

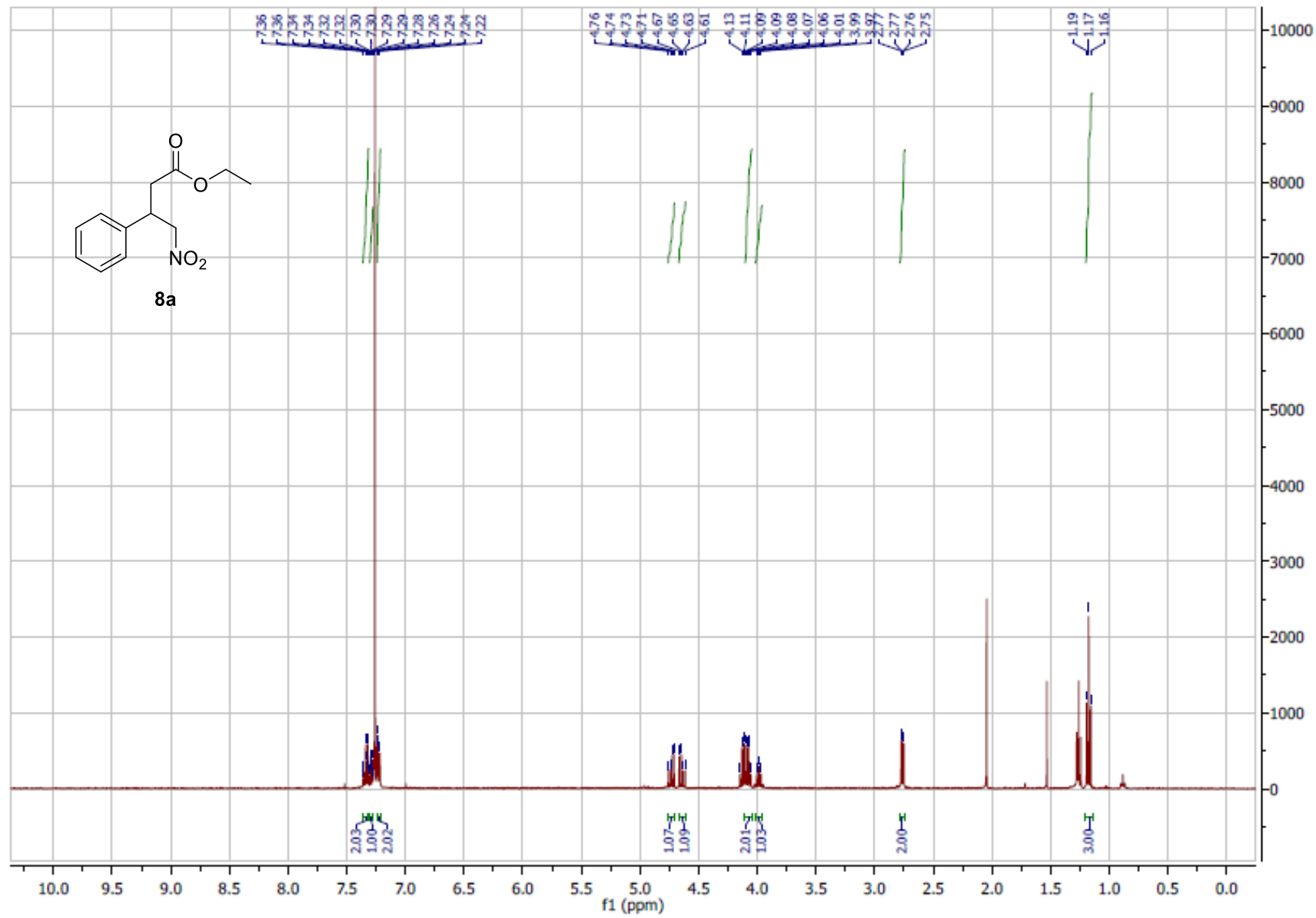
Asymmetric Synthesis of Piperidines using the nitro-Mannich Reaction

James C. Anderson, Eva Bouvier-Israel, Christopher D. Rundell and Xiangyu Zhang

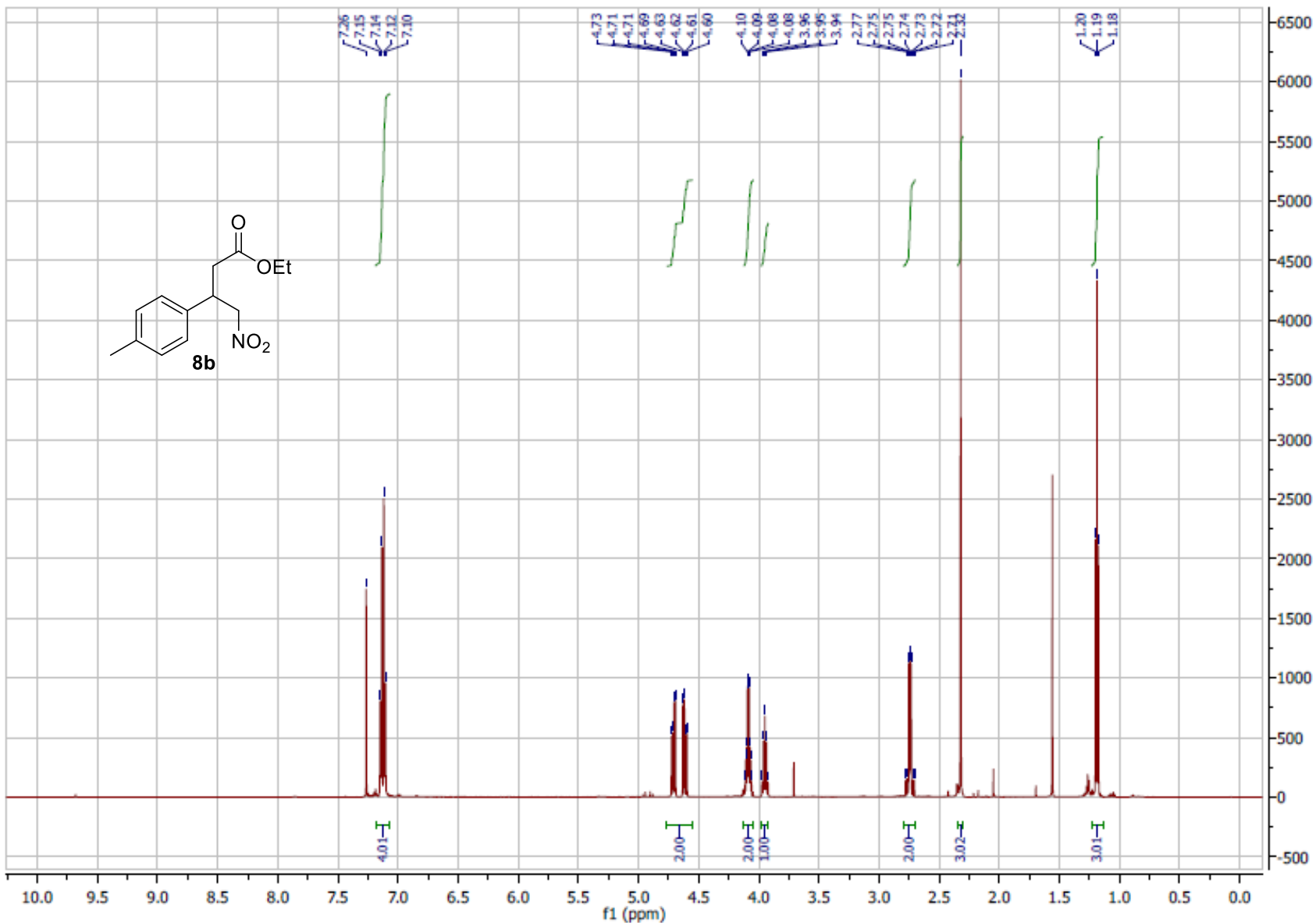
Supplementary Information

Copies of ^1H and ^{13}C NMR spectra for all new compounds

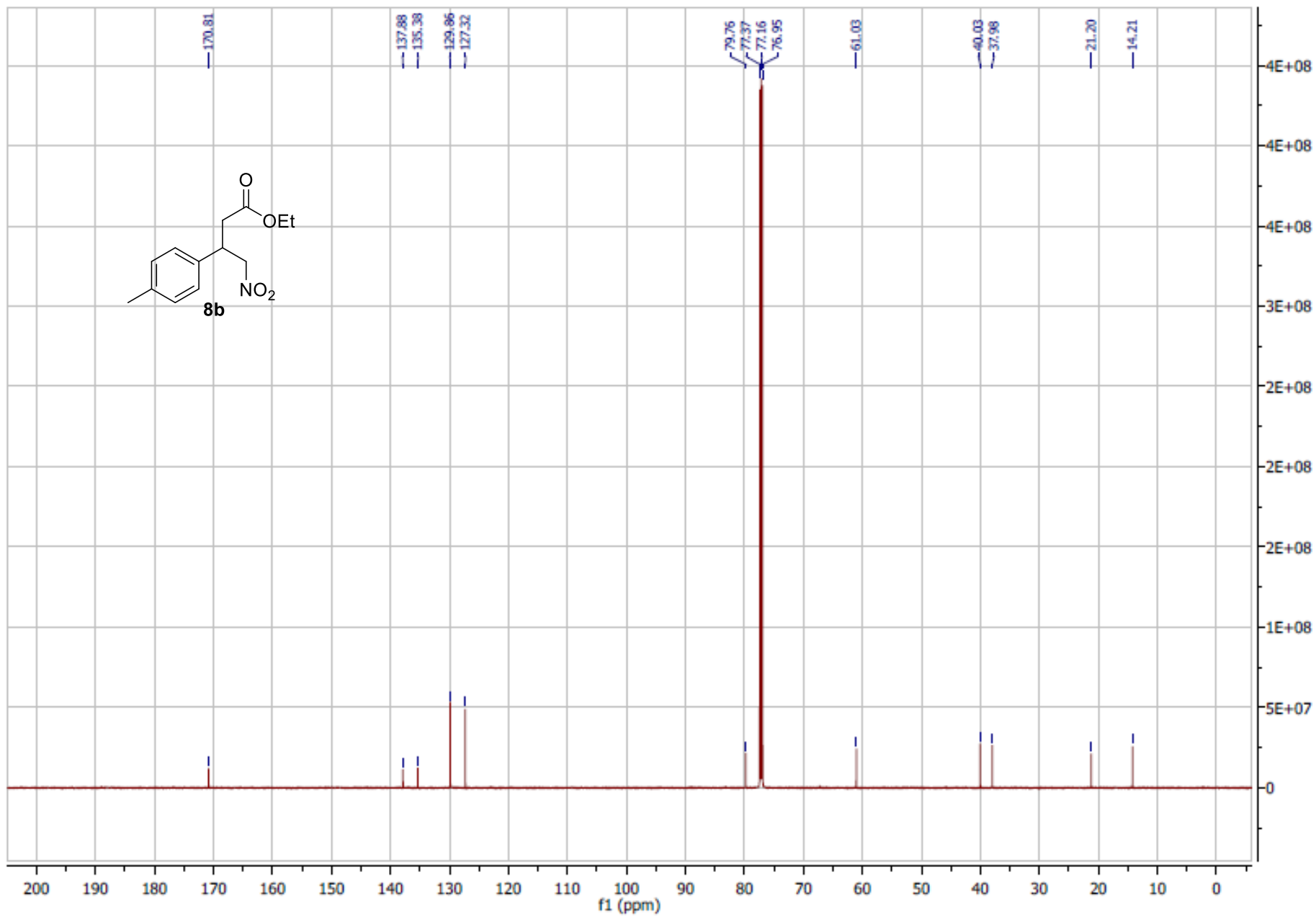
Ethyl 4-nitro-3-phenylbutanoate (8a) ^1H NMR



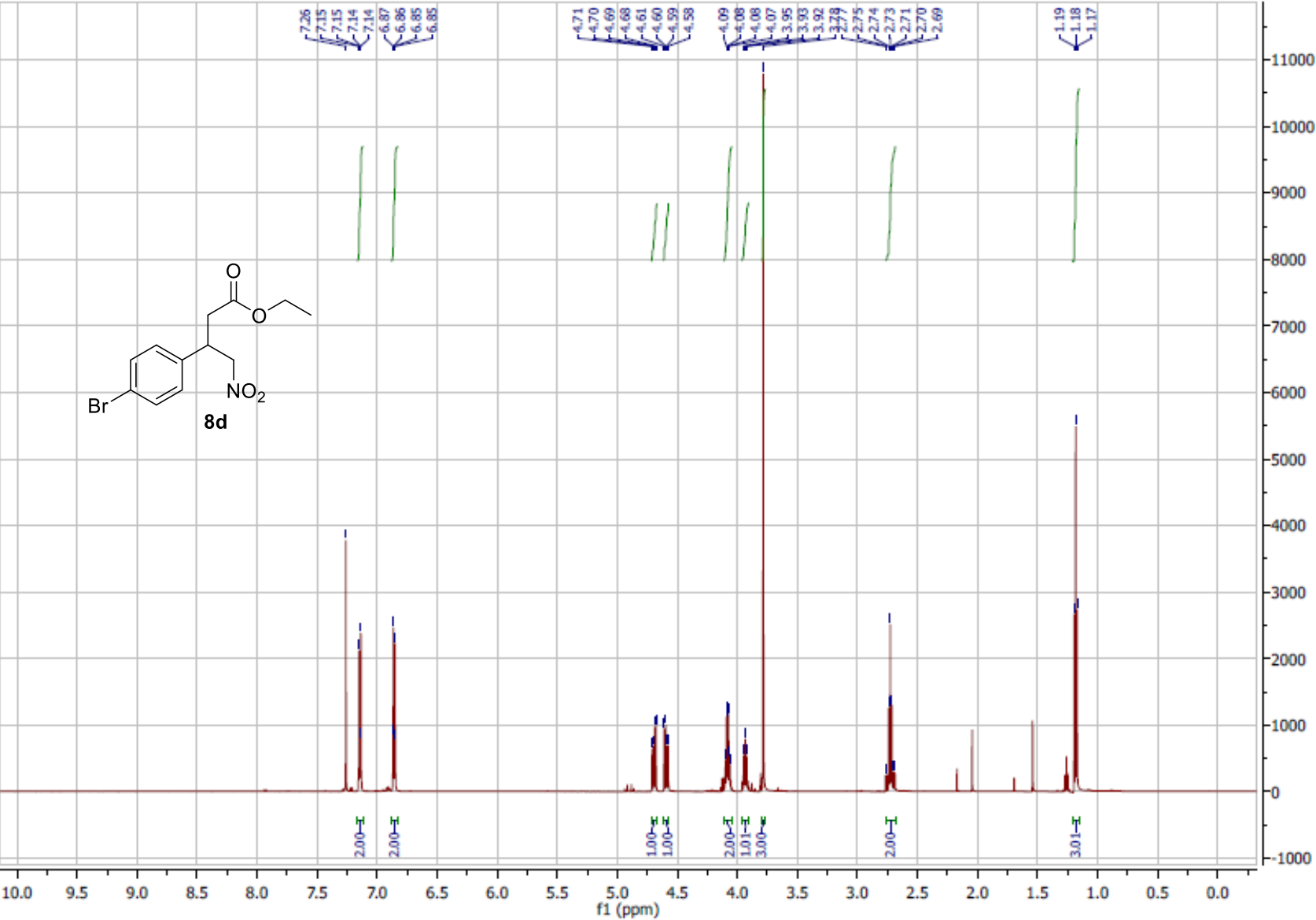
Ethyl 4-nitro-3-(p-tolyl)butanoate (8b) ¹H NMR



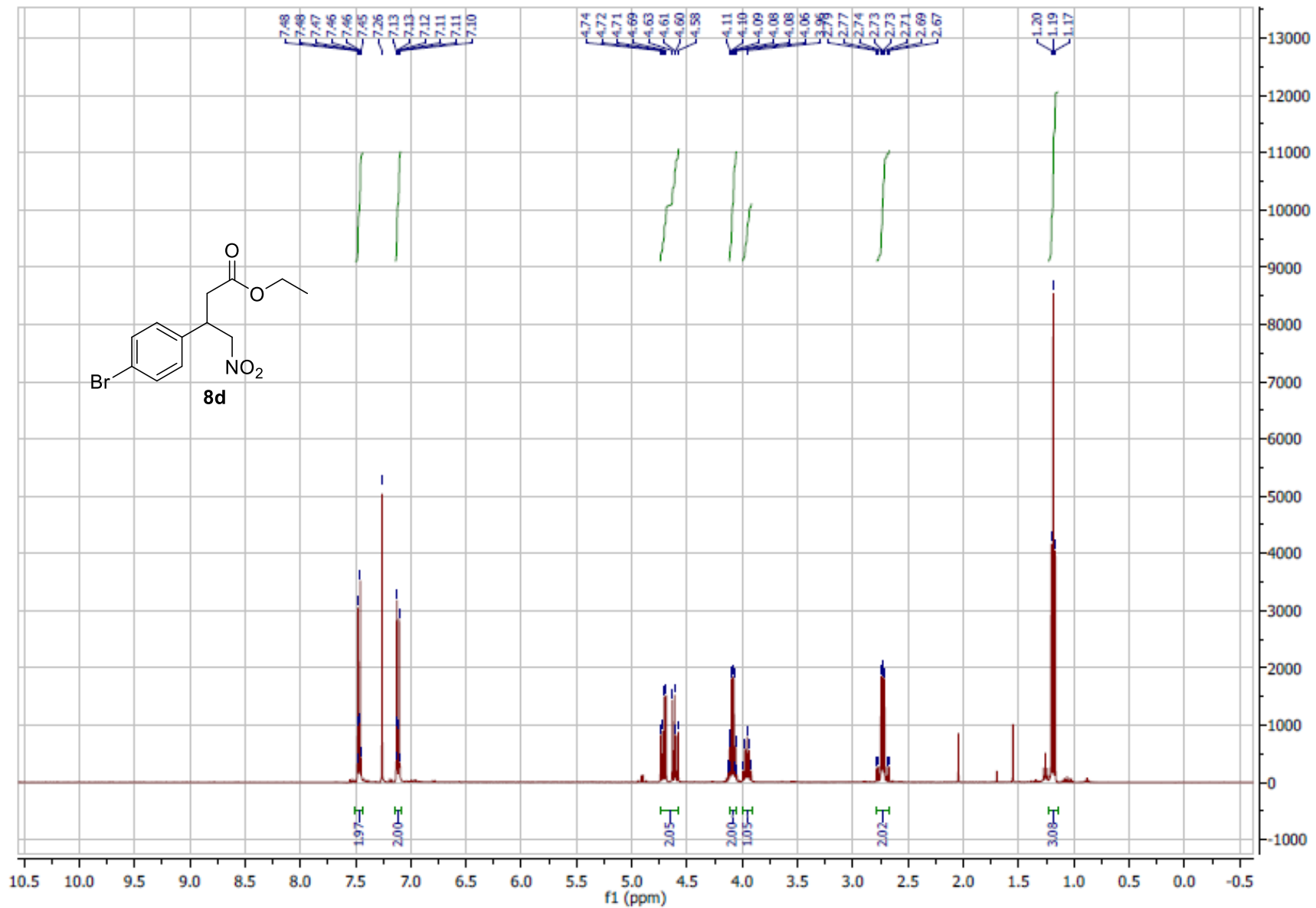
Ethyl 4-nitro-3-(p-tolyl)butanoate (8b) ¹³C NMR



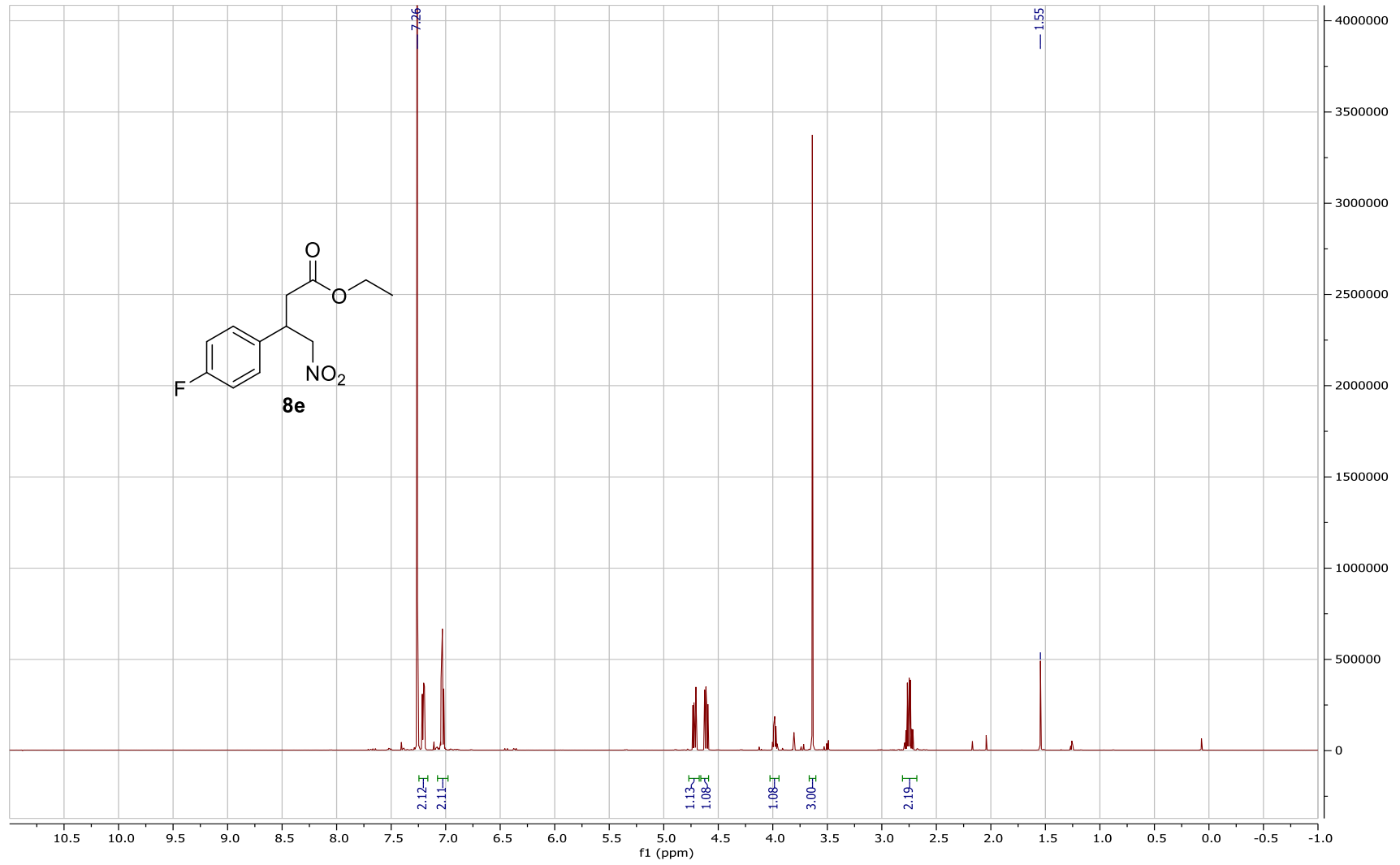
Ethyl 3-(4-methoxyphenyl)-4-nitrobutanoate (8c) ¹H NMR

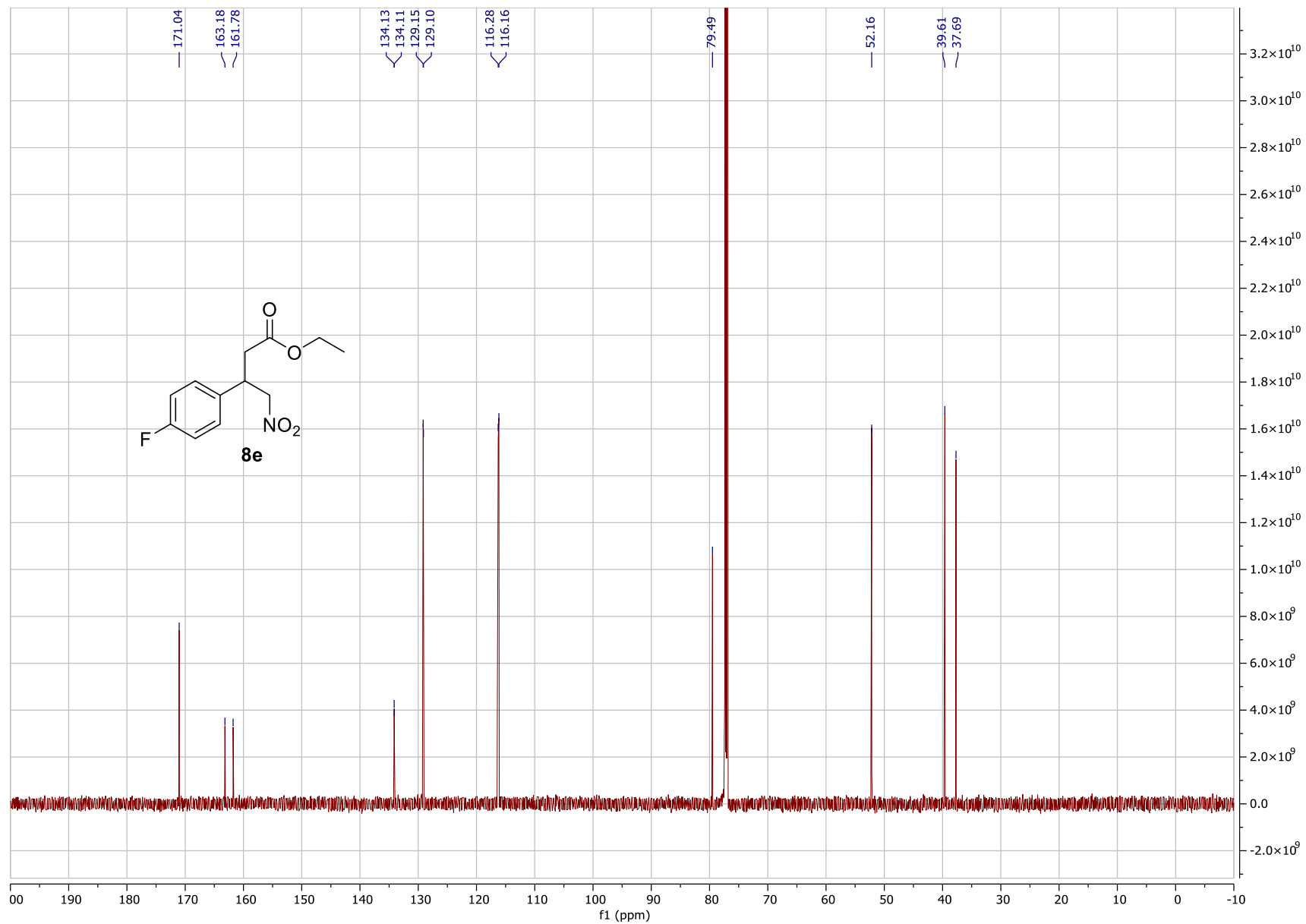


Ethyl 3-(4-bromophenyl)-4-nitrobutanoate (8d) ¹H NMR

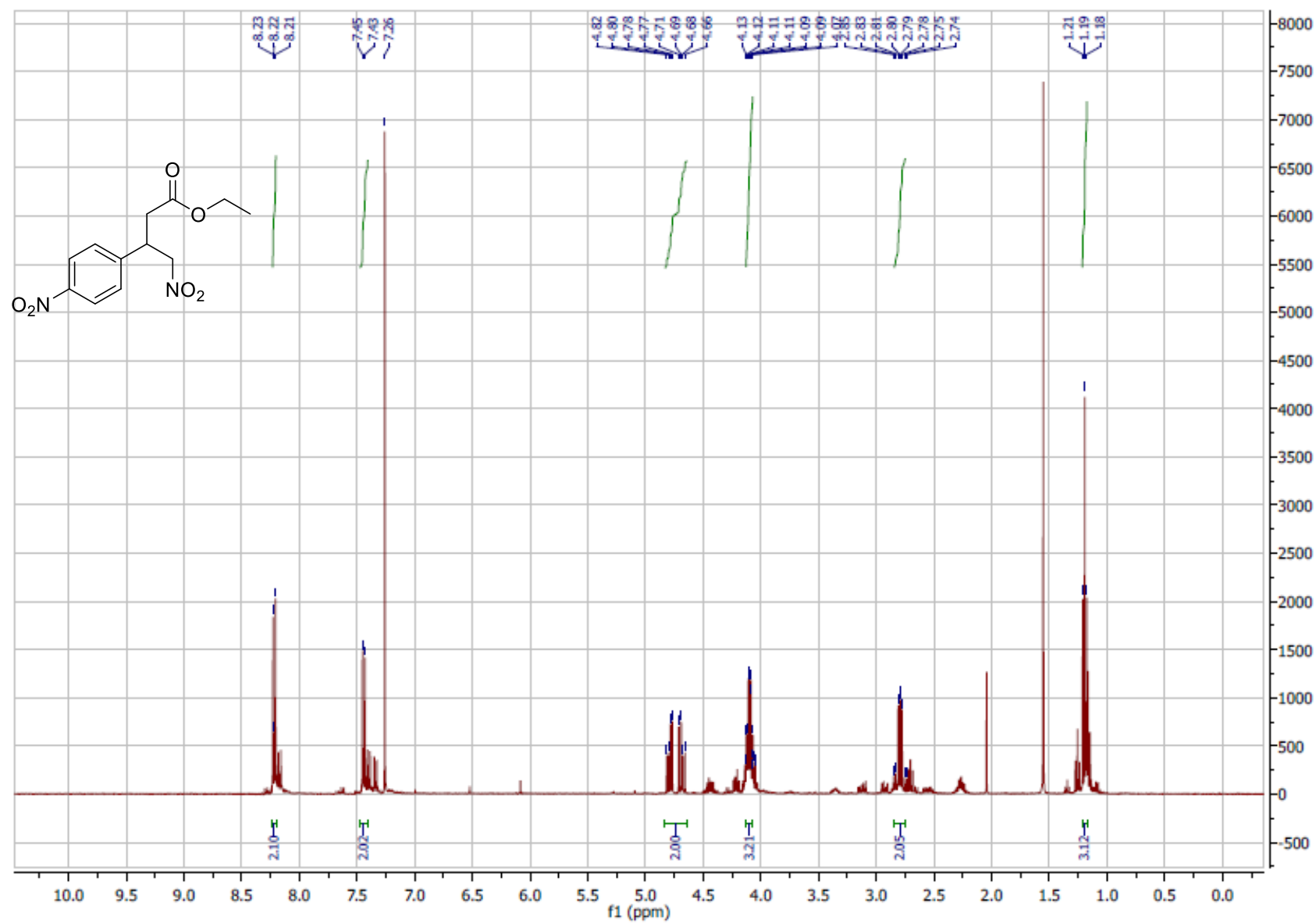


Ethyl 3-(4-fluorophenyl)-4-nitrobutanoate (8e) ¹H NMR

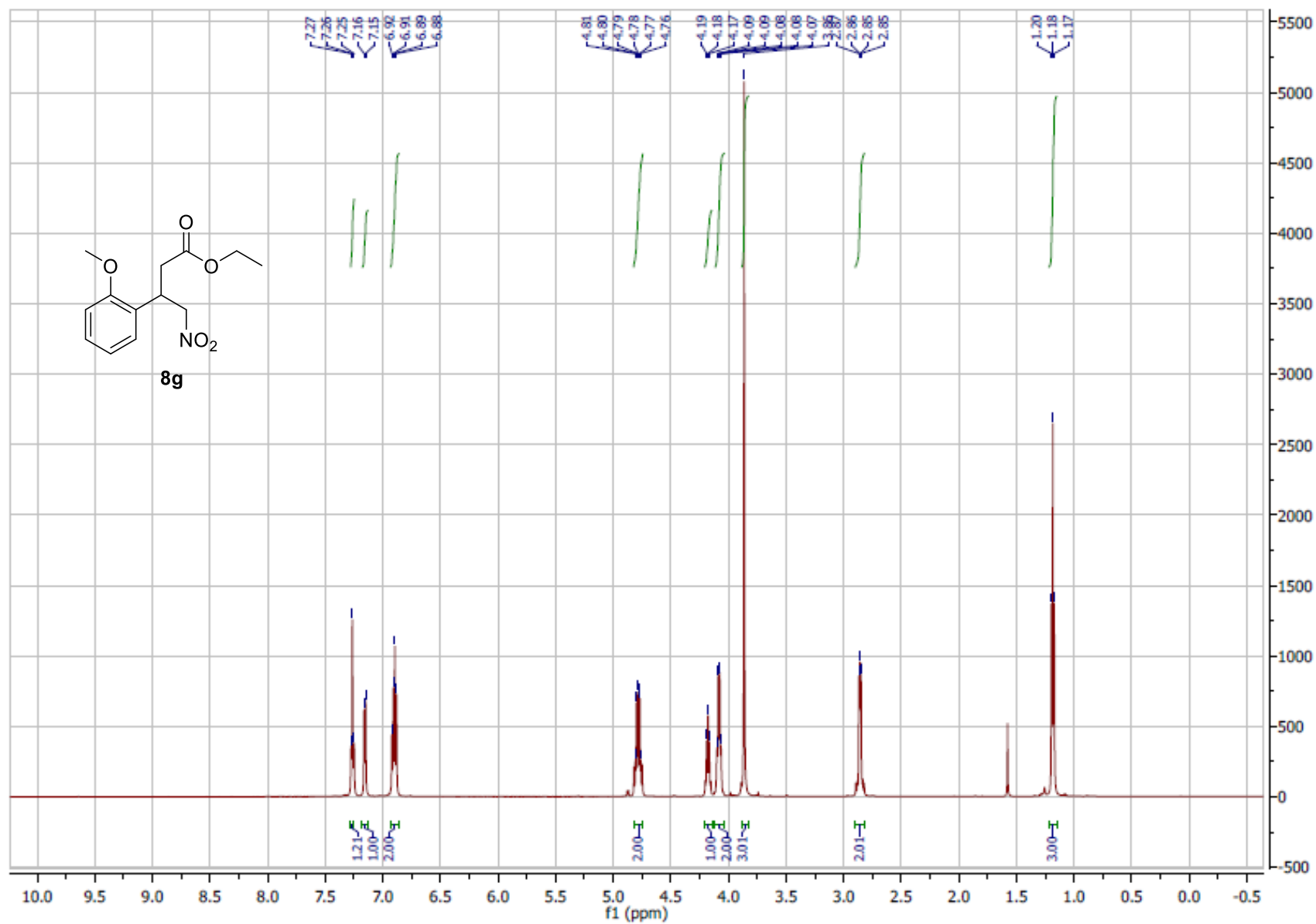




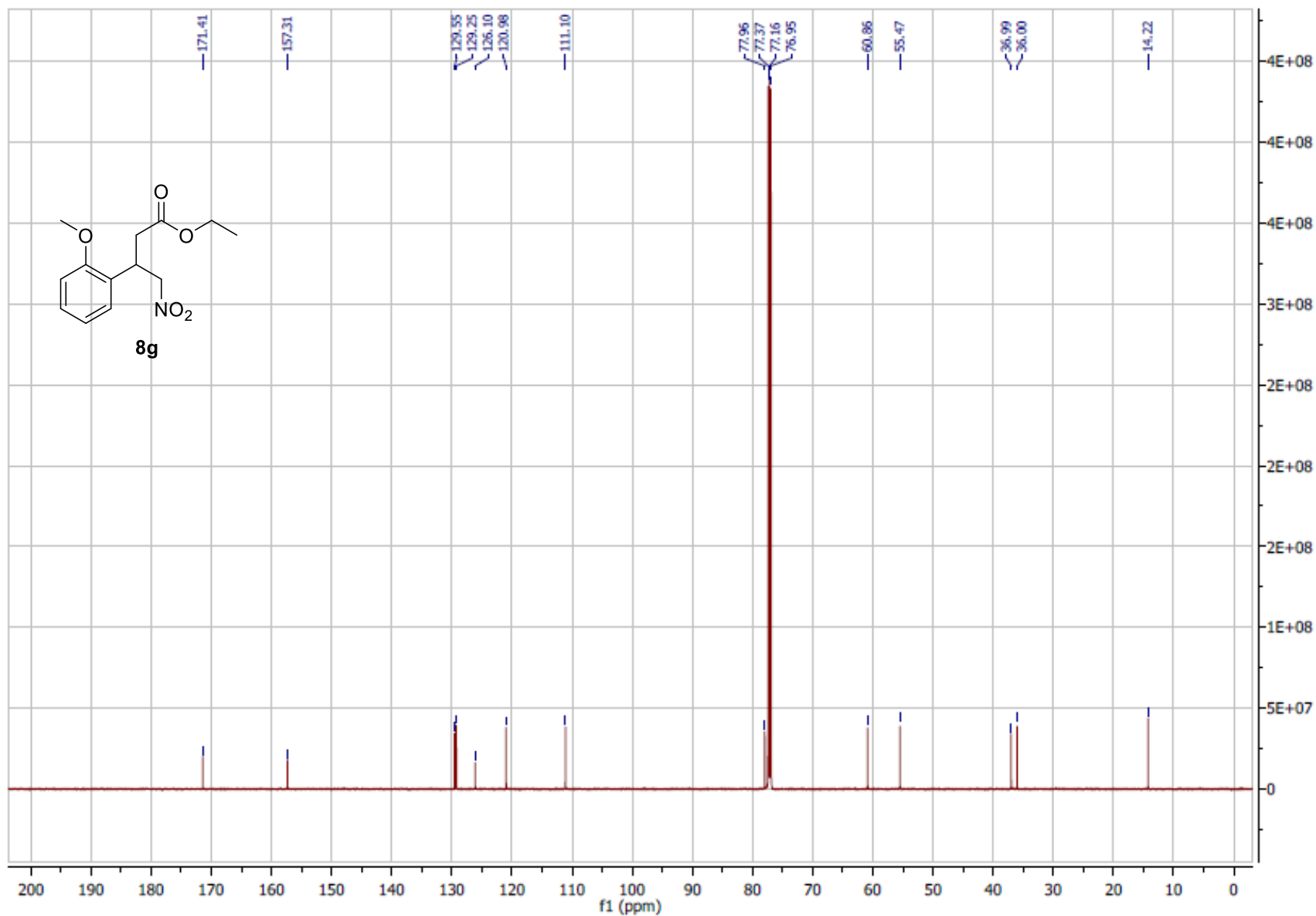
Ethyl 4-nitro-3-(4-nitrophenyl)butanoate (8f) ¹H NMR



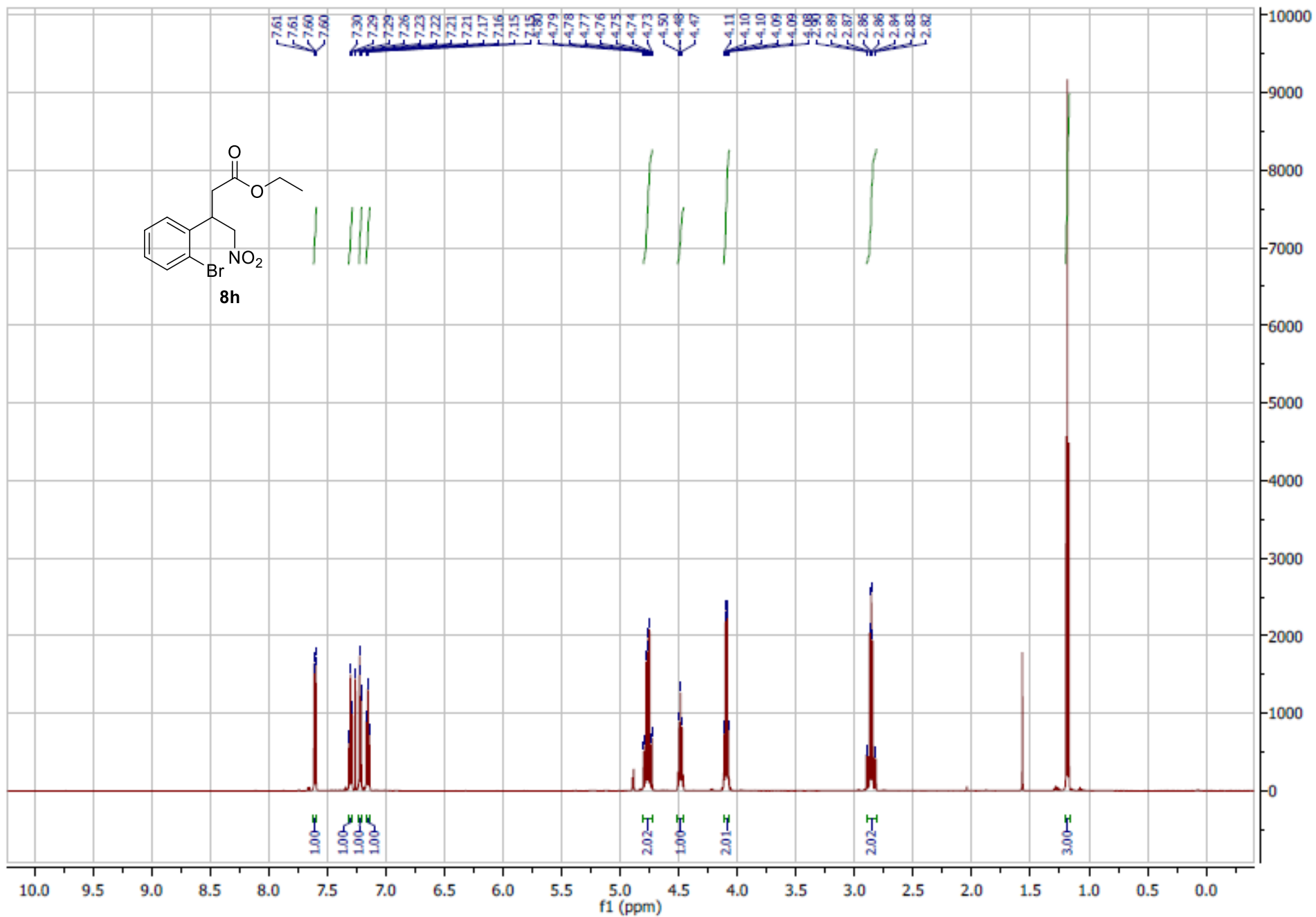
Ethyl 3-(2-methoxyphenyl)-4-nitrobutanoate (8g) ¹H NMR



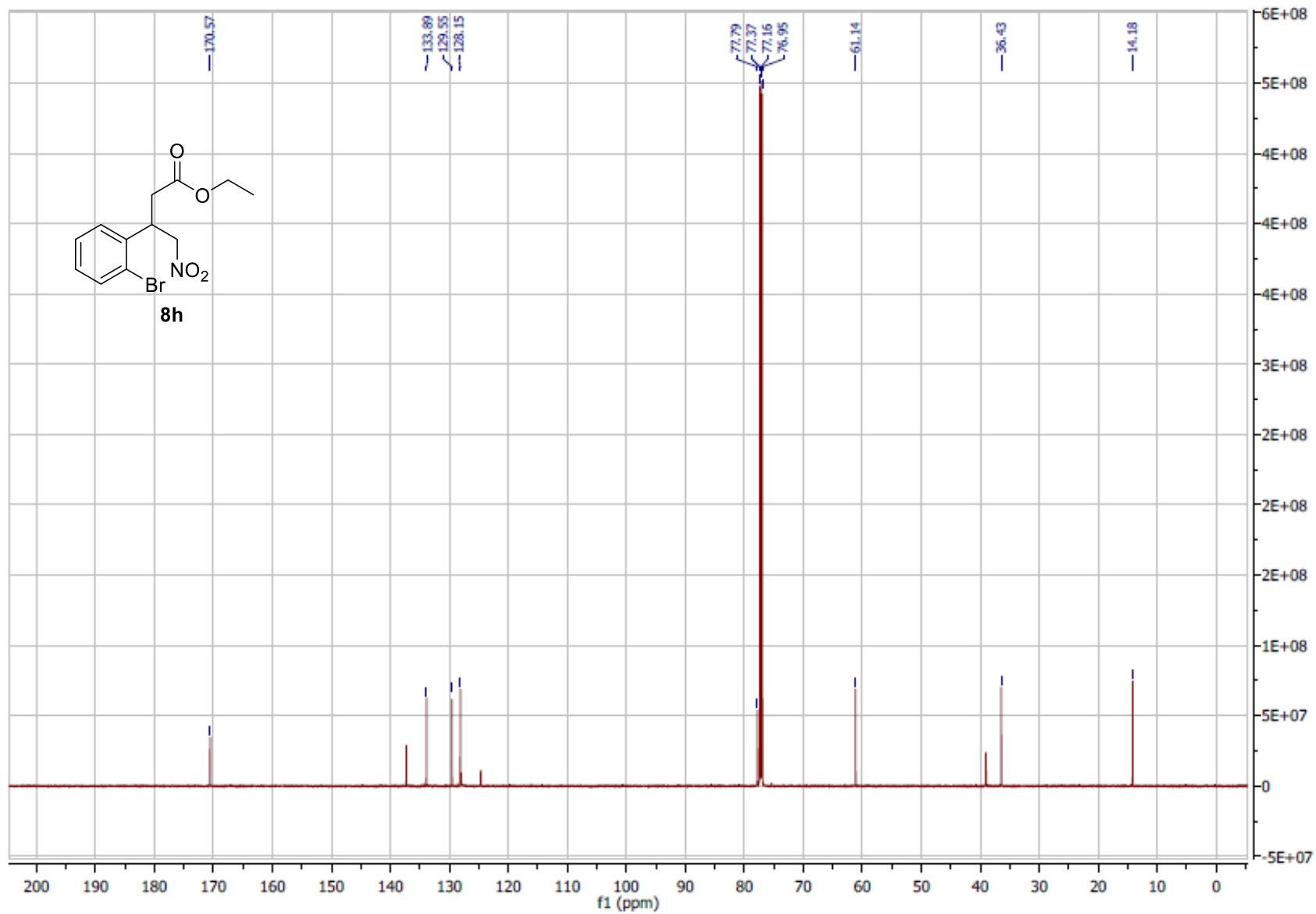
Ethyl 3-(2-methoxyphenyl)-4-nitrobutanoate (8g) ¹³C NMR



