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Friedel–Crafts reaction of electron-rich (het)arenes with nitroalkenes

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Table of contents

Experimental S1
Friedel–Crafts alkylation. General procedure. S1
Characterization of the products S2
References S8
^{1}H, ^{13}C spectra of the Friedel–Crafts products. S9

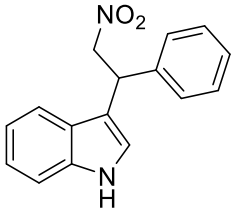
Experimental

All commercially available reagents were used without further purification. Solvents were purified using known procedures. Compounds **2a** [S1] and **2b** [S2] were prepared according to reported methods. All reactions were performed under an air atmosphere. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ with Bruker Avance-400 at ambient temperature. ^{13}C spectra were ^{1}H decoupled. Chemical shifts are reported in δ-scale in parts per million (ppm) relative to the residual solvent peak ($CHCl_3$: δ = 7.26 ppm for ^{1}H) or to solvent ($CDCl_3$: δ = 77.00 ppm for ^{13}C) as internal standards. Accurate-mass measurements (HRMS) were performed by ESI-TOF with a Thermo Scientific Orbitrap Elite mass spectrometer. Analytical TLC was carried out using Macherey-Nagel silica gel 60 F254 plates, the spots were visualized by UF. Preparative column chromatography was performed using Macherey-Nagel silica gel 60 (0.040–0.063 mm, 230–400 mesh). Melting points were measured with an Electrothermal IA 9200 apparatus and are uncorrected.

Friedel–Crafts alkylation. General procedure.

Magnesium iodide (0.025 mmol, 10 mol%, 6.9 mg) or calcium bis(trifluoromethane-sulfonimide) (0.025 mmol, 10 mol%, 15 mg) and nitroalkene (0.25 mmol) were dissolved in CH_2Cl_2 or $CHCl_3$ (0.5 ml). The mixture was stirred at room temperature for 30 min in a glass vial, and the appropriate (het)arene (0.5 mmol) was added. After the reaction completion, the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography to afford the desired product.

3-(2-Nitro-1-phenylethyl)-1*H*-indole (3a) [S3]

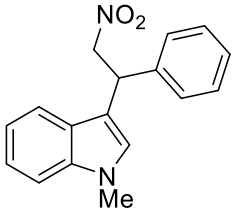


was obtained following the general procedure using indole **1a** (58 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/light petroleum, 1:1, then CH_2Cl_2/light petroleum, 3:1), the product was obtained as a grey solid, yield: 61 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 7.20–7.35 (m, 6 H), 7.22 (t, J = 7.5 Hz, 1 H), 7.08 (t, J = 7.5 Hz, 1 H), 6.99 (d, J = 1.8 Hz, 1 H), 5.20 (t, J = 8.2 Hz, 1 H), 5.07 (dd, J = 12.5, 8.2 Hz, 1 H), 4.95 (dd, J = 12.5, 8.2 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.1, 136.4, 128.9 (2C), 127.7 (2C), 127.50, 126.0, 122.6, 121.6, 119.9, 118.8, 114.3, 111.4, 76.7, 41.5.

1-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3b) [S4]

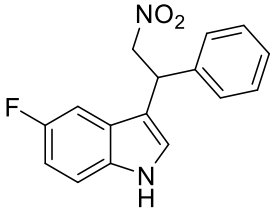


was obtained following the general procedure using indole **1b** (66 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a light-yellow oil, yield: 58 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d; 8.0 Hz; 1H), 7.26-7.40 (m; 7H), 7.12 (ddd, J = 8.6, 6.9, 1.0 Hz; 1H), 6.89 (s; 1H), 5.23 (t, J = 8.0 Hz; 1H), 5.07 (dd, J = 12.5, 8.0 Hz; 1H), 4.96 (dd, J = 12.5, 8.0 Hz; 1H), 3.75 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.2, 128.8 (2C), 127.7 (2C), 127.4, 126.5, 126.3, 122.1, 119.4, 118.9, 112.7, 109.5, 79.5, 41.4, 32.7.

5-Fluoro-3-(2-nitro-1-phenylethyl)-1*H*-indole (3c) [S5]

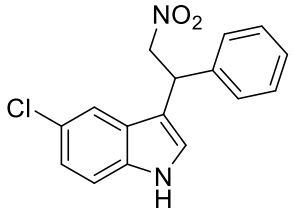


was obtained following the general procedure using indole **1c** (68 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a white solid.

Yield: 64 mg (90%).

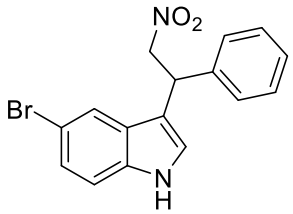
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s; 1H), 7.28-7.35 (m; 5H), 7.23 (dd, J = 9.0, 4.3 Hz; 1H), 7.05-7.07 (m; 2H), 6.94 (dt, J = 9.1, 2.3 Hz; 1H), 5.12 (t, J = 8.0 Hz; 1H), 5.04 (dd, J = 12.4, 8.0 Hz; 1H), 4.93 (dd, J = 12.4, 8.0 Hz; 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (d, J = 235.2 Hz), 138.8, 132.9, 129.0 (2C), 127.6 (3C), 126.4 (d, J = 10 Hz), 123.2, 114.3 (d, J = 4.2 Hz), 112.1 (d, J = 9.2 Hz), 111.1 (d, J = 26.1 Hz), 103.8 (d, J = 26.1 Hz), 79.35, 41.39.

5-Chloro-3-(2-nitro-1-phenylethyl)-1*H*-indole (3d) [S6]



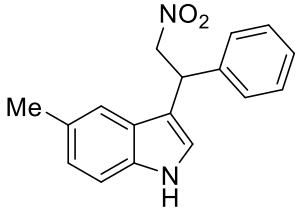
was obtained following the general procedure using indole **1d** (76 mg, 0.5 mmol), **2f** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a light-yellow oil, yield: 58 mg (77%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s; 1H), 7.40 (s; 1H), 7.22-7.36 (m; 1H), 7.14 (dd, J = 8.7, 1.6 Hz; 1H), 7.05 (d, J = 2.2 Hz; 1H), 5.13 (t, J = 8.0 Hz; 1H), 5.02 (dd, J = 12.5, 8.0 Hz; 1H), 4.91 (dd, J = 12.5, 8.0 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 134.8, 129.0 (2C), 127.7, 127.6 (2C), 127.1, 125.6, 123.0, 122.8, 118.2, 113.9, 112.4, 79.3, 41.3.

5-Bromo-3-(2-nitro-1-phenylethyl)-1*H*-indole (3e) [S4]



was obtained following the general procedure using indole **1e** (76 mg, 0.5 mmol), **2f** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a light-yellow oil, yield: 81 mg (94%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s;1H), 7.56 (d, J = 1.64 Hz; 1H), 7.25-7.35 (m; 6H), 7.19 (d, J = 8.7 Hz; 1H), 7.03 (d, J = 2.4 Hz; 1H), 5.12 (t, J = 8.0 Hz; 1H), 5.02 (dd, J = 12.5, 8.0 Hz; 1H), 4.91 (dd, J = 12.5, 8.0 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 135.0, 129.0 (2C), 127.8, 127.7, 127.60 (2C), 125.6, 122.7, 121.4, 113.9, 113.2, 112.8, 79.3, 41.2.

5-Methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole (3f) [S6]

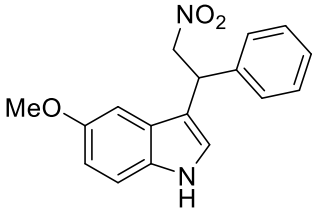


was obtained following the general procedure using indole **1f** (66 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a light-yellow oil, yield: 64 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s; 1H), 7.23-7.36 (m; 7H), 7.05 (d, J = 8.3 Hz; 1H), 6.93 (d, J = 2.5 Hz; 1H), 5.18 (t, J = 7.8 Hz; 1H), 5.05 (dd, J = 12.5, 7.8 Hz; 1H), 4.94 (dd, J = 12.5, 7.8 Hz; 1H), 2.44 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 134.7, 129.2, 128.9 (2C), 127.7 (2C), 127.5, 126.2, 124.3, 121.8, 118.3, 113.7, 111.0, 79.5, 41.3, 21.5.

5-Methoxy-3-(2-nitro-1-phenylethyl)-1*H*-indole (3g) [S4]

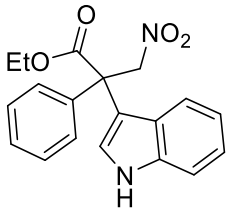


was obtained following the general procedure using indole **1g** (73 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a light-yellow oil, yield: 57 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s; 1H), 7.31-7.35 (m; 4H), 7.26-7.29 (m; 1H), 7.21 (dd, J = 6.8, 2.7 Hz; 1H), 6.96 (d, J = 2.4 Hz; 1H), 6.86-6.89 (m; 2H), 5.15 (dd, J = 8.5, 7.5 Hz; 1H), 5.04 (dd, J = 12.5, 7.5 Hz), 4.93 (dd, J = 12.5, 8.5 Hz; 1H) 3.79 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 139.0, 131.5, 128.9 (2C), 127.7 (2C), 127.5, 126.5, 122.2, 113.8, 112.6, 112.1, 100.7, 79.4, 55.8, 41.4.

Ethyl 2-(1*H*-Indol-3-yl)-3-nitro-2-phenylpropanoate(3h) [S3]

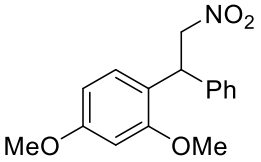


was obtained following the general procedure using indole **1a** (58 mg, 0.5 mmol), **2b** (55 mg, 0.25 mmol) in $CHCl_3$ and $Ca(NTf_2)_2$ as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 4:1, then CH_2Cl_2), the product was obtained as a white solid, yield: 76 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 7.49 (d, J = 2.5 Hz, 1 H), 7.30–7.38 (m, 6 H), 7.11 (t, J = 7.6 Hz, 1 H), 6.87 (t, J = 7.6 Hz, 1 H), 6.77(d, J = 8.21 Hz, 1 H), 5.66 (d, J = 13.6 Hz, 1 H), 5.45 (d, J = 13.6 Hz, 1 H), 4.20–4.33 (m, 2 H), 1.21 (t, J = 7.07 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 137.8, 136.4, 128.2 (2 C), 127.7 (2 C), 127.7, 125.1, 124.9, 121.5, 120.2, 119.1, 111.4, 80.6, 61.8, 54.5, 13.6 (one aromatic quaternary carbon atom was not unambiguously assigned).

2,4-Dimethoxy-1-(2-nitro-1-phenylethyl)benzene (4a)



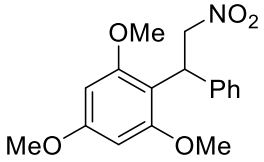
was obtained following the general procedure using 1,3-dimethoxybenzene (69 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a light-yellow oil, yield: 49 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.34 (m; 5H), 6.96 (d, J = 9.3 Hz; 1H), 6.44 (d, J = 2.4 Hz; 1H), 6.42 (dd, J = 8.5, 2.4 Hz; 1H), 5.19 (dd, J = 8.8, 7.4 Hz; 1H), 5.02 (dd, J = 12.8, 7.4 Hz; 1H), 4.94 (dd, J = 128, 8.8 Hz; 1H), 3.81 (s; 3H), 3.78 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 157.8, 139.2, 129.0, 128.7, 127.8, 127.1, 119.9, 104.2, 100.0, 78.0, 55.4, 55.9, 42.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{17}NO_4$: 288.1236; found: 288.1231.

1,3,5-Trimethoxy-2-(2-nitro-1-phenylethyl)benzene (4b) [S7]

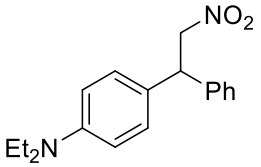


was obtained following the general procedure using 1,3,5-trimethoxybenzene (84 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a light-yellow oil, yield: 44 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.6 Hz; 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.0 Hz; 1H), 6.13 (s; 2H), 5.50 (t, J = 7.8 Hz; 1H), 5.24 (dd, J = 12.5, 8.4 Hz, 1H), 5.13 (dd, J = 12.5, 7.4 Hz; 1H), 3.80 (s; 6H), 3.79 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 158.9 (2C), 140.5, 128.2 (2C), 127.5 (2C), 126.5, 92.8, 91.1 (2C), 78.2, 55.7 (2C), 55.2, 38.5.

***N*,*N*-diethyl-4-(2-nitro-1-phenylethyl)aniline (4c)** [S8]

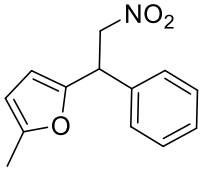


was obtained following the general procedure using *N*,*N*-diethylaniline (75 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a light-yellow oil, yield: 62 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.35 (m; 2H), 7.22-7.27 (m; 3H), 7.06 (d, J = 8.7 Hz; 2H), 6.61 (d, J = 8.7 Hz; 2H), 4.97 (dd, J = 12.5, 8.2 Hz; 1H), 4.92 (dd, J = 12.5, 8.2 Hz; 1H), 4.80 (t, J = 8.2 Hz; 1H), 3.33 (q, J = 7.1 Hz; 4H), 1.14 (t, J = 7.1 Hz; 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 140.0, 128.8 (2C), 128.5 (2C), 127.6 (2C), 127.22, 125.3, 111.8 (2C), 79.6, 48.2, 44.2, 12.5.

2-Methyl-5-(2-nitro-1-phenylethyl)furan (4d) [S9]

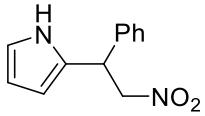


was obtained following the general procedure using 2-methylfuran (42 mg, 0.5 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a light-yellow oil, yield: 26 mg (44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.37 (m; 5H), 5.97 (d, J = 3.0 Hz; 1H), 5.88-5.89 (m; 1H), 4.99 (dd, J = 12.0, 7.6 Hz; 1H), 4.87 (t, J = 7.6 Hz; 1H), 4.89 (dd, J = 12.0, 7.6 Hz; 1H), 2.25 (s; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 150.0, 137.1, 129.0 (2C), 128.0 (2C), 127.9, 108.1, 106.3, 78.2, 43.6, 13.5.

2-(2-Nitro-1-phenylethyl)-1*H*-pyrrole (5) [S6]

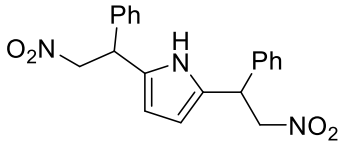


was obtained following the general procedure using pyrrole (67 mg, 1 mmol), **2a** (37 mg, 0.25 mmol) in CH_2Cl_2 and MgI_2 as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:2, then CH_2Cl_2/ light petroleum, 1:1), the product was obtained as a brown oil, yield: 30 mg (46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s; 1H), 7.29-7.38 (m; 3H), 7.23-7.26 (m; 2H), 6.69 (dd, J = 2.5, 1.6 Hz; 1H), 6.18 (q, J = 2.8 Hz; 1H), 6.08-6.10 (m; 1H), 4.99 (dd, J = 11.8, 7.5 Hz; 1H), 4.90 (t, J = 7.5 Hz; 1H), 4.81 (dd, J = 11.8, 7.5 Hz; 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 129.2 (2C), 128.1, 127.9 (2C), 118.2, 108.6, 105.7, 79.2, 42.9 (one quaternary aromatic carbon was not unambiguously assigned).

2,5-Bis(2-nitro-1-phenylethyl)-1*H*-pyrrole (*dl*-6 + *meso*-6) [S10]

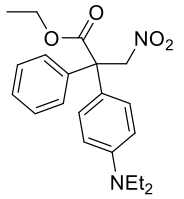


was the second product in the above reaction, yield: 22 mg (31%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s; 1H), 7.51 (s; 1H), 7.24-7.36 (m; 6H), 7.14-7.17 (m; 4H), 6.01 (d, J = 2.6 Hz; 2H), 5.99 (d, J = 2.6 Hz; 2H), 4.87-4.91 (m; 2H), 4.69-4.81 (m; 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.71, 137.65, 129.49, 129.18, 129.12, 128.16, 128.12, 127.8, 127.7, 106.5, 106.1, 79.11, 79.06, 42.7 (two quaternary carbons were not unambiguously assigned).

Ethyl 2-(4-(diethylamino)phenyl)-3-nitro-2-phenylpropanoate (7a)



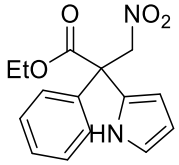
was obtained following the general procedure using *N*,*N*-diethylaniline (75 mg, 0.5 mmol), **2b** (55 mg, 0.25 mmol) in $CHCl_3$ and $Ca(NTf_2)_2$ as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as an light-yellow oil, yield: 35 mg (38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.32 (m; 5H), 7.03 (d, J = 9.0 Hz; 2H), 6.57 (d, J = 9.0 Hz; 1H), 5.47 (d, J = 14 Hz; 1H), 5.31 (d, J = 14 Hz; 1H), 4.22-4.33 (m; 2H), 3.33 (q, J = 7.1 Hz; 4H), 1.25 (t, J = 7.2 Hz; 3H), 1.15 (t, J = 7.1 Hz; 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 147.0, 139.7, 129.2 (2C), 128.4 (2C), 128.1 (2C), 127.5, 124.9, 111.0 (2C), 81.6, 61.9, 57.9, 44.2 (2C), 13.9, 12.7 (2C).

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{27}N_2O_4$: 371.1971; found: 371.1978.

Ethyl 3-nitro-2-phenyl-2-(1*H*-pyrrol-2-yl)propanoate (7b)



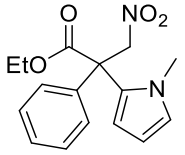
was obtained following the general procedure using pyrrole (67 mg, 1 mmol), **2b** (55 mg, 0.25 mmol) in $CHCl_3$ and $Ca(NTf_2)_2$ as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as a white solid, yield: 58 mg (81%), m.p. 112-113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s; 1H), 7.30-7.34 (m; 3H), 7.09-7.11 (m, 2H), 6.82 (dt, J = 2.6, 1.4 Hz; 1H), 6.20 (q, J = 3.1 Hz; 1H), 6.10 – 6.02 (m; 1H), 5.44 (d, J = 15.0 Hz; 1H), 5.17 (d, J = 15.0 Hz; 1H), 4.43 – 4.28 (m; 2H), 1.32 (t, J = 7.1 Hz; 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 138.3, 128.8 (2C), 128.4 (2C), 127.3, 127.0, 118.5, 108.1, 106.9, 79.8, 62.6, 54.1, 13.8.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{17}N_2O_4$: 289.1188; found: 289.1183.

