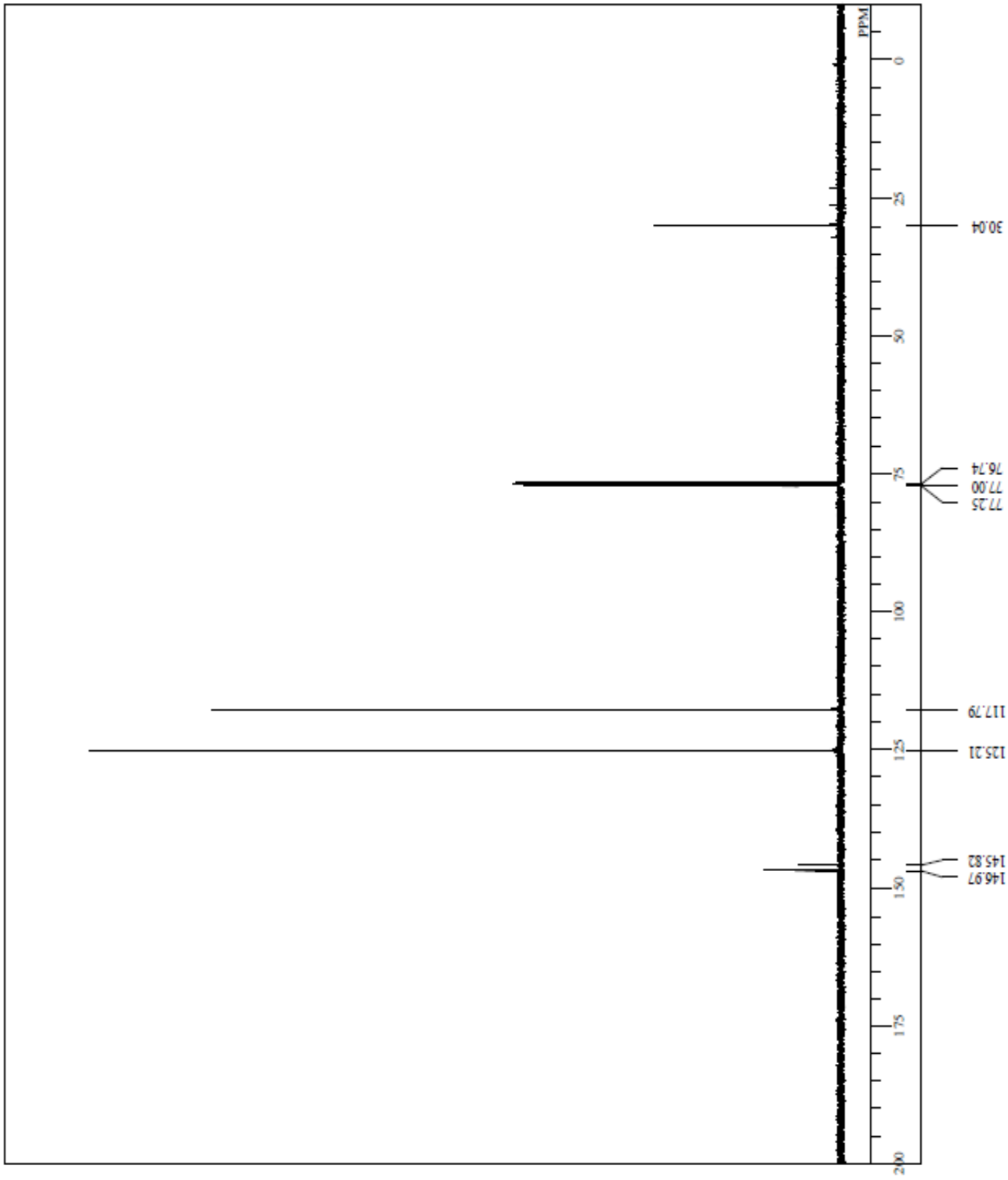
NO
O2N

10a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50
75
100
125
150
175
200
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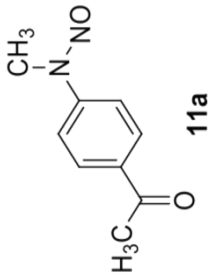
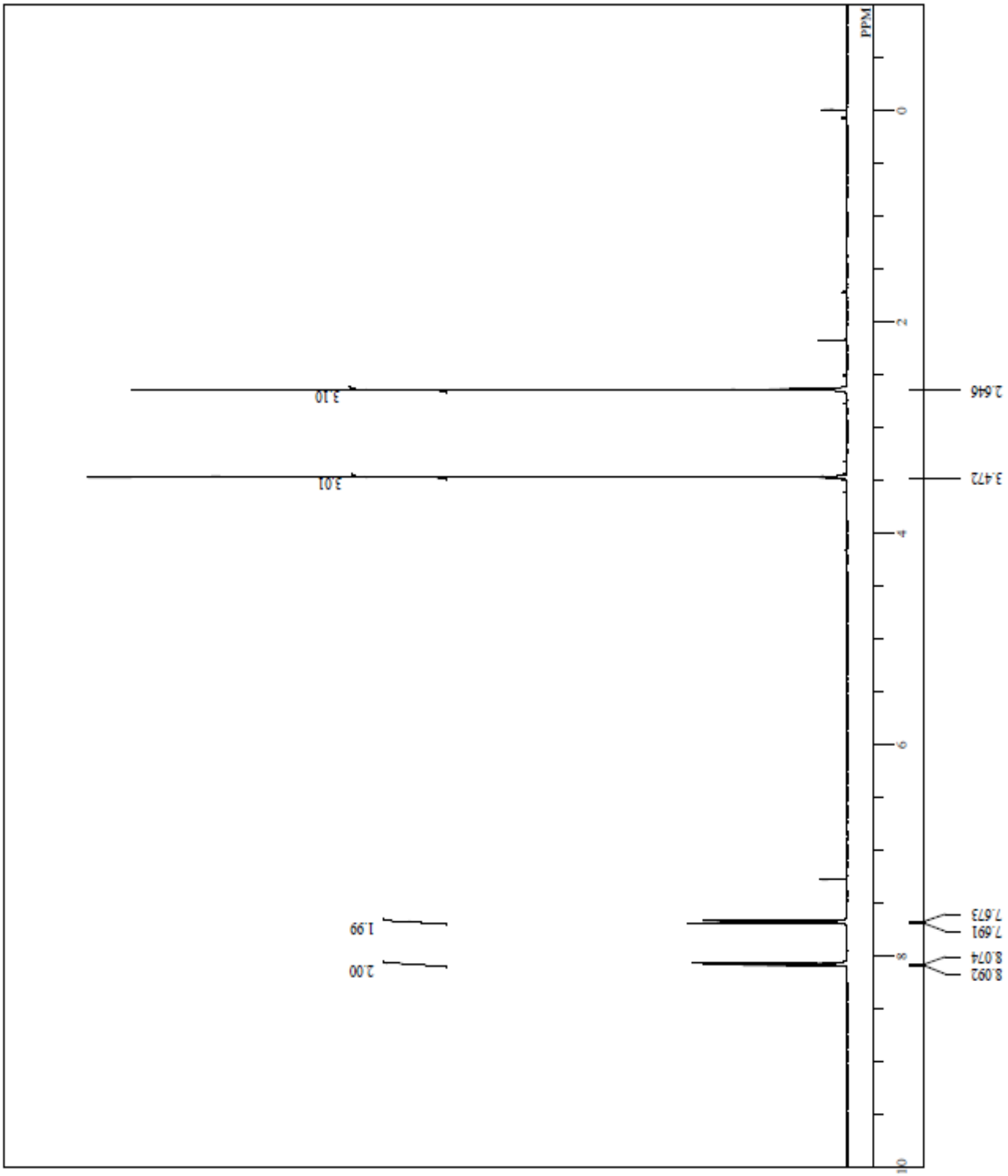
77.00
77.25
117.79
125.21
145.82
146.97


