

Supporting Information for

Copper-catalyzed [3+2]-cycloaddition of α -halonitroalkenes with azomethine ylides: facile synthesis of multisubstituted pyrrolidines and pyrroles

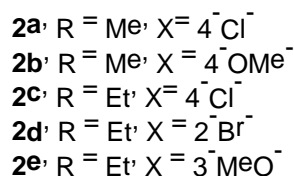
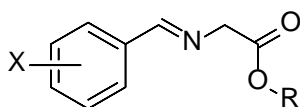
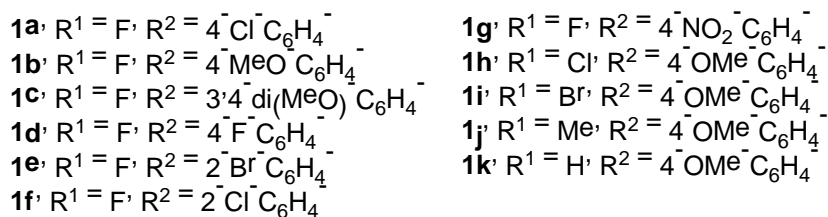
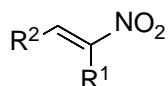
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^b*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, Moscow, 119991, Russia.*

^c*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119991, Russia.*

Starting compounds were prepared according to literature procedures: fluoronitroalkenes **1a-1e,g**,^{s1} **1f**,^{s2} other nitroalkenes: **1h**,^{s3} **1i**,^{s4} **1j**,^{s5} **1k**,^{s6} Schiff bases **2**.^{s7}



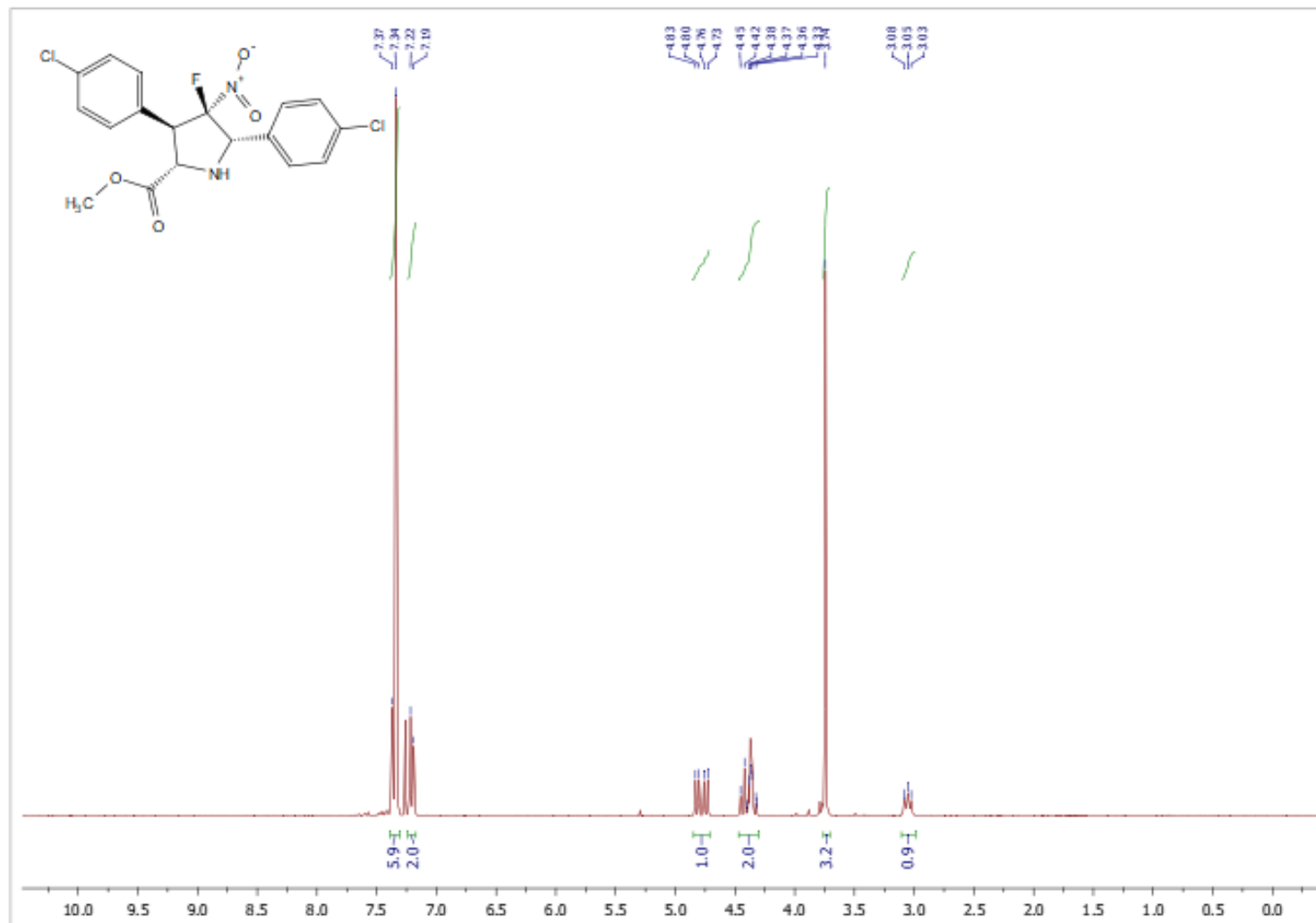
References

- s1. V. A. Motornov, V. M. Muzalevskiy, A. A. Tabolin, R. A. Novikov, Yu. V. Nelyubina, V. G. Nenajdenko and S. L. Ioffe, *J. Org. Chem.* 2017, **82**, 5274.
- s2. V. A. Motornov, A. A. Tabolin, R. A. Novikov, Yu. V. Nelyubina, S. L. Ioffe, I. S. Smolyar and V. G. Nenajdenko, *Eur. J. Org. Chem.*, 2017, 6851.
- s3. A. A. Fadeeva, S. L. Ioffe and A. A. Tabolin, *Synthesis*, 2020, **52**, 2679.
- s4. K. Huang, Q. Ma, X. Shen, L. Gong and E. Meggers, *Asian J. Org. Chem.*, 2016, **5**, 1198.
- s5. A. A. Tabolin, Yu. A. Khomutova, Yu. V. Nelyubina, S. L. Ioffe and V. A. Tartakovsky, *Synthesis*, 2011, 2415.
- s6. V. Ashokkumar and A. Siva, *Org. Biomol. Chem.*, 2015, **13**, 10216.
- s7. R. Lasch and M. R. Heinrich, *Tetrahedron*, 2015, **71**, 4282.

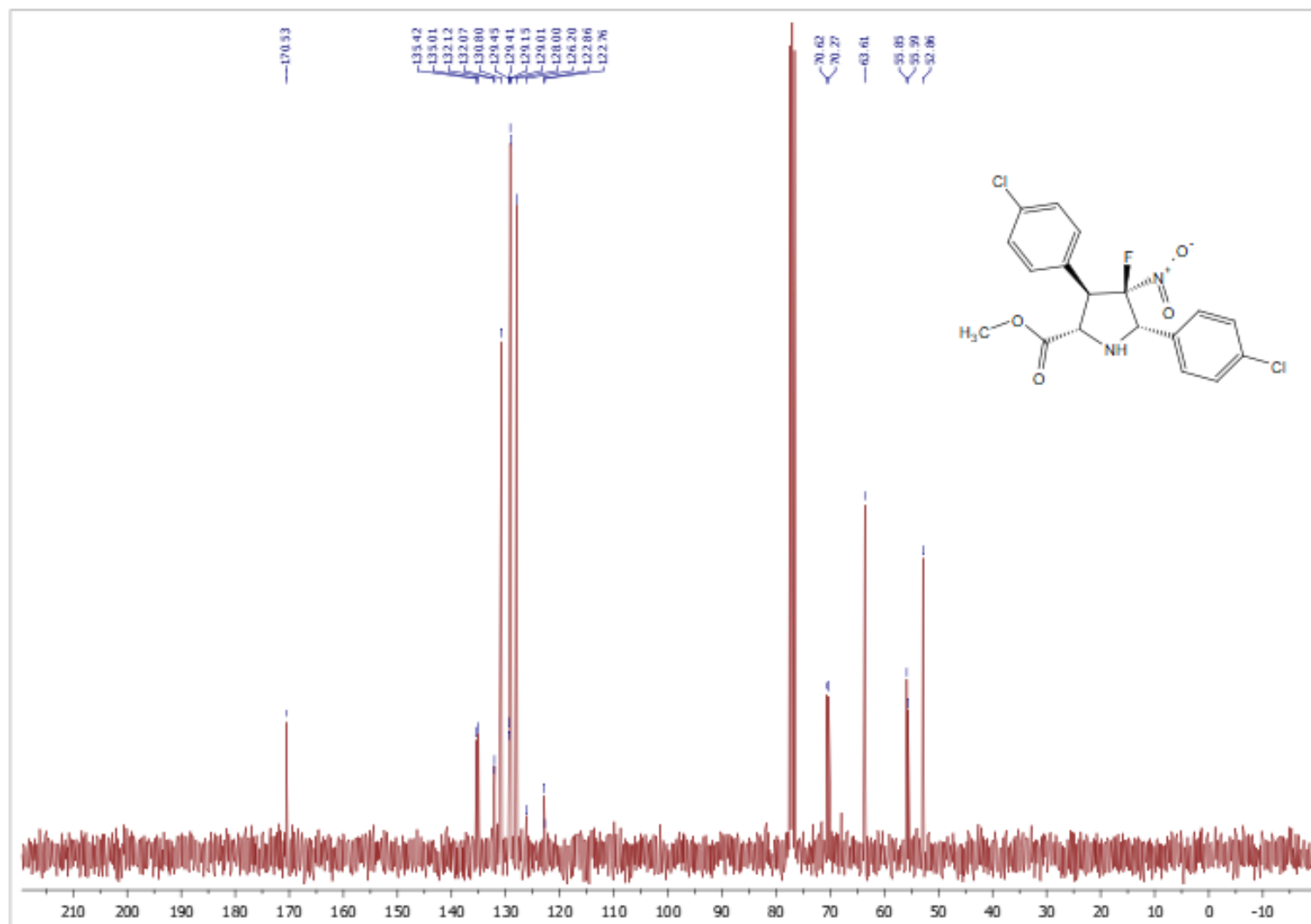
Copies of ^1H , ^{13}C and ^{19}F NMR spectra

methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3,5-bis(4-chlorophenyl)-pyrrolidine-2-carboxylate **3a**

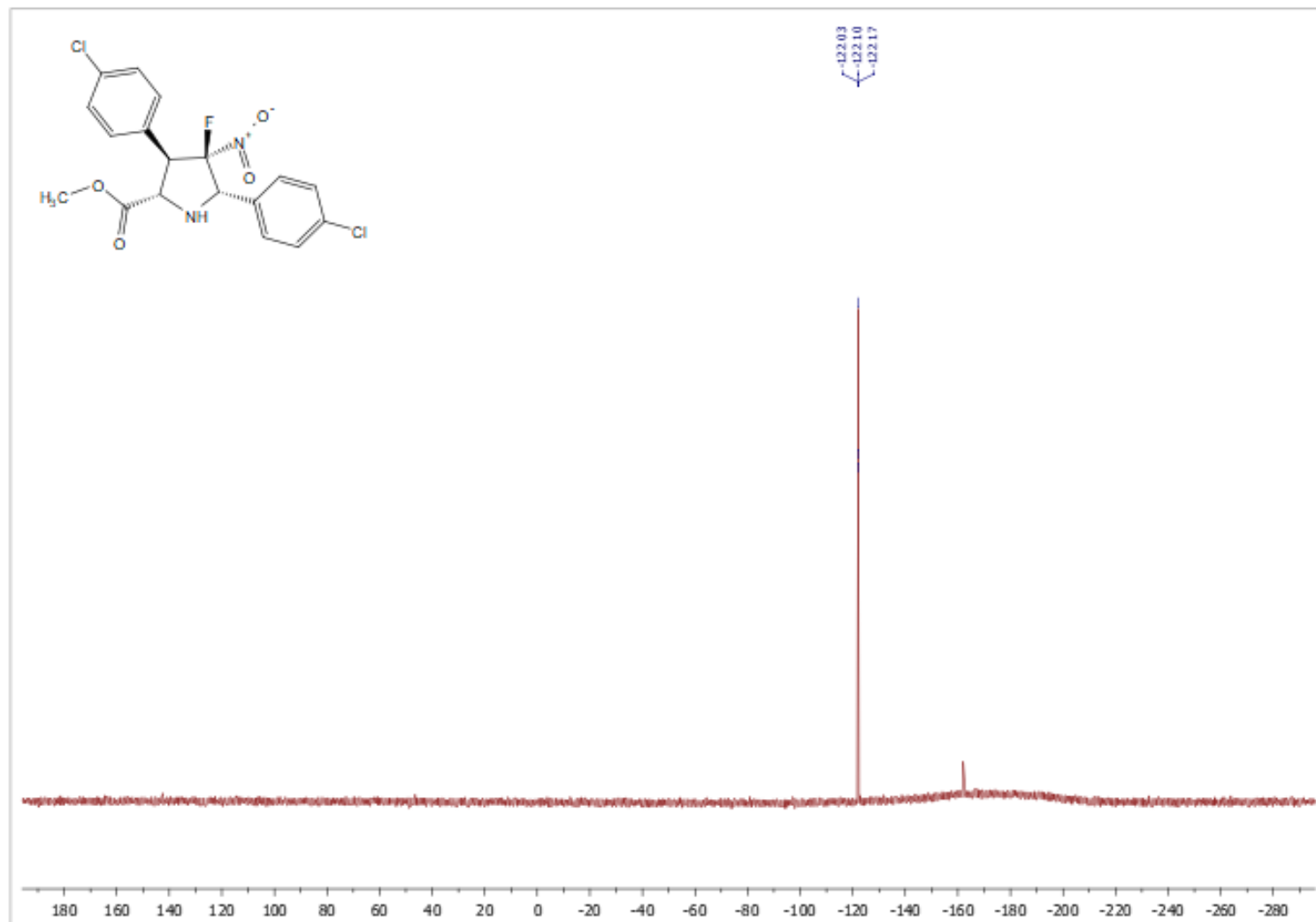
^1H NMR



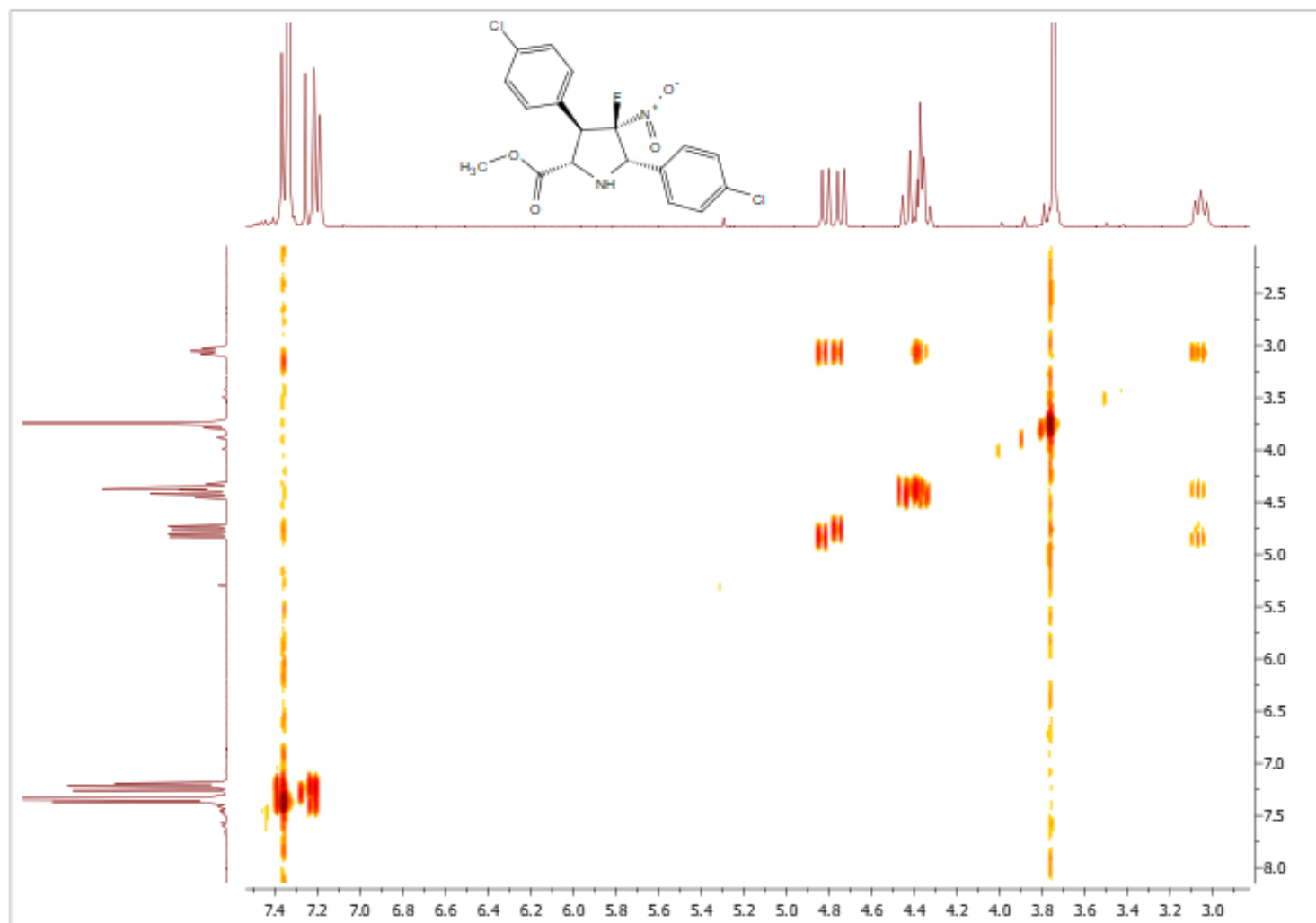
^{13}C NMR



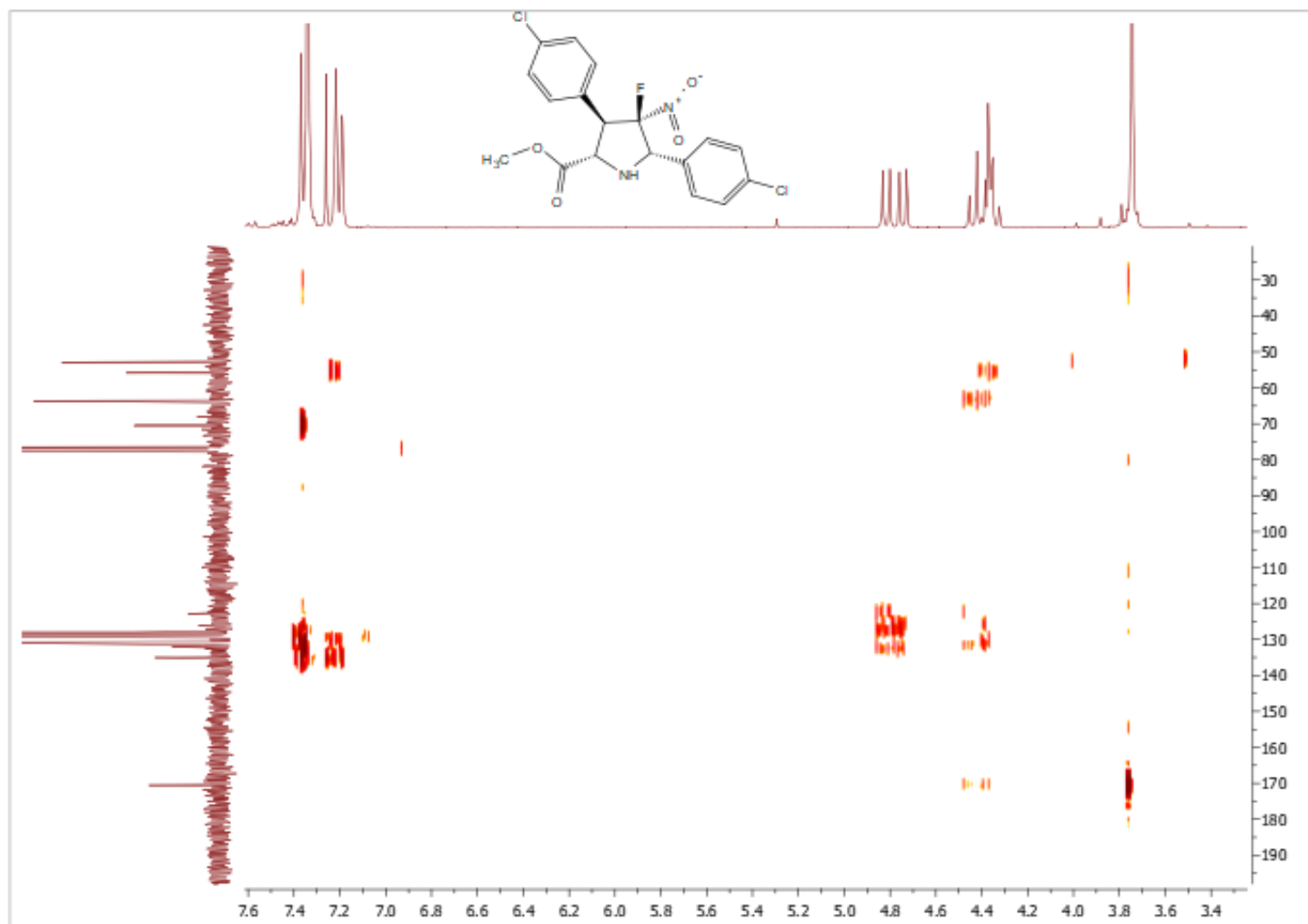
^{19}F NMR



^1H - ^1H COSY NMR

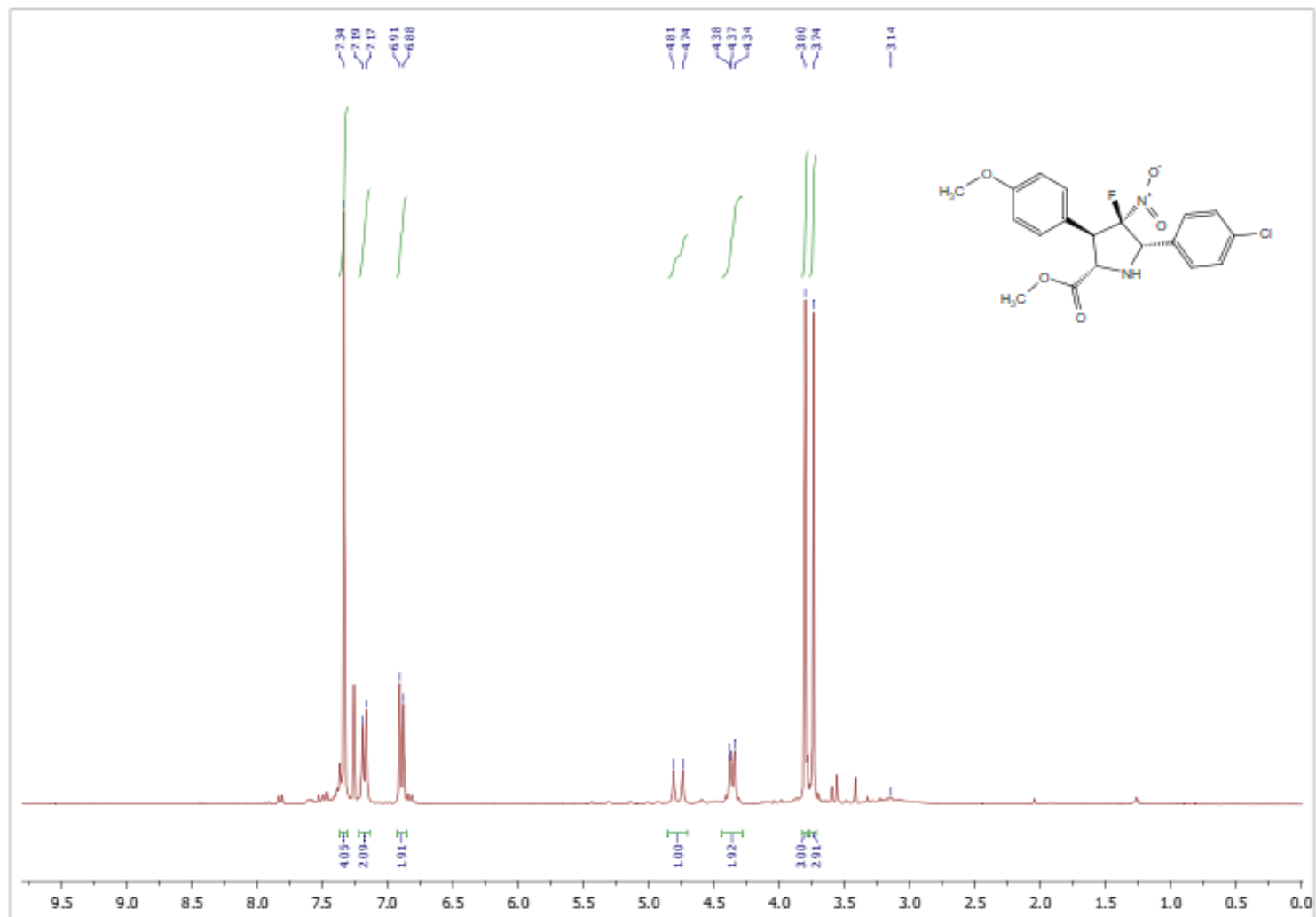


^1H - ^{13}C HMBC NMR

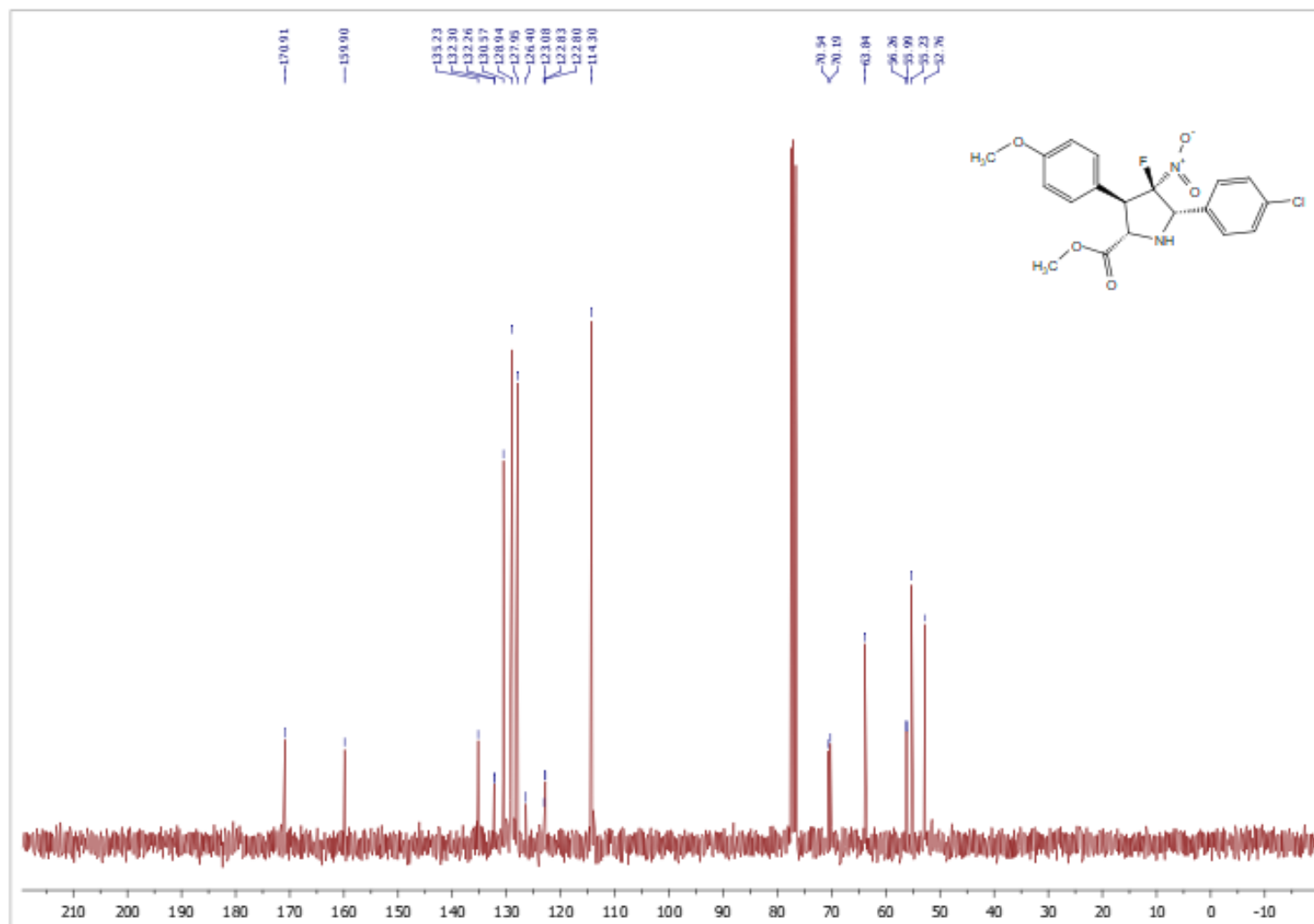


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3b**

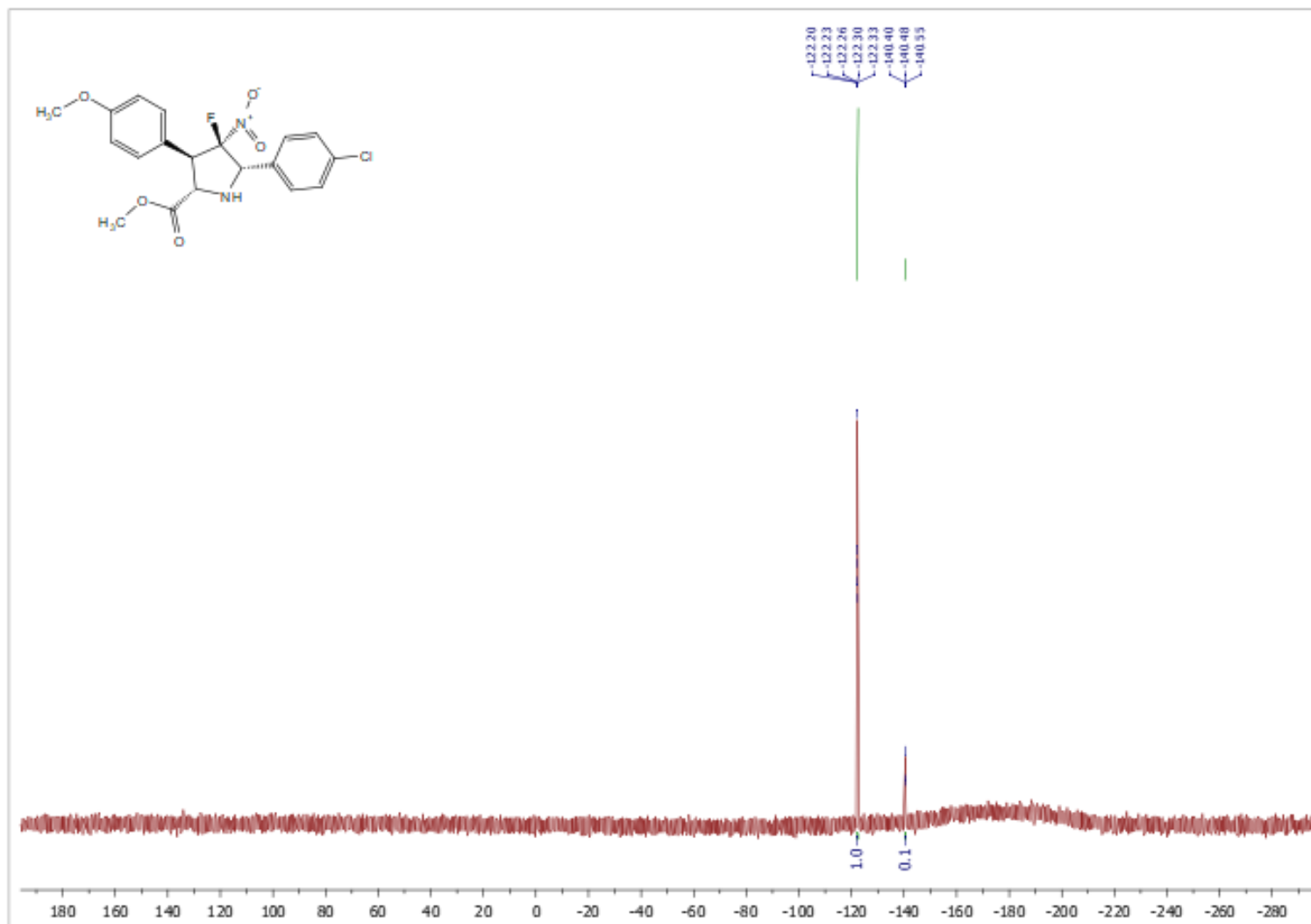
¹H NMR



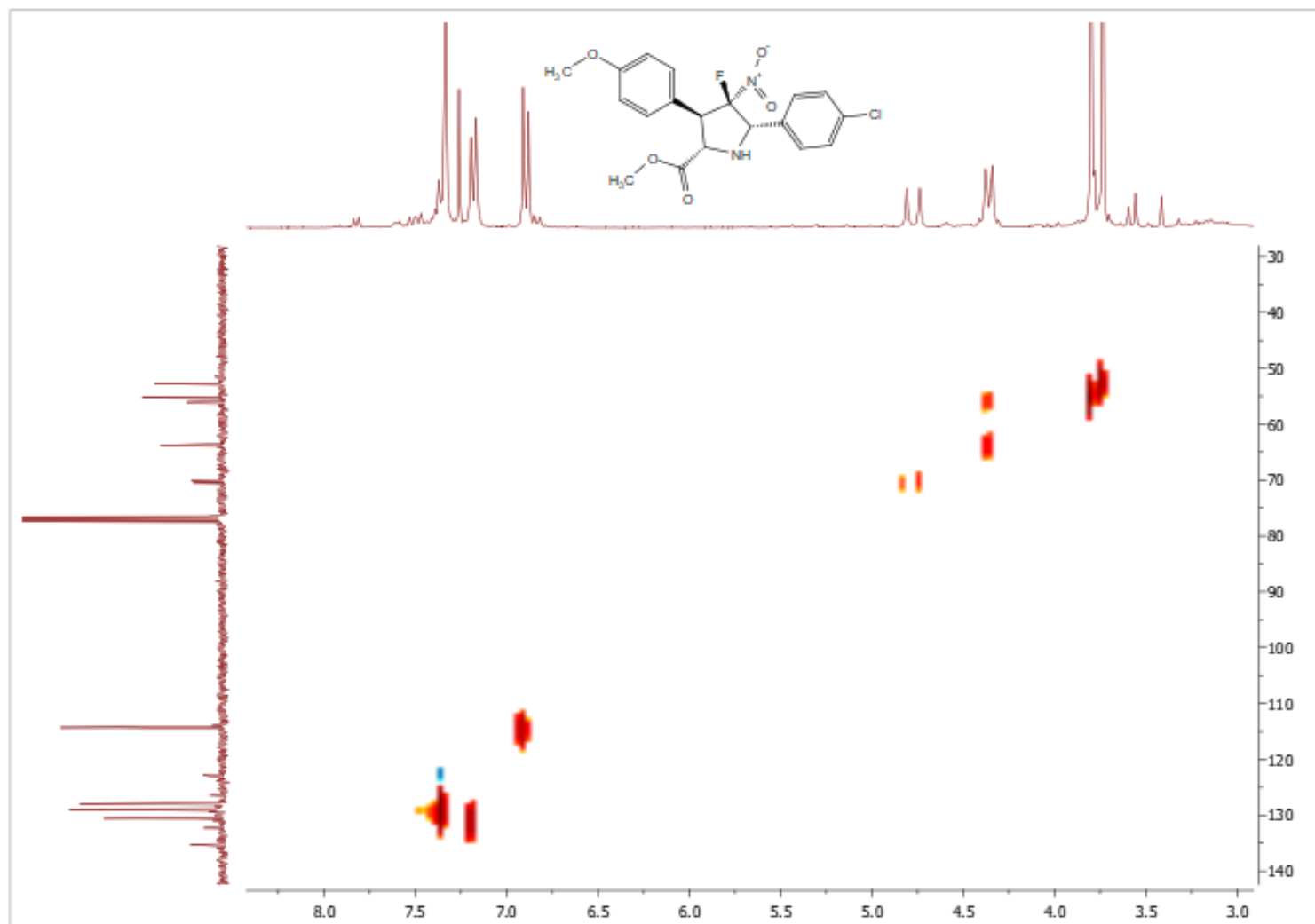
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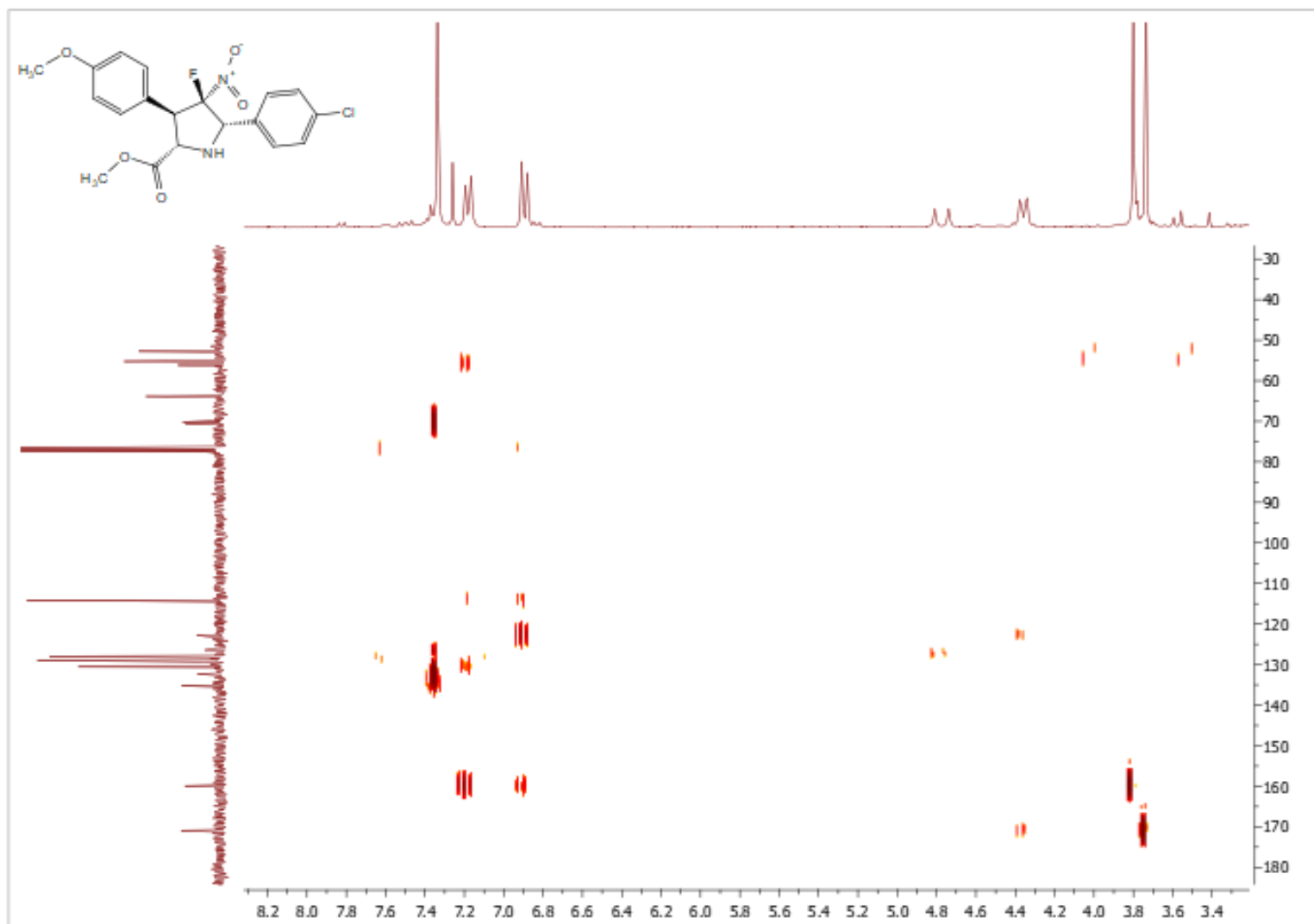
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^1H - ^{13}C HSQC NMR

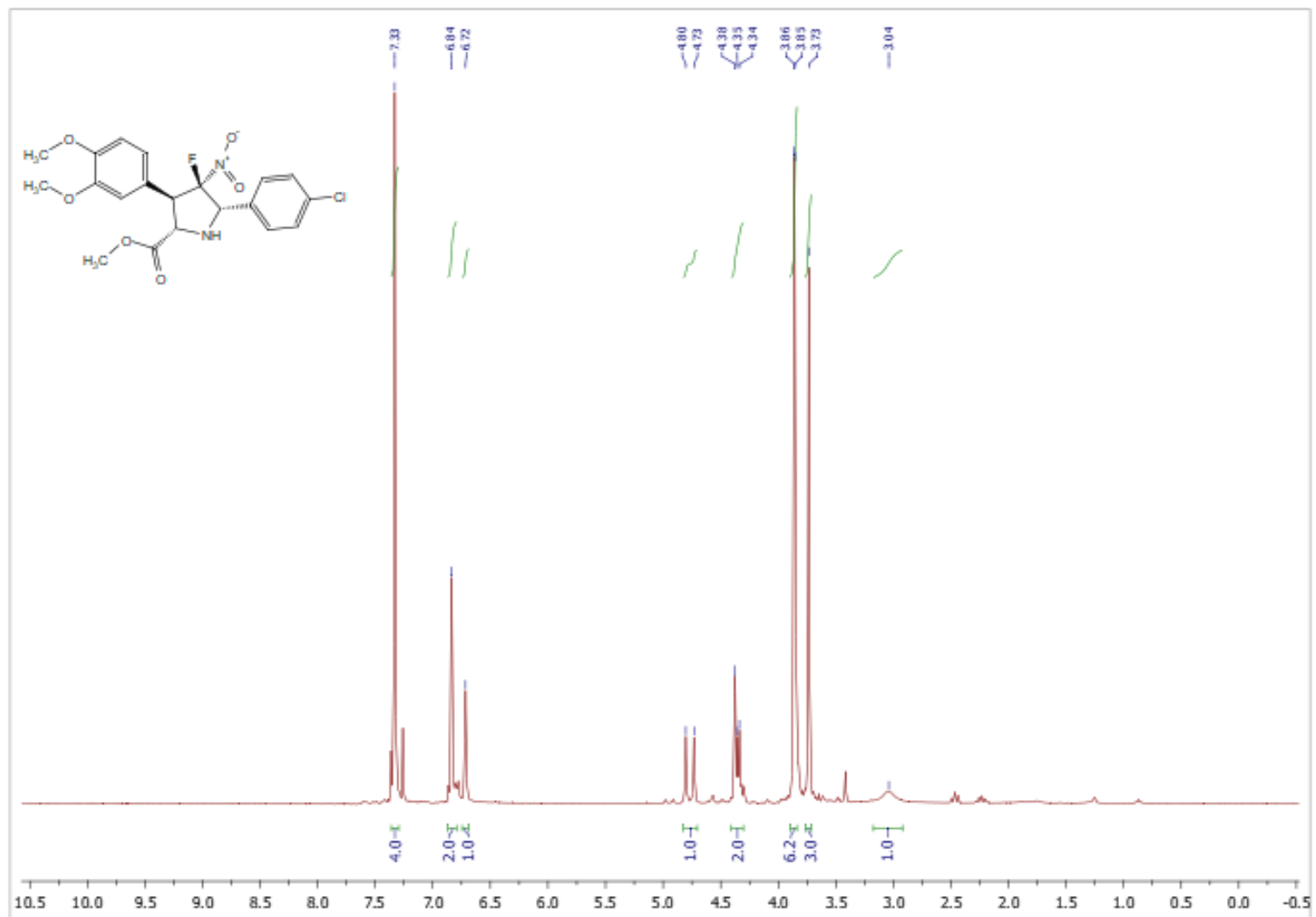


^1H - ^{13}C HMBC NMR

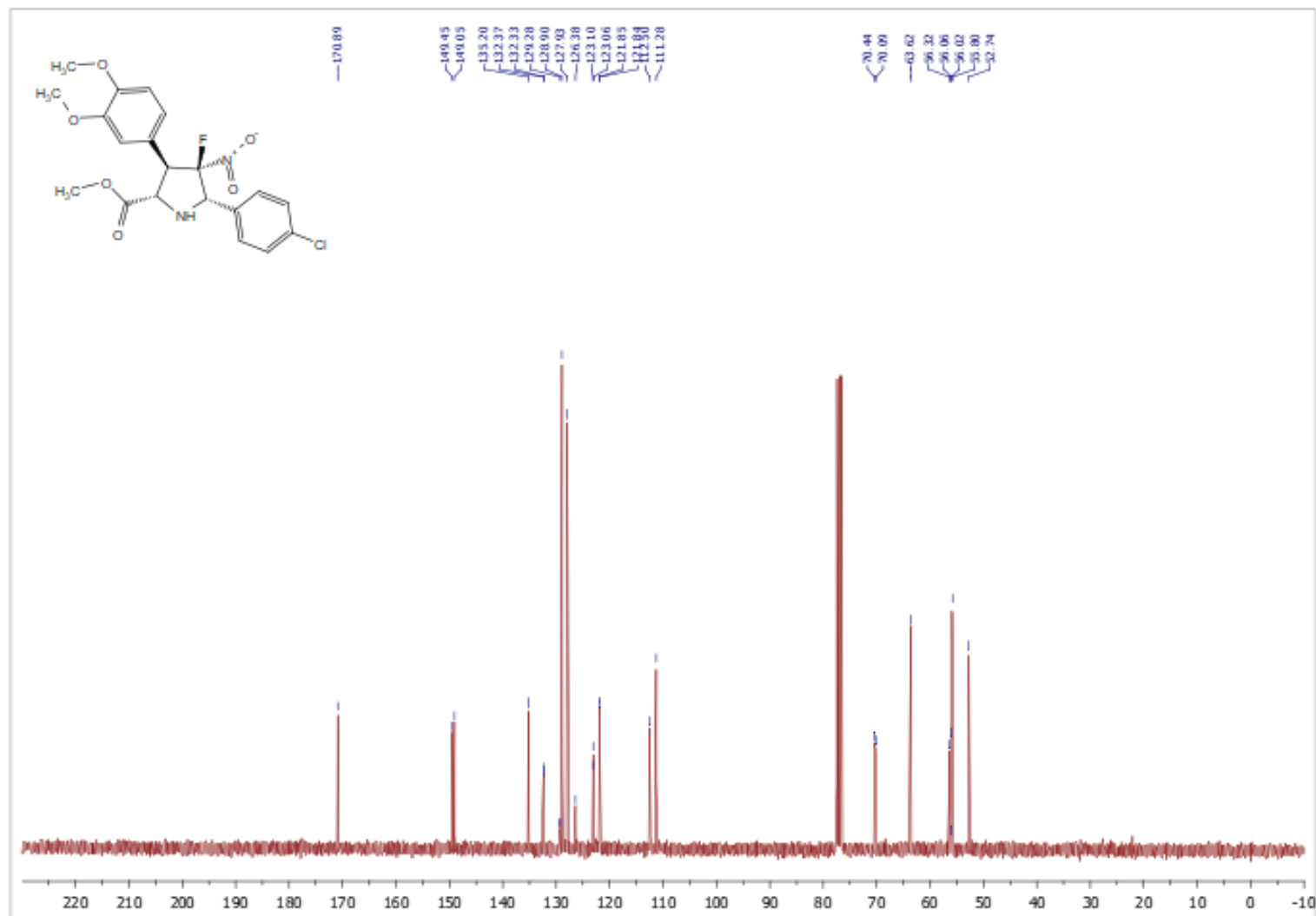


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(3,4-dimethoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3c**

