Deacylative allylation: allylic alkylation via retro-Claisen activation.

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Supporting Information

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General Information:

All reactions were run in flame-dried glassware. CH_2Cl_2 and toluene were dried over activated alumina. THF dried over sodium and distilled. Anhydrous dichloroethane, acetonitrile, NMP, DMF and DMSO were purchased from Aldrich, stored in the glove box and used as is. All palladium catalysts and ligands were purchased from Strem and used as is. 95% Sodium hydride was purchased from Aldrich, stored in a glove box and used as is. Allyl alcohol was purchased from Aldrich and stored over activated 3Å mol sieves in a vial with a rubber septum. β-methyl allyl alcohol, hexenyl alcohol, cinnamyl alcohol were commercially available from Aldrich and/or Fluka and used without furthur purification. Dienyl alcohol and cylcopropyl allyl alcohol were prepared via Wittig reaction/reduction (see below).[1,2] Acetyl imidazole was prepared by the literature procedure.[3] Nitroketones were prepared by literature procedures.[4,5,6] All allyl *tert*-butyl carbonates were prepared from the literature procedure.[5] All Allyl acetates used were commercially available from Aldrich. For all other substrate preparations, see the experimental section below.

Compound purification was effected by flash chromatography using 230x400 mesh, 60Å porosity silica obtained from Sorbent Technologies. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX spectrometer equipped with a QNP cryoprobe and referenced to residual protio solvent signals. Product nitroalkanes **3** and *para*-nitrophenylketones **4a**-**d** were previously reported by us.[8]

References

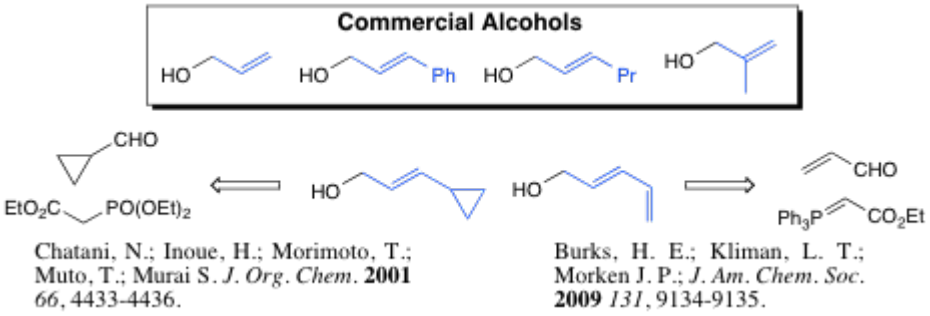
1. Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai S. *J. Org. Chem.* **2001** *66*, 4433-4436.
2. Burks, H. E.; Kliman, L. T.; Morken J. P.; *J. Am. Chem. Soc.* **2009** *131*, 9134-9135.
3. Boyer, J. H.; *J. Am. Chem. Soc. 1952*, 74, 6274.

4. Linton, B. R.; Reutershan, M. H.; Aderman, C. M.; Richardson, E. A.; Brownell, K. R.; Ashley, C. W.; Evans, C. A.; Miller, S. J.; *Tet. Lett. 2007*, 48, 1993.
5. Crumbie, R. L.; Nimitz, J. S.; Mosher, H. S.; *J. Org. Chem. 1982, 47,* 4040
6. Dampawan, P.; Zajac, W. W., Jr.; *Synthesis 1983*, 7, 545.
7. Houlihan, F.; Bouchard, F.; Frechet, J. M. J.; Willson, C. G.; *Canadian Journal of Chemistry 1985*, 63, 153.
8. Grenning, A. J.; Tunge, J. A. *Angew. Chem. Int. Ed.* **2011**, 50, 1688.

Experimental Procedures:

Allyl Alcohol Synthesis:

See the following references for the synthesis of cyclopropane allyl alcohol and dienyl allyl alcohol. **NOTE: Diene-alcohols are light sensitive: store wrapped in aluminum foil in a freezer.**



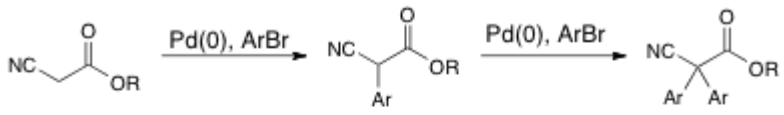
Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai S. *J. Org. Chem.* **2001** *66*, 4433-4436.

Burks, H. E.; Kliman, L. T.; Morken J. P.; *J. Am. Chem. Soc.* **2009** *131*, 9134-9135.

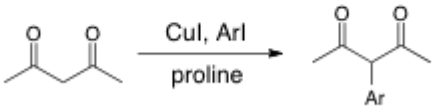
Substrate Synthesis:

α-Arylation of acetylacetone and cyanoacetates:

All acetylacetone derivates and cycano aceteates were prepared via arylation. Please see the following references for their synthesis:



Beare, N. A.; Hartwig, J. F. *J. Org. Chem.* **2002,** *67*, 541-555

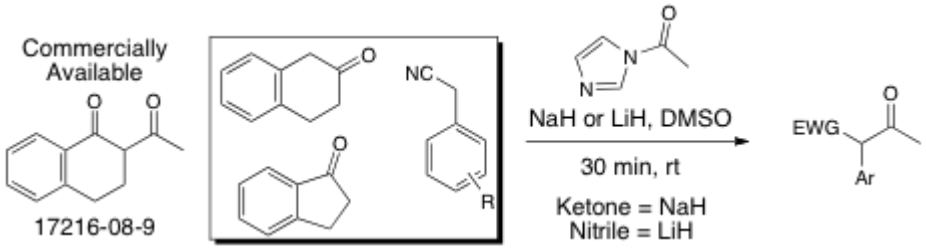


Jiang, Y. F.; Wu, N.; Wu, H. H.; He, M. Y. *Synlett*. **2005**, *18*, 2731-2734.

Acetylation of enolates and nitrile anions:

The procedure utilized in this paper was based on the method reported by Crumbie et al. for the acetylation of nitroalkanes.

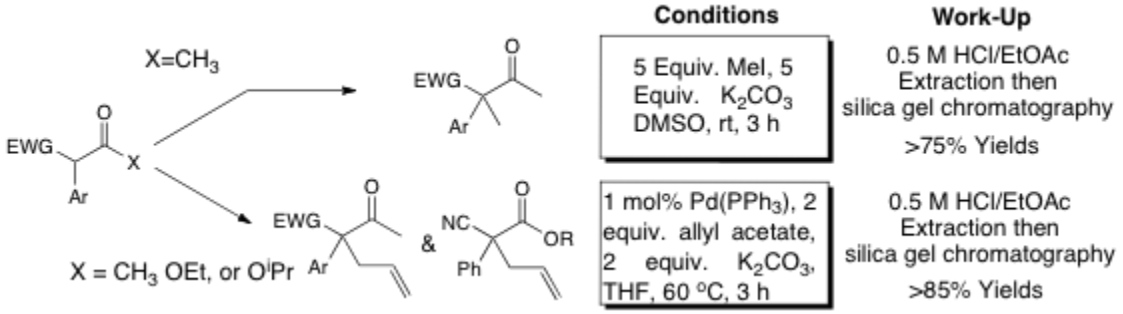
Crumbie, R. L.; Nimitz, J. S.; Mosher, H. S.; *J. Org. Chem. 1982, 47,* 4040



In a glove box, a flame dried 250 mL Schlenk flask is charged with hydride (40 mmol) (NaH for ketones and LiH for nitriles). A slurry of this hydride is made in 15 mL of DMSO. An additional 5 mL of DMSO is syringed and both the DMSO-filled syringe and vessel are removed from the glove box. The ketone or nitrile (20 mmol) is then added neat to the mixture while stirring. The sides of the vessel are washed with 2.5 mL of DMSO if there is any residual solid not in the basin. N-Acetylimidazole is then added neat slowly. Use the final 2.5 mL of DMSO to wash any residual N-Acetylimidazole into the reaction basin.

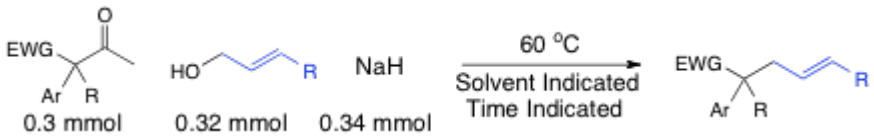
After reaction for 30 min., the mixture is diluted with 50 mL of EtOAc and 100 mL of 0.5 M HCl (at least until acidic). The biphasic mixture is transferred to a separatory funnel for extraction. The reaction vessel is washed with ~50 mL of EtOAc to ensure complete transfer into the separatory funnel. After vigourous shaking, the water layer is removed. The organic layer is again washed with 0.5 M HCl and brine (100 and 50 mL, respectively). The organic layer is dried with anhydrous magnesium sulfate and evaporated yielding the pure acetylated product (commonly, > 85% yields for cyano compounds. The ketones were less consistent, though usually > 70 % Yields).

Procedure for alkylation of the α-arylacetylketones, α-arylcyanoketones, and α-arylcyanoacetates compounds:

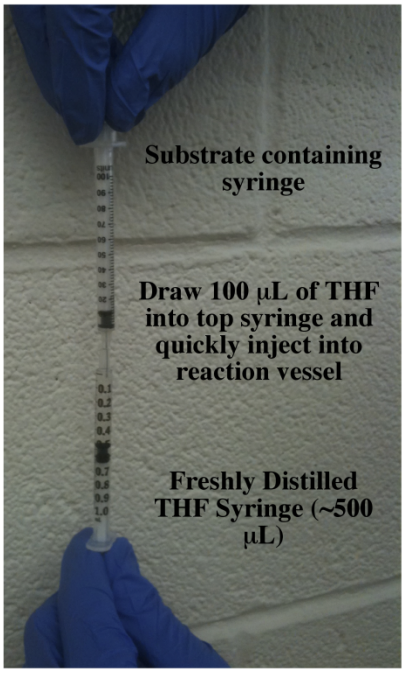


Note*:* Only one equiv. of higher boiling allyl acetates were used (cinnamyl, prenyl, etc.). Monitor reaction by TLC (7% EtOAc in Hexanes) until completion. Reaction "overnight" also sufficed with little/no effect in yield.

Representative procedure for the DaA of α-aryl ketones and nitriles:



A 10 mL flame-dried Schlenk flask is charged with $Pd(PPh_3)_4$ (2-3 mol %, 6-8 mg, FW:1155.57) and NaH (0.34 mmol, 8 mg, FW: 24.00) in a glove box. The vessel is capped and removed from the glove box. The vessel is then attached to a Schlenk apparatus. Over argon, freshly distilled THF (~1 mL) is added to the reaction mixture. The allylic alcohol (0.32 mmol) is syringed and diluted with ~0.1 mL of THF and injected into the Schlenk flask (see **technique image** below). Rapid effervescence occurs forming the alkoxide. The syringe is washed with an additional 0.4 mL of THF and this is injected. Once H_2 effervescence ceases, the acylpronucleophile (0.3 mmol), diluted in ~0.1 mL of solvent using the same addition technique as above is added. The vessel is the washed with an additional 0.4 mL of THF and this is injected. The reaction mixture is then submerged in an oil bath at 60 °C where it is left to react for the indicated time.



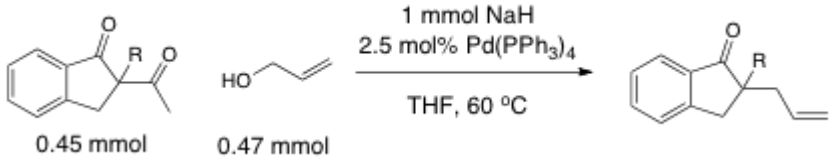
Technique image: This technique was a practical way to inject the reagents without exposing the solvent/substrates to much moisture. Any contaminate water can induce an undesired retro-Claisen reaction, decreasing the yield of desired product (and increasing the yield of protonation byproduct). Use the most effective dry techniques possible.

Note: Small amounts of protonation can often be overcome by simply using a slight excess of NaH/Allyl alcohol (e.g. 1.1-1.3 equiv. of NaH/Allyl alcohol)

After the desired reaction time, the mixture was transferred to a separatory funnel with 3 x ~10 mL portions of EtOAc. The organic layer was extracted with 0.5 M HCl then brine (~25 mL of each water mixture). The organic layer is then dried, evaporated and purified by column chromatography to yield the desired compound.

NOTE: Elution solvent mixtures for purification varied from 2-10% EtOAc in Hexanes.

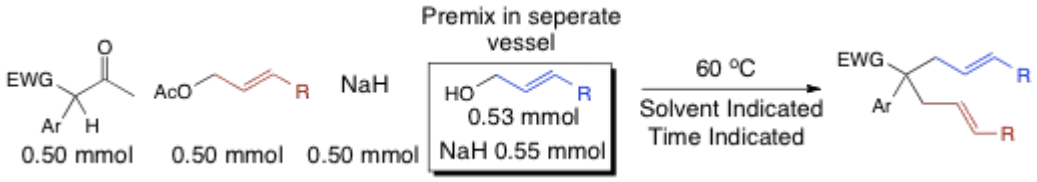
Representative procedure for the DaA of 1-indanone and other α,α-dialkylketones: (e.g. 1-indanone **4m-n**, 1-tetralone **4o**, α,α-dialkylacetylacetone **4p**)



A flame-dried 10 mL Schlenk flask is charged with NaH (25 mg, 1 mmol, 2 equivalents, 95% NaH) and $Pd(PPh_3)_4$ (10 mg, 0.010 mmol) in a glove box. This vessel is capped and removed from the glove box. Outside the glove box, the vessel is attached to a inert atmosphere Schlenk line. Over argon, freshly distilled THF (~1 mL) is added to the reaction mixture and stirred. Allyl alcohol (28 mg, 0.47 mmol) is added to the reaction vessel in ~0.1 mL THF (the transfer technique utilized is described in the image above). Wash the transfer syringe with ~0.4 mL of THF. Upon addition of the alcohol, rapid effervescence occurs. Once H_2 effervescence ceases, the 2-acetyl-1-indanone derivative (87 mg, 0.45 mmol) is added to the reaction vessel in 0.1 mL of THF. Wash the transfer syringe with ~0.4 mL of THF. The vessel is submerged in an oil bath at 60 °C for 1 h.

After reaction for 1 h, the vessel is diluted with 5 mL EtOAc and transferred to a separatory funnel. The reaction vessel is washed twice with 5 mL of EtOAc and added to the separatory funnel. The organic layer is extracted with ~20 mL of 0.5 M HCl. The organic layer is then washed with brine, dried over magnesium sulfate and evaporated. Silica gel column chromatography affords the product (2.5% EtOAc in Hexanes).

Representative procedure for 3-component Tsuji-Trost/DaA:



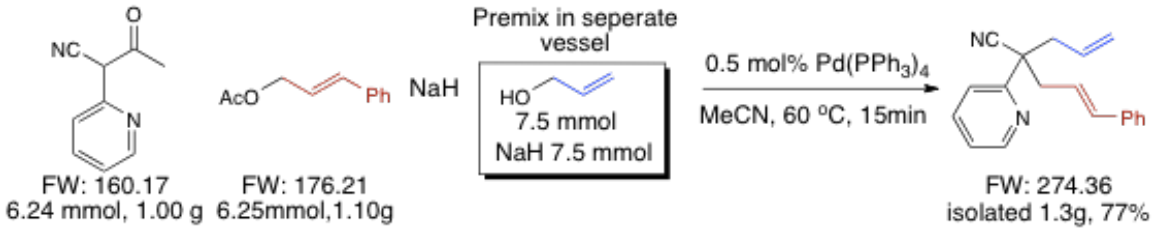
A 10 mL flame dried Schlenk flask is charged with $Pd(PPh_3)_4$ (2-3 mol%, 6-8 mg, FW:1155.57) and NaH (0.50 mmol, 12.5 mg, FW: 24.00/95% purity) in a glove box. A separate flame-dried Schlenk flask is charged with NaH (0.55 mmol, 13.5 mg, FW: 24.00) and capped. The vessel is capped and removed from the glove box. Outside the glove box the vessels are attached to a Schlenk apparatus. Over argon, freshly distilled THF (~1 mL) is added to the reaction mixture and stirred. α-EWG acetone (0.5 mmol) derivative is diluted in 0.1 mL of THF and injected into the vessel. The syringe is then washed with an additional ~0.4 mL of solvent. The allylic acetate (0.5 mmol) is diluted with ~0.1 mL of THF and injected in the mixture. The syringe is then washed with an additional ~0.4 mL of THF. This mixture is then submerged in an oil bath for 5-15 mins. to allow the Tsuji-Trost to complete.

In the mean time, sodium allyl alkoxide in 1 mL of THF is prepared in the other vessel. This is done by adding THF and allyl alcohol consecutively. Make sure to wash

the syringe containing the alcohol to ensure complete transfer. Once the alkoxide solution is prepared, inject it into the reaction vessel. Wash the transfer vessel with an addition 1 mL of THF to ensure complete transfer. Allow the reaction to react at the 60 °C for the time indicated.

Work-up is the same as for the 2-component deacylative allylation above.

Gram-Scale 3-Component Bisallylation:



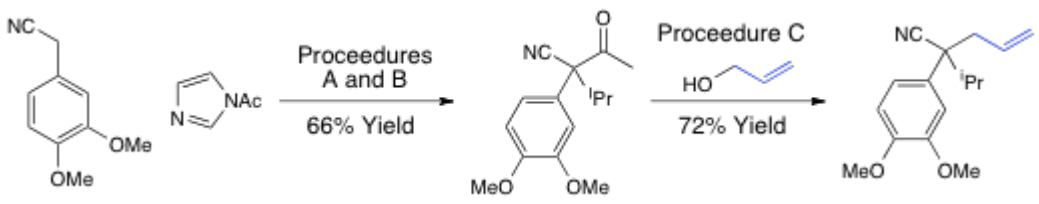
In a glove box, a 50 mL Schlenk flask is charged with NaH (6.25 mmol, 157mg) and $Pd(PPh_3)_4$(0.5 mol%, 36mg). The vessel is capped, removed from the glove box and attached to a Schlenk Apparatus. Over argon, 5 mL of anhydrous acetonitrile is added to the flask followed by the cyanoketone substrate. Rapid effervescence occurs. While stirring, cinnamyl acetate is added via syringe. The syringe is washed with 2 x 0.5 mL portions of acetonitrile to ensure complete transfer of the reagent.

In a separate Schlenk tube, a solution of sodium allyl alkoxide in anhydrous acetonitrile (5mL) is prepared by the reaction of NaH and allyl alcohol. Once effervescence ceases (~5 min.),

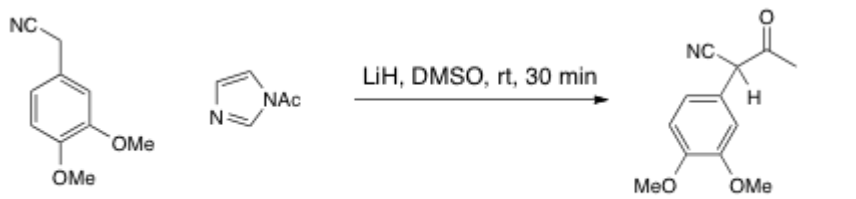
The alkoxide solution is injected into the reaction mixture containing the cyanoketone. Wash the transfer vessel with an additional 5 mL of solvent to ensure complete transfer of the reagent to the reaction vessel. After complete transfer of reagents, cap the vessel and heat it at 60 °C for 15 min.

After reaction, transfer the contents to a separatory funnel and extract with EtOAc and aqueous sat. $NaHCO_3$ and brine consecutively. The pure product (1.3 g, 77%) is afforded by silica gel chromatography (10% EtOAc in Hexanes).

Synthesis of verapamil precursor from homoveratronitrile:



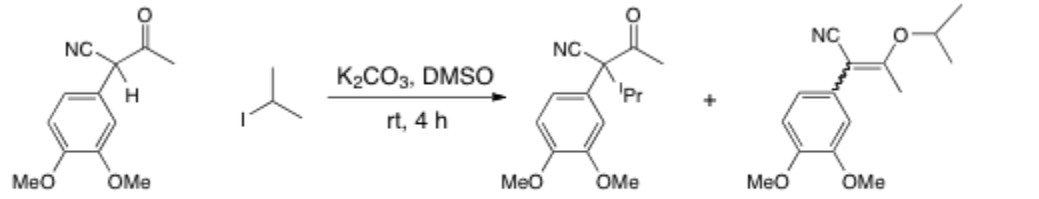
Procedure A: Acetylation of homoveratronitrile



FW: 177.20 20 mmol, 3.54 g | FW: 110.11 22 mmol | FW: 219.24 isolated 4.13 g, 94% Yield

See the general procedure for acetylation of arylacetonitrile derivatives above. Yield = 94%.

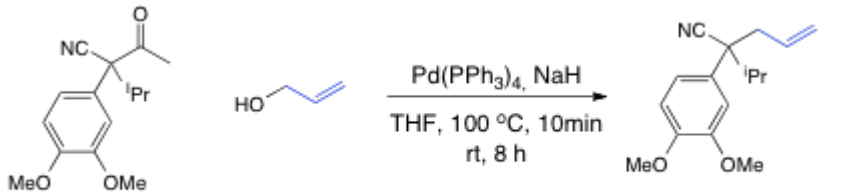
Procedure B: Alkylation of acetylhomoveratronitrile with 2-iodopropane



FW: 219.24 17.5 mmol, 3.9 g | FW: 169.99 72 mmol, 12.2 g | FW: 388.22 Isolated 3.1 g, 71% | Byproduct: seen in crude NMR, ~30%, but not isolated

A flame-dried 50 mL Schlenk flask is charge with 10 g of K_2CO_3 (72 mmol, FW = 138). 10 mL of DMSO is added and the slurry is stirred. To this stirring mixture, acetylhomoveratronitrile (17.5 mmol, 3.9 g) is added as a solid. The sides of the vessel are washed with 10 mL DMSO. This ensures all reacts are in the solution. 2-iodopropane (72 mmol, 12.17 g) is added via syringe in a single shot. After 4 hours, the reaction is complete (monitor by NMR via aliquot removal). The reaction is transferred to a separatory funnel and diluted with ~40 mL EtOAc. The organic layer is extracted with 2 50 mL portions of aqueous $NaHCO_3$. The organic layer is concentrated under vacuum and the residual was purified by gradient column chromatography, 10-15% w/v EtOAc in hexanes.

Procedure C: Deacylative allylation

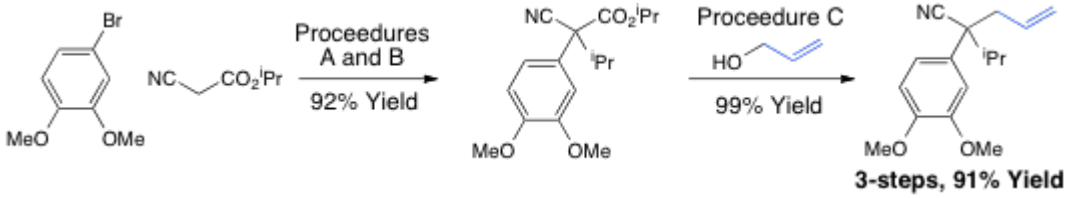


FW: 388.22 5.0 mmol, 1.30 g | FW: 58.08 5.0 mmol, 291 mg | FW: 259.34 Isolated 927 mg, 72%

A pressure vial (20 mL Biotage microwave vial was used), is charged with 95% pure NaH (FW: 24.00, 10 mmol, 240mg) and 2.5 mol % $Pd(PPh_3)_4$ (FW: 1155.57, 0.05 mmol, 57 mg). A stir bar is added and the vial is capped with an injectable pressure septum. The vial is secured to a ring stand and connected to an argon source via a syringe. A needle is inserted for exhaust of the H_2 gas byproduct. 4 mL of THF is added the vial and while stirring, a solution of allyl alcohol (5.7 mmol, 331 mg) in THF (~0.7 mL, total volume = 1 mL) is then added. The syringe is washed with a 2 x 0.5 mL portion of THF. Chill the alkoxided solution to 0 °C. To this slurry, the cyanoacetone derivative is added as a solution in THF dropwise (4 mL solution). The syringe and transfer vessel are washed with ~1 mL of THF and the argon line is removed. The vessel is then submerged in an oil bath at 100 °C for 10 min. It then cooled to room temperature and left to react for 8 h.

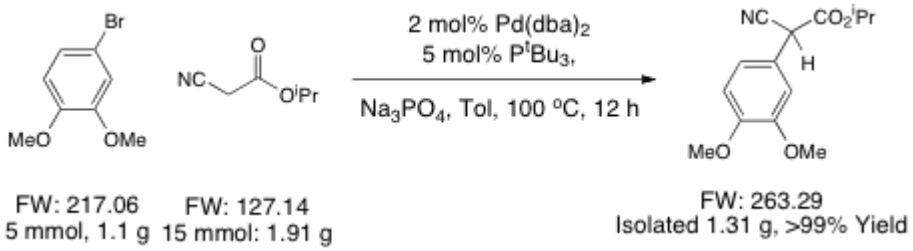
After reaction for 8 h, the vessel is diluted with EtOAc and poured into a separatory funnel. The reaction mixture is further diluted with ~30 mL of EtOAc then extracted with 30 mL 1 M HCl and brine, sequentially. The organic layer is dried of Mg_2SO_4 and then concentrated under reduced pressure. The residue is purified by gradient column chromatography: 11-13% w/v EtOAc in hexanes. Isolated 0.927 g, 72% yield.

Synthesis of verapamil precursor from isopropyl cyanoacetate and bromoveratrole:



Procedure A: Palladium-catalyzed arylation of isopropyl cyanoacetate

This procedure is based on the published work by Hartwig and Coworkers: (a) Stauffer, S.; Beare, N. A.; Stambuli, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001,** *123,* 4641 (b) Beare, N. A; Hartwig, J. F. *J. Org. Chem.* **2002,** *67,* 541.

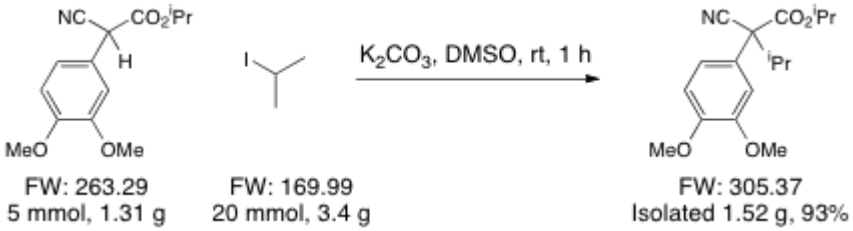


A flame-dried 25 mL Schlenk flask is charged with Na_3PO_4 (20 mmol, 3.3 g), $Pd(dba)_2$ (0.1 mmol, 58 mg), and P^tBu_3 (0.25 mmol, 50 mg). The vessel is capped and removed from the glove box. 5 mL of toluene is added and the mixture is stirred. Isopropyl cyanoacetate is then added via syringe. The transfer syringe is washed with ~1

mL toluene. Bromoveratrole is then added via syringe. The transfer syringe is again washed with ~1 mL toluene. The heterogeneous mixture is recapped and submerged in an oil bath at 100 °C for 12 h.

After reaction for the allotted time, the mixture is transferred to a separatory funnel and extracted with EtOAc and 1 M HCl. 1 M HCl is added until the aqueous layer is acidic. A brine wash, drying over magnesium sulfate, and evaporation then follows yielding the crude product. The product is rendered pure by column chromatography: 3% EtOAc, 25% DCM, Hexanes. Isolated 1.31 g of pure product as an orange oil.

Procedure B: Addition of 2-iodopropane to isopropyl 3,4-dimethoxyphenylcyanoacetate

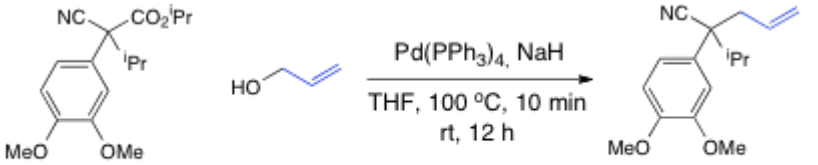


FW: 263.29 5 mmol, 1.31 g | FW: 169.99 20 mmol, 3.4 g | FW: 305.37 Isolated 1.52 g, 93%

A round-bottom flask is charged with anhydrous K_2CO_3 (20 mmol, 2.8 g). The nitrile containing substrate is transferred to the reaction vessel with the aid of 2 x 2.5 mL portions of DMSO. 2-iodopropane is then added as a neat shot and the reaction is capped and stirred for 1h.

After reaction for the allotted time, the mixture is diluted with 30 mL EtOAc and transferred to a separatory funnel. The vessel is washed twice with 10 mL of EtOAc to ensure complete transfer. The organic layer is extracted with 2 x 40 mL portions of 0.5 M HCl and Brine. The organic layer is then dried over magnesium sulfate and evaporated. The resulting orange product is quite pure by ^{1}H NMR (>90% purity), but is nonetheless purified via gradient silica gel column chromatography: 10-15% EtOAc in hexanes. 1.52 g of a clear pale yellow oil is isolated, 93%.

Procedure C: Synthesis of verapamil precursor via retro-Claisen allylation



FW: 305.37 0.34 mmol, 105 mg | FW: 58.08 0.36 mmol, 21 mg | FW: 259.34 Isolated 88 mg, 99%

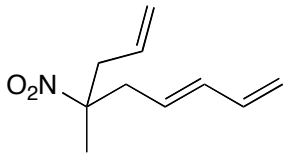
A flame-dried 10 mL pressure vial is charged with NaH (0.70 mmol, 17.7 mg, 2 equiv.) in a glove box. The vessel is capped with a rubber septum capable of holding pressure (Biotage microwave vessel was used) and removed from the glove box. The vessel is connected to an argon line via needle to relieve the vessel of pressure from H_2 effervescence. 1.5 mL of THF is added and while stirring, a solution of allyl alcohol in 0.5 mL of THF is added. Rapid H_2 effervescence occurs.

The transfer syringe is washed with an additional 0.5 mL portion of THF. The cyanoacetate substrate is then added in 0.5 mL of THF via syringe. The transfer vessel is washed with an additional 0.5 mL portion of THF. The argon bleed is removed and the vessel is placed in an oil bath at 100 °C for 10 min. The vessel is then cooled to room temperature and THF solution of $Pd(PPh_3)_4$ is injected. The vessel is then stirred for 12 h.

After the allotted reaction time, the cap is removed and vessel's contents are transferred to a separatory funnel with the aid of 2 x 5 mL portions of EtOAc. The organic layer is extracted with 0.5 M HCl and brine. The organic layer is then dried over magnesium sulfate and evaporated.

88 mg (99% Yield) of pure product is obtained by silica gel chromatography: 11-13% EtOAc in Hexanes.

Spectroscopic Data for Compounds 3f, 4e-z, 4aa-ll, 5a-w
3f



^{1}H NMR (500 MHz, CDCl3):

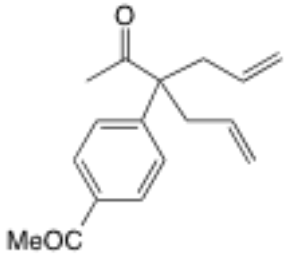
δ 6.22 (dt, *J* = 16.9, 10.3 Hz, 1H), 6.06 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.60 (m, 1H), 5.45 (dt, *J* = 15.1, 7.8, Hz, 1H), 5.11 (d, *J* = 9.35 Hz, 2H), 5.08 (d, *J* = 8.4 Hz, 1H), 5.01 (d, *J* = 10.3 Hz, 1H), 2.68 (dt, *J* = 14.7, 7.2 Hz, 2H), 2.49 (dt, *J* = 22.8, 7.5 Hz, 2H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 135.23, 135.16, 129.77, 125.02, 119.64, 116.49, 89.72, 42.38, 41.17, 20.98.

GC/MS data: 181.4 (M^+), 135.3 (M-NO_2), 67.1 (base peak).

4e:



^{1}H NMR (500 MHz, CDCl3):

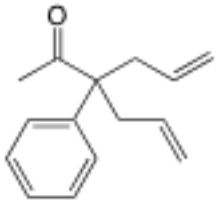
δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.36 (m, 2H), 5.00 (dd, *J* = 8.0, 10.2 Hz, 4H), 2.69 (d, *J* = 7.3 Hz, 4H), 2.54 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.43, 197.60, 146.63, 135.98, 132.61, 128.81, 127.00, 119.10, 59.33, 37.45, 26.64, 26.41.

GC/MS data: 256.1 (M^+), 114.2 (M-Ac), 173.1 (base peak).

4f:



^{1}H NMR (500 MHz, CDCl3):

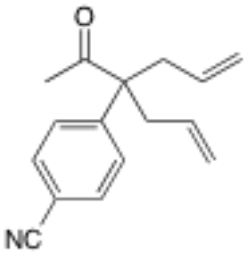
δ 7.25 (m, aromatics, 3H), 7.11 (m, aromatics, 2H), 5.37 (m, 2H), 4.98 (dd, *J* = 15.3, 6.0 Hz, 4H), 2.67 (m, 4H), 1.83 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.45, 141.13, 133.24, 128.81, 127.14, 126.66, 118.57, 58.93, 37.44, 26.24.

GC/MS data: 214.1 (M^+), 271.1 (M-Ac, base peak).

4g:



^{1}H NMR (500 MHz, CDCl3):

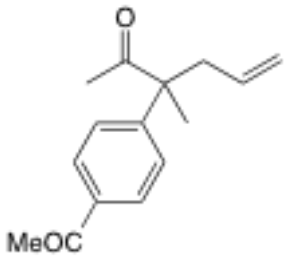
δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.43 (m, 2H), 5.08 (m, 4H), 2.76 (d, *J* = 7.2 Hz, 4H), 1.93 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 207.81, 146.70, 132.58, 132.14, 127.62, 119.47, 118.46, 111.29, 59.43, 37.42, 26.46.

GC/MS data: 239.1 (M^+), 196.1 (M-Ac, base peak).

4h:



^{1}H NMR (500 MHz, CDCl3):

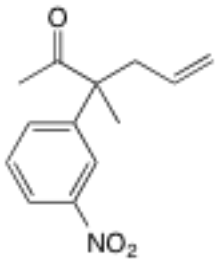
δ 7.97 (d, *J* = 8.6 Hz 2H), 7.35 (d, *J* = 8.6 Hz 2H), 5.47 (m, 1H), 5.04 (dd, *J* = 12.4, 4.3 Hz 2H), 2.71 (d, *J* = 7.3 Hz, 2H), 2.62 (s, 3H), 1.95 (s, 3H), 1.52 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.36, 197.62, 147.76, 135.89, 133.47, 128.81, 126.72, 118.71, 55.87, 42.26, 26.64, 26.09, 21.11.

GC/MS data: 230.1 (M^+), 188.2 (M-Ac, base peak).

4i:



^{1}H NMR (500 MHz, CDCl3):

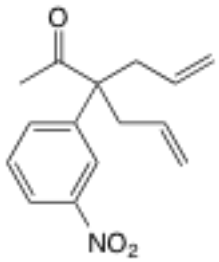
δ 8.17 (m, aromatics, 2H), 7.57 (m, aromatics, 2H), 5.48 (m, 1H), 5.07 (m, 2H), 2.73 (d, *J* = 7.6 2H), 1.98 (s, 3H), 1.58 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.76, 148.67, 144.64, 132.96, 132.91, 129.74, 122.26, 121.32, 119.27, 55.65, 42.33, 26.09, 21.24.

GC/MS data: 233.1 (M^+), 190.1 (M-Ac, base peak).

4j:



^{1}H NMR (500 MHz, CDCl3):

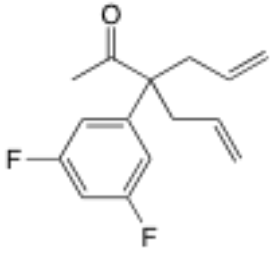
δ 8.10 (ddd, *J* = 8.1, 2.2, 1.1 Hz, 1H), 8.05 (t, *J* = 2.0 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.42 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 5.36 (m, 2H), 5.01 (m, 4H), 2.72 (d, *J* = 7.2 Hz, 4H), 1.87 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

13C NMR (126 MHz, CDCl3) δ 207.83, 148.67, 143.56, 133.18, 132.04, 129.80, 122.40, 121.59, 119.60, 59.10, 37.55, 26.38.

GC/MS data: 259.1 (M^+), 216.1 (M-Ac, base peak).

4k:



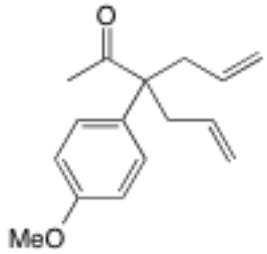
^{1}H NMR (500 MHz, CDCl3):

δ 6.67 (m, 3H), 5.35 (m, 2H), 5.01 (dd, *J* = 12.9, 3.1 Hz, 4H), 2.62 (d, *J* = 7.4 Hz, 4H), 1.87 (s, 3H).

^{13}C NMR (126 MHz, CDCl3): δ 207.74, 163.30 (dd, *J* = 249.5, 14.02 Hz), 145.5, 132.27, 131.16 (d, *J* = 645.5 Hz), 119.31, 109.93 (d, *J* = 19.5 Hz), 102.85 (t, *J* = 27.4 Hz), 58.89, 37.33, 26.20.

GC/MS data: 250.1 (M^+), 207.1 (M-Ac, base peak).

4l:



^{1}H NMR (500 MHz, CDCl3):

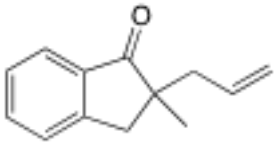
δ 7.12 (d *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.47 (m, *J* = 17.1, 10.1, 7.2 Hz, 2H), 5.08 (d, *J* = 14. 8 Hz, 2H), 5.05 (d ,*J* = 6.7 Hz, 2H), 3.83 (s, 3H), 2.72 (m, 4H), 1.92 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.69, 158.55, 133.38, 133.05, 127.72, 118.46, 114.13, 58.19, 55.24, 37.48, 26.03.

GC/MS data: 244.1 (M^+), 201.2 (M-Ac, base peak).

4m:



^{1}H NMR (500 MHz, CDCl3):

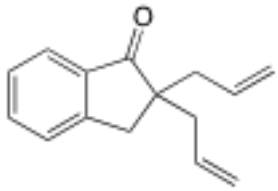
δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.39 (td, *J* = 7.5, 1.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 5.45 (m, 1H), 4.87 (d, *J* = 17.0 Hz, 1H), 4.81 (d, *J* = 10.1 Hz, 1H), 2.97 (d, *J* = 17.2 Hz, 1H), 2.64 (d, *J* = 17.2 Hz, 1H), 2.19 (ddt, *J* = 13.6, 6.7, 1.2 Hz, 1H), 2.10 (dd, *J* = 13.7, 8.0 Hz, 1H), 1.02 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 210.81, 152.60, 135.87, 134.90, 133.89, 127.42, 126.60, 124.27, 118.36, 48.84, 42.54, 39.41, 23.81.

GC/MS data: 186.1 (M^+), 145.1 (base peak).

4n:



^{1}H NMR (500 MHz, CDCl3):

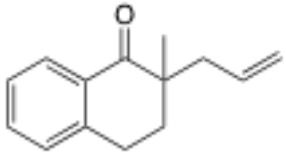
δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.1 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.42 (m, 2H), 4.89 (d, *J* = 16.9 Hz, 2H), 4.81 (d, *J* = 10.2 Hz, 2H), 2.86 (s, 2H), 2.28 (ddt, *J* = 13.7, 6.6, 1.2 Hz, 2H), 2.14 (dd, *J* = 13.7, 8.2 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 210.11, 153.07, 136.72, 134.95, 133.42, 127.37, 126.47, 123.91, 118.54, 52.24, 41.75, 36.04.

GC/MS data: 212.1 (M^+), 170.0, 128.1 (base peak).

4o:



^{1}H NMR (500 MHz, CDCl3):

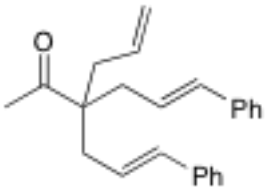
δ 7.98 (dd, J = 7.9, 1.2 Hz, 1H), 7.39 (td, J = 7.5, 1.4 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.15 (m, 1H), 5.72 (m, 1H), 5.03 (d, J = 0.91 Hz, 1H), 5.00 (d, J = 4.8 Hz, 1H), 2.91 (m, 2H), 2.40 (dd, J = 13.8, 7.3 Hz, 1H), 2.21 (ddt, J = 13.8, 7.5, 1.1 Hz, 1H), 2.01 (m, 1H), 1.84 (m, 1H), 1.12 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 202.09, 143.33, 133.98, 133.08, 131.59, 128.68, 128.03, 126.64, 118.22, 44.62, 41.12, 33.35, 25.35, 21.92.

GC/MS data: 212.1 (M^+), 170.0, 128.1 (base peak).

4p:



^{1}H NMR (500 MHz, CDCl3):

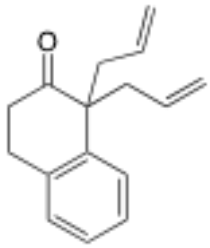
δ 7.34 (m, 8H), 7.25 (m, 2H), 6.48 (d, *J* = 15.7 Hz, 2H), 6.11 (dt, *J* = 15.7, 7.3 Hz, 2H), 5.76 (m, 1H), 5.18 (m, 2H), 2.56 (dd, *J* = 7.5, 1.2 Hz, 4H), 2.46 (d, *J* = 7.4 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 211.67, 137.19, 133.58, 133.22, 128.57, 127.38, 126.15, 124.90, 118.71, 55.41, 38.86, 37.68, 26.43.

GC/MS data: 330.2 (M^+), 287.1 (M-Ac, base peak).

4q:



^{1}H NMR (500 MHz, CDCl3):

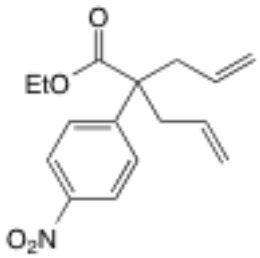
δ 7.24 (m, aromatics, 2H), 7.11 (m, aromatics, 2H), 5.30 (m, 2H), 4.84 (d, *J* = 17.9 Hz, 2H), 4.80 (d, *J* = 9.9 Hz, 2H), 2.89 (dd, *J* = 6.8, 6.8 Hz, 2H), 2.71 (dd, *J* = 8.2, 8.2 Hz, 2H), 2.46 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 213.73, 139.15, 137.01, 133.82, 133.67, 133.38, 128.72, 128.53, 128.47, 128.03, 127.01, 126.90, 126.37, 118.32, 56.01, 45.10, 40.32, 27.86.

GC/MS data: 226.1 (M^+).

4r:



^{1}H NMR (500 MHz, CDCl3):

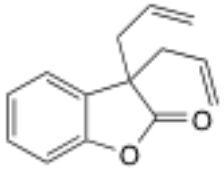
δ 8.21 (d, *J* = 9.4 Hz, 2H), 7.43 (d, *J* = 9.4 Hz, 2H), 5.53 (m, 2H), 5.09 (m, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.86 (dd, *J* = 13.9, 7.6 Hz, 2H), 2.79 (dd, *J* = 13.9, 6.9 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 173.74, 149.39, 146.73, 132.32, 127.64, 123.49, 119.58, 61.37, 53.94, 39.09, 14.07.

GC/MS data: 289.1 (M^+), 128.1 (base peak), 216.1.

4s:



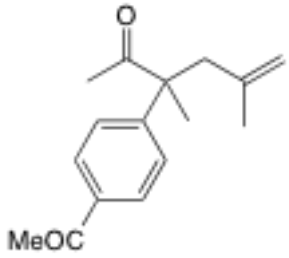
^{1}H NMR (500 MHz, CDCl3):

δ 7.22 (td, J = 7.5, 1.6 Hz, 1H), 7.14 (dd, J = 7.4, 1.5 Hz, 1H), 7.09 (td, J = 7.4, 1.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 5.39 (m, 2H), 4.97 (d, 17.1 Hz 4H), 4.94 (d, 10.0 Hz 1H), 2.55 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 178.58, 152.97, 131.18, 129.41, 128.78, 124.11, 123.65, 120.06, 110.68, 52.37, 41.73.

4t:



^{1}H NMR (500 MHz, CDCl3):

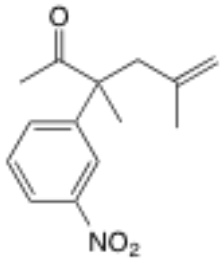
δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 4.80 (s,1H), 4.58 (s, 1H), 2.79 (d, *J* = 13.9, 1H), 2.69 (d, *J* = 14.0 Hz, 1H), 2.62 (s, 3H), 1.95 (s, 3H), 1.58 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.54, 197.63, 148.10, 141.79, 135.86, 128.71, 126.98, 115.54, 55.60, 45.56, 26.64, 26.04, 24.19, 20.65.

GC/MS data: 244.1(M^+), 201.2 (M-Ac, base peak).

4u:



^{1}H NMR (500 MHz, CDCl3):

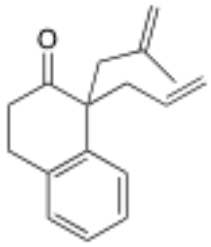
δ 8.22 (t, *J* = 2.0 Hz, 1H), 8.17 (ddd, *J* = 8.0, 2.2, 1.2 Hz, 1H), 7.61 (ddd, *J* = 7.8, 1.8, 1.2 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 4.83 (apparent quintet, *J* = 1.5 Hz, 1H), 4.57 (s, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.69 (d, *J* = 14.1 Hz, 1H), 1.99 (s, 3H), 1.63 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.97, 148.61, 145.02, 141.16, 133.19, 129.61, 122.26, 121.49, 116.02, 55.37, 45.60, 26.07, 24.29, 20.90.

GC/MS data: 247.1 (M^+), 204.1 (M-Ac, base peak).

4v:



^{1}H NMR (500 MHz, CDCl3):

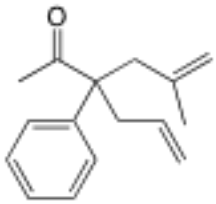
δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.3, 1.3 Hz, 2H), 7.12 (td, *J* = 7.3, 1.3 Hz, 1H), 7.07 (d, *J* = 7.5, 0.7 Hz, 1H), 5.28 (m, *J* = 16.7, 10.1, 8.3, 6.4 Hz, 1H), 4.84 (d, *J* = 16.9 1H), 4.80 (d, *J* = 10.0 Hz, 1H), 2.91 (m, 2H), 2.82 (d, *J* = 13.5 Hz, 1H), 2.71 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.50 (m, 3H), 2.35 (d, *J* = 13.5 Hz, 1H), 1.19 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 213.64, 141.87, 139.42, 136.76, 133.31, 128.08, 127.35, 126.71, 126.38, 118.35, 115.11, 56.17, 48.26, 46.04, 40.28, 27.80, 24.22.

GC/MS data: 240.2 (M^+), 199.2 (base peak).

4w:



^{1}H NMR (500 MHz, CDCl3):

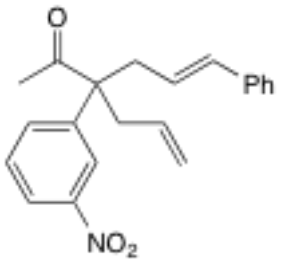
δ 7.27 (m, aromatics, 2H), 7.20 (m, aromatics, 1H), 7.14 (m, 2H), 5.48 (m, 1H), 5.01 (dd, *J* = 16.85, 7.71, 2H), 4.74 (s, 1H), 4.56 (s, *J* = 0.9 Hz, 1H), 2.84 (dd, *J* = 5.86, 5.86 Hz, 1H), 2.73 (dt, 2H), 2.59 (d, *J* = 14.4 Hz, 1H), 1.83 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.78, 141.89, 141.68, 133.53, 128.76, 127.14, 126.85, 118.63, 115.17, 58.80, 41.13, 36.77, 26.32, 24.15

GC/MS data: 228.2 (M^+), 185.1 (M-Ac, base peak).

4x:



^{1}H NMR (500 MHz, CDCl3):

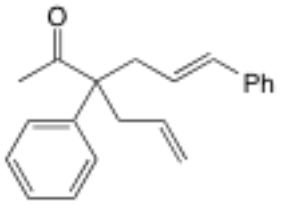
δ 8.11 (m, 2H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.5 1H), 7.16 (m, 5H), 6.34 (d, *J* = 15.7 Hz, 1H), 5.71 (dt, *J* = 16.2, 7.5 1H), 5.42 (m, 1H), 5.05 (m, 2H), 2.87 (d, *J* = 7.2 Hz, 2H), 2.77 (d, *J* = 7.2 Hz, 2H), 1.92 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 207.84, 148.72, 143.58, 136.84, 134.49, 133.19, 132.05, 129.87, 128.56, 127.58, 126.15, 123.48, 122.49, 121.62, 119.73, 59.47, 37.77, 36.99, 26.45.

GC/MS data: 335.2 (M^+), 292.2 (M-Ac, base peak).

4y:



^{1}H NMR (500 MHz, CDCl3):

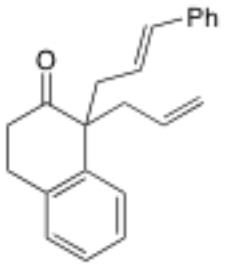
δ 7.31 (m, 2H), 7.18 (m, 9H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.72 (dt, *J* = 15.7, 7.4 Hz, 1H), 5.44 (m, 1H), 5.02 (dd, *J* = 12.1, 3.57 2H), 2.80 (dd, *J* = 7.4, 1.3 Hz, 2H), 2.71 (dd, *J* = 8.4, 7.3 Hz, 2H), 1.85 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.46, 141.13, 137.29, 133.51, 133.19, 128.89, 128.47, 127.23, 126.68, 126.09, 125.03, 118.73, 59.31, 37.54, 36.94, 26.30.

GC/MS data: 290.2 (M^+), 247.1 (M-Ac, base peak).

4z:



^{1}H NMR (500 MHz, CDCl3):

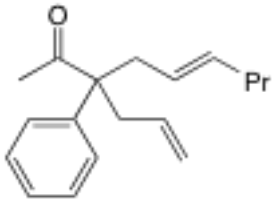
δ 7.32 (d, *J* = 7.9 Hz, 1H), 7.25 (td, *J* = 7.9, 1.4 Hz, 1H), 7.14 (m, 3H), 7.08 (m, 4H), 6.16 (d, *J* = 15.8 Hz, 1H), 5.67 (m, 1H), 5.32 (m, 1H), 4.86 (d, *J* = 17.2 Hz, 1H), 4.81 (d, *J* = 10.2 Hz, 1H), 2.85 (m, 3H), 2.77 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.56 (ddd, *J* = 13.6, 6.8, 1.5 Hz, 1H), 2.51 (ddt, *J* = 13.6, 6.8, 1.1 Hz, 1H) 2.45 (ddd, *J* = 7.8, 6.5, 3.4 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 213.96, 139.07, 137.21, 137.10, 133.37, 133.27, 128.42, 128.10, 127.18, 126.99, 126.98, 126.46, 126.08, 124.86, 118.37, 56.35, 44.95, 44.53, 40.42, 27.80.

GC/MS data: 302.2 (M^+).

4aa:



^{1}H NMR (500 MHz, CDCl3):

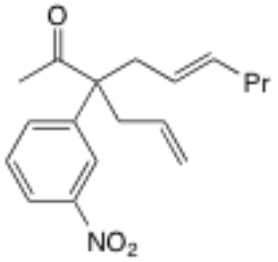
δ 7.28 (m, 2H), 7.20 (m, 1H), 7.10 (m, 2H), 5.36 (m, 2H), 4.96 (m, 3H), 2.62 (m, 4H), 1.86 (apparent quartet, *J* = 7.12, 2H), 1.82 (s, 3H), 1.25 (apparent sextet, *J* = 7.12, Hz, 2H), 0.77 (t, *J* = 7.12 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

13C NMR (126 MHz, CDCl3) δ 209.70, 141.39, 134.76, 133.54, 128.72, 127.01, 126.71, 124.26, 118.29, 59.15, 37.65, 36.03, 34.75, 26.29, 22.60, 13.60.

GC/MS data: 256.2 (M^+), 213.1 (M-Ac, base peak).

4bb:



^{1}H NMR (500 MHz, CDCl3):

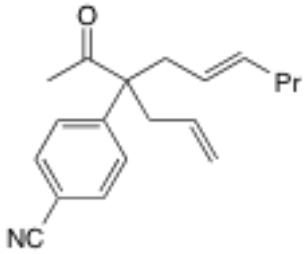
δ 8.09 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 8.04 (t, *J* = 2.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.41 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 5.36 (m, 2H), 4.98 (m, 3H), 2.69 (d, *J* = 7.3 Hz, 2H), 2.66 (d, *J* = 7.3 Hz, 2H), 1.87 (s, 3H), 1.84 (apparent quartet, *J* = 6.9 Hz, 2H), 1.23 (apparent sextet, *J* = 6.9 Hz, 2H), 0.77 (t, *J* = 6.9, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.10, 148.63, 143.84, 135.84, 133.25, 132.30, 129.68, 123.14, 122.28, 121.66, 119.37, 59.36, 37.73, 36.26, 34.70, 26.45, 22.50, 13.56.

GC/MS data: 301.2 (M^+), 258.1 (M-Ac, base peak).

4cc:



^{1}H NMR (500 MHz, CDCl3):

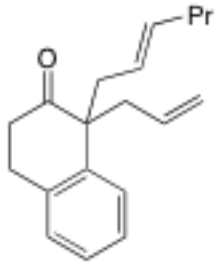
δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 5.37 (m, 1H), 5.31 (m, 1H), 4.96 (m, 3H), 2.64 (d, *J* = 7.3 Hz, 2H), 2.61 (d, *J* = 7.3 Hz, 2H), 1.86 (second order apparent quartet, *J* = 7.0 Hz, 1H), 1.83 (s, 3H), 1.24 (apparent sextet, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.08, 147.00, 135.68, 132.50, 132.40, 127.66, 123.24, 119.22, 118.53, 111.13, 59.68, 37.59, 36.09, 34.69, 26.52, 22.50, 13.57.

GC/MS data: 281.2 (M^+), 238.1 (M-Ac, base peak).

4dd:



^{1}H NMR (500 MHz, CDCl3):

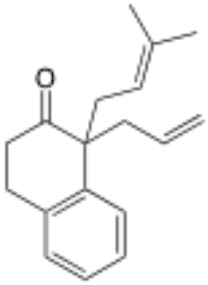
δ 7.25 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.22 (td, *J* = 7.3, 1.4 Hz, 1H), 7.12 (td, *J* = 7.3, 1.4 Hz, 1H), 7.08 (dd, *J* = 7.9, 1.1 Hz, 1H), 5.29 (m, 1H), 5.21 (dt, *J* = 15.0, 6.8 Hz, 1H), 4.90 (m, 1H), 4.83 (d, *J* = 17.3 Hz, 1H), 4.78 (d, *J* = 10.1 Hz, 1H), 2.87 (t, *J* = 6.9 Hz, 2H), 2.71 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.63 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.44 (td, *J* = 6.8, 2.5 Hz, 2H), 2.41 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.36 (dd, *J* = 13.4, 6.4 Hz, 1H), 1.71 (m, 2H), 1.13 (apparent sextet, *J* = 7.4 Hz, 2H), 0.67 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 214.06, 139.41, 137.07, 134.52, 133.60, 127.92, 127.04, 126.81, 126.22, 124.51, 118.11, 56.28, 44.90, 44.41, 40.44, 34.57, 27.84, 22.43, 13.55.

GC/MS data: 268.2 (M^+) 268.18 (base peak).

4ee:



^{1}H NMR (500 MHz, CDCl3):

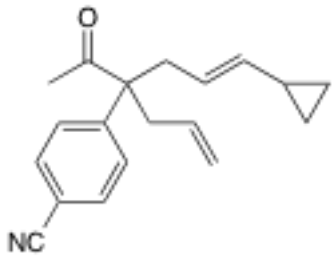
δ 7.25 (d, *J* = 7.5 Hz, 1H), 7.20 (td, *J* = 7.3, 1.4 Hz, 2H), 7.12 (td, *J* = 7.3, 1.4 Hz, 1H), 7.08 (d, *J* = 7.5, 1H), 5.29 (m, 1H), 4.83 (d, *J* = 17.4 Hz, 1H), 4.78 (d, *J* = 10.1 Hz, 1H), 4.66 (t, 7.9 Hz, 1H), 2.87 (t, *J* = 6.9 Hz, 2H), 2.73 (td, *J* = 14.8, 8.3 Hz, 2H), 2.45 (m, 3H), 2.30 (dd, *J* = 14.0, 6.5 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 214.39, 139.57, 137.15, 134.65, 133.67, 127.89, 127.11, 126.78, 126.20, 118.95, 118.06, 56.12, 44.60, 40.34, 39.93, 27.89, 25.82, 17.72.

GC/MS data: 254.2 (M^+), 186.2 (base peak).

4ff



^{1}H NMR (500 MHz, CDCl3):

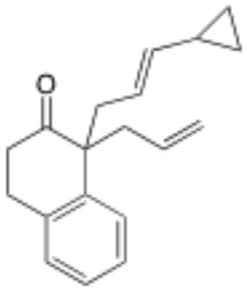
δ 7.59 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 5.29 (m, 1H), 4.96 (m, 4H), 2.65 (d, J = 7.3 Hz, 2H), 2.59 (d, J = 7.4 Hz, 2H), 1.85 (s, 3H), 1.22 (m, 1H), 0.58 (dd, J = 8.1, 2.0 Hz, 2H), 0.19 (m, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.12, 146.97, 139.23, 132.50, 132.40, 127.67, 120.52, 119.23, 118.52, 111.14, 59.72, 37.59, 35.98, 26.52, 13.64, 6.60, 6.53.

GC/MS data: 279.2 (M^+), 236.1 (M-Ac, base peak).

4gg



^{1}H NMR (500 MHz, CDCl3):

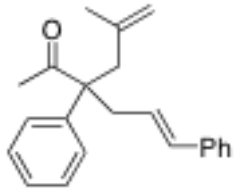
δ 7.29 (m, 3H), 7.17 (m, 2H), 7.14 (d, J = 7.5 Hz, 1H), 5.34 (m, 1H), 5.03 (m, Hz, 1H), 4.88 (d, J = 16.8 Hz, 3H), 4.83 (d, J = 10.0 Hz, 1H), 4.79 (dd, J = 15.3, 8.6 Hz, 1H), 2.94 (t, J = 6.9 Hz, 2H), 2.77 (dd, J = 13.6, 8.2 Hz, 1H), 2.66 (dd, J = 13.6, 8.2 Hz, 1H), 2.50 (m, 3H), 2.40 (ddd, J = 13.5, 6.3, 1.2 Hz, 1H), 1.13 (m, 1H), 0.53 (dd, J = 8.2, 2.0 Hz, 2H), 0.15 (m, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 214.15, 139.39, 137.99, 137.18, 133.58, 127.92, 127.02, 126.81, 126.23, 121.91, 118.11, 56.39, 44.71, 44.22, 40.46, 27.82, 13.41, 6.35, 6.27.

GC/MS data: 266.1 (M^+), 223.1 (M-Ac, base peak)

4hh:



^{1}H NMR (500 MHz, CDCl3):

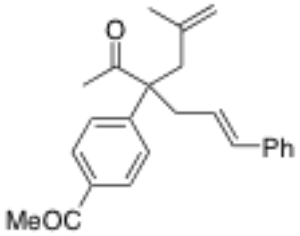
δ 7.29 (m, 2H), 7.18 (m, 8H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.80 (dt, *J* = 15.8, 8.0, Hz, 1H), 4.78 (s, 1H), 4.61 (s, 1H), 2.98 (dd, *J* = 14.5, 6.4, Hz, 1H), 2.89 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.78 (d, *J* = 14.5 Hz, 1H), 2.65 (d, *J* = 14.5 Hz, 1H), 1.88 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 209.84, 141.80, 141.64, 137.30, 133.60, 128.83, 128.49, 127.26, 127.22, 126.85, 126.14, 126.10, 125.26, 115.22, 59.04, 41.25, 36.25, 26.38, 24.20.

GC/MS data: 304.2 (M^+), 261.1 (M-Ac, base peak).

4ii:



^{1}H NMR (500 MHz, CDCl3):

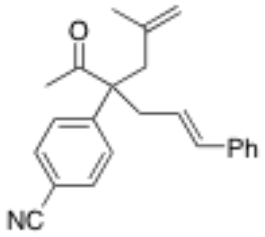
δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.17 (m, 5H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.78 (dt, *J* = 15.8, 7.6 Hz, 1H), 4.80 (s, 1H), 4.61 (s, 1H), 2.99 (dd, *J* = 14.8, 6.5 Hz, 1H), 2.94 (dd, *J* = 14.8, 8.1 Hz, 1H), 2.81 (d, *J* = 14.8 Hz, 1H), 2.69 (d, *J* = 14.8 Hz, 1H), 2.56 (s, 3H), 1.85 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.84, 197.62, 147.19, 141.19, 137.06, 136.00, 134.04, 128.81, 128.53, 127.44, 127.20, 126.12, 124.48, 115.65, 59.45, 41.26, 36.34, 26.66, 26.54, 24.29.

GC/MS data: 346.2 (M^+), 303.2 (M-Ac, base peak).

4jj:



^{1}H NMR (500 MHz, CDCl3):

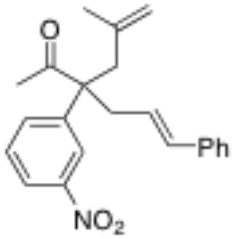
δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.18 (m, 7H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.75 (dt, *J* = 15.6, 7.6,Hz, 1H), 4.81 (s, 1H), 4.60 (s, 1H), 2.96 (dd, *J* = 14.6, 6.7 Hz, 1H), 2.90 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.79 (d, *J* = 14.6 Hz, 1H), 2.66 (d, *J* = 14.6 Hz, 1H), 1.89 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.25, 147.25, 140.73, 136.88, 134.37, 132.55, 128.58, 127.82, 127.58, 126.12, 123.89, 118.46, 115.94, 111.33, 59.58, 41.23, 36.39, 26.59, 24.30.

GC/MS data: 329.2 (M^+), 286.1 (M-Ac, base peak).

4kk:



^{1}H NMR (500 MHz, CDCl3):

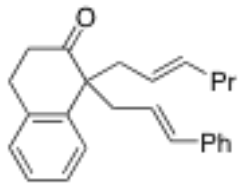
δ 8.11 (m, 2H), 7.50 (m, 2H), 7.18 (m, 6H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.77 (dt, *J* = 15.7, 7.7, Hz, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 3.03 (dd, *J* = 14.7, 6.7 Hz, 1H), 2.95 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.84 (d, *J* = 14.7 Hz, 1H), 2.71 (d, *J* = 14.7 Hz, 1H), 1.91 (m, 3H), 1.35 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 208.25, 148.67, 144.08, 140.59, 136.87, 134.50, 133.40, 129.74, 128.57, 127.58, 126.14, 123.77, 122.46, 121.77, 116.09, 59.23, 41.35, 36.59, 26.50, 24.38.