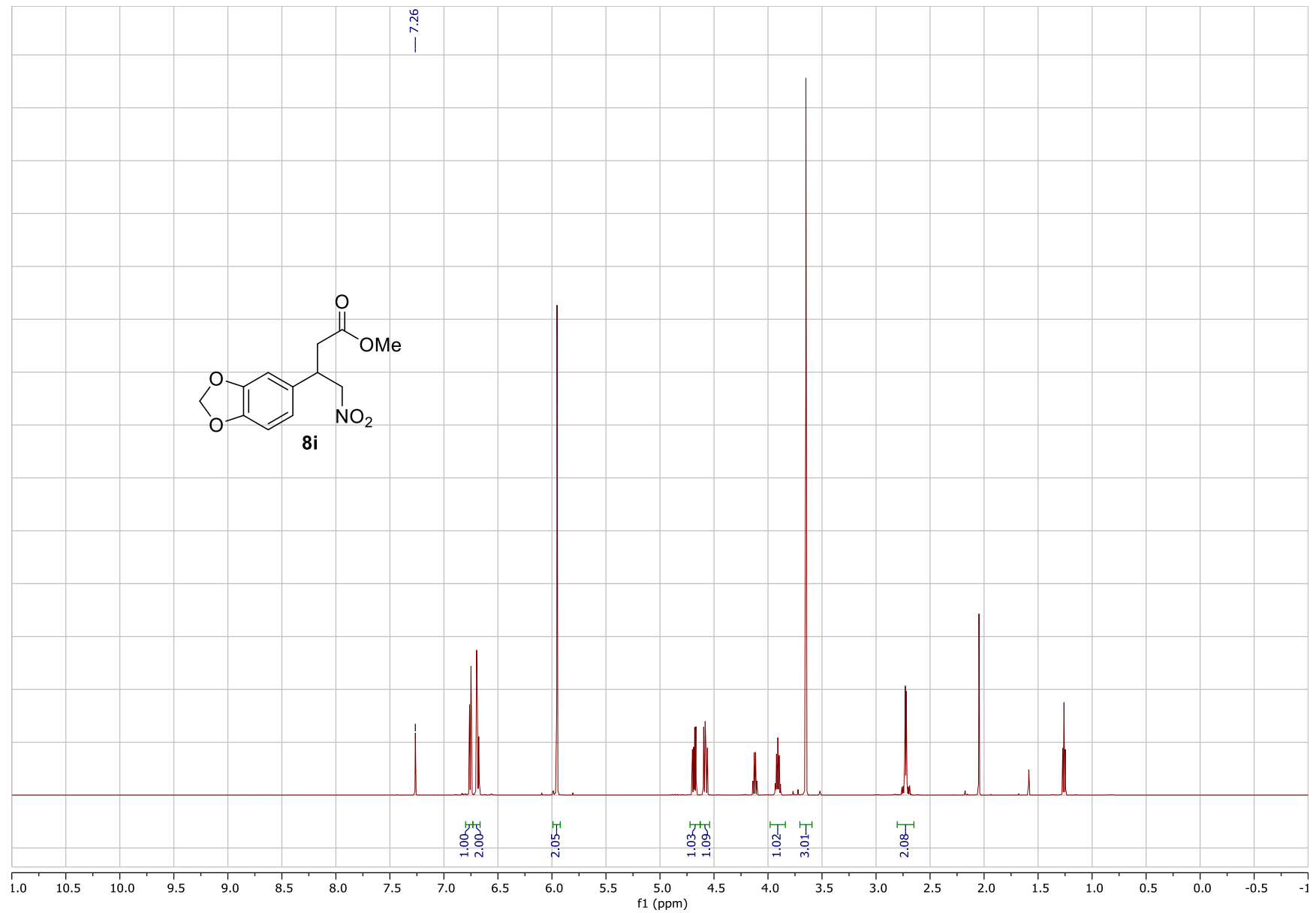
Ethyl 3-(2-bromophenyl)-4-nitrobutanoate (8h) ¹H NMR



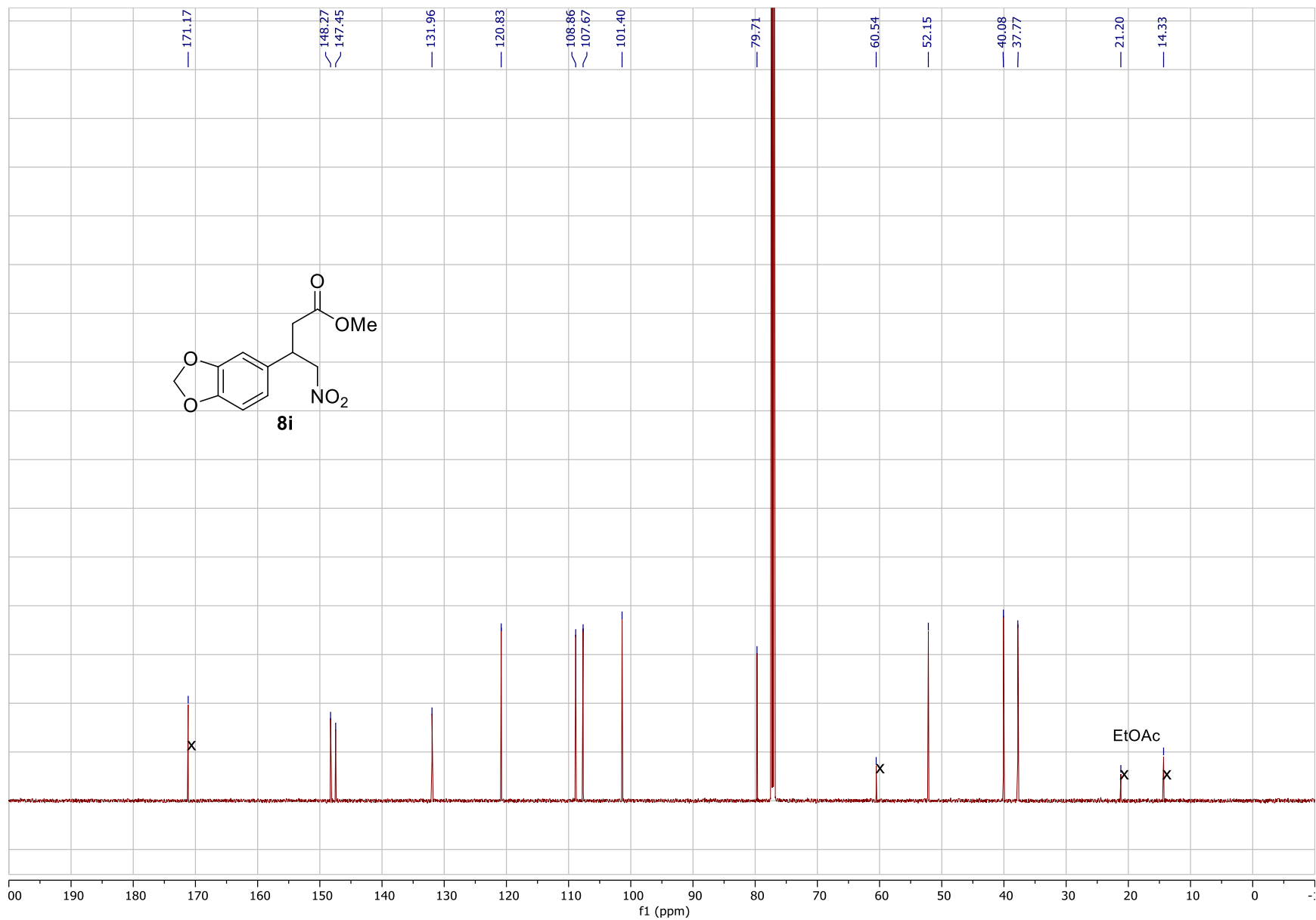
Ethyl 3-(2-bromophenyl)-4-nitrobutanoate (8h) ¹³C NMR



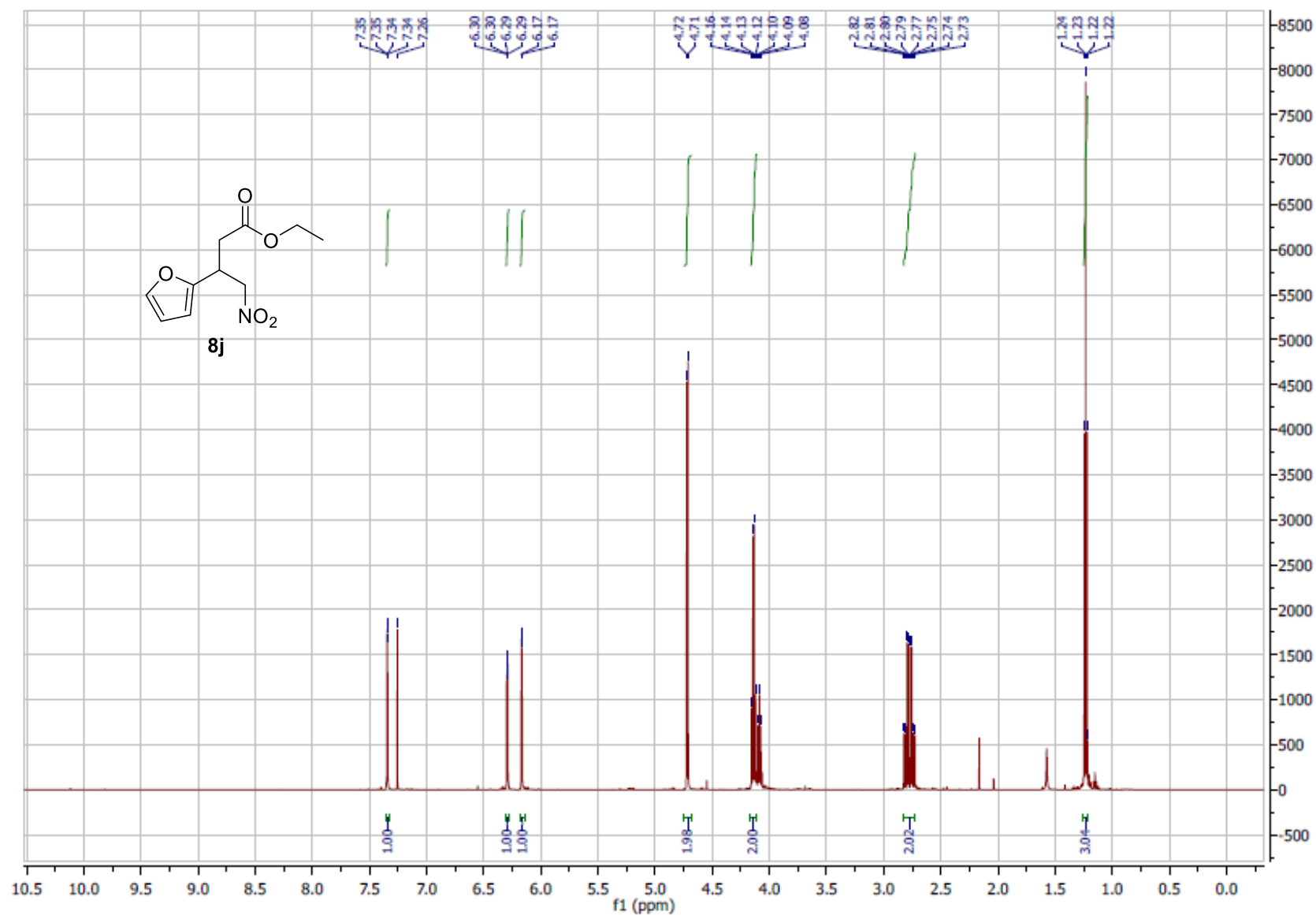
Methyl 3-(benzo[d][1,3]dioxol-5-yl)-4-nitrobutanoate (8i) ¹H NMR



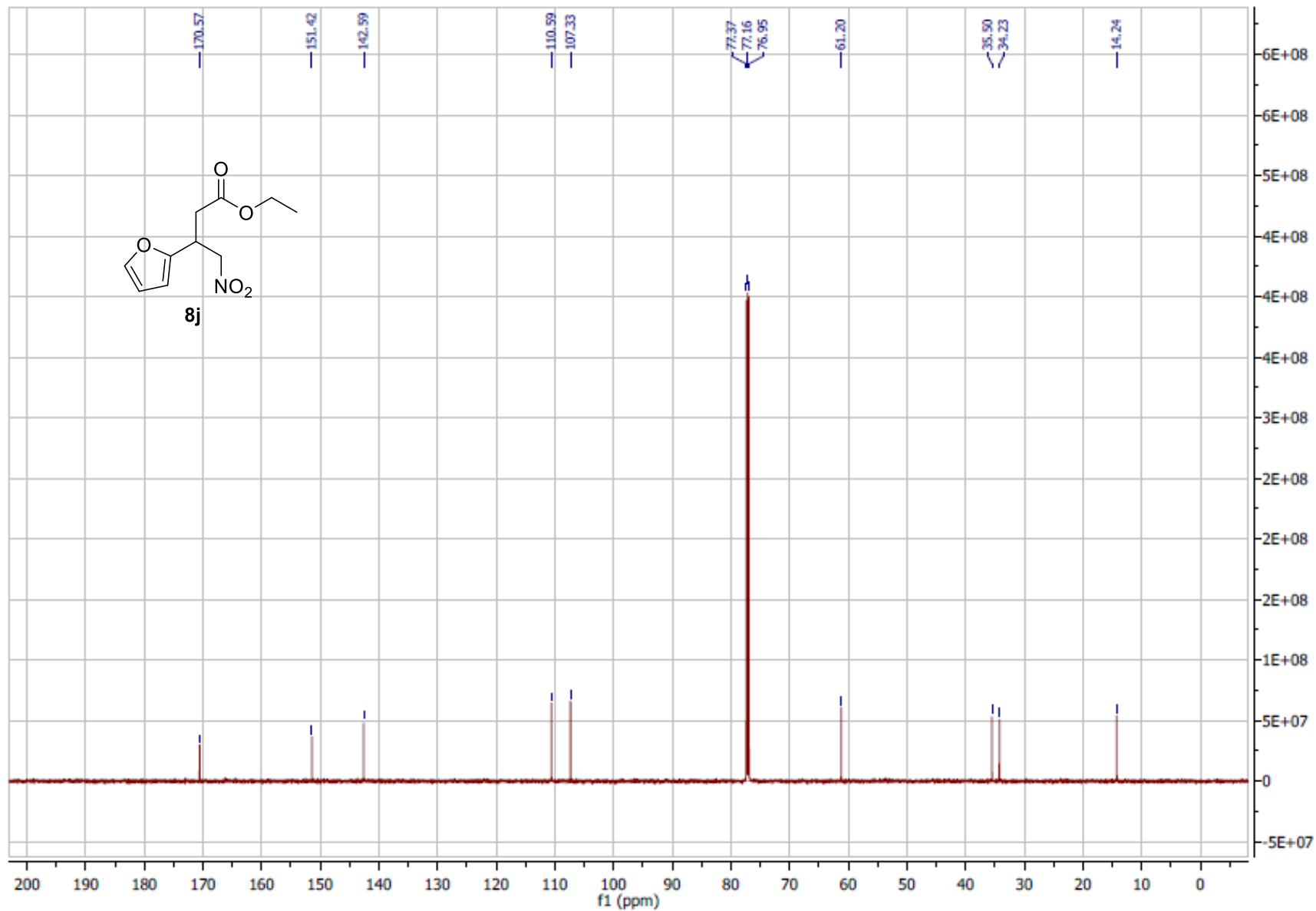
Methyl 3-(benzo[d][1,3]dioxol-5-yl)-4-nitrobutanoate (8i) ¹³C NMR



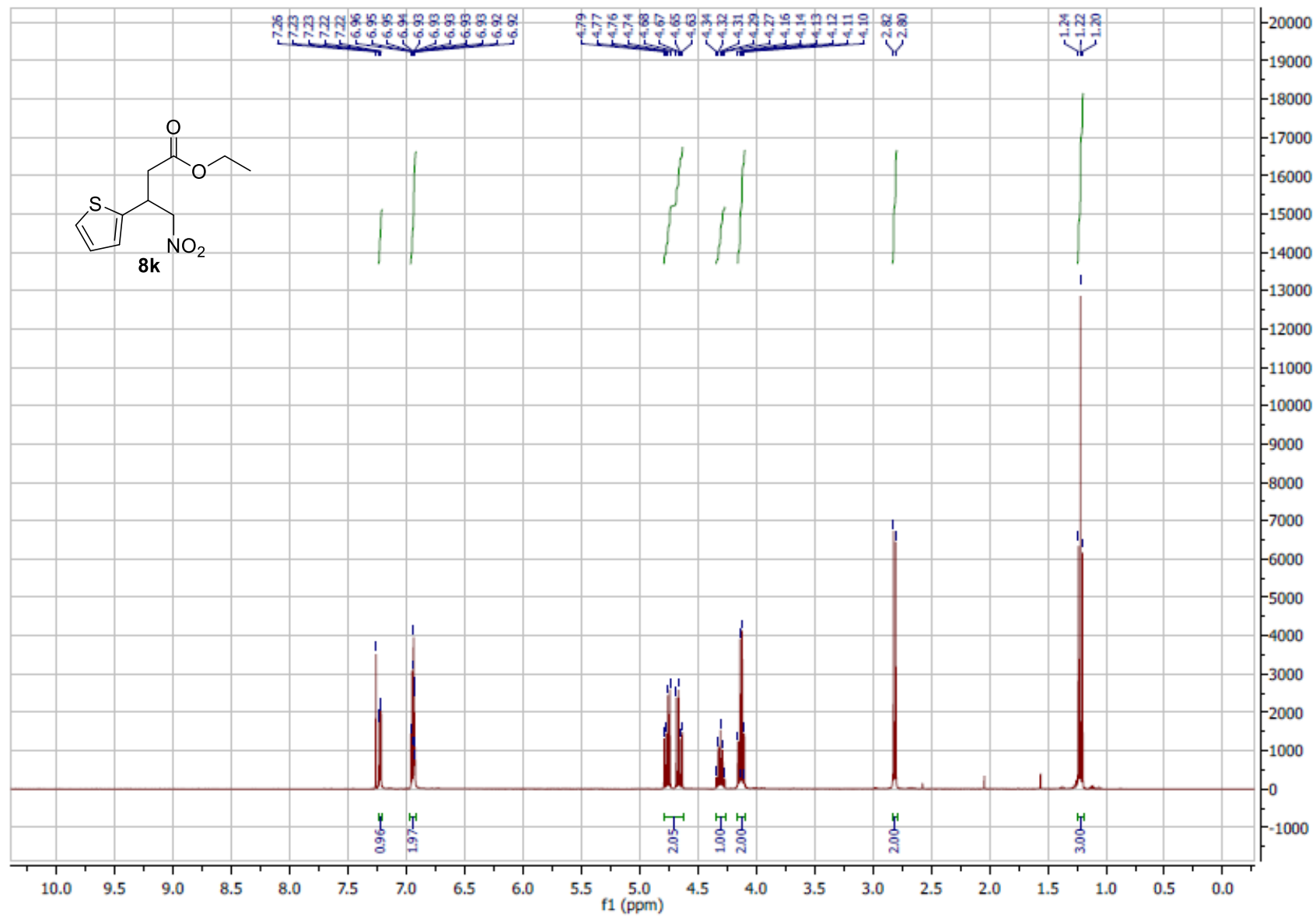
Ethyl 3-(furan-2-yl)-4-nitrobutanoate (8j) ¹H NMR



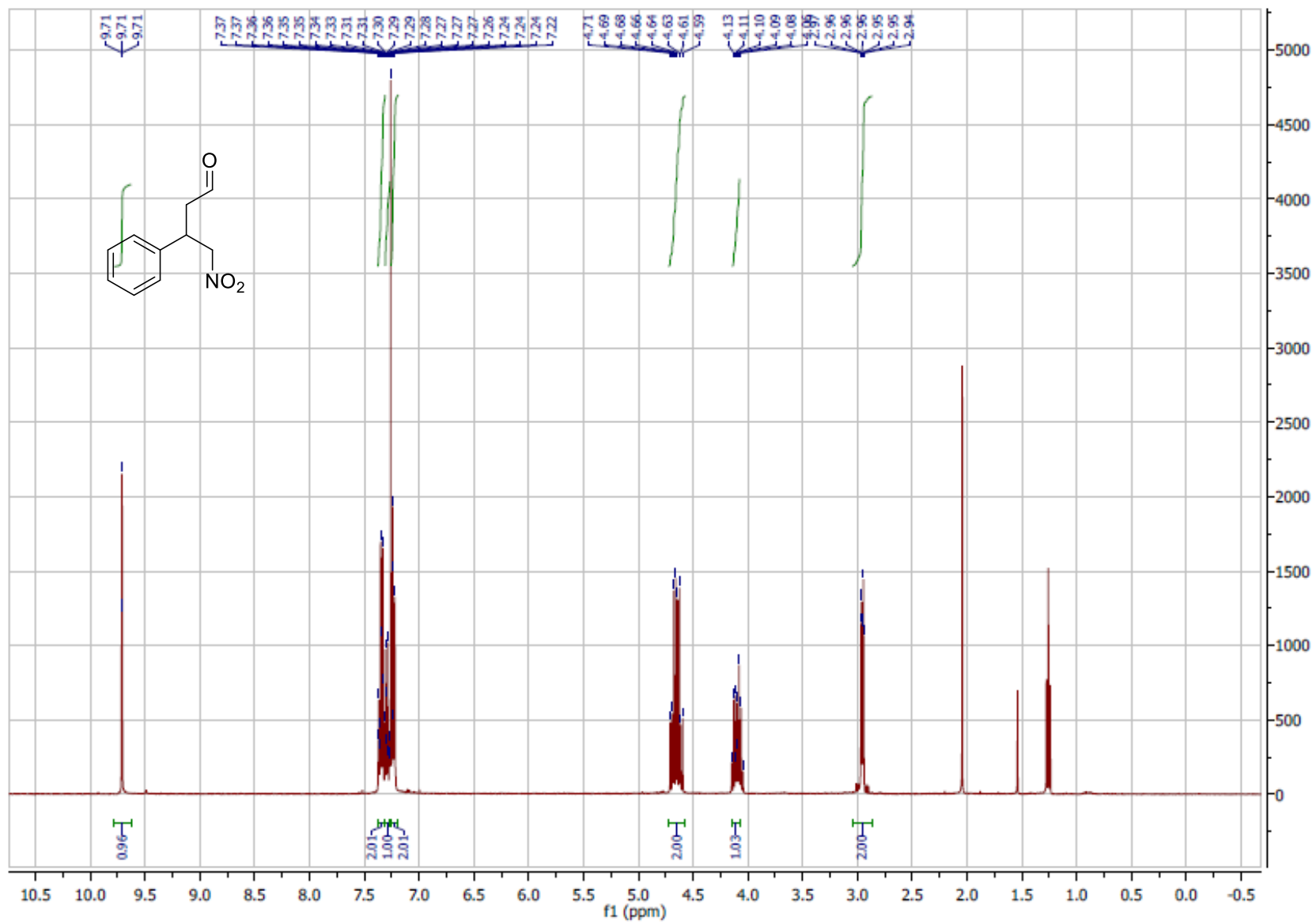
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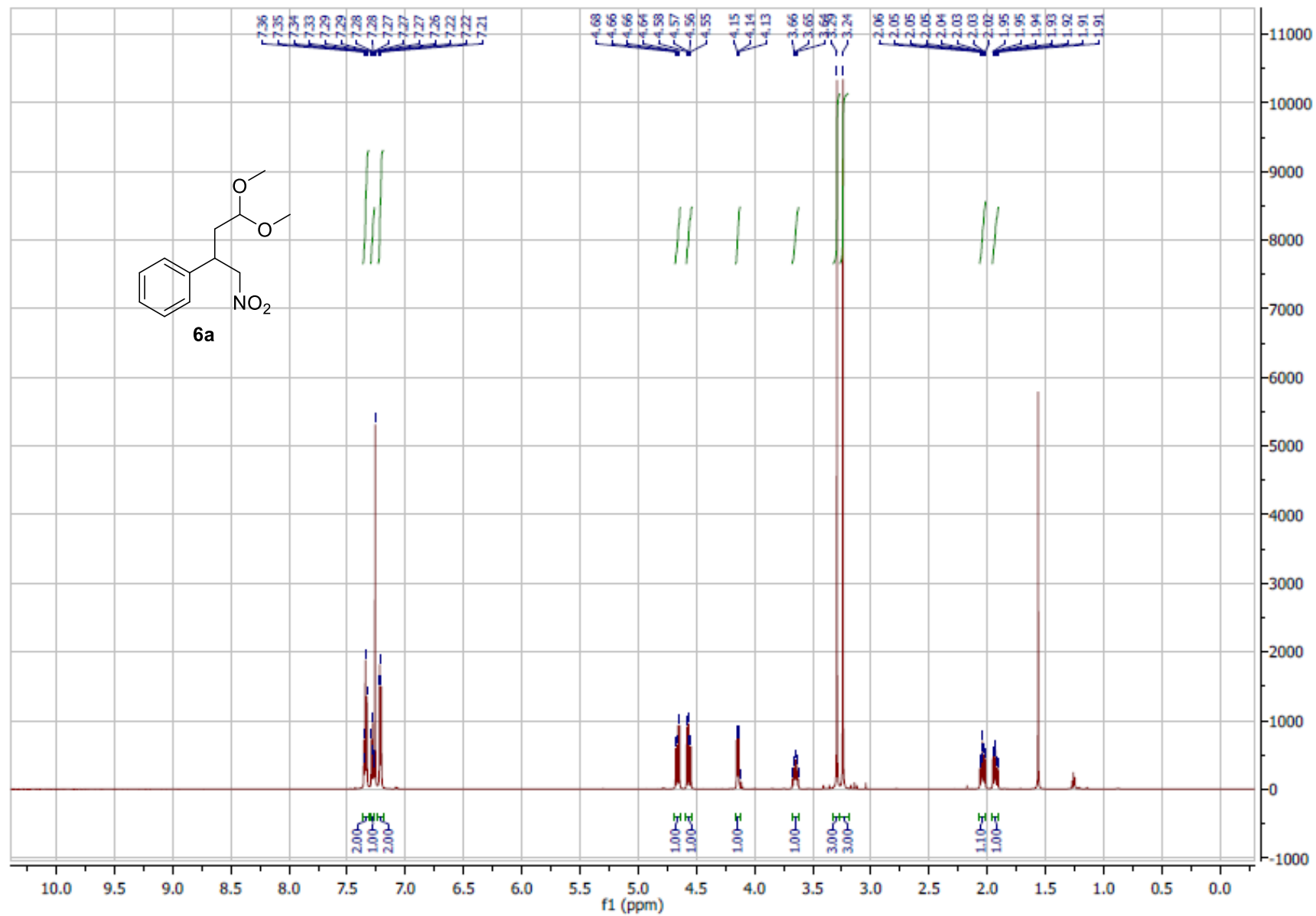
Ethyl 4-nitro-3-(thiophen-2-yl)butanoate (8k) ¹H NMR



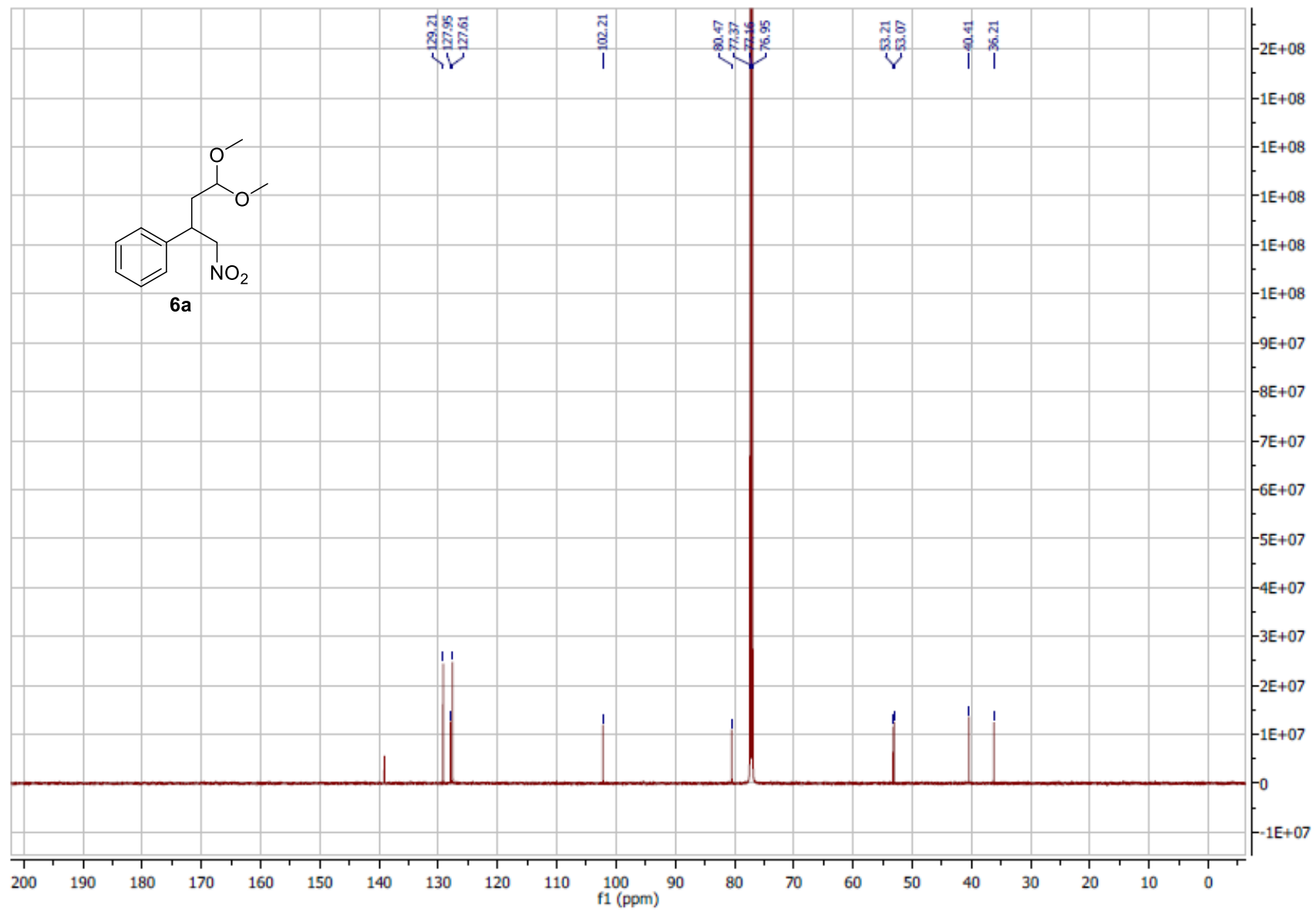
4-nitro-3-phenylbutanal ¹H NMR



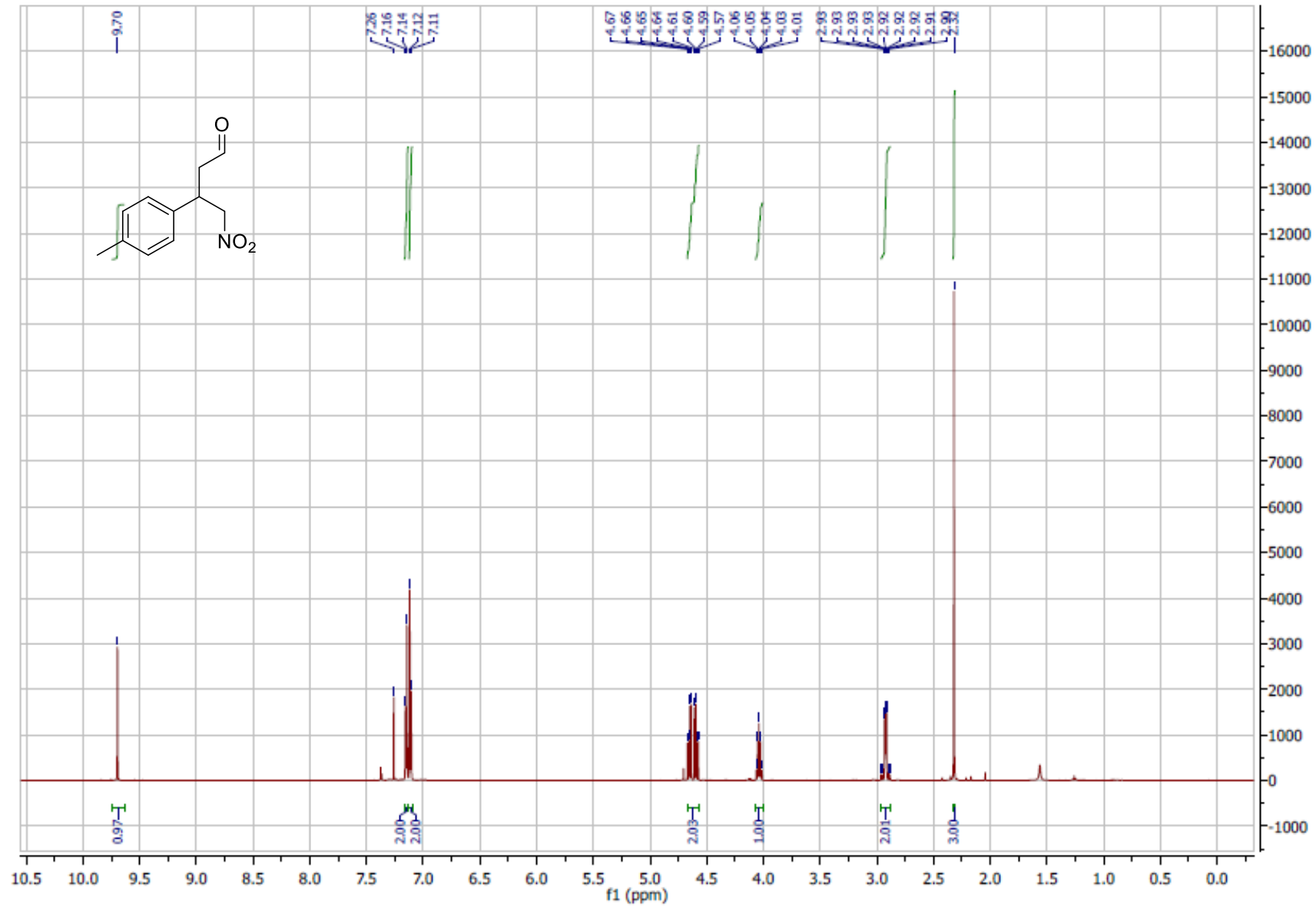
(4,4-dimethoxy-1-nitrobutan-2-yl)benzene (6a) ¹H NMR



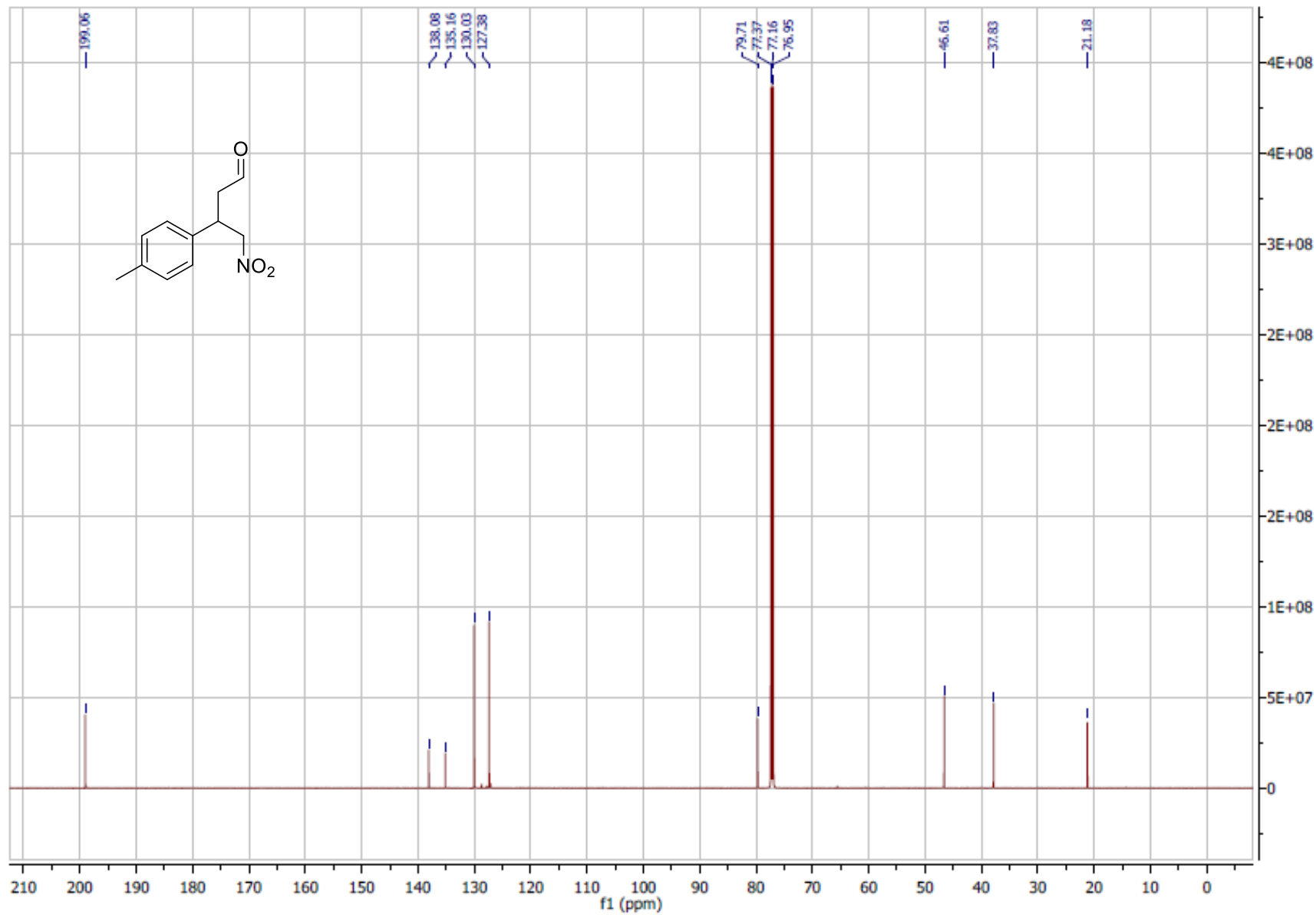
(4,4-dimethoxy-1-nitrobutan-2-yl)benzene (6a) ^{13}C NMR



