Supporting Information

Tunable Aziridinium Ylide Reactivity: Non-covalent Interactions Enable Divergent Product Outcomes

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I. General information

Unless otherwise specified, all reactions were run under an inert atmosphere of N_2. Glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Procedures for compounds requiring purification were obtained from "Purification of Laboratory Chemicals."[1a] All standard solvents (acetonitrile, dichloromethane, toluene) were obtained from a PureSolv MD5 5 column solvent purification system. All other solvents were also purified in accordance with methods reported in "Purification of Laboratory Chemicals".[1a] Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[1b] The mobile phases for column chromatography varied depending on the substrate; however, hexanes/ethyl acetate, or dichloromethane/ethyl acetate were commonly employed. Columns were typically run using a gradient method, beginning with 100% of the less polar eluent and gradually increasing the polarity with the other solvent. For reactions producing products without a UV signature, a potassium permanganate stain or acidic anisaldehyde stain was employed to visualize the reaction products. ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-400, Bruker Avance-500 or Varian Inova-600 NMR spectrometers. For ^{1}H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 4.80 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and CD_3OD respectively). ^{13}C NMR spectra were measured at either 125 MHz or 150 MHz on the same instruments noted above for recording ^{1}H NMR spectra. Chemical shifts were again reported in accordance to residual protiated solvent peaks (δ 77.1, 39.5, 128.0 and 49.0 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and CD_3OD, respectively). Accurate mass measurements were acquired at the University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). Crystal structure data was collected on a Bruker D8 VENTURE Phot on II funded by NSF CHE-1919350. The Paul Bender Chemistry Instrumentation Center (NMR, mass spectrometry and X-ray crystallography) is funded

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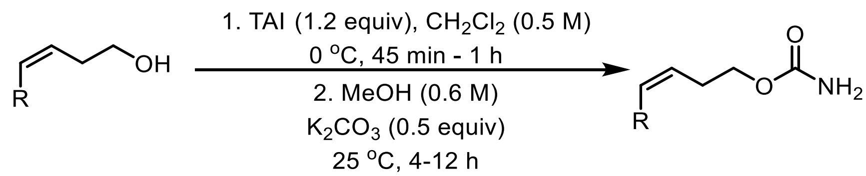
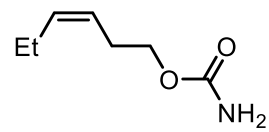
II. Substrate synthesis

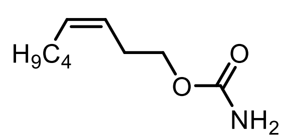
Preparation of carbamate aziridine precursors. All carbamates, if not explicitly mentioned in the subsequent sections, were synthesized according to reported literature procedures.[2]



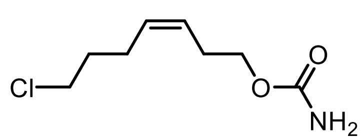
General procedure for carbamate formation. The homoallylic alcohol (1 equiv) was dissolved in CH_2Cl_2 (0.5 M) and cooled to 0 ˚C. Trichloroacetylisocyanate (TAI) (1.2 equiv) was then added dropwise to the cooled solution. The reaction was stirred at 0 ˚C until TLC indicated complete consumption of the starting material (usually between 45 min to 1 h). The solvent was then removed under reduced pressure and the crude reaction mixture was dissolved in MeOH (0.6 M). K_2CO_3 (0.5 eq.) was added in a single portion, and the mixture was stirred at room temperature until TLC indicated complete consumption of the starting material. Saturated aqueous NH_4Cl was added to quench the reaction and the mixture was extracted with three portions of CH_2Cl_2. The combined organic phases were washed with brine. The crude product was then diluted with CH_2Cl_2 (0.05 M) and 1 M aqueous NaOH solution (10 mL/mmol) was added. The biphasic solution was vigorously stirred for 30 min to remove the trichloroacetamide impurity. *Note: it is imperative that this step is done carefully. If not, it is likely that the aziridination will not proceed to completion.* The mixture was extracted with three portions of CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4 or $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (40% EtOAc/Hexanes).



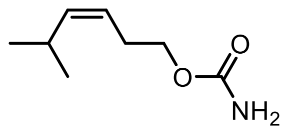
Carbamate precursor to Compound 1. Following the general procedure, the reaction to furnish the carbamate precursor to **1** was conducted on 22.1 mmol scale. The product was purified by silica gel flash column chromatography (0% to 50% EtOAc/Hex) to yield **1** as a white solid (2.92 g, 92% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (dtd, *J* = 10.5, 7.2, 1.6 Hz, 1H), 5.32 (dtt, *J* = 10.6, 7.3, 1.6 Hz, 1H), 4.68 (br s, 2H), 4.06 (t, *J* = 6.9 Hz, 2H), 2.37 (dt, *J* = 8.2, 6.3 Hz, 2H), 2.06 (td, *J* = 7.5, 1.5 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 134.6, 123.8, 64.7, 27.0, 20.6, 14.2. *m/z* matched already published data.[2]



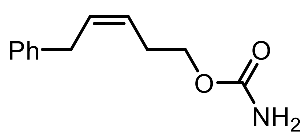
Carbamate precursor to Compound 12. Following the general procedure, the reaction to furnish the carbamate precursor to **12** was conducted on a 15.7 mmol scale. The product was purified by silica gel flash column chromatography (40% EtOAc/Hex) to yield **12** as a white solid (1.19 g, 44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 – 5.46 (m, 1H), 5.43 – 5.28 (m, 1H), 4.56 (bs, 2H), 4.06 (t, *J* = 6.9 Hz, 2H), 2.59 – 2.35 (m, 2H), 2.05 (m, 2H), 1.44 – 1.28 (m, 4H), 1.03 – 0.80 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 133.1, 124.5, 64.9, 31.9, 27.3, 27.2, 22.5, 14.1. HRMS (ESI) *m/z* calculated for $C_9H_{17}NO_2$ $[M+H]^+$ 172.1332; found, 172.1330.



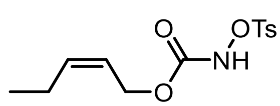
Carbamate precursor to Compound 13. Following the general procedure, the reaction to furnish carbamate precursor to **13** was conducted on a 4.6 mmol scale. The product was purified by silica gel flash column chromatography (30% EtOAc/Hex) to yield **13** as a white solid (0.830 g, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 – 5.27 (m, 2H), 4.60 (br s, 2H), 4.08 (t, *J* = 6.8 Hz, 2H), 3.54 (t, *J* = 6.5 Hz, 2H), 2.51 – 2.33 (m, 2H), 2.33 – 2.17 (m, 2H), 1.93 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 130.5, 126.3, 64.5, 44.4, 32.2, 27.1, 24.4. HRMS (ESI) *m/z* calculated for $C_8H_{14}NO_2$ [M+H]$^+$ 192.0786; found, 192.0784.



Carbamate precursor to Compound 14. Following the general procedure, the reaction to furnish carbamate precursor to **14** was conducted on a 6.02 mmol scale. The product was purified by silica gel flash column chromatography (40% EtOAc/Hex) to yield **14** as a white solid (0.690 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (ddt, *J* = 11.0, 9.4, 1.5 Hz, 1H), 5.23 (dt, *J* = 10.7, 7.2 Hz, 1H), 4.53 (br s, 2H), 4.06 (t, *J* = 6.9 Hz, 2H), 2.60 (m, 1H), 2.39 (qd, *J* = 7.0, 1.5 Hz, 2H), 0.96 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 140.4, 121.9, 64.8, 27.2, 26.6, 23.1. HRMS (ESI) *m/z* calculated for $C_8H_{15}NO_2$ [M+H]$^+$ 158.1176; found, 158.1175.

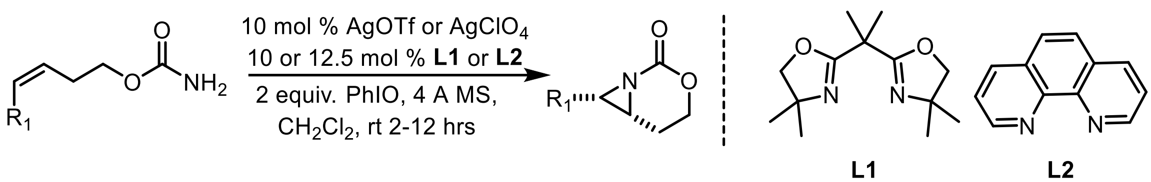


Carbamate precursor to Compound 15. Following the general procedure, the reaction to furnish the carbamate precursor to **15** was conducted on a 10 mmol scale. The product was purified by silica gel flash column chromatography (20% to 50% EtOAc/Hex) to yield **15** as a white solid (1.81g, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.72 (dtt, *J* = 10.8, 7.5, 1.6 Hz, 1H), 5.52 (dtt, *J* = 10.7, 7.3, 1.7 Hz, 1H), 4.55 (br s, 2H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.43 (dd, *J* = 7.5, 1.5 Hz, 2H), 2.50 (tdd, *J* = 6.8, 6.8, 1.8 Hz); (app qd, *J* = 6.8, 1.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 140.8, 131.1, 128.6, 128.5, 126.1, 125.8, 64.6, 33.6, 27.3. HRMS (ESI) *m/z* calculated for $C_{12}H_{15}NO_2$ [M+H]$^+$ 206.1176; found, 206.1173.

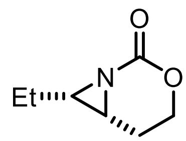


Carbamate precursor to Compound 18. The *N*-tosyl carbamate **18** was synthesized following Lebel's reported procedure.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.77 (br s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.62 (dtt, *J* = 10.3, 7.5, 1.4 Hz, 1H), 5.29 (dtt, *J* = 10.4, 7.0, 1.6 Hz, 1H), 4.56 (dd, *J* = 7.0, 1.2 Hz, 2H), 2.46 (s, 3H), 2.04 (qdd, *J* = 7.6 Hz, 7.6 Hz, 1.6 Hz); (app pd, *J* = 7.6, 1.6 Hz). , 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 146.2, 138.2, 130.5, 129.9, 129.7, 121.5, 62.8, 21.9, 21.0, 14.1. δ HRMS (ESI) *m/z* calculated for $C_{13}H_{21}N_2O_5S$ $[M+NH_4]^+$ 317.1166; found, 317.1166.

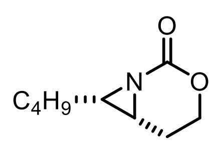
III. Preparation of aziridine precursors. All aziridines, if not explicitly mentioned in the subsequent sections, were synthesized according to reported literature procedures.[2]



General procedure for silver-catalyzed aziridination of homoallylic carbamates. A cooled, flame-dried round bottom flask was charged with AgOTf (0.1 equiv) and dimethyl bisoxazoline (dmBox) **L1** or 1,10-phenanthroline ligand **L2** (0.1 equiv). Dry CH_2Cl_2 (0.05 M) was added to the flask and the mixture was stirred vigorously for 10 min. *Note: Both* ***L1*** *and* ***L2*** *will furnish the aziridine product.* ***L2*** *may result in varying ratios of aziridine to C-H insertion product if the metal/ligand ratio is not carefully measured to be 1:1.*[2] ***L1*** *is the preferable ligand, as the ratio of metal/ligand is not as important to the aziridine/C-H insertion product ratio. However,* ***L2*** *is a good commercially available alternative if* ***L1*** *is unavailable.* After 10 min of pre-stirring, powdered 4Å molecular sieves (1g of sieves /mmol of substrate) were added. *Note: It is not necessary to use rigorously dried molecular sieves*. After 5 min, the carbamate ester (1 equiv) and iodosobenzene (2 equiv) were added. The reaction was then capped, covered in aluminum foil (if AgOTf is used), and allowed to stir at room temperature for 2-12 h. After TLC indicated complete consumption of the starting material, the reaction mixture was filtered over Celite and concentrated. The crude mixture was then purified by column chromatography – once with a gradient elution of 0-2.5% MeOH/CH_2Cl_2, followed by a second column with a gradient elution of 0-50% EtOAc/Hex or 5% EtOAc/CH_2Cl_2. *Note*: *omitting the first plug with CH_2Cl_2 leaves silver* *byproducts in the mixture, which, upon concentration, can degrade the aziridine over time or cause decreased reactivity in the subsequent carbene transfer reaction.* The compounds were stored at -20 ˚C to prevent decomposition. All aziridines not described below were prepared according to published literature procedures.

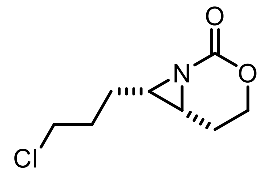


Compound 1. Following the general procedure, the aziridination reaction to furnish **1** was conducted on 6.98 mmol scale. The product was purified by silica gel flash column chromatography (0-2.5% MeOH/CH_2Cl_2, then 0 to 5% EtOAc/CH_2Cl_2) to yield **1** as a white solid (0.660 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 – 4.27 (m, 2H), 2.84 (ddd, *J* = 9.0, 6.9, 4.9 Hz, 1H), 2.57 (dt, *J* = 8.3, 5.2 Hz, 1H), 2.16 (dddd, *J* = 14.7, 7.0, 2.0, 2.0 Hz, 1H); app ddt, *J* = 14.7, 7.0, 2.0 Hz, 1H), 1.83 (dqd, *J* = 14.4, 7.3, 5.3 Hz, 1H), 1.44 (dddd, *J* = 14.3, 12.1, 9.0, 4.9 Hz, 1H), 1.29 – 1.14 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 68.0, 44.0, 37.3, 19.0 (d, *J* = 2.0 Hz), 10.9. HRMS (ESI) *m/z* matched already published data.[2]

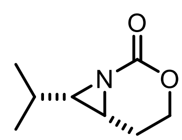


Compound 12. Following the general procedure, the aziridination reaction to furnish **12** was conducted on an 8.76 mmol scale. The product was purified by silica gel flash column chromatography (2.5% MeOH/CH_2Cl_2 and 5% EtOAc/CH_2Cl_2) to yield **12** as a colorless oil (329.9 mg, 33%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48 – 4.29 (m, 2H), 2.87 (ddd, *J* = 8.9, 6.9, 4.9 Hz, 1H), 2.63 (dt, *J* = 9.4, 4.9 Hz, 1H), 2.18 (ddt, *J* = 14.6, 6.9, 2.0 Hz, 1H), 1.88 (ddt, *J* = 14.2, 9.6, 5.2 Hz, 1H), 1.63 – 1.32 (m, 5H), 1.16 (dtd, *J* = 14.6, 9.2, 5.2 Hz, 1H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 68.0, 42.9, 37.5, 28.8,

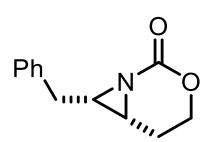
25.2, 22.6, 19.3, 14.1. HRMS (ESI) *m/z* calculated for $C_9H_{16}NO_2$ $[M+H]^+$ 170.1176; found, 170.1174.



Compound 13. Following the general procedure, the aziridination reaction to furnish **13** was conducted on 0.42 mmol scale. The product was purified by silica gel flash column chromatography (2.5% MeOH/CH_2Cl_2 and then 0 to 50% EtOAc/Hex) to yield **13** as a colorless oil (49.7 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 – 4.33 (m, 2H), 3.63 (ddd, J = 11.0, 6.8, 5.2 Hz, 1H), 3.55 (ddd, J = 11.0, 7.6, 5.2 Hz, 1H), 2.90 (ddd, J = 9.0, 6.9, 4.9 Hz, 1H), 2.65 (ddd, J = 7.5, 6.0, 4.9 Hz, 1H), 2.30 – 2.11 (m, 2H), 1.97 – 1.87 (m, 1H), 1.83 (dddd, J = 14.5, 9.6, 5.9, 4.8 Hz, 1H), 1.65 – 1.47 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 68.0, 44.3, 42.0, 37.4, 29.6, 23.2, 19.3 HRMS (ESI) *m/z* calculated for $C_8H_{12}ClNO_2$$[M+H]^+$ 190.0629; found, 190.0630.

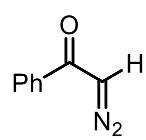


Compound 14. Following the general procedure, the aziridination reaction to furnish **14** was conducted on a 2.05 mmol scale. The product was purified by silica gel flash column chromatography (2.5% MeOH/CH_2Cl_2 and 5% EtOAc/CH_2Cl_2) to yield **14** as a white solid (0.316 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 – 4.22 (m, 2H), 2.81 (ddd, J = 9.1, 6.8, 5.0 Hz, 1H), 2.38 (dd, J = 9.9, 5.0 Hz, 1H), 2.19 (ddt, J = 14.6, 6.8, 2.0 Hz, 1H), 1.62 – 1.35 (m, 2H), 1.30 (d, J = 6.4 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 67.7, 49.4, 36.9, 26.9, 20.1, 20.0, 19.6. HRMS-(ESI) *m/z* calculated for $C_8H_{14}NO_4$ $[M+Na]^+$ 156.1019; found, 156.1019.

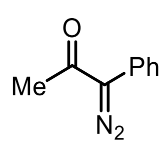


Compound 15. Following the general procedure, the aziridination reaction to furnish **15** was conducted on 0.48 mmol scale. The product was purified by silica gel flash column chromatography (0-2.5% MeOH/CH_2Cl_2, then 0 to 5% EtOAc/CH_2Cl_2) to yield **15** as a white solid (84.9 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (tt, *J* = 8.1, 1.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 4.50 – 4.39 (m, 2H), 3.34 (dd, *J* = 15.4, 3.9 Hz, 1H), 2.98 (ddd, *J* = 8.9, 6.8, 4.8 Hz, 1H), 2.90 (ddd, *J* = 10.1, 4.8, 3.9 Hz, 1H), 2.41 (dd, *J* = 15.3, 10.1 Hz, 1H), 2.29 (ddt, *J* = 14.6, 6.8, 1.9 Hz, 1H), 1.69 (dddd, *J* = 14.4, 12.1, 8.9, 4.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 136.7, 129.0, 128.5, 127.2, 68.1, 42.8, 37.8, 31.1, 19.7. HRMS (ESI) *m/z* calculated for $C_{12}H_{13}NO_2$[M+H]$^+$ 204.1019; found, 204.1020.

IV. Preparation of diazoketones. All diazoketone compounds, if not directly mentioned in the subsequent sections, were synthesized according to the reported literature procedures described therein. All spectroscopic data either matched that reported in the literature for the indicated compounds or new compounds were fully characterized in our facilities. When the data was not specifically obtained by us, a reference is provided so that the data may be easily located. [4-9] Frequently, the signal to noise ratio for the diazo-carbon is not intense enough to be seen on ^{13}C NMR.

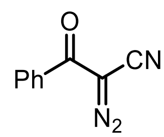


Compound 2a. The formation of **2a** was conducted on 1.5 mmol scale. The product was used without further purification and was isolated as a red solid (0.220 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 7.1, 1.4 Hz, 2H), 7.67 – 7.52 (m, 1H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.90 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.4, 136.9, 132.9, 128.8, 126.9, 54.3. *m/z* matched already published data.[8]

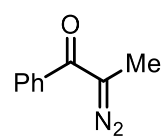


Compound 2b. The formation of **2b** was conducted on 14.2 mmol scale. The product was used without further purification and **2b** was obtained as an orange solid (1.56 g, 69%). ^{1}H

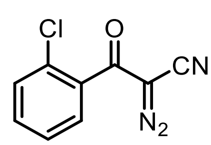
NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.26 (dt, *J* = 14.7, 1.3 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 129.1, 127.03, 125.9, 125.6, 72.7, 27.0. *m/z* matched already published data.[8]



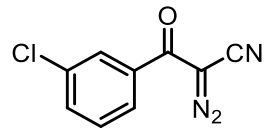
Compound 2c. The formation of **2e** was conducted on 4.0 mmol scale. The product was used without the need for purification by column chromatography and yielded **2e** as a red solid (0.405 g, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.80 (m, 2H), 7.70 – 7.56 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.0, 134.8, 134.0, 129.0, 128.2, 109.3. *m/z* matched already published data.[8]



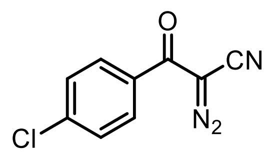
Compound 2d. The formation of **2d** was conducted on 1.5 mmol scale. The product **2d** was used without further purification as an orange solid (121.8 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.43 (dd, *J* = 8.2, 6.5 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3, 137.8, 131.5, 128.7, 127.3, 68.1, 25.8. *m/z* matched already published data.[8]



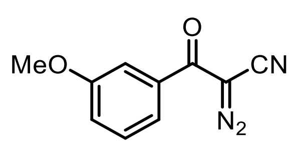
Diazoketone precursor to 6c. The formation of diazoketone precursor to **6c** was conducted on a 3.0 mmol scale according to the procedure reported by Krasavin.[8b] The product was additionally subjected to silica flash column chromatography (0% to 50% EtOAc/Hex) to yield the diazoketone precursor to **6c** as an orange solid (0.185 g, 30% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.46 – 7.43 (m, 1H), 7.39 (ddd, *J* = 7.7, 4.9, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.8, 134.8, 133.1, 131.4, 130.8, 128.8, 127.3, 107.9. HRMS (ESI) *m/z* calculated for $C_9H_4ClNO_3$ [M+Na]+ 227.9935; found, 227.9933.



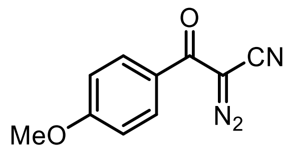
Diazoketone precursor to 7c. The formation of the diazoketone precursor to **7c** was conducted on a 4.0 mmol scale. The product was pure and required no purification by column chromatography. The diazoketone precursor to **7c** was produced as an orange solid (0.400 g, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, *J* = 2.0 Hz, 1H), 7.78 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.8, 136.1, 135.5, 134.0, 130.3, 128.3, 126.2, 108.9. *m/z* matched already published data.[8]



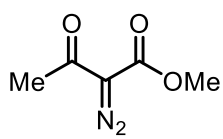
Diazoketone precursor to 8c. The formation of diazoketone precursor to **8c** was conducted on a 3.0 mmol scale according to the procedure reported by Krasavin.[8b] The product was additionally subjected to silica flash column chromatography (0% to 50% EtOAc/Hex) to yield the diazoketone precursor to **8c** as an orange solid (0.280 g, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 7.89 – 7.81 (m, 2H), 7.52 – 7.40 (m, 2H). δ ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.8, 140.6, 133.0, 129.7, 129.4, 109. HRMS (ASAP) $C_9H_4ClNO_3$ [M-N_2+H]+ 178.0054; found, 178.0055.



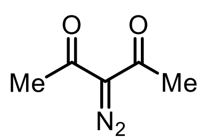
Diazoketone precursor to 10c. The formation of the diazoketone precursor to **10c** was conducted on a 4.0 mmol scale. The product was used without further purification by chromatography to yield the diazoketone precursor to **10c** as a red solid (0.142 g, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 2.6, 1.7 Hz, 1H), 7.16 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.8, 160.0, 135.9, 130.1, 120.7, 120.6, 112.6, 109.3, 55.7. The *m/z* matched previously published data.[8]



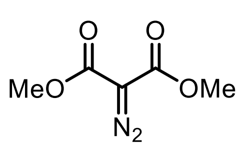
Diazoketone precursor to 11c. The formation of the diazoketone precursor to **11c** was conducted on a 3.0 mmol scale according to the procedure reported by Krasavin.[8b,9] The product was additionally subjected to silica flash column chromatography (0% to 50% EtOAc/Hex) to yield the diazoketone precursor to **11c** as a bright yellow solid (0.280 g, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.79 (m, 2H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.2, 164.3, 130.7, 127.5, 114.3, 109.9, 55.8. *m/z* matched already published data.[9]



Compound 2e. The formation of **2e** was conducted on a 21.5 mmol scale. The product was purified by trituration with pentane/diethyl ether (2:1 v/v) to yield **2e** as a yellow oil (2.50 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ. δ 3.84 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 162.0, 52.4, 28.4. *m/z* matched already published data.[4]



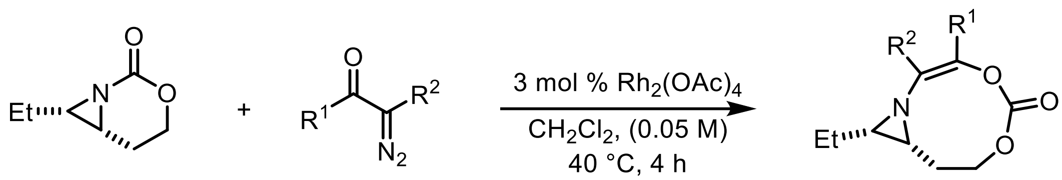
Compound 2f. The formation of **2f** was conducted on a 50 mmol scale. The product was purified by trituration with pentane/diethyl ether (2:1 v/v) to yield **2f** as a yellow oil (5.2 g, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.4, 28.6 *m/z* matched already published data.[6]



Compound SI-1. The formation of **SI-1** was conducted on a 7.6 mmol scale. The product was used without further purification and isolated as an off-white solid (1.20 g, quantitative yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 52.7. *m/z* matched already published data.[7]

V. General procedures for carbene transfer.

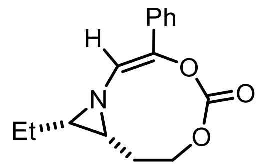
General Procedure A:



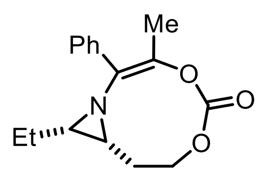
A flame-dried round bottom flask was placed under N_2 and charged with $Rh_2(OAc)_4$ (0.03 equiv), followed by a solution of the aziridine (0.1 M in dry CH_2Cl_2). The reaction setup was equipped with a reflux condenser and purged with N_2. *Note: Upon the addition of aziridine, a color change of green to purple will be observed. This does not signify catalyst death; rather, experiments show that if this color change is not observed, the reaction is less likely to proceed*. To this mixture was added a solution of the diazoketone compound (2.5 equiv, brought to 0.1 M in CH_2Cl_2) dropwise over 4 h using a syringe pump. The conversion was checked by TLC and NMR after the addition was complete, and once all the starting material had been consumed, the crude material was concentrated *in vacuo* and subjected to flash column chromatography using silica-9, a basified silica gel with a pH of 9 in an aqueous solution (see below for procedure). *Note: Any exposure to standard silica gel or basic alumina led to extensive decomposition. On occasion, the [3,9]-aziridines generated via this method were unstable towards any purification media, including silica-9. Those results are reported as NMR yields using 1,3,5-trimethoxybenzene as the internal standard.* A gradient of 0% to 50% EtOAc/hexanes was used, with most compounds eluting around ~30% EtOAc/hexanes.

Procedure for generation of silica-9.

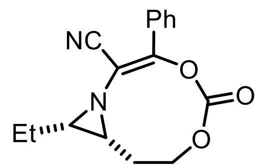
Silica-9 was prepared via a modified procedure described by both Deli[10a] and Yoon.[10b] Silica gel (200 g) was added to 2 L of saturated aqueous $NaHCO_3$. The resulting slurry was vigorously stirred for 2 h, at which point the mixture was diluted with 200 mL acetone and filtered. The silica gel was washed three times with a 1:1 H_2O/acetone mixture and once with acetone, and the filtrate was allowed to air dry overnight before use.



Compound 3a. Following the general procedure, the carbene transfer to furnish **3a** was conducted on 0.2 mmol scale. The product was purified by flash column chromatography using silica-9 (0% to 50% EtOAc/Hex) to yield **3a** as a white solid (40.0 mg, 78% yield, >20:1 *dr*). A crystal structure for this compound can be found in Section X. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.12 (m, 1H), 6.48 (s, 1H), 4.77 – 4.68 (m, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 2.05 (q, *J* = 6.6 Hz, 1H), 1.98 (dt, *J* = 14.6, 2.8 Hz, 1H), 1.85 (ddd, *J* = 11.2, 6.4, 1.8 Hz, 1H), 1.71 (dtd, *J* = 14.5, 11.3, 3.0 Hz, 1H), 1.51 (dp, *J* = 14.7, 7.4 Hz, 1H), 1.45 – 1.30 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 143.7, 132.9, 128.7, 128.6, 127.7, 123.0, 69.7, 45.5, 28.5, 22.0, 11.7. HRMS (ESI) *m/z* calculated for $C_{15}H_{17}NO_3$ [M+Na]+ 282.1101; found, 382.1096.



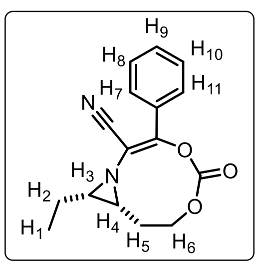
Compound 3b. Following the general procedure, the carbene transfer to furnish **3b** was conducted on a 0.3 mmol scale. The product was purified by flash column chromatography using silica-9 (0 to 50% EtOAc/Hex) to yield **3b** as a white solid (75.0 mg, 92% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 4.74 (t, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 2.04 (m, 4H), 1.99 (ddd, *J* = 11.1, 6.5, 1.9 Hz, 1H), 1.79 (ddd, *J* = 14.8, 11.0, 3.0 Hz, 1H), 1.73 (q, *J* = 6.6 Hz, 1H), 1.63 – 1.48 (m, 1H), 1.39 – 1.27 (m, 1H), 0.78 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 140.0, 137.6, 134.7, 129.0, 128.3, 128.1, 69.34, 43.5, 29.0, 22.1, 17.1, 11.6. HRMS (ESI) *m/z* calculated for $C_{16}H_{19}NO_3$ [M+H]+ 274.1438; found, 274.1434.



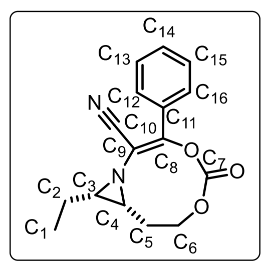
Compound 3c. Following the general procedure, the carbene transfer to furnish **3c** was conducted on a 0.2 mmol scale. Unfortunately, this compound was unstable to all forms of chromatography, including purification with silica-9. As a result, the yield reported below is an NMR yield using 1,3,5-trimethoxybenzene as an internal standard (68% yield, >20:1 *dr* 87% mass balance). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 2H), 7.50 – 7.40 (m, 3H), 4.66 (td, *J* = 11.6, 2.3 Hz, 1H), 4.62 – 4.55 (m, 1H), 2.56 (q, *J* = 6.7 Hz, 1H), 2.10 (dddd, *J* = 15.3, 7.4, 5.8, 2.3 Hz, 2H), 1.92 (dtd, *J* = 15.3, 11.3, 4.0 Hz, 1H), 1.59 (tt, *J* = 14.0, 7.0 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 150.0, 130.9, 130.3, 128.9, 126.9, 123.4, 114.7, 69.5, 49.5, 46.4, 21.5, 11.5. HRMS (ESI) *m/z* calculated for $C_{16}H_{16}N_2O_3$ [M+H]+ 285.1234; found, 285.1230.

Given the overlapping peaks and complex nature of the NMR spectrum, an NMR key is provided below for both the ^{1}H NMR and ^{13}C NMR data:

^{1}HNMR assignments



^{13}CNMR assignments

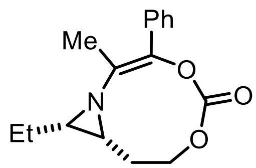


H_1	t, 1.09 ppm
H_2	m, 1.57 ppm
H_3	apq, 2.56 ppm
H_4	m, 2.10 ppm
H_5	dtd, 1.92 ppm, m 2.10 ppm
H_6	td, 4.66 ppm, m, 4.60 ppm

H_7, H_8, H_9, H_{10}, H_{11}	m, 7.77 ppm m, 7.43 ppm

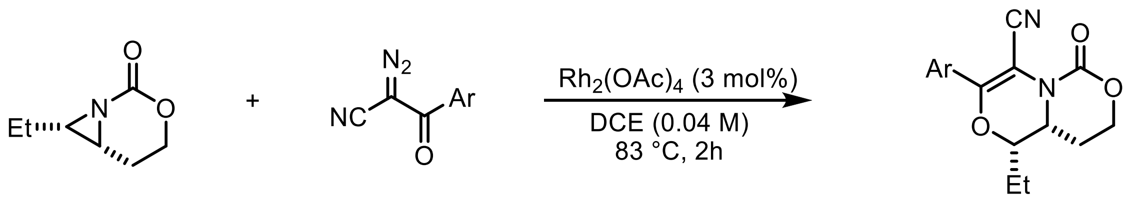
C_1	11.5 ppm
C_2	21.5 ppm
C_3	46.4 ppm
C_4	49.5 ppm
C_5	26.7 ppm
C_6	69.5 ppm
C_7	149.6 ppm
C_8	130.2 ppm
C_9	114.7 ppm
C_{10}	123.4 ppm

C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}	154.4 ppm 130.8 ppm 128.9 ppm 126.9 ppm

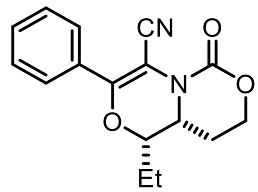


Compound 3d. Following the general procedure, the carbene transfer to furnish **3d** was conducted on a 0.3 mmol scale. The product was purified by flash column chromatography using silica-9 (0% to 50% EtOAc/Hex) to yield **3d** as a white solid (61.4 mg, 75% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.25 – 7.22 (m, 1H), 4.81 (t, *J* = 11.6 Hz, 1H), 4.35 (bd, 1H), 2.17 (q, J= 6.3 Hz, 1H), 2.07 – 2.01 (m, 2H), 1.99 (s, 3H), 1.77 (dtd, *J* = 15.4, 12.4, 11.9, 3.3 Hz, 1H), 1.62 – 1.43 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 137.7, 137.1, 133.9, 128.1, 127.6, 127.3, 69.3, 43.0, 28.9, 22.0, 15.5, 11.9. HRMS (ESI) *m/z* calculated for $C_{16}H_{19}NO_3$ [M+H]+ 274.1438; found, 274.1434.

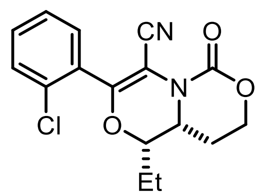
General Procedure B:



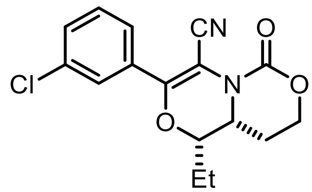
A flame-dried round bottom flask was placed under nitrogen and charged with $Rh_2(OAc)_4$ (0.03 equiv), followed by a solution of the aziridine (0.1 M in dry 1,2-dichloroethane). *Note: Unlike the previous experiments, addition of aziridine to 1,2-dichloroethane does not produce a color change of green to purple. These solutions remain green, and the reactions proceed as normal.* To this mixture was added a solution of the diazoketone (1.5 equiv, brought to 0.1 M in 1,2-dichloroethane) dropwise over 2 h using a syringe pump. The conversion was checked by TLC and NMR after the addition was complete; once all the starting material had been consumed, the crude material was subjected to silica flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer, 0% to 100% EtOAc/He, with a hold at 52% EtOAc/Hex). *Note: The R_f differences between the aziridine and the morpholine product can be very small. Purification can be extremely challenging if the reaction does not go to completion.*



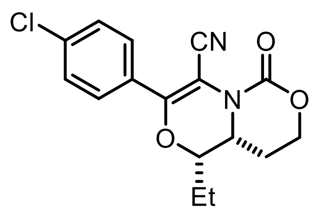
Compound 4c. Following the general procedure, the carbene transfer to furnish **4c** was conducted on 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **4c** as a light brown solid (26.6 mg, 47% yield, >19:1 *dr*).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.50 – 7.37 (m, 3H), 4.42 (dt, *J* = 10.2, 2.9 Hz, 1H), 4.40 – 4.30 (m, 2H), 4.02 (ddd, *J* = 10.4, 7.6, 2.4 Hz, 1H), 2.24 (ddt, *J* = 14.2, 7.5, 2.1 Hz, 1H), 2.08 – 1.96 (m, 1H), 1.76 – 1.54 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 149.8, 131.5, 131.0, 128.6, 128.5, 114.4, 91.9, 79.5, 64.3, 54.0, 23.6, 19.9, 10.2. *m/z* calculated for $C_{16}H_{16}N_2O_3$ [M+H]+ 285.1234; found, 285.1230.



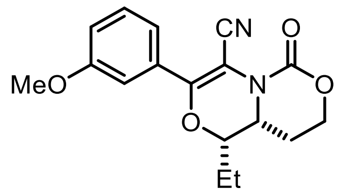
Compound 6c. Following the general procedure, the carbene transfer to furnish **6c** was conducted on 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex with a hold at 52% EtOAc/Hex) to yield **6c** as a pale yellow solid (21.1 mg, 33% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 3H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 4.52 – 4.31 (m, 3H), 4.07 (ddd, *J* = 11.1, 7.3, 2.4 Hz, 1H), 2.24 (ddt, *J* = 14.3, 7.4, 2.2 Hz, 1H), 2.08 – 1.92 (m, 1H), 1.78 – 1.52 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 149.5, 134.0, 132.1, 131.7, 131.0, 130.3, 127.3, 113.0, 94.8, 80.2, 64.4, 54.1, 23.5, 20.0, 10.3. δ *m/z* calculated for $C_{16}H_{15}N_2O_3$ [M+H]+ 319.0844 ; found, 319.0836.



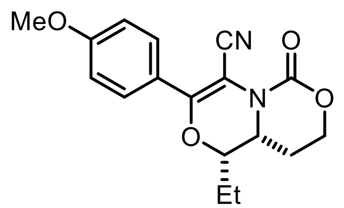
Compound 7c. Following the general procedure, the carbene transfer to furnish **7c** was conducted on 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **7c** as a brown solid (21.8 mg, 34% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.43 (dt, *J* = 8.1, 1.4 Hz, 1H), 7.36 (t, *J* = 8.2 Hz, 1H), 4.42 (dt, *J* = 10.7, 2.6 Hz, 1H), 4.40 – 4.29 (m, 2H), 4.01 (ddd, *J* = 10.9, 7.5, 2.4 Hz, 1H), 2.24 (ddt, *J* = 14.2, 7.5, 2.1 Hz, 1H), 1.97 (dtd, *J* = 14.2, 11.3, 5.5 Hz, 1H), 1.66 (dtd, *J* = 14.9, 7.4, 2.8 Hz, 1H), 1.57 (ddt, *J* = 14.4, 7.3, 3.6 Hz, 1H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 149.7, 134.6, 133.3, 130.9, 129.9, 128.4, 126.7, 114.1 92.5, 79.6, 64.4, 54.0, 23.5, 20.0, 10.2. *m/z* calculated for $C_{16}H_{15}N_2O_3$ [M+H]+ 341.0663; found, 341.0659.



Compound 8c. Following the general procedure, the carbene transfer to furnish **8c** was conducted on 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **8c** as a beige solid (19.1 mg, 29% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.59 (m, 2H), 7.48 – 7.34 (m, 2H), 4.42 (dt, *J* = 10.6, 2.7 Hz, 1H), 4.40 – 4.31 (m, 2H), 4.01 (ddd, *J* = 11.0, 7.5, 2.4 Hz, 1H), 2.24 (ddt, *J* = 14.2, 7.6, 2.1 Hz, 1H), 2.08 – 1.86 (m, 1H), 1.63 (ddddd, *J* = 35.9, 14.2, 10.8, 7.0, 3.2 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 149.7, 137.1, 129.9, 129.8, 128.9, 114.2, 92.2, 79.6, 64.3, 54.0, 23.6, 20.0, 10.2. *m/z* calculated for $C_{16}H_{15}N_2O_3$ [M+NH4]+ 336.1110 ; found, 336.1106.

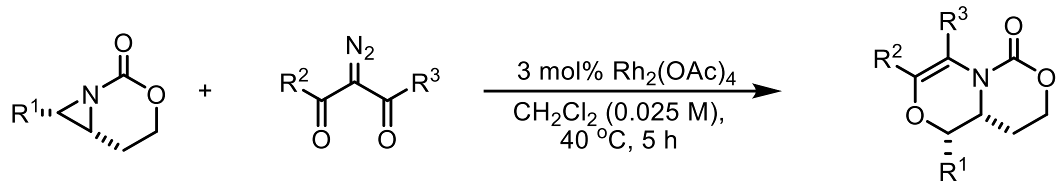


Compound 10c. Following the general procedure, the carbene transfer to furnish **10c** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **10c** as a brown solid (21.5 mg, 43% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.28 – 7.21 (m, 1H), 6.99 (dt, *J* = 6.7, 2.7 Hz, 1H), 4.41 (dt, *J* = 10.5, 2.7 Hz, 1H), 4.39 – 4.24 (m, 2H), 4.01 (ddd, *J* = 10.4, 7.7, 2.4 Hz, 1H), 3.82 (s, 3H), 2.23 (ddt, *J* = 14.2, 7.6, 2.1 Hz, 1H), 1.97 (dtd, *J* = 14.2, 11.4, 5.3 Hz, 1H), 1.72 – 1.54 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 154.5, 149.8, 132.7, 129.7, 120.8, 117.0, 114.3, 113.6, 91.9, 79.5, 64.3, 55.6, 54.0, 23.6, 19.9, 10.2. *m/z* calculated for $C_{17}H_{18}NO_4$ [M+H]+ 315.1339; found, 315.1333.

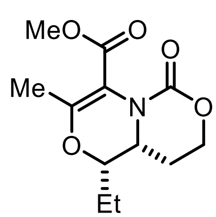


Compound 11c. Following the general procedure, the carbene transfer to furnish **11c** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **11c** as a beige solid (14.4 mg, 23% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) 7.74 – 7.64 (m, 2H), 6.99 – 6.88 (m, 2H), 4.39 (ddd, *J* = 10.2, 3.5, 2.4 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.00 (ddd, *J* = 10.5, 7.6, 2.4 Hz, 1H), 2.23 (ddt, *J* = 14.2, 7.6, 2.1 Hz, 1H), 1.98 (dtd, *J* = 14.1, 11.5, 5.1 Hz, 1H), 1.65 (dddd, *J* = 17.0, 10.0, 7.1, 3.1 Hz, 2H), 1.12 (t, *J* = 7.3 Hz, 3H). δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 154.4, 149.8, 130.0, 123.7, 114.8, 114.0, 90.9, 79.5, 64.2, 55.5, 54.0, 23.7, 19.9, 10.2. *m/z* calculated for $C_{17}H_{18}NO_4$ [M+H]+ 315.1339; found, 315.1332

General Procedure C:

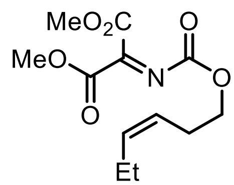


A flame-dried round bottom flask was placed under N_2 and charged with $Rh_2(OAc)_4$ (0.03 equiv), followed by a solution of the aziridine (0.1 M in dry CH_2Cl_2). The reaction setup was equipped with a reflux condenser and purged with N_2. *Note: Upon the addition of aziridine, a color change of green to purple will be observed. This does not signify catalyst death; rather, experiments show that if this color change is not observed, the reaction is less likely to proceed*. To this mixture was added a solution of the diazoketone compound (3.0 equiv, brought to 0.1 M in CH_2Cl_2, unless otherwise noted) dropwise over 5 h using a syringe pump. The conversion was checked by TLC and NMR after the addition was complete; and once all the starting material had been consumed, the crude material was concentrated *in vacuo* and subjected to silica flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex). *Note: The R_f differences between the aziridine and the morpholine product can be very small. Purification can be extremely challenging if the reaction does not go to completion.*



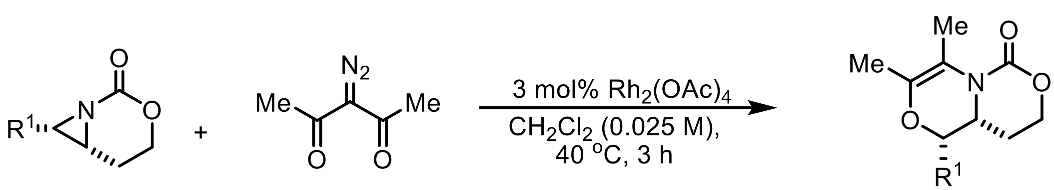
Compound 4c. Following the general procedure, the carbene transfer to furnish **4c** was conducted on 0.3 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex), with a hold at 52% EtOAc/Hex) to yield **4c** as a white solid (27.1 mg, 38% yield, >20:1 *dr*). A crystal structure for this compound can be found in Section X. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 – 4.22 (m, 2H), 4.13 (dt, J = 10.4, 2.6 Hz, 1H), 3.85 (ddd, J = 13.6, 8.0, 3.9 Hz, 1H), 3.73 (s, 3H), 2.21 – 2.15 (m, 1H), 2.13 (s, 3H), 1.97 – 1.83 (m, 1H), 1.59 – 1.39 (m, 2H), 1.02 (t, J = 7.4

Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 152.0, 149.7, 107.8, 78.9, 64.0, 53.1, 52.0, 23.8, 19.7, 17.8, 10.2. HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_5$ [M+Na]+ 278.0999; found, 278.0990.

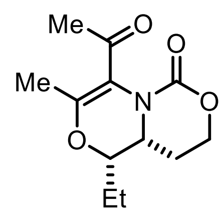


Compound SI-2. Following the general procedure, the carbene transfer to furnish **SI-2** was conducted on 0.1 mmol scale. This compound was unstable to all forms of chromatography; therefore, the NMR yield was determined using 10 μL of mesitylene as the internal standard. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 – 5.47 (m, 1H), 5.38 – 5.27 (m, 1H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.84 (s, 6H) (over integrating as a result of excess diazoester), 2.53 – 2.43 (m, 2H), 2.06 (td, *J* = 7.6, 1.8 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 161.5, 159.7, 151.6, 135.2, 122.9, 67.2, 52.6, 26.6, 20.7, 14.2. HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_6$[M+H]+ 272.1129; found, 272.1125.

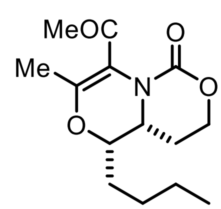
General Procedure D:



A flame-dried round bottom flask was placed under nitrogen and charged with $Rh_2(OAc)_4$ (0.03 equiv), followed by a solution of the aziridine (1.0 equiv, 0.1 M in dry CH_2Cl_2). The reaction setup was equipped with a reflux condenser and purged with N_2. *Note: Upon the addition of aziridine, a color change of green to purple will be observed. This does not signify catalyst death; rather, experiments show that if this color change is not observed, the reaction is less likely to proceed*. To this mixture was added a solution of the diazoketone (10.0 equiv, brought to 0.3 M in CH_2Cl_2) dropwise over 3 h using a syringe pump. *Note: the excess equivalents of the diazoketone coupling partner were necessary to achieve full conversion of the aziridine. If the equivalents are dropped, the unproductive dimerization process, along with other diazo-based side reactions, outcompetes the* *productive ylide-forming reaction and prevents full conversion of the starting material*. The conversion was checked by TLC and NMR after the addition was complete; once all the starting material had been consumed, the crude material was subjected to silica flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex). *Note: The R_f differences between the aziridine and the morpholine product can be very small dependent on the substrate. Purification can be extremely challenging if the reaction does not go to completion.*

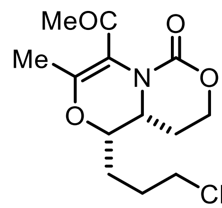


Compound 4f. Following the general procedure, the carbene transfer to furnish **4f** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 24g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/He, with a hold at 52% EtOAc/Hex) to yield **4f** as a white solid (27.9 mg, 58% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40 – 4.27 (m, 2H), 4.14 (dt, *J* = 10.7, 2.6 Hz, 1H), 3.92 (ddd, *J* = 10.6, 8.6, 2.5 Hz, 1H), 2.25 (ddt, *J* = 14.2, 8.5, 2.1 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.04 – 1.93 (m, 1H), 1.55 (dtd, *J* = 15.1, 7.5, 2.9 Hz, 1H), 1.51 – 1.41 (m, 1H), 1.03 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 152.8, 148.9, 116.0, 78.7, 64.1, 53.0, 27.8, 23.7, 19.6, 18.0, 10.2. HRMS (ESI) *m/z* calculated for $C_{12}H_{17}NO_4$ [M+H]+ 240.1230; found, 240.1228.

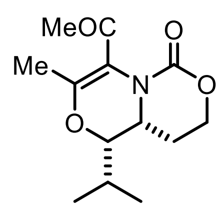


Compound 12f. Following the general procedure, the carbene transfer to furnish **12f** was conducted on a 0.3 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 24g gold resolution column with a 30 min method

generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **12f** as a bluish-white solid (46.8 mg, 58% yield, >2:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$ δ 4.43 – 4.26 (m, 2H), 4.19 (ddd, *J* = 7.6, 5.5, 2.5 Hz, 1H), 3.89 (ddd, *J* = 10.7, 8.6, 2.5 Hz, 1H), 2.22 (ddt, *J* = 14.2, 8.5, 2.0 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.03 – 1.92 (m, 2H), 1.54 – 1.39 (m, 2H), 1.38 – 1.28 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 195.1, 152.7, 148.9, 116.0, 77.4, 64.1, 53.1, 27.9 (d, *J* = 16.4 Hz), 26.1, 23.8, 22.5, 18.0, 14.1. HRMS (ESI) *m/z* calculated for $C_{14}H_{21}NO_4$ [M+H]+ 268.1543; found, 268.1541.

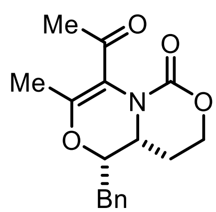


Compound 13f. Following the general procedure, the carbene transfer to furnish **13f** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 12g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex with a hold at 52% EtOAc/Hex) to yield **13f** as a white solid (29.50 mg, 51% yield, >20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 – 4.28 (m, 2H), 4.26 (dt, *J* = 11.1, 2.4 Hz, 1H), 3.95 (ddd, *J* = 10.8, 8.5, 2.5 Hz, 1H), 3.72 – 3.60 (m, 1H), 3.54 (ddd, *J* = 11.0, 7.5, 5.6 Hz, 1H), 2.27 (ddt, *J* = 14.4, 8.6, 2.1 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.00 (qdd, *J* = 14.3, 7.0, 4.8 Hz, 2H), 1.87 (dddd, *J* = 16.0, 8.4, 5.5, 3.8 Hz, 1H), 1.78 (dddd, *J* = 15.8, 8.9, 6.2, 2.3 Hz, 1H), 1.52 (dtd, *J* = 11.2, 9.0, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 152.6, 148.4, 116.1, 76.4, 64.1, 53.0, 44.3, 28.5, 27.9, 23.8, 23.5, 17.9. HRMS (ESI) *m/z* calculated for $C_{13}H_{18}ClNO_4$ [M+H]+ 288.0997; found, 288.0092.



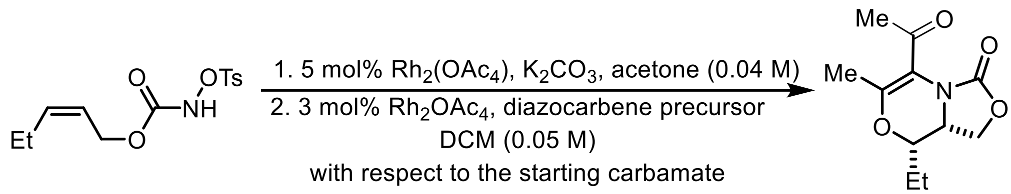
Compound 14f. Following the general procedure, the carbene transfer to furnish **14f** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column

chromatography using a Combiflash™ 24g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **14f** as a white solid (36.5 mg, 48% yield, >20:1 *dr*). This product coelutes with a minor NMR impurity that has two corresponding signals at 1.96 ppm and 1.92 ppm. These are likely a byproduct of the corresponding diazo precursor, but were inseparable from the dehydromorpholine compound in this case. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (ddd, *J* = 10.8, 4.6, 2.3 Hz, 1H), 4.30 (ddd, *J* = 13.2, 11.0, 2.4 Hz, 1H), 4.08 (t, *J* = 3.8 Hz, 1H), 3.96 (ddd, *J* = 11.2, 7.9, 3.5 Hz, 1H), 2.21 (ddt, *J* = 14.2, 7.9, 2.5 Hz, 1H), 2.17 – 2.12 (m, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.01 (dqd, *J* = 9.1, 6.6, 3.2 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 151.8, 150.6, 116.3, 81.0, 64.4, 53.1, 29.0, 27.9, 23.7, 22.7, 17.8, 17.0. HRMS (ESI) *m/z* calculated for $C_{13}H_{19}NO_4$ [M+Na]+ 276.1206; found, 276.1204.



Compound 15f. Following the general procedure, the carbene transfer to furnish **15f** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 24g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **15f** as a white solid (21.6 mg, 36% yield, >20:1 *dr*). This product coelutes with a minor NMR impurity that has two corresponding signals at 1.96 ppm and 1.92 ppm. These are likely a byproduct of the corresponding diazo precursor, but were inseparable from the dehydromorpholine compound in this case. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.21 – 7.15 (m, 2H), 4.45 (ddd, *J* = 9.8, 3.3, 2.4 Hz, 1H), 4.43 – 4.33 (m, 2H), 4.00 (ddd, *J* = 10.7, 8.6, 2.4 Hz, 1H), 2.83 (dd, *J* = 14.4, 3.3 Hz, 1H), 2.74 (dd, *J* = 14.4, 9.8 Hz, 1H), 2.30 (ddt, *J* = 14.3, 8.6, 2.1 Hz, 1H), 2.18 (s, 3H), 2.16 – 2.03 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 152.6, 148.4, 136.7, 129.4, 128.8, 127.0, 116.4, 78.0, 64.1, 53.3, 33.1, 28.0, 24.0, 18.0. HRMS (ESI) *m/z* calculated for $C_{17}H_{19}NO_4$ [M+H]+ 302.1387; found, 302.1384.

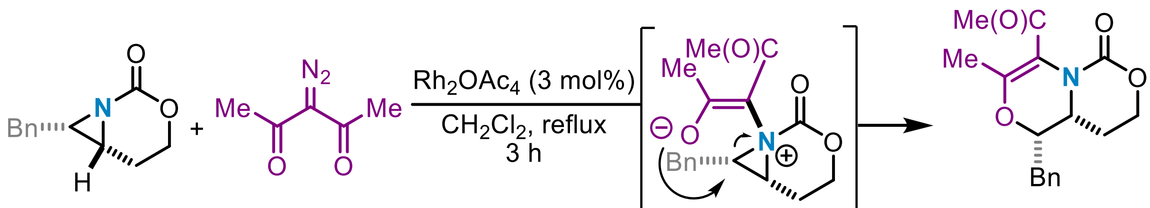
VI. One-pot nitrene-carbene transfer reaction.



Preparation of Compound 18.

To a flame dried round bottom flask equipped with a stir bar was added K_2CO_3 (484.8 mg, 3.5 mmol, 7 equiv) and 5 mol % $Rh_2(OAc)_4$ (11.0 mg, 0.025 mmol, 0.05 equiv). The flask was subjected to three freeze-pump-thaw cycles and placed under N_2. This mixture was diluted with 8.0 mL of freshly distilled acetone and the *N*-tosyloxycarbamate precursor to **18** (150.0 mg, 0.50 mmol, 1.0 equiv) was added in 4.0 mL of distilled acetone. This mixture was stirred vigorously for ~12 h (generally overnight). *Note: the reaction will start off as a deep green color, however, overnight, this color will change to a purple/gray*. The next morning CH_2Cl_2 was added to the reaction mixture and the combined organics were filtered through Celite using a fritted funnel *Note: generally coarse frits were used but medium were also acceptable*. The solution was concentrated *in vacuo* and transferred to a 50 mL flame dried round bottom flask. This flask was charged with an additional 3 mol% of $Rh_2(OAc)_4$ (6.6 mg, 0.015 mmol, 0.03 equiv), equipped with a reflux condenser and subjected to three freeze-pump-thaw cycles. The combined crude aziridine and Rh catalyst were then diluted to 0.1 M with CH_2Cl_2 (5 mL). Separately, a solution 0.3 M solution of diazoketone (632.0 mg, 5.0 mmol, 10 eq) in 15 mL of CH_2Cl_2 was prepared. This solution was added to the first solution *via* slow addition over 3 h. Once the addition of diazoketone was complete, the solution was concentrated *in vacuo* and purified by silica gel flash column chromatography using a Combiflash™ 24g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **18** as an off-white solid (37.3 mg, 46% yield over two steps, >20:1 *dr*). *Note: Sometimes a residual tosyl acid impurity from the nitrene transfer step was identified in the final product. The residual acid was not always detected in the final purified compound. If tosyl acid is identified in the NMR after column chromatography, the best way to remove the impurity is by diluting the product in CH_2Cl_2 to 0.05 M and stirring with 10 mL of 1 M NaOH for 2 h. No product degradation has been observed when this purification technique has been applied after silica gel flash column chromatography*. ^1H NMR (500 MHz, $CDCl_3$) δ 4.64 (dd, J = 9.6, 8.2 Hz, 1H), 4.29 (dd, J = 9.6, 2.0 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.88 (ddd, J = 8.1, 3.5, 1.9 Hz, 1H), 2.32 (s, 3H), 2.17 (s, 3H), 1.62 – 1.48 (m, 3H), 1.44 (ddt, J = 14.2, 11.3, 7.1 Hz, 1H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 156.3, 150.8, 114.0, 77.3, 64.0, 51.1, 28.3, 19.0, 18.0, 10.1. HRMS (ESI) *m/z* calculated for $C_{11}H_{15}NO_4$ [M+H]+ 226.1074; found 226.1072.

VII. Transfer of chirality experiment.

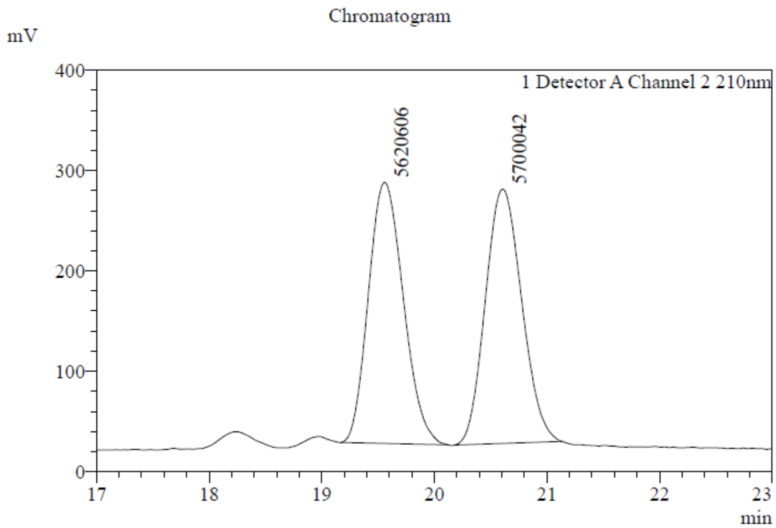


***(S,R)*-15** 94% *ee* **2f** ***(S,R)*-15f** 39%[a], >20:1 *dr* 97% *ee*

Transfer of chirality experiment.

Enantioenriched bicyclic aziridine **15**: $AgClO_4$ (155.5 mg, 0.75 mmol, 0.20 equiv) and (***S***,***S***)-*t*BuBox (110.5 mg, 0.375 mmol, 0.10 equiv) were vigorously stirred in DCM (60 mL) for 15 min at room temperature. A charge of 4 Å MS (3.75 g; 1 g/mmol substrate) was added and the mixture was stirred for an additional 5 min. After cooling to -20 °C, a solution of the carbamate precursor to **15** (770 mg, 3.75 mmol, 1 equiv) in DCM (15 mL) was sequentially added along with iodosobenzene (1.651 g, 7.5 mmol, 2 equiv). The reaction was capped and stirred at -20 °C for 72 h. The reaction was filtered over Celite and concentrated, then passed through a short plug of silica gel, eluting with 5% EtOH/DCM to remove any silver salts. Purification by silica gel column chromatography (0-50% EtOAc/Hex) gave a white solid (313.6 mg, 41% yield, 87% *ee*). Recrystallization from 30% *i*PrOH/Hex gave the major enantiomer from the mother liquor (187.3 mg, 59% recovery, 94% *ee*).

HPLC conditions: Shimadzu Prominence HPLC equipped with a 5 µm phase Chiralcel OJ-H column. Flow rate: 1 mL/min.; Oven temp: 40 °C; Solvent: 5% *i*PrOH/Hex, increased to 30% over 5 minutes, then to 35% over 10 minutes. The eluent was held at this solvent composition for 10 min to complete the analysis. The detector was set @ 210 nm.

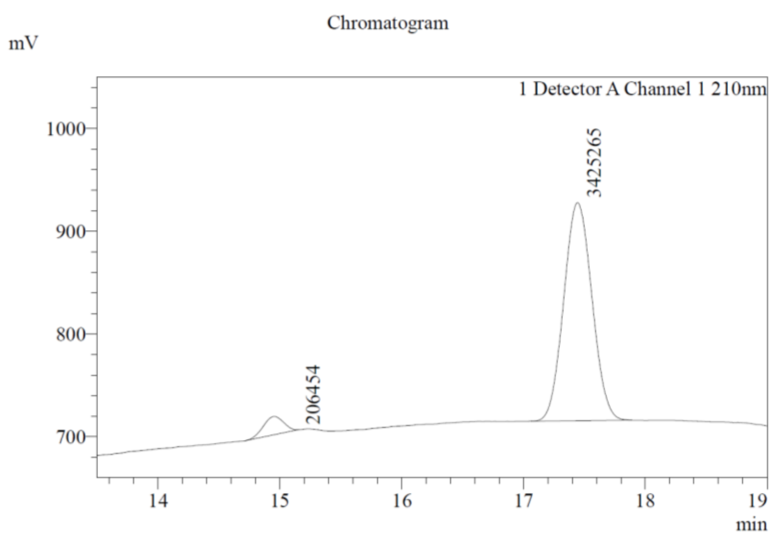


Peak Table

Detector A Channel 2 210nm

Peak#	Ret. Time	Area	Area%
1	19.558	5620606	49.649
2	20.608	5700042	50.351
Total		11320647	100.000

Figure S-1. Racemic bicyclic aziridine **15** HPLC data.