Ethyl 2-(1-methyl-1*H*-pyrrol-2-yl)-3-nitro-2-phenylpropanoate (7c)



was obtained following the general procedure using *N*-methylpyrrole (81 mg, 1 mmol), **2b** (55 mg, 0.25 mmol) in $CHCl_3$ and $Ca(NTf_2)_2$ as the catalyst. After purification by gradient column chromatography (CH_2Cl_2/ light petroleum, 1:1, then CH_2Cl_2/ light petroleum, 3:1), the product was obtained as an oil, yield: 50 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.36 (m, 3H), 7.20-7.27 (m, 2H), 6.60 (t, J = 2.1 Hz; 1H), 6.14 (d, J = 2.3 Hz; 2H), 5.55 (d, J = 14.1 Hz; 1H), 4.99 (d, J = 14.1 Hz; 1H), 4.47-4.22 (m; 2H), 3.07 (s, 3H), 1.30 (t, J = 7.1 Hz; 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 137.0, 128.7 (2C), 128.1 (2C), 128.1, 127.8, 125.3, 108.3, 106.8, 82.2, 62.2, 54.7, 35.8, 13.8.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_4$: 303.1345; found: 303.1350.

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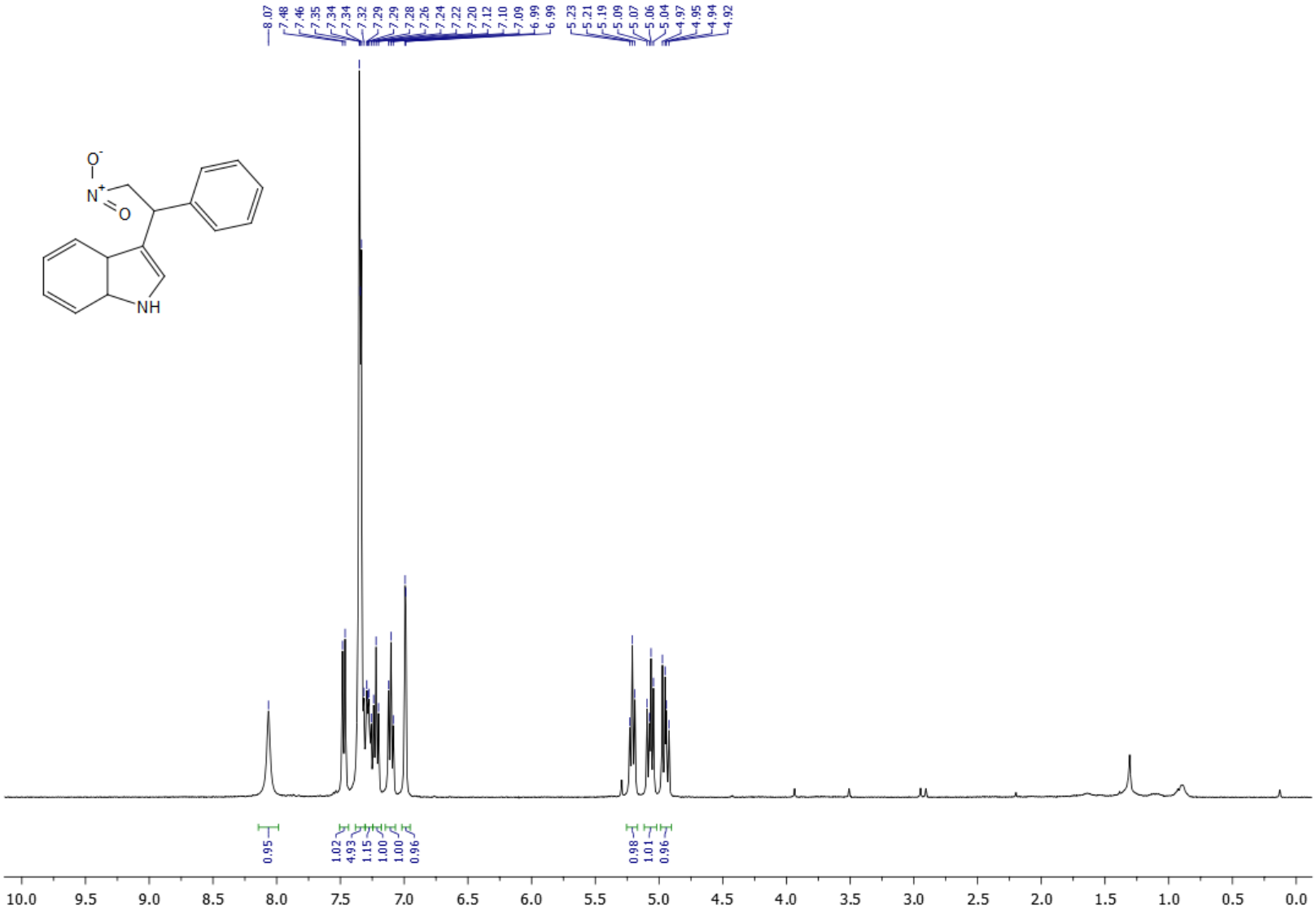
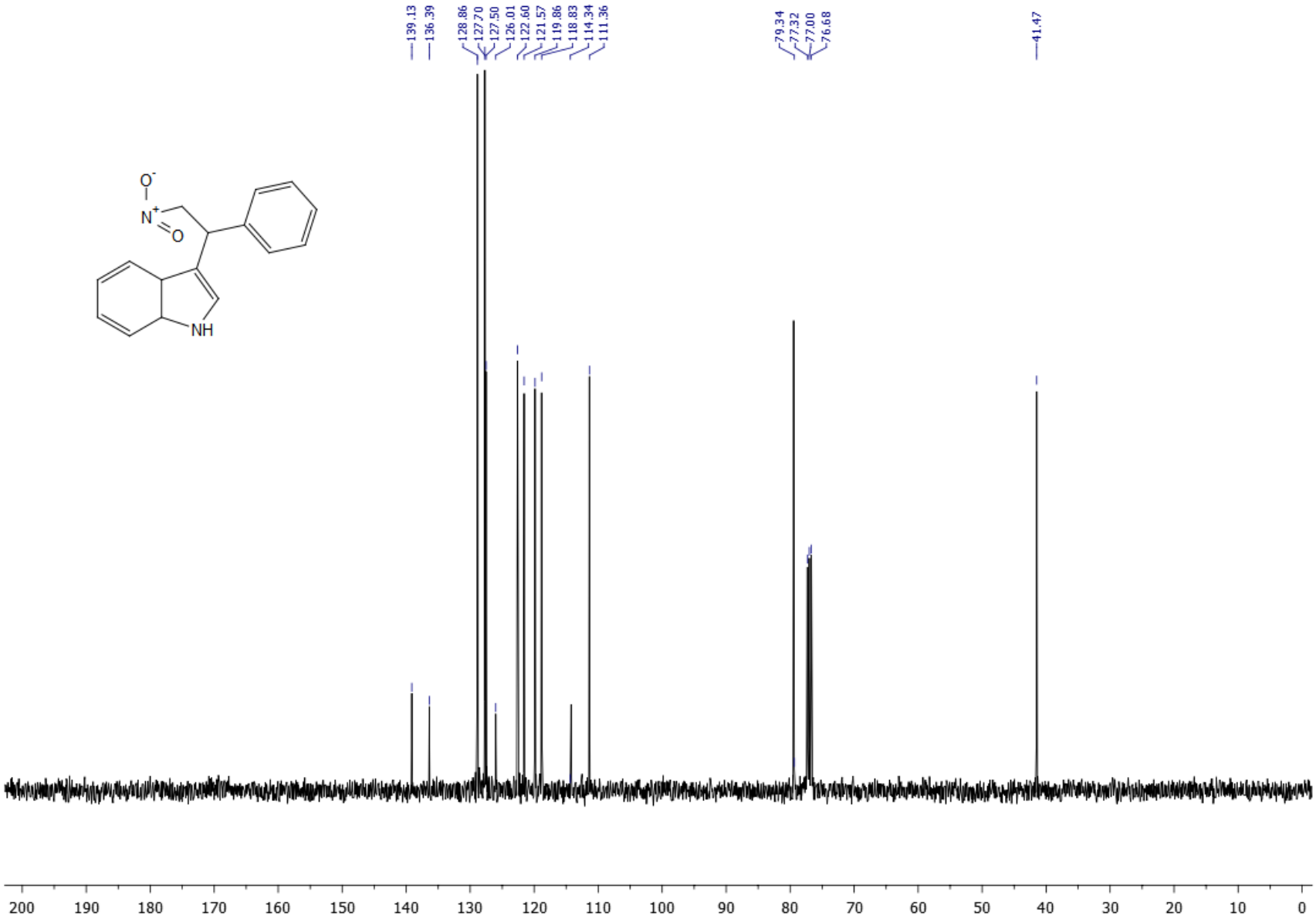
^{1}H, ^{13}C spectra of Friedel-Crafts products.