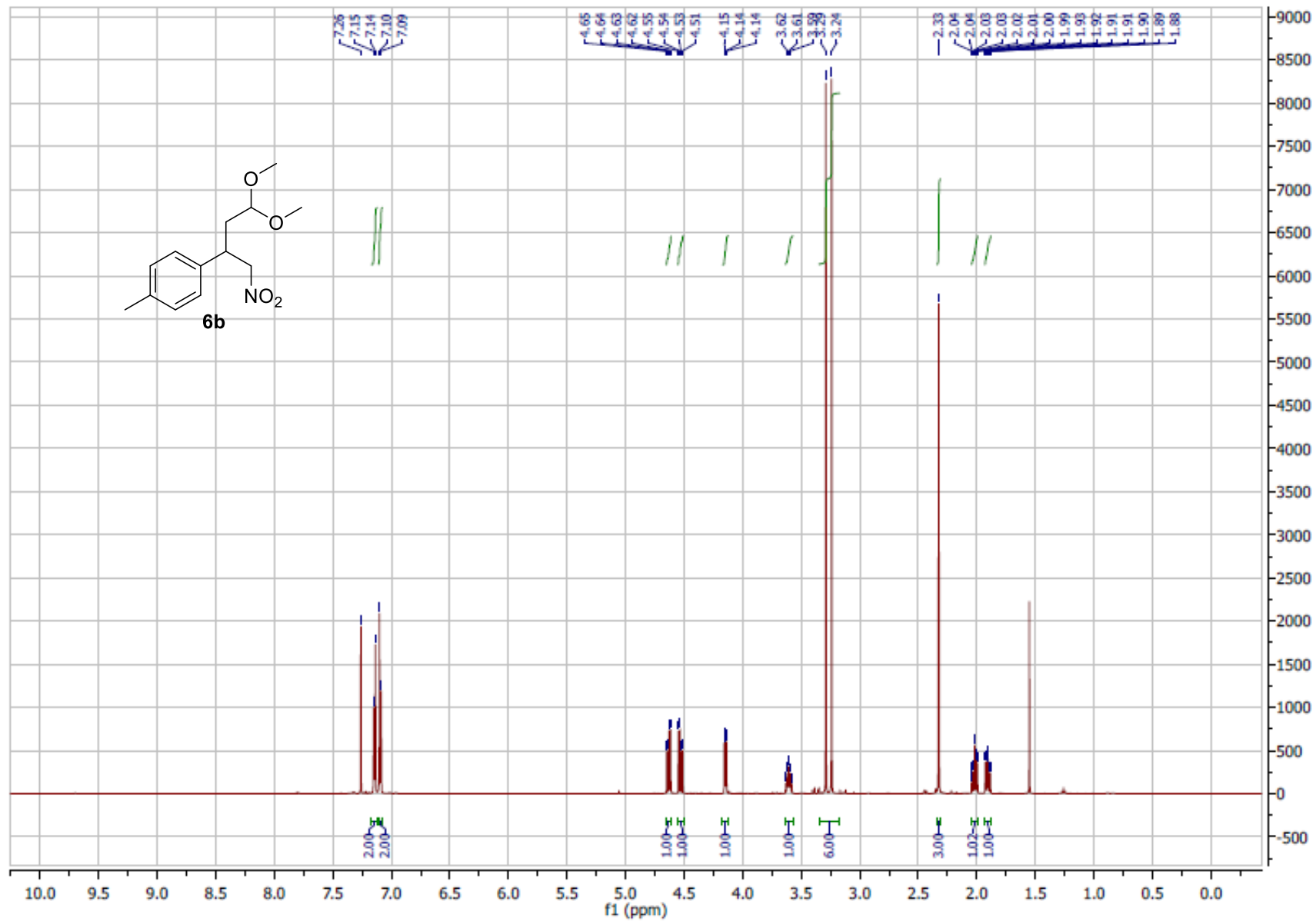
4-nitro-3-(p-tolyl)butanal ¹H NMR



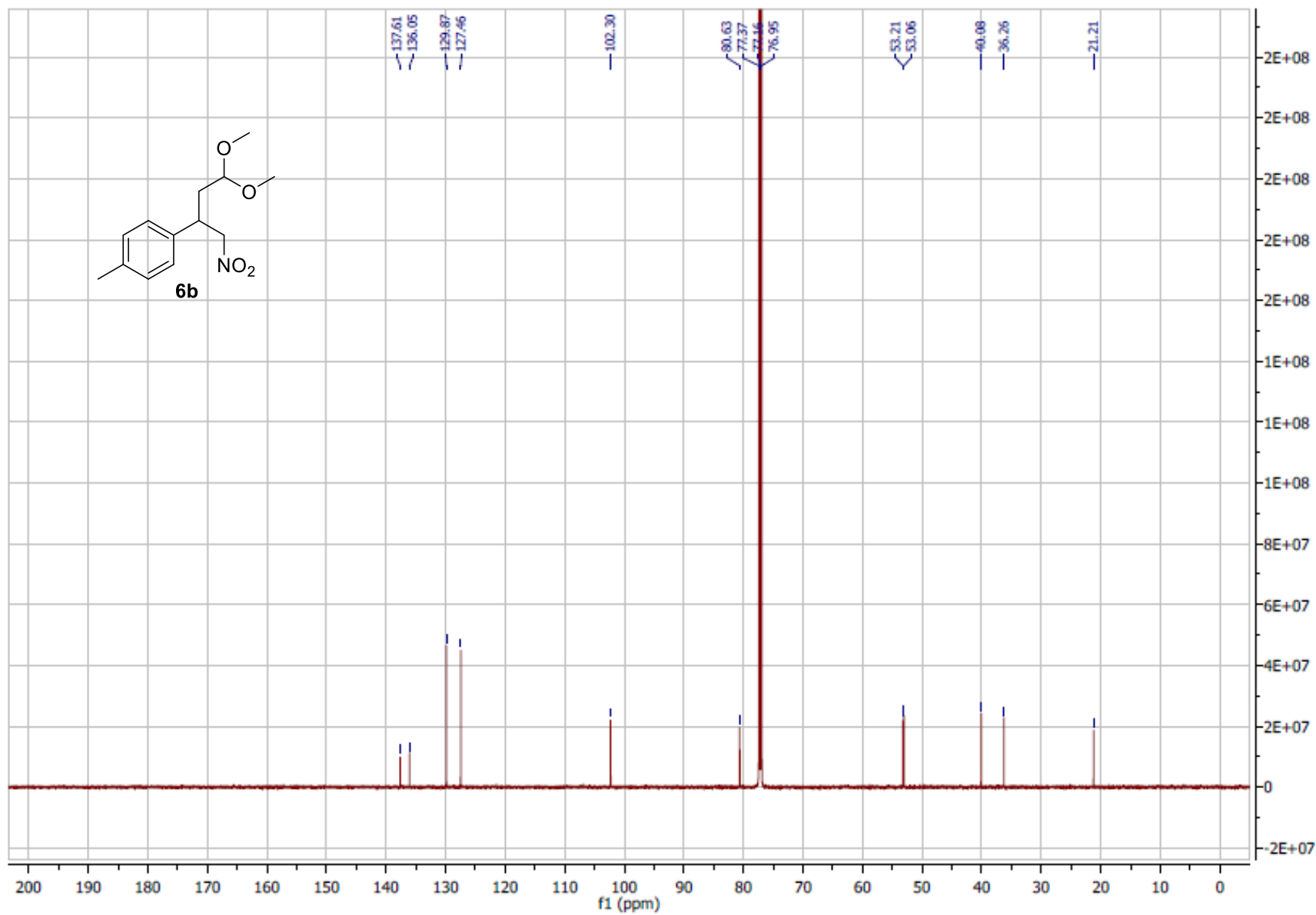
4-nitro-3-(p-tolyl)butanal ^{13}C NMR



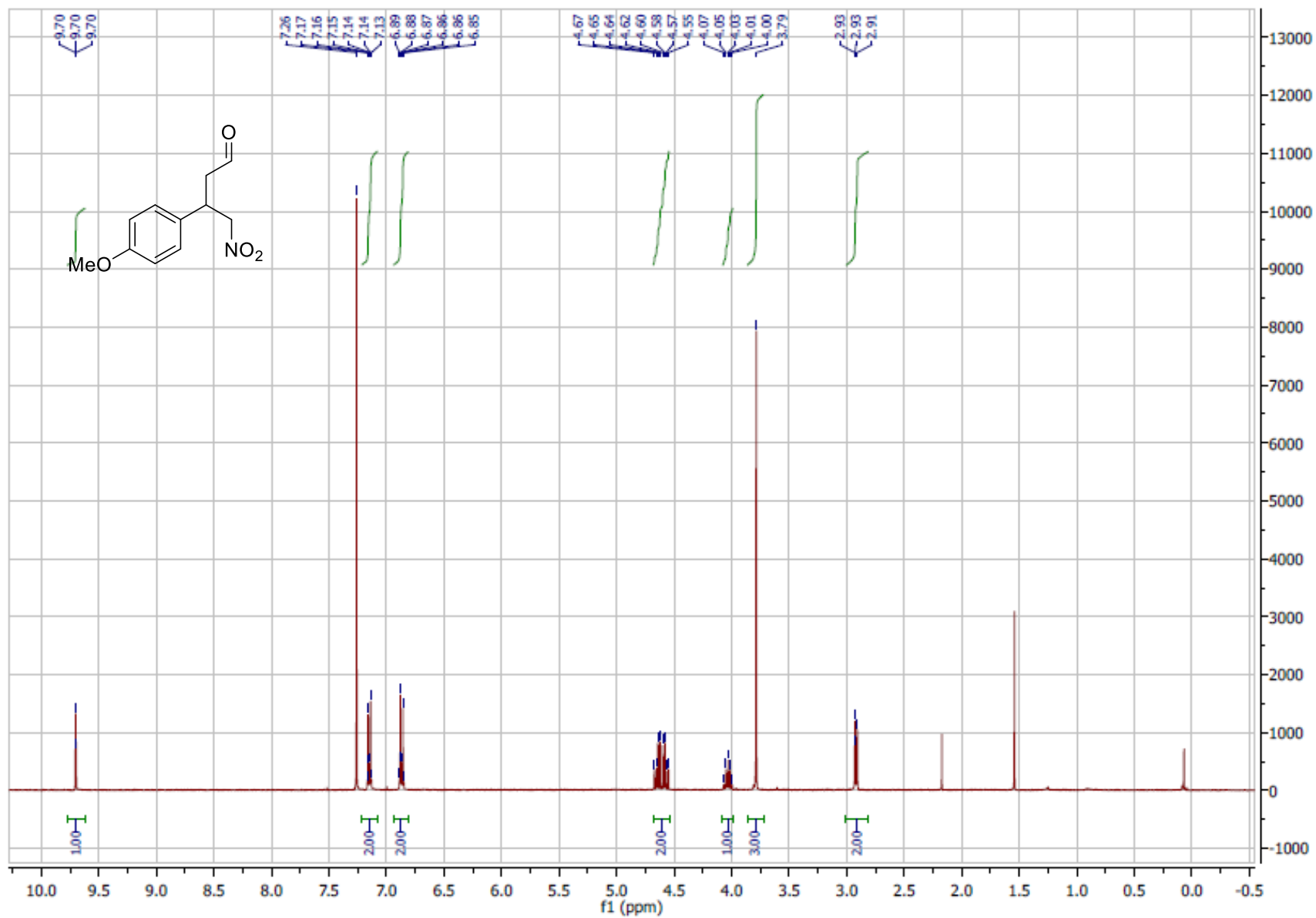
1-(4,4-dimethoxy-1-nitrobutan-2-yl)-4-methylbenzene (6b) ¹H NMR



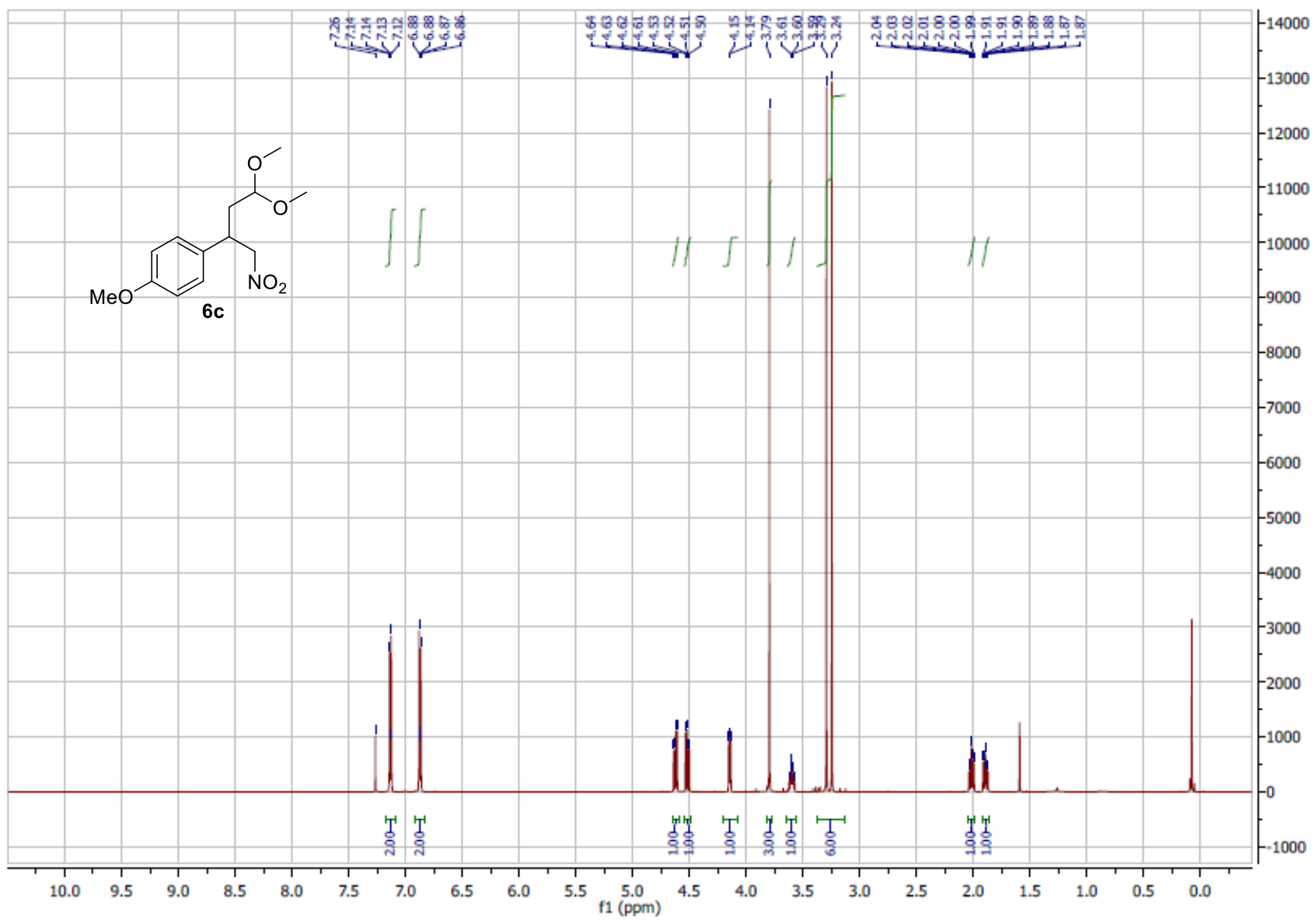
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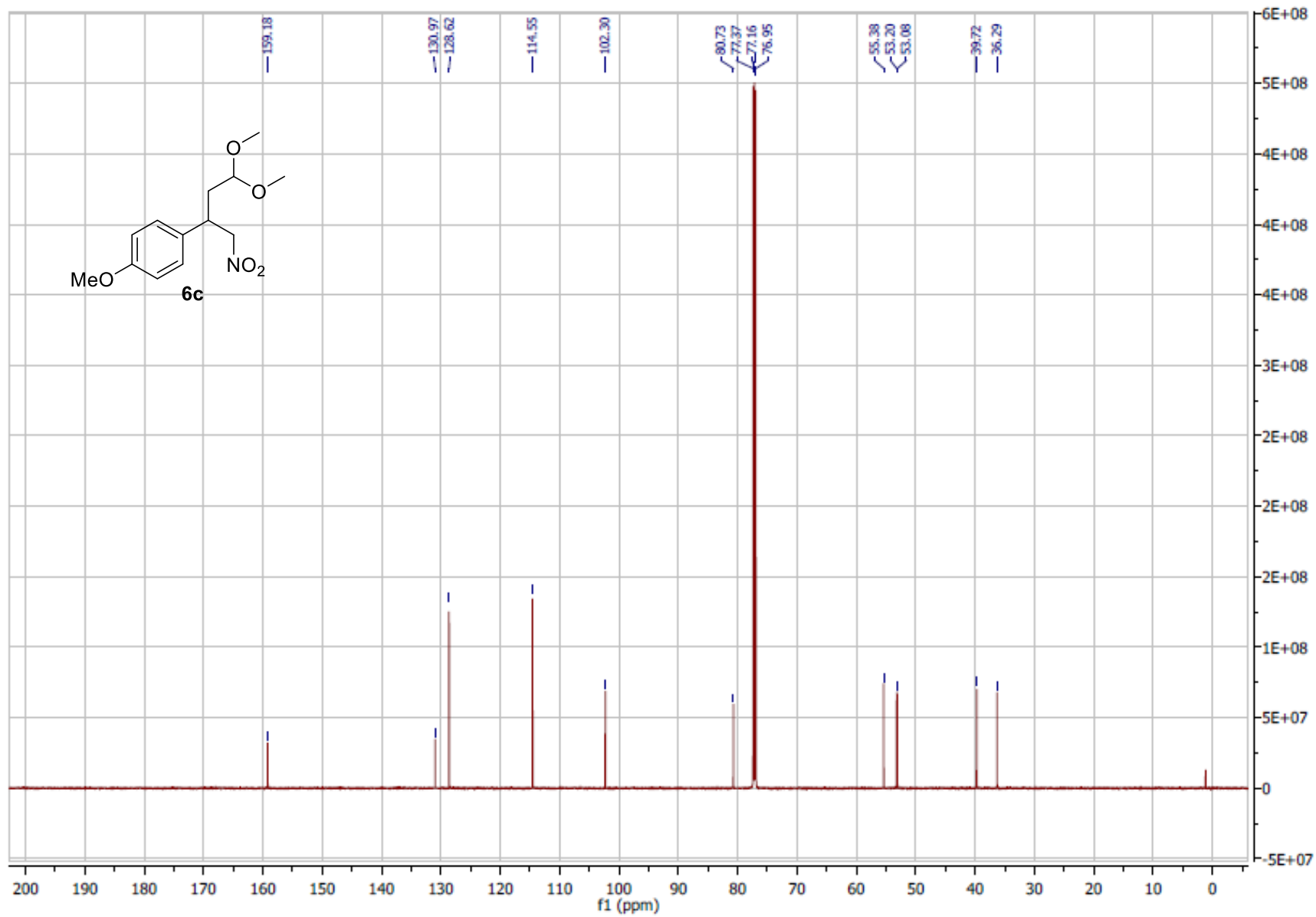
3-(4-methoxyphenyl)-4-nitrobutanal ¹H NMR



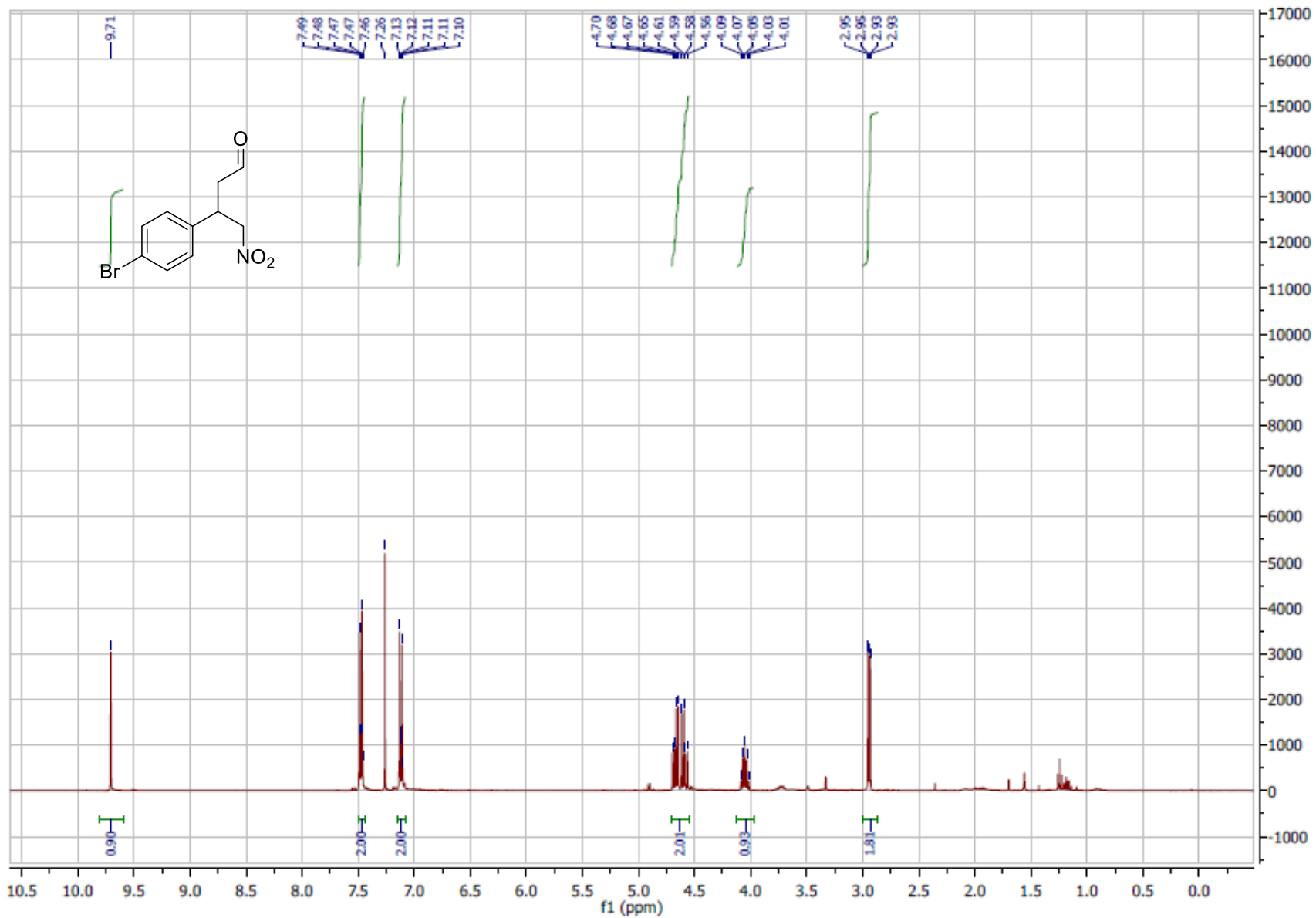
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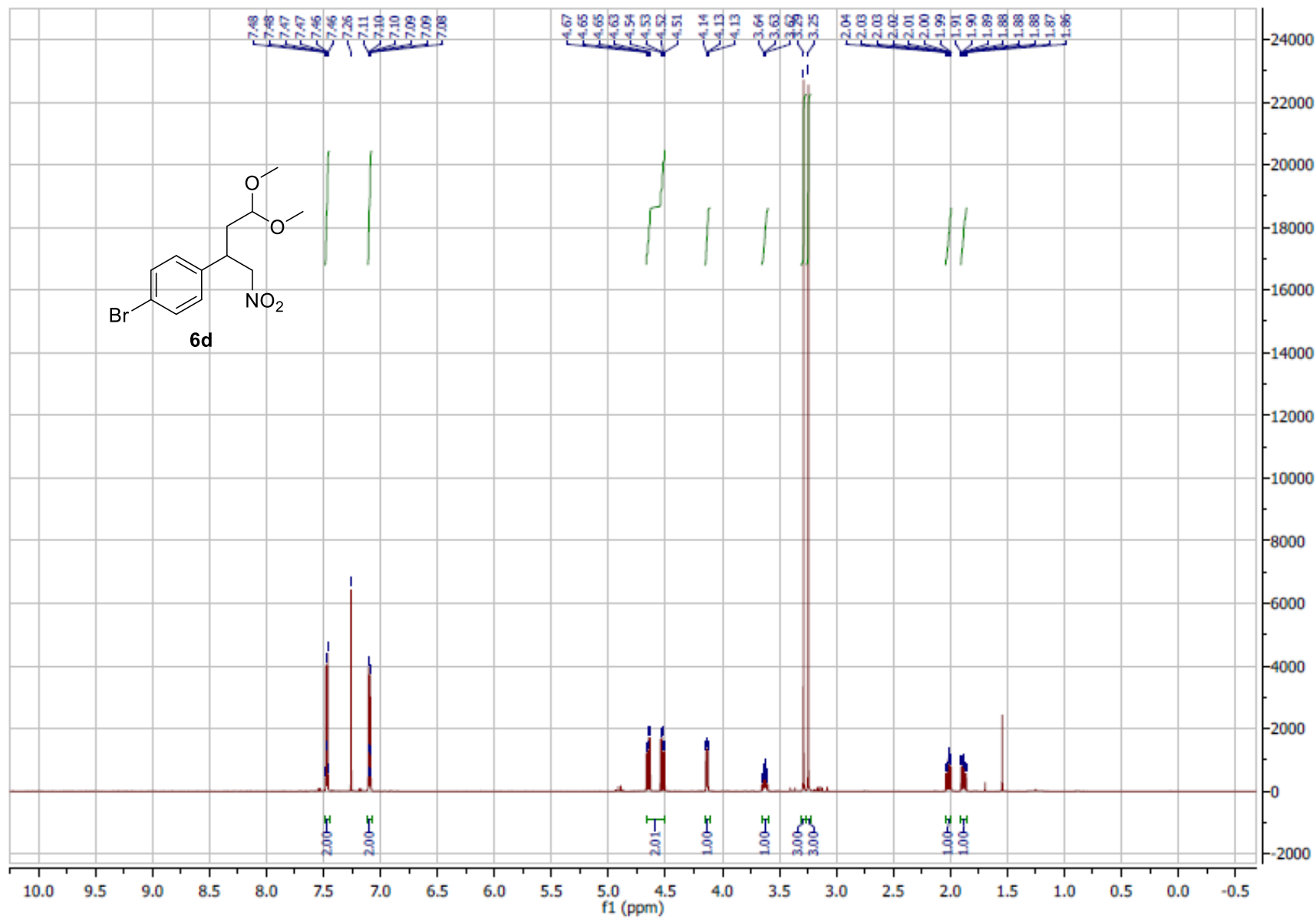
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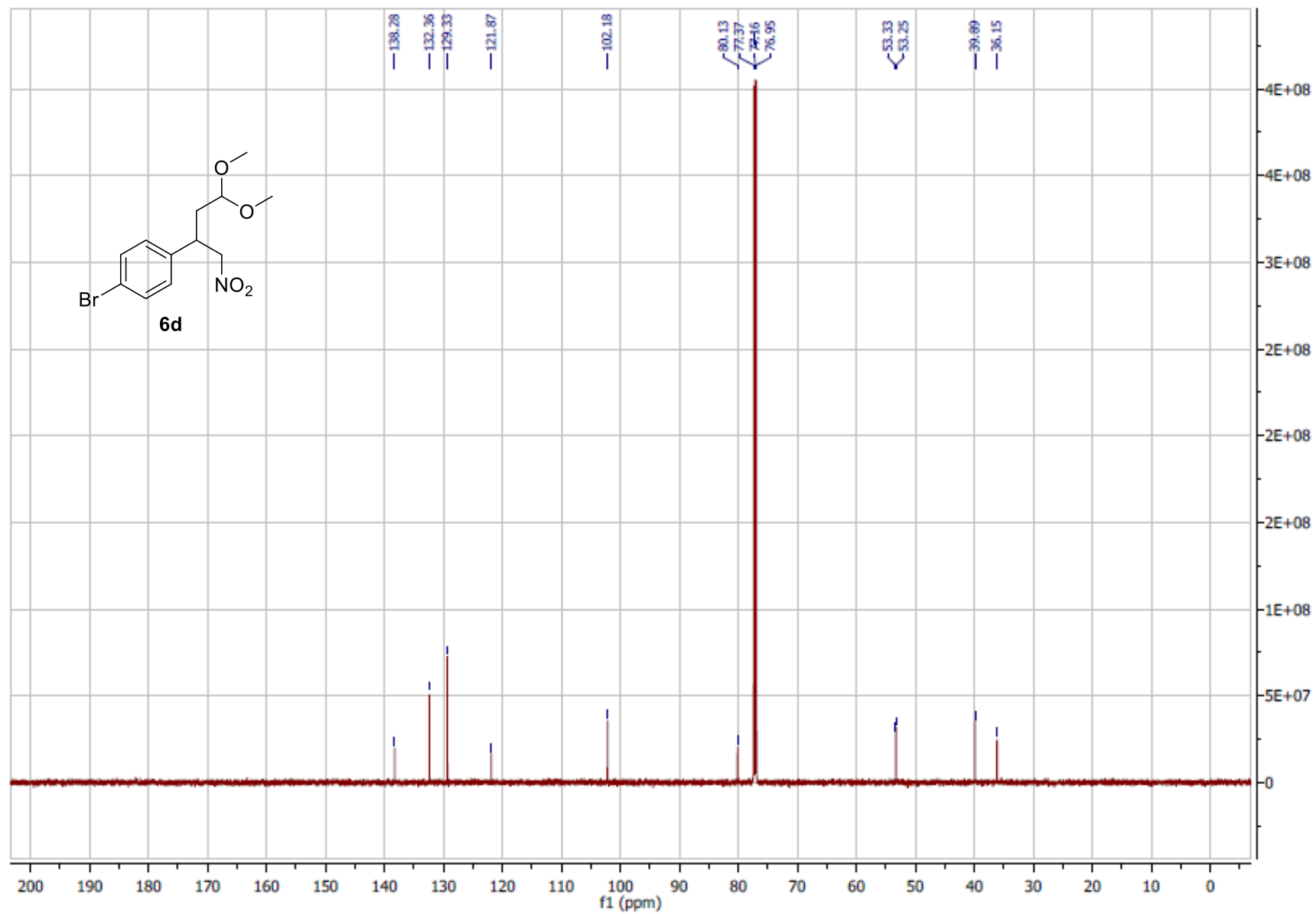
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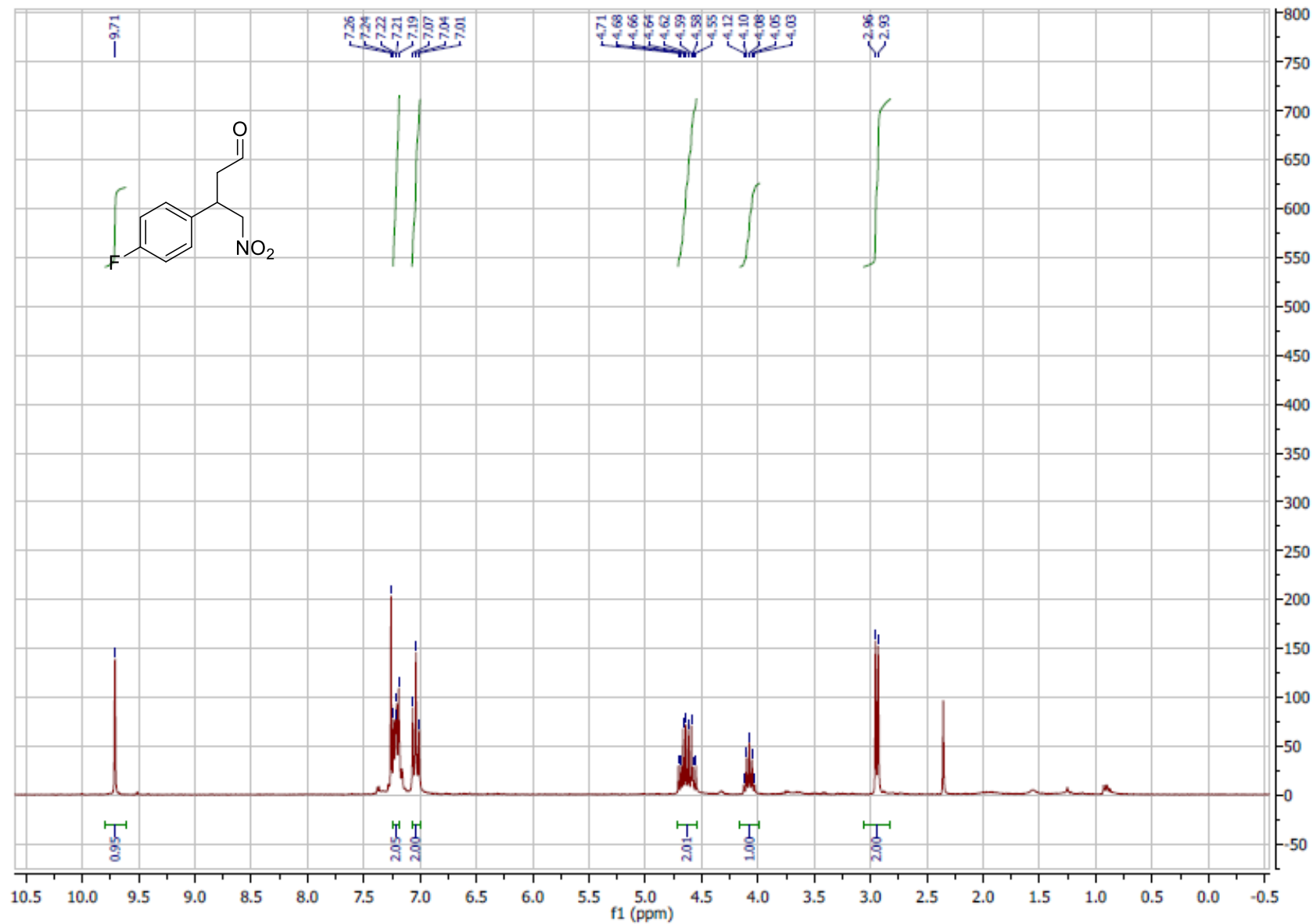
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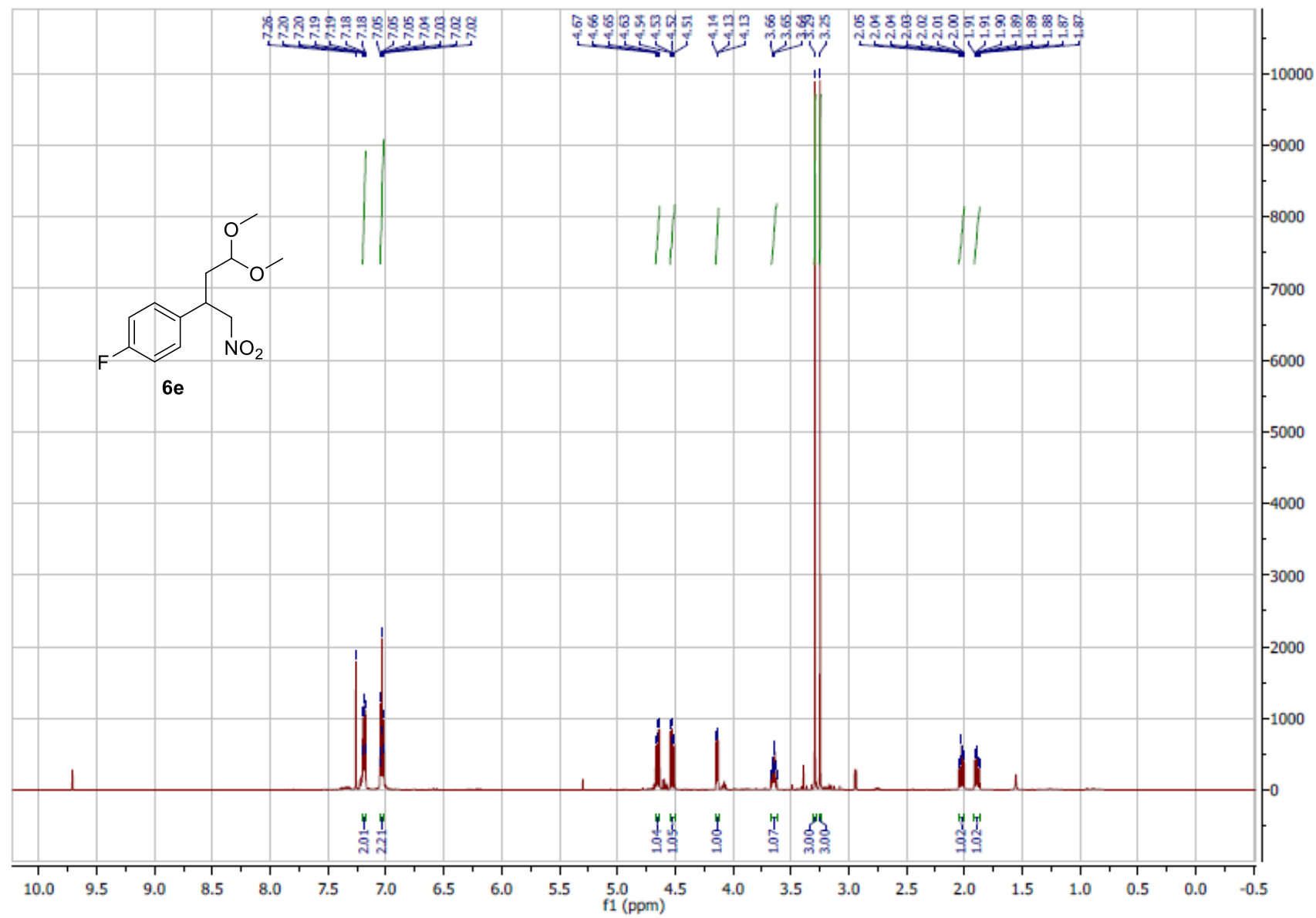
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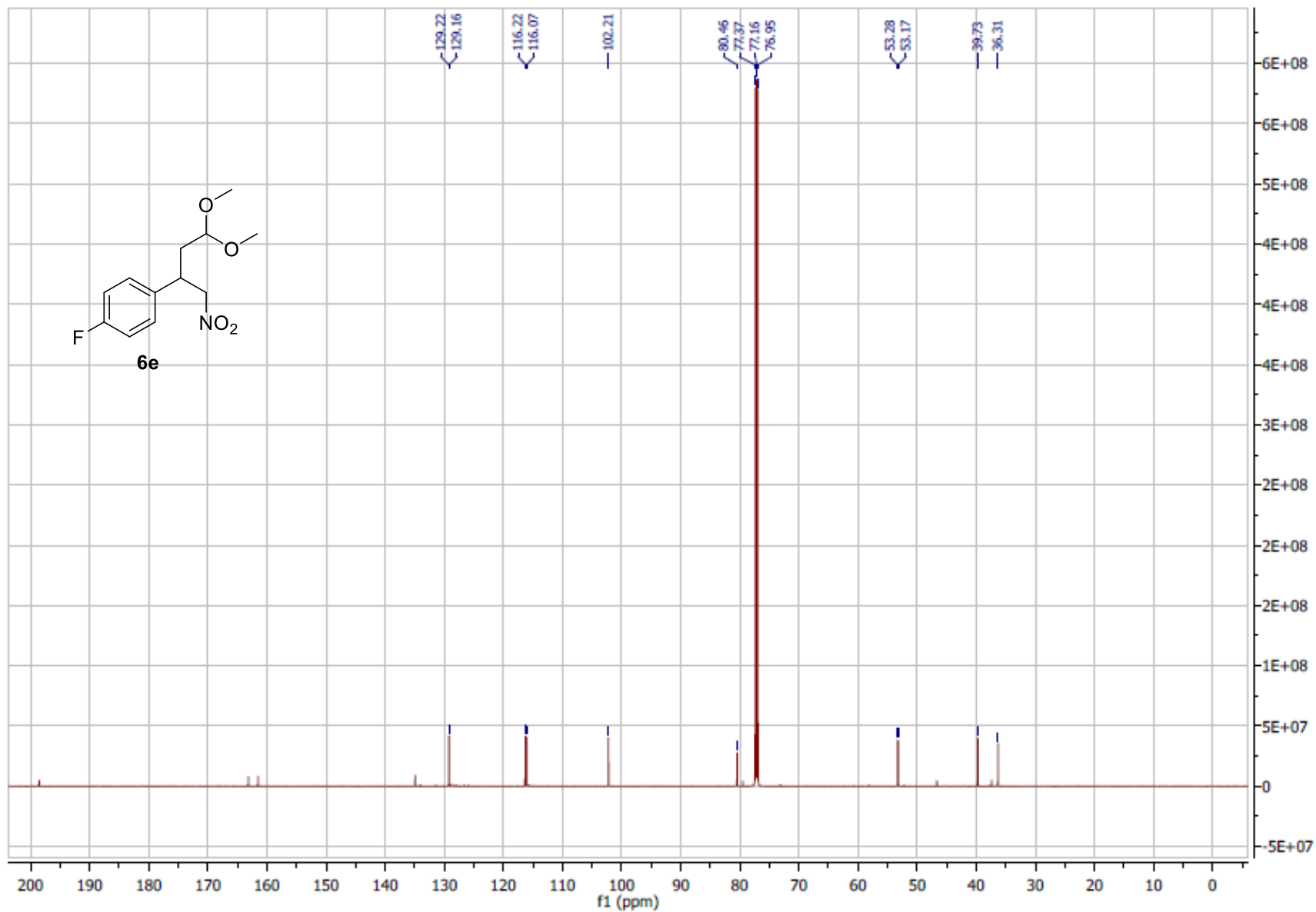
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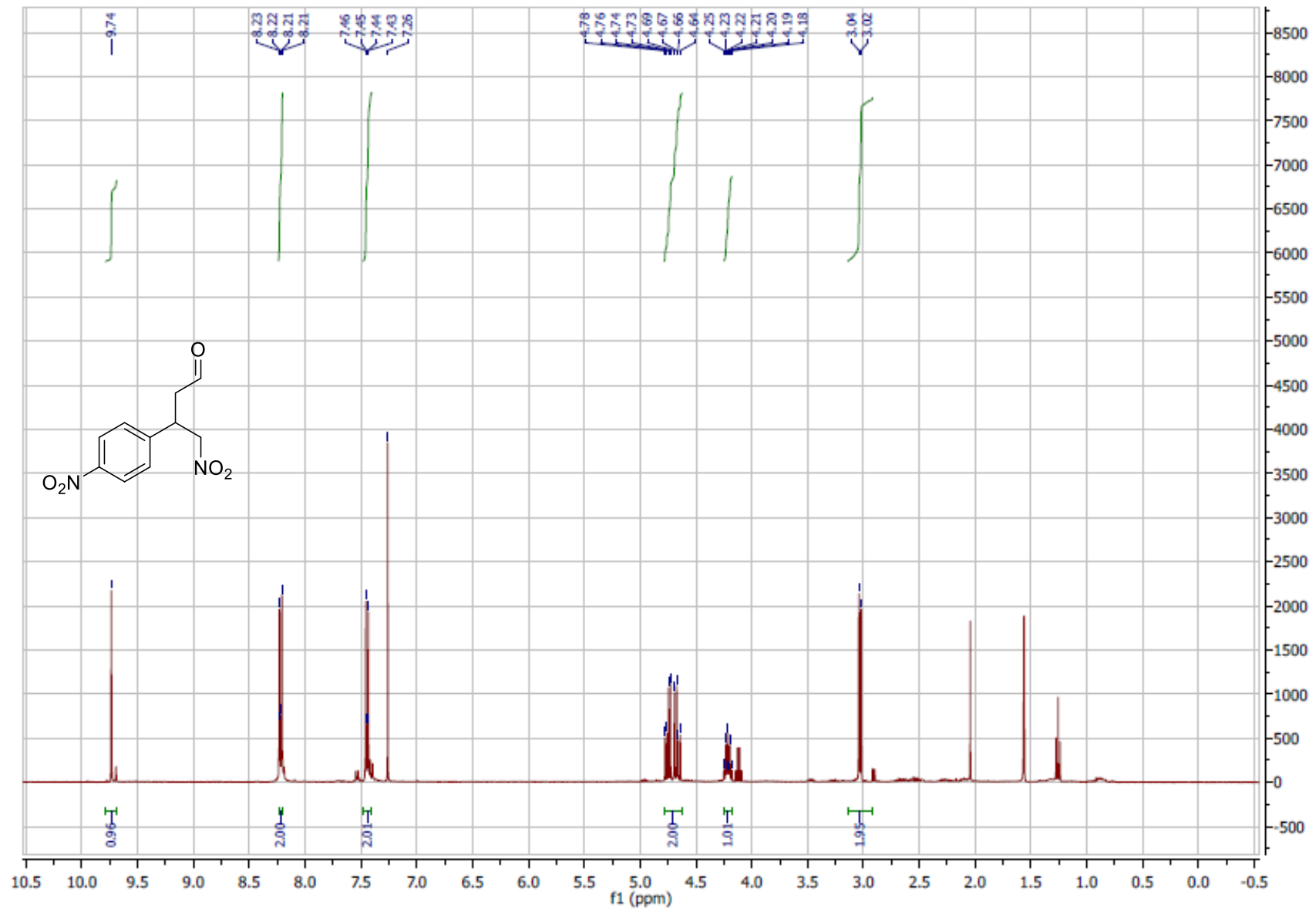
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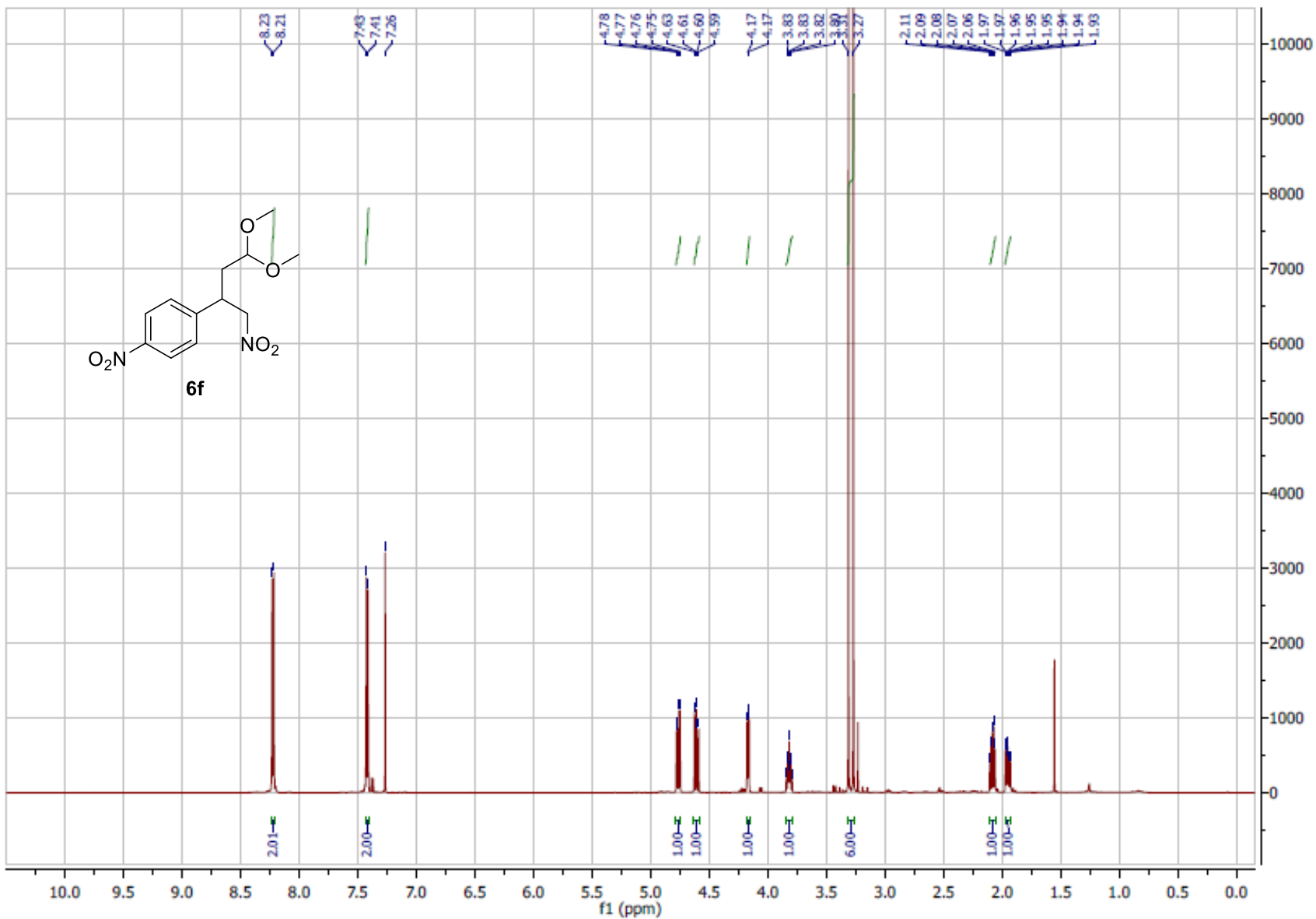
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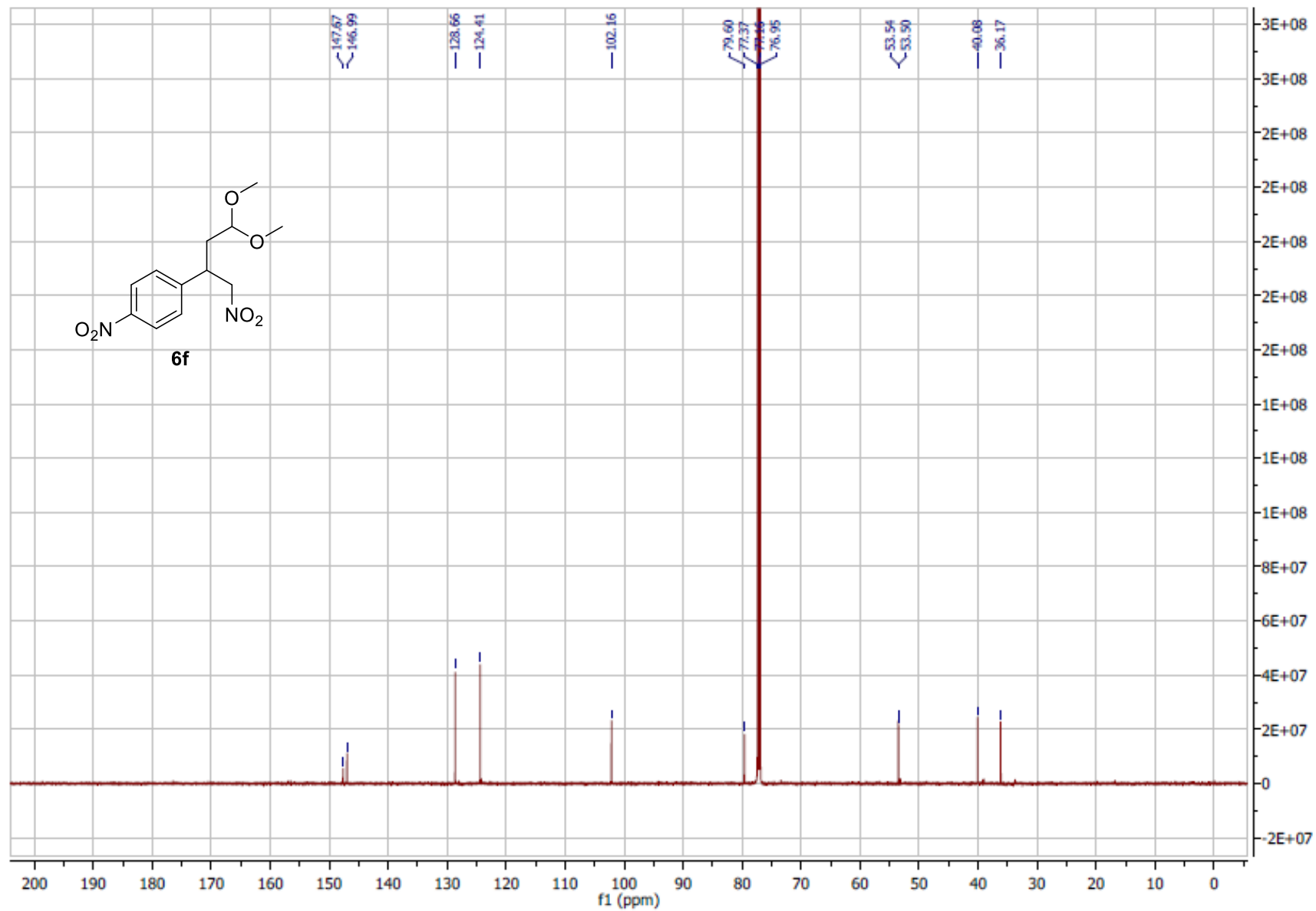
4-nitro-3-(4-nitrophenyl)butanal ¹H NMR