Peak Table

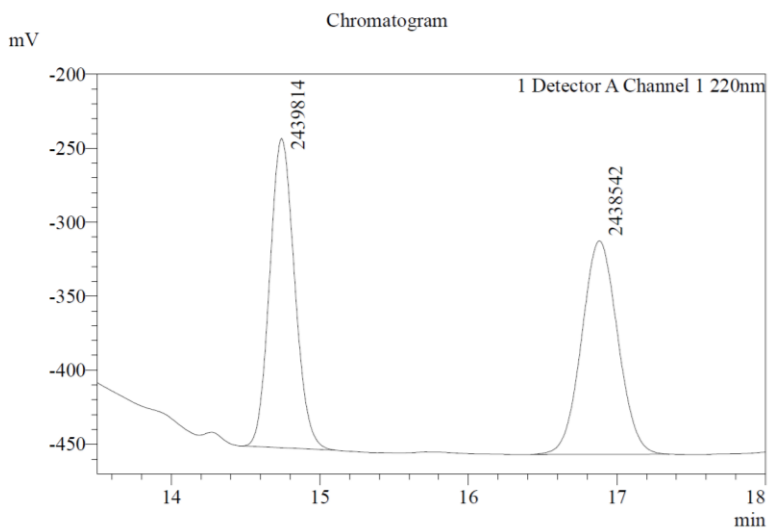
Detector A Channel 1 210nm

Peak#	Ret. Time	Area	Area%
1	15.138	206454	5.685
2	17.444	3425265	94.315
Total		3631719	100.000

Figure S-2. Enantioenriched bicyclic aziridine (*S*,*R*)-**15** HPLC data.

Enantioenriched morpholine **15f**. Following the General Procedure D, the carbene transfer reaction to furnish enantioenriched **15f** was conducted on a 0.2 mmol scale. The product was purified by silica gel flash column chromatography using a Combiflash™ 24g gold resolution column with a 30 min method generated *via* the gradient optimizer (0% to 100% EtOAc/Hex, with a hold at 52% EtOAc/Hex) to yield **15f** as a white solid (23.9 mg, 39% yield, >20:1 *dr*, 97% *ee*).

HPLC Conditions. Shimadzu Prominence HPLC equipped with a 5 µm phase Chiralpak IC column. Flow rate: 1 mL/min.; Oven temp: 40.0 °C; Solvent: 30% MeOH/H_2O (1% HCO_2H), increased to 80% over 10 minutes. The eluent was held at this composition for 15 minutes to complete analysis. Detector @ 220 nm.

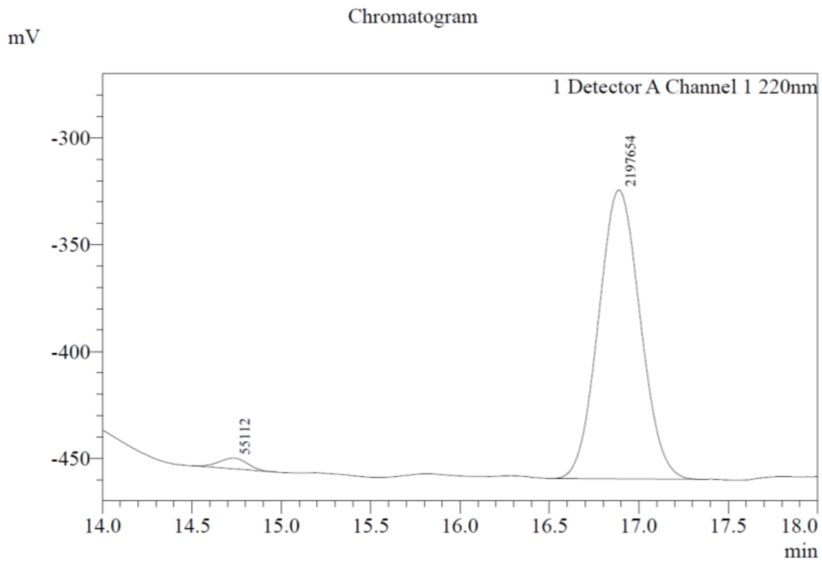


Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Area%
1	14.742	2439814	50.013
2	16.882	2438542	49.987
Total		4878356	100.000

Figure S-3. Racemic morpholine **15f** HPLC data.



Peak Table

Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Area%
1	14.730	55112	2.446
2	16.888	2197654	97.554
Total		2252766	100.000

Figure S-4. Enantioenriched morpholine (*S*,*R*)-**15f** HPLC data

VIII. Limitations in substrate scope.

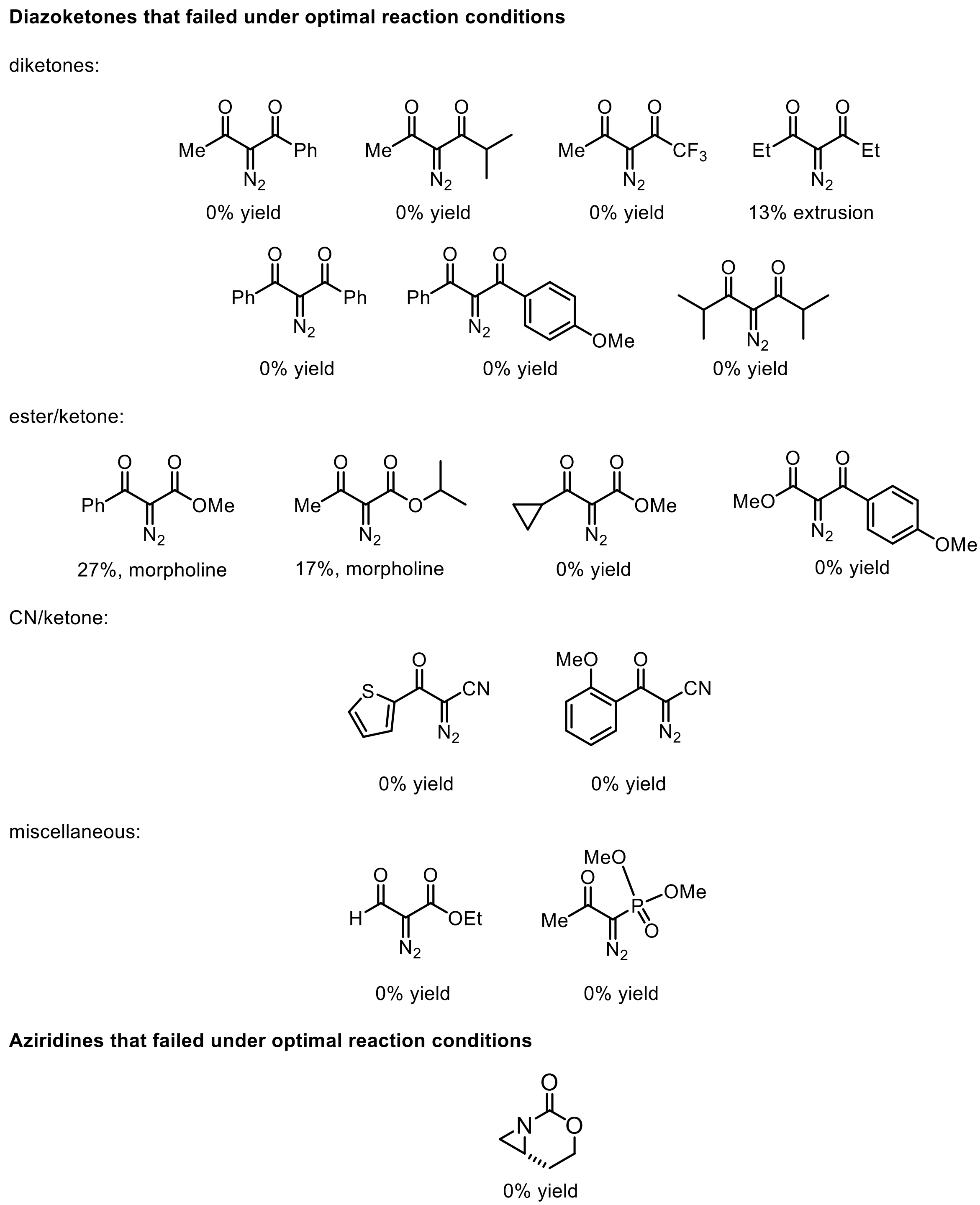
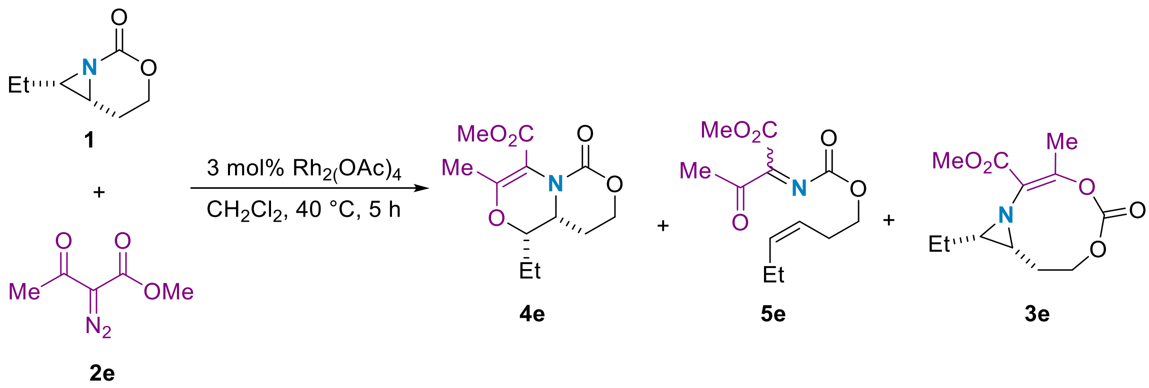


Figure S-5. Limitations of reaction scope.

IX. NMR time course studies of the transformation of 1 and 2e to 3e, 4e and 5e.

A. Time course experiments to identify presence of additional products or intermediates.

The following reaction was run under standard reaction conditions reported in the General Procedure C:



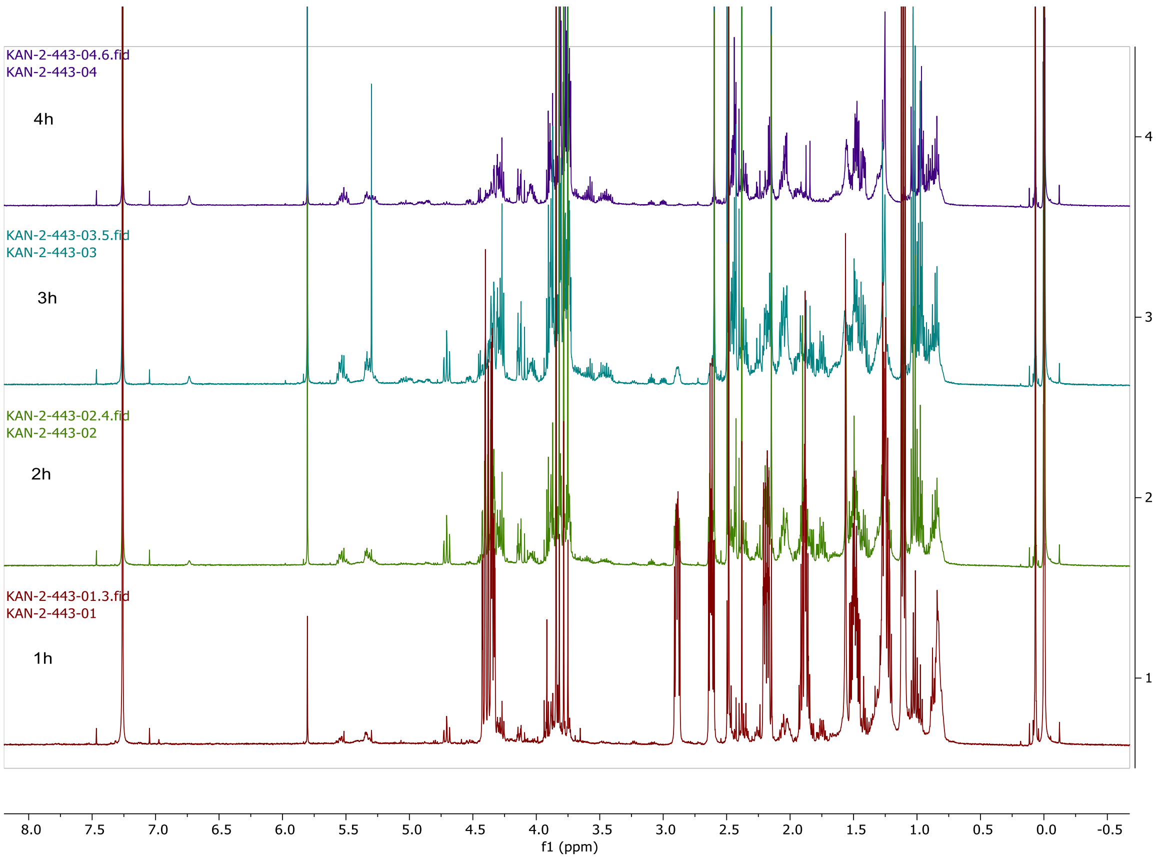


Figure S-6. Time course data was collected on a 500 MHz NMR, aliquots taken every hour to determine the presence of unique peaks that may provide insight into potential reaction intermediates or additional products.

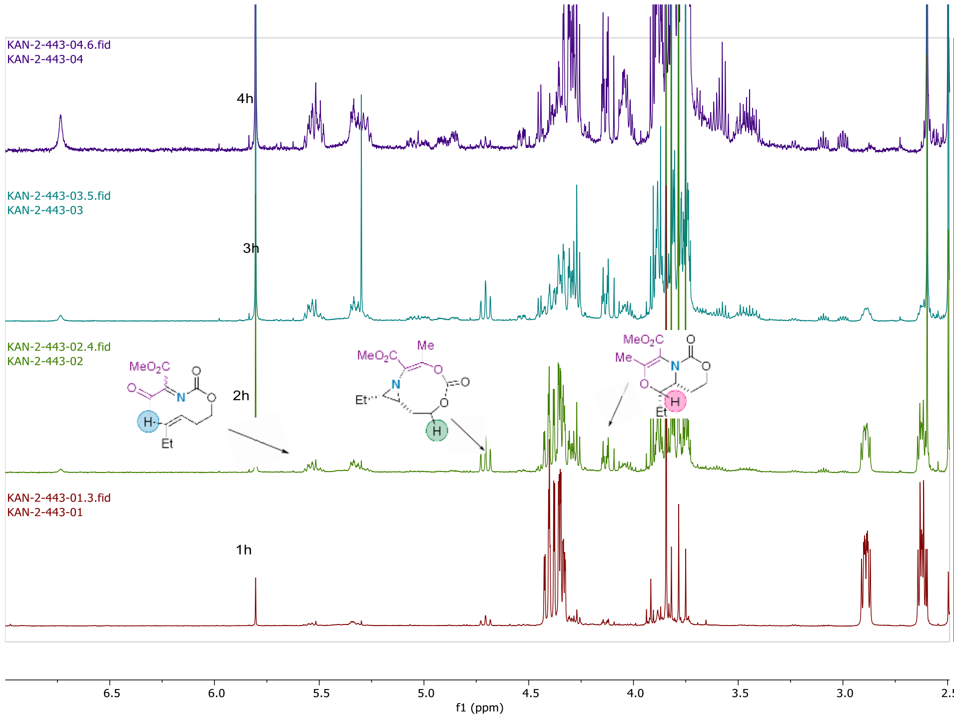


Figure S-7. Zoom-in of relevant peaks. As the reaction begins, after 1 h, little-to-no conversion is seen. After 2 h, conversion is seen primarily in the peaks corresponding to the morpholine **4e**, and [3,9]-aziridine **3e** with a small amount of cheletropic extrusion **5e.** The reaction appears to continue to consistently generate **4e** while **3e** grows in and disappears with a steady increase of **5e**, appearing as **3e** begins to disappear.

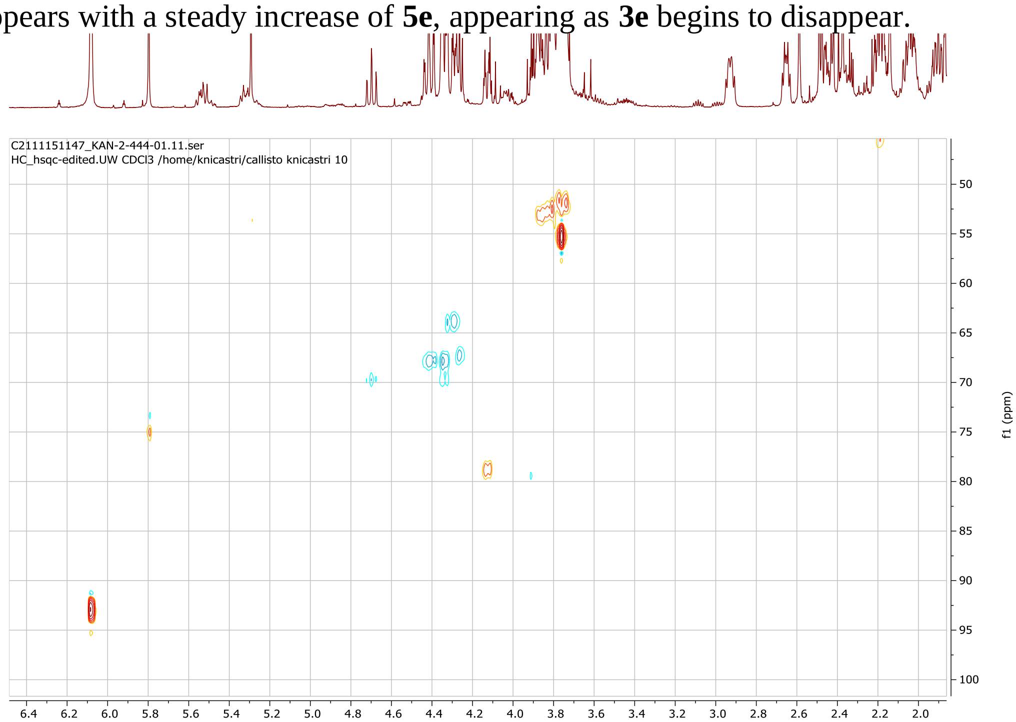


Figure S-8. HSQC spectrum of reaction aliquot that demonstrates the apparent t at 4.69 ppm corresponds to a CH_2 peak with a unique ^{13}CNMR shift at 69.9 ppm that matches known data for the [3,9]-aziridine.

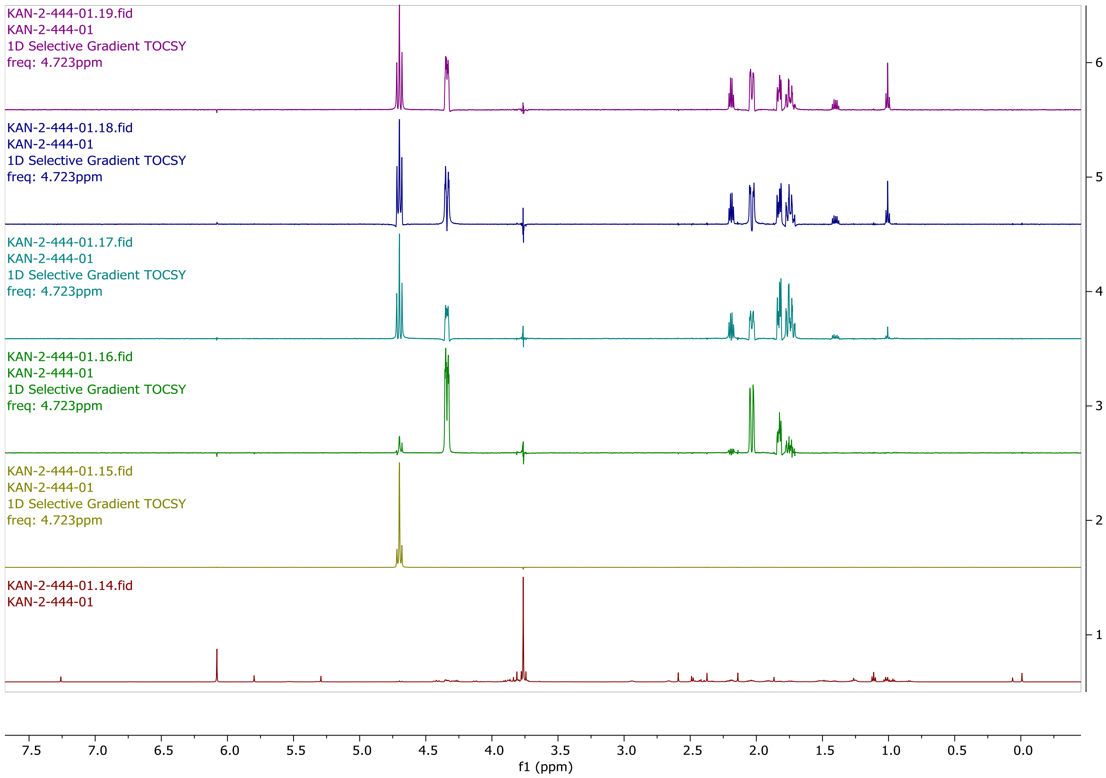


Figure S-9. 1D-TOCSY of an aliquot of **2h**. Irradiation of the apparent t at 4.69 ppm reveals the full chain for the unique compound proposed to be compound **3e**.

X. Crystallographic information for Compounds 3a and 4e.

Crystallographic Experimental Section

Data Collection for Compound 3a (CCDC Deposition Number 2124058).

A colorless crystal with approximate dimensions 0.40 x 0.09 x 0.09 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 VENTURE PhotonIII four-circle diffractometer with Cu Kα (λ = 1.54178 Å) radiation and the detector to crystal distance of 4.0 cm.[11]

The initial cell constants were obtained from a 180° φ scan conducted at a 2θ = 55° angle with the exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program. The final cell constants were calculated from a set of 9321 strong reflections from the actual data collection.

The data were collected by using an automated data collection routine to survey the reciprocal space to the extent of a hemisphere to a resolution of 0.78 Å. A total of 26326 data were harvested by collecting 33 sets of frames with 0.8º scans in ω and φ with an exposure time 0.5–6 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[12]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.[13-18]

A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

This compound crystallizes as a racemate with two symmetry-independent molecules in the asymmetric unit.

The final least-squares refinement of 345 parameters against 5590 data resulted in residuals R (based on F^2 for $I\geq2\sigma$) and wR (based on F^2 for all data) of 0.0367 and 0.0889, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{15}H_{17}NO_3$ (M =259.29 g/mol): triclinic, space group $P\bar{1}$ (no. 2), a = 8.5412(8) Å, b = 11.6388(10) Å, c = 13.9486(14) Å, α = 75.092(6)°, β = 89.692(8)°, γ = 85.847(7)°, V = 1336.3(2) Å^3, Z = 4, T = 100.0 K, μ(Cu Kα) = 0.732 mm^{-1}, $Dcalc$ = 1.289 g/cm^3, 26326 reflections measured (6.558° ≤ 2Θ ≤ 157.15°), 5590 unique (R_{int} = 0.0337, R_{sigma} = 0.0295) which were used in all calculations. The final R_1 was 0.0367 (I > 2σ(I)) and wR_2 was 0.0889 (all data).

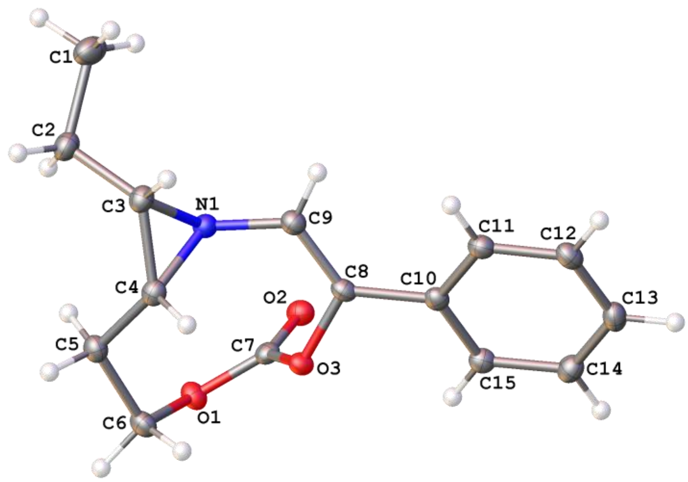


Figure S-10. A molecular drawing of the first symmetry-independent molecule in **3a** shown with 50% probability ellipsoids.

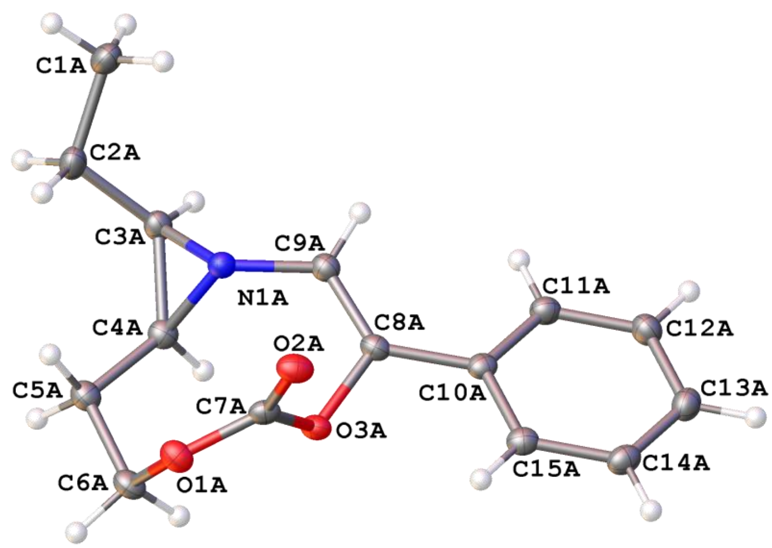


Figure S-11. A molecular drawing of the second symmetry-independent molecule in **3a** shown with 50% probability ellipsoids.

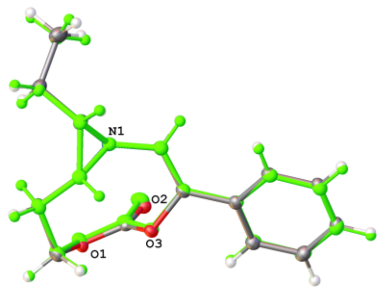


Figure S-12. An overlay of the two symmetry-independent molecules in **3a** shown with 50% probability ellipsoids. One of the enantiomers was inverted to demonstrate the conformation similarity.

Table S-1. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{15}H_{17}NO_3$
Formula weight	259.29
Temperature/K	100.0
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	8.5412(8)
b/Å	11.6388(10)
c/Å	13.9486(14)
α/°	75.092(6)
β/°	89.692(8)
γ/°	85.847(7)
Volume/Å^3	1336.3(2)
Z	4
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	0.732
F(000)	552.0
Crystal size/mm^3	0.4 × 0.09 × 0.09
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	6.558 to 157.15
Index ranges	$-10 \le h \le 10$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	26326
Independent reflections	5590 [R_{int} = 0.0337, R_{sigma} = 0.0295]
Data/restraints/parameters	5590/0/345
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0874
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.26/-0.23

Table S-2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	8185.8(9)	6704.7(7)	4383.3(6)	18.02(17)
O2	9547.1(9)	5725.9(7)	5729.6(6)	18.05(17)
O3	7171.9(9)	5135.2(7)	5414.8(6)	15.18(16)
N1	6064.2(11)	6760.6(8)	6324.3(7)	15.99(19)
C1	4941.4(17)	8780.1(12)	7495.9(10)	28.4(3)
C2	4714.3(14)	8745.2(10)	6421.3(9)	21.2(2)
C3	4585.5(13)	7488.9(10)	6342.5(9)	17.7(2)
C4	5000.7(12)	7067.2(10)	5440.8(8)	16.6(2)
C5	5623.5(13)	7801.3(10)	4485.3(8)	18.1(2)
C6	6626.4(13)	7049.7(10)	3930.0(8)	18.6(2)
C7	8385.2(12)	5853.5(10)	5225.3(8)	14.9(2)
C8	6821.7(12)	4727.9(10)	6433.9(8)	15.0(2)
C9	6211.3(12)	5558.7(10)	6865.0(8)	16.4(2)
C10	7130.2(12)	3445.4(10)	6865.8(8)	15.2(2)
C11	6341.3(13)	2862.1(10)	7713.7(8)	17.5(2)
C12	6646.5(13)	1646.3(10)	8115.0(8)	19.4(2)
C13	7742.3(14)	993.3(10)	7682.1(9)	20.1(2)
C14	8520.9(13)	1569.2(10)	6837.9(9)	19.5(2)
C15	8216.5(13)	2785.3(10)	6425.6(8)	16.7(2)
O1A	3156.0(9)	6708.7(7)	9754.2(6)	19.20(17)
O2A	4575.9(9)	5647.5(8)	8910.7(6)	20.50(18)
O3A	2217.0(9)	5050.8(7)	9518.2(6)	15.82(16)
N1A	1144.8(11)	6521.4(8)	7839.9(7)	15.83(19)
C1A	472.3(15)	8395.0(11)	5708.7(9)	23.6(2)
C2A	0.2(15)	8475.0(10)	6748.5(9)	21.8(2)
C3A	-276.5(13)	7271.0(10)	7418.9(8)	17.5(2)
C4A	25.0(13)	6946.2(10)	8516.6(8)	17.0(2)
C5A	613.2(13)	7750.4(10)	9107.5(8)	18.6(2)
C6A	1576.0(13)	7068.4(11)	10020.8(8)	18.9(2)
C7A	3399.4(13)	5800.7(10)	9343.0(8)	15.9(2)
C8A	1880.7(12)	4533.1(10)	8733.7(8)	15.7(2)
C9A	1279.3(13)	5291.5(10)	7906.3(8)	16.5(2)
C10A	2166.4(12)	3232.6(10)	8965.3(8)	15.5(2)
C11A	1389.7(13)	2567.8(10)	8431.4(8)	18.3(2)
C12A	1660.4(14)	1333.7(11)	8663.9(9)	20.7(2)
C13A	2689.4(14)	742.6(10)	9433.8(9)	20.9(2)
C14A	3456.6(13)	1397.8(11)	9967.0(9)	19.6(2)
C15A	3203.1(13)	2633.4(10)	9739.0(8)	17.3(2)

Table S-3. Anisotropic Displacement Parameters (Å^2×10^3) for **3a**. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	15.5(4)	20.2(4)	16.1(4)	-0.5(3)	1.3(3)	-1.7(3)
O2	15.5(4)	21.0(4)	18.3(4)	-6.5(3)	-0.6(3)	-0.6(3)
O3	16.5(4)	16.3(4)	12.8(4)	-3.4(3)	1.4(3)	-3.1(3)
N1	16.0(4)	16.6(4)	15.7(4)	-5.0(4)	0.3(3)	0.0(3)
C1	37.1(7)	24.0(6)	27.4(7)	-11.4(5)	4.6(5)	-6.0(5)
C2	23.4(6)	16.3(5)	24.1(6)	-5.9(4)	1.9(4)	-0.3(4)
C3	16.1(5)	16.5(5)	20.4(6)	-5.0(4)	1.7(4)	-0.2(4)
C4	14.4(5)	16.4(5)	18.9(5)	-4.7(4)	-1.0(4)	-0.8(4)
C5	17.5(5)	17.5(5)	17.9(5)	-2.4(4)	-1.7(4)	-0.2(4)
C6	17.9(5)	21.7(5)	14.7(5)	-2.0(4)	-1.8(4)	-0.2(4)
C7	15.3(5)	15.1(5)	15.2(5)	-6.0(4)	3.0(4)	-0.5(4)
C8	14.0(5)	18.4(5)	12.1(5)	-2.7(4)	0.7(4)	-2.4(4)
C9	15.8(5)	17.9(5)	15.3(5)	-3.6(4)	0.5(4)	-1.7(4)
C10	14.4(5)	16.9(5)	14.5(5)	-4.3(4)	-2.4(4)	-1.6(4)
C11	17.3(5)	20.2(5)	15.2(5)	-5.3(4)	0.0(4)	-0.8(4)
C12	20.8(5)	20.9(5)	15.3(5)	-1.4(4)	-0.6(4)	-3.9(4)
C13	21.9(5)	15.7(5)	21.0(6)	-1.9(4)	-3.4(4)	-1.0(4)
C14	17.8(5)	18.6(5)	22.8(6)	-7.0(4)	-0.6(4)	0.7(4)
C15	15.2(5)	18.6(5)	16.6(5)	-4.6(4)	0.8(4)	-2.8(4)
O1A	15.2(4)	23.4(4)	21.4(4)	-9.7(3)	-0.2(3)	-3.0(3)
O2A	15.9(4)	28.3(4)	17.6(4)	-6.5(3)	1.1(3)	-0.9(3)
O3A	16.5(4)	18.5(4)	13.0(4)	-4.6(3)	0.5(3)	-2.9(3)
N1A	17.0(4)	16.2(4)	14.1(4)	-3.8(3)	-0.6(3)	-0.4(3)
C1A	30.7(6)	18.1(5)	20.0(6)	-1.9(4)	-3.8(5)	-0.1(5)
C2A	27.1(6)	15.2(5)	22.4(6)	-4.5(4)	-4.0(5)	1.7(4)
C3A	16.9(5)	17.2(5)	18.6(5)	-5.9(4)	-2.9(4)	1.3(4)
C4A	14.3(5)	18.6(5)	18.1(5)	-5.1(4)	0.4(4)	-0.8(4)
C5A	18.0(5)	19.8(5)	19.4(5)	-7.5(4)	1.3(4)	-1.4(4)
C6A	17.6(5)	23.1(6)	18.2(5)	-9.5(4)	2.5(4)	-1.4(4)
C7A	14.7(5)	19.8(5)	12.3(5)	-2.5(4)	-2.5(4)	-0.9(4)
C8A	15.0(5)	18.9(5)	14.6(5)	-6.3(4)	0.7(4)	-2.0(4)
C9A	16.5(5)	17.2(5)	16.4(5)	-5.2(4)	0.5(4)	-1.9(4)
C10A	14.1(5)	18.0(5)	13.8(5)	-3.1(4)	2.4(4)	-0.3(4)
C11A	18.1(5)	20.1(5)	16.1(5)	-4.4(4)	-1.1(4)	0.4(4)
C12A	22.9(6)	20.0(6)	20.6(6)	-7.7(4)	-1.1(4)	-1.3(4)
C13A	22.2(5)	16.9(5)	22.2(6)	-3.2(4)	1.7(4)	1.4(4)

C14A	16.6(5)	21.6(6)	18.0(5)	-1.3(4)	-0.6(4)	1.9(4)
C15A	14.6(5)	20.6(5)	16.2(5)	-4.0(4)	1.0(4)	-1.8(4)

Table S-4. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C6	1.4615(13)	O1A	C6A	1.4586(13)
O1	C7	1.3299(14)	O1A	C7A	1.3295(14)
O2	C7	1.1976(14)	O2A	C7A	1.1950(14)
O3	C7	1.3607(14)	O3A	C7A	1.3625(14)
O3	C8	1.4157(13)	O3A	C8A	1.4180(13)
N1	C3	1.4731(14)	N1A	C3A	1.4732(14)
N1	C4	1.4866(14)	N1A	C4A	1.4873(14)
N1	C9	1.4050(14)	N1A	C9A	1.4067(14)
C1	C2	1.5238(17)	C1A	C2A	1.5273(17)
C2	C3	1.5060(16)	C2A	C3A	1.5052(16)
C3	C4	1.4954(15)	C3A	C4A	1.4986(16)
C4	C5	1.5038(16)	C4A	C5A	1.5092(15)
C5	C6	1.5271(15)	C5A	C6A	1.5250(16)
C8	C9	1.3383(16)	C8A	C9A	1.3384(16)
C8	C10	1.4638(15)	C8A	C10A	1.4665(15)
C10	C11	1.3994(16)	C10A	C11A	1.4035(16)
C10	C15	1.4005(15)	C10A	C15A	1.4031(15)
C11	C12	1.3872(16)	C11A	C12A	1.3910(16)
C12	C13	1.3948(17)	C12A	C13A	1.3933(17)
C13	C14	1.3886(17)	C13A	C14A	1.3905(17)
C14	C15	1.3897(16)	C14A	C15A	1.3915(16)

Table S-5. Bond Angles for **3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	C6	120.74(9)	C7A	O1A	C6A	120.53(9)
C7	O3	C8	114.19(8)	C7A	O3A	C8A	115.25(8)
C3	N1	C4	60.69(7)	C3A	N1A	C4A	60.82(7)
C9	N1	C3	120.14(9)	C9A	N1A	C3A	121.20(9)
C9	N1	C4	116.73(9)	C9A	N1A	C4A	117.39(9)
C3	C2	C1	111.27(10)	C3A	C2A	C1A	111.86(10)
N1	C3	C2	117.05(10)	N1A	C3A	C2A	115.67(10)
N1	C3	C4	60.10(7)	N1A	C3A	C4A	60.06(7)
C4	C3	C2	124.35(10)	C4A	C3A	C2A	123.27(10)
N1	C4	C3	59.21(7)	N1A	C4A	C3A	59.12(7)
N1	C4	C5	117.47(9)	N1A	C4A	C5A	117.72(9)
C3	C4	C5	126.40(10)	C3A	C4A	C5A	126.18(10)
C4	C5	C6	112.57(9)	C4A	C5A	C6A	112.82(9)
O1	C6	C5	111.78(9)	O1A	C6A	C5A	111.41(9)
O1	C7	O3	112.75(9)	O1A	C7A	O3A	112.80(9)
O2	C7	O1	122.35(10)	O2A	C7A	O1A	122.34(11)
O2	C7	O3	124.85(10)	O2A	C7A	O3A	124.76(10)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	C8	C10	115.44(9)	O3A	C8A	C10A	115.13(9)
C9	C8	O3	115.80(10)	C9A	C8A	O3A	115.53(10)
C9	C8	C10	128.73(10)	C9A	C8A	C10A	129.26(10)
C8	C9	N1	119.76(10)	C8A	C9A	N1A	119.38(10)
C11	C10	C8	120.78(10)	C11A	C10A	C8A	120.71(10)
C11	C10	C15	119.21(10)	C15A	C10A	C8A	120.23(10)
C15	C10	C8	120.01(10)	C15A	C10A	C11A	119.05(10)
C12	C11	C10	120.13(10)	C12A	C11A	C10A	120.17(10)
C11	C12	C13	120.56(11)	C11A	C12A	C13A	120.56(11)
C14	C13	C12	119.40(11)	C14A	C13A	C12A	119.44(11)
C13	C14	C15	120.54(10)	C13A	C14A	C15A	120.61(11)
C14	C15	C10	120.16(10)	C14A	C15A	C10A	120.17(11)

Table S-6. Torsion Angles for **3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C8	C9	N1	-4.57(15)	O3A	C8A	C9A	N1A	5.04(15)
O3	C8	C10	C11	-156.30(10)	O3A	C8A	C10A	C11A	156.78(10)
O3	C8	C10	C15	23.18(14)	O3A	C8A	C10A	C15A	-22.06(14)
N1	C3	C4	C5	-103.17(12)	N1A	C3A	C4A	C5A	103.54(12)
N1	C4	C5	C6	82.16(12)	N1A	C4A	C5A	C6A	-79.59(12)
C1	C2	C3	N1	-83.30(13)	C1A	C2A	C3A	N1A	79.23(13)
C1	C2	C3	C4	-154.09(11)	C1A	C2A	C3A	C4A	148.93(11)
C2	C3	C4	N1	104.04(12)	C2A	C3A	C4A	N1A	-102.70(12)
C2	C3	C4	C5	0.86(17)	C2A	C3A	C4A	C5A	0.83(17)
C3	N1	C4	C5	117.95(11)	C3A	N1A	C4A	C5A	-117.57(11)
C3	N1	C9	C8	133.29(11)	C3A	N1A	C9A	C8A	-137.12(11)
C3	C4	C5	C6	152.68(10)	C3A	C4A	C5A	C6A	-150.08(10)
C4	N1	C3	C2	-115.92(12)	C4A	N1A	C3A	C2A	115.19(11)
C4	N1	C9	C8	63.25(13)	C4A	N1A	C9A	C8A	-66.28(13)
C4	C5	C6	O1	-76.04(12)	C4A	C5A	C6A	O1A	76.86(12)
C6	O1	C7	O2	-163.10(10)	C6A	O1A	C7A	O2A	162.38(10)
C6	O1	C7	O3	19.51(13)	C6A	O1A	C7A	O3A	-21.01(14)
C7	O1	C6	C5	75.10(12)	C7A	O1A	C6A	C5A	-75.69(13)
C7	O3	C8	C9	68.73(12)	C7A	O3A	C8A	C9A	-67.03(12)
C7	O3	C8	C10	-113.17(10)	C7A	O3A	C8A	C10A	116.01(10)
C8	O3	C7	O1	-145.12(9)	C8A	O3A	C7A	O1A	145.27(9)

C8	O3	C7	O2	37.57(14)	C8A	O3A	C7A	O2A	-38.22(15)
C8	C10	C11	C12	-179.96(10)	C8A	C10A	C11A	C12A	-179.44(10)
C8	C10	C15	C14	179.52(10)	C8A	C10A	C15A	C14A	179.11(10)
C9	N1	C3	C2	138.39(11)	C9A	N1A	C3A	C2A	-138.68(11)
C9	N1	C3	C4	-105.69(11)	C9A	N1A	C3A	C4A	106.13(11)
C9	N1	C4	C3	111.23(10)	C9A	N1A	C4A	C3A	-112.26(11)
C9	N1	C4	C5	-130.82(10)	C9A	N1A	C4A	C5A	130.16(11)
C9	C8	C10	C11	21.51(18)	C9A	C8A	C10A	C11A	-19.67(18)
C9	C8	C10	C15	-159.01(11)	C9A	C8A	C10A	C15A	161.49(11)
C10	C8	C9	N1	177.62(10)	C10A	C8A	C9A	N1A	-178.52(10)
C10	C11	C12	C13	0.19(17)	C10A	C11A	C12A	C13A	0.69(18)
C11	C10	C15	C14	-0.99(16)	C11A	C10A	C15A	C14A	0.25(16)
C11	C12	C13	C14	-0.50(17)	C11A	C12A	C13A	C14A	-0.44(18)
C12	C13	C14	C15	0.05(17)	C12A	C13A	C14A	C15A	0.10(17)
C13	C14	C15	C10	0.70(17)	C13A	C14A	C15A	C10A	-0.01(17)
C15	C10	C11	C12	0.55(16)	C15A	C10A	C11A	C12A	-0.59(16)

Table S-7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

Atom	***x***	***y***	***Z***	**U(eq)**
H1A	4957.7	9610.13	7528.88	43
H1B	5937.68	8342.56	7755.79	43
H1C	4074.96	8410.09	7894.14	43
H2A	3749.34	9239.18	6143.7	25
H2B	5613.9	9087.38	6025.69	25
H3	3744.94	7056.46	6756.05	21
H4	4395.17	6392.6	5361.94	20
H5A	6261.93	8414.44	4631.08	22
H5B	4730.35	8217.92	4054.19	22
H6A	6092.17	6323.45	3927.59	22
H6B	6734.58	7510.16	3232.51	22
H9	5878.6	5336.63	7534.17	20

Table S-7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

Atom	***x***	***y***	***Z***	**U(eq)**
H11	5595.14	3299.64	8015.13	21
H12	6104.68	1255.17	8689.57	23
H13	7954.08	161.91	7962.25	24
H14	9267.7	1128.41	6539.88	23
H15	8746.57	3169.87	5843.74	20
H1AA	808.66	9166.53	5329.01	35
H1AB	-427.47	8185.33	5372.23	35
H1AC	1338.54	7781.86	5757.69	35
H2AA	839.75	8828.85	7039.25	26
H2AB	-969.69	9007.47	6702.47	26
H3A	-1118.39	6843.15	7192.52	21
H4A	-640.81	6319.44	8902.46	20
H5AA	-295.83	8197.54	9320.2	22
H5AB	1267.51	8336.64	8676.33	22
H6AA	1643.14	7578.3	10486.08	23
H6AB	1042.16	6351.36	10363.06	23
H9A	946.37	5001.88	7368.95	20
H11A	677.15	2961.65	7909.89	22
H12A	1139.41	890.07	8294.65	25
H13A	2865.32	-100.88	9593.12	25
H14A	4160.37	998.28	10491.78	24
H15A	3733.29	3072.25	10108.14	21

Data Collection for Compound 4e (CCDC Deposition Number 2124059).

A colorless crystal with approximate dimensions 0.09 x 0.06 x 0.06 mm^3 was selected under oil under ambient conditions selected under oil and attached to the tip of a MiTeGen MicroMount© . The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 VENTURE PhotonIII four-circle diffractometer with Cu Kα (λ = 1.54178 Å) radiation and the detector to crystal distance of 4.0 cm.[11]

The initial cell constants were obtained from a 180° φ scan conducted at a 2θ = 50° angle with an exposure time of 1 second per frame. The reflections were successfully indexed by an automated indexing routine built into the APEX3 program. The final cell constants were calculated from a set of 9897 strong reflections from the actual data collection.

The data were collected by using a full sphere data collection routine to survey reciprocal space to the extent of a full sphere to a resolution of 0.79 Å. A total of 46757 data were harvested by collecting 33 sets of frames with 0.9º scans in ω and φ with exposure times of 2 - 25 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[12]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *Pnma* and $Pna2_1$. The *E*-statistics strongly suggested the non-centrosymmetric space group $Pna2_1$ that yielded chemically reasonable and computationally stable results of refinement.[13-18]

A successful solution by direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located with an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The compound crystallizes as a racemate. The molecule shown in Figure S-13 with stereocenters C1 (*S*) and C7 (*R*) was chosen arbitrarily.

The compound crystallizes as an inversion twin, with a 43(9)% contribution from the minor component.

The final least-squares refinement of 167 parameters against 2554 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0335 and 0.0856, respectively. The final difference Fourier map was featureless.

Summary.

Crystal Data for **4e.** $C_{12}H_{17}NO_5$ (M =255.26 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 11.2137(19) Å, b = 16.314(4) Å, c = 6.706(3) Å, V = 1226.8(6) Å^3, Z = 4, T = 100.0 K, μ(Cu Kα) = 0.907 mm^{-1}, *Dcalc* = 1.382 g/cm^3, 37289 reflections measured (9.57° ≤ 2Θ ≤ 157.854°), 2554 unique (R_{int} = 0.0576, R_{sigma} = 0.0215) which were used in all calculations. The final R_1 was 0.0335 (I > 2σ(I)) and wR_2 was 0.0856 (all data).

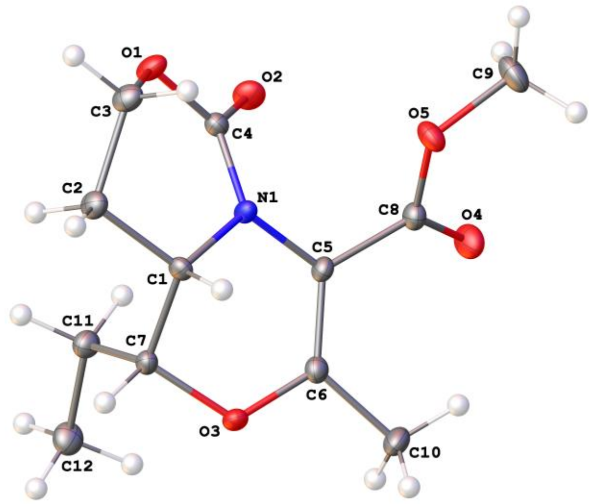


Figure S-13. A molecular drawing of **4e** shown with 50% probability ellipsoids.

Table S-8. Crystal data and structure refinement for **4e.**

Empirical formula	$C_{12}H_{17}NO_5$
Formula weight	255.26
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	11.2137(19)
b/Å	16.314(4)
c/Å	6.706(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1226.8(6)
Z	4
ρ_{calc}g/cm^3	1.382
μ/mm^{-1}	0.907
F(000)	544.0
Crystal size/mm^3	0.09 × 0.06 × 0.06
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	9.57 to 157.854
Index ranges	$-14 \leq h \leq 14$, $-20 \leq k \leq 20$, $-8 \leq l \leq 7$
Reflections collected	37289
Independent reflections	2554 [R_{int} = 0.0576, R_{sigma} = 0.0215]
Data/restraints/parameters	2554/1/167
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0840
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0856

Largest diff. peak/hole / e Å^{-3}	0.30/-0.18
Flack parameter	0.43(9)

Table S-9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4e**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	8601.7(14)	5012.9(9)	4357(2)	16.9(3)
O2	7800.4(14)	4105.6(10)	2287(2)	17.9(4)
O3	6165.9(13)	3080.1(9)	8124(2)	13.9(3)
O4	7542.5(14)	1944.9(10)	2756(3)	21.7(4)
O5	9162.3(13)	2704.5(9)	3463(2)	17.5(4)
N1	7887.5(15)	3788.2(11)	5616(3)	11.3(4)
C1	7696.5(18)	4098.8(12)	7657(3)	11.9(4)
C2	8085(2)	4992.9(13)	7839(3)	15.7(4)
C3	9067(2)	5149.6(14)	6352(3)	16.6(5)
C4	8059.8(18)	4290.3(13)	3990(3)	12.4(4)
C5	7445.4(18)	2980.7(12)	5294(3)	12.2(4)
C6	6655.8(19)	2649.9(13)	6597(3)	13.6(4)
C7	6380.7(17)	3954.3(12)	8183(3)	12.3(4)
C8	8016.4(19)	2487.3(13)	3700(3)	14.3(4)
C9	9763(2)	2313.6(15)	1808(4)	22.9(5)
C10	6252(2)	1780.6(13)	6689(4)	18.6(5)
C11	5486.4(19)	4391.9(13)	6853(3)	16.2(4)
C12	4199.6(19)	4127.4(14)	7237(4)	19.7(5)

Table S-10. Anisotropic Displacement Parameters (Å^2×10^3) for **4e**. The Anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	24.1(8)	12.3(7)	14.4(8)	1.6(5)	0.8(6)	-4.9(6)
O2	24.3(8)	19.1(8)	10.4(8)	1.1(6)	-0.4(6)	-0.9(6)
O3	17.0(7)	11.4(7)	13.2(7)	1.8(6)	4.0(6)	-0.8(5)
O4	22.6(8)	18.8(8)	23.9(9)	-9.4(6)	2.1(6)	-3.8(6)
O5	14.3(7)	20.3(8)	18.0(8)	-6.7(6)	3.3(6)	0.8(6)
N1	15.6(8)	9.4(8)	8.9(8)	-1.0(6)	1.2(7)	-1.4(6)
C1	13.7(9)	12.6(10)	9.3(10)	-1.4(7)	1.9(7)	0.1(7)
C2	19.6(11)	13.1(10)	14.4(11)	-2.9(7)	0.7(8)	-2.5(8)
C3	19.5(11)	14.5(10)	15.7(11)	-0.8(8)	-0.9(8)	-4.6(8)
C4	12.8(9)	12.4(9)	12.0(10)	-0.2(7)	1.8(7)	0.7(8)
C5	13.4(9)	9.0(9)	14.2(10)	-1.0(7)	0.3(8)	-0.6(7)
C6	12.6(10)	11.9(10)	16.3(10)	-0.8(7)	0.4(8)	1.4(8)
C7	14.6(9)	10.1(9)	12.3(10)	-0.5(7)	2.1(8)	0.9(7)
C8	15.9(9)	11.8(9)	15.3(10)	-2.1(8)	0.7(8)	0.6(8)
C9	19.2(11)	26.6(12)	22.8(12)	-9.7(9)	5.2(9)	3.5(9)

Atom	*x*		*y*	*z*	U(eq)	
C10	18.2(10)	11.3(10)	26.2(12)	0.9(9)	2.9(9)	-1.0(8)
C11	15.7(10)	14.4(10)	18.3(11)	2.0(8)	0.6(8)	1.3(8)
C12	14.7(10)	19.4(11)	25.1(12)	0.0(9)	-1.8(9)	1.7(8)

Table S-11. Bond Lengths for **4e**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.453(3)	N1	C5	1.424(3)
O1	C4	1.349(3)	C1	C2	1.527(3)
O2	C4	1.216(3)	C1	C7	1.535(3)
O3	C6	1.358(3)	C2	C3	1.507(3)
O3	C7	1.447(2)	C5	C6	1.356(3)
O4	C8	1.211(3)	C5	C8	1.483(3)
O5	C8	1.342(3)	C6	C10	1.490(3)
O5	C9	1.446(3)	C7	C11	1.520(3)
N1	C1	1.476(3)	C11	C12	1.528(3)
N1	C4	1.377(3)			

Table S-12. Bond Angles for **4e**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O1	C3	117.65(17)	N1	C5	C8	117.45(18)
C6	O3	C7	117.56(16)	C6	C5	N1	119.85(19)
C8	O5	C9	114.88(17)	C6	C5	C8	122.02(18)
C4	N1	C1	123.41(17)	O3	C6	C10	109.73(18)
C4	N1	C5	118.62(17)	C5	C6	O3	123.00(19)
C5	N1	C1	114.07(17)	C5	C6	C10	127.2(2)
N1	C1	C2	111.13(17)	O3	C7	C1	107.76(16)
N1	C1	C7	107.44(16)	O3	C7	C11	109.70(16)
C2	C1	C7	113.72(17)	C11	C7	C1	115.30(17)
C3	C2	C1	108.52(18)	O4	C8	O5	123.44(19)
O1	C3	C2	108.71(18)	O4	C8	C5	125.71(19)
O1	C4	N1	116.00(18)	O5	C8	C5	110.82(17)
O2	C4	O1	119.72(19)	C7	C11	C12	113.05(18)
O2	C4	N1	124.21(19)				

Table S-13. Torsion Angles for **4e**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C7	C11	C12	49.5(2)	C4	N1	C1	C2	-17.3(3)
N1	C1	C2	C3	-28.7(2)	C4	N1	C1	C7	107.7(2)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C7	O3	61.7(2)	C4	N1	C5	C6	-142.0(2)
N1	C1	C7	C11	-61.2(2)	C4	N1	C5	C8	47.2(3)
N1	C5	C6	O3	6.5(3)	C5	N1	C1	C2	-174.64(16)
N1	C5	C6	C10	-169.4(2)	C5	N1	C1	C7	-49.6(2)
N1	C5	C8	O4	-152.5(2)	C5	N1	C4	O1	-172.94(17)
N1	C5	C8	O5	29.3(3)	C5	N1	C4	O2	4.0(3)
C1	N1	C4	O1	30.6(3)	C6	O3	C7	C1	-42.4(2)
C1	N1	C4	O2	-152.4(2)	C6	O3	C7	C11	83.9(2)
C1	N1	C5	C6	16.5(3)	C6	C5	C8	O4	37.0(3)
C1	N1	C5	C8	-154.22(18)	C6	C5	C8	O5	-141.2(2)
C1	C2	C3	O1	61.8(2)	C7	O3	C6	C5	8.5(3)
C1	C7	C11	C12	171.32(18)	C7	O3	C6	C10	-175.07(17)
C2	C1	C7	O3	-174.90(16)	C7	C1	C2	C3	-150.05(18)
C2	C1	C7	C11	62.2(2)	C8	C5	C6	O3	176.78(19)
C3	O1	C4	O2	-170.25(19)	C8	C5	C6	C10	1.0(3)
C3	O1	C4	N1	6.8(3)	C9	O5	C8	O4	7.6(3)
C4	O1	C3	C2	-53.0(2)	C9	O5	C8	C5	-174.19(18)

Table S-14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4e**.

Atom	*x*	*y*	*z*	U(eq)
H1	8195.65	3764.85	8588.63	14
H2A	7400.36	5359.74	7566.82	19
H2B	8374.85	5103.73	9206.54	19
H3A	9354.95	5720.83	6478.86	20
H3B	9744.49	4775.47	6608.48	20
H7	6250.35	4145.26	9582.9	15
H9A	9331.6	2431.11	569.94	34
H9B	9786.96	1719.91	2026.59	34
H9C	10579.19	2525.14	1705.9	34
H10A	6403.04	1560.94	8025.72	28
H10B	6690.25	1456.1	5702.08	28
H10C	5395.84	1752.99	6400.87	28
H11A	5687.69	4281.31	5440.98	19
H11B	5553.62	4990.17	7073.53	19
H12A	3659.22	4460.66	6423.7	30
H12B	4008.91	4203.65	8651.28	30
H12C	4105.28	3548.17	6883.13	30

XI. Computational Methods.

Computational details

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.[19] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[20] in conjunction with the D3 dispersion correction suggested by Grimme et al.[21] using the standard double-ζ quality def2-SVP[22] basis set for all atoms. The SMD continuum model was used to model the effects of the solvent. This level is denoted SMD(dichloromethane)-B3LYP-D3/def2-SVP. This DFT level has been selected to enable a direct comparison with our previous reports on the chemistry of strongly related systems.[23] Geometries were fully optimized in solution without any geometry or symmetry constraints. Reactants, intermediates, and products were characterized by frequency calculations[24], and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[25]

Donor-acceptor interactions were computed using the natural bond orbital (NBO6) method.[26] The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi^*} = -n_{\phi}\frac{\langle\phi^*|\hat{F}|\phi\rangle^2}{\varepsilon_{\phi^*}-\varepsilon_{\phi}}$$

where F is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled Natural Bond Orbitals having ε_{ϕ} and $\varepsilon_{\phi*}$ energies, respectively; ; n_{ϕ} stands for the occupation number of the filled orbital. Noncovalent interactions were visualized with the help of the NCIPLOT method.[27]

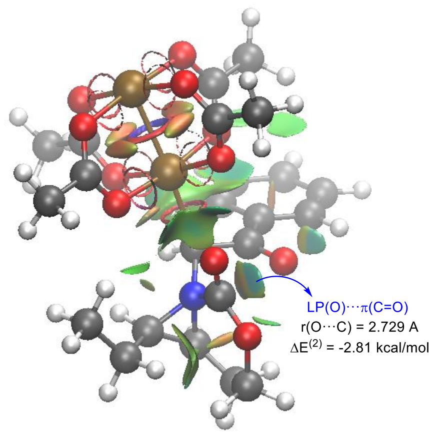


Figure S-14. Contour plots of the reduced density gradient isosurfaces (density cutoff of 0.04 a.u.) for intermediate **INT2-Rh** (the green surfaces indicate attractive noncovalent interactions) and associated SOPT-NBO stabilizing energy.

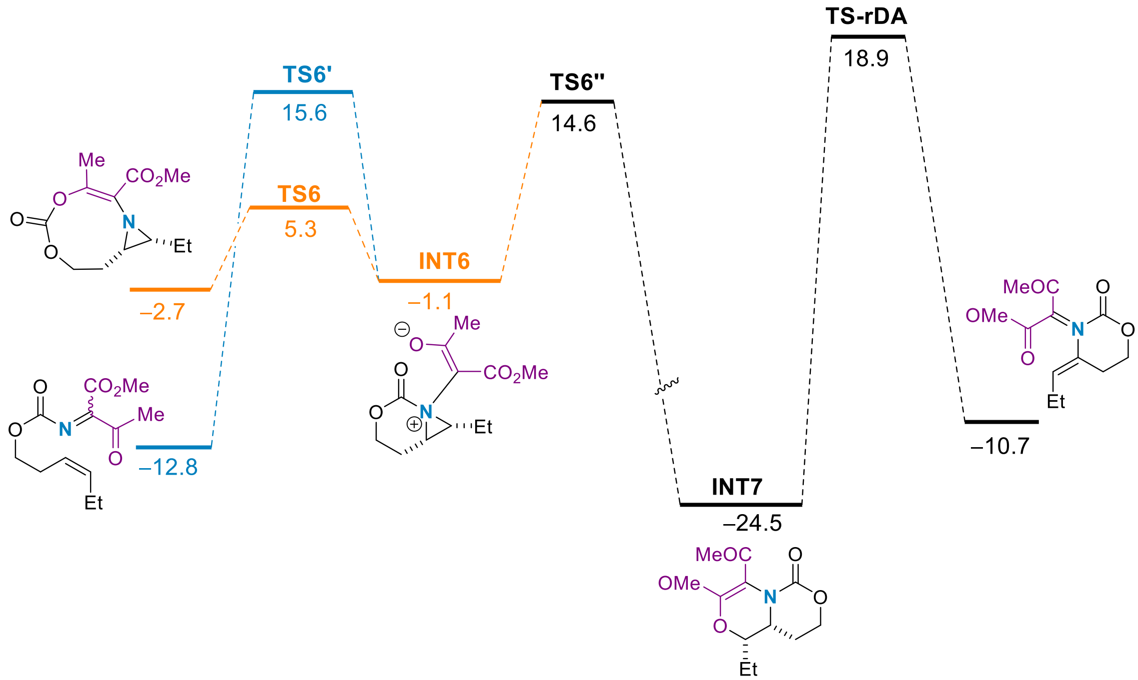


Figure S-15. Computed (SMD-B3LYP-D3/def2-SVP level) alternative pathways from ylide **INT6**. Relative free enrgies DG, at 298 K) are given in kcal/mol

Cartesian coordinates (in Å) and energies (in free energies, in a.u.) of all the stationary points discussed in the text. All calculations have been performed at the SMD(dichloromethane)-B3LYP-D3/def2-SVP level.

