Ag-catalysed protodecarboxylation of *ortho* substituted benzoic acids

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General Information

All reactions were carried out opened to air except when indicated. DMF, anhydrous DMSO and all the reagents were purchased from chemical companies and used without further purification. ^{1}H NMR spectra, recorded at 400 MHz are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$). ^{13}C NMR spectra, recorded at 101 MHz, are referenced to the residual solvent peak at 77.0 ppm ($CDCl_3$).

General procedure for the Ag-catalysed protodecarboxylation of *ortho* benzoic acids

A mixture of benzoic acid (0.5 mmol) and Ag_2CO_3 (14 mg, 0.05 mmol) in dry DMSO (2.5 mL) was stirred for 16 hours at 120 ºC. After this time the reaction was partitioned with Et_2O (10 mL) and saturated aqueous $NaHCO_3$ (10 mL). The two layers were separated and the organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL). The ethereal layer was dried over anhydrous $MgSO_4$, filtered and evaporated to dryness under reduced pressure. The product was obtained without further purification.

The benzene derivatives obtained are all known compounds, which are commercially available or previously described. Their analytical data are identical with those reported in the literature.

^{1}H and ^{13}C NMR spectra for compounds **2a**, **2d**, **2h** and **2m** are provided as an example of the purities obtained.

1-Chloro-4-nitrobenzene (2a)

The reaction was carried out following the general procedure with 2-chloro-5-nitrobenzoic acid (0.102 g, 0.5 mmol) to afford **2a** as a yellow solid (0.071 g, 90%).

Nitrobenzene (2b)

The reaction was carried out following the general procedure with 2-nitrobenzoic acid (0.084 g, 0.5 mmol) to afford **2b** as a yellow oil (0.057 g, 91%).

The same reaction was scaled up following the general procedure with 2-nitrobenzoic acid (4.2 g, 25 mmol) to afford **2b** as a yellow oil (2.8 g, 91%).

1,3-Dinitrobenzene (2c)

The reaction was carried out following the general procedure with 2,4-dinitrobenzoic acid (0.111 g, 0.5 mmol) to afford **2c** as a yellow solid (0.079 g, 94%).

1-Methoxy-3-nitrobenzene (2d)

The reaction was carried out following the general procedure with 4-methoxy-2-nitrobenzoic acid (0.100 g, 0.5 mmol) to afford **2d** as a yellow solid (0.074 g, 96%).

1,2-Dimethoxy-4-nitrobenzene (2e)

The reaction was carried out following the general procedure with 4,5-methoxy-2-nitrobenzoic acid (0.116 g, 0.5 mmol) to afford **2e** as a yellow solid (0.092 g, 100%).

3-Nitrotoluene (2f)

The reaction was carried out following the general procedure with 2-methyl-6-nitrobenzoic acid (0.093 g, 0.5 mmol) to afford **2f** as a yellow liquid (0.059 g, 86%).

1-Bromo-4-nitrobenzene (2h)

The reaction was carried out following the general procedure using 2-bromo-5-nitrobenzoic acid (0.125 g, 0.5 mmol) to afford **2h** as a white solid (0.098 g, 97%).

1-Bromo-3-chlorobenzene (2i)

The reaction was carried out following the general procedure in a sealed vessel with 4-bromo-2-chlorobenzoic acid (0.024 g, 0.1 mmol)) and d_6-DMSO (0.5 mL) to afford **2i** (99%) calculated by ^{1}H NMR using mesitylene as the internal standard.

1,3-Dichlorobenzene (2j)

The reaction was carried out following the general procedure in a sealed vessel with 2,6-dichlorobenzoic acid (0.020 g, 0.1 mmol) and d_6-DMSO (0.5 mL) to afford **2j** (96%) calculated by ^{1}H NMR using mesitylene as the internal standard.

1,3-Difluorobenzene (2k)

The reaction was carried out following the general procedure in a sealed vessel with 2,6-difluorobenzoic acid (0.016 g, 0.1 mmol) and d_6-DMSO (0.5 mL) to afford **2k** (99%) calculated by ^{1}H NMR using mesitylene as the internal standard.

1,3-Dimethoxybenzene (2l)

From **1l**: the reaction was carried out following the general procedure with 2,6-dimethoxybenzoic acid (0.092 g, 0.5 mmol) to afford **2l** as a colorless oil (0.063 g, 91%).