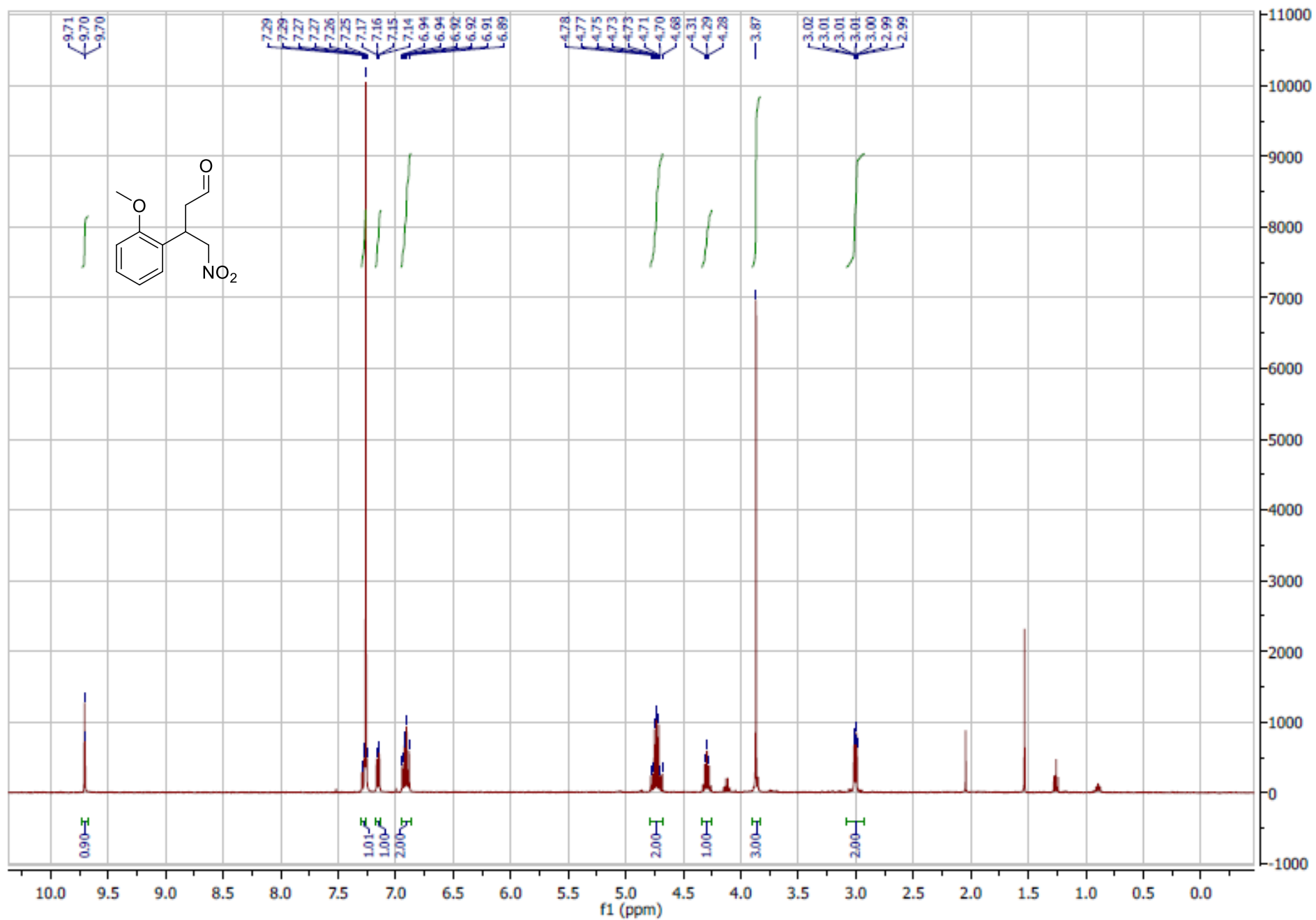
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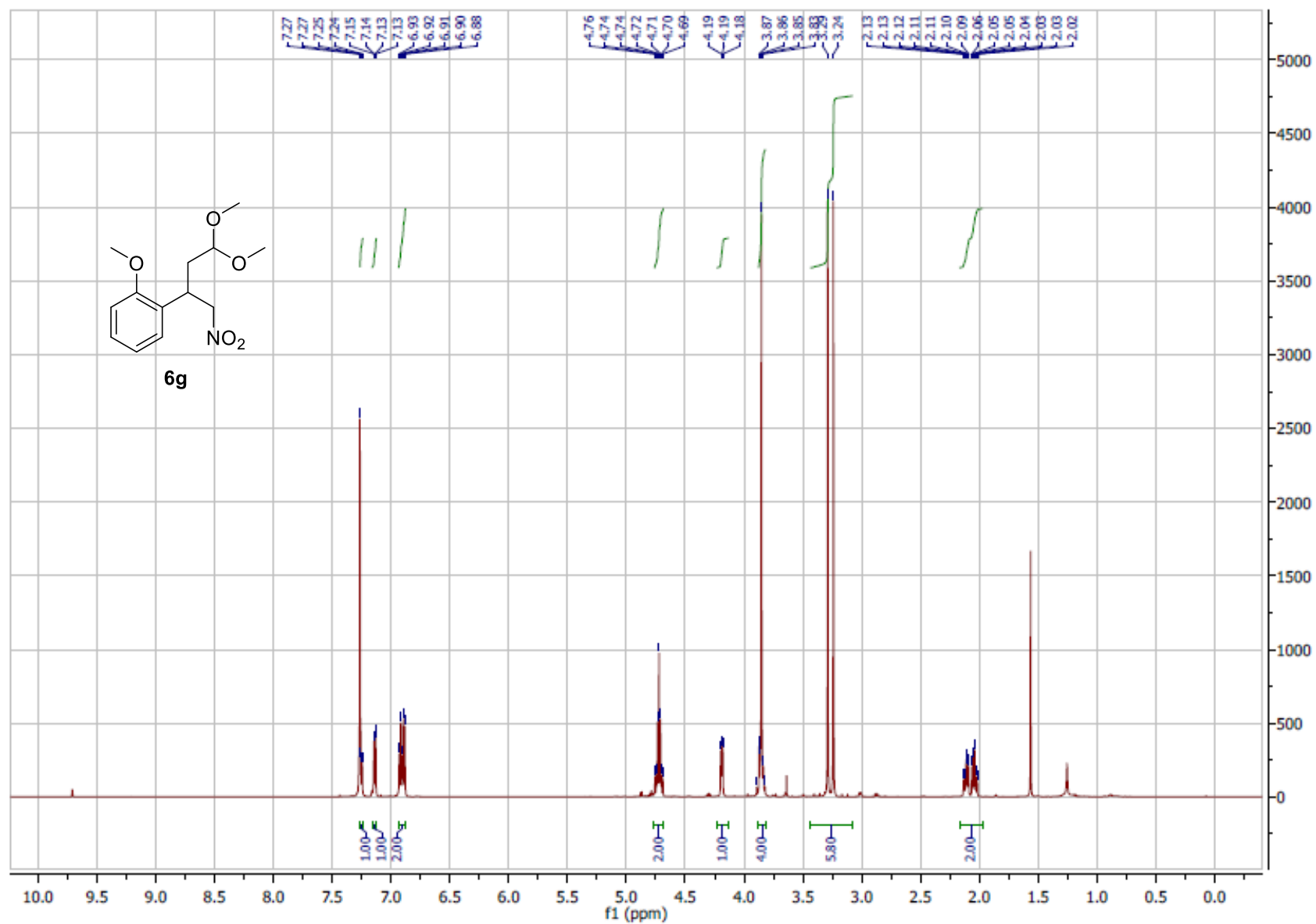
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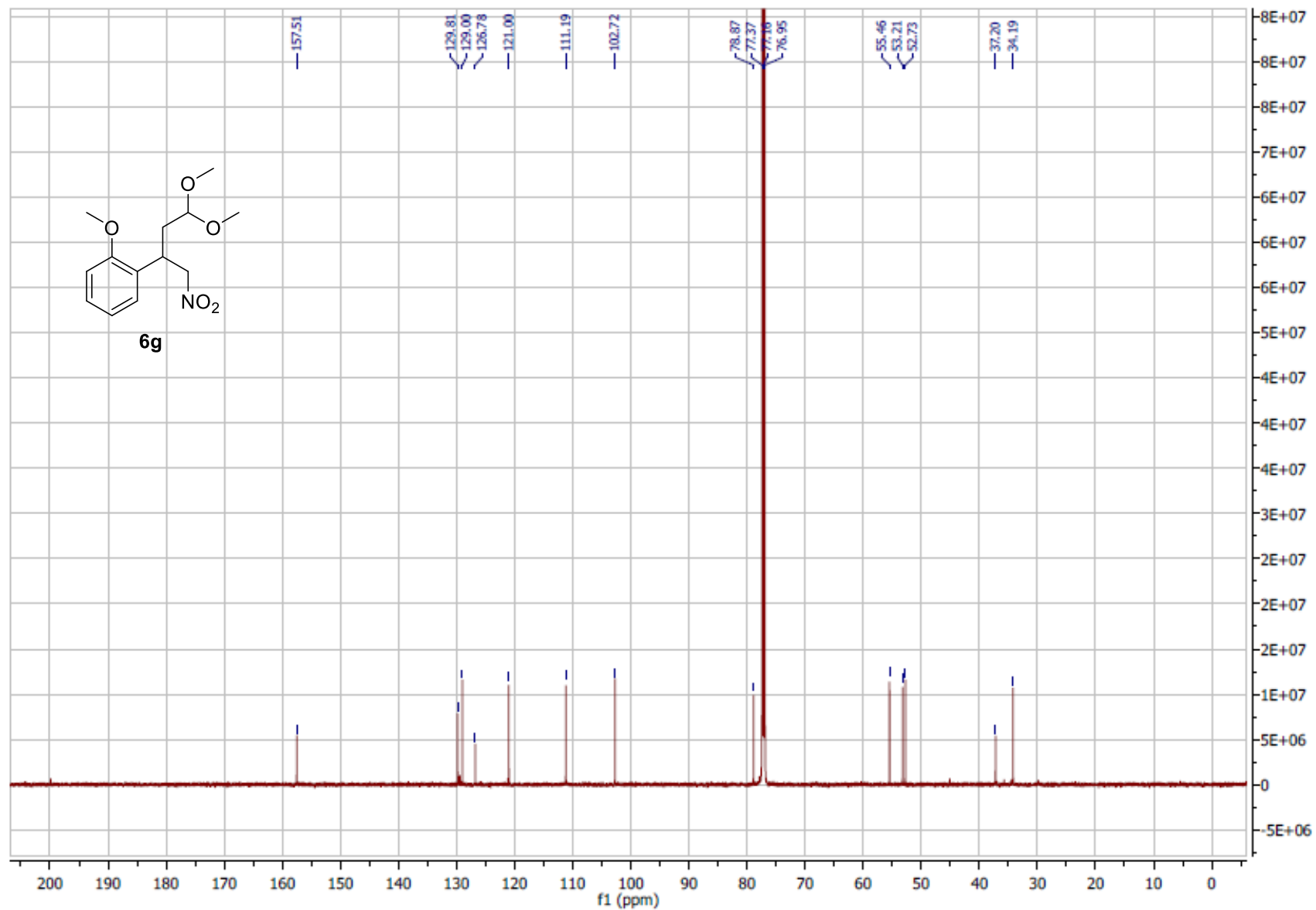
3-(2-methoxyphenyl)-4-nitrobutanal ¹H NMR



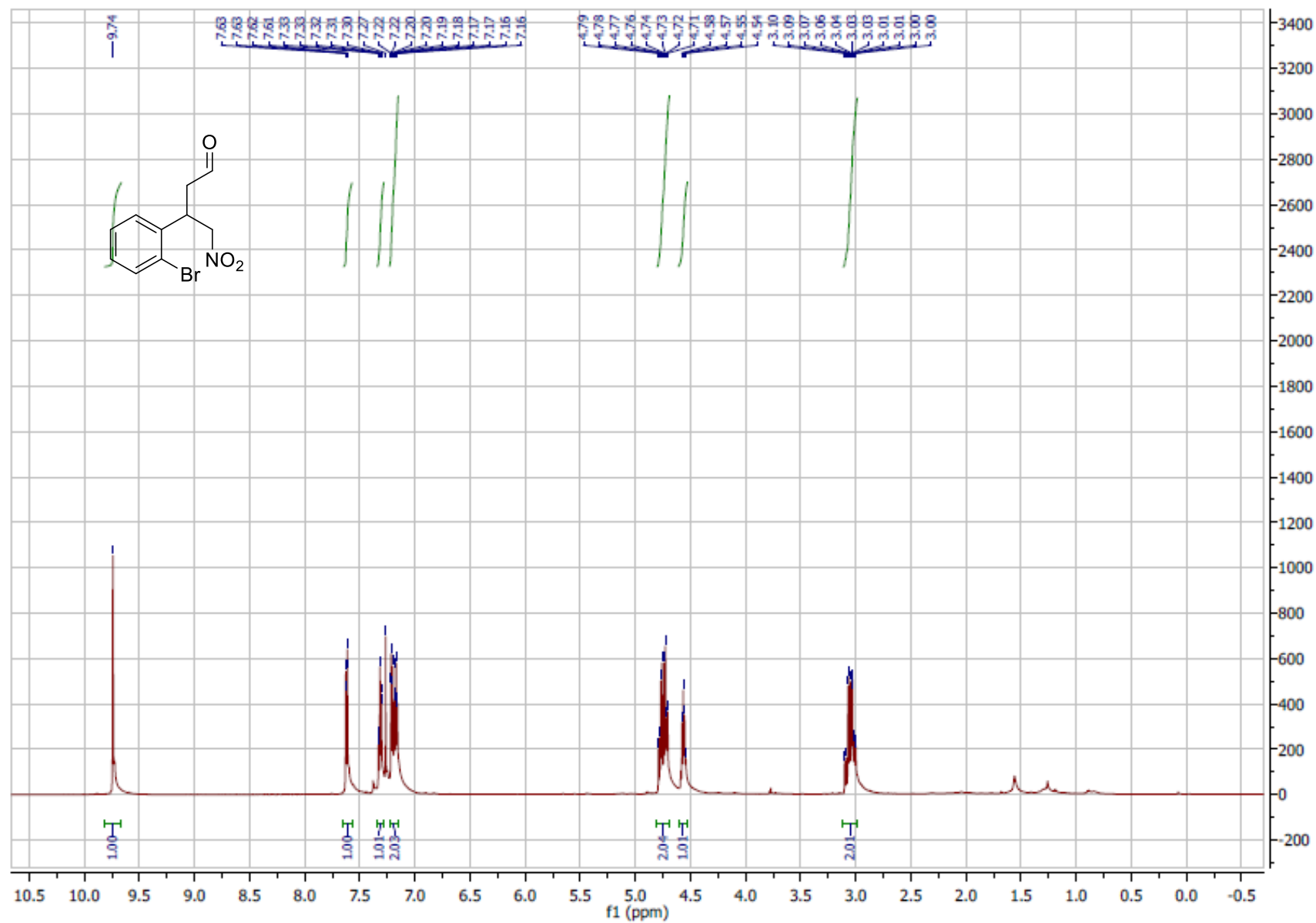
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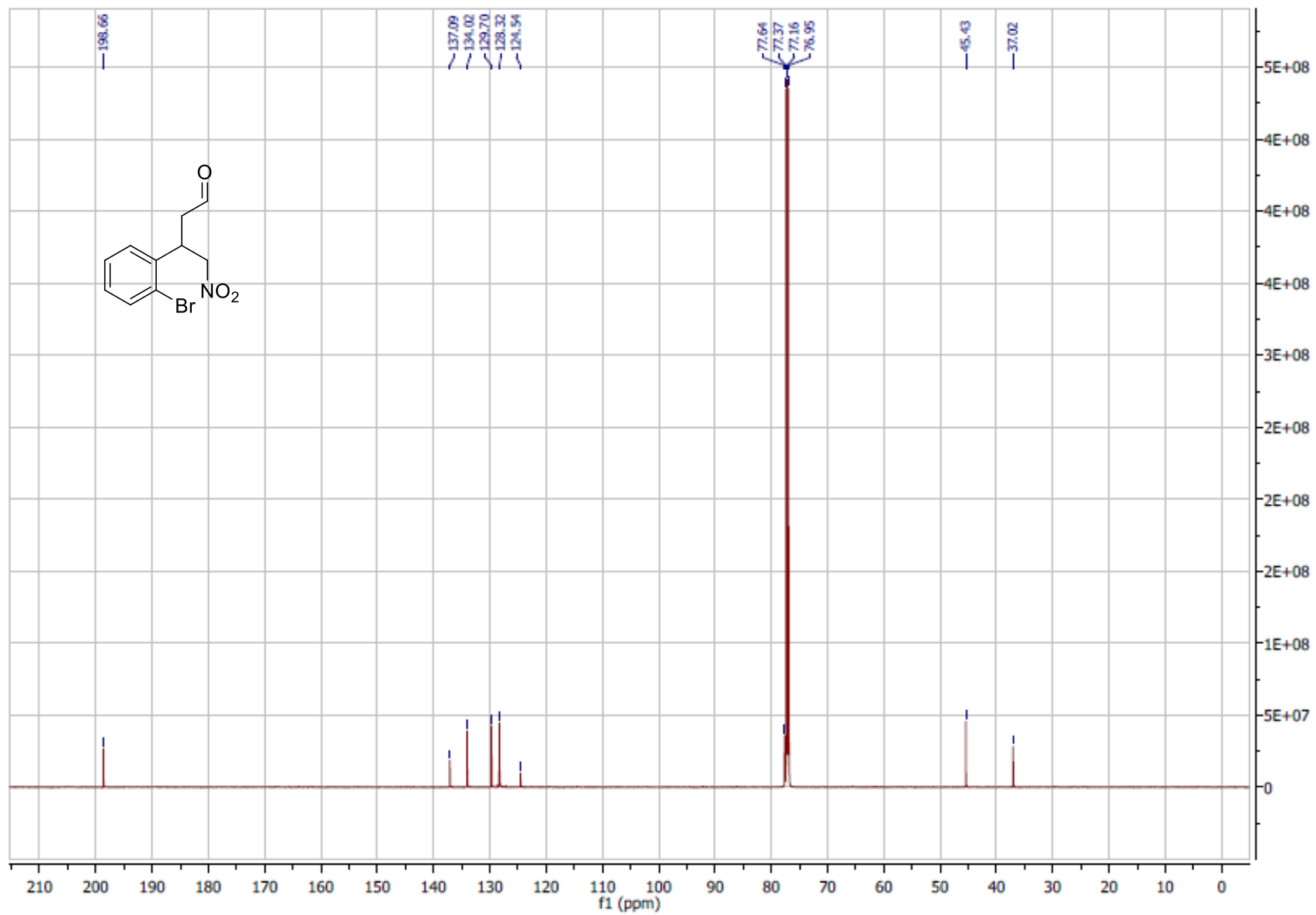
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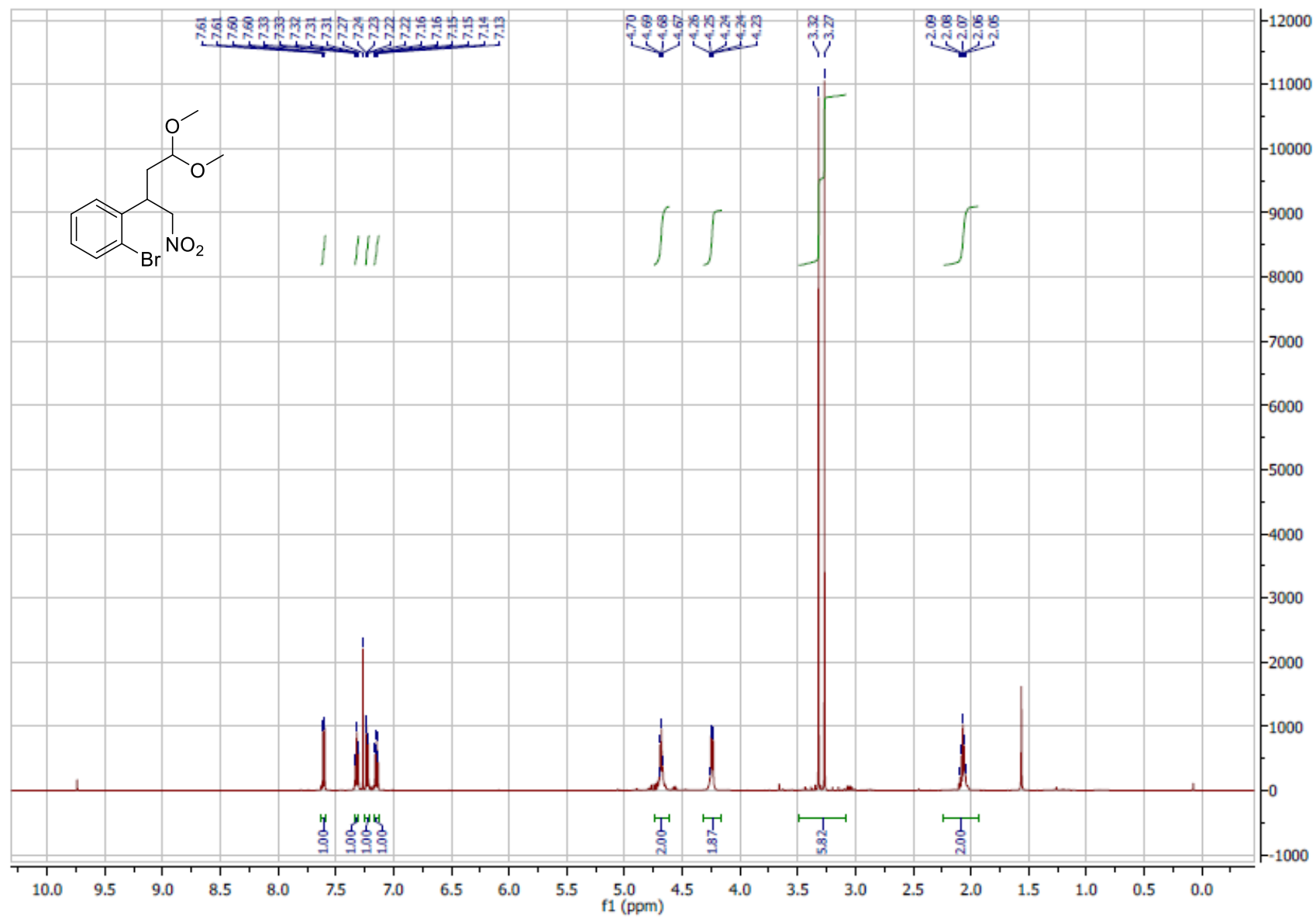
3-(2-bromophenyl)-4-nitrobutanal ¹H NMR



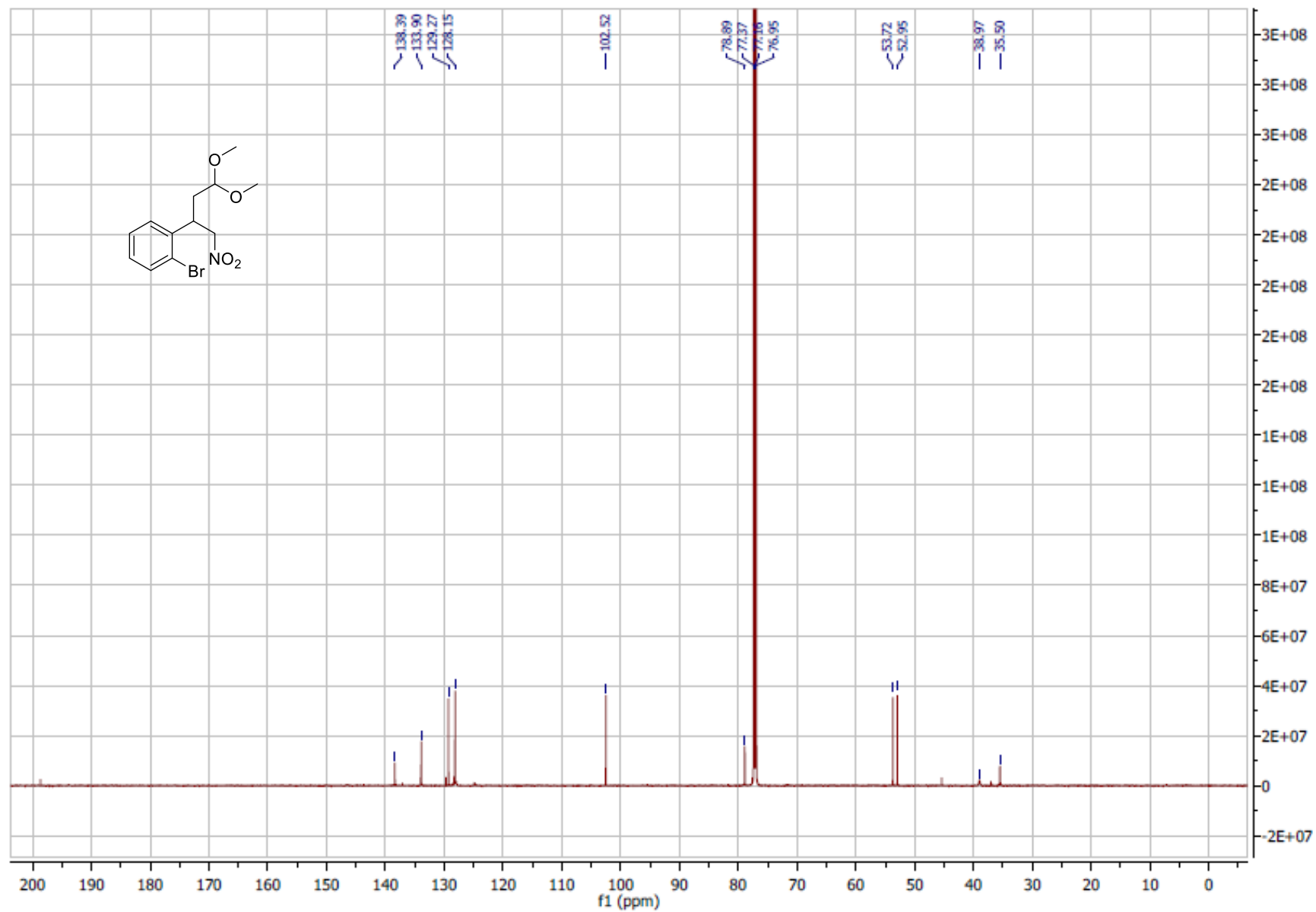
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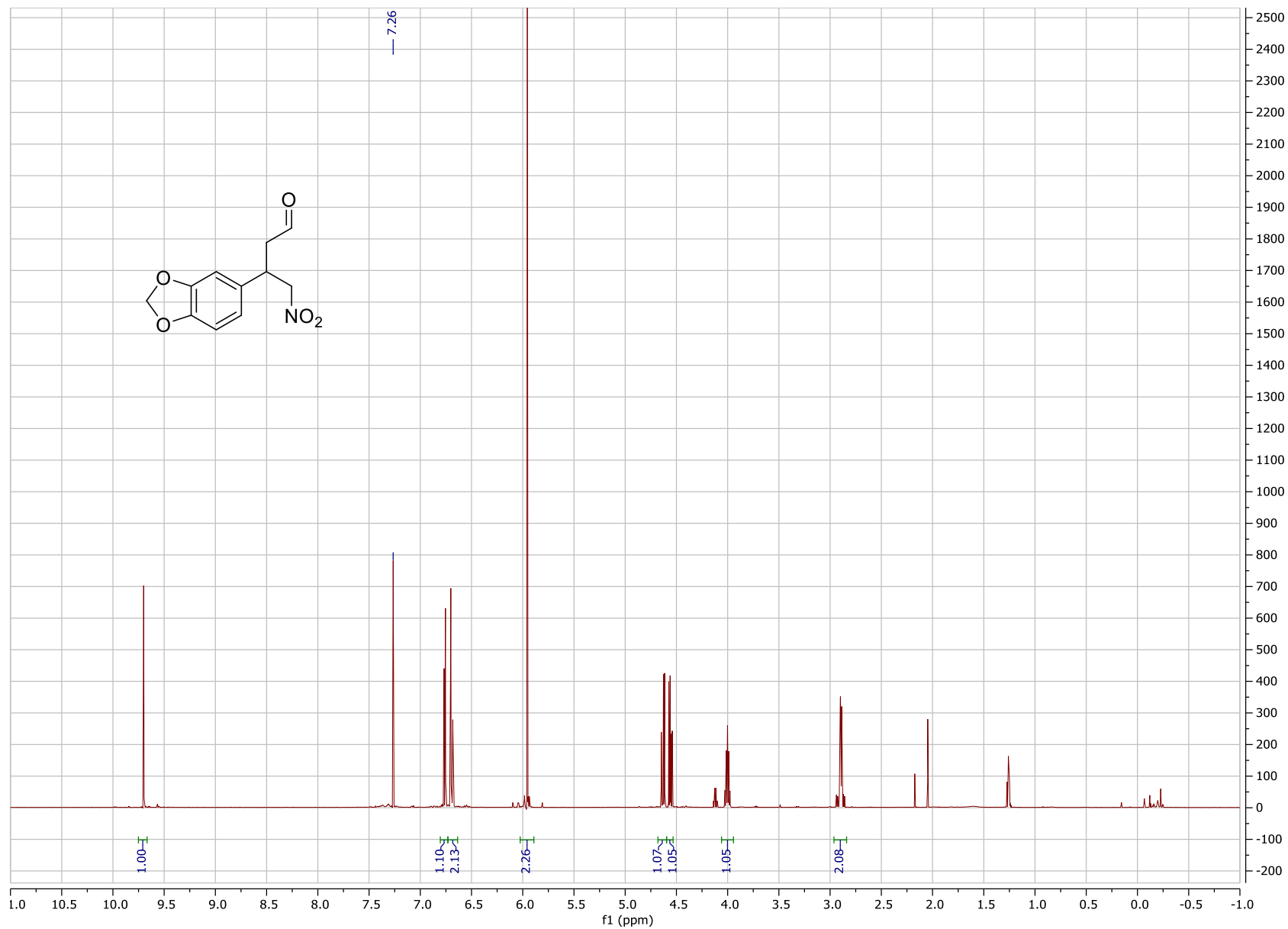
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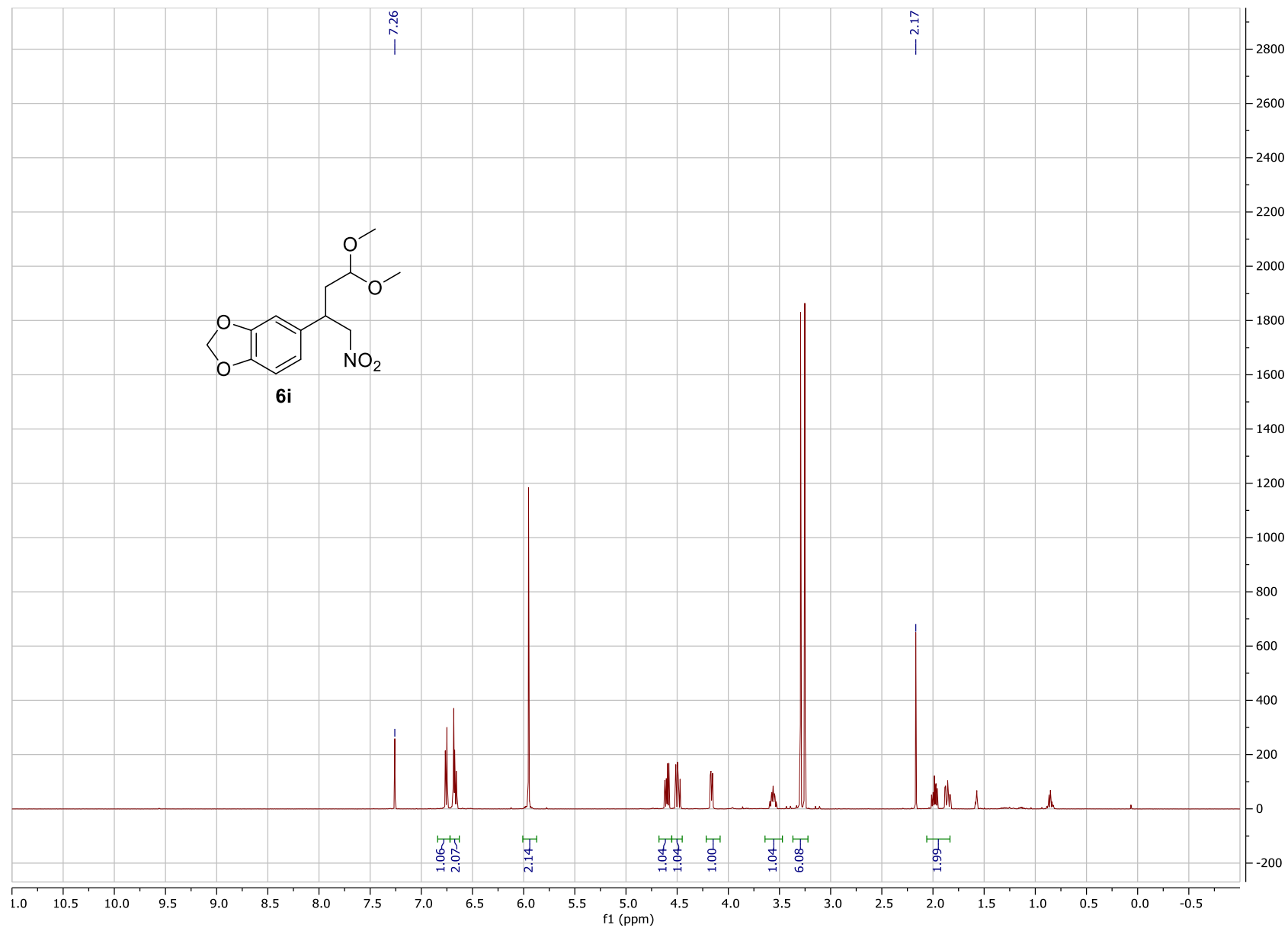
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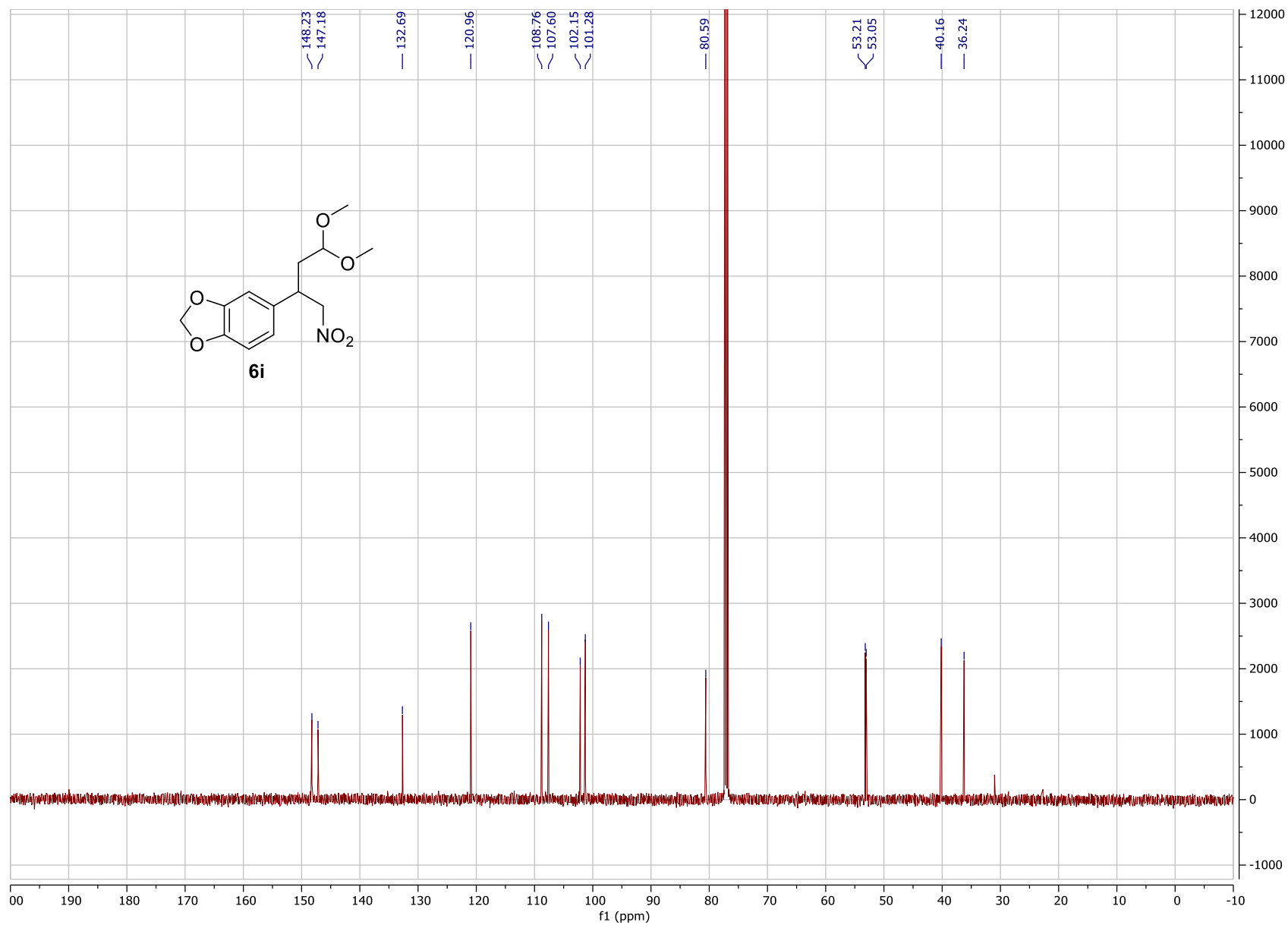
3-(benzo[1,3]dioxol-5-yl)-4-nitrobutanal ¹H NMR