INT1-Rh, G = -1995.875237

Rh	0.376539000	-0.244547000	-0.055558000
C	-1.515318000	0.981021000	-0.185397000
N	-2.895546000	0.367058000	-0.036059000
C	-4.049881000	1.258977000	0.374702000
C	-3.669328000	0.139435000	1.268128000
H	-3.671727000	2.220585000	0.723952000
C	-5.194607000	1.404484000	-0.594344000
C	-5.431739000	0.184028000	-1.459129000
O	-4.185686000	-0.423613000	-1.891671000

C	-3.182188000	-0.679891000	-1.063813000
O	-2.500994000	-1.649938000	-1.136004000
H	-6.013977000	-0.593447000	-0.943647000
H	-5.956788000	0.443726000	-2.386035000
H	-6.115305000	1.648765000	-0.041497000
H	-4.959439000	2.269297000	-1.233478000
Rh	2.476966000	-1.524128000	-0.064946000
O	3.340391000	0.061020000	-1.067220000
C	2.639071000	1.078334000	-1.341479000
O	1.410514000	1.227247000	-1.060848000
O	1.854823000	-2.348704000	-1.854228000
C	0.790454000	-1.927738000	-2.397917000
O	0.012715000	-1.048239000	-1.920938000
O	2.945611000	-0.605713000	1.725985000
C	2.119665000	0.201491000	2.245157000
O	0.982362000	0.504588000	1.771884000
O	1.475650000	-3.007464000	0.951704000
C	0.255424000	-2.850371000	1.253414000
O	-0.453629000	-1.837003000	0.972187000
C	-0.422682000	-3.974007000	2.001087000
H	-1.174381000	-4.440169000	1.344528000
H	0.308420000	-4.731713000	2.310701000
H	-0.950952000	-3.576370000	2.879605000
C	2.526734000	0.900101000	3.519088000
H	3.300926000	0.329864000	4.049702000
H	2.938286000	1.888536000	3.254212000
H	1.652008000	1.060053000	4.164595000
C	0.401311000	-2.507356000	-3.736199000
H	1.080114000	-3.317914000	-4.031090000
H	-0.633587000	-2.878742000	-3.684188000
H	0.427547000	-1.709942000	-4.496341000
C	3.305123000	2.231693000	-2.049786000

H	2.718177000	2.509811000	-2.937987000
H	3.312053000	3.103989000	-1.377447000
H	4.333030000	1.978087000	-2.338851000
H	-3.044034000	0.460517000	2.103463000
C	-4.429451000	-1.144521000	1.492693000
H	-4.945604000	-1.490262000	0.585272000
H	-5.229737000	-0.882387000	2.206556000
C	-1.211898000	2.034845000	0.781193000
O	-1.612912000	2.034614000	1.952788000
H	-1.460063000	1.287167000	-1.234755000
C	-0.305624000	3.153118000	0.340788000
C	0.577014000	3.689297000	1.292507000
C	-0.341888000	3.708873000	-0.946159000
C	1.422603000	4.747399000	0.958081000
C	0.486664000	4.785589000	-1.276079000
C	1.376871000	5.301718000	-0.328550000
H	0.595456000	3.246303000	2.289034000
H	-1.023944000	3.306757000	-1.698029000
H	2.119704000	5.145428000	1.700666000
H	0.442911000	5.217841000	-2.279351000
H	2.033947000	6.135512000	-0.590688000
C	-3.548005000	-2.258516000	2.051647000
H	-4.140877000	-3.167972000	2.235341000
H	-2.737284000	-2.492639000	1.350948000
H	-3.084497000	-1.952107000	3.003025000

INT2-Rh, G = -1995.884377

Rh	-0.500375000	-0.186460000	0.008702000
C	1.603120000	0.459144000	-0.381425000
N	2.796774000	-0.456619000	-0.263513000
C	4.013288000	0.005974000	-1.034951000

C	3.304252000	-1.217633000	-1.479781000
H	3.762042000	0.898274000	-1.613209000
C	5.293258000	0.157653000	-0.260124000
C	5.466369000	-0.878832000	0.827433000
O	4.237246000	-1.160901000	1.535087000
C	3.005539000	-1.126248000	1.054097000
O	2.087103000	-1.640951000	1.605971000
H	5.840351000	-1.833755000	0.431671000
H	6.167226000	-0.533924000	1.598021000
H	6.150609000	0.111978000	-0.949822000
H	5.274781000	1.164416000	0.182148000
Rh	-2.876957000	-0.812315000	0.140860000
O	-3.305317000	1.152974000	0.596734000
C	-2.353166000	1.983667000	0.669743000
O	-1.125508000	1.715471000	0.498652000
O	-2.569285000	-1.214818000	2.136692000
C	-1.434347000	-0.973872000	2.651014000
O	-0.415868000	-0.539797000	2.036391000
O	-3.001590000	-0.343730000	-1.876307000
C	-1.976606000	0.053224000	-2.499798000
O	-0.812890000	0.190390000	-2.001438000
O	-2.315104000	-2.731924000	-0.330183000
C	-1.093829000	-2.997364000	-0.536577000
O	-0.132487000	-2.169507000	-0.475915000
C	-0.748804000	-4.427437000	-0.879992000
H	-0.097712000	-4.845168000	-0.096526000
H	-1.658088000	-5.036129000	-0.963251000
H	-0.189595000	-4.460245000	-1.826539000
C	-2.128017000	0.426317000	-3.954051000
H	-3.095116000	0.090601000	-4.349939000
H	-2.061596000	1.523162000	-4.044671000
H	-1.304091000	-0.005245000	-4.541533000

C	-1.272794000	-1.204734000	4.134210000
H	-2.138663000	-1.737177000	4.548669000
H	-0.348386000	-1.770775000	4.322413000
H	-1.171478000	-0.228744000	4.636547000
C	-2.688793000	3.428407000	0.943452000
H	-1.939502000	3.871662000	1.614445000
H	-2.645803000	3.979809000	-0.010524000
H	-3.696694000	3.525803000	1.367855000
H	2.616971000	-1.056180000	-2.316118000
C	3.776886000	-2.648089000	-1.370365000
H	4.326178000	-2.831231000	-0.437850000
H	4.510368000	-2.777765000	-2.184704000
H	1.472376000	0.631216000	-1.452188000
C	2.634030000	-3.650812000	-1.500493000
H	3.015614000	-4.682117000	-1.448541000
H	1.900292000	-3.500901000	-0.698493000
H	2.107187000	-3.527928000	-2.460243000
C	1.924355000	1.655404000	0.406964000
O	2.659699000	1.558895000	1.399084000
C	1.404188000	2.999587000	-0.013997000
C	1.701957000	4.103912000	0.801995000
C	0.672284000	3.206410000	-1.197324000
C	1.276003000	5.386561000	0.451210000
C	0.251838000	4.489694000	-1.551722000
C	0.550509000	5.583340000	-0.729542000
H	2.269779000	3.934169000	1.718953000
H	0.393657000	2.363351000	-1.830235000
H	1.509770000	6.235721000	1.099094000
H	-0.321115000	4.637373000	-2.471146000
H	0.216045000	6.586454000	-1.007990000

Rh2(AOc)4, G = -1134.513729

Rh	0.000007000	0.000031000	-1.194774000
Rh	-0.000069000	-0.000011000	1.196480000
O	1.414789000	-1.487532000	1.125943000
C	1.868866000	-1.864363000	0.001673000
O	1.489053000	-1.413770000	-1.123393000
O	-1.485550000	-1.417053000	1.125754000
C	-1.864709000	-1.868590000	0.001136000
O	-1.410985000	-1.491602000	-1.123525000
O	1.485447000	1.417024000	1.125711000
C	1.864749000	1.868518000	0.001150000
O	1.411037000	1.491625000	-1.123569000
O	-1.414836000	1.487571000	1.125928000
C	-1.868846000	1.864464000	0.001644000
O	-1.489076000	1.413803000	-1.123414000
C	-2.961820000	2.898234000	-0.001356000
H	-3.928550000	2.381473000	-0.122943000
H	-2.975850000	3.454233000	0.945071000
H	-2.835914000	3.582924000	-0.851769000
C	2.958274000	2.901675000	-0.003731000
H	2.981276000	3.448276000	0.948314000
H	3.923560000	2.384023000	-0.133926000
H	2.827088000	3.594314000	-0.846410000
C	-2.958018000	-2.901981000	-0.003882000
H	-2.981661000	-3.447976000	0.948496000
H	-3.923309000	-2.384689000	-0.135365000
H	-2.825877000	-3.595166000	-0.845974000
C	2.961904000	-2.898076000	-0.001324000
H	2.835722000	-3.583133000	-0.851397000
H	3.928542000	-2.381292000	-0.123544000
H	2.976341000	-3.453667000	0.945338000

INT1, G = -861.359966

O	2.720223000	-1.579524000	-1.123459000
O	1.642274000	0.107764000	-2.078118000
O	-0.789480000	1.660716000	-0.136667000
N	1.271854000	-0.250165000	0.205452000
C	2.116750000	-0.470615000	1.445978000
H	1.490112000	-0.865237000	2.249176000
C	3.401094000	-1.228569000	1.184552000
H	4.221833000	-0.570556000	0.863663000
H	3.718632000	-1.741420000	2.103292000
C	3.116168000	-2.254741000	0.101193000
H	4.006092000	-2.834730000	-0.172354000
H	2.312149000	-2.948695000	0.394638000
C	1.900245000	-0.539226000	-1.107653000
C	-0.141716000	-0.575785000	0.223203000
C	-1.075226000	0.445042000	0.013025000
C	1.825531000	0.916358000	1.014080000
H	0.998158000	1.409443000	1.526501000
H	-0.345953000	-1.623465000	0.426586000
C	2.820746000	1.855110000	0.381987000
H	3.545739000	1.303862000	-0.237661000
H	3.403112000	2.282446000	1.217210000
C	2.160911000	2.967027000	-0.434095000
H	2.928059000	3.628267000	-0.867458000
H	1.495467000	3.576297000	0.196579000
H	1.548315000	2.544793000	-1.241606000
C	-2.542563000	0.045937000	0.030175000
C	-3.492221000	1.064468000	0.218737000
C	-3.004361000	-1.270085000	-0.154965000
C	-4.859845000	0.779151000	0.245893000
C	-4.372263000	-1.558570000	-0.132635000
C	-5.306407000	-0.536093000	0.072117000

H	-3.124886000	2.086096000	0.337893000
H	-2.295478000	-2.079660000	-0.341160000
H	-5.582316000	1.586066000	0.399387000
H	-4.711163000	-2.587409000	-0.284600000
H	-6.376036000	-0.763038000	0.088151000

INT2, G = -861.366629

O	-2.223382000	-1.600002000	0.859470000
O	-1.328220000	0.038756000	2.059530000
O	0.657391000	-1.456892000	0.249297000
N	-1.230734000	0.279421000	-0.262485000
C	-3.404761000	2.494357000	1.004007000
H	-4.346490000	2.663070000	1.548674000
H	-2.630061000	2.221467000	1.736329000
H	-3.109450000	3.445814000	0.532565000
C	-3.578483000	1.391990000	-0.042744000
H	-4.354695000	1.674402000	-0.774342000
H	-3.930131000	0.462169000	0.430065000
C	-2.318186000	1.152017000	-0.837792000
H	-1.877038000	2.058718000	-1.262023000
C	-1.973090000	-0.110974000	-1.536154000
H	-1.292481000	-0.015470000	-2.384568000
C	-2.807814000	-1.374650000	-1.477282000
H	-3.863509000	-1.154937000	-1.259735000
H	-2.765160000	-1.878517000	-2.453270000
C	-2.237020000	-2.292743000	-0.413255000
H	-1.201964000	-2.588317000	-0.636938000
H	-2.862822000	-3.178418000	-0.248739000
C	-1.549181000	-0.476093000	1.005484000
C	1.056183000	-0.287992000	-0.058745000
C	0.150825000	0.723148000	-0.343572000
H	0.310922000	1.794245000	-0.417839000

C	2.533540000	0.002777000	-0.071298000
C	3.092684000	1.141264000	-0.680336000
H	2.448781000	1.857608000	-1.195831000
C	4.473111000	1.357034000	-0.655677000
H	4.892253000	2.245029000	-1.137293000
C	5.320346000	0.436909000	-0.025176000
H	6.400450000	0.606538000	-0.008265000
C	4.775207000	-0.703553000	0.575514000
H	5.429904000	-1.429094000	1.066780000
C	3.394722000	-0.918443000	0.548567000
H	2.951814000	-1.805455000	1.006204000

TS1, G = -861.349113 (i = -128 cm-1)

O	-3.144244000	-0.887472000	1.067987000
O	-1.262252000	-0.491887000	2.185555000
O	0.642663000	1.274518000	0.575153000
N	-1.151764000	-0.713959000	-0.118458000
C	-1.980497000	-0.487504000	-1.393282000
H	-1.376806000	-0.869638000	-2.221529000
C	-3.388101000	-1.087430000	-1.346825000
H	-4.137275000	-0.302938000	-1.525645000
H	-3.503809000	-1.840852000	-2.138927000
C	-3.620179000	-1.741571000	0.002917000
H	-4.685753000	-1.905102000	0.207770000
H	-3.097110000	-2.709236000	0.073170000
C	-1.815340000	-0.670485000	1.137719000
C	0.226885000	-0.898171000	-0.198366000
C	1.078109000	0.165727000	0.186754000
C	-1.785448000	0.934806000	-1.116679000
H	-0.822962000	1.359500000	-1.408757000
H	0.547013000	-1.681210000	-0.889075000

C	-2.772690000	1.854066000	-0.505274000
H	-3.492078000	1.301350000	0.119107000
H	-3.378202000	2.238000000	-1.356500000
C	-2.148448000	3.018115000	0.265321000
H	-2.931285000	3.677079000	0.671559000
H	-1.498284000	3.621899000	-0.388010000
H	-1.526732000	2.641423000	1.089291000
C	2.568549000	-0.027184000	0.035010000
C	3.384390000	1.115834000	-0.026645000
C	3.178073000	-1.293070000	-0.025744000
C	4.768910000	1.001391000	-0.169746000
C	4.564604000	-1.409946000	-0.164756000
C	5.364845000	-0.263883000	-0.241063000
H	2.904138000	2.094245000	0.043230000
H	2.568713000	-2.195640000	0.060827000
H	5.387918000	1.901605000	-0.222057000
H	5.024345000	-2.401486000	-0.203420000
H	6.449209000	-0.356738000	-0.347439000

TS2, G = -861.364226 (i = -101 cm-1)

O	-2.053699000	-1.658586000	0.759171000
O	-1.257045000	0.017788000	1.990797000
O	0.518365000	-1.214714000	0.463904000
N	-1.225967000	0.338729000	-0.354482000
C	-3.457757000	2.337944000	1.192177000
H	-4.370758000	2.408198000	1.803996000
H	-2.614919000	2.101315000	1.858018000
H	-3.276896000	3.327698000	0.741319000
C	-3.611551000	1.261837000	0.116198000
H	-4.462513000	1.499374000	-0.545562000
H	-3.838213000	0.287787000	0.573919000

C	-2.398622000	1.160088000	-0.777738000
H	-2.067771000	2.117824000	-1.192188000
C	-2.035593000	-0.041866000	-1.579469000
H	-1.448509000	0.147709000	-2.481280000
C	-2.771150000	-1.367103000	-1.525256000
H	-3.823464000	-1.230885000	-1.233654000
H	-2.758620000	-1.826444000	-2.523996000
C	-2.081410000	-2.289970000	-0.531646000
H	-1.048338000	-2.519887000	-0.833855000
H	-2.639006000	-3.225192000	-0.390785000
C	-1.336368000	-0.542347000	0.932731000
C	1.013669000	-0.132137000	-0.047192000
C	0.131745000	0.813595000	-0.506041000
H	0.291162000	1.826249000	-0.862320000
C	2.491878000	0.056127000	-0.060240000
C	3.122969000	1.028343000	-0.858319000
H	2.526910000	1.667499000	-1.514044000
C	4.512001000	1.171003000	-0.836528000
H	4.989274000	1.928645000	-1.464171000
C	5.294086000	0.341875000	-0.021830000
H	6.381704000	0.453210000	-0.008677000
C	4.675600000	-0.632963000	0.768885000
H	5.279463000	-1.285340000	1.405835000
C	3.285810000	-0.776341000	0.747578000
H	2.789439000	-1.533272000	1.357983000

TS_{rot}(INT1-INT2), G = -861.354625 (i = -59 cm-1)

O	-2.900357000	-1.786518000	0.451535000
O	-1.869959000	-0.724704000	2.099030000
O	0.945273000	1.665586000	-0.832350000
N	-1.238234000	-0.167594000	-0.073001000

C	-2.653959000	2.466738000	1.529422000
H	-3.547723000	2.874912000	2.026336000
H	-2.138954000	1.803768000	2.240701000
H	-1.978688000	3.305898000	1.297470000
C	-3.042439000	1.709966000	0.258111000
H	-3.556372000	2.386190000	-0.447483000
H	-3.766209000	0.910871000	0.487797000
C	-1.844388000	1.183460000	-0.487979000
H	-1.011094000	1.877363000	-0.642066000
C	-1.863419000	0.055824000	-1.447869000
H	-1.068611000	0.070365000	-2.197859000
C	-3.078577000	-0.792886000	-1.758820000
H	-4.016111000	-0.273359000	-1.510848000
H	-3.097799000	-1.025553000	-2.833001000
C	-2.980307000	-2.084028000	-0.971614000
H	-2.091028000	-2.670925000	-1.250659000
H	-3.873380000	-2.711526000	-1.075531000
C	-2.031472000	-0.918726000	0.932188000
C	1.159268000	0.539369000	-0.291050000
C	0.198816000	-0.385500000	0.104434000
H	0.417329000	-1.396084000	0.437960000
C	2.609126000	0.130710000	-0.082140000
C	3.033386000	-0.845756000	0.837915000
H	2.304535000	-1.354614000	1.472585000
C	4.389599000	-1.155791000	0.978501000
H	4.699291000	-1.912757000	1.704757000
C	5.350409000	-0.493430000	0.204938000
H	6.410800000	-0.735914000	0.317152000
C	4.941972000	0.489244000	-0.704057000
H	5.684661000	1.019000000	-1.307809000
C	3.586232000	0.799968000	-0.839150000
H	3.251852000	1.575638000	-1.531201000

3a, G = -861.397067

O	1.179366000	2.609991000	0.491485000
O	-0.182079000	1.614930000	1.935073000
O	-0.347531000	1.167003000	-0.284431000
N	1.540785000	-0.667583000	0.049771000
C	3.781952000	-2.826638000	1.013395000
H	4.713549000	-3.014100000	1.571140000
H	2.968962000	-2.700067000	1.747933000
H	3.559007000	-3.728820000	0.418709000
C	3.905563000	-1.589321000	0.122834000
H	4.730131000	-1.721685000	-0.599450000
H	4.155663000	-0.710439000	0.737419000
C	2.633825000	-1.322511000	-0.650742000
H	2.335601000	-2.141482000	-1.322042000
C	2.154211000	0.034028000	-1.080170000
H	1.546327000	0.023494000	-1.995341000
C	2.844815000	1.357049000	-0.841650000
H	3.446144000	1.333024000	0.079637000
H	3.535913000	1.548452000	-1.680436000
C	1.881395000	2.541928000	-0.773790000
H	1.159127000	2.527469000	-1.603516000
H	2.438823000	3.487411000	-0.812306000
C	0.199280000	1.770971000	0.808173000
C	-0.780898000	-0.160279000	-0.121104000
C	0.212229000	-1.071611000	0.017952000
H	0.001606000	-2.128596000	0.194376000
C	-2.229296000	-0.377136000	-0.128846000
C	-2.786212000	-1.668177000	-0.262948000
H	-2.134290000	-2.535005000	-0.391059000
C	-4.168114000	-1.852671000	-0.248777000

H	-4.576896000	-2.861490000	-0.352148000
C	-5.031512000	-0.756799000	-0.116025000
H	-6.114393000	-0.905063000	-0.111102000
C	-4.492112000	0.527701000	0.003307000
H	-5.153291000	1.392542000	0.105494000
C	-3.108004000	0.718087000	-0.003280000
H	-2.698254000	1.724315000	0.097305000

4a, G = -861.448979

O	-3.747147000	-1.362999000	0.207390000
O	-2.126082000	-2.509193000	1.189004000
O	0.450321000	1.173300000	-0.763720000
N	-1.531011000	-0.693969000	-0.066199000
C	-1.868679000	0.515944000	-0.834891000
H	-1.688786000	0.295257000	-1.901943000
C	-3.337364000	0.861900000	-0.646674000
H	-3.522682000	1.284760000	0.352493000
H	-3.645992000	1.605592000	-1.396107000
C	-4.143088000	-0.410145000	-0.795219000
H	-5.216795000	-0.243888000	-0.635263000
H	-4.003882000	-0.861850000	-1.793038000
C	-2.445617000	-1.574010000	0.483817000
C	-0.163613000	-0.961552000	0.085138000
C	0.784640000	-0.068426000	-0.285975000
C	-0.872564000	1.626464000	-0.448493000
H	-1.041014000	2.480588000	-1.122443000
H	0.080282000	-1.924870000	0.523551000
C	-0.962832000	2.101082000	1.005414000
H	-0.943714000	1.230026000	1.681035000
H	-1.943832000	2.582982000	1.142784000
C	0.149448000	3.078025000	1.382742000

H	0.017741000	3.440683000	2.414612000
H	0.157128000	3.956591000	0.715398000
H	1.139073000	2.601109000	1.316286000
C	2.238748000	-0.305908000	-0.211122000
C	3.132323000	0.767937000	-0.400551000
C	2.779539000	-1.584991000	0.041955000
C	4.514408000	0.572289000	-0.324435000
C	4.158619000	-1.773729000	0.123257000
C	5.036711000	-0.696809000	-0.059253000
H	2.732243000	1.761165000	-0.606801000
H	2.119338000	-2.445266000	0.168304000
H	5.186908000	1.421519000	-0.473637000
H	4.552862000	-2.773874000	0.322729000
H	6.117395000	-0.850026000	-0.000217000

INT3, G = -953.555890

O	-2.947871000	-0.858063000	1.435091000
O	-1.514697000	0.733063000	2.013132000
O	0.709187000	1.757389000	-0.143142000
N	-1.306305000	-0.151470000	-0.139106000
C	-2.168458000	-0.630992000	-1.304037000
H	-1.558585000	-1.231037000	-1.982816000
C	-3.500341000	-1.230274000	-0.902479000
H	-4.301112000	-0.477532000	-0.876808000
H	-3.784153000	-2.000677000	-1.632872000
C	-3.347962000	-1.868625000	0.464328000
H	-4.293568000	-2.266964000	0.850120000
H	-2.588542000	-2.665928000	0.466568000
C	-1.936246000	-0.043126000	1.213232000
C	0.111332000	-0.506431000	-0.103756000
C	1.058673000	0.566420000	-0.112345000

C	-1.830581000	0.804589000	-1.216013000
H	-0.998279000	1.140913000	-1.835901000
C	-2.802832000	1.886342000	-0.820864000
H	-3.547050000	1.505309000	-0.103666000
H	-3.369853000	2.116679000	-1.740045000
C	-2.132380000	3.147453000	-0.276977000
H	-2.893849000	3.907295000	-0.041377000
H	-1.434410000	3.572704000	-1.014057000
H	-1.553907000	2.925660000	0.629516000
C	2.533436000	0.244461000	-0.079416000
C	3.371670000	1.138510000	0.610095000
C	3.110521000	-0.848977000	-0.746608000
C	4.750225000	0.926823000	0.661392000
C	4.493897000	-1.053248000	-0.706843000
C	5.316079000	-0.172123000	0.002729000
H	2.921047000	2.002228000	1.103628000
H	2.486635000	-1.536969000	-1.319578000
H	5.388015000	1.622779000	1.213211000
H	4.930765000	-1.903143000	-1.238102000
H	6.396428000	-0.336922000	0.037170000
C	0.338065000	-1.879845000	0.072782000
N	0.454431000	-3.036994000	0.212396000

INT4, G = -953.561464

O	-2.285963000	-1.824999000	0.814172000
O	-1.396594000	-0.244454000	2.096188000
O	0.631010000	-1.658860000	0.105181000
N	-1.273786000	0.092469000	-0.206210000
C	-3.546085000	2.213982000	1.033625000
H	-4.520021000	2.361954000	1.524591000
H	-2.817560000	1.916838000	1.803073000
H	-3.221941000	3.180856000	0.616834000

C	-3.655762000	1.150812000	-0.061408000
H	-4.400813000	1.451819000	-0.817478000
H	-4.013758000	0.197171000	0.355395000
C	-2.362028000	0.965593000	-0.813346000
H	-1.924329000	1.898868000	-1.178541000
C	-1.948275000	-0.261884000	-1.529052000
H	-1.234031000	-0.125957000	-2.343781000
C	-2.775313000	-1.532542000	-1.547557000
H	-3.841519000	-1.314944000	-1.388268000
H	-2.673955000	-2.011519000	-2.531575000
C	-2.272495000	-2.484516000	-0.481378000
H	-1.241245000	-2.809798000	-0.672677000
H	-2.930052000	-3.353133000	-0.358798000
C	-1.629684000	-0.705640000	1.021569000
C	1.048908000	-0.489452000	-0.056429000
C	0.109995000	0.569524000	-0.199774000
C	2.527308000	-0.229183000	-0.054919000
C	3.128102000	0.836264000	-0.747483000
H	2.518561000	1.532035000	-1.326215000
C	4.515883000	1.003015000	-0.721316000
H	4.971577000	1.832374000	-1.268687000
C	5.319439000	0.110030000	-0.004376000
H	6.404195000	0.245133000	0.017680000
C	4.729914000	-0.960973000	0.678682000
H	5.353373000	-1.664549000	1.236995000
C	3.345440000	-1.133189000	0.646143000
H	2.873018000	-1.970024000	1.164352000
C	0.303379000	1.951426000	-0.078132000
N	0.427860000	3.113211000	-0.003265000

TS3, G = -953.542486 (i = -145 cm-1)

O	-3.180028000	-0.596186000	1.282207000
O	-1.216361000	-0.306254000	2.292434000
O	0.432285000	1.417973000	0.317804000
N	-1.247969000	-0.660192000	0.008592000
C	-2.082987000	-0.374830000	-1.234096000
H	-1.559985000	-0.844989000	-2.072507000
C	-3.536150000	-0.854976000	-1.112213000
H	-4.228264000	-0.021395000	-1.295995000
H	-3.737667000	-1.623191000	-1.871936000
C	-3.771105000	-1.441036000	0.268651000
H	-4.838544000	-1.500227000	0.515639000
H	-3.333160000	-2.448278000	0.356550000
C	-1.836317000	-0.495601000	1.282332000
C	0.146426000	-0.847123000	-0.092561000
C	0.967461000	0.304204000	0.138420000
C	-1.794869000	1.064220000	-1.125985000
H	-0.884211000	1.423226000	-1.609064000
C	-2.674566000	2.061904000	-0.505067000
H	-3.336176000	1.601576000	0.245998000
H	-3.361508000	2.318133000	-1.348164000
C	-1.994901000	3.323611000	0.019555000
H	-2.751013000	4.056111000	0.339502000
H	-1.367930000	3.790291000	-0.756253000
H	-1.347552000	3.077429000	0.871468000
C	2.465353000	0.210678000	0.094997000
C	3.185290000	1.350154000	-0.306990000
C	3.172969000	-0.941474000	0.478436000
C	4.579571000	1.328688000	-0.357796000
C	4.570395000	-0.958980000	0.435503000
C	5.276861000	0.171448000	0.011519000
H	2.630025000	2.250563000	-0.577665000
H	2.637680000	-1.823708000	0.833130000

H	5.126903000	2.217944000	-0.682056000
H	5.109378000	-1.859344000	0.742031000
H	6.369541000	0.154227000	-0.023297000
C	0.553355000	-2.049454000	-0.707701000
N	0.851484000	-3.054267000	-1.227016000

TS4, G = -953.553095 (i = -183 cm-1)

O	-1.964182000	-2.054571000	0.166313000
O	-1.246310000	-0.847252000	1.901467000
O	0.399146000	-1.394692000	0.173252000
N	-1.277031000	0.279765000	-0.240096000
C	-3.528798000	1.483918000	1.966798000
H	-4.412207000	1.279357000	2.591975000
H	-2.640975000	1.101546000	2.491054000
H	-3.431903000	2.577632000	1.866560000
C	-3.670861000	0.812901000	0.600154000
H	-4.569775000	1.187331000	0.080654000
H	-3.803450000	-0.272271000	0.715876000
C	-2.505698000	1.111736000	-0.314003000
H	-2.263373000	2.177423000	-0.392802000
C	-2.114670000	0.287801000	-1.493905000
H	-1.605401000	0.824504000	-2.299405000
C	-2.766774000	-1.030239000	-1.871593000
H	-3.812912000	-1.062659000	-1.532378000
H	-2.769277000	-1.129116000	-2.966590000
C	-1.999661000	-2.195716000	-1.261357000
H	-0.971699000	-2.254859000	-1.652615000
H	-2.505716000	-3.151326000	-1.452330000
C	-1.227723000	-1.068676000	0.718365000
C	0.961287000	-0.243645000	-0.037674000
C	0.071608000	0.804202000	-0.235456000

C	2.434545000	-0.160838000	0.006412000
C	3.155086000	0.842350000	-0.668263000
H	2.634121000	1.587725000	-1.270776000
C	4.548503000	0.878081000	-0.589613000
H	5.099443000	1.658719000	-1.120141000
C	5.237492000	-0.084419000	0.157294000
H	6.328532000	-0.052097000	0.217494000
C	4.527541000	-1.091937000	0.821278000
H	5.062144000	-1.846841000	1.403431000
C	3.135421000	-1.135374000	0.742620000
H	2.572625000	-1.916970000	1.255711000
C	0.301454000	2.183048000	-0.356342000
N	0.452469000	3.335215000	-0.470226000

TS4‘, G = -953.535200 (i = -408 cm-1)

C	0.128266000	0.607671000	0.046521000
N	-1.171117000	0.372329000	0.271940000
C	-2.218118000	-0.574623000	-1.640281000
C	-2.391972000	0.699760000	-1.081923000
H	-1.332317000	-0.733768000	-2.262091000
C	-3.032853000	-1.762741000	-1.280410000
C	-2.483661000	-2.358330000	0.017509000
O	-2.532189000	-1.399368000	1.097006000
C	-1.586709000	-0.478733000	1.326552000
O	-1.208375000	-0.249199000	2.446836000
H	-3.108642000	-3.195829000	0.358136000
H	-1.446085000	-2.695723000	-0.107481000
H	-4.095577000	-1.509170000	-1.141580000
H	-2.957649000	-2.536260000	-2.061326000
H	-1.823792000	1.504532000	-1.560009000
C	-3.658827000	1.181771000	-0.418764000

H	-4.094256000	0.388640000	0.206088000
H	-4.377535000	1.361678000	-1.238925000
C	1.086109000	-0.514582000	0.102910000
O	0.643453000	-1.660657000	0.200391000
C	-3.471456000	2.461730000	0.395997000
H	-4.438645000	2.817958000	0.783279000
H	-2.803545000	2.294754000	1.255097000
H	-3.034840000	3.267049000	-0.217452000
C	0.463069000	1.896901000	-0.456581000
N	0.688732000	2.947501000	-0.907763000
C	2.557788000	-0.271843000	0.026471000
C	3.170080000	0.884182000	0.542472000
C	3.359551000	-1.280589000	-0.540271000
C	4.558248000	1.031891000	0.477057000
C	4.742593000	-1.122498000	-0.619072000
C	5.344938000	0.035533000	-0.110059000
H	2.573147000	1.661576000	1.022024000
H	2.878665000	-2.184587000	-0.919750000
H	5.026574000	1.928098000	0.891624000
H	5.355902000	-1.904759000	-1.073705000
H	6.429894000	0.157784000	-0.165794000

TS$_{rot}$(INT3-INT4), G = -953.541306 (i = -55 cm-1)

O	-2.718808000	-0.757866000	1.768866000
O	-2.346679000	1.405088000	1.458604000
O	0.869444000	-1.374593000	-1.468023000
N	-1.326636000	-0.078627000	-0.034630000
C	-2.879144000	2.534266000	-1.560007000
H	-3.802914000	3.111380000	-1.719406000
H	-2.438599000	2.850038000	-0.602871000
H	-2.172884000	2.794194000	-2.365203000

C	-3.176787000	1.034270000	-1.557020000
H	-3.621907000	0.730670000	-2.520864000
H	-3.924845000	0.783680000	-0.788968000
C	-1.935132000	0.193838000	-1.411488000
H	-1.124780000	0.459212000	-2.097425000
C	-1.864031000	-1.203611000	-0.918889000
H	-1.022134000	-1.774811000	-1.312918000
C	-2.992272000	-1.990104000	-0.290688000
H	-3.974365000	-1.518452000	-0.444194000
H	-3.021240000	-2.994816000	-0.735288000
C	-2.708624000	-2.097659000	1.196195000
H	-1.731680000	-2.560934000	1.404577000
H	-3.491055000	-2.639309000	1.740591000
C	-2.189425000	0.266881000	1.139791000
C	1.112002000	-0.547429000	-0.564134000
C	0.126483000	0.103298000	0.237742000
C	2.567015000	-0.236832000	-0.294571000
C	3.074822000	1.069249000	-0.210484000
H	2.400834000	1.924165000	-0.290502000
C	4.446572000	1.284891000	-0.041610000
H	4.830686000	2.306961000	0.013515000
C	5.323726000	0.199724000	0.052623000
H	6.394738000	0.370239000	0.191447000
C	4.825871000	-1.106096000	-0.040386000
H	5.507404000	-1.958494000	0.026665000
C	3.459139000	-1.321200000	-0.226331000
H	3.066672000	-2.336053000	-0.323652000
C	0.448544000	0.981841000	1.286714000
N	0.735472000	1.689962000	2.172370000

3c, G = -953.572534

O	-1.225062000	-2.802994000	0.481993000
O	0.053158000	-1.767567000	1.976089000
O	0.363654000	-1.392395000	-0.241126000
N	-1.551629000	0.395483000	0.029493000
C	-3.824306000	2.527065000	0.969747000
H	-4.771366000	2.701730000	1.504852000
H	-3.030296000	2.389971000	1.722363000
H	-3.585650000	3.439319000	0.397683000
C	-3.922237000	1.305267000	0.054757000
H	-4.728769000	1.446456000	-0.685719000
H	-4.180621000	0.413222000	0.646145000
C	-2.631750000	1.064312000	-0.693432000
H	-2.316667000	1.908349000	-1.323319000
C	-2.125633000	-0.266752000	-1.153829000
H	-1.488350000	-0.222875000	-2.047210000
C	-2.814477000	-1.598683000	-0.970183000
H	-3.486522000	-1.584383000	-0.099354000
H	-3.434598000	-1.794182000	-1.861494000
C	-1.846374000	-2.770445000	-0.829230000
H	-1.072040000	-2.759998000	-1.610192000
H	-2.387603000	-3.723935000	-0.883844000
C	-0.272102000	-1.961000000	0.839753000
C	0.794027000	-0.080766000	-0.116335000
C	-0.215890000	0.833852000	0.012022000
C	2.244219000	0.119376000	-0.155731000
C	2.828339000	1.292385000	-0.676011000
H	2.200734000	2.077809000	-1.099606000
C	4.215002000	1.447548000	-0.679727000
H	4.653413000	2.361242000	-1.088969000
C	5.041820000	0.434263000	-0.181013000
H	6.127755000	0.558093000	-0.189662000
C	4.472039000	-0.742246000	0.319553000

H	5.111053000	-1.539391000	0.707974000
C	3.086707000	-0.903248000	0.329004000
H	2.646472000	-1.816518000	0.732280000
C	0.008234000	2.223710000	0.259039000
N	0.120678000	3.361791000	0.466524000

4c, G = -953.620596

O	-3.727374000	-1.105931000	0.266971000
O	-2.164520000	-1.800104000	1.681544000
O	0.409390000	1.377127000	-0.641417000
N	-1.507822000	-0.619966000	-0.172520000
C	-1.795837000	0.513872000	-1.067398000
H	-1.389988000	0.249765000	-2.058018000
C	-3.298873000	0.752994000	-1.191172000
H	-3.666935000	1.432950000	-0.409150000
H	-3.521003000	1.211147000	-2.165559000
C	-4.011581000	-0.573133000	-1.039927000
H	-5.103118000	-0.467872000	-1.087153000
H	-3.691866000	-1.299503000	-1.806941000
C	-2.446284000	-1.202609000	0.666724000
C	-0.119986000	-0.839799000	0.045772000
C	0.791076000	0.142516000	-0.263126000
C	-0.990515000	1.721870000	-0.558045000
H	-1.109262000	2.554107000	-1.268375000
C	-1.325312000	2.189558000	0.858794000
H	-1.177868000	1.352412000	1.561201000
H	-2.395959000	2.443654000	0.894314000
C	-0.496302000	3.395864000	1.297418000
H	-0.778861000	3.714369000	2.313071000
H	-0.648163000	4.253210000	0.620469000
H	0.579412000	3.162023000	1.306075000

C	2.263411000	-0.001211000	-0.234557000
C	3.034916000	1.068014000	0.262023000
C	2.918004000	-1.147567000	-0.720193000
C	4.426568000	0.976446000	0.301186000
C	4.311603000	-1.232653000	-0.681331000
C	5.069504000	-0.175493000	-0.167149000
H	2.534370000	1.966560000	0.626670000
H	2.341787000	-1.968116000	-1.149246000
H	5.012782000	1.808308000	0.700011000
H	4.807075000	-2.127621000	-1.066030000
H	6.160015000	-0.245512000	-0.137988000
C	0.298850000	-2.128878000	0.492339000
N	0.669559000	-3.175369000	0.838479000

5c, G = -953.576426

C	0.575864000	0.674007000	-0.381319000
N	-0.638312000	0.542169000	-0.028645000
C	-3.727146000	0.706938000	-1.174442000
C	-4.372483000	1.067534000	-0.054160000
H	-3.220683000	1.492537000	-1.748992000
C	-3.562019000	-0.688498000	-1.714907000
C	-2.161201000	-1.248748000	-1.483045000
O	-1.924666000	-1.399766000	-0.064278000
C	-1.136594000	-0.600615000	0.635062000
O	-0.949682000	-0.751708000	1.817933000
H	-2.065035000	-2.260760000	-1.901430000
H	-1.387303000	-0.617886000	-1.942310000
H	-4.290881000	-1.384254000	-1.272483000
H	-3.730329000	-0.695661000	-2.806188000
H	-4.364873000	2.134035000	0.209115000
C	-5.092326000	0.185147000	0.929182000

H	-5.125764000	-0.857682000	0.577212000
H	-6.142568000	0.524494000	1.004792000
C	1.584506000	-0.495633000	-0.352646000
O	1.123118000	-1.587044000	-0.627238000
C	-4.460202000	0.234341000	2.328096000
H	-5.042070000	-0.368015000	3.045175000
H	-3.429646000	-0.154787000	2.316635000
H	-4.422877000	1.267657000	2.713341000
C	0.973290000	1.943008000	-0.958716000
N	1.302753000	2.940273000	-1.449307000
C	3.002114000	-0.259825000	-0.011416000
C	3.429765000	0.892580000	0.675859000
C	3.935501000	-1.264463000	-0.338583000
C	4.773672000	1.037728000	1.023349000
C	5.277133000	-1.106517000	-0.003043000
C	5.696819000	0.044476000	0.679098000
H	2.719558000	1.668652000	0.967322000
H	3.589741000	-2.158428000	-0.861443000
H	5.100323000	1.927852000	1.565842000
H	6.000992000	-1.880712000	-0.268264000
H	6.750017000	0.165257000	0.945792000

INT5, G = -897.496004

O	-1.042416000	-1.828351000	1.262548000
O	-0.707213000	0.179231000	2.130960000
O	-0.491398000	2.747576000	-0.034884000
N	-0.349141000	-0.033884000	-0.157677000
C	-0.700915000	-0.869954000	-1.383952000
H	0.081147000	-0.747838000	-2.134810000
C	-1.191057000	-2.283965000	-1.138185000
H	-2.286940000	-2.332136000	-1.210084000

H	-0.780638000	-2.945667000	-1.913924000
C	-0.732464000	-2.787741000	0.215344000
H	-1.261927000	-3.700794000	0.512395000
H	0.348951000	-2.967265000	0.239277000
C	-0.706085000	-0.554642000	1.190574000
C	0.840581000	0.816500000	-0.186661000
C	0.637454000	2.233009000	-0.088343000
C	-1.522756000	0.319675000	-1.087693000
H	-1.282559000	1.229699000	-1.636739000
C	-2.931000000	0.263038000	-0.551625000
H	-3.082091000	-0.633078000	0.070164000
H	-3.573853000	0.120886000	-1.438300000
C	-3.351361000	1.517847000	0.213980000
H	-4.396724000	1.423592000	0.547844000
H	-3.264430000	2.415331000	-0.415818000
H	-2.709992000	1.677328000	1.091350000
C	1.864458000	3.132795000	-0.068502000
H	1.520578000	4.176538000	-0.036140000
H	2.497202000	2.918254000	0.806551000
H	2.500798000	2.968423000	-0.950691000
C	2.098525000	0.132408000	-0.126411000
O	3.220415000	0.619471000	-0.149564000
O	1.930805000	-1.233915000	-0.025585000
C	3.123685000	-2.011783000	0.015615000
H	3.733568000	-1.765903000	0.899493000
H	2.808544000	-3.063273000	0.066297000
H	3.736442000	-1.852130000	-0.885770000

INT6, G = -953.572534

O	-1.225062000	-2.802994000	0.481993000
O	0.053158000	-1.767567000	1.976089000

O	0.363654000	-1.392395000	-0.241126000
N	-1.551629000	0.395483000	0.029493000
C	-3.824306000	2.527065000	0.969747000
H	-4.771366000	2.701730000	1.504852000
H	-3.030296000	2.389971000	1.722363000
H	-3.585650000	3.439319000	0.397683000
C	-3.922237000	1.305267000	0.054757000
H	-4.728769000	1.446456000	-0.685719000
H	-4.180621000	0.413222000	0.646145000
C	-2.631750000	1.064312000	-0.693432000
H	-2.316667000	1.908349000	-1.323319000
C	-2.125633000	-0.266752000	-1.153829000
H	-1.488350000	-0.222875000	-2.047210000
C	-2.814477000	-1.598683000	-0.970183000
H	-3.486522000	-1.584383000	-0.099354000
H	-3.434598000	-1.794182000	-1.861494000
C	-1.846374000	-2.770445000	-0.829230000
H	-1.072040000	-2.759998000	-1.610192000
H	-2.387603000	-3.723935000	-0.883844000
C	-0.272102000	-1.961000000	0.839753000
C	0.794027000	-0.080766000	-0.116335000
C	-0.215890000	0.833852000	0.012022000
C	2.244219000	0.119376000	-0.155731000
C	2.828339000	1.292385000	-0.676011000
H	2.200734000	2.077809000	-1.099606000
C	4.215002000	1.447548000	-0.679727000
H	4.653413000	2.361242000	-1.088969000
C	5.041820000	0.434263000	-0.181013000
H	6.127755000	0.558093000	-0.189662000
C	4.472039000	-0.742246000	0.319553000
H	5.111053000	-1.539391000	0.707974000
C	3.086707000	-0.903248000	0.329004000

H	2.646472000	-1.816518000	0.732280000
C	0.008234000	2.223710000	0.259039000
N	0.120678000	3.361791000	0.466524000

TS5, G = -897.478147 (i = -196 cm-1)

O	-1.332595000	-1.808971000	1.320667000
O	-0.600074000	0.022706000	2.355315000
O	-0.731822000	2.333507000	0.056230000
N	-0.091140000	-0.269021000	0.122611000
C	-0.649249000	-0.818767000	-1.166119000
H	0.143212000	-0.715728000	-1.912530000
C	-1.151290000	-2.266774000	-1.052184000
H	-2.226632000	-2.327953000	-1.270486000
H	-0.629712000	-2.899462000	-1.784317000
C	-0.874407000	-2.775439000	0.349253000
H	-1.416264000	-3.703914000	0.569996000
H	0.203583000	-2.943703000	0.502297000
C	-0.678096000	-0.627463000	1.346711000
C	0.925976000	0.709606000	0.091739000
C	0.490849000	2.065480000	0.100994000
C	-1.632665000	0.280681000	-1.230891000
H	-1.356326000	1.172812000	-1.793826000
C	-3.006149000	0.202083000	-0.712056000
H	-3.092333000	-0.553232000	0.085214000
H	-3.550848000	-0.250196000	-1.575667000
C	-3.656937000	1.525088000	-0.318559000
H	-4.718647000	1.367344000	-0.075770000
H	-3.594783000	2.260671000	-1.135812000
H	-3.145164000	1.950602000	0.554415000
C	1.496818000	3.198249000	0.102825000
H	0.957420000	4.152656000	0.181530000

H	2.209963000	3.094388000	0.933679000
H	2.098378000	3.184374000	-0.819334000
C	2.278677000	0.255182000	-0.120426000
O	3.287929000	0.943030000	-0.193746000
O	2.342342000	-1.110415000	-0.241034000
C	3.640828000	-1.661923000	-0.432960000
H	4.307291000	-1.424029000	0.412129000
H	3.507625000	-2.750342000	-0.501654000
H	4.108843000	-1.286011000	-1.357562000

TS6, G = -897.487520 (i = -160 cm-1)

O	2.507014000	-1.018156000	0.071406000
O	1.477982000	-0.633205000	-1.869883000
O	0.393976000	-2.330404000	-0.351907000
N	0.325775000	0.085423000	0.092000000
C	1.573096000	2.584566000	-1.903761000
H	2.468387000	3.043164000	-2.352643000
H	1.276867000	1.728107000	-2.526203000
H	0.762519000	3.331675000	-1.929229000
C	1.859625000	2.132390000	-0.471590000
H	2.153164000	2.998860000	0.146972000
H	2.706978000	1.433870000	-0.444765000
C	0.642763000	1.550021000	0.209147000
H	-0.258975000	2.152361000	0.105590000
C	0.685776000	0.692945000	1.425734000
H	-0.201324000	0.747940000	2.061758000
C	1.962365000	0.199056000	2.082442000
H	2.779220000	0.922830000	1.939389000
H	1.796377000	0.091418000	3.163942000
C	2.365212000	-1.145295000	1.493907000
H	1.622366000	-1.927136000	1.717079000

H	3.346372000	-1.471833000	1.863025000
C	1.412928000	-0.794727000	-0.680215000
C	-0.811077000	-1.896916000	-0.332211000
C	-0.983719000	-0.524948000	-0.134817000
C	-1.926873000	-2.880112000	-0.531881000
H	-2.453757000	-2.670092000	-1.475568000
H	-1.507216000	-3.894982000	-0.563740000
H	-2.678591000	-2.799153000	0.265995000
C	-2.266705000	0.123713000	0.001404000
O	-3.341992000	-0.408017000	-0.227576000
O	-2.196363000	1.406258000	0.454138000
C	-3.440546000	2.086638000	0.630675000
H	-4.071962000	1.570011000	1.370085000
H	-3.188671000	3.092909000	0.990498000
H	-3.994199000	2.156282000	-0.318612000

TS6‘, G = -897.471166 (i = -411 cm-1)

C	0.920243000	-0.689280000	0.049112000
N	-0.186361000	0.033291000	0.281067000
C	-1.453650000	0.343112000	-1.687291000
C	-0.749452000	1.287961000	-0.924558000
H	-0.870902000	-0.292383000	-2.360385000
C	-2.885149000	0.004063000	-1.486503000
C	-2.994426000	-0.980017000	-0.320078000
O	-2.457373000	-0.417994000	0.894318000
C	-1.155813000	-0.405052000	1.219697000
O	-0.815754000	-0.588216000	2.361730000
H	-4.047783000	-1.193223000	-0.087713000
H	-2.464829000	-1.916381000	-0.539890000
H	-3.495575000	0.894516000	-1.266966000
H	-3.298410000	-0.488622000	-2.380952000

H	0.241870000	1.555823000	-1.295196000
C	-1.410897000	2.401237000	-0.145395000
H	-2.288475000	2.020319000	0.396514000
H	-1.801256000	3.109592000	-0.898909000
C	2.205197000	-0.001274000	-0.158841000
O	3.258628000	-0.538779000	-0.451643000
C	0.774383000	-2.154838000	-0.042872000
O	-0.355117000	-2.643856000	0.029955000
C	1.979279000	-3.048346000	-0.201173000
H	2.717850000	-2.855055000	0.591128000
H	1.646208000	-4.094800000	-0.166367000
H	2.493881000	-2.842631000	-1.151763000
O	2.109166000	1.334961000	0.019575000
C	3.310098000	2.088216000	-0.155207000
H	3.702840000	1.978956000	-1.178570000
H	3.043960000	3.135980000	0.034933000
H	4.084755000	1.763228000	0.556593000
C	-0.471012000	3.130861000	0.813944000
H	-1.008763000	3.936463000	1.338438000
H	-0.058522000	2.444047000	1.567587000
H	0.378467000	3.582340000	0.277572000

TS_{rot}(INT5-INT6), G = -897.464750 (i = -38 cm-1)

O	0.970042000	0.307910000	-2.153821000
O	1.271164000	1.885927000	-0.616406000
O	-0.737437000	-2.701798000	1.010189000
N	0.459004000	-0.237898000	0.079674000
C	1.877509000	1.636917000	2.501783000
H	2.669759000	2.326336000	2.832871000
H	1.147570000	2.208648000	1.910139000
H	1.366538000	1.251580000	3.399438000

C	2.464189000	0.494662000	1.672367000
H	3.176855000	-0.090309000	2.280643000
H	3.032279000	0.879601000	0.814522000
C	1.418307000	-0.499044000	1.238730000
H	0.834295000	-0.924731000	2.060208000
C	1.469404000	-1.402755000	0.064865000
H	0.935663000	-2.340262000	0.218311000
C	2.386714000	-1.362112000	-1.132593000
H	3.188980000	-0.612922000	-1.046237000
H	2.854122000	-2.348068000	-1.266436000
C	1.504087000	-1.039981000	-2.334277000
H	0.665190000	-1.746521000	-2.430424000
H	2.062881000	-1.005325000	-3.278090000
C	0.925188000	0.789330000	-0.921275000
C	-1.479183000	-1.796250000	0.571852000
C	-1.012760000	-0.514982000	0.118499000
C	-2.974720000	-2.089246000	0.559012000
H	-3.409800000	-1.971130000	-0.443103000
H	-3.100295000	-3.123550000	0.910014000
H	-3.530513000	-1.403240000	1.215227000
C	-1.925007000	0.587981000	-0.100357000
O	-3.135505000	0.510897000	-0.264696000
O	-1.308597000	1.800891000	-0.100062000
C	-2.102908000	2.933144000	-0.434684000
H	-2.884290000	3.110837000	0.321523000
H	-1.415612000	3.789415000	-0.465898000
H	-2.588893000	2.808327000	-1.415592000

4e, G = -897.558269

O	0.052377000	-2.760382000	0.540028000
O	1.080085000	-1.200596000	1.741203000

O	-1.535162000	1.661709000	-0.766058000
N	0.042020000	-0.574363000	-0.209840000
C	-1.179615000	-0.711963000	-1.016534000
H	-0.901784000	-0.476011000	-2.057243000
C	-1.721594000	-2.140077000	-0.954462000
H	-2.434839000	-2.267255000	-0.127176000
H	-2.246341000	-2.383389000	-1.889585000
C	-0.559185000	-3.082725000	-0.721126000
H	-0.881065000	-4.129250000	-0.639284000
H	0.195779000	-3.005738000	-1.523345000
C	0.424126000	-1.483295000	0.761133000
C	0.577514000	0.741045000	-0.170383000
C	-0.221259000	1.803397000	-0.481385000
C	-2.162375000	0.380692000	-0.554231000
H	-3.034675000	0.385889000	-1.226490000
C	-2.629306000	0.271716000	0.898767000
H	-1.747909000	0.234967000	1.560558000
H	-3.158973000	-0.685953000	1.022607000
C	-3.545051000	1.422209000	1.314318000
H	-3.871878000	1.303996000	2.359521000
H	-4.447986000	1.464847000	0.681865000
H	-3.030731000	2.391566000	1.227258000
C	0.199257000	3.231058000	-0.621462000
H	-0.261683000	3.652105000	-1.529198000
H	-0.181291000	3.810760000	0.236869000
H	1.286048000	3.350354000	-0.658173000
C	2.036288000	0.883204000	0.054477000
O	2.587100000	1.847091000	0.547149000
O	2.708298000	-0.195309000	-0.387180000
C	4.100062000	-0.250318000	-0.072571000
H	4.252875000	-0.233608000	1.018183000
H	4.470865000	-1.197272000	-0.485995000

H	4.644688000	0.594783000	-0.521885000

3e, G = -897.500278

O	2.762020000	-0.631617000	0.304281000
O	1.998916000	-0.863016000	-1.772766000
O	1.003619000	-2.020899000	-0.095210000
N	0.151457000	0.400535000	0.145947000
C	0.842953000	2.387628000	-2.266745000
H	1.595482000	2.894376000	-2.892689000
H	0.807757000	1.330024000	-2.572195000
H	-0.137602000	2.843523000	-2.486132000
C	1.192683000	2.497338000	-0.781511000
H	1.281408000	3.557633000	-0.484385000
H	2.171676000	2.027087000	-0.601802000
C	0.142519000	1.842773000	0.090226000
H	-0.843292000	2.320137000	0.053139000
C	0.436769000	1.119867000	1.381738000
H	-0.388173000	1.140546000	2.104885000
C	1.828984000	0.917230000	1.969551000
H	2.537500000	1.671584000	1.592330000
H	1.784141000	1.045596000	3.062963000
C	2.414872000	-0.468843000	1.699009000
H	1.730157000	-1.270916000	2.011623000
H	3.363980000	-0.594156000	2.238376000
C	1.881824000	-1.057347000	-0.596265000
C	-0.348479000	-1.843992000	-0.195108000
C	-0.843131000	-0.578502000	-0.062400000
C	-1.066974000	-3.136880000	-0.352615000
H	-0.900277000	-3.520565000	-1.374316000
H	-0.641159000	-3.877009000	0.344123000
H	-2.143528000	-3.033775000	-0.188950000

C	-2.298419000	-0.297427000	-0.067628000
O	-3.165972000	-1.000190000	-0.545822000
O	-2.572615000	0.864569000	0.559165000
C	-3.950020000	1.250371000	0.621782000
H	-4.369429000	1.374283000	-0.388722000
H	-4.543414000	0.497373000	1.163033000
H	-3.974659000	2.206445000	1.159700000

5e, G = -897.516431

C	1.572981000	-0.206047000	0.191744000
N	0.321382000	-0.139382000	0.382979000
C	-2.157768000	1.091930000	-1.255687000
C	-2.934045000	1.446261000	-0.219777000
H	-1.325773000	1.755717000	-1.522140000
C	-2.253964000	-0.174309000	-2.064048000
C	-1.166917000	-1.188190000	-1.710055000
O	-1.318850000	-1.626037000	-0.344005000
C	-0.541855000	-1.212041000	0.651280000
O	-0.685030000	-1.622139000	1.779111000
H	-1.269091000	-2.097979000	-2.319156000
H	-0.160509000	-0.781155000	-1.881168000
H	-3.234122000	-0.659311000	-1.940481000
H	-2.139923000	0.051540000	-3.138966000
H	-2.697941000	2.392631000	0.285621000
C	-4.085475000	0.686024000	0.379824000
H	-4.305599000	-0.223018000	-0.201055000
H	-4.992184000	1.318082000	0.328981000
C	2.341586000	1.084899000	-0.016255000
O	3.426110000	1.120309000	-0.553498000
C	2.298404000	-1.559491000	0.067293000
O	1.621228000	-2.510700000	-0.262086000

C	3.757883000	-1.653222000	0.388364000
H	3.988086000	-1.108308000	1.318114000
H	4.043112000	-2.709950000	0.476151000
H	4.336793000	-1.167150000	-0.412204000
O	1.674742000	2.144814000	0.417514000
C	2.296585000	3.424319000	0.213420000
H	2.466404000	3.604926000	-0.858923000
H	1.598661000	4.166666000	0.619002000
H	3.259009000	3.474762000	0.745044000
C	-3.835024000	0.306491000	1.847069000
H	-4.716676000	-0.194836000	2.279695000
H	-2.975452000	-0.375790000	1.944722000
H	-3.624430000	1.199126000	2.460591000

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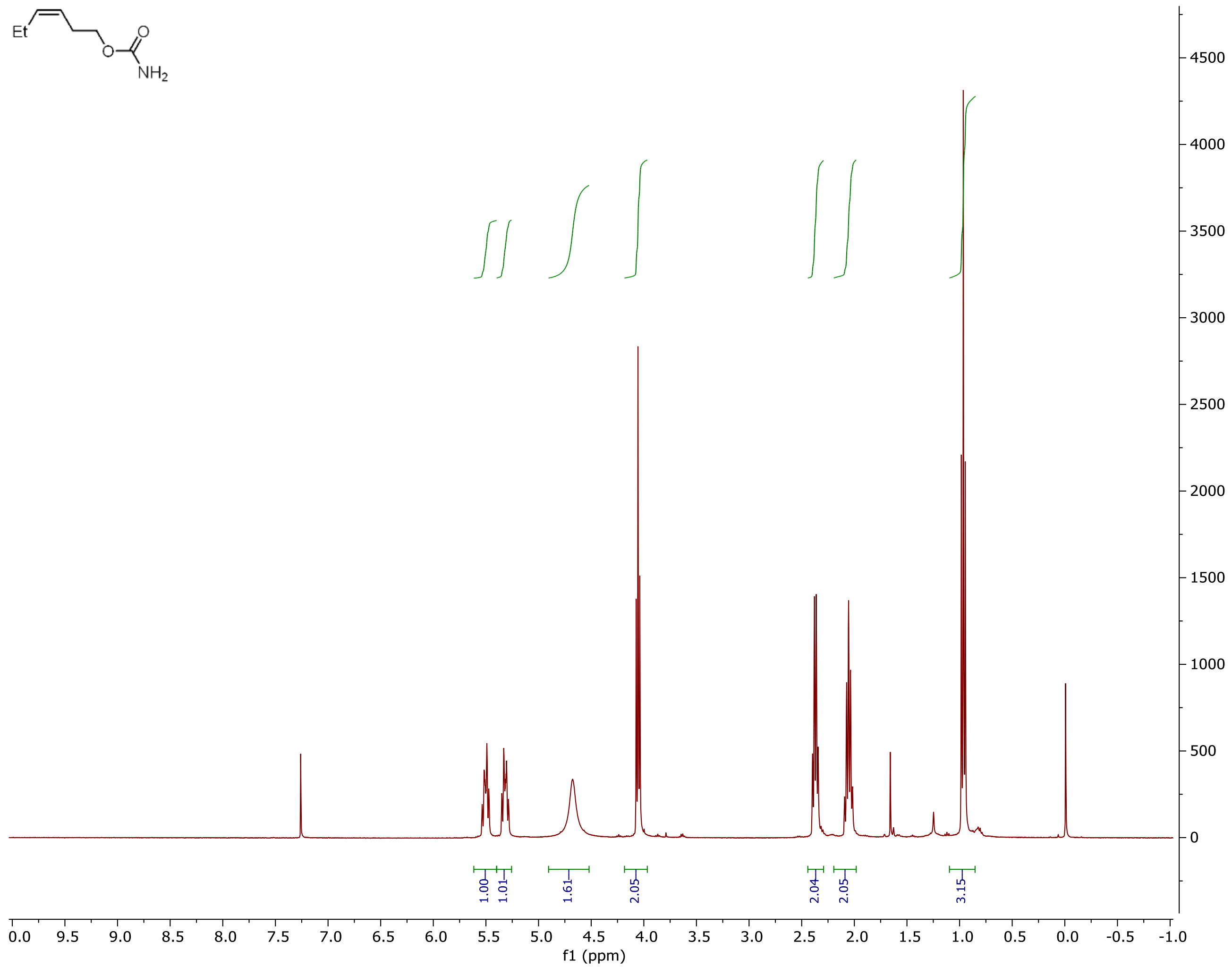
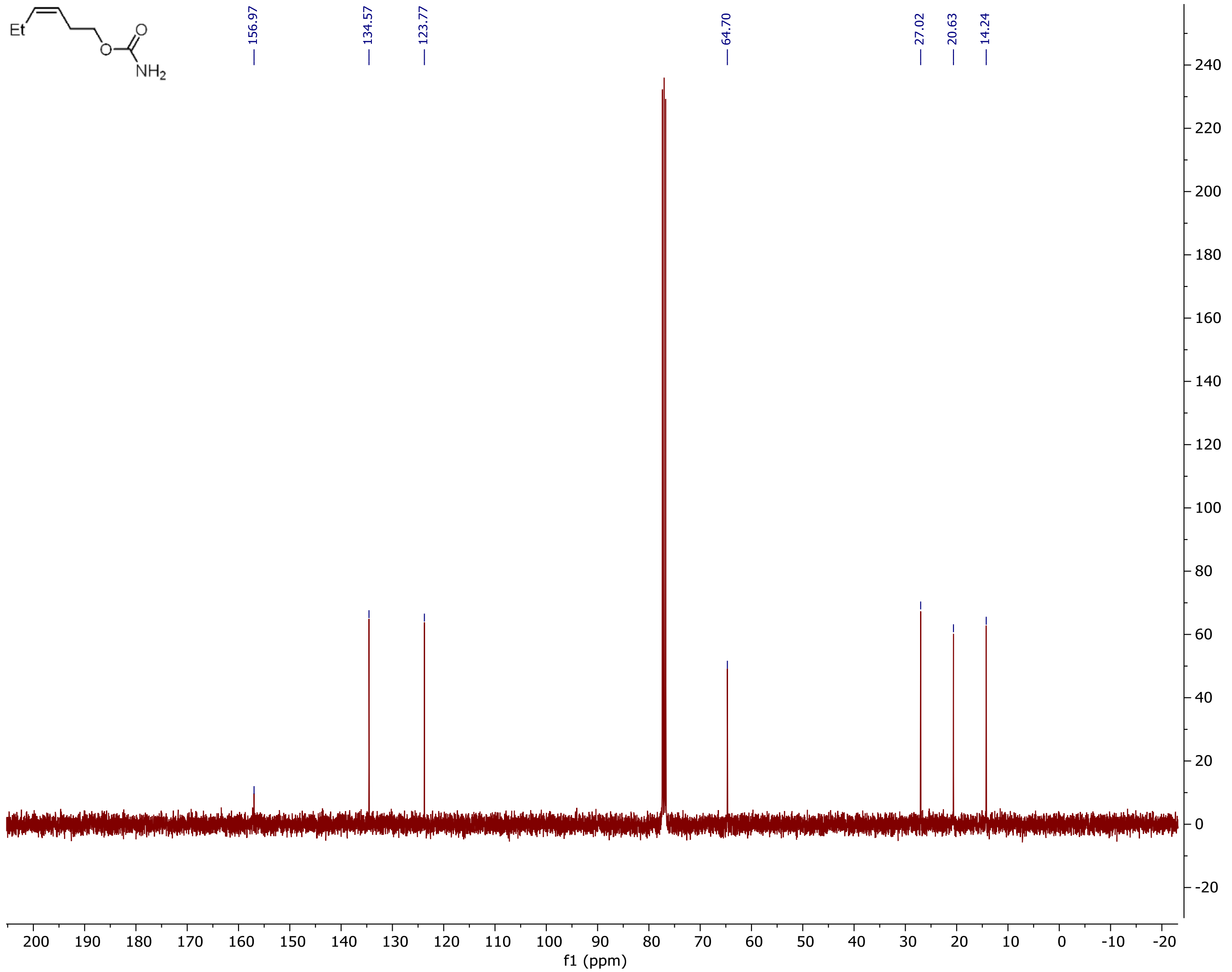
XIII. NMR Spectra

