Supporting Information

Chemo- and Enantioselective Intramolecular Silver-Catalyzed Aziridinations of Carbamimidates

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I. General Information

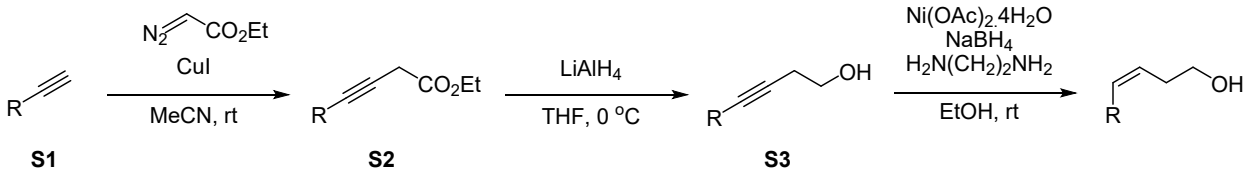
All glassware was either oven-dried overnight at 130 °C or flame-dried using a Bunsen burner. All glassware was then allowed to cool to room temperature in a desiccator filled with Drierite™ as a desiccant or under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from Sigma-Aldrich, Oakwood Products, Alfa Aesar, Tokyo Chemical Industry, Combi-Blocks, Acros Organics or Cayman Chemicals and directly used without further purification. Diethyl ether (Et_2O), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), and toluene were passed through an alumina column before use. All other solvents were purified using accepted procedures from the sixth edition of "Purification of Laboratory Chemicals".[1] Air- and moisture-sensitive reactions were performed using standard Schlenk techniques under a nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{24} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh). Product purification was typically carried out by preparative TLC, or by column chromatography using a gradient method employing mixtures of hexanes and ethyl acetate (EtOAc), or dichloromethane (DCM) and methanol (MeOH). Various stains were used to visualize reaction products, including ninhydrin and $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-400 (400 and 100 MHz) and Bruker Avance-500 (500 and 125 MHz) spectrometers. ^1H chemical shifts were reported using tetramethylsilane (TMS) ($CDCl_3$ referenced at δ 0.00) or protiated solvent peaks as an internal standard (CD_3CN referenced at δ 1.94). ^{13}C chemical shifts were reported using absolute referencing (TMS in $CDCl_3$, $\phi = 1\%$, $\Xi = 25.145020$). High-performance liquid chromatography (HPLC) analyses were performed using Shimadzu LC-20AB. A CHIRALCEL® OD-H (0.46 cm diameter x 25 cm), CHIRALCEL® OJ-H column (0.46 cm diameter x 25 cm), or CHIRALPAK® IC (0.46 cm diameter x 25 cm) was employed, maintained at a temperature of 40 °C, using ^{i}PrOH/hexane or 0.1% HCO_2H/H_2O/MeCN mobile phase. Accurate mass measurements were acquired at the University of Wisconsin-Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer, or electron impact methods).

II. Synthesis and Characterization of Carbamimidate Substrates

1. General Methods for the Synthesis of (Homo)allylic Alcohol Precursors

Alcohol precursors of **Compounds 1f**, **1u**, **1v**, **1w**, and **1y** are commercially available. Alcohol precursors of **Compounds 1s**[2] and **1t**[3] were synthesized following reported procedures.

General Method A:[4,5] Alcohol precursors of Compounds **1a**, **1c**, **1d**, **1e**, **1h**, **1k**, **1l,** and **1m**



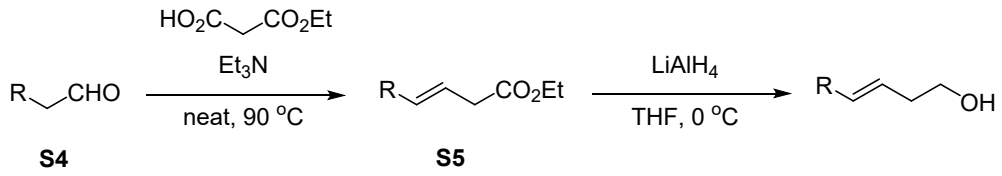
To a solution of CuI (5 mol %) in dry MeCN under N_2 atmosphere was added terminal alkyne **S1** (1 equiv.). Ethyl diazoacetate (87 wt % DCM, 1.05 equiv.) was then added dropwise, and the reaction mixture was stirred overnight at rt. Upon removal of solvent, the resulting residue was dissolved in Et_2O and filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Flash column chromatography using a gradient of hexane/Et_2O mixtures afforded **S2**.

A solution of ester **S2** (1 equiv.) in THF at 0 °C was treated with portionwise addition of LAH (0.6 equiv.), and the mixture was stirred at 0 °C for 30 min. The reaction was quenched using Fieser's work-up procedure: a mixture containing *x* g of LAH at 0 °C was treated with slow addition of *x* mL of H_2O, 2*x* mL of a 10% aqueous NaOH solution, and 2*x* mL of H_2O, then diluted with Et_2O and dried over $MgSO_4$ with vigorous stirring for 15 min at rt. The resulting mixture was filtered through a pad of $MgSO_4$. The filtrate was concentrated under reduced pressure to afford homopropargyl alcohol **S3**, which was used in the next step without purification.

To a solution of $Ni(OAc)_2.4H_2O$ (1 equiv.) in EtOH under H_2 atmosphere, was added $NaBH_4$ (1 equiv.) in EtOH at rt. After stirring for 30 min, ethylenediamine (4 equiv.) and **S3** (1 equiv.) in EtOH were added sequentially. The reaction mixture was allowed to stir for 4 h. Upon completion of the reaction and removal

of EtOH under reduced pressure, the crude product was purified by column chromatography (hexane/EtOAc gradient) gradients to afford the corresponding *Z*-homoallylic alcohol.

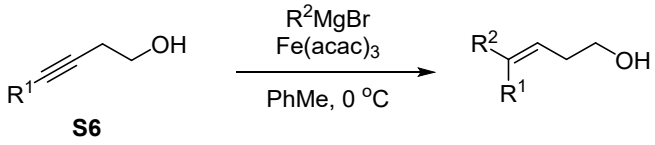
General Method B:[6] Alcohol precursors of Compounds **1b, 1g, 1i**, **1j**, and **1n**



The aldehyde **S4** (1 equiv.) was treated with monoethylmalonate (1.5 equiv.) and Et_3N (2.0 equiv.). The reaction mixture was heated to 90 °C under neat conditions overnight, then cooled to rt and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexane/Et_2O gradient) to afford **S5**.

To a solution of ester **S5** (1 equiv.) in THF at 0 °C was added LAH portionwise (0.6 equiv.), and the mixture was stirred at 0 °C for 30 min. The reaction was quenched using Fieser's work-up procedure as described above and filtered through a pad of $MgSO_4$. The filtrate was concentrated under reduced pressure to afford the corresponding *E*-homoallylic alcohol, which was used in the next step without purification.

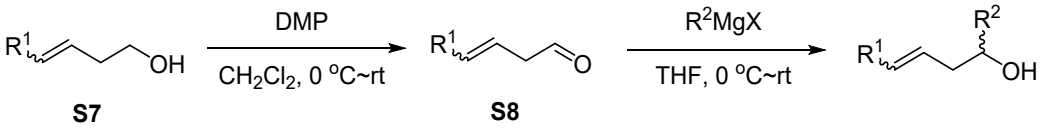
General Method C:[7] Alcohol precursors of Compounds **1q** and **1r**



A solution of homopropargyl alcohol **S6** (1 equiv.) and $Fe(acac)_3$ (20 mol%) in toluene at -78 °C was treated with dropwise addition of the appropriate Grignard reagent (5 equiv.). The resulting black mixture was warmed to 0 °C and stirred for 7 h at this temperature. After cooling to -78 °C, saturated aqueous NH_4Cl and Et_2O were added. The organic layer was extracted with Et_2O, dried over Na_2SO_4, and concentrated

under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc gradient) to afford the corresponding 1,2,2′-trisubstituted homoallylic alcohol.

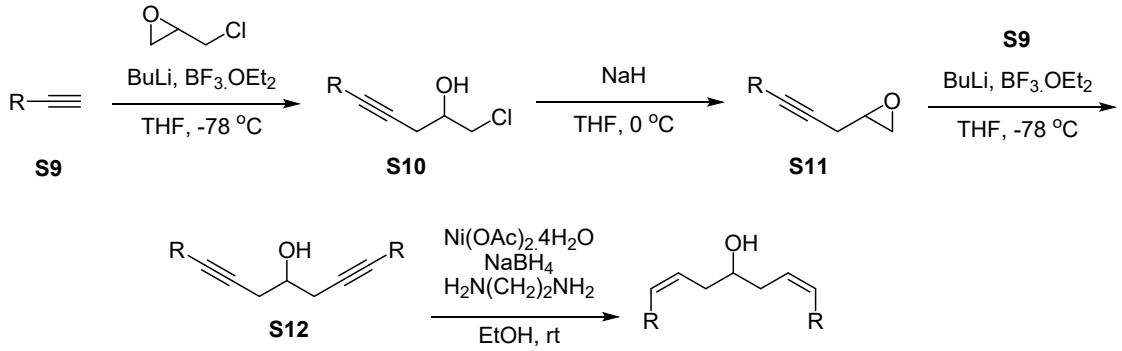
General Method D: Alcohol precursor of Compound **1o**



To a solution of homoallylic alcohol **S7** (1 equiv.) in CH_2Cl_2 at 0 °C was added Dess-Martin periodinane (1.2 equiv.) portionwise. The reaction mixture was stirred for 3 h at rt and quenched by the addition of saturated aqueous $Na_2S_2O_3$. After washing with saturated aqueous $Na_2S_2O_3$, then saturated aqueous $NaHCO_3$, and brine, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford **S8**, which was used in the next step without purification.

A solution of aldehyde **S8** (1 equiv.) in THF at 0 °C was treated by dropwise addition to the appropriate Grignard reagent (1.2 equiv.). The reaction mixture was warmed to rt at stirred for 4 h, then it was cooled to 0 °C and quenched by the addition of saturated aqueous NH_4Cl. The organic layer was extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc gradient) to afford the corresponding secondary homoallylic alcohol.

General Method E:[5,8] Alcohol precursor of Compound **1p**



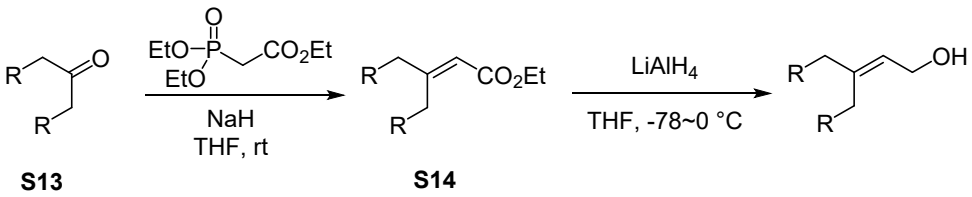
To a solution of terminal alkyne **S9** (1.5 equiv.) in THF at -78 °C was added *n*-BuLi (2.5 M in THF, 1.6 equiv.) dropwise. After stirring for 10 min, $BF_3.Et_2O$ (1.6 equiv.) was added dropwise. The mixture was stirred for another 10 min before epichlorohydrin (1 equiv.) was added dropwise. After stirring for another hour at -78 °C, the mixture was warmed to 0 °C and quenched by the addition of saturated aqueous NH_4Cl. The organic layer was extracted with Et_2O, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford **S10**, which was used in the next step without purification.

To a solution of chlorohydrin **S10** (1 equiv.) in THF was added NaH (60% dispersion in mineral oil, 1.5 equiv.) at 0 °C. The mixture was stirred at 0 °C for 2 h then quenched by the addition of water and Et_2O. The organic layer was extracted with Et_2O, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by passing through a short pad of silica gel using hexane/Et_2O (1:1) as an eluent to afford **S11**.

To a solution of terminal alkyne **S9** (1.5 equiv.) in THF at -78 °C was added *n*-BuLi (2.5 M in THF, 1.6 equiv.) dropwise. After stirring for 10 min, $BF_3.Et_2O$ (1.6 equiv.) was added dropwise. The mixture was stirred for another 10 min before a solution of **S11** (1 equiv.) in THF was added dropwise. After stirring for another hour at -78 °C, the mixture was warmed to 0 °C and quenched by the addition of saturated aqueous NH_4Cl. The organic layer was extracted by Et_2O, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford **S12**, which was used in the next step without purification.

A solution of $Ni(OAc)_2.4H_2O$ (2 equiv.) in EtOH under H_2 atmosphere was treated with $NaBH_4$ (2 equiv.) in EtOH at rt. After stirring for 30 min, ethylenediamine (8 equiv.) and **S12** (1 equiv.) in EtOH were added sequentially. The reaction mixture was allowed to stir for 4 h. Upon completion of the reaction and removal of EtOH under reduced pressure, the crude product was purified by column chromatography (hexane/EtOAc gradient) gradients to afford the corresponding symmetrical secondary bis-(*Z*-homoallyl) alcohol.

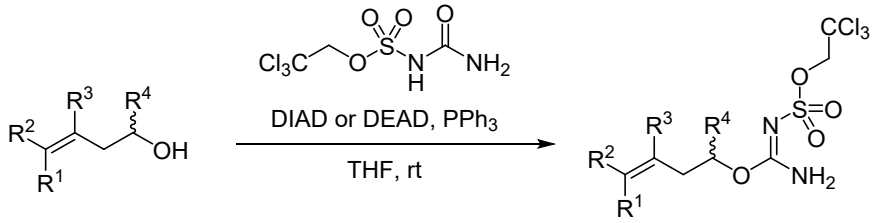
General Method F: Alcohol precursor of **Compounds 1q-s**



To a suspension of NaH (60% dispersion in mineral oil, 1.2 equiv.) in THF (0.2 M) at rt was added triethyl phosphonoacetate (1.05 equiv.) dropwise. The resulting mixture was stirred at rt for 1 h before ketone **S13** (1equiv.) was added dropwise. The reaction mixture was stirred at rt overnight then diluted with Et_2O and quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford **S14**, which was used in the next step without purification.

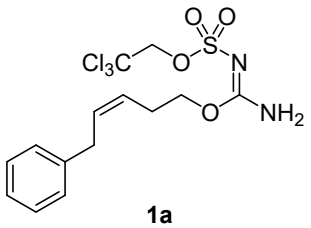
To a solution of **S14** (1 equiv.) in Et_2O (0.25 M) at -78 °C was added LAH (0.6 equiv.) in one portion. The reaction mixture was stirred at -78 °C for 2 h and allowed to warm up to 0 °C over a period of 30 min. The reaction was then quenched using Fieser's work-up procedure as described above and filtered through a pad of $MgSO_4$. The filtrate was concentrated under reduced pressure to afford the corresponding 1,1',2-trisubstituted allylic alcohol, which was used in the next step without purification.

2. General Procedure for the Synthesis of Carbamimidate Substrates



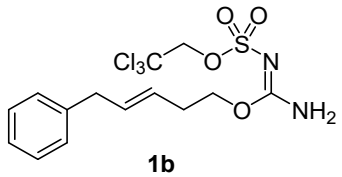
Diisopropyl azodicarboxylate or diethyl azodicarboxylate (1.30 equiv.) were added dropwise to a solution of homoallylic alcohol precursor (1 equiv.), *N*-(2,2,2-trichloroethoxysulfonyl)urea (TcesNHC(O)NH_2, 1.33 equiv.), and PPh_3 (1.30 equiv.) in THF (0.3 M) at 0 °C. The reaction mixture was then warmed to rt and allowed to stir overnight until TLC indicated complete consumption of the starting alcohol. The solvent was removed under reduced pressure. Flash column chromatography on silica gel using a gradient of

EtOAc/hexanes mixtures afforded the corresponding carbamimidate. *Note:* TcesNHC(O)NH_2 was synthesized at multiple-gram scale following a previously reported procedure.[9]



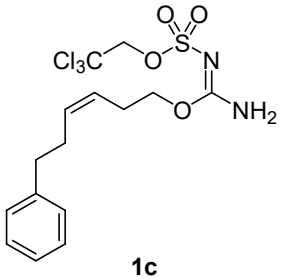
1a

Compound 1a: Off-white solid, 723 mg (38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.17 (m, 3H), 6.95 (br s, 1H), 5.80 (dtt, *J* = 10.8, 7.6, 1.5 Hz, 1H), 5.55 – 5.46 (m, 1H), 5.22 (br s, 1H), 4.65 (s, 2H), 4.29 (t, *J* = 6.6 Hz, 2H), 3.43 (d, *J* = 7.8 Hz, 2H), 2.56 (qd, *J* = 6.6, 1.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 140.4, 131.7, 128.5, 128.2, 126.1, 124.7, 93.7, 78.5, 68.4, 33.4, 26.6. HRMS (ESI) m/z calculated for $C_{14}H_{17}Cl_3N_2O_4S$ $[M-H]^-$, 412.9902; found, 412.9905.



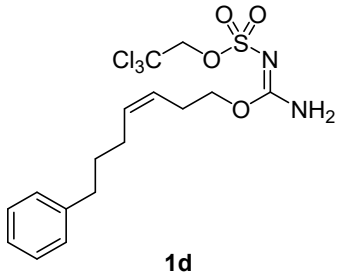
1b

Compound 1b: White solid, 151 mg (32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (td, *J* = 7.0, 1.4 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 2H), 7.02 (br s, 1H), 5.71 (dtt, *J* = 15.3, 6.9, 1.4 Hz, 1H), 5.50 – 5.31 (m, 2H), 4.67 (s, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.35 (d, *J* = 6.7 Hz, 2H), 2.42 (qd, *J* = 6.7, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 140.2, 133.0, 128.47, 128.46, 126.1, 125.5, 93.7, 78.5, 68.6, 39.0, 31.6. HRMS (ESI) m/z calculated for $C_{14}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 415.0047; found, 415.0043.



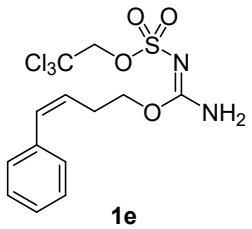
1c

Compound 1c: White solid, 337 mg (52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 6.99 (br s, 1H), 5.63 – 5.52 (m, 1H), 5.33 (dtt, *J* = 10.5, 7.2, 1.6 Hz, 2H), 4.65 (s, 2H), 4.13 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.36 (dqd, *J* = 20.8, 7.1, 1.6 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 141.6, 132.4, 128.5, 128.3, 125.9, 124.2, 93.7, 78.5, 68.5, 35.6, 29.2, 26.5. HRMS (ESI) m/z calculated for $C_{15}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 429.0204; found, 429.0201.



1d

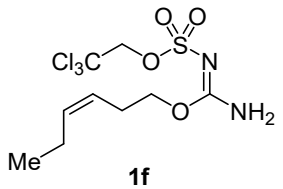
Compound 1d: White solid, 322 mg (29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.18 (td, *J* = 7.2, 1.6 Hz, 3H), 7.01 (br s, 1H), 5.61 – 5.53 (m, 1H), 5.47 – 5.28 (m, 2H), 4.66 (s, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 2.66 – 2.59 (m, 2H), 2.41 (qd, *J* = 6.9, 1.7 Hz, 2H), 2.09 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.70 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 142.2, 133.2, 128.4, 128.3, 125.8, 123.8, 93.7, 78.5, 68.7, 35.4, 31.1, 26.9, 26.6. HRMS (ESI) m/z calculated for $C_{16}H_{21}Cl_3N_2O_4S$ $[M+H]^+$, 443.0360; found, 443.0356.



1e

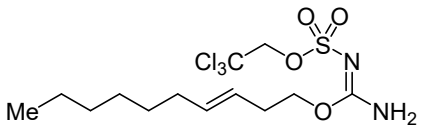
Compound 1e: White solid, 388 mg (50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.29 – 7.22 (m, 3H), 7.03 (br s, 1H), 6.59 (dt, *J* = 11.6, 2.0 Hz, 1H), 5.62 (dt, *J* = 11.7, 7.3 Hz, 1H), 5.42 (br s, 1H), 4.65 (s, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 2.73 (qd, *J* = 6.7, 1.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3,

136.8, 132.3, 128.6, 128.4, 127.1, 126.0, 93.7, 78.5, 68.6, 27.8. HRMS (ESI) m/z calculated for $C_{13}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 400.9891; found, 400.9887.



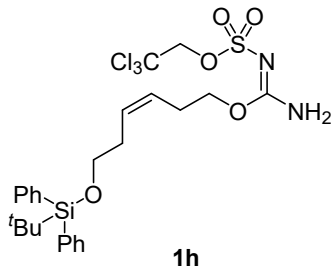
1f

Compound 1f: White solid, 220 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.58 – 5.51 (m, 1H), 5.43 (br s, 1H), 5.32 – 5.25 (m, 1H), 4.67 (s, 2H), 4.26 (t, *J* = 6.9 Hz, 2H), 2.49 – 2.40 (m, 2H), 2.12 – 2.01 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 135.4, 122.6, 93.7, 78.5, 68.7, 26.5, 20.7, 14.2. HRMS (ESI) m/z calculated for $C_9H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 352.9891; found, 352.9886.



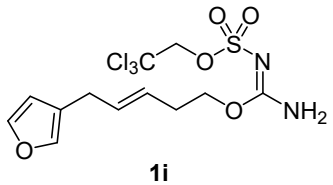
1g

Compound 1g: White solid, 324 mg (51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 5.54 (dtt, *J* = 15.0, 6.7, 1.4 Hz, 1H), 5.44 (br s, 1H), 5.33 (dtt, *J* = 15.3, 6.9, 1.5 Hz, 1H), 4.67 (s, 2H), 4.25 (t, *J* = 6.8 Hz, 2H), 2.37 (qd, *J* = 6.8, 1.3 Hz, 2H), 2.00 (qd, *J* = 6.9, 1.4 Hz, 2H), 1.39 – 1.21 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 134.6, 123.9, 93.7, 78.5, 68.9, 32.6, 31.7 (overlapped), 29.3, 28.8, 22.6, 14.1. HRMS (ESI) m/z calculated for $C_{13}H_{23}Cl_3N_2O_4S$ $[M+H]^+$, 409.0517; found, 409.0514.



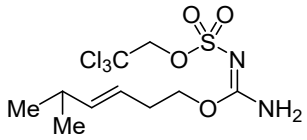
1h

Compound 1h: Colorless semisolid, 607 mg (32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 4H), 7.46 – 7.41 (m, 2H), 7.41 – 7.35 (m, 4H), 6.92 (br s, 1H), 5.61 – 5.52 (m, 1H), 5.44 – 5.35 (m, 1H), 5.30 (br s, 1H), 4.65 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 2.37 (qd, *J* = 6.6, 1.5 Hz, 2H), 2.31 (q, *J* = 6.9 Hz, 2H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 135.6, 133.8, 129.7, 129.6, 127.7, 125.4, 93.7, 78.5, 68.5, 63.4, 30.9, 26.8, 26.6, 19.2. HRMS (ESI) m/z calculated for $C_{25}H_{33}Cl_3N_2O_5SSi$ $[M+NH_4]^+$, 624.1283; found, 624.1281.



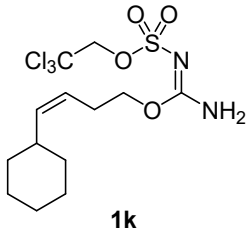
1i

Compound 1i: Off-white solid, 210 mg (41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.12 – 6.94 (m, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.00 (dq, *J* = 3.0, 0.9 Hz, 1H), 5.72 – 5.64 (m, 1H), 5.50 (dtt, *J* = 15.1, 6.8, 1.5 Hz, 1H), 5.46 – 5.34 (m, 1H), 4.67 (s, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.36 (dt, *J* = 6.6, 1.1 Hz, 2H), 2.43 (qd, *J* = 6.7, 1.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 153.8, 141.3, 129.4, 126.7, 110.3, 105.4, 93.7, 78.5, 68.5, 31.5, 31.4. HRMS (ESI) m/z calculated for $C_{12}H_{15}Cl_3N_2O_5S$ $[M+H]^+$, 404.9840; found, 404.9835.



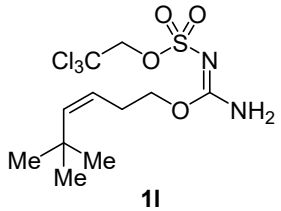
1j

Compound 1j: White solid, 221 mg (24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 5.51 (ddt, *J* = 15.4, 6.6, 1.4 Hz, 1H), 5.44 (br s, 1H), 5.29 (dtd, *J* = 15.3, 6.8, 1.4 Hz, 1H), 4.67 (s, 2H), 4.25 (t, *J* = 6.9 Hz, 2H), 2.37 (qt, *J* = 6.9, 1.2 Hz, 2H), 2.26 (dq, *J* = 13.4, 6.7 Hz, 1H), 0.97 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 141.5, 120.9, 93.7, 78.5, 68.9, 31.6, 31.1, 22.4. HRMS (ESI) m/z calculated for $C_{11}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 367.0047; found, 367.0045.



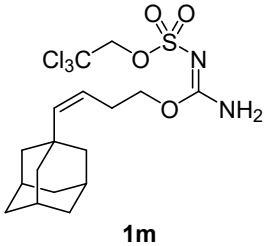
1k

Compound 1k: White solid, 239 mg (54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.51 – 5.33 (m, 2H), 5.21 (dtd, *J* = 10.8, 7.2, 1.1 Hz, 1H), 4.67 (s, 2H), 4.25 (t, *J* = 6.9 Hz, 2H), 2.45 (qd, *J* = 6.9, 1.5 Hz, 2H), 2.29 – 2.16 (m, 1H), 1.71 (dt, *J* = 13.3, 3.7 Hz, 2H), 1.66 (ddt, *J* = 14.5, 3.5, 1.5 Hz, 1H), 1.62 – 1.55 (m, 2H), 1.35 – 1.23 (m, 2H), 1.18 (tt, *J* = 12.5, 3.3 Hz, 1H), 1.08 (qd, *J* = 12.8, 3.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 139.8, 121.3, 93.8, 78.5, 68.9, 36.5, 33.2, 26.8, 25.9, 25.8. HRMS (ESI) m/z calculated for $C_{13}H_{21}Cl_3N_2O_4S$ $[M+H]^+$, 407.0360; found, 407.0357.



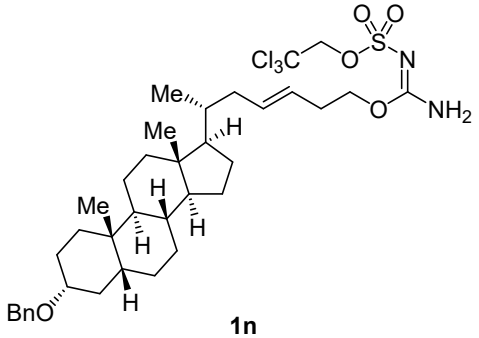
1l

Compound 1l: White solid, 201 mg (49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.49 (dt, *J* = 12.1, 1.8 Hz, 2H), 5.10 (dt, *J* = 12.1, 7.3 Hz, 1H), 4.67 (s, 2H), 4.27 (t, *J* = 6.8 Hz, 2H), 2.60 (qd, *J* = 6.9, 1.8 Hz, 2H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 143.4, 121.9, 93.7, 78.5, 69.0, 33.4, 31.0, 27.5. HRMS (ESI) m/z calculated for $C_{11}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 381.0204; found, 381.0200.



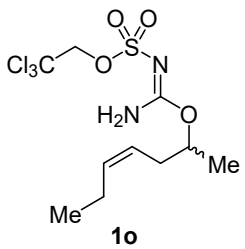
1m

Compound 1m: White solid, 288 mg (42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.44 (br s, 1H), 5.22 (dt, *J* = 12.2, 1.8 Hz, 1H), 5.08 (dt, *J* = 12.2, 7.3 Hz, 1H), 4.67 (s, 2H), 4.25 (t, *J* = 6.9 Hz, 2H), 2.62 (qd, *J* = 7.0, 1.8 Hz, 2H), 2.01 – 1.92 (m, 3H), 1.78 – 1.64 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 143.6, 121.6, 93.7, 78.5, 69.2, 43.0, 36.7, 36.0, 28.6, 28.0. HRMS (ESI) m/z calculated for $C_{17}H_{25}Cl_3N_2O_4S$ $[M+H]^+$, 459.0673; found, 459.0668.



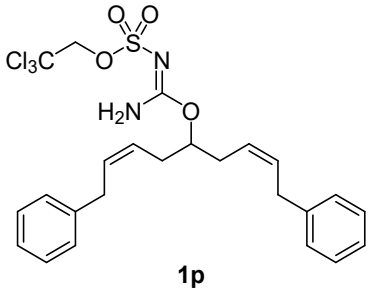
1n

Compound 1n: White solid, 383 mg (54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 7.03 (br s, 1H), 5.50 (ddd, *J* = 14.7, 8.1, 6.3 Hz, 1H), 5.43 (br s, 1H), 5.32 (dt, *J* = 14.7, 6.8 Hz, 1H), 4.67 (s, 2H), 4.56 (s, 2H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.37 (td, *J* = 11.0, 5.4 Hz, 1H), 2.39 (q, *J* = 6.8 Hz, 2H), 2.12 (d, *J* = 13.8 Hz, 1H), 1.94 (dt, *J* = 12.4, 3.3 Hz, 1H), 1.90 – 1.77 (m, 4H), 1.73 (dt, *J* = 13.9, 8.3 Hz, 1H), 1.64 (d, *J* = 12.8 Hz, 1H), 1.57 (ddd, *J* = 9.5, 6.5, 3.6 Hz, 1H), 1.49 – 1.30 (m, 7H), 1.30 – 1.16 (m, 4H), 1.16 – 0.99 (m, 5H), 0.94 – 0.89 (m, 4H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 139.2, 132.8, 128.3, 127.6, 127.3, 125.3, 93.7, 78.6, 78.5, 69.9, 68.9, 56.5, 55.9, 42.7, 42.1, 40.3, 40.1, 39.2, 36.0, 35.9, 35.4, 34.9, 33.2, 31.8, 28.3, 27.3, 27.2, 26.4, 24.2, 23.4, 20.8, 18.6, 12.1. HRMS (ESI) m/z calculated for $C_{36}H_{53}Cl_3N_2O_5S$ $[M+NH_4]^+$, 748.3079; found, 748.3077.



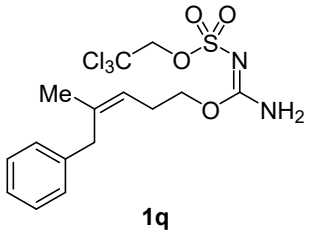
1o

Compound 1o: White solid, 97.0 mg (21%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 5.61 – 5.49 (m, 1H), 5.38 (br s, 1H), 5.32 – 5.23 (m, 1H), 5.14 – 5.04 (m, 1H), 4.66 (s, 2H), 2.46 – 2.38 (m, 1H), 2.31 (dt, *J* = 13.4, 6.1 Hz, 1H), 2.05 (pd, *J* = 7.5, 1.9 Hz, 2H), 1.30 (d, *J* = 6.3 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 135.3, 122.4, 93.7, 78.5, 76.5, 33.3, 20.7, 19.4, 14.1. HRMS (ESI) m/z calculated for $C_{10}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 367.0047; found, 367.0043.



1p

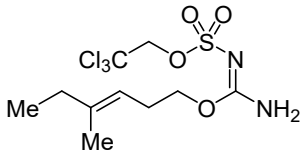
Compound 1p: Colorless semisolid, 68.8 mg (17%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H), 7.22 – 7.16 (m, 6H), 6.84 (br s, 1H), 5.80 (dtt, *J* = 10.7, 7.7, 1.5 Hz, 2H), 5.55 – 5.46 (m, 2H), 5.13 (tt, *J* = 7.0, 5.4 Hz, 1H), 4.97 (d, *J* = 7.1 Hz, 1H), 4.59 (s, 2H), 3.41 (d, *J* = 7.6 Hz, 4H), 2.61 – 2.53 (m, 2H), 2.47 (dddd, *J* = 14.6, 7.1, 5.4, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 140.4, 131.9, 128.5, 128.3, 126.1, 124.2, 93.6, 78.8, 78.4, 33.4, 31.4. HRMS (ESI) m/z calculated for $C_{24}H_{27}Cl_3N_2O_4S$ $[M+Na]^+$, 567.0649; found, 567.0646.



1q

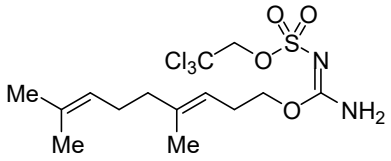
Compound 1q: Colorless semisolid, 140 mg (44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 7.00 (br s, 1H), 5.34 (br s, 1H), 5.29 (td, *J* = 7.2, 1.5 Hz, 1H), 4.65 (s, 2H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.39 (s, 2H), 2.53 (qd, *J* = 6.9, 1.2 Hz, 2H), 1.68 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 139.5, 137.9, 128.46, 128.45, 126.1, 120.5, 93.7, 78.5, 68.9, 37.8, 27.5, 23.6. HRMS (ESI) m/z calculated for $C_{15}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 429.0204; found, 429.0199.



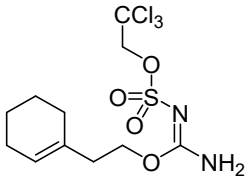
1r

Compound 1r: White solid, 92.6 mg (39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.43 (br s, 1H), 5.07 (tq, *J* = 7.2, 1.4 Hz, 1H), 4.67 (s, 2H), 4.23 (t, *J* = 7.0 Hz, 2H), 2.40 (q, *J* = 7.0 Hz, 2H), 2.01 (q, *J* = 7.4 Hz, 2H), 1.63 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 141.1, 116.5, 93.7, 78.5, 69.0, 32.3, 27.2, 16.1, 12.6. HRMS (ESI) m/z calculated for $C_{10}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 367.0047; found, 367.0049.



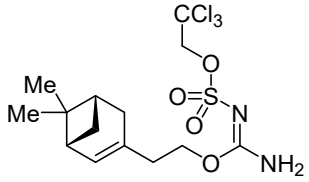
1s

Compound 1s: Colorless semisolid, 161 mg (21%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (br s, 1H), 5.44 (br s, 1H), 5.14 – 5.04 (m, 2H), 4.67 (s, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 2.40 (q, *J* = 7.5 Hz, 2H), 2.08 (q, *J* = 7.3 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.63 (d, *J* = 1.4 Hz, 3H), 1.61 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 139.2, 131.7, 123.9, 117.9, 93.7, 78.5, 68.9, 39.6, 27.2, 26.5, 25.7, 17.7, 16.2. HRMS (ESI) m/z calculated for $C_{14}H_{23}Cl_3N_2O_4S$ $[M+Na]^+$, 443.0336; found, 443.0333.



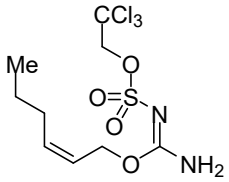
1t

Compound 1t: White solid, 75.2 mg (38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.58 – 5.31 (m, 2H), 4.68 (s, 2H), 4.31 (t, *J* = 6.9 Hz, 2H), 2.34 – 2.28 (m, 2H), 1.99 (ddt, *J* = 9.4, 6.4, 2.9 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.67 – 1.60 (m, 2H), 1.56 (dp, *J* = 8.4, 2.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 132.7, 124.3, 93.7, 78.5, 67.8, 36.7, 28.4, 25.2, 22.7, 22.2. HRMS (ESI) m/z calculated for $C_{11}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 379.0047; found, 379.0044.



1u

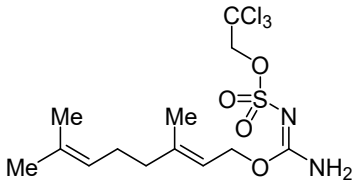
Compound 1u: White solid, 184 mg (44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (br s, 1H), 5.41 (br s, 1H), 5.34 – 5.23 (m, 1H), 4.67 (s, 2H), 4.32 – 4.20 (m, 2H), 2.42 – 2.36 (m, 1H), 2.34 (tt, *J* = 6.8, 1.6 Hz, 2H), 2.30 – 2.16 (m, 2H), 2.10 (dddd, *J* = 8.6, 5.7, 2.7, 1.2 Hz, 1H), 2.02 (td, *J* = 5.6, 1.6 Hz, 1H), 1.28 (s, 3H), 1.14 (d, *J* = 8.6 Hz, 1H), 0.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 143.1, 119.5, 93.7, 78.5, 67.4, 45.6, 40.7, 38.0, 35.6, 31.6, 31.3, 26.2, 21.1. HRMS (ESI) m/z calculated for $C_{14}H_{21}Cl_3N_2O_4S$ $[M+H]^+$, 419.0360; found, 419.0355.



1v

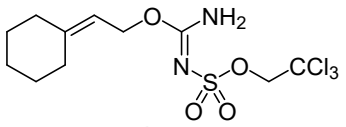
Compound 1v: White solid, 321 mg (61%, isolated as a 1.5:1 mixture of two rotamers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (br s, 1H), 5.78 – 5.61 (m, 1H), 5.59 – 5.52 (m, 1H), 5.45 (br s, 1H), 4.89 – 4.42 (m, 4H), 2.18 – 2.06 (m, 2H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.92 (td, *J* = 7.4, 3.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2 – 151.4, 137.0 – 135.1, 123.5 – 121.8, 93.7 – 92.6, 78.8 – 78.5, 65.0 – 45.0, 29.6 – 29.3,

22.5 – 22.4, 13.7 – 13.6. HRMS (ESI) m/z calculated for $C_9H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 352.9891; found, 352.9886.



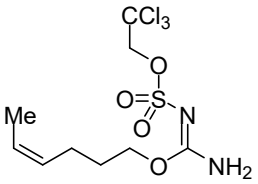
1w

Compound 1w: Colorless semisolid, 180 mg (44%, isolated as a 1:1 mixture of two rotamers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (br s, 1H), 5.41 (br s, 1H), 5.36 (dddd, *J* = 9.8, 5.7, 2.6, 1.3 Hz, 1H), 5.06 (dddt, *J* = 6.9, 4.0, 2.7, 1.3 Hz, 1H), 4.78 (d, *J* = 7.3 Hz, 2H) (for rotamer 1) or 4.46 (d, *J* = 7.0 Hz, 2H) (for rotamer 2), 4.66 (d, *J* = 5.9 Hz, 2H), 2.15 – 1.99 (m, 4H), 1.74 (dd, *J* = 8.8, 1.4 Hz, 3H), 1.68 (dt, *J* = 4.0, 1.3 Hz, 3H), 1.60 (dd, *J* = 5.1, 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 – 151.6, 144.7 – 141.7, 132.1 – 131.9, 123.6 – 123.4, 118.5 – 116.7, 93.7 – 92.6, 78.7 – 78.5, 66.1 – 46.1, 39.6 – 39.5, 26.3 – 26.2, 25.7, 17.7, 16.7 – 16.4. HRMS (ESI) m/z calculated for $C_{13}H_{21}Cl_3N_2O_4S$ $[M+Na]^+$, 429.0180; found, 429.0173.



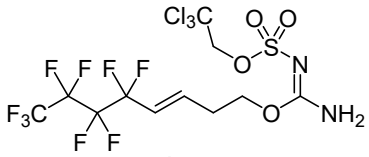
1x

Compound 1x: Colorless semisolid, 117 mg (32%, isolated as a 1.5:1 mixture of two rotamers). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (br s, 1H), 5.42 (br s, 1H), 5.31 (tdt, *J* = 7.3, 4.5, 1.2 Hz, 1H), 4.77 (d, *J* = 7.4 Hz, 2H) (for rotamer 1) or 4.45 (d, *J* = 7.2 Hz, 2H) (for rotamer 2), 4.67 (d, *J* = 2.9 Hz, 2H), 2.23 (dt, *J* = 19.8, 5.2 Hz, 2H), 2.16 – 2.07 (m, 2H), 1.61 – 1.54 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 – 151.6, 149.3 – 146.1, 115.5 – 113.6, 93.7 – 92.6, 78.7 – 78.5, 65.4 – 45.3, 37.0, 29.2 – 28.9, 28.3 – 28.2, 27.7 – 27.6, 26.6 – 26.5. HRMS (ESI) m/z calculated for $C_{11}H_{17}Cl_3N_2O_4S$ $[M+Na]^+$, 400.9867; found, 400.9862.



1y

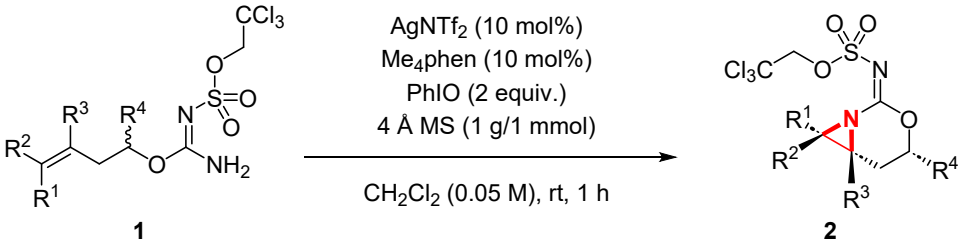
Compound 1y: White solid, 310 mg (58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (br s, 1H), 5.52 (dtt, *J* = 13.9, 6.9, 5.3 Hz, 1H), 5.44 (br s, 1H), 5.35 (dddd, *J* = 10.8, 9.0, 7.4, 3.8 Hz, 1H), 4.67 (s, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 2.20 – 2.05 (m, 2H), 1.85 – 1.70 (m, 2H), 1.61 (dd, *J* = 6.8, 1.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 128.4, 125.5, 93.7, 78.5, 68.9, 28.1, 22.8, 12.7. HRMS (ESI) m/z calculated for $C_9H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 352.9891; found, 352.9888.



1z

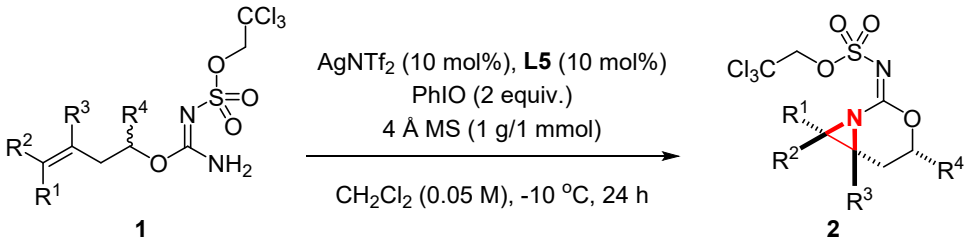
Compound 1z: Off-white solid, 198 mg (29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 10.5 Hz, 1H), 6.18 – 6.11 (m, 1H), 5.77 – 5.63 (m, 1H), 5.46 (br s, 1H), 4.67 (s, 2H), 4.36 (t, *J* = 6.3 Hz, 2H), 2.84 – 2.70 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 139.3 – 119.5 (m), 119.3 – 119.1 (m), 118.9 – 106.1 (m, 4C), 93.6, 78.5, 67.3, 27.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -80.9 – -81.1 (m, 3F), -107.3 – -107.4 (m, 2F), -124.6 (t, *J* = 10.0 Hz, 2F), -125.8 (dt, *J* = 12.6, 6.6 Hz, 2F). HRMS (ESI) m/z calculated for $C_{11}H_{10}Cl_3F_9N_2O_4S$ $[M+H]^+$, 542.9356; found, 542.9352.

III. Enantioselective Aziridinations with Carbamimidate Substrates

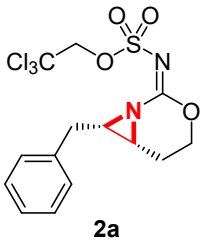


1 **2**

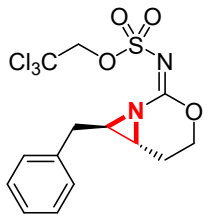
General procedure for the racemic reaction: In a pre-dried vial equipped with a magnetic stir bar, $AgNTf_2$ (10 mol %) and 3,4,7,8-tetramethyl-1,10-phenanthroline (10 mol %) were dissolved in CH_2Cl_2 (0.05 M). After stirring vigorously for 15 minutes at rt, 4 Å molecular sieves (100 mg) and carbamimidate **1** (1.0 equiv.) were added. The mixture was left stirred at rt for 2 min before PhIO (2.0 equiv.) was added in one portion. Upon completion of the reaction indicated by TLC analysis (~1 h), the mixture was filtered through a pad of Celite using EtOAc as an eluent. The resulting clear solution was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexane/EtOAc gradient) to afford bicyclic aziridine *rac*-**2**.



General procedure for the enantioselective reaction: In a pre-dried test tube (0.1 mmol scale) or a round-bottom flask (large scale) equipped with a magnetic stir bar, $AgNTf_2$ (10 mol %) and **L5** (10 mol %) were dissolved in CH_2Cl_2 (0.05 M). After stirring vigorously for 15 min at rt, 4 Å molecular sieves (100 mg) and carbamimidate **1** (1.0 equiv.) were added. The mixture was then cooled to -10 °C before PhIO (2.0 equiv.) was added in one portion. After stirring for 24 h, the mixture was filtered through a pad of Celite using EtOAc as an eluent. The resulting clear solution was concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexane/EtOAc gradient) to afford bicyclic aziridine **2**.

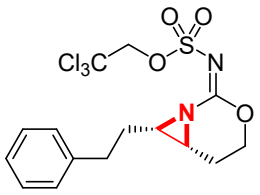


Compound 2a: The reaction was run on a 2.5 mmol scale. Off-white solid, 922 mg (89%, 95% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 4.70 (d, *J* = 1.8 Hz, 2H), 4.67 (ddd, *J* = 10.3, 4.6, 1.5 Hz, 1H), 4.44 (ddd, *J* = 12.9, 10.7, 2.4 Hz, 1H), 3.46 (dd, *J* = 15.3, 4.3 Hz, 1H), 3.26 (dt, *J* = 9.6, 4.6 Hz, 1H), 3.16 (ddd, *J* = 9.1, 6.9, 4.9 Hz, 1H), 2.49 – 2.38 (m, 2H), 1.75 (dddd, *J* = 14.8, 12.4, 9.1, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 135.5, 129.0, 128.4, 127.4, 93.7, 78.8, 68.3, 46.8, 37.9, 30.8, 19.0. HRMS (ESI) m/z calculated for $C_{14}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 412.9891, found 412.9887. The *ee* value was determined by chiral HPLC analysis of **2a** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 27.8 min (major) and 30.1 min (minor).



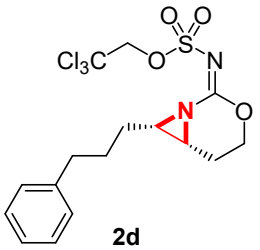
2b

Compound 2b: The reaction was run on a 0.1 mmol scale. White solid, 32.9 mg (80%, 97% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 4.69 (s, 2H), 4.50 (ddd, *J* = 10.7, 4.3, 1.8 Hz, 1H), 4.34 (ddd, *J* = 12.7, 10.8, 2.2 Hz, 1H), 3.32 (dd, *J* = 15.3, 3.4 Hz, 1H), 3.03 (dd, *J* = 14.6, 6.3 Hz, 1H), 2.82 (q, *J* = 4.0 Hz, 1H), 2.75 (ddd, *J* = 9.6, 6.3, 3.7 Hz, 1H), 2.47 (ddt, *J* = 14.6, 6.3, 2.0 Hz, 1H), 1.41 (dddd, *J* = 14.8, 12.7, 8.9, 4.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 135.4, 129.4, 128.6, 127.2, 93.6, 78.9, 68.3, 53.1, 39.6, 36.6, 24.5. HRMS (ESI) m/z calculated for $C_{14}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 412.9891; found, 412.9886. The *ee* value was determined by chiral HPLC analysis of **2b** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 20.9 min (minor) and 24.7 min (major).



2c

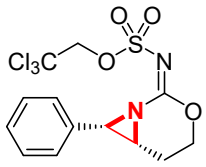
Compound 2c: The reaction was run on a 0.1 mmol scale. White semisolid, 38.6 mg (90%, 99% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 7.6, 5.6, 1.6 Hz, 2H), 7.24 – 7.14 (m, 3H), 4.70 (s, 2H), 4.50 (ddd, *J* = 10.7, 4.5, 1.5 Hz, 1H), 4.30 (ddd, *J* = 13.0, 10.7, 2.4 Hz, 1H), 3.06 – 2.90 (m, 3H), 2.74 (dt, *J* = 13.9, 7.9 Hz, 1H), 2.43 – 2.29 (m, 1H), 1.96 (ddt, *J* = 15.0, 6.6, 2.3 Hz, 1H), 1.50 – 1.36 (m, 1H), 1.20 (dddd, *J* = 15.0, 13.1, 8.9, 4.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 139.8, 128.7, 128.5, 126.6, 93.7, 78.8, 68.4, 46.5, 37.9, 32.5, 26.9, 18.5. HRMS (ESI) m/z calculated for $C_{15}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 427.0047; found, 427.0040. The *ee* value was determined by chiral HPLC analysis of **2c** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 22.2 min (minor) and 23.8 min (major).



2d

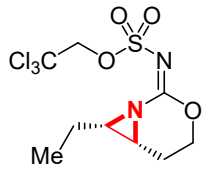
Compound 2d: The reaction was run on a 0.1 mmol scale. White semisolid, 34.3 mg (78%, 75% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 4.69 (d, *J* = 0.6 Hz, 2H), 4.56 (ddd, *J* = 10.6, 4.6, 1.5 Hz, 1H), 4.36 (ddd, *J* = 12.9, 10.7, 2.4 Hz, 1H), 3.04 (ddd, *J* = 9.0, 6.9, 5.0 Hz, 1H), 2.96 (dt, *J* = 8.7, 5.0 Hz, 1H), 2.76 – 2.60 (m, 2H), 2.28 (dddd, *J* = 14.8, 6.9, 2.4, 1.5 Hz, 1H), 2.09 – 1.92 (m, 2H), 1.79 – 1.67 (m, 1H), 1.41 (dddd, *J* = 14.9, 12.4, 9.1, 4.6 Hz, 1H), 1.25 – 1.16 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 141.0, 128.5, 128.3, 126.2, 93.7, 78.8, 68.2, 46.8, 37.6, 35.3, 27.9, 24.7, 18.5. HRMS (ESI) m/z calculated for $C_{16}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 441.0204; found, 441.0199. The *ee* value was

determined by chiral HPLC analysis of **2d** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 27.0 min (major) and 31.1 min (minor).



2e

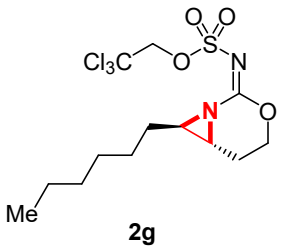
Compound 2e: The reaction was run on a 0.1 mmol scale. White semisolid, 14.9 mg (37%, 62% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 4.65 (ddd, *J* = 10.8, 4.7, 1.6 Hz, 1H), 4.55 – 4.43 (m, 3H), 4.17 (d, *J* = 5.1 Hz, 1H), 3.32 (ddd, *J* = 9.2, 6.5, 5.1 Hz, 1H), 2.33 (dddd, *J* = 15.0, 6.6, 2.5, 1.6 Hz, 1H), 1.72 (dddd, *J* = 14.8, 12.5, 9.2, 4.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 129.30, 129.27, 129.25, 128.8, 93.6, 78.6, 68.2, 48.5, 37.9, 18.9. HRMS (ESI) m/z calculated for $C_{13}H_{13}Cl_3N_2O_4S$ $[M+H]^+$, 398.9734; found, 398.9728. The *ee* value was determined by chiral HPLC analysis of **2e** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 31.6 min (major) and 38.9 min (minor).



2f

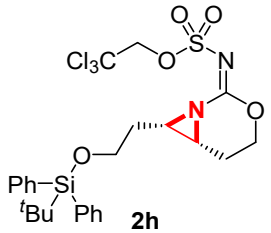
Compound 2f: The reaction was run on a 0.1 mmol scale. White solid, 27.9 mg (79%, 95% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (d, *J* = 1.0 Hz, 2H), 4.60 (ddd, *J* = 10.7, 4.6, 1.5 Hz, 1H), 4.39 (ddd, *J* = 12.9, 10.7, 2.4 Hz, 1H), 3.07 (ddd, *J* = 9.1, 6.9, 5.0 Hz, 1H), 2.95 (dt, *J* = 9.7, 5.0 Hz, 1H), 2.34 (dddd, *J* = 14.8, 7.0, 2.4, 1.5 Hz, 1H), 2.08 (dp, *J* = 13.3, 6.8 Hz, 1H), 1.59 – 1.47 (m, 1H), 1.24 – 1.14 (m, 1H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 93.7, 78.8, 68.1, 48.1, 37.5, 18.8, 18.4, 10.5. HRMS

(ESI) m/z calculated for $C_9H_{13}Cl_3N_2O_4S$ $[M+H]^+$, 350.9734; found, 350.9736. The *ee* value was determined by chiral HPLC analysis of **2f** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 21.3 min (major) and 22.0 min (minor).



2g

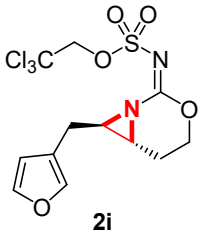
Compound 2g: The reaction was run on a 0.1 mmol scale. White semisolid, 37.0 mg (91%, 93% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (s, 2H), 4.54 (ddd, *J* = 10.7, 4.3, 1.8 Hz, 1H), 4.39 (ddd, *J* = 12.7, 10.7, 2.1 Hz, 1H), 2.77 (ddd, *J* = 8.9, 6.1, 3.5 Hz, 1H), 2.57 – 2.47 (m, 2H), 1.96 (s, 1H), 1.58 (dq, *J* = 14.3, 7.5 Hz, 1H), 1.49 – 1.24 (m, 9H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 93.7, 78.9, 68.4, 53.5, 40.4, 31.6, 31.0, 28.8, 25.8, 24.8, 22.5, 14.0. HRMS (ESI) m/z calculated for $C_{13}H_{21}Cl_3N_2O_4S$ $[M+H]^+$, 407.0360; found, 407.0354. The *ee* value was determined by chiral HPLC analysis of **2g** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 17.6 min (minor) and 18.8 min (major).



2h

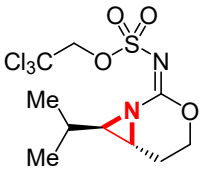
Compound 2h: The reaction was run on a 0.1 mmol scale. White solid, 39.2 mg (65%, 90% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (ddt, *J* = 6.5, 4.9, 1.5 Hz, 4H), 7.48 – 7.42 (m, 2H), 7.40 (dd, *J* = 8.0, 6.5 Hz, 4H), 4.66 (s, 2H), 4.56 (ddd, *J* = 10.8, 4.5, 1.5 Hz, 1H), 4.35 (ddd, *J* = 12.9, 10.7, 2.4 Hz, 1H), 3.91 – 3.81 (m, 2H), 3.08 (dt, *J* = 9.4, 4.5 Hz, 1H), 3.02 (ddd, *J* = 9.0, 6.9, 5.0 Hz, 1H), 2.33 – 2.18 (m, 2H), 1.59 – 1.47

(m, 1H), 1.41 (dtd, J = 14.6, 8.9, 5.4 Hz, 1H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 135.5, 133.0, 129.9, 127.9, 93.7, 78.7, 68.3, 60.7, 45.4, 38.0, 28.0, 26.8, 19.14, 19.13. HRMS (ESI) m/z calculated for $C_{25}H_{31}Cl_3N_2O_5SSi$ $[M+H]^+$, 605.0861; found, 605.0856. The *ee* value was determined by chiral HPLC analysis of **2h** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 17.7 min (major) and 20.1 min (minor).



2i

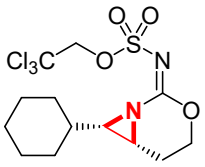
Compound 2i: The reaction was run on a 0.1 mmol scale. Yellow solid, 30.0 mg (74%, 95% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 1.8, 0.9 Hz, 1H), 6.33 (dd, J = 3.2, 1.8 Hz, 1H), 6.25 (dd, J = 3.2, 0.8 Hz, 1H), 4.71 (s, 2H), 4.53 (ddd, J = 10.8, 4.3, 1.8 Hz, 1H), 4.39 (ddd, J = 12.8, 10.8, 2.2 Hz, 1H), 3.45 (d, J = 13.1 Hz, 1H), 2.97 (dd, J = 15.7, 6.9 Hz, 1H), 2.88 (ddd, J = 8.9, 6.3, 3.6 Hz, 1H), 2.81 (dt, J = 7.8, 4.0 Hz, 1H), 2.54 (ddt, J = 14.8, 6.3, 2.1 Hz, 1H), 1.44 (dddd, J = 14.8, 13.0, 8.9, 4.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 149.7, 142.1, 110.6, 108.0, 93.6, 79.0, 68.3, 51.0, 39.9, 29.8, 24.5. HRMS (ESI) m/z calculated for $C_{12}H_{13}Cl_3N_2O_5S$ $[M+H]^+$, 402.9683; found, 402.9679. The *ee* value was determined by chiral HPLC analysis of **2i** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 24.1 min (minor) and 25.0 min (major).



2j

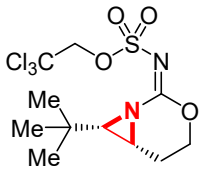
Compound 2j: The reaction was run on a 0.1 mmol scale. White semisolid, 27.5 mg (75%, 96% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (d, J = 1.6 Hz, 2H), 4.57 (ddd, J = 10.7, 4.2, 1.7 Hz, 1H), 4.42 (ddd, J =

12.7, 10.7, 2.2 Hz, 1H), 2.86 – 2.77 (m, 1H), 2.51 (ddt, *J* = 14.8, 6.2, 2.0 Hz, 1H), 2.35 (dd, *J* = 6.4, 3.6 Hz, 1H), 1.91 (h, *J* = 6.4 Hz, 1H), 1.49 – 1.38 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 93.7, 78.9, 68.8, 58.4, 38.4, 29.2, 24.8, 19.2, 17.8. HRMS (ESI) m/z calculated for $C_{10}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 364.9891; found, 364.9888. The *ee* value was determined by chiral HPLC analysis of **2j** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 16.6 min (minor) and 18.1 min (major).



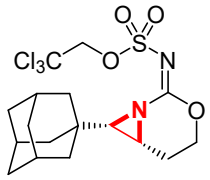
2k

Compound 2k: The reaction was run on a 0.1 mmol scale. White solid, 34.2 mg (84%, 96% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.4 Hz, 2H), 4.63 (ddd, *J* = 10.7, 4.4, 1.7 Hz, 1H), 4.40 (ddd, *J* = 12.8, 10.7, 2.4 Hz, 1H), 2.98 (ddd, *J* = 9.3, 6.7, 5.0 Hz, 1H), 2.68 (dd, *J* = 9.5, 5.2 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.36 (ddt, *J* = 14.8, 6.9, 2.1 Hz, 1H), 1.82 – 1.72 (m, 2H), 1.72 – 1.65 (m, 1H), 1.52 (dddd, *J* = 14.6, 12.4, 9.5, 4.4 Hz, 2H), 1.36 – 1.06 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 93.7, 78.7, 68.5, 51.3, 36.9, 35.6, 30.5, 29.8, 25.9, 25.5, 25.2, 19.4. HRMS (ESI) m/z calculated for $C_{13}H_{19}Cl_3N_2O_4S$ $[M+H]^+$, 405.0204; found, 405.0202. The *ee* value was determined by chiral HPLC analysis of **2k** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 19.3 min (minor) and 19.7 min (major).



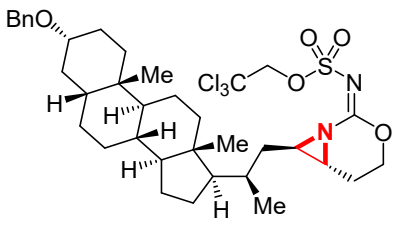
2l

Compound 2l: The reaction was run on a 0.1 mmol scale. White solid, 29.5 mg (78%, 95% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 – 4.64 (m, 3H), 4.36 (ddd, *J* = 12.1, 10.7, 2.6 Hz, 1H), 2.92 (ddd, *J* = 9.8, 7.0, 5.3 Hz, 1H), 2.80 (d, *J* = 5.3 Hz, 1H), 2.31 (dddd, *J* = 14.8, 6.9, 2.7, 1.6 Hz, 1H), 2.19 (dddd, *J* = 14.6, 12.4, 9.8, 4.5 Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 93.8, 78.6, 68.2, 56.0, 37.8, 33.7, 28.6, 18.8. HRMS (ESI) m/z calculated for $C_{11}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 379.0047; found, 379.0044. The *ee* value (95%) was determined by chiral HPLC analysis of **2l** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 21.4 min (major) and 22.1 min (minor).



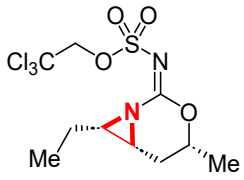
2m

Compound 2m: The reaction was run on a 0.1 mmol scale. White solid, 34.7 mg (82%, 96% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 – 4.69 (m, 2H), 4.66 (ddd, *J* = 10.5, 4.3, 1.8 Hz, 1H), 4.33 (td, *J* = 11.3, 3.1 Hz, 1H), 2.88 (ddd, *J* = 9.8, 7.0, 5.3 Hz, 1H), 2.57 (d, *J* = 5.5 Hz, 1H), 2.38 – 2.23 (m, 2H), 2.07 – 1.96 (m, 6H), 1.81 – 1.67 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 93.8, 78.6, 68.2, 56.7, 40.2, 37.9, 36.5, 36.1, 28.0, 19.9. HRMS (ESI) m/z calculated for $C_{17}H_{23}Cl_3N_2O_4S$ $[M+H]^+$, 457.0517; found, 457.0511. The *ee* value was determined by chiral HPLC analysis of **2m** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 21.7 min (minor) and 23.6 min (major).



2n

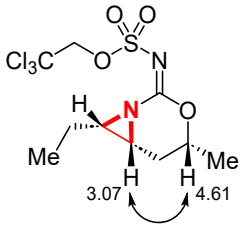
Compound 2n: The reaction was run on a 0.1 mmol scale. White semisolid, 42.0 mg (58%, *dr* > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 4.71 (s, 2H), 4.59 – 4.51 (m, 3H), 4.39 (ddd, *J* = 12.7, 10.7, 2.1 Hz, 1H), 3.37 (tt, *J* = 11.1, 4.3 Hz, 1H), 2.76 (ddd, *J* = 9.3, 6.2, 3.5 Hz, 1H), 2.57 – 2.45 (m, 2H), 1.96 (dt, *J* = 12.2, 3.2 Hz, 1H), 1.90 – 1.75 (m, 5H), 1.72 (ddt, *J* = 13.1, 6.5, 3.3 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.57 (qd, *J* = 5.0, 2.9 Hz, 1H), 1.50 – 1.30 (m, 7H), 1.30 – 1.20 (m, 5H), 1.20 – 0.99 (m, 8H), 0.98 – 0.88 (m, 4H), 0.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 139.1, 128.3, 127.6, 127.4, 93.6, 78.9, 78.6, 69.9, 68.5, 56.5, 56.2, 52.2, 42.9, 42.1, 41.7, 40.3, 40.2, 37.7, 35.8, 35.4, 34.9, 34.6, 33.2, 28.4, 27.3, 27.2, 26.3, 24.7, 24.2, 23.4, 20.8, 18.9, 12.1. HRMS (ESI) m/z calculated for $C_{36}H_{51}Cl_3N_2O_5S$ $[M+NH_4]^+$, 746.2928; found, 746.2917. The *dr* value was determined by ^{1}H NMR analysis of the crude mixture in comparison with the crude ^{1}H NMR spectrum of a reaction using an achiral catalyst.



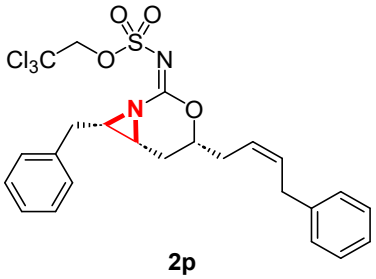
2o

Compound 2o: The reaction was run on a 0.1 mmol scale. White semisolid, 20.7 mg (57%, 6.4:1 *dr*, major: 71% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.99 – 4.55 (m, 3H), 3.07 (tdd, *J* = 9.2, 6.9, 5.0 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.39 – 2.15 (m, 1H), 2.14 – 2.00 (m, 1H), 1.66 – 1.44 (m, 4H), 1.23 – 1.06 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 93.8, 78.7, 76.8, 48.9, 36.3, 24.1, 20.1, 18.8, 10.5. HRMS (ESI) m/z calculated for $C_{10}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 364.9891; found, 364.9889. The *dr* value was determined by ^{1}H NMR analysis of the crude mixture. Each diastereomer was isolated as a mixture of two NMR-distinguishable, inseparable rotamers. The *ee* value of the major diastereomer was determined by chiral HPLC analysis of **2o** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 12.1 min (minor) and 12.4 min (major).

The identity of the major diastereomer was determined by NOESY (see Section VI for the NMR spectrum).



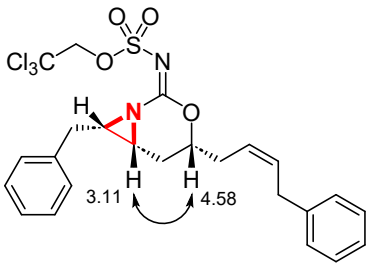
2o



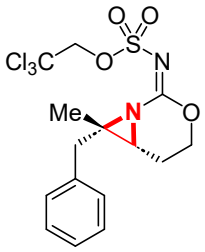
2p

Compound 2p: The reaction was run on a 0.1 mmol scale. Off-white solid, 27.7 mg (51%, > 20:1 *dr*, major: 94% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 3H), 7.23 – 7.14 (m, 5H), 5.93 – 5.83 (m, 1H), 5.62 (tdd, *J* = 10.8, 5.3, 3.7 Hz, 1H), 4.74 – 4.65 (m, 2H), 4.58 (dtd, *J* = 11.7, 6.0, 2.2 Hz, 1H), 3.50 – 3.40 (m, 3H), 3.24 (dt, *J* = 9.6, 4.5 Hz, 1H), 3.11 (ddd, *J* = 9.1, 6.8, 4.9 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.69 – 2.59 (m, 1H), 2.44 – 2.31 (m, 2H), 1.42 (ddd, *J* = 14.6, 11.3, 9.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 140.1, 135.6, 133.1, 129.0, 128.6, 128.4, 128.2, 127.3, 126.2, 122.5, 93.8, 80.1, 78.8, 47.5, 38.1, 33.6, 31.9, 30.8, 24.0. HRMS (ESI) m/z calculated for $C_{24}H_{25}Cl_3N_2O_4S$ $[M+Na]^+$, 565.0493; found, 565.0490. The *dr* value was determined by ^{1}H NMR analysis of the crude mixture. The *ee* value of the major diastereomer was determined by chiral HPLC analysis of **2p** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 50 min, 0.7 mL/min, 210 nm): t_R: 25.0 min (major) and 34.9 min (minor).

The identity of the major diastereomer was determined by NOESY (see Section VI for the NMR spectrum).

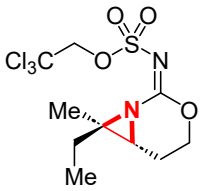


2p



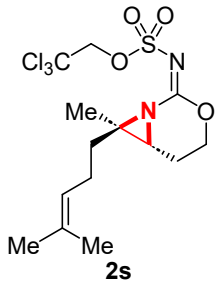
2q

Compound 2q: The reaction was run on a 0.1 mmol scale. White solid, 34.2 mg (80%, 96% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.16 (dd, *J* = 7.0, 2.0 Hz, 2H), 4.75 (s, 2H), 4.63 (ddd, *J* = 10.7, 4.6, 1.7 Hz, 1H), 4.41 (ddd, *J* = 13.0, 10.6, 2.4 Hz, 1H), 3.37 (d, *J* = 15.3 Hz, 1H), 3.03 (dd, *J* = 9.2, 6.9 Hz, 1H), 2.59 – 2.48 (m, 2H), 1.82 (dddd, *J* = 14.6, 12.4, 9.2, 4.7 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 135.5, 128.9, 128.7, 127.3, 93.8, 78.8, 67.8, 54.1, 45.2, 36.1, 22.3, 20.5. HRMS (ESI) m/z calculated for $C_{15}H_{17}Cl_3N_2O_4S$ $[M+H]^+$, 407.0360; found, 407.0354. The *ee* value was determined by chiral HPLC analysis of **2q** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 23.3 min (minor) and 24.2 min (major).



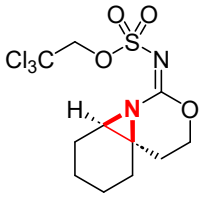
2r

Compound 2r: The reaction was run on a 0.1 mmol scale. White semisolid, 22.5 mg (62%, 94% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (d, *J* = 1.5 Hz, 2H), 4.57 (ddd, *J* = 10.7, 4.6, 1.6 Hz, 1H), 4.34 (ddd, *J* = 13.0, 10.6, 2.4 Hz, 1H), 2.90 (dd, *J* = 9.0, 7.0 Hz, 1H), 2.33 (ddt, *J* = 14.8, 7.2, 2.1 Hz, 1H), 1.90 – 1.78 (m, 1H), 1.69 (dt, *J* = 14.2, 7.4 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.34 (s, 3H), 1.01 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 93.8, 78.8, 67.8, 55.4, 43.4, 31.0, 19.4, 14.3, 9.2. HRMS (ESI) m/z calculated for $C_{10}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 364.9891; found, 364.9886. The *ee* value was determined by chiral HPLC analysis of **2r** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 19.1 min (minor) and 20.1 min (major).



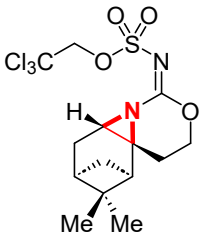
2s

Compound 2s: The reaction was run on a 0.1 mmol scale. White solid, 25.2 mg (60%, 95% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 – 5.04 (m, 1H), 4.70 (d, *J* = 1.7 Hz, 2H), 4.56 (ddd, *J* = 10.7, 4.7, 1.6 Hz, 1H), 4.33 (ddd, *J* = 12.8, 10.6, 2.5 Hz, 1H), 2.91 (dd, *J* = 9.0, 7.0 Hz, 1H), 2.31 (ddt, *J* = 15.0, 7.2, 2.2 Hz, 1H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.88 (p, *J* = 7.8 Hz, 1H), 1.69 (d, *J* = 1.2 Hz, 3H), 1.67 – 1.54 (m, 5H), 1.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 132.8, 122.6, 93.8, 78.8, 67.7, 54.4, 44.0, 38.1, 25.7, 23.8, 19.4, 17.7, 14.6. HRMS (ESI) m/z calculated for $C_{14}H_{21}Cl_3N_2O_4S$ $[M+H]^+$, 419.0360; found, 419.0358. The *ee* value was determined by chiral HPLC analysis of **2s** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 11.7 min (minor) and 14.0 min (major).



2t

Compound 2t: The reaction was run on a 0.1 mmol scale. White solid, 31.4 mg (83%, 42% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (s, 2H), 4.50 (ddd, *J* = 10.8, 4.2, 1.8 Hz, 1H), 4.40 (ddd, *J* = 12.8, 10.9, 2.0 Hz, 1H), 2.88 (d, *J* = 4.9 Hz, 1H), 2.44 – 2.32 (m, 1H), 2.25 (dt, *J* = 14.6, 2.0 Hz, 1H), 2.15 (dt, *J* = 14.2, 5.6 Hz, 1H), 1.98 (dq, *J* = 15.8, 5.6 Hz, 1H), 1.75 (ddd, *J* = 14.2, 8.4, 5.7 Hz, 1H), 1.64 – 1.47 (m, 3H), 1.44 (dtd, *J* = 13.5, 6.7, 4.1 Hz, 1H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 93.8, 78.8, 67.4, 54.6, 44.0, 32.2, 28.9, 23.3, 19.6, 19.3. HRMS (ESI) m/z calculated for $C_{11}H_{15}Cl_3N_2O_4S$ $[M+H]^+$, 376.9891; found, 376.9890. The *ee* value of the major diastereomer was determined by chiral HPLC analysis of **2t** in comparison with a sample of racemic material (CHIRALCEL® OJ-H, 5 to 35% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 12.7 min (minor) and 13.1 min (major).

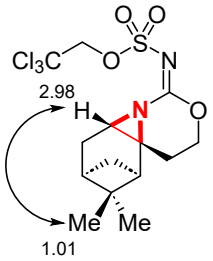


2u

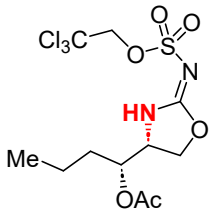
Compound 2u: The reaction was run on a 0.1 mmol scale. White solid, 40.9 mg (98%, > 20:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (d, *J* = 0.8 Hz, 2H), 4.49 (ddd, *J* = 10.7, 4.1, 1.8 Hz, 1H), 4.30 (ddd, *J* = 12.7, 10.7, 2.0 Hz, 1H), 2.98 (d, *J* = 5.7 Hz, 1H), 2.46 (dd, *J* = 15.6, 2.9 Hz, 1H), 2.21 (dt, *J* = 14.5, 2.0 Hz, 1H), 2.17 – 2.08 (m, 3H), 1.89 (tt, *J* = 5.6, 3.1 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.65 (ddd, *J* = 14.4, 12.3, 4.1 Hz, 1H), 1.36 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 93.8, 78.8, 67.1, 51.3, 48.2, 44.3,

40.2, 40.0, 30.9, 26.2, 25.8, 25.5, 20.4. HRMS (ESI) m/z calculated for $C_{14}H_{19}Cl_3N_2O_4S$ $[M+Na]^+$, 439.0023; found, 439.0017.

The identity of the major diastereomer was determined by NOESY (see Section VI for the NMR spectrum).

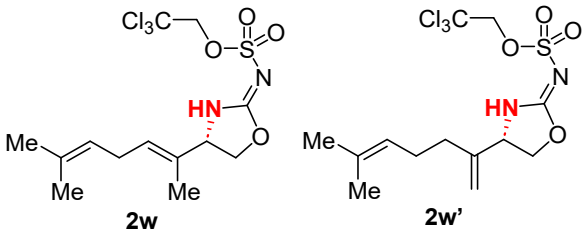


2u



2v

Compound 2v: The reaction was run on a 0.1 mmol scale. 79% *ee*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (br s, 1H), 5.02 (dt, *J* = 8.9, 4.3 Hz, 1H), 4.69 (s, 2H), 4.62 (t, *J* = 9.2 Hz, 1H), 4.40 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.24 (dt, *J* = 9.1, 4.7 Hz, 1H), 2.12 (s, 3H), 1.67 – 1.57 (m, 1H), 1.50 (dddd, *J* = 13.8, 9.5, 6.4, 4.3 Hz, 1H), 1.44 – 1.30 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 163.0, 93.6, 78.6, 72.4, 69.3, 57.3, 32.5, 20.8, 18.4, 13.7. HRMS (ESI) m/z calculated for $C_{11}H_{17}Cl_3N_2O_6S$ $[M+H]^+$, 410.9946; found, 410.9943. The *ee* value was determined by chiral HPLC analysis of **2v** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 20.7 min (major) and 24.5 min (minor).

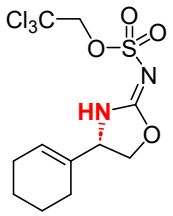


Compounds 2w and 2w': The reaction was run on a 0.1 mmol scale. White solid, 8.40 mg (21% total yield of an inseparable mixture, **2w**:**2w'** = 1.7:1, 49% *ee*). HRMS (ESI) m/z calculated for $C_{13}H_{19}Cl_3N_2O_4S$ $[M+Na]^+$, 427.0023; found, 427.0018. The *ee* value was determined by chiral HPLC analysis of **2w** and **2w'** in comparison with a sample of racemic materials (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: **2w**: 16.5 min (major) and 18.8 min (minor), **2w'**: 17.8 min (major) and 20.2 min (minor).

Assignments of ^{1}H and ^{13}C NMR data for **Compounds 2w** and **2w'** were determined using ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC NMR (see Section VI for the NMR spectra).

Compound 2w: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 5.50 (t, J = 7.3 Hz, 1H), 5.08 – 4.99 (m, 1H), 4.69 (s, 2H), 4.72 – 4.63 (m, 2H), 4.29 (m, 1H), 2.80 – 2.67 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 133.2, 130.9, 129.3, 120.8, 93.7, 78.6, 71.9, 59.6, 26.9, 25.6, 17.8, 11.0.

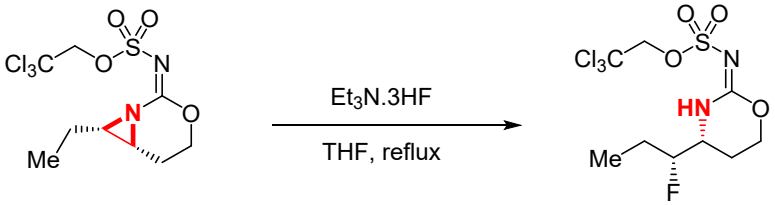
Compound 2w': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 5.17 (s, 1H), 5.10 (d, J = 1.6 Hz, 1H), 5.08 – 4.99 (m, 1H), 4.70 (s, 2H), 4.68 – 4.58 (m, 2H), 4.29 (m, 1H), 2.18 (q, J = 7.4 Hz, 2H), 2.04 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 144.3, 133.3, 122.6, 113.8, 93.7, 78.6, 71.0, 62.1, 31.0, 25.9, 25.6, 17.8.



2x

Compound 2x: The reaction was run on a 0.1 mmol scale. White solid, 13.8 mg (37%, 67% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 1H), 5.81 (tt, *J* = 3.6, 1.7 Hz, 1H), 4.70 (s, 2H), 4.64 (t, *J* = 8.9 Hz, 1H), 4.57 (dd, *J* = 9.2, 6.1 Hz, 1H), 4.31 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.06 (ddd, *J* = 8.5, 5.9, 3.3 Hz, 2H), 2.01 – 1.88 (m, 2H), 1.75 – 1.57 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 132.7, 128.3, 93.7, 78.6, 71.1, 60.9, 24.9, 22.9, 22.0, 21.9. HRMS (ESI) m/z calculated for $C_{11}H_{15}Cl_3N_2O_4S$ $[M+Na]^+$, 398.9710; found, 398.9704. The *ee* value of the major diastereomer was determined by chiral HPLC analysis of **2y** in comparison with a sample of racemic material (CHIRALCEL® OD-H, 5 to 30% ^{i}PrOH/hexanes gradient over 45 min, 0.7 mL/min, 210 nm): t_R: 17.8 min (major) and 19.6 min (minor).

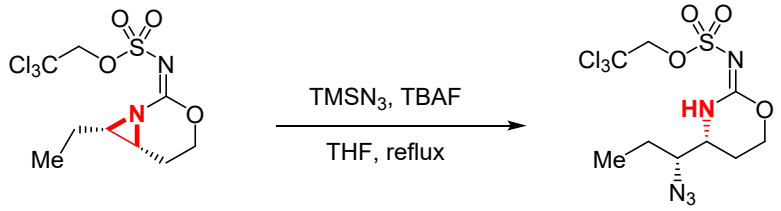
IV. Post-Functionalization of Enantioenriched Bicyclic Aziridines



2f **3**

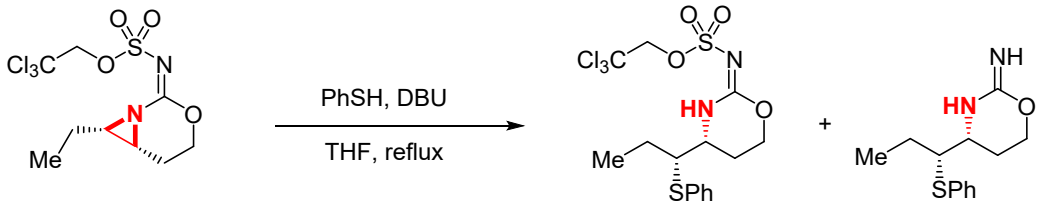
Compound 3: To a solution of aziridine **2f** (35.2 mg, 0.1 mmol, 1 equiv.) in 1 mL of anhydrous THF at rt was added 3HF·Et_3N (33 µL, 0.2 mmol, 2 equiv.). The reaction was heated under reflux overnight. The reaction mixture was diluted with water (5 mL) and EtOAc (5 mL). The aqueous layer was extracted with EtOAc three times. The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of CH_2Cl_2/EtOAc mixtures (25:1 ✂ 5:1). The product was obtained in 58% yield (21.4 mg, white solid). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 4.68 (s, 2H), 4.56 (dtd, *J* = 11.3, 4.3, 1.4 Hz, 1H), 4.40 – 4.22 (m, 2H), 3.74 – 3.62 (m, 1H), 2.16 – 2.08 (m, 1H), 1.91 (dtd, *J* = 14.2, 10.1, 4.2 Hz, 1H), 1.78 – 1.64 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 96.3, 95.6 (d), 78.4, 66.0 (d), 52.7 (d), 24.3 (d), 22.7 (d), 8.9 (d). ^{19}F NMR (377 MHz, $CDCl_3$) δ -192.6 (s). HRMS (ESI) m/z calculated for $C_9H_{14}Cl_3FN_2O_4S$ $[M+H]^+$, 370.9797; found, 370.9798.