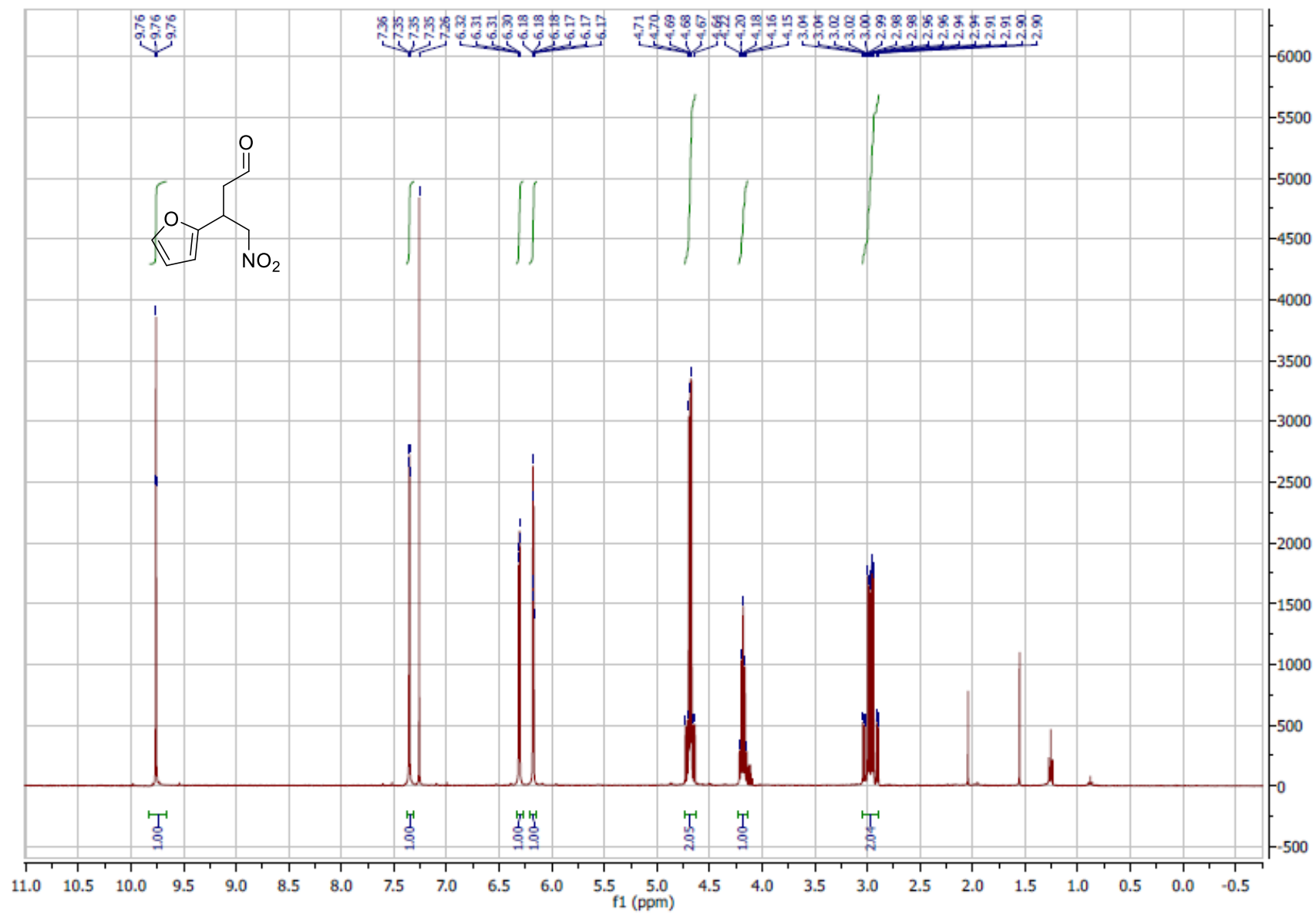
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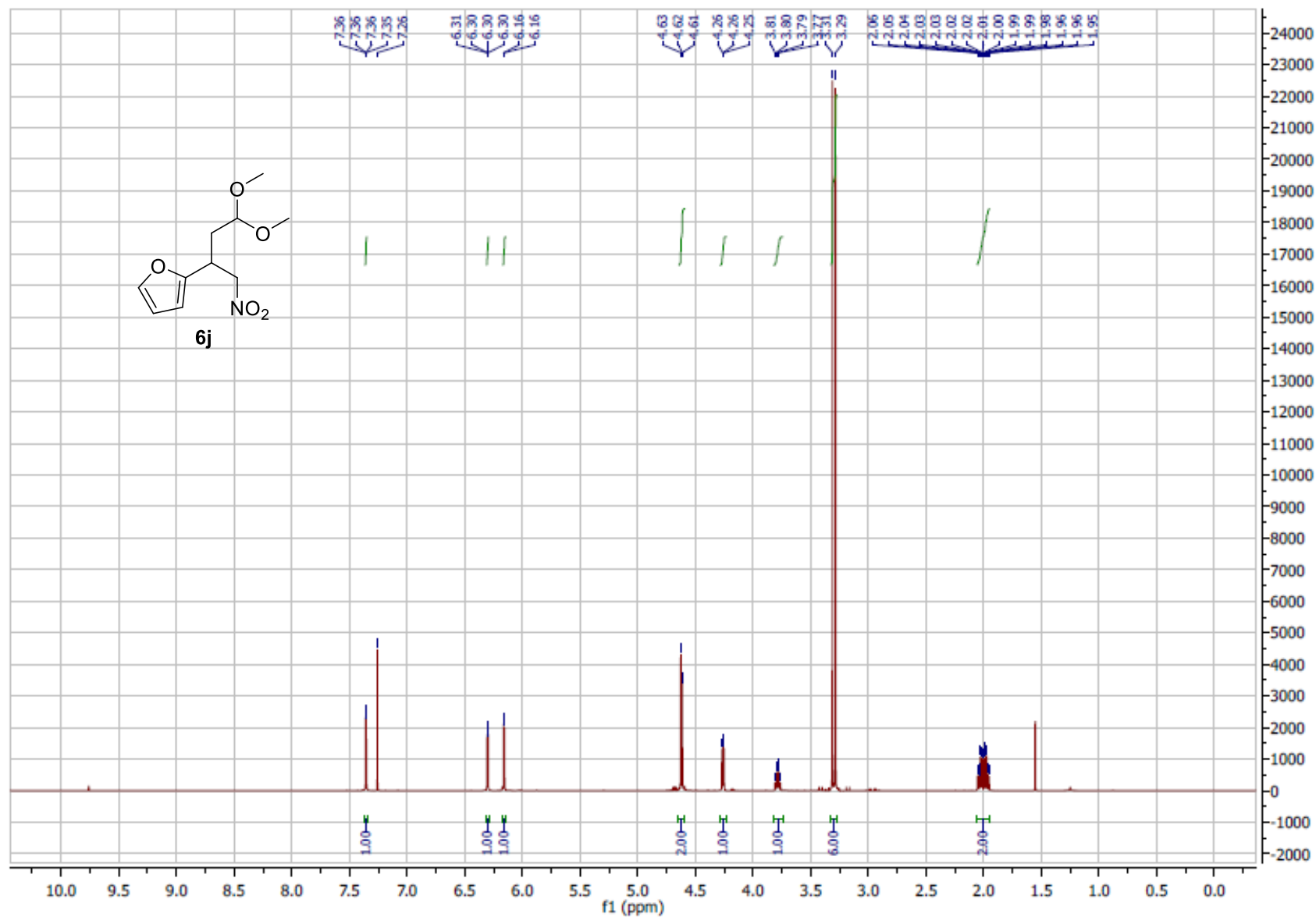
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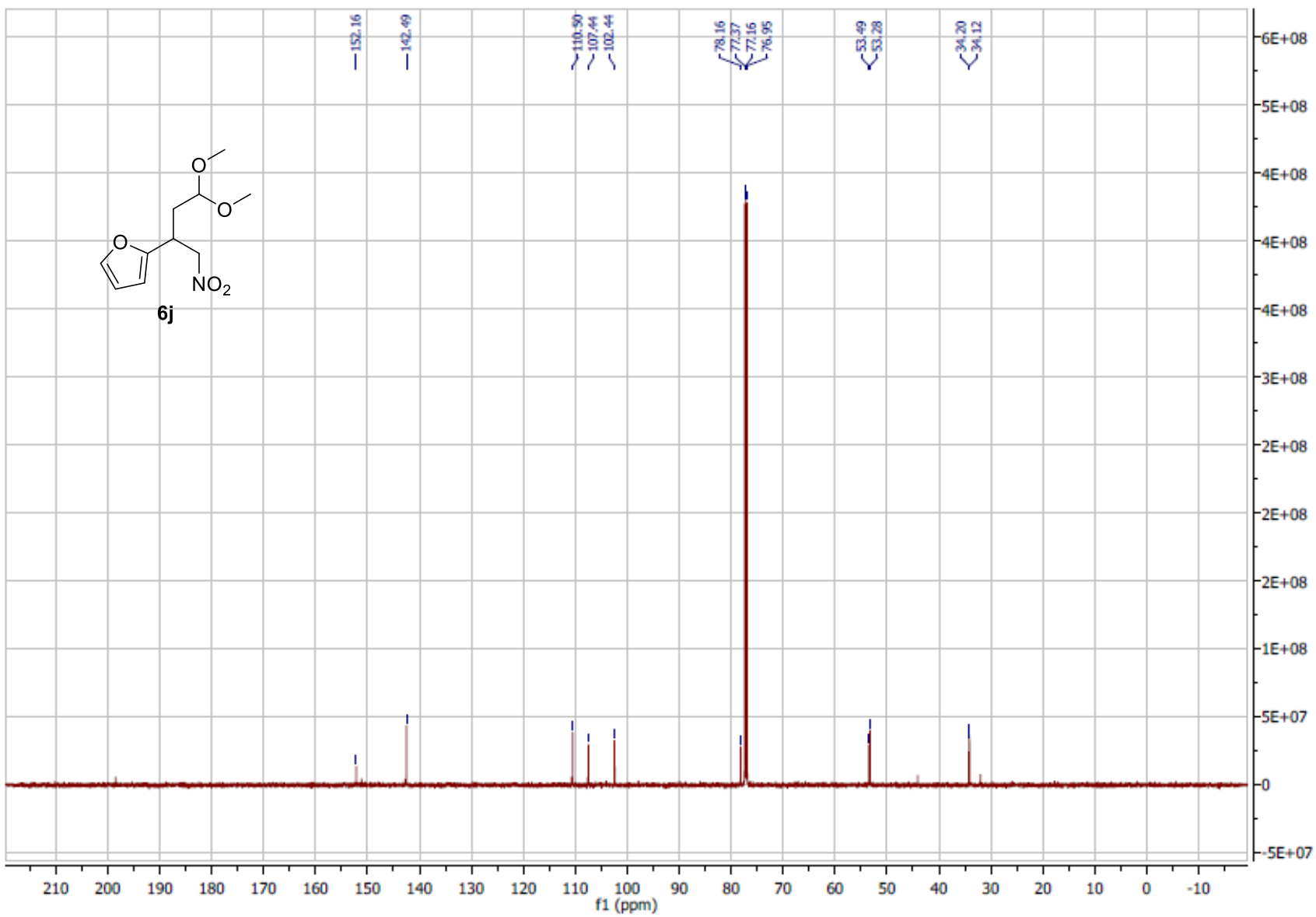
3-(furan-2-yl)-4-nitrobutanal ¹H NMR



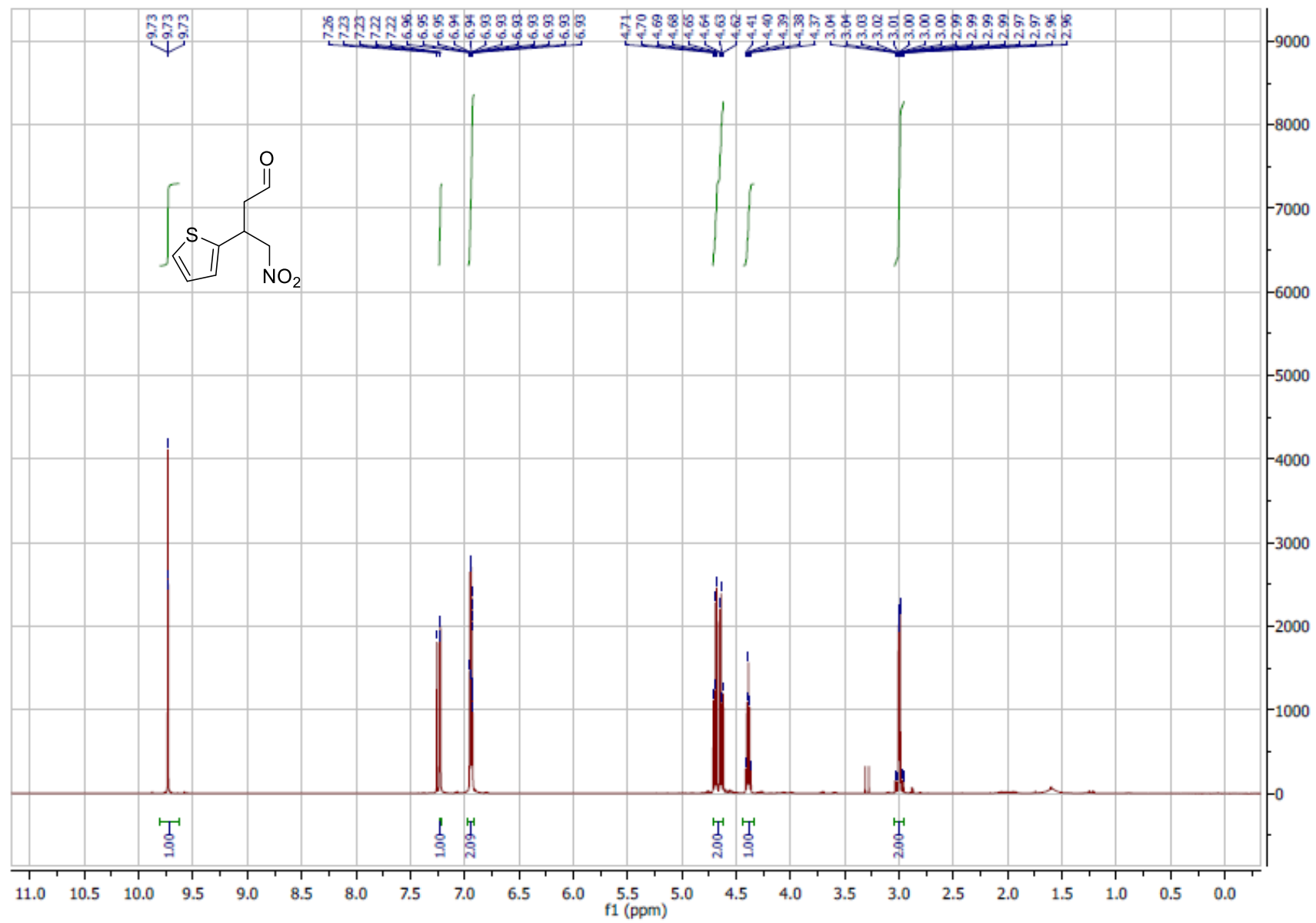
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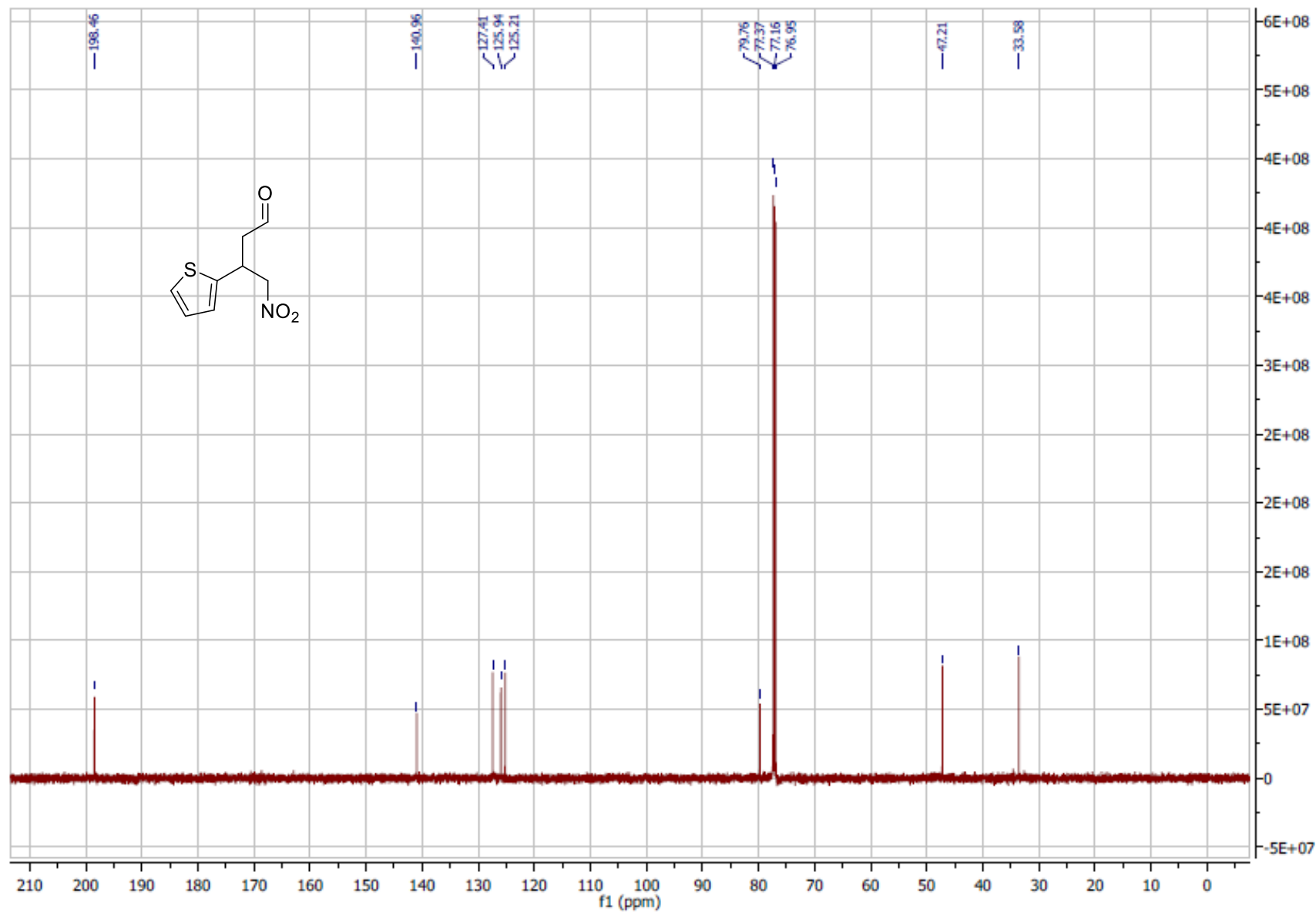
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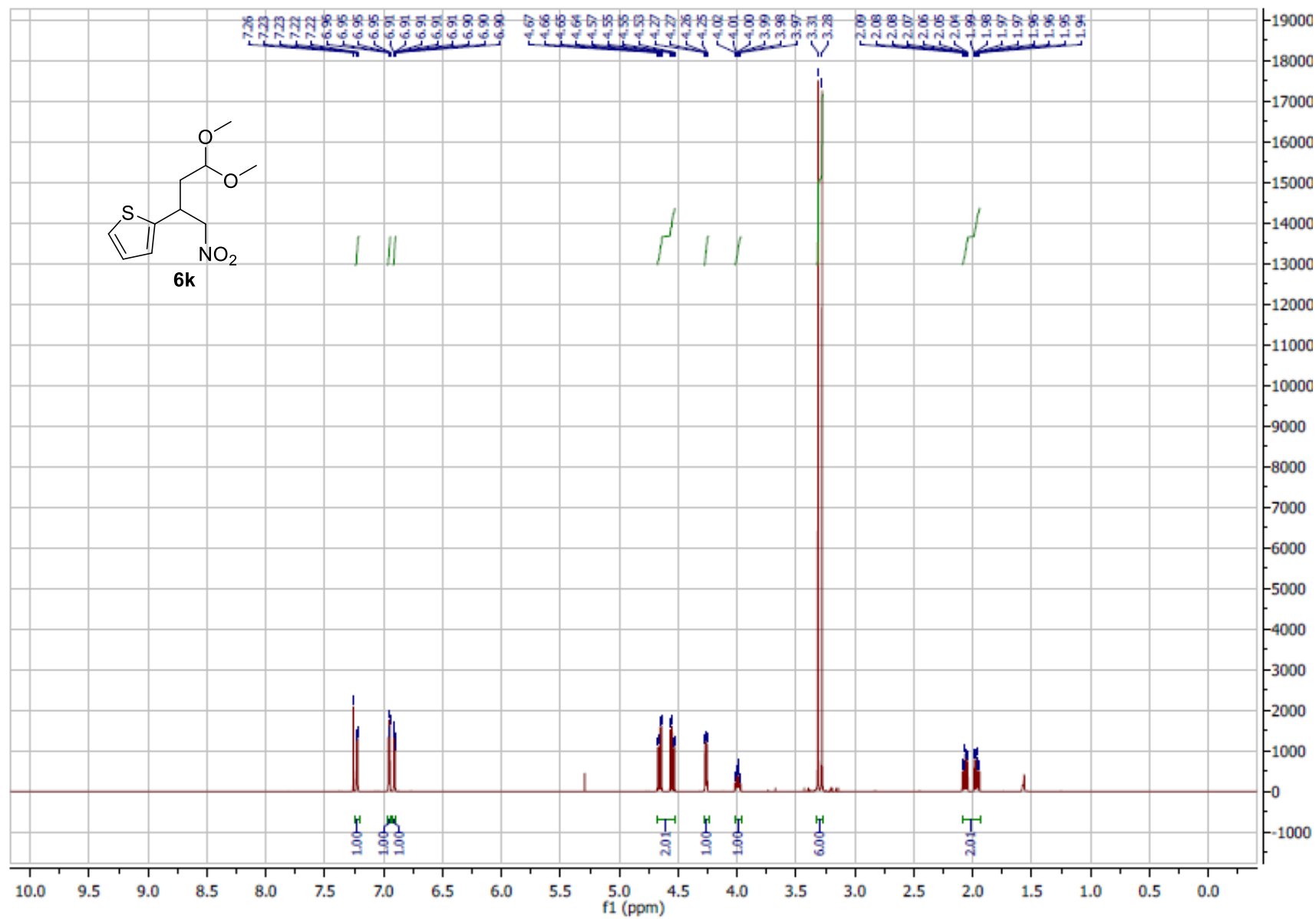
4-nitro-3-(thiophen-2-yl)butanal ¹H NMR



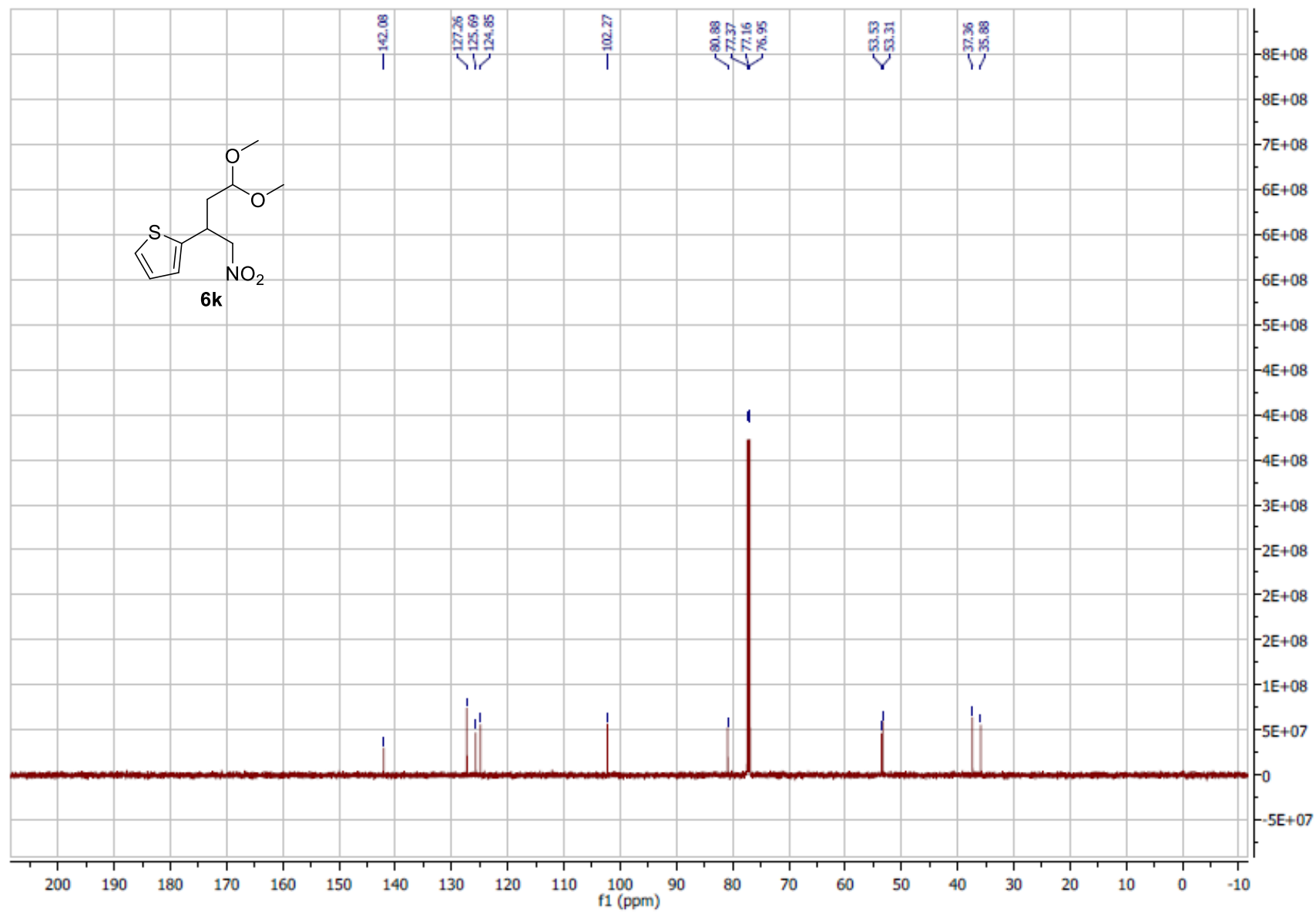
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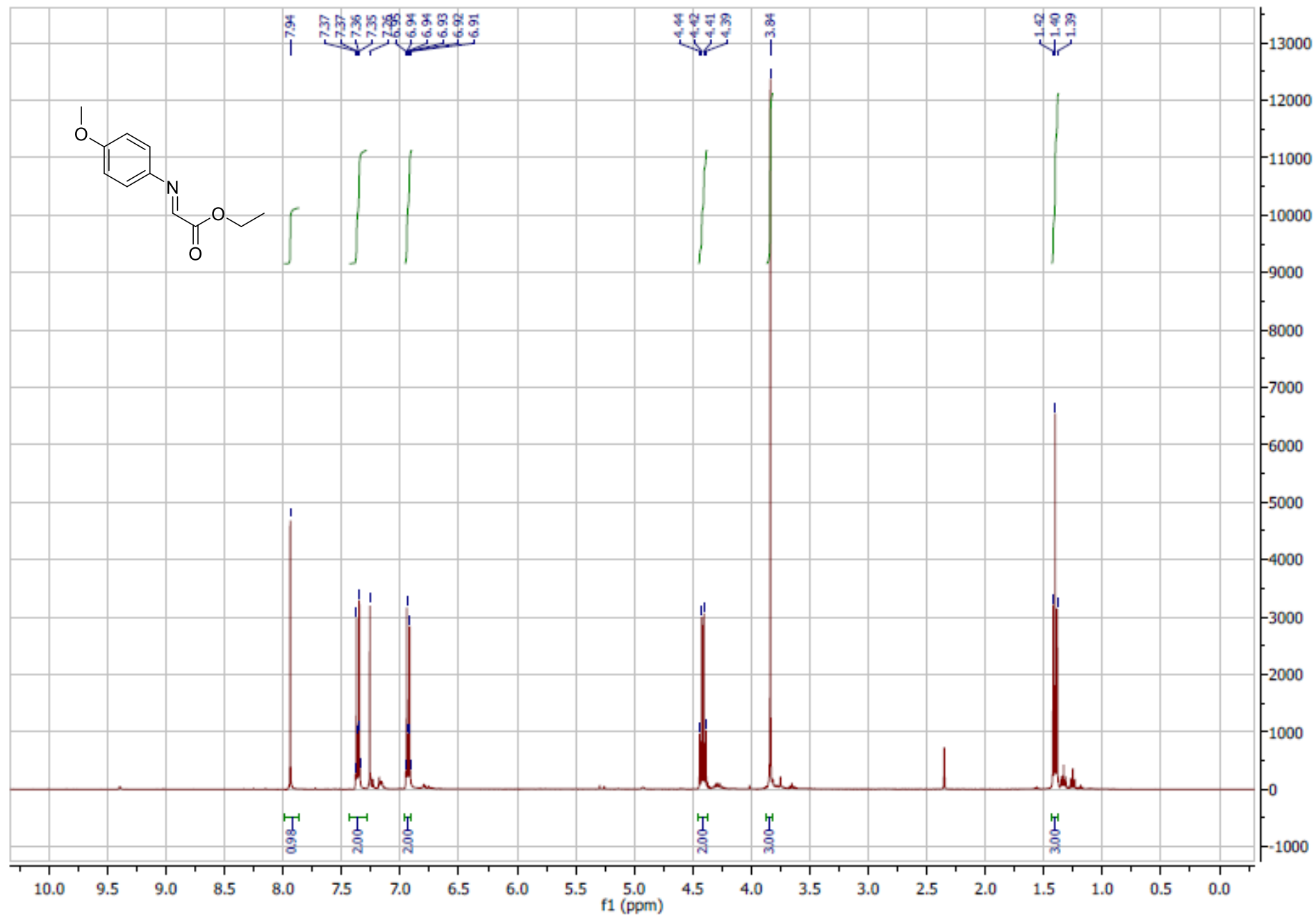
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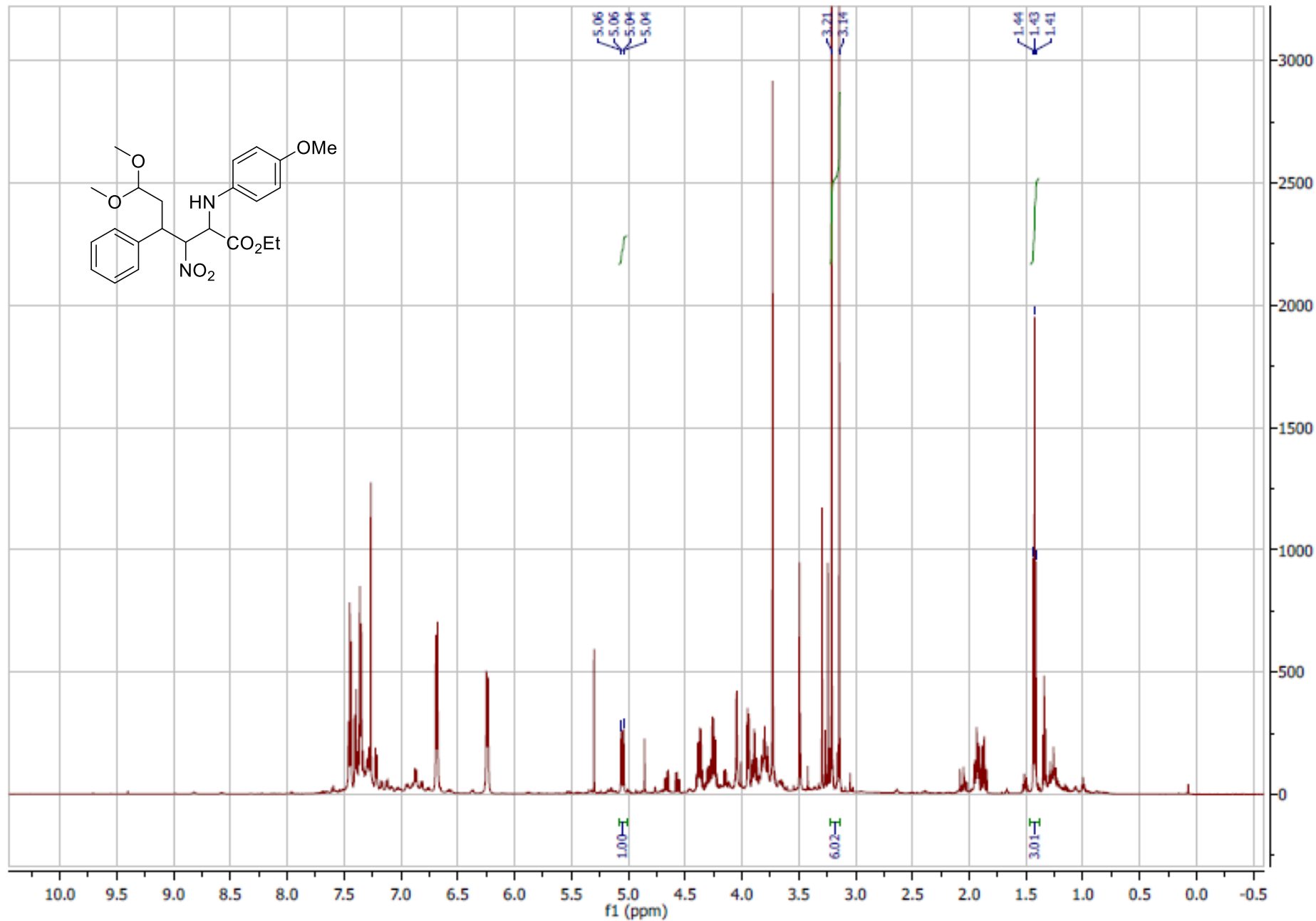
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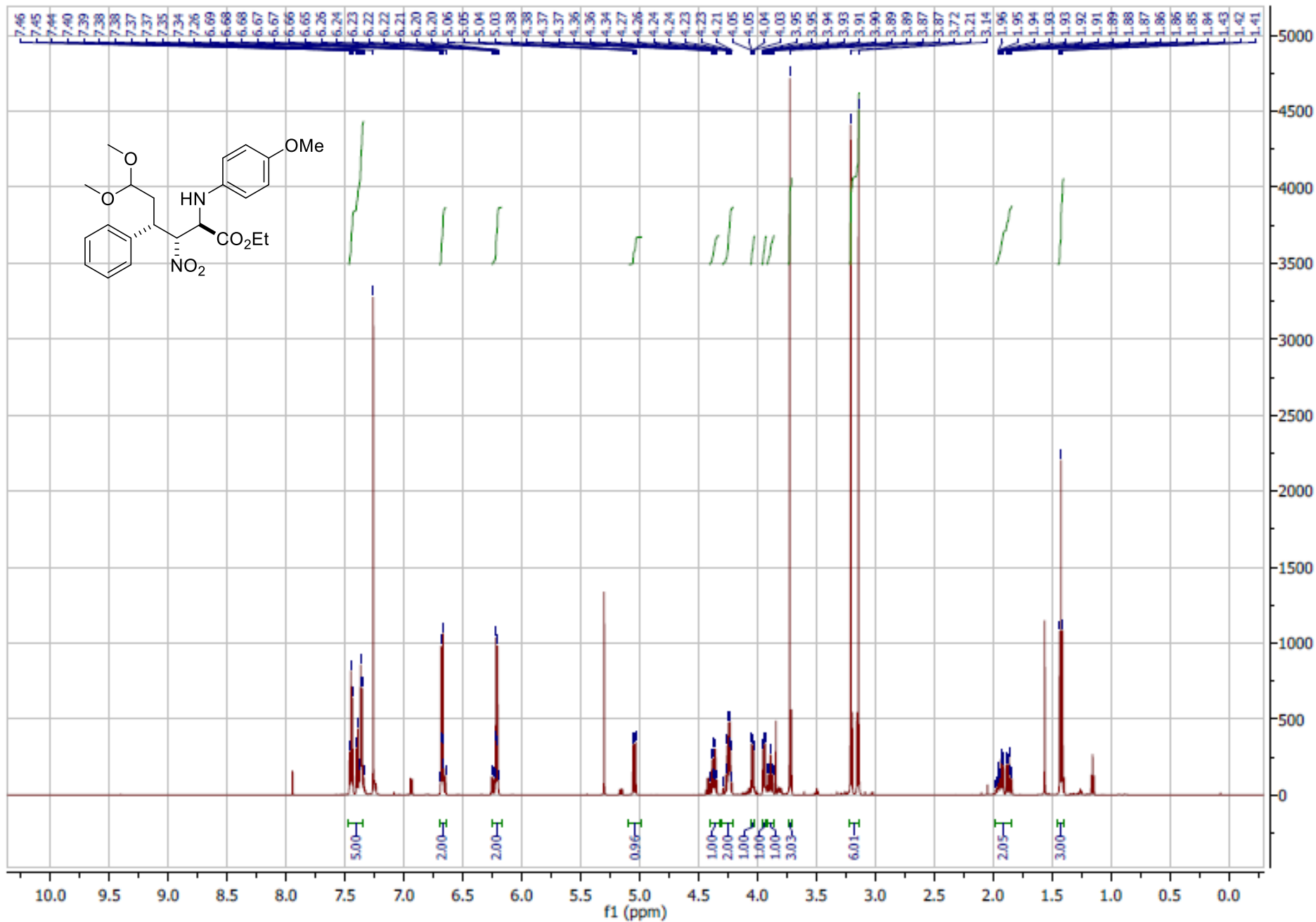
Ethyl (E)-2-((4-methoxyphenyl)imino)acetate (5) ¹H NMR



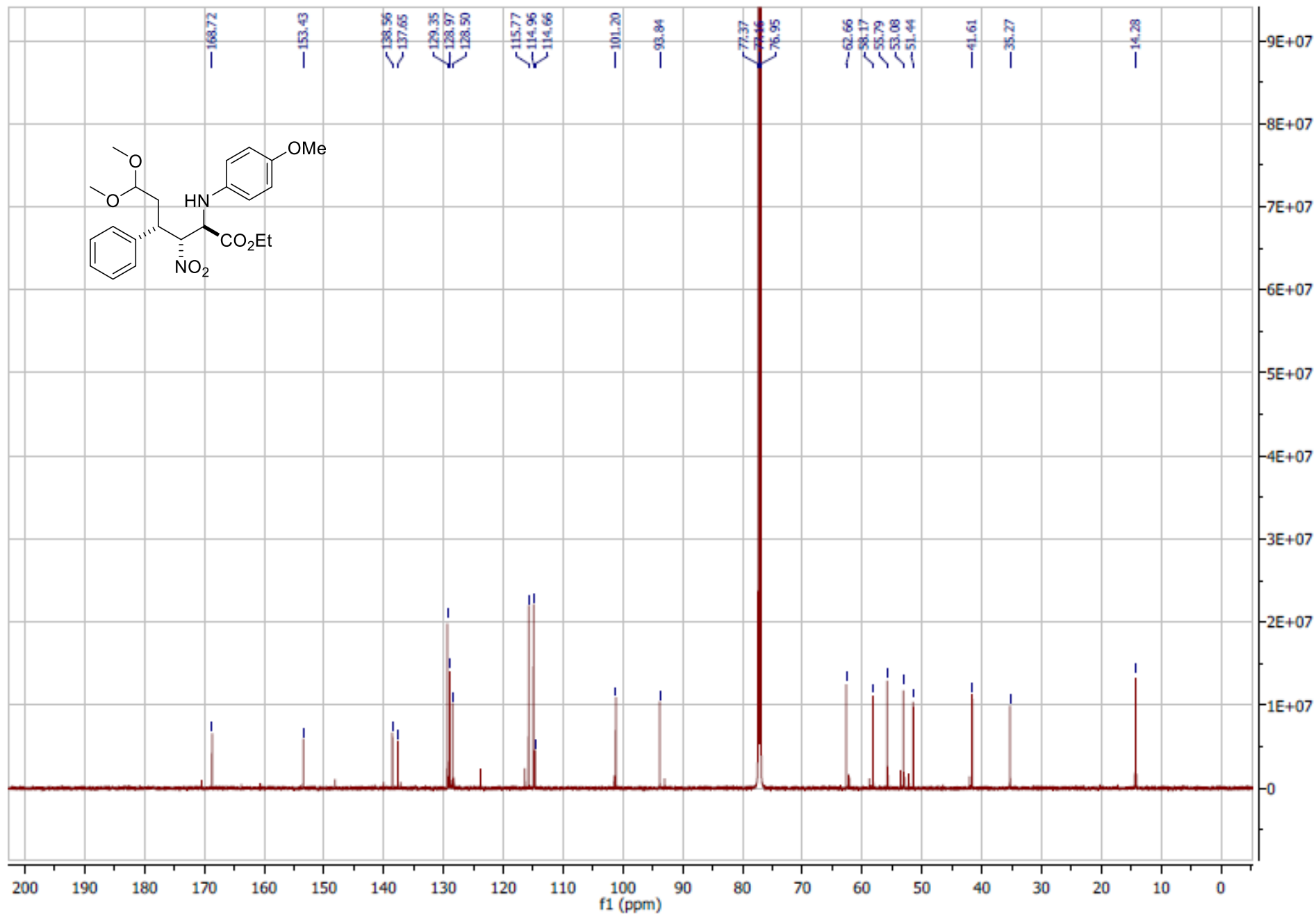
Ethyl 6,6-dimethoxy-2-((4-methoxyphenyl)amino)-3-nitro-4-phenylhexanoate (2a) ¹H NMR crude for dr calculation