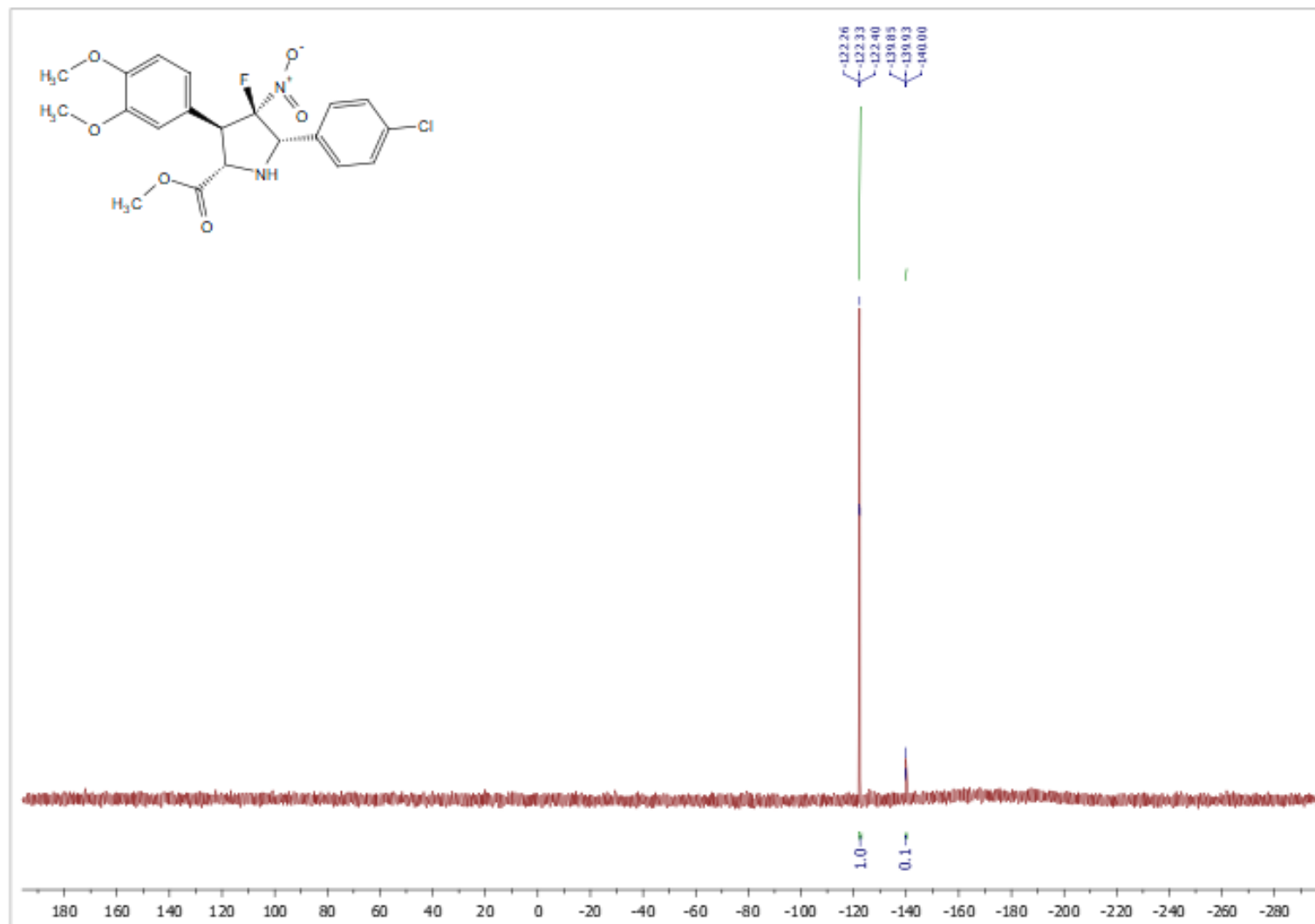
¹H NMR



^{13}C NMR

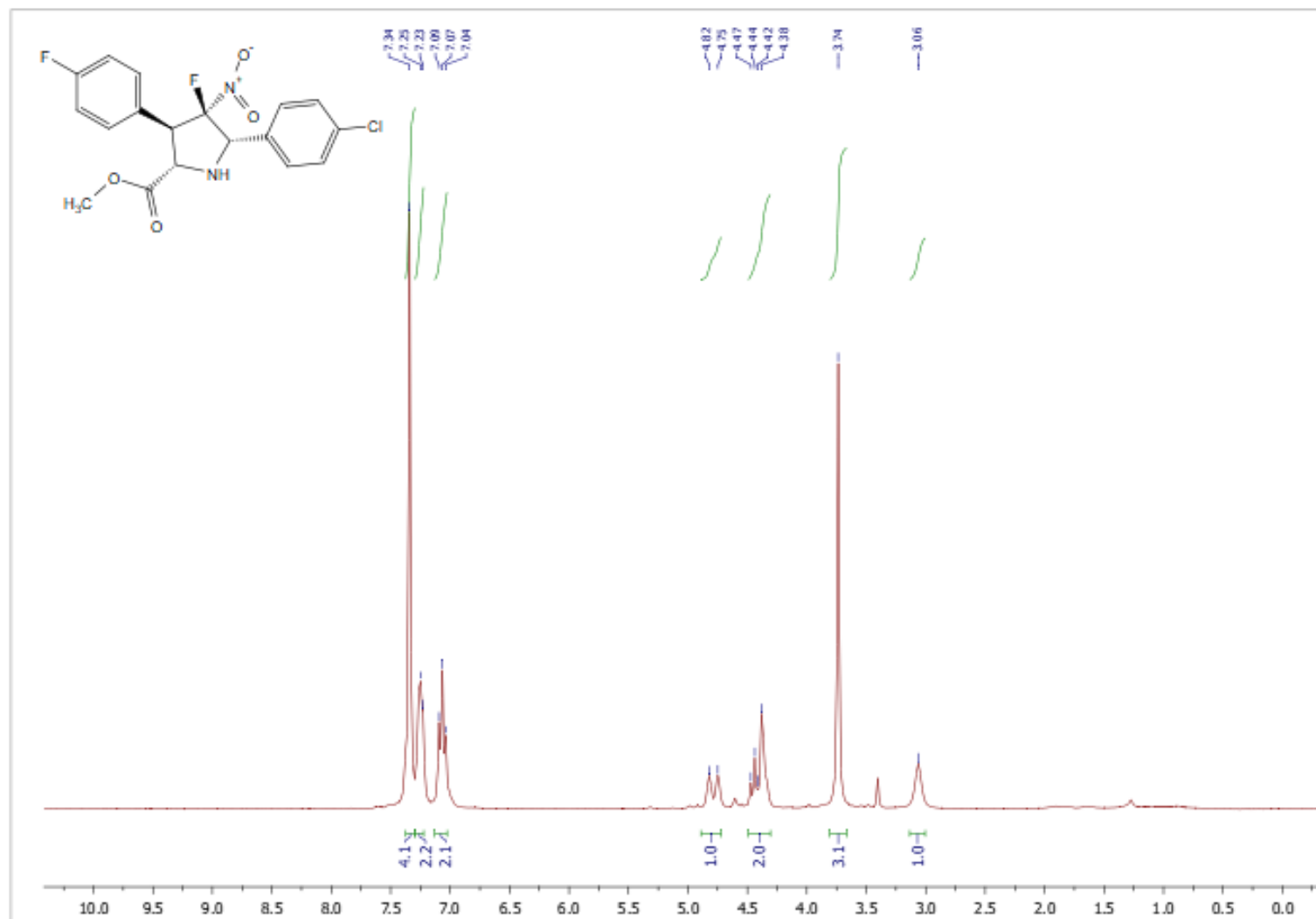


^{19}F NMR

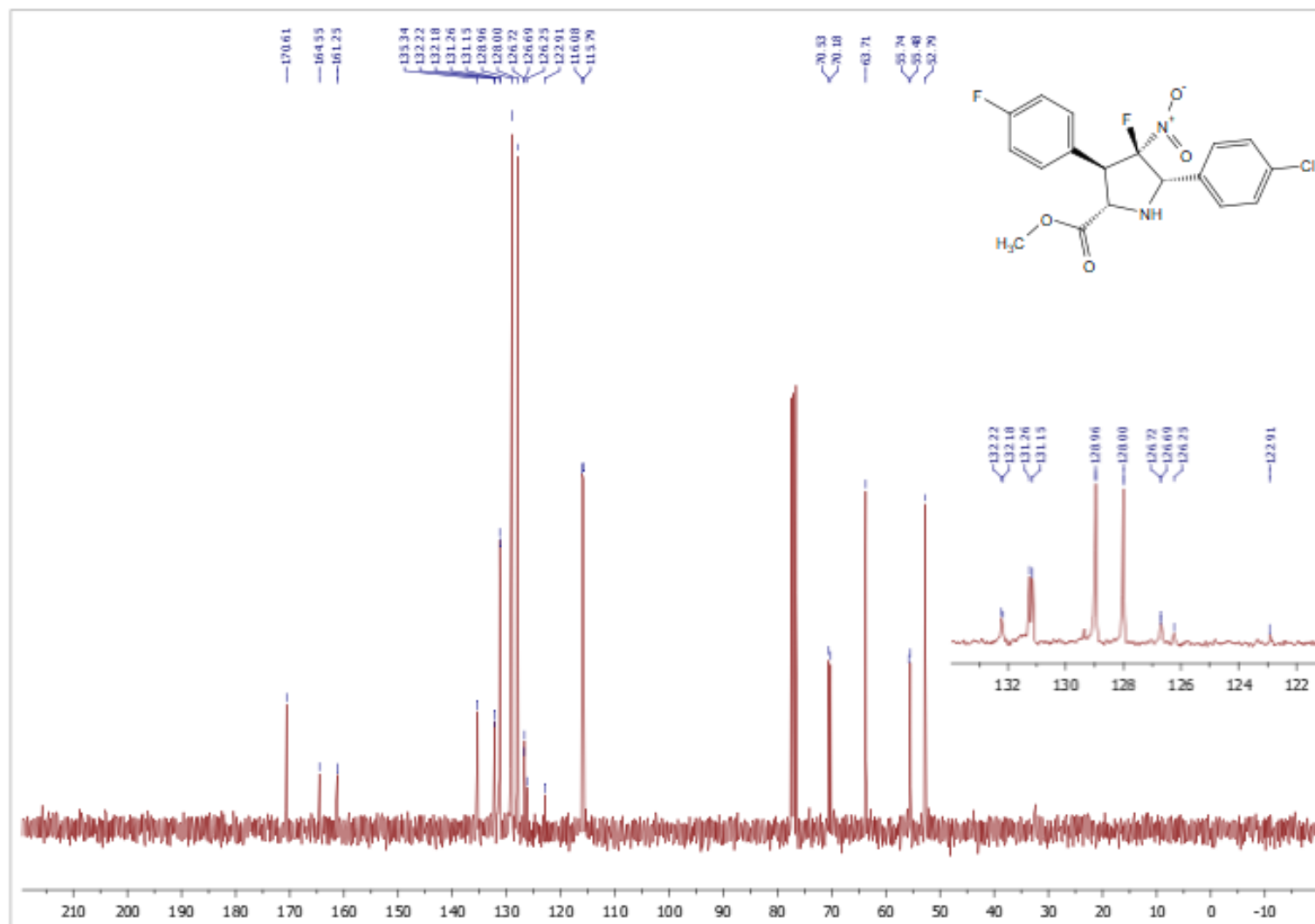


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-fluorophenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3d**

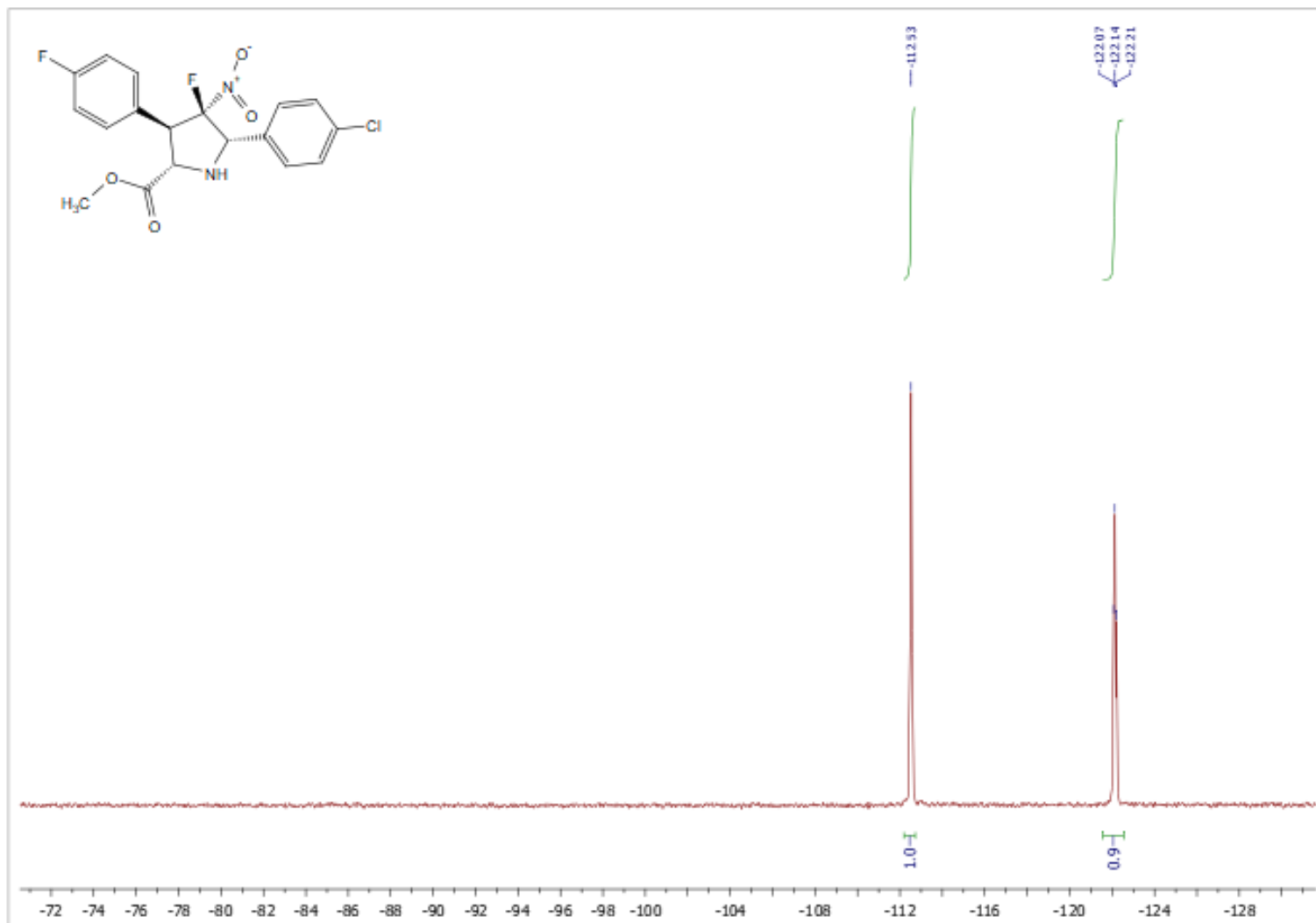
¹H NMR



¹³C NMR

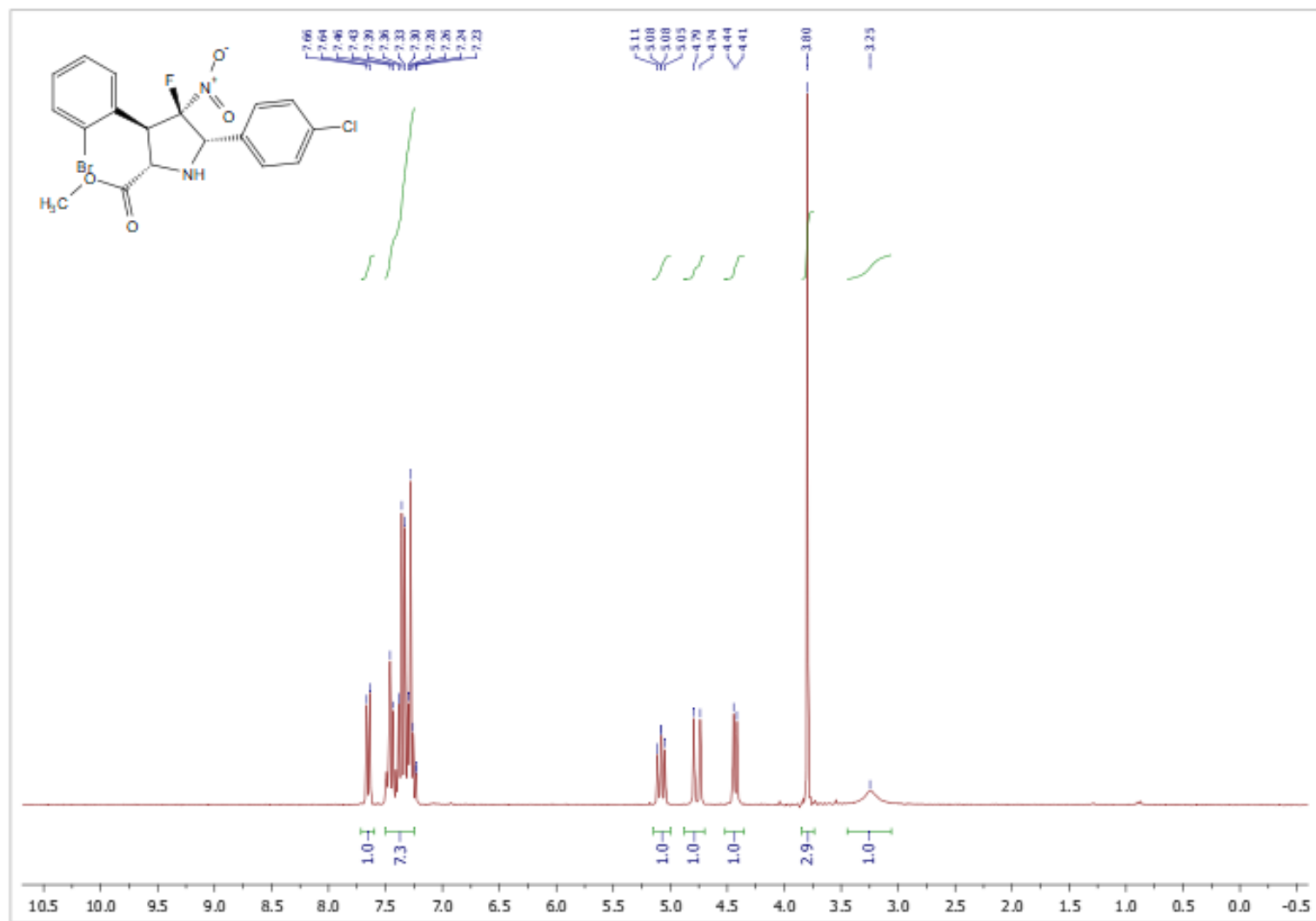


^{19}F NMR

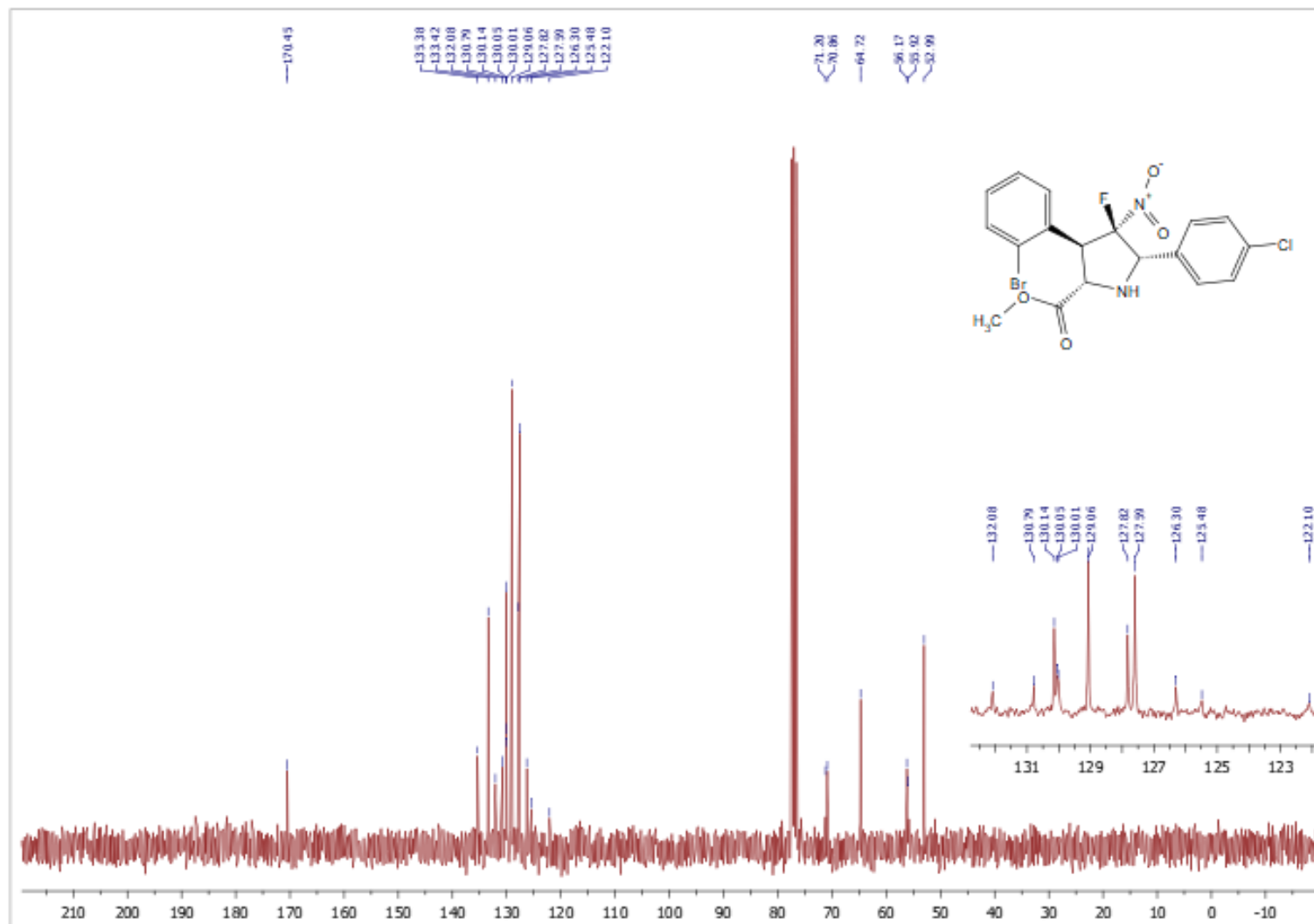


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(2-bromophenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3e**

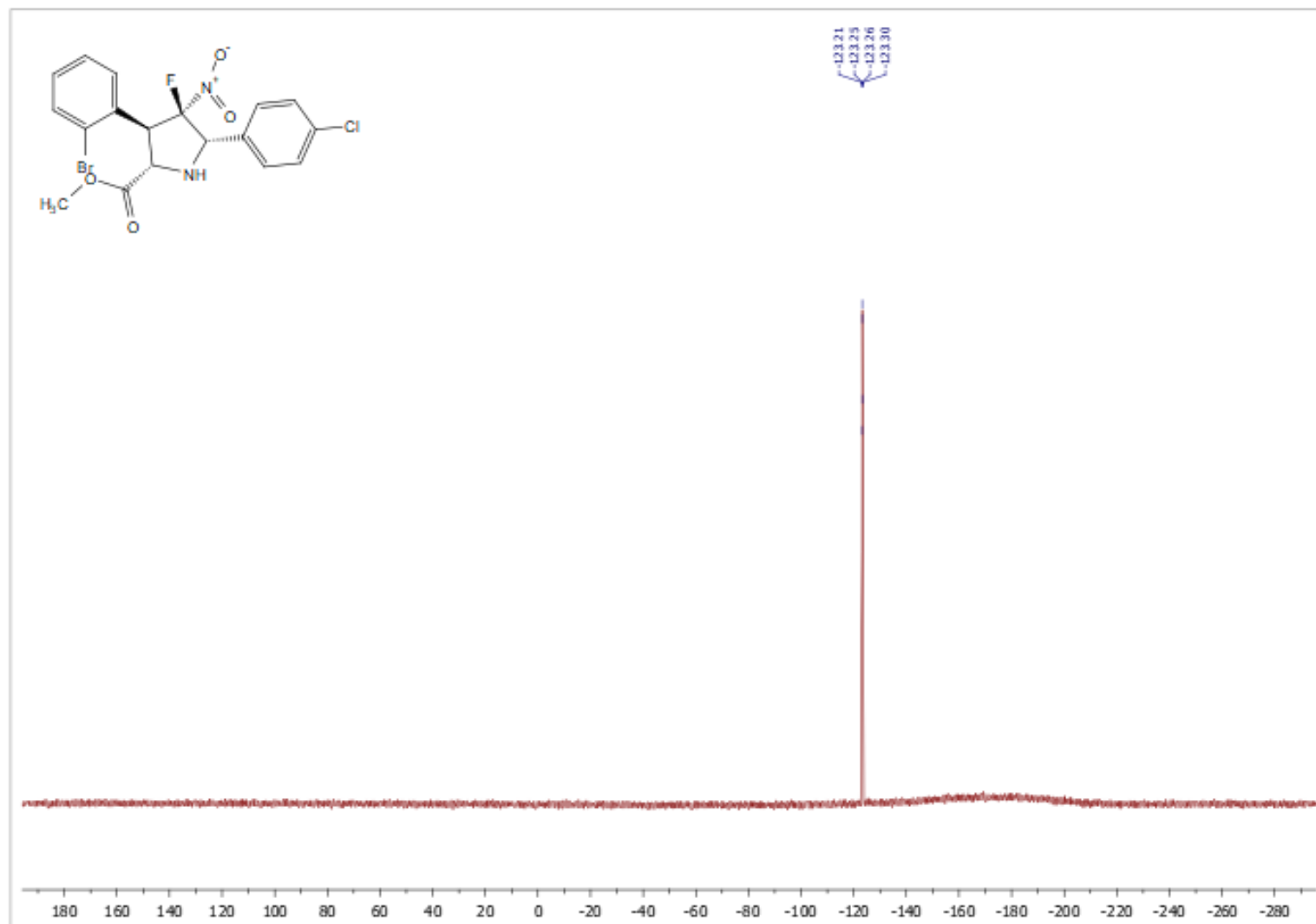
^1H NMR



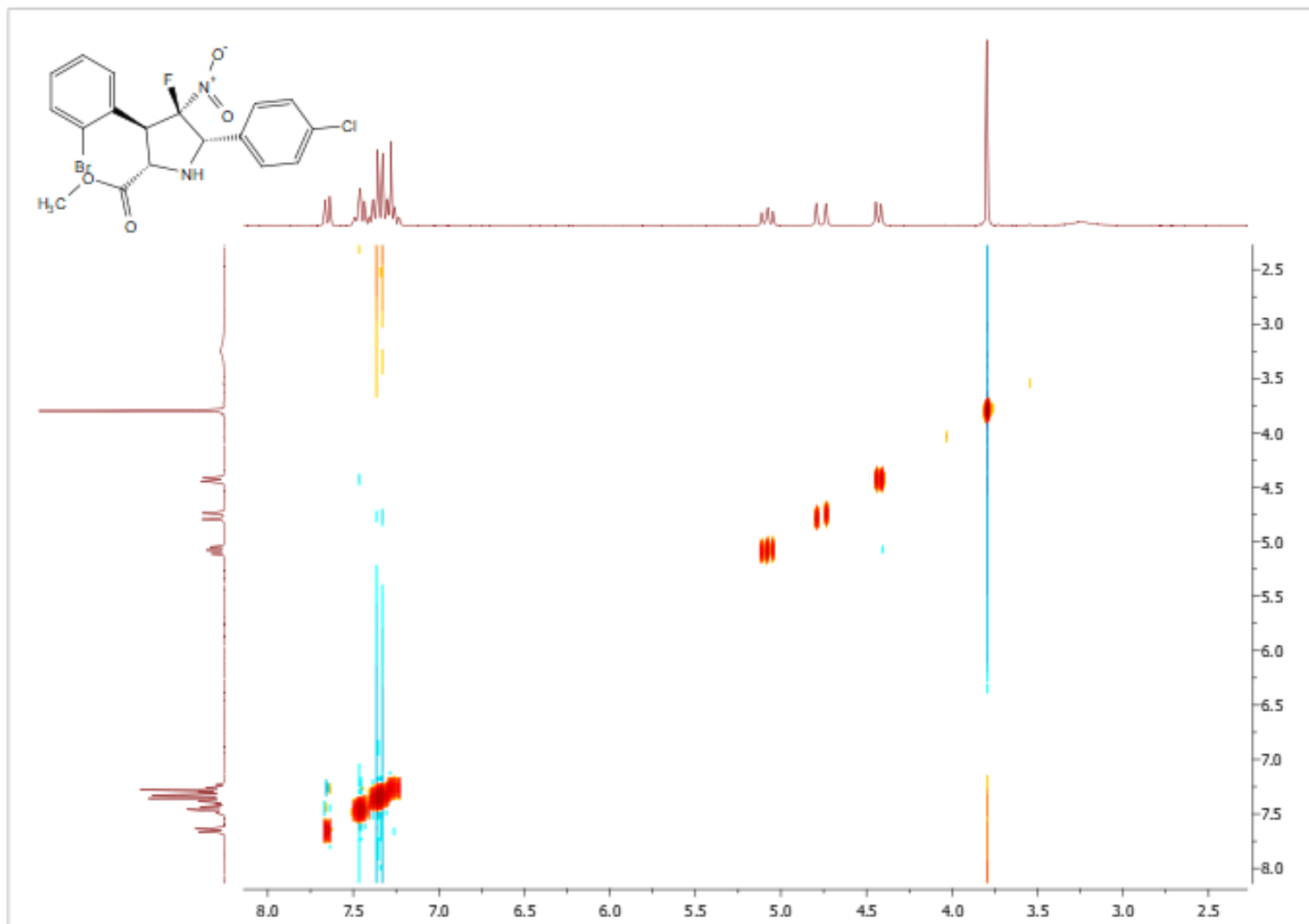
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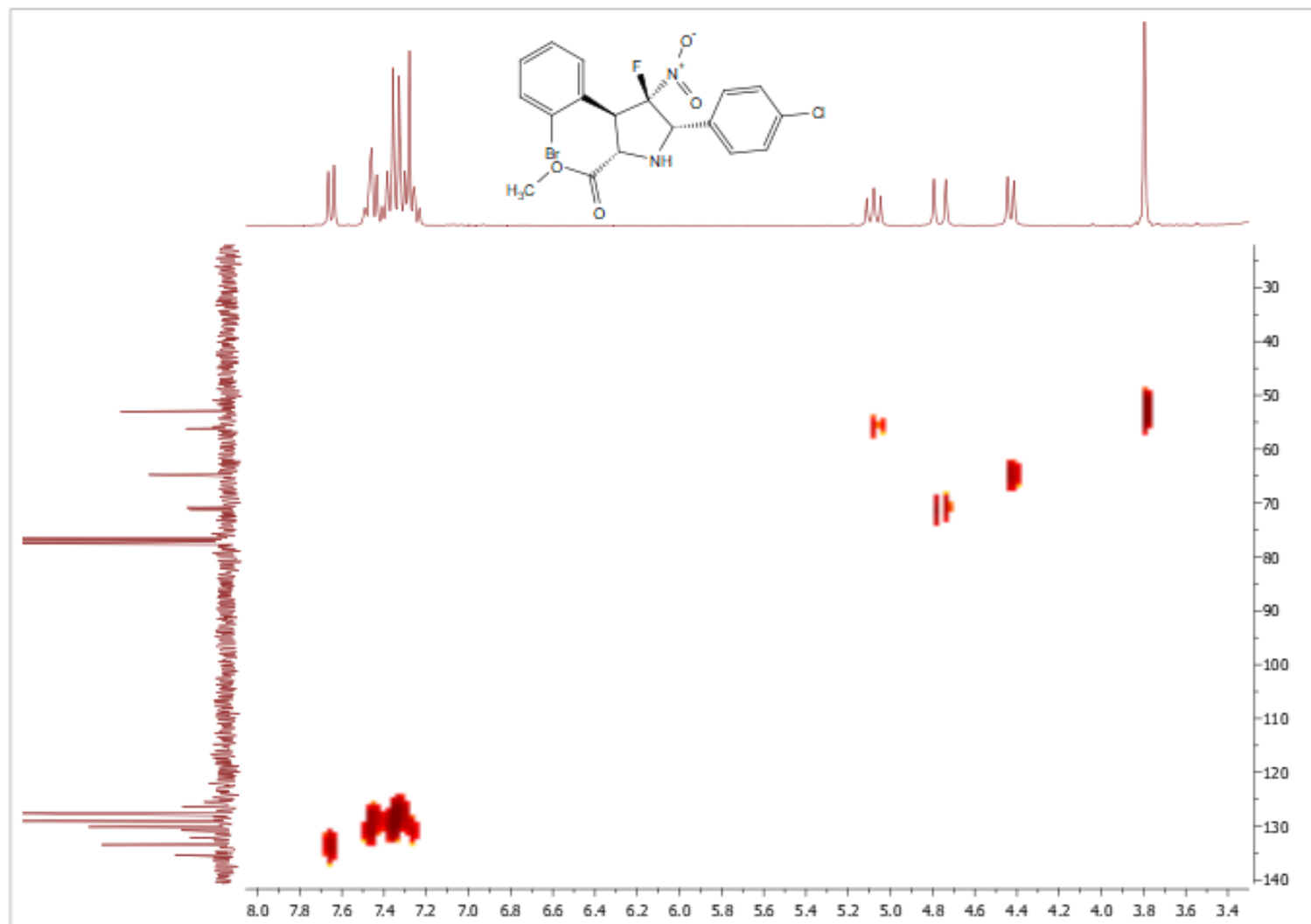
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^1H - ^1H NOESY NMR

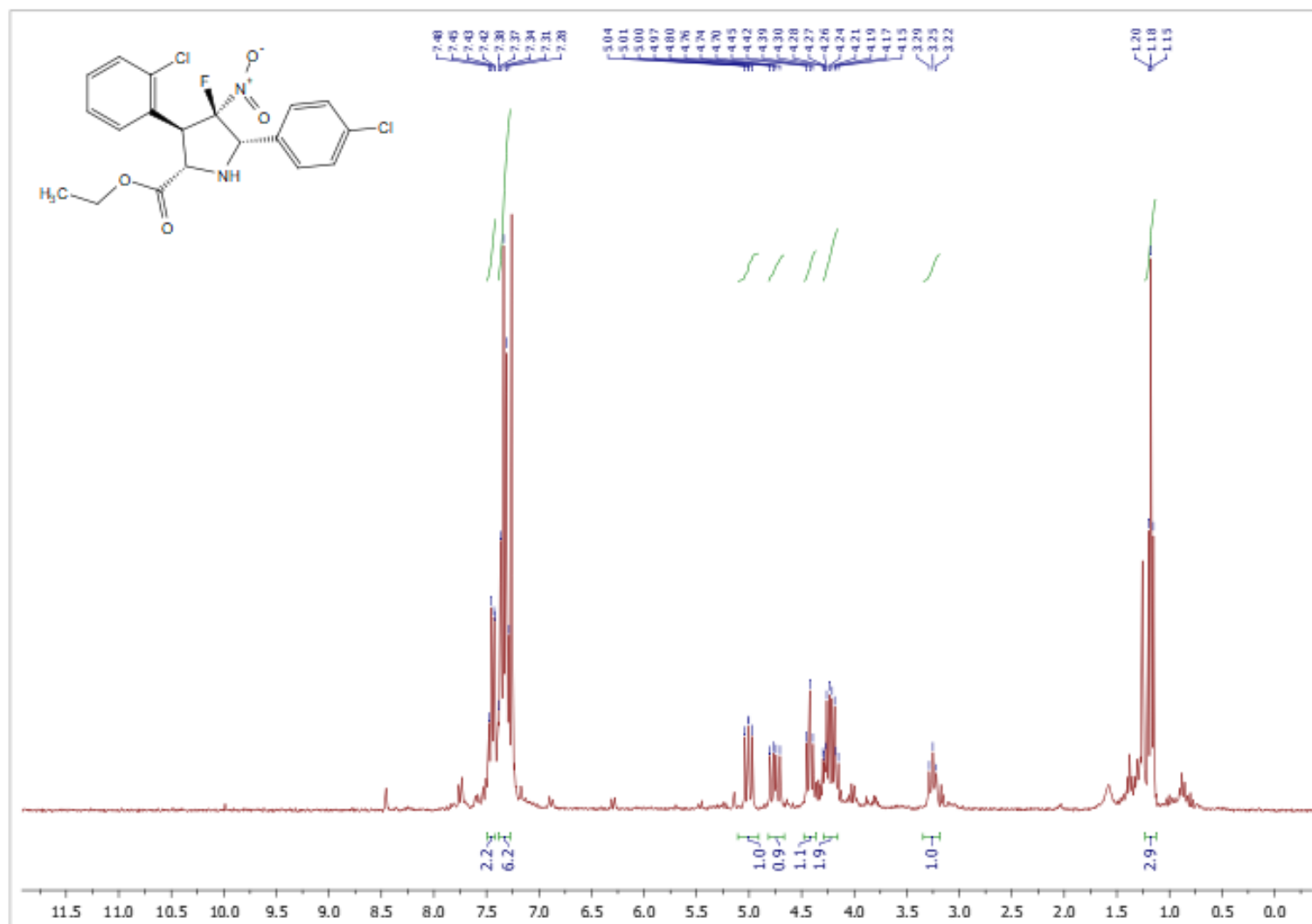


$^1\text{H} - ^{13}\text{C}$ HSQC NMR

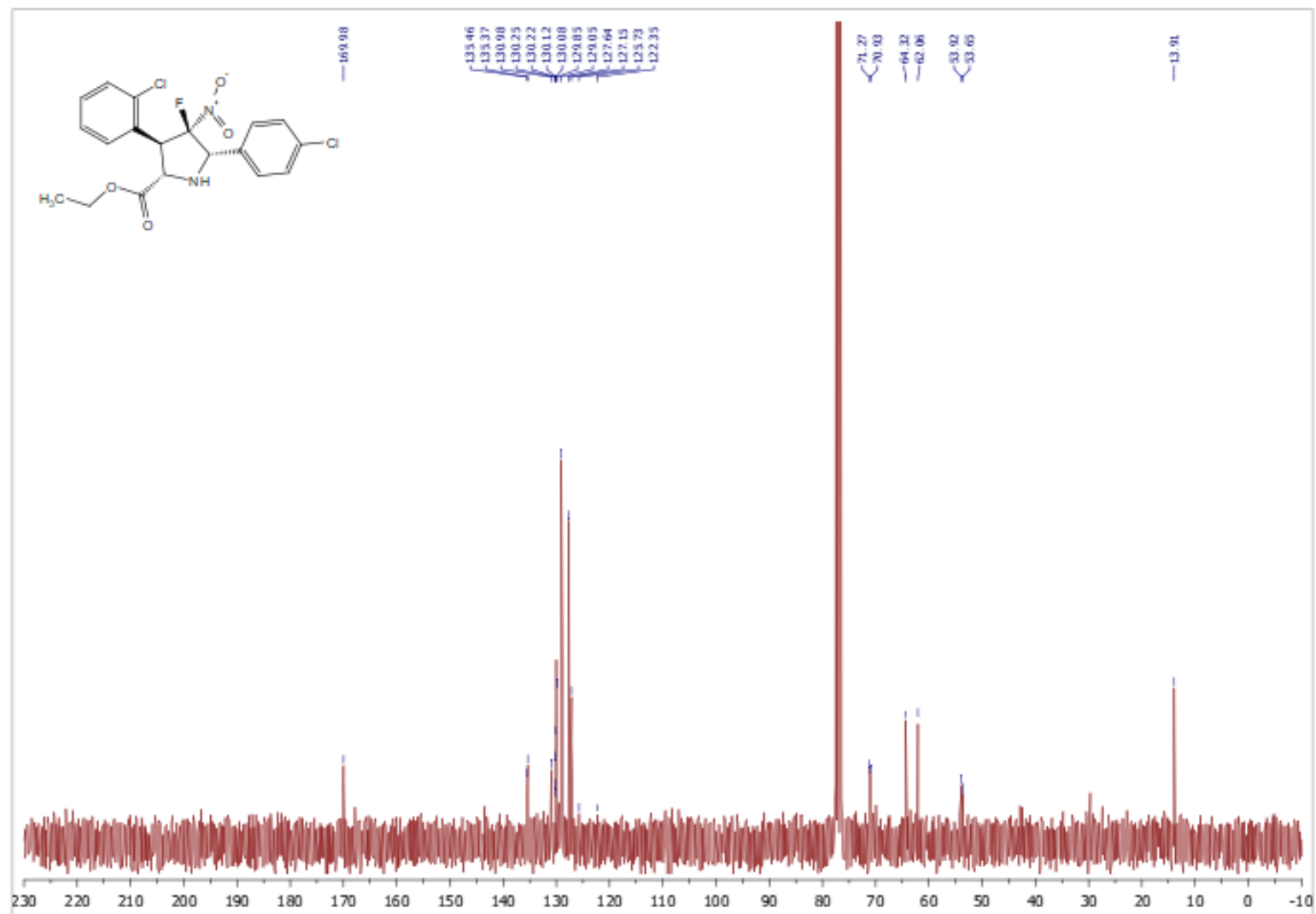


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(2-chlorophenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3f**

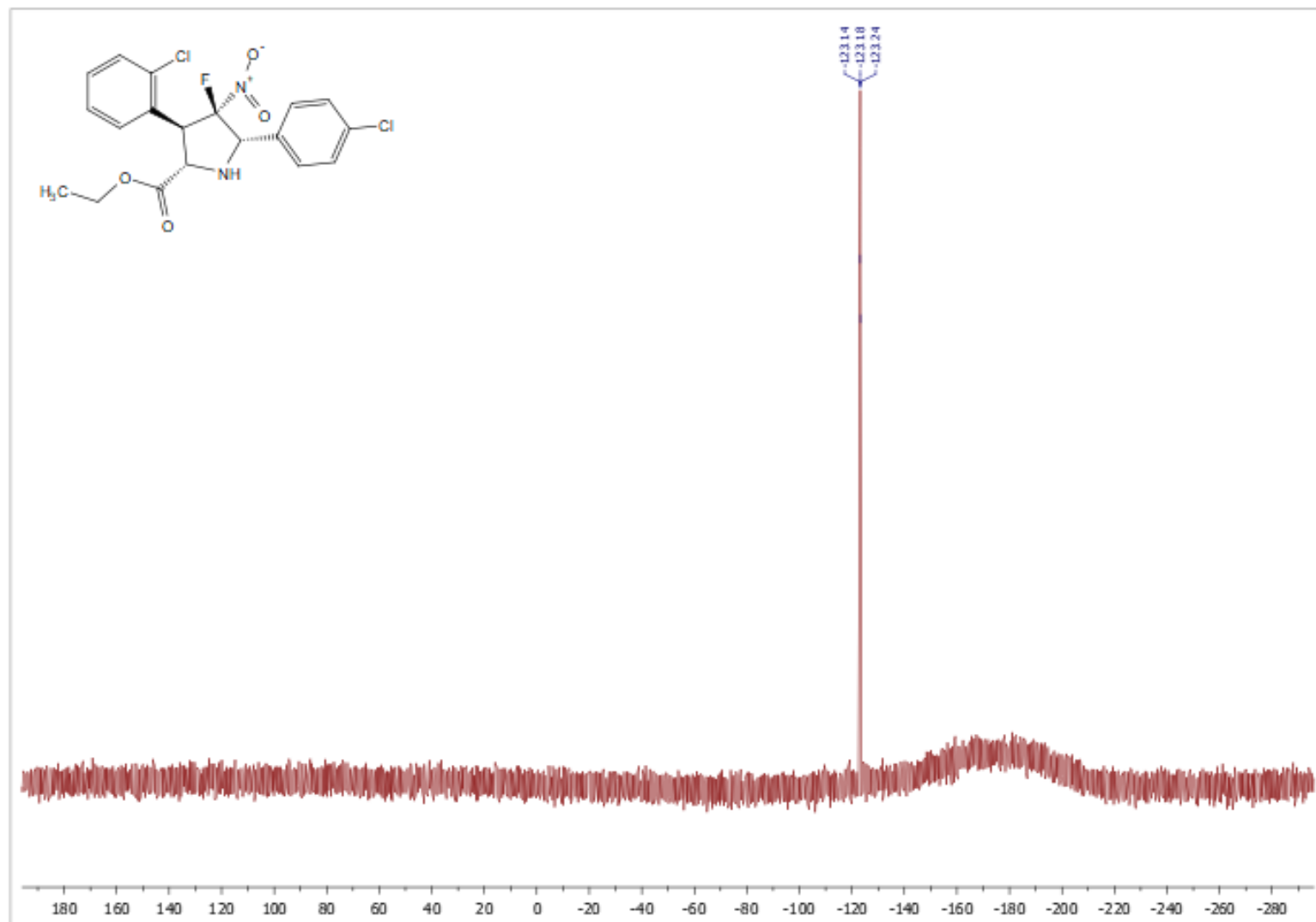
¹H NMR



^{13}C NMR

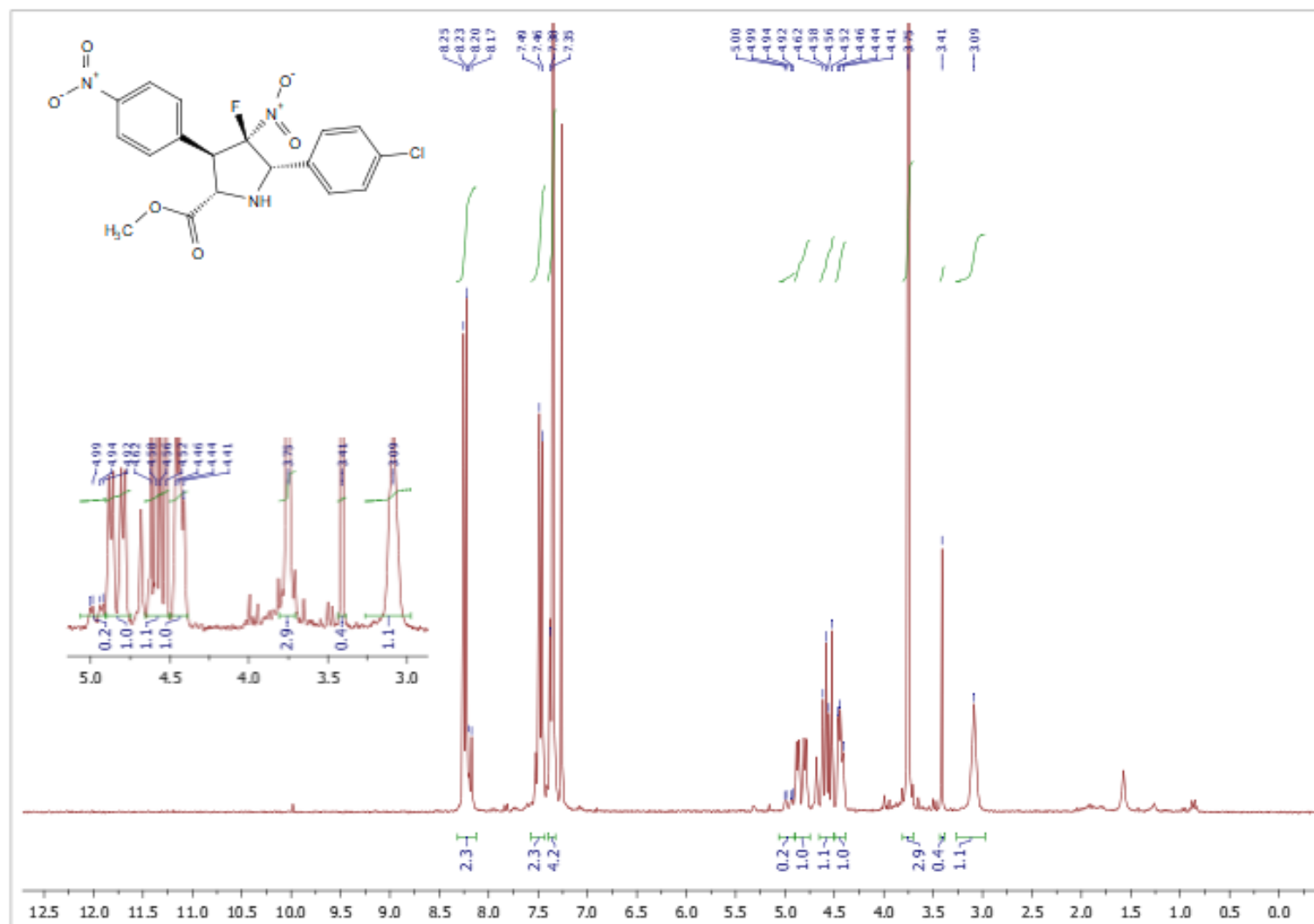


^{19}F NMR

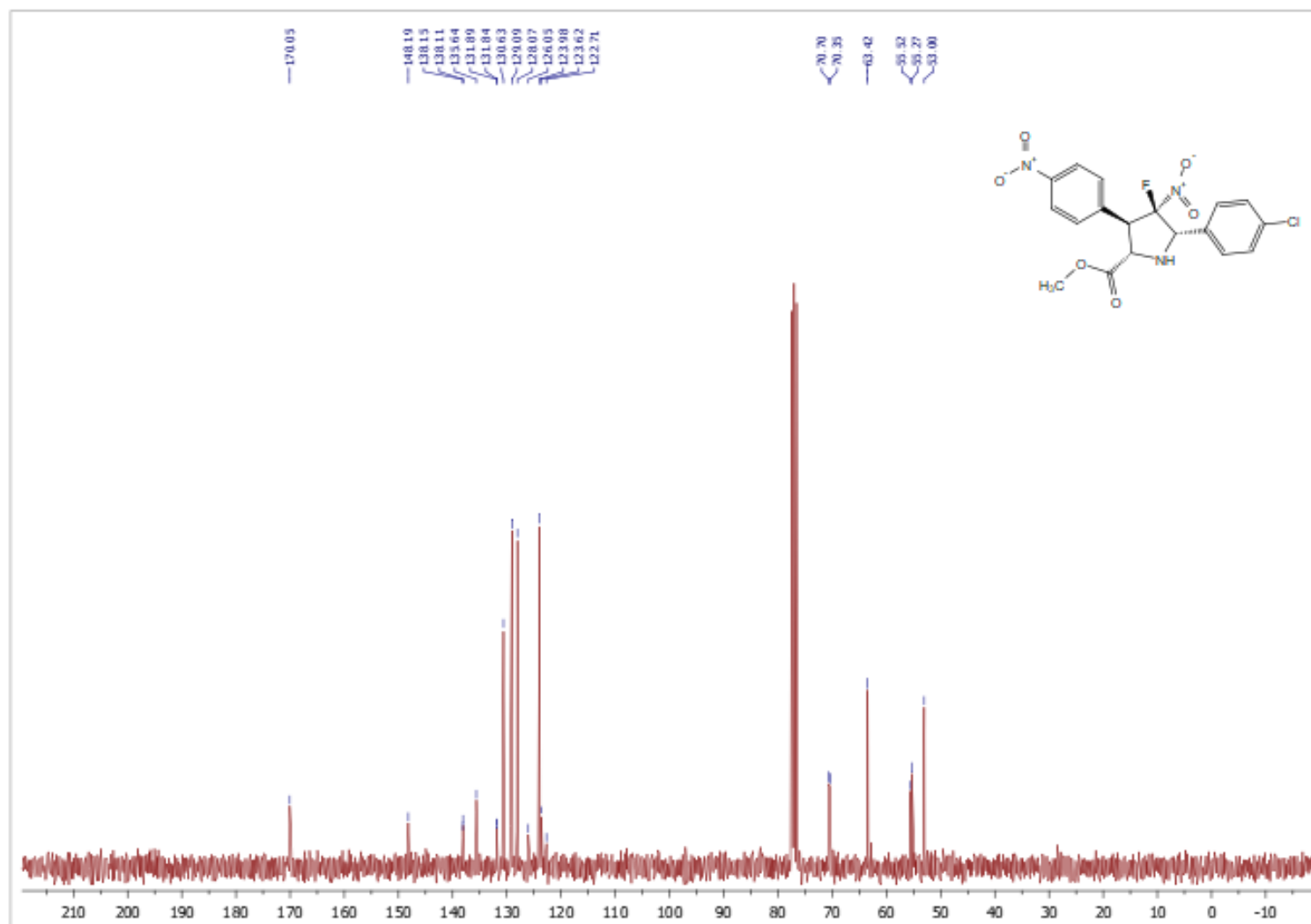


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-nitrophenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3g**