GC/MS data: 349.2 (M^+), 306.1 (M-Ac, base peak).

4ll:



^{1}H NMR (500 MHz, CDCl3):

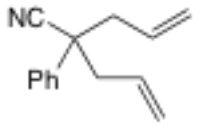
7.31 (d, *J* = 7.9 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.13 (m, 3H), 7.08 (m, 4H), 6.14 (d, *J* = 15.8 Hz, 1H), 5.66 (m, 1H), 5.23 (dt, *J* = 14.9, 6.8 Hz, 1H), 4.92 (dt, *J* = 14.9, 6.8 Hz 1H), 2.83 (m, 3H), 2.68 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.54 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.46 (m, 3H), 1.72 (apparent quintet, *J* = 7.4 Hz, 2H), 1.14 (apparent sextet, *J* = 7.4 Hz, 2H), 0.67 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 214.28, 139.34, 137.29, 137.15, 134.56, 133.08, 128.39, 127.99, 127.11, 127.00, 126.90, 126.31, 126.05, 125.12, 124.51, 56.62, 44.31, 44.22, 40.53, 34.58, 27.79, 22.44, 13.55.

GC/MS data: 344.2 (M^+), 301.1 (M-Ac, base peak).

5a



^{1}H NMR (500 MHz, CDCl3):

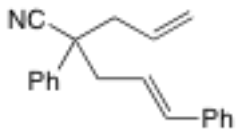
δ 7.33 (m, 4H), 7.24 (m, 1H), 5.58 (dddd, *J* = 23.6, 10.3, 7.5, 6.9 Hz, 2H), 5.08 (m, 4H), 2.63 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 137.62, 131.65, 128.84, 127.88, 126.28, 121.68, 120.20, 47.68, 44.18.

GC/MS data: 197.1 (M^+), 156.1, 129.0 (base peak).

5b



^{1}H NMR (500 MHz, CDCl3):

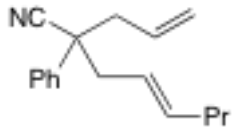
δ 7.35 (m, 4H), 7.25 (m, 1H), 7.19 (m, 5H), 7.14 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.96 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.61 (m, 1H), 5.09 (m, *J* = 9.3, 3.0, 1.6 Hz, 2H), 2.78 (m, 2H), 2.68 (m, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 137.66, 136.71, 135.05, 131.68, 128.91, 128.52, 127.95, 127.66, 126.36, 126.30, 122.96, 121.77, 120.24, 47.98, 43.97, 43.62.

GC/MS data: 273.2 (M^+), 117.1 (base peak), 115.1, 91.1.

5c



^{1}H NMR (500 MHz, CDCl3):

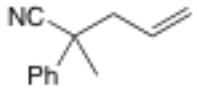
δ 7.27 (m, 6H), 5.58 (m, 1H), 5.45 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.19 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.07 (d, *J* = 7.9 Hz, 1H), 5.04 (s, 1H), 2.59 (m, 4H), 1.85 (apparant quartet, *J* = 7.5 Hz, 2H), 1.24 (apparent sextet, *J* = 7.5 Hz, 2H), 0.74 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 137.92, 136.56, 131.86, 128.73, 127.72, 126.33, 123.03, 121.91, 119.98, 48.05, 43.97, 43.27, 34.55, 22.33, 13.50.

GC/MS data: 239.2 (M^+), 157.1, 156.2 (base peak).

5d



^{1}H NMR (500 MHz, CDCl3):

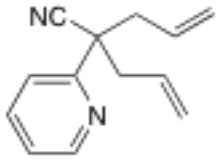
δ 7.37 (m, 2H), 7.32 (m, 2H), 7.25 (m, 1H), 5.64 (m, 1H), 5.11 (m, 1H), 5.08 (d, *J* = 8.2 Hz, 1H), 2.61 (ddt, *J* = 13.9, 6.7, 1.1 Hz 1H), 2.55 (ddt, *J* = 13.9, 7.5, 1.1 Hz, 1H), 1.65 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 139.83, 131.90, 128.89, 127.86, 125.61, 123.14, 120.20, 46.32, 42.17, 26.56.

GC/MS data: 171.1 (M^+), 130.0, 103.0, 83.0 (base peak).

5e



^{1}H NMR (500 MHz, CDCl3):

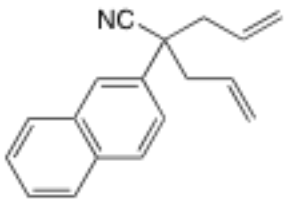
δ 8.56 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1H), 7.63 (td, *J* = 7.9, 1.8 Hz, 1H), 7.48 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.16 (ddd, *J* = 7.9, 4.8, 1.1 Hz, 1H), 5.57 (m, 2H), 5.03 (m, 4H), 2.82 (ddt, *J* = 13.7, 6.8, 1.1 Hz, 2H), 2.66 (dd, *J* = 13.7, 7.8 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 156.57, 149.69, 136.79, 131.78, 122.68, 122.18, 121.52, 120.08, 49.72, 43.17.

GC/MS data: 198.1 (M^+), 157.1 (base peak), 83.0.

5f



^{1}H NMR (500 MHz, CDCl3):

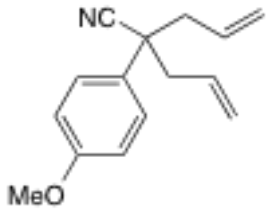
δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.78 (m, 3H), 7.45 (m, 2H), 7.38 (dd, *J* = 8.7, 2.0 Hz, 1H), 5.59 (m, 2H), 5.09 (d, *J* = 17.0 Hz, 2H), 5.05 (d, *J* = 9.9 Hz, 2H), 2.74 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 134.79, 133.07, 132.65, 131.61, 128.87, 128.20, 127.56, 126.69, 126.57, 126.16, 123.08, 121.74, 120.26, 47.98, 44.11.

GC/MS data: 247.1 (M^+), 206.2, 179.1 (base peak).

5g



^{1}H NMR (500 MHz, CDCl3):

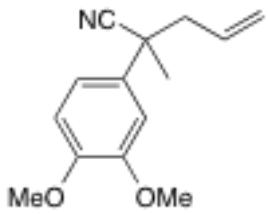
δ 7.24 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.58 (m, 2H), 5.07 (m, 4H), 3.74 (s, 3H), 2.59 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 159.02, 131.79, 129.57, 127.43, 121.94, 120.08, 114.10, 55.30, 46.94, 44.27.

GC/MS data: 227.1 (M^+), 186.1 (base peak).

5h



^{1}H NMR (500 MHz, CDCl3):

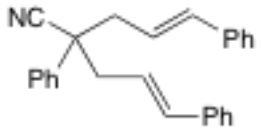
δ 6.90 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.64 (m, 1H), 5.09 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 2.59 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.52 (dd, *J* = 13.6, 6.7 Hz, 1H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 149.05, 148.55, 132.32, 131.99, 123.34, 120.12, 117.72, 111.12, 109.12, 56.02, 55.95, 46.40, 41.73, 26.67.

GC/MS data: 231.1 (M^+), 190.1 (base peak).

5i



^{1}H NMR (500 MHz, CDCl3):

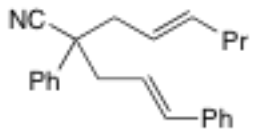
δ 7.40 (m, 2H), 7.34 (m, 2H), 7.26 (m, 2H), 7.21 (m, 7H), 7.14 (m, 2H), 6.41 (d, *J* = 15.8 Hz, 2H), 5.98 (dt, *J* = 15.7, 7.4 Hz, 2H), 2.84 (m, 4H).

^{13}C NMR (126 MHz, CDCl3):

δ 137.72, 136.71, 135.10, 128.98, 128.53, 128.03, 127.68, 126.38, 126.32, 122.98, 121.85, 48.27, 43.43.

GC/MS data: 349.2 (M^+), 115.0, 117.1 (base peak).

5j



^{1}H NMR (500 MHz, CDCl3):

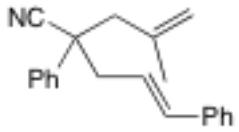
δ 7.33 (m, 4H), 7.23 (m, 6H), 7.13 (m, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 5.95 (dt, *J* = 15.7, 7.8, Hz, 1H), 5.47 (dt, *J* = 15.0, 6.9 Hz, 1H), 5.22 (dt, *J* = 15.0, 6.9 Hz, 1H), 2.76 (m, 2H), 2.60 (m, 2H), 1.87 (apparent quartet, *J* = 7.4 Hz, 2H), 1.25 (apparent sextet, *J* = 7.4 Hz Hz, 2H), 0.76 (t, *J* =7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 137.96, 136.78, 136.61, 134.85, 128.80, 128.50, 127.79, 127.59, 126.35, 123.22, 123.05, 121.99, 48.33, 43.41, 43.06, 34.57, 22.35, 13.52.

GC/MS data: 315. 2 (M^+).

5k



^{1}H NMR (500 MHz, CDCl3):

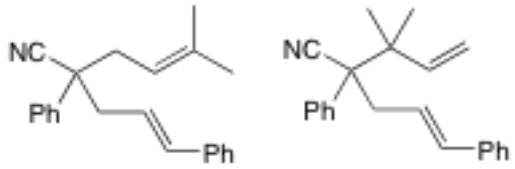
δ 7.38 (m, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 7.19 (m, 4H), 7.14 (m, 1H), 6.40 (d, *J* = 15.7, Hz, 1H), 5.97 (dt, *J* = 15.7, 7.4 Hz, 1H), 4.80 (s, 1H), 4.67 (s, 1H), 2.80 (dt, *J* = 7.5, 1.1 Hz, 2H), 2.71 (d, *J* = 14.1 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 139.81, 137.86, 136.74, 135.05, 128.81, 128.51, 127.88, 127.63, 126.38, 126.31, 123.08, 122.09, 116.68, 47.71, 47.65, 44.87, 23.66.

GC/MS data: 287.2 (M^+), 117.1 (base peak), 91.1.

5l and 5m:



55:45 l:b

^{1}H NMR (500 MHz, CDCl3):

Linear regioisomer reported. Please see Reprint of Proton NMR spectrum below for further analysis

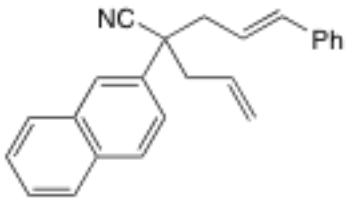
δ 7.23 (m, 10H), 6.40 (m, 2H), 5.96 (m, 1H), 5.03 (m, 1H), 2.80 (m, 4H), 1.61 (s, 3H), 1.49 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

See Reprint of Carbon spectrum below for analysis

GC/MS data: 301.2 (M^+), 172.1, 117.1 (base peak), 69.1.

5n



^{1}H NMR (500 MHz, CDCl3):

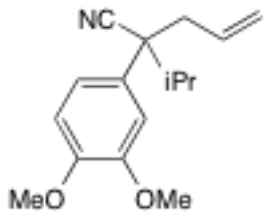
δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.80 (m, 3H), 7.44 (m, 3H), 7.17 (m, 5H), 7.12 (m, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 5.97 (dt, *J* = 15.7, 7.2 Hz 1H), 5.61 (m, 1H), 5.11 (d, *J* = 17.0, 1H), 5.06 (d, *J* = 10.1 Hz 1H), 2.88 (dd, *J* = 7.4, 1.2 Hz, 2H), 2.77 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 136.64, 135.11, 134.86, 133.12, 132.70, 131.64, 128.92, 128.50, 128.23, 127.66, 127.58, 126.70, 126.59, 126.38, 126.12, 123.15, 122.90, 121.81, 120.31, 48.27, 43.98, 43.55.

GC/MS data: 323.2 (M^+), 179.0, 117.1 (base peak), 115.1, 91.1.

5o: Verapamil Precursor



^{1}H NMR (500 MHz, CDCl3):

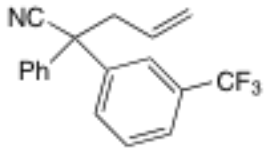
δ 6.94 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.87 (m, 2H), 5.51 (m, 1H), 5.11 (d, *J* = 16.9 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H) 3.92 (s, 3H), 3.90 (s, 3H), 2.85 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.63 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.15 (apparent septet, *J* = 6.7 Hz, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 148.87, 148.29, 132.34, 130.00, 121.10, 119.39, 119.02, 110.91, 109.93, 55.99, 55.87, 53.33, 42.17, 37.23, 18.81, 18.56.

GC/MS data: 259.2 (M^+), 218.2 (base peak), 138.0, 76.9.

5p



^{1}H NMR (500 MHz, CDCl3):

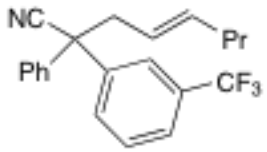
δ 7.57 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.29 (m, 5H), 5.62 (m, 1H), 5.15 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 4.6 Hz, 1H), 3.08 (m, 2H).

^{13}C NMR (126 MHz, CDCl3):

Complex Splitting due to Fluorine. See **^{13}C** NMR reproduction

GC/MS data: 301.1 (M^+), 260.1 (base peak), 233.0, 190.1.

5q



^{1}H NMR (500 MHz, CDCl3):

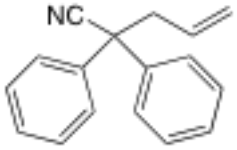
δ 7.56 (s, 1H), 7.49 (m,, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.28 (m, 5H), 5.49 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.23 (dt, *J* = 15.1, 6.9 Hz, 1H), 3.02 (m, 2H), 1.86 (apparent quartet, *J* = 7.4 Hz, 2H), 1.21 (apparent sextet, *J* = 7.4 Hz 2H), 0.72 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

Complex Splitting due to Fluorine. See **^{13}C** NMR reproduction

GC/MS data: 343.2 (M^+), 261.2 (base peak), 190.1, 165.0.

5r



^{1}H NMR (500 MHz, CDCl3):

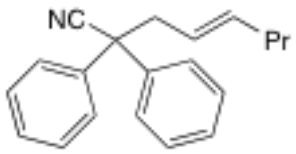
δ 7.27 (m, 10H), 5.64 (m, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.2, 1H), 3.07 (dt, *J* = 7.0, 1.1 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 139.74, 131.79, 128.86, 127.95, 127.06, 121.97, 120.44, 51.72, 43.95.

GC/MS data: 233.1 (M^+), 192.1, 165.1 (base peak).

5s



^{1}H NMR (500 MHz, CDCl3):

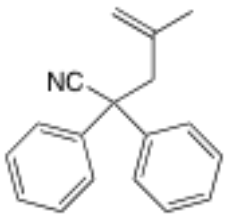
δ 7.26 (m, 10H), 5.50 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.24 (dt, *J* = 15.1, 6.9 Hz, 1H), 2.99 (d, *J* = 7.0, Hz, 2H), 1.86 (apparent quartet, *J* = 7.4 Hz, 2H), 1.22 (apparent sextet, *J* = 7.4 Hz, 3H), 0.73 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 140.00, 136.83, 128.76, 127.81, 127.14, 123.15, 52.13, 42.96, 34.58, 22.30, 13.50.

GC/MS data: 275.2 (M^+), 193.1 (base peak), 165.1.

5t



1H NMR (500 MHz, CDCl3)

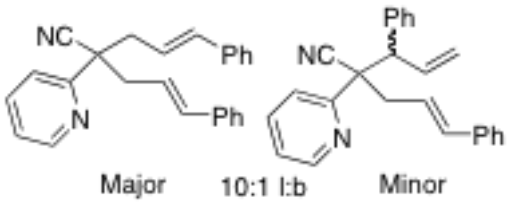
δ 7.30 (m, 8H), 7.22 (m, 2H), 4.85 (s, 1H), 4.69 (s,, 1H), 3.05 (s, 2H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, CDCl3):

δ 140.32, 139.48, 128.77, 127.89, 127.10, 122.36, 117.07, 51.08, 46.90, 23.74.

GC/MS data: 247. (M^+), 192.1, 165.1 (base peak).

5u:



^{1}H NMR (500 MHz, CDCl3):

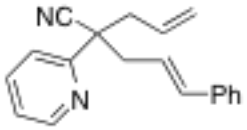
δ 8.60 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.15 (m, 13H), 6.37 (d, *J* = 15.7 Hz, 2H), 5.99 (m, 2H), 3.01 (ddd, *J* = 13.7, 7.1, 1.3 Hz, 2H), 2.88 (ddd, *J* = 13.8, 7.9, 1.1 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3):

δ 156.63, 149.77, 136.94, 136.80, 134.98, 128.49, 127.59, 126.35, 123.18, 122.81, 122.27, 50.34, 42.51.

GC/MS data: 350.2 (M^+).

5v:



^{1}H NMR (500 MHz, CDCl3):

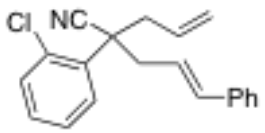
δ 8.58 (dd, *J* = 4.8, 1.8, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.15 (m, 6H), 6.35 (d, *J* = 15.7 Hz, 1H), 5.97 (dt, *J* = 15.7, 7.6 Hz, 1H), 5.60 (m, 1H), 5.05 (m, 2H), 2.97 (ddd, *J* = 13.7, 7.1, 1.3 Hz, 1H), 2.86 (m, 2H), 2.71 (dd, *J* = 13.7, 7.8 Hz, 1H).

^{13}C NMR (126 MHz, CDCl3):

δ 156.60, 149.73, 136.86, 136.79, 134.93, 131.81, 128.48, 127.58, 126.33, 123.16, 122.75, 122.23, 121.60, 120.13, 50.03, 43.18, 42.49.

GC/MS data: 274.1 (M^+)

5w



^{1}H NMR (500 MHz, CDCl3):

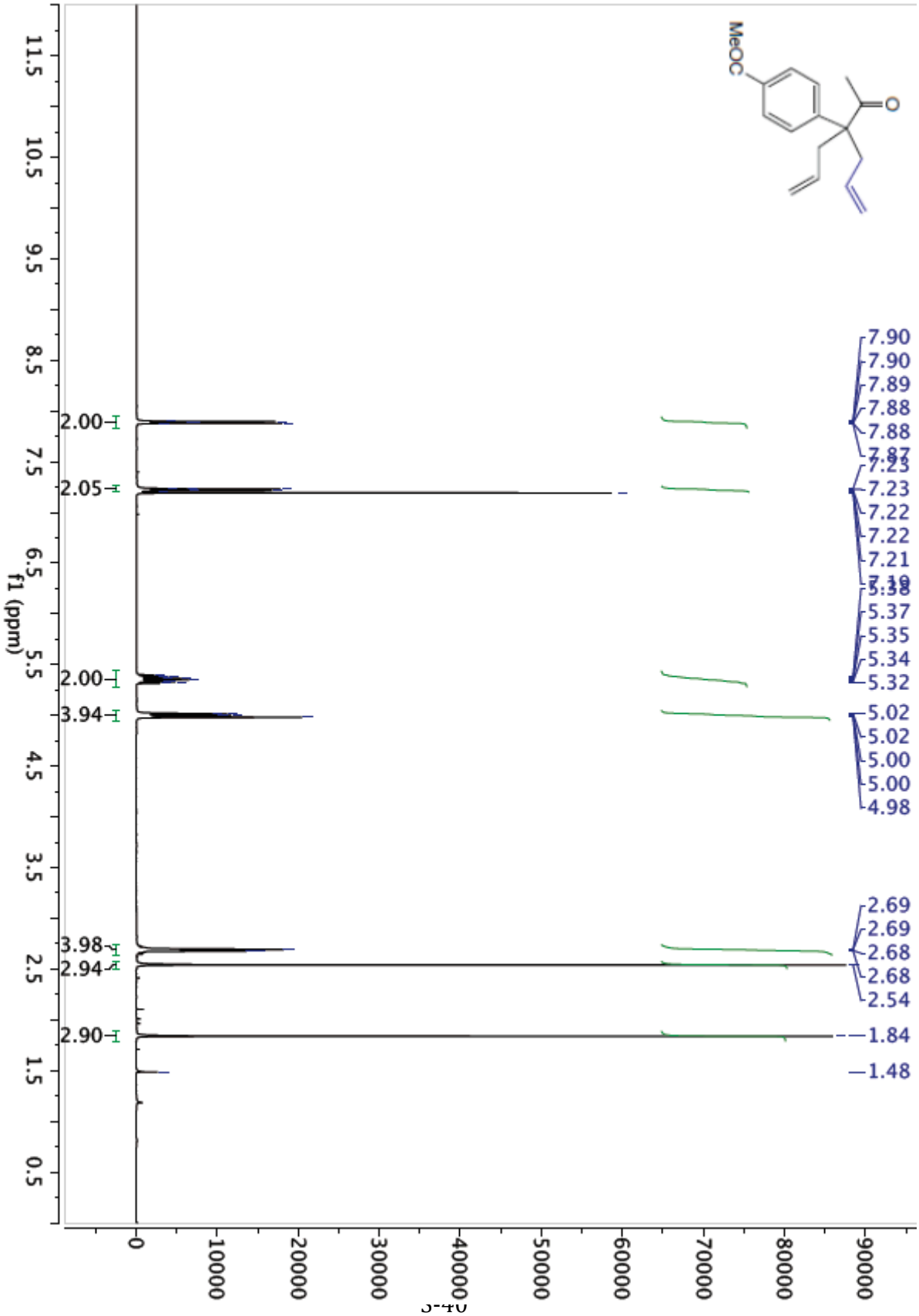
δ 7.54 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.35 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.19 (m, 6H), 7.14 (ddd, *J* = 9.3, 6.2, 3.3 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 5.96 (dt, *J* = 15.6, 7.4 Hz, 1H), 5.60 (m, 1H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 3.28 (ddd, *J* = 14.2, 7.2, 1.3 Hz, 1H), 3.20 (ddt, *J* = 14.2, 7.2, 1.0 Hz, 1H), 2.96 (ddd, *J* = 14.2, 7.7, 1.2 Hz, 1H), 2.82 (ddt, *J* = 14.2, 7.4, 1.0 Hz, 1H).

^{13}C NMR (126 MHz, CDCl3):

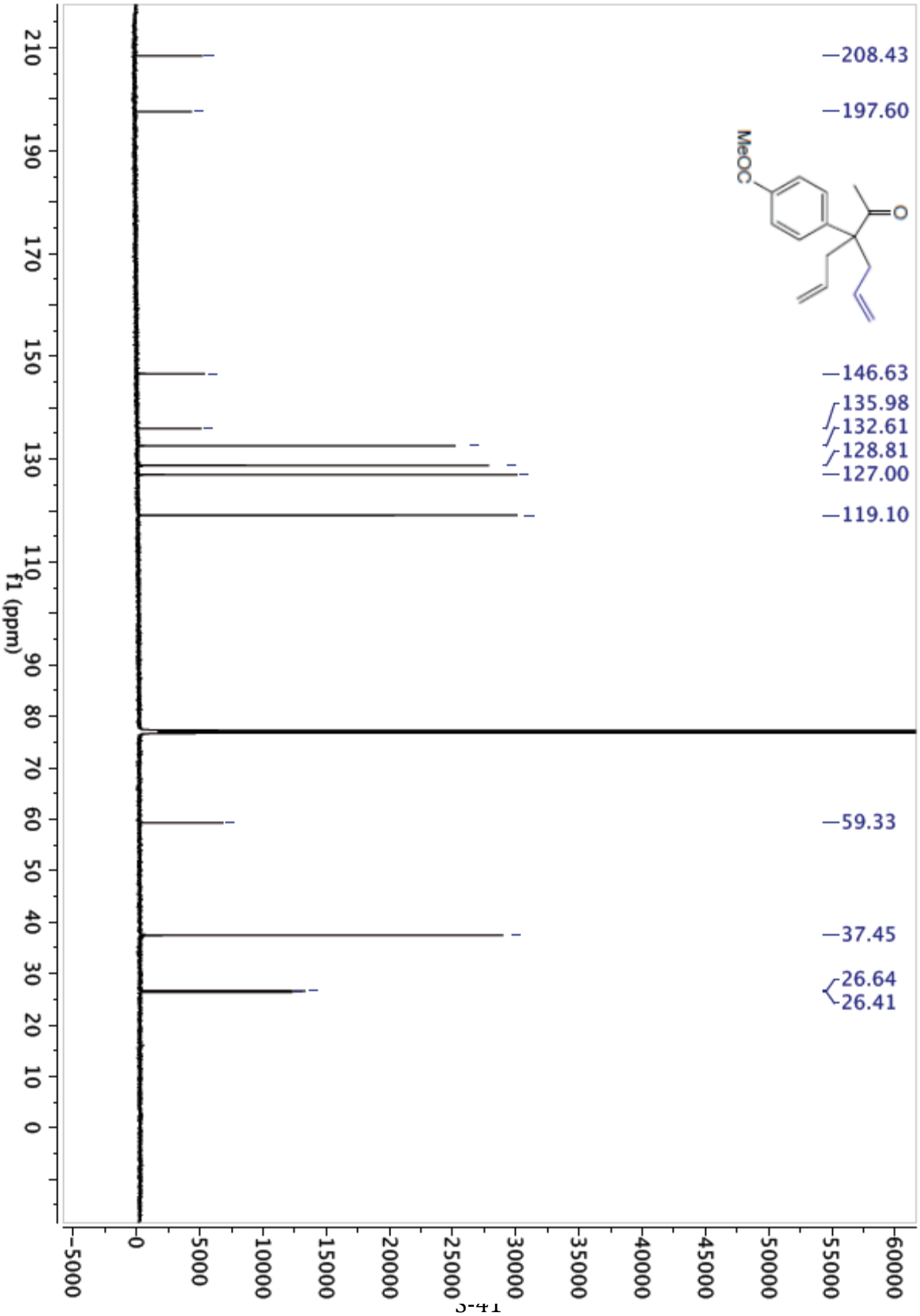
δ 136.73, 134.89, 133.24, 132.23, 132.08, 131.69, 130.79, 129.52, 128.50, 127.63, 127.28, 126.36, 123.02, 121.63, 120.12, 49.21, 40.57, 39.87.

GC/MS data: 307.1 (M^{+}).