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O
NH
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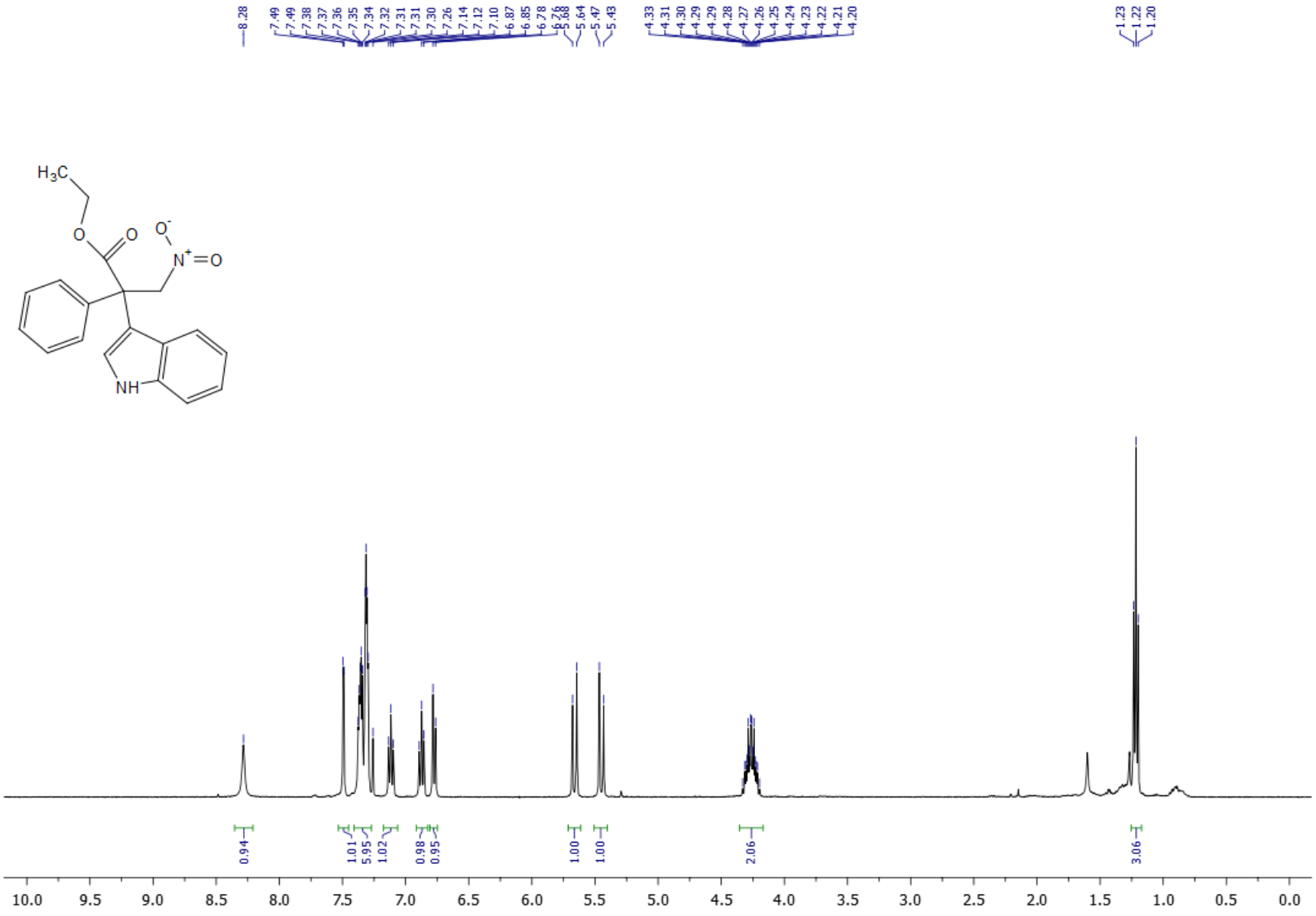
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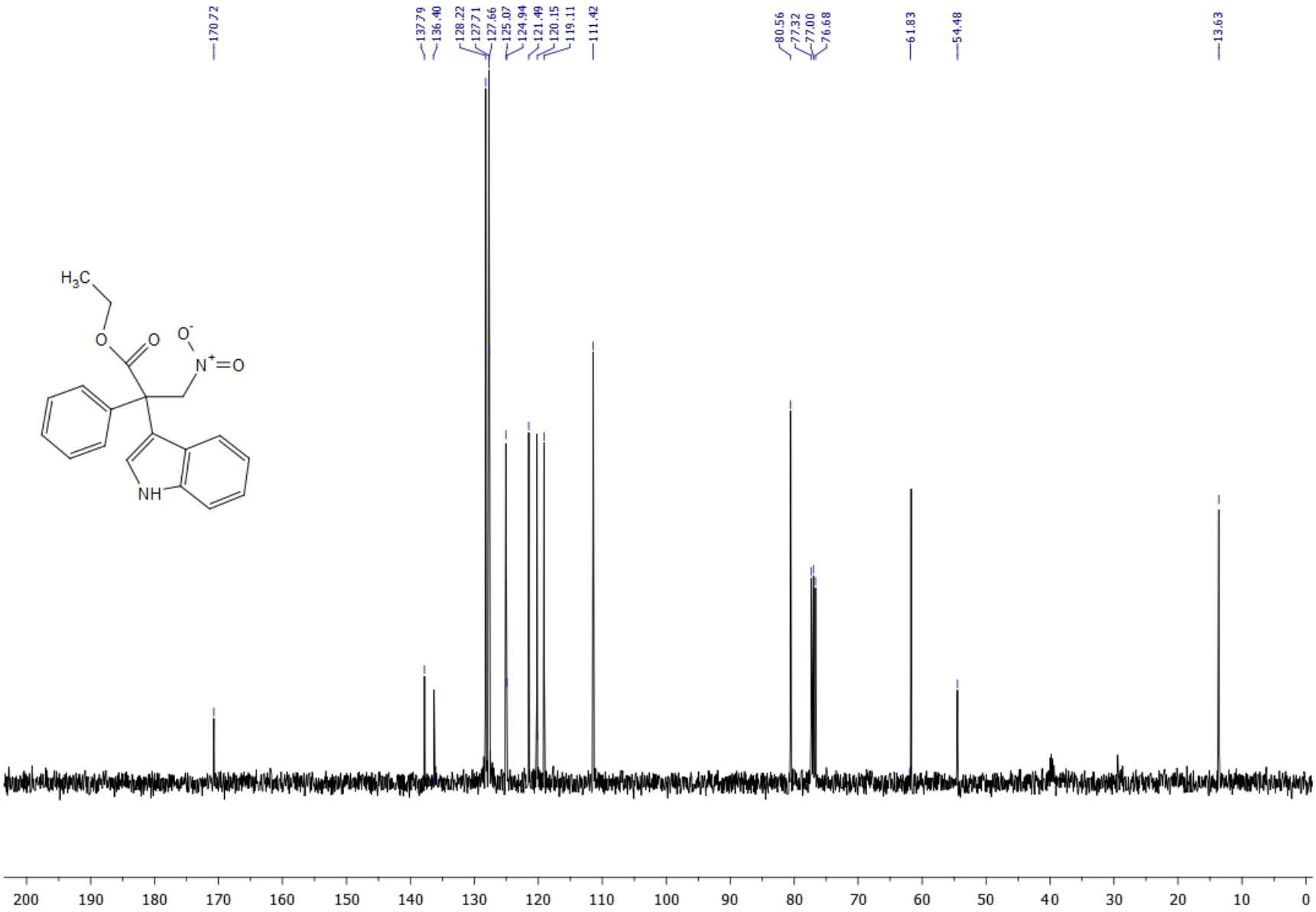
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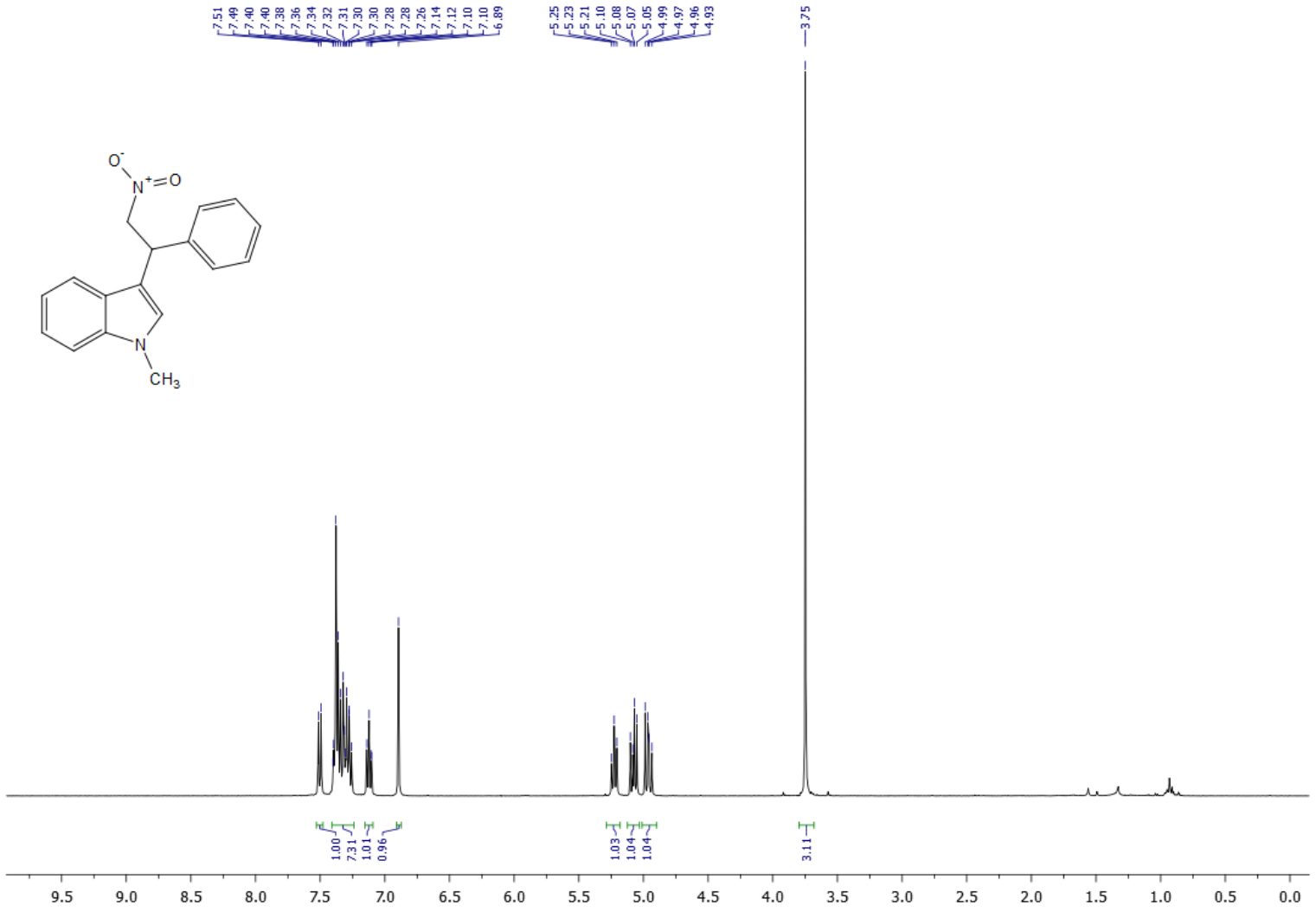
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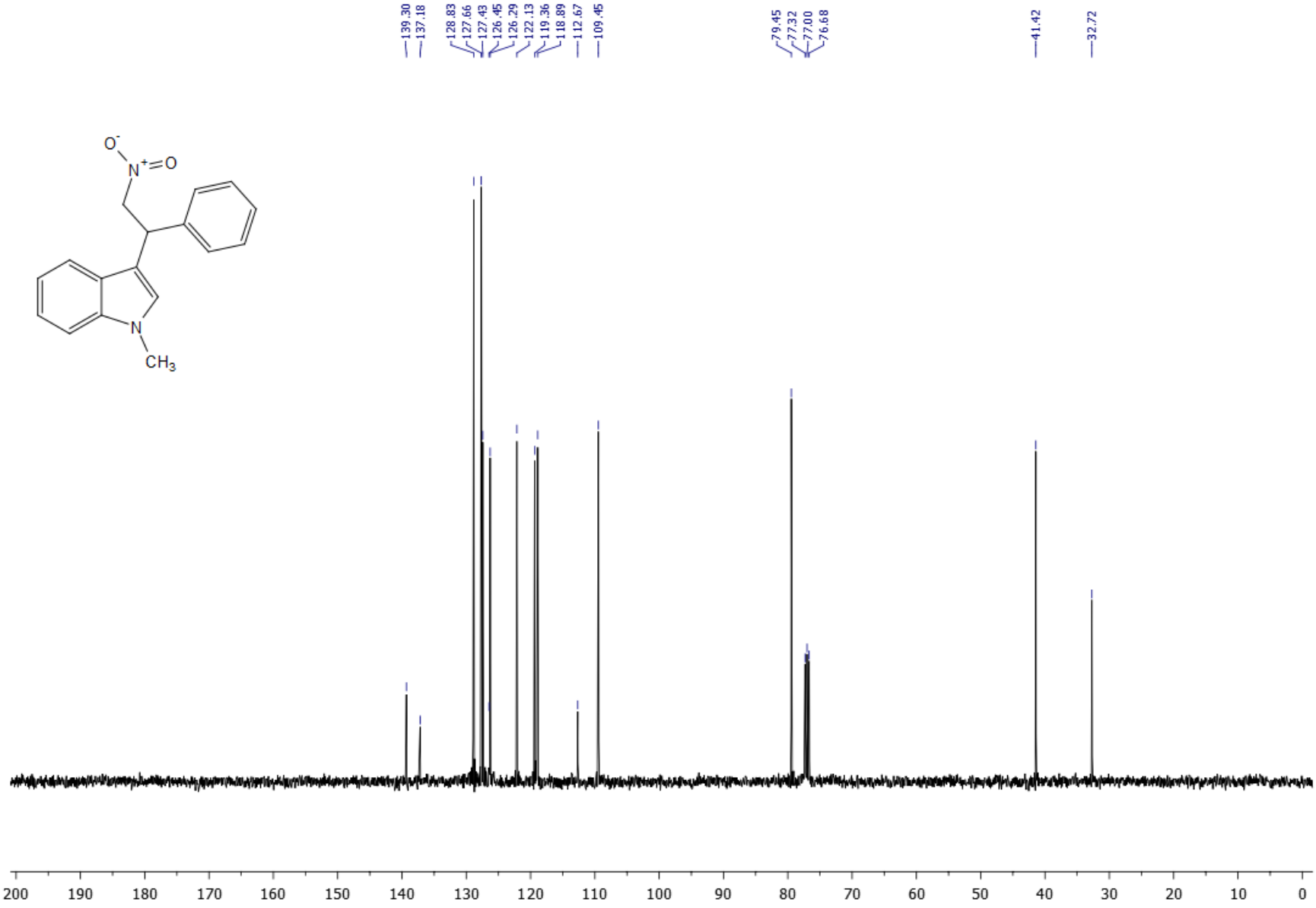
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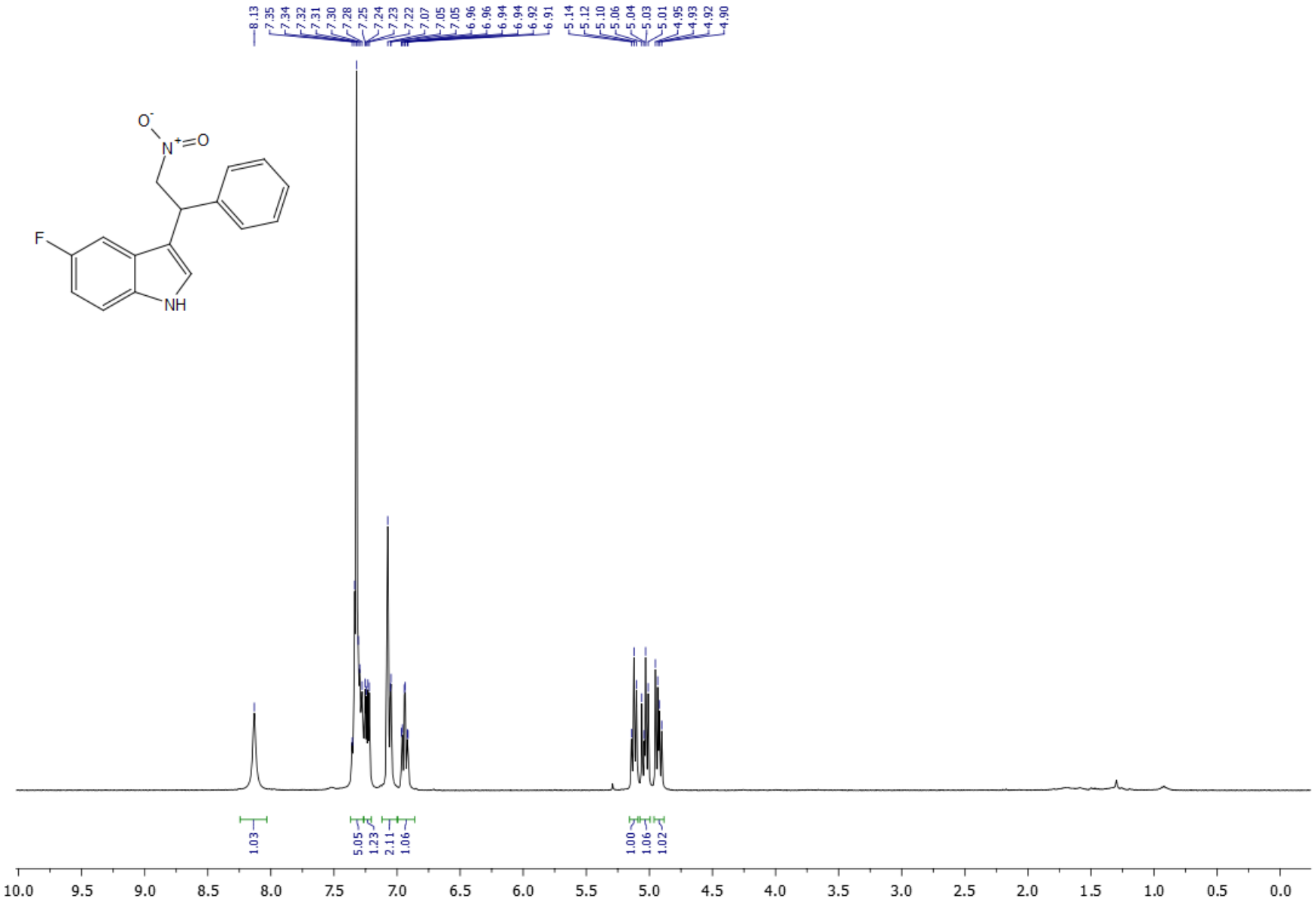
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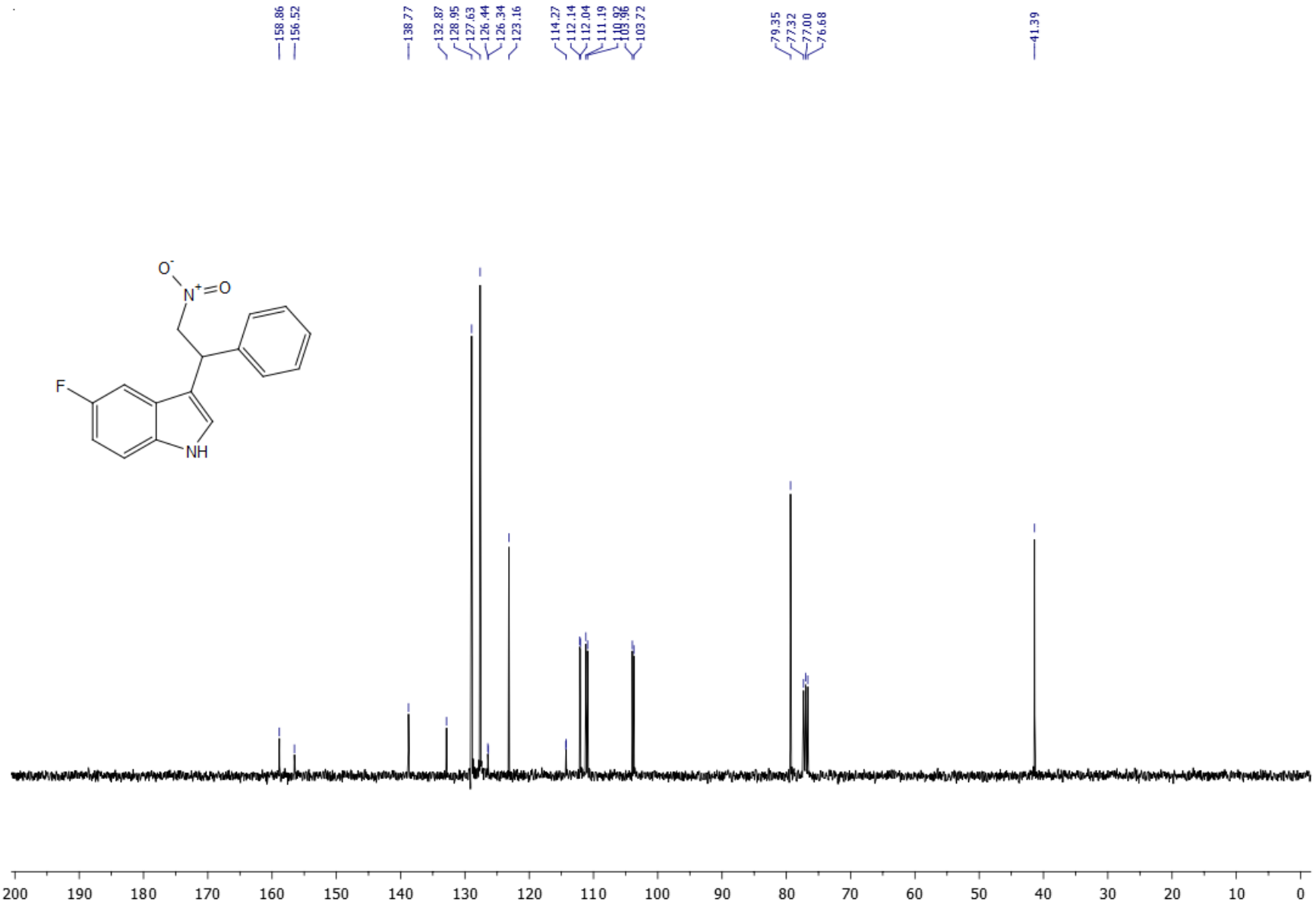
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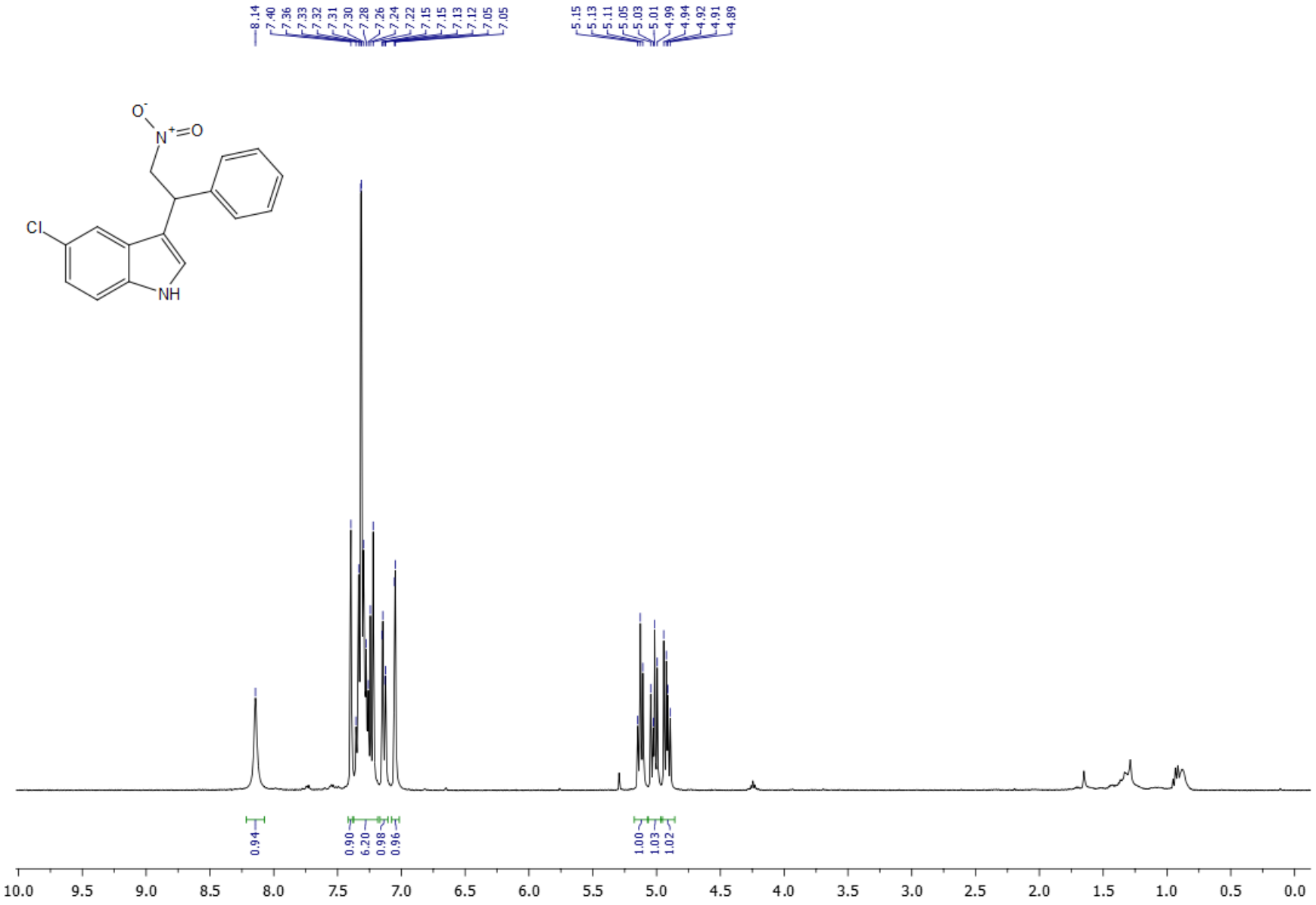
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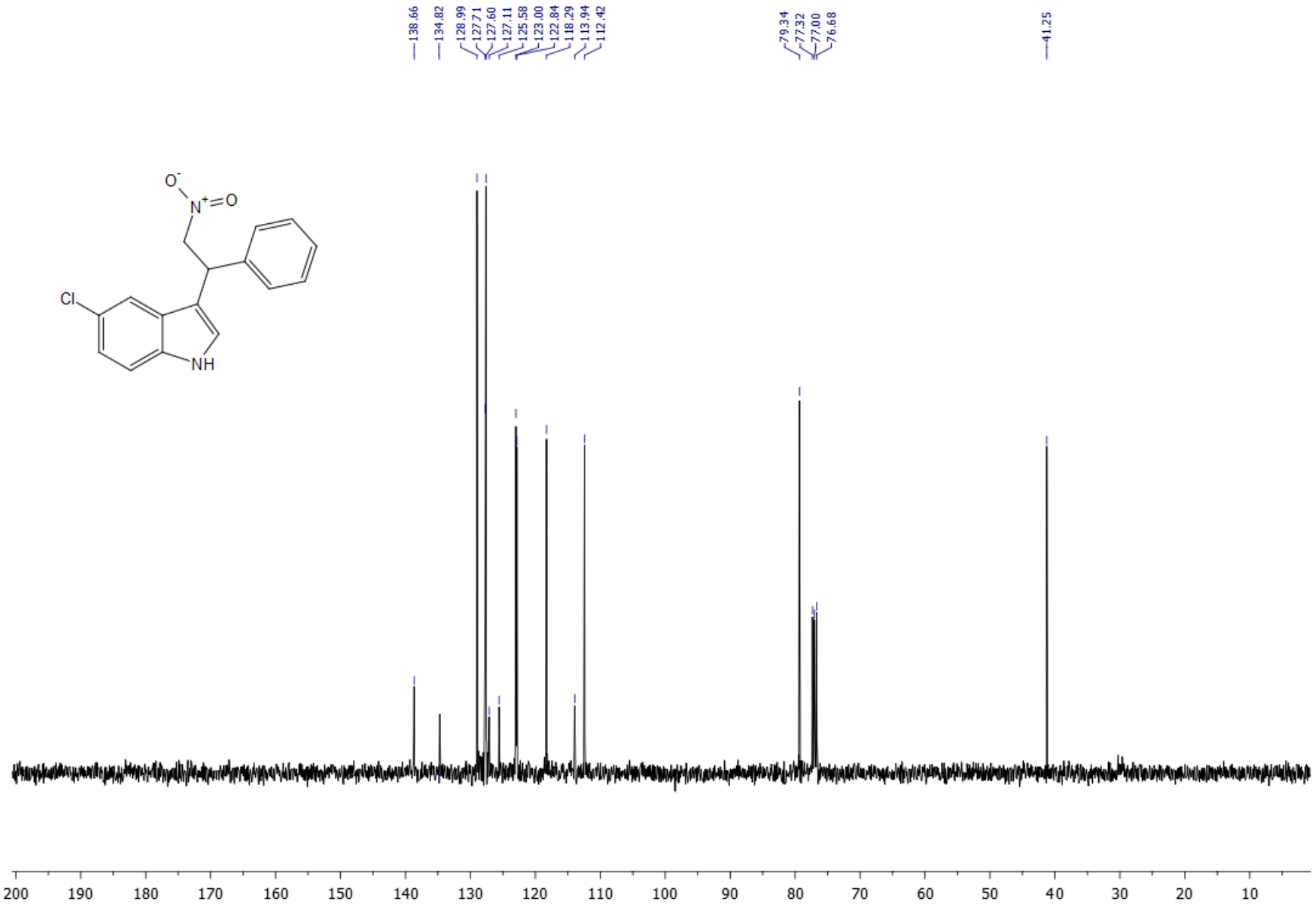
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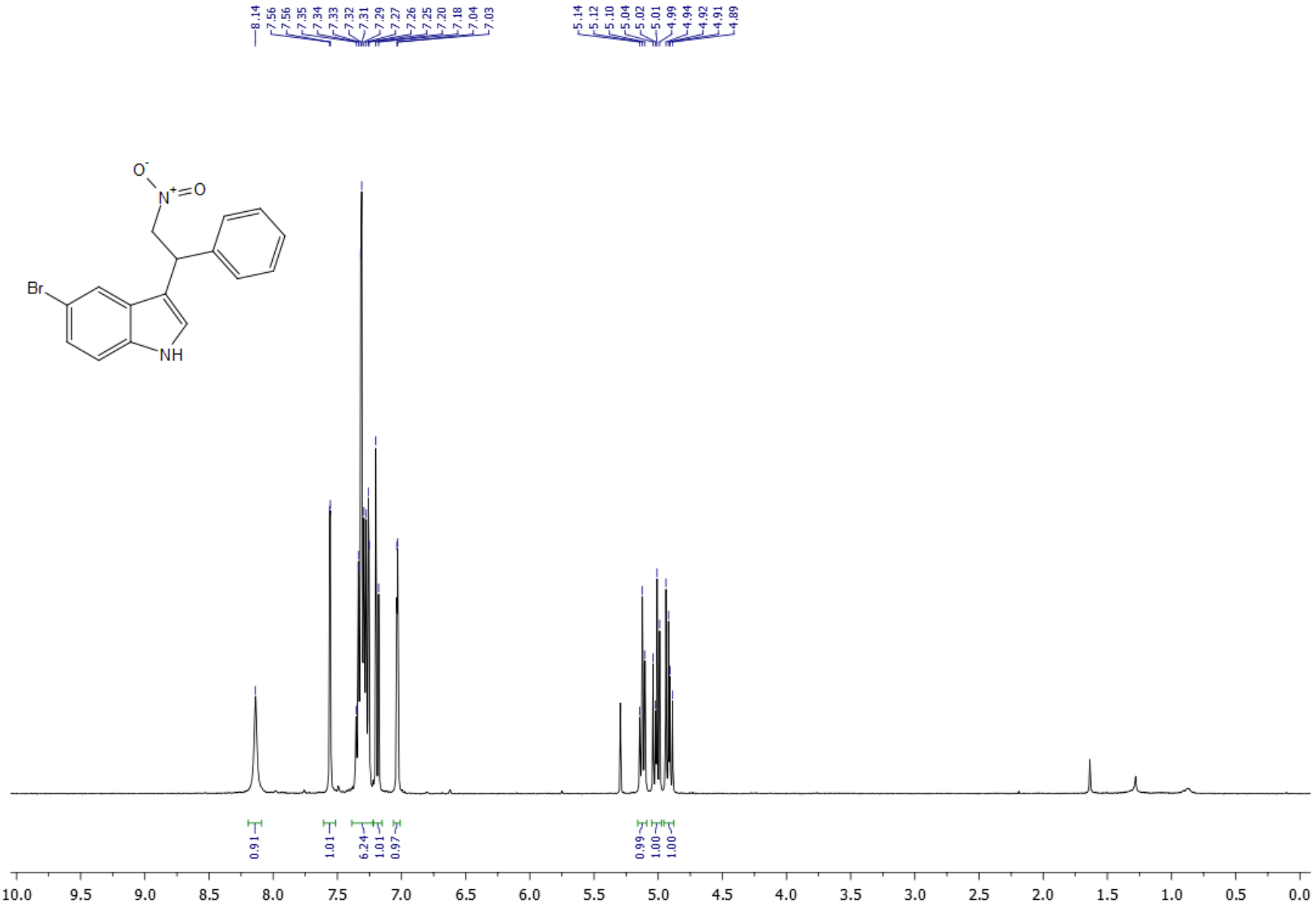