2f **4**

Compound 4: To a solution of aziridine **2f** (35.2 mg, 0.1 mmol, 1 equiv.) in 1 mL of anhydrous THF under N_2 atmosphere at 0 °C were added 1 M TBAF solution in THF (10 µL, 0.01 mmol, 0.1 equiv.) and $TMSN_3$ (14.6 µL, 0.11 mmol, 1.1 equiv.). The reaction was heated under reflux overnight. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of CH_2Cl_2/EtOAc mixtures (25:1 ✂ 5:1). The product was obtained in 61% yield (23.9 mg, white solid). ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 4.68 (s, 2H), 4.57 (dt, *J* = 11.4, 4.0 Hz, 1H), 4.35 (td, *J* = 11.3, 2.7 Hz, 1H), 3.51 (tt, *J* = 11.1, 5.7 Hz, 1H), 3.33 (td, *J* = 8.0, 3.9 Hz, 1H), 2.22 – 2.11 (m, 1H), 1.92 (dtd, *J* = 14.3, 10.4, 4.1 Hz, 1H), 1.82 (dqd, *J* = 14.7, 7.4, 3.7 Hz, 1H), 1.68 (dp, *J* = 14.9, 7.5 Hz, 1H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 94.0, 78.4, 66.8, 66.3, 52.2, 23.9, 23.8, 9.9. HRMS (ESI) m/z calculated for $C_9H_{14}Cl_3N_5O_4S$ $[M+H]^+$, 393.9905; found, 393.9906.



2f **5a** **5b**

Compounds 5a and **5b**: To a solution of aziridine **2f** (35.2 mg, 0.1 mmol, 1 equiv.) in 1 mL of anhydrous THF at rt were added PhSH (12 µL, 0.12 mmol, 1.2 equiv.) and DBU (16 µL, 0.11 mmol, 1.1 equiv.). The reaction was heated under reflux for 2 h. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of CH_2Cl_2/EtOAc mixtures (25:1 ✂ 5:1). The products **5a** and **5b** were obtained in 21% yield (9.8 mg, white solid) and 79% yield (19.9 mg, white solid), respectively.

Compound 5a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.52 – 7.45 (m, 2H), 7.35 (dt, *J* = 4.6, 3.0 Hz, 3H), 4.69 (s, 2H), 4.54 (ddd, *J* = 11.4, 4.4, 2.8 Hz, 1H), 4.26 (td, *J* = 11.7, 2.5 Hz, 1H), 3.43 (ddd, *J* = 10.9, 8.3, 4.9 Hz, 1H), 2.82 – 2.74 (m, 1H), 2.27 – 2.18 (m, 1H), 1.91 (dddd, *J* = 14.7, 12.0, 10.6, 4.4 Hz, 1H), 1.78 (dqd, *J* = 14.6, 7.3, 3.5 Hz, 1H), 1.47 (ddq, *J* = 14.3, 9.6, 7.2 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 134.2, 131.4, 129.4, 128.7, 94.1, 78.4, 66.8, 56.6, 52.4, 24.7, 23.1, 11.4. HRMS (ESI) m/z calculated for $C_{15}H_{19}Cl_3N_2O_4S_2$ $[M+H]^+$, 460.9925; found, 460.9925.

Compound 5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.53 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 7.12 (s, 1H), 4.57 (ddd, *J* = 11.4, 4.3, 2.7 Hz, 1H), 4.29 (td, *J* = 11.8, 2.5 Hz, 1H), 3.42 (ddd, *J* = 10.6, 8.5, 4.9 Hz, 1H), 2.76 (ddd, *J* = 9.8, 8.6, 3.5 Hz, 1H), 2.28 – 2.19 (m, 1H), 1.93 (dddd, *J* = 14.7, 12.2, 10.6, 4.4 Hz, 1H), 1.78 (dqd, *J* = 14.5, 7.3, 3.5 Hz, 1H), 1.48 (ddq, *J* = 14.3, 9.7, 7.3 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.9, 134.3, 129.5, 128.8, 67.0, 56.6, 52.4, 24.8, 23.1, 11.3.

V. X-ray Crystallographic Data of Compound 2a.

1. Data Collection for CDC deposition number 2279283

A colorless crystal with approximate dimensions 0.22 × 0.16 × 0.12 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 4.96 cm.[10]

The initial cell constants were obtained from one 180° ω scan with frames collected at 1° intervals with the exposure time of 1 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program suite. The final cell constants were calculated from a set of 9766 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.67 Å. A total of 54085 data were harvested by collecting 6 sets of frames with 0.4º scans in ω and φ with exposure times of 10 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[11]

2. Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2_1/m$. The *E*-statistics strongly suggested the non-centrosymmetric space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement.[12-17]

A successful solution by intrinsic phasing provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference

Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless indicated otherwise. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There are two symmetry-independent molecules with identical compositions but slightly different conformations in the asymmetric unit. There is positional disorder in the **2a** molecule: atoms Cl1a, Cl2a, C1a, C2a, O1a, S1a, O2a, O3a are disordered over two positions with the major component contribution of 92.1(2) %. The minor disorder components were refined isotropically with geometrical restraints.

The absolute structure was unambiguously established by resonant scattering effects. The absolute configuration is assigned as follows: atoms C6 and C6a are *R*; atoms C7 and C7a are *S*. The crystal may contain 0.029(10) % of the other enantiomer.

The final least-squares refinement of 466 parameters against 11914 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0231 and 0.0584, respectively. The final difference Fourier map was featureless.

3. Summary

Crystal Data for $C_{14}H_{15}Cl_3N_2O_4S$ (M =413.69 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 11.978(3) Å, b = 9.923(3) Å, c = 14.449(4) Å, β = 96.646(13)°, V = 1705.8(8) Å^3, Z = 4, T = 100 K, μ(Mo Kα) = 0.681 mm^{-1}, *Dcalc* = 1.611 g/cm^3, 54085 reflections measured (2.838° ≤ 2Θ ≤ 64.316°), 11914 unique (R_{int} = 0.0315, R_{sigma} = 0.0247) which were used in all calculations. The final R_1 was 0.0231 (I > 2σ(I)) and wR_2 was 0.0584 (all data).

4. Acknowledgement

The Bruker Quazar APEX2 was purchased by the UW–Madison Department of Chemistry with a portion of a generous gift from Paul J. and Margaret M. Bender.

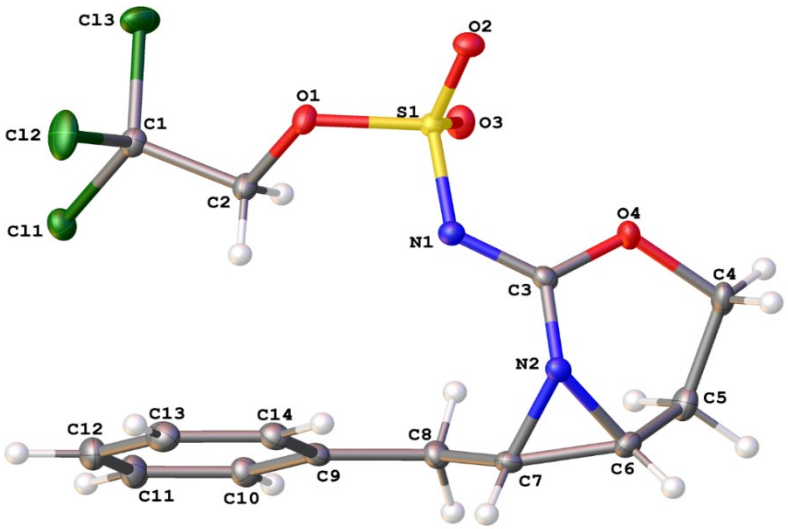


Figure S1. A molecular drawing of the first symmetry-independent molecule of **2a** shown with 50% probability ellipsoids.

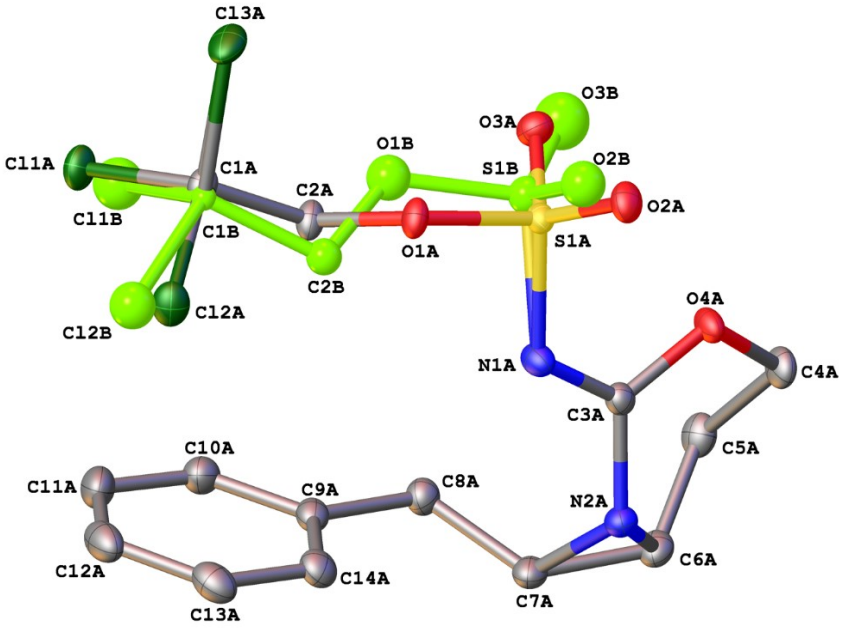


Figure S2. A molecular drawing of the second symmetry-independent molecule of **2a** shown with 50% probability ellipsoids. All H atoms are omitted. The portion colored green highlights the disordered atoms.

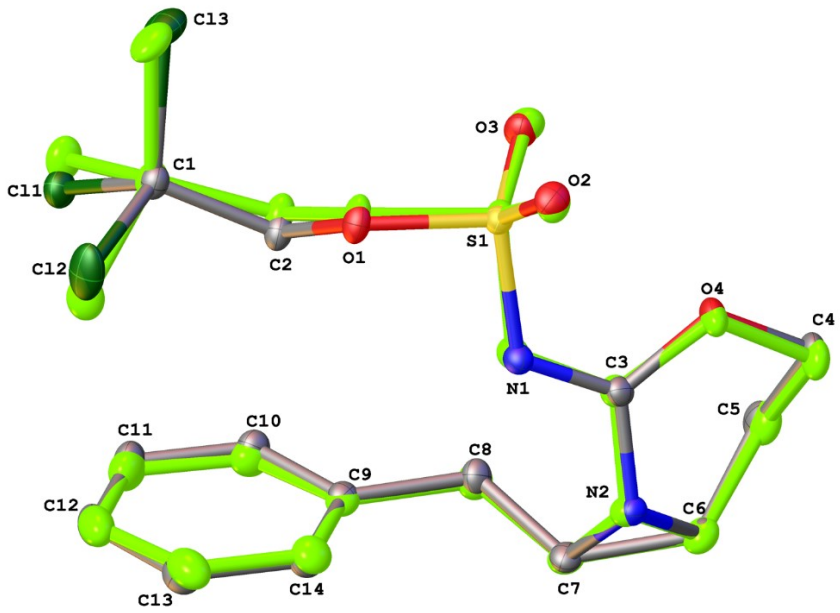


Figure S3. A molecular drawing of a superposition of the two symmetry-independent molecules of **2a** shown with 50% probability ellipsoids. The minor disorder component atoms and H atoms are omitted. Molecule **2a** is colored green.

Table S1. Crystal data and structure refinement for **2a.**

Identification code	Schomaker100
Empirical formula	$C_{14}H_{15}Cl_3N_2O_4S$
Formula weight	413.69
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.978(3)
b/Å	9.923(3)
c/Å	14.449(4)
α/°	90
β/°	96.646(13)
γ/°	90

Volume/Å^3	1705.8(8)
Z	4
ρ_{calc}g/cm^3	1.611
μ/mm^{-1}	0.681
F(000)	848.0
Crystal size/mm^3	0.22 × 0.16 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	2.838 to 64.316
Index ranges	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	54085
Independent reflections	11914 [R_{int} = 0.0315, R_{sigma} = 0.0247]
Data/restraints/parameters	11914/24/466
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0231, wR_2 = 0.0577
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0584
Largest diff. peak/hole / e Å^{-3}	0.55/-0.25
Flack parameter	0.026(9)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl1	6153.6(3)	3430.6(4)	5861.8(3)	17.45(7)
Cl2	5736.7(4)	6146.3(4)	5214.5(4)	27.24(10)
Cl3	5594.4(4)	3963.2(5)	3891.8(3)	24.92(9)
S1	8839.6(3)	5448.4(4)	3668.2(2)	11.30(6)
O1	7708.9(9)	5603.7(12)	4126.4(8)	14.3(2)

Atom	*x*	*y*	*z*	U(eq)
O2	8702.6(10)	6353.8(12)	2895.4(8)	15.7(2)
O3	9004.6(10)	4047.0(12)	3486.1(9)	16.4(2)
O4	11219.4(9)	5277.0(13)	3807.6(8)	16.3(2)
N1	9705.5(11)	6031.2(13)	4509.7(9)	12.8(2)
N2	11491.7(11)	6382.2(13)	5234.2(9)	12.2(2)
C1	6317.1(13)	4577.8(16)	4946.9(11)	14.3(3)
C2	7569.2(12)	4700.8(16)	4883.6(11)	13.8(3)
C3	10785.1(12)	5862.7(15)	4511.4(10)	11.7(2)
C4	12410.8(13)	4879.1(18)	3953.2(12)	17.6(3)
C5	12709.1(14)	4411.7(17)	4953.2(12)	18.5(3)
C6	12522.7(12)	5609.6(16)	5556.5(10)	14.7(3)
C7	11602.4(12)	5714.5(15)	6166.2(10)	13.6(3)
C8	10878.7(13)	4525.6(16)	6344.6(11)	14.4(3)
C9	9851.5(13)	4856.8(15)	6821.6(10)	12.6(2)
C10	9290.1(13)	3792.7(16)	7209.1(11)	15.6(3)
C11	8334.5(14)	4025.9(18)	7647.3(12)	18.8(3)
C12	7925.6(14)	5333.8(18)	7706.4(12)	19.5(3)
C13	8477.1(15)	6395.2(18)	7328.7(11)	19.1(3)
C14	9432.3(14)	6162.2(17)	6882.1(11)	15.6(3)
Cl1A	6607.3(6)	3667.1(5)	-414.3(3)	19.00(11)
Cl2A	6399.9(6)	6566.7(5)	-275.6(4)	20.06(11)
Cl3A	7211.8(3)	5007.2(5)	1340.8(3)	23.17(9)
S1A	3733.4(3)	5446.9(7)	1691.8(3)	11.91(11)
O1A	4822.5(10)	5738.7(13)	1196.8(9)	14.9(2)
O2A	3765.7(11)	6458.4(16)	2398.1(9)	17.7(3)

Atom	*x*	*y*	*z*	U(eq)
O3A	3737.6(12)	4053.9(15)	1954.4(10)	17.7(3)
N1A	2794.1(11)	5767.6(14)	825.5(9)	15.8(2)
C1A	6268.8(15)	5006(3)	304.2(12)	14.0(4)
C2A	5068.6(13)	4772.6(18)	509.0(12)	15.0(3)
Cl1B	6232(9)	3744(9)	-329(6)	34(2)
Cl2B	6694(8)	6609(8)	-448(6)	27.6(19)
S1B	3735(5)	4917(9)	1668(4)	18.4(15)
O1B	4749(11)	4634(15)	1106(10)	26(4)
O2B	4031(16)	6085(16)	2244(12)	26(5)
O3B	3420(19)	3712(17)	2050(16)	41(6)
C1B	6310(11)	5289(14)	290(8)	7(7)
C2B	5127(11)	5622(16)	512(11)	17(4)
O4A	1391.3(9)	5015.9(13)	1654.9(8)	16.5(2)
N2A	951.8(11)	5886.7(14)	164.0(9)	15.0(2)
C3A	1741.0(12)	5521.7(16)	884.1(10)	13.1(2)
C4A	243.8(13)	4493.9(18)	1585.5(12)	18.5(3)
C5A	-41.7(14)	3836.9(18)	637.9(12)	19.3(3)
C6A	-20.0(14)	4963.4(18)	-55.0(12)	18.0(3)
C7A	818.5(13)	5135.0(18)	-735.1(11)	17.1(3)
C8A	1652.5(14)	4078.4(18)	-944.4(11)	17.4(3)
C9A	2615.0(14)	4614.8(17)	-1441.6(11)	16.6(3)
C10A	3263.3(15)	3696.3(19)	-1875.5(12)	21.4(3)
C11A	4166.5(16)	4124(2)	-2324.0(13)	26.1(4)
C12A	4420.4(15)	5490(2)	-2358.0(12)	25.7(4)
C13A	3770.9(16)	6413(2)	-1936.1(12)	23.7(3)

Atom	*x*	*y*	*z*	U(eq)
C14A	2876.6(15)	5976.2(19)	-1473.9(12)	19.7(3)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	17.76(16)	18.39(16)	16.98(16)	1.55(12)	5.34(13)	-2.41(13)
Cl2	22.67(19)	17.30(17)	44.7(3)	2.72(17)	16.57(18)	6.61(14)
Cl3	21.10(18)	33.8(2)	18.47(17)	2.92(16)	-3.40(14)	-11.05(16)
S1	10.56(14)	11.99(14)	11.41(14)	0.24(11)	1.44(11)	-0.39(12)
O1	10.6(4)	14.8(5)	18.0(5)	3.6(4)	3.8(4)	1.4(4)
O2	15.7(5)	18.2(5)	12.6(5)	3.0(4)	-0.1(4)	-1.1(4)
O3	16.6(5)	13.0(5)	20.5(5)	-2.6(4)	5.3(4)	-0.8(4)
O4	11.8(5)	24.7(6)	13.1(5)	-4.1(4)	4.4(4)	-1.4(4)
N1	12.1(5)	15.2(5)	11.2(5)	-0.5(4)	1.1(4)	0.2(4)
N2	12.1(5)	13.5(5)	11.0(5)	0.0(4)	1.8(4)	-2.2(4)
C1	12.6(6)	14.0(6)	16.8(7)	0.6(5)	2.9(5)	0.0(5)
C2	10.9(6)	15.8(6)	15.0(6)	2.8(5)	3.0(5)	0.3(5)
C3	13.1(6)	12.4(6)	10.0(6)	0.6(4)	2.4(5)	-1.3(5)
C4	12.1(6)	23.1(8)	18.8(7)	-4.6(6)	6.4(5)	-1.6(5)
C5	13.0(7)	20.3(7)	22.9(8)	-0.3(6)	5.3(6)	1.8(5)
C6	10.4(6)	18.6(7)	14.9(6)	1.5(5)	0.3(5)	-1.6(5)
C7	13.2(6)	17.2(7)	9.8(6)	0.7(5)	-0.5(5)	-1.2(5)
C8	14.6(6)	15.3(6)	13.8(6)	2.4(5)	3.7(5)	-0.4(5)
C9	13.6(6)	14.5(6)	9.7(6)	1.1(5)	0.8(5)	-0.8(5)
C10	16.5(7)	15.1(6)	15.6(6)	0.9(5)	3.5(5)	-2.0(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	17.5(7)	20.9(7)	18.9(7)	1.8(6)	6.0(6)	-3.1(6)
C12	15.8(7)	25.0(8)	18.7(7)	-0.2(6)	5.6(5)	1.7(6)
C13	19.5(7)	19.4(7)	18.2(7)	0.4(6)	1.6(6)	3.3(6)
C14	17.4(7)	15.8(6)	13.7(6)	1.5(5)	1.8(5)	-0.6(5)
Cl1A	19.7(3)	17.0(2)	21.2(2)	-6.21(14)	5.99(18)	0.91(16)
Cl2A	21.8(3)	15.46(19)	23.7(2)	-1.28(15)	6.1(2)	-2.43(16)
Cl3A	13.00(16)	35.2(2)	19.96(17)	-6.23(16)	-3.93(13)	4.74(15)
S1A	9.64(17)	15.1(3)	11.00(17)	-0.09(15)	1.29(12)	-0.64(14)
O1A	10.5(5)	17.7(6)	17.1(6)	-4.5(4)	4.5(4)	-1.7(4)
O2A	16.5(6)	22.0(7)	14.9(6)	-5.2(5)	2.8(5)	-0.9(5)
O3A	16.1(6)	17.3(6)	19.4(6)	2.1(5)	1.5(5)	1.8(5)
N1A	12.6(6)	21.2(6)	13.4(5)	2.1(5)	0.5(4)	-2.2(5)
C1A	11.8(9)	14.3(9)	15.9(10)	-4.0(6)	1.5(5)	-0.3(6)
C2A	11.3(7)	18.2(8)	15.8(7)	-5.7(6)	3.0(5)	-1.6(6)
O4A	11.6(5)	26.0(6)	12.3(5)	2.9(4)	3.0(4)	-2.2(4)
N2A	13.1(6)	17.5(6)	14.1(6)	0.8(4)	0.1(4)	1.3(5)
C3A	13.6(6)	13.7(6)	12.1(6)	-1.0(5)	1.7(5)	0.0(5)
C4A	12.0(6)	25.7(8)	18.6(7)	0.4(6)	5.3(6)	-3.3(6)
C5A	14.6(7)	20.4(7)	23.6(8)	-2.5(6)	4.6(6)	-3.8(6)
C6A	12.7(6)	23.5(7)	17.3(7)	-2.2(6)	-0.7(5)	0.1(6)
C7A	14.9(6)	22.1(7)	13.7(6)	-0.3(5)	-1.2(5)	2.5(5)
C8A	16.9(7)	19.5(7)	15.9(7)	-1.5(6)	2.1(5)	0.7(6)
C9A	14.0(6)	23.2(7)	12.1(6)	-1.4(5)	-0.3(5)	1.3(6)
C10A	22.1(8)	23.6(8)	18.5(7)	1.2(6)	2.6(6)	4.5(6)
C11A	21.6(8)	36.2(10)	21.5(8)	1.6(7)	6.3(6)	8.4(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12A	16.9(7)	41.8(10)	18.6(7)	5.4(8)	2.3(6)	-1.8(7)
C13A	24.0(8)	29.6(9)	16.8(7)	1.9(6)	-0.9(6)	-6.3(7)
C14A	21.2(8)	24.1(8)	13.5(7)	-2.2(6)	0.5(6)	0.0(6)

Table S4. Bond Lengths for **2a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1	1.7724(17)	S1A	O2A	1.4287(16)
Cl2	C1	1.7656(17)	S1A	O3A	1.4333(16)
Cl3	C1	1.7719(17)	S1A	N1A	1.6148(14)
S1	O1	1.5824(12)	O1A	C2A	1.436(2)
S1	O2	1.4278(12)	N1A	S1B	1.774(6)
S1	O3	1.4332(13)	N1A	C3A	1.297(2)
S1	N1	1.6114(14)	C1A	C2A	1.519(3)
O1	C2	1.4387(19)	Cl1B	C1B	1.772(12)
O4	C3	1.3285(18)	Cl2B	C1B	1.783(12)
O4	C4	1.4721(19)	S1B	O1B	1.563(10)
N1	C3	1.3036(19)	S1B	O2B	1.447(11)
N2	C3	1.3668(19)	S1B	O3B	1.387(11)
N2	C6	1.482(2)	O1B	C2B	1.411(12)
N2	C7	1.4929(19)	C1B	C2B	1.525(12)
C1	C2	1.518(2)	O4A	C3A	1.3325(18)
C4	C5	1.520(2)	O4A	C4A	1.4615(19)
C5	C6	1.506(2)	N2A	C3A	1.3710(19)
C6	C7	1.492(2)	N2A	C6A	1.486(2)
C7	C8	1.504(2)	N2A	C7A	1.491(2)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C8	C9	1.514(2)	C4A	C5A	1.519(2)
C9	C10	1.403(2)	C5A	C6A	1.503(2)
C9	C14	1.396(2)	C6A	C7A	1.494(2)
C10	C11	1.390(2)	C7A	C8A	1.503(2)
C11	C12	1.393(3)	C8A	C9A	1.523(2)
C12	C13	1.388(3)	C9A	C10A	1.393(2)
C13	C14	1.396(2)	C9A	C14A	1.389(3)
Cl1A	C1A	1.762(3)	C10A	C11A	1.390(3)
Cl2A	C1A	1.776(3)	C11A	C12A	1.392(3)
Cl3A	C1A	1.7686(18)	C12A	C13A	1.387(3)
Cl3A	C1B	1.781(11)	C13A	C14A	1.395(3)
S1A	O1A	1.5854(13)			

Table S5. Bond Angles for **2a.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	99.01(7)	C3A	N1A	S1B	114.3(2)
O2	S1	O1	103.86(7)	Cl1A	C1A	Cl2A	109.91(11)
O2	S1	O3	118.22(7)	Cl1A	C1A	Cl3A	109.36(13)
O2	S1	N1	111.71(7)	Cl3A	C1A	Cl2A	108.43(15)
O3	S1	O1	108.32(7)	C2A	C1A	Cl1A	106.71(18)
O3	S1	N1	113.35(7)	C2A	C1A	Cl2A	111.23(16)
C2	O1	S1	115.98(9)	C2A	C1A	Cl3A	111.18(13)
C3	O4	C4	117.84(12)	O1A	C2A	C1A	107.93(15)
C3	N1	S1	120.47(11)	O1B	S1B	N1A	101.5(6)
C3	N2	C6	117.70(12)	O2B	S1B	N1A	96.1(8)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	N2	C7	120.29(12)	O2B	S1B	O1B	106.8(10)
C6	N2	C7	60.21(10)	O3B	S1B	N1A	120.2(10)
Cl2	C1	Cl1	108.82(9)	O3B	S1B	O1B	108.4(12)
Cl2	C1	Cl3	109.04(9)	O3B	S1B	O2B	121.5(12)
Cl3	C1	Cl1	109.60(8)	C2B	O1B	S1B	121.0(11)
C2	C1	Cl1	106.96(10)	Cl3A	C1B	Cl2B	116.9(8)
C2	C1	Cl2	111.04(11)	Cl1B	C1B	Cl3A	106.6(7)
C2	C1	Cl3	111.32(11)	Cl1B	C1B	Cl2B	109.6(7)
O1	C2	C1	107.37(12)	C2B	C1B	Cl3A	109.9(9)
O4	C3	N2	119.15(13)	C2B	C1B	Cl1B	107.3(10)
N1	C3	O4	122.06(13)	C2B	C1B	Cl2B	106.1(9)
N1	C3	N2	118.66(13)	O1B	C2B	C1B	110.4(11)
O4	C4	C5	109.57(12)	C3A	O4A	C4A	117.40(12)
C6	C5	C4	105.96(14)	C3A	N2A	C6A	116.93(13)
N2	C6	C5	113.60(13)	C3A	N2A	C7A	121.61(13)
N2	C6	C7	60.25(9)	C6A	N2A	C7A	60.25(11)
C7	C6	C5	124.47(14)	N1A	C3A	O4A	121.83(13)
N2	C7	C8	120.67(12)	N1A	C3A	N2A	119.42(14)
C6	C7	N2	59.53(10)	O4A	C3A	N2A	118.55(13)
C6	C7	C8	121.76(13)	O4A	C4A	C5A	109.01(13)
C7	C8	C9	115.00(13)	C6A	C5A	C4A	105.17(14)
C10	C9	C8	118.07(14)	N2A	C6A	C5A	112.97(13)
C14	C9	C8	123.17(13)	N2A	C6A	C7A	60.02(11)
C14	C9	C10	118.76(14)	C7A	C6A	C5A	126.00(15)
C11	C10	C9	120.96(15)	N2A	C7A	C6A	59.74(10)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C11	C12	119.79(15)	N2A	C7A	C8A	121.19(13)
C13	C12	C11	119.74(15)	C6A	C7A	C8A	124.47(15)
C12	C13	C14	120.58(16)	C7A	C8A	C9A	114.09(15)
C9	C14	C13	120.17(15)	C10A	C9A	C8A	118.40(16)
O1A	S1A	N1A	98.64(7)	C14A	C9A	C8A	122.80(15)
O2A	S1A	O1A	103.78(8)	C14A	C9A	C10A	118.80(16)
O2A	S1A	O3A	119.31(9)	C11A	C10A	C9A	120.99(18)
O2A	S1A	N1A	111.97(8)	C10A	C11A	C12A	119.91(18)
O3A	S1A	O1A	108.52(9)	C13A	C12A	C11A	119.44(17)
O3A	S1A	N1A	112.09(8)	C12A	C13A	C14A	120.40(18)
C2A	O1A	S1A	115.84(11)	C9A	C14A	C13A	120.45(17)
C3A	N1A	S1A	120.53(11)				

Table S6. Torsion Angles for **2a.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C1	C2	O1	178.54(10)	S1A	N1A	C3A	N2A	175.60(12)
Cl2	C1	C2	O1	-62.87(14)	O1A	S1A	N1A	C3A	172.69(13)
Cl3	C1	C2	O1	58.83(14)	O2A	S1A	O1A	C2A	173.75(12)
S1	O1	C2	C1	-156.37(10)	O2A	S1A	N1A	C3A	-78.58(15)
S1	N1	C3	O4	3.7(2)	O3A	S1A	O1A	C2A	45.90(14)
S1	N1	C3	N2	179.47(11)	O3A	S1A	N1A	C3A	58.59(16)
O1	S1	N1	C3	166.90(12)	N1A	S1A	O1A	C2A	-70.98(13)
O2	S1	O1	C2	174.43(11)	N1A	S1B	O1B	C2B	41.8(16)
O2	S1	N1	C3	-84.18(13)	Cl1B	C1B	C2B	O1B	63.4(15)
O3	S1	O1	C2	47.95(12)	Cl2B	C1B	C2B	O1B	-179.4(12)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	S1	N1	C3	52.38(14)	S1B	N1A	C3A	O4A	18.7(4)
O4	C4	C5	C6	-61.85(16)	S1B	N1A	C3A	N2A	-166.5(3)
N1	S1	O1	C2	-70.42(12)	S1B	O1B	C2B	C1B	162.4(12)
N2	C6	C7	C8	109.38(15)	O2B	S1B	O1B	C2B	-58.3(18)
N2	C7	C8	C9	-97.86(17)	O3B	S1B	O1B	C2B	169.2(17)
C3	O4	C4	C5	35.22(19)	O4A	C4A	C5A	C6A	-64.57(17)
C3	N2	C6	C5	6.65(19)	N2A	C6A	C7A	C8A	109.07(17)
C3	N2	C6	C7	-110.84(14)	N2A	C7A	C8A	C9A	-91.06(18)
C3	N2	C7	C6	106.61(15)	C3A	N1A	S1B	O1B	145.7(6)
C3	N2	C7	C8	-4.6(2)	C3A	N1A	S1B	O2B	-105.7(9)
C4	O4	C3	N1	-167.55(14)	C3A	N1A	S1B	O3B	26.4(13)
C4	O4	C3	N2	16.7(2)	C3A	O4A	C4A	C5A	35.7(2)
C4	C5	C6	N2	41.26(17)	C3A	N2A	C6A	C5A	6.8(2)
C4	C5	C6	C7	110.35(16)	C3A	N2A	C6A	C7A	-112.75(15)
C5	C6	C7	N2	-99.62(16)	C3A	N2A	C7A	C6A	105.12(16)
C5	C6	C7	C8	9.8(2)	C3A	N2A	C7A	C8A	-9.3(2)
C6	N2	C3	O4	-39.34(19)	C4A	O4A	C3A	N1A	-166.51(15)
C6	N2	C3	N1	144.73(14)	C4A	O4A	C3A	N2A	18.7(2)
C6	N2	C7	C8	-111.17(16)	C4A	C5A	C6A	N2A	43.22(18)
C6	C7	C8	C9	-168.82(13)	C4A	C5A	C6A	C7A	111.94(17)
C7	N2	C3	O4	-109.27(16)	C5A	C6A	C7A	N2A	-97.91(17)
C7	N2	C3	N1	74.80(18)	C5A	C6A	C7A	C8A	11.2(3)
C7	N2	C6	C5	117.50(15)	C6A	N2A	C3A	N1A	143.36(15)
C7	C8	C9	C10	-165.03(14)	C6A	N2A	C3A	O4A	-41.7(2)
C7	C8	C9	C14	15.8(2)	C6A	N2A	C7A	C8A	-114.37(18)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C8	C9	C10	C11	-179.27(15)	C6A	C7A	C8A	C9A	-163.65(14)
C8	C9	C14	C13	179.70(14)	C7A	N2A	C3A	N1A	73.3(2)
C9	C10	C11	C12	-0.1(2)	C7A	N2A	C3A	O4A	-111.75(17)
C10	C9	C14	C13	0.6(2)	C7A	N2A	C6A	C5A	119.51(16)
C10	C11	C12	C13	-0.1(3)	C7A	C8A	C9A	C10A	-163.84(15)
C11	C12	C13	C14	0.6(3)	C7A	C8A	C9A	C14A	16.7(2)
C12	C13	C14	C9	-0.8(2)	C8A	C9A	C10A	C11A	-178.70(16)
C14	C9	C10	C11	-0.1(2)	C8A	C9A	C14A	C13A	179.73(15)
Cl1A	C1A	C2A	O1A	172.03(13)	C9A	C10A	C11A	C12A	-1.2(3)
Cl2A	C1A	C2A	O1A	-68.10(16)	C10A	C9A	C14A	C13A	0.2(3)
Cl3A	C1A	C2A	O1A	52.8(2)	C10A	C11A	C12A	C13A	0.5(3)
Cl3A	C1B	C2B	O1B	-52.1(16)	C11A	C12A	C13A	C14A	0.6(3)
S1A	O1A	C2A	C1A	-165.37(14)	C12A	C13A	C14A	C9A	-0.9(3)
S1A	N1A	C3A	O4A	0.8(2)	C14A	C9A	C10A	C11A	0.8(3)

Table S7. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **2a.**

Atom	*x*	*y*	*z*	U(eq)
H2A	7957.44	5061.21	5474.06	17
H2B	7891.68	3806.75	4766.36	17
H4A	12889.76	5654.3	3824.48	21
H4B	12548.87	4141.4	3519.36	21
H5A	12222.09	3651.12	5095.66	22
H5B	13502.93	4115.19	5057.14	22
H6	13205.55	6164.85	5753.92	18
H7	11762.05	6342.39	6706.67	16

Atom	*x*	*y*	*z*	U(eq)
H8A	11343.29	3867.45	6733.86	17
H8B	10628.77	4084.45	5741.59	17
H10	9567.03	2899.58	7171.55	19
H11	7961.46	3295.81	7905.63	23
H12	7271.92	5498.55	8003.92	23
H13	8202.26	7287.95	7374.52	23
H14	9797.85	6894.14	6618.76	19
H2AA	4542.45	4885.91	-66.59	18
H2AB	4985.71	3846.14	745.87	18
H2BA	5127.68	6514.64	817.92	20
H2BB	4609.11	5663.93	-72.75	20
H4AA	-288.05	5238.44	1661.91	22
H4AB	179.14	3824.49	2084.58	22
H5AA	519.63	3138.16	532.12	23
H5AB	-795.05	3414.65	589.46	23
H6A	-758.5	5419.42	-231.18	22
H7A	542.42	5705.38	-1284.99	21
H8AA	1252.65	3370.3	-1335.66	21
H8AB	1969.7	3652.95	-351.91	21
H10A	3085.69	2763.82	-1864.72	26
H11A	4609.74	3483.71	-2606.98	31
H12A	5033.31	5788.73	-2667.42	31
H13A	3936.08	7347.6	-1962.16	28
H14A	2443.65	6614.57	-1179.17	24

Table S8. Atomic Occupancy for **2a.**

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Cl1A	0.921(2)	Cl2A	0.921(2)	S1A	0.921(2)
O1A	0.921(2)	O2A	0.921(2)	O3A	0.921(2)
C1A	0.921(2)	C2A	0.921(2)	H2AA	0.921(2)
H2AB	0.921(2)	Cl1B	0.079(2)	Cl2B	0.079(2)
S1B	0.079(2)	O1B	0.079(2)	O2B	0.079(2)
O3B	0.079(2)	C1B	0.079(2)	C2B	0.079(2)
H2BA	0.079(2)	H2BB	0.079(2)		

VI. Computational Studies.

Density functional theory (DFT) calculations, including geometry optimization, vibrational frequency calculations, and single-point energy calculations, were performed with the Gaussian 16 software package.[18] Geometries were optimized in the gas phase using the ωB97X-D[19] functional and a mixed basis set of def2-TZVPP for Ag and def2-SVP for other atoms. Single-point energies were calculated using ωB97X-D and the def2-TZVPP basis set for all atoms in dichloromethane (DCM) using the SMD solvation model.[20] Gibbs free energies were calculated at the standard conditions (298 K, 1 M solution). Quasiharmonic approximation from Grimme[21] was applied for vibrational entropy calculations using 100 cm^{-1} as the frequency cut-off. Quasiharmonic approximations were computed using GoodVibes.[22] The 3D images of optimized structures were prepared using CYLView.[23]

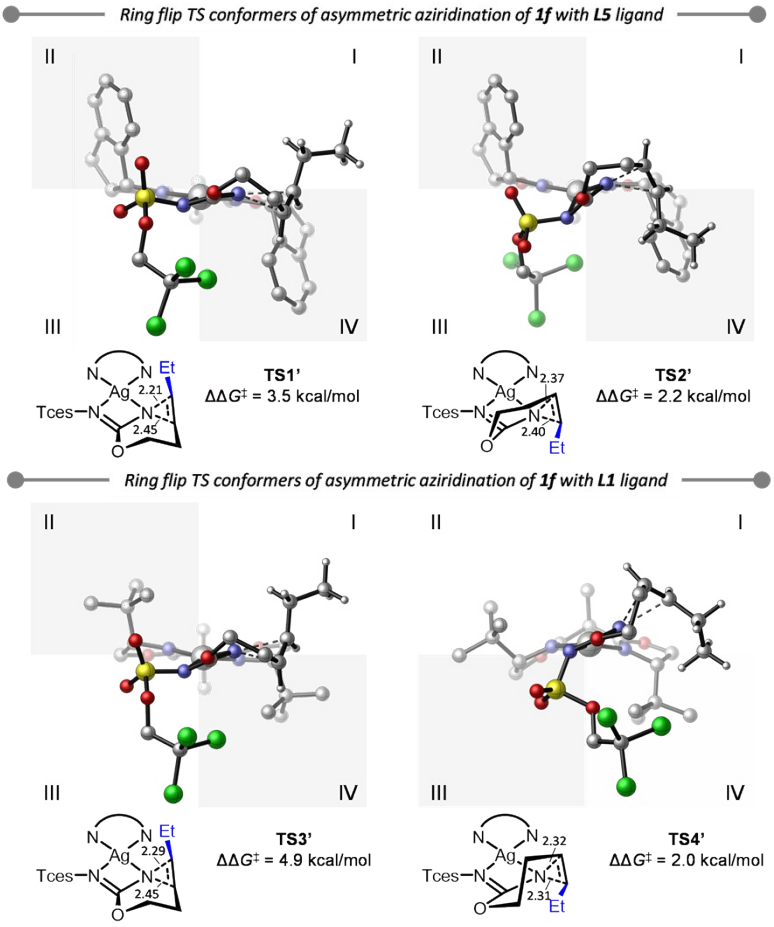


Figure S4. Alternative ring-flipped TS isomers. The relative Gibbs free energies ($\Delta\Delta G^{\ddagger}$) of **TS1'** and **TS2'** are with respect to the **TS1**. The relative Gibbs free energies ($\Delta\Delta G^{\ddagger}$) of **TS3'**-**TS4'** are with respect to **TS3**.

Cartesian Coordinates (Å) and Energies of Optimized Structures

3a *(planar conformer)*

ωB97X-D SCF energy:	-3832.58809321 a.u.
ωB97X-D enthalpy:	-3831.918974 a.u.
ωB97X-D free energy:	-3832.042142 a.u.
ωB97X-D SCF energy in solution:	-3835.43139061 a.u.
ωB97X-D enthalpy in solution:	-3834.762271 a.u.
ωB97X-D free energy in solution:	-3834.885439 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ag	-0.395842	-0.466908	0.654991
N	-1.094786	1.340282	1.097784
C	-0.887778	1.828672	-0.078780
O	-1.114353	3.023936	-0.517113
C	-0.707132	4.312662	1.555127
C	0.723031	4.535945	1.152485
H	-1.103021	5.220134	2.041965
H	-0.796605	3.501622	2.290321
H	0.895665	5.387519	0.484319
C	-1.628240	4.035181	0.370655
H	-2.630600	3.728646	0.706071
H	-1.726249	4.912602	-0.279334
C	1.784582	3.805901	1.513448
H	2.760664	4.120508	1.123260
C	1.819312	2.584692	2.388574
H	2.407259	2.812920	3.294195
H	0.808282	2.318253	2.729194
C	2.448416	1.388011	1.673179
H	2.421064	0.481957	2.299241
H	1.923673	1.174997	0.729393
H	3.500664	1.575935	1.410603
O	-0.525241	-2.530836	4.335172
N	-0.691661	-1.229476	2.559847
C	-1.201517	-1.354389	4.860363
H	-0.493578	-0.874217	5.548220
C	-2.532214	-1.737870	5.504198
H	-2.716645	-1.107464	6.388265
H	-2.514154	-2.780878	5.852265
C	-3.551357	-1.470787	4.423614
C	-4.903135	-1.806992	4.411371
H	-5.347698	-2.361281	5.240826

C	-5.683693	-1.422266	3.321655
H	-6.743795	-1.682317	3.298056
C	-5.124919	-0.701405	2.262358
H	-5.751255	-0.400871	1.420389
C	-3.773647	-0.358935	2.274578
H	-3.339100	0.219037	1.456679
C	-2.994745	-0.758457	3.359124
C	-1.511720	-0.546467	3.575115
H	-1.227325	0.513649	3.619407
C	-0.255013	-2.331474	3.060937
C	0.497935	-3.403392	2.386006
C	0.261194	-4.829047	2.916725
H	-0.500941	-4.917778	3.692106
H	0.264470	-5.610913	2.156149
O	1.446096	-4.313494	0.428014
N	0.563569	-2.299692	0.147997
C	1.609991	-4.092925	-0.997964
H	0.945771	-4.809091	-1.498703
C	3.076639	-4.218384	-1.409385
H	3.150989	-4.711296	-2.391259
H	3.633697	-4.842224	-0.695017
C	3.561844	-2.791034	-1.479565
C	4.860764	-2.329273	-1.683671
H	5.692657	-3.030683	-1.778698
C	5.084537	-0.955462	-1.774455
H	6.097689	-0.582923	-1.938092
C	4.023880	-0.052009	-1.664246
H	4.204623	1.021352	-1.748659
C	2.724993	-0.513389	-1.456944
H	1.899596	0.193456	-1.361885
C	2.505533	-1.885658	-1.363461
C	1.194728	-2.610695	-1.151808
H	0.475232	-2.419341	-1.956985
C	0.812216	-3.278412	0.946307
C	1.529420	-4.159816	3.244635
H	2.435682	-4.465677	2.719846
H	1.669729	-3.769176	4.253803
N	-0.321920	0.874012	-0.911524
S	-1.136972	0.524208	-2.331150
O	-2.543862	0.784834	-2.200097
O	-0.635518	-0.756859	-2.778811
O	-0.567887	1.672258	-3.292837
C	0.701461	1.514810	-3.908183
H	1.248868	0.655643	-3.495492
H	0.546729	1.354839	-4.984441
C	1.546279	2.778027	-3.731914

Cl	0.717657	4.181358	-4.430947
Cl	1.884883	3.093594	-2.007113
Cl	3.080202	2.475156	-4.591491

3b *(boat conformer)*

ωB97X-D SCF energy:	-3832.56988802 a.u.
ωB97X-D enthalpy:	-3831.901614 a.u.
ωB97X-D free energy:	-3832.031441 a.u.
ωB97X-D SCF energy in solution:	-3835.41240807 a.u.
ωB97X-D enthalpy in solution:	-3834.744134 a.u.
ωB97X-D free energy in solution:	-3834.873961 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ag	0.503729	-0.439535	-0.238834
N	-1.367941	-0.369255	-0.909351
C	-1.789891	-1.280276	-0.101176
O	-3.001124	-1.700894	0.083102
C	-5.385170	-1.590274	-0.119158
C	-6.548121	-0.822535	-0.690897
H	-5.411946	-2.649500	-0.413648
H	-5.417974	-1.563978	0.980965
H	-6.833730	0.085426	-0.148256
C	-4.070671	-0.986171	-0.572813
H	-3.939756	-1.073435	-1.662448
H	-3.990910	0.077553	-0.298692
C	-7.232825	-1.133577	-1.796796
H	-8.059414	-0.470119	-2.078920
C	-7.033094	-2.319799	-2.695463
H	-6.874885	-1.952793	-3.724179
H	-6.119370	-2.871683	-2.424936
C	-8.234084	-3.268689	-2.683150
H	-9.157377	-2.744926	-2.974672
H	-8.086217	-4.102840	-3.384224
H	-8.392847	-3.689587	-1.679026
O	2.939291	2.269260	-2.339089
N	1.369336	1.000266	-1.454566
C	1.921435	2.242774	-3.378241
H	2.327163	1.633273	-4.196944
C	1.538017	3.661872	-3.778151
H	1.225337	3.679721	-4.834394
H	2.393661	4.345703	-3.682747
C	0.385281	3.984334	-2.860600
C	-0.205481	5.221844	-2.618409
H	0.172631	6.124768	-3.102794
C	-1.289138	5.290323	-1.743318
H	-1.759310	6.254548	-1.539929

C	-1.780202	4.136795	-1.126176
H	-2.627991	4.209090	-0.442601
C	-1.196087	2.895093	-1.371807
H	-1.580093	1.989274	-0.900552
C	-0.107138	2.833691	-2.238350
C	0.722397	1.623221	-2.624370
H	0.160692	0.868225	-3.191030
C	2.552842	1.495849	-1.344432
C	3.507675	1.419225	-0.189548
C	3.642045	2.580902	0.782265
H	3.021735	3.455556	0.572037
H	3.730978	2.316867	1.838378
O	4.652811	-0.490339	0.653444
N	2.481067	-0.795463	0.387422
C	4.467533	-1.847979	1.128994
H	4.733853	-1.842470	2.193100
C	5.285717	-2.839368	0.295031
H	5.775724	-3.576686	0.949376
H	6.083646	-2.317977	-0.253995
C	4.269611	-3.503229	-0.602608
C	4.493801	-4.416982	-1.630359
H	5.509600	-4.711020	-1.903514
C	3.398804	-4.959470	-2.302667
H	3.562114	-5.676984	-3.109253
C	2.094202	-4.607565	-1.944426
H	1.248370	-5.057703	-2.467501
C	1.866306	-3.696849	-0.913376
H	0.847222	-3.439981	-0.612354
C	2.965496	-3.141773	-0.260322
C	2.964836	-2.111746	0.844336
H	2.379723	-2.408206	1.725143
C	3.485322	-0.007221	0.270308
C	4.758698	2.247057	-0.146626
H	5.642085	1.754449	0.261539
H	4.930747	2.898600	-1.004301
N	-0.735675	-1.818005	0.629018
S	-0.840867	-1.879879	2.284184
O	0.493932	-1.723308	2.824876
O	-1.682534	-2.972821	2.666255
O	-1.661073	-0.493986	2.564730
C	-1.295107	0.386775	3.600413
H	-2.107669	0.423392	4.340516
H	-0.360570	0.070814	4.087590
C	-1.105445	1.798560	3.038956
Cl	-0.819118	2.889702	4.405096
Cl	0.325367	1.851909	1.945892

Cl	-2.546835	2.303321	2.131595

4a *(planar conformer)*

ωB97X-D SCF energy:	-3610.24647141 a.u.
ωB97X-D enthalpy:	-3609.504267 a.u.
ωB97X-D free energy:	-3609.633155 a.u.
ωB97X-D SCF energy in solution:	-3612.85876684 a.u.
ωB97X-D enthalpy in solution:	-3612.116562 a.u.
ωB97X-D free energy in solution:	-3612.245450 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	4.370339	-0.786134	1.081416
C	3.461099	-1.099519	-0.111014
N	2.588352	0.100046	-0.119633
C	3.185724	1.018048	0.553071
O	4.271602	0.648349	1.203100
C	2.870838	2.486992	0.691425
C	1.622410	2.913592	-0.039067
N	0.585002	2.216319	-0.351046
C	-0.494884	3.153907	-0.735584
C	0.328830	4.402401	-1.061948
O	1.539387	4.201709	-0.296683
C	4.085909	3.279485	0.162334
C	2.635818	2.799191	2.191126
H	5.425461	-1.042315	0.940374
H	4.008828	-1.223276	2.023524
H	0.618610	4.468836	-2.120797
H	-0.120122	5.349210	-0.745817
H	3.919018	4.353061	0.309835
H	4.246169	3.095846	-0.909522
H	4.988084	2.980388	0.708858
H	2.397694	3.863511	2.318082
H	1.809026	2.197432	2.595297
H	3.548611	2.571894	2.756200
Ag	0.568743	0.174723	-0.826897
N	-1.202418	0.215563	-1.729821
C	-1.221811	-1.043726	-2.018695
O	-2.162179	-1.727645	-2.589042
C	-4.247090	-1.259321	-1.412982
C	-5.685976	-0.856894	-1.603256
H	-4.189688	-2.306550	-1.079042
H	-3.755322	-0.650496	-0.638673
H	-6.356728	-1.638464	-1.975460
C	-3.473804	-1.138098	-2.718838

H	-3.949234	-1.709928	-3.524168
H	-3.376881	-0.090259	-3.040282
C	-1.544204	3.353072	0.397612
C	-2.699166	4.170208	-0.198094
H	-3.461146	4.364271	0.570652
H	-2.369215	5.149403	-0.579145
H	-3.185683	3.629049	-1.023972
C	-0.954414	4.090021	1.608236
H	-0.118443	3.531669	2.054772
H	-0.607393	5.106864	1.371536
H	-1.723289	4.186712	2.388484
C	-2.070901	1.995256	0.870843
H	-2.435467	1.386791	0.032655
H	-1.291986	1.420316	1.391954
H	-2.898087	2.140558	1.580580
C	4.200781	-1.297228	-1.464701
C	3.182337	-1.420948	-2.604048
H	2.636747	-0.479154	-2.773900
H	3.698244	-1.667456	-3.543500
H	2.448188	-2.212230	-2.403436
C	4.984871	-2.614328	-1.365832
H	4.310395	-3.460216	-1.163029
H	5.504036	-2.817312	-2.313799
H	5.752185	-2.590478	-0.576770
C	5.153027	-0.133364	-1.768070
H	4.608832	0.820163	-1.858014
H	5.938214	-0.013091	-1.006291
H	5.659177	-0.304771	-2.729285
H	2.842219	-1.983659	0.077602
H	-1.008973	2.754652	-1.620307
C	-6.193699	0.360593	-1.387155
H	-7.266423	0.501591	-1.562859
C	-5.454763	1.563767	-0.873557
H	-4.368349	1.434346	-0.999259
H	-5.732627	2.436944	-1.487230
C	-5.772845	1.857984	0.594199
H	-6.855236	1.980545	0.749979
H	-5.436372	1.033137	1.240955
H	-5.280789	2.782282	0.930959
N	-0.037041	-1.641630	-1.636468
S	-0.080454	-3.060836	-0.793687
O	1.208604	-3.255327	-0.164708
O	-0.673960	-4.088165	-1.596058
O	-1.149575	-2.655390	0.380195
C	-0.972162	-3.129534	1.695176
H	-1.801139	-3.804418	1.953574

H	-0.014001	-3.658360	1.805539
C	-0.992545	-1.954265	2.674663
Cl	-0.784986	-2.602278	4.309092
Cl	0.377770	-0.837356	2.307493
Cl	-2.524046	-1.067007	2.551477

4b *(boat conformer)*

ωB97X-D SCF energy:	-3610.24353500 a.u.
ωB97X-D enthalpy:	-3609.501943 a.u.
ωB97X-D free energy:	-3609.629847 a.u.
ωB97X-D SCF energy in solution:	-3612.85647675 a.u.
ωB97X-D enthalpy in solution:	-3612.114885 a.u.
ωB97X-D free energy in solution:	-3612.242789 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.112449	4.176812	0.507945
C	0.670375	2.794505	1.030734
N	1.377605	1.907741	0.100122
C	2.234539	2.587411	-0.564677
O	2.231710	3.885418	-0.364910
C	3.219768	2.007793	-1.562879
C	3.780236	0.723163	-0.964817
N	3.120986	-0.261185	-0.457377
C	4.098868	-1.172420	0.191028
C	5.407445	-0.699338	-0.456392
O	5.091052	0.619528	-0.940288
C	4.346751	3.010934	-1.843272
C	2.465466	1.682951	-2.876251
H	1.464233	4.871642	1.278894
H	0.340358	4.662581	-0.102986
H	6.249531	-0.617832	0.238258
H	5.703303	-1.305451	-1.325383
H	4.900243	3.268936	-0.931468
H	3.919630	3.930564	-2.260934
H	5.052124	2.587080	-2.568021
H	3.164193	1.248936	-3.604367
H	1.632333	0.979416	-2.734166
H	2.053770	2.609374	-3.298956
Ag	0.998121	-0.110041	-0.370739
N	0.345511	-1.911529	-0.935998
C	-0.892766	-1.571982	-0.934421
O	-1.942850	-2.260124	-1.255135
C	-1.950471	-4.620240	-0.643417
C	-0.816527	-4.614731	0.344123

H	-2.919464	-4.445060	-0.153662
H	-2.017410	-5.611167	-1.121755
H	0.118038	-5.061644	-0.014294
C	-1.787440	-3.603417	-1.762800
H	-0.810434	-3.687355	-2.261805
H	-2.582012	-3.704542	-2.511884
C	3.834032	-2.691064	0.106275
C	5.115500	-3.403451	0.574284
H	4.935723	-4.486071	0.640468
H	5.957068	-3.260533	-0.120828
H	5.428921	-3.060020	1.573380
C	3.486024	-3.119412	-1.323200
H	4.276719	-2.851711	-2.041721
H	3.371901	-4.212774	-1.364684
H	2.539107	-2.673777	-1.656317
C	2.701215	-3.067218	1.071803
H	1.741325	-2.615558	0.792010
H	2.548906	-4.157073	1.061753
H	2.948397	-2.777300	2.105606
C	1.017751	2.466466	2.505331
C	0.647458	1.002965	2.791660
H	0.682051	0.802388	3.872468
H	-0.366142	0.760277	2.438230
H	1.354385	0.300212	2.319516
C	0.169022	3.380835	3.398977
H	-0.906275	3.219640	3.225053
H	0.372185	3.175966	4.460180
H	0.383507	4.446922	3.227106
C	2.510074	2.674593	2.788687
H	3.132715	2.037297	2.139758
H	2.825391	3.719923	2.649459
H	2.740318	2.403955	3.829666
H	-0.409374	2.657402	0.884054
H	4.102044	-0.900704	1.262518
C	-0.829341	-4.111551	1.582933
H	0.098693	-4.194542	2.162421
C	-1.948760	-3.406895	2.291013
H	-2.858049	-3.381376	1.672749
H	-2.205519	-3.976763	3.200146
C	-1.564139	-1.980378	2.687692
H	-2.362428	-1.501749	3.272794
H	-0.645552	-1.969857	3.296419
H	-1.393169	-1.354178	1.799290
N	-1.042664	-0.252299	-0.497339
S	-1.670121	0.818977	-1.632567
O	-1.267459	0.428762	-2.960372

O	-1.435862	2.164407	-1.154987
O	-3.230611	0.474823	-1.510240
C	-4.145911	1.291874	-0.804907
H	-3.833539	2.345870	-0.815949
H	-5.097818	1.181579	-1.339703
C	-4.376746	0.854464	0.650487
Cl	-4.622614	-0.899739	0.743167
Cl	-3.005044	1.322078	1.701308
Cl	-5.832537	1.714860	1.206825

TS1

ωB97X-D SCF energy:	-3832.57394285 a.u.
ωB97X-D enthalpy:	-3831.907141 a.u.
ωB97X-D free energy:	-3832.032028 a.u.
ωB97X-D SCF energy in solution:	-3835.41051067 a.u.
ωB97X-D enthalpy in solution:	-3834.743709 a.u.
ωB97X-D free energy in solution:	-3834.868596 a.u.
Imaginary frequency:	-259.5311 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ag	-0.378619	0.005539	0.467136
N	1.374574	-0.688874	1.570887
C	1.150836	-1.952989	1.271147
O	1.958727	-2.974610	1.444482
C	3.974782	-2.157170	2.550779
C	3.342149	-0.831699	2.833813
H	3.857024	-2.847276	3.398757
H	5.053816	-2.029786	2.377901
H	3.781389	0.049355	2.357238
C	3.372072	-2.792222	1.304309
H	3.553139	-2.185754	0.403756
H	3.769316	-3.800723	1.140436
C	2.260668	-0.645056	3.646697
H	1.932674	0.387130	3.803719
C	1.559136	-1.674103	4.474969
H	0.474541	-1.504366	4.379771
H	1.751339	-2.686530	4.092757
C	1.963591	-1.577312	5.950599
H	1.759619	-0.576212	6.358848
H	1.399470	-2.306157	6.548585
H	3.035645	-1.784112	6.083800
O	-0.405512	4.327835	0.864871
N	-0.034424	2.141603	0.771338
C	0.790462	4.177393	1.662225

H	0.508862	4.407585	2.698639
C	1.924186	5.050373	1.126208
H	2.517639	5.456155	1.960680
H	1.526786	5.910120	0.567419
C	2.744774	4.106705	0.282270
C	3.798213	4.414037	-0.575972
H	4.112609	5.449555	-0.723857
C	4.444175	3.377990	-1.249339
H	5.266686	3.605509	-1.930388
C	4.046892	2.051177	-1.063076
H	4.553703	1.252953	-1.607894
C	2.997369	1.740094	-0.199611
H	2.680015	0.705876	-0.053096
C	2.350291	2.779393	0.465525
C	1.167500	2.695743	1.407136
H	1.391592	2.126960	2.320343
C	-0.804551	3.122477	0.469485
C	-2.081091	3.109424	-0.278073
C	-2.323759	4.317212	-1.199564
H	-1.499539	5.028306	-1.270945
H	-2.843788	4.093036	-2.131944
O	-3.839140	1.952514	-1.354847
N	-2.253382	0.633664	-0.527055
C	-4.285896	0.635464	-1.756038
H	-4.223436	0.602856	-2.851680
C	-5.684926	0.339629	-1.212318
H	-6.270552	-0.220120	-1.958462
H	-6.232171	1.271604	-1.008189
C	-5.433230	-0.498985	0.017246
C	-6.350413	-0.919367	0.978211
H	-7.398642	-0.618016	0.918194
C	-5.910925	-1.737099	2.018810
H	-6.619856	-2.074060	2.777841
C	-4.573741	-2.137375	2.094438
H	-4.248314	-2.788201	2.908358
C	-3.655126	-1.719918	1.132483
H	-2.613073	-2.040773	1.185493
C	-4.096894	-0.893629	0.101610
C	-3.284029	-0.292358	-1.023258
H	-2.815720	-1.057597	-1.655808
C	-2.684018	1.825639	-0.708701
C	-3.075644	4.230405	0.064737
H	-4.128105	3.947342	0.026789
H	-2.782778	4.879879	0.890400
N	-0.049111	-2.122743	0.691918
S	-0.248952	-3.236483	-0.510947

O	-1.337994	-2.784583	-1.349416
O	-0.219660	-4.565521	0.024448
O	1.149695	-3.021456	-1.349563
C	1.139477	-2.824009	-2.741620
H	1.733986	-3.619407	-3.214071
H	0.115867	-2.838839	-3.144381
C	1.781768	-1.480630	-3.099406
Cl	1.876285	-1.378535	-4.865697
Cl	0.794133	-0.119493	-2.481874
Cl	3.422610	-1.380048	-2.399075

TS2

ωB97X-D SCF energy:	-3832.56768594 a.u.
ωB97X-D enthalpy:	-3831.900924 a.u.
ωB97X-D free energy:	-3832.024739 a.u.
ωB97X-D SCF energy in solution:	-3835.40810113 a.u.
ωB97X-D enthalpy in solution:	-3834.741339 a.u.
ωB97X-D free energy in solution:	-3834.865154 a.u.
Imaginary frequency:	-268.7030 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ag	0.361668	-0.005262	-0.588115
N	-1.373260	-0.808597	-1.795209
C	-0.935685	-2.051325	-1.741401
O	-1.400343	-3.139189	-2.293493
C	-2.616069	-3.188042	-3.030072
C	-2.681018	-2.101733	-4.093876
C	-2.637741	-0.721111	-3.499441
H	-3.452033	-3.126642	-2.319868
H	-2.623002	-4.186131	-3.482518
H	-1.848840	-2.237154	-4.798625
H	-3.609905	-2.245848	-4.670082
H	-1.920933	-0.015631	-3.922915
C	-3.601811	-0.224652	-2.657586
H	-3.456807	0.795346	-2.285460
C	-4.841471	-0.902912	-2.190305
H	-5.669050	-0.196728	-2.377804
H	-5.057598	-1.798793	-2.789879
C	-4.832386	-1.242757	-0.693382
H	-5.773940	-1.735187	-0.414405
H	-3.998364	-1.911919	-0.434892
H	-4.730016	-0.333200	-0.086868
O	0.268889	4.349530	-0.841150
N	-0.016315	2.146917	-0.812778

C	-0.934453	4.176709	-1.621692
H	-0.678899	4.425845	-2.660807
C	-2.086466	5.004571	-1.055170
H	-2.738073	5.352674	-1.872487
H	-1.713114	5.900182	-0.538043
C	-2.809572	4.040500	-0.146632
C	-3.794969	4.314150	0.799135
H	-4.146201	5.335939	0.958886
C	-4.316274	3.263472	1.553981
H	-5.080533	3.465724	2.307016
C	-3.857683	1.956524	1.368354
H	-4.253112	1.149524	1.988049
C	-2.879546	1.677992	0.413922
H	-2.511803	0.657883	0.276835
C	-2.368185	2.729655	-0.342437
C	-1.258179	2.684629	-1.371186
H	-1.527197	2.127631	-2.280677
C	0.724393	3.145347	-0.496710
C	2.014471	3.153744	0.224250
C	2.244964	4.350473	1.161766
H	1.406364	5.040903	1.261500
H	2.788779	4.122037	2.079337
O	3.807927	2.020847	1.267952
N	2.259070	0.678745	0.402515
C	4.286305	0.706791	1.640841
H	4.204451	0.639612	2.733935
C	5.701879	0.469134	1.114432
H	6.280423	-0.122251	1.841688
H	6.235913	1.420625	0.976169
C	5.491514	-0.303116	-0.165191
C	6.431508	-0.635265	-1.138586
H	7.468903	-0.305417	-1.047562
C	6.028571	-1.400293	-2.232676
H	6.755326	-1.667763	-3.002498
C	4.704947	-1.834444	-2.349178
H	4.407913	-2.441942	-3.206365
C	3.763688	-1.505332	-1.374917
H	2.732296	-1.852284	-1.458615
C	4.169004	-0.732850	-0.289058
C	3.325867	-0.224952	0.860385
H	2.890681	-1.041030	1.451667
C	2.654184	1.875959	0.619441
C	2.974667	4.303854	-0.118088
H	4.034280	4.046059	-0.105323
H	2.650807	4.960463	-0.926517
N	0.203470	-2.116146	-1.020137

S	0.433748	-3.261799	0.125247
O	1.580126	-2.870653	0.916365
O	0.325846	-4.586723	-0.416285
O	-0.913227	-3.005345	1.040388
C	-0.824297	-3.024668	2.443028
H	-1.422858	-3.860134	2.835329
H	0.218586	-3.128165	2.778058
C	-1.387618	-1.726041	3.025712
Cl	-1.313209	-1.846203	4.793222
Cl	-0.417246	-0.319878	2.485732
Cl	-3.080165	-1.507822	2.504237

TS3

ωB97X-D SCF energy: -3610.23937452 a.u.
ωB97X-D enthalpy: -3609.499589 a.u.
ωB97X-D free energy: -3609.628229 a.u.
ωB97X-D SCF energy in solution: -3612.84701563 a.u.
ωB97X-D enthalpy in solution: -3612.107230 a.u.
ωB97X-D free energy in solution: -3612.235870 a.u.
Imaginary frequency: -249.3186 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.681579	-2.433275	-0.025594
C	-2.485236	-2.089322	0.875796
N	-2.210404	-0.693968	0.483167
C	-3.225977	-0.259787	-0.161192
O	-4.178772	-1.144467	-0.429769
C	-3.549778	1.135292	-0.643776
C	-2.462604	2.156951	-0.391849
N	-1.193247	1.994824	-0.295617
C	-0.561602	3.325197	-0.366964
C	-1.759026	4.243460	-0.080090
O	-2.890874	3.412747	-0.387150
C	-4.853982	1.572875	0.057600
C	-3.755660	1.087948	-2.178262
H	-4.496198	-2.972612	0.470483
H	-3.386972	-2.978083	-0.934349
H	-1.835651	4.534609	0.978051
H	-1.814058	5.141467	-0.704880
H	-5.173568	2.550663	-0.321485
H	-4.712457	1.650338	1.145210
H	-5.643144	0.837951	-0.141106
H	-3.981613	2.093984	-2.556382
H	-2.854798	0.711905	-2.684595

H	-4.596747	0.424285	-2.415484
Ag	-0.195350	0.228887	0.545795
N	1.703824	1.148961	1.003118
C	2.295270	-0.002061	1.254396
O	3.579988	-0.226553	1.397961
C	4.707241	1.931989	1.462464
C	3.412399	2.679124	1.539020
H	5.118068	1.730967	2.462338
H	5.453662	2.527627	0.916022
H	3.170913	3.342615	0.703995
C	4.526532	0.611604	0.726003
H	4.183018	0.763804	-0.309298
H	5.455894	0.030336	0.715540
C	0.140073	3.578820	-1.731887
C	0.874831	4.922986	-1.633355
H	1.400554	5.139813	-2.574736
H	0.192132	5.765453	-1.442616
H	1.625988	4.908658	-0.827144
C	-0.870132	3.615853	-2.886332
H	-1.408758	2.660995	-2.976673
H	-1.610290	4.423605	-2.783507
H	-0.343314	3.780081	-3.837715
C	1.159863	2.469122	-2.008389
H	1.869723	2.354543	-1.177156
H	0.668078	1.498225	-2.161501
H	1.726187	2.698768	-2.923387
C	-2.741587	-2.219189	2.402807
C	-1.530363	-1.676518	3.173031
H	-1.430727	-0.585928	3.055761
H	-1.643047	-1.880865	4.248158
H	-0.597394	-2.146882	2.832645
C	-2.898681	-3.712720	2.720839
H	-1.993081	-4.272025	2.439804
H	-3.064540	-3.857816	3.798528
H	-3.756012	-4.164182	2.197843
C	-3.996206	-1.447461	2.830344
H	-3.901228	-0.372859	2.608099
H	-4.910557	-1.820325	2.344138
H	-4.145807	-1.542674	3.916037
H	-1.608734	-2.702074	0.627957
H	0.200005	3.394742	0.423055
C	2.522782	2.615052	2.571367
H	1.630196	3.244592	2.490039
C	2.658589	1.870345	3.860825
H	3.439246	1.099103	3.792427
H	3.014144	2.602991	4.608782

C	1.345783	1.255822	4.349763
H	0.549865	2.014021	4.411071
H	1.000681	0.451972	3.683594
H	1.475061	0.825652	5.351894
N	1.407628	-1.007130	1.332005
S	1.784336	-2.528205	0.821835
O	0.543059	-3.250443	0.639223
O	2.851517	-3.080373	1.604364
O	2.386383	-2.185654	-0.666760
C	2.002483	-2.941510	-1.789944
H	2.901339	-3.388337	-2.238991
H	1.290670	-3.735092	-1.518428
C	1.349009	-2.042090	-2.843870
Cl	1.010390	-3.037824	-4.270399
Cl	-0.199384	-1.372597	-2.216131
Cl	2.433444	-0.700303	-3.272994

TS4

ωB97X-D SCF energy:	-3610.23081408 a.u.
ωB97X-D enthalpy:	-3609.491363 a.u.
ωB97X-D free energy:	-3609.622236 a.u.
ωB97X-D SCF energy in solution:	-3612.84271021 a.u.
ωB97X-D enthalpy in solution:	-3612.103259 a.u.
ωB97X-D free energy in solution:	-3612.234132 a.u.
Imaginary frequency:	-223.8201 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.052551	3.635302	1.409990
C	-1.820837	2.714779	1.583525
N	-1.920382	1.832177	0.408127
C	-2.973221	2.147214	-0.247794
O	-3.699378	3.146131	0.224251
C	-3.473876	1.493721	-1.526421
C	-3.707059	0.015146	-1.262509
N	-2.975152	-0.765461	-0.558056
C	-3.604915	-2.090096	-0.523793
C	-4.696872	-1.947116	-1.606238
O	-4.753996	-0.531533	-1.856292
C	-2.388341	1.624614	-2.621581
C	-4.773530	2.159494	-2.000564
H	-2.797334	4.688754	1.237331
H	-3.769269	3.574451	2.238330
H	-4.435273	-2.443746	-2.550838
H	-5.695817	-2.274063	-1.295065

H	-2.740827	1.152192	-3.548702
H	-1.437807	1.154596	-2.336235
H	-2.195592	2.687074	-2.823943
H	-5.574833	2.067403	-1.256542
H	-4.596019	3.226423	-2.183051
H	-5.109320	1.692339	-2.933799
Ag	-0.943127	-0.138640	0.055145
N	0.102077	-2.005717	0.104670
C	1.226068	-1.510526	-0.353317
O	2.292087	-2.150919	-0.760941
C	2.194928	-3.501313	-1.225264
C	2.097883	-4.473388	-0.058032
C	0.873497	-4.206737	0.762595
H	3.111823	-3.660561	-1.804434
H	1.323827	-3.579130	-1.894363
H	2.061949	-5.493810	-0.468221
H	3.013155	-4.397053	0.546686
H	-0.052555	-4.698671	0.452017
C	-4.114159	-2.454042	0.897161
C	-2.920312	-2.500393	1.859167
H	-3.238065	-2.867683	2.846345
H	-2.135992	-3.170604	1.476677
H	-2.472476	-1.505007	2.005960
C	-4.751657	-3.849177	0.837640
H	-5.081338	-4.160653	1.839636
H	-5.636418	-3.879810	0.183903
H	-4.034100	-4.601293	0.473021
C	-5.133182	-1.423472	1.397785
H	-5.485417	-1.694993	2.403833
H	-4.685568	-0.419502	1.464104
H	-6.021120	-1.361581	0.749951
C	-0.464553	3.449845	1.717501
C	-0.146596	4.246991	0.448229
H	-0.053752	3.584650	-0.423930
H	-0.906251	5.015167	0.233717
H	0.813818	4.770534	0.564764
C	0.647904	2.424132	1.970242
H	1.593122	2.938708	2.198997
H	0.408297	1.776683	2.830178
H	0.835889	1.792407	1.092805
C	-0.556141	4.383846	2.933778
H	-0.800836	3.825927	3.852015
H	0.409337	4.884466	3.097181
H	-1.310175	5.175439	2.803982
H	-1.941888	2.086182	2.482552
H	-2.856804	-2.842101	-0.818503

C	0.829646	-3.423576	1.874725
H	-0.136513	-3.345264	2.383988
C	1.961049	-2.708215	2.542793
H	2.323850	-3.371181	3.349984
H	2.809521	-2.570180	1.856175
C	1.548050	-1.365760	3.147238
H	0.695548	-1.482768	3.834123
H	2.379179	-0.929502	3.718192
H	1.263581	-0.643294	2.368063
N	1.197499	-0.161493	-0.378114
S	1.625510	0.613016	-1.789581
O	1.429173	2.025968	-1.564751
O	1.022379	-0.060857	-2.914121
O	3.201480	0.312498	-1.911243
C	4.179080	1.206472	-1.417740
H	4.886395	1.391261	-2.237759
H	3.727324	2.158356	-1.102405
C	4.965871	0.605826	-0.246675
Cl	5.605037	-0.995916	-0.677360
Cl	6.305040	1.727598	0.093432
Cl	3.938409	0.462965	1.207959

TS1'

ωB97X-D SCF energy: -3832.56297147 a.u.
ωB97X-D enthalpy: -3831.895943 a.u.
ωB97X-D free energy: -3832.020929 a.u.
ωB97X-D SCF energy in solution: -3835.40524021 a.u.
ωB97X-D enthalpy in solution: -3834.738212 a.u.
ωB97X-D free energy in solution: -3834.863198 a.u.
Imaginary frequency: -231.8408 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ag	-0.656082	0.025413	0.197031
N	1.099928	0.716071	1.386077
C	1.729552	-0.432307	1.186860
O	2.820448	-0.901402	1.737162
C	4.076823	0.961837	2.649868
C	3.164415	1.906151	1.933935
H	4.417880	1.381232	3.611041
H	4.966535	0.762822	2.037980
H	3.411898	2.159670	0.899214
C	3.362234	-0.355078	2.933504
H	4.060111	-1.116562	3.300140
H	2.550385	-0.234050	3.666314

C	2.010112	2.423906	2.445210
H	1.464648	3.105823	1.786520
C	1.527715	2.386852	3.862062
H	0.543558	1.890434	3.876055
H	2.193594	1.783750	4.496334
C	1.398630	3.799755	4.436932
H	2.368891	4.317262	4.452230
H	0.702446	4.410690	3.841648
H	1.017541	3.763689	5.466700
O	-3.355374	3.385628	-0.232909
N	-1.766411	1.891290	0.173375
C	-2.387839	4.150584	0.521151
H	-2.849770	4.373897	1.492378
C	-1.941006	5.393228	-0.247136
H	-1.769303	6.228095	0.450604
H	-2.717810	5.720134	-0.953476
C	-0.657947	4.966037	-0.916832
C	0.075054	5.644578	-1.888339
H	-0.265756	6.609634	-2.269712
C	1.249289	5.070611	-2.374573
H	1.829251	5.591036	-3.139285
C	1.686194	3.831477	-1.897936
H	2.600878	3.388397	-2.297286
C	0.956111	3.152251	-0.923423
H	1.288820	2.180393	-0.552835
C	-0.214236	3.732502	-0.434810
C	-1.187808	3.174517	0.584758
H	-0.753464	3.073136	1.589690
C	-2.929583	2.128379	-0.315572
C	-3.866885	1.197543	-0.979275
C	-4.711779	1.798206	-2.116388
H	-4.483575	2.832308	-2.378070
H	-4.907669	1.125571	-2.952621
O	-4.473402	-0.977773	-1.677786
N	-2.466192	-0.851998	-0.732878
C	-3.985083	-2.336516	-1.793948
H	-3.830848	-2.525870	-2.864467
C	-4.946935	-3.318770	-1.125982
H	-4.978767	-4.261004	-1.695566
H	-5.971005	-2.918149	-1.109060
C	-4.353522	-3.536472	0.244480
C	-4.910909	-4.207672	1.330544
H	-5.916666	-4.629357	1.268612
C	-4.162171	-4.339399	2.499805
H	-4.586864	-4.864758	3.357625
C	-2.868821	-3.815985	2.579628

H	-2.286274	-3.942465	3.494050
C	-2.310229	-3.144442	1.493153
H	-1.289872	-2.762734	1.559219
C	-3.065782	-3.003638	0.332011
C	-2.687357	-2.291620	-0.948980
H	-1.805201	-2.735402	-1.430453
C	-3.526985	-0.239830	-1.106730
C	-5.361933	1.521639	-0.823716
H	-6.020185	0.655799	-0.745167
H	-5.593488	2.361154	-0.167136
N	1.089914	-1.172789	0.272549
S	1.259525	-2.806623	0.151461
O	0.435943	-3.208149	-0.966944
O	1.174225	-3.459809	1.429790
O	2.814385	-2.936268	-0.270247
C	3.234010	-2.724392	-1.599230
H	3.729835	-3.644207	-1.940015
H	2.387720	-2.507126	-2.267733
C	4.266487	-1.590983	-1.701745
Cl	4.946062	-1.668980	-3.344772
Cl	3.514396	0.025319	-1.481528
Cl	5.550517	-1.801941	-0.494253

TS2'

ωB97X-D SCF energy:	-3832.57030193 a.u.
ωB97X-D enthalpy:	-3831.903709 a.u.
ωB97X-D free energy:	-3832.027657 a.u.
ωB97X-D SCF energy in solution:	-3835.40729012 a.u.
ωB97X-D enthalpy in solution:	-3834.740697 a.u.
ωB97X-D free energy in solution:	-3834.864645 a.u.
Imaginary frequency:	-196.7800 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Ag	0.021461	0.414882	-0.505618
N	1.555920	1.892754	-1.008749
C	1.319732	2.587467	0.078659
O	1.638290	3.837918	0.329432
C	1.733072	4.767618	-0.761100
C	3.049946	4.619566	-1.508923
C	3.216140	3.230318	-2.044805
H	1.648511	5.755346	-0.293295
H	0.870017	4.609550	-1.426736
H	3.050883	5.346267	-2.335311
H	3.874933	4.890710	-0.834674

H	2.784803	3.019532	-3.026630
C	3.894489	2.227194	-1.421288
H	3.945942	1.264249	-1.940859
C	4.625894	2.287961	-0.119596
H	4.679332	3.317730	0.261106
H	4.036777	1.725343	0.627875
C	6.022082	1.669798	-0.214783
H	6.522646	1.698421	0.762839
H	5.967104	0.618488	-0.536096
H	6.651752	2.215090	-0.932742
O	-3.549698	-2.056424	-0.400399
N	-1.981235	-0.485405	-0.352178
C	-4.268367	-0.911485	0.115511
H	-4.568434	-1.161269	1.140975
C	-5.444969	-0.547779	-0.794668
H	-6.318508	-0.257925	-0.189937
H	-5.748393	-1.411128	-1.404713
C	-4.939333	0.619112	-1.607725
C	-5.551658	1.248826	-2.689523
H	-6.509112	0.890752	-3.074467
C	-4.924258	2.348378	-3.274459
H	-5.393595	2.849868	-4.123276
C	-3.706227	2.822073	-2.777905
H	-3.237484	3.694186	-3.238043
C	-3.094916	2.195941	-1.692837
H	-2.160157	2.579306	-1.277688
C	-3.718136	1.088862	-1.122646
C	-3.216133	0.223980	0.010675
H	-3.058145	0.781148	0.943864
C	-2.287935	-1.699759	-0.611397
C	-1.402495	-2.785272	-1.097781
C	-2.076255	-4.086494	-1.527587
H	-3.165837	-4.070234	-1.531359
H	-1.601598	-4.610467	-2.357082
O	0.470337	-3.452326	-2.391153
N	0.530461	-1.336903	-1.723052
C	1.680002	-2.956593	-3.010666
H	1.485633	-2.903848	-4.090554
C	2.878680	-3.824800	-2.637972
H	3.603375	-3.842087	-3.467566
H	2.573321	-4.864986	-2.454583
C	3.452912	-3.137491	-1.423701
C	4.412113	-3.612369	-0.531834
H	4.847752	-4.605723	-0.659885
C	4.803505	-2.804745	0.536044
H	5.549665	-3.169244	1.244808