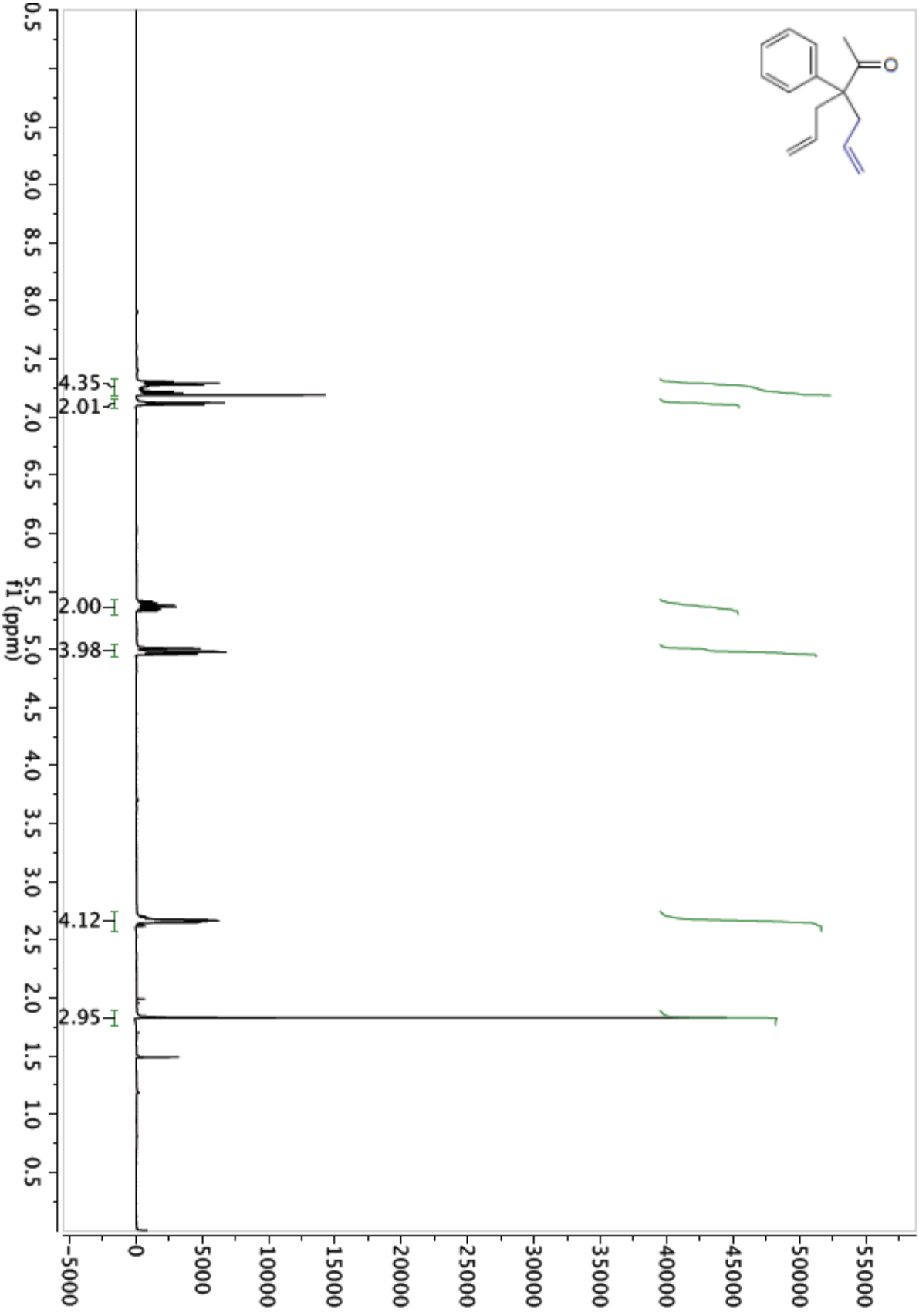
^{1}H NMR for Compound 4e



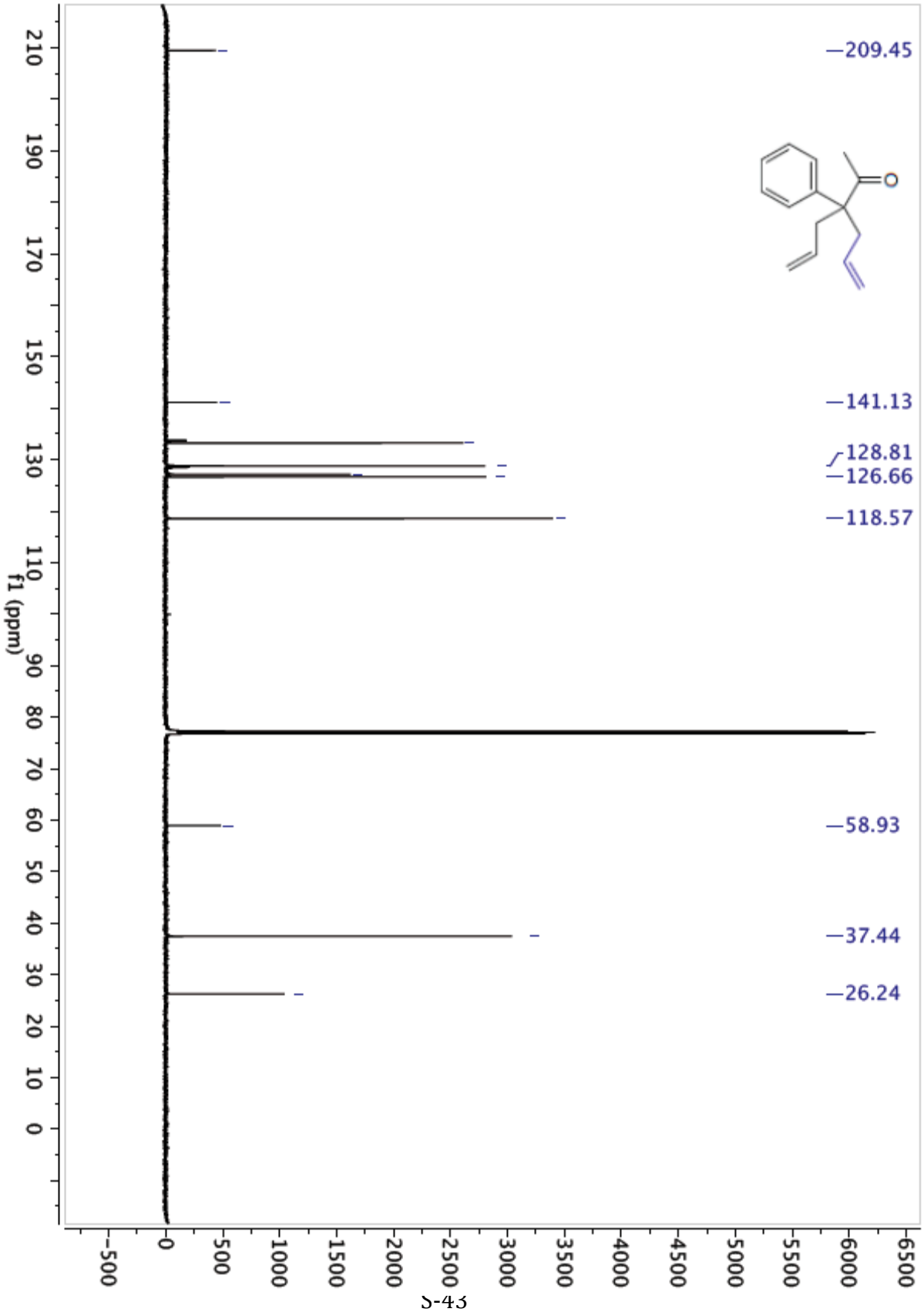
^{13}C NMR for Compound 4e



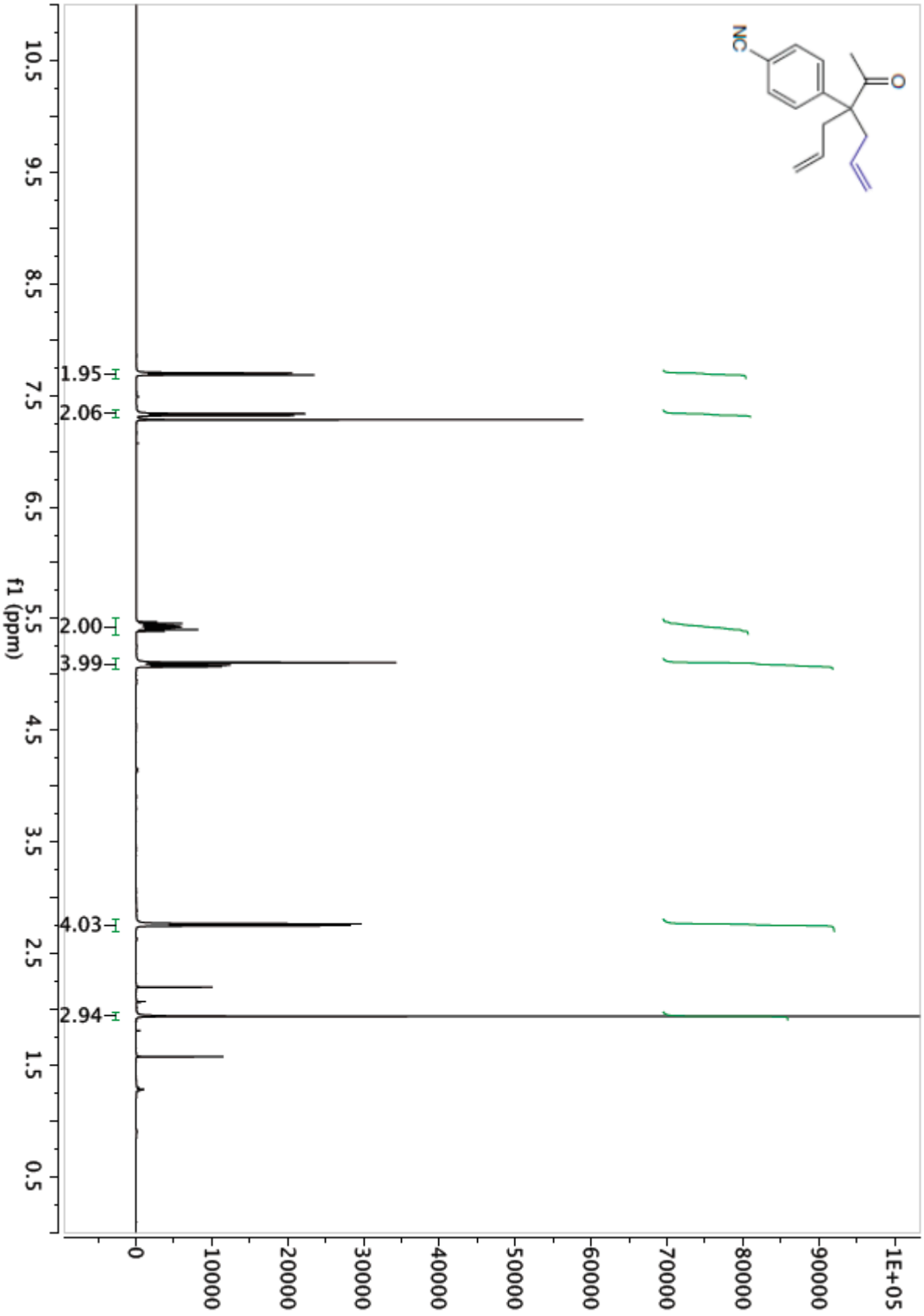
^{1}H NMR for Compound 4f



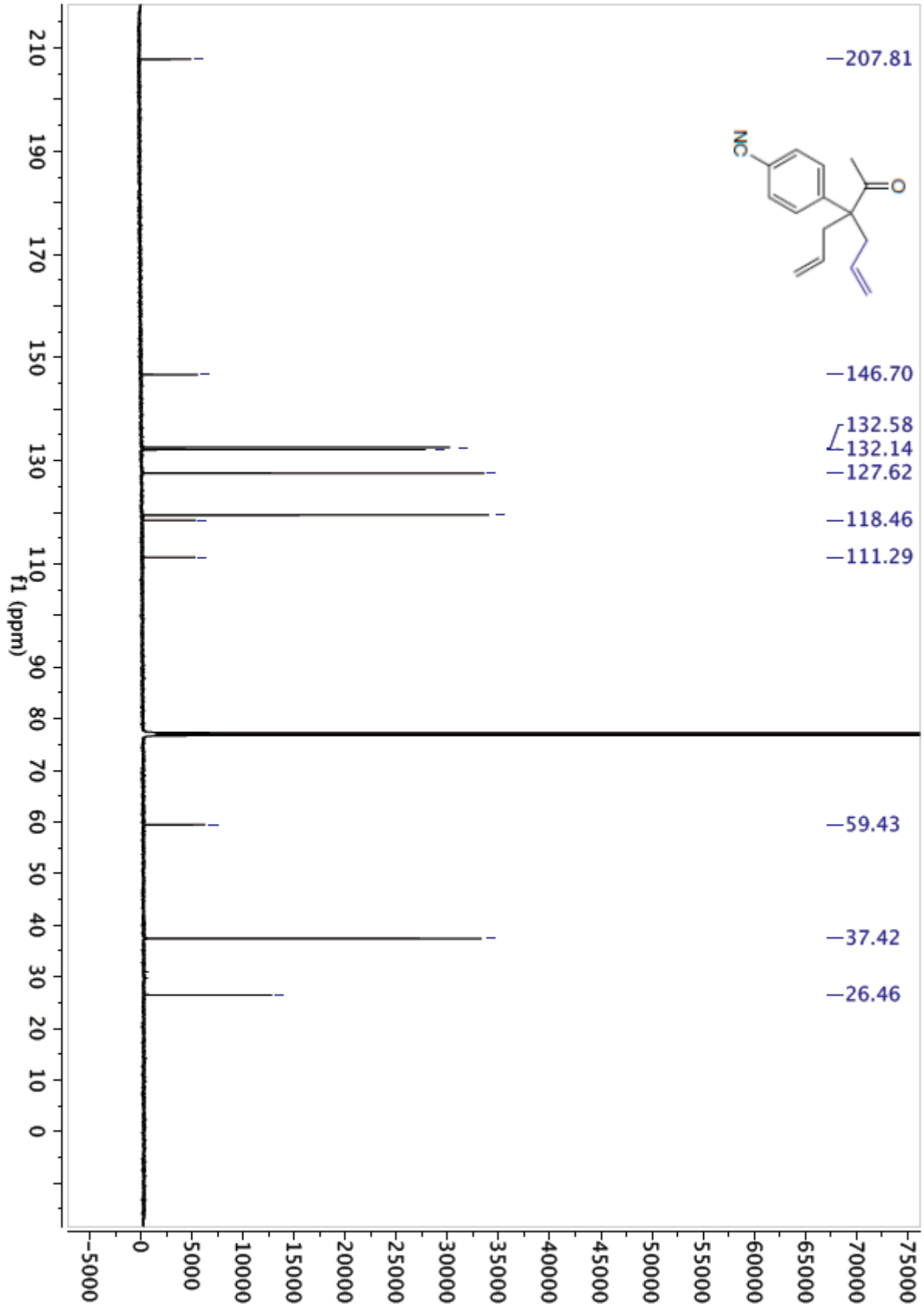
^{13}C NMR for Compound 4f



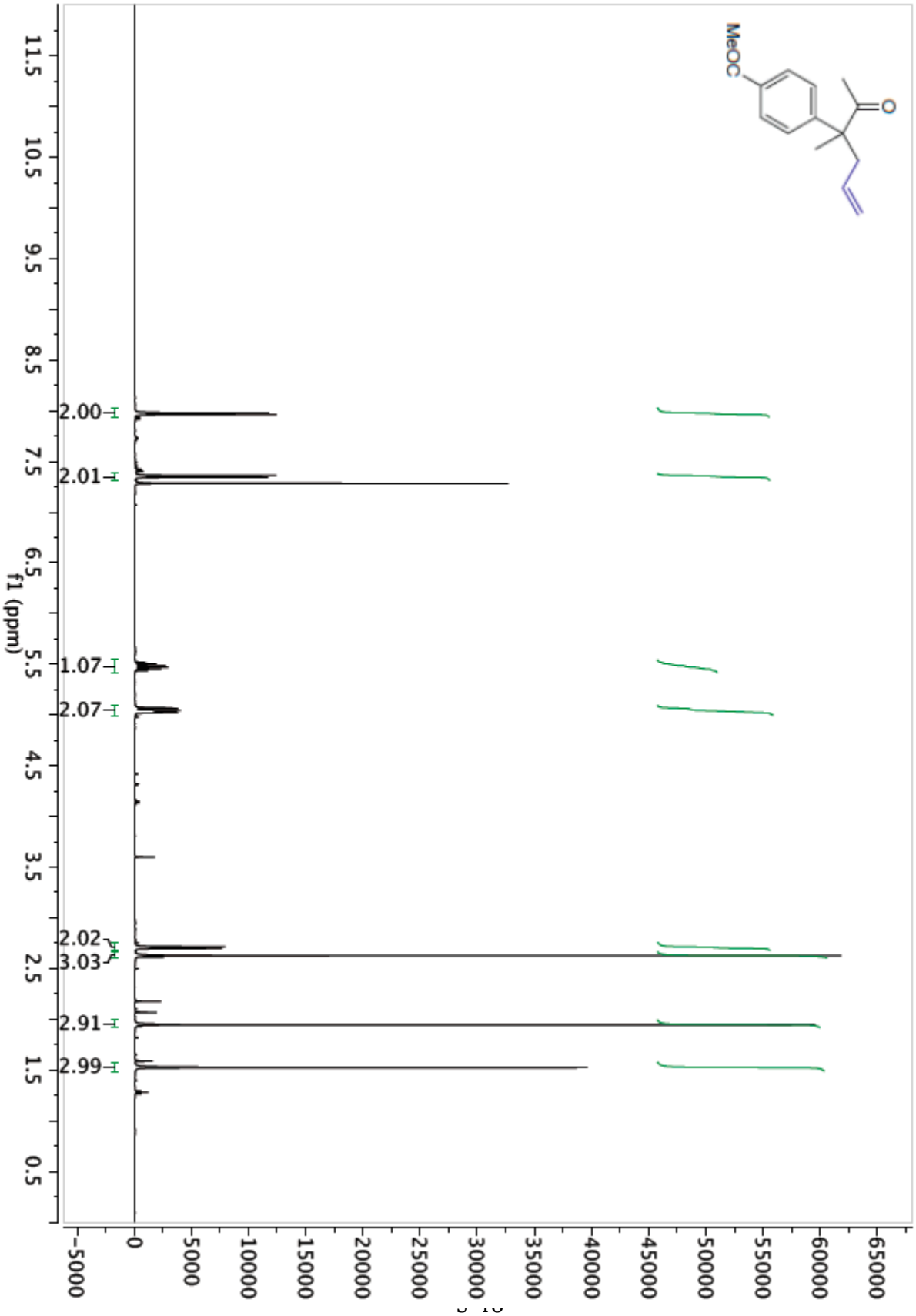
^{1}H NMR for Compound 4g



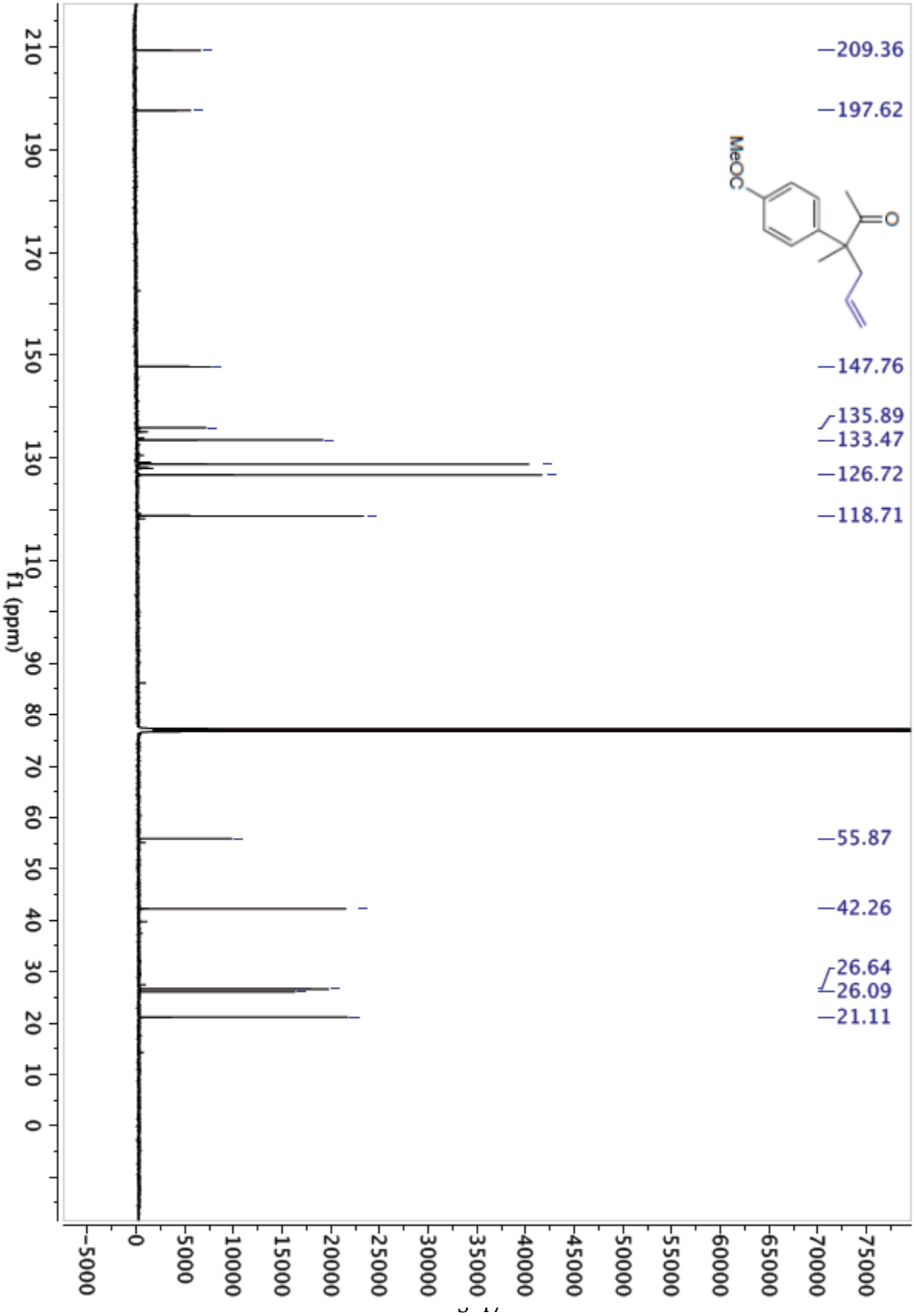
^{13}C NMR for Compound 4g



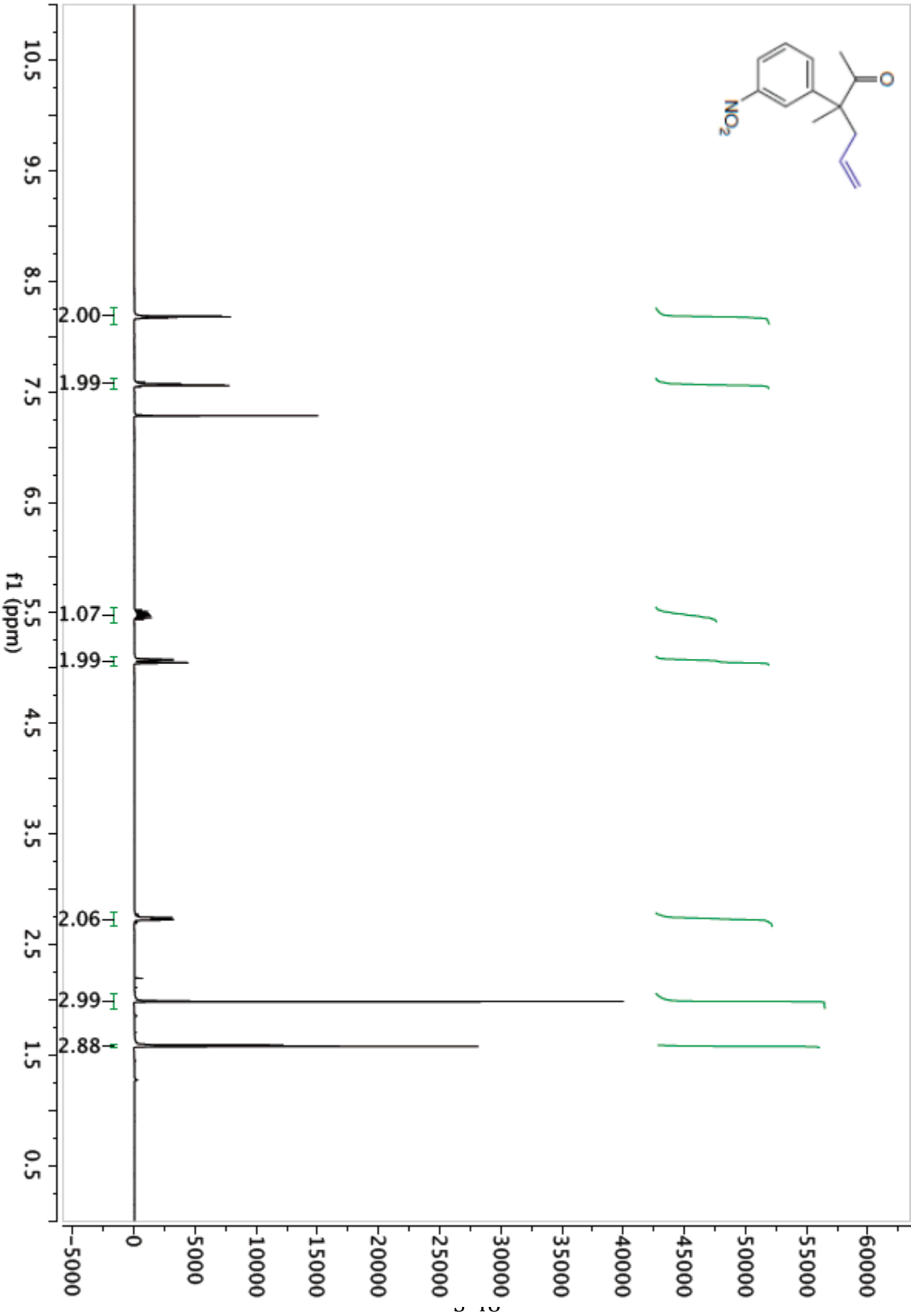
^{1}H NMR for Compound 4h



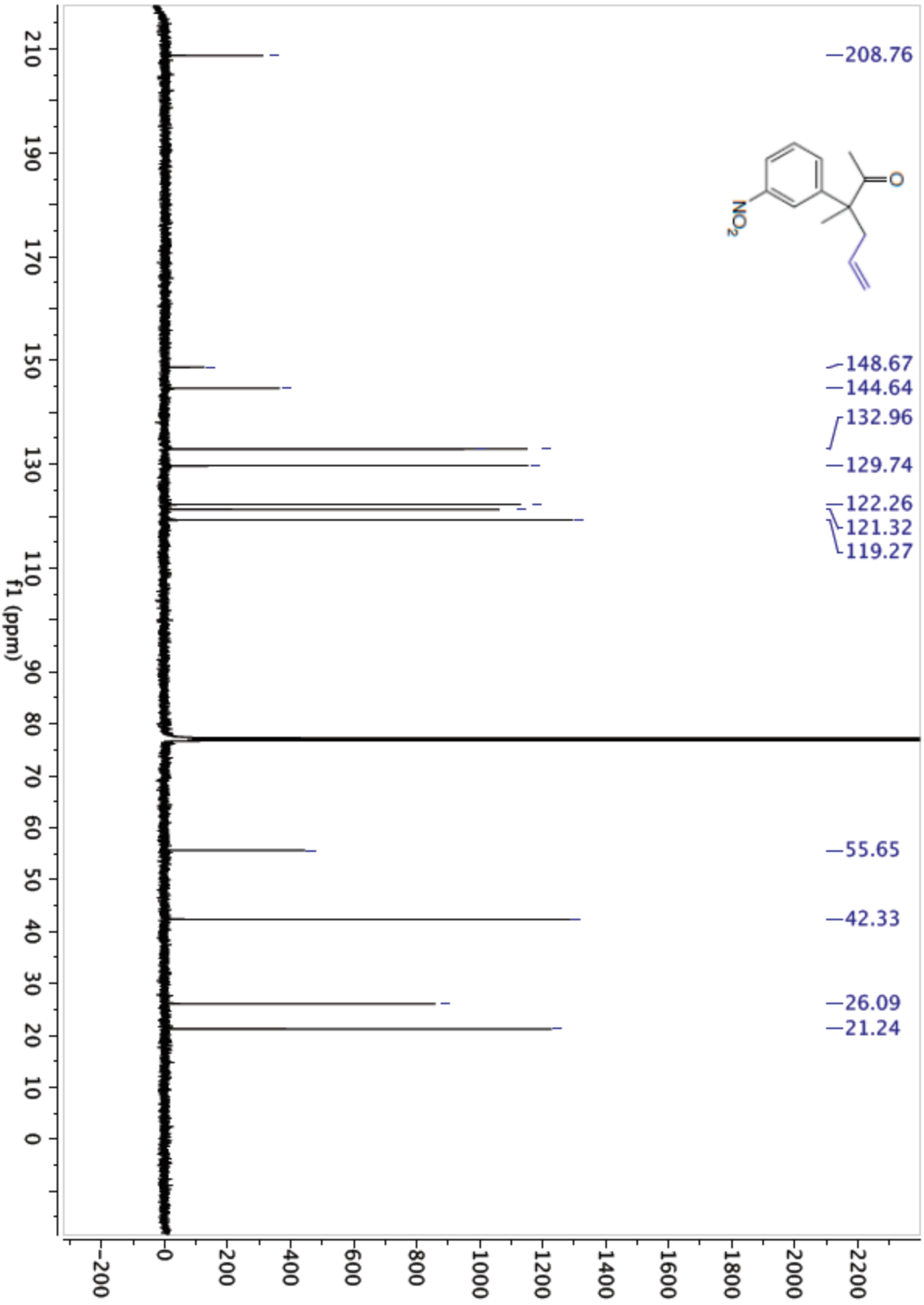
^{13}C NMR for Compound 4h



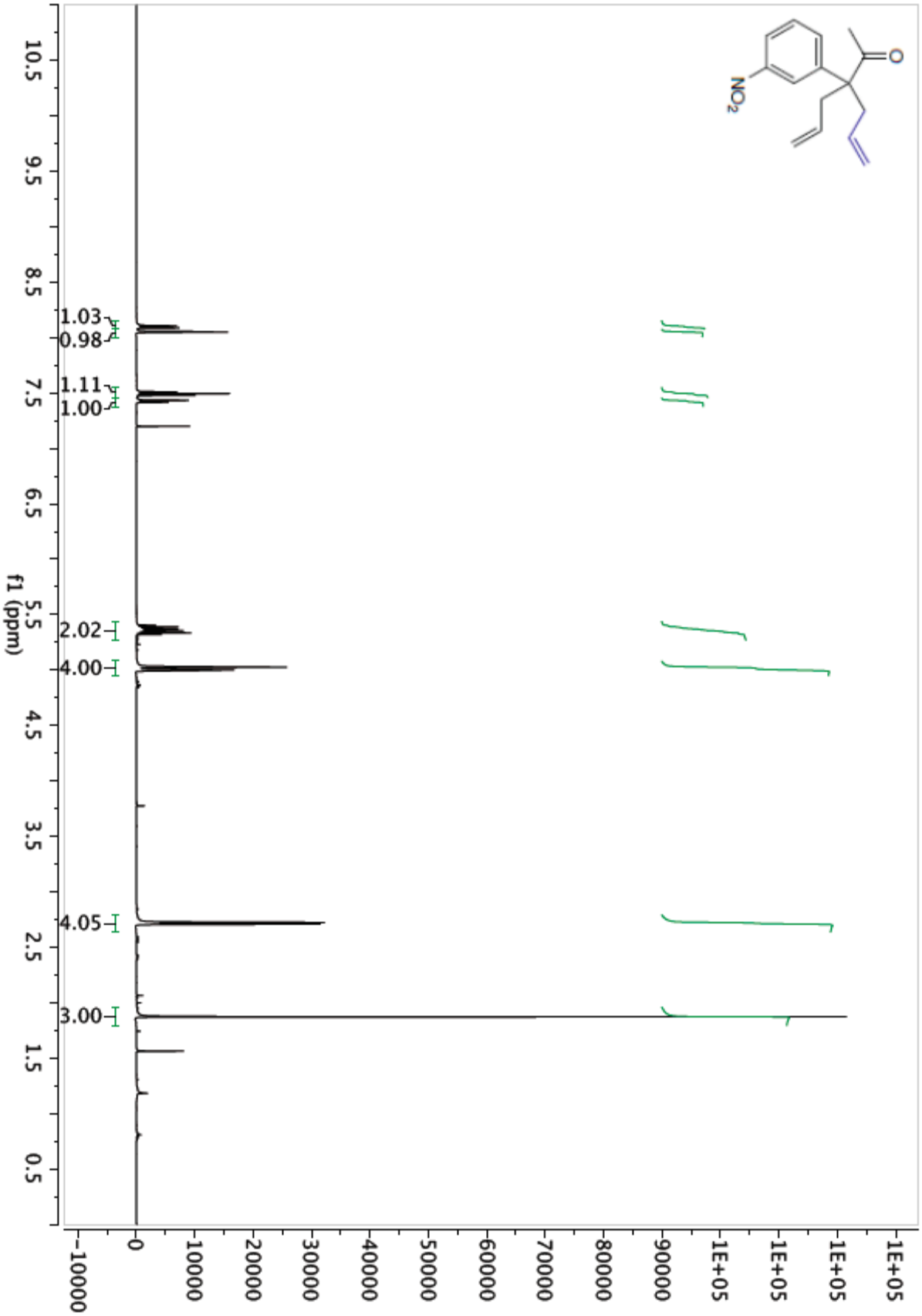
^{1}H NMR for Compound 4i



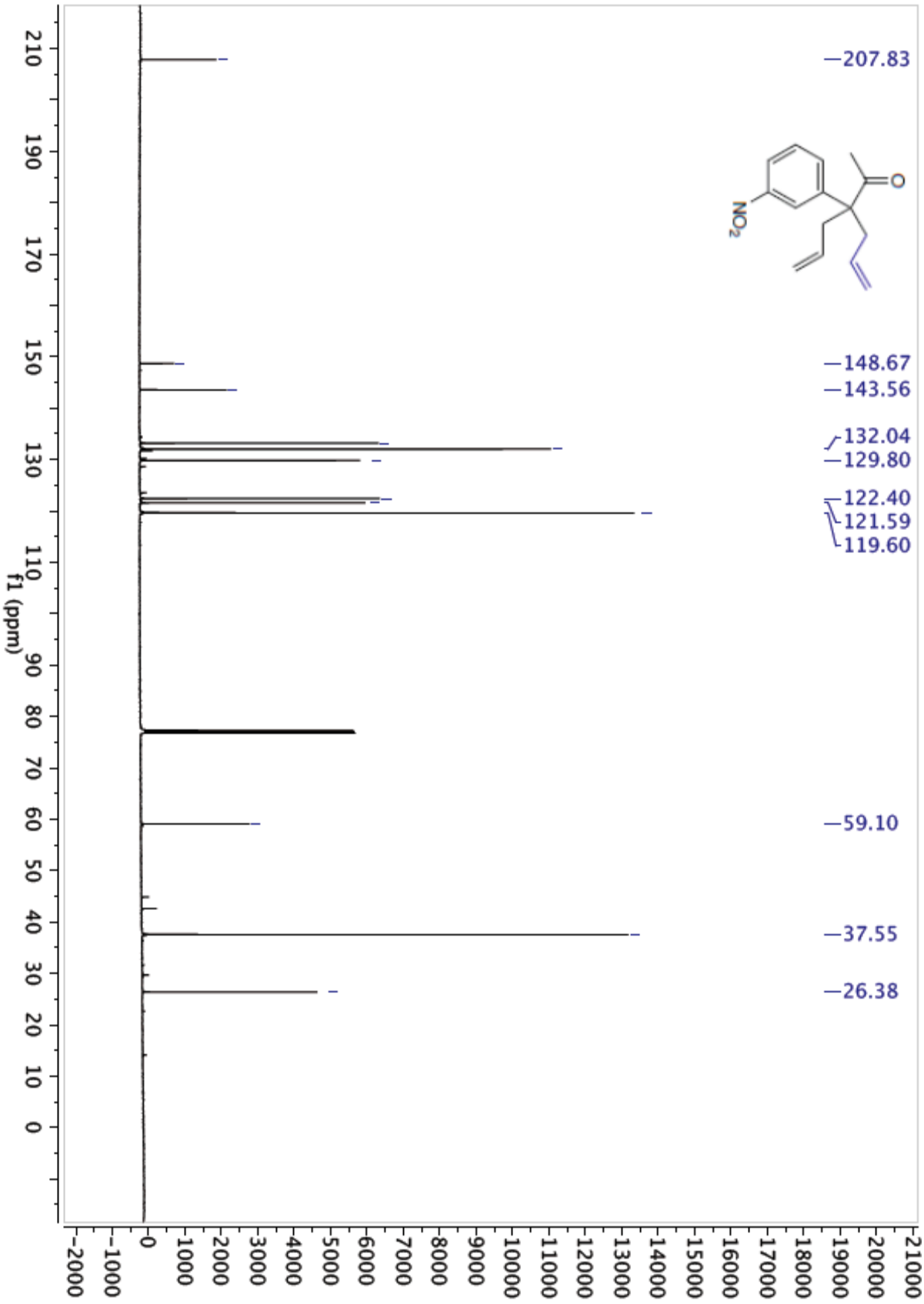
^{13}C NMR for Compound 4i



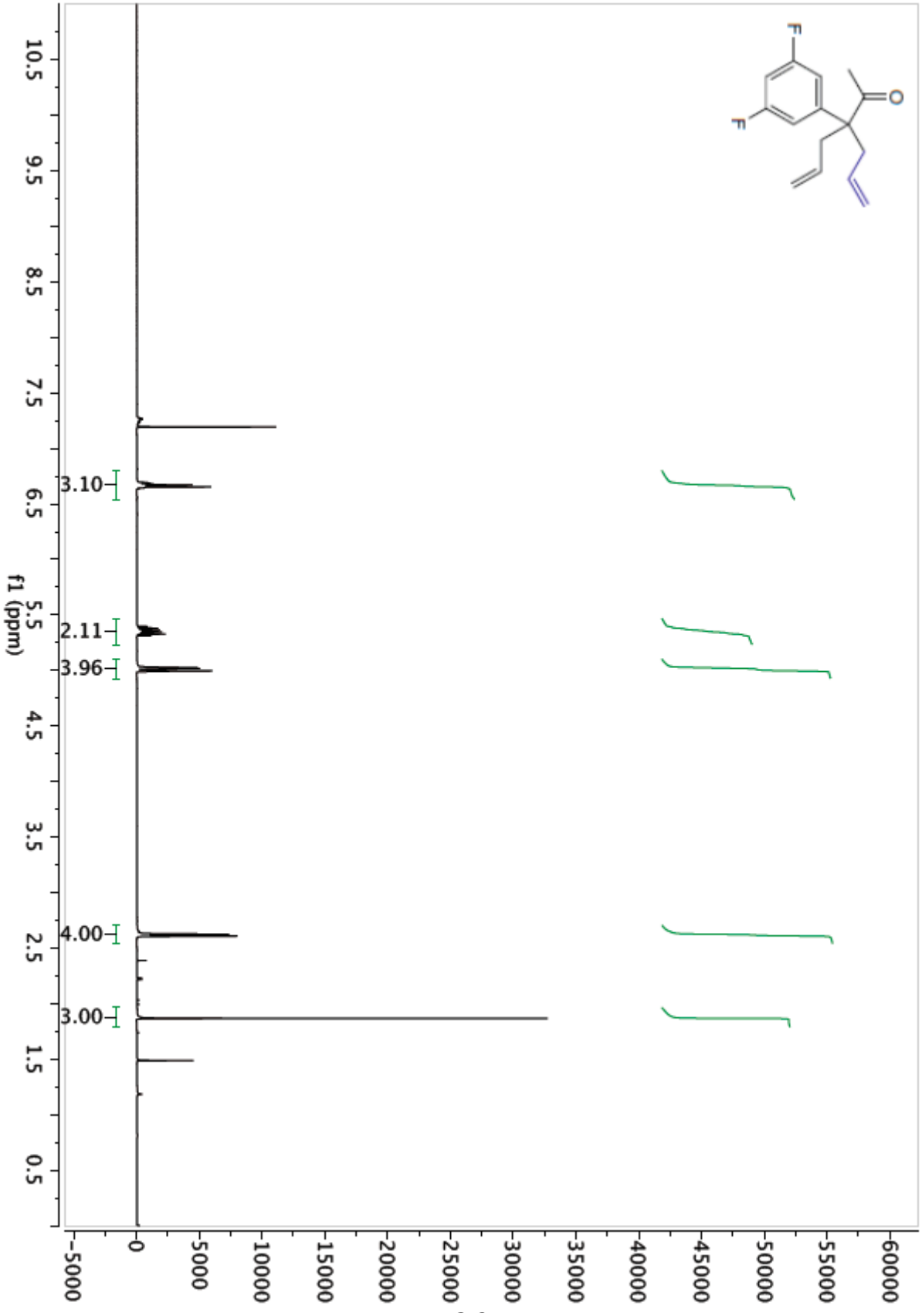
^{1}H NMR for Compound 4j



^{13}C NMR for Compound 4j



^{1}H NMR for Compound 4k



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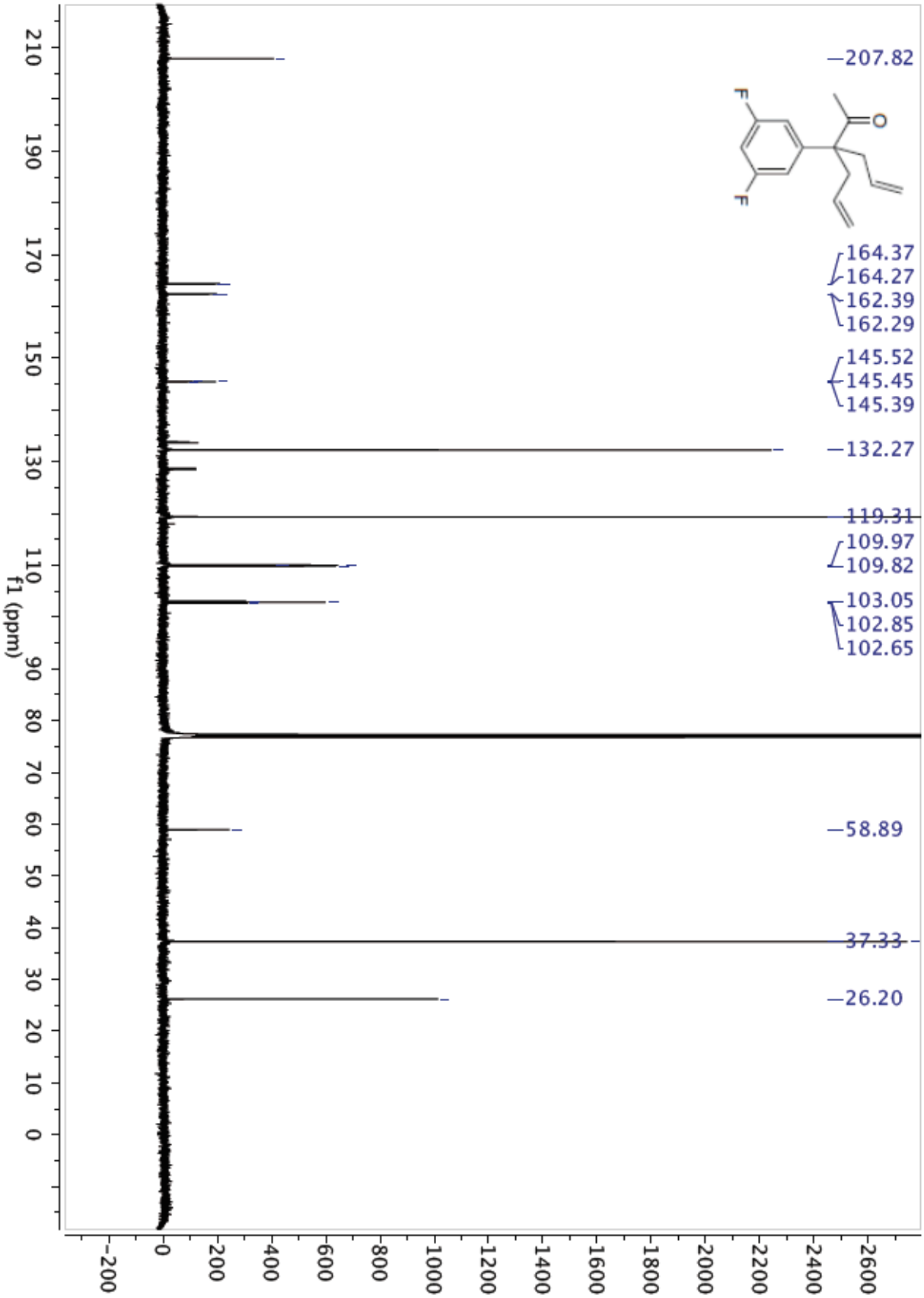
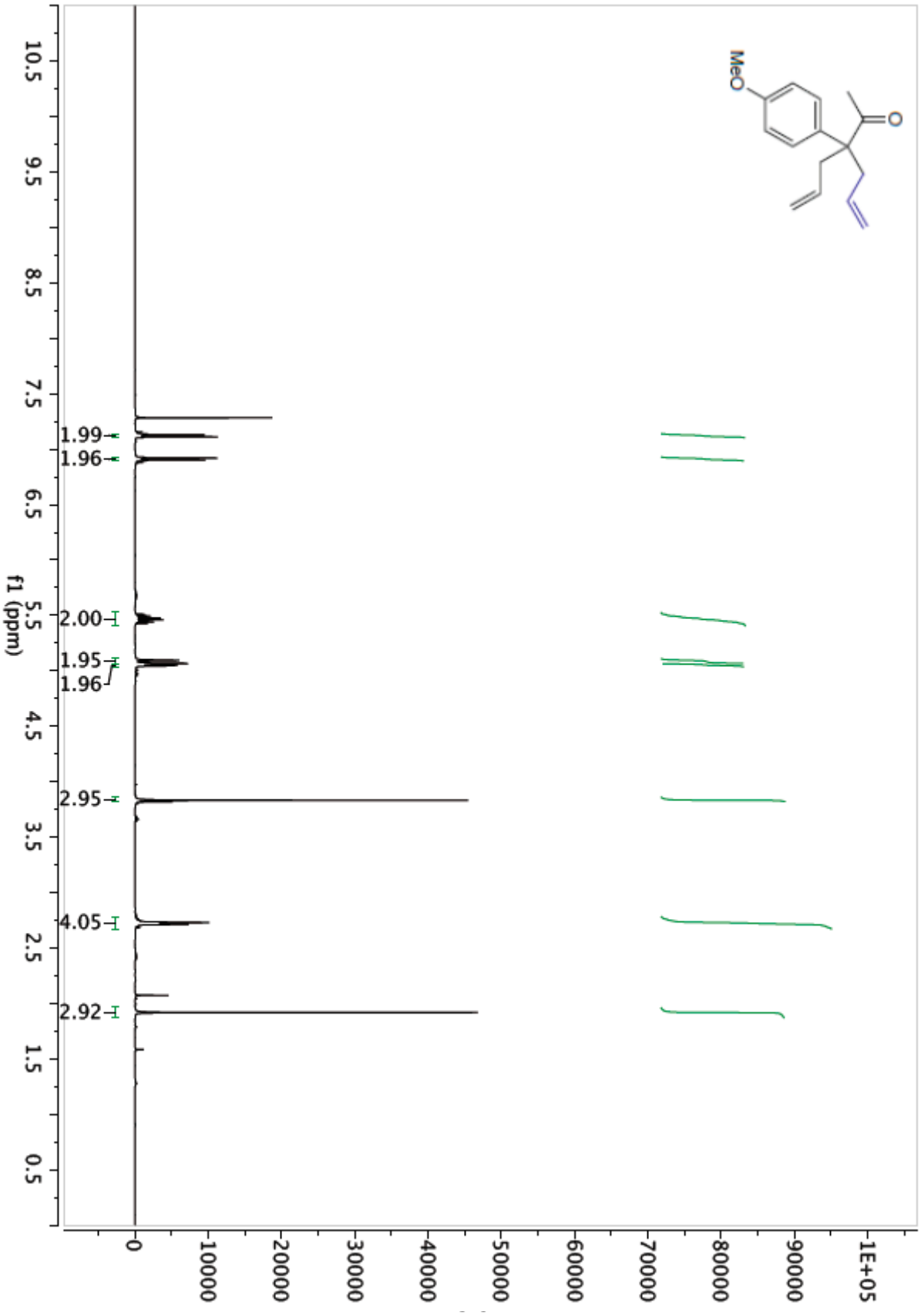
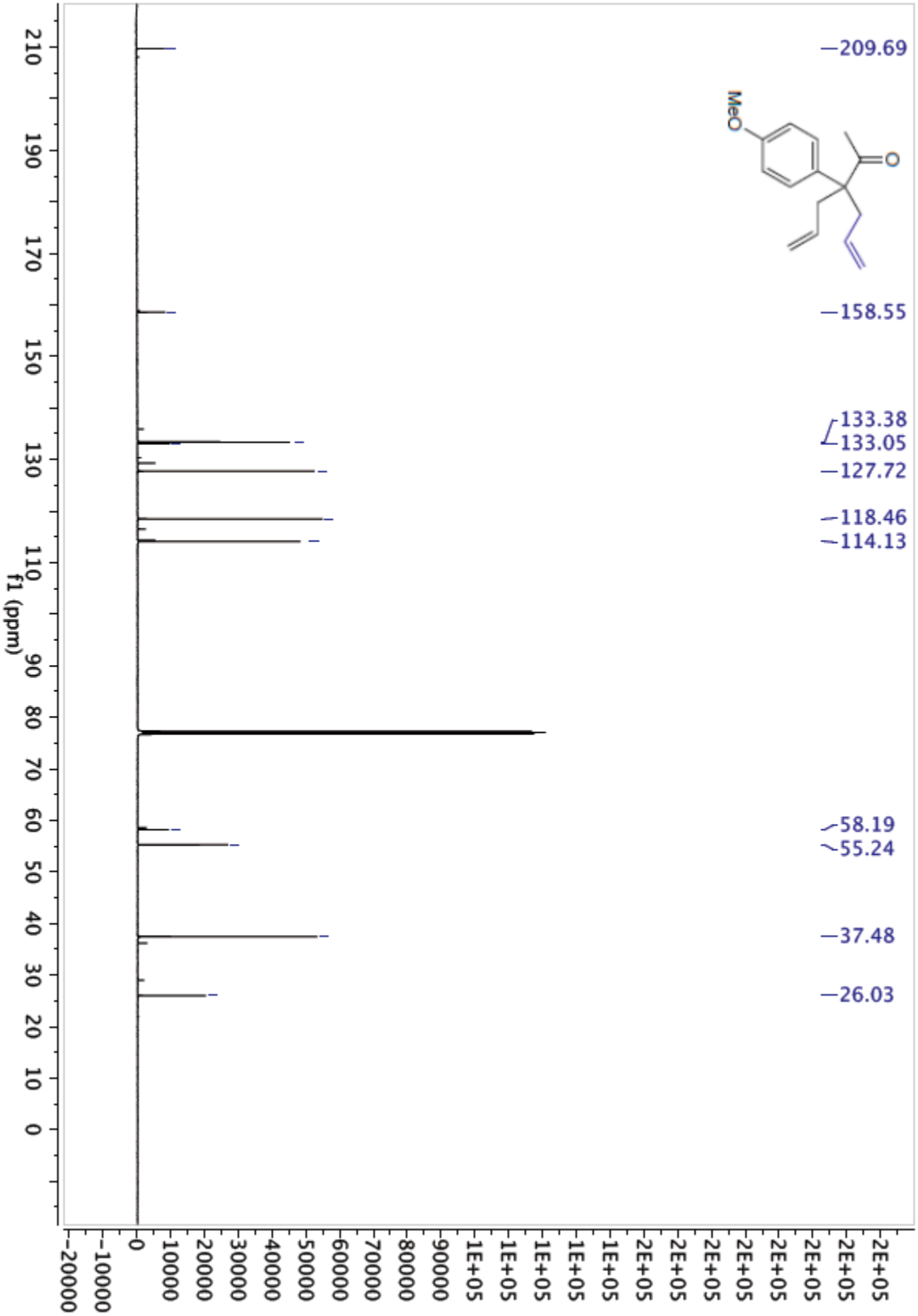


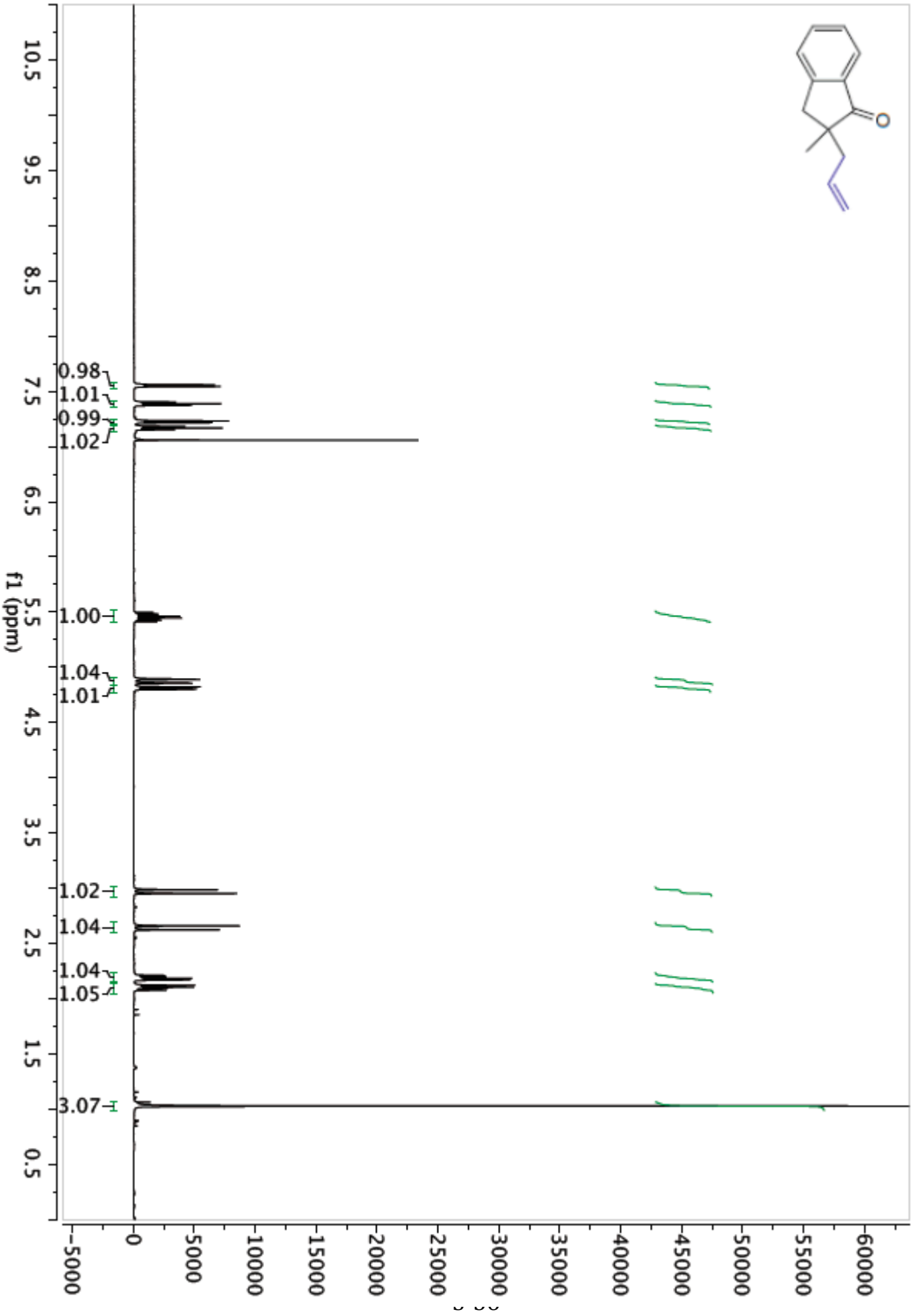
^{1}H NMR for Compound 4l



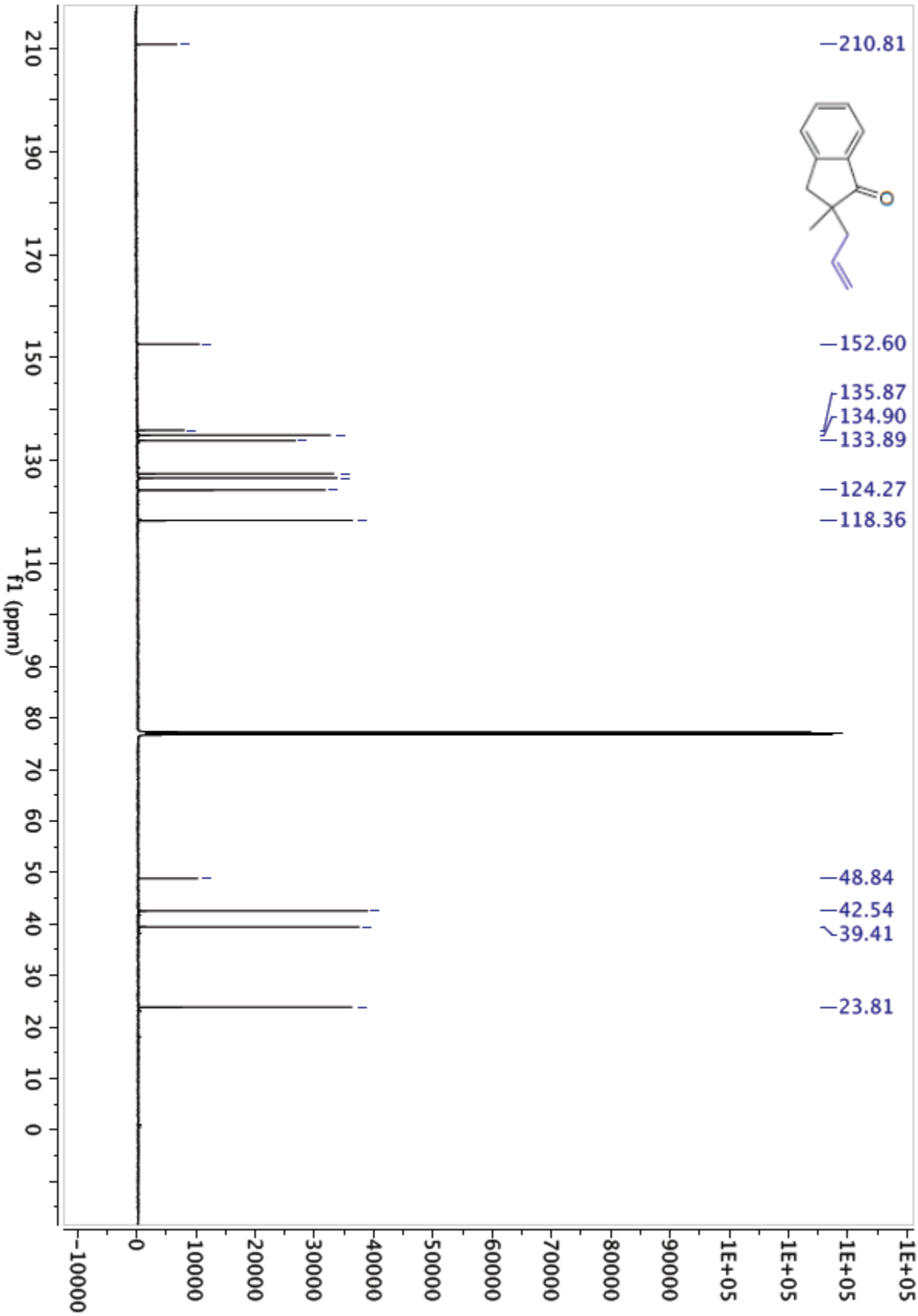
^{13}C NMR for Compound 4l



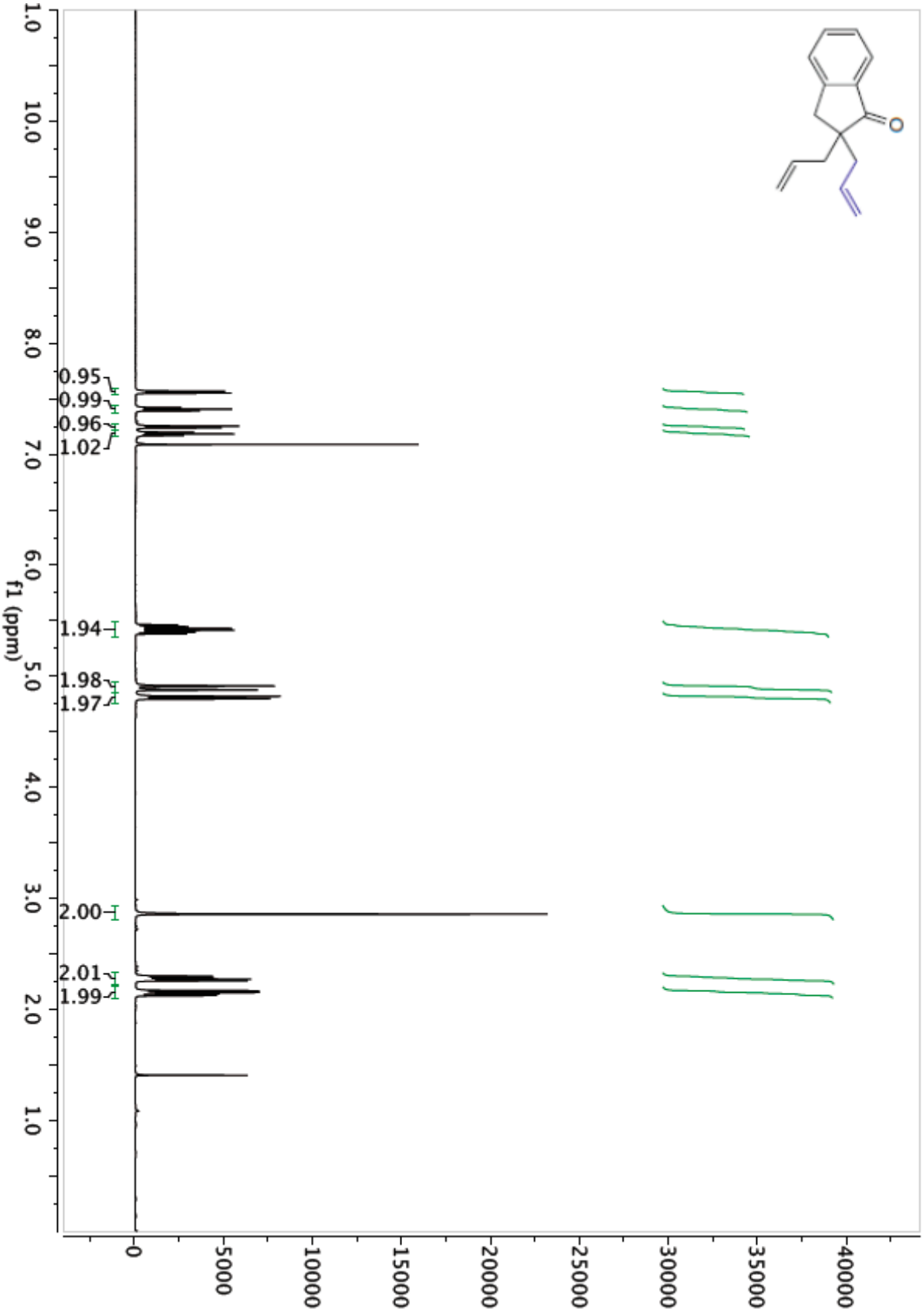
^{1}H NMR for Compound 4m



^{13}C NMR for Compound 4m



^{1}H NMR for Compound 4n



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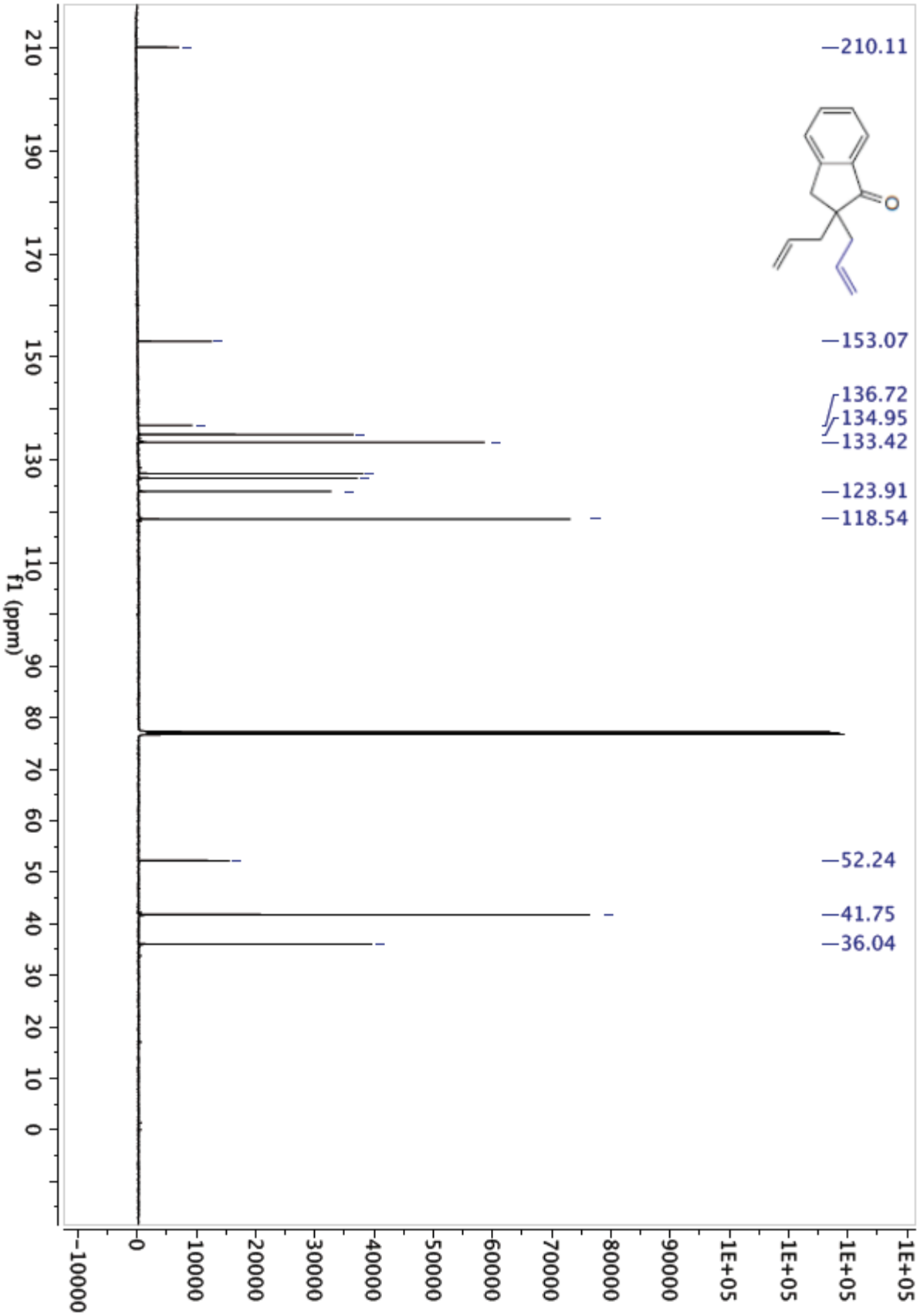
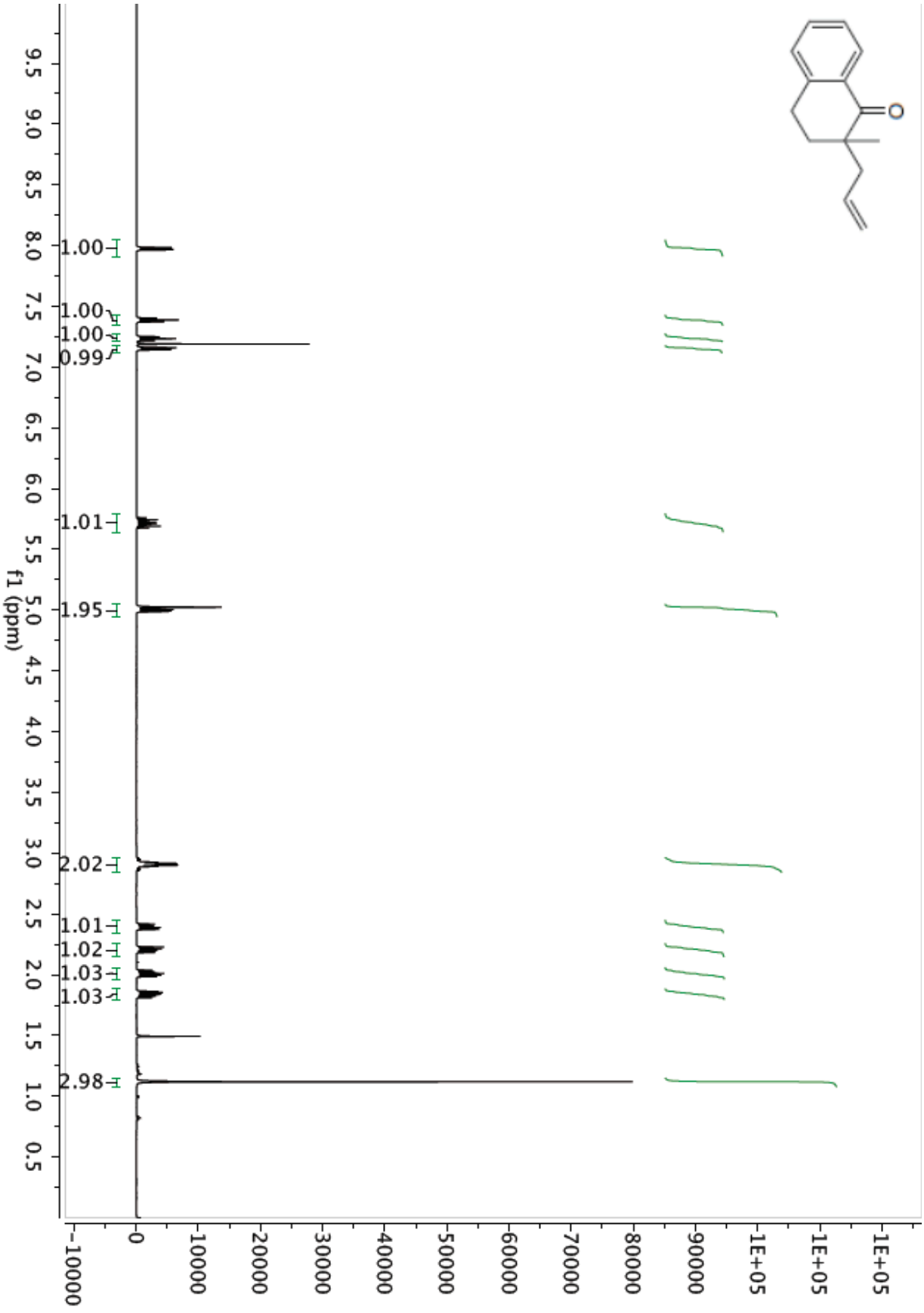
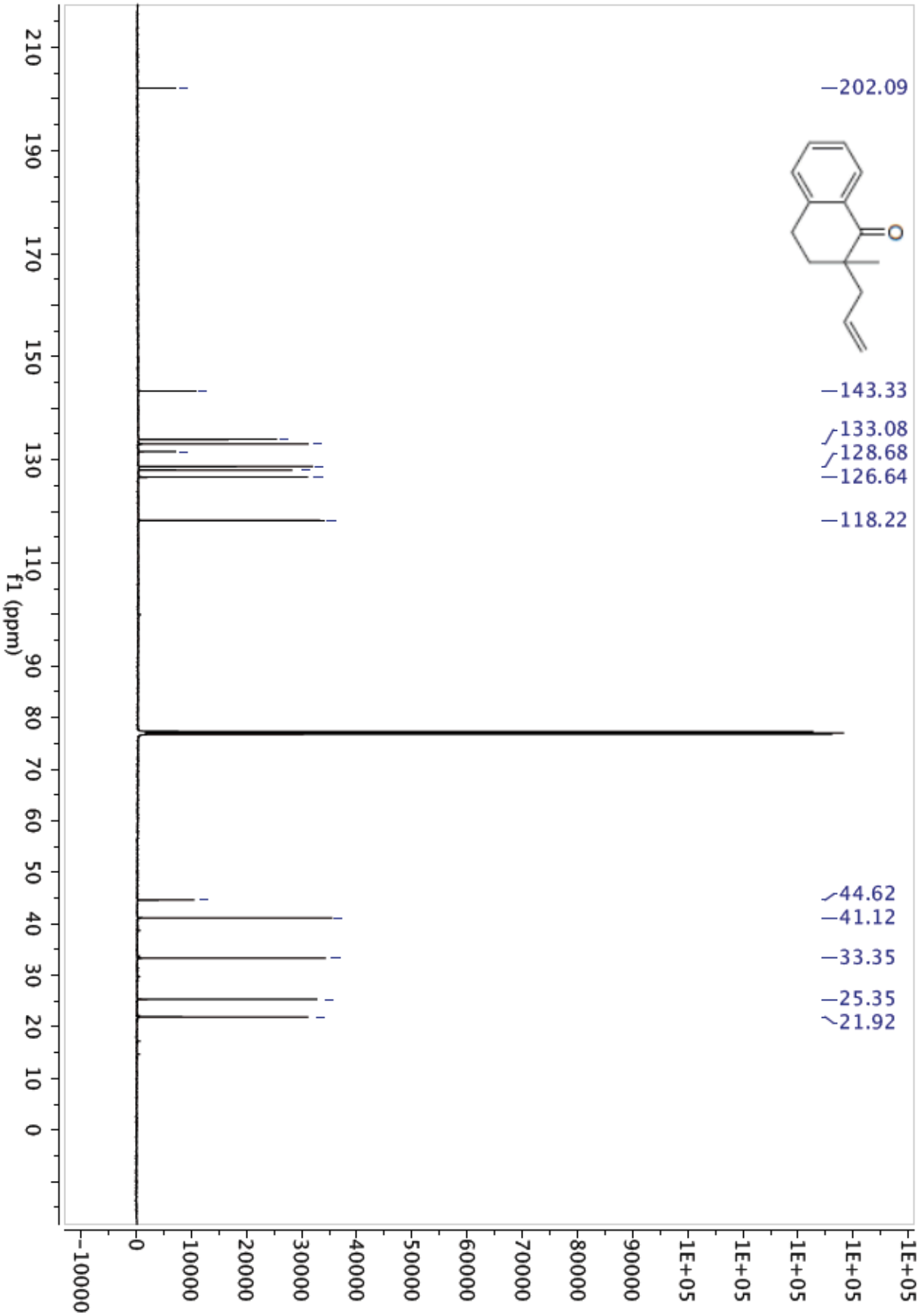


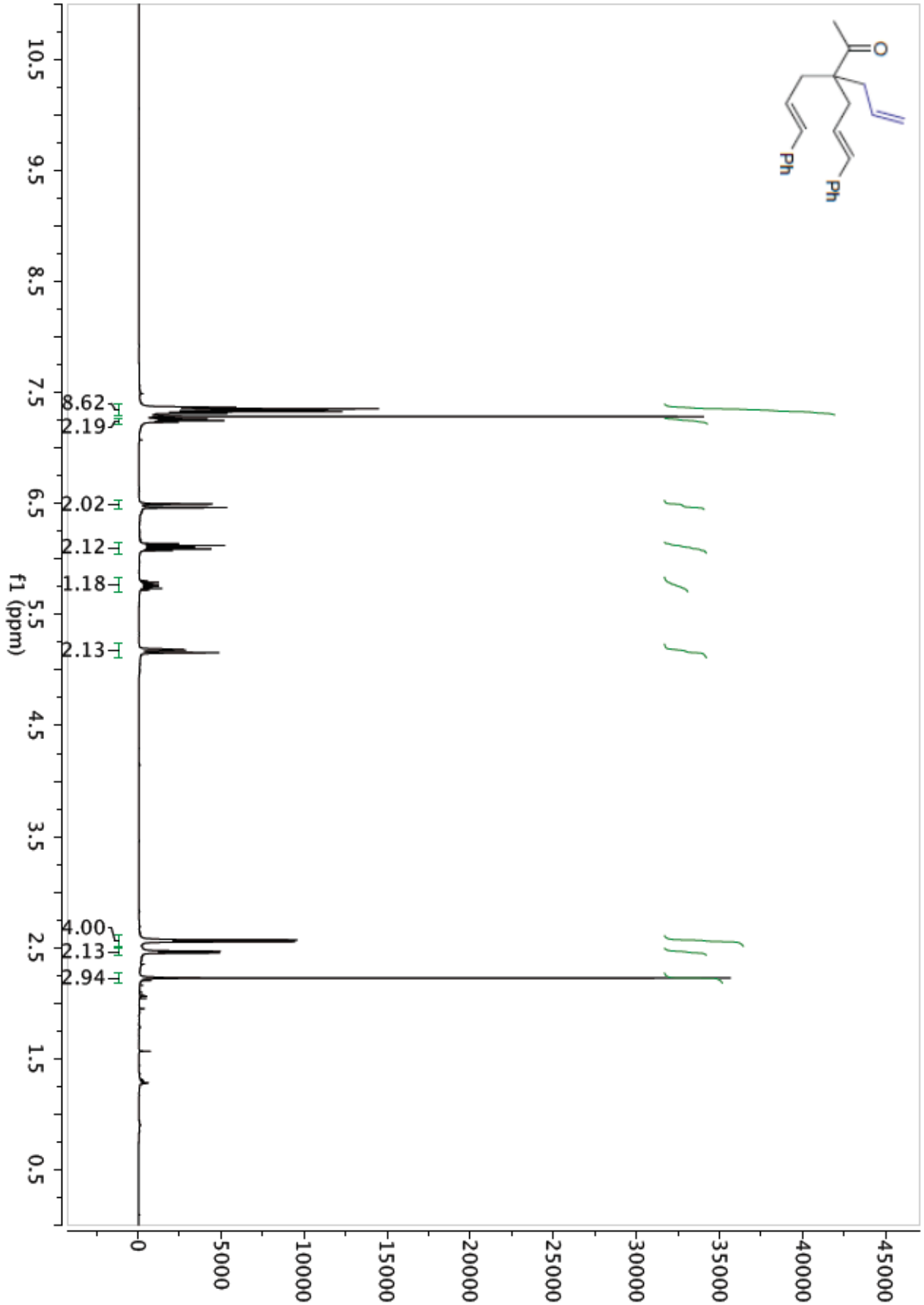
^{1}H NMR for Compound 4o



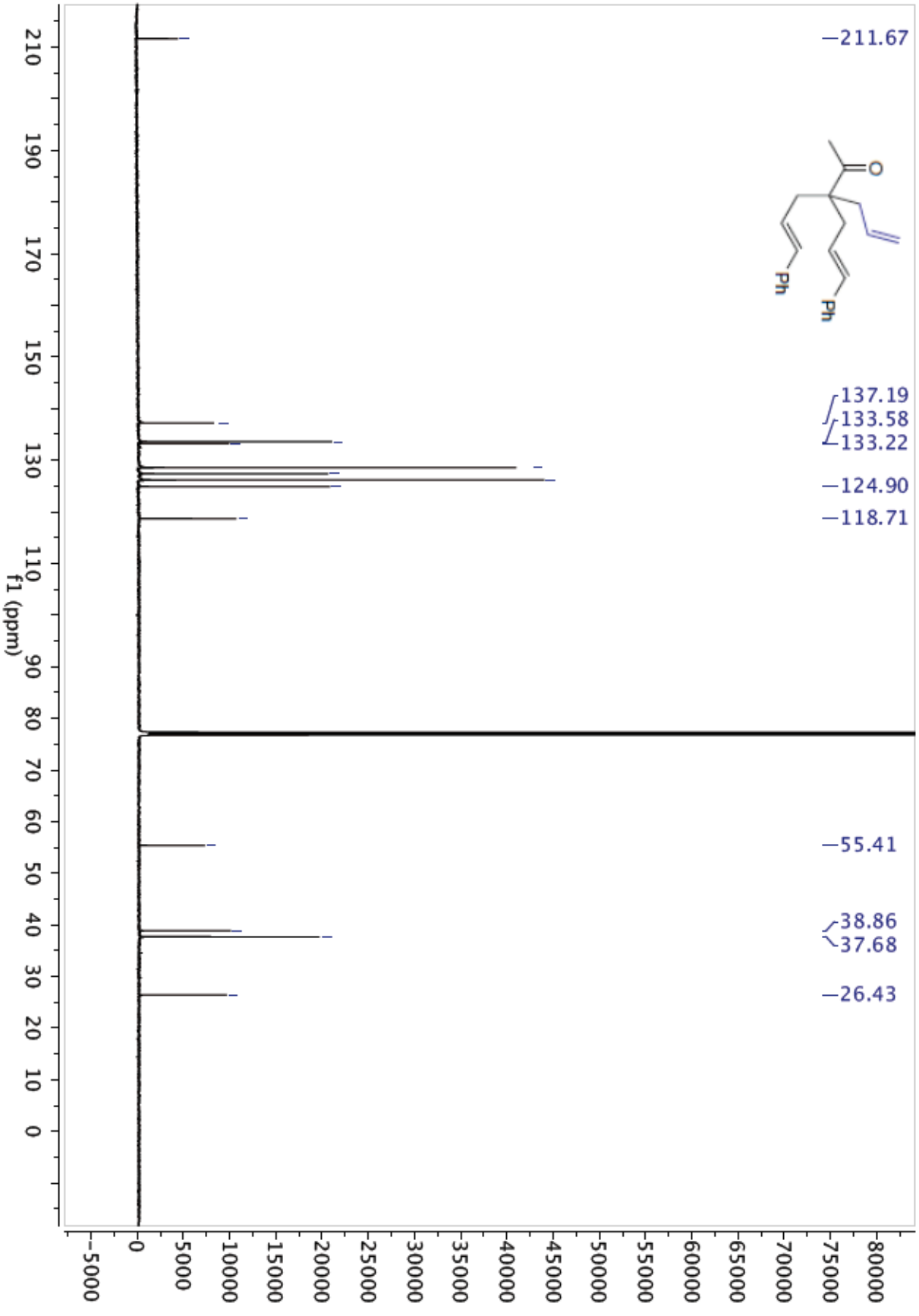
^{13}C NMR for Compound 4o



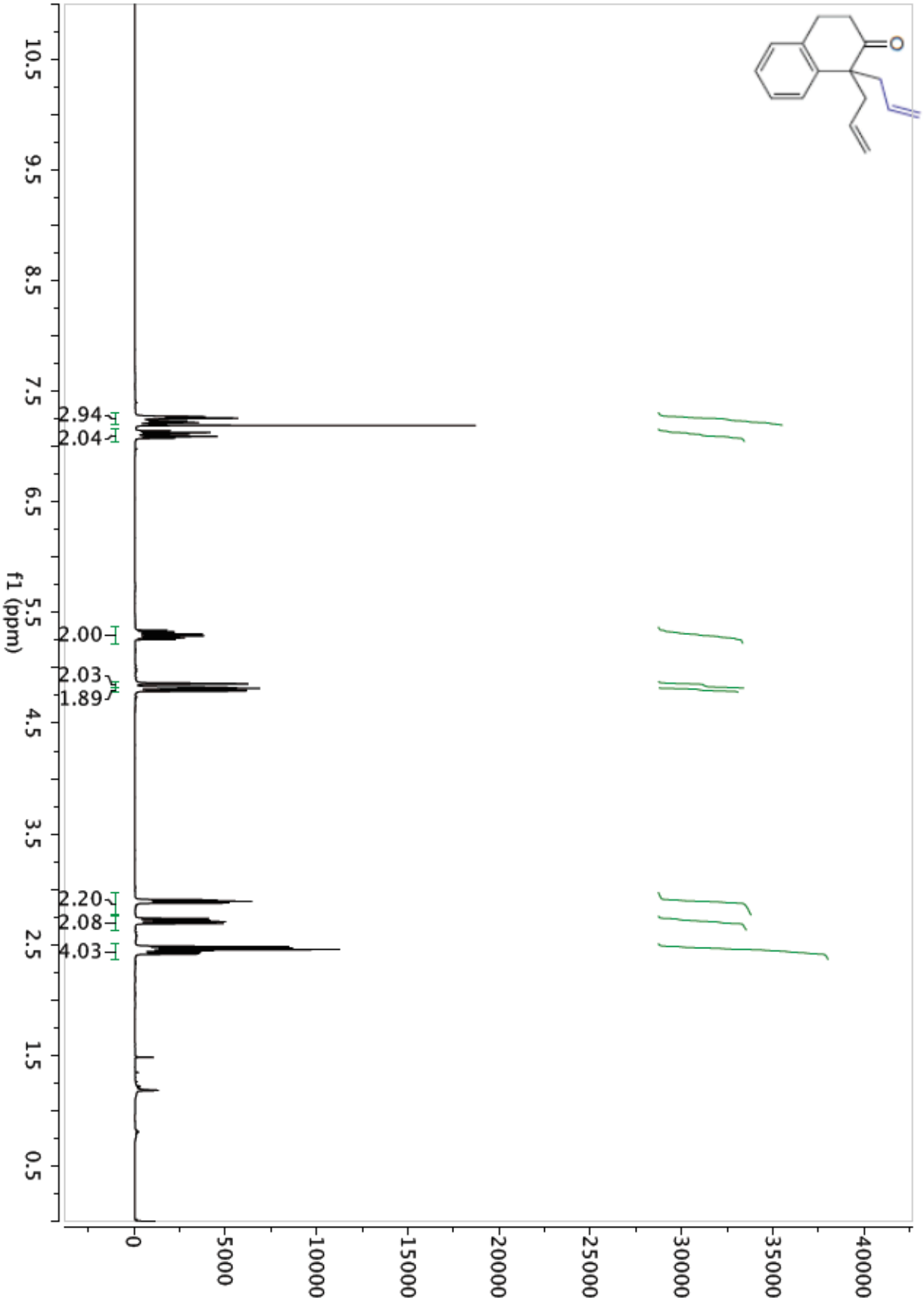
^{1}H NMR for Compound 4p



^{13}C NMR for Compound 4p



^{1}H NMR for Compound 4q



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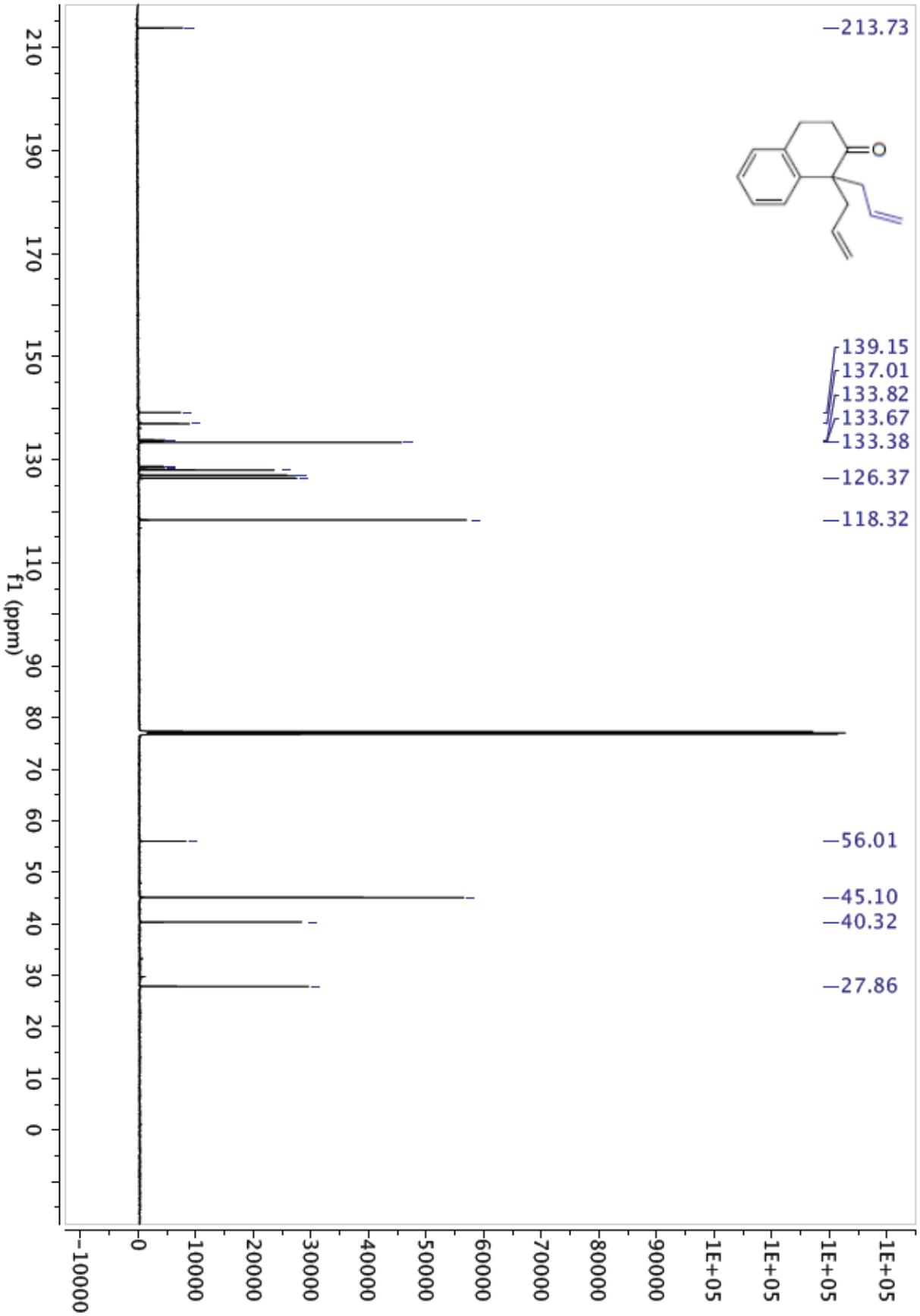
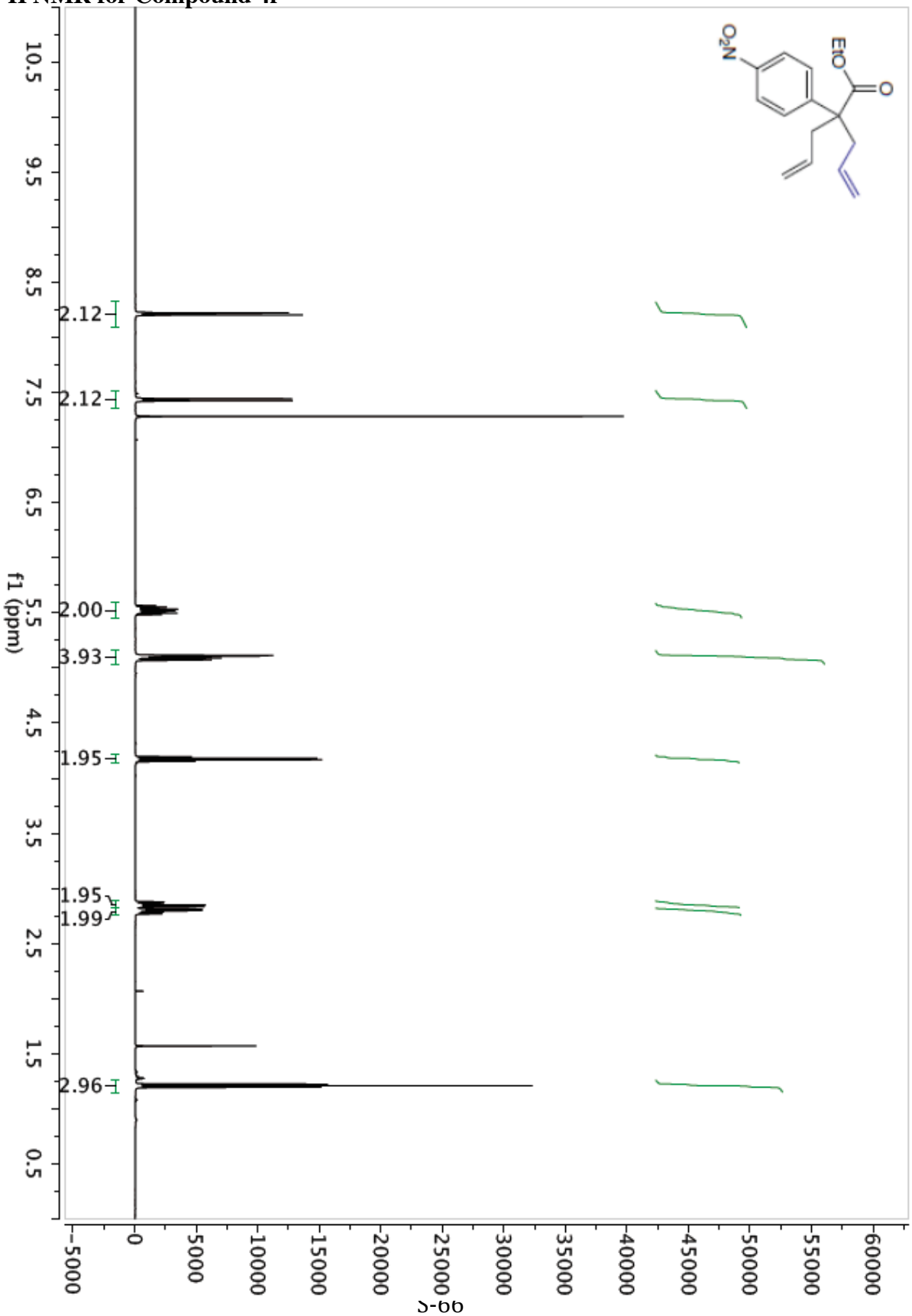
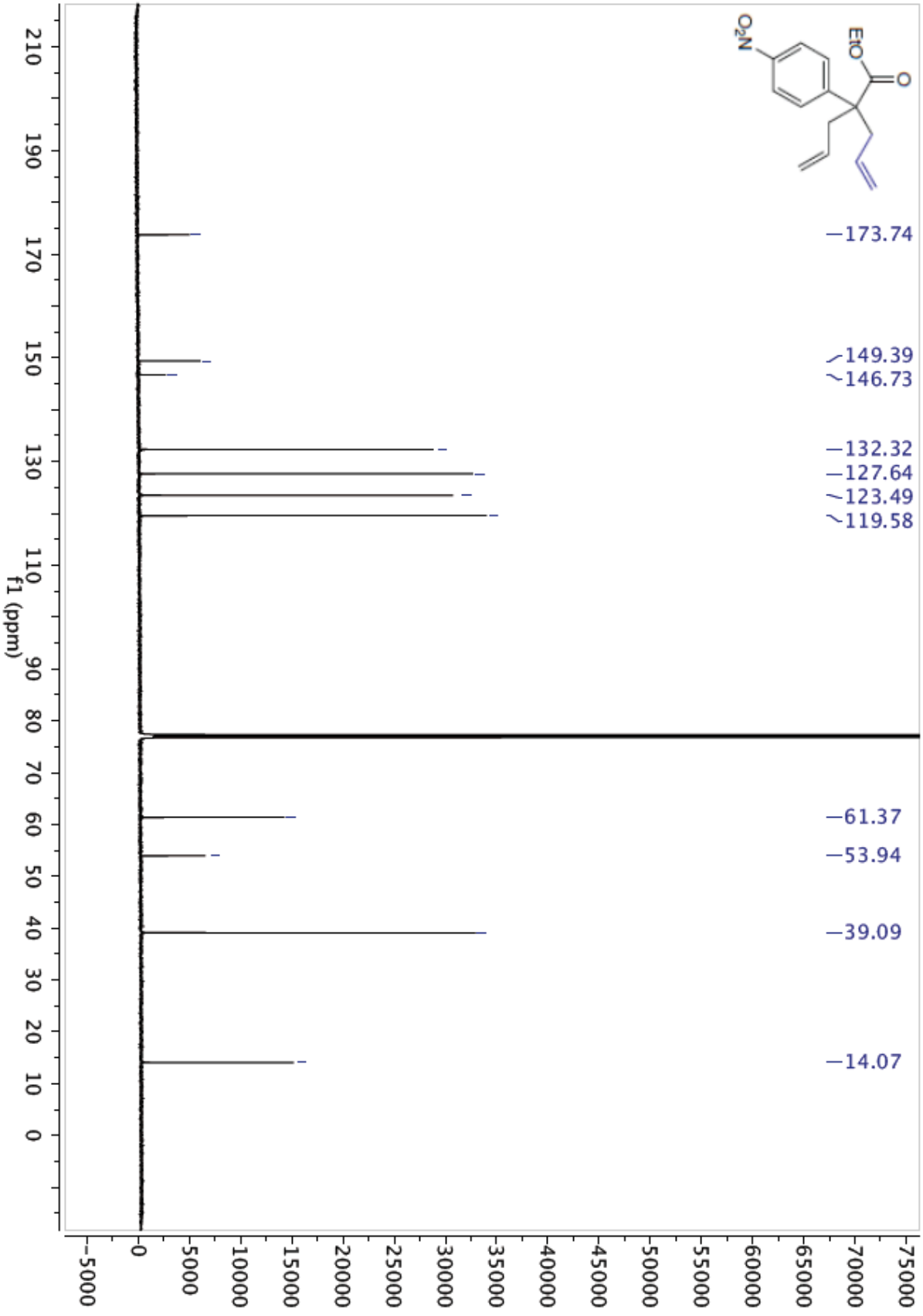