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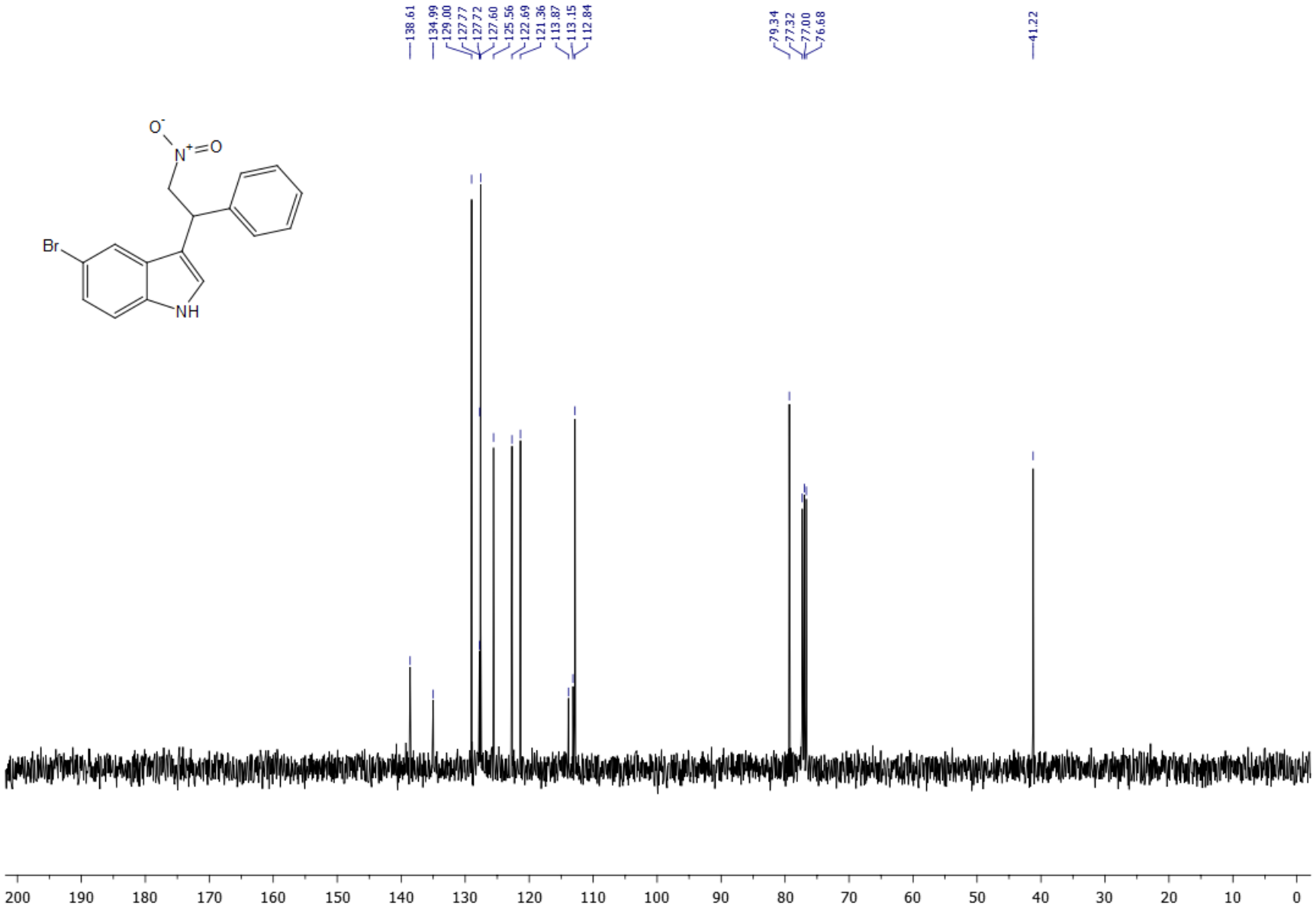
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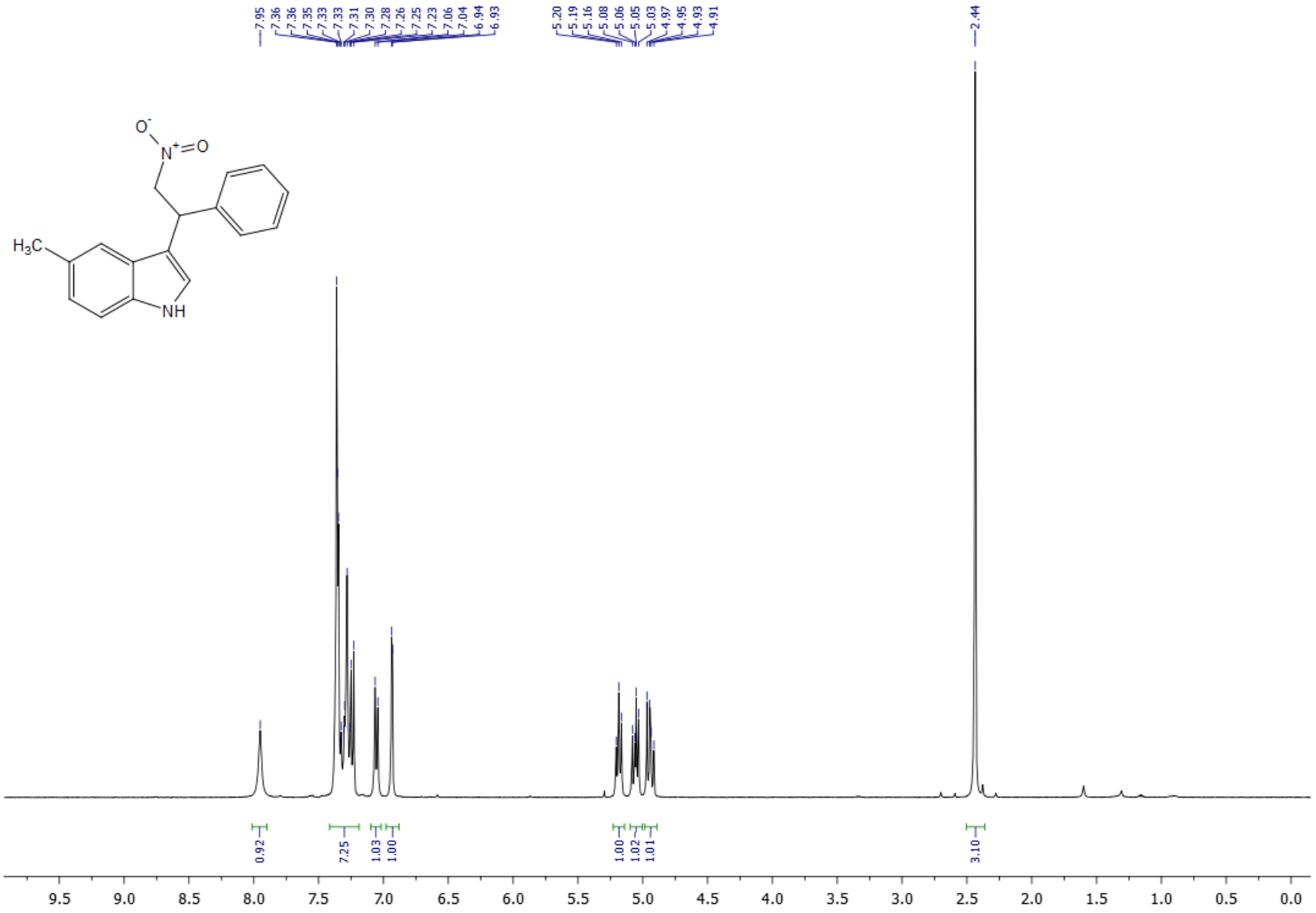
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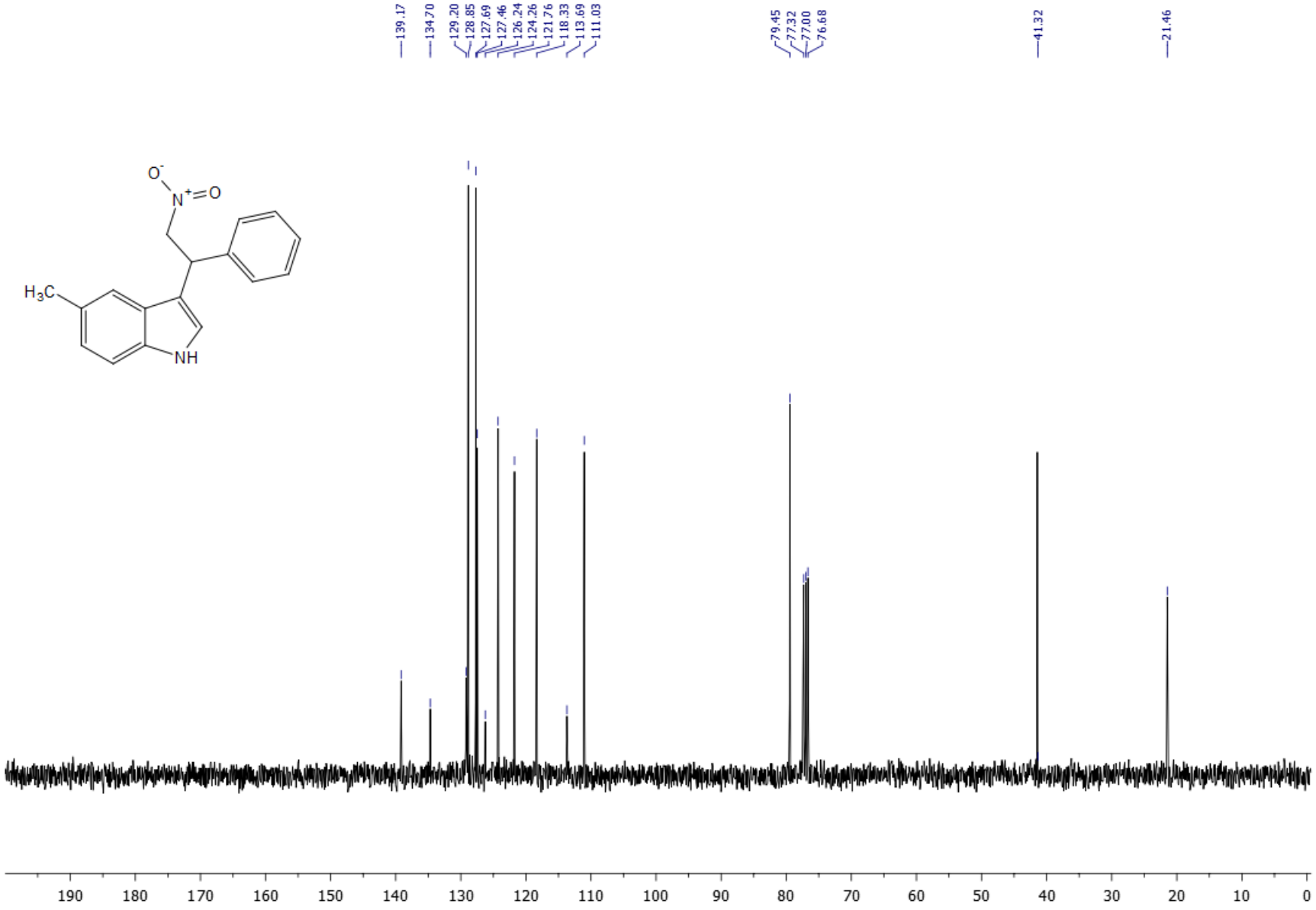
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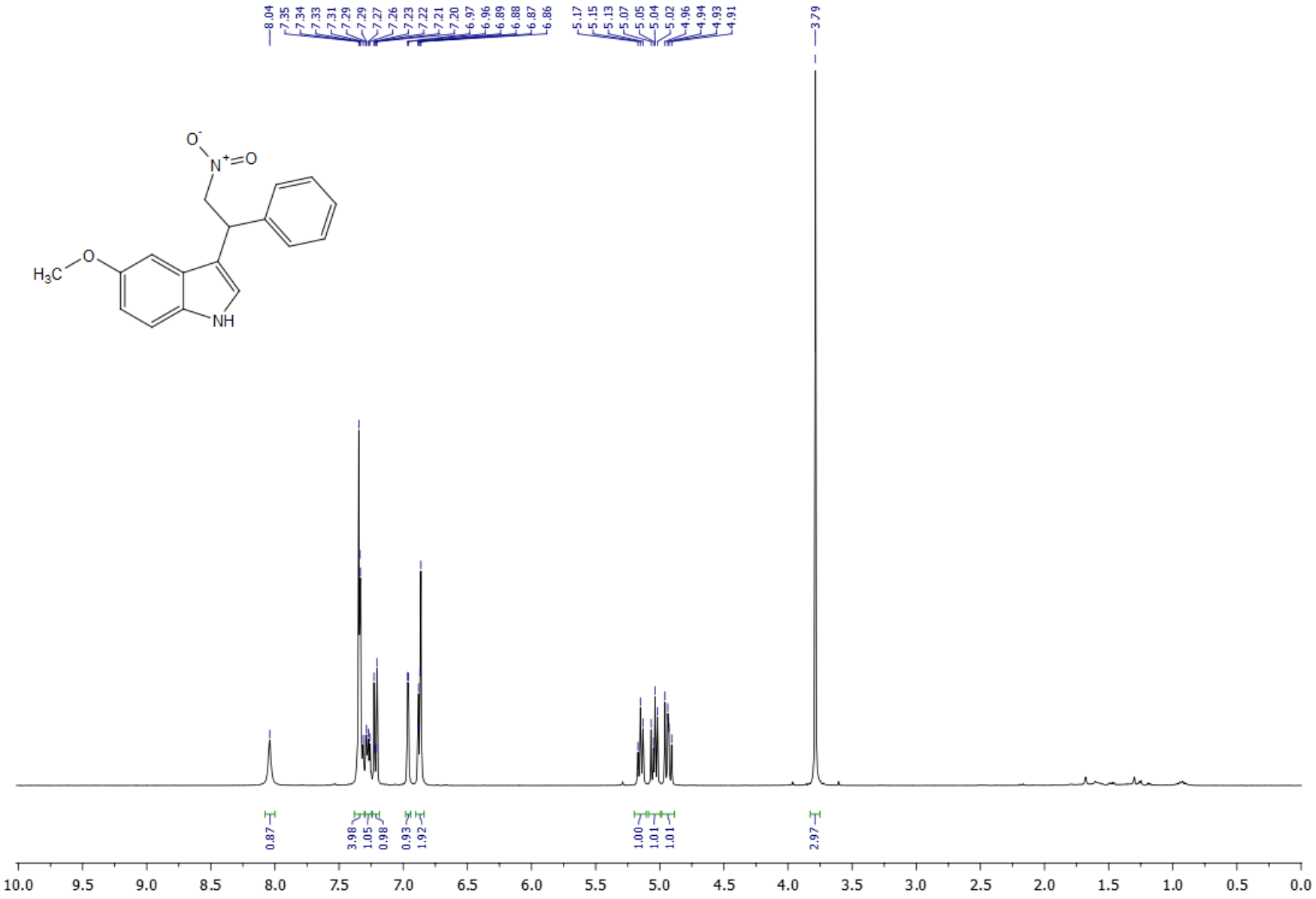
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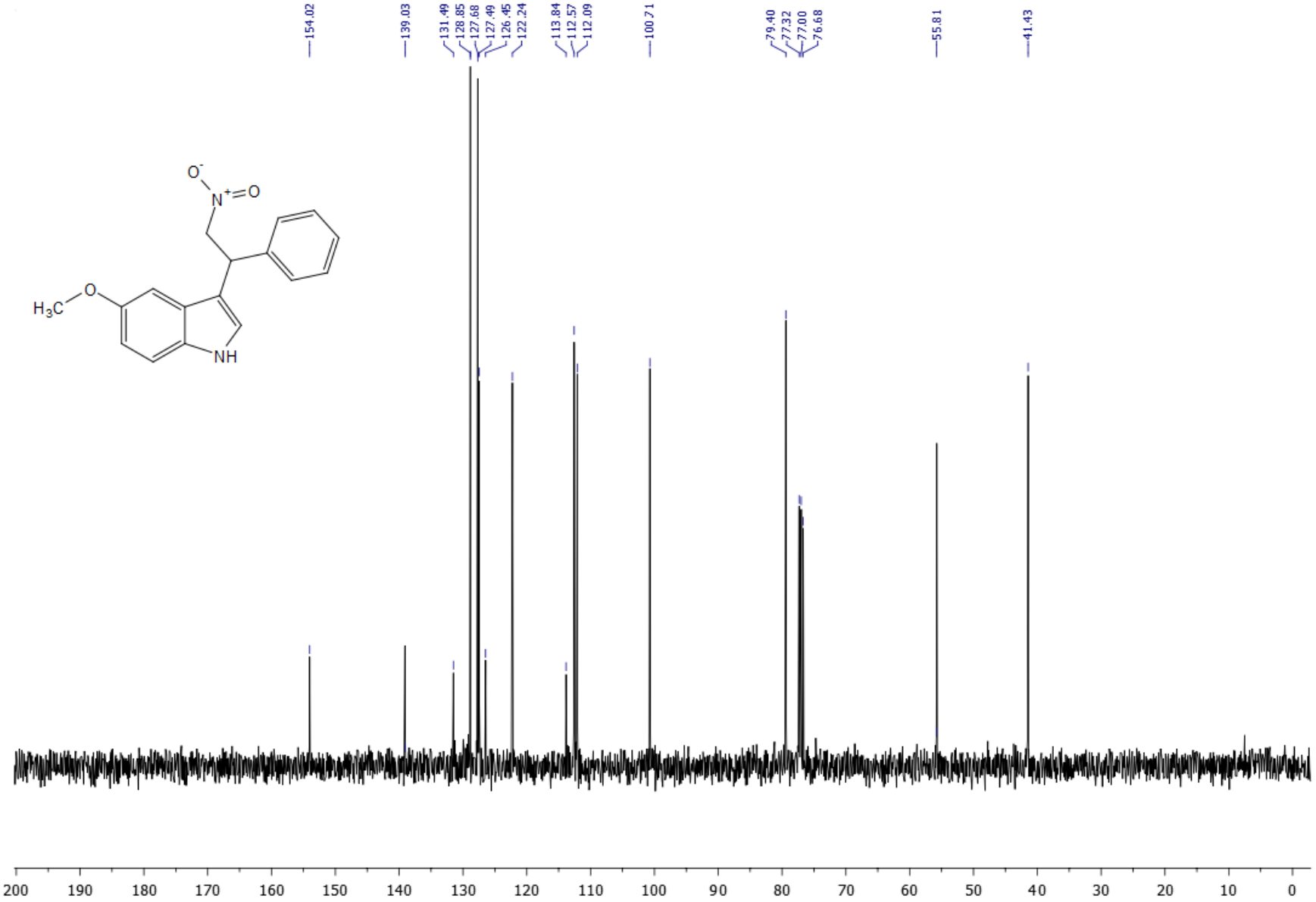
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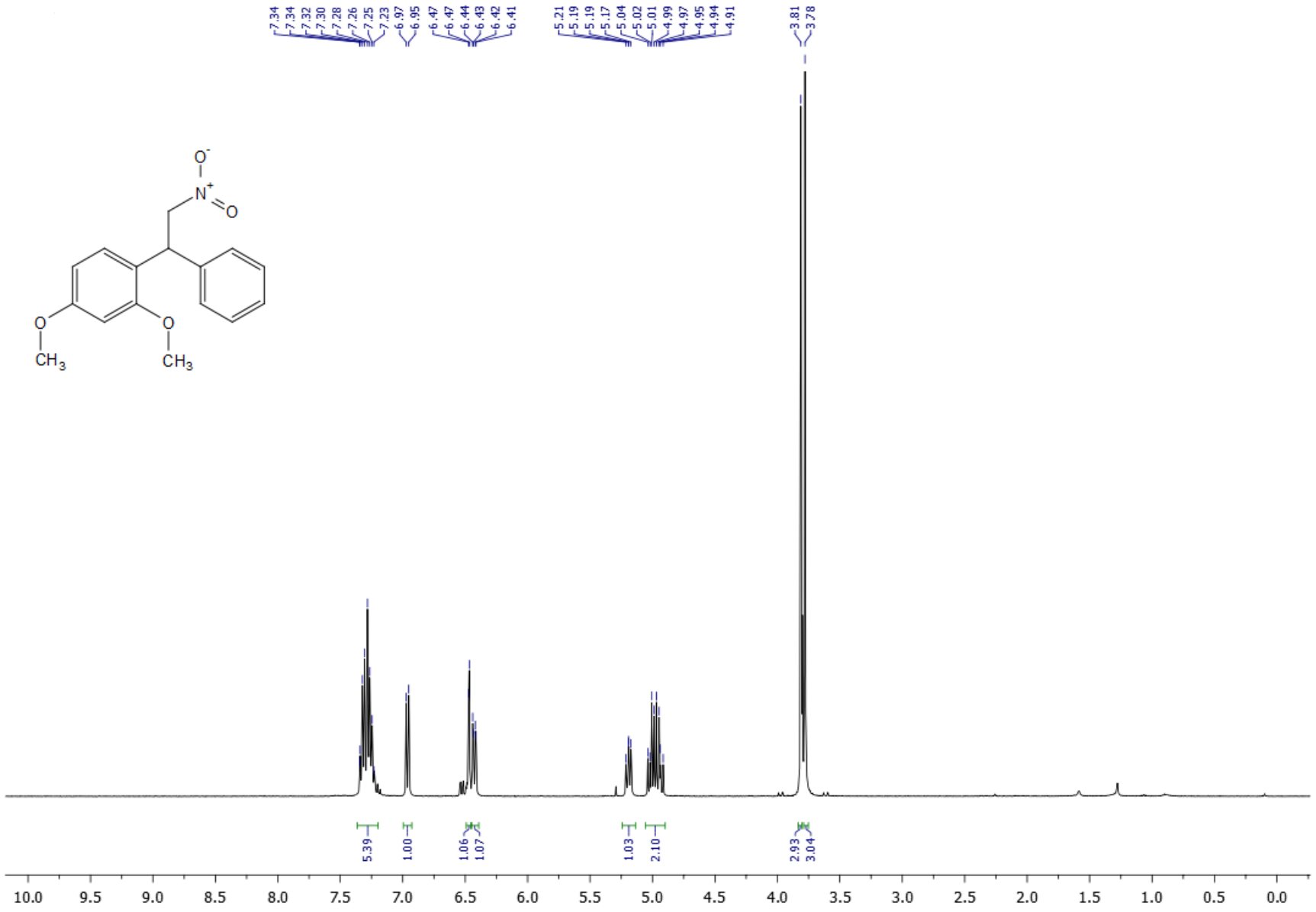
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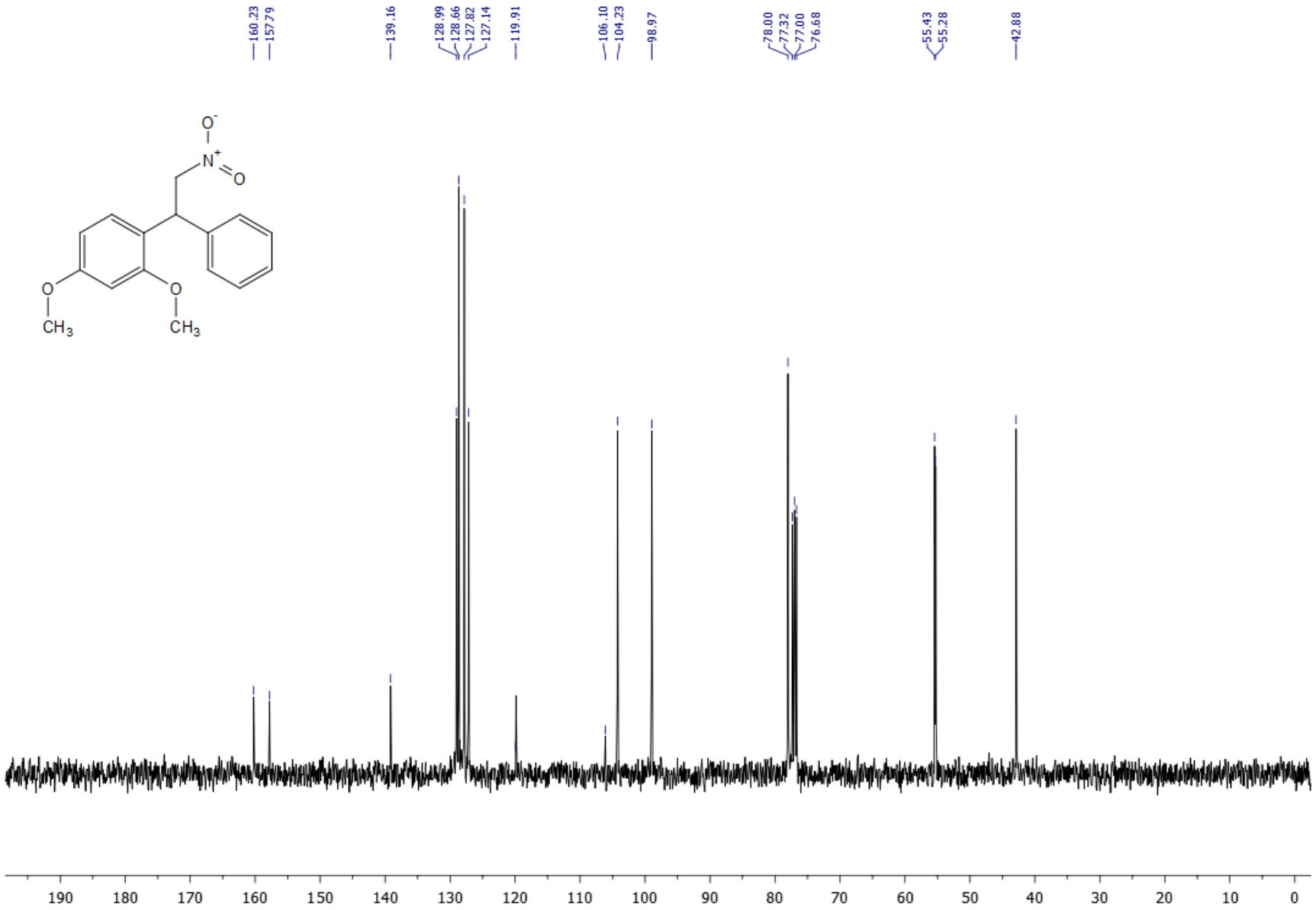
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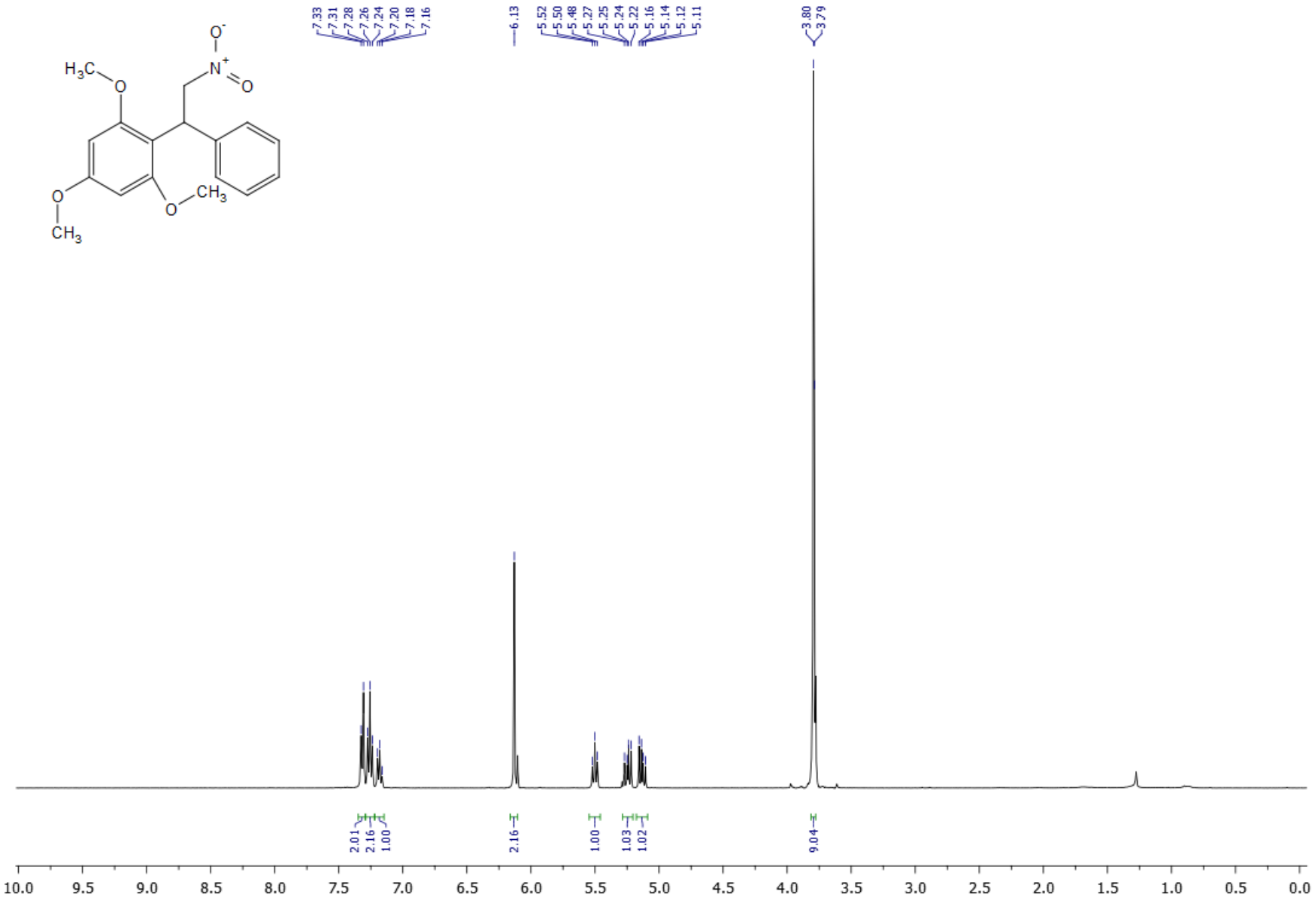
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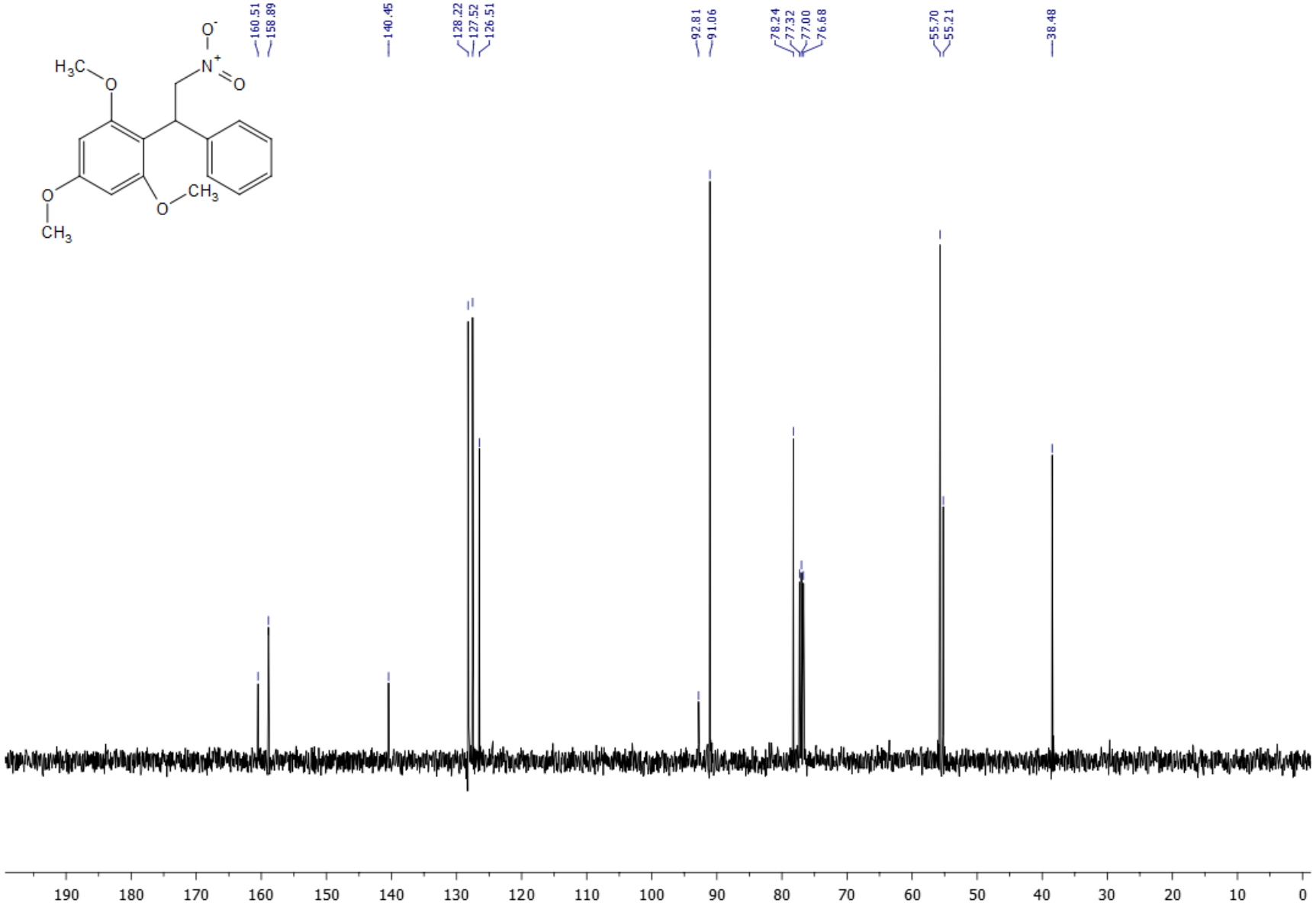
