Supporting Information

Biomimetic 2-Imino-Nazarov Cyclizations via Eneallene Aziridination

Joshua R. Corbin[†], Devin R. Ketelboeter[†], Israel Fernández[‡,*], and Jennifer M. Schomaker[†,*]

[†]Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States

[‡]Departmento de Química Orgánica I and Centro de Innovación en Química Avazanda (ORFEO-CINQA), Facultad de Ciencias Químcas, Universidad Complutense de Madrid, 28040, Madrid, Spain

Corresponding Authors *schomakerj@chem.wisc.edu, *israel@quim.ucm.es

I. General information

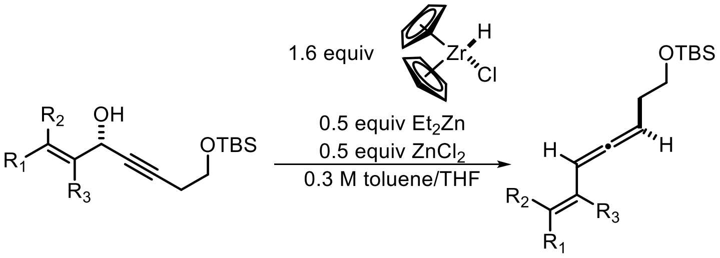
All glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Tetrahydrofuran and diethyl ether were distilled from purple Na/benzophenone ketyl. Dichloromethane, benzene, toluene, acetonitrile, triethyl amine, and diisopropyl amine were dried over CaH_2 and freshly distilled prior to use. All other solvents and reagents were purified in accordance with "Purification of Laboratory Chemicals".[1a] Air- and moisture-sensitive reactions were performed either in an MBraun LabStar glovebox under an atmosphere of nitrogen or using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F254 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 substrate as hexanes/ether, pentane/ether, hexanes/ethyl acetate, or benzene/ethyl acetate were used. 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, potassium permanganate or ceric ammonium molybdate was employed to visualize the reaction products.

^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance III 500, Bruker Avance III 400, Bruker Avance III 600, and Varian Mercury-300 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 Thermo Q Exactive™ Plus (electrospray ionization or atmospheric solids analysis probe (ASAP-MS) methods). The NMR facilities are funded by the NSF (CHE-1048642, CHE-0342998), the University of Wisconsin, the NIH (S10 OD012245), and a generous gift from Paul J. and Margaret M. Bender. The purchase of the Thermo Q Exactive™ Plus in 2015 was funded by NIH Award 1S10 OD020022-1 to the Department of Chemistry.

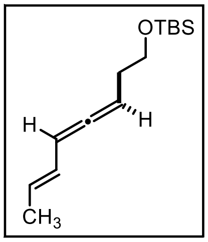
II. Substrate preparation

Conjugated allenes were typically prepared using the following general procedure reported by Ready[2], though base-catalyzed prototropic rearrangement of 1,4-enynes[3a-b] and alkoxy-directed rearrangement of 1,3-enynes are alternative preparative methods.[4a-b] The Schwartz reagent was prepared routinely on 100 g scale using a straightforward procedure in *Organic Syntheses* reported by Buchwald, then it was stored in the glovebox protected from light.[5] The starting allyl propargyl alcohols were prepared according to reports involving lithium acetylide addition into α,β-unsaturated aldehydes.[6]

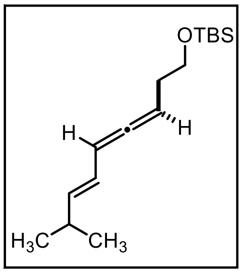
General procedure for eneallene synthesis:



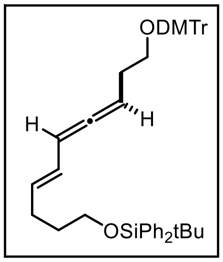
A round-bottom flask equipped with a stir bar was charged with $ZnCl_2$ (0.5 equiv) and the solid was freshly fused by flame torching under vacuum. After cooling to room temperature under a slight positive pressure of nitrogen, Et_2Zn (1 M in toluene, 0.5 equiv) was added, followed by anhydrous THF (3 M with respect to Et_2Zn). This mixture was stirred at room temperature for 30 minutes until solid $ZnCl_2$ was completely dissolved, then toluene was added (0.3 M with respect to ROH). The solution was cooled to 0 °C before allyl propargyl alcohol (1.0 equiv) in toluene (0.3 M with respect to Et_2Zn) was added to the EtZnCl solution. The mixture was stirred for 20 min before the addition of $Cp_2Zr(H)Cl$ (1.6 equiv) in a single portion under the protection of nitrogen atmosphere. The reaction was stirred vigorously for 12-24 hours until starting material was consumed according to TLC. The process was quenched by adding saturated $NaHCO_3$. The aqueous phase was extracted thrice with ether, and the combined organic layers were dried by Na_2SO_4 before concentrating under reduced pressure. The desired eneallene was easily purified by SiO_2 column chromatography using hexanes/EtOAc or pentane/Et_2O solvent systems. **NOTE:** While some substrates in the report by Ready could be synthesized using EtMgCl as the base instead of EtZnCl, the eneallene class of substrates could not be prepared successfully using EtMgCl.[5]



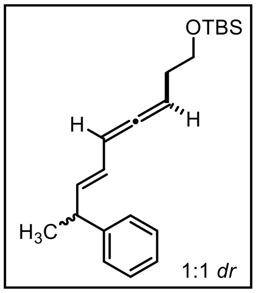
Compound S-1. Following the general procedure (14.3 mmol scale), **S-1** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (2.33 g, 9.8 mmol, 69% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.87 – 5.81 (m, 1H), 5.75 (ddt, *J* = 10.3, 5.8, 2.7 Hz, 1H), 5.61 (dqd, *J* = 14.8, 6.7, 1.4 Hz, 1H), 5.28 (dtd, *J* = 8.4, 5.8, 1.4 Hz, 1H), 3.67 (t, *J* = 6.7 Hz, 2H), 2.23 (qd, *J* = 6.8, 2.7 Hz, 2H), 1.73 (dt, *J* = 6.7, 1.6 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.8, 127.1, 127.0, 94.0, 88.9, 63.0, 32.8, 26.1, 18.5, 18.2, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{14}H_{26}OSi$ [M+H]$^+$ 239.1826, measured 239.1822 (1.7 ppm).



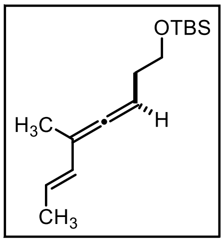
Compound S-2. Following the general procedure (14 mmol scale), **S-2** was purified on silica gel using a 0-25% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a deep yellow oil (1.37 g, 5.1 mmol, 37% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.83 – 5.73 (m, 2H), 5.59 (ddd, *J* = 14.8, 6.6, 1.4 Hz, 1H), 5.33 – 5.26 (m, 1H), 3.68 (t, *J* = 6.7 Hz, 2H), 2.33 (dqt, *J* = 13.4, 6.7, 1.2 Hz, 1H), 2.24 (qd, *J* = 6.8, 2.5 Hz, 2H), 1.00 (d, *J* = 6.7 Hz, 6H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.0, 139.5, 122.8, 94.0, 88.8, 62.8, 32.6, 31.1, 25.9, 22.33, 22.31, 18.3, -5.3. **HRMS** (ASAP-MS) *m/z* calculated for $C_{16}H_{30}OSi$ [M+H]$^+$ 267.2139, measured 267.2138 (0.4 ppm).



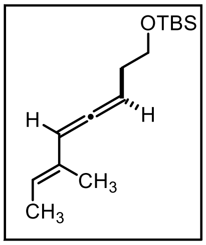
Compound S-3. The *O*-TBS protected homopropargyl acetylide was replaced with a 4,4'-dimethoxytrityl *O*-protecting group. Following the general procedure (5 mmol scale), **S-3** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a light yellow oil (1.829 g, 2.6 mmol, 52% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.67 (dt, *J* = 7.7, 1.7 Hz, 4H), 7.47 – 7.31 (m, 13H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.83 – 6.80 (m, 4H), 5.82 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.76 – 5.68 (m, 1H), 5.57 (dt, *J* = 14.5, 6.8 Hz, 1H), 5.38 – 5.31 (m, 1H), 3.78 (s, 6H), 3.66 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 6.5 Hz, 2H), 2.31 (qd, *J* = 6.7, 2.5 Hz, 2H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.64 (p, *J* = 6.8 Hz, 2H), 1.05 (d, *J* = 2.0 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.1, 158.5, 145.4, 136.7, 135.7, 134.2, 132.1, 130.2, 129.7, 128.4, 127.7, 126.8, 126.1, 113.1, 94.1, 89.4, 86.0, 63.4, 63.2, 55.3, 32.4, 30.3, 29.1, 27.0, 19.4, 0.1. **HRMS** (ESI-MS) *m/z* calculated for $C_{47}H_{52}O_4Si$ [M+H]$^+$ 731.3527, measured 731.3522 (0.7 ppm).



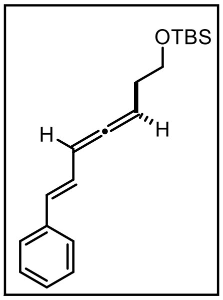
Compound S-4. Following the general procedure (2.9 mmol scale), **S-4** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (0.830 g, 2.5 mmol, 87% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 5.91 – 5.74 (m, 3H), 5.34 – 5.27 (m, 1H), 3.68 (td, *J* = 6.7, 4.7 Hz, 2H), 3.50 (q, *J* = 6.9 Hz, 1H), 2.27 – 2.21 (m, 2H), 1.38 (dd, *J* = 7.0, 1.3 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.4, 136.8, 128.6, 127.4, 126.3, 124.8, 124.7, 94.0, 89.1, 62.9, 42.5, 32.7, 26.1, 21.3, 18.5, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{21}H_{32}OSi$ $[M+H]^+$ 329.2295, measured 329.2290 (1.5 ppm).



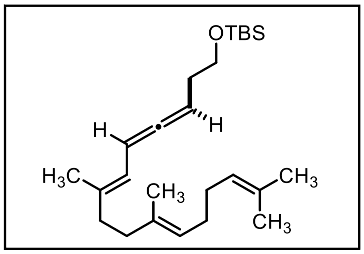
Compound S-5. Following the general procedure (15 mmol scale), **S-5** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a clear oil (1.726 g, 6.8 mmol, 45% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.04 – 5.93 (m, 1H), 5.52 (dqd, *J* = 14.7, 6.7, 1.4 Hz, 1H), 5.23 – 5.13 (m, 1H), 3.67 (t, *J* = 6.7 Hz, 2H), 2.21 (q, *J* = 6.8 Hz, 2H), 1.77 (dt, *J* = 3.8, 1.6 Hz, 6H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.7, 130.1, 123.7, 99.9, 87.0, 63.2, 33.0, 26.1, 18.5, 18.4, 15.8, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{15}H_{28}OSi$ $[M+H]^+$ 253.1982, measured 253.1978 (1.6 ppm).



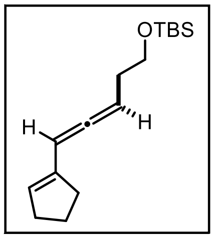
Compound S-6. Following the general procedure (27 mmol scale), **S-6** was purified on silica gel using a 0-25% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a deep yellow oil (4.83 g, 19.1 mmol, 70% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.84 (dt, *J* = 6.0, 2.8 Hz, 1H), 5.47 – 5.36 (m, 2H), 3.69 (t, *J* = 6.8 Hz, 2H), 2.26 (qd, *J* = 6.9, 2.8 Hz, 2H), 1.70 (dt, *J* = 7.0, 1.3 Hz, 3H), 1.67 (d, *J* = 1.4 Hz, 3H), 0.90 (d, *J* = 1.0 Hz, 9H), 0.06 (d, *J* = 0.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.2, 130.9, 123.0, 99.4, 90.7, 63.1, 33.1, 26.1, 18.5, 14.1, 13.4, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{15}H_{28}OSi$ $[M+H]^+$ 253.1982, measured 253.1977 (2.0 ppm).



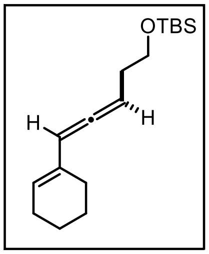
Compound S-7. Following the general procedure (14.5 mmol scale), **S-7** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a light yellow oil (2.40 g, 8.0 mmol, 41% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.18 (m, 1H), 6.59 (ddd, *J* = 15.7, 10.3, 1.0 Hz, 1H), 6.48 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.02 – 5.94 (m, 1H), 5.42 (q, *J* = 6.8 Hz, 1H), 3.72 (t, *J* = 6.6 Hz, 2H), 2.30 (qd, *J* = 6.7, 2.7 Hz, 2H), 0.92 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.9, 137.5, 130.1, 128.7, 127.4, 126.3, 125.4, 94.7, 89.5, 62.8, 32.7, 26.1, 18.5, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{19}H_{28}OSi$ $[M+H]^+$ 301.1982, measured 301.1979 (1.0 ppm).



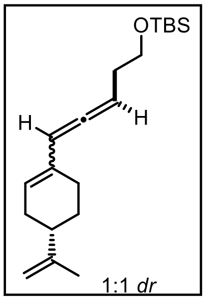
Compound S-8. Following the general procedure (15 mmol scale), **S-8** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a deep yellow/orange oil (4.70 g, 12.1 mmol, 80% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.97 (ddt, *J* = 10.8, 6.3, 2.7 Hz, 1H), 5.62 (dp, *J* = 10.9, 1.3 Hz, 1H), 5.32 – 5.26 (m, 1H), 5.14 – 5.07 (m, 2H), 3.68 (t, *J* = 6.7 Hz, 2H), 2.24 (qd, *J* = 6.8, 2.7 Hz, 2H), 2.15 – 2.03 (m, 6H), 1.98 (dd, *J* = 9.1, 6.1 Hz, 2H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.60 (d, *J* = 1.3 Hz, 6H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.8, 137.6, 135.4, 131.4, 124.5, 124.0, 119.7, 90.6, 88.5, 63.0, 40.1, 39.9, 32.9, 26.9, 26.7, 26.1, 25.8, 18.5, 17.8, 16.6, 16.1, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{25}H_{44}OSi$ $[M+H]^+$ 389.3234, measured 389.3231 (0.8 ppm).



Compound S-9. Following the general procedure (11 mmol scale), **S-9** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a deep yellow oil (2.9 g, 11 mmol, quantitative yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.03 – 6.01 (m, 1H), 5.62 (d, *J* = 2.3 Hz, 1H), 5.38 – 5.32 (m, 1H), 3.68 (t, *J* = 6.8 Hz, 2H), 2.40 (ddt, *J* = 9.8, 4.8, 2.3 Hz, 2H), 2.34 – 2.30 (m, 2H), 2.25 (qd, *J* = 6.9, 2.7 Hz, 2H), 1.89 (p, *J* = 7.6 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.1, 138.6, 127.9, 91.4, 89.5, 63.1, 33.3, 32.9, 32.8, 26.1, 23.3, 18.5, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{16}H_{28}OSi$ $[M+H]^+$ 265.1982, measured 265.1977 (1.9 ppm).

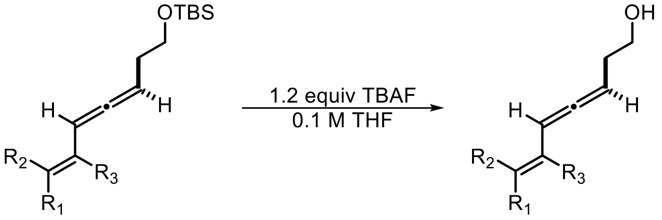


Compound S-10. Following the general procedure (15.0 mmol scale), **S-10** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (2.89 g, 10.4 mmol, 69% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.80 (dt, *J* = 5.9, 2.8 Hz, 1H), 5.64 (ddt, *J* = 5.1, 3.7, 1.8 Hz, 1H), 5.41 – 5.34 (m, 1H), 3.68 (t, *J* = 6.8 Hz, 2H), 2.25 (qd, *J* = 6.9, 2.8 Hz, 2H), 2.09 (dh, *J* = 5.9, 1.9 Hz, 2H), 2.02 (dp, *J* = 6.3, 2.0 Hz, 2H), 1.69 – 1.56 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.9, 132.4, 125.7, 97.8, 90.8, 63.1, 33.1, 26.1, 26.0, 25.9, 22.7, 22.6, 18.5, -5.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{17}H_{30}OSi$ $[M+H]^+$ 279.2139, measured 279.2136 (1.0 ppm).

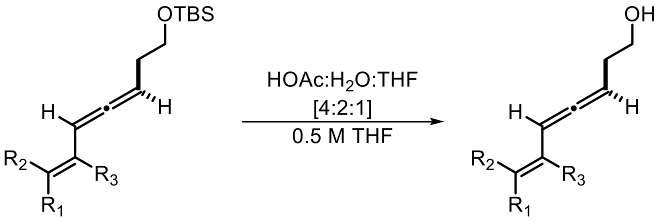


Compound S-11. Following the general procedure (15.0 mmol scale), **S-11** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (3.93 g, 12.3 mmol, 82% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.87 – 5.82 (m, 1H), 5.69 – 5.65 (m, 1H), 5.40 (dq, *J* = 13.0, 6.6, 6.2 Hz, 1H), 4.77 – 4.73 (m, 2H), 3.70 (tt, *J* = 6.8, 1.5 Hz, 2H), 2.31 – 2.15 (m, 5H), 2.12 – 2.00 (m, 2H), 1.86 (ddd, *J* = 10.6, 5.4, 2.6 Hz, 1H), 1.76 (d, *J* = 1.2 Hz, 3H), 1.55 – 1.47 (m, 1H), 0.92 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.1, 205.0, 149.81, 149.78, 132.1, 132.0, 126.7, 126.6, 124.87, 124.85, 108.7, 97.3, 97.2, 90.8, 90.7, 63.0, 62.9, 41.3, 41.2, 33.0, 32.9, 31.4, 31.3, 27.53, 27.51, 26.3, 26.2, 26.0, 20.82, 20.81, 18.38, 18.37, -5.23, -5.24. **HRMS** (ASAP-MS) *m/z* calculated for $C_{20}H_{34}OSi$ $[M+H]^+$ 319.2452, measured 319.2447 (1.6 ppm).

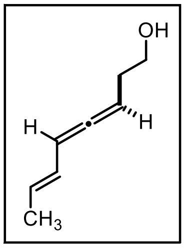
Procedure for alcohol deprotection: NOTE: The acidic deprotection (method B, *vide infra*) must be used on the indicated substrates instead of the basic method A or the formation of undesired alkylidene THF was observed (*i.e.* intramolecular addition of alkoxide into the allene).



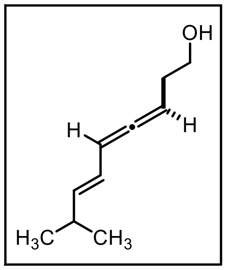
Method A – A dry round-bottom flask equipped with a stirbar was charged with the homoallenic silyl ether (1.0 equiv) and diluted in anhydrous tetrahydrofuran (0.1 M). The solution was stirred and tetrabutylammonium fluoride (1 M in THF, 1.2 equiv) was added. The reaction stirred for 30-60 min until complete consumption of starting material was observed by TLC. At this point water was added to quench the reaction and the aqueous layer was extracted thrice with ether. The combined organic extracts were dried over Na_2SO_4 before concentrating the volatiles under reduced pressure. The crude mixture was purified by SiO_2 column chromatography using pentane/Et_2O or hexanes/EtOAc as eluent.



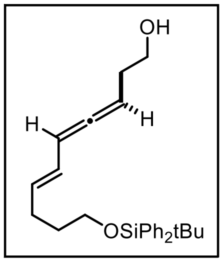
Method B – A round-botton flask equipped with a stirbar was charged with the homoallenic silyl ether (1.0 equiv) and diluted in tetrahydrofuran (0.5 M). The solution was stirred and DI H_2O (twice the amount of THF by volume) was added, followed by HOAc (four times the amount of THF by volume). The reaction stirred until starting material was completely consumed by TLC. At this point the reaction was quenched slowly with a large excess of saturated $NaHCO_3$ solution and transferred to a separatory funnel. The organic layer was washed with portions of $NaHCO_3$ until the formation of bubbles stopped and all AcOH was removed. The organic layer was dried over Na_2SO_4 before concentrating the volatiles under reduced pressure. The pure homoallenic alcohol was purified by SiO_2 column chromatography using pentane/ether or hexanes/EtOAc as eluent.



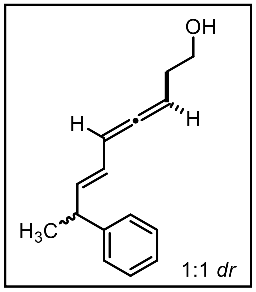
Compound S-12. Following method A (17.9 mmol scale), **S-12** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (1.83 g, 14.7 mmol, 76% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.89 – 5.77 (m, 2H), 5.68 – 5.59 (m, 1H), 5.30 (dddd, *J* = 7.8, 6.2, 4.3z, 2.3 Hz, 1H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.28 (qd, *J* = 6.4, 2.6 Hz, 2H), 1.74 (dt, *J* = 6.3, 1.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.8, 127.8, 126.6, 94.6, 88.7, 62.1, 32.4, 18.2. **HRMS** (ASAP-MS) *m/z* calculated for $C_8H_{12}O$ $[M+H]^+$ 125.0961, measured 125.0959 (1.6 ppm).



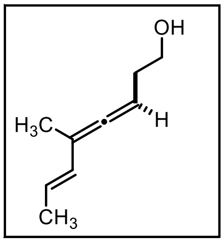
Compound S-13. Following method A (5.1 mmol scale), **S-13** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (0.761 g, 5.0 mmol, 98% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.85 – 5.75 (m, 2H), 5.62 (ddd, *J* = 14.8, 6.6, 1.4 Hz, 1H), 5.33 – 5.29 (m, 1H), 3.72 (q, *J* = 5.9 Hz, 2H), 2.36 – 2.25 (m, 3H), 1.59 (s, 1H), 1.00 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.1, 140.4, 122.4, 94.9, 88.7, 62.1, 32.4, 31.3, 25.8, 22.4. **HRMS** (ASAP-MS) *m/z* calculated for $C_{10}H_{16}O$ $[M+H]^+$ 153.1274, measured 153.1273 (0.7 ppm).



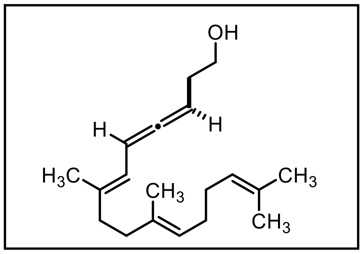
Compound S-14. Method B (2.4 mmol scale) was slightly modified. Allene was dissolved in THF and AcOH/H_2O were added. After 1 h, additional THF (5 mL) and AcOH (20 mL) were added to obtain a homogenous 67% AcOH solution. The reaction progress was monitored closely by TLC and the reaction was quenched after complete consumption of starting material as described above (1 h after extra AcOH was added). **S-14** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a viscous yellow oil (0.199 g, 0.5 mmol, 20% yield). Up to 1.6 mmol of additional product was collected as a mixture with DMTrOH byproduct that is more easily purified after converting the homoallenic alcohol to the corresponding sulfamate. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 – 7.66 (m, 4H), 7.42 – 7.36 (m, 6H), 5.87 – 5.78 (m, 2H), 5.62 (dtd, *J* = 14.3, 6.9, 1.5 Hz, 1H), 5.31 (tdd, *J* = 6.9, 5.6, 1.6 Hz, 1H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.29 (tt, *J* = 6.5, 3.2 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.69 – 1.62 (m, 2H), 1.50 (bs, 1H), 1.05 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.0, 135.7, 132.8, 129.7, 127.7, 125.6, 113.3, 94.7, 88.8, 63.4, 62.1, 32.4, 32.3, 29.1, 27.0, 19.4. **HRMS** (ASAP-MS) *m/z* calculated for $C_{26}H_{34}O_2Si$ $[M+H]^+$ 407.2401, measured 407.2401 (<0.1 ppm).



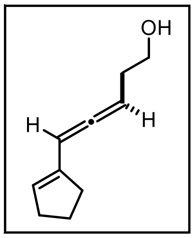
Compound S-15. Following method A (2.5 mmol scale), **S-15** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (0.478 g, 2.2 mmol, 89% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.20 (tt, *J* = 7.1, 1.5 Hz, 3H), 5.91 – 5.78 (m, 3H), 5.32 (tdd, *J* = 8.0, 6.0, 3.3 Hz, 1H), 3.73 (q, *J* = 5.4 Hz, 2H), 3.51 (p, *J* = 6.8 Hz, 1H), 2.30 (tdd, *J* = 9.0, 7.0, 4.4 Hz, 2H), 1.51 (bs, 1H), 1.38 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.42, 207.41, 145.74, 145.71, 137.54, 137.51, 128.61, 128.60, 127.35, 126.33, 126.32, 124.29, 124.25, 94.67, 94.66, 88.88, 88.87, 62.11, 62.10, 42.49, 42.48, 32.34, 32.33, 21.32, 21.26. **HRMS** (ASAP-MS) *m/z* calculated for $C_{15}H_{18}O$ $[M+H]^+$ 215.1430, measured 215.1428 (0.9 ppm).



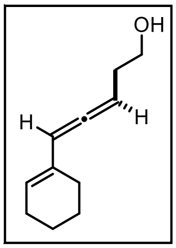
Compound S-16. Following method A (6.8 mmol scale), **S-16** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (0.691 g, 5.0 mmol, 74% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.97 (dd, *J* = 15.6, 2.3 Hz, 1H), 5.60 – 5.50 (m, 1H), 5.22 – 5.16 (m, 1H), 3.71 – 3.67 (m, 2H), 2.26 (q, *J* = 6.1 Hz, 2H), 1.79 (d, *J* = 2.7 Hz, 3H), 1.78 – 1.75 (m, 3H), 1.70 – 1.58 (bs, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.7, 129.5, 124.5, 100.7, 86.7, 62.2, 32.5, 18.4, 15.9. **HRMS** (ASAP-MS) *m/z* calculated for $C_9H_{14}O$ $[M+H]^+$ 139.1117, measured 119.1117 (<0.1 ppm).



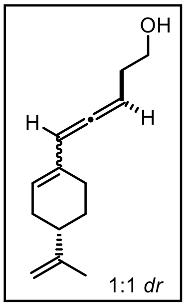
Compound S-17. Following method A (12.1 mmol scale), **S-17** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (2.670 g, 9.7 mmol, 80% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.94 (ddt, *J* = 11.0, 6.0, 3.0 Hz, 1H), 5.51 (dq, *J* = 10.9, 1.3 Hz, 1H), 5.20 (q, 1H), 5.04 – 4.95 (m, 2H), 3.61 (t, *J* = 6.1 Hz, 2H), 2.18 (qd, *J* = 6.5, 2.9 Hz, 2H), 1.97 (ddd, *J* = 19.2, 13.5, 6.8 Hz, 7H), 1.87 (dd, *J* = 9.1, 6.2 Hz, 2H), 1.62 (d, *J* = 1.3 Hz, 3H), 1.57 (d, *J* = 1.7 Hz, 3H), 1.49 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.8, 138.4, 135.5, 131.4, 124.5, 123.9, 119.2, 91.3, 88.3, 62.1, 40.1, 39.8, 32.4, 26.8, 26.6, 25.8, 17.8, 16.6, 16.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_{19}H_{30}O$ $[M+H]^+$ 275.2369, measured 275.2365 (1.5 ppm).



Compound S-18. Following method A (11.0 mmol scale), **S-18** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (1.054 g, 7.0 mmol, 64% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.08 (dt, *J* = 6.2, 2.9 Hz, 1H), 5.64 (q, *J* = 2.1 Hz, 1H), 5.36 (dt, *J* = 10.5, 6.7 Hz, 1H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.40 (tt, *J* = 7.4, 2.5 Hz, 2H), 2.30 (dddd, *J* = 12.8, 9.3, 6.7, 2.6 Hz, 4H), 1.89 (p, *J* = 7.5 Hz, 2H), 1.71 – 1.66 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.1, 138.1, 128.7, 92.1, 89.3, 62.1, 33.3, 32.7, 32.5, 23.3. **HRMS** (ASAP-MS) *m/z* calculated for $C_{10}H_{14}O$ $[M+H]^+$ 151.1117, measured 151.1117 (<0.1 ppm).



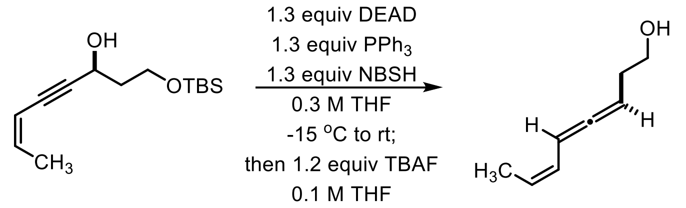
Compound S-19. Following method A (10.4 mmol scale), **S-19** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide an yellow oil (1.186 g, 7.2 mmol, 69% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.87 (dt, *J* = 6.0, 2.9 Hz, 1H), 5.66 (dt, *J* = 5.3, 2.5 Hz, 1H), 5.39 (tt, *J* = 7.8, 4.0 Hz, 1H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.29 (qd, *J* = 6.4, 2.9 Hz, 2H), 2.13 – 1.94 (m, 4H), 1.68 – 1.55 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.0, 131.9, 126.4, 98.5, 90.6, 62.2, 32.6, 26.0, 25.9, 22.6, 22.5. **HRMS** (ASAP-MS) *m/z* calculated for $C_{11}H_{16}O$ $[M+H]^+$ 165.1274, measured 165.1275 (0.6 ppm).



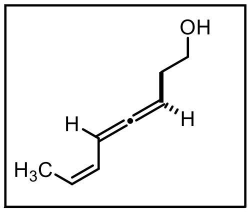
1:1 *dr*

Compound S-20. Following method A (12.3 mmol scale), **S-20** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (2.052 g, 10.0 mmol, 82% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.88 (dt, *J* = 5.5, 2.8 Hz, 1H), 5.70 – 5.64 (m, 1H), 5.39 (tdd, *J* = 13.2, 6.6, 1.8 Hz, 1H), 4.74 – 4.69 (m, 2H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.33 – 2.08 (m, 6H), 2.04 (m, 1H), 1.85 (ddp, *J* = 12.8, 4.9, 2.3 Hz, 1H), 1.73 (t, *J* = 1.1 Hz, 3H), 1.63 (s, 1H), 1.49 (dtt, *J* = 12.7, 11.0, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.2, 205.1, 149.9, 149.8, 131.72, 131.67, 125.74, 125.69, 108.84, 108.83, 98.04, 98.02, 90.7, 90.6, 62.2, 62.1, 41.2, 41.2, 32.63, 32.55, 31.42, 31.40, 27.58, 27.56, 26.4, 26.3, 20.92, 20.91. **HRMS** (ASAP-MS) *m/z* calculated for $C_{14}H_{20}O$ $[M+H]^+$ 205.1587, measured 205.1586 (0.5 ppm).

Procedure for (*Z*)-eneallene substrate:

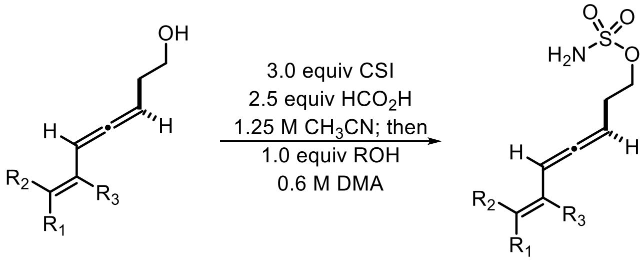


The starting enyne was prepared using a previously reported Sonogashira reaction.[7] A portion of THF (0.325 M with respect to DEAD) was used to dissolve PPh_3 and the solution was cooled to -15 °C before adding DEAD dropwise. After 10 min, alcohol in THF (0.33 M with respect to ROH) was added to the yellow mixture. After another 10 min, a solution of *o*-nitrobenzenesulfonylhydrazide (NBSH) in THF (0.65 M with respect to NBSH) was added. The temperature was held at -15 °C for 1-2 h until starting material was consumed according to TLC analysis. The reaction was warmed to room temperature and the mixture stirred overnight (>8 h). At this point the crude mixture was concentrated and directly purified by SiO_2 column chromatography. The resulting alcohol was immediately deprotected according to method A using TBAF (*vide supra*).

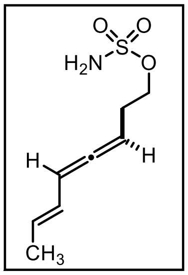


Compound S-21. The Mitsunobu outlined above was conducted twice on 10 mmol scale and purified on silica gel using a 0-15% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc providing ~4.7 mmol (47% yield) of allene each run. The deprotection was conducted following method A (8.4 mmol scale), **S-21** was purified on silica gel using a 0-30% hexanes:EtOAc solvent system with increasing 5% increments of EtOAc to provide a yellow oil (0.463 g, 3.7 mmol, 44% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.10 (dddq, *J* = 10.7, 5.9, 2.9, 1.5 Hz, 1H), 5.80 (tq, *J* = 11.0, 1.5 Hz, 1H), 5.46 (ddt, *J* = 10.4, 8.8, 6.2 Hz, 1H), 5.32 (q, *J* = 6.8 Hz, 1H), 3.70 (tt, *J* = 6.3, 1.6 Hz, 2H), 2.28 (qd, *J* = 6.3, 5.3, 2.5 Hz, 2H), 1.72 (dd, *J* = 7.0, 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.3, 125.9, 124.6, 90.0, 88.5, 62.0, 32.2, 13.3. **HRMS** (ASAP-MS) *m/z* calculated for $C_8H_{12}O$ $[M+H]^+$ 125.0961, measured 125.0960 (0.8 ppm).

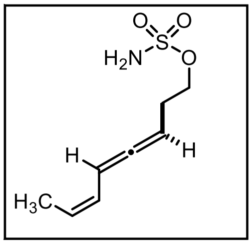
General procedure for the synthesis of homoallenic sulfamates:



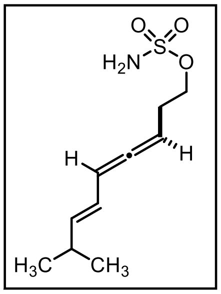
A dry, 3-necked round-bottom flask was equipped with a stirbar and chlorosulfonyl isocyanate (3.0 equiv) was added and cooled to 0 °C. At this temperature, formic acid (2.5 equiv) was added dropwise with vigorous stirring. Gas evolves and the reaction mixture solidified within 5 minutes. Acetonitrile (1.25 M with respect to formic acid) was then added and the solution stirs at 0 °C for 30 min before warming to room temperature for 4-6 hours. At this point the flask was cooled to 0 °C and to the cold solution was added alcohol (1.0 equiv) in *N,N*-dimethylacetamide (0.6 M with respect to alcohol). The solution was warmed to room temperature and the mixture was stirred for 1-2 hours or until starting material was completely consumed according to TLC. The reaction was quenched by the addition of H_2O and the aqueous phase was extracted thrice with ether. The combined organic extracts were then washed with five portions of water, once with brine, then dried over Na_2SO_4 before concentrating under reduced pressure. The crude products were purified by SiO_2 column chromatography using a pentane/ether gradient. The purified sulfamate was dried for 1-2 hours to remove residual solvent before being stored in a -78 °C freezer. **NOTE**: The homoallenic sulfamates change color if left under vacuum overnight, so the use of diethyl ether instead of EtOAc for these purifications was critical for fast solvent removal.



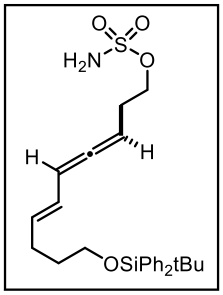
Compound 4. Following the general procedure (7.0 mmol scale), **4** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide an off-white solid upon drying and freezing at -78 °C (0.978 g, 4.8 mmol, 69% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.88 – 5.80 (m, 2H), 5.70 – 5.61 (m, 1H), 5.33 – 5.27 (m, 1H), 5.02 – 4.93 (s, 2H), 4.25 (td, *J* = 6.7, 1.1 Hz, 2H), 2.46 (qd, *J* = 6.6, 2.2 Hz, 2H), 1.74 (dt, *J* = 7.0, 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.9, 128.4, 126.2, 95.4, 87.2, 70.3, 28.4, 18.2. **HRMS** (ESI-MS) *m/z* calculated for $C_8H_{13}NO_3S$ $[M–H]^-$ 202.0543, measured 202.0544 (0.5 ppm).



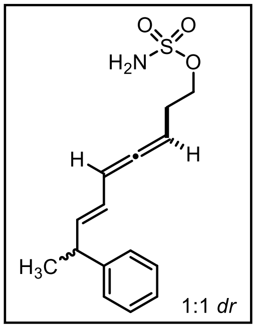
Compound 5. Following the general procedure (3.7 mmol scale), **5** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a yellow oil that solidified upon storing at -78 °C (0.597 g, 2.9 mmol, 79% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.14 (ddtd, *J* = 10.8, 6.1, 2.9, 1.4 Hz, 1H), 5.84 – 5.77 (m, 1H), 5.49 (dddd, *J* = 10.7, 8.7, 7.0, 5.5 Hz, 1H), 5.32 (dtdt, *J* = 7.6, 5.1, 2.4, 1.2 Hz, 1H), 4.96 (s, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 2.47 (qd, *J* = 6.6, 2.9 Hz, 2H), 1.72 (dt, *J* = 7.1, 1.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.5, 126.5, 124.3, 90.7, 87.0, 70.3, 28.3, 13.3. **HRMS** (ESI-MS) *m/z* calculated for $C_8H_{13}NO_3S$ $[M–H]^-$ 202.0543, measured 202.0544 (0.5 ppm).



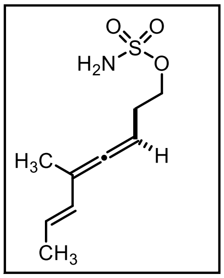
Compound 6. Following the general procedure (5.0 mmol scale), **6** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a clear, yellow-tinted oil (0.882 g, 3.8 mmol, 76% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.87 – 5.75 (m, 2H), 5.64 (ddd, *J* = 14.5, 6.6, 1.3 Hz, 1H), 5.30 (q, *J* = 6.4 Hz, 1H), 4.87 (s, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 2.47 (qd, *J* = 6.6, 2.7 Hz, 2H), 2.34 (dddd, *J* = 13.4, 7.9, 6.8, 5.5 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.2, 141.0, 122.1, 95.6, 87.2, 70.3, 31.3, 28.4, 22.38, 22.36. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{17}NO_3S$ $[M–H]^-$ 230.0856, measured 230.0858 (0.9 ppm).



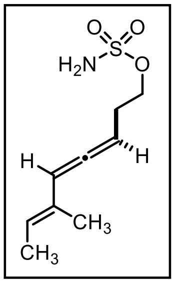
Compound 7. Following the general procedure (0.8 mmol scale), **7** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a red oil (94.8 mg, 0.2 mmol, 25% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 – 7.65 (m, 4H), 7.45 – 7.35 (m, 6H), 5.86 – 5.79 (m, 2H), 5.67 – 5.58 (m, 1H), 5.35 – 5.28 (m, 1H), 4.64 (bs, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.47 (qd, *J* = 6.7, 2.3 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.69 – 1.62 (m, 2H), 1.05 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.2, 135.7, 134.2, 133.5, 129.7, 127.8, 125.3, 95.5, 87.2, 70.3, 63.3, 32.2, 29.1, 28.4, 27.0, 19.4. **HRMS** (ESI-MS) *m/z* calculated for $C_{26}H_{35}NO_4S$ $[M+Na]^+$ 508.1948, measured 508.1946 (0.4 ppm).



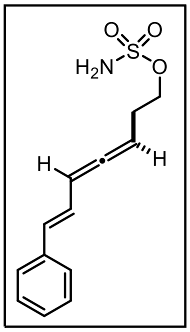
Compound 8. Following the general procedure (2.2 mmol scale), **8** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a white solid (0.423 g, 1.4 mmol, 66% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.22 – 7.18 (m, 3H), 5.90 – 5.81 (m, 3H), 5.36 – 5.30 (m, 1H), 4.67 (bs, 2H), 4.26 (q, *J* = 6.5 Hz, 2H), 3.51 (h, *J* = 6.7 Hz, 1H), 2.51 – 2.44 (m, 2H), 1.39 (dd, *J* = 7.0, 2.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.55, 207.54, 145.7, 145.6, 138.15, 138.13, 128.68, 128.65, 127.4, 127.3, 126.41, 126.39, 123.95, 123.90, 95.41, 95.36, 87.39, 87.36, 70.24, 70.18, 42.55, 42.47, 28.4, 28.3, 21.3, 21.2. **HRMS** (ESI-MS) *m/z* calculated for $C_{15}H_{19}NO_3S$ $[M+Na]^+$ 316.0978, measured 316.0974 (1.3 ppm).



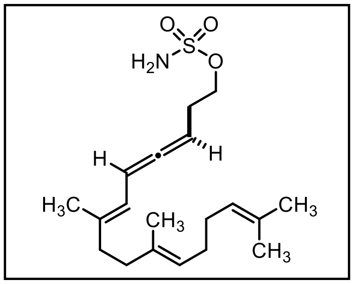
Compound 9. Following the general procedure (5.0 mmol scale), **9** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a yellow oil (0.225 g, 1.0 mmol, 20% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.00 – 5.93 (m, 1H), 5.62 – 5.52 (m, 1H), 5.19 (dddd, *J* = 6.4, 5.0, 3.2, 1.5 Hz, 1H), 4.86 (bs, 2H), 4.24 (t, *J* = 6.7 Hz, 2H), 2.44 (q, *J* = 6.6 Hz, 2H), 1.78 (dd, *J* = 7.7, 2.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.8, 129.2, 125.0, 101.5, 85.2, 70.5, 28.6, 18.4, 15.7. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{15}NO_3S$ $[M–H]^-$ 216.0700, measured 216.0701 (0.5 ppm).



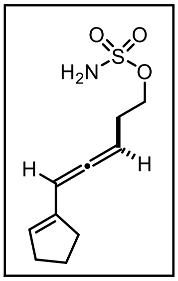
Compound 10. The sulfamate was characterized over two steps from TBS-ether **S-6** after being deprotected using method A. Following the general procedure (10.0 mmol scale), **10** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide an orange oil (0.629 g, 2.9 mmol, 29% yield over two steps). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.92 (dt, *J* = 6.1, 3.0 Hz, 1H), 5.47 (qq, *J* = 7.0, 1.3 Hz, 1H), 5.42 – 5.36 (m, 1H), 4.81 (s, 2H), 4.27 (t, *J* = 6.6 Hz, 2H), 2.48 (qdd, *J* = 6.7, 2.9, 1.1 Hz, 2H), 1.70 (dt, *J* = 6.9, 1.3 Hz, 3H), 1.69 – 1.66 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 205.4, 130.3, 124.3, 100.9, 89.0, 70.3, 28.7, 14.1, 13.34. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{15}NO_3S$ $[M–H]^-$ 216.0700, measured 216.0701 (0.5 ppm).



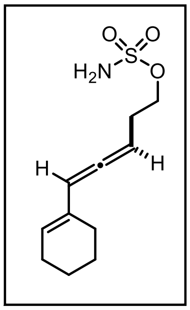
Compound 11. The sulfamate was characterized over two steps from TBS-ether **S-7** after being deprotected using method B. Following the general procedure (2.8 mmol scale), **11** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a light yellow solid (0.237 g, 0.9 mmol, 32% yield over two steps). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.22 (dd, *J* = 7.8, 5.9 Hz, 1H), 6.64 – 6.44 (m, 2H), 6.06 (ddt, *J* = 9.4, 6.0, 2.8 Hz, 1H), 5.44 (q, *J* = 6.5 Hz, 1H), 4.70 (s, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.53 (qd, *J* = 6.6, 2.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.0, 137.2, 131.3, 128.8, 127.7, 126.4, 124.4, 96.1, 87.8, 70.2, 28.4. **HRMS** (ESI-MS) *m/z* calculated for $C_{13}H_{15}NO_3S$ $[M–H]^-$ 264.0700, measured 264.0700 (<0.1 ppm).



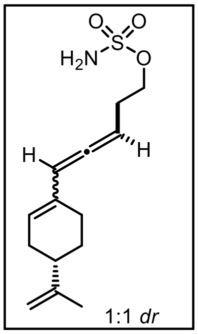
Compound 12. Following the general procedure (9.7 mmol scale), **12** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a yellow-orange oil (1.944 g, 5.5 mmol, 57% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.07 (ddt, *J* = 10.8, 6.1, 2.9 Hz, 1H), 5.61 (dt, *J* = 10.9, 1.3 Hz, 1H), 5.30 (q, *J* = 4.9 Hz, 1H), 5.09 (qt, *J* = 7.0, 1.5 Hz, 2H), 4.86 (s, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 2.47 (qd, *J* = 6.7, 2.9 Hz, 2H), 2.16 – 2.02 (m, 6H), 1.97 (dd, *J* = 9.1, 6.1 Hz, 2H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.6 Hz, 3H), 1.60 (d, *J* = 1.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.0, 139.1, 135.6, 131.5, 124.5, 123.9, 118.9, 92.0, 86.8, 70.4, 40.1, 39.8, 28.5, 26.8, 26.6, 25.8, 17.8, 16.7, 16.1. **HRMS** (ESI-MS) *m/z* calculated for $C_{19}H_{31}NO_3S$ $[M–H]^-$ 352.1952, measured 352.1948 (1.1 ppm).



Compound 13. Following the general procedure (7.0 mmol scale), **13** was purified on silica gel using a 0-100% pentane:Et_2O solvent system with increasing 20% increments of Et_2O to provide a dark red-brown oil (0.474 g, 2.1 mmol, 30% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.11 (dt, *J* = 6.2, 3.0 Hz, 1H), 5.67 (q, *J* = 2.1 Hz, 1H), 5.41 – 5.33 (m, 1H), 4.91 (s, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 2.48 (qd, *J* = 6.6, 3.0 Hz, 2H), 2.41 (ddt, *J* = 7.4, 5.0, 2.3 Hz, 2H), 2.32 (tt, *J* = 7.3, 1.8 Hz, 2H), 1.95 – 1.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.2, 137.9, 129.3, 92.8, 87.8, 70.2, 33.3, 32.7, 28.5, 23.3. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{15}NO_3S$ $[M–H]^-$ 228.0700, measured 228.0703 (0.5 ppm).

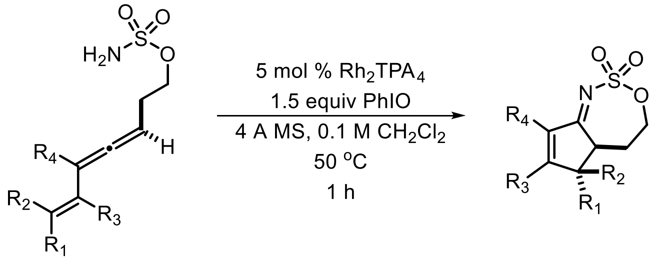


Compound 14. Following the general procedure (7.2 mmol scale), **14** was purified on silica gel using a 0-100% pentane:Et$_2$O solvent system with increasing 20% increments of Et$_2$O to provide an orange oil (1.293 g, 5.3 mmol, 74% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.89 (dd, *J* = 6.3, 3.1 Hz, 1H), 5.68 (dq, *J* = 4.6, 2.0 Hz, 1H), 5.41 – 5.35 (m, 1H), 4.86 (s, 2H), 4.26 (dd, *J* = 8.0, 5.4 Hz, 2H), 2.47 (qq, *J* = 6.9, 2.3 Hz, 2H), 2.10 (dtq, *J* = 6.5, 4.6, 2.2 Hz, 2H), 2.00 (ddt, *J* = 7.1, 4.9, 2.7 Hz, 2H), 1.69 – 1.55 (m, 4H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 205.1, 131.9, 127.0, 99.3, 89.0, 70.3, 28.6, 26.0, 25.8, 22.6, 22.5. **HRMS** (ESI-MS) *m/z* calculated for $C_{11}H_{17}NO_3S$ [M–H]$^-$ 242.0856, measured 242.0858 (0.8 ppm).

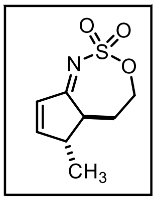


Compound 15. Following the general procedure (10.0 mmol scale), **15** was purified on silica gel using a 0-100% pentane:Et$_2$O solvent system with increasing 20% increments of Et$_2$O to provide an orange oil that becomes solid after storing at -78 ^{o}C (1.921 g, 6.8 mmol, 68% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.91 (dt, *J* = 6.4, 3.0 Hz, 1H), 5.69 (d, *J* = 5.1 Hz, 1H), 5.39 (dq, *J* = 13.4, 6.6 Hz, 1H), 4.94 – 4.77 (m, 2H), 4.75 – 4.70 (m, 2H), 4.26 (tt, *J* = 6.6, 2.0 Hz, 2H), 2.48 (ddt, *J* = 7.2, 5.0, 2.7 Hz, 2H), 2.28 – 2.11 (m, 3H), 2.10 – 1.99 (m, 2H), 1.89 – 1.82 (m, 1H), 1.74 (s, 3H), 1.55 – 1.43 (m, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 205.33, 205.29, 149.80, 149.77, 131.60, 131.58, 126.26, 126.25, 108.91, 108.90, 98.78, 98.77, 89.10, 89.09, 70.30, 70.26, 41.17, 41.16, 31.41, 31.40, 28.67, 28.65, 28.61, 27.5, 26.3, 26.2, 20.94, 20.93. **HRMS** (ESI-MS) *m/z* calculated for $C_{14}H_{21}NO_3S$ [M–H]$^-$ 282.1169, measured 282.1168 (0.4 ppm).

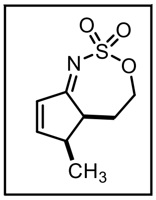
III. Procedure for eneallene aziridination/electrocyclization



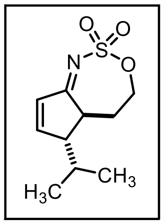
A dry round-bottom flask equipped with a stir bar was charged with 4 A molecular sieves before adding Rh$_2$TPA$_4$ (5 mol %, 0.05 equiv) and homoallenic sulfamate (1.0 equiv) using anhydrous CH$_2$Cl$_2$ (0.1 M) to transfer quantitatively. The solution was placed in an oil bath preheated to 50 ^{o}C and stirred vigorously. As soon as boiling starts, PhIO (1.5 equiv) was added in a single portion and the reaction was fit with a reflux condenser and stirred for 1 h at which point all allene is consumed by ^{1}H NMR analysis of reaction aliquots or TLC. The reaction was cooled to room temperature, diluted with CH_2Cl_2, and filtered over a fritted funnel. The filtrate was concentrated under reduced pressure and the crude mixture was purified by SiO_2 column chromatography using a gradient of either hexanes/EtOAc or pentane/Et_2O.



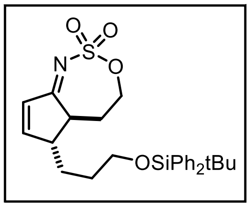
Compound 4a. Following the general procedure (0.3 mmol scale), **4a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a light-yellow oil (38.2 mg, 0.19 mmol, 63% yield, >19:1 *dr*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 5.5, 2.3 Hz, 1H), 6.29 (dd, *J* = 5.5, 2.0 Hz, 1H), 4.73 – 4.66 (m, 1H), 4.50 (dt, *J* = 12.0, 3.9 Hz, 1H), 2.99 (ddd, *J* = 10.4, 6.1, 2.3 Hz, 1H), 2.80 (dddd, *J* = 9.5, 7.3, 5.0, 2.2 Hz, 1H), 2.08 (ddd, *J* = 10.4, 7.7, 4.2 Hz, 2H), 1.28 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.2, 167.1, 132.9, 71.3, 52.2, 47.8, 29.6, 18.1. **HRMS** (ESI-MS) *m/z* calculated for $C_8H_{11}NO_3S$ $[M+H]^+$ 202.0532, measured 202.0530 (1.0 ppm).



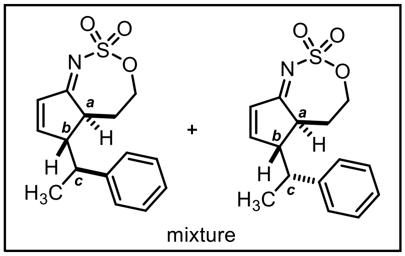
Compound 5a. Following the general procedure (0.5 mmol scale), **5a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a yellow solid (35.9 mg, 0.18 mmol, 36% yield, 2.4:1 *syn:anti*). **Major *(syn)* diastereomer ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 5.5, 2.7 Hz, 1H), 6.32 (dd, *J* = 5.5, 1.9 Hz, 1H), 4.64 (dd, *J* = 11.2, 4.2 Hz, 1H), 4.57 – 4.52 (m, 1H), 3.52 (ddd, *J* = 11.0, 6.0, 4.0 Hz, 1H), 3.38 – 3.31 (m, 1H), 2.03 – 1.95 (m, 2H), 1.14 (d, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.8, 168.6, 132.5, 71.2, 46.7, 43.2, 26.4, 15.7. **HRMS** (ESI-MS) *m/z* calculated for $C_8H_{11}NO_3S$ $[M+H]^+$ 202.0532, measured 202.0531 (1.4 ppm). **NOTE:** the minor *(anti)* diastereomer is characterized as compound **4a**.



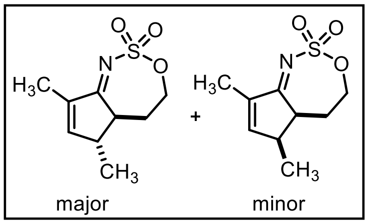
Compound 6a. Following the general procedure (3.26 mmol scale), **6a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a light-brown oil (0.553 g, 2.4 mmol, 74% yield, >19:1 *dr*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 5.6, 2.4 Hz, 1H), 6.32 (dd, *J* = 5.6, 2.0 Hz, 1H), 4.70 (td, *J* = 11.8, 3.7 Hz, 1H), 4.46 (ddd, *J* = 12.0, 4.9, 2.5 Hz, 1H), 3.20 (ddd, *J* = 11.8, 3.6, 2.1 Hz, 1H), 2.59 (dq, *J* = 6.4, 2.1 Hz, 1H), 2.11 – 1.97 (m, 2H), 1.87 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.00 (dd, *J* = 10.8, 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.7, 165.4, 133.6, 71.1, 59.6, 47.4, 31.3, 30.7, 20.5, 20.0. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{15}NO_3S$ $[M+H]^+$ 230.0845, measured 230.0844 (0.4 ppm).



Compound 7a. Following the general procedure (0.195 mmol scale), **7a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a yellow oil (61.2 mg, 0.127 mmol, 65% yield, *dr* >19:1 *anti*:*syn*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.65 (dt, *J* = 6.7, 1.6 Hz, 4H), 7.46 – 7.37 (m, 6H), 7.34 (dd, *J* = 5.6, 2.3 Hz, 1H), 6.28 (dd, *J* = 5.5, 2.0 Hz, 1H), 4.65 (td, *J* = 11.9, 3.5 Hz, 1H), 4.45 (ddd, *J* = 12.0, 5.0, 2.3 Hz, 1H), 3.73 – 3.68 (m, 2H), 3.04 (ddd, *J* = 12.1, 3.4, 2.1 Hz, 1H), 2.71 (ddq, *J* = 6.8, 4.6, 2.4 Hz, 1H), 2.02 – 1.91 (m, 2H), 1.64 (ddq, *J* = 12.2, 6.2, 3.8, 2.9 Hz, 4H), 1.06 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.2, 166.0, 135.7, 133.8, 133.2, 129.9, 127.9, 71.1, 63.4, 52.7, 50.2, 30.3, 30.1, 29.8, 27.0, 19.3. **HRMS** (ESI-MS) *m/z* calculated for $C_{26}H_{33}NO_4SSi$ $[M+H]^+$ 484.1972, measured 484.1968 (0.8 ppm).

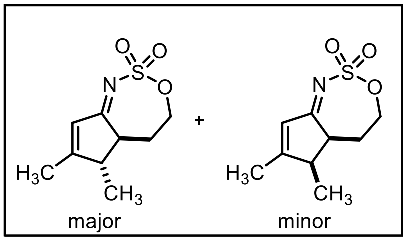


Compound 8a. Following the general procedure (0.259 mmol scale), **8a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a yellow oily solid (55.2 mg, 0.189 mmol, 73% yield, $dr_{a,b}$ >19:1 *anti*:*syn* and $dr_{ab,c}$ = 1.2:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 5.6, 2.3 Hz, 1H), 7.35 (td, *J* = 7.7, 2.2 Hz, 4H), 7.29 – 7.23 (m, 4H), 7.21 – 7.16 (m, 3H), 6.36 (dd, *J* = 5.6, 2.0 Hz, 1H), 6.26 (d, *J* = 5.6 Hz, 1H), 4.55 (td, *J* = 12.1, 3.3 Hz, 1H), 4.38 (ddd, *J* = 12.0, 5.1, 2.2 Hz, 1H), 4.18 – 4.09 (m, 2H), 3.23 (dd, *J* = 12.5, 2.9 Hz, 1H), 3.08 (dt, *J* = 12.2, 2.6 Hz, 1H), 2.99 – 2.93 (m, 2H), 2.84 (dq, *J* = 9.9, 2.2 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.04 – 1.96 (m, 2H), 1.81 (ddt, *J* = 14.6, 11.6, 5.9 Hz, 1H), 1.70 (dq, *J* = 14.9, 2.9 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.36 (d, *J* = 5.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.2, 192.6, 165.5, 164.3, 143.9, 143.2, 134.0, 133.4, 129.1, 129.0, 127.5, 127.3, 127.14, 127.05, 70.8, 60.0, 59.4, 49.2, 47.6, 44.1, 43.1, 30.5, 29.8, 19.1, 18.5. **HRMS** (ESI-MS) *m/z* calculated for $C_{15}H_{17}NO_3S$ $[M+H]^+$ 292.1002, measured 292.0999 (1.0 ppm). **NOTE:** Relative stereochemistry of the major diastereomers was determined by analogy to other substrates with nOe data and by comparing coupling constants. $J_{a,b}$ = 2-3 Hz is consistent with *anti* cyclopentene while $J_{a,b}$ = 6-8 Hz for *syn* cyclopentene.

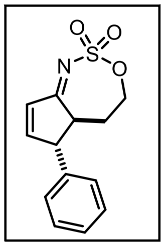


Compound 9a. Following the general procedure (0.32 mmol scale), **9a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a light-yellow oil (44.4 mg, 0.21 mmol, 65% yield, *dr* = 4.1:1 *anti*:*syn*). **Major *(anti)* diastereomer ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.01 (s, 1H), 4.67 (qd, *J* = 10.7, 10.1, 5.3 Hz, 1H), 4.55 – 4.43 (m, 1H), 3.01 – 2.95 (m, 1H), 2.63 (dtt, *J* = 9.7, 5.0, 2.4 Hz, 1H), 2.08 – 2.01 (m, 2H), 1.83 (q, *J* = 2.3, 1.8 Hz, 3H), 1.21 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz,

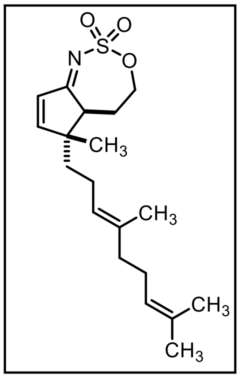
$CDCl_3$) δ 192.1, 161.2, 139.6, 70.3, 51.5, 43.9, 28.5, 17.1, 10.35. **Minor *(syn)* diastereomer ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 2.8 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.52 (dt, *J* = 9.6, 2.9 Hz, 1H), 3.52 (dt, *J* = 10.9, 5.3 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.03 (d, *J* = 3.5 Hz, 2H), 1.83 (s, 3H), 1.08 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.4, 162.4, 139.2, 70.1, 46.0, 39.3, 25.4, 14.9, 10.38. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{13}NO_3S$ $[M+H]^+$ 216.0689, measured 216.0687 (0.9 ppm).



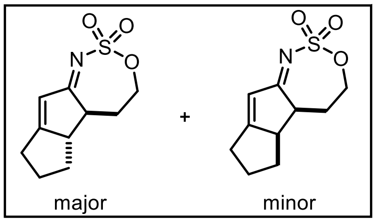
Compound 10a. Following the general procedure (0.5 mmol scale), **10a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a yellow-brown oil (45.9 mg, 0.21 mmol, 46% yield, 2.0:1 *anti*:*syn*). **NOTE:** Using 1 mol % Rh_2TPA_4 seemed to improve the *dr* to 3.9:1. **Major (*Anti)* diastereomer ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.02 (t, *J* = 1.5 Hz, 1H), 4.66 (ddd, *J* = 11.8, 9.1, 6.8 Hz, 1H), 4.44 (dt, *J* = 12.0, 3.8 Hz, 1H), 3.04 (ddd, *J* = 8.6, 6.7, 2.4 Hz, 1H), 2.59 (tdd, *J* = 8.9, 4.8, 1.9 Hz, 1H), 2.10 (d, *J* = 1.3 Hz, 3H), 2.05 – 2.00 (m, 2H), 1.24 (d, *J* = 7.4 Hz, 3H). **Minor *(Syn)* diastereomer ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.07 (t, *J* = 1.5 Hz, 1H), 4.63 – 4.55 (m, 1H), 4.49 (dt, *J* = 11.9, 3.8 Hz, 1H), 3.54 (dt, *J* = 8.6, 6.3 Hz, 1H), 3.12 (p, *J* = 7.4 Hz, 1H), 2.13 (s, 3H), 1.98 – 1.93 (m, 2H), 1.12 (d, *J* = 7.5 Hz, 3H). **Mixed ^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.4, 192.7, 182.9, 181.8, 129.3, 129.2, 71.2, 70.8, 53.1, 50.2, 47.7, 45.9, 30.0, 26.5, 17.7, 17.2, 16.8, 14.8. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{13}NO_3S$ $[M+H]^+$ 216.0689, measured 216.0688 (0.5 ppm).



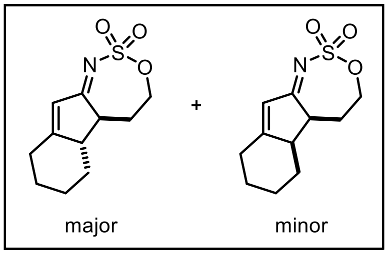
Compound 11a. Following the general procedure (0.2 mmol scale), **11a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a light-yellow oil (19.0 mg, 0.072 mmol, 36% yield, >19:1 *anti*:*syn*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 4H), 7.15 (dd, *J* = 6.9, 1.8 Hz, 2H), 6.49 (dd, *J* = 5.5, 2.2 Hz, 1H), 4.56 (td, *J* = 11.6, 4.3 Hz, 1H), 4.48 (ddd, *J* = 12.0, 5.1, 2.5 Hz, 1H), 3.87 (q, *J* = 2.5 Hz, 1H), 3.33 – 3.27 (m, 1H), 2.29 – 2.17 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.4, 164.1, 138.9, 134.1, 129.5, 128.4, 127.3, 71.0, 58.3, 54.0, 29.5. **HRMS** (ESI-MS) *m/z* calculated for $C_{13}H_{13}NO_3S$ $[M+H]^+$ 262.0543, measured 262.0543 (<0.1 ppm).



Compound 12a. Following the general procedure (0.5 mmol scale), **12a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a yellow solid (56.2 mg, 0.16 mmol, 31% yield, >19:1 *anti*:*syn*). ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 5.5 Hz, 1H), 6.24 (d, *J* = 5.6 Hz, 1H), 5.07 (qdt, *J* = 5.3, 2.7, 1.4 Hz, 2H), 4.59 – 4.51 (m, 2H), 3.14 (dd, *J* = 12.3, 2.7 Hz, 1H), 2.17 – 2.02 (m, 4H), 2.00 – 1.88 (m, 4H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.57 (m, 8H), 1.11 (s, 3H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 192.2, 171.2, 136.7, 131.8, 131.1, 124.2, 123.1, 70.8, 52.2, 52.0, 40.0, 39.8, 26.8, 26.7, 25.9, 23.5, 22.6, 17.8, 16.3. **HRMS** (ESI-MS) *m/z* calculated for $C_{19}H_{29}NO_3S$ [M+H]$^+$ 352.1941, measured 352.1936 (1.4 ppm).

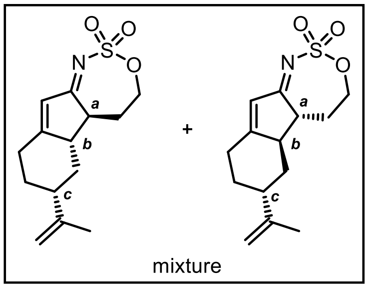


Compound 13a. Following the general procedure (0.21 mmol scale), **13a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide an off-white solid (28.9 mg, 0.13 mmol, 62% yield, 13.7:1 *anti*:*syn*). **Major *(Anti)* diastereomer** ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 6.05 (d, *J* = 1.9 Hz, 1H), 4.61 (td, *J* = 12.1, 3.3 Hz, 1H), 4.46 (ddd, *J* = 11.9, 5.0, 2.1 Hz, 1H), 3.11 (dt, *J* = 12.3, 3.1 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.61 (m, 2H), 2.24 – 2.07 (m, 4H), 1.35 – 1.24 (m, 2H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 195.4, 190.6, 124.5, 70.4, 58.5, 50.9, 30.8, 29.7, 26.6, 26.4. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{13}NO_3S$ [M+H]$^+$ 228.0688, measured 228.0683 (2.2 ppm).



Compound 14a. Following the general procedure (0.5 mmol scale), **14a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide an off-white solid (89.8 mg, 0.37 mmol, 74% yield, 3.0:1 *anti*:*syn*). Characterized as the mixture of diastereomers before isolating and characterizing pure ***anti*-14a**. ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 6.02 (m, 1H), 4.75 – 4.60 (m, 1H), 4.47 (m, 1H), 3.63 – 3.06 (m, 1H), 2.99 – 2.82 (m, 1H), 2.45 – 2.21 (m, 3H), 2.10 – 1.99 (m, 3H), 1.96 – 1.87 (m, 1H), 1.53 – 1.32 (m, 2H), 1.28 – 1.14 (m, 1H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 194.1, 193.0, 185.0, 183.6, 126.3, 126.0, 71.2, 71.0, 53.0, 51.8, 48.5, 47.0, 33.30, 33.29, 31.3, 30.9, 30.3, 27.3, 26.5, 26.1, 25.1, 24.9. **Compound *anti*-14a.** ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 6.00 (d, *J* = 1.8 Hz, 1H), 4.74 – 4.65 (m, 1H), 4.45 (dt, *J* = 12.1, 3.9 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.84 (ddt, *J* = 14.0, 3.9, 1.9 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.33 – 2.20 (m, 2H), 2.08 – 1.99 (m, 3H), 1.94 – 1.87 (m, 1H), 1.51 – 1.32 (m, 2H), 1.23 – 1.17 (m, 1H). ^{13}**C NMR**

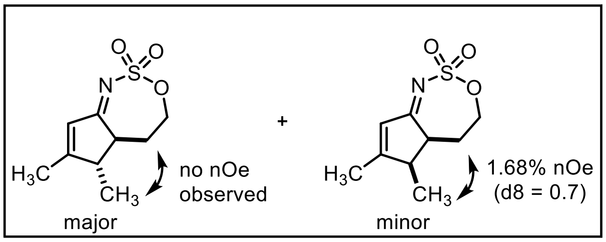
(126 MHz, $CDCl_3$) δ 193.0, 183.6, 126.3, 71.2, 53.0, 51.8, 33.3, 30.9, 30.3, 26.5, 24.9. **HRMS** (ESI-MS) *m/z* calculated for $C_{11}H_{15}NO_3S$ $[M+H]^+$ 242.0845, measured 228.0843 (0.8 ppm).

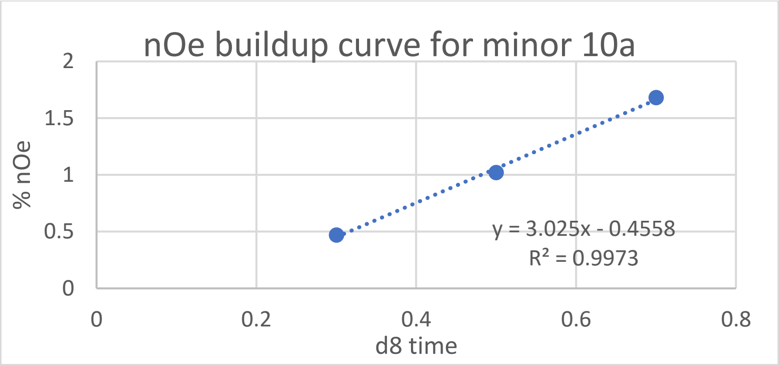


Compound 15a. Following the general procedure (0.5 mmol scale), **15a** was purified on silica gel using a 0-60% hexanes:EtOAc solvent system with increasing 10% increments of EtOAc to provide a light-brown oil (108.2 mg, 0.385 mmol, 77% yield, $dr_{a,b}$ >19:1 *anti*:*syn* and $dr_{ab,c}$ = 1.2:1). Characterized as a mixture of diastereomers. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.03 (dt, *J* = 3.5, 1.7 Hz, 1H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.03 (q, *J* = 1.5 Hz, 1H), 4.89 (s, 1H), 4.76 (p, *J* = 1.5 Hz, 1H), 4.73 – 4.66 (m, 3H), 4.45 (dddd, *J* = 12.2, 5.8, 4.8, 2.6 Hz, 2H), 3.11 (ddt, *J* = 7.8, 5.6, 2.4 Hz, 1H), 3.06 (dt, *J* = 11.7, 3.0 Hz, 1H), 2.90 (ddd, *J* = 14.3, 4.3, 2.2 Hz, 1H), 2.68 (ddd, *J* = 14.5, 4.6, 2.6 Hz, 1H), 2.62 – 2.46 (m, 5H), 2.42 – 2.28 (m, 2H), 2.27 – 2.15 (m, 2H), 2.09 – 2.05 (m, 1H), 2.03 – 1.93 (m, 4H), 1.80 (d, *J* = 3.4 Hz, 3H), 1.74 – 1.72 (m, 3H), 1.68 – 1.61 (m, 1H), 1.46 (td, *J* = 13.0, 4.7 Hz, 1H), 1.42 – 1.33 (m, 1H), 1.28 – 1.23 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.1, 192.9, 184.2, 182.5, 147.8, 144.6, 126.5, 125.9, 112.0, 110.2, 71.19, 71.16, 52.7, 51.9, 51.8, 48.7, 43.9, 38.1, 37.9, 34.8, 31.5, 30.4, 30.3, 30.2, 28.2, 26.9, 22.6, 20.9. **HRMS** (ESI-MS) *m/z* calculated for $C_{14}H_{19}NO_3S$ $[M+H]^+$ 282.1158, measured 282.1157 (0.4 ppm). **NOTE:** Trace amounts of a third diastereomer could be detected (major:minor = 22.2:1). Relative stereochemistry of the major diastereomers was determined by analogy to other substrates with nOe data and by comparing coupling constants.

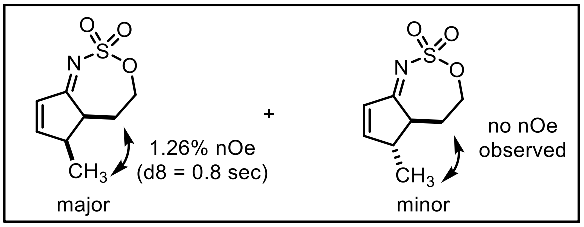
IV. Representative nOe studies

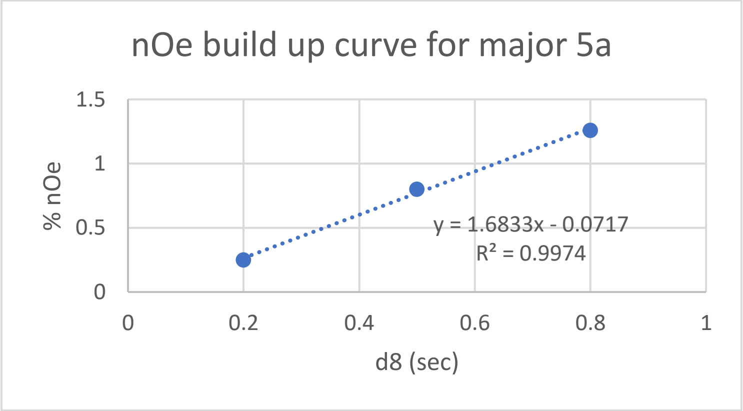
*Selective 1-D NOESY to determine relative stereochemistry for major & minor diastereomers of **10a***



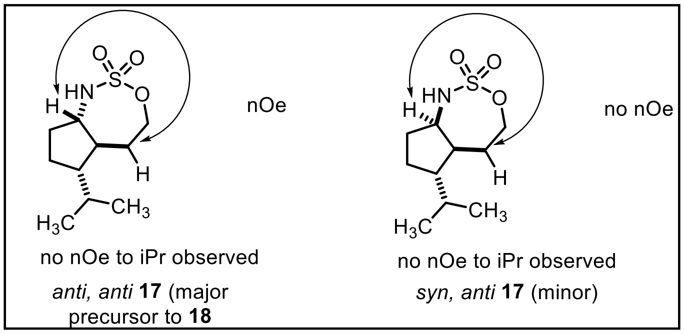


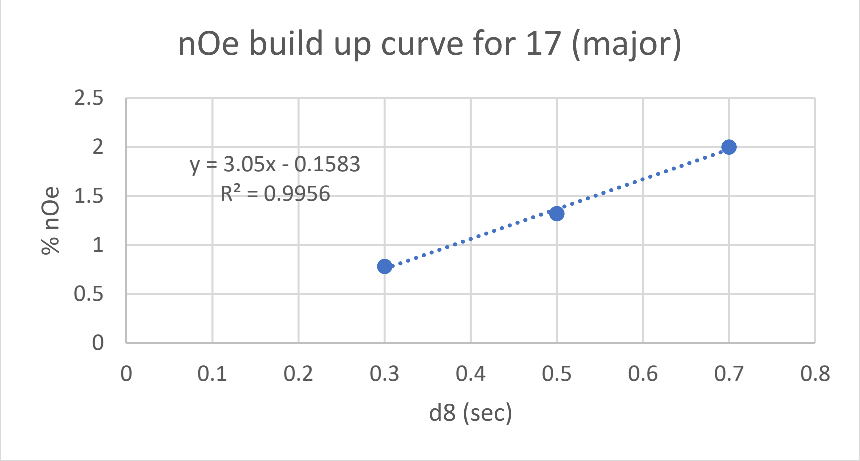
Selective 1-D NOESY to determine relative stereochemistry for major & minor diastereomers of ***5a***



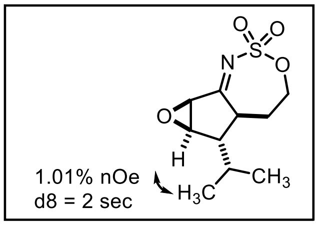


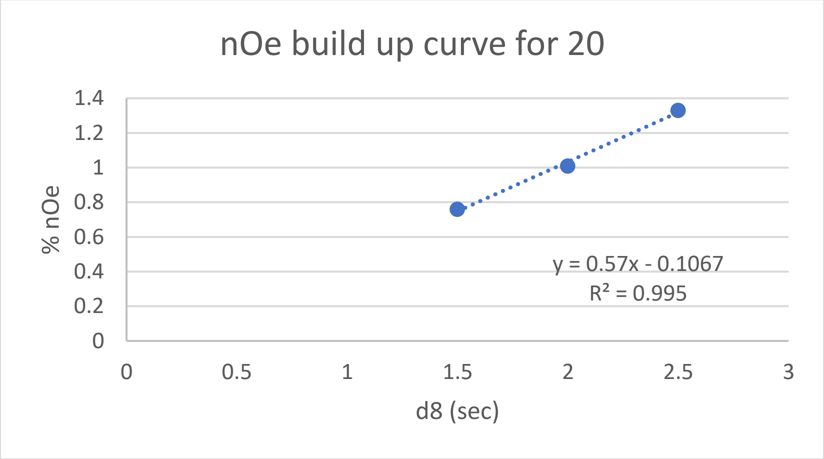
Selective 1-D NOESY to determine relative stereochemistry for ***17*** *and linear build-up curve*





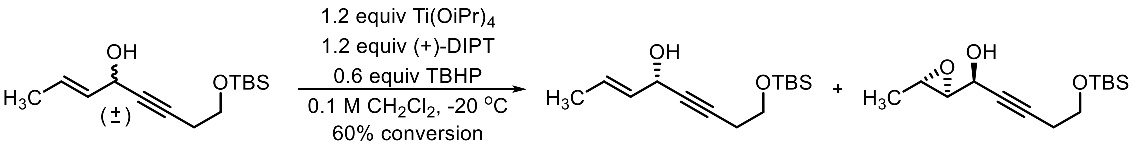
Selective 1-D NOESY to determine relative stereochemistry for ***20*** *and linear build-up curve*



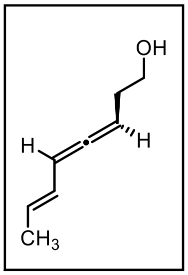


V. Axial-to-point chirality transfer and chiral catalyst experiment

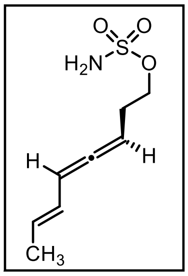
Chiral substrate preparation: Enantioenriched allyl propargyl alcohol was prepared by Sharpless kinetic resolution.[8a-b]



A dry round-bottom flask equipped with a stir bar was charged with anhydrous CH_2Cl_2 (0.1 M) and cooled to -20 °C. At this temperature, $Ti(OiPr)_4$ (1.2 equiv) was added followed by (+)-diisopropyl tartrate (1.2 equiv) and stir 10 min. Alcohol (1.0 equiv) was then added, followed by tert-butyl hydroperoxide (0.6 equiv). The reaction was maintained at -20 °C for 48 h at which point ^1H NMR aliquot showed 60% conversion to the undesired epoxide (alternatively, reaction can be monitored by titration of residual TBHP). The reaction was then quenched with acetone (90 mL) containing water (3 mL) precooled to -20 °C and the mixture was warmed to room temperature over 1 h before filtering the salts over celite. The filtrate was evaporated and the residue was taken up in Et_2O and treated with 1 N NaOH solution at 0 °C. After stirring for 30 min, the organic layer was separated, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting oil was purified by SiO_2 column chromatography using hexanes/EtOAc to collect pure, enantioenriched allyl propargyl alcohol. The enantioenriched alcohol was then taken forward to the UV-active homoallenic sulfamate before determining *ee*. **NOTE**: During the stereospecific reduction of propargyl alcohols using the Schwartz reagent, Ready warns that $ZnCl_2$ will erode axial chirality. Besides being a precursor to EtZnCl, $ZnCl_2$ is a byproduct of the reaction between ROZnCl and $Cp_2Zr(H)Cl$ to generate Cp_2ZrO and $ZnCl_2$.[2] Deprotection of the TBS-ether was conducted using Method A before using the alcohol in the general procedure for synthesizing sulfamate esters (*vide supra*).