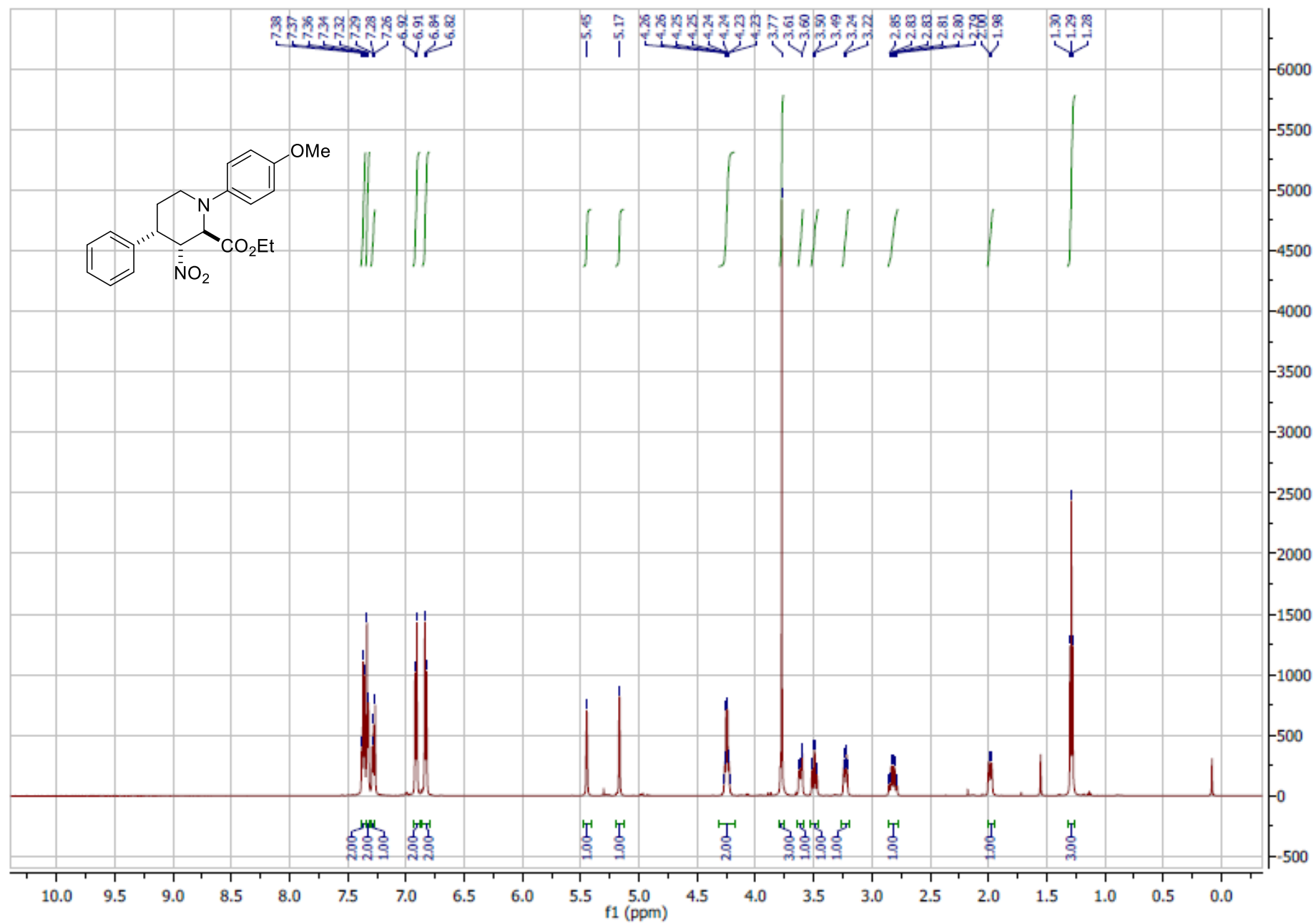
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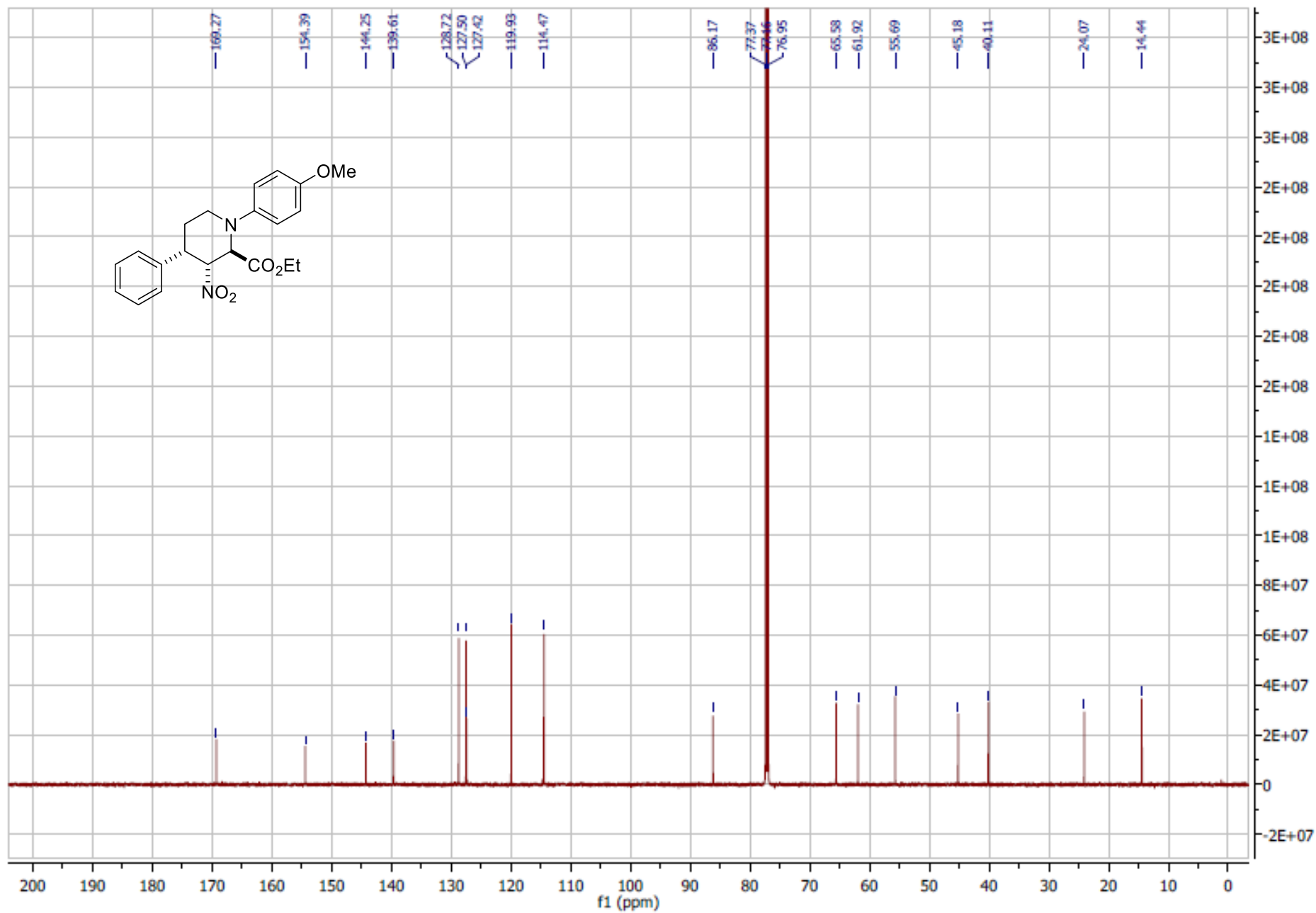
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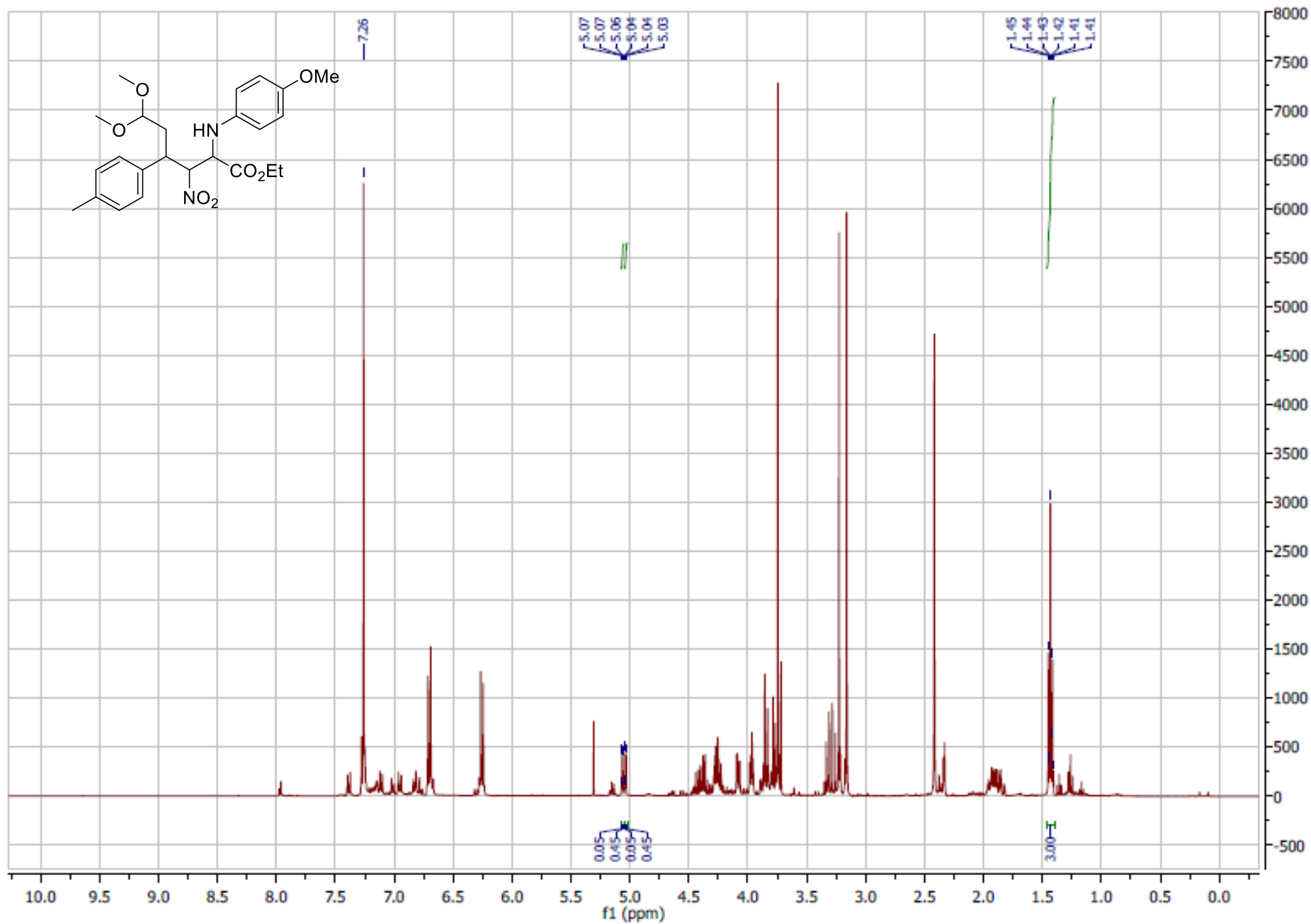
Ethyl 1-(4-methoxyphenyl)-3-nitro-4-phenylpiperidine-2-carboxylate (1a) ¹H NMR



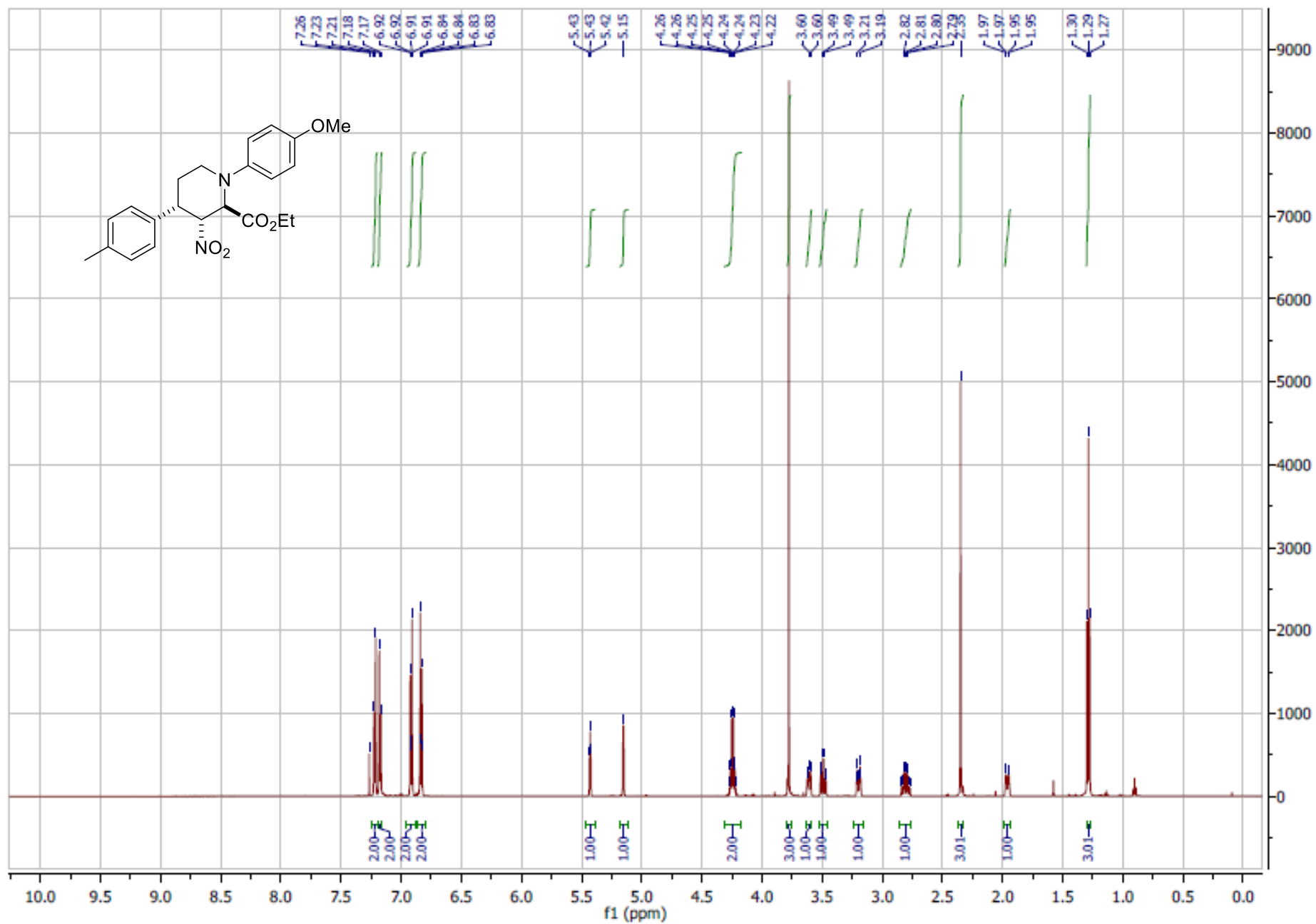
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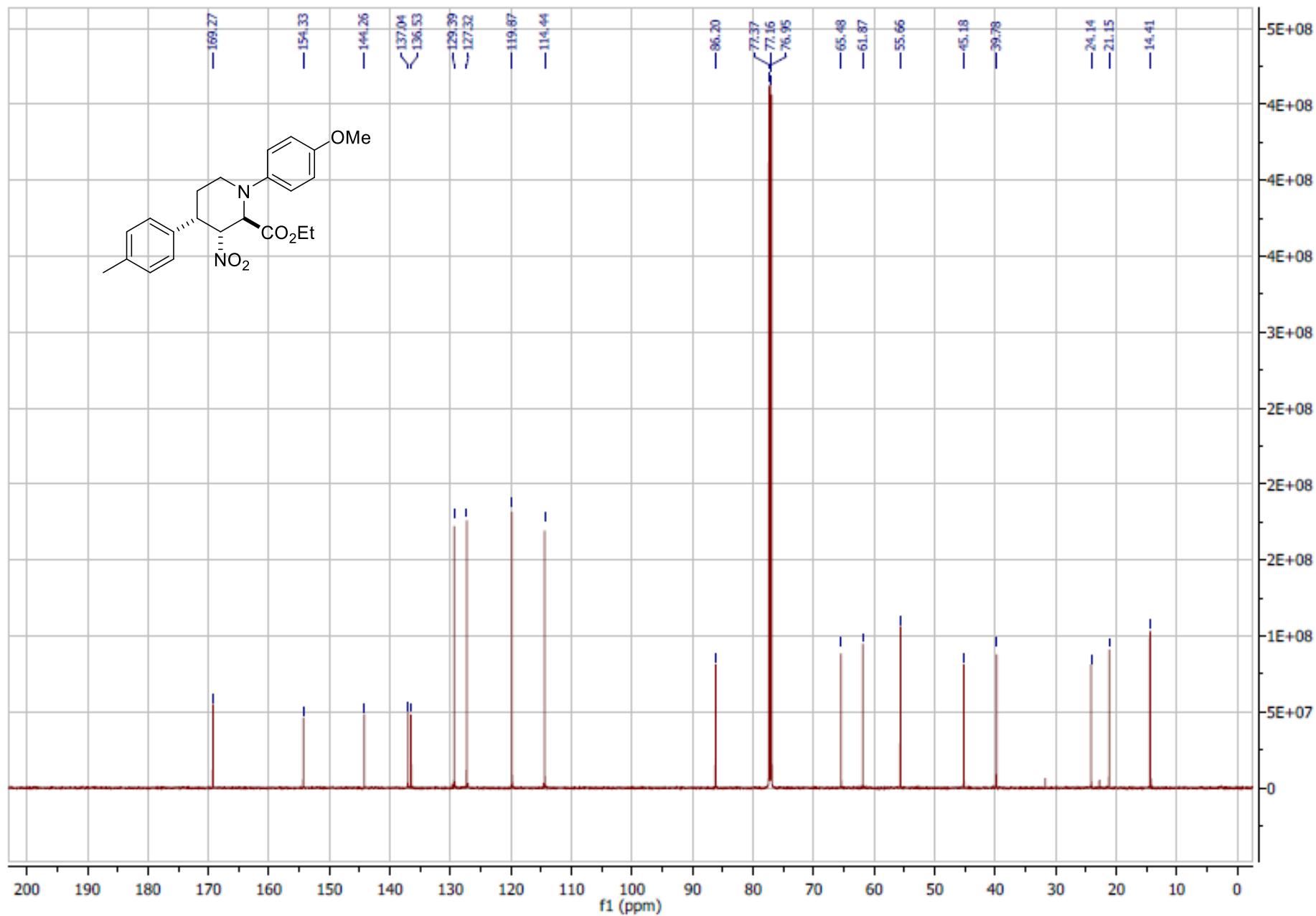
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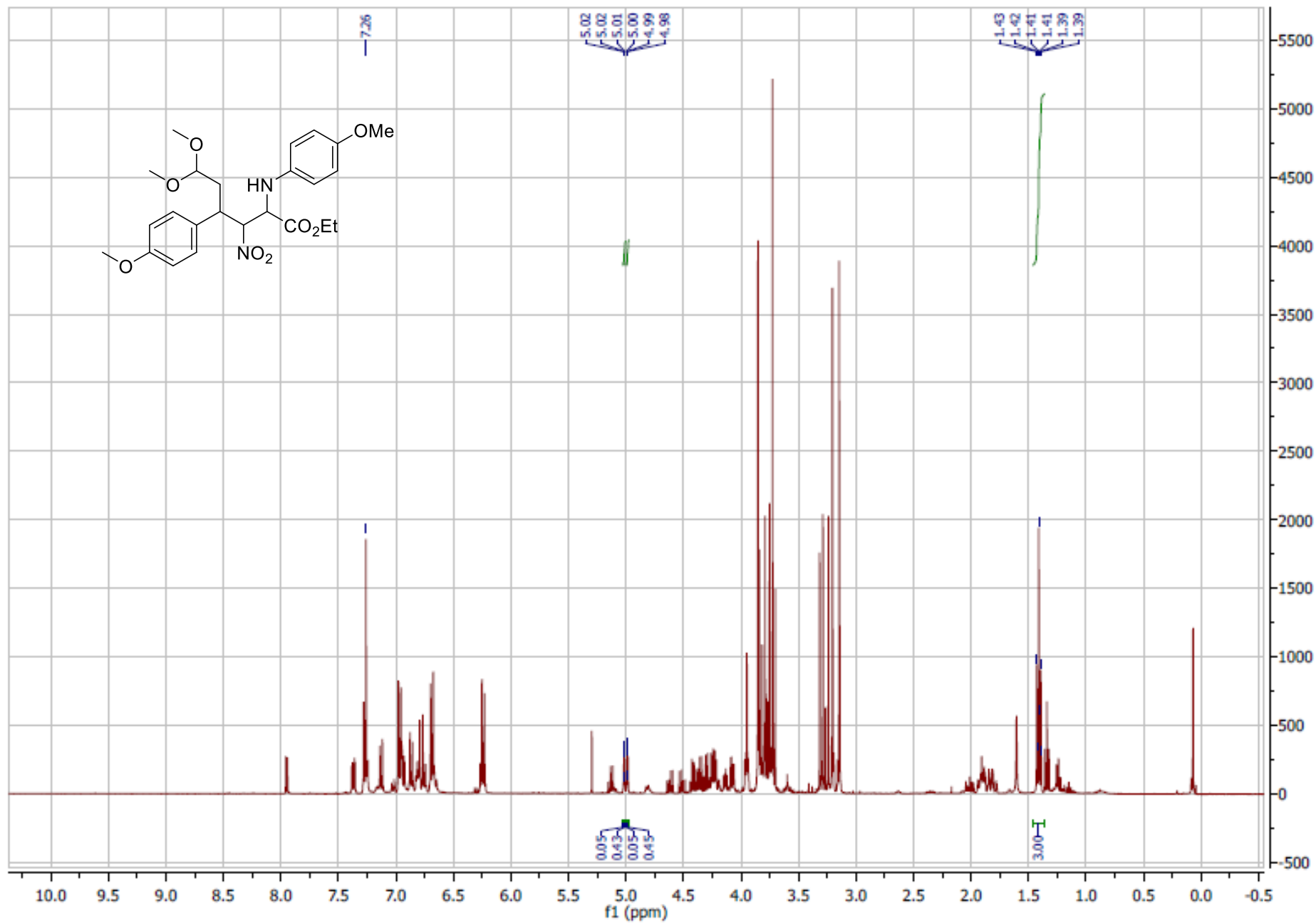
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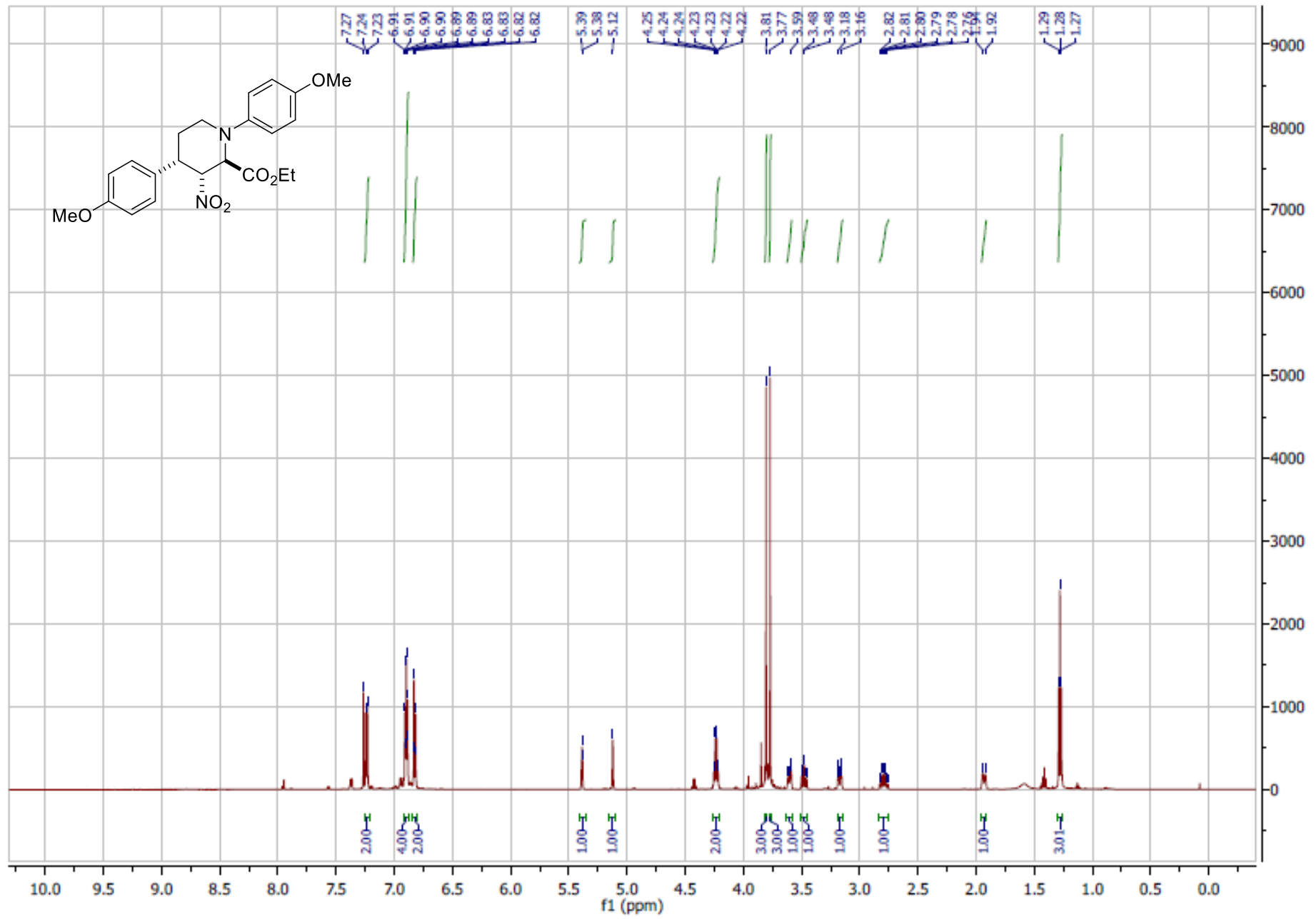
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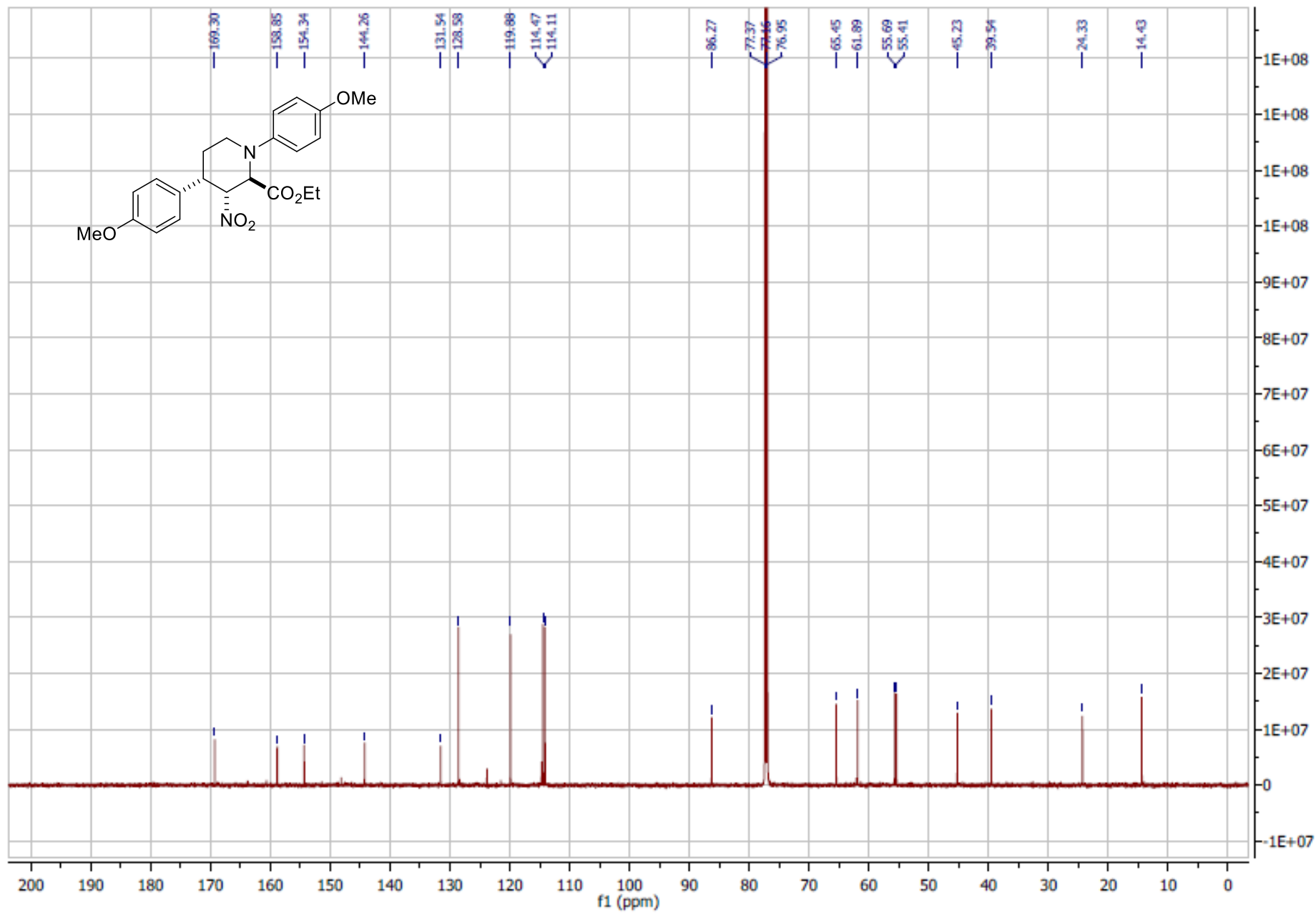
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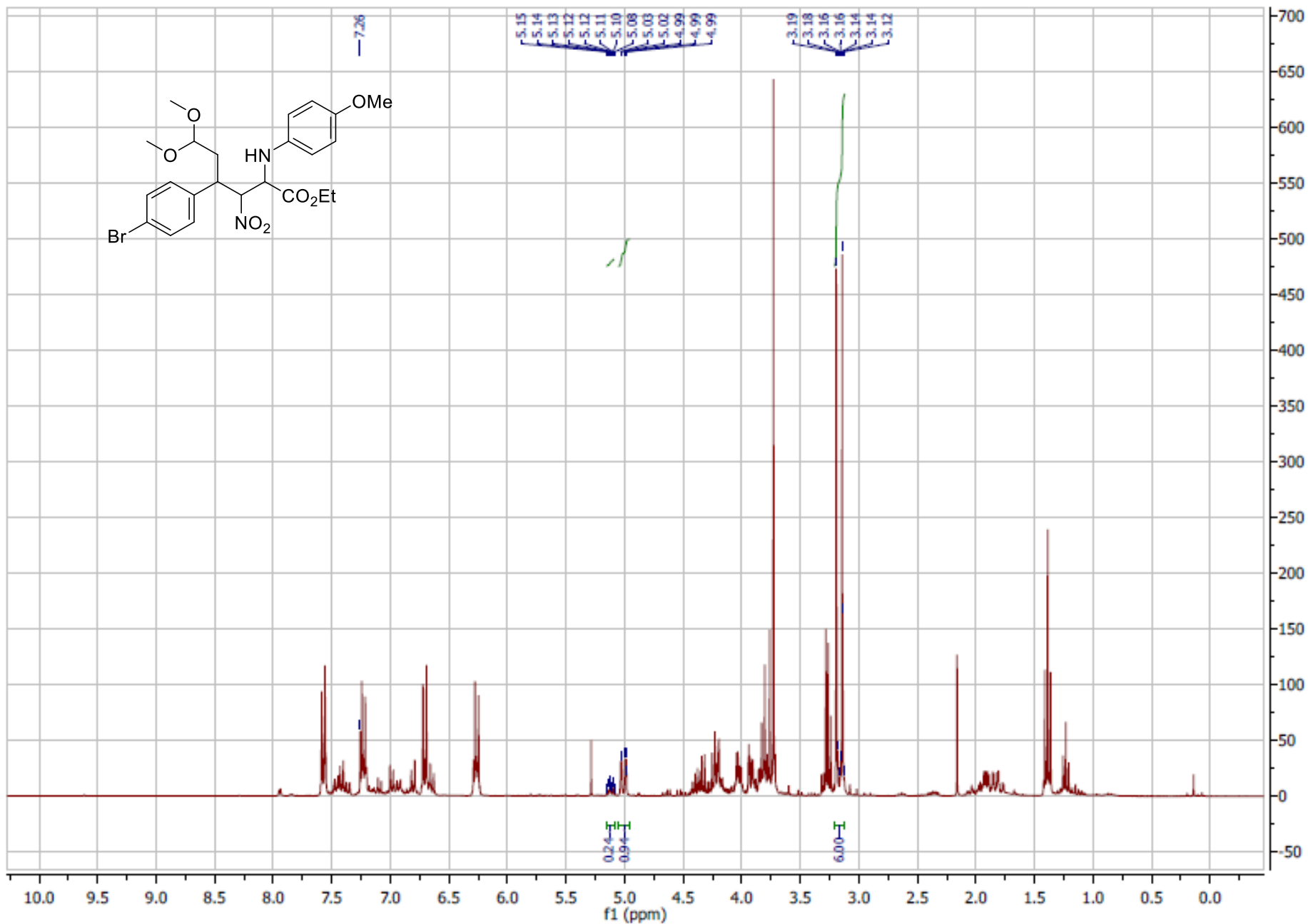
Ethyl 1,4-bis(4-methoxyphenyl)-3-nitropiperidine-2-carboxylate (1c) ¹H NMR



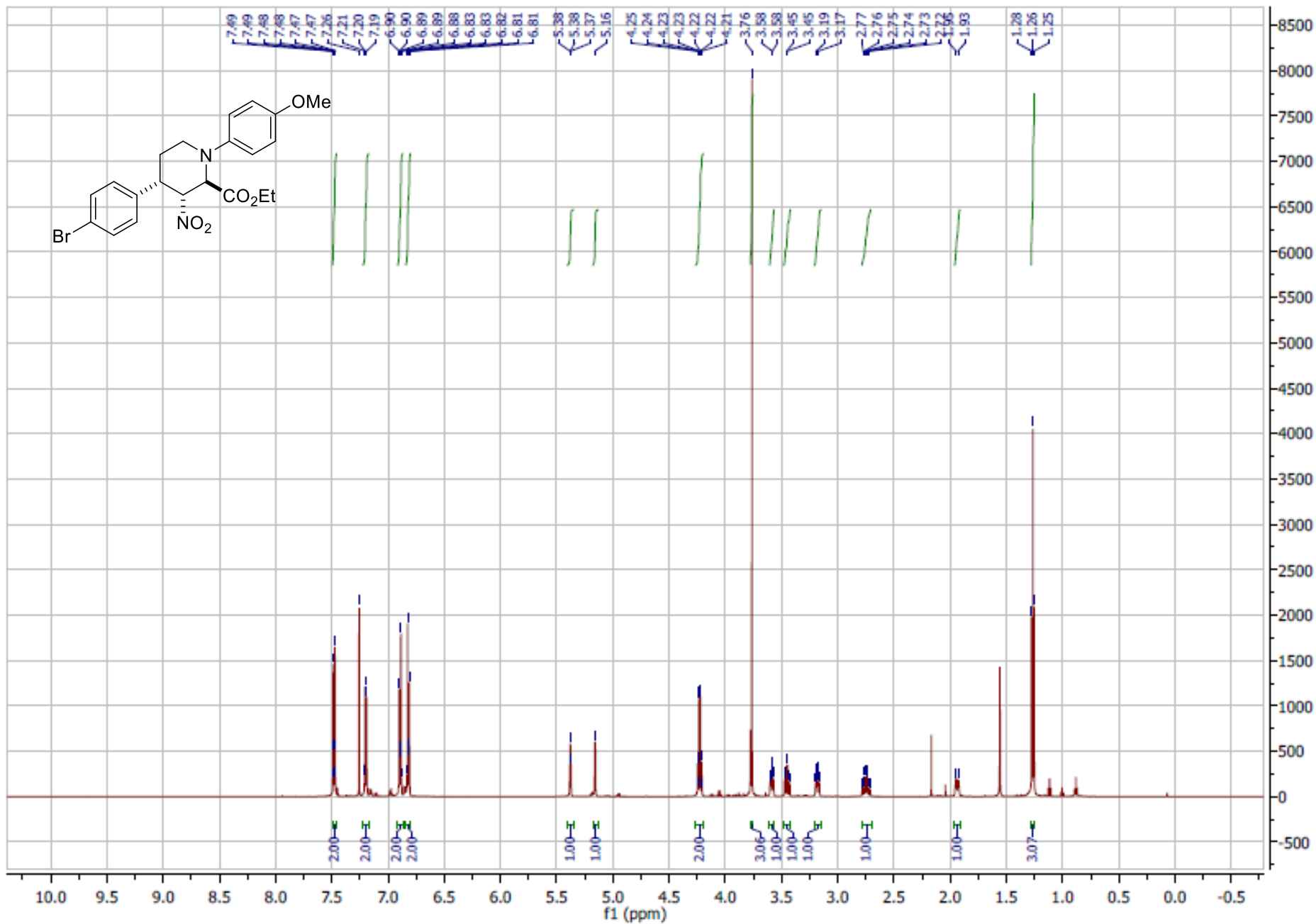
Ethyl 1,4-bis(4-methoxyphenyl)-3-nitropiperidine-2-carboxylate (1c) ¹³C NMR



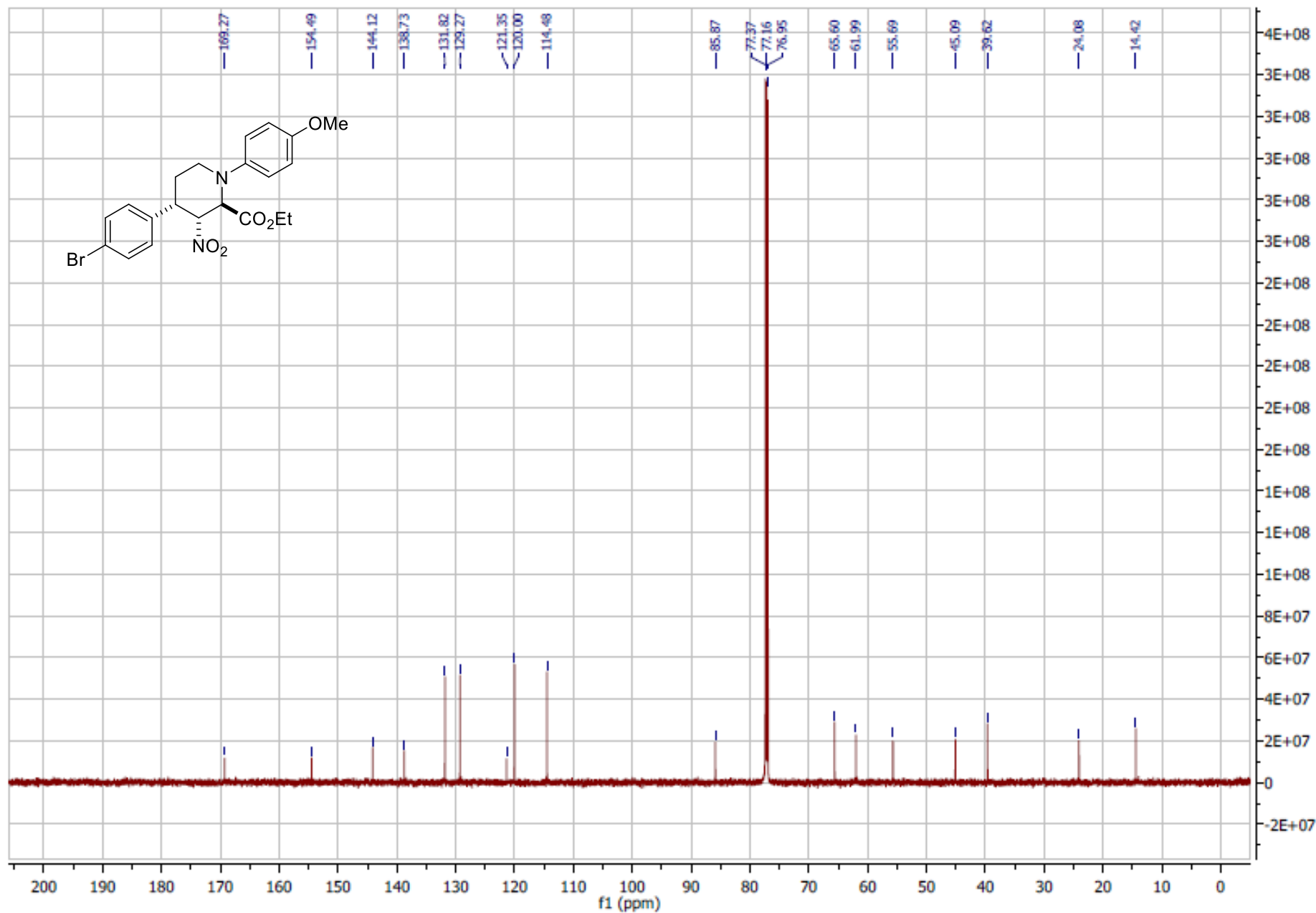
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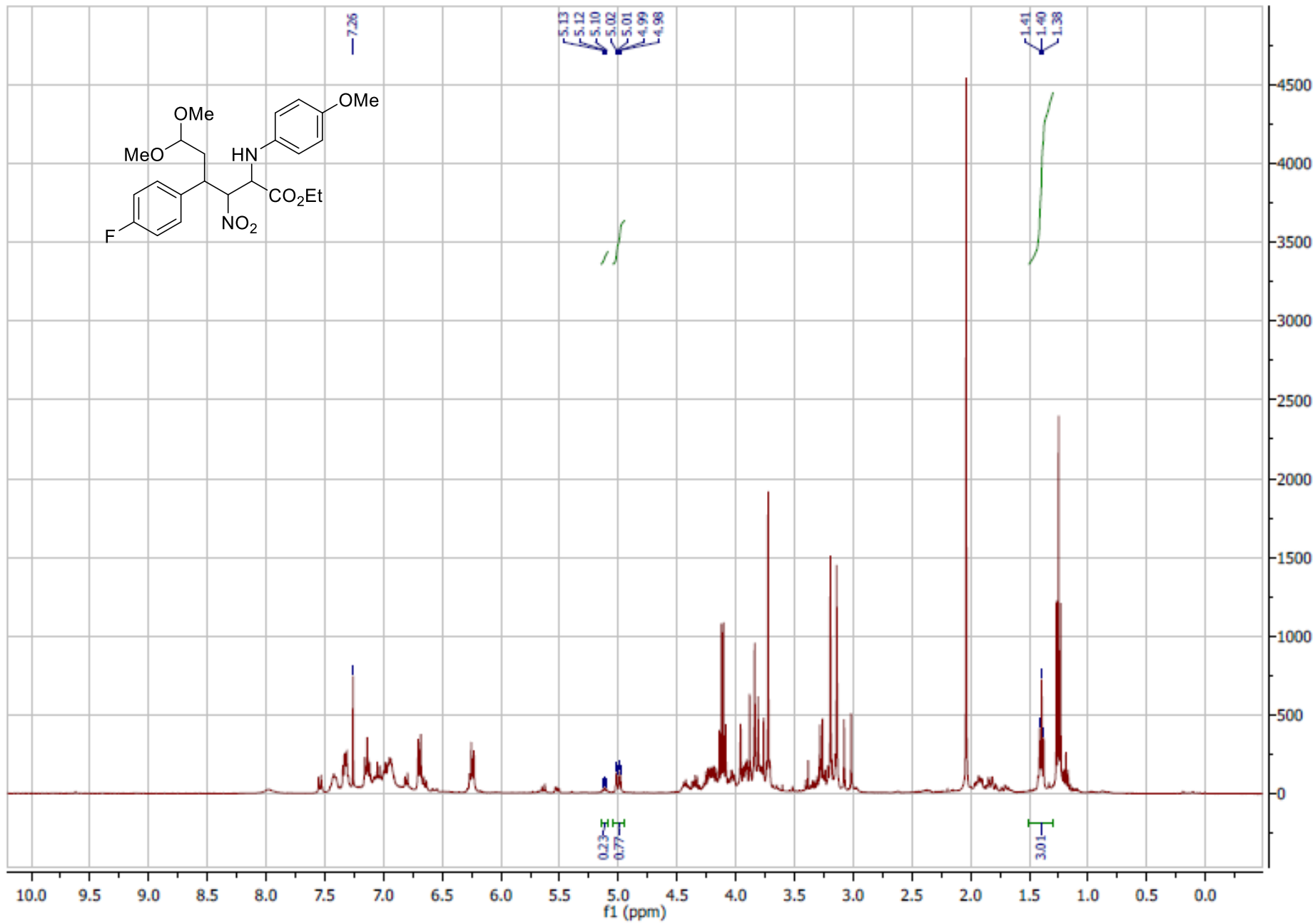
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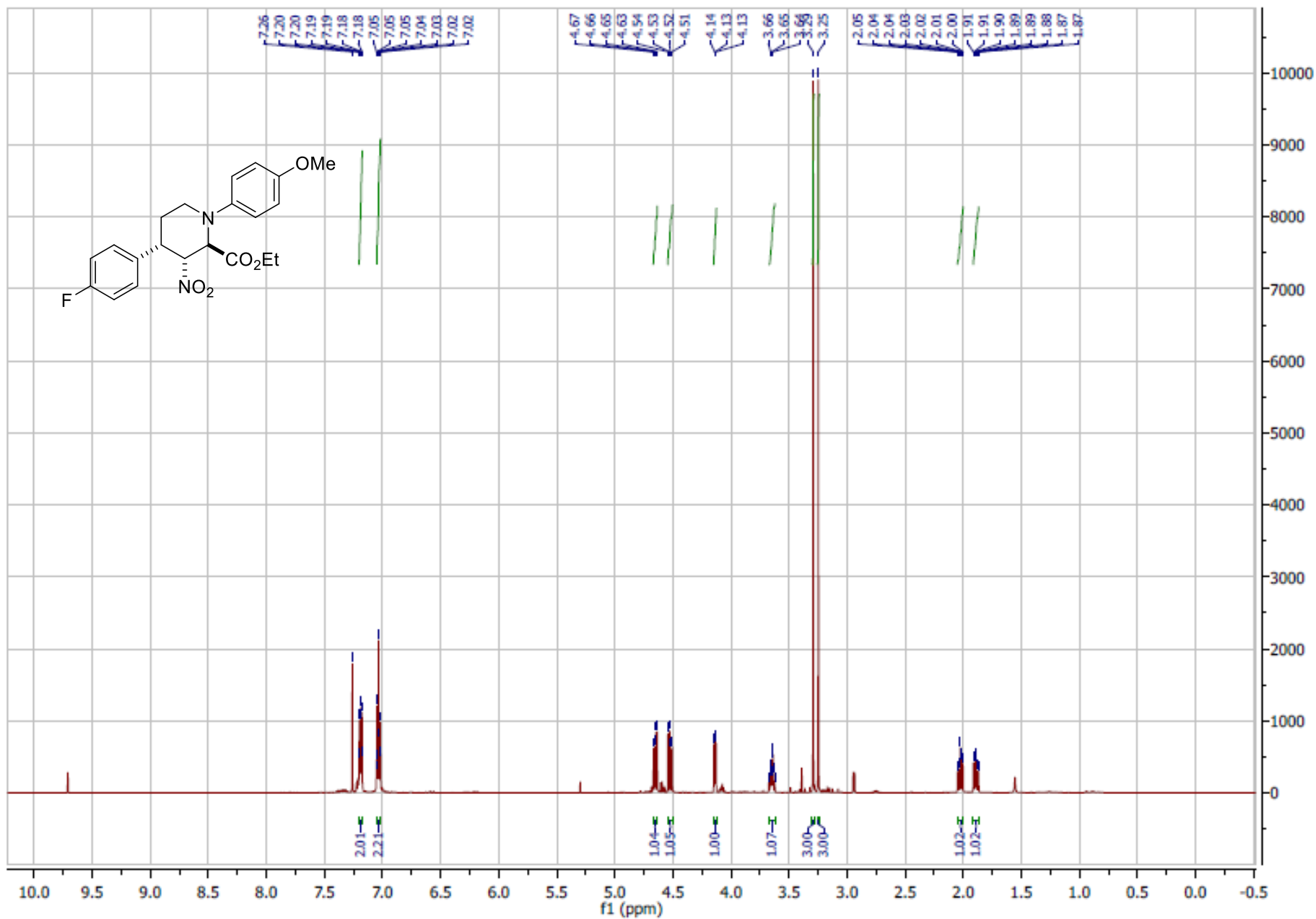
Ethyl 4-(4-bromophenyl)-1-(4-methoxyphenyl)-3-nitropiperidine-2-carboxylate (1d) ¹³C NMR