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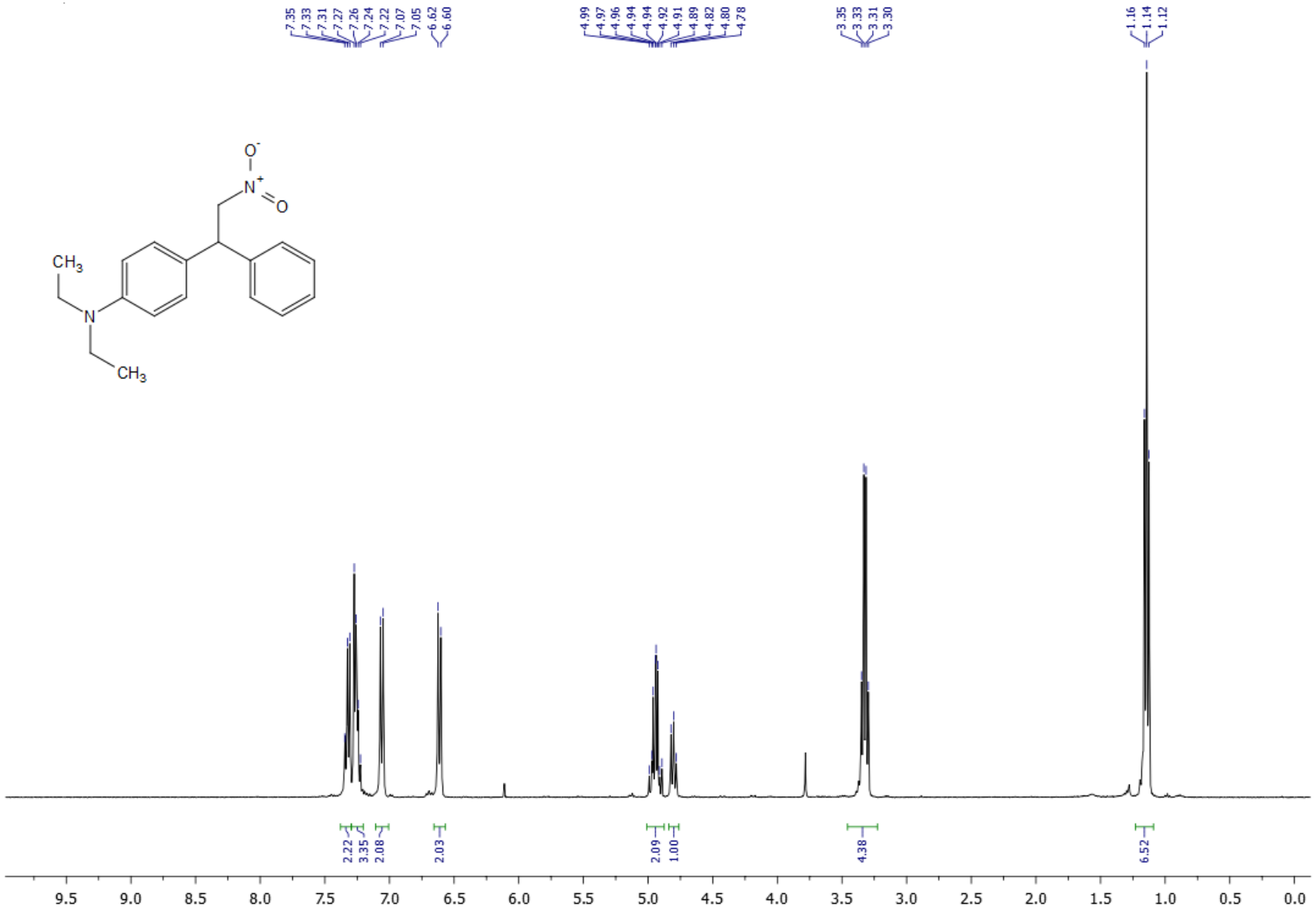
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4.94
4.92
4.91
4.89
4.82
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3.30
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1.14
1.12
O
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O
CH3
N
CH3
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3.35
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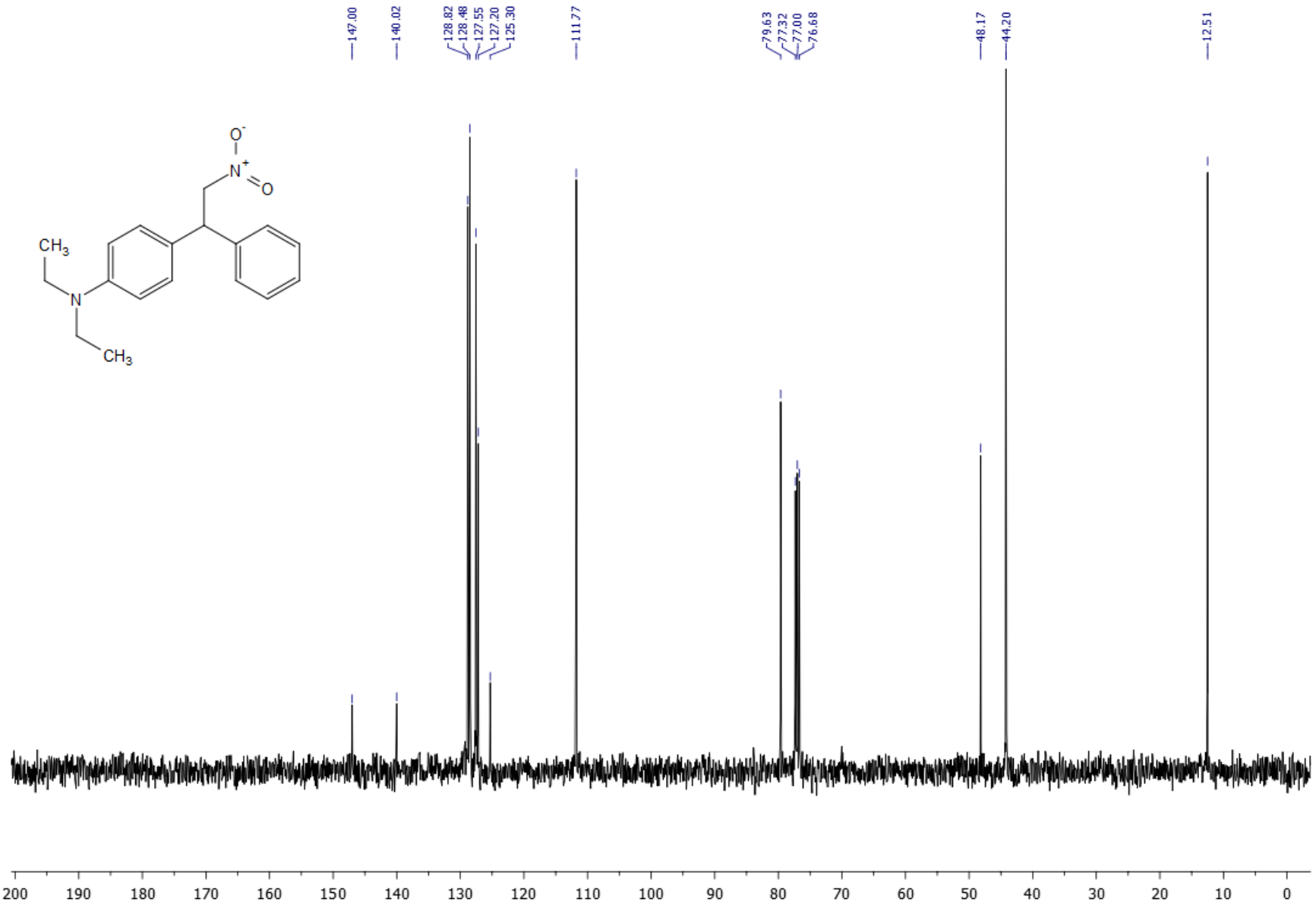
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44.20
12.51
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N
O
CH3
N
CH3
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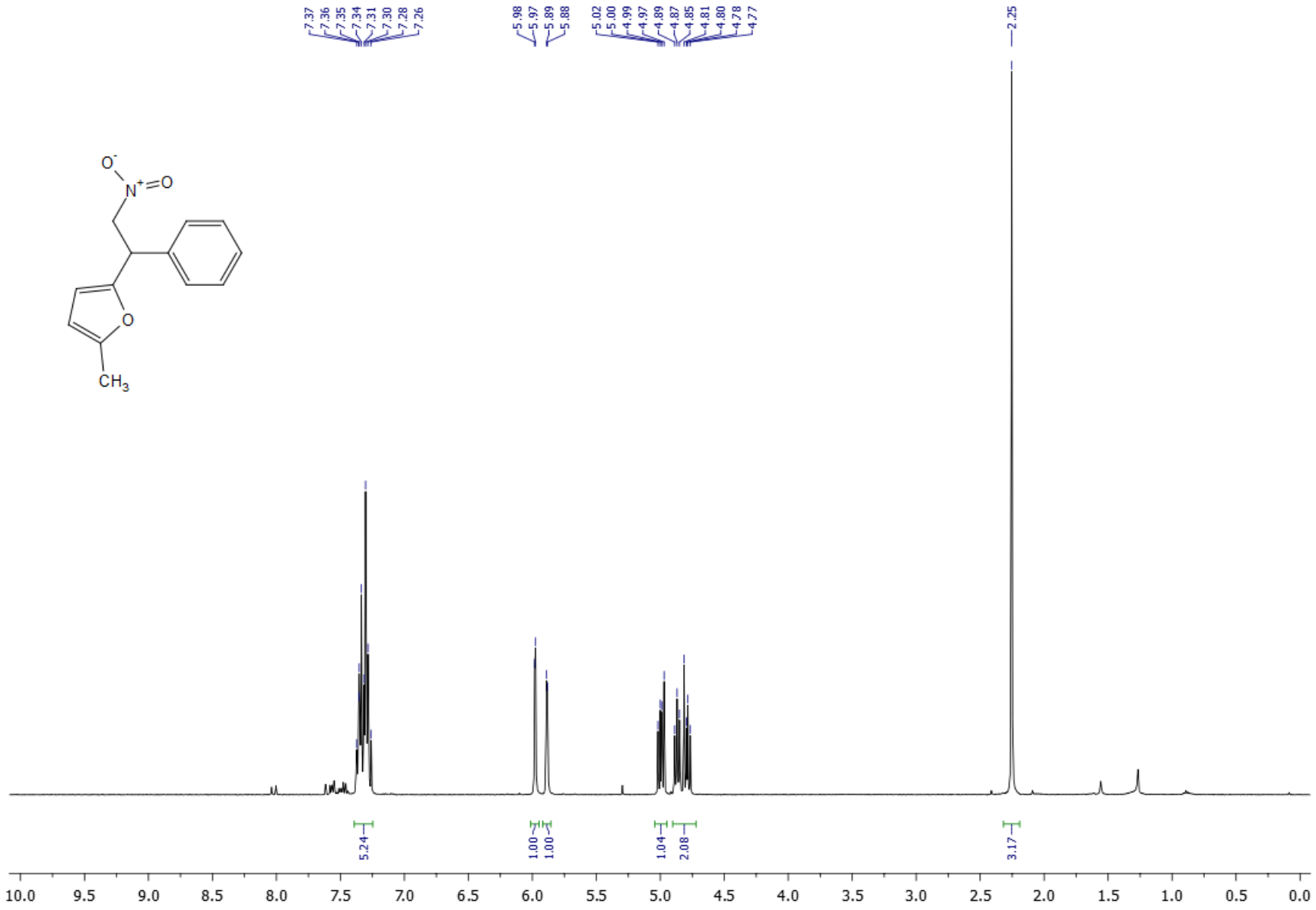
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4.80
4.78
4.77
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O