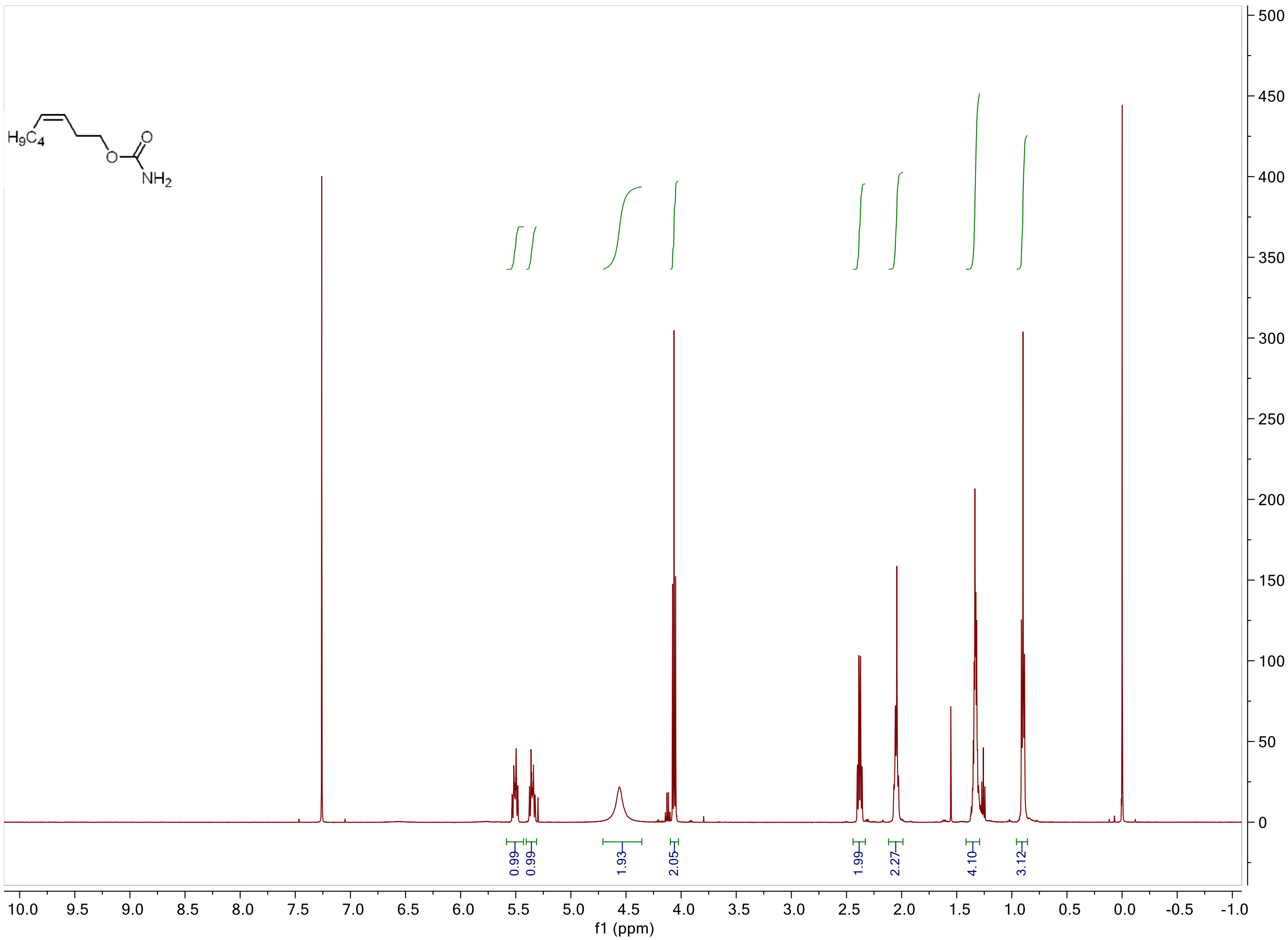
Precursor to compound **1.** ^{1}H NMR (500 MHz, $CDCl_3$)



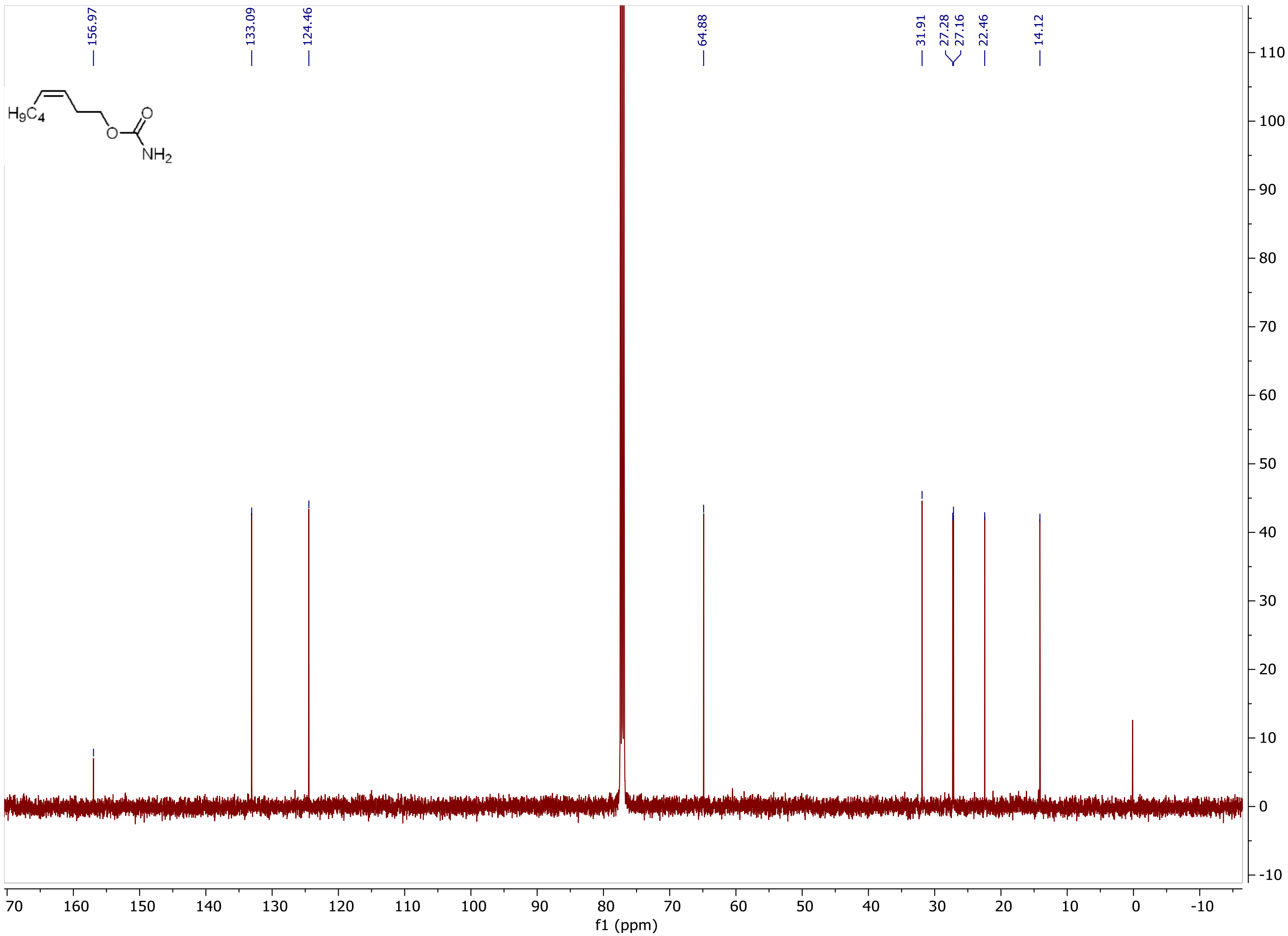
Precursor to compound **1.** ^{13}C NMR (126 MHz, $CDCl_3$)



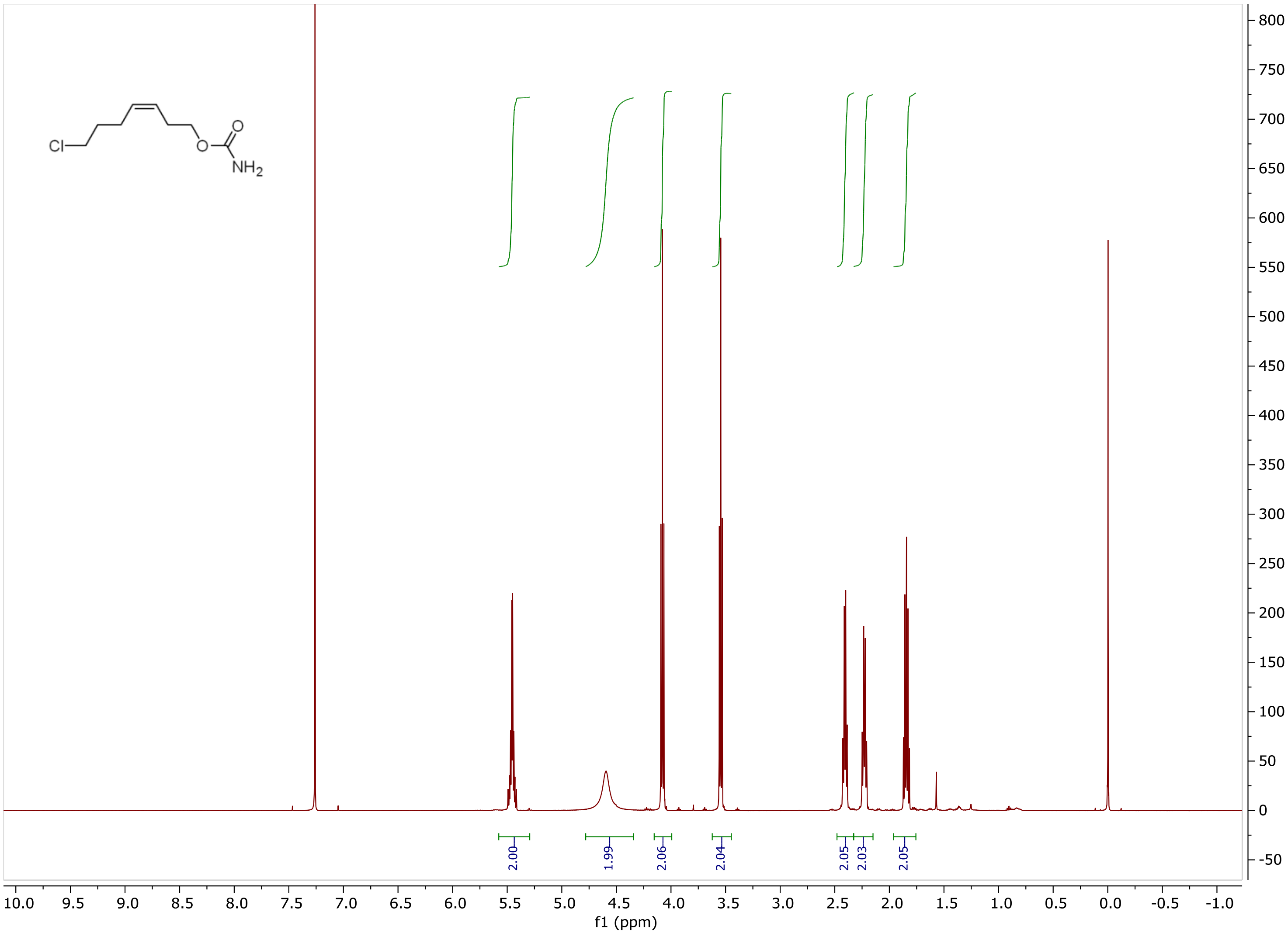
Precursor to compound **12.** ^{1}H NMR (500 MHz, $CDCl_3$)



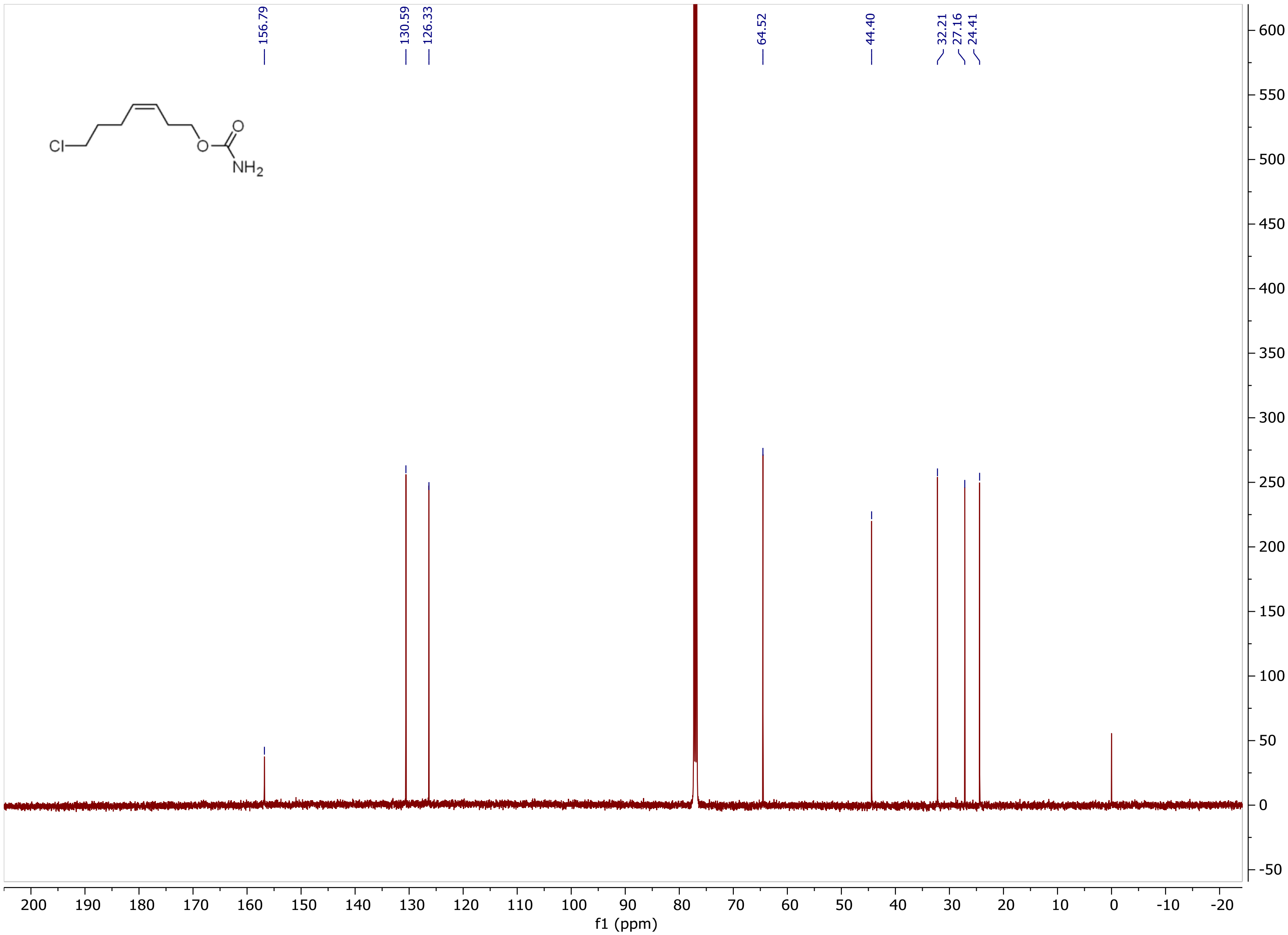
Precursor to compound **12.** ^{13}C NMR (126 MHz, $CDCl_3$)



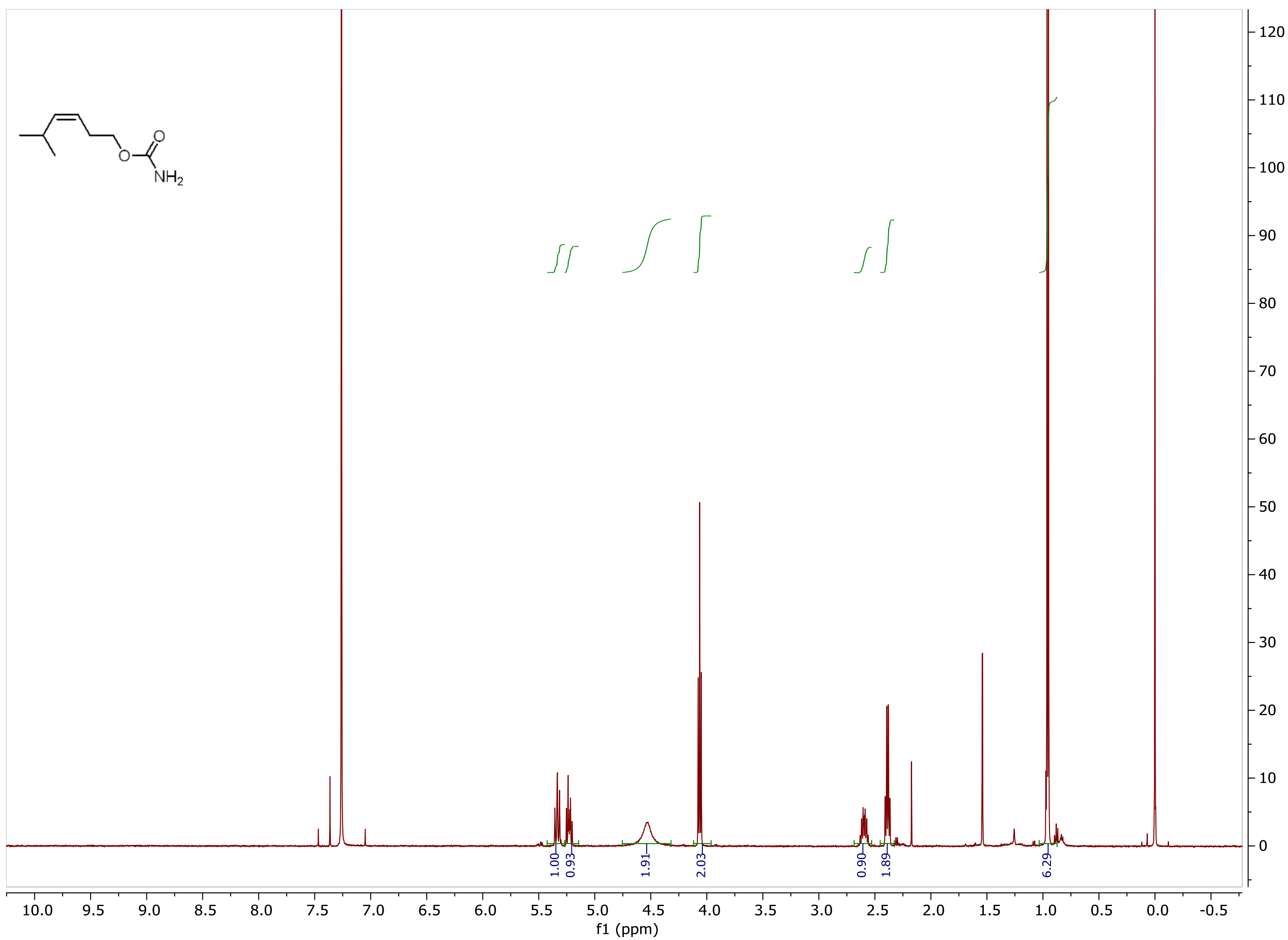
Precursor to compound **13.** ^{1}H NMR (500 MHz, $CDCl_3$)



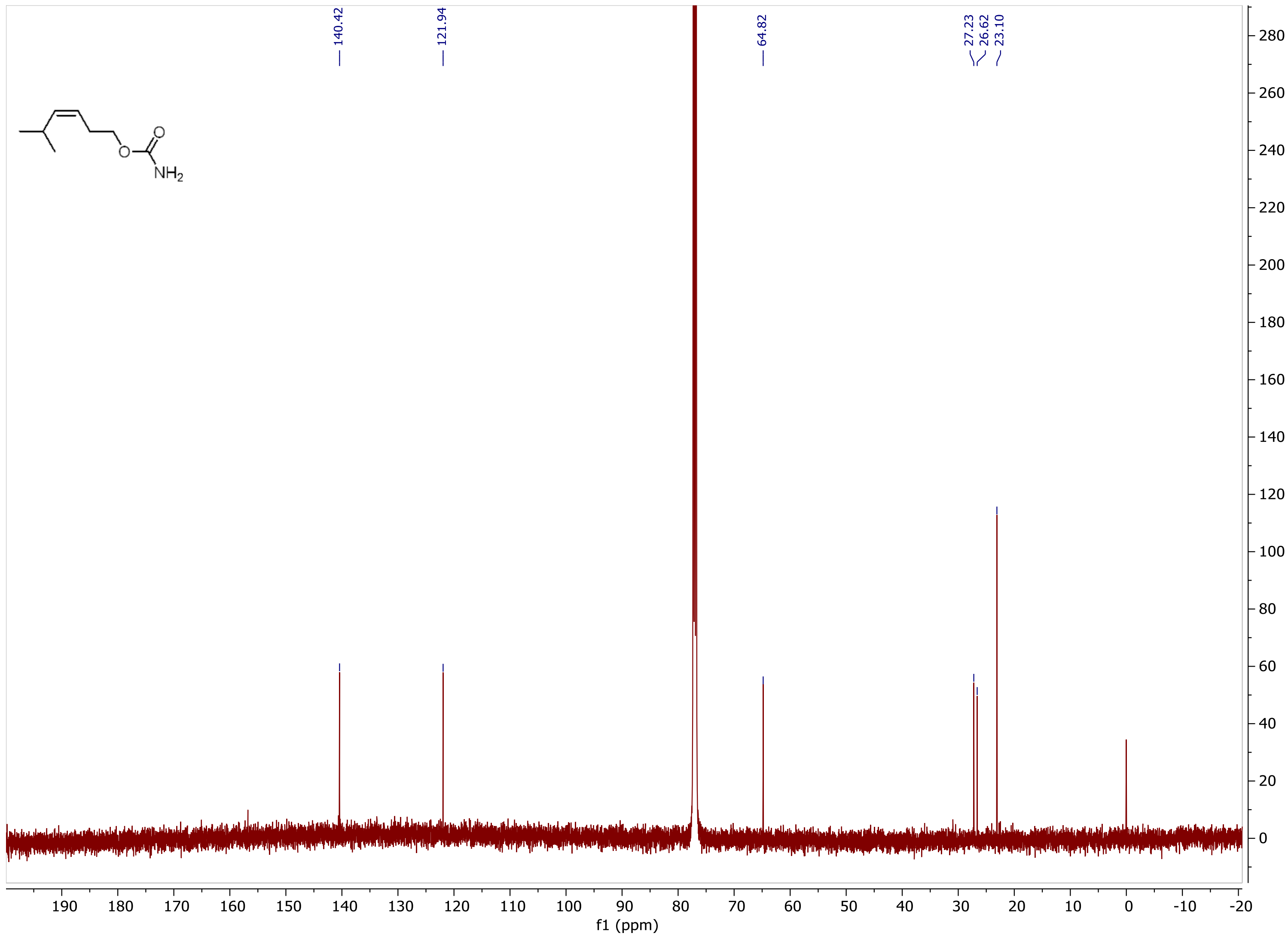
Precursor to compound **13.** ^{13}C NMR (126 MHz, $CDCl_3$)



Precursor to compound **14.** ^{1}H NMR (500 MHz, $CDCl_3$)



Precursor to compound **14.** ^{13}C NMR (126 MHz, $CDCl_3$)



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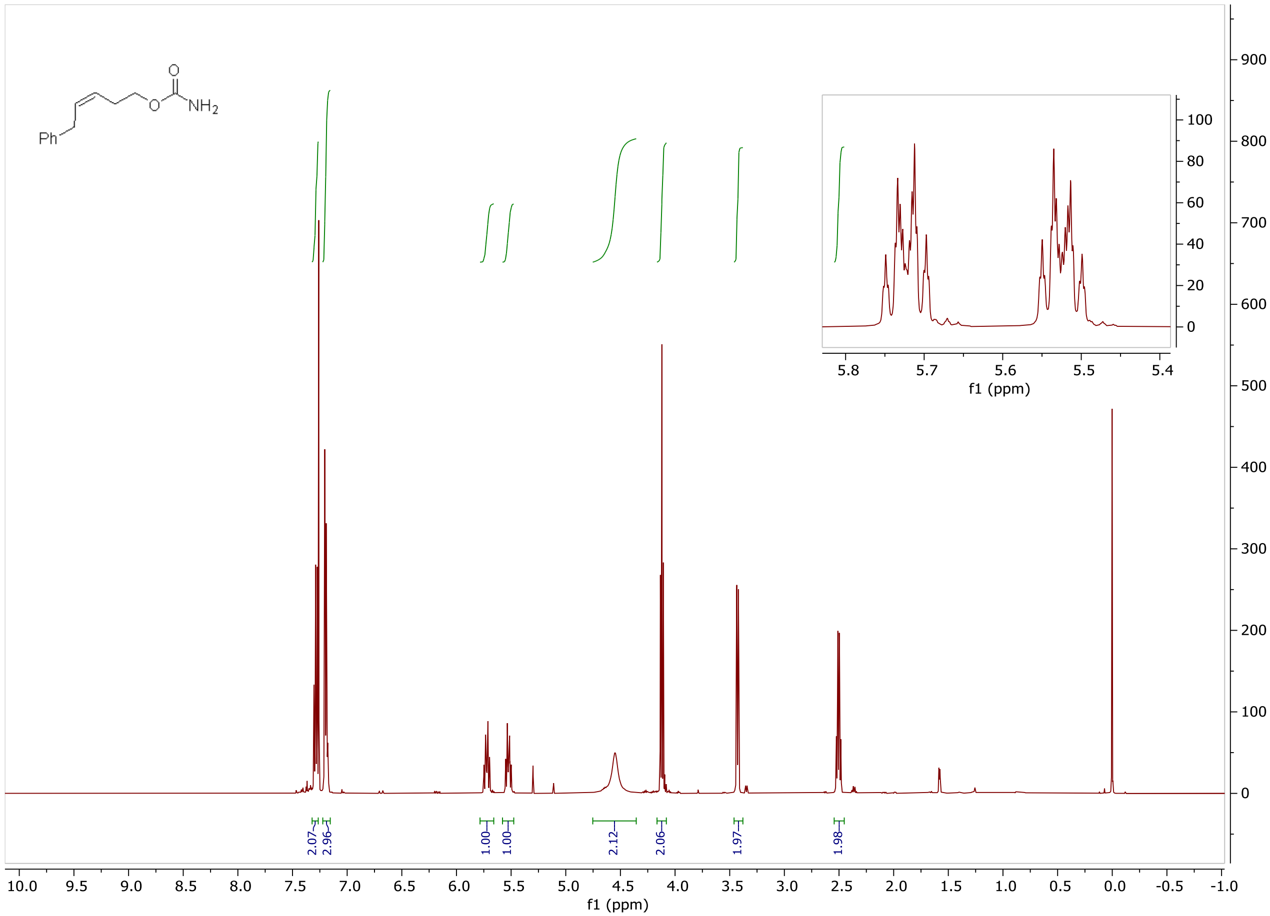
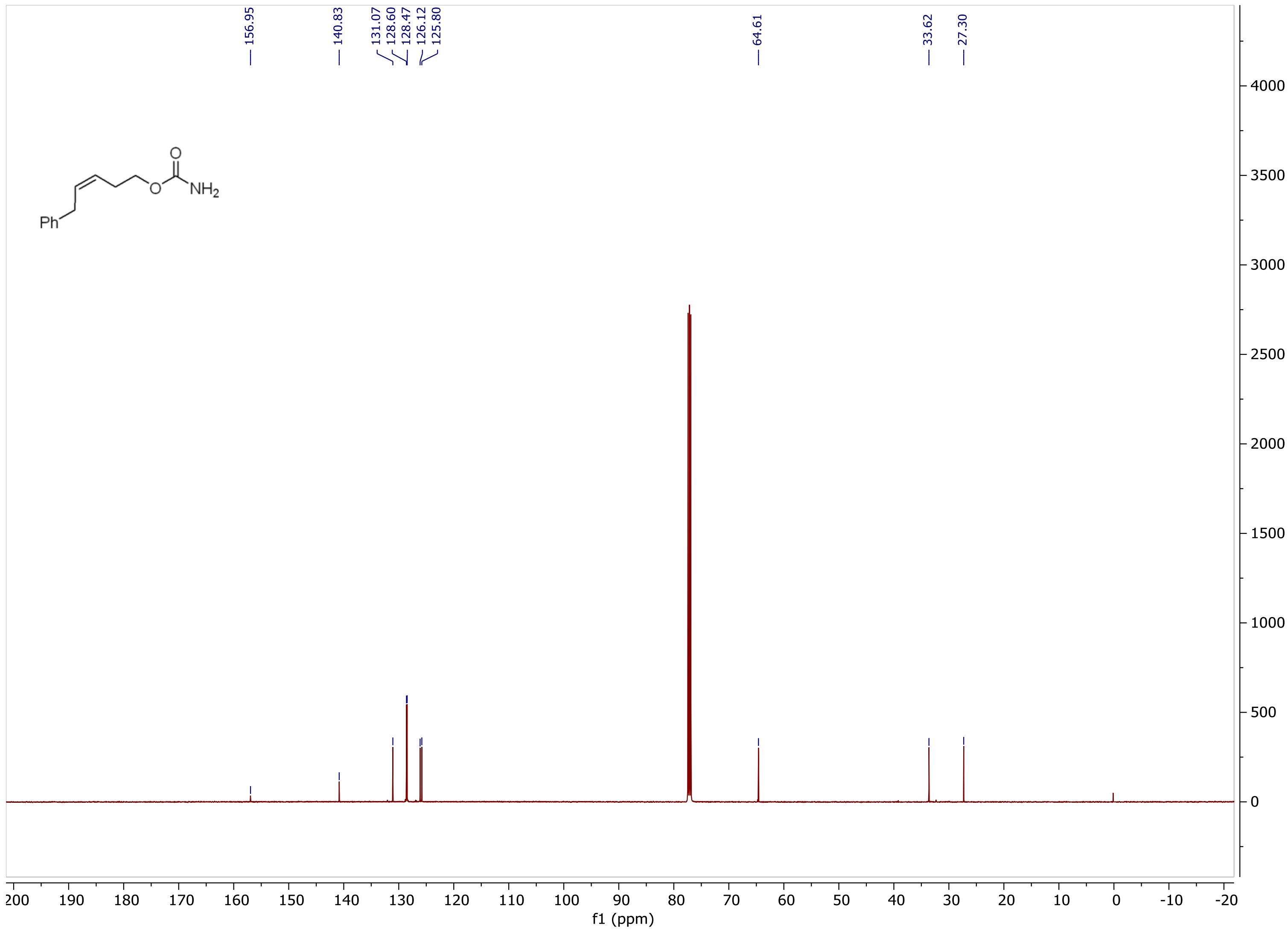
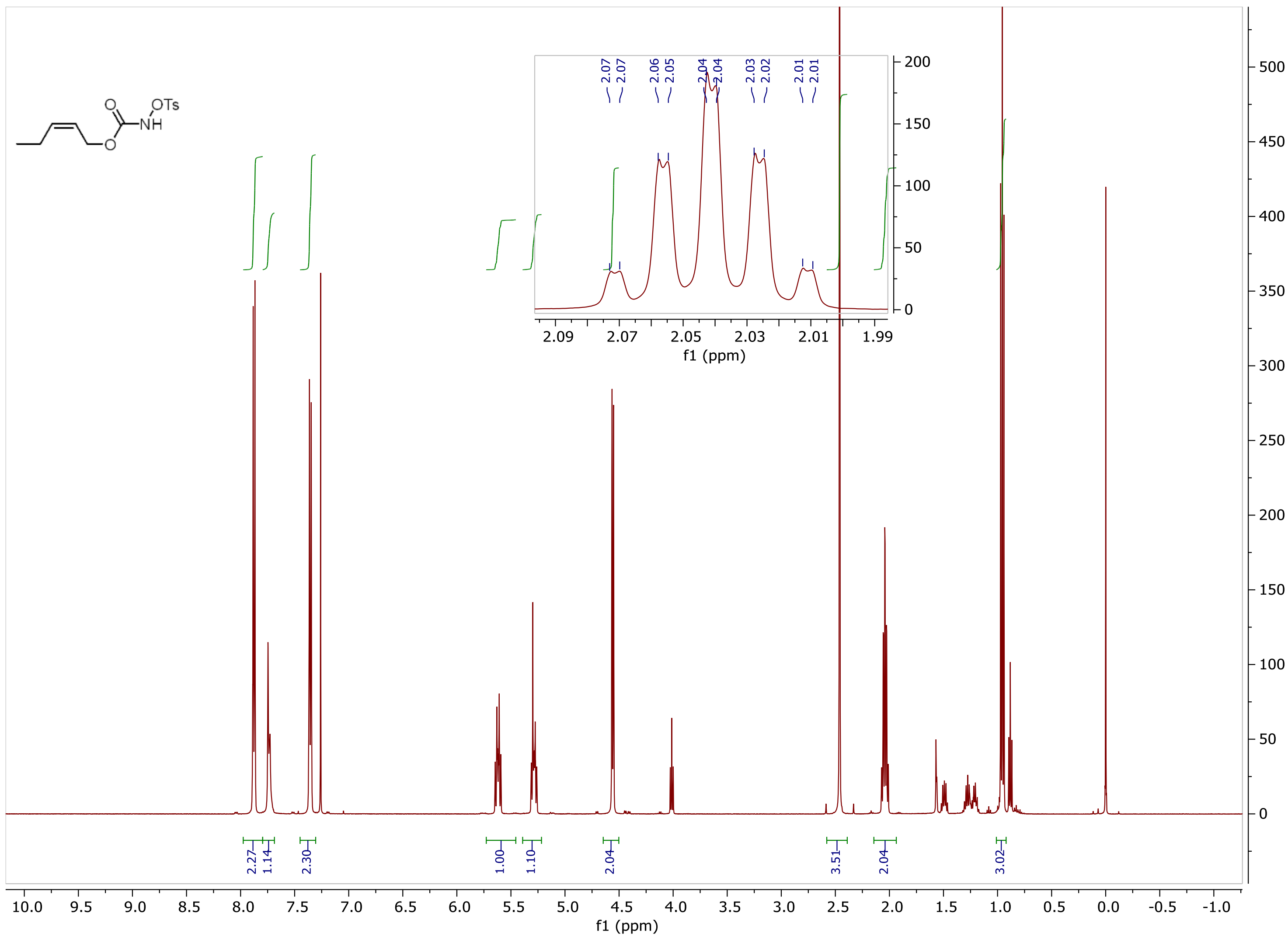


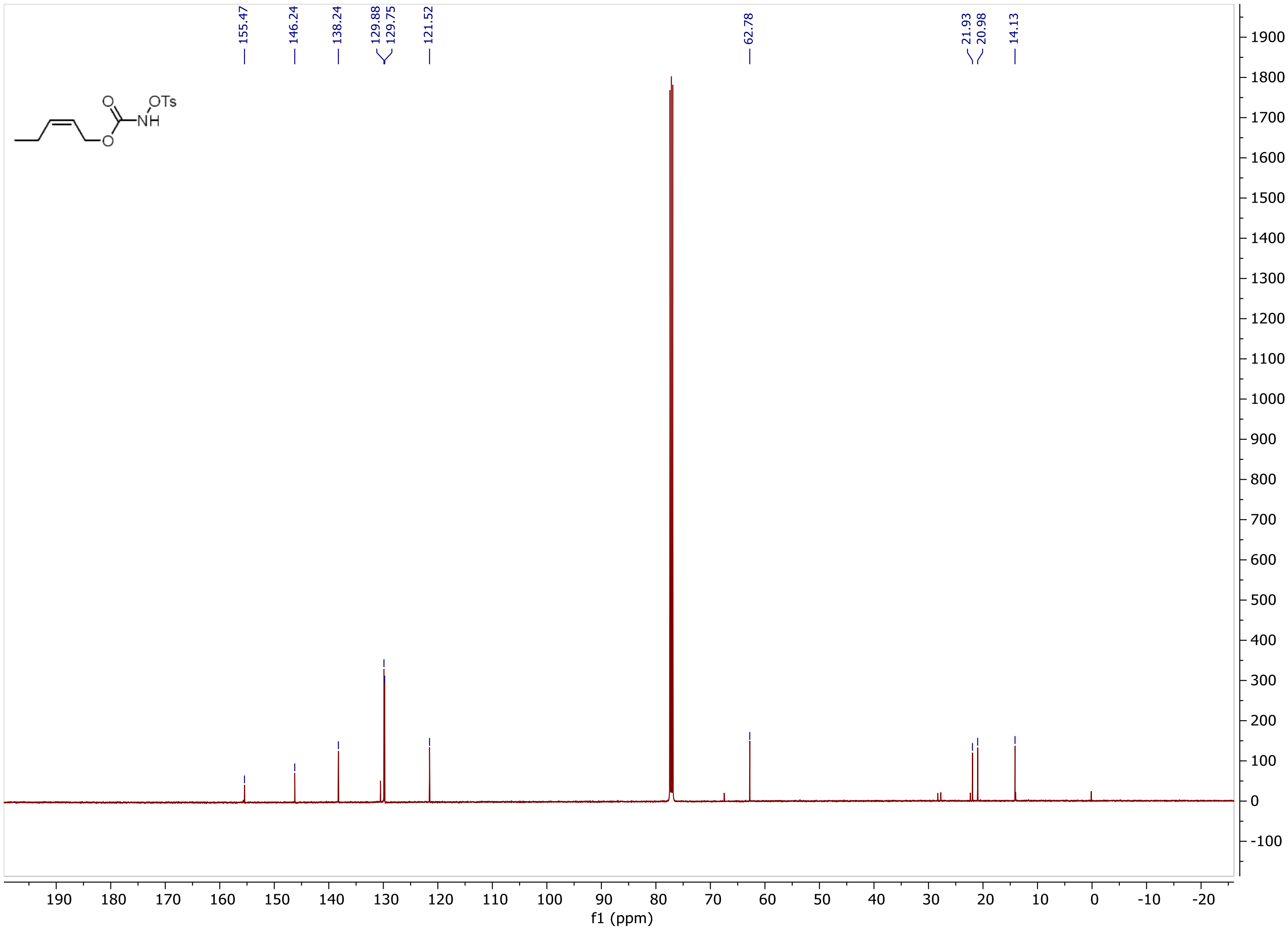
Precursor to compound **15.** ^{13}C NMR (126 MHz, $CDCl_3$)



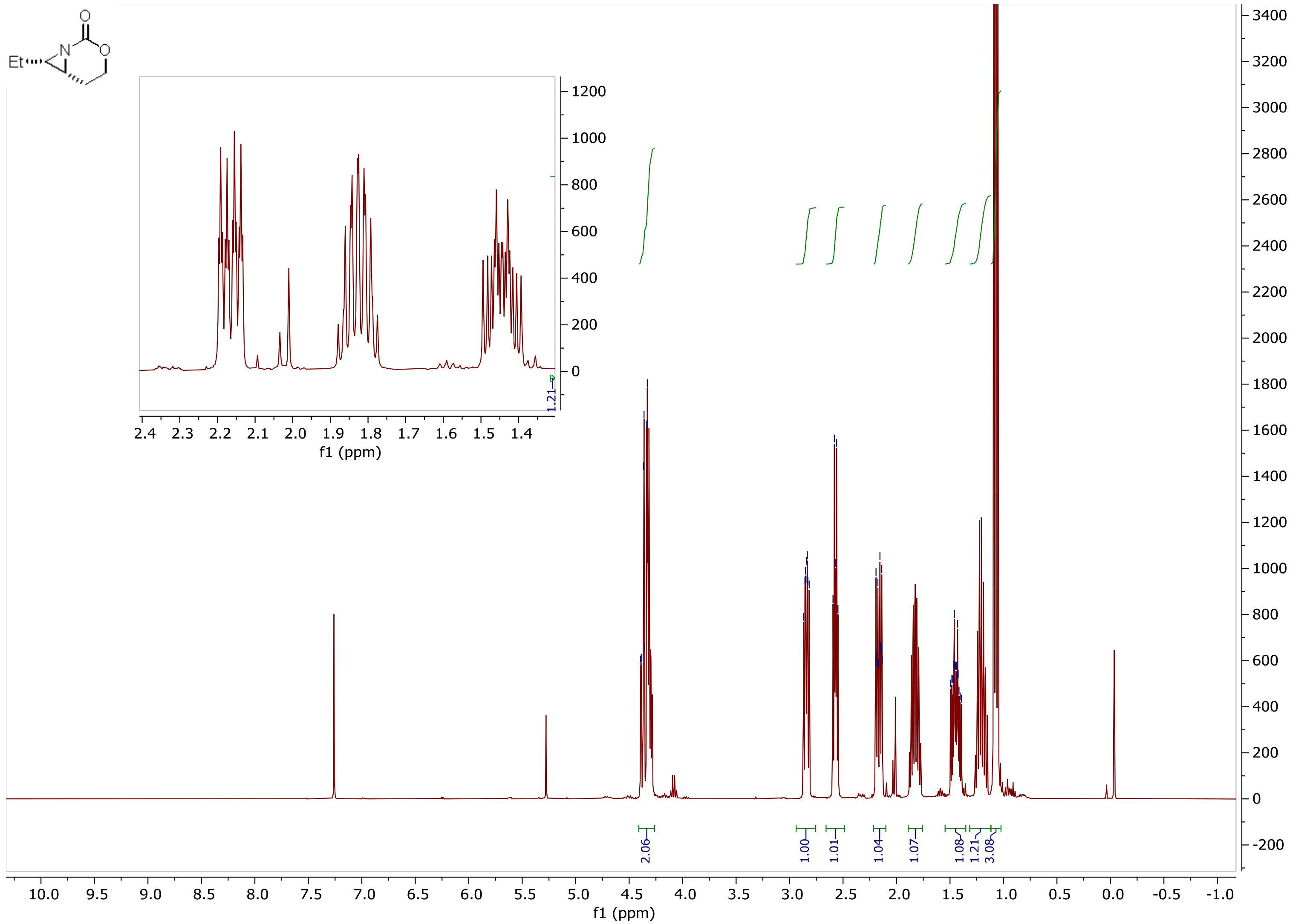
Precursor to compound **18.** ^{1}H NMR (500 MHz, $CDCl_3$)


OTs
O
NH
O
2.07
2.07
2.06
2.05
2.04
2.04
2.03
2.02
2.01
2.01
f1 (ppm)
2.27
1.14
2.30
1.00
1.10
2.04
3.51
2.04
3.02
f1 (ppm)

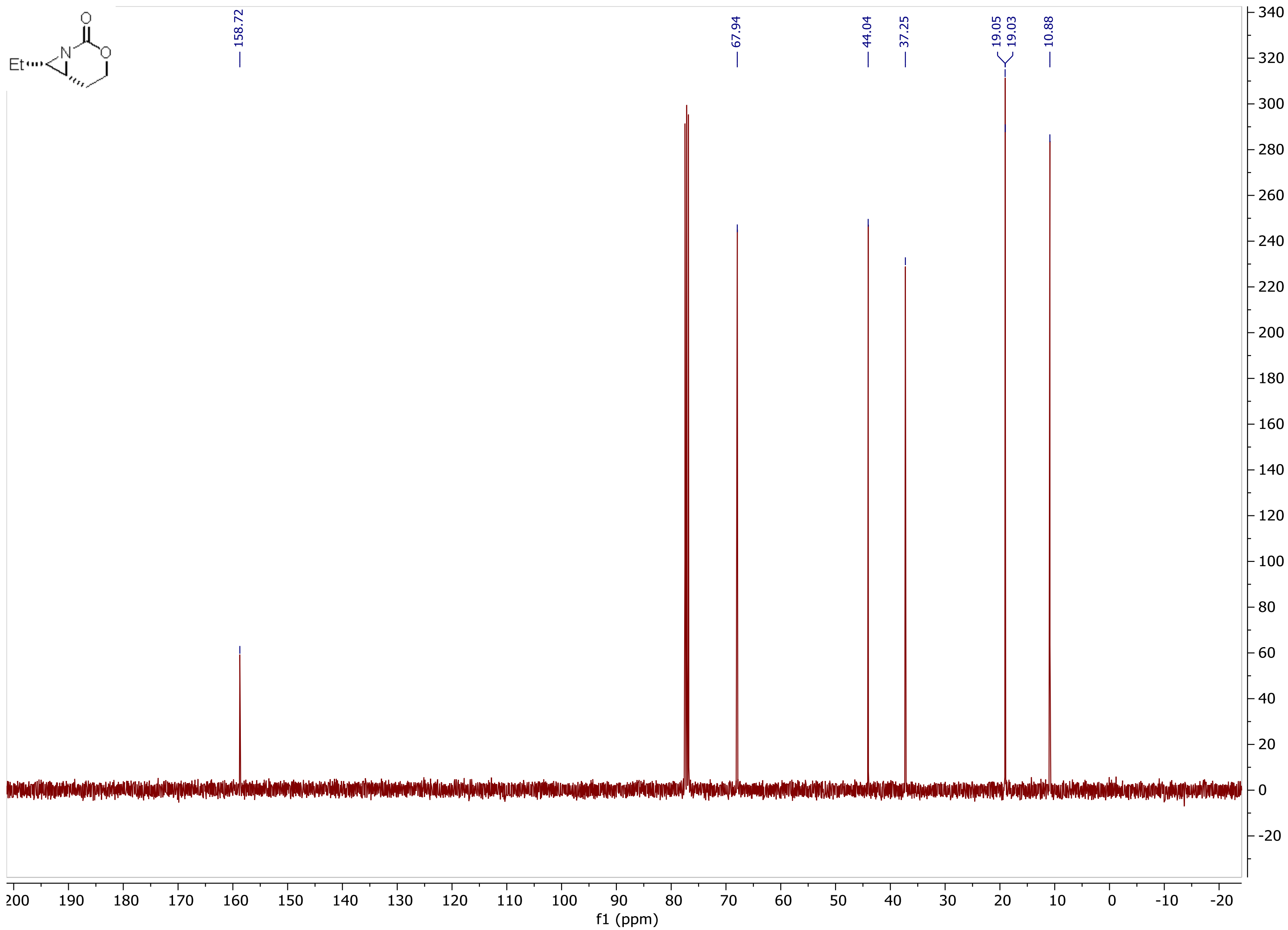
Precursor to compound **18.** ^{13}C NMR (126 MHz, $CDCl_3$)



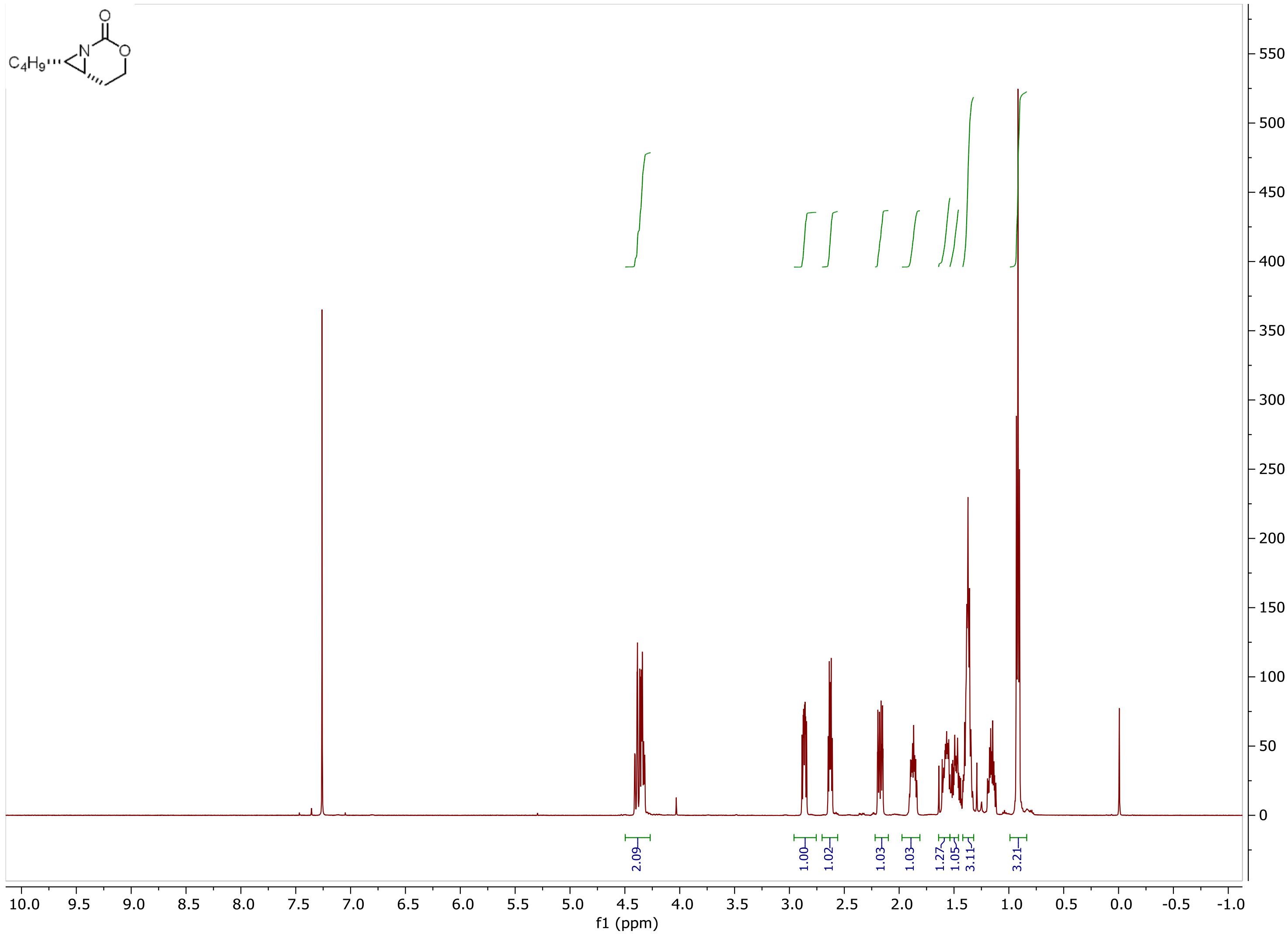
Compound **1.** ^{1}H NMR (500 MHz, $CDCl_3$)



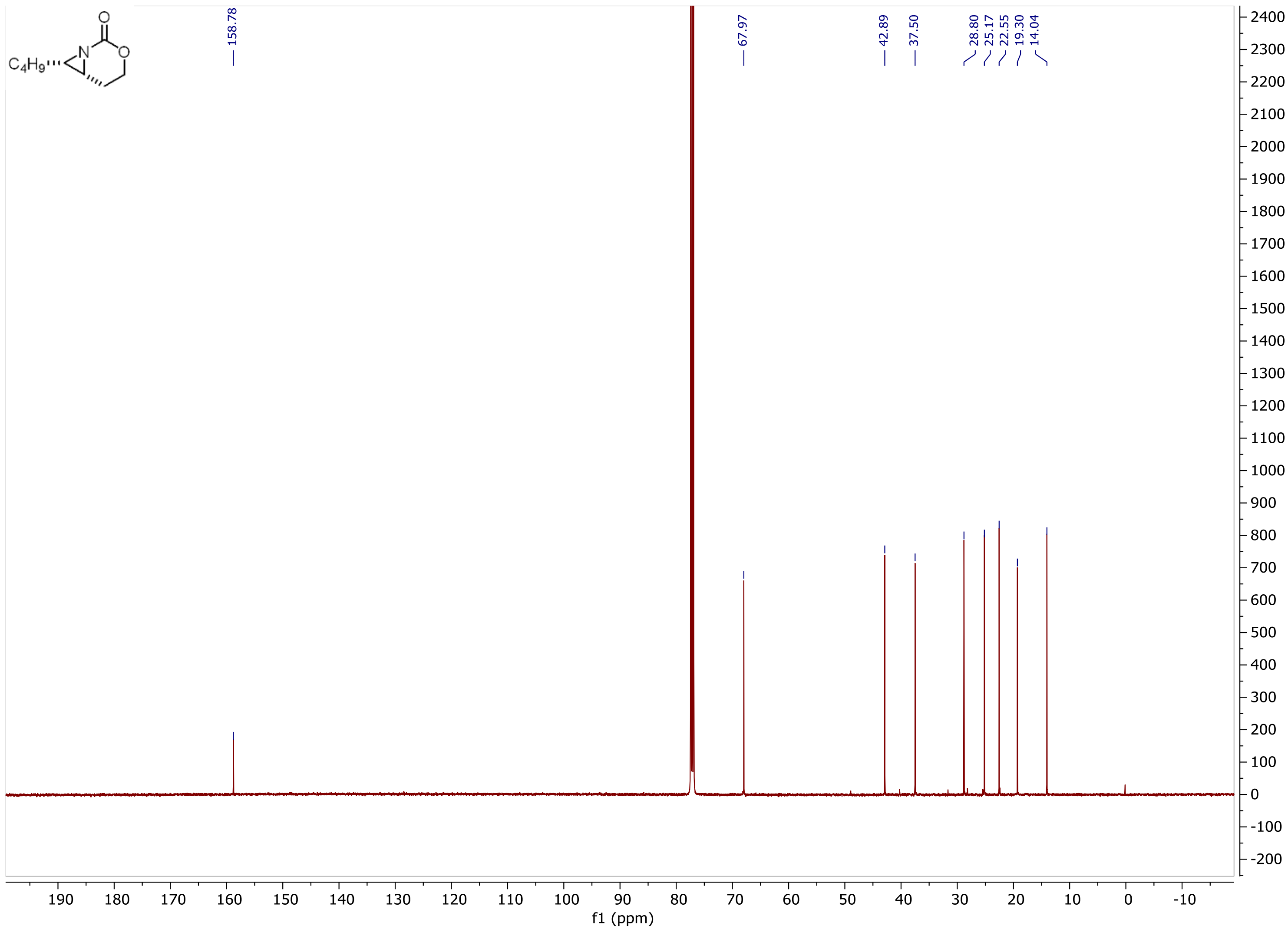
Compound **1.** ^{13}C NMR (126 MHz, $CDCl_3$)



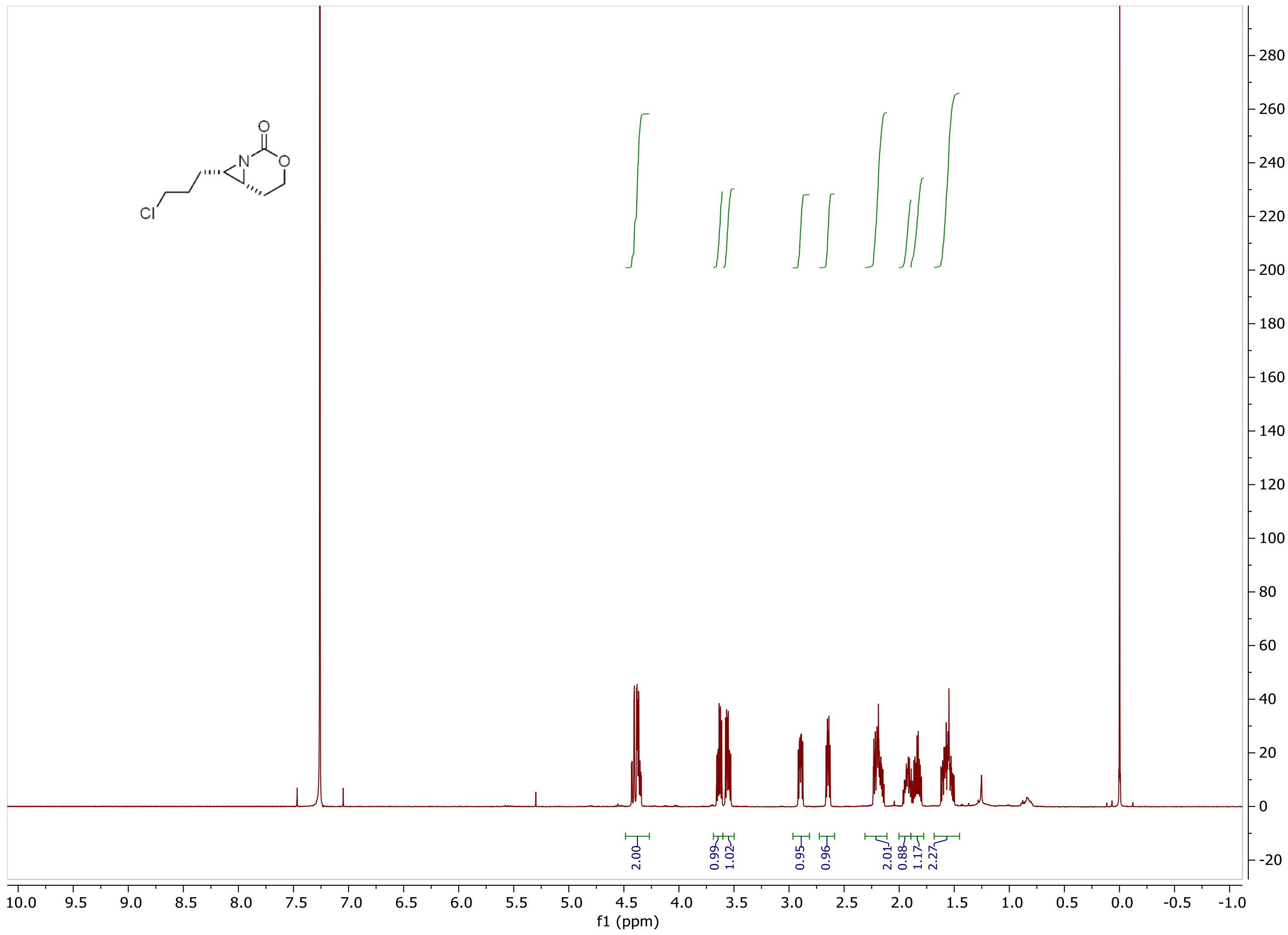
Compound **12.** ^{1}H NMR (500 MHz, $CDCl_3$)



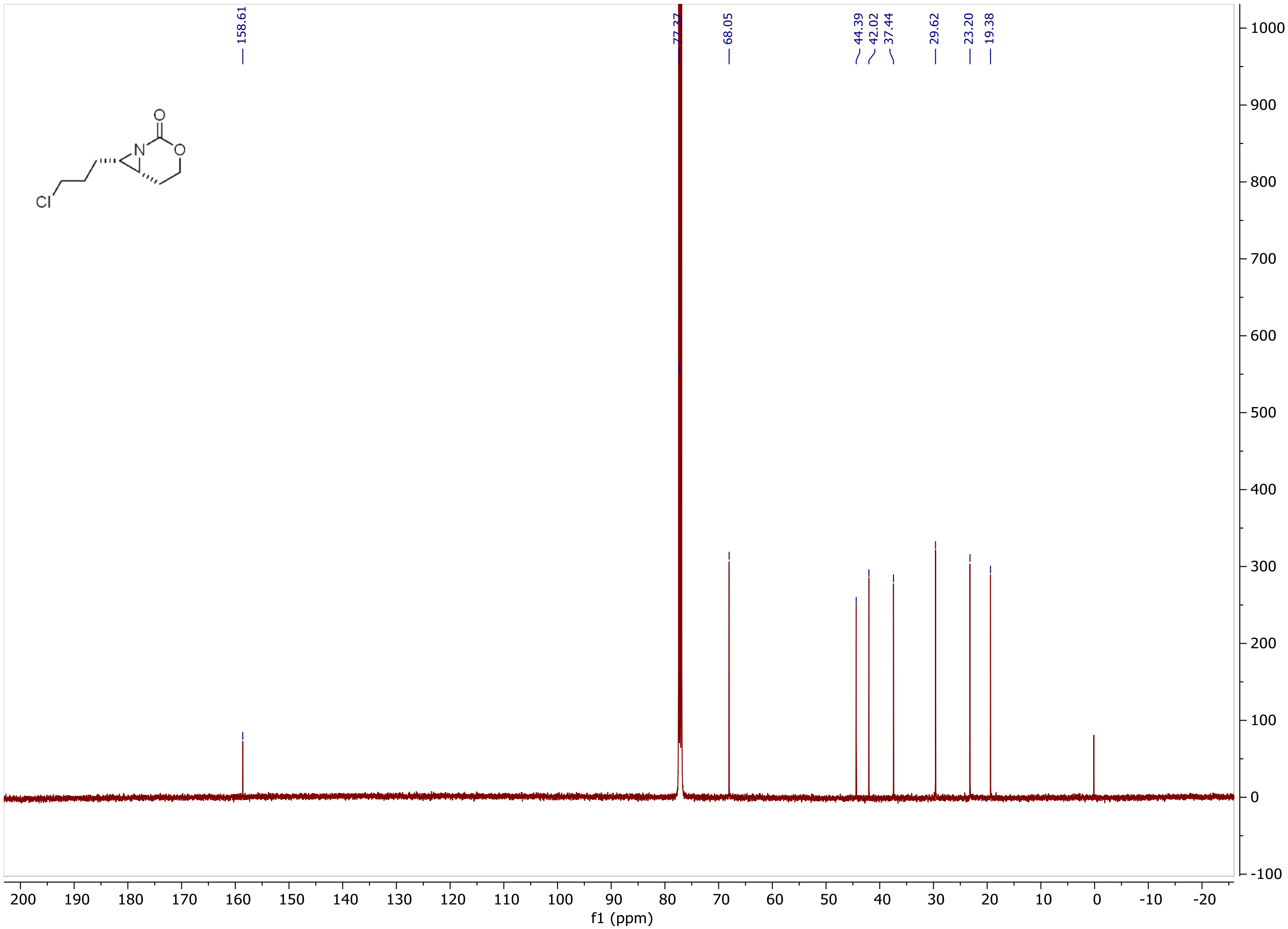
Compound **12.** ^{13}C NMR (126 MHz, $CDCl_3$)