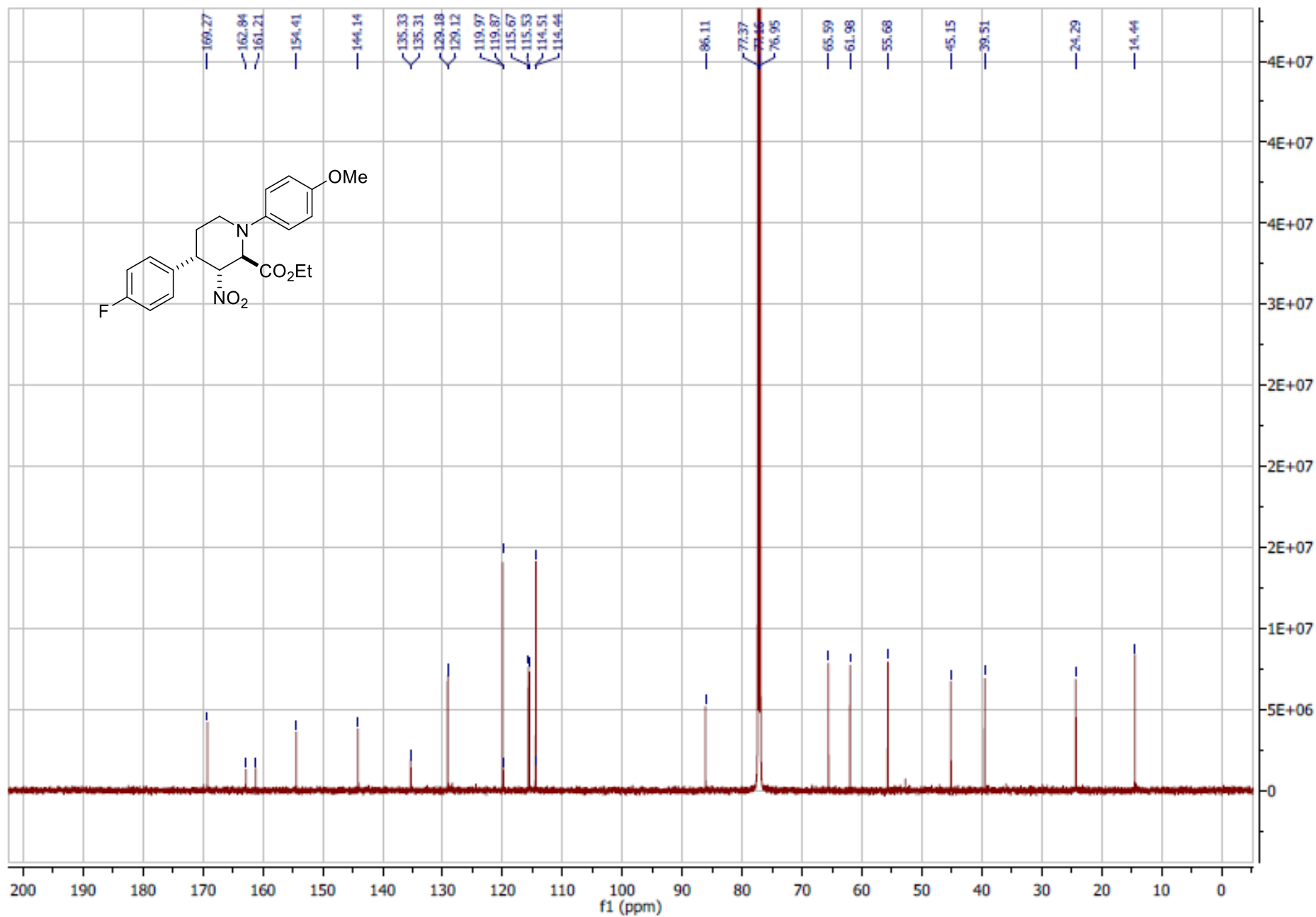
Ethyl 4-(4-fluorophenyl)-6,6-dimethoxy-2-((4-methoxyphenyl)amino)-3-nitrohexanoate (2e) ¹H NMR crude for dr calculation



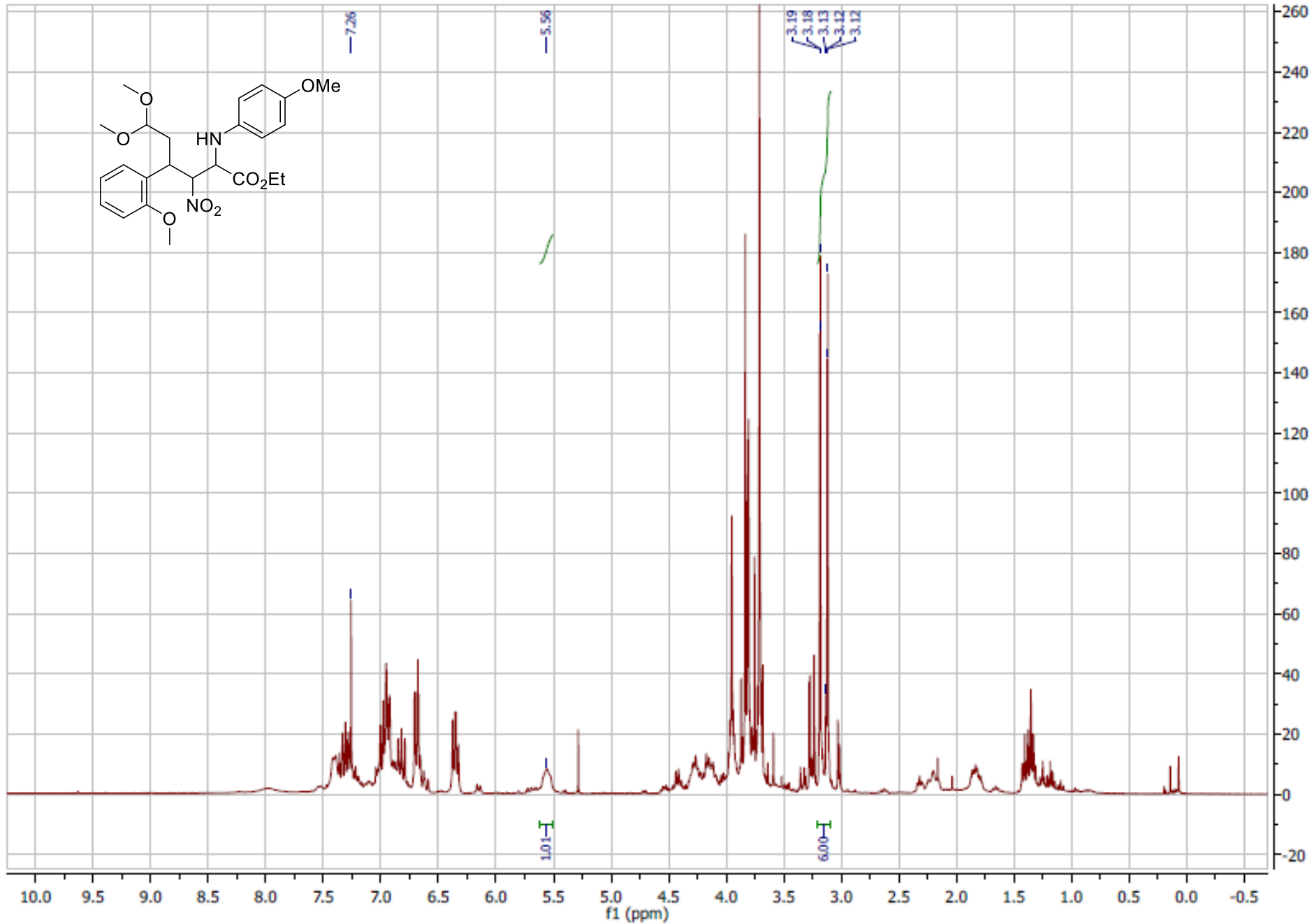
Ethyl 4-(4-fluorophenyl)-1-(4-methoxyphenyl)-3-nitropiperidine-2-carboxylate (1e) ¹H NMR



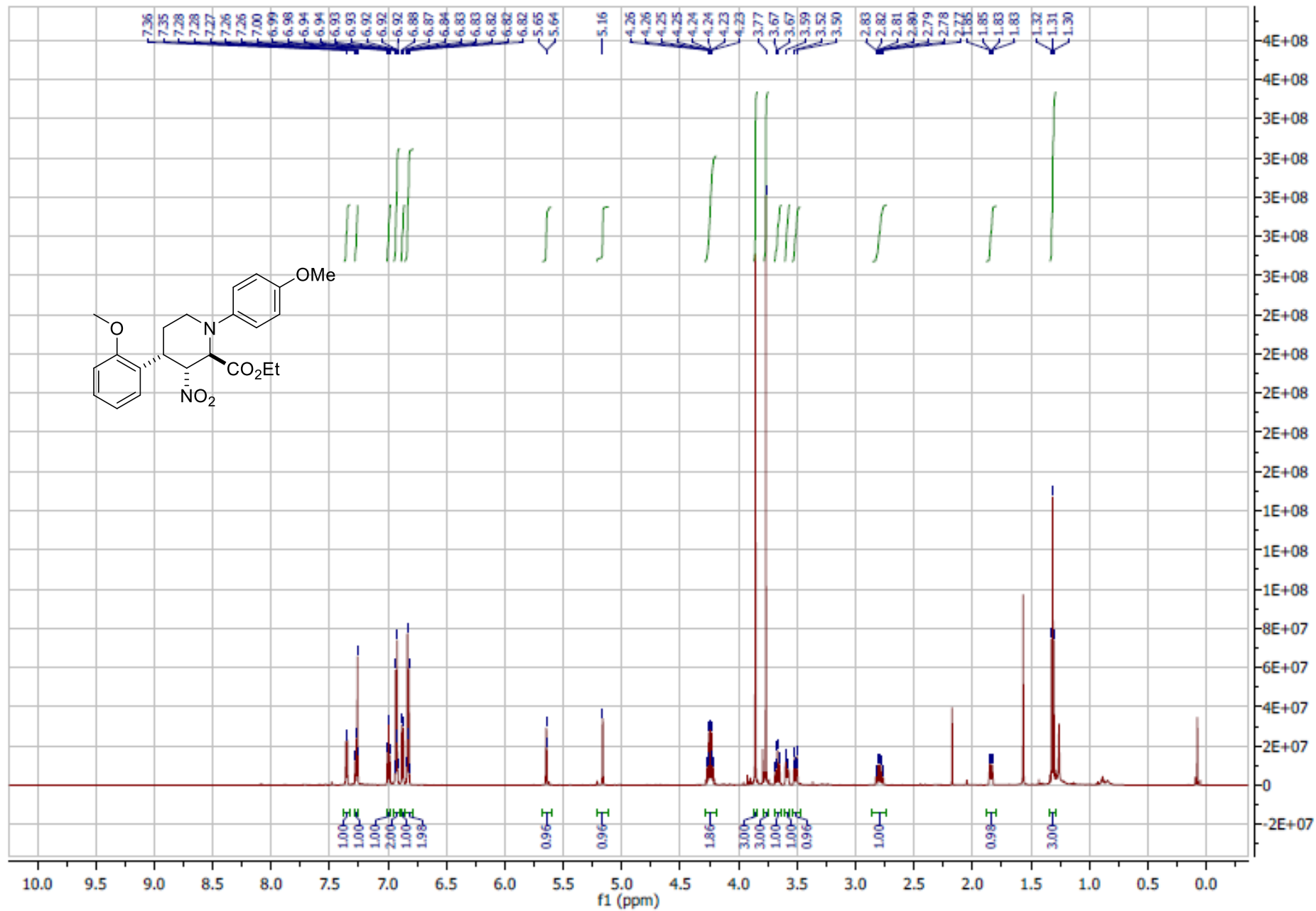
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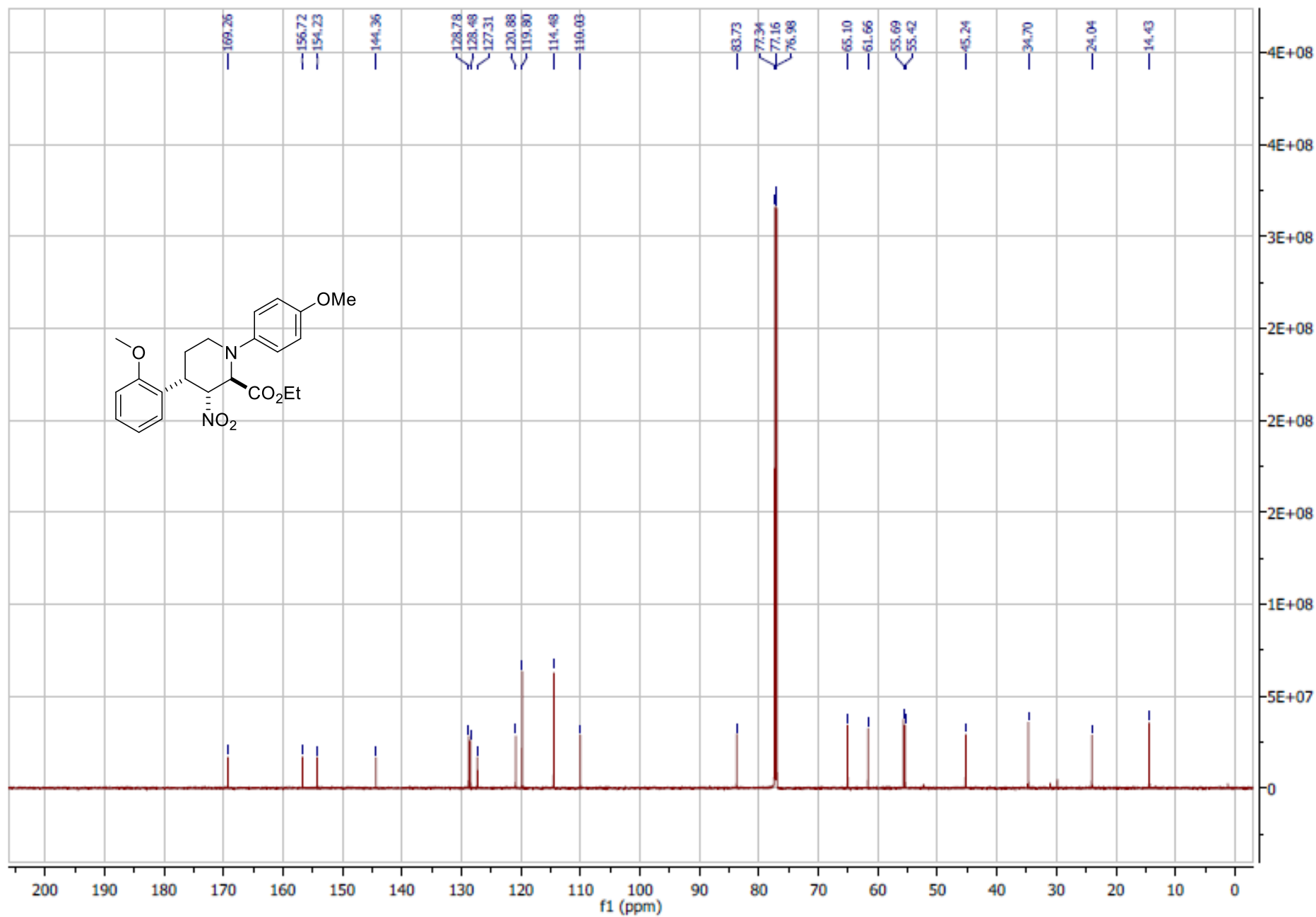
Ethyl 6,6-dimethoxy-4-(2-methoxyphenyl)-2-((4-methoxyphenyl)amino)-3-nitrohexanoate (2g) ¹H NMR crude for dr calculation



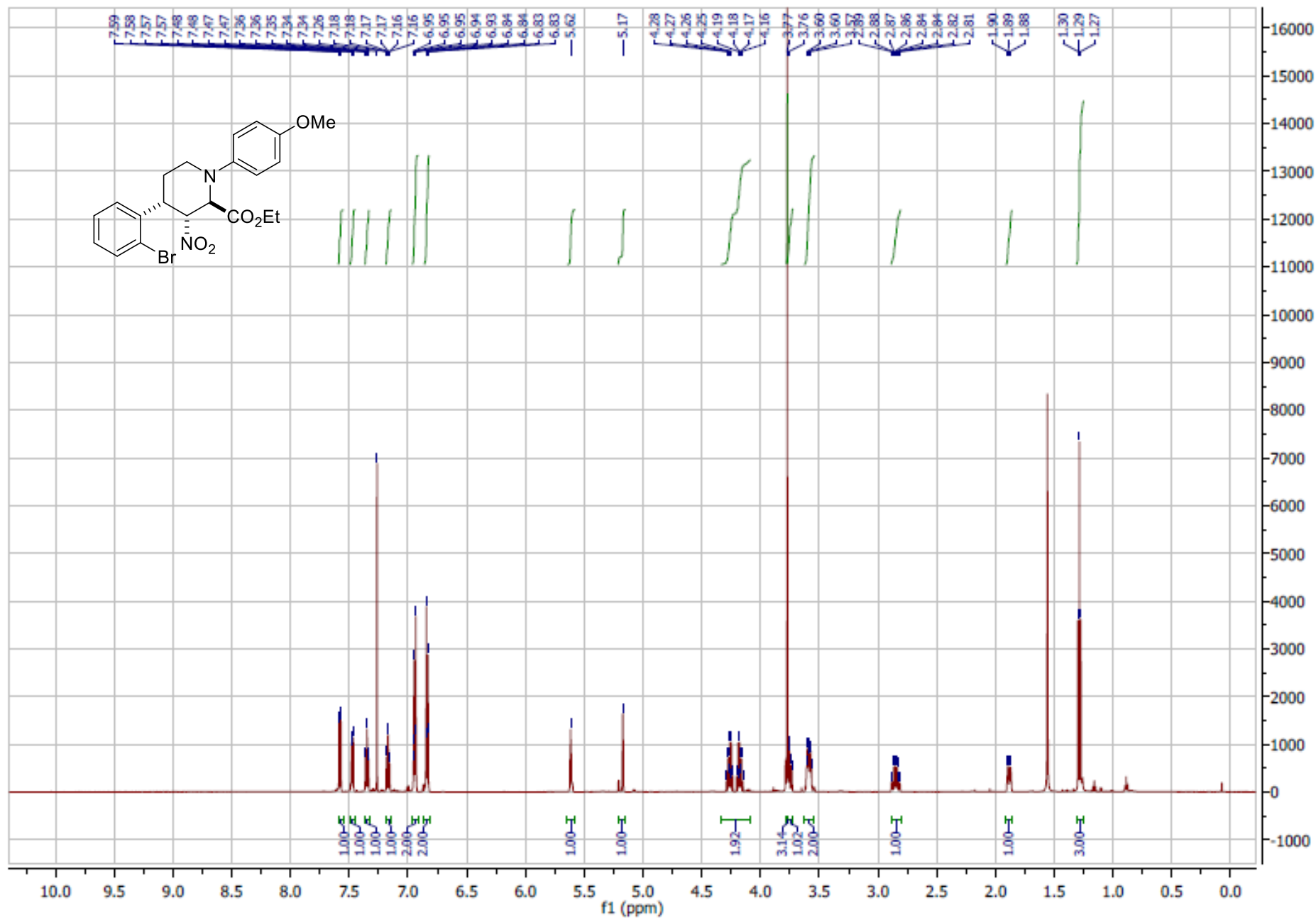
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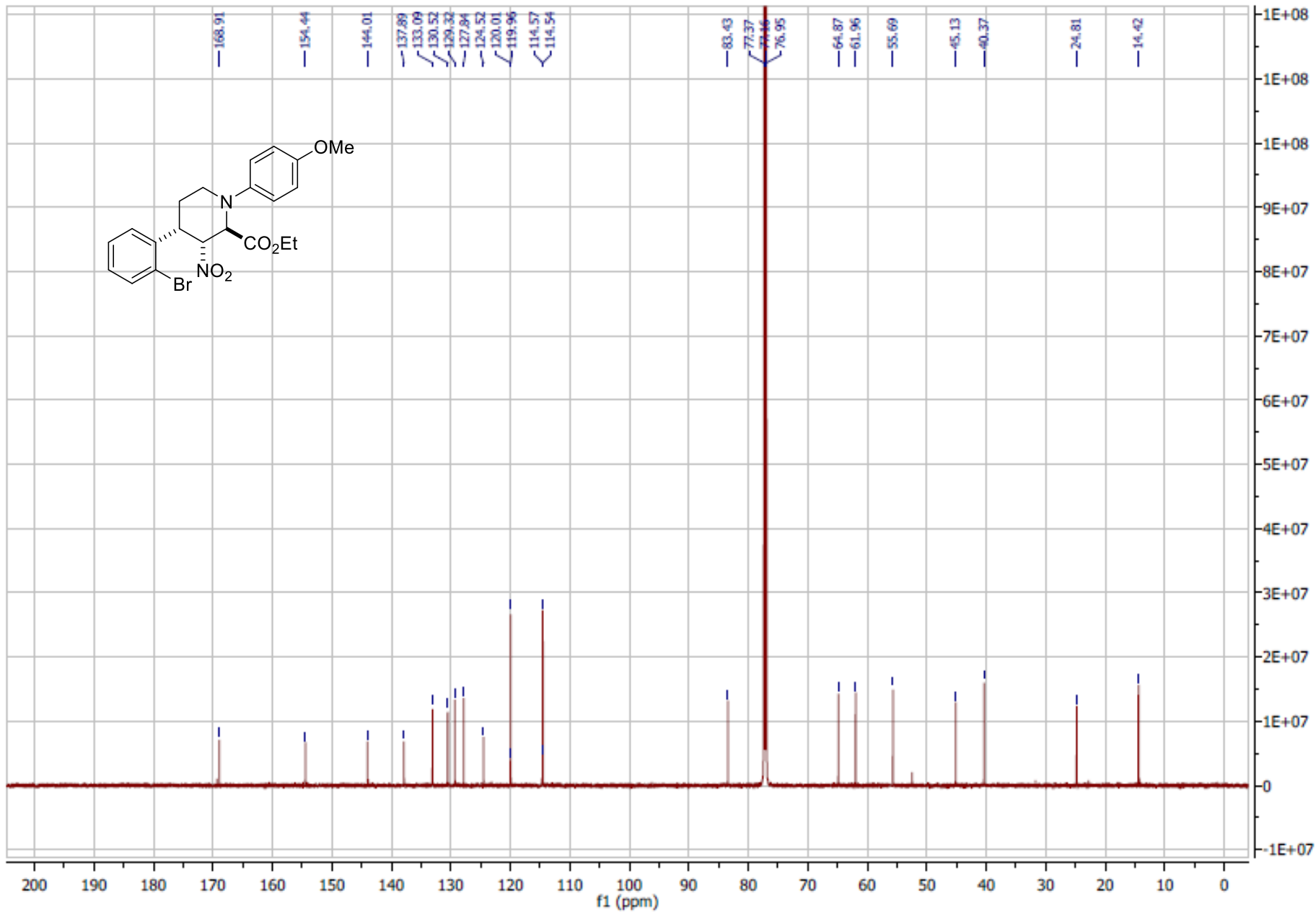
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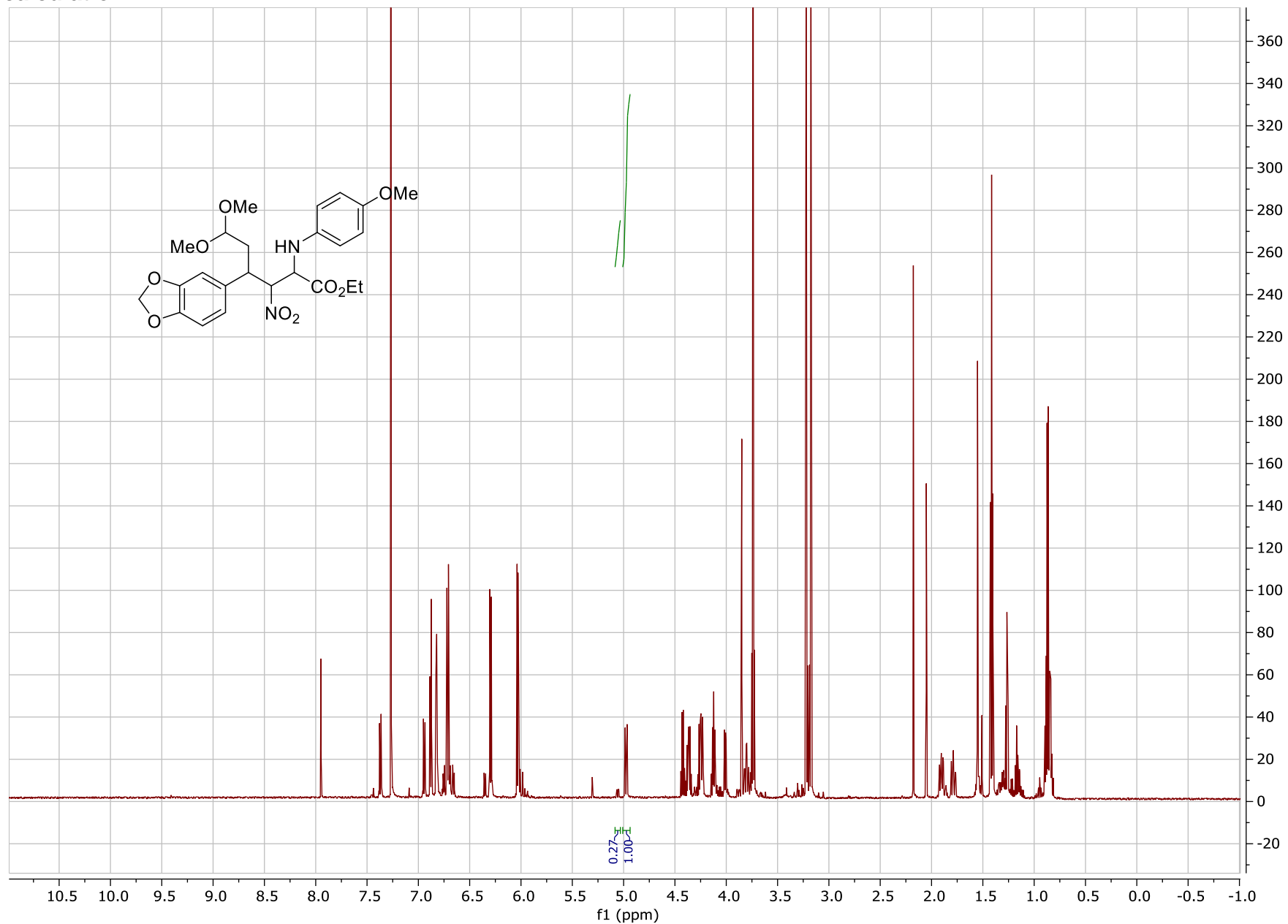
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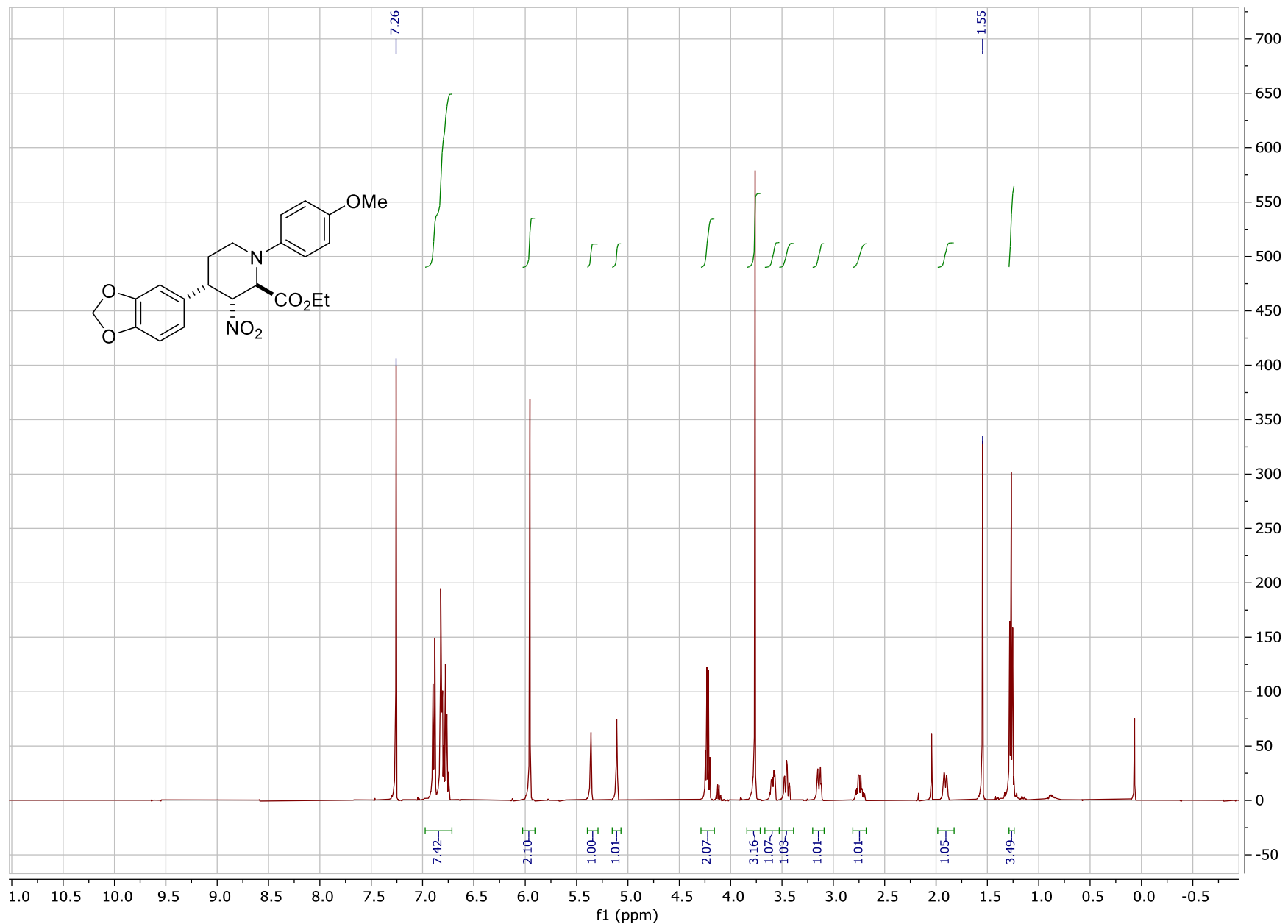
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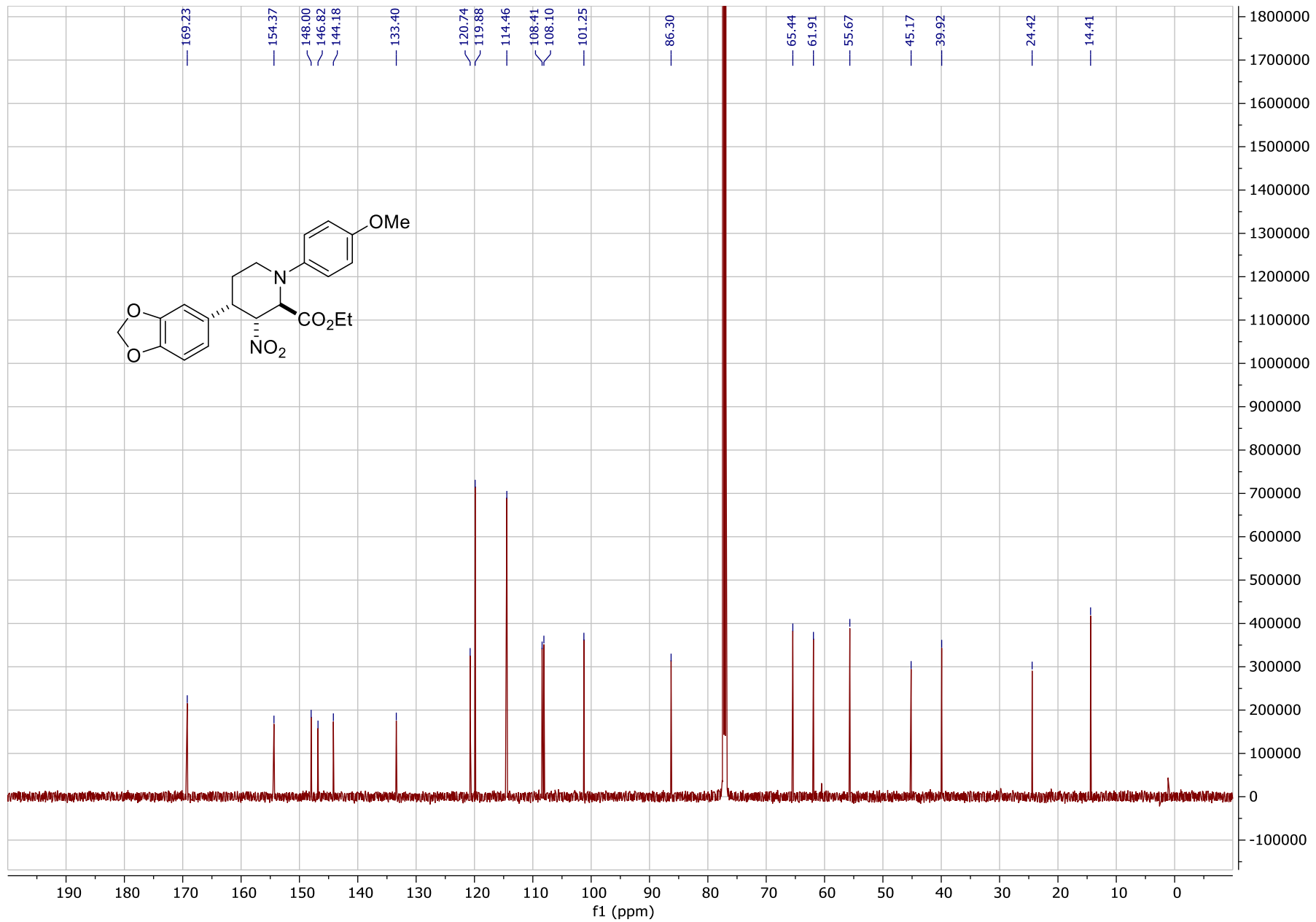
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-6,6-dimethoxy-2-((4-methoxyphenyl)amino)-3-nitrohexanoate (2i) ¹H NMR for dr calculation



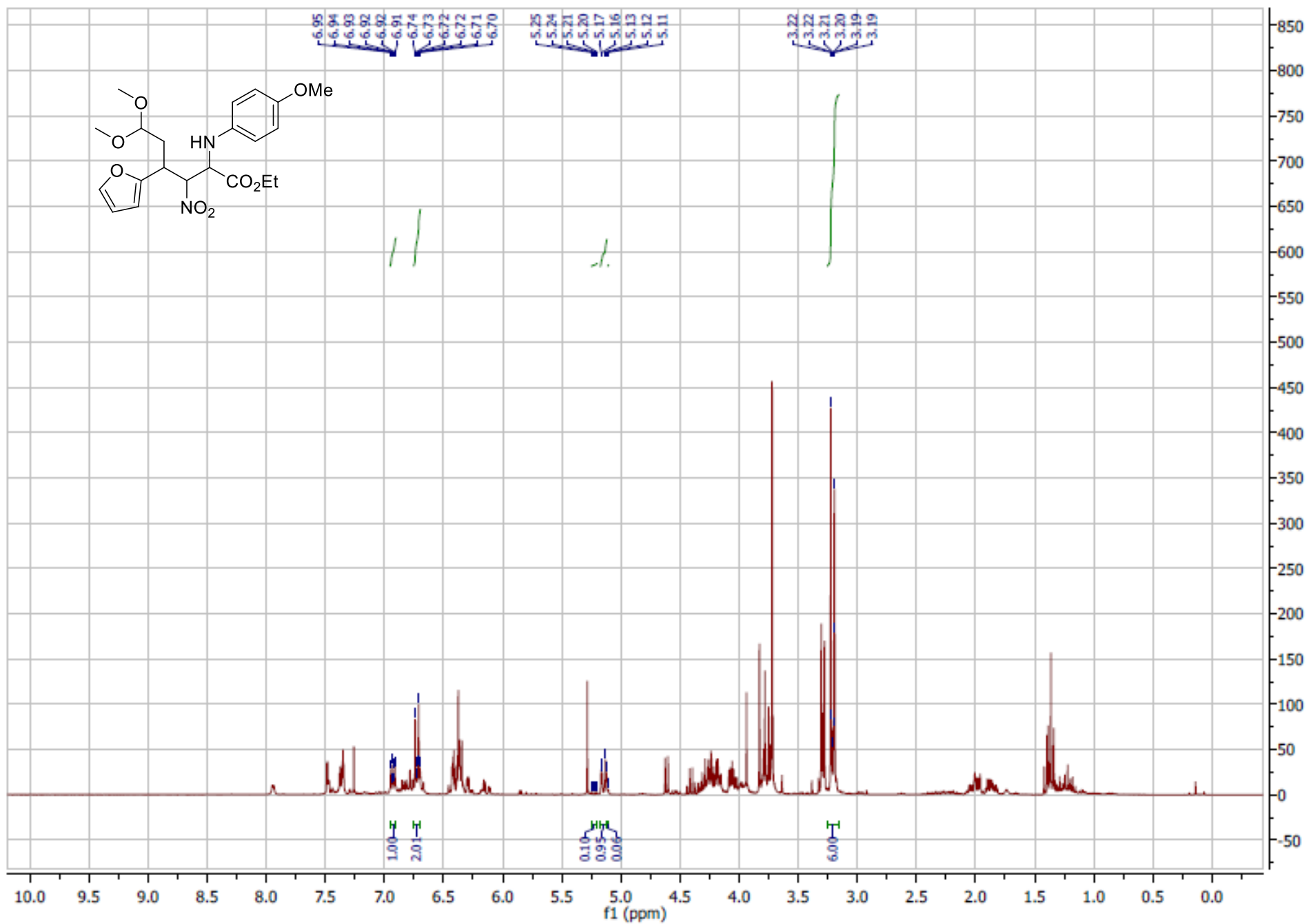
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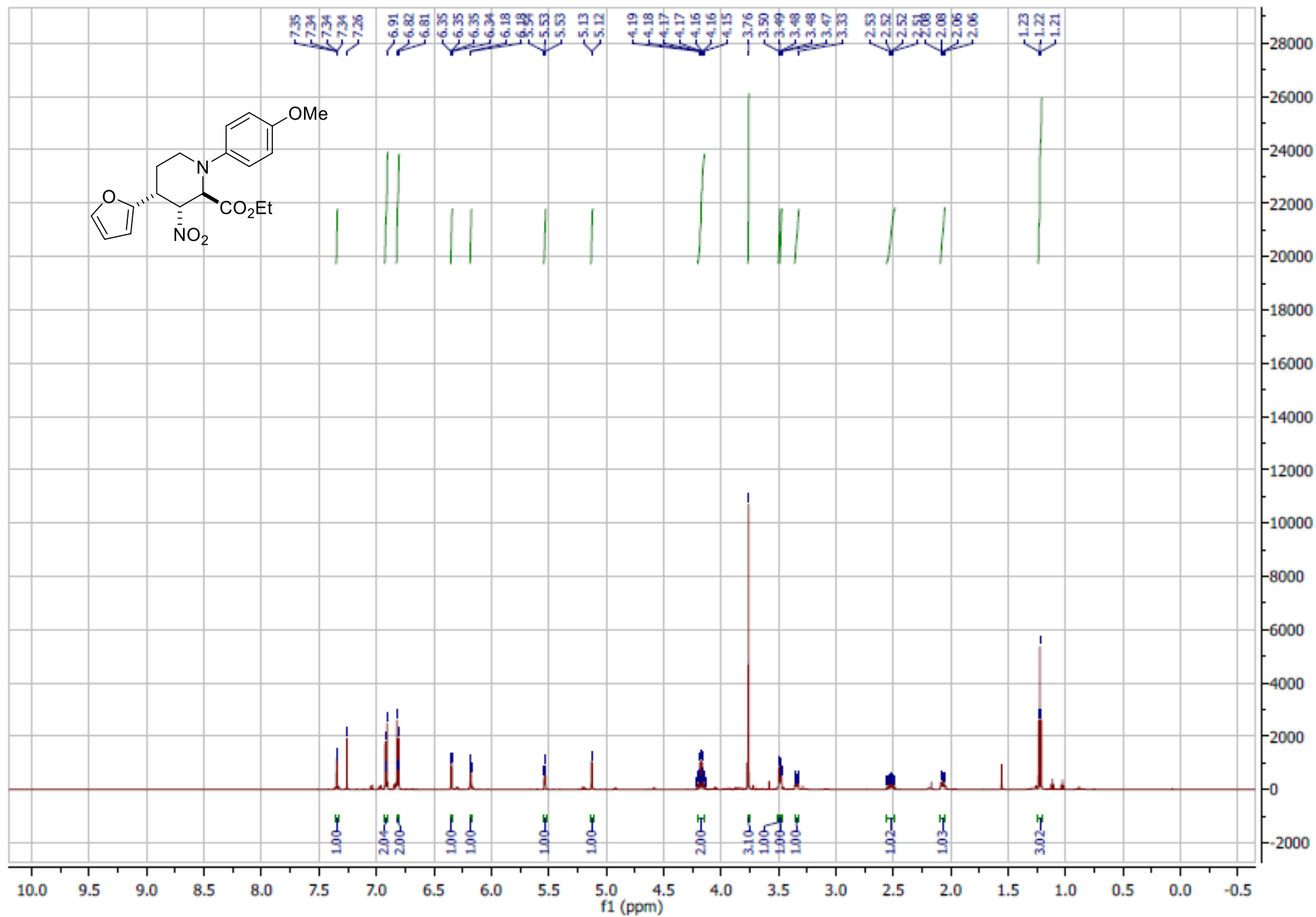
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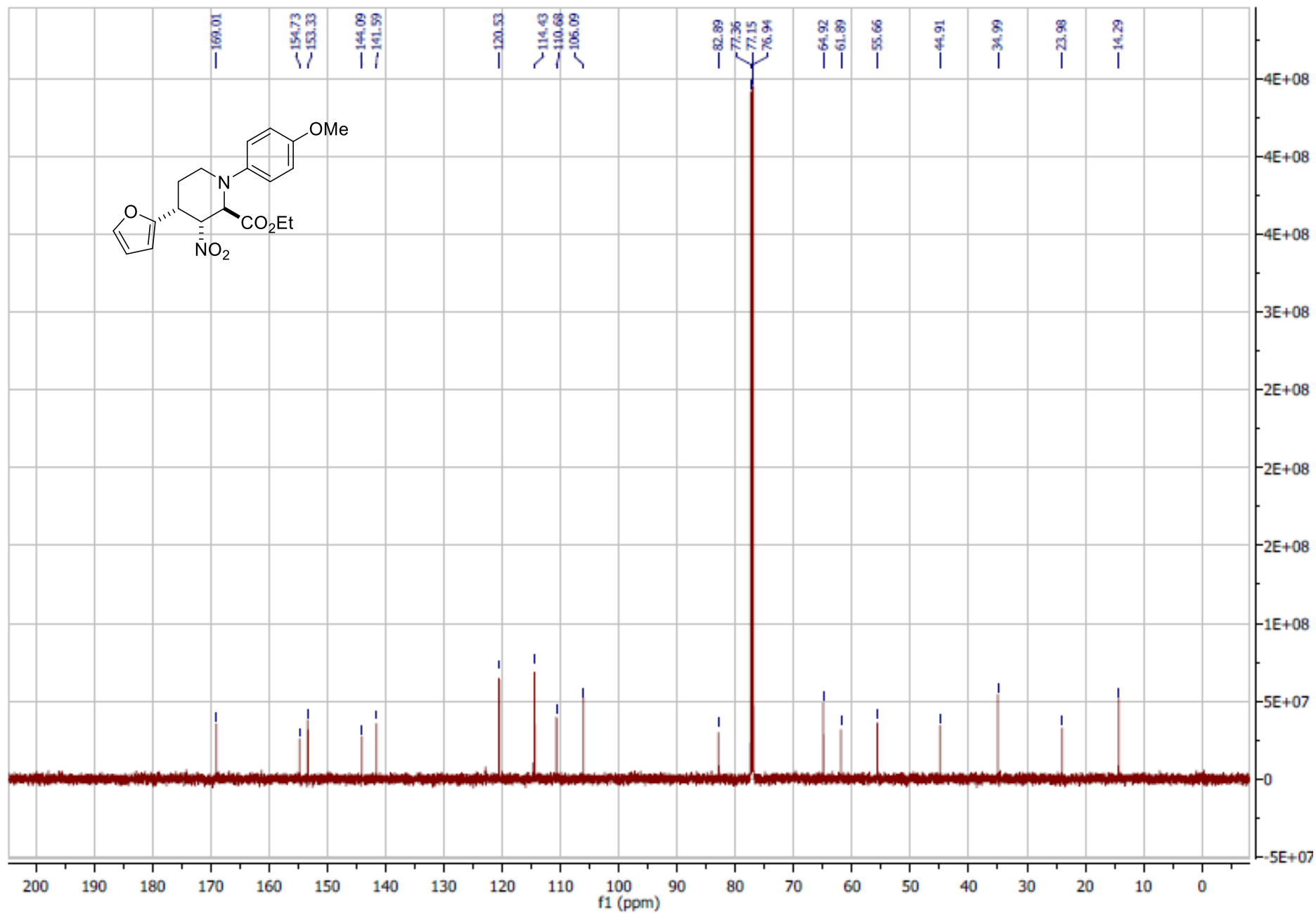
Ethyl 4-(furan-2-yl)-6,6-dimethoxy-2-((4-methoxyphenyl)amino)-3-nitrohexanoate (2j) ¹H NMR for dr calculation



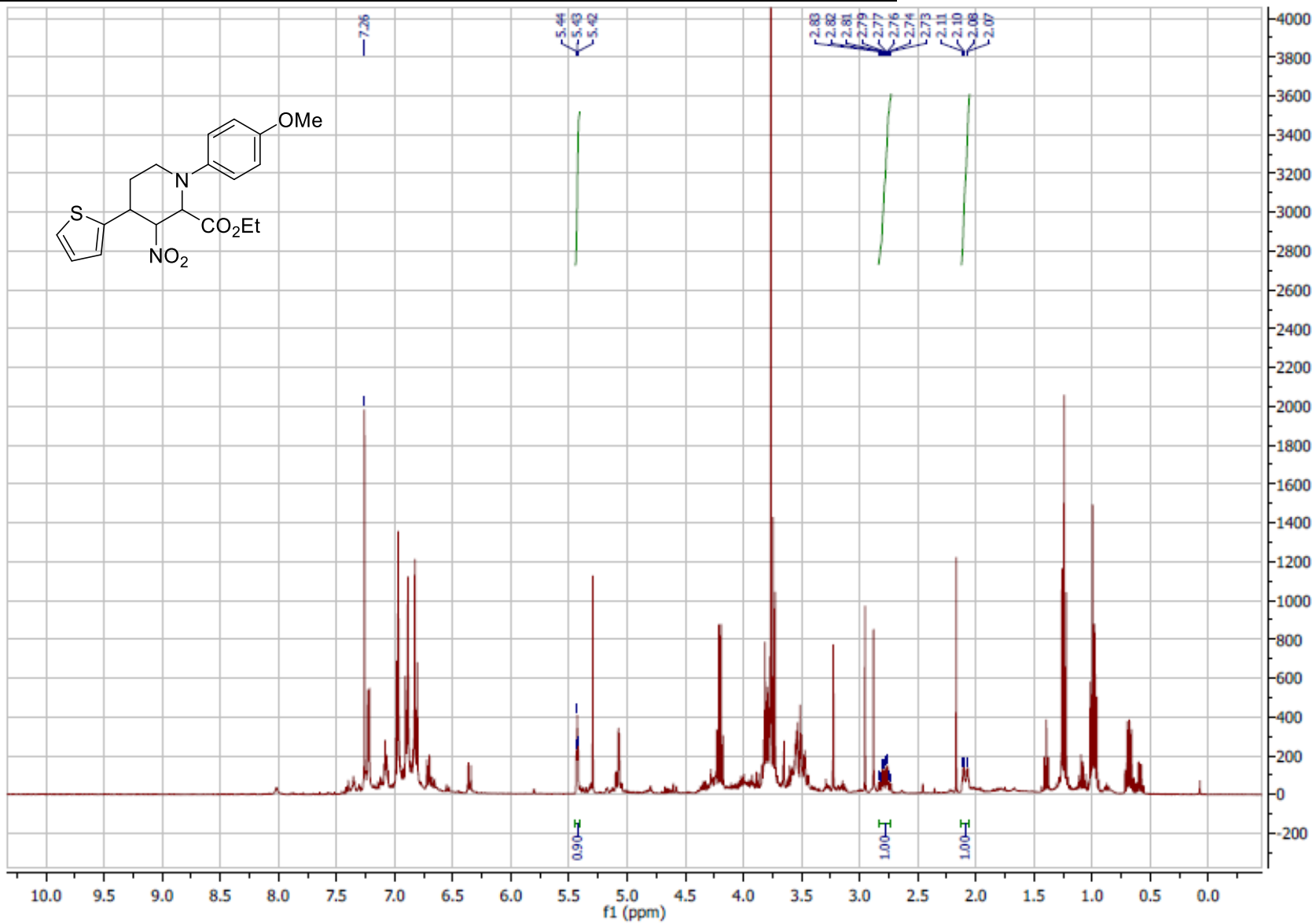
Ethyl 4-(furan-2-yl)-1-(4-methoxyphenyl)-3-nitropiperidine-2-carboxylate (1j) ¹H NMR



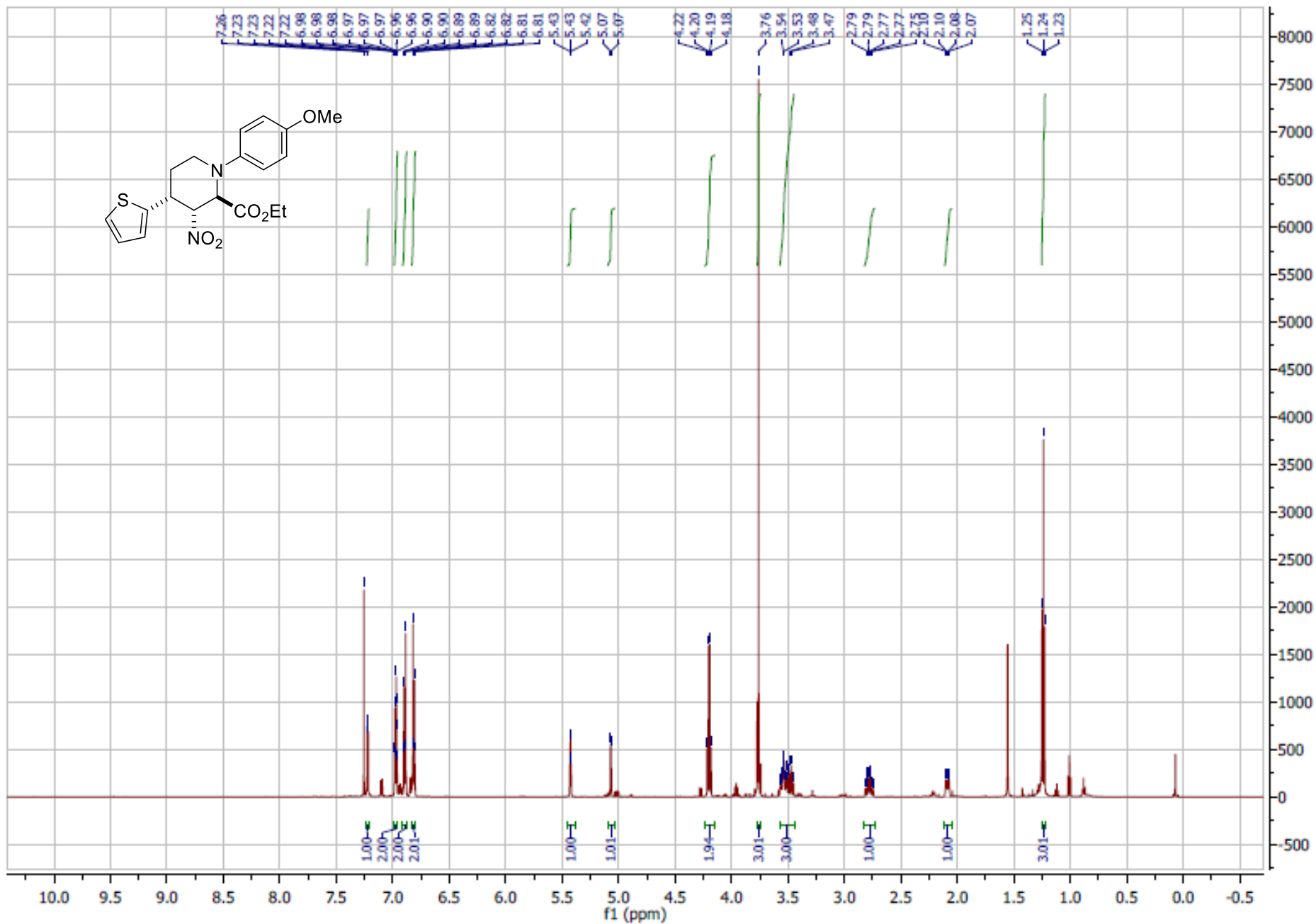
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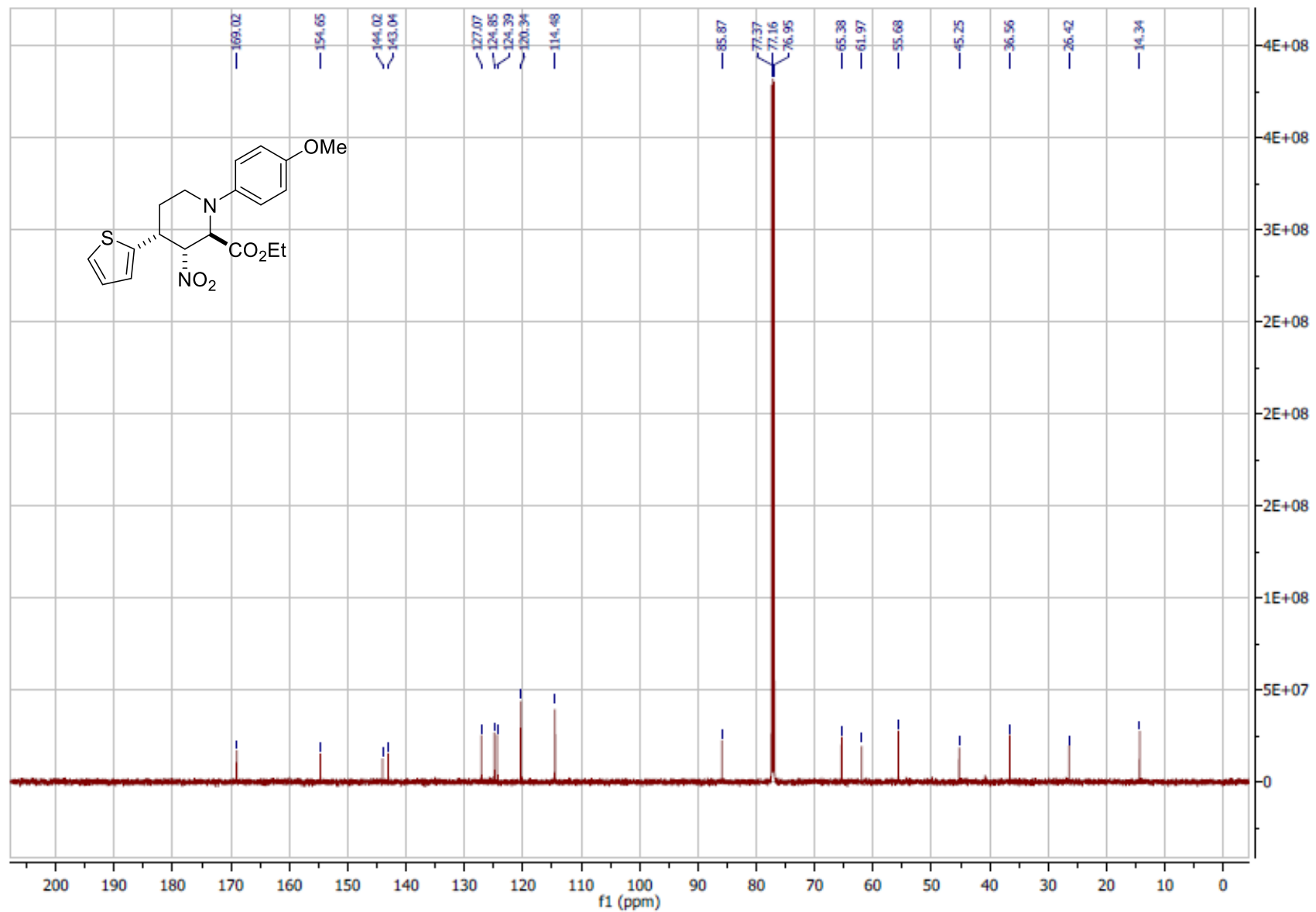
Ethyl 1-(4-methoxyphenyl)-3-nitro-4-(thiophen-2-yl)piperidine-2-carboxylate (2k) ¹H NMR crude for dr calculation



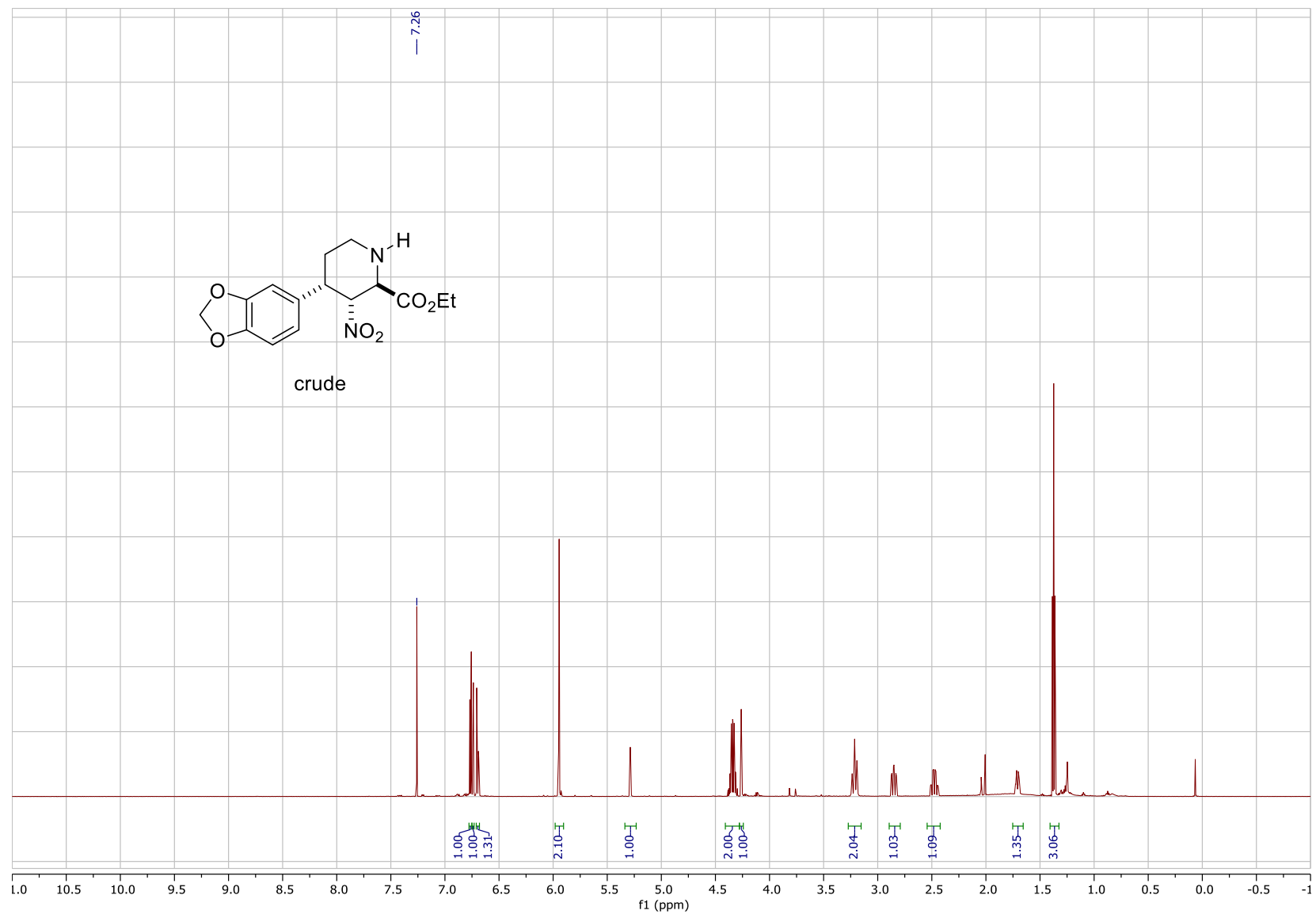
Ethyl 1-(4-methoxyphenyl)-3-nitro-4-(thiophen-2-yl)piperidine-2-carboxylate (1k) ¹H NMR



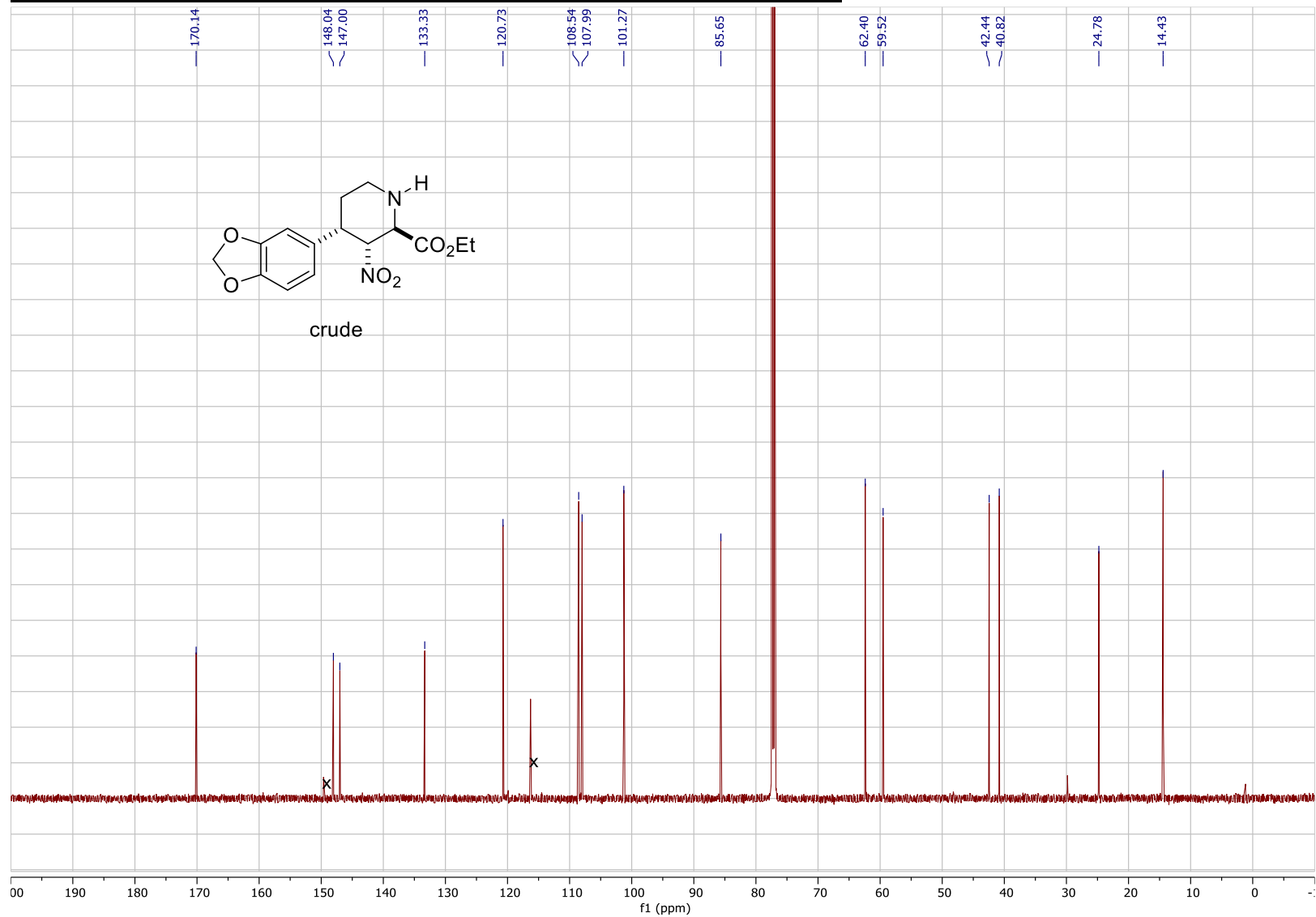
Ethyl 1-(4-methoxyphenyl)-3-nitro-4-(thiophen-2-yl)piperidine-2-carboxylate (2k) ¹³C NMR



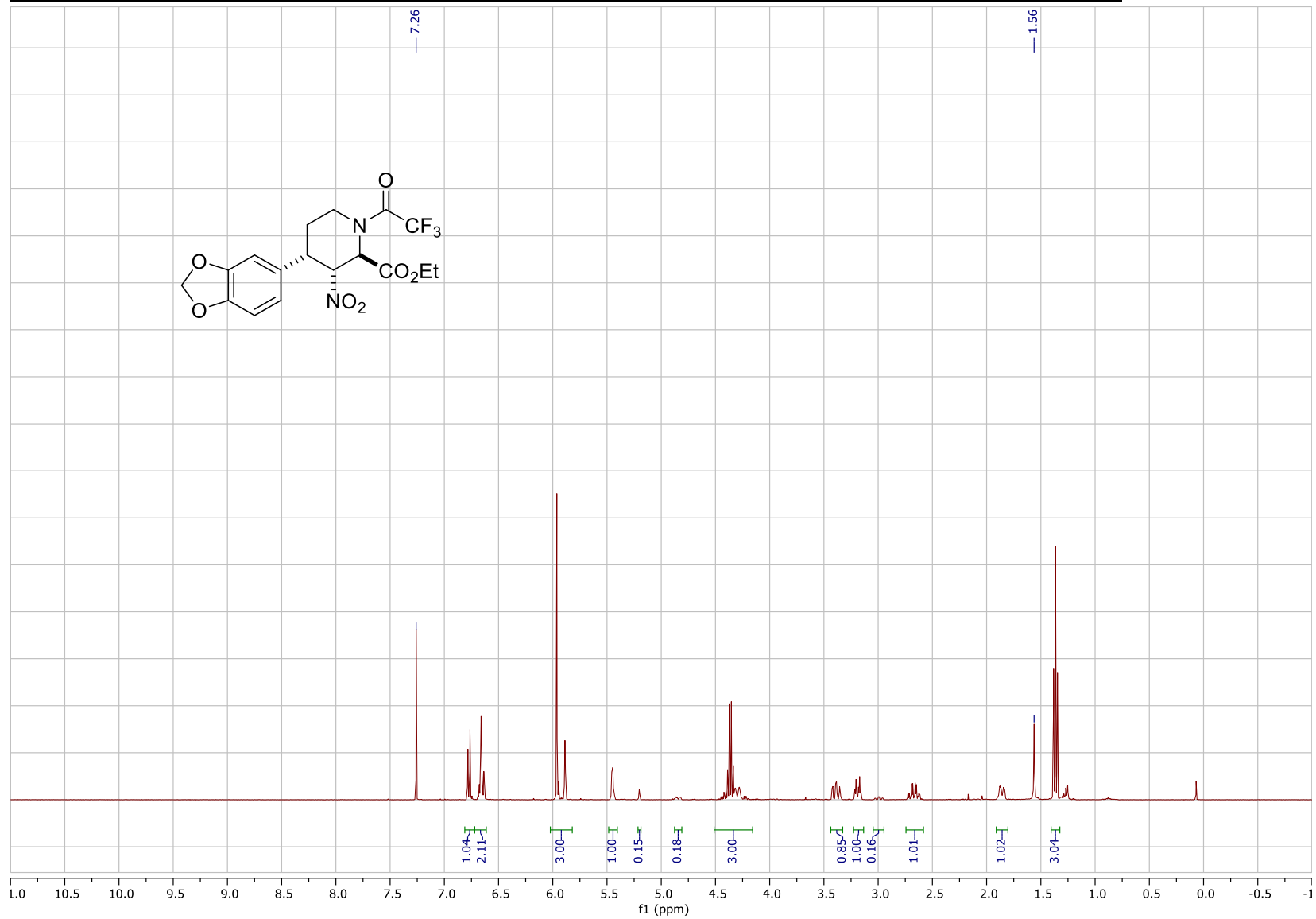
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-3-nitropiperidine-2-carboxylate (9) Crude ¹H NMR



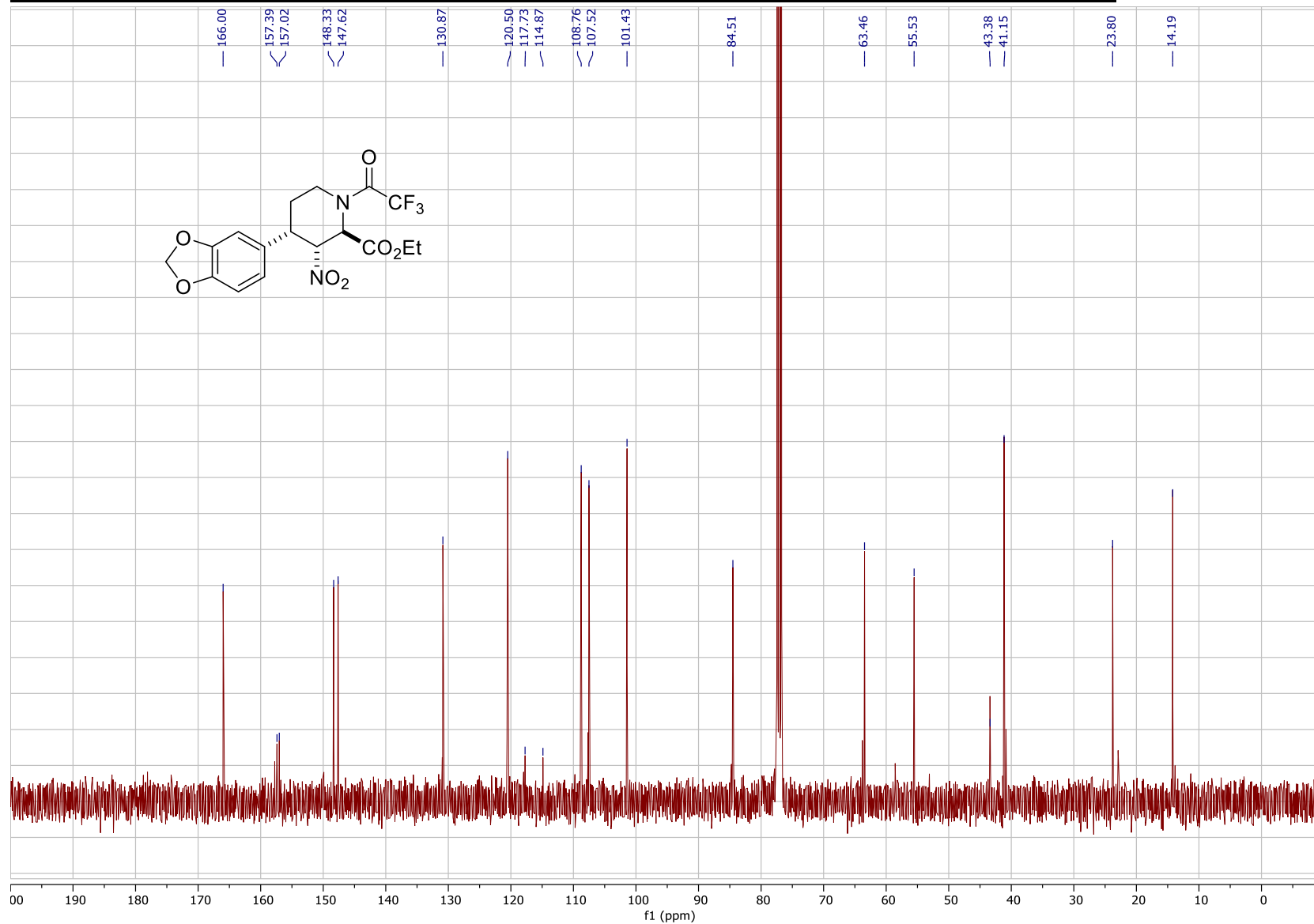
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-3-nitropiperidine-2-carboxylate (9) Crude ¹³C NMR



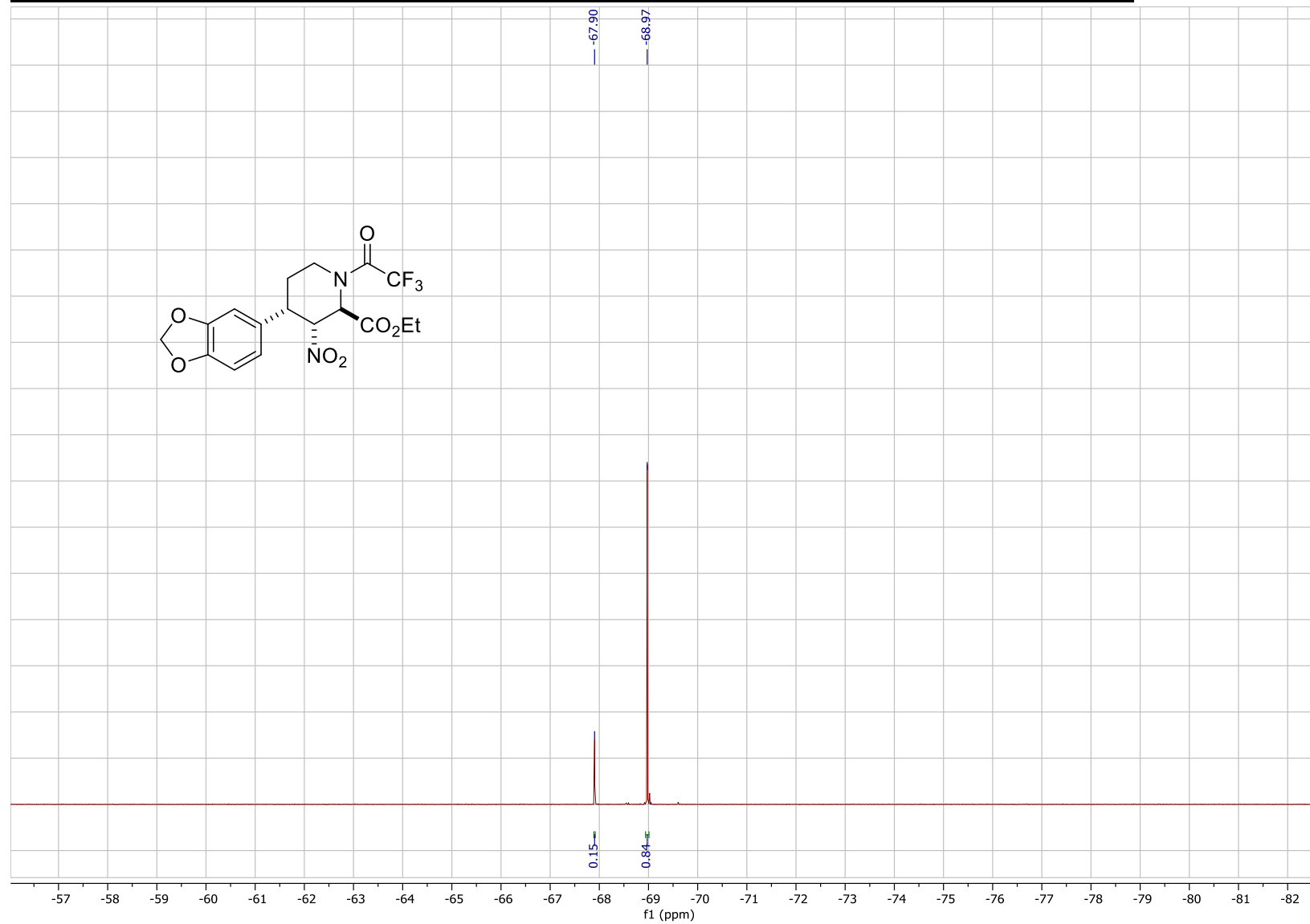
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-3-nitro-1-(2,2,2-trifluoroacetyl)piperidine-2-carboxylate (10) ¹H NMR



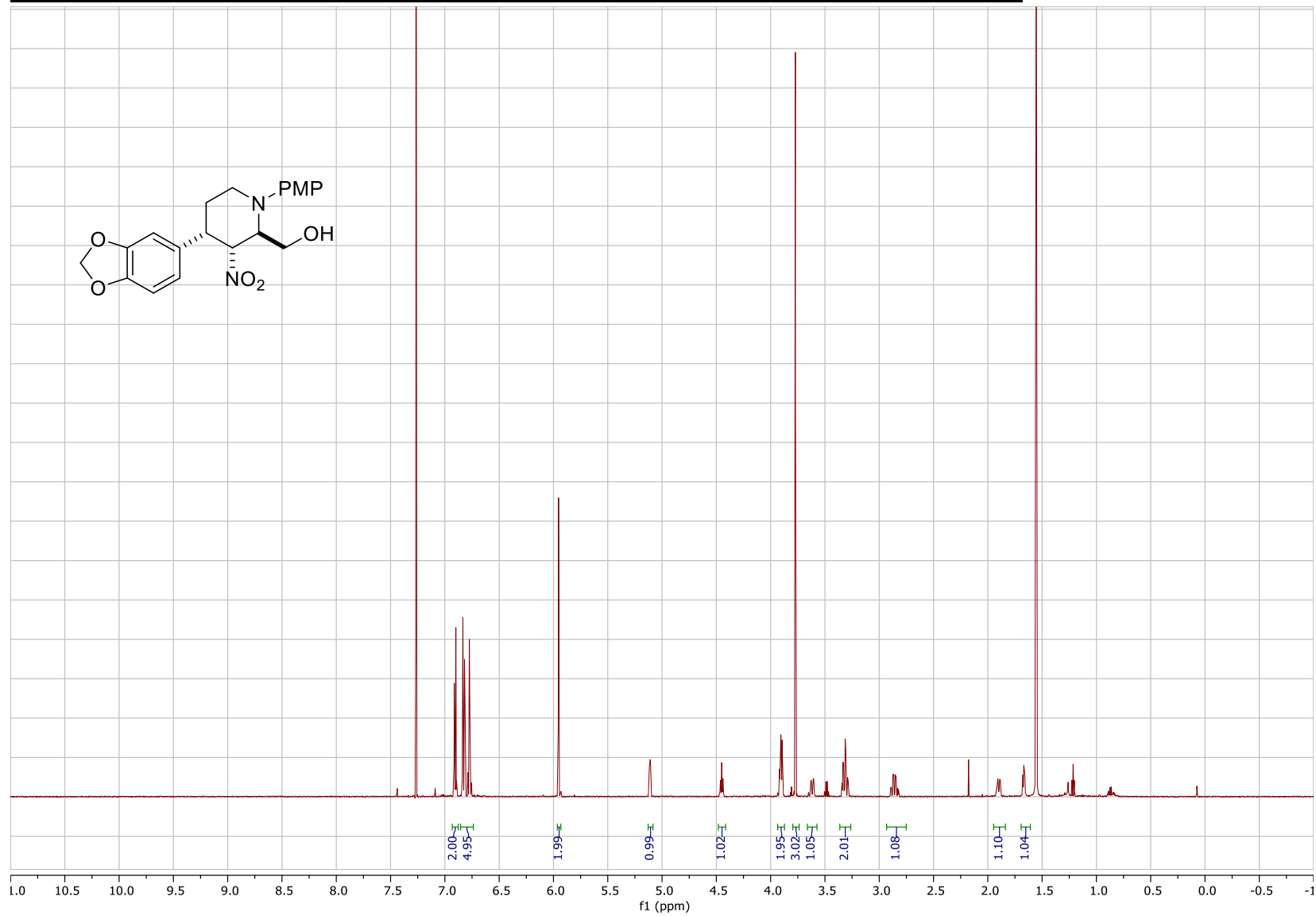
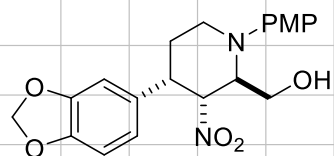
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-3-nitro-1-(2,2,2-trifluoroacetyl)piperidine-2-carboxylate (10) ¹³C NMR



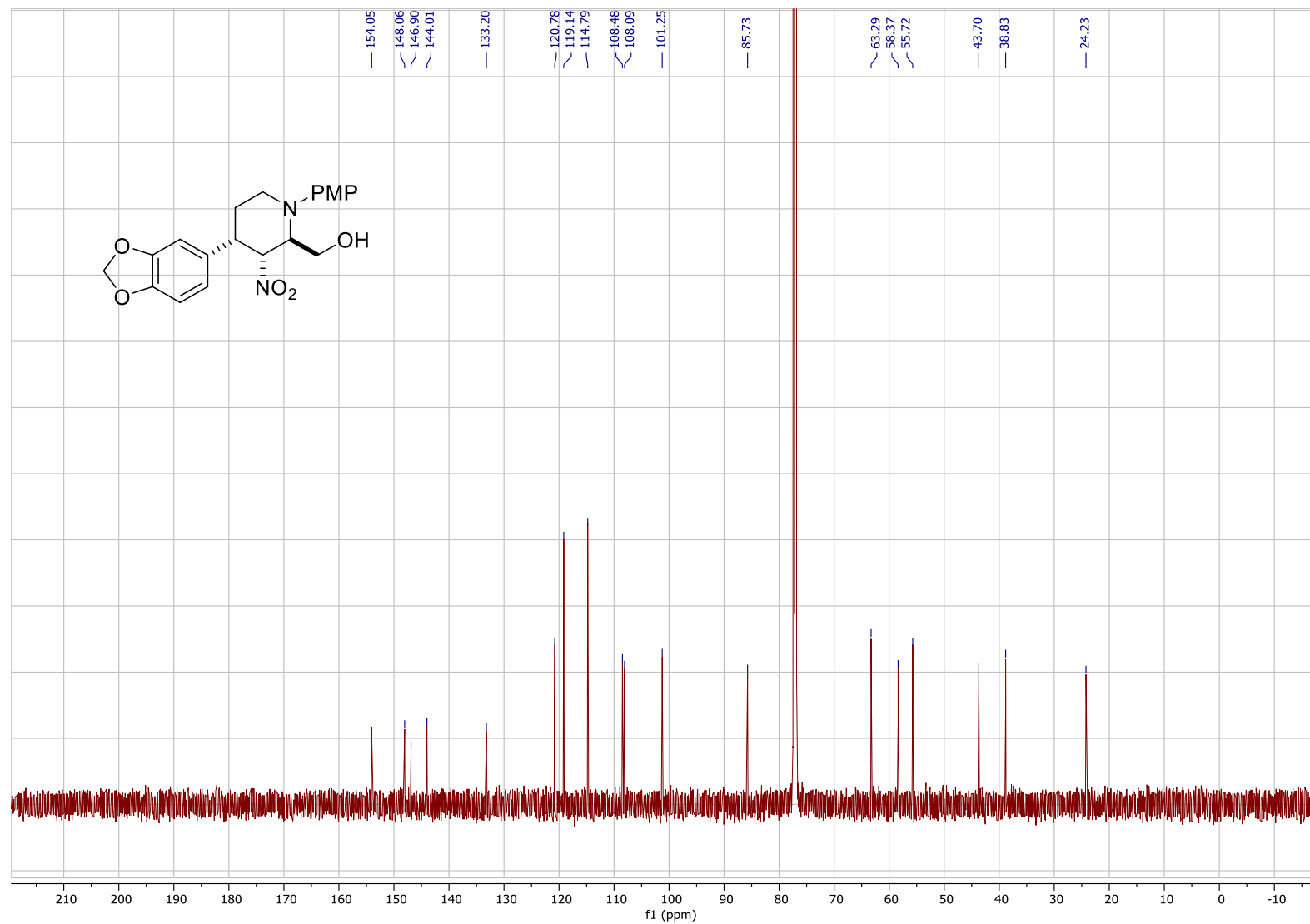
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-3-nitro-1-(2,2,2-trifluoroacetyl)piperidine-2-carboxylate (10) ¹⁹F NMR



4-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)-3-nitropiperidin-2-yl)-methanol (11) 1H NMR

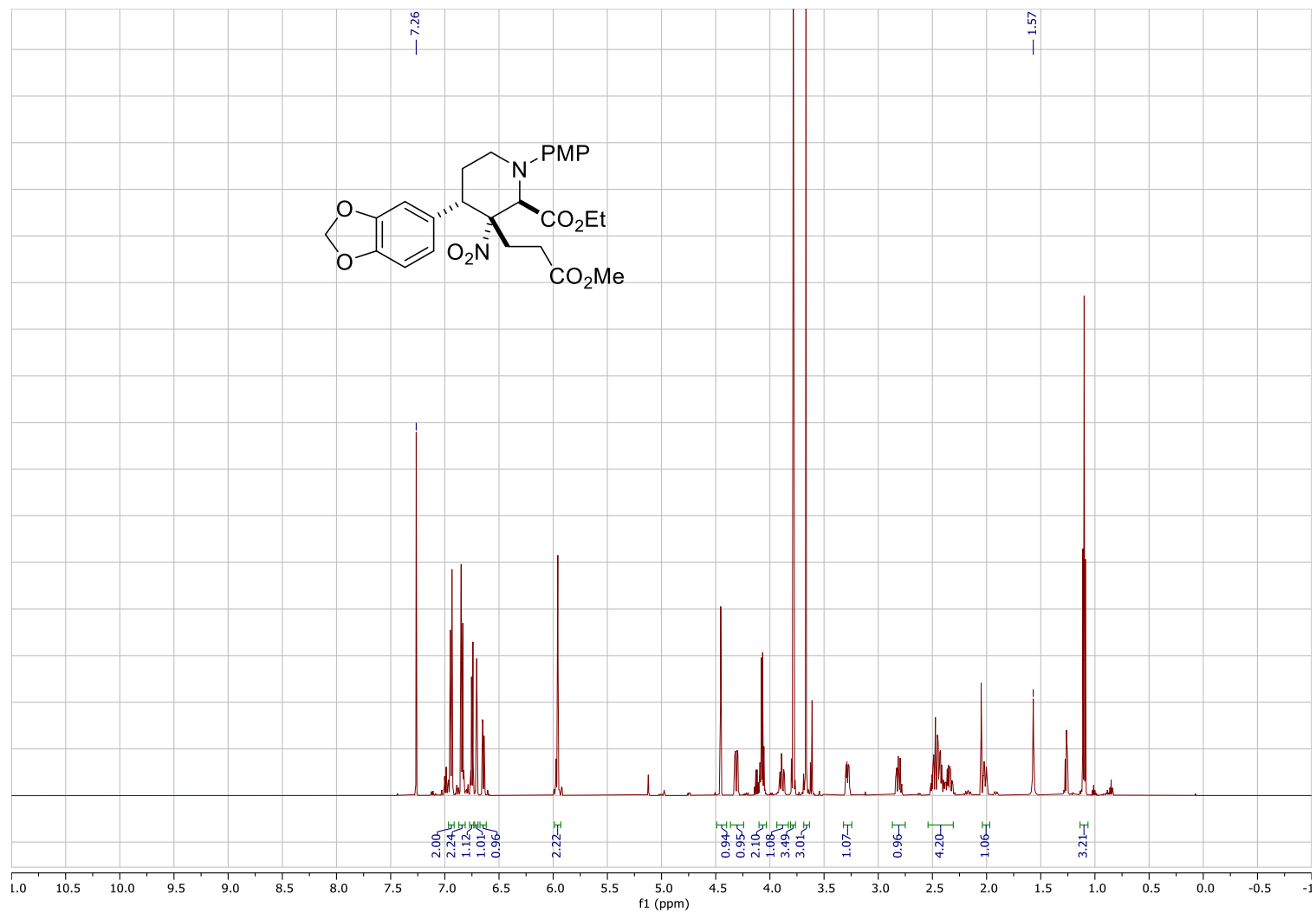


4-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)-3-nitropiperidin-2-yl)-methanol (11) ¹³C NMR



Ethyl-4-(benzo[d][1,3]dioxol-5-yl)-3-(3-methoxy-3-oxopropyl)-1-(4-methoxy-phenyl)-3-nitropiperidine-2-carboxylate (12)

¹H NMR



Ethyl-4-(benzo[d][1,3]dioxol-5-yl)-3-(3-methoxy-3-oxopropyl)-1-(4-methoxy-phenyl)-3-nitropiperidine-2-carboxylate (12)

¹³C NMR