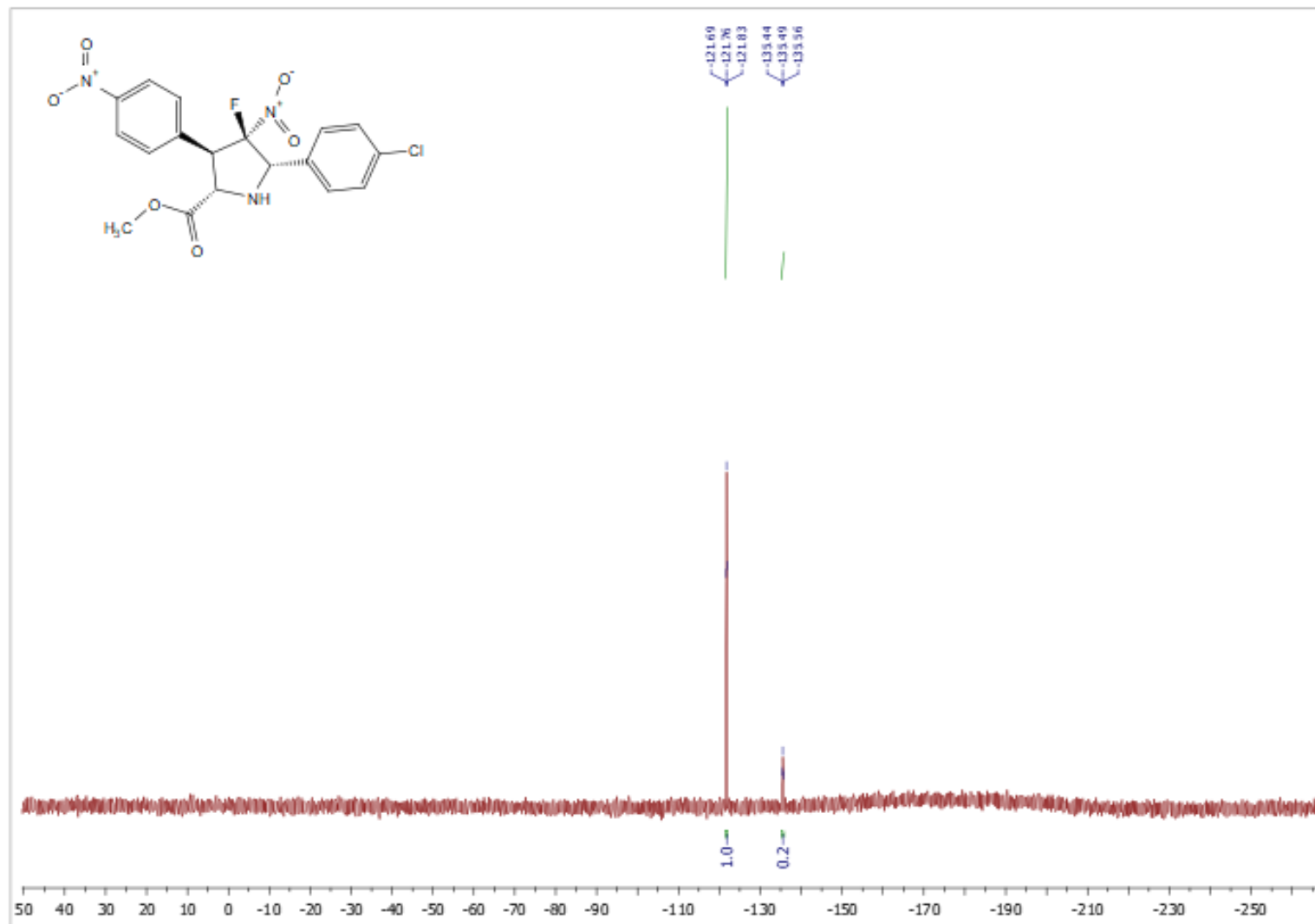
^1H NMR



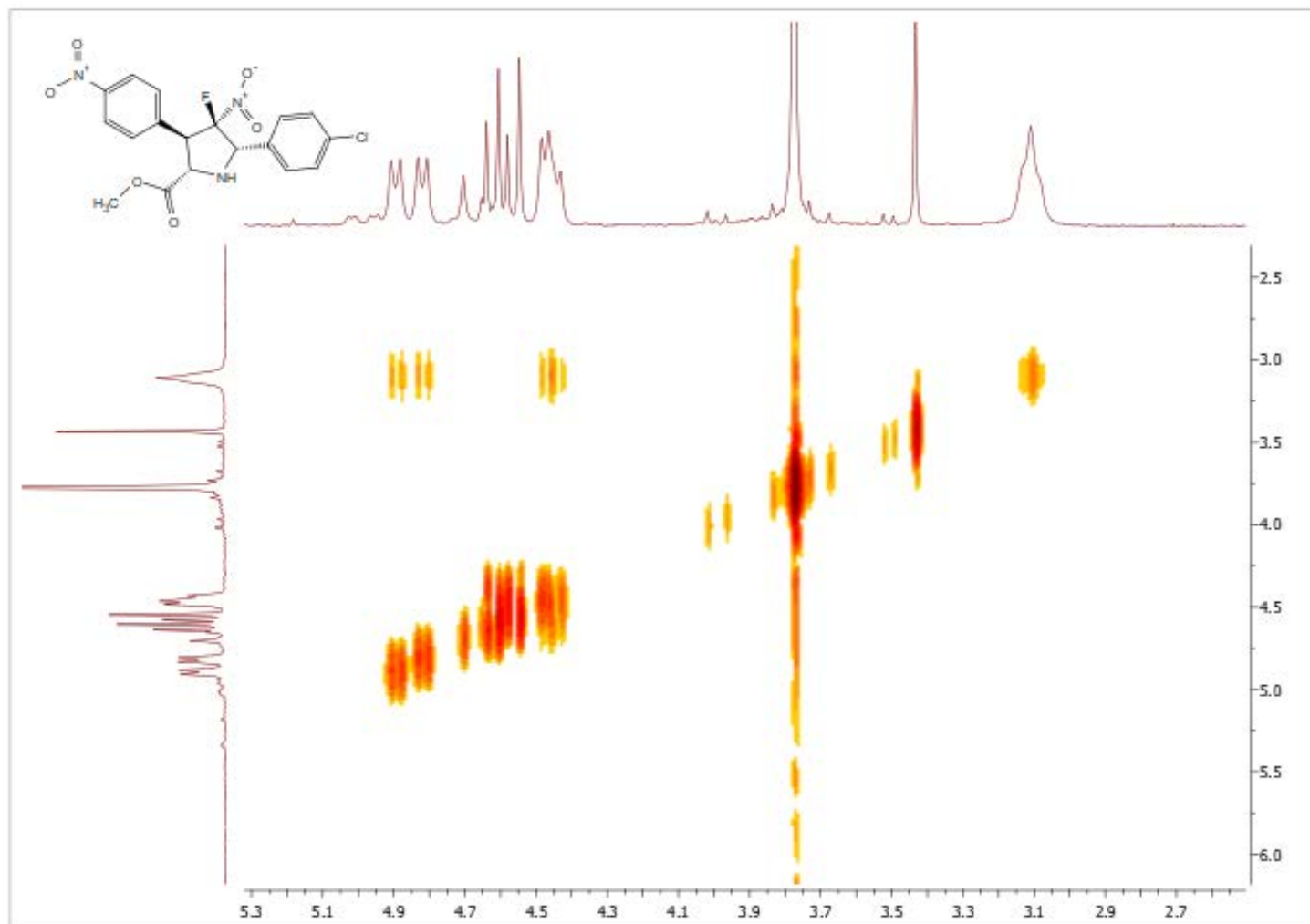
¹³C NMR



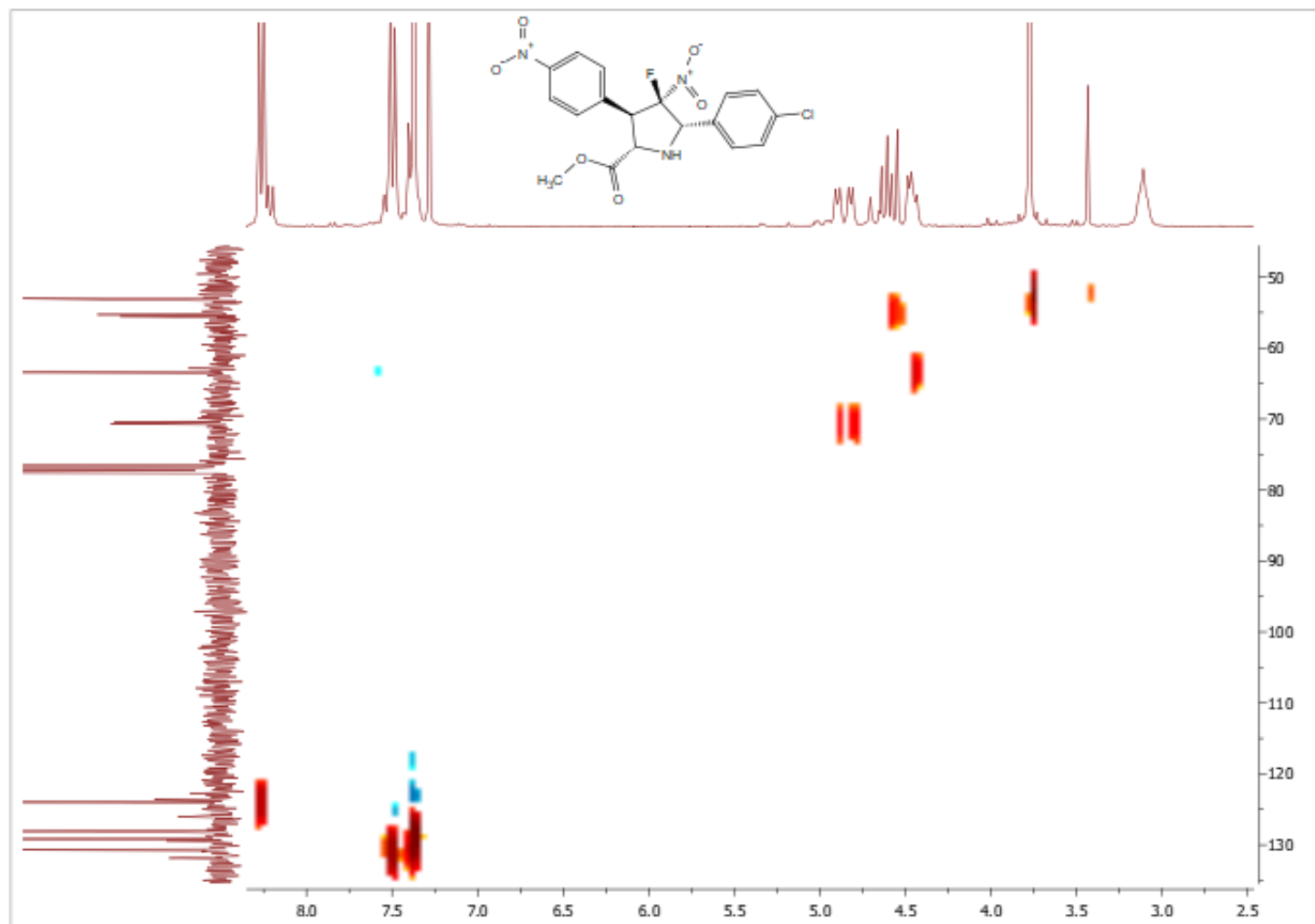
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^1H - ^1H COSY NMR

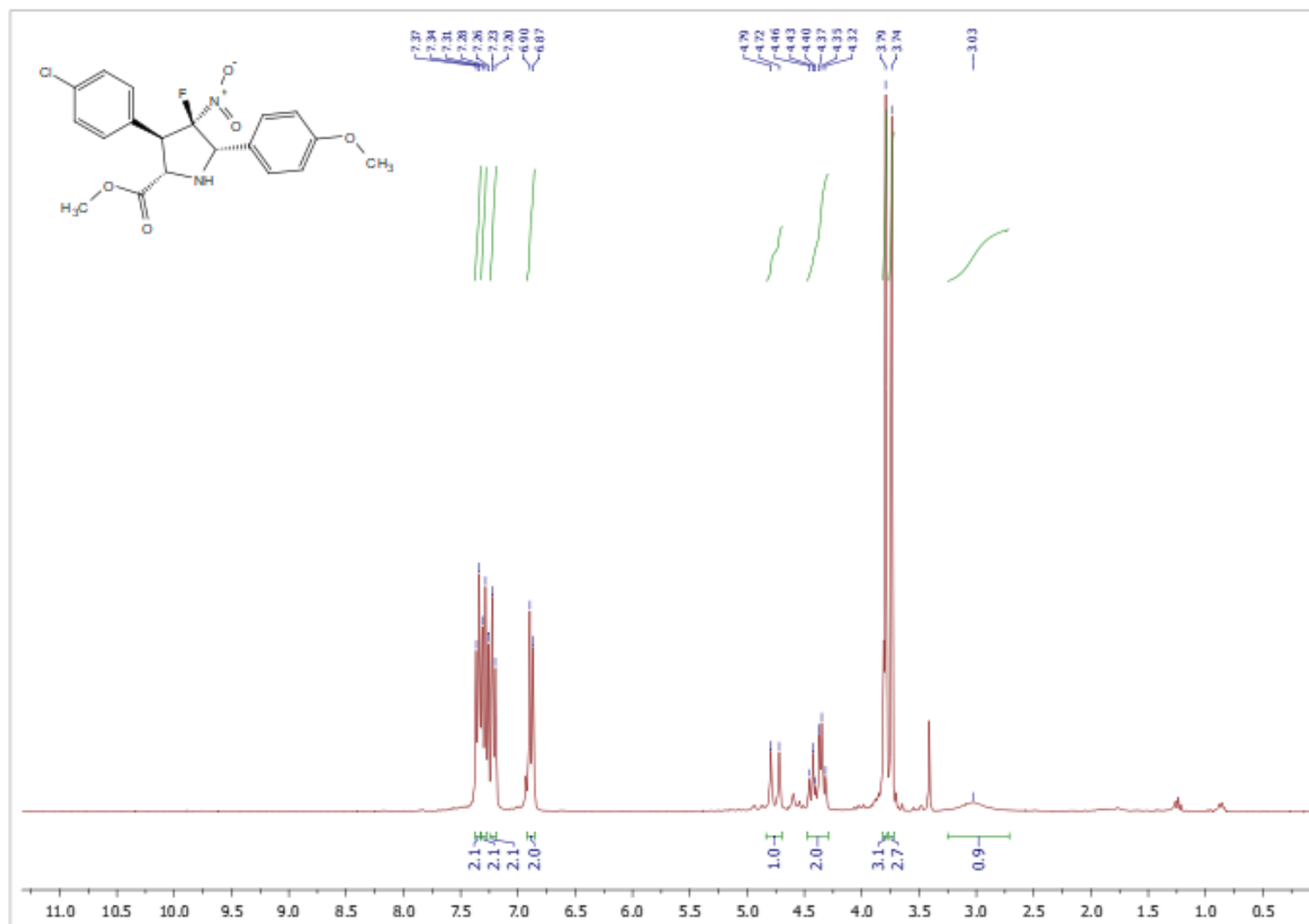


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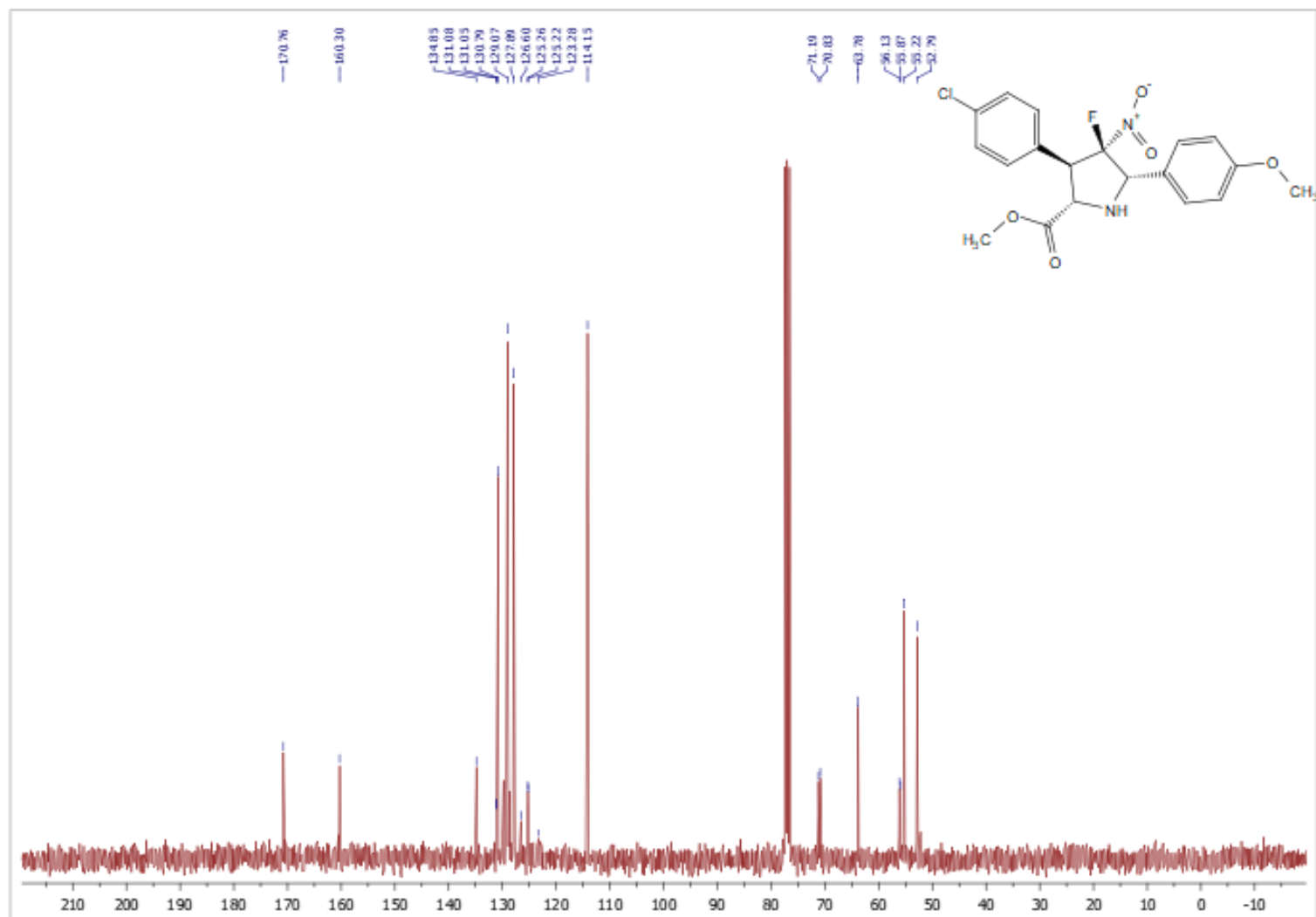


methyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(chlorophenyl)-5-(4-methoxyphenyl)-pyrrolidine-2-carboxylate **3h**

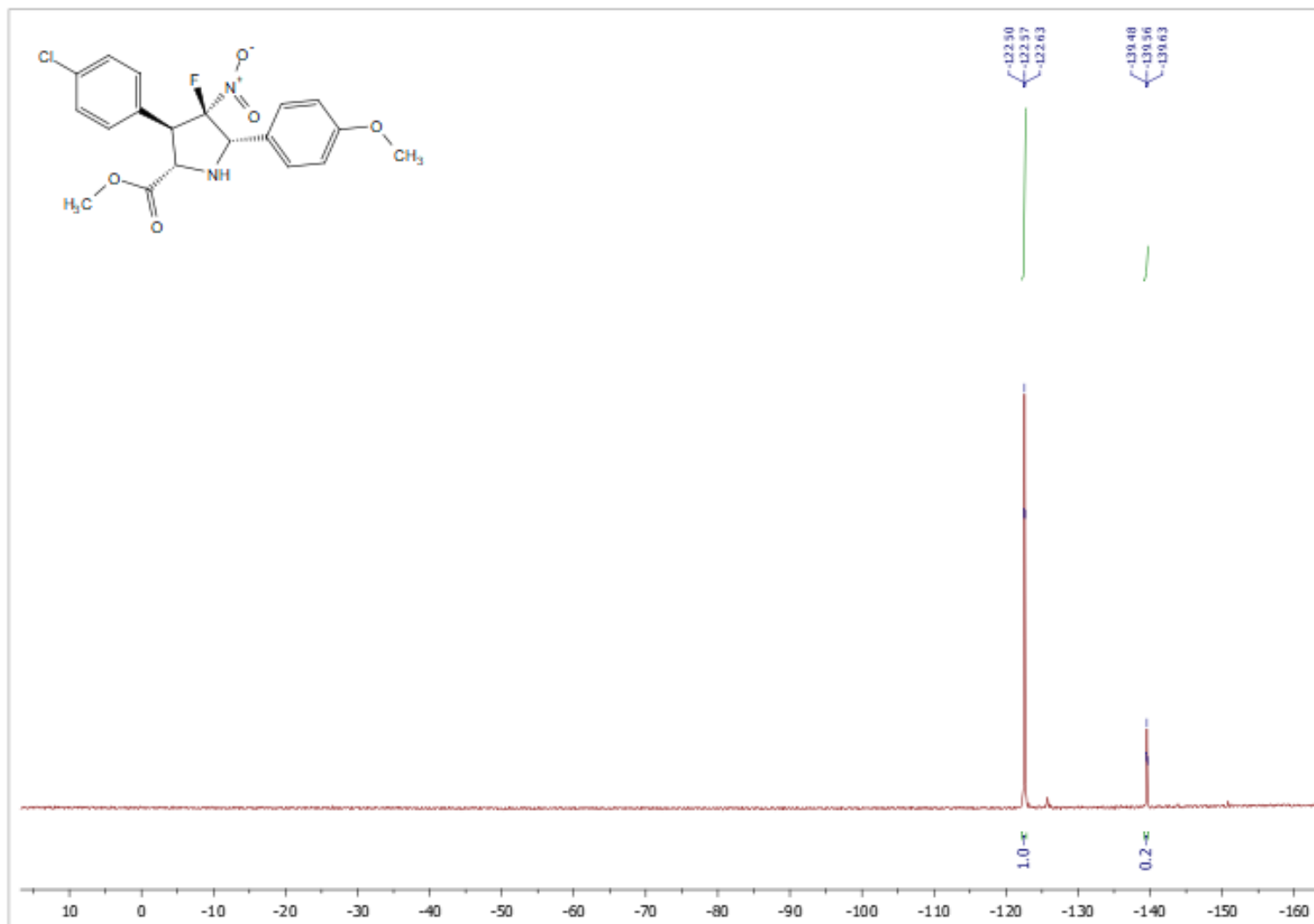
¹H NMR



^{13}C NMR

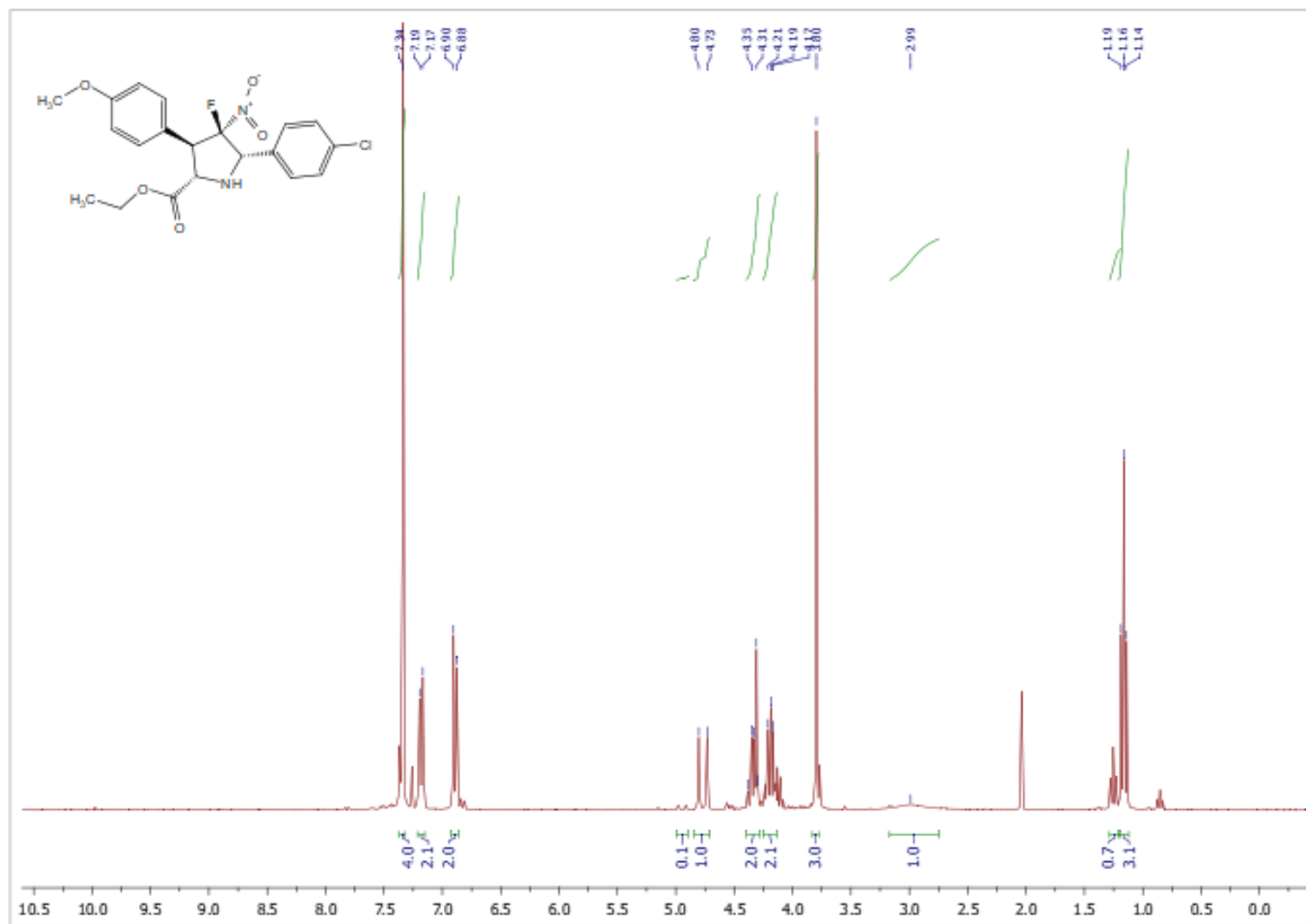


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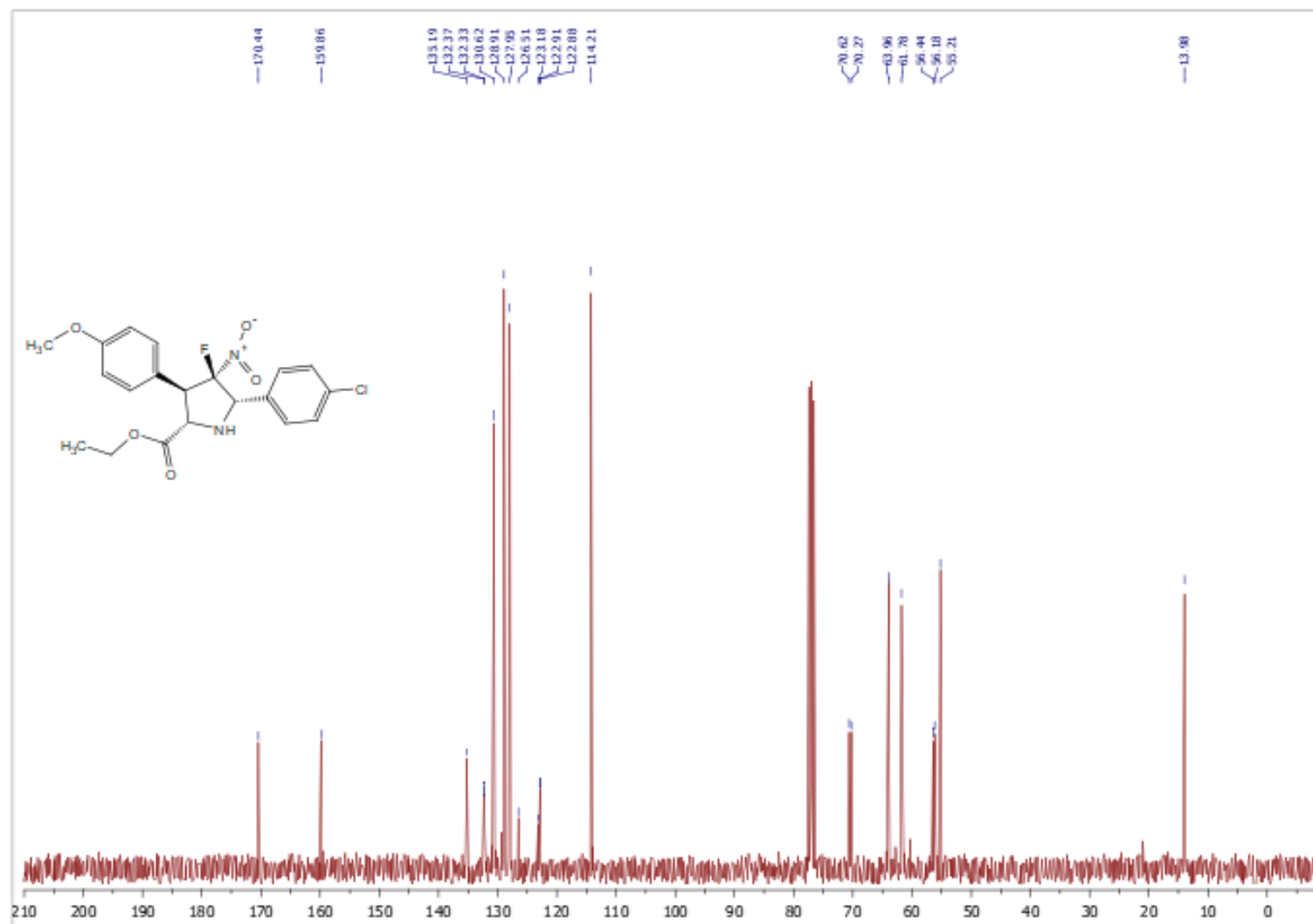


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3i**

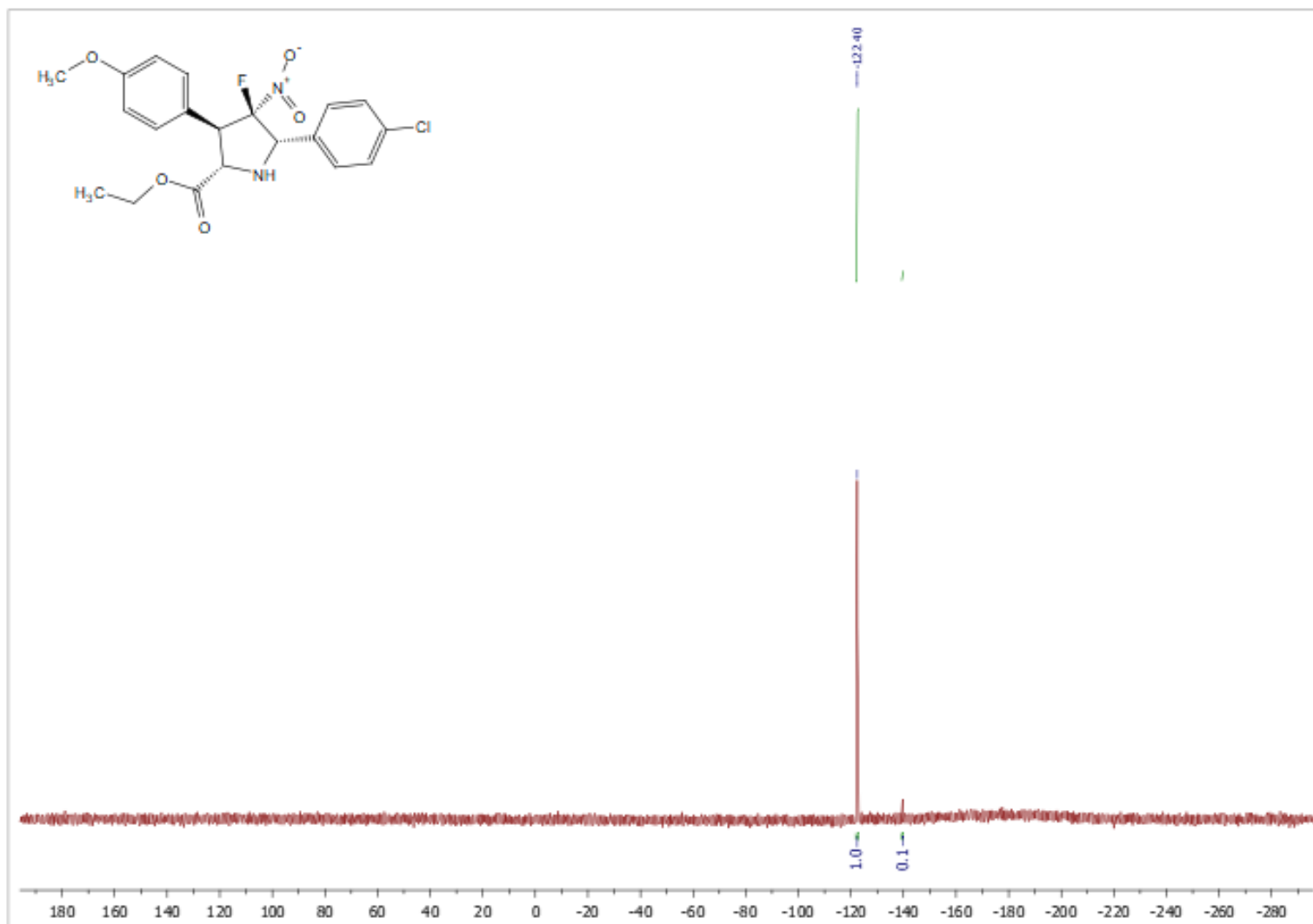
¹H NMR



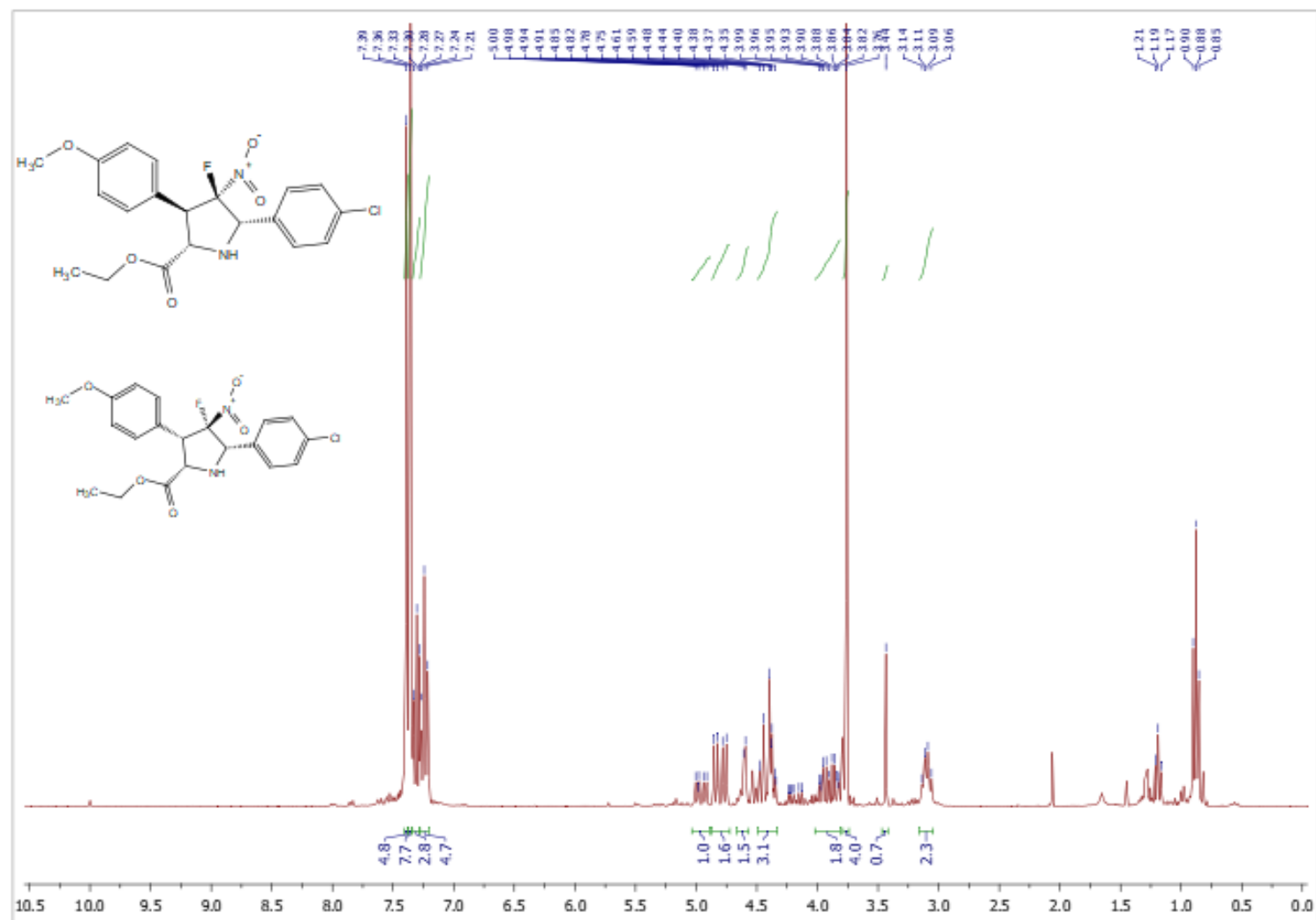
¹³C NMR



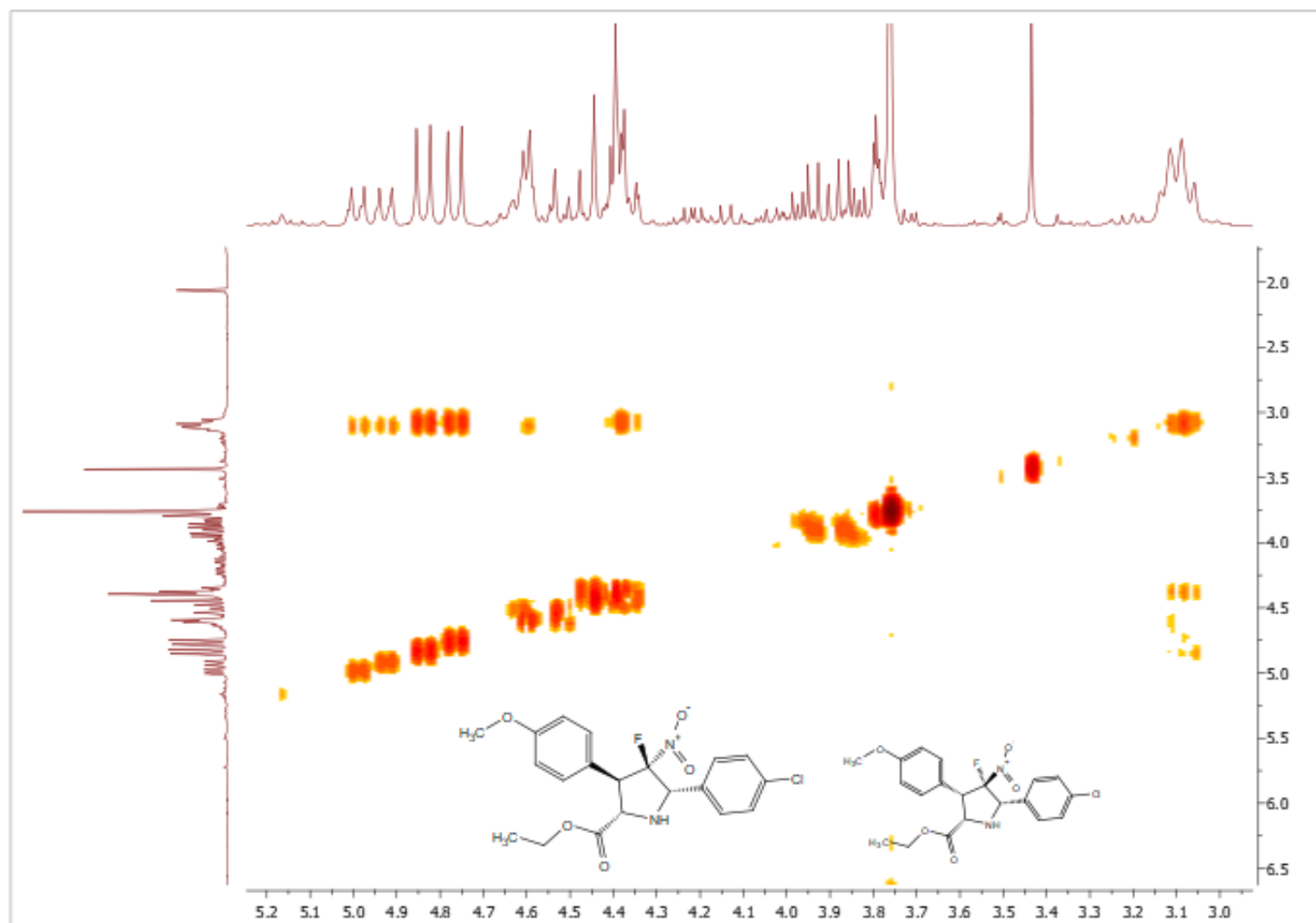
^{19}F NMR



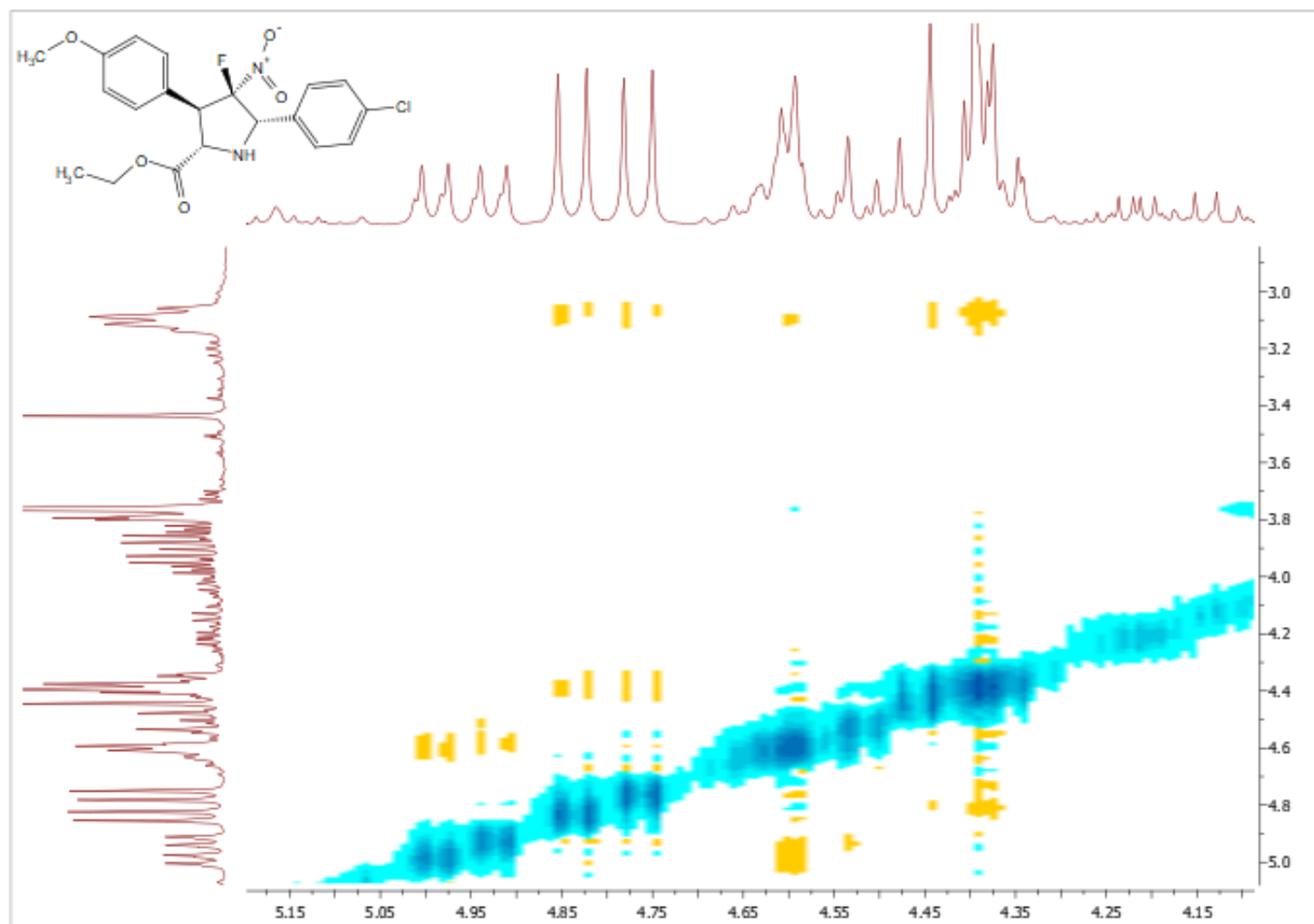
^1H NMR of mixture **3i/3i'** (dr = 1.6:1)



^1H - ^1H COSY NMR of mixture **3i/3i'** (dr = 1.6:1)

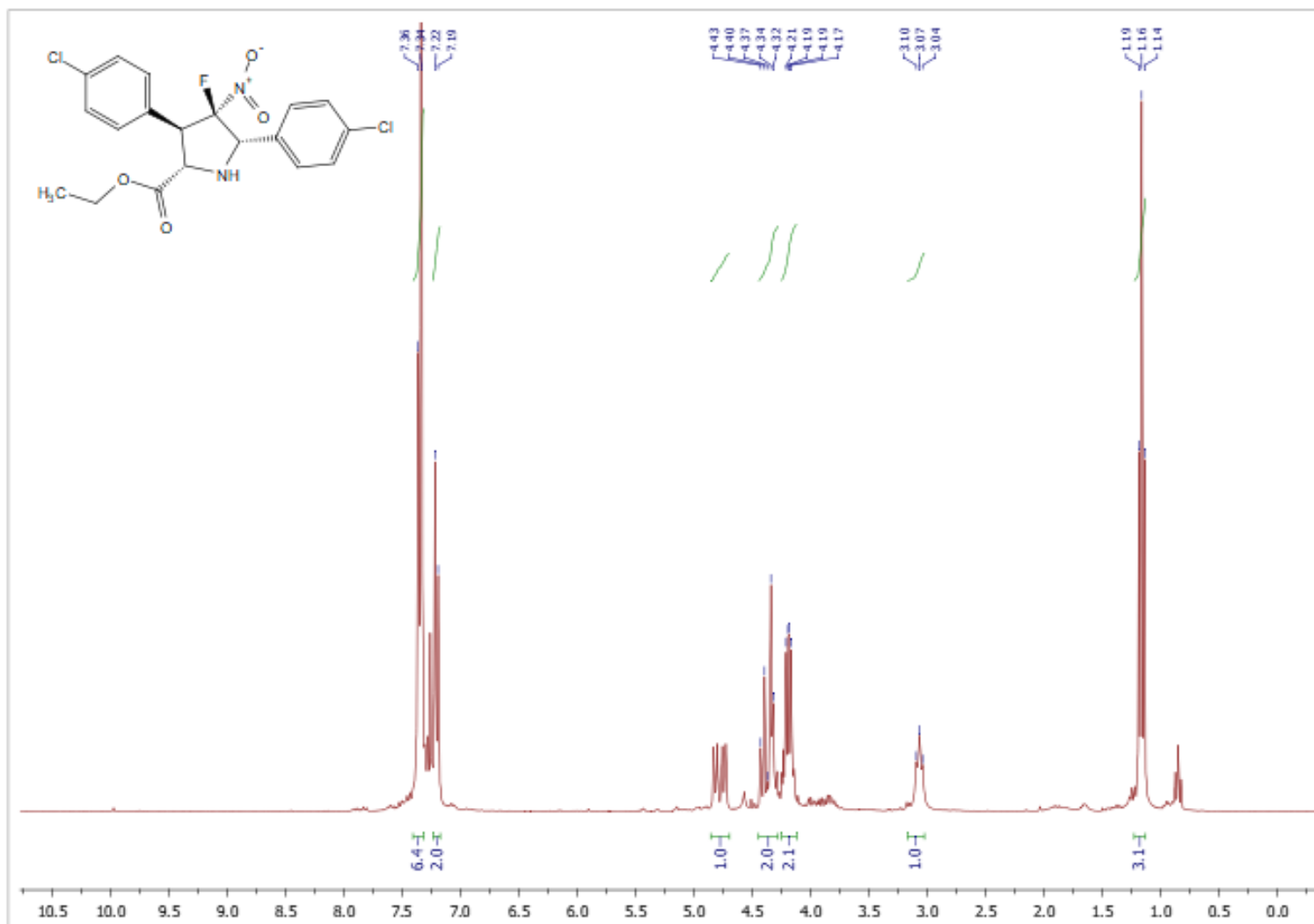


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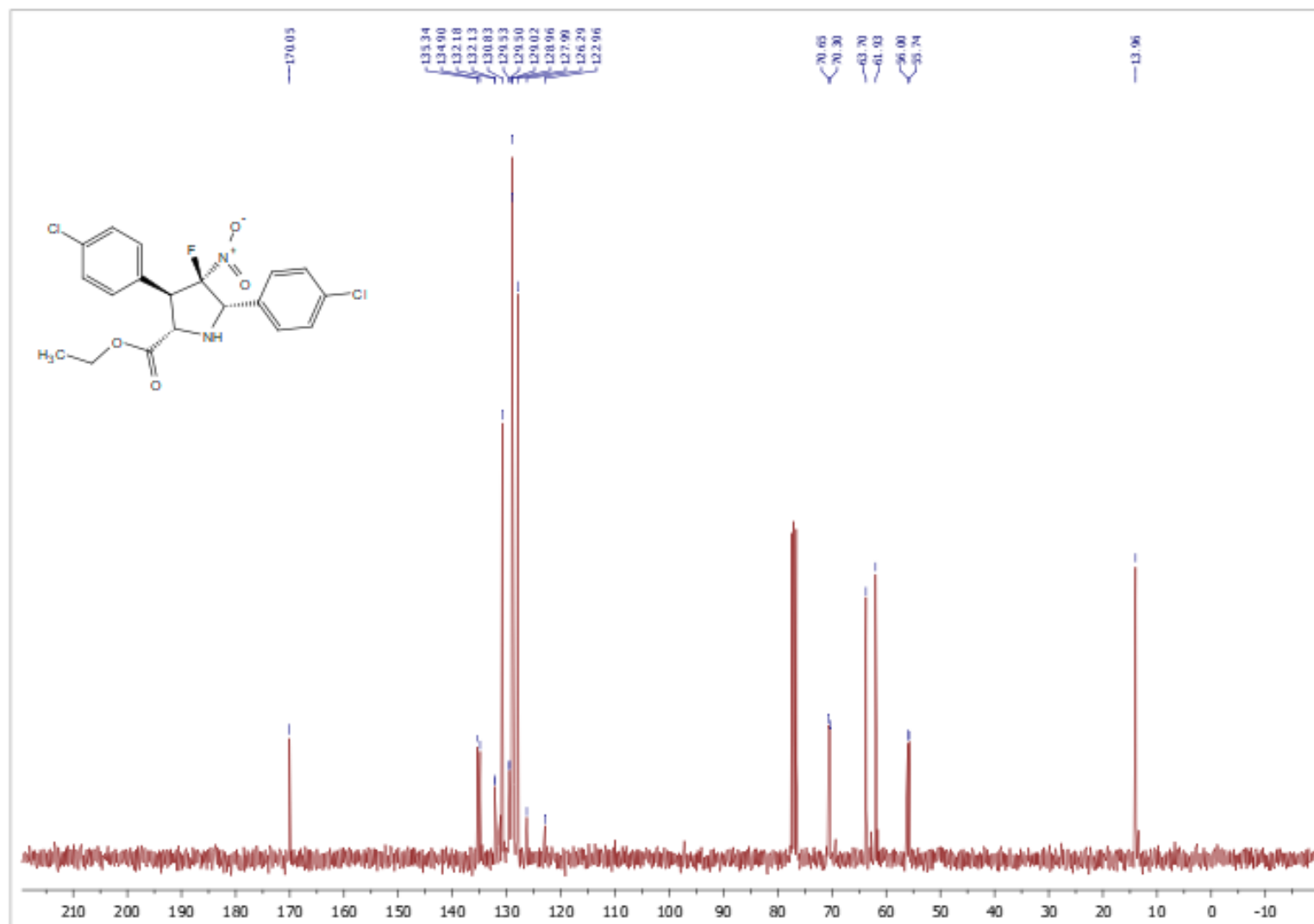