C	4.241296	-1.537616	0.711828
H	4.547506	-0.920809	1.559445
C	3.285872	-1.059015	-0.184100
H	2.836819	-0.074805	-0.043891
C	2.901159	-1.865613	-1.252588
C	1.850108	-1.586834	-2.311336
H	2.123503	-0.765128	-2.988626
C	-0.115484	-2.446365	-1.748480
C	-1.377483	-4.057358	-0.227564
H	-0.406911	-4.548785	-0.135818
H	-1.962150	-4.001578	0.692737
N	0.623134	1.858550	0.969325
S	-0.558614	2.540569	1.919950
O	-1.605515	3.110022	1.109189
O	0.048257	3.256091	3.011533
O	-1.190660	1.156856	2.487550
C	-0.592048	0.521440	3.598824
H	0.433825	0.880428	3.768412
H	-1.192664	0.724219	4.497373
C	-0.552150	-0.996010	3.394792
Cl	-2.184205	-1.623749	3.034453
Cl	0.564006	-1.459165	2.075855
Cl	0.034145	-1.704078	4.915352

TS3'

ωB97X-D SCF energy:	-3610.22412408 a.u.
ωB97X-D enthalpy:	-3609.484255 a.u.
ωB97X-D free energy:	-3609.614572 a.u.
ωB97X-D SCF energy in solution:	-3612.83834535 a.u.
ωB97X-D enthalpy in solution:	-3612.098476 a.u.
ωB97X-D free energy in solution:	-3612.228793 a.u.
Imaginary frequency:	-185.6274 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.318113	-3.544241	-0.852234
C	-2.304716	-2.958472	0.142518
N	-2.426544	-1.514368	-0.133718
C	-3.514921	-1.329367	-0.778234
O	-4.164400	-2.421076	-1.164710
C	-4.223363	-0.044944	-1.143180
C	-3.511924	1.220053	-0.711871
N	-2.273374	1.428268	-0.447953
C	-2.062891	2.884884	-0.380509
C	-3.504689	3.392550	-0.226674

O	-4.291807	2.294667	-0.713672
C	-5.625549	-0.092390	-0.495790
C	-4.349207	0.023932	-2.685379
H	-3.949374	-4.346127	-0.453700
H	-2.849899	-3.882313	-1.788045
H	-3.787865	3.569502	0.821445
H	-3.749785	4.280108	-0.820050
H	-6.208404	0.784658	-0.800581
H	-5.555332	-0.100998	0.601520
H	-6.149770	-0.999508	-0.819168
H	-4.859178	0.950920	-2.979158
H	-3.359094	-0.005141	-3.162913
H	-4.936302	-0.831634	-3.042660
Ag	-0.788160	-0.056751	0.181773
N	0.758610	1.190320	1.148126
C	1.643972	0.210300	1.118681
O	2.819769	0.114210	1.683010
C	3.599613	2.355821	2.195020
C	2.455221	2.941206	1.427319
H	3.879617	2.995270	3.048649
H	4.480692	2.263401	1.546168
H	2.587487	3.068201	0.349231
C	3.234675	0.978568	2.735337
H	4.104935	0.481064	3.178486
H	2.433027	1.029623	3.487493
C	-1.305852	3.436610	-1.624130
C	-1.009649	4.920539	-1.363989
H	-0.480430	5.360509	-2.221745
H	-1.925333	5.511969	-1.210059
H	-0.369855	5.052821	-0.476520
C	-2.140729	3.285489	-2.902850
H	-2.384276	2.230987	-3.100623
H	-3.079940	3.857507	-2.871499
H	-1.568540	3.652454	-3.767465
C	0.020591	2.689388	-1.814730
H	0.617101	2.675615	-0.892110
H	-0.140215	1.644372	-2.119602
H	0.613993	3.173371	-2.604589
C	-2.582855	-3.279993	1.638870
C	-1.648670	-2.454157	2.533604
H	-1.874801	-1.377323	2.473474
H	-1.776852	-2.751943	3.584966
H	-0.590695	-2.612969	2.281226
C	-2.281194	-4.769611	1.854215
H	-1.230330	-4.996245	1.616947
H	-2.456991	-5.047432	2.903856

H	-2.919605	-5.418654	1.234851
C	-4.035658	-2.968806	2.021782
H	-4.271062	-1.903061	1.873290
H	-4.764220	-3.565152	1.452280
H	-4.198921	-3.190706	3.086719
H	-1.281724	-3.280626	-0.095771
H	-1.465630	3.110166	0.514398
C	1.248385	3.279012	1.959170
H	0.509397	3.683364	1.260989
C	0.853974	3.338359	3.400808
H	0.073666	2.577842	3.571872
H	1.698592	3.076792	4.055186
C	0.311191	4.719695	3.774959
H	1.070881	5.501717	3.630561
H	-0.564839	4.983101	3.162311
H	0.001166	4.739950	4.828655
N	1.183017	-0.808555	0.380254
S	1.714025	-2.359207	0.536511
O	0.975881	-3.129626	-0.441422
O	1.809019	-2.780169	1.908668
O	3.246100	-2.219366	0.049290
C	3.581139	-2.153955	-1.319659
H	4.258589	-2.992562	-1.533295
H	2.693652	-2.239046	-1.964108
C	4.337282	-0.861261	-1.662520
Cl	4.986586	-1.075025	-3.306239
Cl	3.254451	0.569587	-1.666766
Cl	5.659006	-0.585931	-0.509813

TS4'

ωB97X-D SCF energy:	-3610.22897853 a.u.
ωB97X-D enthalpy:	-3609.489539 a.u.
ωB97X-D free energy:	-3609.618823 a.u.
ωB97X-D SCF energy in solution:	-3612.84269326 a.u.
ωB97X-D enthalpy in solution:	-3612.103254 a.u.
ωB97X-D free energy in solution:	-3612.232538 a.u.
Imaginary frequency:	-211.3519 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-4.346055	-1.927176	-1.729653
C	-3.174590	-2.224543	-0.772391
N	-2.967789	-0.912119	-0.135244
C	-3.972856	-0.174220	-0.417211
O	-4.872119	-0.674253	-1.252398

C	-4.277286	1.199209	0.163995
C	-3.126741	2.142145	-0.132869
N	-1.876627	1.874907	-0.067487
C	-1.134950	3.041826	-0.561307
C	-2.221924	4.133051	-0.525850
O	-3.448407	3.385268	-0.458860
C	-4.388252	1.062979	1.700717
C	-5.586635	1.755084	-0.411756
H	-5.157146	-2.663913	-1.708612
H	-4.023250	-1.778291	-2.770051
H	-2.165953	4.765917	0.371892
H	-2.262832	4.774542	-1.413302
H	-3.470890	0.641400	2.134539
H	-5.228362	0.400892	1.952696
H	-4.577728	2.047815	2.150486
H	-6.408554	1.062139	-0.194165
H	-5.811645	2.727029	0.043345
H	-5.529019	1.885446	-1.499823
Ag	-0.996897	-0.043789	0.585273
N	0.767209	0.495485	1.863189
C	1.365925	-0.665157	1.699645
O	2.517139	-1.102227	2.131986
C	3.490195	-0.220941	2.682032
C	3.033763	0.322846	4.032526
C	1.720916	1.035039	3.912685
H	3.687926	0.575696	1.949166
H	4.395241	-0.829137	2.785580
H	2.952774	-0.507467	4.746656
H	3.819512	0.998071	4.408839
H	0.857359	0.610214	4.429818
C	-0.496159	2.788111	-1.956451
C	0.341541	4.023479	-2.315707
H	0.807646	3.894845	-3.303521
H	-0.261645	4.943334	-2.360200
H	1.149114	4.181013	-1.583411
C	-1.570369	2.541569	-3.023301
H	-2.191397	1.667796	-2.769725
H	-2.233580	3.407565	-3.168385
H	-1.095847	2.331501	-3.993186
C	0.429126	1.565222	-1.894654
H	1.116349	1.603223	-1.036442
H	-0.134648	0.621149	-1.839179
H	1.044456	1.514036	-2.805517
C	-3.443680	-3.342906	0.271792
C	-2.234874	-3.464738	1.207062
H	-2.090482	-2.554887	1.808262

H	-2.376247	-4.305286	1.902712
H	-1.311740	-3.647006	0.639033
C	-4.698588	-3.040008	1.099738
H	-4.583543	-2.105394	1.670216
H	-5.604961	-2.957078	0.479930
H	-4.876589	-3.846666	1.826208
C	-3.613369	-4.667741	-0.485279
H	-2.720785	-4.896390	-1.088186
H	-3.757597	-5.494832	0.225442
H	-4.486803	-4.662507	-1.155453
H	-2.263968	-2.493433	-1.326140
H	-0.322330	3.267744	0.142224
C	1.540533	2.199098	3.221440
H	0.527395	2.612582	3.202404
C	2.600624	3.061090	2.619612
H	2.680903	3.938705	3.287819
H	3.584030	2.573261	2.649115
C	2.286364	3.543639	1.205991
H	3.091759	4.189460	0.830527
H	2.172959	2.693527	0.518750
H	1.355262	4.130058	1.187830
N	0.586466	-1.477664	0.955016
S	1.207879	-2.224174	-0.368488
O	0.130681	-2.397660	-1.319387
O	2.064941	-3.332039	-0.038938
O	2.144011	-0.983494	-0.894906
C	3.087220	-1.213719	-1.915334
H	3.221405	-2.288492	-2.113526
H	2.759600	-0.705531	-2.834014
C	4.441059	-0.636908	-1.495621
Cl	5.531078	-0.756232	-2.890007
Cl	4.249378	1.085422	-1.029263
Cl	5.107280	-1.548295	-0.123089

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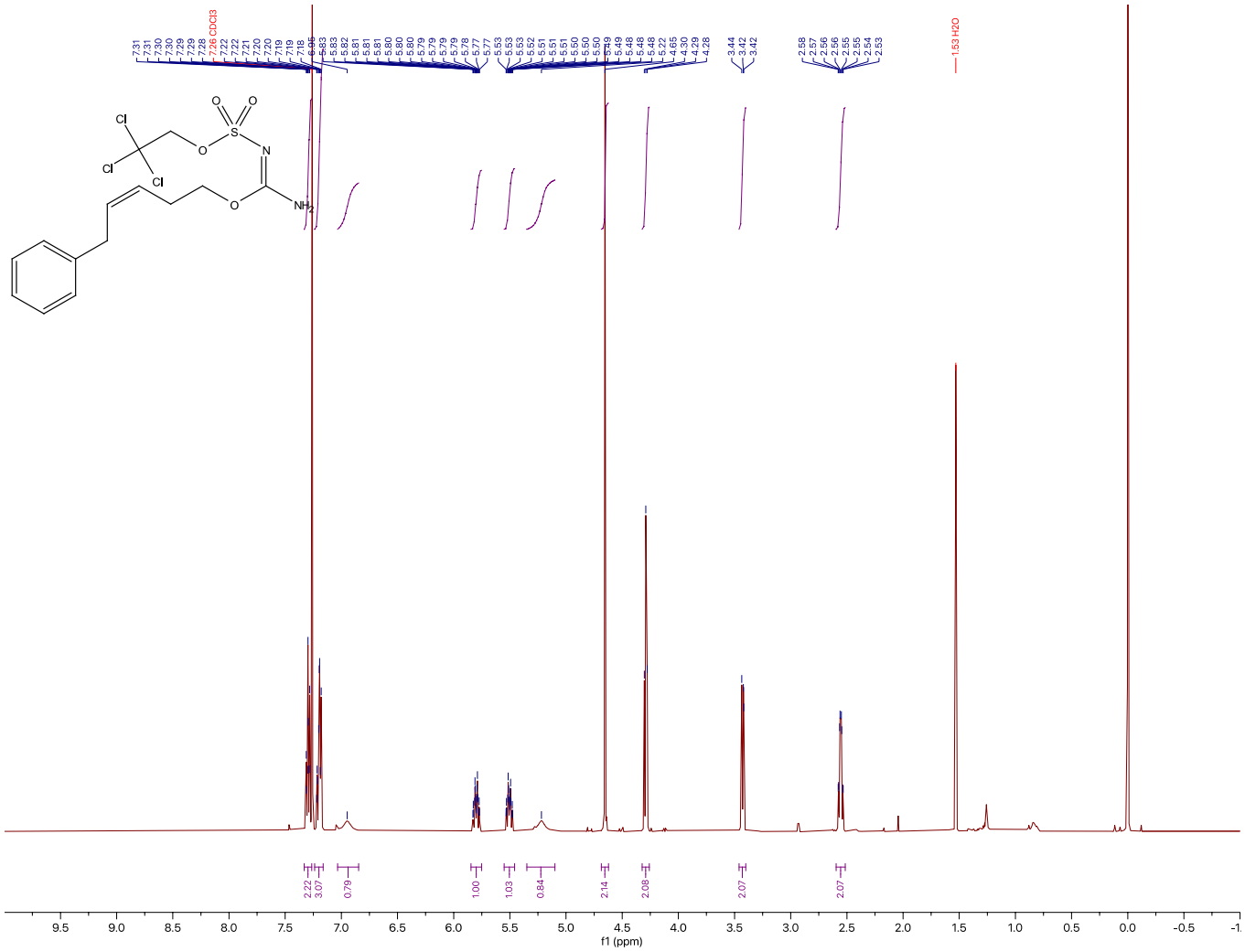
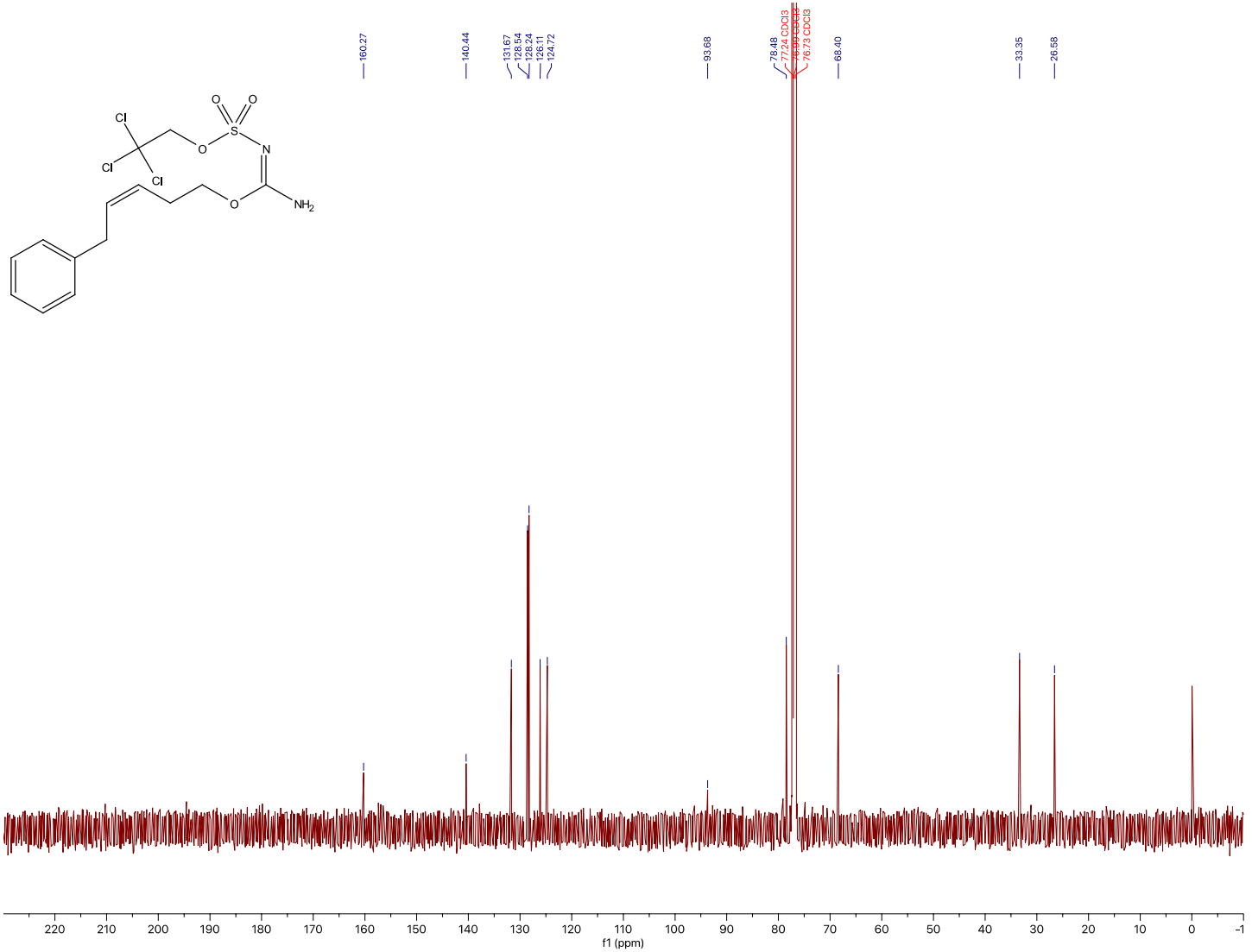
VIII. NMR Spectral Data

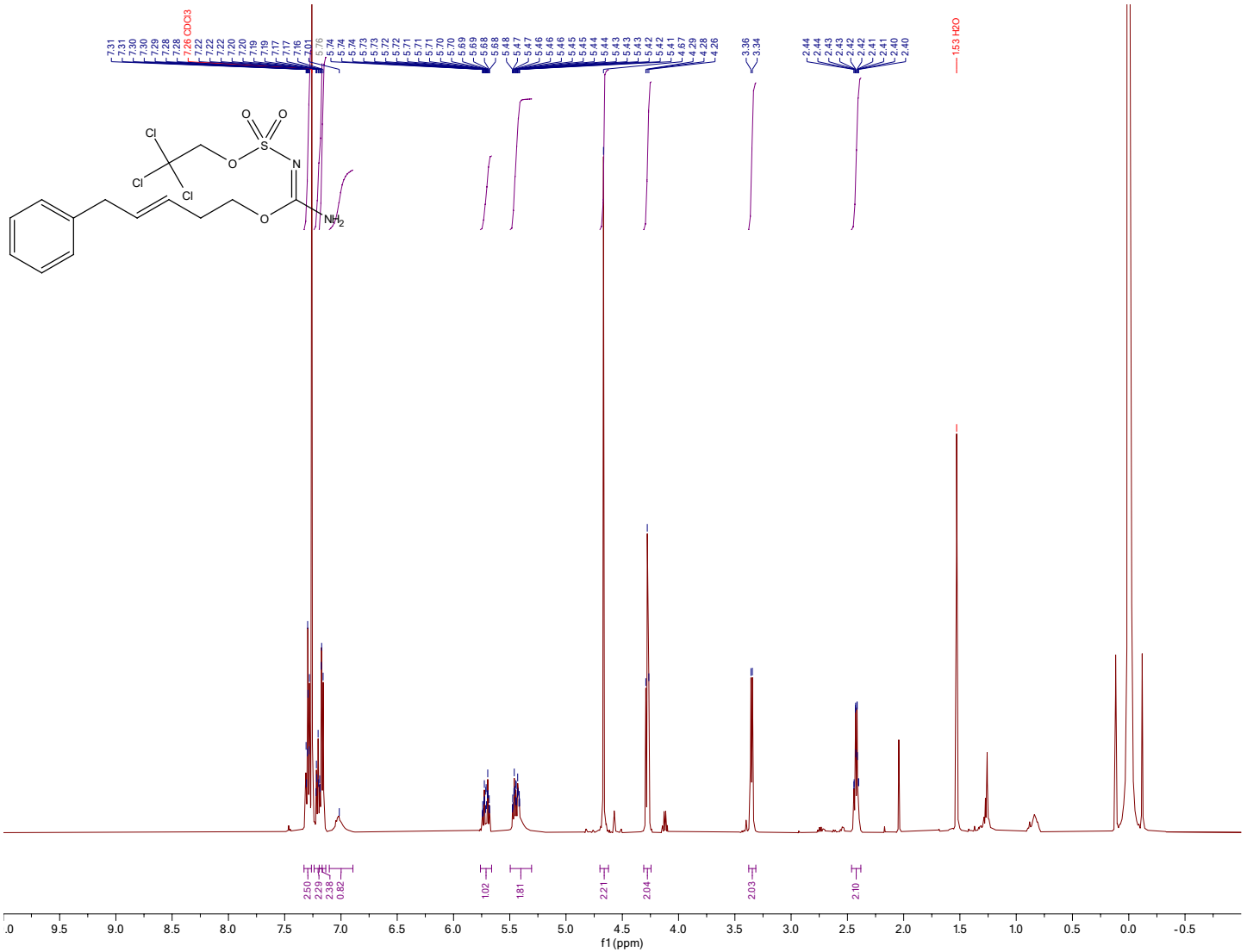
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1a**



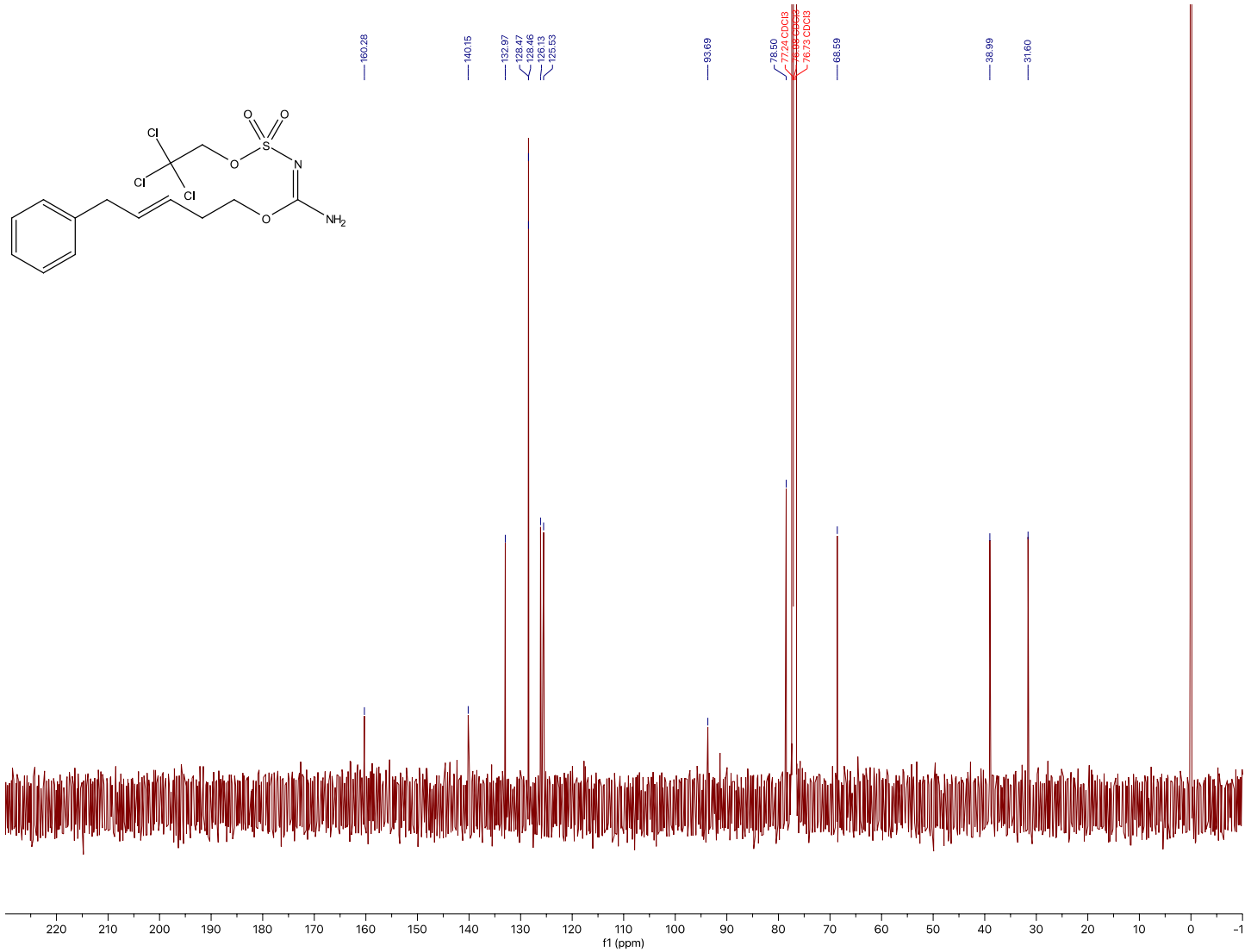
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1a**



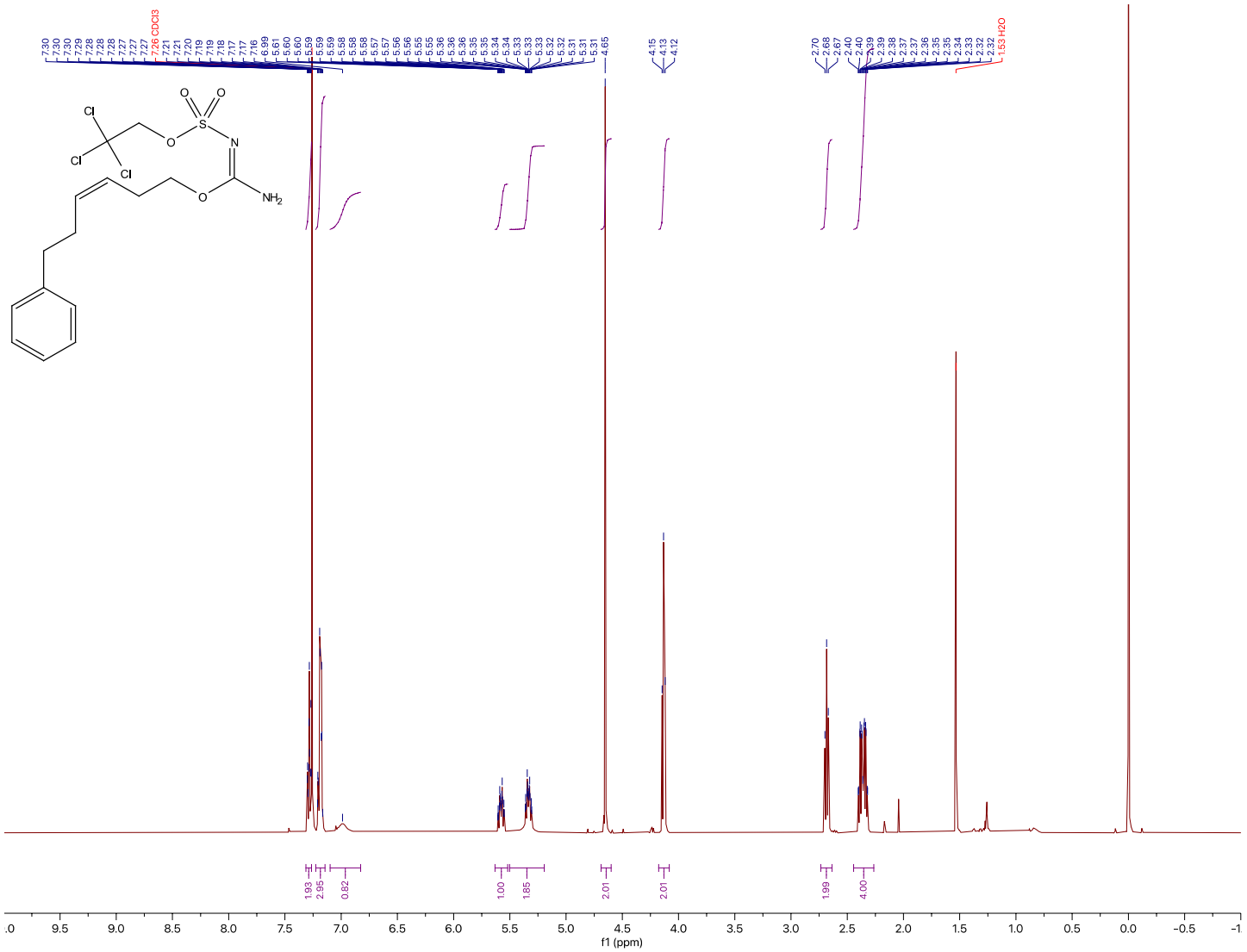
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1b**



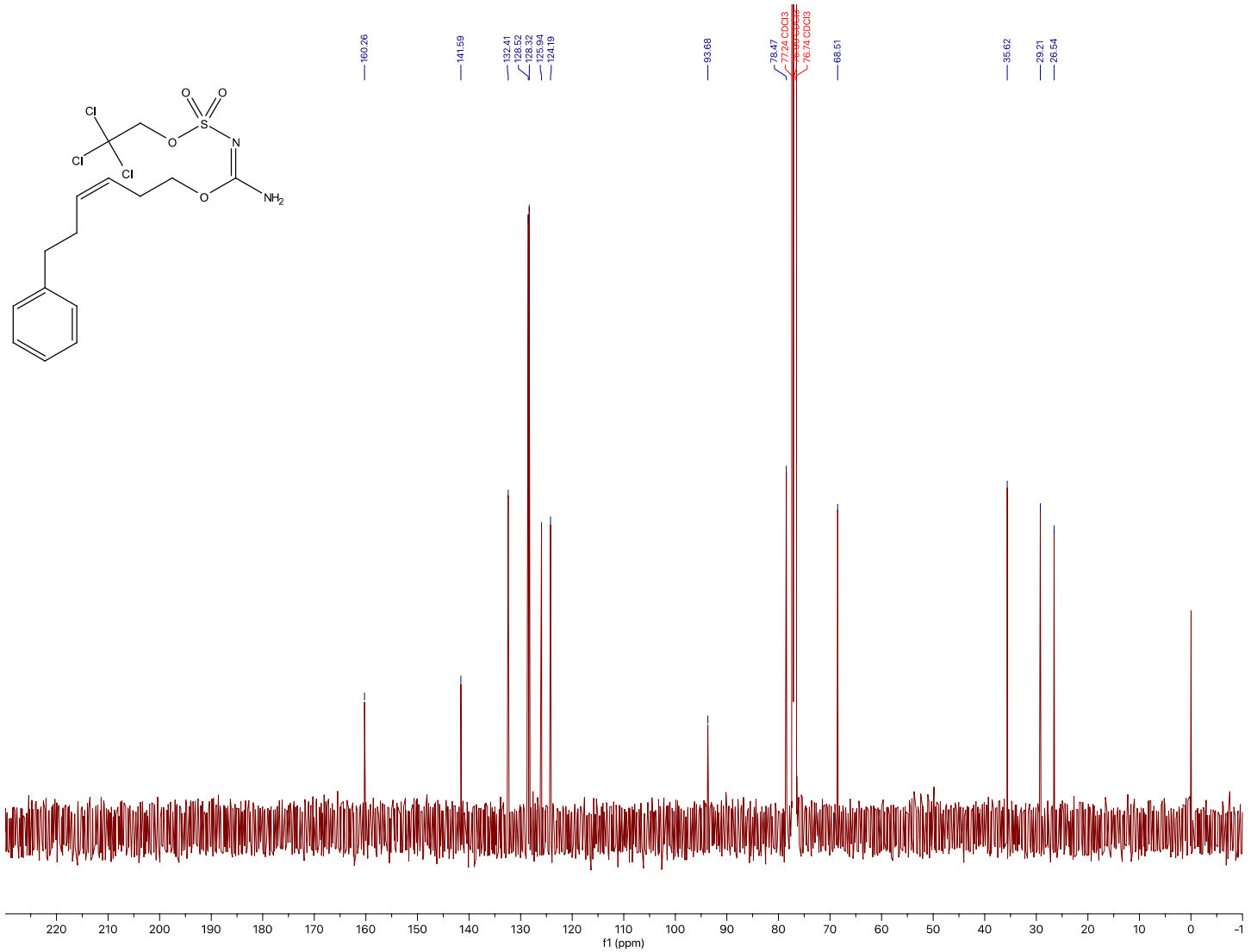
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1b**



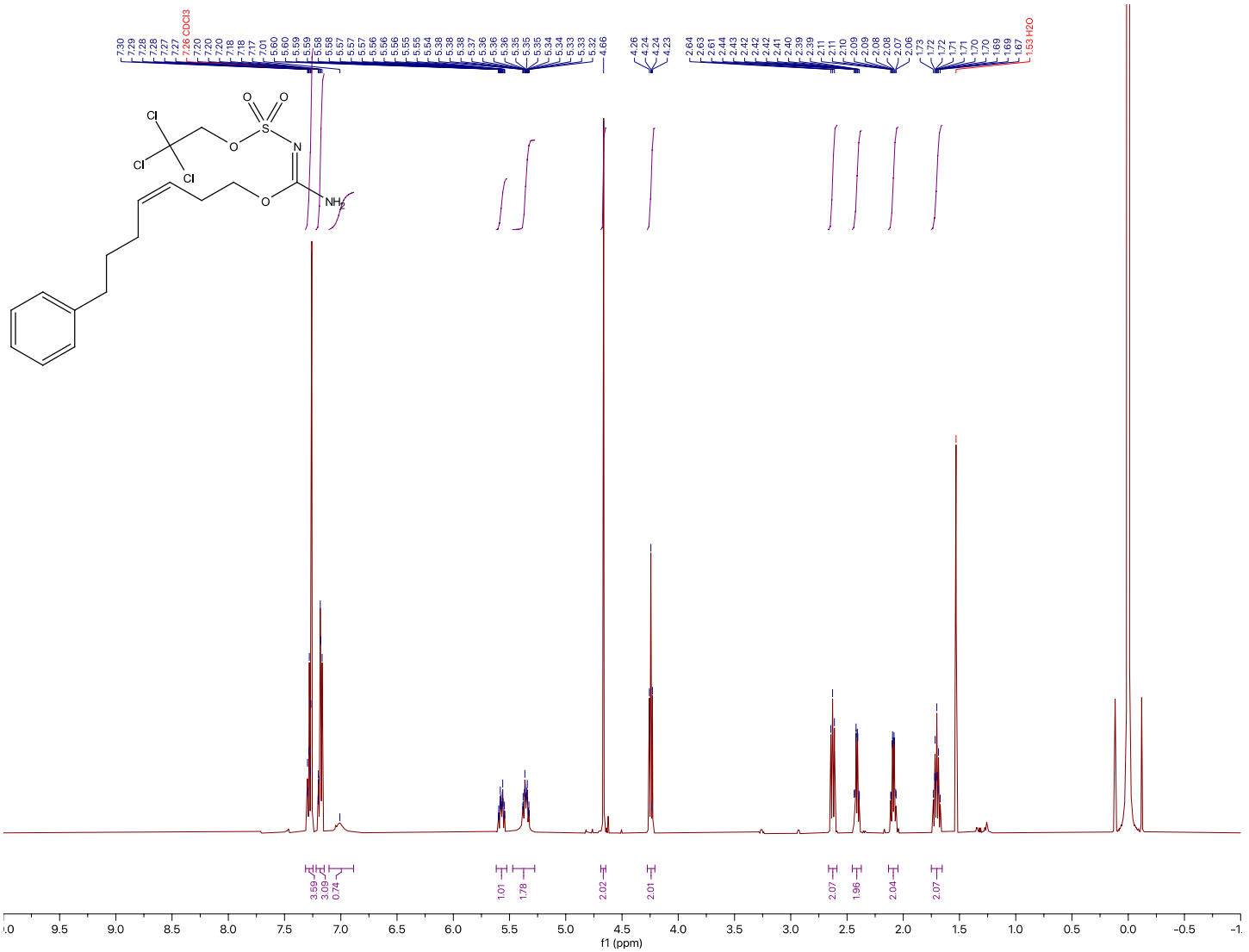
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1c**



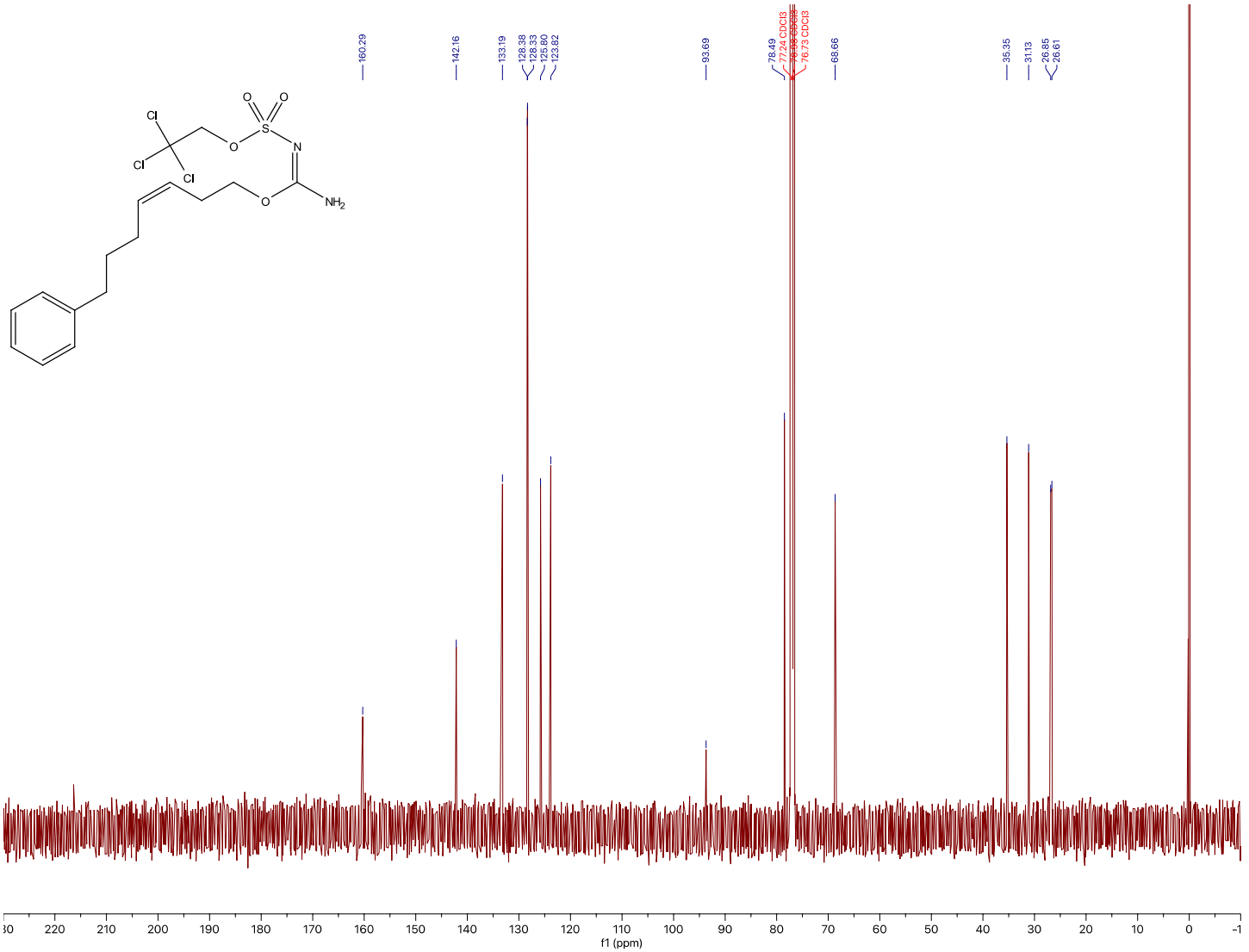
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1c**



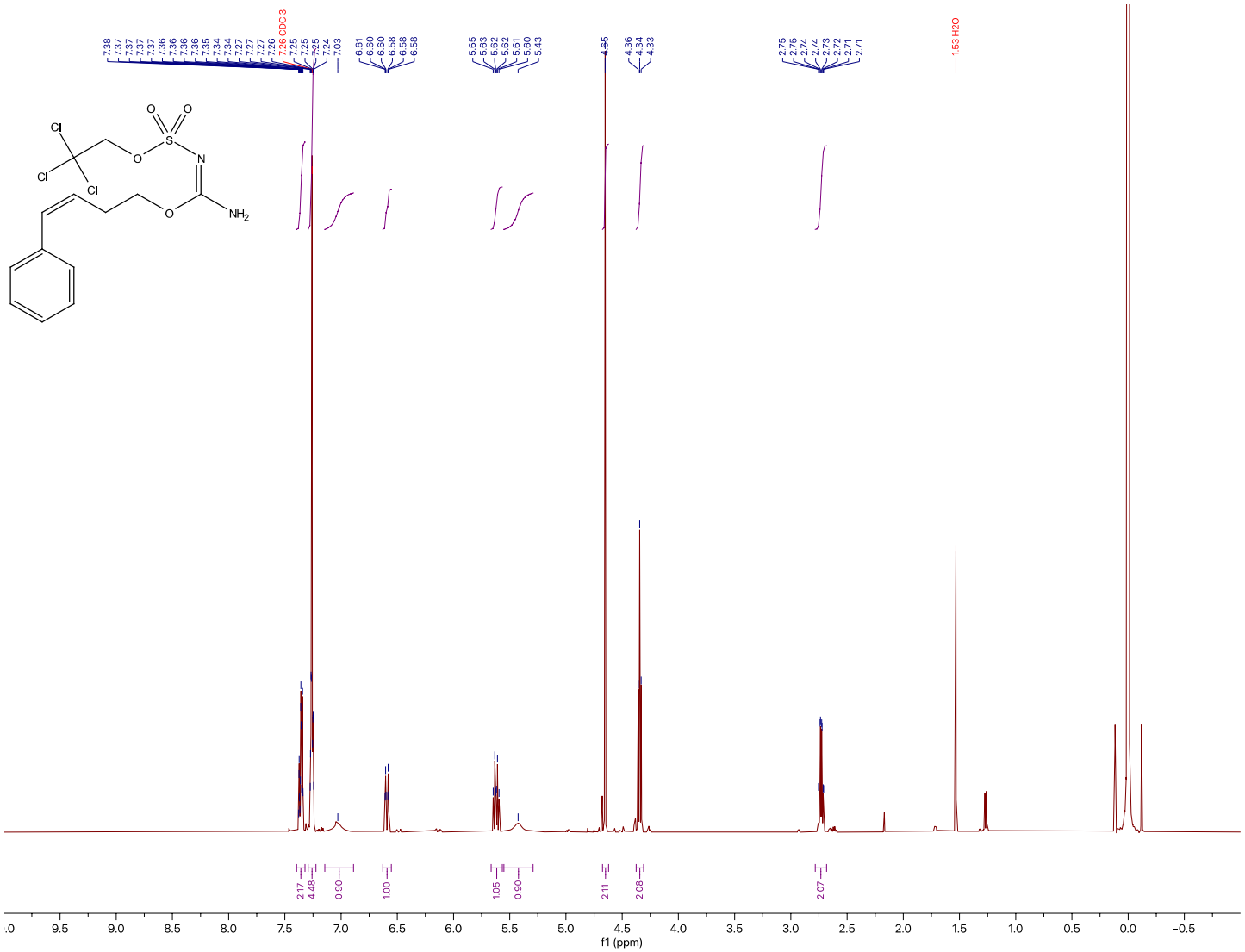
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1d**



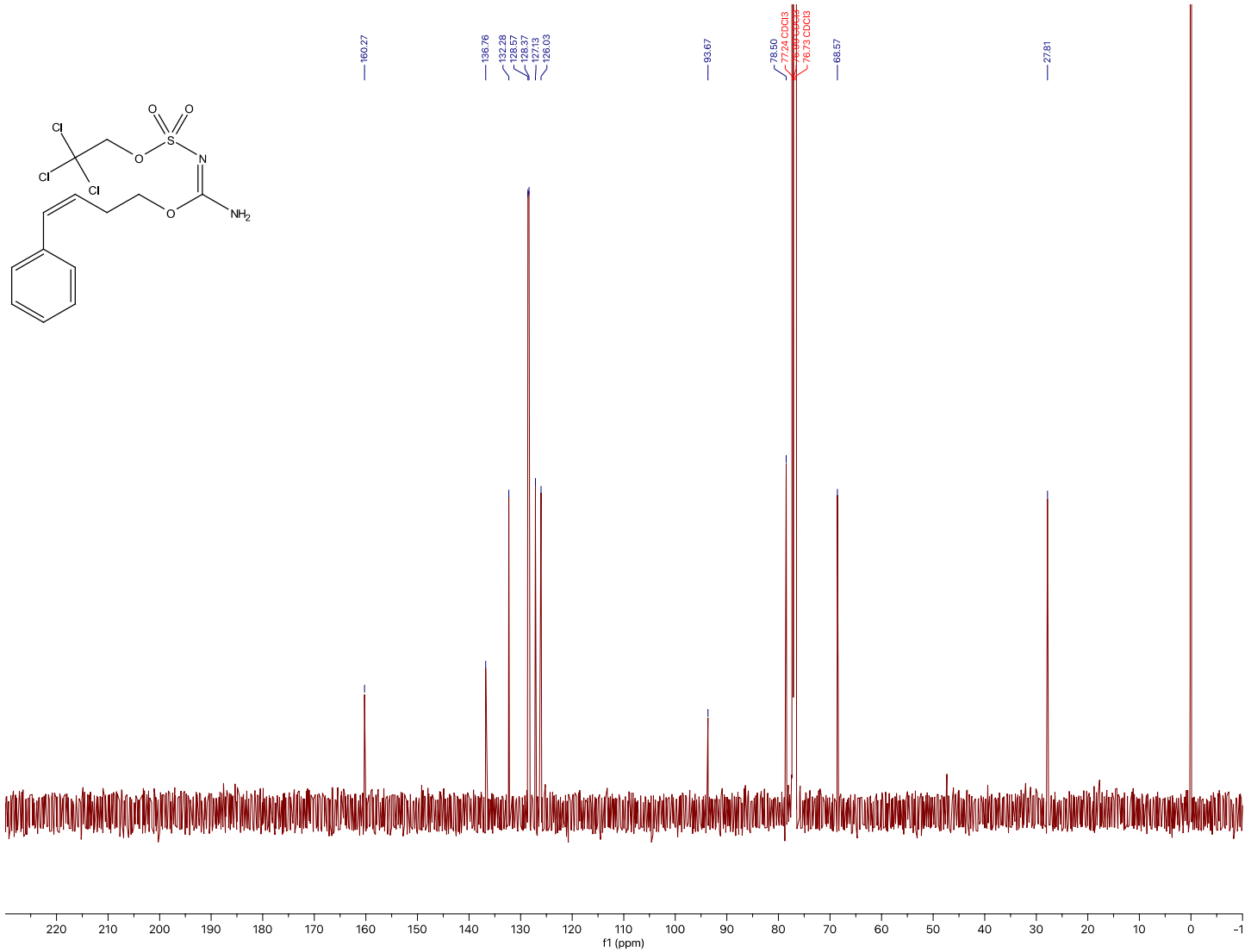
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1d**



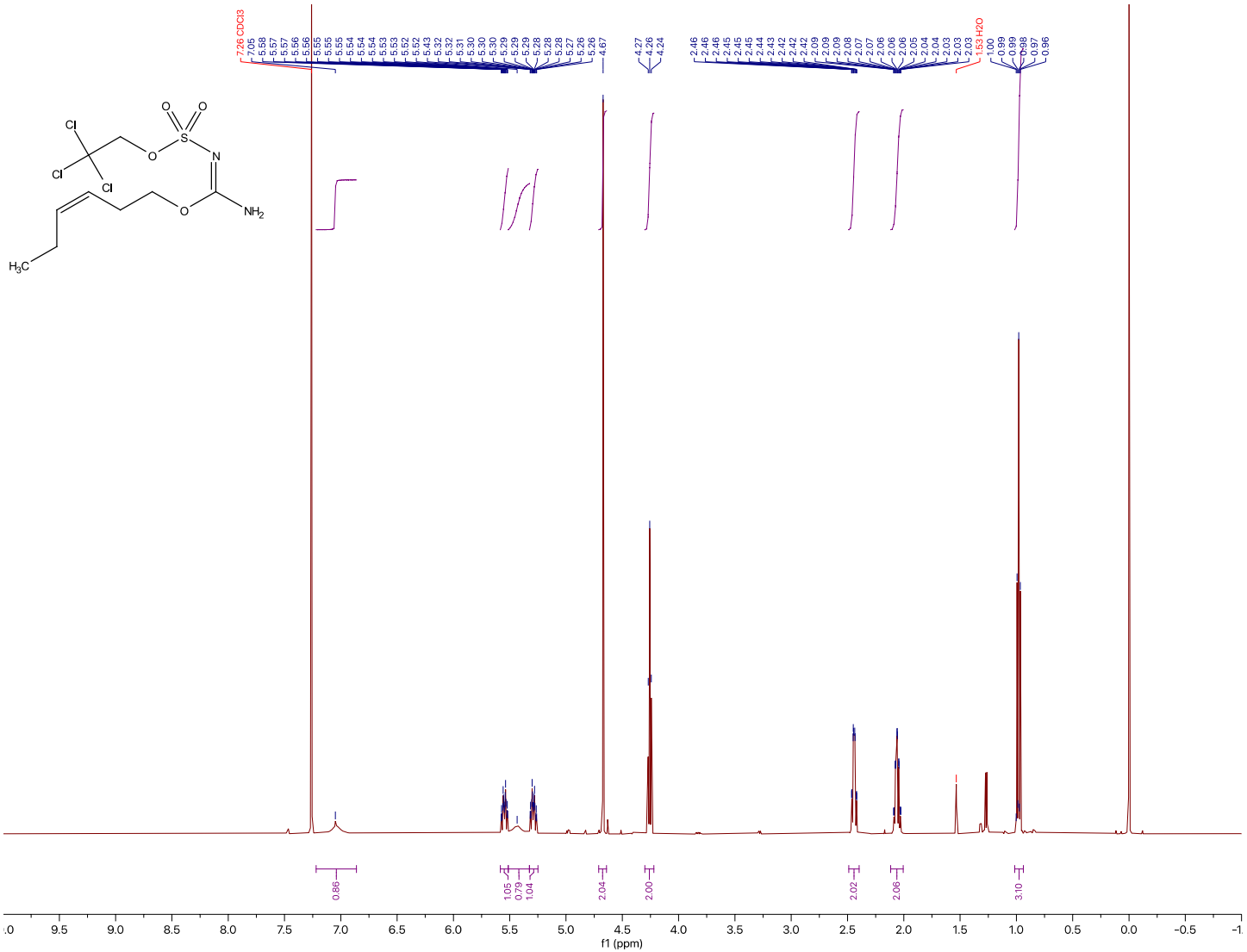
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1e**



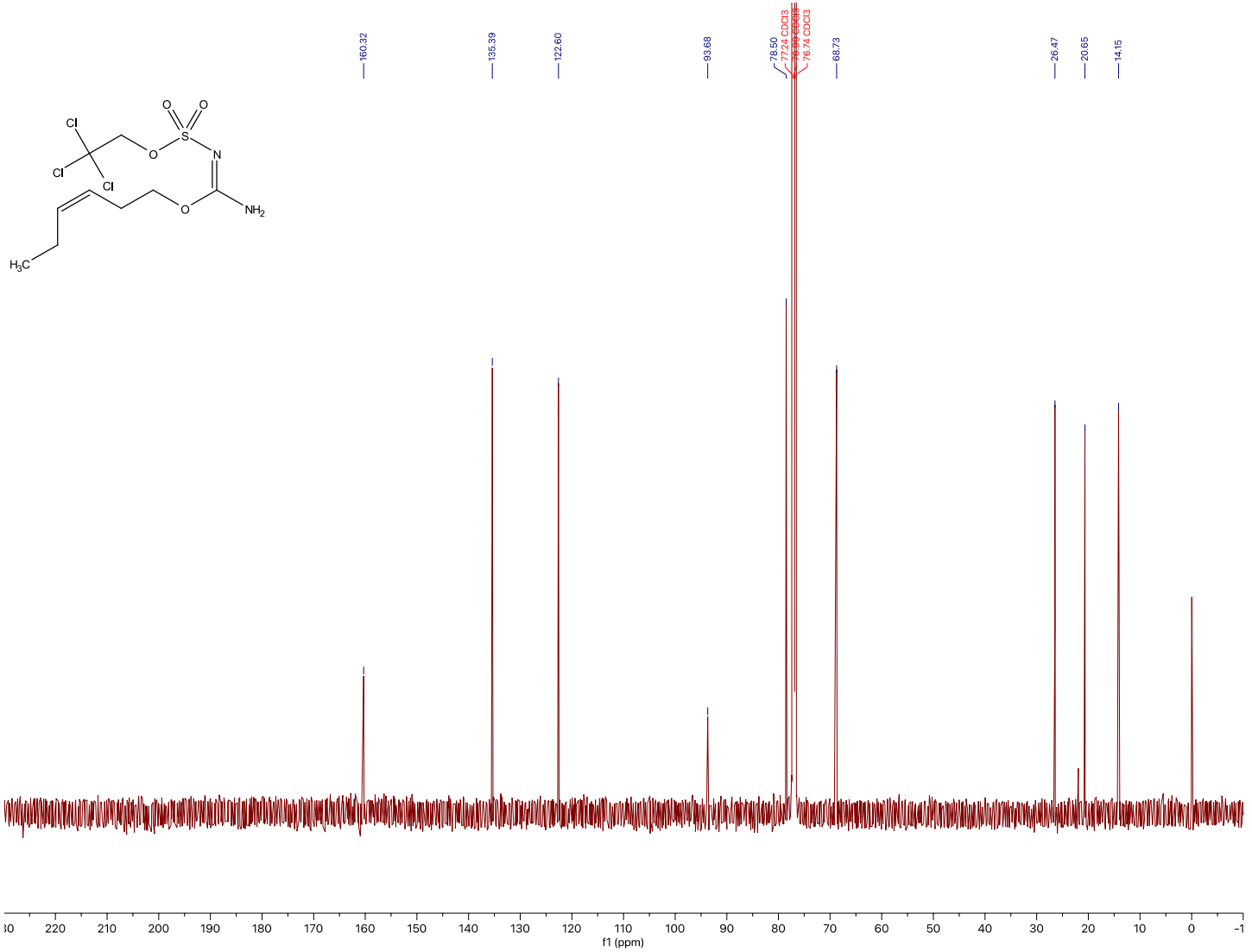
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1e**



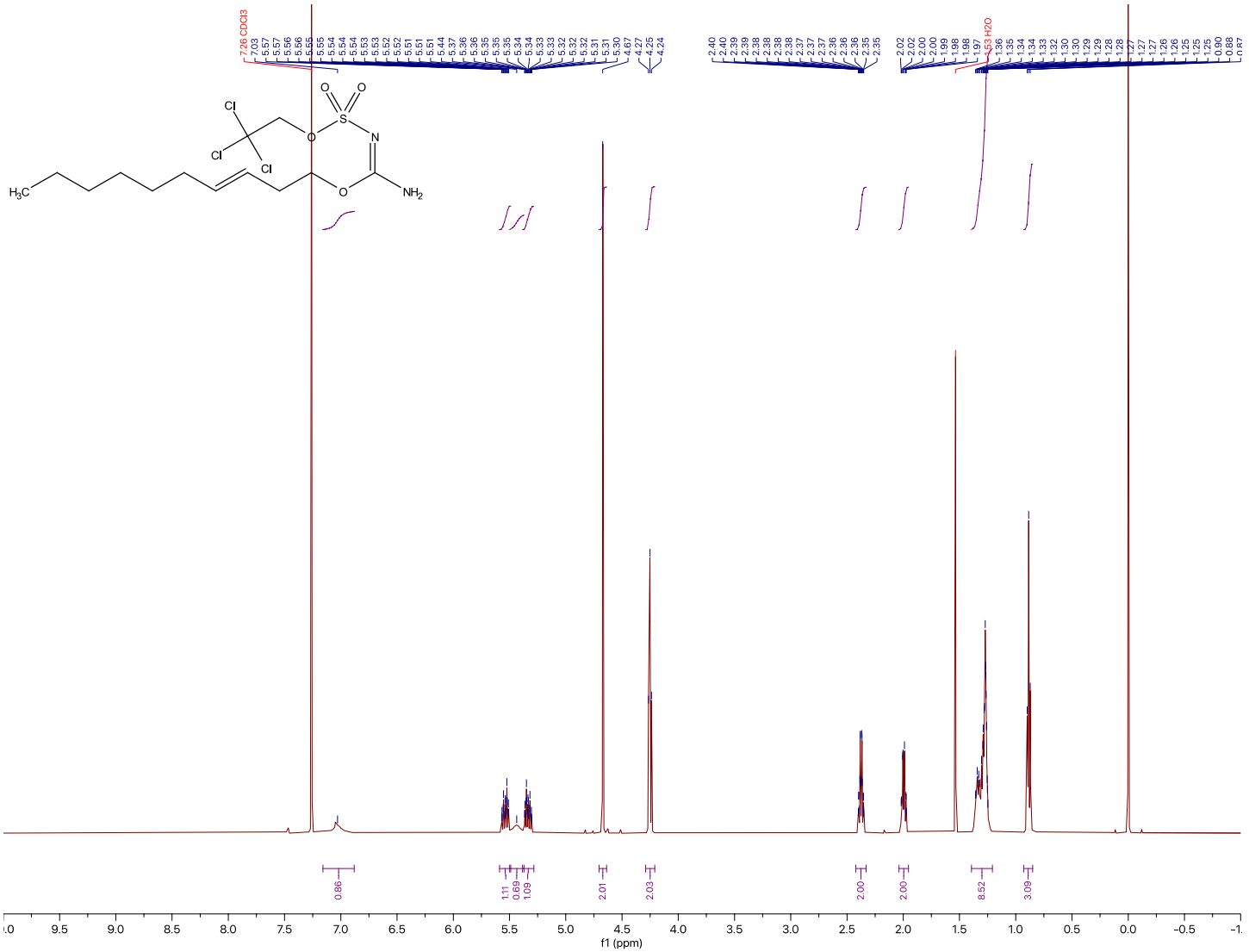
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1f**



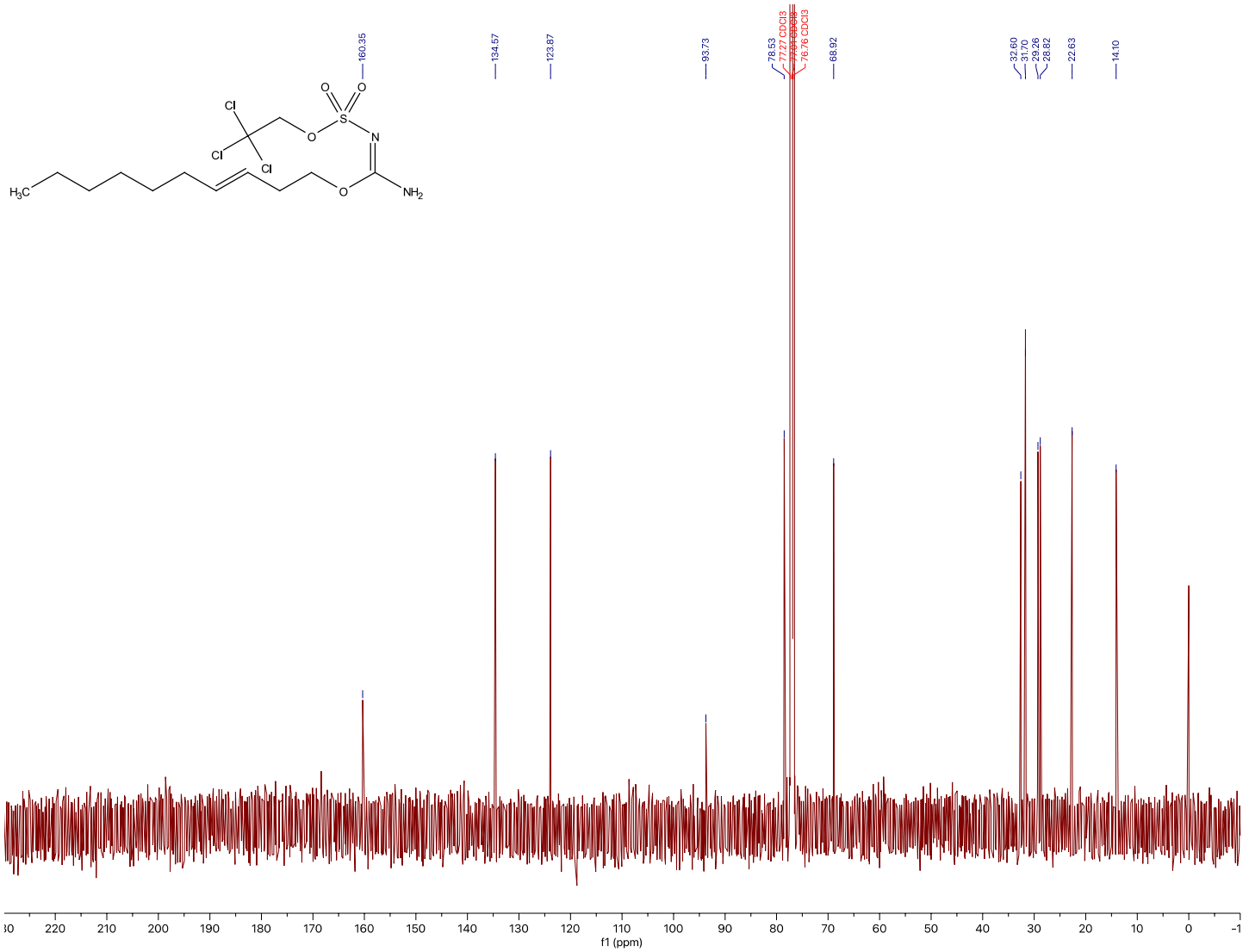
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1f**



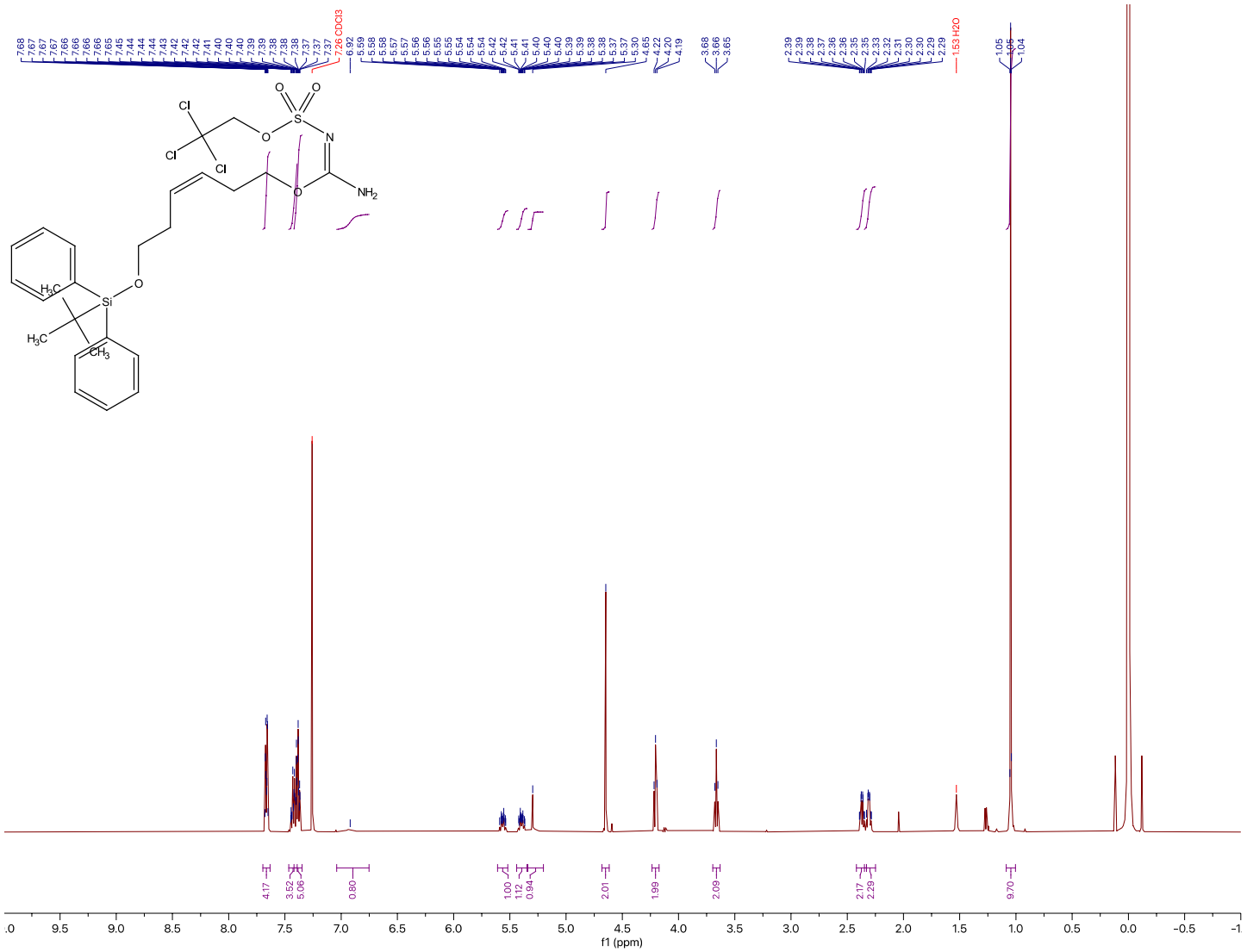
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1g**



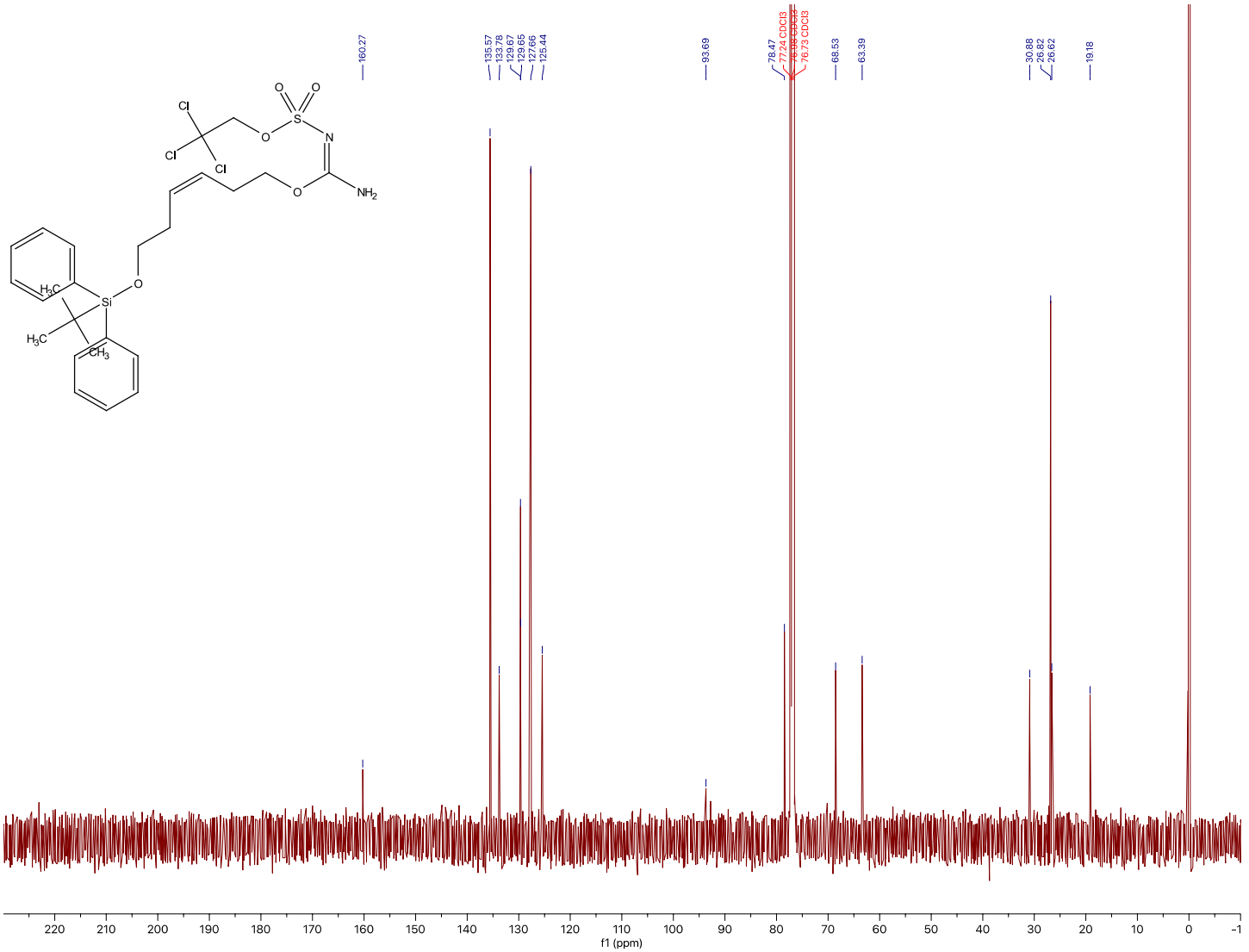
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1g**



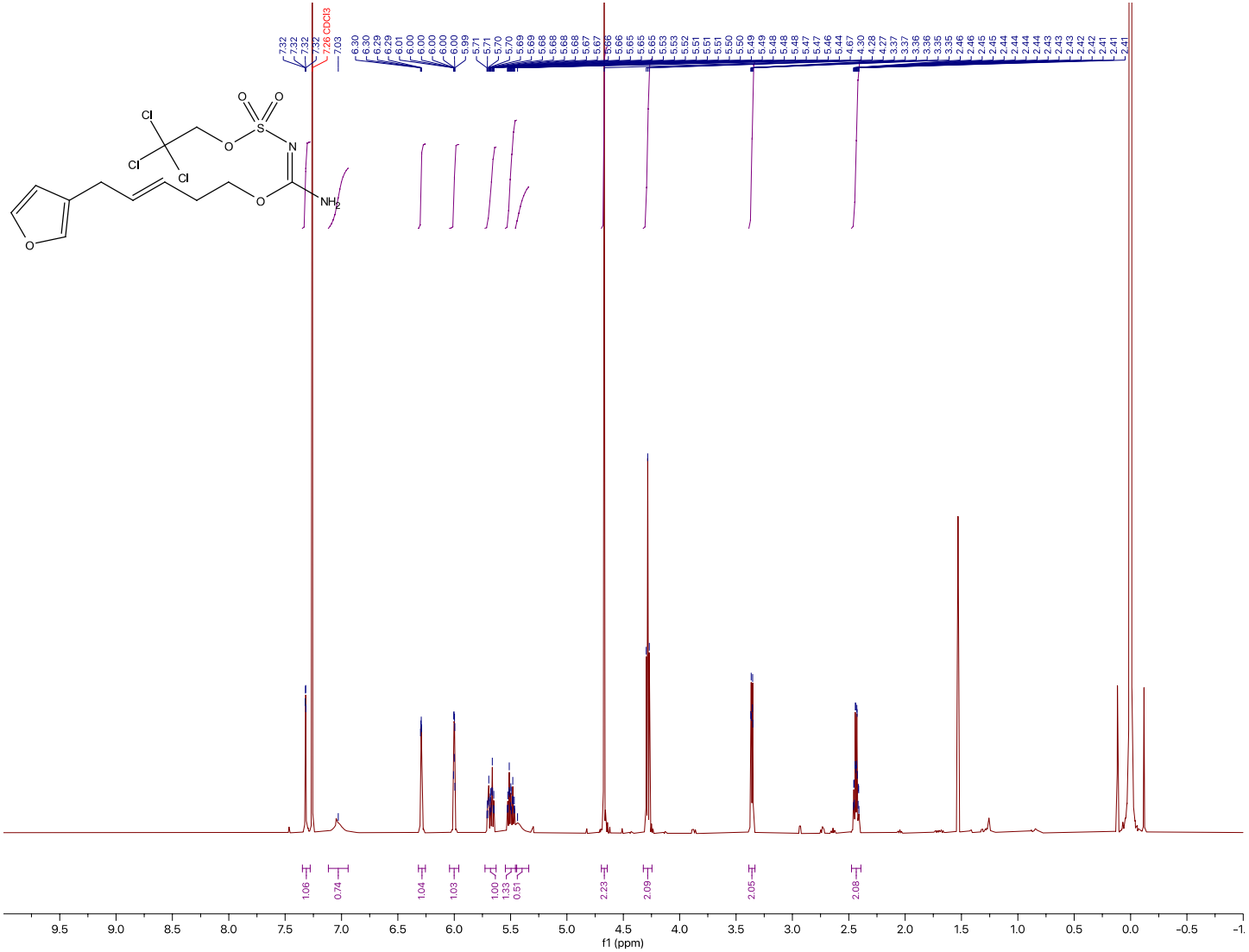
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1h**



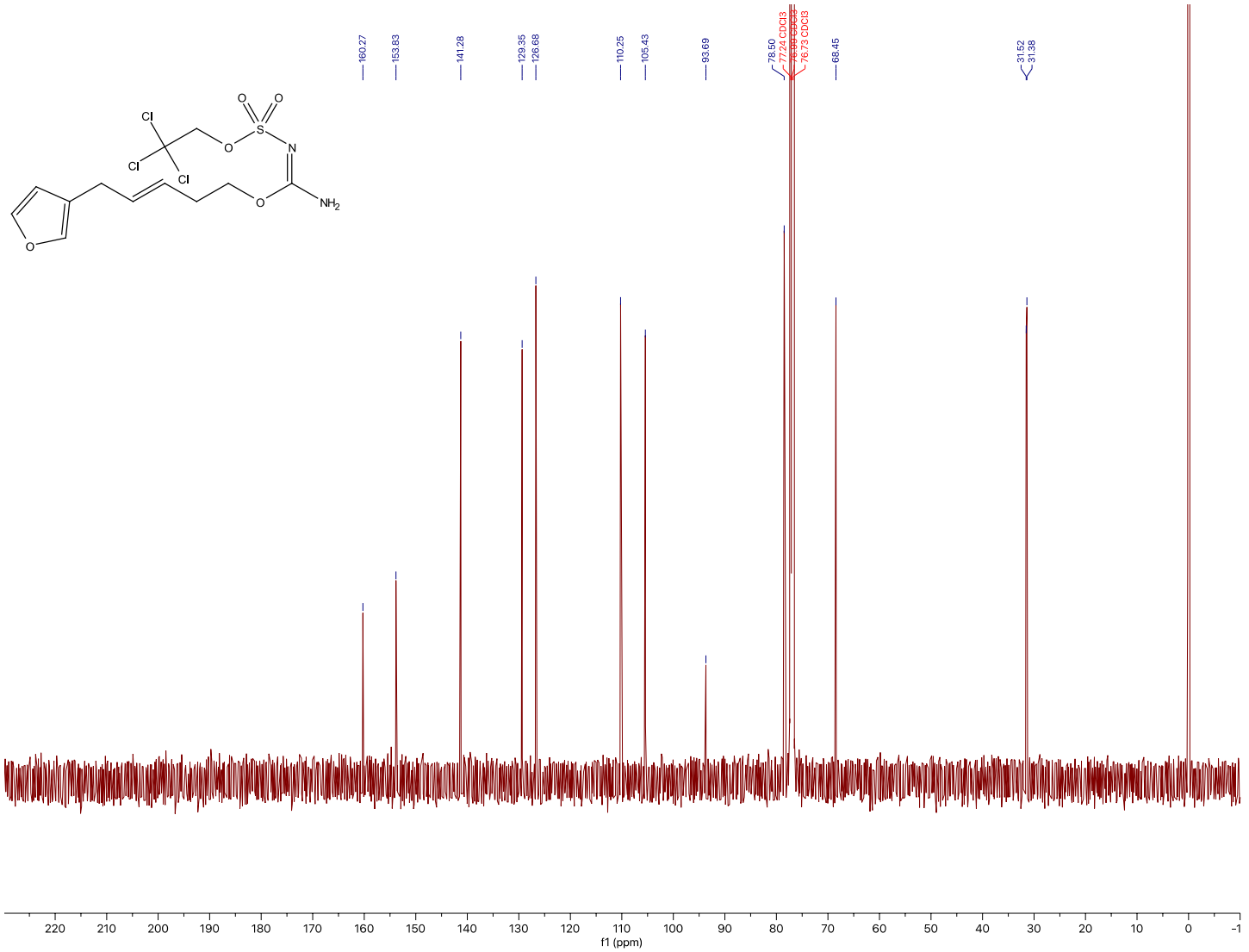
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1h**



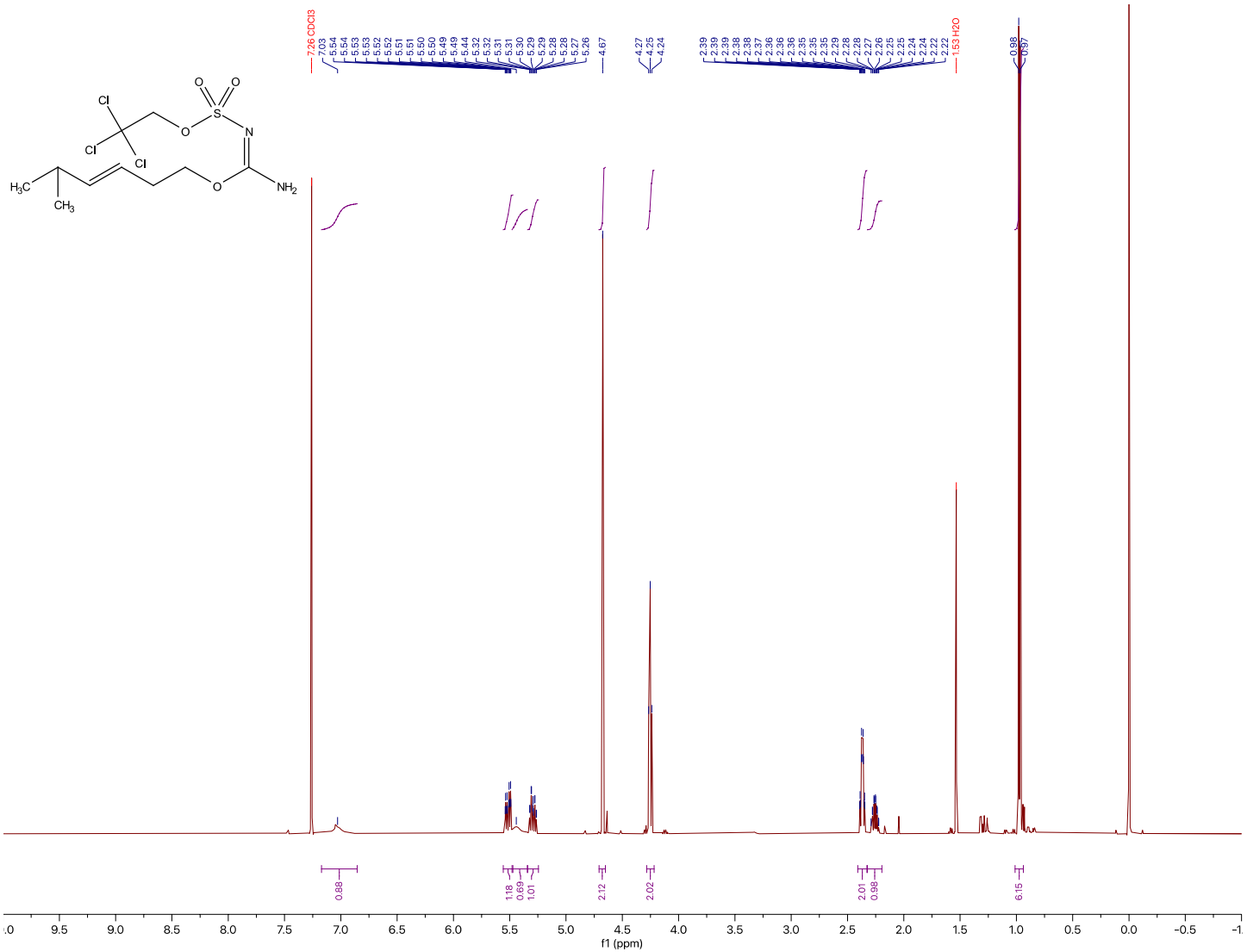
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1i**



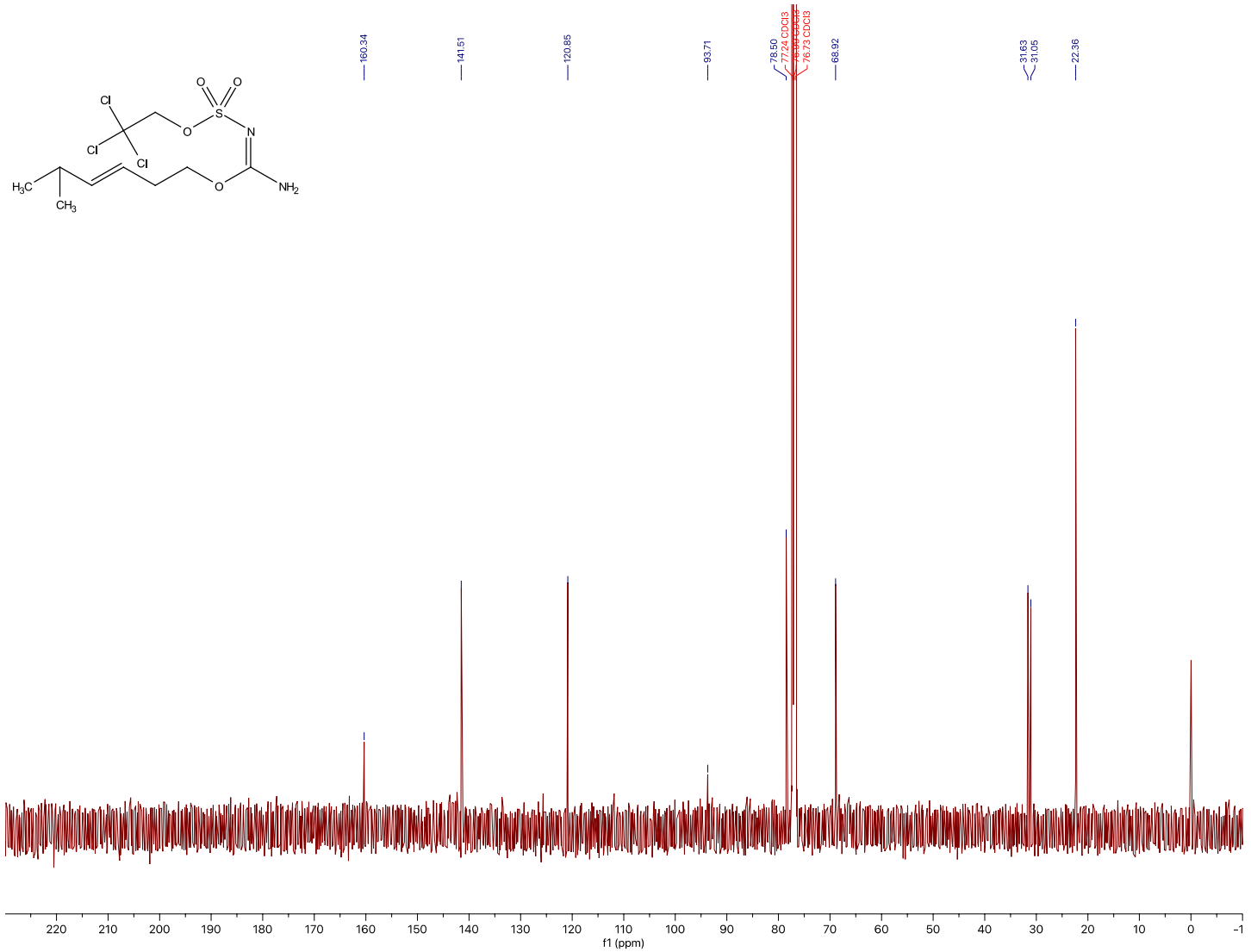
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1i**



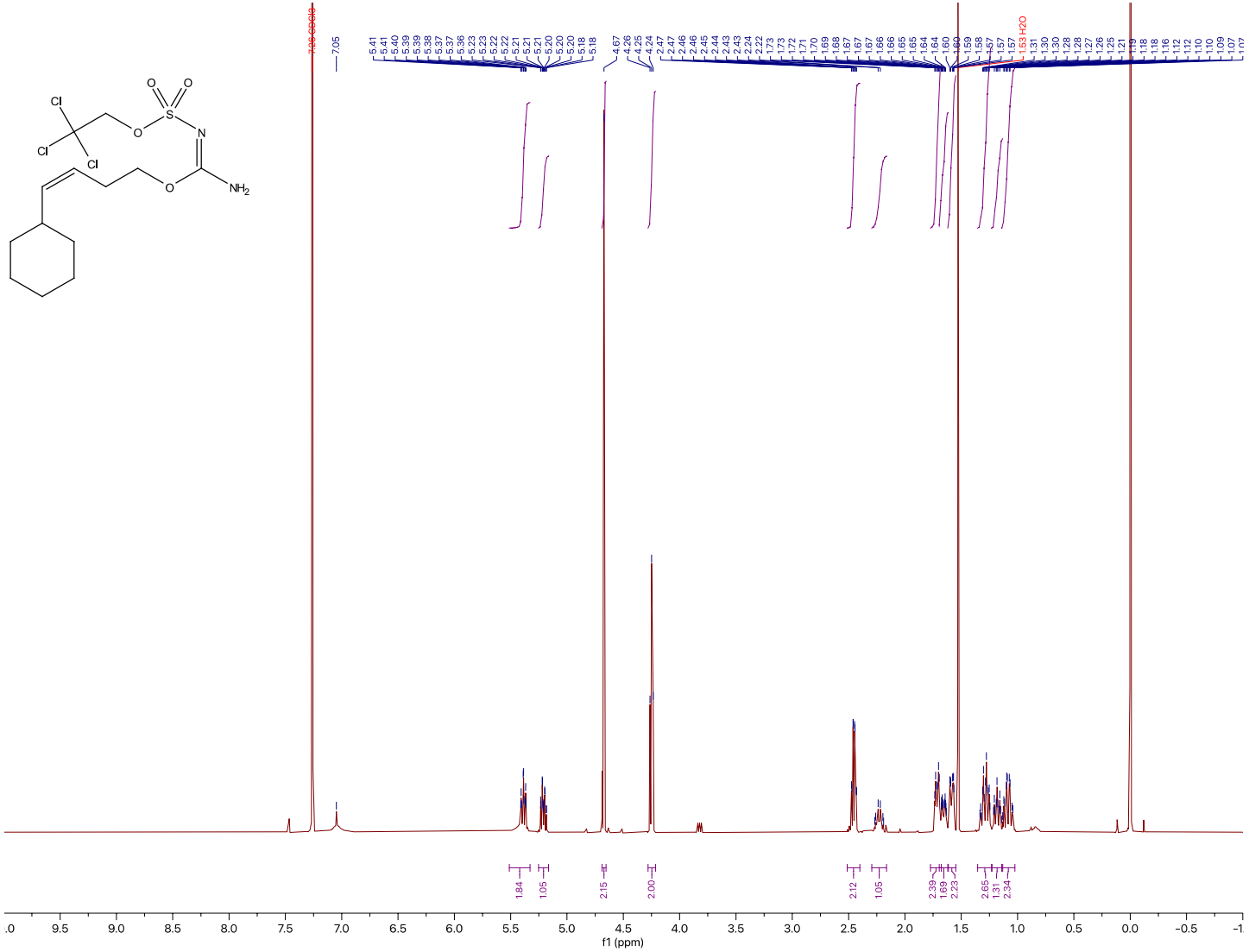
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1j**



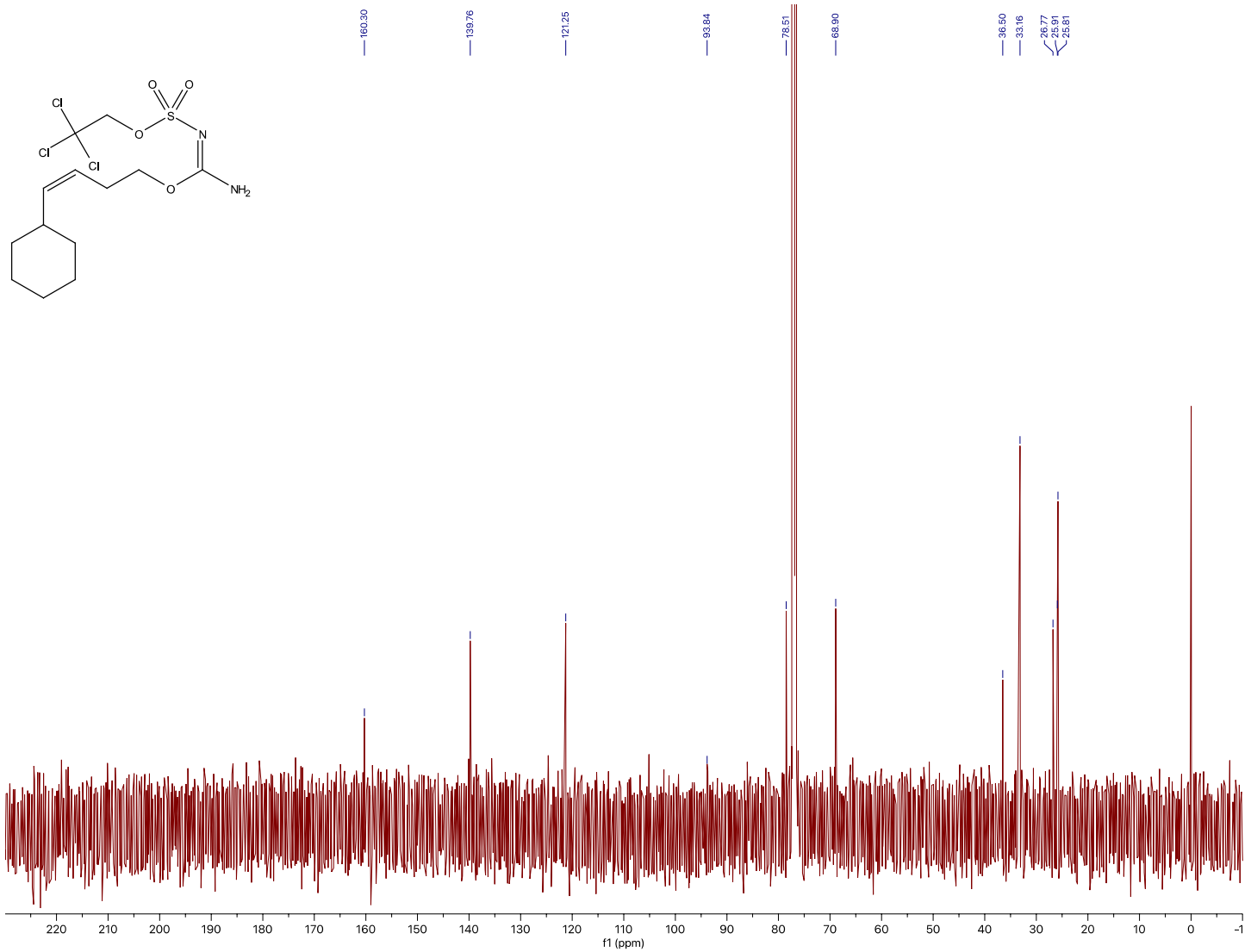
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1j**



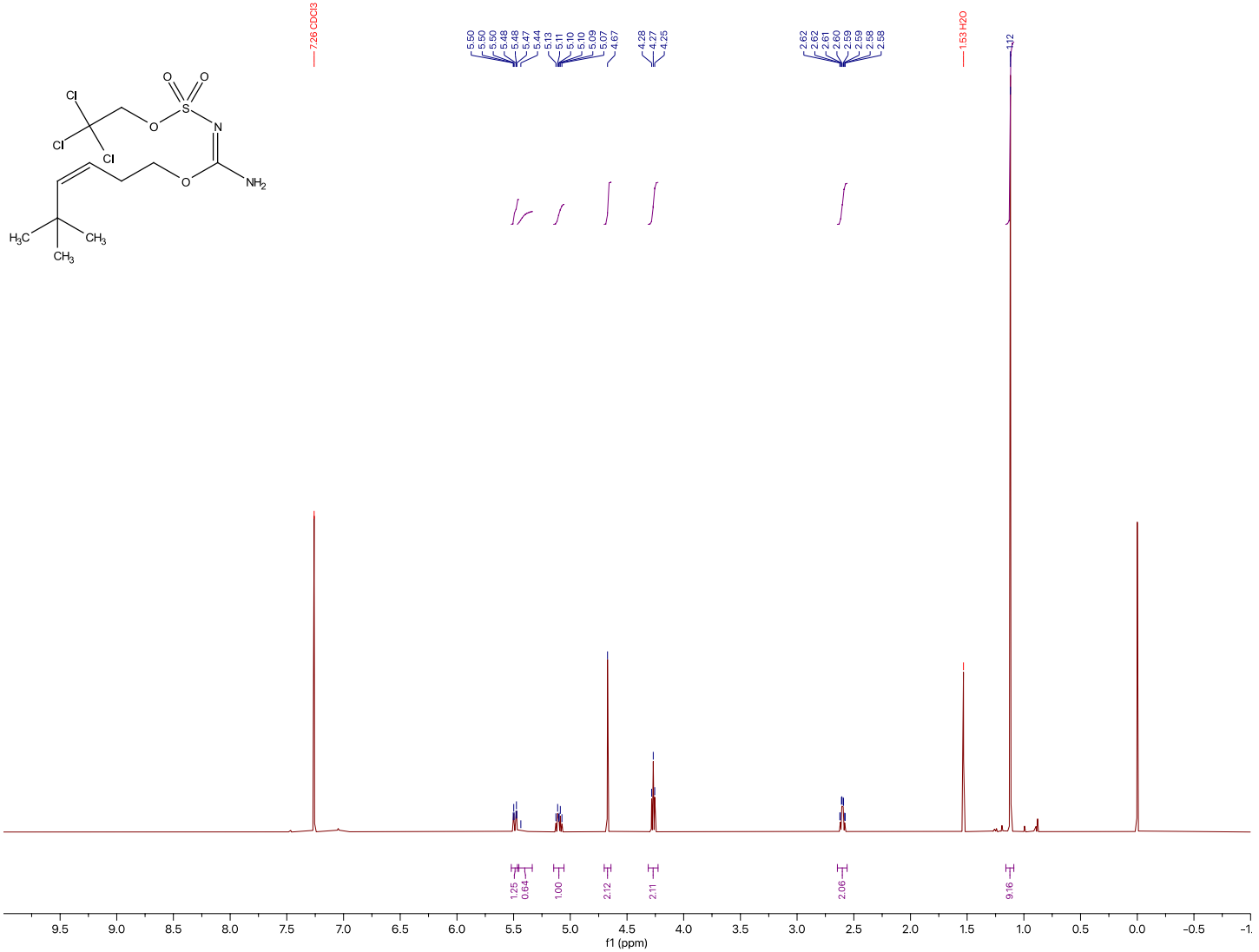
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1k**



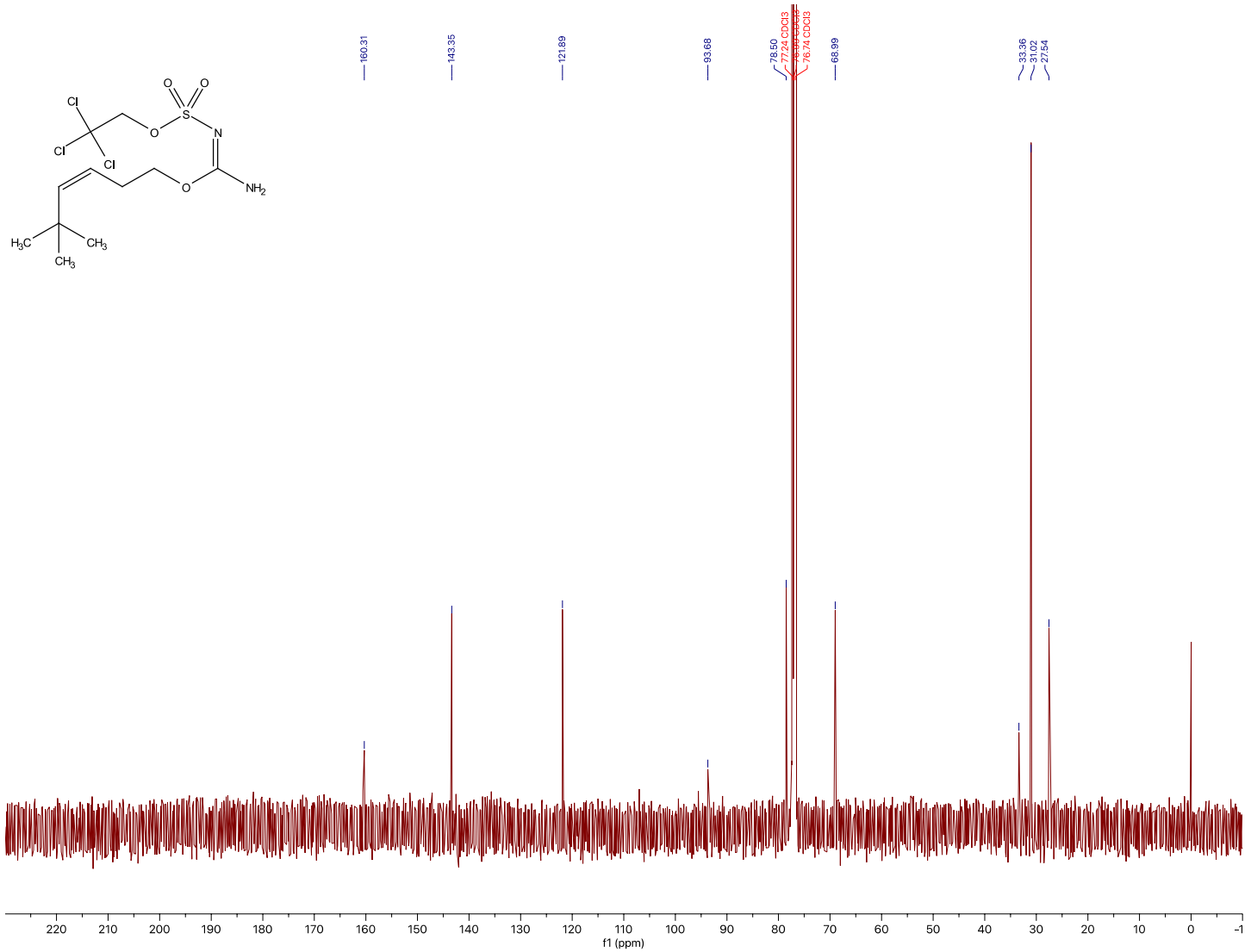
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1k**



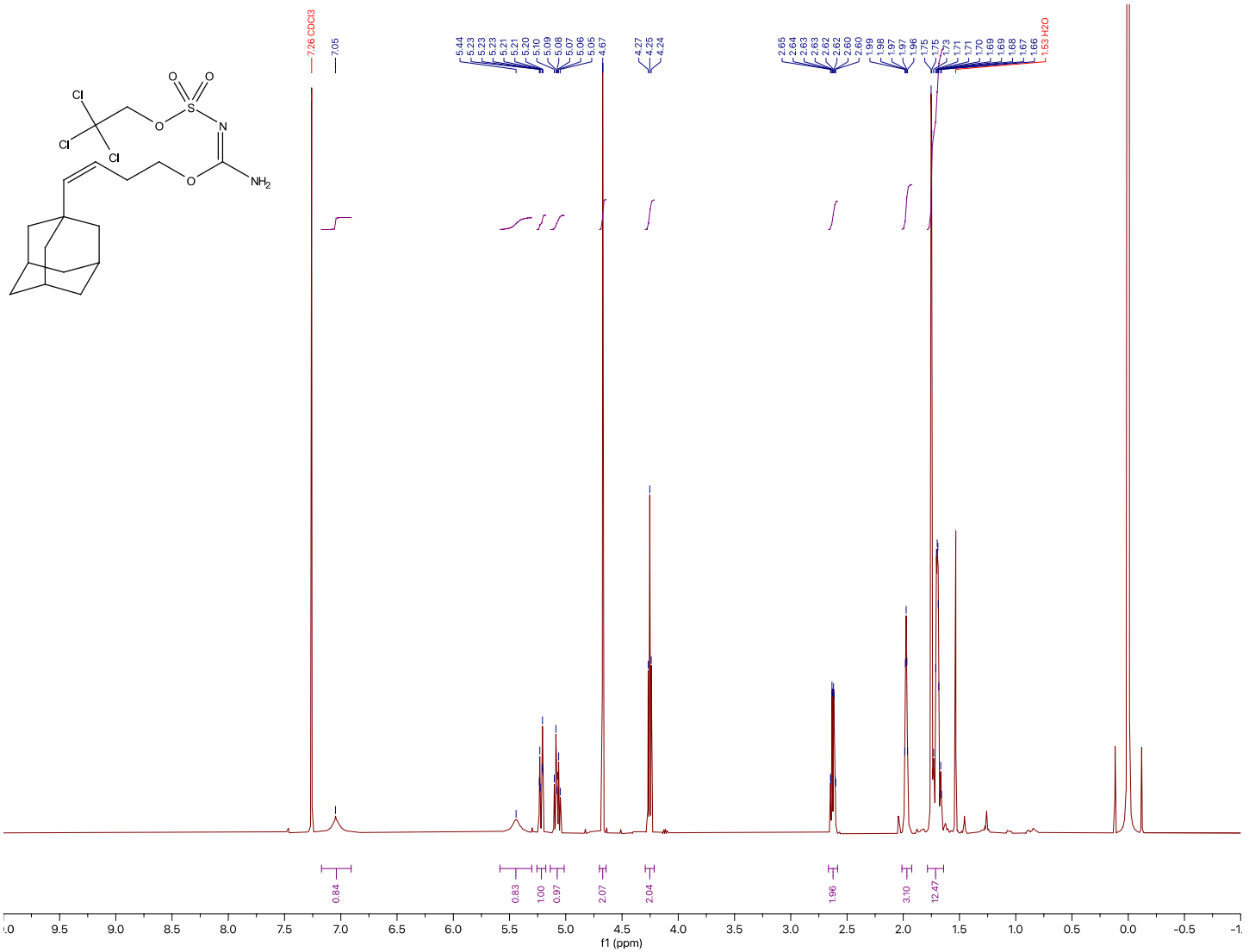
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1l**



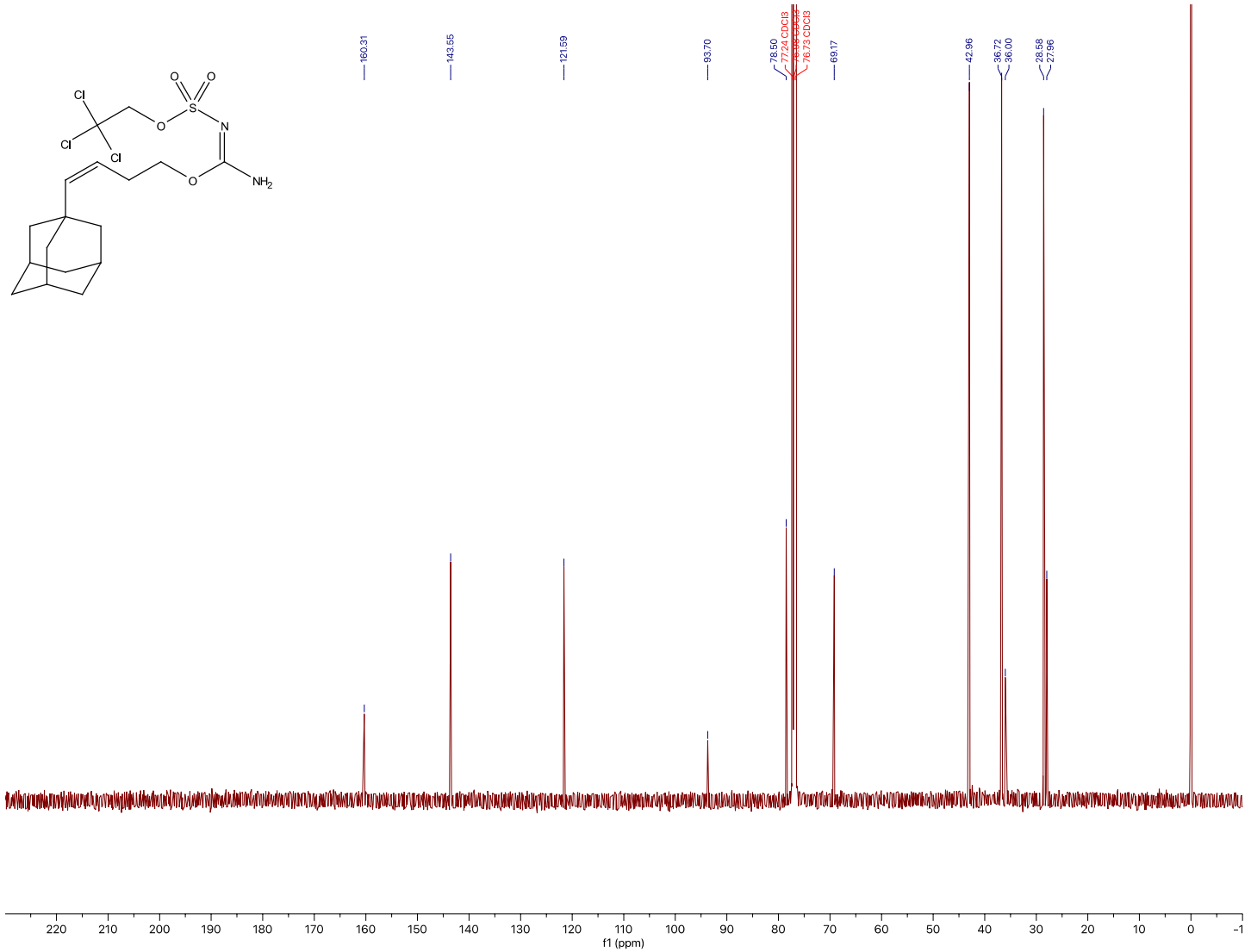
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1l**



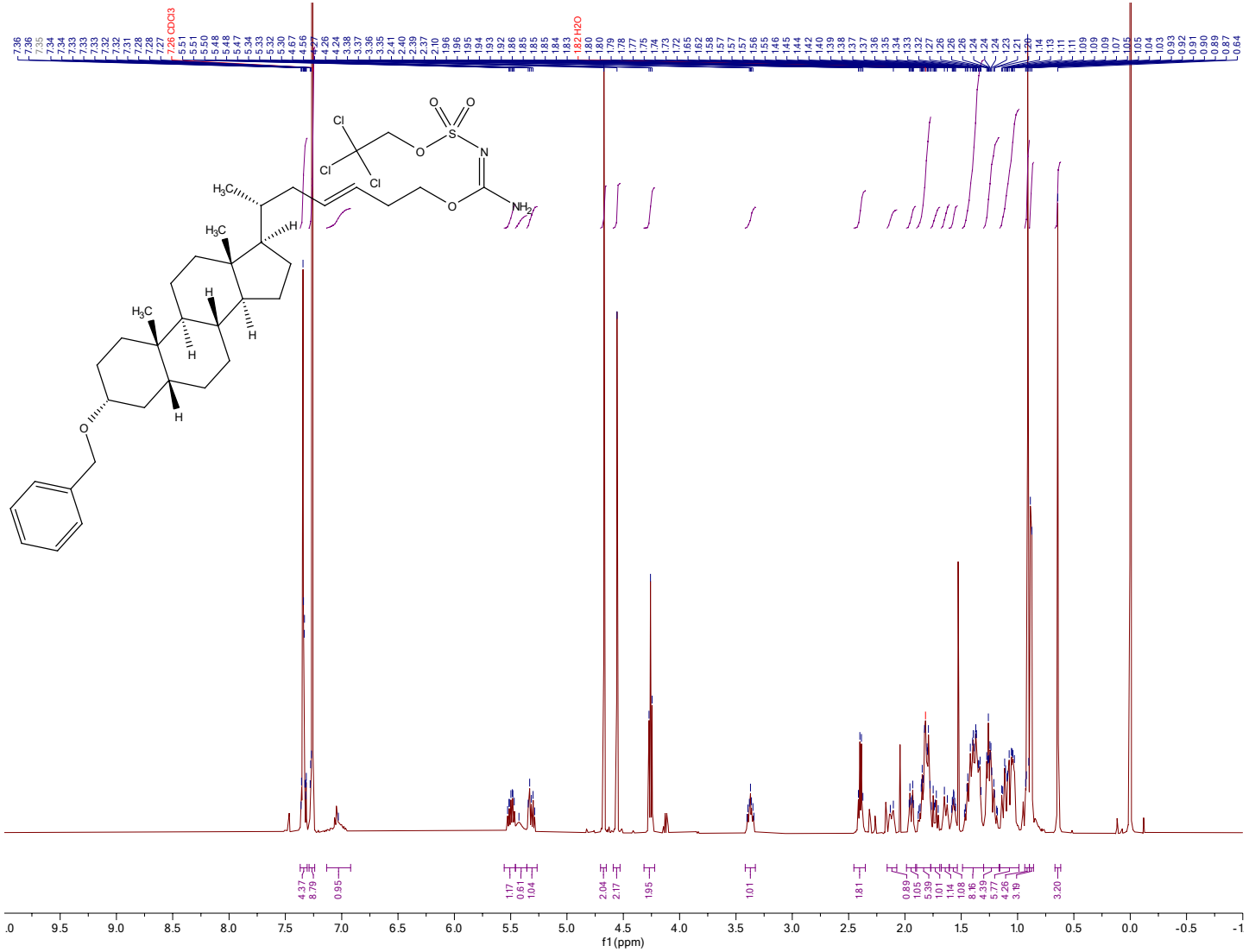
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1m**



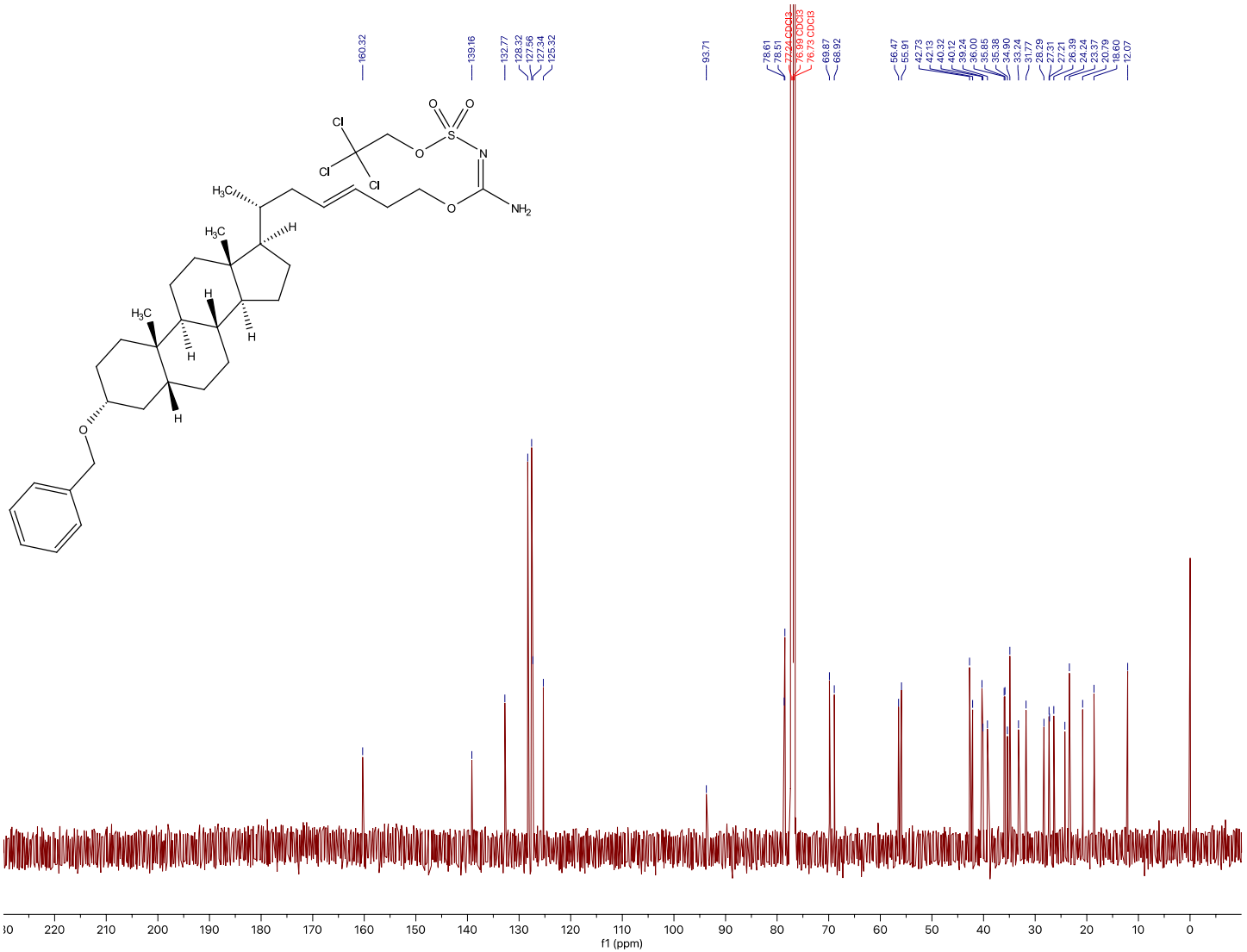
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1m**



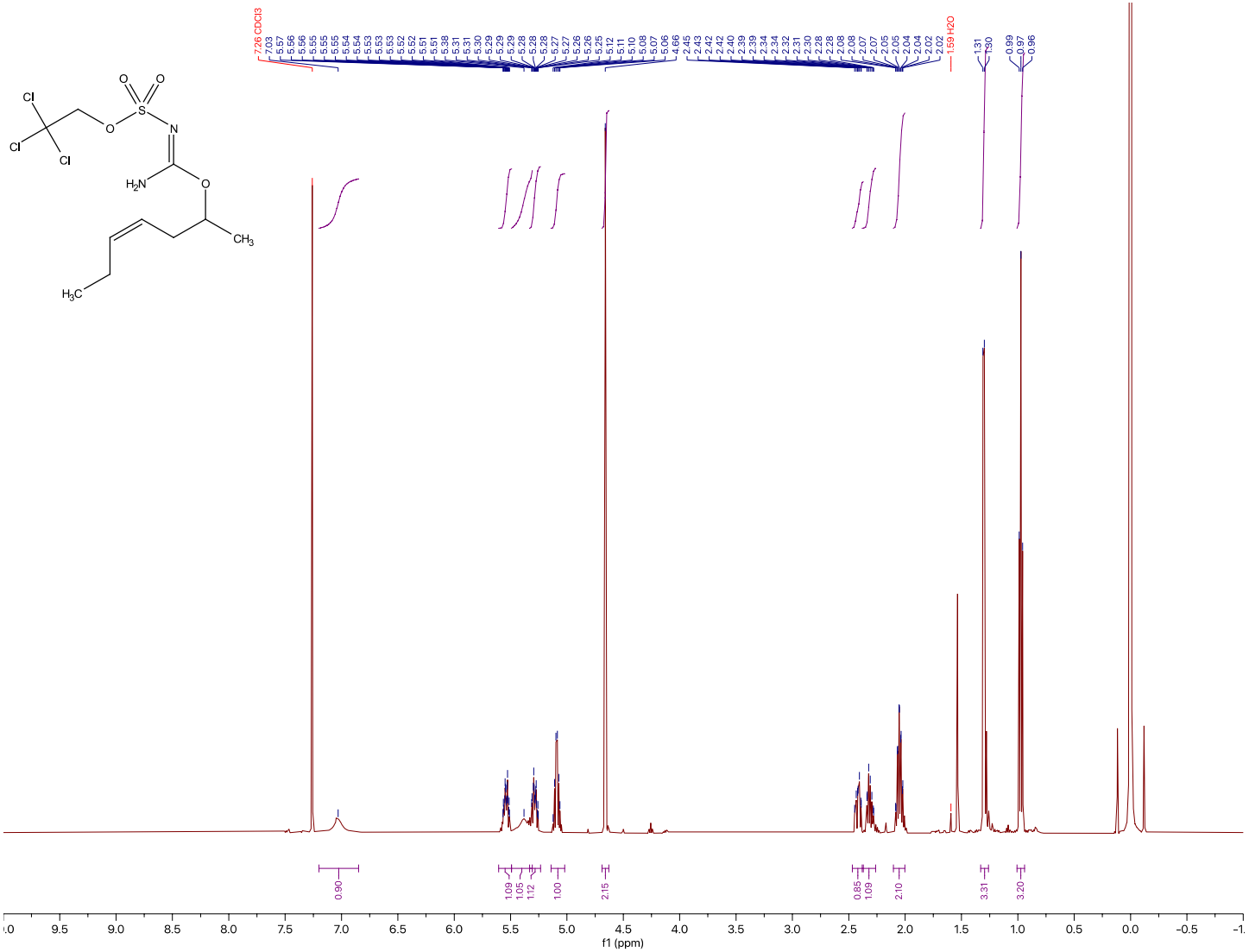
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1n**



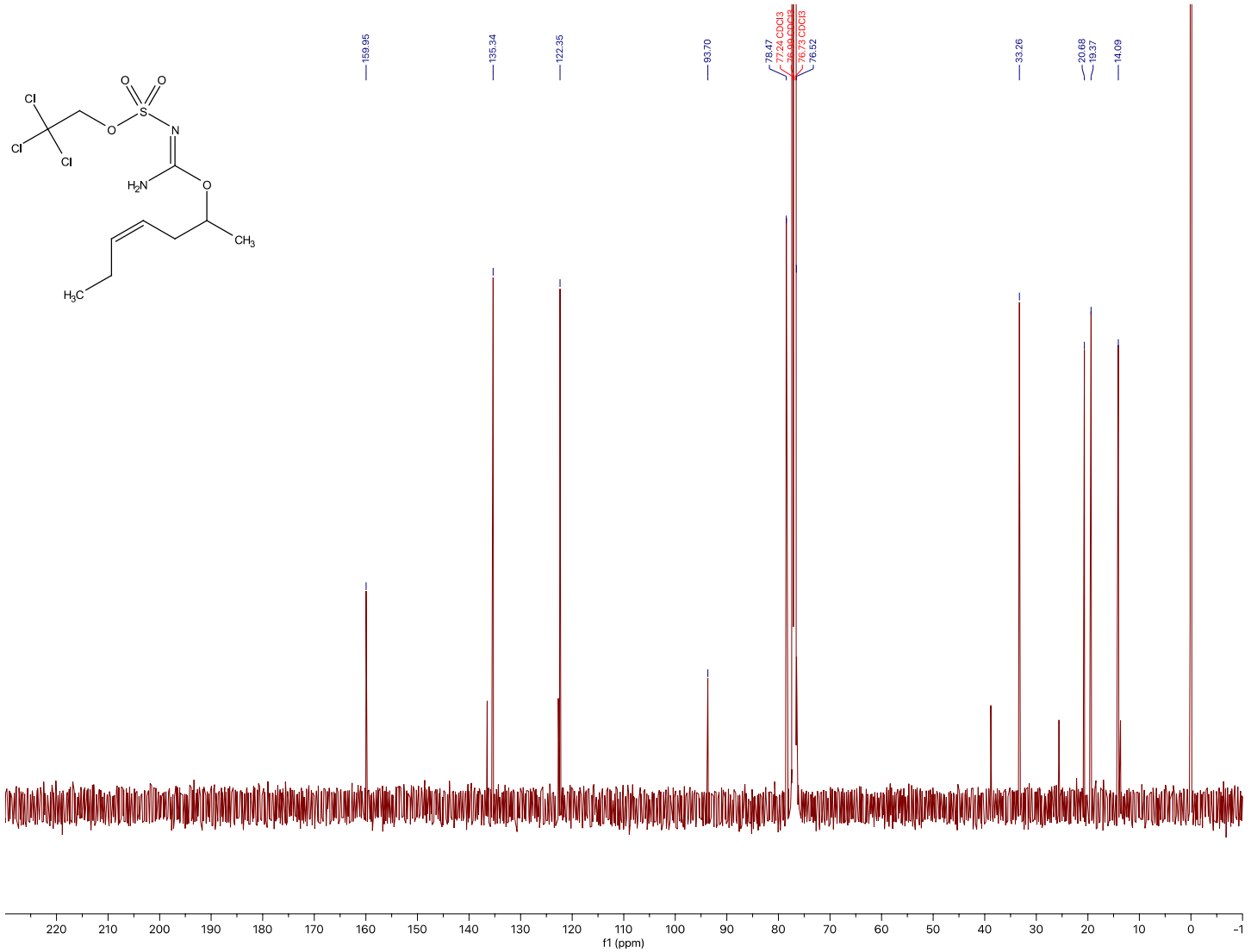
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1n**



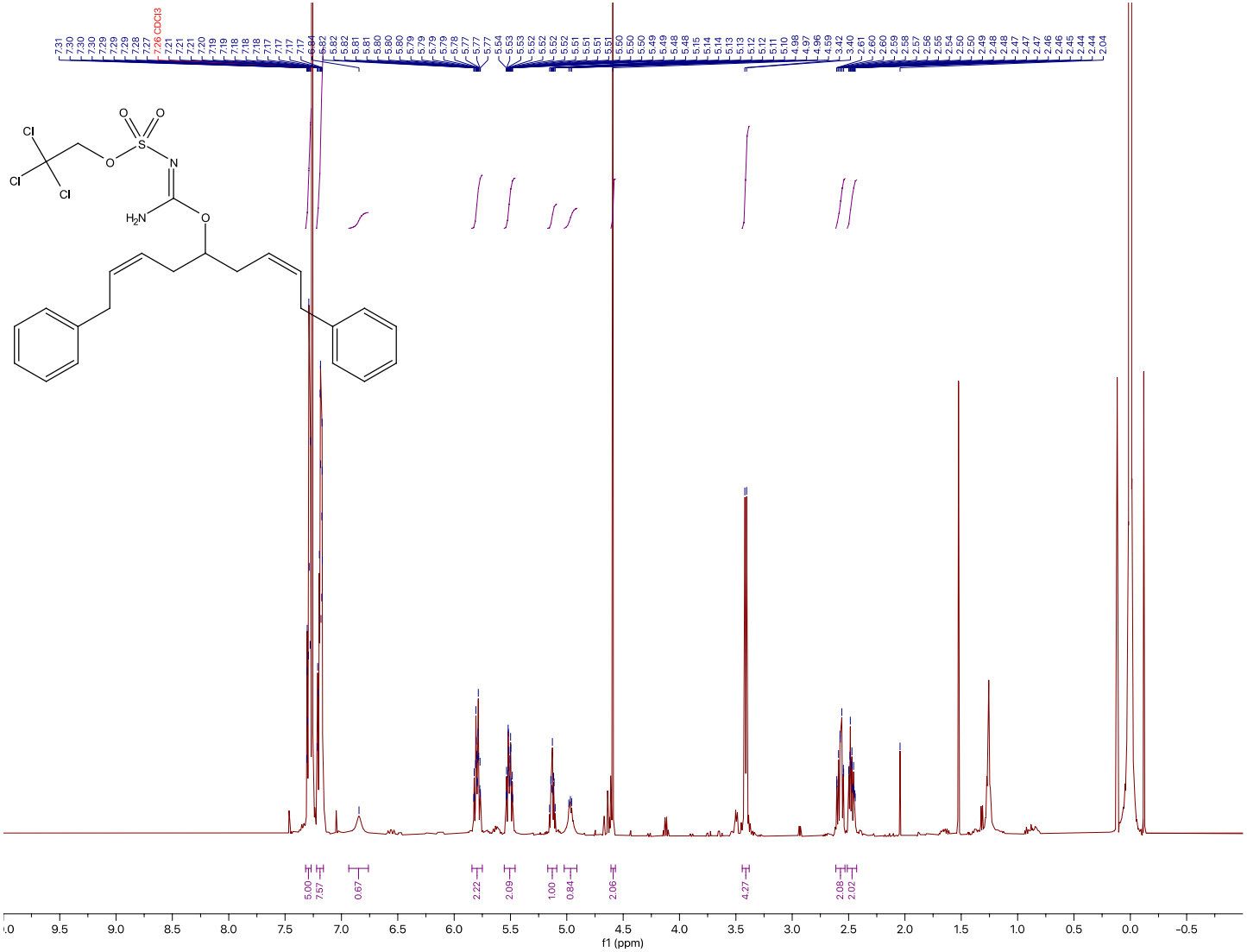
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1o**



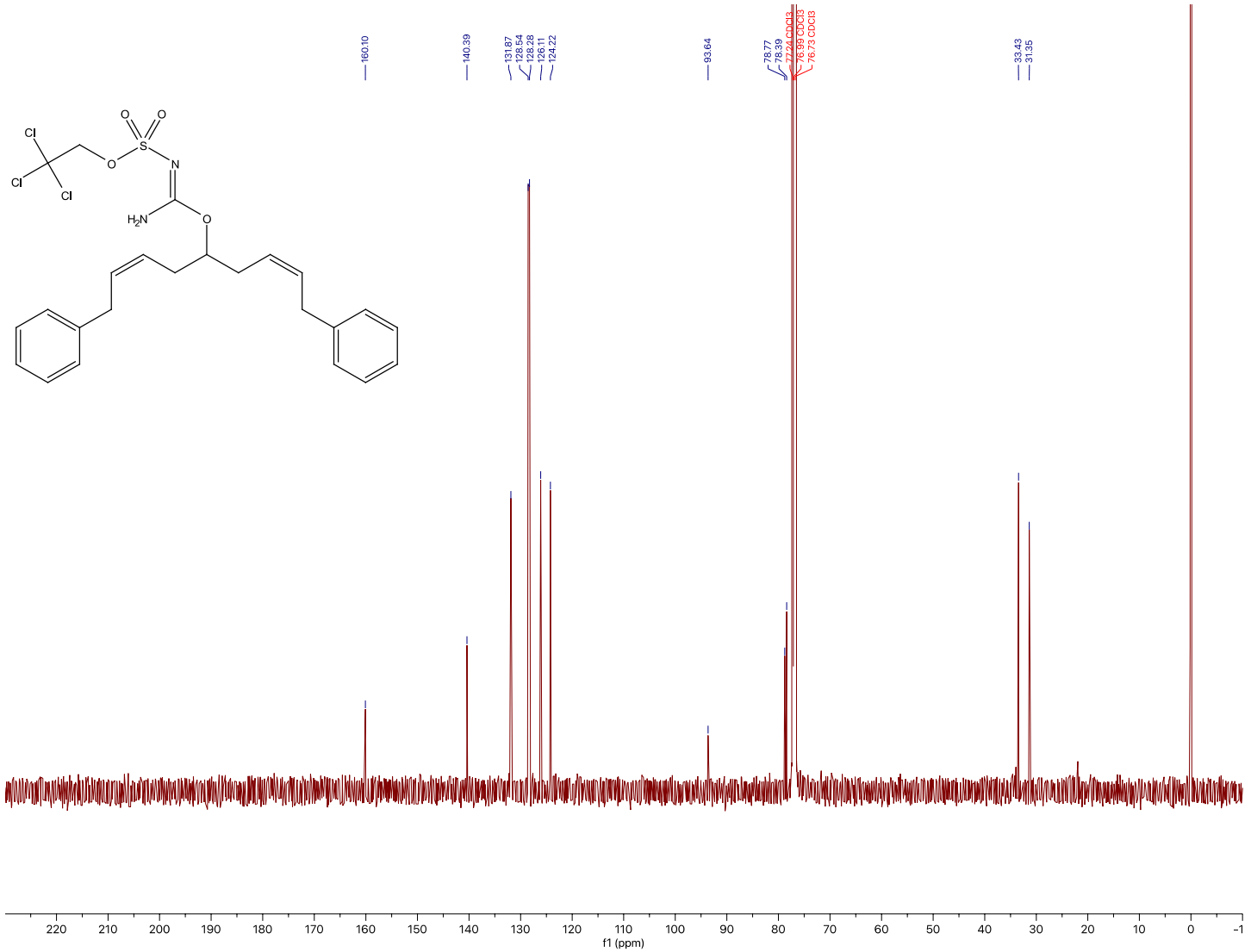
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1o**



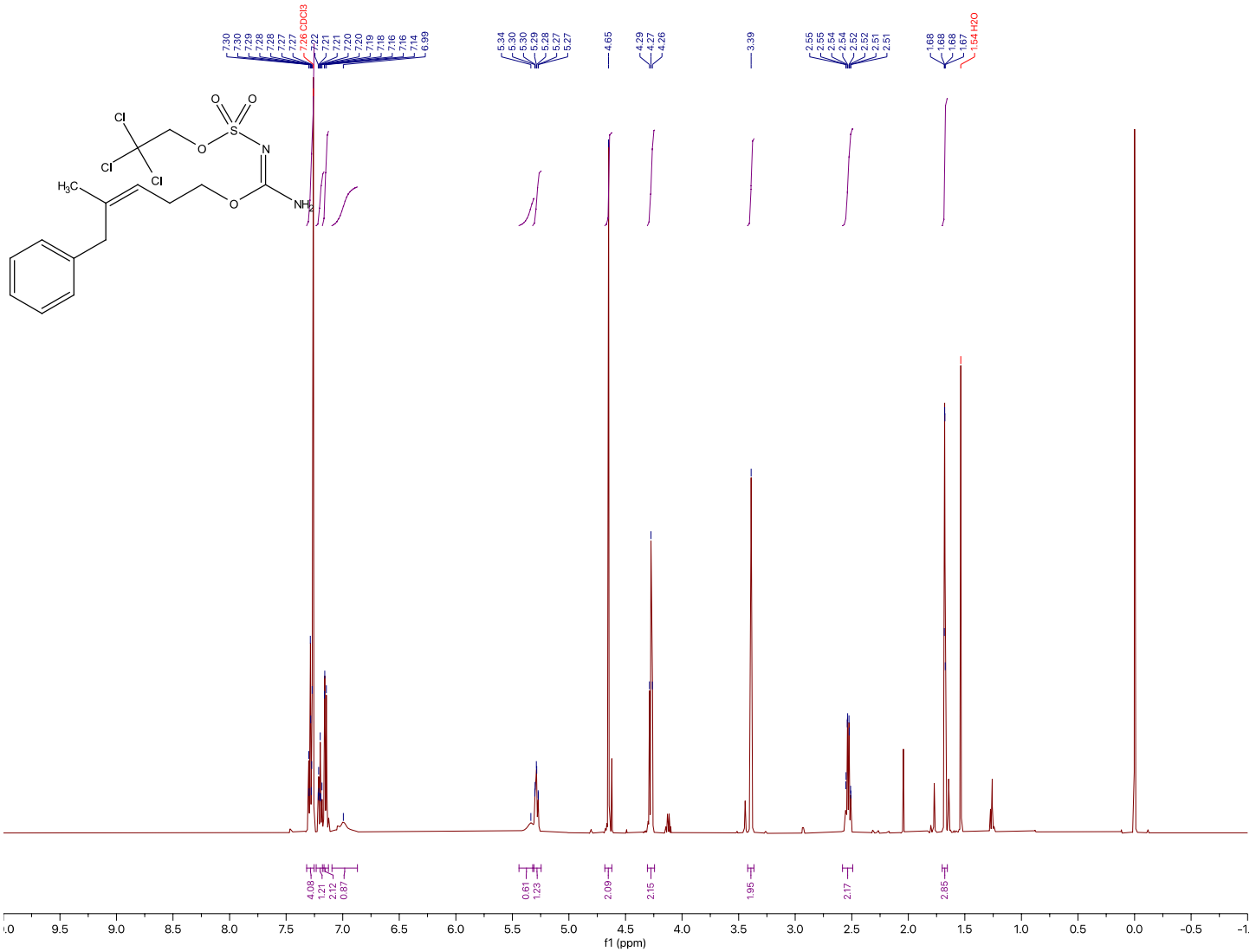
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1p**



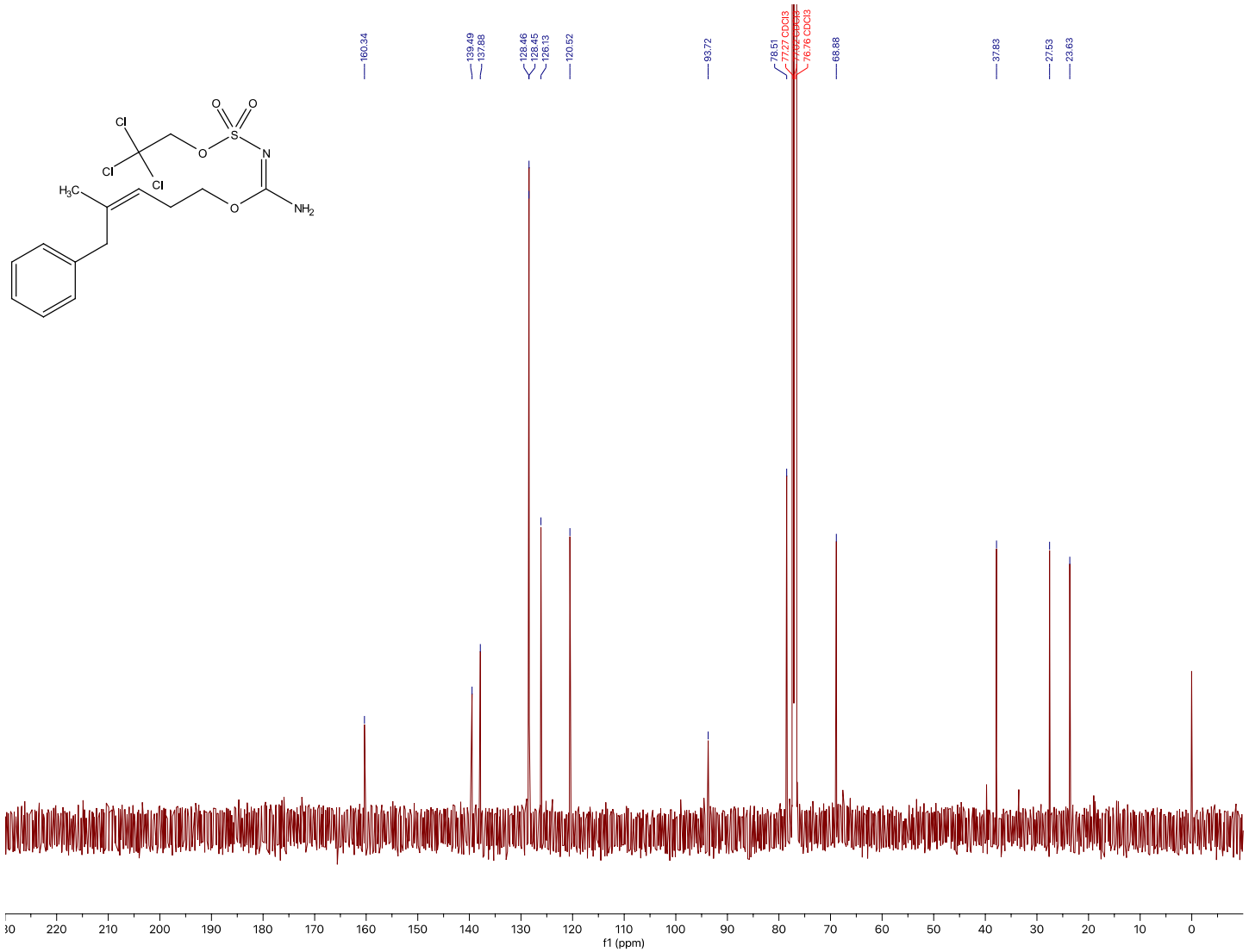
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1p**



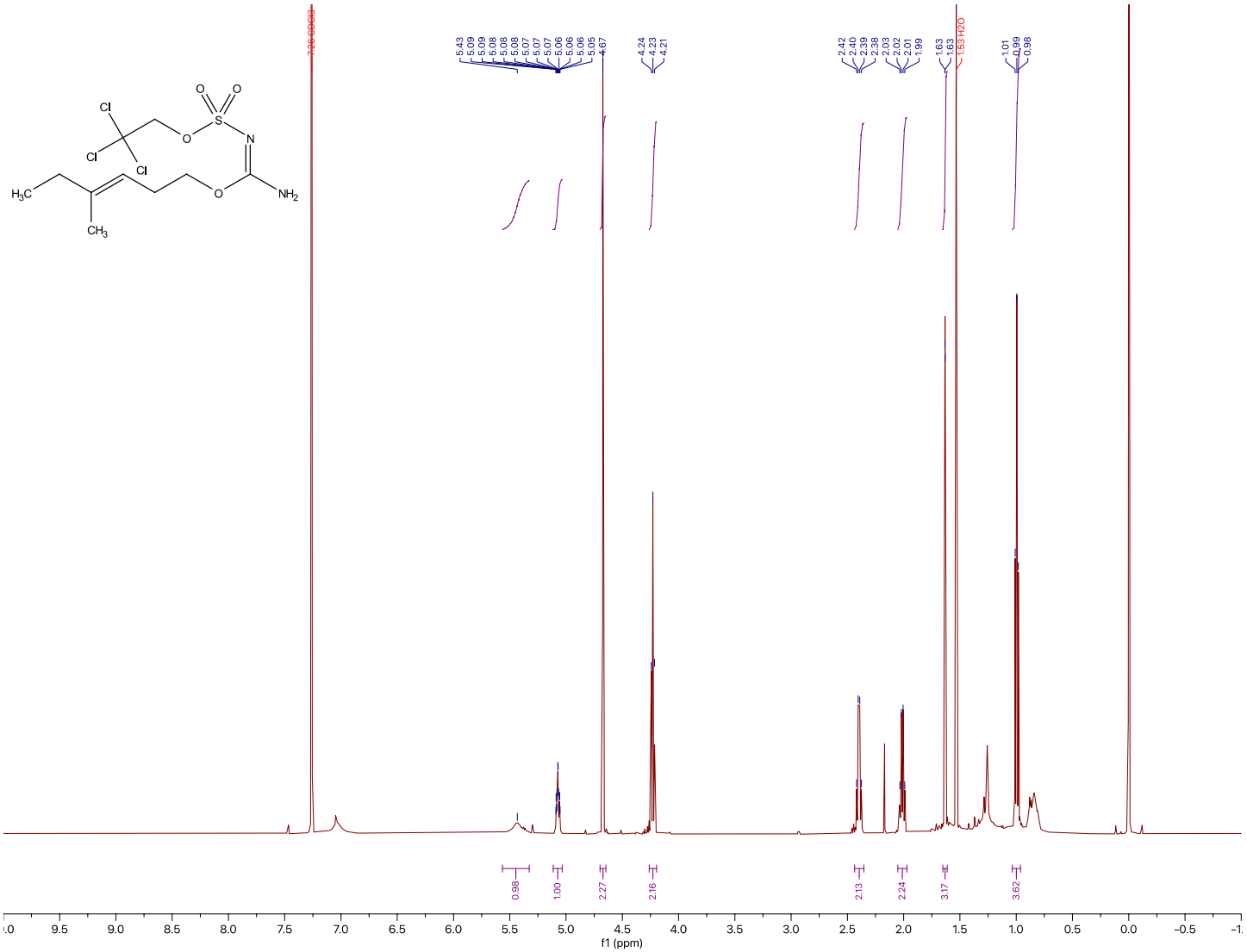
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1q**



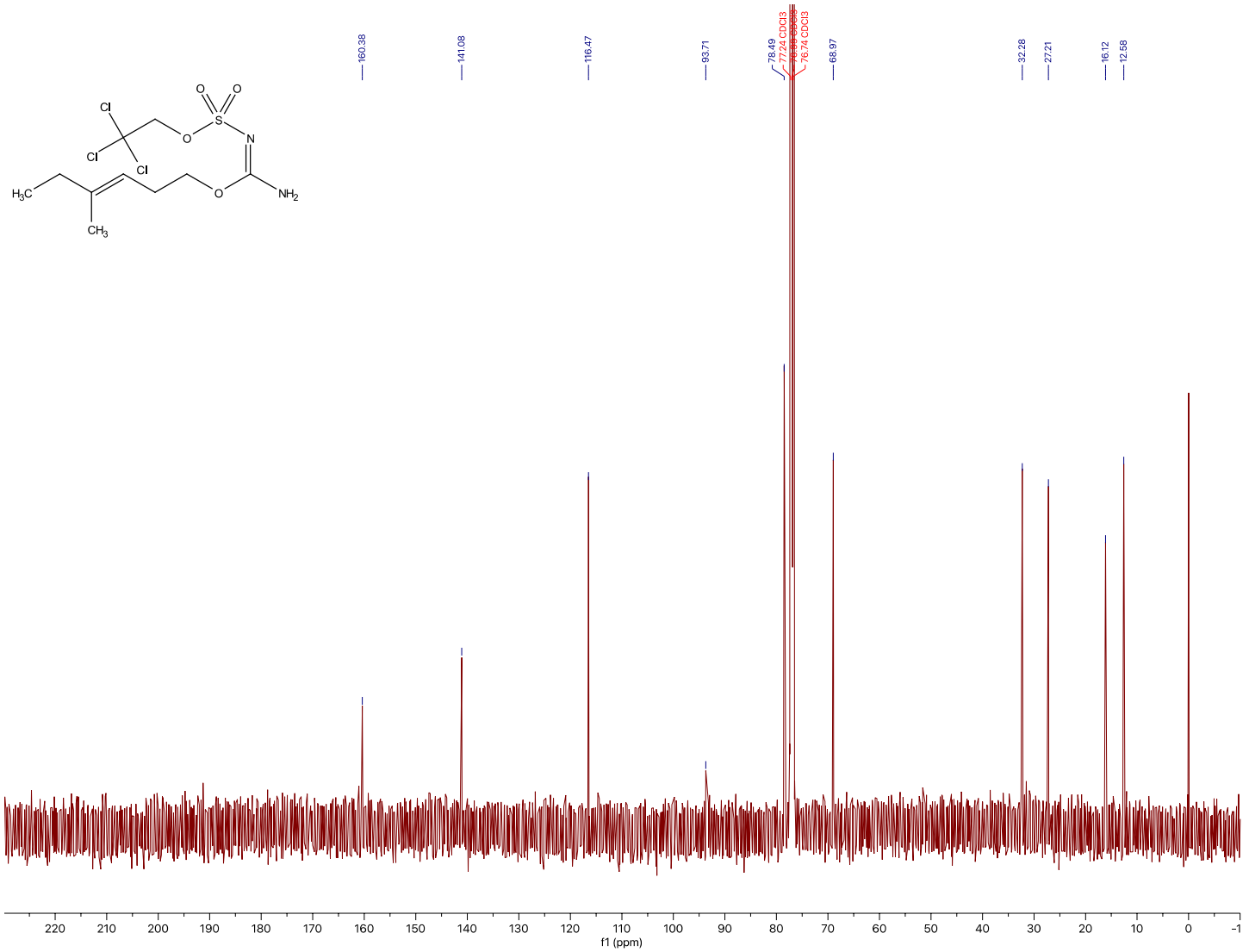
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1q**



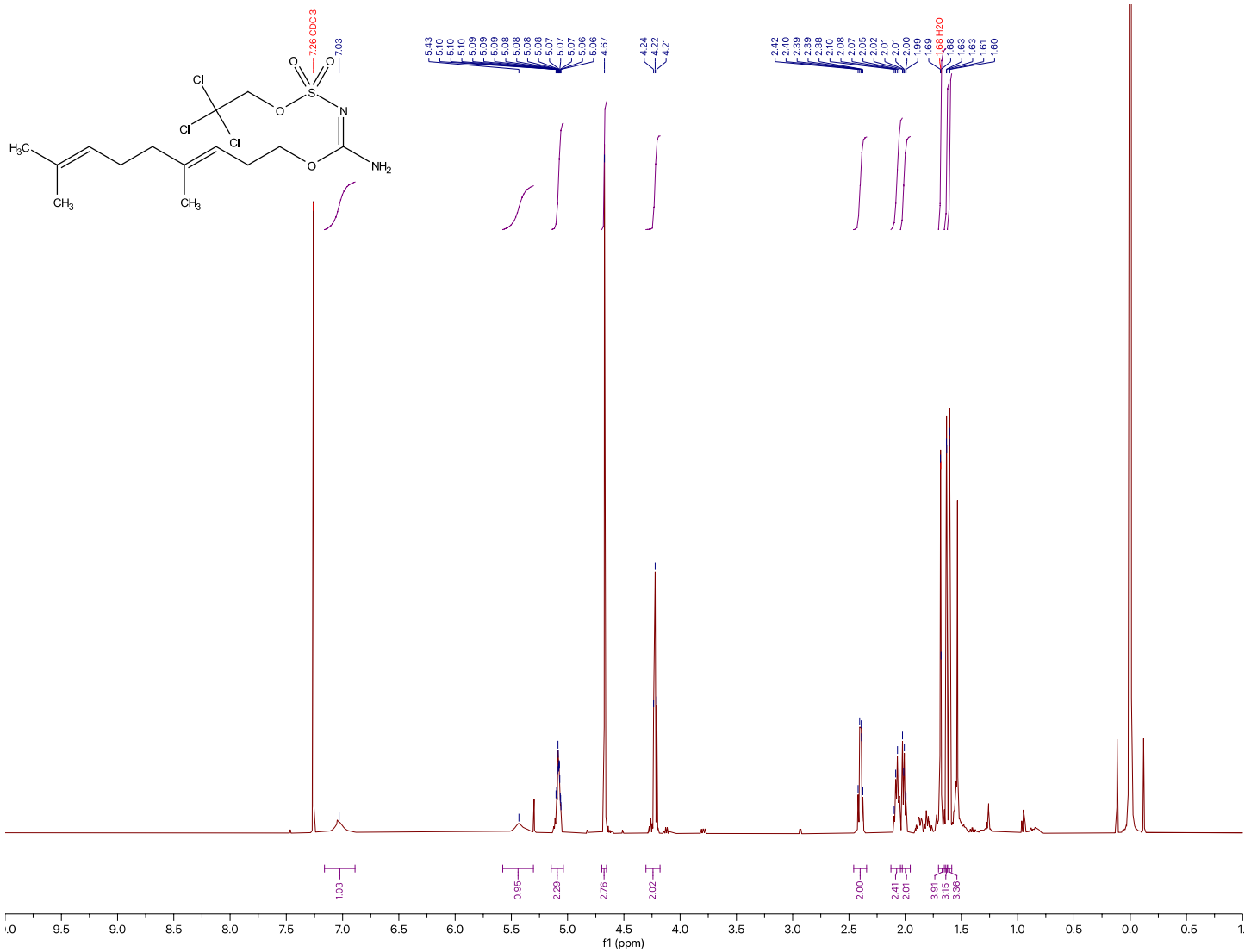
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1r**



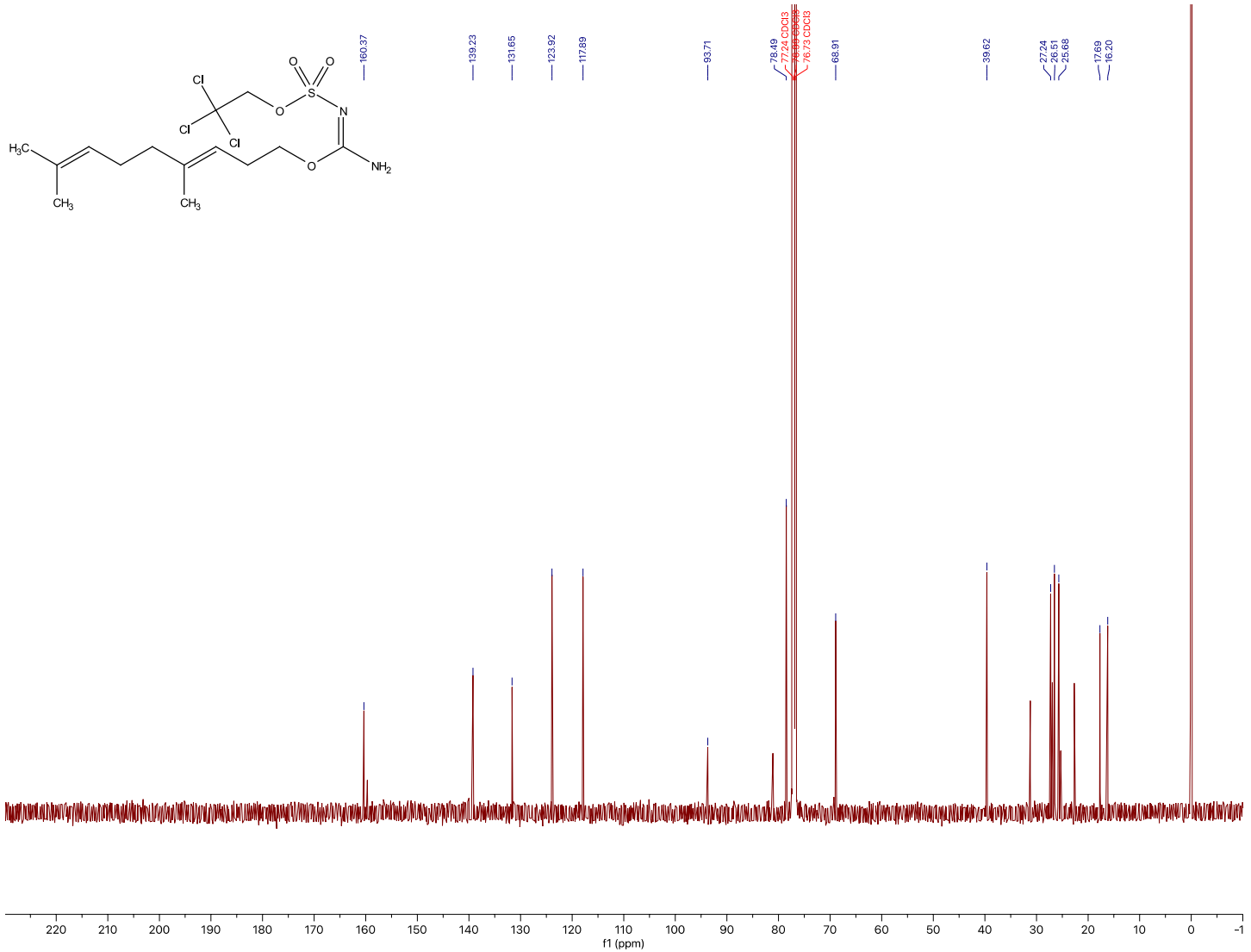
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1r**



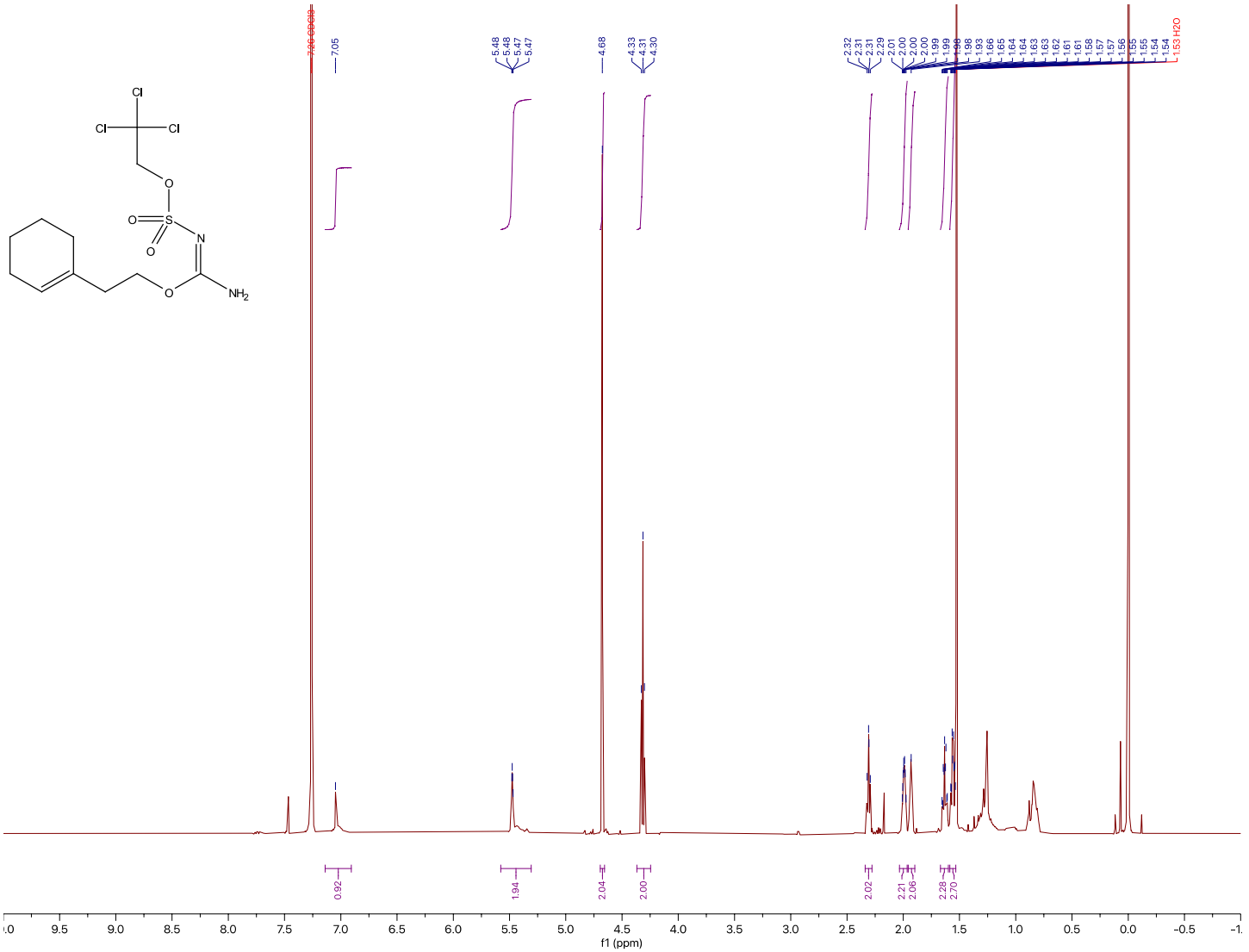
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1s**



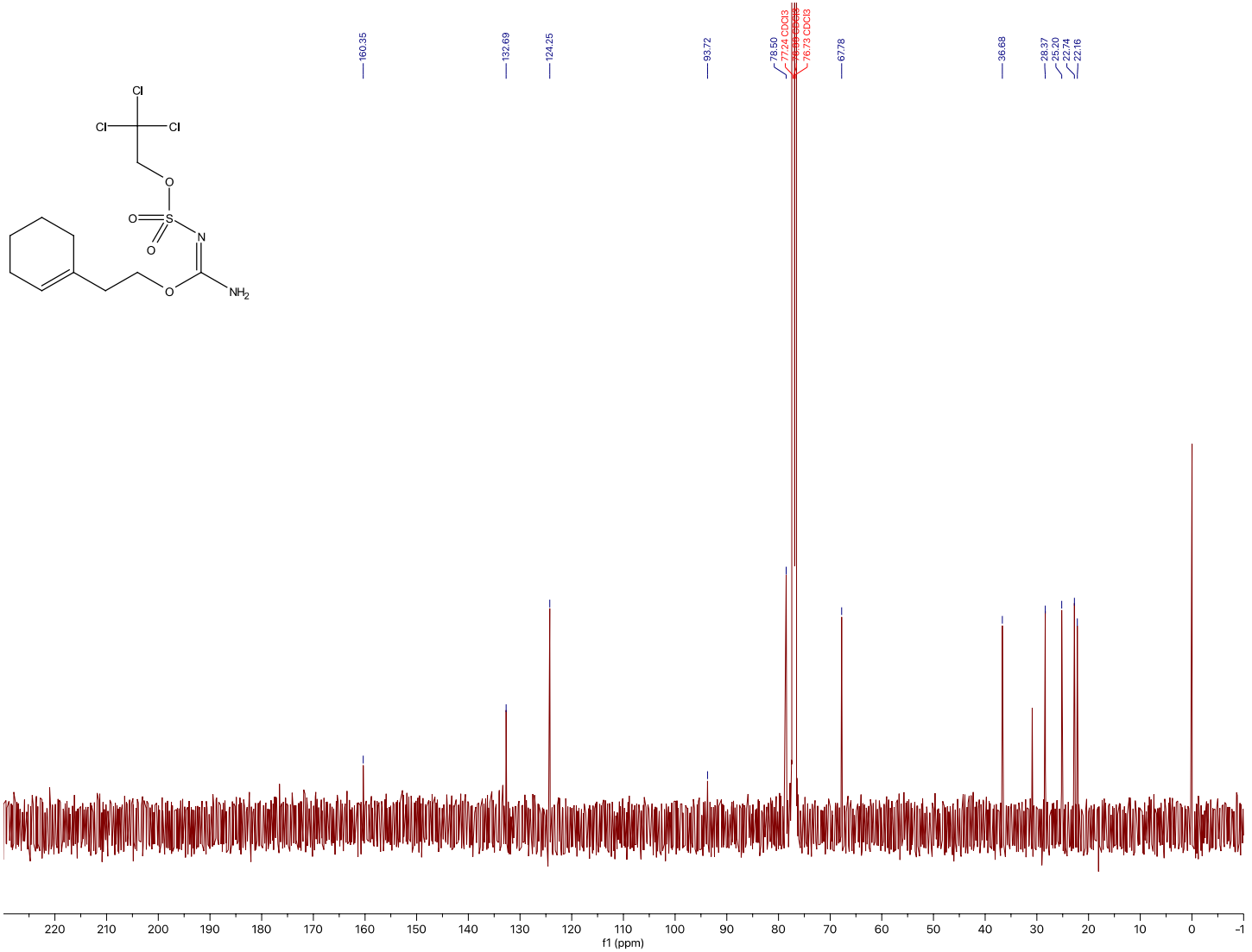
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1s**



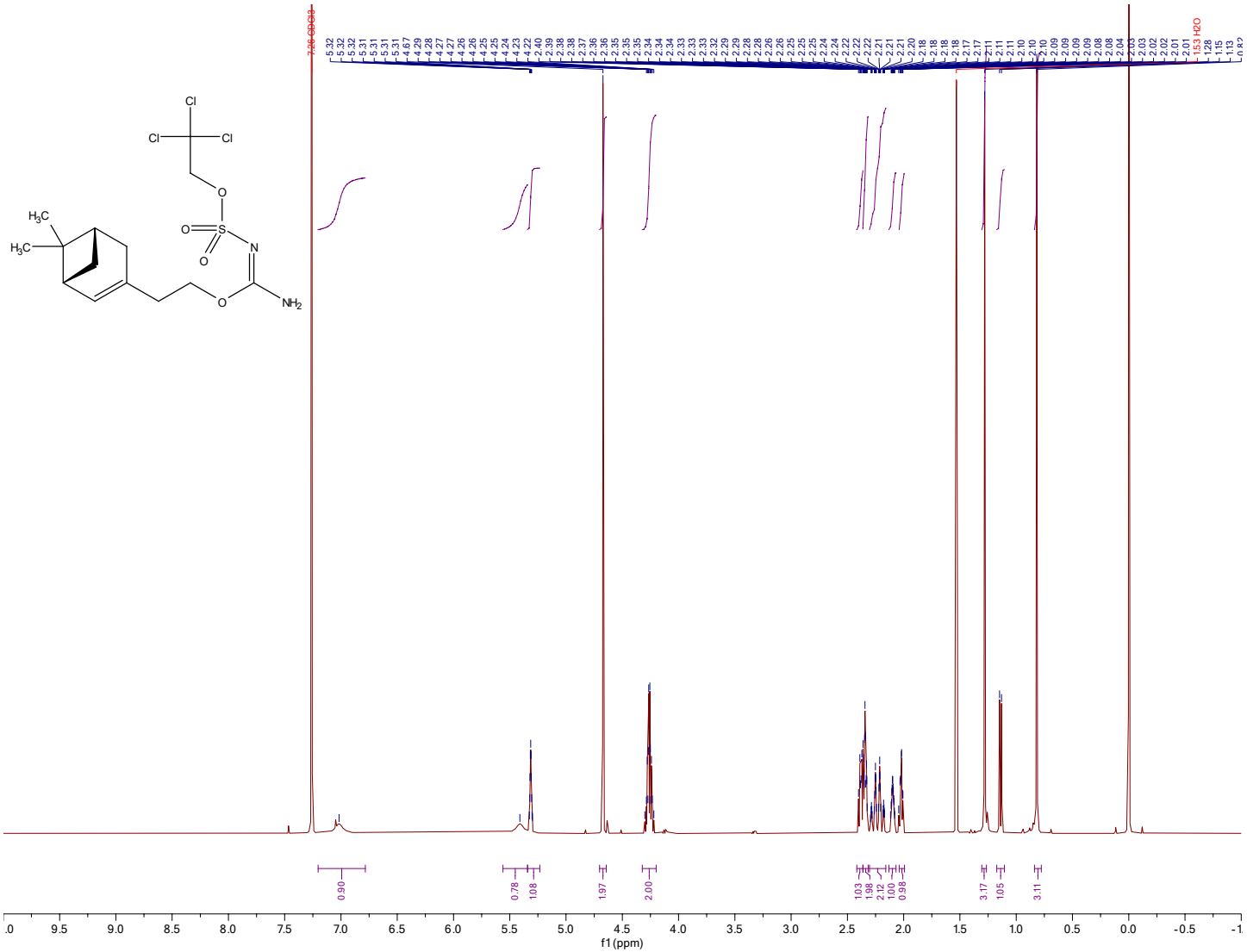
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1t**



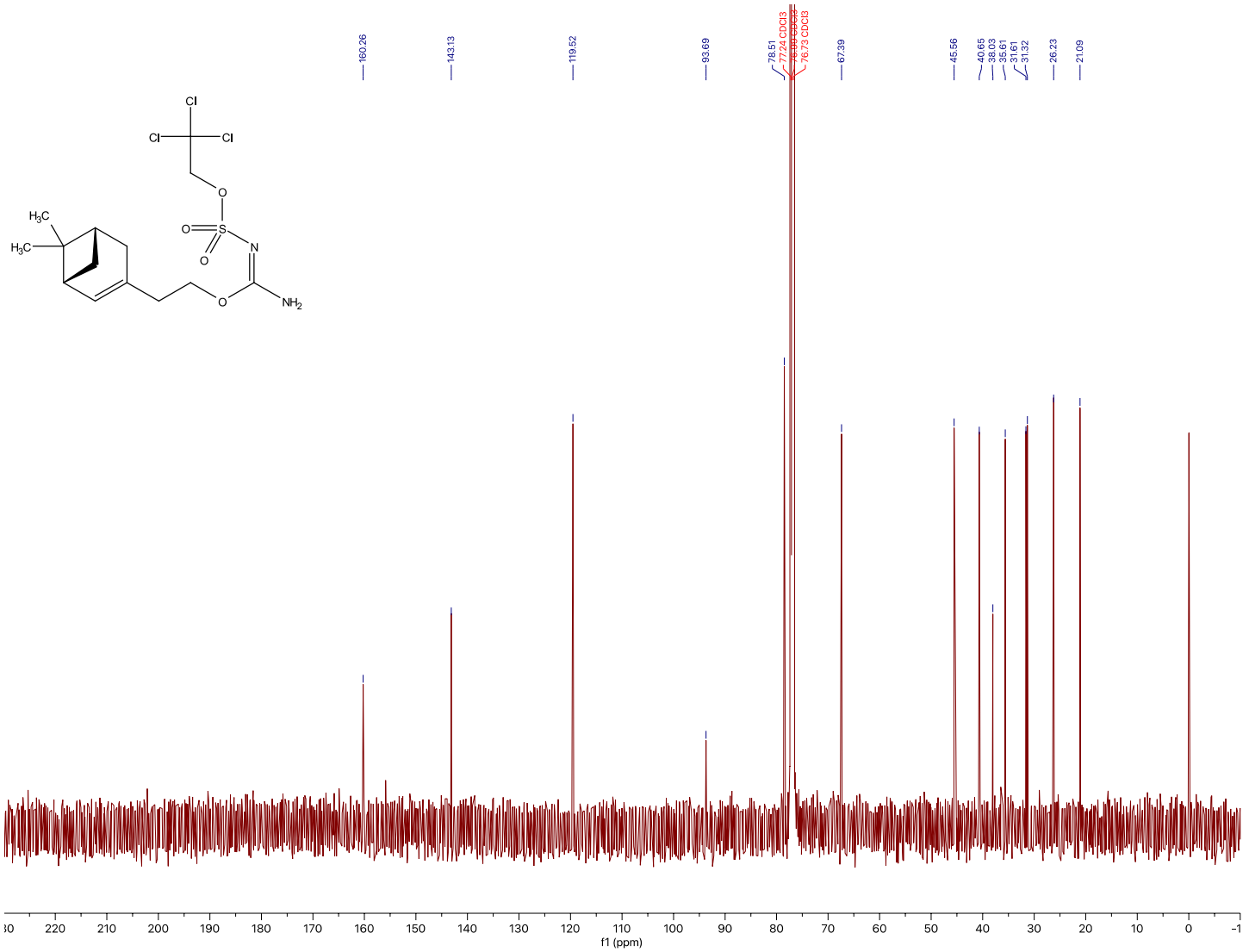
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1t**



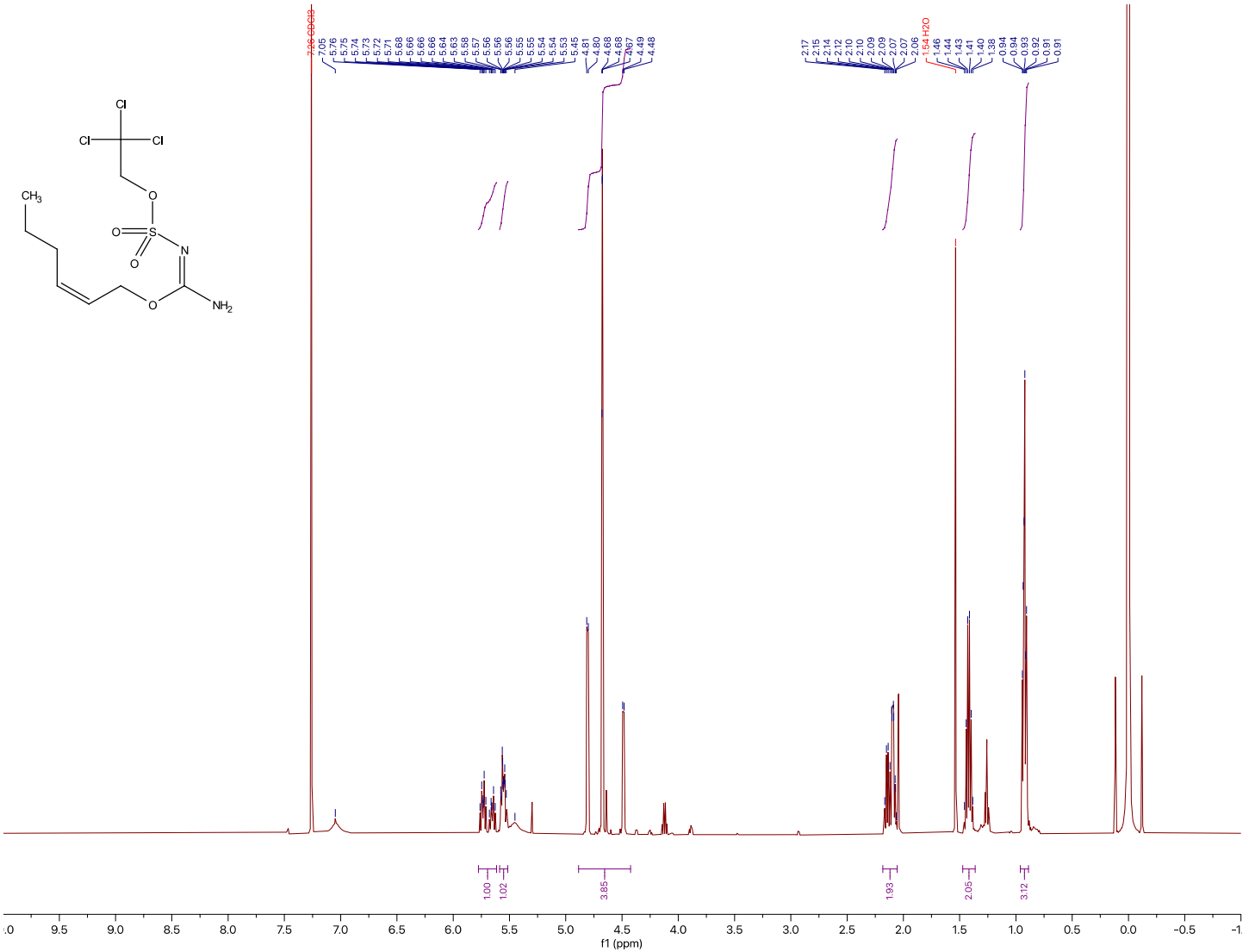
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1u**



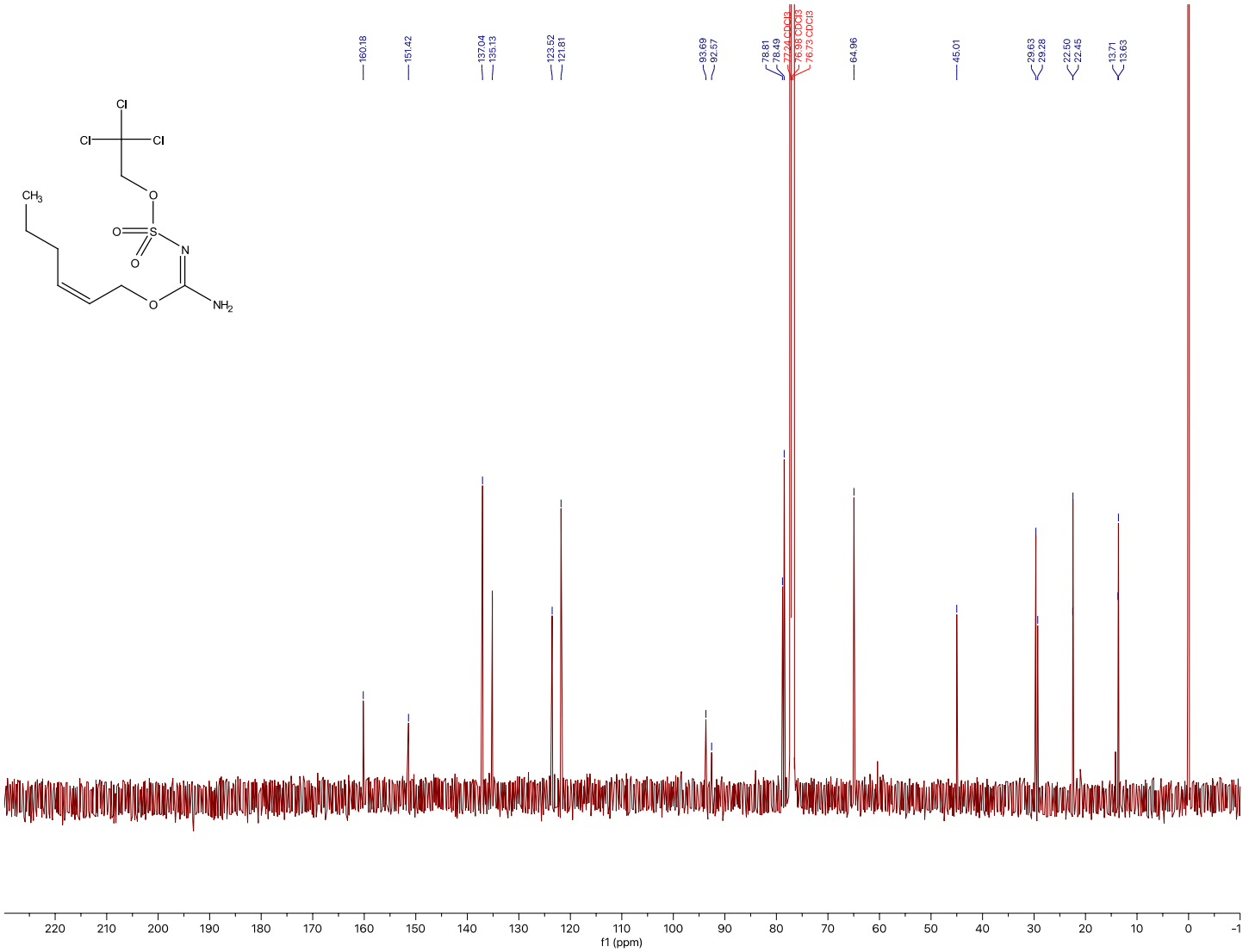
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1u**



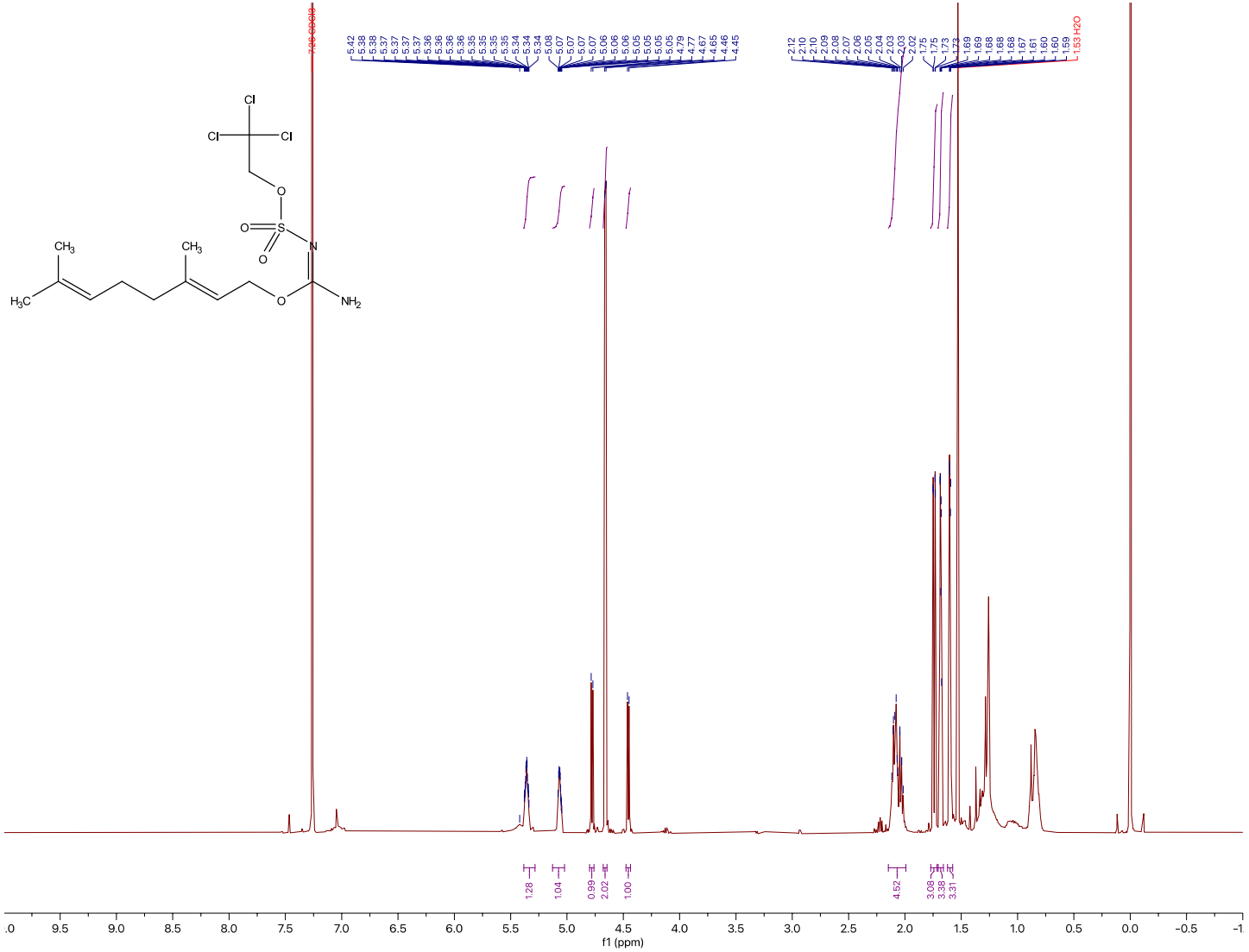
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1v**



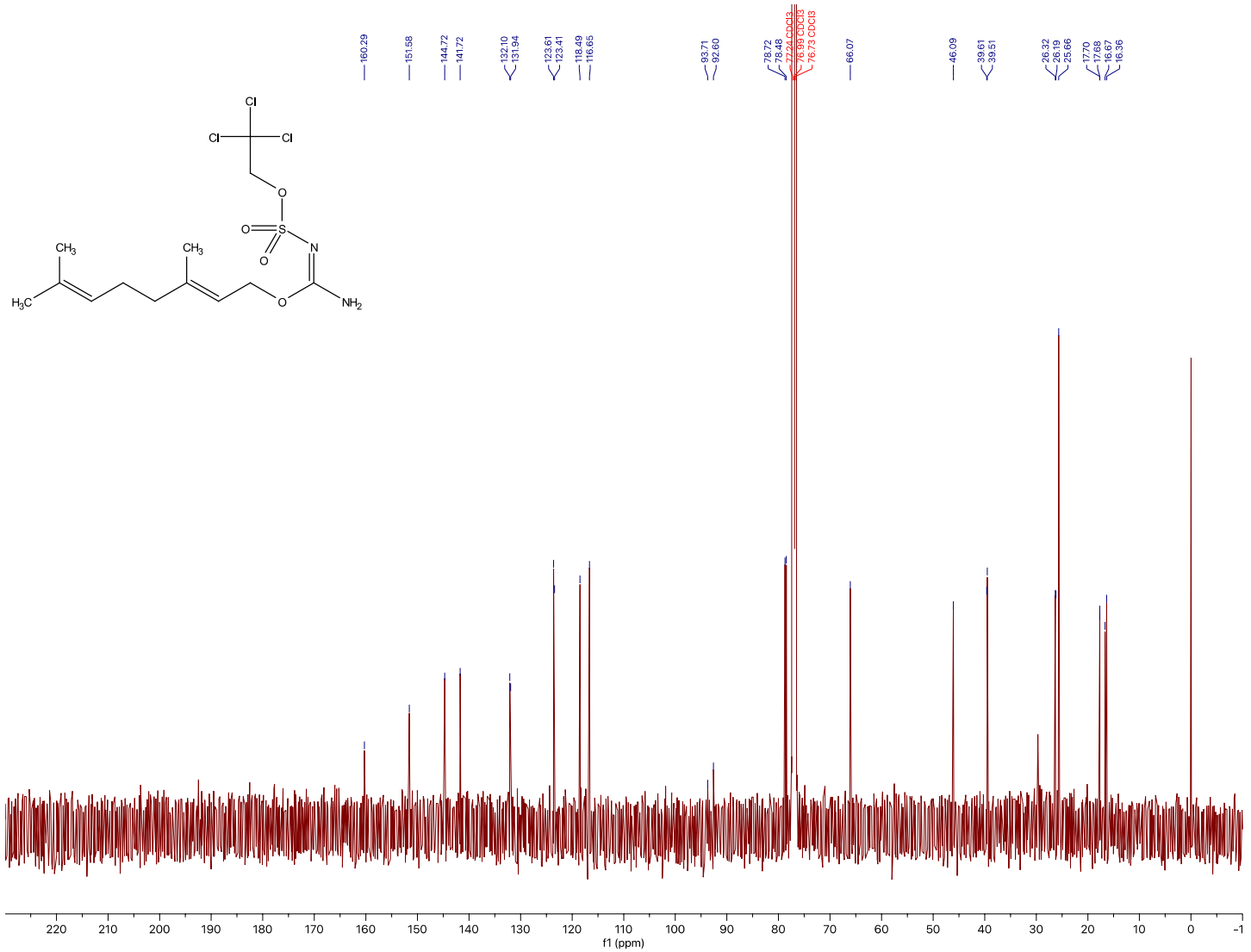
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1v**



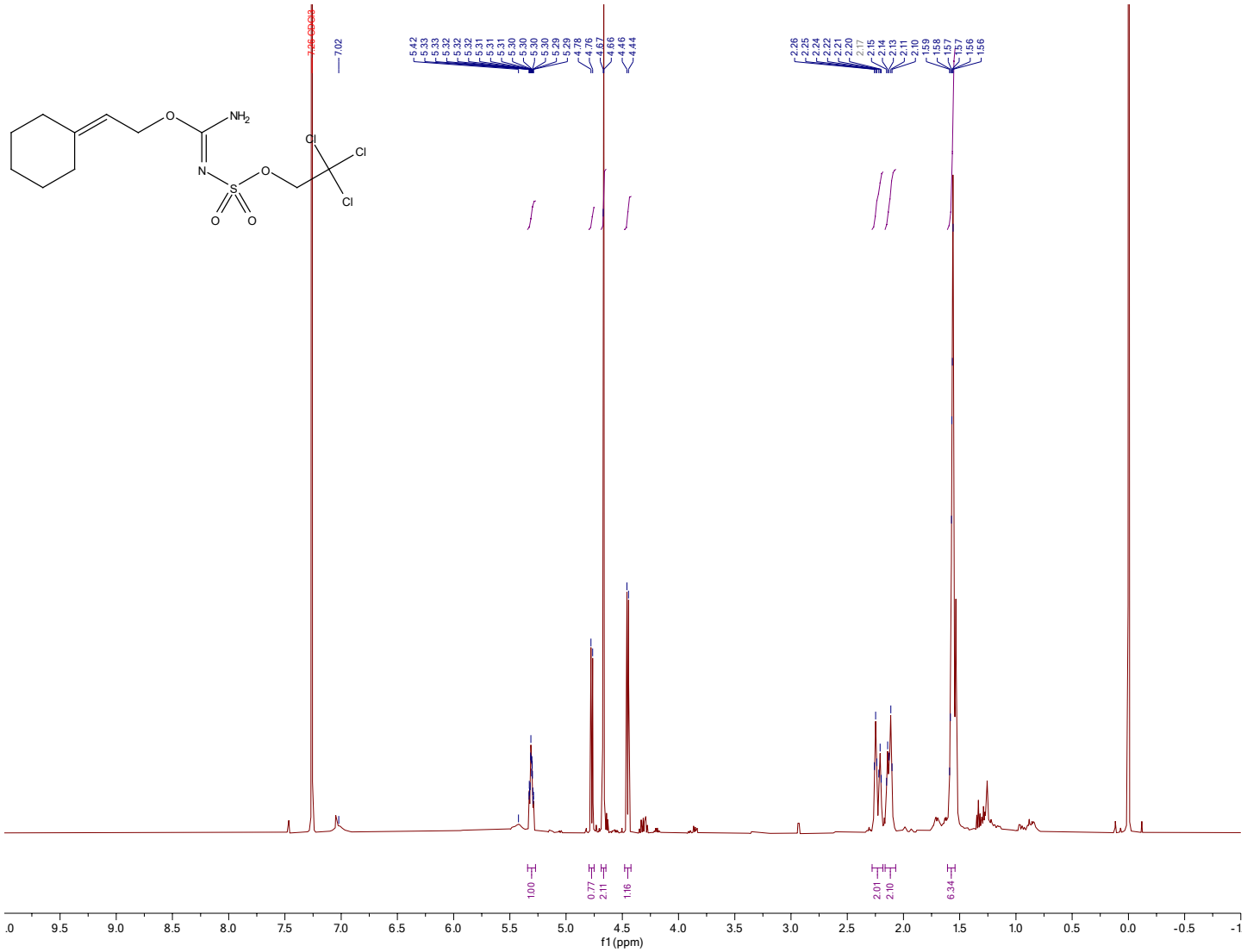
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1w**



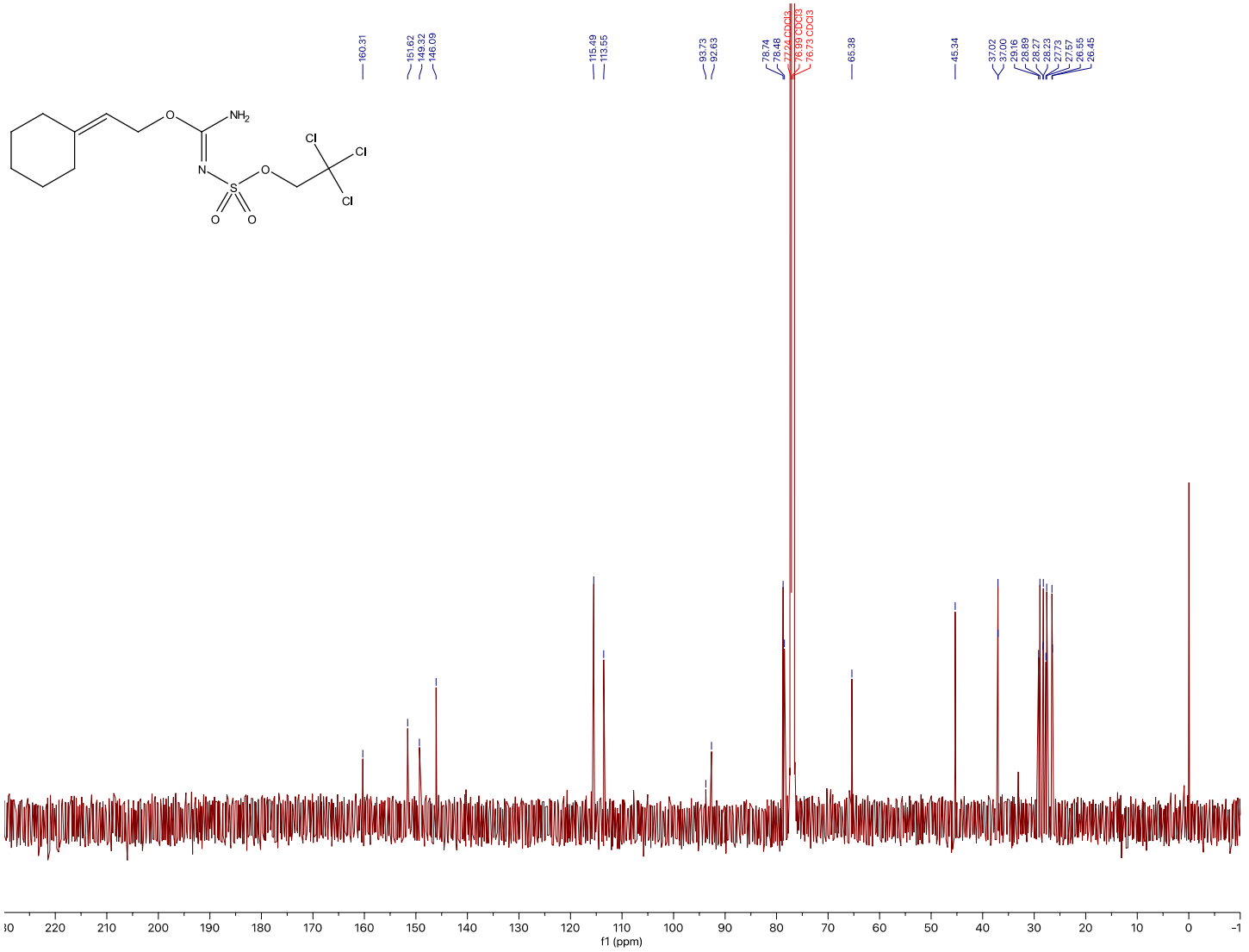
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1w**



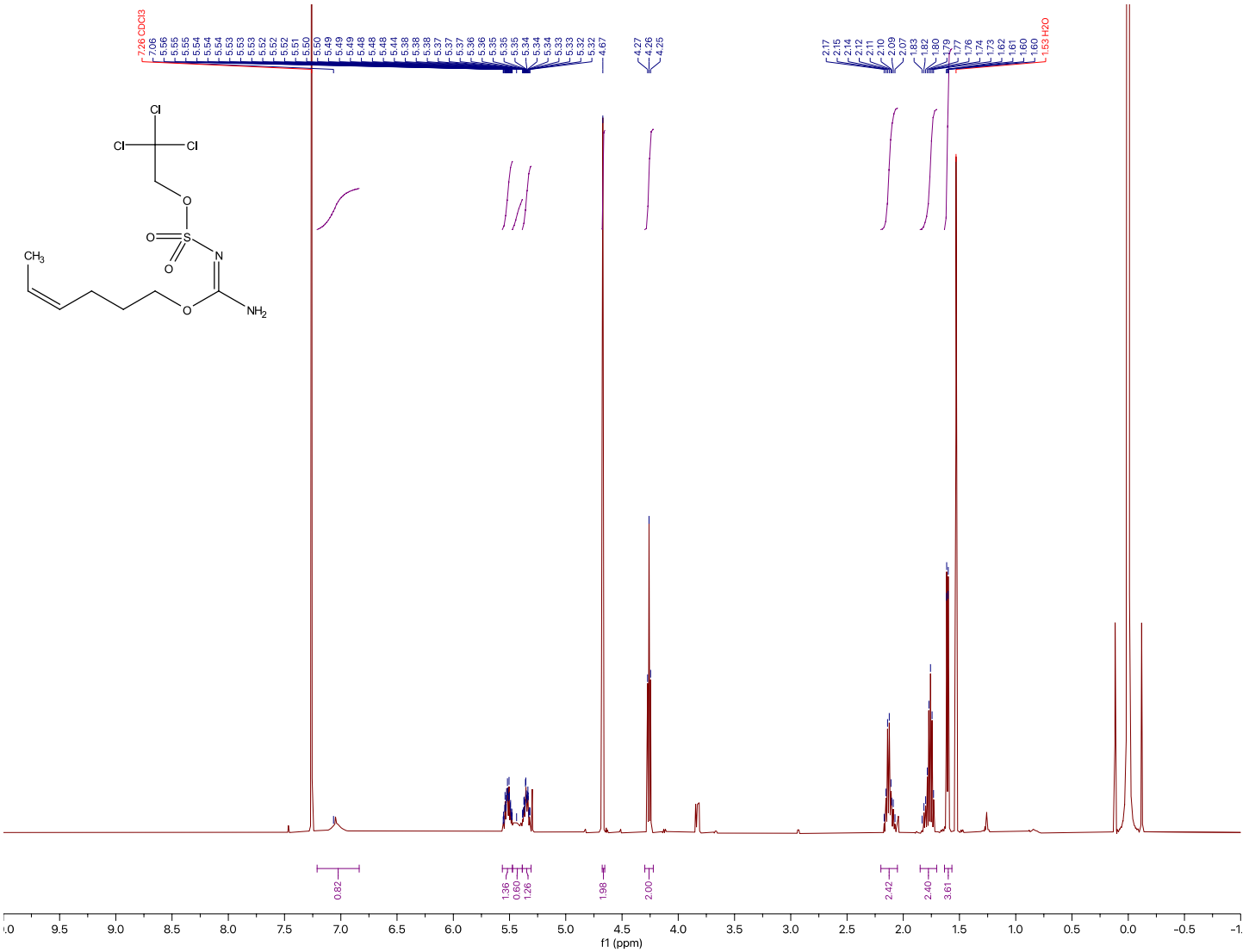
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1x**



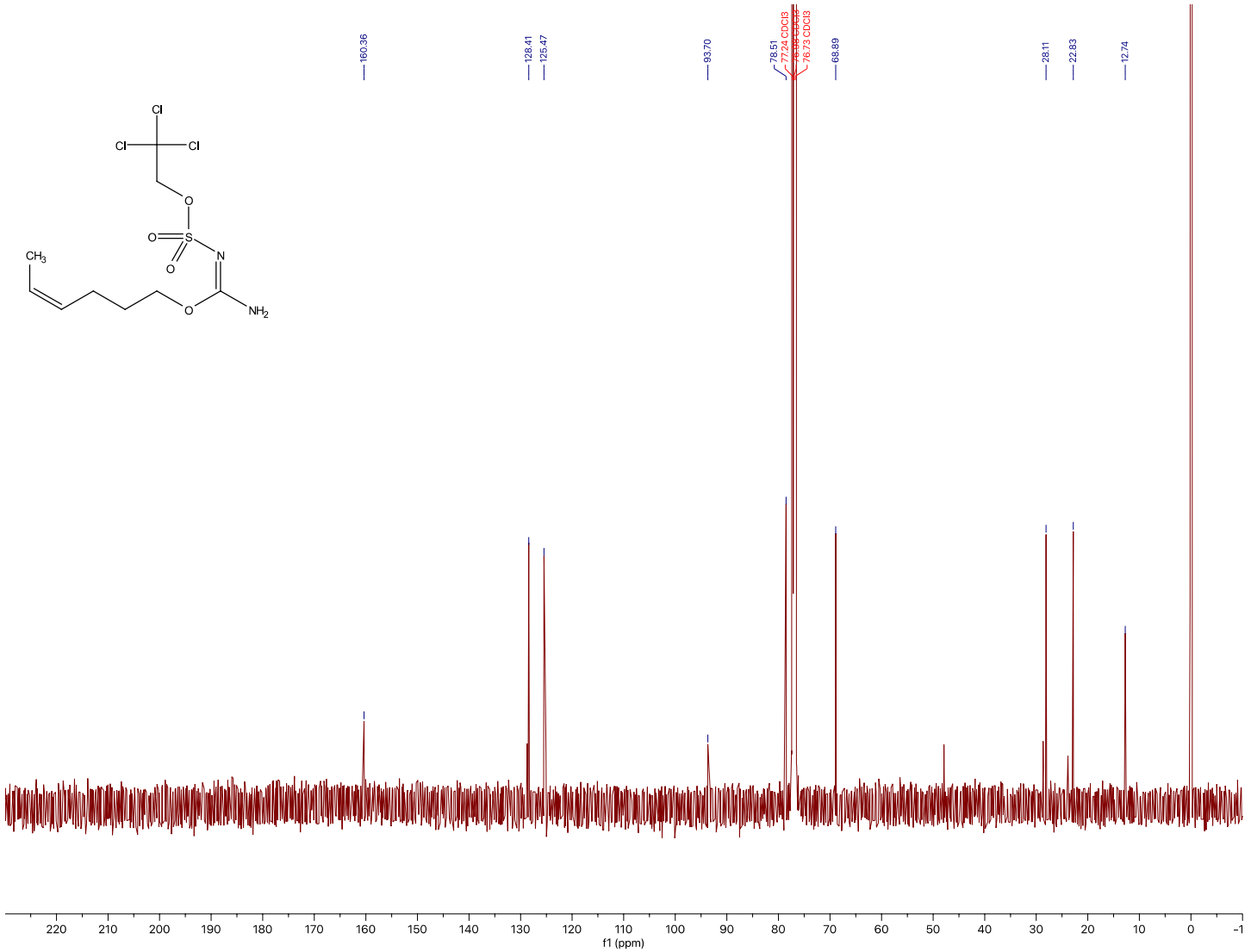
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1x**



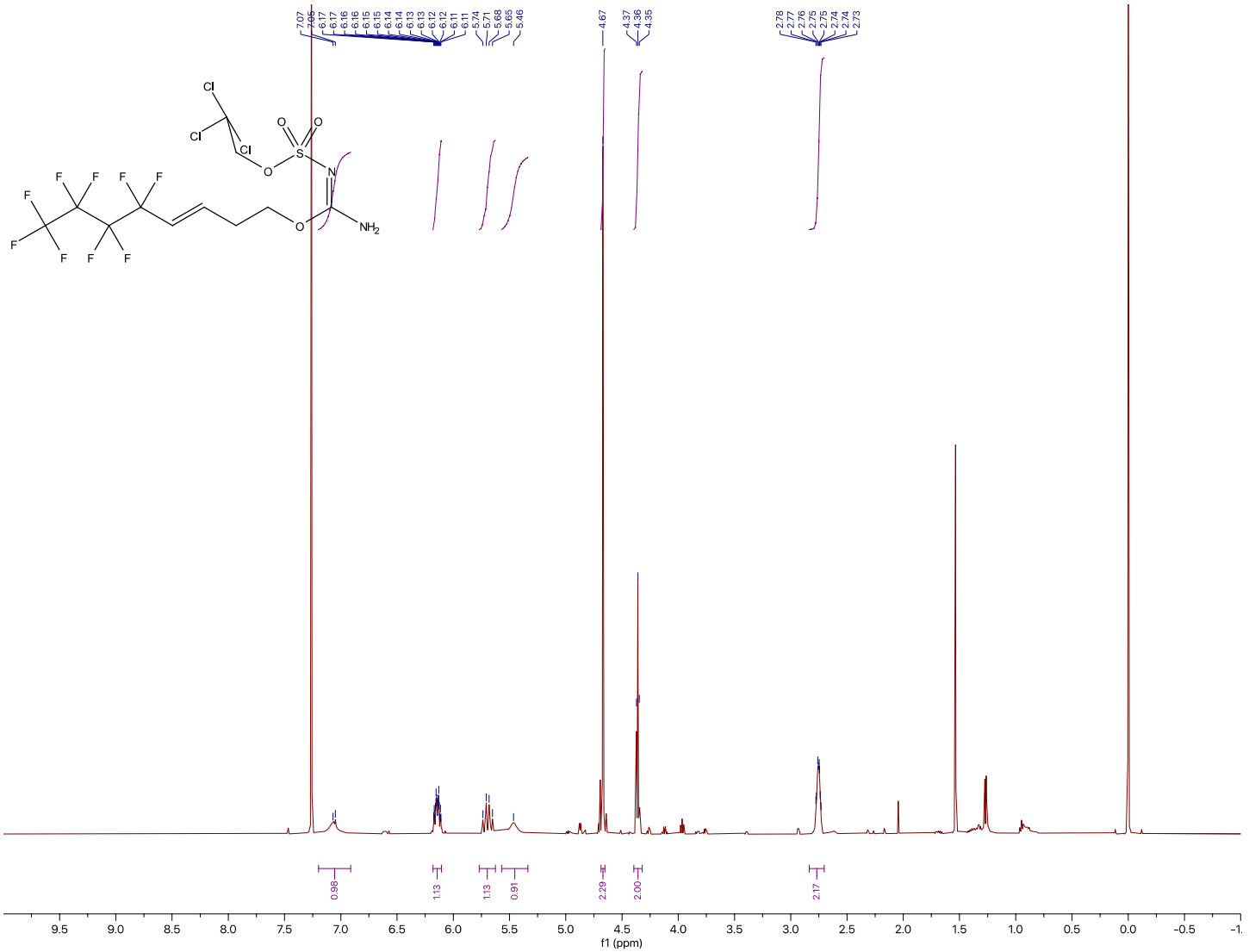
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1y**



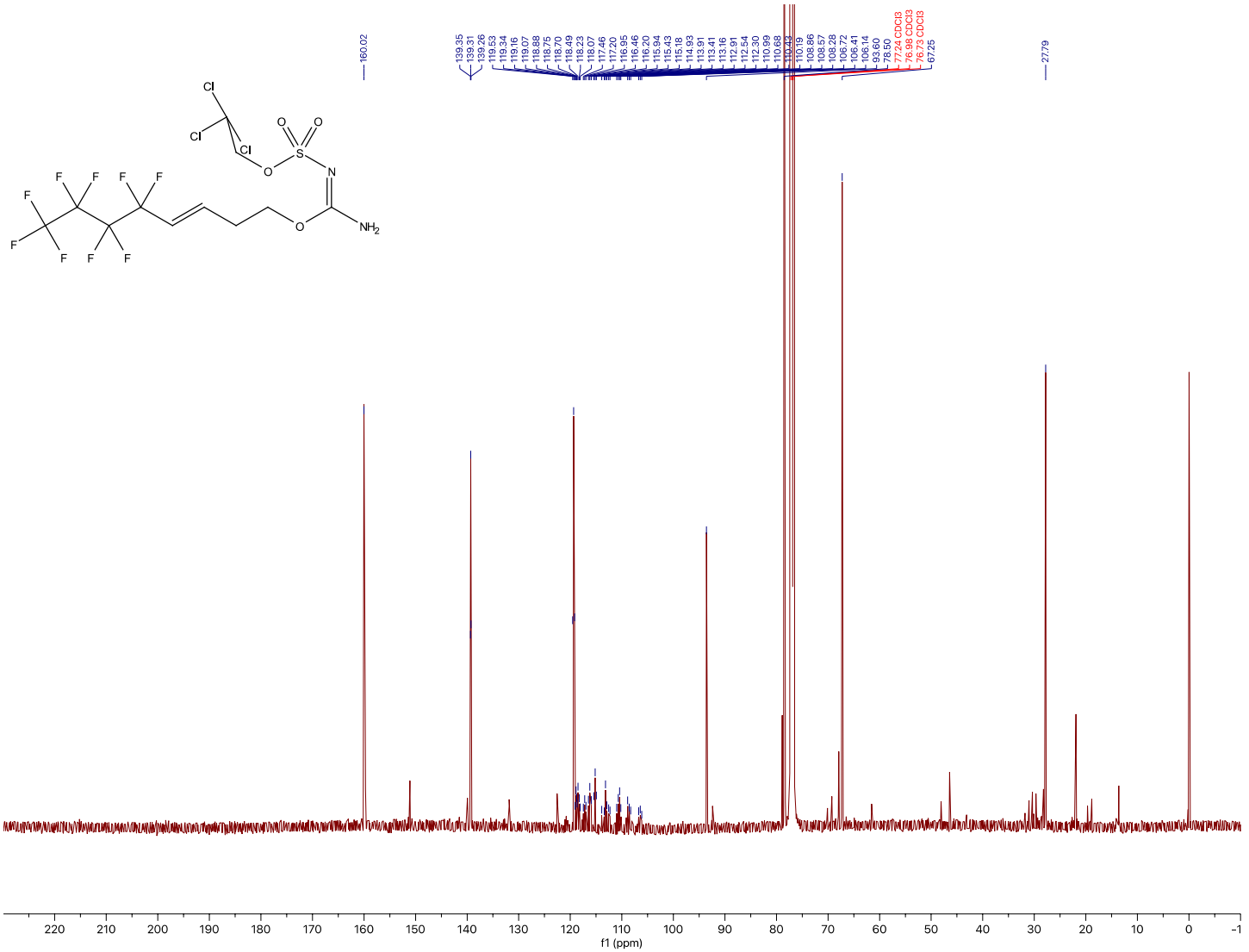
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1y**



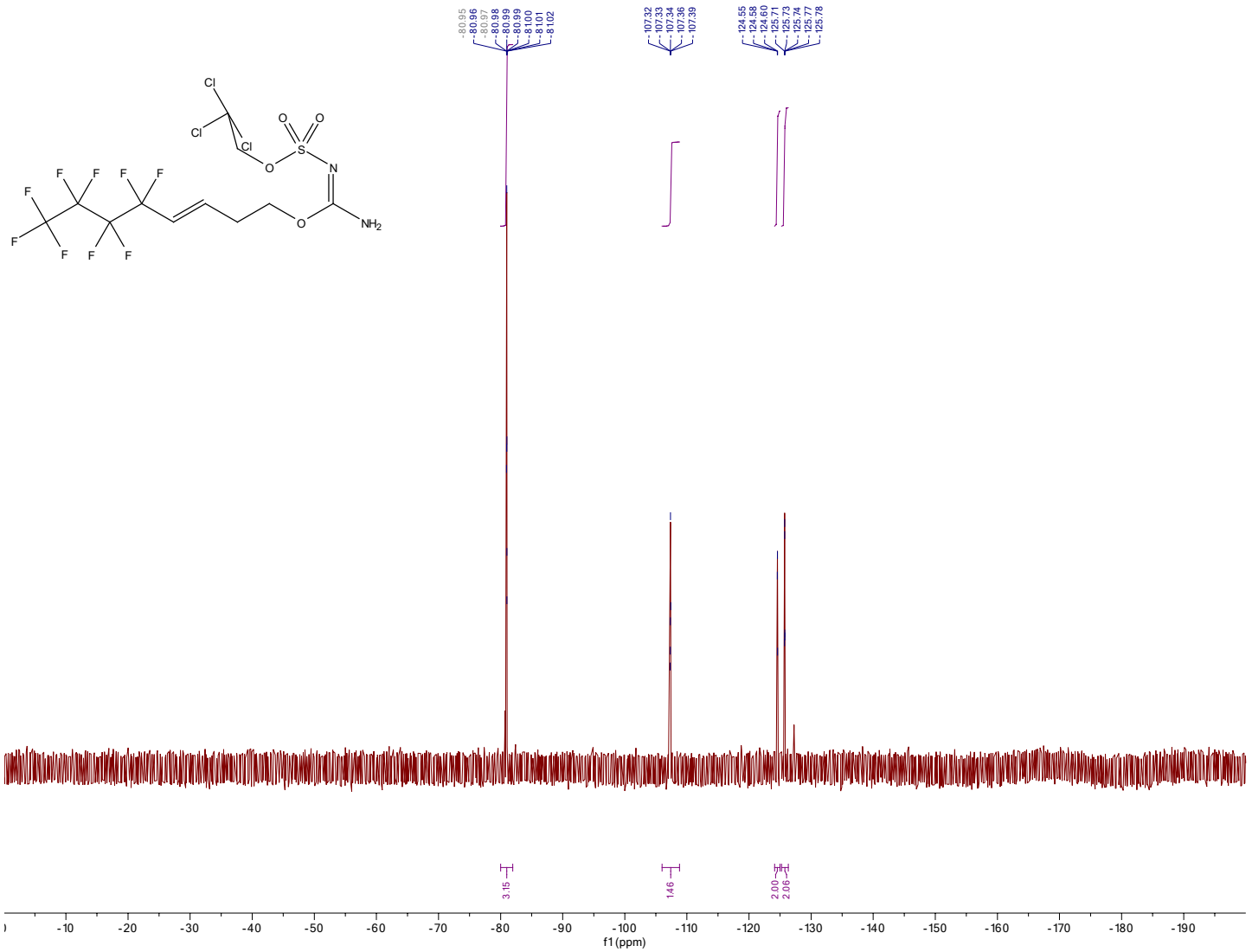
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 1z**



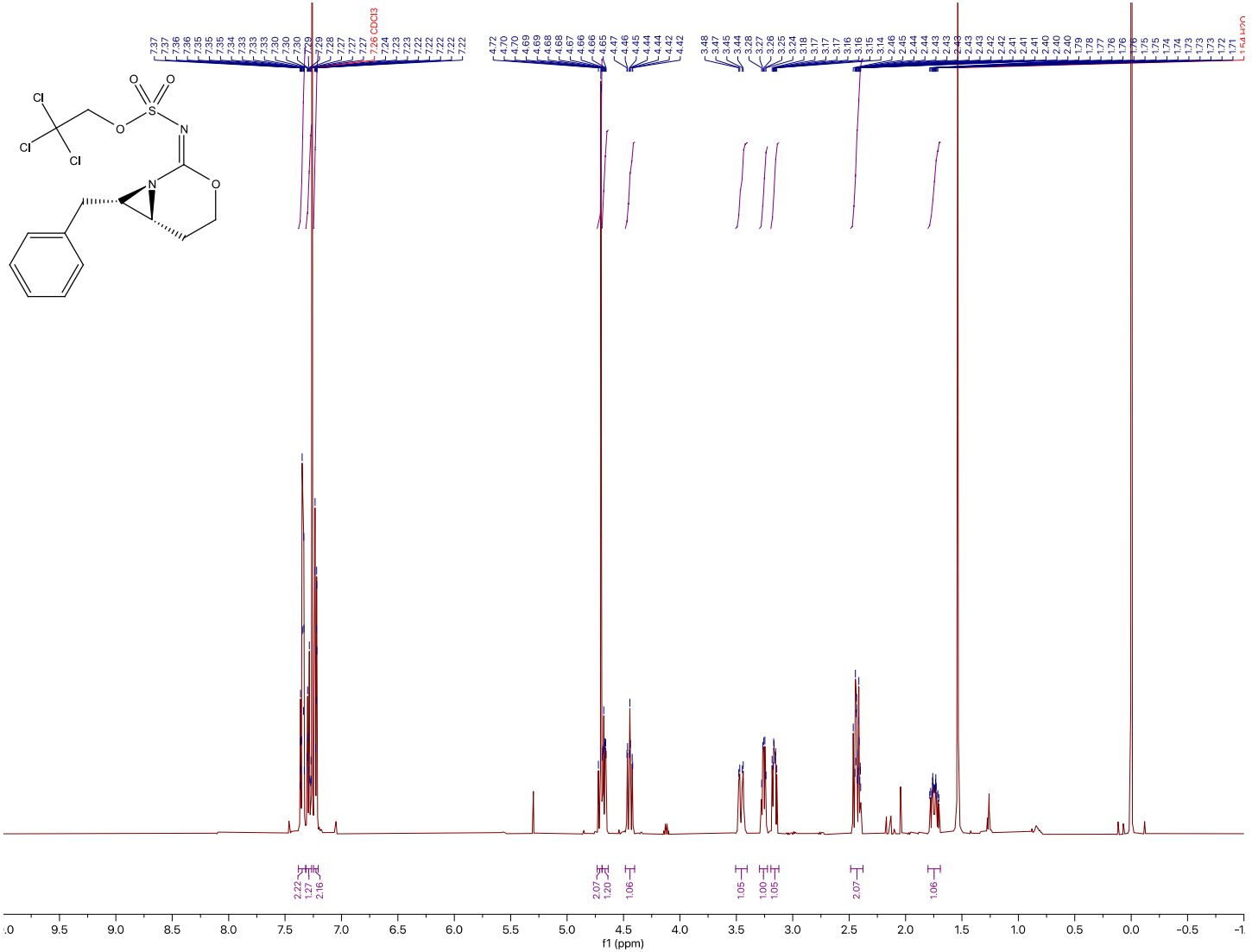
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 1z**



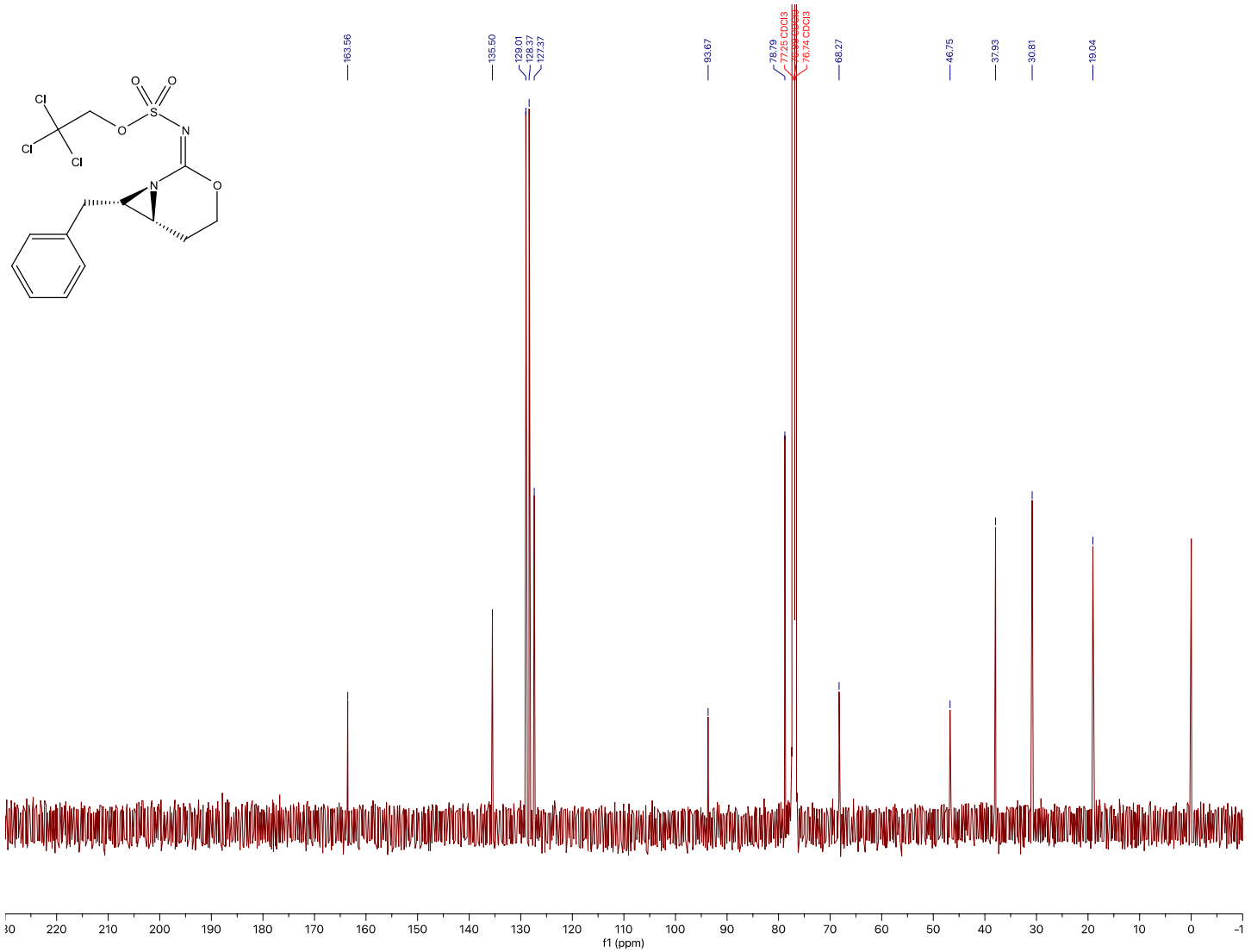
^{19}F NMR (377 MHz, $CDCl_3$) for **Compound 1z**



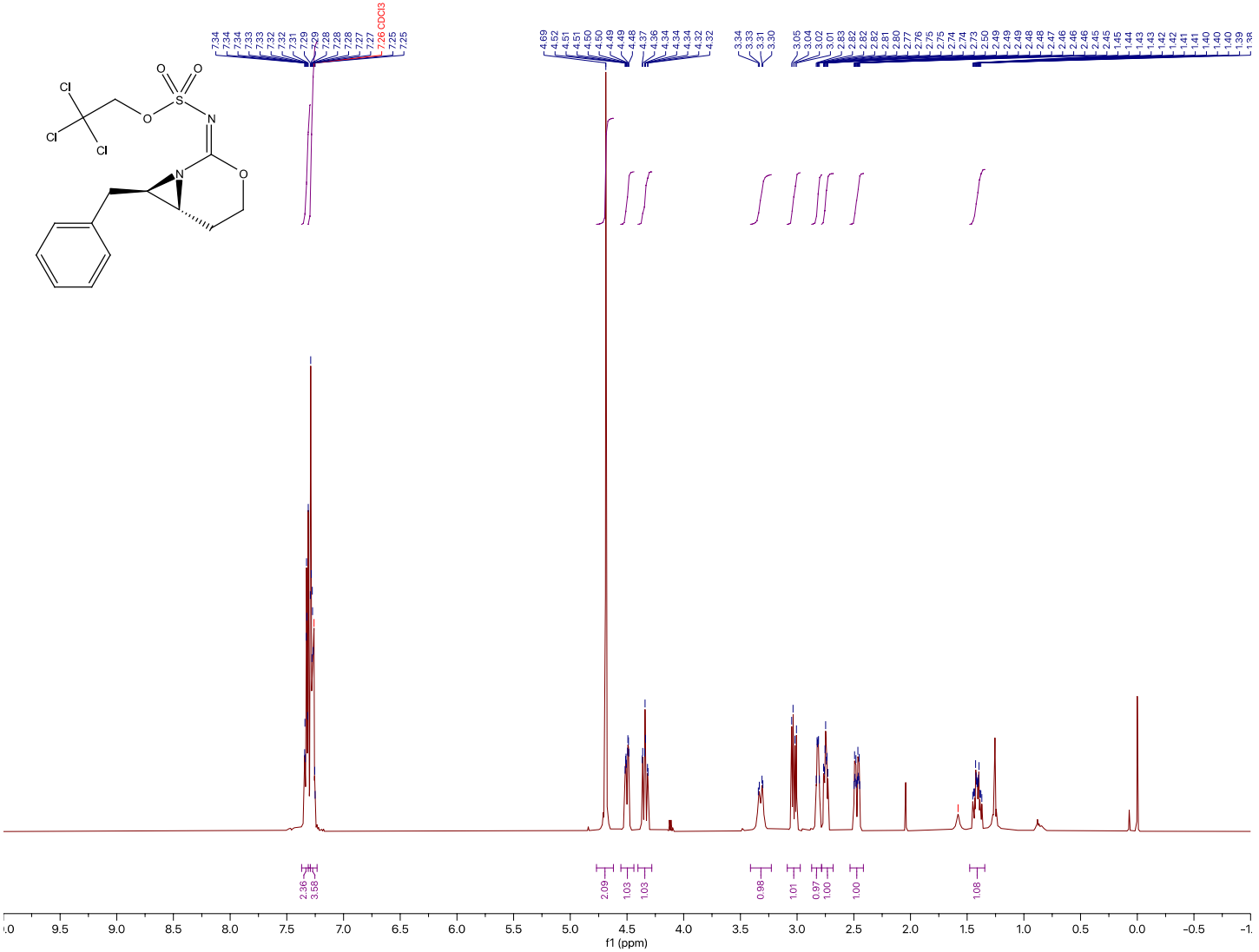
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2a**



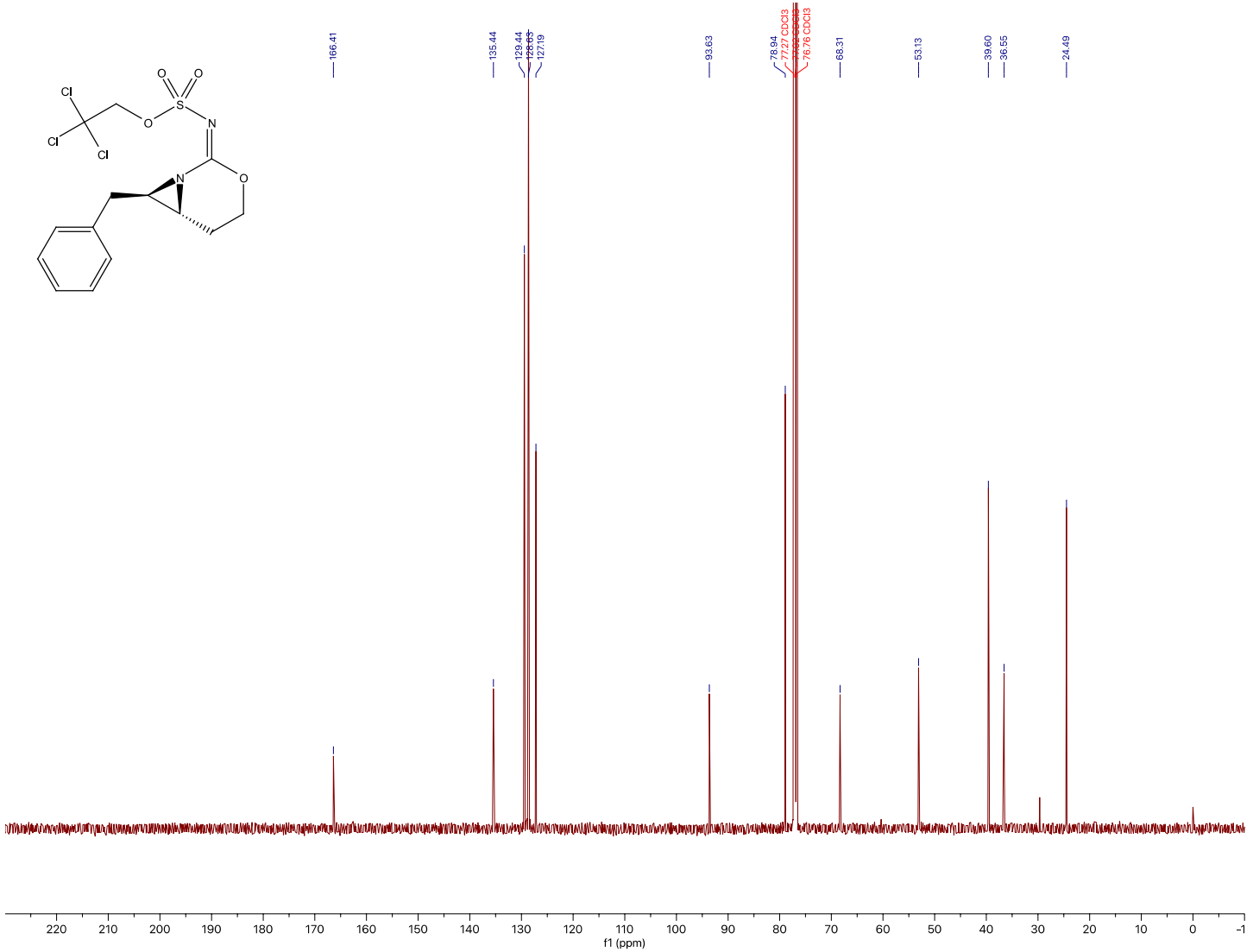
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2a**



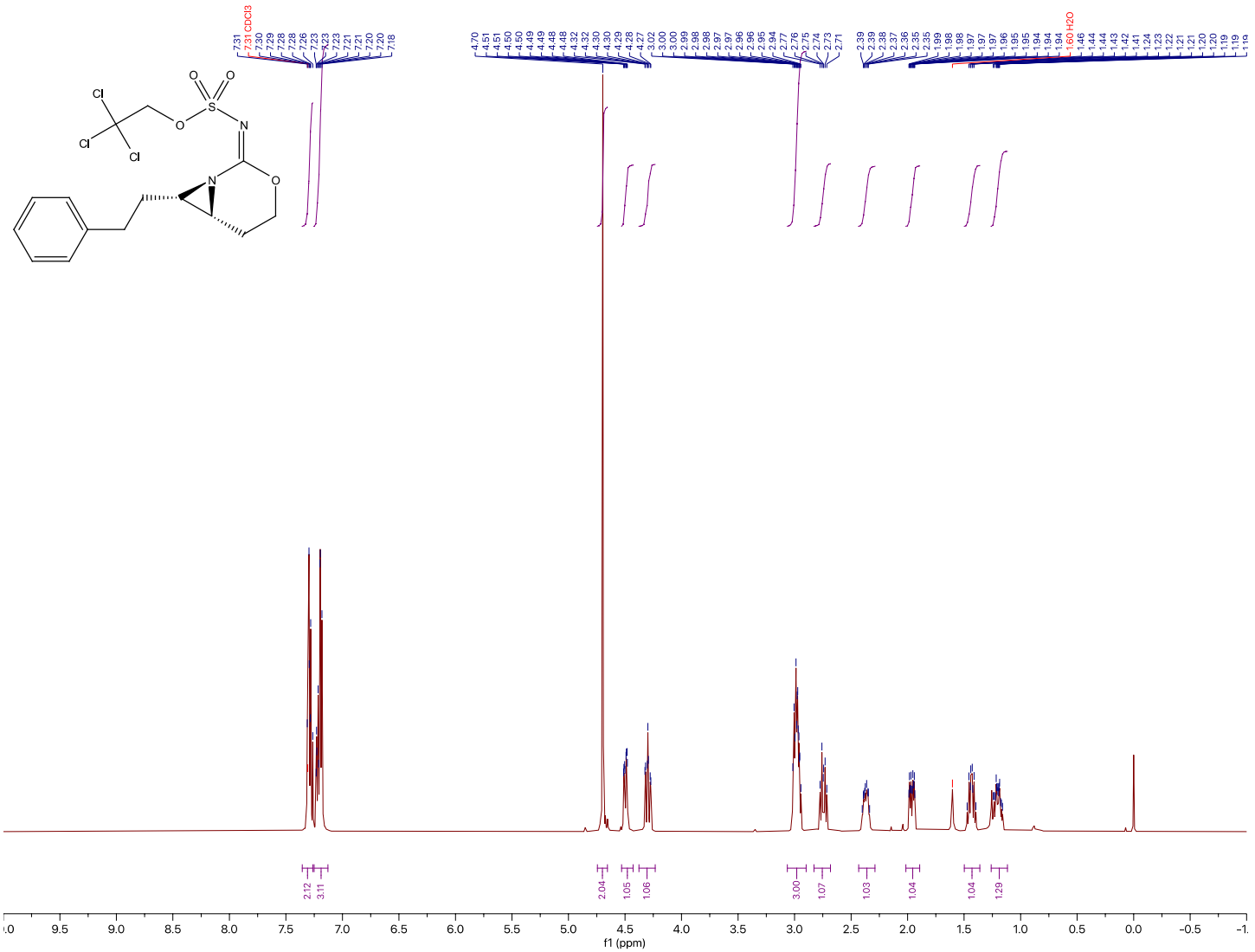
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2b**



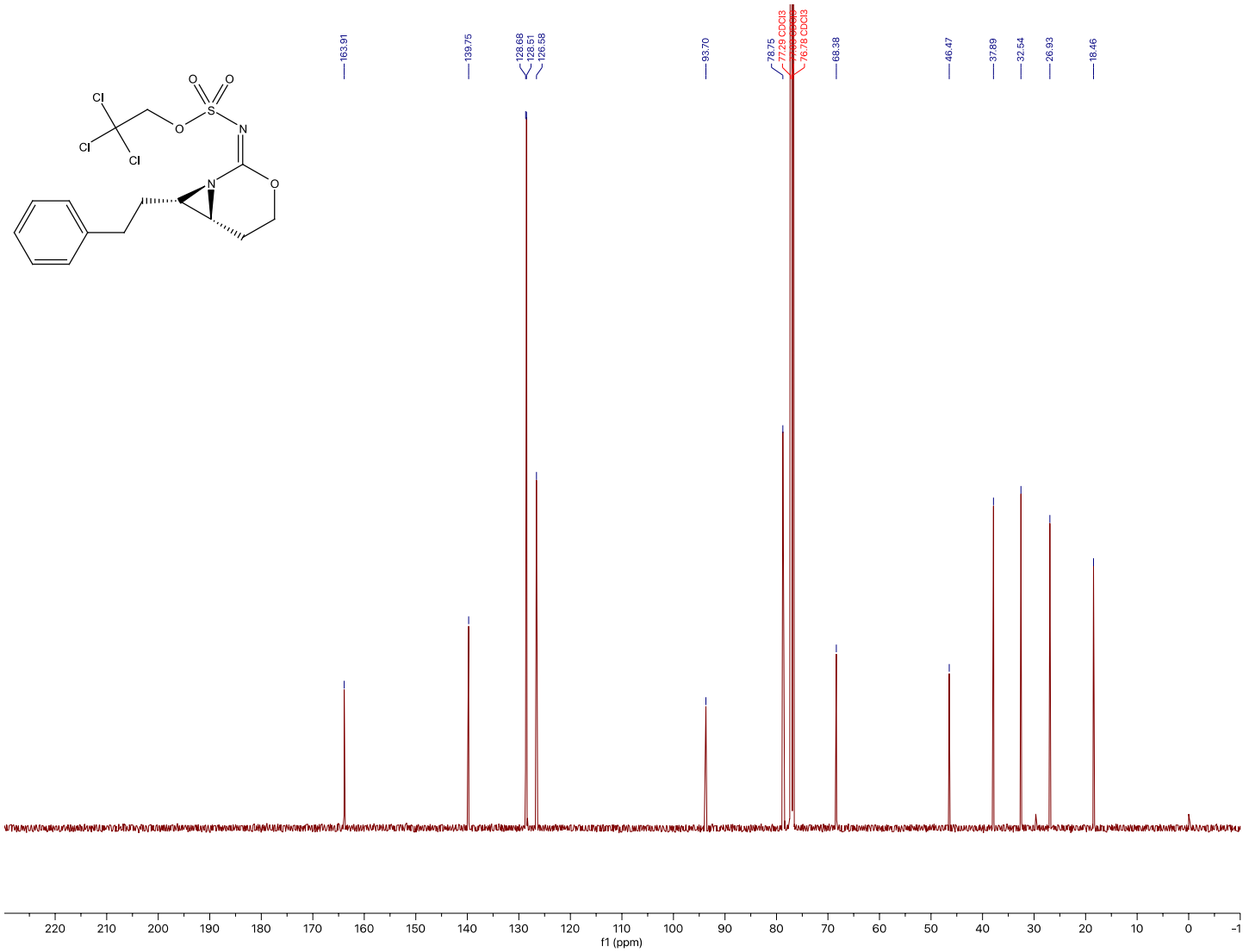
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2b**



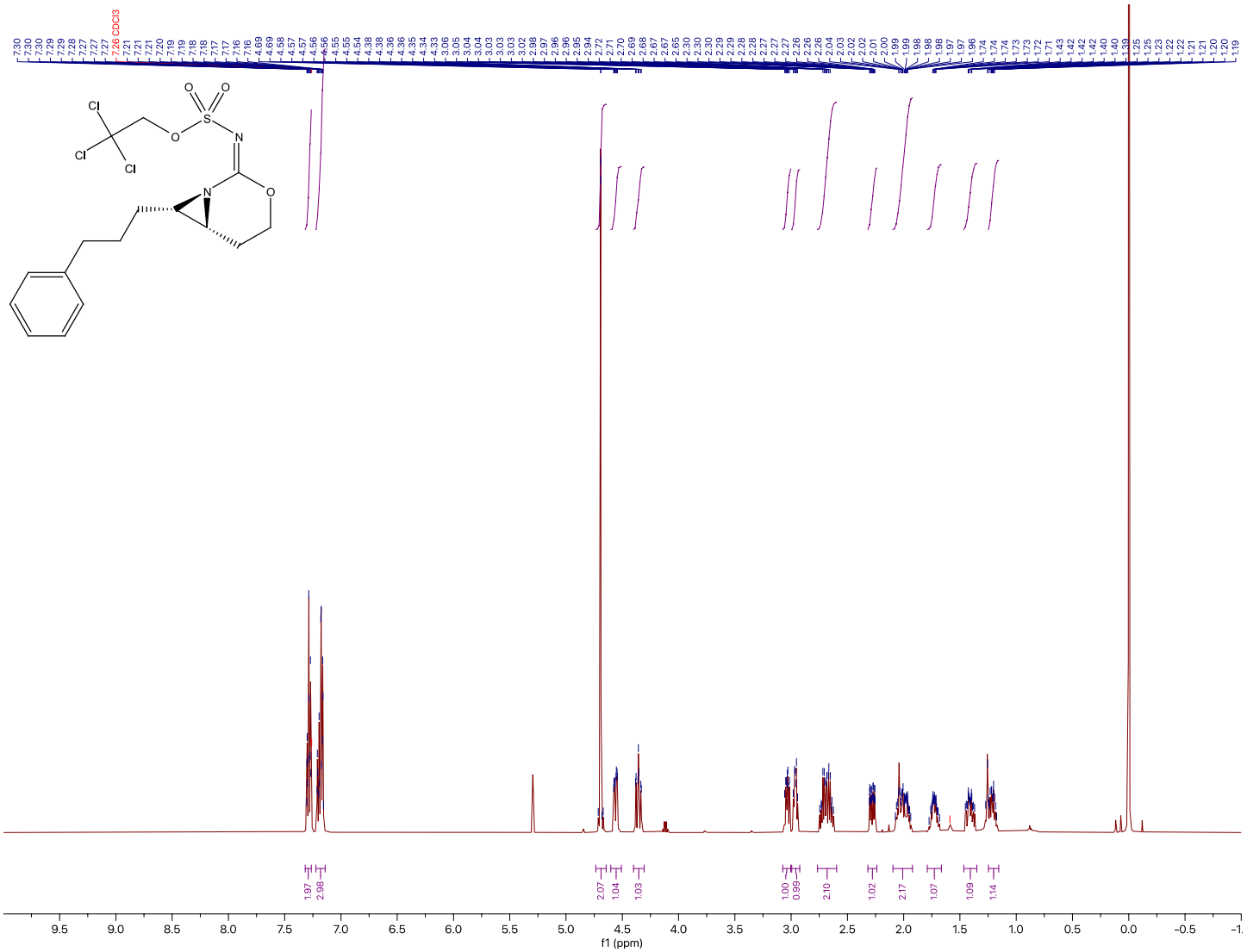
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2c**



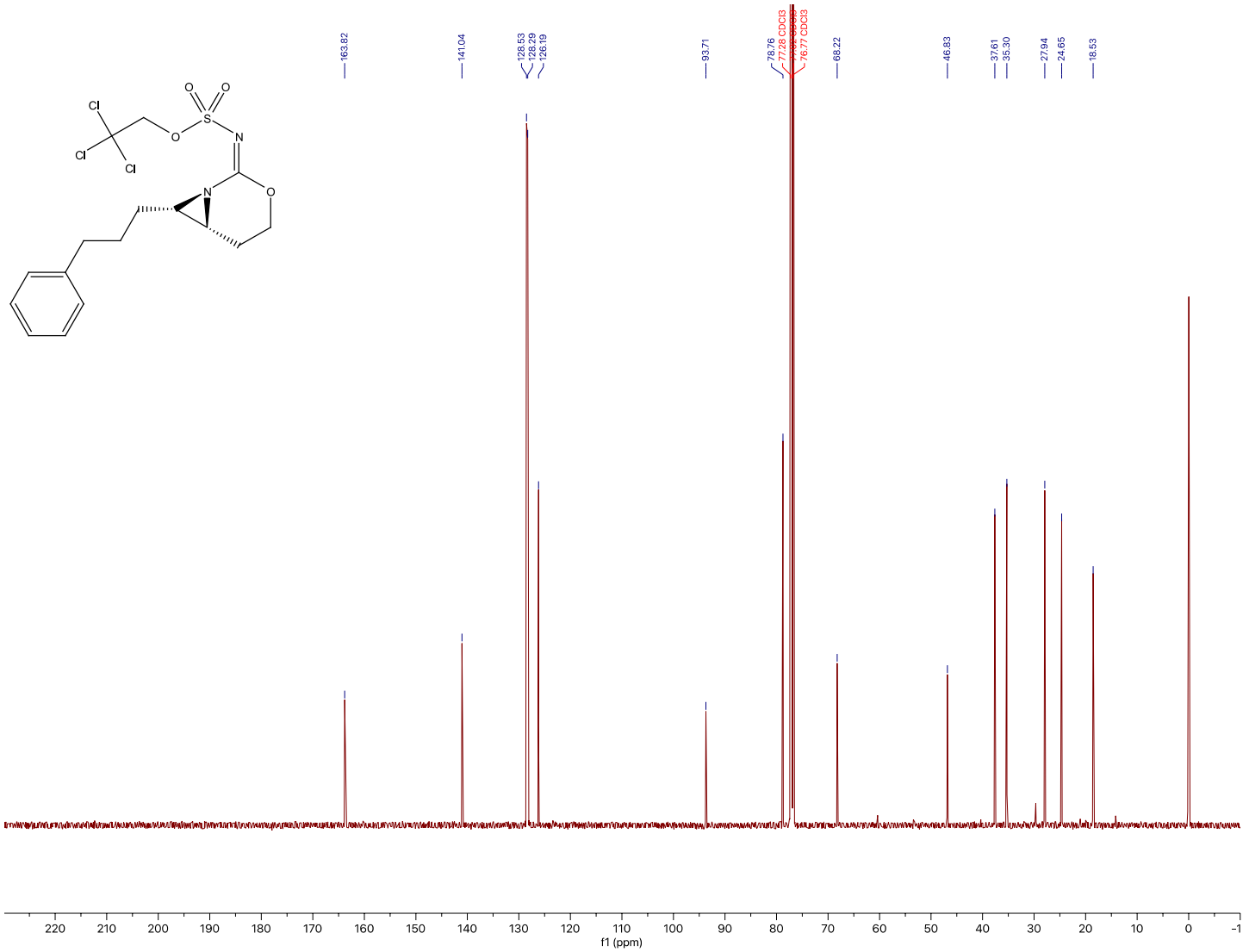
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2c**



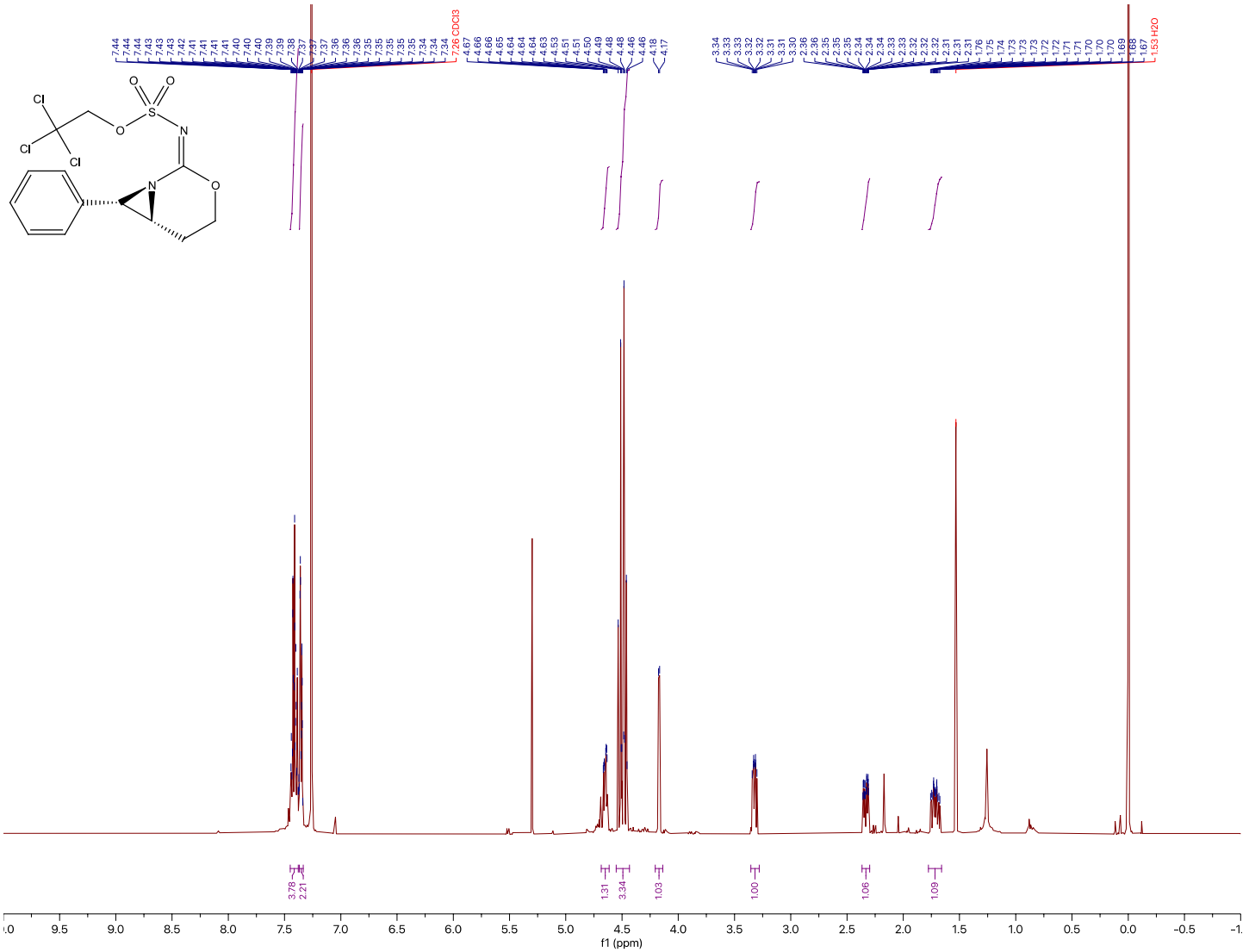
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2d**



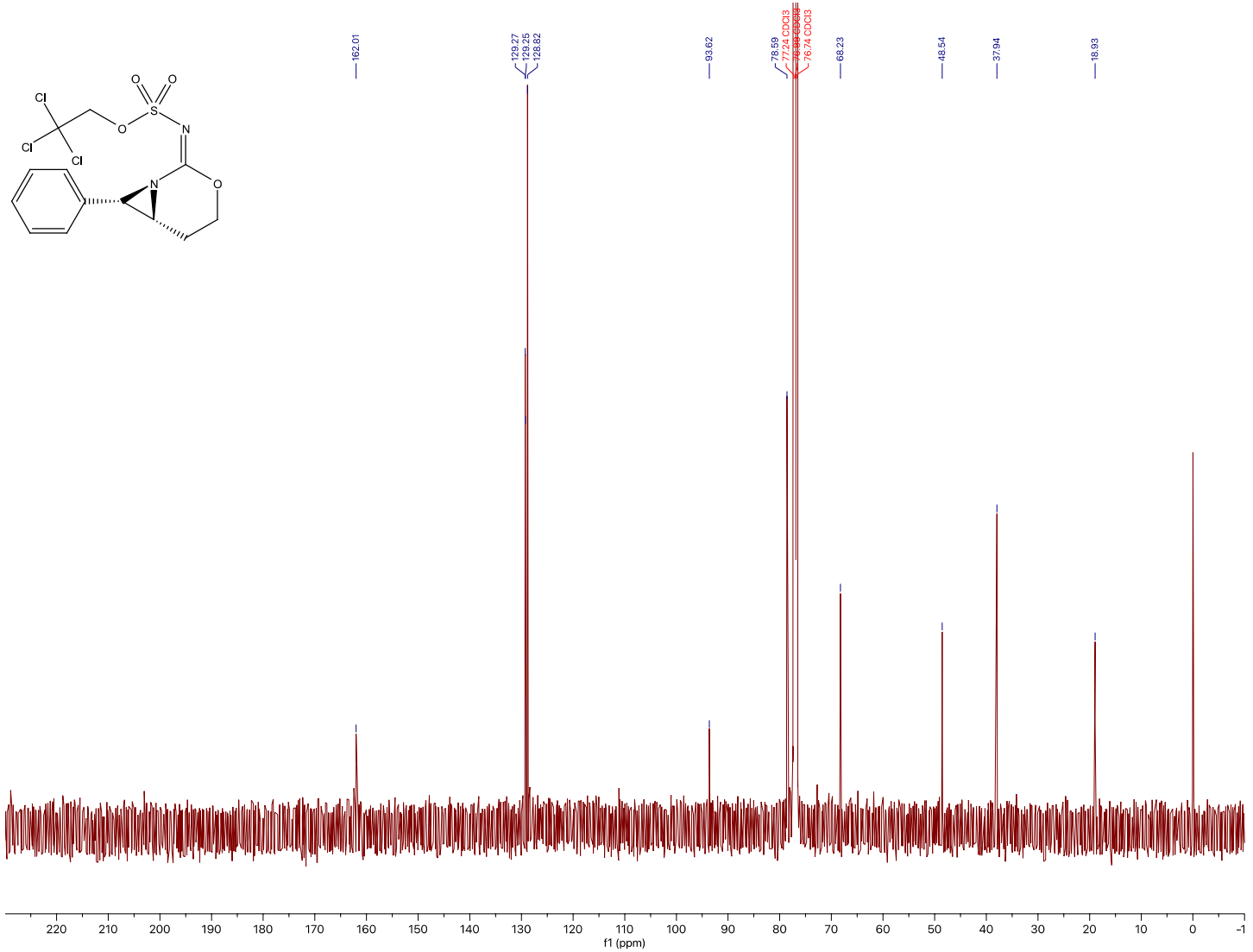
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2d**



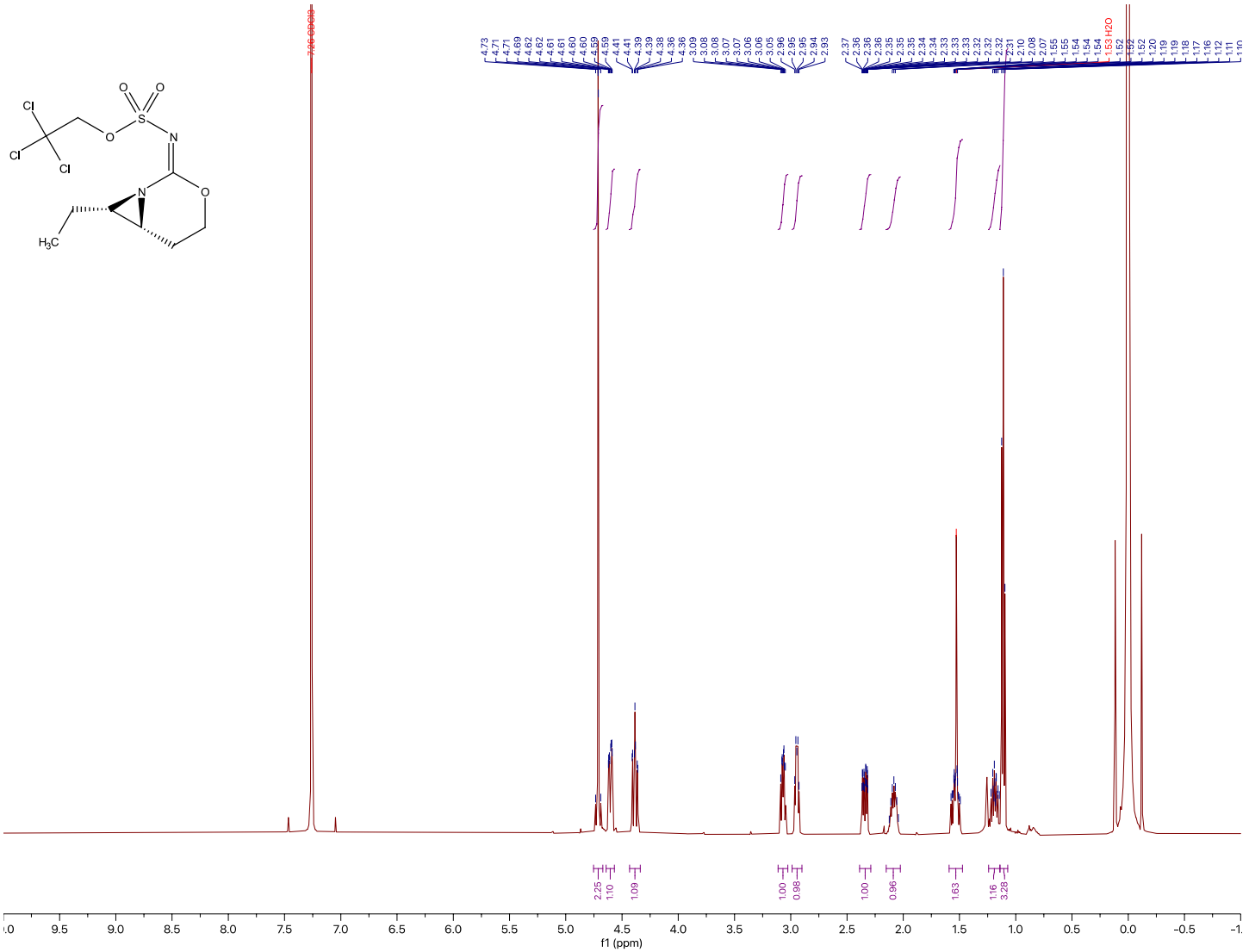
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2e**



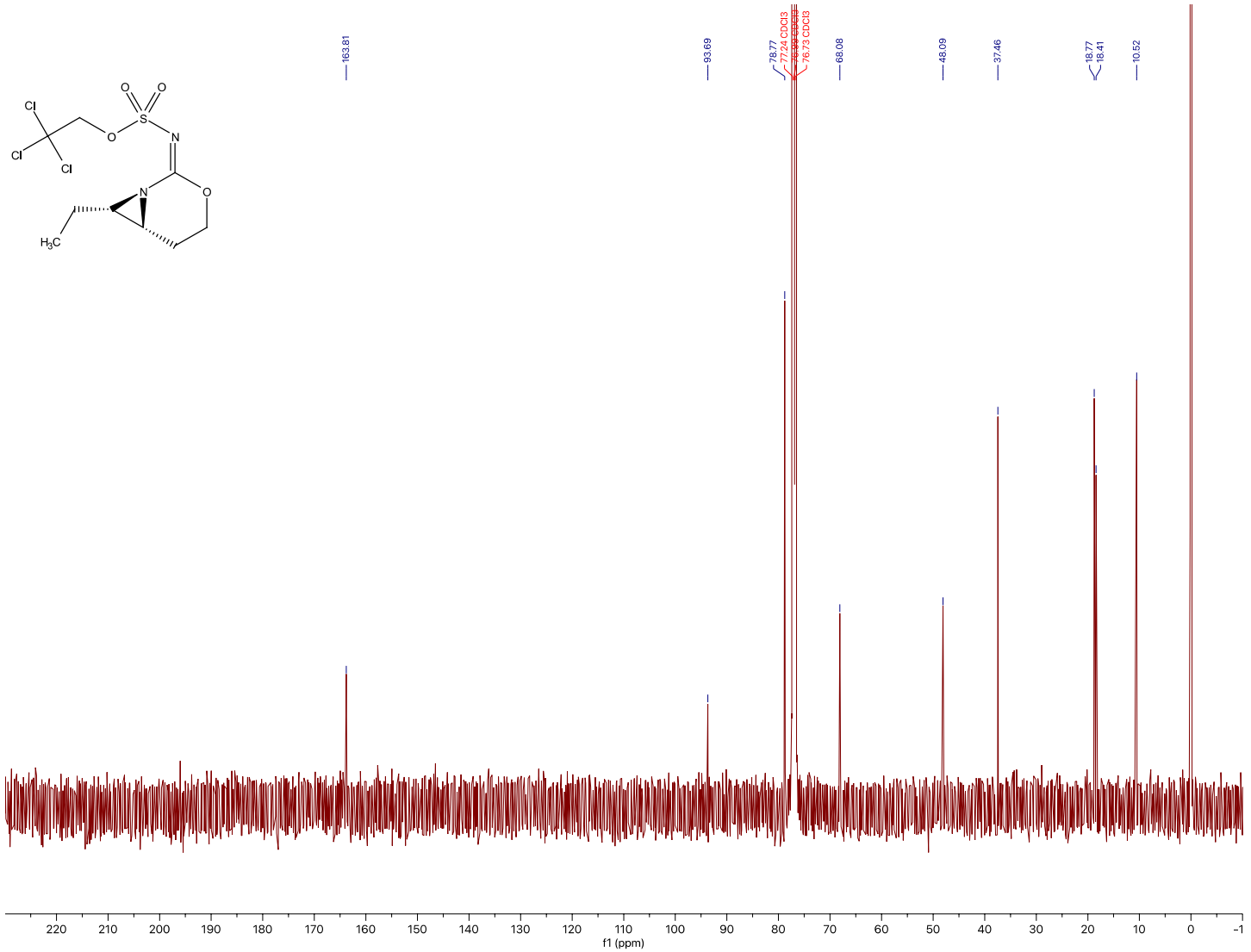
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2e**



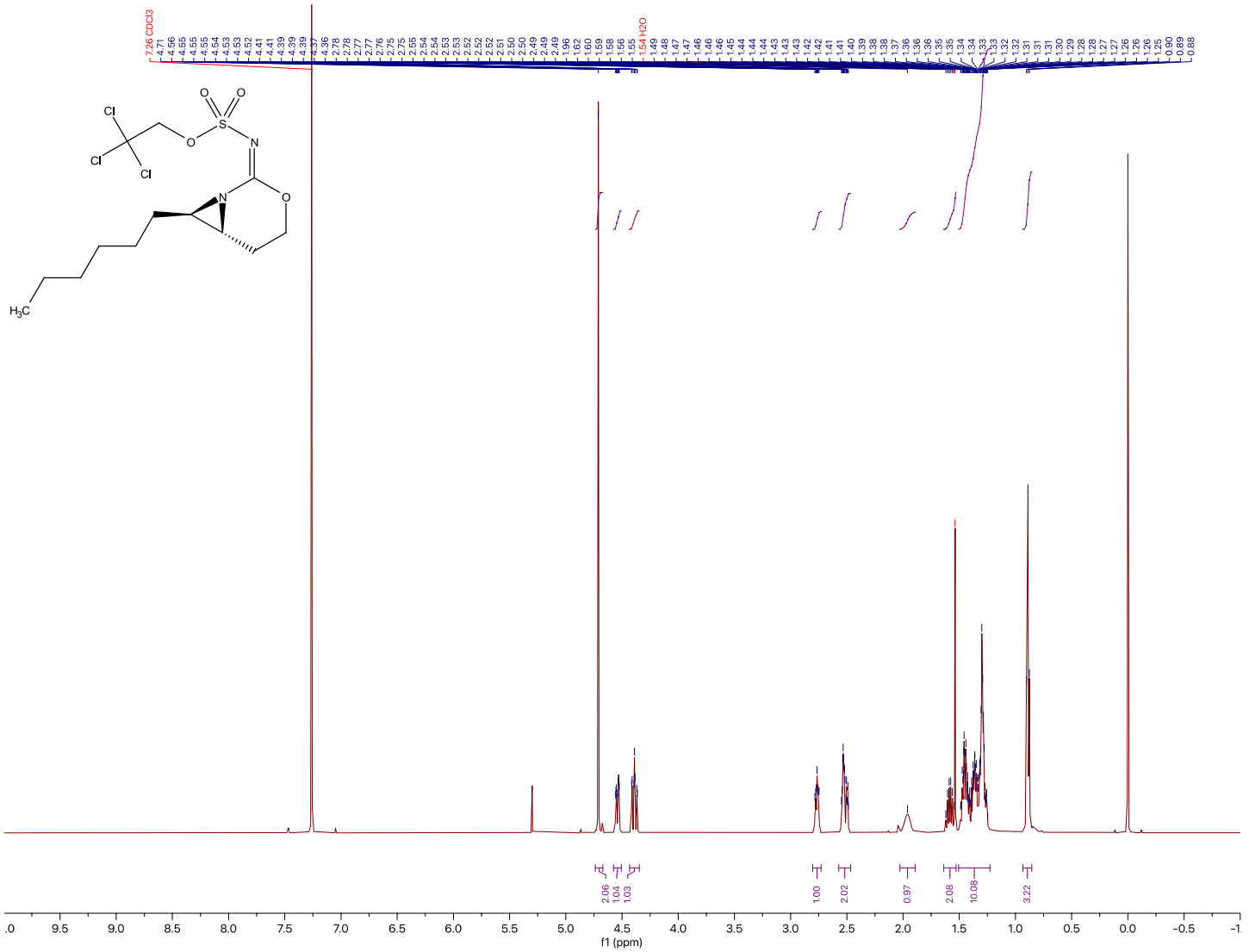
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2f**



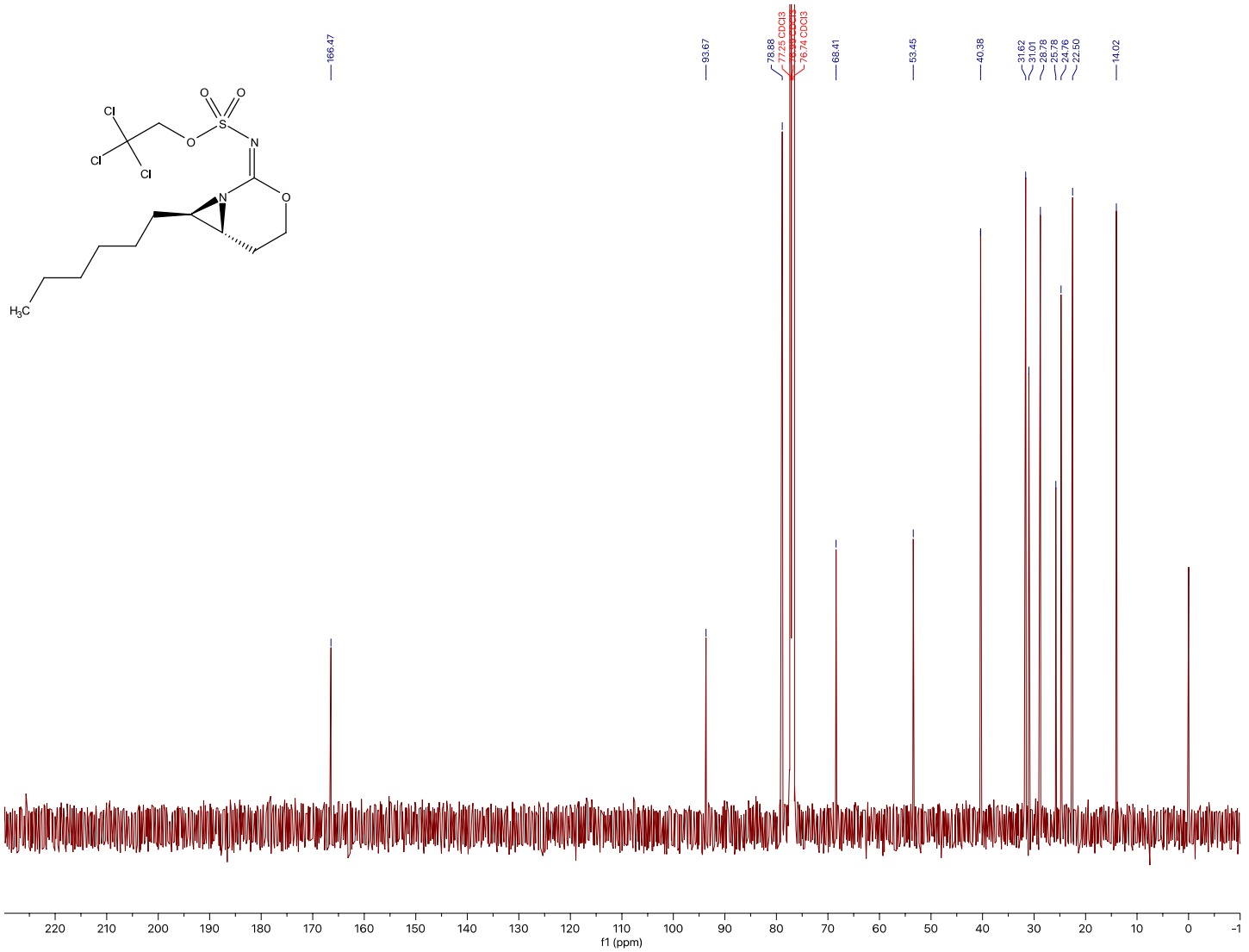
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2f**



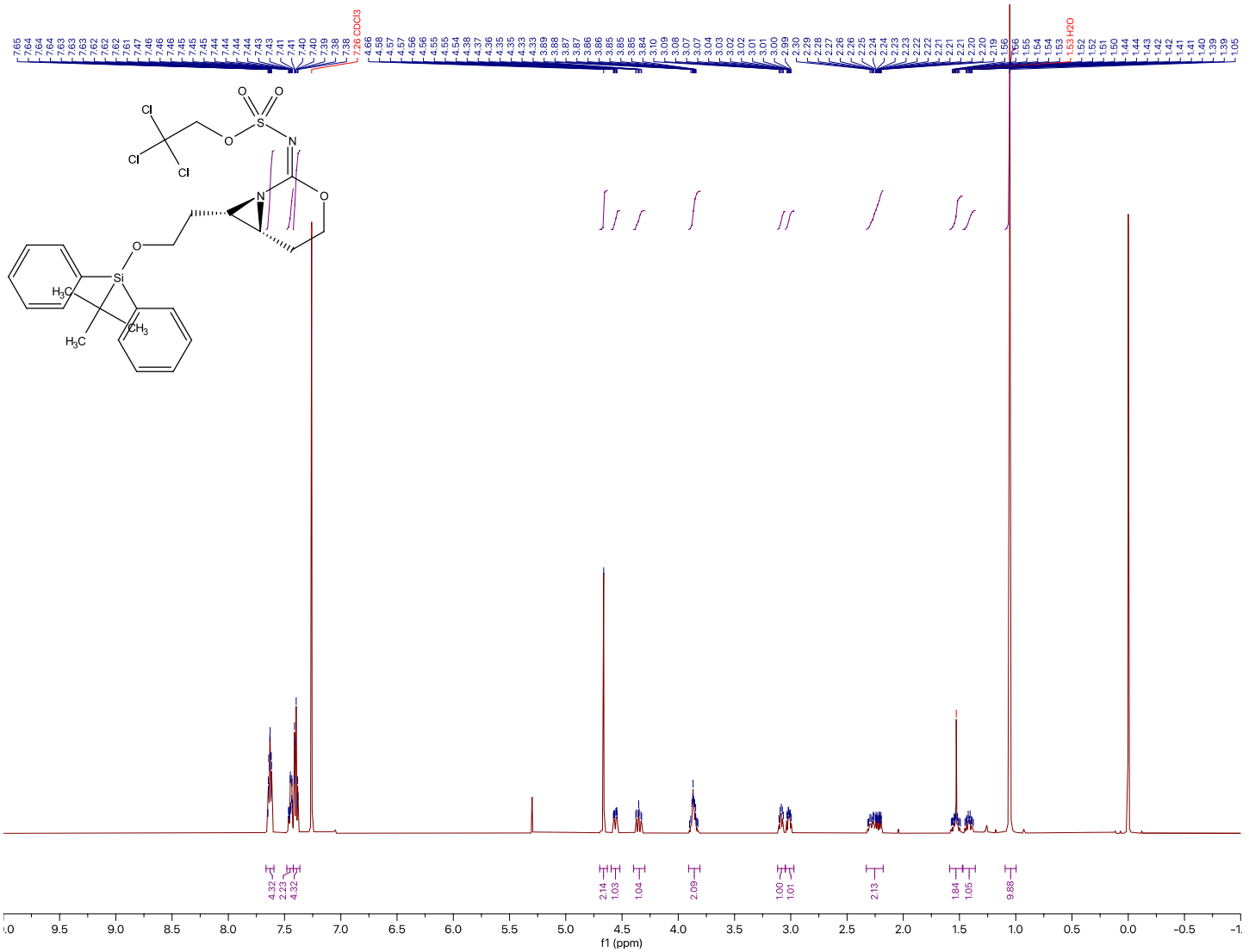
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2g**



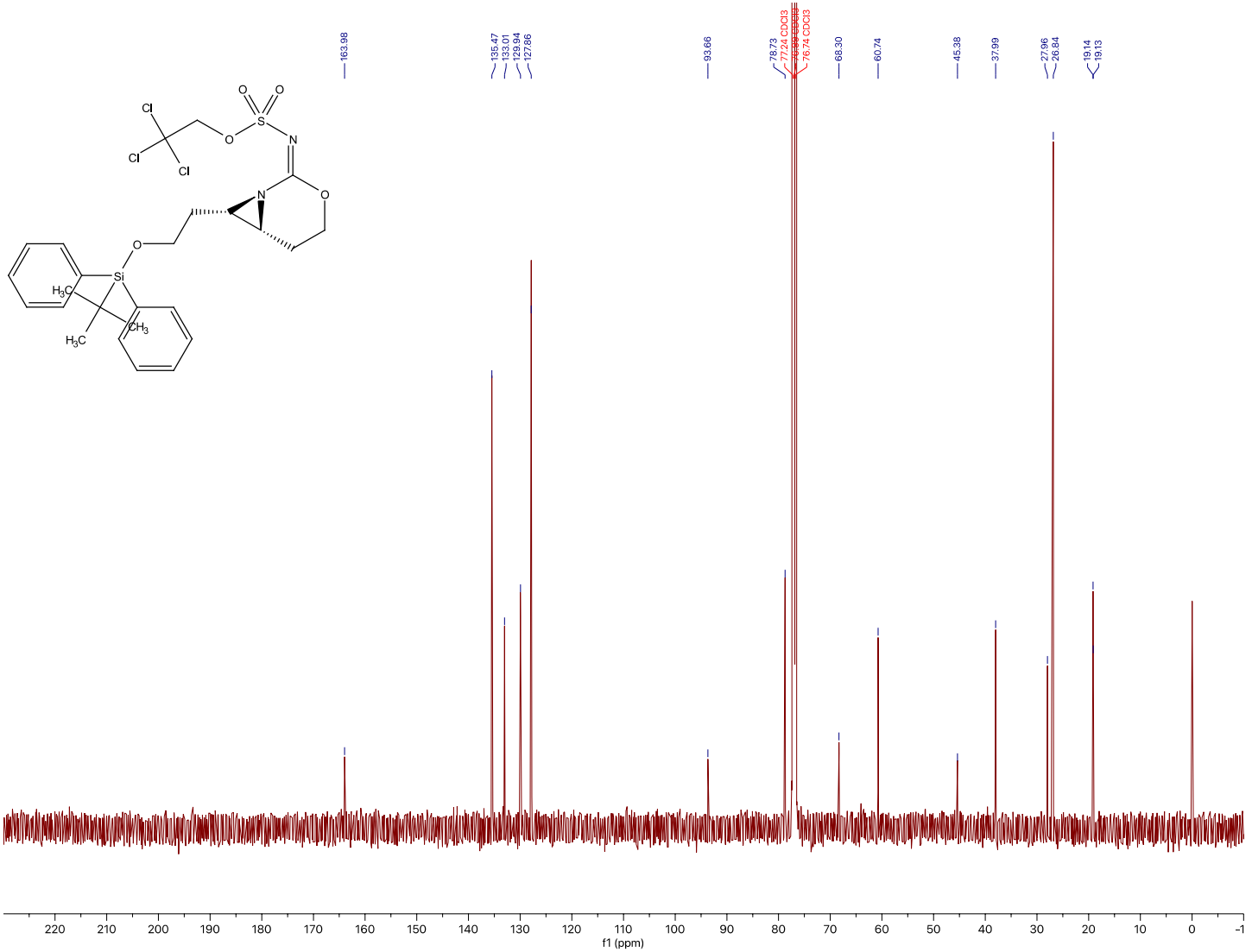
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2g**



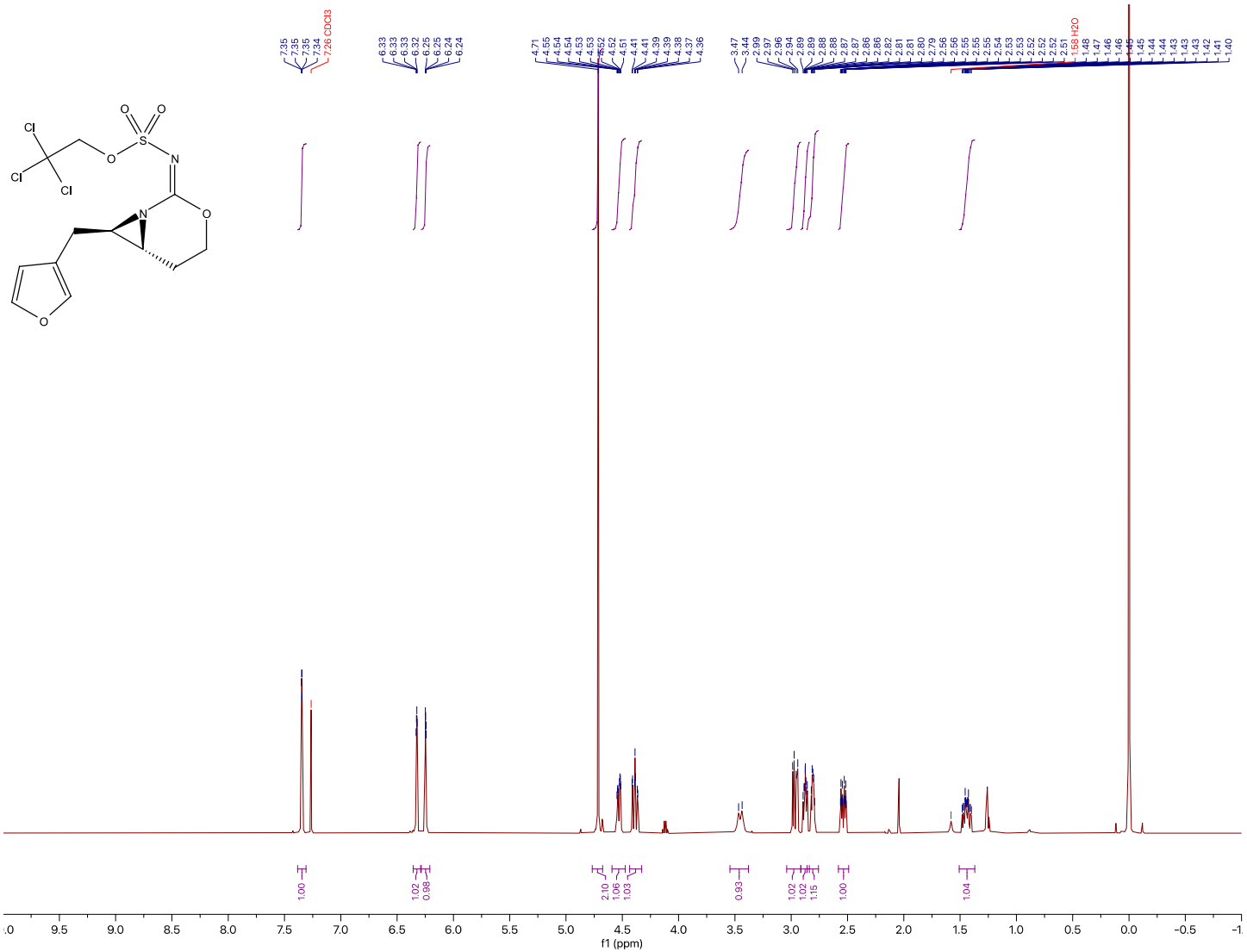
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2h**



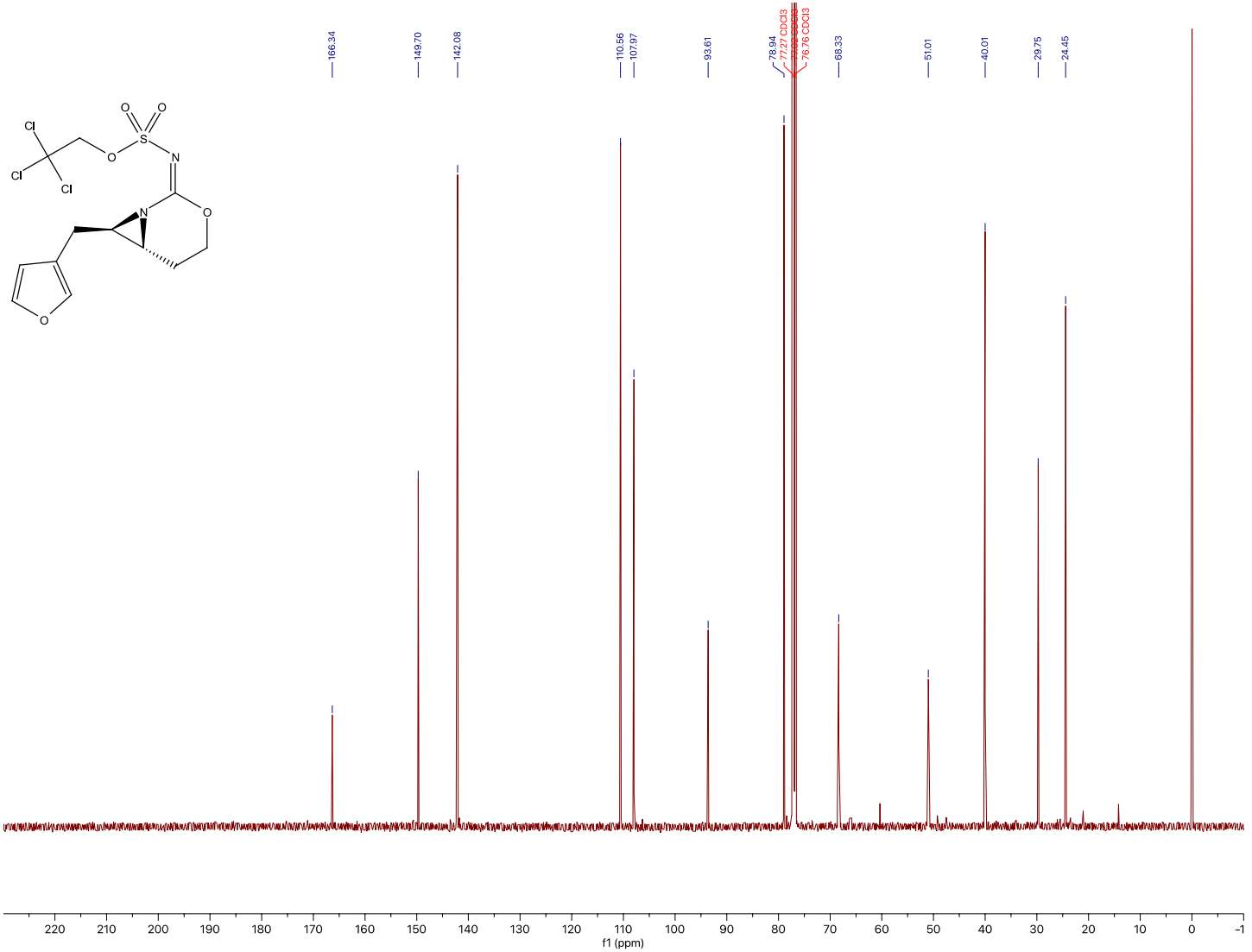
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2h**



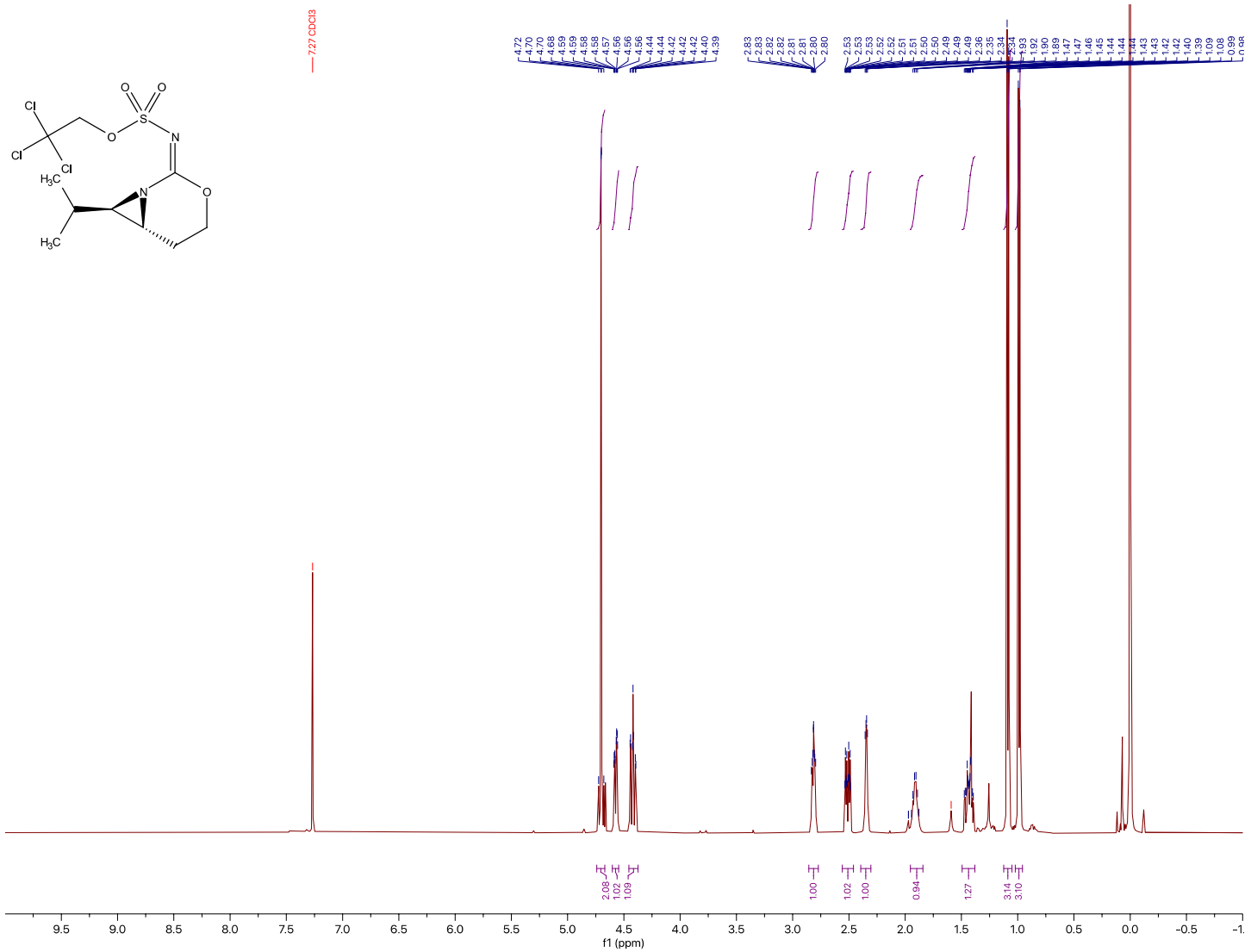
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2i**



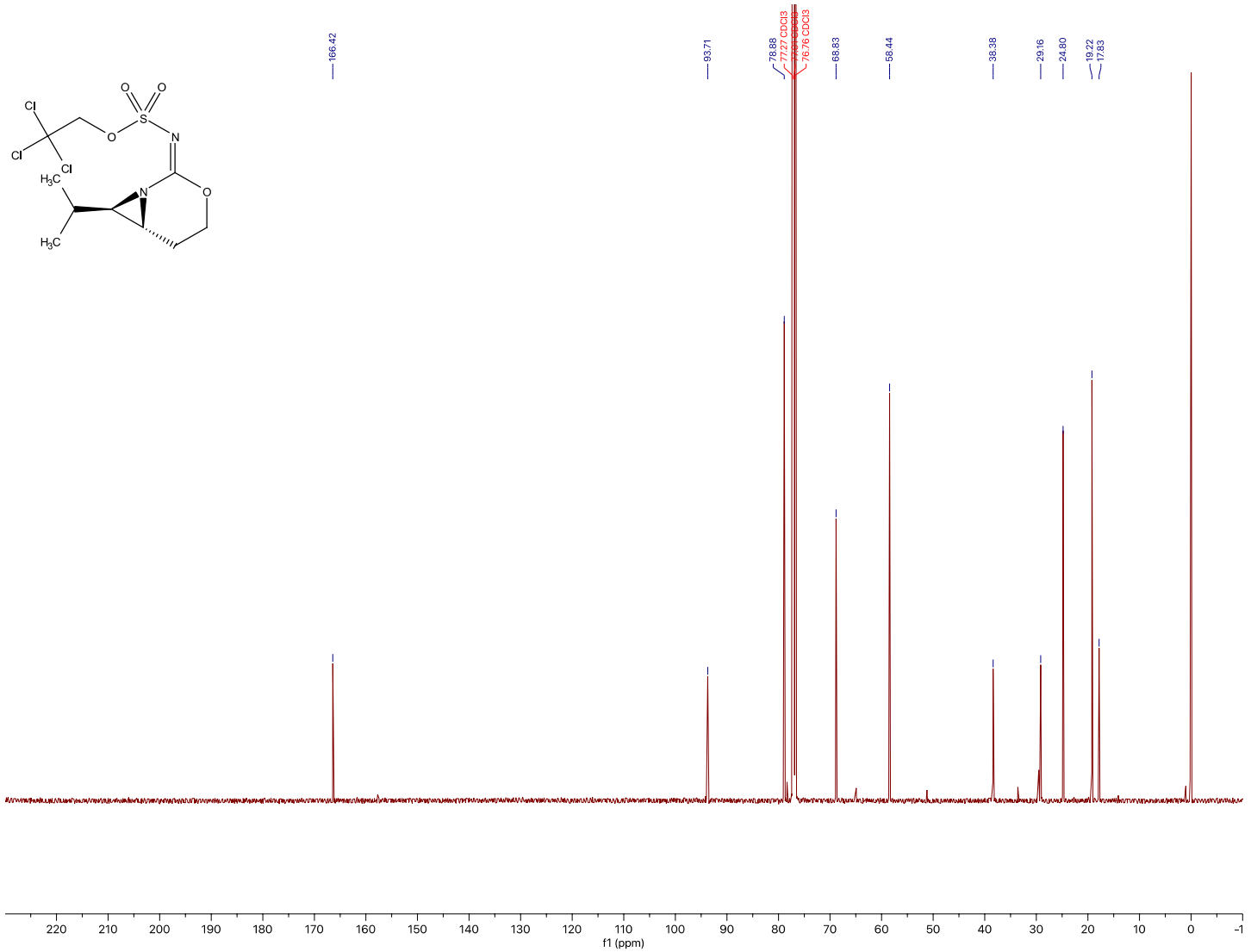
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2i**



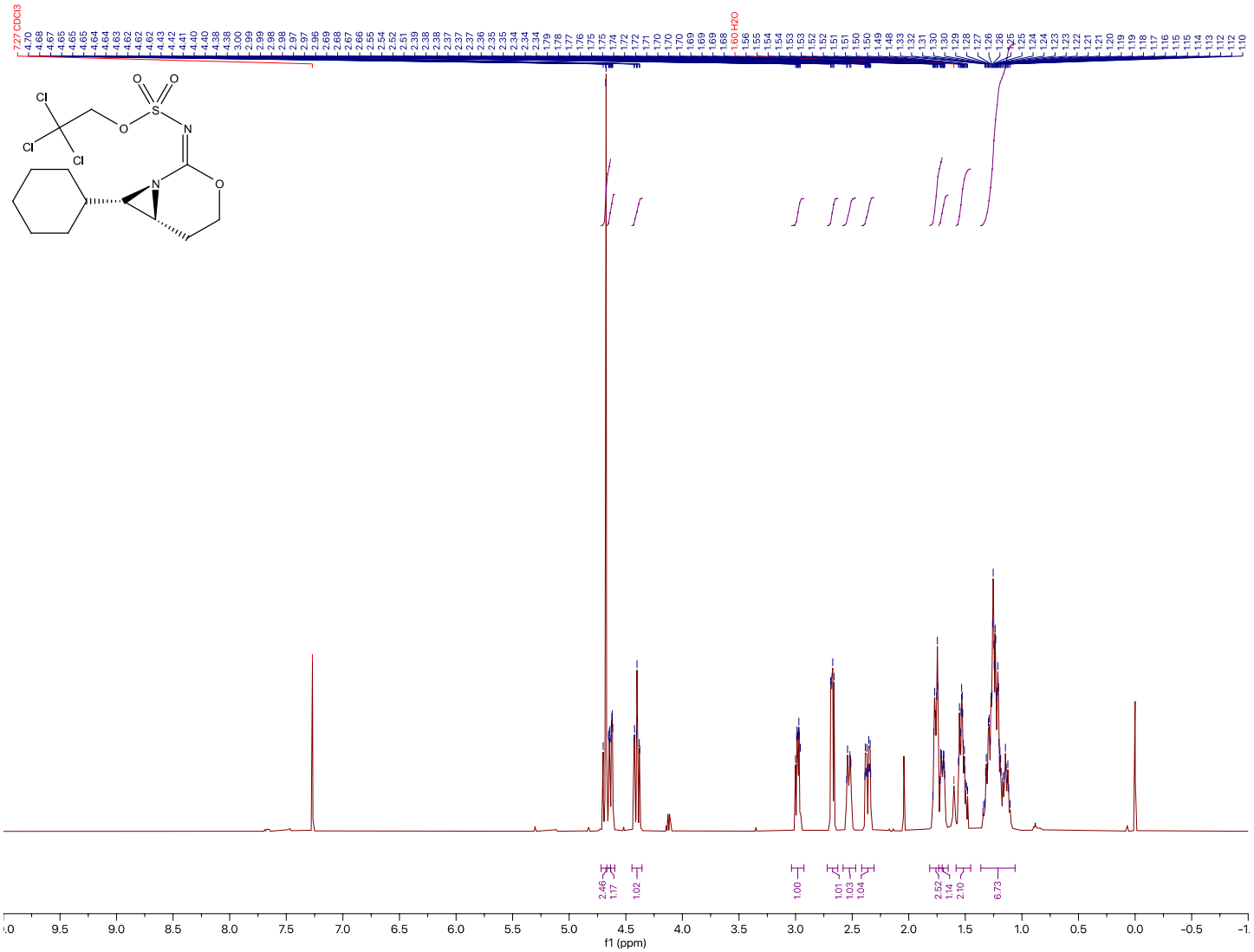
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2j**



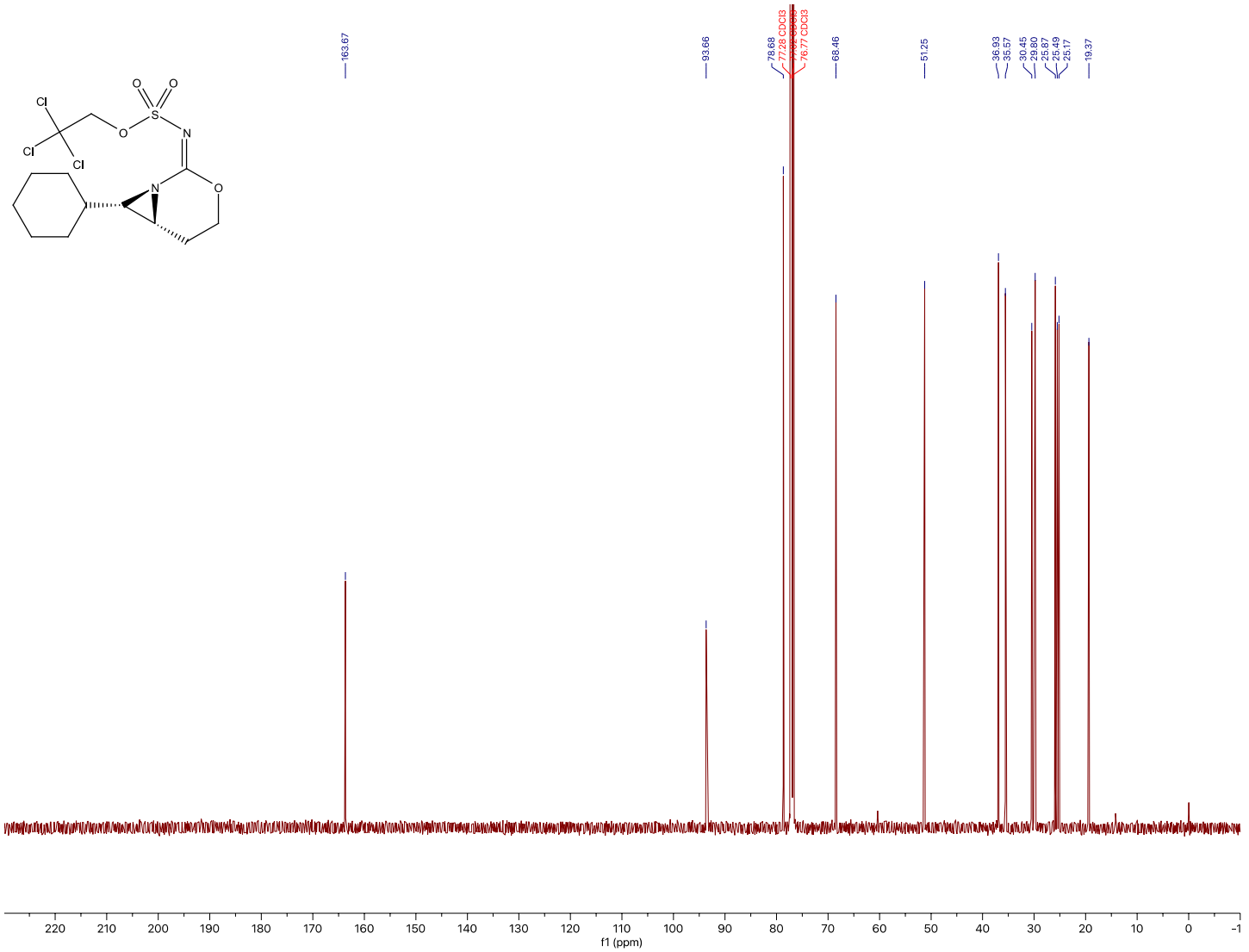
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2j**



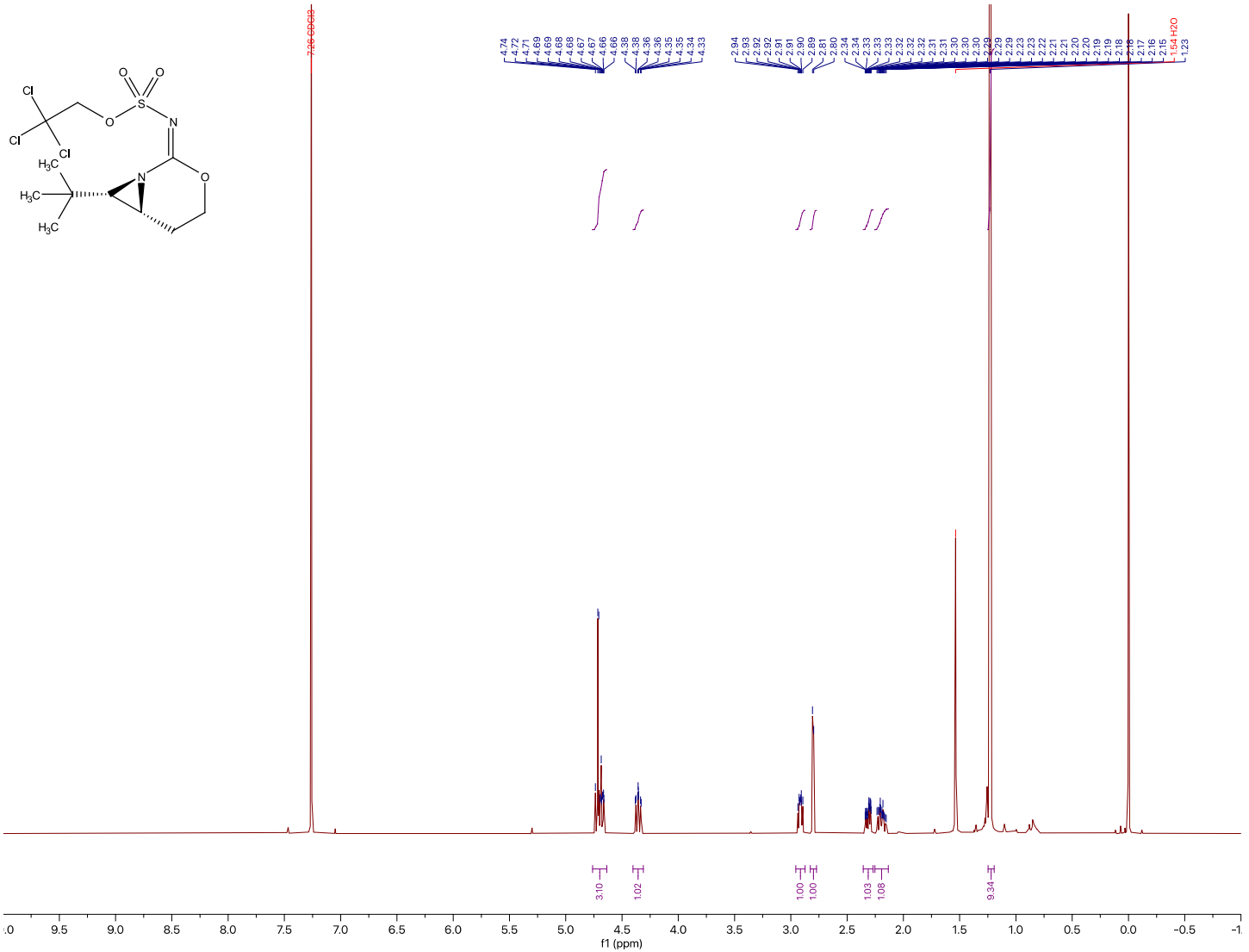
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2k**



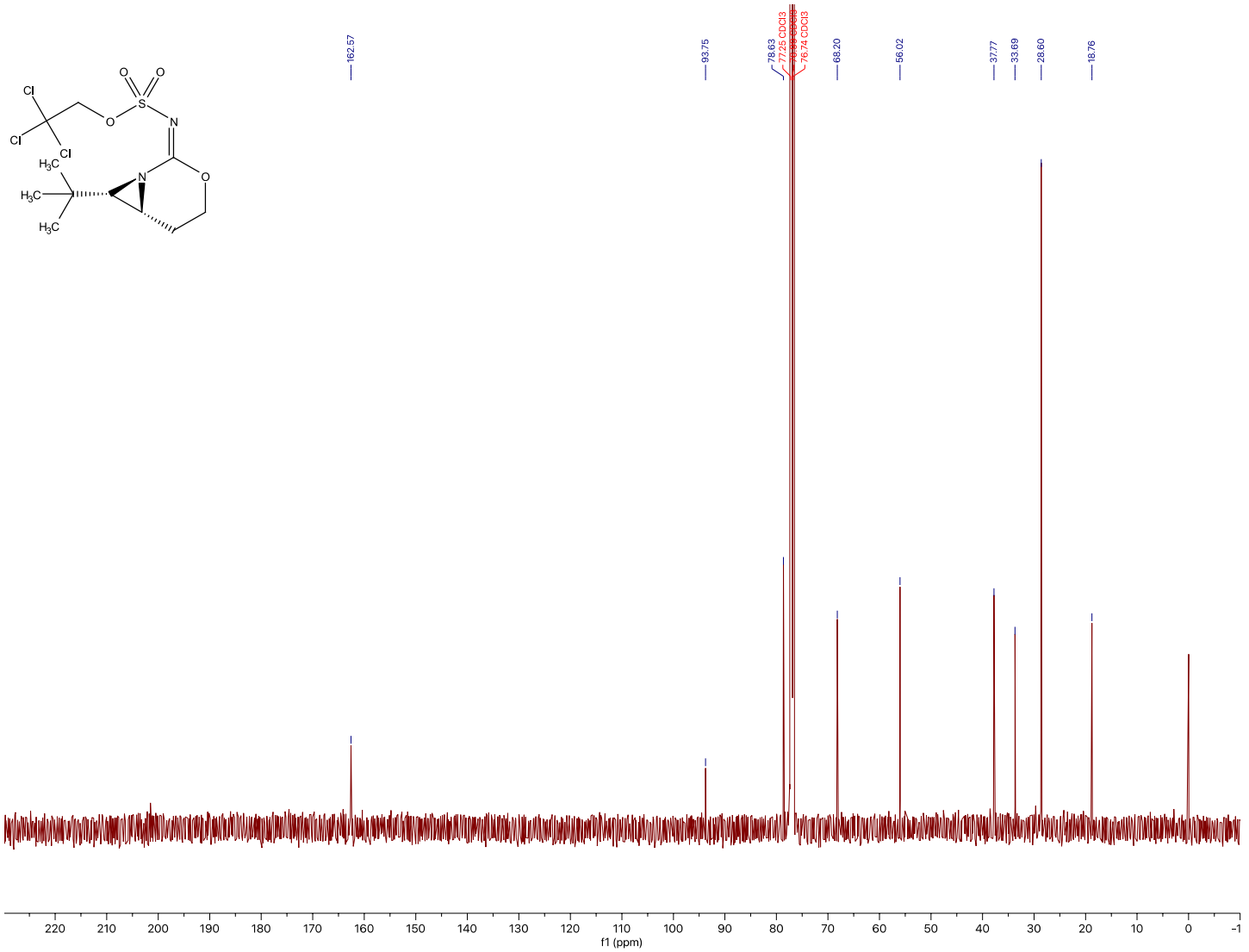
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2k**



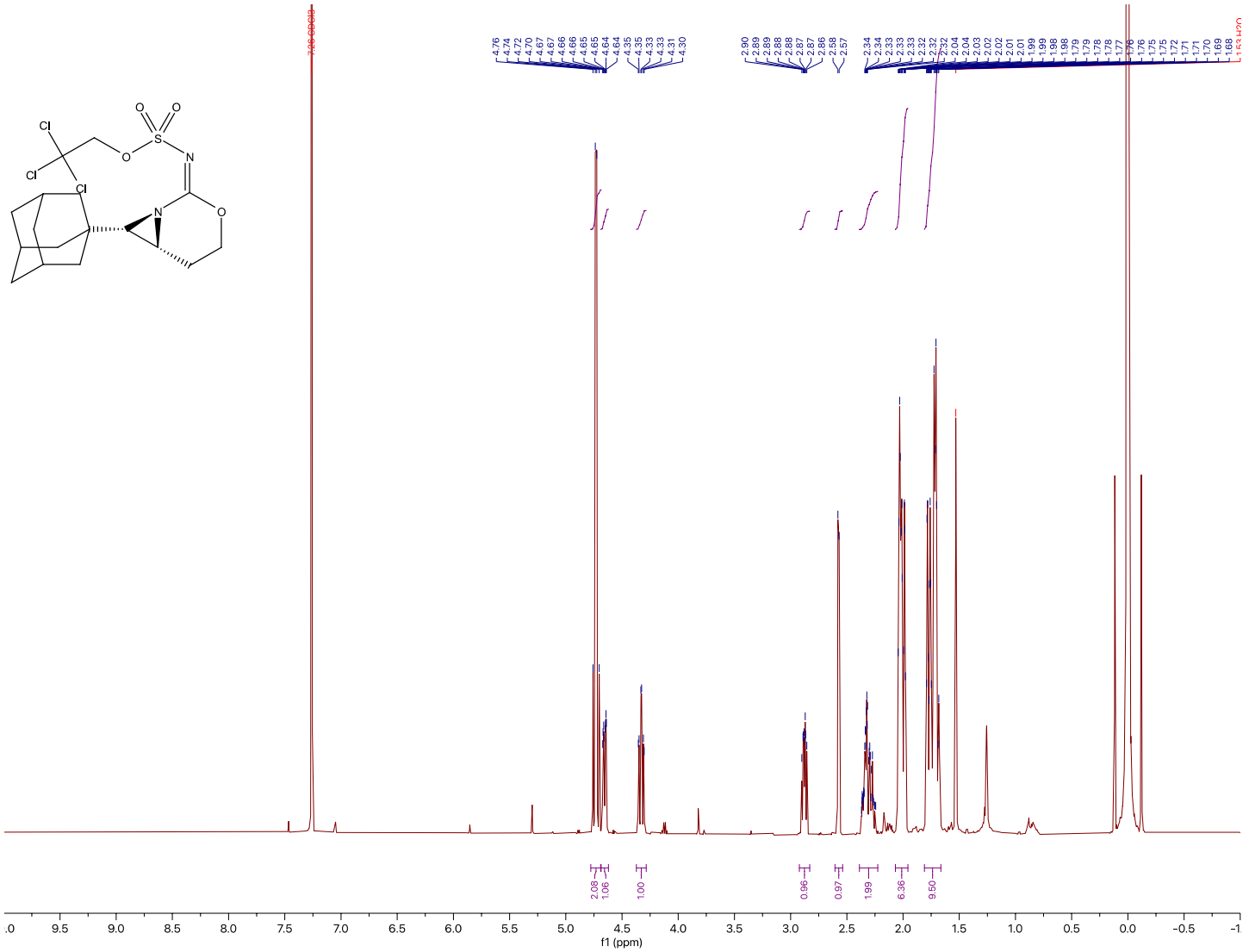
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2l**



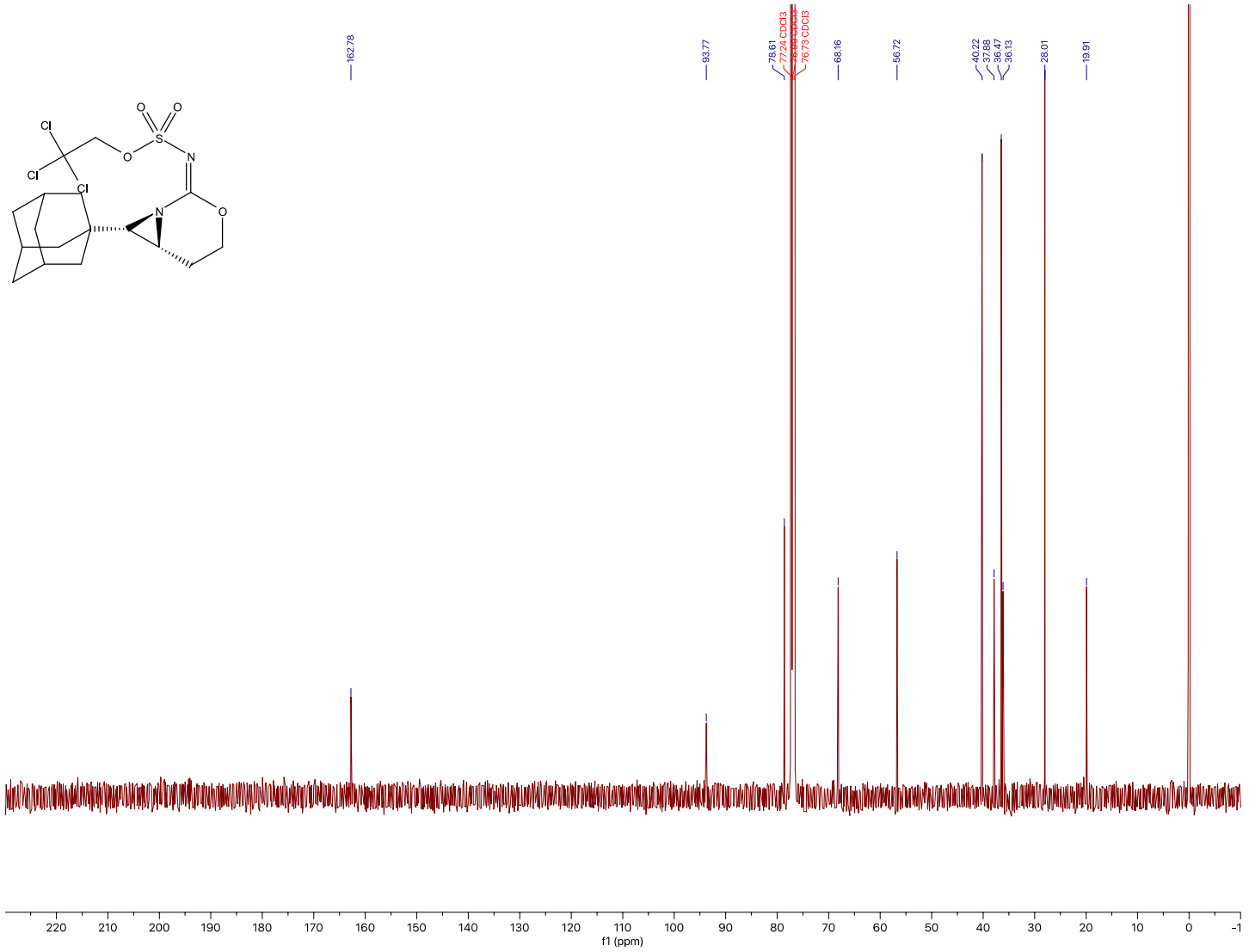
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2l**



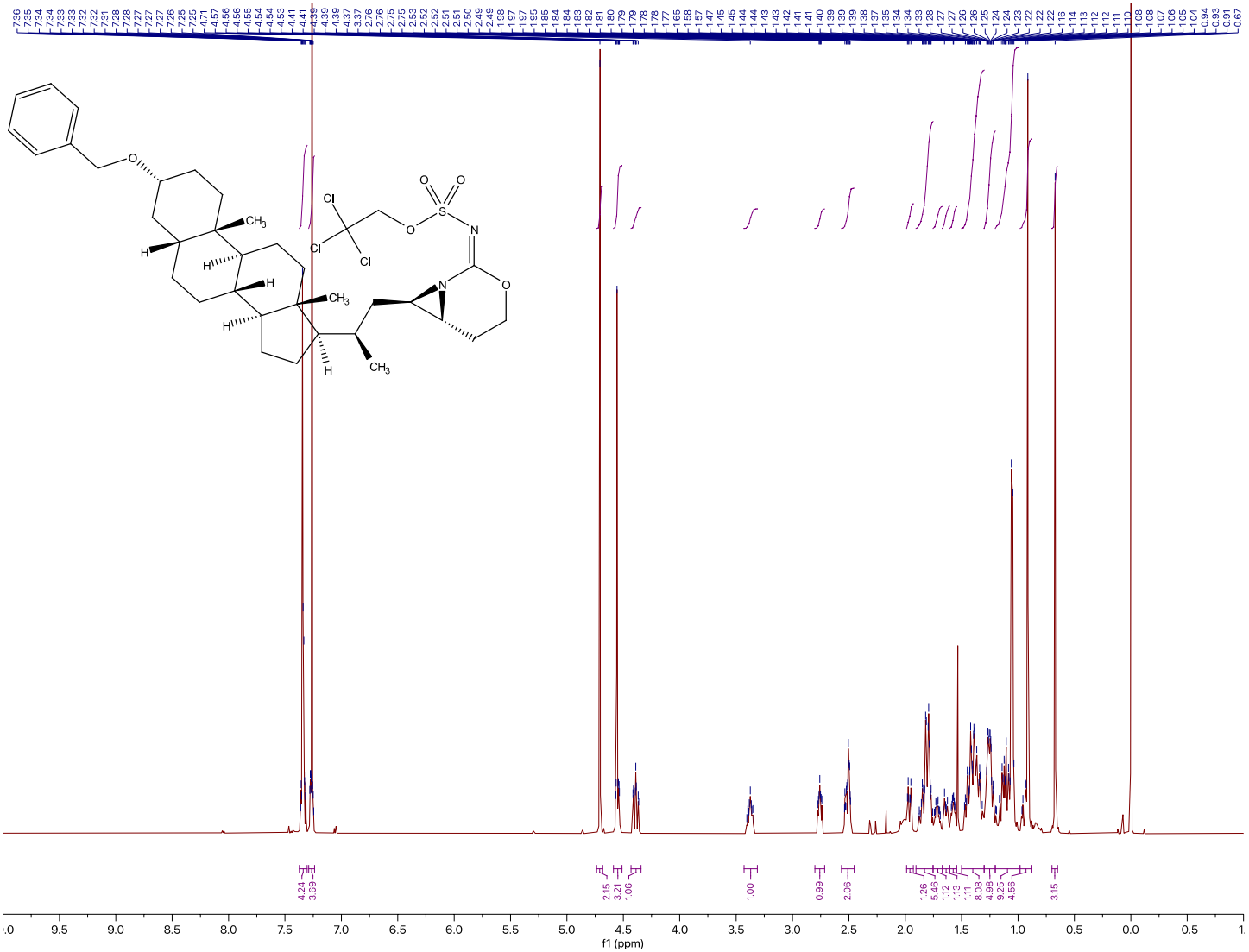
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2m**



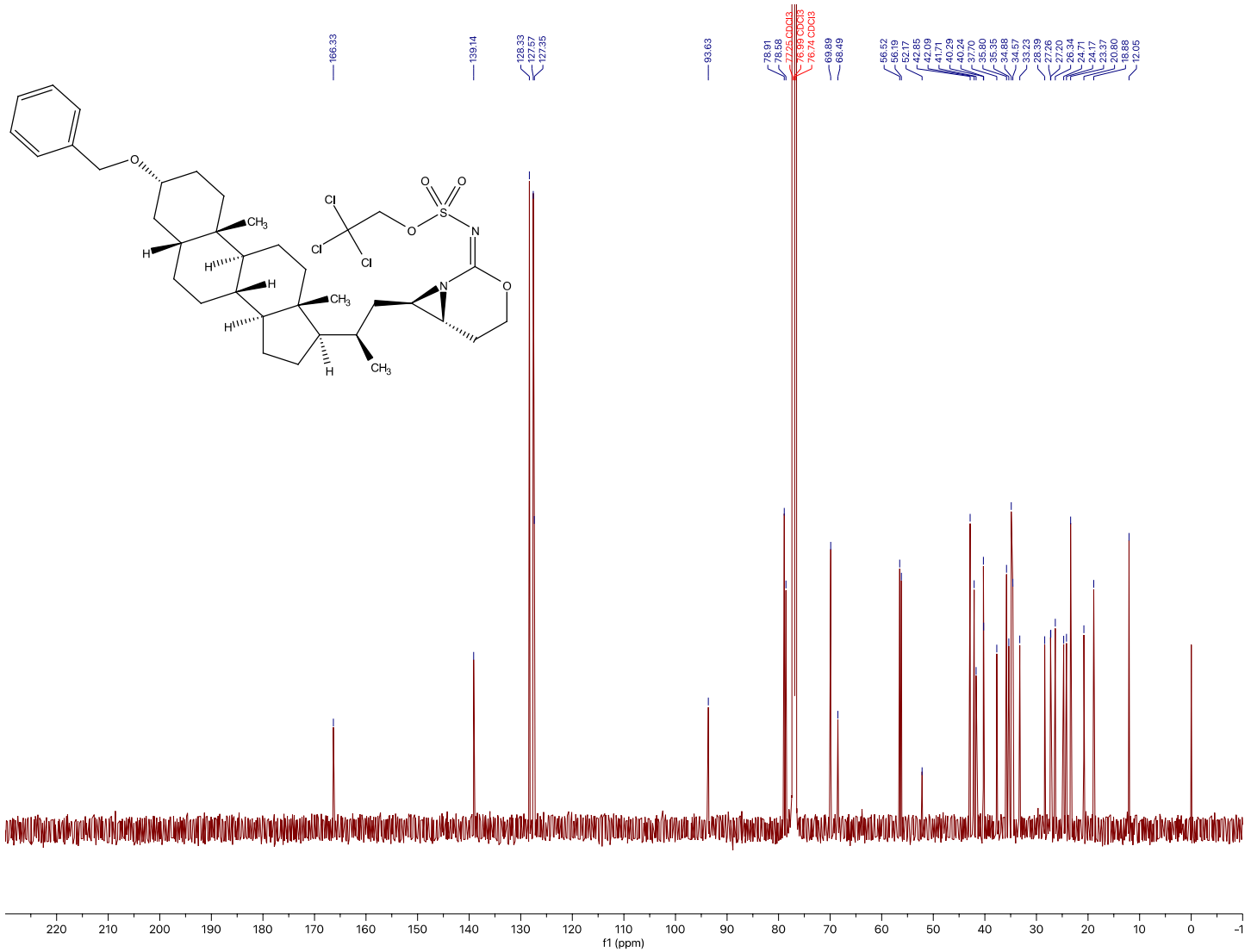
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2m**



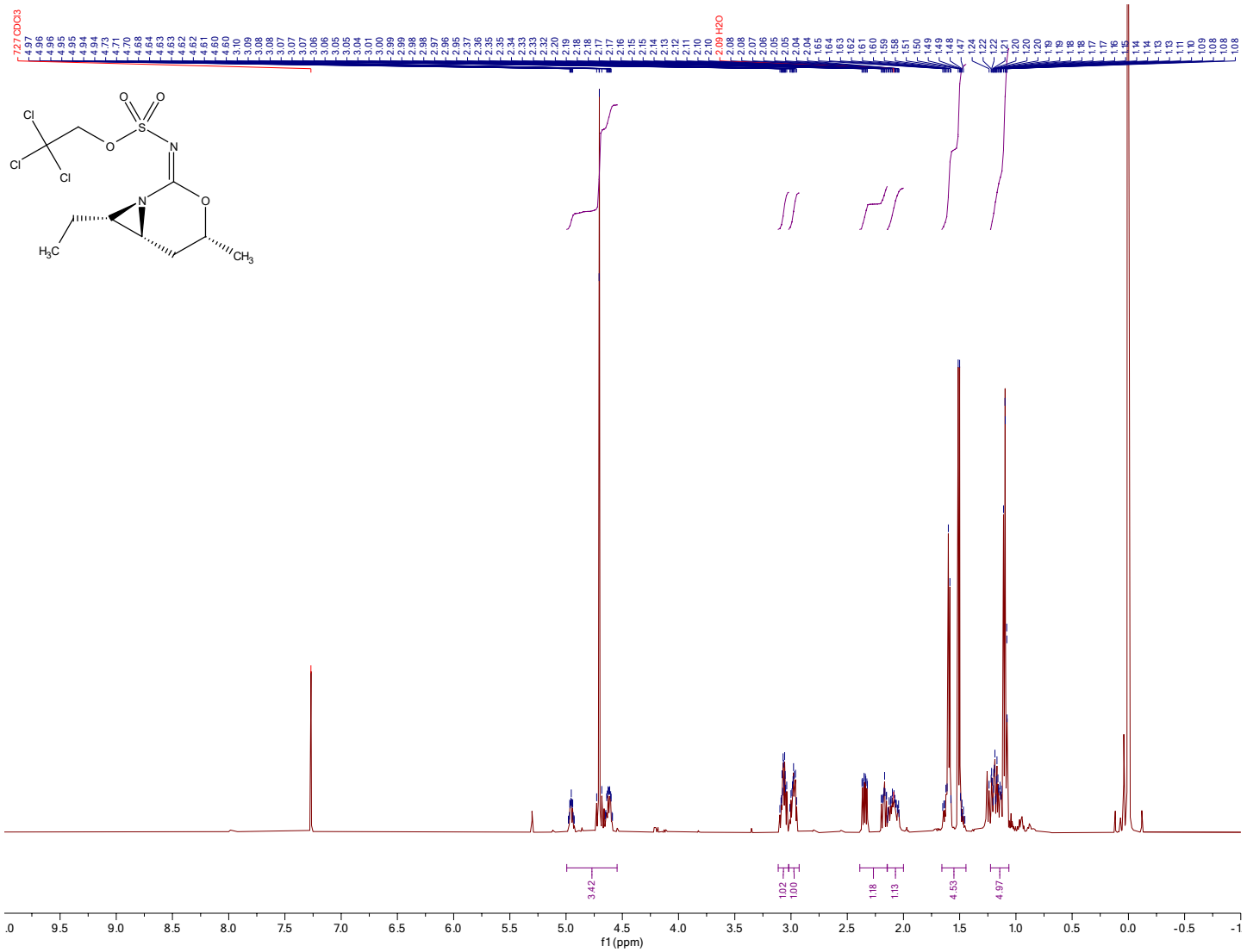
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2n**



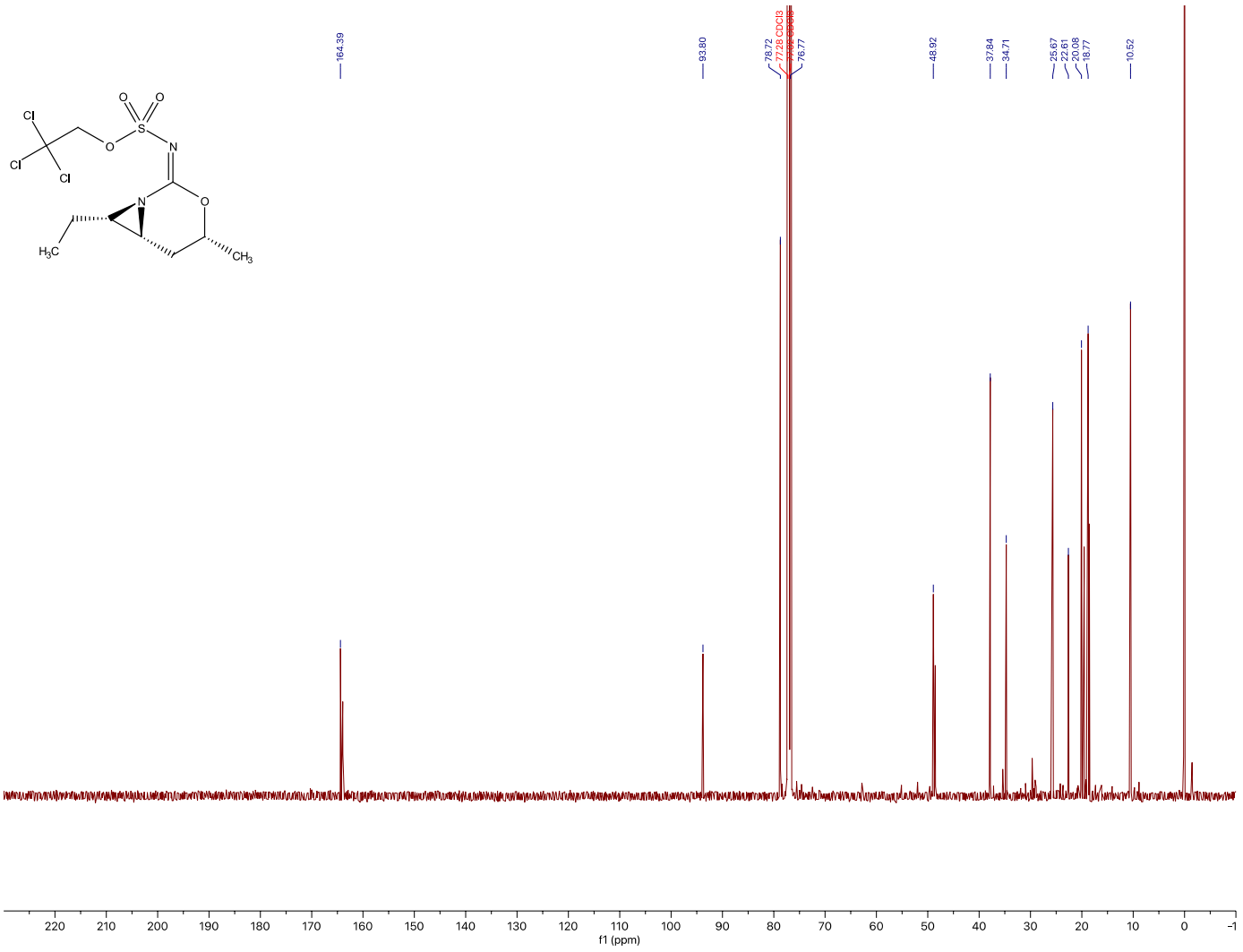
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2n**



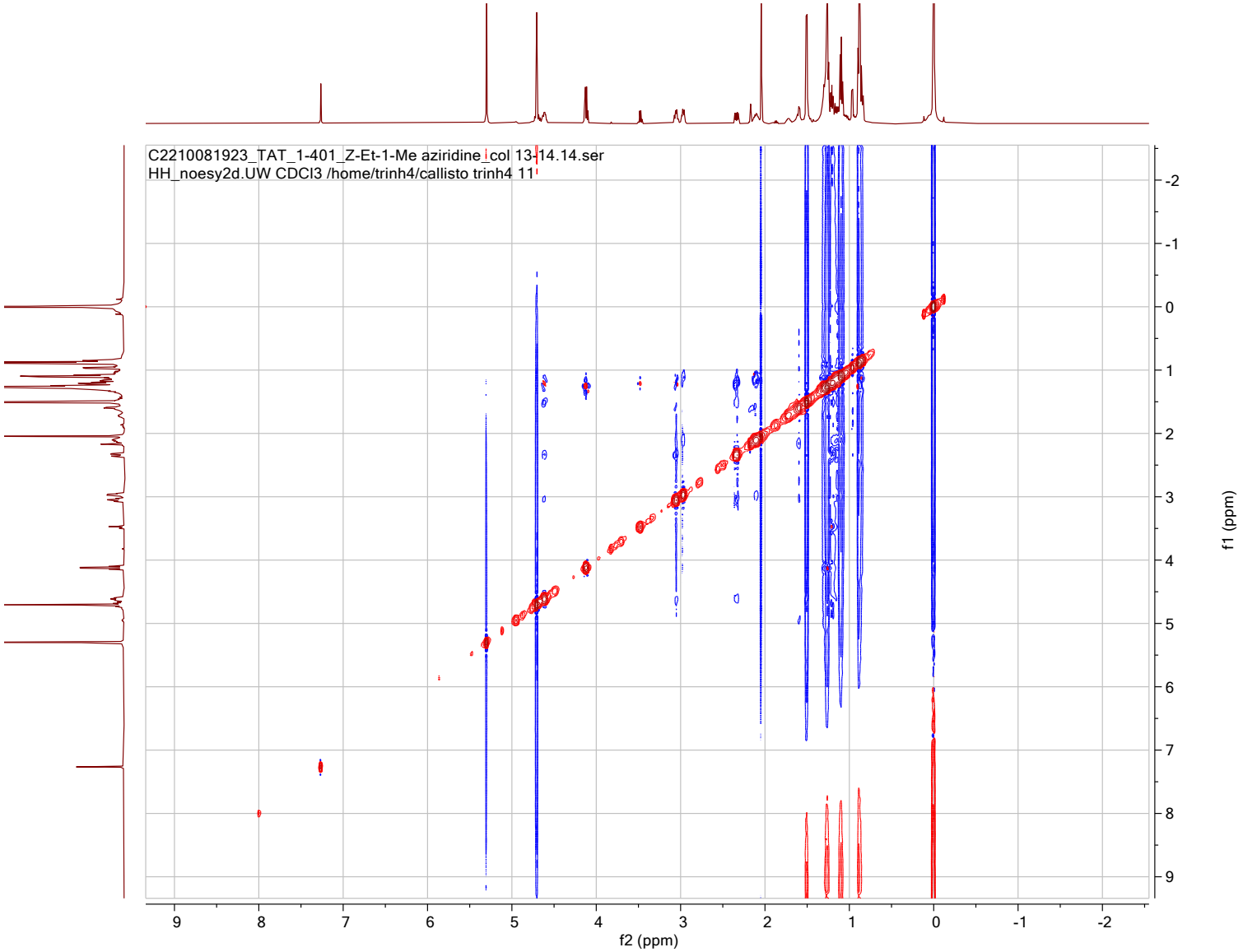
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2o** (major diastereomer)



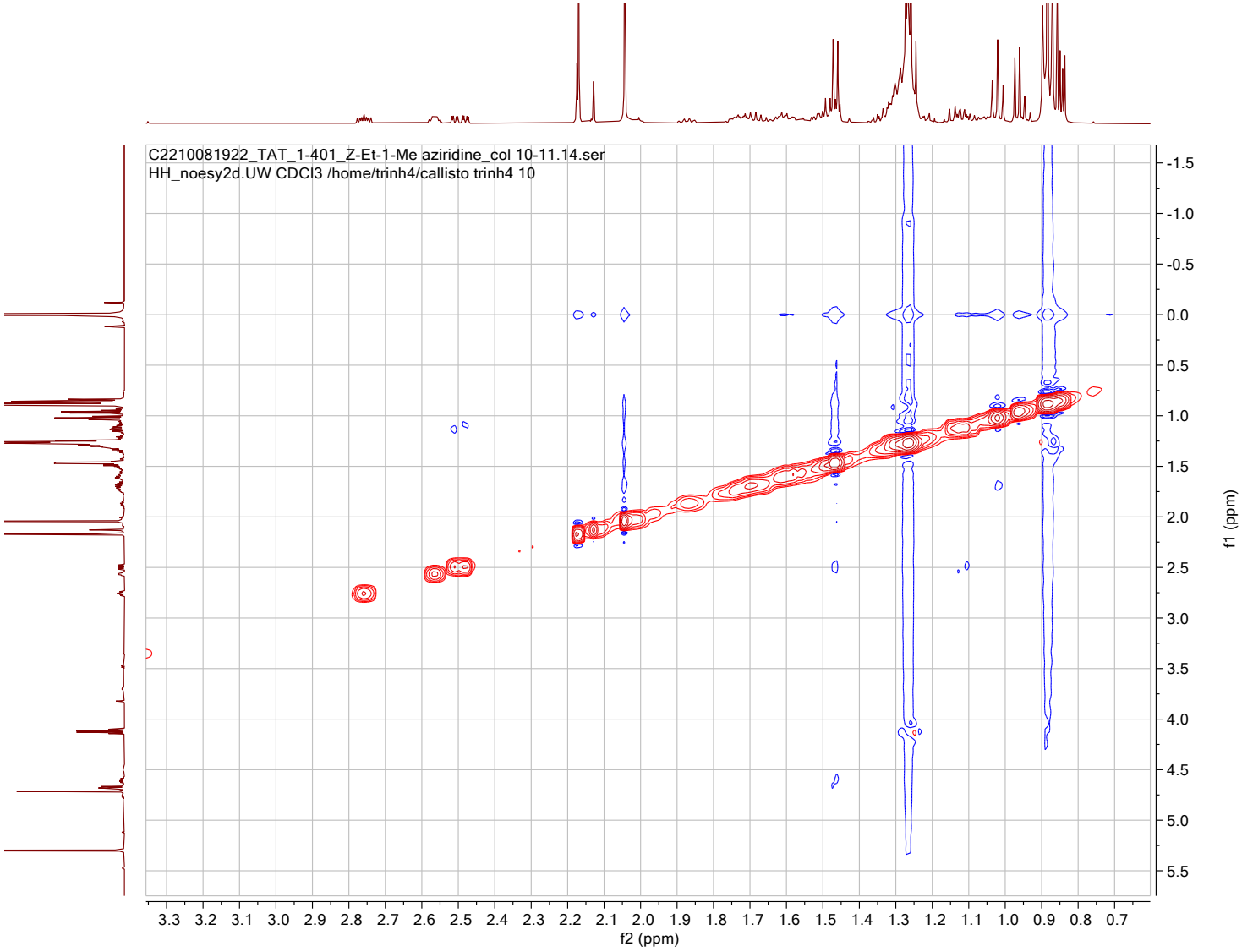
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2o** (major diastereomer)



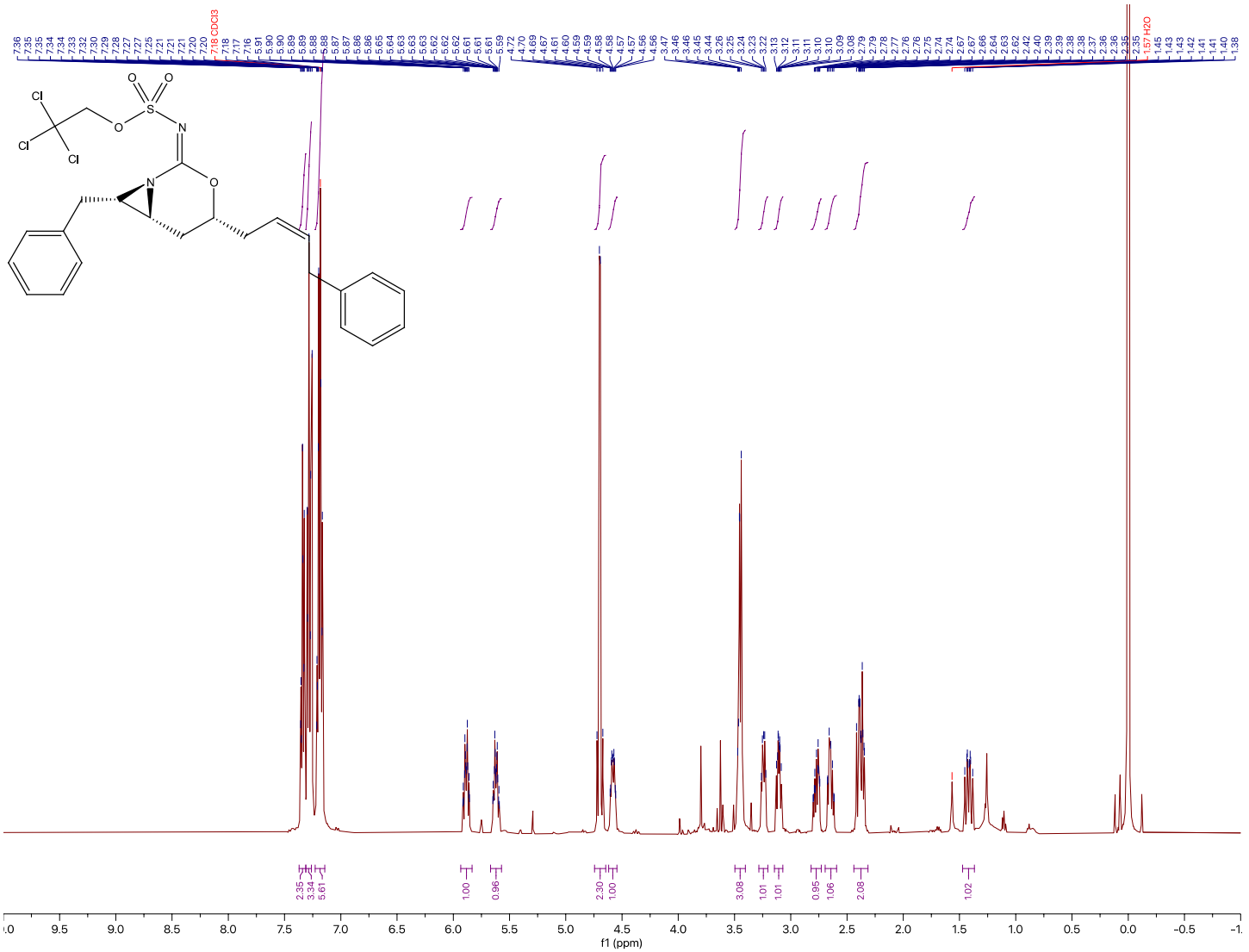
NOESY NMR (500 MHz, $CDCl_3$) for **Compound 2o** (major diastereomer).



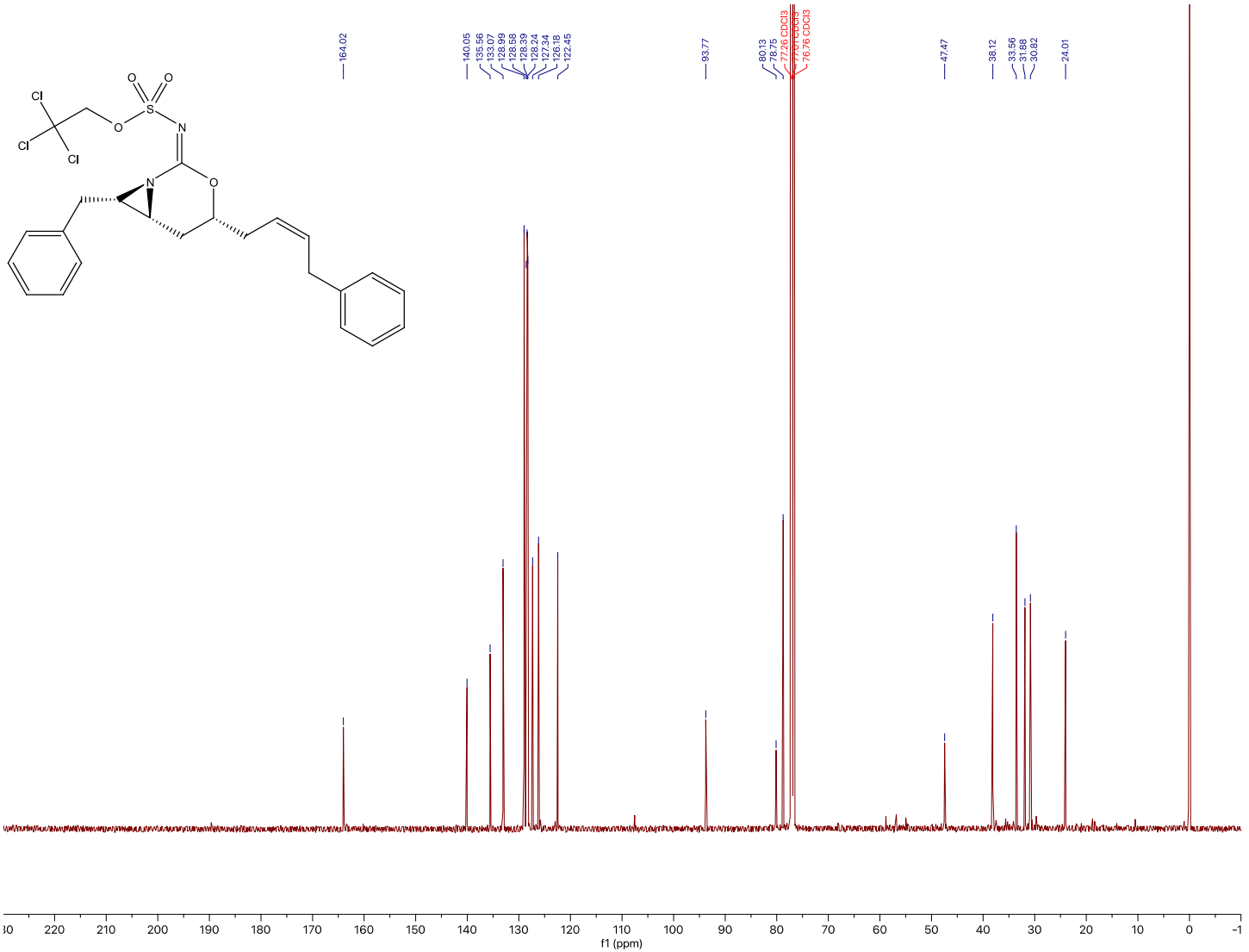
NOESY NMR (500 MHz, $CDCl_3$) for **Compound 2o** (minor diastereomer).



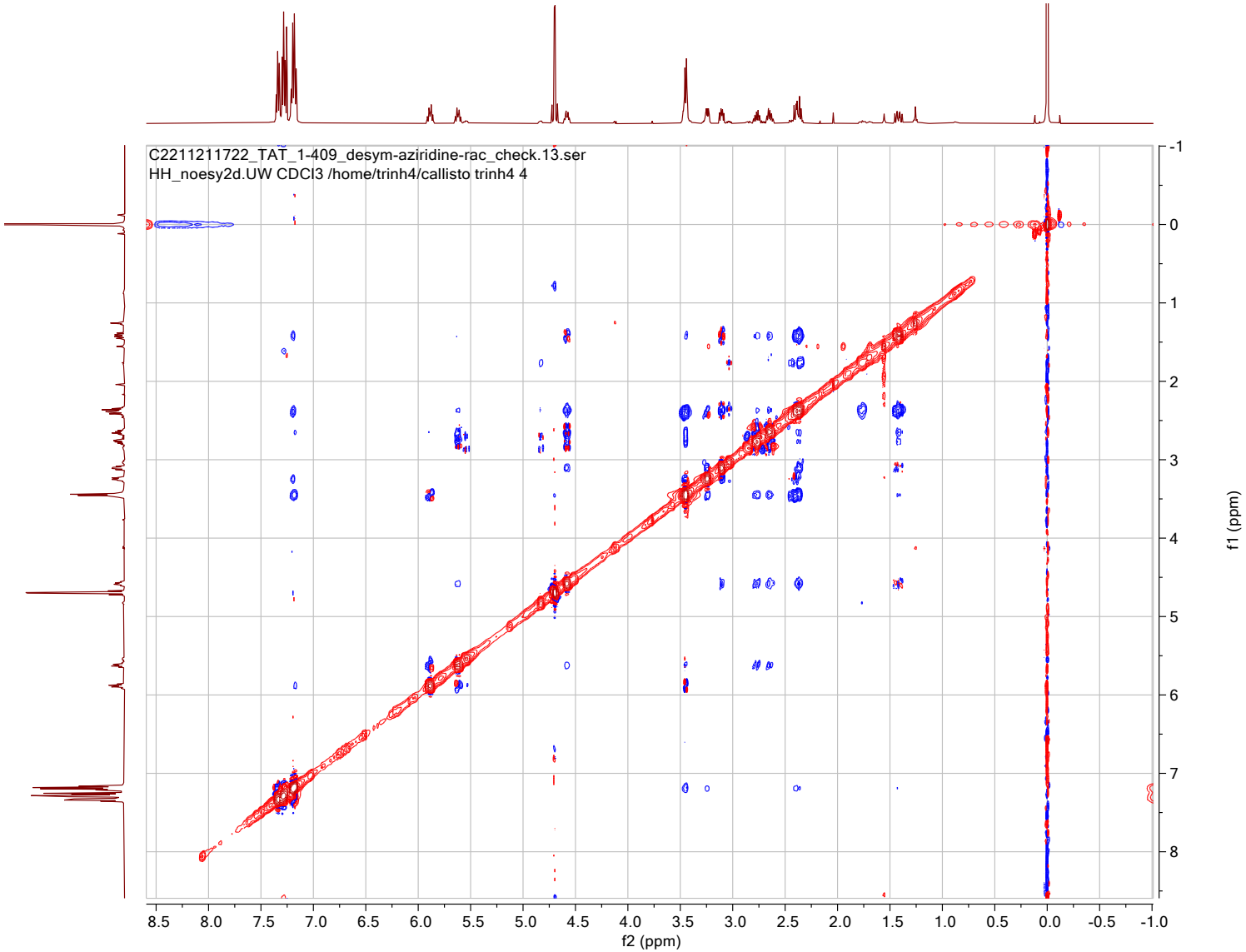
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2p**



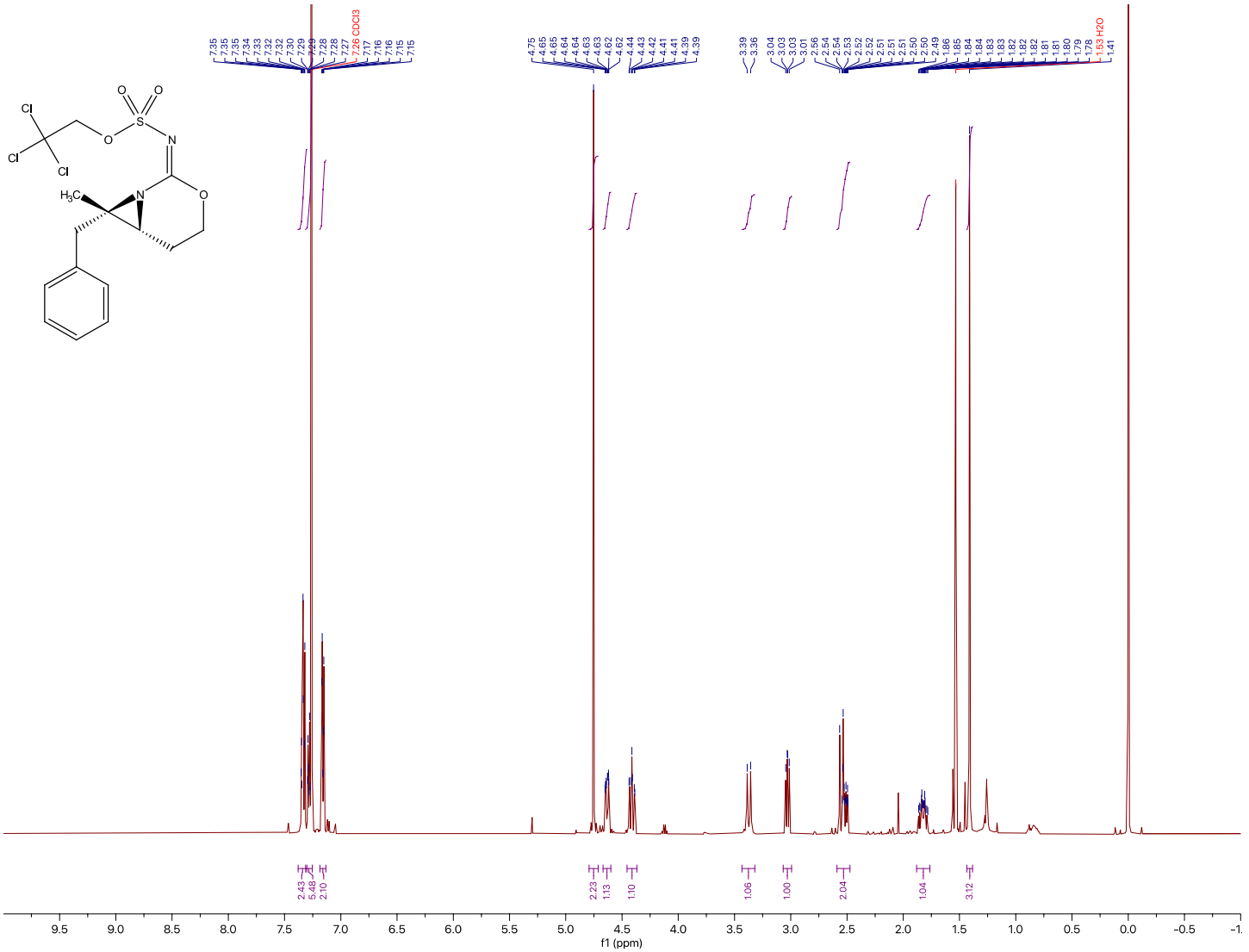
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2p**



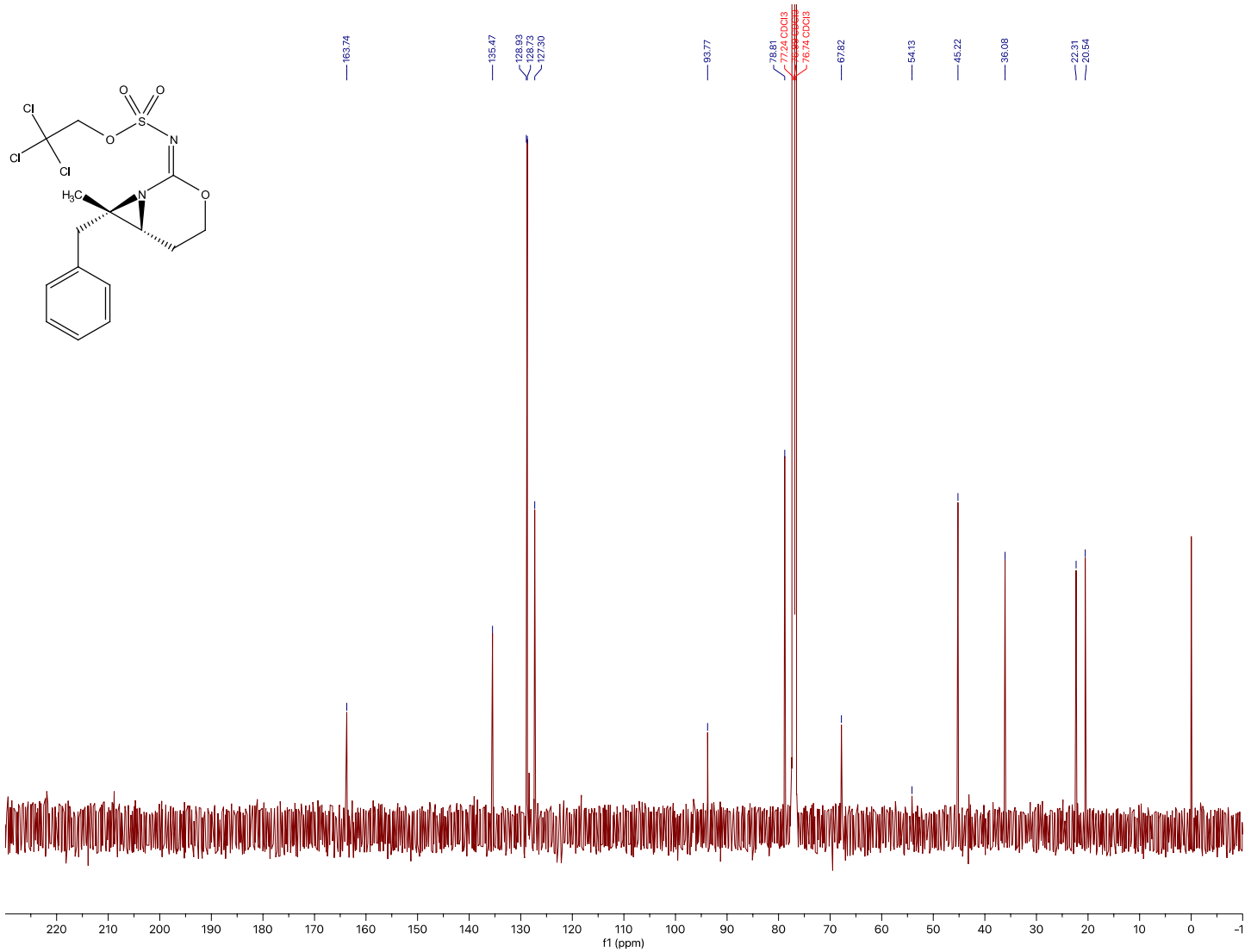
NOESY NMR (500 MHz, $CDCl_3$) for **Compound 2p**



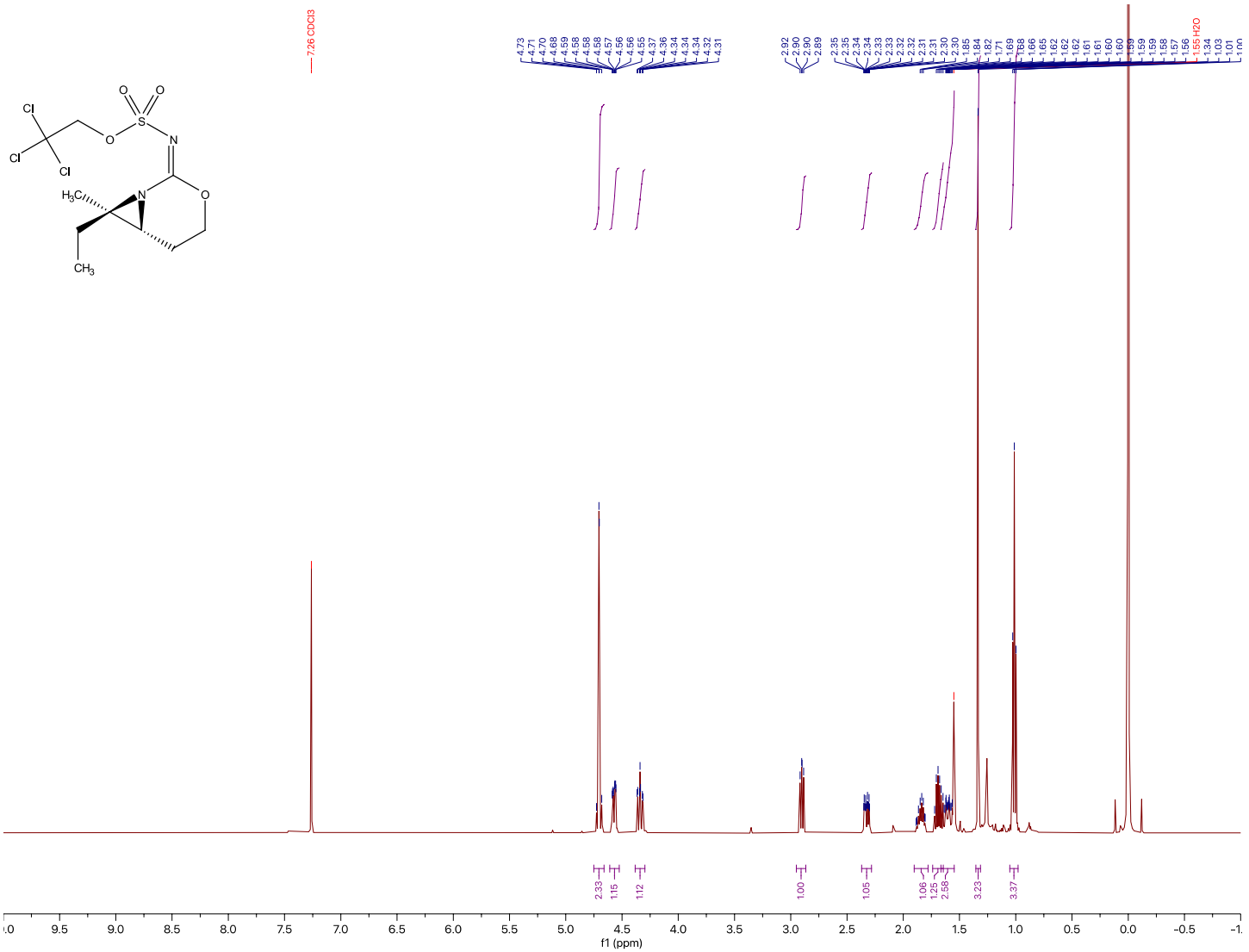
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2q**



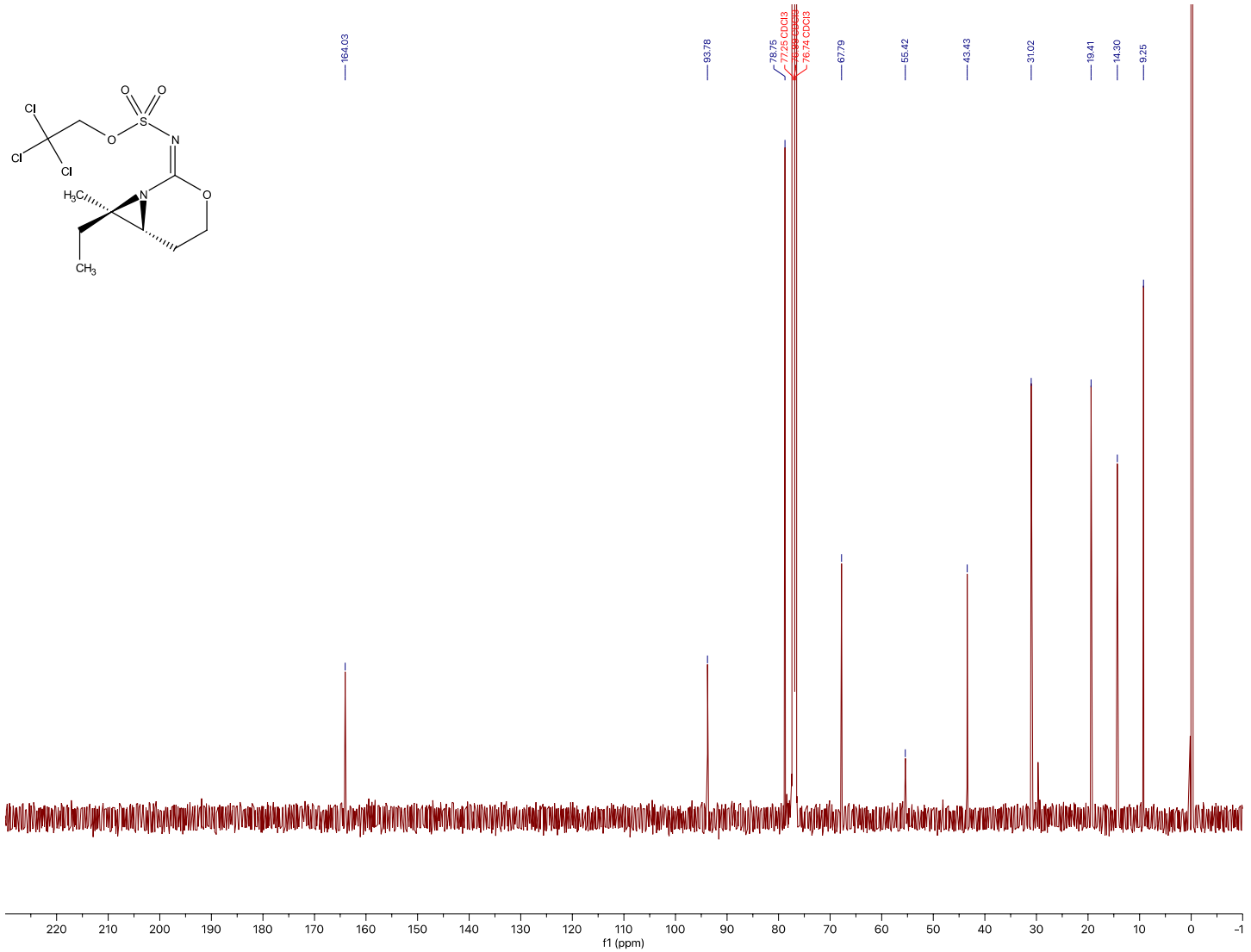
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2q**



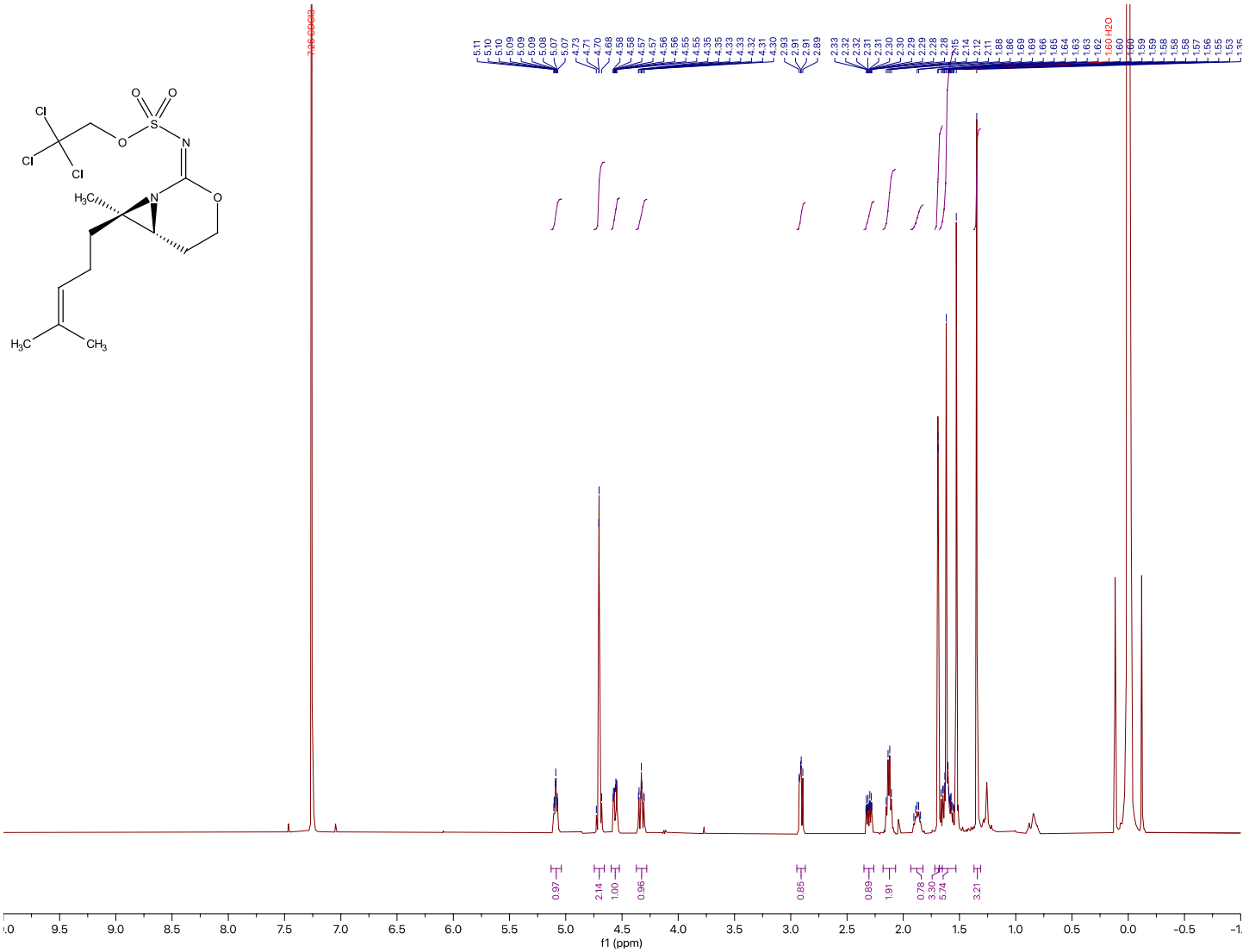
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2r**



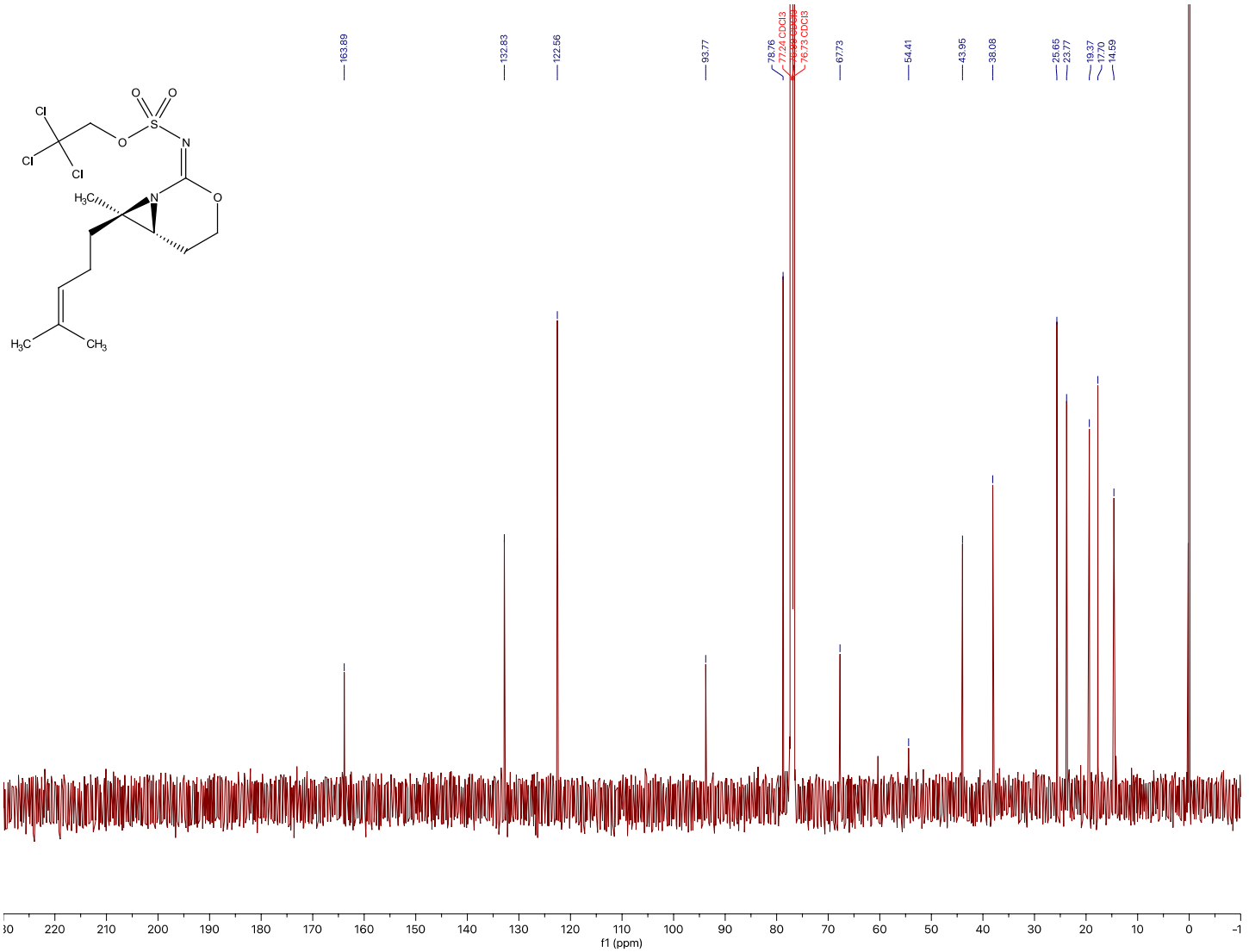
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2r**



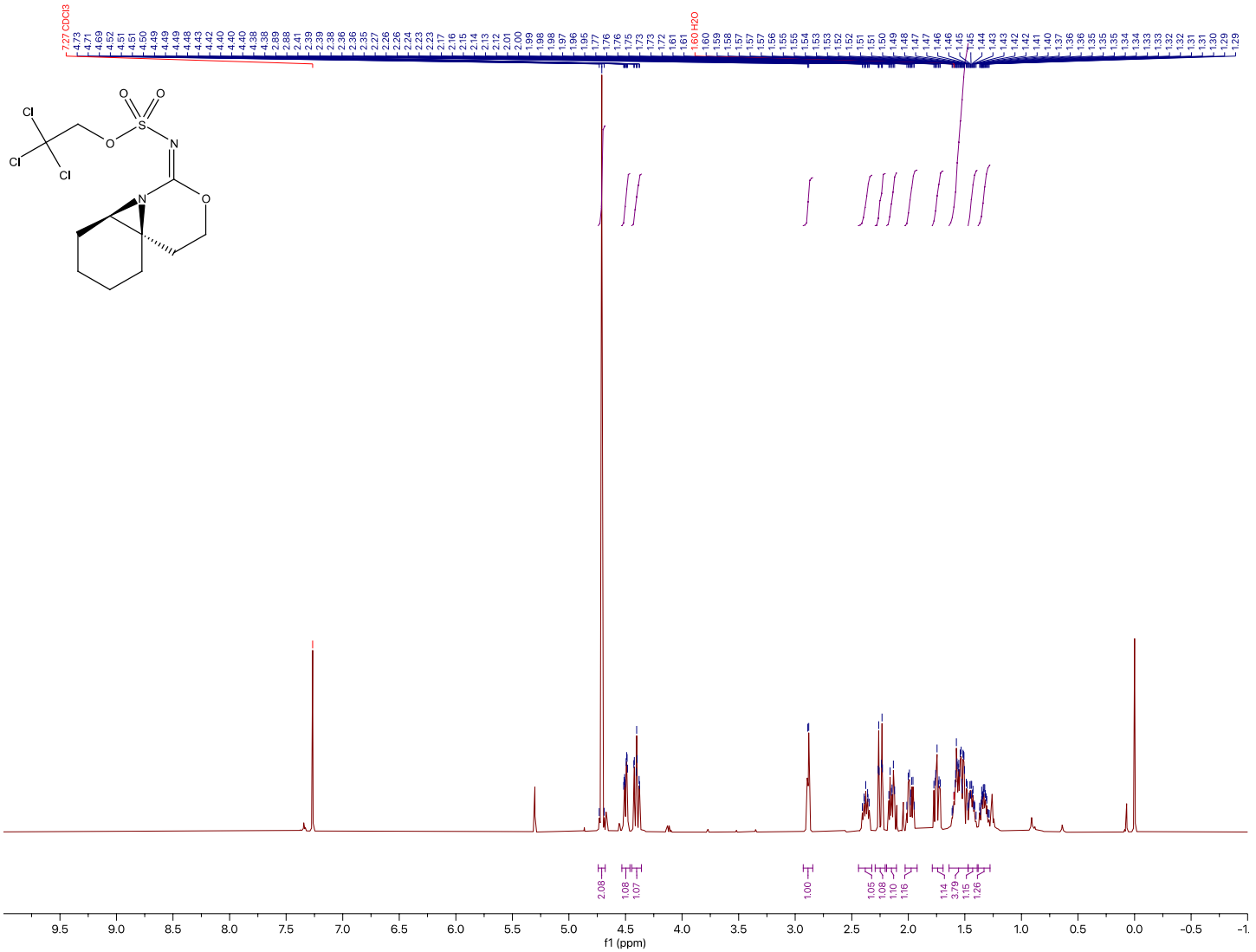
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2s**



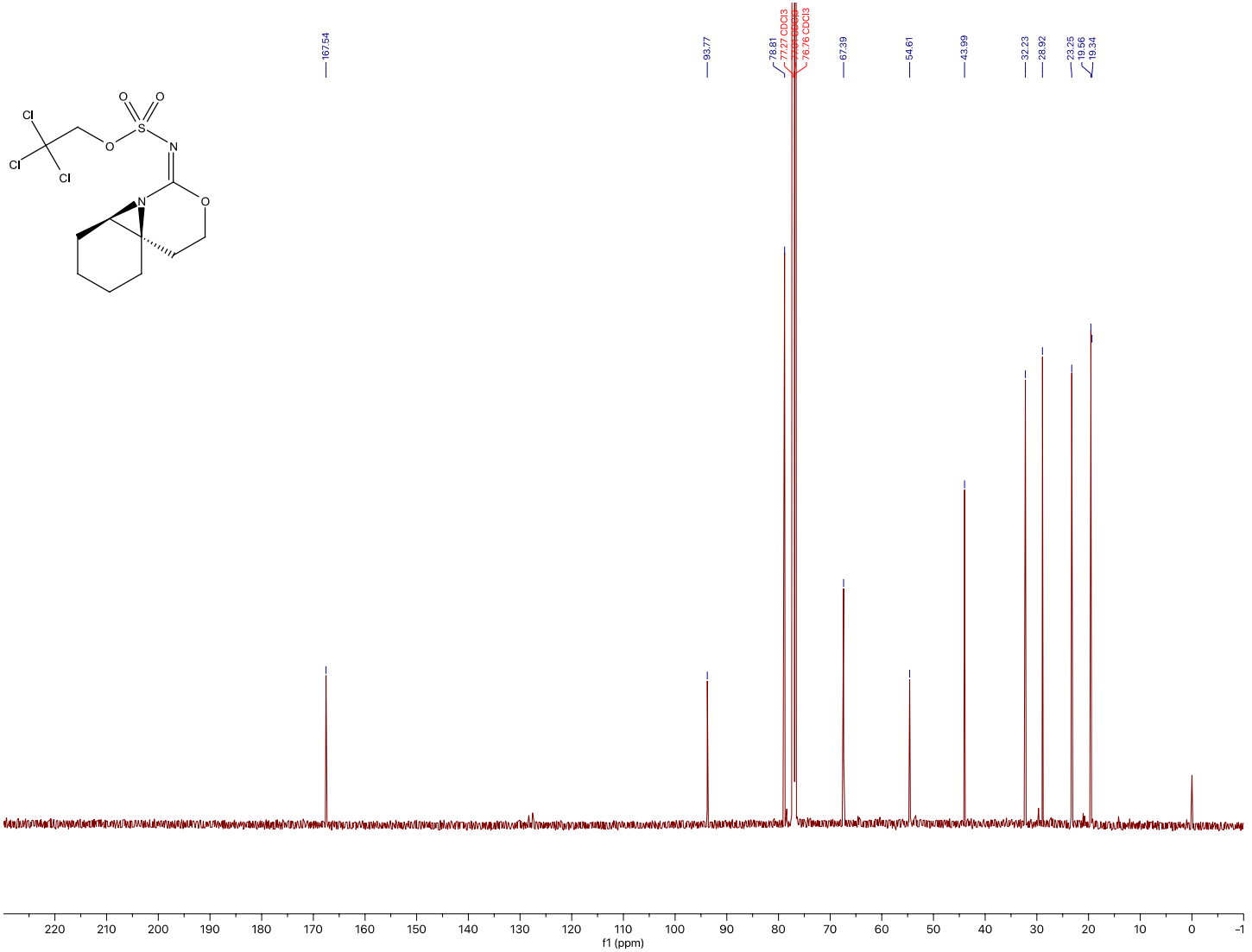
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2s**



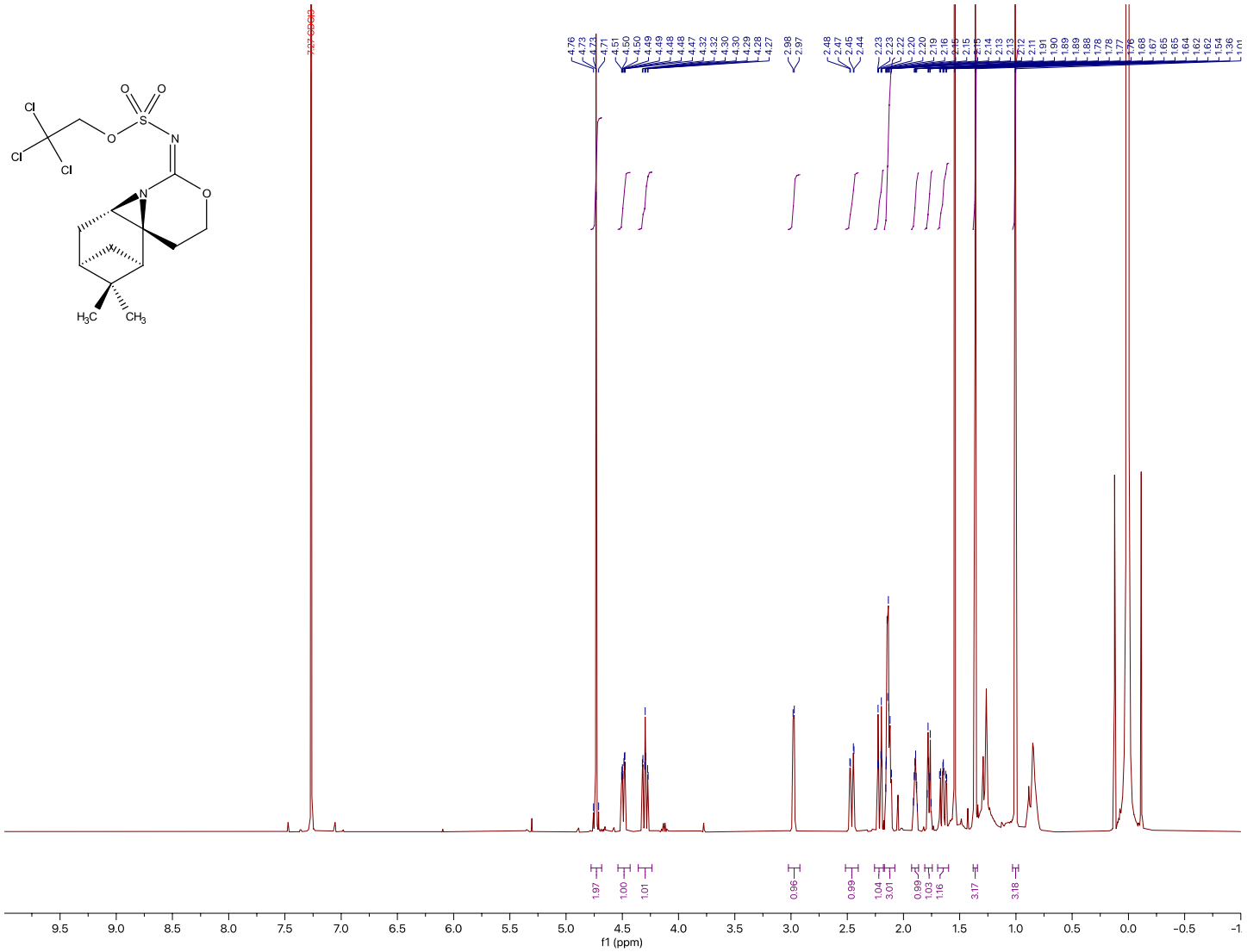
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2t**



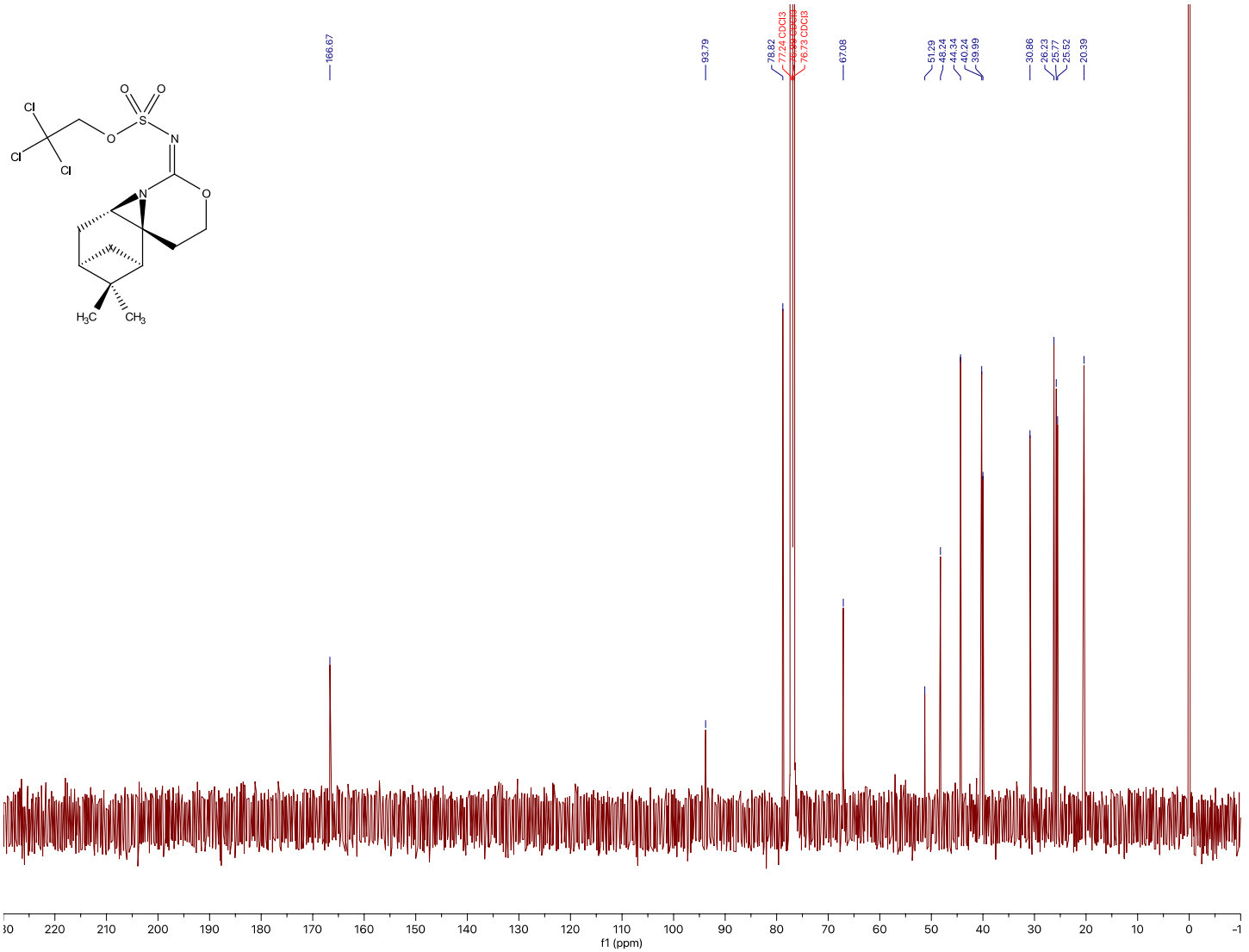
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2t**



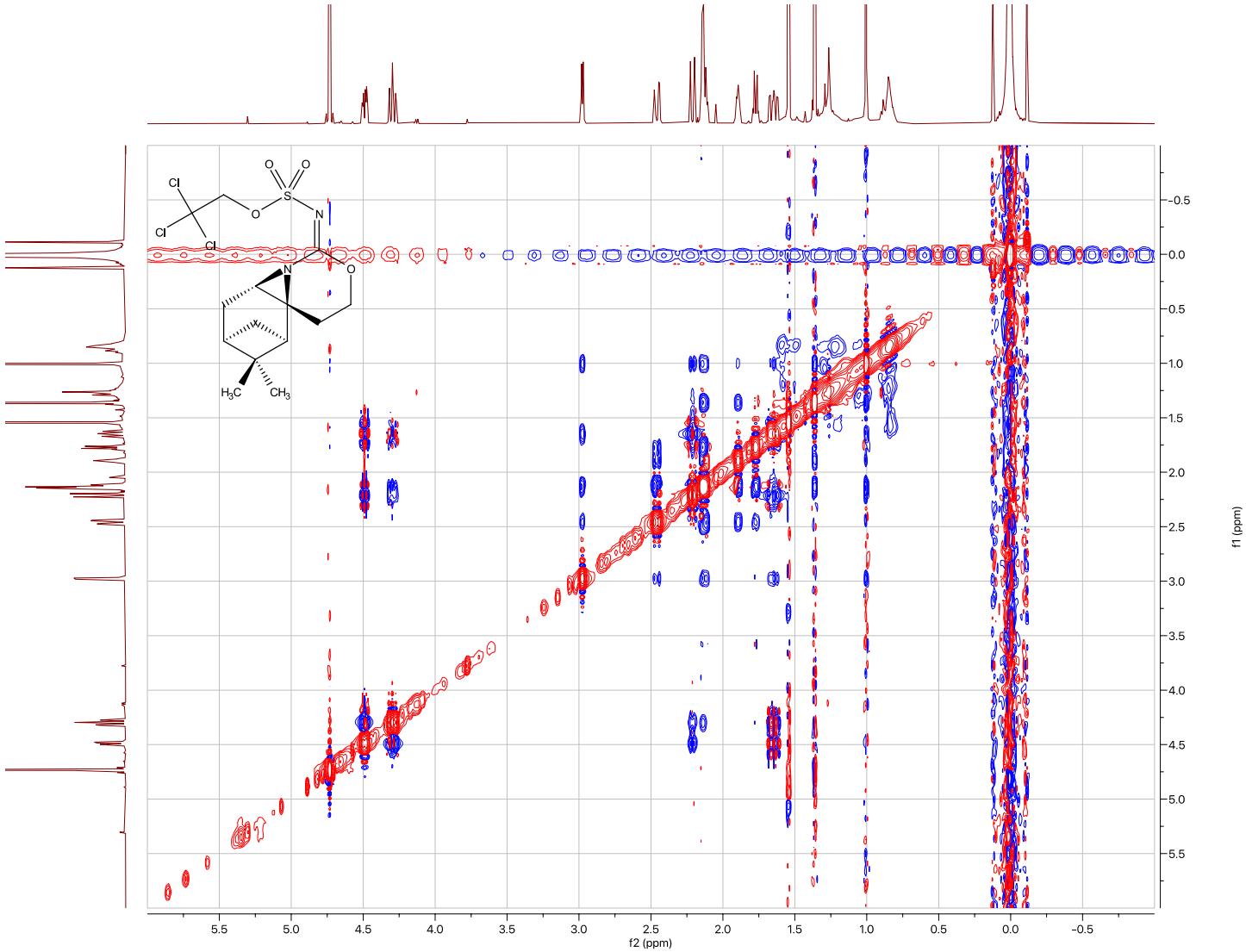
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2u**



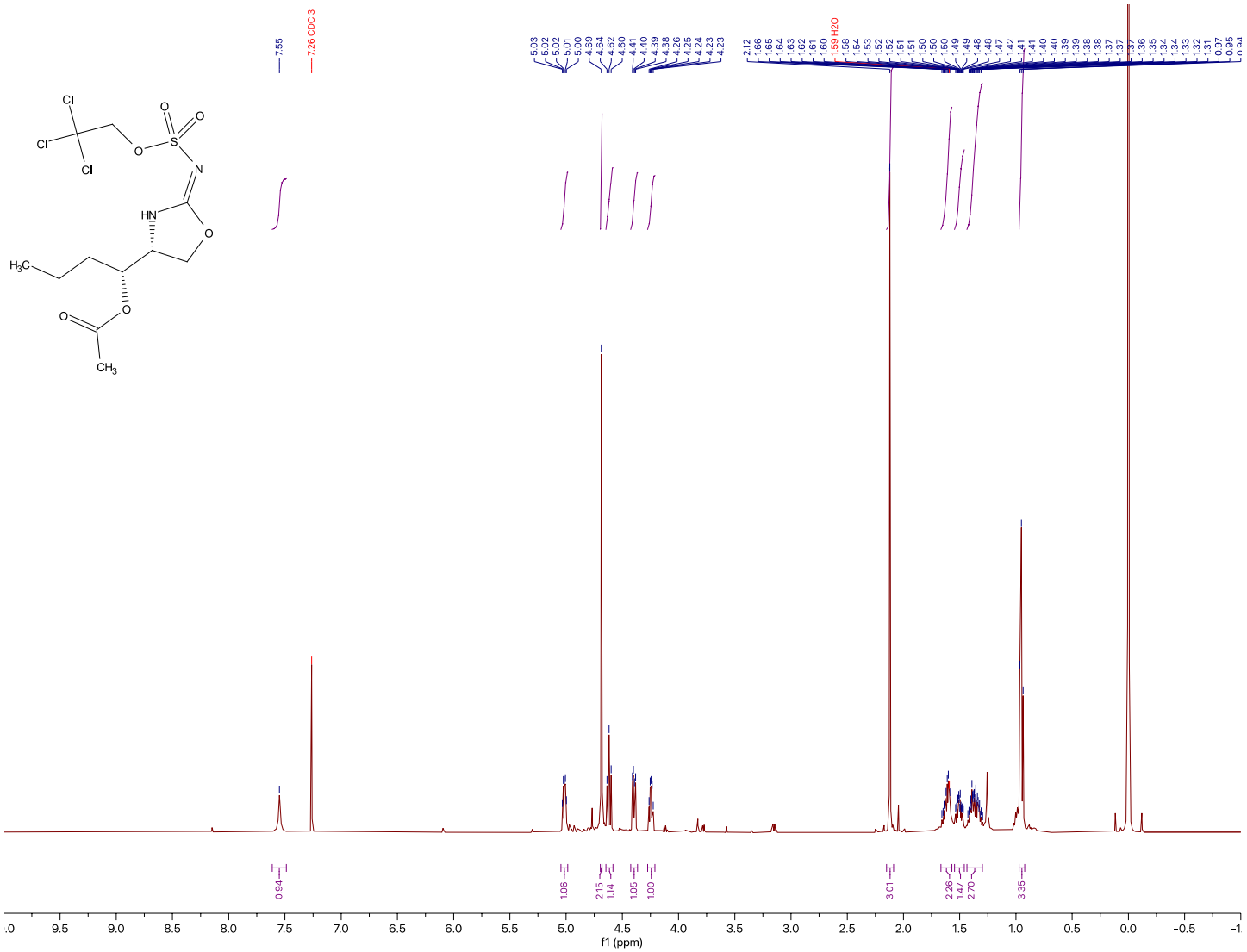
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2u**



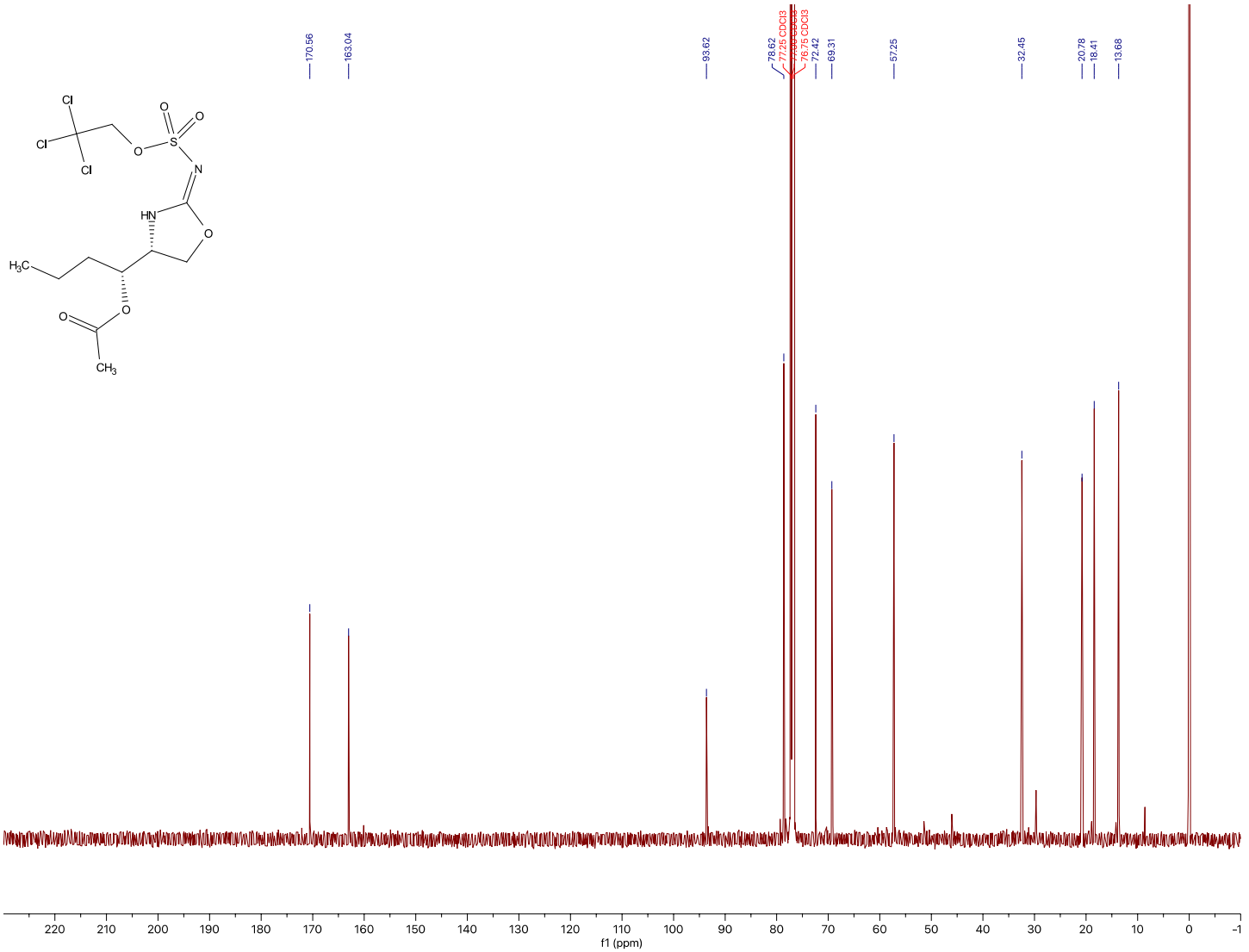
NOESY NMR (500 MHz, $CDCl_3$) for **Compound 2u**



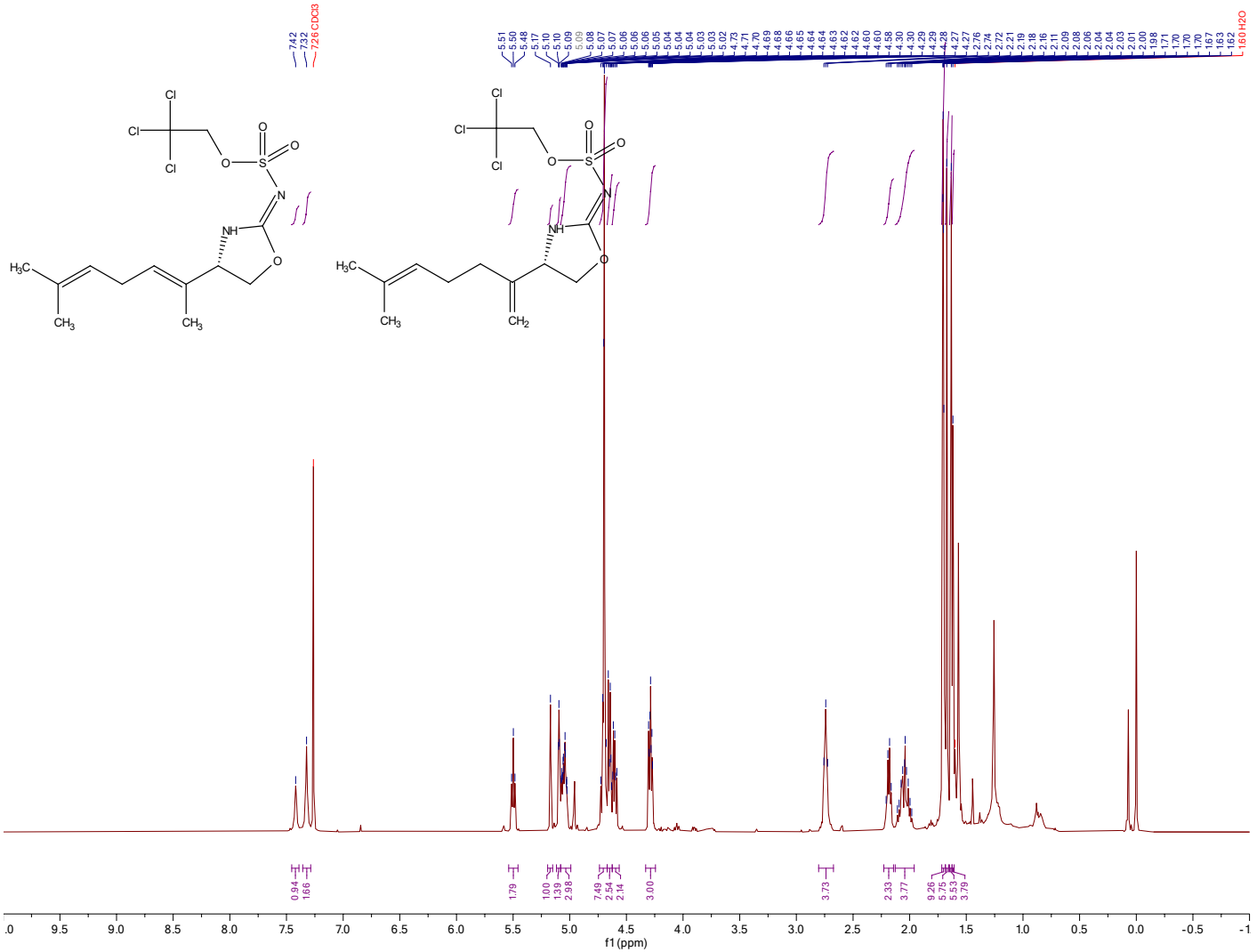
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2v**



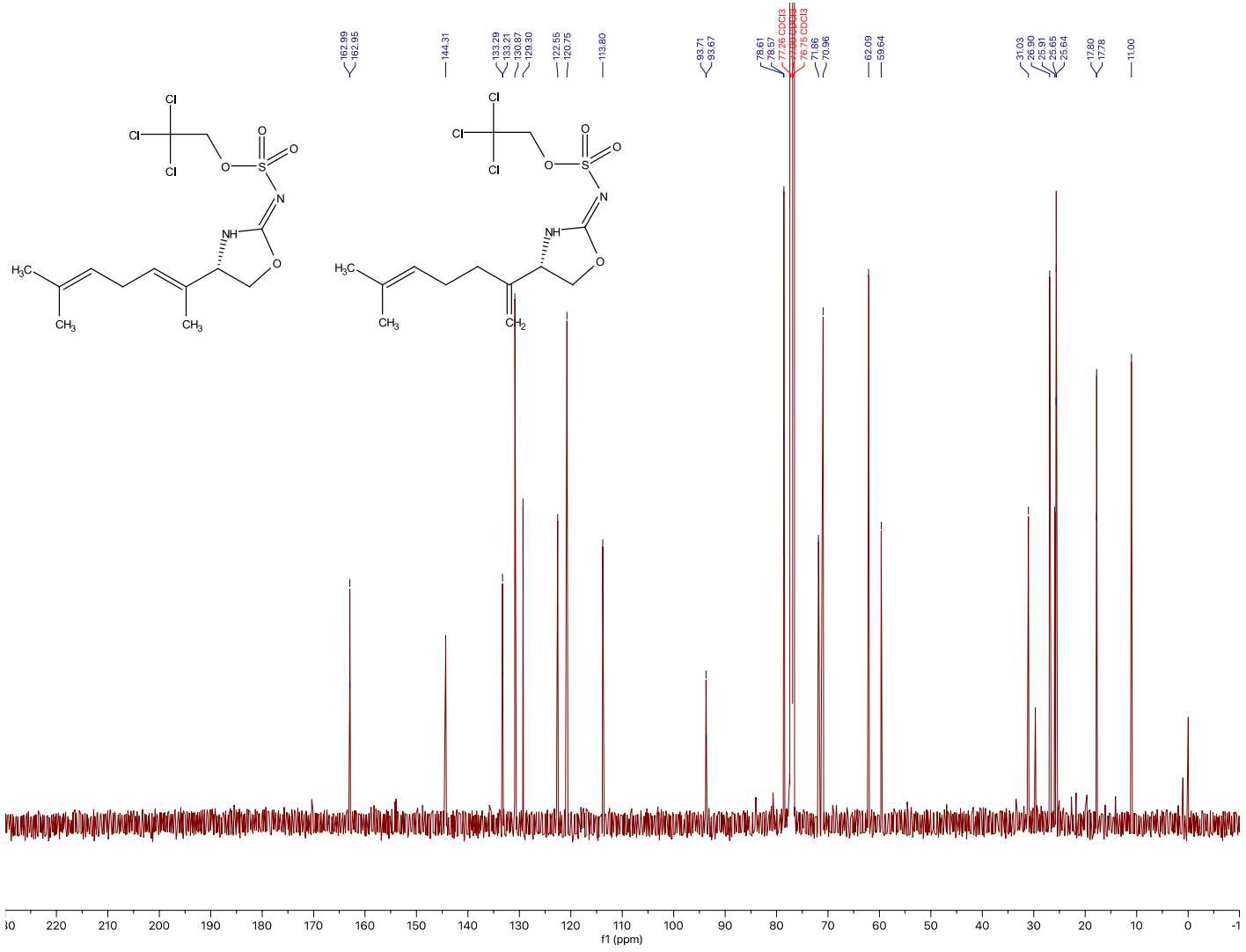
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2v**



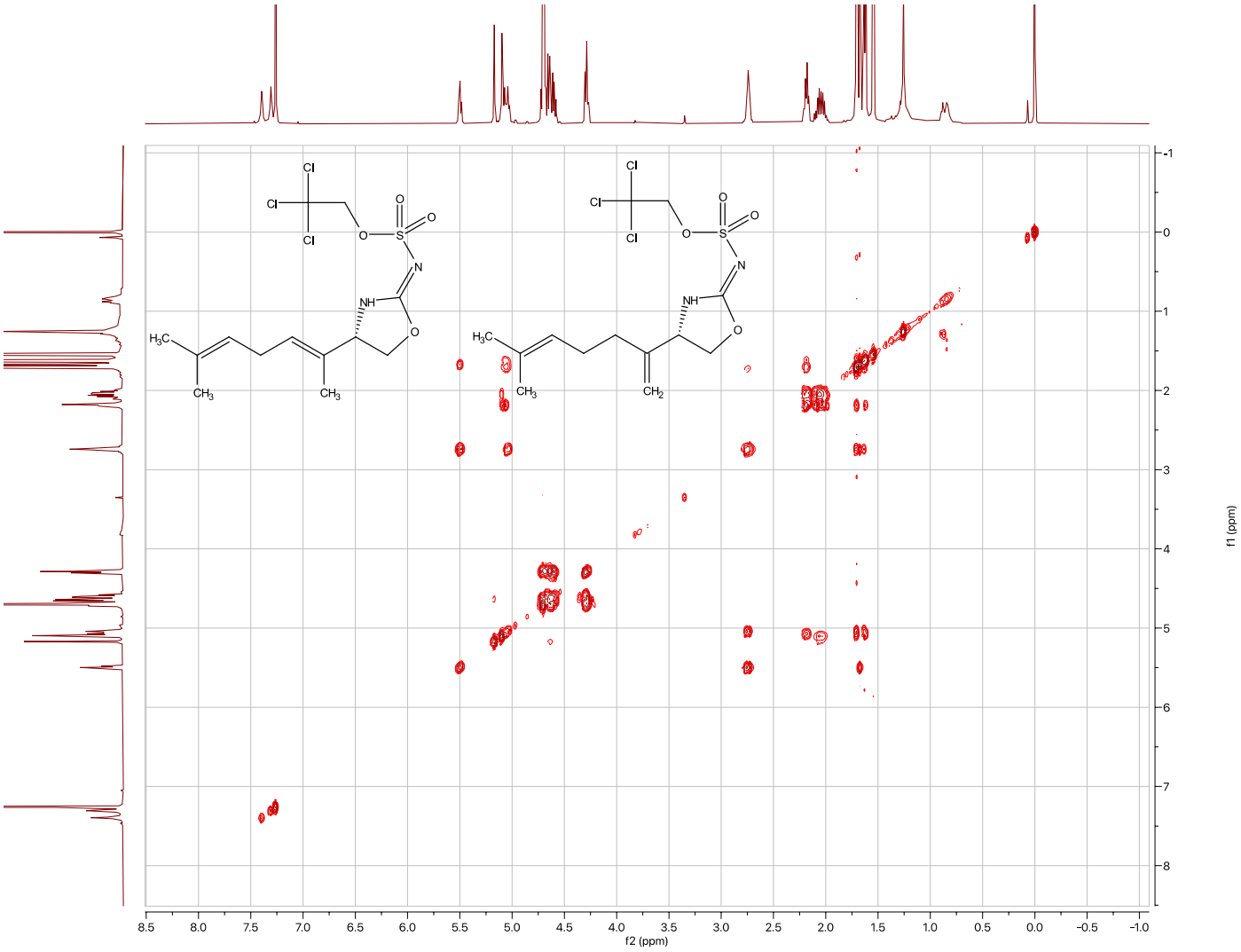
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2w** and **2w'**



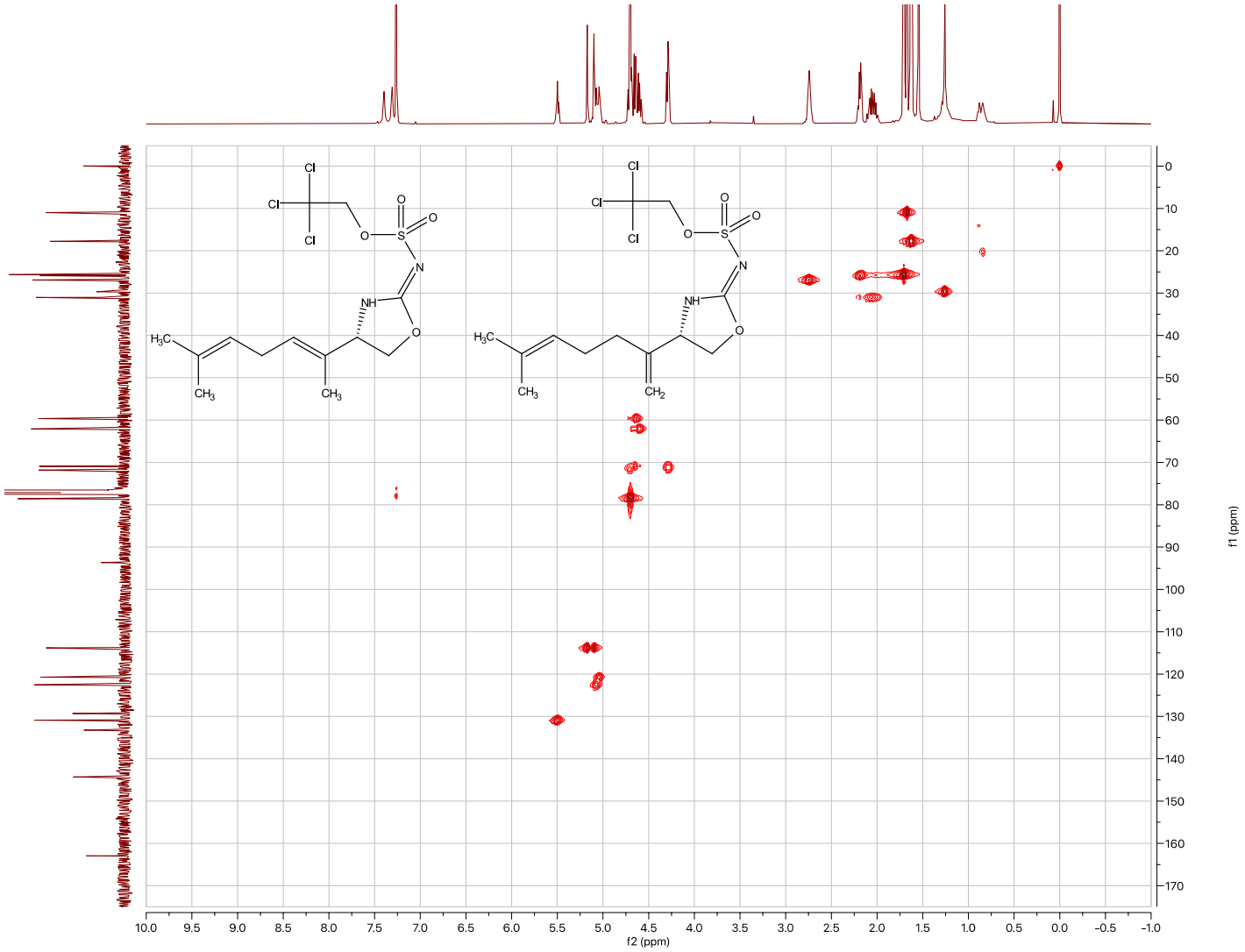
^{13}C NMR (126 MHz, $CDCl_3$) for **Compounds 2w** and **2w'**



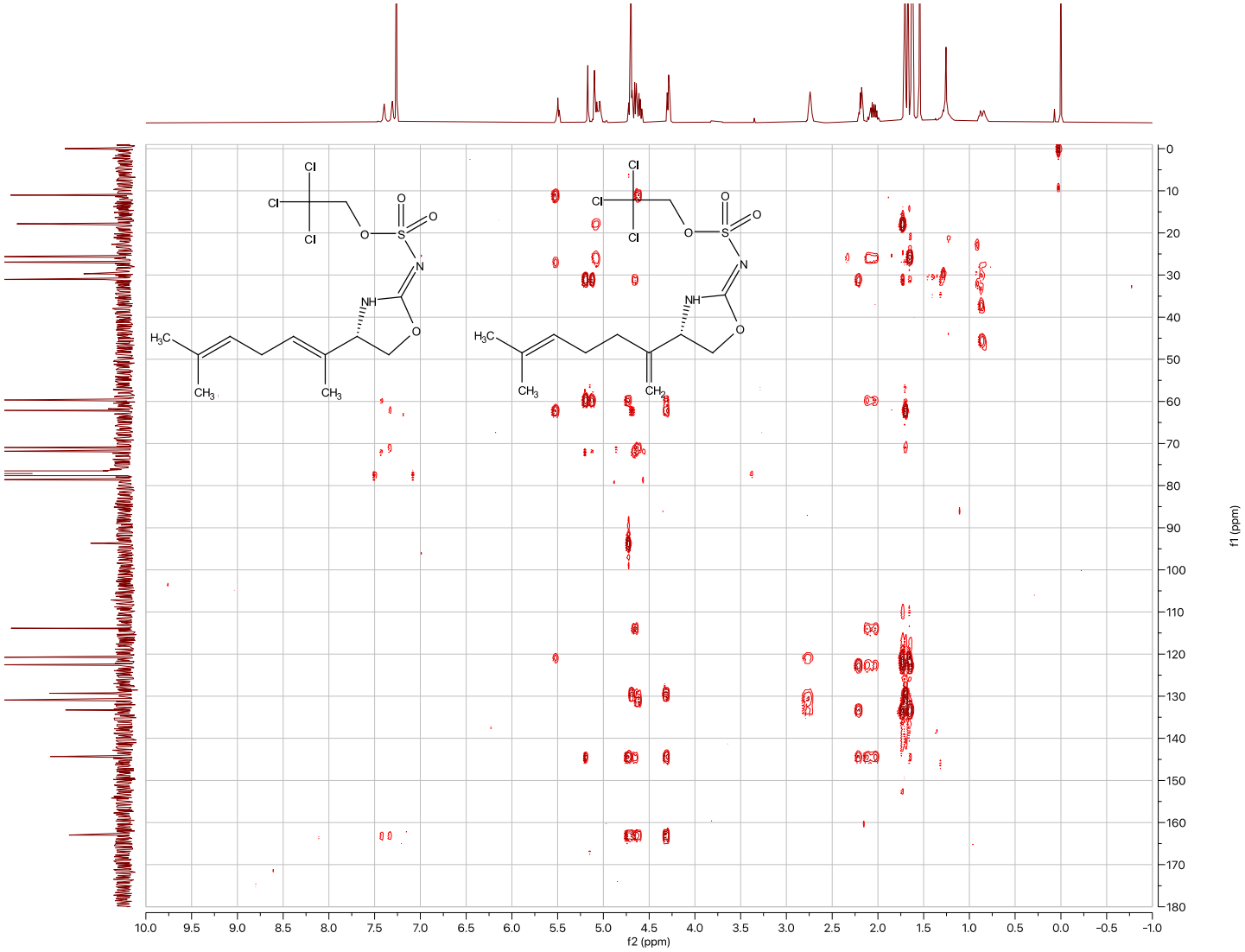
COSY NMR (500 MHz, $CDCl_3$) for **Compounds 2w** and **2w'**



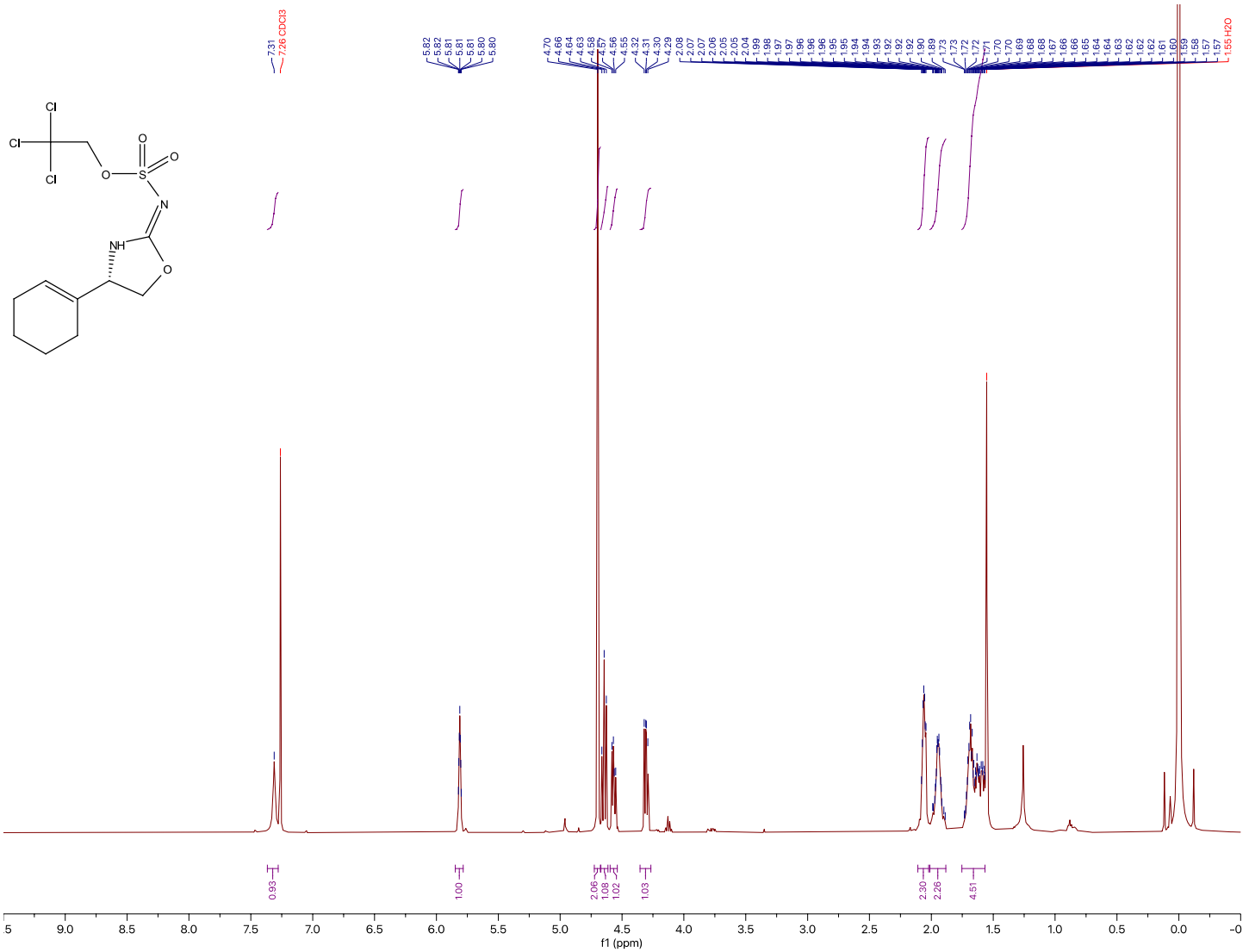
HSQC NMR (500 MHz/126 MHz, $CDCl_3$) for **Compounds 2w** and **2w'**



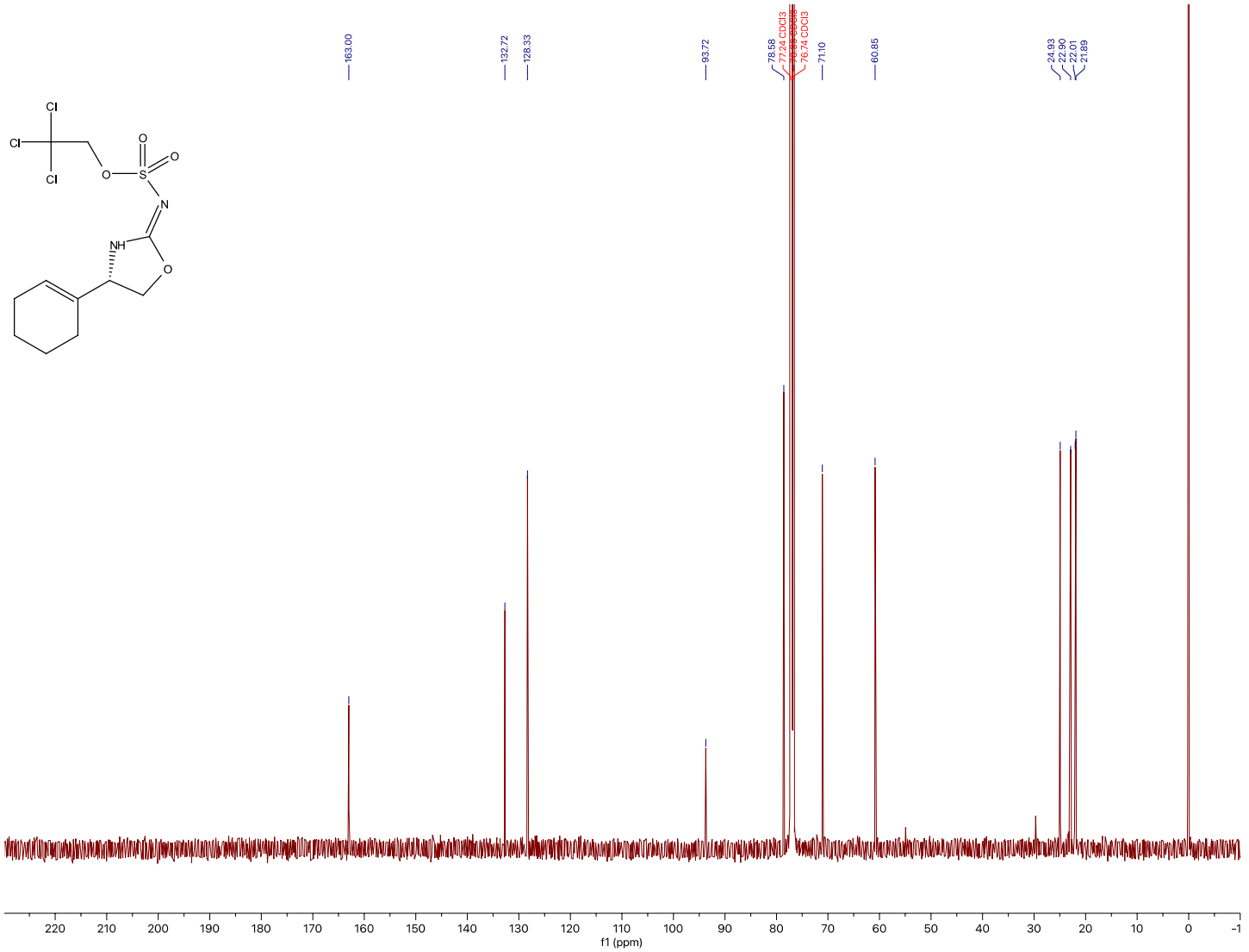
HMBC NMR (500 MHz/126 MHz, $CDCl_3$) for **Compounds 2w** and **2w'**



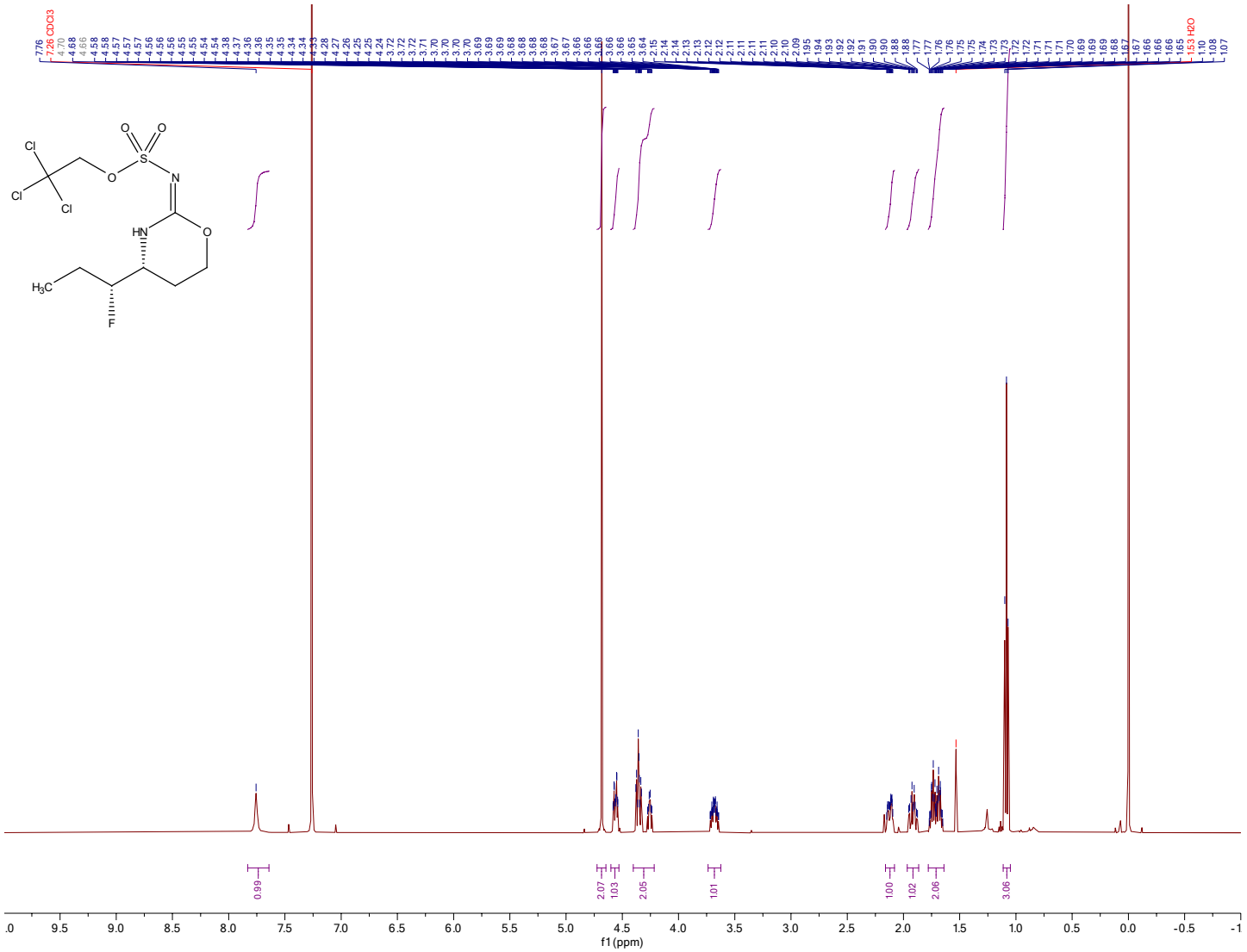
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 2x**



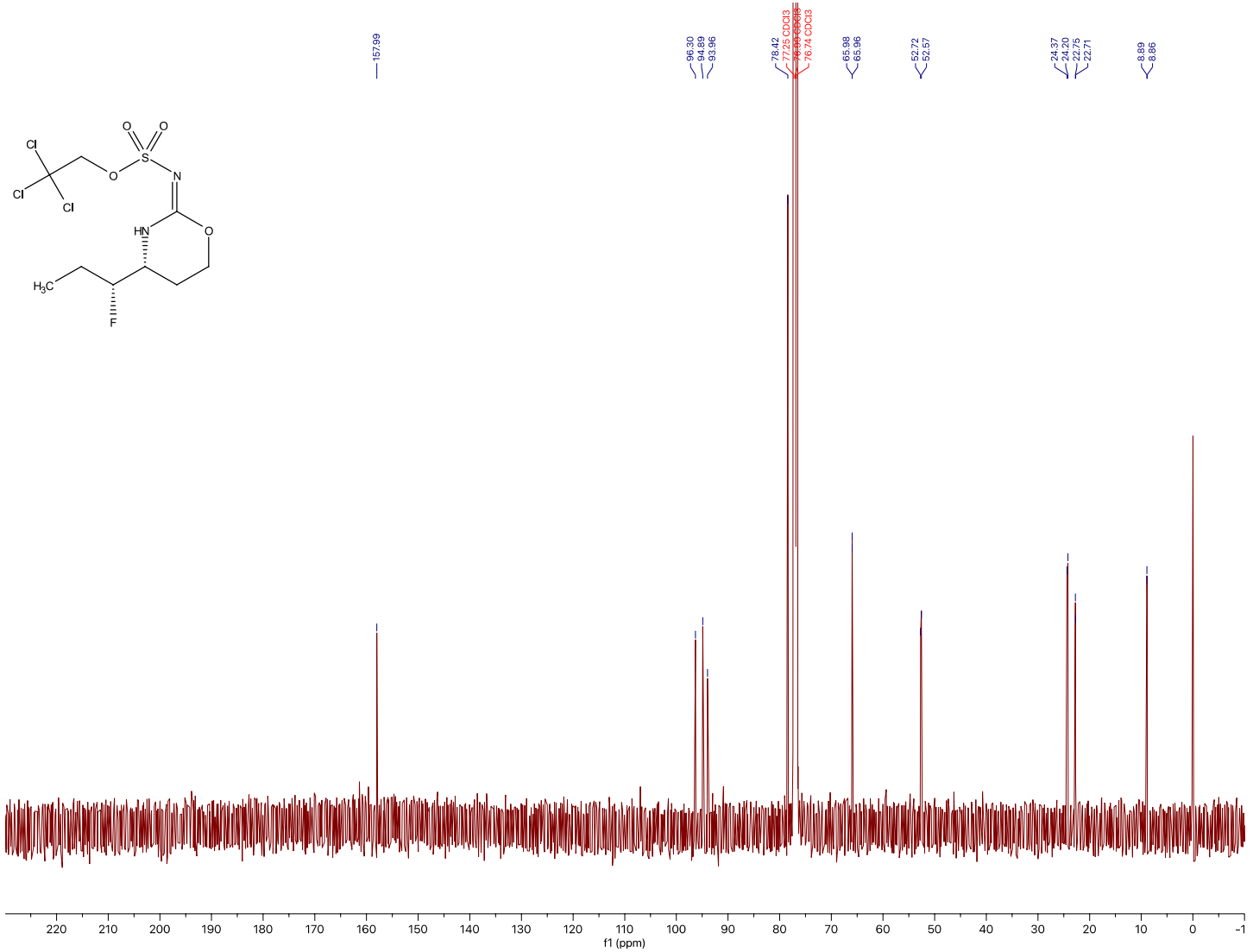
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 2x**



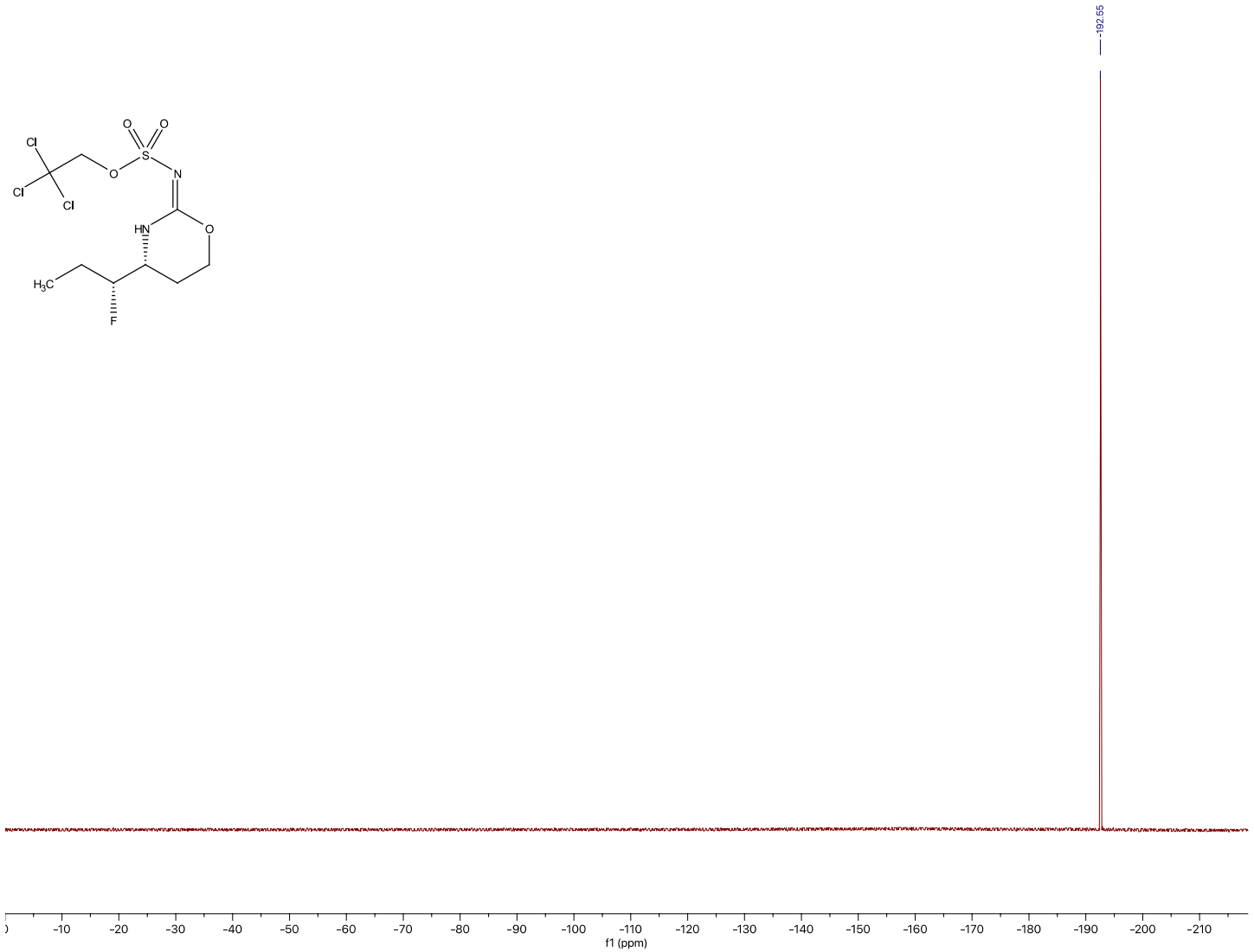
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 3**



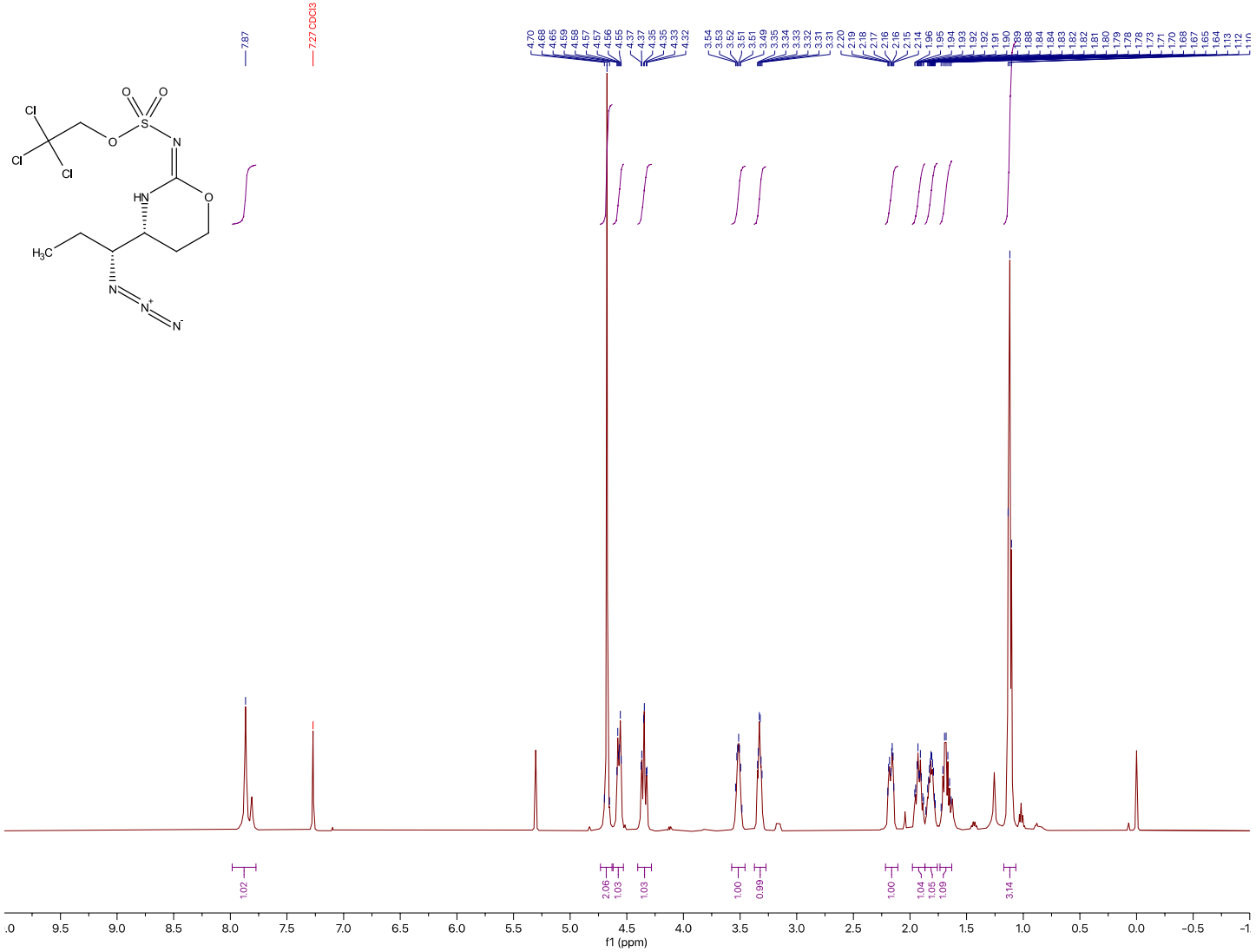
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 3**



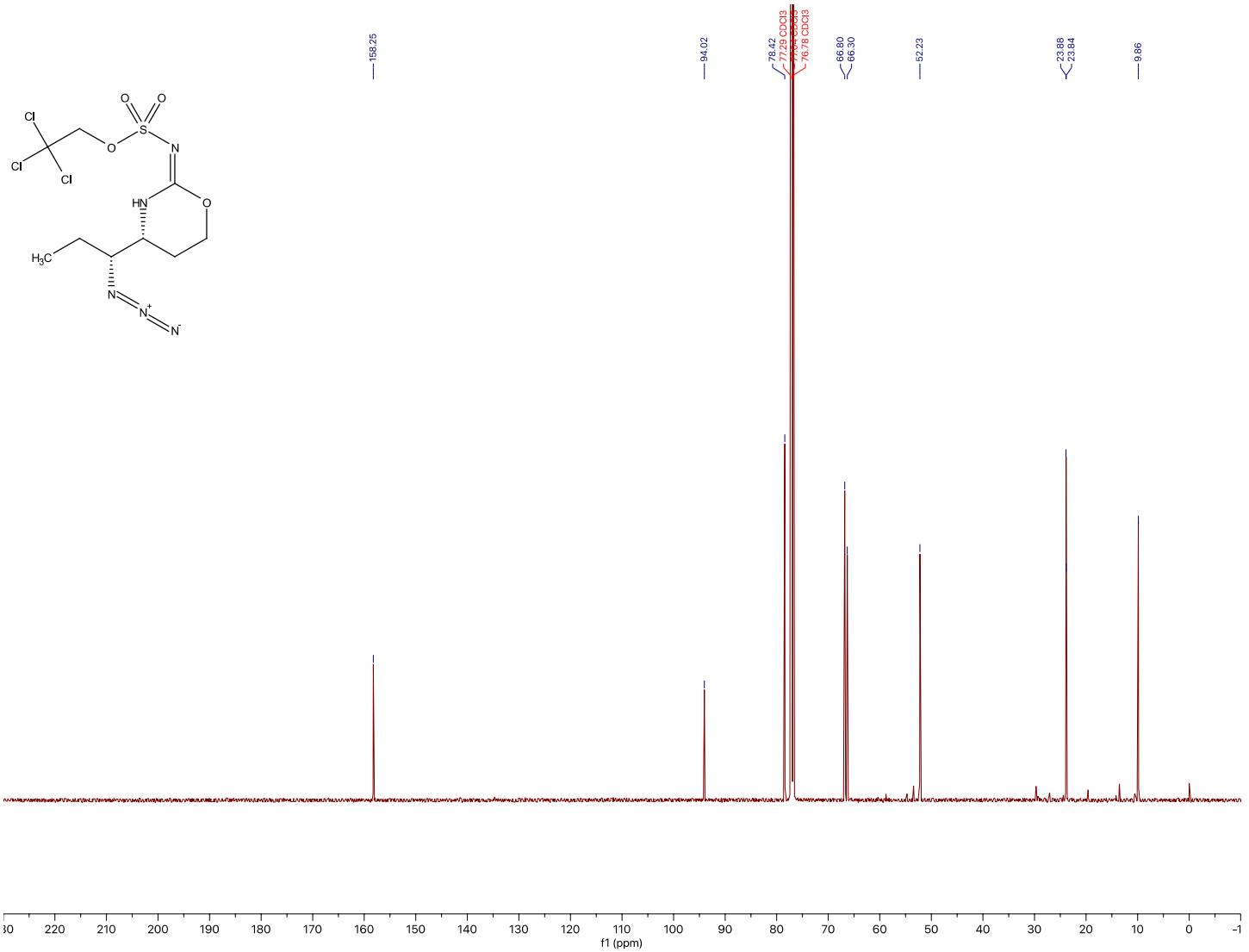
^{19}F NMR (377 MHz, $CDCl_3$) for **Compound 3**



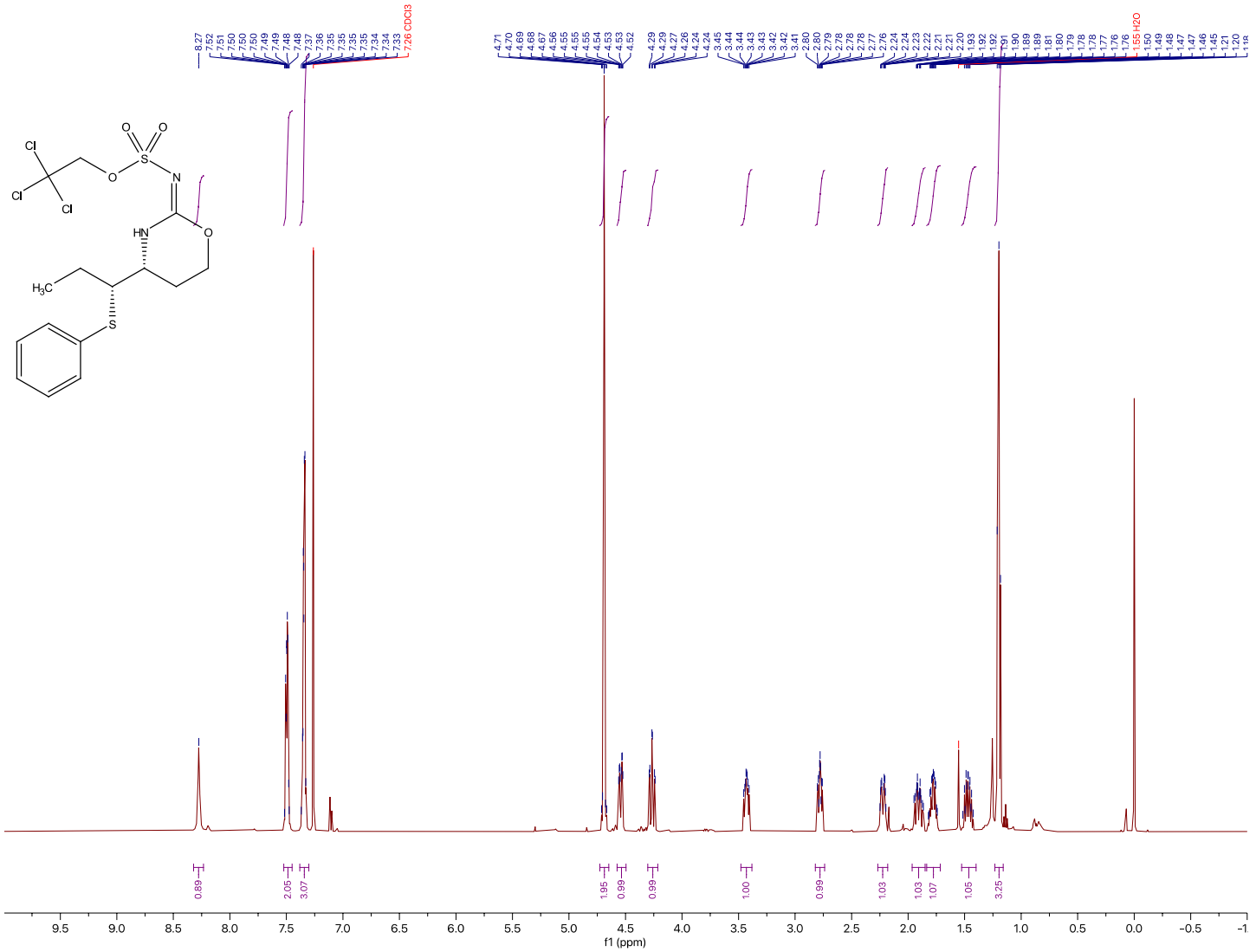
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 4**



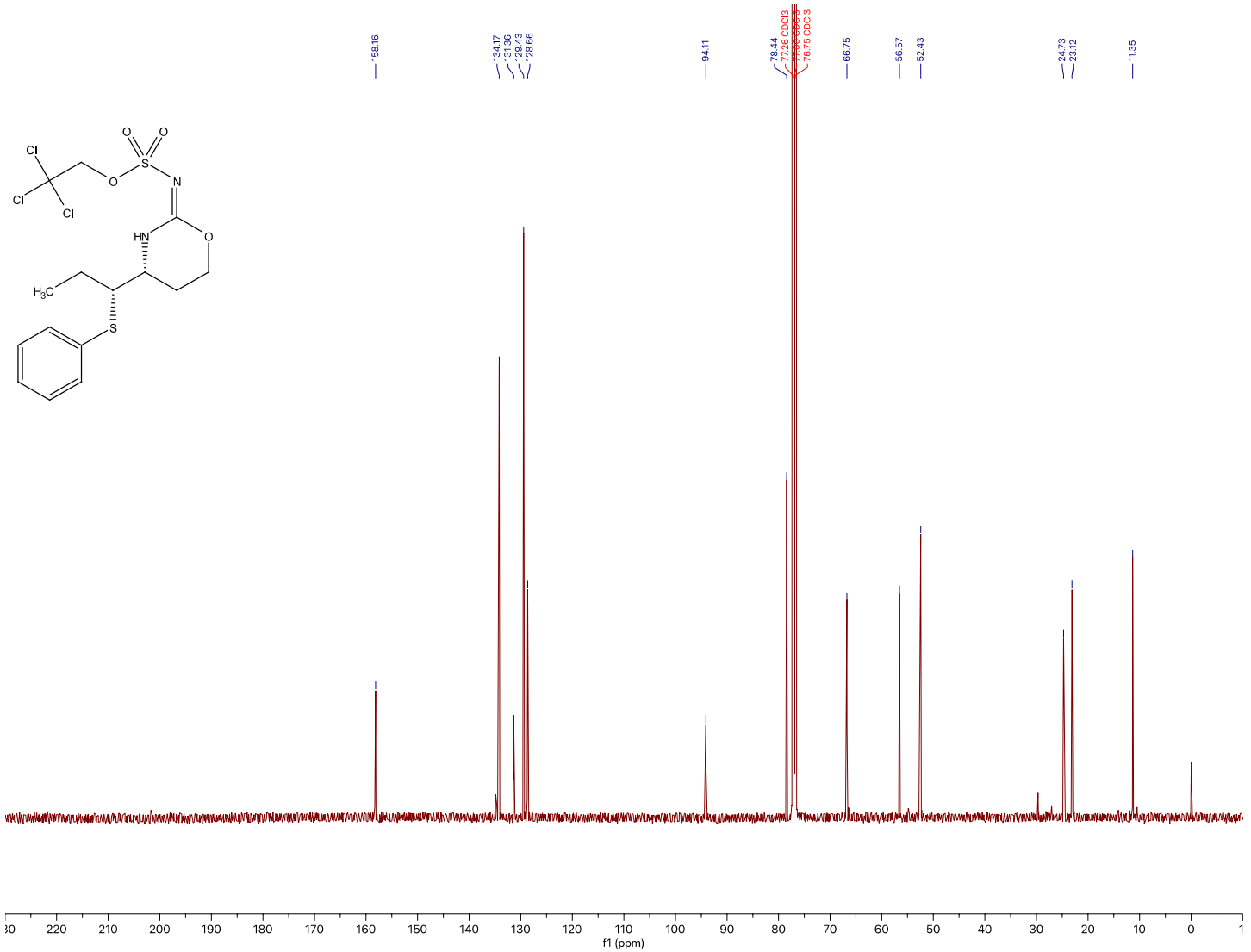
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 4**



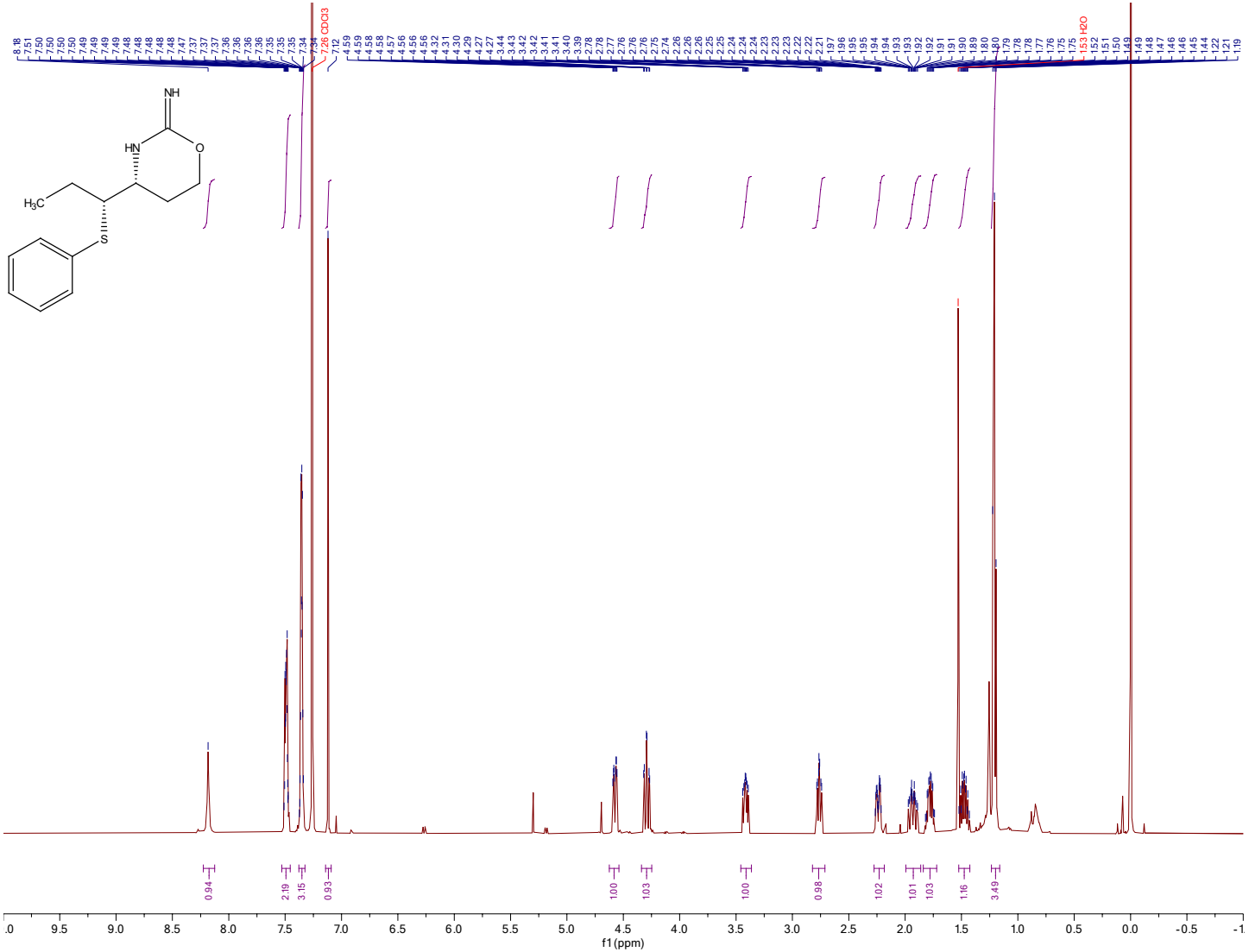
^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 5a**



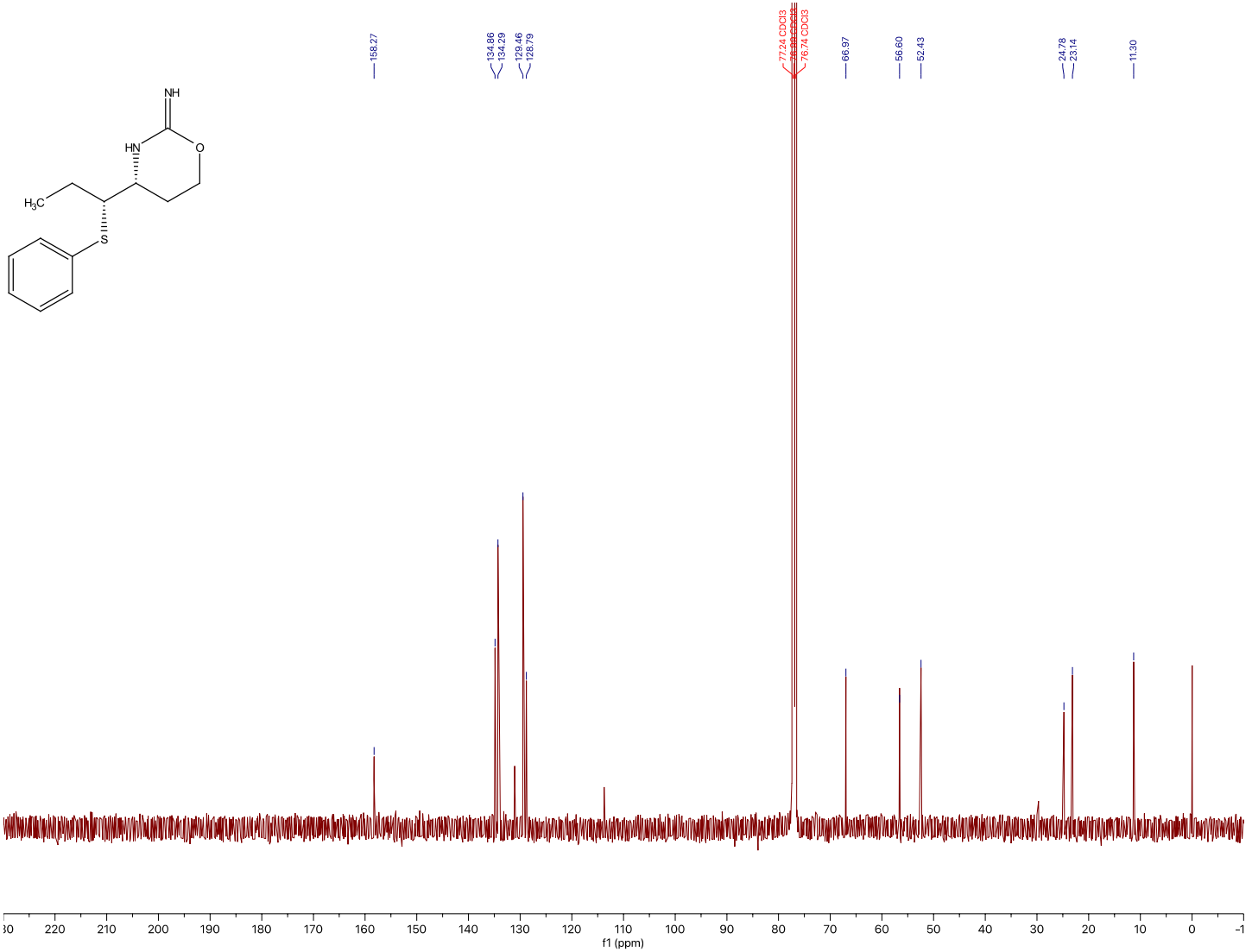
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 5a**



^{1}H NMR (500 MHz, $CDCl_3$) for **Compound 5b**



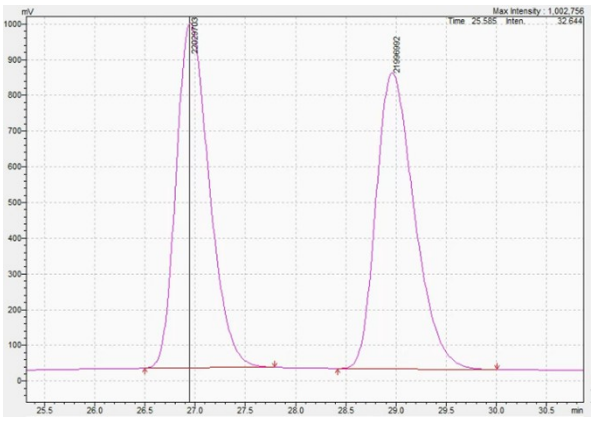
^{13}C NMR (126 MHz, $CDCl_3$) for **Compound 5b**



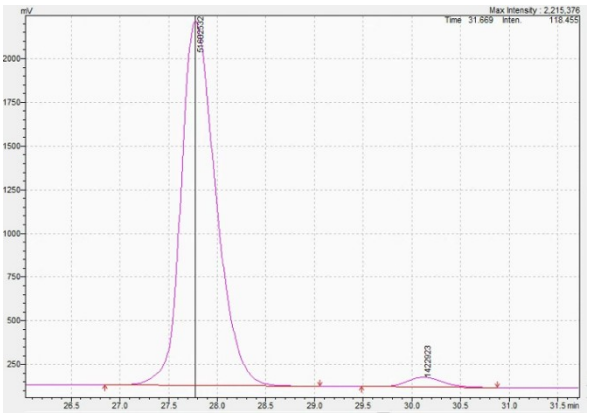
IX. HPLC Chromatograms

Refer to section III for all HPLC method parameters.

Compound 2a:

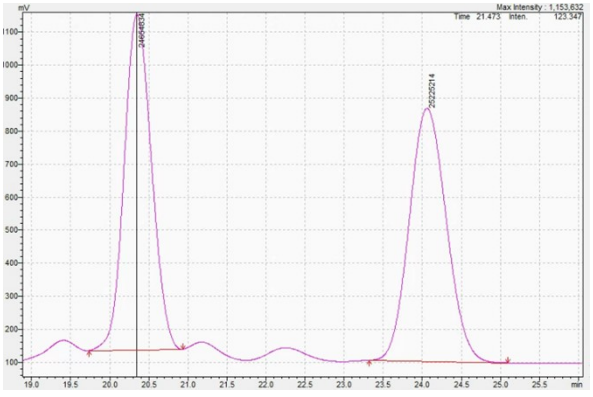


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	26.949	50.037	22029703
2	28.959	49.963	21996992
Total		100.000	44026695

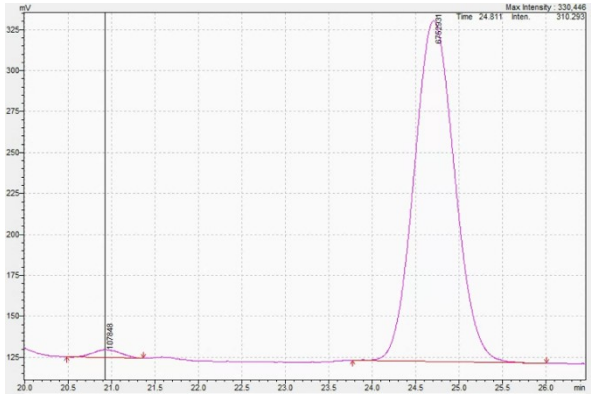


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	27.773	97.317	51602532
2	30.109	2.683	1422923
Total		100.000	53025455

Compound 2b:

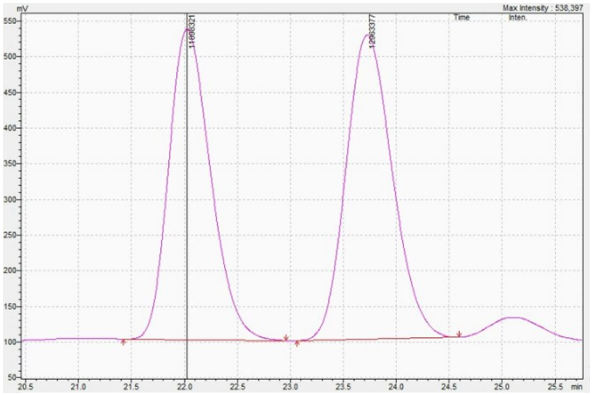


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	20.347	49.428	24654834
2	24.061	50.572	25225214
Total		100.000	49880048

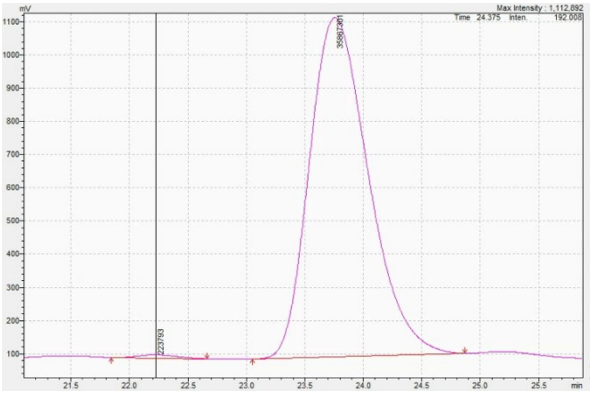


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	20.926	1.572	107848
2	24.712	98.428	6752931
Total		100.000	6860779

Compound 2c:

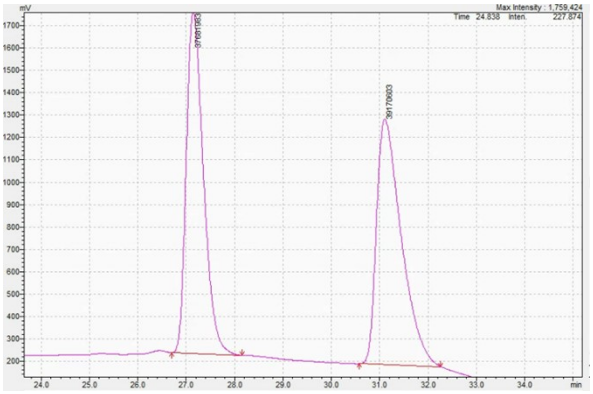


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	22.025	47.858	11898321
2	23.727	52.142	12963377
Total		100.000	24861697

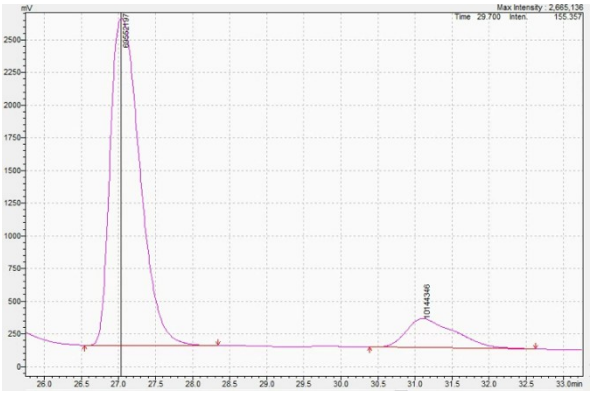


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	22.227	0.620	223793
2	23.758	99.380	35867301
Total		100.000	36091094

Compound 2d:

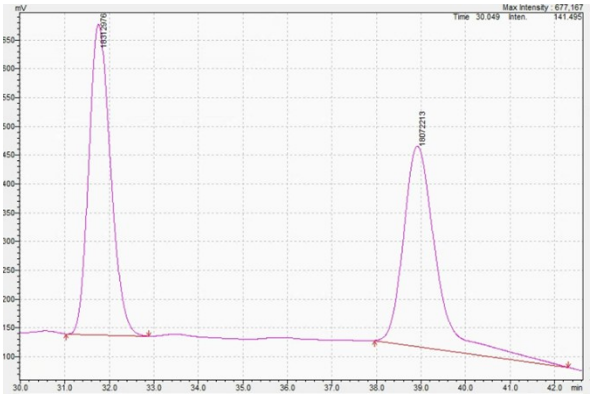


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	27.141	49.032	37681983
2	31.104	50.968	39170603
Total		100.000	76852586

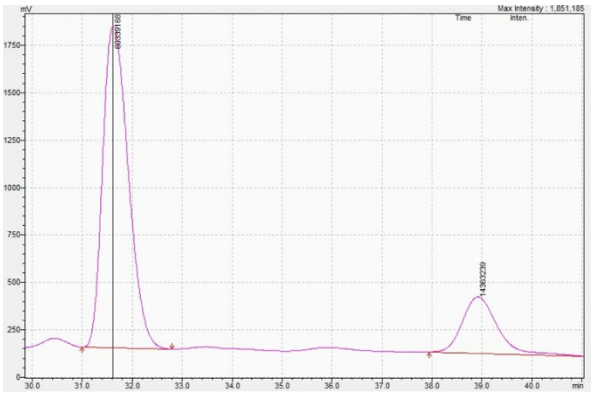


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	27.037	87.271	69552197
2	31.099	12.729	10144346
Total		100.000	79696543

Compound 2e:

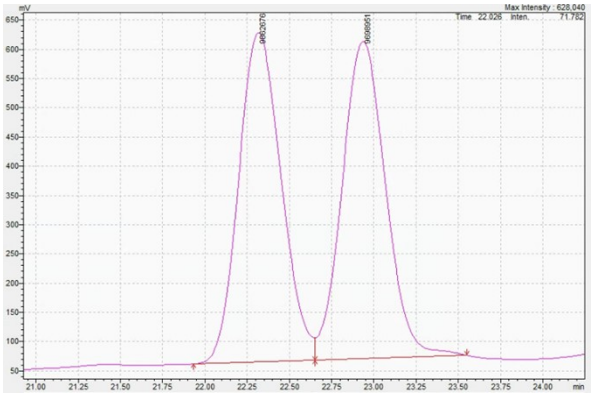


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	31.753	50.331	18312976
2	38.912	49.669	18072213
Total		100.000	36385189

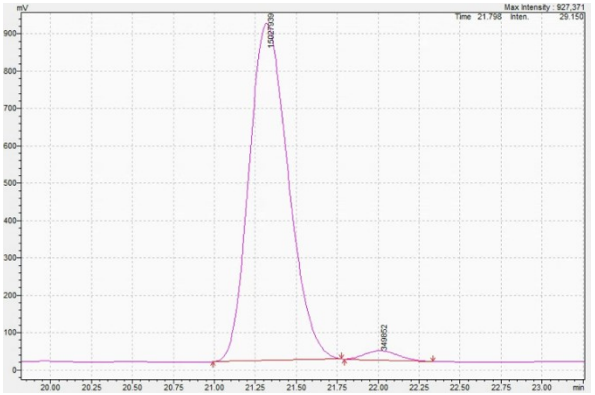


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	31.618	80.773	60339168
2	38.917	19.227	14363239
Total		100.000	74702407

Compound 2f:

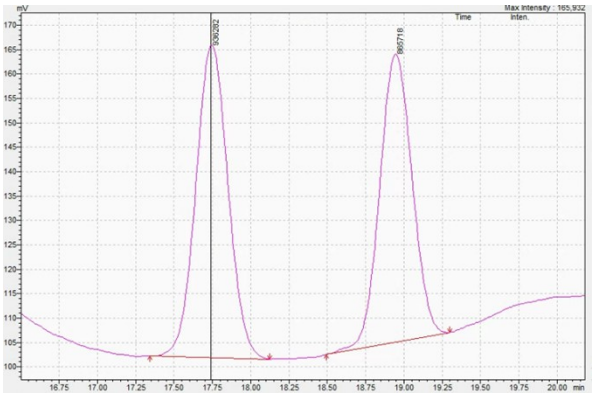


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	22.313	50.418	9862676
2	22.932	49.582	9698951
Total		100.000	19561627

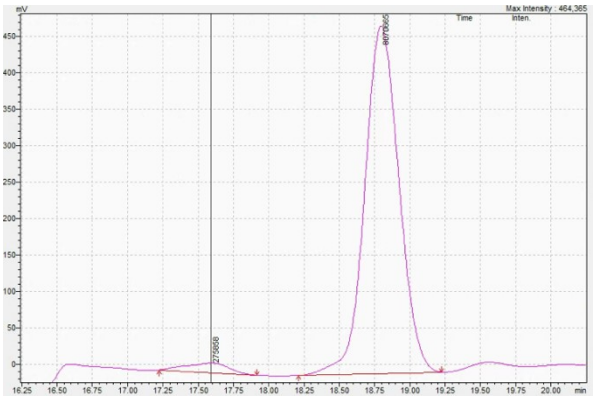


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	21.315	97.725	15027939
2	22.007	2.275	349852
Total		100.000	15377791

Compound 2g:

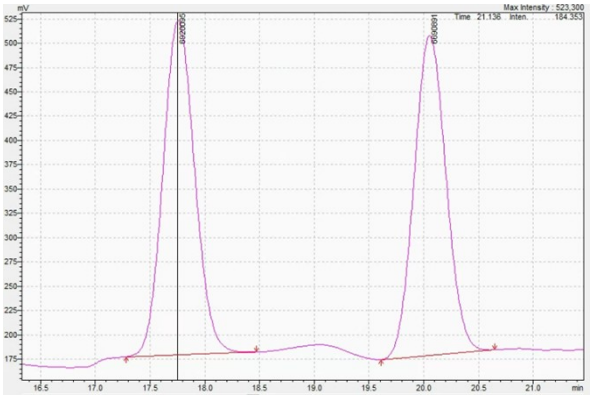


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.741	51.958	936282
2	18.942	48.082	865718
Total		100.000	1802001

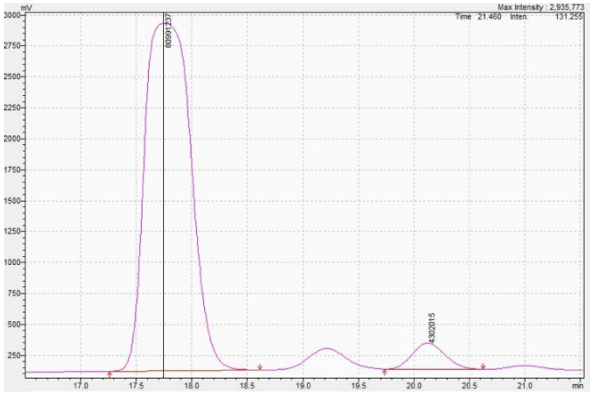


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.590	3.305	275858
2	18.792	96.695	8070665
Total		100.000	8346523

Compound 2h:

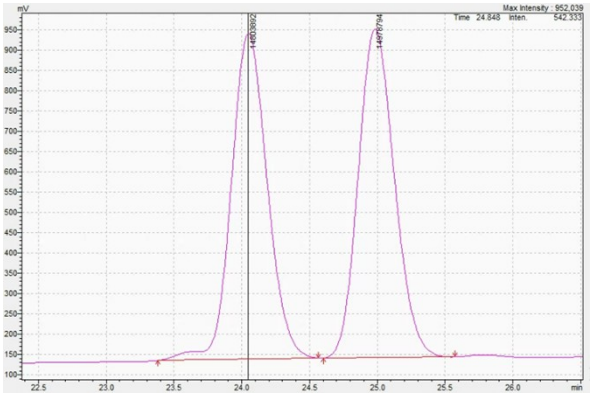


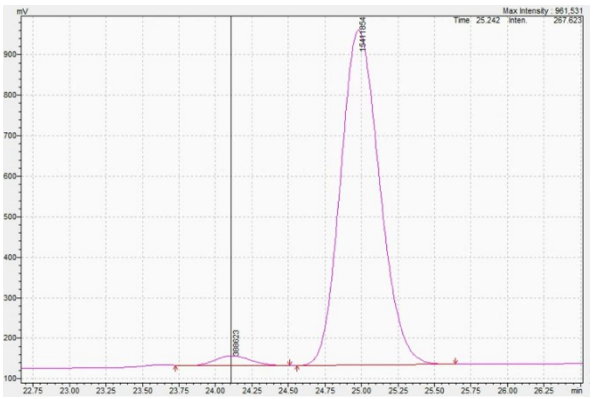
Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.754	50.842	6920095
2	20.050	49.158	6690891
Total		100.000	13610985



Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.748	94.956	80991237
2	20.121	5.044	4302015
Total		100.000	85293252

Compound 2i:

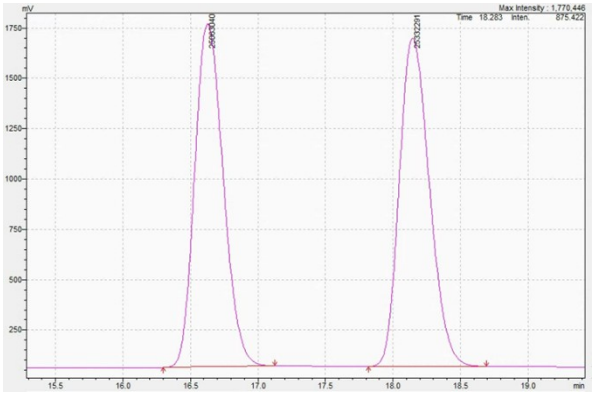


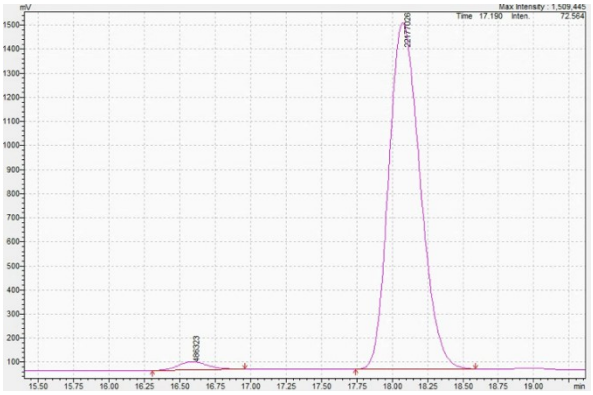


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	24.045	49.706	14803892
2	24.979	50.294	14978794
Total		100.000	29782686

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	24.106	2.460	388623
2	24.977	97.540	15411854
Total		100.000	15800478

Compound 2j:

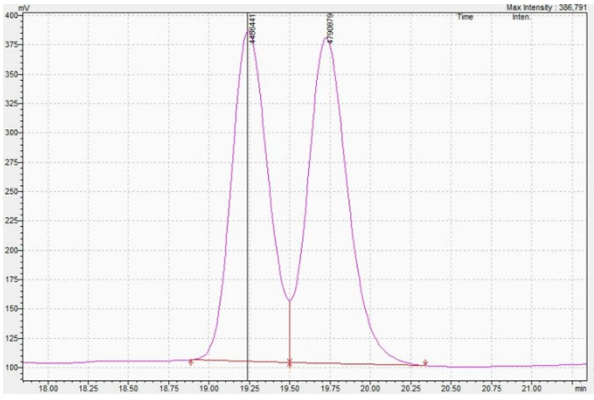


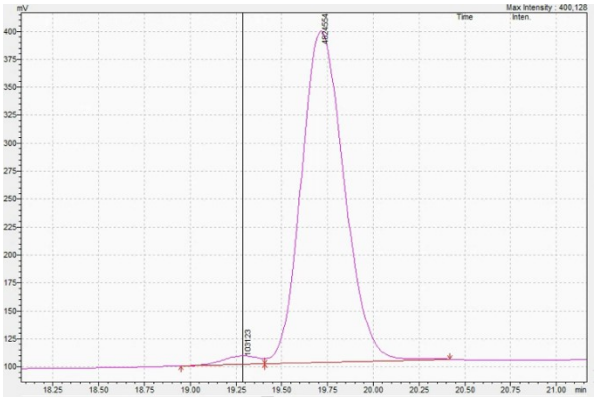


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	16.624	49.733	25063040
2	18.143	50.267	25332291
Total		100.000	50395332

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	16.583	2.146	486323
2	18.071	97.854	22177026
Total		100.000	22663349

Compound 2k:

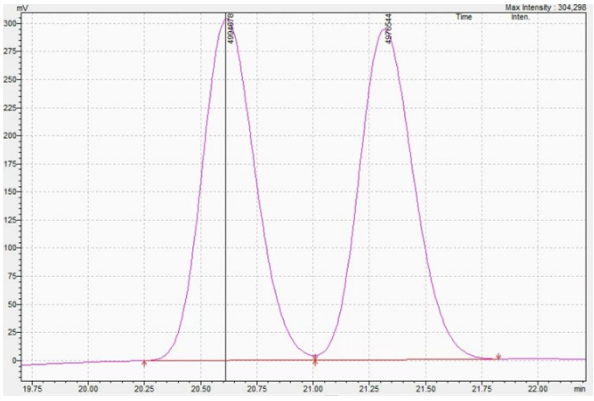


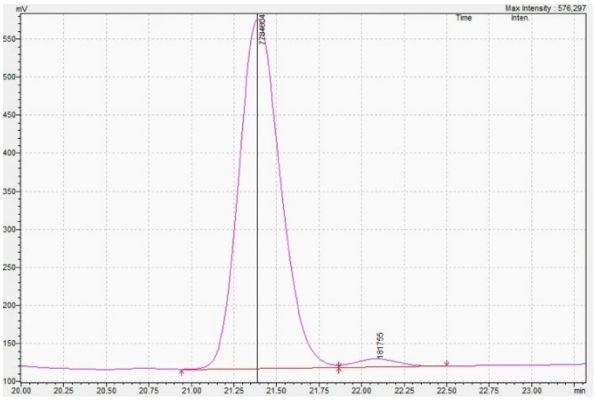


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	19.239	48.359	4486441
2	19.721	51.641	4790879
Total		100.000	9277319

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	19.286	2.093	103123
2	19.711	97.907	4824554
Total		100.000	4927677

Compound 2l:

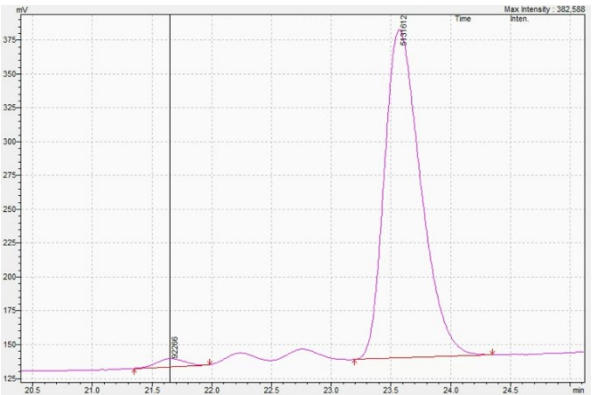


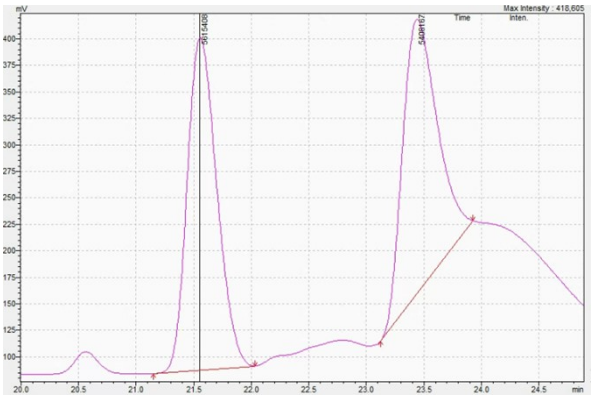


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	20.611	50.091	4994678
2	21.313	49.909	4976544
Total		100.000	9971222

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	21.386	97.719	7784804
2	22.082	2.281	181755
Total		100.000	7966558

Compound 2m:

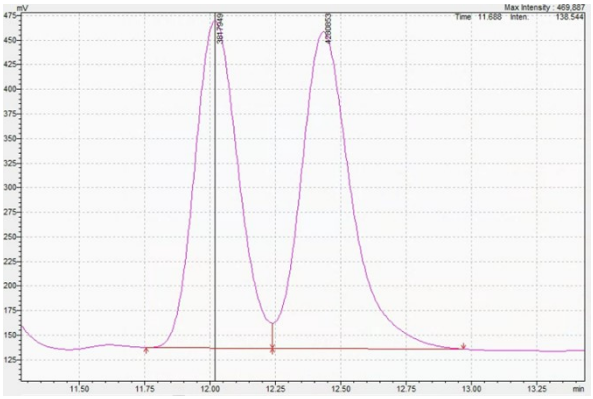


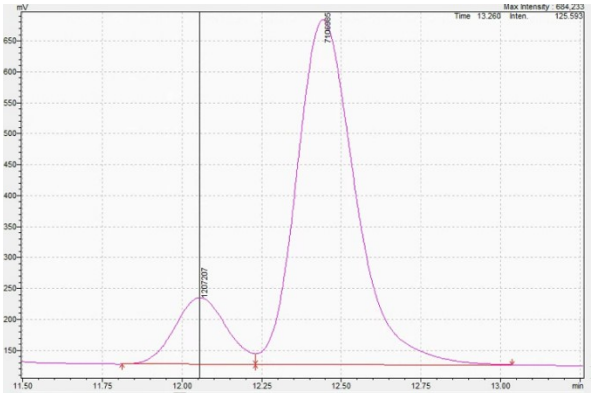


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	21.552	50.940	5615408
2	23.437	49.060	5408167
Total		100.000	11023575

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	21.651	1.766	92266
2	23.566	98.234	5131612
Total		100.000	5223877

Compound 2o:

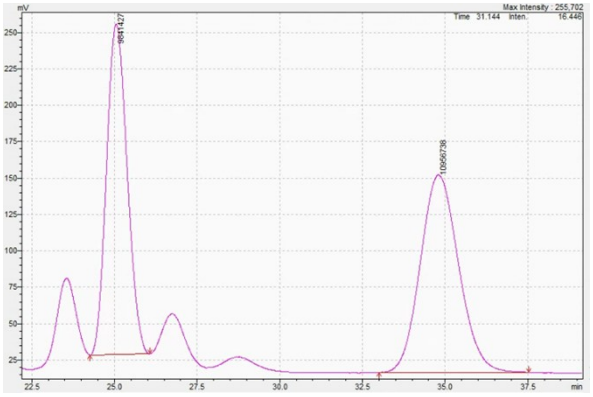




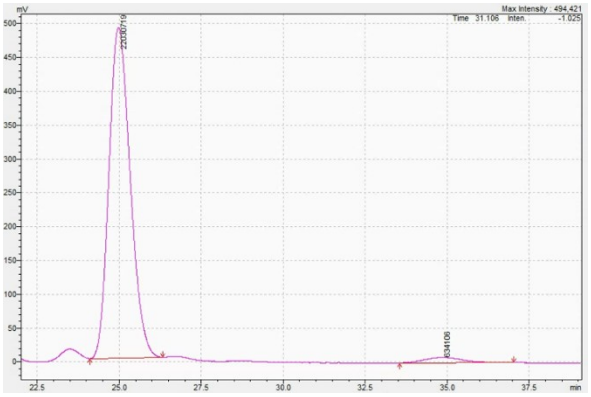
Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	12.018	47.142	3817949
2	12.433	52.858	4280853
Total		100.000	8098802

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	12.056	14.520	1207207
2	12.443	85.480	7106985
Total		100.000	8314192

Compound 2p:

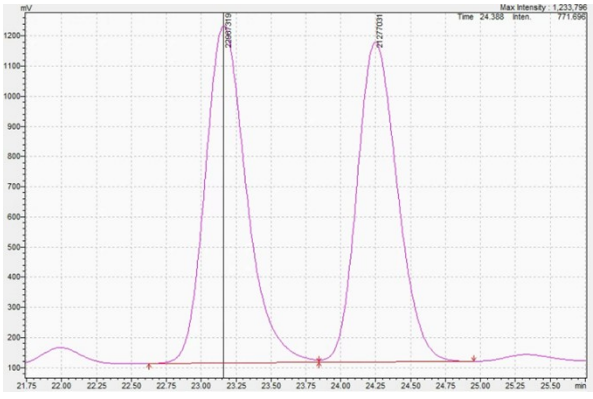


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	25.052	47.319	9841427
2	34.799	52.681	10956738
Total		100.000	20798166

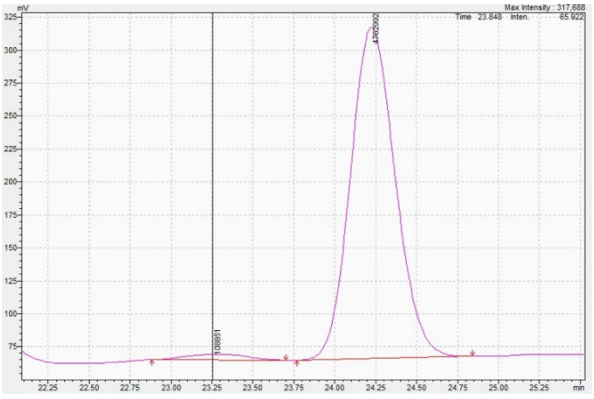


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	24.976	97.202	22030719
2	34.855	2.798	634106
Total		100.000	22664825

Compound 2q:

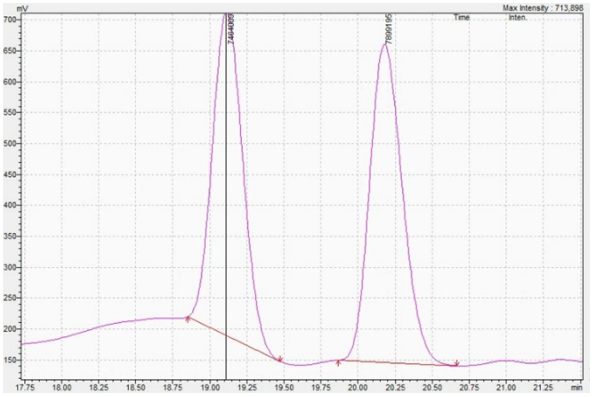


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	23.157	51.910	22967319
2	24.243	48.090	21277031
Total		100.000	44244349

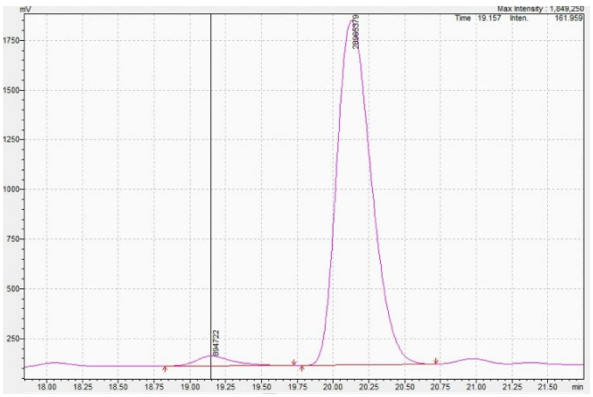


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	23.253	2.234	108851
2	24.221	97.766	4762992
Total		100.000	4871843

Compound 2r:

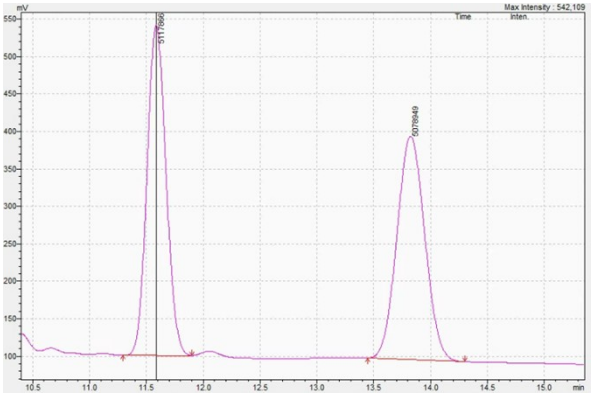


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	19.110	48.584	7464009
2	20.174	51.416	7899195
Total		100.000	15363204

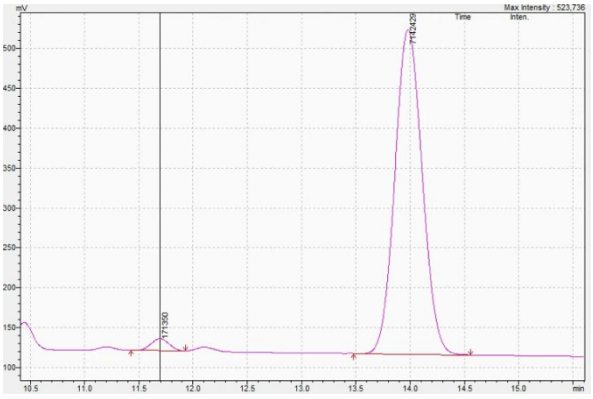


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	19.146	2.996	894722
2	20.124	97.004	28965379
Total		100.000	29860102

Compound 2s:

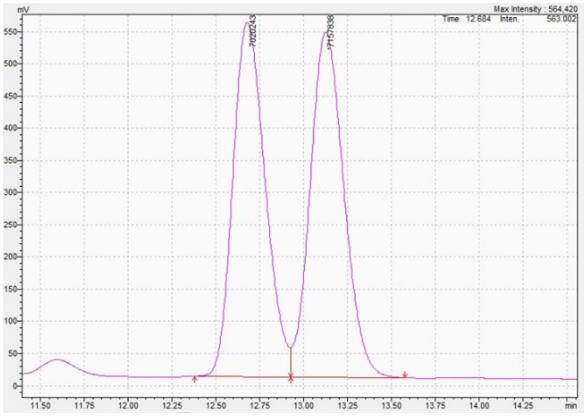


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	11.587	50.191	5117866
2	13.824	49.809	5078949
Total		100.000	10196815

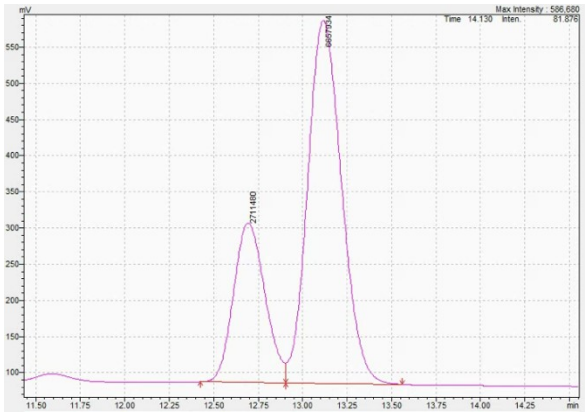


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	11.694	2.343	171350
2	13.982	97.657	7142429
Total		100.000	7313779

Compound 2t:

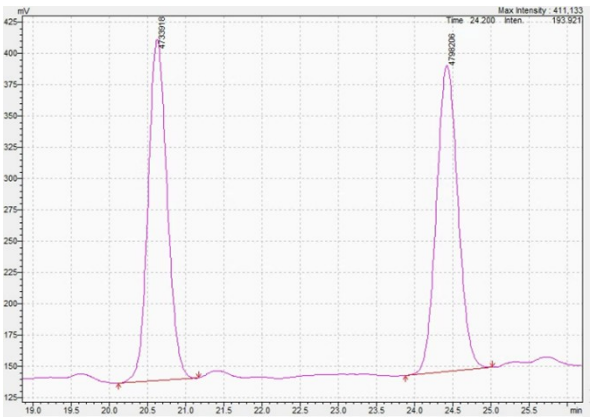


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	12.678	49.515	7020243
2	13.125	50.485	7157838
Total		100.000	14178081

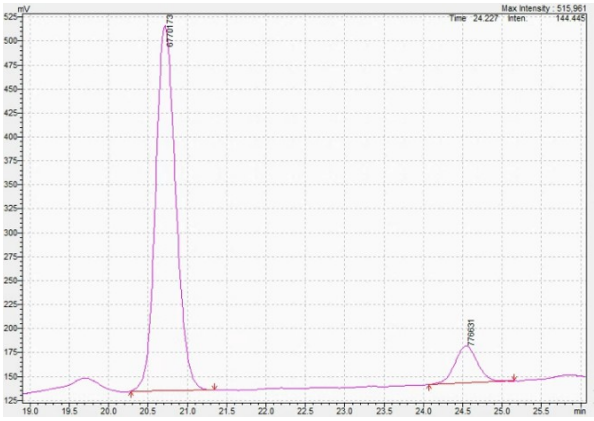


Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	12.694	28.940	2711480
2	13.117	71.060	6657934
Total		100.000	9369414

Compound 2v:

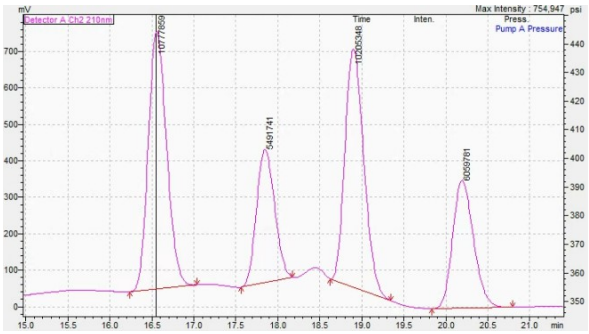


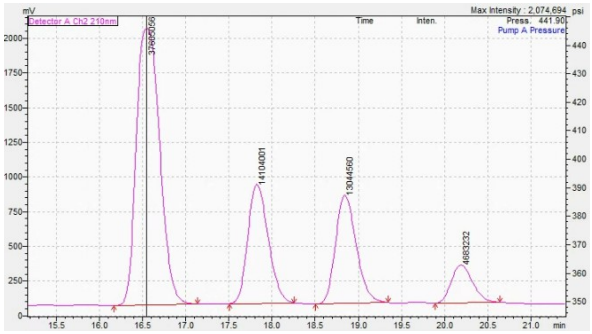
Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	20.624	49.663	4733918
2	24.419	50.337	4798206
Total		100.000	9532125



Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	20.710	89.709	6770173
2	24.539	10.291	776631
Total		100.000	7546804

Compound 2w and **2w'**:

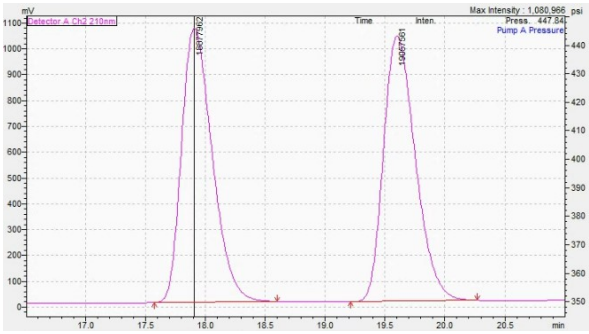


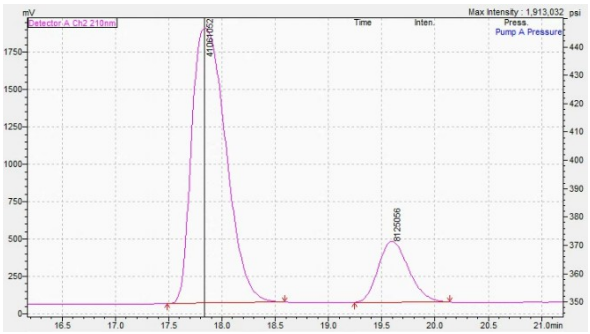


Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	16.554	33.127	10777859
2	17.842	16.880	5491741
3	18.896	31.368	10205348
4	20.190	18.626	6059781
Total		100.000	32534729

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	16.543	54.157	37605056
2	17.821	20.312	14104001
3	18.839	18.786	13044560
4	20.186	6.745	4683232
Total		100.000	69436849

Compound 2x:





Racemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.905	49.763	18877962
2	19.597	50.237	19057561
Total		100.000	37935522

Scalemic			
Peak	**Ret. Time**	**Area%**	**Area**
1	17.838	83.481	41061052
2	19.592	16.519	8125056
Total		100.000	49186107