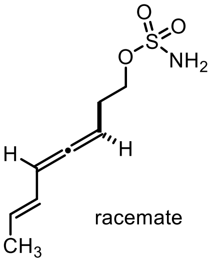


Enantioenriched Compound S-12. The described Sharpless kinetic resolution was ran to 55% conversion to further increase the *ee* of the recovered allyl propargyl alcohol. Following the general procedure for allene formation and deprotection using Method A (*vide supra*), **S-12** was isolated as described for **S-12** to provide an orange oil (0.563 g, 4.5 mmol, 86% yield). The spectroscopic and HRMS data was consistent with that reported for racemic **S-12**. Axial chirality is drawn by analogy to that reported by Ready invoking Sharpless's mnemonic.[2]

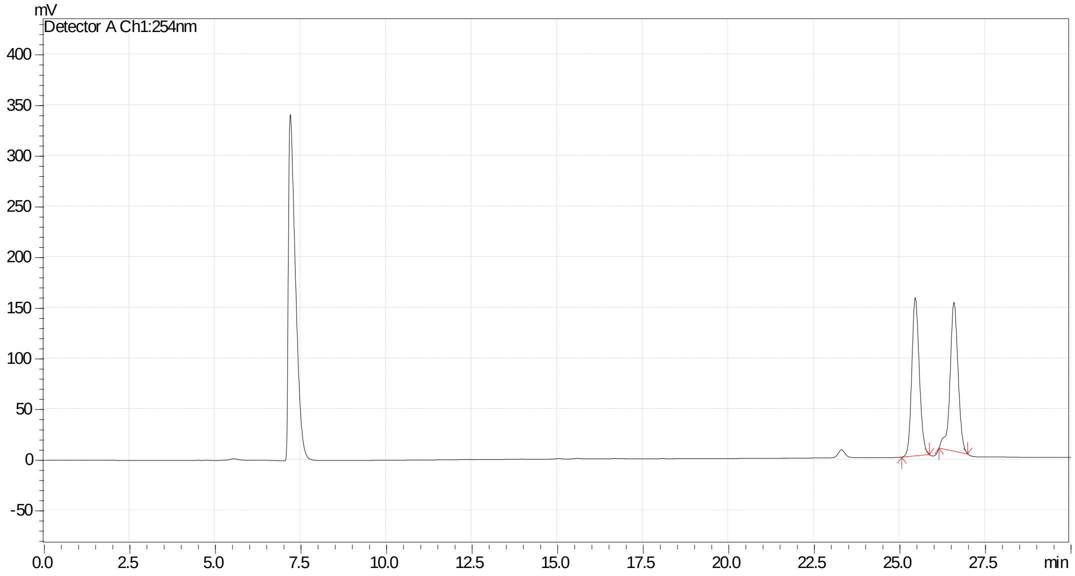


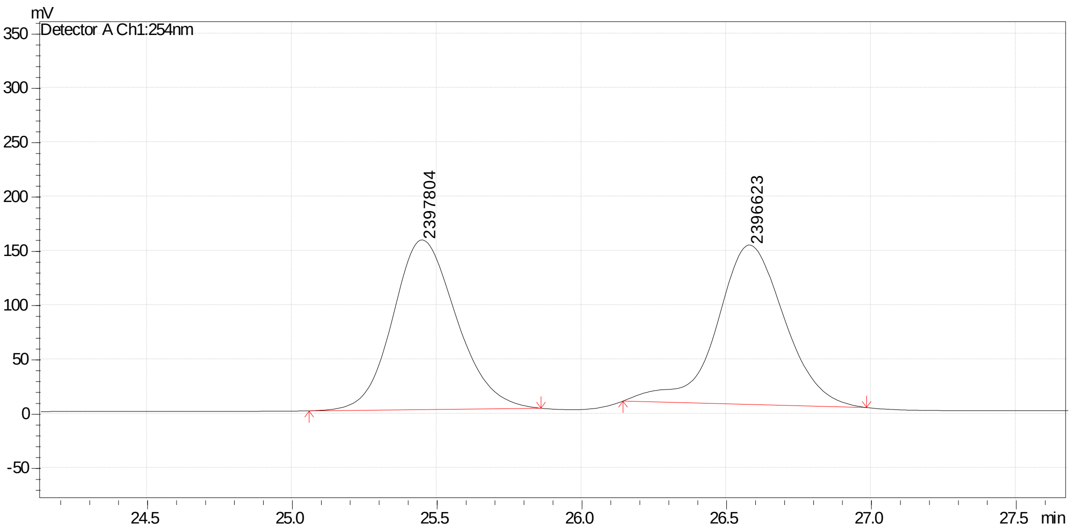
Enantioenriched Compound 4. Following the general procedure for synthesizing sulfamate esters (4.5 mmol scale), **4** was isolated as described for **4** to provide a white solid (0.644 g, 3.2 mmol, 70% yield, 92% *ee* [see chromatograms below]). The spectroscopic and HRMS data was consistent with that reported for racemic **4**.

Separation of eneallene enantiomers and HPLC traces: HPLC conditions – chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel OJ-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 ºC; Solvent: 5:95 iPrOH:hexane held for 2 min and polarity was increased to 20:80 iPrOH:hexane over 20 minutes. The eluent composition was held at this ratio for another 5 minutes before dropping back down to 5:95 iPrOH:hexane over 30 sec. The solvent composition stayed at this ratio for 2.5 min to complete the 30 min analysis. Detector: UV 254 nm and 210 nm.

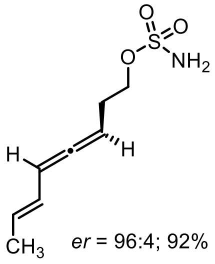


racemate

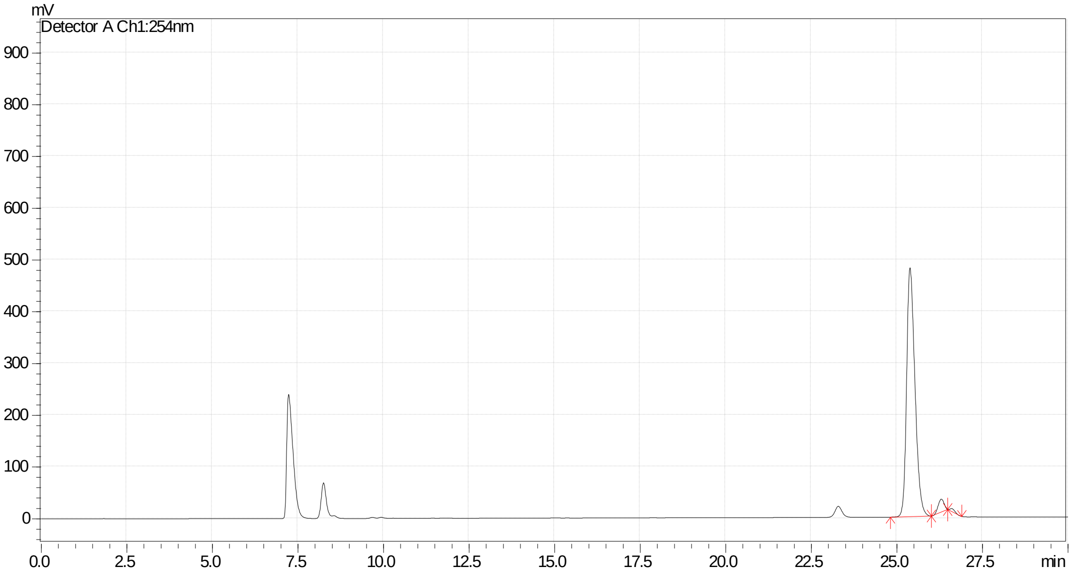


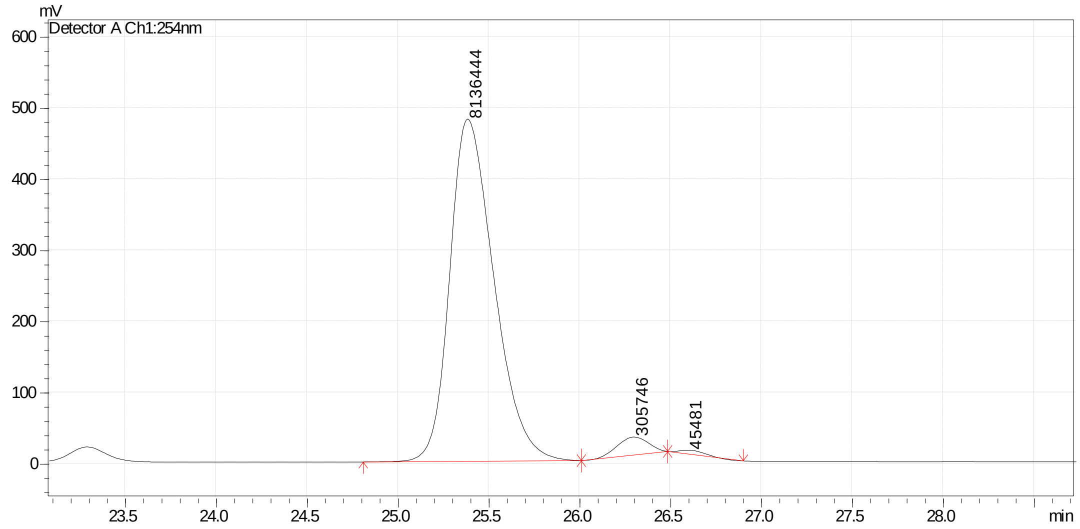


Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
2397804	2396623	50:50	0



er = 96:4; 92% *ee*

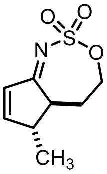




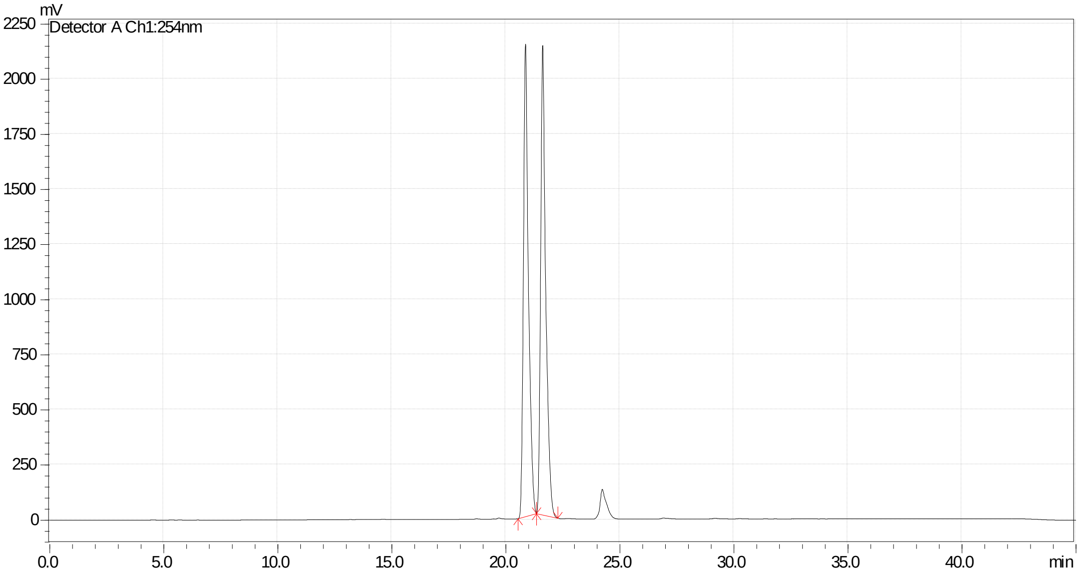
Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
8136444	305746	96:4	92
8136444	45481	99:1	98

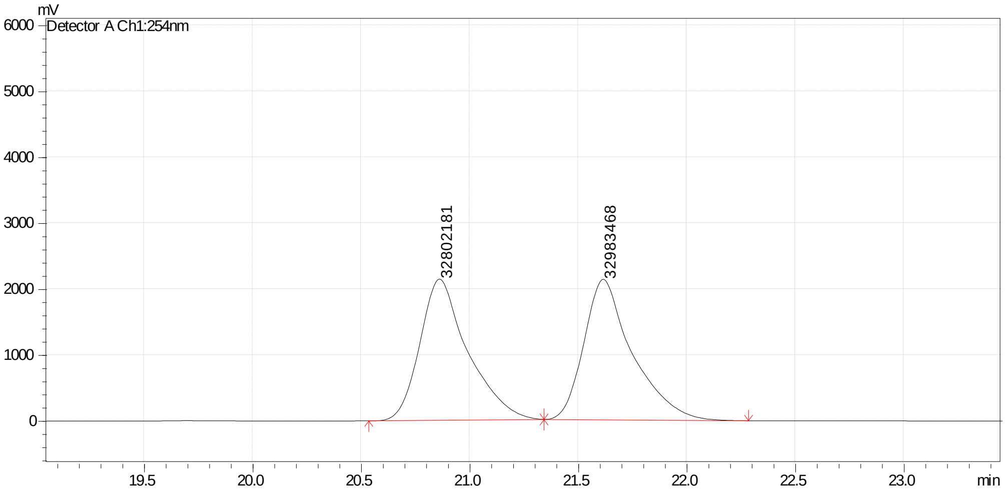
NOTE: We reported the lower *ee* despite this assignment likely being incorrect. Even though the higher *ee* is likely the correct peak assignment by comparison to racemate retention times, we were able to confirm significant erosion of *ee* following amination and cyclization regardless the peak assignment.

Separation of cyclopentene enantiomers and HPLC traces: HPLC conditions – chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 ºC; Solvent: 5:95 iPrOH:hexane held for 2 min and polarity was increased to 50:50 iPrOH:hexane over 33 minutes. The eluent composition was held at this ratio for another 3 minutes before dropping back down to 5:95 iPrOH:hexane over 30 sec. The solvent composition stayed at this ratio for 2.5 min to complete the 40 min analysis. Detector: UV 254 nm and 210 nm.

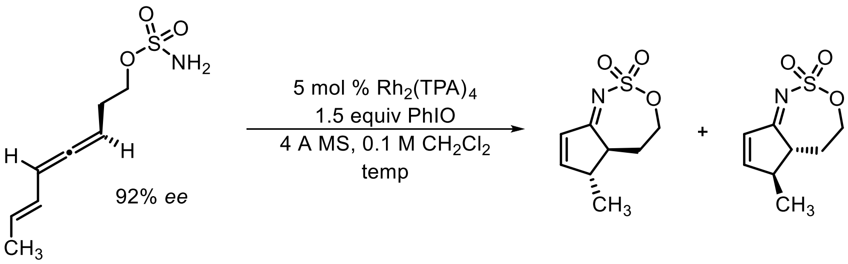


racemate





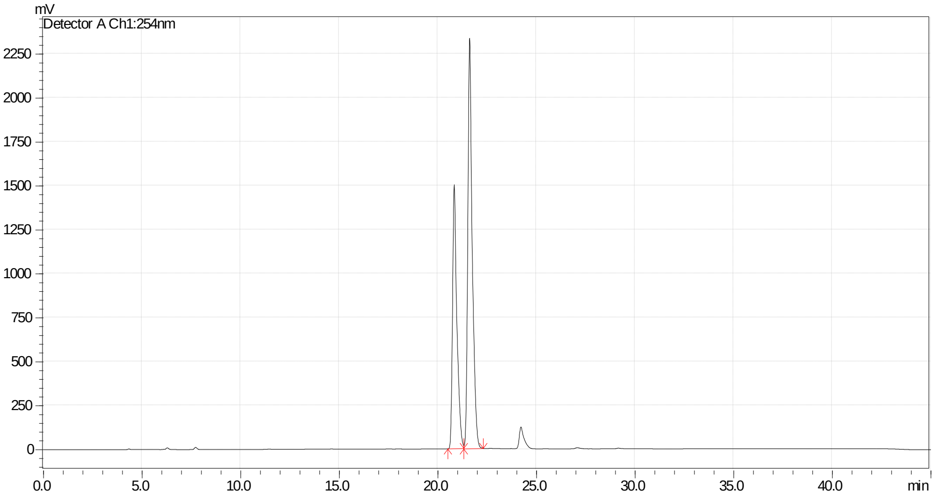
Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
32802181	32983468	50:50	0

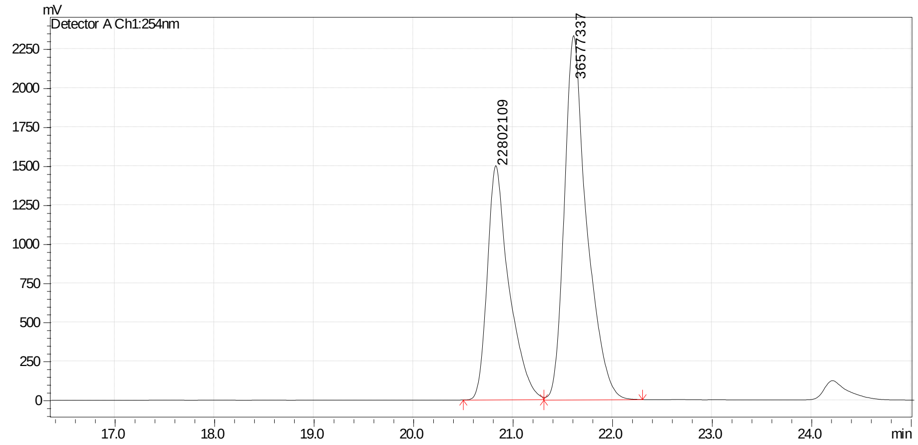


entry	temperature (°C)	% yield[a]	*er*	% *ee*
1	23	63	62:38	24
2	50	57	56:44	12

[a] Isolated yields

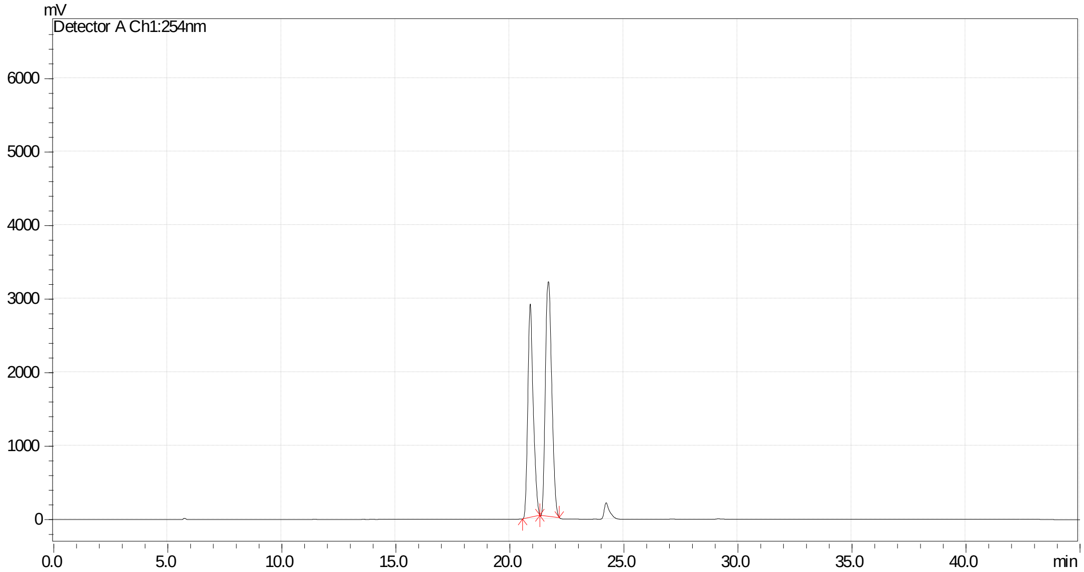
Room temperature (entry 1)

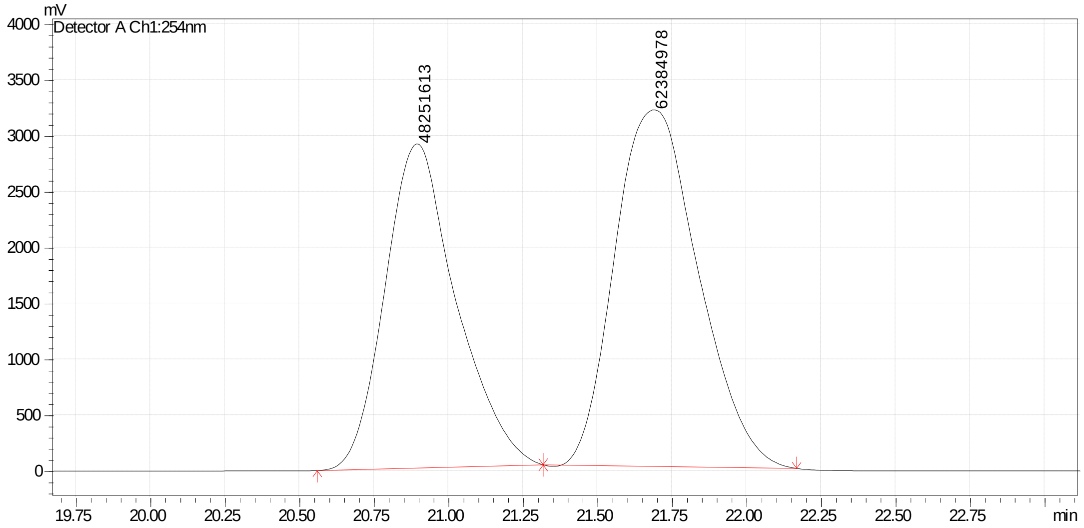




Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
36577337	22802109	62:38	24

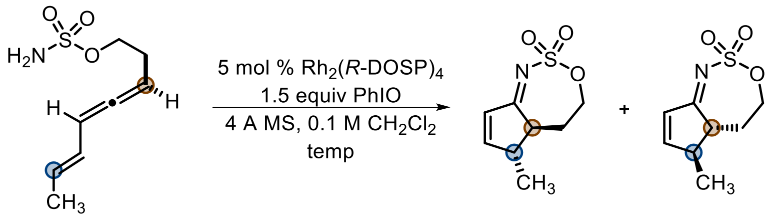
Elevated temperature (entry 2)





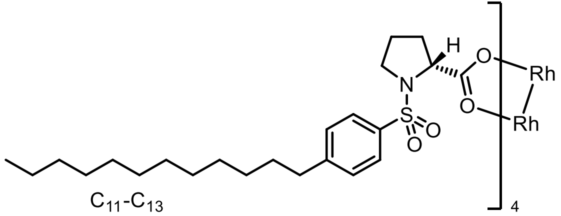
Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
62384978	48251613	56:44	12

Asymmetric catalysis with racemic substrate.

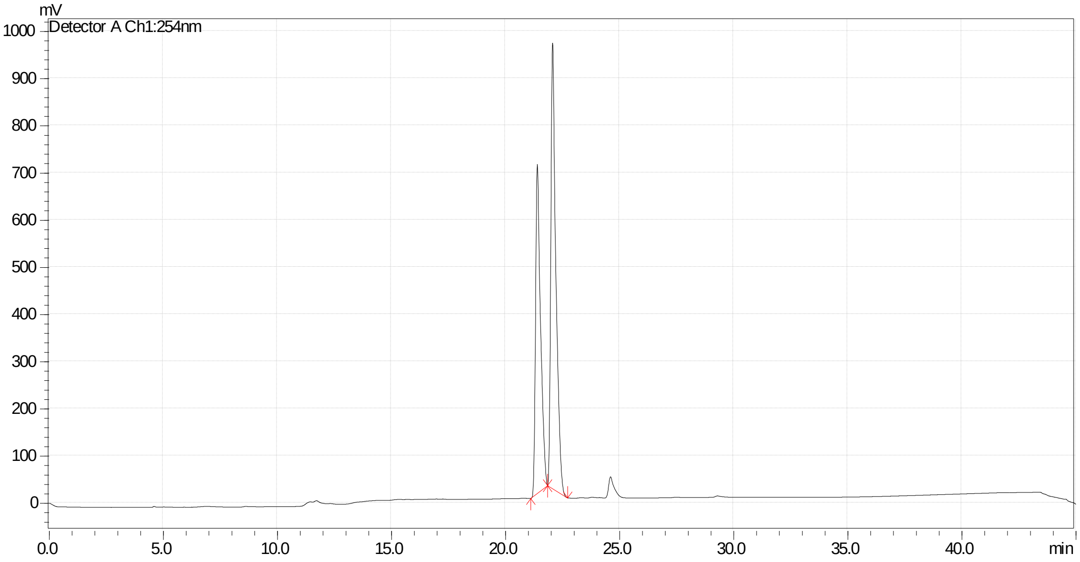


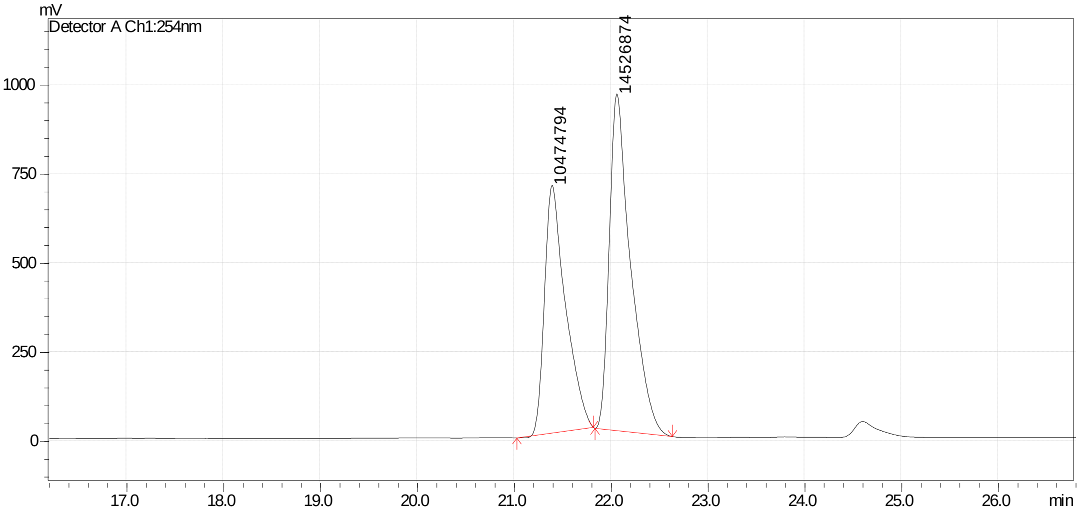
entry	temperature (° C)	% yield[a]	*er*	% *ee*
1	50	54	58:42	16

[a] Isolated yields

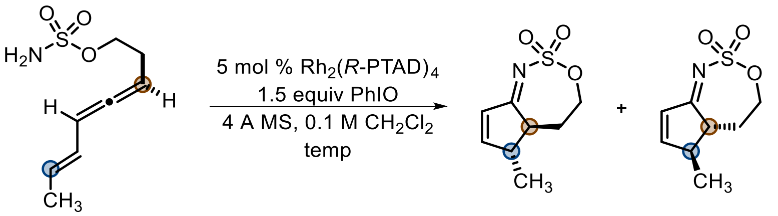


Rh$_2$(*R*-DOSP)$_4$



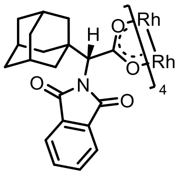


Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
14526872	10474794	58:42	16

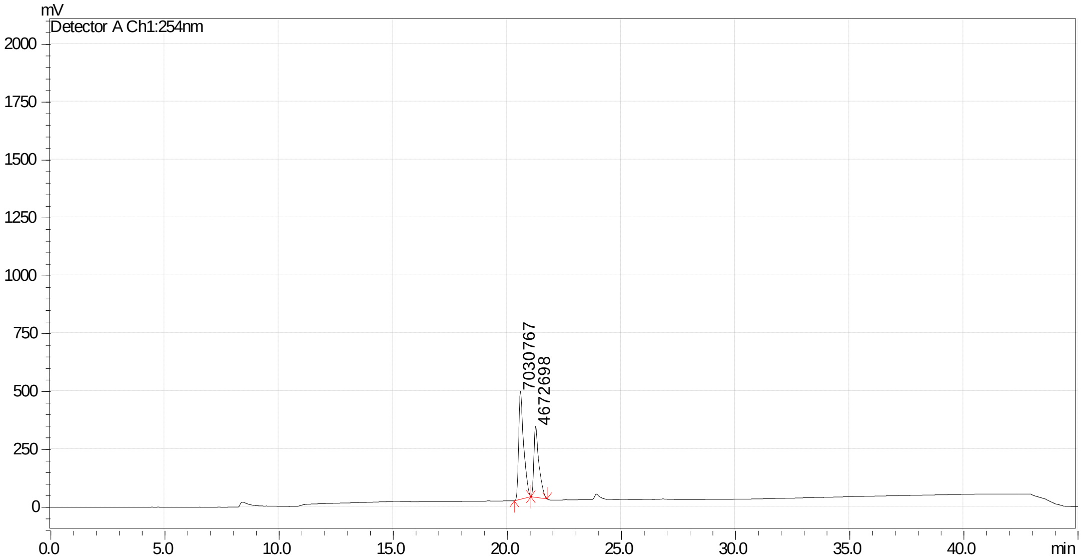


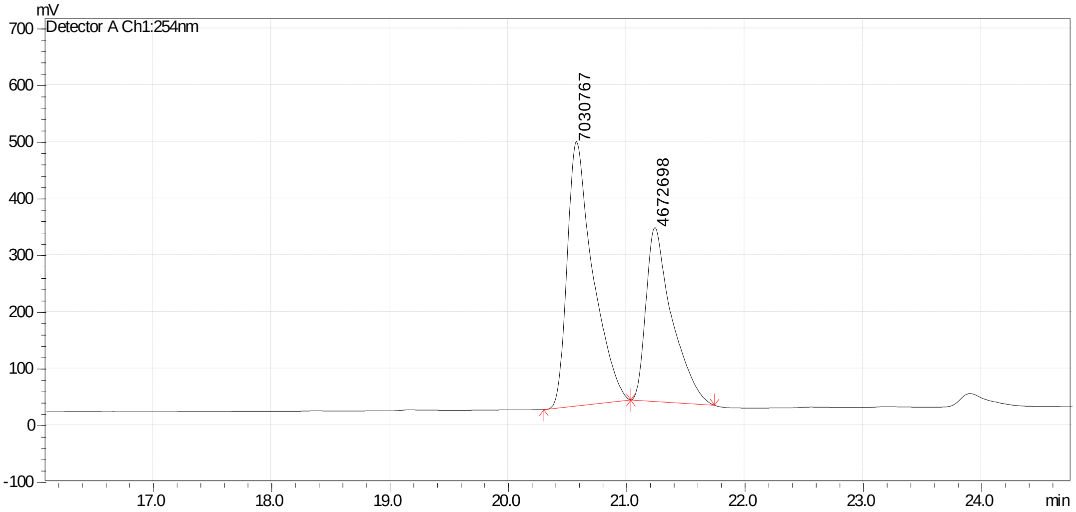
entry	temperature (°C)	% yield[a]	*er*	% *ee*
1	50	47	60:40	20

[a] Isolated yields



Rh_2(*R*-PTAD)$_4$

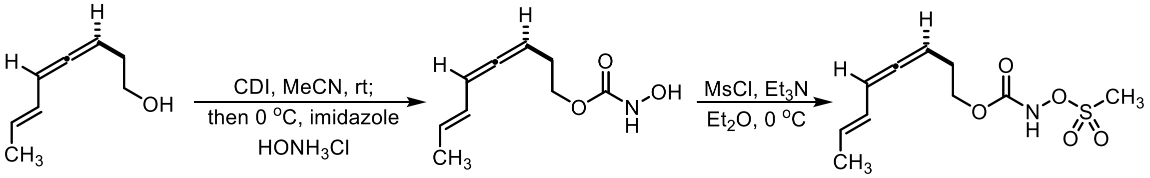




Major Peak Area	Minor Peak Area	*er* (major:minor)	% *ee*
7030767	4672698	60:40	20

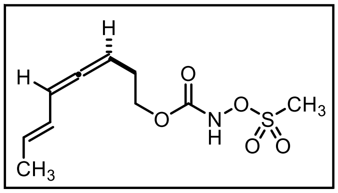
VI. Tether length/*N*-source optimization and reaction monitoring

Synthesis of homoallenic N-mesyloxycarbamate and procedure for nitrene transfer

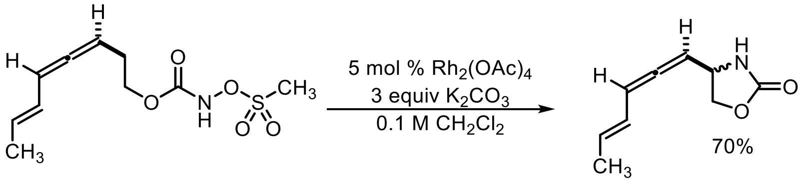


Solid 1,1’-carbonyldiimidazole (8.2 mmol, 1.2 equiv) was added to a solution of alcohol **S-12** (6.8 mmol, 1.0 equiv) in acetonitrile (36 mL, 0.19 M) and the clear solution stirred at room temperature for 2 hours. The resulting mixture was cooled to 0 ºC and hydroxylamine-HCl (27.2 mmol, 4.0 equiv) was added, followed by imidazole (20.4 mmol, 3.0 equiv) and vigorous stirring was maintained for 1 hour at 0 ºC. After the reaction is complete according to TLC analysis, the suspension was concentrated. The white residue was dissolved in a 1:1 mixture of EtOAc:10% HCl (aq). The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The resulting *N*-hydroxycarbamate is obtained as a white solid and was sufficiently pure to be used in the next step.

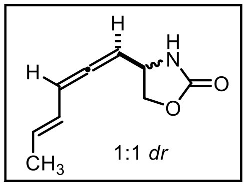
The resulting *N*-hydroxycarbamate (3.4 mmol, 1.0 equiv) was dissolved in Et_2O and cooled to 0 °C. The solution is stirred and MsCl (3.4 mmol, 1.0 equiv) is added dropwise, followed by Et_3N (3.4 mmol, 1.0 equiv). The resulting white suspension stirs for 1 h at 0 °C. The mixture was quenched with H_2O and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude material was columned over SiO_2 using hexanes:EtOAc gradient (0 to 25% EtOAc with increasing 5% increments) followed by recrystallization in $CHCl_3$/hexanes to give *N*-mesyloxylcarbamate **S-22**.



Compound S-22. Following the described procedure, **S-22** was obtained as a clear oil (0.130 g, 0.5 mmol, 15% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.47 – 8.28 (m, 1H), 5.85 – 5.78 (m, 2H), 5.70 – 5.59 (m, 1H), 5.28 – 5.21 (m, 1H), 4.30 (td, *J* = 6.6, 1.7 Hz, 2H), 3.17 (s, 3H), 2.39 (qd, *J* = 6.7, 3.7 Hz, 2H), 1.77 – 1.72 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.9, 156.0, 128.3, 126.2, 95.2, 87.4, 66.5, 36.4, 28.4, 18.2. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{15}NO_5S$ $[M+NH_4]^+$ 279.1009, measured 279.1006 (1.1 ppm).

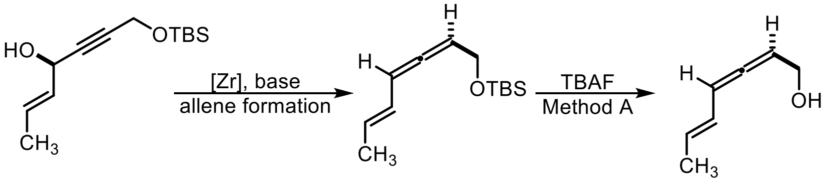


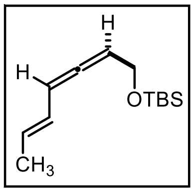
To a solution of **S-22** (0.15 mmol, 1.0 equiv) in CH_2Cl_2 (1.5 mL, 0.1 M) was added K_2CO_3 (0.45 mmol, 3.0 equiv) and $Rh_2(OAc)_4$ (0.0075 mmol, 0.05 equiv). The resulting suspension stirs until complete consumption of starting material is observed by TLC. The crude solution is washed with water and the aqueous layer is extracted three times with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Allenic C–H amination product **S-23** was observed (70% ^{1}H-NMR yield with respect to mesitylene internal standard) instead of the desired eneallene aziridination/electrocyclization.



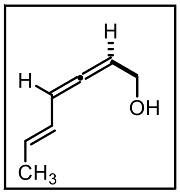
Compound S-23. Characterized as a 1:1 mix of diastereomers. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.01 (tdd, *J* = 10.3, 6.2, 1.7 Hz, 1H), 5.88 – 5.78 (m, 1H), 5.73 (ddd, *J* = 15.2, 6.3, 1.2 Hz, 1H), 5.40 – 5.32 (m, 1H), 5.02 (s, 1H), 4.55 (td, *J* = 8.4, 1.8 Hz, 1H), 4.43 – 4.34 (m, 1H), 4.19 (dt, *J* = 8.6, 5.3 Hz, 1H), 1.77 (dt, *J* = 6.5, 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.1, 206.0, 158.9, 158.8, 130.41, 130.39, 124.89, 124.86, 98.10, 98.07, 92.67, 92.65, 70.4, 70.3, 52.10, 52.07, 18.34, 18.33. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{11}NO_2$ $[M+H]^+$ 166.0863, measured 166.0861 (1.2 ppm).

Synthesis of allenic carbamate and procedure for nitrene transfer

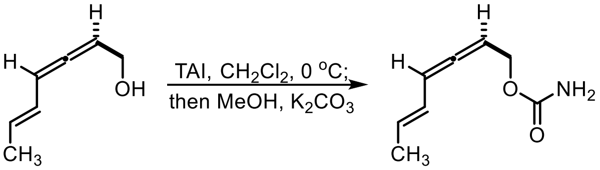




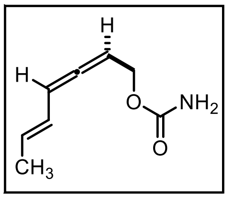
Compound S-24. Following the general procedure for allene formation (36.9 mmol scale), **S-24** was isolated a dark yellow/orange oil (4.98 g, 22.2 mmol, 60% yield**).** ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 5.90 – 5.81 (m, 2H), 5.64 (ddtd, *J* = 15.9, 8.1, 6.6, 1.5 Hz, 1H), 5.39 (dtt, *J* = 8.1, 4.5, 1.5 Hz, 1H), 4.22 – 4.17 (m, 2H), 1.74 (dt, *J* = 6.7, 1.5 Hz, 3H), 0.90 (s, 9H), 0.08 (d, *J* = 2.2 Hz, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 205.6, 127.9, 126.3, 95.4, 93.2, 61.9, 26.1, 18.5, 18.2, -4.9. **HRMS** (ASAP-MS) *m/z* calculated for $C_{13}H_{24}OSi$ $[M+H]^+$ 225.1669, measured 225.1665 (1.8 ppm).



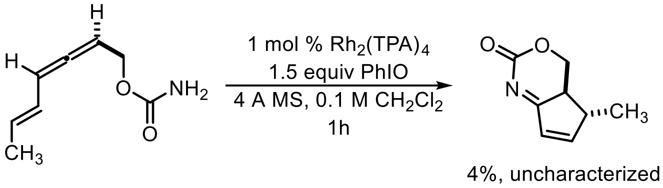
Compound S-25. Following Method A for TBS-ether deprotection (9.6 mmol scale), **S-25** was isolated as a yellow oil (0.822 g, 6.6 mmol, 69% yield). ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 5.93 (ddt, *J* = 11.5, 5.7, 2.7 Hz, 1H), 5.89 – 5.81 (m, 1H), 5.71 – 5.62 (m, 1H), 5.49 (tdd, *J* = 9.2, 5.0, 1.9 Hz, 1H), 4.14 – 4.11 (m, 2H), 1.92 – 1.78 (m, 1H), 1.76 – 1.72 (m, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 205.1, 128.5, 125.9, 96.6, 93.1, 60.6, 18.1. **HRMS** (ASAP-MS) *m/z* calculated for $C_7H_{10}O$ $[M+H]^+$ 111.0804, measured 111.0803 (0.9 ppm).



Allenic alcohol **S-25** (0.165 g, 1.5 mmol, 1 equiv) was dissolved in CH_2Cl_2 (5 mL, 0.3 M) and placed in an ice bath. Trichloroacetyl isocyanate (TAI, 0.2 mL, 1.5 mmol, 1 equiv) was then added slowly dropwise. The reaction was stirred at 0 °C until starting material was consumed by TLC (~20 min). At this point the solvent was removed and the crude reaction was redissolved in MeOH (3.8 mL, 0.4 M). Potassium carbonate (0.104 g, 0.75 mmol, 0.5 equiv) was added and the mixture stirs at room temperature until TLC shows complete consumption of the starting material (~3 h). At this point H_2O was added to the reaction and the mixture was extracted with three portions of CH_2Cl_2. The organic extracts were dried over Na_2SO_4, the salts were filtered, and then the solvent was removed under decreased pressure. The crude material was purified using silica column chromatography using hexanes:EtOAc with a 0% to 30% EtOAc gradient using increasing 5% EtOAc increments.

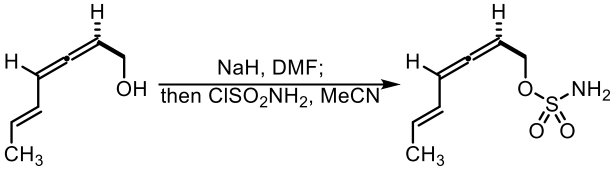


Compound S-26. Allenic carbamate was isolated as an orange solid (0.165 g, 1.1 mmol, 72% yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.95 – 5.81 (m, 2H), 5.73 – 5.64 (m, 1H), 5.45 (q, *J* = 6.6 Hz, 1H), 4.56 (dd, *J* = 6.6, 2.2 Hz, 4H), 1.75 (dt, *J* = 6.8, 1.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.4, 156.5, 128.9, 125.6, 95.9, 88.7, 63.1, 18.3. **HRMS** (ESI-MS) *m/z* calculated for $C_8H_{11}NO_2$ $[M+Na]^+$ 176.0682, measured 176.0681 (0.6 ppm).

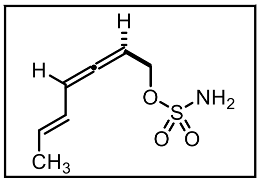


The general eneallene aziridination/electrocyclization was followed on **S-26** with the following exceptions (0.1 mmol scale). Only 1 mol % Rh_2TPA_4 was used (1.4 mg, 0.001 mmol), and the reaction was not heated. This resulted in ~4-15% imino-Nazarov electrocyclization product (uncharacterized) and ~38% recovered starting material according to quantitative analysis of the crude ^{1}H-NMR using mesitylene as an internal standard.

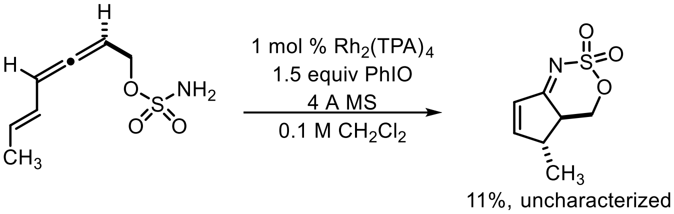
Synthesis of allenic sulfamate and nitrene transfer



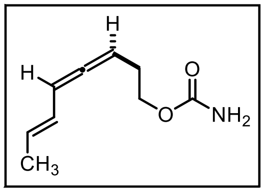
NaH (60% dispersion in mineral oil) was washed 3 times with 10 mL Et_2O to remove the mineral oil (92 mg, 2.31 mmol, 1.1 equiv) and then suspended in DMF (2.1 mL). A solution of allenic alcohol **S-25** (0.231 g, 2.1 mmol, 1.0 equiv) in DMF (1.6 mL, final concentration of 0.56 M) was added dropwise at 0 °C. The reaction was stirred for 1 h at room temperature. At this point, the reaction was cooled to 0 °C and a solution of $ClSO_2NH_2$ in MeCN (3 mL, 0.7 M) was added dropwise and the resulting solution stirs for ~2 h. The reaction is quenched with 10 mL H_2O and extracted 3 times with 30 mL Et_2O. The combined organic extracts were washed 5 times with 20 mL H_2O, 1 time with 25 mL brine, and dried over Na_2SO_4 before concentrating. The crude mixture was purified by silica chromatography using pentane/Et_2O solvent gradient (0% to 100% Et_2O with increasing 20% increments). This provided pure **S-27** (87 mg, 0.5 mmol, 24% yield). Significant elimination to the triene is observed and is the only product using the general sulfamate ester synthesis using acidic CSI described above.



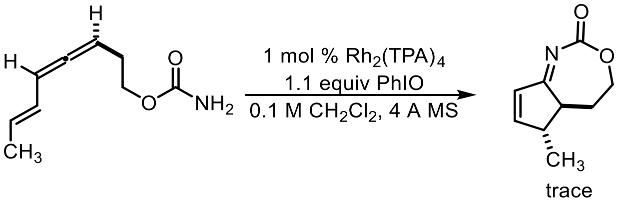
Compound S-27. Isolated as a yellow oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.02 – 5.96 (m, 1H), 5.89 – 5.81 (m, 1H), 5.78 – 5.68 (m, 1H), 5.52 (q, *J* = 6.9 Hz, 1H), 4.74 – 4.66 (m, 4H), 1.77 (dt, *J* = 6.5, 1.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.7, 130.2, 124.6, 96.4, 87.3, 69.6, 18.4. **HRMS** (ESI-MS) *m/z* calculated for $C_7H_{11}NO_3S$ $[M+H]^+$ 188.0387, measured 188.0387 (<0.1 ppm).



The general eneallene aziridination/electrocyclization was followed on **S-27** with the following exceptions (0.1 mmol scale). Only 1 mol % Rh_2TPA_4 was used (1.4 mg, 0.001 mmol), and the reaction was not heated. This resulted in ~11% imino-Nazarov electrocyclization product (uncharacterized) and no recovered starting material according to quantitative analysis of the crude ^{1}H-NMR using mesitylene as an internal standard.

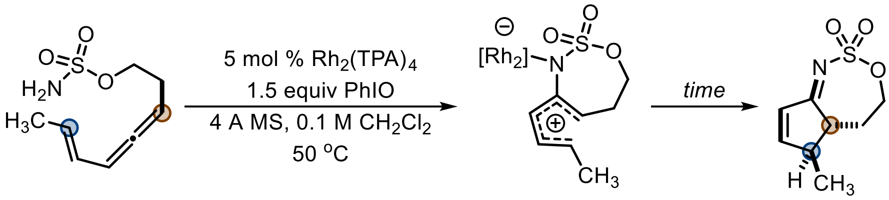


Compound S-28. Following the procedure for synthesizing the allenic carbamate above (1.0 mmol scale), homoallenic carbamate **S-28** was isolated as a yellow oil that solidifies upon dryness (107.8 mg, 0.64 mmol, 64% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.87 – 5.77 (m, 2H), 5.67 – 5.59 (m, 1H), 5.27 (ddd, *J* = 8.7, 6.9, 3.5 Hz, 1H), 4.57 (s, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.34 (qd, *J* = 6.8, 2.6 Hz, 2H), 1.74 (dt, *J* = 6.4, 1.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.9, 156.8, 127.7, 126.6, 94.8, 88.1, 64.4, 28.8, 18.3. **HRMS** (ESI-MS) *m/z* calculated for $C_9H_{13}NO_2$ $[M+Na]^+$ 190.0839, measured 190.0836 (1.6 ppm).



The general eneallene aziridination/electrocyclization was followed on **S-28** with the following exceptions (0.15 mmol scale). Only 1 mol % Rh_2TPA_4 was used (1.4 mg, 0.001 mmol) with 1.1 equiv PhIO, and the reaction was not heated. This resulted in trace amounts of imino-Nazarov electrocyclization product (uncharacterized) and no recovered starting material according to quantitative analysis of the crude ^{1}H-NMR using mesitylene as an internal standard.

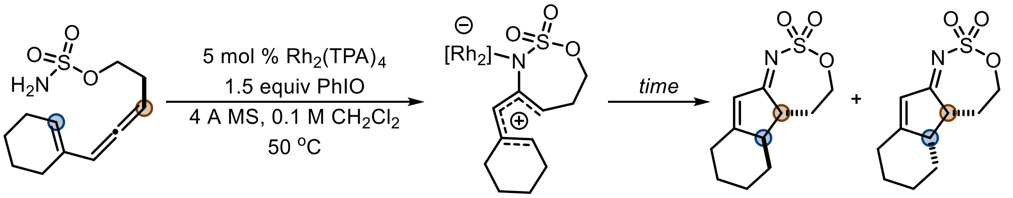
Monitoring mass balance by quantitative ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard



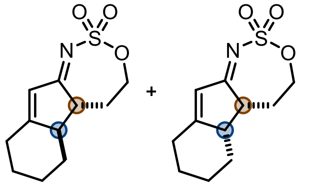
entry	time	% rsm	% yield[a]	% mass balance
1	18 min	33	15	48
2	33 min	24	22	45
3	48 min	7	29	36
4	63 min	5	37	42
5	117 min	2	48	50

[a] NMR yields using 1,3,5-trimethoxybenzene as internal standard

Monitoring the diastereomeric ratio over time to investigate epimerization under the reaction conditions

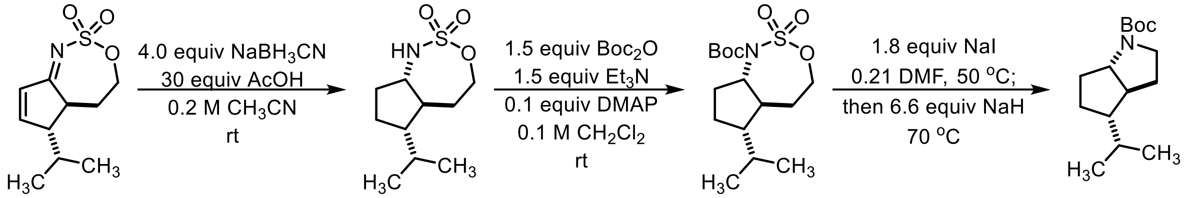


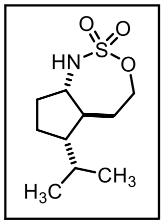
entry	time	*anti* : *syn*
1	15 min	3.0 : 1
2	30 min	3.0 : 1
3	45 min	2.9 : 1
4	60 min	3.1 : 1
5	120 min	3.0 : 1
6	180 min	2.9 : 1
7	300 min	3.0 : 1
8	24 h	3.0 : 1



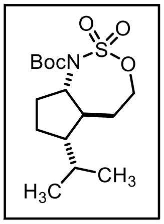
ΔΔG = 2.12 kcal/mol
dr = 3 : 1

VII. Procedures for functionalization of α,β-unsaturated iminocyclopentene 6a

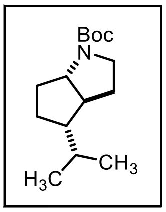




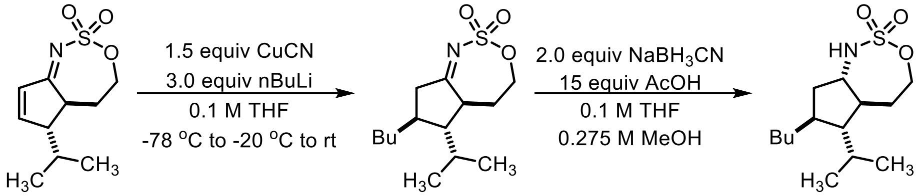
Compound 17. Iminocyclopentene **6a** was added to a dry round-bottom flask equipped with a stirbar (75.3 mg, 0.3 mmol, 1.0 equiv). After adding CH_3CN (0.2 M), $NaBH_3CN$ (50.3 mg, 0.8 mmol, 4.0 equiv) was added in a single portion, followed by the dropwise addition of AcOH (0.34 mL, 6 mmol, 30 equiv). The reaction was stirred at room temperature until starting material was consumed according to TLC analysis (12 h). The reaction was quenched with the dropwise addition of saturated aqueous $NaHCO_3$ and extracted thrice with EtOAc. The organic extracts were washed once with brine before drying over Na_2SO_4, filtering the salts, and evaporating the volatiles *in vacuo*. The crude mixture was purified on silica gel using a 0-50% EtOAc:hexanes gradient with increasing 10% EtOAc increments. Amine **17** was isolated as a white solid (57 mg, 0.246 mmol, 82% yield, 4.8:1 *dr*). **Major diastereomer**: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.86 (d, *J* = 7.0 Hz, 1H), 4.32 – 4.20 (m, 2H), 3.84 (ddt, *J* = 10.7, 8.9, 6.8 Hz, 1H), 2.22 (dddd, *J* = 11.8, 9.4, 7.4, 2.8 Hz, 1H), 2.09 – 1.97 (m, 2H), 1.78 (dddd, *J* = 17.8, 9.6, 5.6, 1.8 Hz, 2H), 1.59 – 1.49 (m, 1H), 1.39 (m, 2H), 1.28 – 1.17 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 71.1, 56.7, 53.9, 47.5, 33.0, 32.2, 31.9, 27.6, 21.8, 19.4. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{19}NO_3S$ $[M-H]^-$ 232.1013, measured 232.1014 (0.4 ppm).

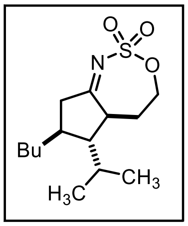


Compound S-29. Aminocyclopentane **17** (46.7 mg, 0.2 mmol, 1 equiv) was dissolved as in dry CH_2Cl_2 (0.1 M) in a dry round-bottom flask equipped with a stirbar as a 4.8:1 mixture of diastereomers. The solution was stirred and Boc_2O (65.8 mg, 0.3 mmol, 1.5 equiv), Et_3N (0.05 mL, 0.3 mmol, 1.5 equiv), and DMAP (3.2 mg, 0.02 mmol, 0.1 equiv) were added in sequence. When the starting material was consumed according to TLC analysis (~40 min), the reaction was quenched with saturated aqueous NH_4Cl and extracted thrice with CH_2Cl_2. The combined organic extracts were washed once with saturated NH_4Cl, followed by brine. The organic extracts were dried over Na_2SO_4, the salts were filtered, and the volatiles were concentrated *in vacuo*. The crude mixture was purified on silica gel using a 0-50% CH_2Cl_2:pentane gradient with increasing 10% CH_2Cl_2 increments. The column was then flushed with 100% CH_2Cl_2 (one column volume). This provided Boc-protected amine **S-29** as a clear oil (40.8 mg, 0.122 mmol, 74%, >19:1 *dr*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.81 (td, *J* = 11.2, 7.8 Hz, 1H), 4.56 (ddd, *J* = 11.4, 6.5, 1.7 Hz, 1H), 4.34 (td, *J* = 12.0, 5.0 Hz, 1H), 2.33 – 2.22 (m, 2H), 2.17 – 2.00 (m, 2H), 1.93 – 1.81 (m, 2H), 1.73 (ddt, *J* = 11.8, 9.4, 6.3 Hz, 1H), 1.54 (s, 10H), 1.13 (qd, *J* = 12.4, 6.6 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 151.8, 85.0, 69.8, 61.4, 46.9, 39.9, 31.9, 29.4, 28.0, 27.5, 26.1, 21.9, 19.8. **HRMS** (ESI-MS) *m/z* calculated for $C_{15}H_{27}NO_5S$ [M+NH$_4$]$^+$ 351.1948, measured 351.1942 (1.7 ppm).

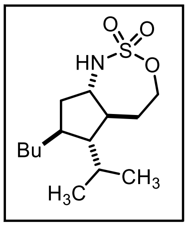


Compound 18. Boc-protected amine **S-29** (38 mg, 0.116 mmol, 1 equiv) was dissolved in dry DMF (0.21 M) in a scintillation vial equipped with a stirbar, followed by the addition of NaI (33.0 mg, 0.22 mmol, 1.8 equiv). The solution was capped and warmed to 50 °C in an oil bath with stirring and this temperature was maintained for 15 minutes. At this point, unwashed NaH (60% dispersion in mineral oil, 31.6 mg, 0.79 mmol, 6.6 equiv) was added and the solution turned yellow. The oil bath temperature was raised to 70 °C and this temperature was maintained until the reaction was complete (15 h). The yellow color fades over the course of the reaction. The reaction is then placed in an ice bath to cool to 0 °C, prior to cautiously quenching with the dropwise addition of H$_2$O. The aqueous layer was extracted thrice with Et$_2$O and the combined organic extracts were dried over Na$_2$SO$_4$ before filtering the salts and concentrating the volatiles *in vacuo*. The crude mixture was purified on silica gel using a 0-50% Et$_2$O:pentane gradient with increasing 10% Et$_2$O increments. This provided pyrrolidine **18** as a clear oil (25.6 mg, 0.101 mmol, 87% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.16 – 3.95 (m, 1H), 3.57 – 3.39 (m, 1H), 3.36 – 3.26 (m, 1H), 2.29 (qd, *J* = 7.4, 3.4 Hz, 1H), 2.19 – 2.02 (m, 1H), 1.91 (dq, *J* = 12.5, 8.1 Hz, 1H), 1.80 (dtd, *J* = 12.6, 6.4, 2.8 Hz, 1H), 1.62 (ddt, *J* = 11.8, 7.0, 4.5 Hz, 2H), 1.45 (s, 10H), 1.38 – 1.30 (m, 1H), 1.24 – 1.16 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 154.6, 78.9, 63.0, 52.5, 47.8, 45.8, 33.9, 32.6, 30.8, 30.6, 28.7, 21.9, 20.6. **HRMS** (ESI-MS) *m/z* calculated for $C_{15}H_{27}NO_2$ [M+H]$^+$ 254.2115, measured 254.2110 (2.0 ppm).

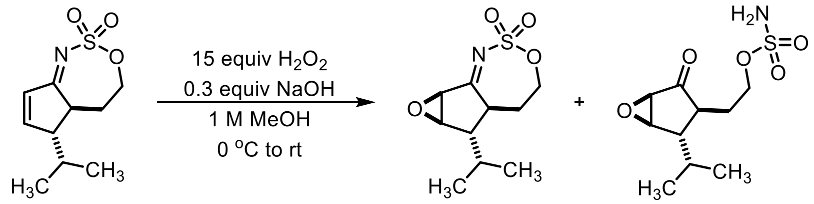


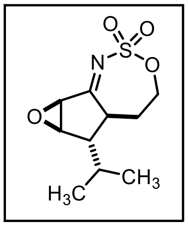


Compound S-30. A flame-dried round-bottom flask equipped with a stir bar was cooled under N$_2$. The reaction vessel was charged with CuCN (26.9 mg, 0.3 mmol, 1.5 equiv) and diluted with anhydrous THF (1 mL). The solution was cooled to -78 °C with stirring, and recently titrated nBuLi (2.5 M in hexanes, 0.24 mL, 0.6 mmol, 3.0 equiv) was added dropwise. These components are stirred for 1 h to generate the higher-order cuprate Bu$_2$Cu(CN)Li$_2$. The cuprate solution was then warmed to -20 °C prior to the dropwise addition of iminocyclopentene **6a** (45.9 mg, 0.2 mmol, 1 equiv) in 1 mL THF to bring the final reaction concentration to 0.1 M. The reaction was stirred at -20 °C for 1 h prior to warming to rt for 1 h. The reaction was then quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted thrice with Et_2O and the combined organic extracts were dried over Na_2SO_4, the salts were filtered, and the volatiles were removed under reduced pressure. The crude mixture was purified on silica gel using a 0-20% EtOAc/hexanes gradient with increasing 5% EtOAc increments. This was followed by a 20-50% EtOAc/hexanes gradient with increasing 10% EtOAc increments. This resulted in the isolation of imine **S-30** as a light-yellow oil (31.2 mg, 0.11 mmol, 55% yield, >19:1 *dr*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.55 – 4.42 (m, 2H), 2.98 – 2.91 (m, 1H), 2.80 (ddd, *J* = 18.8, 7.2, 1.5 Hz, 1H), 2.31 (ddd, *J* = 18.8, 10.7, 1.1 Hz, 1H), 2.05 (dtd, *J* = 14.8, 11.6, 5.7 Hz, 1H), 1.93 (m, 3H), 1.70 – 1.63 (m, 1H), 1.56 (td, *J* = 9.5, 3.3 Hz, 1H), 1.32 (tdd, *J* = 11.7, 8.1, 5.9 Hz, 3H), 1.27 – 1.16 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 6H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.4, 70.8, 56.4, 48.8, 44.5, 38.7, 34.6, 31.1, 29.9, 28.5, 22.9, 20.5, 20.0, 14.1. **HRMS** (ESI-MS) *m/z* calculated for $C_{14}H_{25}NO_3S$ $[M+H]^+$ 288.1628, measured 288.1631 (1.0 ppm).



Compound 19. Imine **S-30** (25 mg, 0.085 mmol, 1 equiv) was dissolved in THF (0.1 M with respect to the imine) and the solution was cooled to 0 °C with stirring. At this point, a solution of $NaBH_3CN$ (12.8 mg, 0.2 mmol, 2.0 equiv) and AcOH (0.09 mL, 1.65 mmol, 15 equiv) in MeOH (0.275 M with respect to the hydride) was added in a single portion and the solution was warmed to room temperature. The reaction was stirred until starting material was consumed according to TLC analysis (~2 h). The reaction was transferred to a separatory funnel using Et_2O prior to cautiously quenching with sat. aq. $NaHCO_3$. The organic layer was washed twice more with sat. aq. $NaHCO_3$ before washing once with brine. The organic extracts were dried over Na_2SO_4, the salts were filtered, and the volatiles were removed under reduced pressure. The crude mixture was purified on silica gel using a 0-100% Et_2O:pentane gradient with increasing 20% Et_2O increments. This provided amine **19** as a white solid (19.0 mg, 0.066 mmol, 78% yield, >19:1 *dr*). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.72 (d, *J* = 5.8 Hz, 1H), 4.27 – 4.17 (m, 2H), 3.70 (ddt, *J* = 11.9, 8.7, 6.1 Hz, 1H), 2.38 (dddd, *J* = 11.4, 8.3, 5.8, 2.2 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.74 (pd, *J* = 6.9, 4.3 Hz, 1H), 1.67 – 1.62 (m, 2H), 1.61 – 1.51 (m, 2H), 1.30 (ddt, *J* = 12.8, 9.1, 5.9 Hz, 2H), 1.19 (dt, *J* = 10.0, 5.2 Hz, 2H), 1.14 – 1.05 (m, 2H), 0.89 (dd, *J* = 15.8, 6.9 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 71.2, 59.5, 55.4, 46.0, 40.1, 38.6, 35.2, 34.4, 30.6, 29.8, 23.0, 21.6, 18.7, 14.2. **HRMS** (ESI-MS) *m/z* calculated for $C_{14}H_{27}NO_3S$ $[M+NH_4]^+$ 307.2050, measured 307.2048 (0.7 ppm).





Compound 20. Iminocyclopentene **6a** (71.1 mg, 0.31 mmol, 1 equiv) was added to a round-bottom flask equipped with a stir bar and dissolved in MeOH (1 M). The solution was cooled to 0 °C with vigorous stirring prior to adding H_2O_2 (30% aqueous solution, 0.5 mL, 4.65 mmol, 15 equiv). A grain of solid NaOH was then added (1-3 mg, 0.09 mmol, 0.3 equiv) and the reaction stirred for 3.5 h with no additional ice added to the water bath. At this point, complete consumption of starting material was observed according to TLC analysis and the reaction was poured into an ice-filled beaker of brine to quench. The aqueous layer was extracted thrice with CH_2Cl_2 before drying the combined organic extracts over Na_2SO_4, filtering the salts, and removing the volatiles under reduced pressure (70% NMR yield, 4.8:1 mixture). The crude was sufficiently pure to recommend carrying forward in subsequent transformations; notably, further imine hydrolysis was observed when purifying over silica gel or Al_2O_3. Compound **20** was an off-white/yellow solid (74.8 mg total, 0.24 mmol, 58% yield, >19:1 *dr* of epoxyimine). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.31 (dt, *J* = 12.2, 3.9 Hz, 1H), 4.25 (td, *J* = 11.7, 2.7 Hz, 1H), 4.01 (d, *J* = 2.6 Hz, 1H), 3.55 (d, *J* = 2.6 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.24 – 2.15 (m, 1H), 1.77 – 1.73 (m, 2H), 1.61 (dq, *J* = 15.7, 2.8 Hz, 1H), 1.01 (d, *J* = 5.9 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.5, 70.8, 60.6, 59.4, 55.8, 48.8, 35.0, 29.2, 21.2, 20.7. **HRMS** (ESI-MS) *m/z* calculated for $C_{10}H_{15}NO_4S$ $[M+H]^+$ 246.0795, measured 246.0792 (1.2 ppm).

VIII. References

1. a) Armarego, W.L.F.; Chai, C.L.L. Purification of Laboratory Chemicals 6th ed., Elsevier: Burlington, MA, **2009**. b) Still, W. C.; Kahn, M.; Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **1978**, *43*, 2923- 2925.
2. Stereospecific reduction of propargyl alcohols with $Cp_2Zr(H)Cl$: Pu, X.; Ready, J. M. Direct and Stereospecific Synthesis of Allenes via Reduction of Propargylic Alcohols with $Cp_2Zr(H)Cl$. *J. Am. Chem. Soc.* **2008**, *130*, 10874-10875.
3. Base-catalyzed prototropic rearrangement of 1,4-enynes: a) Oroshnik, W.; Mebane, A.; Karmas, G. Synthesis of Polyenes. III. Prototropic Rearrangements in β-Ionols and Related Compounds. *J. Am. Chem. Soc.* **1953**, *75*, 1050. b) Egenburg, I. Z. The Methods of Synthesis and Properties of Conjugated Enallenic Hydrocarbons. *Russ. Chem. Rev.* **1978**, *47*, 470.

4. Alkoxy-directed rearrangement of 1,3-enynes: a) Brummond, K. M.; Sill, P. C.; Chen, H. The First Total Synthesis of 15-Deoxy-$\Delta^{12,14}$-Prostaglandin J_2 and the Unambiguous Assignment of the C^{14} Stereochemistry. *Org. Lett.*, **2004**, *6*, 149-152. b) Enomoto, M.; Katsuki, T.; Yamaguchi, M. Highly regioselective isomerization of acetylenes to allenes. *Tetrahedron Lett.* **1986**, *27*, 4599.
5. Buchwald, S. L; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. Schwartz's Reagent. *Org. Synth.* **1993**, *71*, 77.
6. Ciesielski, J.; Leboeuf, D.; Stern, H. A.; Frontier, A. J. Gold(III) Chloride-Catalyzed 6-endo-trig Oxa-Michael Addition Reactions for Diastereoselective Synthesis of Fused Tetrahydropyranones. *Adv. Synth. Catal.*, **2013**, *355*, 2077-2082.
7. Burke, C. P.; Shi, Y. Enantioselective Epoxidation of Conjugated *cis*-Enynes by Chiral Dioxirane. *J. Org. Chem.*, **2007**, *72*, 4093-4097.
8. Sharpless kinetic resolution: a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. Asymmetric epoxidation provides shortest routes to four chiral epoxy alcohols which are key intermediates in syntheses of methymycin, erythromycin, leukotriene C-1, and disparlure. *J. Am. Chem. Soc.* **1981**, *103*, 6237-6240. b) Yadav, J. S.; Radhakrishna, P. Synthesis of (9z,15z)-(11s,12s,13s)-11-hydroxy-12,13-epoxyoctadecadienoic acid: Application of 'Sharpless kinetic resolution' to allyl propargyl alcohols. *Tetrahedron*, **1990**, *46*, 5825-5832.

IX. Computational studies

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.[1] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[2] in conjunction with the D3 dispersion correction suggested by Grimme et al.[3] using the standard double-ζ

---

[1] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[2] a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648; b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785; c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys*. **1980**, *58*, 1200.

[3] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. **2010**, *132*, 154104.

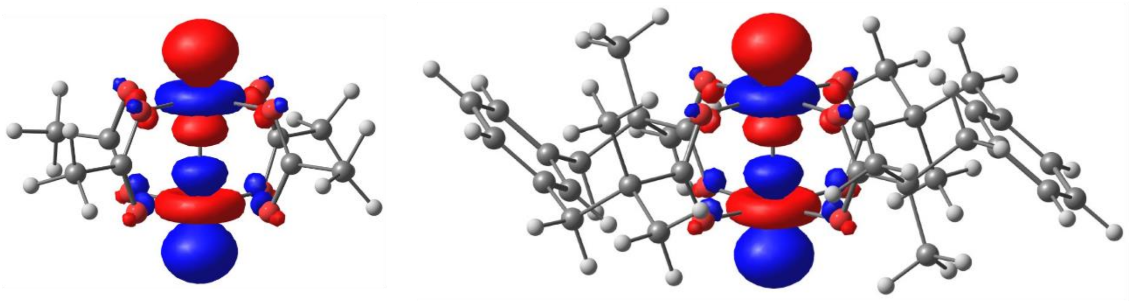
quality def2-SVP[4] basis set for all atoms. The SMD continuum model was used to model the effects of the solvent (CH_2Cl_2). This level is denoted SMD(CH_2Cl_2)-B3LYP-D3/def2-SVP. Geometries were fully optimized in solution without any geometry or symmetry constraints. Reactants, intermediates, and products were characterized by frequency calculations,[5] 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.[6] Potential energies were refined by means of single point calculations at the same level with a larger basis set, def2-TZVPP,[4] where all elements were described with a triple-ζ plus polarization quality basis set. This level is denoted SMD(CH_2Cl_2)-B3LYP-D3/def2-TZVPP//SMD(CH_2Cl_2)-B3LYP-D3/def2-SVP.

---

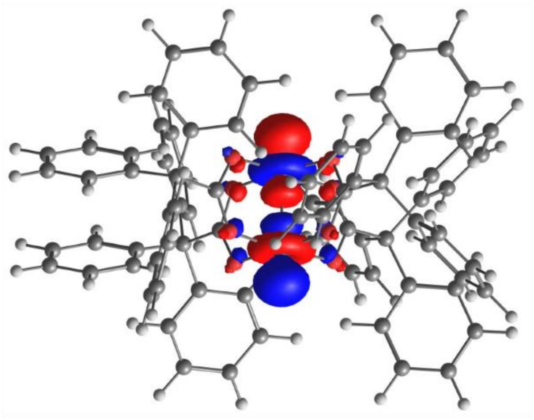
[4] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297

[5] McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[6] González, C.; Schlegel, H. B. *J. Phys. Chem*. **1990**, *94*, 5523.



$Rh_2(OAc)_4$, E(LUMO) = –2.68 eV $Rh_2(esp)_2$, E(LUMO) = –2.71 eV



$Rh_2(TPA)_4$, E(LUMO) = –2.90 eV

Figure S-1. Computed LUMO (in eV, at the SMD-B3LYP-D3/def2-SVP level) for the dirhodium catalysts used in this study.

Table S-1. Cartesian coordinates (in Å) and energies (in a.u.) of all the stationary points discussed in the text. All calculations have been performed at the SCM(dichloromethane)-B3LYP-D3/def2-SVP level.