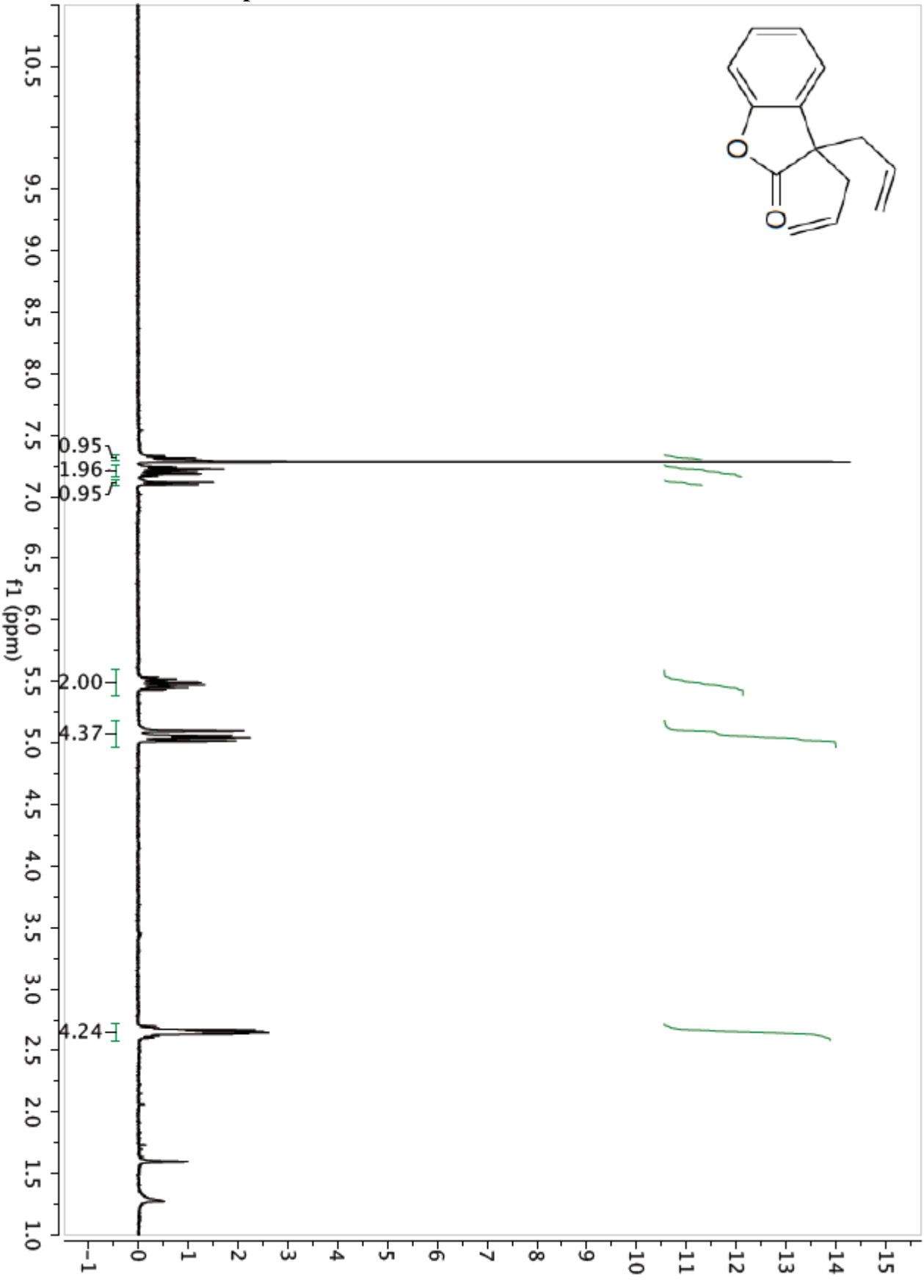
^{1}H NMR for Compound 4r



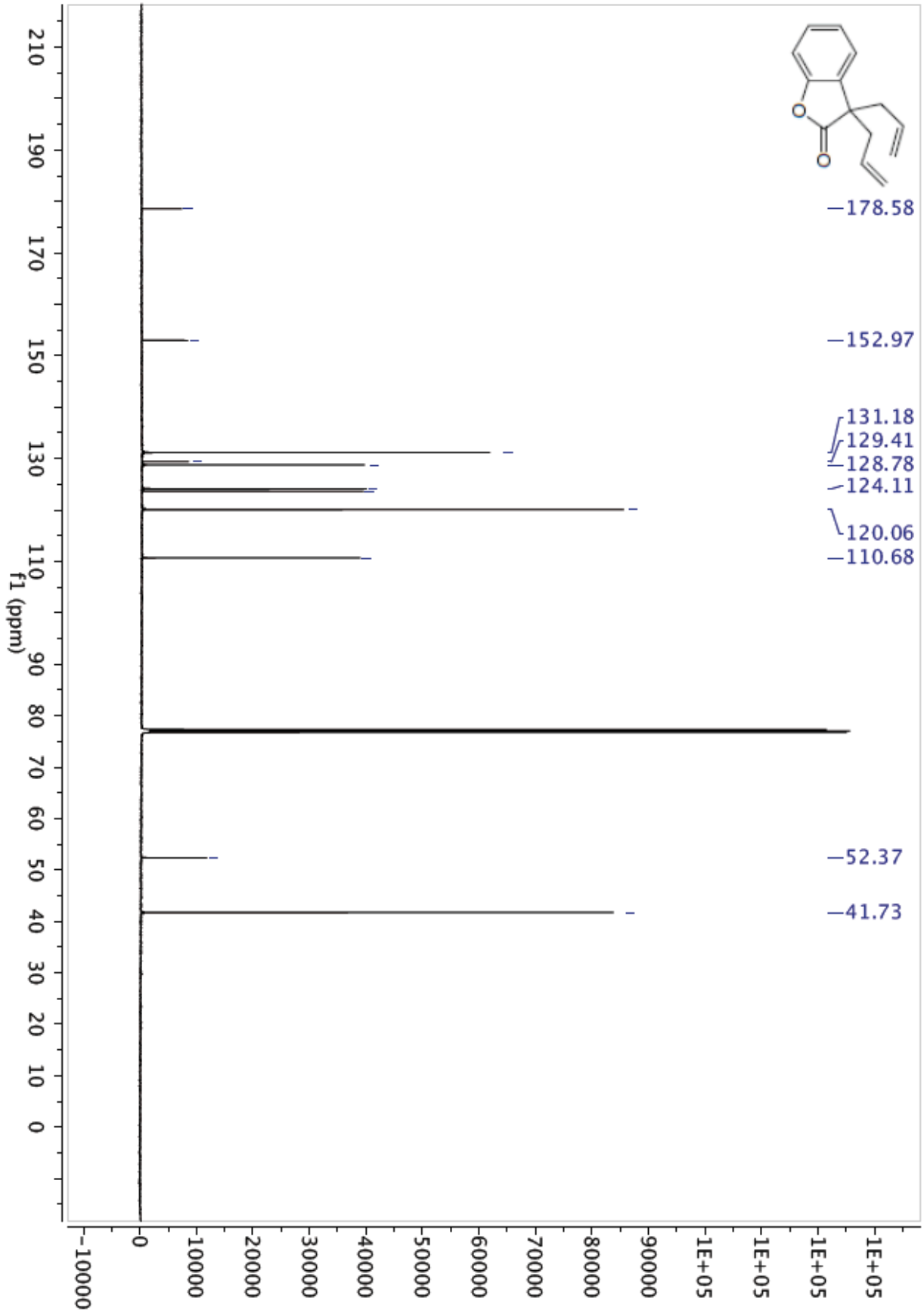
^{13}C NMR for Compound 4r



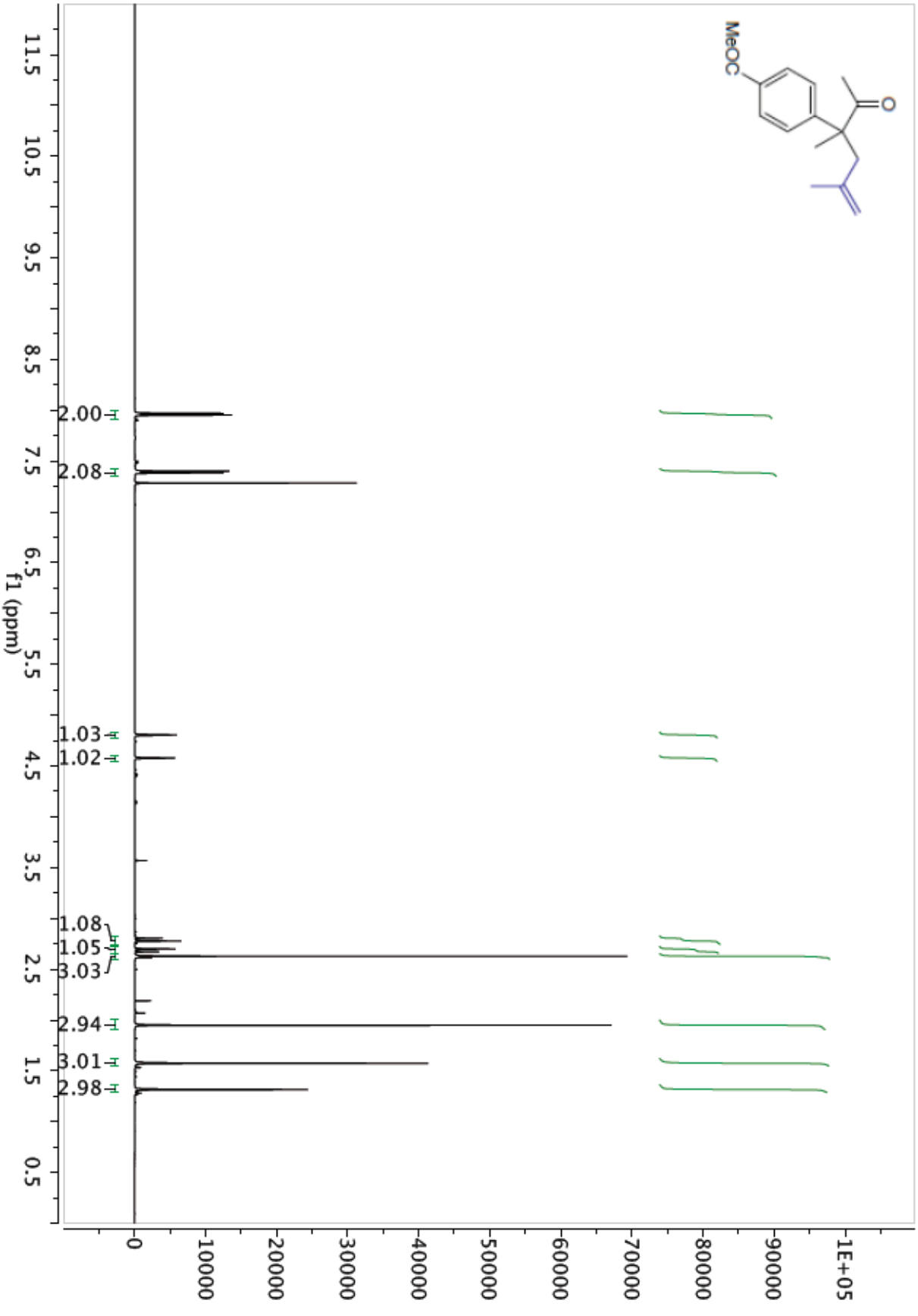
^{1}H NMR for Compound 4s



^{13}C NMR for Compound 4s



^{1}H NMR for Compound 4t



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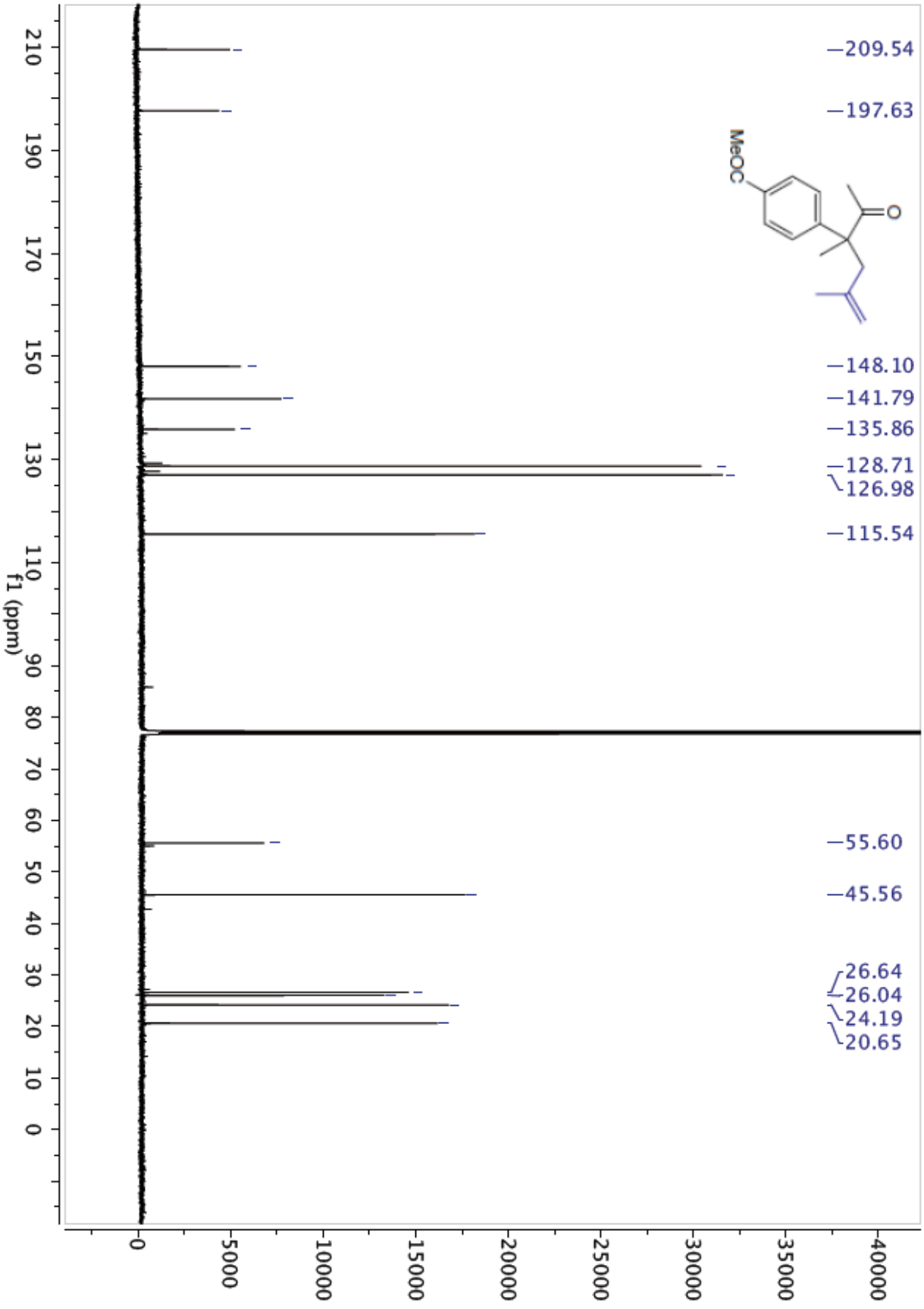
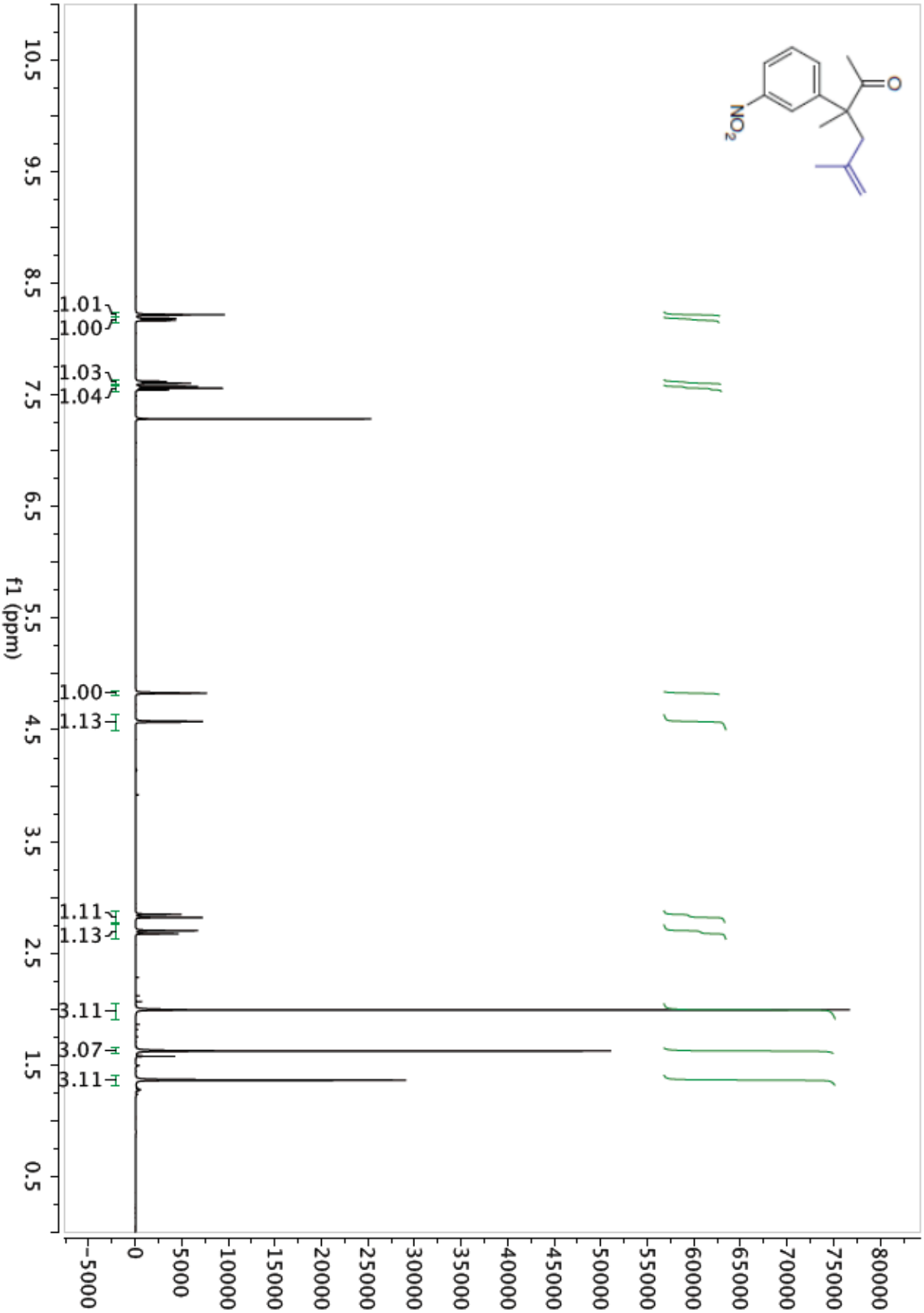
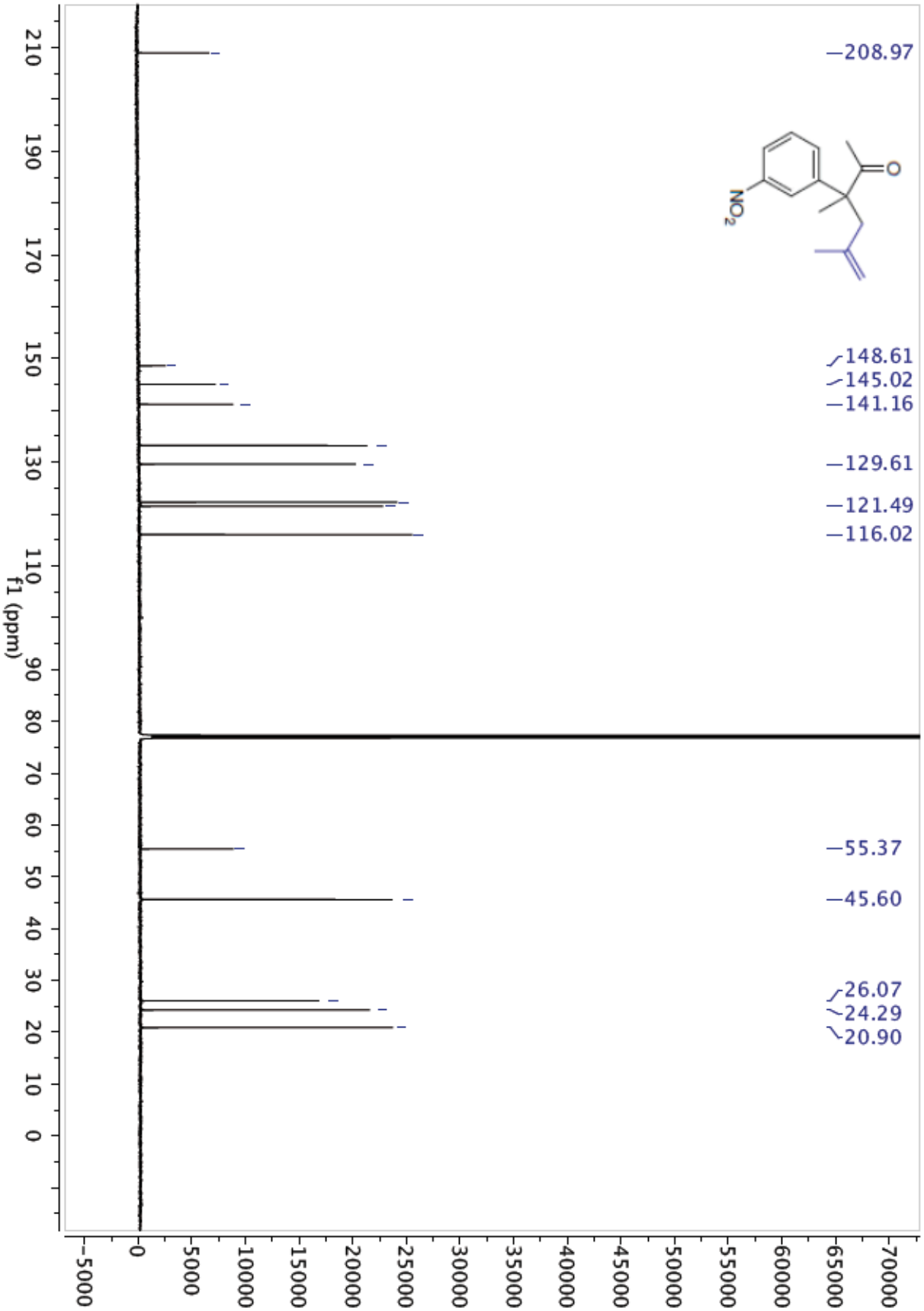


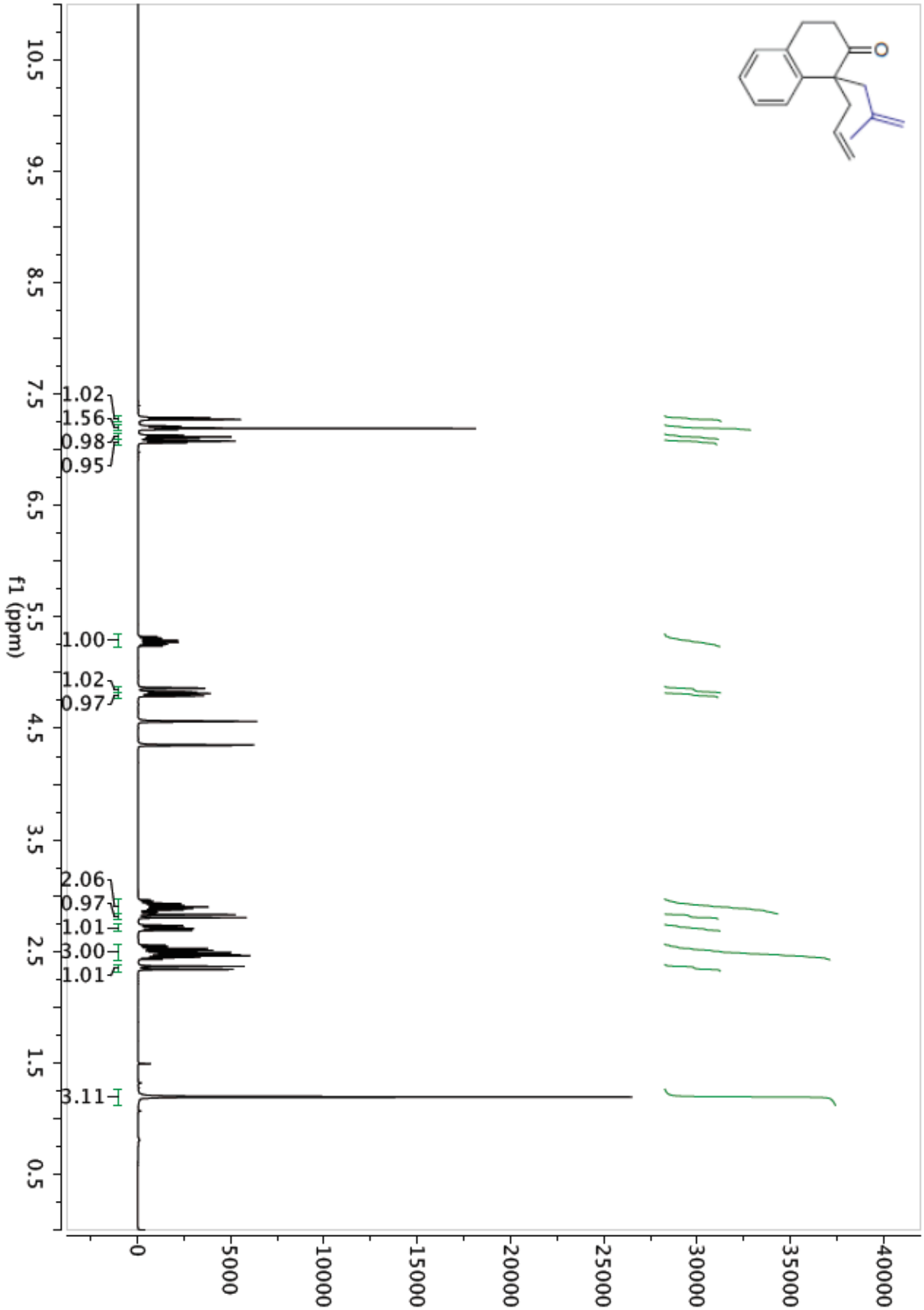
^{1}H NMR for Compound 4u



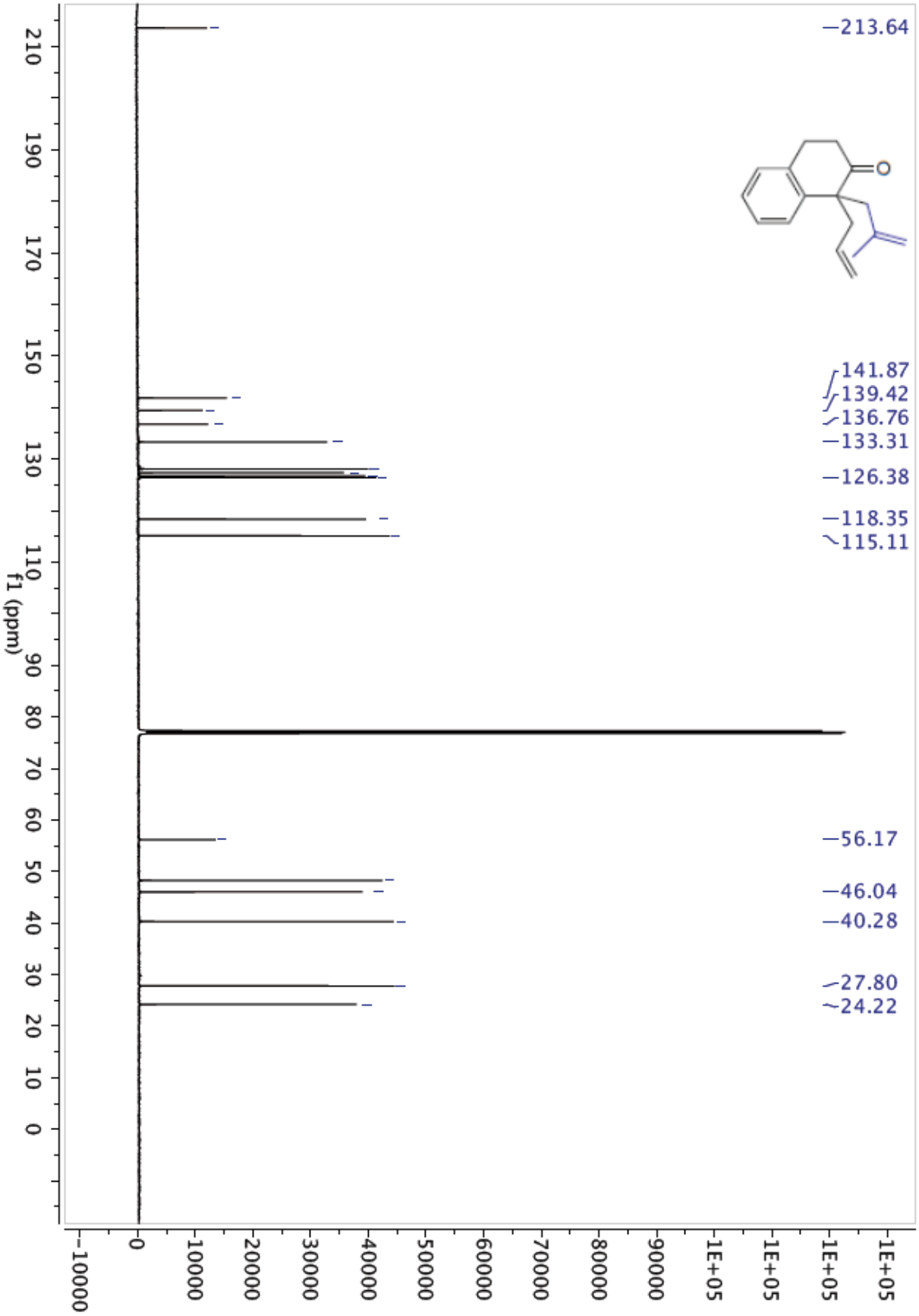
^{13}C NMR for Compound 4u



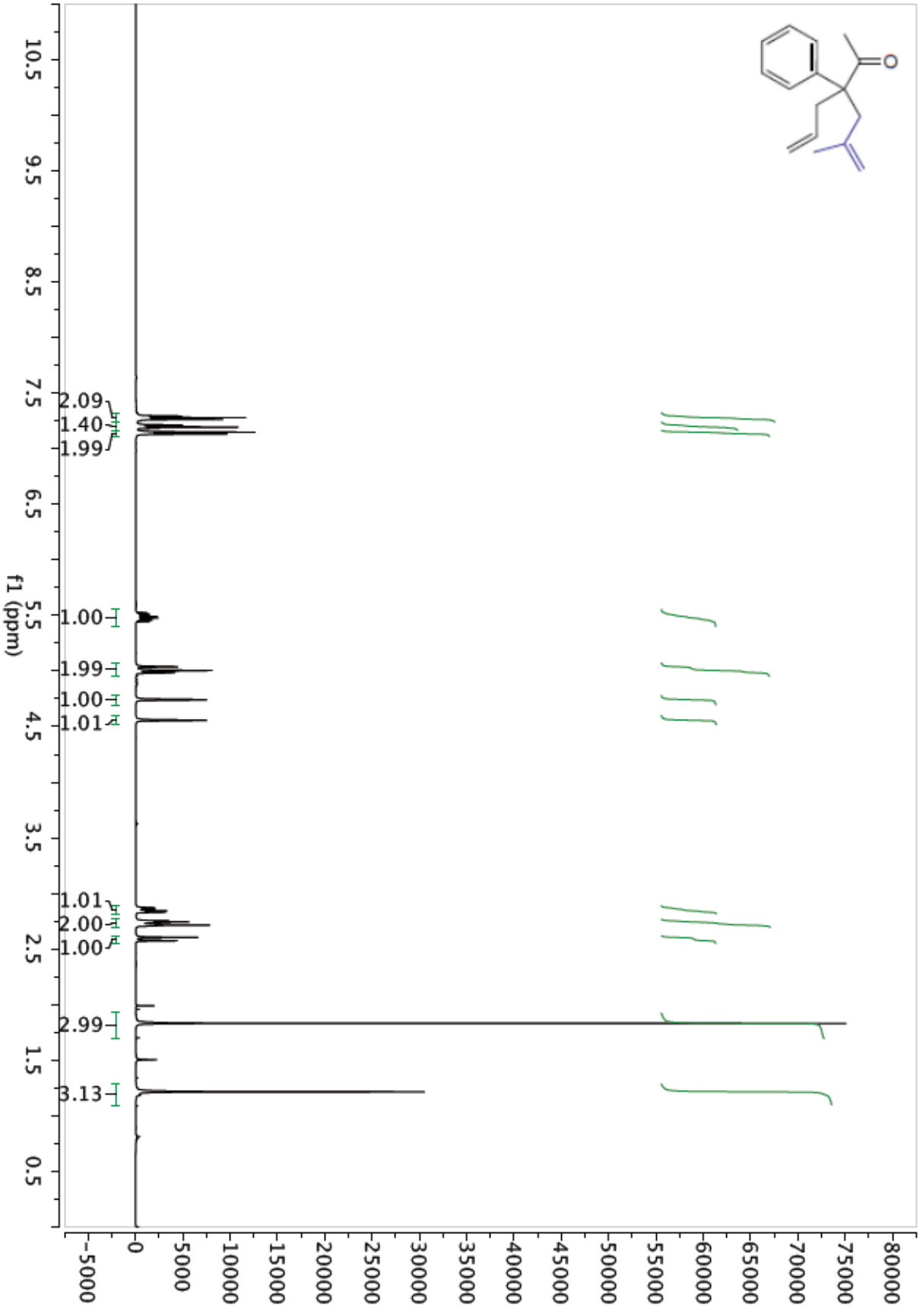
^{1}H NMR for Compound 4v



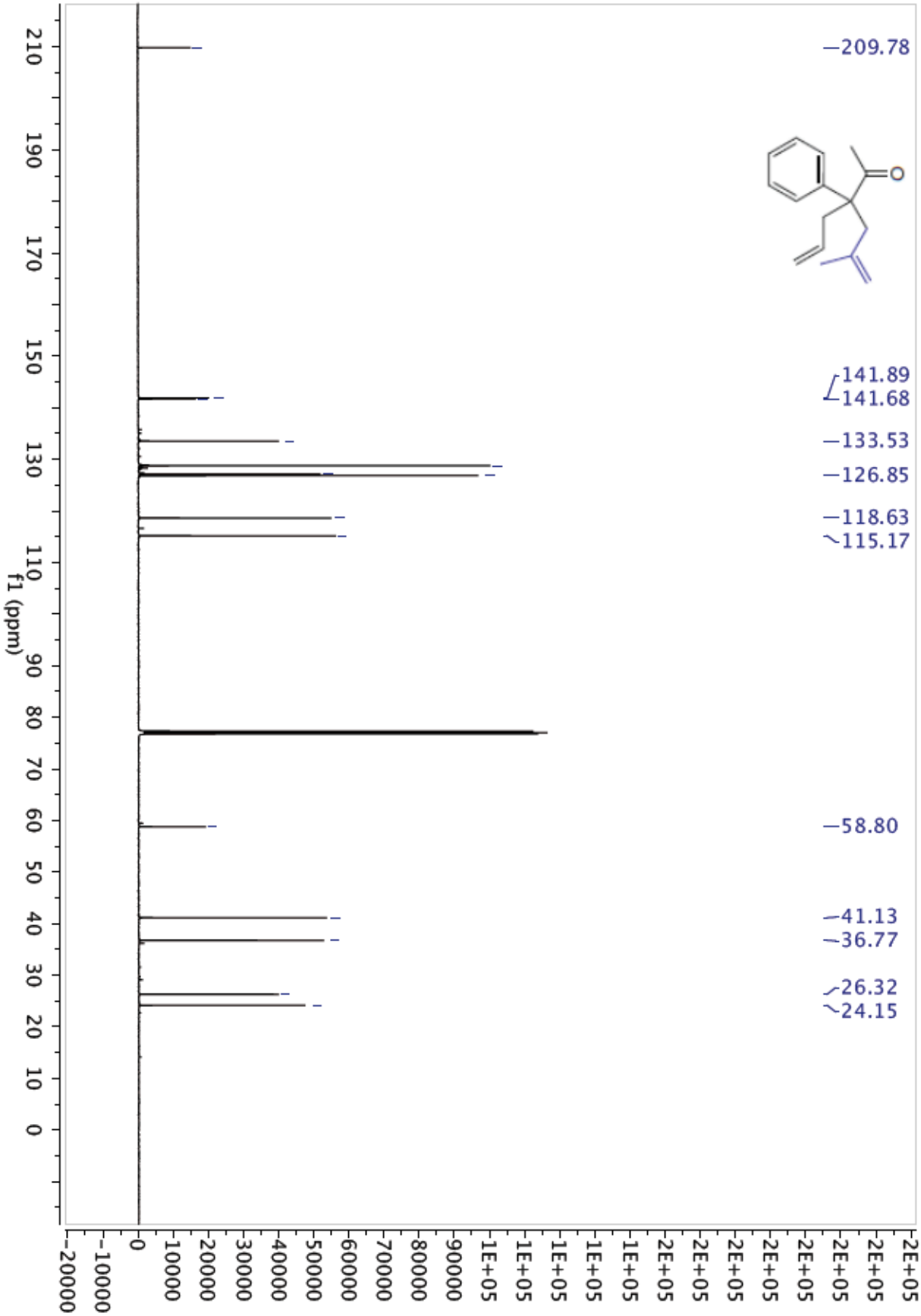
^{13}C NMR for Compound 4v



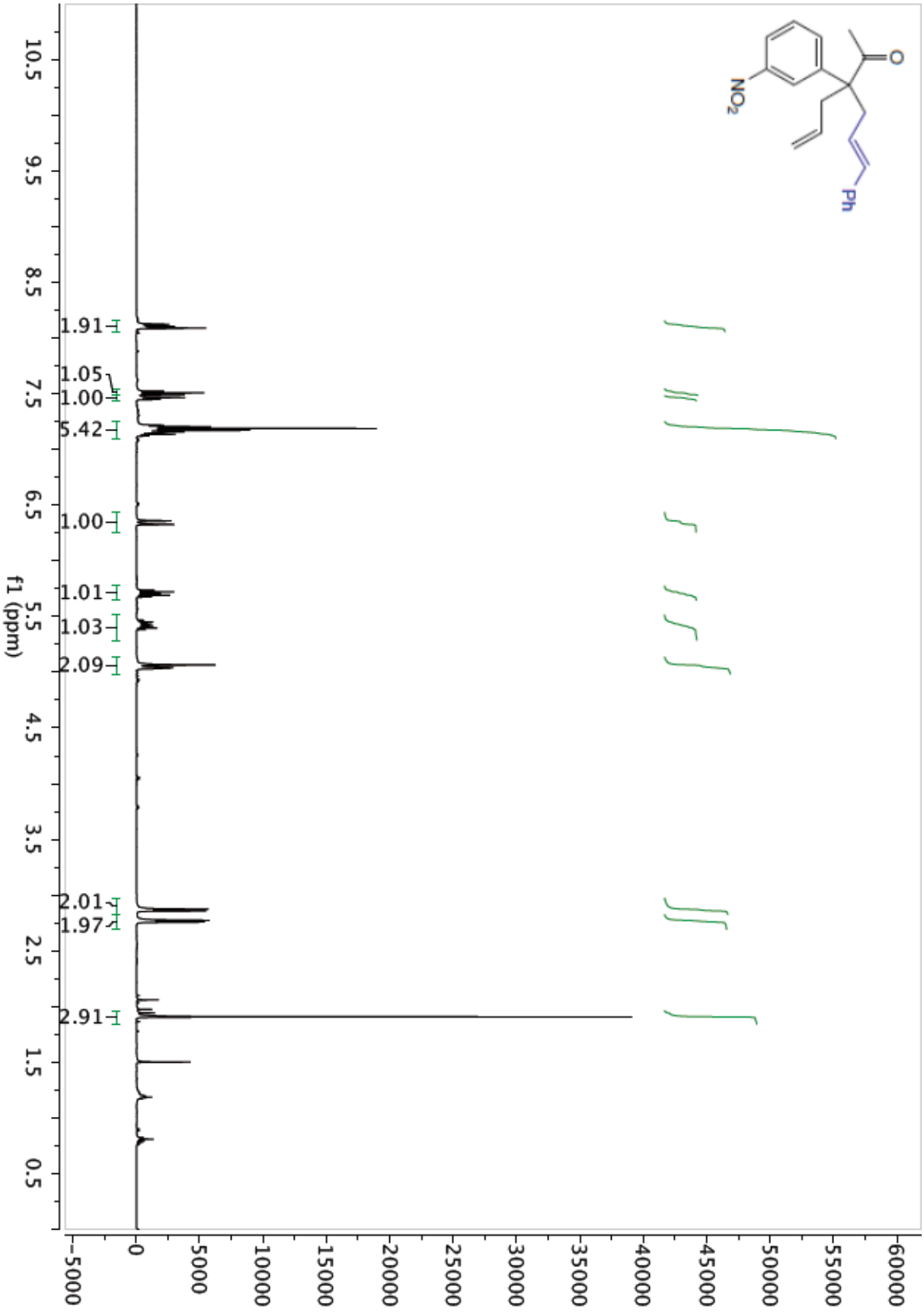
^{1}H NMR for Compound 4w



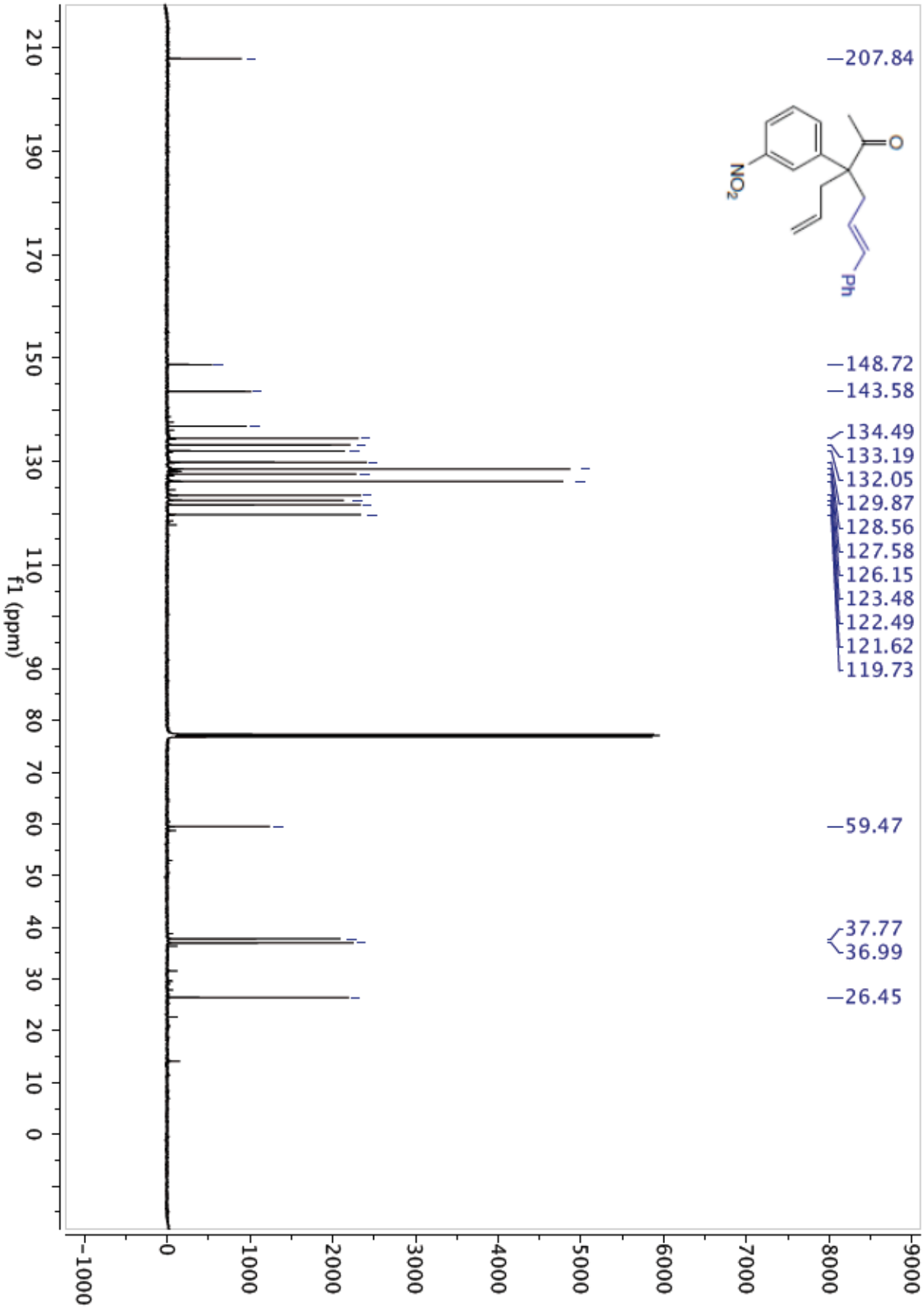
^{13}C NMR for Compound 4w



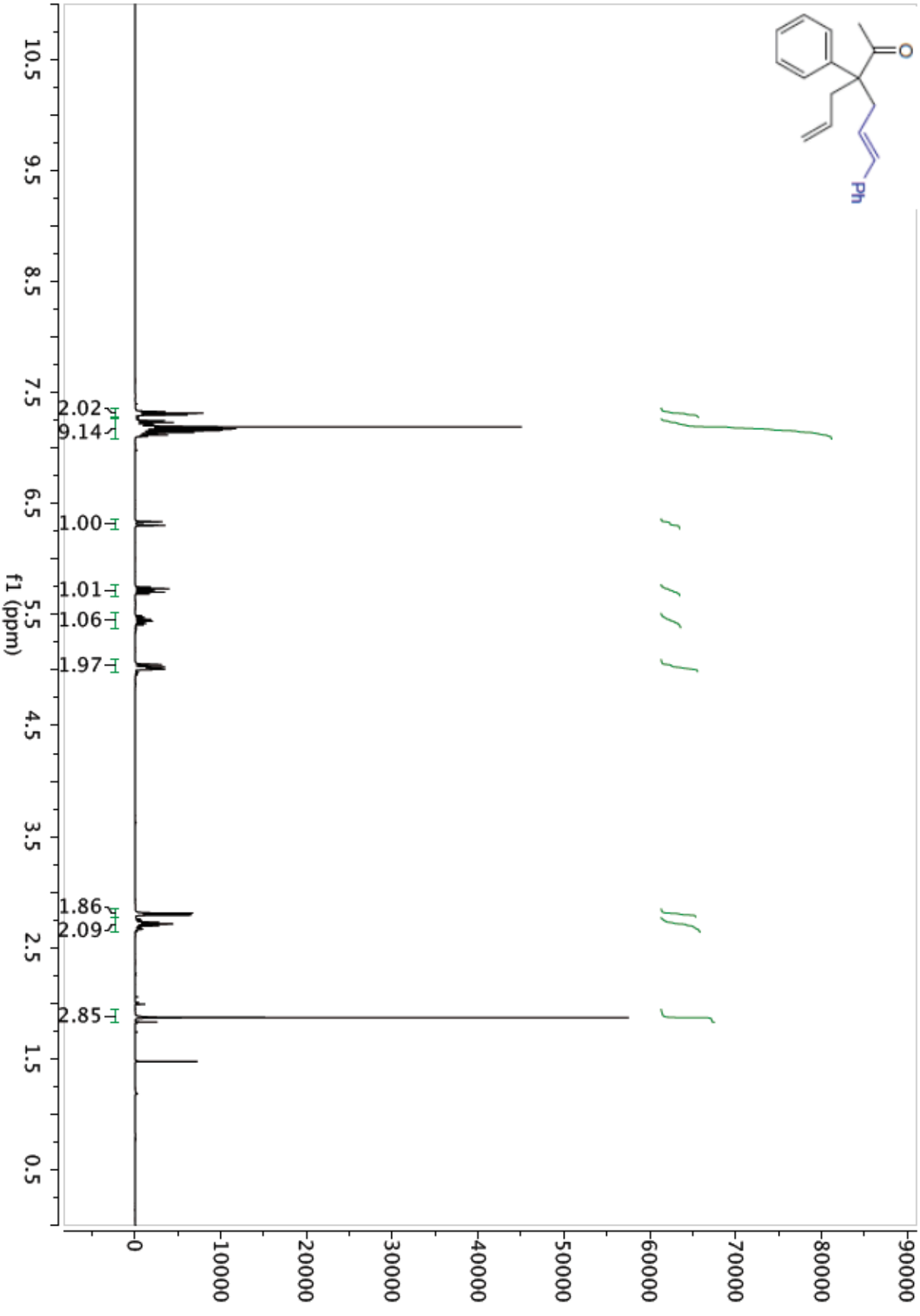
^{1}H NMR for Compound 4x



^{13}C NMR for Compound 4x



^{1}H NMR for Compound 4y



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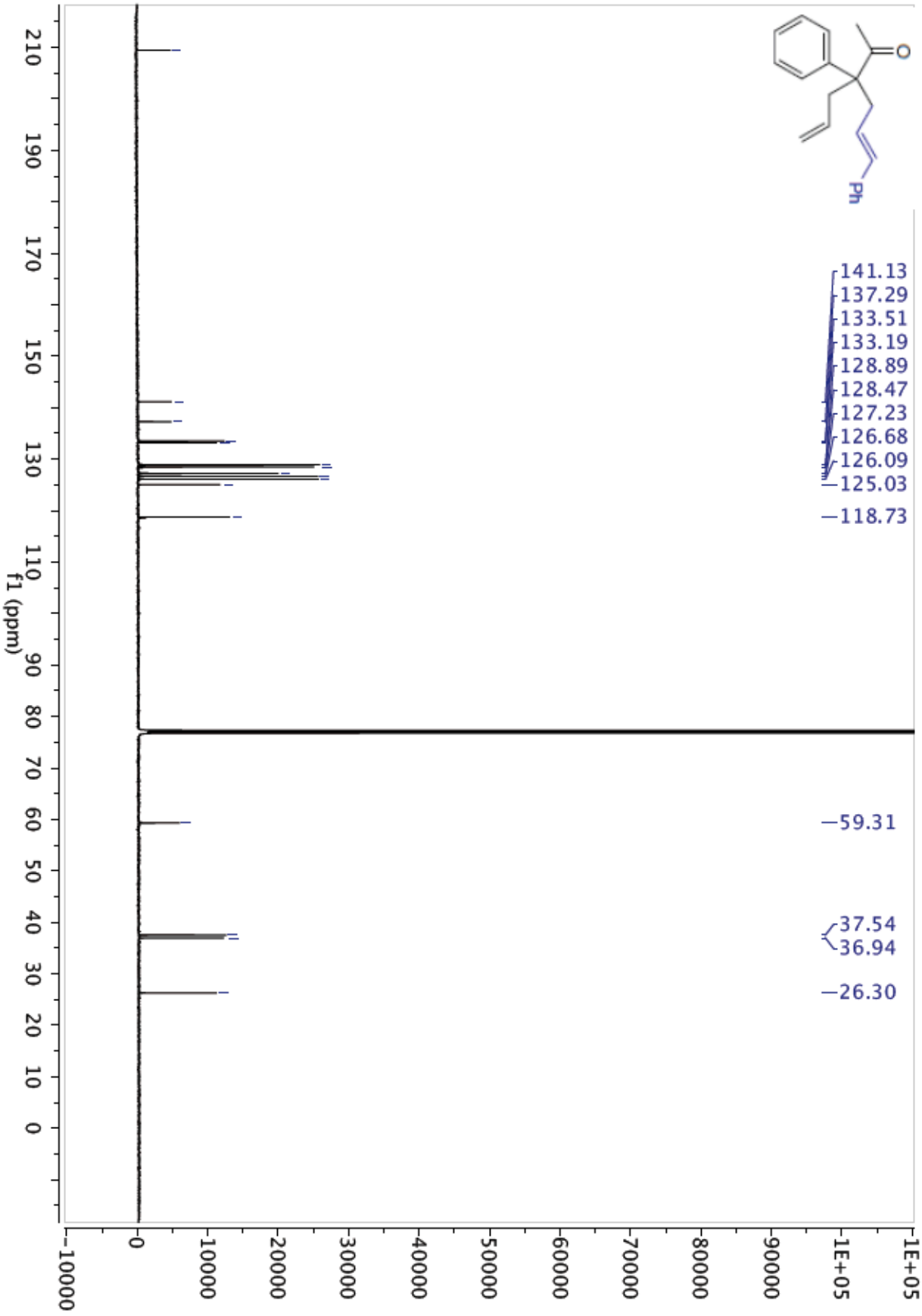
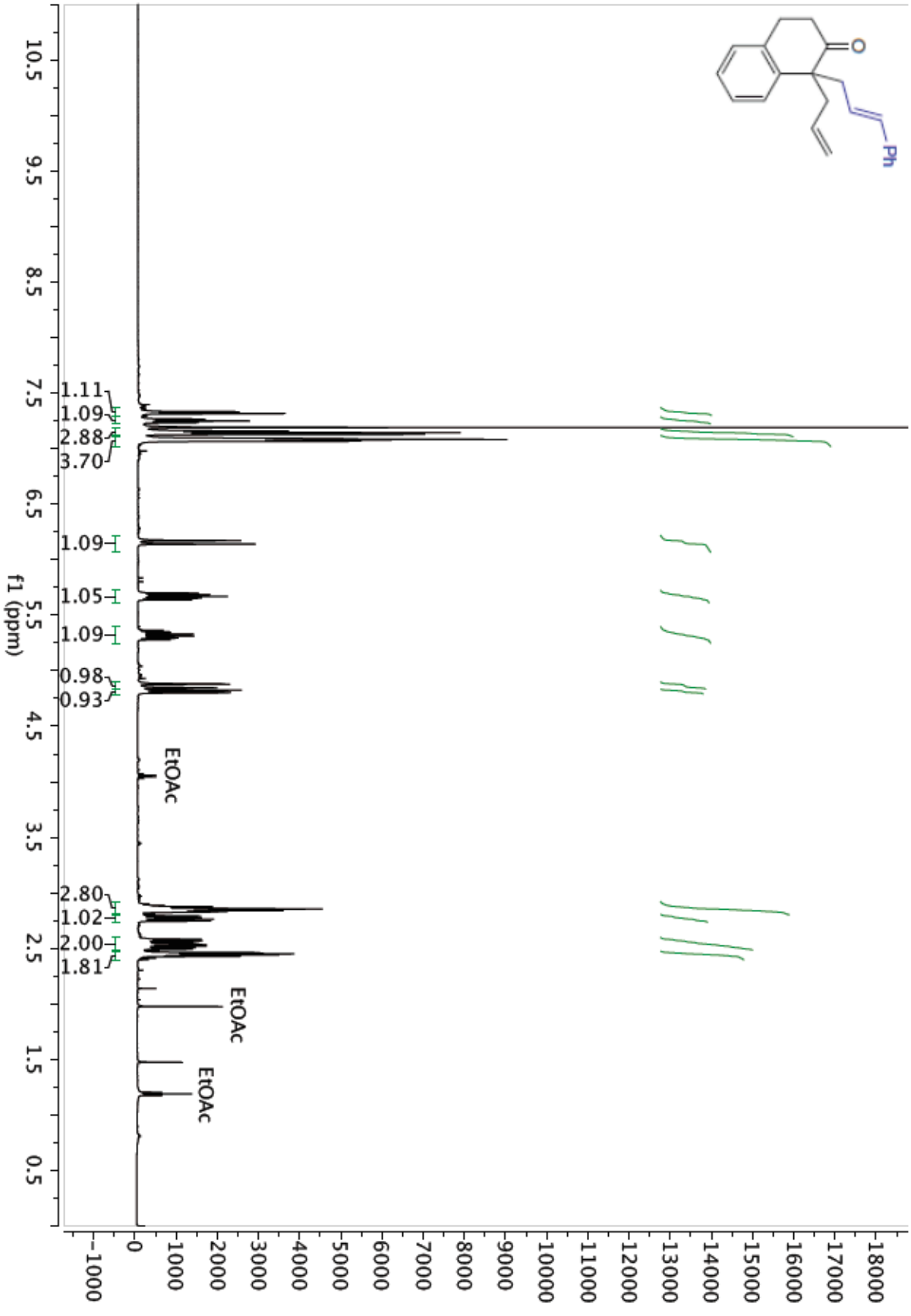


^{1}H NMR for Compound 4z



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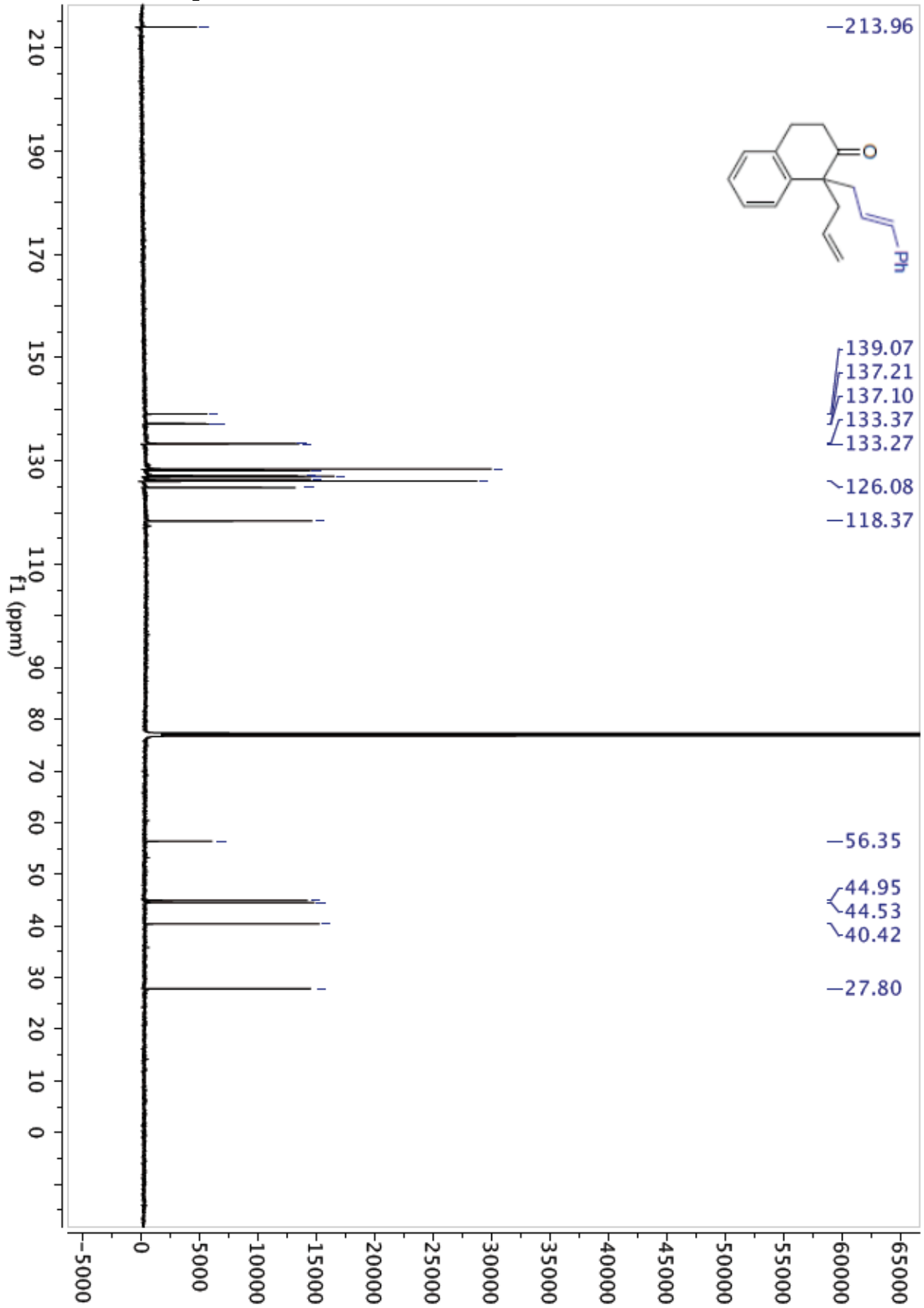
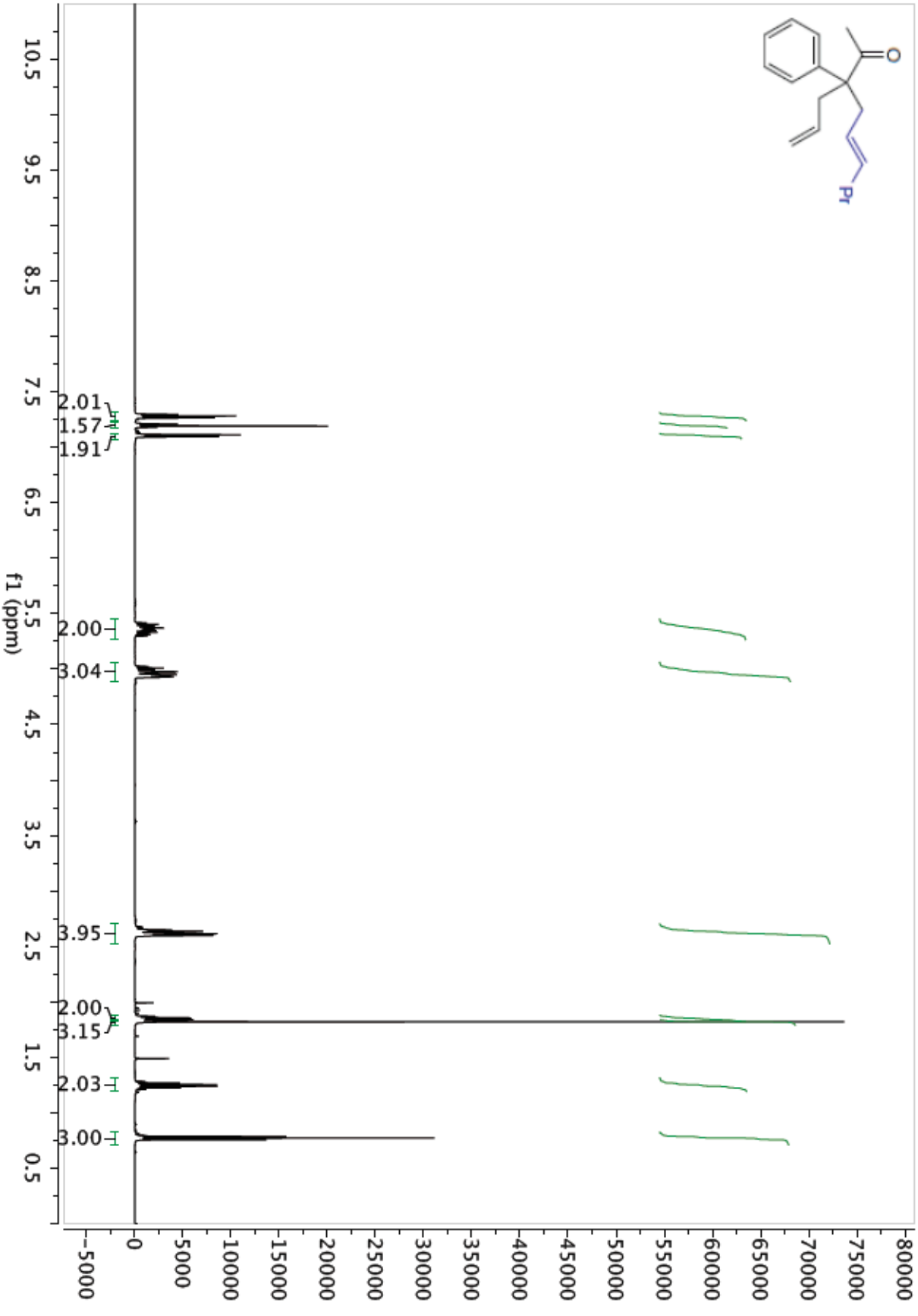
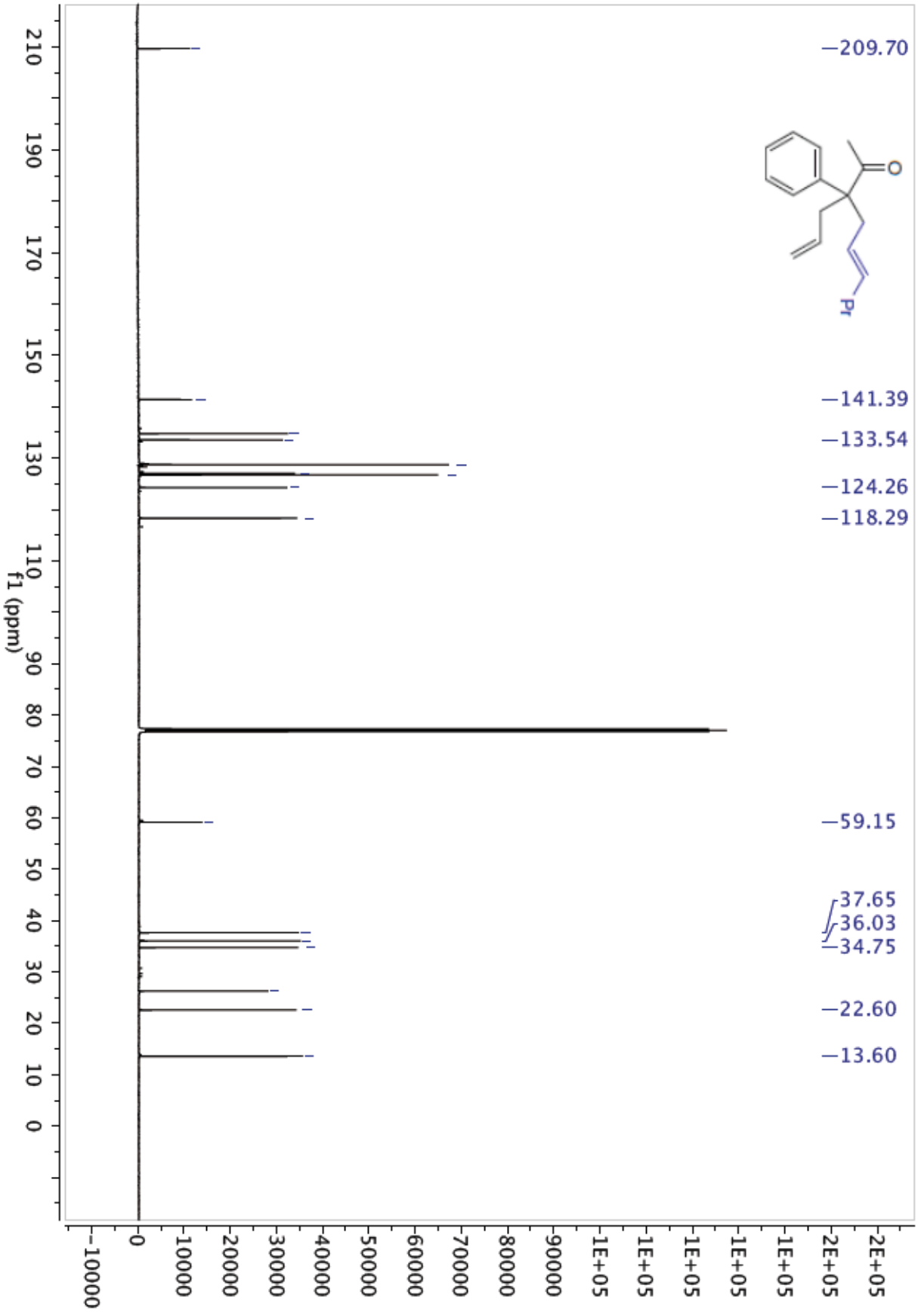