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3,5-bis-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3j**

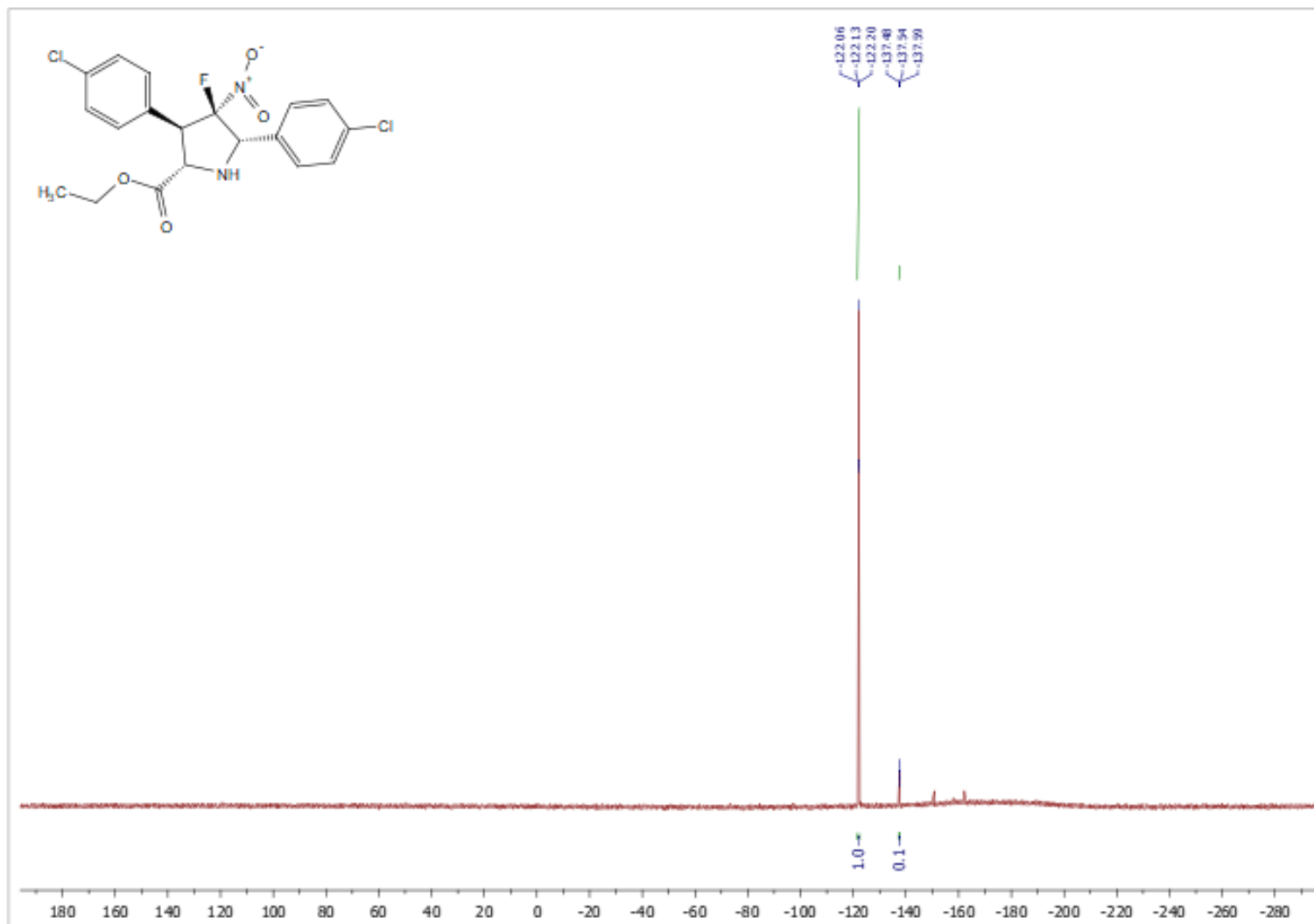
¹H NMR



¹³C NMR

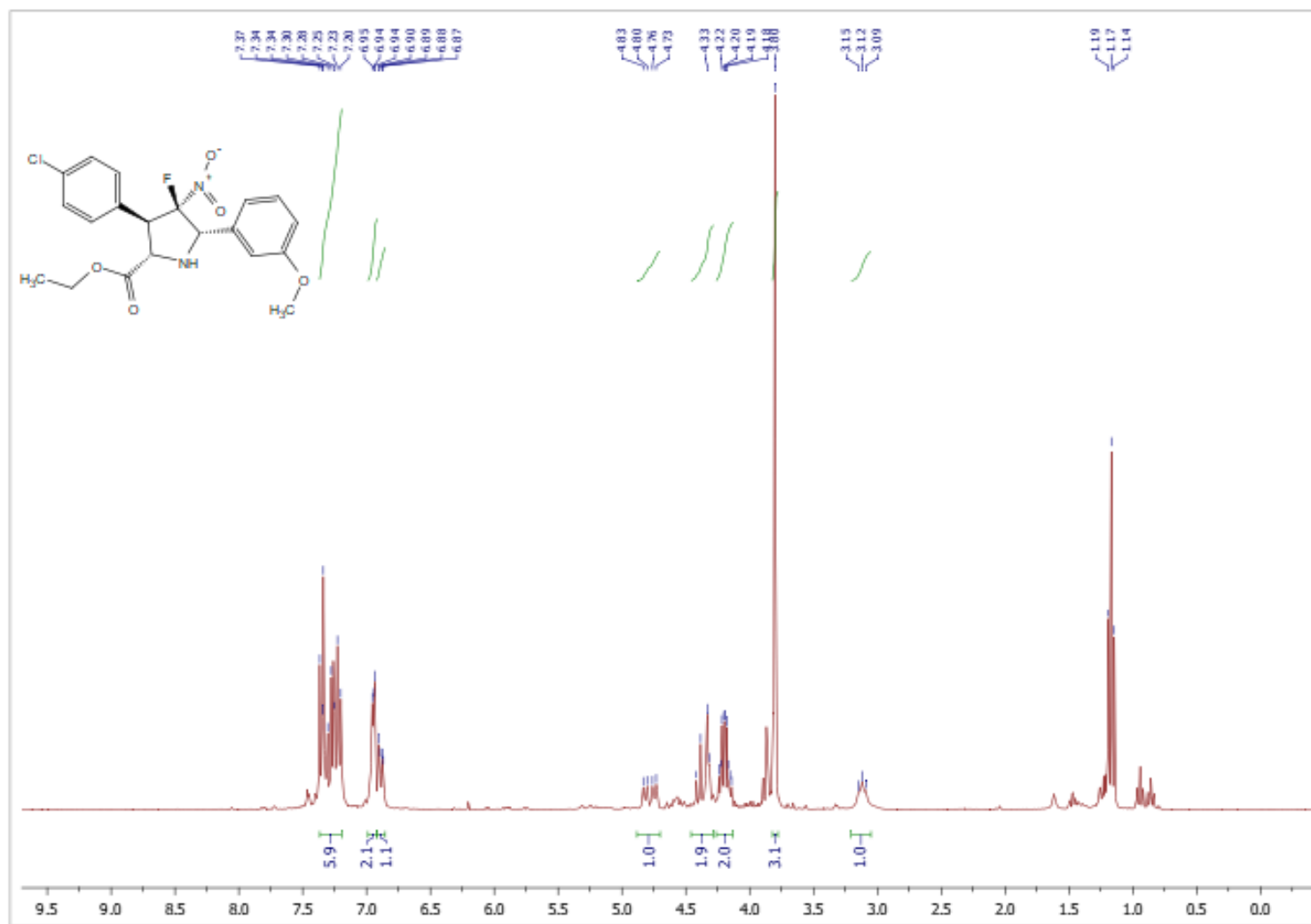


^{19}F NMR

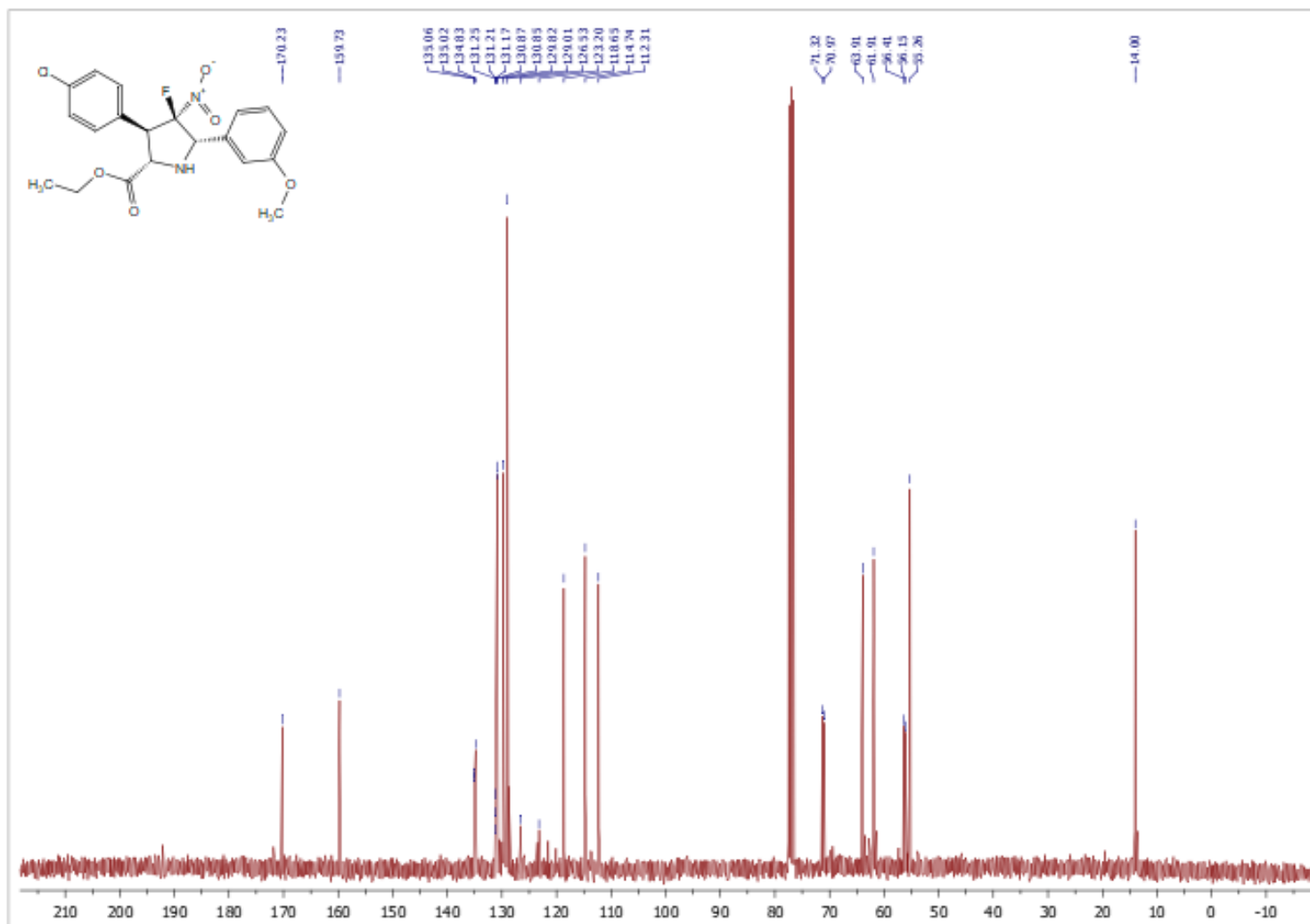


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-chlorophenyl)-5-(3-methoxyphenyl)-pyrrolidine-2-carboxylate **3k**

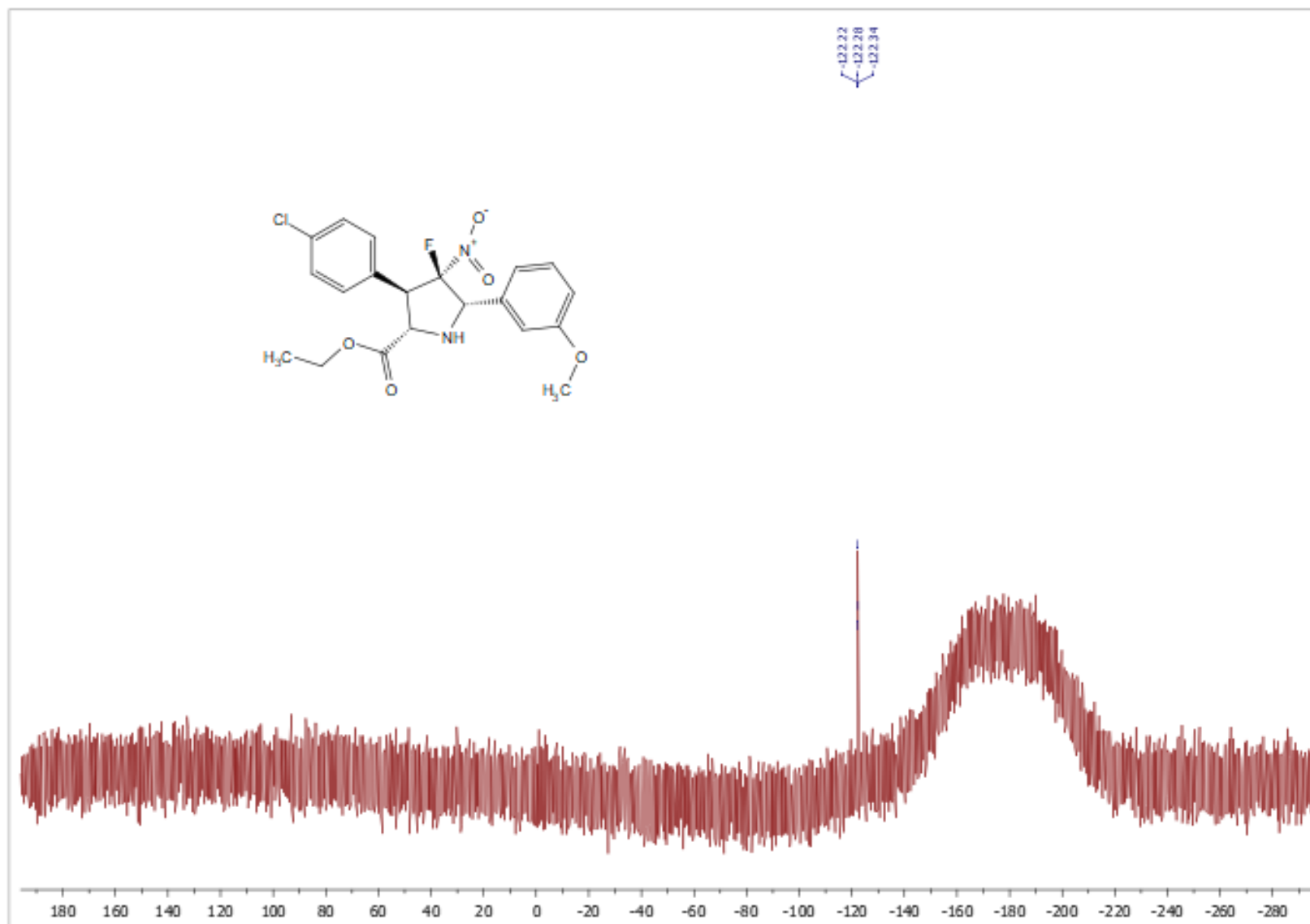
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^{13}C NMR

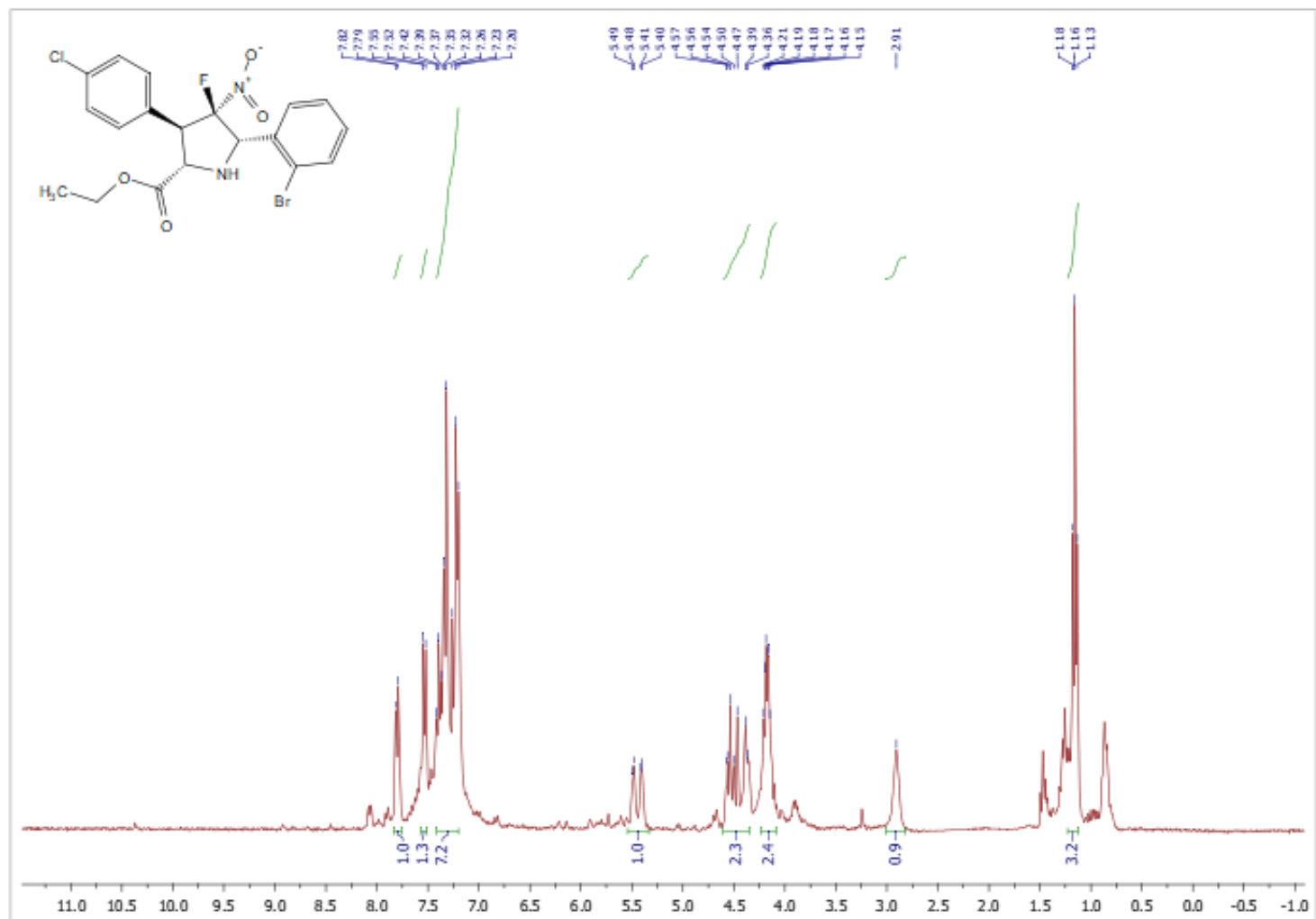


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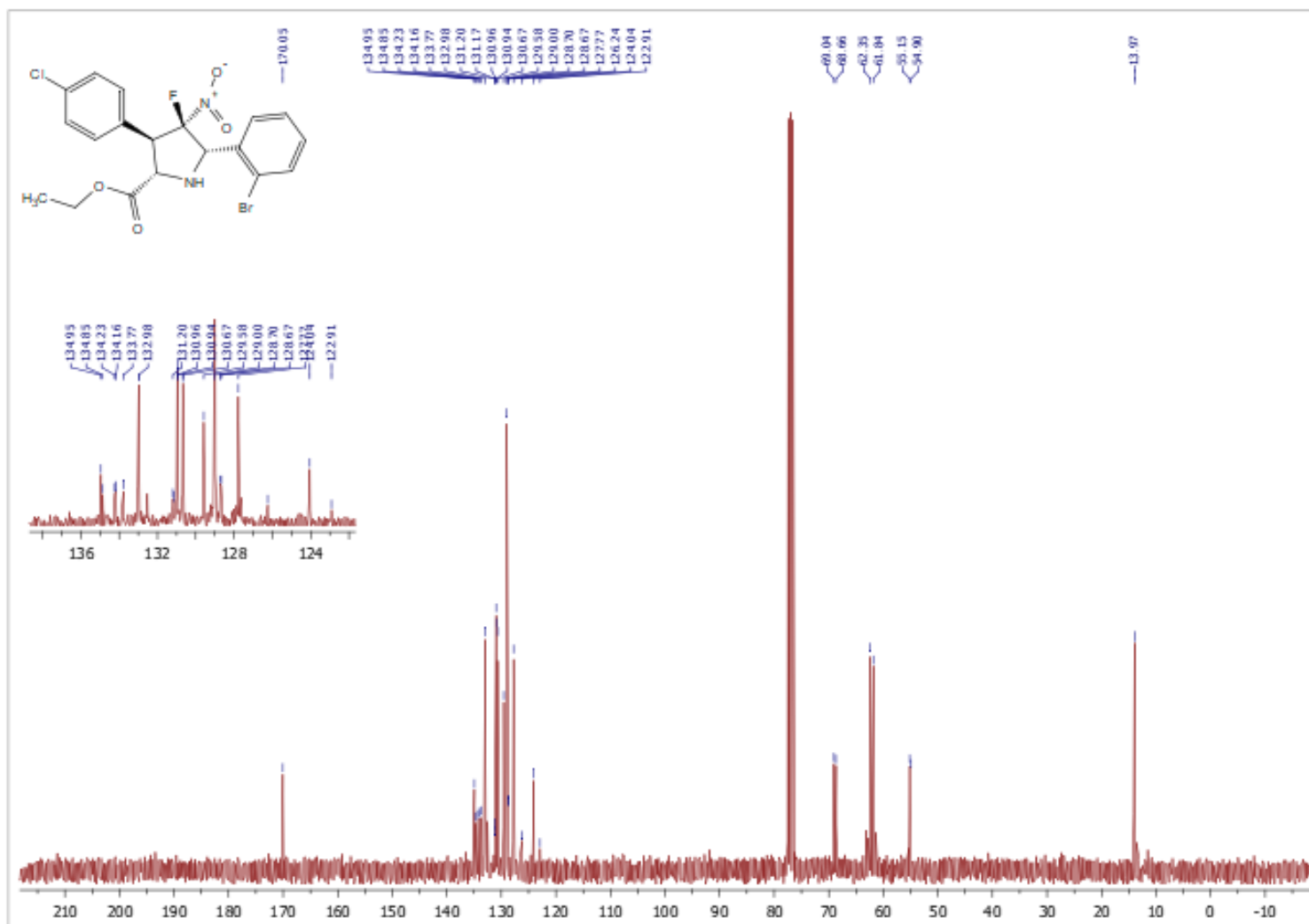


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-chlorophenyl)-5-(2-bromophenyl)-pyrrolidine-2-carboxylate **31**

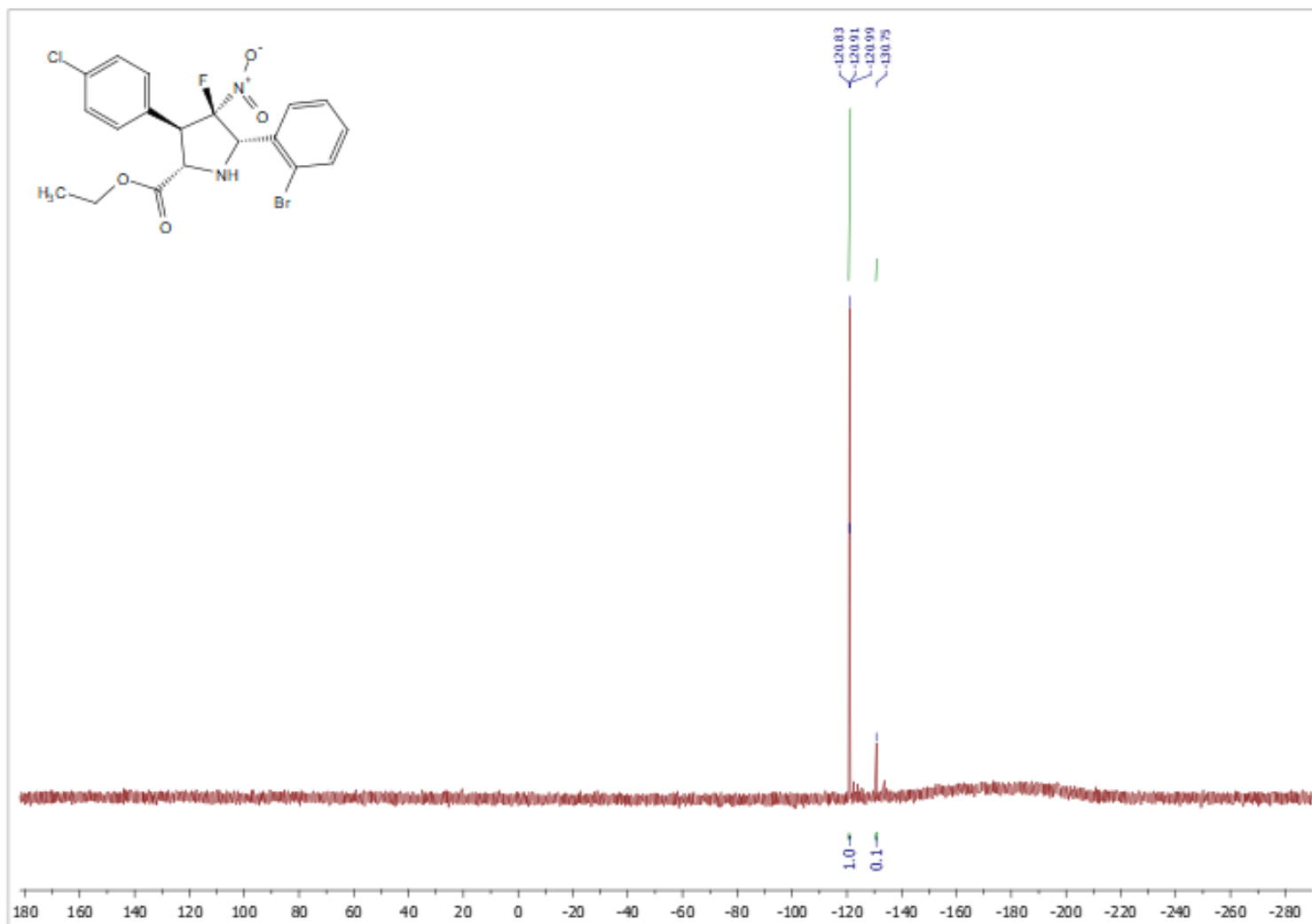
¹H NMR



¹³C NMR

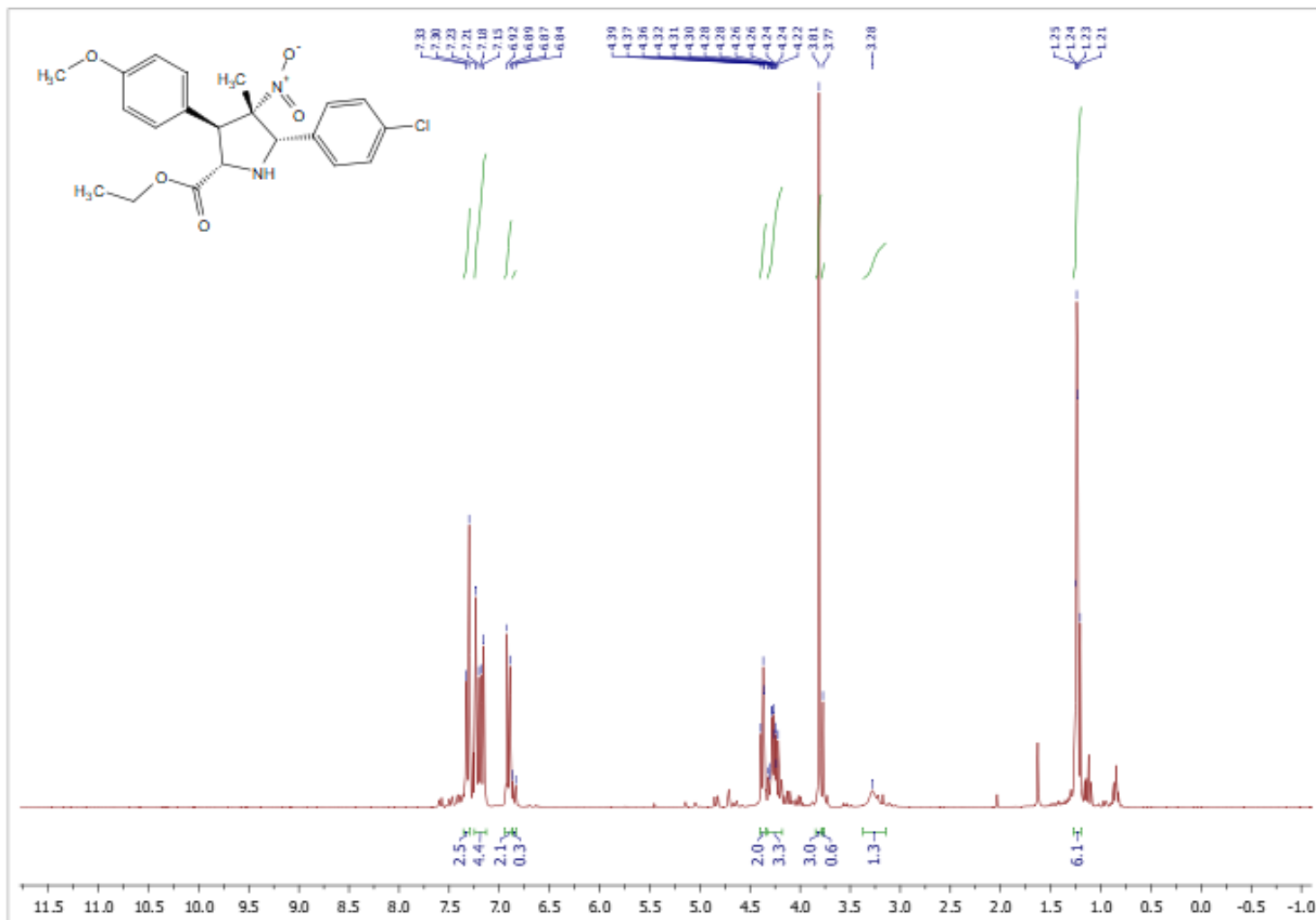


^{19}F NMR

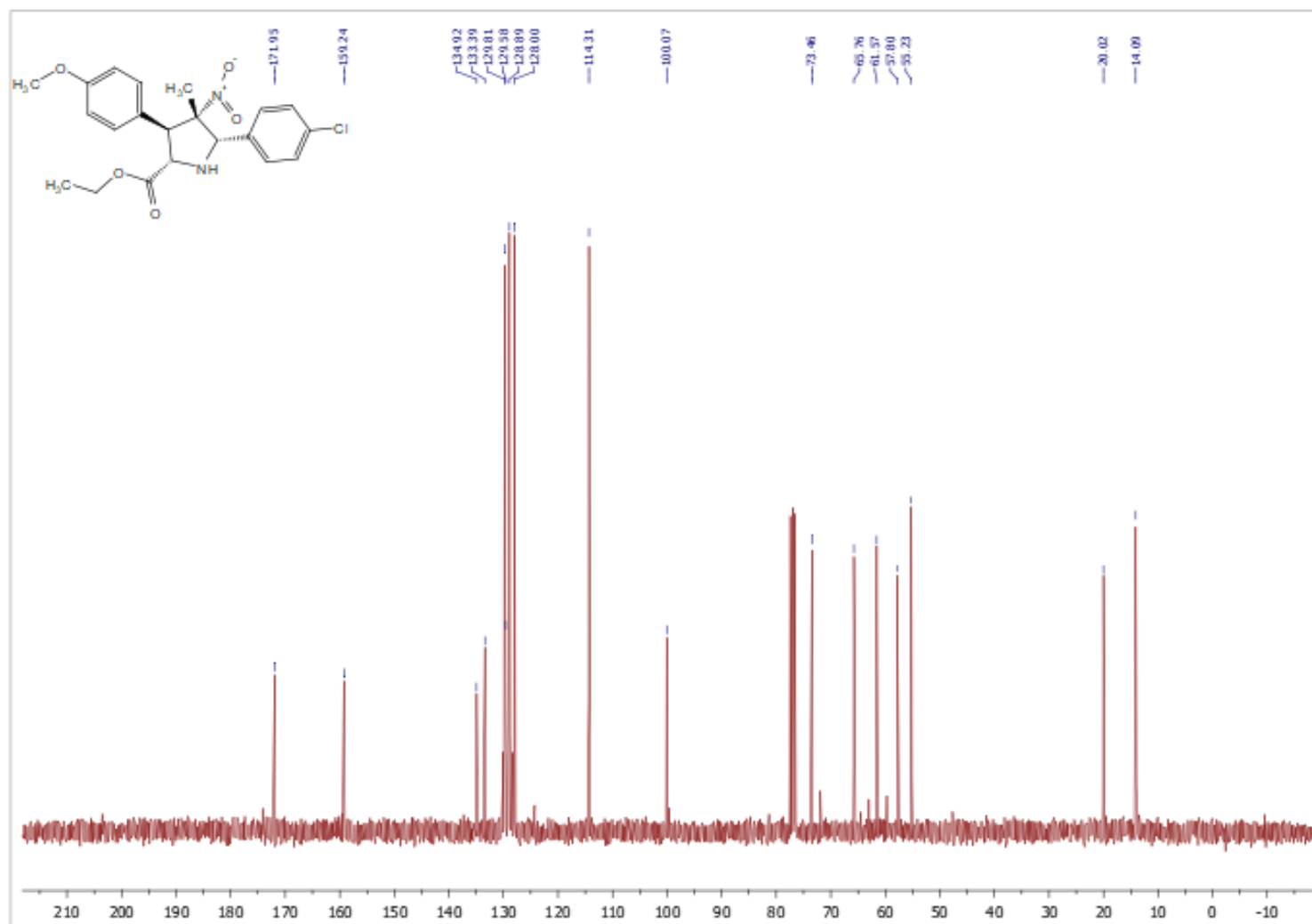


methyl (2*S*,3*R*,4*R*,5*S*)-4-methyl-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate and methyl (2*S*,3*S*,4*S*,5*S*)-4-methyl-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3m/3m'**

¹H NMR

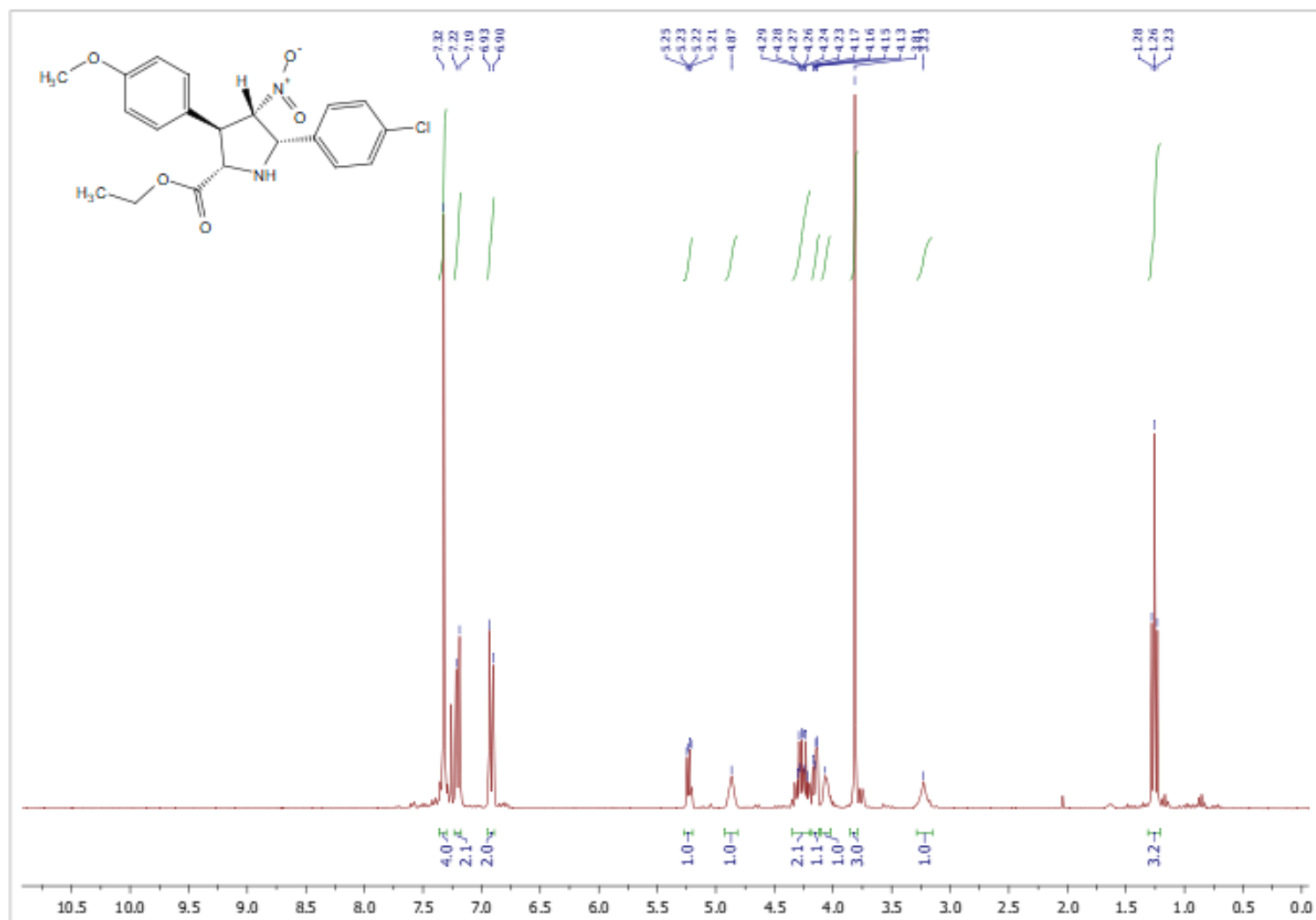


^{13}C NMR

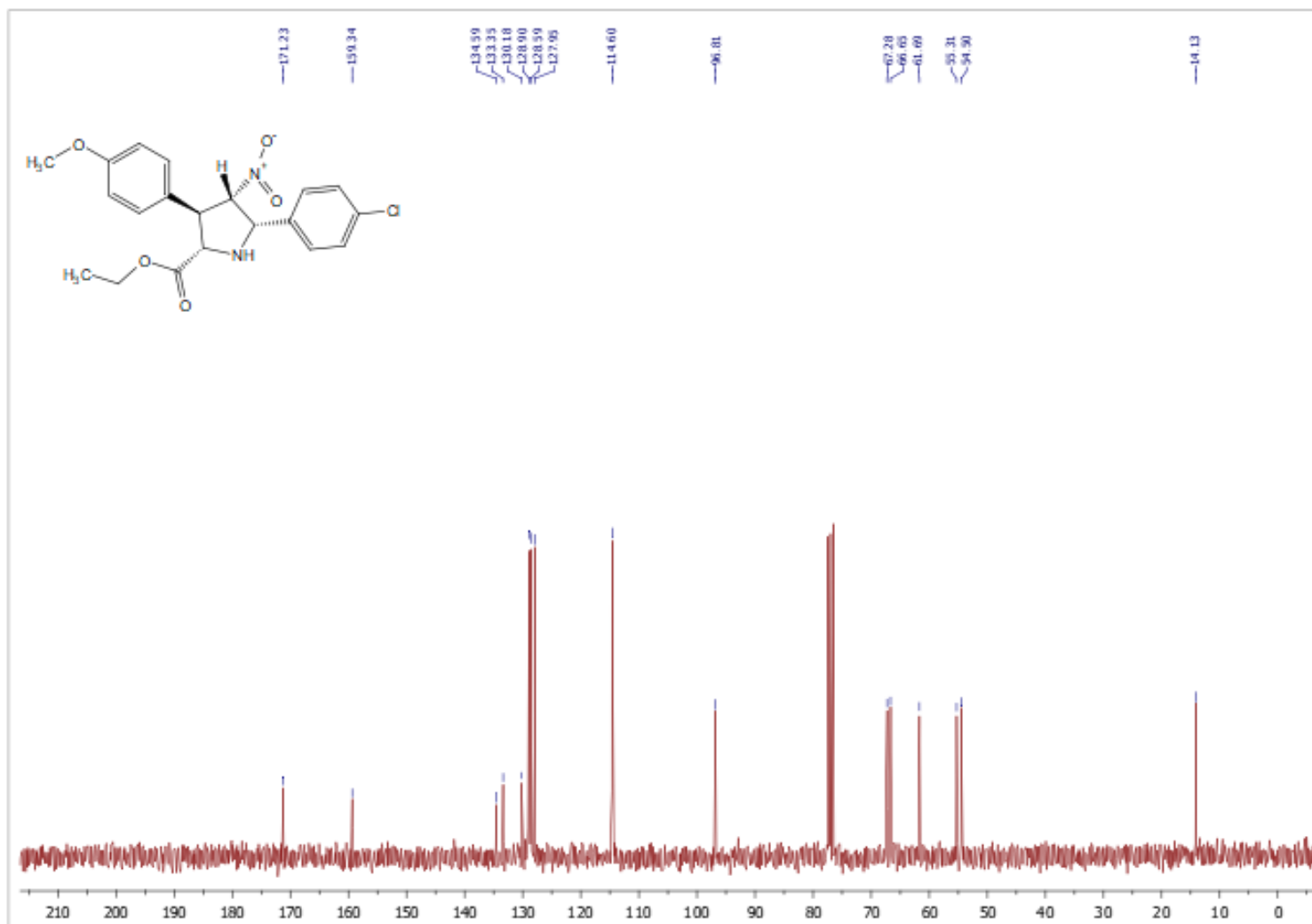


ethyl (2*S*,3*R*,4*S*,5*S*) -4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3n**