Aziridine-4, E = -990.287459

N	0.833266000	-0.396882000	1.085216000
C	-0.115425000	0.796220000	1.214412000
C	-0.511061000	-0.503519000	0.697574000
C	-1.347904000	-1.348680000	0.089820000
H	-0.924620000	-2.306373000	-0.227092000
H	-0.310838000	1.046720000	2.263694000
C	0.051783000	1.980204000	0.279420000
C	0.749545000	1.604228000	-1.018185000
O	2.063432000	1.057036000	-0.710458000
S	2.086923000	-0.445847000	-0.081206000
H	0.176586000	0.876109000	-1.615468000
H	0.946539000	2.485633000	-1.641288000
H	-0.944442000	2.393778000	0.051941000
H	0.631686000	2.765620000	0.788530000
C	-2.762583000	-1.105381000	-0.201373000

H	-3.288224000	-1.948924000	-0.663950000
C	-3.453395000	0.027799000	0.034809000
H	-2.935634000	0.881090000	0.491967000
C	-4.902263000	0.229410000	-0.277186000
H	-5.474192000	0.476371000	0.635947000
H	-5.046103000	1.082414000	-0.965256000
H	-5.355386000	-0.663786000	-0.735888000
O	3.355883000	-0.546077000	0.612022000
O	1.711787000	-1.418284000	-1.101076000

Rh$_2$(OAc)$_4$, E = -1135.797077

Rh	-0.002728000	0.001161000	-1.194894000
Rh	-0.006234000	-0.001684000	1.196216000
O	-1.505171000	1.400991000	1.127942000
C	-1.890482000	1.846876000	0.003283000
O	-1.437624000	1.469818000	-1.121637000
O	1.396905000	1.497760000	1.130344000
C	1.846962000	1.881999000	0.007279000
O	1.472811000	1.429321000	-1.118930000
O	-1.412425000	-1.497585000	1.121268000
C	-1.856661000	-1.881285000	-0.004887000
O	-1.479604000	-1.425127000	-1.128161000
O	1.490034000	-1.408709000	1.122521000
C	1.879204000	-1.850458000	-0.002762000
O	1.428469000	-1.470841000	-1.127380000
C	-2.882677000	-2.981581000	-0.005554000
H	-2.355430000	-3.946900000	0.076300000
H	-3.548459000	-2.884220000	0.863183000
H	-3.459561000	-2.975485000	-0.939663000
C	2.979643000	-2.876442000	0.000418000
H	2.992008000	-3.437767000	-0.942946000
H	3.943340000	-2.351707000	0.111914000
H	2.864359000	-3.556717000	0.855758000
C	2.917845000	2.938886000	-0.000377000
H	3.056960000	3.366472000	1.000512000
H	3.862427000	2.482752000	-0.338643000
H	2.654563000	3.727820000	-0.720601000
C	-2.939840000	2.924930000	-0.002474000
H	-3.644148000	2.762823000	-0.830751000
H	-3.472069000	2.959122000	0.956846000
H	-2.441845000	3.894767000	-0.168666000

INT1, E = -2126.104515

Rh	-0.449383000	-0.115453000	0.053644000
N	1.723484000	-0.845486000	0.149064000
C	2.634948000	-0.277309000	1.267798000
C	2.672667000	0.180231000	-0.103020000
C	3.120389000	0.908620000	-1.125756000
H	2.677910000	0.693175000	-2.100608000

H	2.037595000	0.286625000	1.992525000
C	3.742927000	-1.138263000	1.835589000
C	4.285243000	-2.134222000	0.827784000
O	3.205968000	-3.026295000	0.432923000
S	2.030738000	-2.444039000	-0.523645000
H	4.716200000	-1.651834000	-0.064335000
H	5.043746000	-2.791363000	1.271151000
H	4.554362000	-0.467358000	2.162233000
H	3.374862000	-1.675798000	2.722900000
Rh	-2.684023000	0.790470000	-0.004961000
O	-3.101067000	-0.524559000	-1.524903000
C	-2.194099000	-1.315580000	-1.928851000
O	-1.010292000	-1.364052000	-1.476823000
O	-2.005082000	2.161798000	-1.383317000
C	-0.799781000	2.113148000	-1.771259000
O	0.068267000	1.281884000	-1.361173000
O	-3.216818000	-0.642767000	1.372323000
C	-2.335412000	-1.442677000	1.812017000
O	-1.113063000	-1.447707000	1.470736000
O	-2.122727000	2.057547000	1.526510000
C	-0.942661000	2.006333000	1.980441000
O	-0.034223000	1.216255000	1.568194000
C	-0.340075000	3.140663000	-2.771738000
H	0.385505000	2.695900000	-3.467089000
H	-1.193266000	3.561411000	-3.319758000
H	0.167878000	3.954194000	-2.227144000
C	-2.565333000	-2.305521000	-3.000902000
H	-1.673446000	-2.643156000	-3.544915000
H	-3.029637000	-3.180193000	-2.514832000
H	-3.300579000	-1.868409000	-3.690574000
C	-0.559124000	2.958493000	3.082374000
H	-1.436915000	3.495734000	3.462863000
H	-0.069619000	2.403465000	3.896745000
H	0.172279000	3.682555000	2.687914000
C	-2.775210000	-2.499780000	2.790757000
H	-3.685593000	-2.188390000	3.319759000
H	-2.994117000	-3.422113000	2.226692000
H	-1.968840000	-2.722821000	3.503068000
C	4.126685000	1.967774000	-1.054915000
H	4.297464000	2.505230000	-1.994766000
C	4.837811000	2.329845000	0.032113000
H	4.680810000	1.790520000	0.975469000
C	5.844431000	3.434315000	0.068044000
H	5.554933000	4.205320000	0.805270000
H	6.832868000	3.060683000	0.391566000
H	5.961518000	3.921662000	-0.912708000
O	0.893838000	-3.298551000	-0.262267000
O	2.537792000	-2.232829000	-1.872219000

TS1, E = -2126.082773

Rh	-0.441043000	-0.136751000	-0.069892000
N	1.635677000	-0.863220000	-0.295911000
C	2.869792000	0.117234000	1.068287000
C	2.667794000	0.096180000	-0.351350000
C	3.056948000	0.920045000	-1.347946000
H	2.597268000	0.778169000	-2.328572000
H	2.480255000	0.977767000	1.628597000
C	3.459877000	-0.973983000	1.877057000
C	3.875796000	-2.251693000	1.158441000
O	2.743873000	-2.992131000	0.662200000
S	2.057205000	-2.430797000	-0.723936000
H	4.576015000	-2.041985000	0.332987000
H	4.369181000	-2.929838000	1.866952000
H	4.364153000	-0.524964000	2.338046000
H	2.792504000	-1.193995000	2.729693000
Rh	-2.649376000	0.815042000	0.233019000
O	-3.151389000	-0.883811000	1.278410000
C	-2.277869000	-1.785742000	1.459672000
O	-1.079303000	-1.741882000	1.047112000
O	-3.197213000	-0.107826000	-1.521239000
C	-2.347655000	-0.808443000	-2.151281000
O	-1.143169000	-0.994043000	-1.800481000
O	-1.939824000	1.670236000	1.976808000
C	-0.733094000	1.502532000	2.313387000
O	0.116720000	0.809576000	1.667104000
O	-1.992563000	2.455057000	-0.832566000
C	-0.814978000	2.469917000	-1.298138000
O	0.045692000	1.548470000	-1.145526000
C	-2.807991000	-1.511458000	-3.401834000
H	-2.005548000	-1.516664000	-4.152915000
H	-3.036718000	-2.559622000	-3.146137000
H	-3.713676000	-1.040657000	-3.806028000
C	-2.694061000	-3.031462000	2.198659000
H	-3.653860000	-2.885344000	2.710661000
H	-2.793314000	-3.852554000	1.469732000
H	-1.913982000	-3.320185000	2.918222000
C	-0.393176000	3.656918000	-2.124875000
H	-0.427573000	3.370728000	-3.189324000
H	-1.066400000	4.508681000	-1.963201000
H	0.644016000	3.932919000	-1.886101000
C	-0.235726000	2.191240000	3.557169000
H	0.361760000	1.491925000	4.160520000
H	0.424263000	3.022389000	3.258113000
H	-1.070228000	2.589767000	4.147868000
C	3.979563000	2.019142000	-1.145368000
H	3.888170000	2.856519000	-1.848081000
C	4.910752000	2.094670000	-0.164169000
O	3.098477000	-2.405080000	-1.754942000
O	0.874934000	-3.252369000	-0.891521000
H	5.094041000	1.212172000	0.461776000
C	5.775072000	3.281043000	0.108082000

H	5.635320000	3.631443000	1.146860000
H	6.844653000	3.019353000	0.017335000
H	5.557373000	4.119774000	-0.570984000

INT2, E = -2126.11012

Rh	-0.425478000	-0.044742000	-0.203506000
N	1.665735000	-0.595343000	-0.697961000
C	3.160948000	-0.053962000	1.173330000
C	2.624662000	0.226322000	-0.073218000
C	2.869486000	1.480765000	-0.692670000
H	2.051951000	1.838335000	-1.329691000
H	3.832981000	0.677404000	1.626463000
C	2.766715000	-1.239723000	1.979230000
C	3.045641000	-2.625233000	1.359580000
O	2.120730000	-2.984361000	0.339521000
S	2.165602000	-2.085345000	-1.067322000
H	4.080198000	-2.692182000	0.983081000
H	2.911468000	-3.385551000	2.142505000
H	3.249333000	-1.195602000	2.966008000
H	1.671336000	-1.172273000	2.125821000
Rh	-2.662530000	0.662200000	0.420944000
O	-2.923350000	-1.193891000	1.271048000
C	-1.974842000	-2.035322000	1.228047000
O	-0.838710000	-1.838315000	0.700107000
O	-3.318968000	-0.073303000	-1.383348000
C	-2.479021000	-0.584908000	-2.185828000
O	-1.233072000	-0.694811000	-1.978796000
O	-1.865198000	1.344411000	2.197789000
C	-0.627334000	1.210148000	2.420343000
O	0.210993000	0.689299000	1.618934000
O	-2.243581000	2.478124000	-0.471109000
C	-1.116019000	2.670432000	-1.010310000
O	-0.168249000	1.823032000	-1.052040000
C	-2.999991000	-1.138833000	-3.487451000
H	-2.329540000	-0.856874000	-4.312241000
H	-3.001858000	-2.239585000	-3.423199000
H	-4.021249000	-0.788021000	-3.684533000
C	-2.222960000	-3.400550000	1.815645000
H	-2.993379000	-3.356015000	2.597128000
H	-2.581006000	-4.063214000	1.009757000
H	-1.288989000	-3.822929000	2.211020000
C	-0.862243000	3.999091000	-1.674851000
H	-0.795471000	3.843725000	-2.763900000
H	-1.669956000	4.709237000	-1.456988000
H	0.103452000	4.404987000	-1.337866000
C	-0.079055000	1.728128000	3.725382000
H	0.622155000	0.997264000	4.154283000
H	0.484422000	2.655301000	3.529018000
H	-0.888213000	1.943889000	4.434748000
C	4.017096000	2.295735000	-0.575241000

H	3.909305000	3.352171000	-0.844928000
C	5.269124000	1.813543000	-0.289341000
O	3.585298000	-2.067352000	-1.466695000
O	1.192260000	-2.764302000	-1.908520000
H	5.401720000	0.729077000	-0.198518000
C	6.486351000	2.642236000	-0.175986000
H	6.958911000	2.459921000	0.807771000
H	7.236282000	2.315398000	-0.919689000
H	6.290149000	3.717362000	-0.292969000

TS2, E = -2126.102281

Rh	-0.449985000	-0.097812000	-0.184462000
N	1.622118000	-0.600091000	-0.780522000
C	3.101269000	0.575501000	0.804884000
C	2.500984000	0.436452000	-0.469368000
C	2.820582000	1.429498000	-1.426187000
H	2.151294000	1.628823000	-2.264496000
H	3.250119000	1.590566000	1.177014000
C	3.145779000	-0.495799000	1.842274000
C	3.530609000	-1.916344000	1.425665000
O	2.522497000	-2.597324000	0.672801000
S	2.274180000	-2.066998000	-0.889132000
H	4.485244000	-1.925004000	0.872749000
H	3.657915000	-2.524994000	2.332411000
H	3.817613000	-0.174840000	2.653816000
H	2.124817000	-0.514685000	2.273148000
Rh	-2.689994000	0.604518000	0.427685000
O	-2.892973000	-1.179707000	1.433188000
C	-1.925818000	-2.001351000	1.438045000
O	-0.806948000	-1.825472000	0.868526000
O	-3.358019000	-0.299589000	-1.293351000
C	-2.523400000	-0.863963000	-2.064710000
O	-1.269932000	-0.918243000	-1.880157000
O	-1.870537000	1.459712000	2.119546000
C	-0.624250000	1.379350000	2.320664000
O	0.207690000	0.795986000	1.555734000
O	-2.331897000	2.346560000	-0.625094000
C	-1.218226000	2.516963000	-1.202420000
O	-0.246512000	1.698745000	-1.181285000
C	-3.059995000	-1.558855000	-3.289668000
H	-2.405484000	-1.366643000	-4.151951000
H	-3.054650000	-2.645602000	-3.102953000
H	-4.087320000	-1.238209000	-3.505906000
C	-2.131457000	-3.316639000	2.144645000
H	-2.885118000	-3.220345000	2.937751000
H	-2.493868000	-4.051685000	1.406302000
H	-1.180751000	-3.686072000	2.552828000
C	-1.035350000	3.773497000	-2.014362000
H	-1.270175000	3.541784000	-3.066912000
H	-1.716711000	4.562731000	-1.670159000

H	0.008218000	4.114816000	-1.967441000
C	-0.056705000	2.048108000	3.546548000
H	0.673755000	1.385168000	4.033057000
H	0.477183000	2.960614000	3.233486000
H	-0.852462000	2.321797000	4.251018000
C	4.021157000	2.092550000	-1.208455000
H	4.228864000	3.072100000	-1.654591000
C	4.964691000	1.505298000	-0.347615000
O	3.622095000	-1.970694000	-1.483735000
O	1.320489000	-3.031096000	-1.414277000
H	5.074362000	0.416796000	-0.389613000
C	6.046396000	2.251102000	0.342283000
H	6.194836000	1.850259000	1.358522000
H	7.000819000	2.078745000	-0.190363000
H	5.853643000	3.331505000	0.398513000

INT3, E = -2126.173671

Rh	-0.453987000	-0.063972000	-0.088683000
N	1.812670000	-0.432686000	-0.111556000
C	4.225377000	0.383700000	-0.111904000
C	2.709202000	0.511448000	-0.207813000
C	2.383538000	1.907852000	-0.450854000
H	1.373264000	2.263575000	-0.626645000
H	4.475114000	-0.141392000	0.821681000
C	4.813980000	-0.425266000	-1.290864000
C	4.127713000	-1.778121000	-1.453278000
O	3.769885000	-2.273644000	-0.138458000
S	2.240705000	-2.025886000	0.381474000
H	3.227459000	-1.718267000	-2.084835000
H	4.792653000	-2.534698000	-1.891522000
H	4.715574000	0.143272000	-2.229281000
H	5.888499000	-0.559501000	-1.093931000
Rh	-2.807131000	0.442607000	0.136463000
O	-3.190155000	-1.048428000	-1.221714000
C	-2.217295000	-1.680511000	-1.737936000
O	-0.992422000	-1.477867000	-1.483578000
O	-2.588329000	1.788614000	-1.411839000
C	-1.458293000	1.926270000	-1.965312000
O	-0.397978000	1.310633000	-1.628117000
O	-2.872997000	-0.936906000	1.664054000
C	-1.817921000	-1.565301000	1.981421000
O	-0.682839000	-1.406848000	1.439546000
O	-2.272575000	1.911554000	1.479516000
C	-1.052291000	2.085587000	1.770219000
O	-0.084228000	1.415850000	1.291938000
C	-1.358133000	2.863384000	-3.140126000
H	-2.151600000	3.621408000	-3.103119000
H	-0.367762000	3.338332000	-3.171144000
H	-1.481144000	2.272883000	-4.063808000
C	-2.548874000	-2.789192000	-2.702463000

H	-1.702038000	-2.989437000	-3.372107000
H	-2.755301000	-3.702341000	-2.119163000
H	-3.450827000	-2.541458000	-3.279153000
C	-0.715772000	3.145910000	2.785059000
H	-1.485714000	3.928909000	2.796515000
H	-0.682048000	2.675241000	3.781921000
H	0.273607000	3.575733000	2.576611000
C	-1.926700000	-2.599711000	3.070047000
H	-2.441105000	-3.484786000	2.660480000
H	-0.931926000	-2.896468000	3.426072000
H	-2.536595000	-2.211935000	3.898881000
C	3.509485000	2.649904000	-0.380378000
H	3.539526000	3.736907000	-0.494466000
C	4.737224000	1.846354000	-0.070428000
H	5.493585000	2.014485000	-0.857351000
C	5.361697000	2.237550000	1.278628000
H	4.646093000	2.079272000	2.101713000
H	6.257740000	1.629390000	1.479066000
H	5.660917000	3.297715000	1.282831000
O	1.367222000	-2.932262000	-0.341685000
O	2.346263000	-2.064640000	1.830821000

4a, E = -990.357644

N	0.704486000	-1.227671000	-0.364135000
C	-1.134585000	0.490462000	0.111293000
C	-0.526846000	-0.829536000	-0.358368000
C	-1.604343000	-1.694686000	-0.819417000
H	-1.427731000	-2.690468000	-1.228042000
H	-0.851651000	0.613736000	1.168848000
C	-0.634753000	1.731459000	-0.657647000
C	0.890426000	1.824532000	-0.724615000
O	1.480603000	1.204265000	0.444611000
S	1.983004000	-0.348540000	0.246995000
H	1.292162000	1.341965000	-1.629295000
H	1.239656000	2.866262000	-0.723606000
H	-1.032176000	1.721335000	-1.685148000
H	-1.053596000	2.617332000	-0.155682000
C	-2.792687000	-1.086214000	-0.629836000
H	-3.764077000	-1.527474000	-0.869464000
C	-2.668420000	0.279090000	-0.013629000
H	-3.097866000	1.020664000	-0.711324000
C	-3.422143000	0.396673000	1.318776000
H	-3.038729000	-0.330309000	2.053194000
H	-3.304462000	1.407159000	1.741333000
H	-4.499162000	0.209426000	1.181199000
O	3.020640000	-0.366830000	-0.778812000
O	2.278541000	-0.806180000	1.596159000

Aziridine-4(cis), E = -990.286054

N	-0.548692000	-0.228985000	-1.058541000
C	0.395842000	0.952282000	-0.840828000
C	0.716442000	-0.418499000	-0.478585000
C	1.422473000	-1.363745000	0.150756000
H	0.912784000	-2.322099000	0.295579000
H	0.760817000	1.362794000	-1.788757000
C	0.065846000	1.973741000	0.232517000
C	-0.832879000	1.405268000	1.319566000
O	-2.072885000	0.937994000	0.715359000
S	-1.978563000	-0.442888000	-0.144154000
H	-0.359009000	0.580212000	1.875731000
H	-1.138669000	2.176977000	2.036857000
H	1.007688000	2.326700000	0.682854000
H	-0.430004000	2.840706000	-0.231208000
C	2.764617000	-1.224407000	0.716032000
H	2.991278000	-1.936663000	1.517405000
C	3.738483000	-0.361022000	0.354691000
H	4.674661000	-0.408157000	0.923059000
O	-3.113170000	-0.405680000	-1.045110000
O	-1.769840000	-1.575361000	0.750672000
C	3.682918000	0.644349000	-0.756154000
H	4.692638000	0.880137000	-1.126799000
H	3.075055000	0.286241000	-1.602476000
H	3.235327000	1.598809000	-0.421336000

INT1-Z, E = -2126.101148

Rh	-0.419811000	-0.067447000	0.051480000
N	1.814187000	-0.561657000	0.092852000
C	2.657273000	0.018445000	1.254432000
C	2.676071000	0.559990000	-0.090413000
C	2.905375000	1.426985000	-1.077836000
H	2.366073000	1.209171000	-2.004463000
H	2.001229000	0.503729000	1.986108000
C	3.778637000	-0.811060000	1.842213000
C	4.417271000	-1.744705000	0.831733000
O	3.401029000	-2.667863000	0.353324000
S	2.279669000	-2.089293000	-0.666187000
H	4.864788000	-1.215101000	-0.024774000
H	5.184809000	-2.380734000	1.289965000
H	4.536823000	-0.125016000	2.250415000
H	3.381446000	-1.402448000	2.681455000
Rh	-2.774133000	0.466462000	0.050206000
O	-3.054031000	-1.193832000	1.237775000
C	-2.057223000	-1.895956000	1.586341000
O	-0.852786000	-1.670398000	1.258568000
O	-2.957339000	-0.711692000	-1.632470000
C	-1.919490000	-1.239529000	-2.135411000
O	-0.745691000	-1.137508000	-1.665335000
O	-2.426782000	1.612144000	1.729458000
C	-1.259106000	1.684261000	2.213178000

O	-0.235658000	1.088855000	1.747283000
O	-2.334775000	2.092964000	-1.136639000
C	-1.130951000	2.309370000	-1.468204000
O	-0.136345000	1.598236000	-1.123765000
C	-2.077030000	-2.023333000	-3.411509000
H	-3.104911000	-2.395580000	-3.515190000
H	-1.858980000	-1.354065000	-4.260679000
H	-1.357425000	-2.853168000	-3.438792000
C	-2.324296000	-3.116215000	2.428255000
H	-3.242075000	-2.986729000	3.017518000
H	-2.462159000	-3.978110000	1.753917000
H	-1.468378000	-3.328892000	3.083221000
C	-0.838408000	3.491382000	-2.355287000
H	-0.501972000	3.122520000	-3.337827000
H	-1.729381000	4.118412000	-2.485255000
H	-0.015472000	4.081415000	-1.924410000
C	-1.041975000	2.558915000	3.419511000
H	-0.436258000	2.023209000	4.165301000
H	-0.474807000	3.451895000	3.109308000
H	-1.998481000	2.871522000	3.857040000
C	3.683286000	2.664894000	-1.049692000
H	3.291326000	3.437860000	-1.721323000
C	4.800503000	2.958101000	-0.352690000
H	5.202774000	3.970837000	-0.475070000
O	2.890732000	-1.747074000	-1.943479000
O	1.188802000	-3.033036000	-0.576651000
C	5.579498000	2.048633000	0.543952000
H	5.388188000	0.990130000	0.320615000
H	6.661064000	2.236148000	0.442699000
H	5.331372000	2.220182000	1.607405000

TS1-Z, E = -2126.078892

Rh	-0.425455000	-0.102557000	-0.099014000
N	1.701012000	-0.573517000	-0.391329000
C	2.832536000	0.451850000	1.063903000
C	2.646924000	0.474580000	-0.359609000
C	2.924389000	1.403327000	-1.298795000
H	2.448011000	1.275983000	-2.275131000
H	2.391276000	1.272411000	1.644007000
C	3.454852000	-0.623616000	1.862249000
C	3.975374000	-1.861745000	1.144012000
O	2.915604000	-2.647864000	0.567715000
S	2.280214000	-2.080211000	-0.840559000
H	4.709617000	-1.599563000	0.365090000
H	4.461885000	-2.528663000	1.867659000
H	4.310762000	-0.130291000	2.369304000
H	2.769434000	-0.895239000	2.685430000
Rh	-2.728240000	0.534664000	0.301779000
O	-2.966398000	-1.260643000	1.279351000
C	-1.981121000	-2.054052000	1.378242000

O	-0.815085000	-1.837990000	0.929158000
O	-3.204444000	-0.381187000	-1.476930000
C	-2.281359000	-0.891324000	-2.182619000
O	-1.052465000	-0.926147000	-1.871963000
O	-2.080590000	1.403937000	2.062549000
C	-0.857511000	1.355858000	2.376893000
O	0.052831000	0.794907000	1.686180000
O	-2.331335000	2.294013000	-0.704962000
C	-1.168451000	2.500685000	-1.162302000
O	-0.187703000	1.698216000	-1.067279000
C	-2.667241000	-1.472041000	-3.518393000
H	-3.703880000	-1.834567000	-3.497422000
H	-2.595560000	-0.674941000	-4.277757000
H	-1.979072000	-2.280041000	-3.801063000
C	-2.224634000	-3.380094000	2.050664000
H	-3.003091000	-3.286595000	2.820255000
H	-2.579628000	-4.092884000	1.287296000
H	-1.294935000	-3.773613000	2.482997000
C	-0.906808000	3.794146000	-1.890064000
H	-0.666127000	3.570085000	-2.941616000
H	-1.778739000	4.458820000	-1.845344000
H	-0.028268000	4.290729000	-1.450228000
C	-0.418948000	2.032641000	3.648968000
H	0.278008000	1.383019000	4.198609000
H	0.120962000	2.957635000	3.386799000
H	-1.281881000	2.286386000	4.277667000
C	3.711033000	2.601013000	-1.052950000
H	3.335103000	3.501454000	-1.554490000
C	4.843932000	2.726311000	-0.320618000
H	5.251775000	3.740747000	-0.231619000
O	3.386437000	-1.923143000	-1.789839000
O	1.185646000	-2.985793000	-1.127812000
C	5.680243000	1.650792000	0.301013000
H	5.386393000	0.641197000	-0.019780000
H	6.740173000	1.806692000	0.036487000
H	5.634319000	1.687963000	1.403766000

INT2-Z, E = -2126. 0918689

Rh	-0.403920000	-0.027148000	-0.198569000
N	1.744953000	-0.312336000	-0.664340000
C	3.145488000	0.312123000	1.248697000
C	2.593274000	0.585113000	0.009230000
C	2.686926000	1.892836000	-0.526773000
H	1.812177000	2.195564000	-1.118209000
H	3.803895000	1.056477000	1.701503000
C	2.812936000	-0.911474000	2.022670000
C	3.259221000	-2.251417000	1.392428000
O	2.433304000	-2.671243000	0.313711000
S	2.433889000	-1.721500000	-1.058350000
H	4.315224000	-2.211030000	1.077168000

H	3.152458000	-3.038814000	2.152345000
H	3.243930000	-0.844451000	3.031513000
H	1.710843000	-0.957827000	2.110927000
Rh	-2.724798000	0.377693000	0.388004000
O	-2.710815000	-1.450245000	1.337864000
C	-1.647949000	-2.141127000	1.346255000
O	-0.547828000	-1.804142000	0.811759000
O	-3.247205000	-0.546083000	-1.372741000
C	-2.335465000	-0.960499000	-2.152378000
O	-1.089351000	-0.888146000	-1.932575000
O	-2.049402000	1.261069000	2.126277000
C	-0.806860000	1.321440000	2.355104000
O	0.105093000	0.894991000	1.578400000
O	-2.564740000	2.183183000	-0.603387000
C	-1.469818000	2.513295000	-1.143650000
O	-0.410042000	1.809257000	-1.144581000
C	-2.765060000	-1.555480000	-3.468930000
H	-3.774188000	-1.982065000	-3.390684000
H	-2.785250000	-0.750735000	-4.223294000
H	-2.045587000	-2.316490000	-3.800235000
C	-1.699646000	-3.492237000	2.010816000
H	-2.409707000	-3.484701000	2.849175000
H	-2.053120000	-4.227030000	1.267903000
H	-0.699796000	-3.797115000	2.347600000
C	-1.395680000	3.842223000	-1.851054000
H	-1.148658000	3.674143000	-2.911112000
H	-2.345573000	4.385675000	-1.771623000
H	-0.582649000	4.442796000	-1.413929000
C	-0.347113000	1.941877000	3.649523000
H	0.209414000	1.188897000	4.229939000
H	0.346011000	2.769547000	3.432823000
H	-1.197151000	2.309838000	4.237757000
C	3.729052000	2.841867000	-0.380482000
H	3.434739000	3.890015000	-0.502747000
C	5.075253000	2.586520000	-0.290808000
H	5.714038000	3.477373000	-0.245136000
O	3.859494000	-1.524231000	-1.388260000
O	1.589990000	-2.477981000	-1.969326000
C	5.809620000	1.299301000	-0.372645000
H	5.185669000	0.434708000	-0.637210000
H	6.629271000	1.406984000	-1.104390000
H	6.306345000	1.096469000	0.594147000

TS2-Z, E = -2126.091869

Rh	-0.412618000	-0.044288000	-0.194576000
N	1.713094000	-0.311164000	-0.777387000
C	3.019956000	0.809524000	0.990979000
C	2.489811000	0.750348000	-0.316368000
C	2.686536000	1.901108000	-1.126702000
H	1.980157000	2.136461000	-1.924902000

H	3.056026000	1.787330000	1.473001000
C	3.143503000	-0.351882000	1.918095000
C	3.627086000	-1.698492000	1.378233000
O	2.670503000	-2.370794000	0.553305000
S	2.424983000	-1.741774000	-0.968233000
H	4.583315000	-1.595990000	0.840342000
H	3.787447000	-2.378521000	2.227120000
H	3.791717000	-0.061327000	2.760400000
H	2.128255000	-0.479082000	2.346372000
Rh	-2.724809000	0.344412000	0.425249000
O	-2.708145000	-1.501988000	1.335727000
C	-1.646281000	-2.196254000	1.309721000
O	-0.553532000	-1.848867000	0.770060000
O	-3.261942000	-0.544187000	-1.350373000
C	-2.358536000	-0.940755000	-2.148706000
O	-1.109933000	-0.866111000	-1.942826000
O	-2.027995000	1.192389000	2.174343000
C	-0.783263000	1.232418000	2.397849000
O	0.119647000	0.824795000	1.600705000
O	-2.575197000	2.169872000	-0.531084000
C	-1.485671000	2.508955000	-1.079593000
O	-0.422978000	1.812449000	-1.096027000
C	-2.801308000	-1.515003000	-3.470105000
H	-2.098885000	-2.289874000	-3.806411000
H	-3.819628000	-1.919637000	-3.396115000
H	-2.801017000	-0.705021000	-4.219097000
C	-1.694138000	-3.565495000	1.937393000
H	-2.028917000	-4.284154000	1.170421000
H	-0.695542000	-3.869711000	2.278992000
H	-2.414325000	-3.587873000	2.766714000
C	-1.446733000	3.828388000	-1.807571000
H	-1.646411000	3.641207000	-2.876039000
H	-2.217214000	4.509705000	-1.422750000
H	-0.450481000	4.284624000	-1.723371000
C	-0.319943000	1.767259000	3.728460000
H	-0.144481000	0.910812000	4.401323000
H	0.630324000	2.307783000	3.614954000
H	-1.082499000	2.416287000	4.178733000
C	3.757985000	2.699789000	-0.769941000
H	3.763831000	3.771454000	-1.006055000
C	4.808947000	2.175675000	0.013527000
O	3.774882000	-1.561921000	-1.538622000
O	1.516035000	-2.697249000	-1.579013000
H	5.318820000	2.900097000	0.664876000
C	5.626779000	0.955502000	-0.274593000
H	5.977281000	0.476287000	0.652116000
H	5.118586000	0.219525000	-0.909530000
H	6.537347000	1.316995000	-0.791558000

INT3-Z, E = -2126.170717

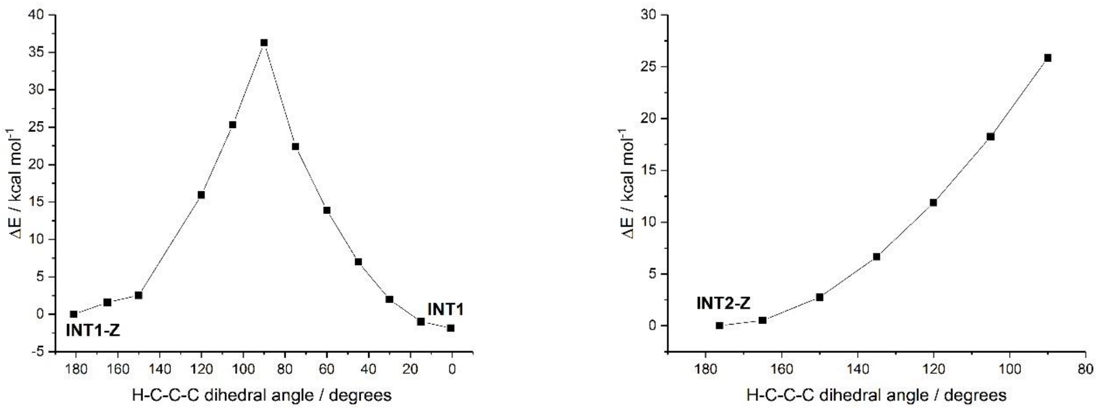
Rh	0.461142000	-0.030913000	0.038893000
N	-1.789215000	-0.443065000	-0.080509000
C	-4.220170000	0.299323000	-0.279861000
C	-2.711295000	0.480050000	-0.146310000
C	-2.423025000	1.902866000	-0.084133000
H	-1.429356000	2.303883000	0.089597000
H	-4.423267000	-0.376673000	-1.122730000
C	-4.822244000	-0.346380000	0.991267000
C	-4.106096000	-1.642495000	1.360076000
O	-3.701062000	-2.313822000	0.139837000
S	-2.162028000	-2.100923000	-0.366729000
H	-3.224977000	-1.468479000	1.997425000
H	-4.764727000	-2.345338000	1.888067000
H	-4.763229000	0.344287000	1.845338000
H	-5.886043000	-0.542766000	0.795956000
Rh	2.832378000	0.437517000	0.002406000
O	3.031723000	-0.808088000	1.627810000
C	1.998507000	-1.365706000	2.110804000
O	0.816915000	-1.223873000	1.675874000
O	2.463540000	2.027861000	1.261667000
C	1.284340000	2.241361000	1.668845000
O	0.262333000	1.558211000	1.343797000
O	3.045310000	-1.180589000	-1.256162000
C	2.016618000	-1.829183000	-1.616271000
O	0.828632000	-1.571244000	-1.257232000
O	2.479731000	1.655226000	-1.624913000
C	1.297724000	1.797522000	-2.057836000
O	0.266258000	1.237221000	-1.570157000
C	1.065537000	3.372154000	2.639378000
H	1.898390000	4.086449000	2.603188000
H	0.112753000	3.878023000	2.427739000
H	1.004084000	2.950501000	3.656670000
C	2.199959000	-2.302582000	3.273265000
H	1.269551000	-2.421327000	3.843869000
H	2.494941000	-3.288081000	2.875230000
H	3.010552000	-1.941677000	3.921593000
C	1.087838000	2.673193000	-3.264984000
H	1.927672000	3.367879000	-3.396735000
H	1.019243000	2.027174000	-4.156286000
H	0.140091000	3.222519000	-3.174228000
C	2.224444000	-3.009190000	-2.528338000
H	2.735594000	-3.805986000	-1.963714000
H	1.264253000	-3.386962000	-2.901893000
H	2.878220000	-2.723552000	-3.365907000
C	-3.553304000	2.599959000	-0.328253000
H	-3.608050000	3.691314000	-0.369968000
C	-4.747375000	1.732598000	-0.592593000
H	-4.946111000	1.786784000	-1.679599000
O	-1.296402000	-2.885156000	0.494425000
O	-2.217230000	-2.332973000	-1.801134000
C	-6.021835000	2.195189000	0.121486000

H	-6.864513000	1.521770000	-0.096807000
H	-5.892030000	2.242553000	1.212961000
H	-6.300191000	3.202487000	-0.226782000

12a, E = -990.354907

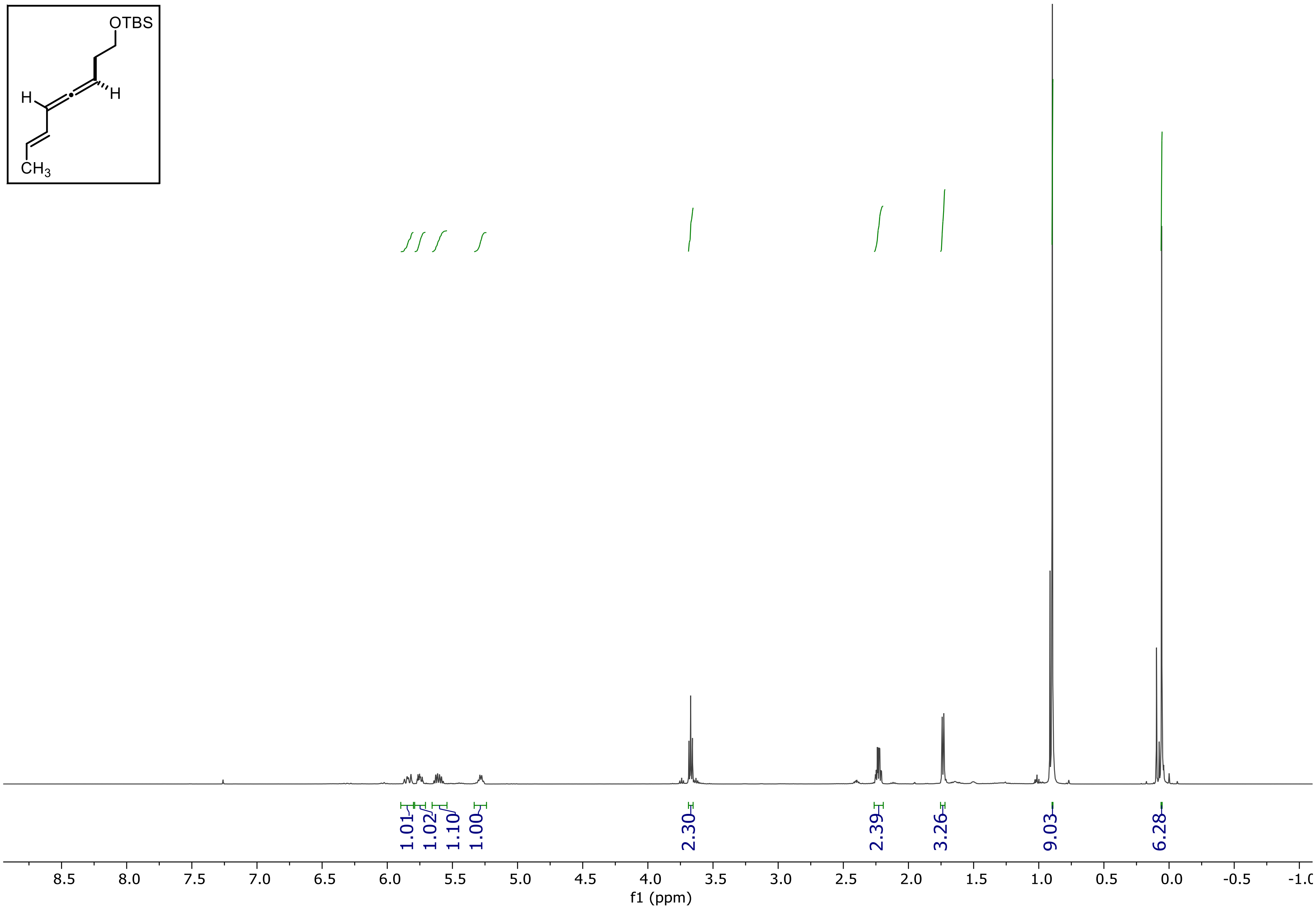
N	0.802716000	-1.204000000	-0.394309000
C	-1.102167000	0.285245000	0.447572000
C	-0.449082000	-0.930557000	-0.207445000
C	-1.496101000	-1.852532000	-0.622268000
H	-1.290008000	-2.773827000	-1.168447000
H	-0.648356000	0.406852000	1.442617000
C	-0.847266000	1.597619000	-0.328250000
C	0.634937000	1.823090000	-0.629303000
O	1.452374000	1.258611000	0.425852000
S	2.060643000	-0.239698000	0.127021000
H	0.930813000	1.379138000	-1.592881000
H	0.885165000	2.892353000	-0.669092000
H	-1.396078000	1.599518000	-1.281512000
H	-1.242097000	2.425614000	0.278058000
C	-2.692729000	-1.407867000	-0.187864000
H	-3.644088000	-1.923923000	-0.343954000
C	-2.604591000	-0.121424000	0.584927000
H	-2.792454000	-0.370367000	1.646166000
O	2.986808000	-0.139285000	-0.995709000
O	2.529476000	-0.705169000	1.423814000
C	-3.662054000	0.908306000	0.171410000
H	-3.562628000	1.836271000	0.754239000
H	-3.594423000	1.163369000	-0.896838000
H	-4.670095000	0.503632000	0.355134000

Figure S-2. Computed *Z*- to *E*- isomerization barriers of **INT1** and **INT2** exceed >20 kcal/mol.

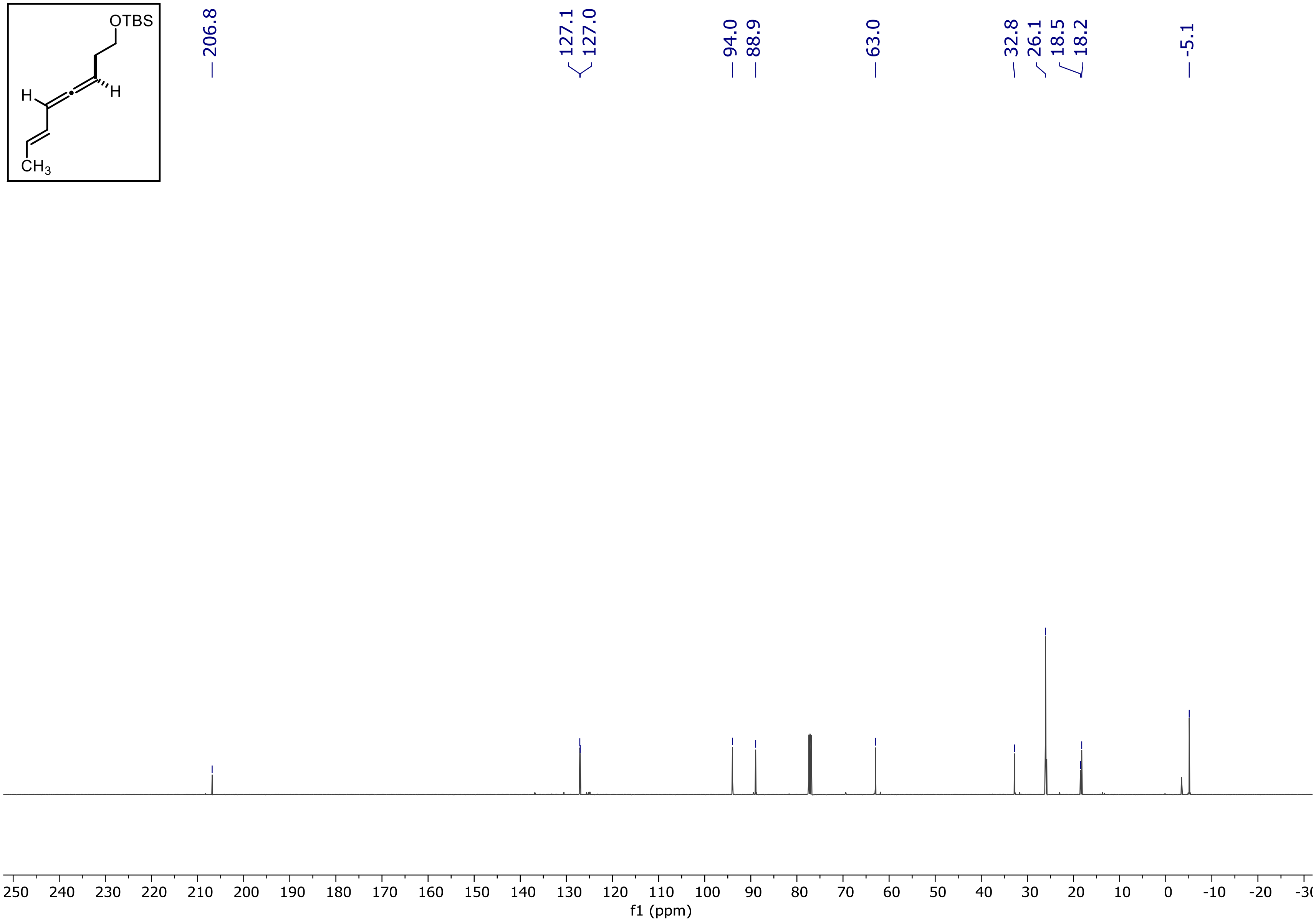


X. NMR data

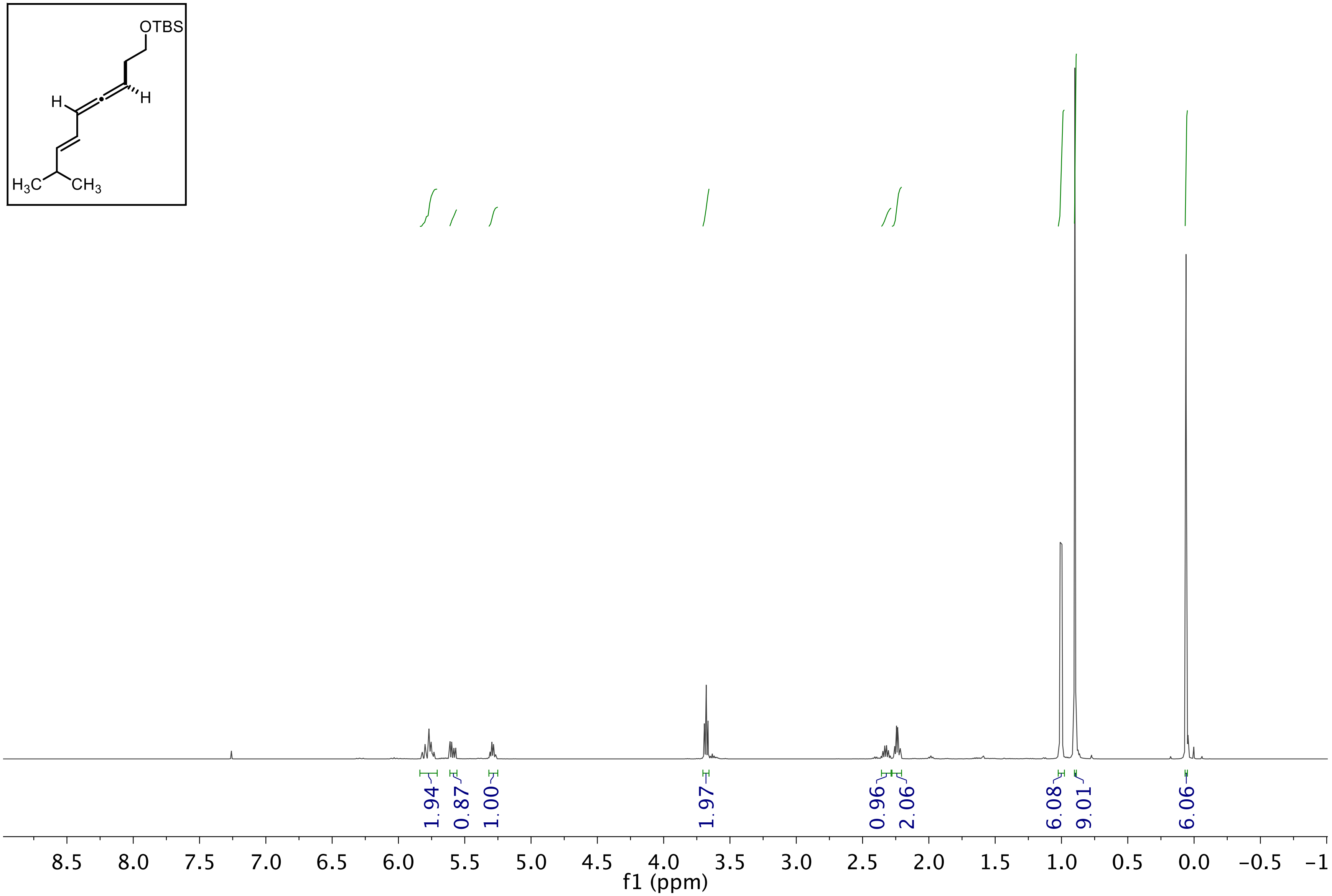
^{1}H NMR for Compound S-1.



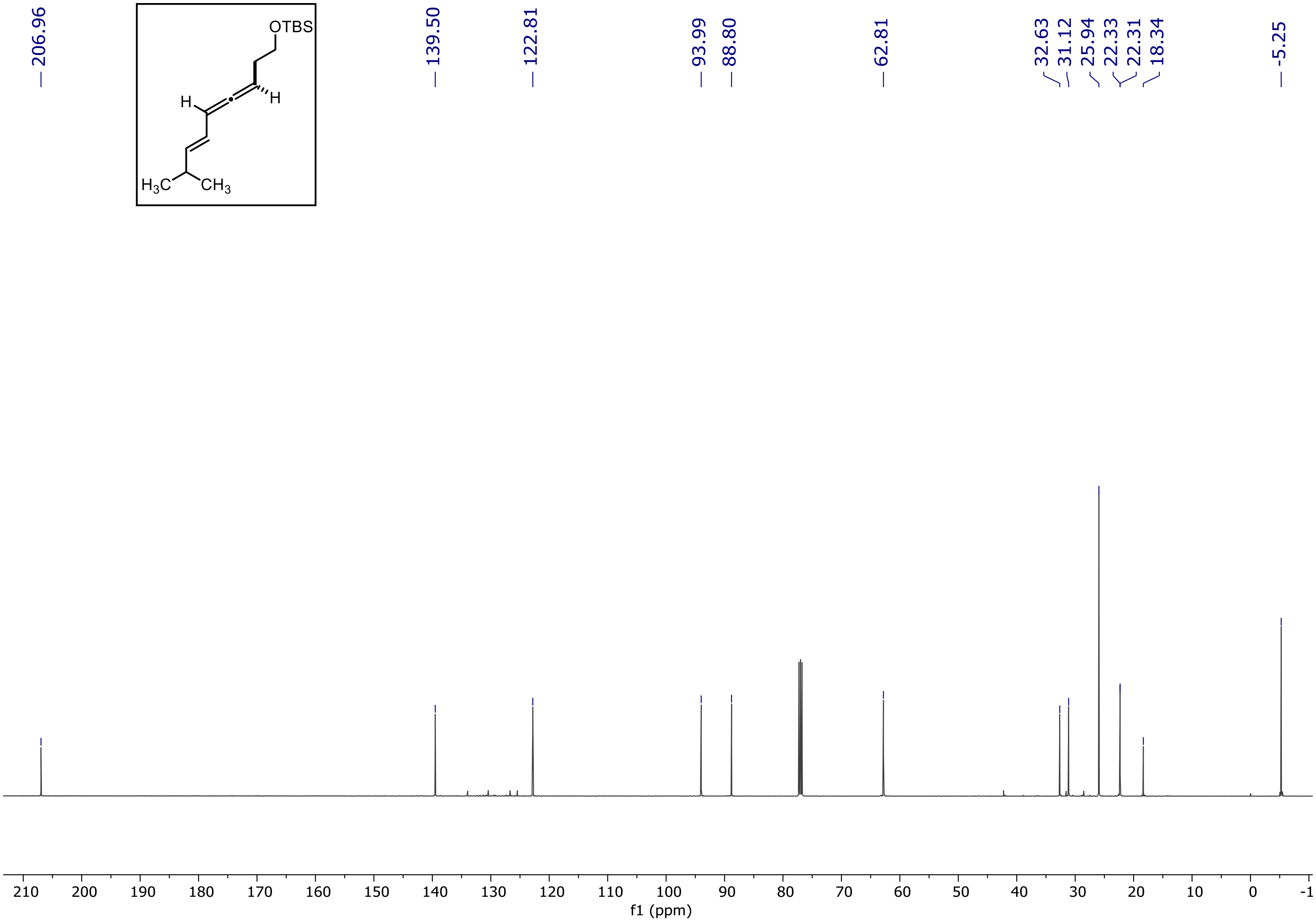
^{13}C NMR for Compound S-1.



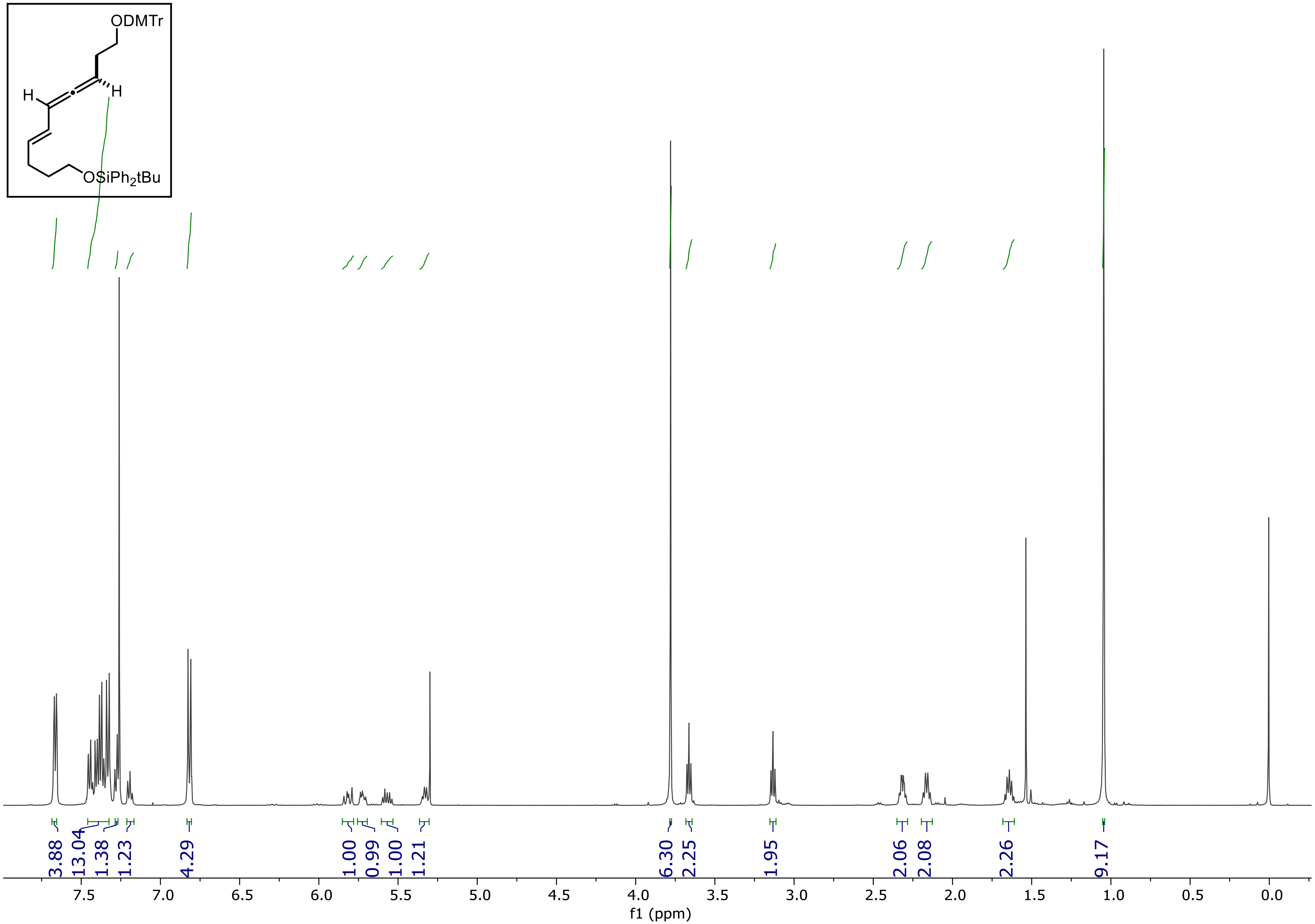
^{1}H NMR for Compound S-2.



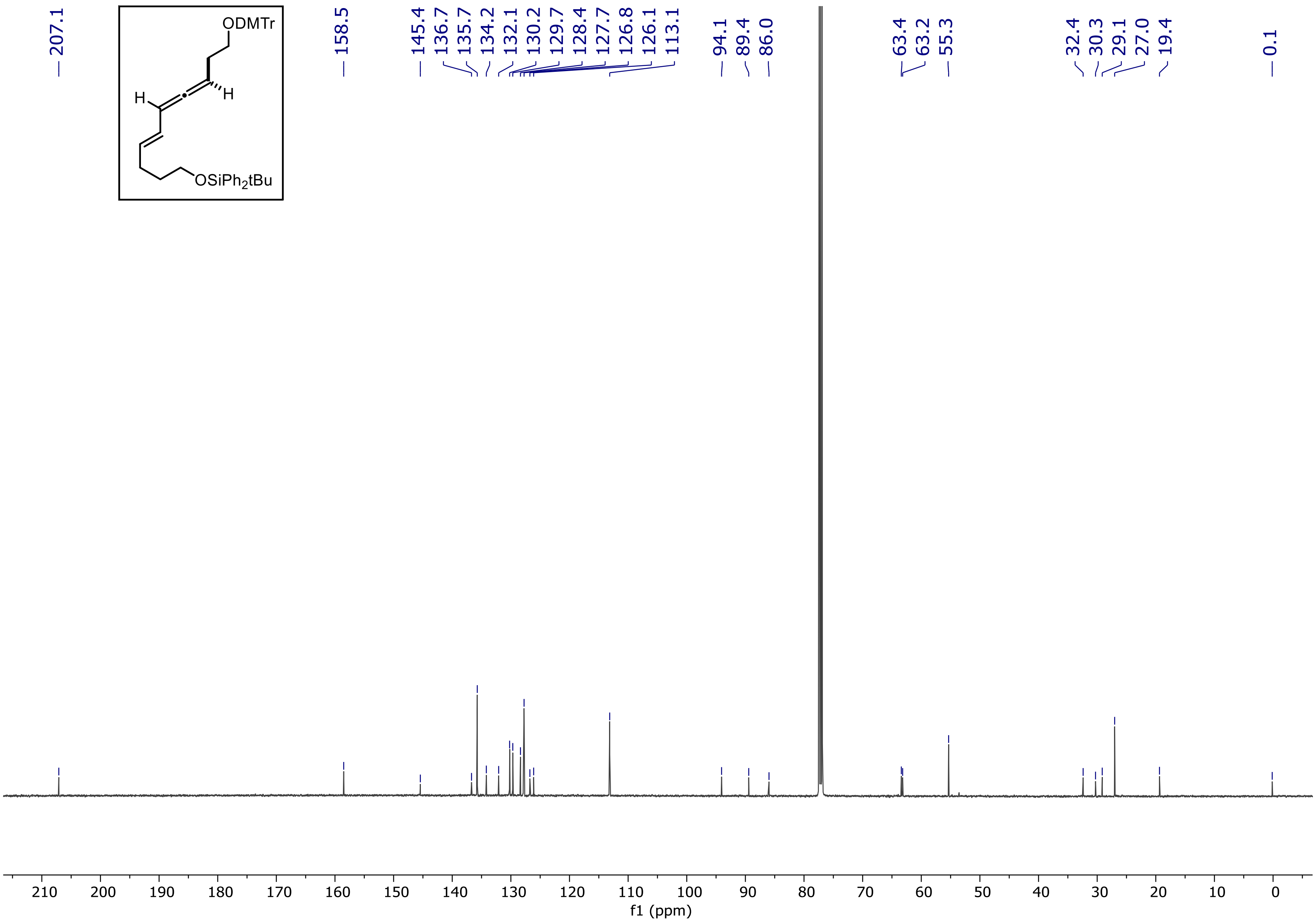
^{13}C NMR for Compound S-2.



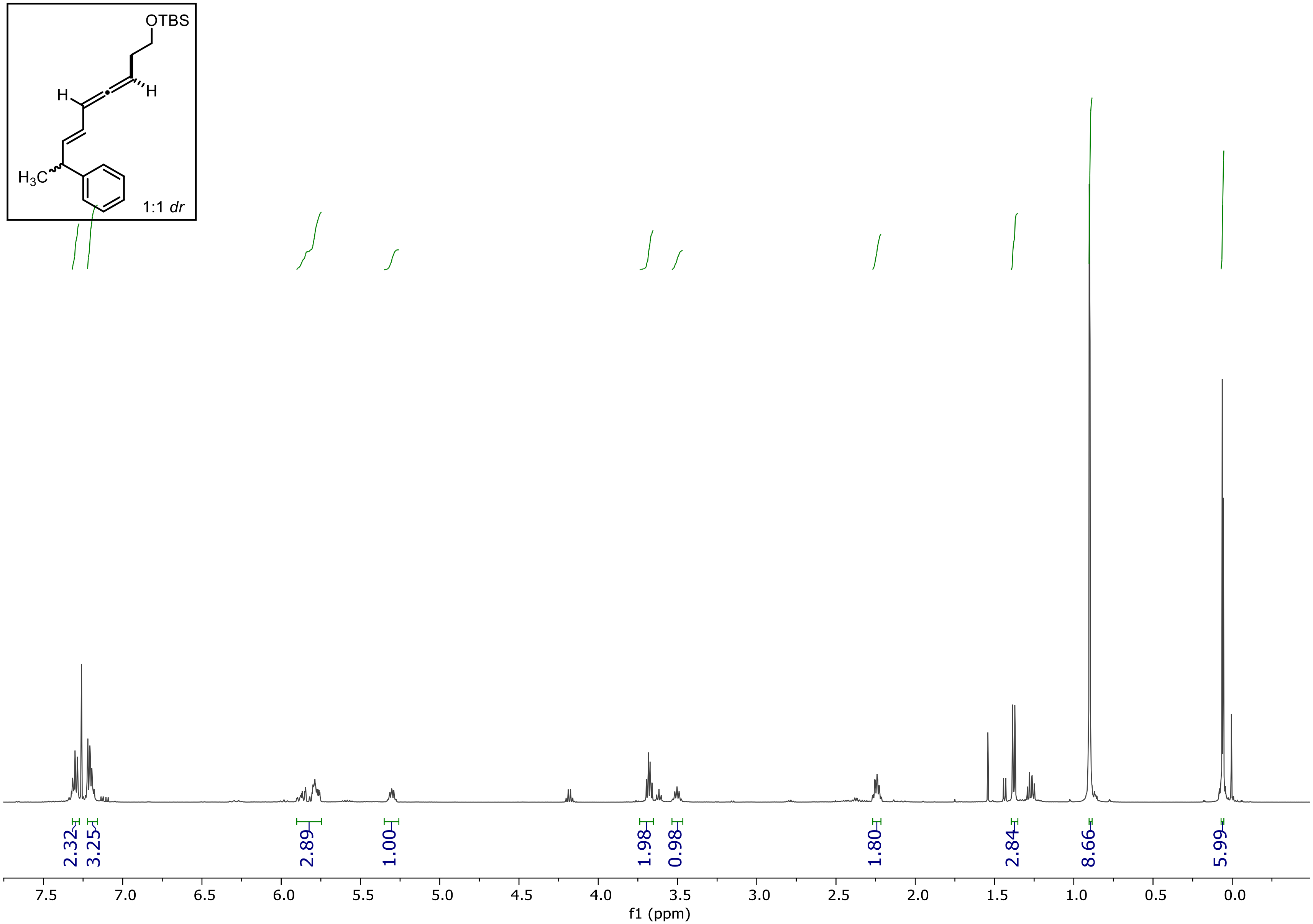
^{1}H NMR for Compound S-3.



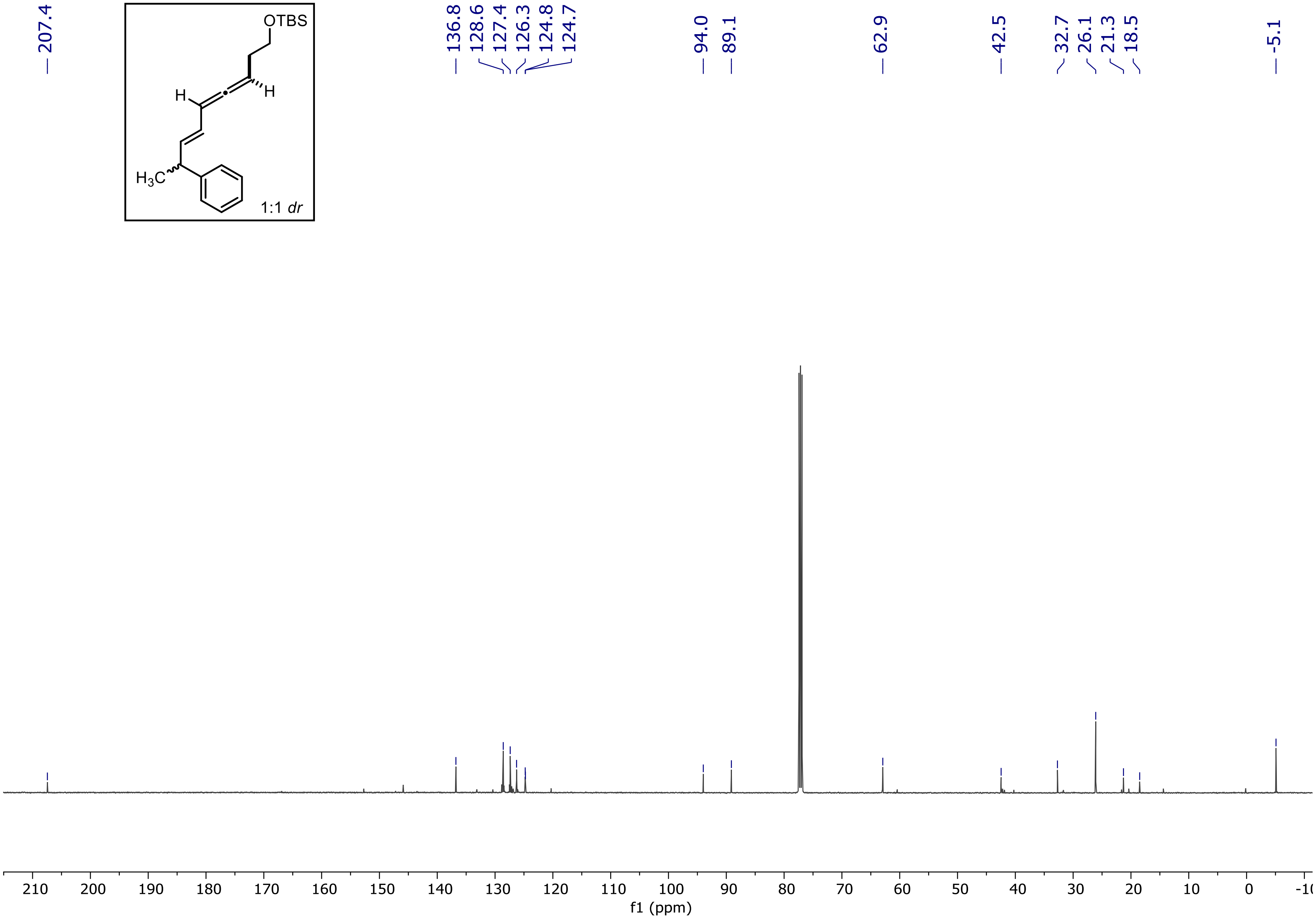
^{13}C NMR for Compound S-3.



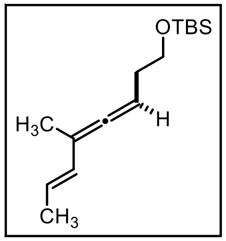
^{1}H NMR for Compound S-4.

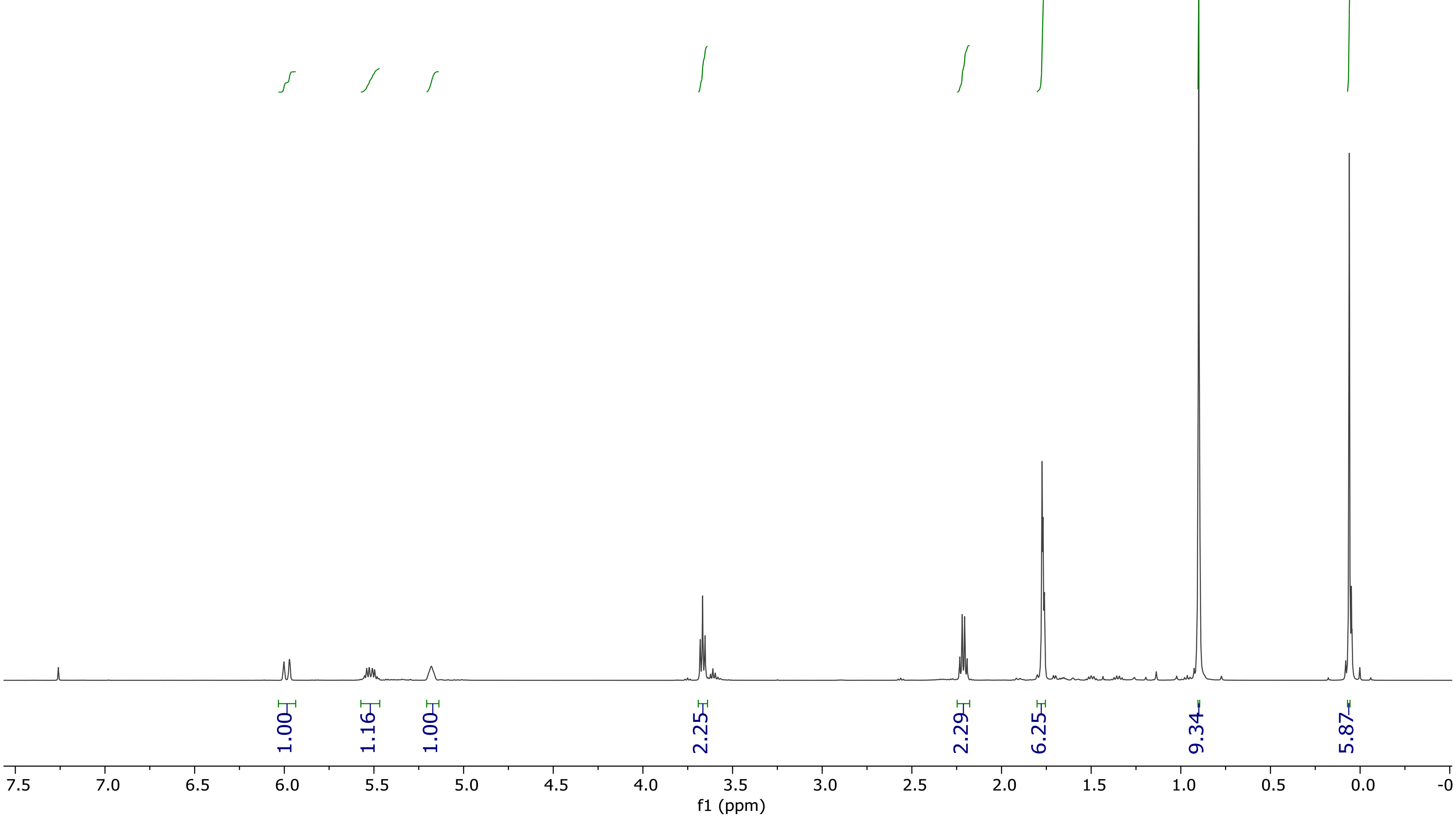


^{13}C NMR for Compound S-4.

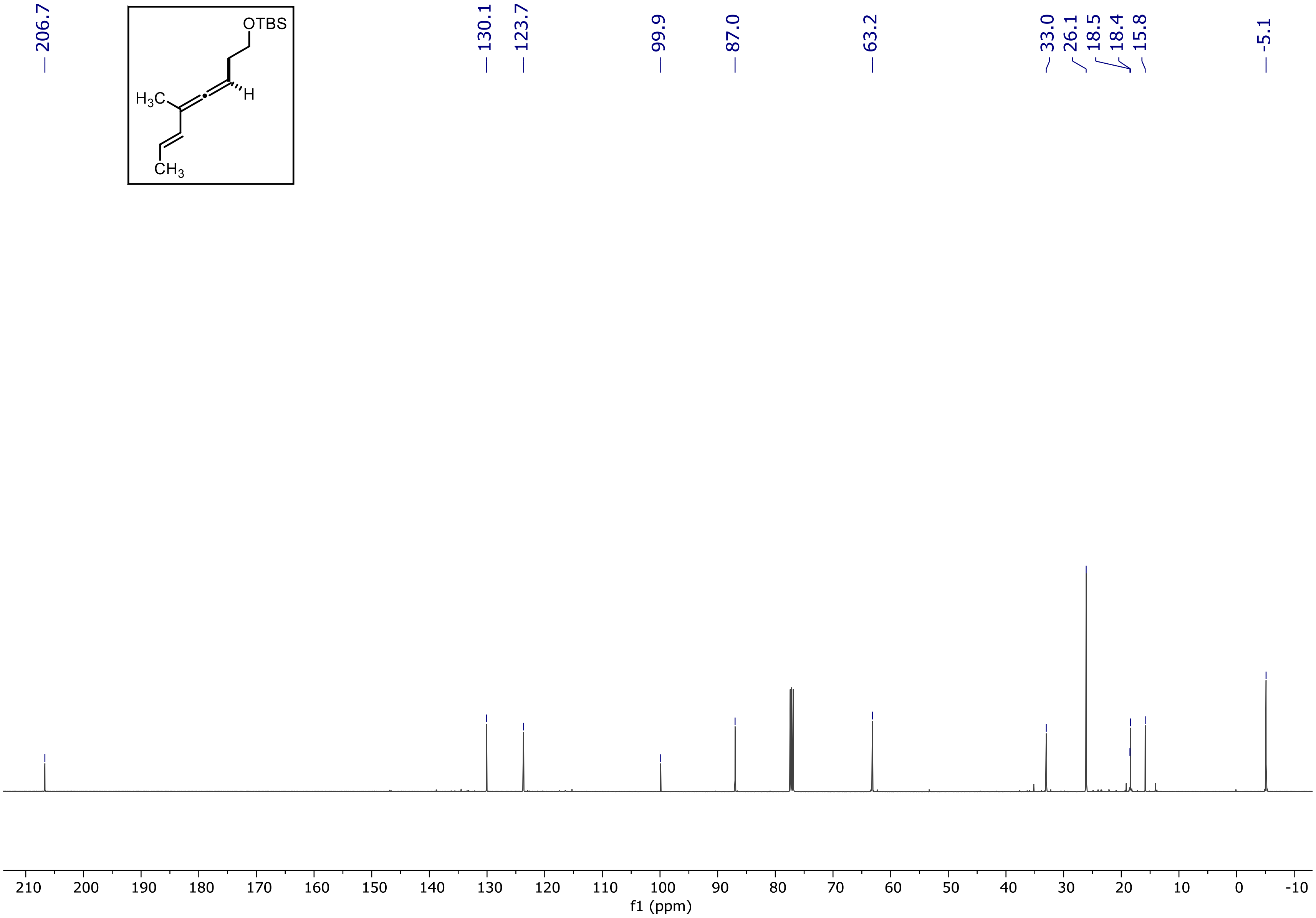


^{1}H NMR for Compound S-5.

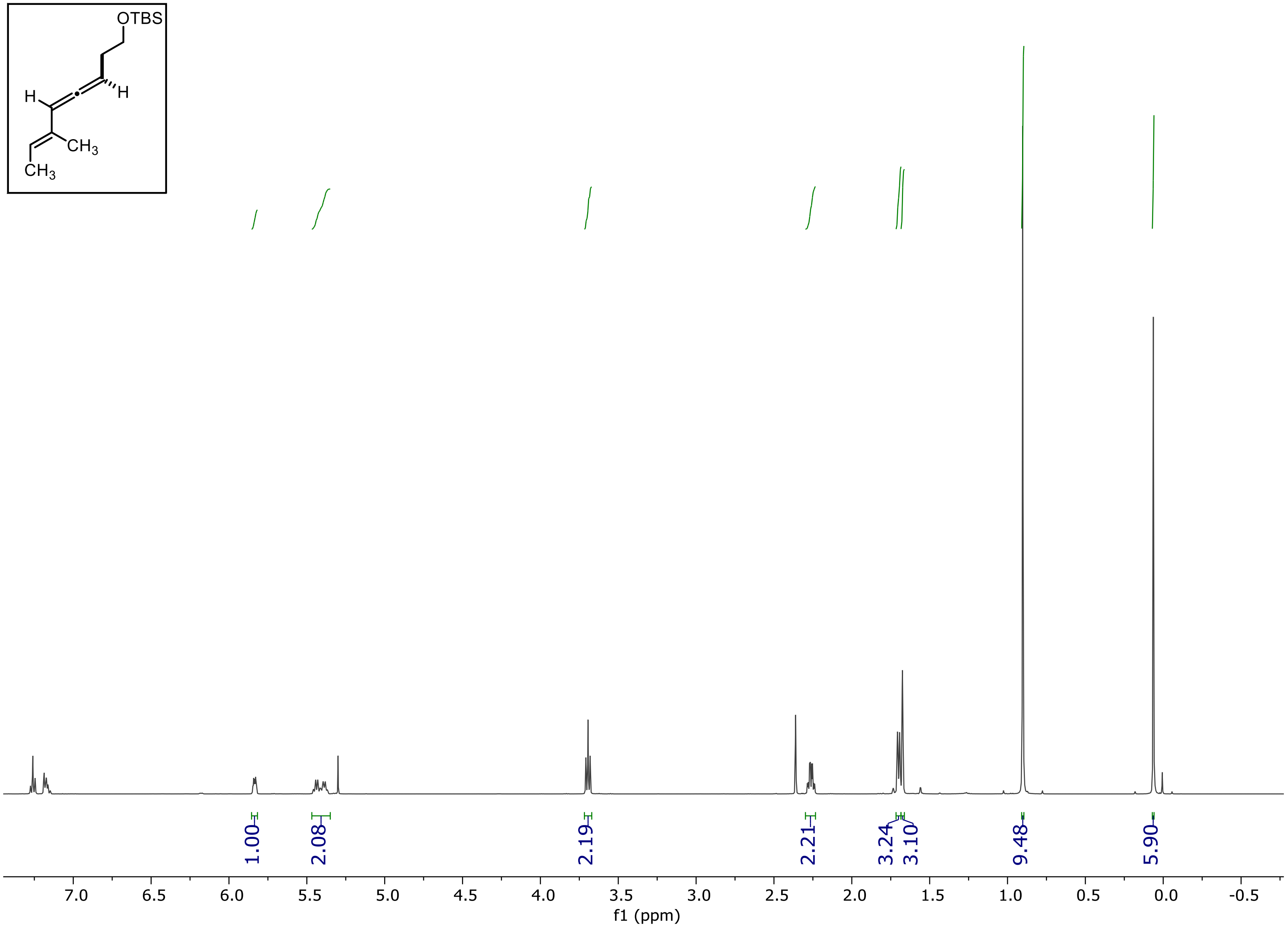




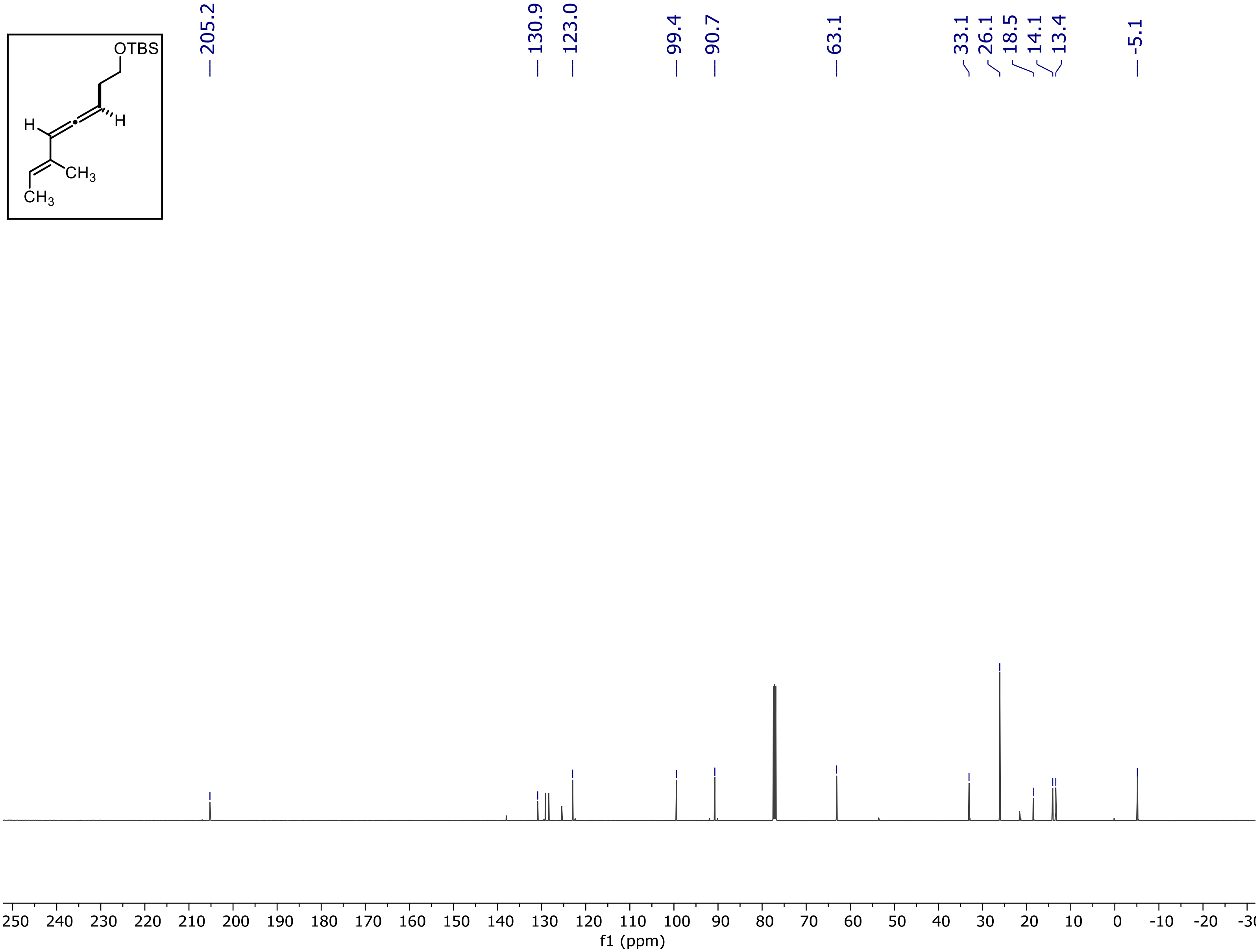
^{13}C NMR for Compound S-5.



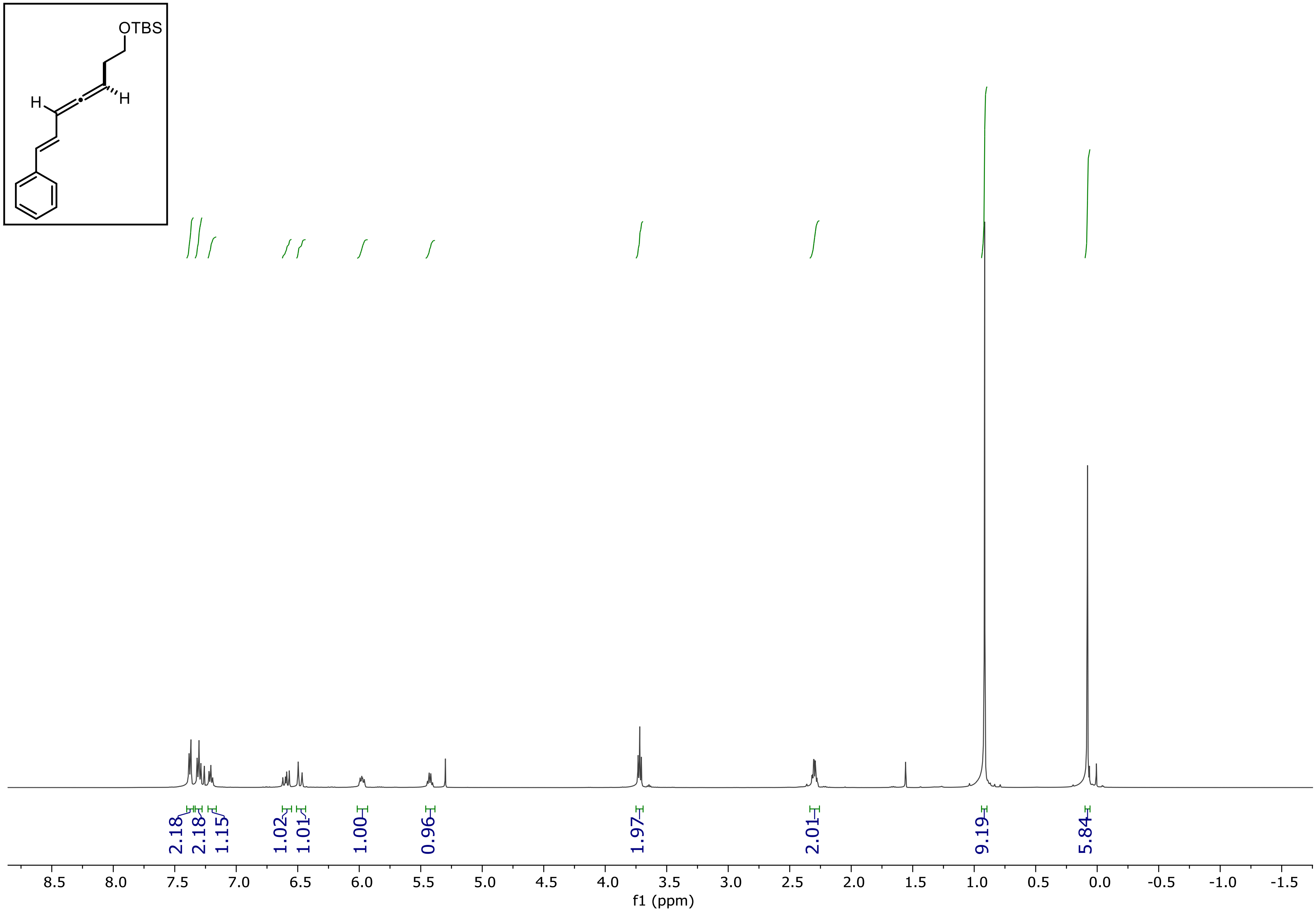
^{1}H NMR for Compound S-6.