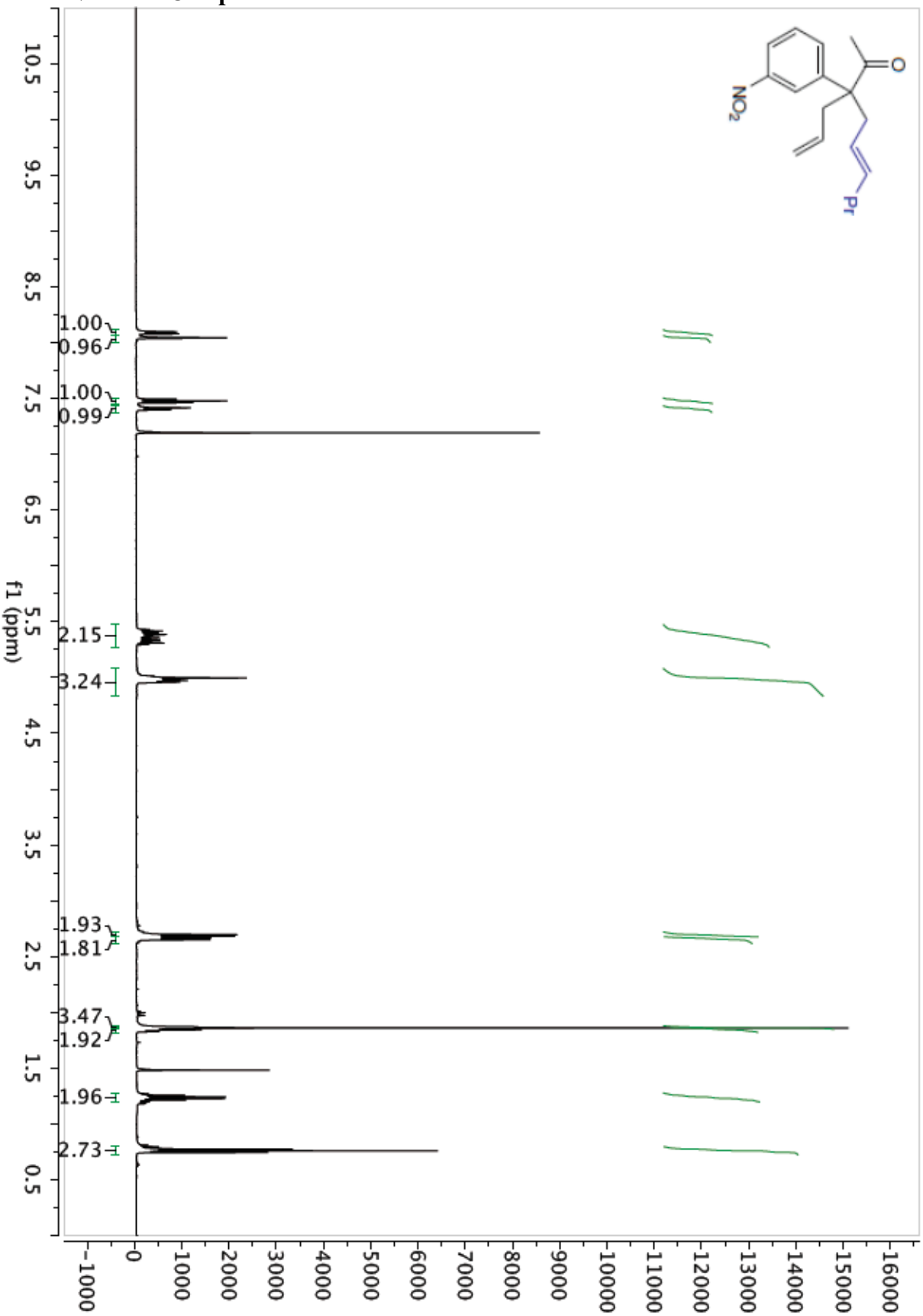
^{1}H NMR for Compound 4aa



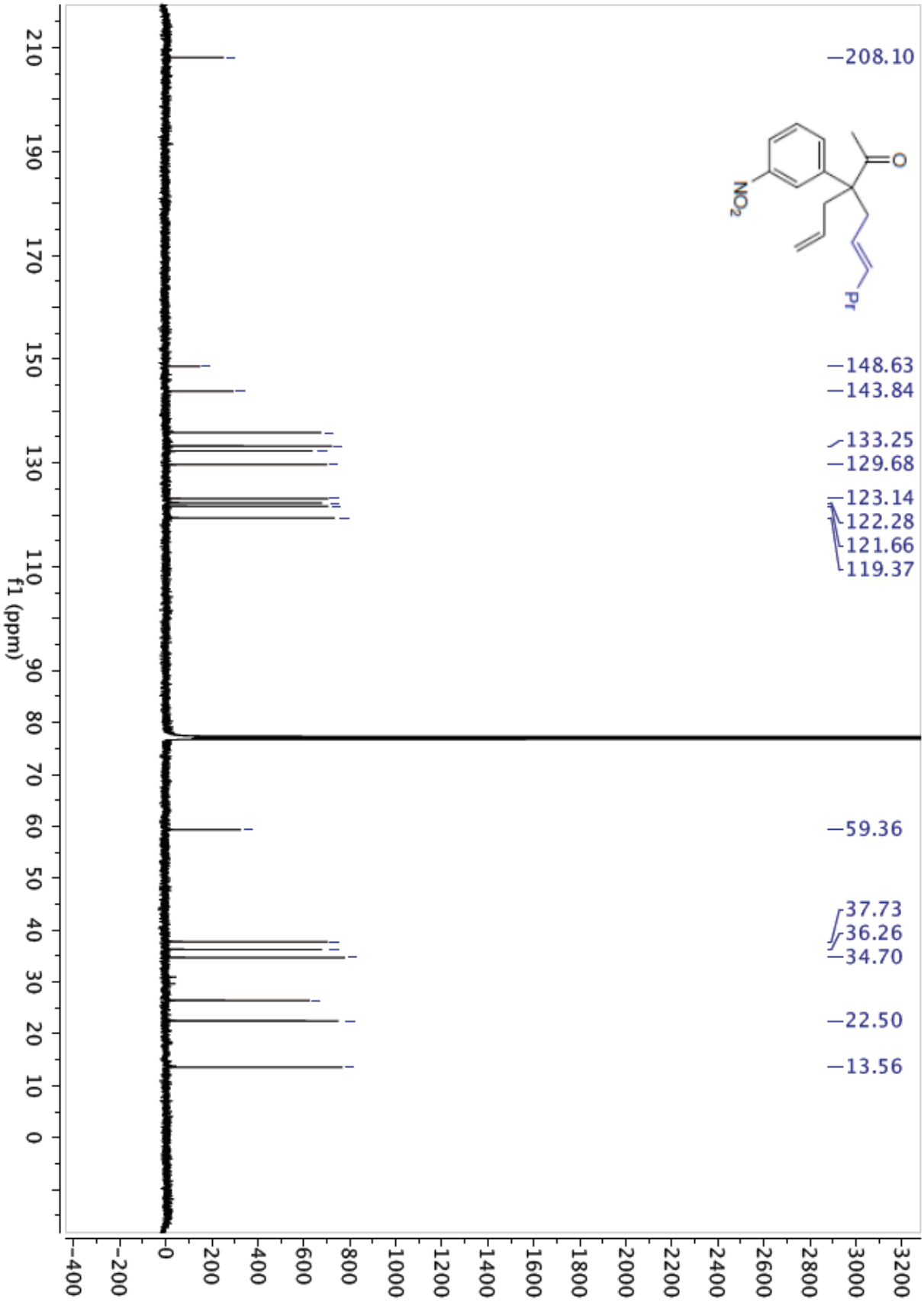
^{13}C NMR for Compound 4aa



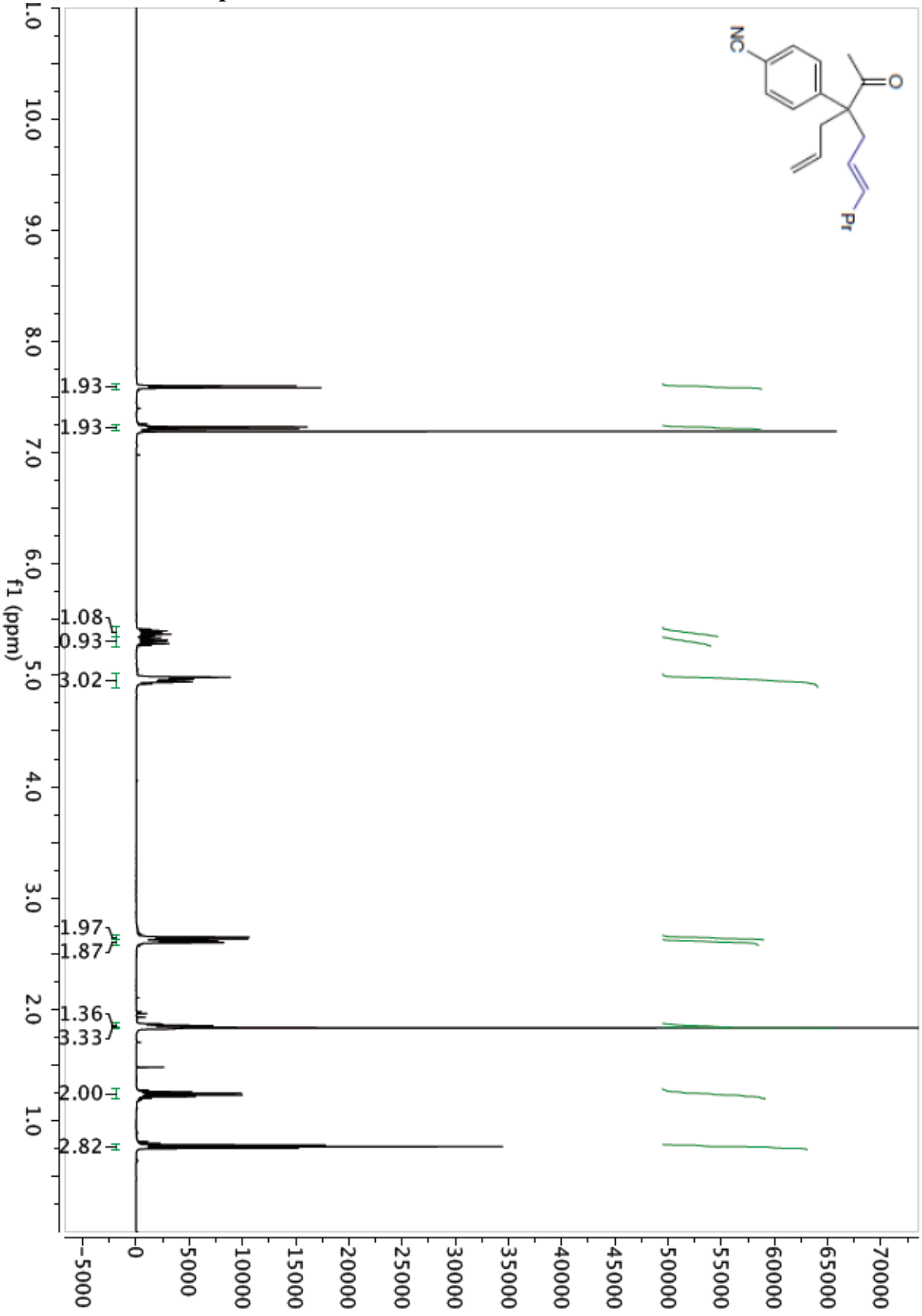
^{1}H NMR for Compound 4bb



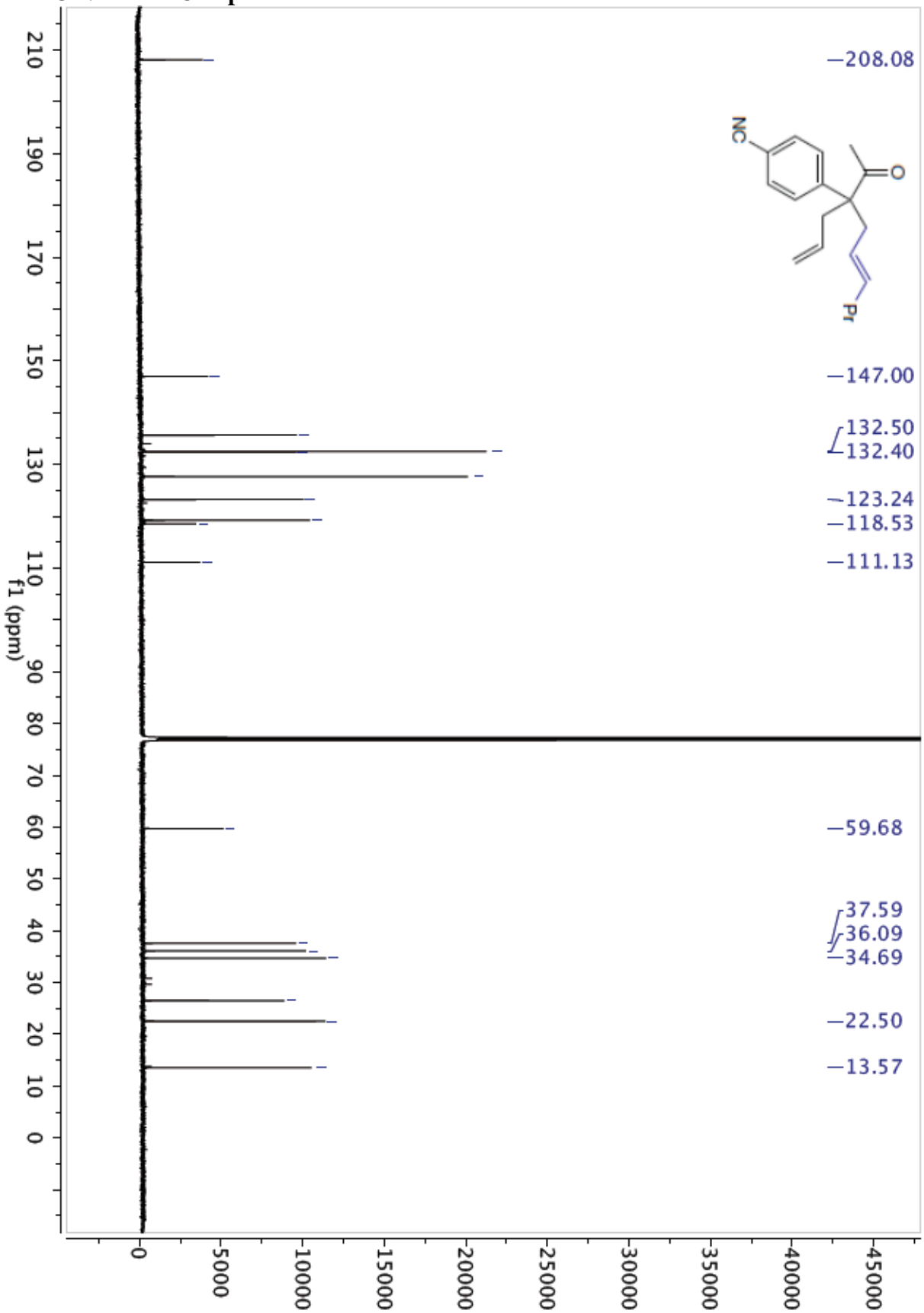
^{13}C NMR for Compound 4bb



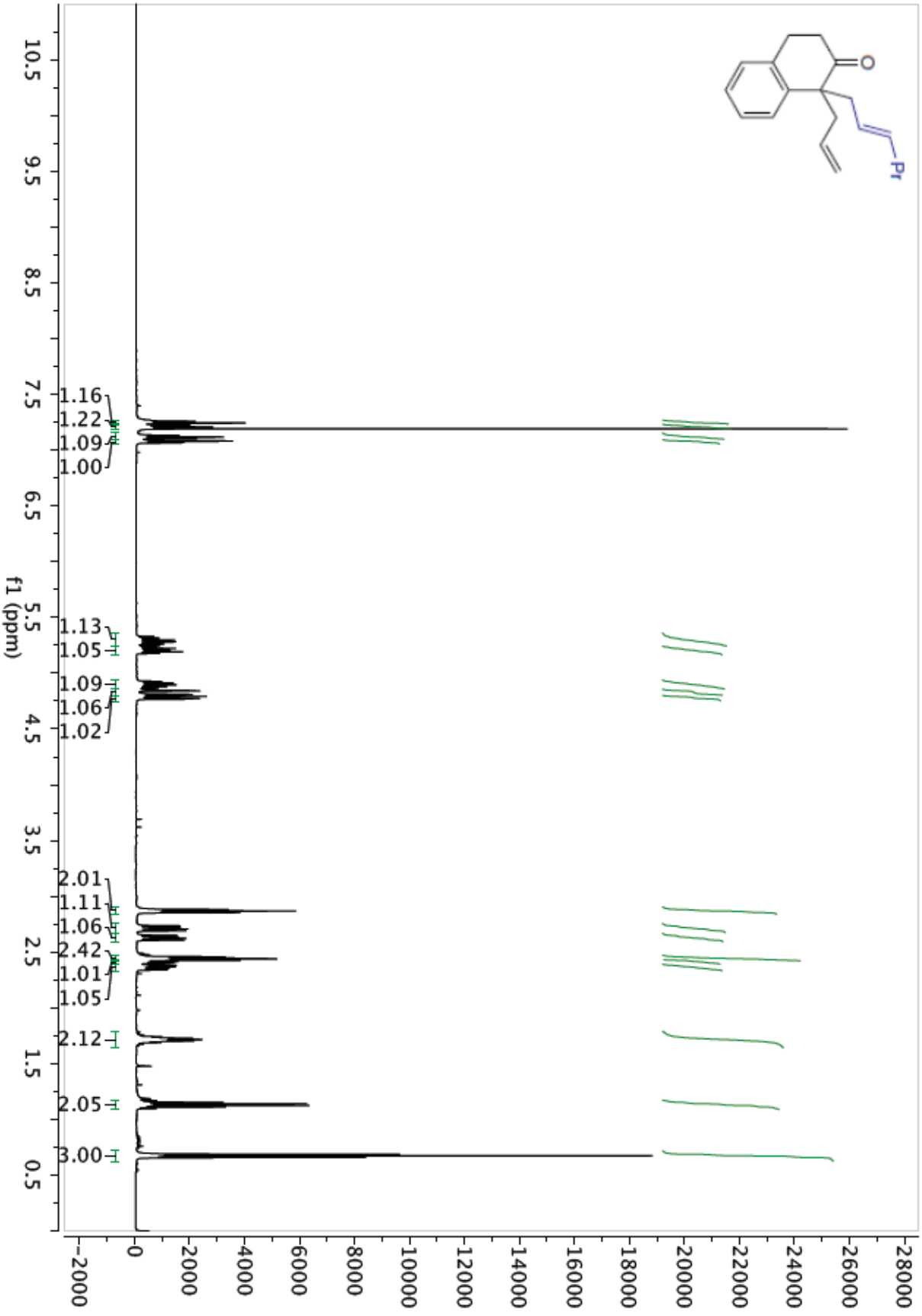
^{1}H NMR for Compound 4cc



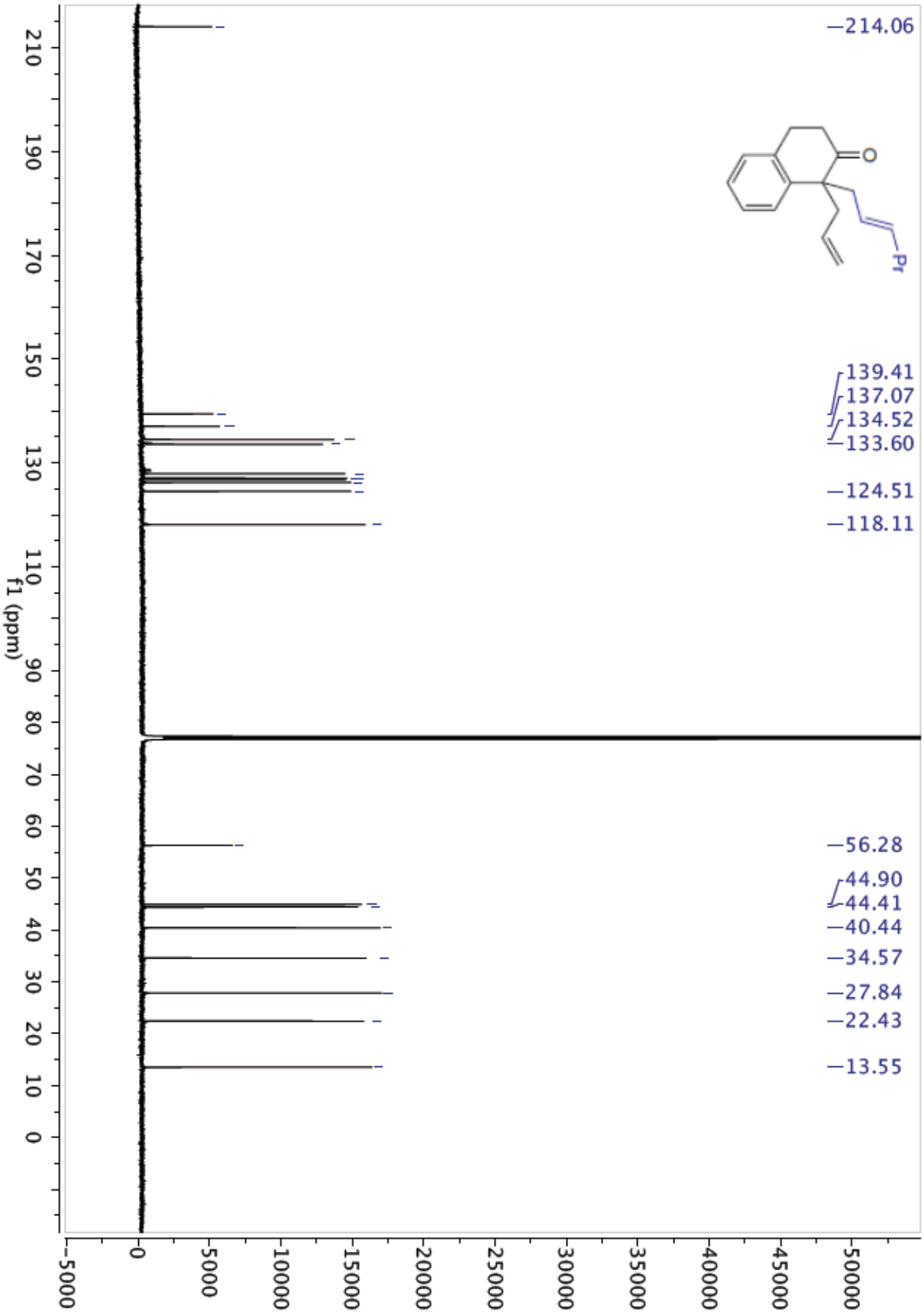
^{13}C NMR for Compound 4cc



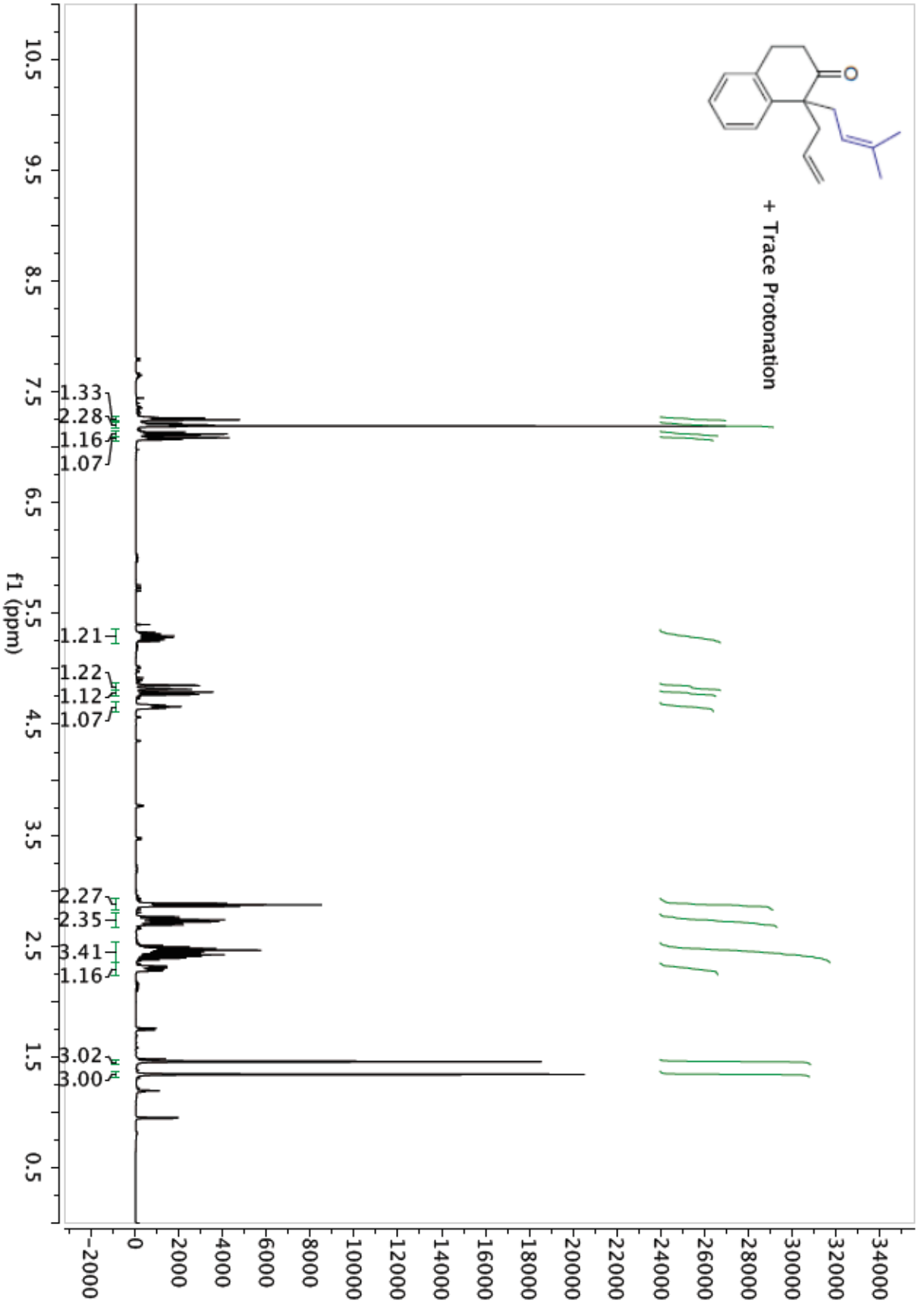
^{1}H NMR for Compound 4dd



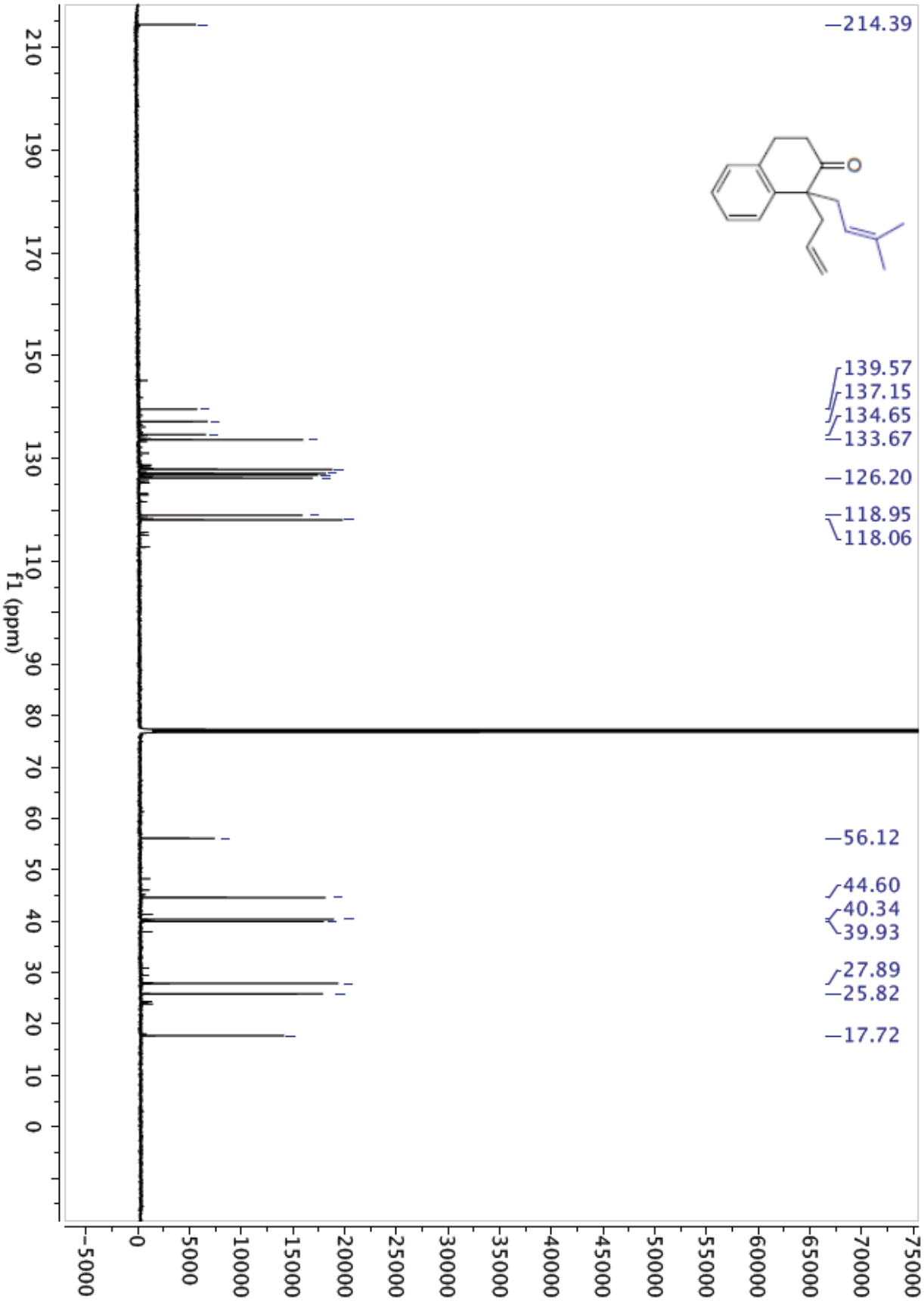
^{13}C NMR for Compound 4dd



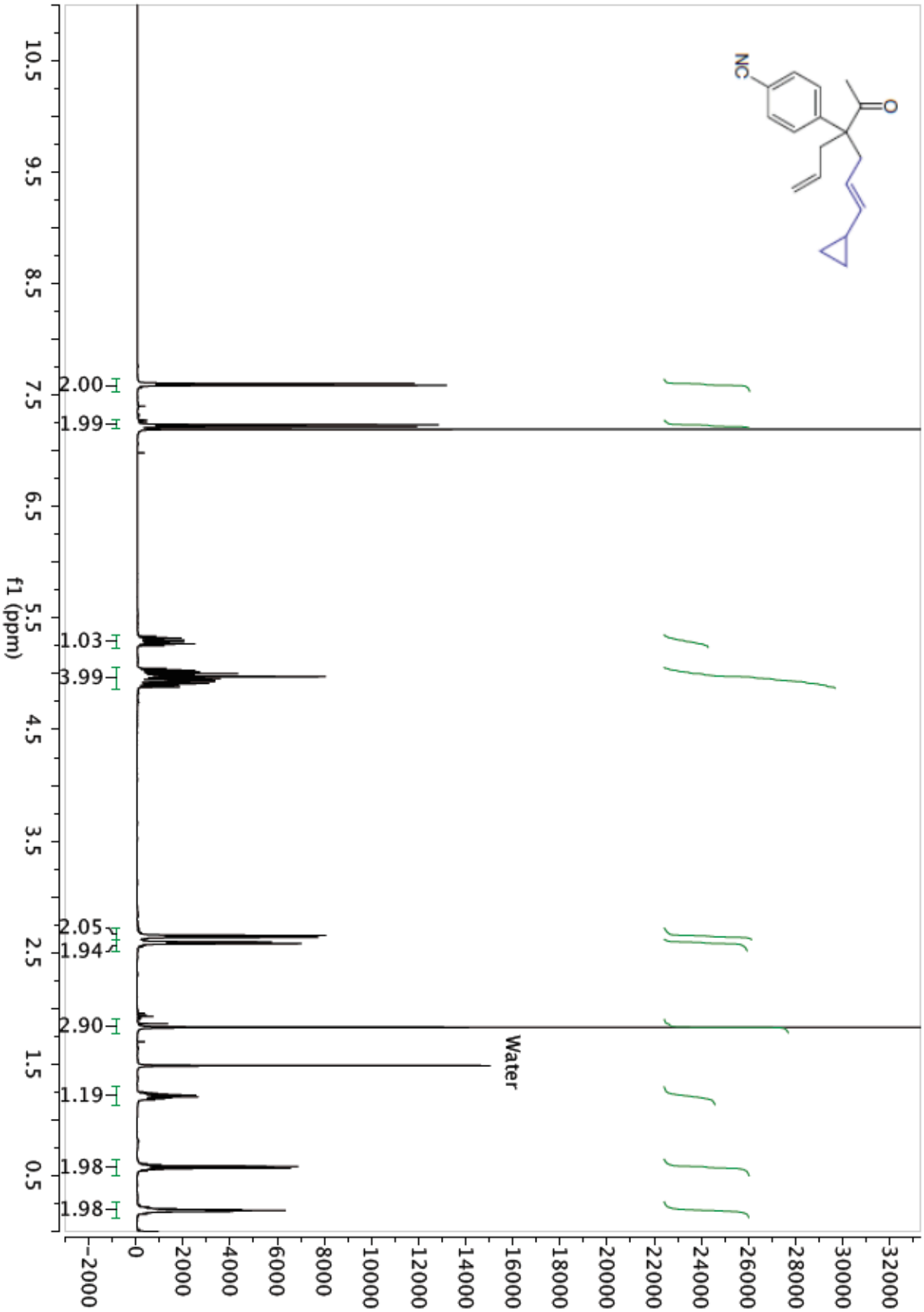
^{1}H NMR for Compound 4ee



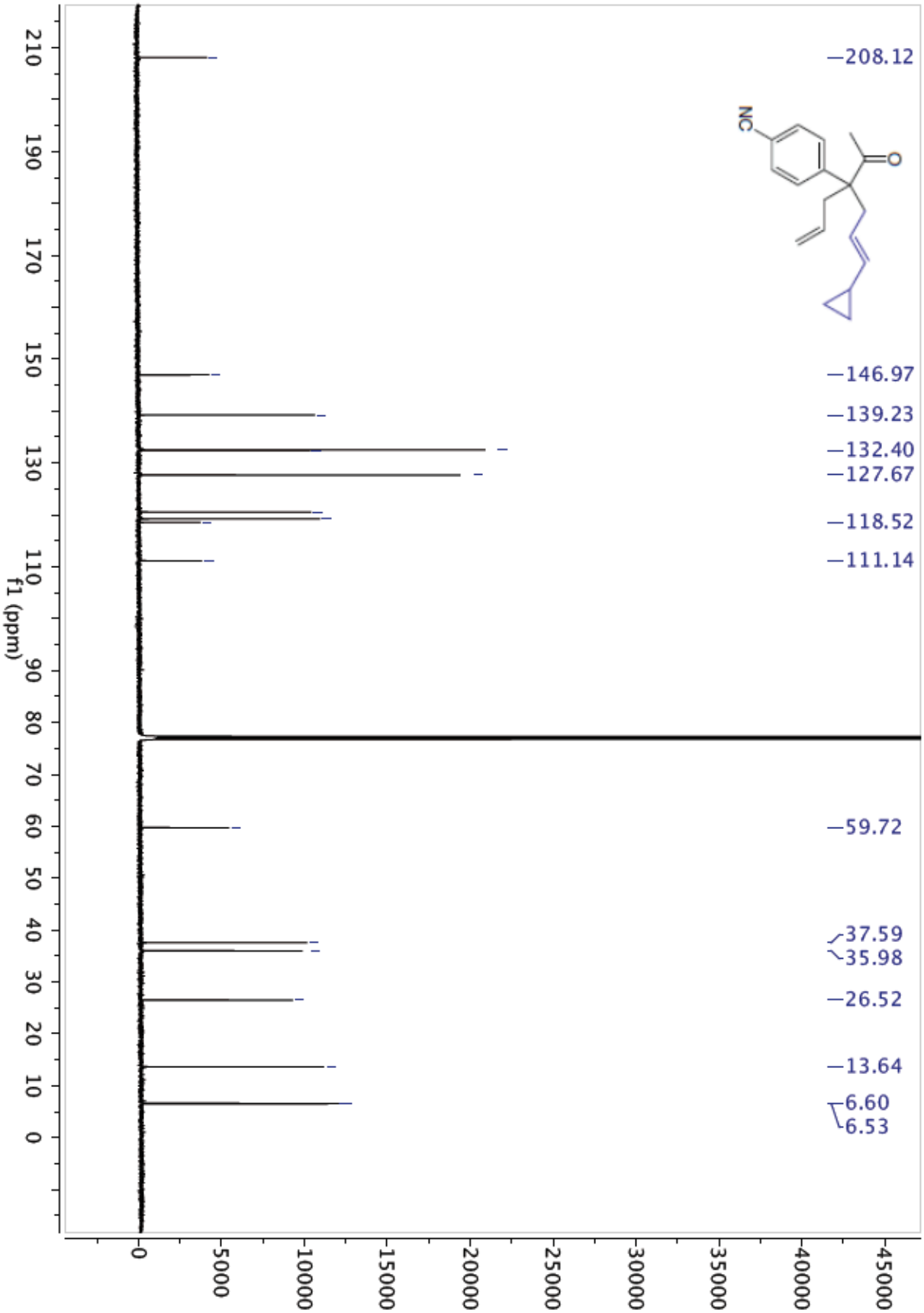
^{13}C NMR for Compound 4ee



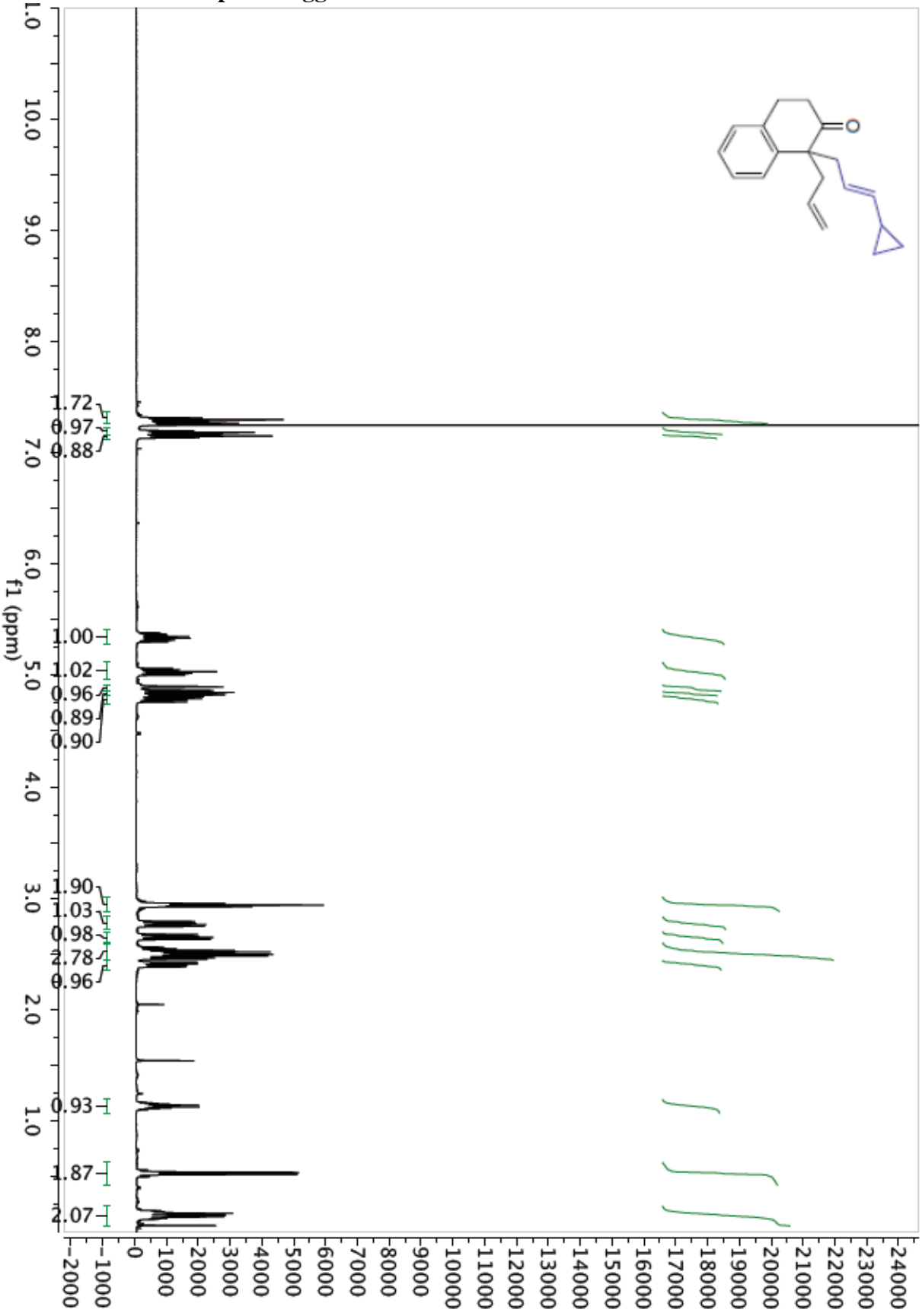
^{1}H NMR for Compound 4ff



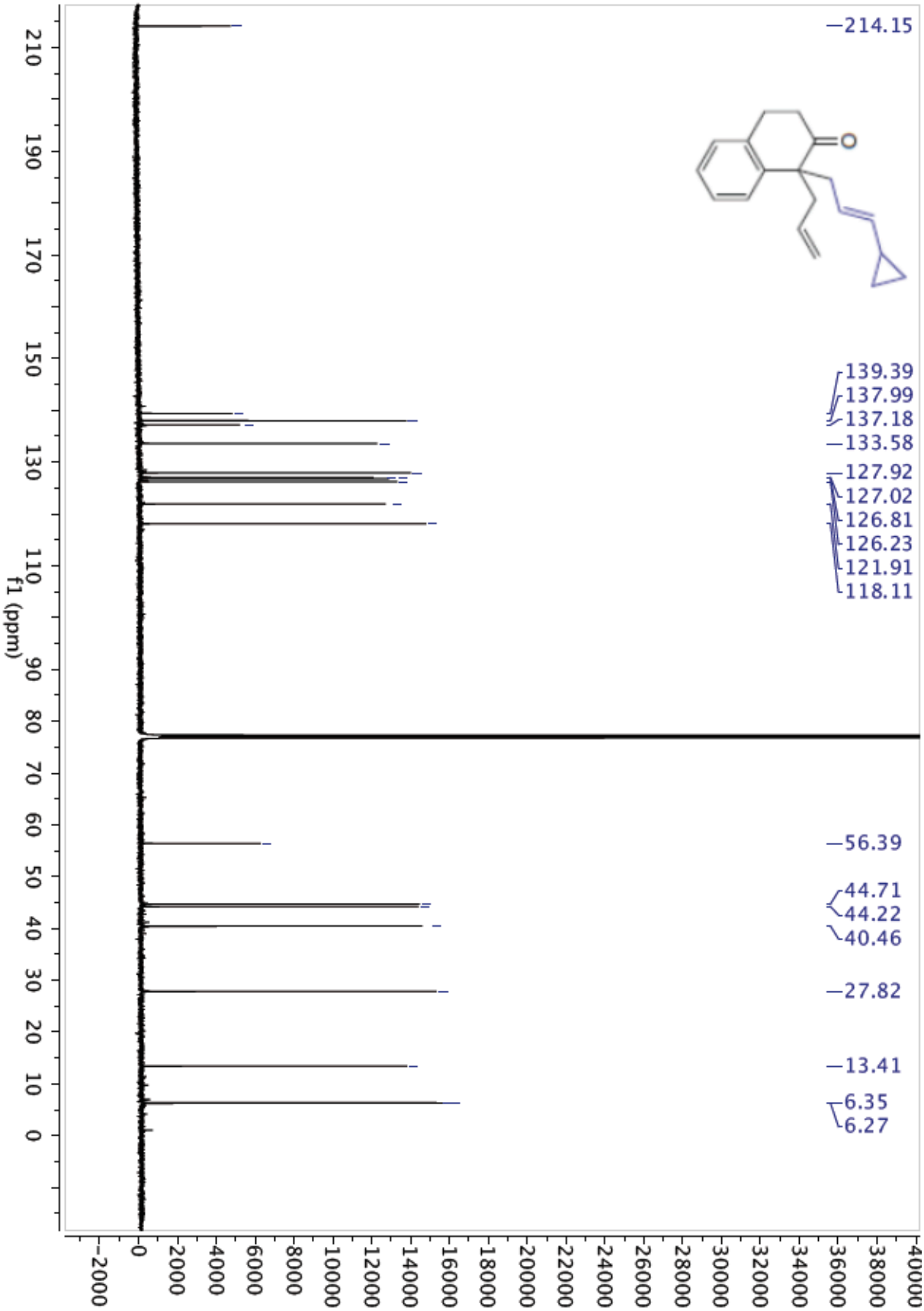
^{13}C NMR for Compound 4ff



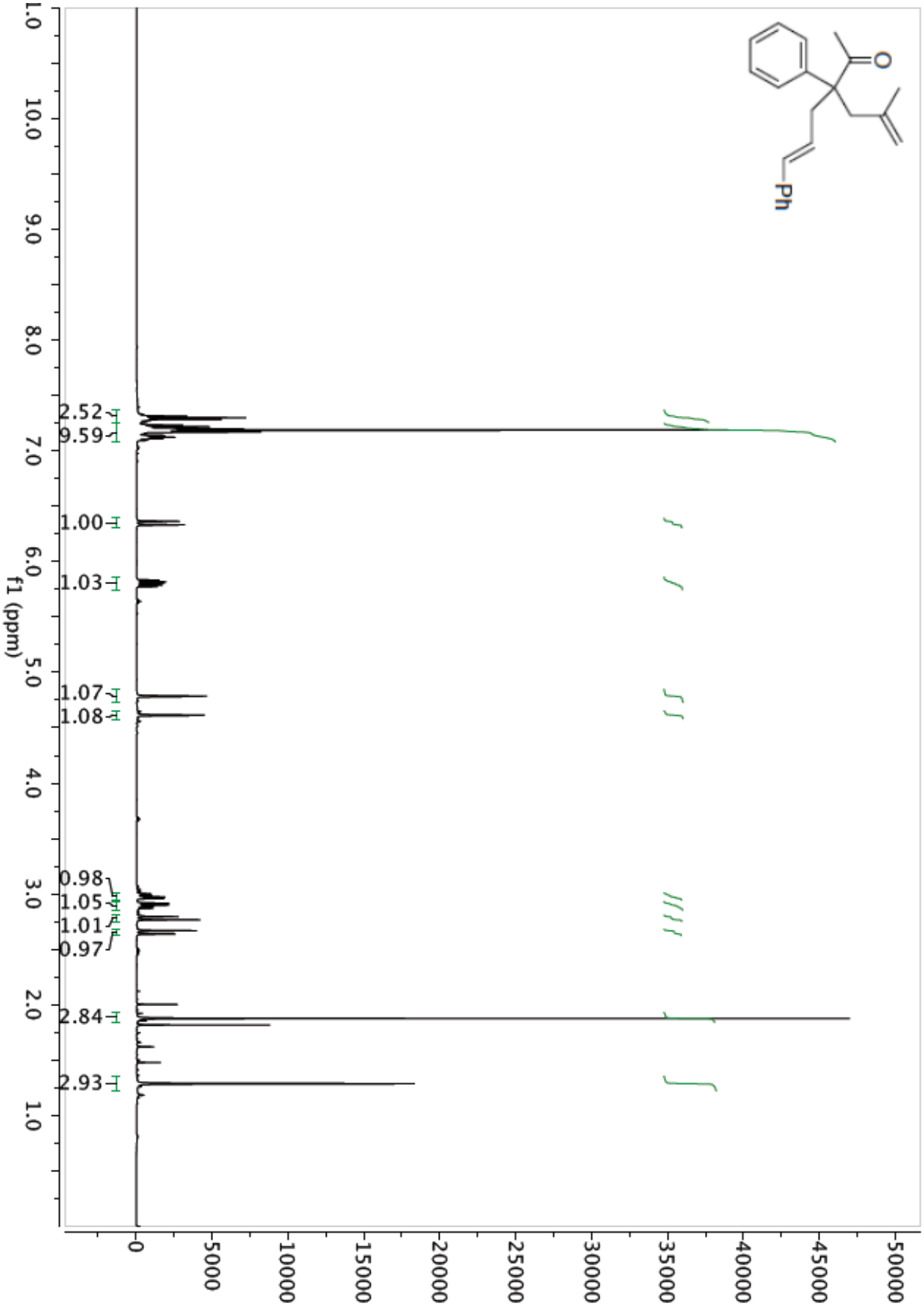
^{1}H NMR for Compound 4gg



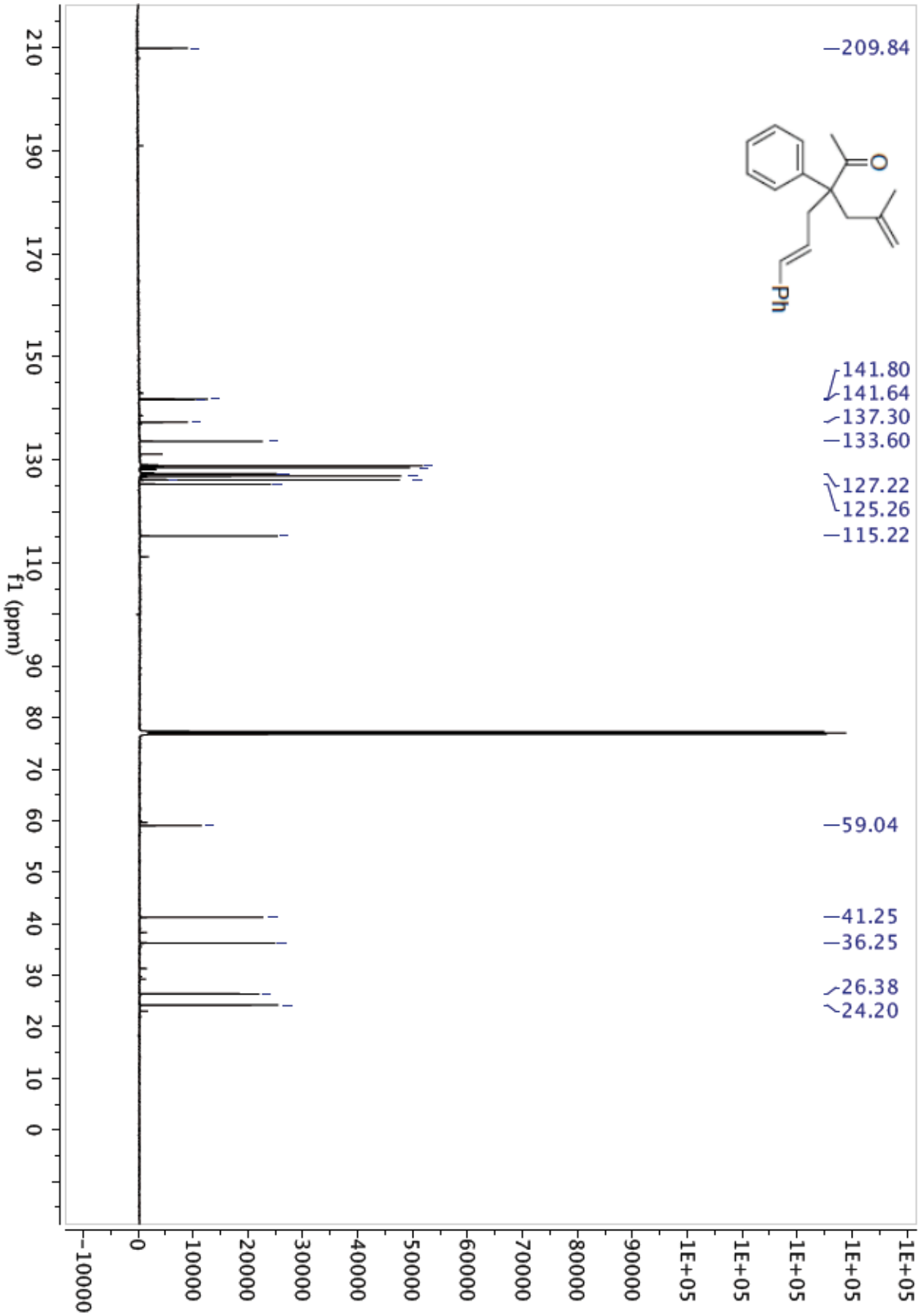
^{13}C NMR for Compound 4gg



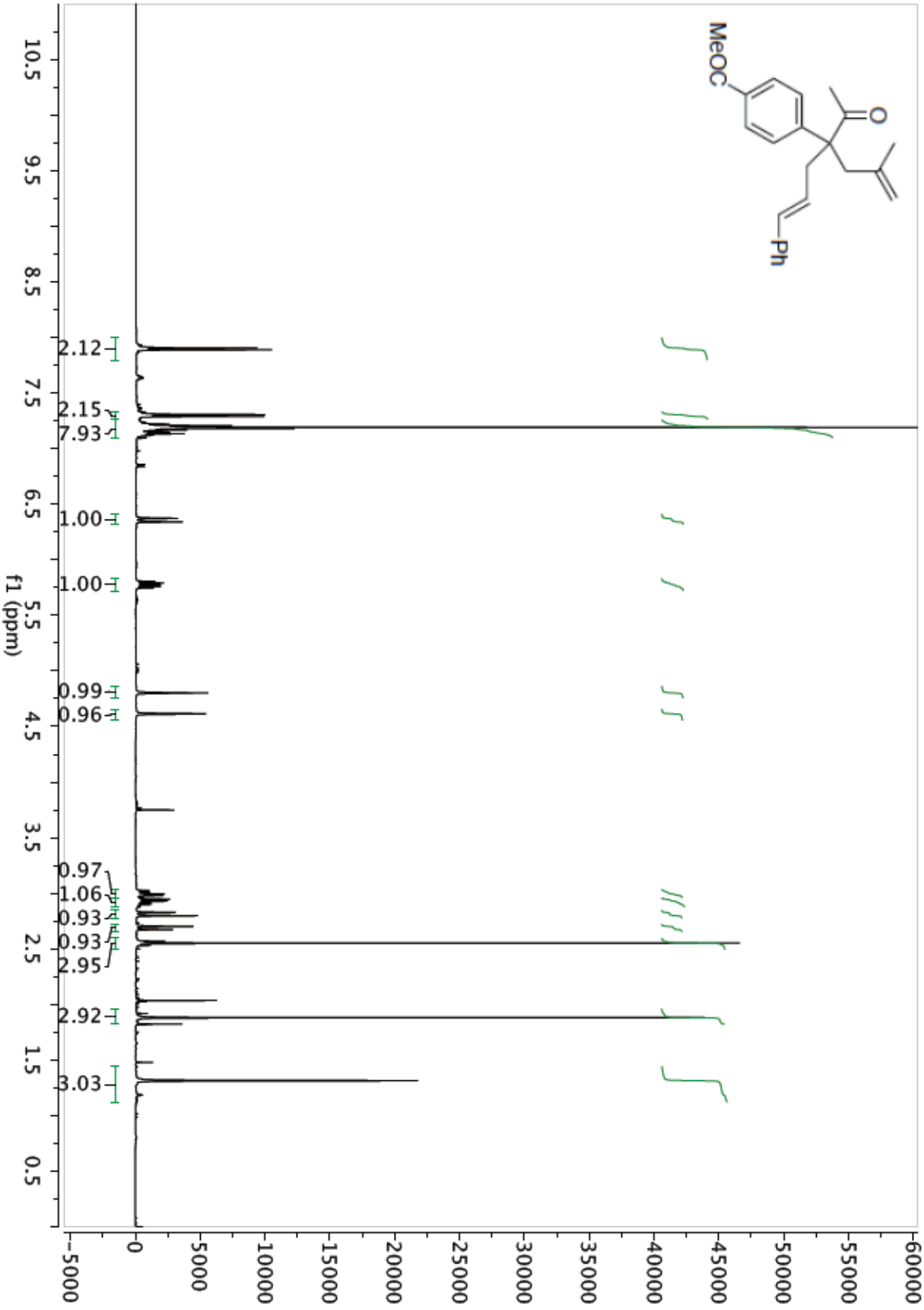
^{1}H NMR for Compound 4hh



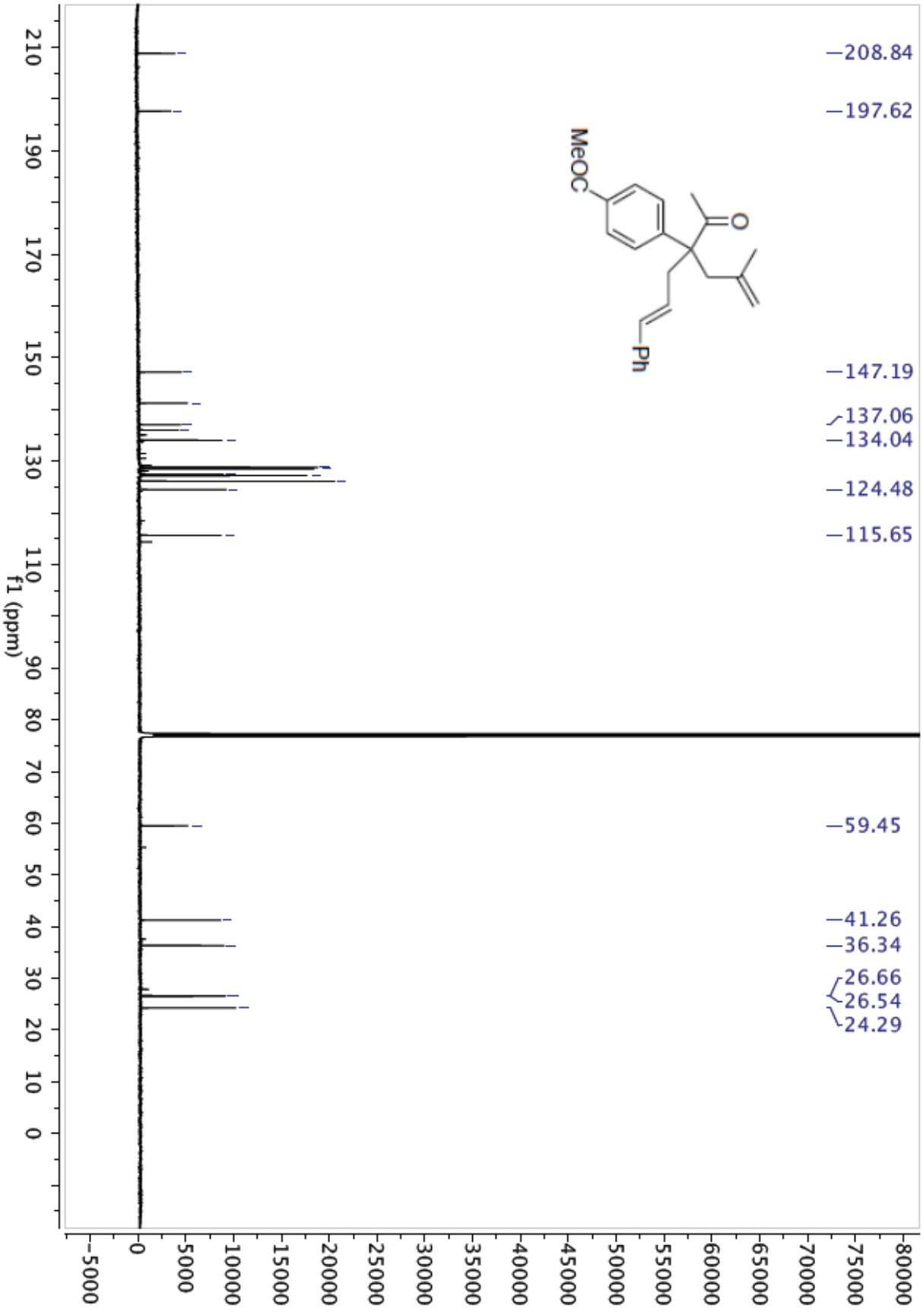
^{13}C NMR for Compound 4hh



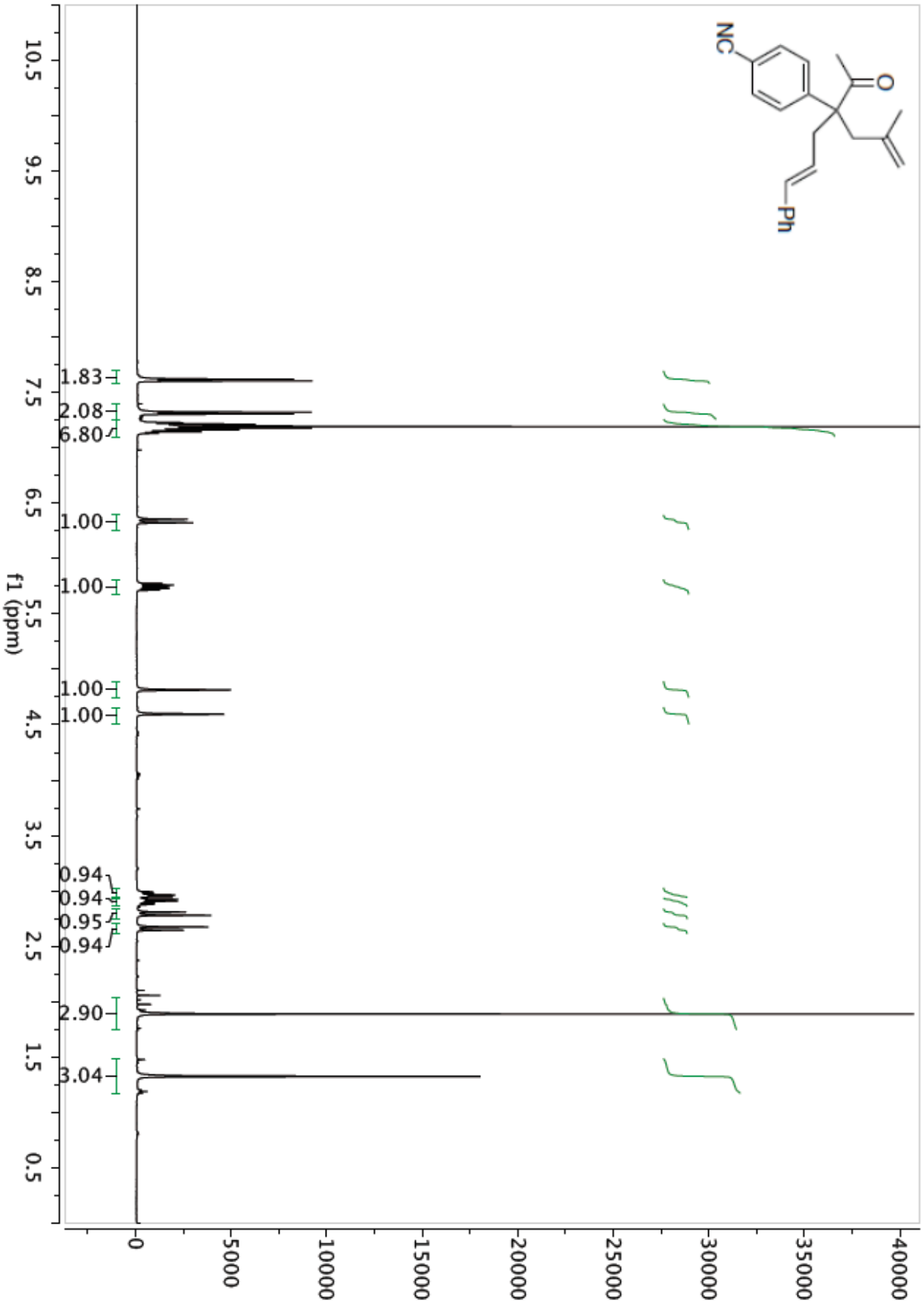
^{1}H NMR for Compound 4ii