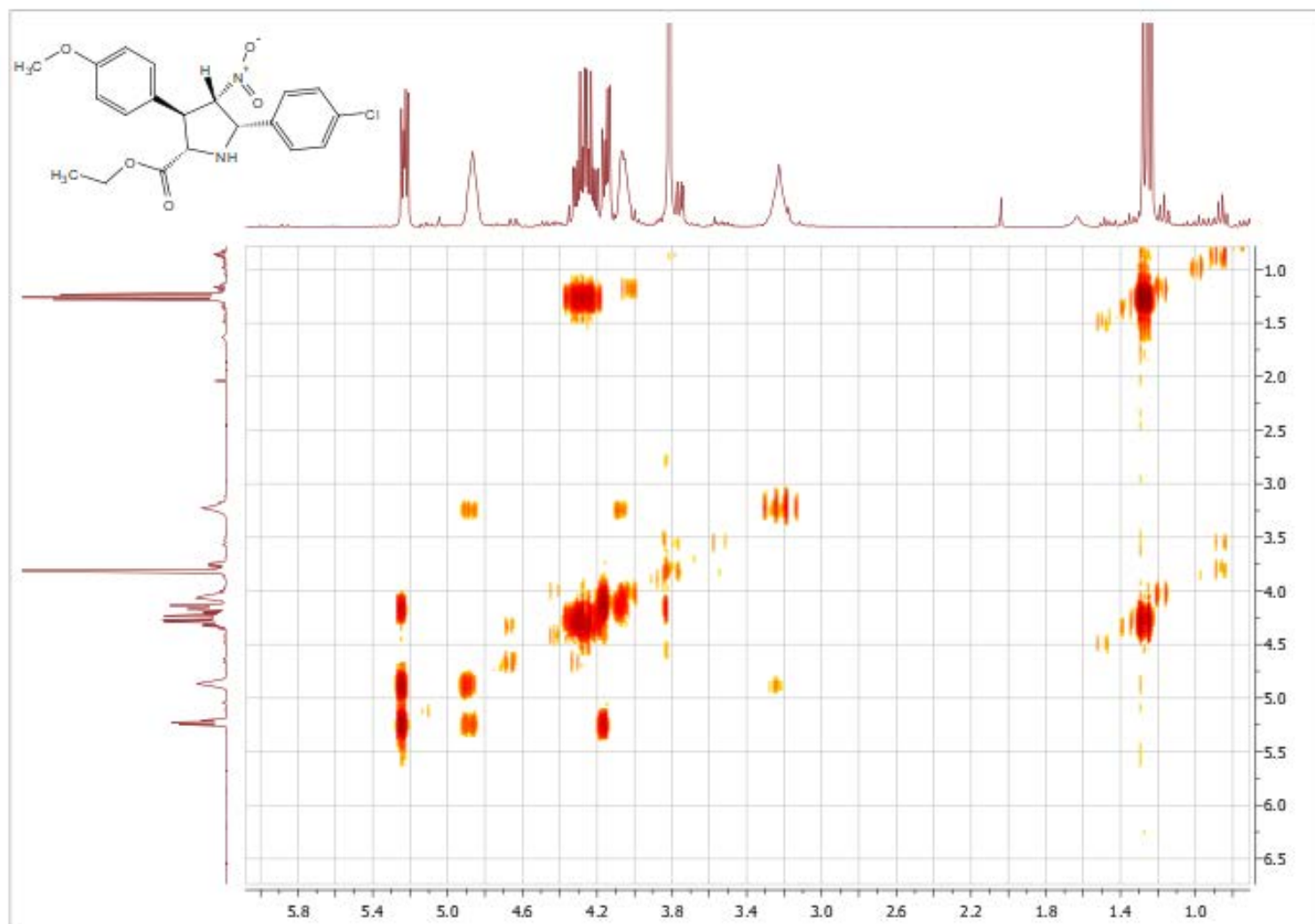
¹H NMR



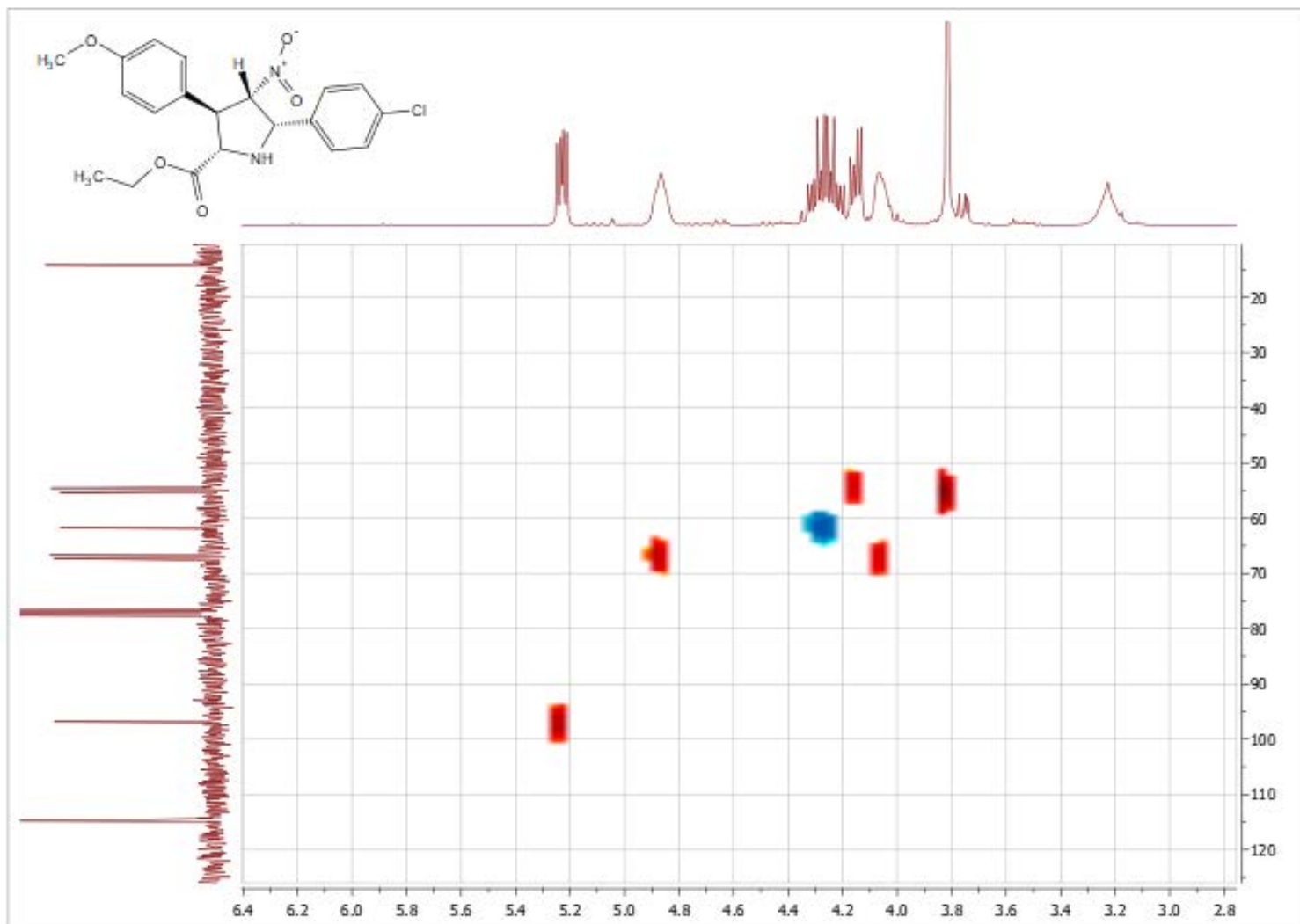
¹³C NMR



^1H - ^1H COSY NMR

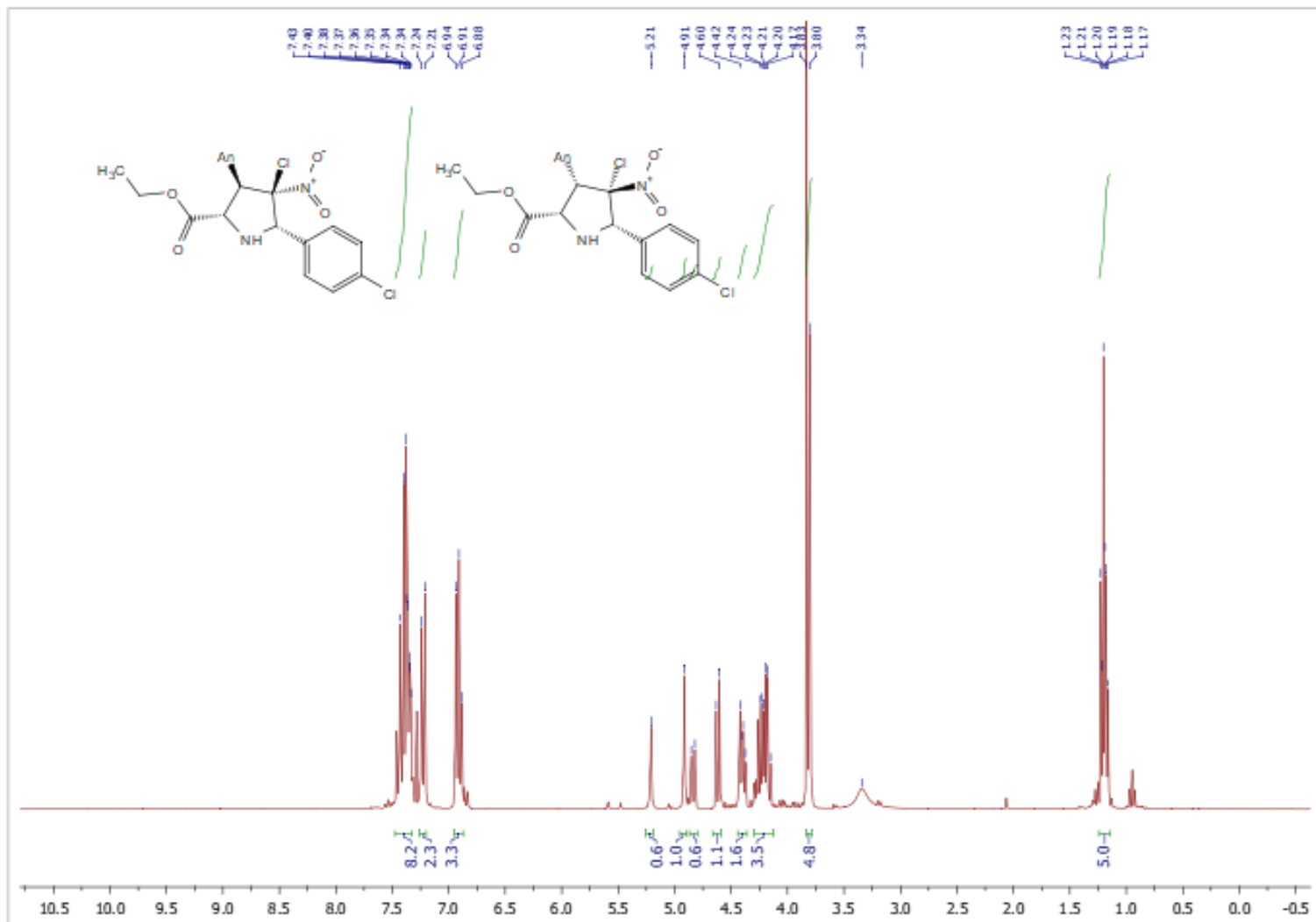


^1H - ^{13}C HSQC NMR

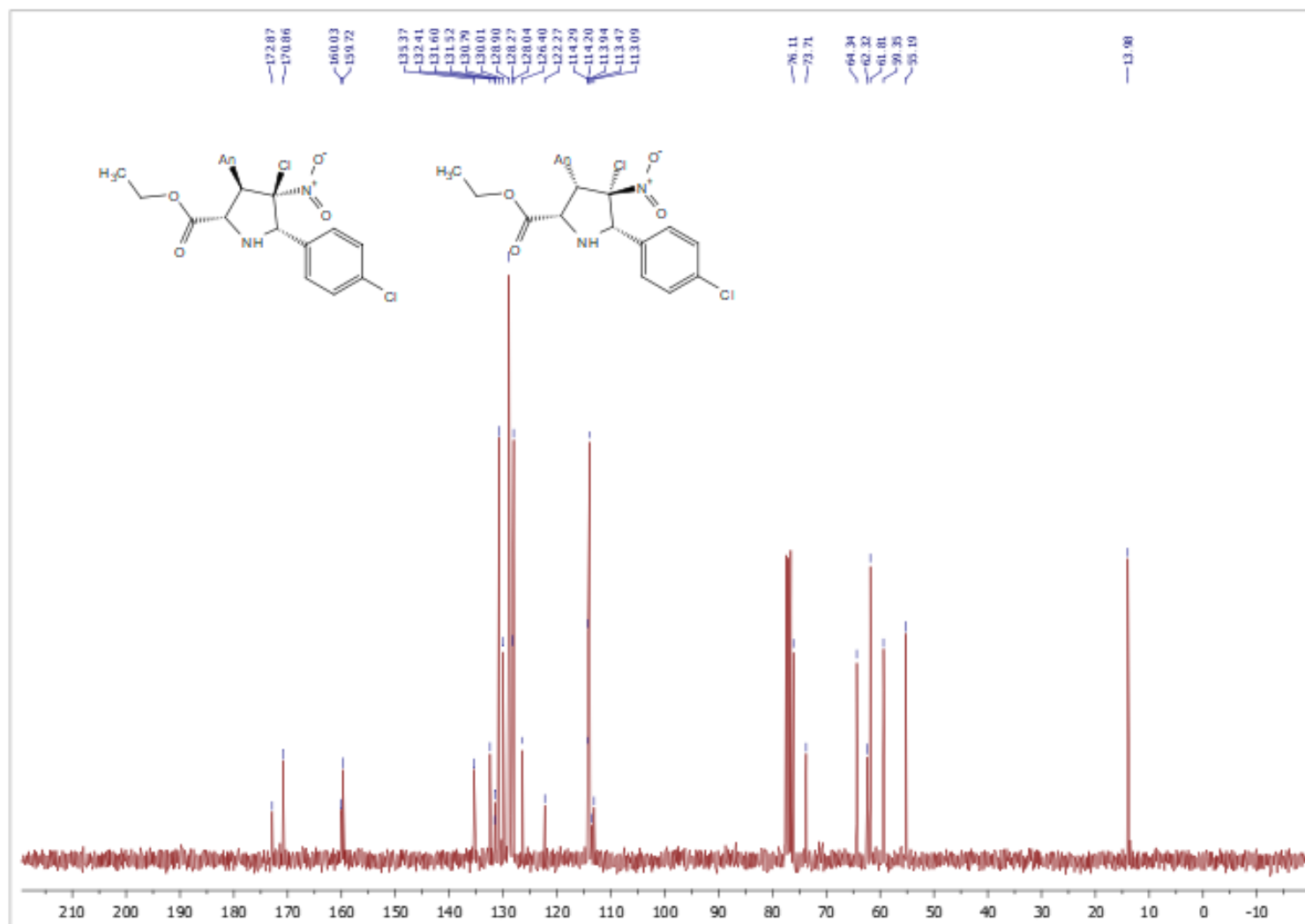


methyl (2*S*,3*R*,4*R*,5*S*)-4-chloro-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate and methyl (2*S*,3*S*,4*S*,5*S*)-4-chloro-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-pyrrolidine-2-carboxylate **3o/3o'** (An = 4-MeO-C₆H₄-)

¹H NMR

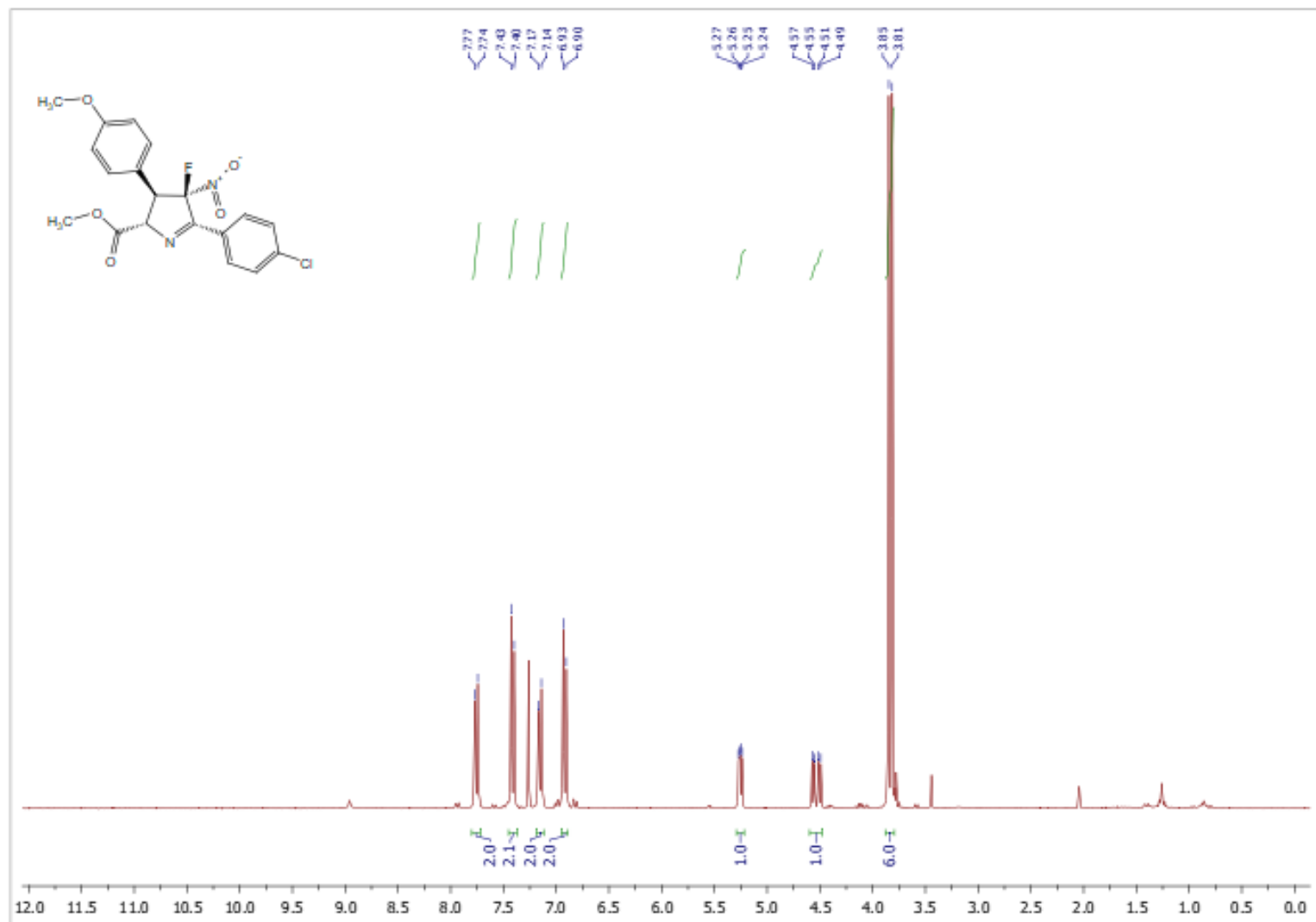


¹³C NMR

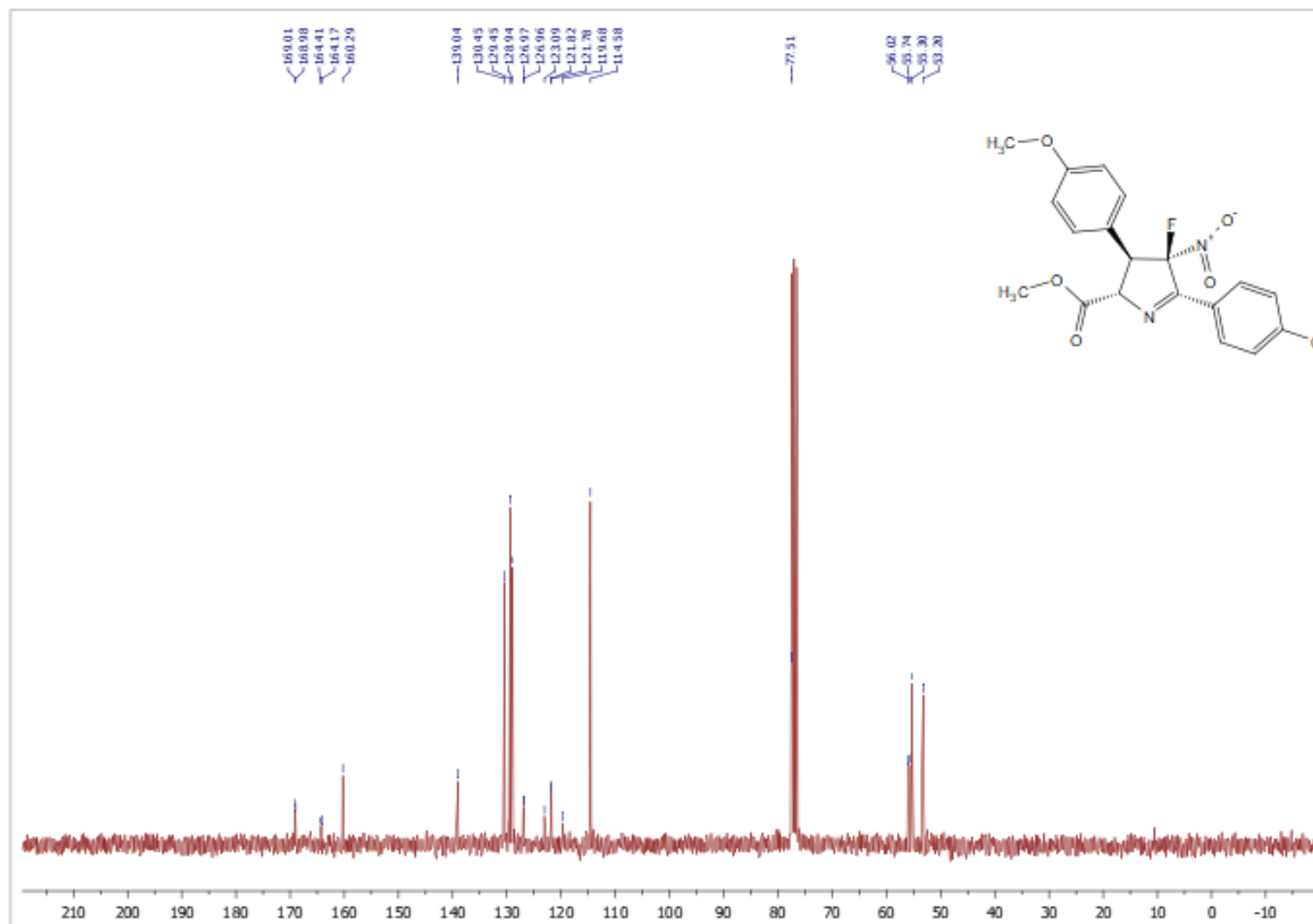


methyl (2*S*,3*R*,4*R*)-4-fluoro-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **4a**

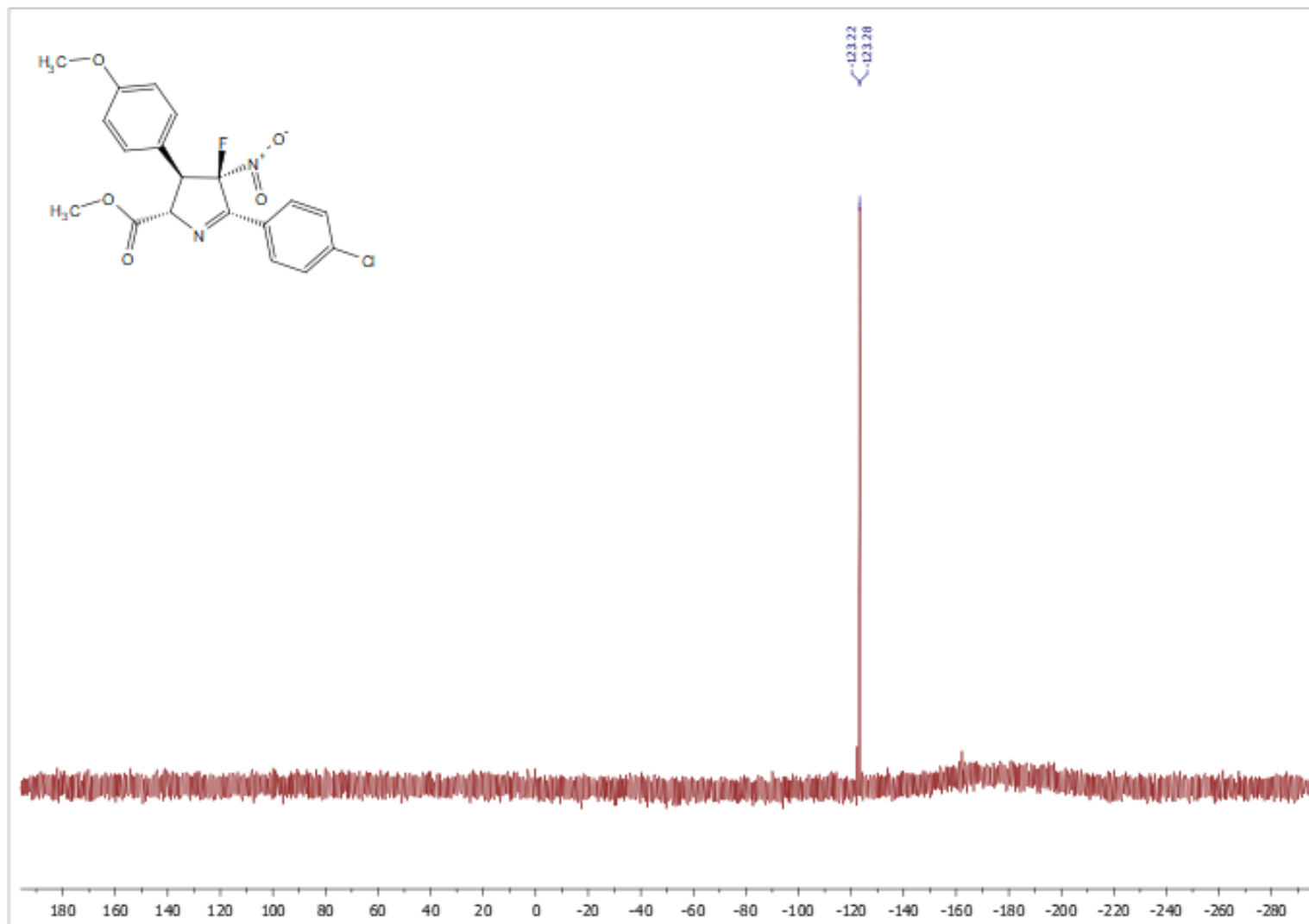
^1H NMR



^{13}C NMR

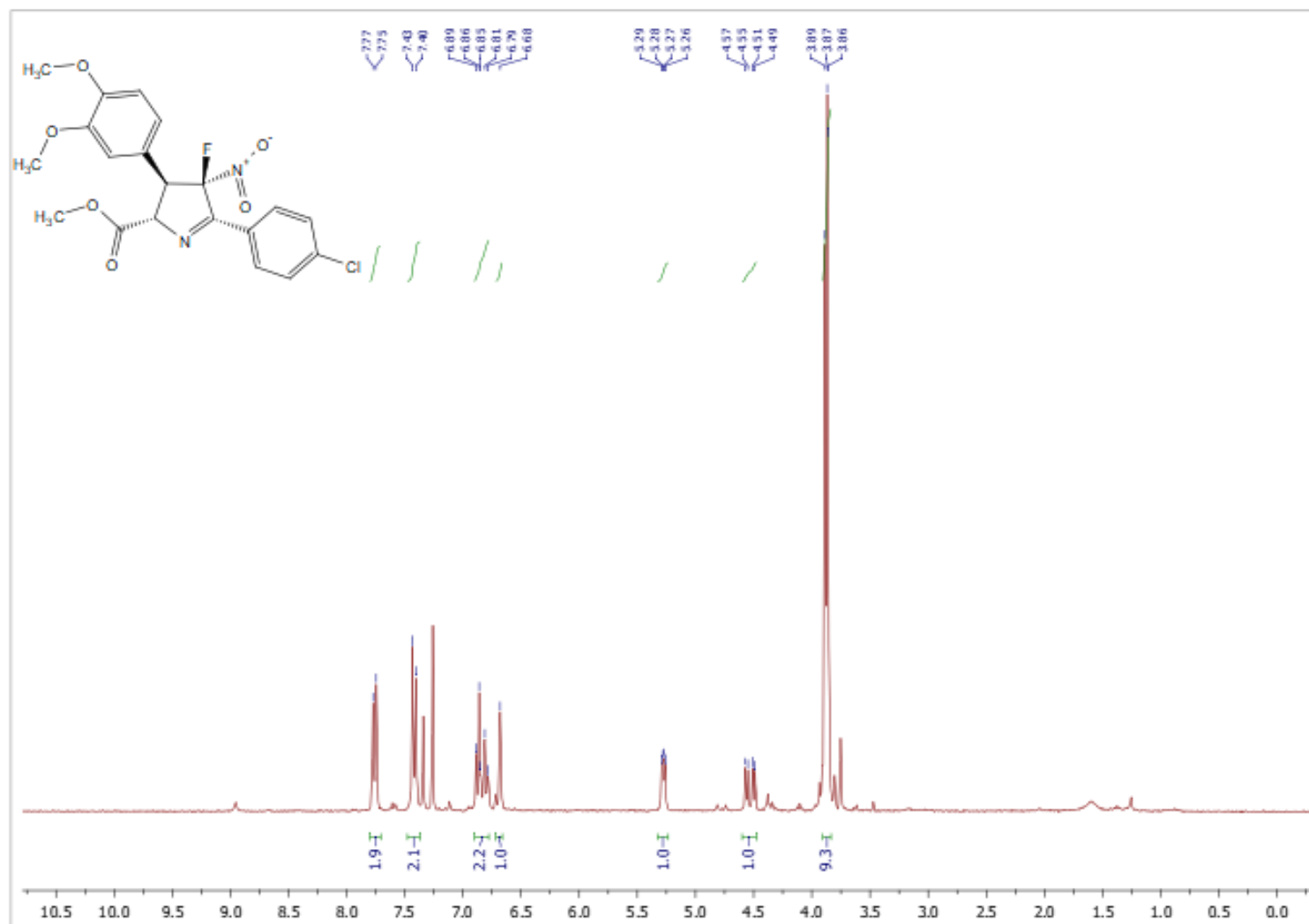


^{19}F NMR

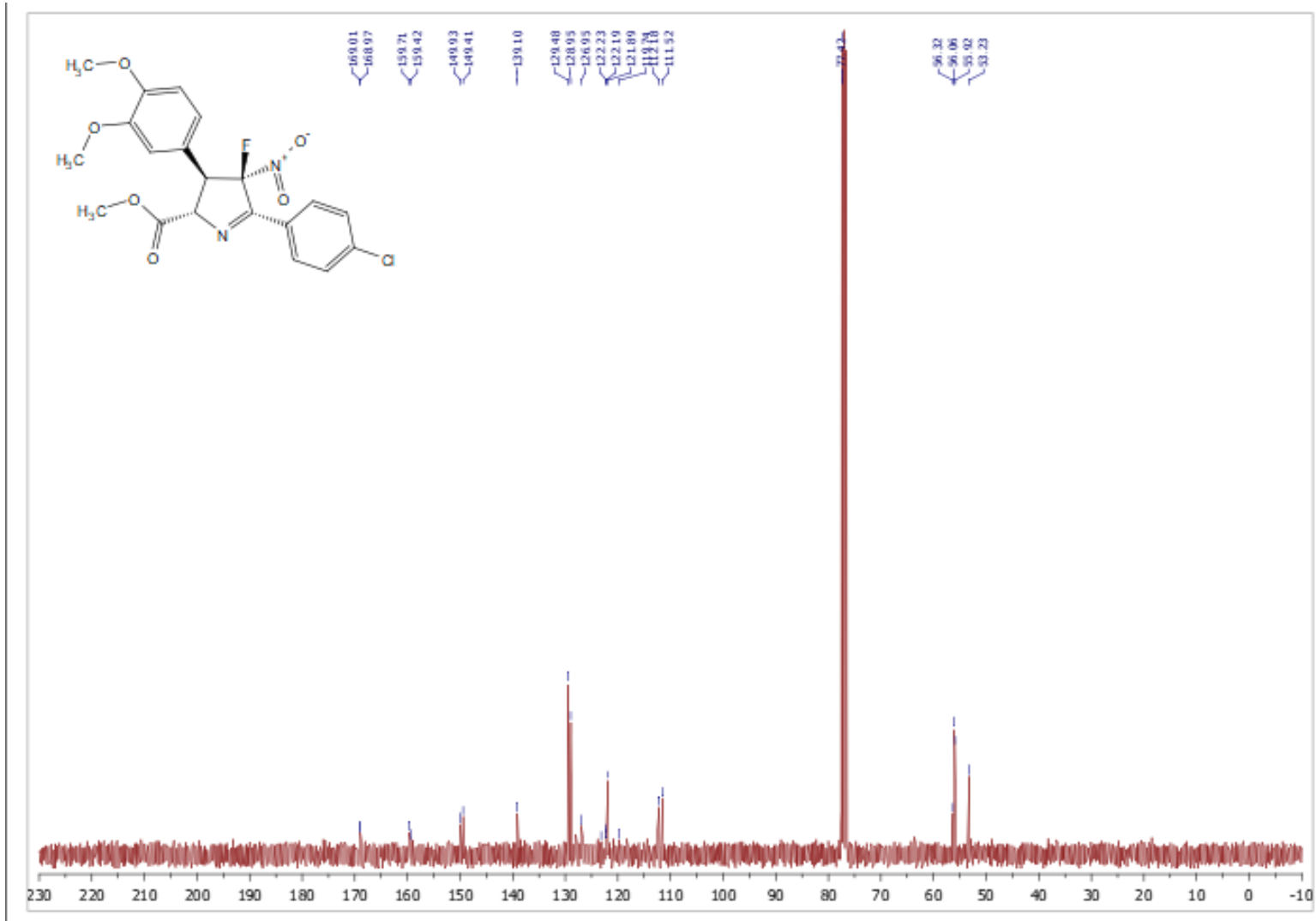


methyl (2*S*,3*R*,4*R*)-4-fluoro-4-nitro-5-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **4b**

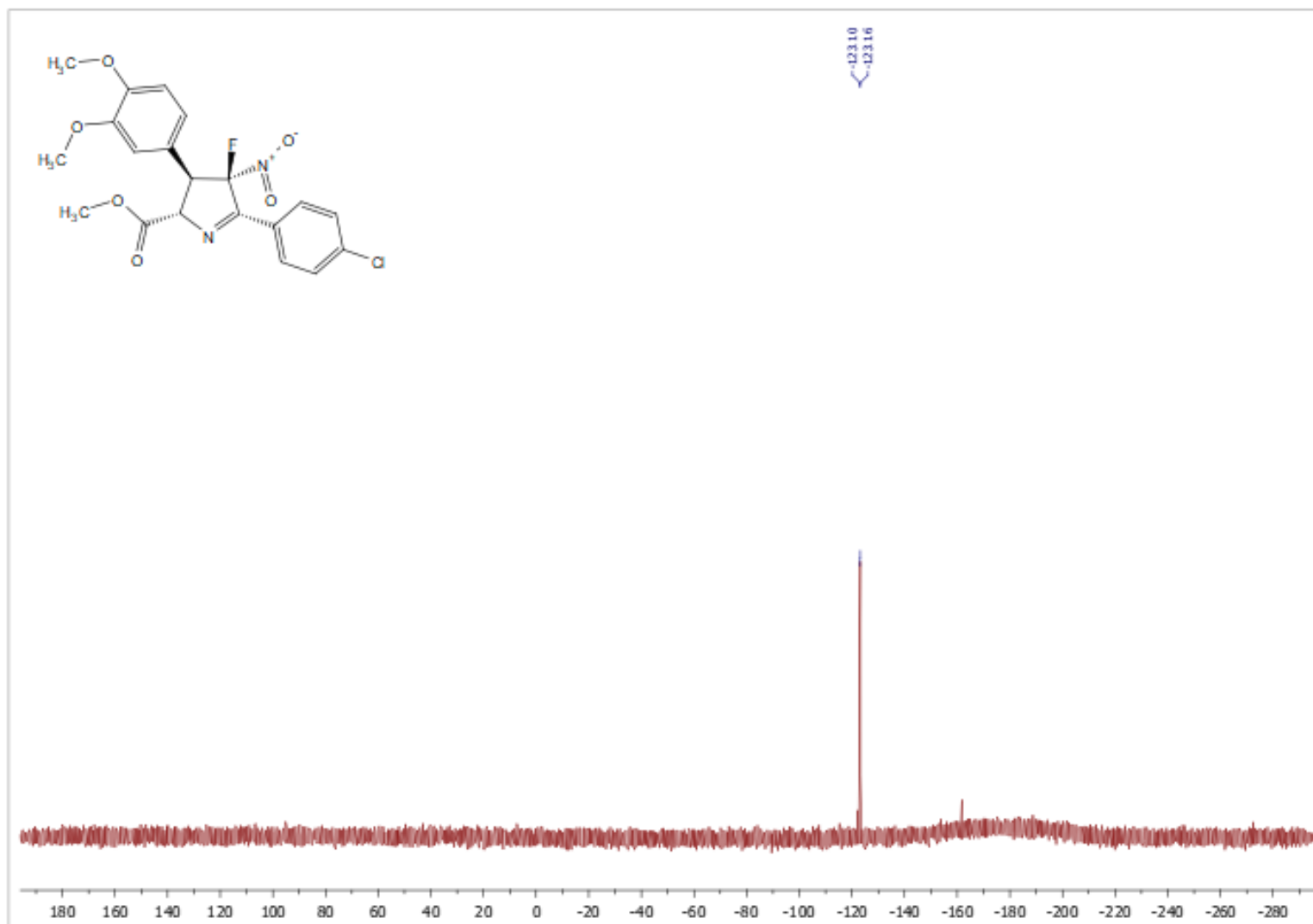
¹H NMR



¹³C NMR

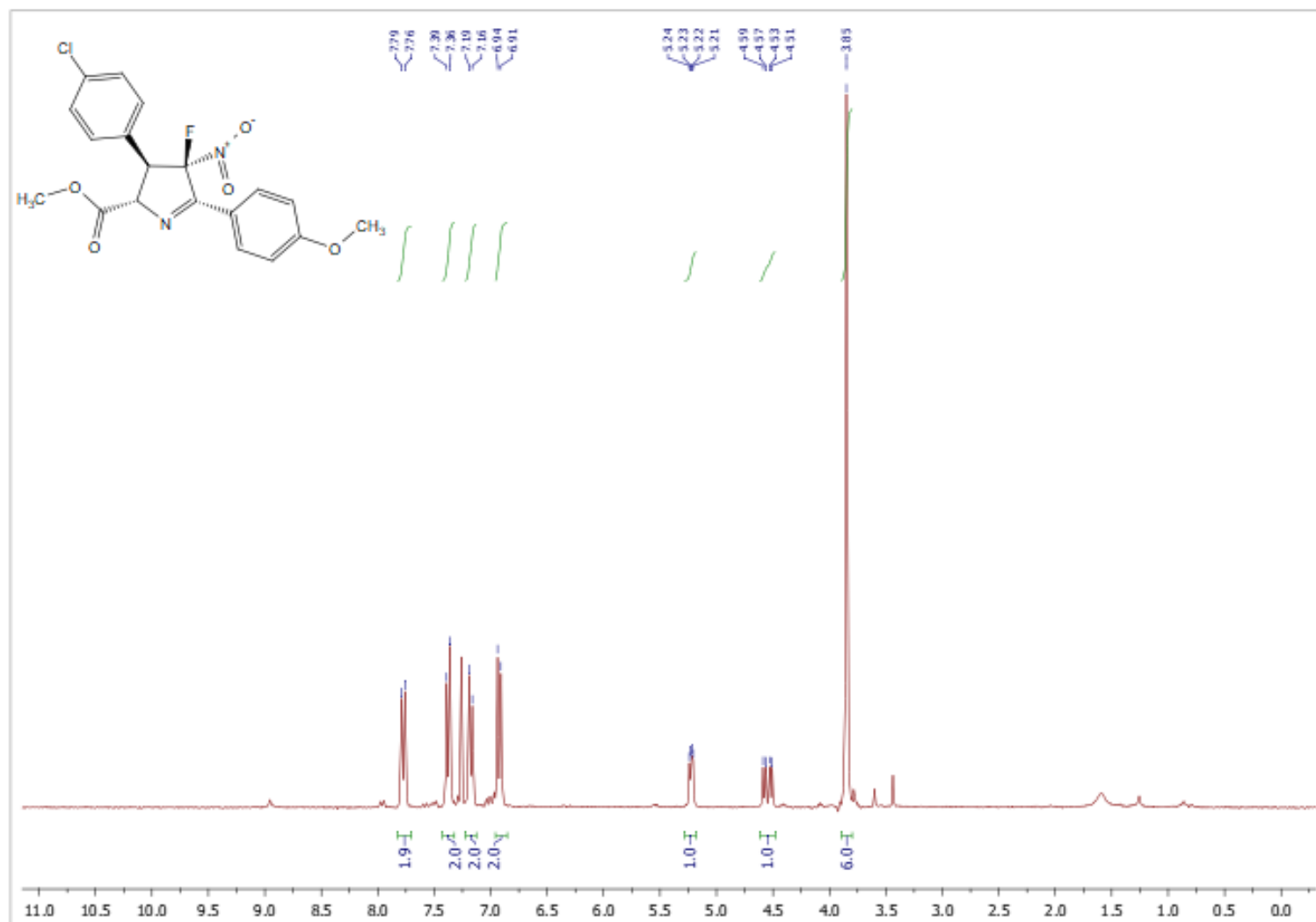


^{19}F NMR

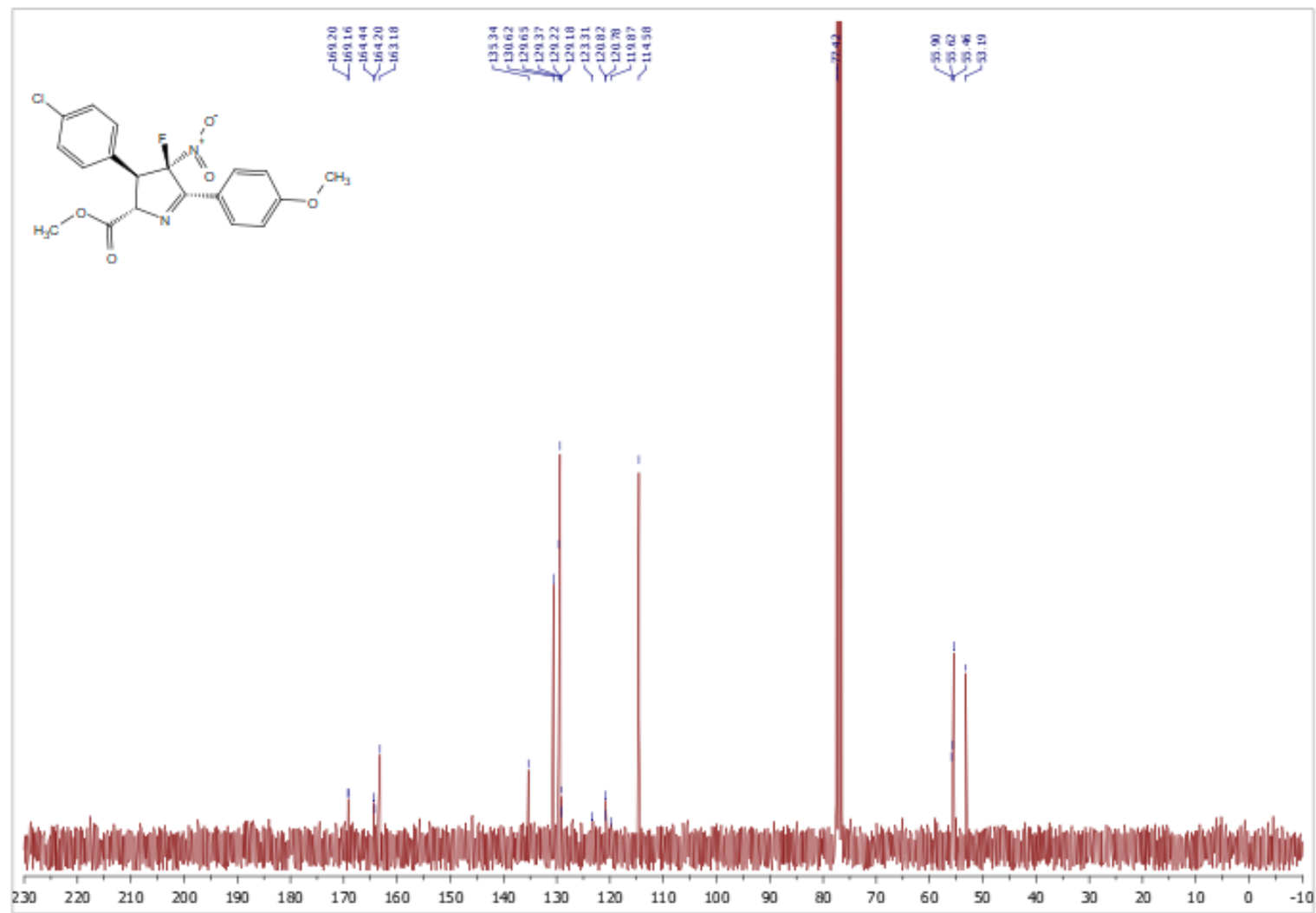


methyl (2*S*,3*R*,4*R*)-4-fluoro-4-nitro-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **4c**

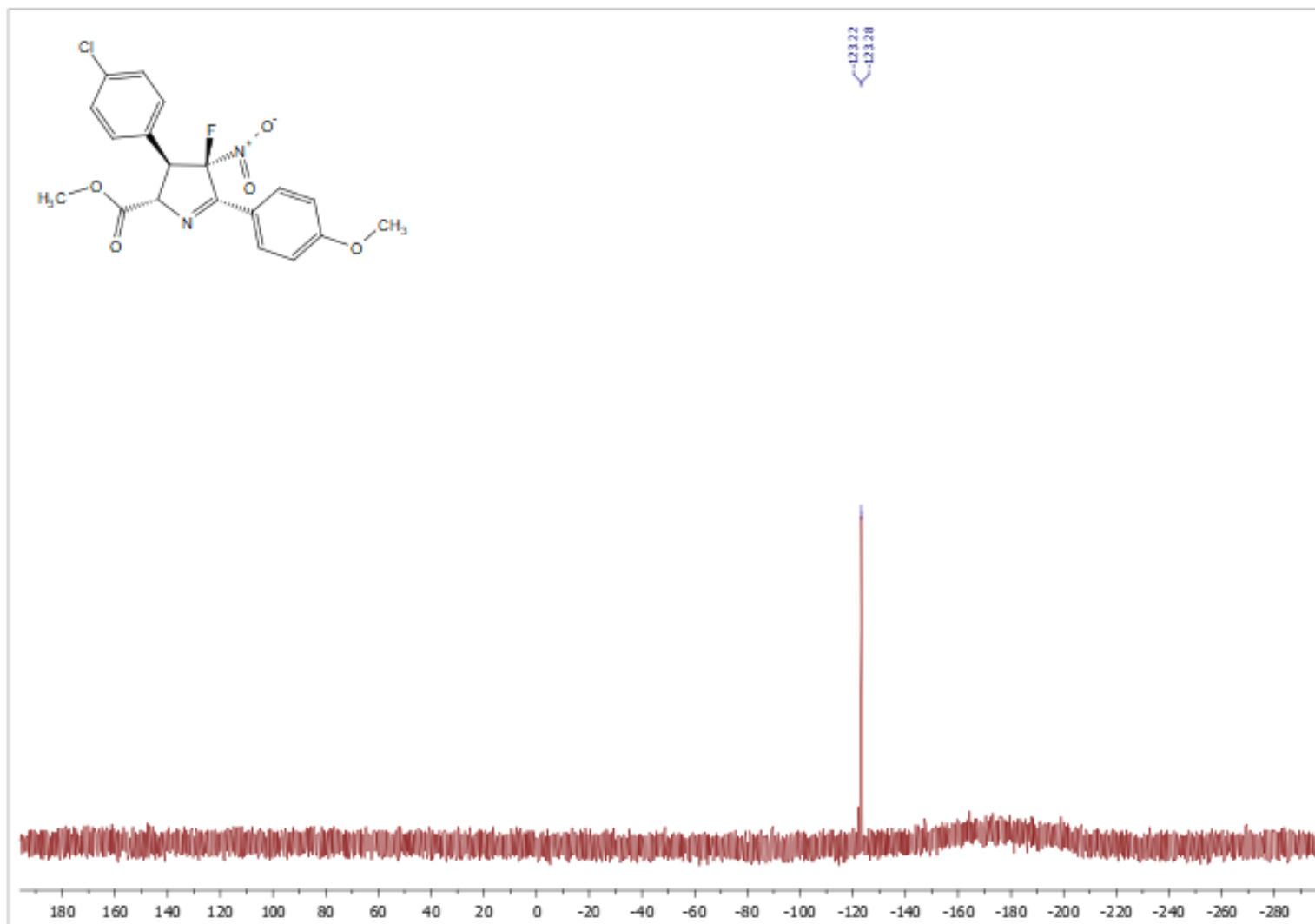
¹H NMR



^{13}C NMR

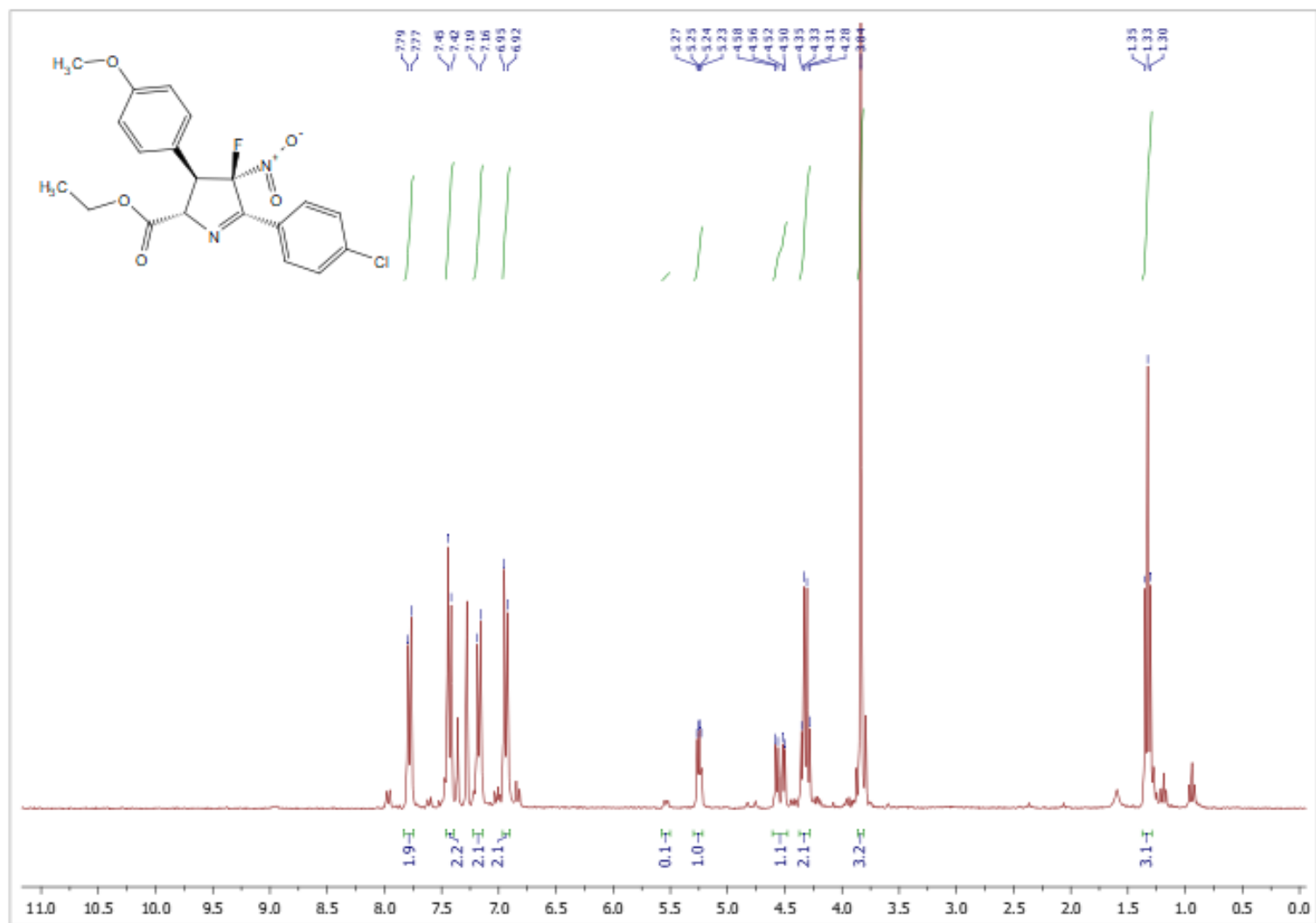


^{19}F NMR

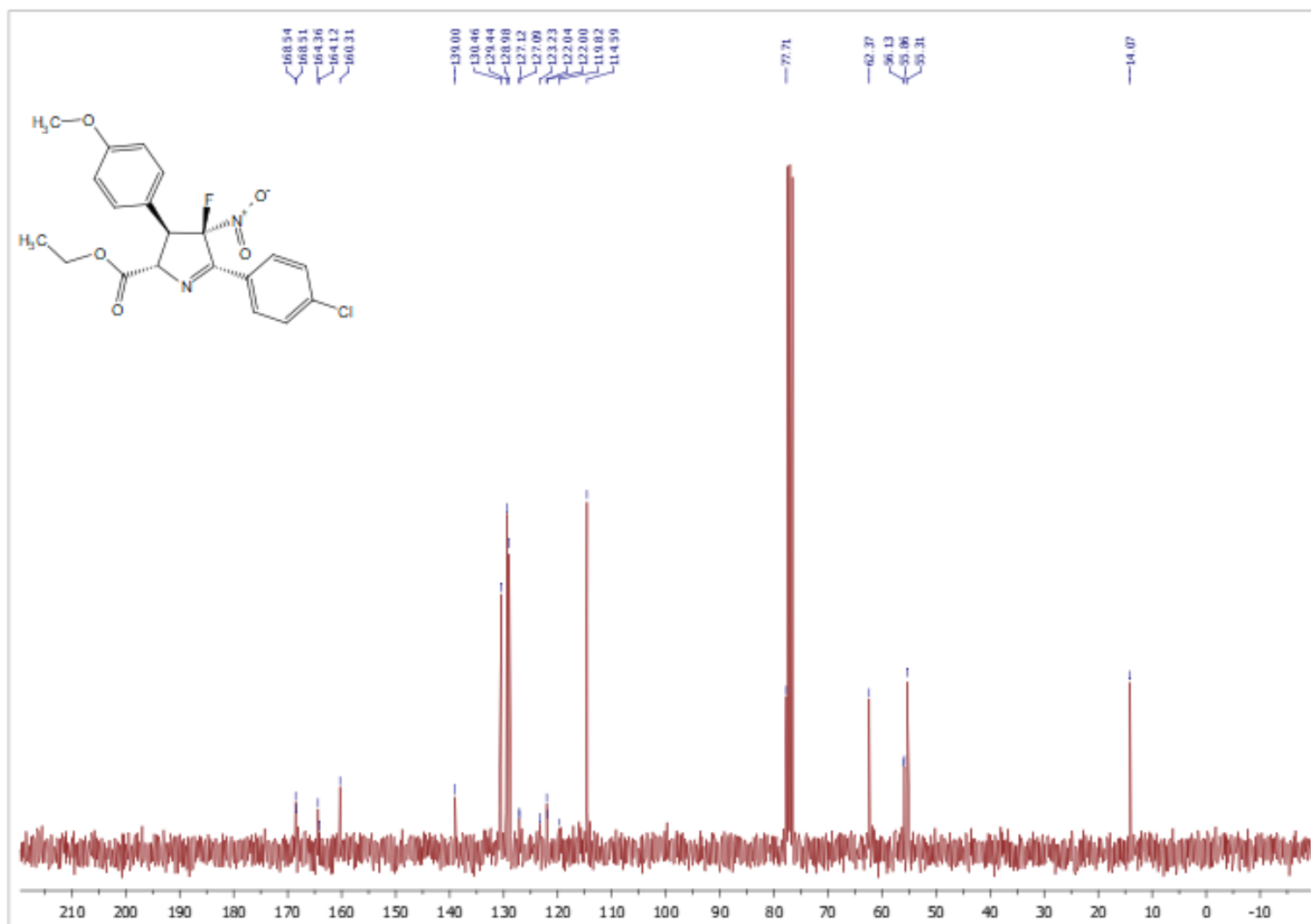


ethyl (2*S*,3*R*,4*R*)-4-fluoro-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **4d**

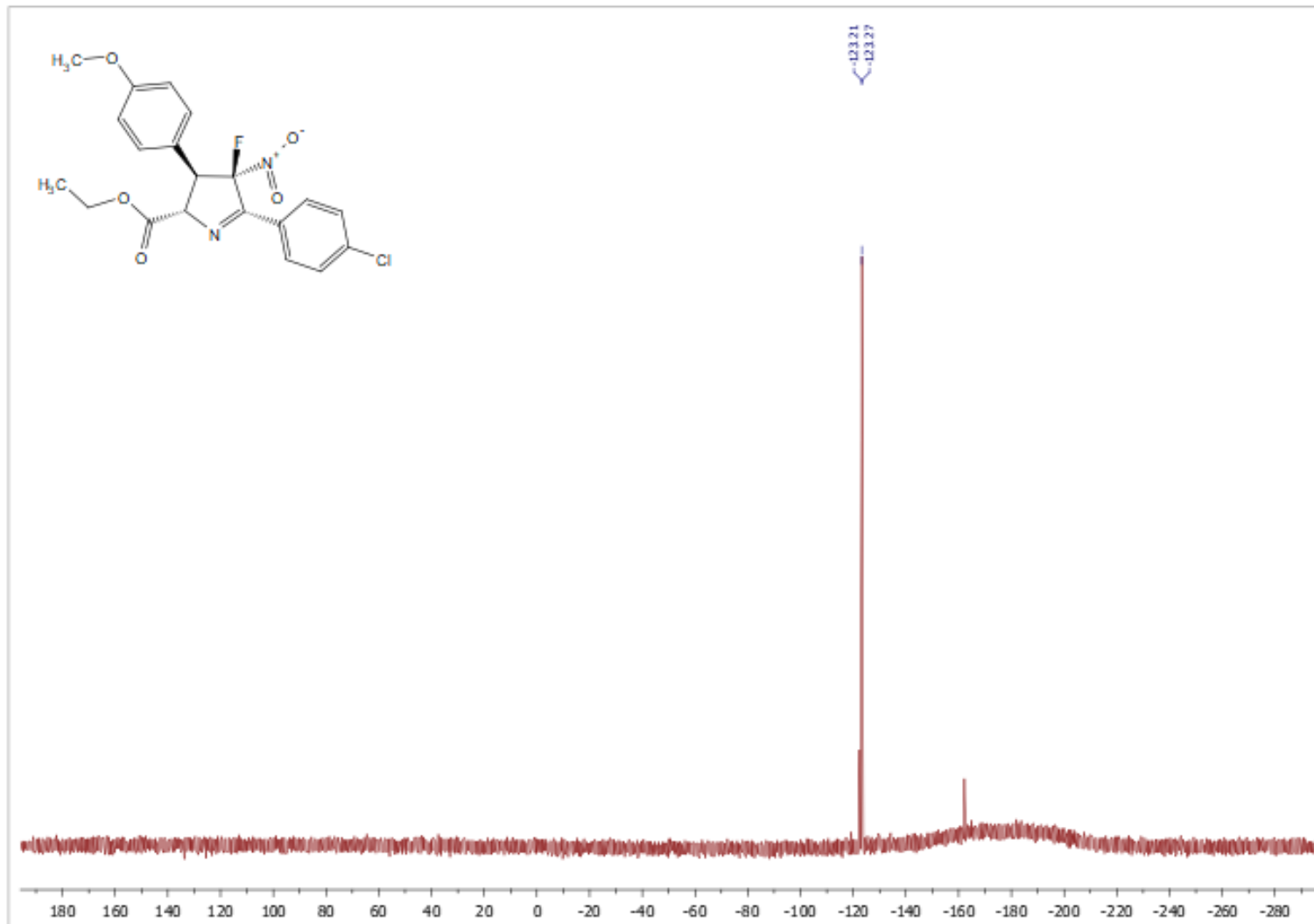
¹H NMR



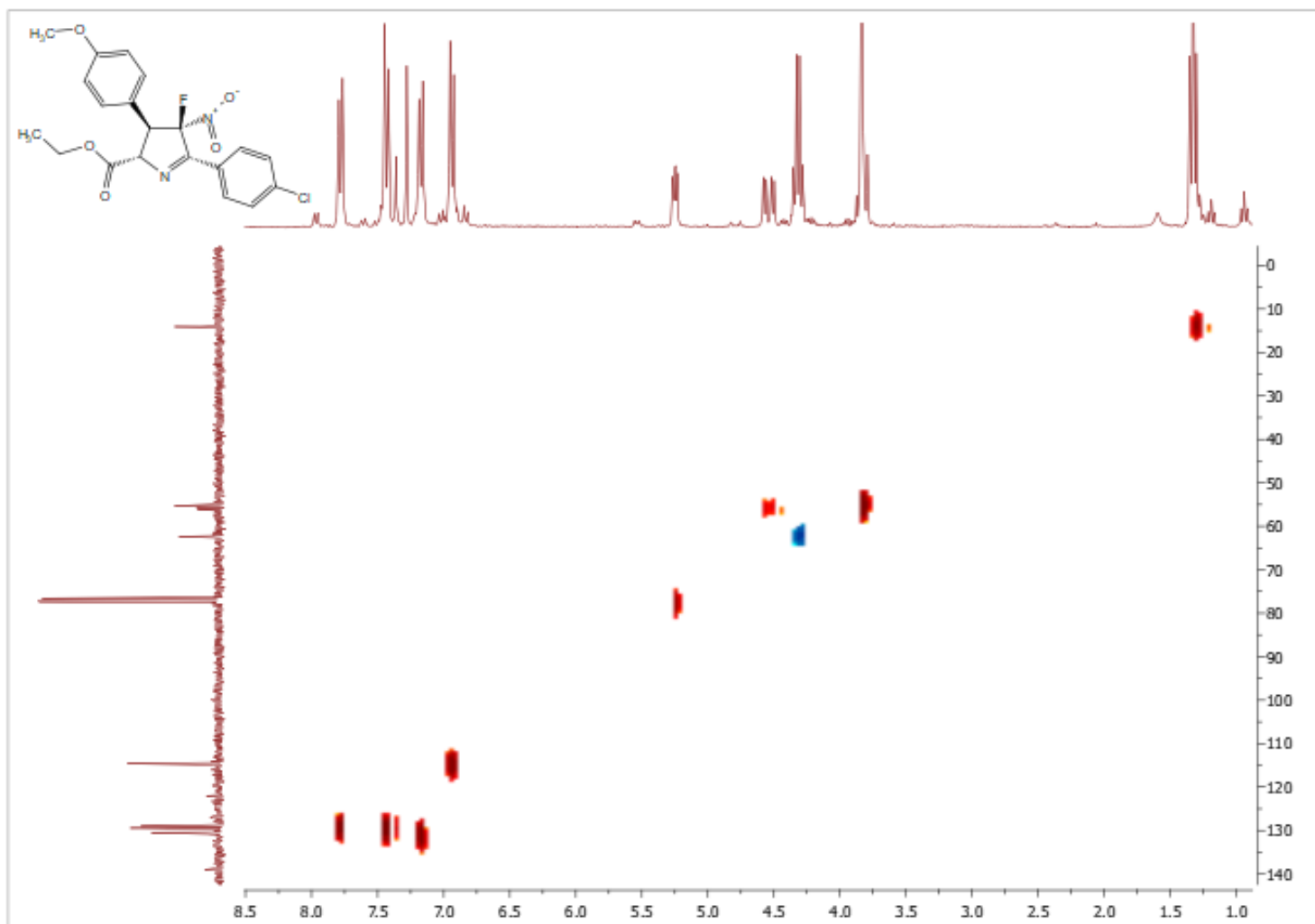
¹³C NMR



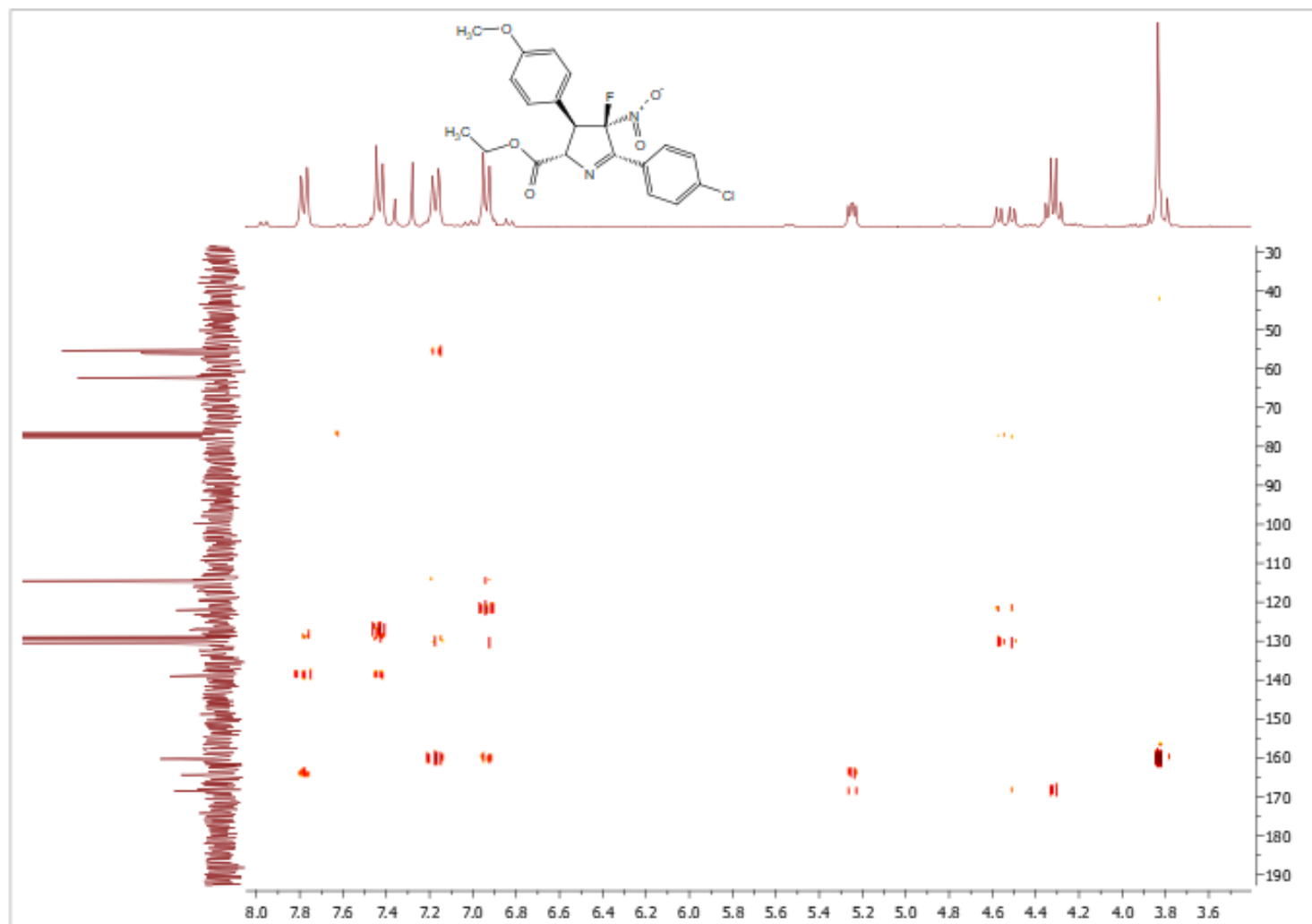
^{19}F NMR



^1H - ^{13}C HSQC NMR

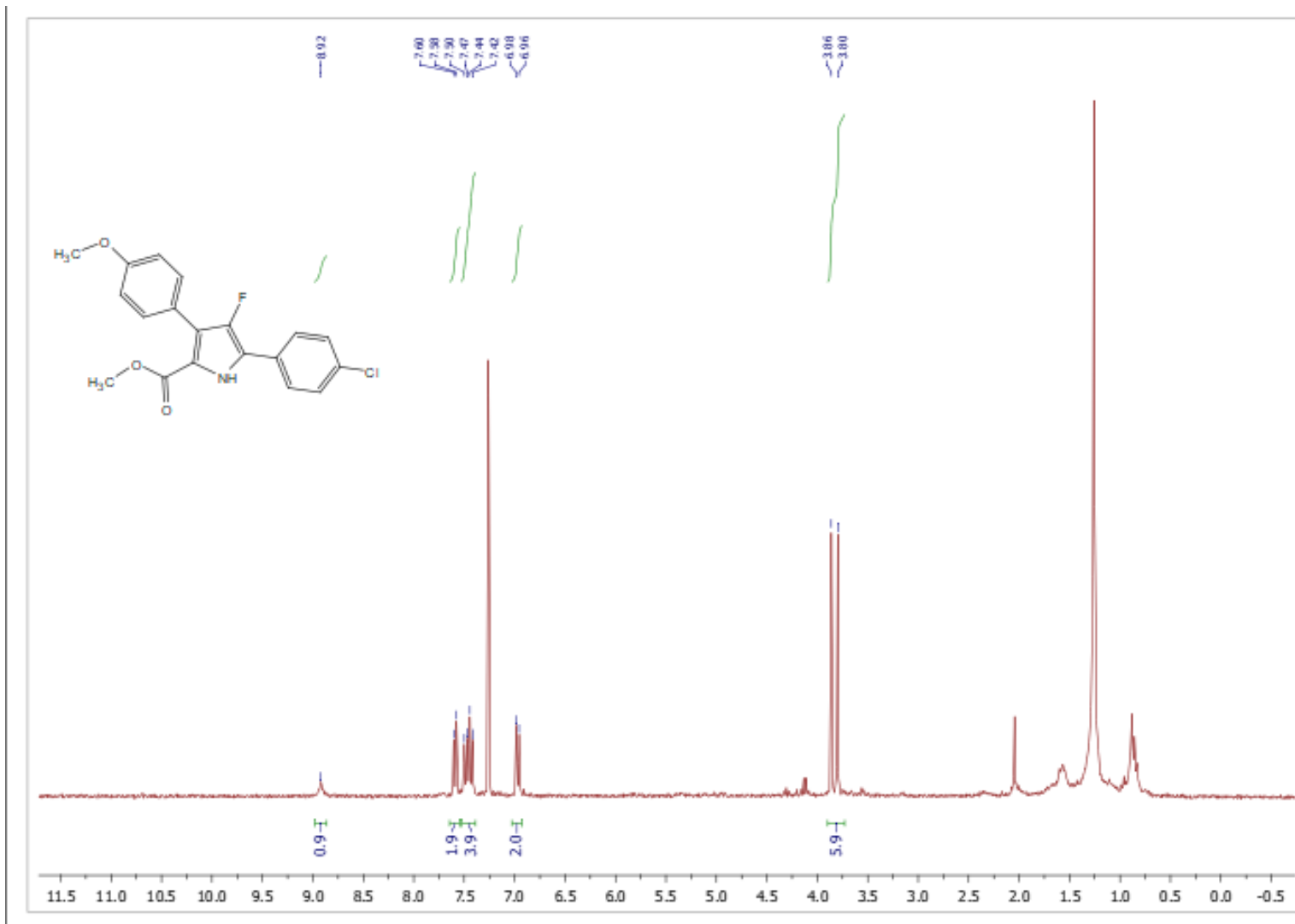


^1H - ^{13}C HMBC NMR

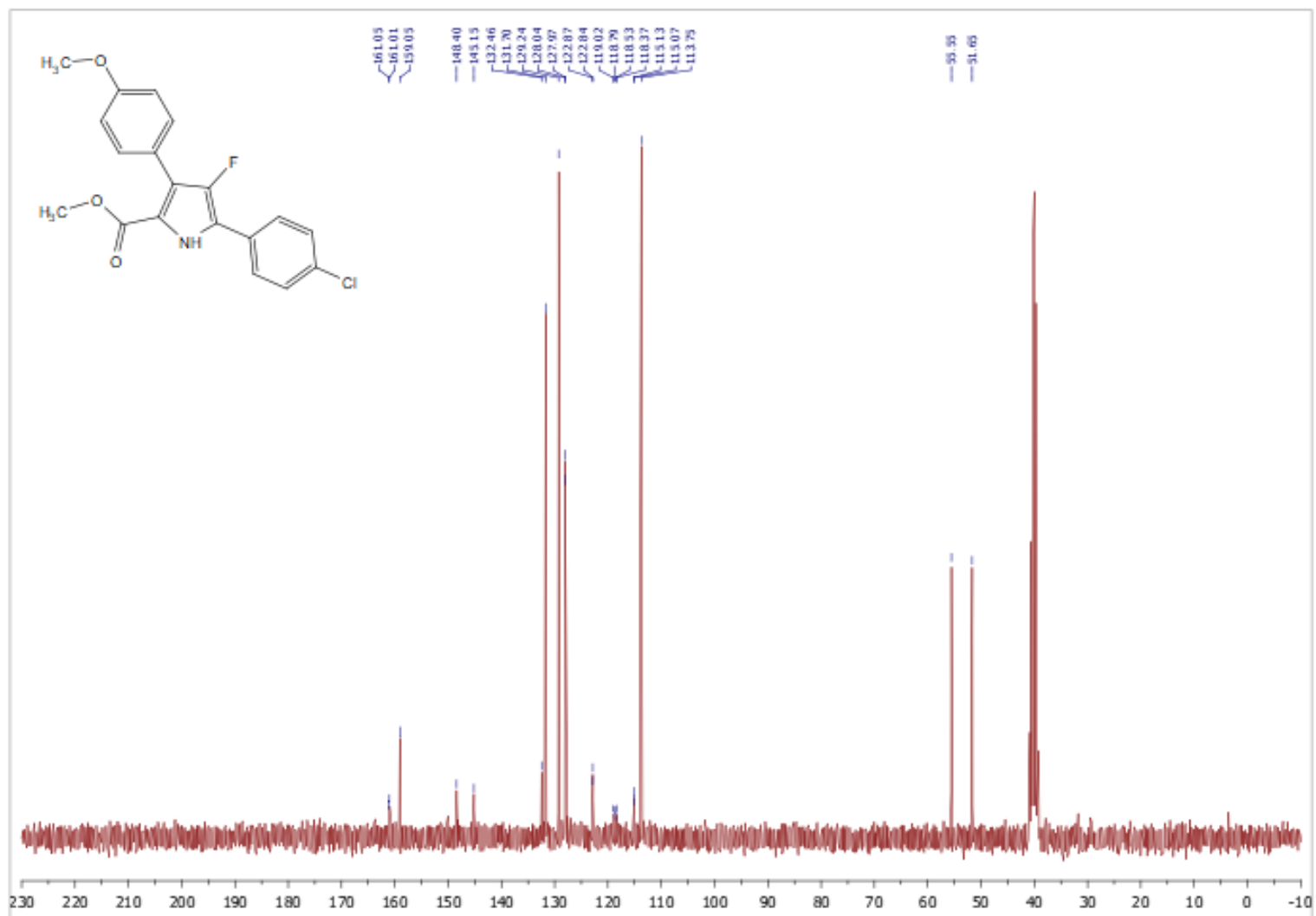


methyl 5-(4-chlorophenyl)-4-fluoro-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **5a**

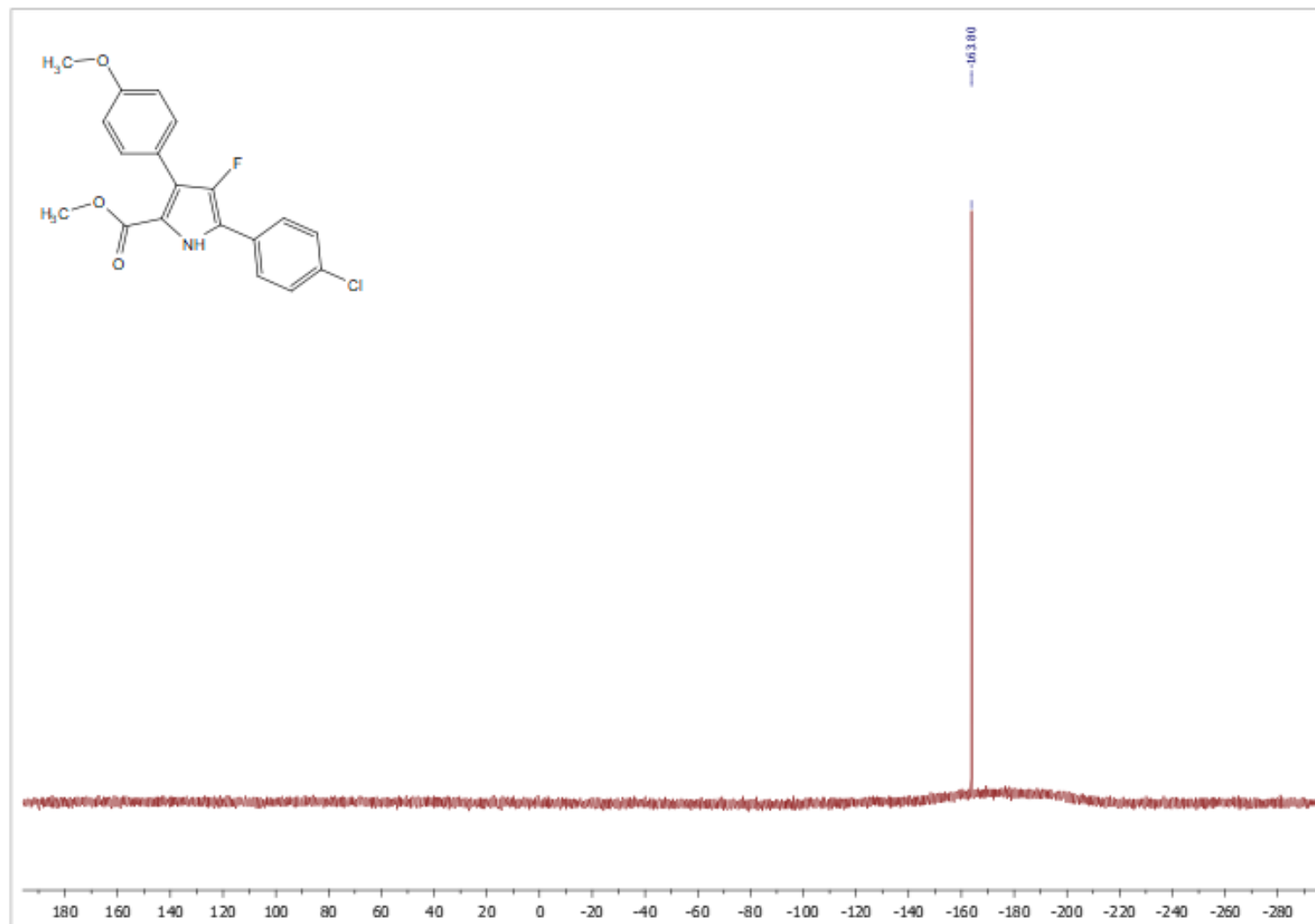
¹H NMR



¹³C NMR

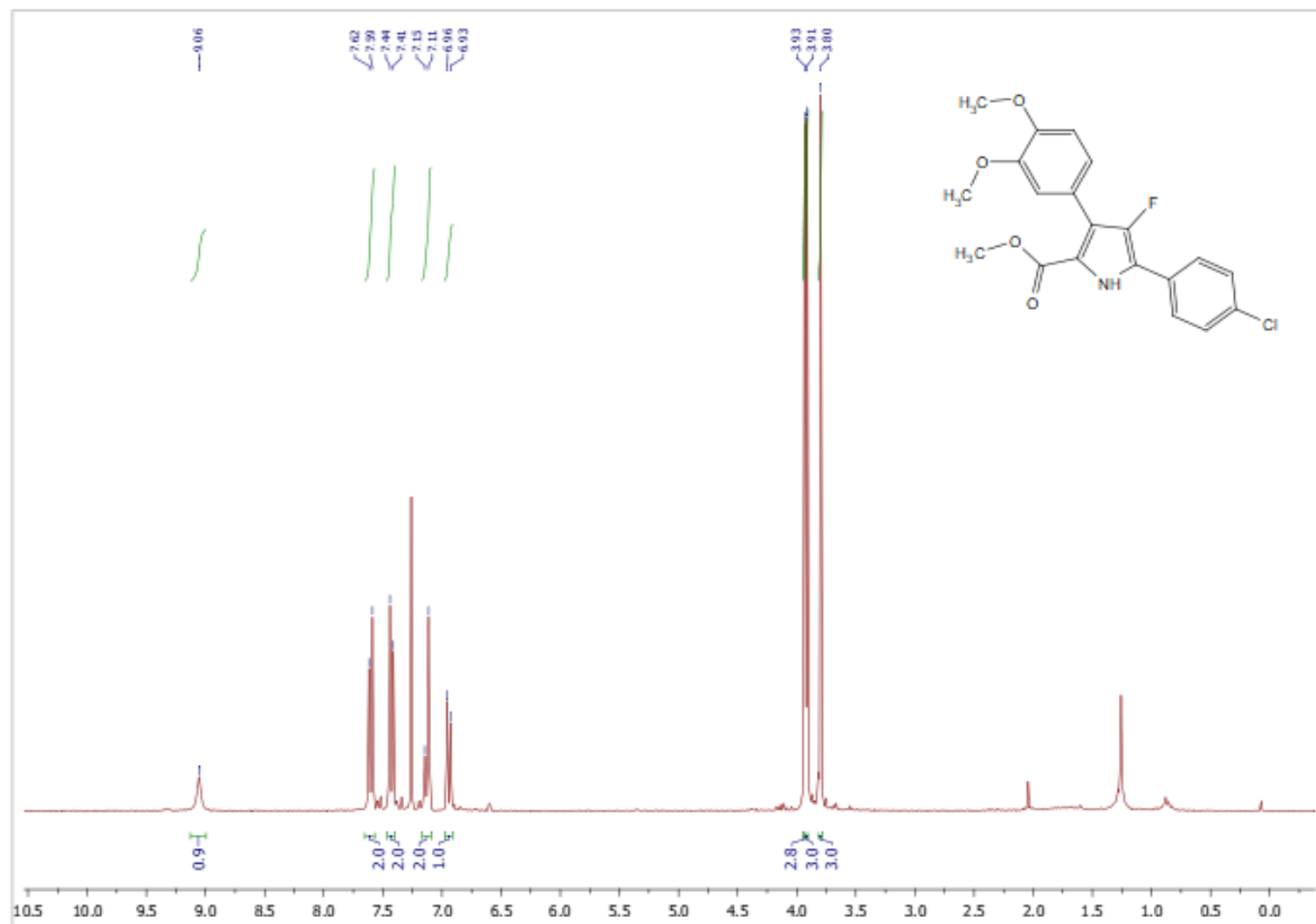


^{19}F NMR

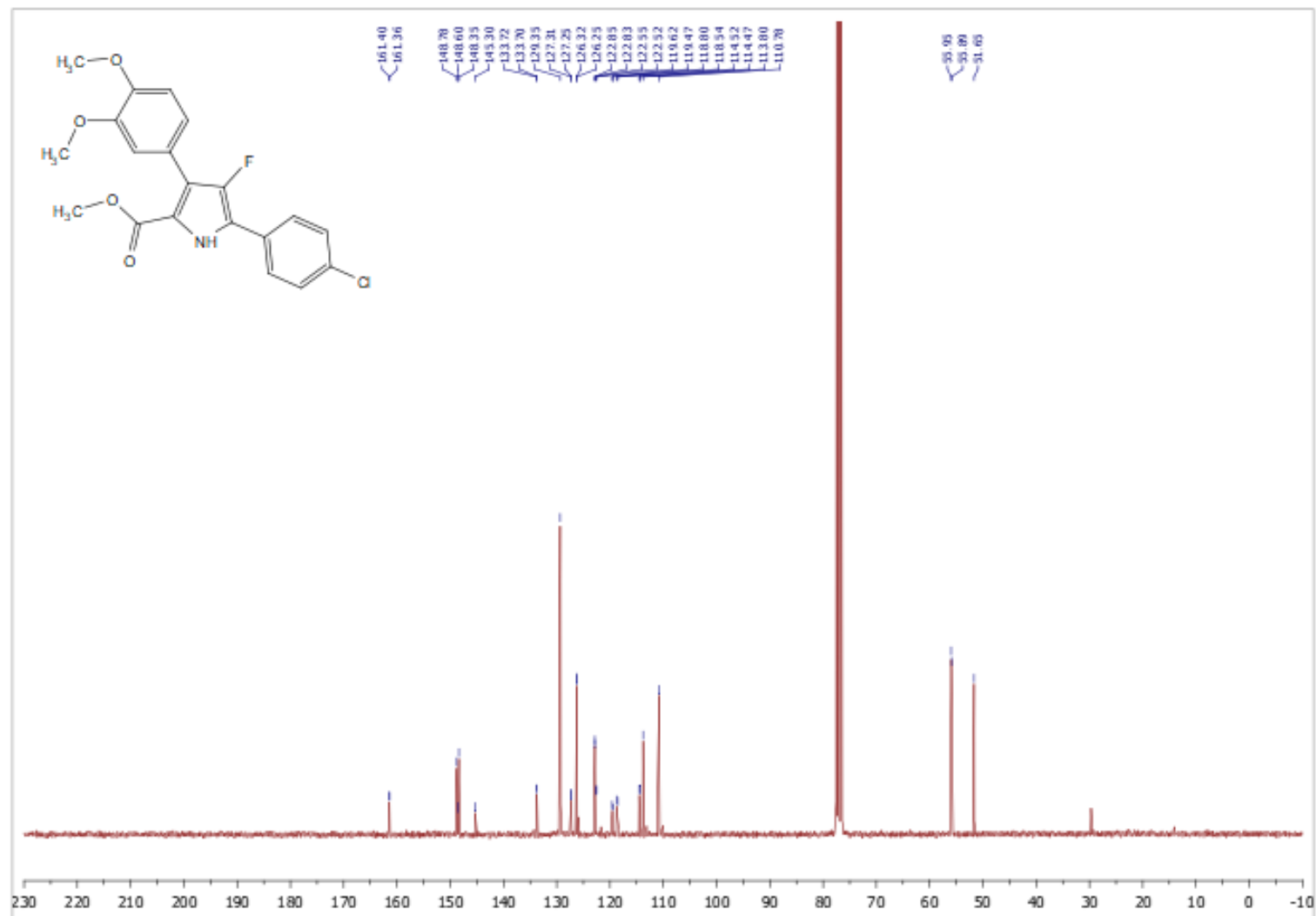


methyl 5-(4-chlorophenyl)-4-fluoro-3-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate **5b**

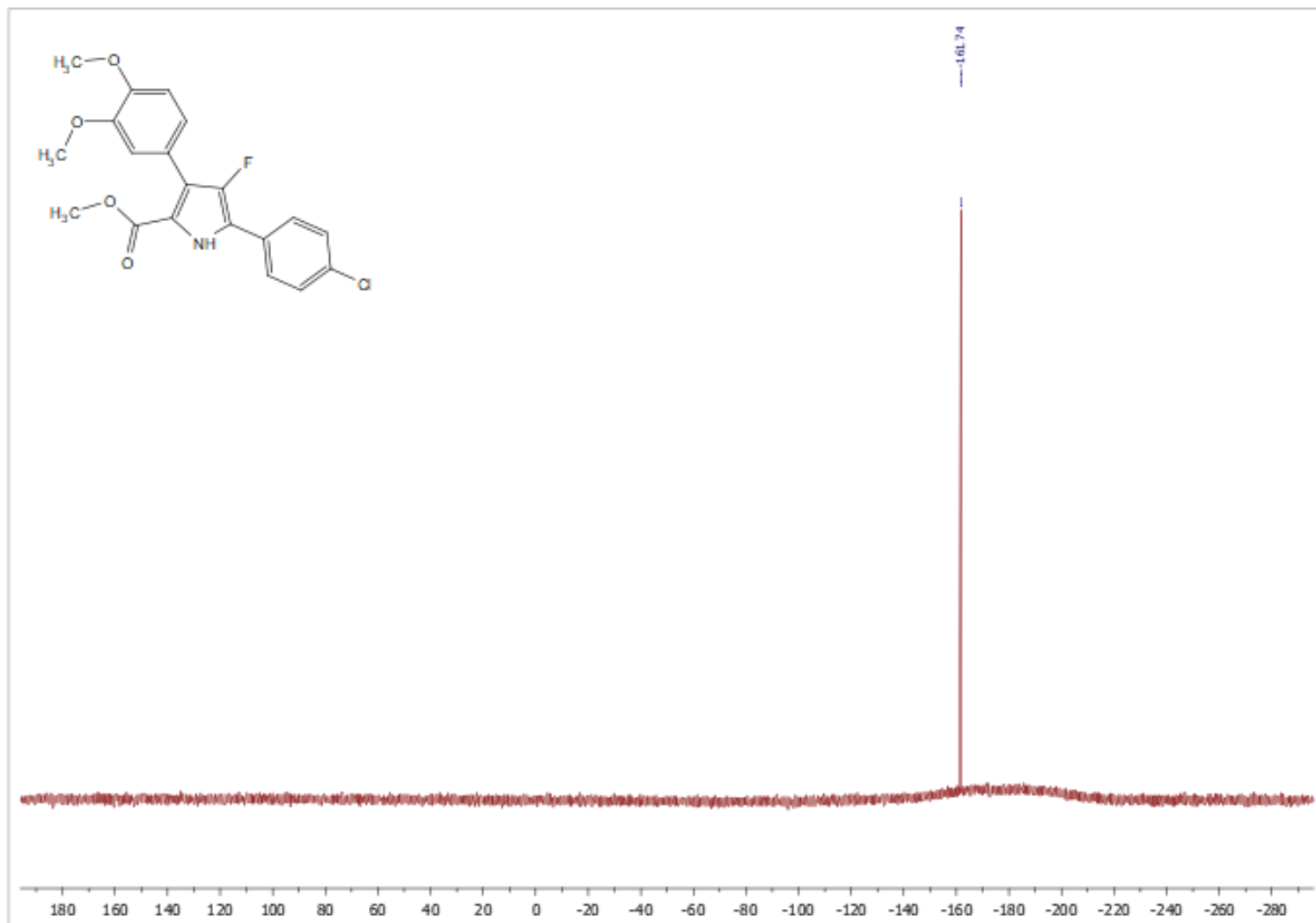
^1H NMR



^{13}C NMR

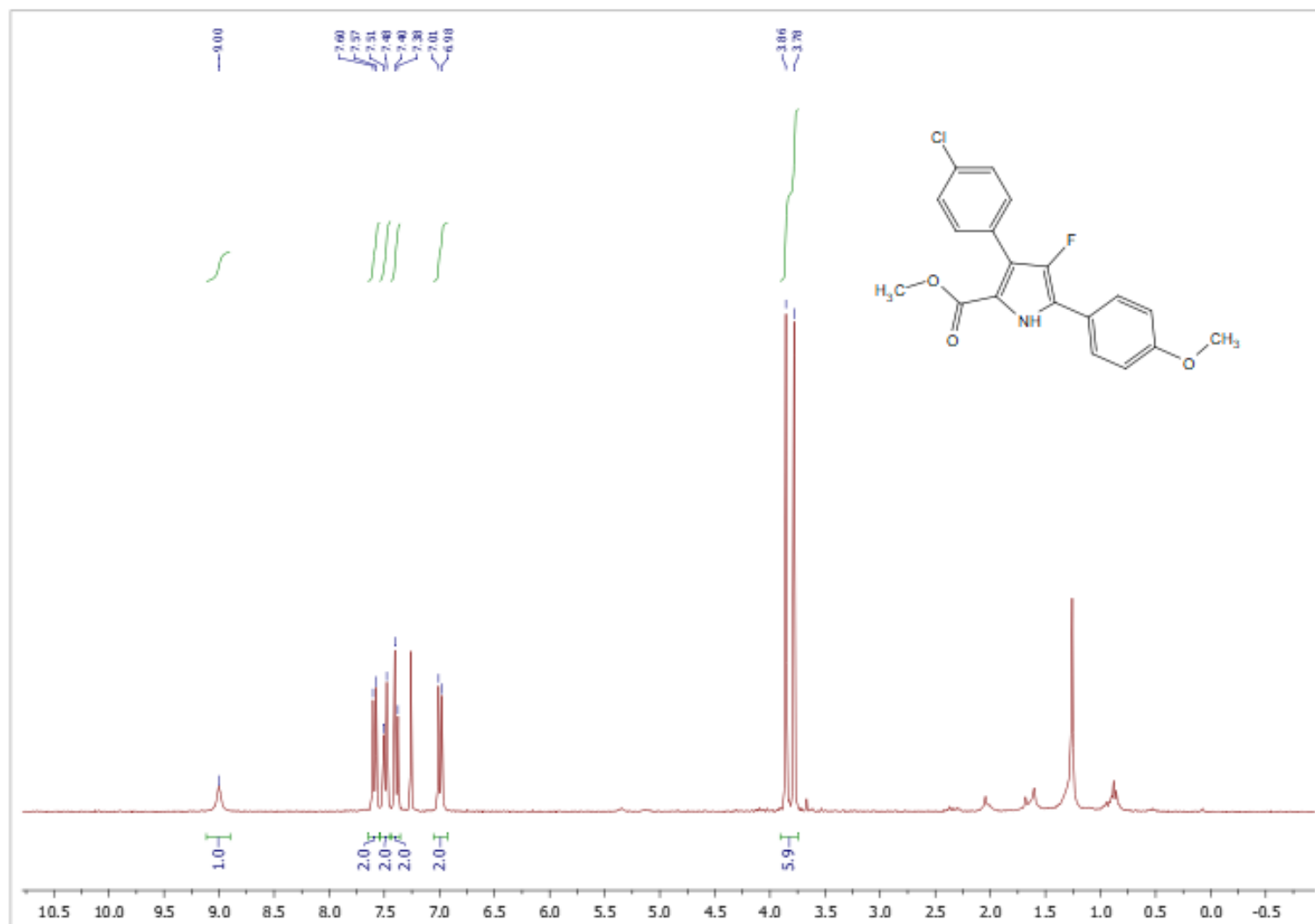


^{19}F NMR

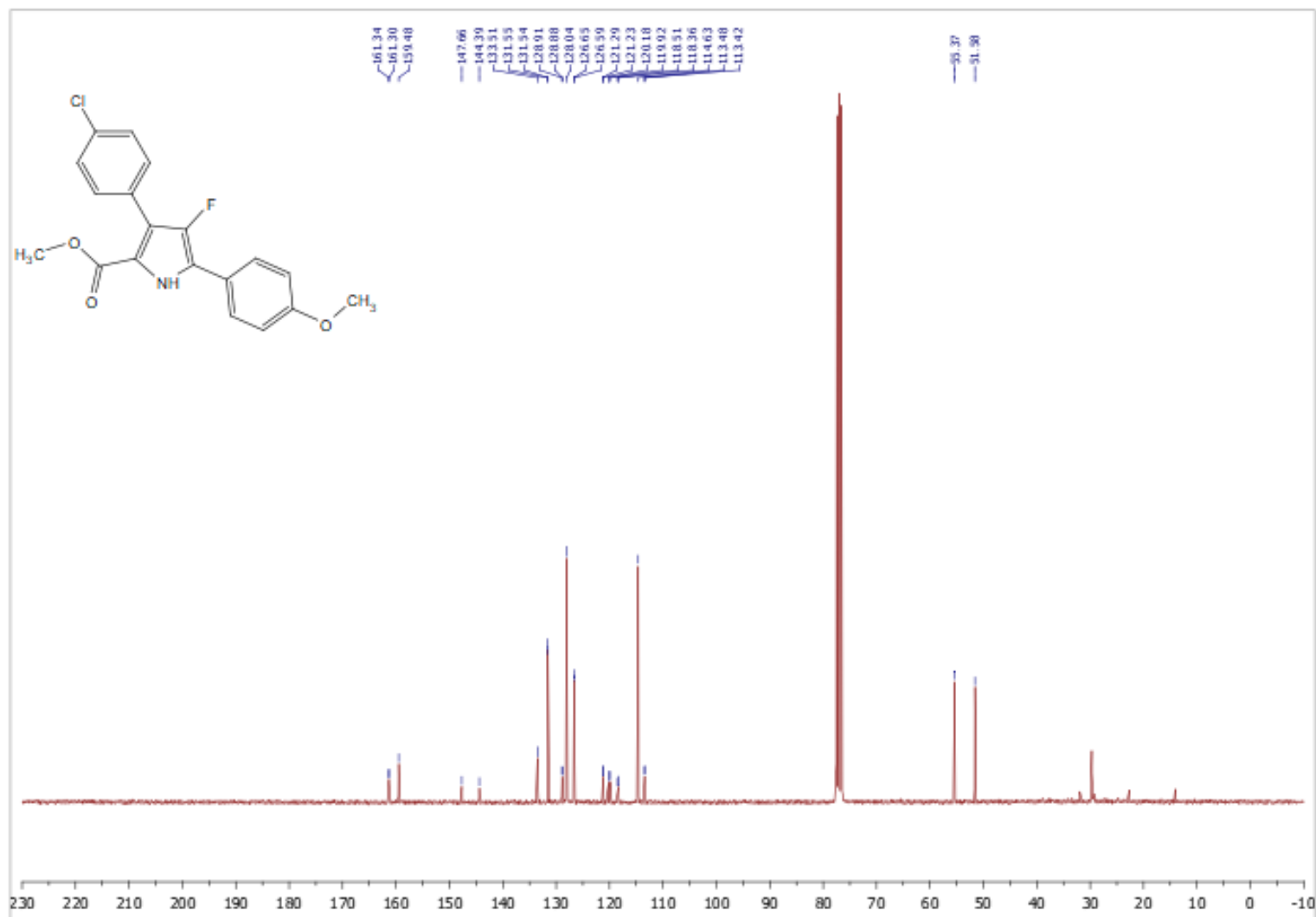


methyl-3-(4-chlorophenyl)-4-fluoro-5-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate **5c**

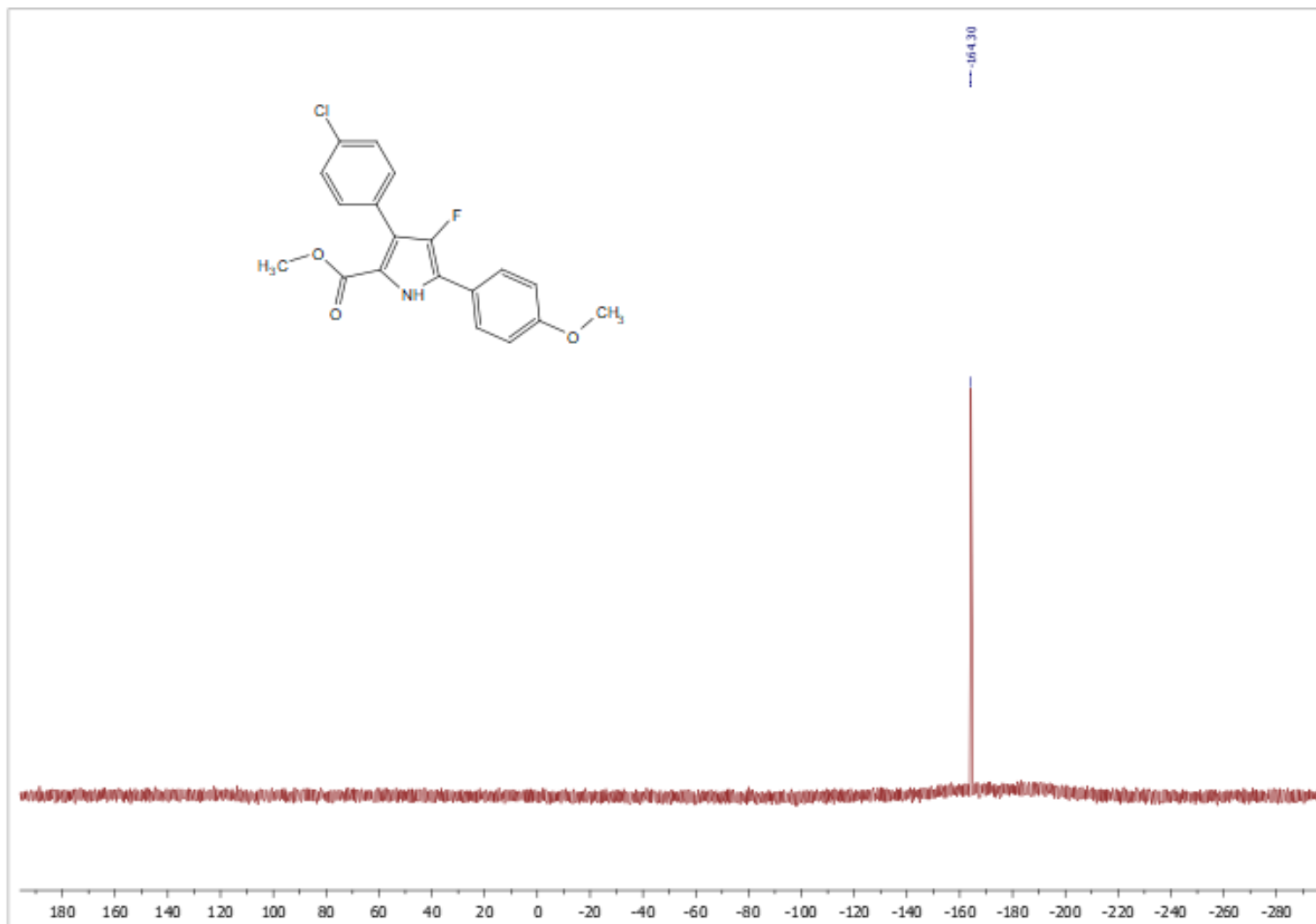
^1H NMR



¹³C NMR

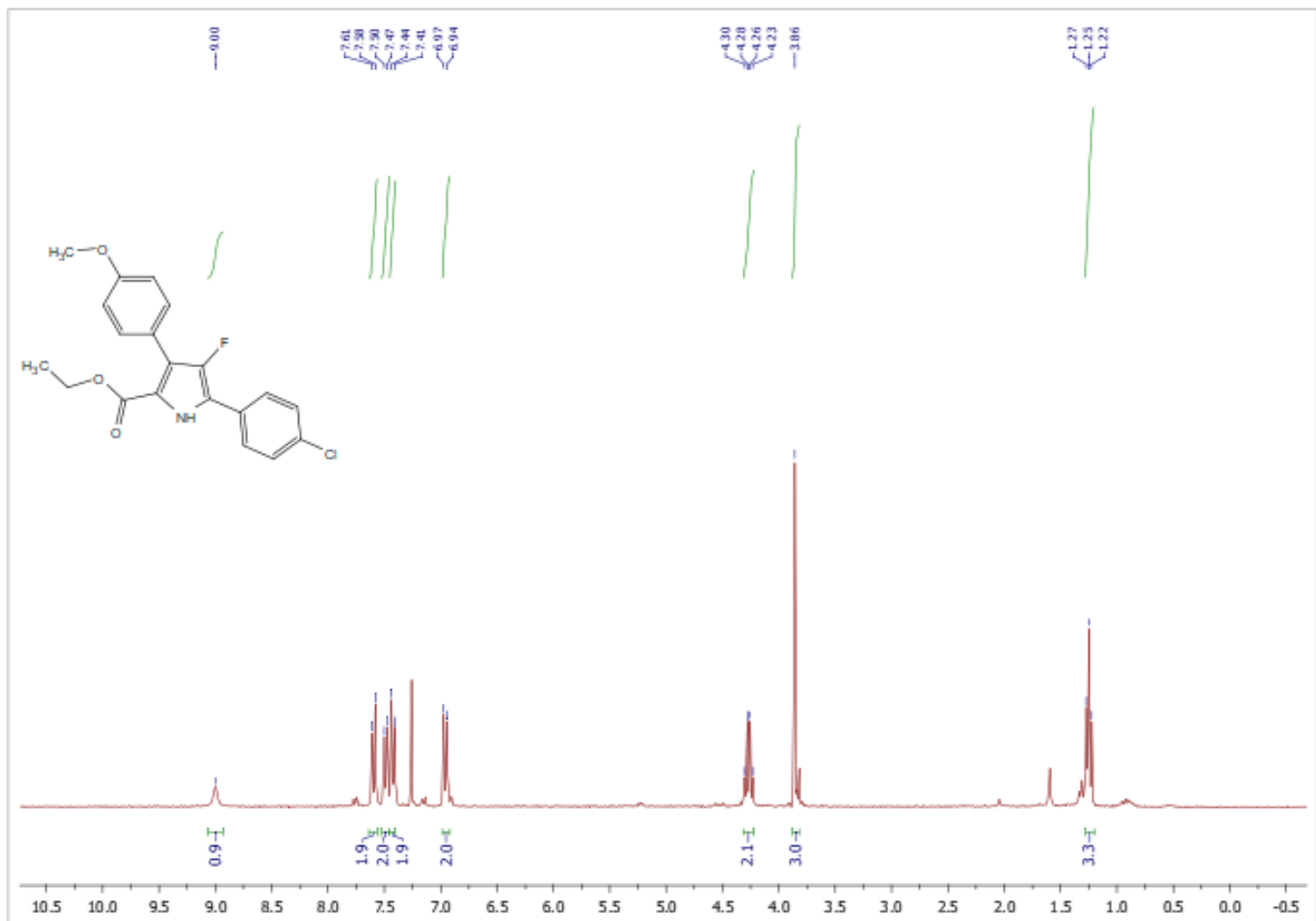


^{19}F NMR

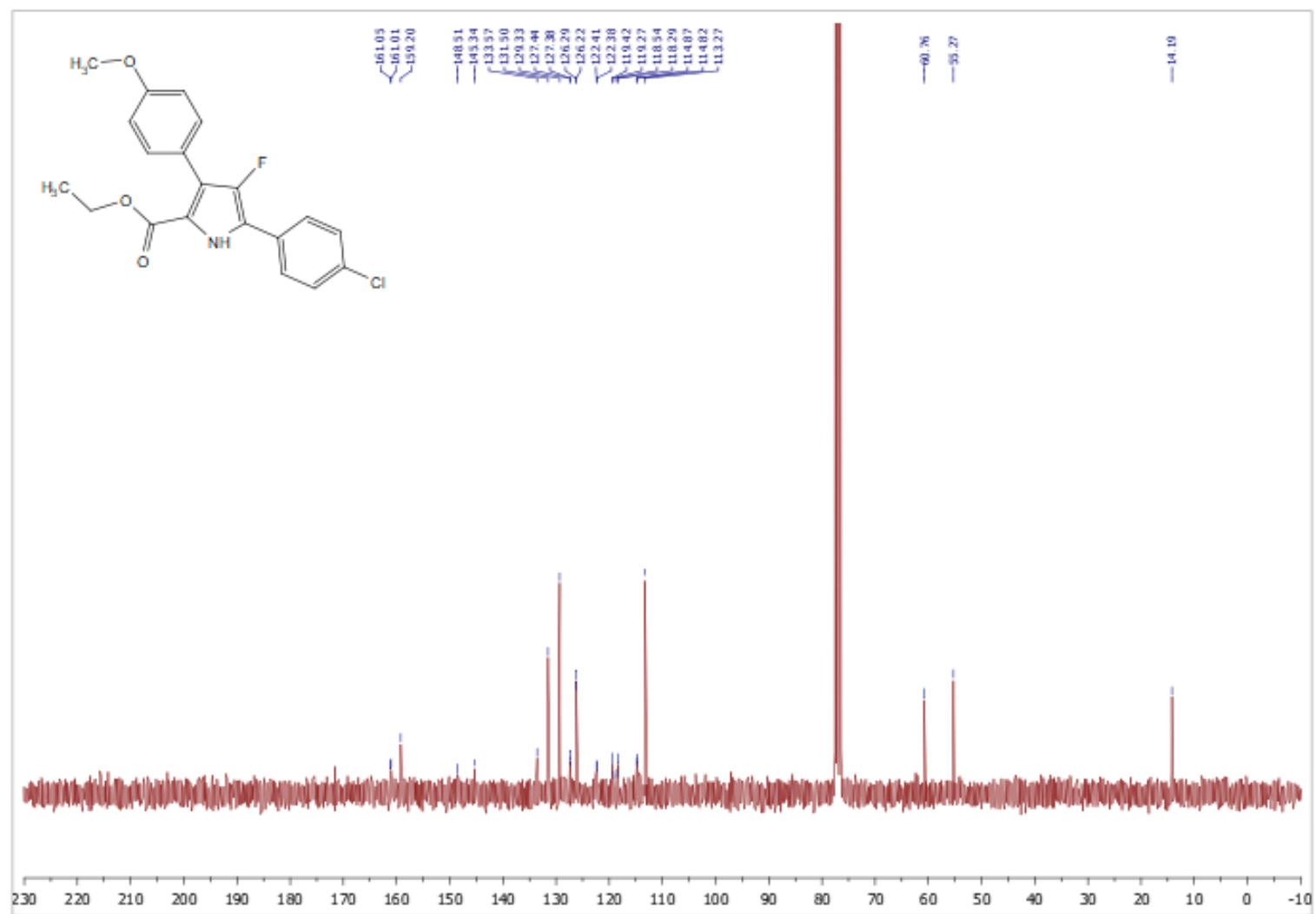


ethyl 5-(4-chlorophenyl)-4-fluoro-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **5d**

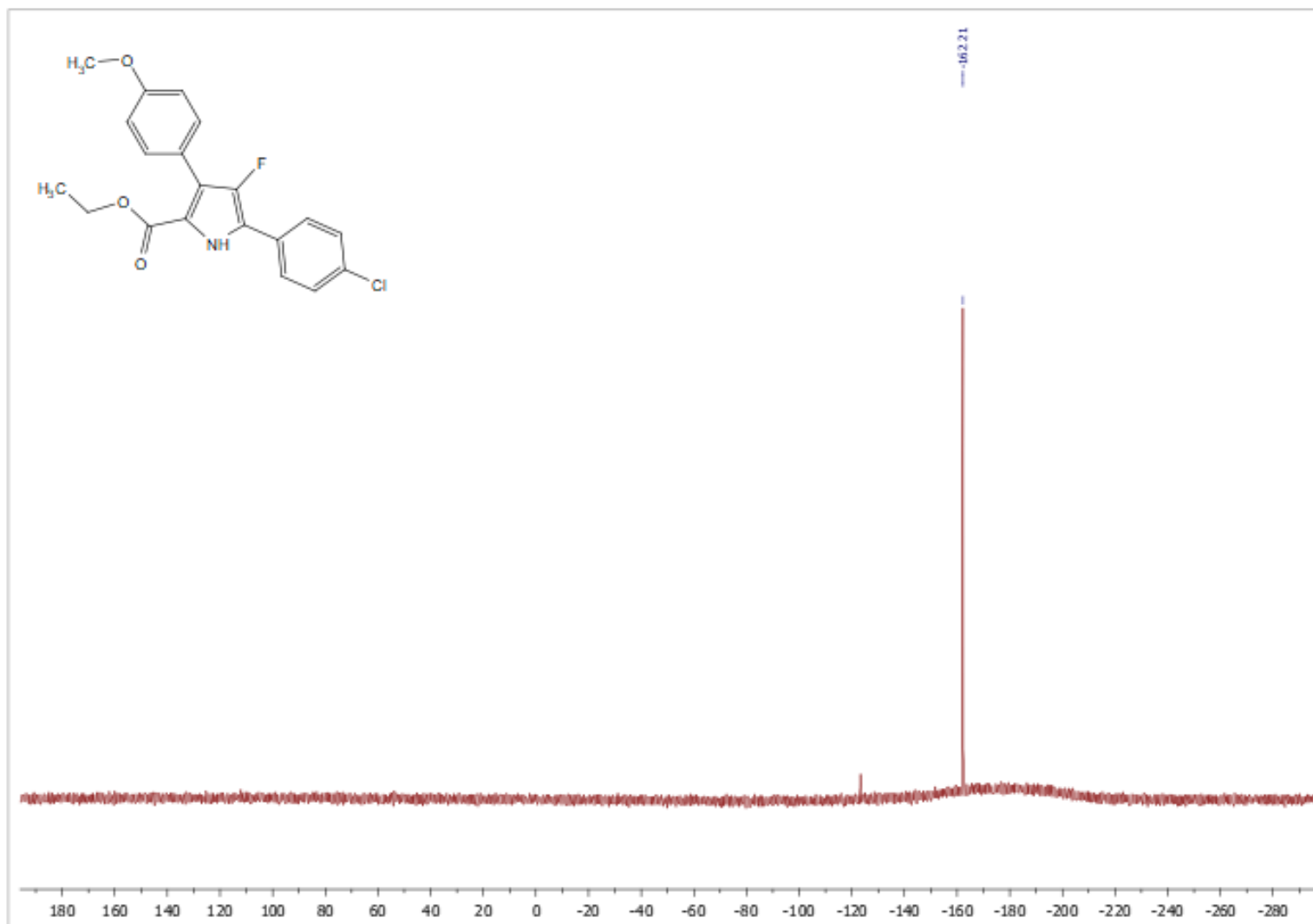
^1H NMR



¹³C NMR

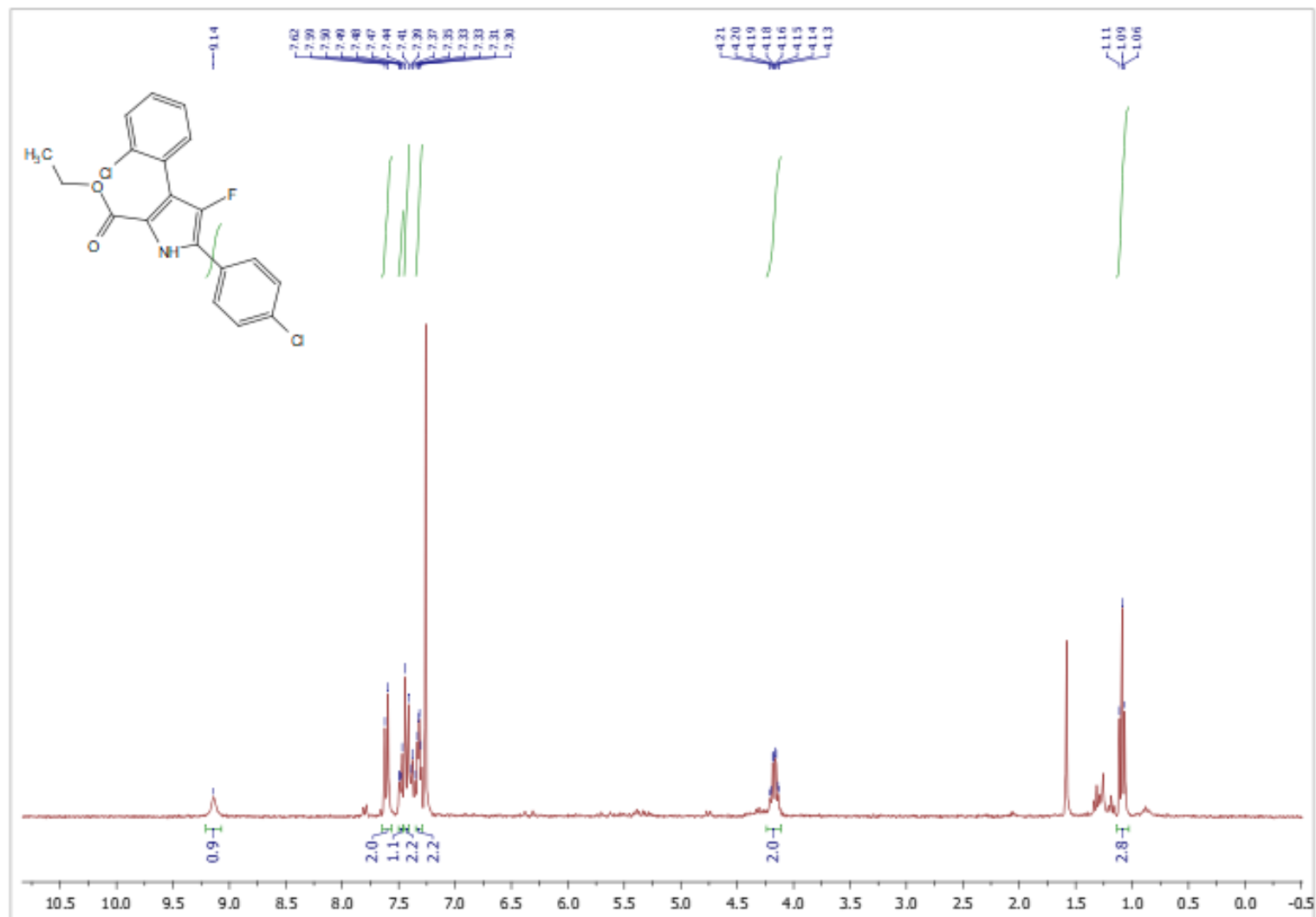


^{19}F NMR

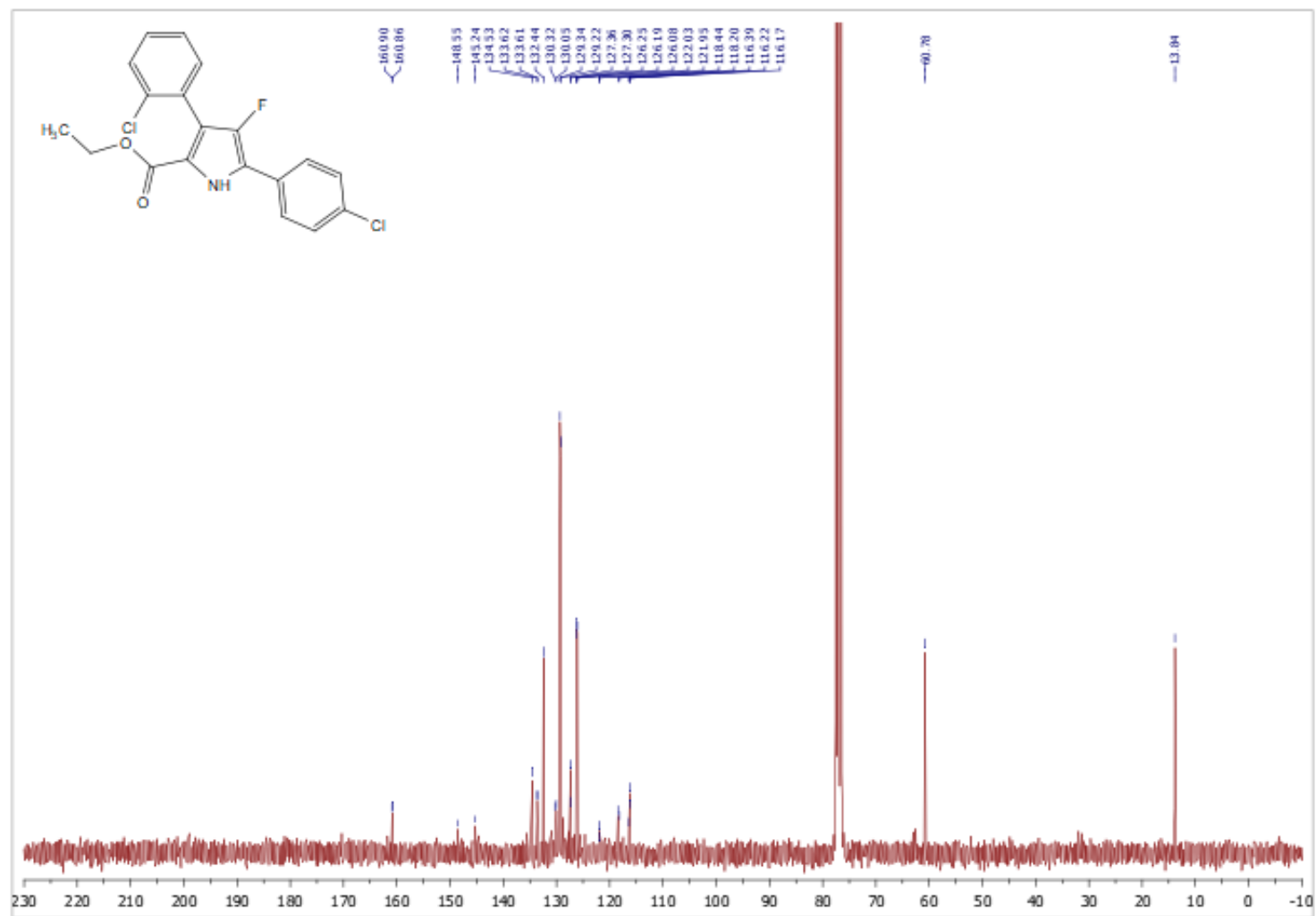


ethyl 5-(4-chlorophenyl)-4-fluoro-3-(2-chlorophenyl)-1H-pyrrole-2-carboxylate **5e**

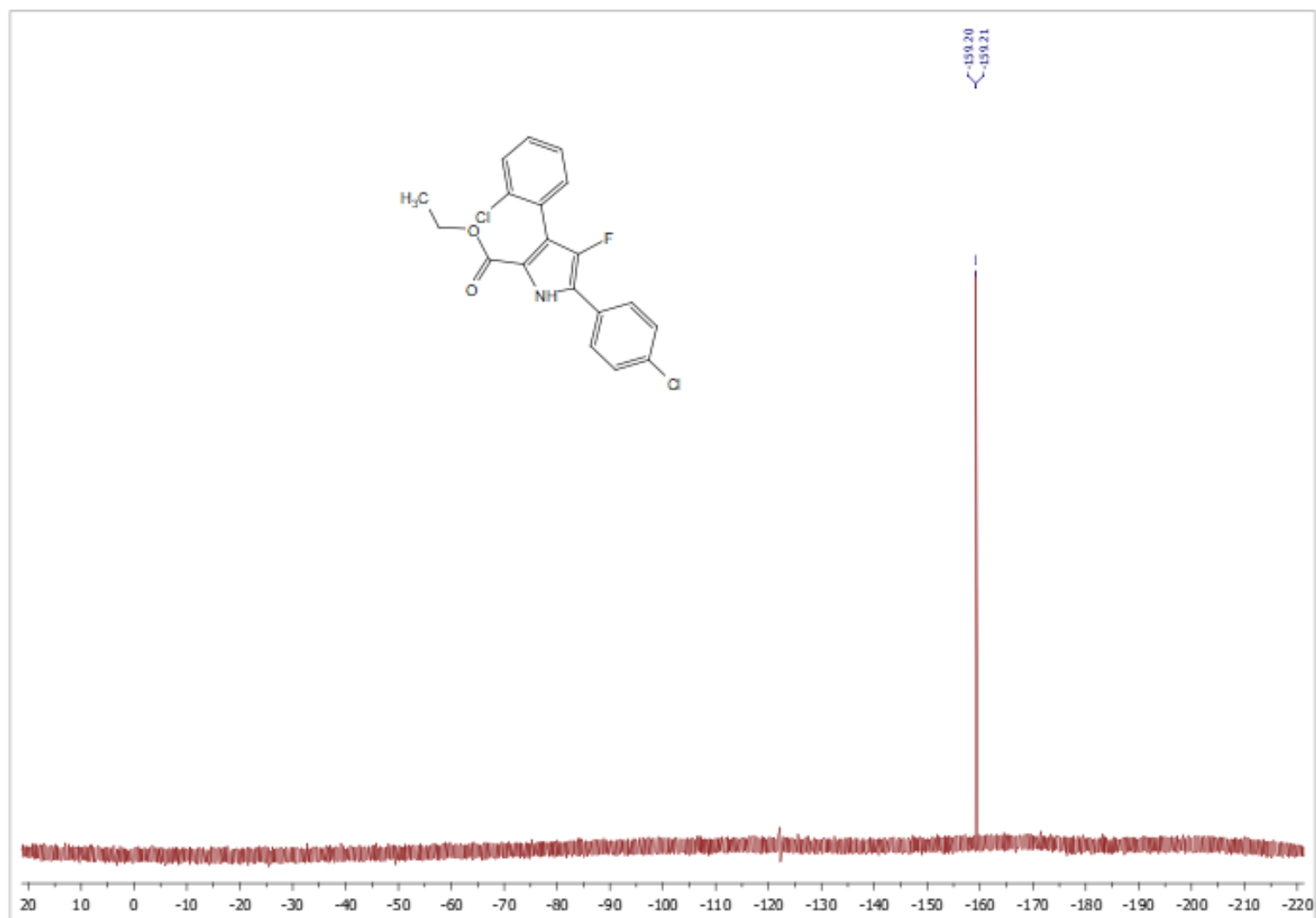
^1H NMR



^{13}C NMR

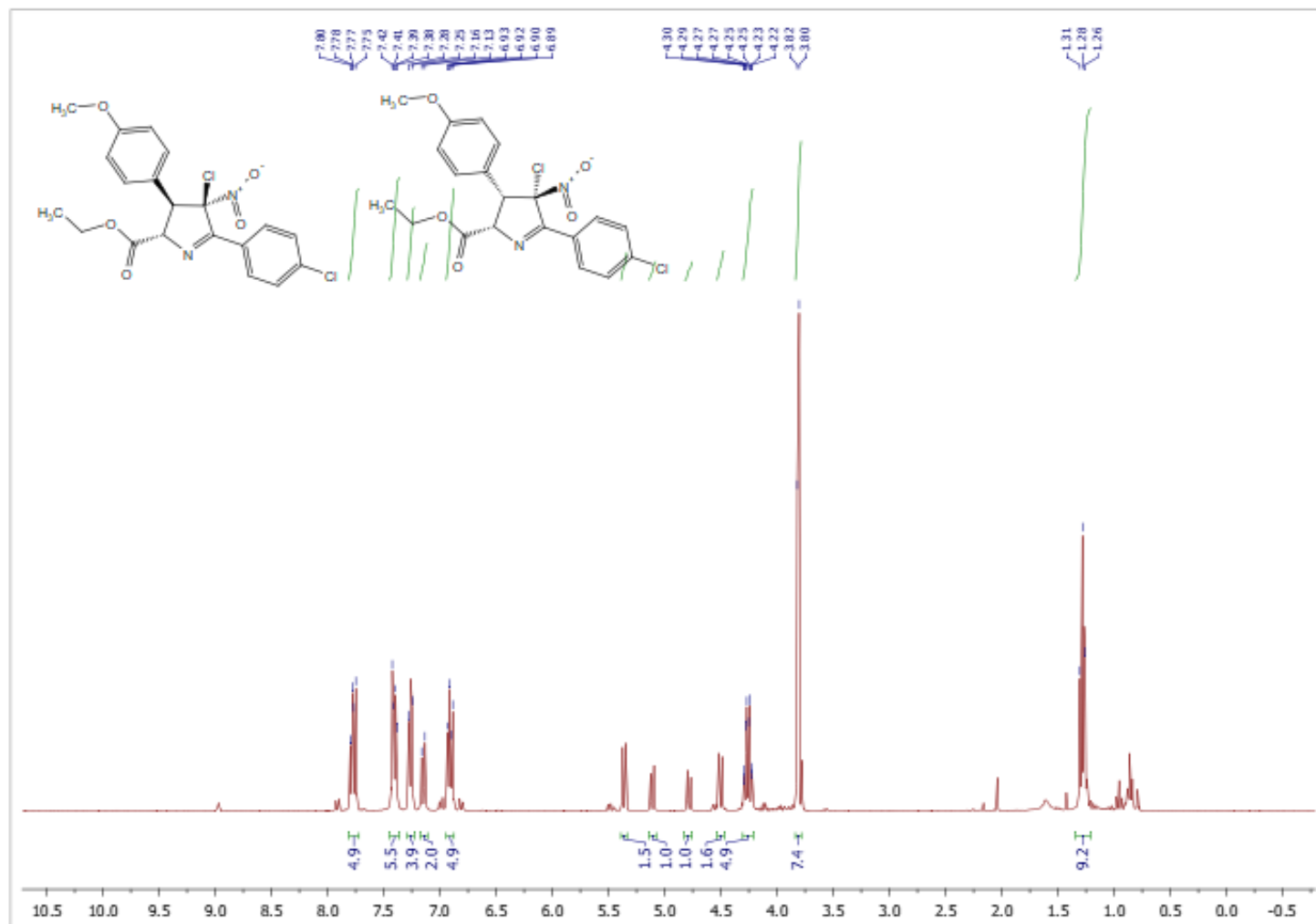


^{19}F NMR

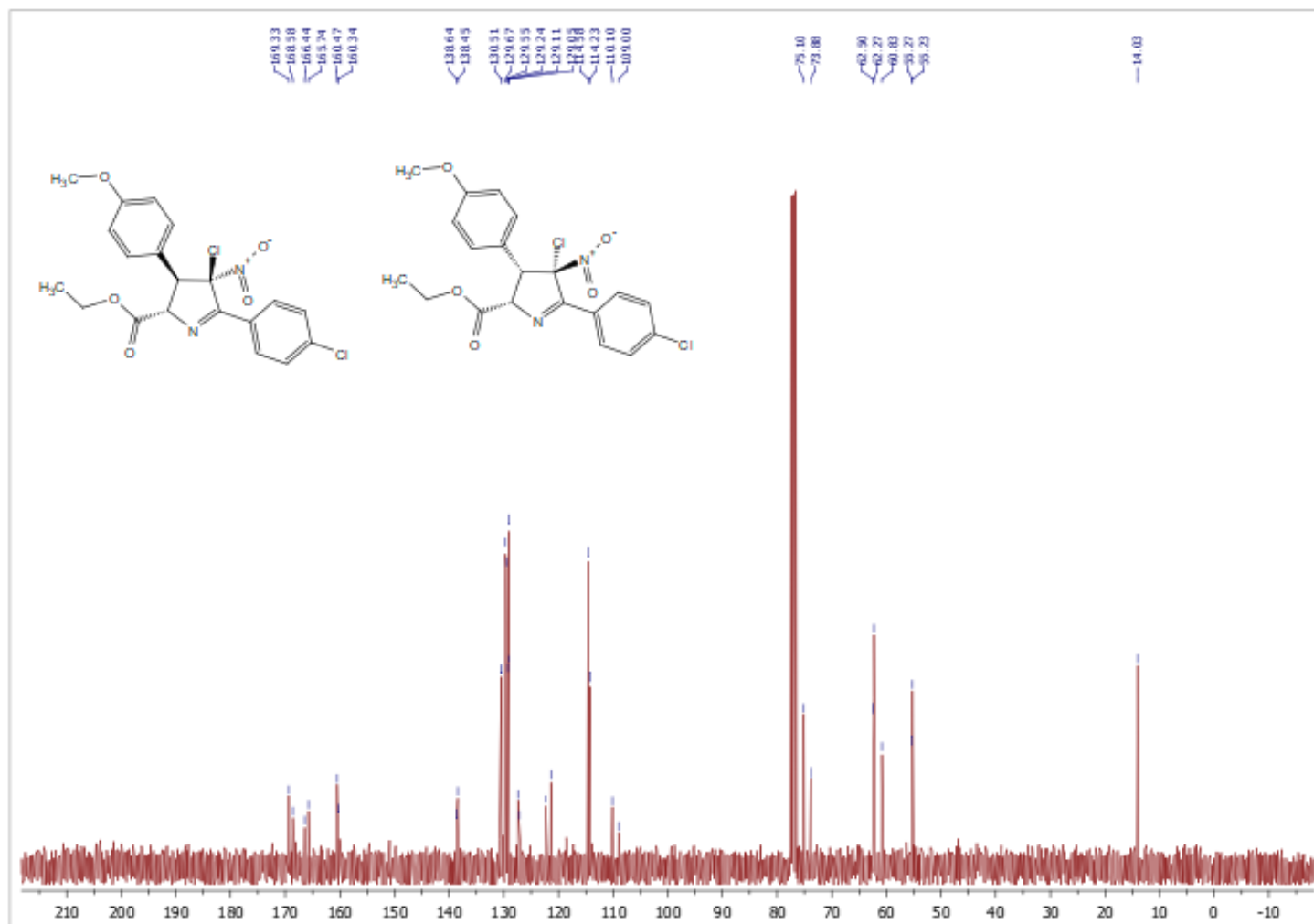


ethyl (2*S*,3*R*,4*R*)-4-chloro-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **60** and ethyl (2*S*,3*S*,4*S*)-4-chloro-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **60'**

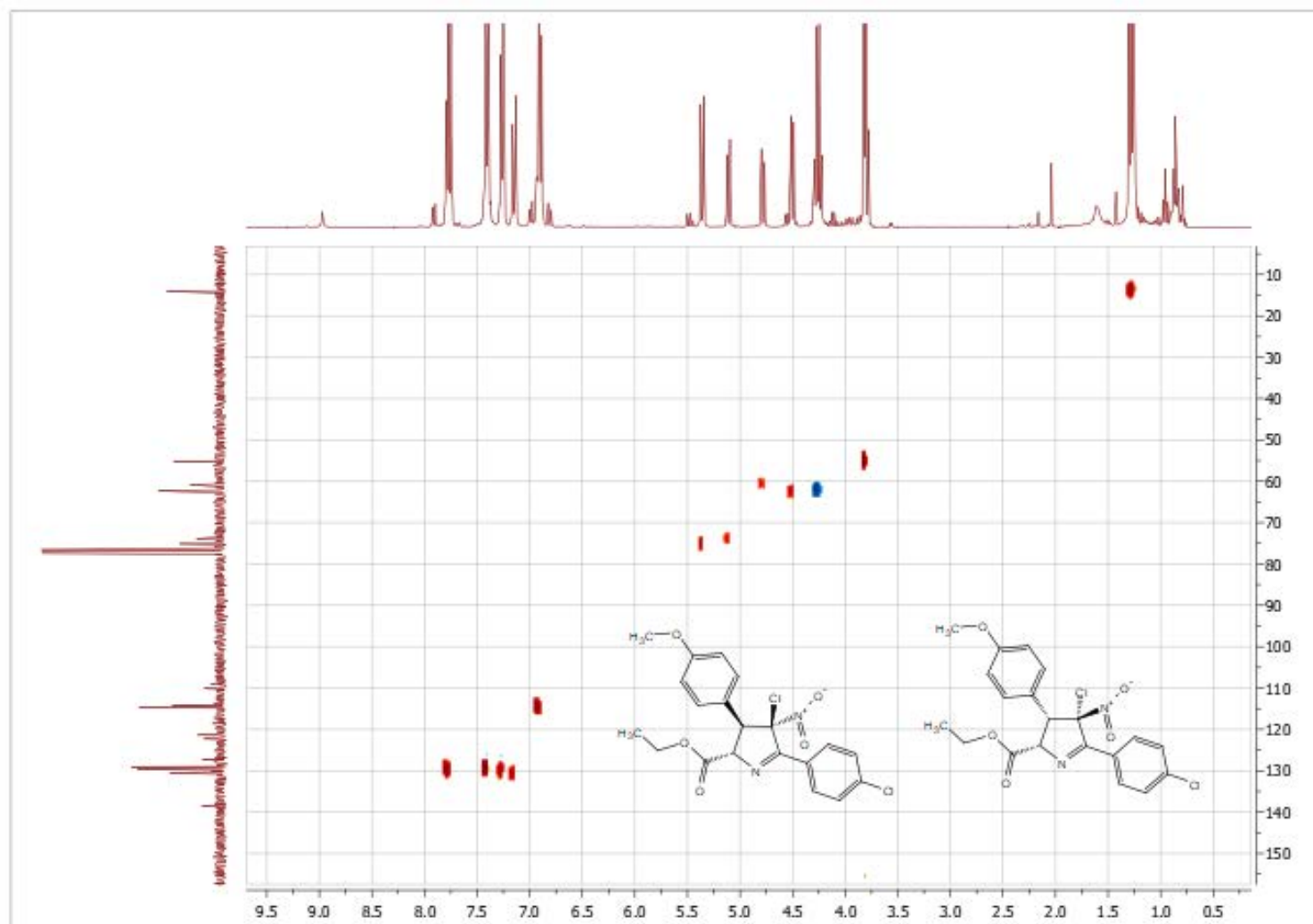
¹H NMR



¹³C NMR

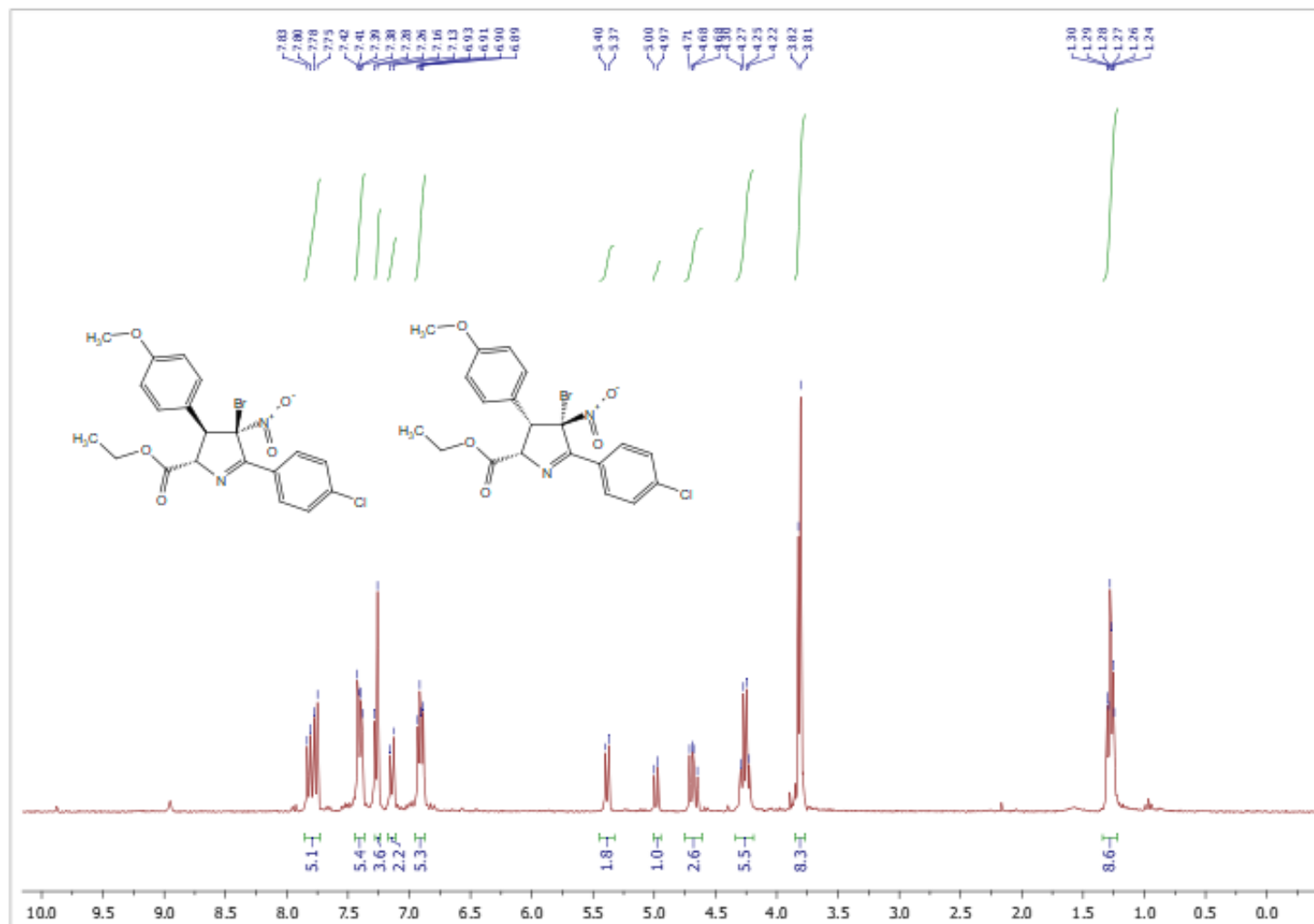


^1H - ^{13}C HSQC NMR

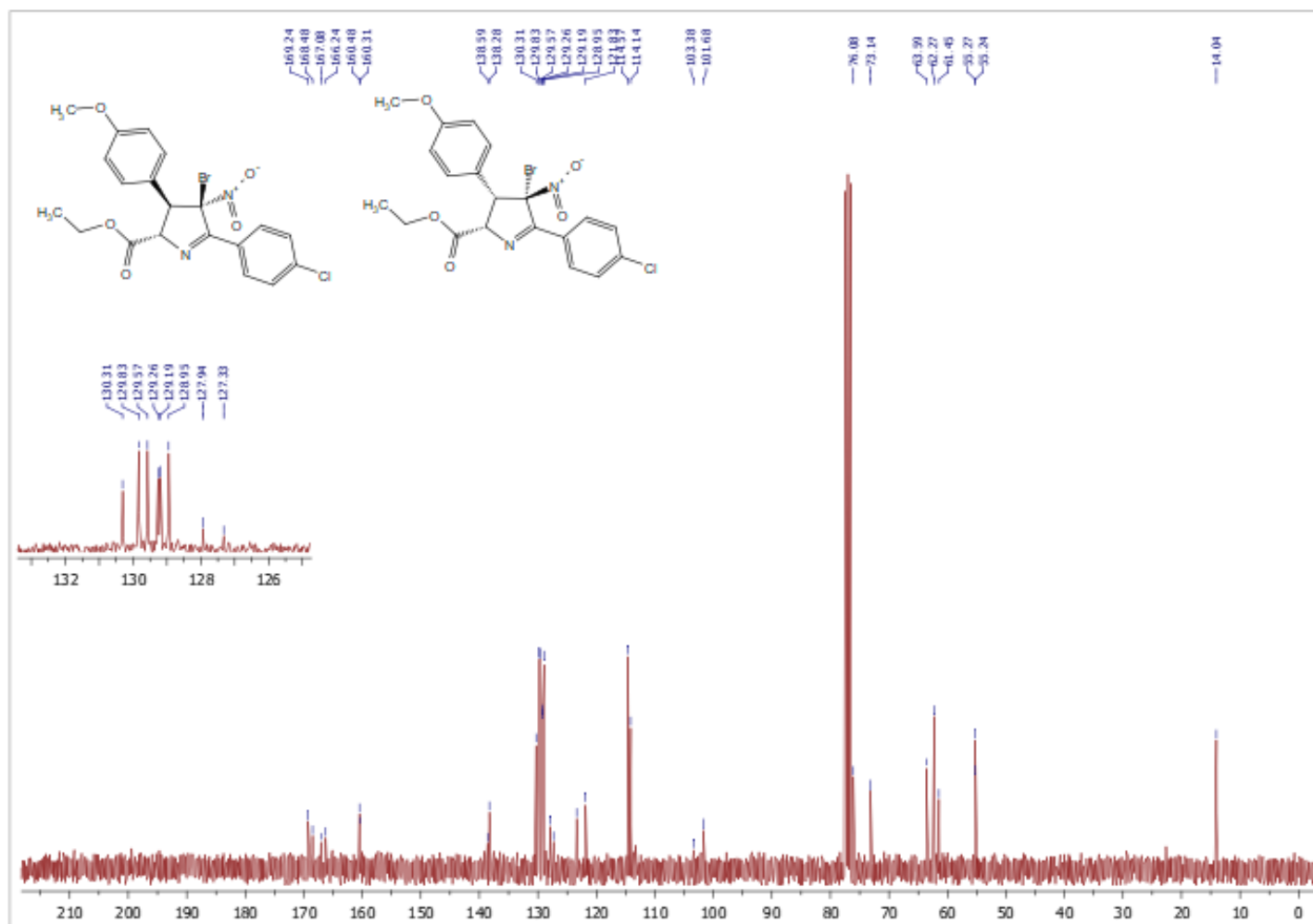


ethyl (2*S*,3*R*,4*R*)-4-bromo-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **6p** and ethyl (2*S*,3*S*,4*S*)-4-bromo-4-nitro-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **6p'**

¹H NMR

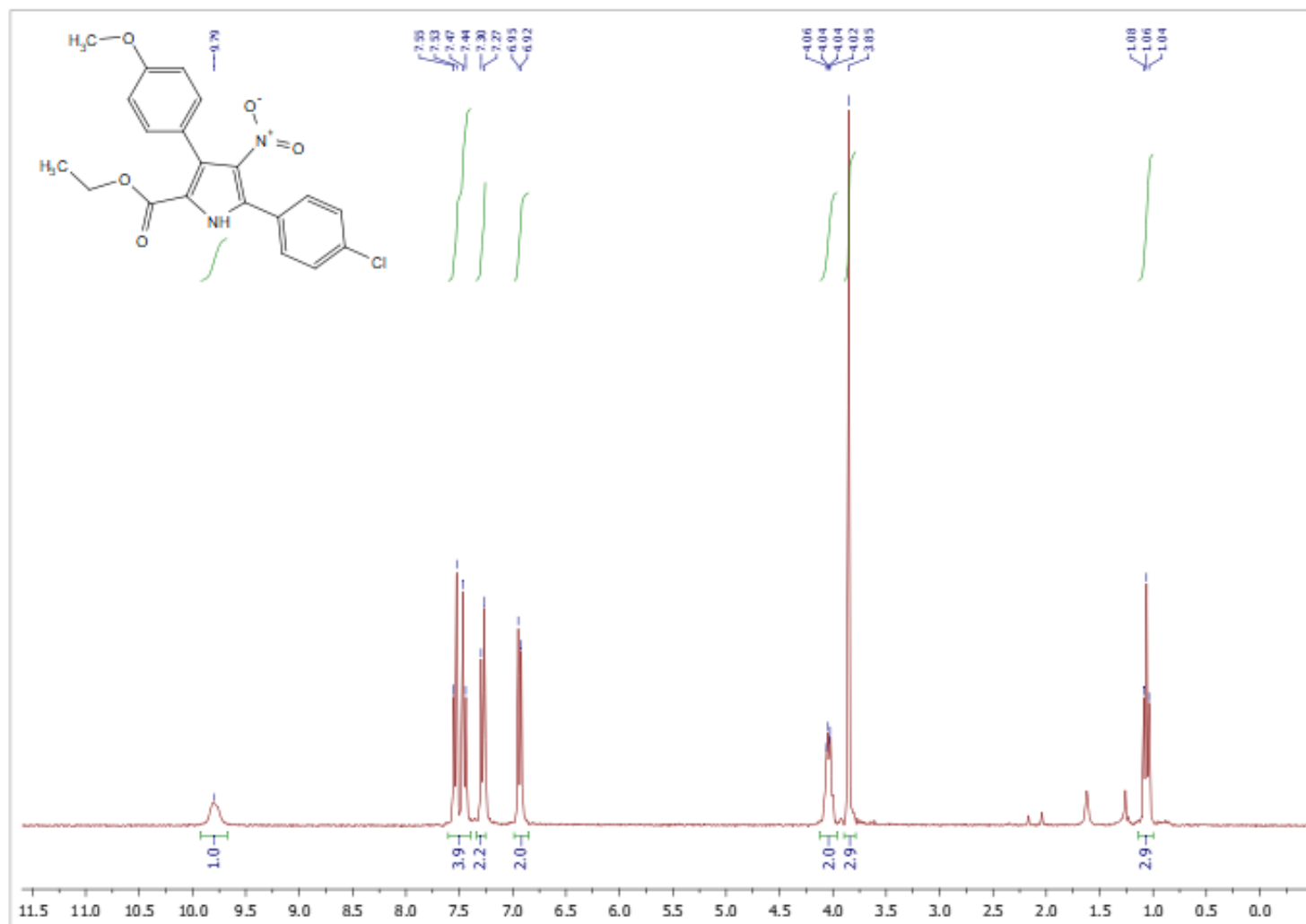


¹³C NMR

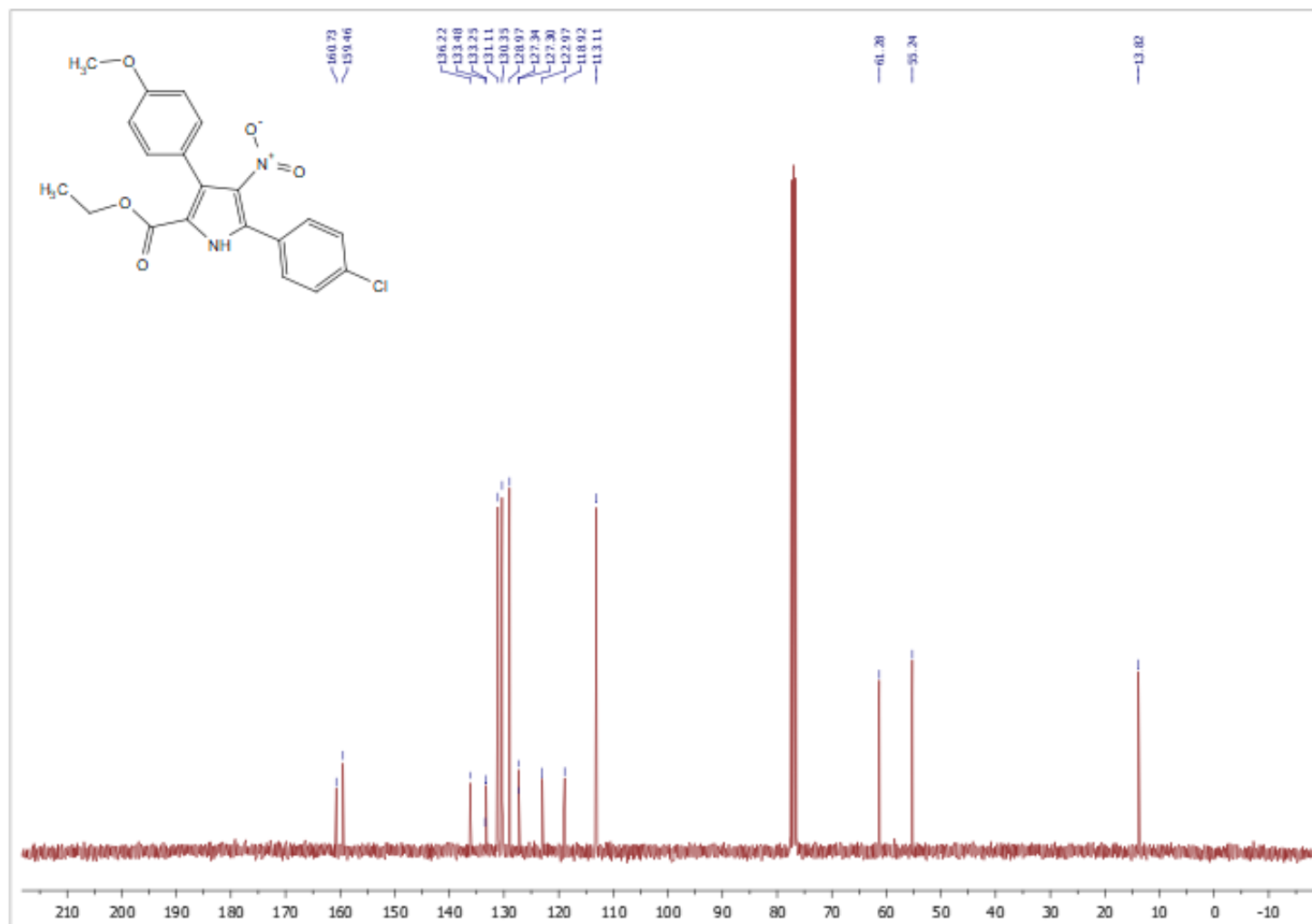


ethyl 5-(4-chlorophenyl)-4-nitro-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **7**

^1H NMR

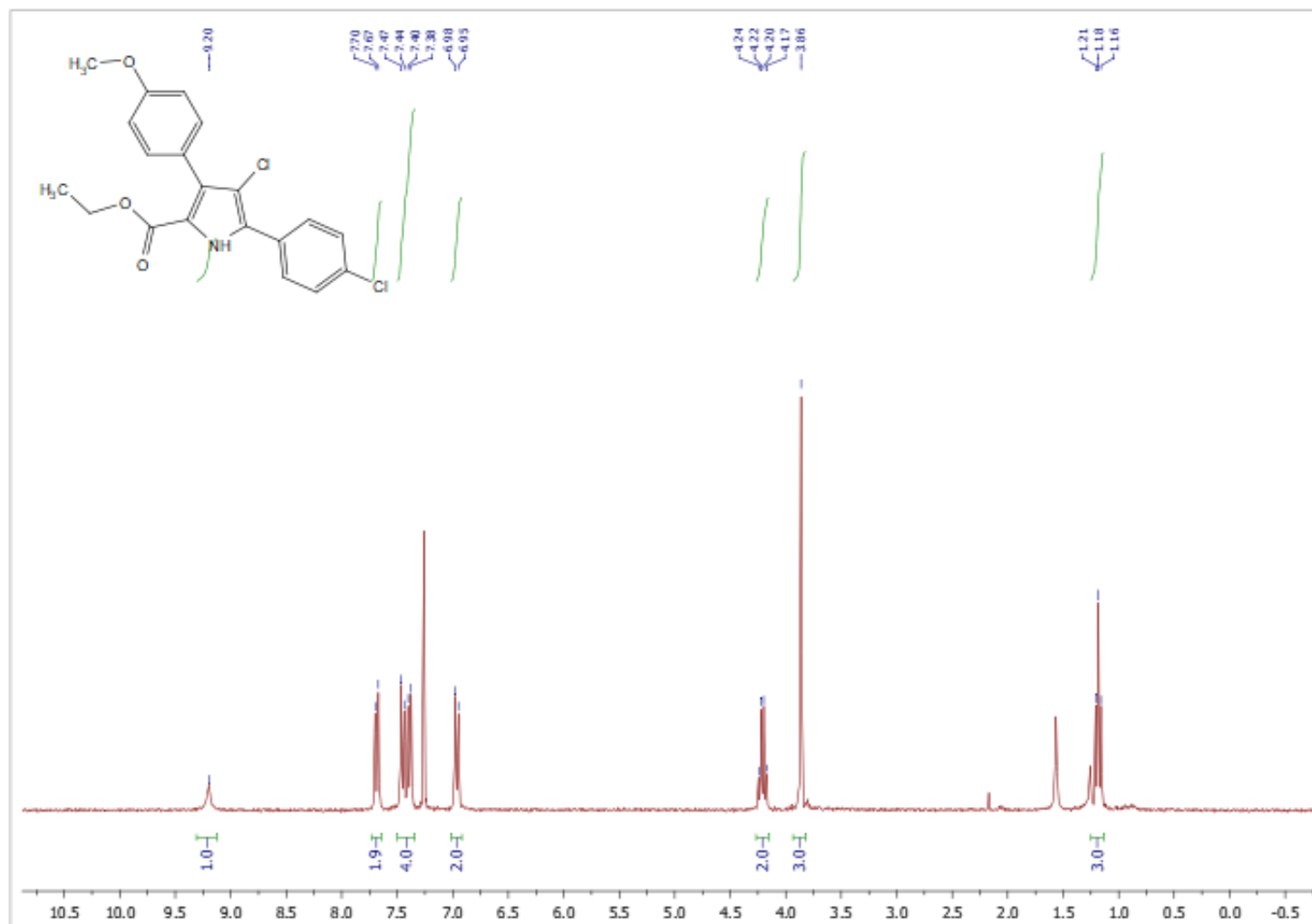


¹³C NMR

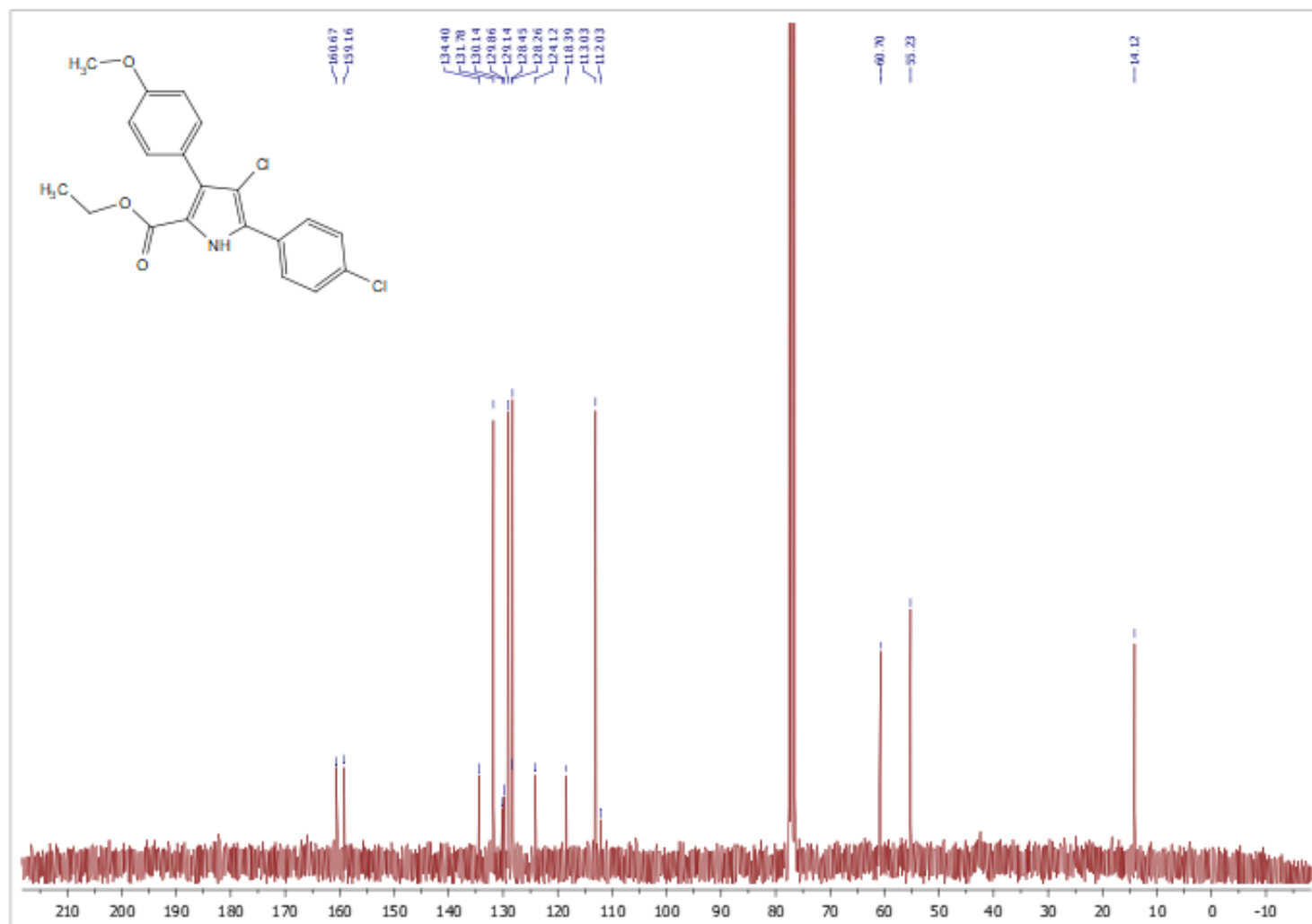


ethyl 5-(4-chlorophenyl)-4-chloro-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **8**