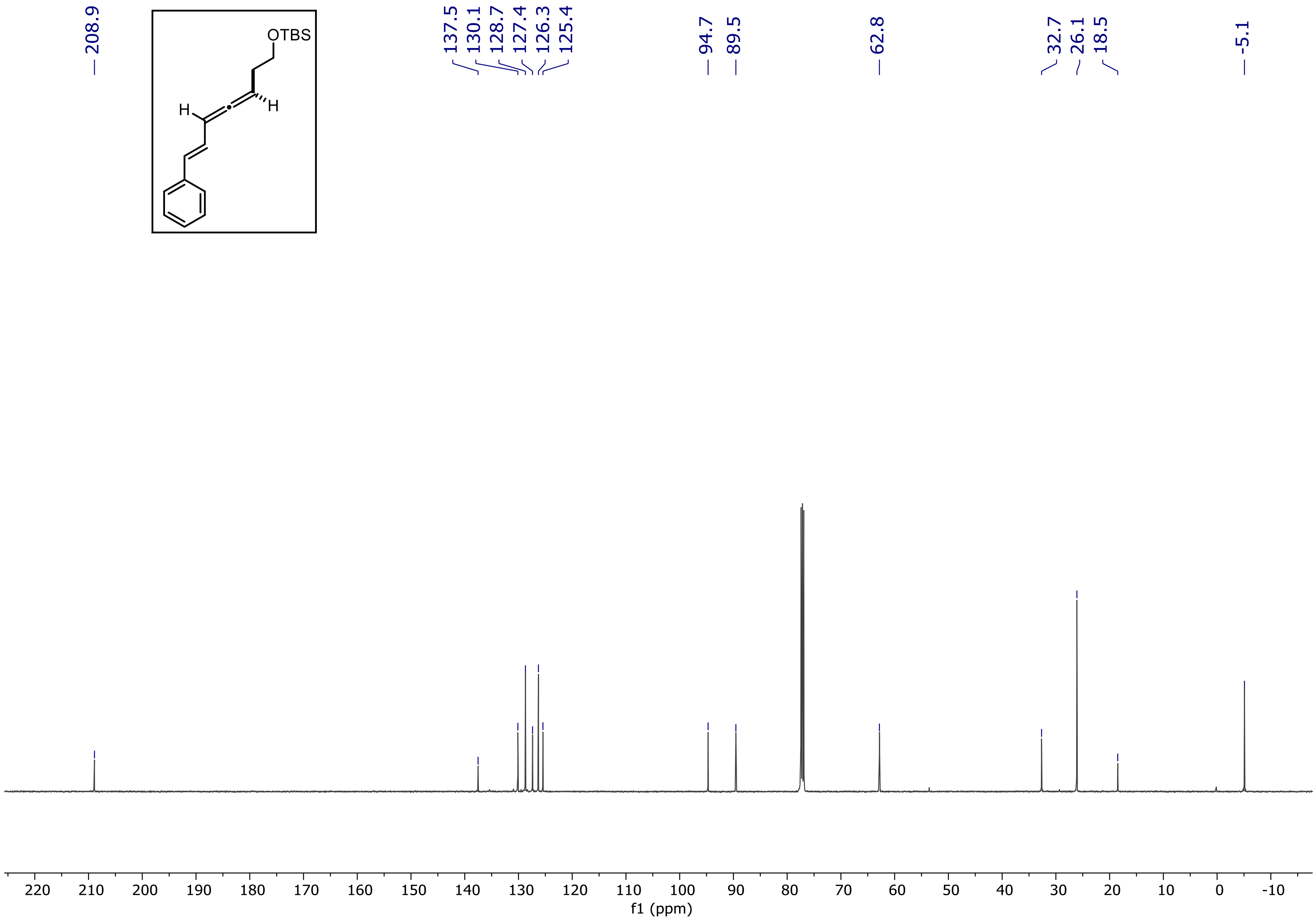
^{13}C NMR for Compound S-6.



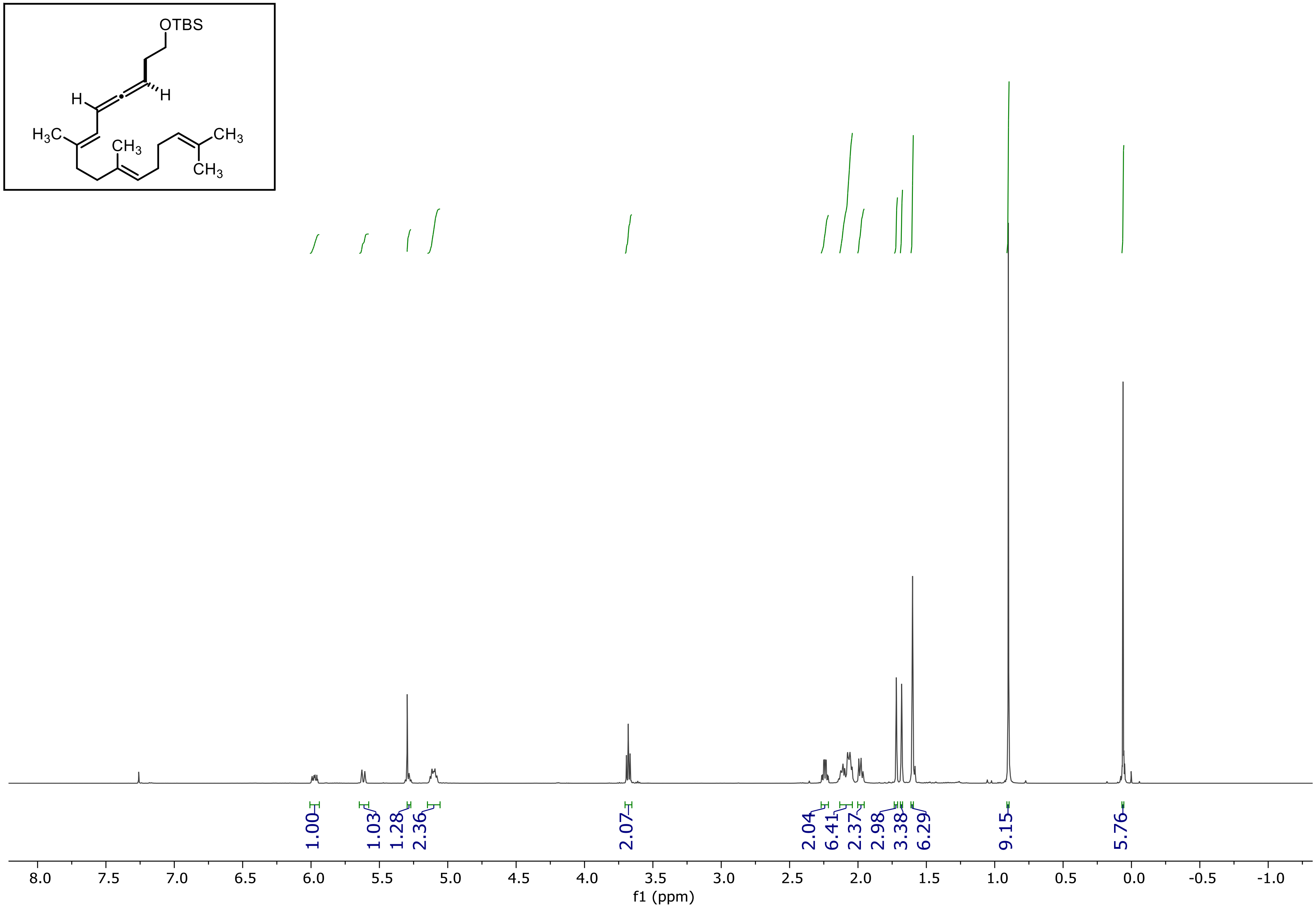
^{1}H NMR for Compound S-7.



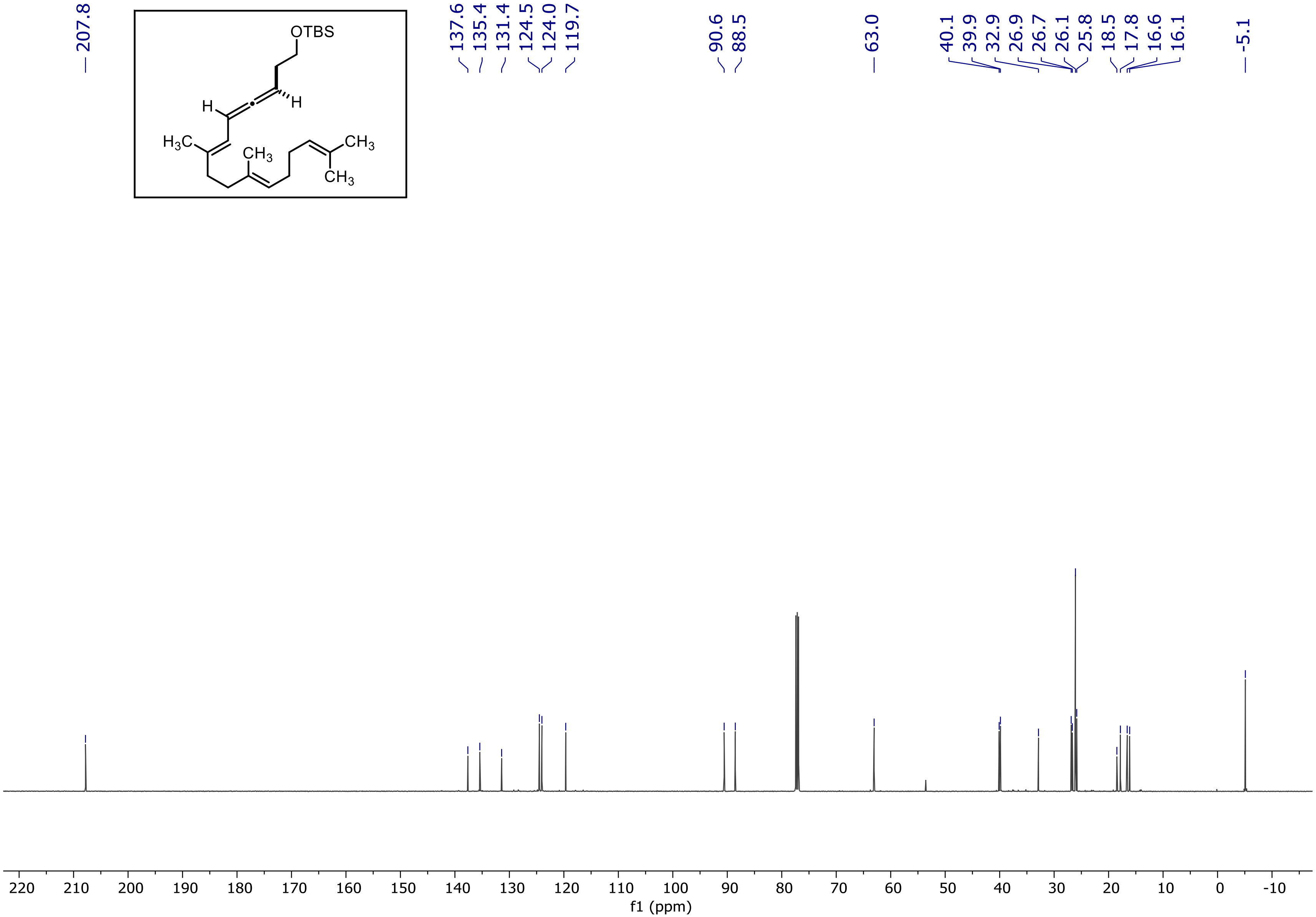
^{13}C NMR for Compound S-7.



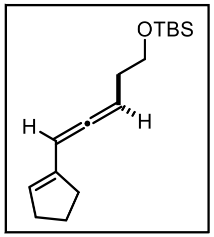
^{1}H NMR for Compound S-8.

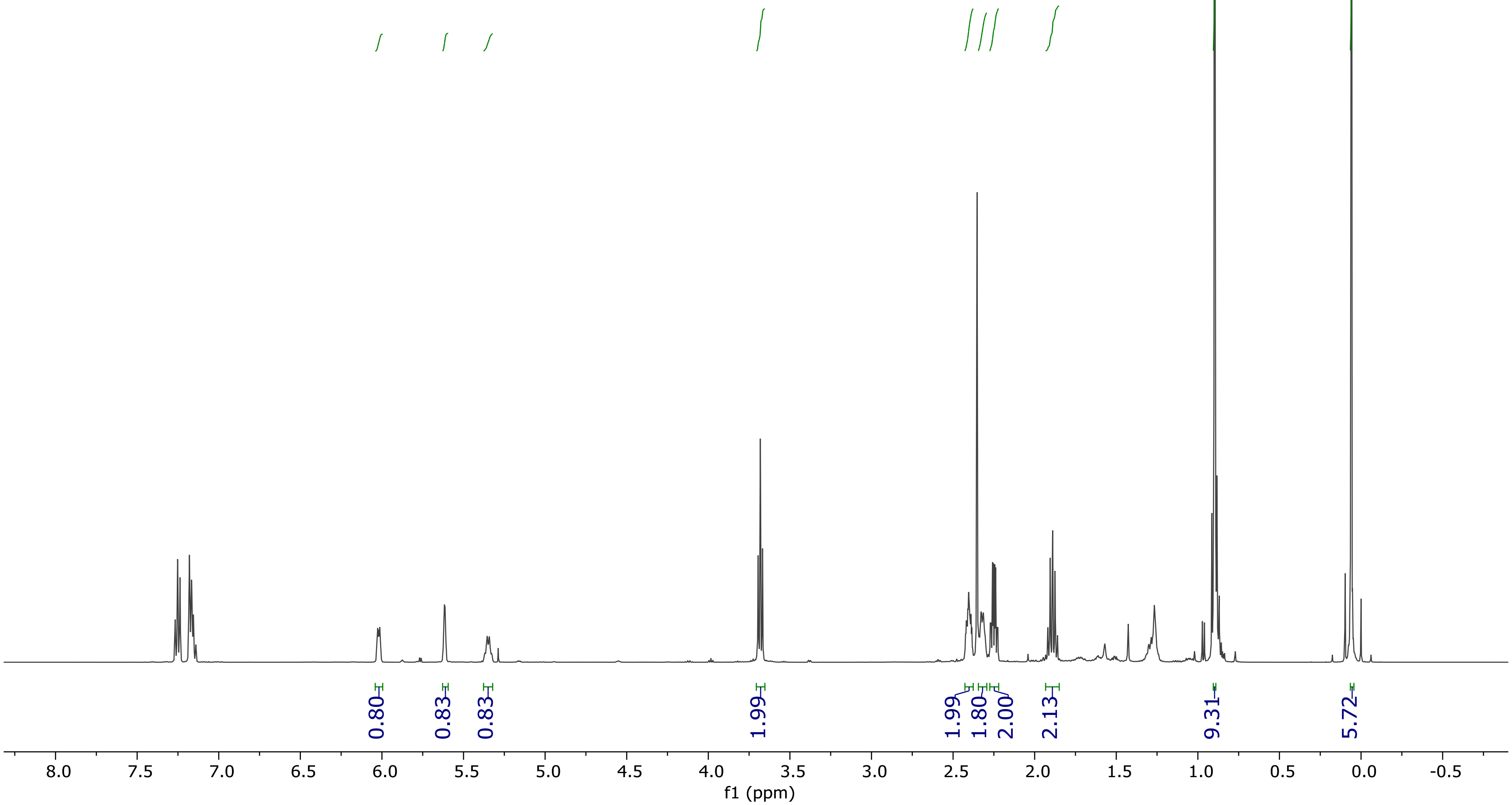


^{13}C NMR for Compound S-8.

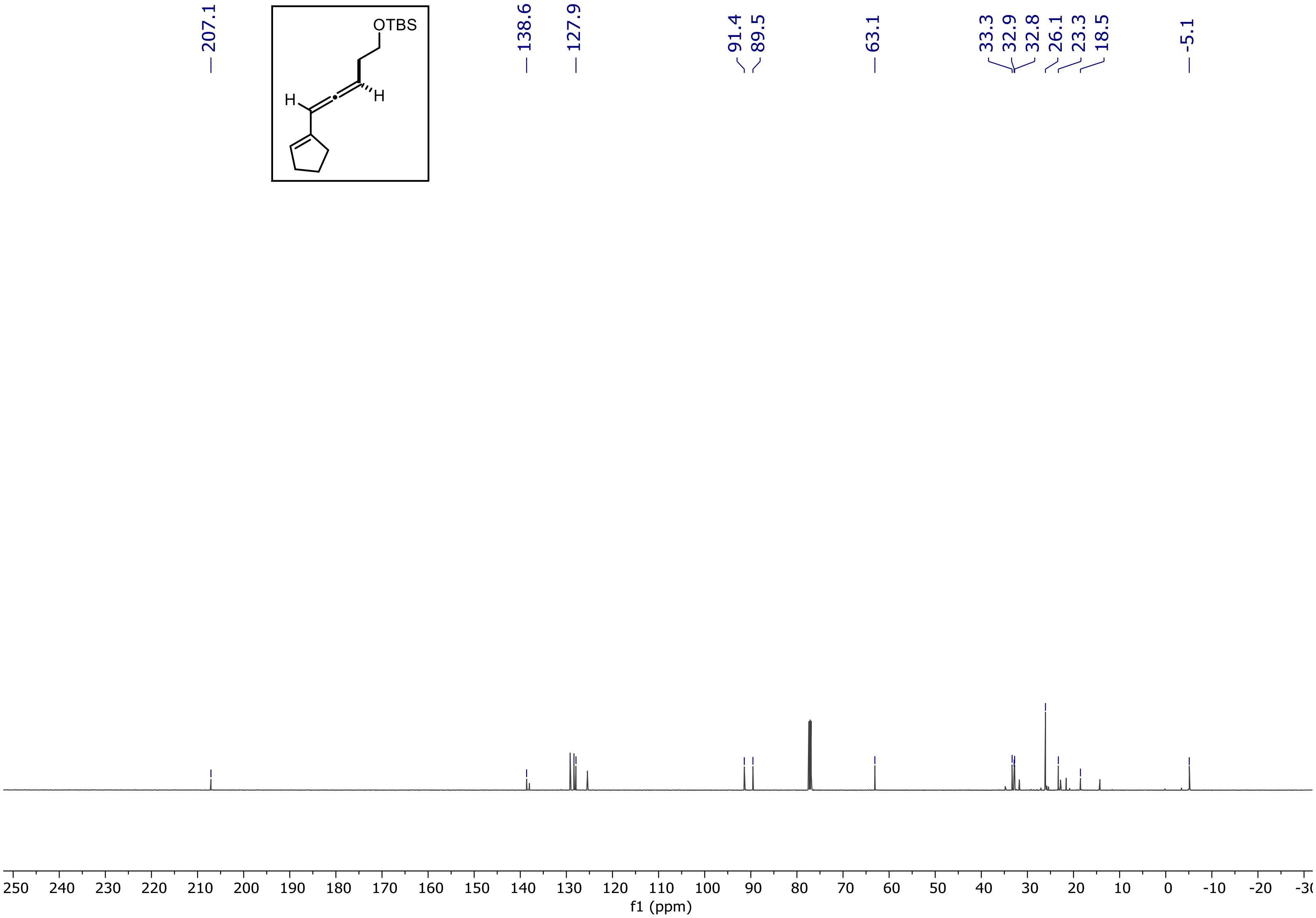


^{1}H NMR for Compound S-9.

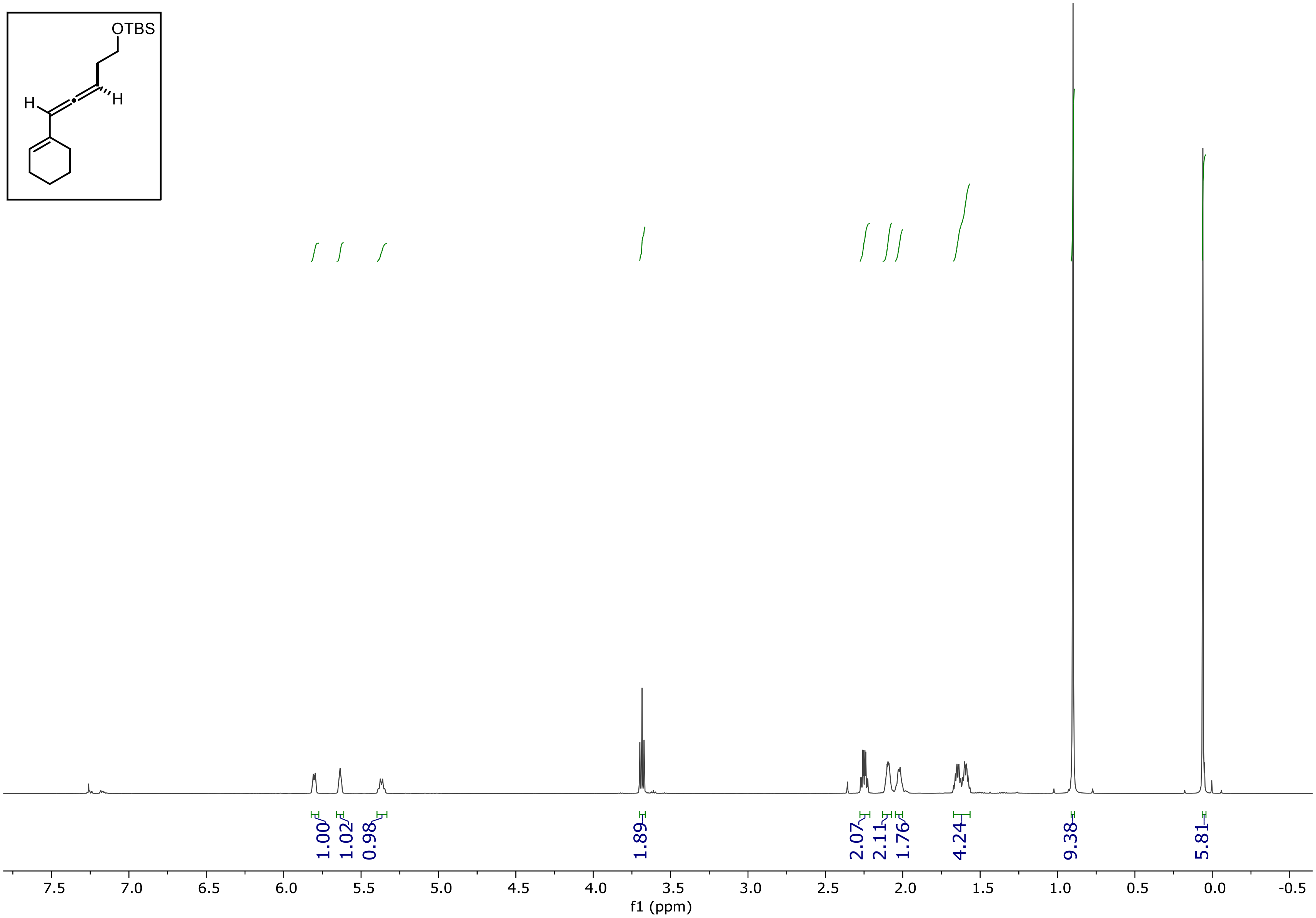




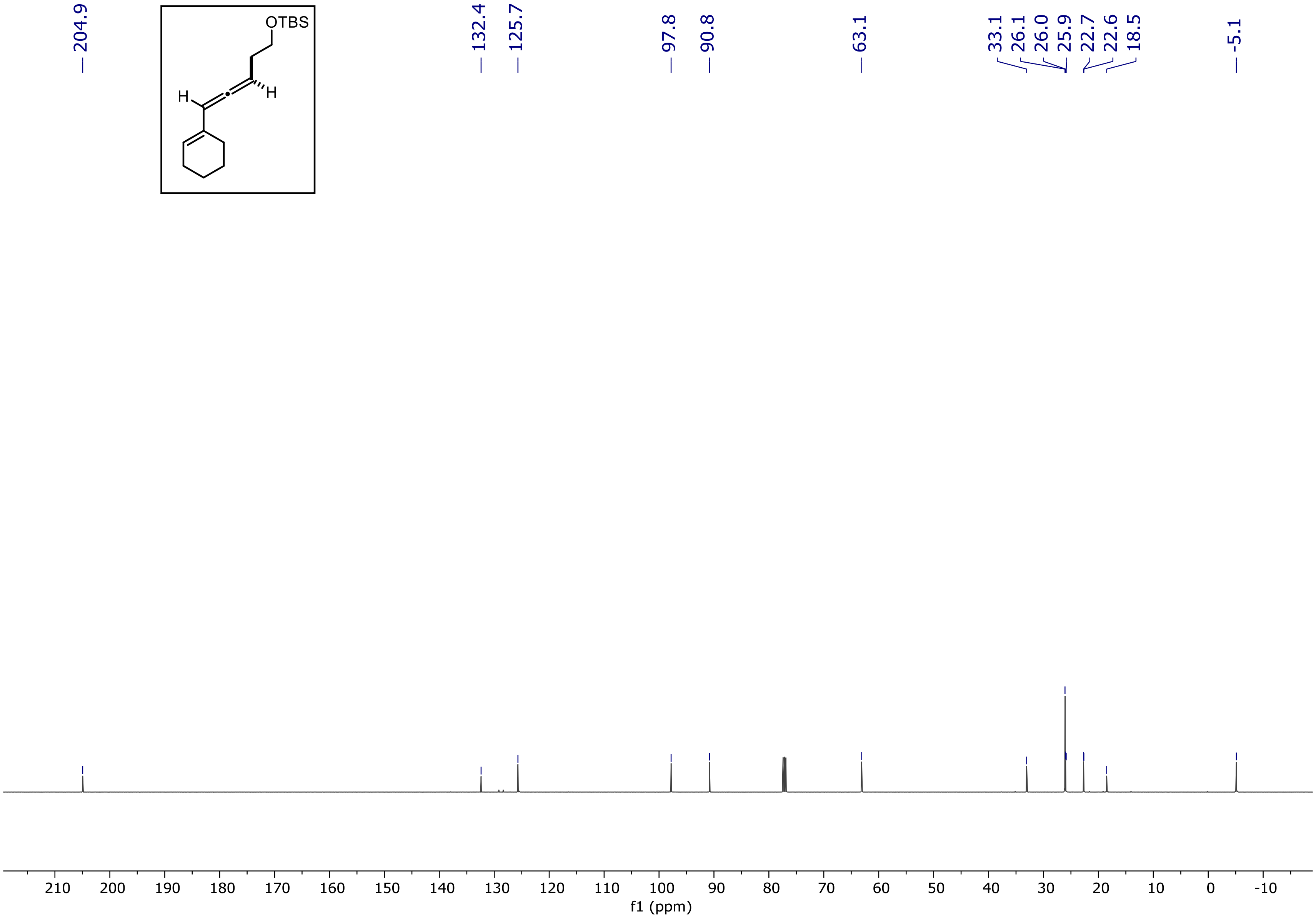
^{13}C NMR for Compound S-9.



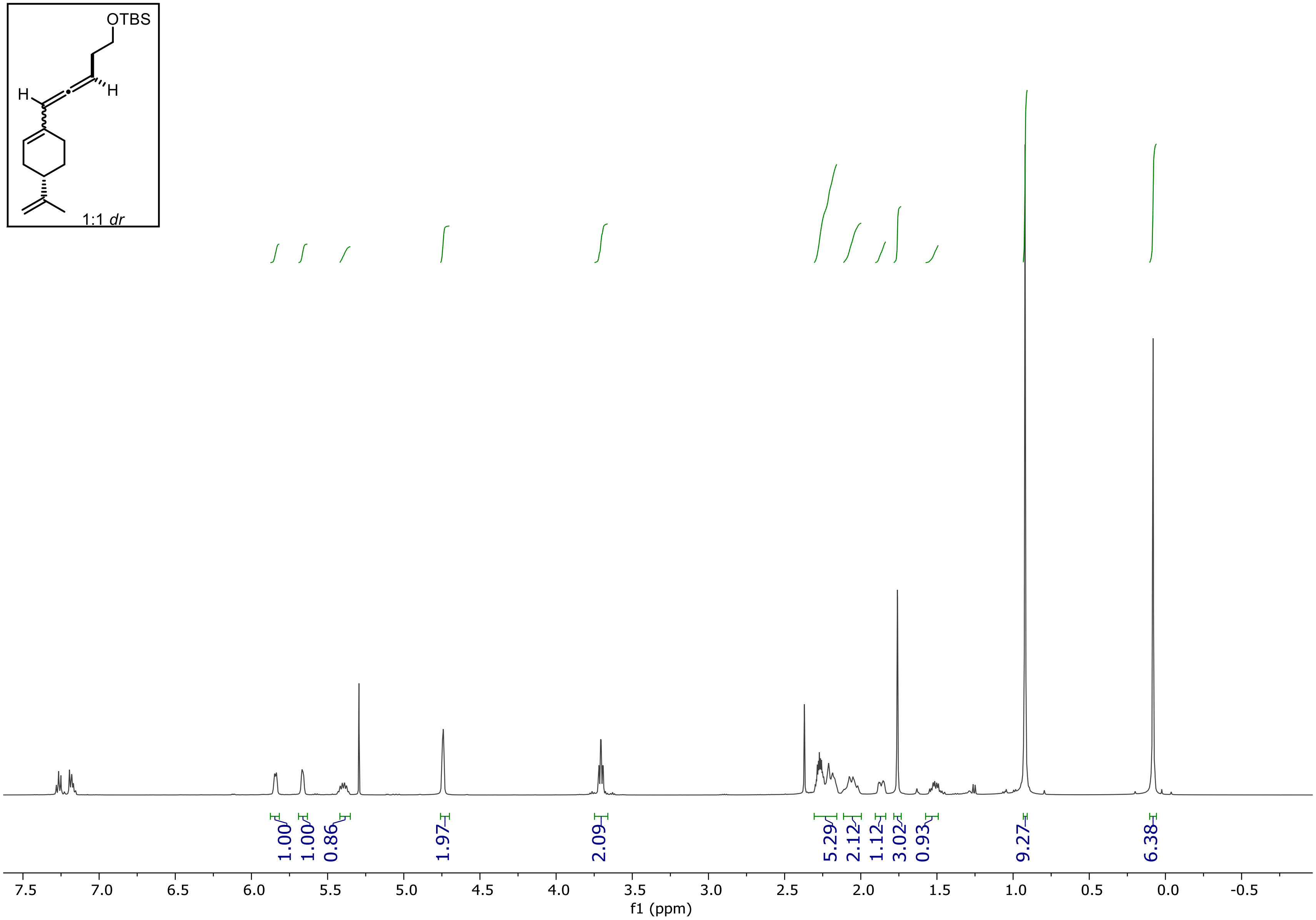
^{1}H NMR for Compound S-10.



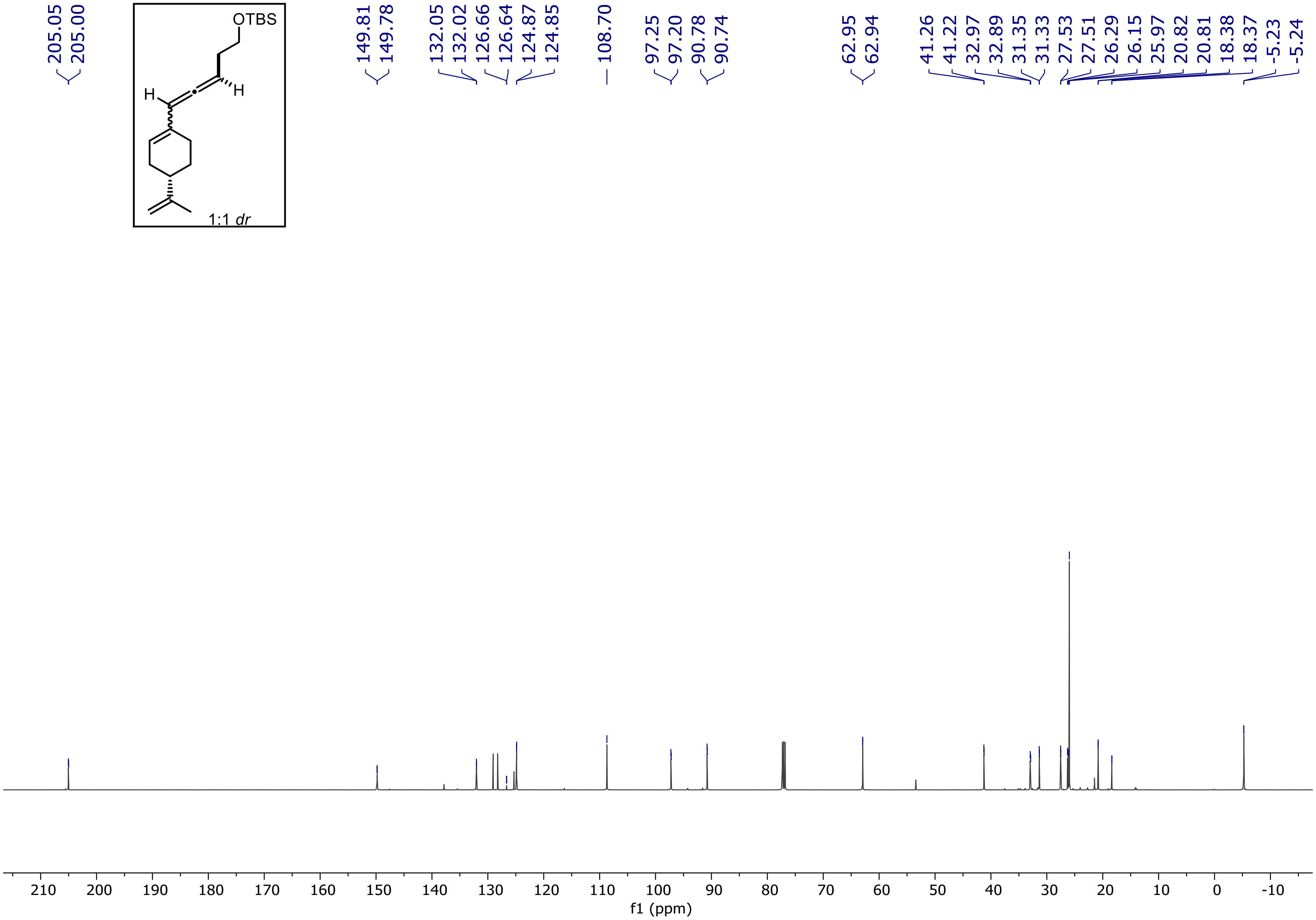
^{13}C NMR for Compound S-10.



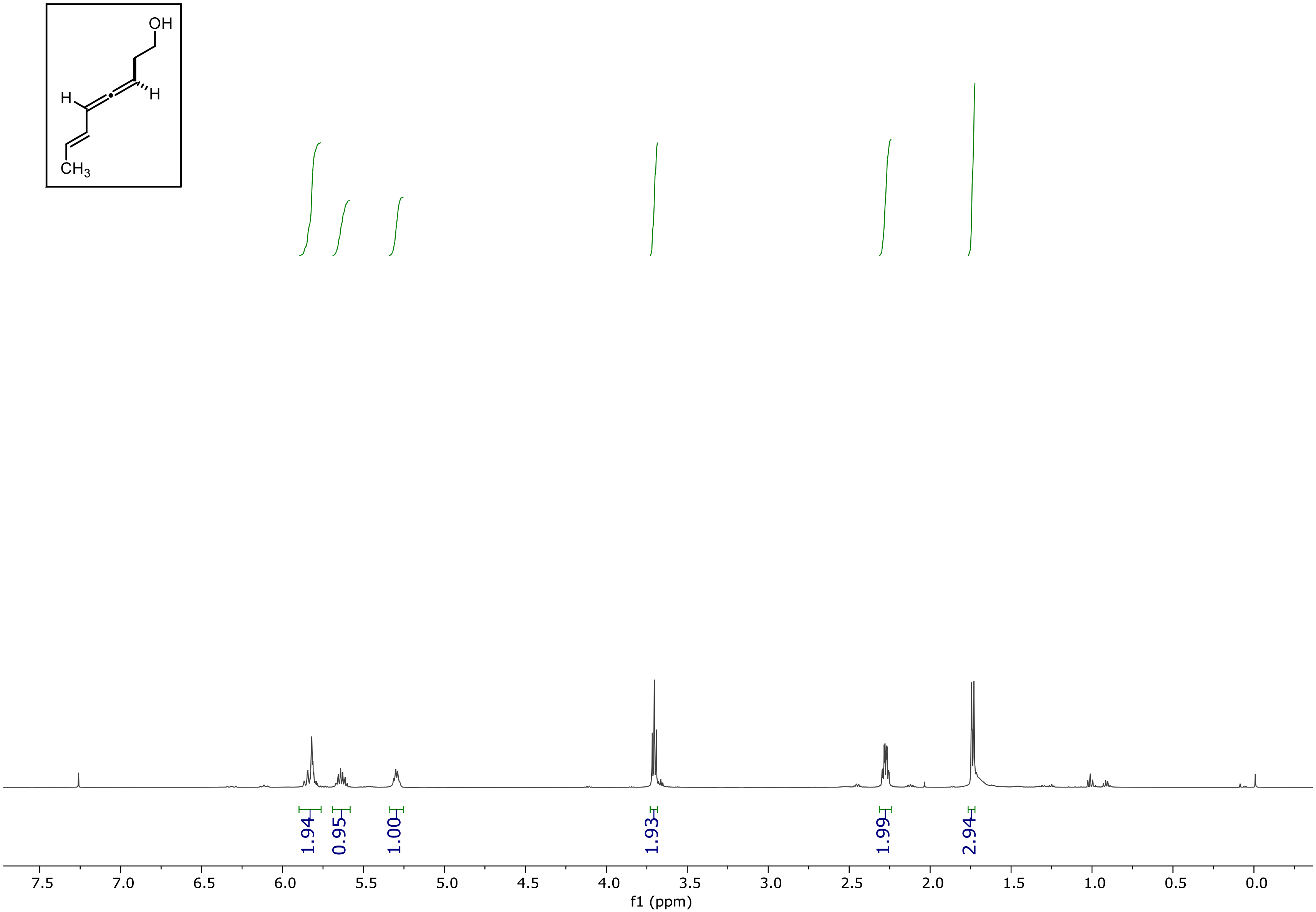
^{1}H NMR for Compound S-11.



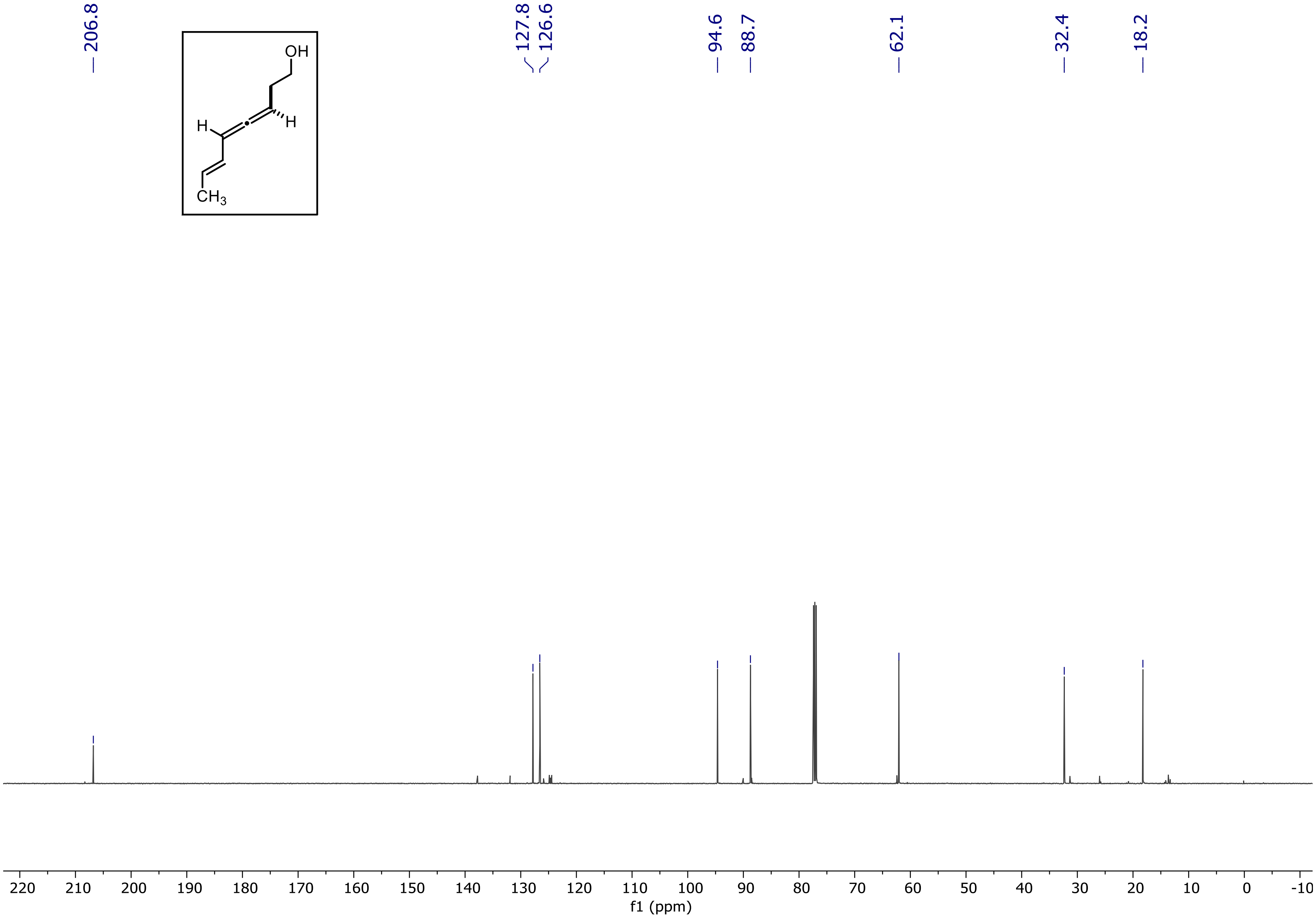
^{13}C NMR for Compound S-11.



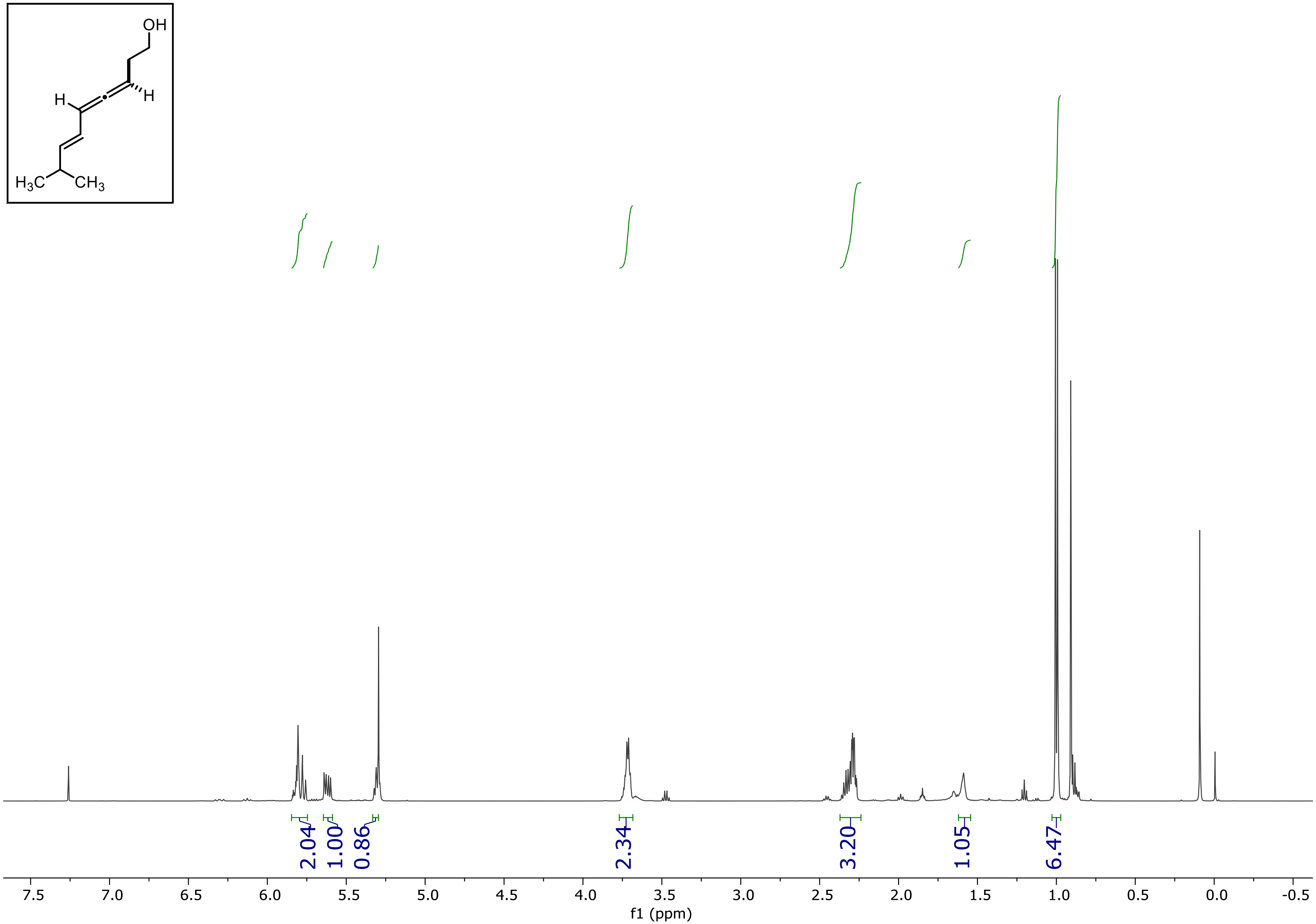
^{1}H NMR for Compound S-12.



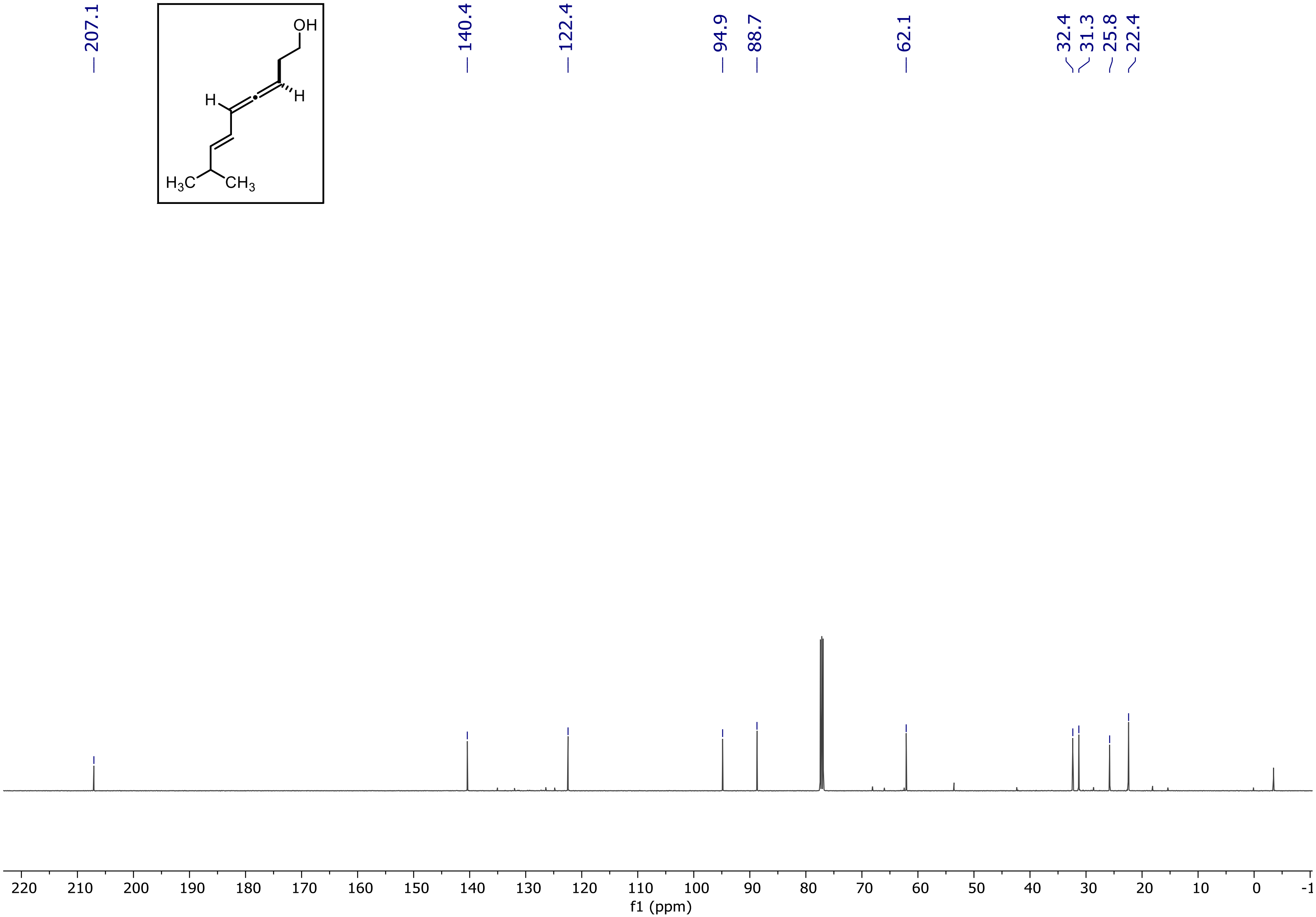
^{13}C NMR for Compound S-12.



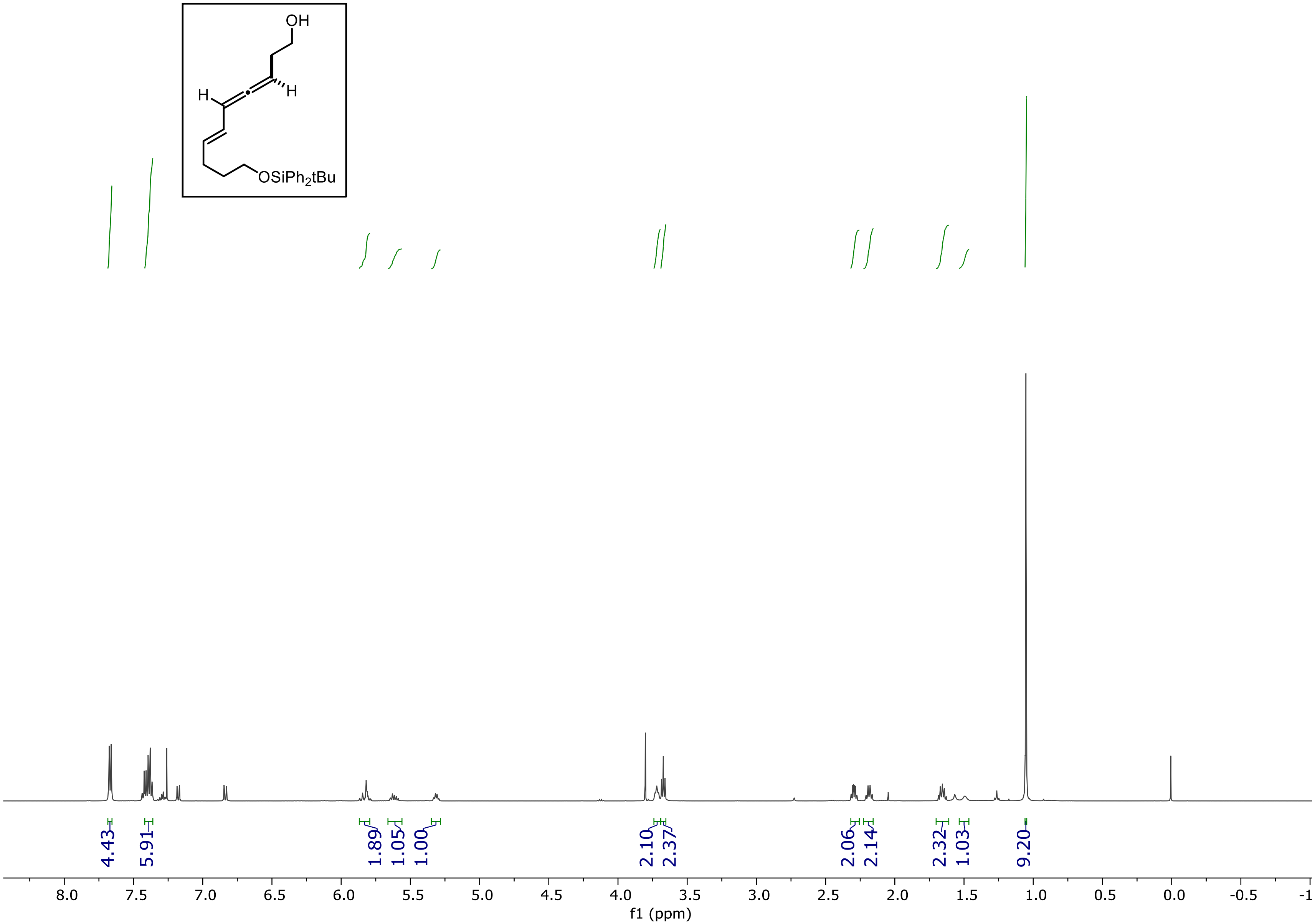
^{1}H NMR for Compound S-13.



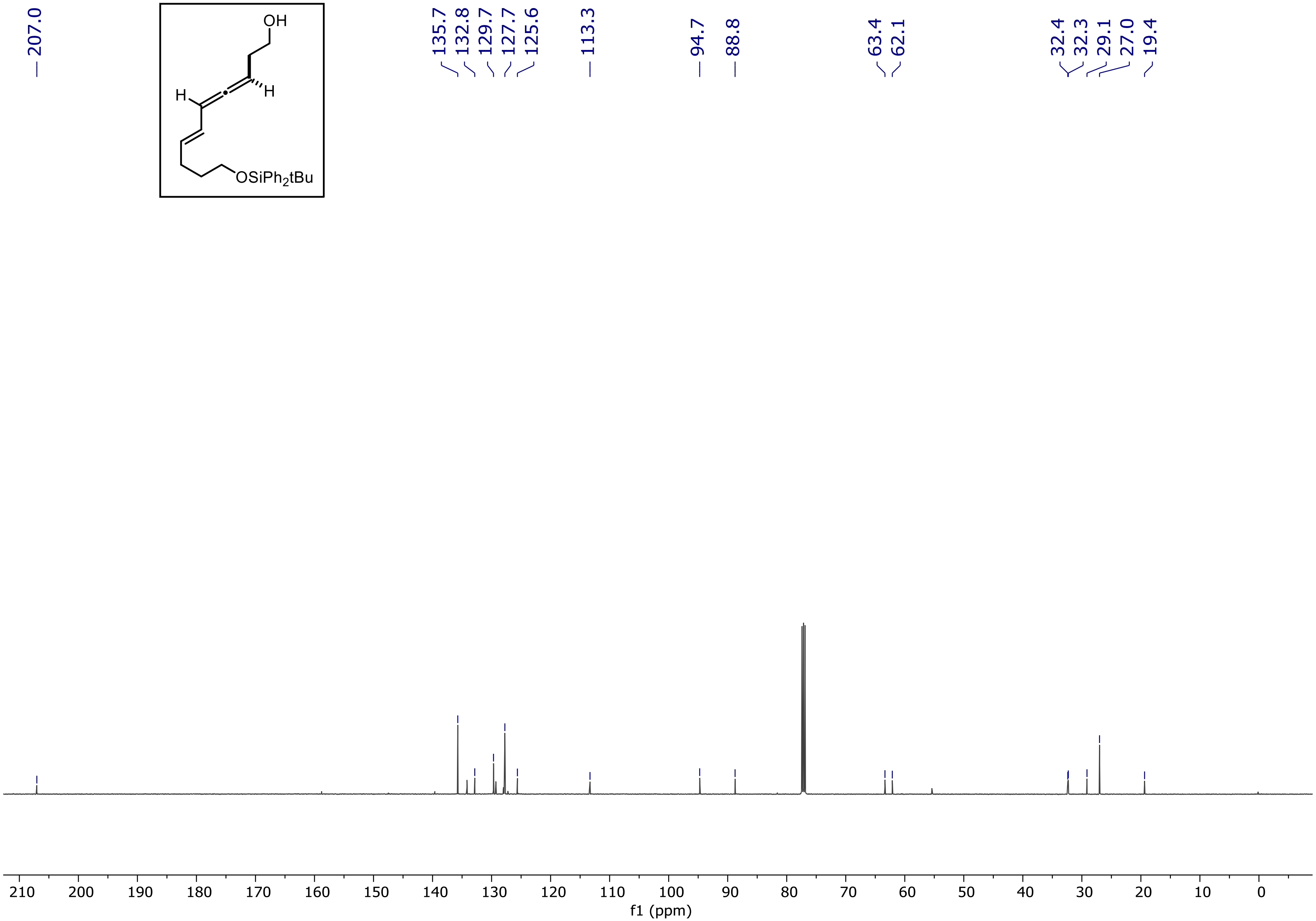
^{13}C NMR for Compound S-13.



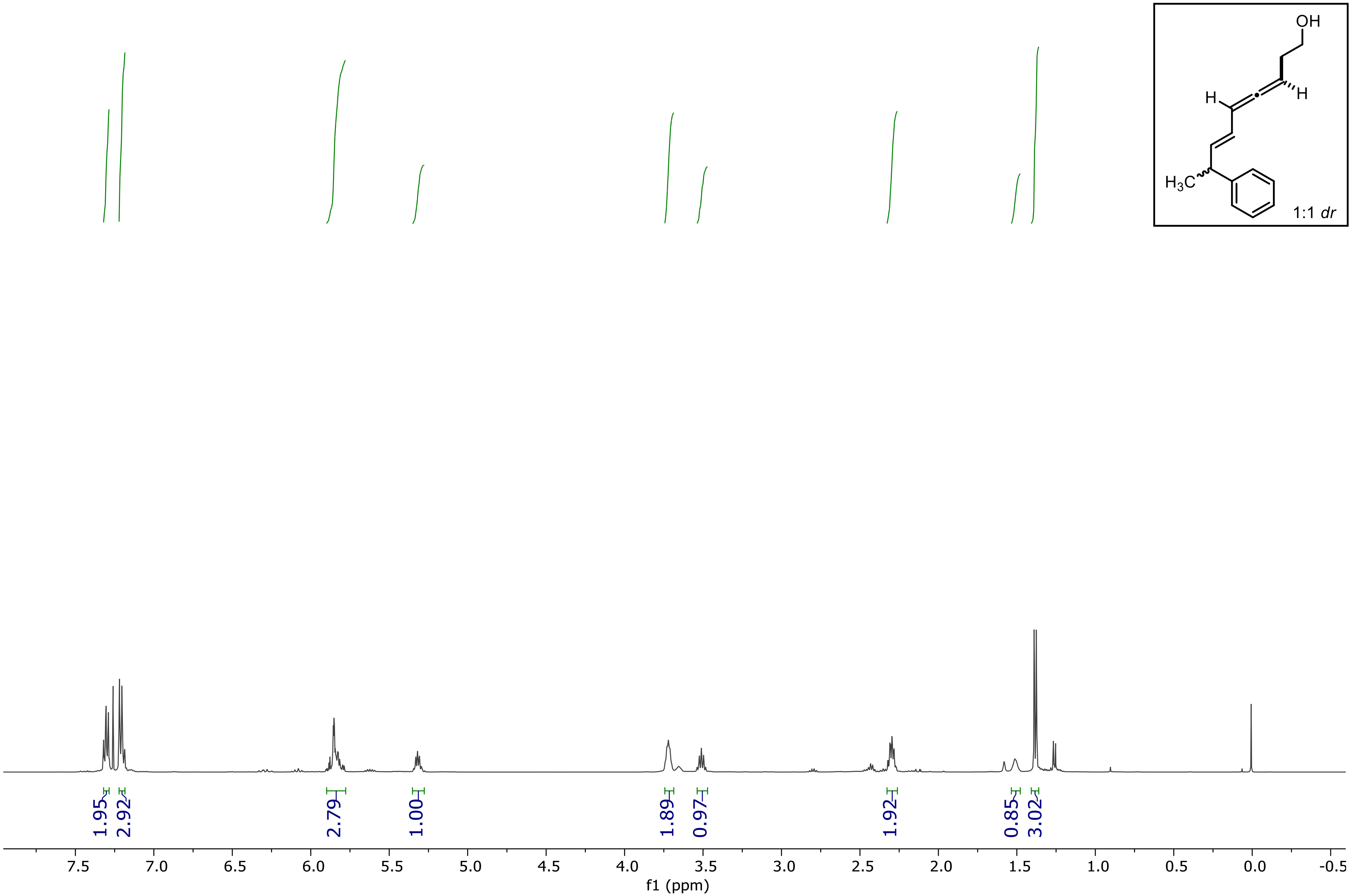
^{1}H NMR for Compound S-14.



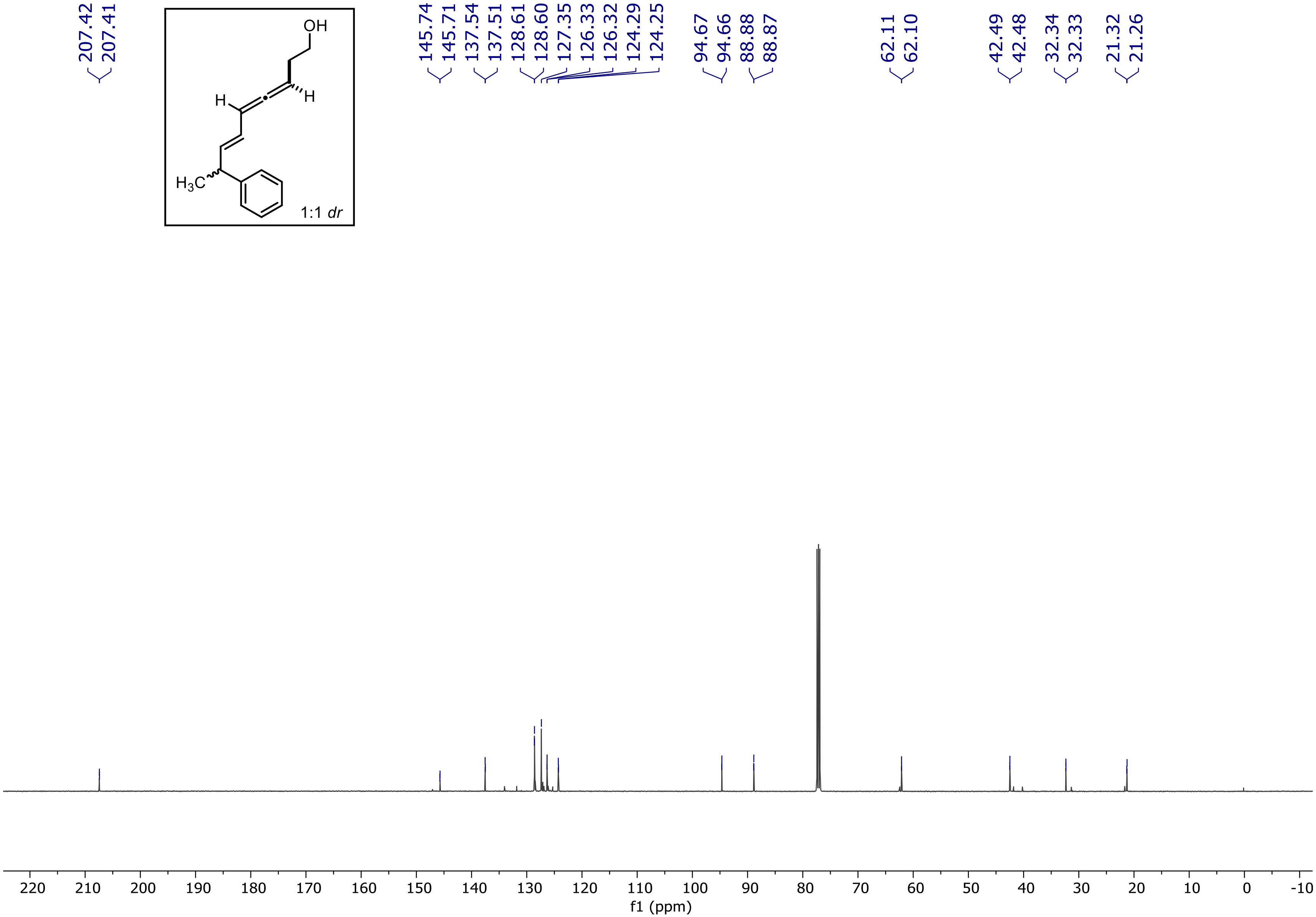
^{13}C NMR for Compound S-14.



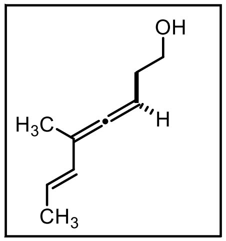
^{1}H NMR for Compound S-15.

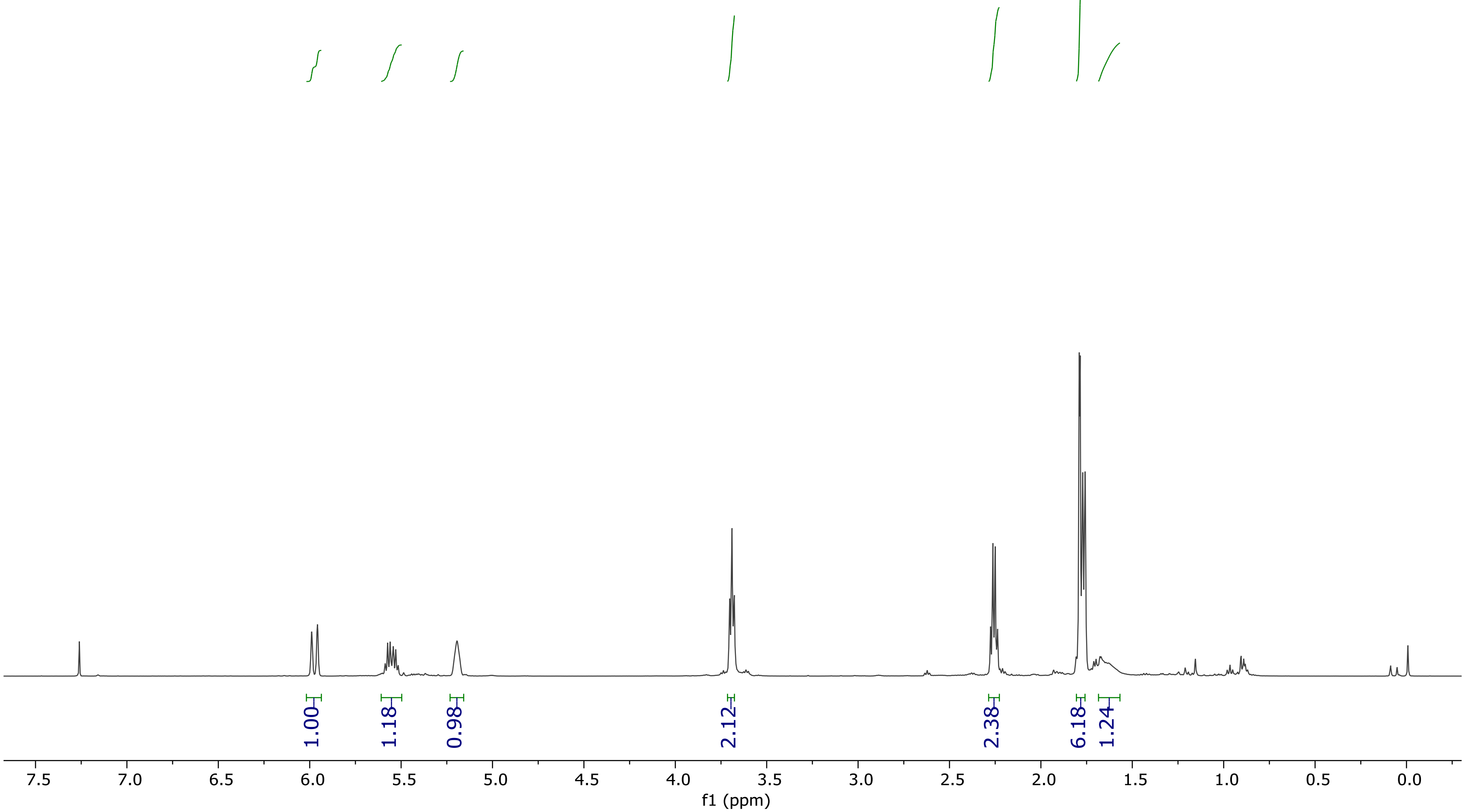


^{13}C NMR for Compound S-15.

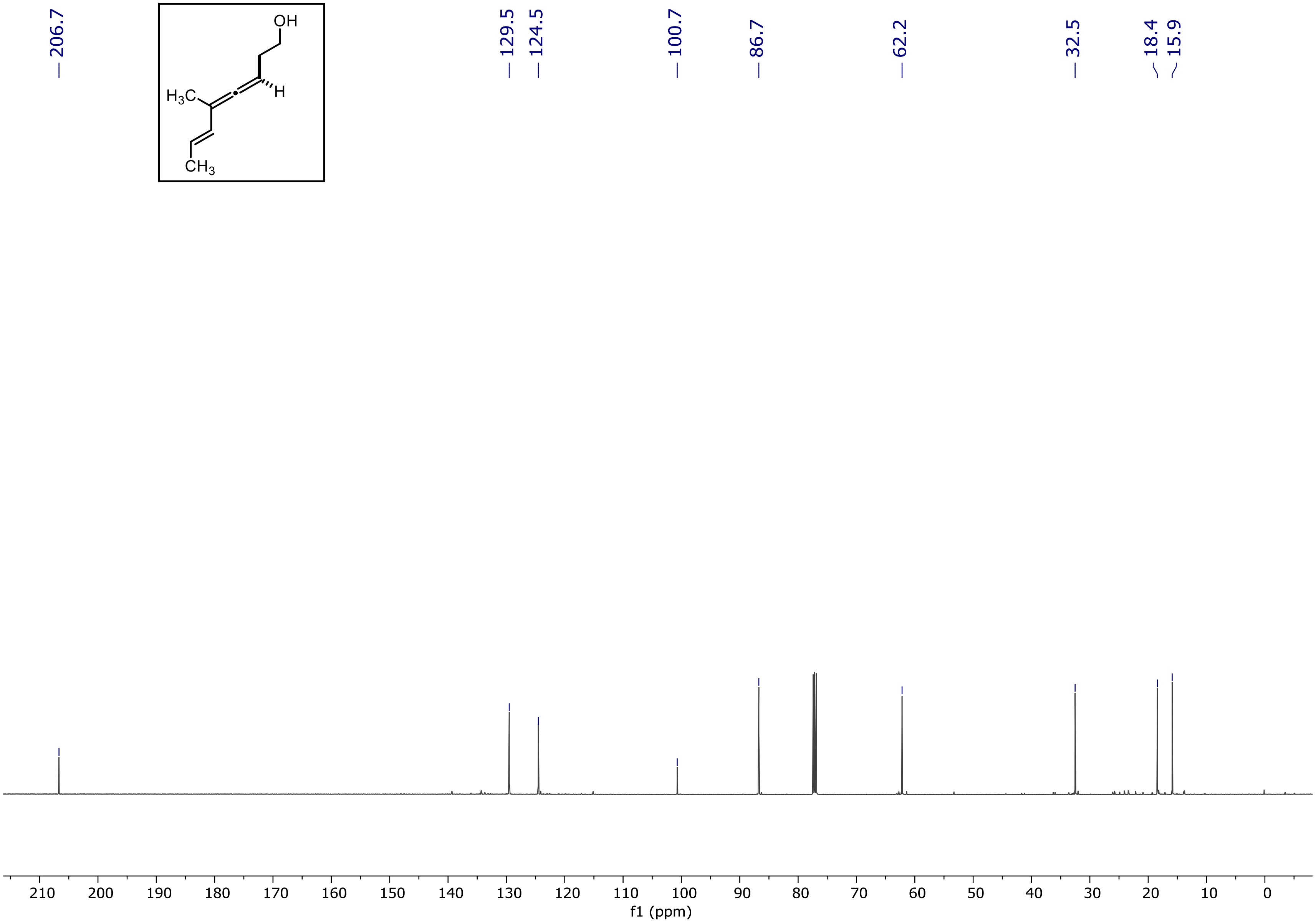


^{1}H NMR for Compound S-16.

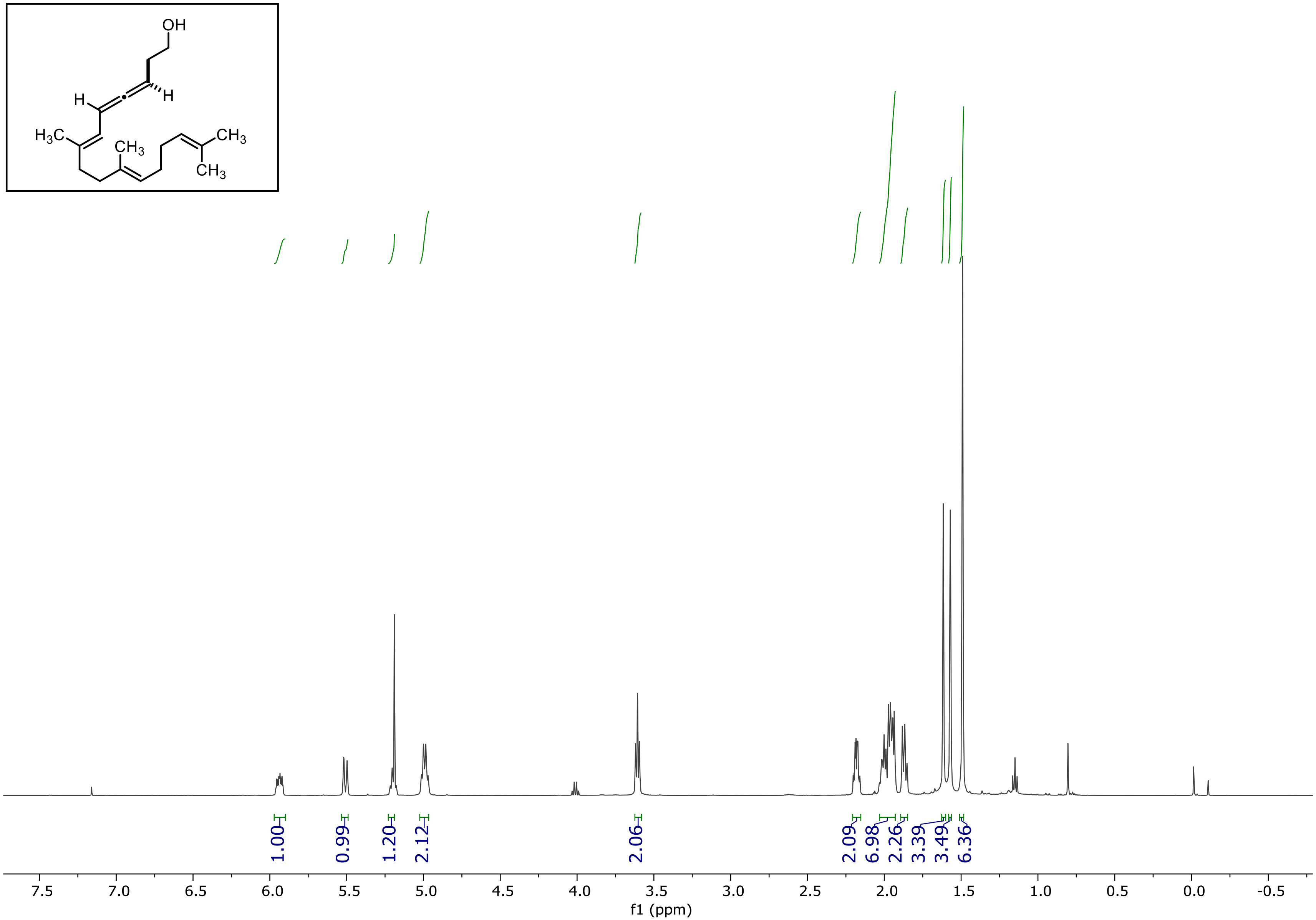




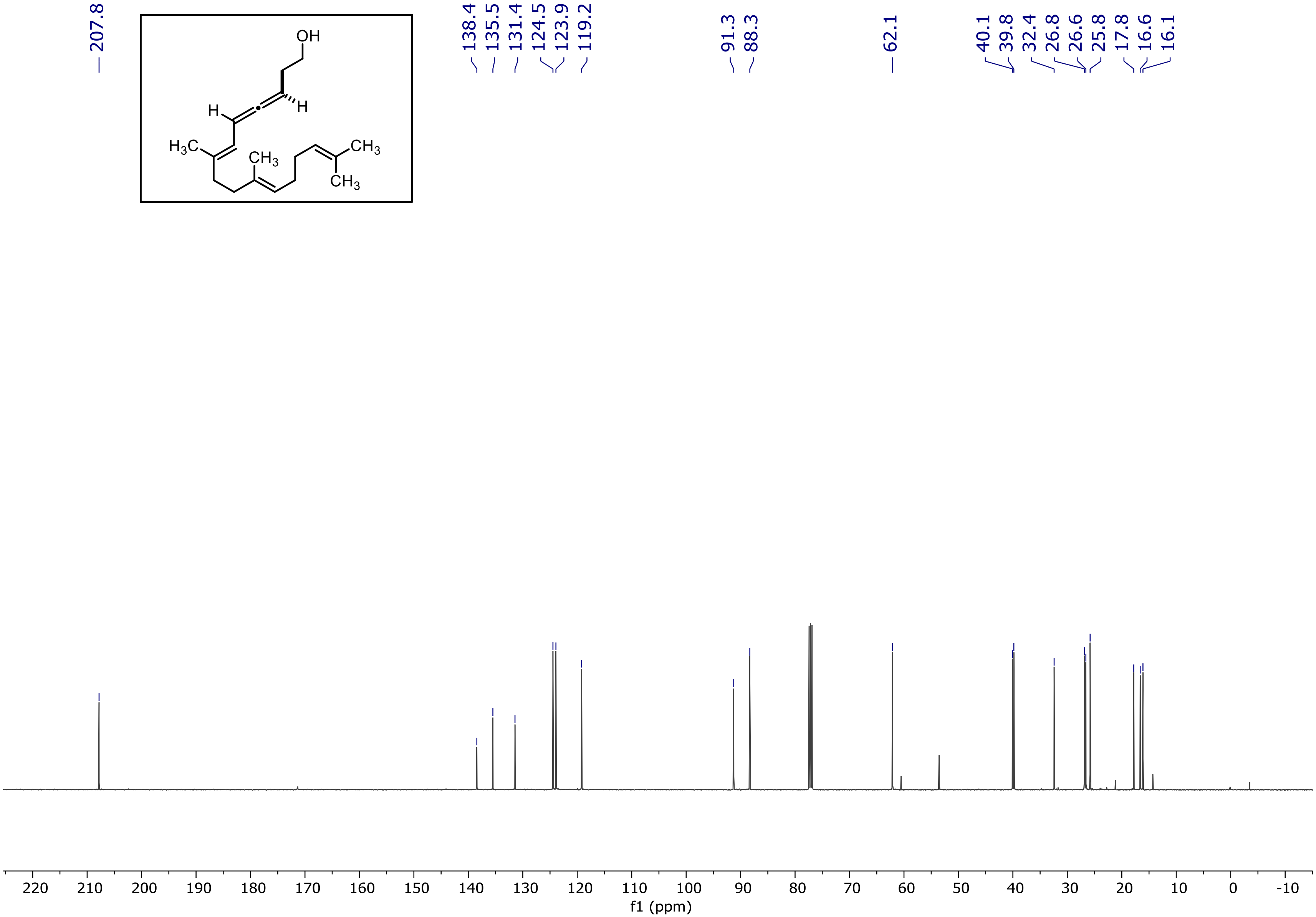
^{13}C NMR for Compound S-16.