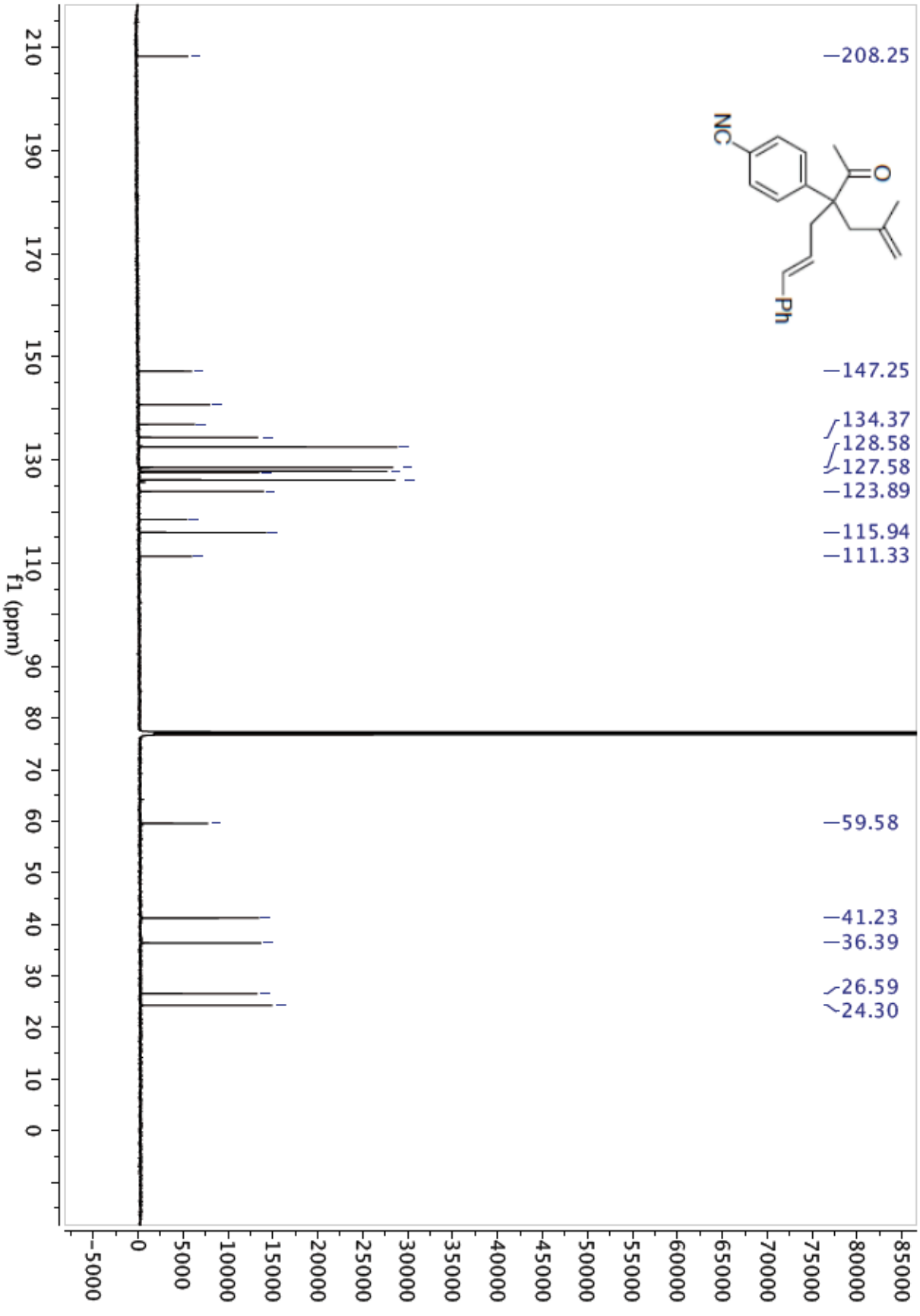
^{13}C NMR for Compound 4ii



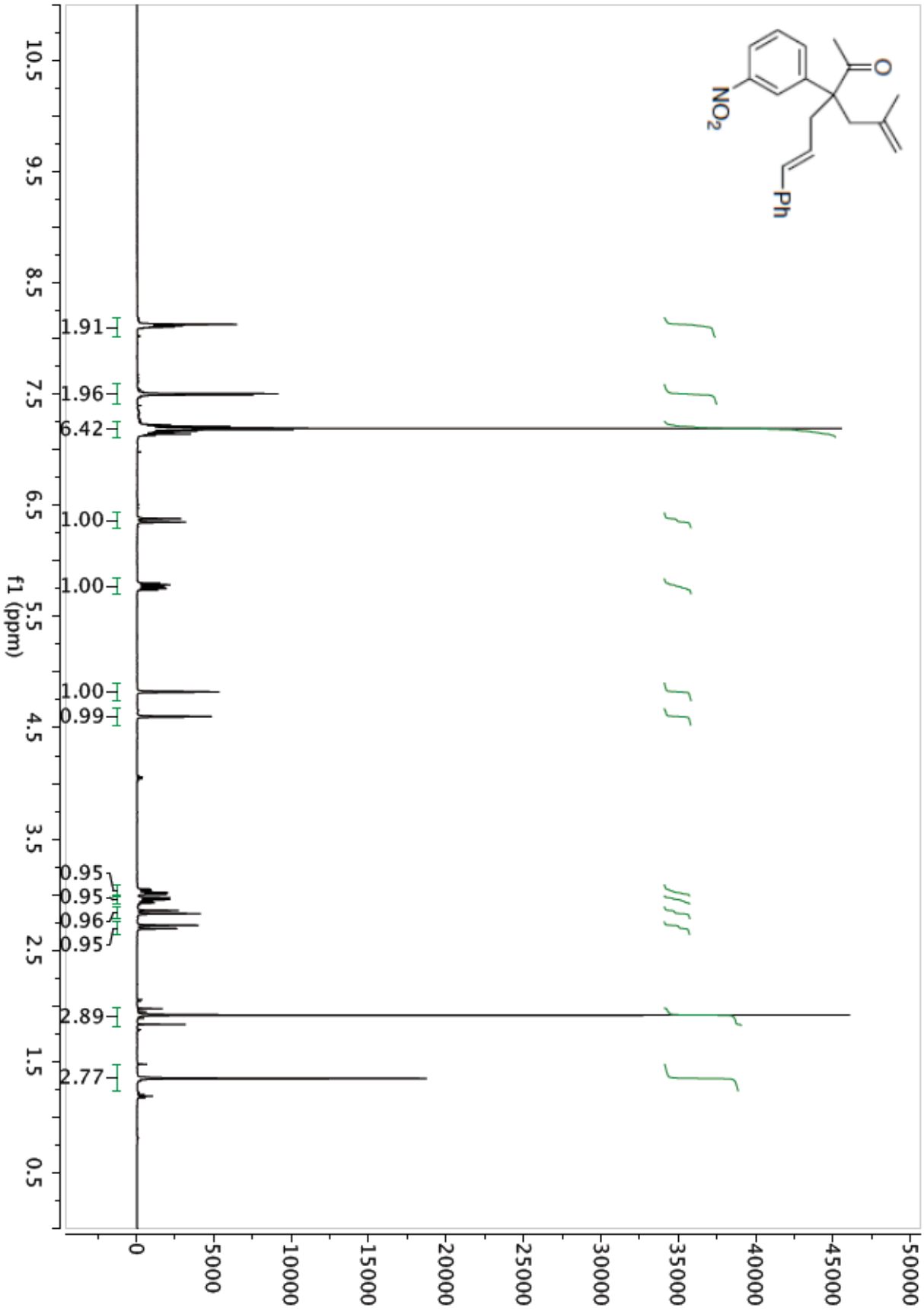
^{1}H NMR for Compound 4jj



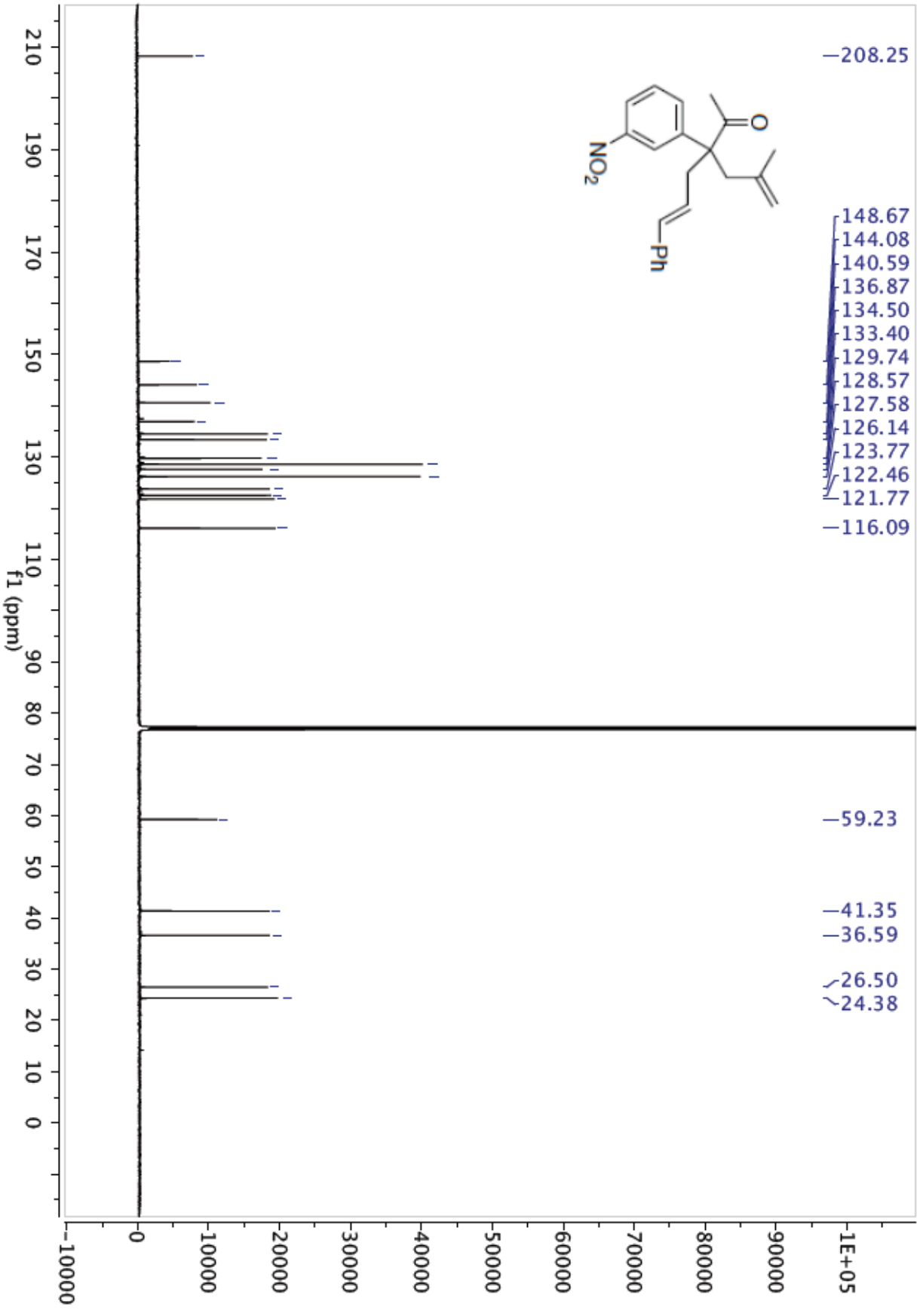
^{13}C NMR for Compound 4jj



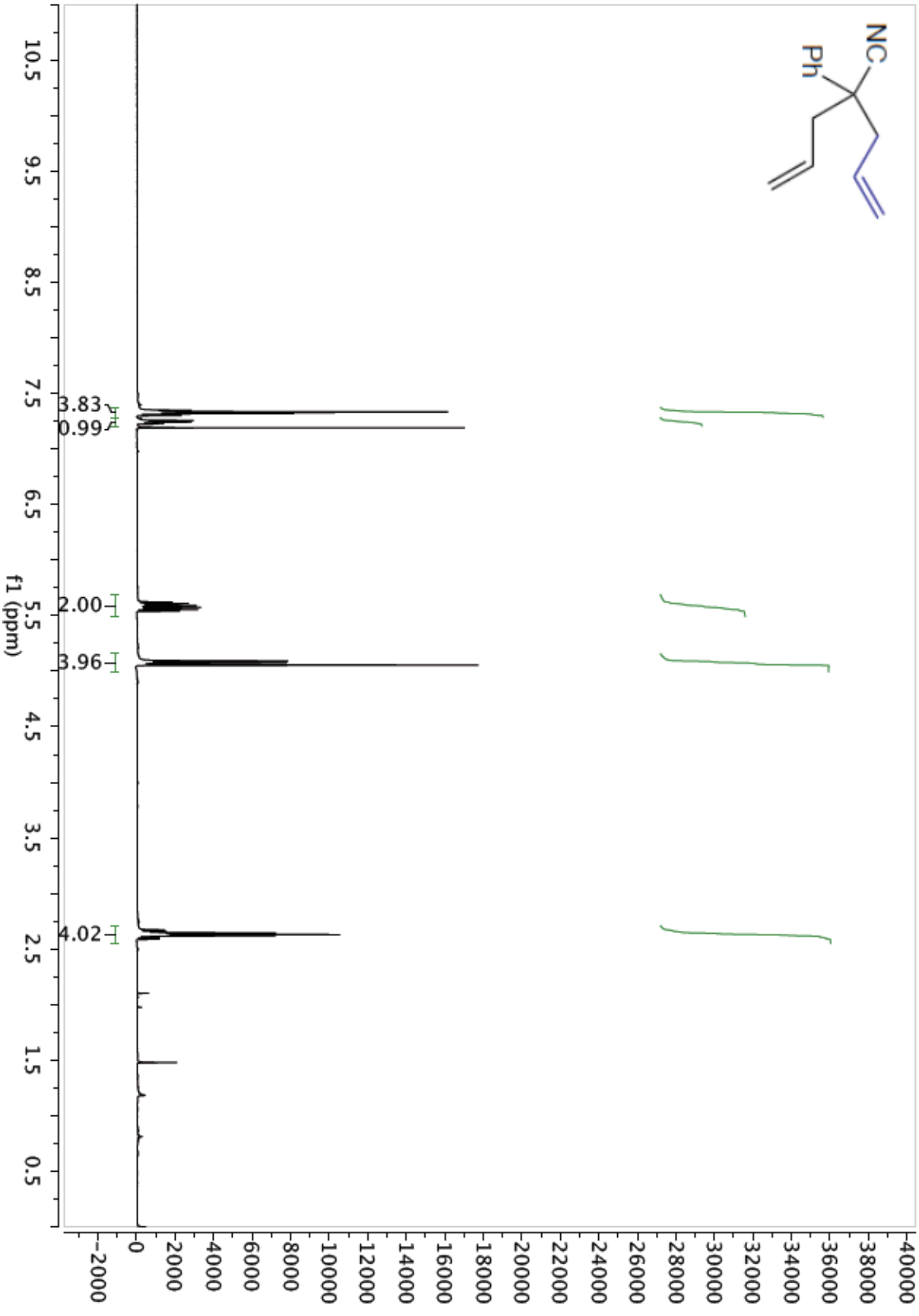
^{1}H NMR for Compound 4kk



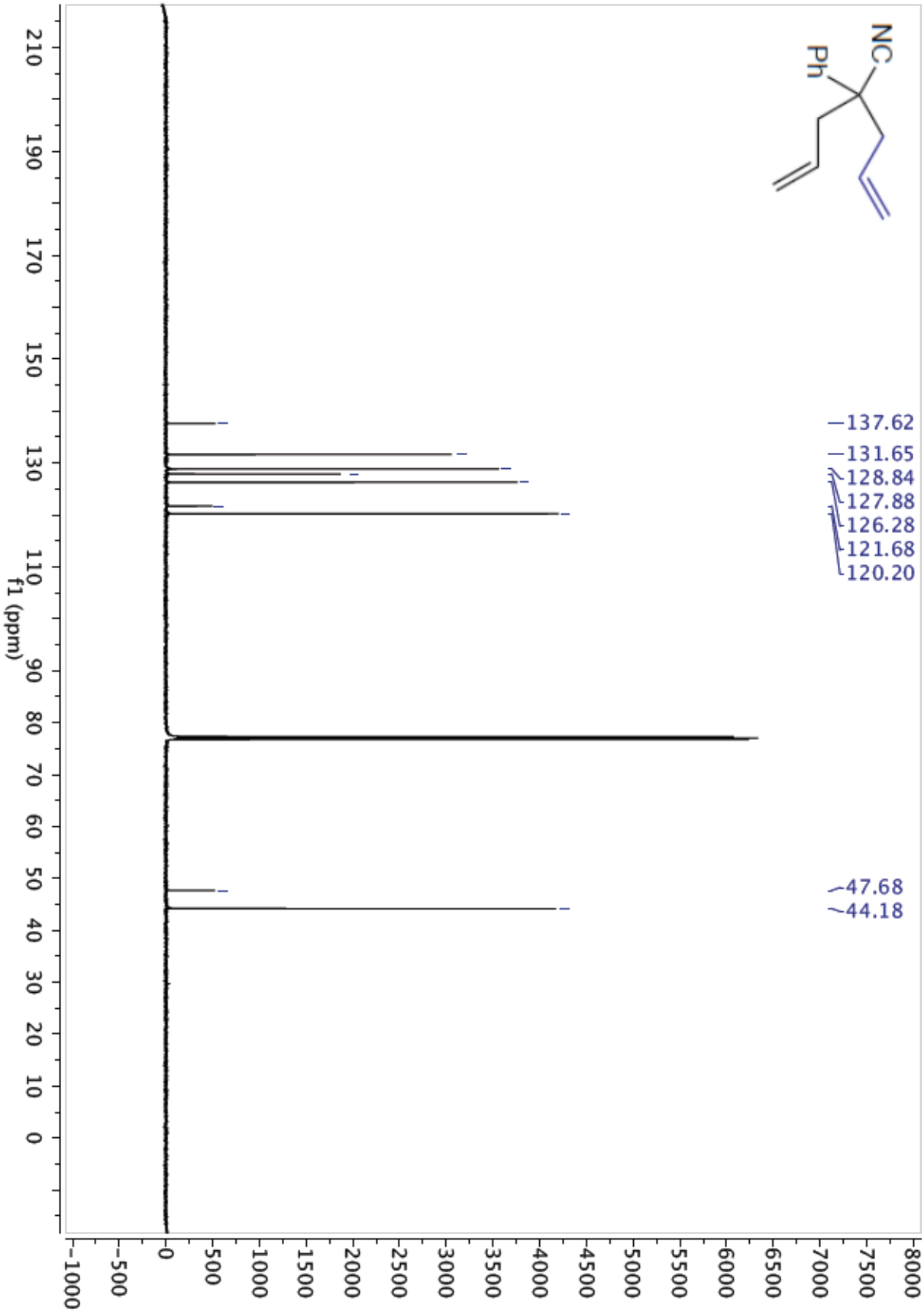
^{13}C NMR for Compound 4kk



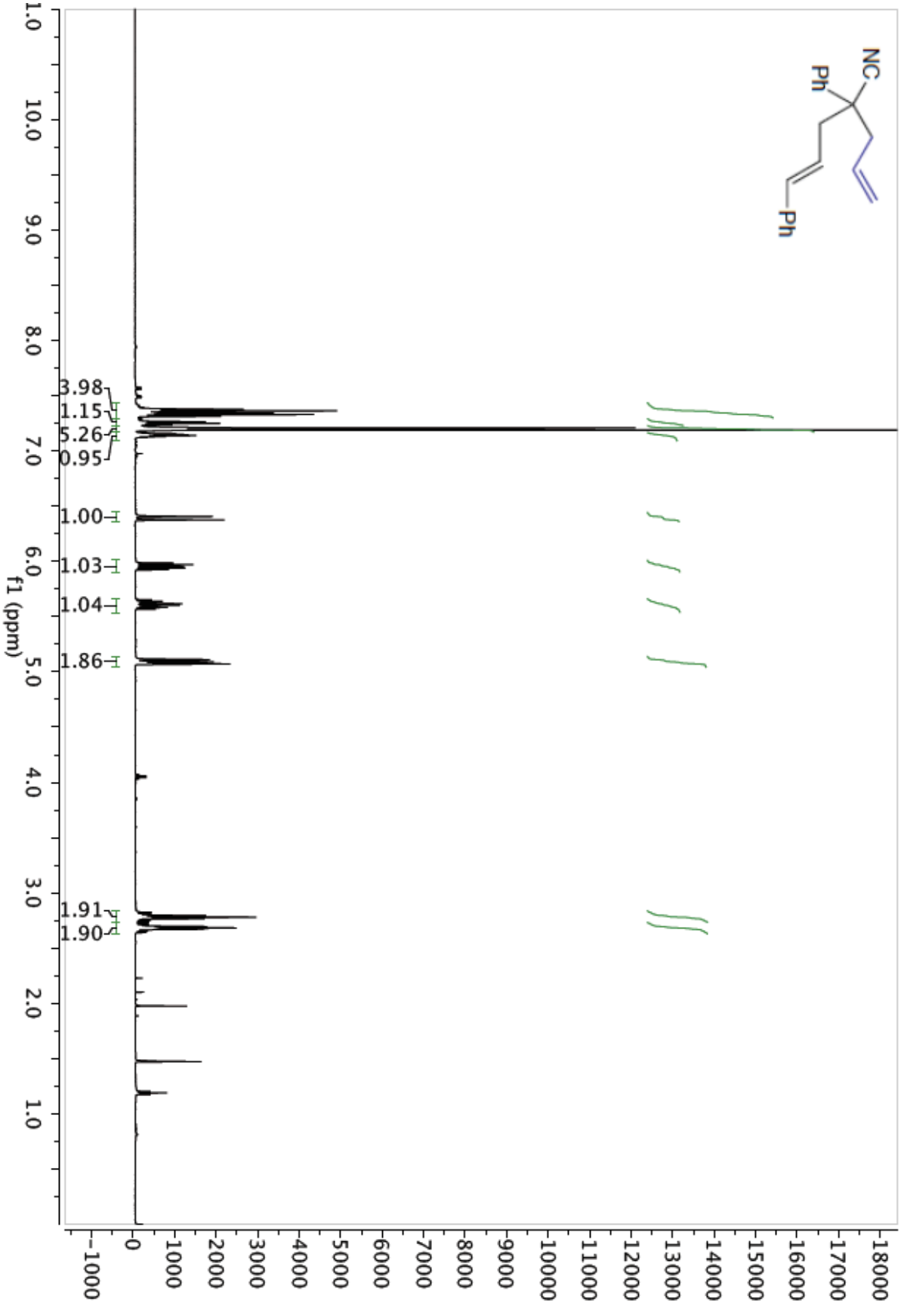
^{1}H NMR for Compound 5a



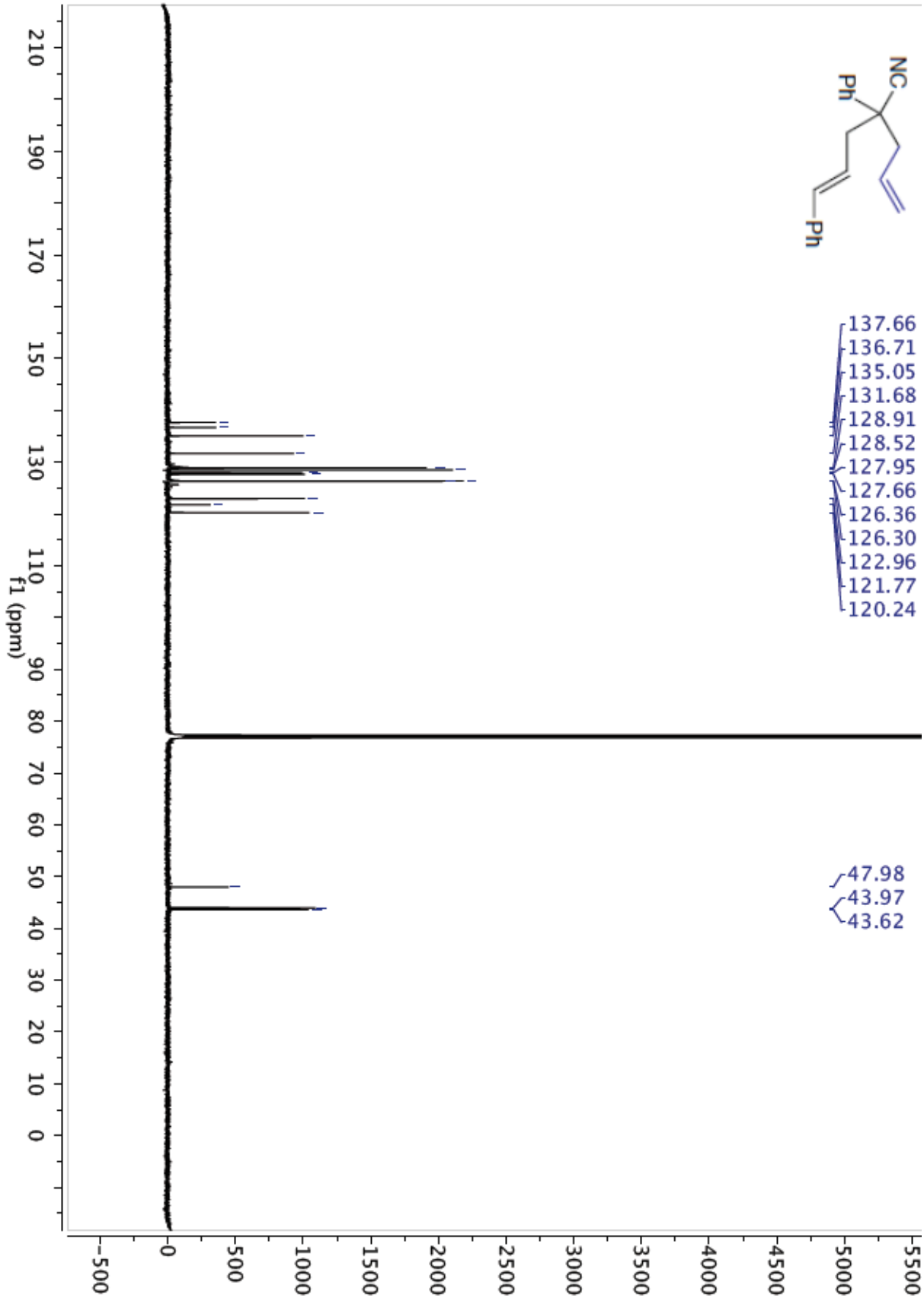
^{13}C NMR for Compound 5a



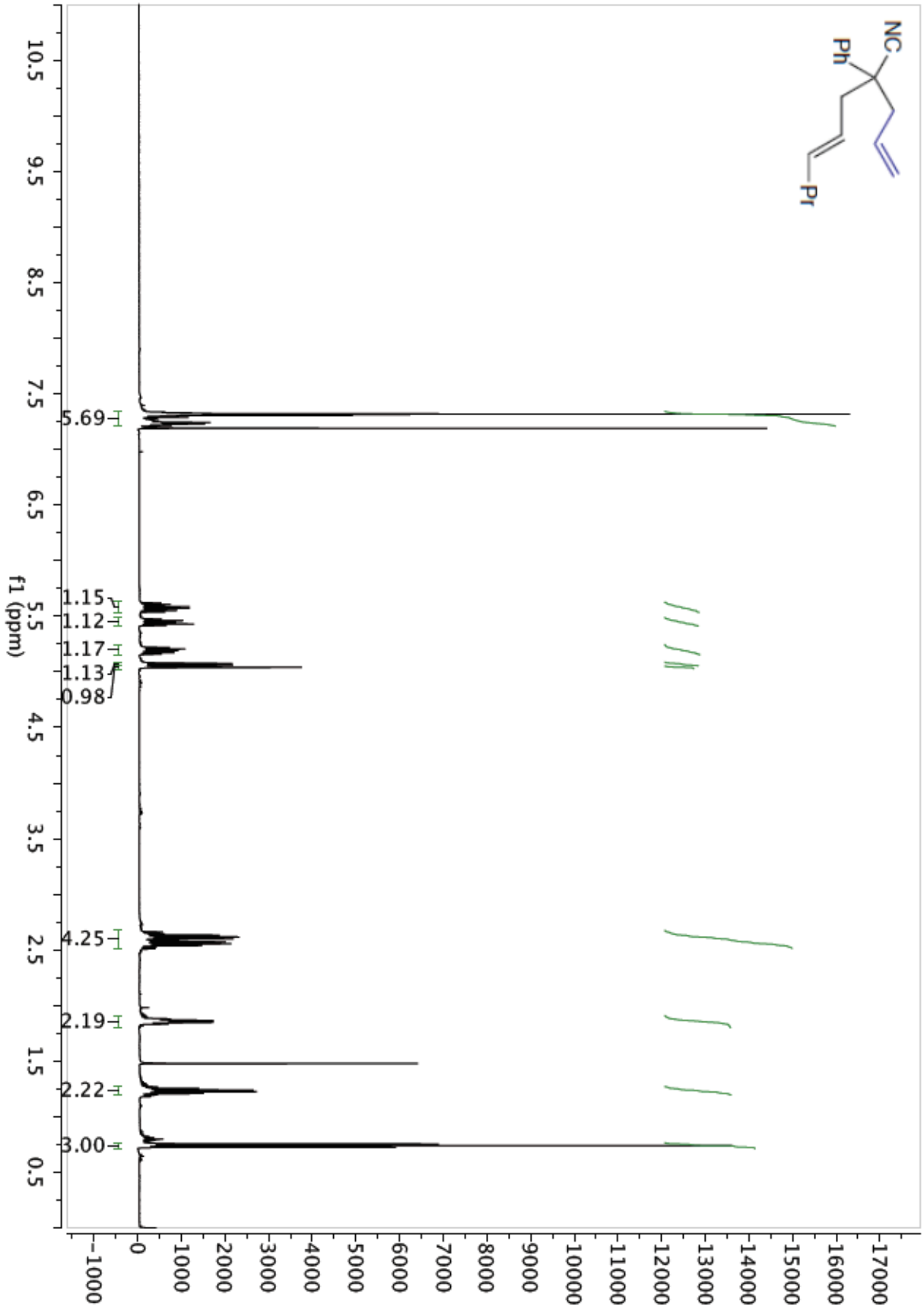
^{1}H NMR for Compound 5b



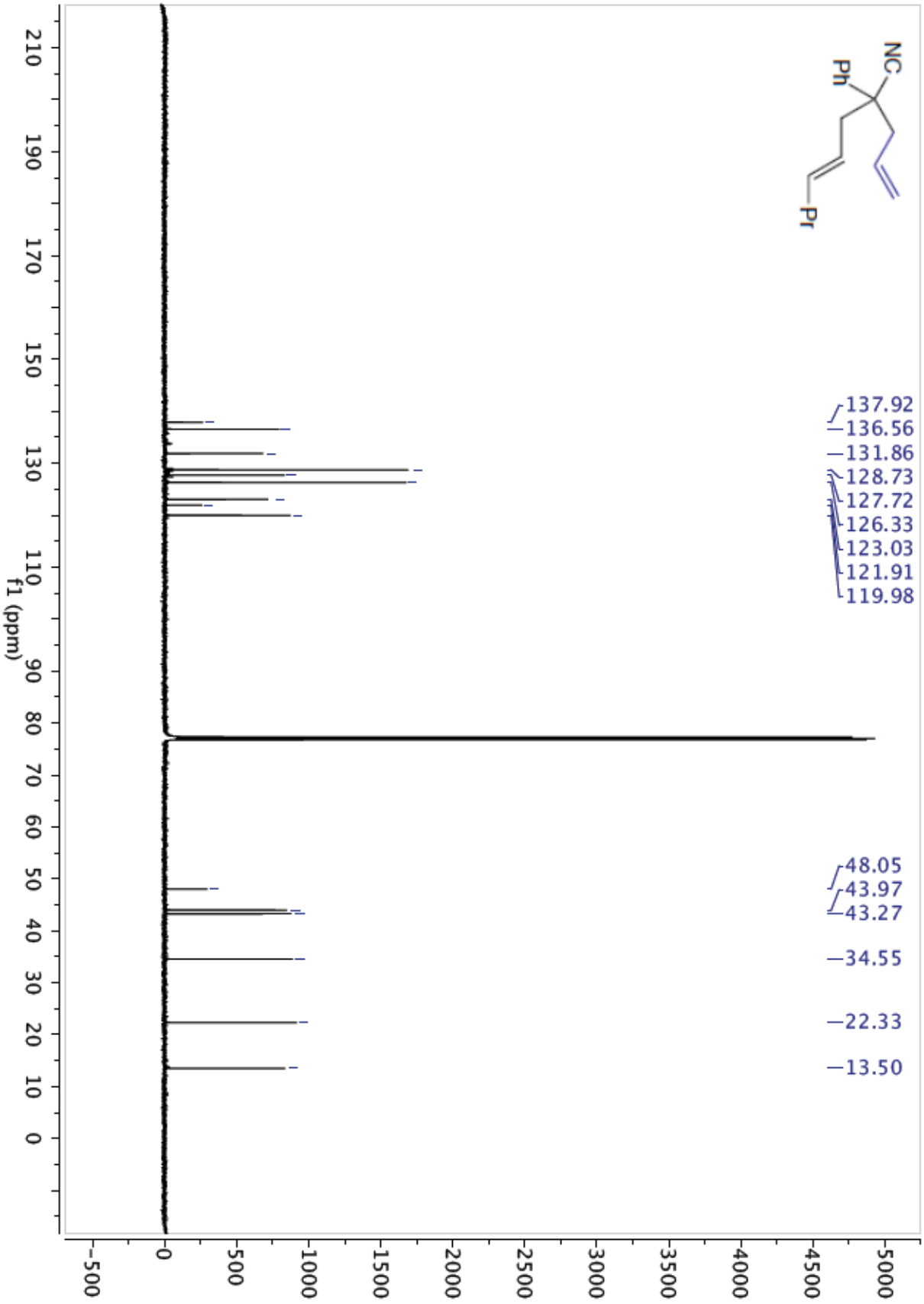
^{13}C NMR for Compound 5b



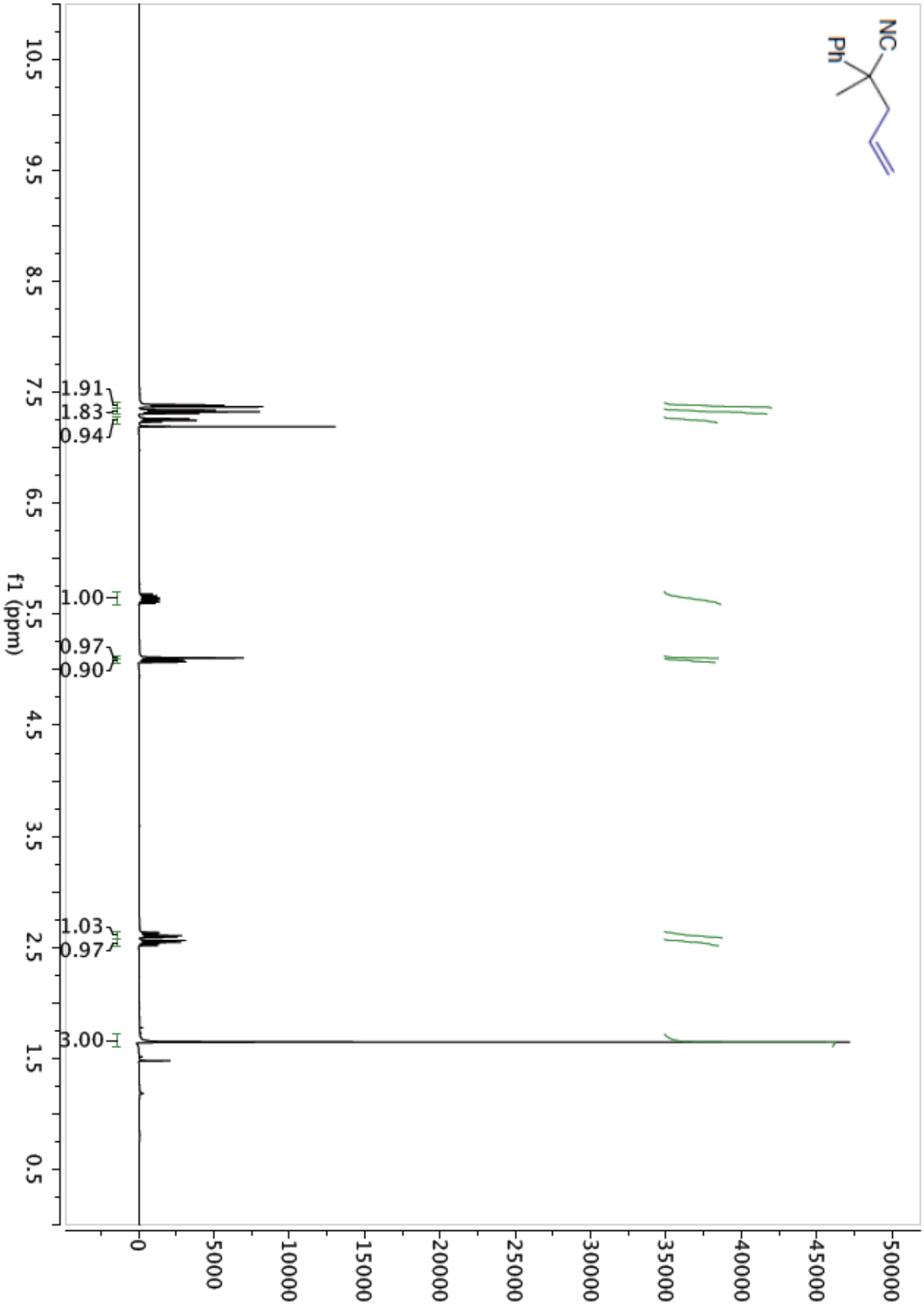
^{1}H NMR for Compound 5c



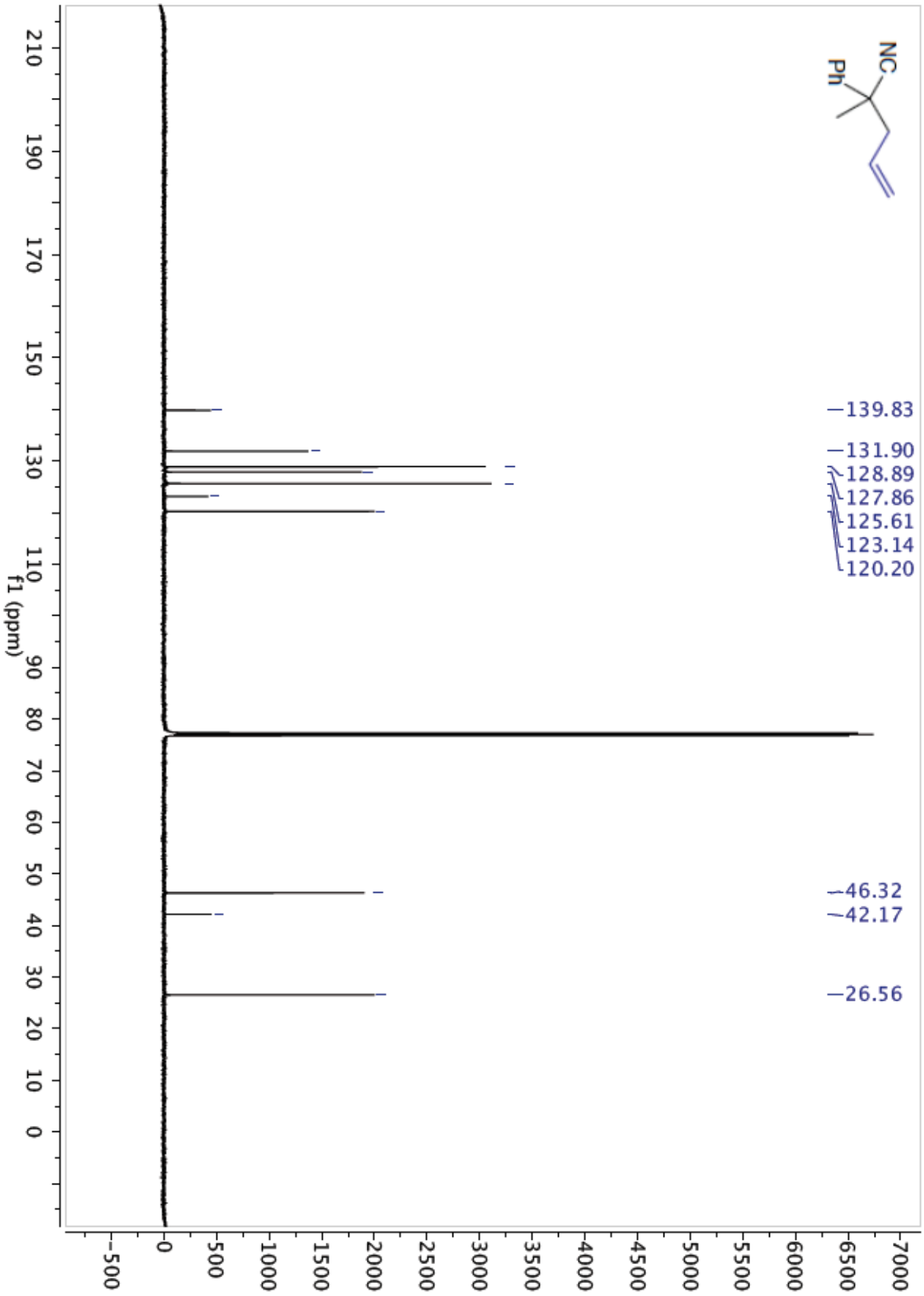
^{13}C NMR for Compound 5c



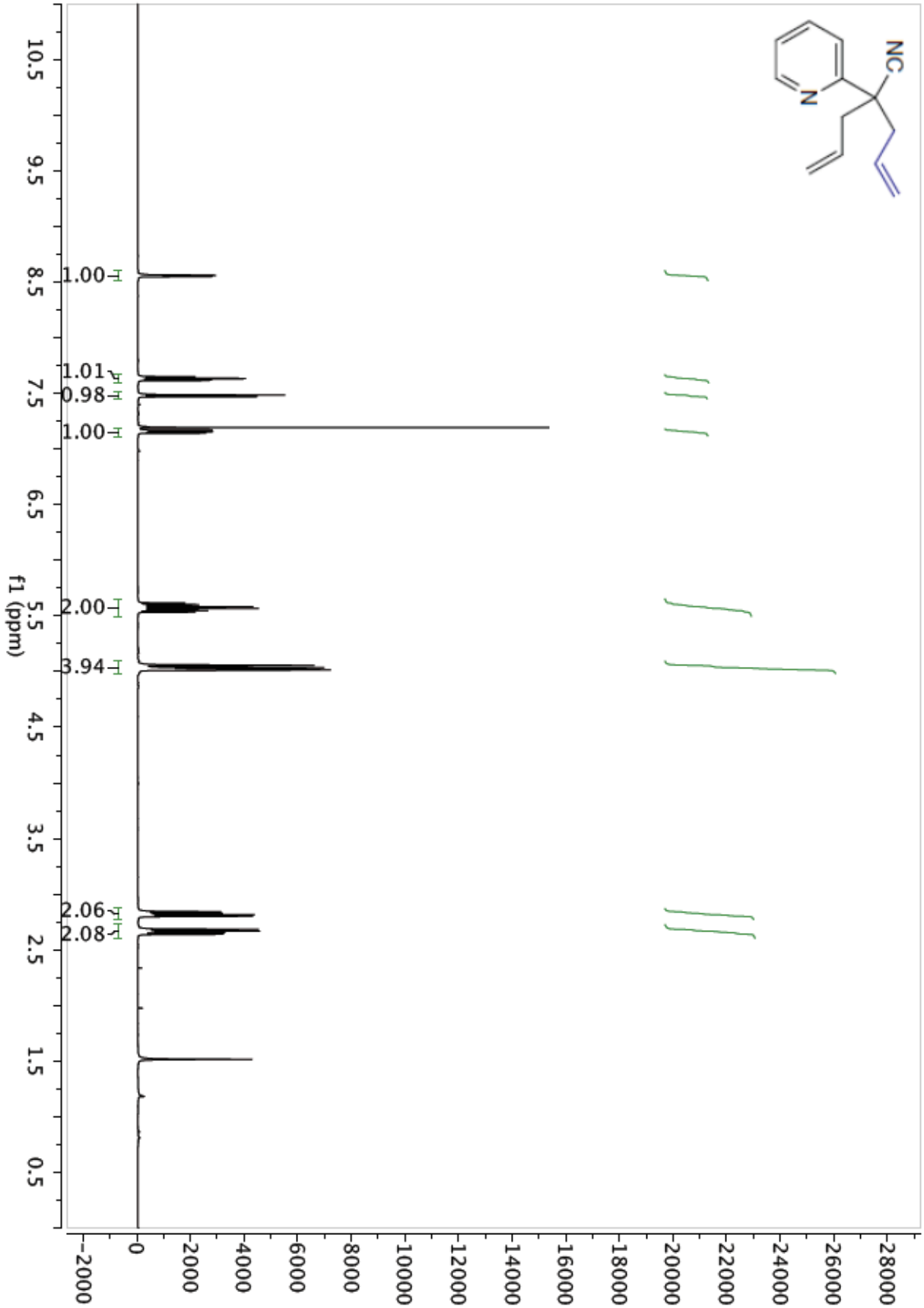
^{1}H NMR for Compound 5d



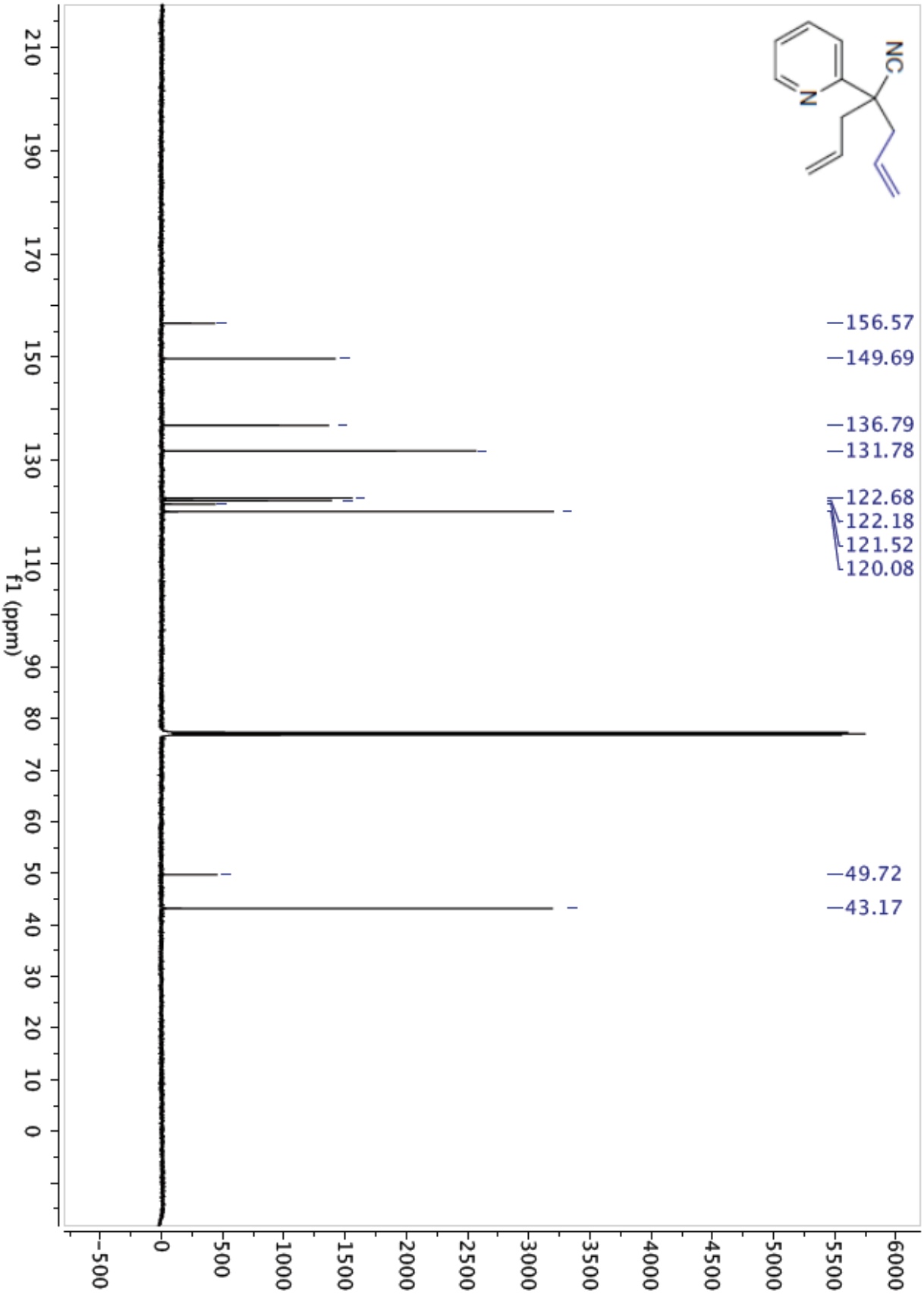
^{13}C NMR for Compound 5d



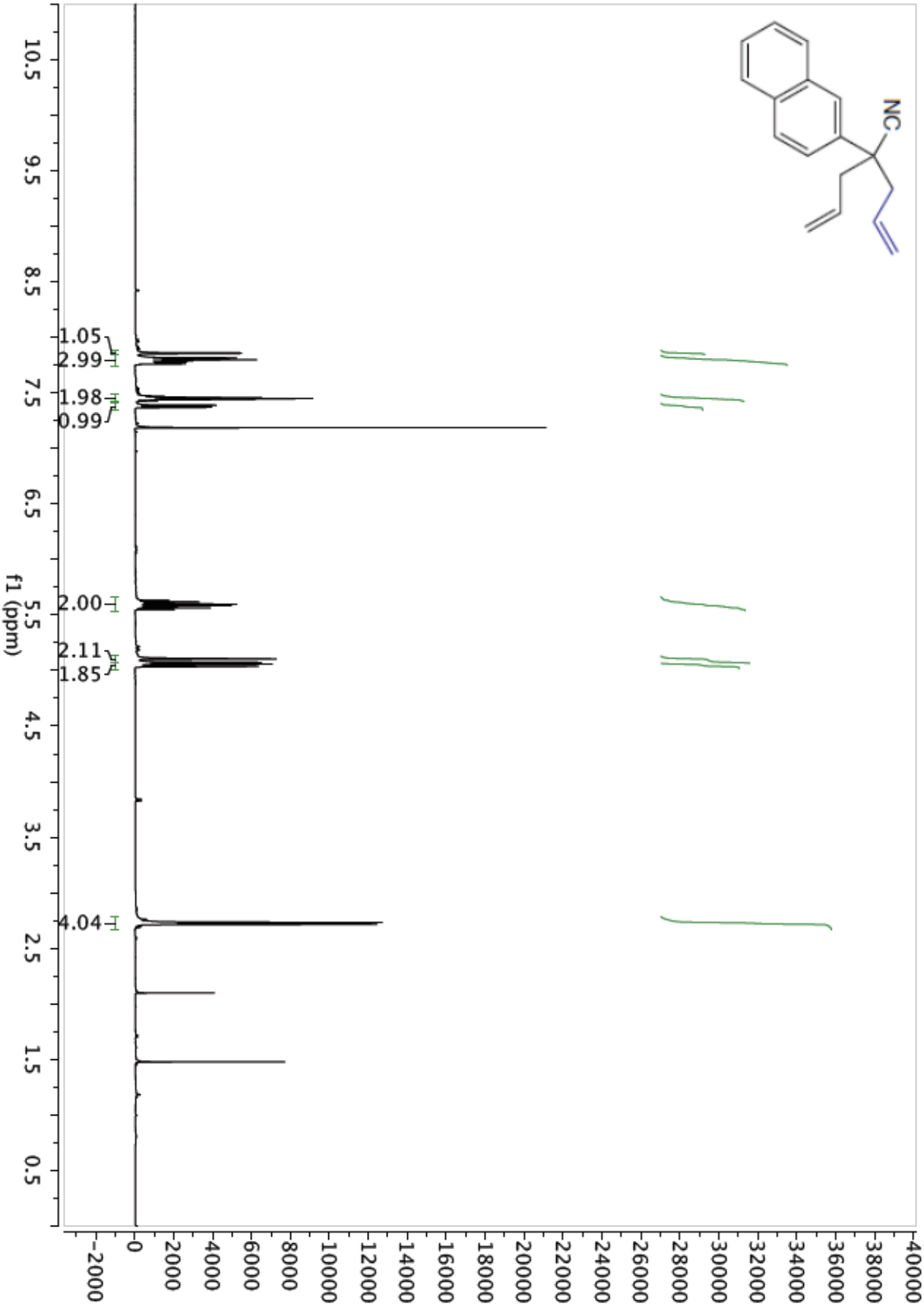
^{1}H NMR for Compound 5e



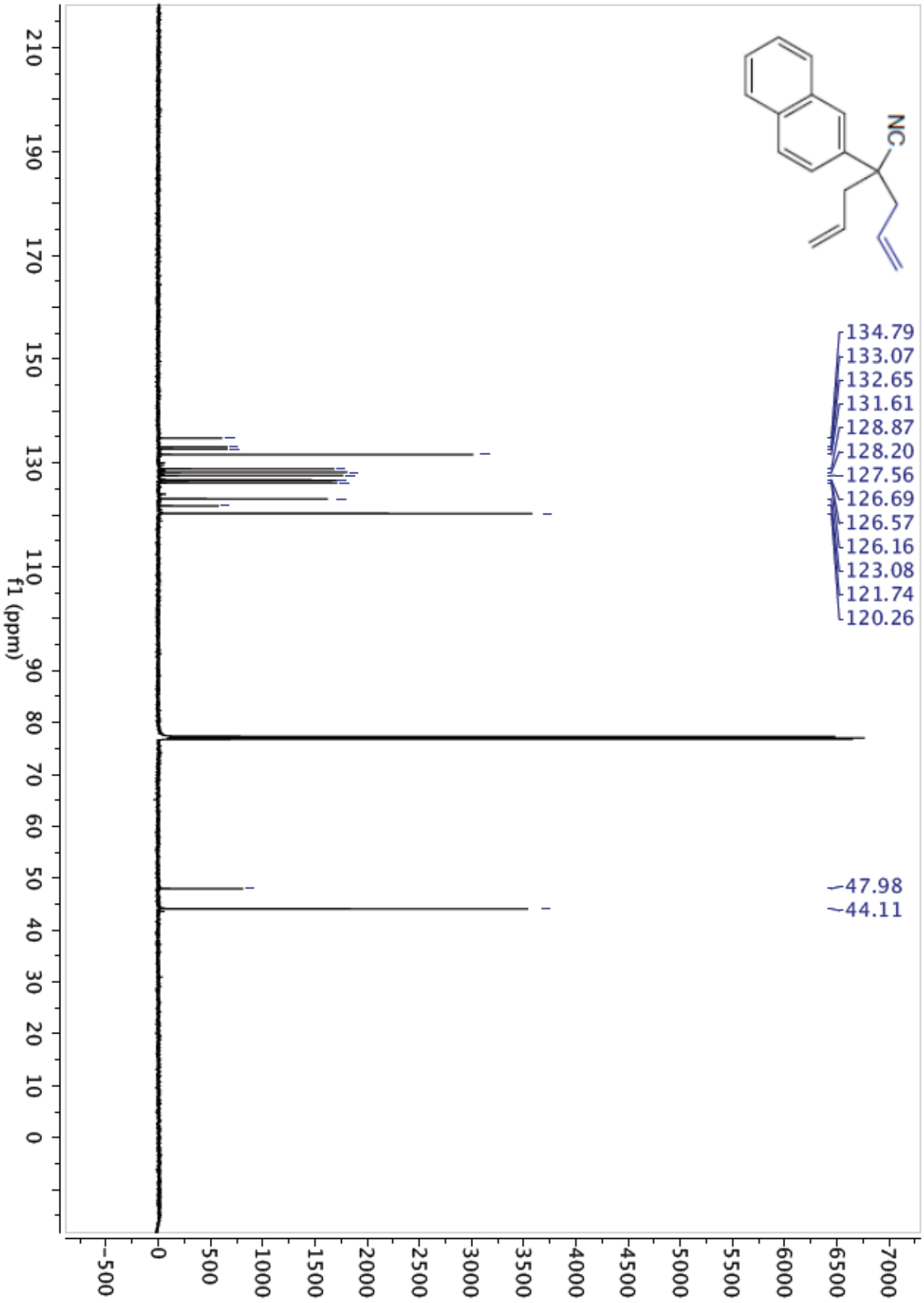
^{13}C NMR for Compound 5e



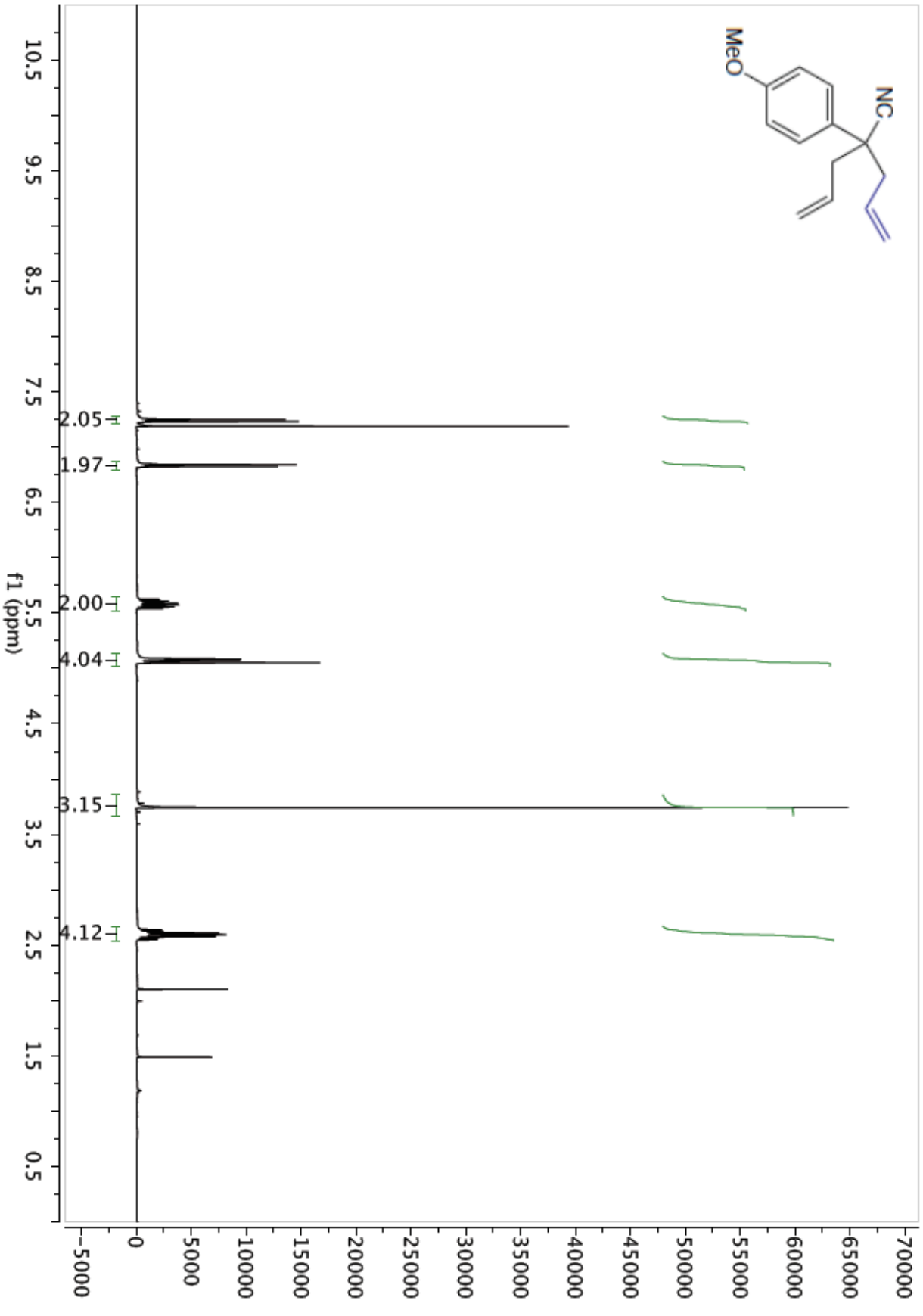
^{1}H NMR for Compound 5f



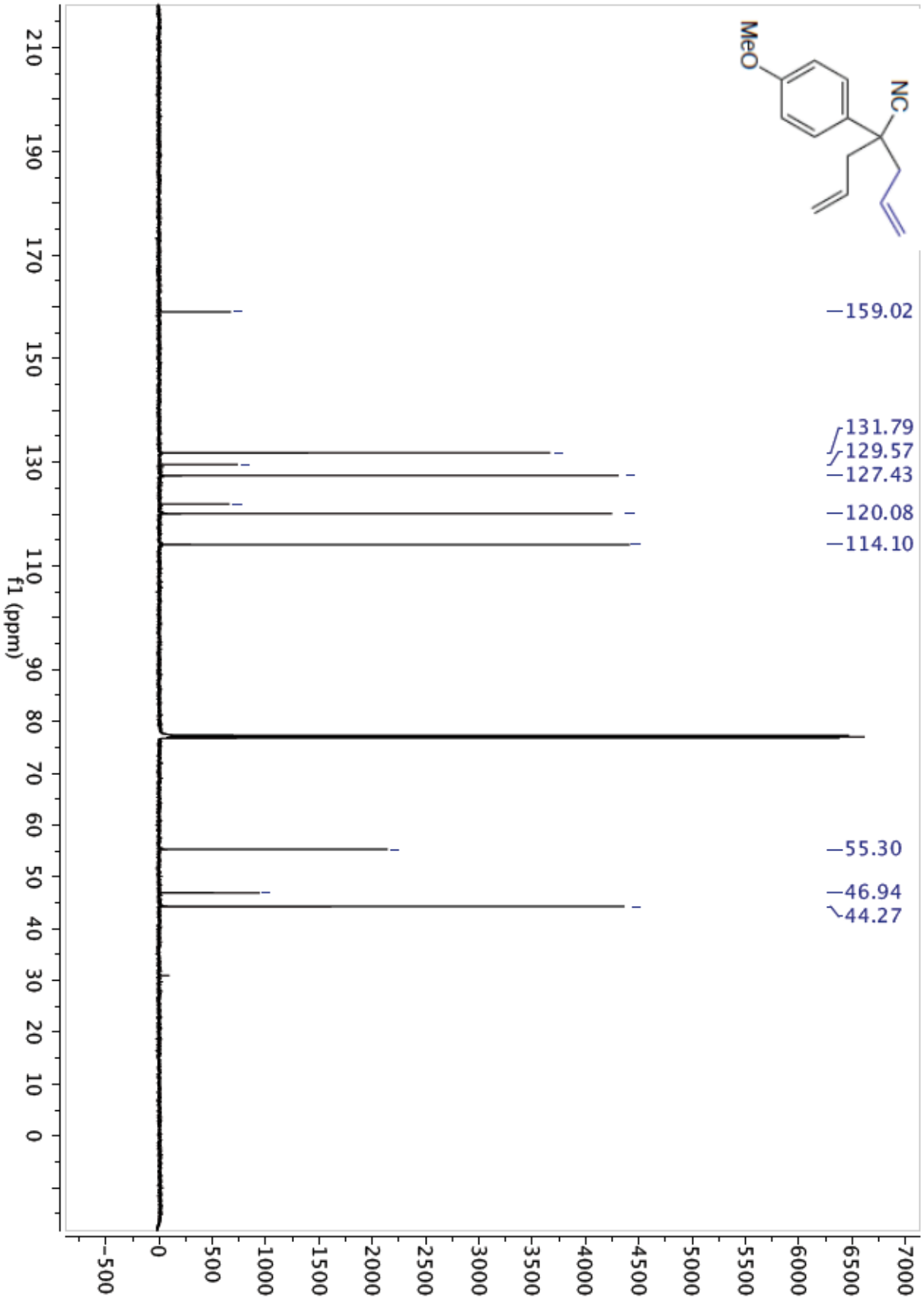
^{13}C NMR for Compound 5f



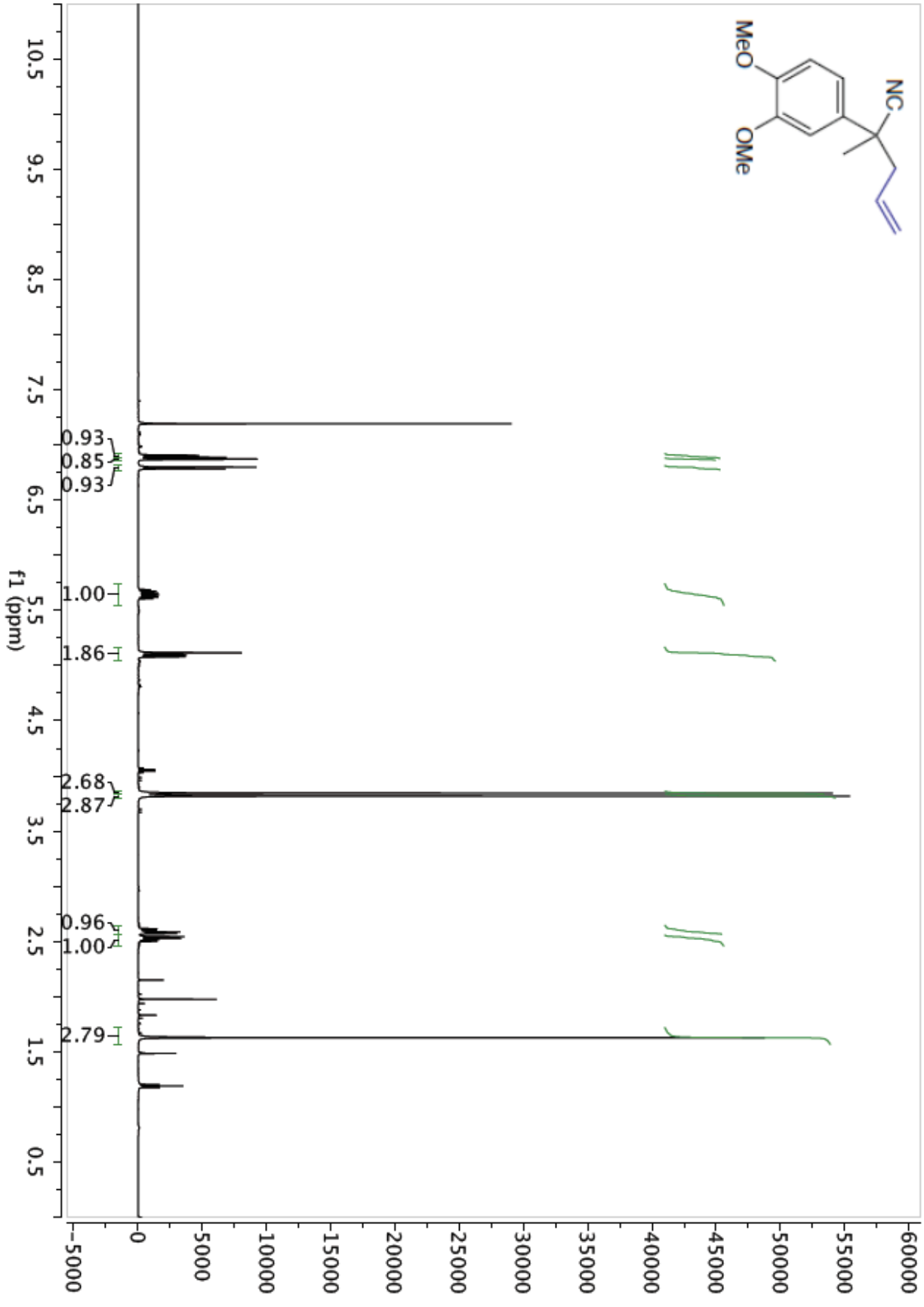