CH3
N
NO
O
H3C

11a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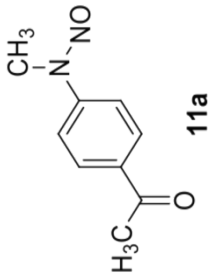
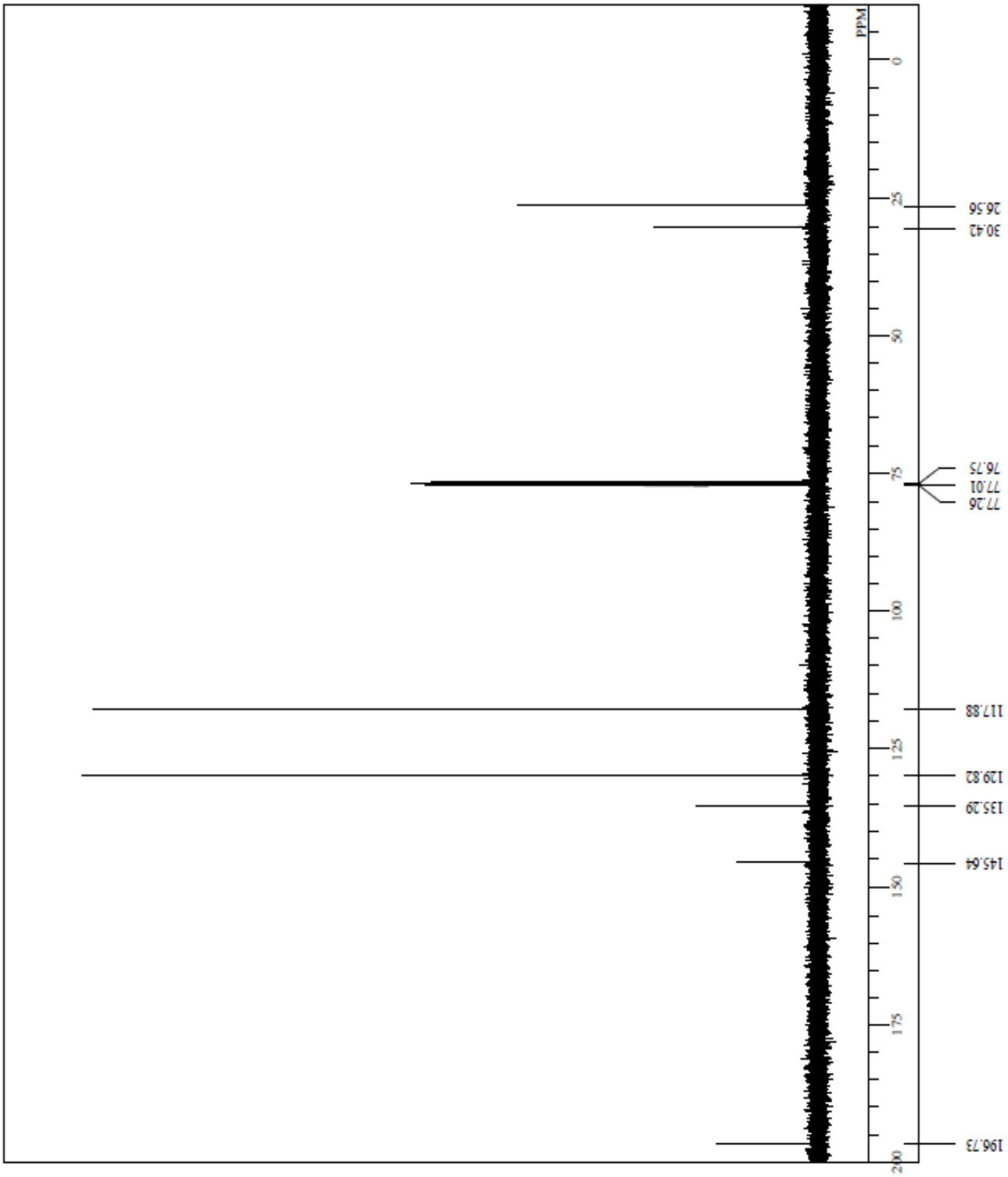
8.092
8.074
7.691
7.673
3.10
3.01
1.99
2.00


CH3
N
NO
O
H3C

11a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50
75
100
125
150
175
200
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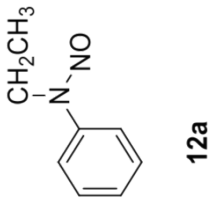
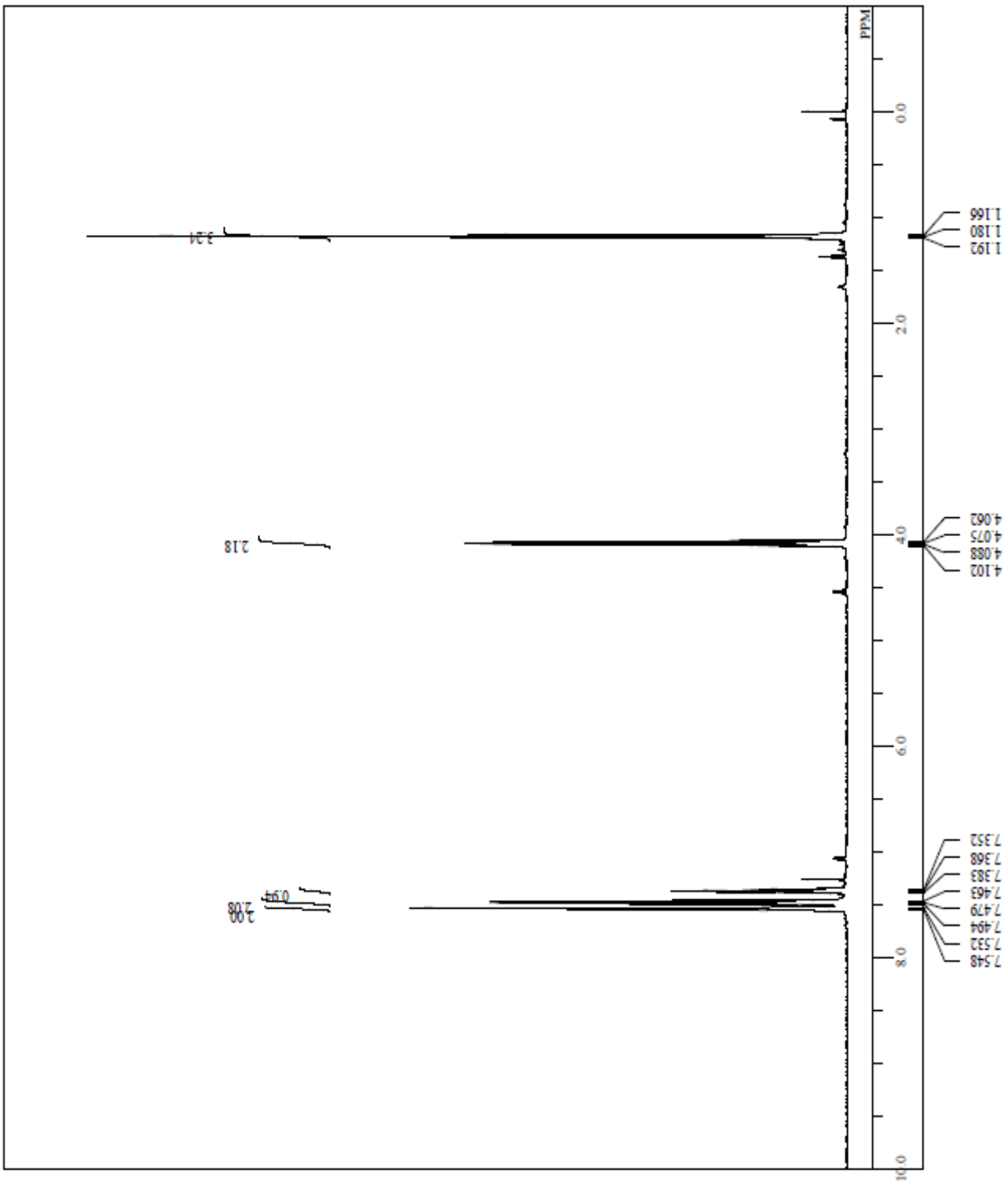
30.42
76.75
77.01
77.26
117.88
129.82
135.29
145.64
196.73


CH2CH3
N
NO

12a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6.0
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10.0
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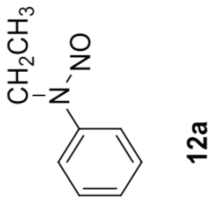
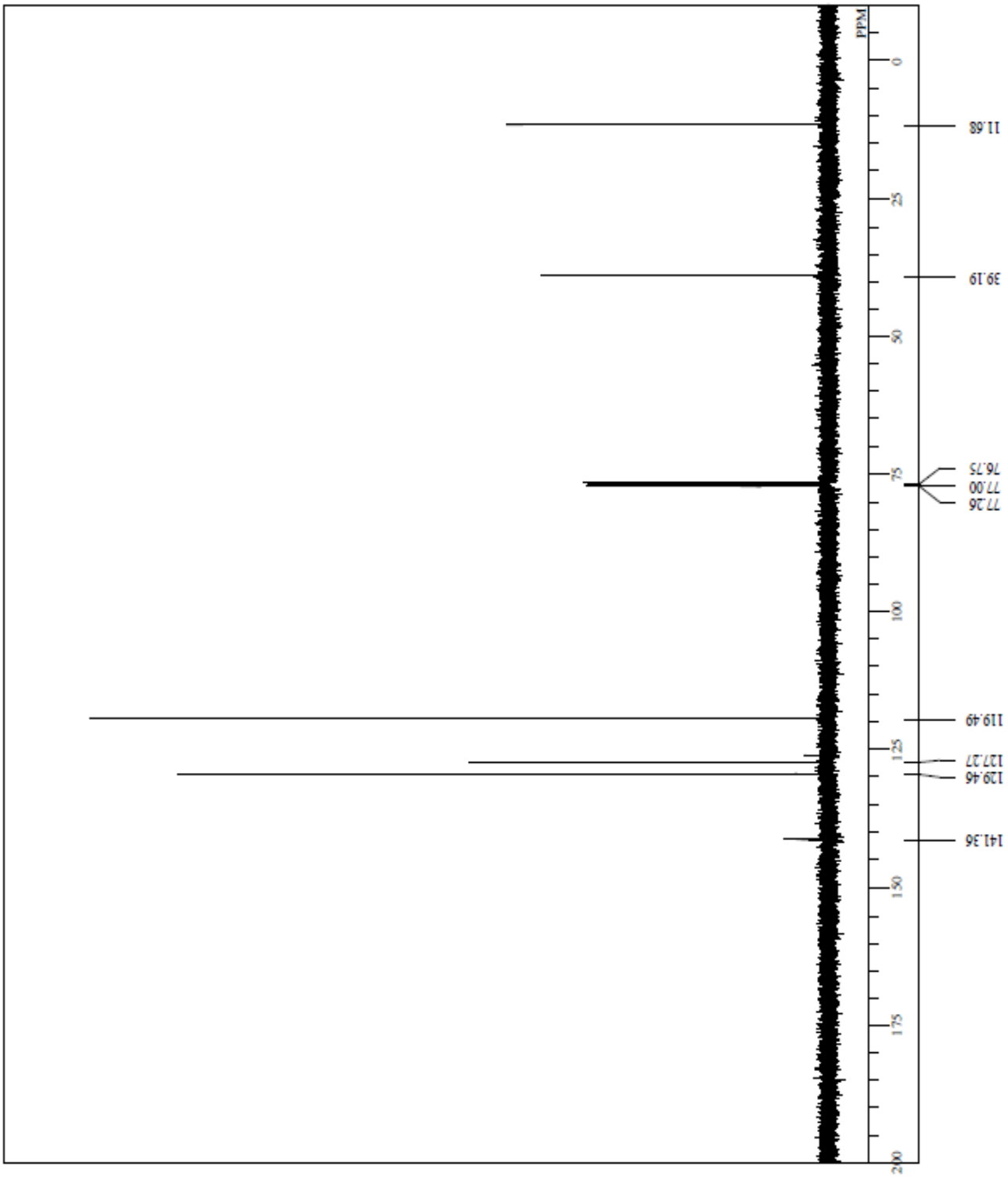
1.180
1.192
4.062
4.075
4.088
4.102
7.352
7.368
7.383
7.463
7.479
7.494
7.532
7.548
3.21
2.18
2.00
0.99
2.08


CH2CH3
N
NO

12a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50
75
100
125
150
175
200
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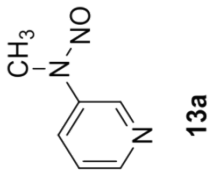
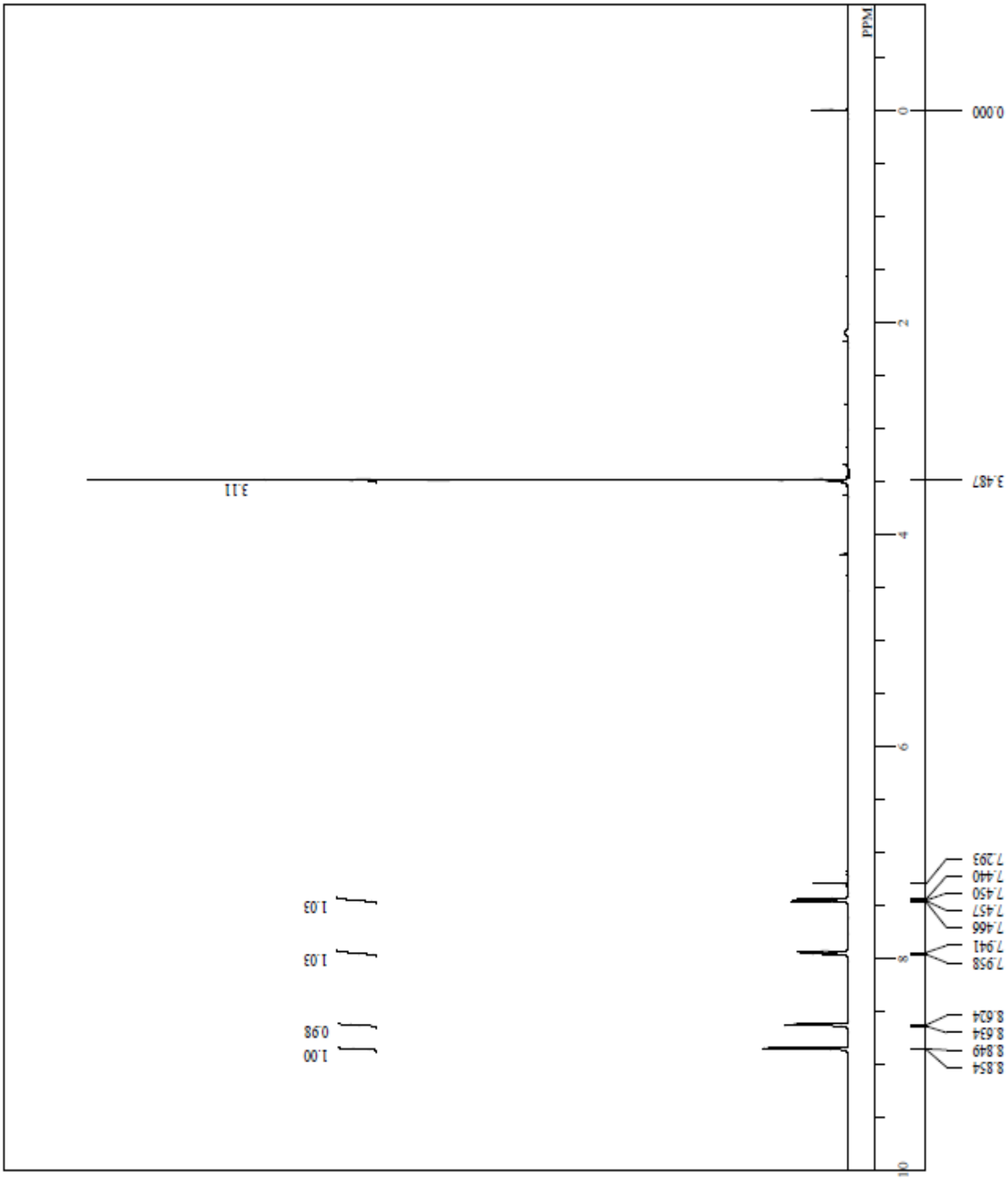
76.75
77.00
77.26
119.49
127.27
129.46
141.36



13a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1.03
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1.00
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7.450
7.457
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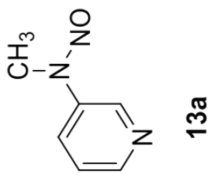
7.941
7.958
8.634
8.849
8.854


CH3
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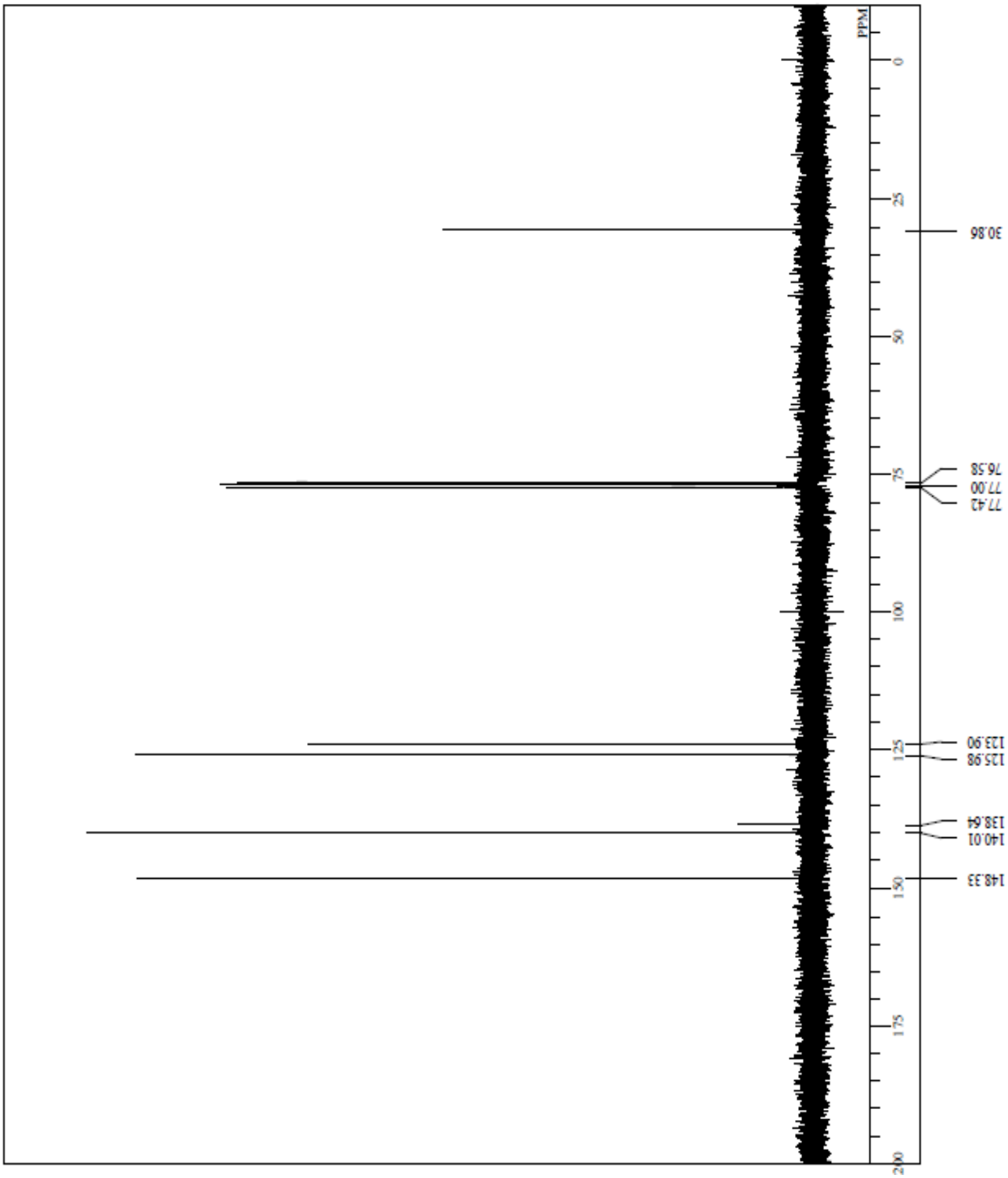
NO
N

13a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75
100
125
150
175
200
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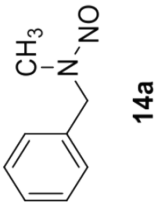
77.00
77.42
123.90
125.98
138.64
140.01
148.33


CH3
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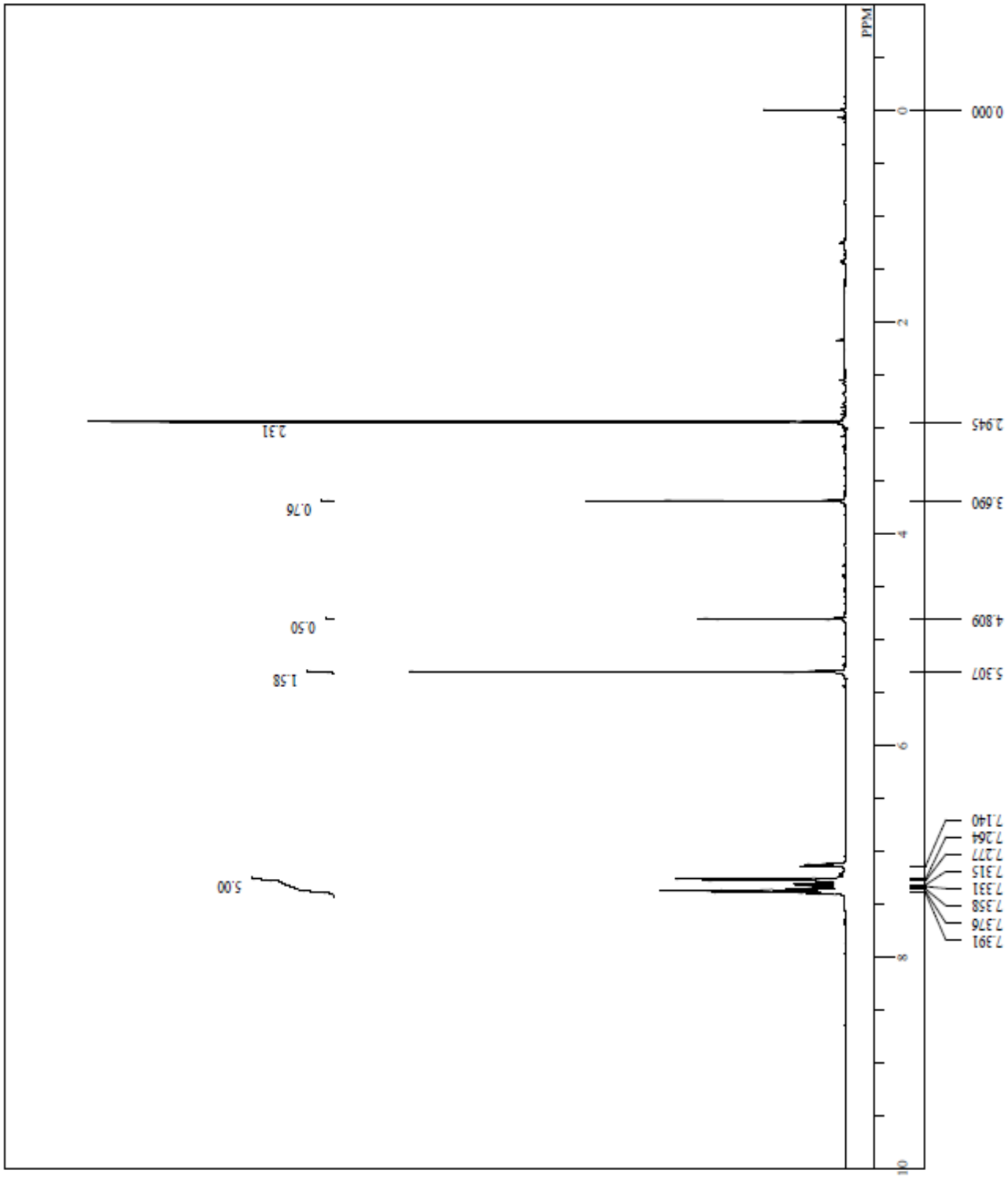
NO

14a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4.809
5.307
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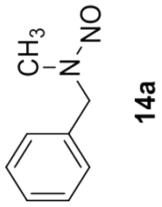
7.264
7.277
7.315
7.331
7.358
7.376
7.391
5.00
1.58
0.50
0.76
2.31


CH3
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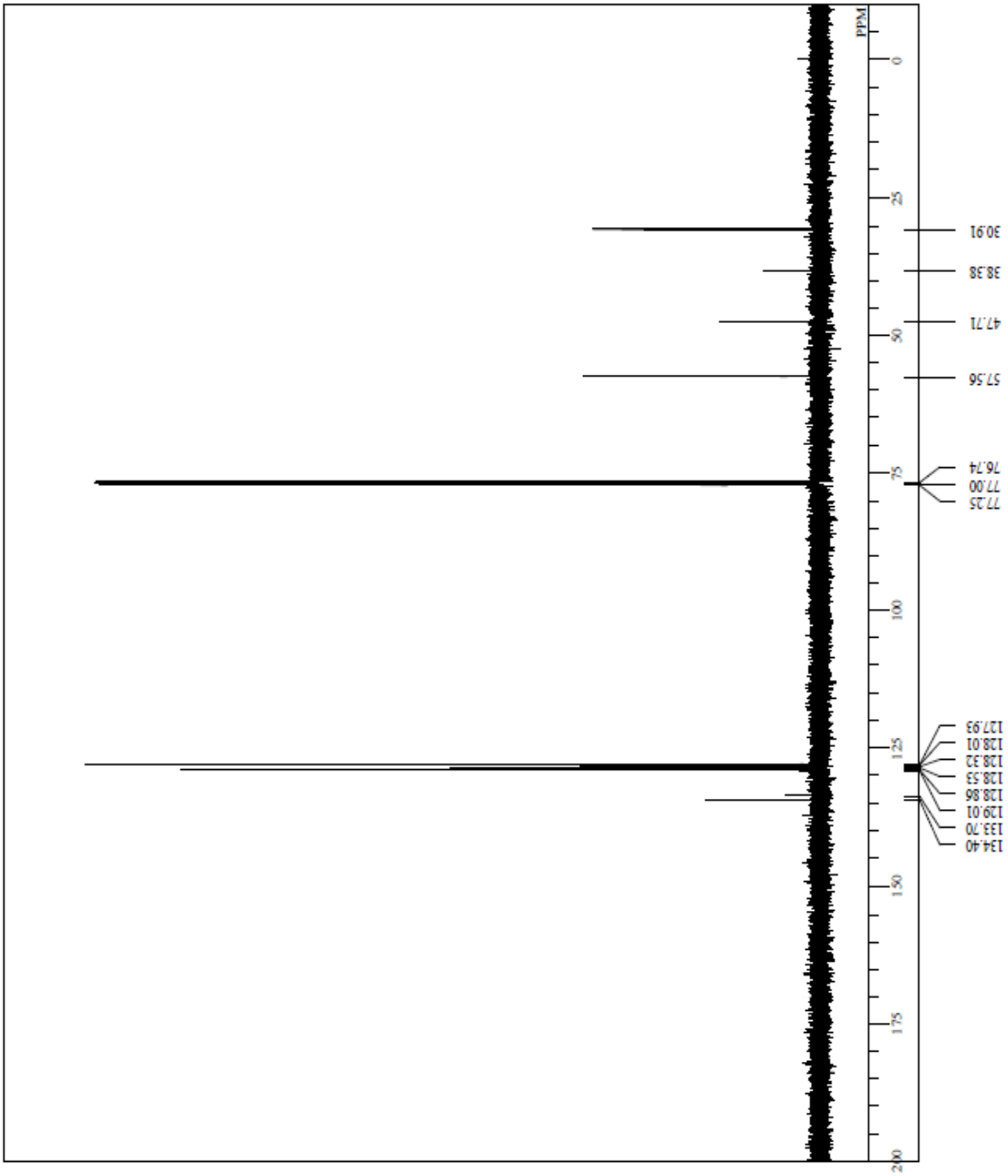
NO

14a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100
125
150
175
200
30.91
38.38
47.71
57.56
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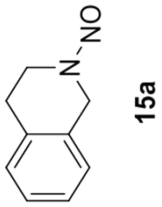
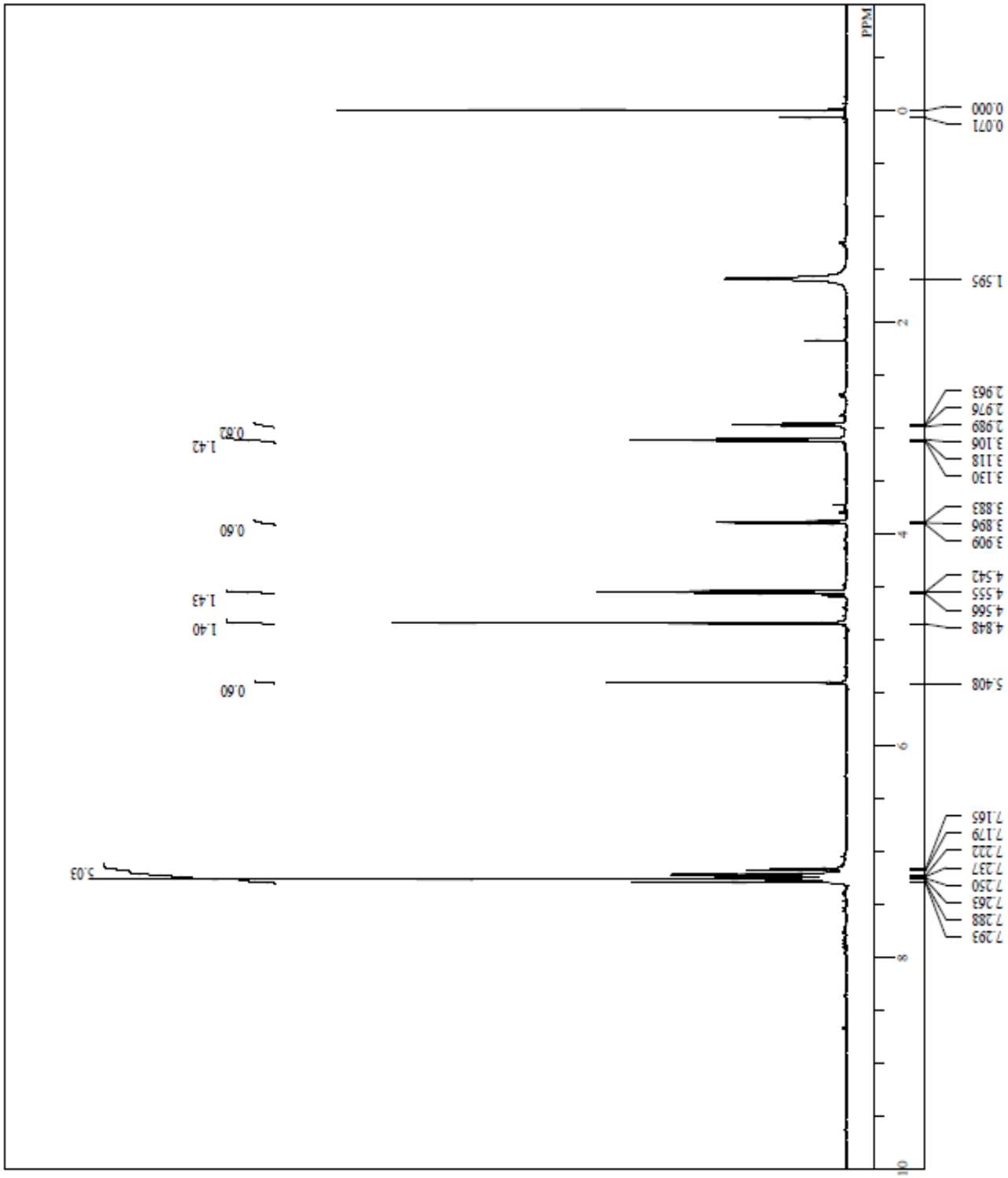
128.32
128.53
128.86
129.01
133.70
134.40



15a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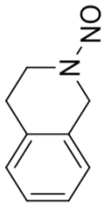
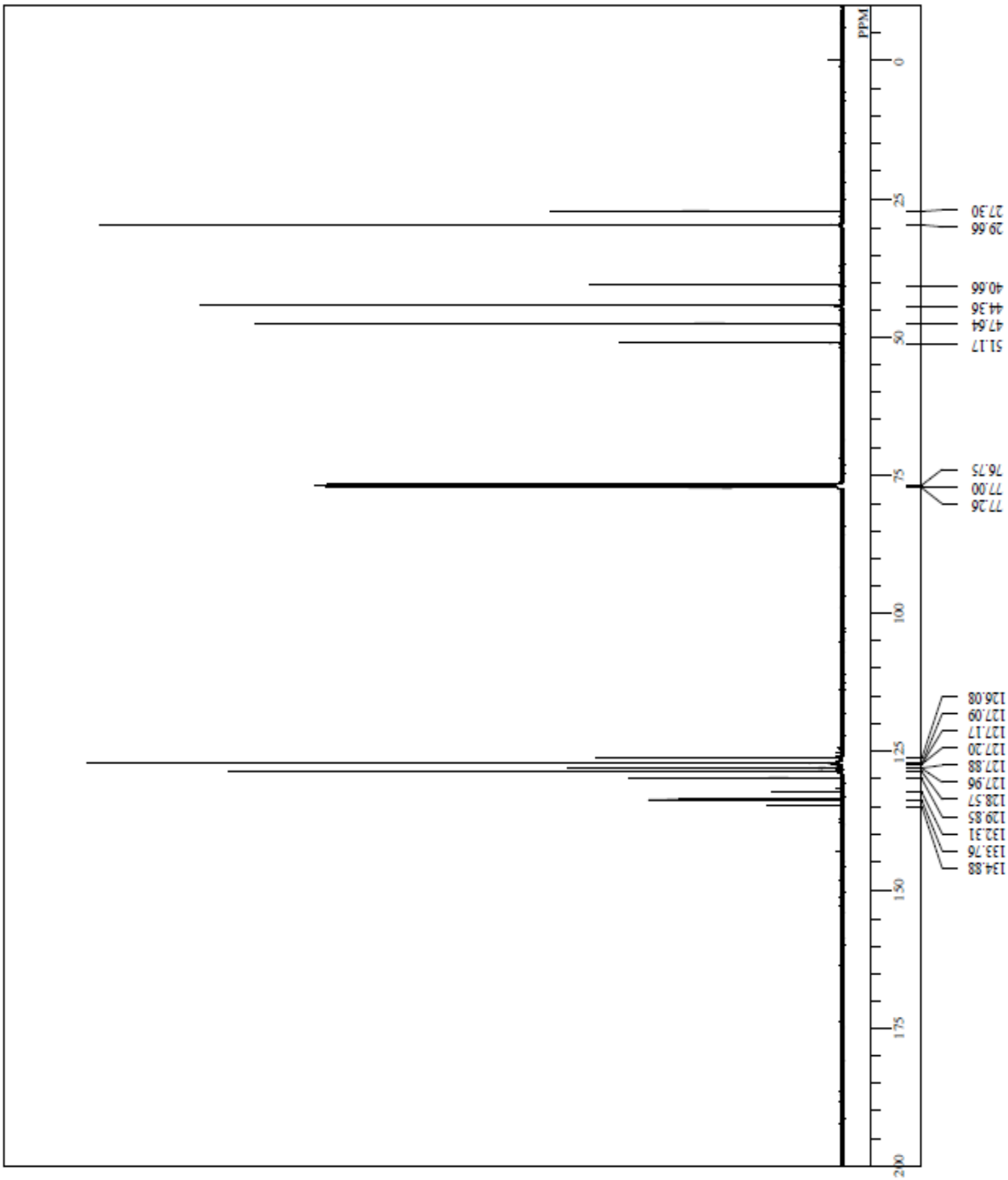
2.976
2.989
3.106
3.118
3.130
3.883
3.896
3.909
4.542
4.555
4.566
4.848
5.408
7.165
7.179
7.222
7.237
7.250
7.263
7.288
7.293
5.03
0.60
1.40
1.43
0.60
1.42
0.83


N
NO

15a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75
100
125
150
175
200
27.30
29.66
40.66
44.36
47.64
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77.00
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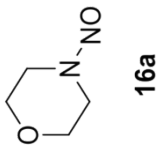
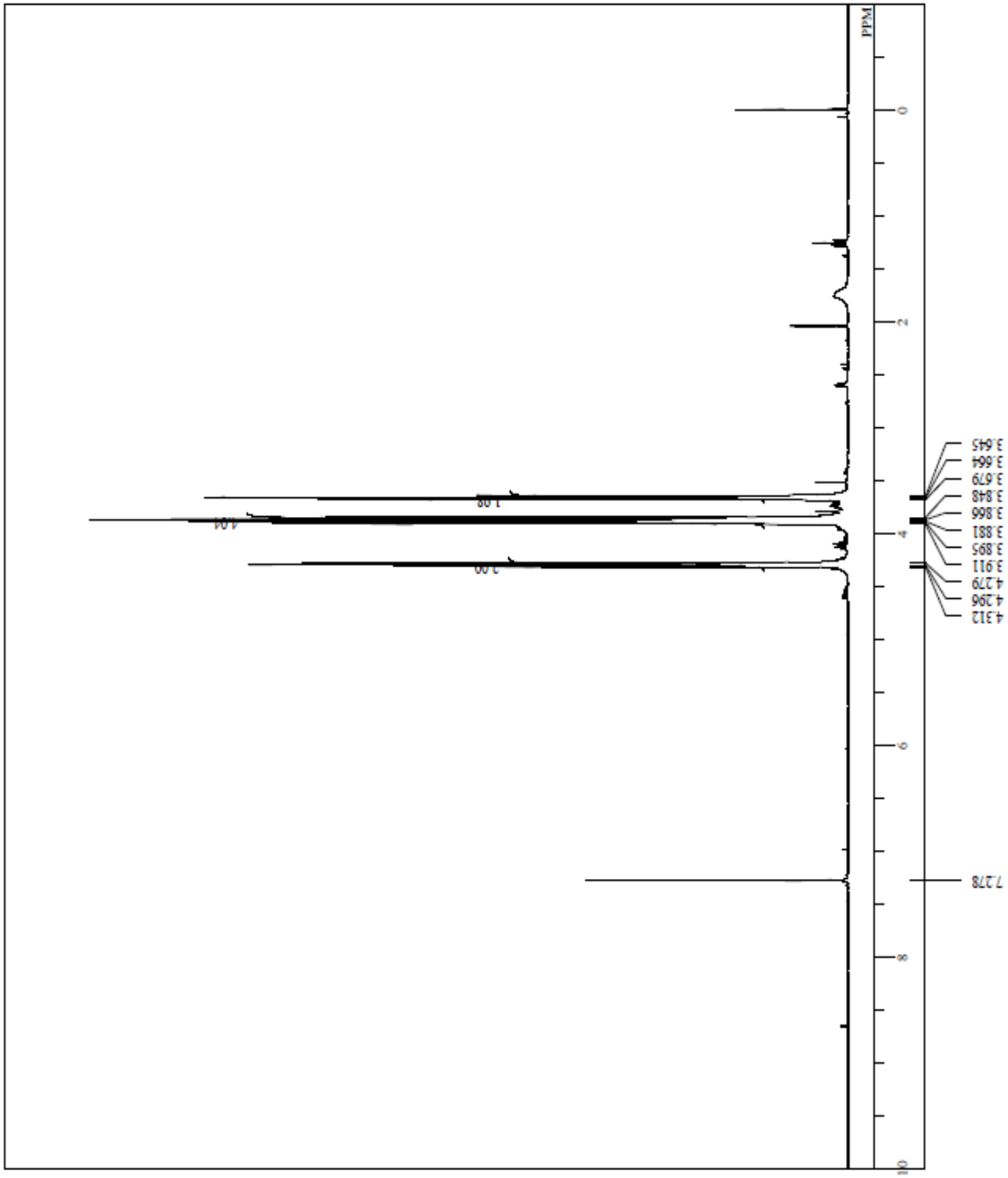
127.96
128.57
129.85
132.31
133.76
134.88


O
N
NO

16a


PPM
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4
6
8
10
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4.312
4.296
4.279
3.911
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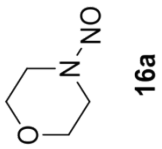
3.881
3.866
3.848
3.679
3.664
3.645
1.08
4.04
2.00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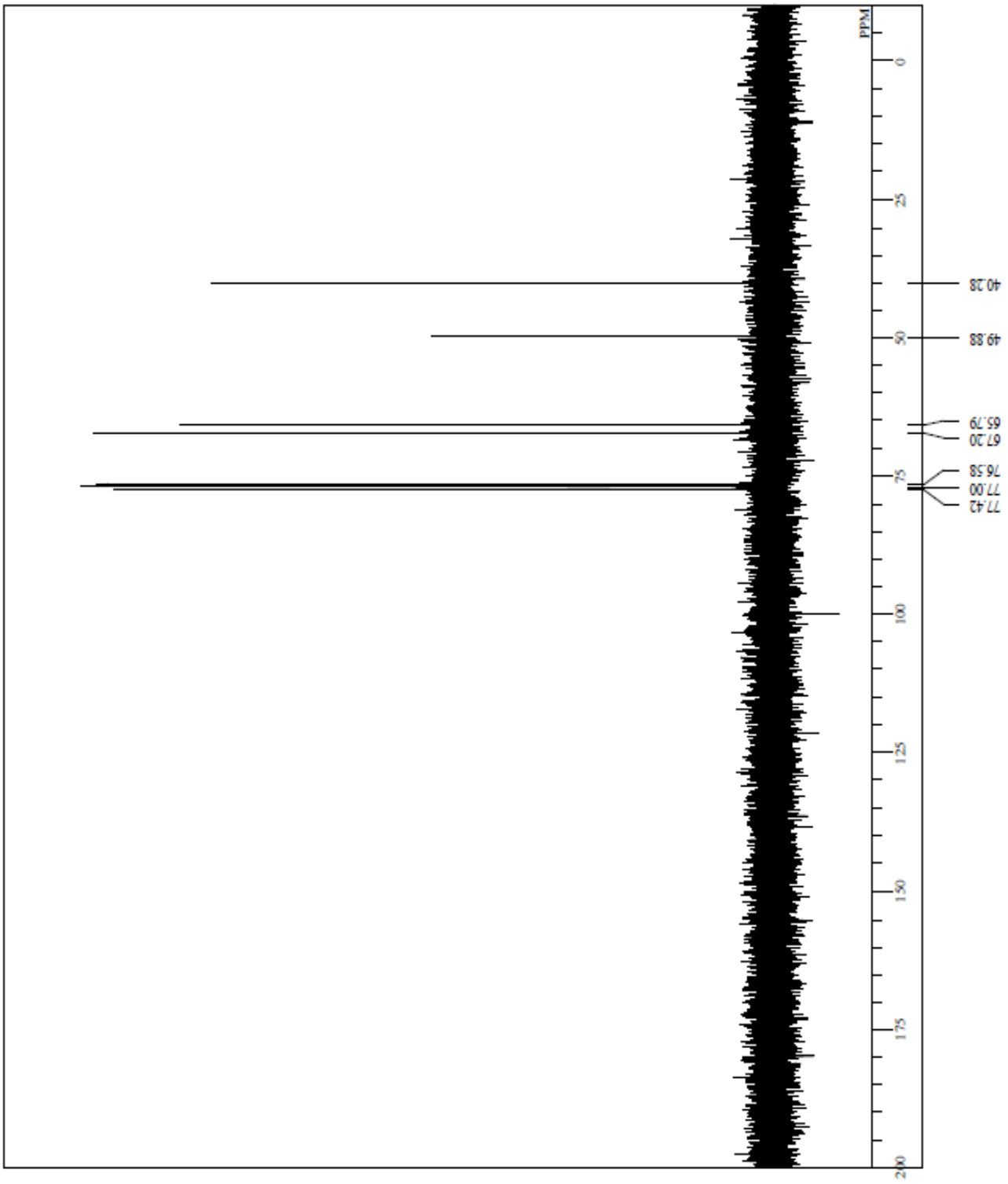
NO
O

16a


PPM
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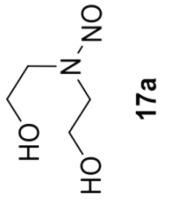
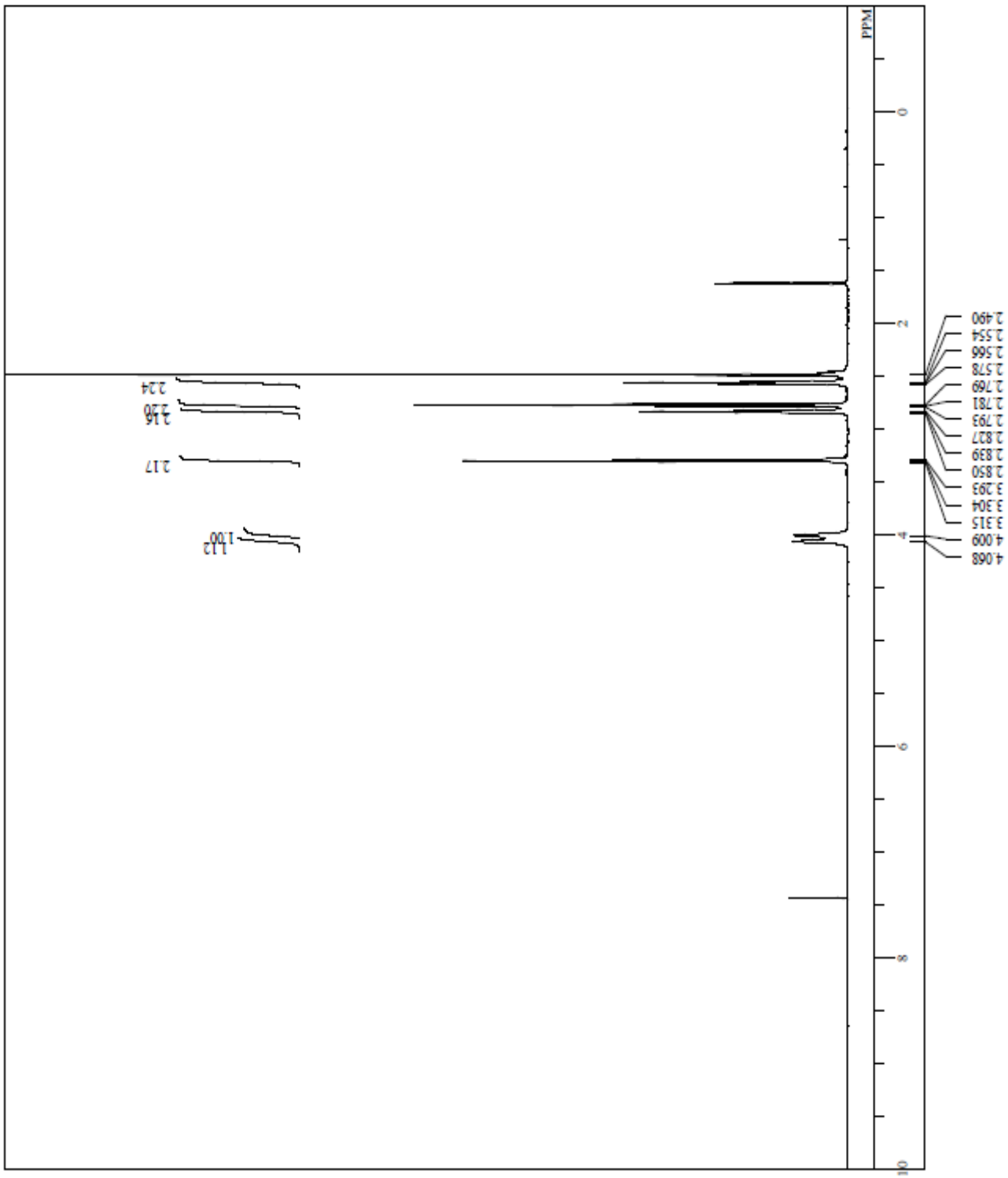
75
100
125
150
175
200
40.28
49.88
65.79
67.30
76.58
77.00
77.42


HO
N
NO
HO

17a


PPM
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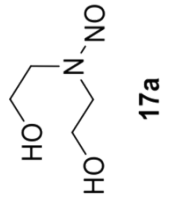
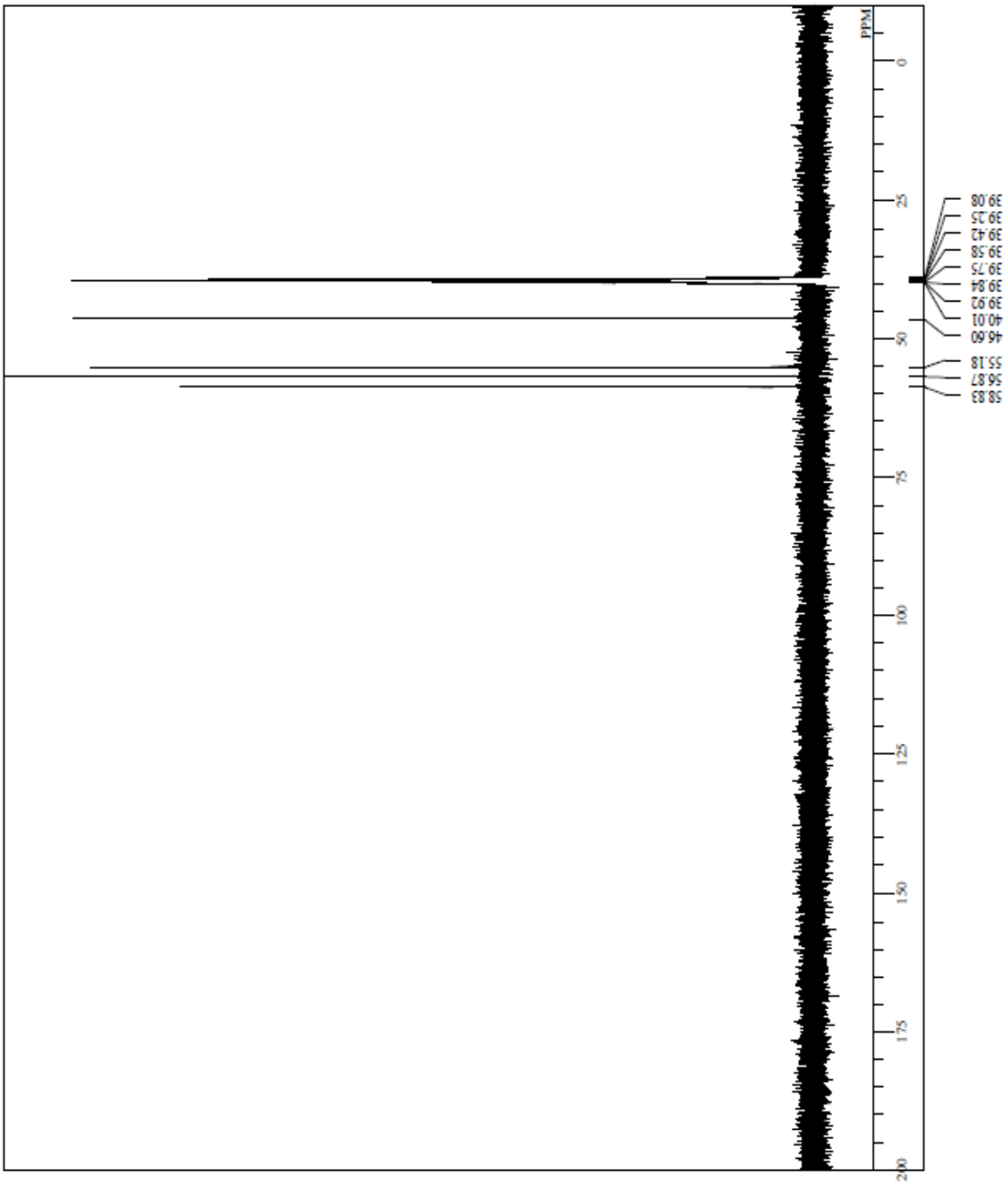
4
6
8
10
4.068
4.009
3.315
3.304
3.293
2.850
2.839
2.827
2.793
2.781
2.769
2.578
2.566
2.554
2.490
1.112
1.100
2.17
2.24
2.26


HO
N
NO
HO

17a


PPM
0
25
50
75
100
125
150
175
200
39.08
39.25
39.42
39.58
39.75
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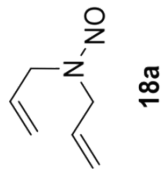
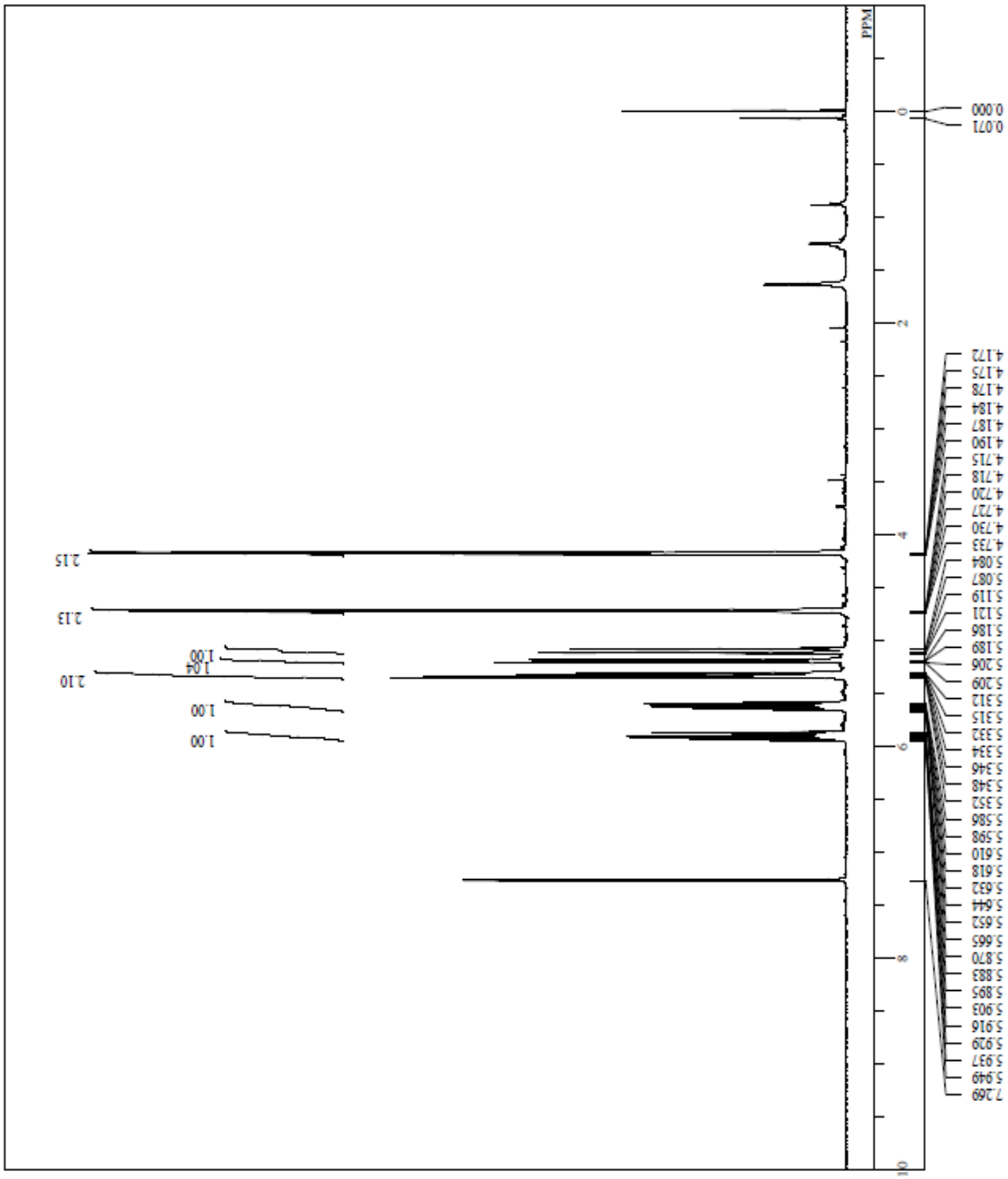
39.92
40.01
46.60
55.18
56.87
58.83


ON
N

18a


PPM
0
2
4
6
8
10
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0.000
4.172
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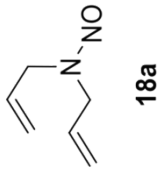
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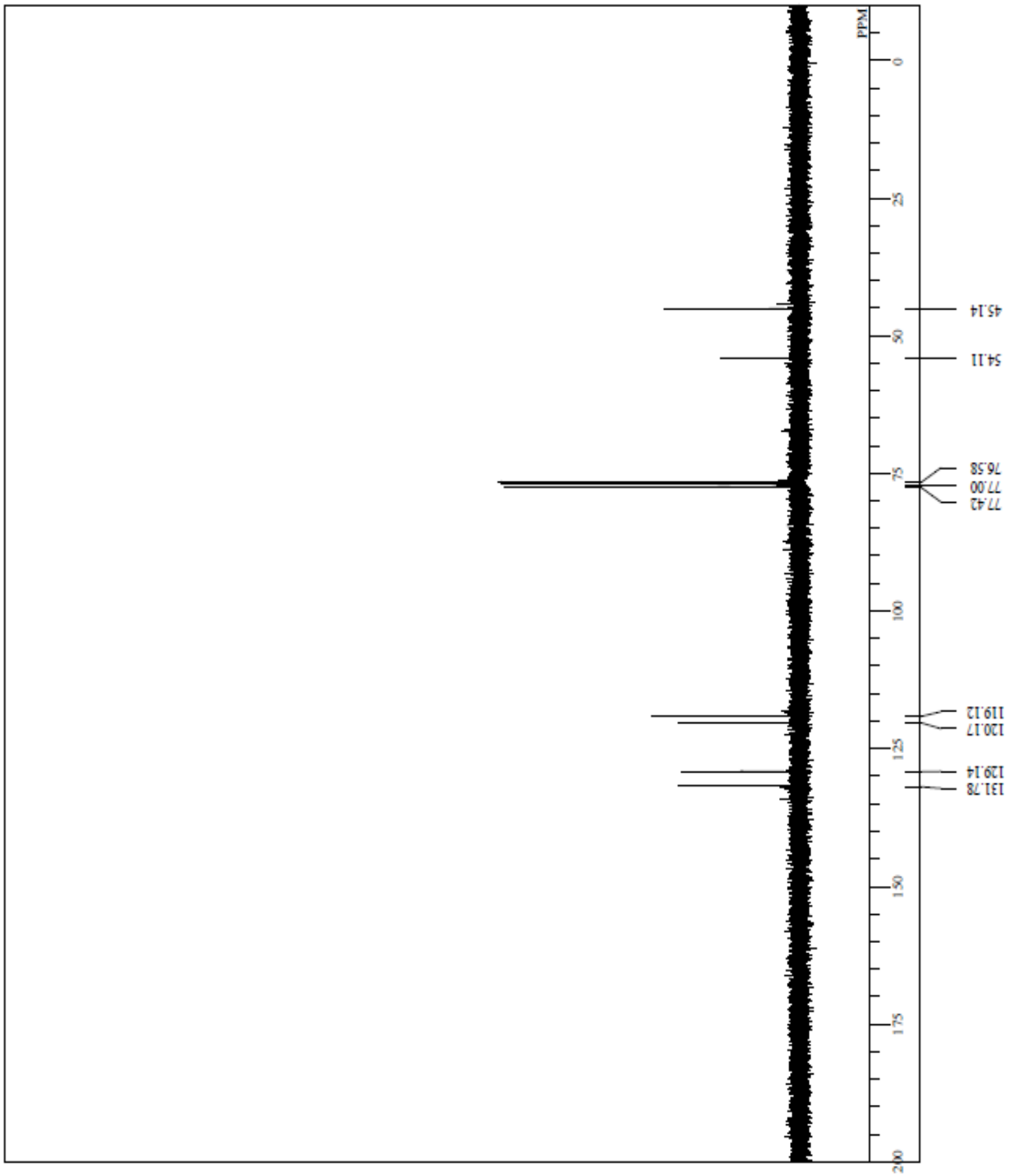
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