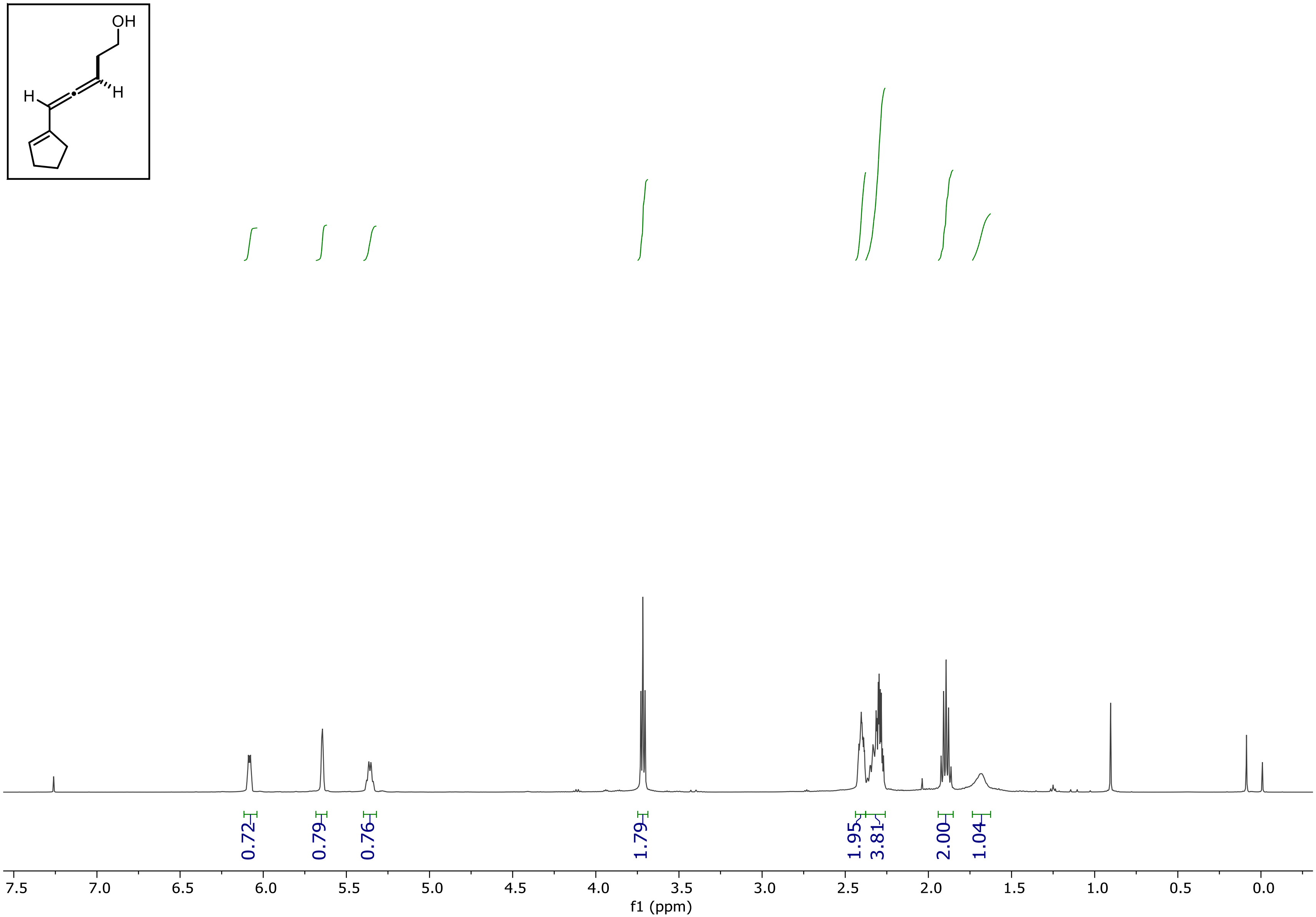
^{1}H NMR for Compound S-17.



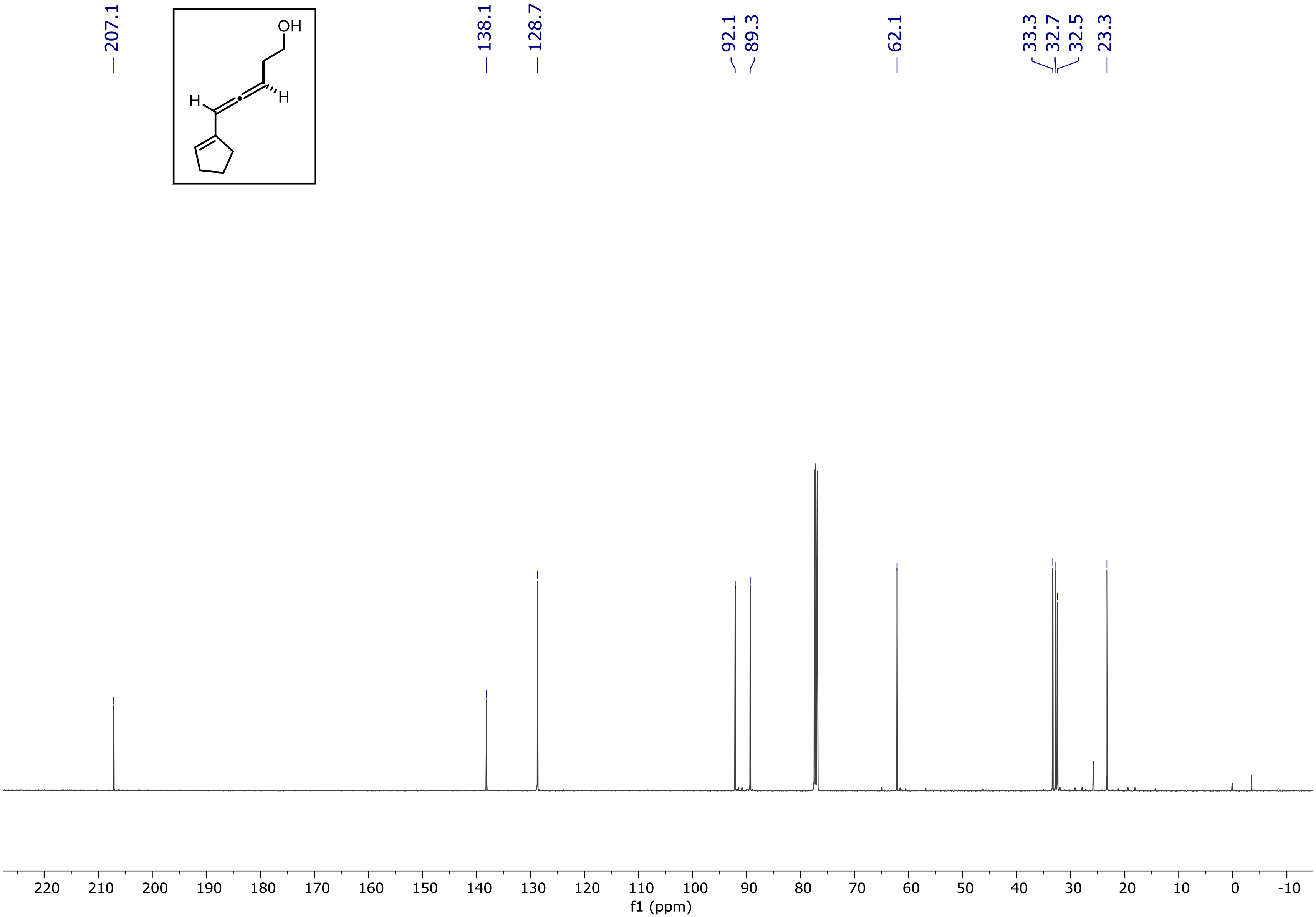
^{13}C NMR for Compound S-17.



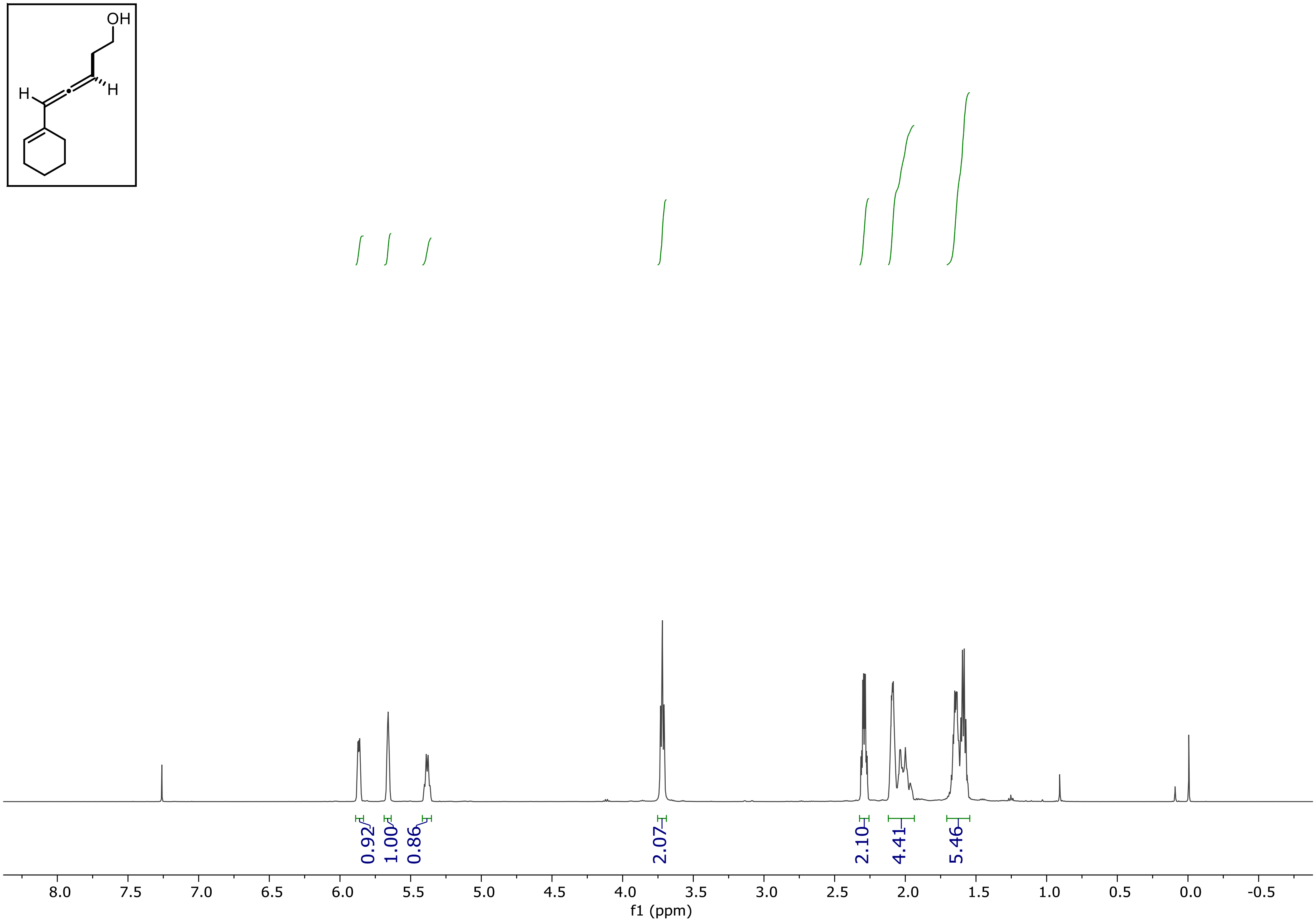
^{1}H NMR for Compound S-18.



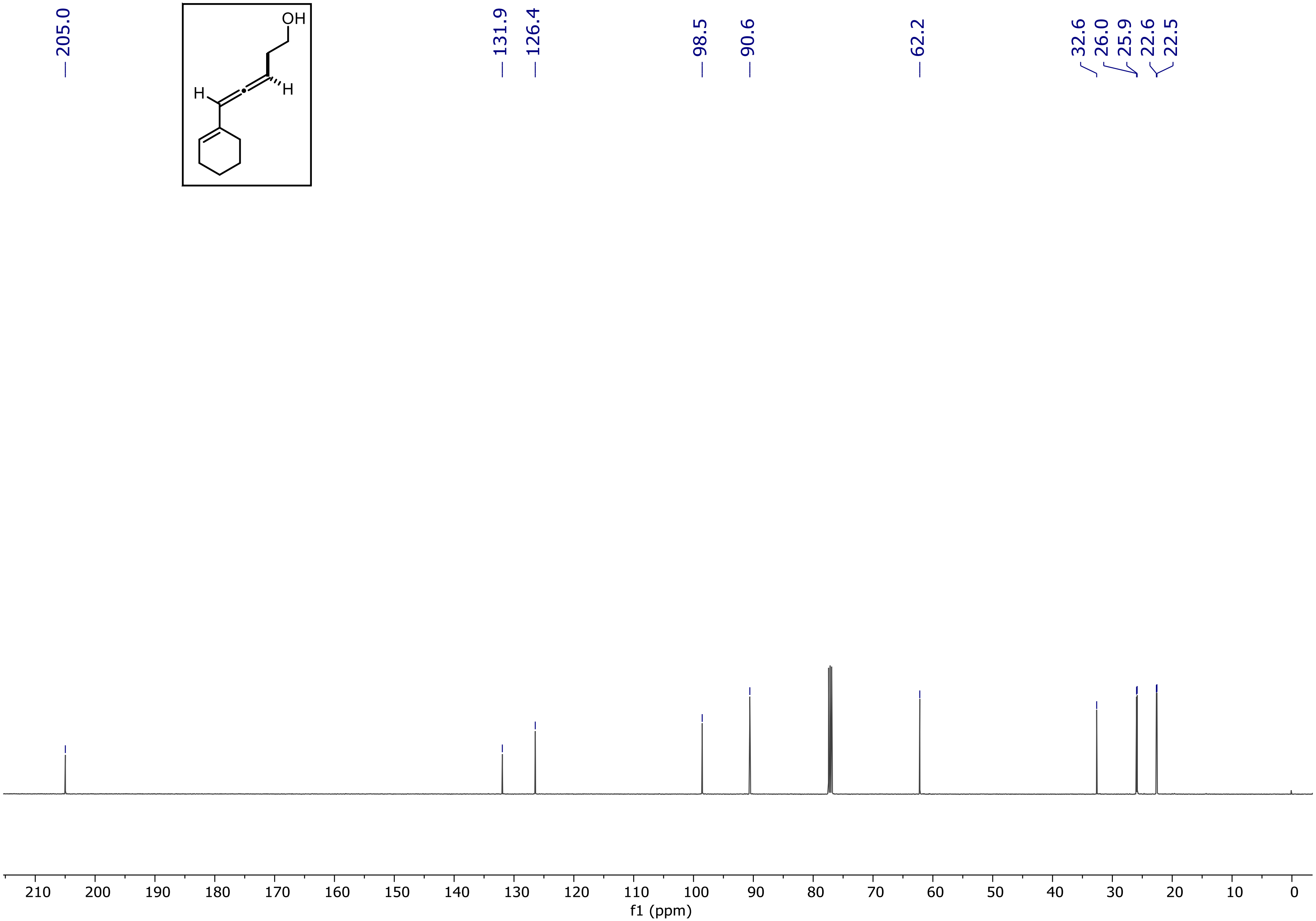
^{13}C NMR for Compound S-18.



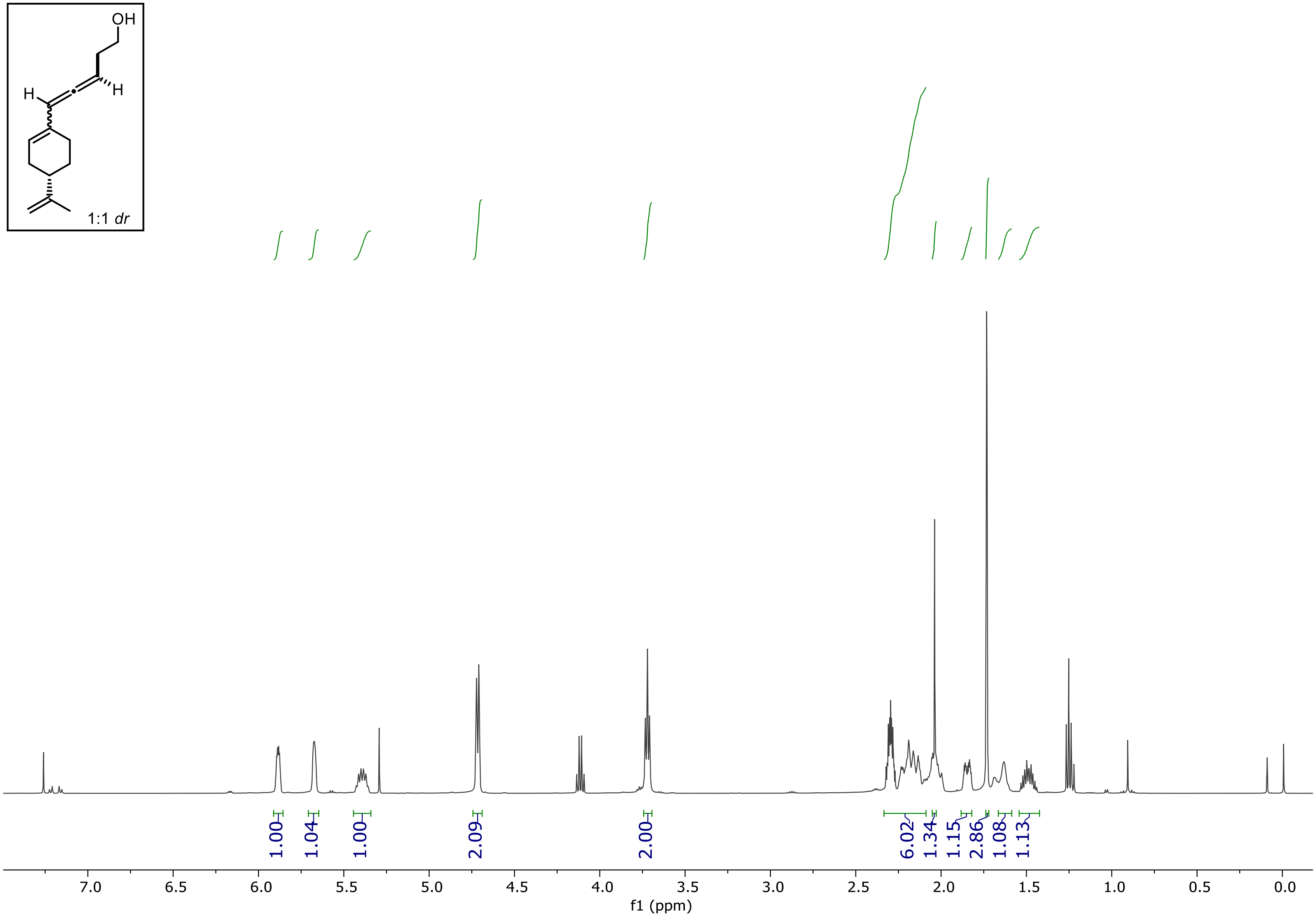
^{1}H NMR for Compound S-19.



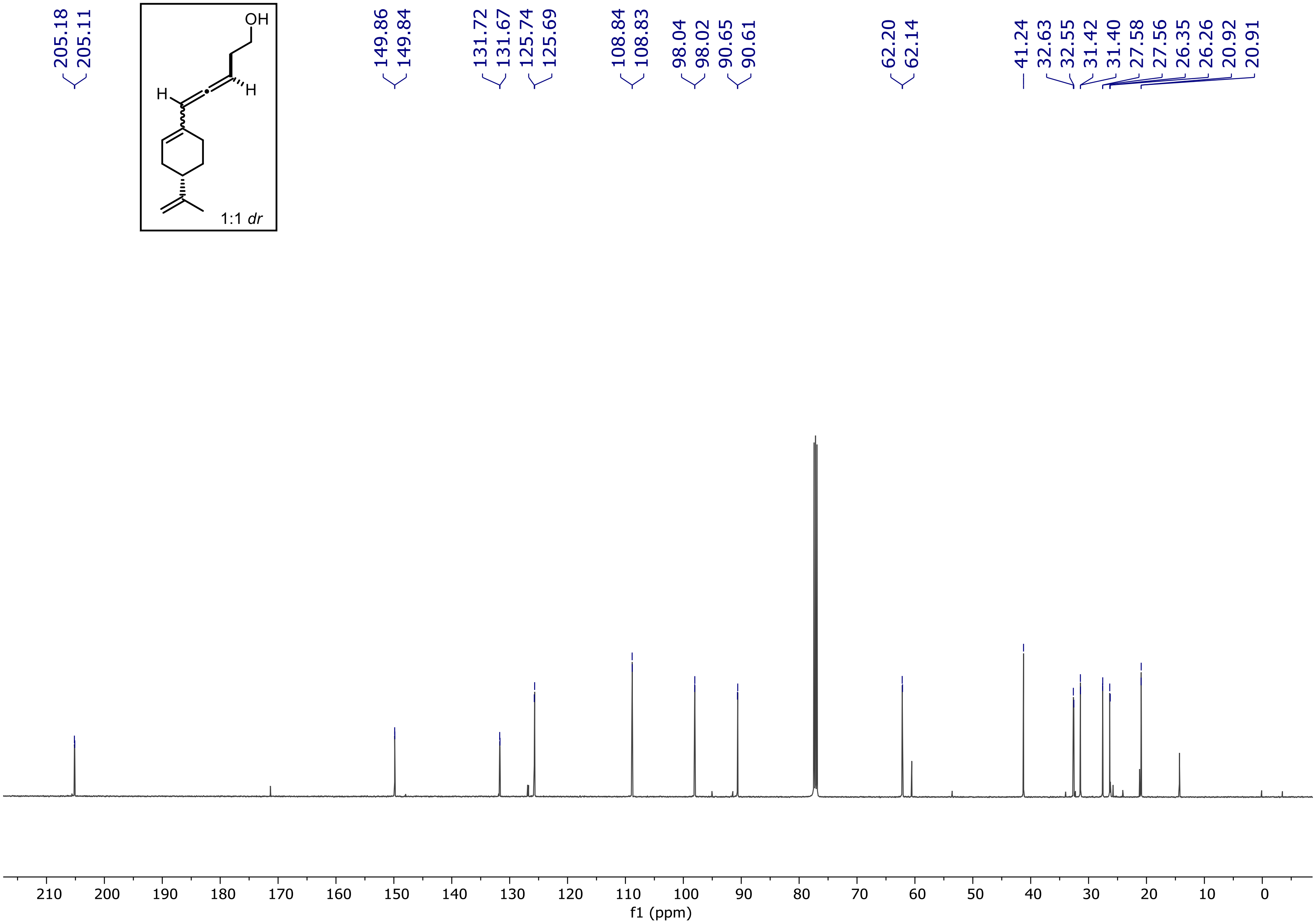
^{13}C NMR for Compound S-19.



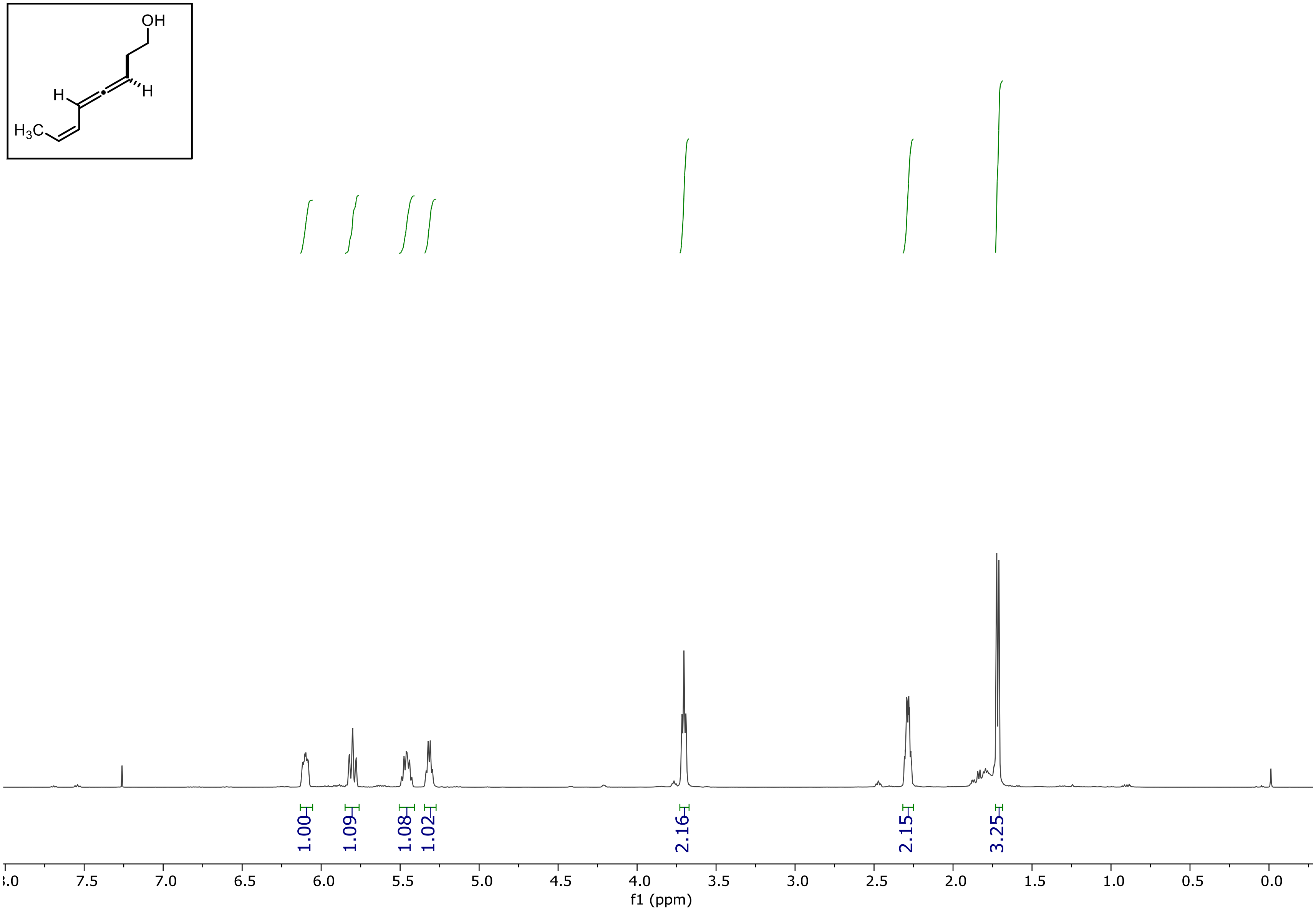
^{1}H NMR for Compound S-20.



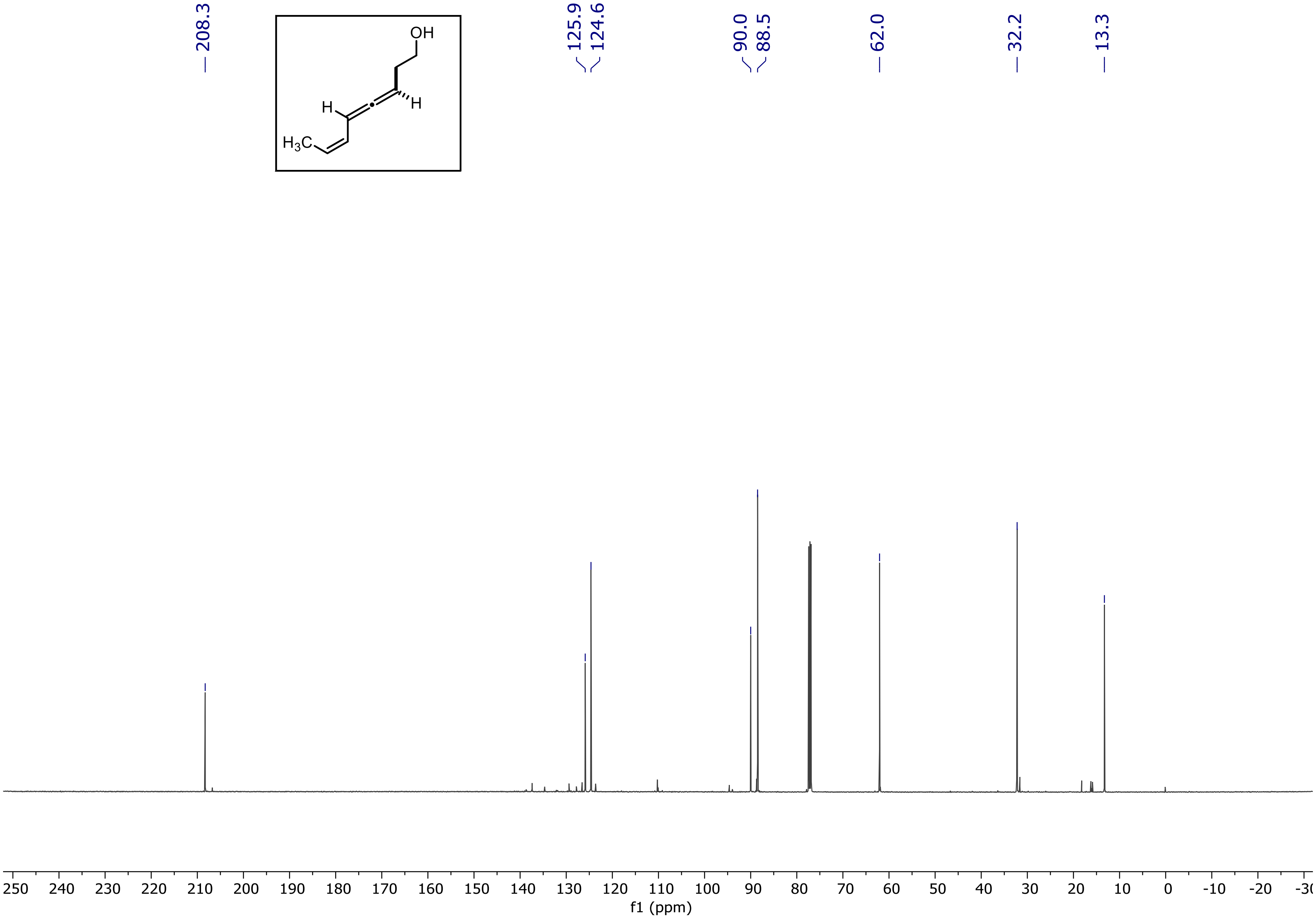
^{13}C NMR for Compound S-20.



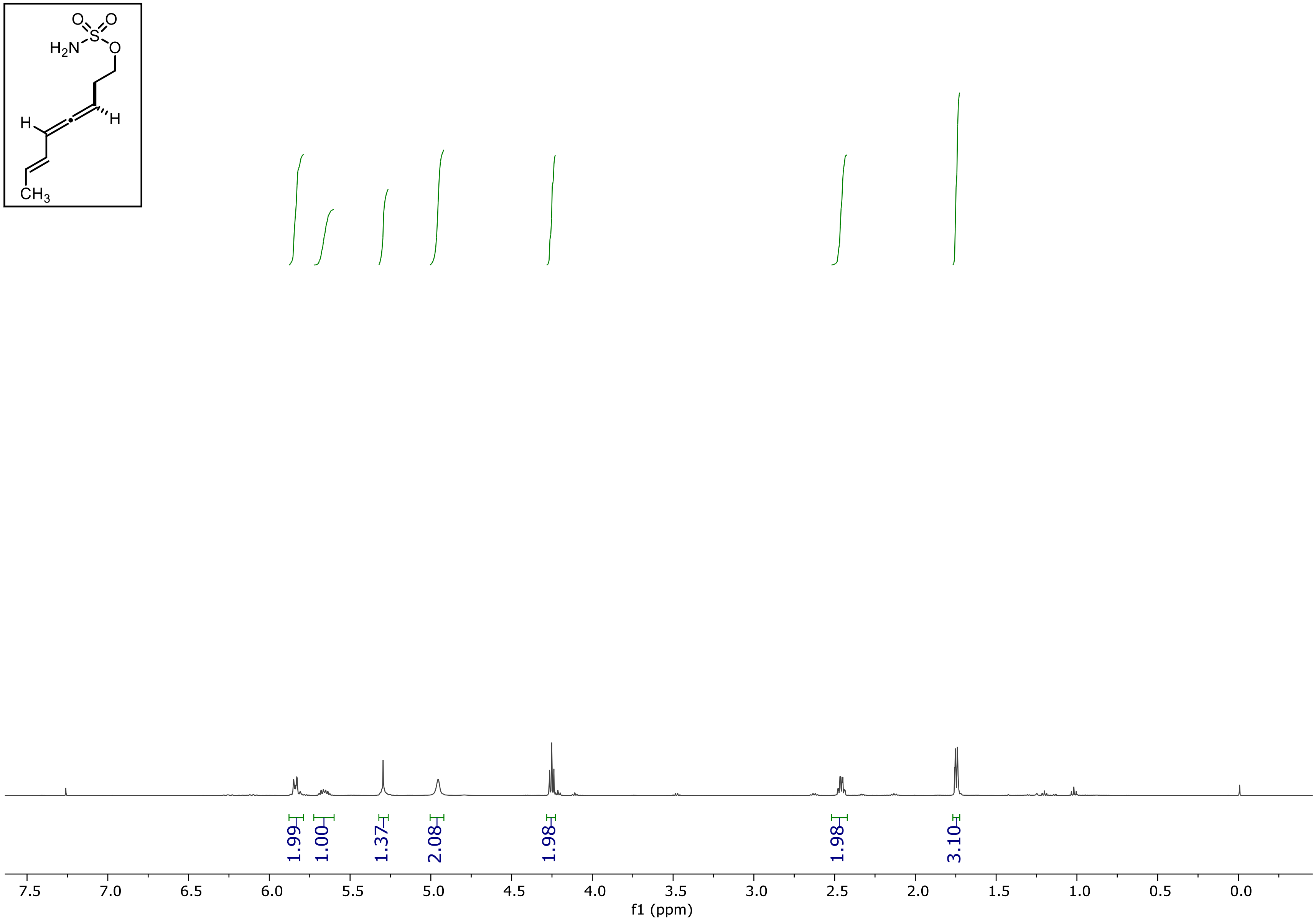
^{1}H NMR for Compound S-21.



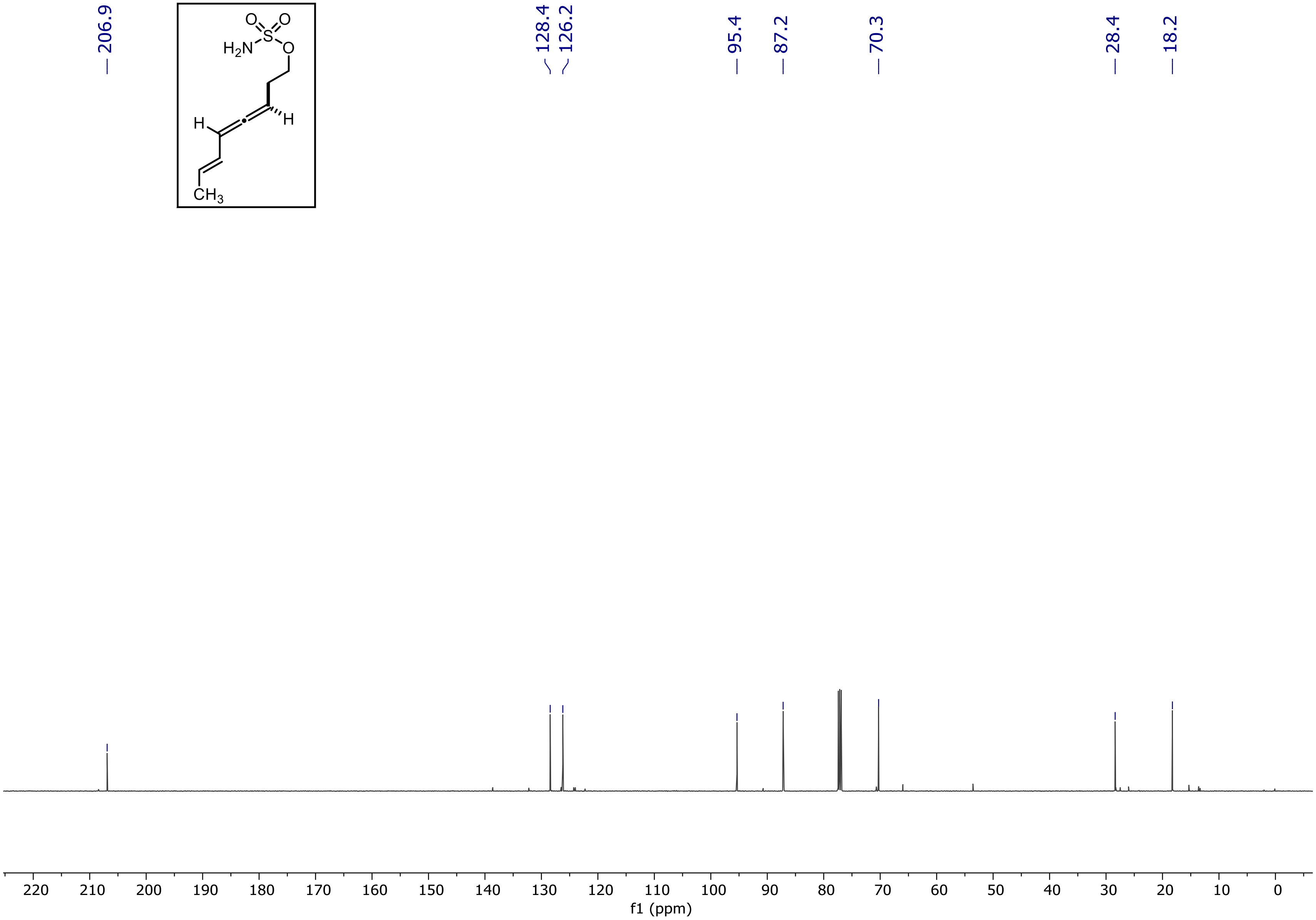
^{13}C NMR for Compound S-21.



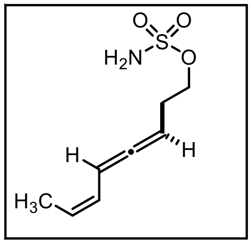
^{1}H NMR for Compound 4.

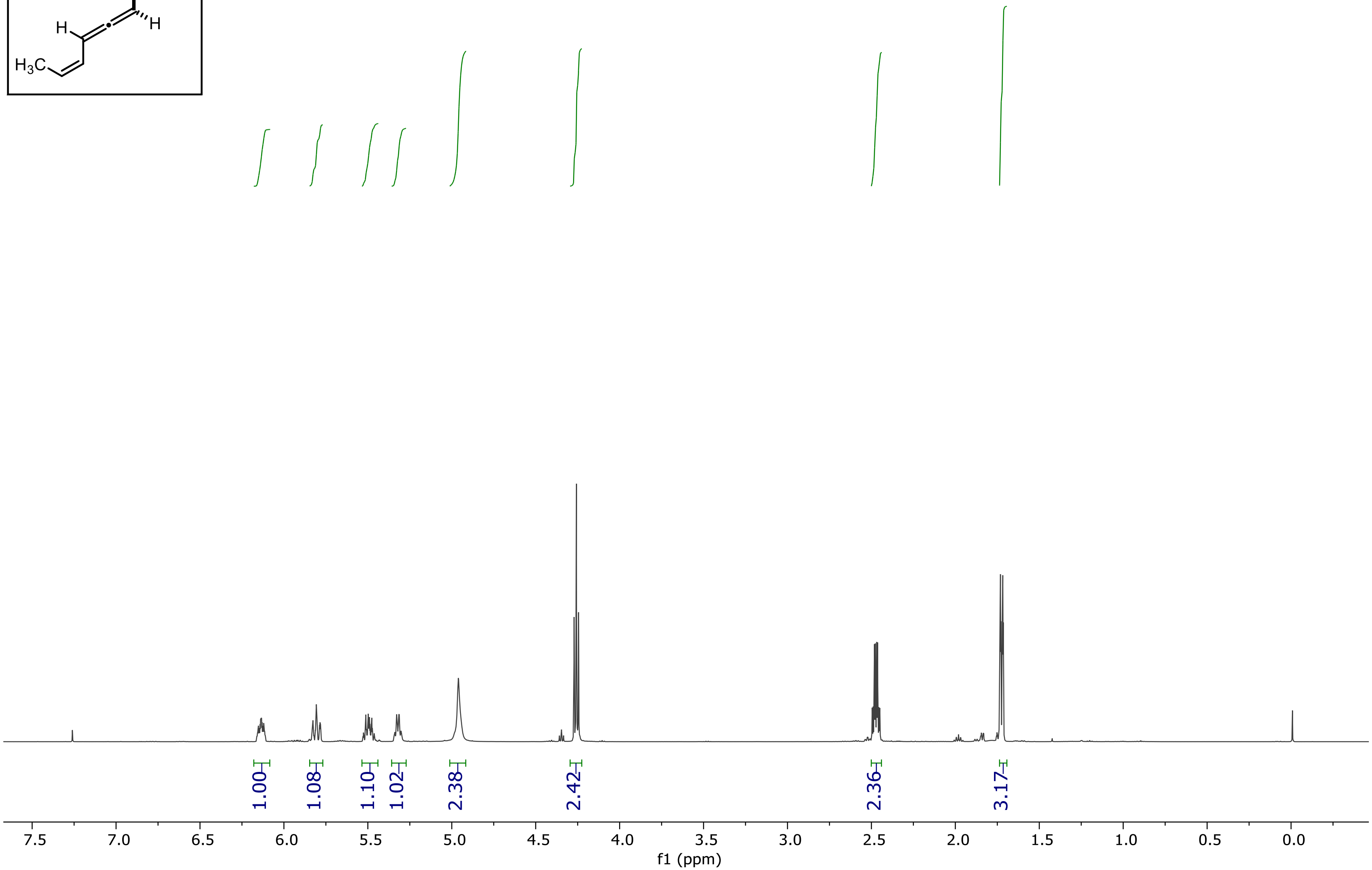


^{13}C NMR for Compound 4.

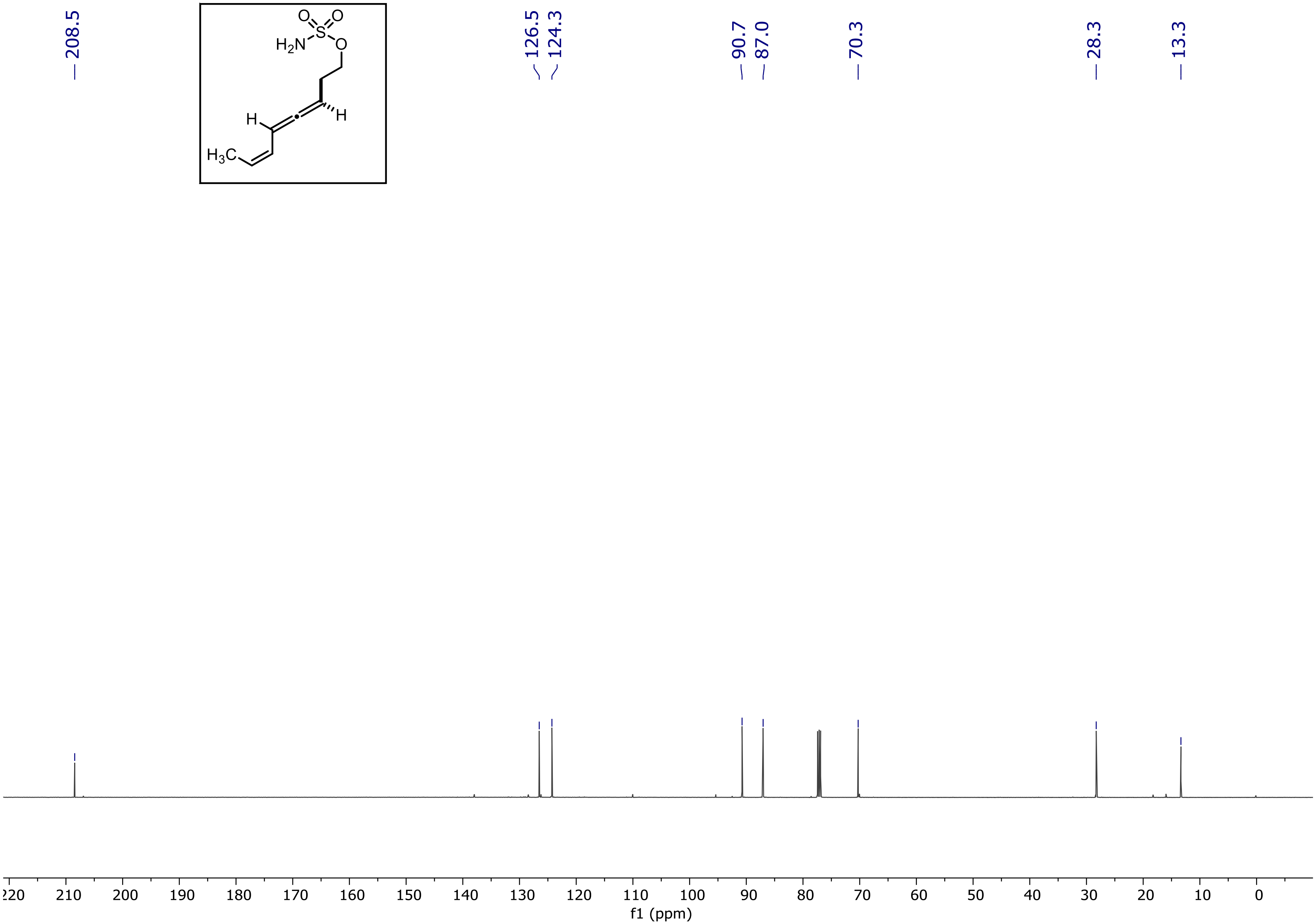


^{1}H NMR for Compound 5.

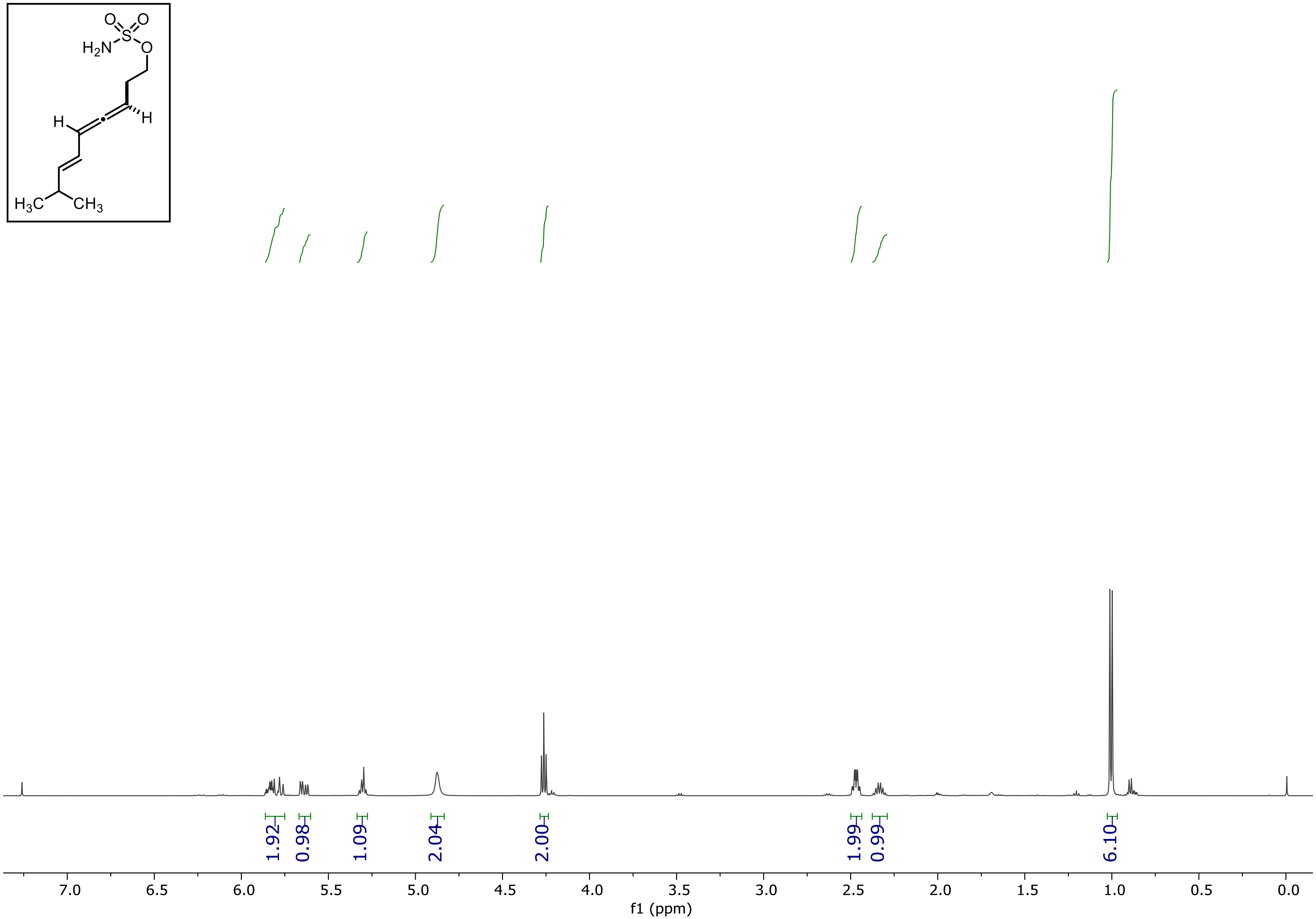




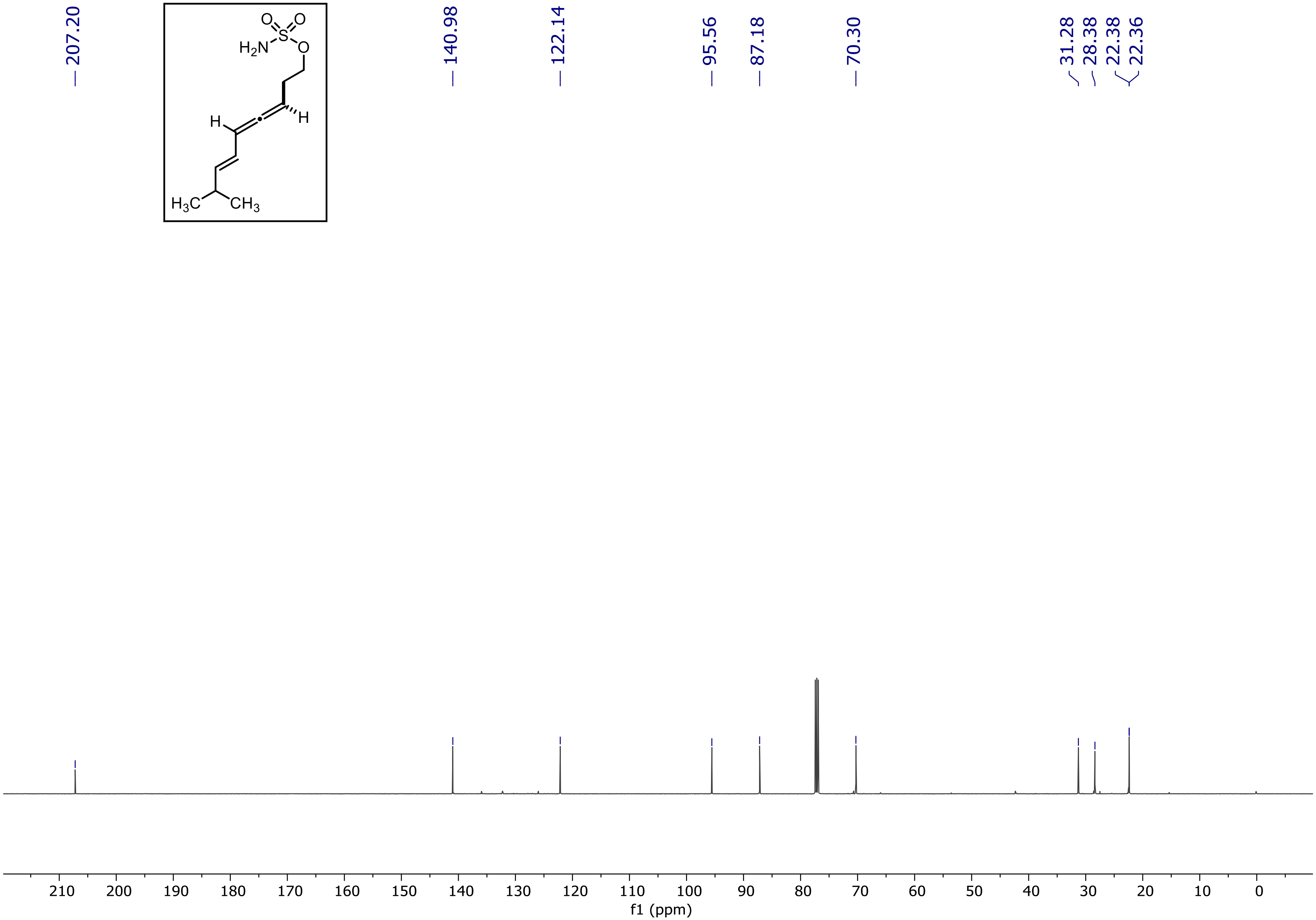
^{13}C NMR for Compound 5.



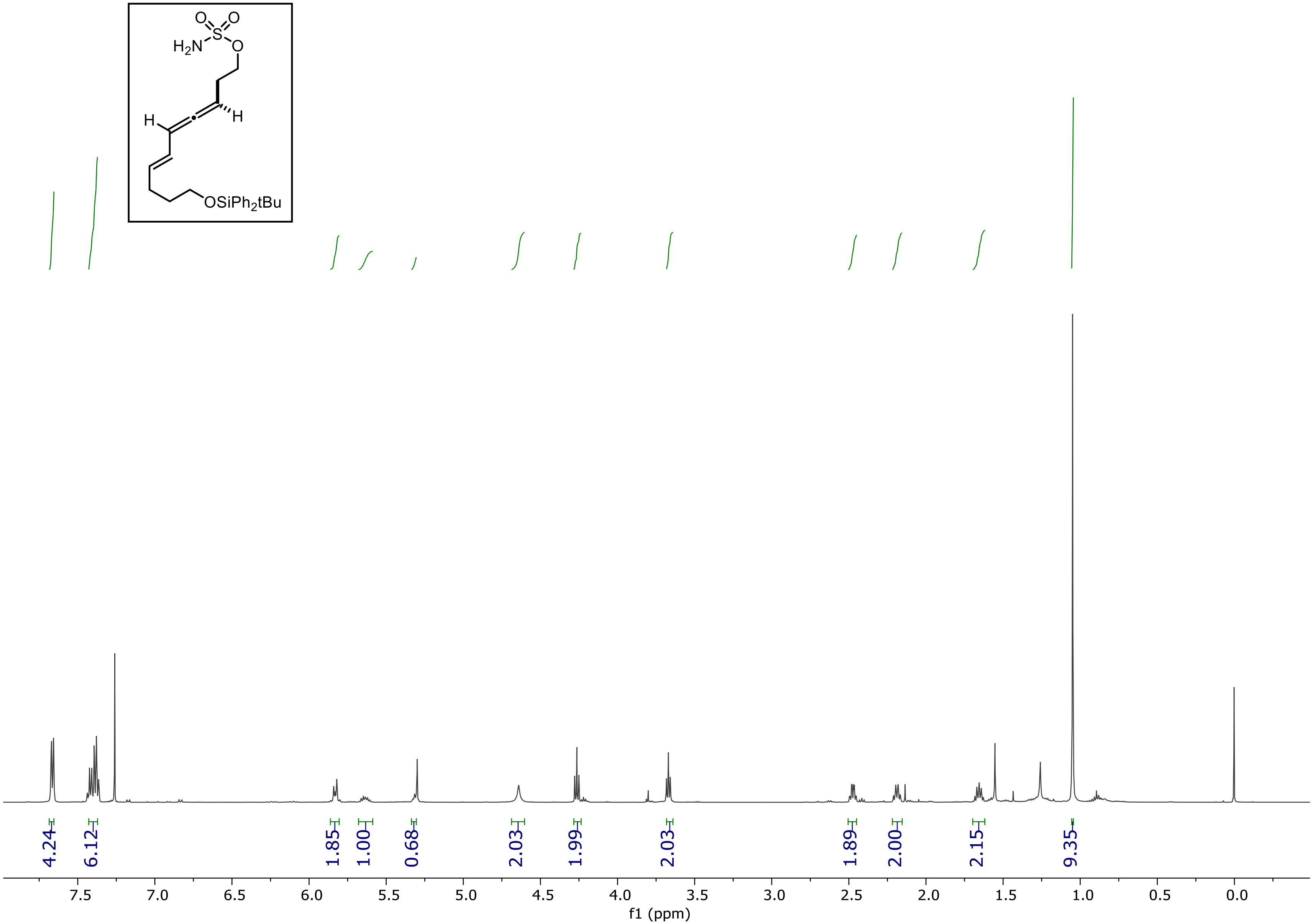
^{1}H NMR for Compound 6.



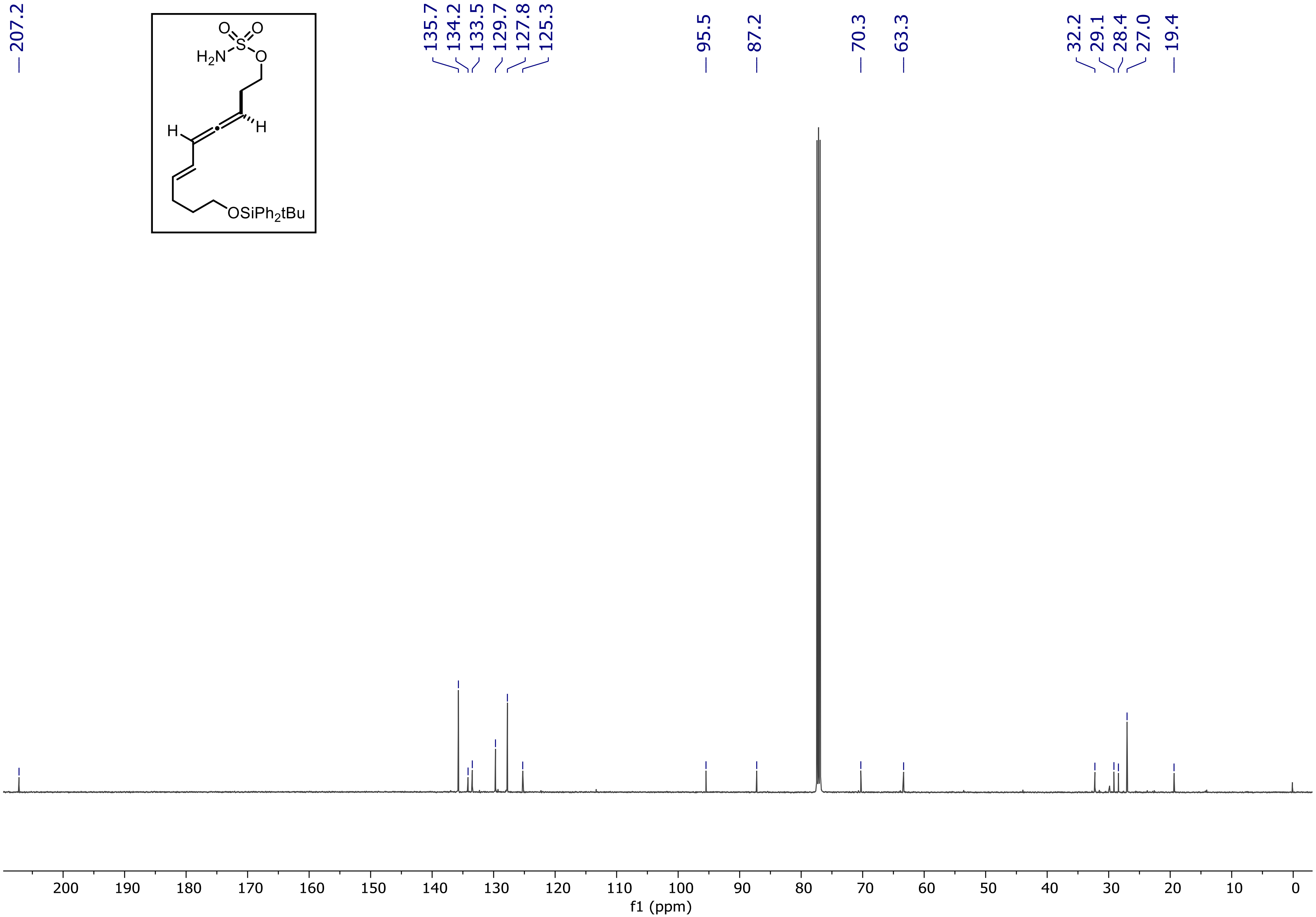
^{13}C NMR for Compound 6.



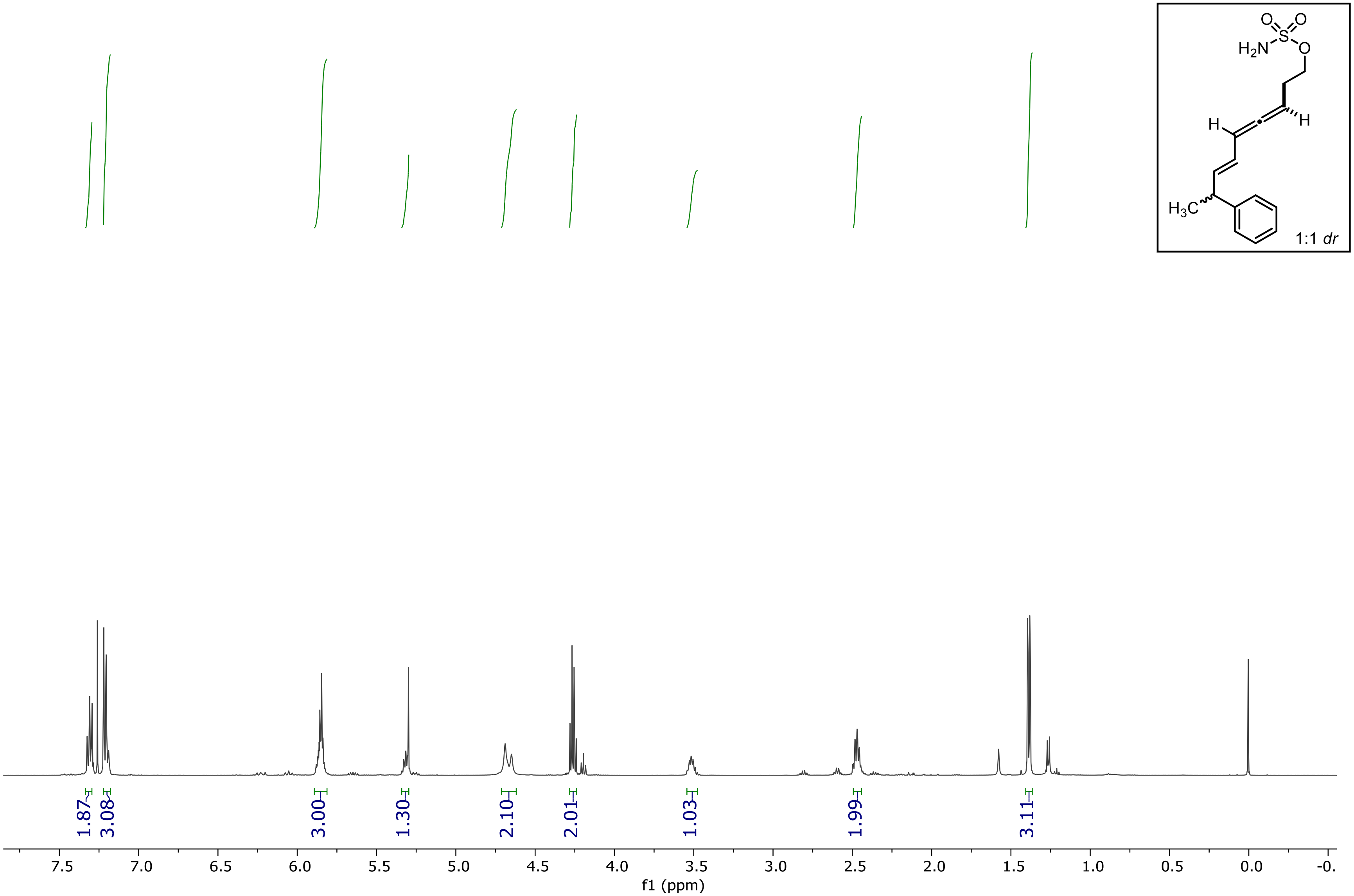
^{1}H NMR for Compound 7.



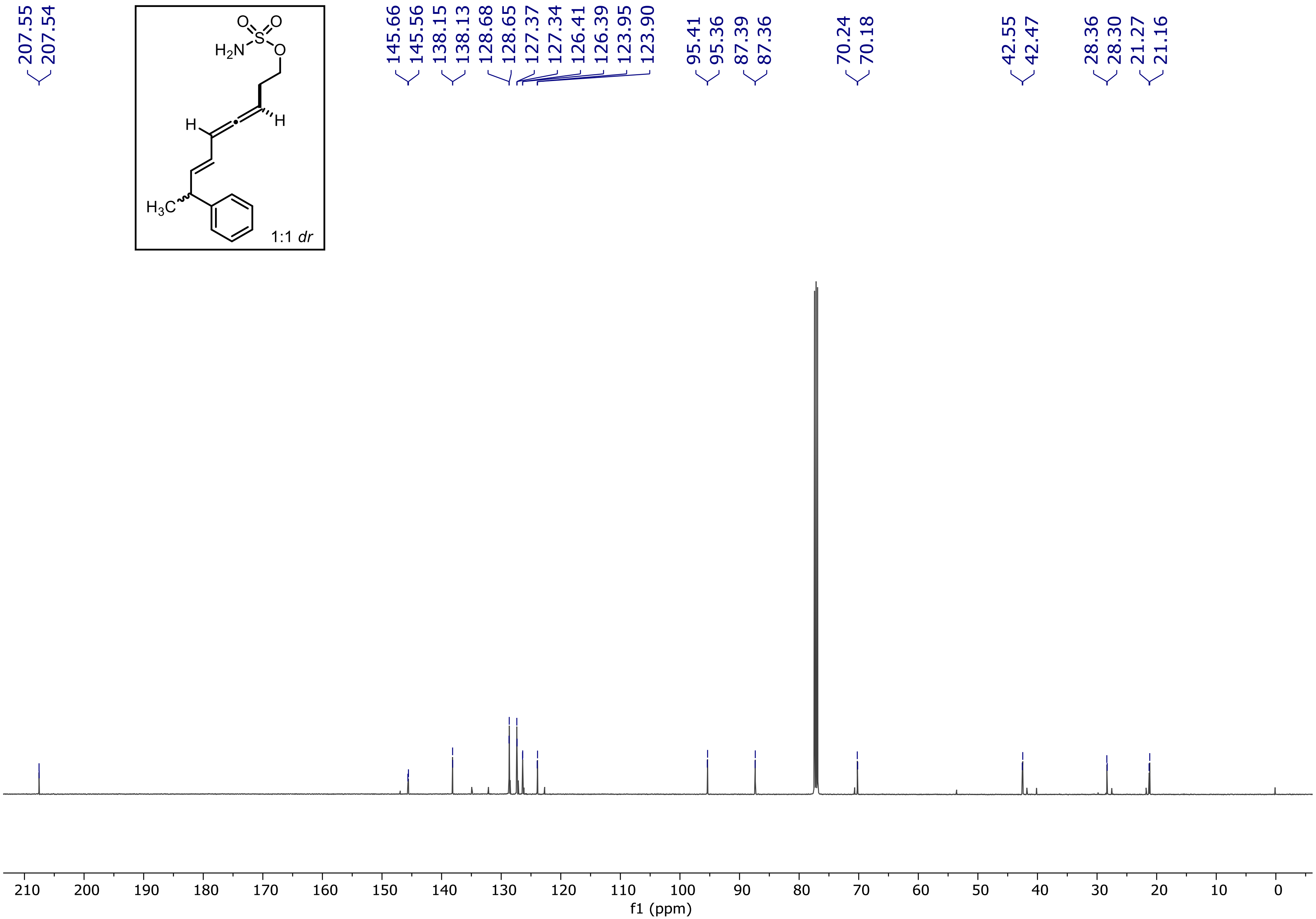
^{13}C NMR for Compound 7.



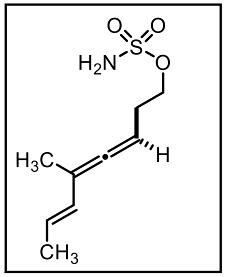
^{1}H NMR for Compound 8.

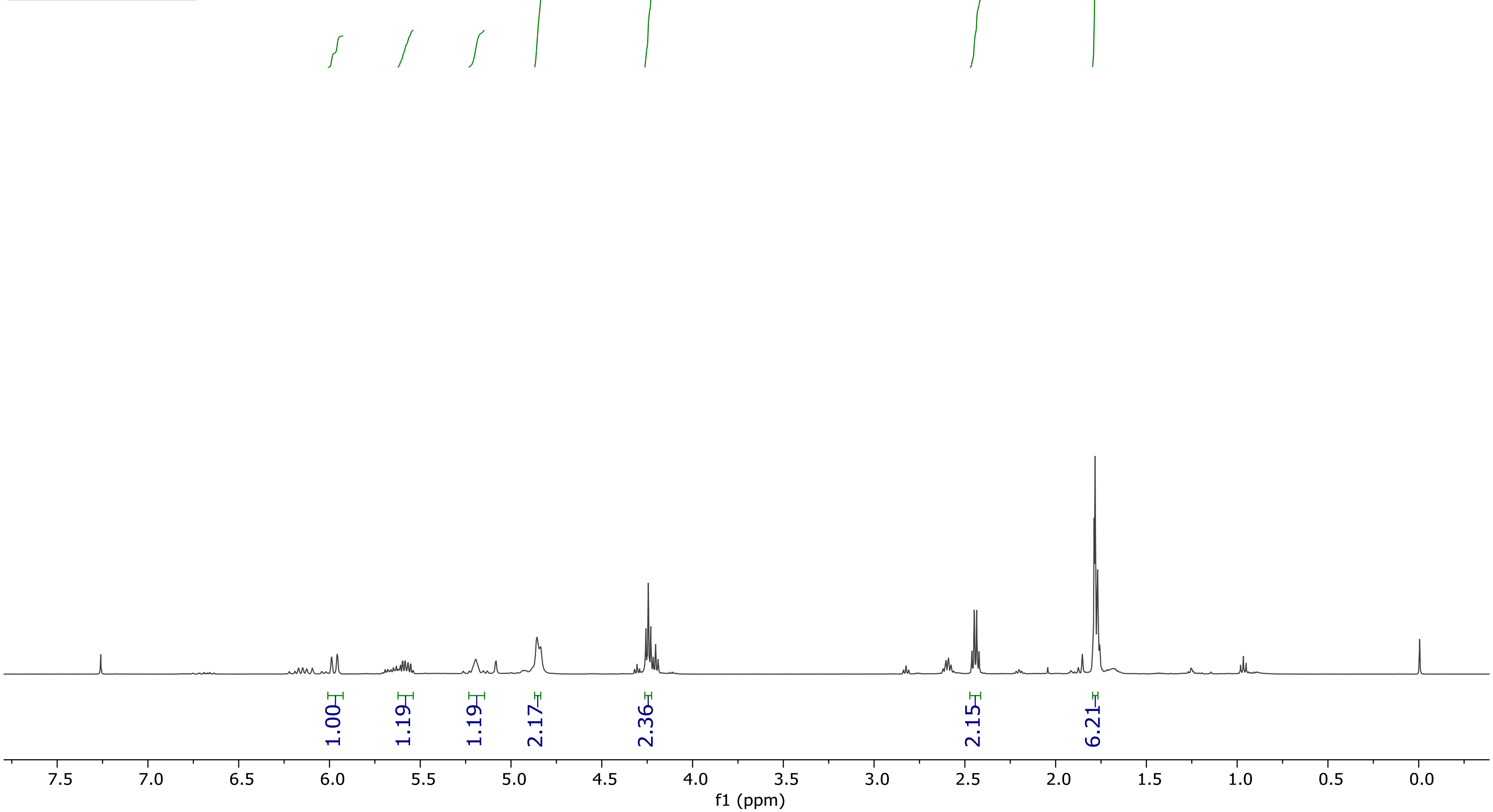


^{13}C NMR for Compound 8.

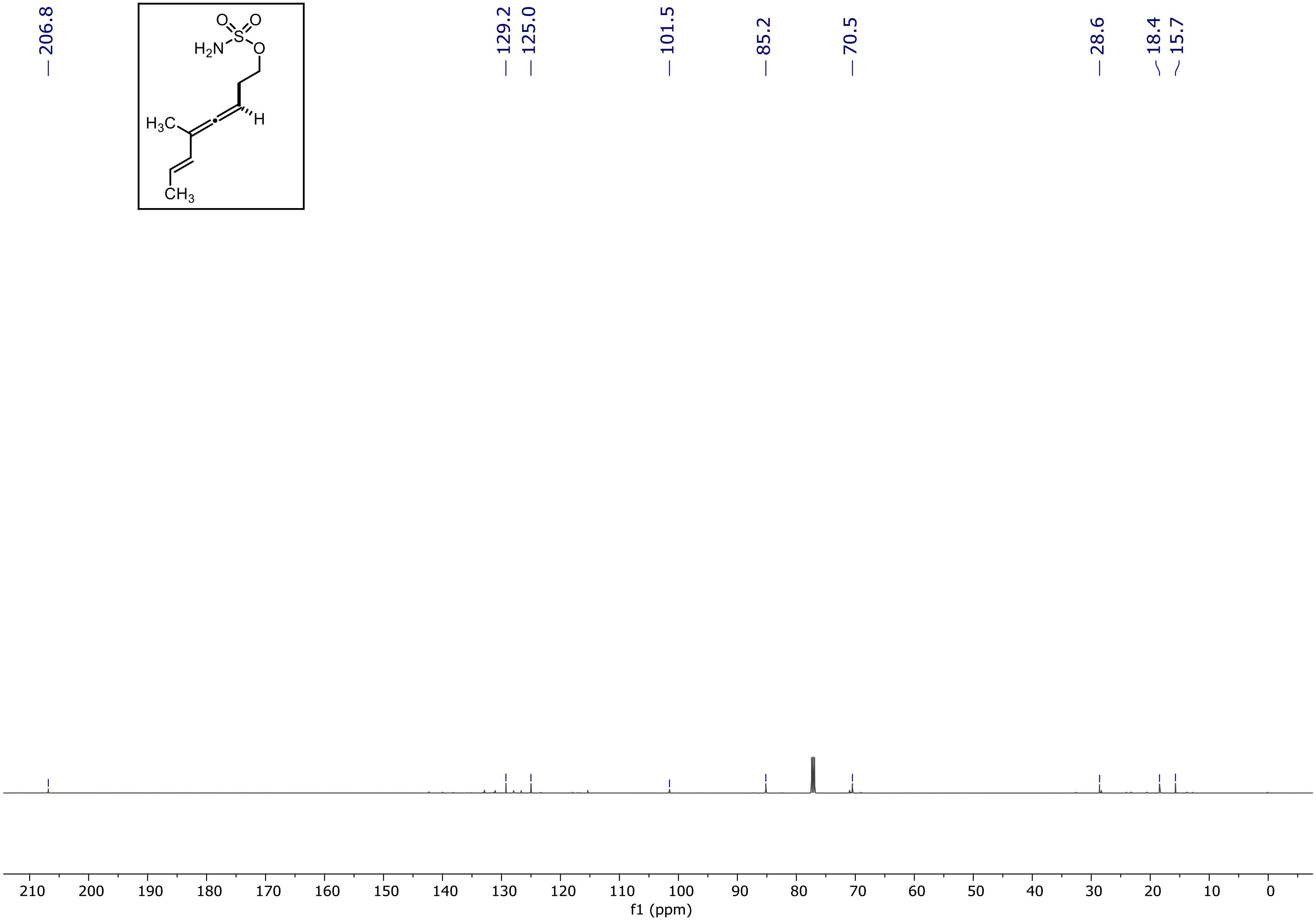


^{1}H NMR for Compound 9.