^{1}H NMR for Compound 5g



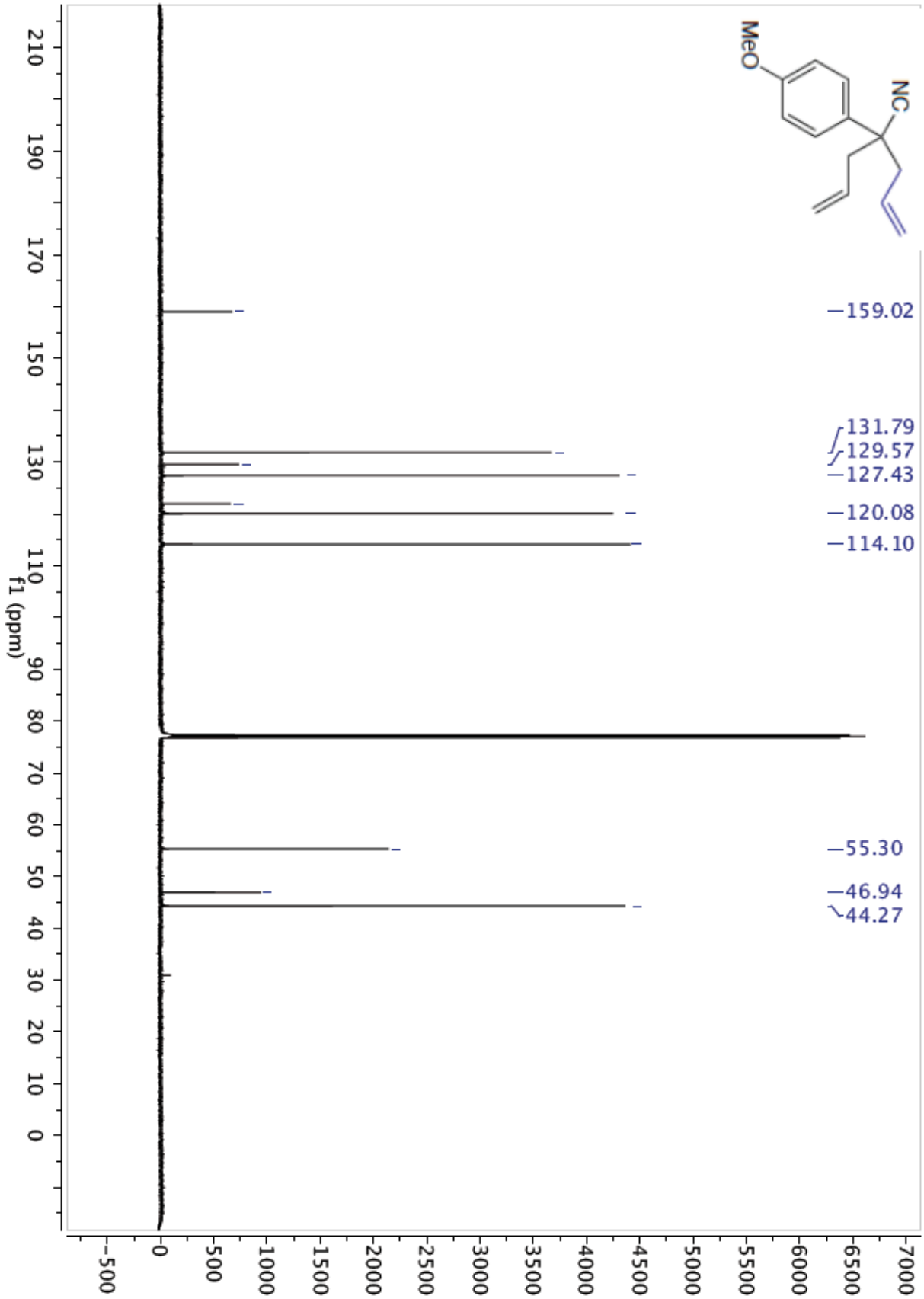
^{13}C NMR for Compound 5g



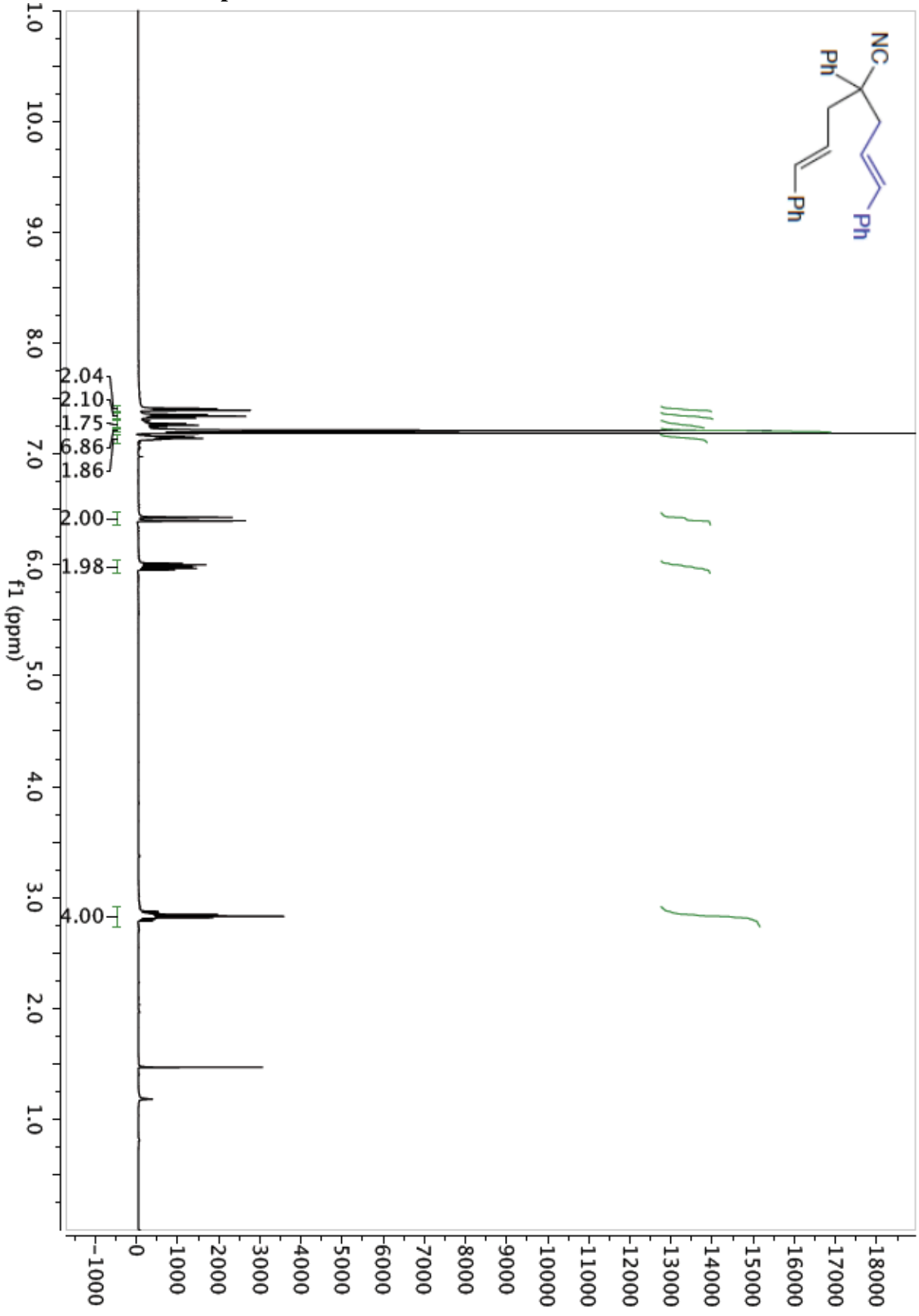
^{1}H NMR for Compound 5h



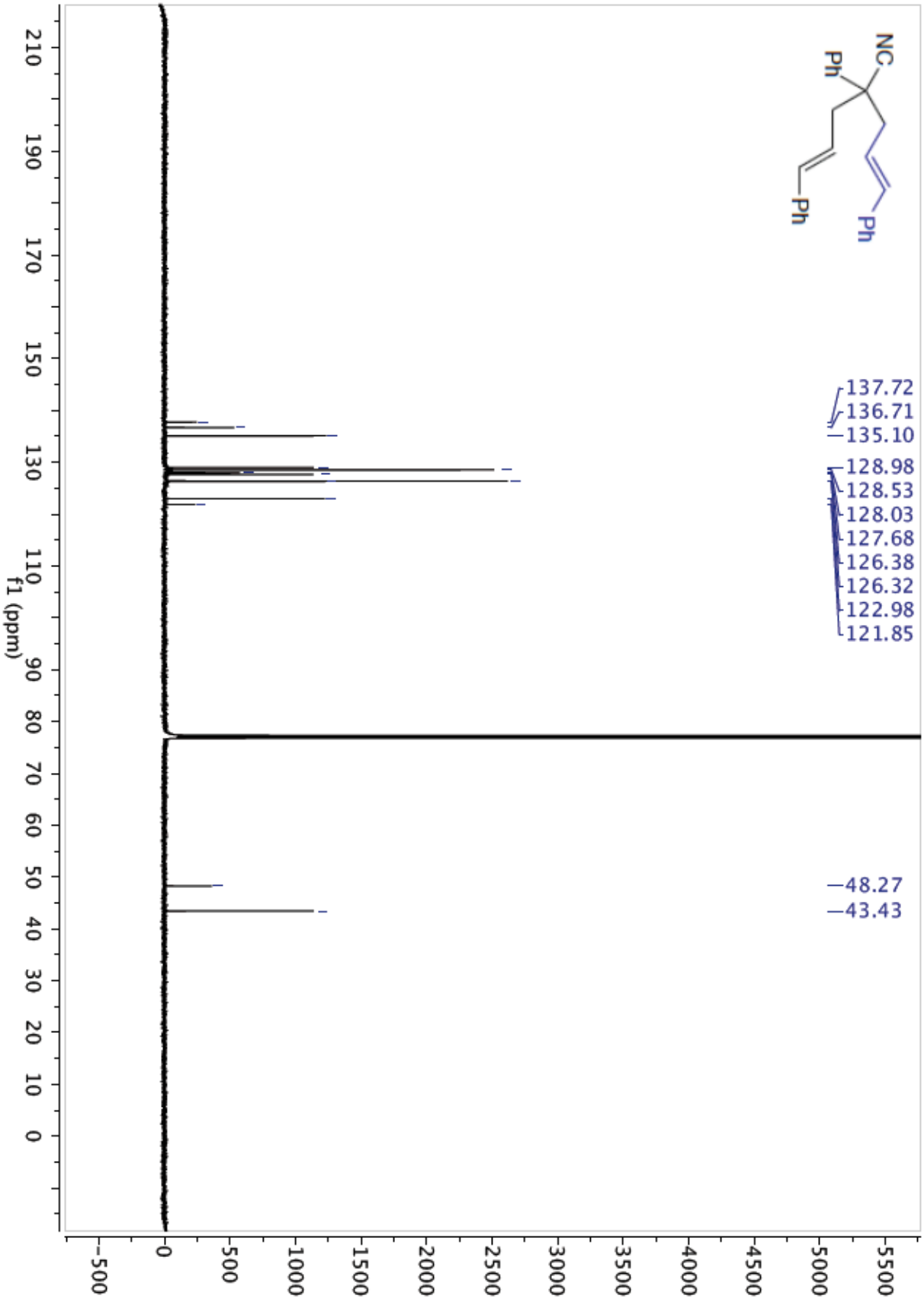
^{13}C NMR for Compound 5h



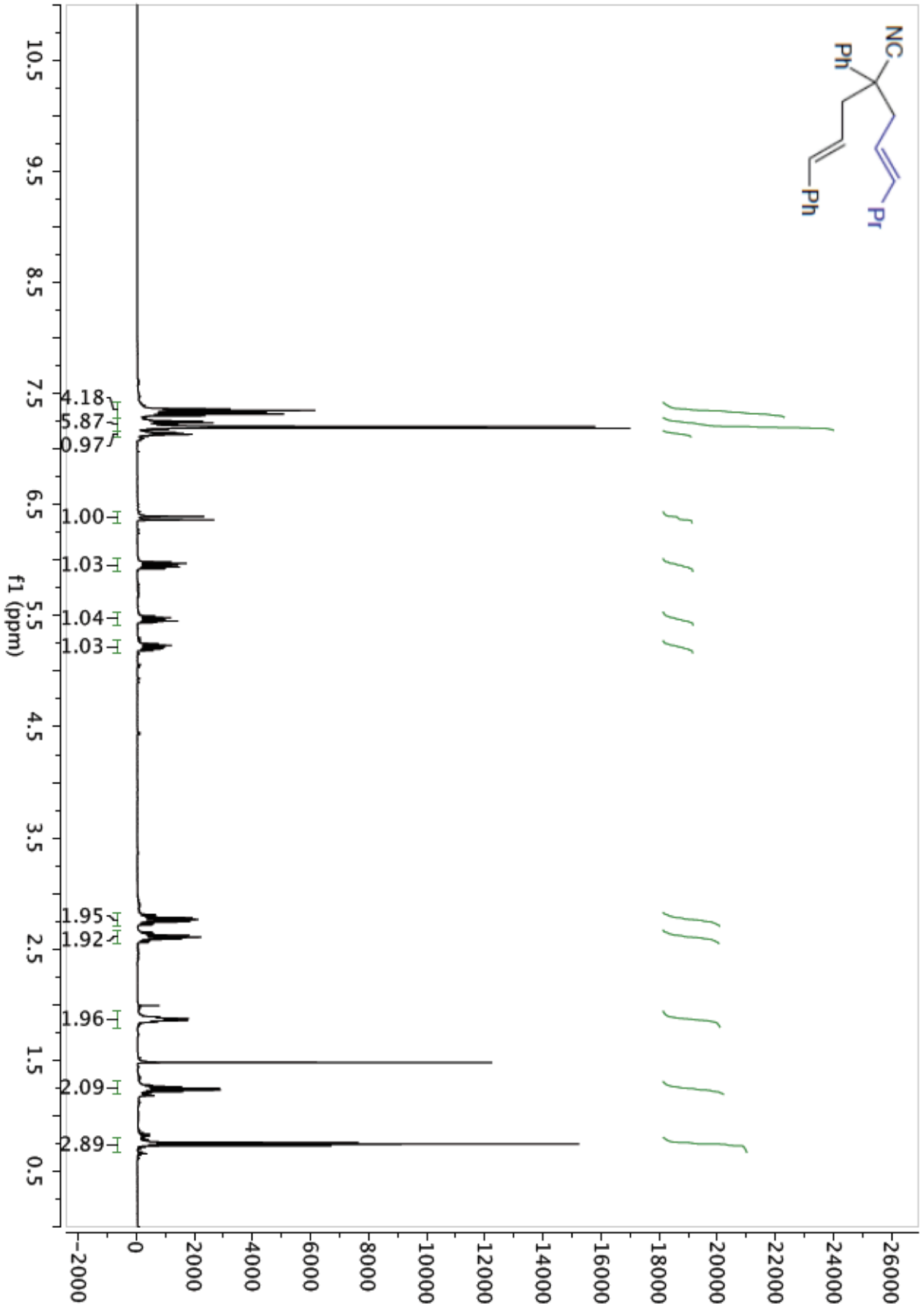
^{1}H NMR for Compound 5i



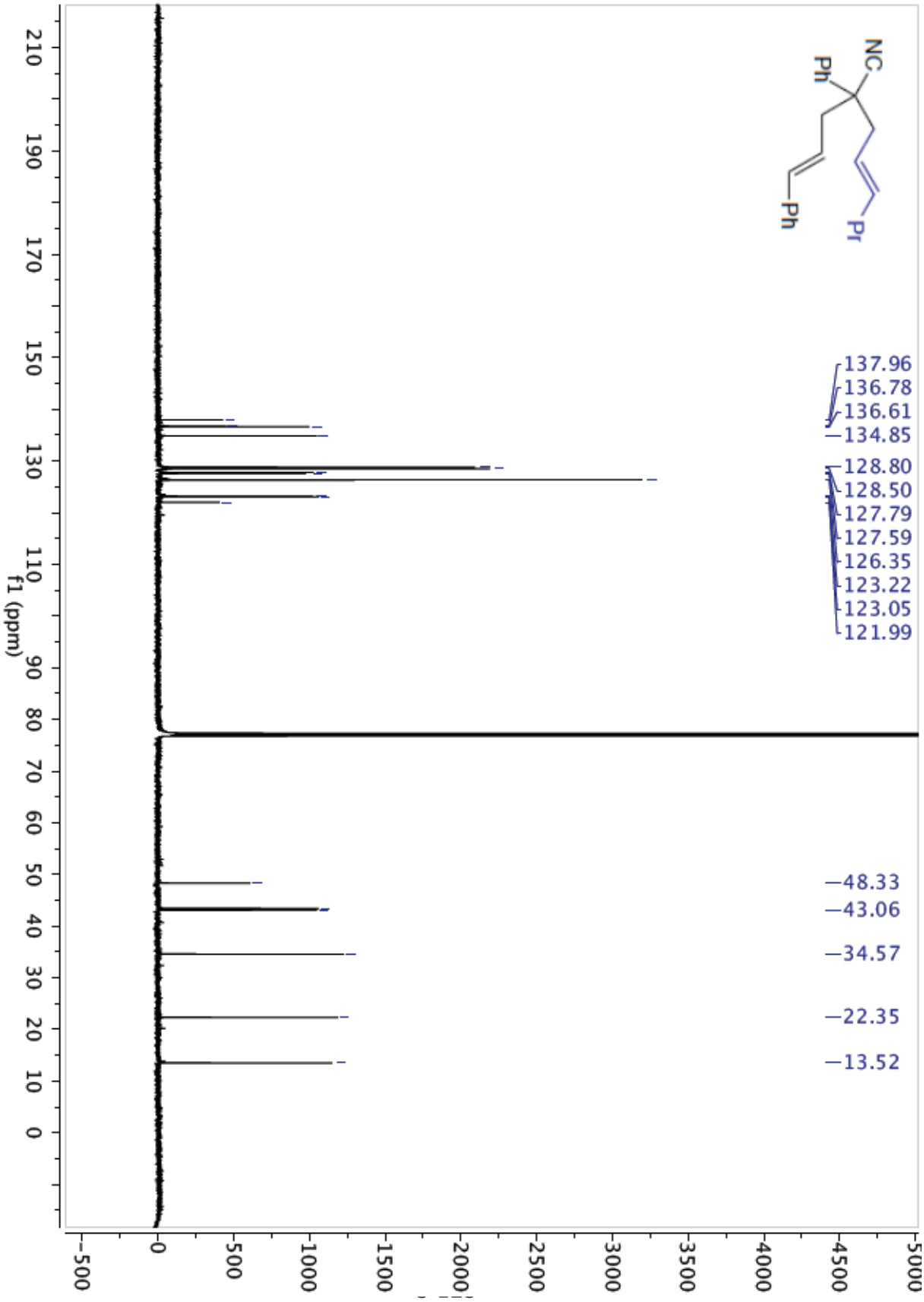
^{13}C NMR for Compound 5i



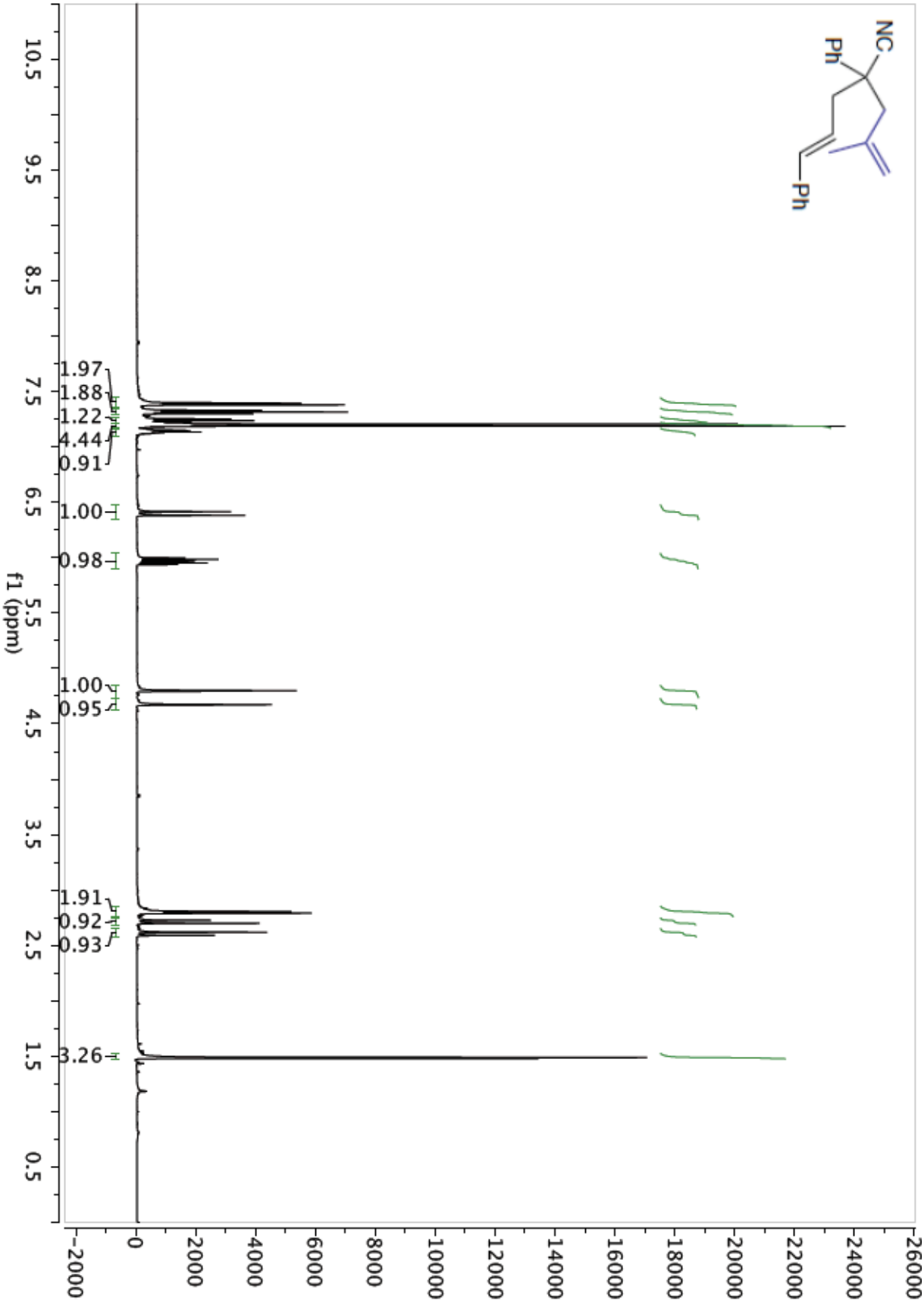
^{1}H NMR for Compound 5j



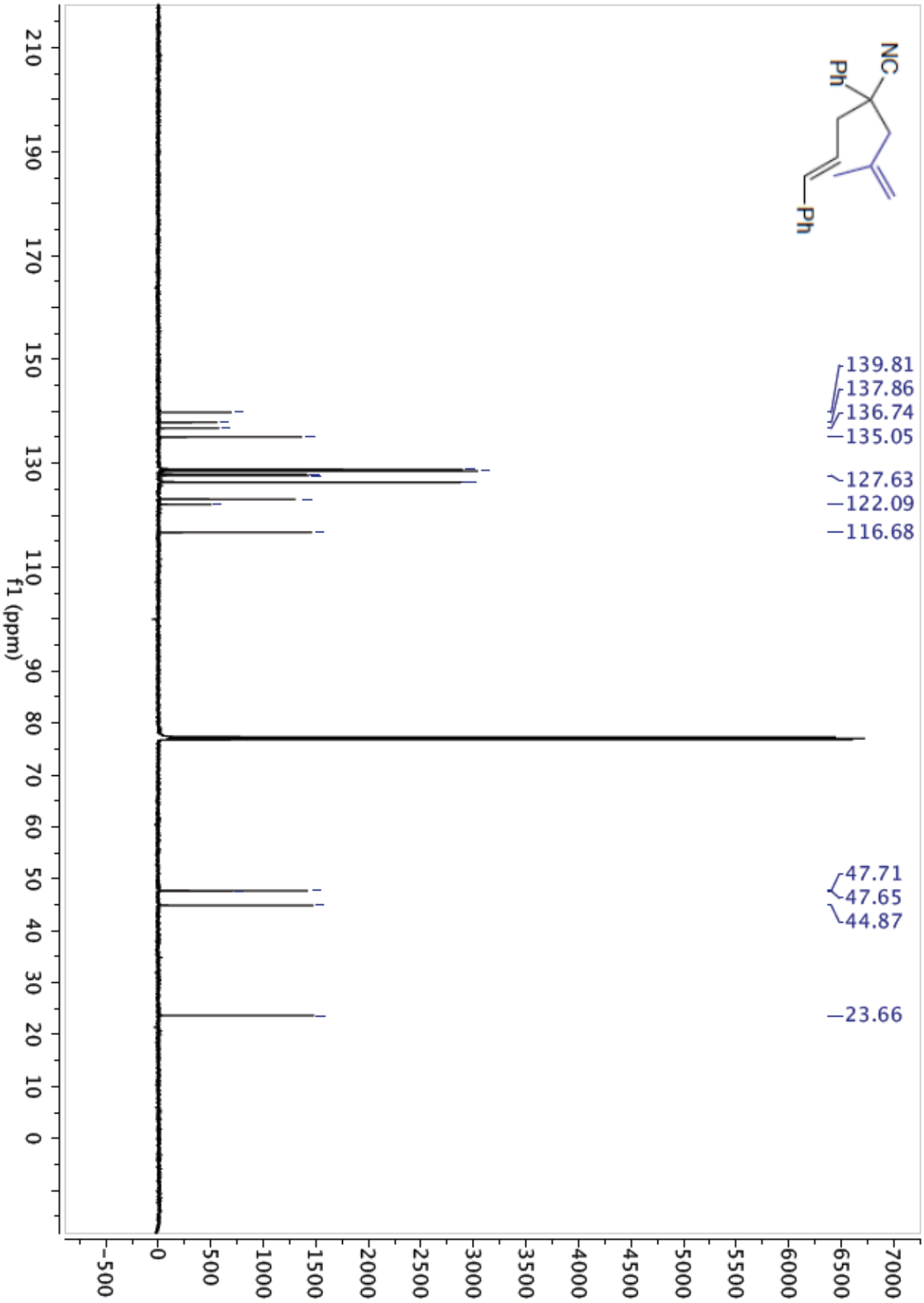
^{13}C NMR for Compound 5j



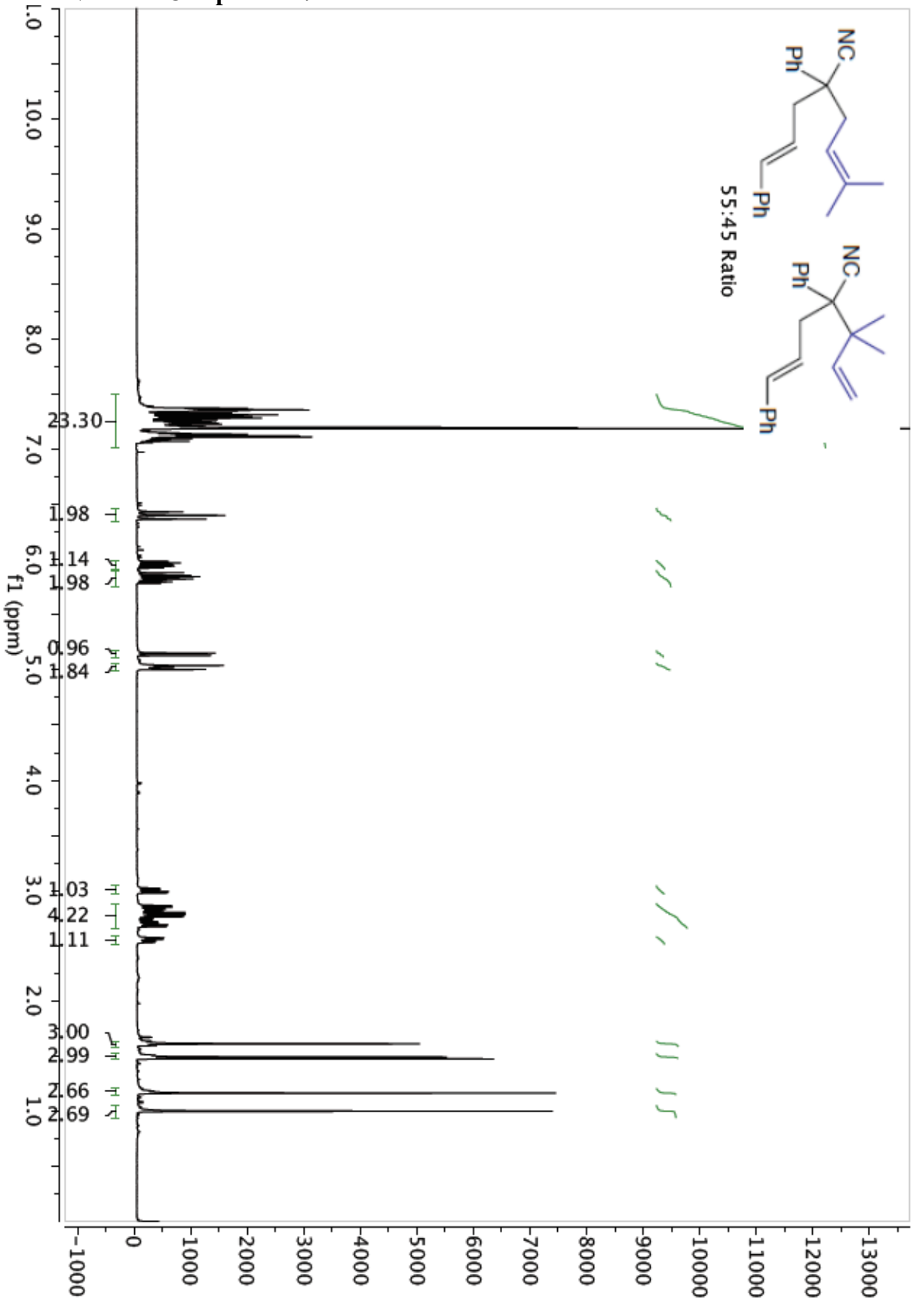
^{1}H NMR for Compound 5k



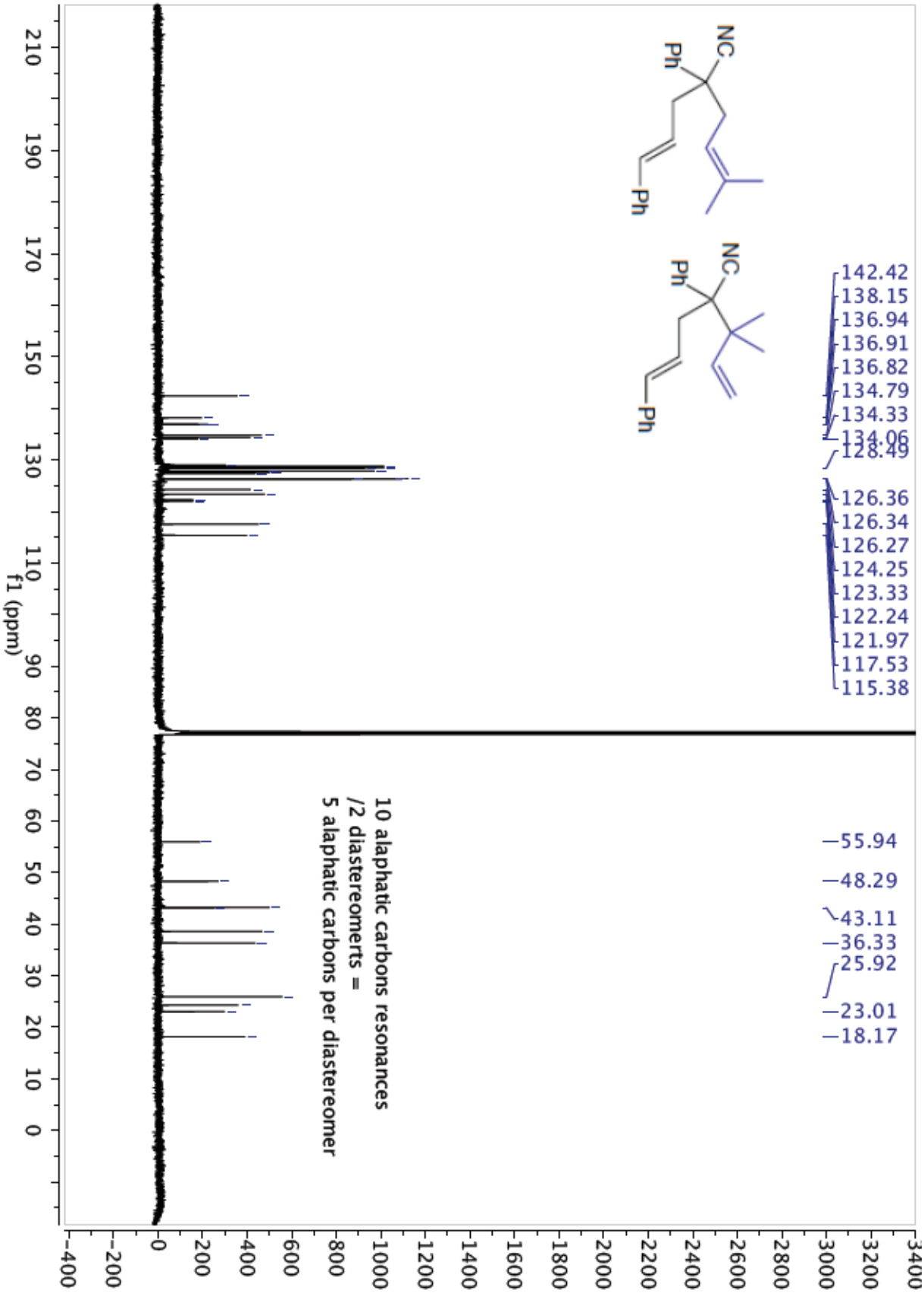
^{13}C NMR for Compound 5k



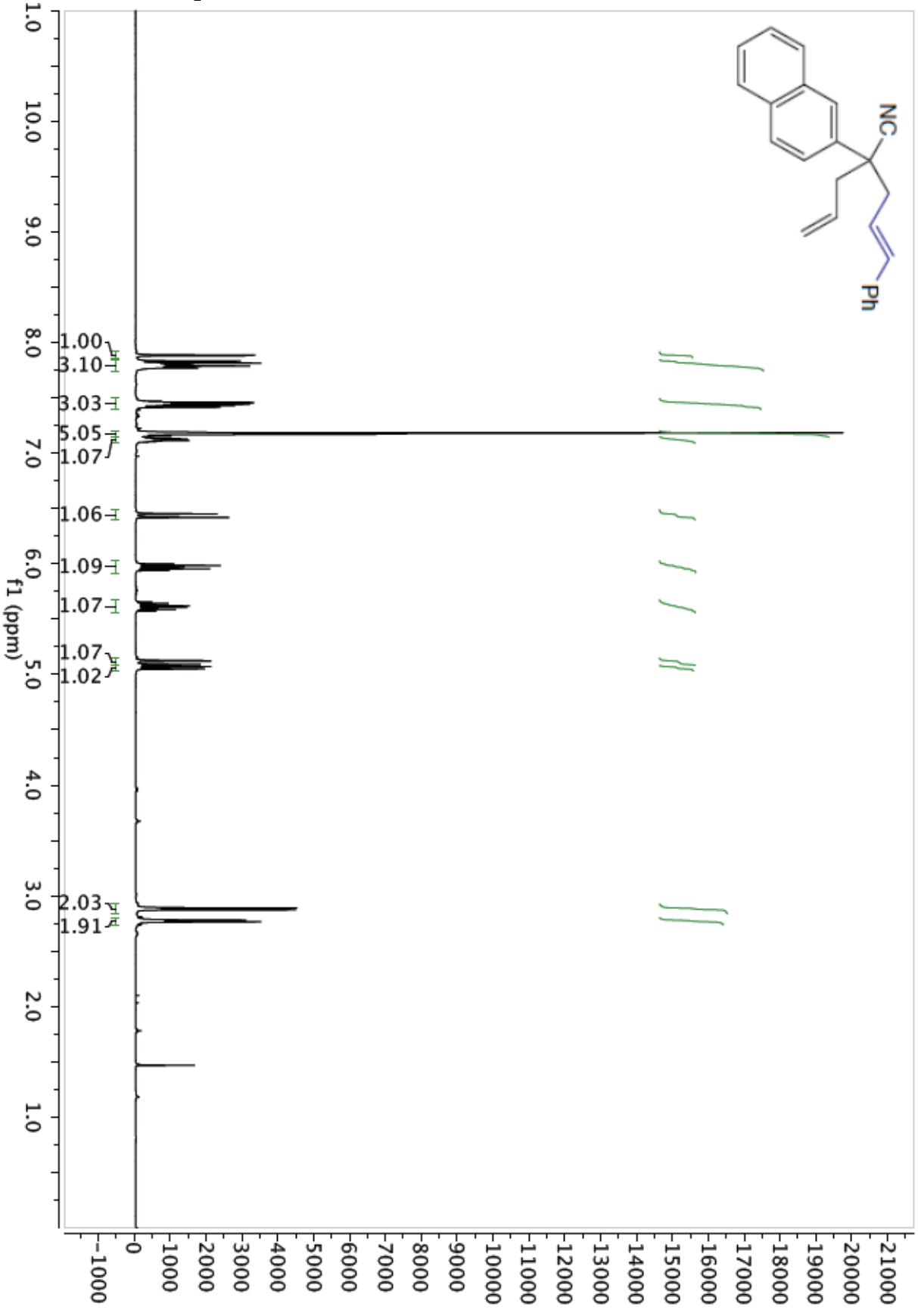
^{1}H NMR for Compound 5l/5m



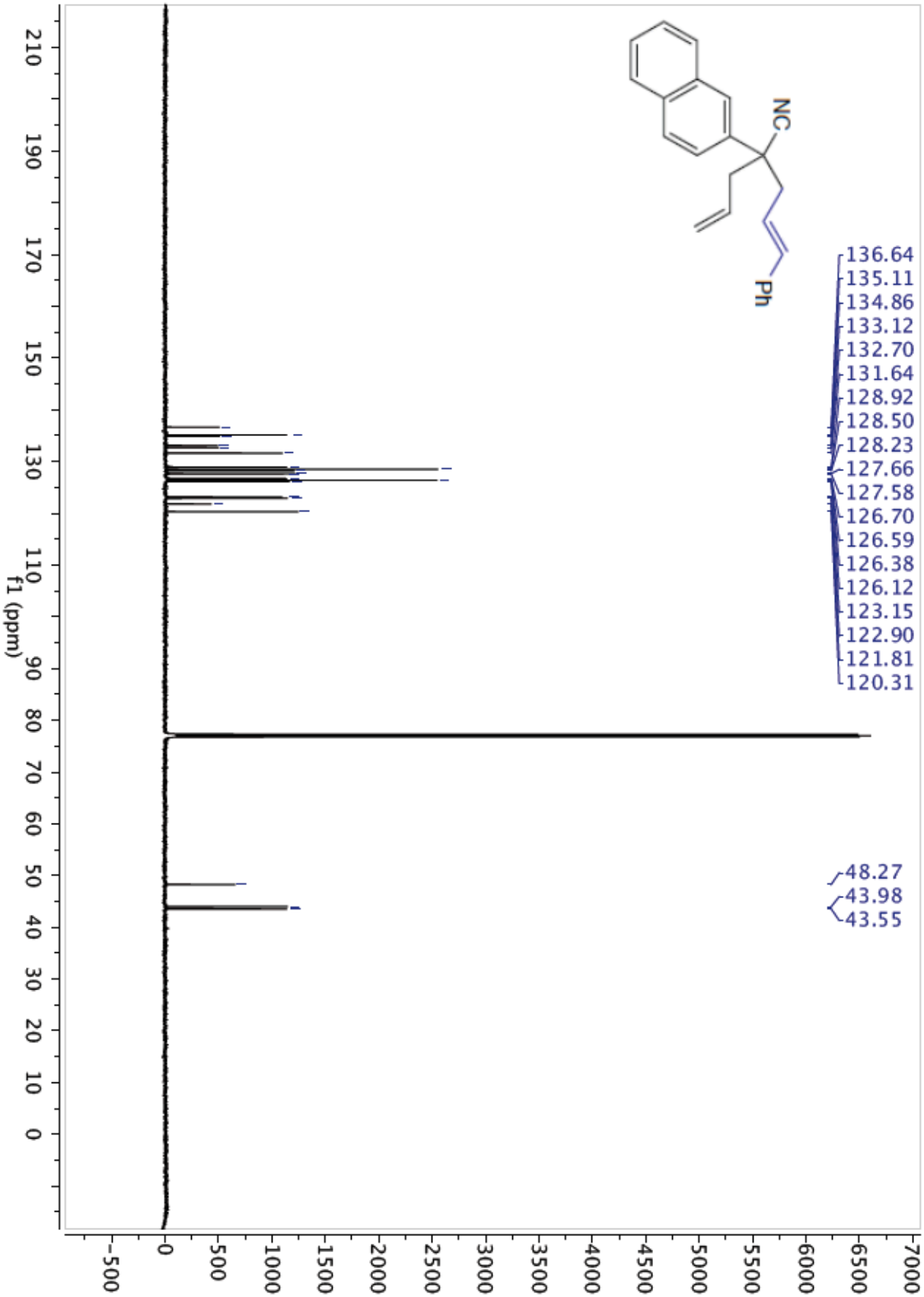
^{13}C NMR for Compound 5l/5m



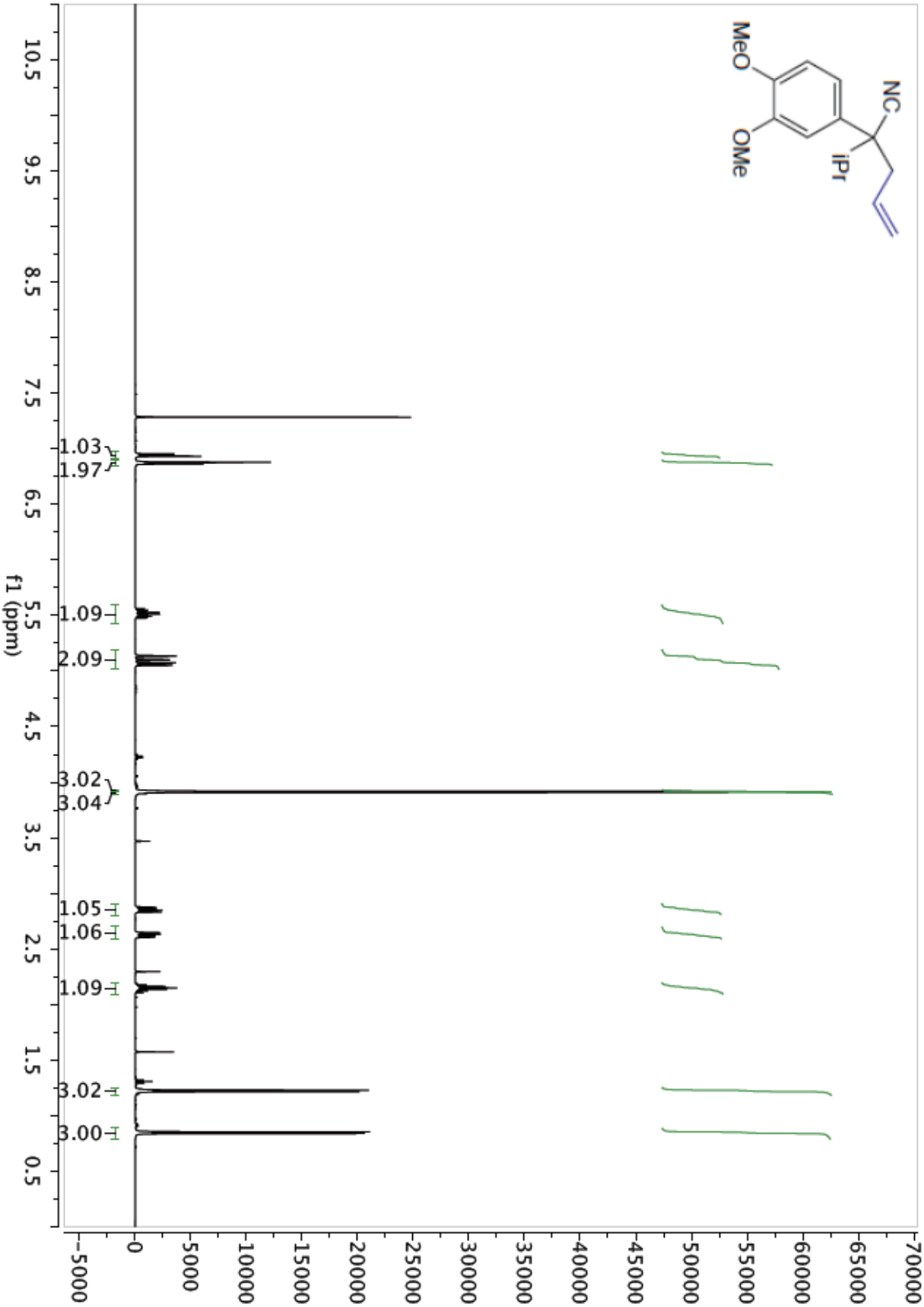
^{1}H NMR for Compound 5n



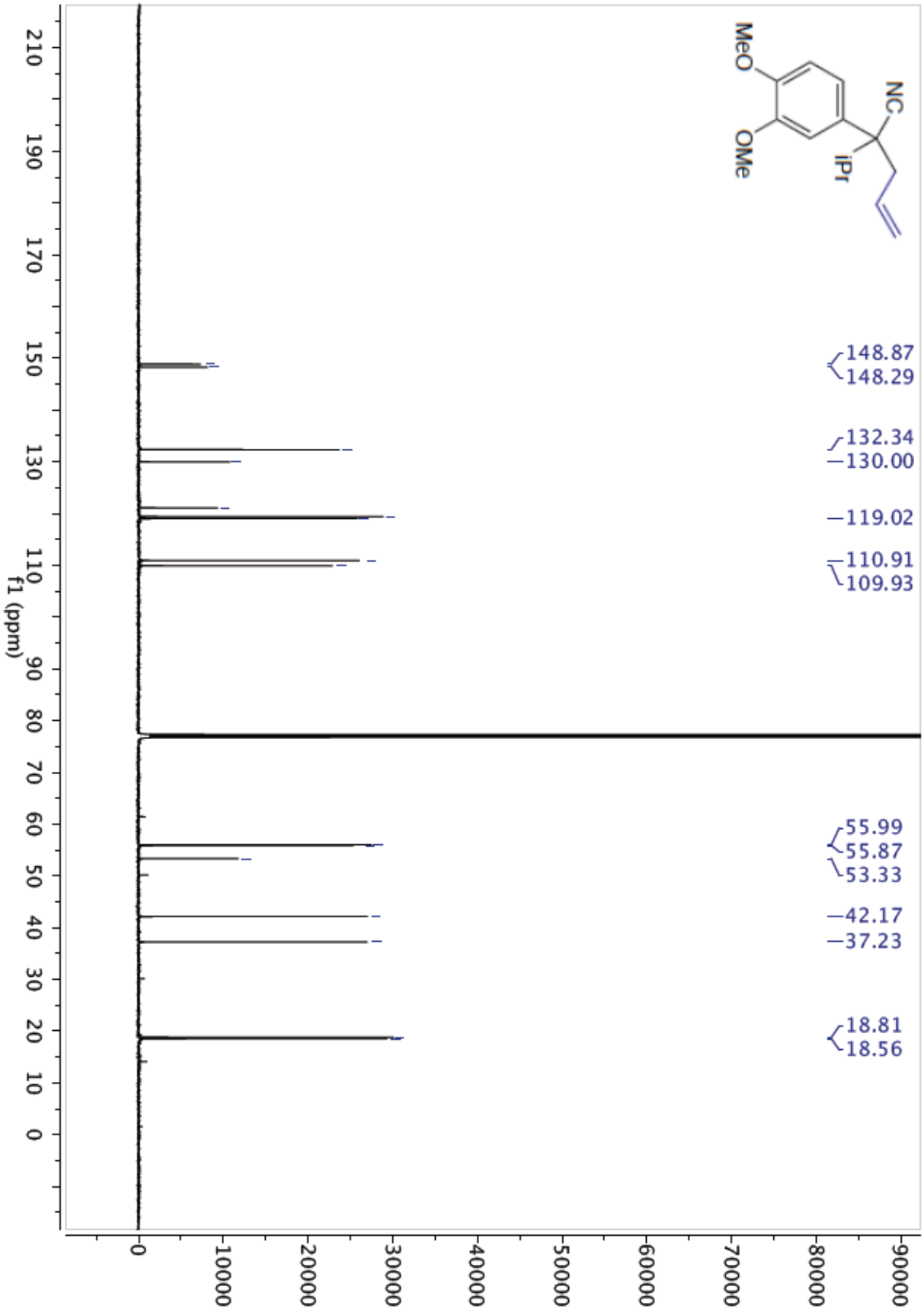
^{13}C NMR for Compound 5n



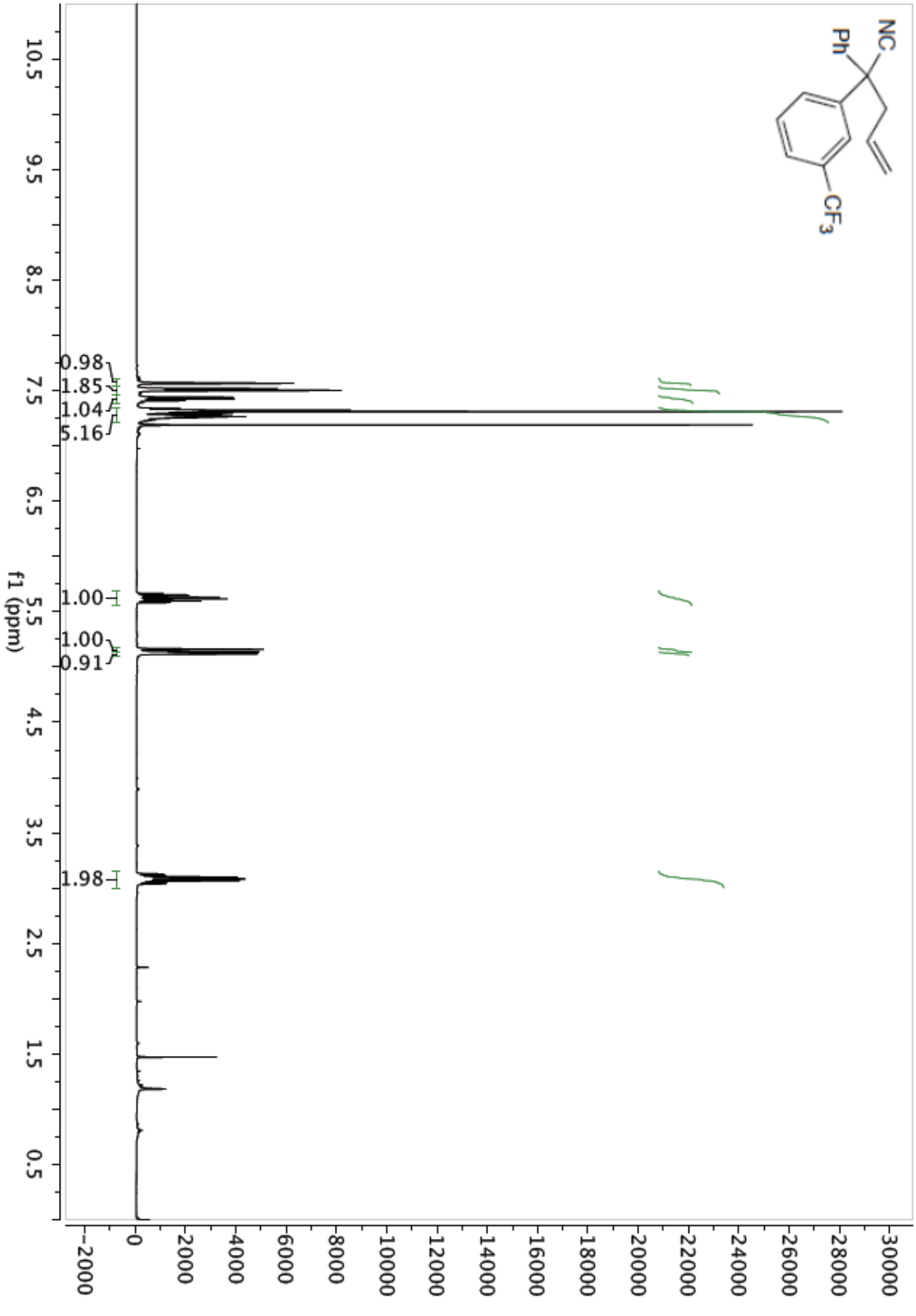
^{1}H NMR for Compound 5o



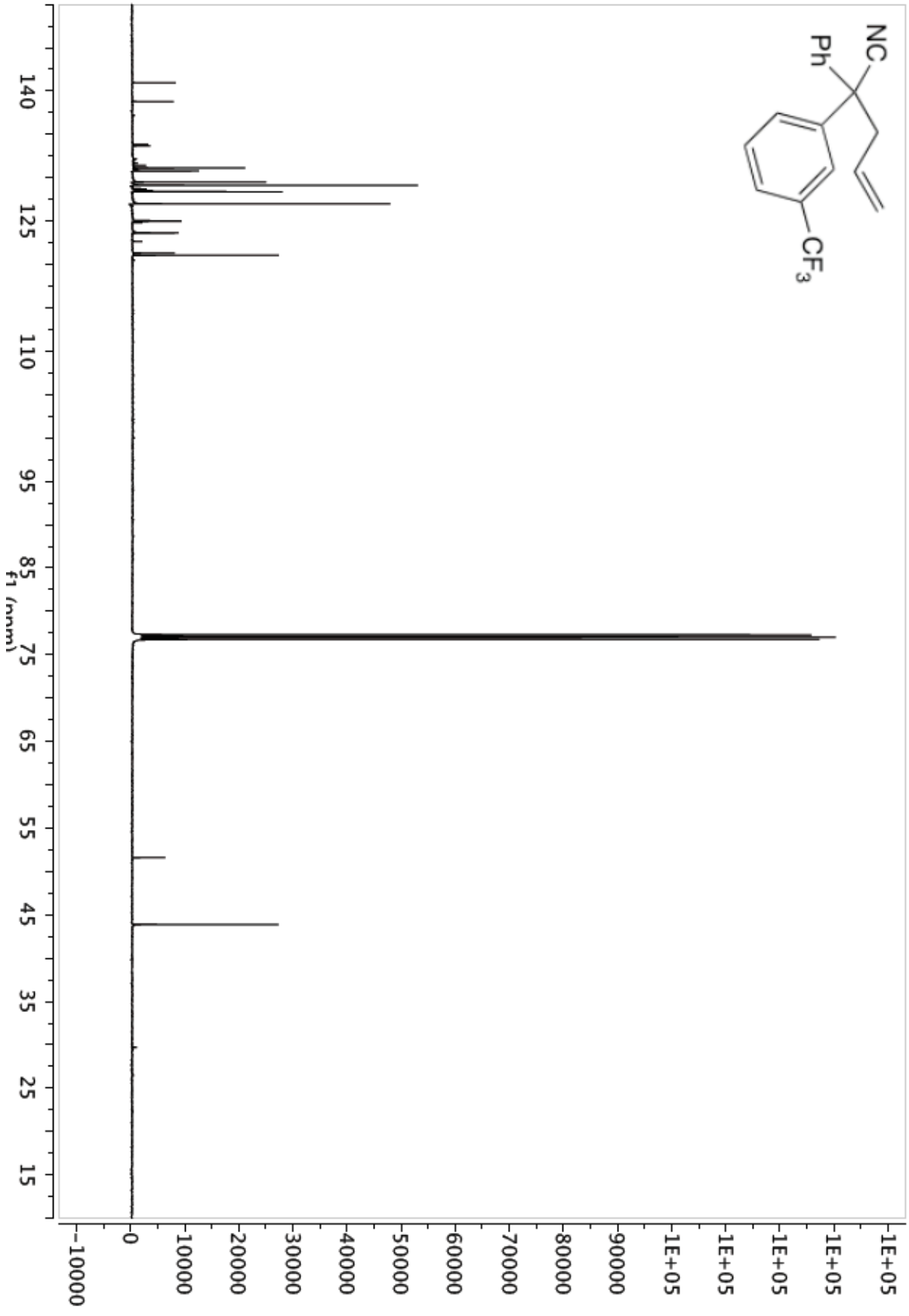
^{13}C NMR for Compound 5o



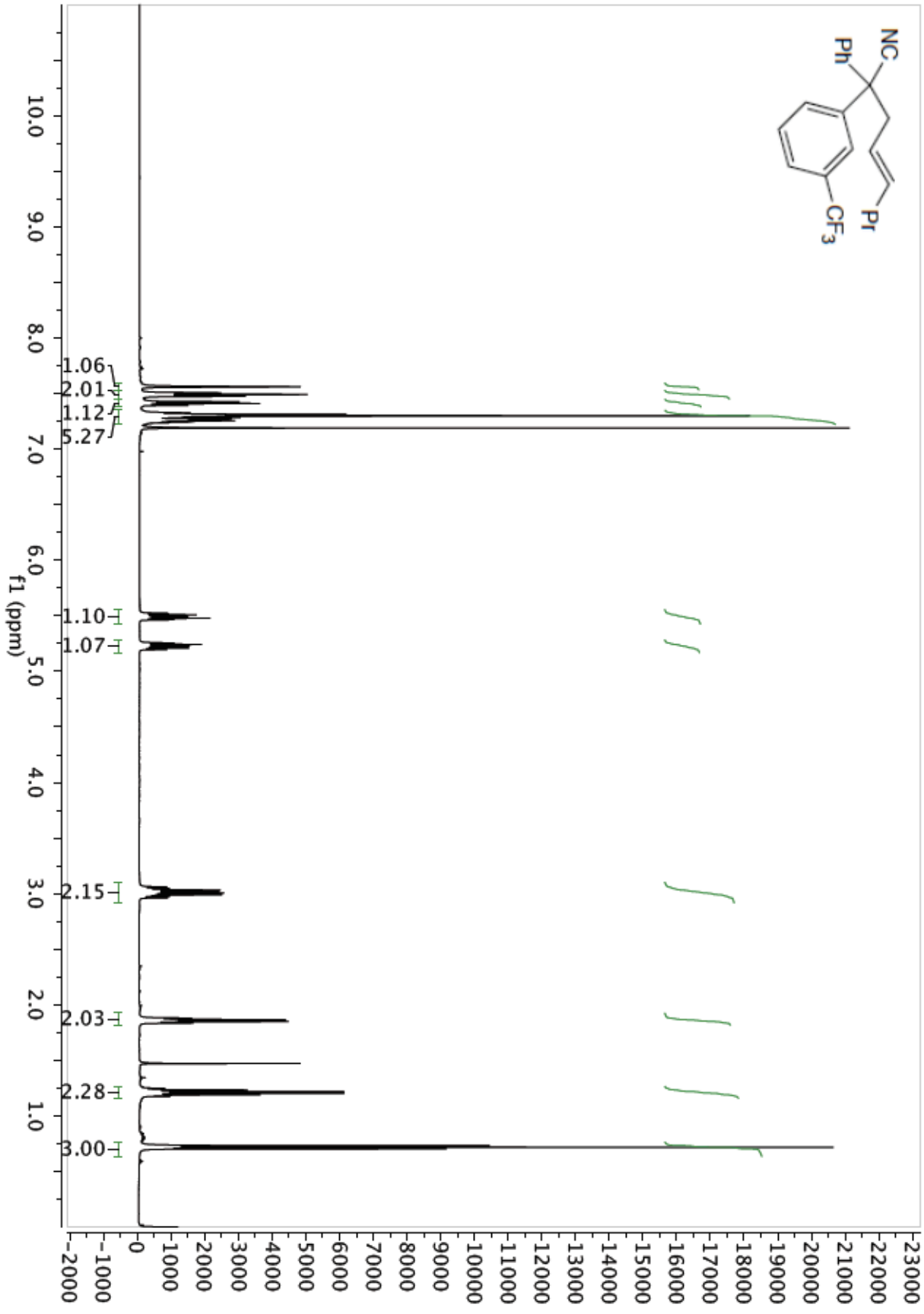
^{1}H NMR for Compound 5p



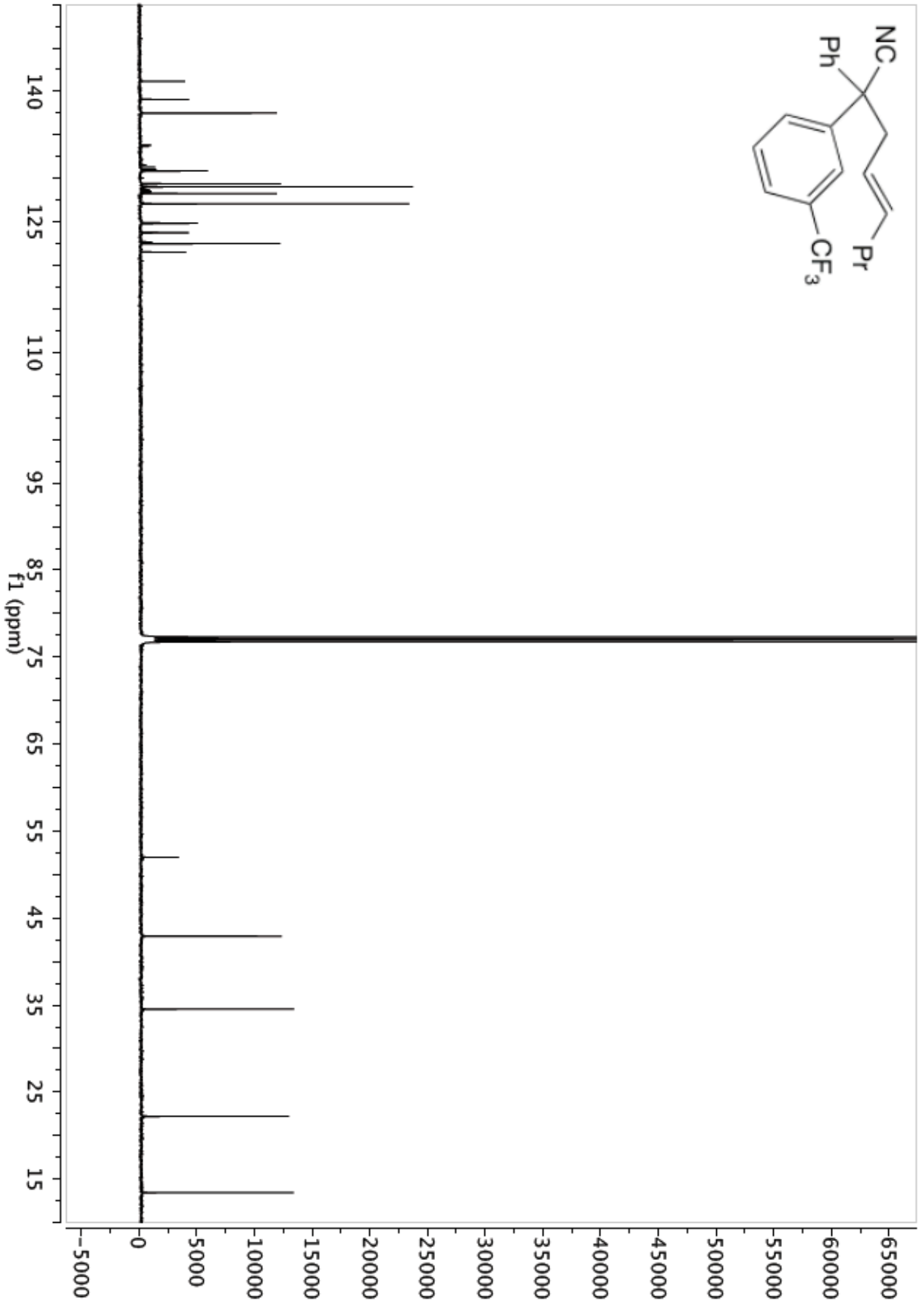
^{13}C NMR for Compound 5p