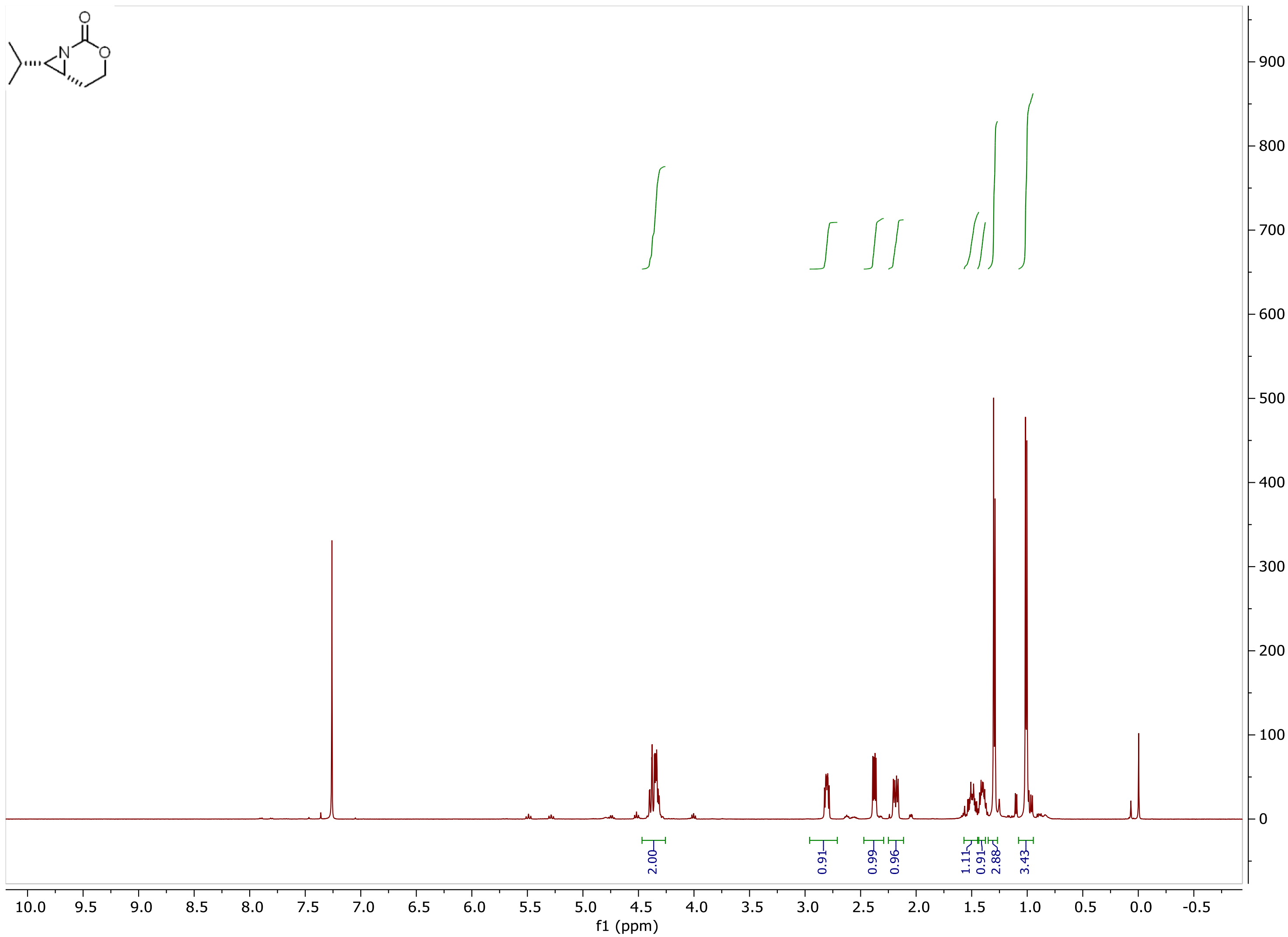
Compound **13.** ^{1}H NMR (500 MHz, $CDCl_3$)



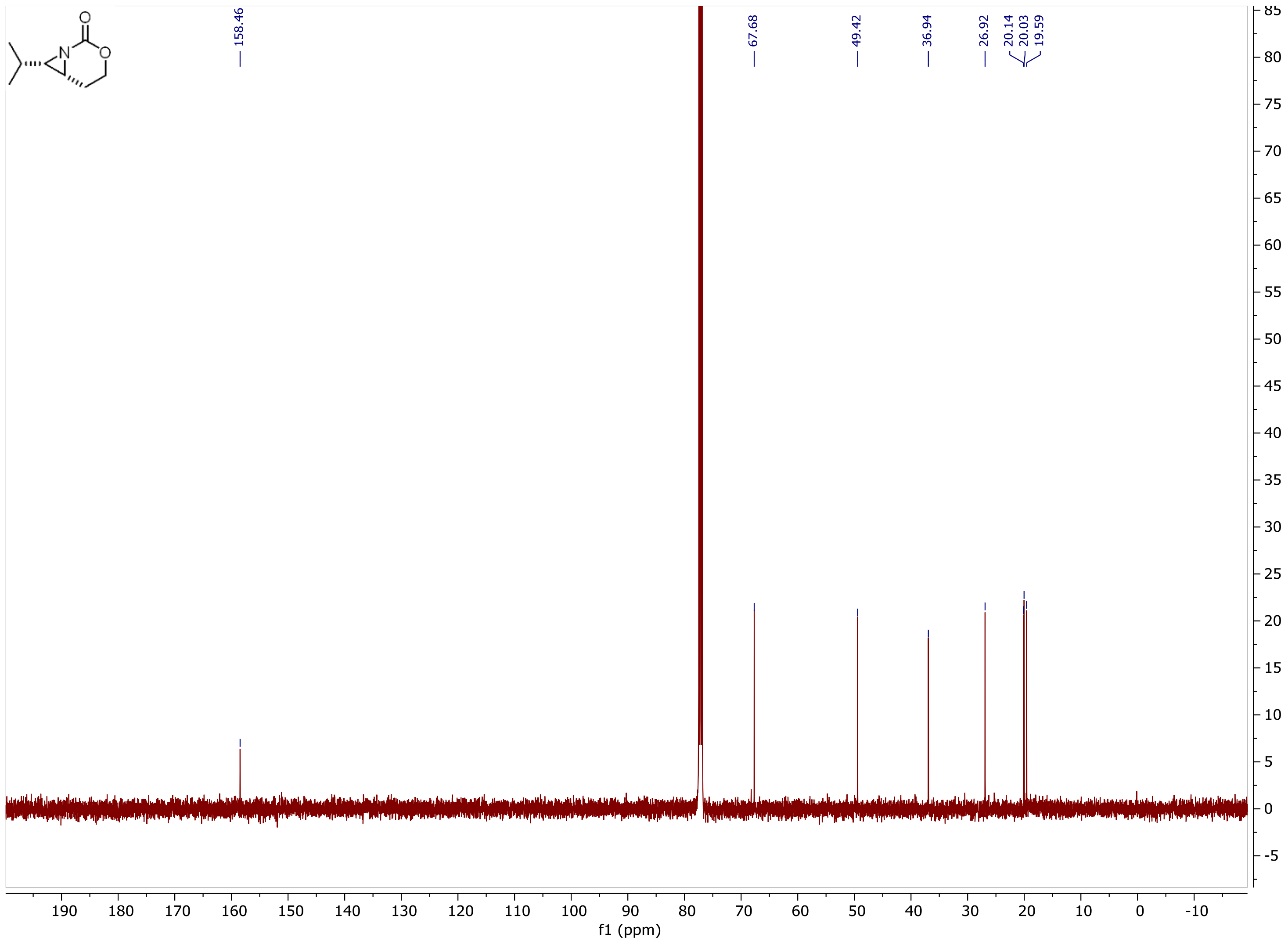
Compound **13.** ^{13}C NMR (126 MHz, $CDCl_3$)



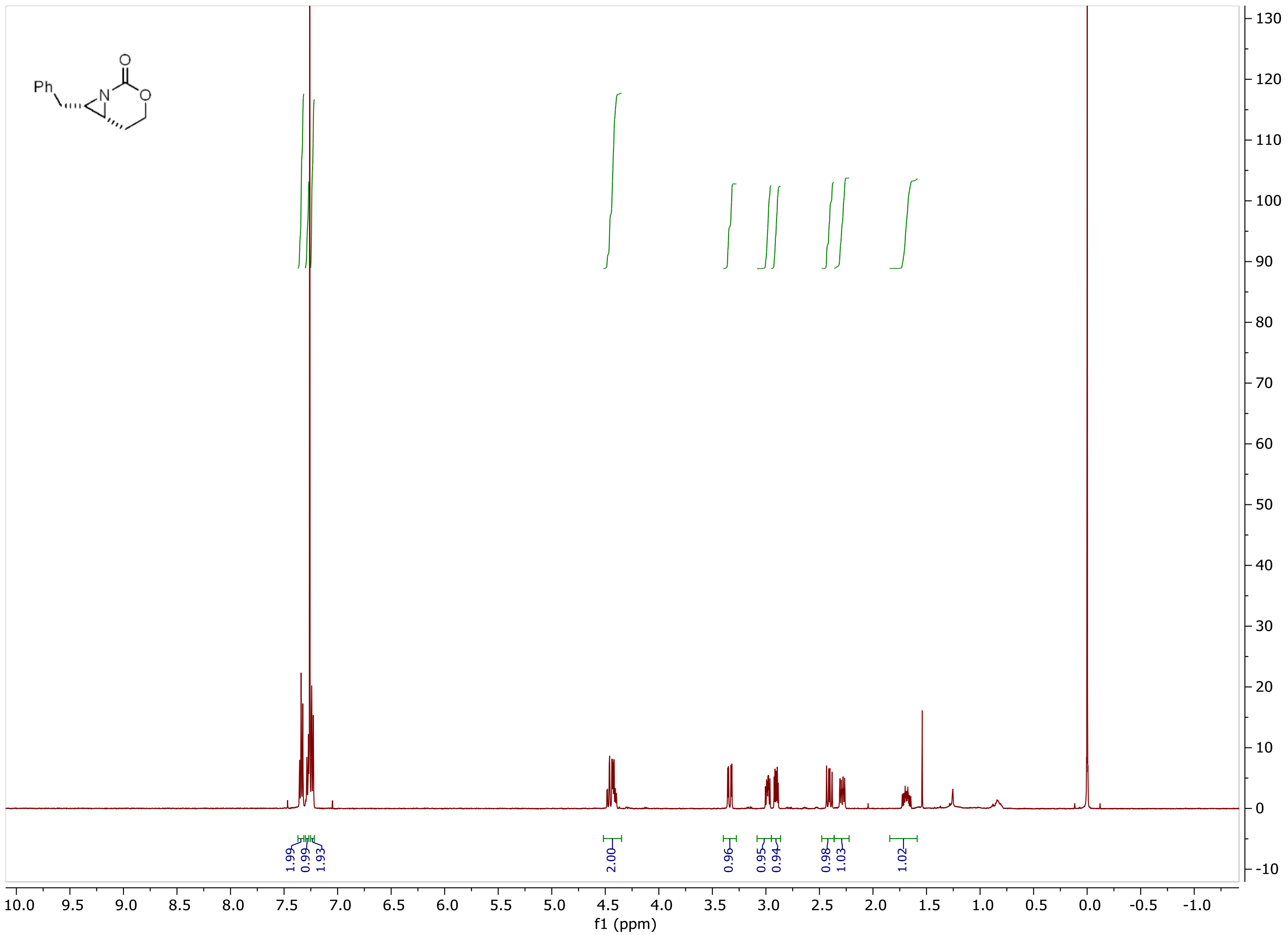
Compound **14.** ^{1}H NMR (500 MHz, $CDCl_3$)



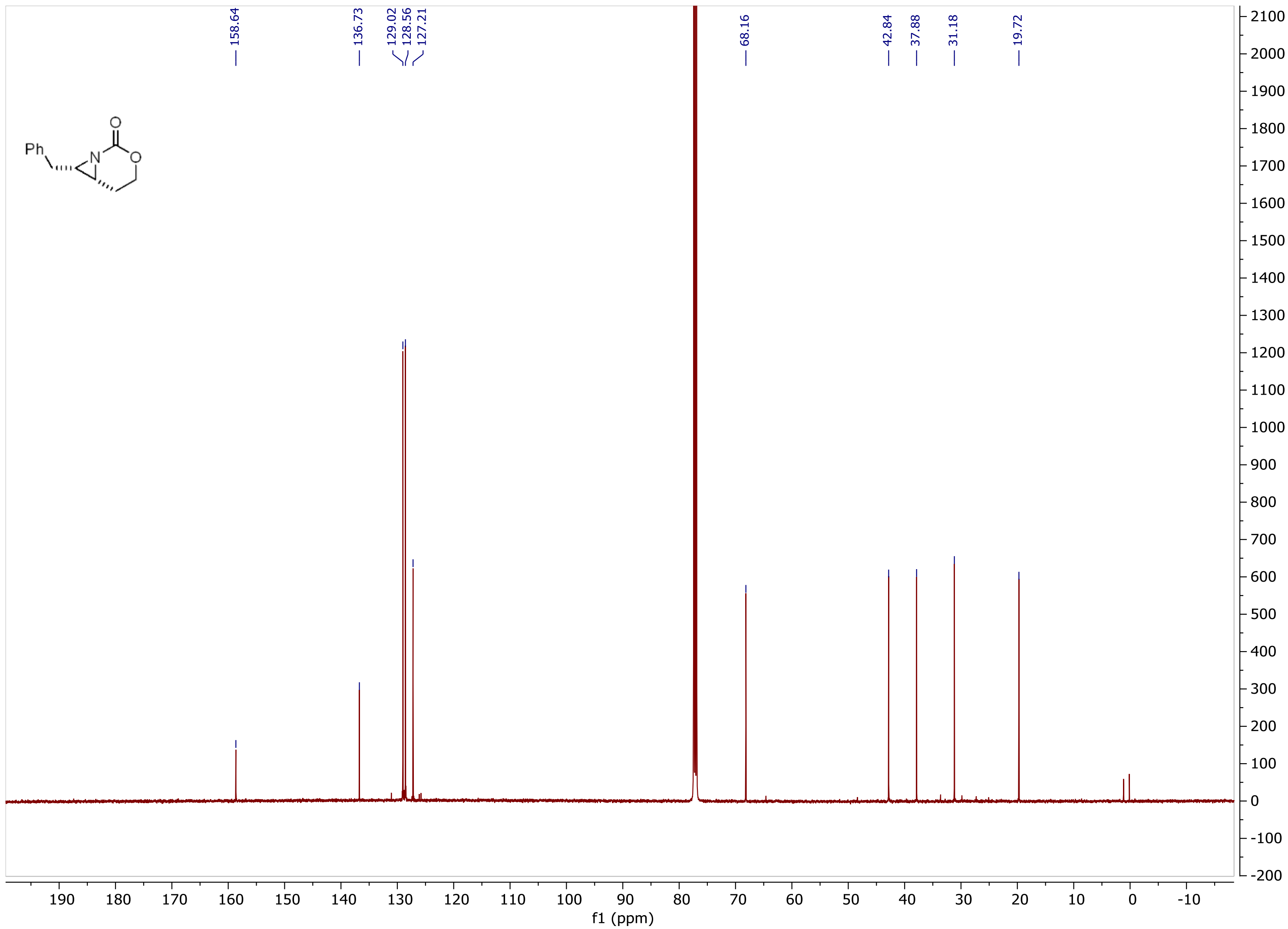
Compound **14.** ^{13}C NMR (126 MHz, $CDCl_3$)



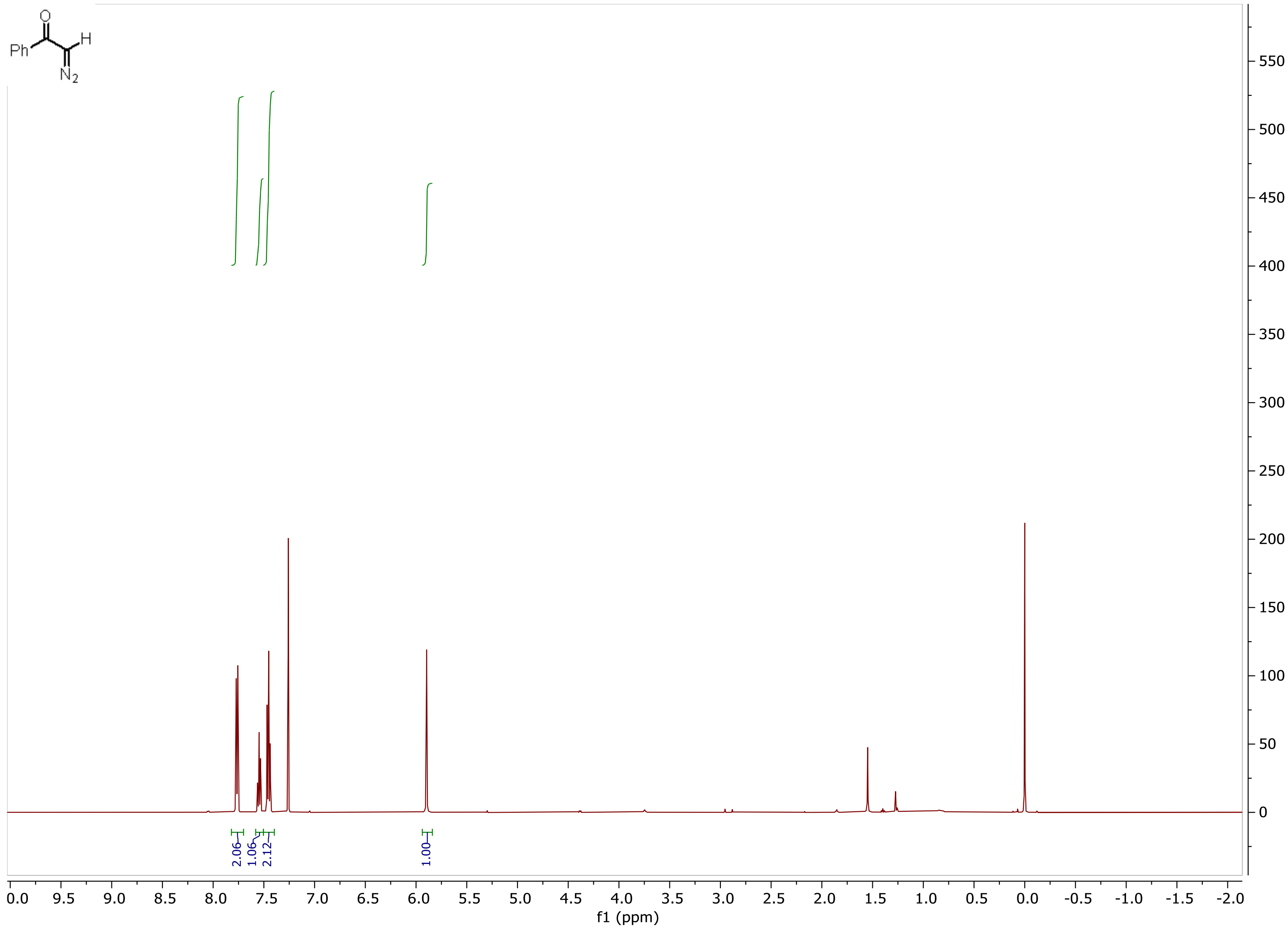
Compound **15.** [1]H NMR (500 MHz, $CDCl_3$)



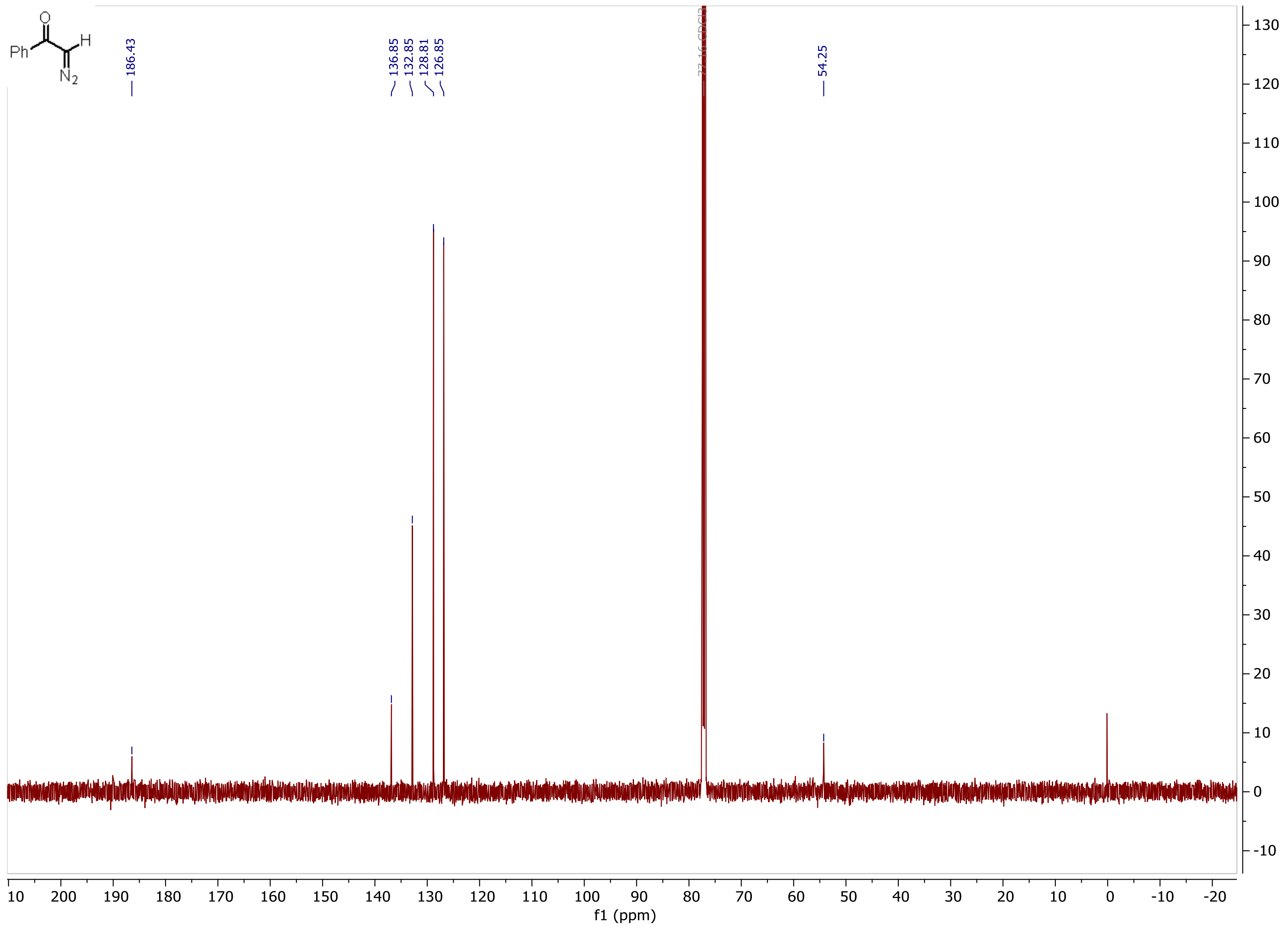
Compound **15.** ^{13}C NMR (126 MHz, $CDCl_3$)



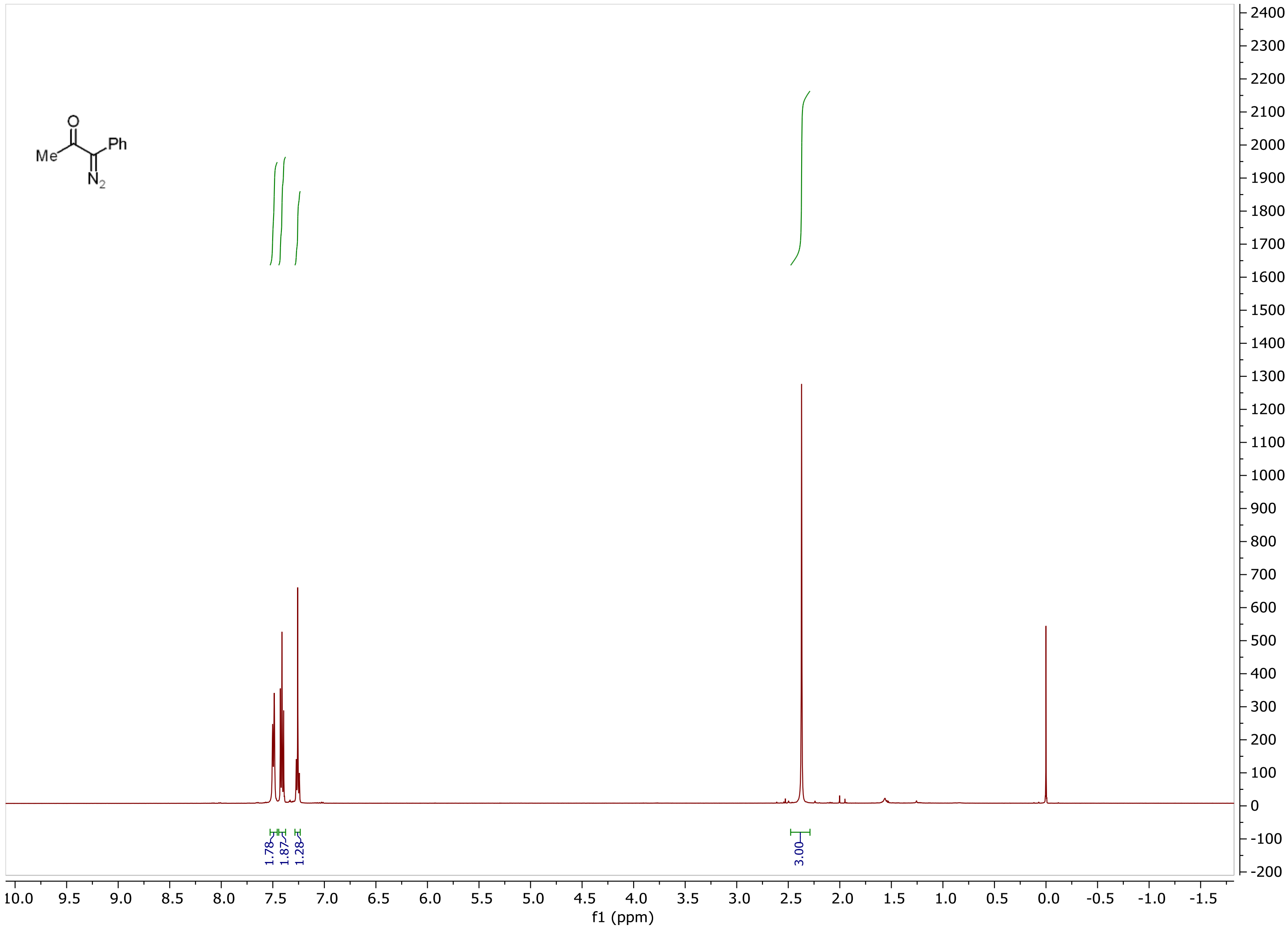
Compound **2a.** ^{1}H NMR (500 MHz, $CDCl_3$)



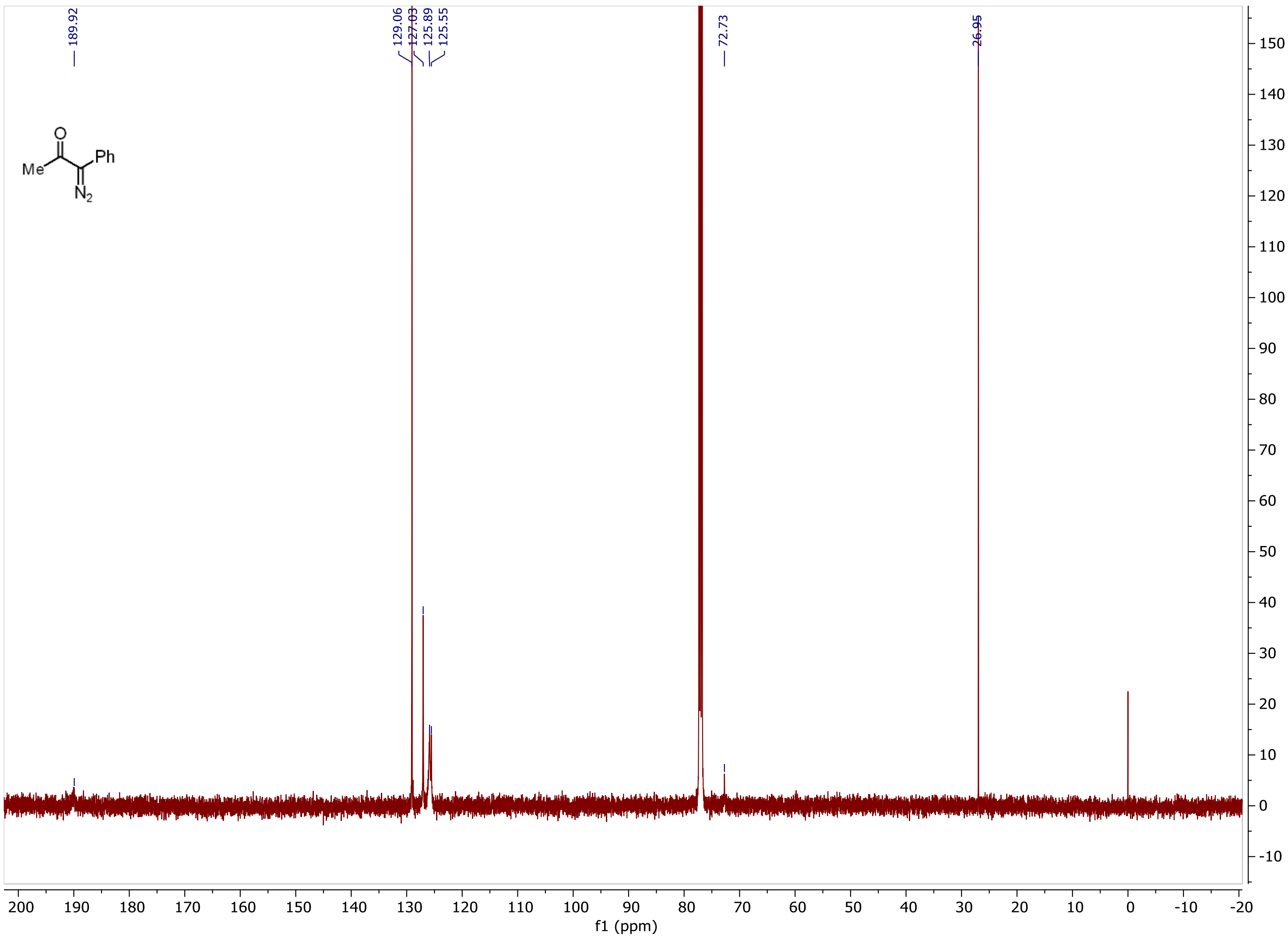
Compound **2a.** ^{13}C NMR (126 MHz, $CDCl_3$)



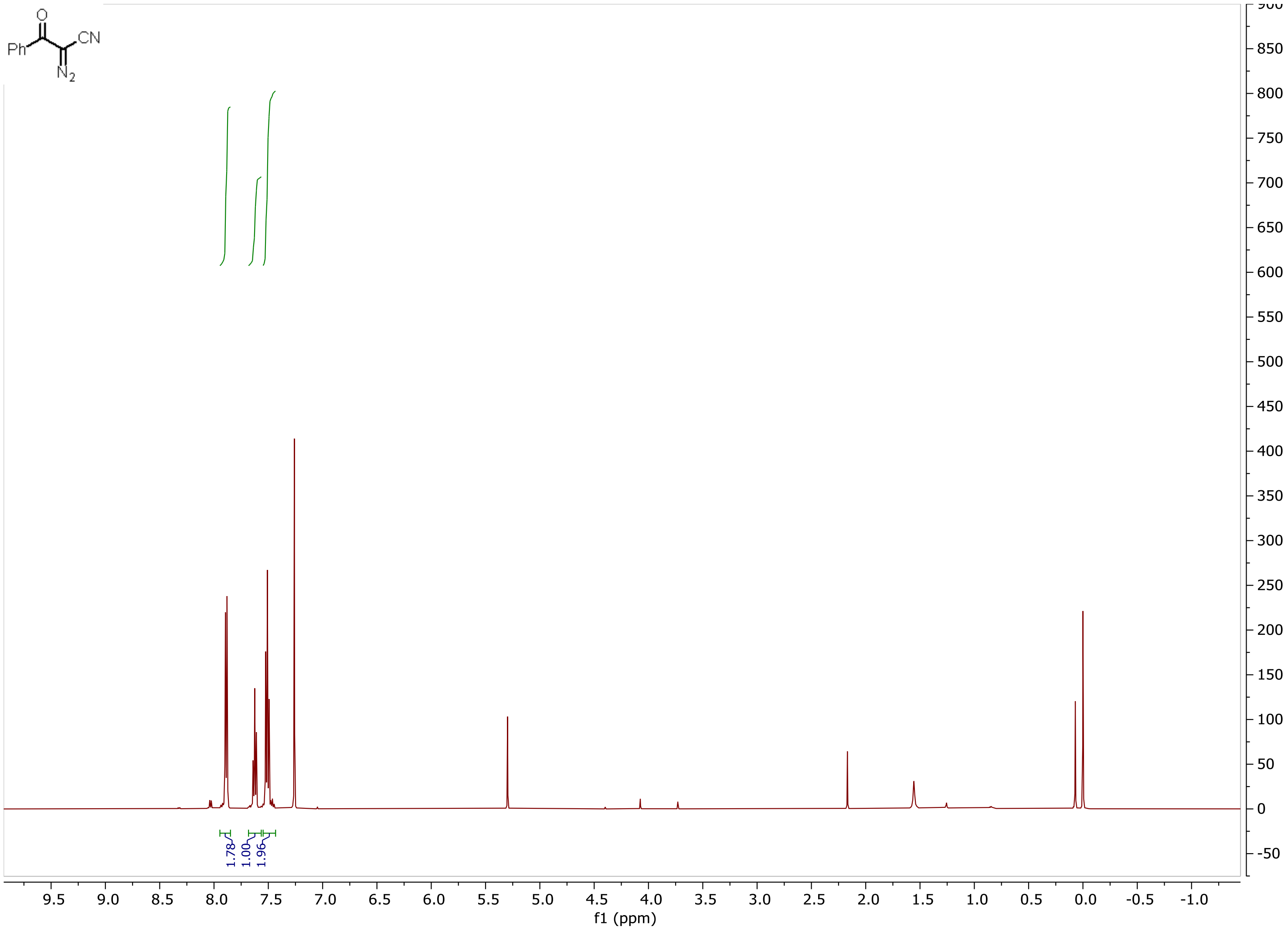
Compound **2b.** ^{1}H NMR (500 MHz, $CDCl_3$)



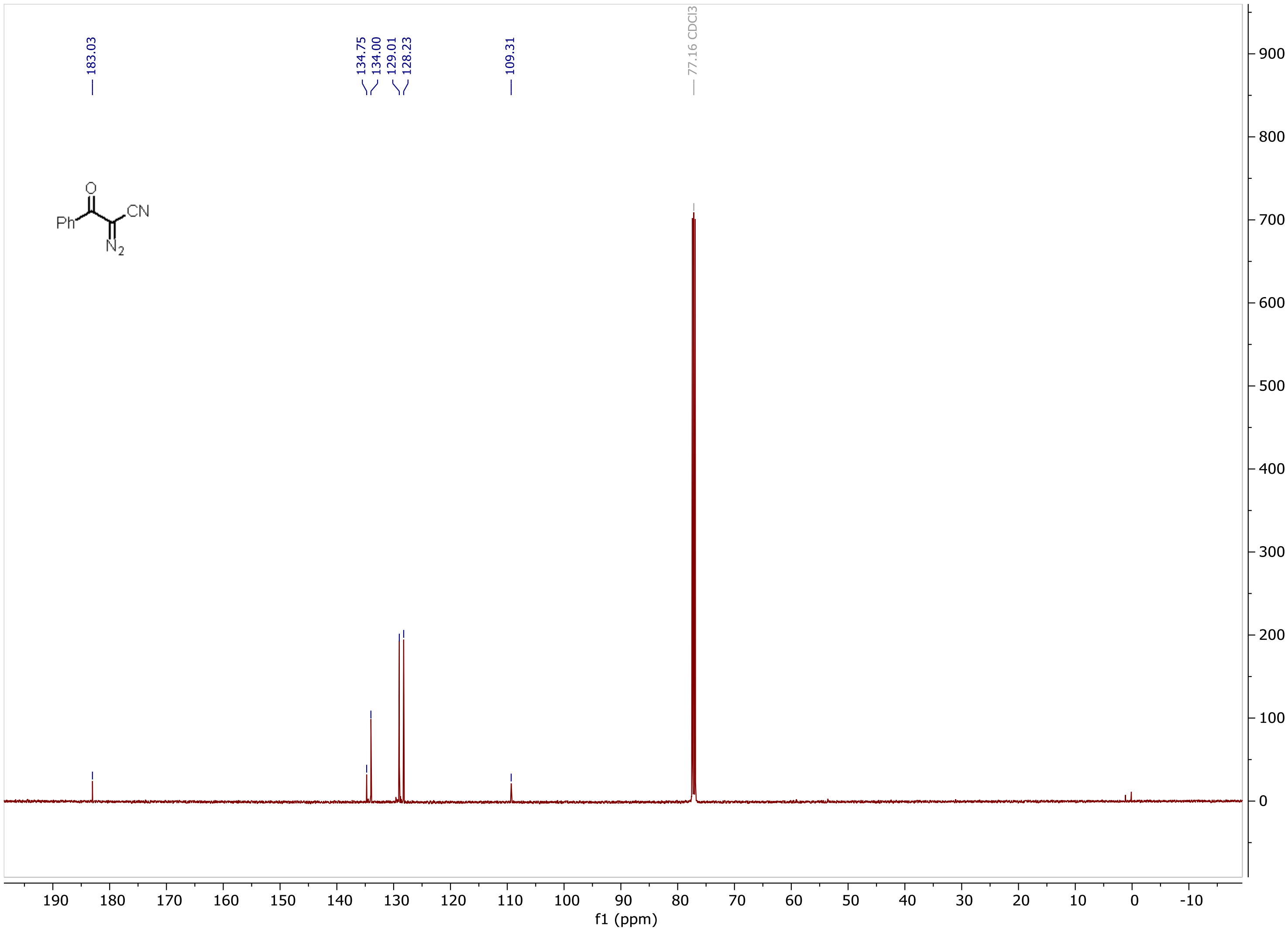
Compound **2b.** ^{13}C NMR (126 MHz, $CDCl_3$)



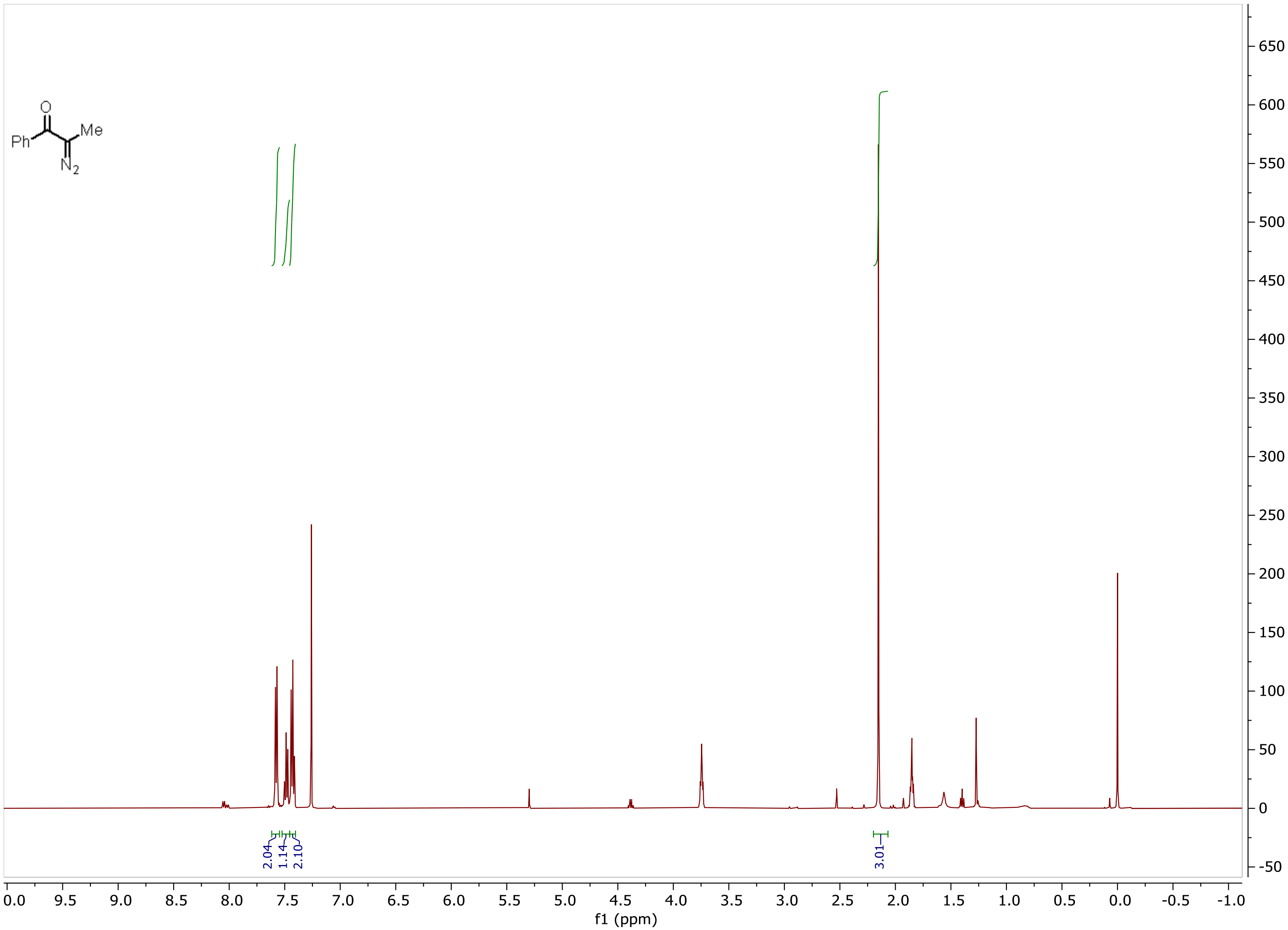
Compound **2c.** ^{1}H NMR (500 MHz, $CDCl_3$)



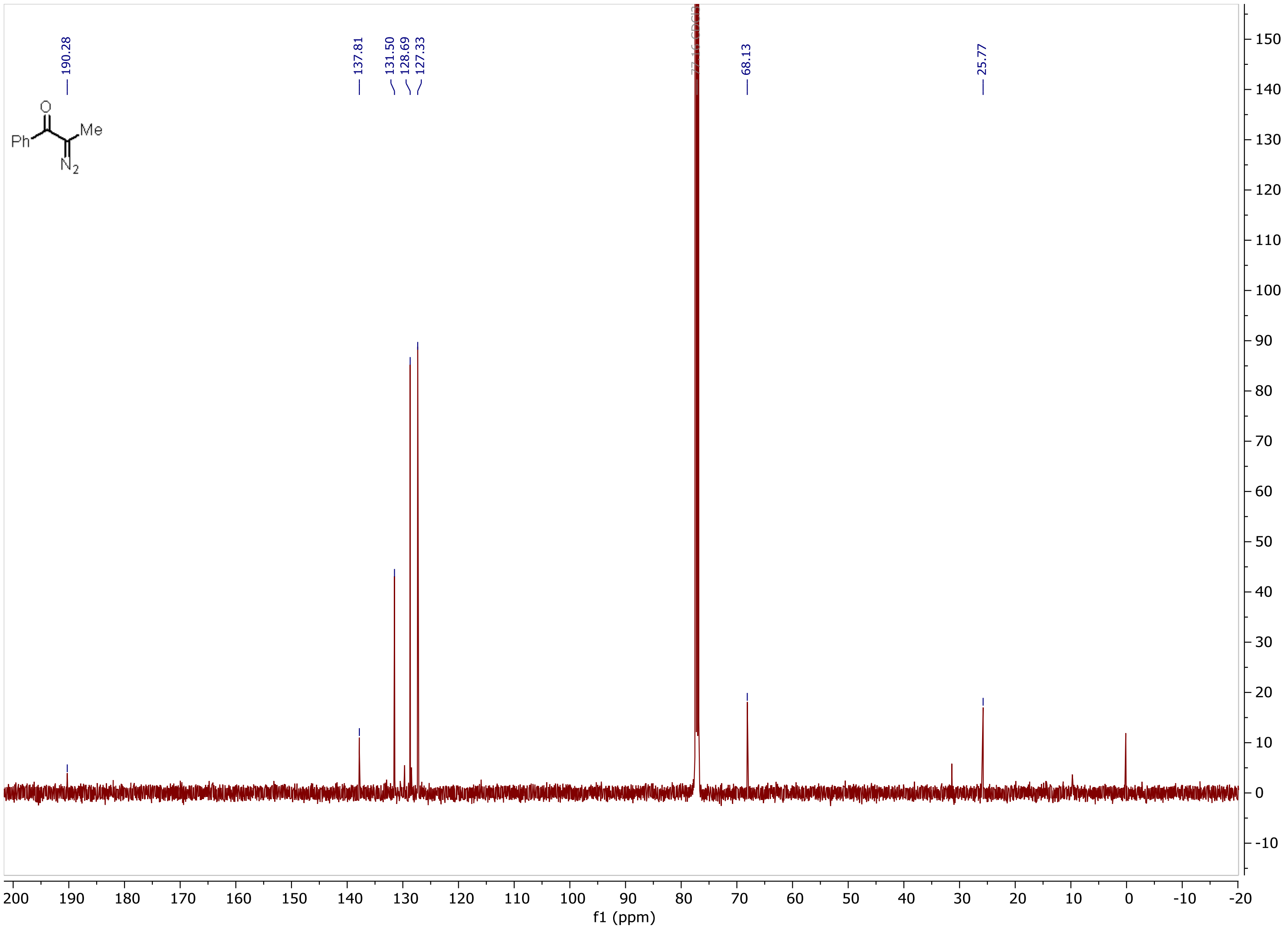
Compound **2c.** ^{13}C NMR (126 MHz, $CDCl_3$)



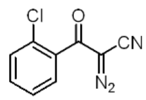
Compound **2d.** [1]H NMR (500 MHz, $CDCl_3$)

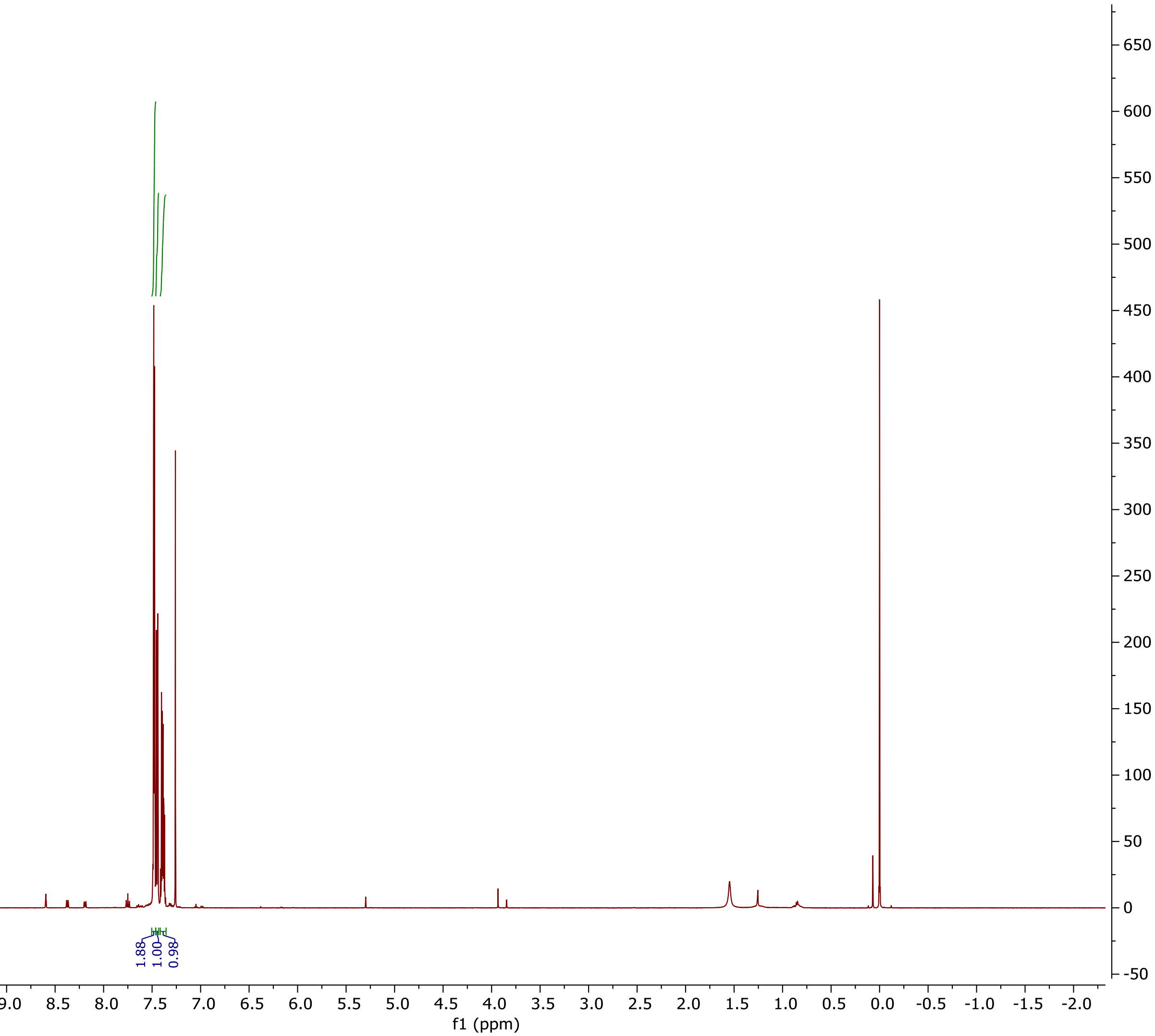


Compound **2d.** ^{13}C NMR (126 MHz, $CDCl_3$)

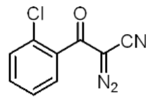


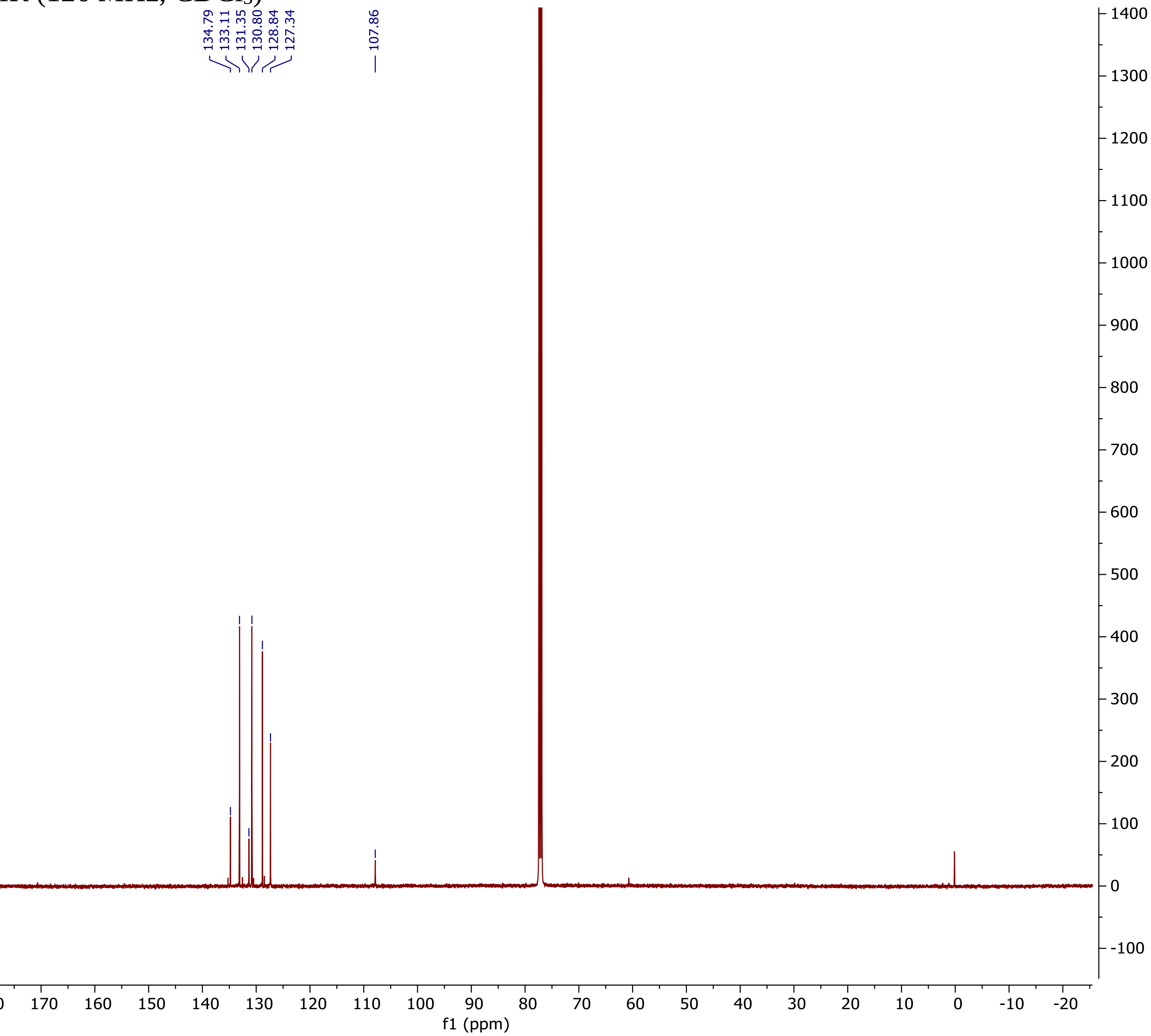
Precursor to **6c.** ^{1}H NMR (500 MHz, $CDCl_3$)



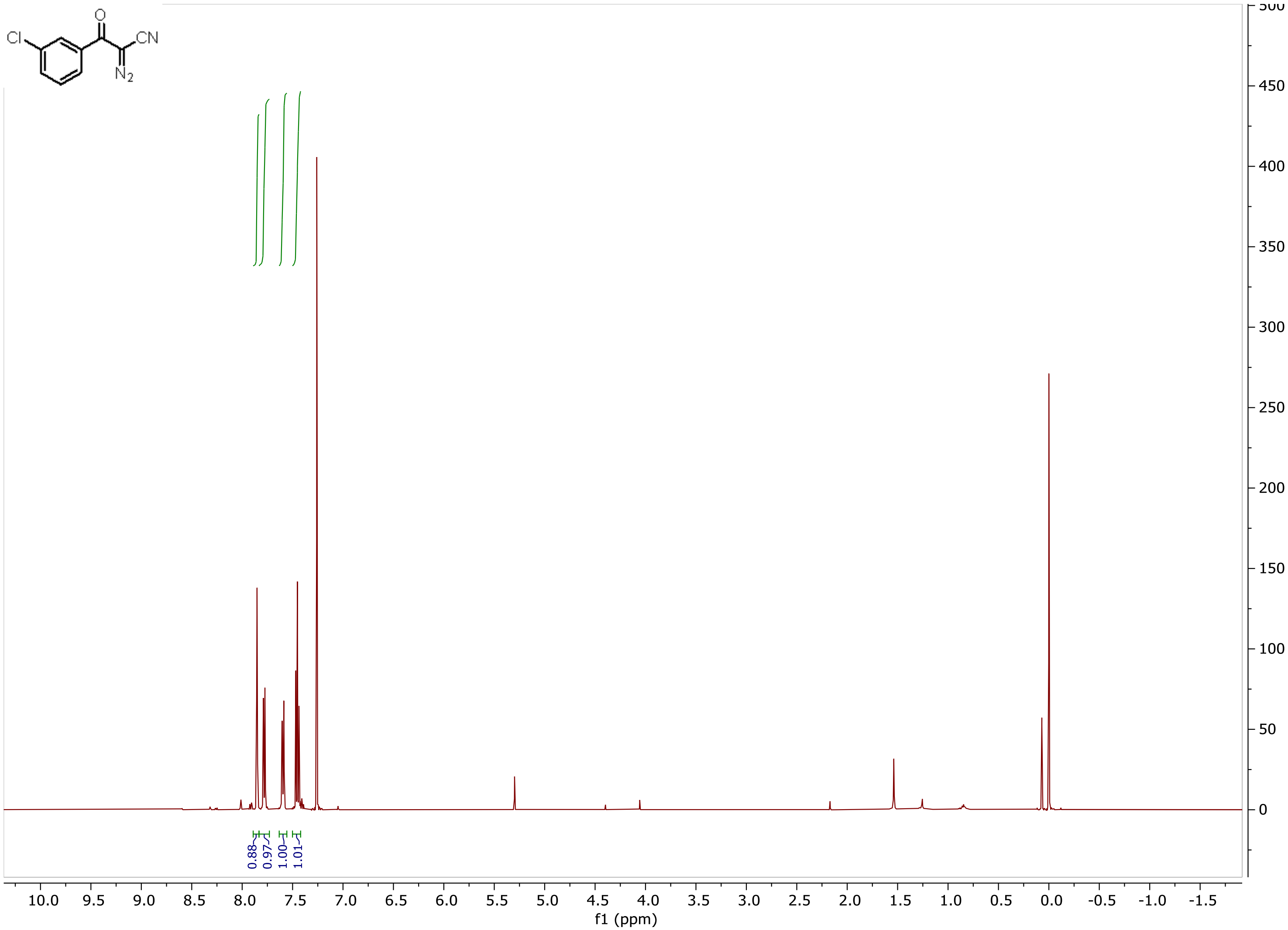


Precursor to **6c.** ^{13}C NMR (126 MHz, $CDCl_3$)

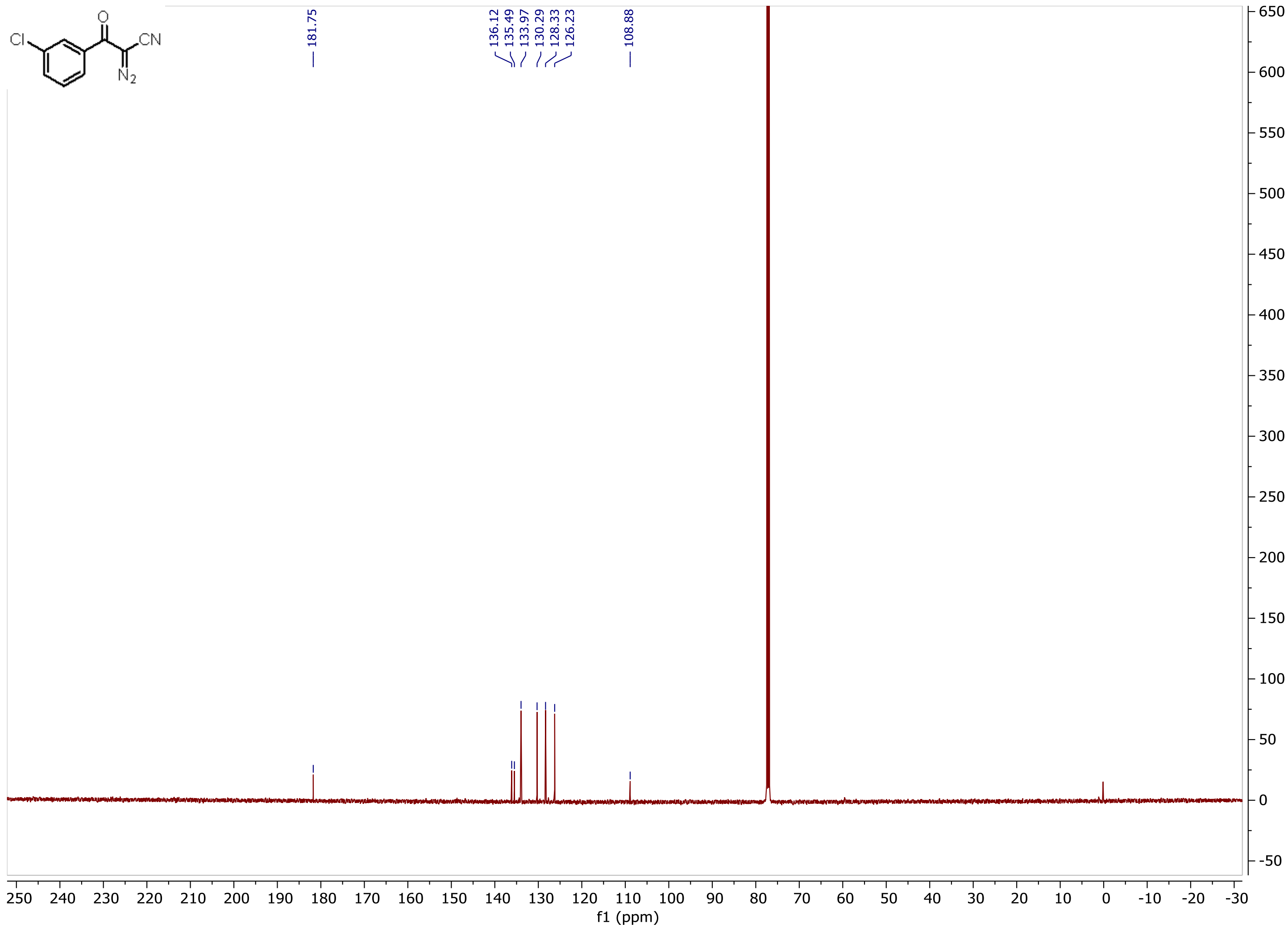




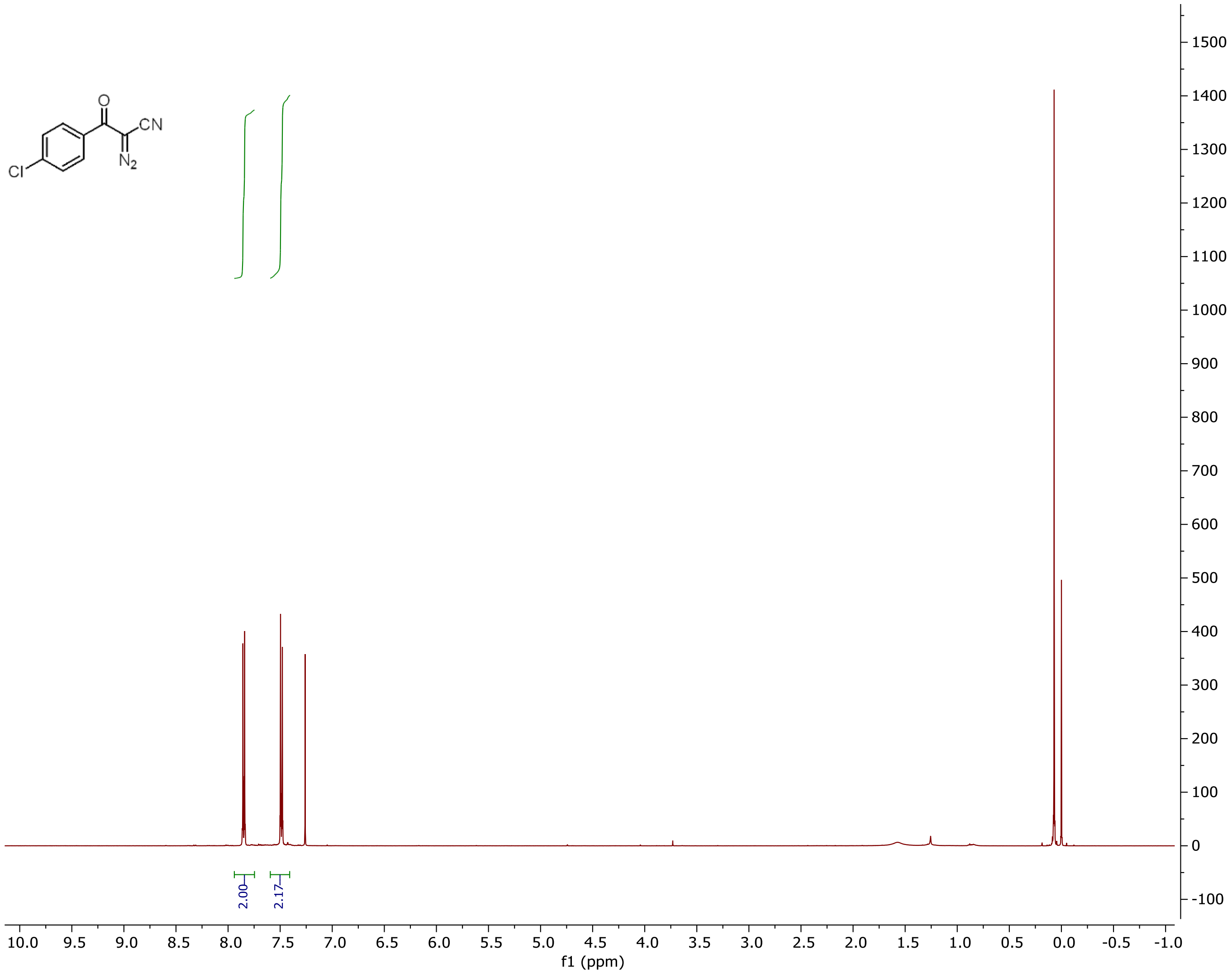
Precursor to **7c.** ^{1}H NMR (500 MHz, $CDCl_3$)