^1H NMR

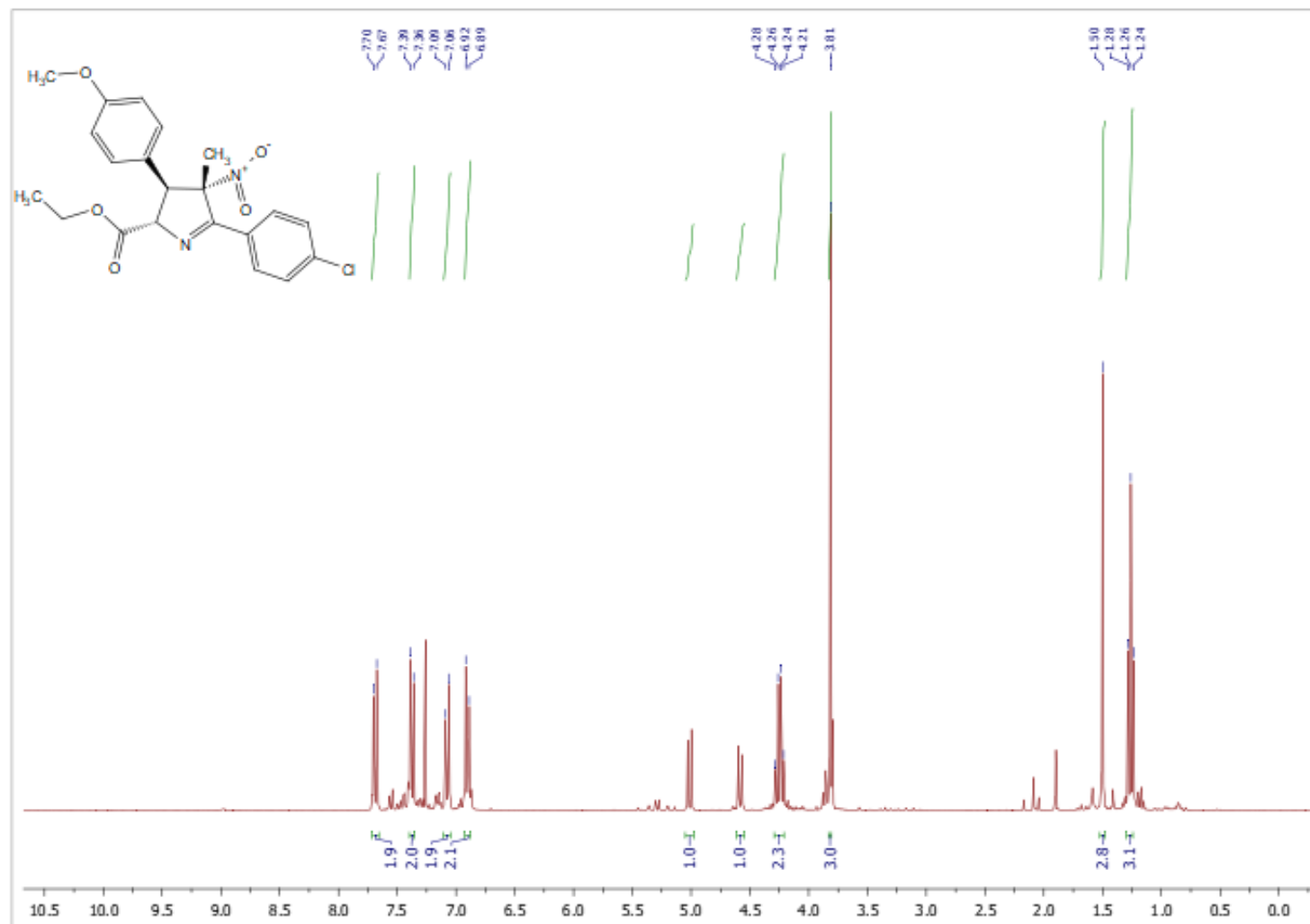


^{13}C NMR

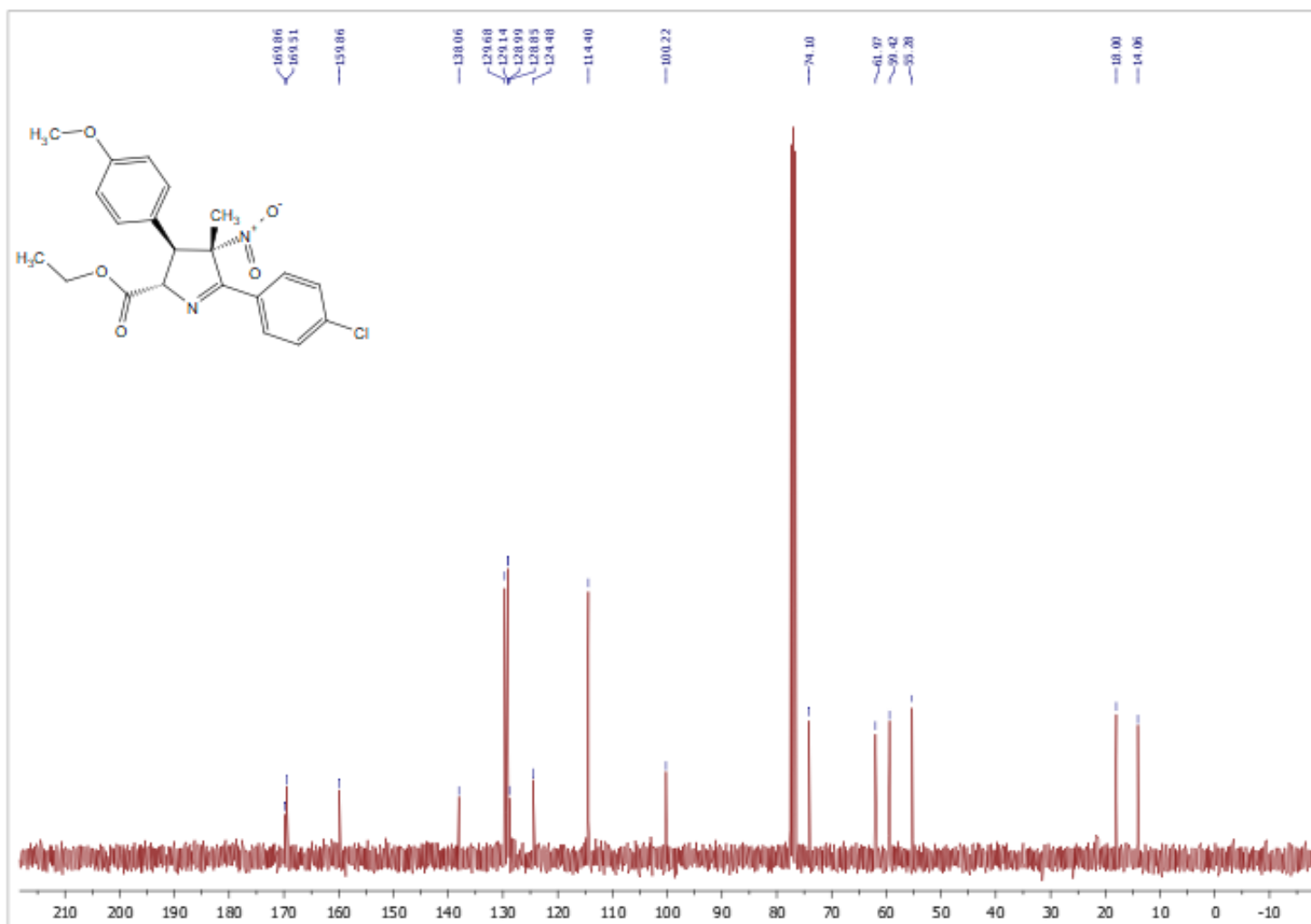


ethyl (2*S*,3*R*,4*R*)-4-nitro-4-methyl-5-(4-chlorophenyl)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate **9**

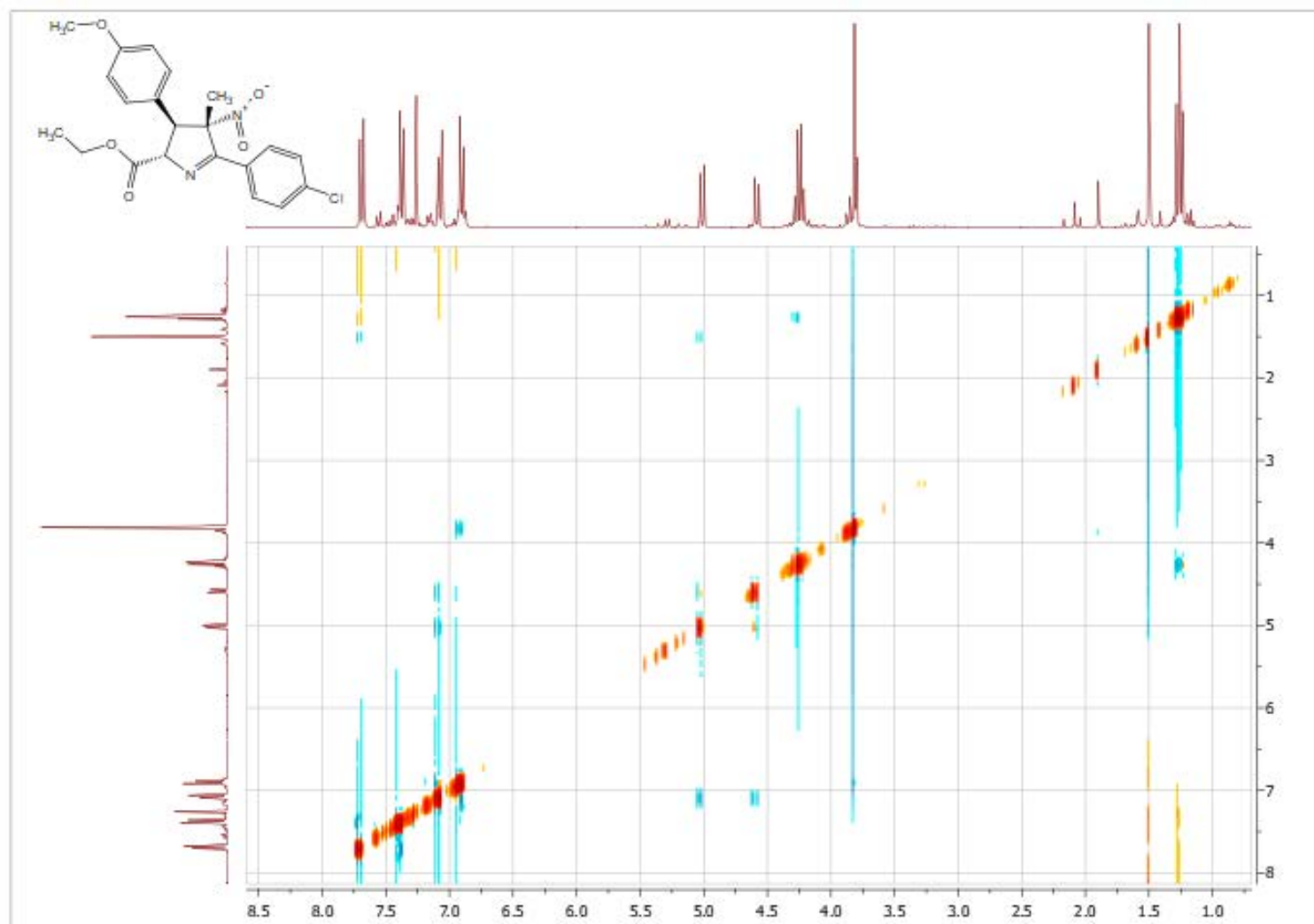
¹H NMR



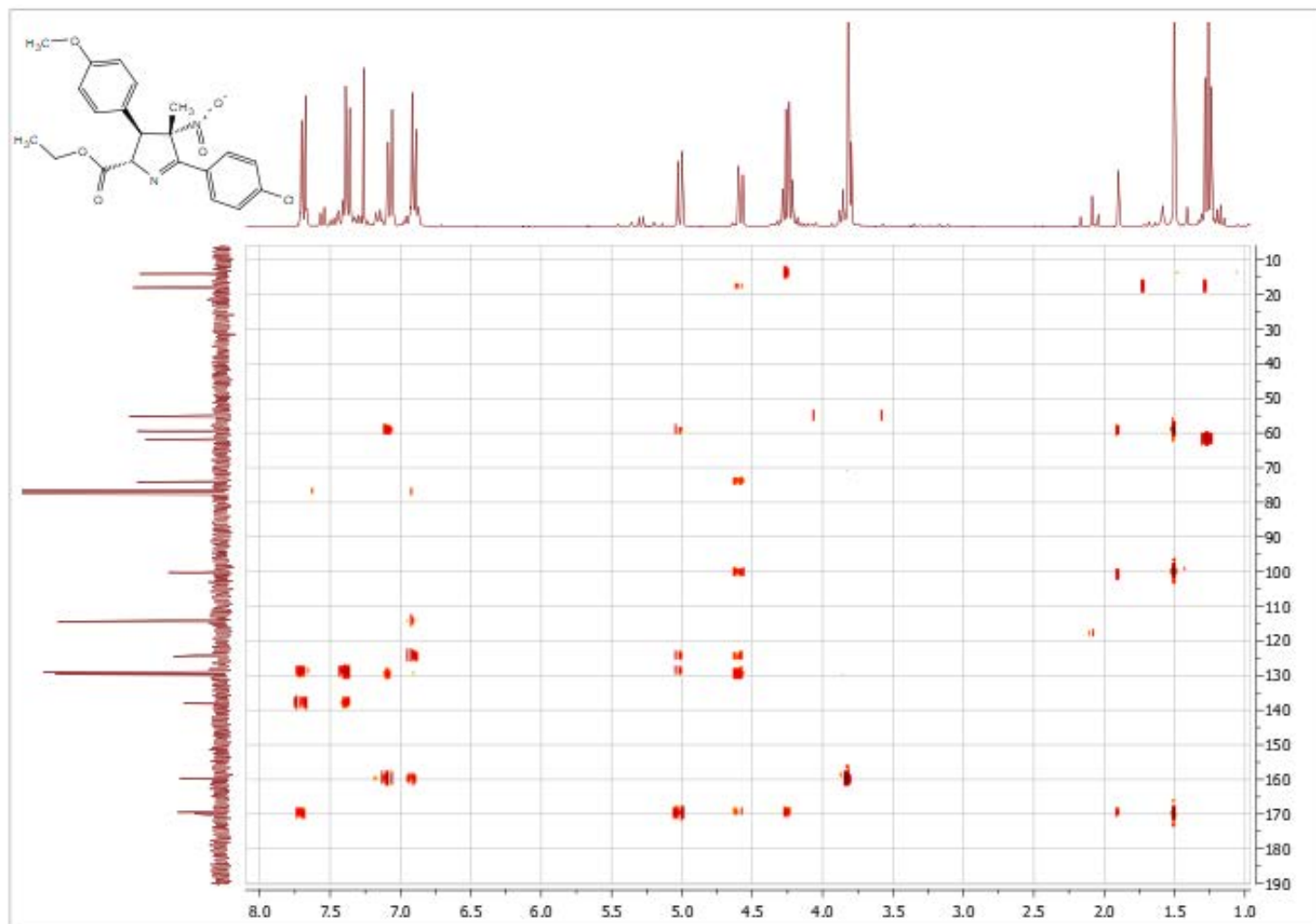
¹³C NMR



^1H - ^1H NOESY NMR

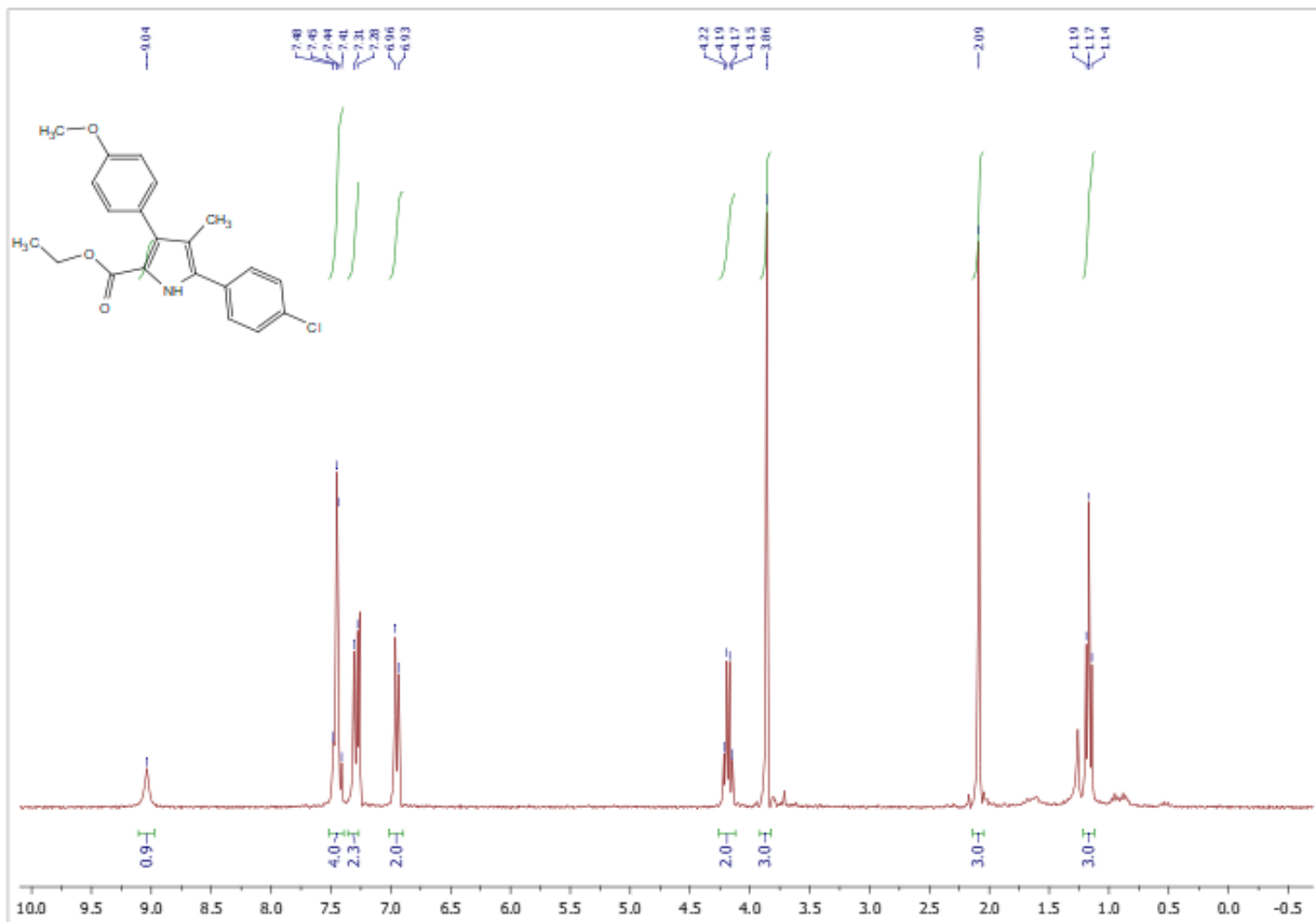


^1H - ^{13}C HMBC NMR

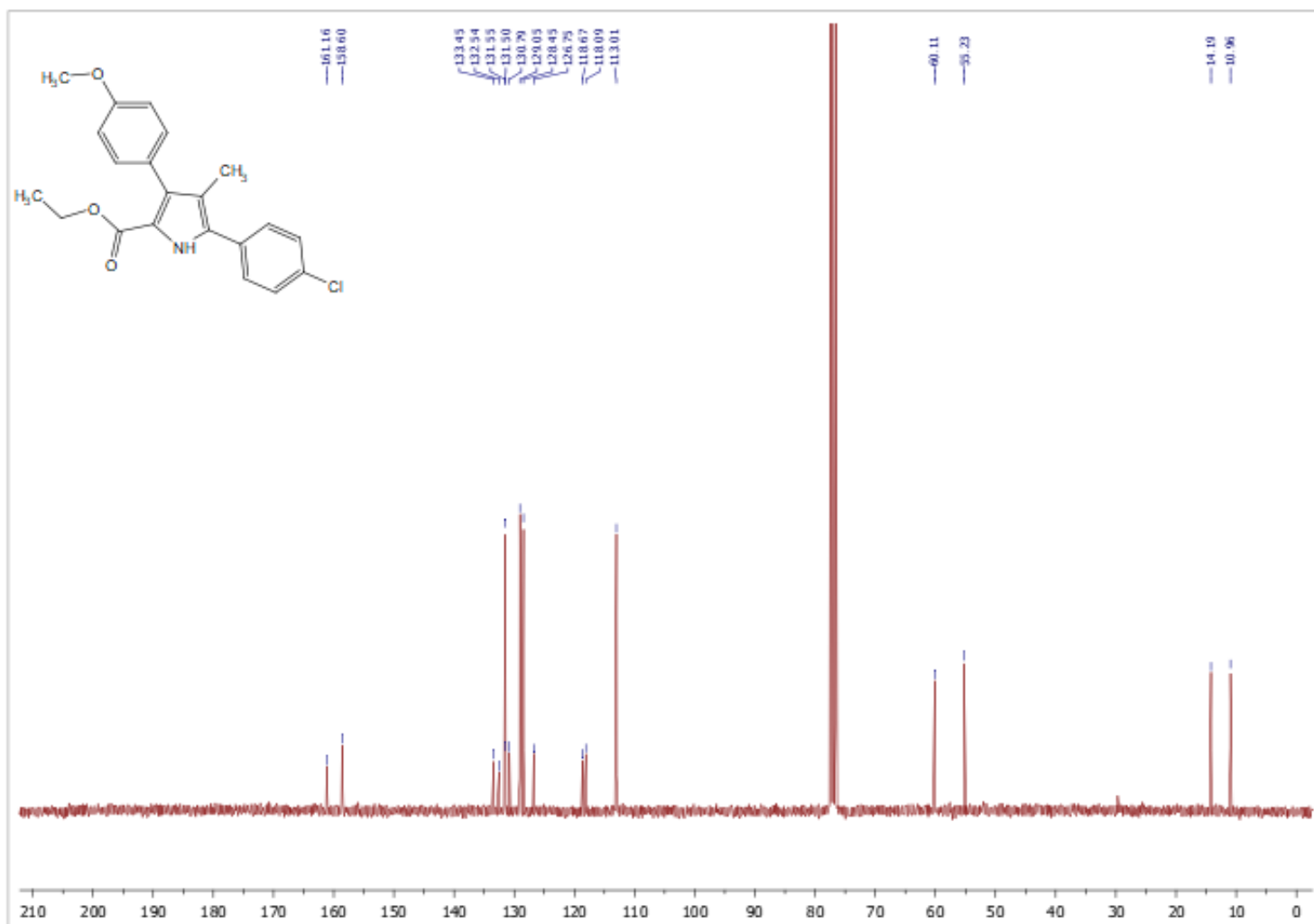


5-(4-chlorophenyl)-4-methyl-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **10**

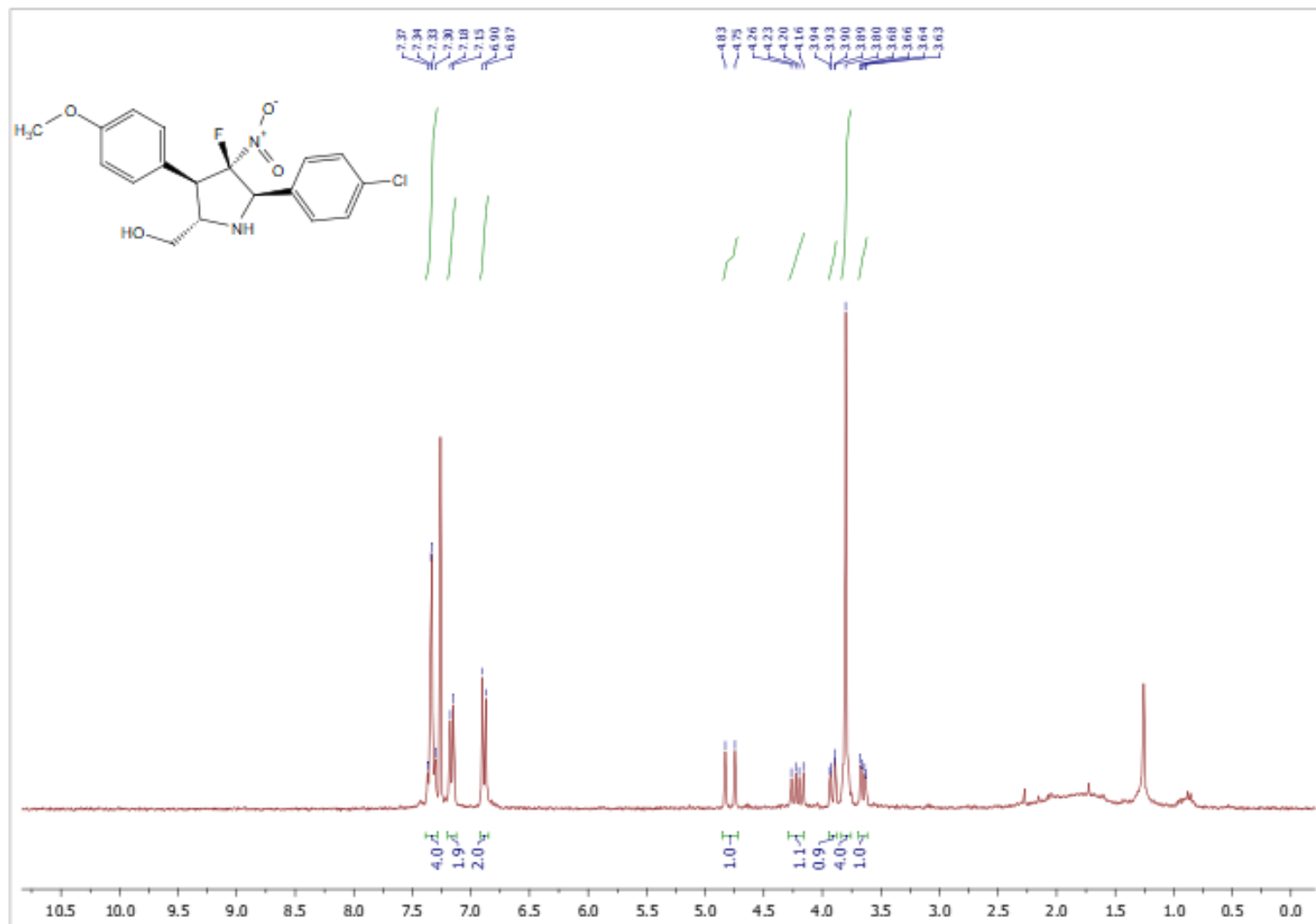
¹H NMR



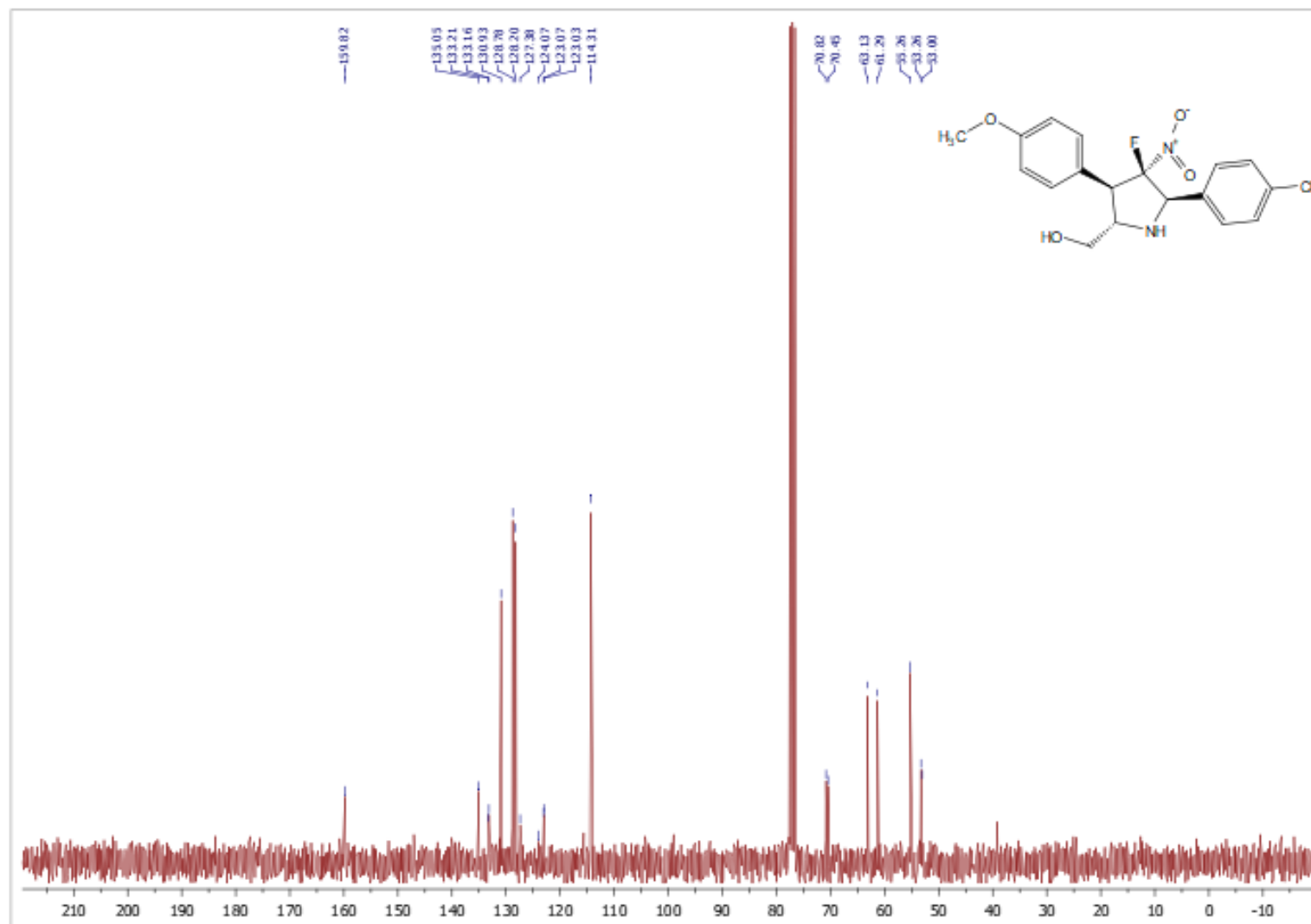
¹³C NMR



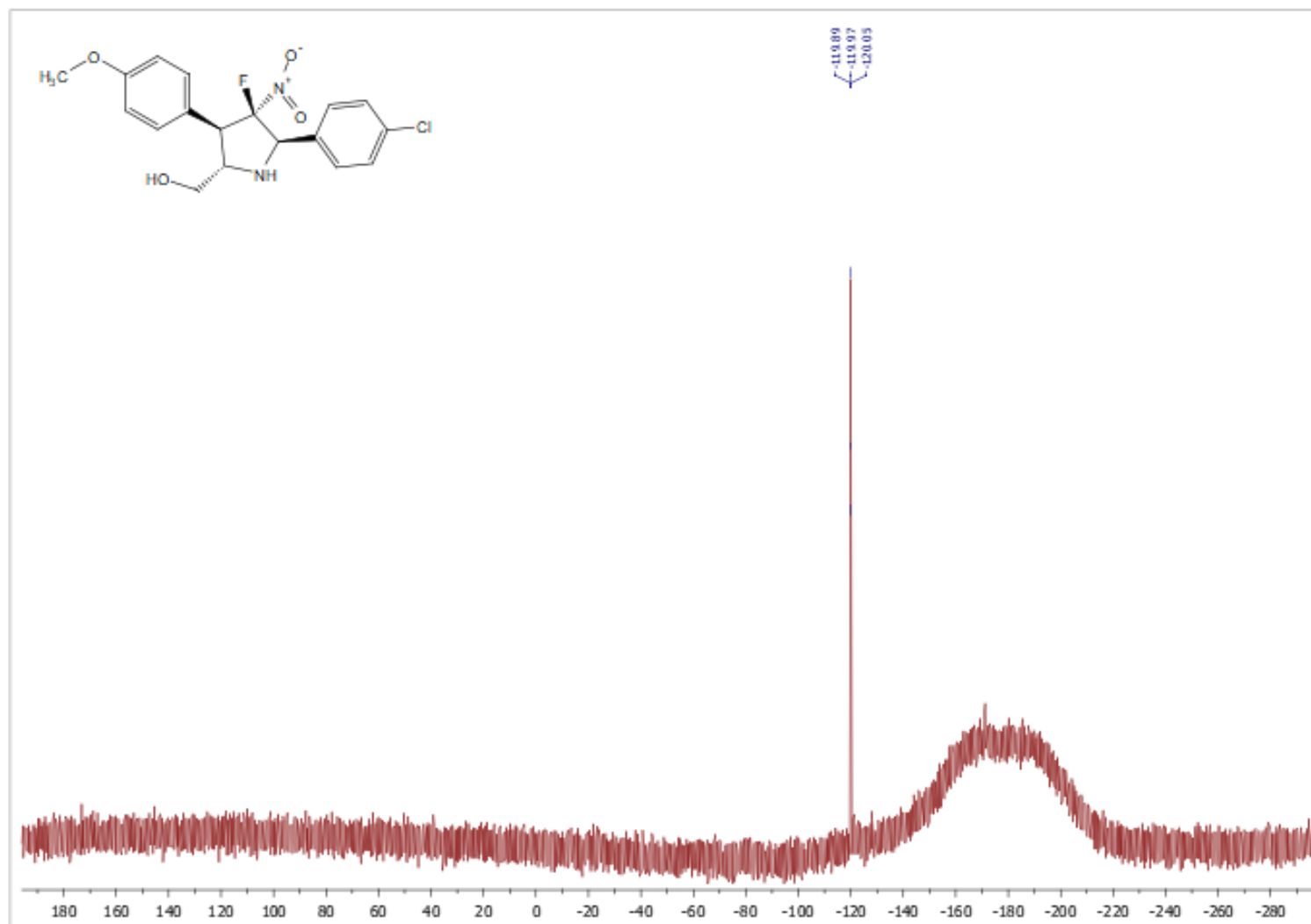
[(2*S*,3*R*,4*R*,5*R*)-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-4-fluoro-4-nitropyrrolidin-2-yl]methanol **11**



^{13}C NMR

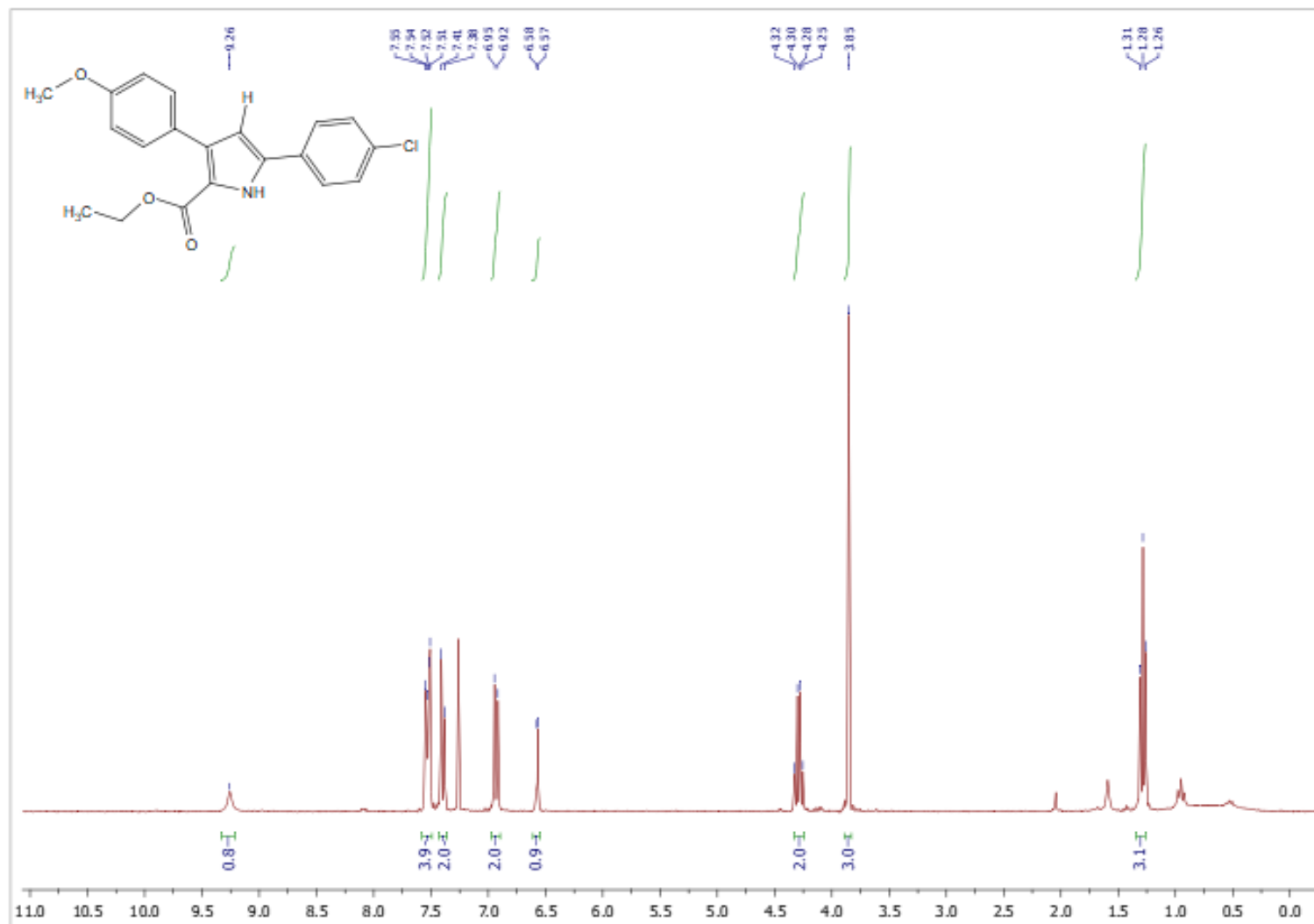


^{19}F NMR

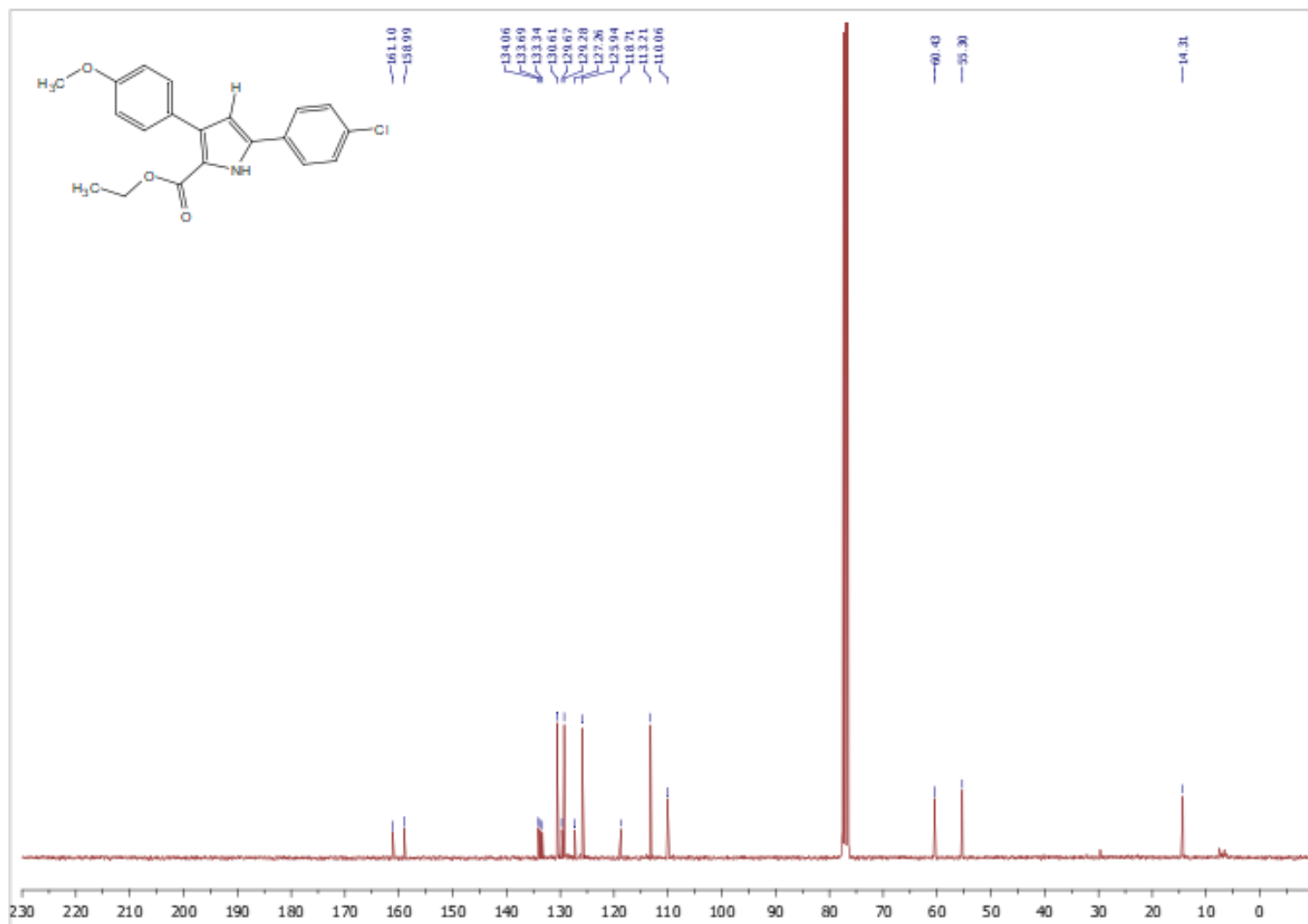


ethyl 5-(4-chlorophenyl)-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate **12**

^1H NMR

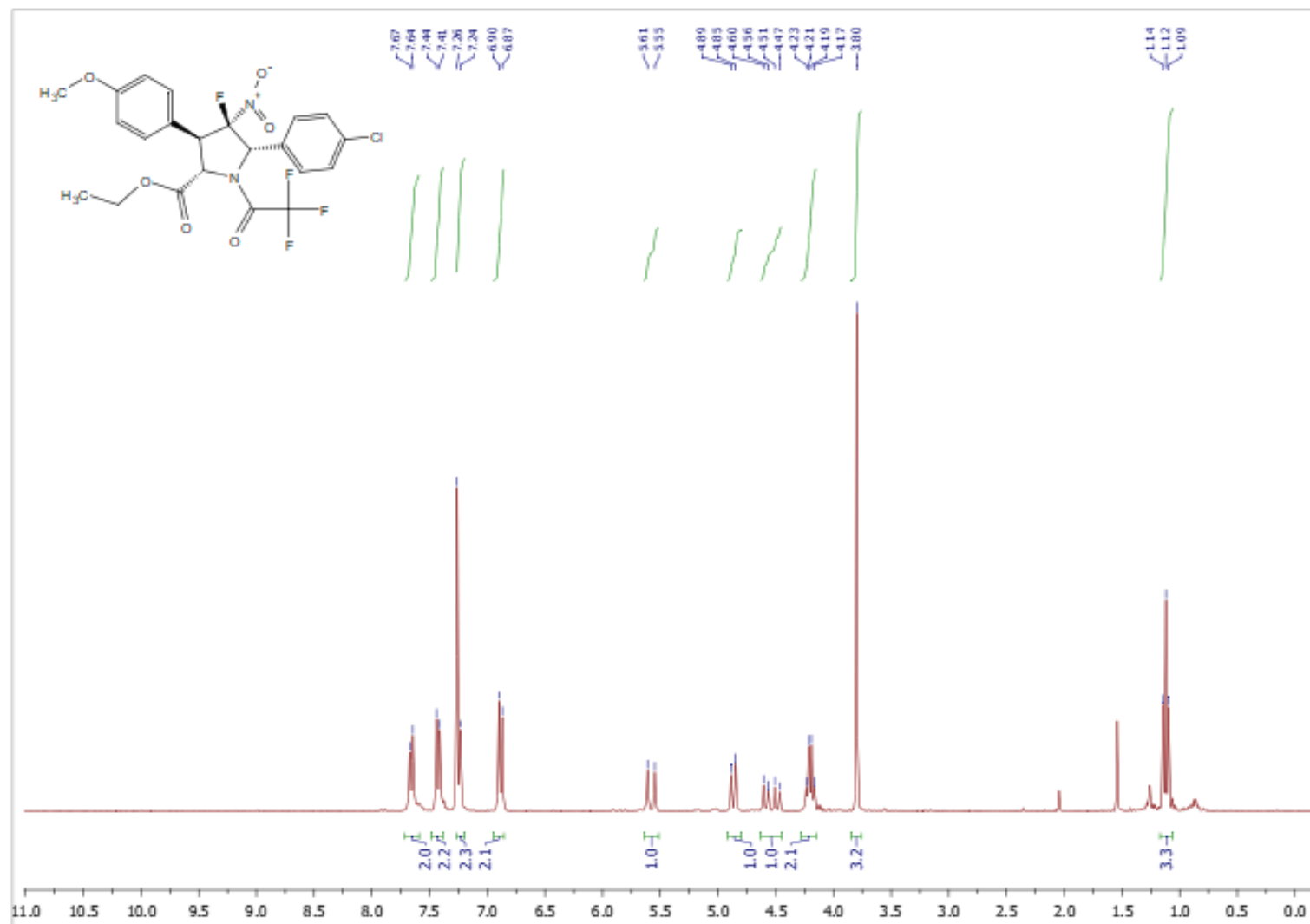


¹³C NMR

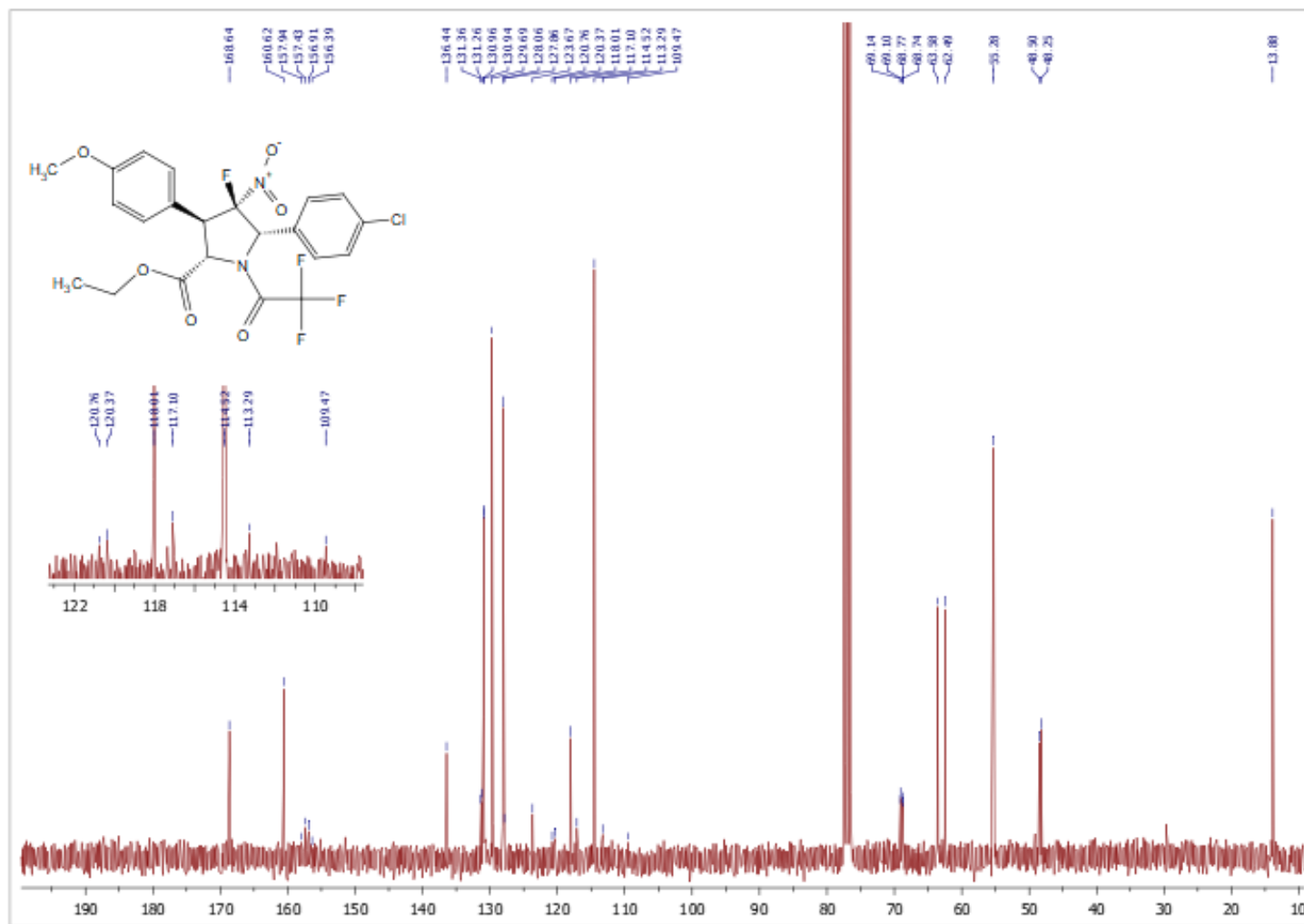


ethyl (2*S*,3*R*,4*R*,5*S*)-4-fluoro-4-nitro-3-(4-methoxyphenyl)-5-(4-chlorophenyl)-1-(trifluoroacetyl)pyrrolidine-2-carboxylate **13**

¹H NMR



¹³C NMR



^{19}F NMR