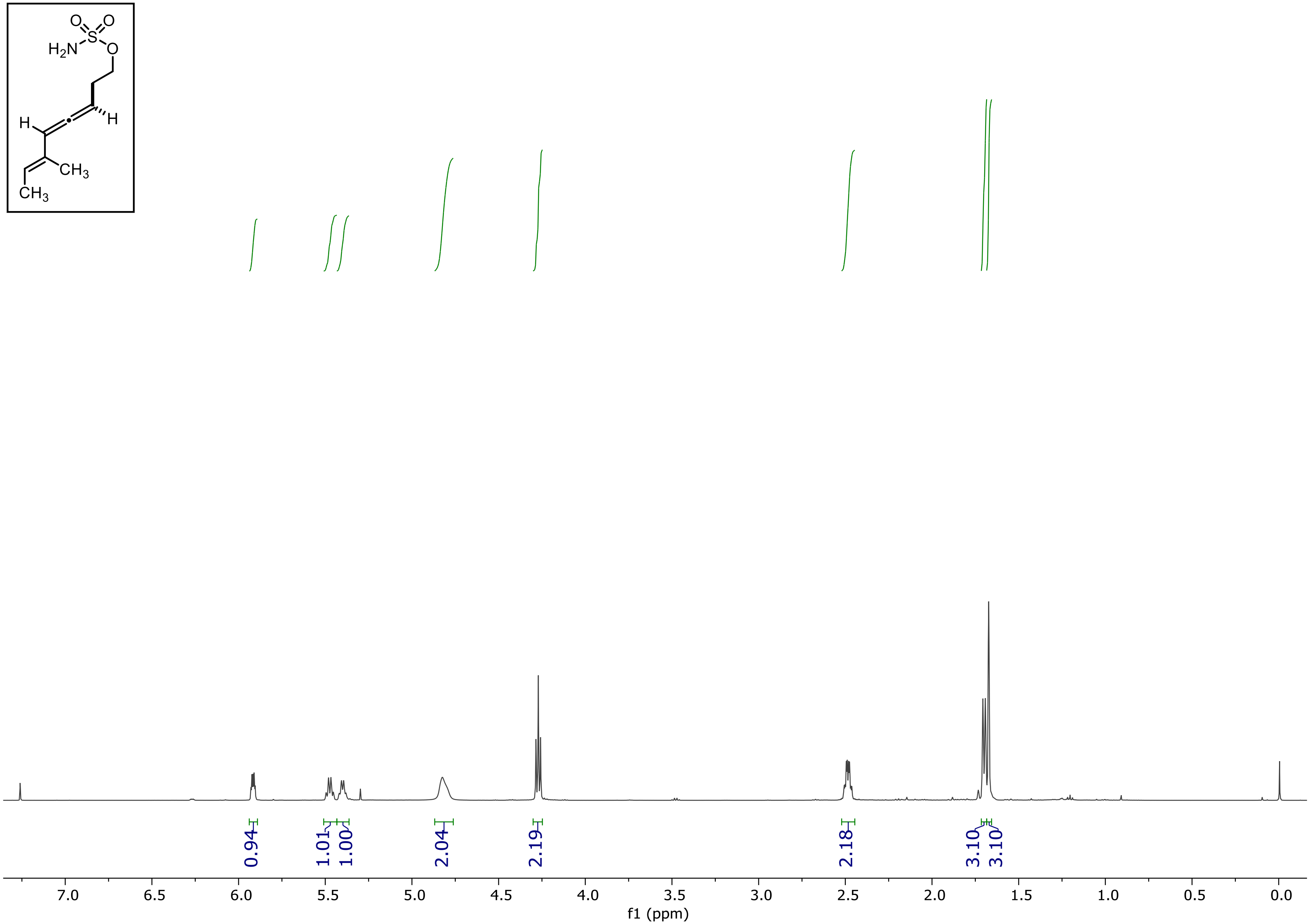




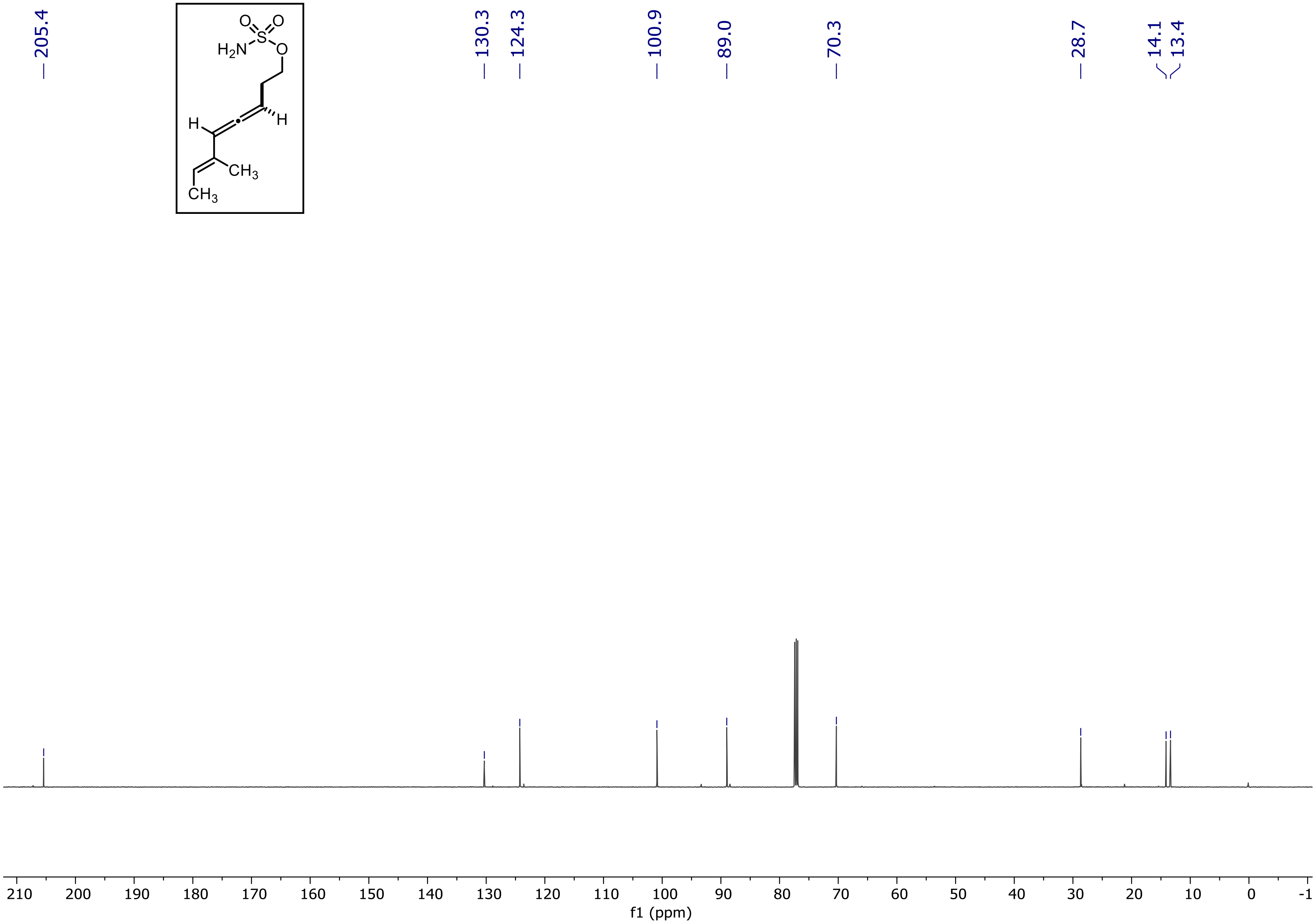
^{13}C NMR for Compound 9.



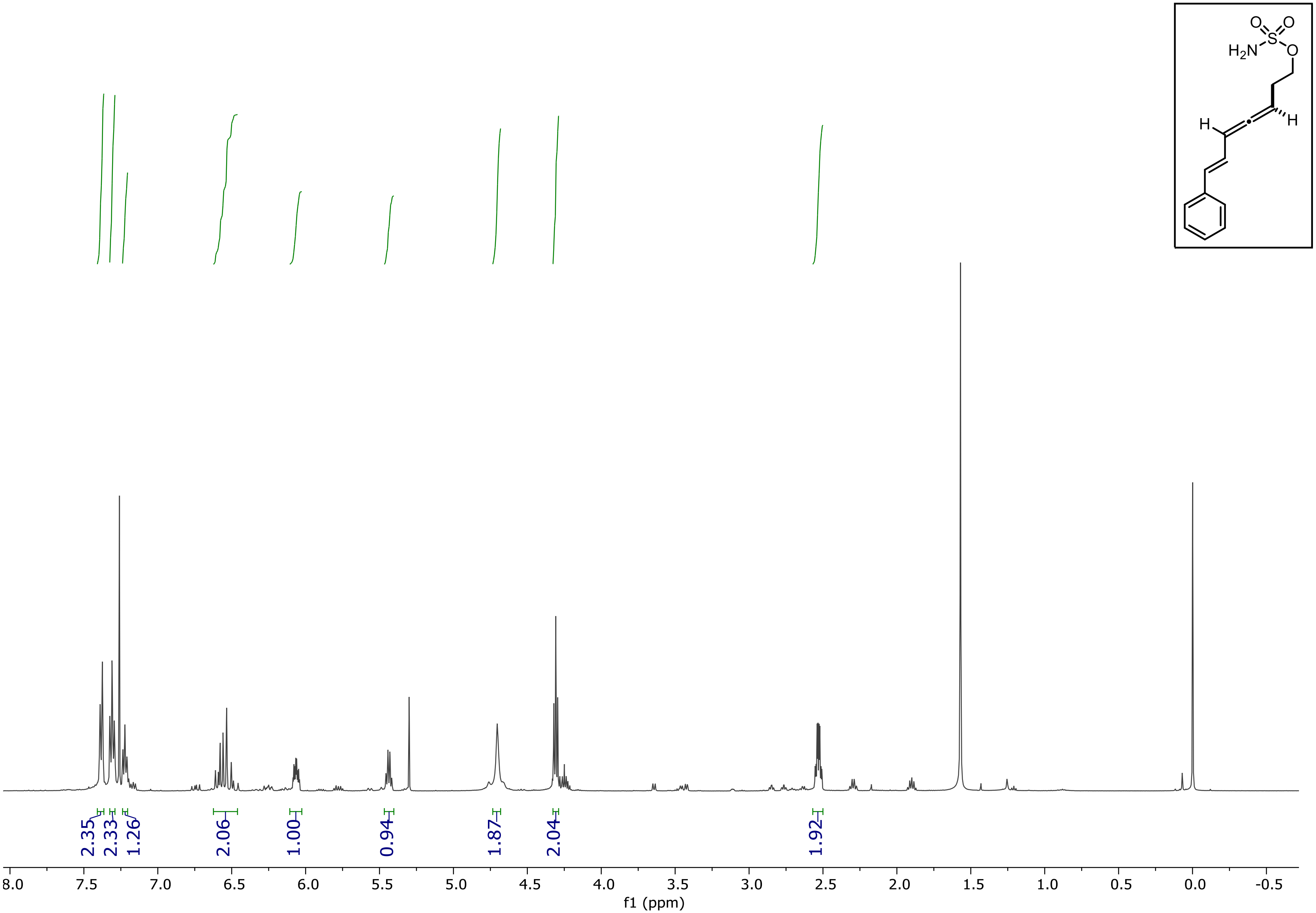
^{1}H NMR for Compound 10.



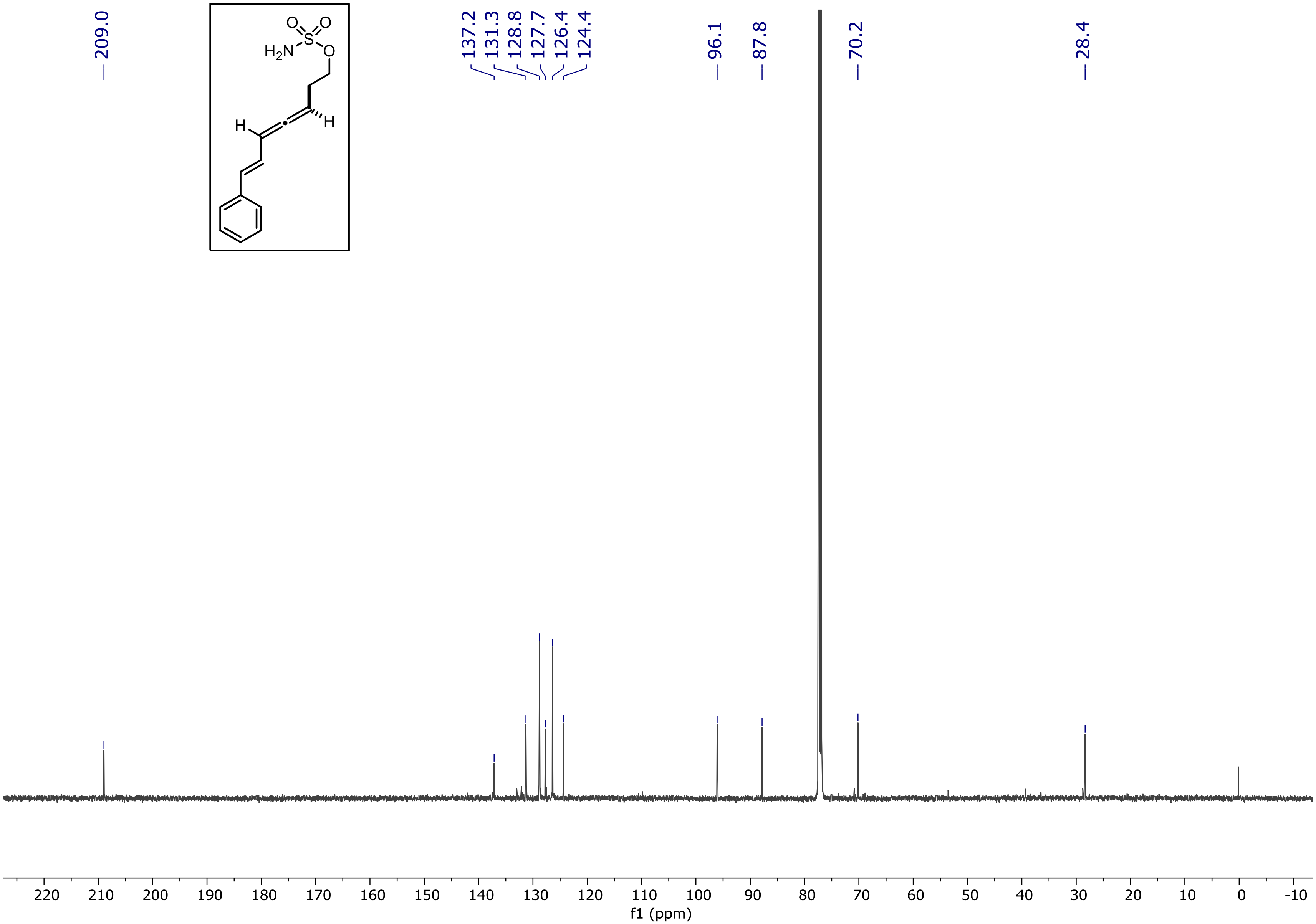
^{13}C NMR for Compound 10.



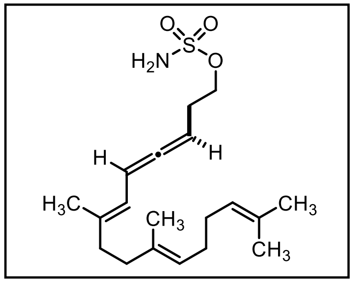
^{1}H NMR for Compound 11.

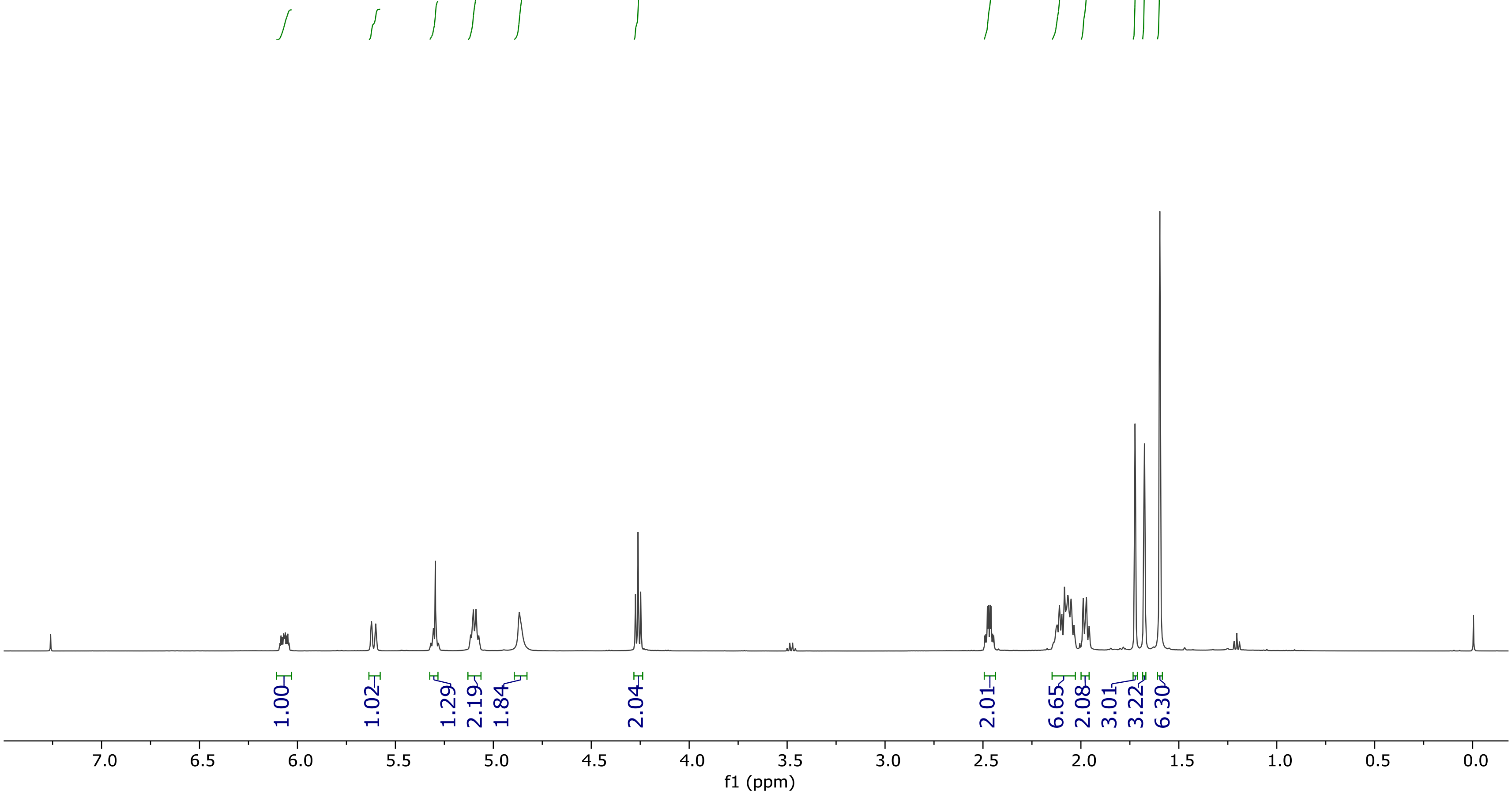


^{13}C NMR for Compound 11.

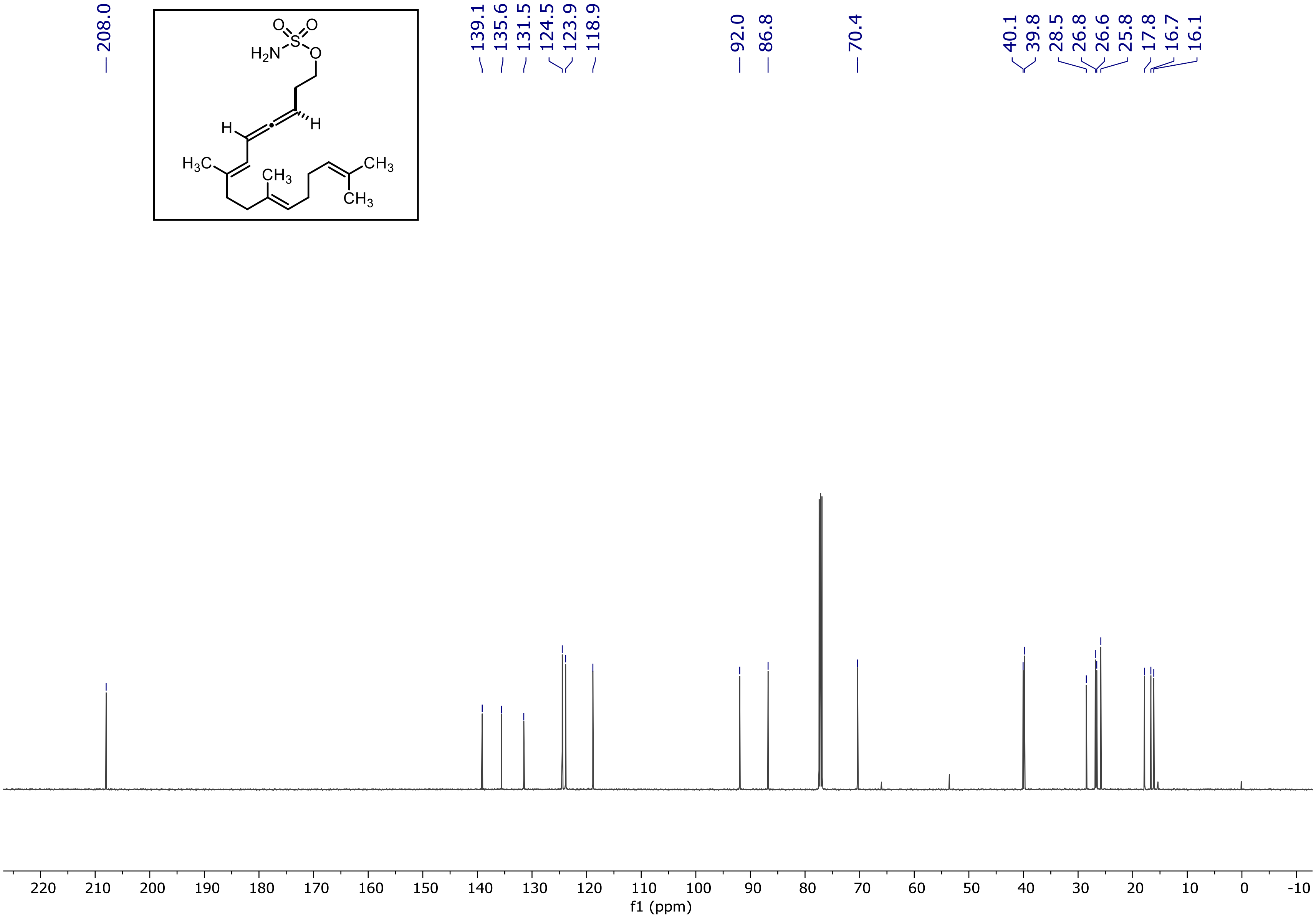


^{1}H NMR for Compound 12.

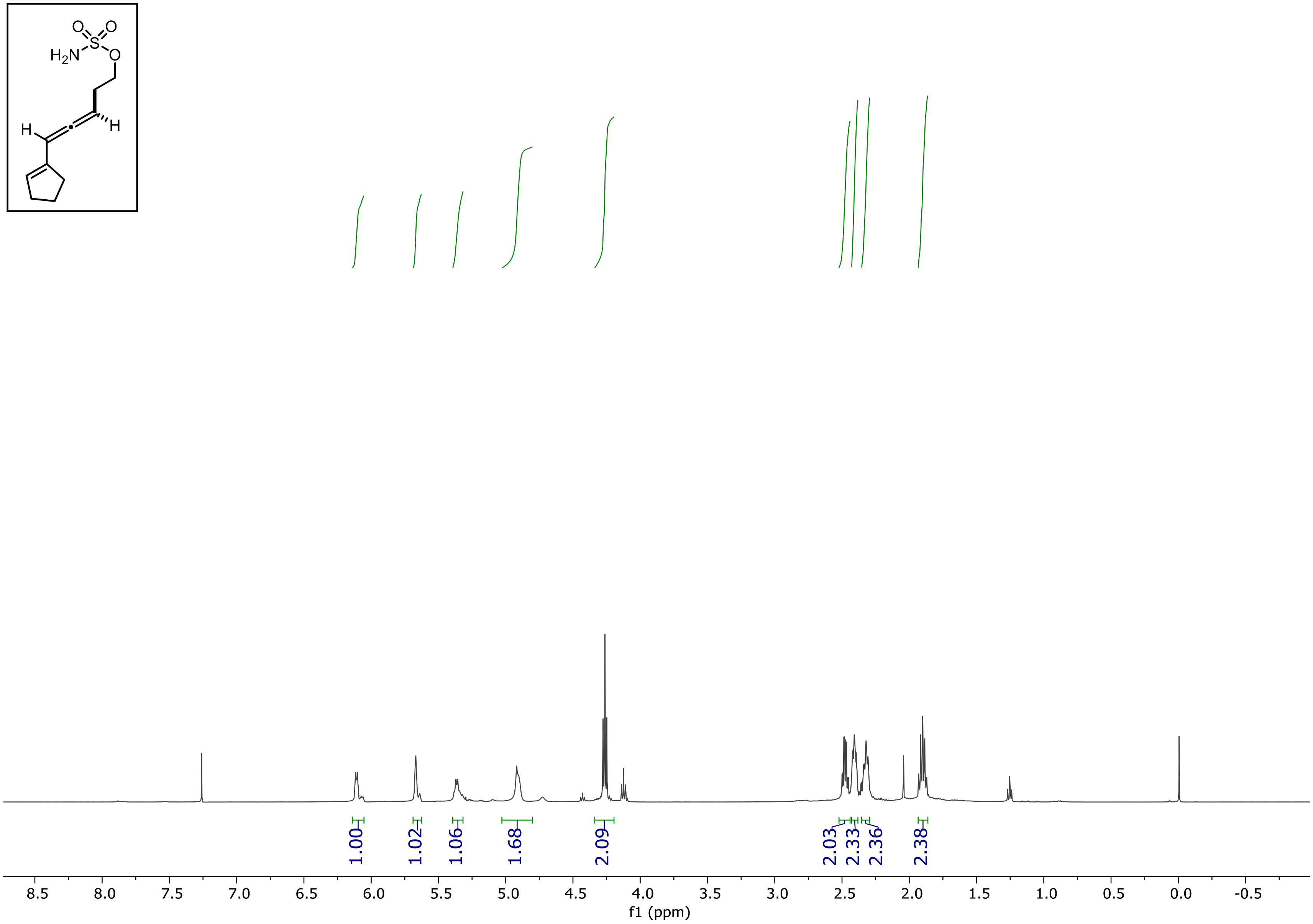




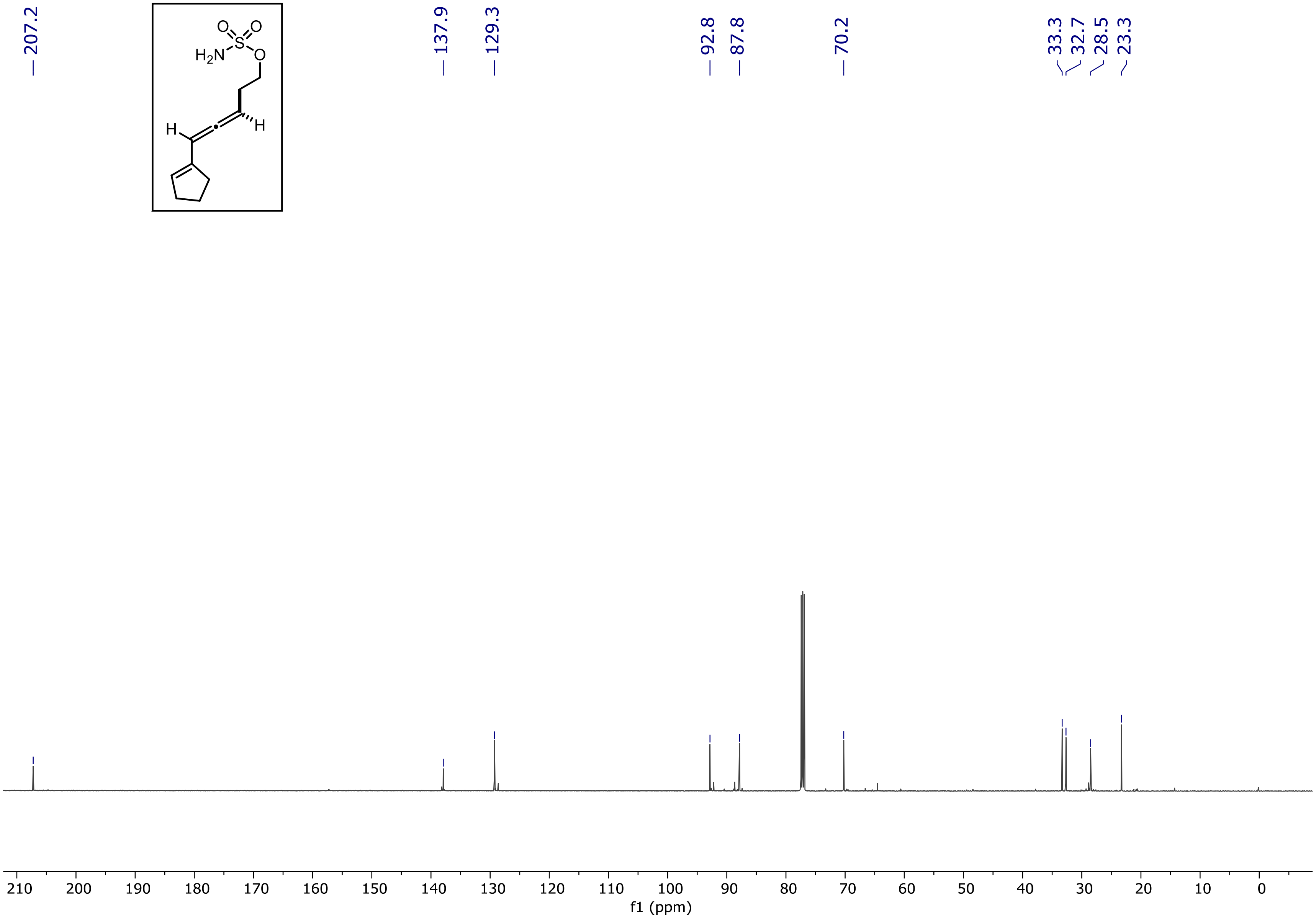
^{13}C NMR for Compound 12.



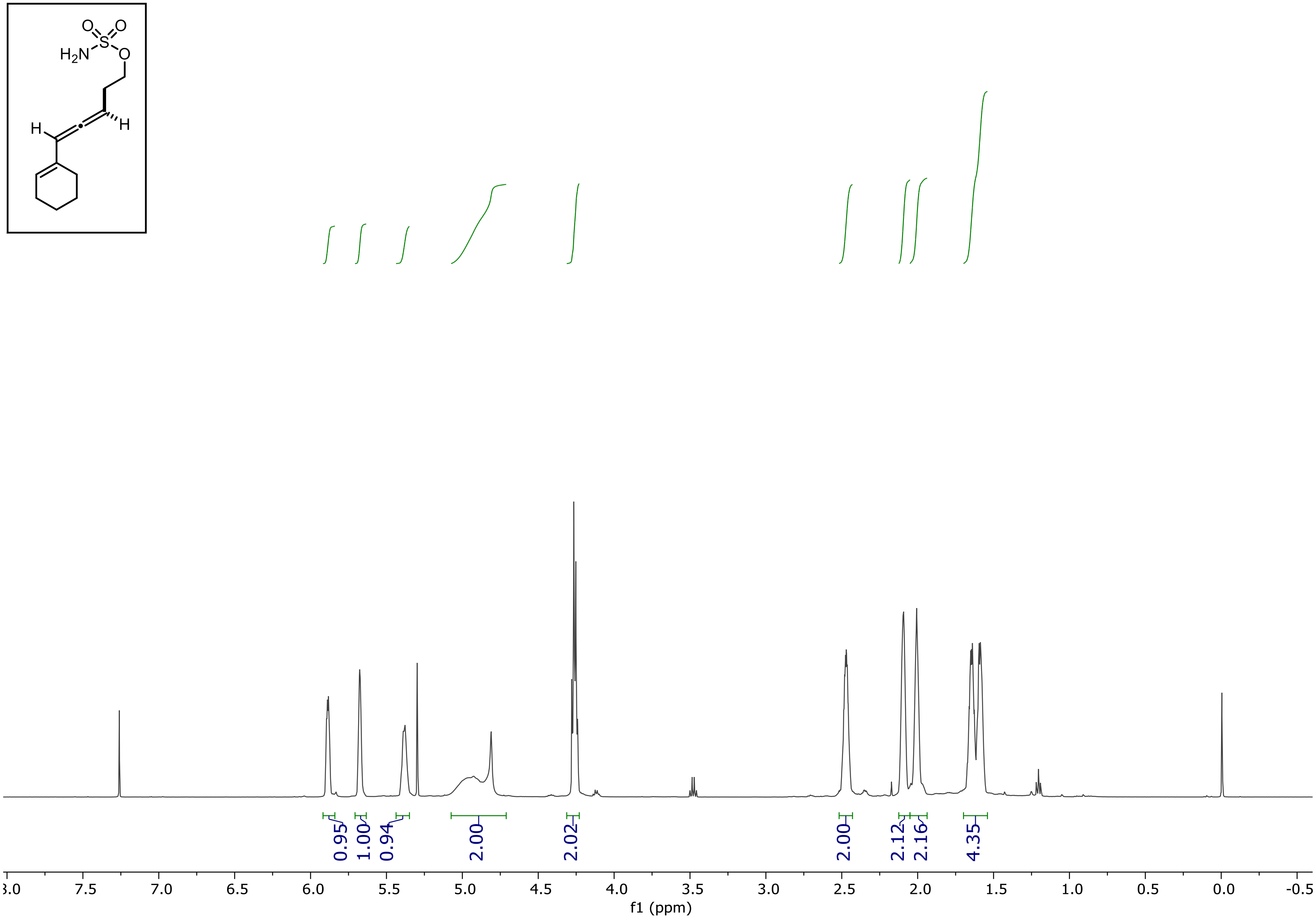
^{1}H NMR for Compound 13.



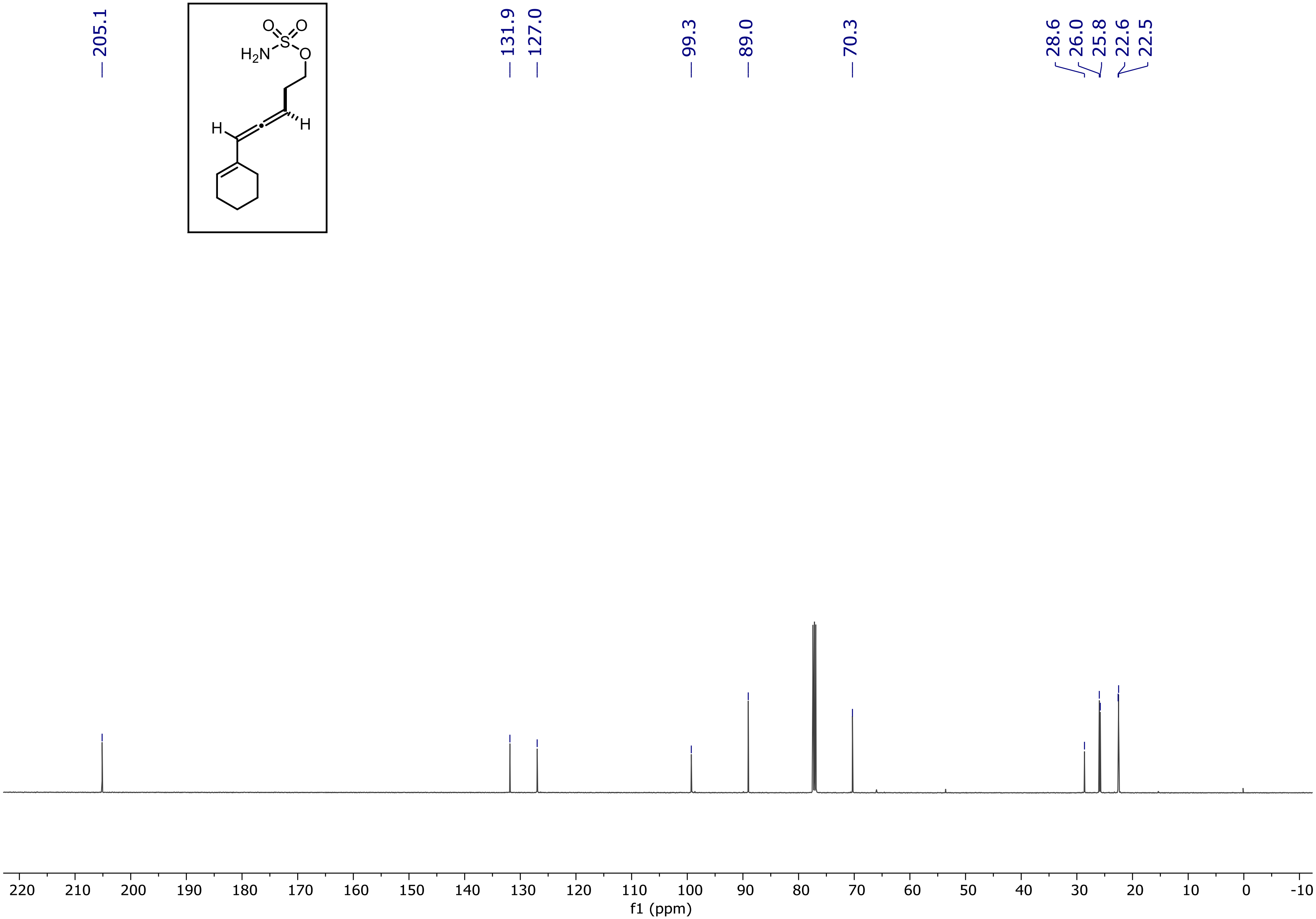
^{13}C NMR for Compound 13.



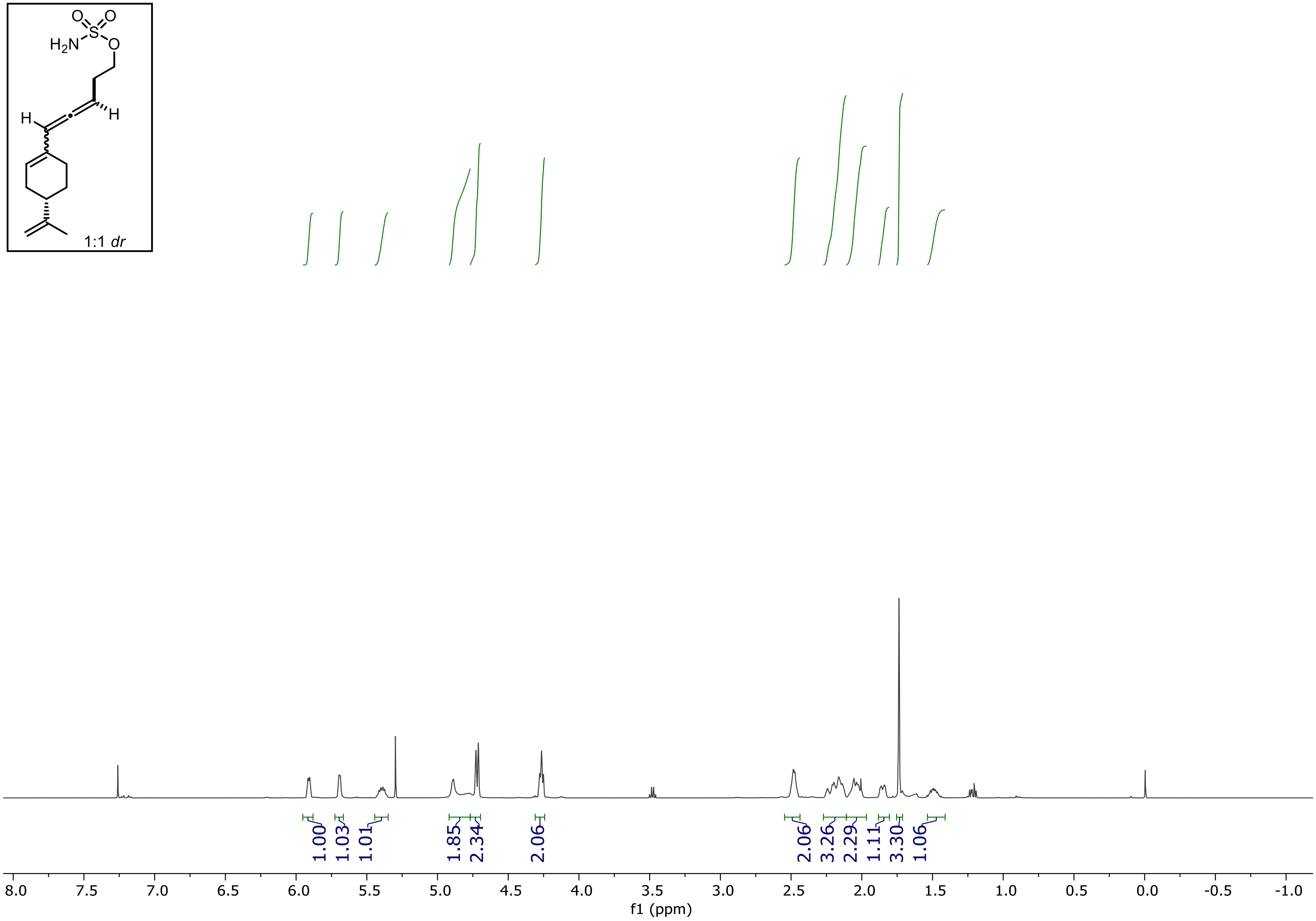
^{1}H NMR for Compound 14.



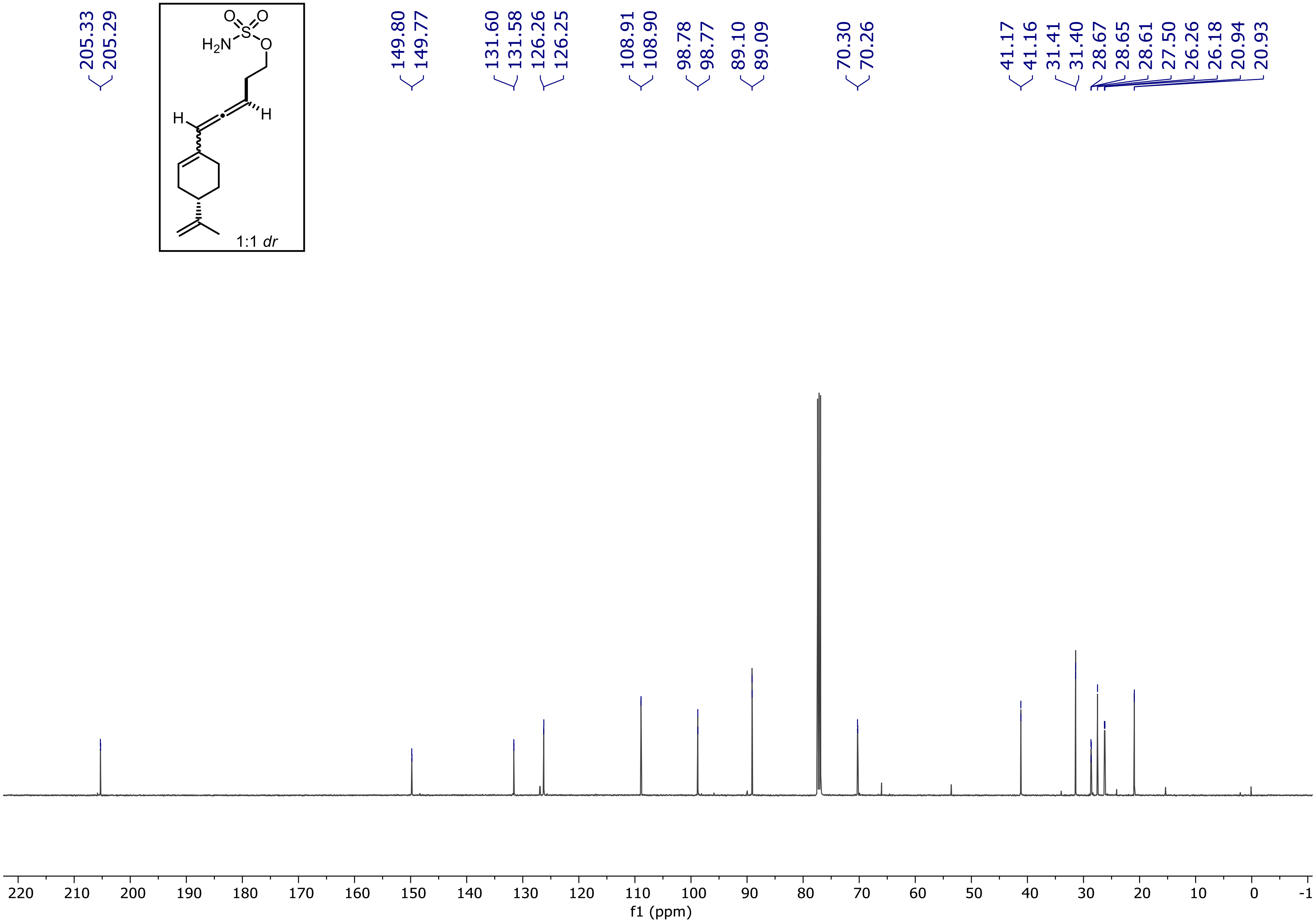
^{13}C NMR for Compound 14.



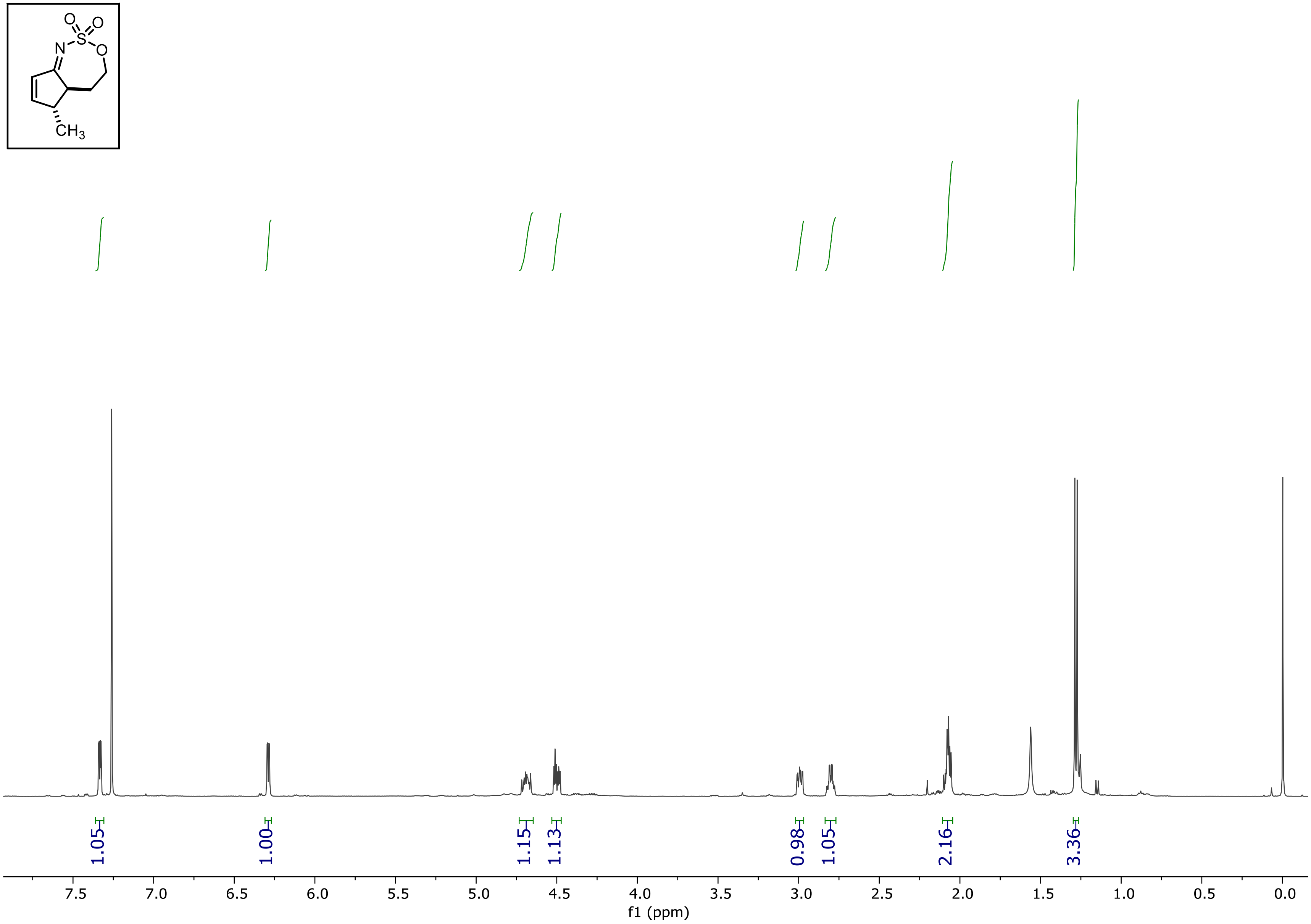
^{1}H NMR for Compound 15.



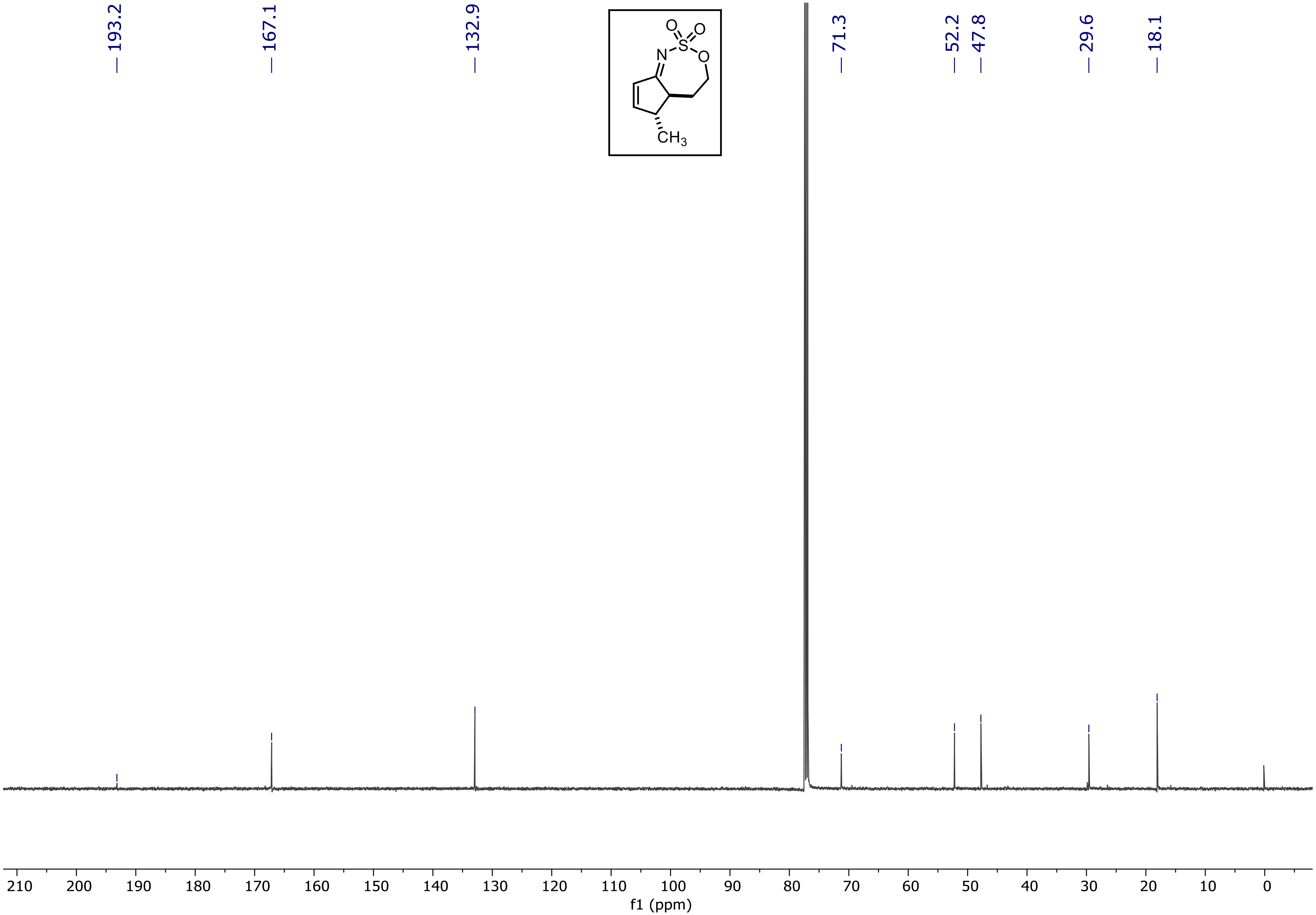
^{13}C NMR for Compound 15.



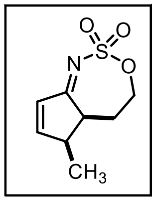
^{1}H NMR for Compound 4a.

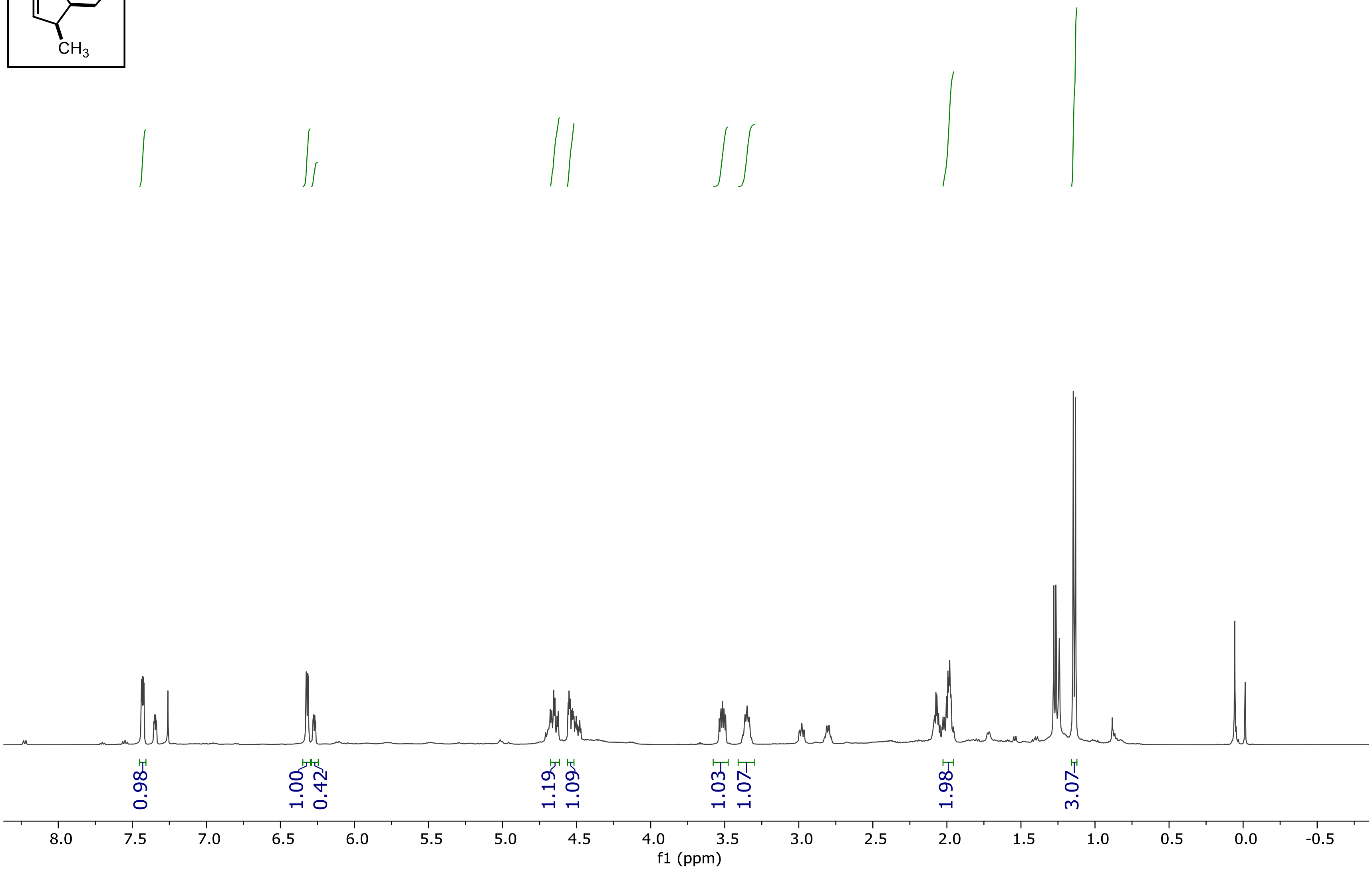


^{13}C NMR for Compound 4a.

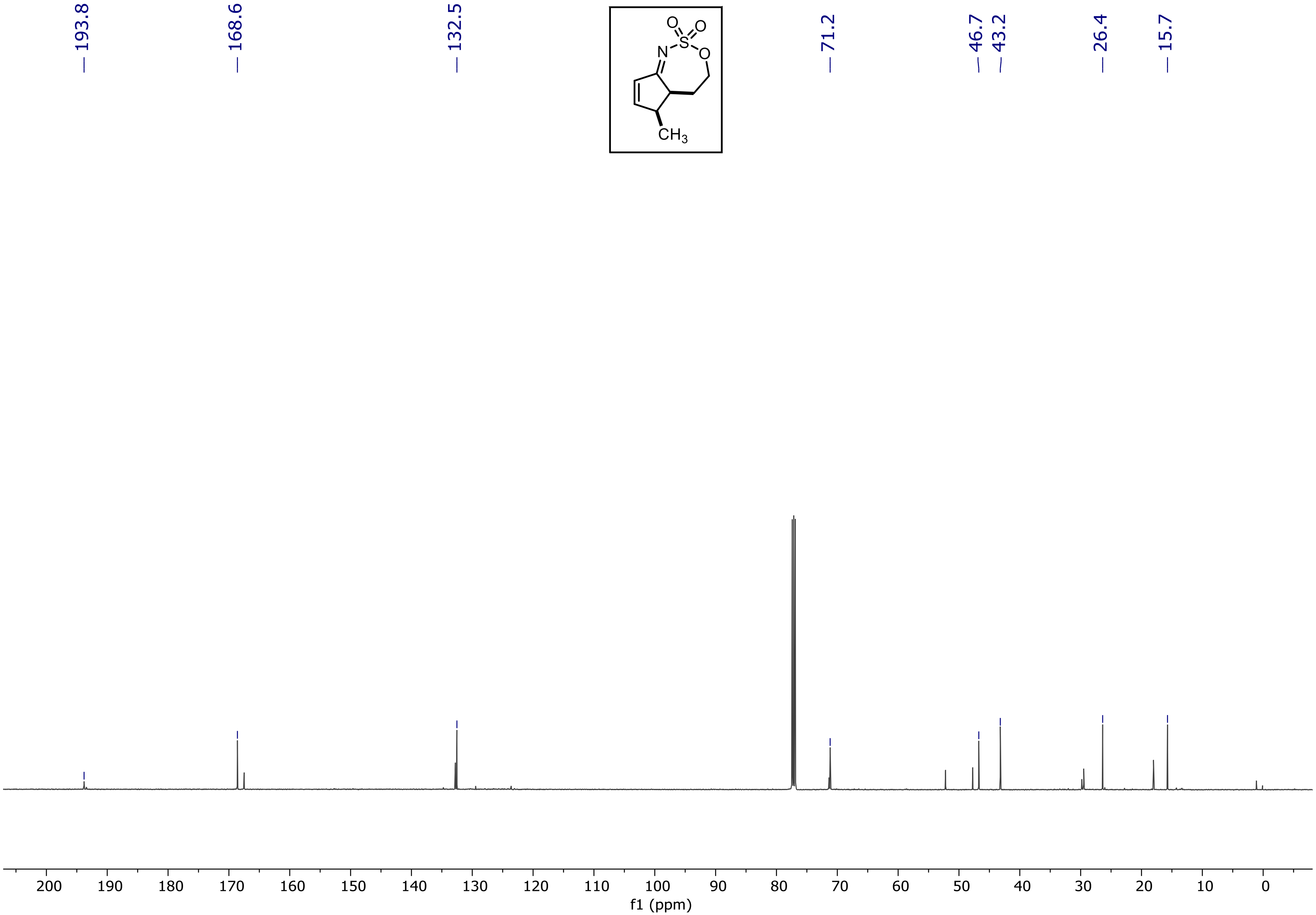


^{1}H NMR for Compound 5a.

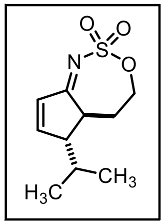


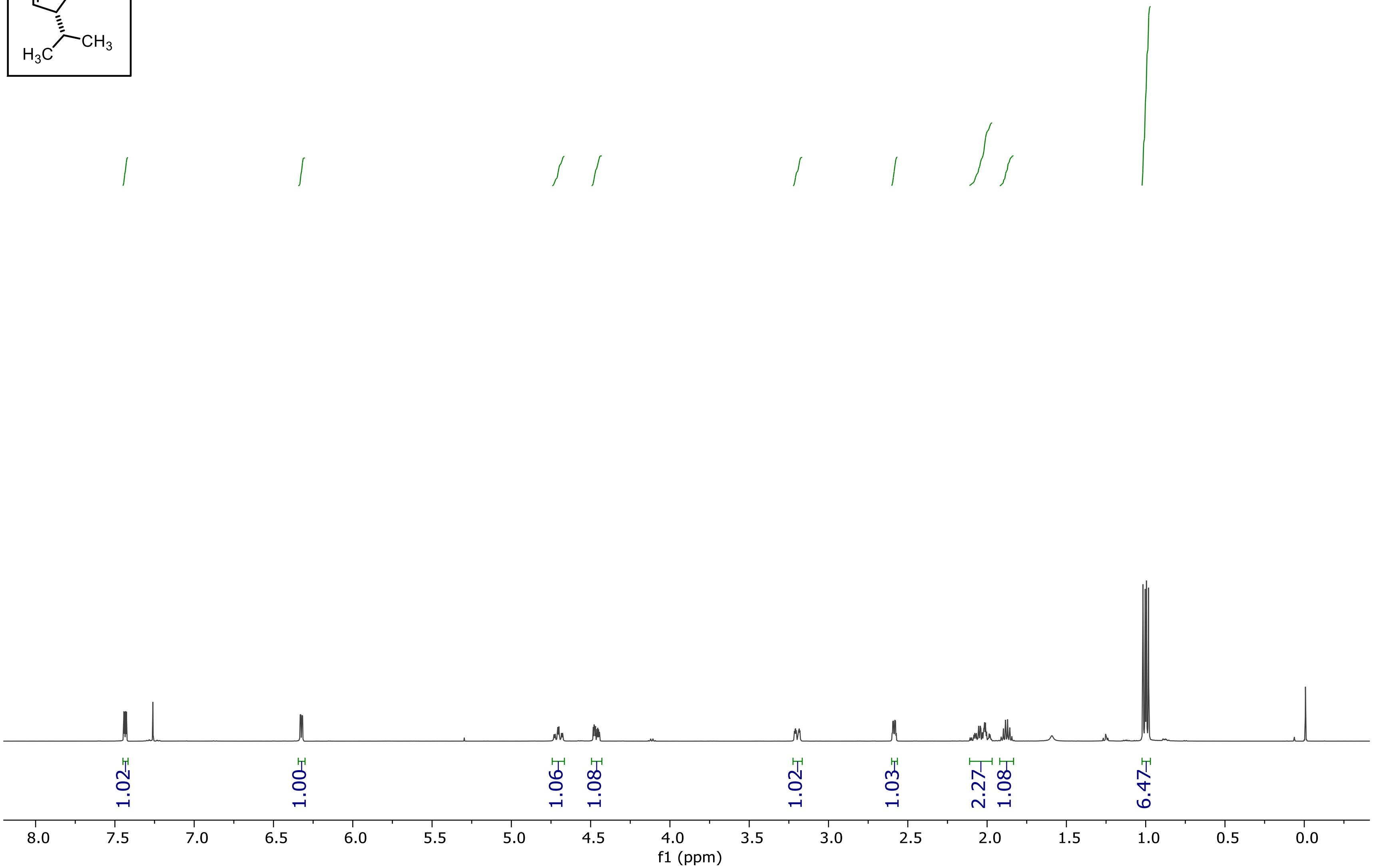


^{13}C NMR for Compound 5a.

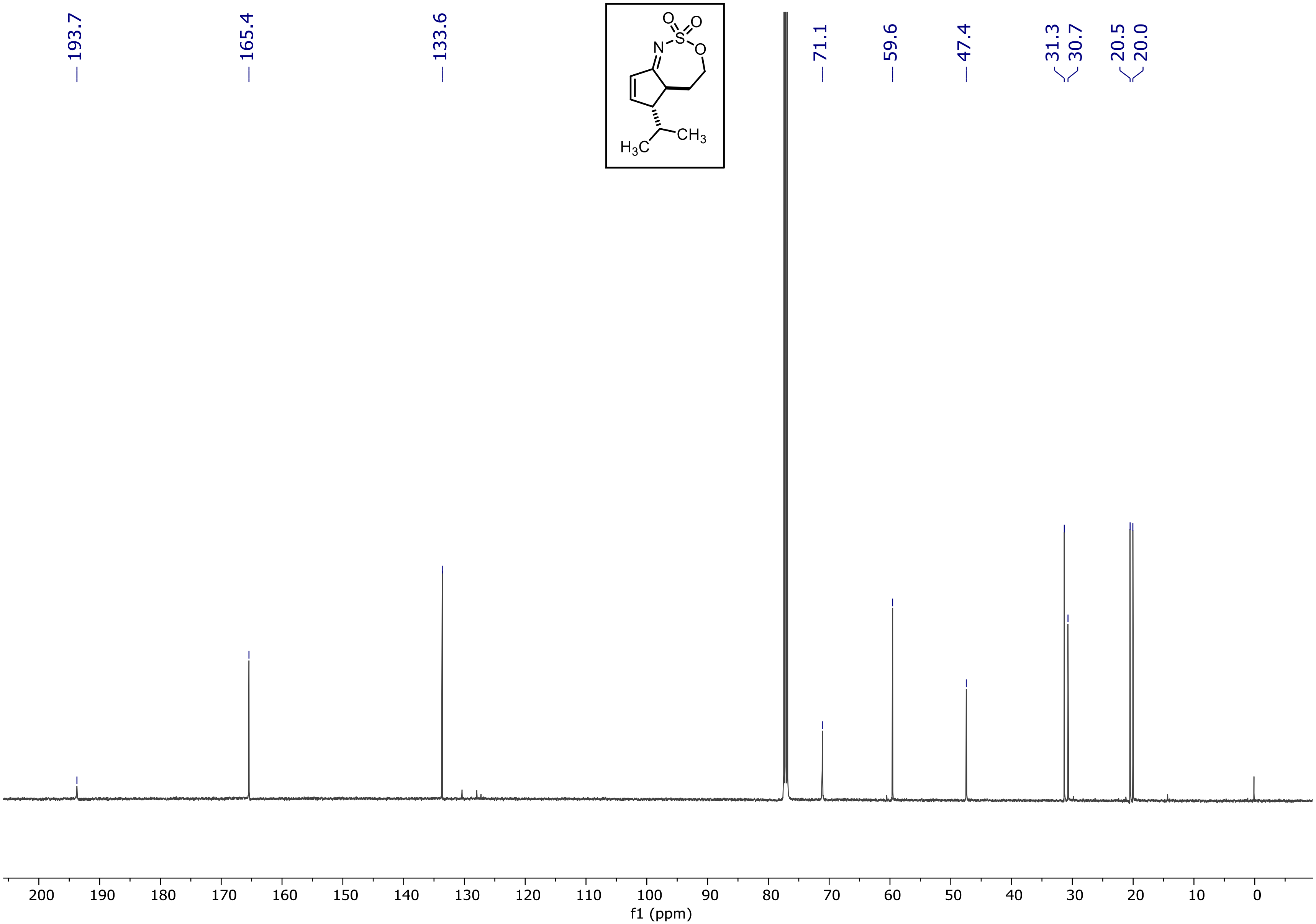


^{1}H NMR for Compound 6a.

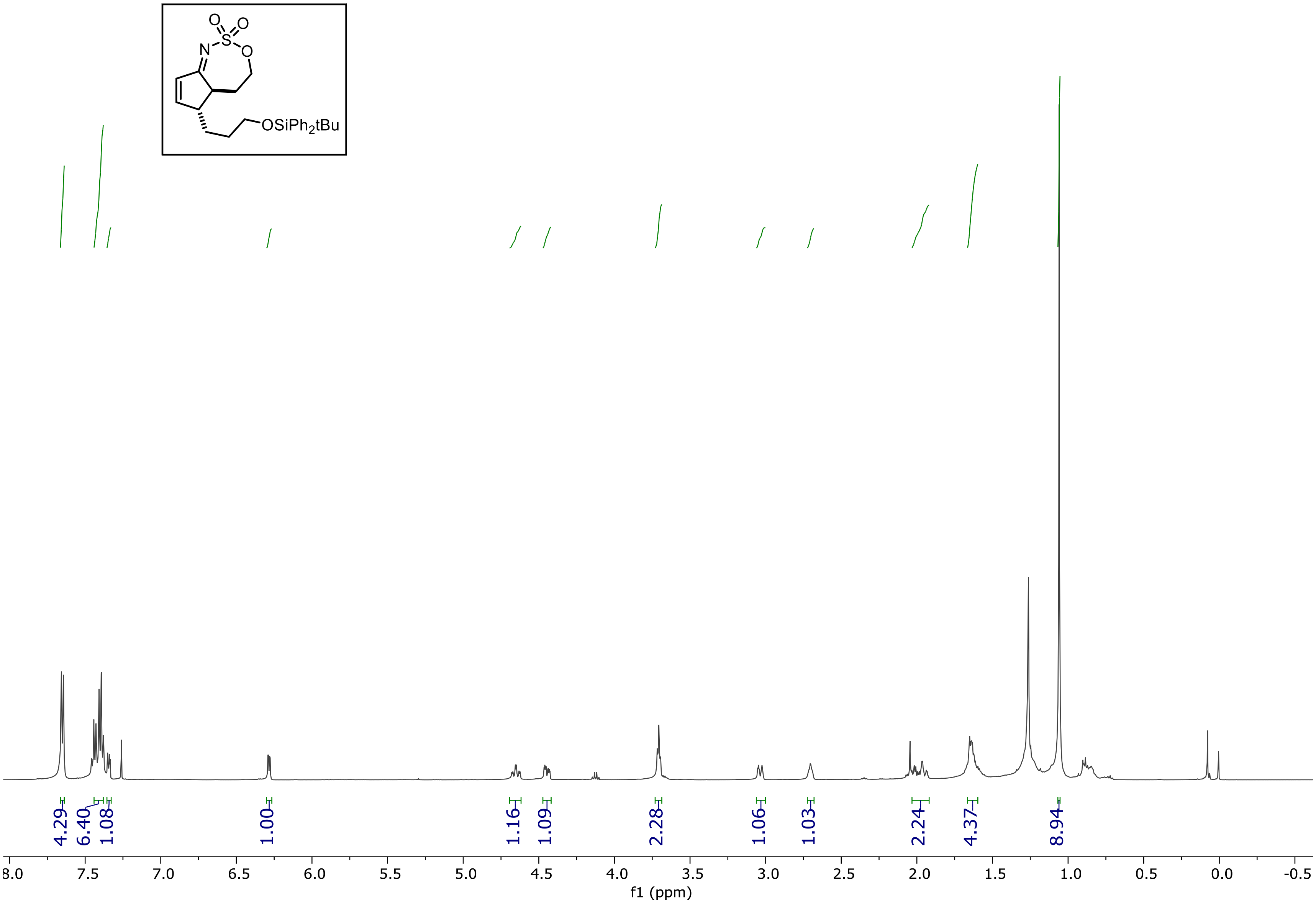




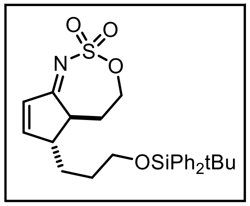
^{13}**C NMR for Compound 6a.**

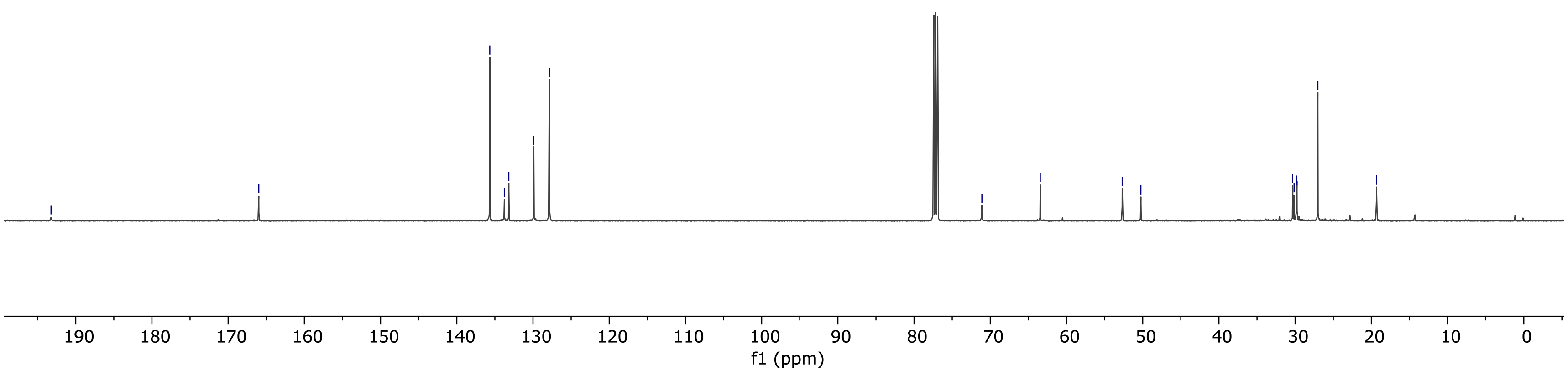


^{1}H NMR for Compound 7a.

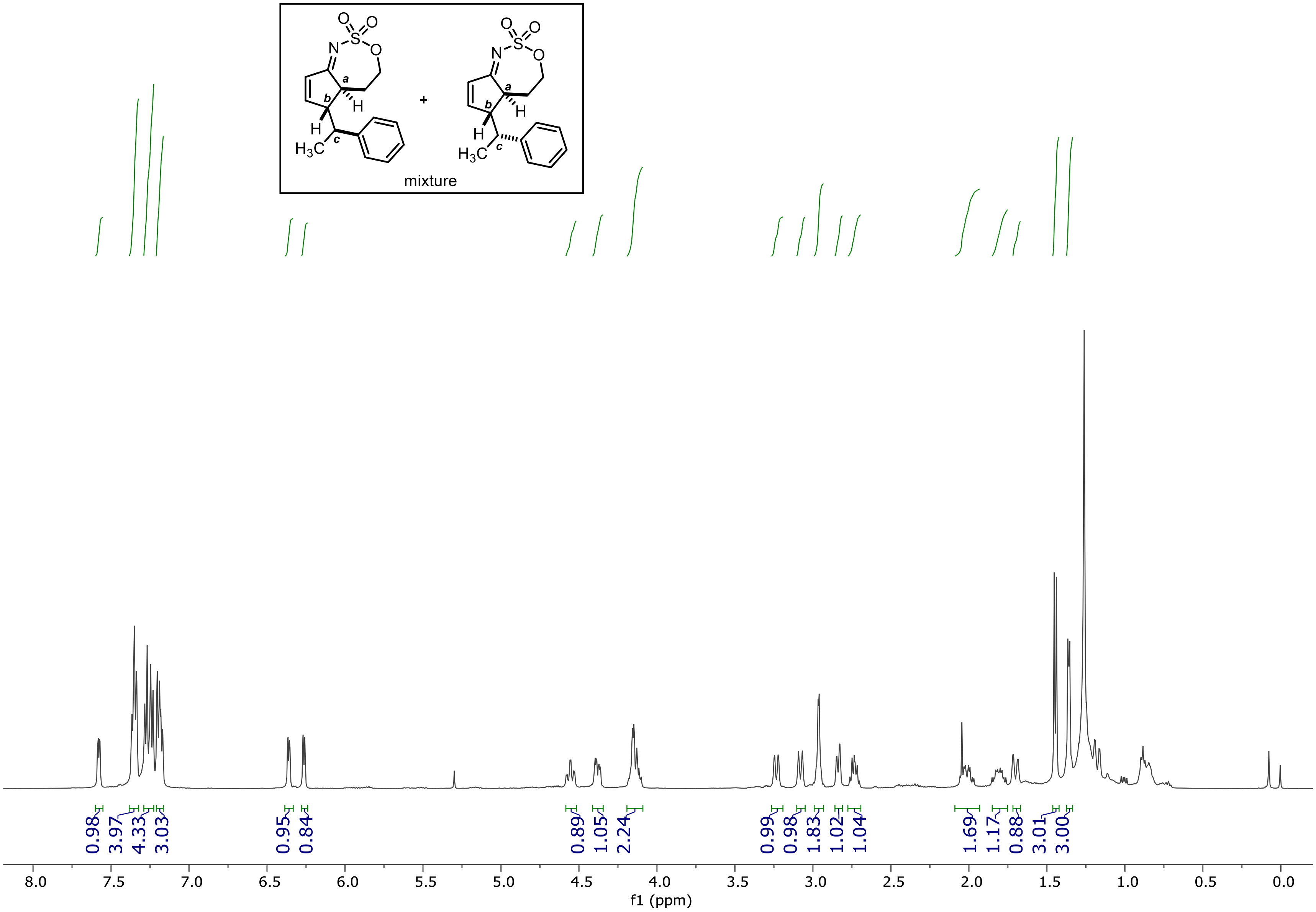


^{13}C NMR for Compound 7a.

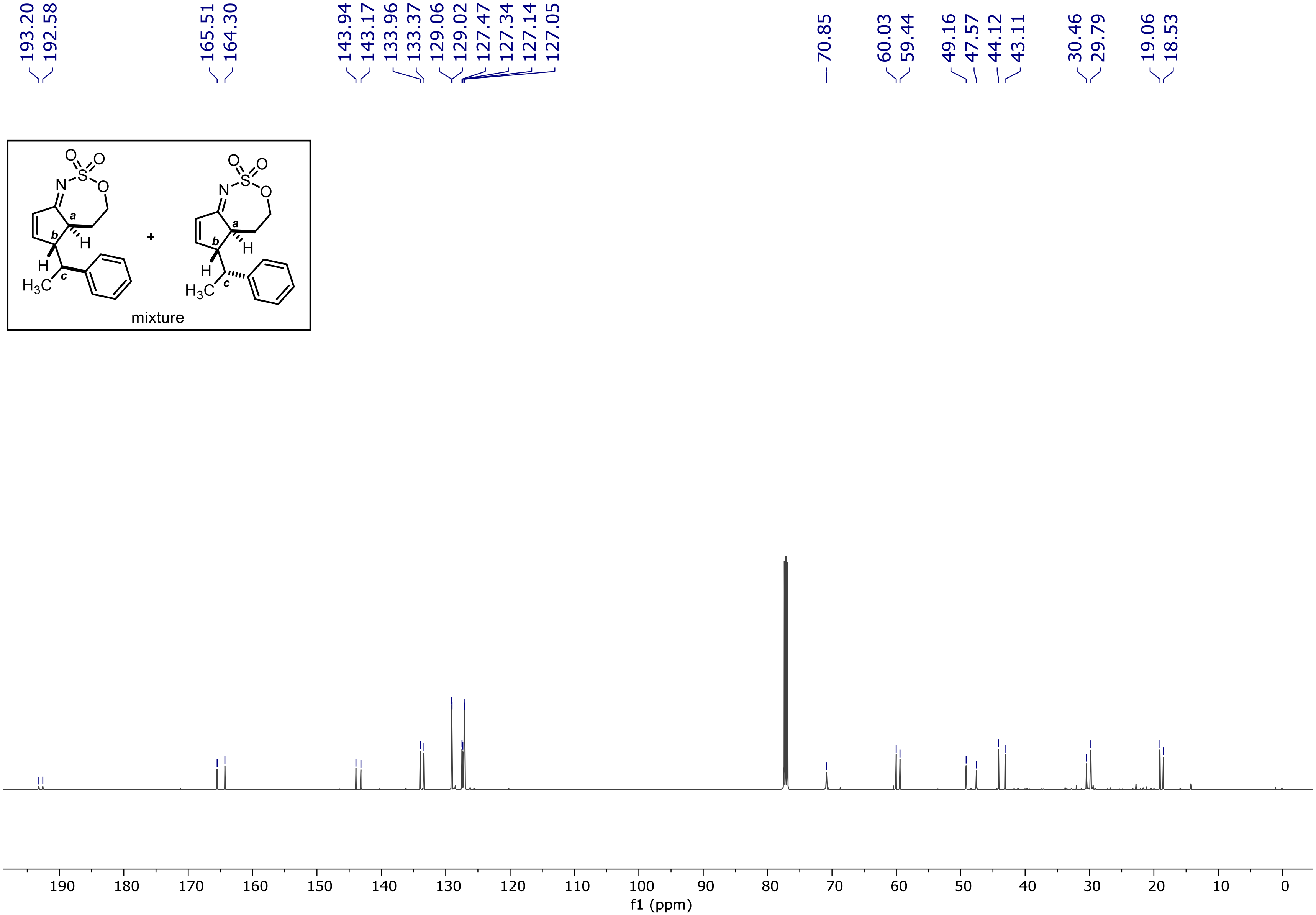




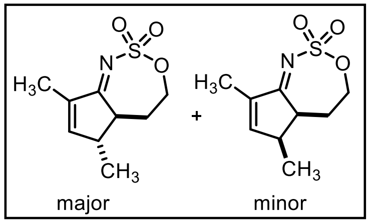
^{1}H NMR for Compound 8a.

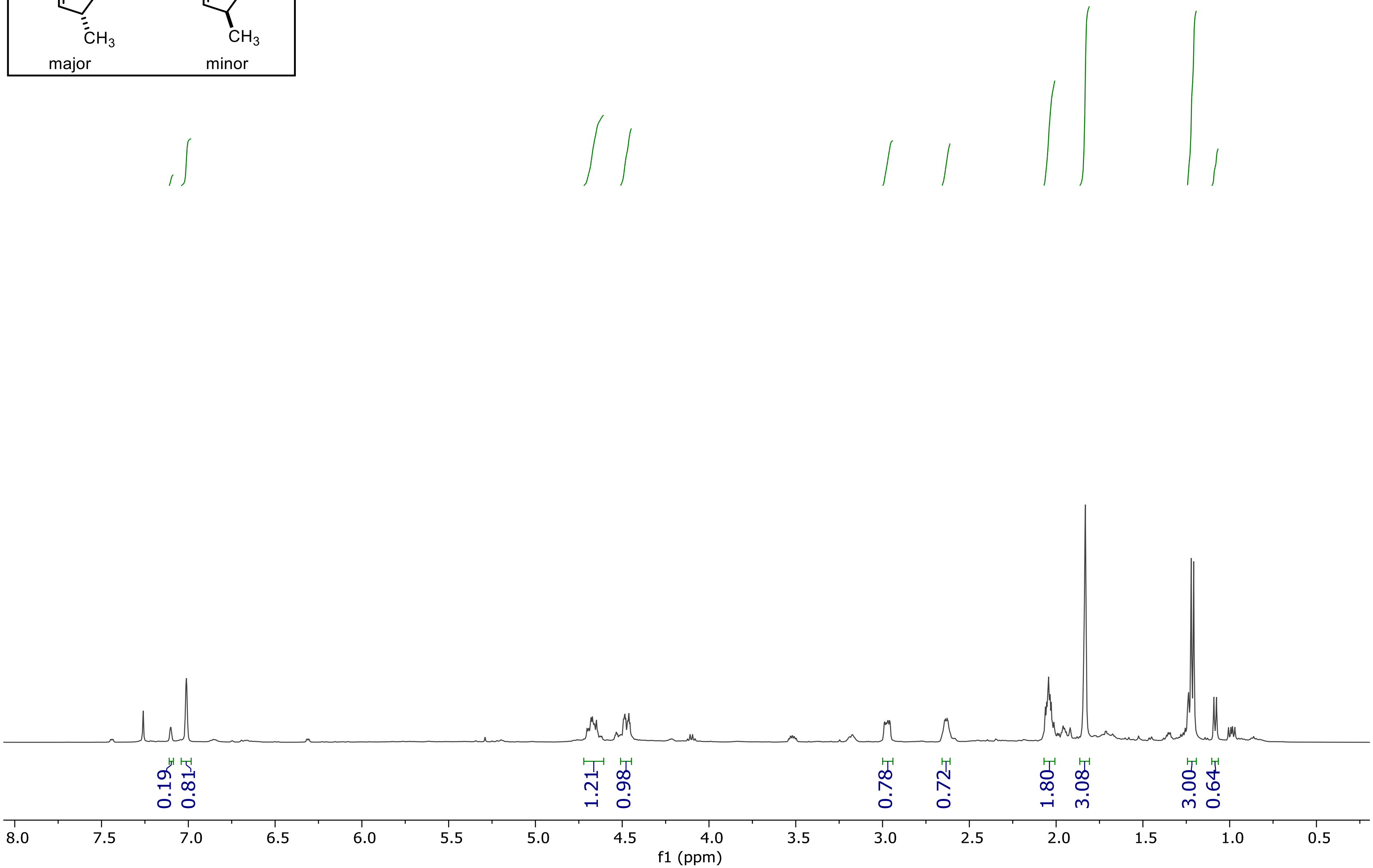


^{13}C NMR for Compound 8a.

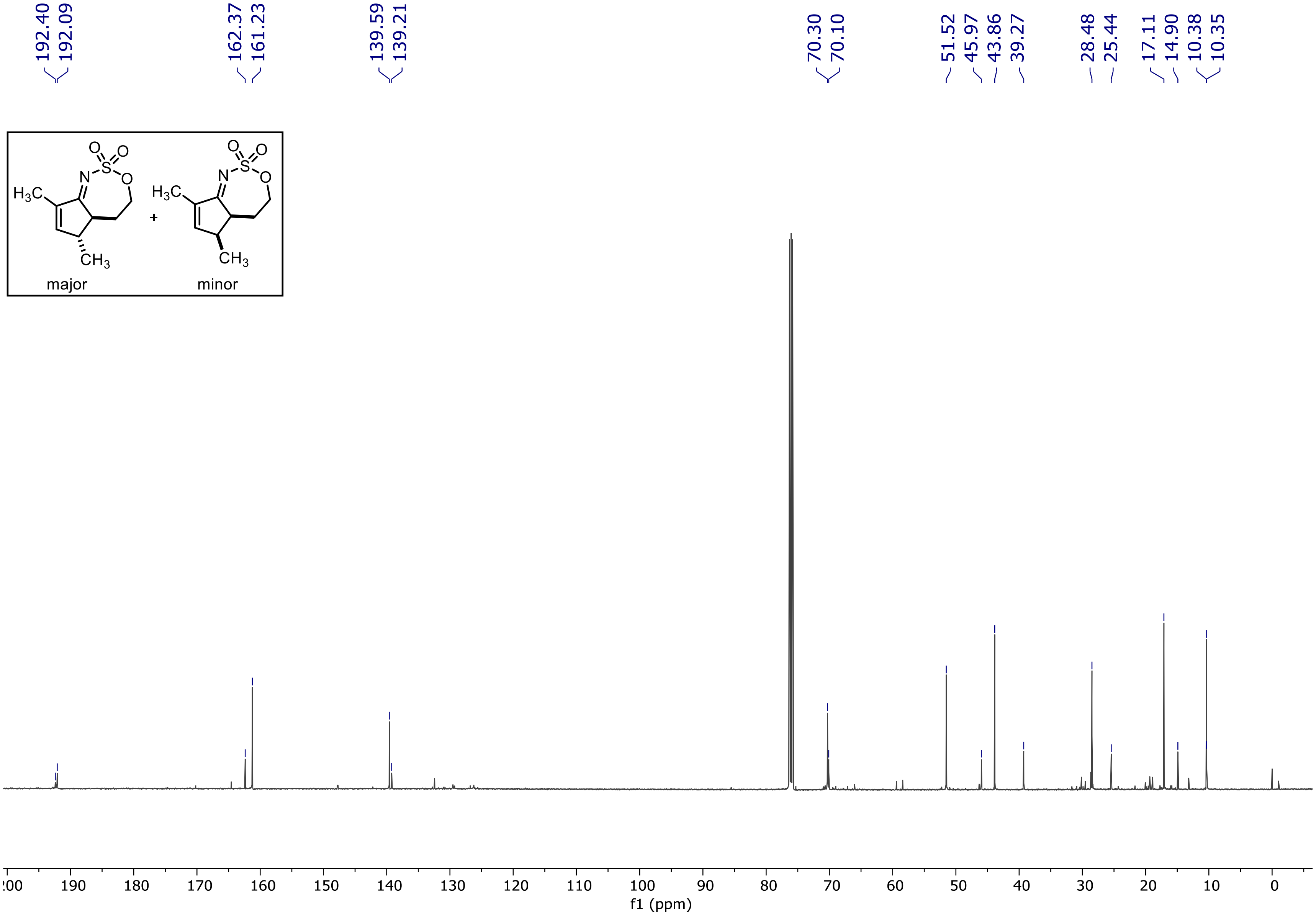


^{1}H NMR for Compound 9a.

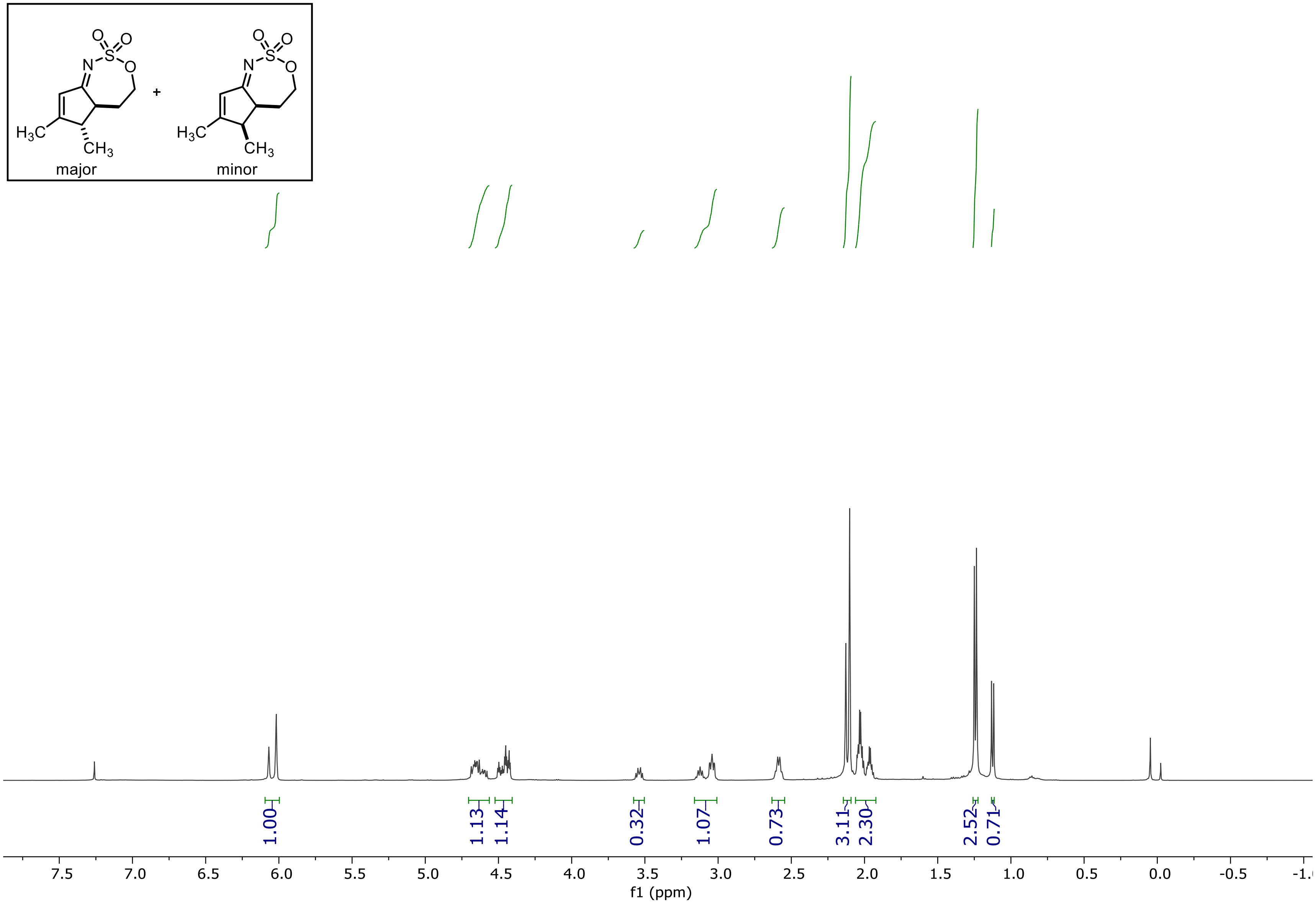




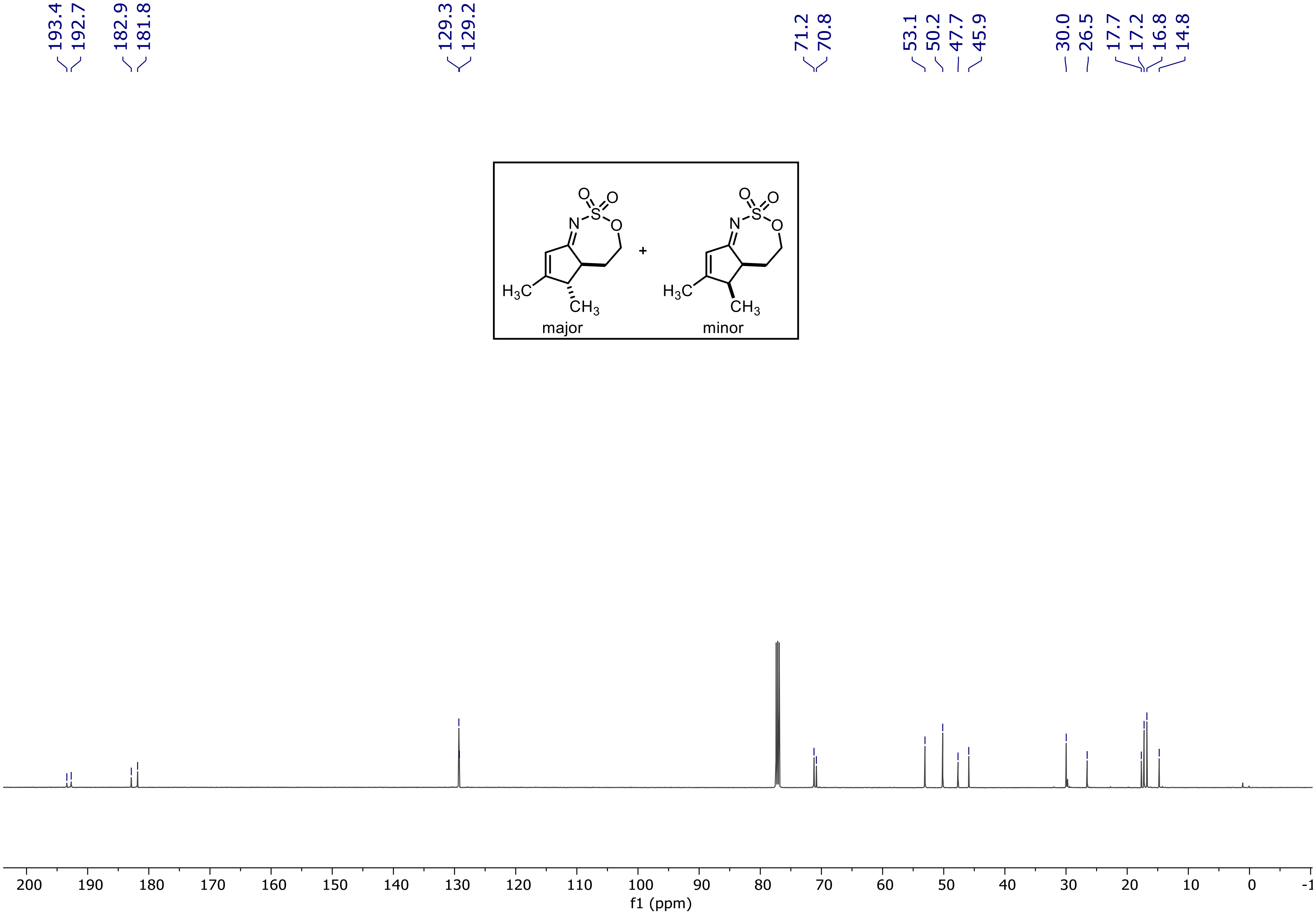
^{13}C NMR for Compound 9a.



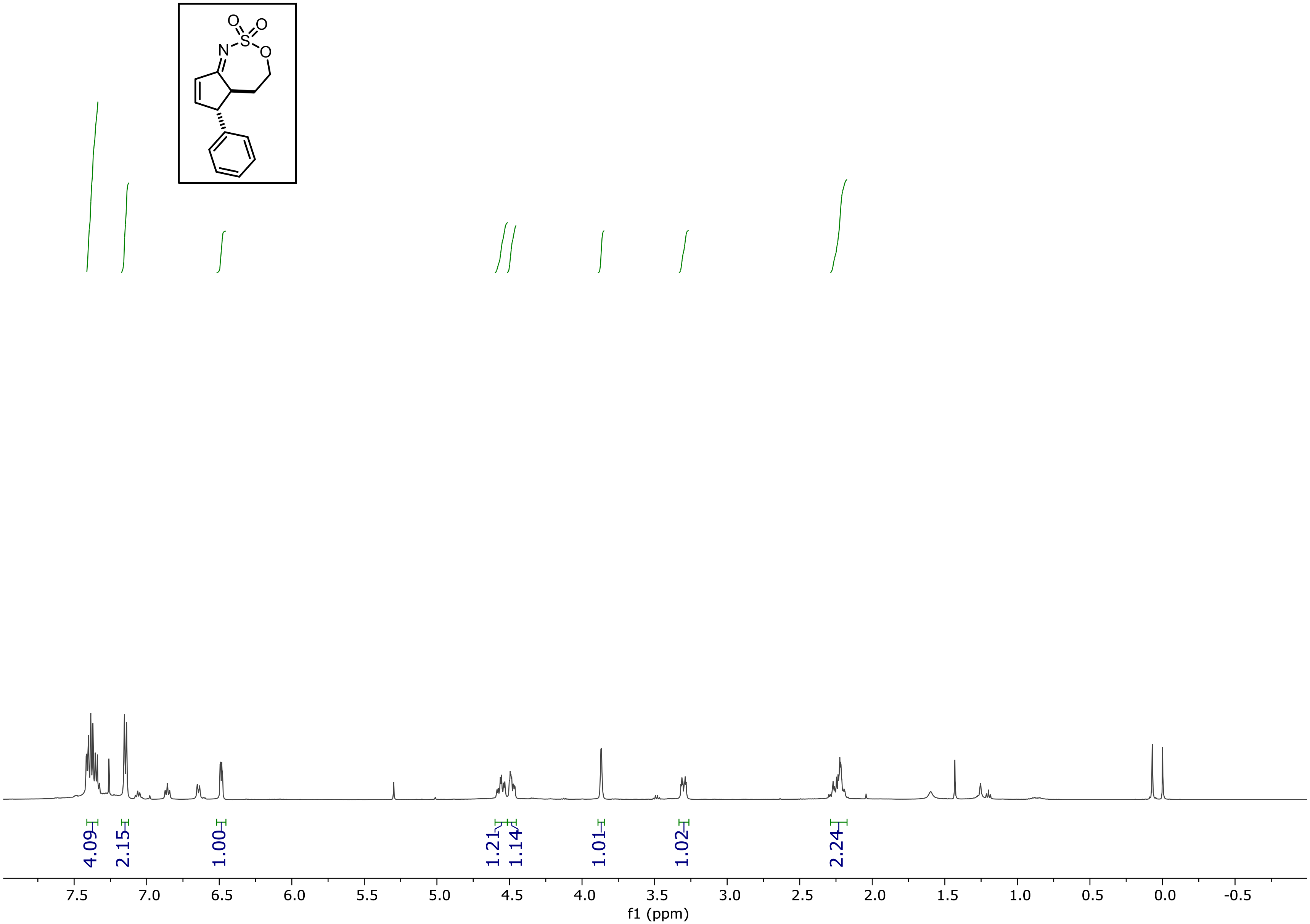
^{1}H NMR for Compound 10a.



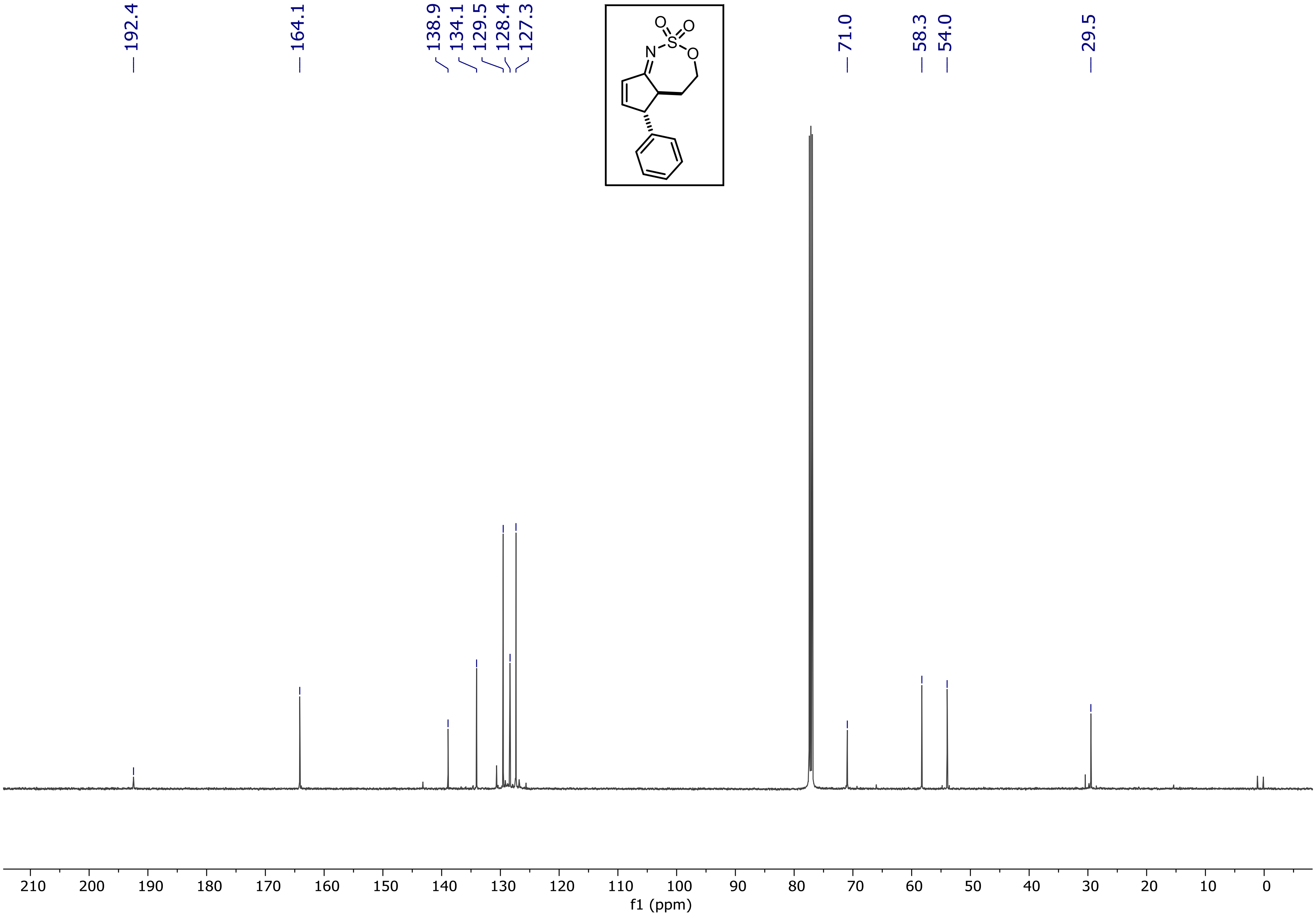
^{13}C NMR for Compound 10a.



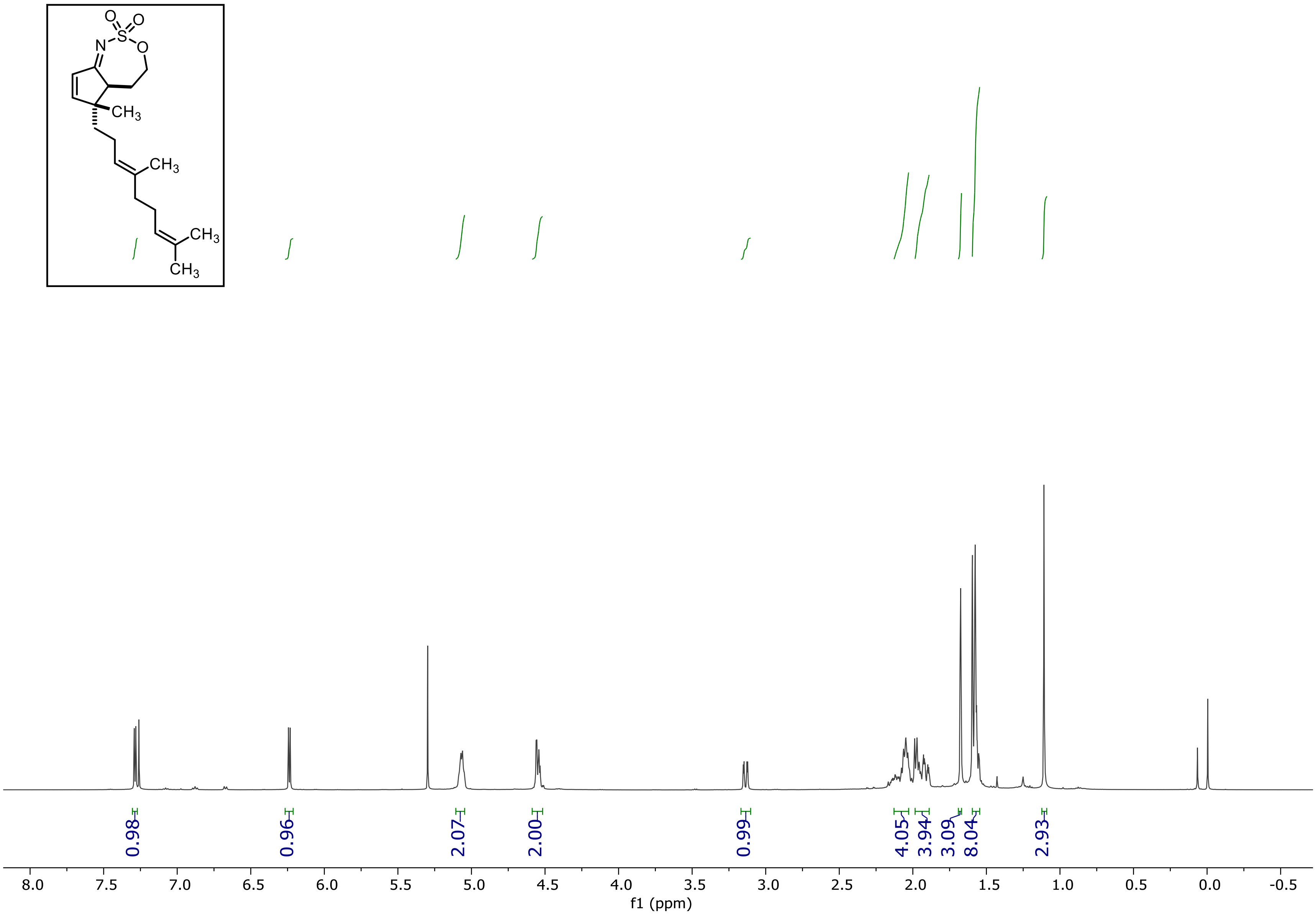
^{1}H NMR for Compound 11a.



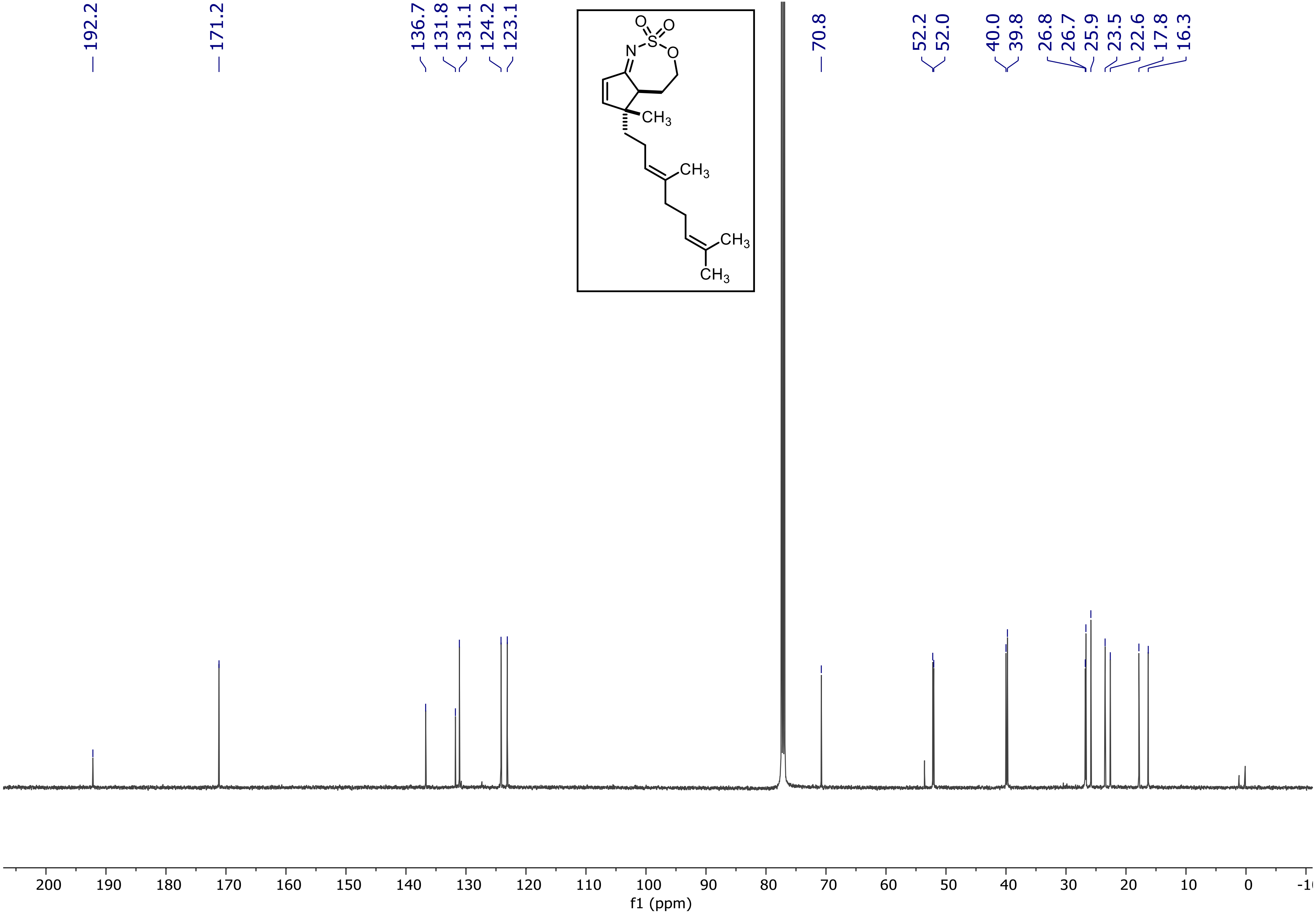
^{13}C NMR for Compound 11a.



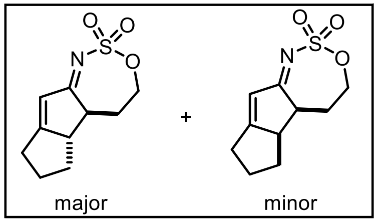
^{1}H NMR for Compound 12a.

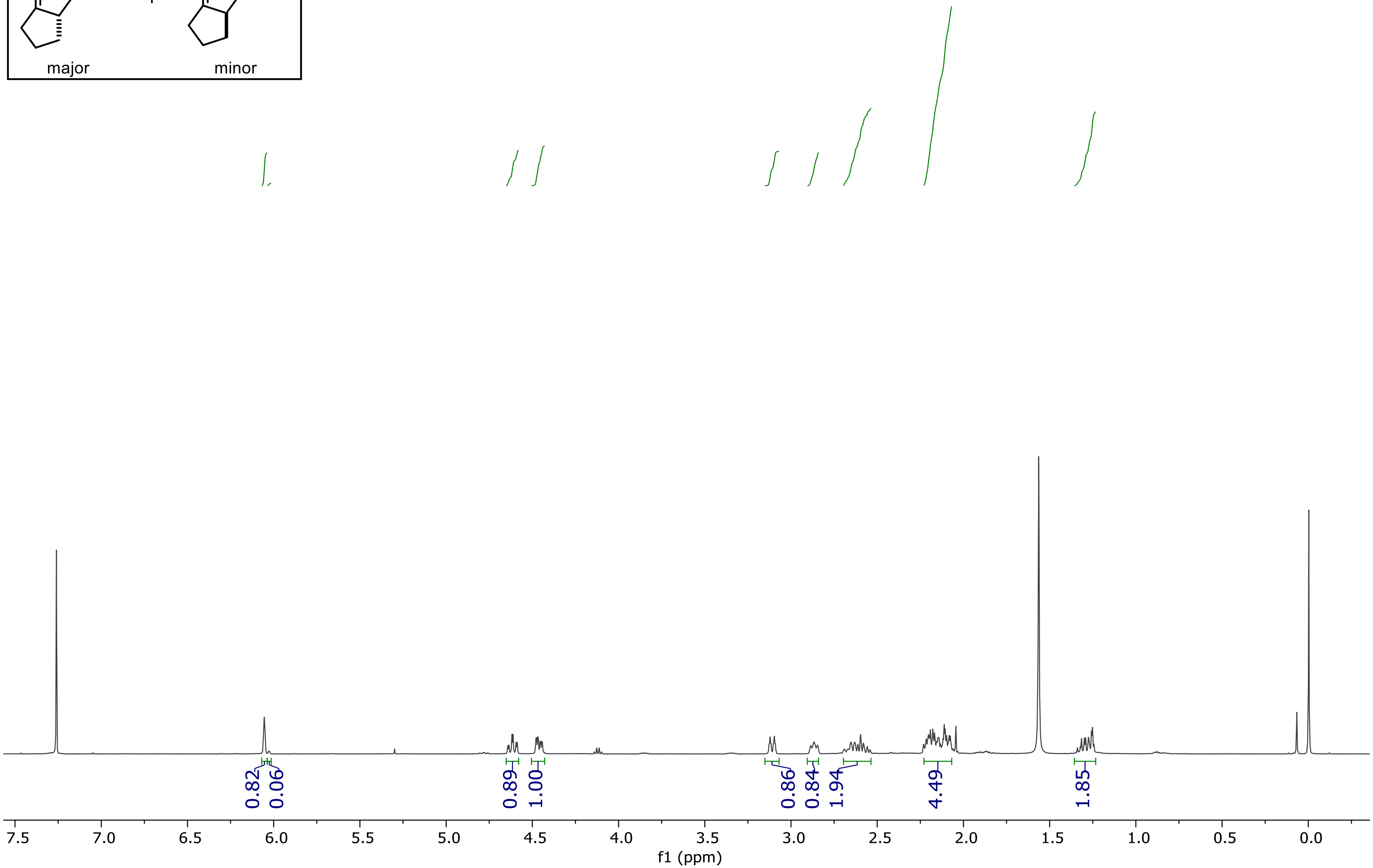


^{13}C NMR for Compound 12a.

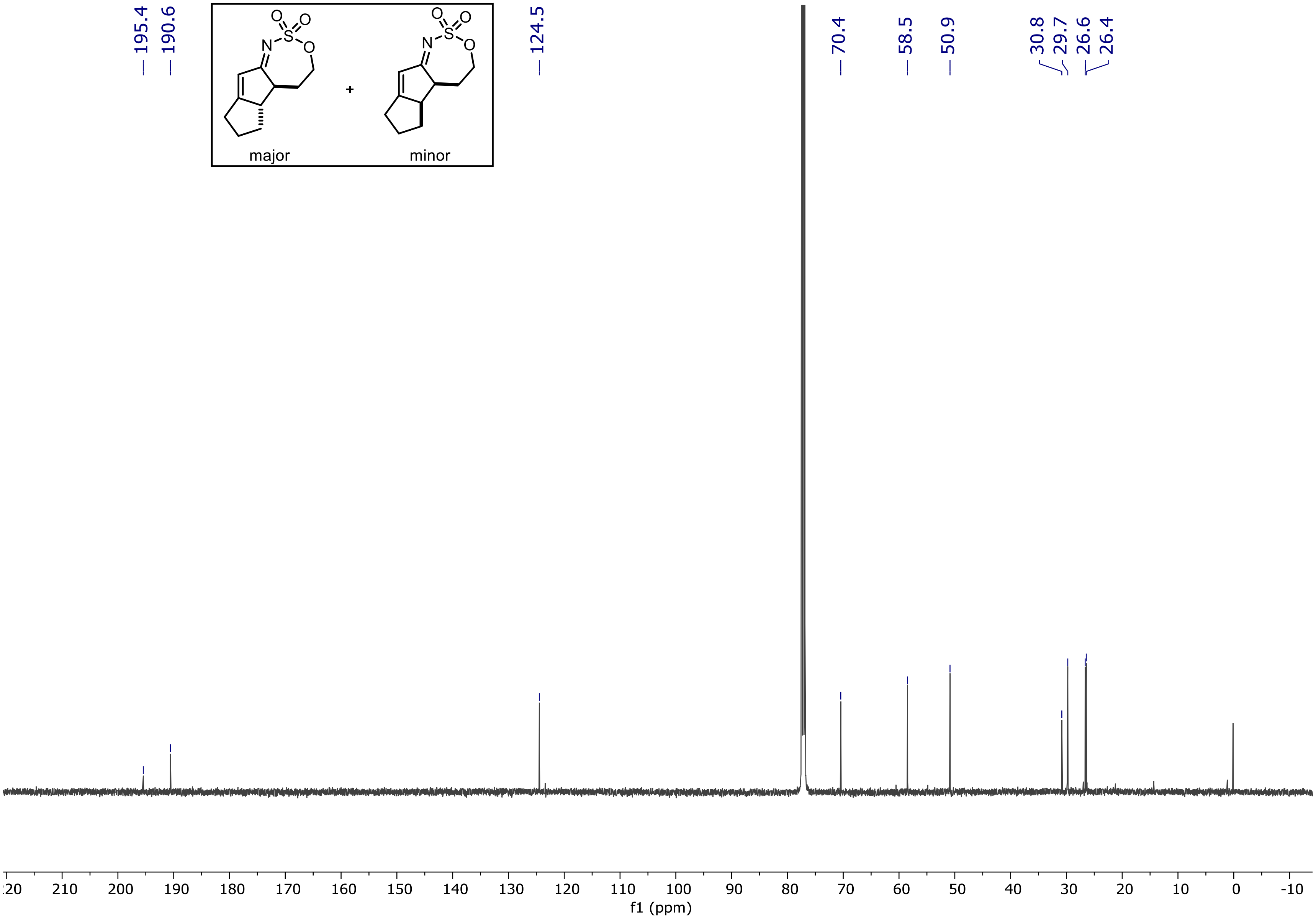


^{1}H NMR for Compound 13a.

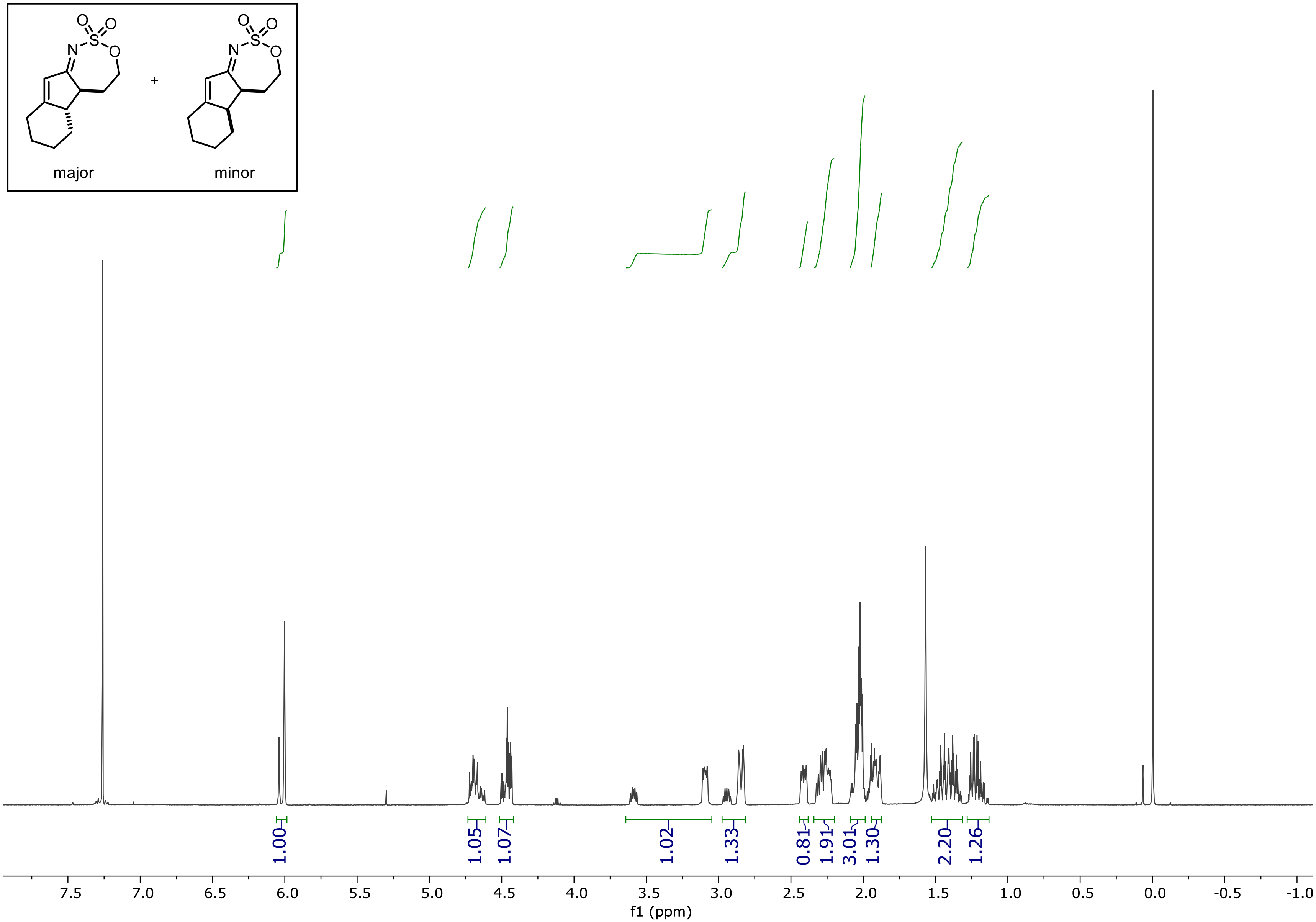




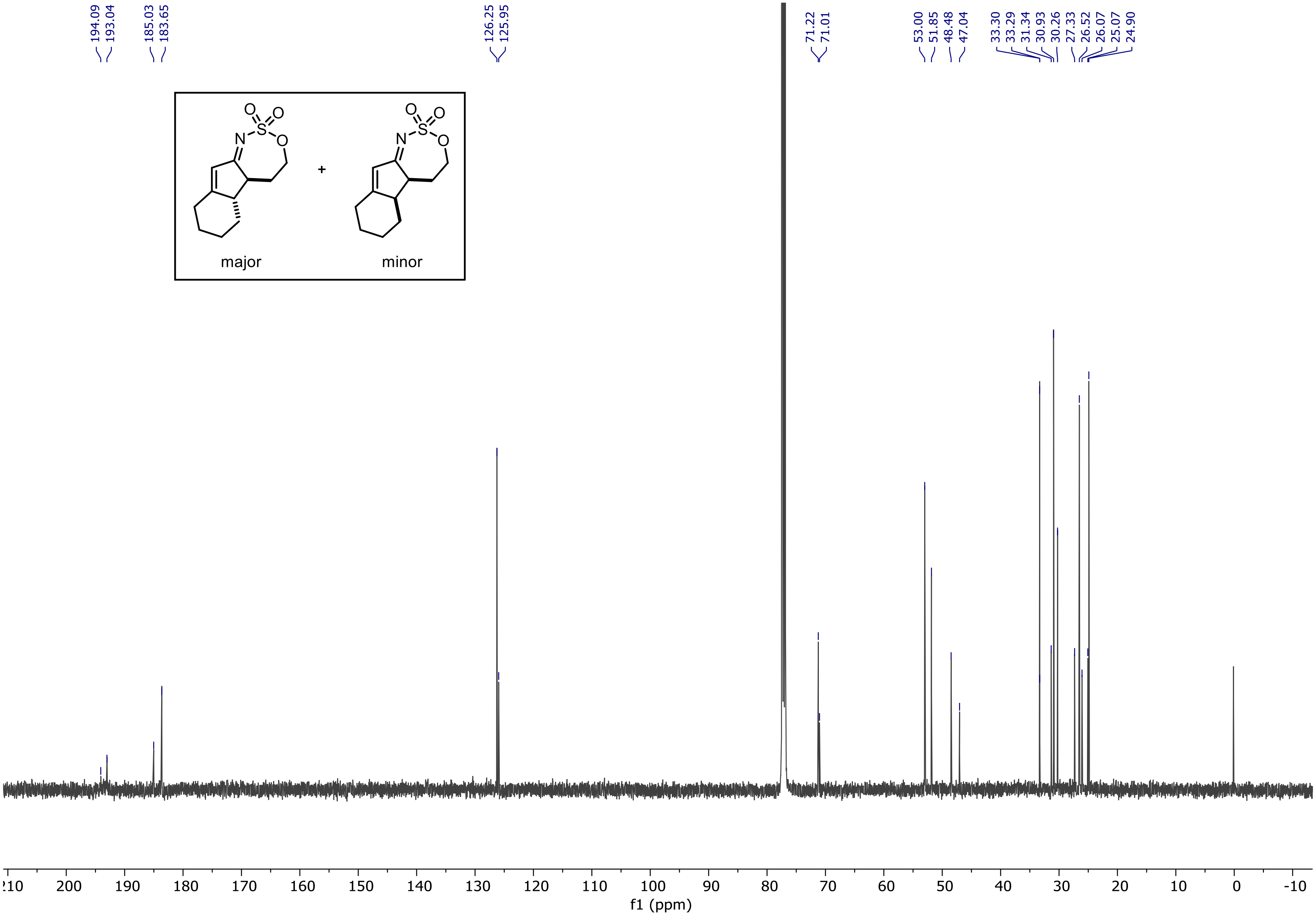
^{13}C NMR for Compound 13a.



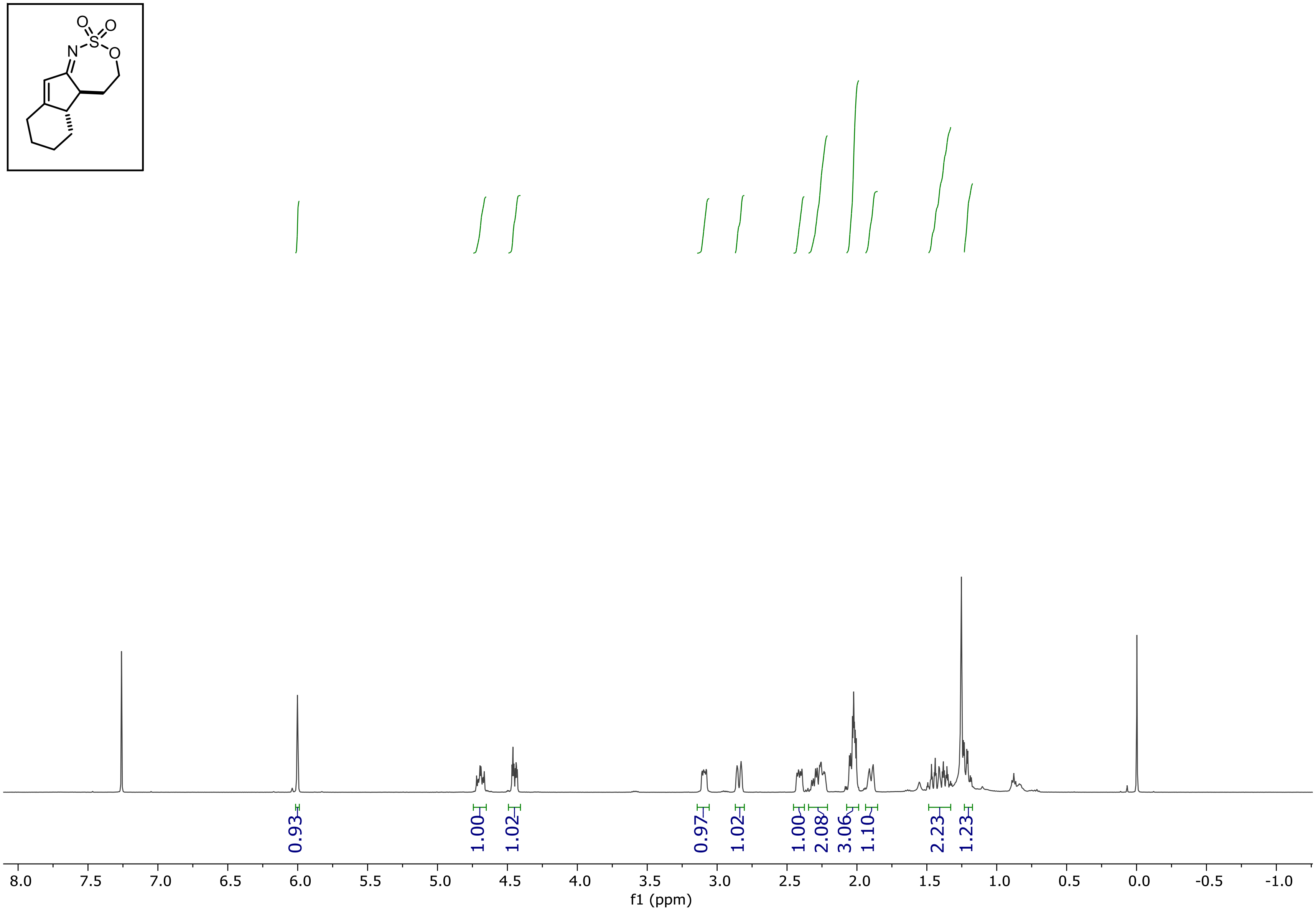
^{1}H NMR for Compound 14a.



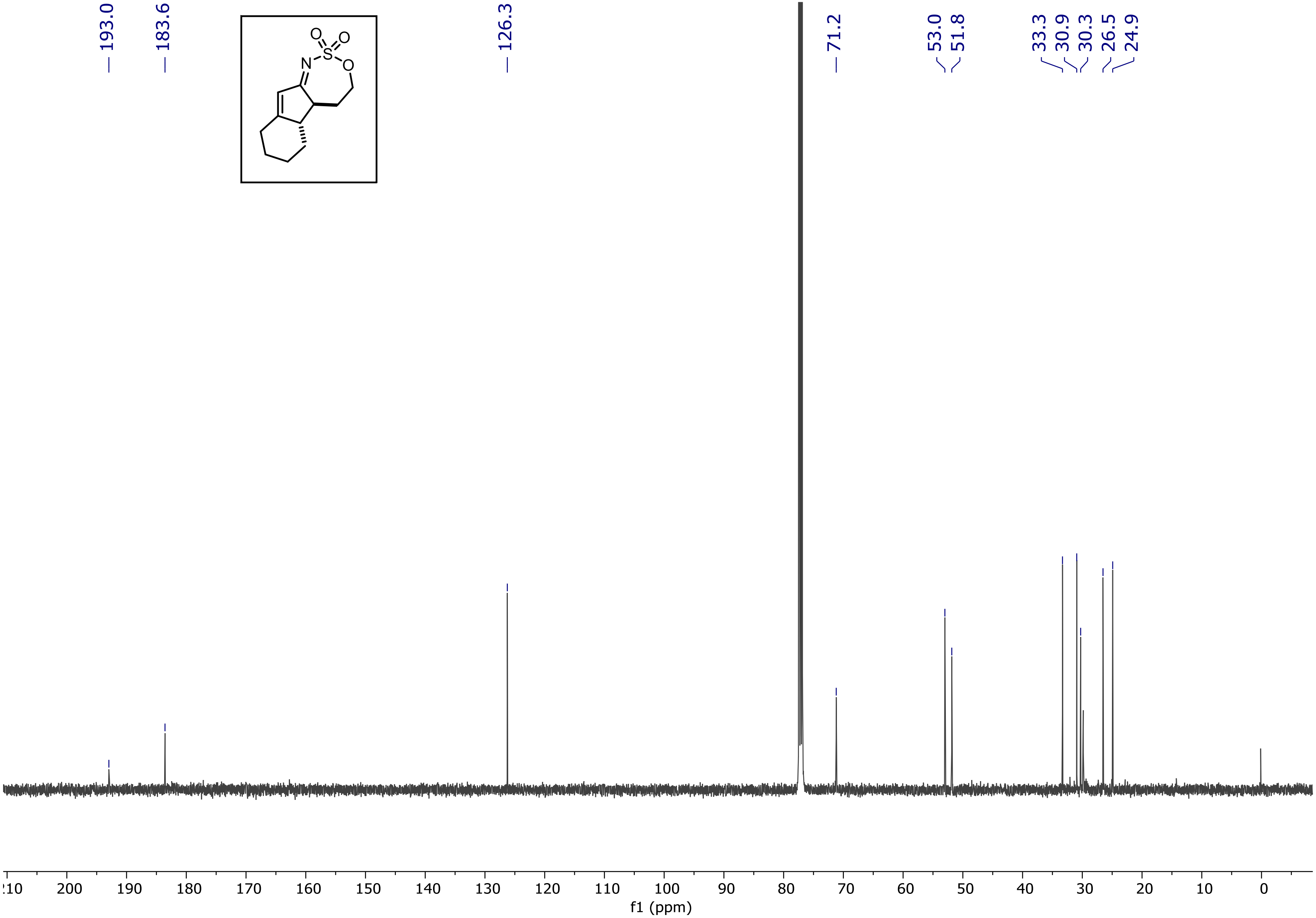
^{13}C NMR for Compound 14a.



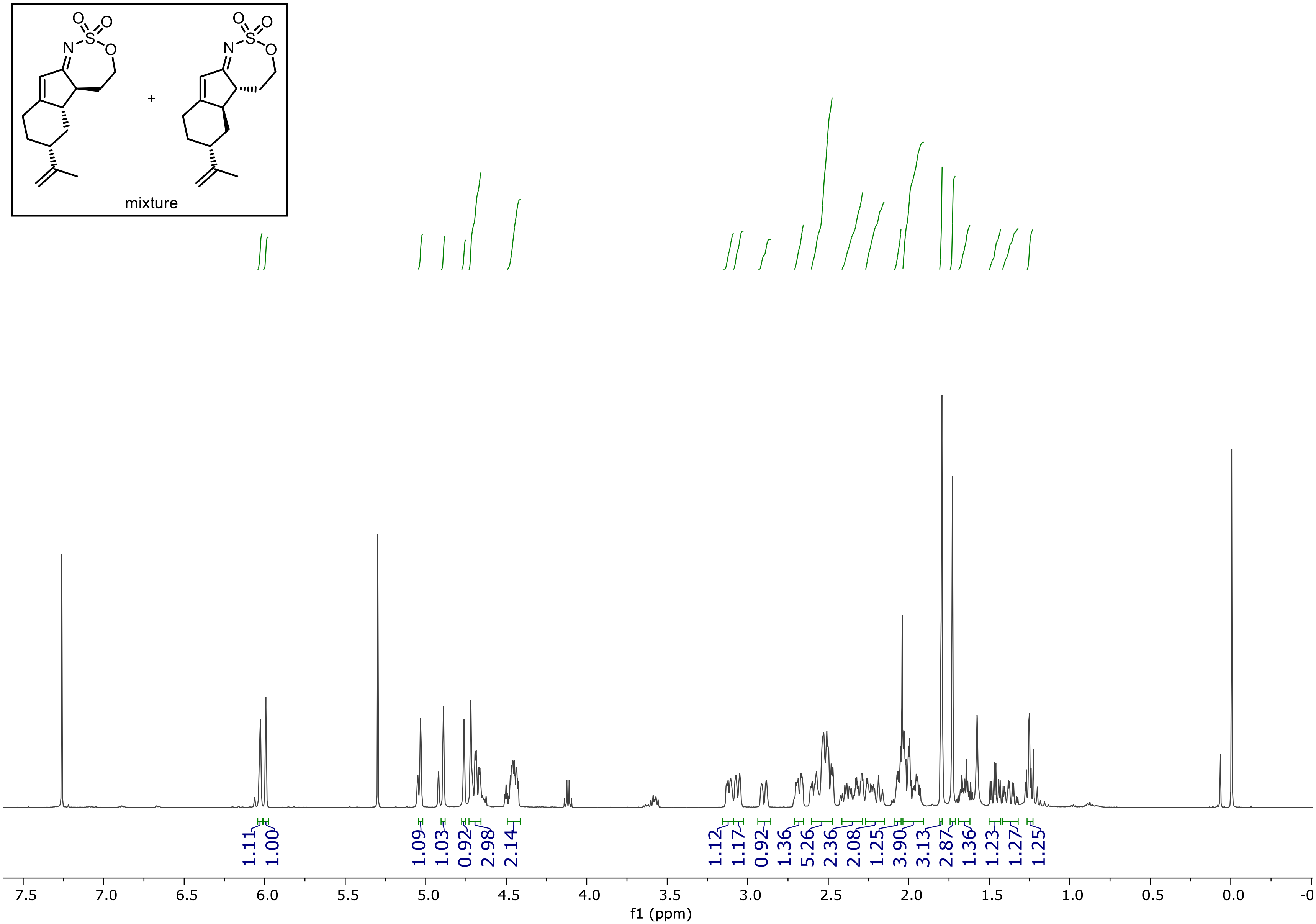
^{1}H NMR for Compound *anti*-14a.



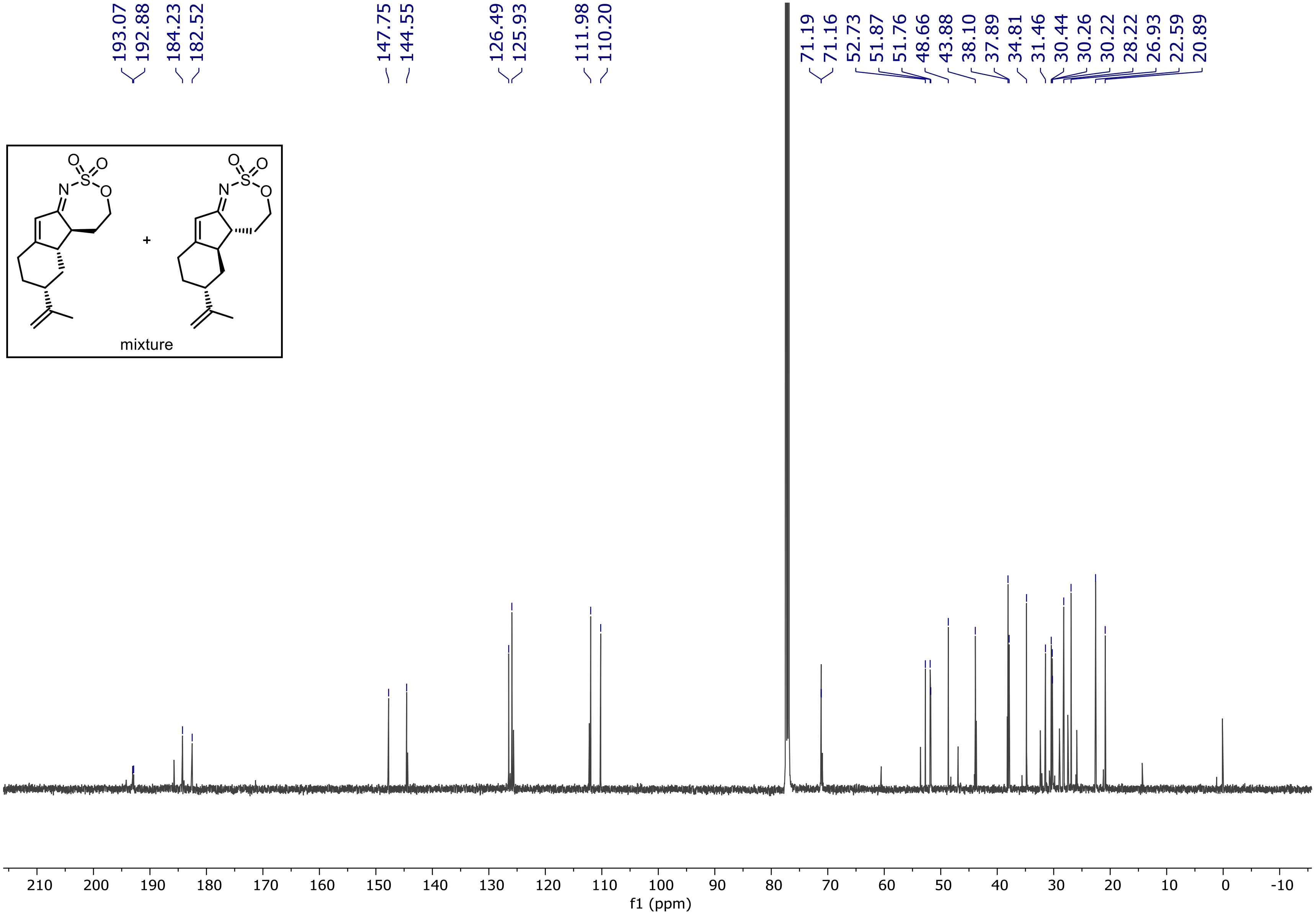
^{13}C NMR for Compound *anti*-14a.



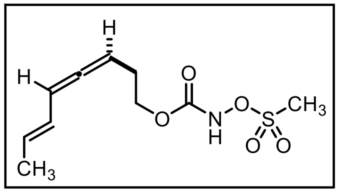
^{1}H NMR for Compound 15a.

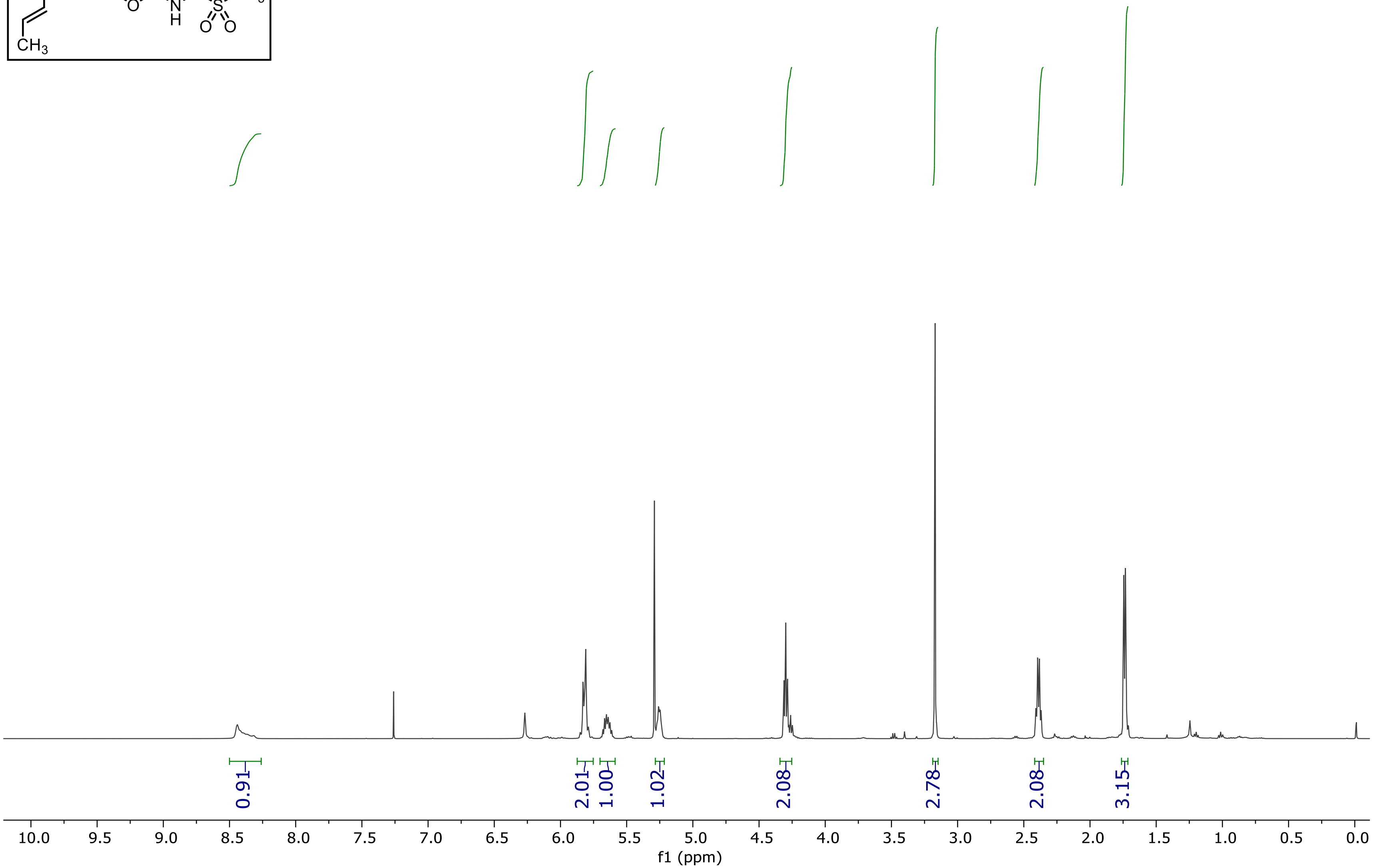


^{13}C NMR for Compound 15a.

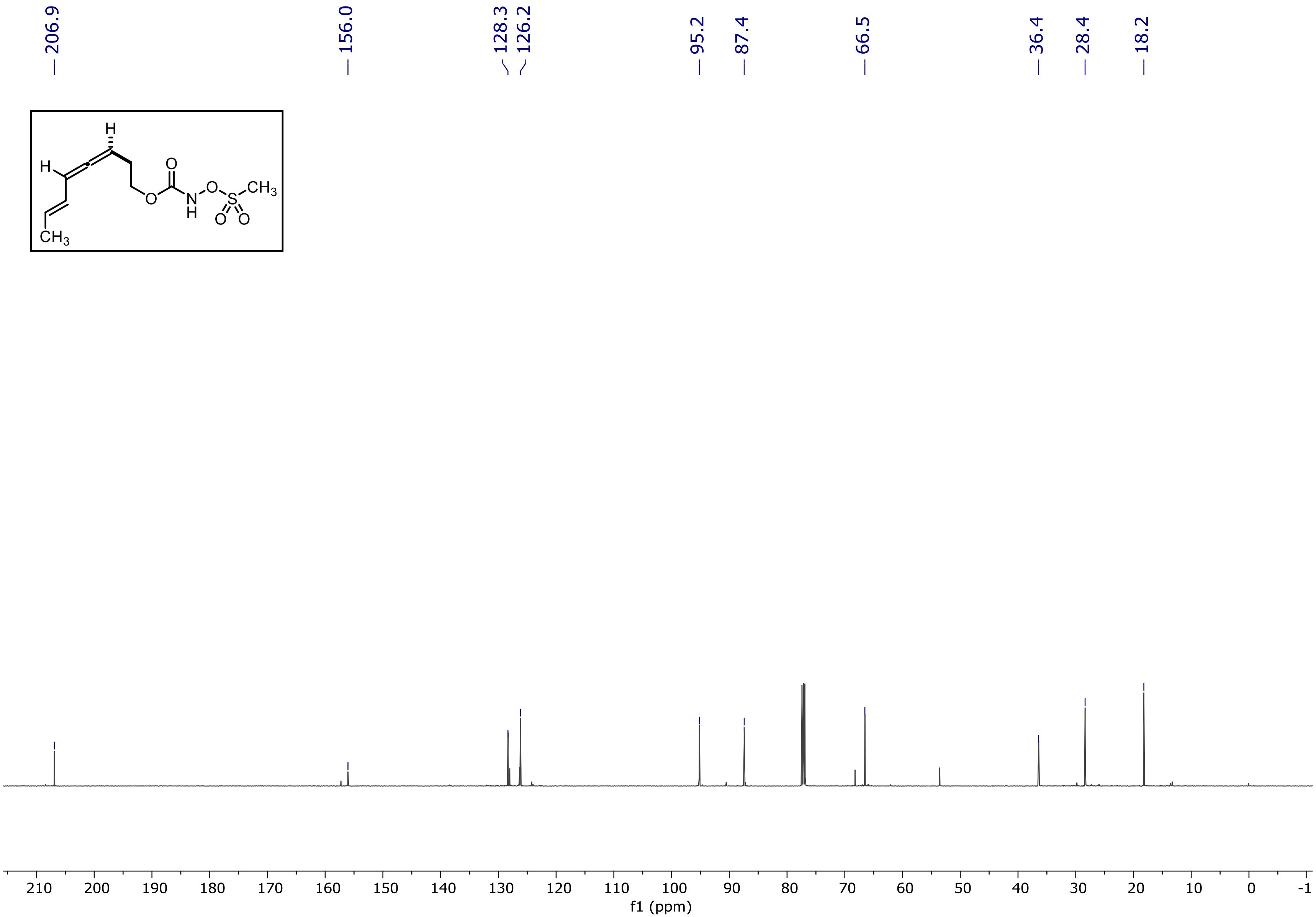


^{1}H NMR for Compound S-22.

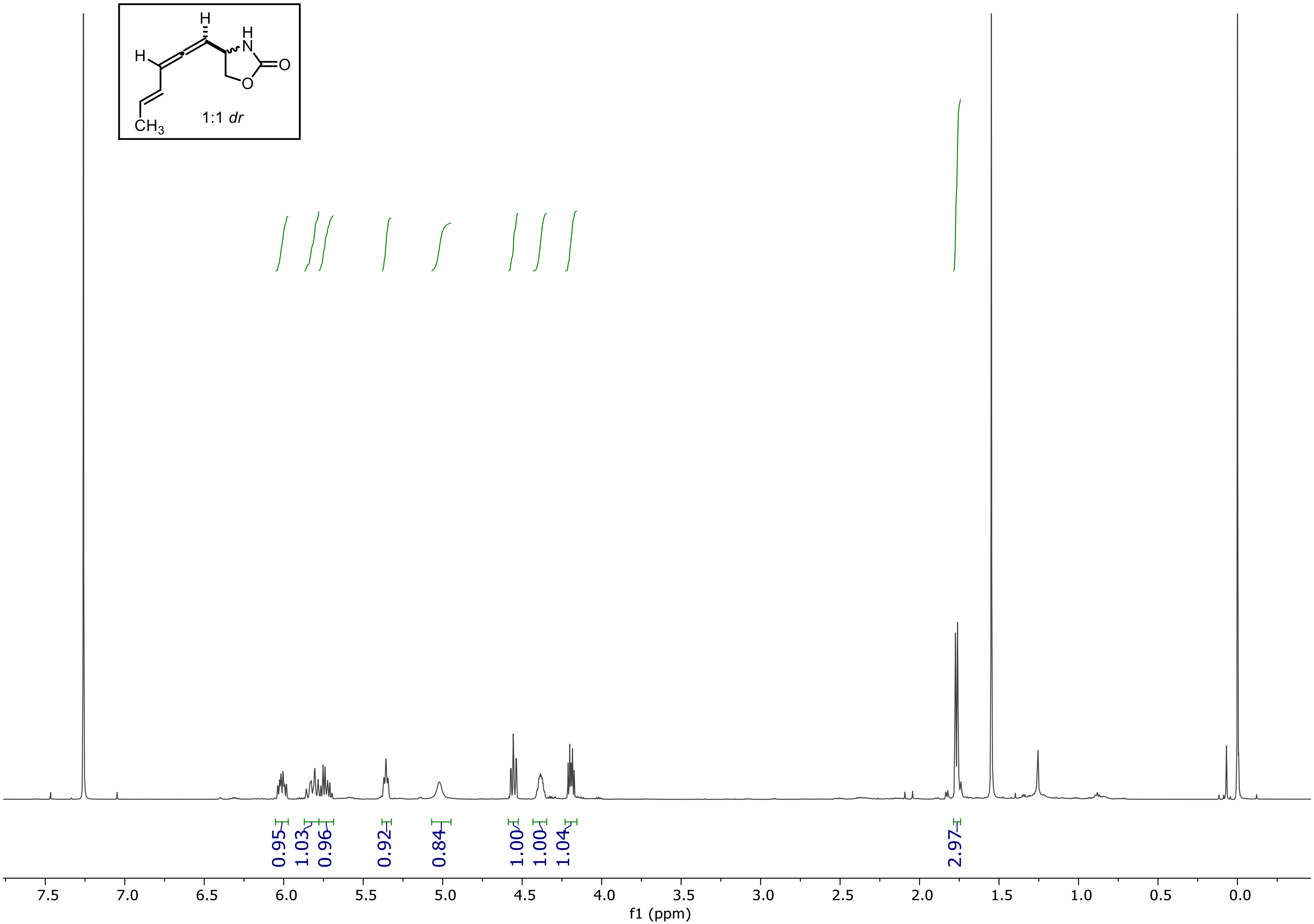




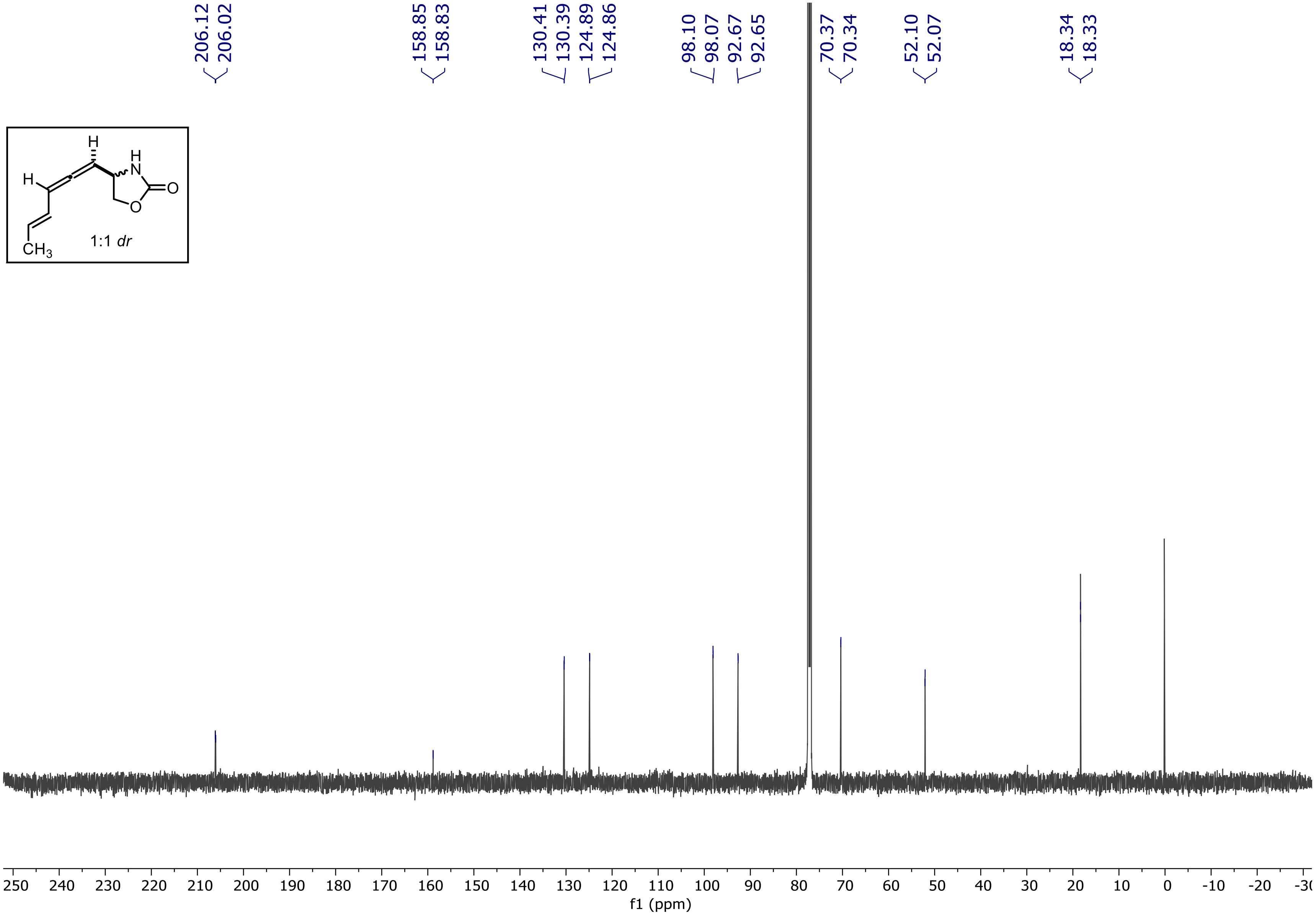
^{13}C NMR for Compound S-22.



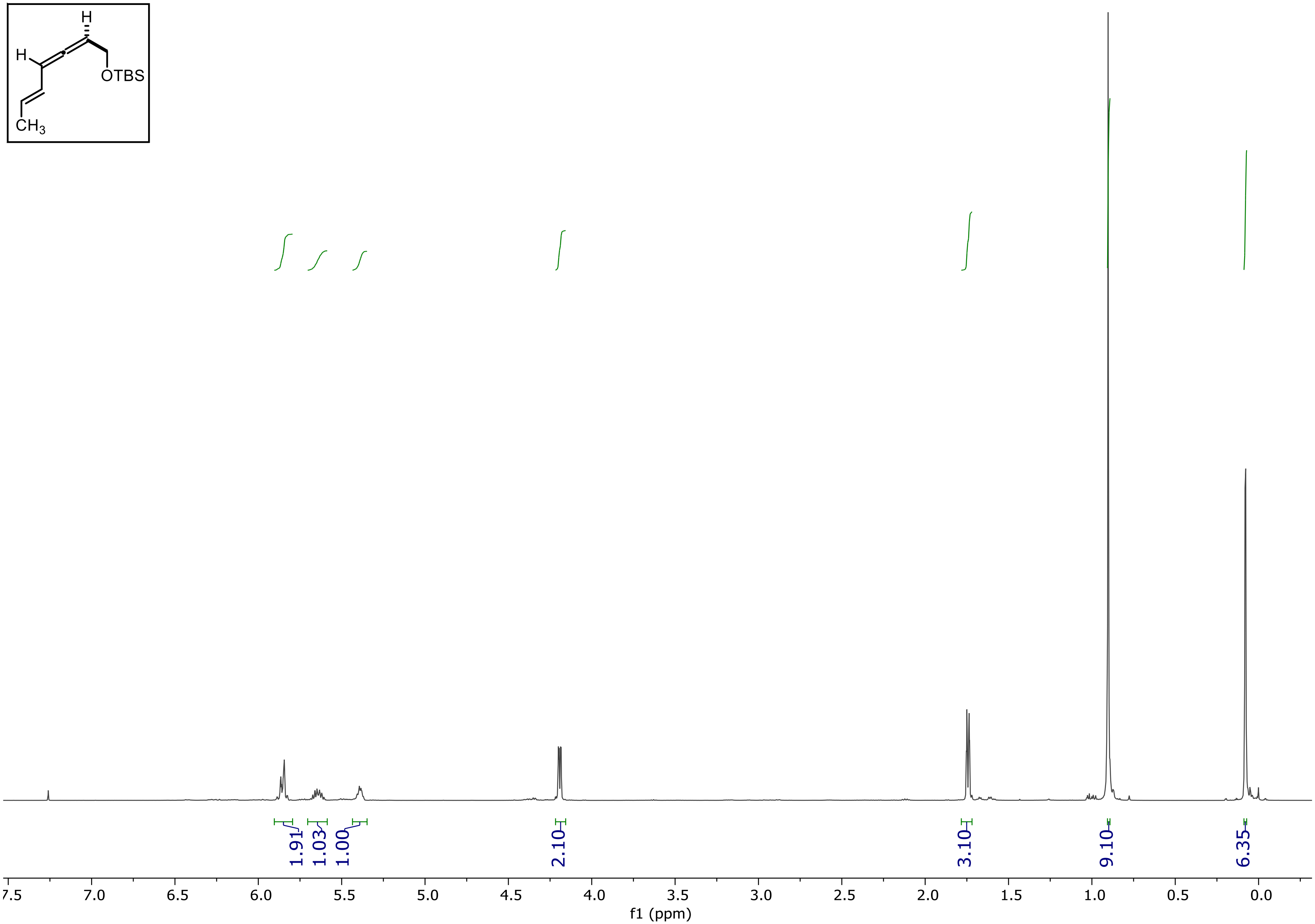
^{1}H NMR for Compound S-23.



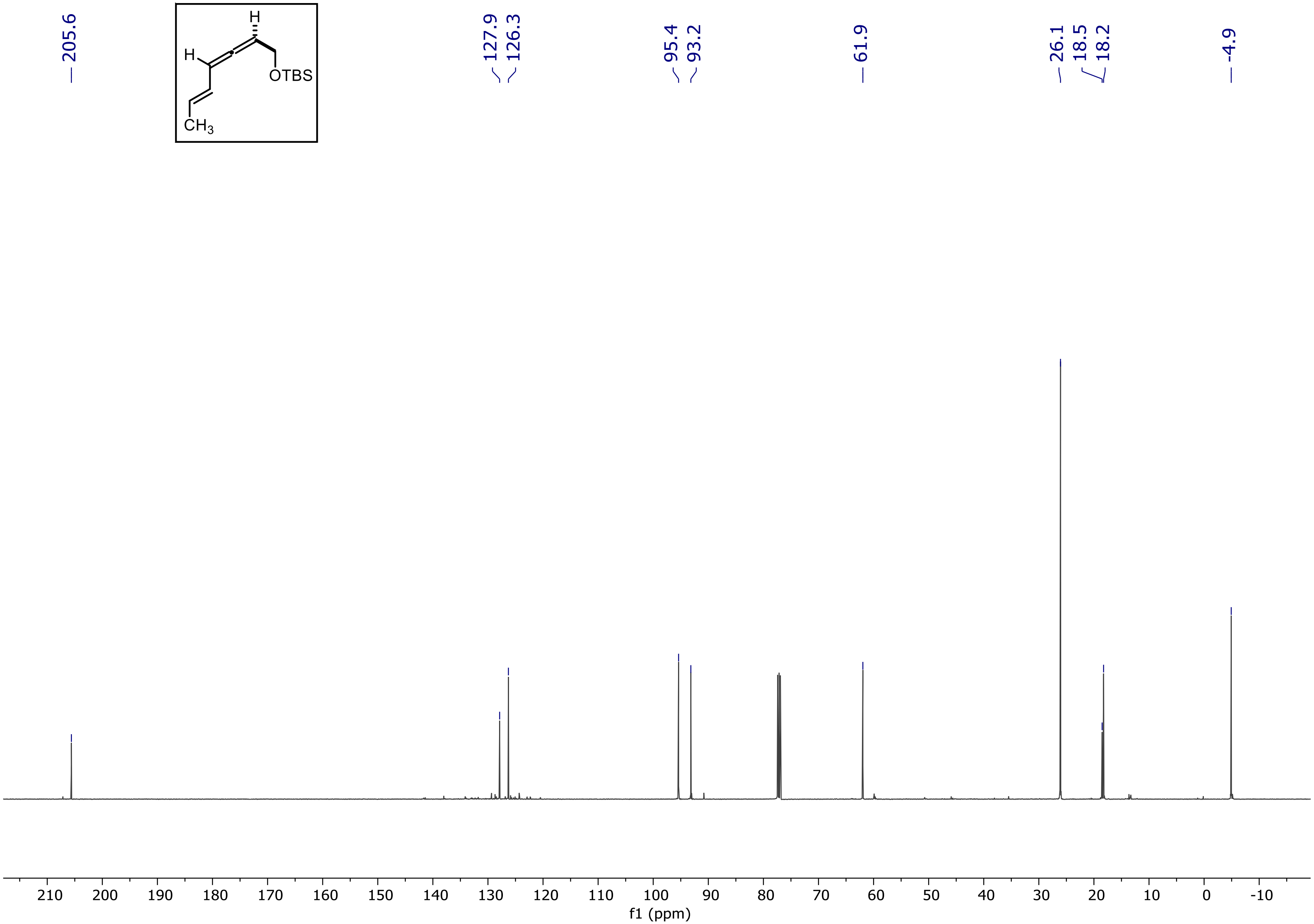
^{13}C NMR for Compound S-23.



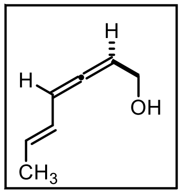
^{1}H NMR for Compound S-24.

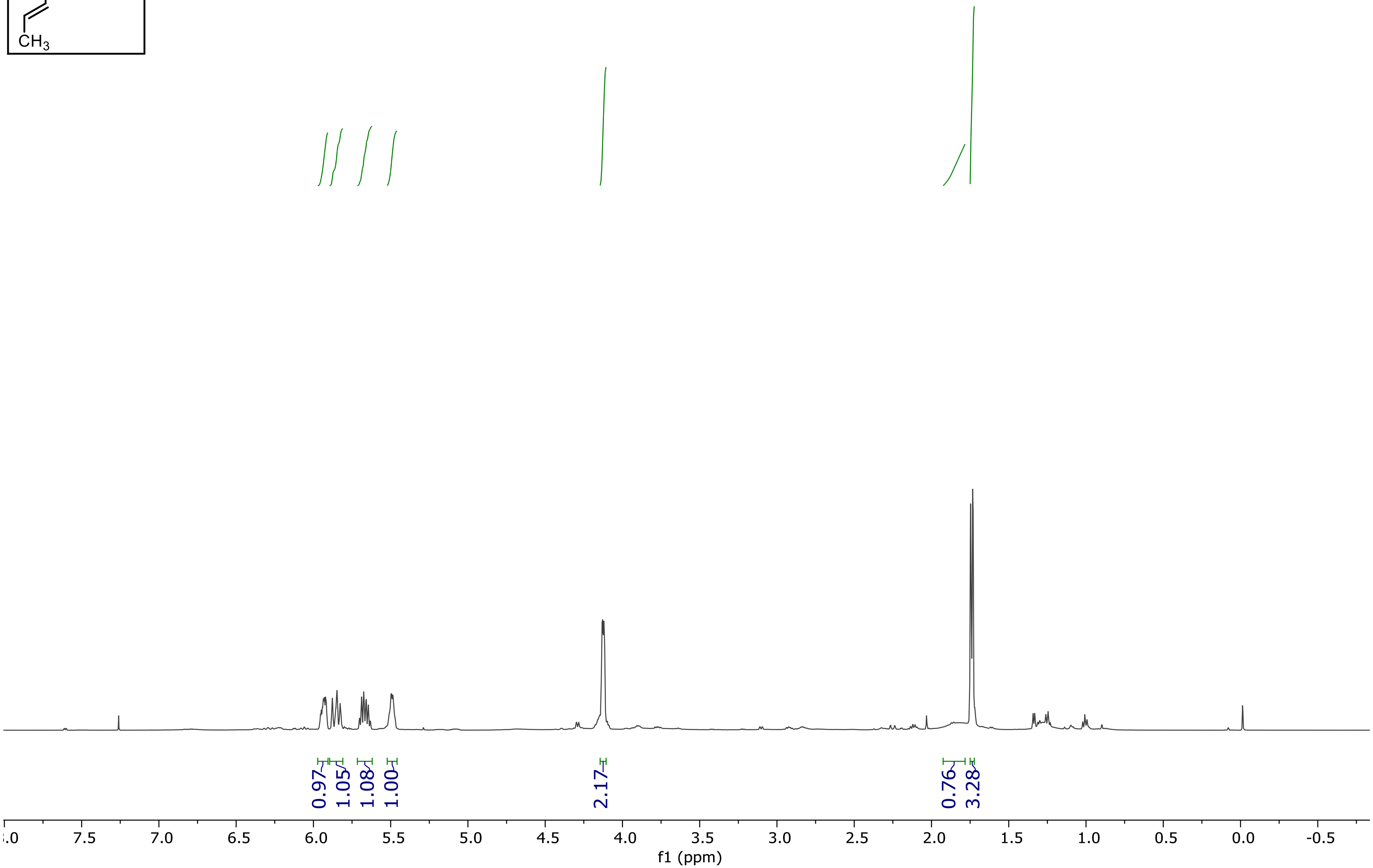


^{13}C NMR for Compound S-24.

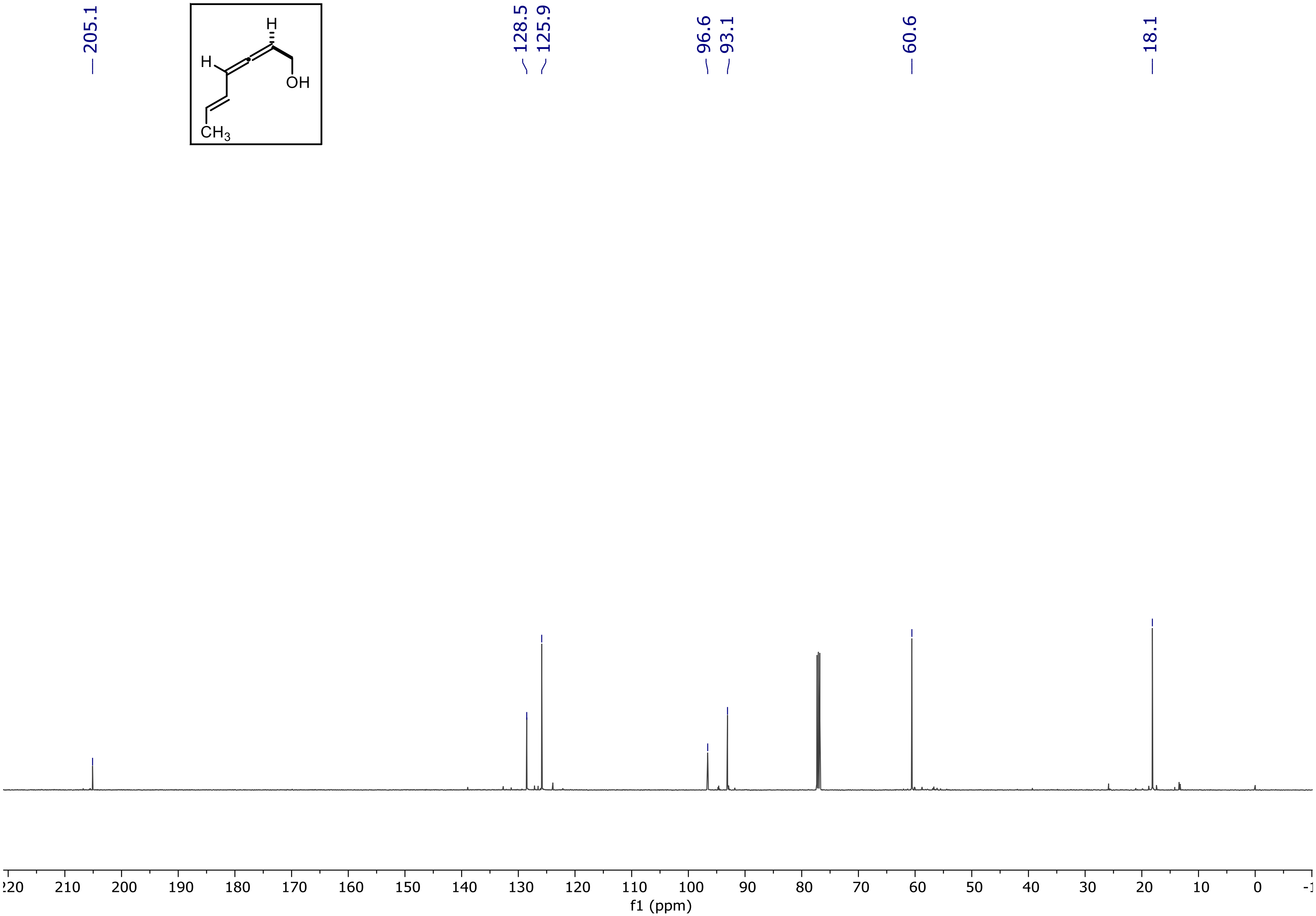


^{1}H NMR for Compound S-25.

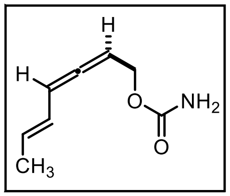


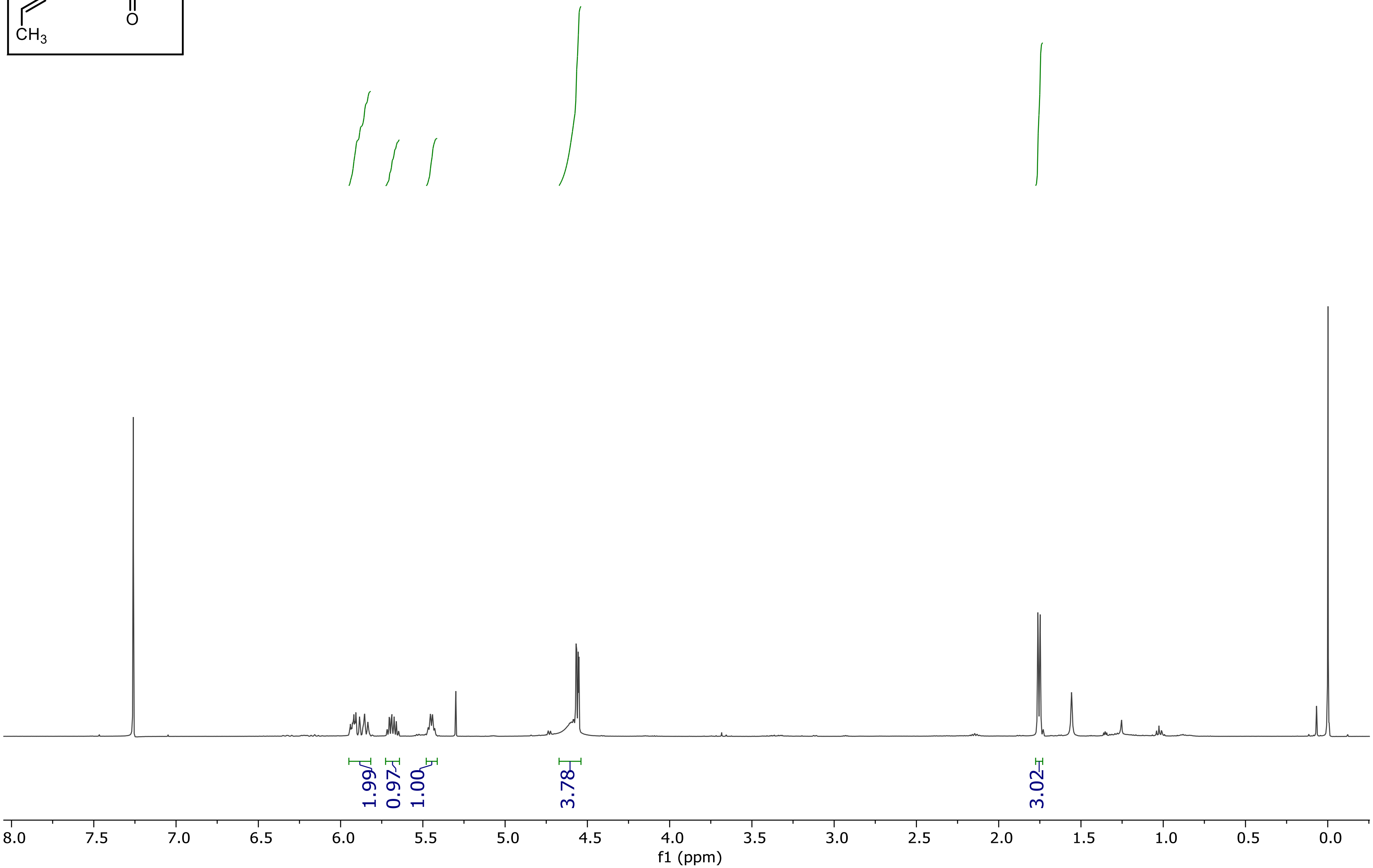


^{13}C NMR for Compound S-25.

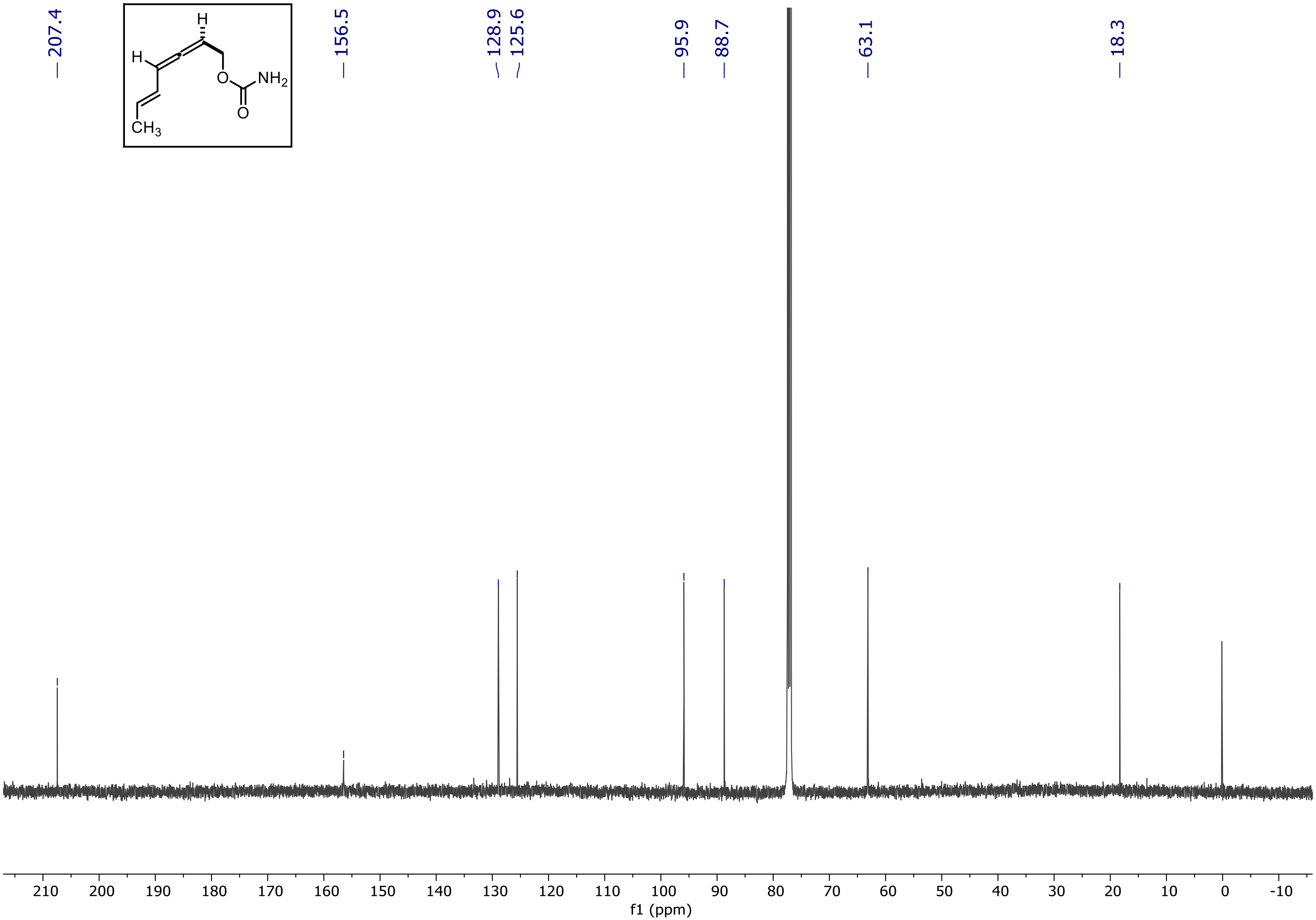


^{1}H NMR for Compound S-26.

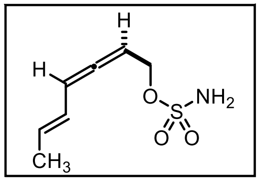


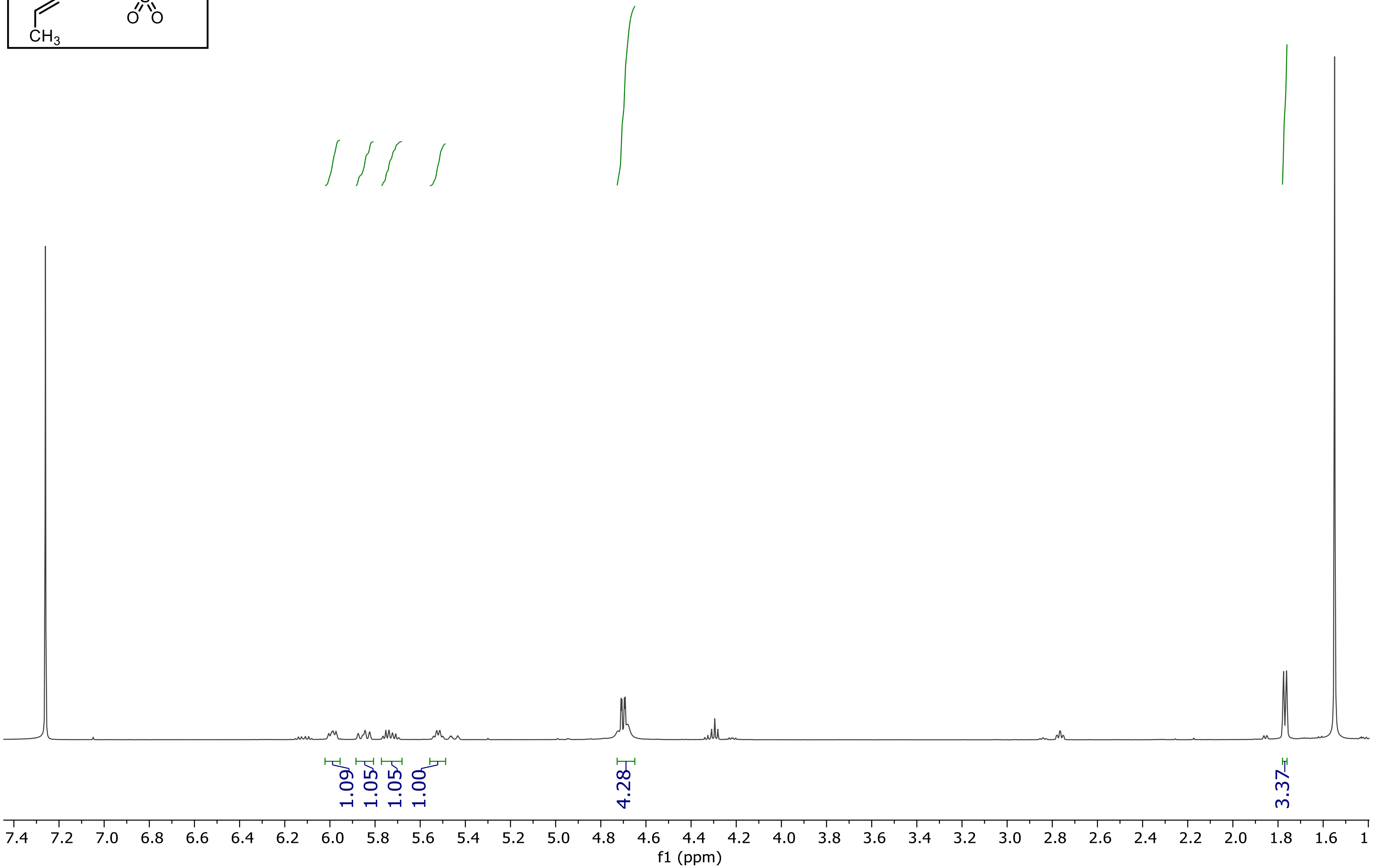


^{13}C NMR for Compound S-26.

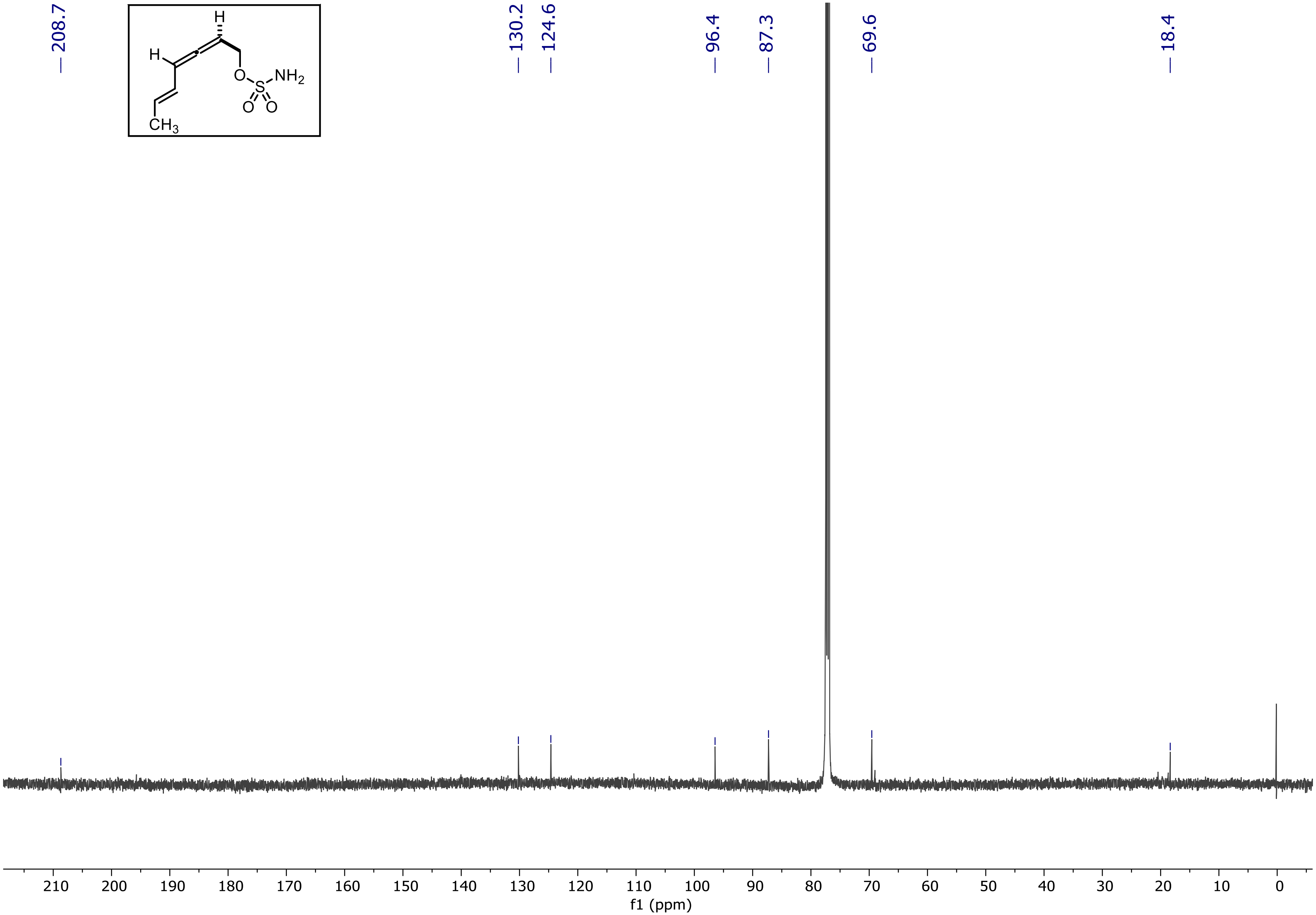


^{1}H NMR for Compound S-27.

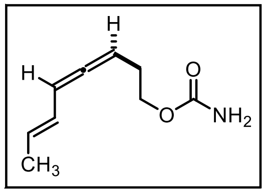


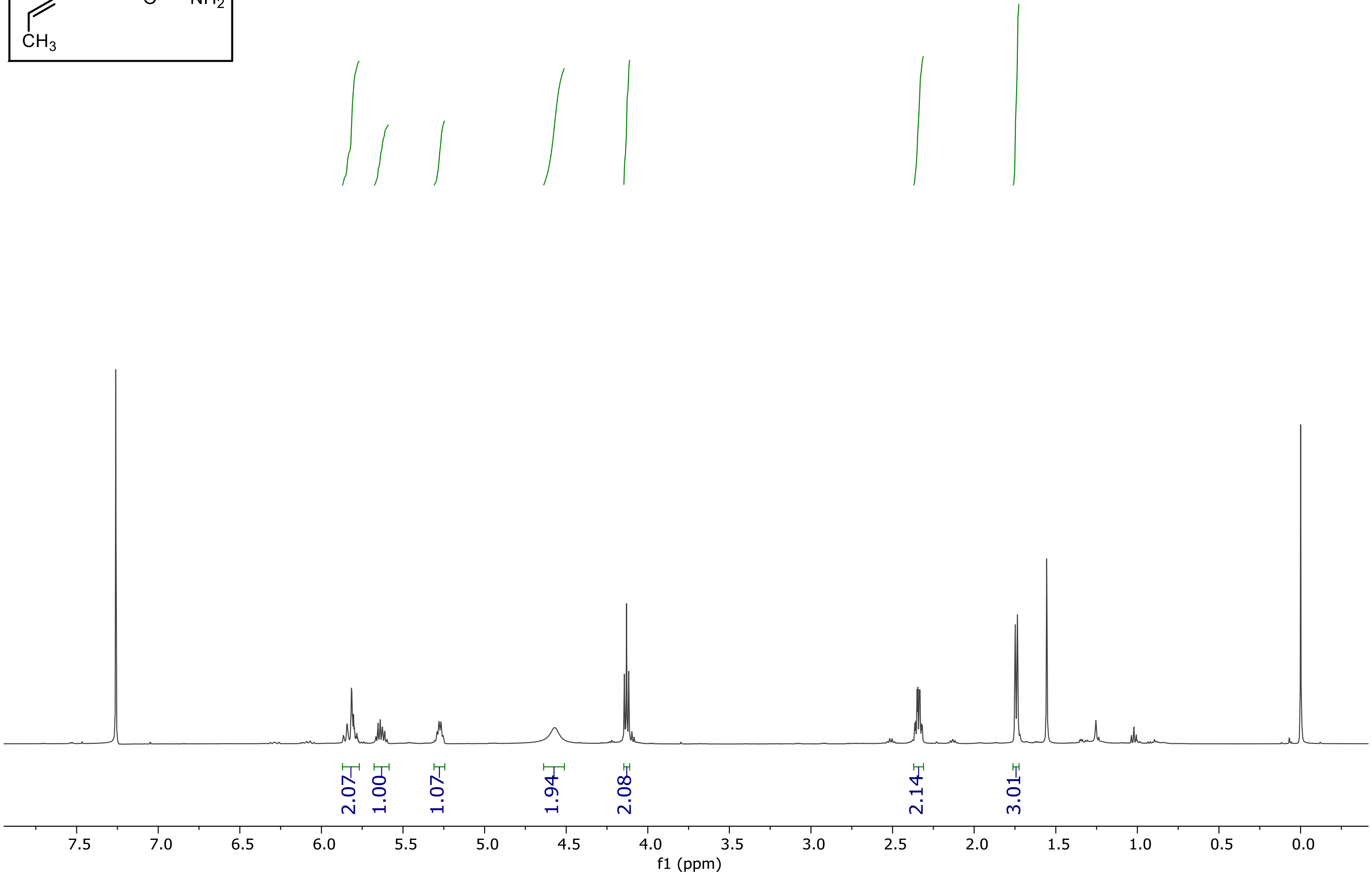


^{13}C NMR for Compound S-27.

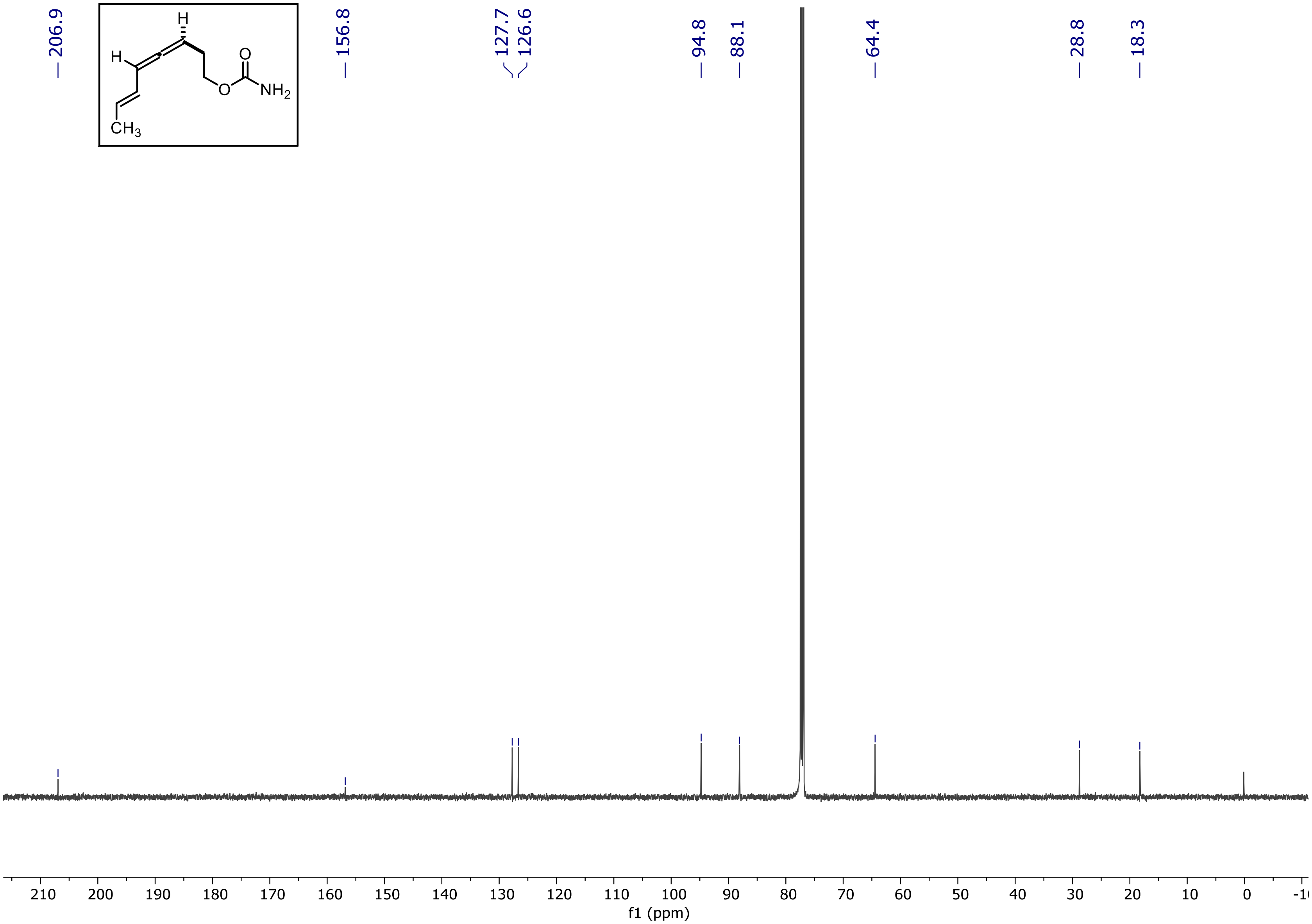


^{1}H NMR for Compound S-28.

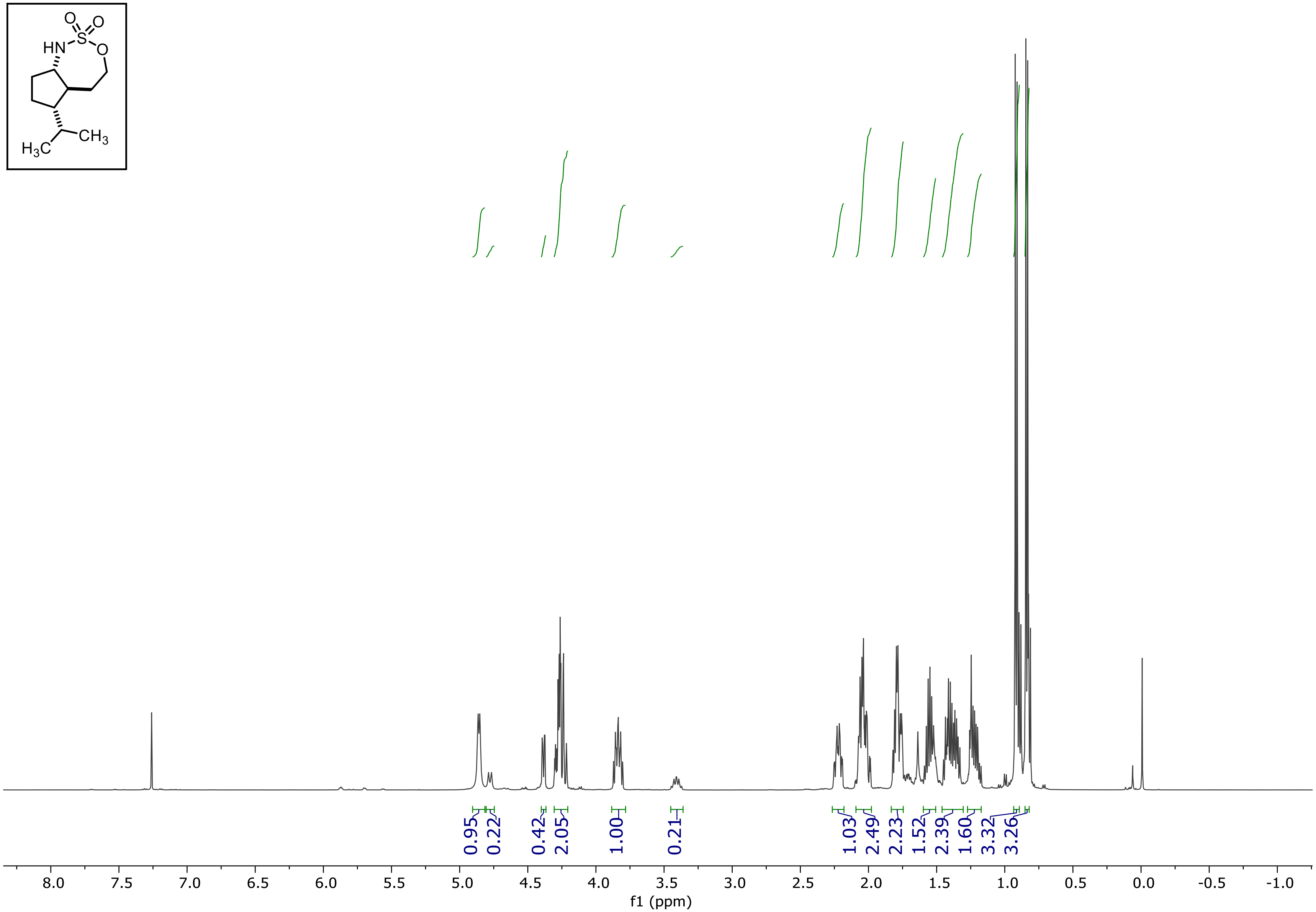




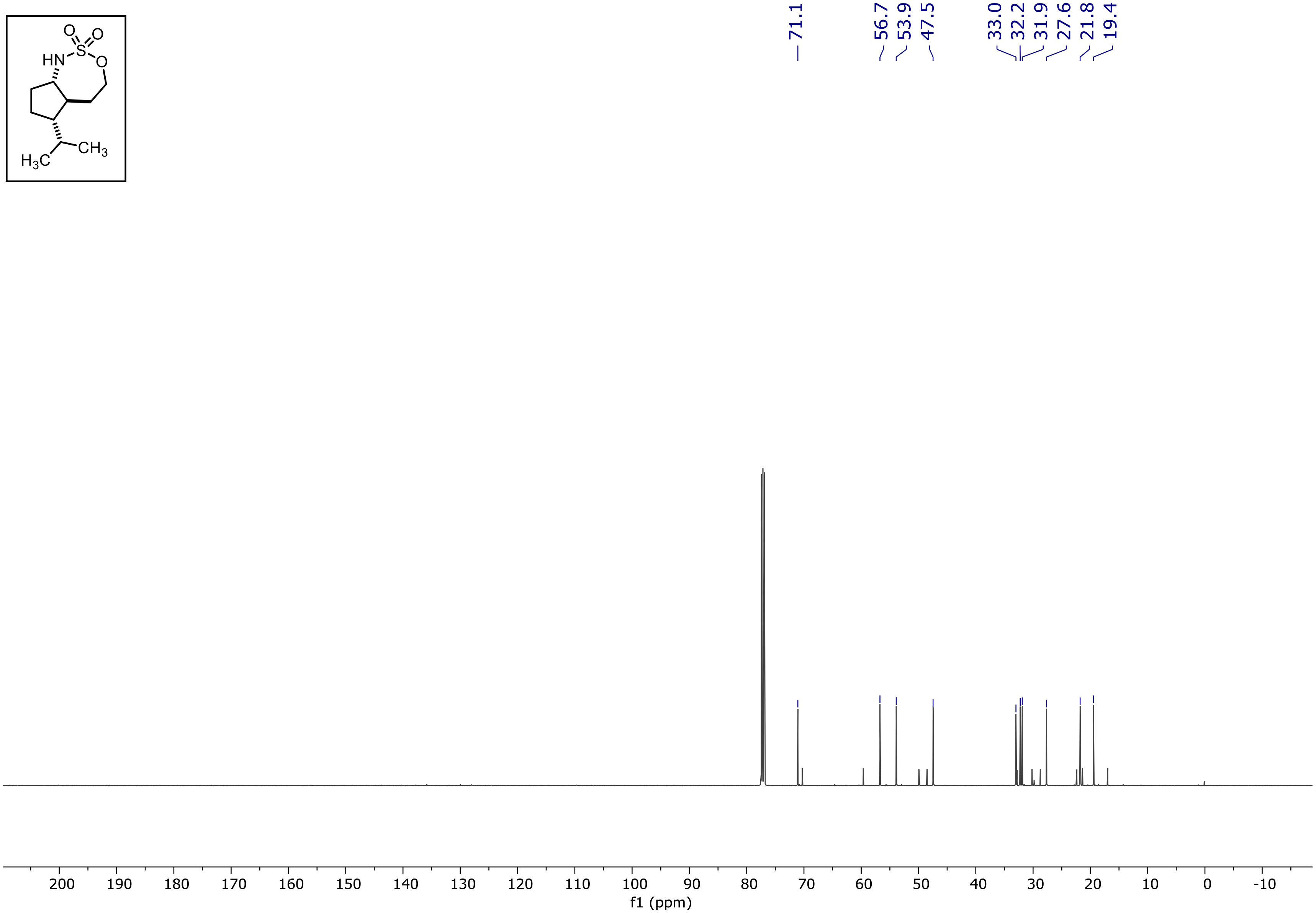
^{13}C NMR for Compound S-28.



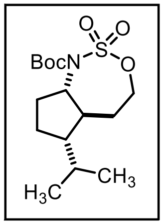
^{1}H NMR for Compound 17.

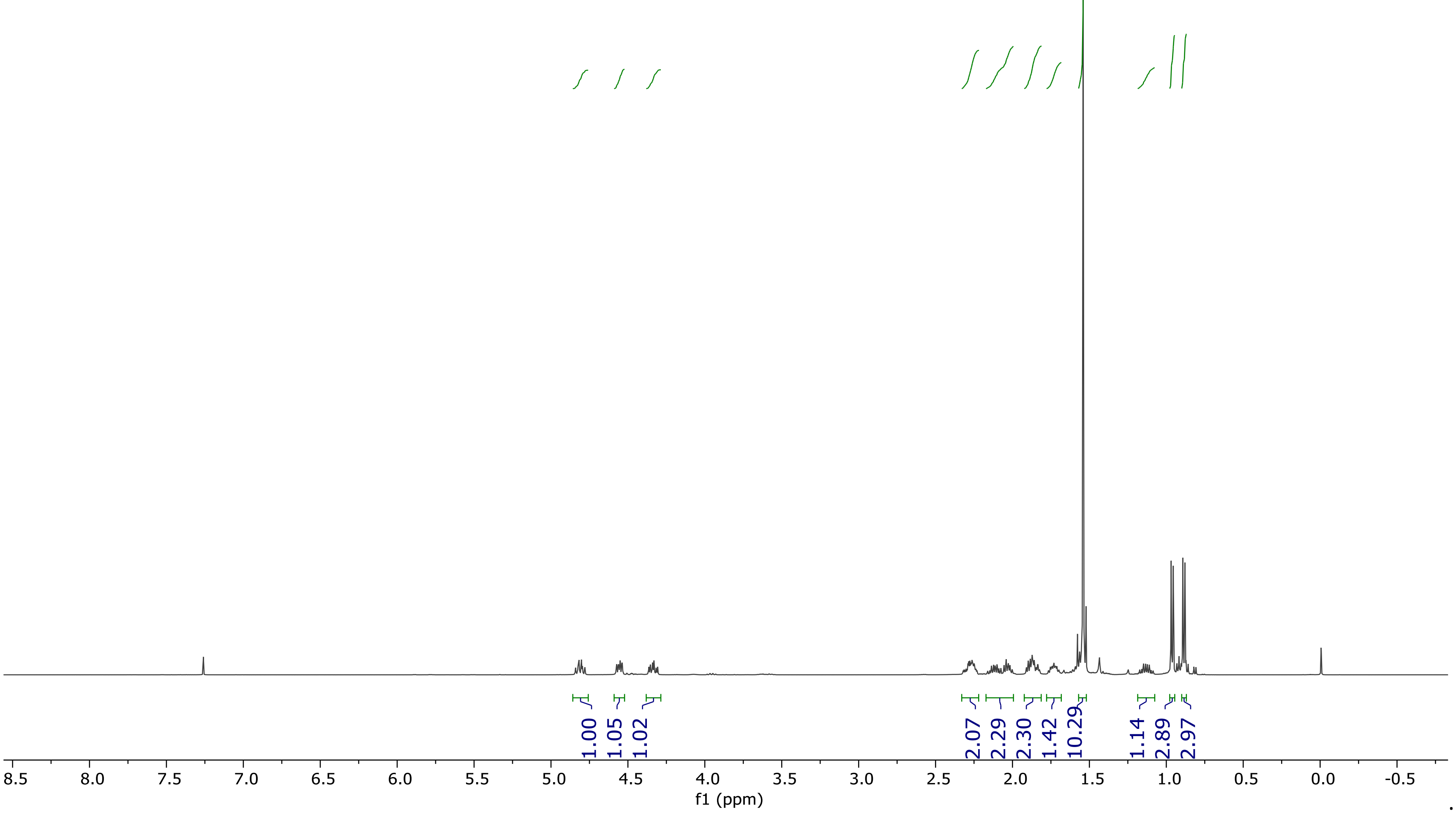


^{13}C NMR for Compound 17.

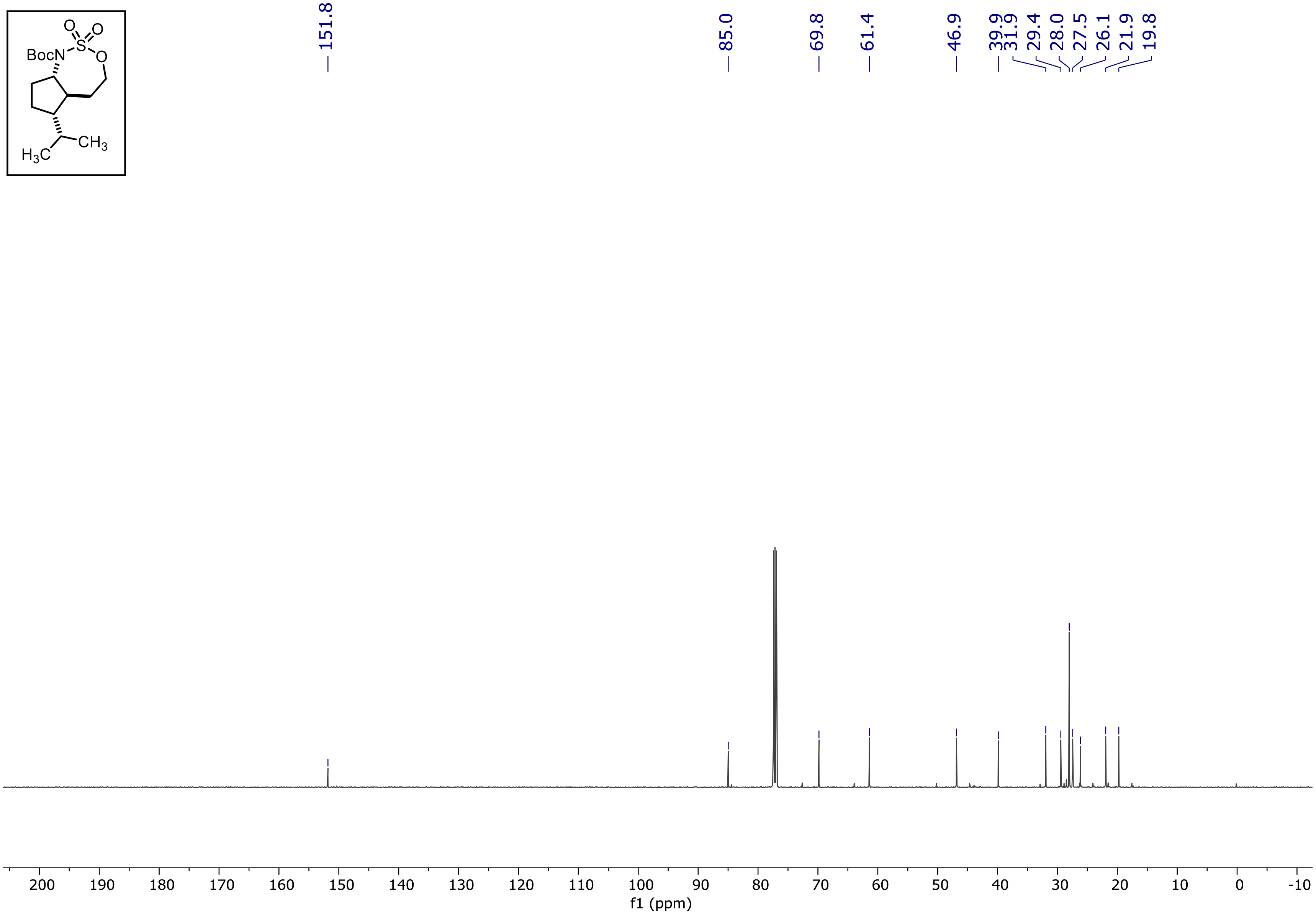


^{1}H NMR for Compound S-29.

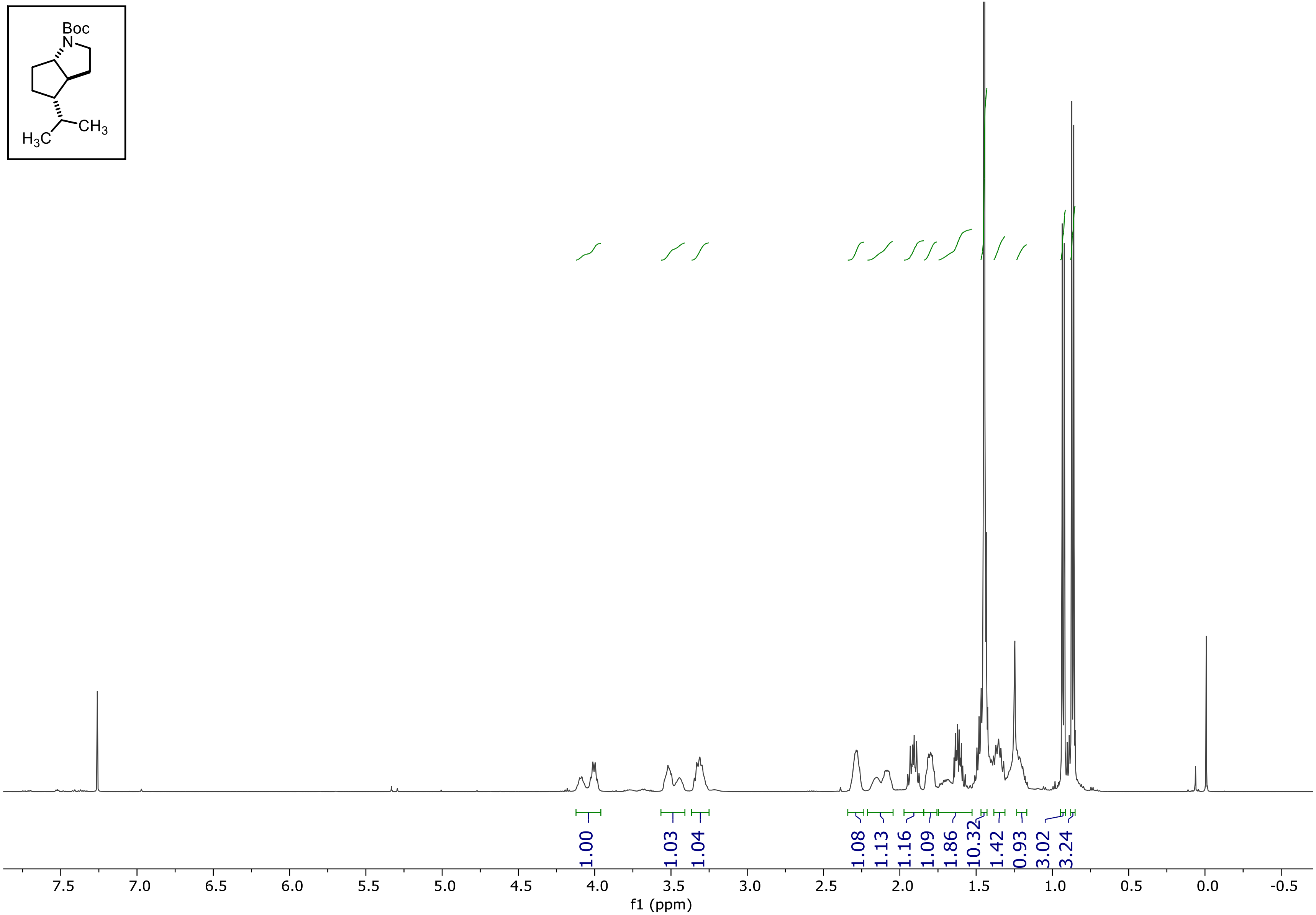




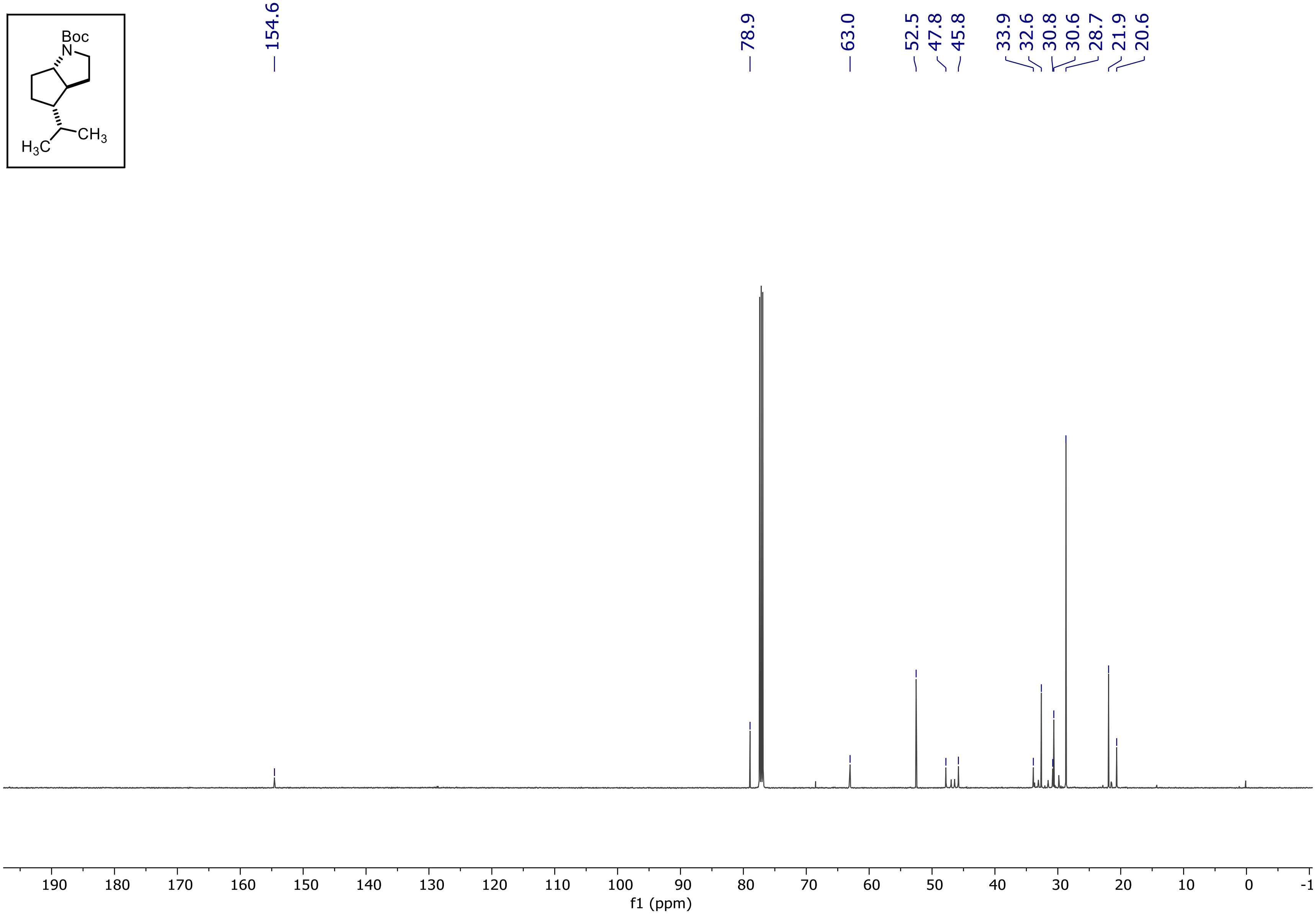
^{13}C NMR for Compound S-29.



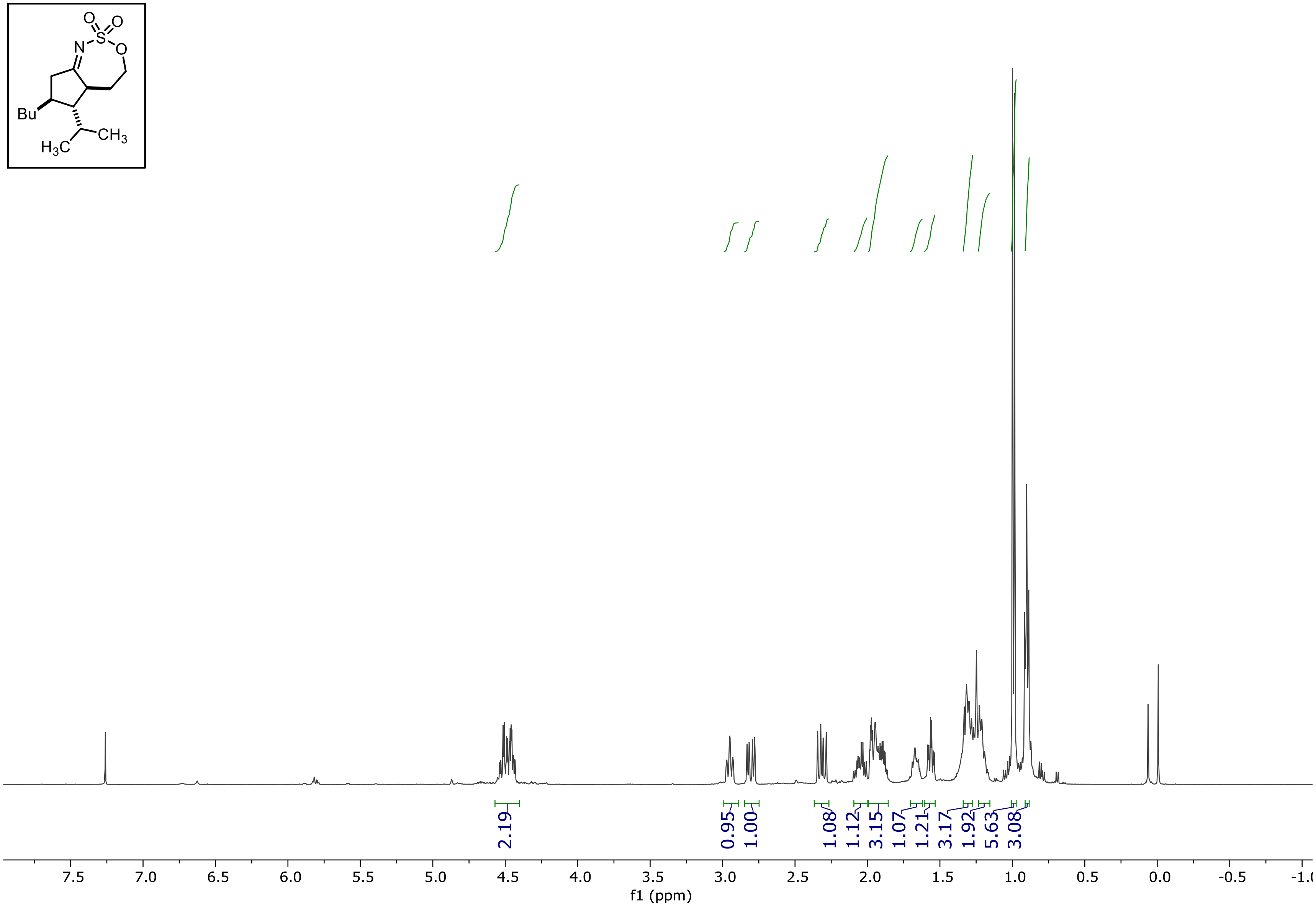
^{1}H NMR for Compound 18.



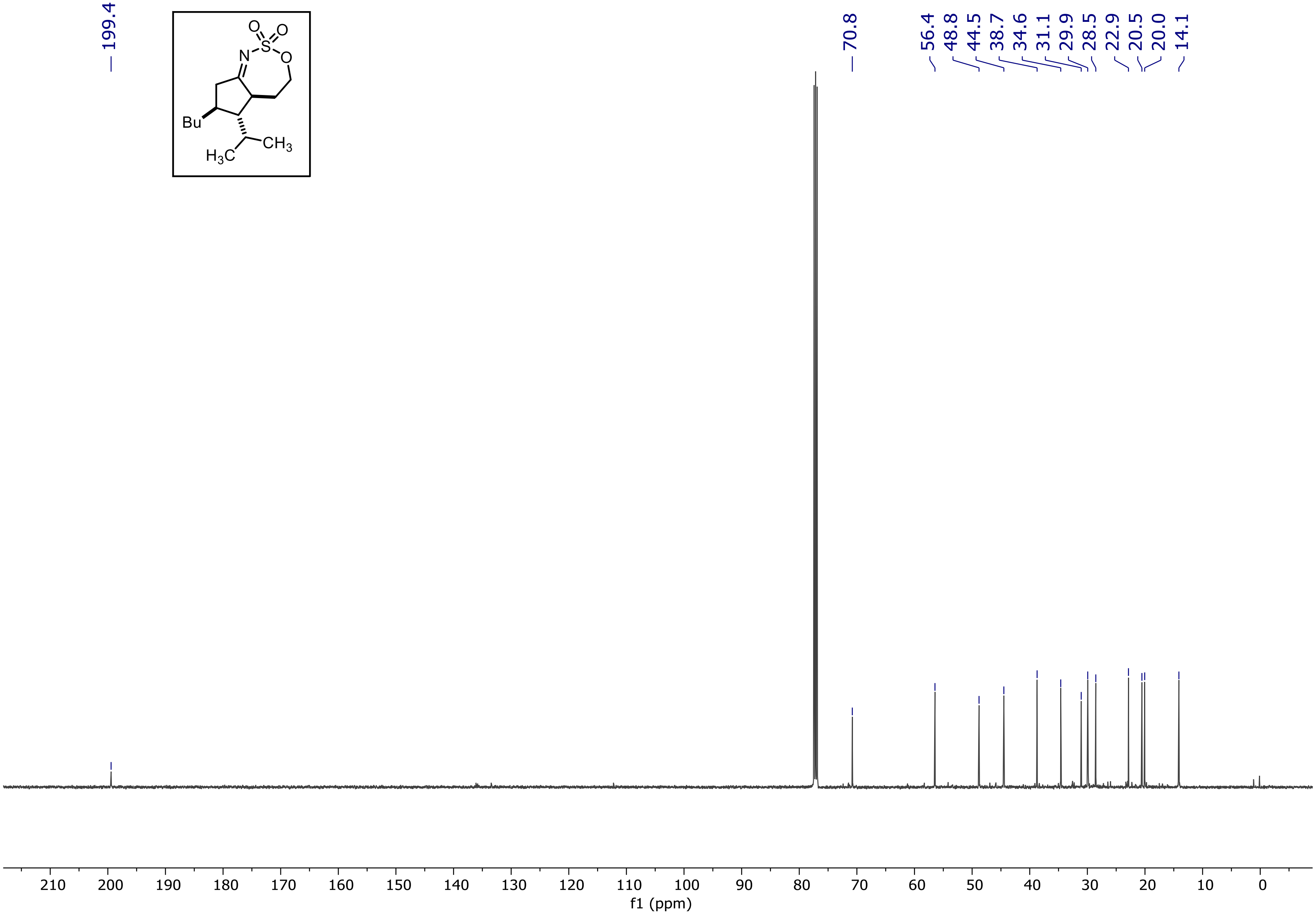
^{13}C NMR for Compound 18.



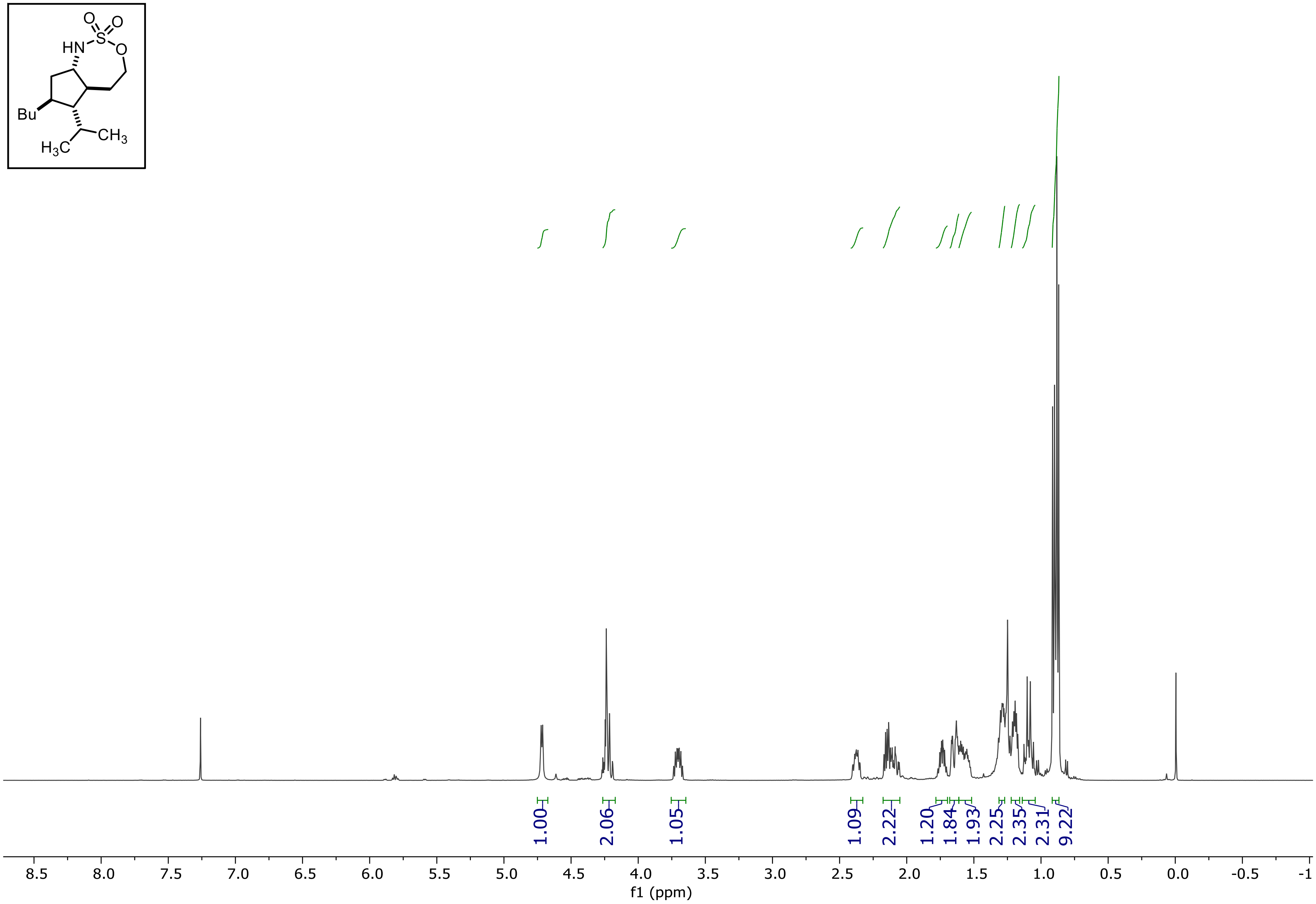
^{1}H NMR for Compound S-30.



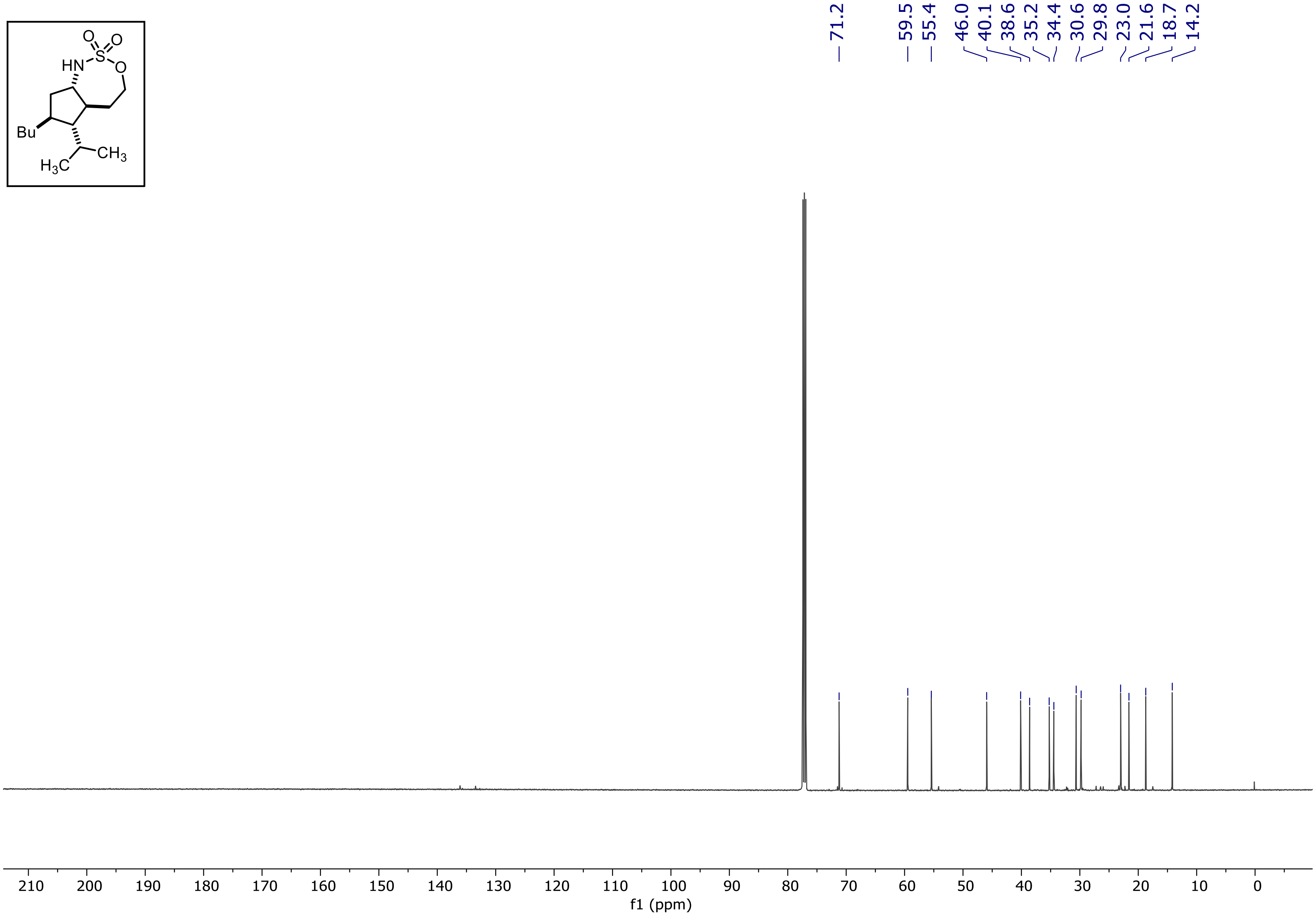
^{13}C NMR for Compound S-30.



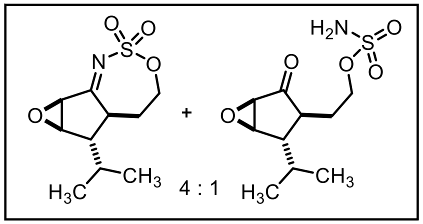
^{1}H NMR for Compound 19.

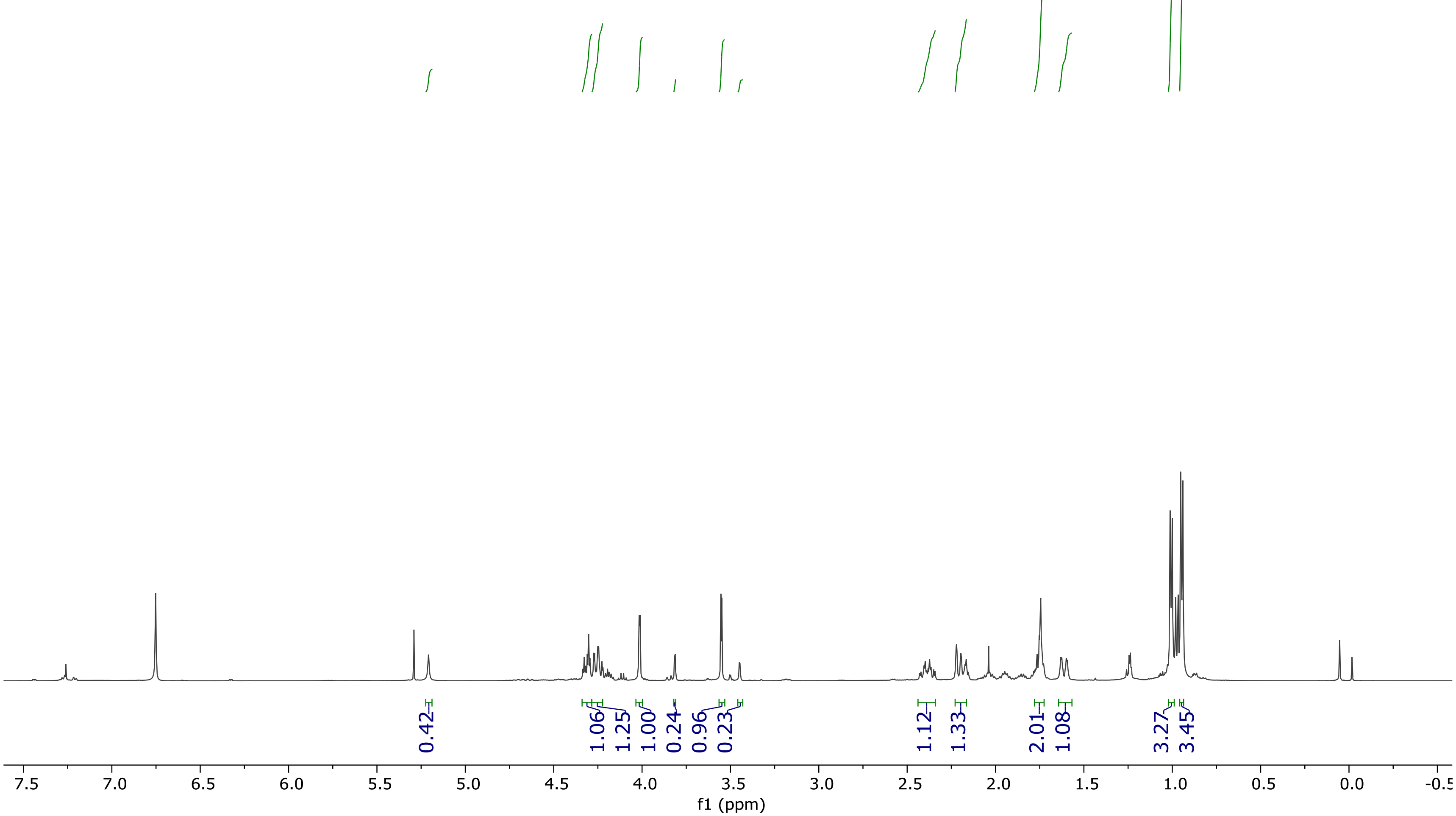


^{13}C NMR for Compound 19.



^{1}H NMR for Compound 20.





^{13}C NMR for Compound 20.