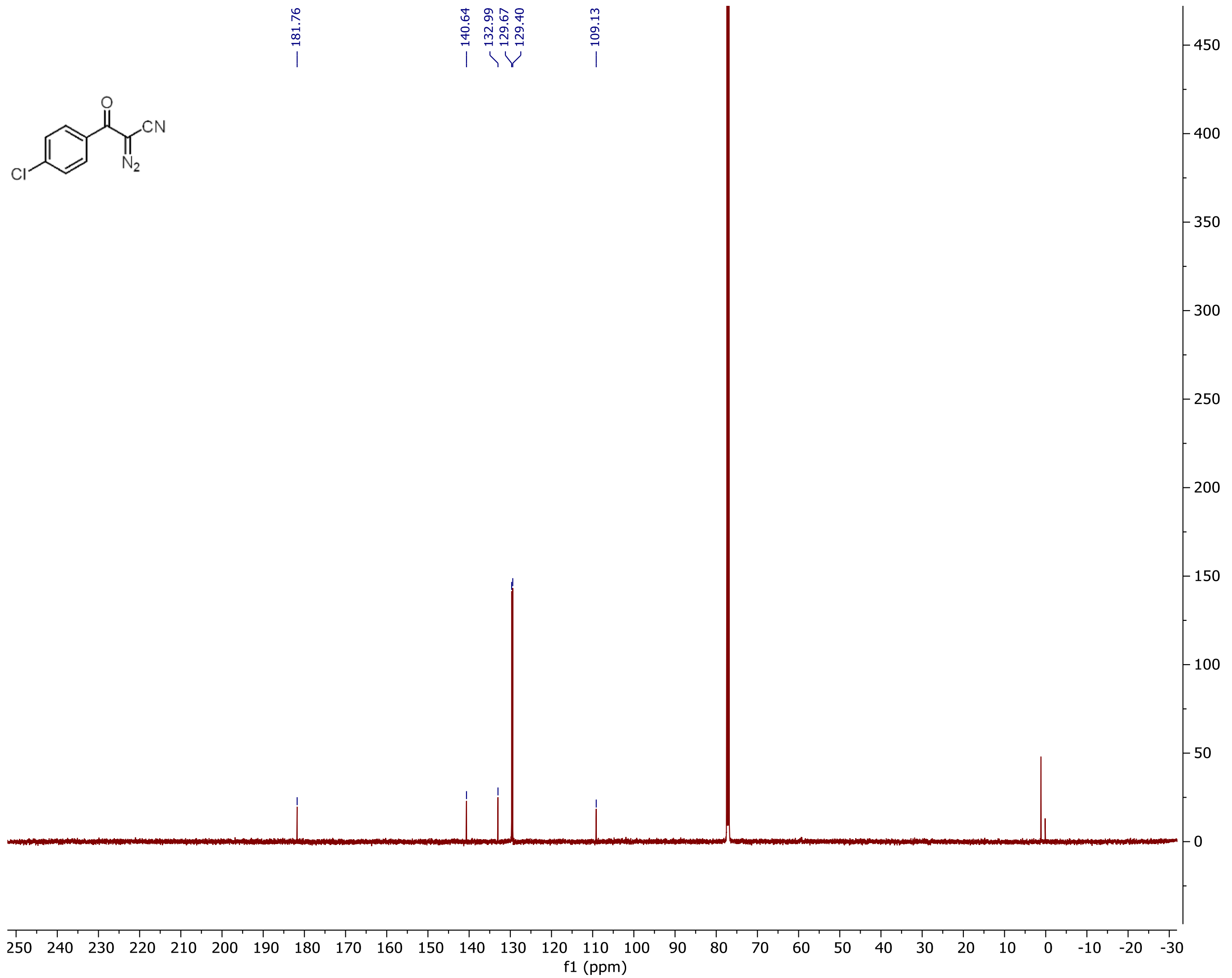
Precursor to **7c.** ^{13}C NMR (126 MHz, $CDCl_3$)



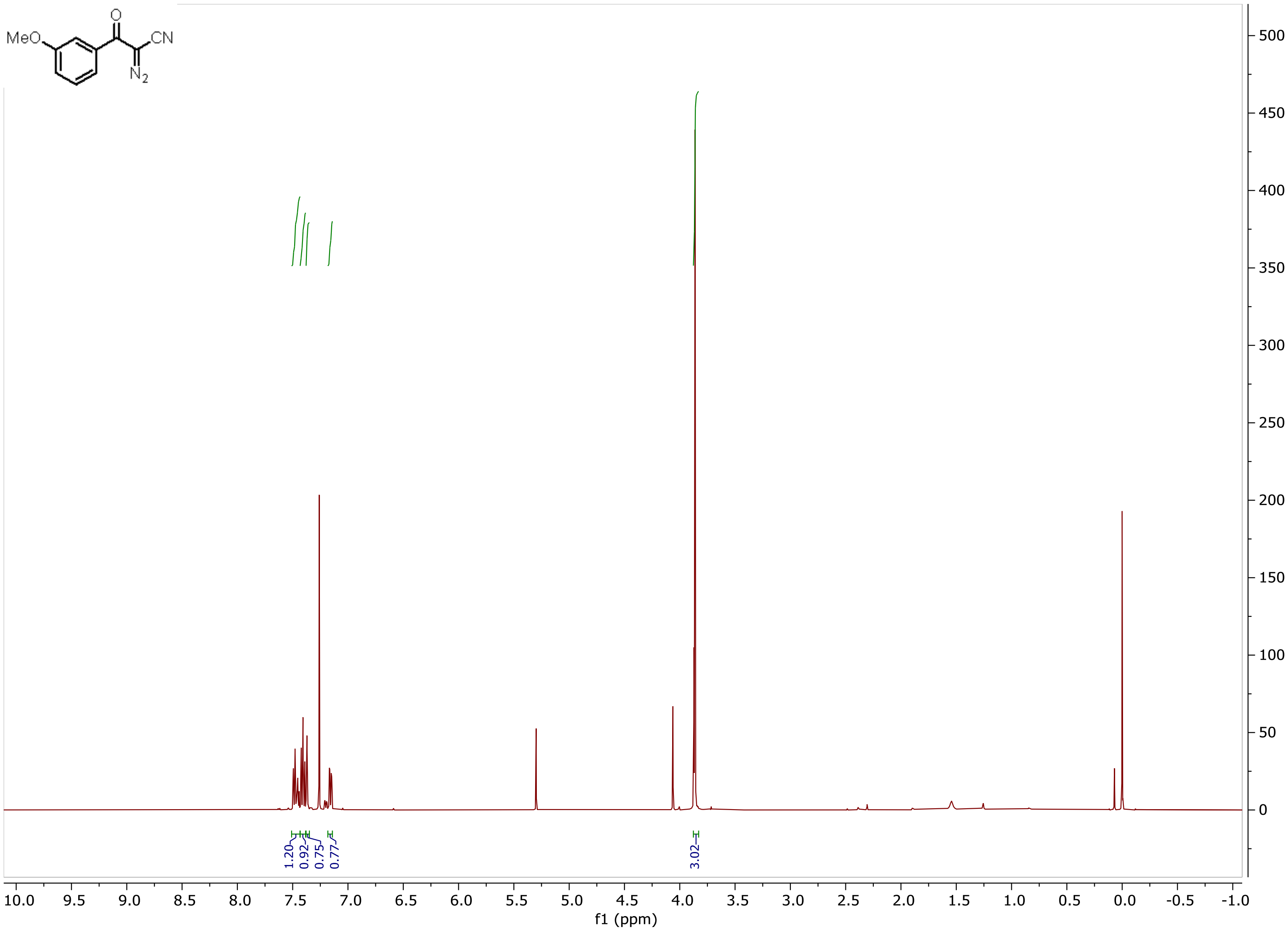
Precursor to **8c.** [1]H NMR (500 MHz, $CDCl_3$)



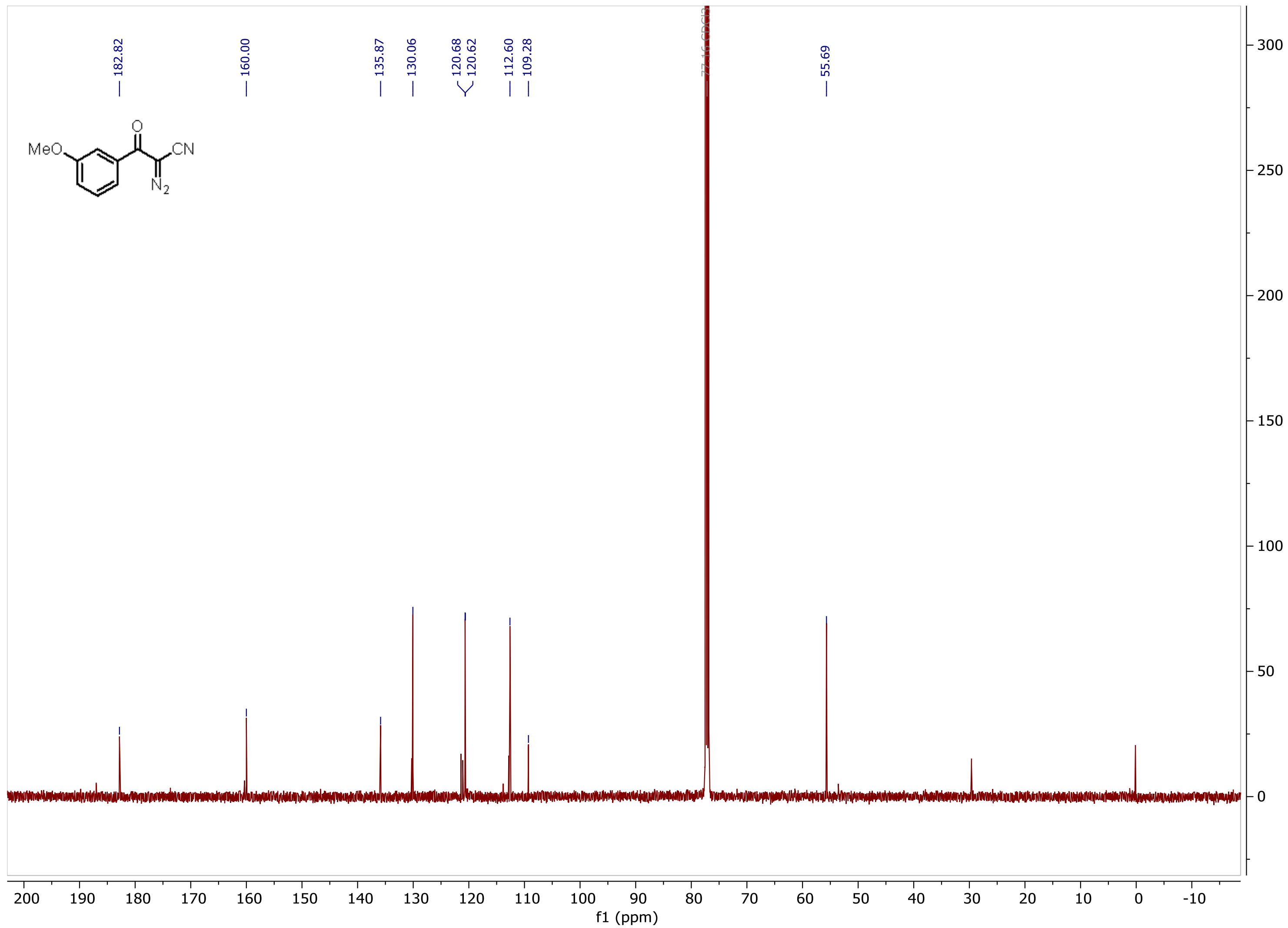
Precursor to **8c.** ^{13}C NMR (500 MHz, $CDCl_3$)



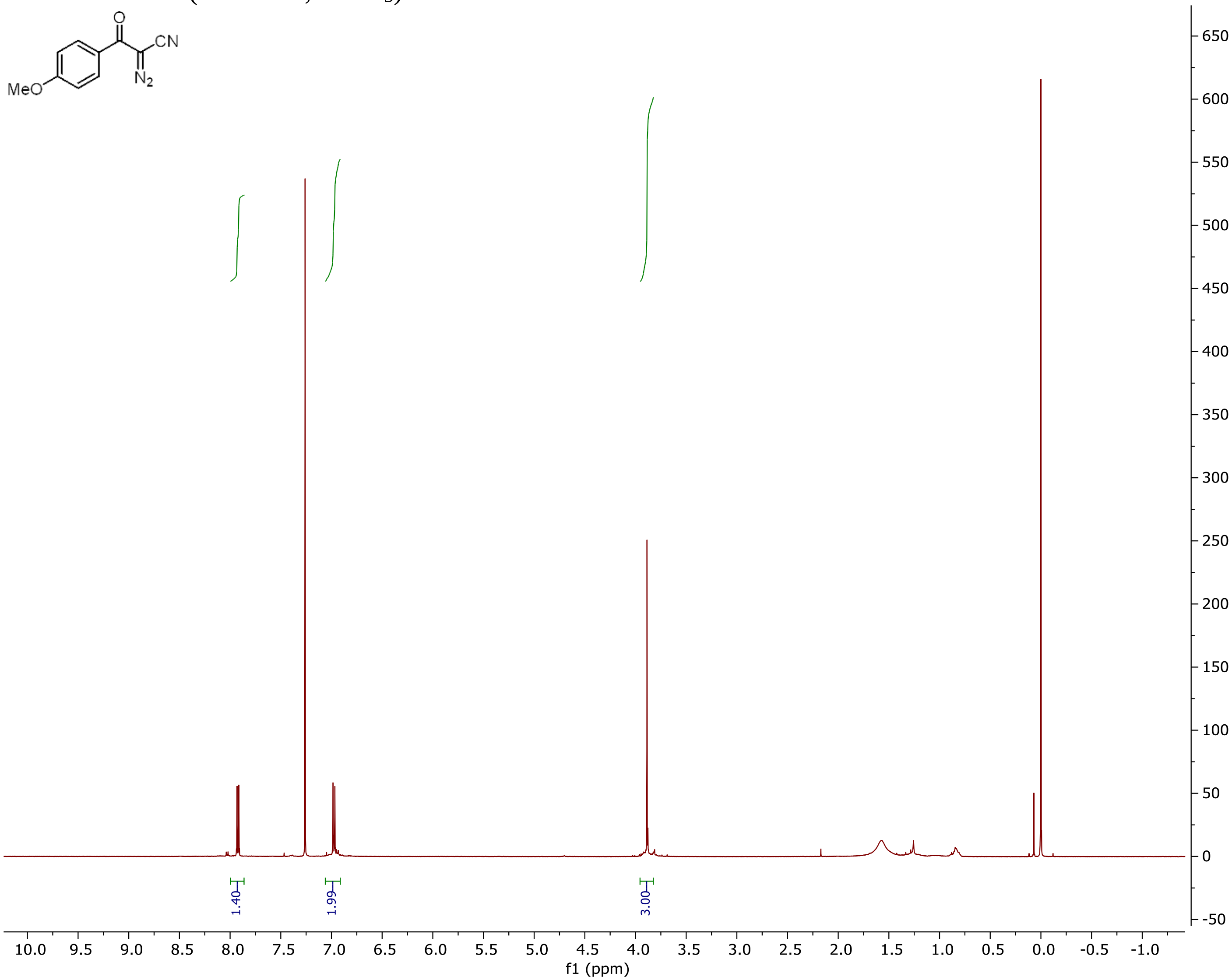
Precursor to **10c.** ^{1}H NMR (500 MHz, $CDCl_3$)



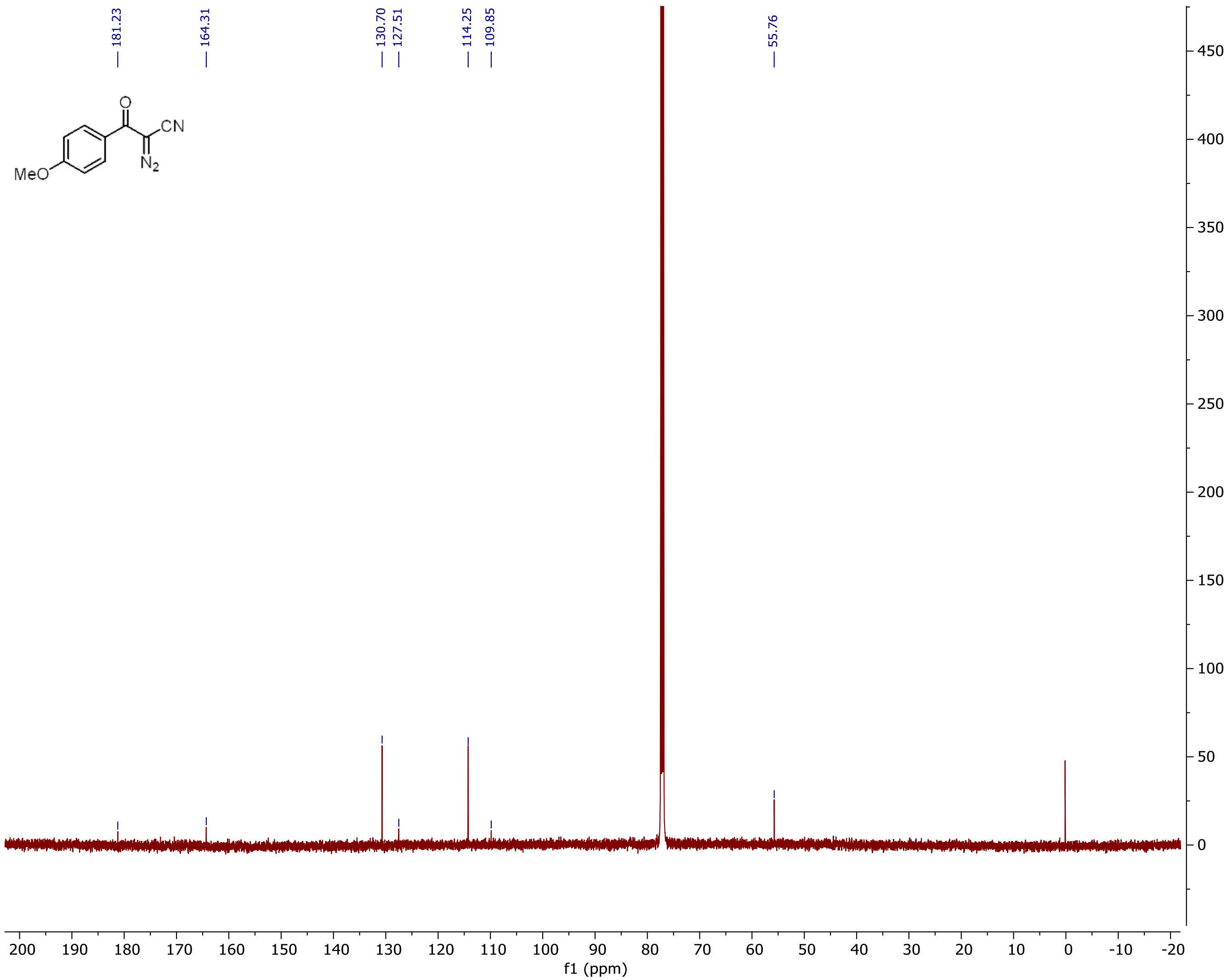
Precursor to **10c.** ^{13}C NMR (126 MHz, $CDCl_3$)



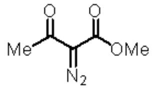
Precursor to **11c.** [1]H NMR (500 MHz, $CDCl_3$)

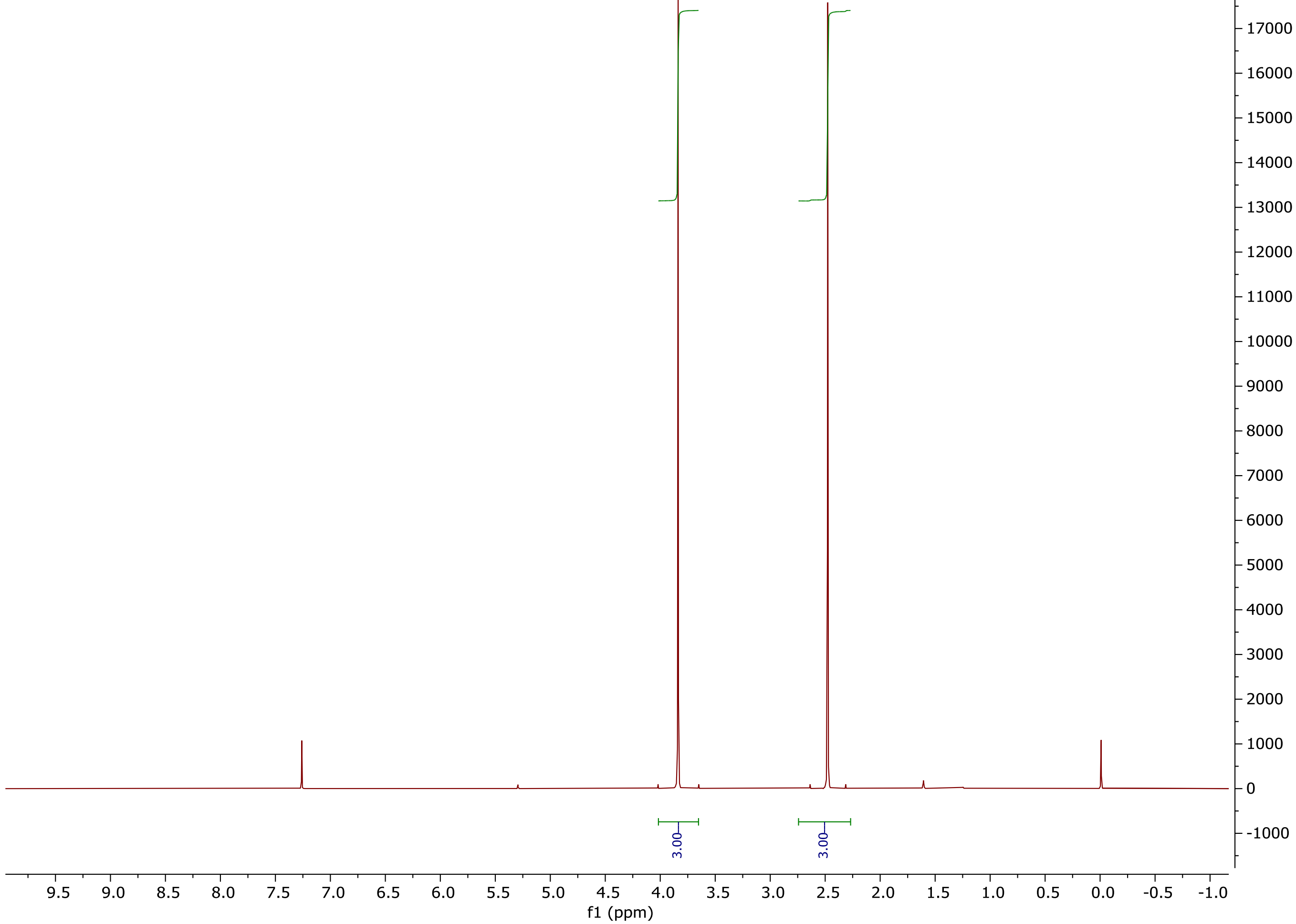


Precursor to **11c.** ^{13}C NMR (126 MHz, $CDCl_3$)

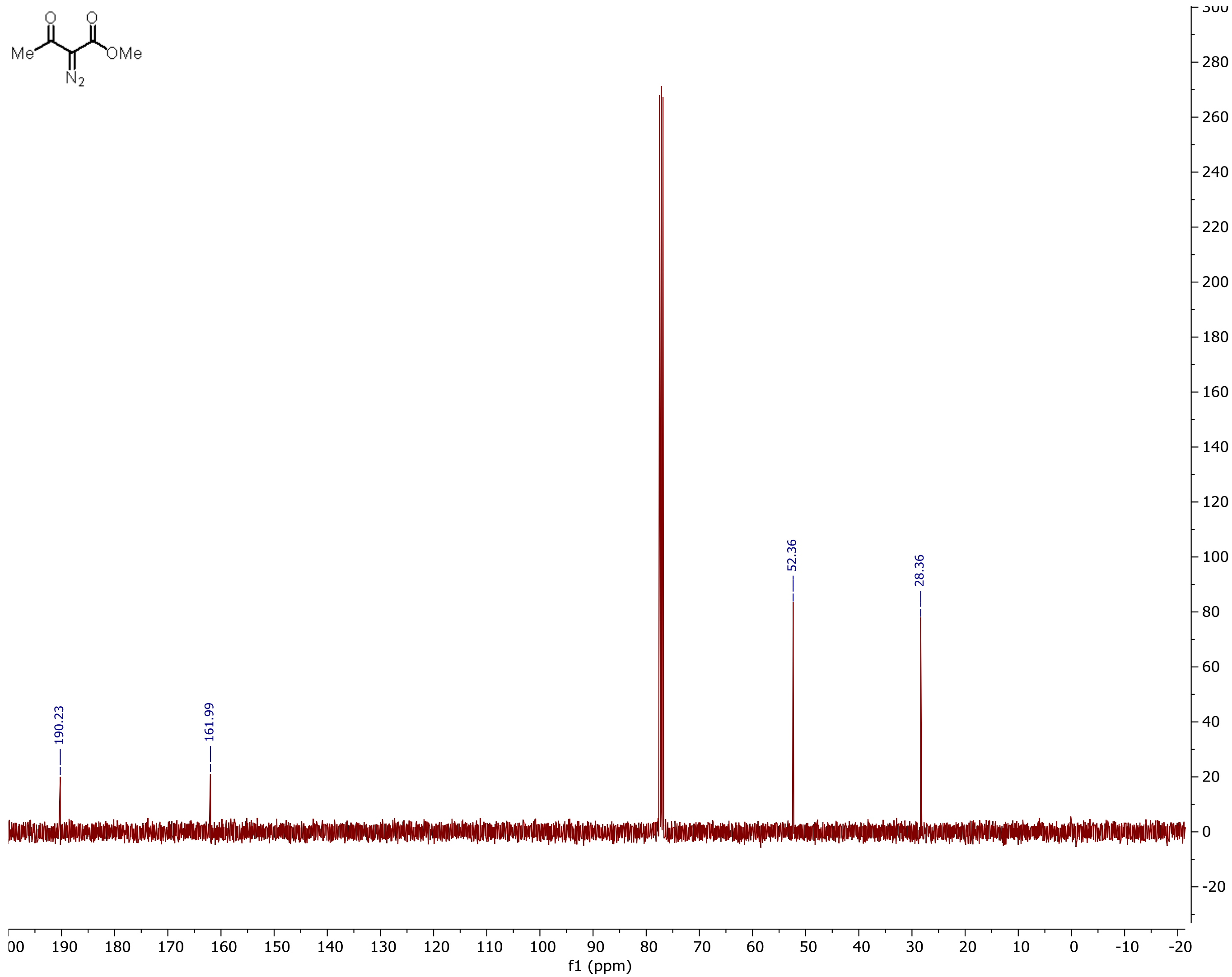


Compound **2e.** ^{1}H NMR (500 MHz, $CDCl_3$)

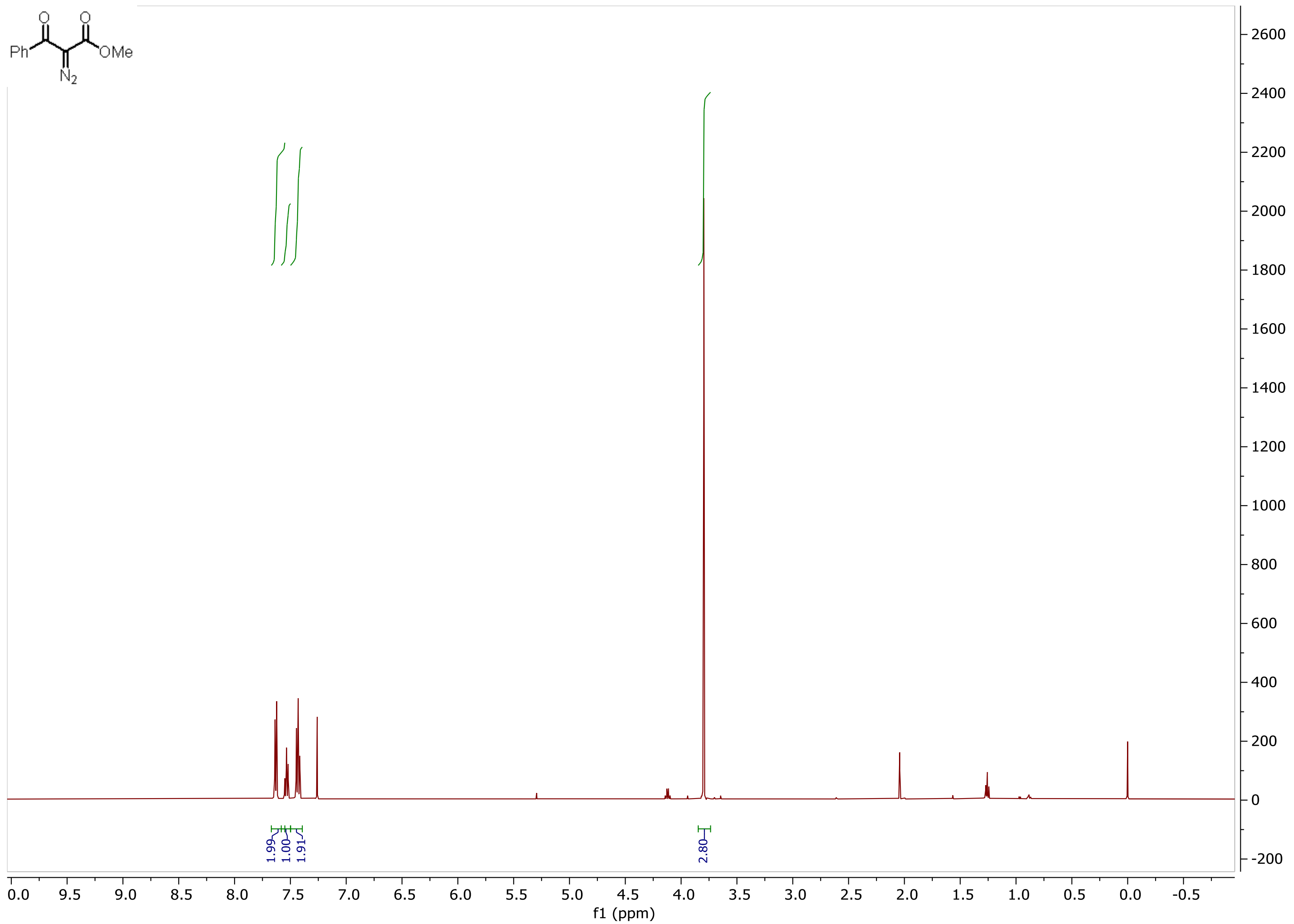




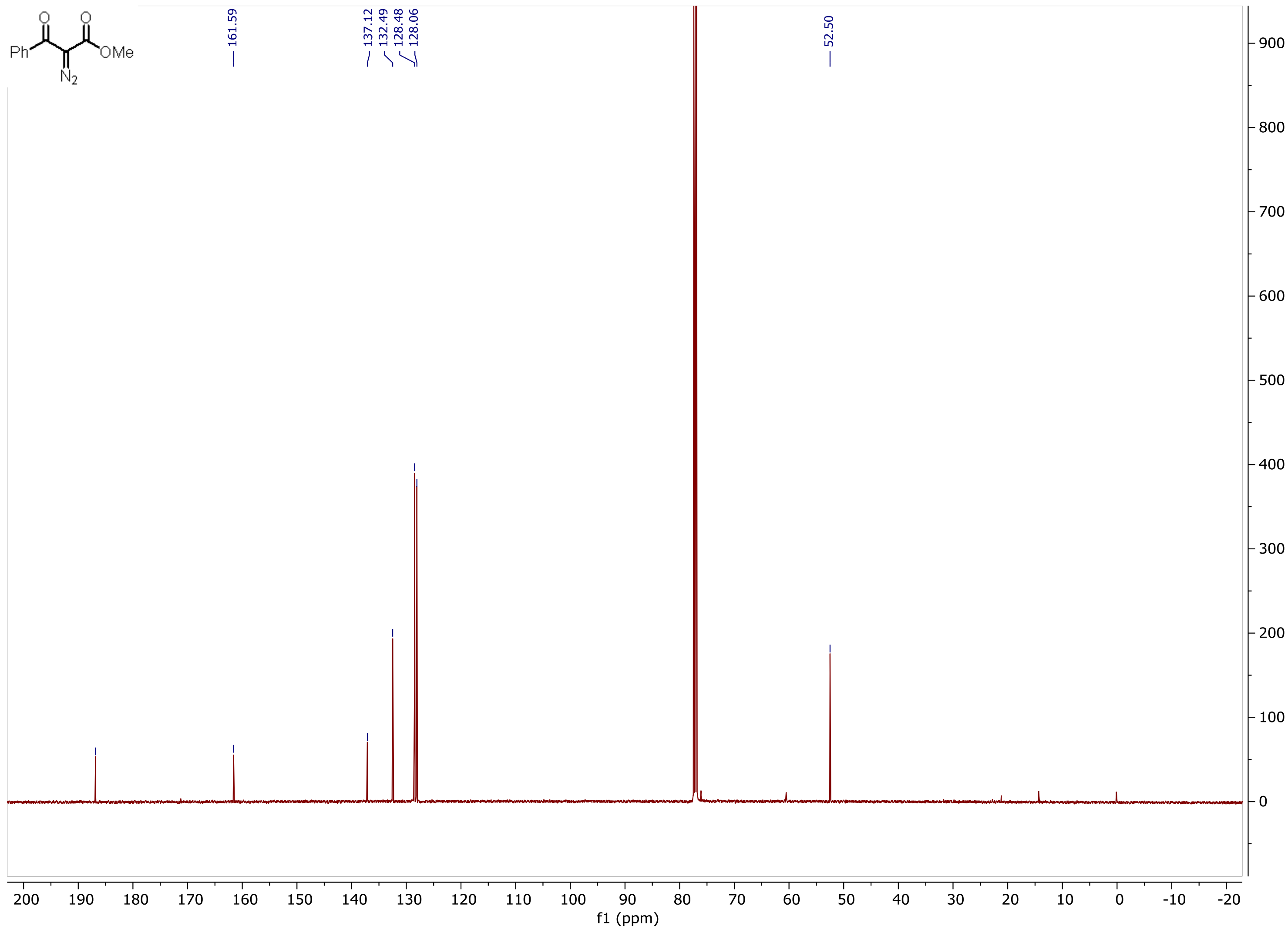
Compound **2e.** ^{13}C NMR (126 MHz, $CDCl_3$)



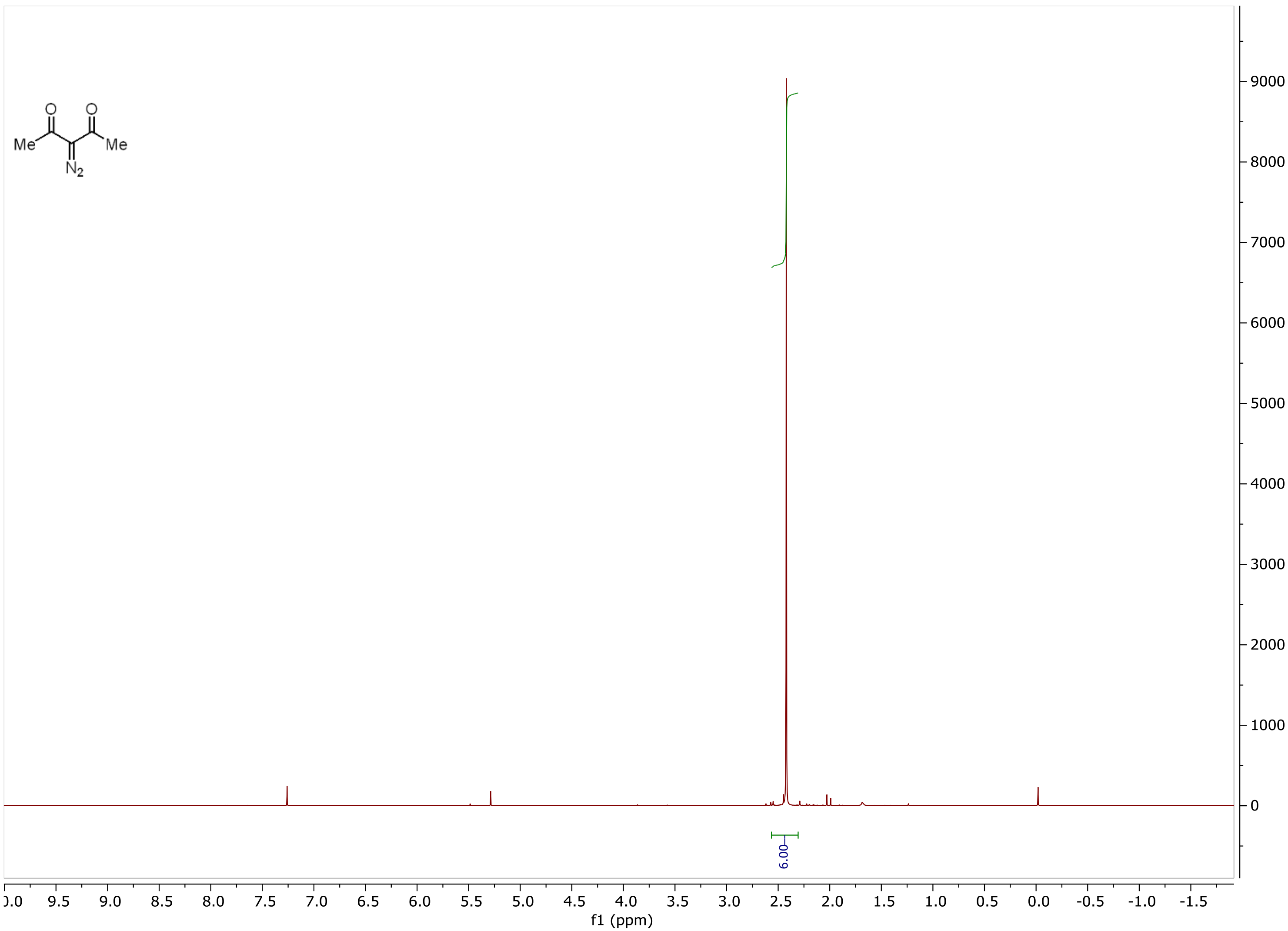
Compound **SI-1.** ^{1}H NMR (500 MHz, $CDCl_3$)



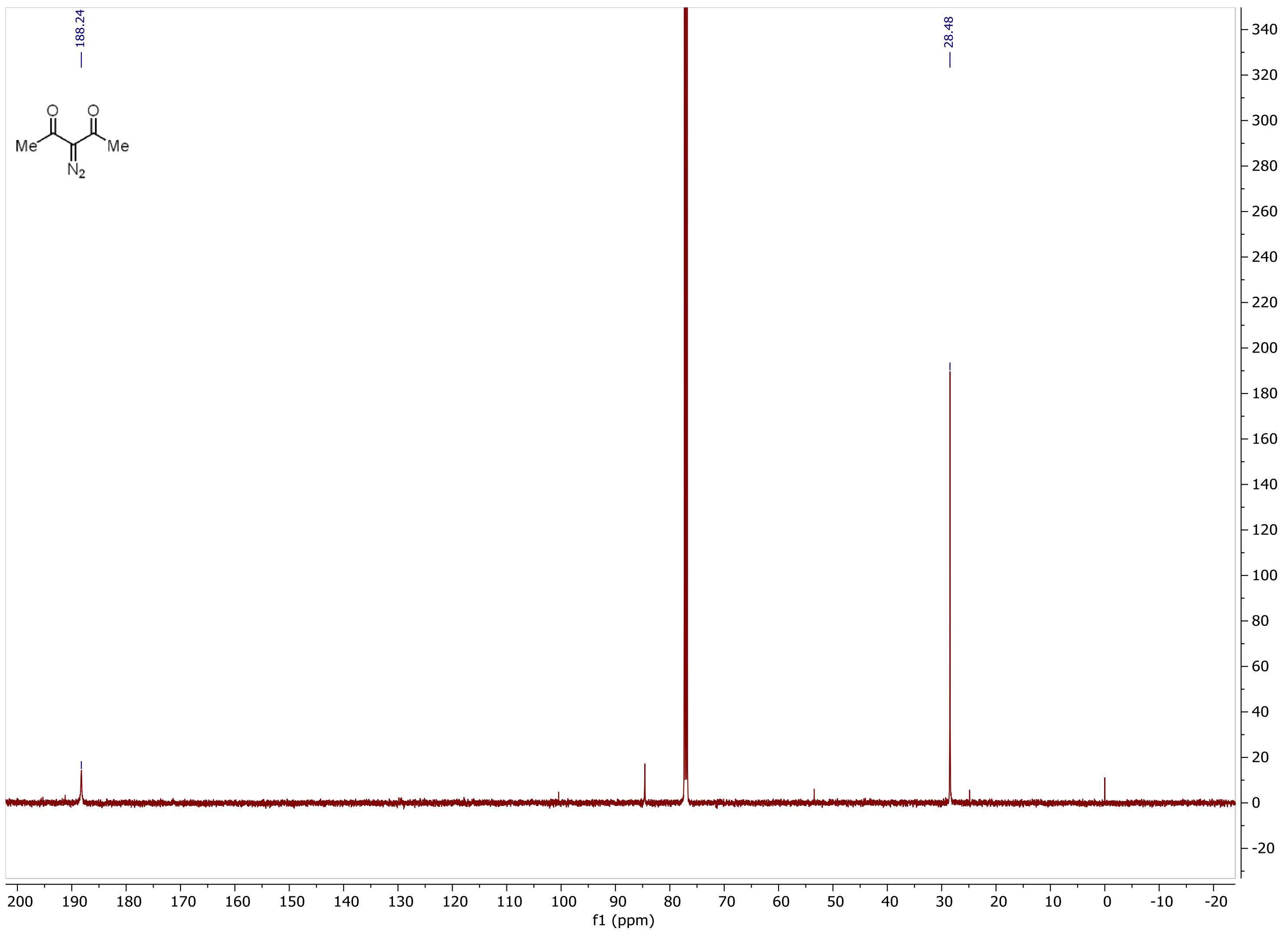
Compound **SI-1.** ^{13}C NMR (126 MHz, $CDCl_3$)



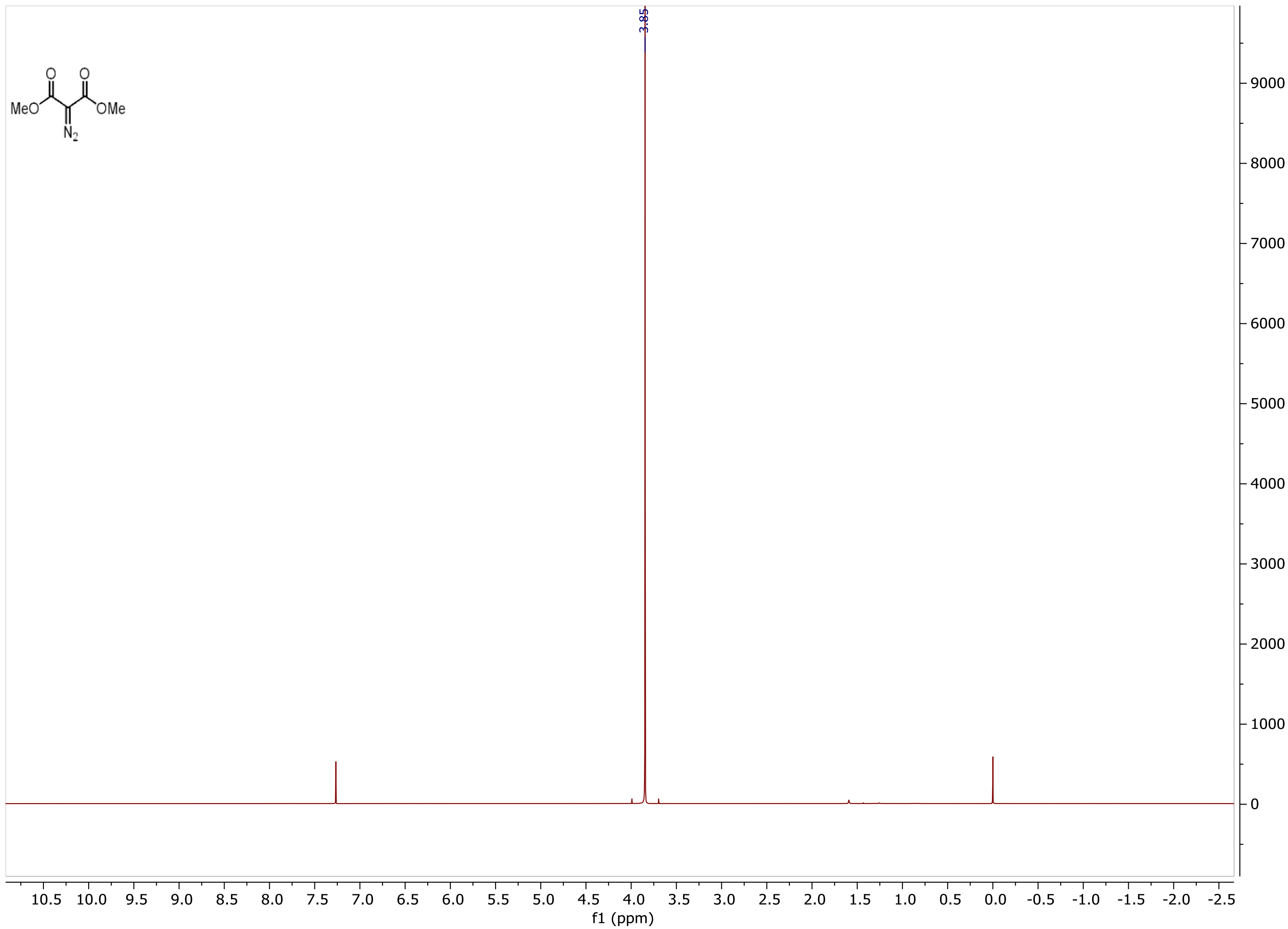
Compound **2f.** ^{1}H NMR (500 MHz, $CDCl_3$)



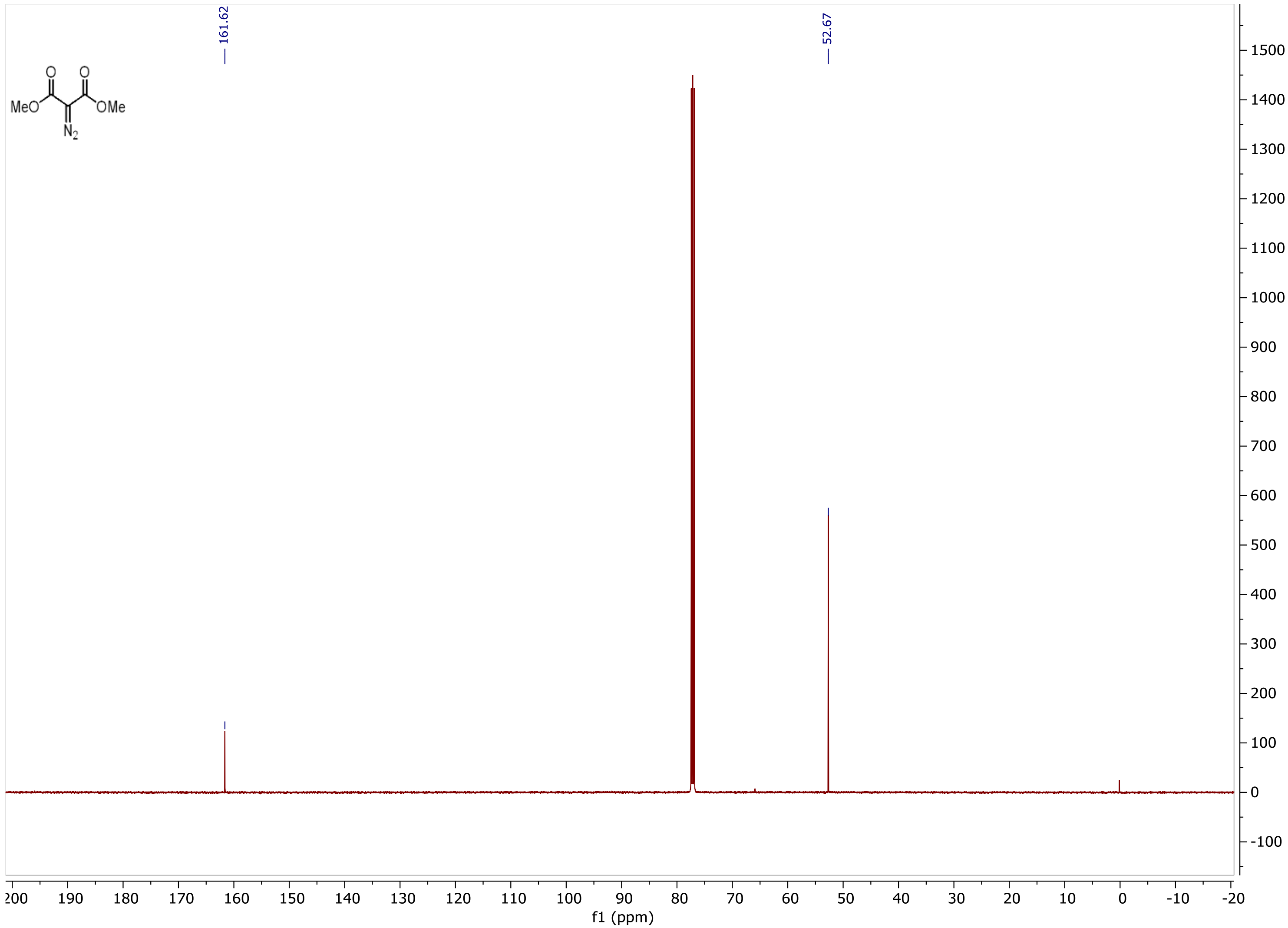
Compound **2f.** ^{13}C NMR (126 MHz, $CDCl_3$)



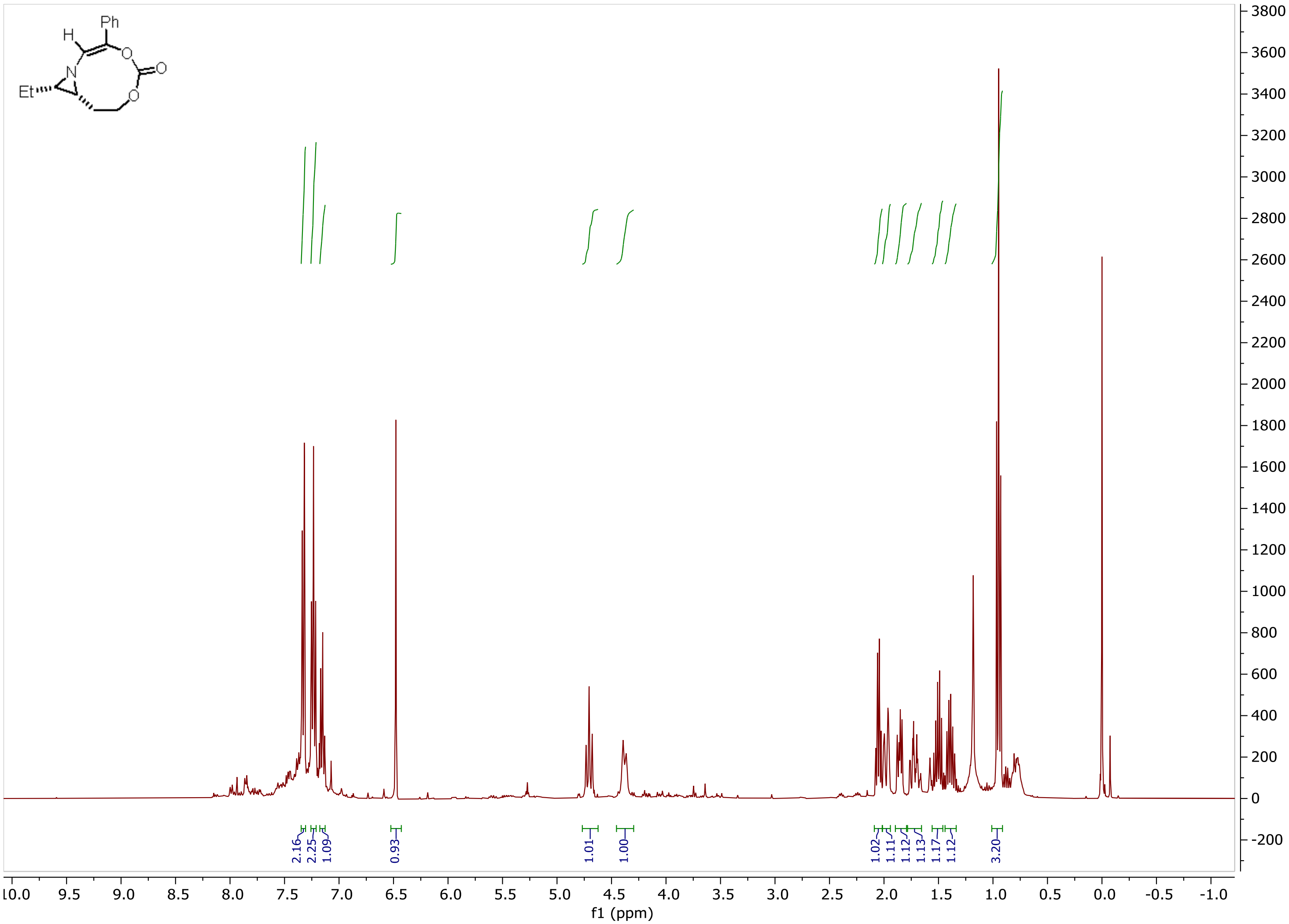
Compound **SI-1.** ^{1}H NMR (500 MHz, $CDCl_3$)



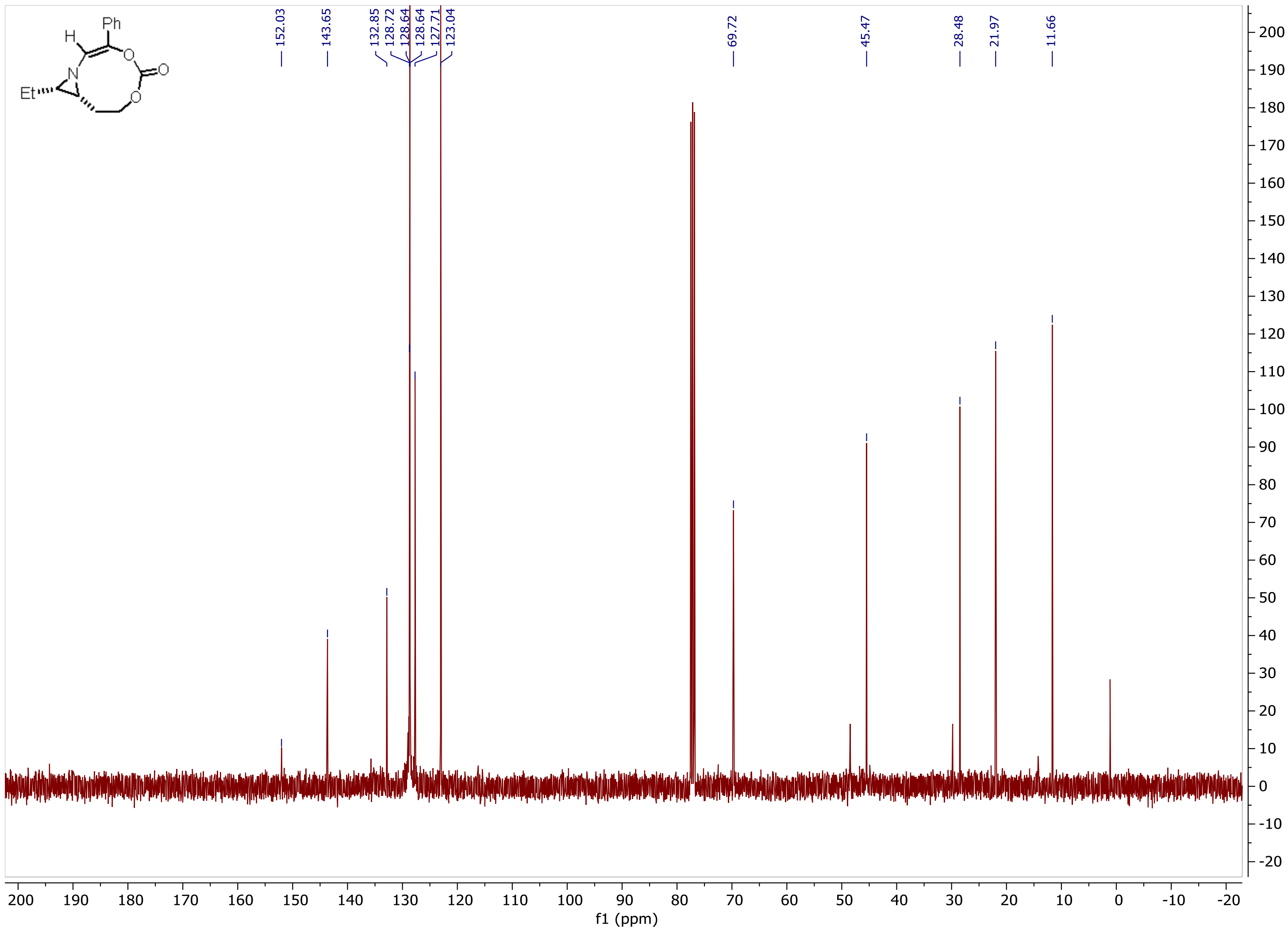
Compound **SI-1.** ^{13}C NMR (126 MHz, $CDCl_3$)



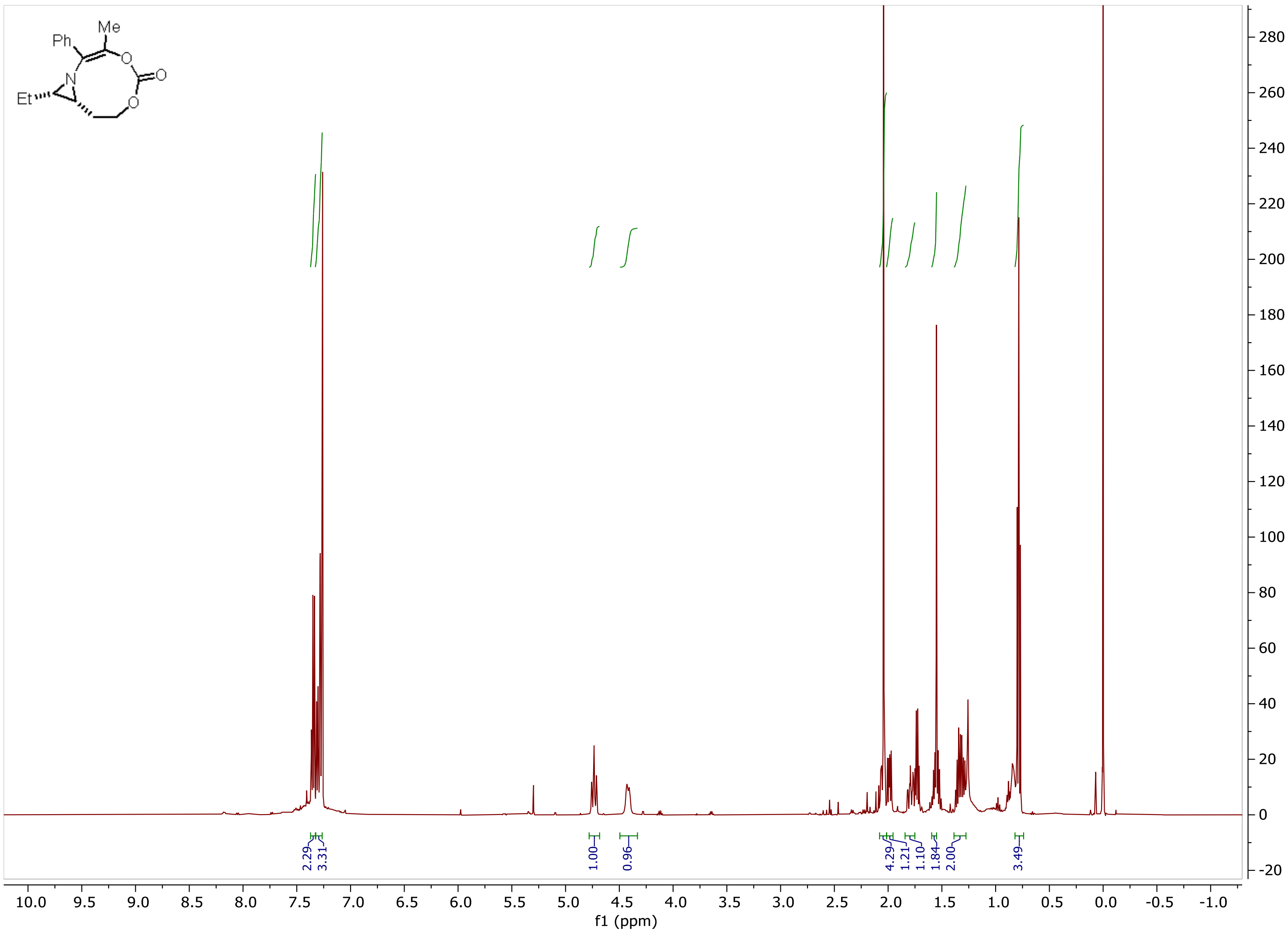
Compound **3a.** [1]H NMR (500 MHz, $CDCl_3$)



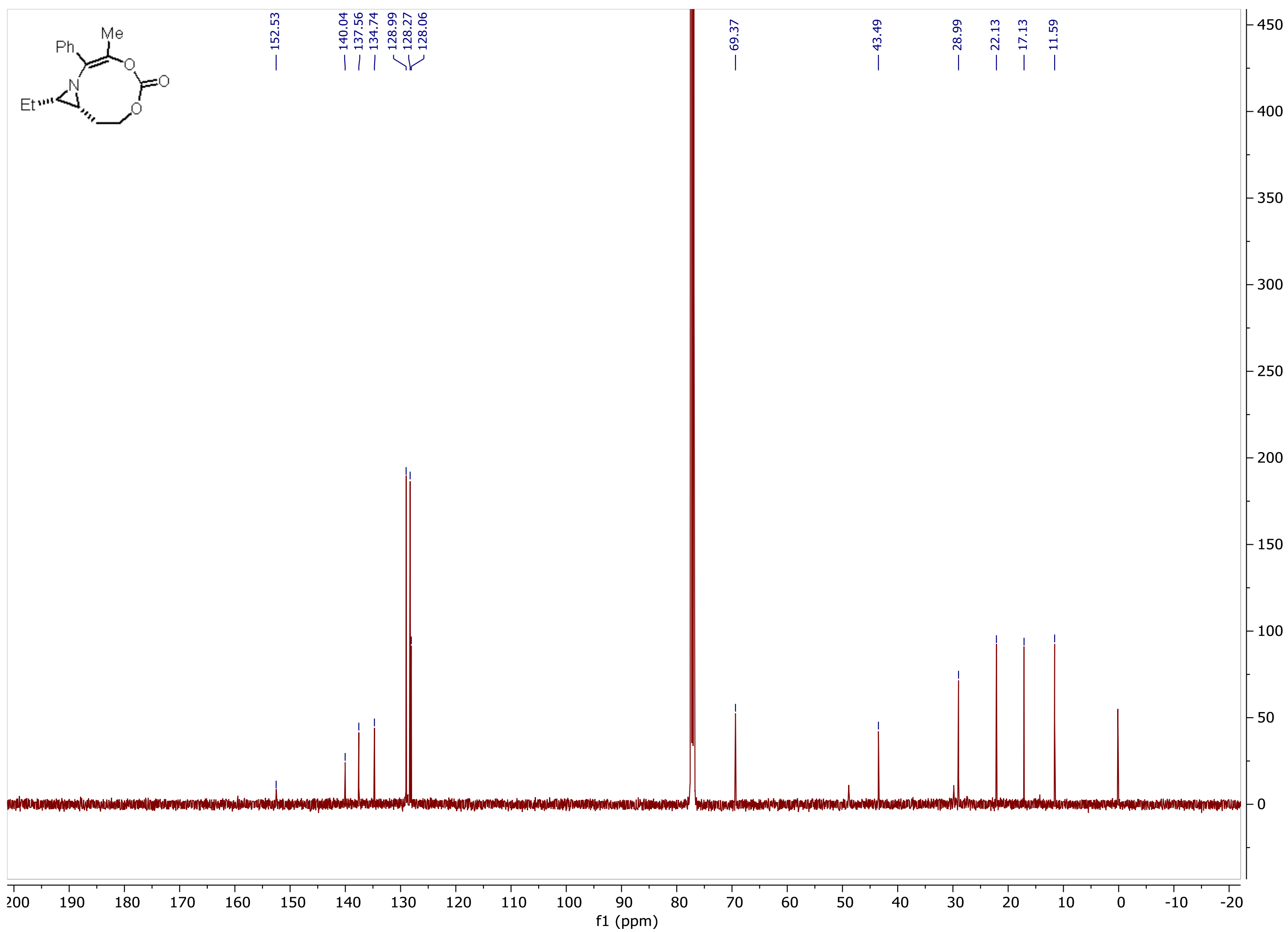
Compound **3a.** [13]C NMR (126 MHz, $CDCl_3$)



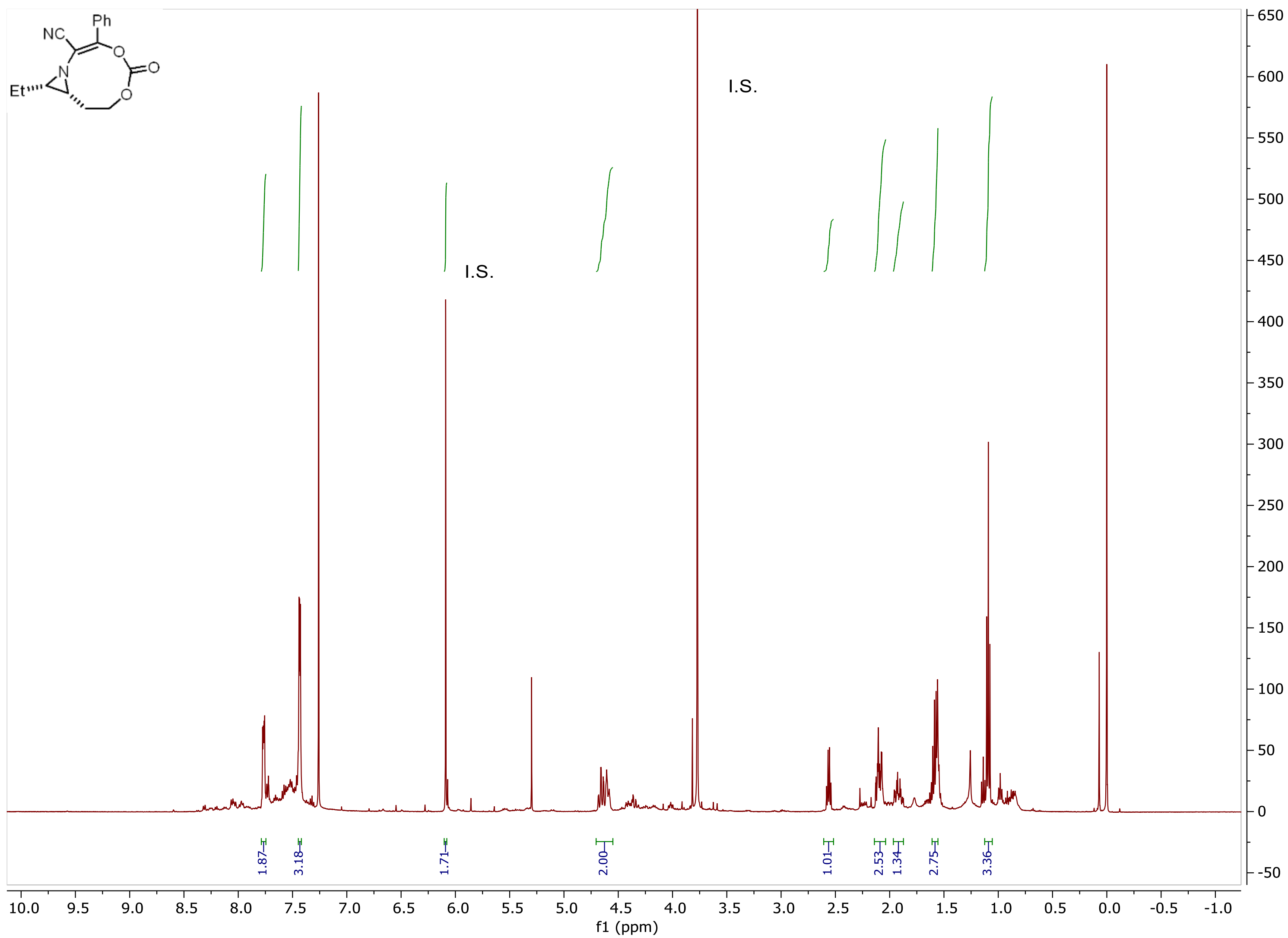
Compound **3b.** ^{1}H NMR (500 MHz, $CDCl_3$)



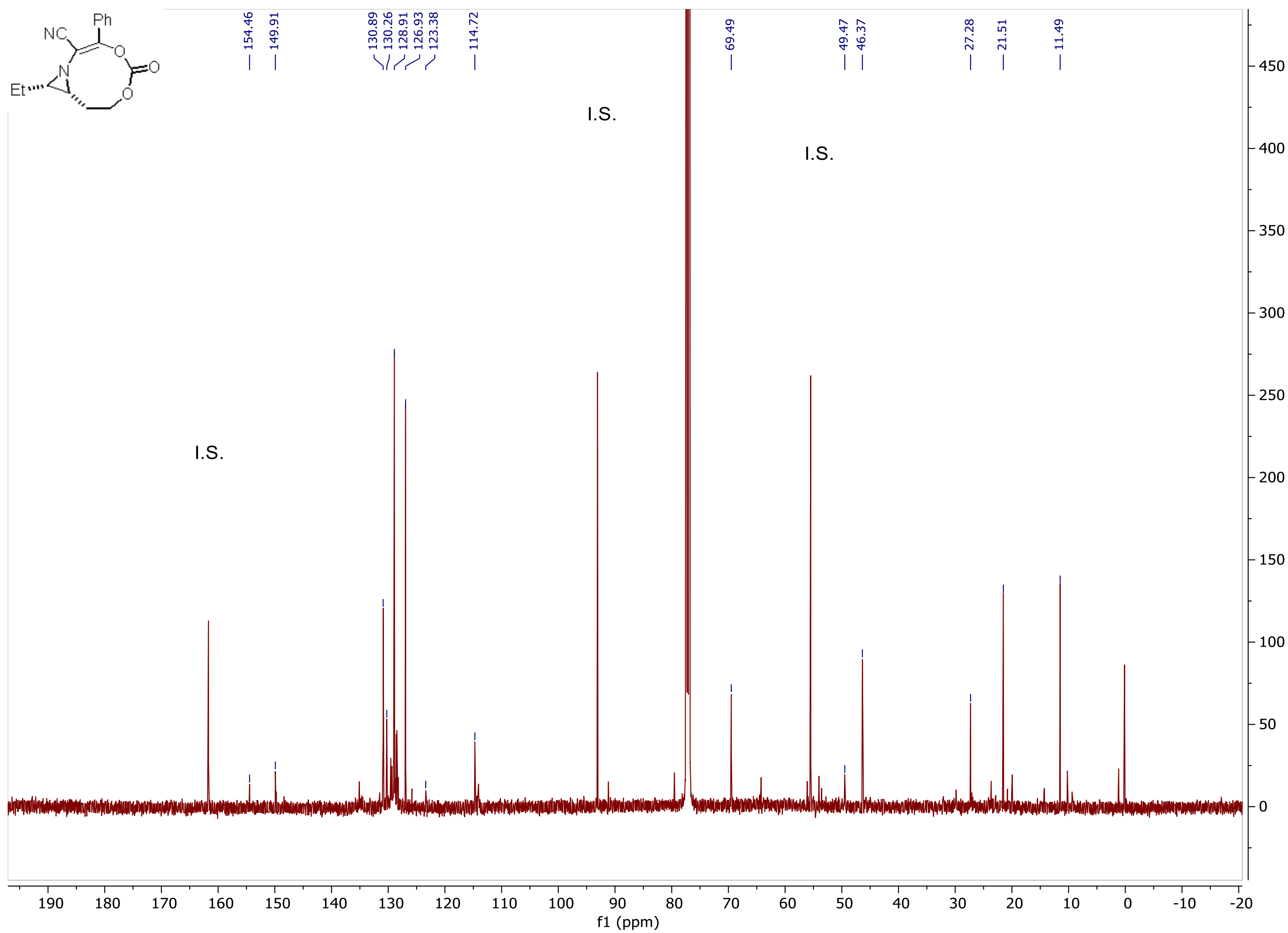
Compound **3b.** ^{13}C NMR (126 MHz, $CDCl_3$)



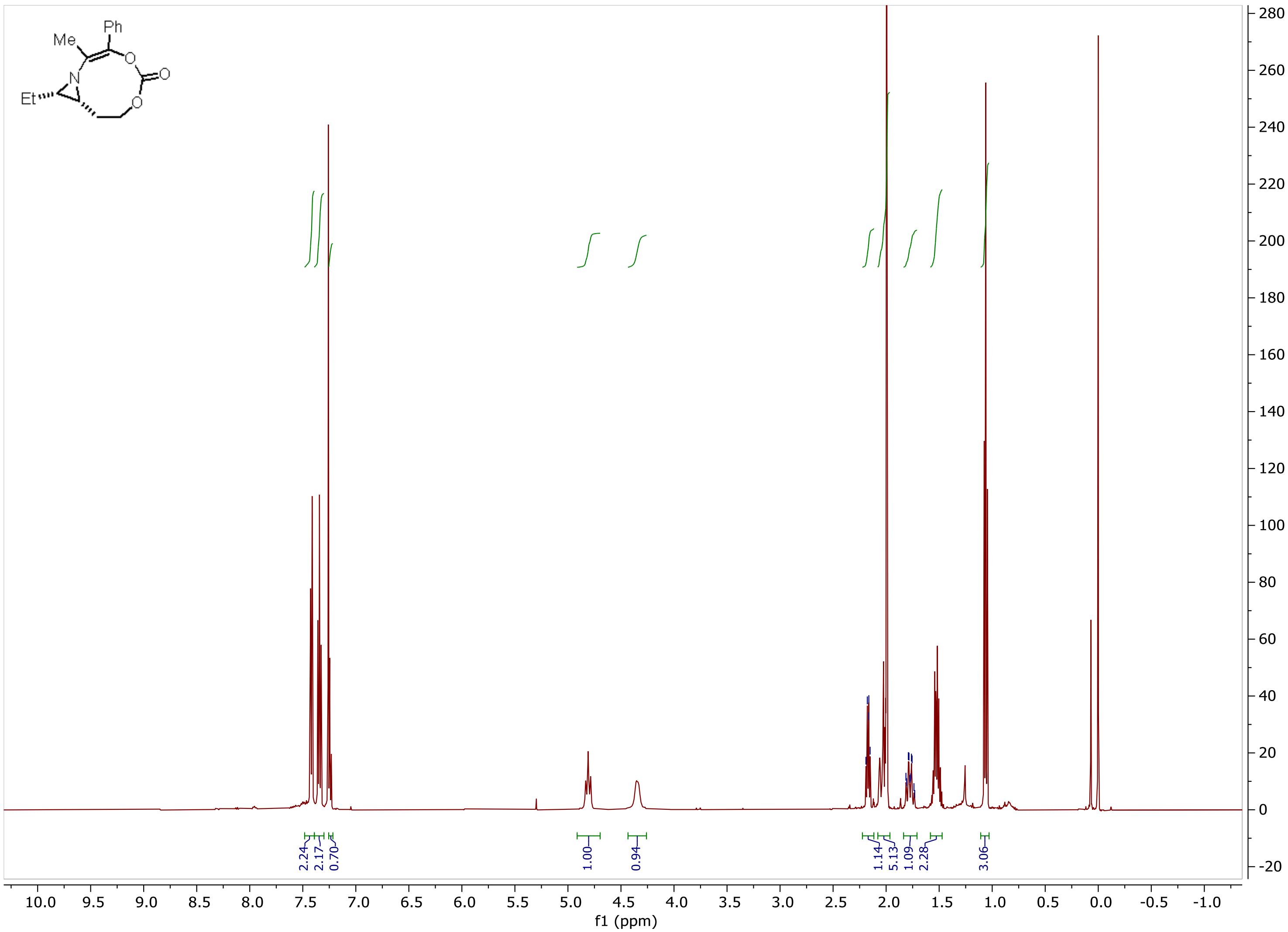
Compound **3c.** ^{1}H NMR (500 MHz, $CDCl_3$)



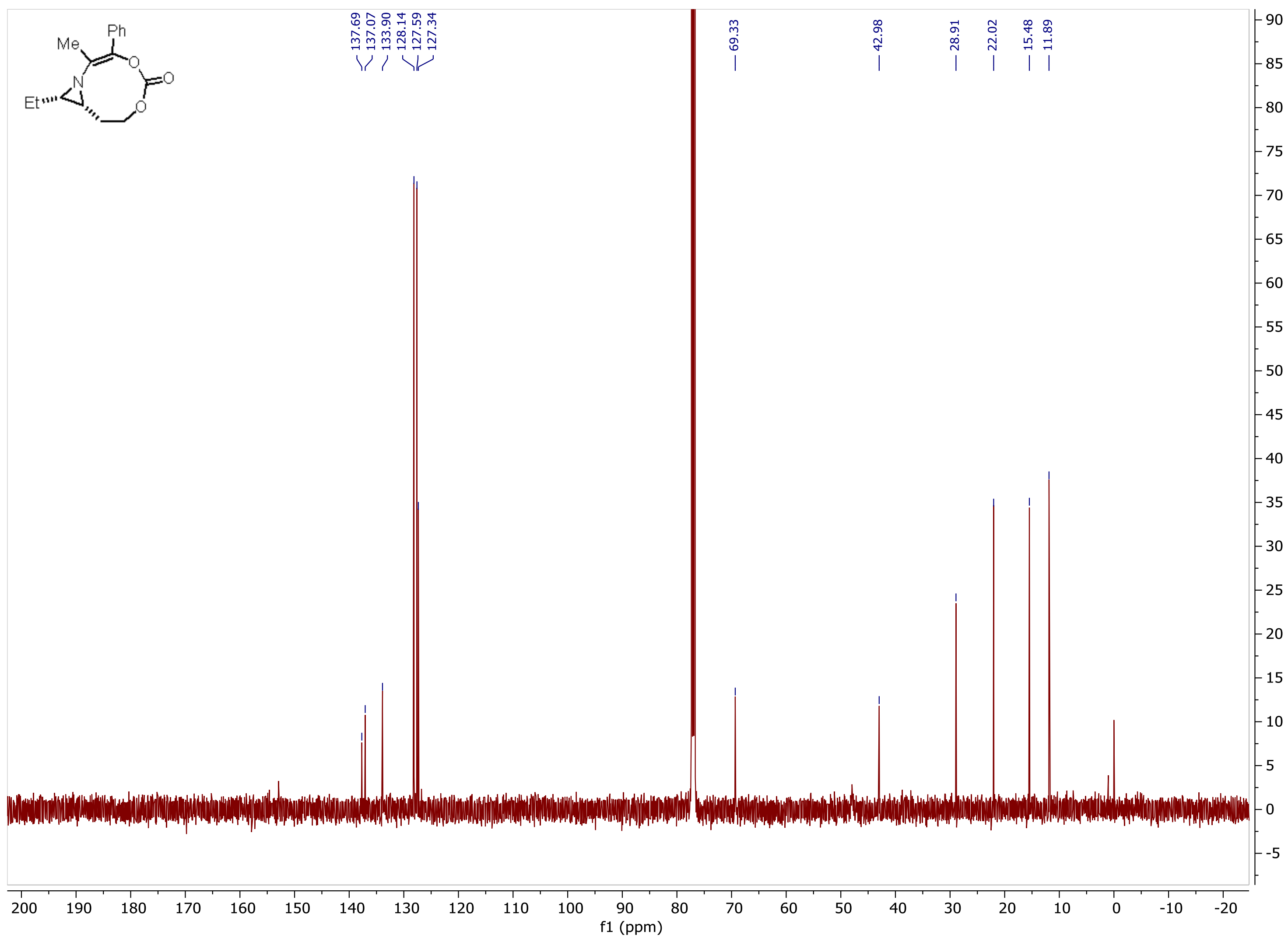
Compound **3c.** ^{13}C NMR (126 MHz, $CDCl_3$)



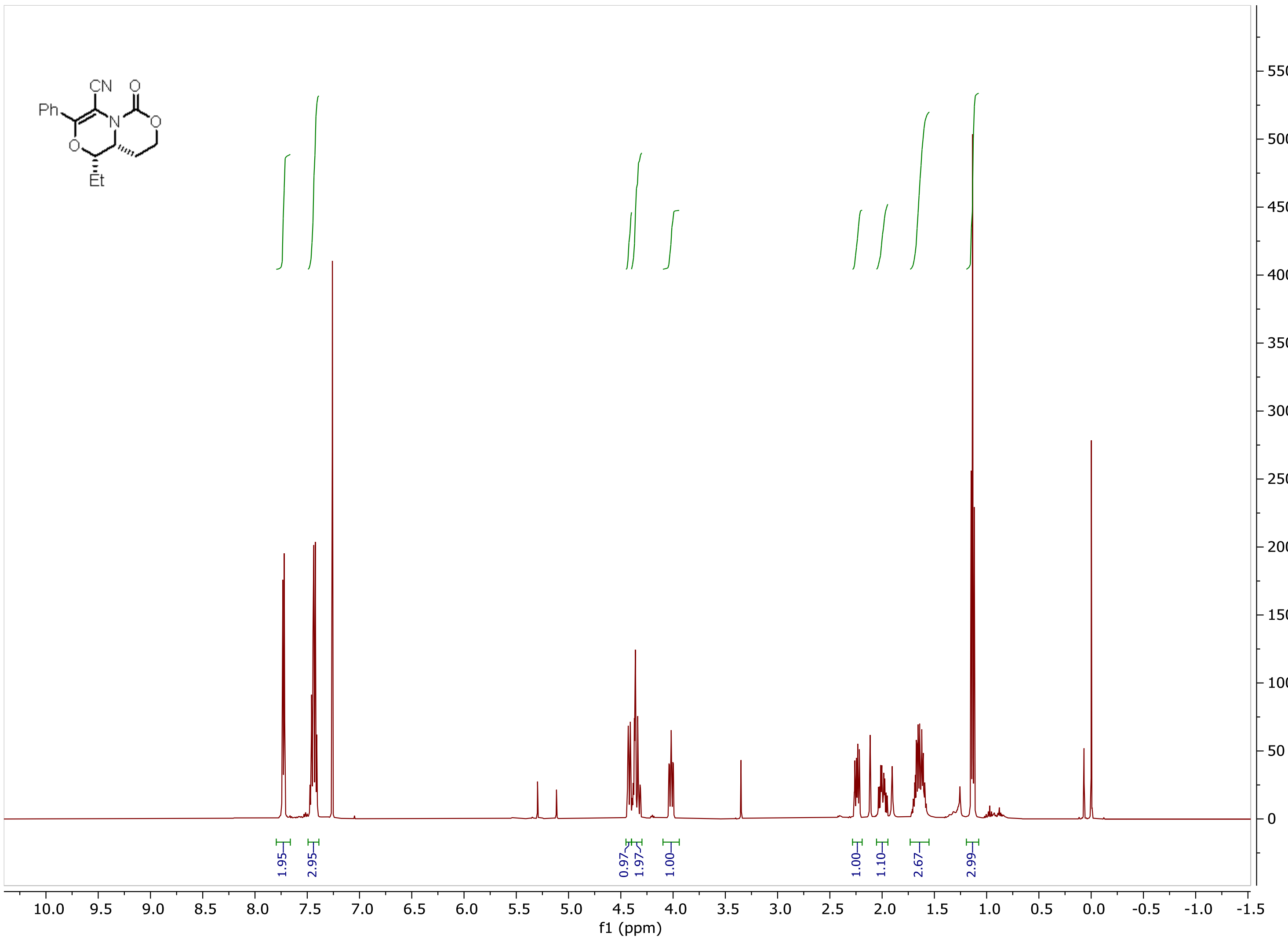
Compound **3d.** [1]H NMR (500 MHz, $CDCl_3$)



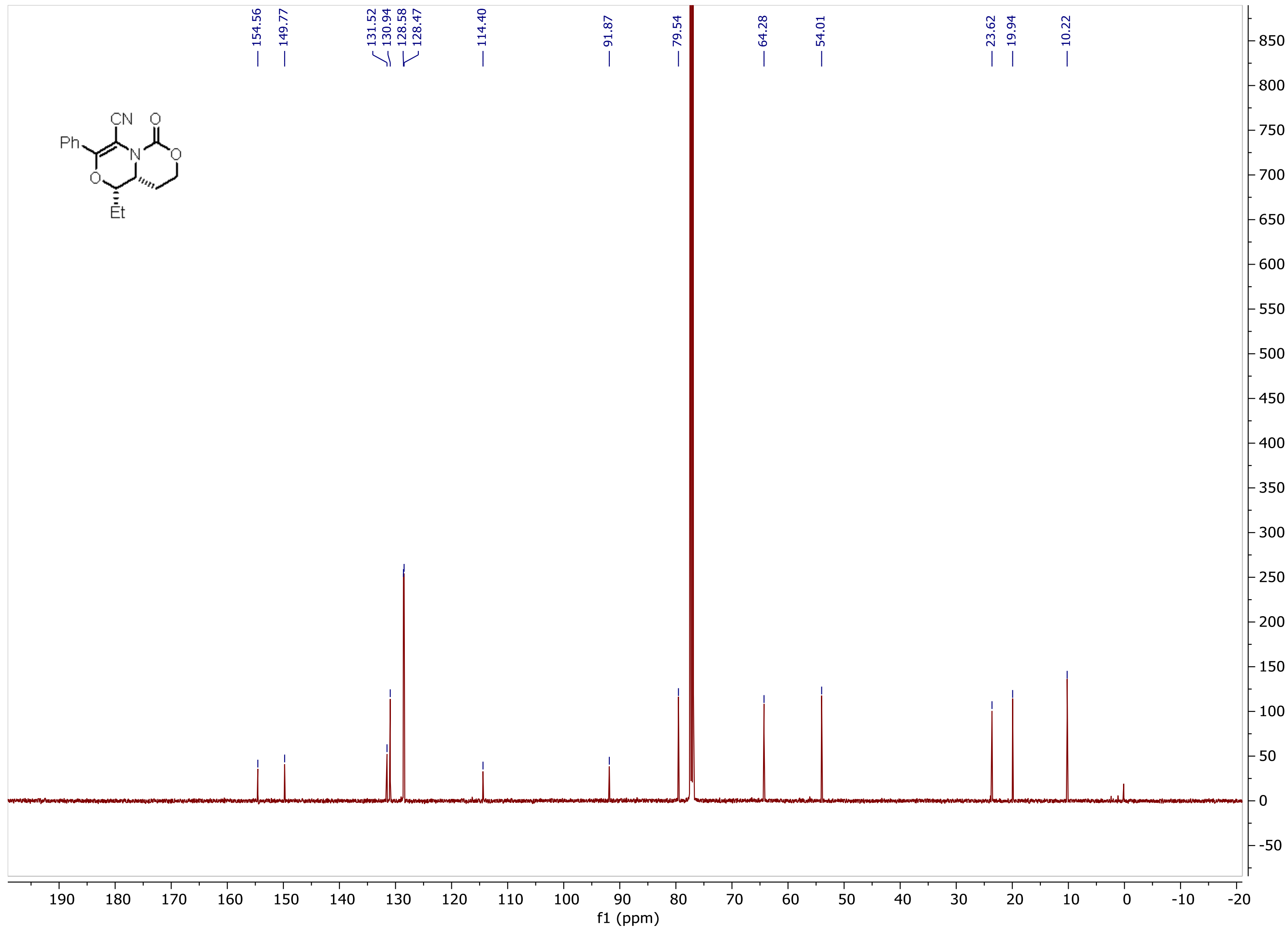
Compound **3d.** ^{13}C NMR (126 MHz, $CDCl_3$)



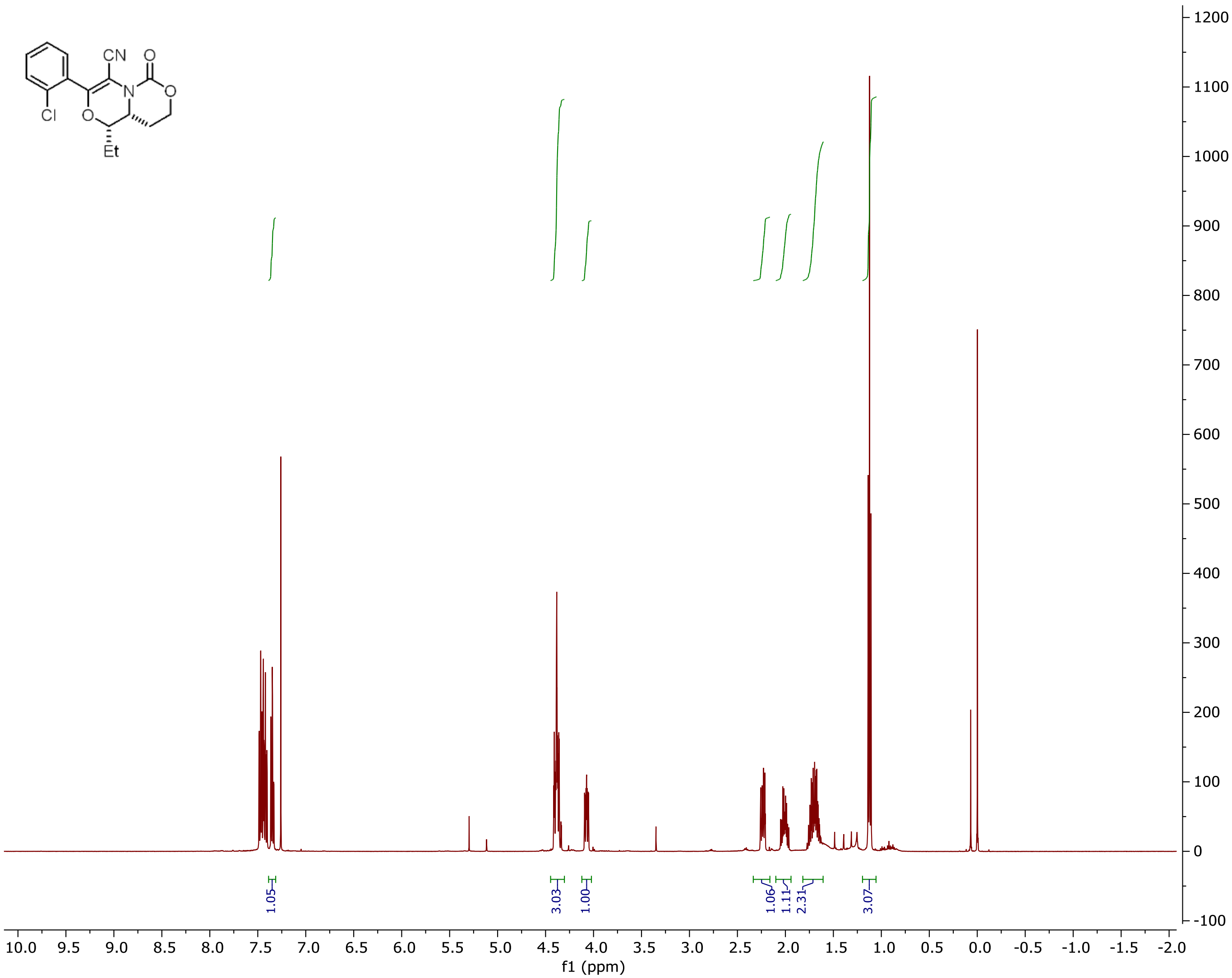
Compound **4c**. ^{1}H NMR (500 MHz, $CDCl_3$)



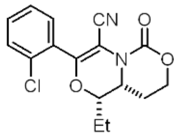
Compound **4c**. ^{13}C NMR (126 MHz, $CDCl_3$)

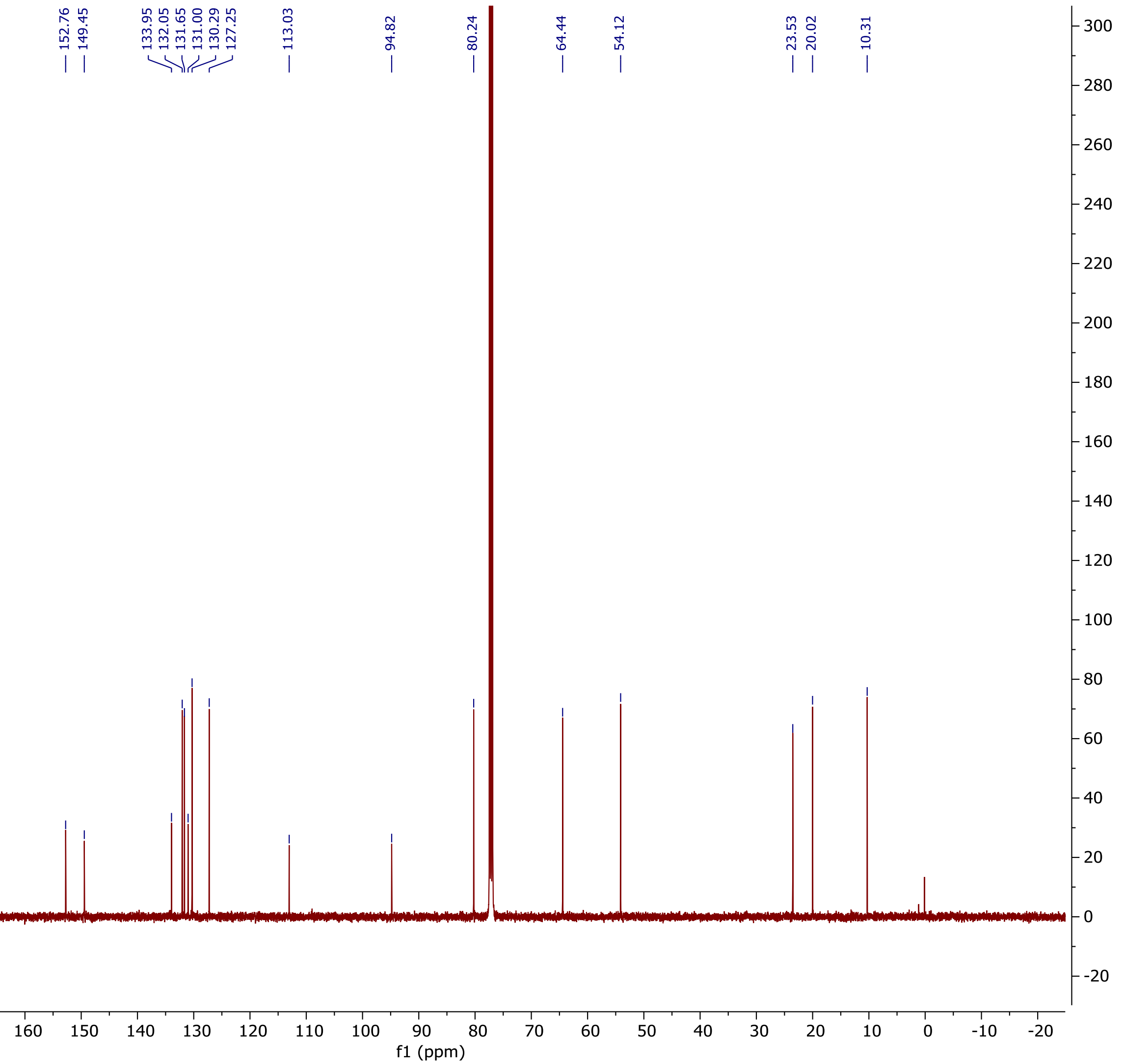


Compound **6c.** ^{1}H NMR (500 MHz, $CDCl_3$)

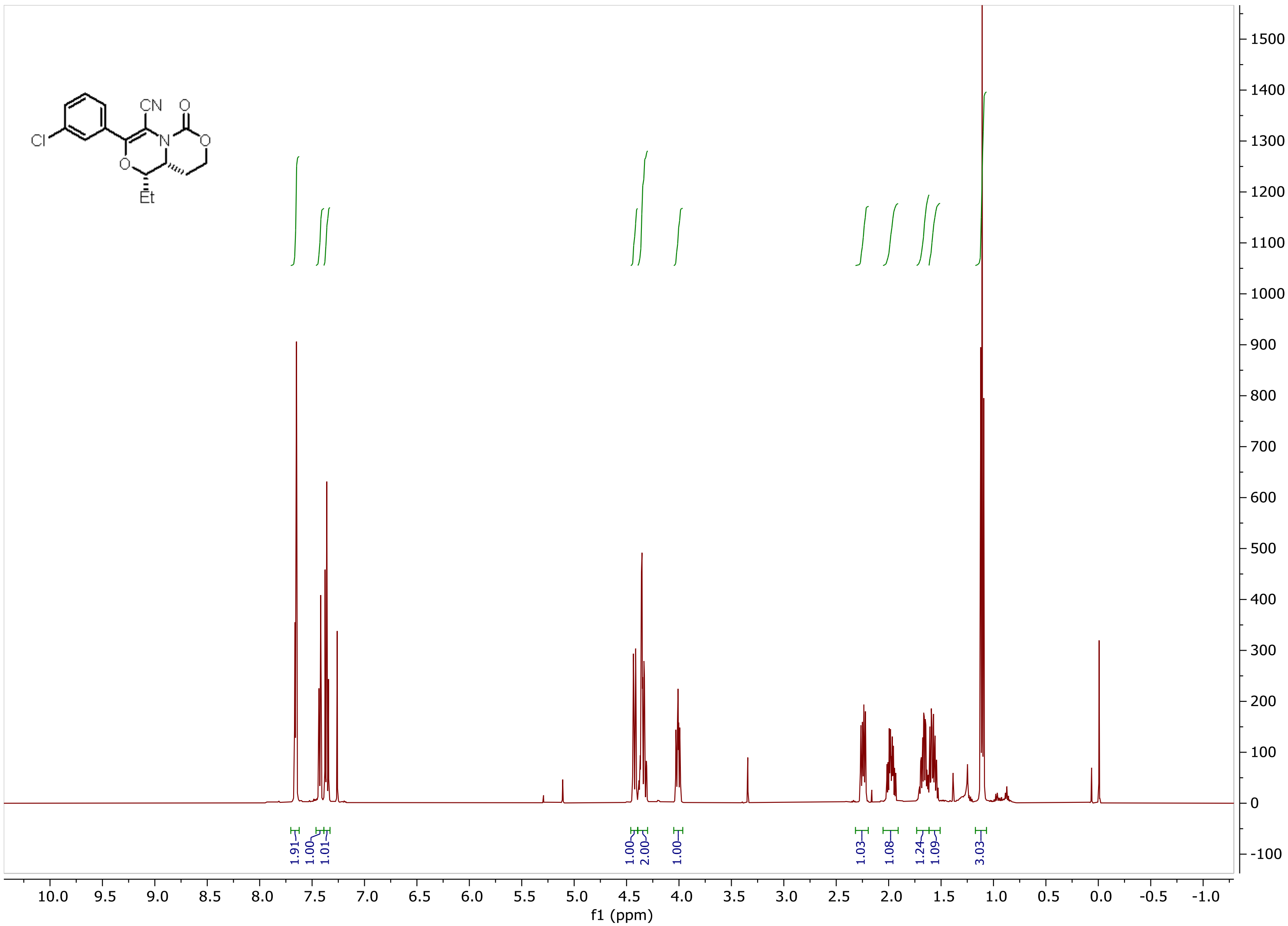


Compound **6c.** ^{13}C NMR (126 MHz, $CDCl_3$)

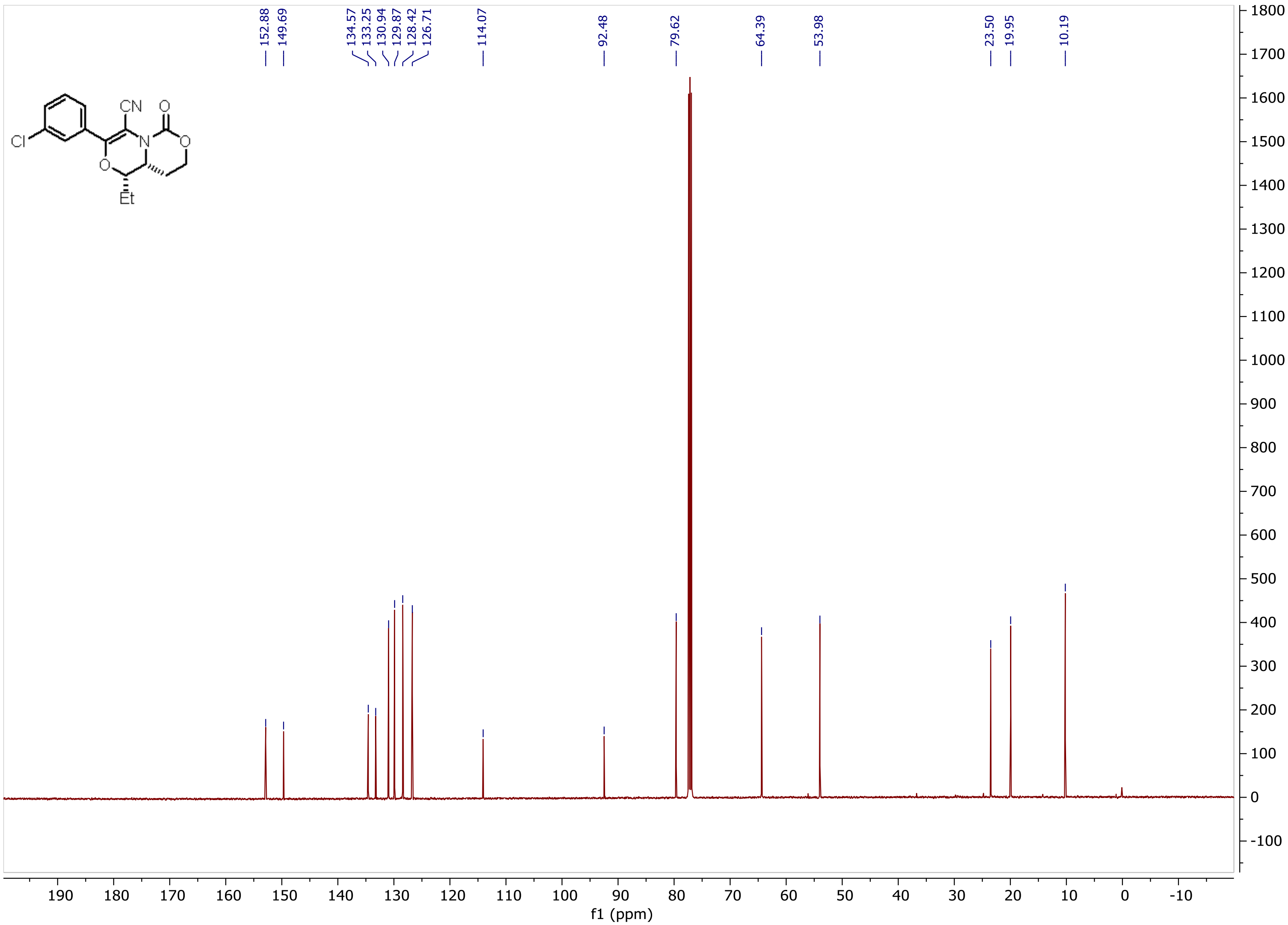




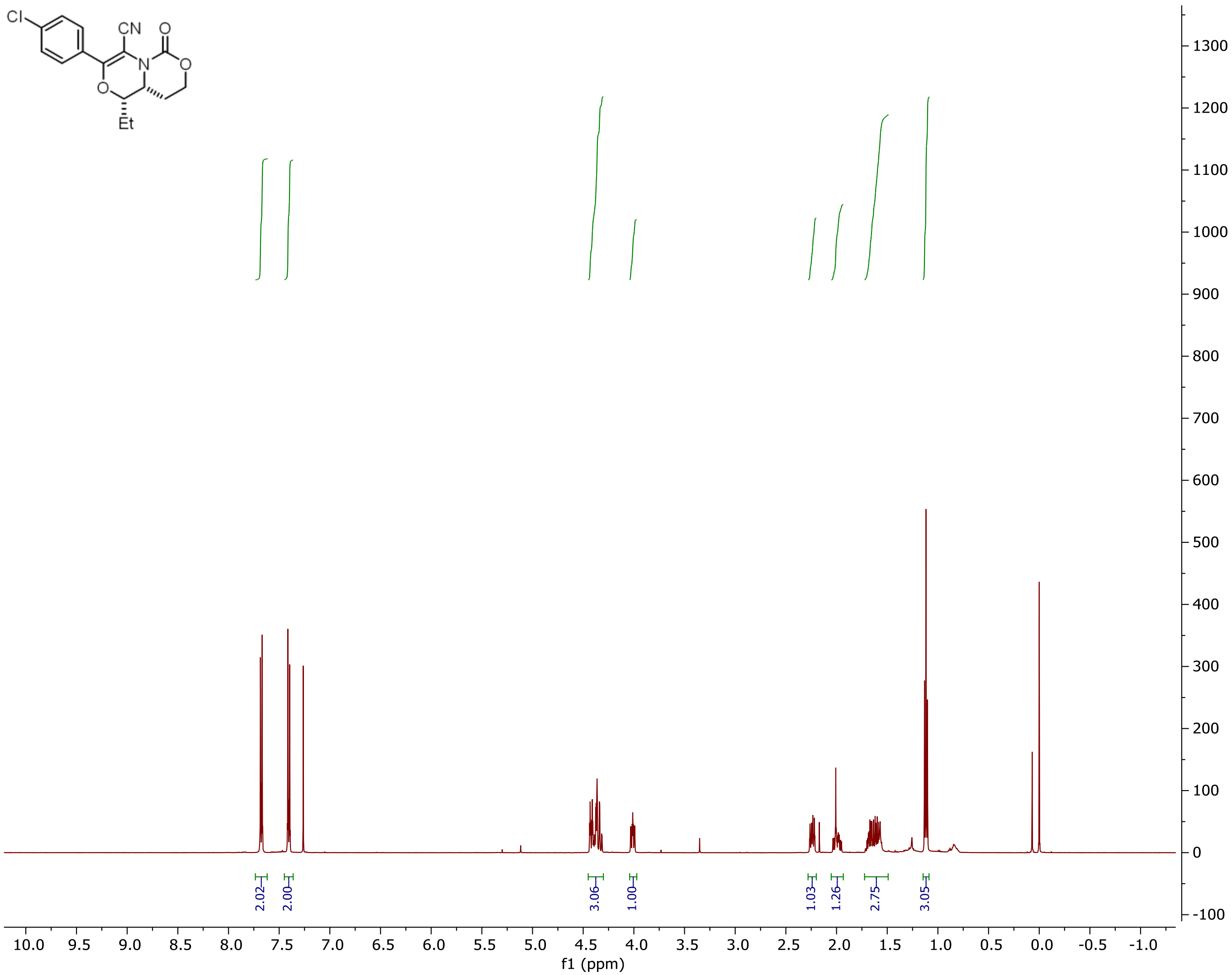
Compound **7c.** ^{1}H NMR (500 MHz, $CDCl_3$)



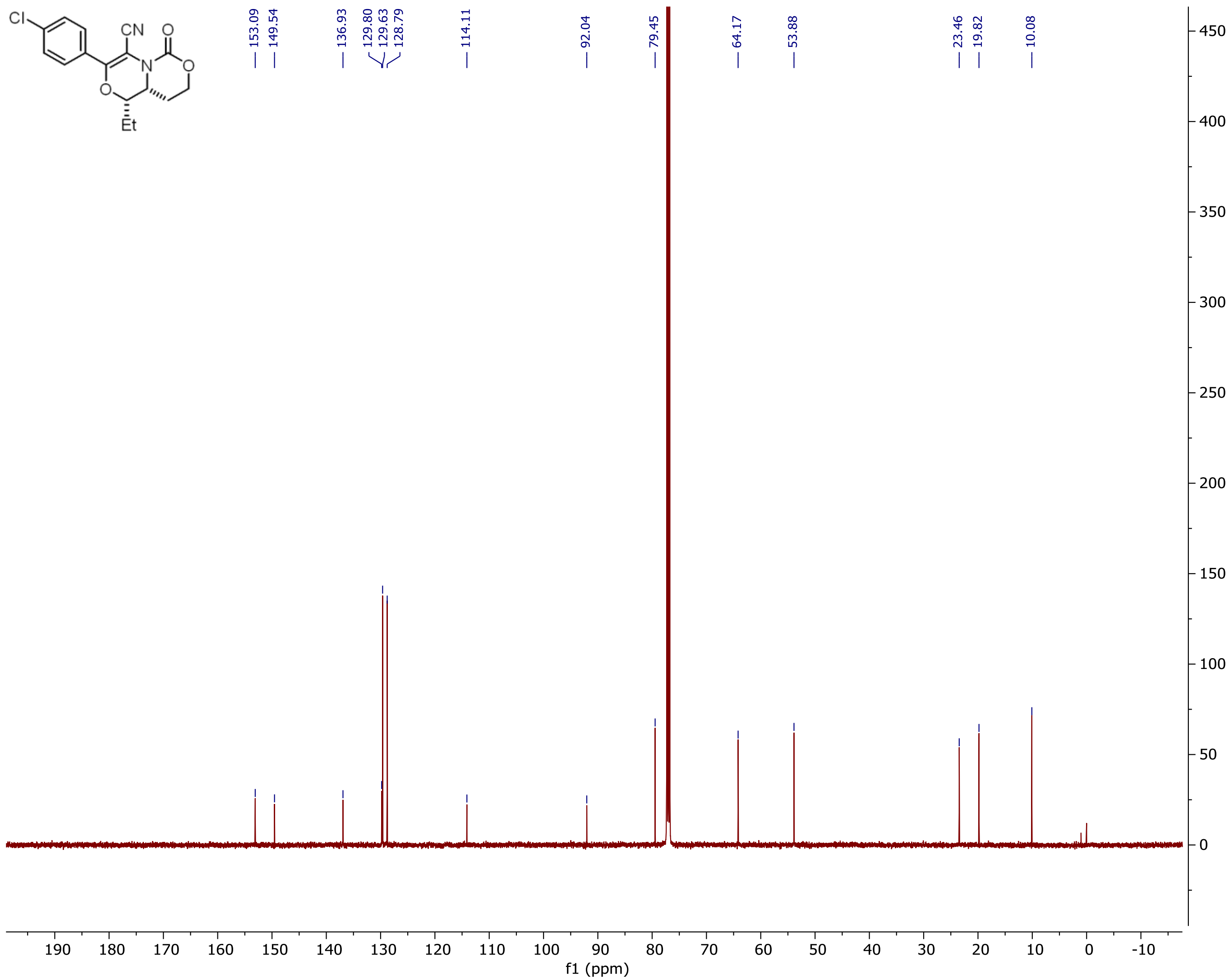
Compound **7c.** ^{13}C NMR (126 MHz, $CDCl_3$)



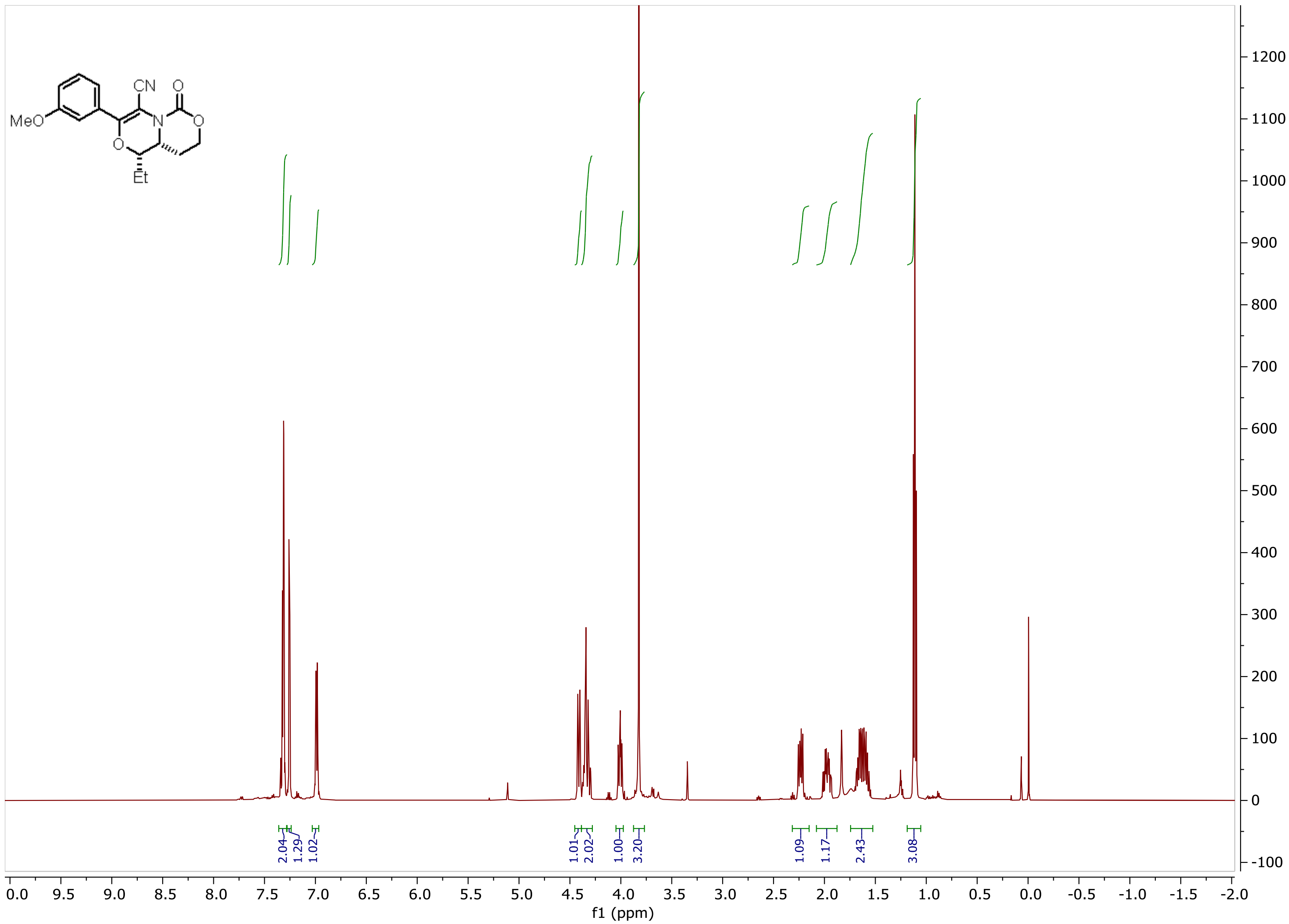
Compound **8c.** ^{1}H NMR (500 MHz, $CDCl_3$)



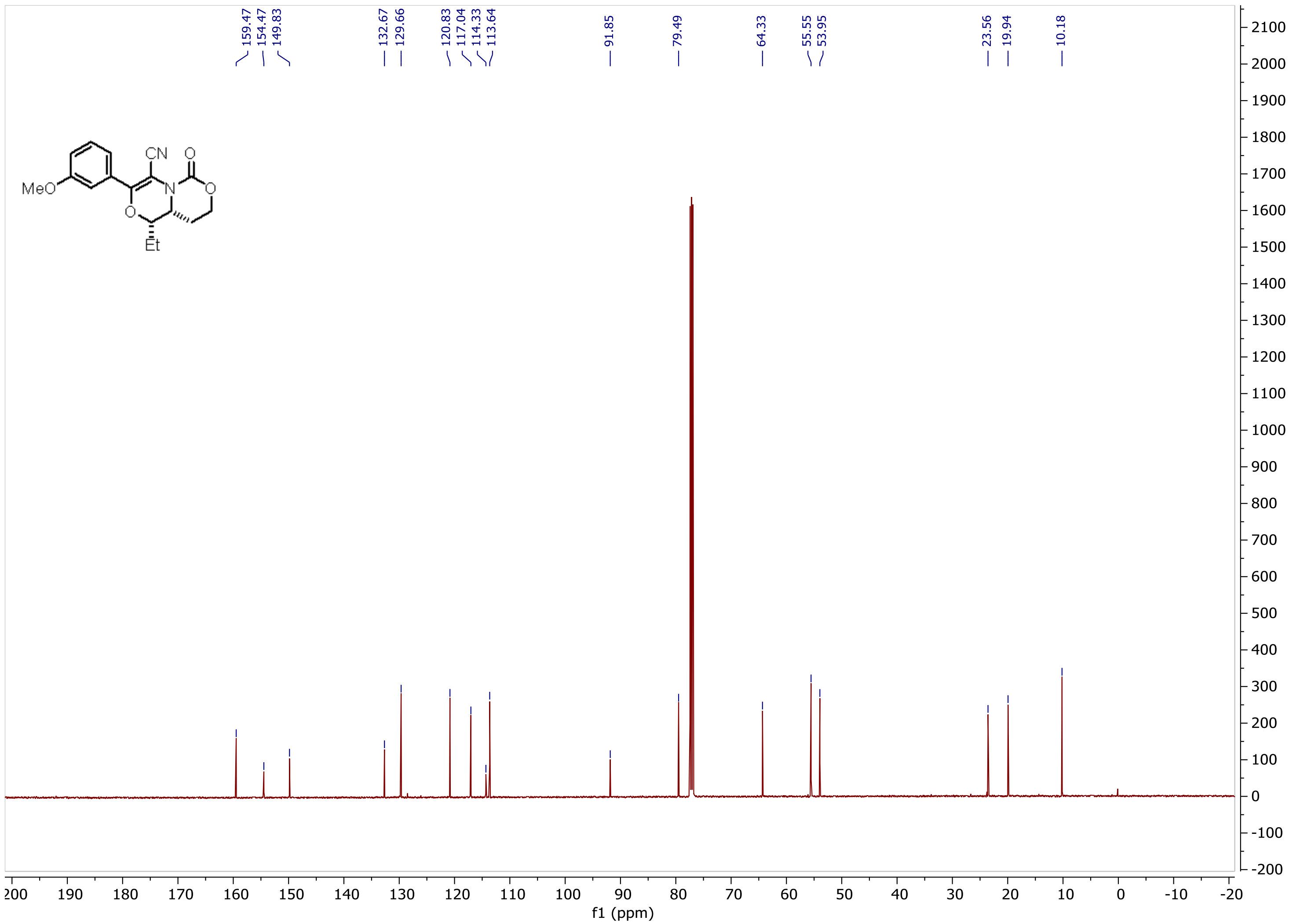
Compound **8c.** ^{13}C NMR (126 MHz, $CDCl_3$)



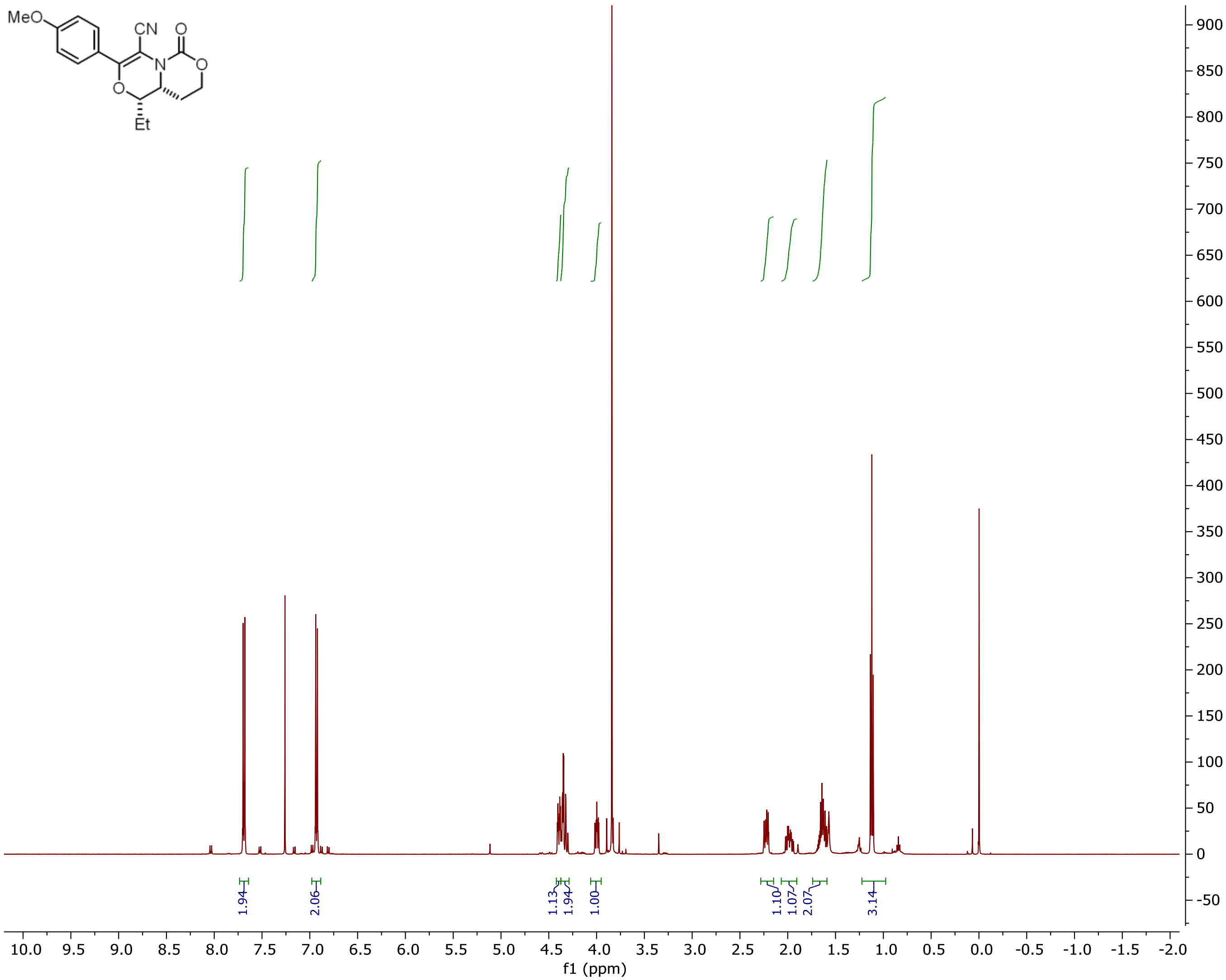
Compound **10c.** ^{1}H NMR (500 MHz, $CDCl_3$)



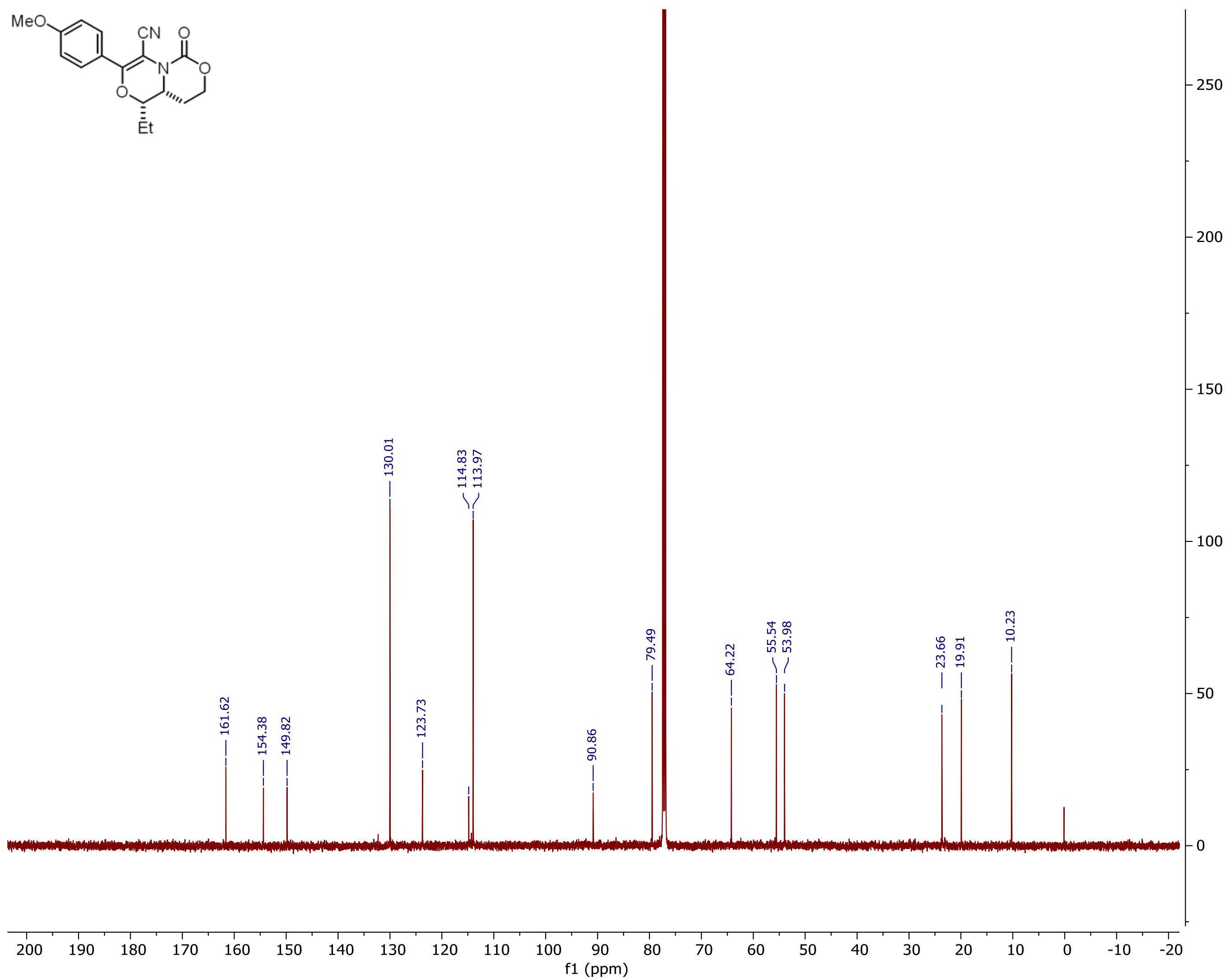
Compound **10c.** ^{13}C NMR (126 MHz, $CDCl_3$)



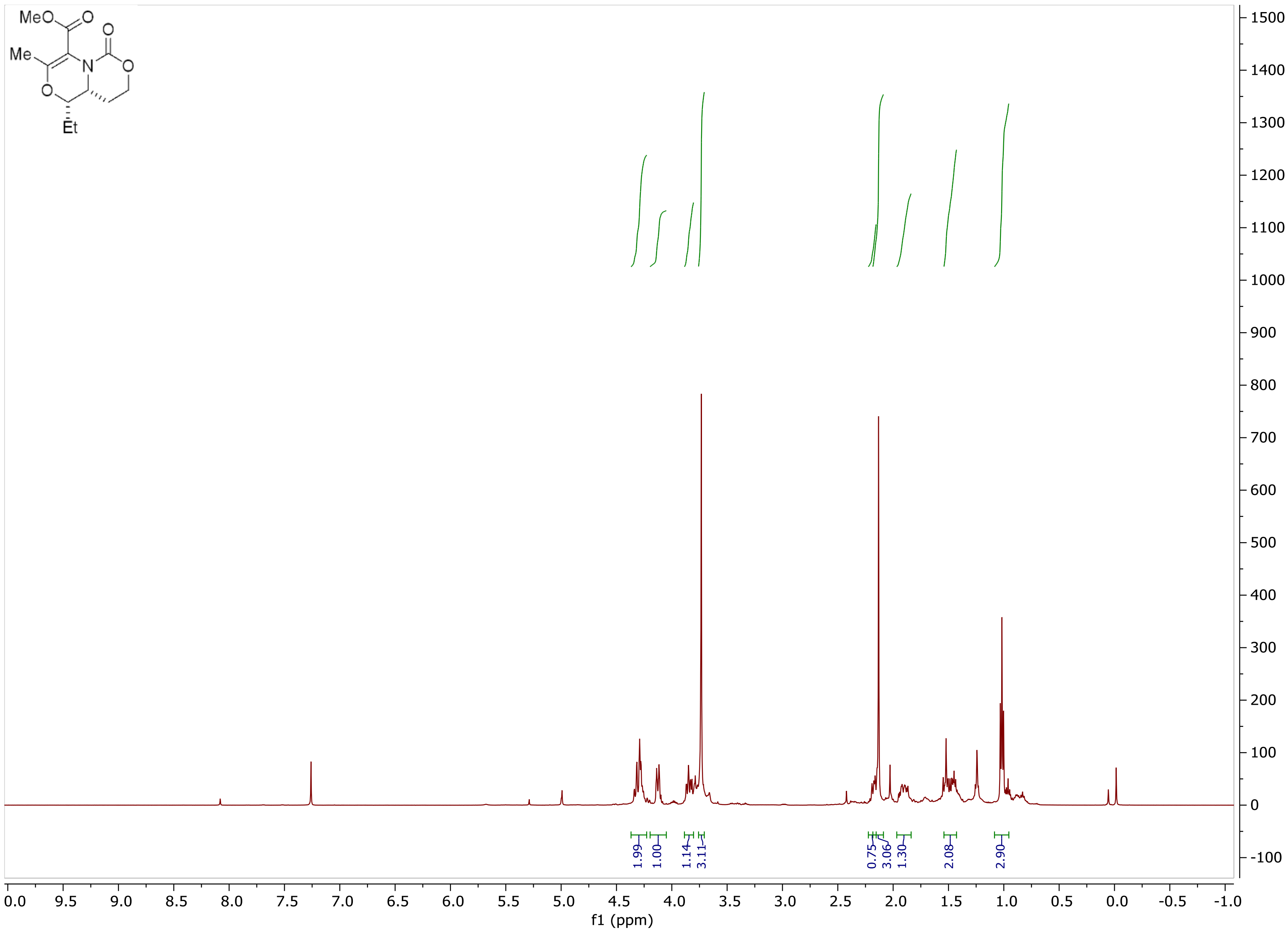
Compound **11c.** [1]H NMR (500 MHz, $CDCl_3$)



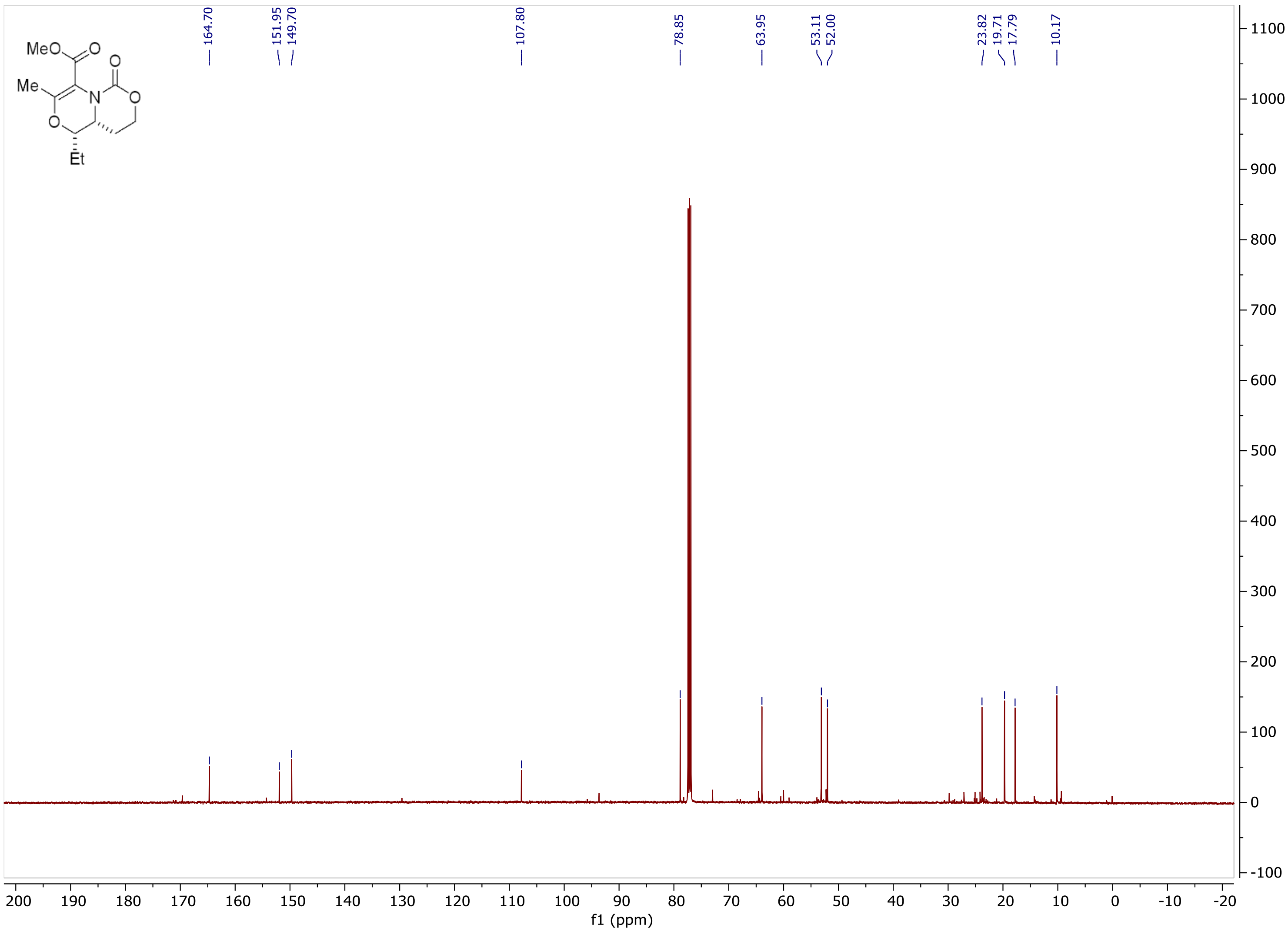
Compound **11c.** ^{13}C NMR (126 MHz, $CDCl_3$)



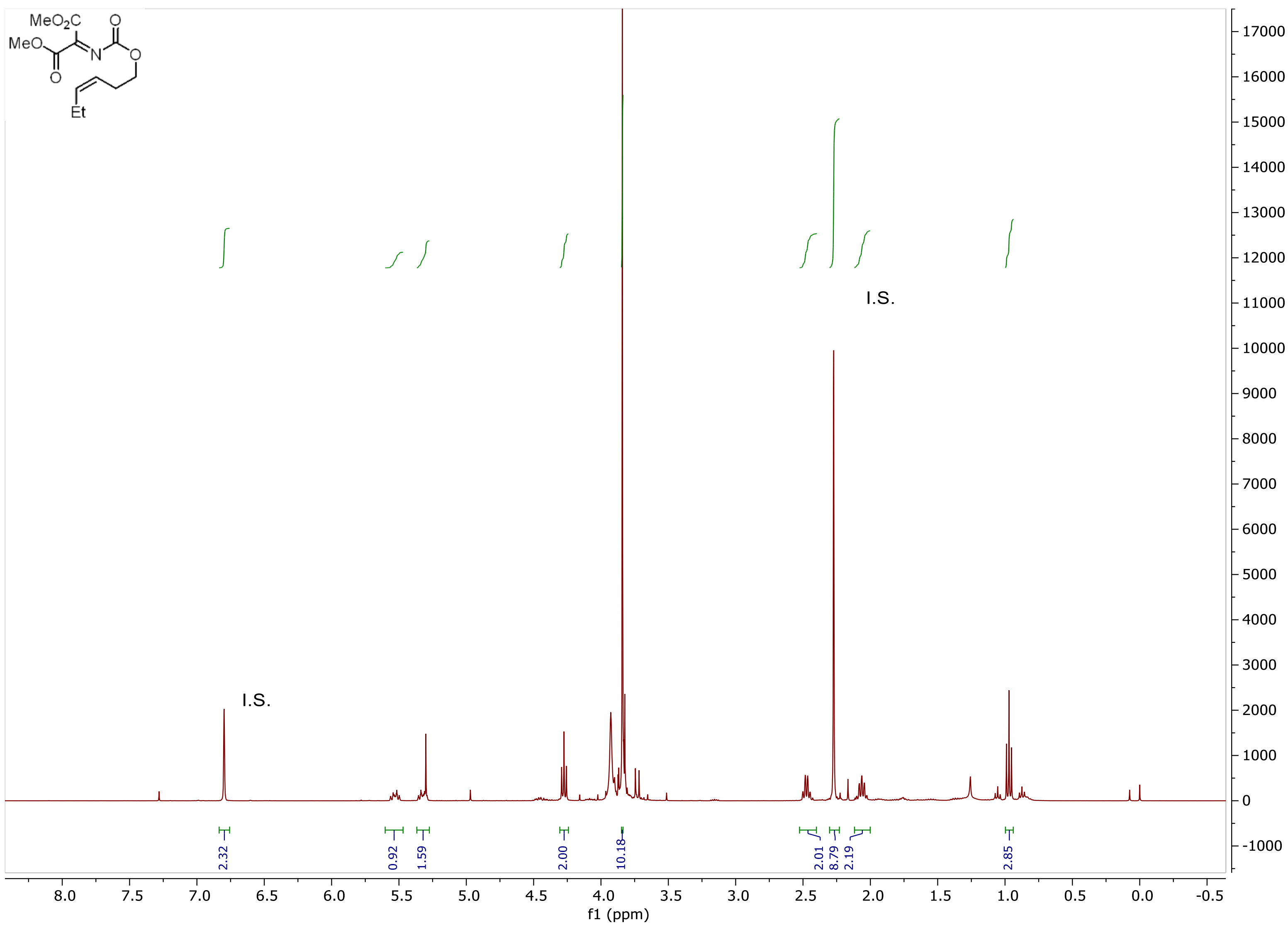
Compound **4e.** ^{1}H NMR (500 MHz, $CDCl_3$)



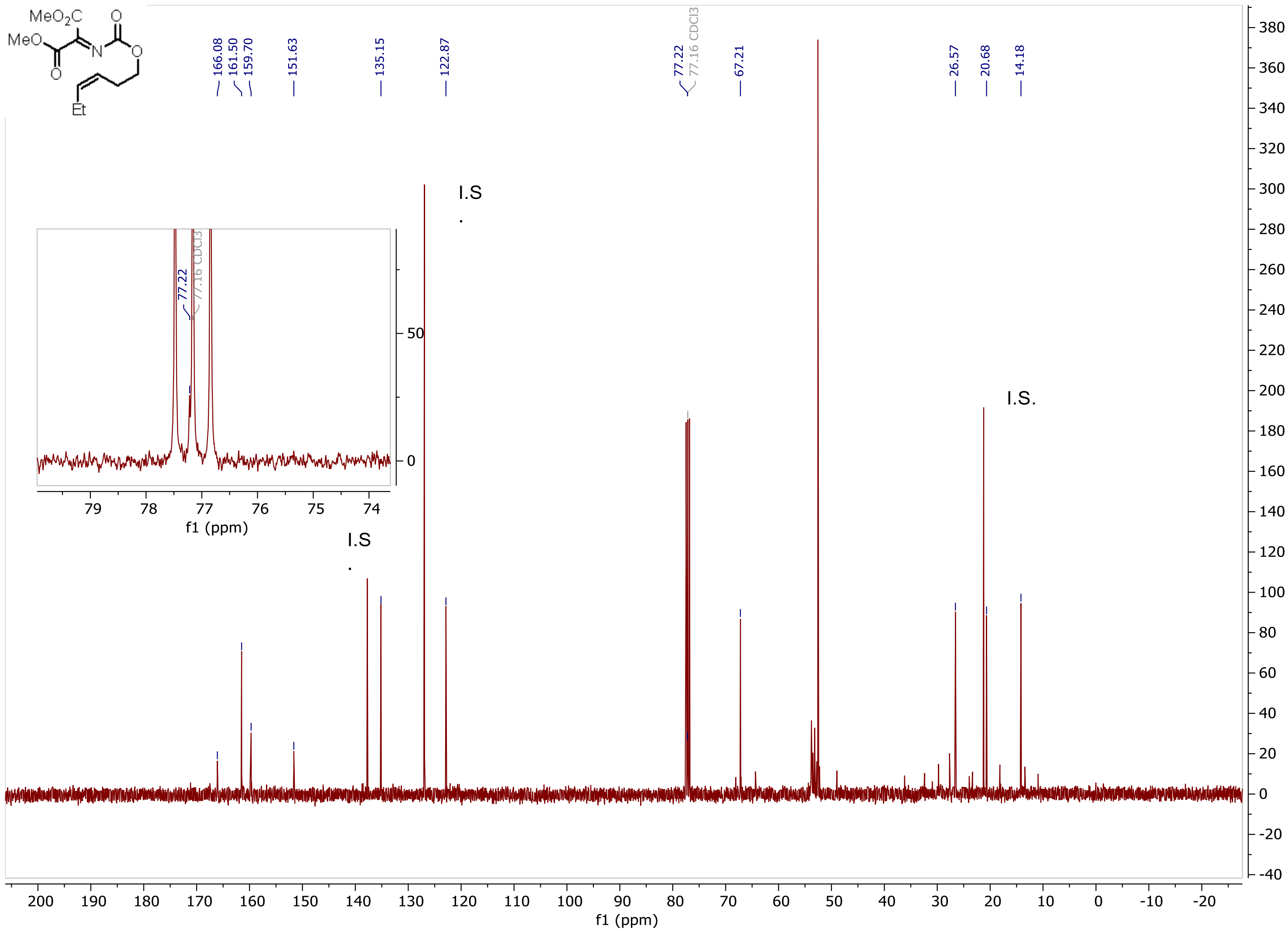
Compound **4e.** ^{13}C NMR (126 MHz, $CDCl_3$)



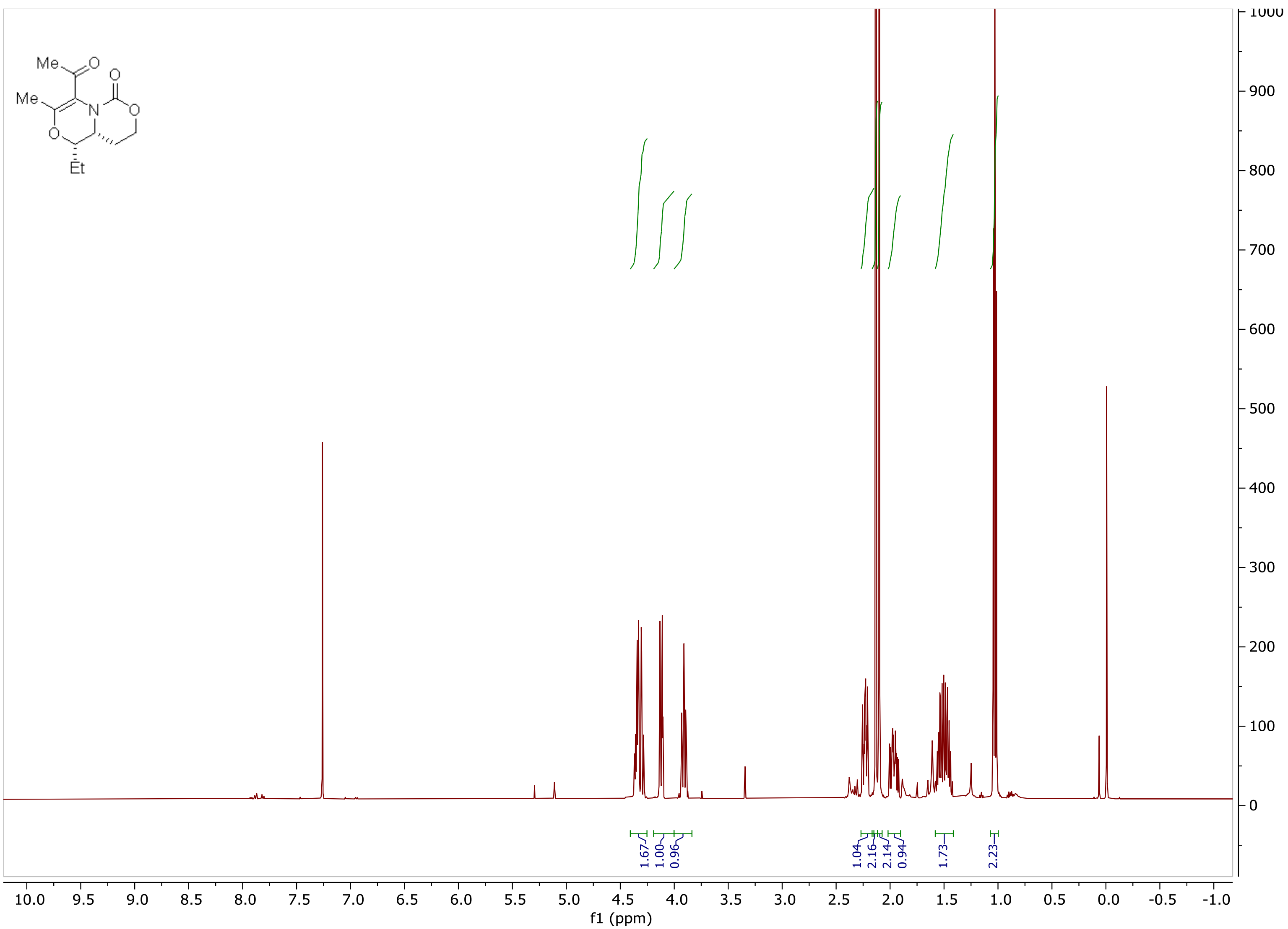
Compound **SI-2.** [1]H NMR (400 MHz, $CDCl_3$)



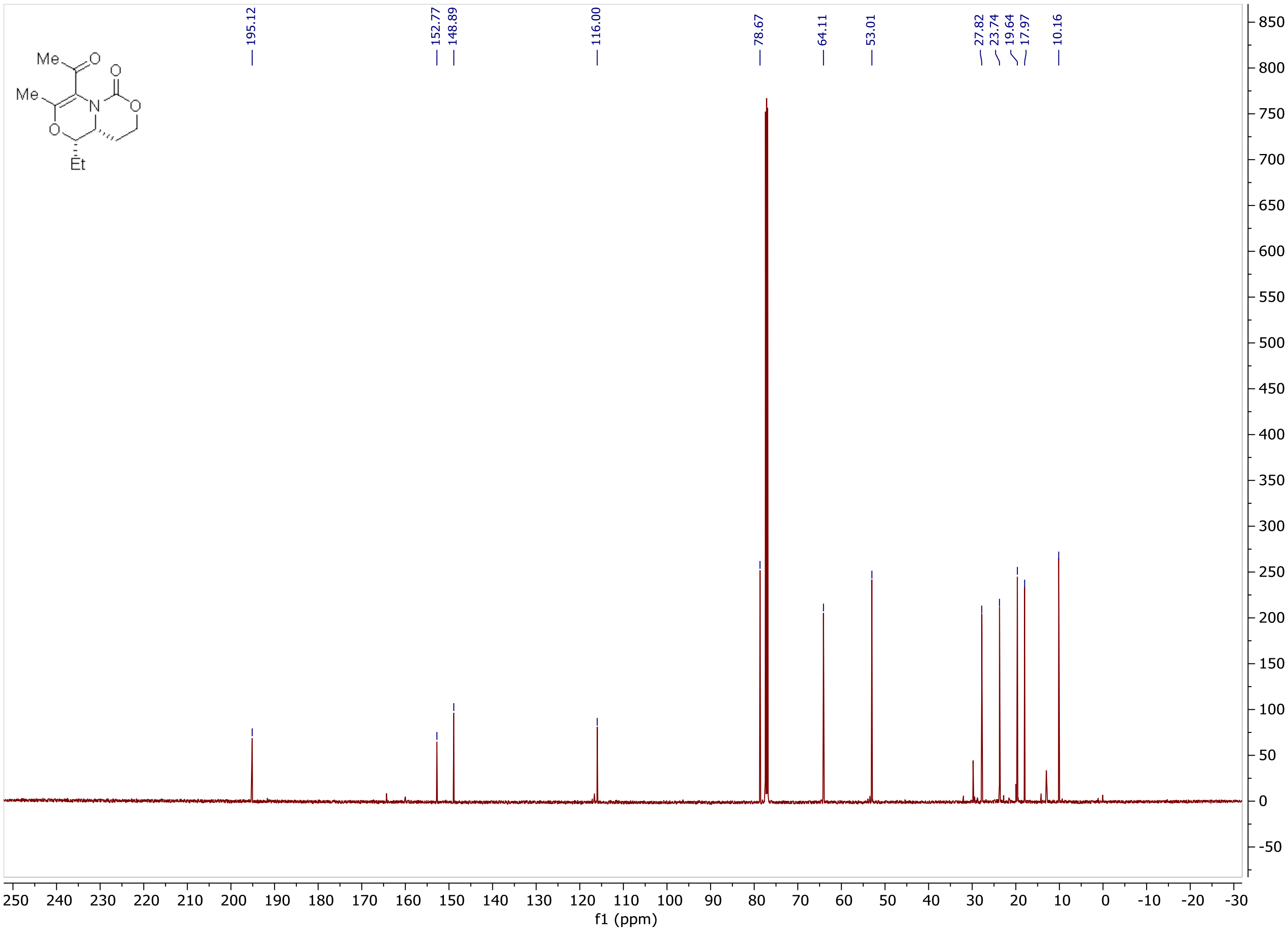
Compound **SI-2.** ^{13}C NMR (101 MHz, $CDCl_3$)



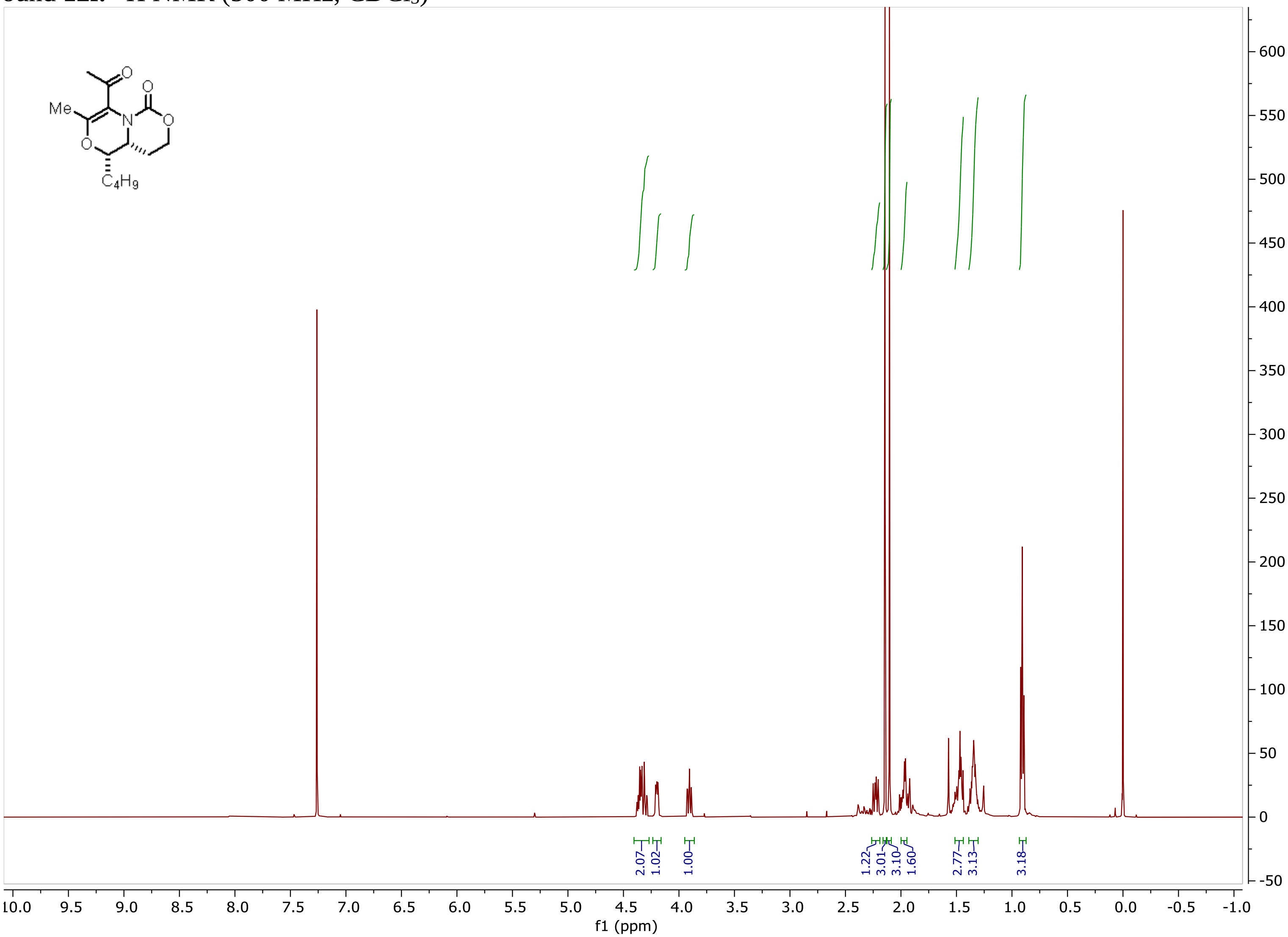
Compound **4f.** ^{1}H NMR (500 MHz, $CDCl_3$)


Me
O
O
Me
N
O
O
Et
1.67
1.00
0.96
1.04
2.16
2.14
0.94
1.73
2.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0

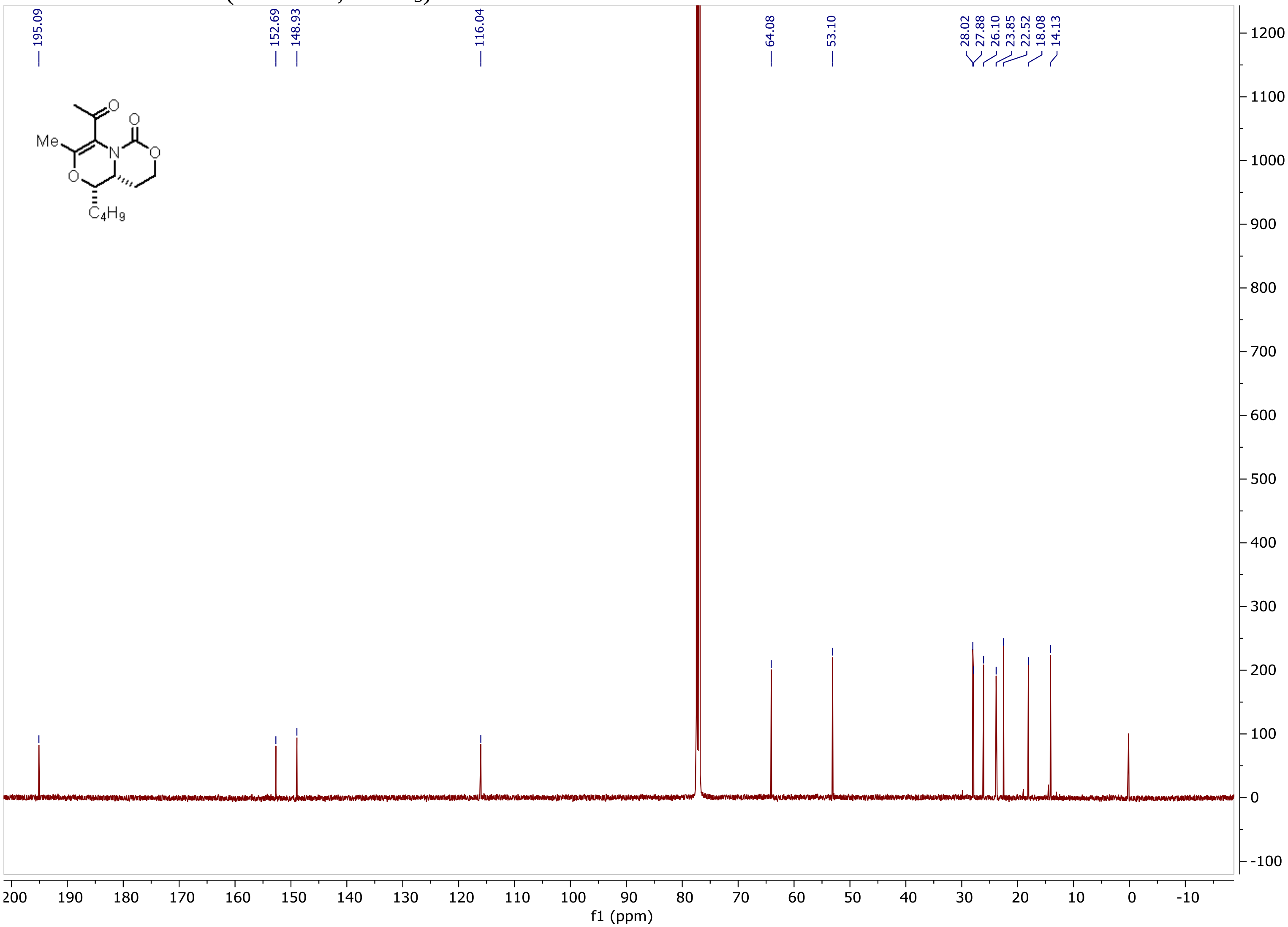
Compound **4f.** ^{13}C NMR (126 MHz, $CDCl_3$)



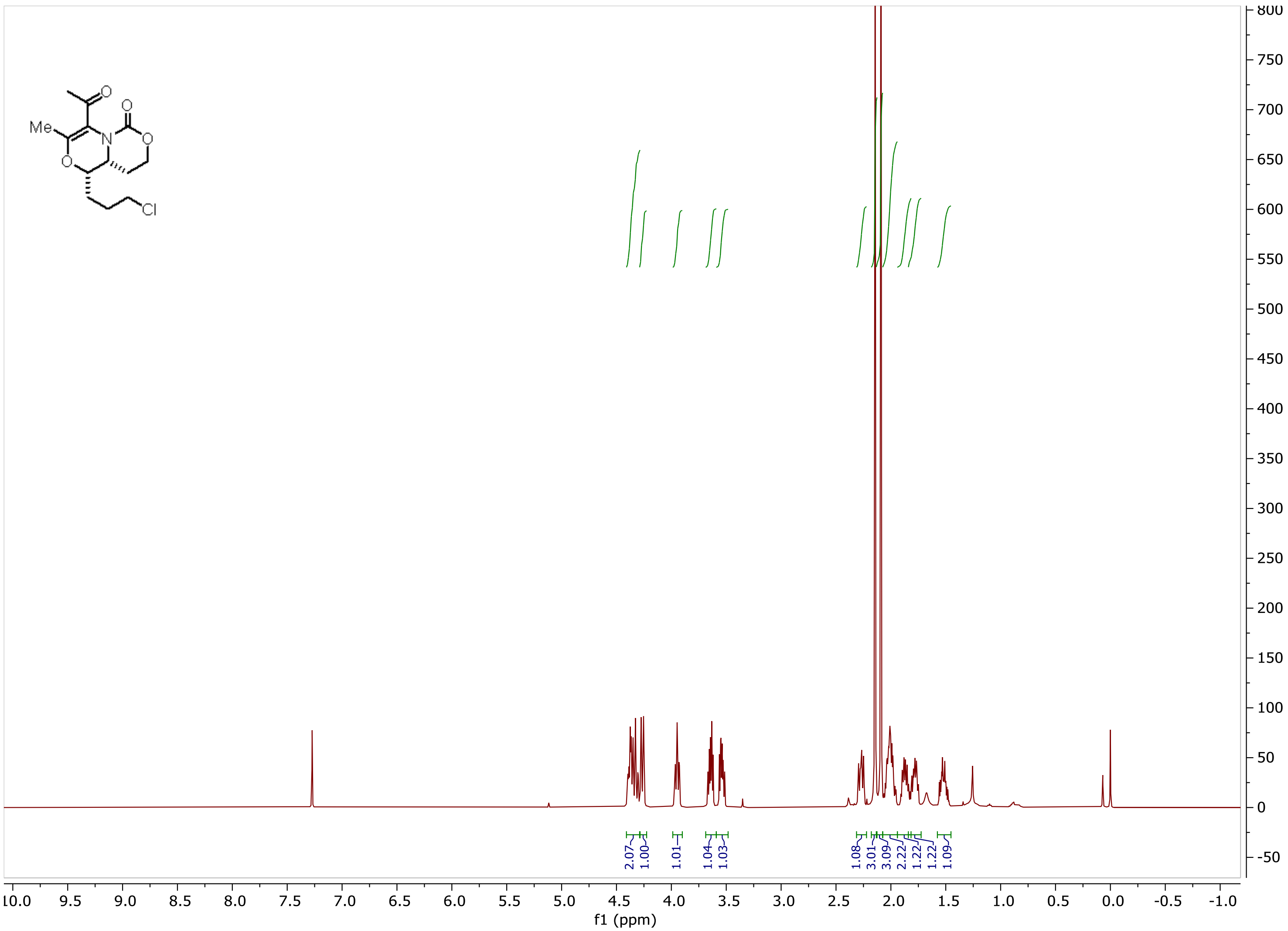
Compound **12f.** ^{1}H NMR (500 MHz, $CDCl_3$)



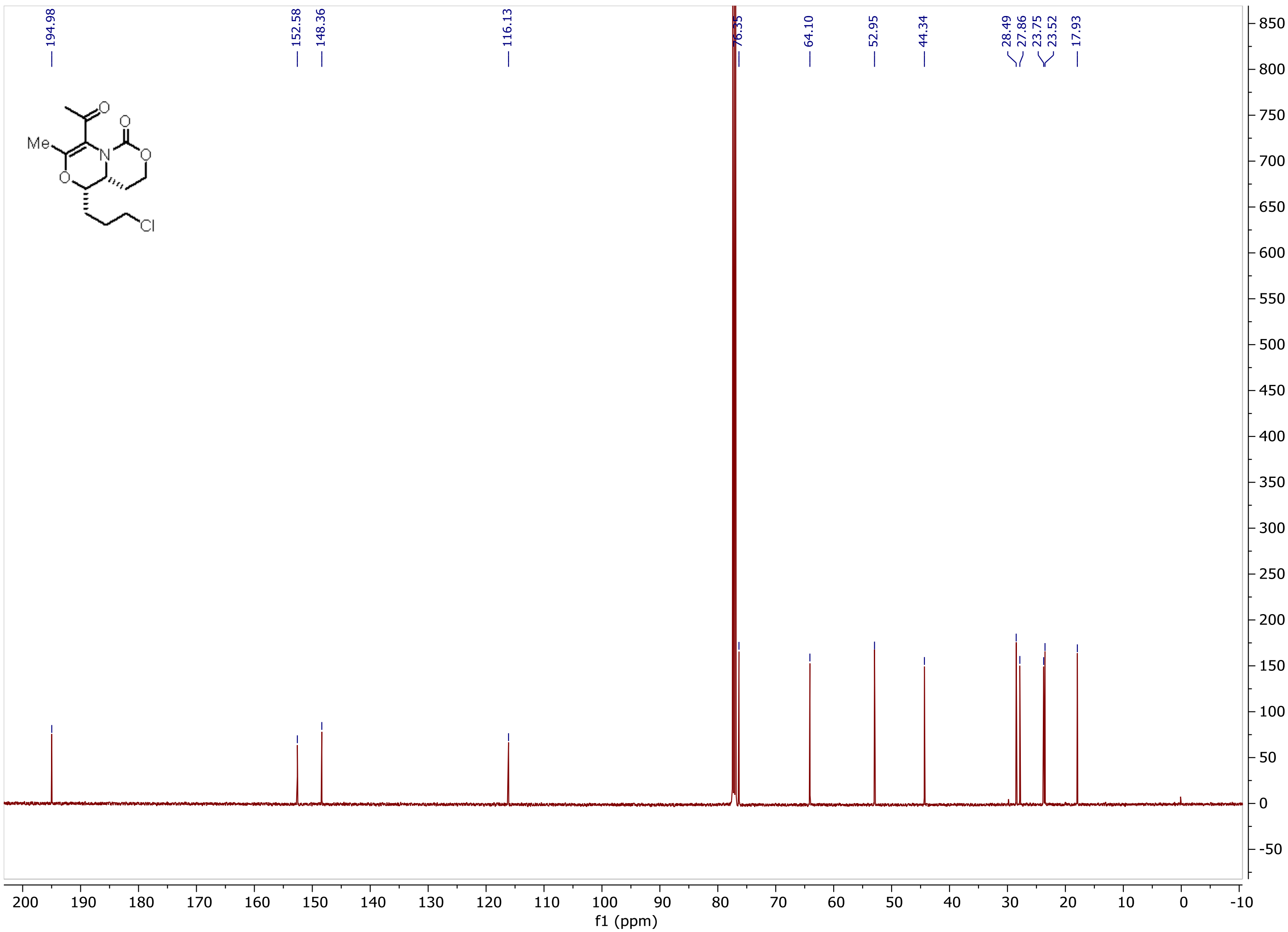
Compound **12f.** ^{13}C NMR (126 MHz, $CDCl_3$)



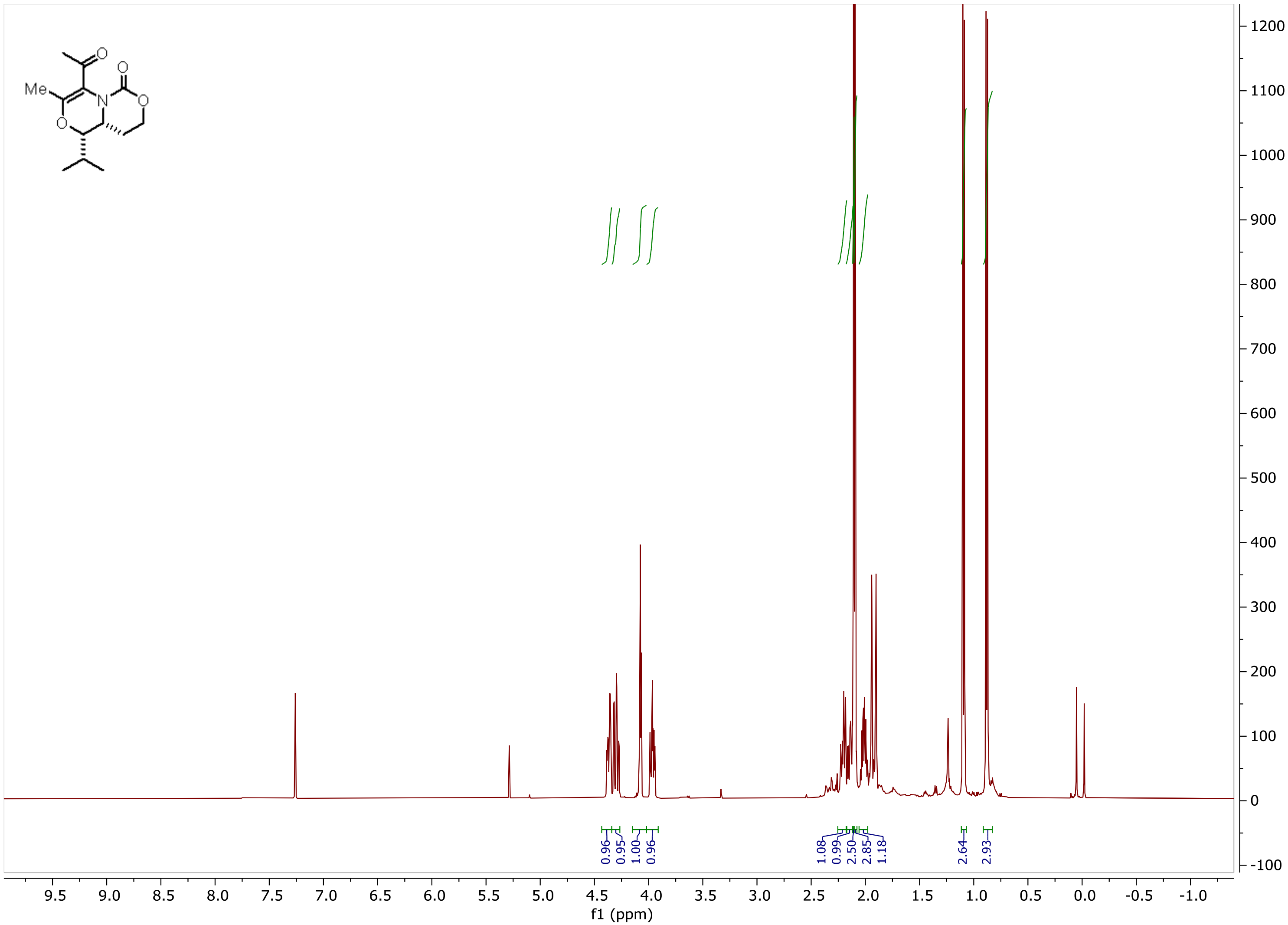
Compound **13f.** [1]H NMR (500 MHz, $CDCl_3$)



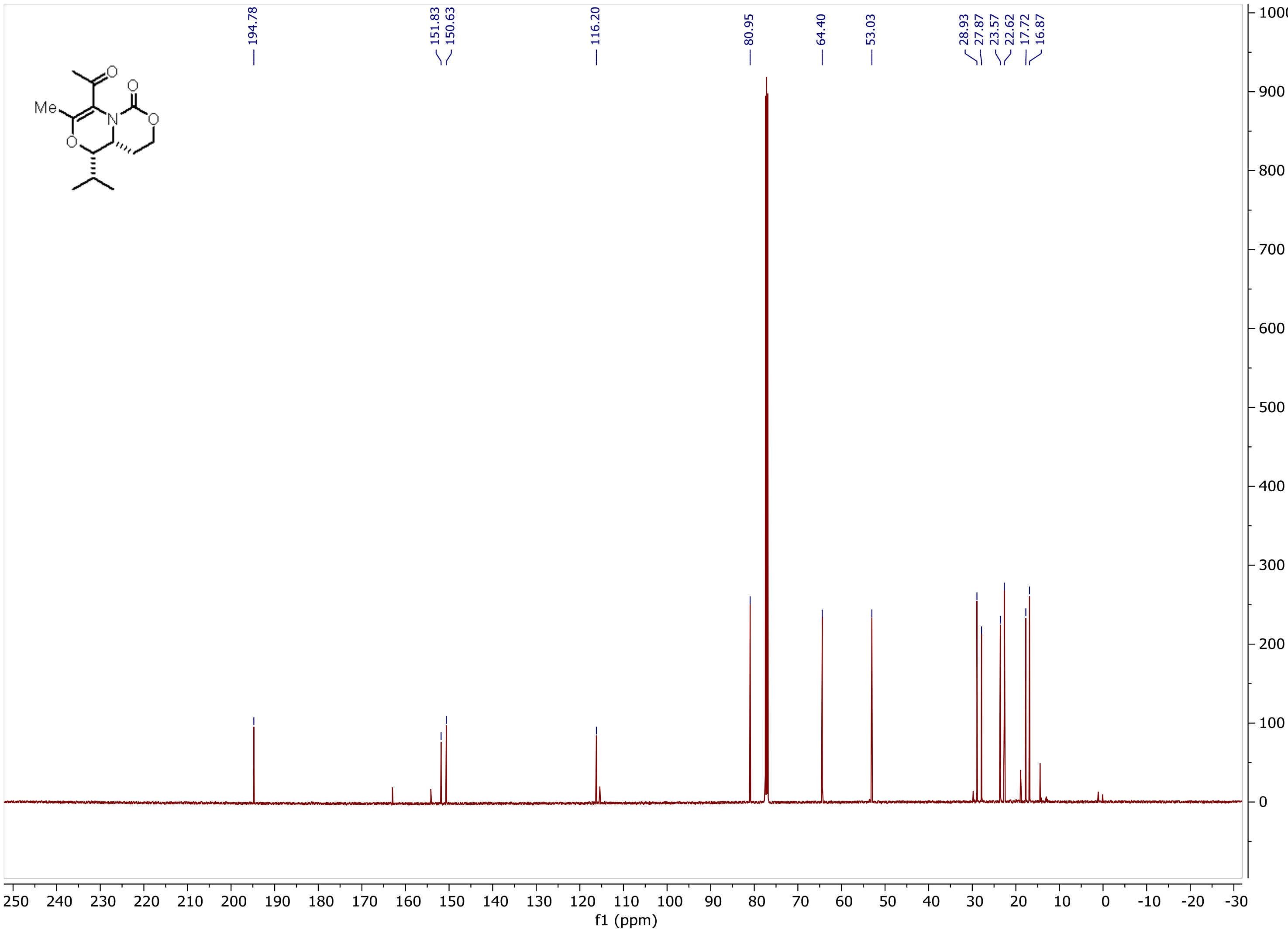
Compound **13f** · ^{13}C NMR (126 MHz, $CDCl_3$)



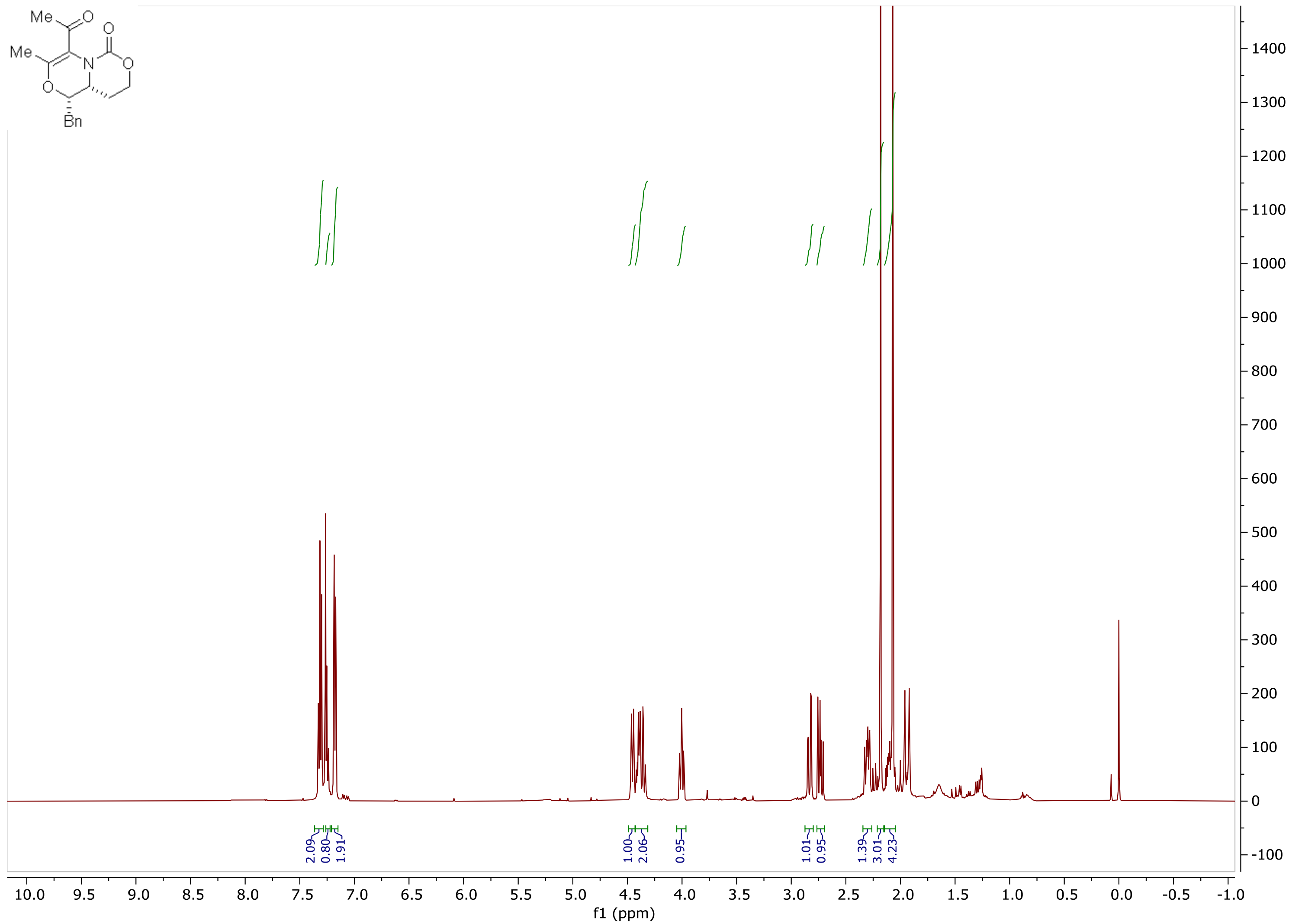
Compound **14f.** ^{1}H NMR (500 MHz, $CDCl_3$)



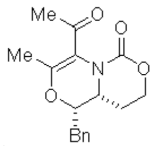
Compound **14f.** ^{13}C NMR (126 MHz, $CDCl_3$)

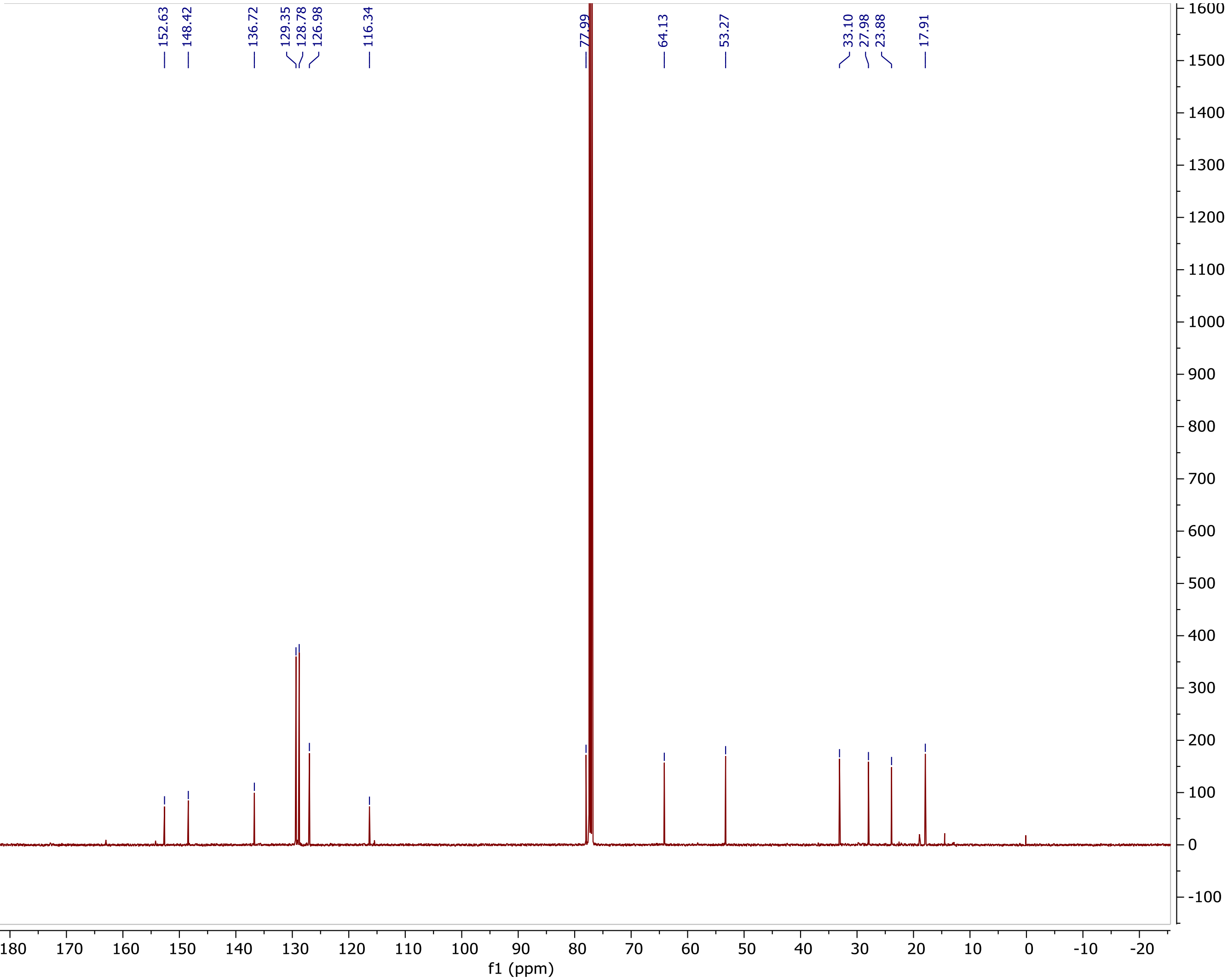


Compound **15f.** ^{1}H NMR (500 MHz, $CDCl_3$)

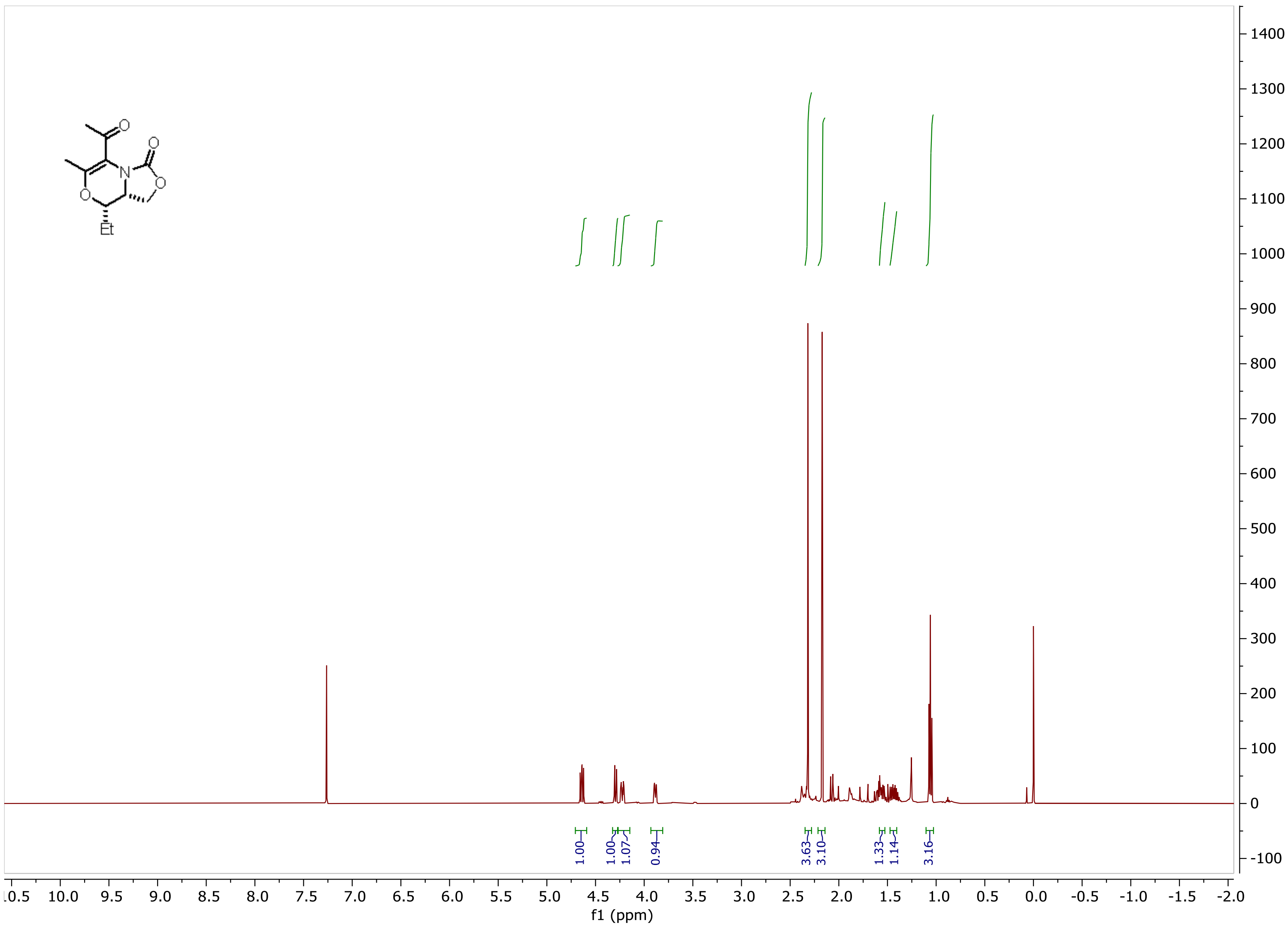


Compound **15f.** ^{13}C NMR (126 MHz, $CDCl_3$)





Compound **18.** ^{1}H NMR (500 MHz, $CDCl_3$)



Compound **18.** ^{13}C NMR (126 MHz, $CDCl_3$)