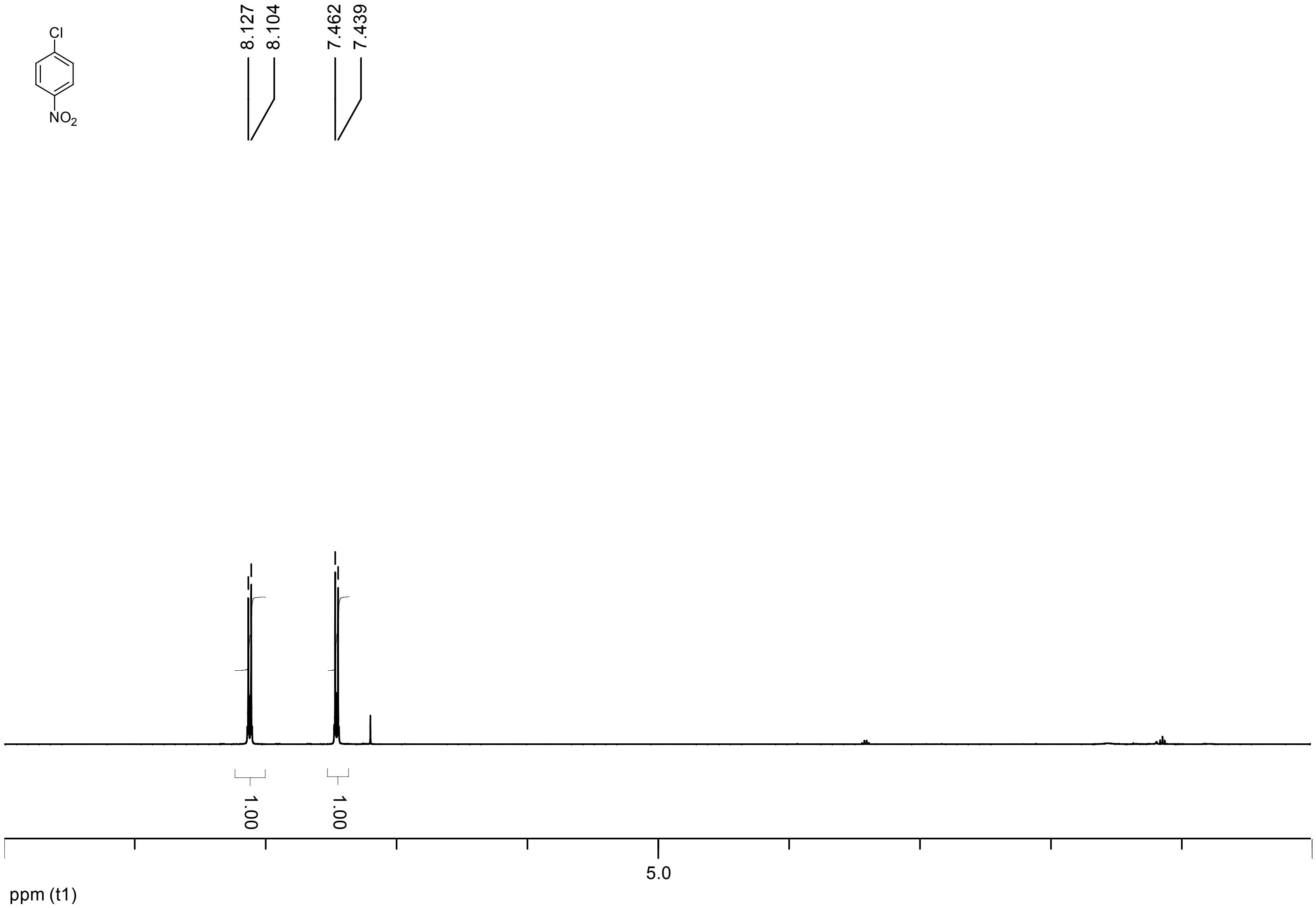
From **1m**: the reaction was carried out following the general procedure with 2,4-dimethoxybenzoic acid (0.092, 0.5 mmol) at 140 ºC to afford **2l** as a colorless oil (0.066 g, 96%).

1,3-Dihydroxybenzene (2n)

The reaction was carried out following the general procedure with 2,6-dihydroxybenzoic acid (0.077 g, 0.5 mmol) to afford **2n** as a white solid (0.041 g, 71%).

3-Fluoroaniline (2o)

The reaction was carried out following the general procedure in a sealed vessel with 2-amino-6-fluorobenzoic acid (0.016 g, 0.1 mmol) and d_6-DMSO (0.5 mL) to afford **2o** (95%) calculated by ^{1}H NMR using mesitylene as the internal standard.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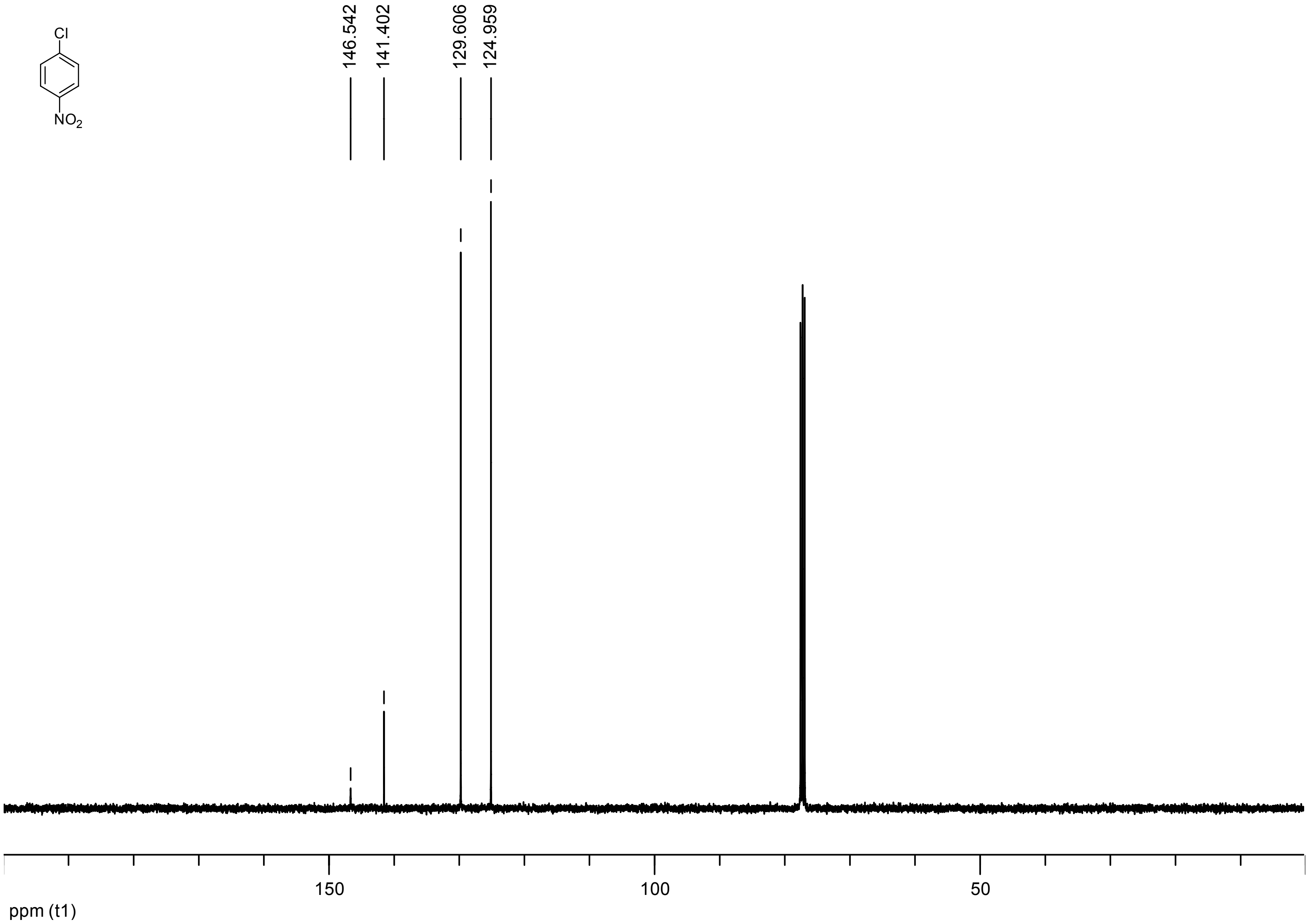
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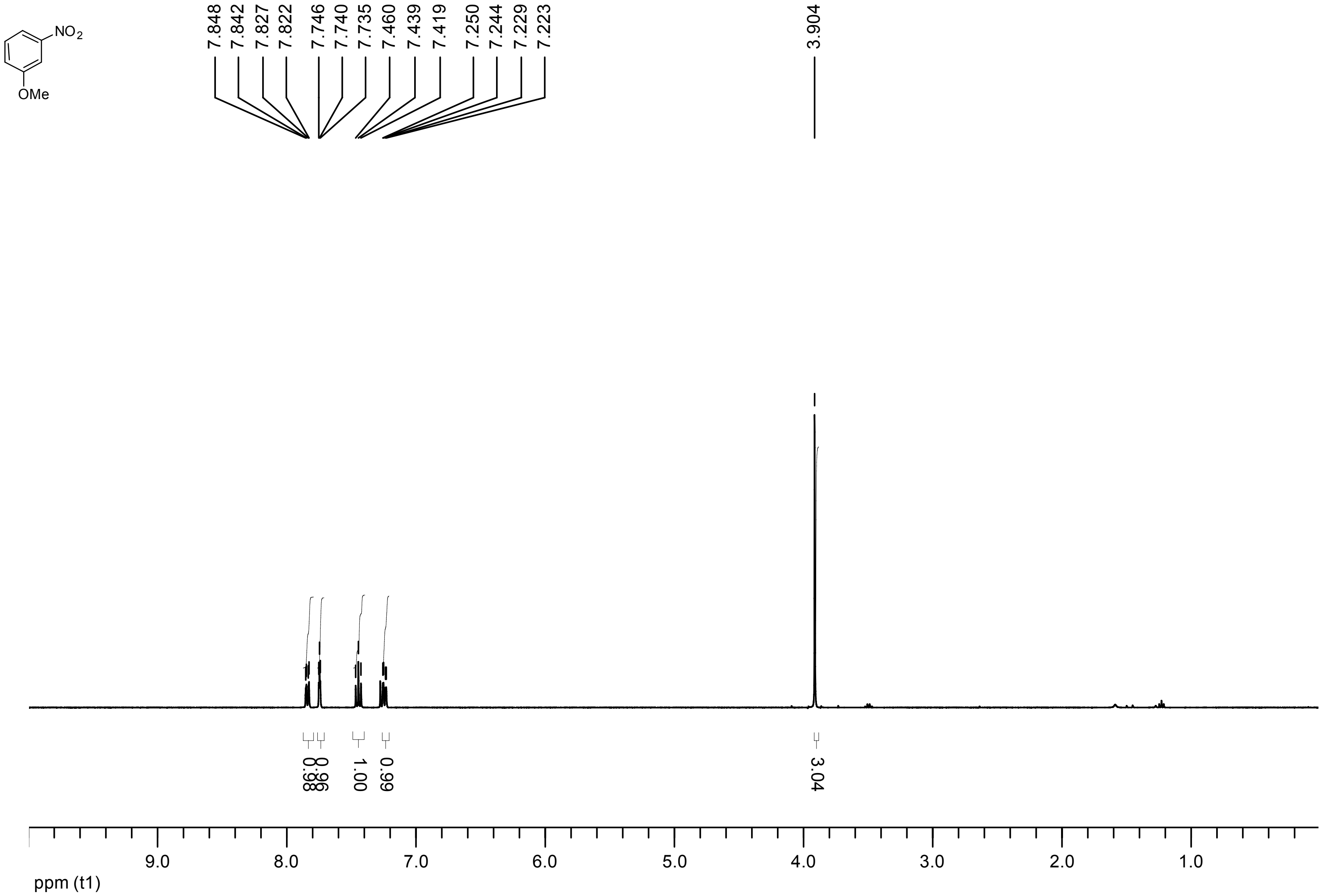
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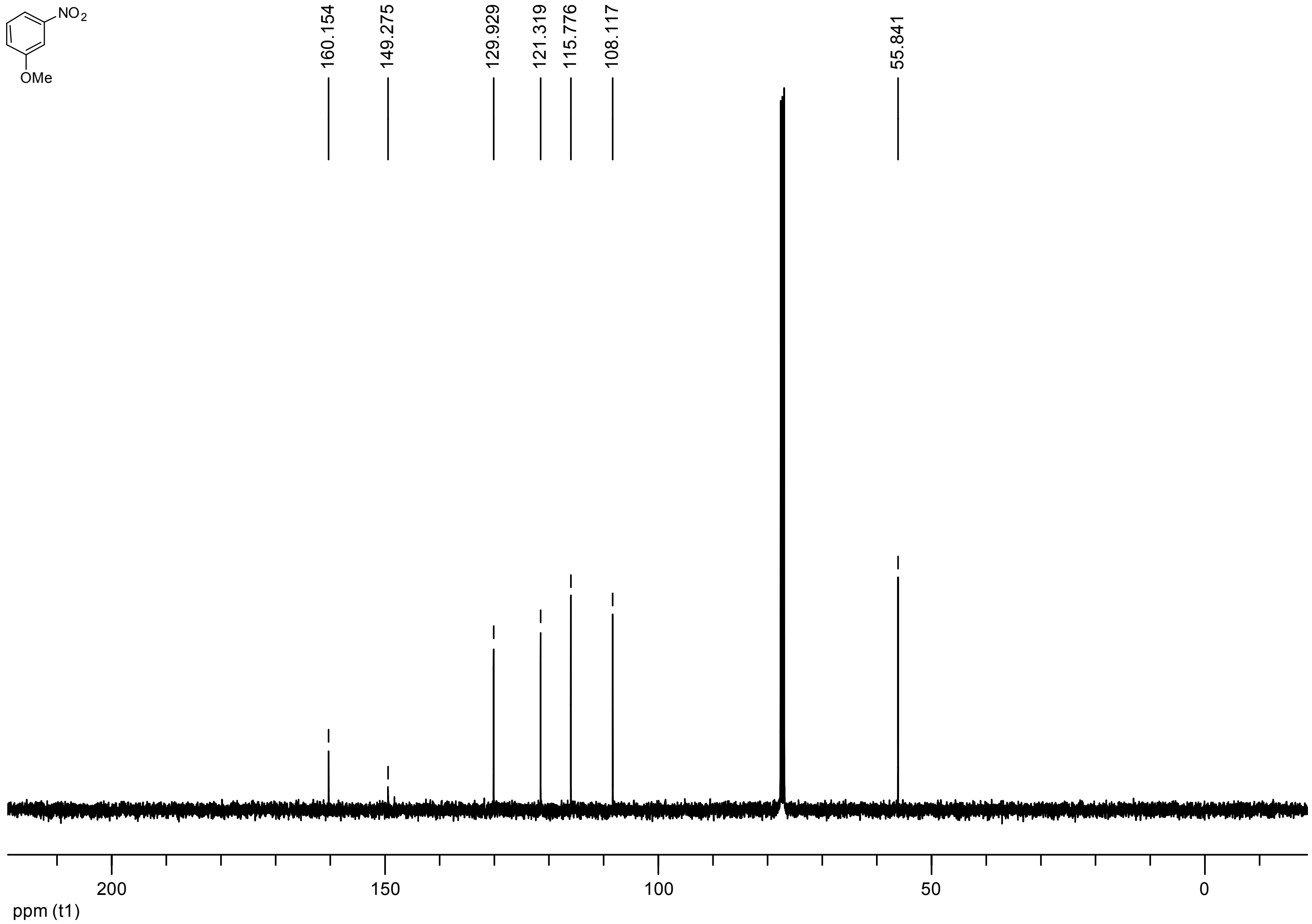
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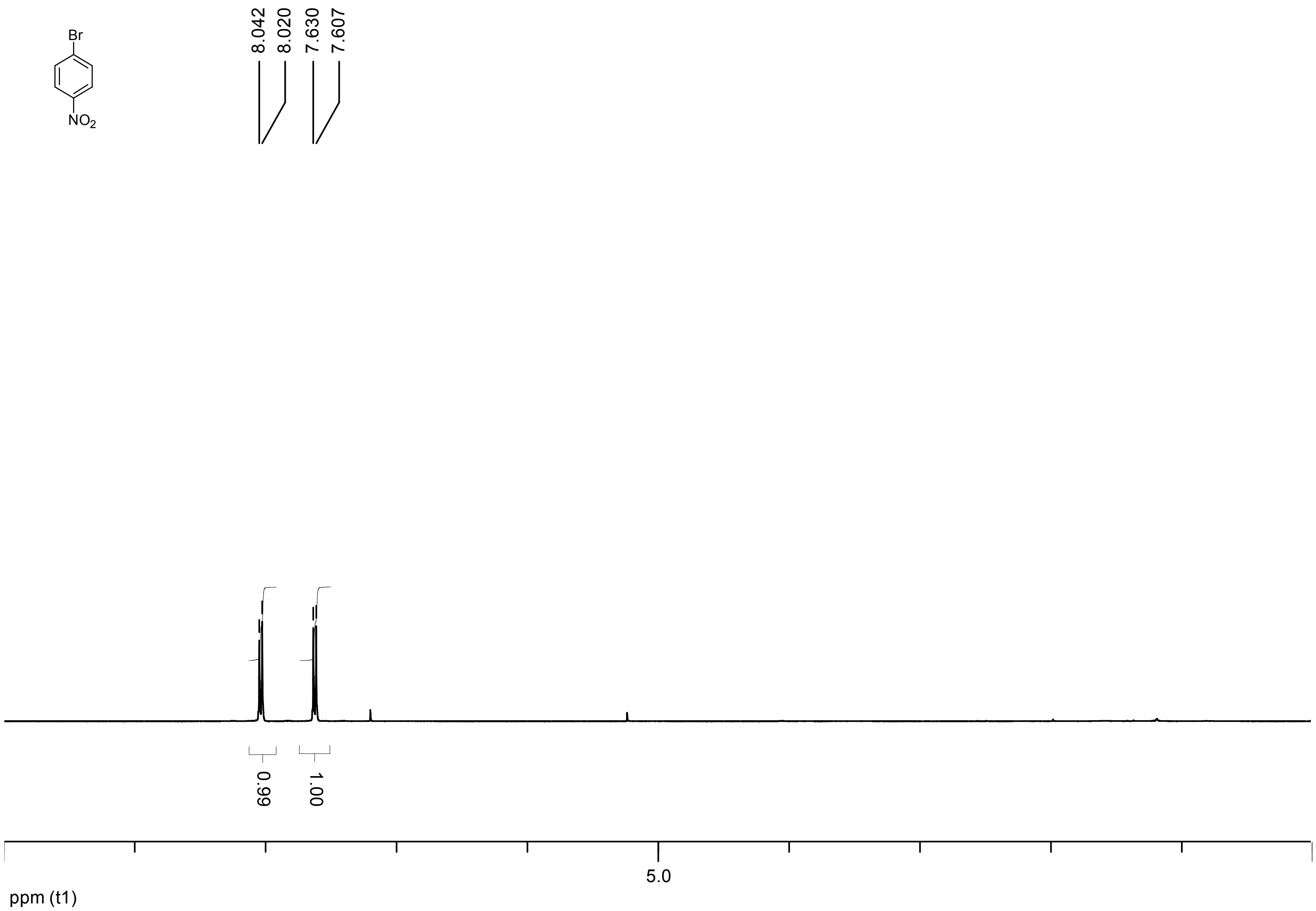
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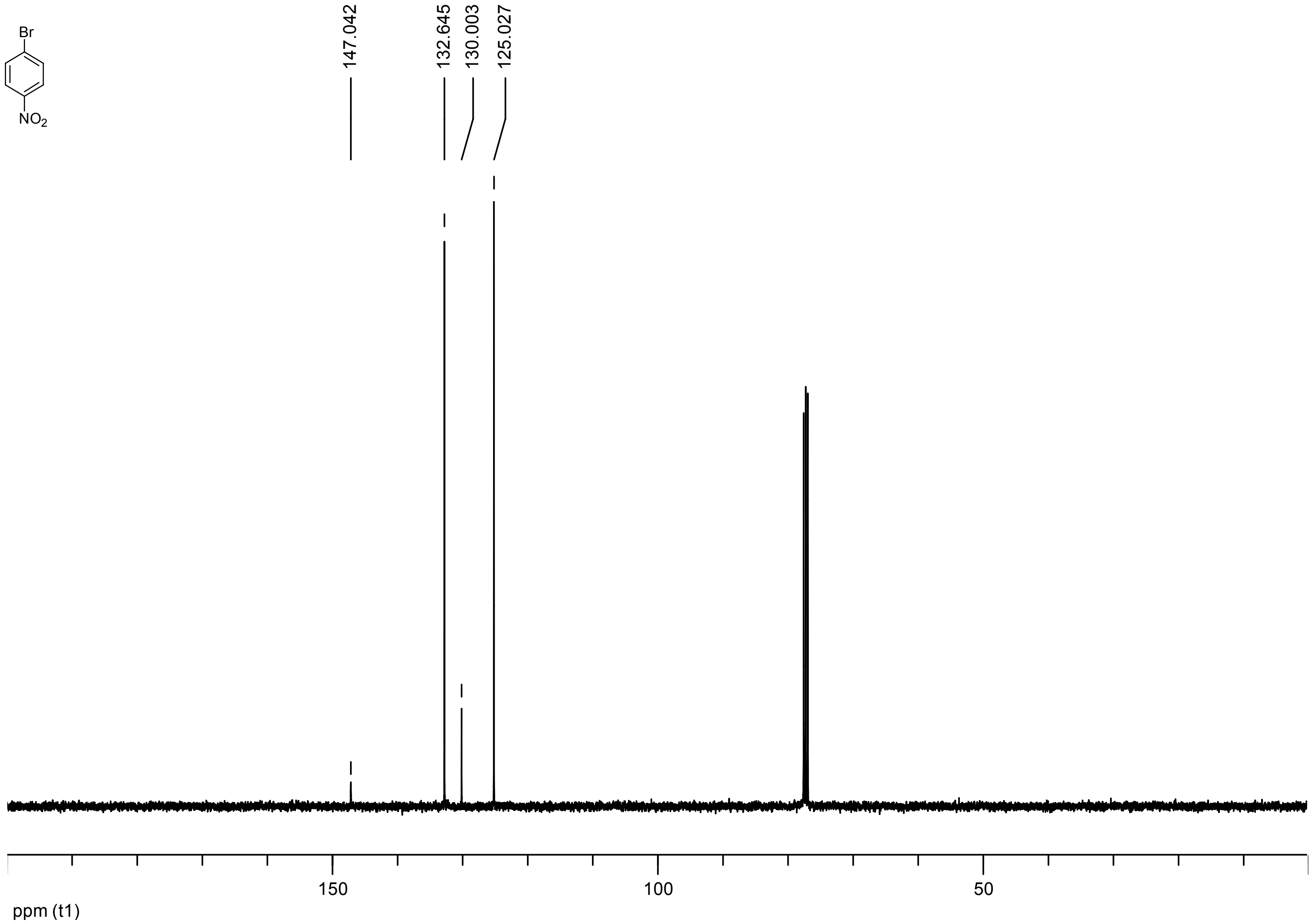
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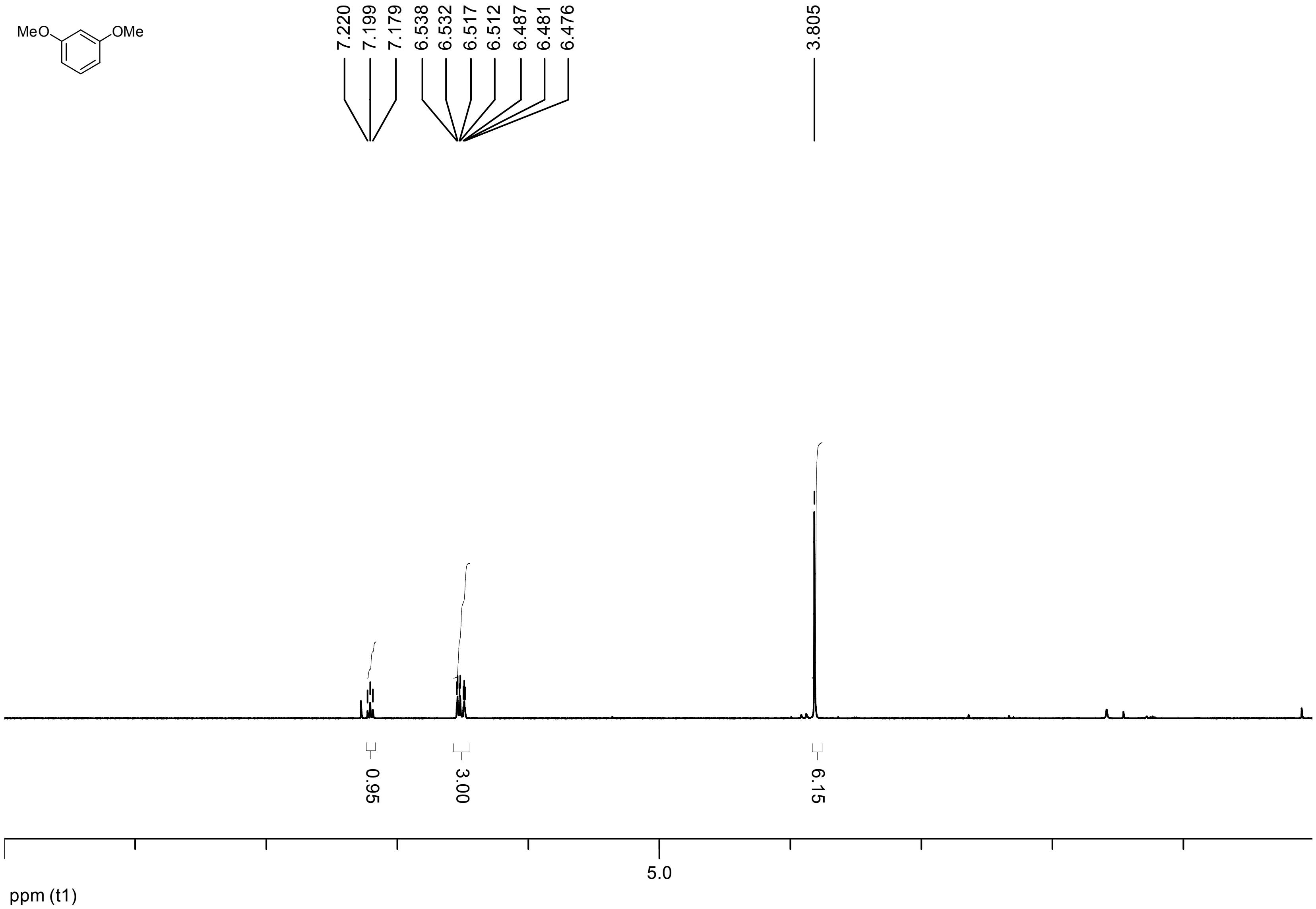
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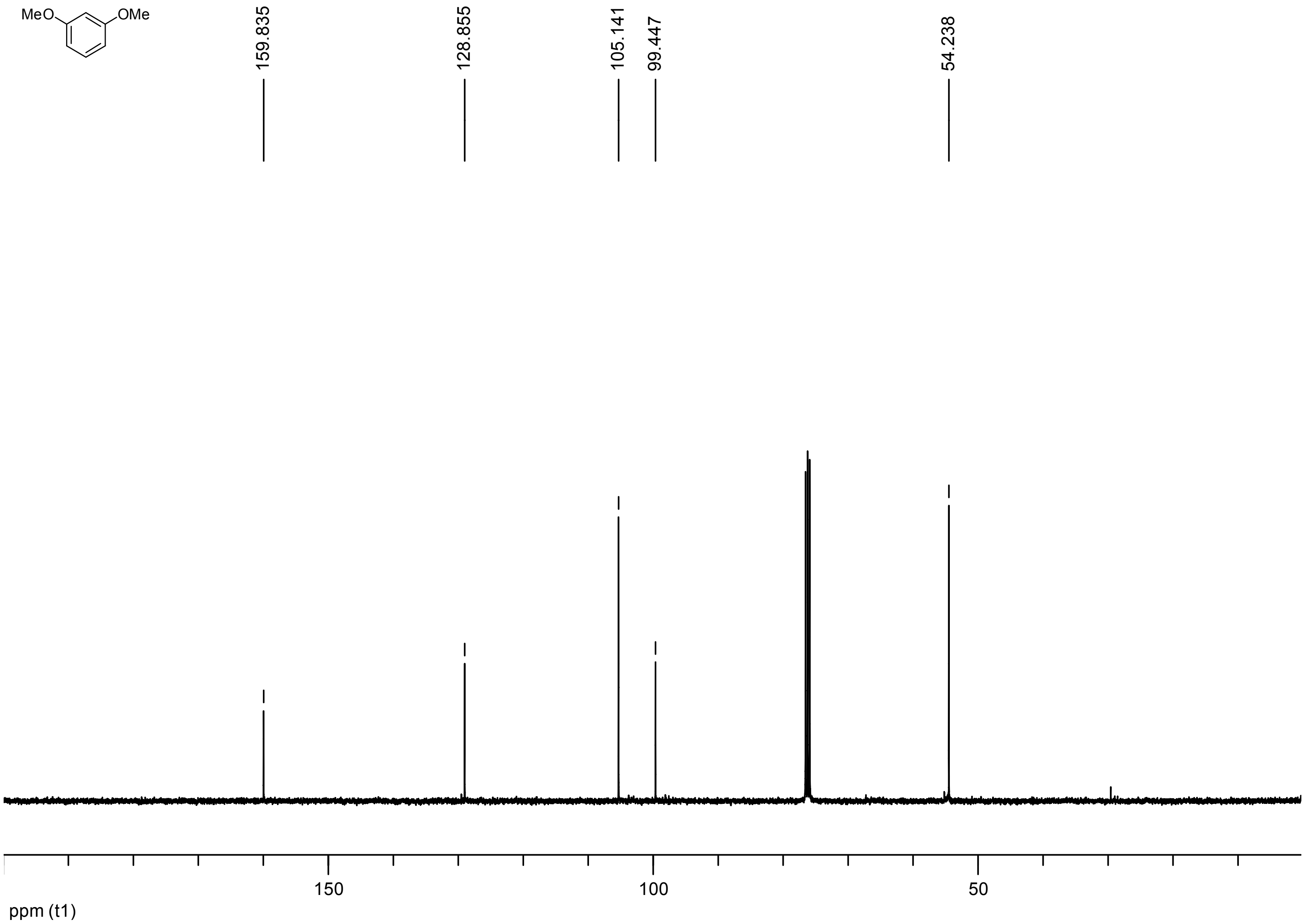
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