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O
CH3
5.24
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1.00
1.04
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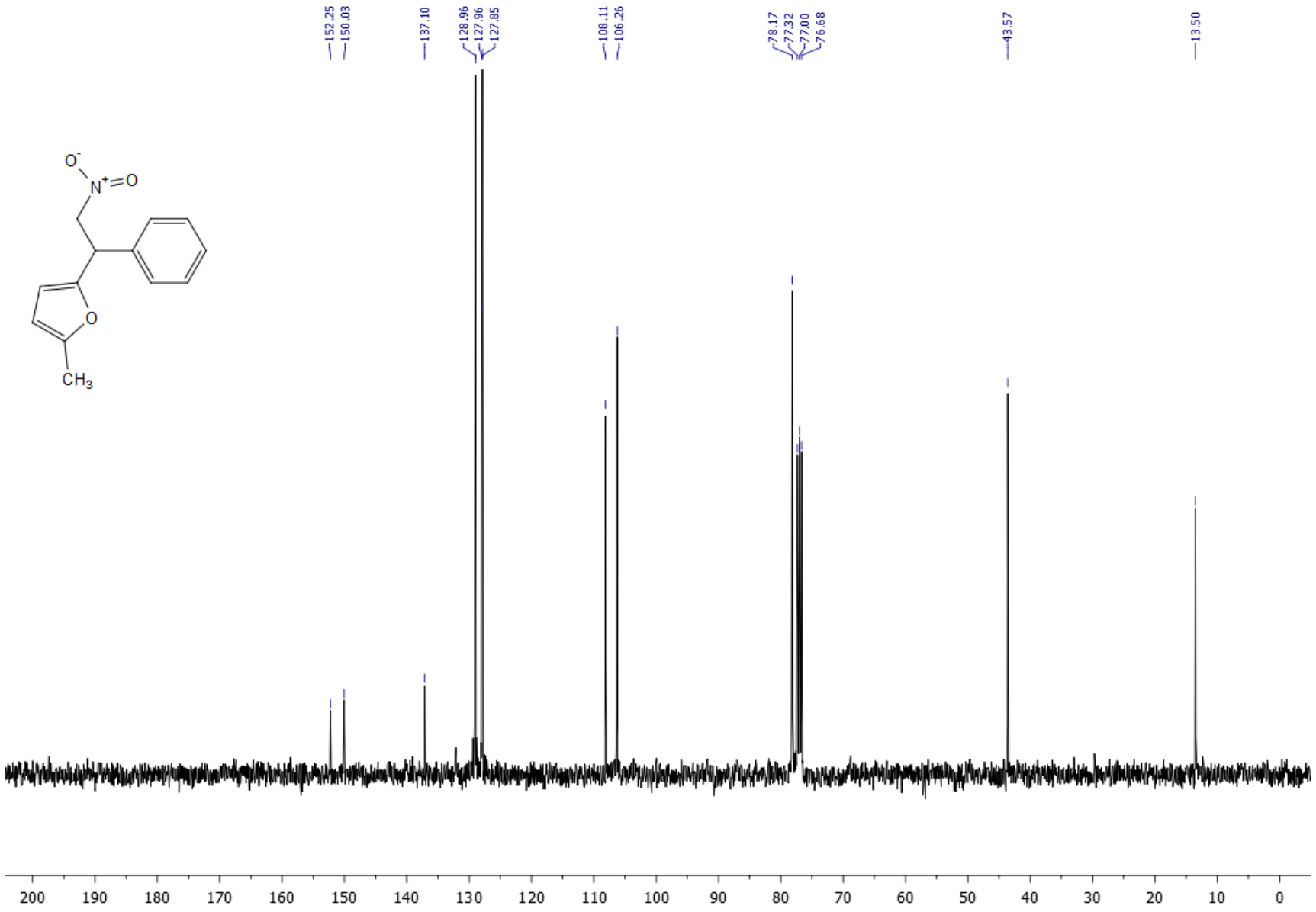
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CH3
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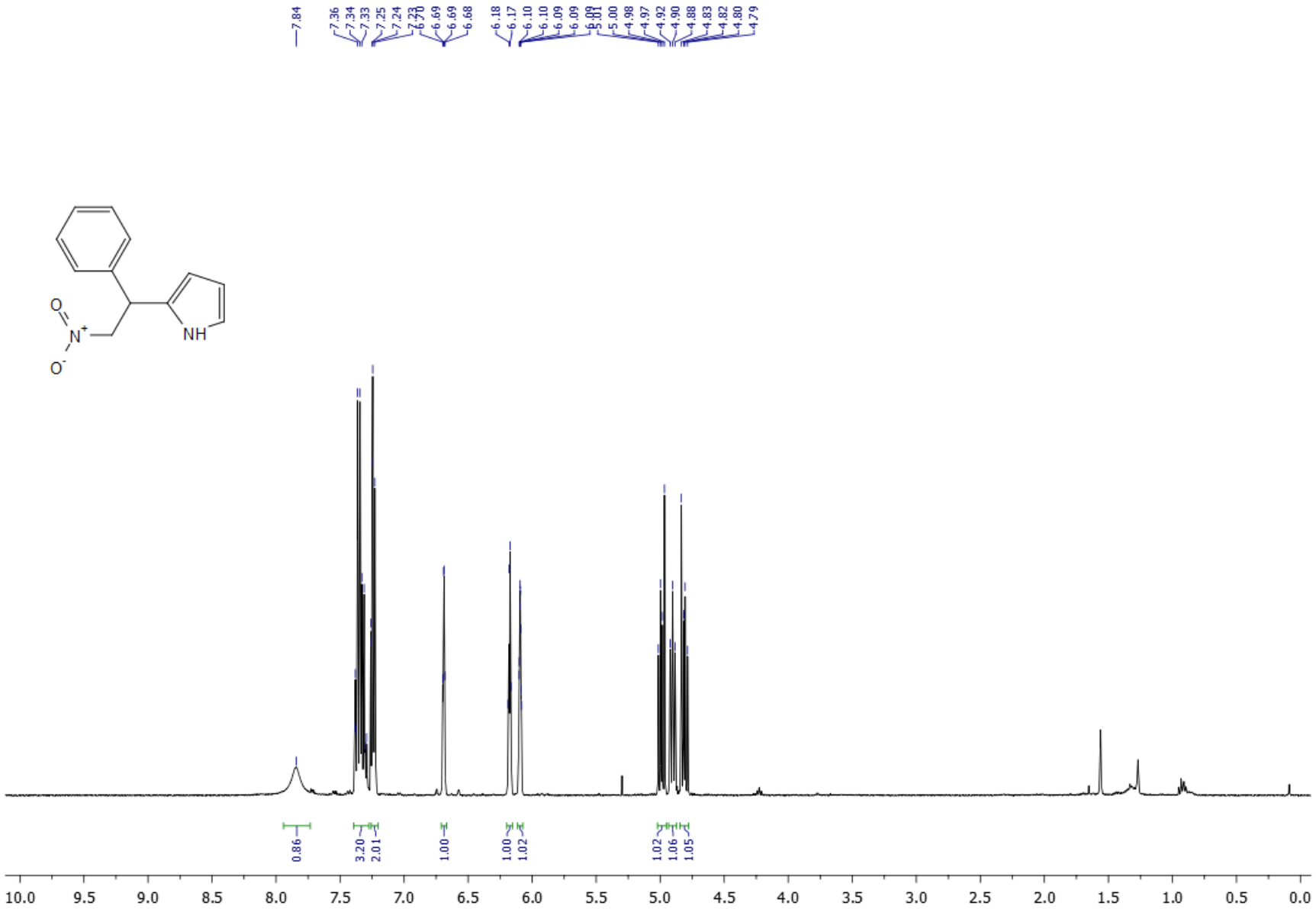
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6.10
6.10
6.09
6.09
6.09
6.01
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4.92
4.90
4.88
4.83
4.82
4.80
4.79
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O-
NH
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1.00
1.02
1.02
1.06
1.05
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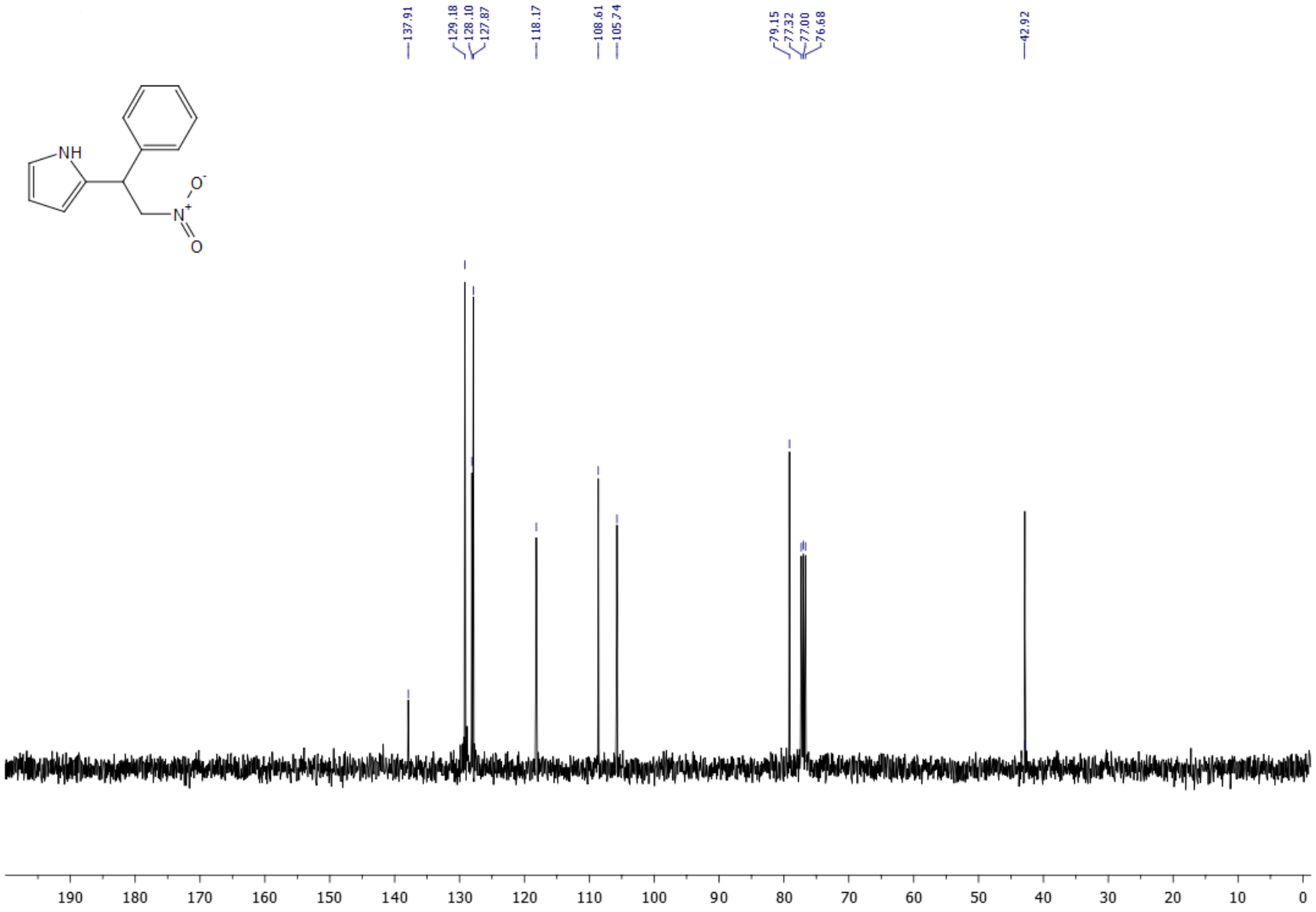
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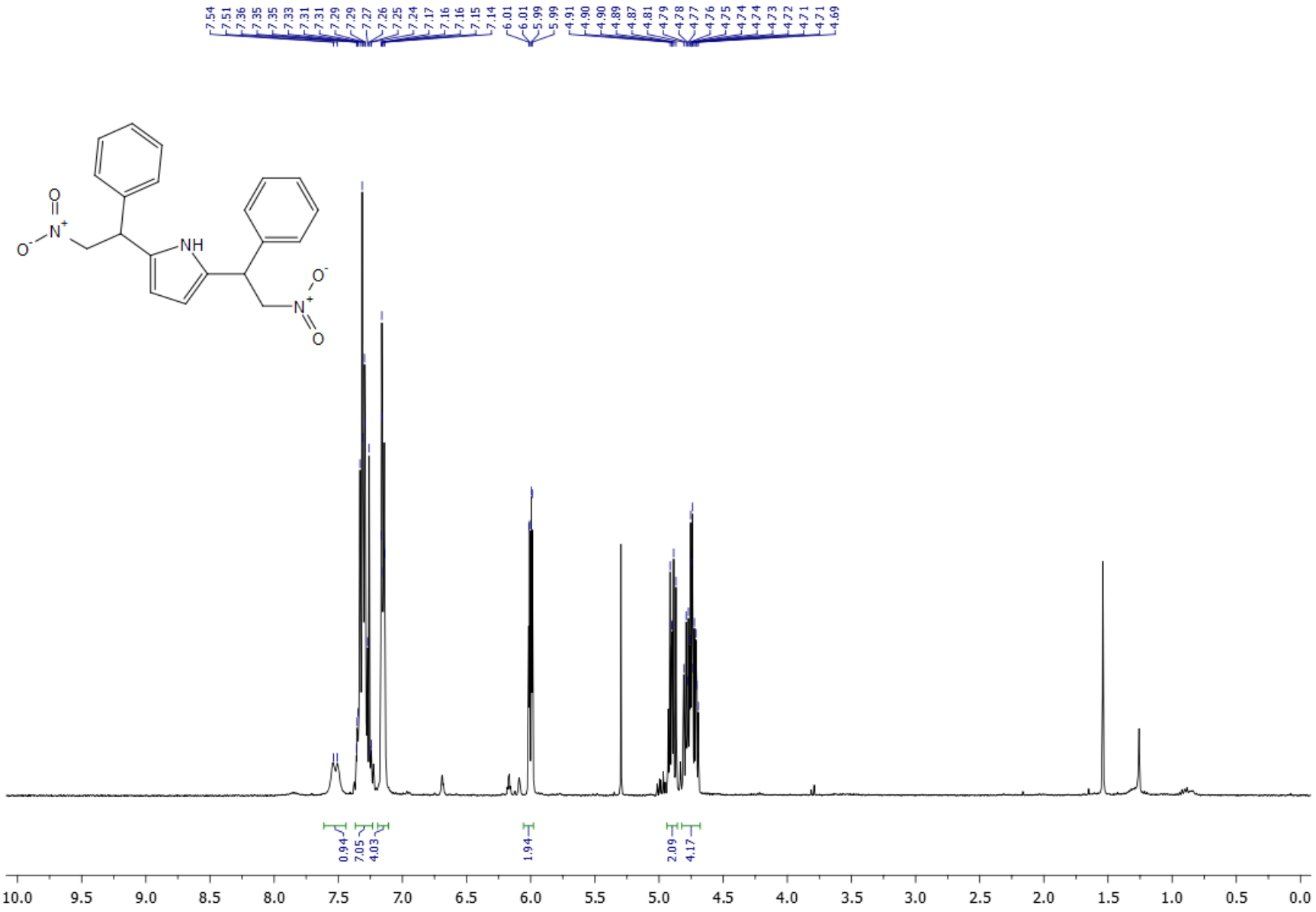
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4.69
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O-
NH
O-
N+
O
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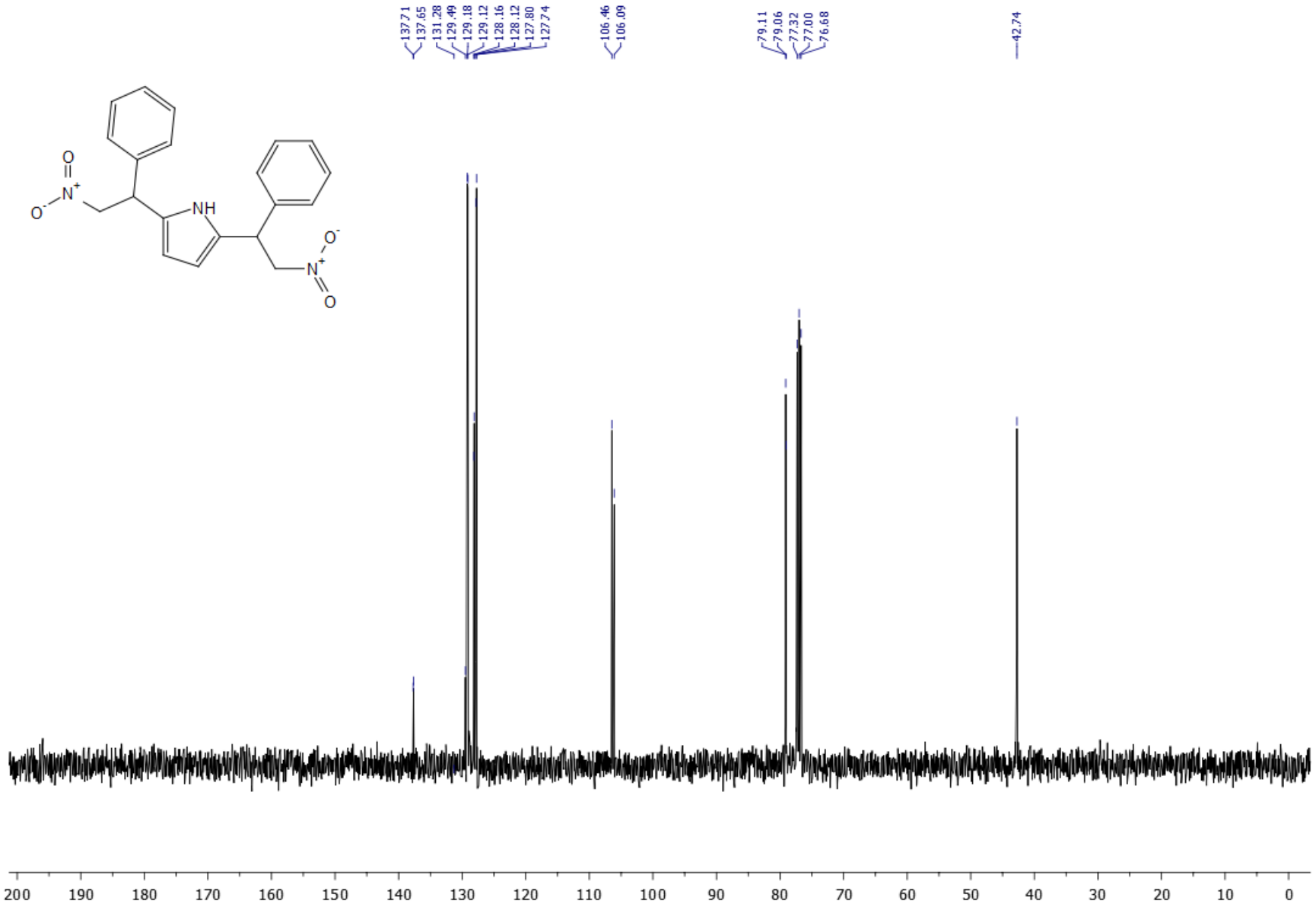
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42.74
NH
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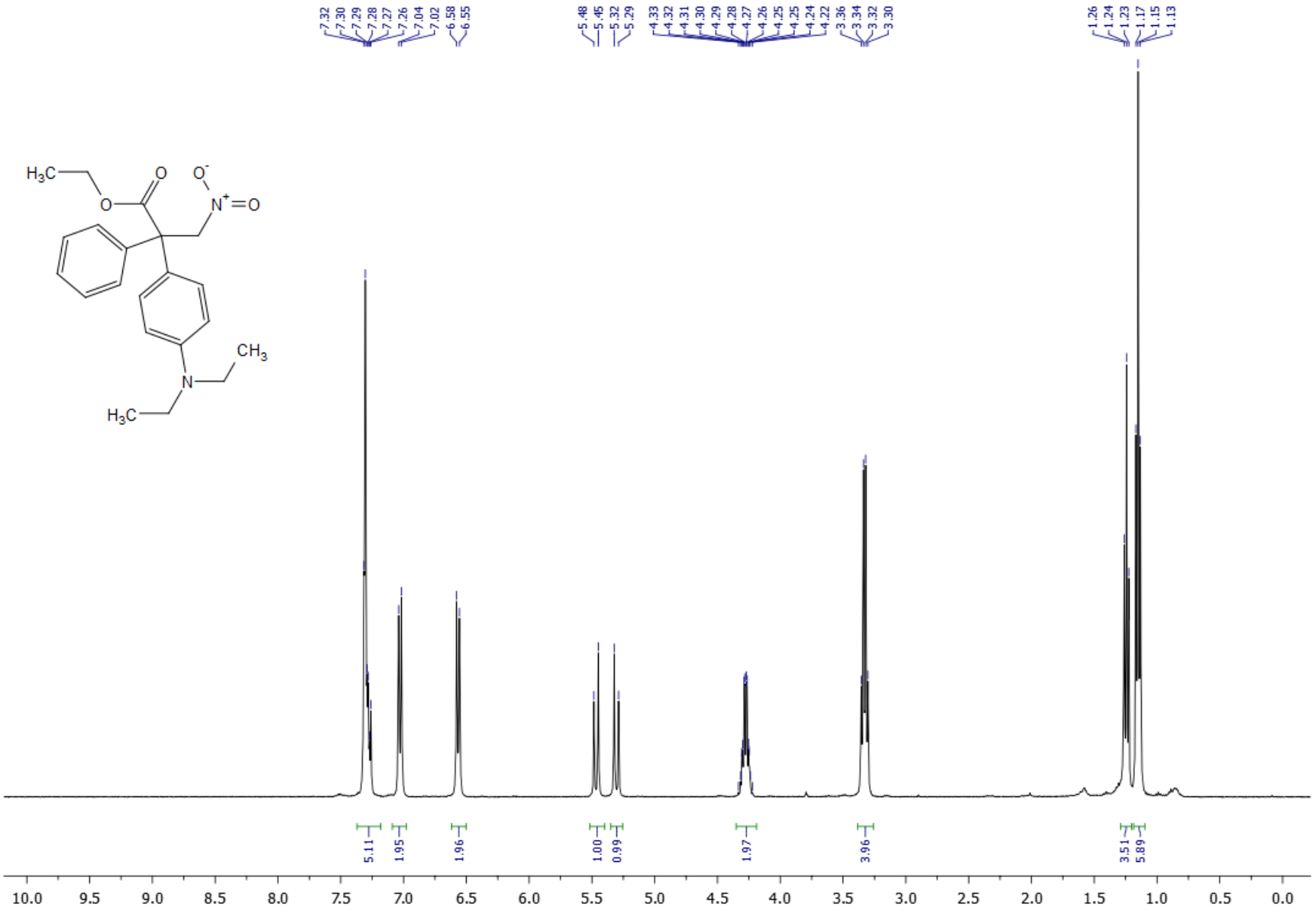
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4.26
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4.24
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H3C
O
O
O-
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CH3
N
H3C
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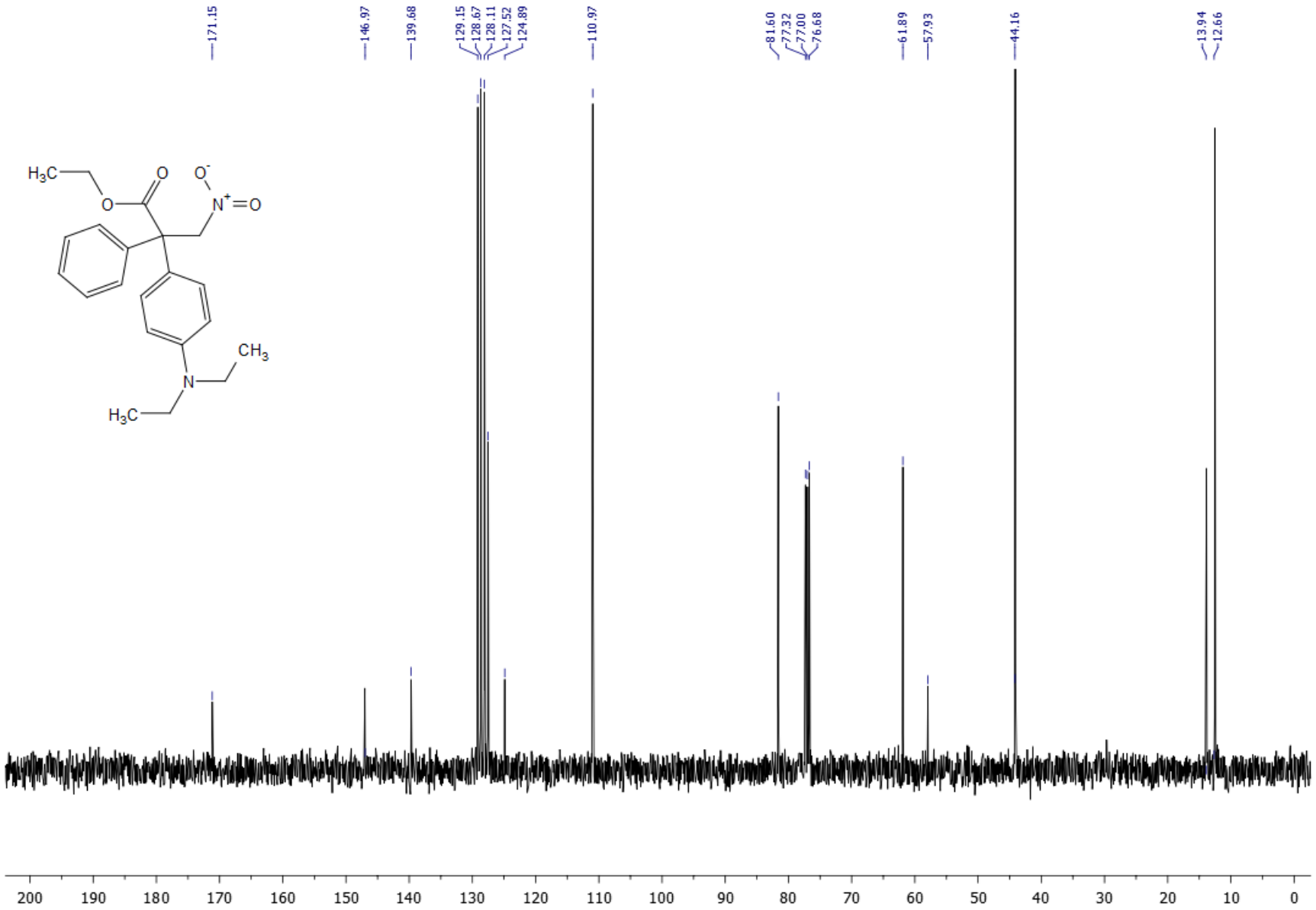
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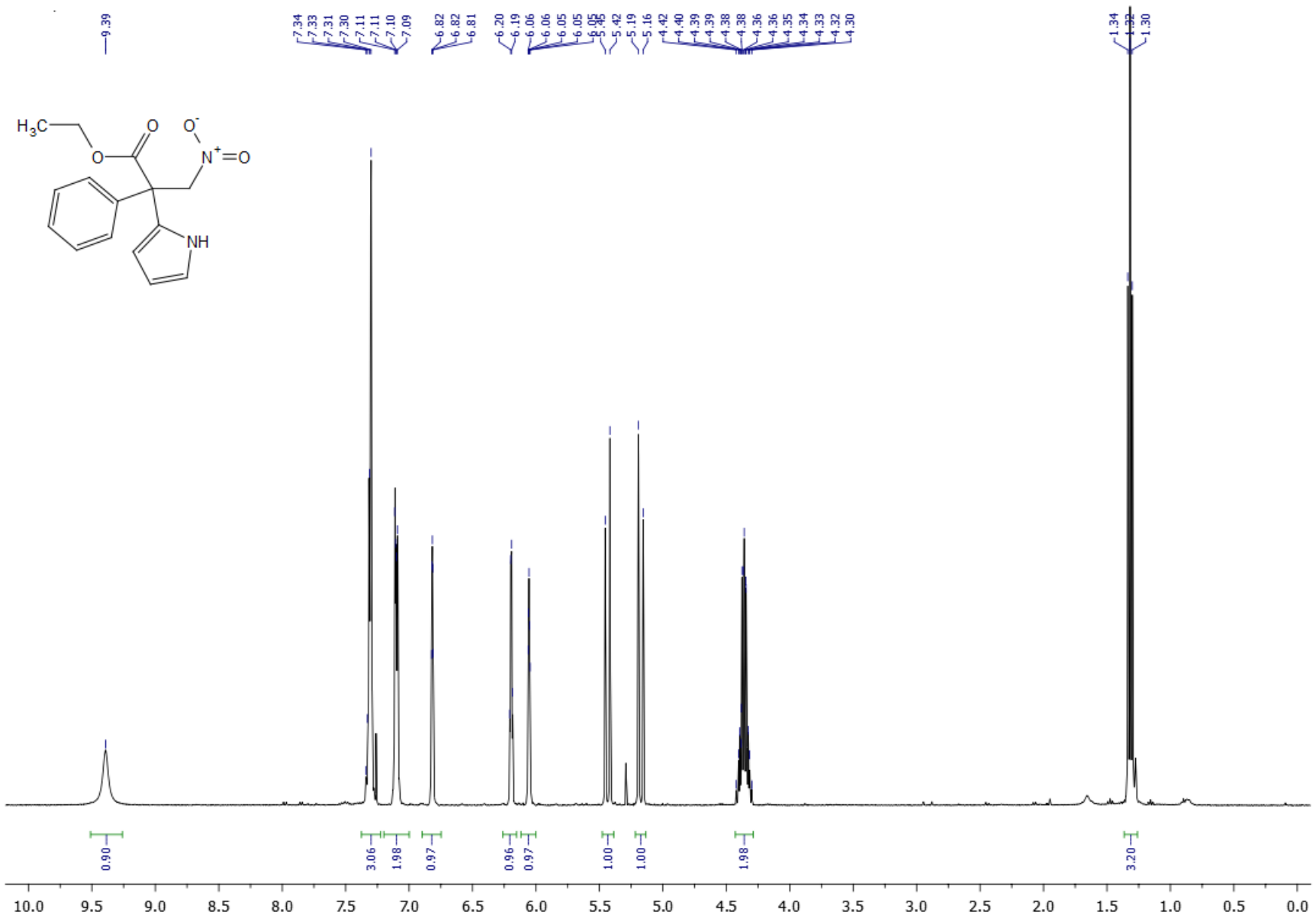
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4.30
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1.32
1.30
H3C
O
O
O-
N+=O
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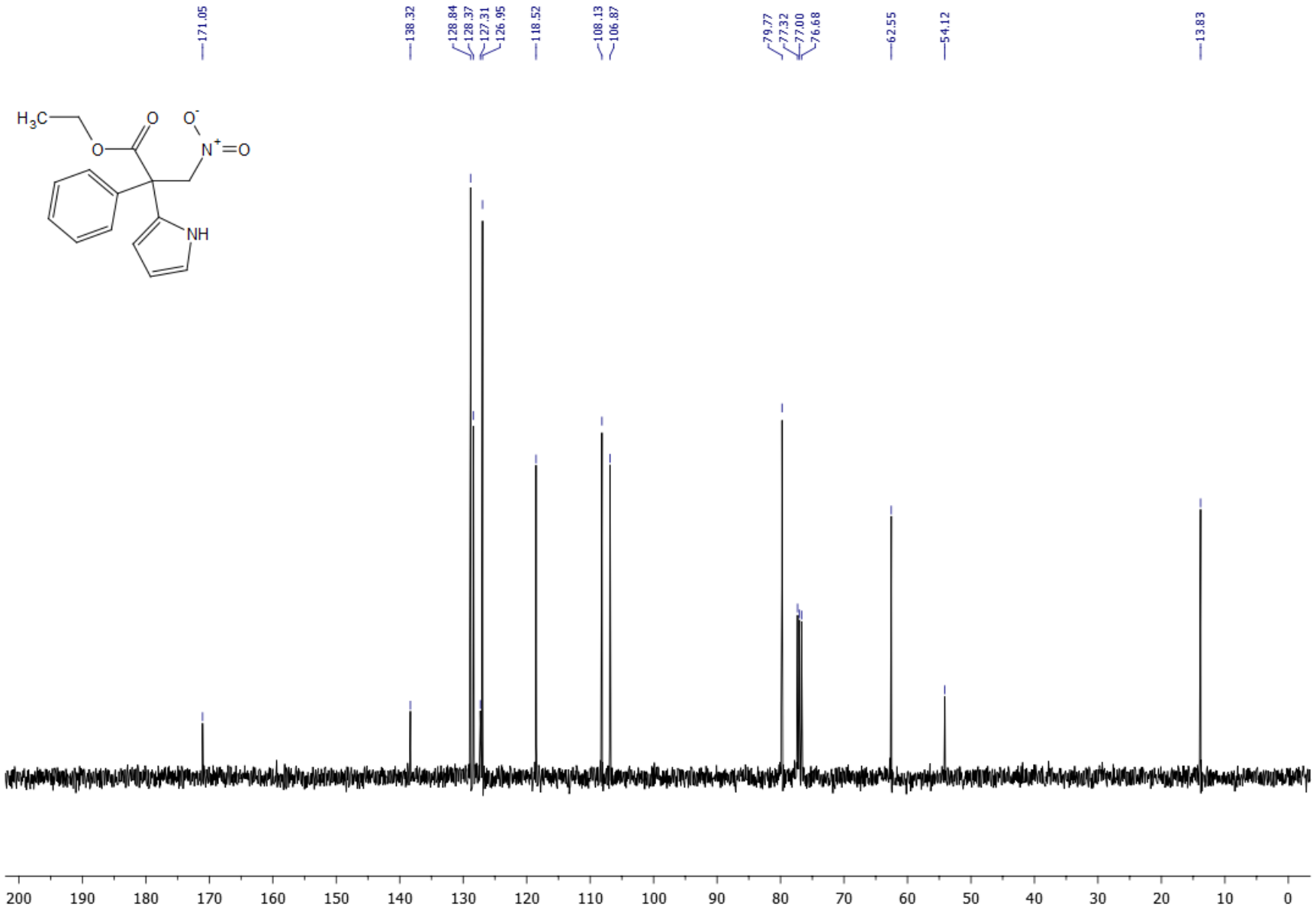
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O-
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NH
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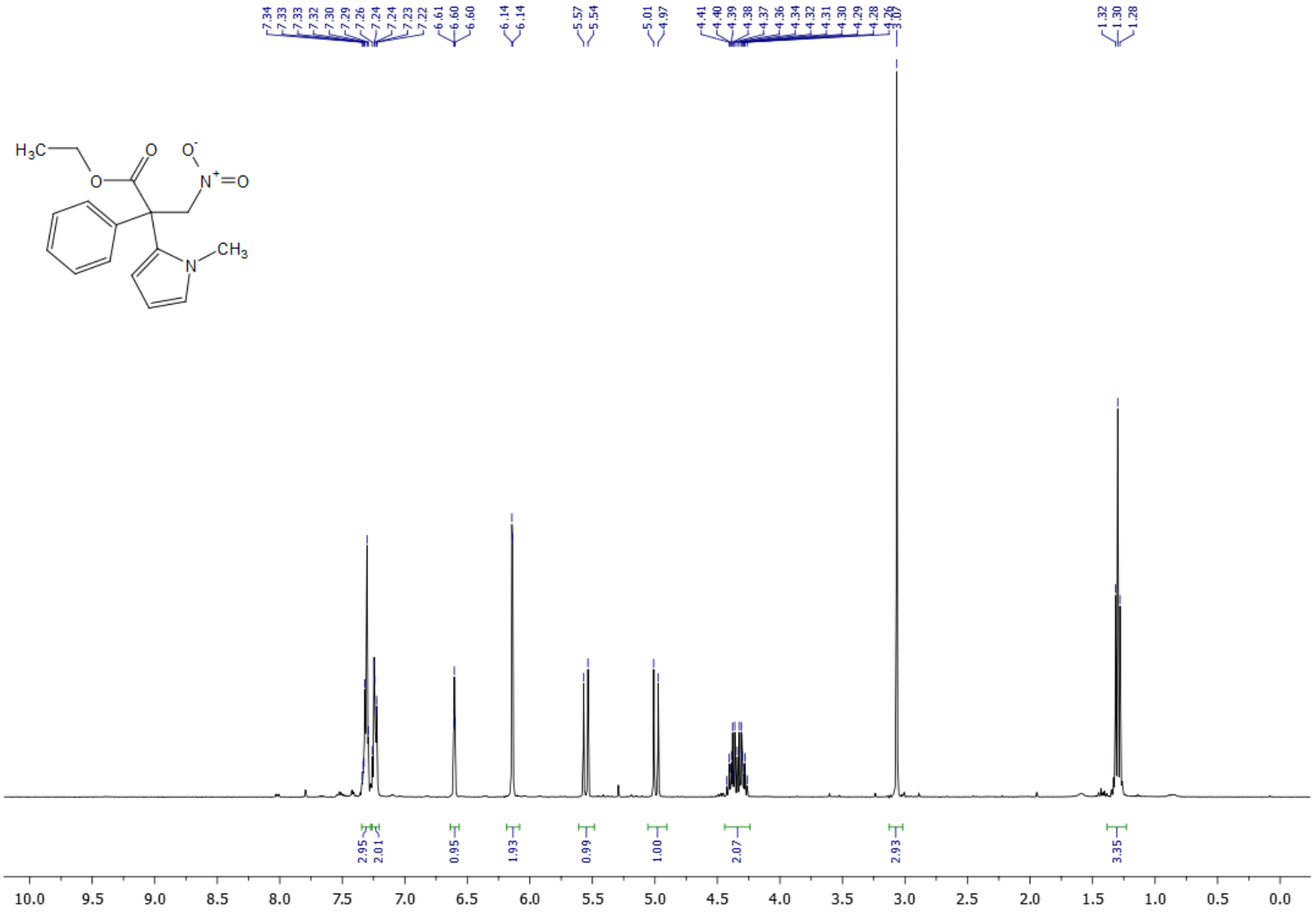
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4.28
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1.28
H3C
O
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O-
N+=O
CH3
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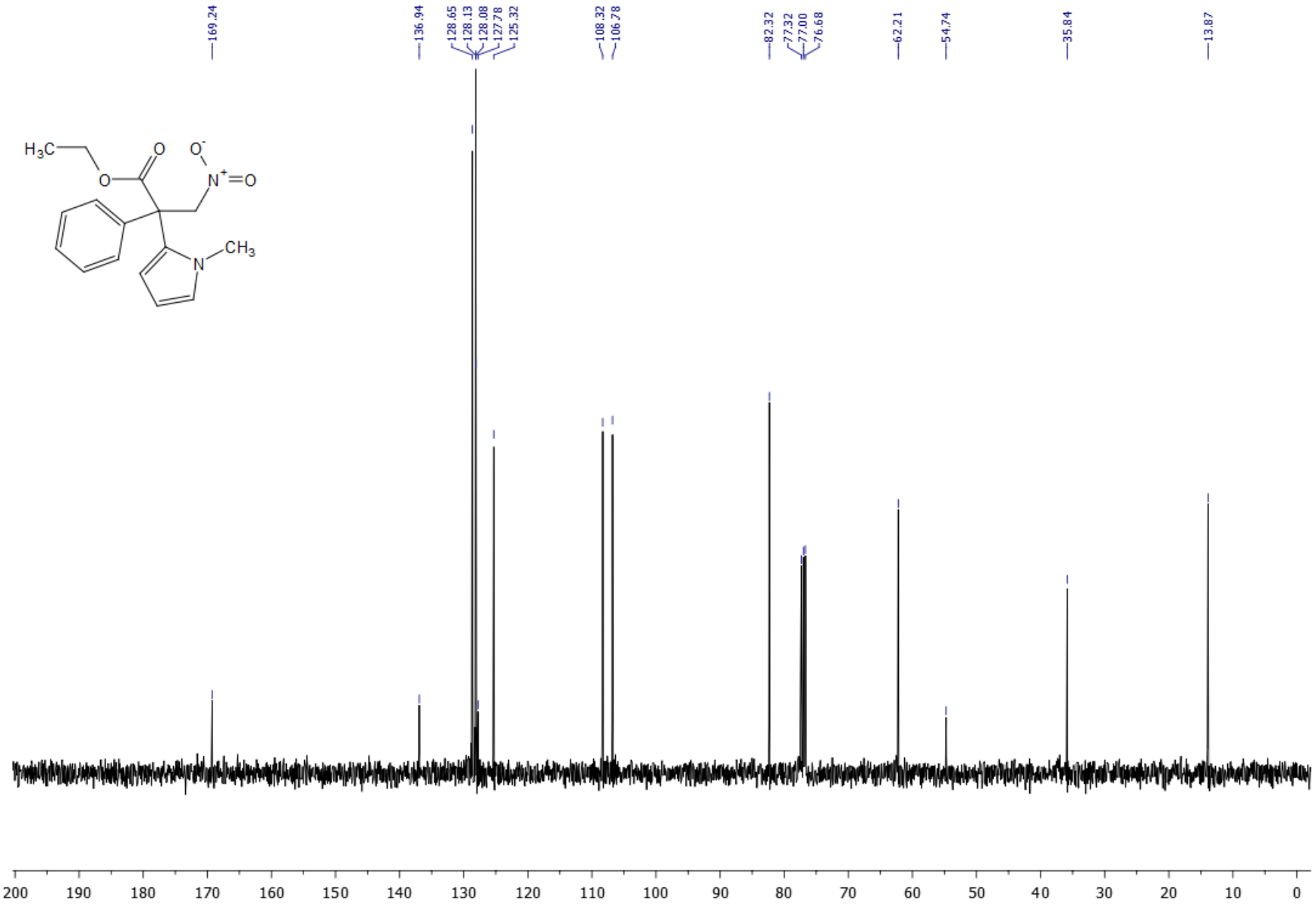
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H3C
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O-
N+=O
CH3
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