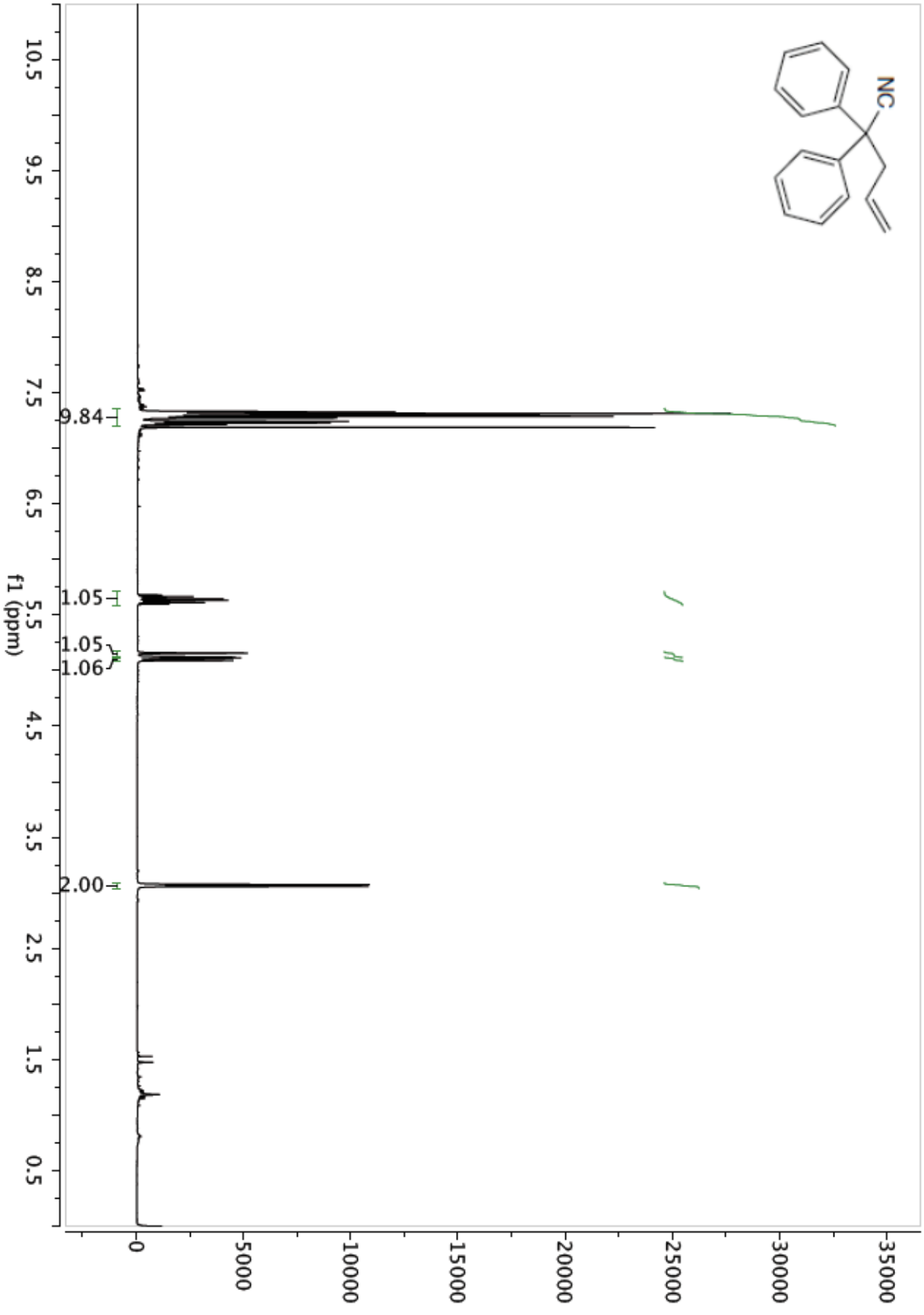
[1]H NMR for Compound 5q



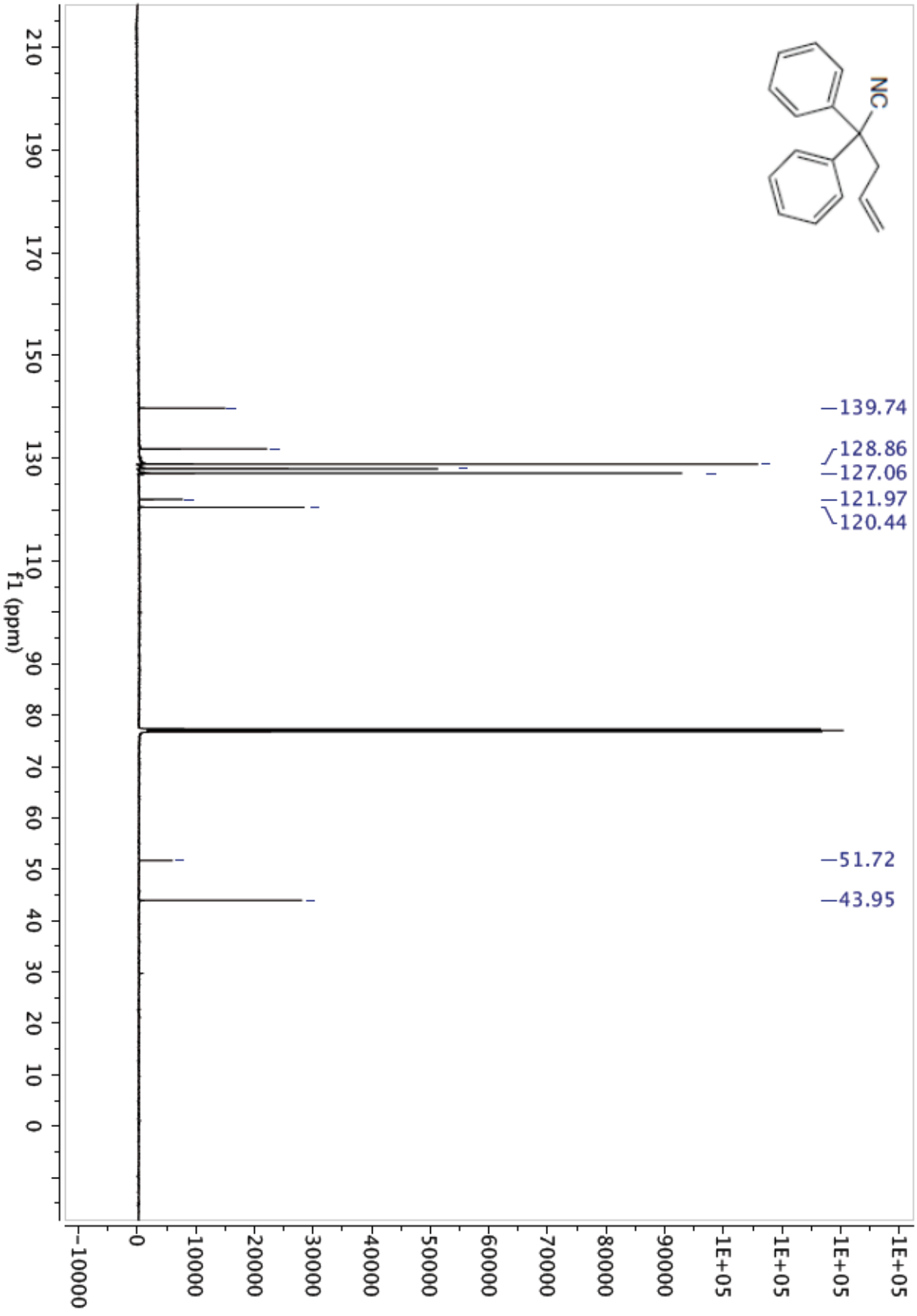
^{13}C NMR for Compound 5q



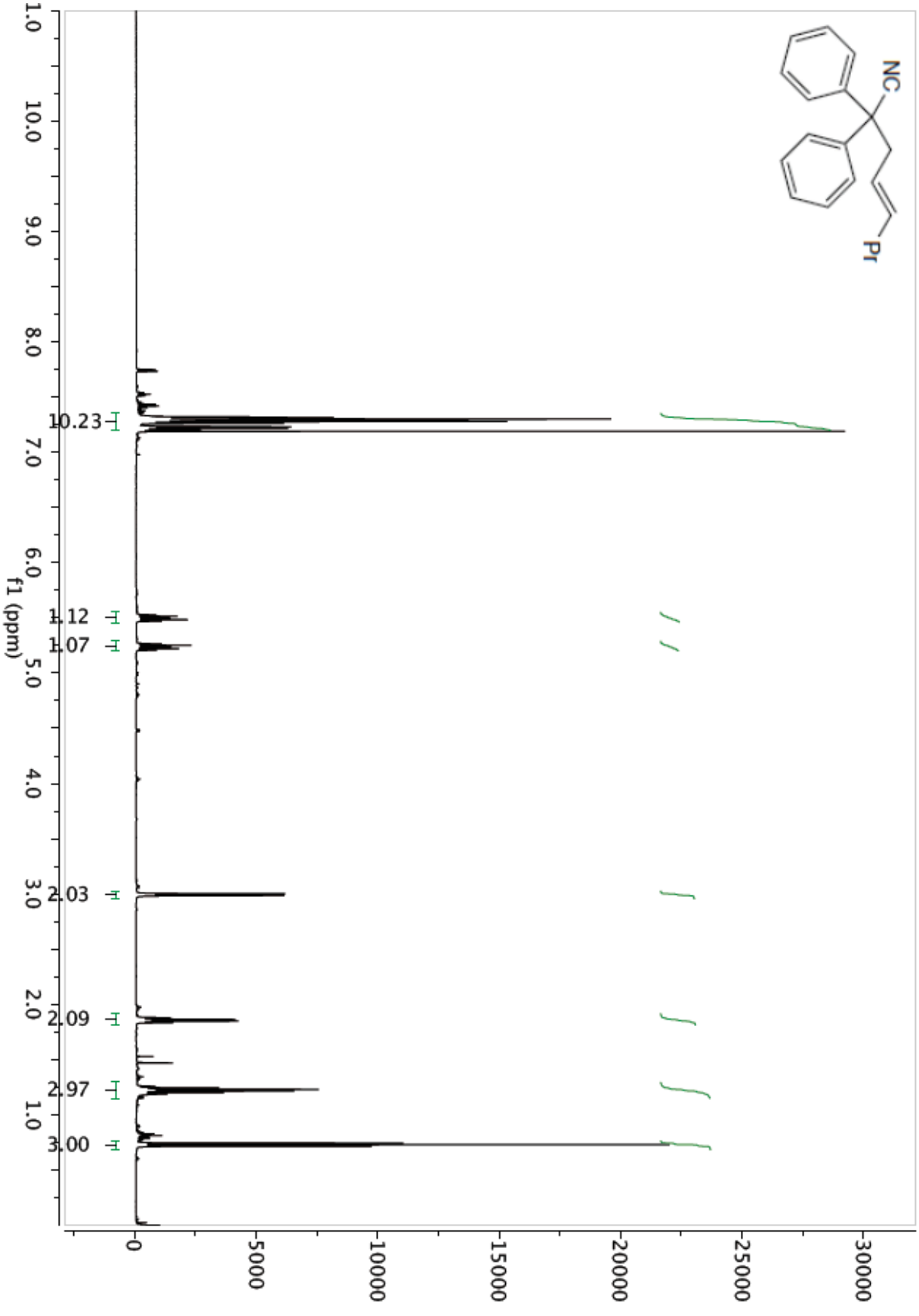
^{1}H NMR for Compound 5r



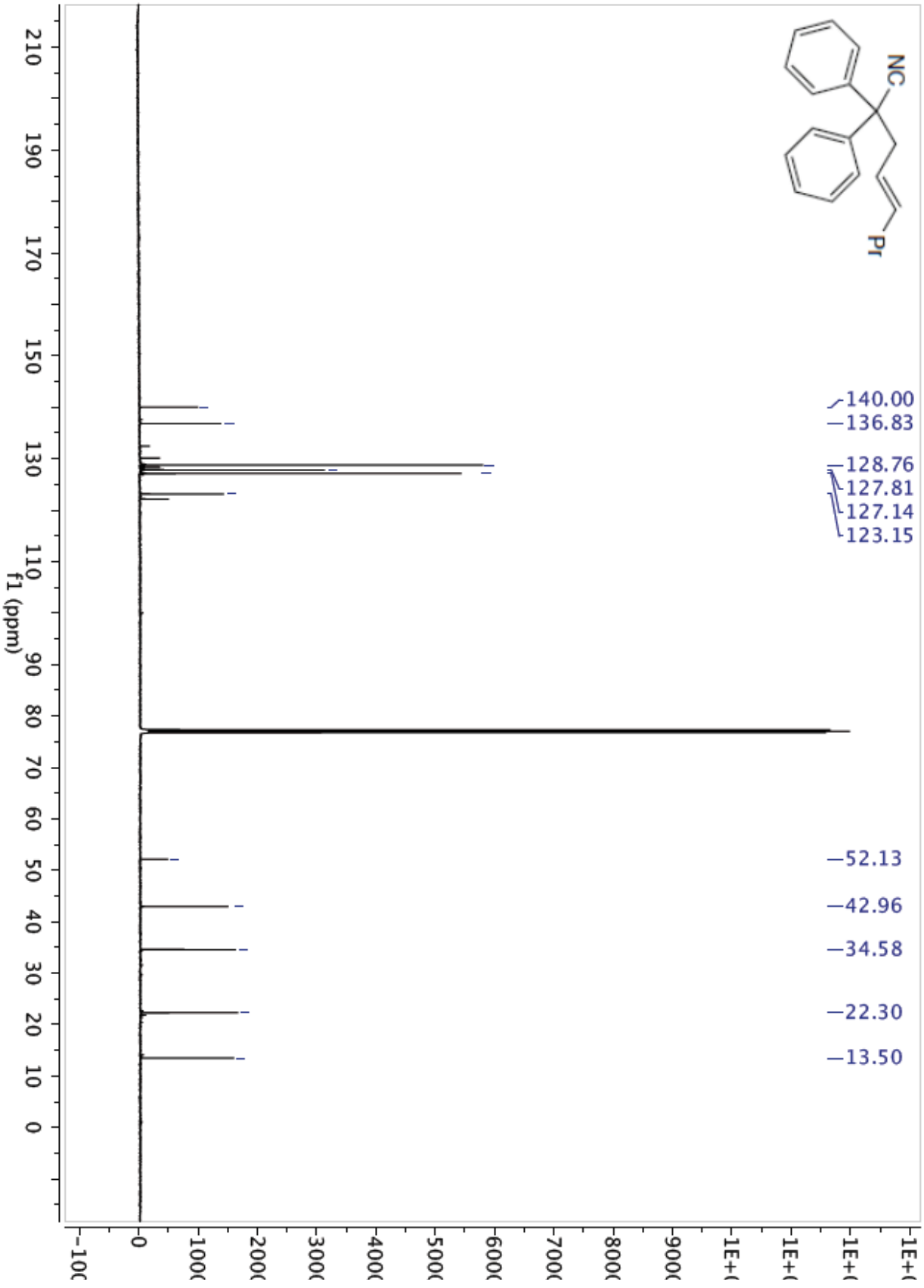
^{13}C NMR for Compound 5r



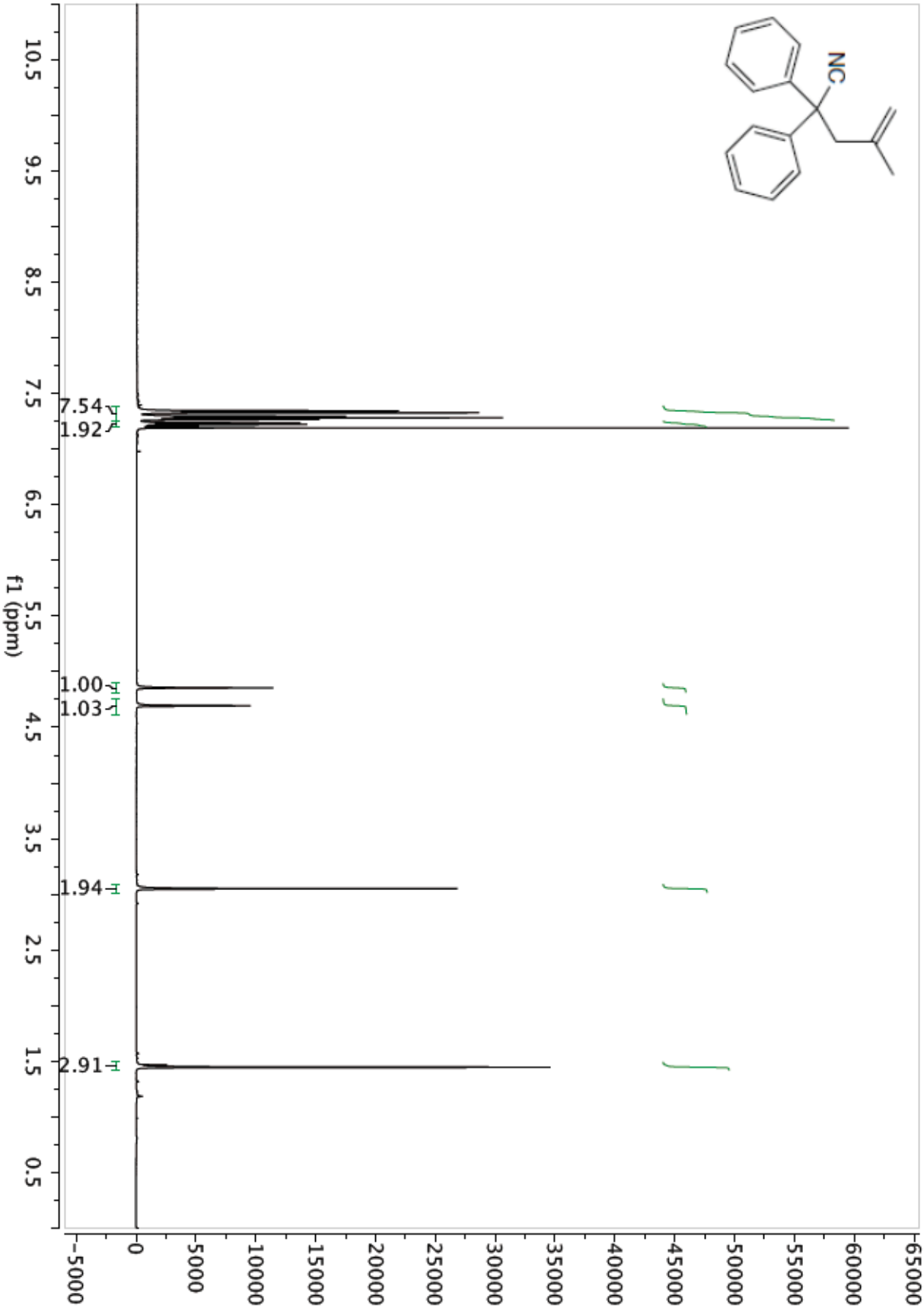
^{1}H NMR for Compound 5s



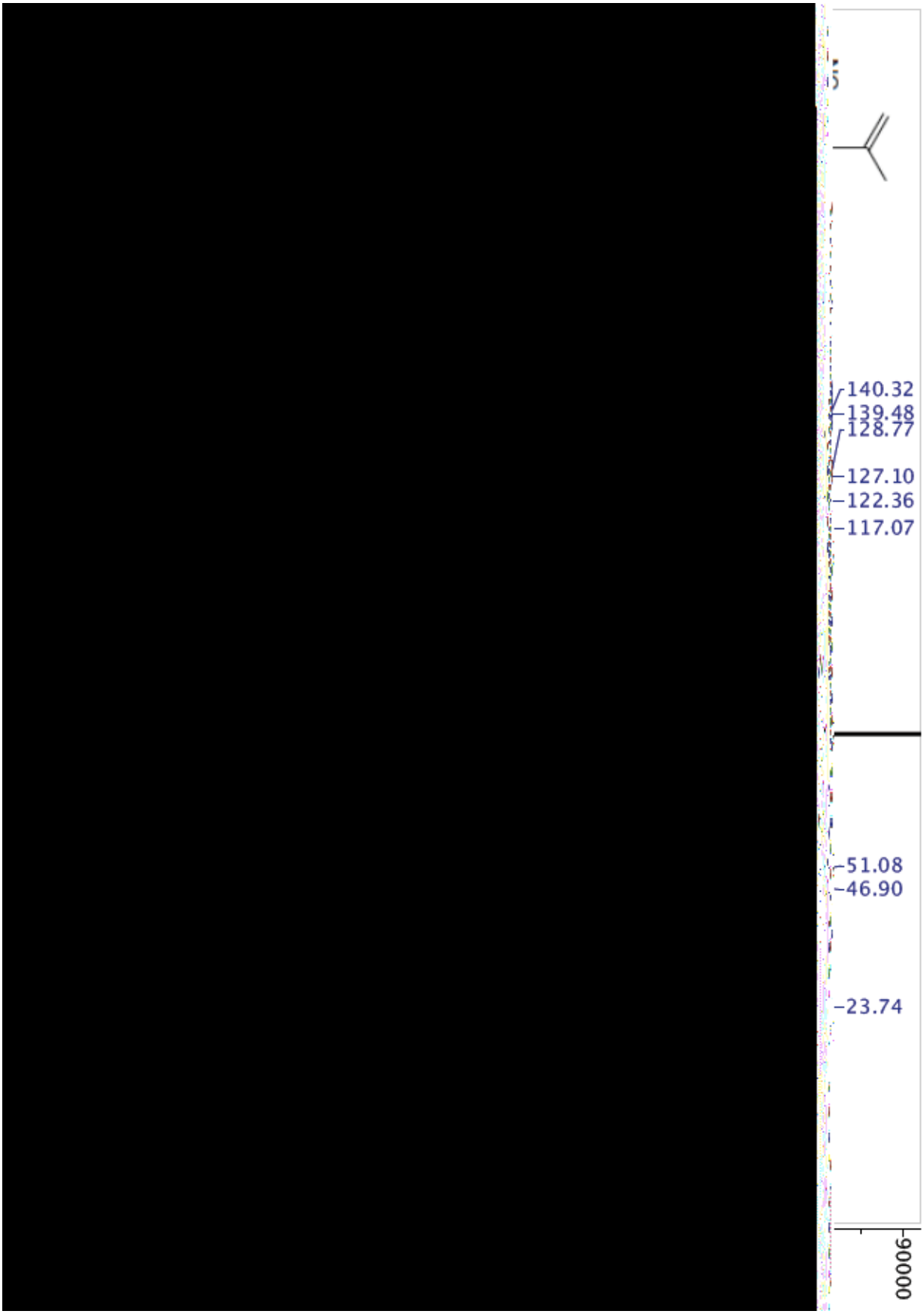
^{13}C NMR for Compound 5s



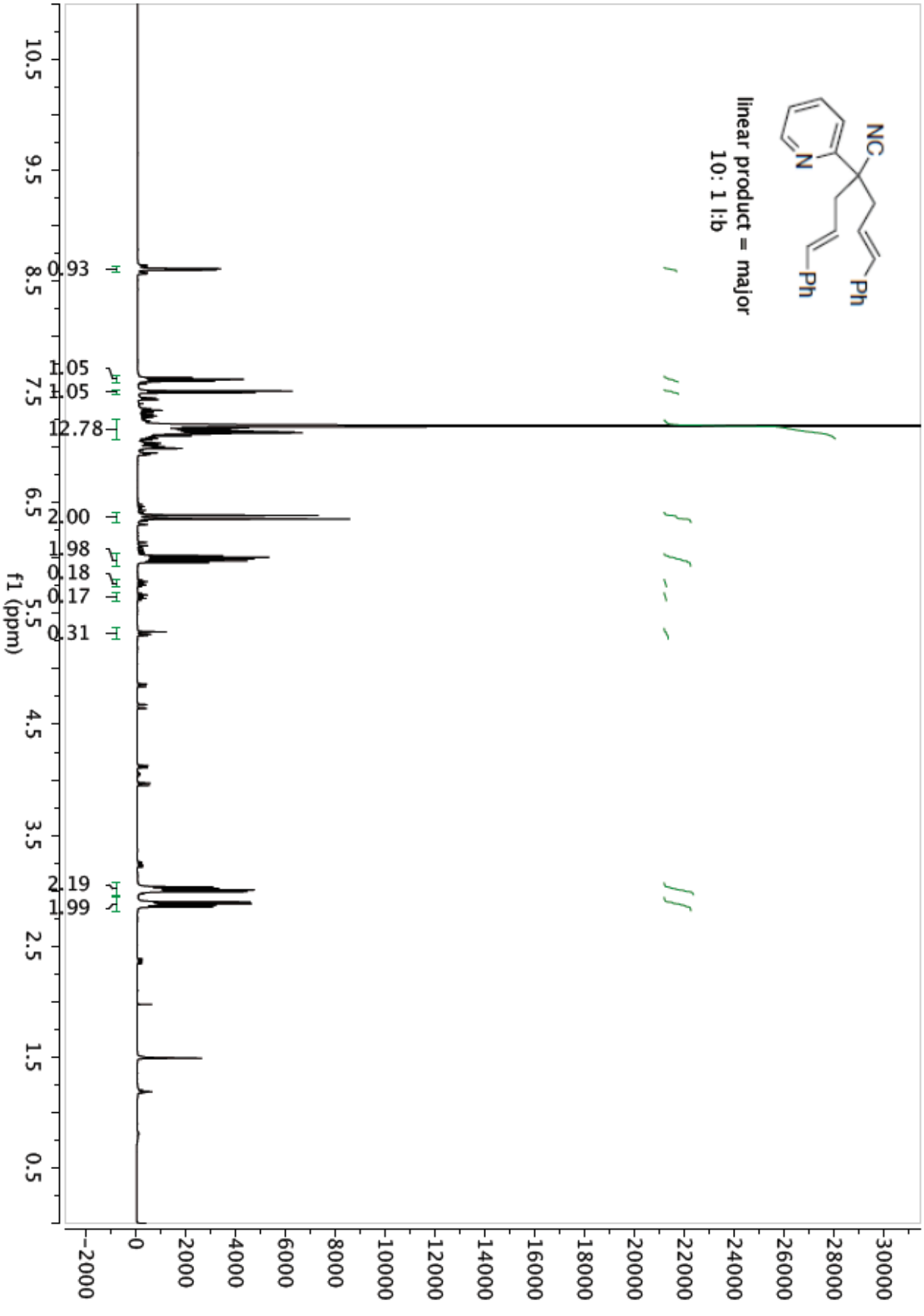
^{1}H NMR for Compound 5t



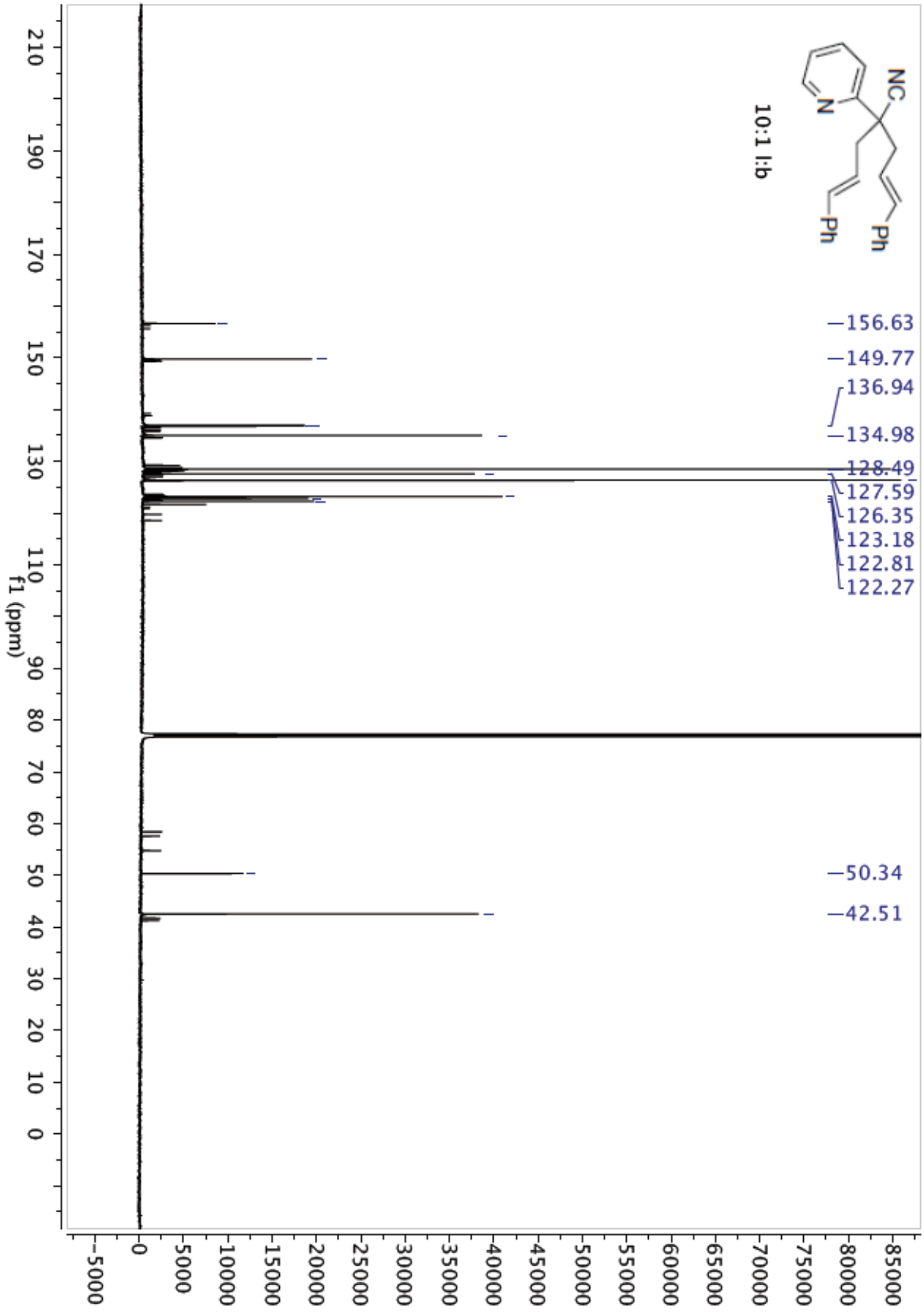
^{13}C NMR for Compound 5t



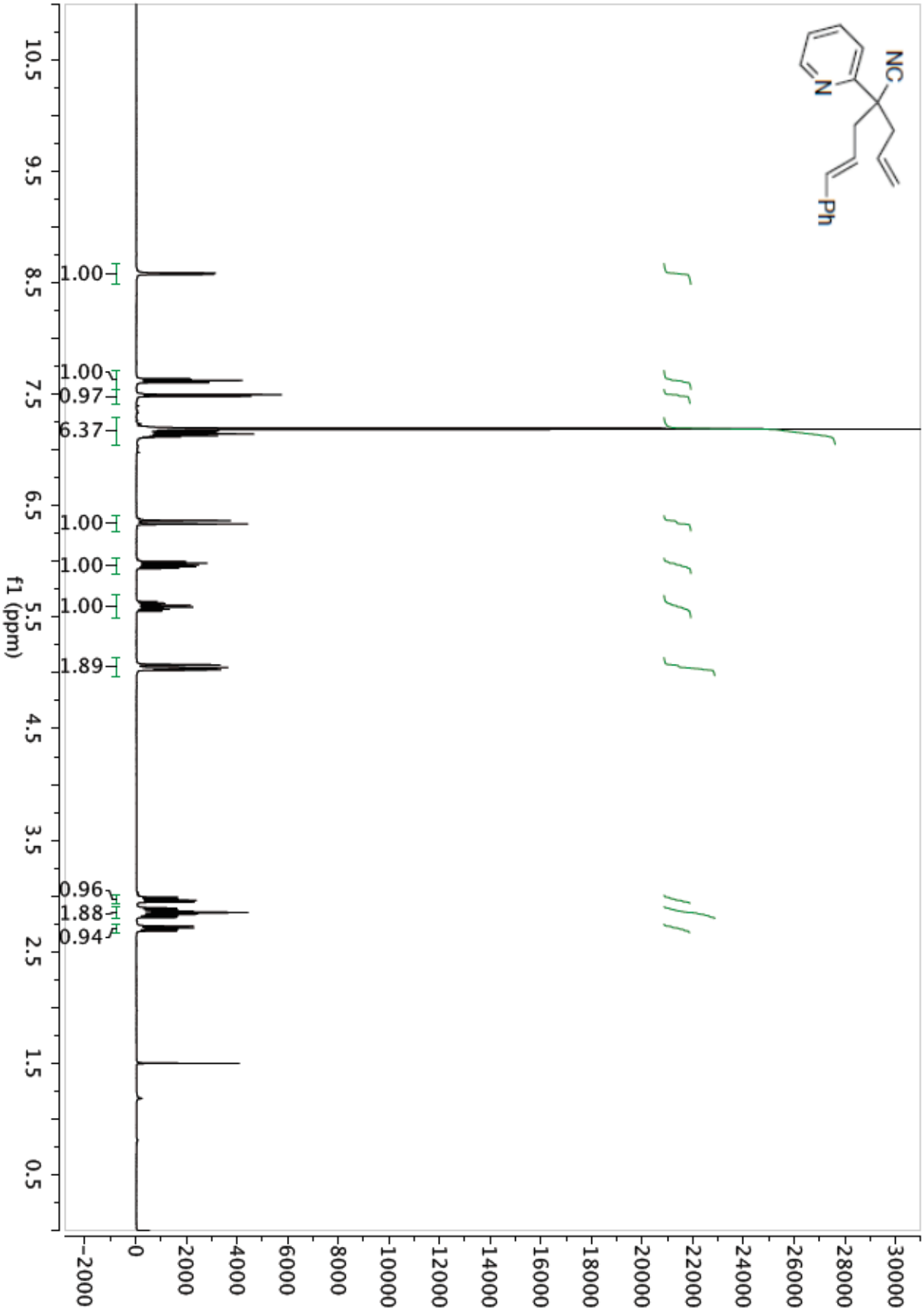
^{1}H NMR for Compound 5u



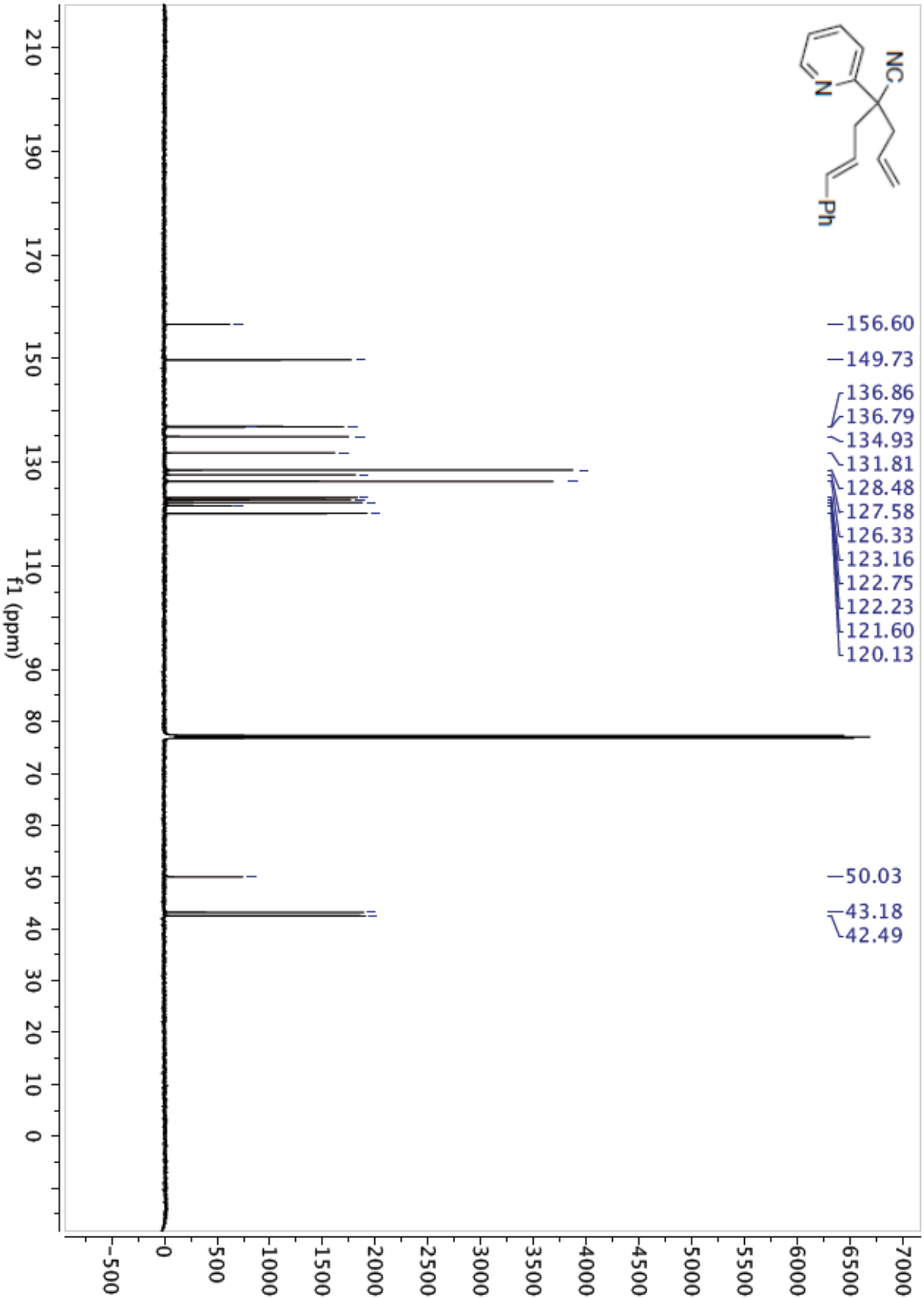
^{13}C NMR for Compound 5u



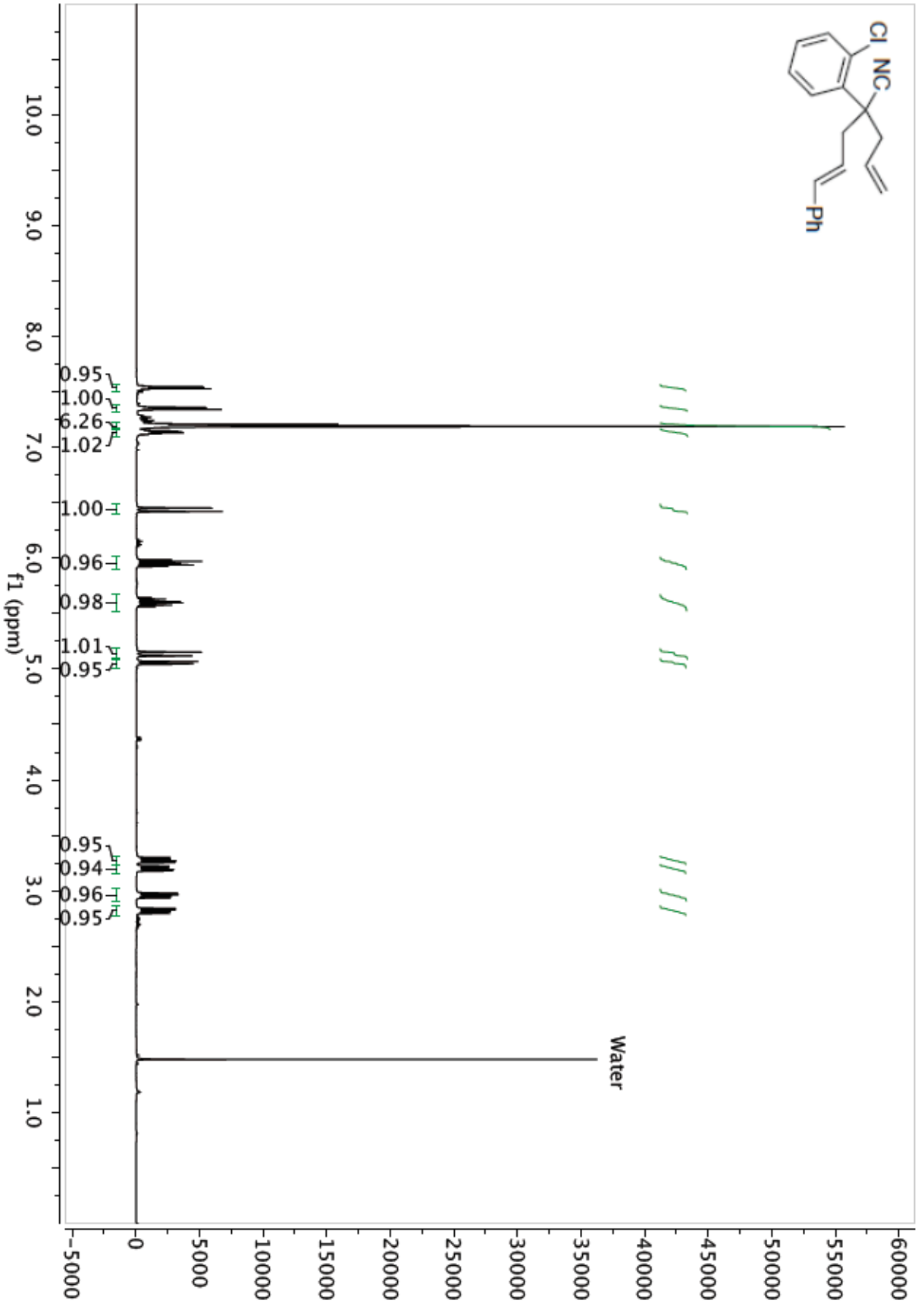
^{1}H NMR for Compound 5v



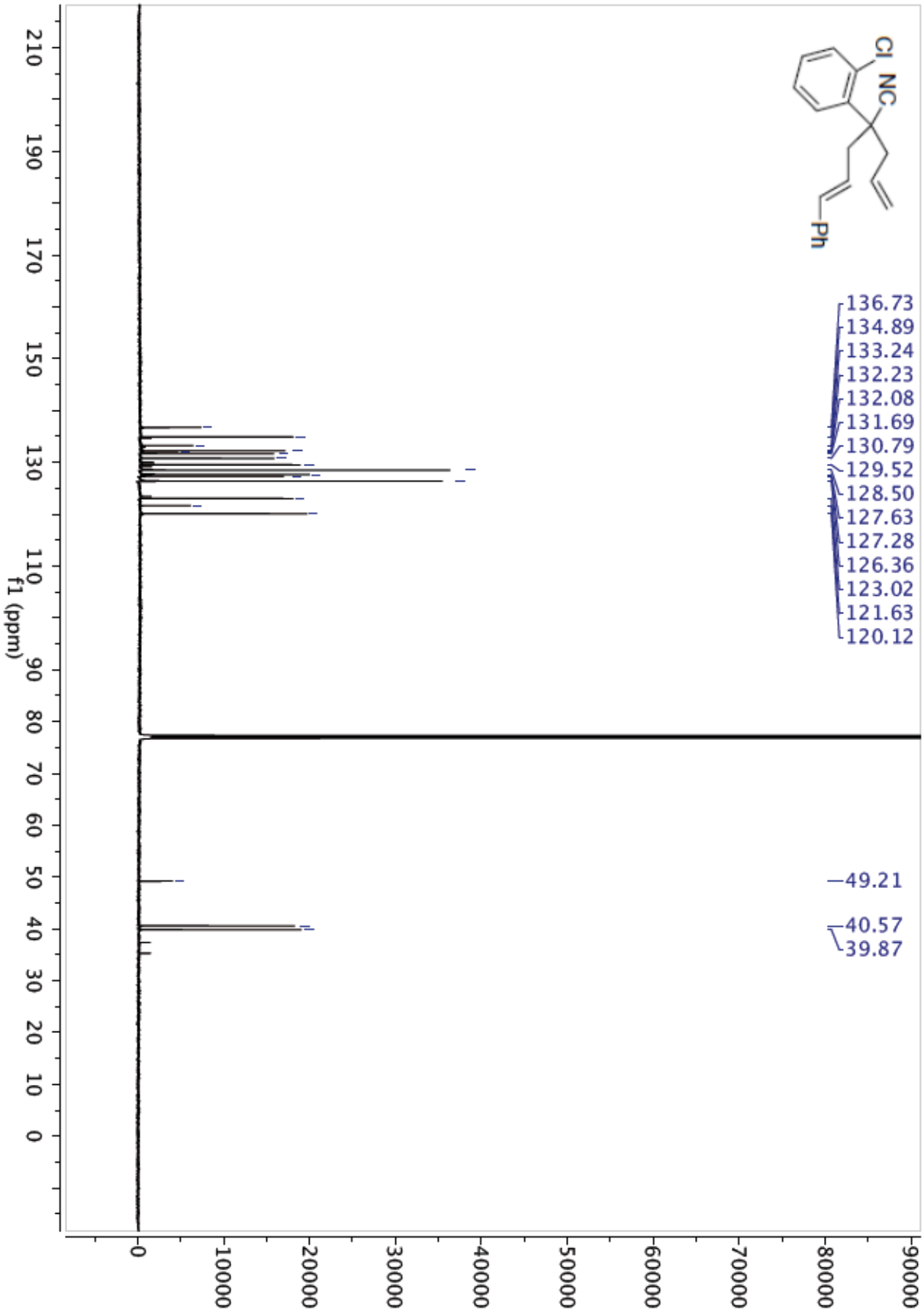
^{13}C NMR for Compound 5v



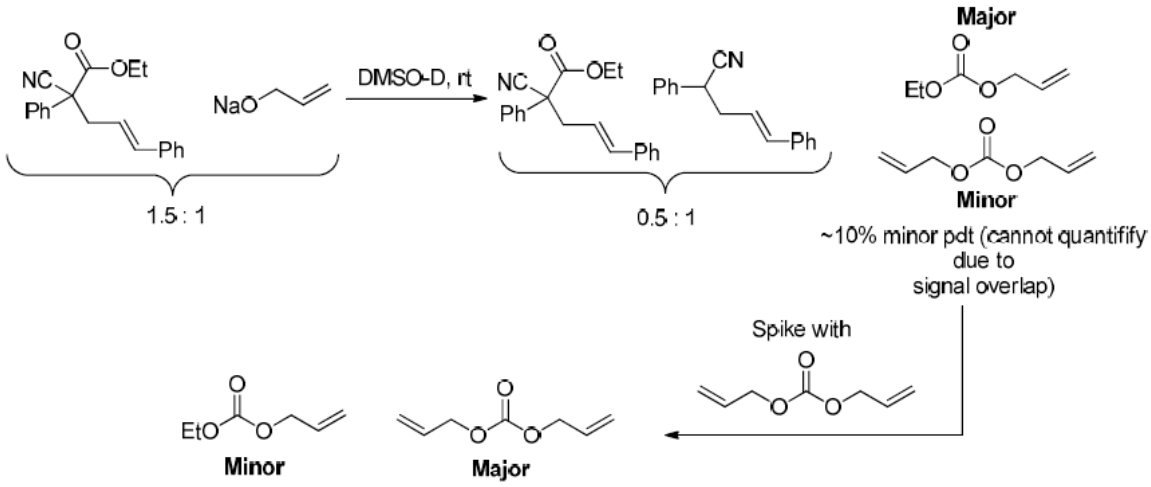
^{1}H NMR for Compound 5w



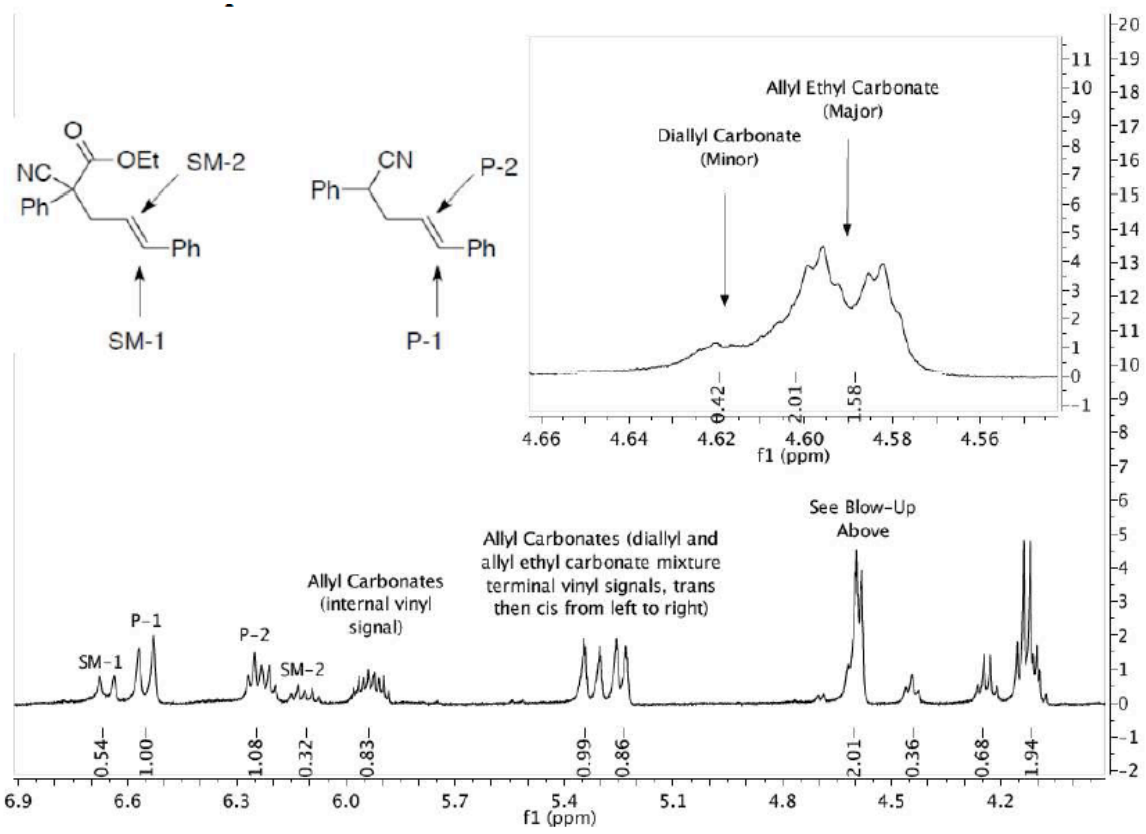
^{13}C NMR for Compound 5w



Diethyl Carbonate is the major product, supporting retro-Claisen activation:



Crude ^{1}H NMR spectrum:



Crude spectrum after addition of excess diallyl carbonate. Positively identifies the downfield doublet at 4.63 as that belonging to diallyl carbonate: