Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Lewis acid mediated allylation of vinyl diazonium ions by allylstannanes

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General Experimental Details

All reactions were performed under an atmosphere of nitrogen in glassware that was flame-dried under vacuum. Tetrahydrofuran (THF), diethyl ether (Et_2O), dimethylformamide (DMF), and dichloromethane (CH_2Cl_2) were dried by passing through activated alumina columns and dispensed from a solvent dispensing system under argon. Triethylamine was freshly distilled from CaH_2 prior to use. Lithium diisopropylamide (LDA) was titrated using N-benzylbenzamide as the color indicator prior to use. All other commercially available reagents were used as received unless otherwise indicated. Silica gel flash column chromatography was performed on manually packed silica gel (230-400 mesh), or on a Teledyne ISCO CombiFlash® automated chromatography system using pre-packaged silica gel columns. For chromatography columns containing K_2CO_3, solid K_2CO_3 was ground to a fine powder with a mortar and pestle, mixed with dry silica, and then packed together as a slurry. NEt_3-deactivated silica was made by preparing a silica gel slurry with 1% Et_3N in hexanes and allowing the hexanes to evaporate. TLC analysis was carried out on glass-backed silica gel plates (250 μm thickness), and plates were visualized using ultraviolet light or I_2 vapor.

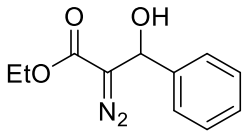
^1H and ^{13}C NMR data were collected at room temperature on a Bruker Avance NMR spectrometer at 500 MHz (^1H) and 125 MHz (^{13}C). Chemical shifts are reported in ppm (δ units) downfield from tetramethylsilane; ^1H NMR spectra are referenced to the TMS signal at 0.00 ppm or the internal $CDCl_3$ signal at 7.26 ppm. ^{13}C NMR spectra are referenced to the internal $CDCl_3$ signal at 77.16 ppm. Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, sept = septet, m = multiplet, app = apparent. Due to the difficulty of observing the diazo carbon in ^{13}C NMR spectra, IR was used to characterize the diazo functional group. IR data was collected on a Bruker Invenio FTIR and values are reported in wavenumbers. Exact mass analysis was performed using a Waters Xevo G2-XS QTof LCMS operated in positive ESI mode or an Agilent 6530 QToF LCMS operated in positive ESI mode.

General Procedure A: Preparation of β-hydroxy-α-diazoesters

LDA in THF (2M, 8 mmol) was added dropwise to a solution of ketone or aldehyde (5 mmol) and ethyl diazoacetate (7.5 mmol) in THF (15mL) at -78 ºC. The reaction mixture was allowed to stir at -78 ºC and was monitored by TLC until the starting material was consumed (1-2 hr). Saturated aqueous NH_4Cl was added at -78 ºC and the mixture was allowed to warm to room temperature. The reaction mixture was diluted with H_2O (~25 mL), extracted with three 50 mL portions of EtOAc and the organic layers were combined then washed with saturated aqueous $NaHCO_3$, brine, dried over magnesium sulfate ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography using EtOAc/Hexanes as eluent to provide the pure β-hydroxy-α-diazoester.

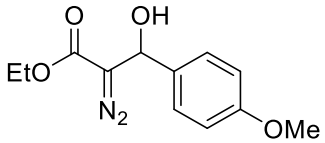
General Procedure B: Preparation of β-hydroxy-α-diazoesters (DBU method)
DBU (0.1 eq.) was added to a mixture of ethyl diazoacetate (1.2 eq.) and the requisite aldehyde (1.0 eq.) in CH_3CN (0.25 M) at room temperature under atmosphere of N_2. The mixture was stirred until consumption of the starting material was observed by TLC, at which point the CH_3CN was removed *in vacuo* and the residue was purified by silica gel flash column chromatography to afford the desired β-hydroxy-α-diazo ester.

Ethyl 2-diazo-3-hydroxy-3-phenylpropanoate



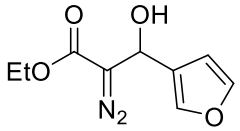
Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and freshly distilled benzaldehyde (0.51 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) to give the title compound as a yellow-orange oil (701 mg, 64% yield). Spectral data matched those previously reported. [1] 1-3 1-3

Ethyl 2-diazo-3-hydroxy-3-(4-methoxyphenyl)propanoate



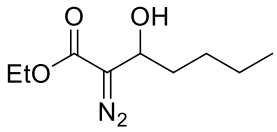
Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and freshly distilled *p*-anisaldehyde (0.61 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) to give the title compound as a yellow-orange solid (1.122 g, 90% yield). Spectral data matched those previously reported. [1b, c] 2, 3 2-3

Ethyl 2-diazo-3-hydroxy-3-(3-furyl)propanoate (S1)



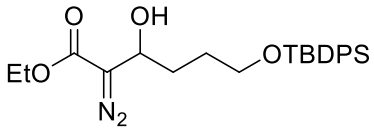
Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and 3-furaldehyde (0.42 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) to give the title compound as a yellow-orange oil (830 mg, 79% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 1H), 7.43 (t, *J* = 1.7 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 5.86 (d, *J* = 3.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.10 (br s, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 144.0, 140.1, 124.3, 108.4, 63.4, 61.4, 14.6. HRMS: [$C_9H_{10}N_2O_4Na^+$] 233.0533, found 233.0536

Ethyl 2-diazo-3-hydroxyheptanoate



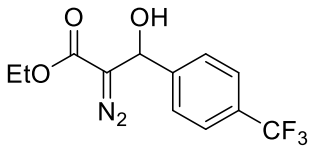
Prepared from ethyl diazoacetate (1.01 mL, 9.6 mmol, 1.6 eq.) and freshly distilled pentanal (0.64 mL, 6.0 mmol, 1.0 eq.) according to General Procedure B. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 20% EtOAc/hexanes) to give the title compound as a yellow oil (780 mg, 65% yield). Spectral data matched those previously reported. [2] 4 4

Ethyl 2-diazo-3-hydroxy-6-(*tert*-butyldiphenylsilyloxy)hexanoate



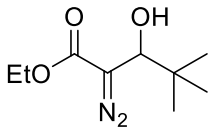
Prepared from ethyl diazoacetate as described previously. Spectral data matched those previously reported. [3] 5 5

Ethyl 2-diazo-3-hydroxy-3-[4-(trifluoromethyl)phenyl]propanoate



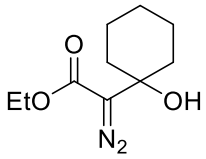
Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and 4-(trifluoromethyl)benzaldehyde (0.68 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 40% EtOAc/hexanes) to give the title compound as an orange solid (1.130 g, 78% yield). Spectral data matched those previously reported. [1c] 3 3

Ethyl 2-diazo-3-hydroxy-4-dimethylpentanoate



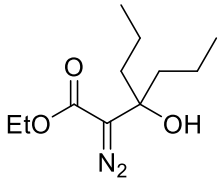
Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and pivaldehye (0.54 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) to give the title compound as bright yellow oil (760 mg, 76% yield). Spectral data matched those previously reported. [4]66

Ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate



Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and freshly distilled cyclohexanone (0.52 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) to give the title compound as bright yellow oil (1.060 g, 100% yield). Spectral data matched those previously reported. [5] 7 7

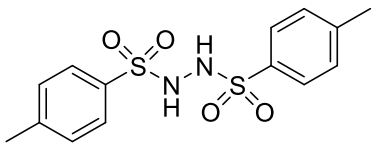
Ethyl 2-diazo-3-hydroxy-3-propylhexanoate



Prepared from ethyl diazoacetate (0.85 mL, 8 mmol, 1.6 eq.) and 4-heptanone (0.70 mL, 5.0 mmol, 1.0 eq.) according to General Procedure A. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 30% EtOAc/hexanes) and left under vacuum overnight to give the title compound as bright yellow oil (633 mg, 55% yield). Spectral data matched those previously reported. [6] 8 8

Preparation of Diazoketone

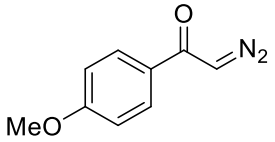
N,N'-ditosylhydrazine



Prepared according to literature procedure[7]. *p*-toluenesulfonyl hydrazide (5.01 g, 26.9 mmol, 1.0 eq.) and *p*-toluenesulfonyl chloride (6.67 g, 35.0 mmol, 1.3 eq.) were dissolved in CH_2Cl_2

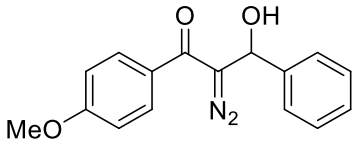
(30 mL) and cooled to 0ºC. Pyridine (2.82 mL, 35.0 mmol, 1.3 eq.) was added dropwise and stirred for 30 min at 0ºC until the formation of a white precipitant. The reaction mixture was then diluted in a 2:3 hexanes/water solution (50 mL) and continued to stir at 0ºC for another 15 min. The precipitant was then isolated via vacuum filtration and rinsed with ice cold Et_2O. The crude precipitant was the recrystallized from a solution 2:1 mixture of boiling acetone/water (45 mL) to produce N,N'-ditosylhydrazine as a white solid (5.82 g, 64% yield). Spectral data matched those previously reported.[7]

2-diazo-1-(4-methoxyphenyl)ethanone



Prepared according to literature procedure[7]. 4'-methoxyphenylacyl bromide (1.37 g, 6.0 mmol, 1.0 eq.) and N,N'-ditosylhydrazine (2.25 g, 6.6 mmol, 1.1 eq.) was dissolved in THF (30 mL) and cooled to 0ºC. DBU was then added dropwise to the reaction mixture and allowed to stir for 30 min at 0ºC. The reaction was then quenched with 3 mL sat. $NaHCO_3$ (aq.), poured into a separatory funnel with 20 mL Et_2O and 30 mL H_2O. The layers were separated, and the aqueous phase was extracted twice more with Et_2O (20 mL). The combined organics were then washed with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was then diluted in CH_2Cl_2 (5 mL) to produce a white precipitant which was subsequently filtered through celite and washed with additional ice cold CH_2Cl_2 (25 mL). The filtrate was then concentrated *in vacuo* and purified via silica gel column chromatography (gradient elution, 10 to 30% EtOAc/hexanes) to provide the title compound as a bright yellow solid (423 mg, 40% isolated yield). Spectral data matched those previously reported.[8]

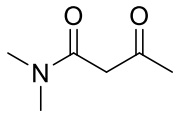
2-diazo-3-hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (S2)



Prepared from 2-diazo-1-(4-methoxyphenyl)ethanone (423 mg, 2.4 mmol, 1.6 eq) and benzaldehyde (0.15 mL, 1.5 mmol, 1.0 eq) according to General Procedure A. The residue was purified twice by silica gel column chromatography (gradient elution, 0 to 70% EtOAc/hexanes, then gradient elution, 0 to 10% EtOAc/CH_2Cl_2) to give title compound as a bright yellow oil (297 mg, 70% isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.19 (d, J = 3.2 Hz, 1H), 3.85 (s, 3H), 3.62 – 3.57 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.3, 162.8, 138.7, 129.9, 129.6, 129.0, 128.6, 126.1, 114.0, 72.6, 69.8, 55.6. IR: 1591 cm^{-1} (C=O stretch), 2075 cm^{-1} (N=N stretch), 3382 (OH). HRMS: [$C_{16}H_{14}N_2O_3Na^+$] 305.0897, found 305.0894.

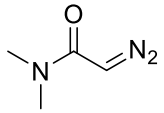
Preparation of Diazoamide

N,N-Dimethyl-3-oxobutanamide[9]



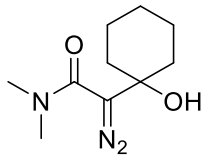
Prepared in accordance with Du *et al.*[10] with the modification that 40% aqueous dimethylamine (Me_2NH) was used. Silica gel flash column chromatography gave title compound as a pale yellow oil (63% yield). ^1H NMR matched previously reported values.[10]

2-Diazo-N,N-dimethylacetamide[9]



Prepared from N,N-Dimethyl-3-oxobutanamide using the procedure specified by Bartlett *et al.* [11]with the modification that para-acetamidobenzenesulfonyl azide (p-ABSA) was used in place of tosyl azide. After stirring in aqueous KOH for 3 hours, the solution was partitioned between 1:1 (v/v) CH_2Cl_2/Et_2O and 2.5N KOH saturated with NaCl. Layers were separated, and the organic layer was dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude material was dissolved in EtOAc and eluted over a plug of neutral alumina. Alumina was washed with EtOAc, and filtrate was concentrated in vacuo to give title compound as a bright yellow oil (43% yield). ^1H NMR matched previously reported values.[11]

2-Diazo-2-(1-hydroxycylohexyl)-N,N-dimethylacetamide[9]



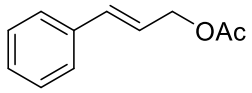
Prepared from 2-Diazo-N,N-dimethylacetamide and cyclohexanone according to procedure specified by Cleary *et al.* The compound was purified by dissolving in 1:1 EtOAc/Hexanes and passing through a plug of neutral alumina. Column was washed three times with 1:1 EtOAc/Hexanes (20 mL) to provide title compound as a bright orange oil (67% yield). ^1H NMR matched previously reported values.[9]

General Procedure C: Preparation of Allyl Stannanes

A modified procedure adapted from Takaki and co-workers[12][149] was followed: Trimethylsilyl chloride (0.13 mL, 1 mmol, 0.2 eq.) was added to a mixture of manganese powder (549 mg, 10 mmol, 2.0 eq), nickel (II) bromide (109 mg, 0.5 mmol, 0.1 eq.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (268 mg, 1 mmol, 0.2 eq.) in DMF (10 mL), and allowed to stir for ~10 min at room

temperature until the reaction mixture turned dark black in color. Allyl acetate (5 mmol, 1 eq) was added followed by tributyltin methoxide (1.74 mL, 6 mmol, 1.2 eq) and the reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was then diluted with Et_2O (50 mL), and then H_2O (50 mL) and 10% *(w/v)* LiCl in 1M HCl (50 mL) were added. The organic layer was separated and the aqueous layer was extracted twice more with Et_2O (50 mL). The combined organics were then washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography using hexanes eluent.

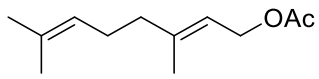
(*E*)-Cinnamyl acetate



Sodium borohydride (500 mg, 13.2 mmol, 1.2 eq.) was added portion wise to a solution of (*E*)-cinnamaldehyde (1.39 mL, 11.0 mmol, 1.0 eq.) in MeOH (20 mL), and the reaction was allowed to stir under nitrogen for 1 hour. 1 M HCl (10 mL) was added and the mixture was extracted three times with EtOAc (25 mL). The organics were combined and washed with saturated $NaHCO_3$ (aq.), brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford crude (*E*)-cinnamyl alcohol as a white crystalline solid.

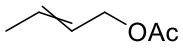
The crude (*E*)-cinnamyl alcohol (11.0 mmol, 1.0 eq) was dissolved in CH_2Cl_2 (25 mL), and 4-dimethylaminopyridine (269 mg, 2.2 mmol, 0.2 eq) and freshly distilled acetic anhydride (2.3 mL, 24 mmol, 2.2 eq) were added and the mixture was cooled to 0 °C. Et_3N (3.1 mL, 22 mmol, 2.0 eq.) was added dropwise and the reaction was removed from the ice bath and stirred for 2 hours. Saturated aqueous NH_4Cl was added and the mixture was extracted three times with CH_2Cl_2, the organics were combined, washed with saturated $NaHCO_3$ (aq.), brine, dried over $MgSO_4$, and concentrated *in vacuo.* The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 20% EtOAc/hexanes) to give the title compound as a colorless oil (1.807 g, 93% yield over 2 steps). Spectral data matched those previously reported. [13] 15 10

Geranyl acetate



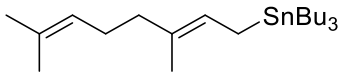
4-dimethylaminopyridine (489 mg, 4.0 mmol, 0.2 eq) and freshly distilled acetic anhydride (4.16 mL, 44 mmol, 2.2 eq) were added to a solution of geraniol (3.5 mL, 20 mmol, 1.0 eq) in CH_2Cl_2 (20 mL), and the mixture was cooled to 0 ºC. Et_3N (5.6 mL, 40 mmol, 2.0 eq.) was added dropwise and the mixture was removed from the cooling bath and stirred for 2 hours. Saturated NH_4Cl (aq) was added and the reaction mixture, extracted three times with CH_2Cl_2 (25 mL), The combine organics were washed with sat. $NaHCO_3$ (aq.), brine, dried over $MgSO_4$, and concentrated *in vacuo.* The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 15% EtOAc/hexanes) to give the title compound as colorless oil (2.962 g, 76% yield). Spectral data matched those previously reported. [14] 16 11

Crotyl Acetate



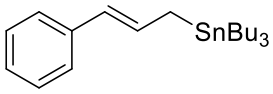
Crotyl alcohol (mixture of cis and trans) (8.5 mL, 100 mmol, 1.0 eq) was added to a mixture of freshly distilled acetic anhydride (21 mL, 220 mmol, 2.2 eq) and dimethylaminopyridine (2.44 g, 20 mmol, 0.2 eq) and the mixture was cooled to 0 ºC. Freshly distilled triethylamine (28 mL, 200 mmol, 2.0 eq.) was added dropwise to the reaction mixture and the ice bath was then removed and the reaction was allowed to stir at room temperature for 1 h. The reaction was quenched with water, the layers were separated and the organic layer was then washed with brine. The organics were fractionally distilled under reduced pressure to yield final product as a clear colorless oil (7.75 g, 68% yield). Spectral data matched those previously reported. [15] 17 12

(*E*)-Geranyl tributyl stannane (15)



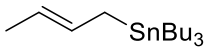
Prepared from geranyl acetate (1.07 mL, 5.0 mmol, 1.0 eq.) as described in general procedure C. The residue was purified via silica gel flash column chromatography in hexanes to yield the title compound as a clear colorless oil (1.945g, 91% yield). Spectral data matched those previously reported. [12] 14 9

(*E*)-Cinnamyl tributyl stannane (14)



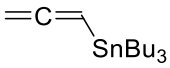
Prepared from cinnamyl acetate (1.52 g, 8.6 mmol, 1.0 eq.) as described in general procedure C. The residue was then purified via silica gel flash column chromatography in hexanes to yield the title compound as a clear colorless oil (2.66 g, 76% yield). Spectral data matched those previously reported. [12] 14 9

***(E)*-Crotyl tributyl stannane (16)**



Prepared from crotyl acetate (0.62 mL, 8.6 mmol, 1.0 eq.) as described in general procedure C. The residue was then purified via silica gel flash column chromatography in hexanes to yield title compound as a clear colorless oil (1.73 g, 100% yield). Spectral data matched those previously reported. [12] 14 9

Allenyl tributyl stannane (13)



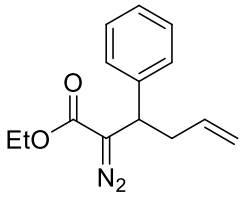
Mercury (II) chloride (543 mg, 2.0 mmol, 0.1 eq.) and magnesium turnings (486 mg, 20 mmol, 1.0 eq) were suspended in Et_2O (20 mL) and cooled to 0 ºC. Propargyl bromide (2.17 mL, 20 mmol, 1 eq.) was added dropwise and allowed to stir for 1 hour at 0 ºC. Tributyl tin chloride (5.4 mL, 20 mmol, 1.0 eq.) was then added dropwise at 0 ºC and the mixture was allowed to warm slowly in the cooling bath to room temperature overnight. Water was added and the reaction was extracted three times with hexanes (25 mL), washed with H_2O, brine, then 10% NH_4F *(w/v)*. The organic layers were combined and then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified via silica gel flash column chromatography in hexanes to yield the title compound as a clear colorless oil (2.168 g, 34% yield). Density determined to be 1.80 g/mL (±0.05 g/mL). Spectral data matched those previously reported. [16] 18, 19 13-14

General Procedure D: Preparation of β-allyl-α-diazoesters

Allyltributylstannane (0.19 mL, 0.6 mmol, 1.2 eq.) was added to a suspension of zinc (II) triflate (182 mg, 0.5 mmol, 1 eq) in CH_2Cl_2 (8 mL) at room temperature. β-hydroxy-α-diazoester (0.5 mmol, 1 eq.) dissolved in of CH_2Cl_2 (0.5 mL) was added to the reaction mixture via syringe. The vial containing the diazo was rinsed three times with 0.5 mL portions of CH_2Cl_2 which were added to the reaction mixture via the same syringe. The reaction mixture was allowed to stir overnight at room temperature. 2M NaOH was added and the reaction mixture was extracted three times with CH_2Cl_2 (25 mL), washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Products were purified by silica gel flash column chromatography over silica gel that contained 10% (*w/w*) K_2CO_3 to remove any excess tin reagents.

Note: *The β-allyl-α-diazoester products showed remarkable stability. All products were stored in a -20ºC freezer up to almost 2 years with no signs of degradation by NMR. The only exception was* ***16*** *which did eventually degrade after 1.5 years. Furthermore, many of the products proved to be stable at room temperature in CH_2Cl_2 after 2 weeks with no signs of degradation by TLC.*

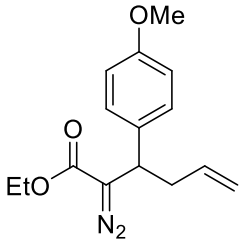
Ethyl 2-diazo-3-phenylhex-5-enoate (3)



Prepared from ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (110 mg, 0.5 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time: 22.5 h). The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (122 mg, 100% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 5.83 – 5.70 (m, 1H), 5.13 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.19 (qd, *J* = 7.1,

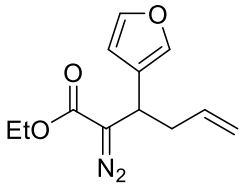
1.7 Hz, 2H), 3.81 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.70 – 2.47 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 141.8, 135.1, 128.8, 127.3, 127.2, 117.5, 60.9, 39.0, 37.3, 14.5. IR: 1690 cm^{-1} (C=O stretch), 2077 cm^{-1} (N=N stretch). HRMS: [$C_{14}H_{16}N_2O_2Na^+$] 267.1104, found 267.1109.

Ethyl 2-diazo-3-(4-methoxyphenyl)hex-5-enoate (4)



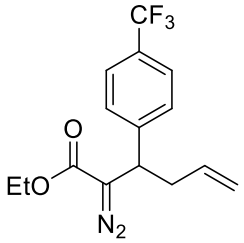
Prepared from ethyl 2-diazo-3-hydroxy-3-(4-methoxyphenyl)propanoate (127 mg, 0.507 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time 24.5 h). The residue was purified by silica gel flash column chromatography with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (122 mg, 88% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.81 – 5.68 (m, 1H), 5.11 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.05 (dd, *J* = 10.0, 1.1 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.79 (s, 3H), 3.84 – 3.75 (m, 1H), 2.64 – 2.49 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ166.9 *(observed in HMBC),* 158.8, 135.3, 133.7, 128.3, 117.4, 114.2, 61.0, 55.4, 38.4, 37.5, 14.6. IR: 1692 cm^{-1} (C=O stretch), 2079 cm^{-1} (N=N stretch). HRMS: [$C_{15}H_{18}N_2O_3Na^+$] 297.1210, found 297.1214.

Ethyl 2-diazo-3-(furan-3-yl)hex-5-enoate (5)



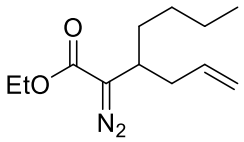
Prepared from ethyl 2-diazo-3-hydroxy-3-(3-furyl)propanoate (211 mg, 1.00 mmol, 1 eq.) and allyltributylstannane (0.37 mL, 1.20 mmol, 1.2 eq.) according to general procedure D (reaction time: 2 h). Reaction was worked up after 2 hours. The residue was purified by silica gel flash column chromatography with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow-orange oil (165 mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (t, *J* = 1.6 Hz, 1H), 7.35 – 7.30 (m, 1H), 6.35 – 6.30 (m, 1H), 5.85 – 5.73 (m, 1H), 5.14 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.08 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.78 (t, *J* = 7.4 Hz, 1H), 2.65 – 2.55 (m, 1H), 2.53 – 2.42 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 143.5, 139.3, 135.0 125.1, 117.7, 109.8, 61.0, 37.1, 30.8, 14.6. IR: 1688 cm^{-1} (C=O stretch), 2081 cm^{-1} (N=N stretch). HRMS: [$C_{12}H_{14}N_2O_3H^+$] 235.1077, found 235.1065.

Ethyl 2-diazo-3-(4-(trifluoromethyl)phenyl)hex-5-enoate (6)



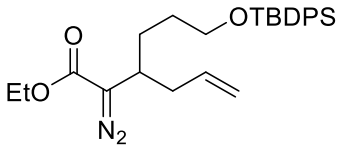
Prepared from ethyl 2-diazo-3-hydroxy-3-[4-(trifluoromethyl)phenyl]propanoate (157 mg, 0.545 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time 23 h). The residue was purified by silica gel flash column chromatography with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 2% EtOAc/hexanes) to give the title compound as a bright yellow oil (9 mg, 5% yield). *Note: In another trial of this reaction starting with 146 mg ethyl 2-diazo-3-hydroxy-3-[4-(trifluoromethyl)phenyl]propanoate, 48 mg of starting material was recovered with similar results in yield. Other attempts of this reaction at increased scaled revealed other unidentifiable byproducts.* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.82 – 5.69 (m, 1H), 5.14 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 4.20 (qd, *J* = 7.1, 2.9 Hz, 2H), 3.87 (t, *J* = 8.3 Hz, 1H), 2.66 – 2.51 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 134.3, 127.5, 125.7 (q, *J* = 3.7 Hz), 118.0, 61.0, 38.2, 37.0, 14.4. *Note: Due to large C-F coupling constant and lack of concentration of the sample, the CF_3 carbon also could not be identified)*. IR: 1715 cm^{-1} (C=O stretch), 2087 cm^{-1} (N=N stretch). HRMS: [$C_{15}H_{15}F_3N_2O_2H^+$] 313.1158, found 313.1172.

Ethyl 3-allyl-2-diazoheptanoate (7)



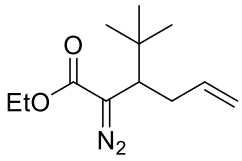
Prepared from ethyl 2-diazo-3-hydroxyheptanoate (108 mg, .539 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.60 mmol, 1.1 eq.) according to general procedure D (reaction time 24.5 h). Reaction was worked up after 2 hours. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (74 mg, 62%) along with the dimer product as a bright yellow oil (17 mg, 16% yield) The dimer product spectral data matched reported literature values. Ethyl 3-allyl-2-diazoheptanoate (7) [17]2015 ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.76 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.09 (d, *J* = 18.8 Hz, 1H), 5.04 (d, *J* = 10.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.53 (tt, *J* = 8.7, 4.3 Hz, 1H), 2.34 – 2.24 (m, 1H), 2.22 – 2.11 (m, 1H), 1.59 – 1.47 (m, 1H), 1.42 – 1.29 (m, 5H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 135.4, 117.1, 60.6, 58.5, 37.6, 33.7. 32.1, 29.3, 22.5, 14.5, 14.0. *Note: a longer relaxation time was used for this ^{13}C NMR experiment, therefore the diazo carbon at 58.5ppm was visible.* IR: 1696 cm^{-1} (C=O stretch), 2079 cm^{-1} (N=N stretch). HRMS: [$C_{12}H_{20}N_2O_2H^+$] 225.1598, found 225.1597.

Ethyl 3-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2-diazohex-5-enoate (8)



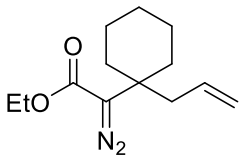
Prepared from ethyl 2-diazo-3-hydroxy-6-(tert-butyldiphenylsilyloxy)hexanoate (233 mg, 0.529 mmol, 1 eq.) and allyltributylstannane (0.33 mL, 1.06 mmol, 2 eq.) according to general procedure D (reaction time 23.5 h). The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil with some small inseparable impurities (92 mg, 37% yield, 50% yield b.r.s.m.). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 4H), 7.45 – 7.35 (m, 6H), 5.80 – 5.70 (m, 1H), 5.10 – 5.05 (m, 1H), 5.05 – 5.02 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.58 – 2.51 (m, 1H), 2.32 – 2.23 (m, 1H), 2.21 – 2.12 (m, 1H), 1.71 – 1.55 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4 *(observed in HMBC*) 135.7, 135.5, 134.1, 129.7, 127.8, 117.3, 63.6, 60.8, 38.4, 34.2, 30.8, 28.0, 27.0, 14.6. IR: 1693 cm^{-1} (C=O stretch), 2081 cm^{-1} (N=N stretch). HRMS: [$C_{27}H_{36}N_2O_3SiNa^+$] 487.2387, found 487.2391.

Ethyl 3-(*tert*-butyl)-2-diazohex-5-enoate (9)



Prepared from ethyl 2-diazo-3-hydroxy-4-dimethylpentanoate (114 mg, 0.518 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time 24.5 h). The residue was purified by silica gel flash column chromatography (2x) with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (3 mg, 2% yield, 11% yield b.r.s.m.). ^{1}H NMR (500 MHz, Chloroform-*d*) δ5.73 (dddd, *J* = 17.0, 10.1, 8.6, 5.0 Hz, 1H) , 5.10 (d, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 2.48 (dtd, *J* = 14.4, 3.5, 1.8 Hz, 1H), 2.34 (dd, *J* = 12.7, 3.6 Hz, 1H), 1.97 (td, *J* = 13.5, 8.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 116.4, 60.8, 43.6, 36.4, 31.1, 27.8, 14.6. *(The carbon signals for the carbonyl and diazo functional groups were not observed due to low sample concentration due to the limited quantity of material available).*

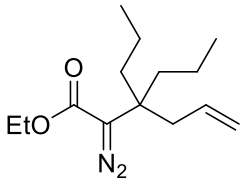
Ethyl 2-(1-allylcyclohexyl)-2-diazoacetate (10)



Prepared from ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate (117 mg, 0.551 mmol, 1 eq.) and allyltributylstannane (0.51 mL, 1.65 mmol, 3.0 eq.) according to general procedure D (reaction time 18 h). The residue was purified by silica gel flash column chromatography (gradient elution,

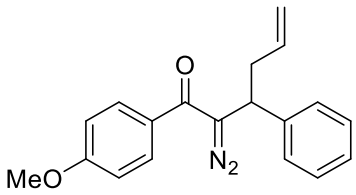
0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (96 mg, 74% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.76 (ddt, *J* = 17.6, 10.2, 7.5 Hz, 1H), 5.09 – 5.06 (m, 1H), 5.06 – 5.01 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.33 (d, *J* = 7.5 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.63 – 1.54 (m, 3H), 1.38 – 1.27 (m, 5H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 134.1, 118.2, 60.2, 44.5, 37.6, 34.3, 25.9, 22.6, 14.6. IR: 1709 cm^{-1} (C=O stretch), 2087 cm^{-1} (N=N stretch). HRMS: [$C_{13}H_{20}N_2O_2H^+$] 237.1598, found 237.1596.

Ethyl 2-diazo-3,3-dipropylhex-5-enoate (11)



Prepared from ethyl 2-diazo-3-hydroxy-3-propylhexanoate (115 mg, 0.50 mmol, 1 eq.) and allyltributylstannane (0.19 mL, 0.60 mmol, 1.2 eq.) according to general procedure D (reaction time: 23 h). The residue was purified by silica gel flash column chromatography (3:1 hexanes/dichloromethane) to give the title compound as a bright yellow oil (66 mg, 52% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.72 (ddt, *J* = 17.7, 10.4, 7.3 Hz, 1H), 5.10 – 5.07 (m, 1H), 5.07 – 5.03 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.33 (d, *J* = 7.3 Hz, 2H), 1.55 – 1.42 (m, 4H), 1.31 – 1.22 (m, 7H), 0.90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 134.1, 118.1, 61.1, 60.3, 39.7, 39.2, 36.9, 17.0, 14.6. IR: 1693 cm^{-1} (C=O stretch), 2077 cm^{-1} (N=N stretch). HRMS: [$C_{14}H_{24}N_2O_2H^+$] 253.1911, found 253.1930.

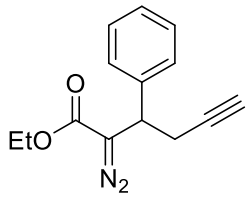
2-diazo-1-(4-methoxyphenyl)-3-phenylhex-5-en-1-one (12)



Prepared from 2-diazo-3-hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (136 mg, 0.48 mmol, 1.0 eq.) and allyltributylstannane (0.18 mL, 0.58 mmol, 1.2 eq.) according to general procedure D (reaction time 24 h). The residue was first purified by silica gel column chromatography (gradient elution, 0 to 6% EtOAc/hexanes), then further purified by another silica gel column (2:1 dichloromethane/hexanes) to give the title compound as a bright yellow oil (43 mg, 29% yield). This reaction yielded significantly more byproducts compared to the diazoesters. It is also noteworthy that the diazoketone was much more prone to acid degradation as noted by the slight degradation on silica gel. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.83 (dddd, *J* = 16.0, 10.2, 7.8, 5.8 Hz, 1H), 5.17 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.08 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.24 (dd, *J* = 9.4, 6.8 Hz, 1H), 3.83 (s, 3H), 2.75 – 2.68 (m, 1H), 2.66 – 2.57 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 162.3, 141.3, 135.3, 130.6, 129.5, 129.0, 127.42, 127.36, 117.5,

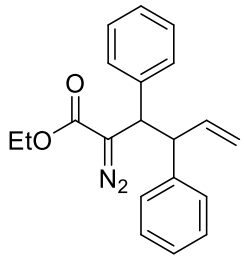
113.9, 70.8, 55.5, 38.7, 36.8. IR: 1601 cm^{-1} (C=O stretch), 2060 cm^{-1} (N=N stretch). HRMS: [$C_{19}H_{18}N_2O_2Na^+$] 329.1260, found 329.1260.

Ethyl 2-diazo-3-phenylhex-5-ynoate (17)



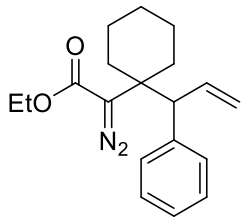
Prepared from ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (110 mg, 0.50 mmol, 1 eq.) and allenyl tributylstannane (0.11 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time: 22 h). The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (70 mg, 58% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.01 (t, *J* = 7.2 Hz, 1H), 2.80 (dd, *J* = 7.2, 2.5 Hz, 2H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 139.9, 128.9 (2C), 127.7, 127.3 (2C), 81.1, 70.9, 61.1, 38.8, 23.1, 14.5. IR: 1688 cm^{-1} (C=O stretch), 2085 cm^{-1} (N=N stretch), 3294 cm^{-1} (C≡C—H stretch). HRMS: [$C_{14}H_{14}N_2O_2H^+$] 243.1128, found 243.1121.

Ethyl 2-diazo-3,4-diphenylhex-5-enoate (18)



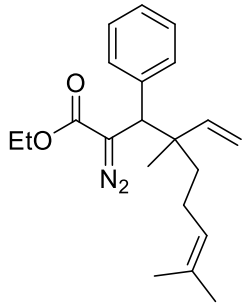
Prepared from ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (119 mg, 0.54 mmol, 1 eq.) and *(E)*-cinnamyltributylstannane (244 mg, 0.6 mmol, 1.1 eq.) according to general procedure D (reaction time: 23 h). The residue was purified by silica gel flash column chromatography with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (116 mg, 67% yield, 2:1 d.r.). ** = *mixture of major and minor diastereomers,* * = *minor diastereomer.* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.26 (m, 11H)**, 7.19 – 7.04 (m, 4H)**, 6.21 – 6.09 (m, 0.5H)*, 5.82 (ddd, *J* = 17.4, 10.3, 7.6 Hz, 1H), 5.26 (d, *J* = 16.9 Hz, 0.5H)*, 5.13 (d, *J* = 10.1 Hz, 0.5H)*, 4.90 (d, *J* = 10.3 Hz, 1H), 4.81 (d, *J* = 17.0 Hz, 1H), 4.23 (qd, *J* = 7.1, 1.7 Hz, 1H)*, 4.11 – 4.03 (m, 3.5H)**, 3.81 (dd, *J* = 11.8, 7.7 Hz, 1H), 3.72 (dd, *J* = 11.8, 9.1 Hz, 0.5H)*, 1.28 (t, *J* = 7.1 Hz, 1.5H)*, 1.13 (t, *J* = 6.6 Hz, 3H). *Due to the complexity of the spectrum major and minor diastereomers were not differentiated.* ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9 *(observed in HMBC),* 166.5 *(observed in HMBC)* 141.5, 141.1, 140.6, 139.7, 139.4, 128.9, 128.9, 128.6, 128.5, 128.0, 127.9, 127.7, 127.5, 127.2, 127.1, 126.6, 116.9, 116.0, 61.1, 60.9, 53.5, 52.5, 44.2, 44.1, 14.6, 14.4. IR: 1688 cm^{-1} (C=O stretch), 2079 cm^{-1} (N=N stretch). HRMS: [$C_{20}H_{20}N_2O_2H^+$] 321.1598, found 321.1591.

Ethyl 2-diazo-2-(1-(1-phenylallyl)cyclohexyl)acetate (19)



Prepared from ethyl 2-diazo-2-(1-hydroxycyclohexyl)acetate (106 mg, 0.5 mmol, 1 eq.) and *(E)*-cinnamyltributylstannane (407 mg, 1.0 mmol, 2.0 eq.) according to general procedure D (reaction time 21 h). Additionally, during aqueous work-up, the reaction mixture was washed five times with 1M KF in H_2O (25 mL) to remove excess tin reagents. The residue was purified by silica gel flash column chromatography (gradient elution, 0 to 2% EtOAc/hexanes) to give the title compound as a bright yellow oil (108 mg, 69% yield) with some small inseparable impurities. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.28 – 6.17 (m, 1H), 5.07 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.03 (d, *J* = 16.8 Hz, 1H), 4.20 – 4.06 (m, 2H), 3.45 (d, *J* = 10.0 Hz, 1H), 1.61 – 1.47 (m, 4H), 1.37 (td, *J* = 13.4, 3.3 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.32 – 0.99 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 140.8, 137.2, 129.2, 128.0, 126.6, 117.6, 60.2, 42.1, 31.9, 25.6, 22.8, 14.6. IR: 1692 cm^{-1} (C=O stretch), 2085 cm^{-1} (N=N stretch). HRMS: [$C_{19}H_{24}N_2O_2H^+$] 313.1911 found 313.1908.

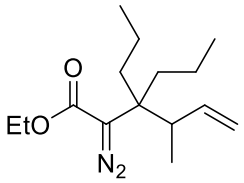
Ethyl 2-diazo-4,8-dimethyl-3-phenyl-4-vinylnon-7-enoate (20)



Prepared from ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (114 mg, 0.518 mmol, 1 eq.) and gernayltributylstannane (244 mg, 0.6 mmol, 1.1 eq.) according to general procedure D (reaction time 18 h). The residue was purified by silica gel flash column chromatography (2x) with 10% *(w/w)* K_2CO_3 (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (74mg, 42% yield, 2:1 d.r.). ** = *mixture of major and minor diasteromers,* * = *minor diastereomer.* ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.25 (m, 5H)**, 7.25 – 7.21 (m, 3H)**, 5.92 – 5.82 (m, 1.5H)**, 5.23 – 5.15 (m, 1.5H)**, 5.12 – 4.91 (m, 3H)**, 4.23 – 4.13 (m, 3H)**, 3.58 (s,0.5H)*, 3.54 (s, 1H), 1.97 – 1.85 (m, 2H), 1.84 – 1.73 (m, 1H)*, 1.66 (s, 1.5H)*, 1.62 (s, 3H), 1.56 (s, 1.5H)*, 1.51 (s, 3H), 1.49 – 1.39 (m, 1H), 1.36 – 1.26 (m, 1.5H)**, 1.25 – 1.20 (m, 7.5H)**, 0.95 (s, 1.5H)*. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 143.2*, 142.7, 140.0*, 139.9, 131.42*, 131.39, 129.2, 128.3, 128.2*, 127.2, 124.6*, 124.5, 115.9, 115.2*, 61.1, 47.8*, 47.6, 45.0*, 44.4, 39.9*, 39.8, 25.8*, 25.7, 22.9*, 22.8, 21.3, 20.5*, 17.70*, 17.66, 14.53, 14.51*.

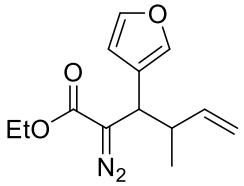
IR: 1690 cm^{-1} (C=O stretch), 2081 cm^{-1} (N=N stretch). HRMS: [$C_{21}H_{28}N_2O_2H^+$] 341.2224 found 341.2221.

Ethyl 2-diazo-4-methyl-3,3-dipropylhex-5-enoate (21)



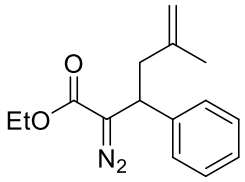
Prepared from ethyl 2-diazo-3-hydroxy-3-propylhexanoate (114 mg, 0.50 mmol, 1 eq.) and *(E)*-crotyl stannane (207 mg, 0.60 mmol, 1.2 eq.) according to general procedure D (reaction time 22 h). The residue was purified by silica gel flash column chromatography (3:1 hexanes/dichloromethane) to give the title compound as a bright yellow oil (12 mg, 9% yield). 28 mg of unknown byproducts were also isolated in the purification. No starting material was recovered from this reaction. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.84 – 5.73 (m, 1H), 5.03 – 5.00 (m, 1H), 4.99 – 4.96 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.56 – 2.45 (m, 1H), 1.74 – 1.64 (m, 1H), 1.61 – 1.45 (m, 3H), 1.37 – 1.16 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H) 1.01 (d, *J* = 6.9 Hz, 3H), 0.90 (dt, *J* = 9.9, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 141.2, 115.3, 60.9, 60.3, 46.4, 42.5, 36.0, 35.2, 17.8, 17.5, 16.0, 14.8, 14.6. IR: 1703 cm^{-1} (C=O stretch), 2077 cm^{-1} (N=N stretch). HRMS: [$C_{15}H_{26}N_2O_2H^+$] 267.2067, found 267.2055.

Ethyl 2-diazo-3-(furan-3-yl)-4-methylhex-5-enoate (22)



Prepared from ethyl 2-diazo-3-hydroxy-3-(3-furyl)propanoate (105 mg, 0.50 mmol, 1 eq.) *(E)*-crotylstannane (207 mg, 0.60 mmol, 1.2 eq.) according to general procedure D. Reaction was worked up after 3 hours. The residue was purified by silica gel flash column chromatography with (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow-orange oil (96 mg, 77% yield). **denotes minor diastereomer, ** denotes major and minor diastereomers.* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (t, *J* = 1.6 Hz, 0.5H)*, 7.36 (t, *J* = 1.6 Hz, 1H), 7.35 (s, 0.5H)*, 7.32 – 7.30 (m, 1H), 6.32 – 6.30 (m, 0.5H)*, 6.30 – 6.28 (m, 1H), 5.75 (m, 1.5H)**, 5.17 – 4.97 (m, 3H)**, 4.28 – 4.16 (m, 3H)**, 3.56 (d, *J* = 8.2 Hz, 1H), 3.48 (d, *J* = 9.6 Hz, 0.5H)*, 2.70-2.59 (m, 1H), 2.59-2.49 (m, 0.5H)*, 1.28 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 1.5H)*, 1.10 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 1.5H)*.). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 143.5*, 143.2, 141.12*. 141.07, 139.9, 139.6*, 124.3*, 123.4, 115.6, 115.3*, 110.2, 109.5*, 61.04, 60.96*, 41.5*, 40.9, 36.6, 36.2*, 19.1*, 18.2, 14.60. 14.57*. IR: 1711 cm^{-1} (C=O stretch), 2079 cm^{-1} (N=N stretch). HRMS: [$C_{13}H_{16}N_2O_3H^+$] 249.1234, found 249.1230.

Ethyl 2-diazo-5-methyl-3-phenylhex-5-enoate (24)

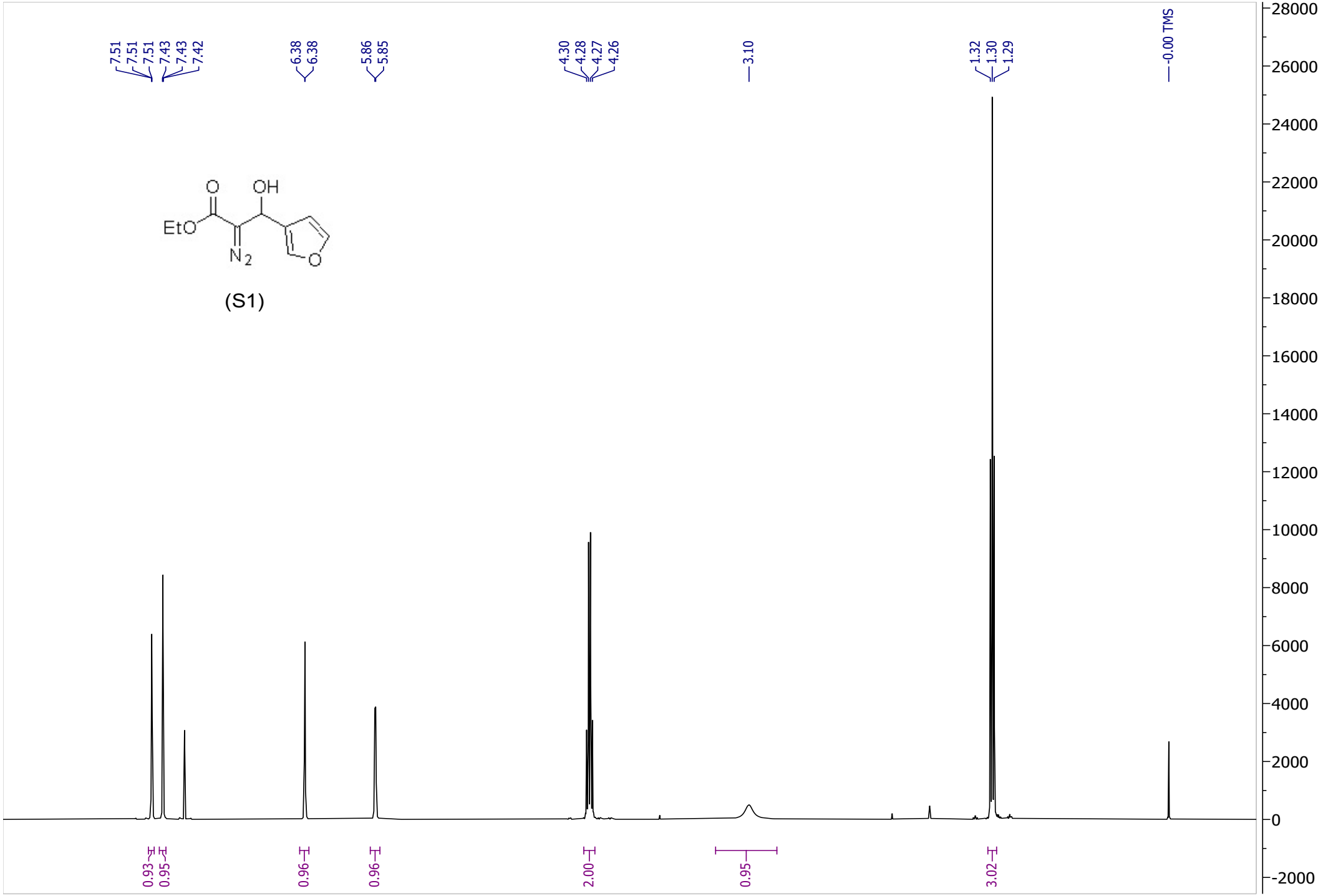


Prepared from ethyl 2-diazo-3-hydroxy-3-phenylpropanoate (110 mg, 0.5 mmol, 1 eq.) and 2-methyl-allyltimethylsilane (0.11 mL, 0.6 mmol, 1.2 eq.) according to general procedure D (reaction time: 25.5 h). The residue was purified by silica gel flash column chromatography twice (gradient elution, 0 to 4% EtOAc/hexanes) to give the title compound as a bright yellow oil (49 mg, 38% yield). A significant amount of product was sacrificed due to difficulty of purification. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 4.81 (s, 1H), 4.76 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.96 (t, *J* = 8.3 Hz, 1H), 2.53 (d, *J* = 8.3 Hz, 2H), 1.77 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 142.20, 142.15, 128.8 , 127.3, 127.1, 113.2, 61.0, 41.4, 37.2, 22.1, 14.6. IR: 1692 cm^{-1} (C=O stretch), 2081 cm^{-1} (N=N stretch). HRMS: [$C_{15}H_{18}N_2O_2H^+$] 259.1441, found 259.1441.

Works Cited

[1] a) S. T. R. Müller, D. Smith, P. Hellier and T. Wirth, *Synlett* **2014**, *25*, 871-875; b) R. A. Maurya, K.-I. Min and D.-P. Kim, *Green Chemistry* **2014**, *16*, 116-120; c) T. Zhong, T. Wu and X. Zhang, *Journal of Chemical Research* **2014**, *38*, 690-691.
[2] M. L. Kantam, V. Balasubrahmanyam, K. B. S. Kumar, G. T. Venkanna and F. Figueras, *Advanced Synthesis & Catalysis* **2007**, *349*, 1887-1890.
[3] E. M. Howard and M. Brewer, *ACS Catalysis* **2021**, *11*, 12203-12207.
[4] W. Qi, X. Xie, T. Zhong and X. Zhang, *Chinese Chemical Letters* **2018**, *29*, 194-196.
[5] D. P. Hari and J. Waser, *Journal of the American Chemical Society* **2016**, *138*, 2190-2193.
[6] J. Fang, E. M. Howard and M. Brewer, *Angew Chem Int Ed Engl* **2020**, *59*, 12827-12831.
[7] T. T. Eiji Ideue, and Jun Shimokawa and Tohru Fukuyama, *Organic Syntheses* **2012**, *89*, 501-509.
[8] Z. Xia, J. Hu, Y.-Q. Gao, Q. Yao and W. Xie, *Chemical Communications* **2017**, *53*, 7485-7488.
[9] S. E. Cleary, X. Li, L.-C. Yang, K. N. Houk, X. Hong and M. Brewer, *Journal of the American Chemical Society* **2019**, *141*, 3558-3565.
[10] H. Du, J. Rodriguez, X. Bugaut and T. Constantieux, *Chemistry – A European Journal* **2014**, *20*, 8458-8466.
[11] P. A. Bartlett, N. I. Carruthers, B. M. Winter and K. P. Long, *The Journal of Organic Chemistry* **1982**, *47*, 1284-1291.
[12] K. Komeyama, Y. Itai and K. Takaki, *Chemistry – A European Journal* **2016**, *22*, 9130-9134.
[13] S. Ghosh, A. Purkait and C. K. Jana, *Green Chemistry* **2020**, *22*, 8721-8727.

[14] C. Oberhauser, V. Harms, K. Seidel, B. Schröder, K. Ekramzadeh, S. Beutel, S. Winkler, L. Lauterbach, J. S. Dickschat and A. Kirschning, *Angewandte Chemie International Edition* **2018**, *57*, 11802-11806.
[15] R. Muto, K. Nagata, Y. Nakazumi, K. Nakamura and S. Ueno, *Organic Letters* **2023**, *25*, 2108-2112.
[16] a) A. Boaretto, D. Marton and G. Tagliavini, *Journal of Organometallic Chemistry* **1985**, *297*, 149-153; b) I. Suzuki, K. Kiyokawa, M. Yasuda and A. Baba, *Organic Letters* **2013**, *15*, 1728-1731.
[17] A. M. Peck and M. Brewer, *Organic Letters* **2023**, *25*, 2647-2651.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5.85
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4.28
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4.26
3.10
1.32
1.30
1.29
-0.00 TMS
O
OH
EtO
N2
O
(S1)
0.93
0.95
0.96
0.96
2.00
0.95
3.02
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
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6.0
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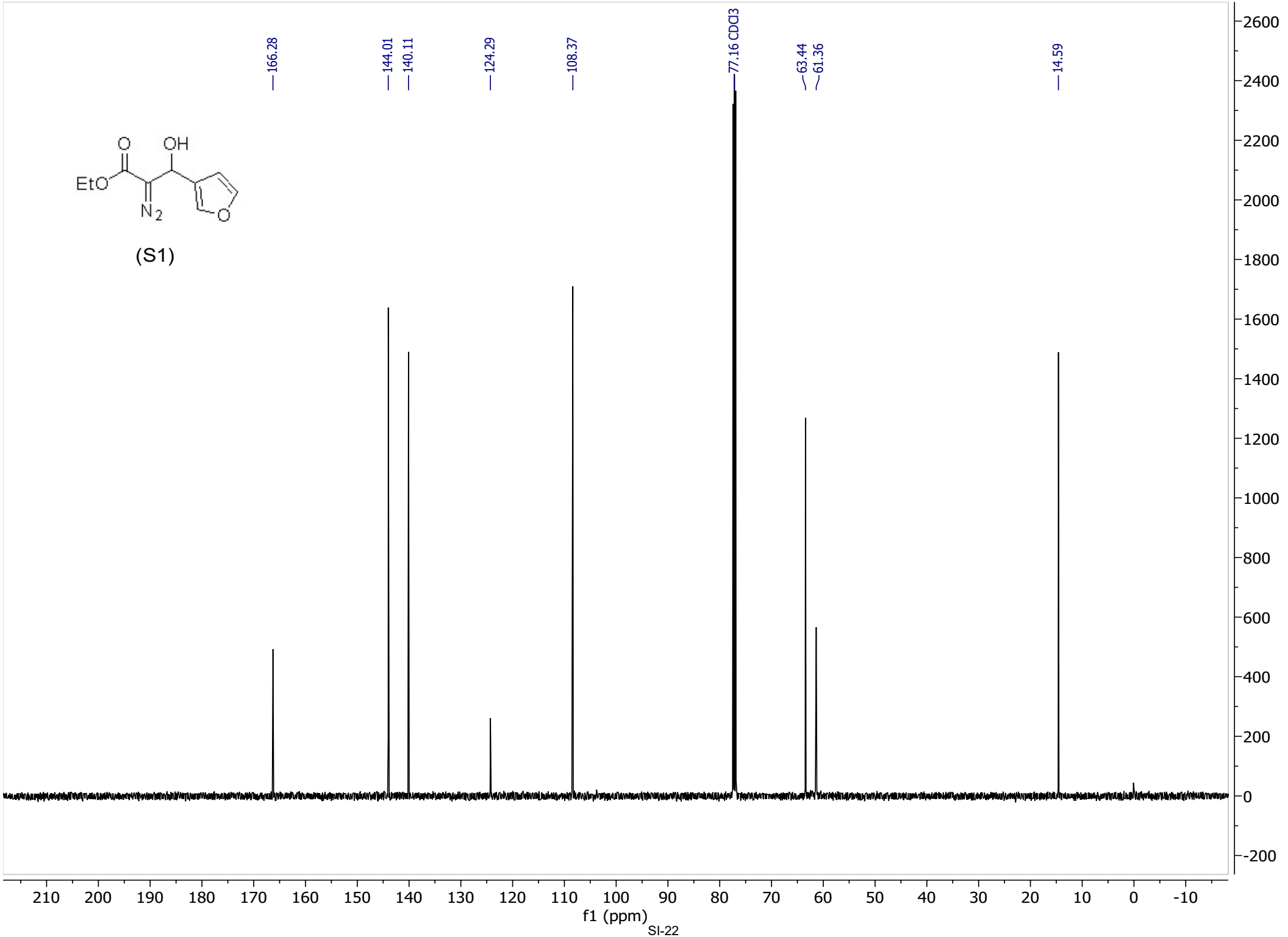
f1 (ppm)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(S1)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
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210
200
190
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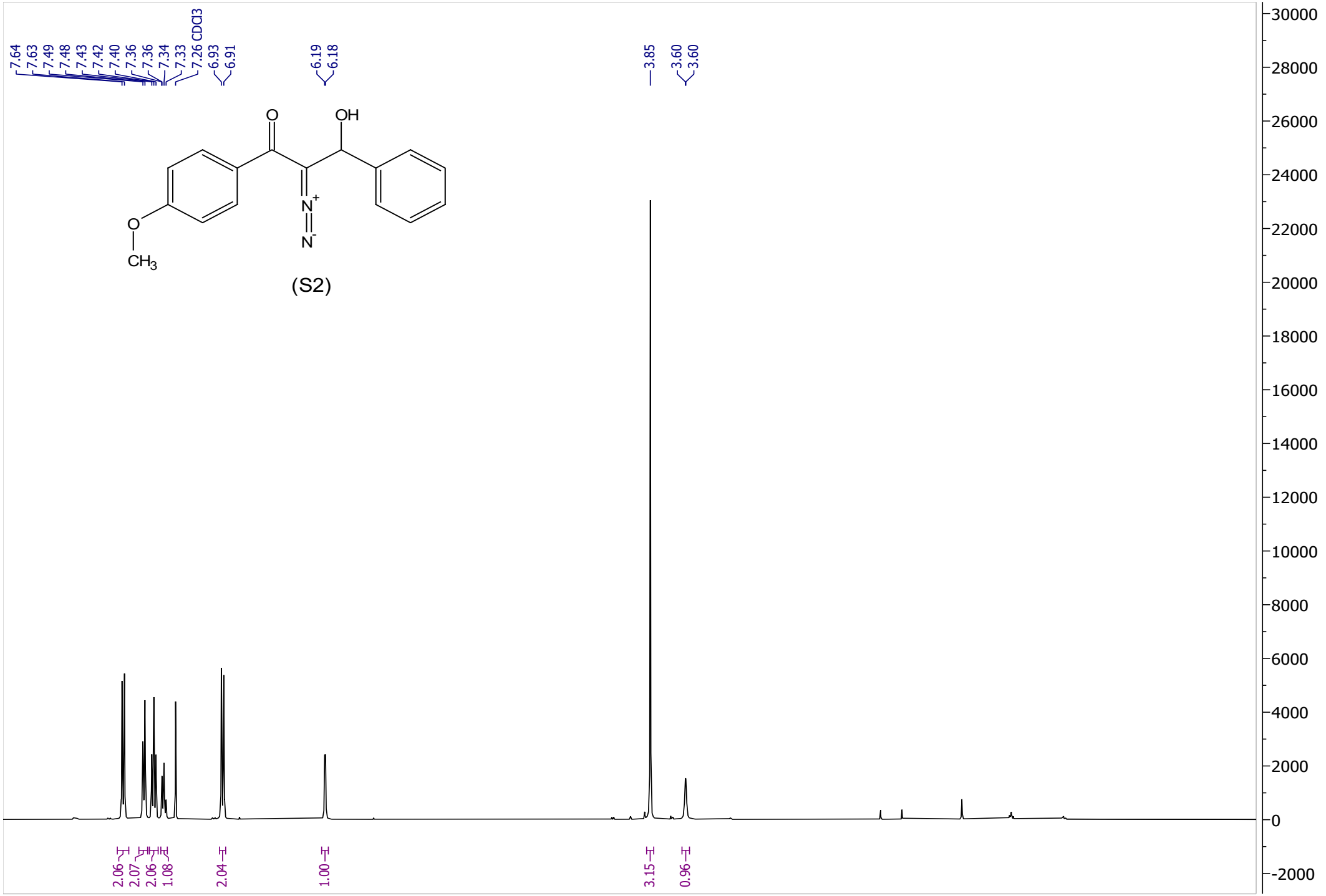
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N-
O
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(S2)
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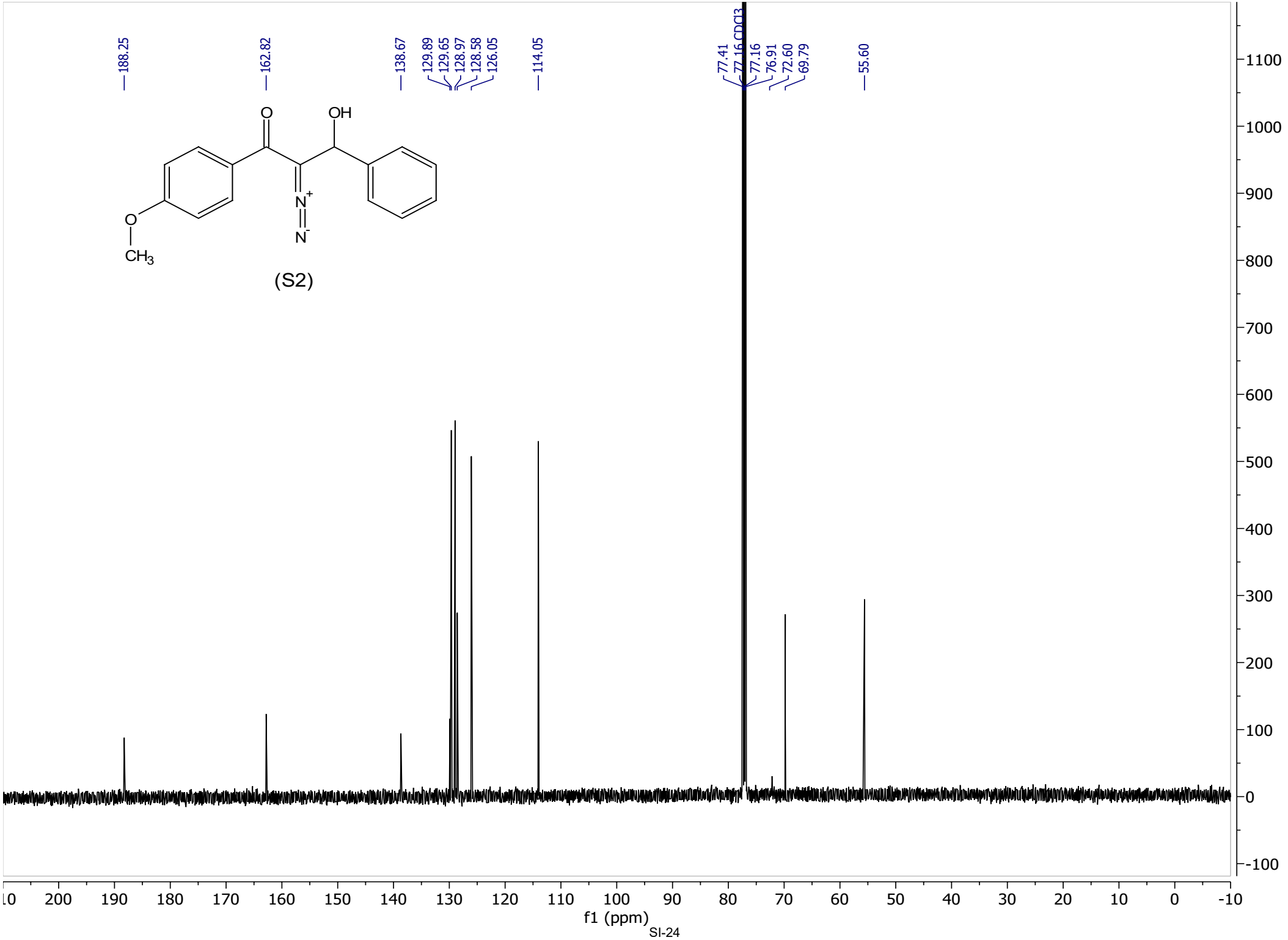
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76.91
72.60
69.79
55.60
O
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N+
N-
O
CH3
(S2)
1100
1000
900
800
700
600
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300
200
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200
190
180
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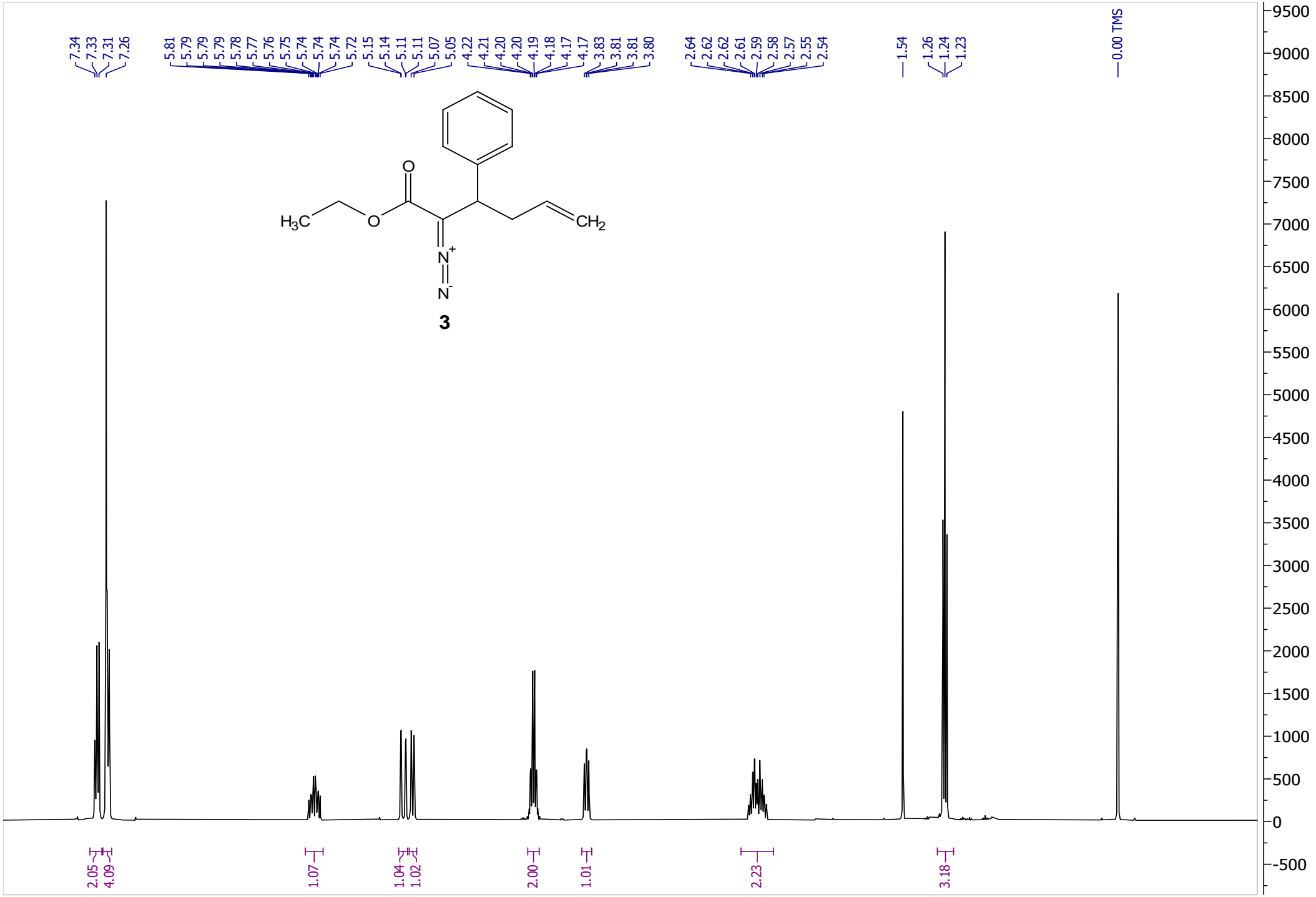
f1 (ppm)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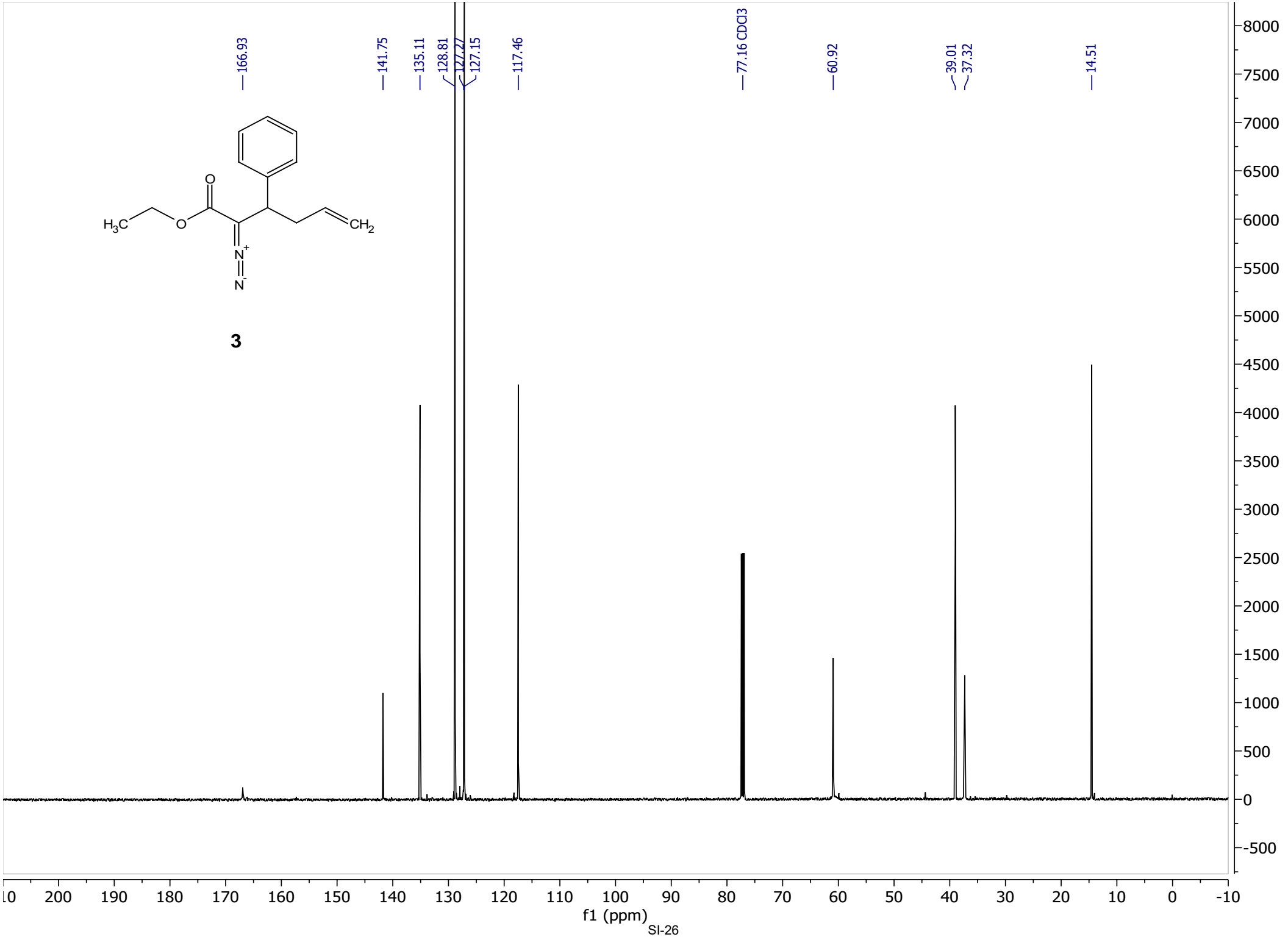
f1 (ppm)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H3C
O
CH2
N+
N-
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6000
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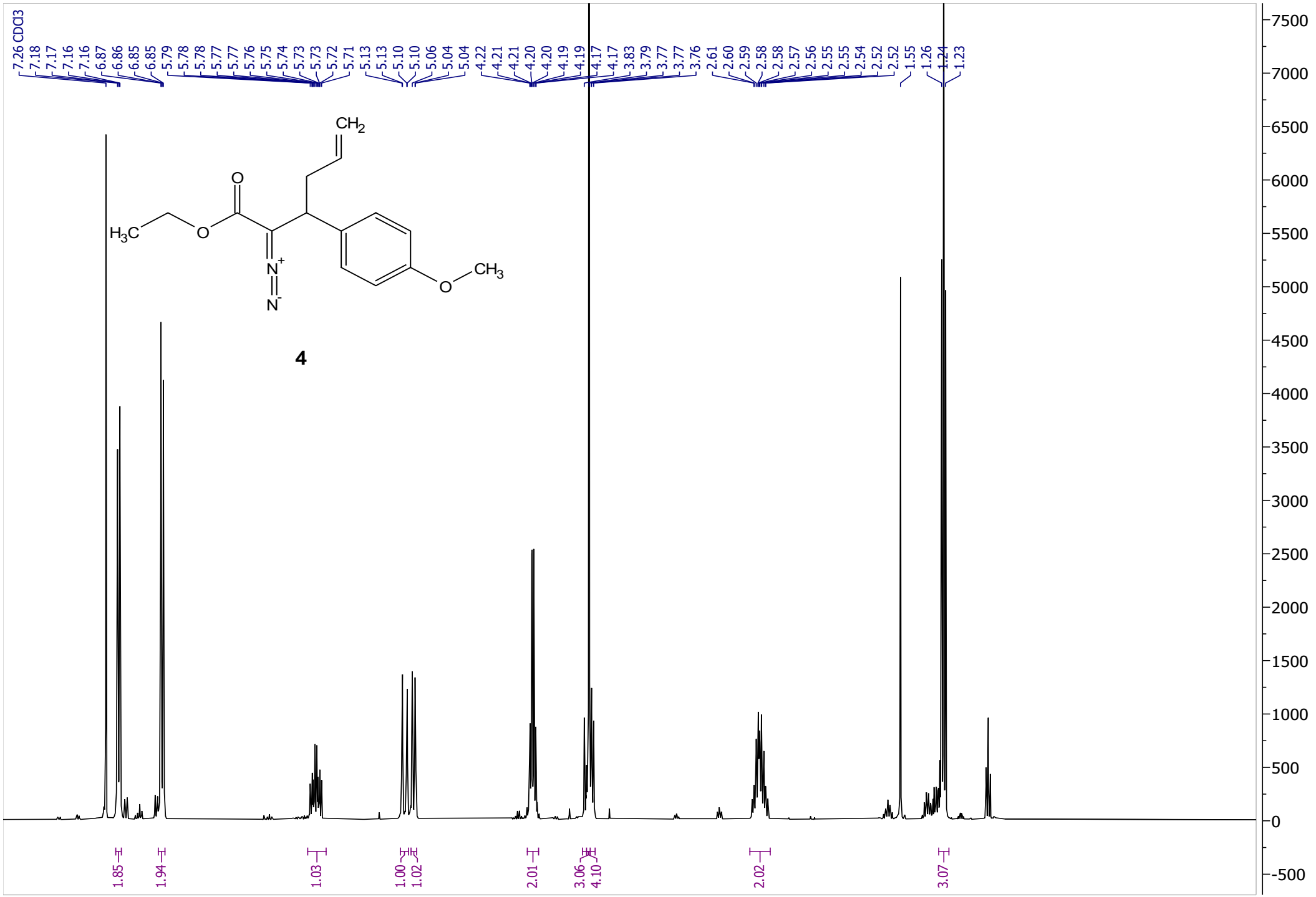
f1 (ppm)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H3C
O
N+
N-
O
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1.00
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5000
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3500
3000
2500
2000
1500
1000
500
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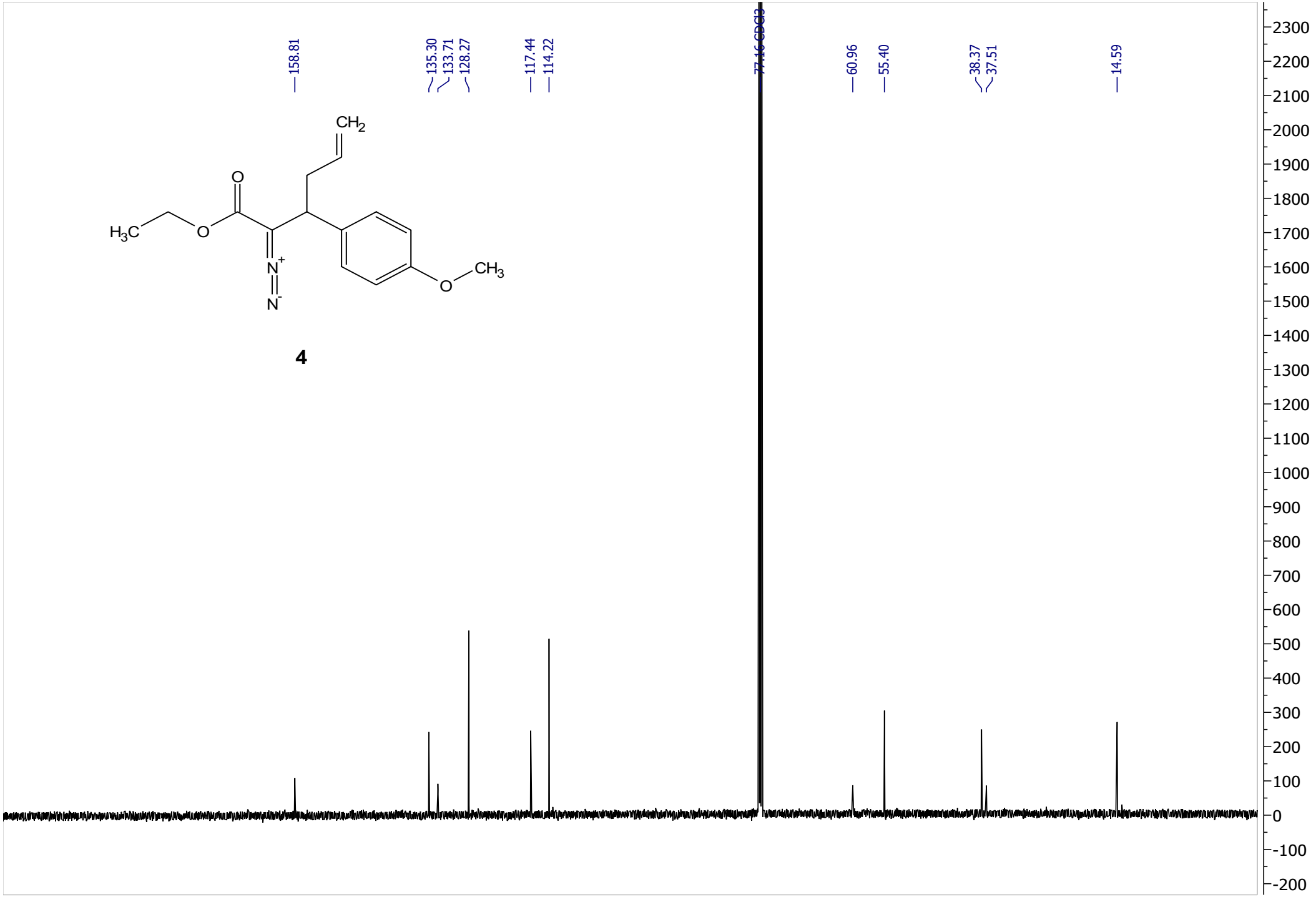
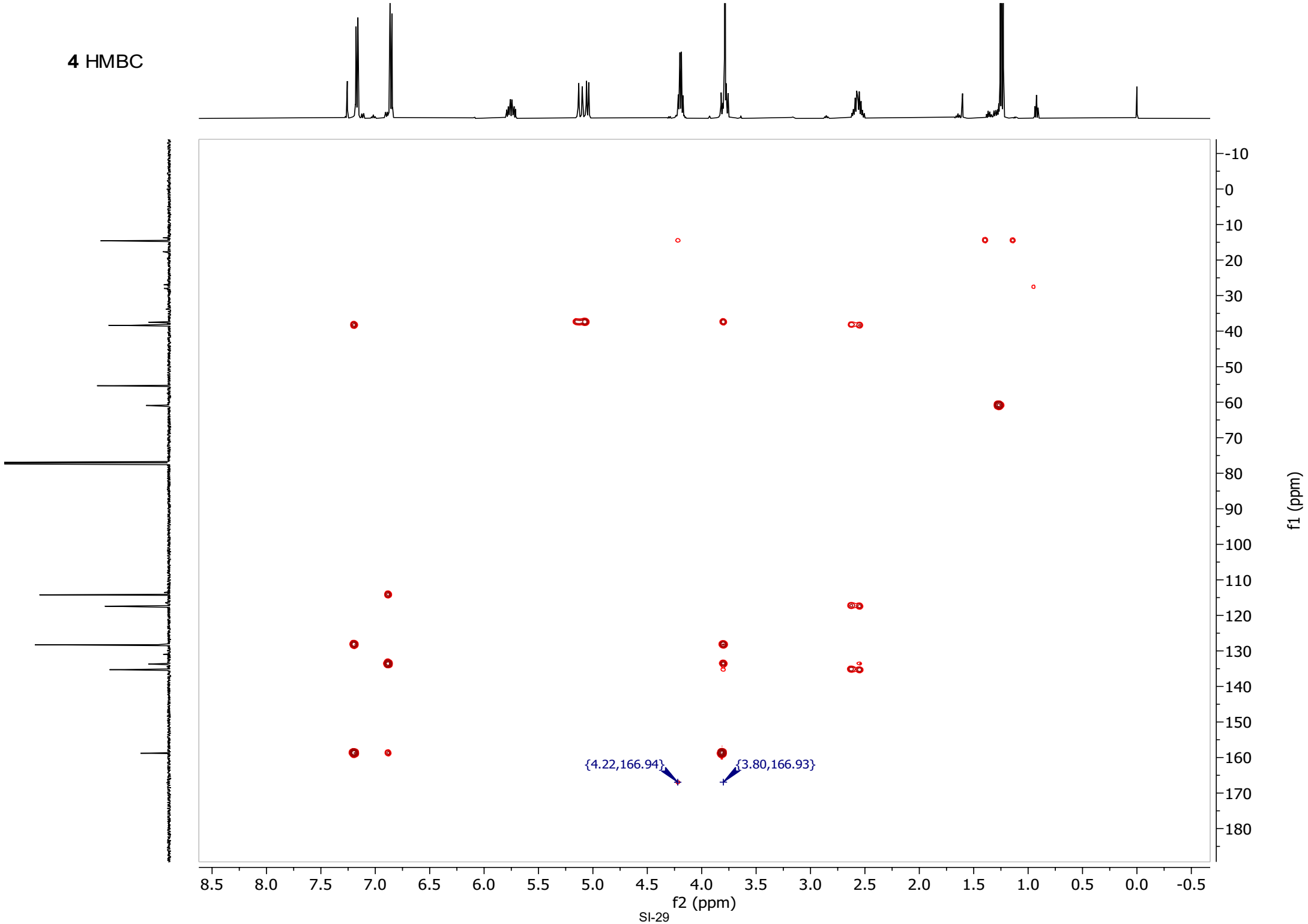
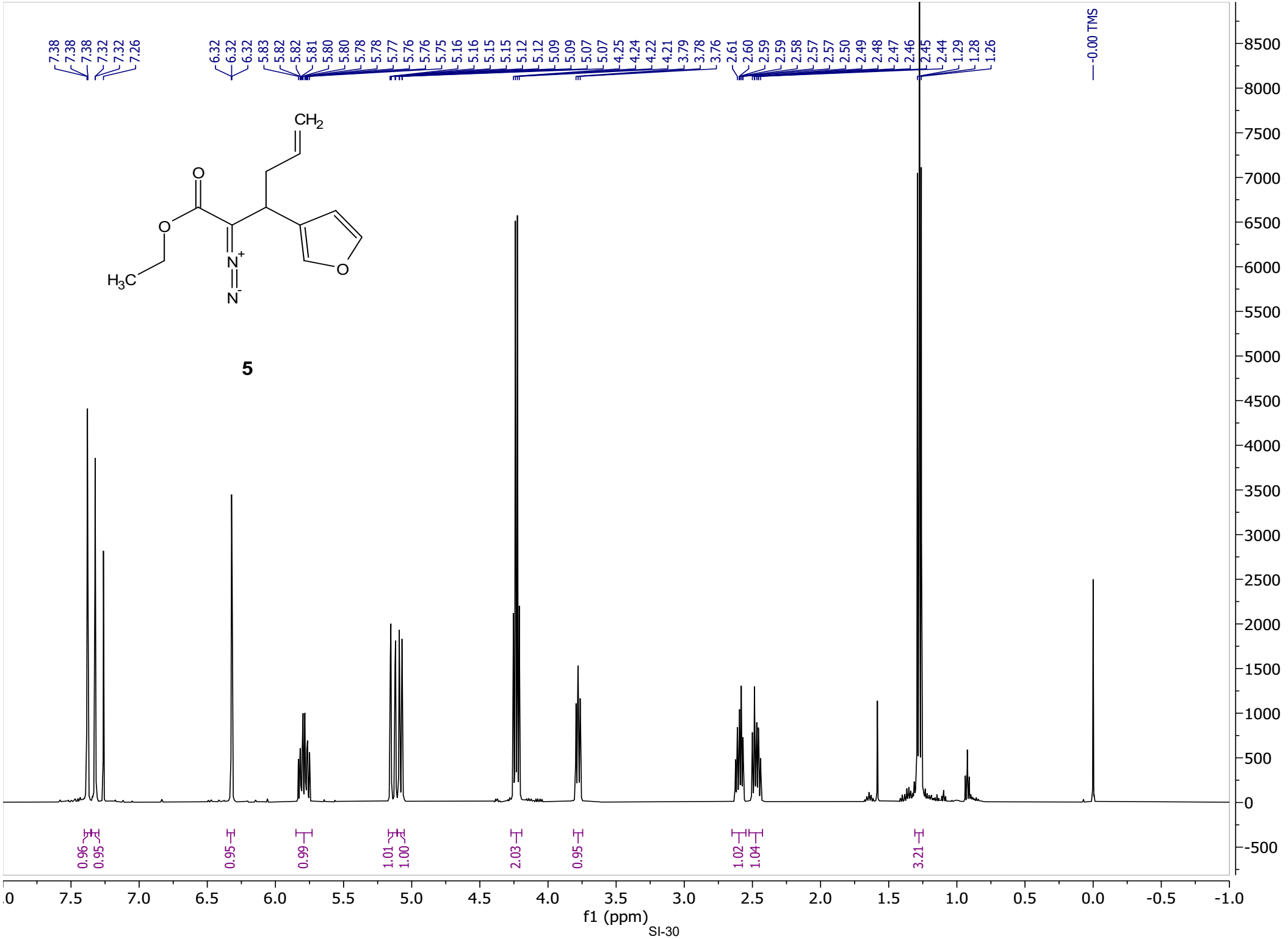
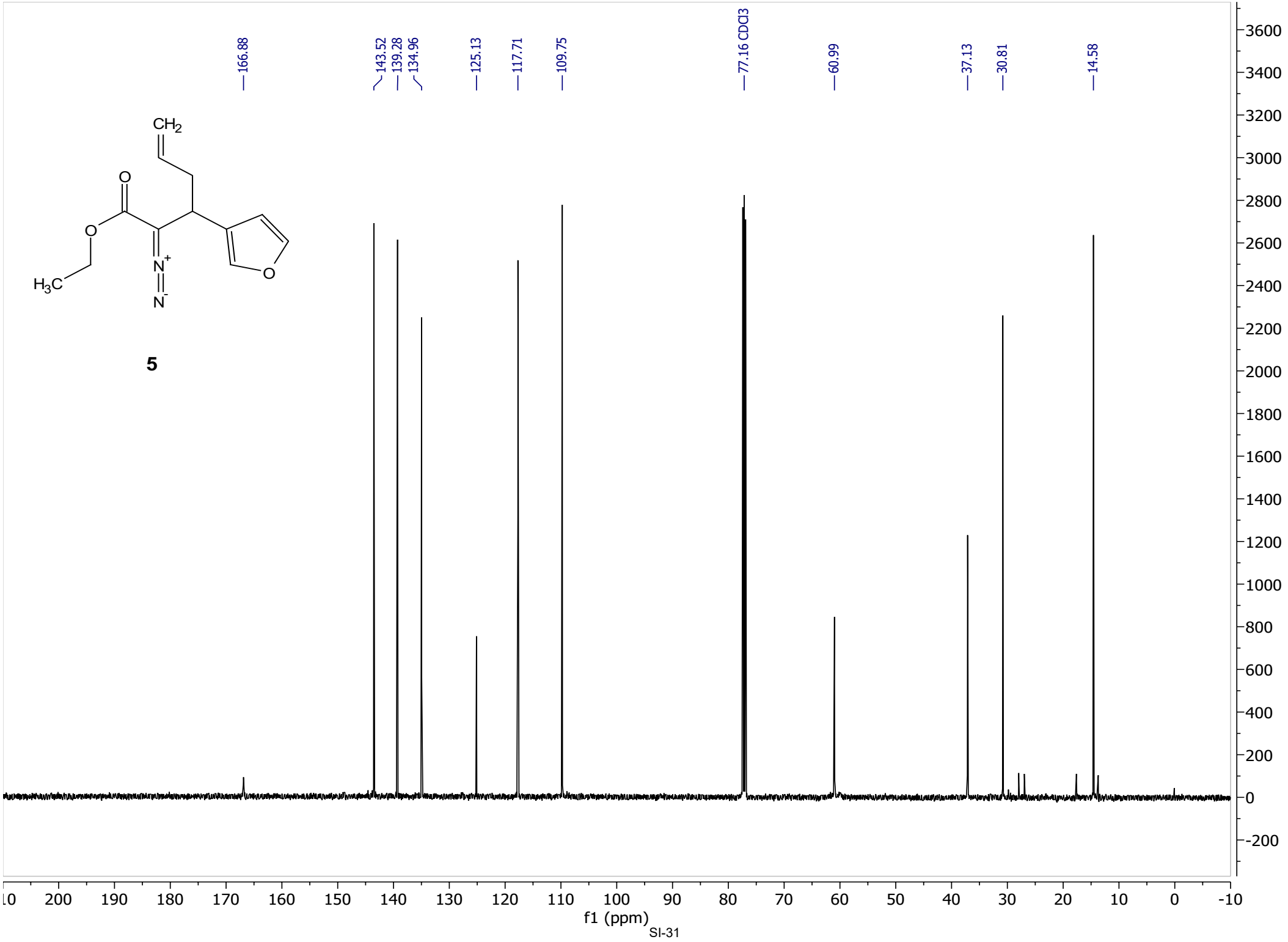
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

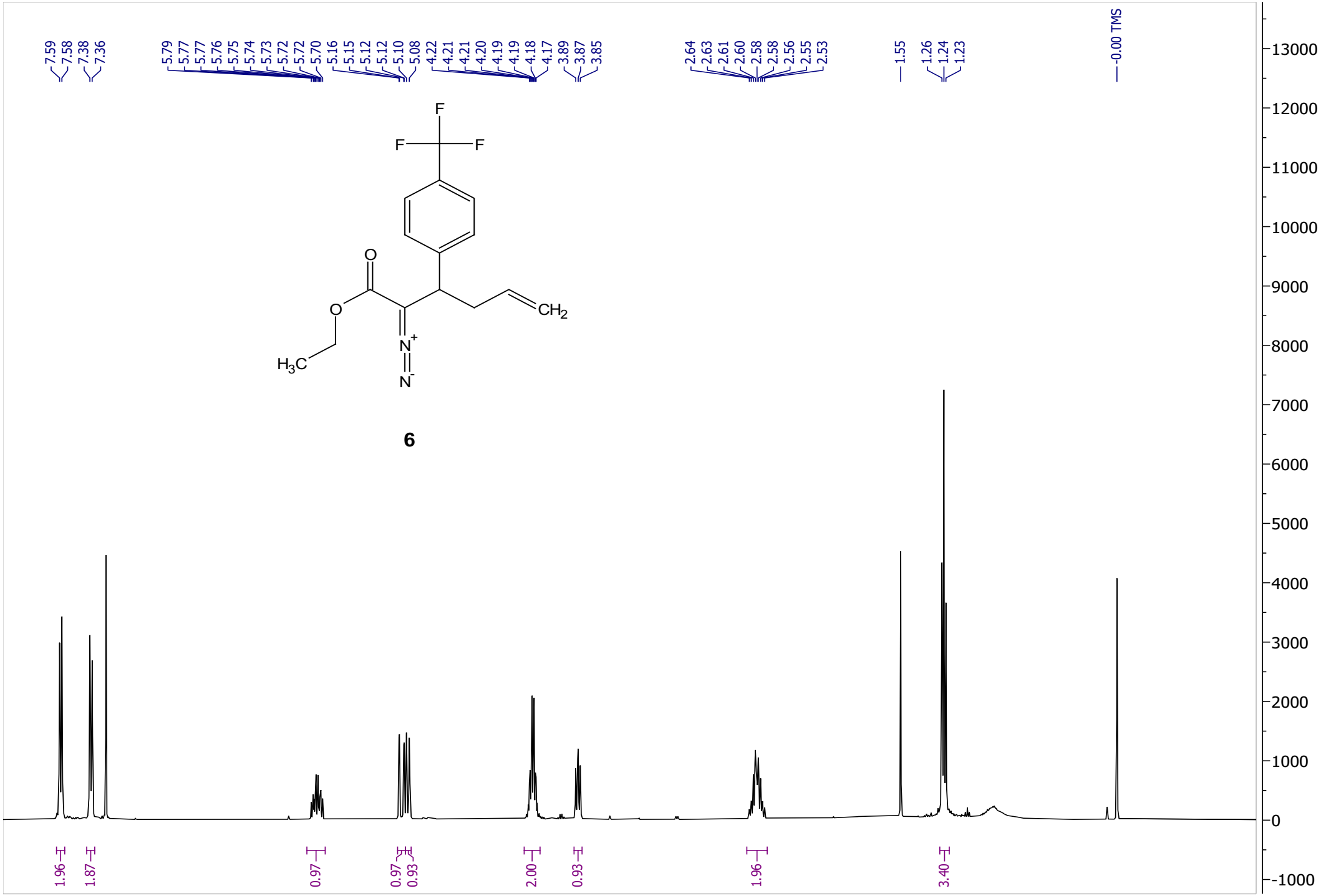

158.81
135.30
133.71
128.27
117.44
114.22
77.16 CDCl3
60.96
55.40
38.37
37.51
14.59
CH2
O
H3C
O
N+
N-
O
CH3
4
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

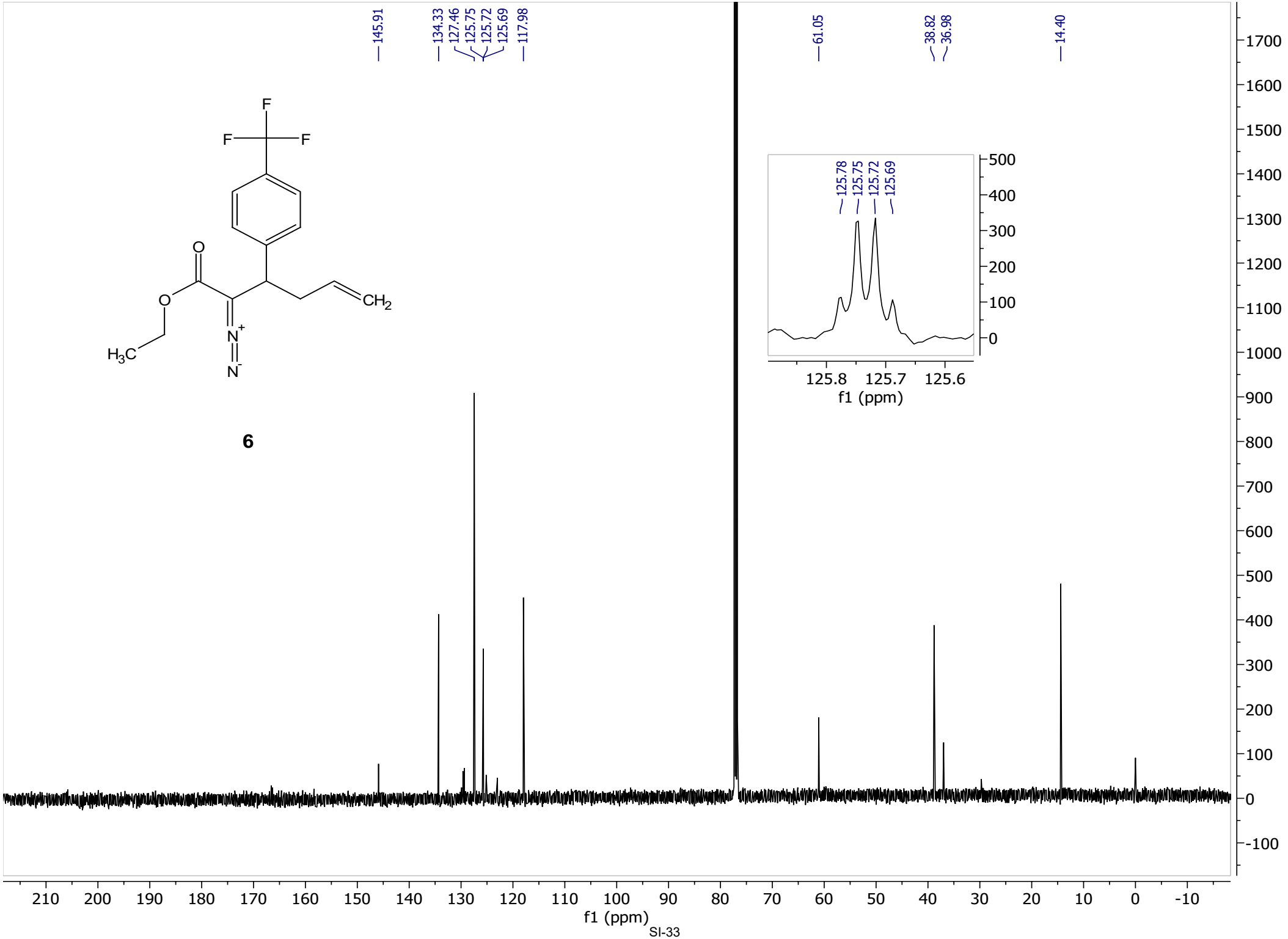
4 HMBC


{4.22,166.94}
{3.80,166.93}
f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

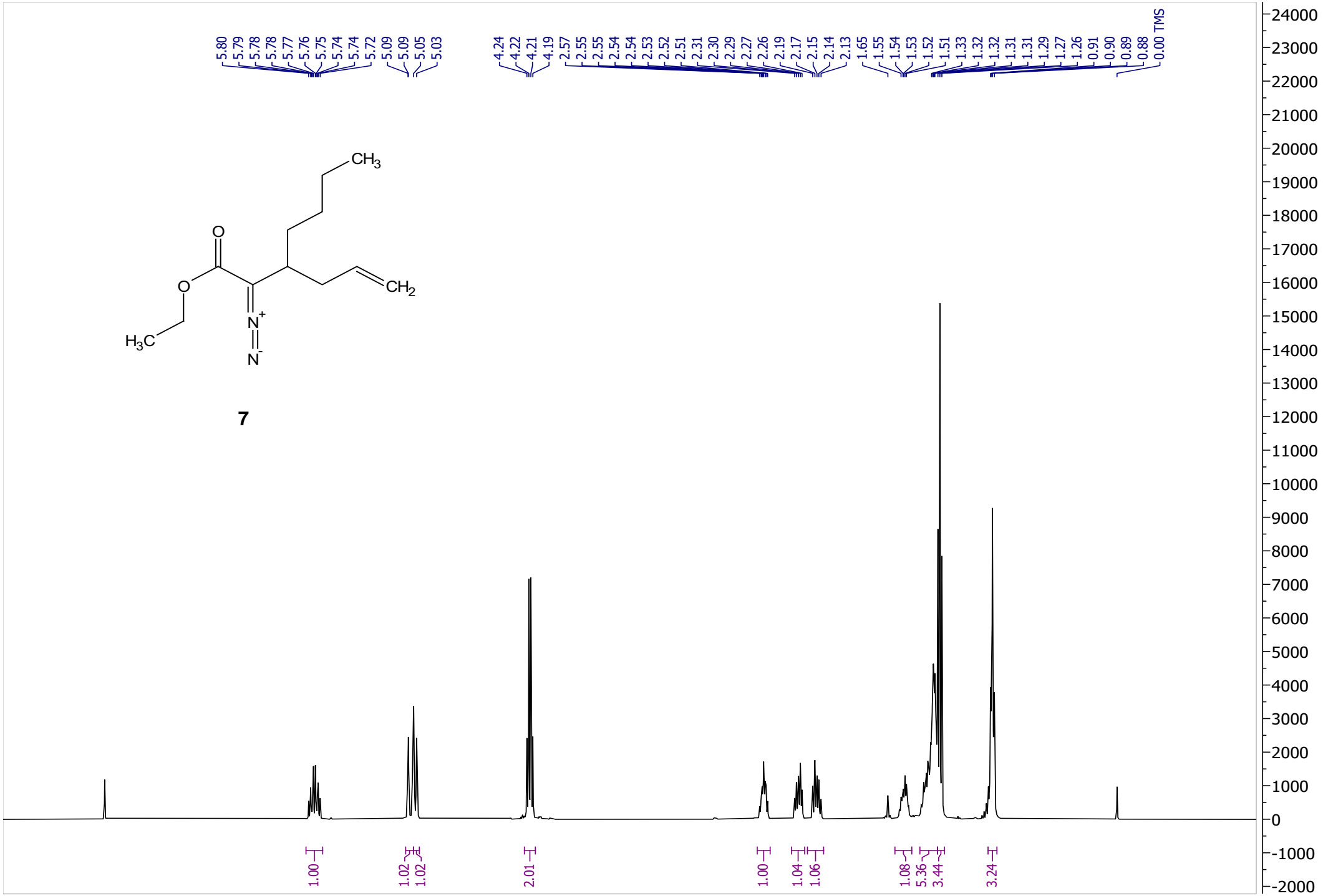

7.38
7.38
7.38
7.32
7.32
7.26
6.32
6.32
6.32
5.83
5.82
5.82
5.81
5.80
5.80
5.78
5.78
5.77
5.76
5.76
5.75
5.16
5.16
5.15
5.15
5.12
5.12
5.09
5.09
5.07
5.07
4.25
4.24
4.22
4.21
3.79
3.78
3.76
2.61
2.60
2.59
2.59
2.58
2.57
2.57
2.50
2.49
2.48
2.47
2.46
2.45
2.44
1.29
1.28
1.26
-0.00 TMS
CH2
O
O
N+
N-
H3C
O
5
0.96
0.95
0.95
0.99
1.01
1.00
2.03
0.95
1.02
1.04
3.21
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


166.88
143.52
139.28
134.96
125.13
117.71
109.75
77.16 CDCl3
60.99
37.13
30.81
14.58
CH2
O
O
H3C
N+
N-
O
5
f1 (ppm)

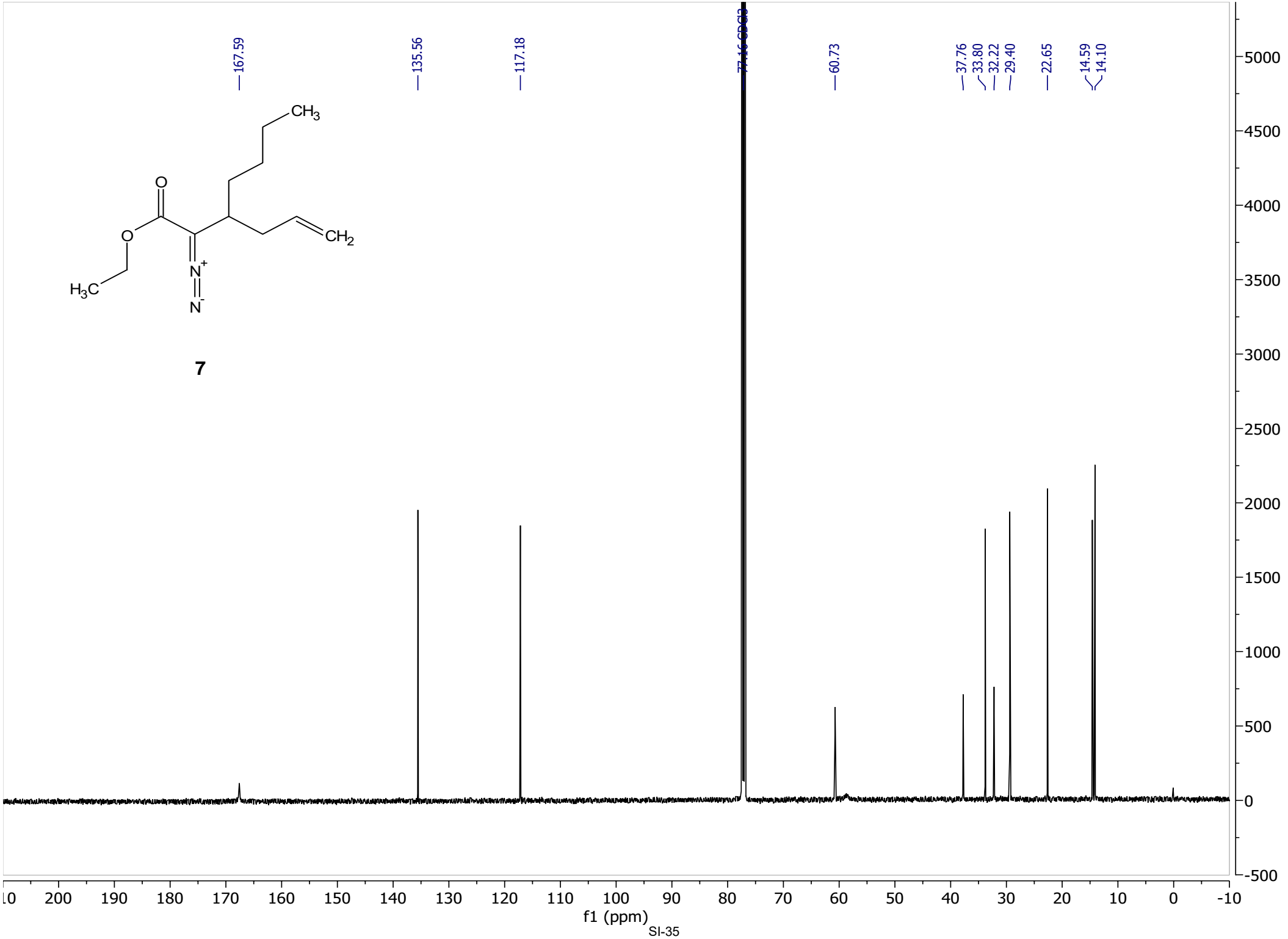

7.59
7.58
7.38
7.36
5.79
5.77
5.77
5.76
5.75
5.74
5.73
5.72
5.72
5.70
5.16
5.15
5.12
5.12
5.10
5.08
4.22
4.21
4.21
4.20
4.19
4.19
4.18
4.17
3.89
3.87
3.85
2.64
2.63
2.61
2.60
2.58
2.58
2.56
2.55
2.53
1.55
1.26
1.24
1.23
-0.00 TMS
F
F
F
O
O
CH2
N+
N-
H3C
6
1.96
1.87
0.97
0.97
0.93
2.00
0.93
1.96
3.40
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

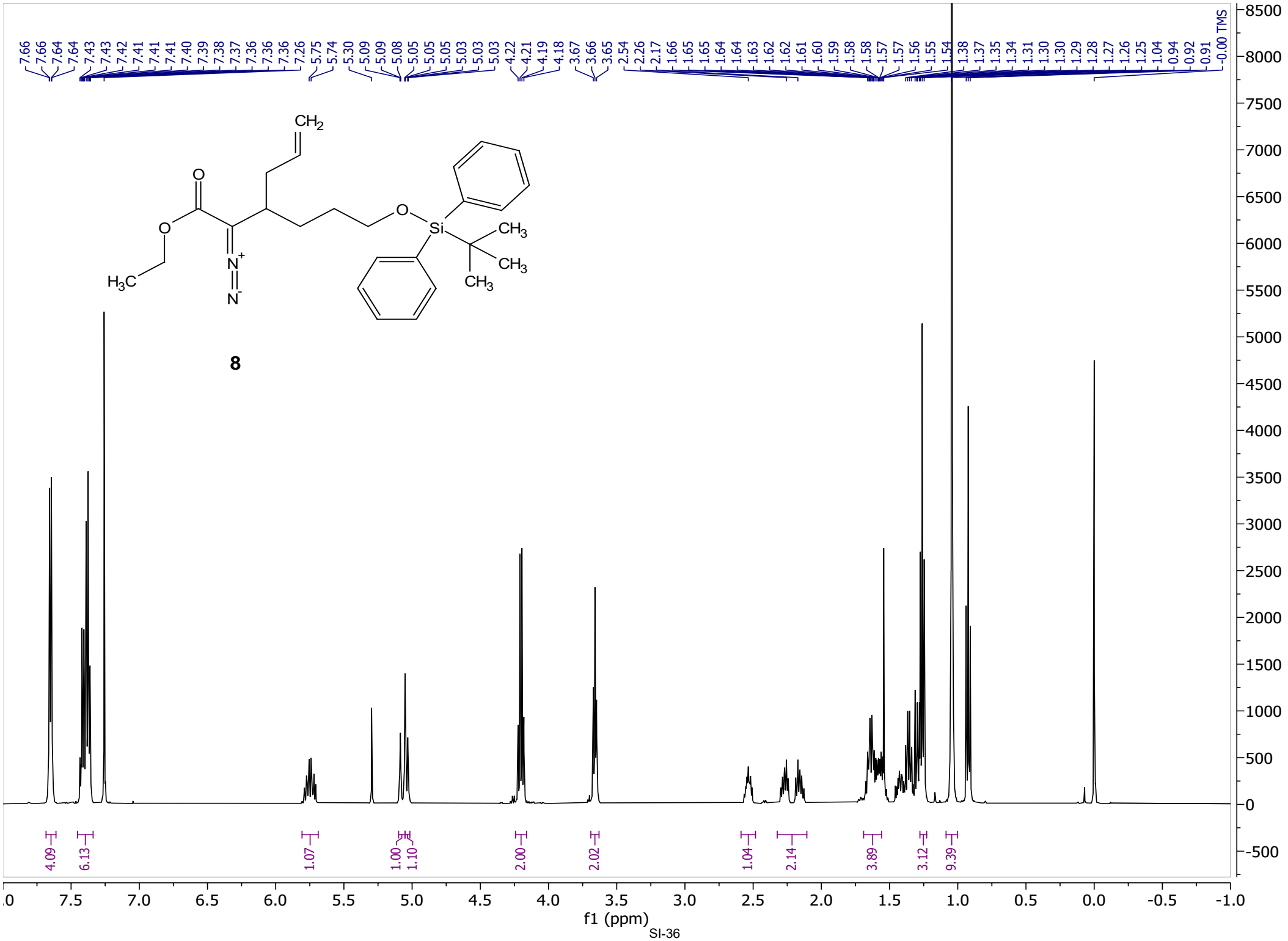

145.91
134.33
127.46
125.75
125.72
125.69
117.98
61.05
38.82
36.98
14.40
125.78
125.75
125.72
125.69
125.8
125.7
125.6
f1 (ppm)
f1 (ppm)

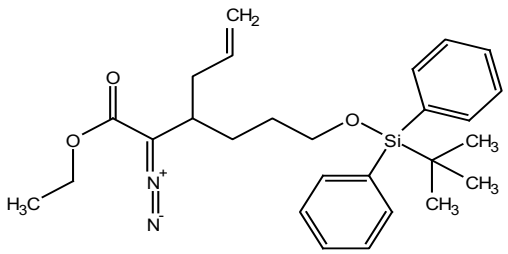
6


5.80 5.79 5.78 5.78 5.77 5.76 5.75 5.74 5.74 5.72 5.09 5.09 5.05 5.03
4.24 4.22 4.21 4.19 2.57 2.55 2.55 2.54 2.54 2.53 2.52 2.51 2.31 2.30 2.29 2.27 2.26 2.19 2.17 2.15 2.14 2.13 1.65 1.55 1.54 1.53 1.52 1.51 1.33 1.32 1.32 1.31 1.31 1.29 1.27 1.26 0.91 0.90 0.89 0.88 0.00 TMS
CH3
O
O
CH2
N+
N-
H3C
1.00 1.02 1.02 2.01 1.00 1.04 1.06 1.08 5.36 3.44 3.24
f1 (ppm)

7


167.59
135.56
117.18
77.16 CDCl3
60.73
37.76
33.80
32.22
29.40
22.65
14.59
14.10
CH3
O
O
CH2
H3C
N+
N-
7
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

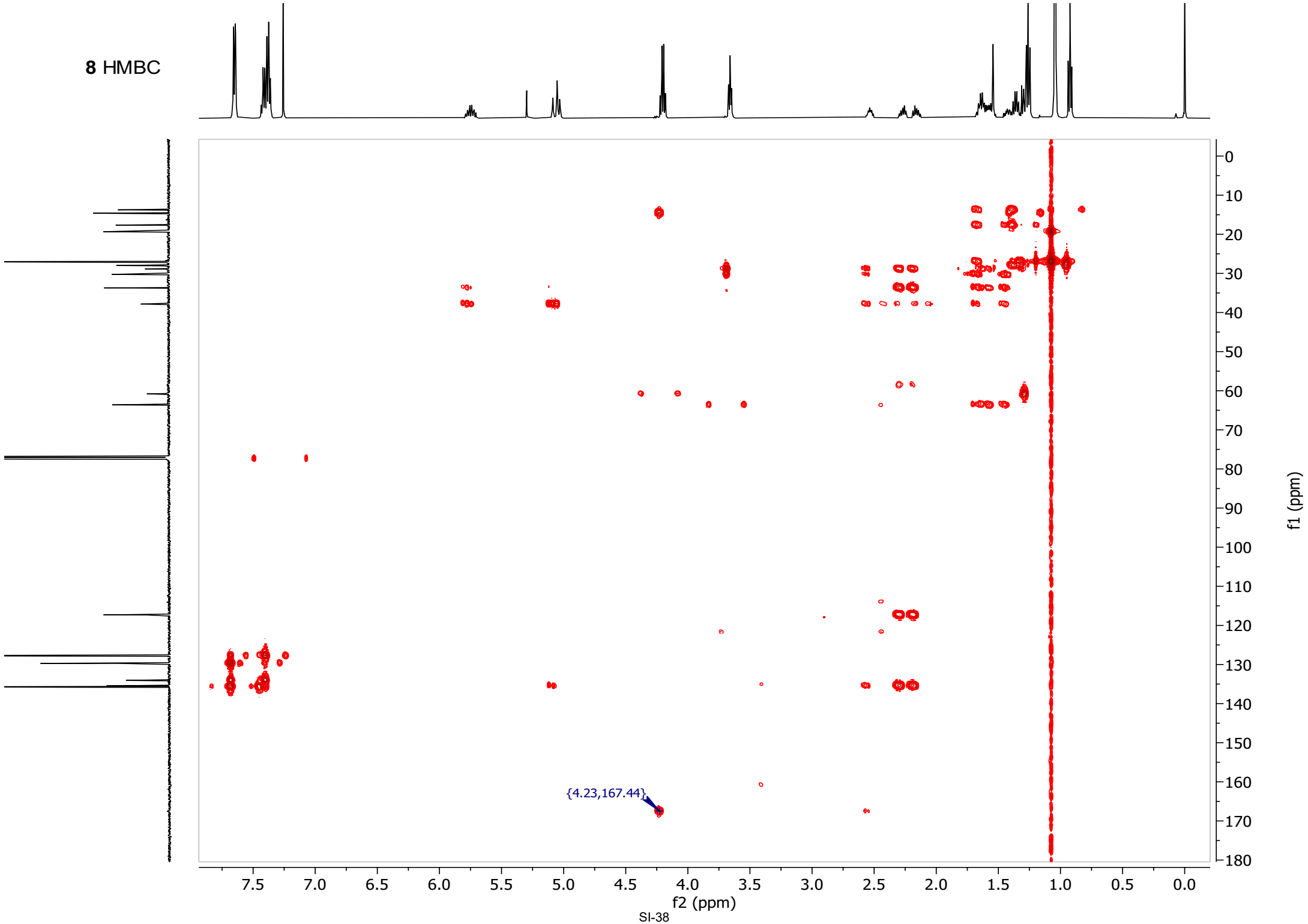

7.66 7.66 7.64 7.64 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.39 7.38 7.37 7.36 7.36 7.36 7.26 5.75 5.74 5.30 5.09 5.09 5.08 5.05 5.05 5.05 5.03 5.03 5.03 4.22 4.21 4.19 4.18 3.67 3.66 3.65 2.54 2.26 2.17 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.55 1.54 1.38 1.37 1.35 1.34 1.31 1.30 1.30 1.29 1.28 1.27 1.26 1.25 1.04 0.94 0.92 0.91 -0.00 TMS
CH2
O
O
O
Si
CH3
CH3
CH3
N+
N-
H3C
8
4.09
6.13
1.07
1.00
1.10
2.00
2.02
1.04
2.14
3.89
3.12
9.39
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


CH2
O
O
H3C
N+
N-
O
Si
CH3
CH3
CH3

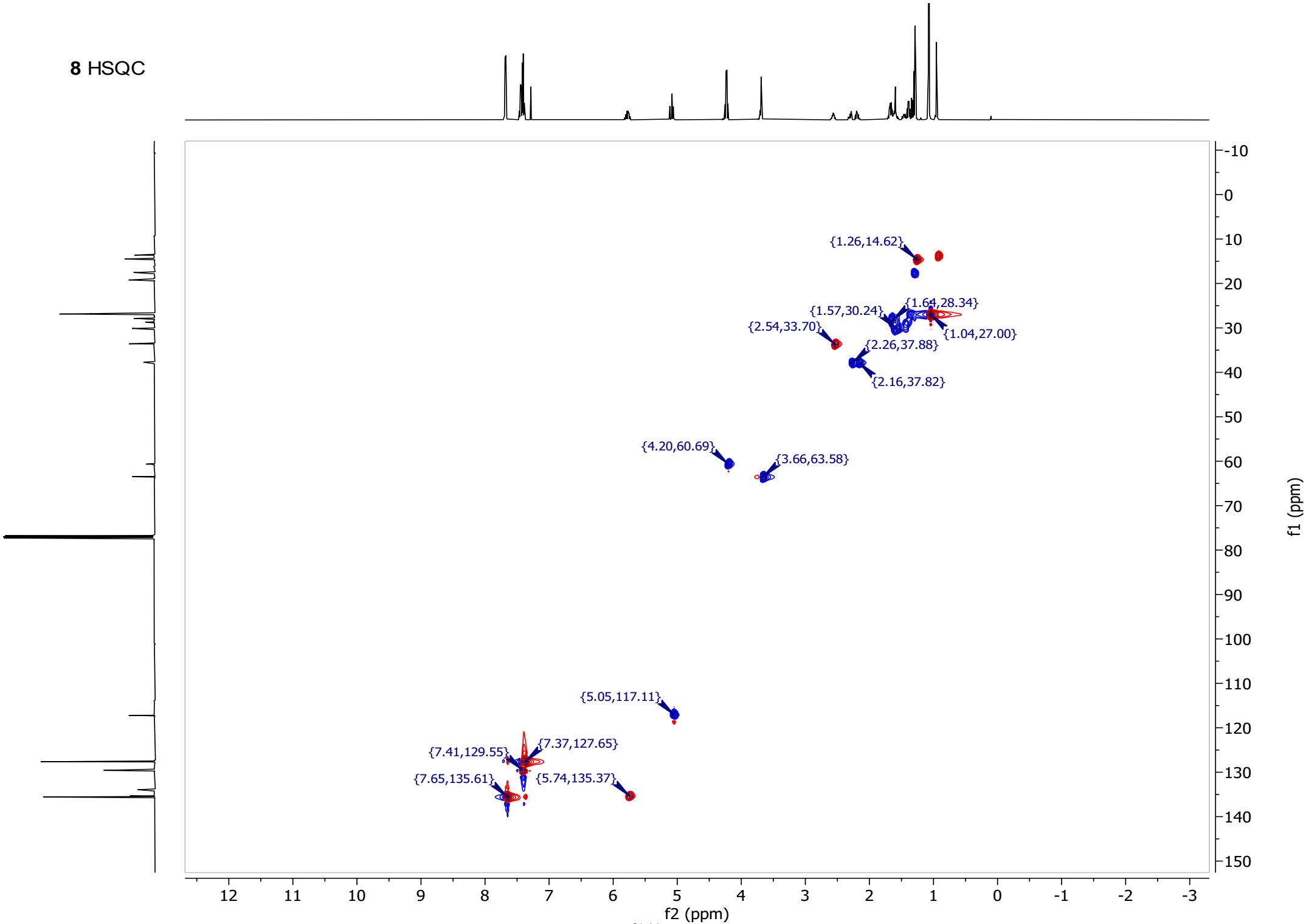
8

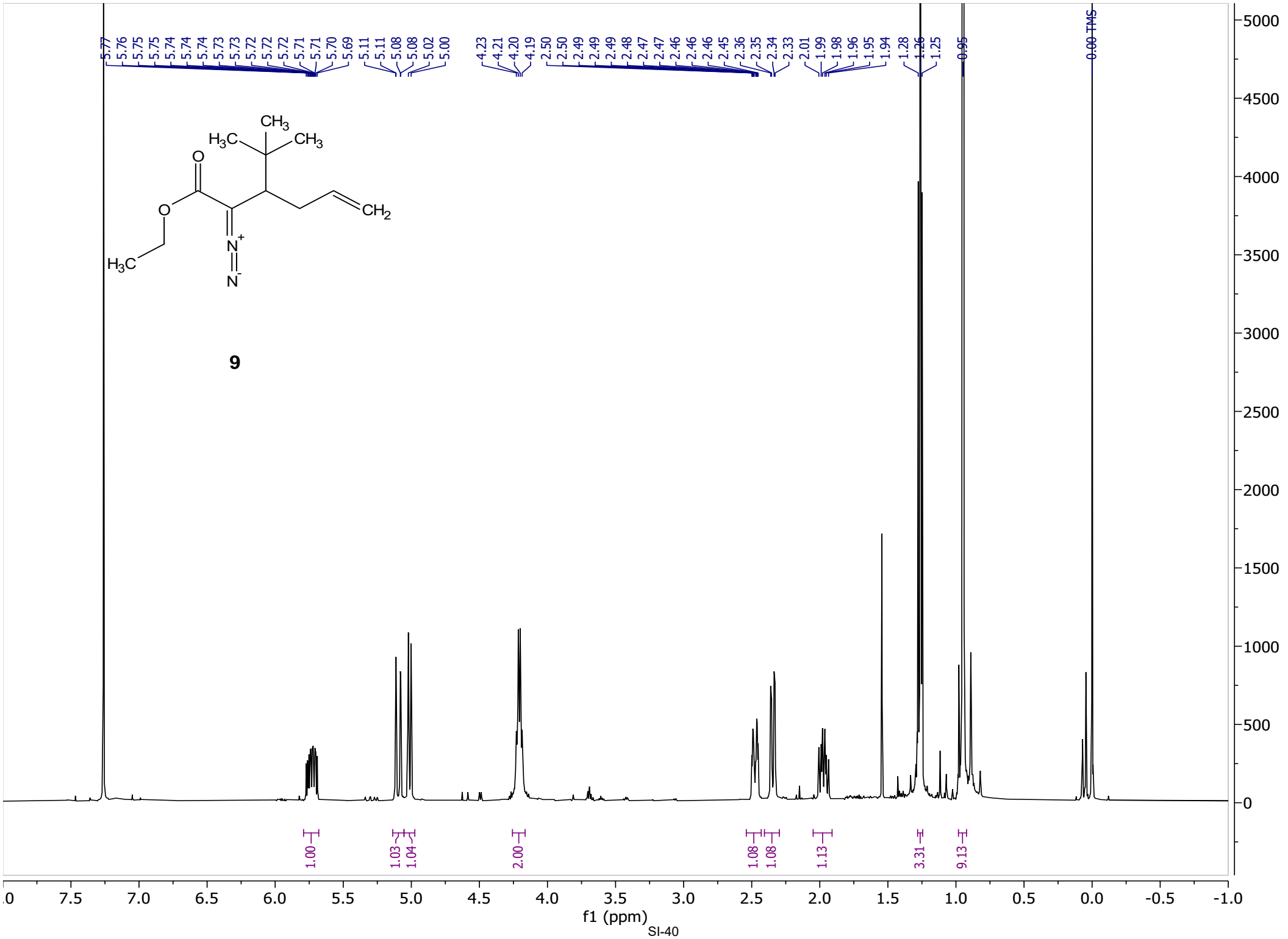
135.70
135.46
134.06
129.71
127.76
117.33
77.16 CDCl3
63.62
60.79
37.84
33.71
30.26
27.99
27.00
14.62
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

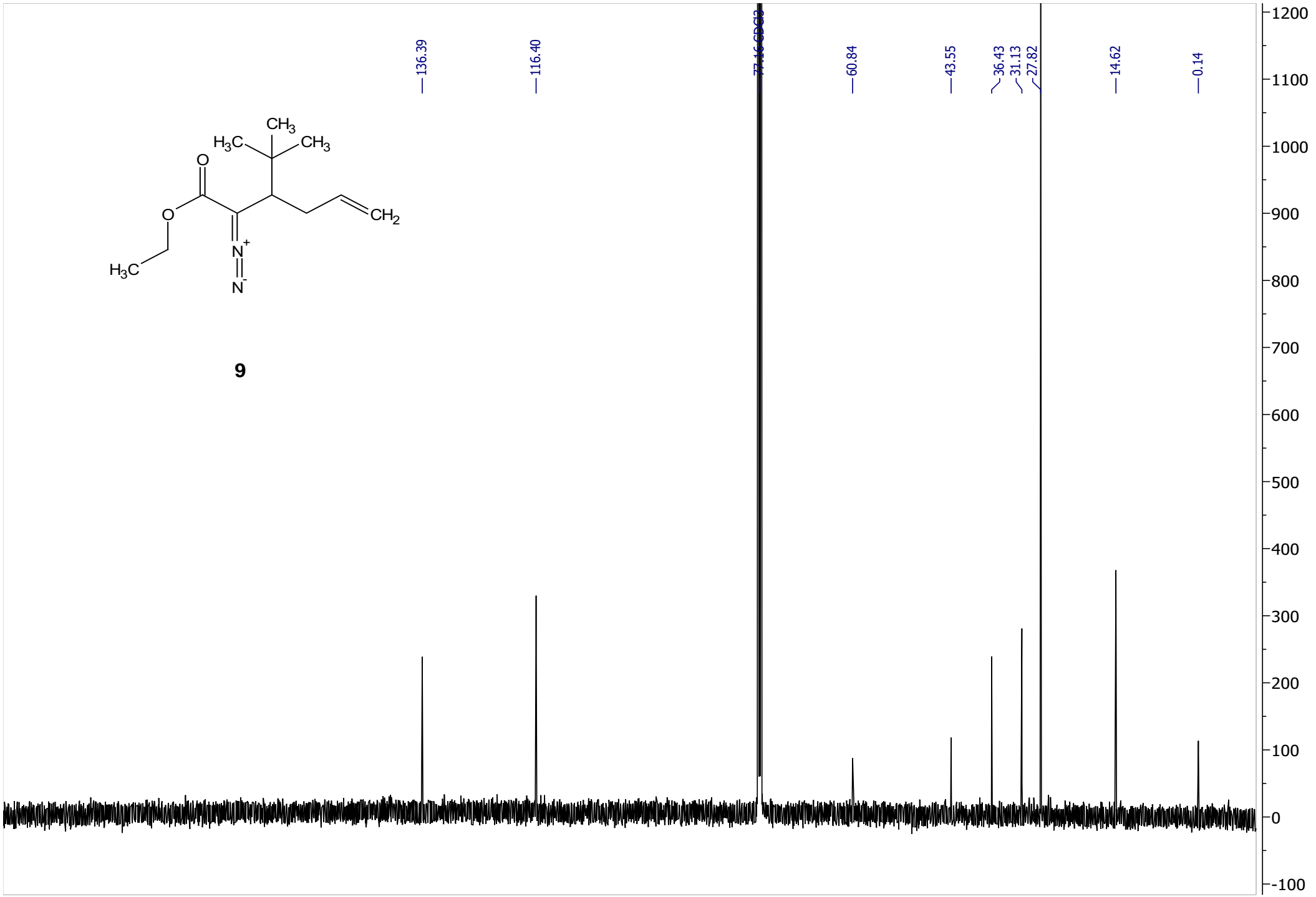
8 HMBC

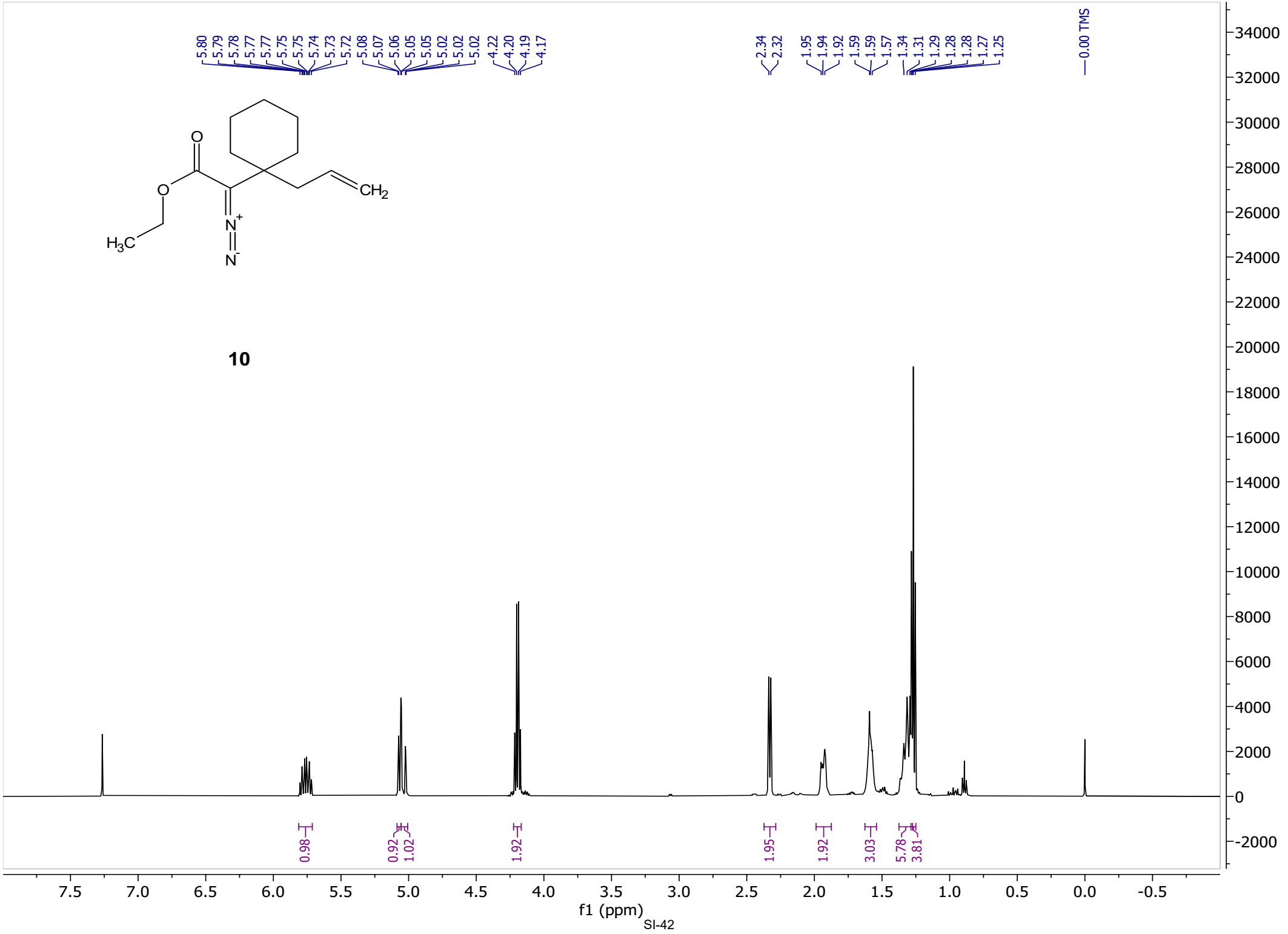

{4.23,167.44}
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

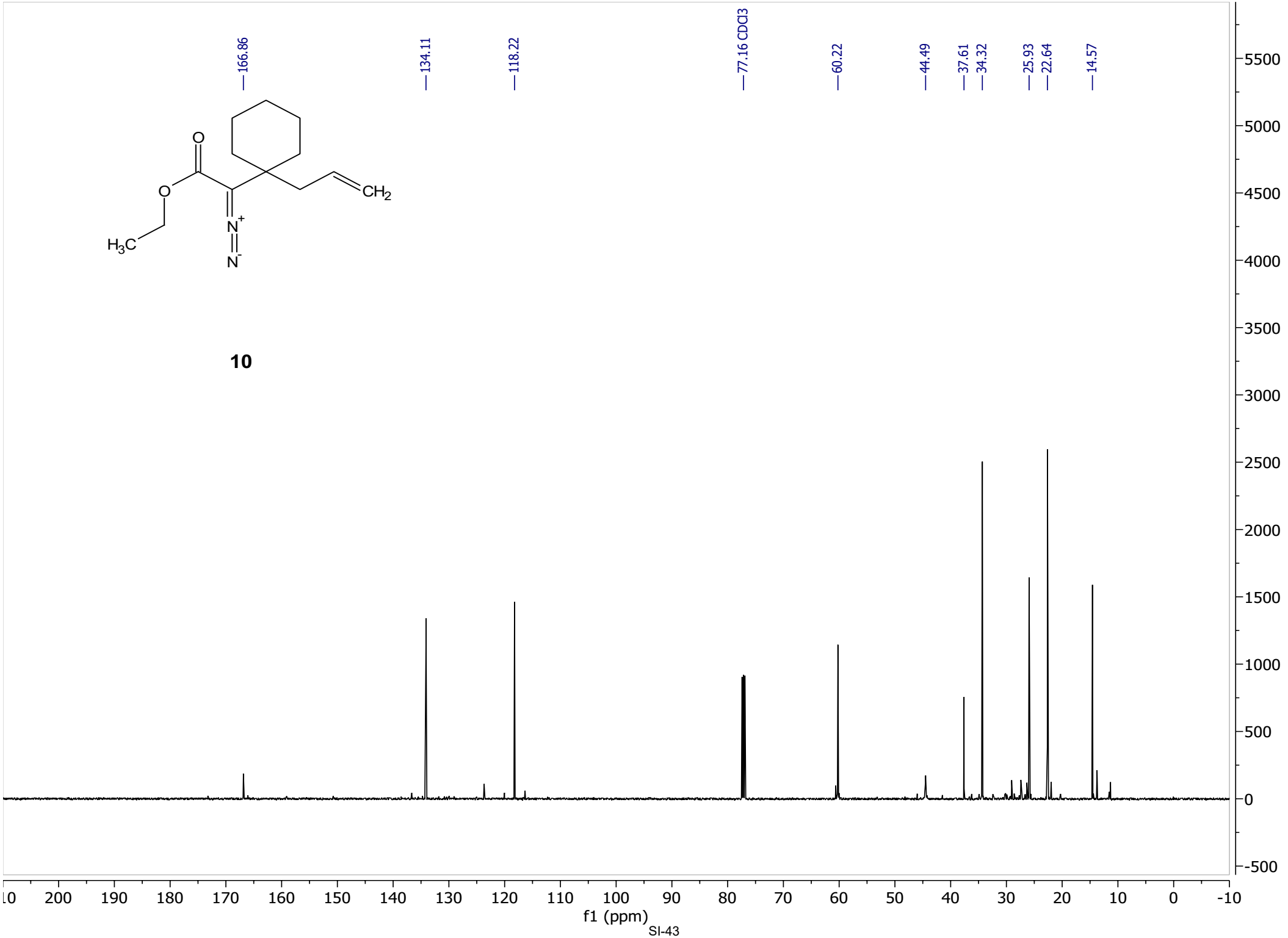
8 HSQC

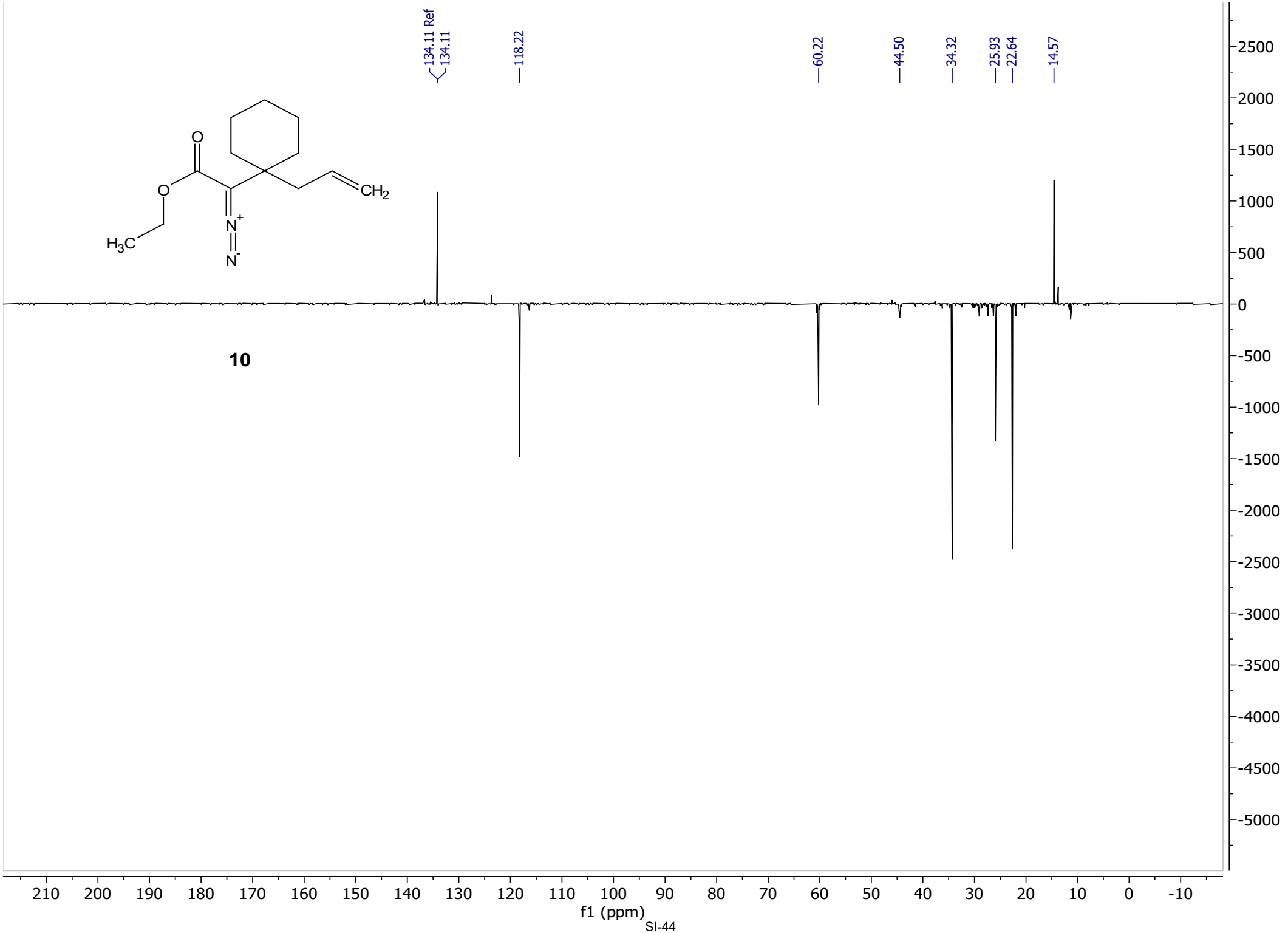

{1.26,14.62}
{1.57,30.24}
{1.64,28.34}
{2.54,33.70}
{1.04,27.00}
{2.26,37.88}
{2.16,37.82}
{4.20,60.69}
{3.66,63.58}
{5.05,117.11}
{7.41,129.55}
{7.37,127.65}
{7.65,135.61}
{5.74,135.37}
f2 (ppm)
f1 (ppm)

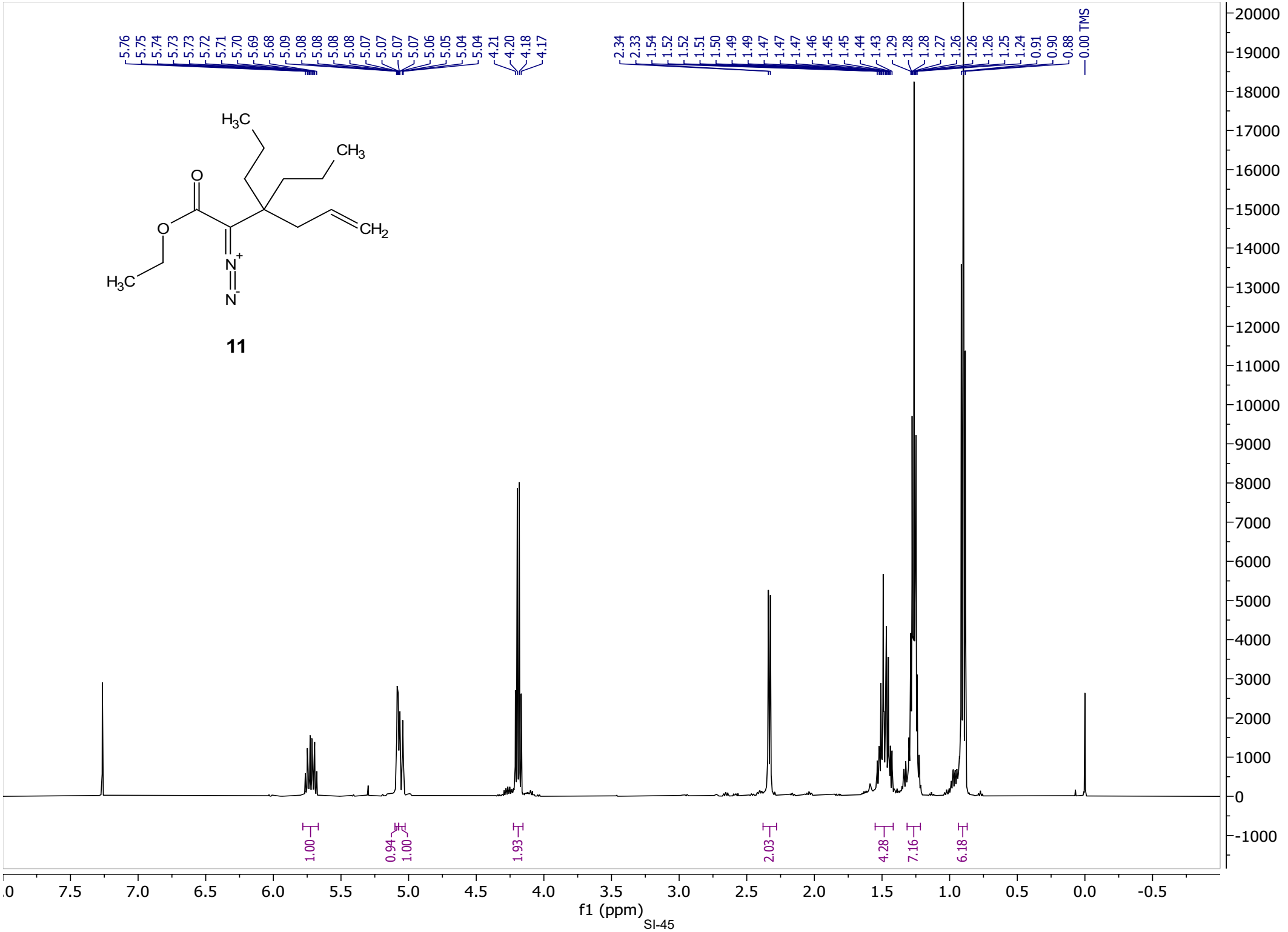

5.77 5.76 5.75 5.75 5.74 5.74 5.74 5.73 5.73 5.72 5.72 5.72 5.71 5.71 5.70 5.69 5.11 5.11 5.08 5.08 5.02 5.00
4.23 4.21 4.20 4.19 2.50 2.50 2.49 2.49 2.49 2.48 2.47 2.47 2.46 2.46 2.46 2.45 2.36 2.35 2.34 2.33 2.01 1.99 1.98 1.96 1.95 1.94 1.28 1.26 1.25 0.95 0.00 TMS
CH3
H3C
CH3
O
O
CH2
N+
N-
H3C
9
1.00
1.03
1.04
2.00
1.08
1.08
1.13
3.31
9.13
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

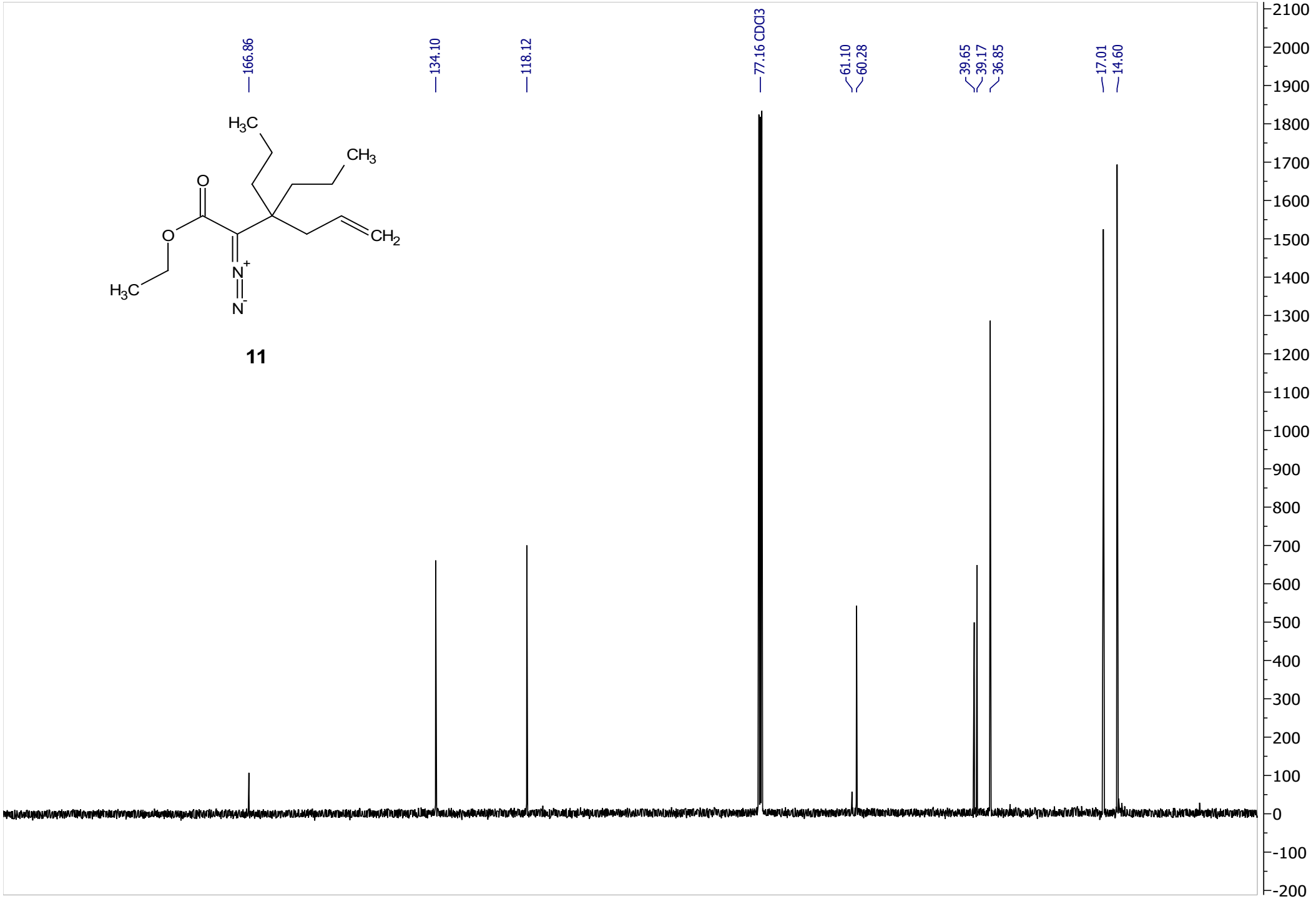

136.39
116.40
77.16 CDCl3
60.84
43.55
36.43
31.13
27.82
14.62
0.14
CH3
H3C
CH3
O
O
CH2
H3C
N+
N-
9
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

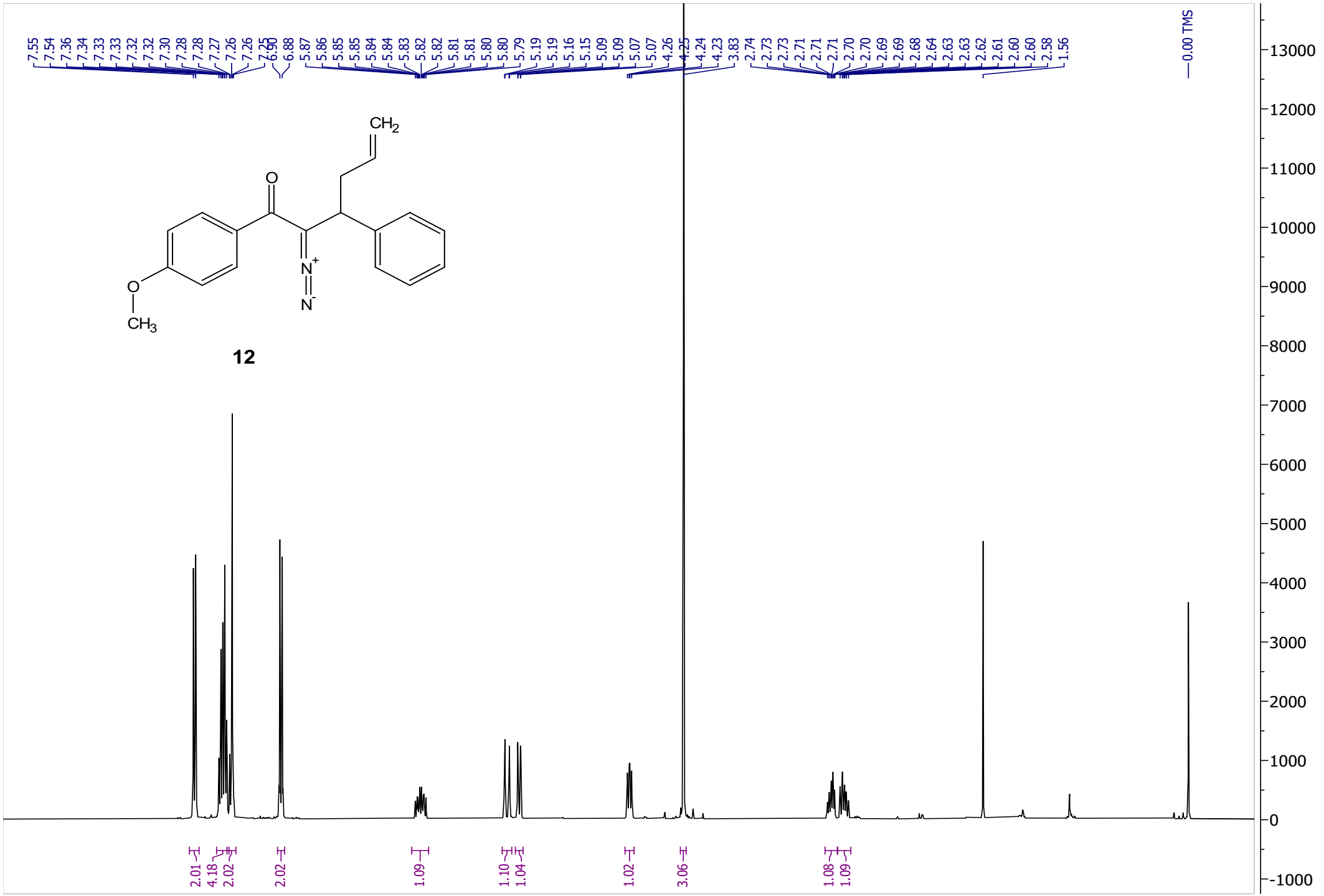

5.80
5.79
5.78
5.77
5.77
5.75
5.75
5.74
5.73
5.72
5.08
5.07
5.06
5.05
5.05
5.02
5.02
5.02
4.22
4.20
4.19
4.17
2.34
2.32
1.95
1.94
1.92
1.59
1.59
1.57
1.34
1.31
1.29
1.28
1.28
1.27
1.25
0.00 TMS
O
O
CH2
N+
N-
H3C
10
0.98
0.92
1.02
1.92
1.95
1.92
3.03
5.78
3.81
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

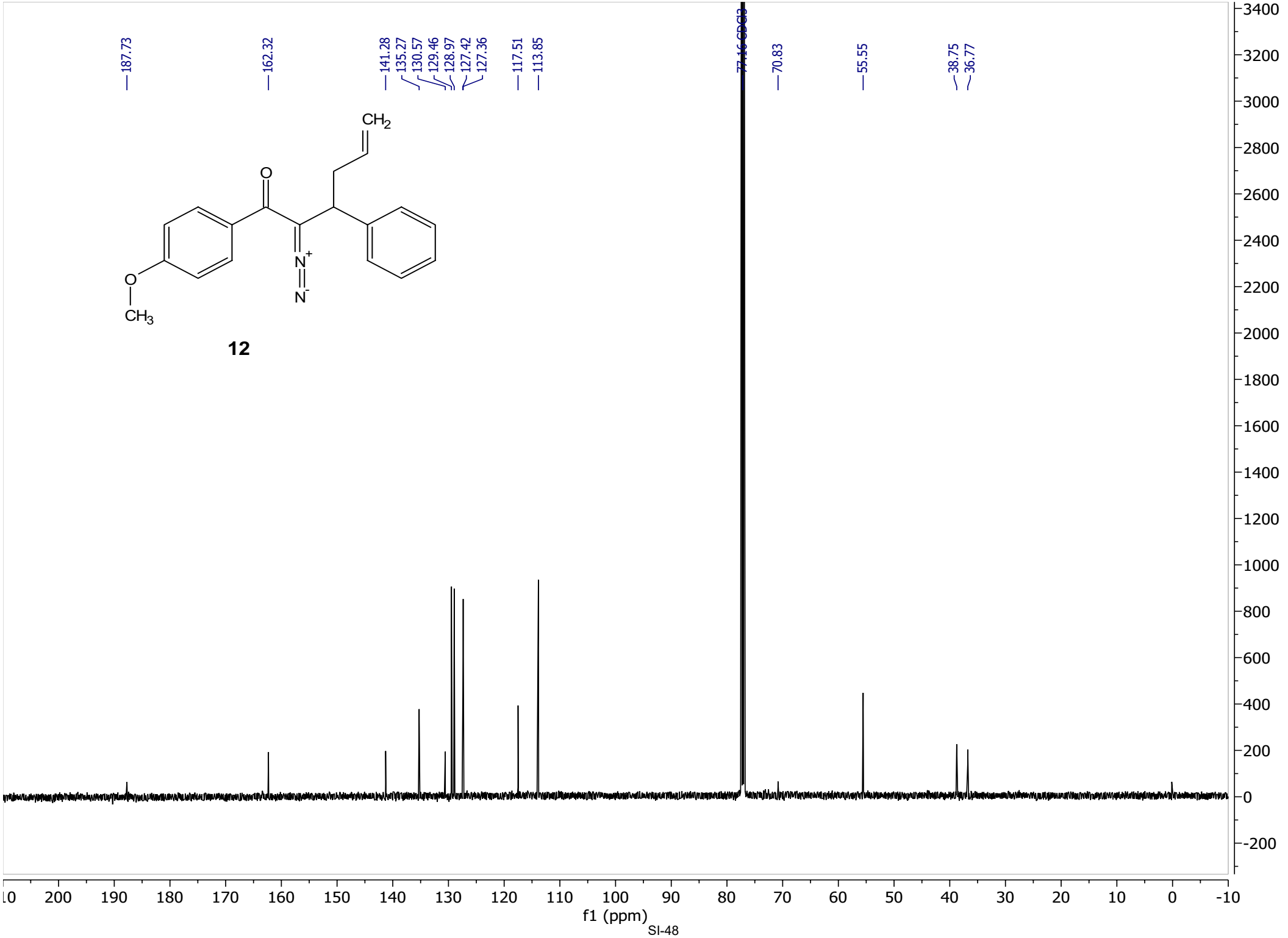

166.86
134.11
118.22
77.16 CDCl3
60.22
44.49
37.61
34.32
25.93
22.64
14.57
O
O
CH2
N+
N-
H3C
10
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

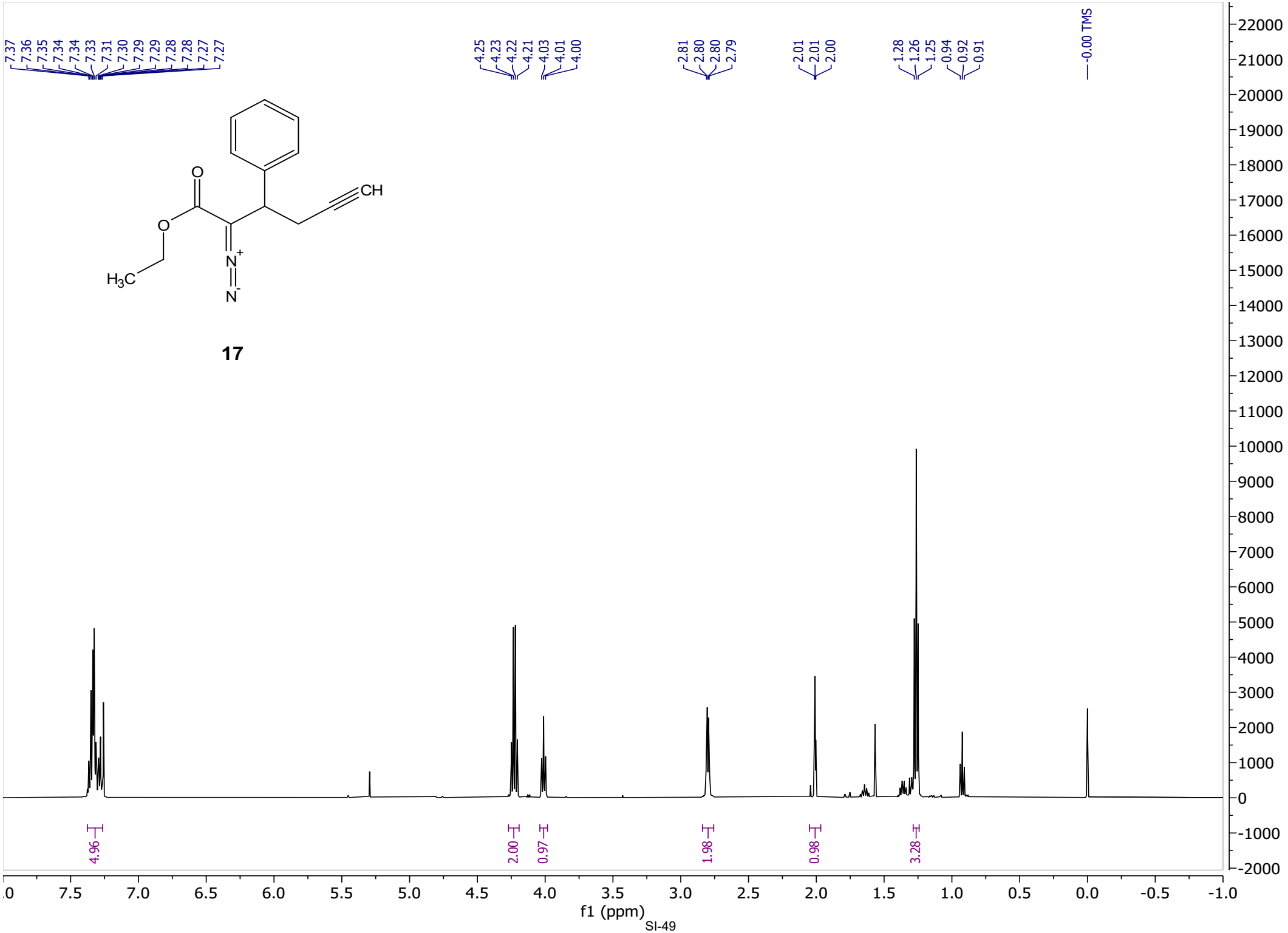

134.11 Ref
134.11
118.22
60.22
44.50
34.32
25.93
22.64
14.57
O
O
CH2
N+
N-
H3C
10
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

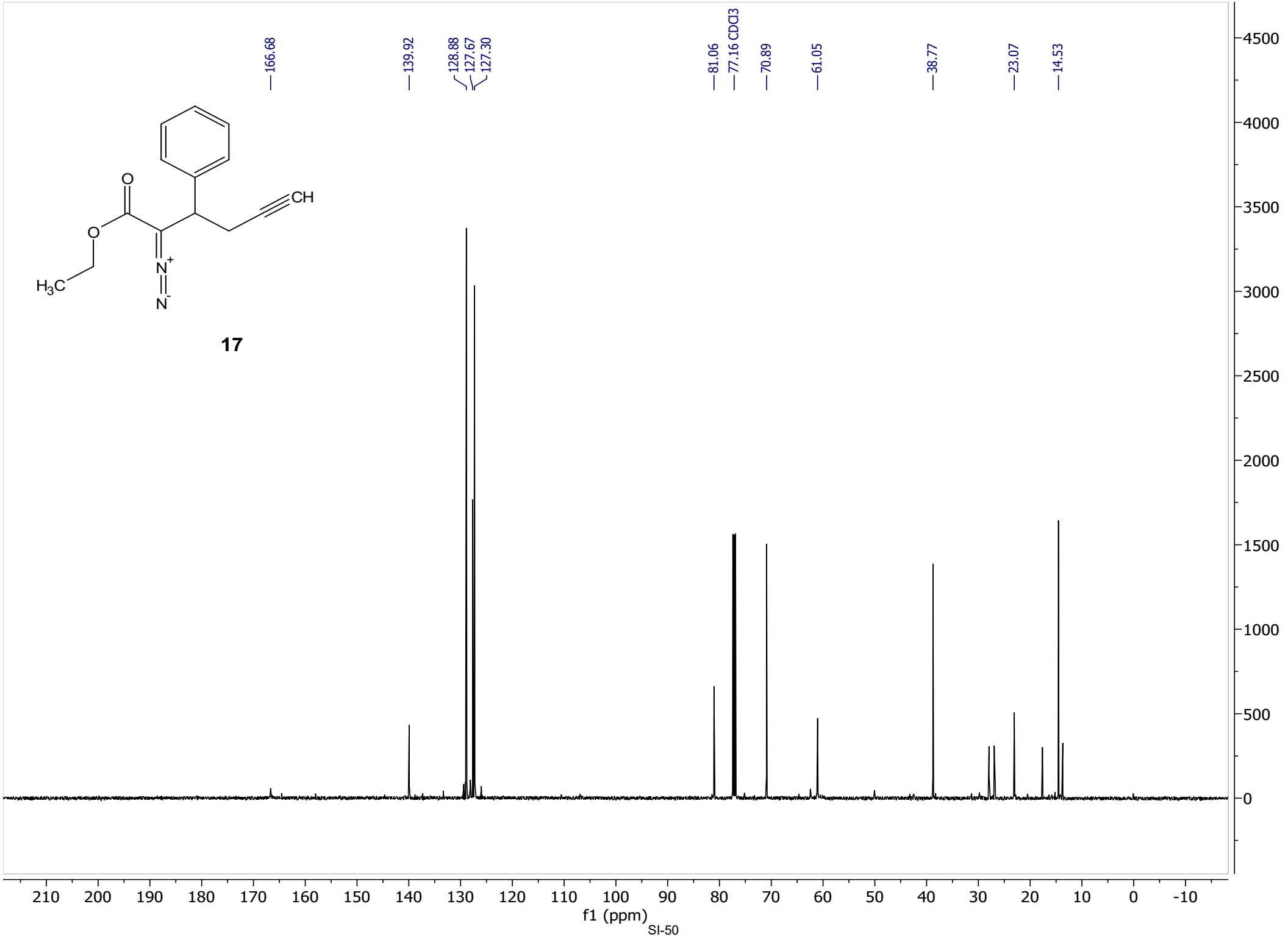

5.76 5.75 5.74 5.73 5.73 5.72 5.71 5.70 5.69 5.68 5.09 5.08 5.08 5.08 5.08 5.07 5.07 5.07 5.07 5.06 5.05 5.04 5.04 4.21 4.20 4.18 4.17
2.34 2.33 1.54 1.52 1.52 1.51 1.50 1.49 1.49 1.47 1.47 1.47 1.46 1.45 1.45 1.44 1.43 1.29 1.28 1.28 1.27 1.26 1.26 1.26 1.25 1.24 0.91 0.90 0.88 0.00 TMS
H3C
CH3
O
O
CH2
N+
N-
H3C
11
1.00
0.94
1.00
1.93
2.03
4.28
7.16
6.18
f1 (ppm)

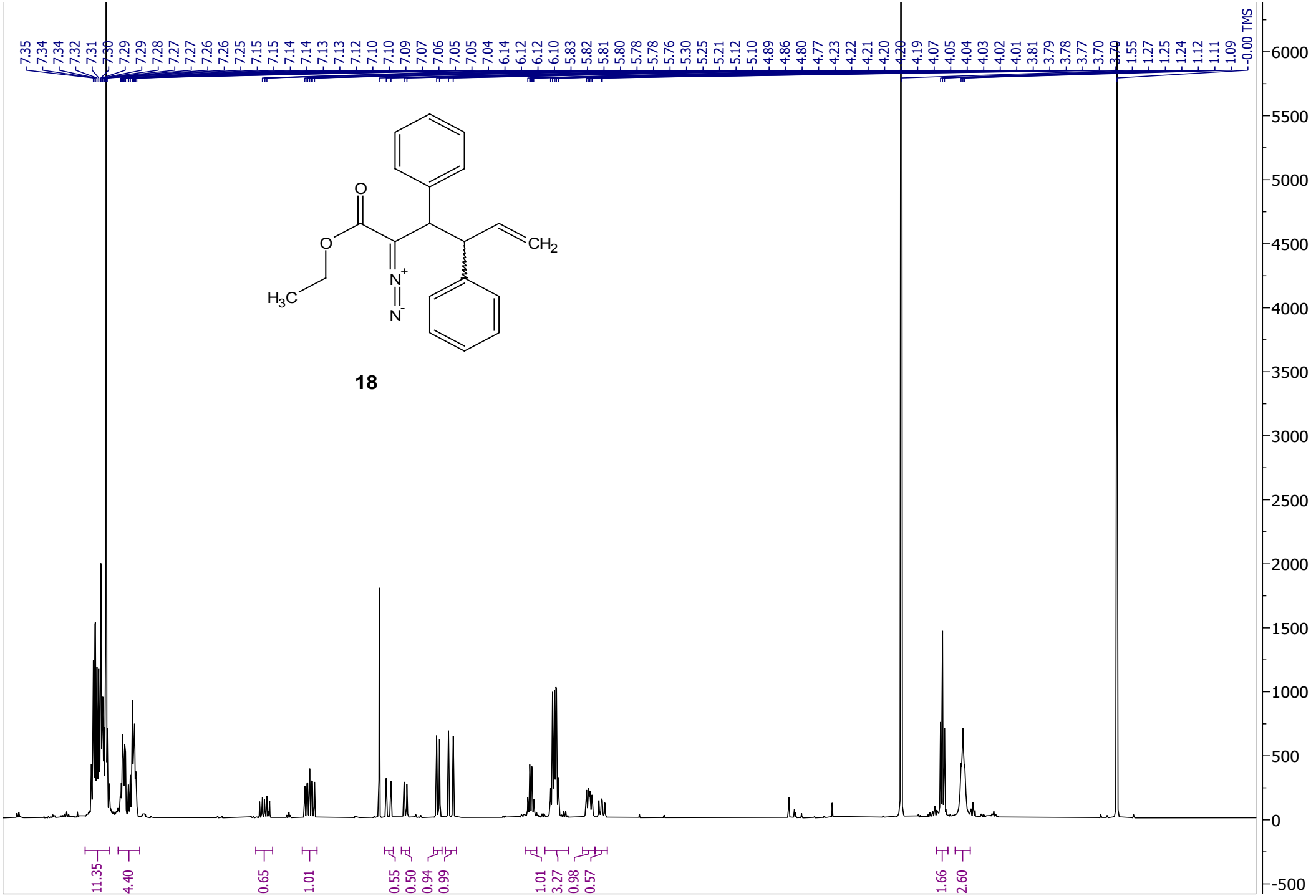

166.86
134.10
118.12
77.16 CDCl3
61.10
60.28
39.65
39.17
36.85
17.01
14.60
H3C
CH3
O
O
CH2
N+
N-
H3C
11
f1 (ppm)

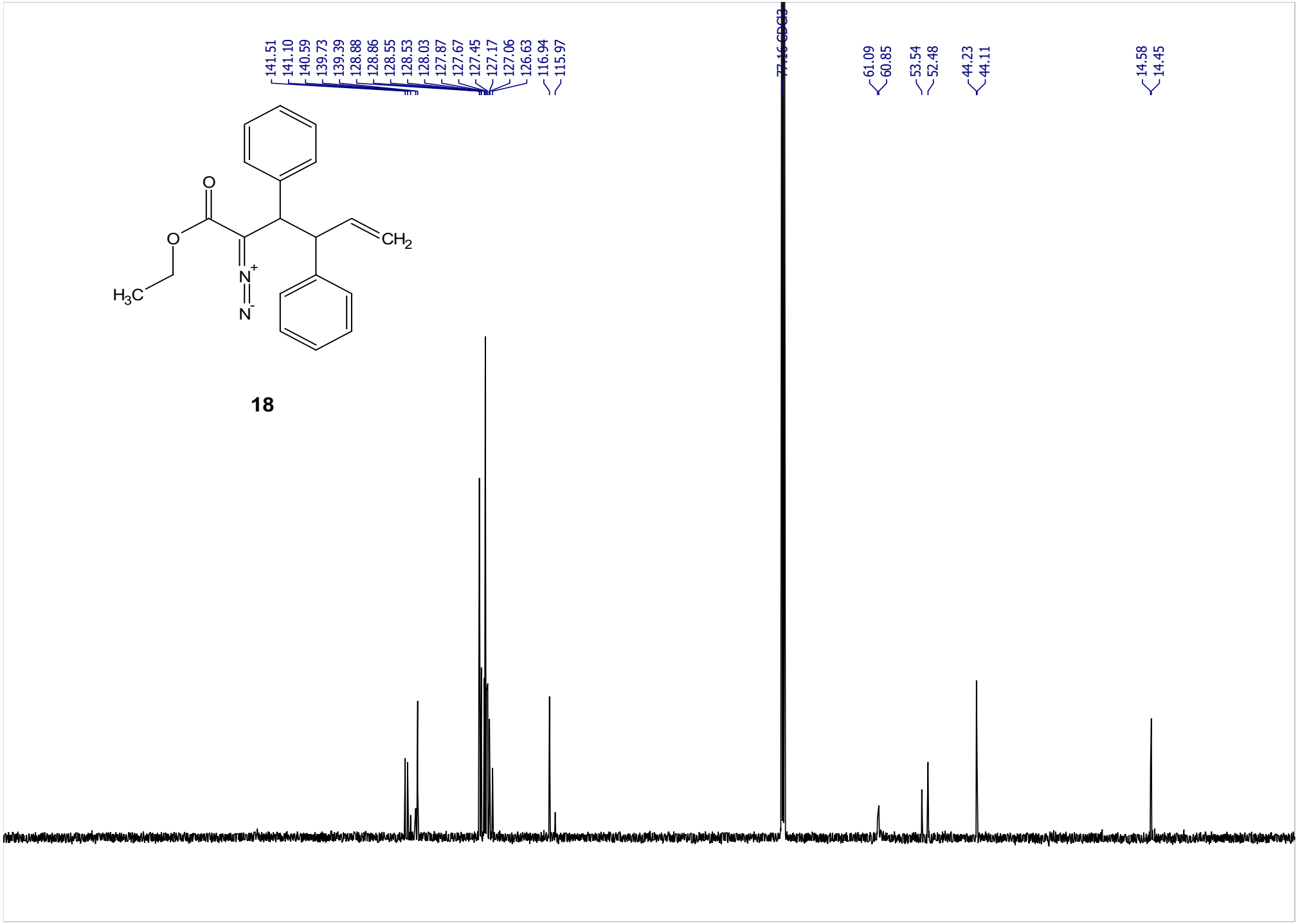

7.55 7.54 7.36 7.34 7.33 7.33 7.32 7.32 7.30 7.28 7.28 7.27 7.26 7.26 7.25 6.90 6.88 5.87 5.86 5.85 5.85 5.84 5.84 5.83 5.82 5.82 5.81 5.81 5.80 5.80 5.79 5.19 5.19 5.16 5.15 5.09 5.09 5.07 5.07 4.26 4.25 4.24 4.23 3.83 2.74 2.73 2.73 2.71 2.71 2.71 2.70 2.70 2.69 2.69 2.68 2.64 2.63 2.63 2.62 2.61 2.60 2.60 2.58 1.56
0.00 TMS
CH2
O
N+
N-
O
CH3
12
2.01 4.18 2.02 2.02 1.09 1.10 1.04 1.02 3.06 1.08 1.09
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

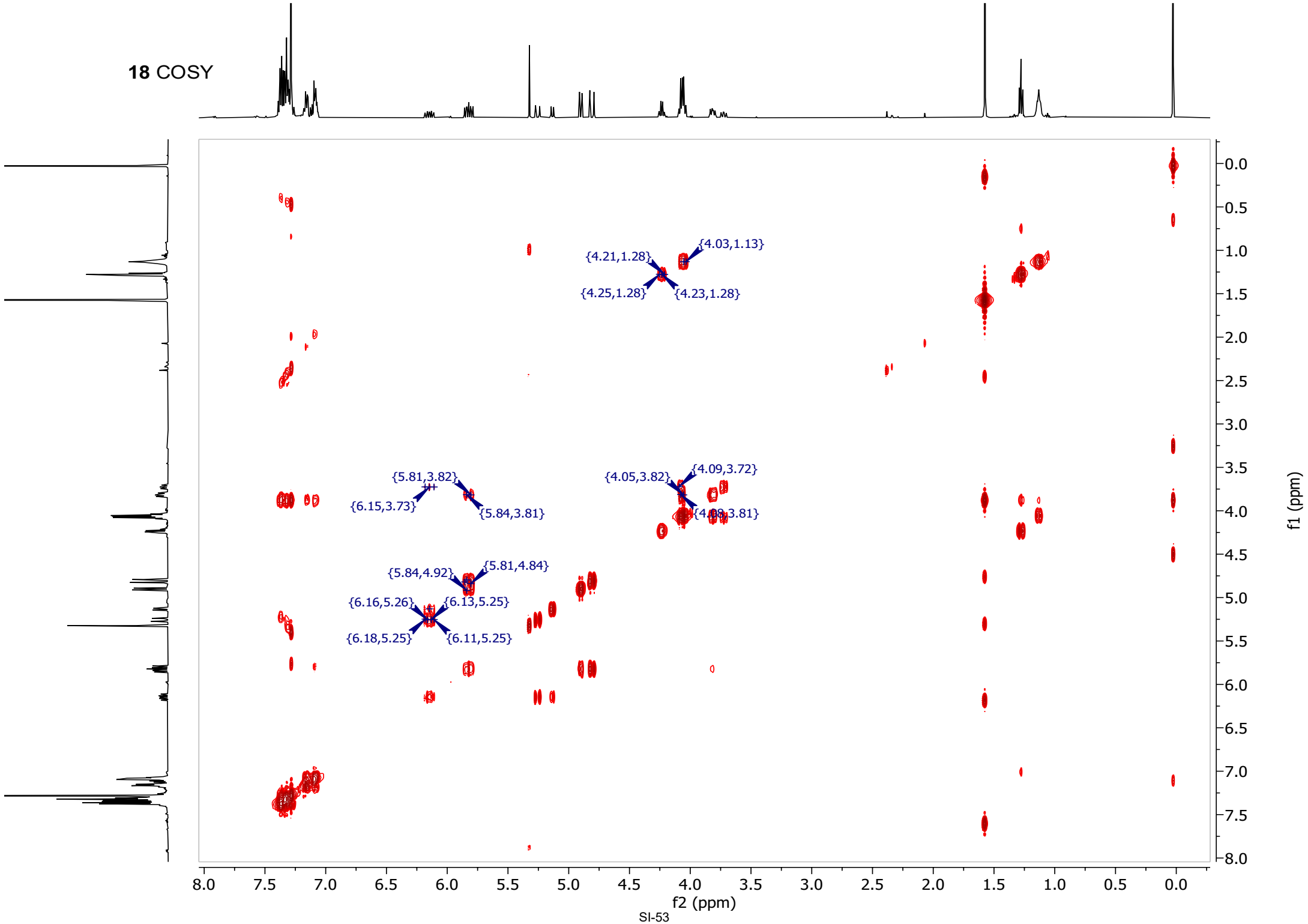

187.73
162.32
141.28
135.27
130.57
129.46
128.97
127.42
127.36
117.51
113.85
77.16 CDCl3
70.83
55.55
38.75
36.77
CH2
O
N+
N-
O
CH3
12
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

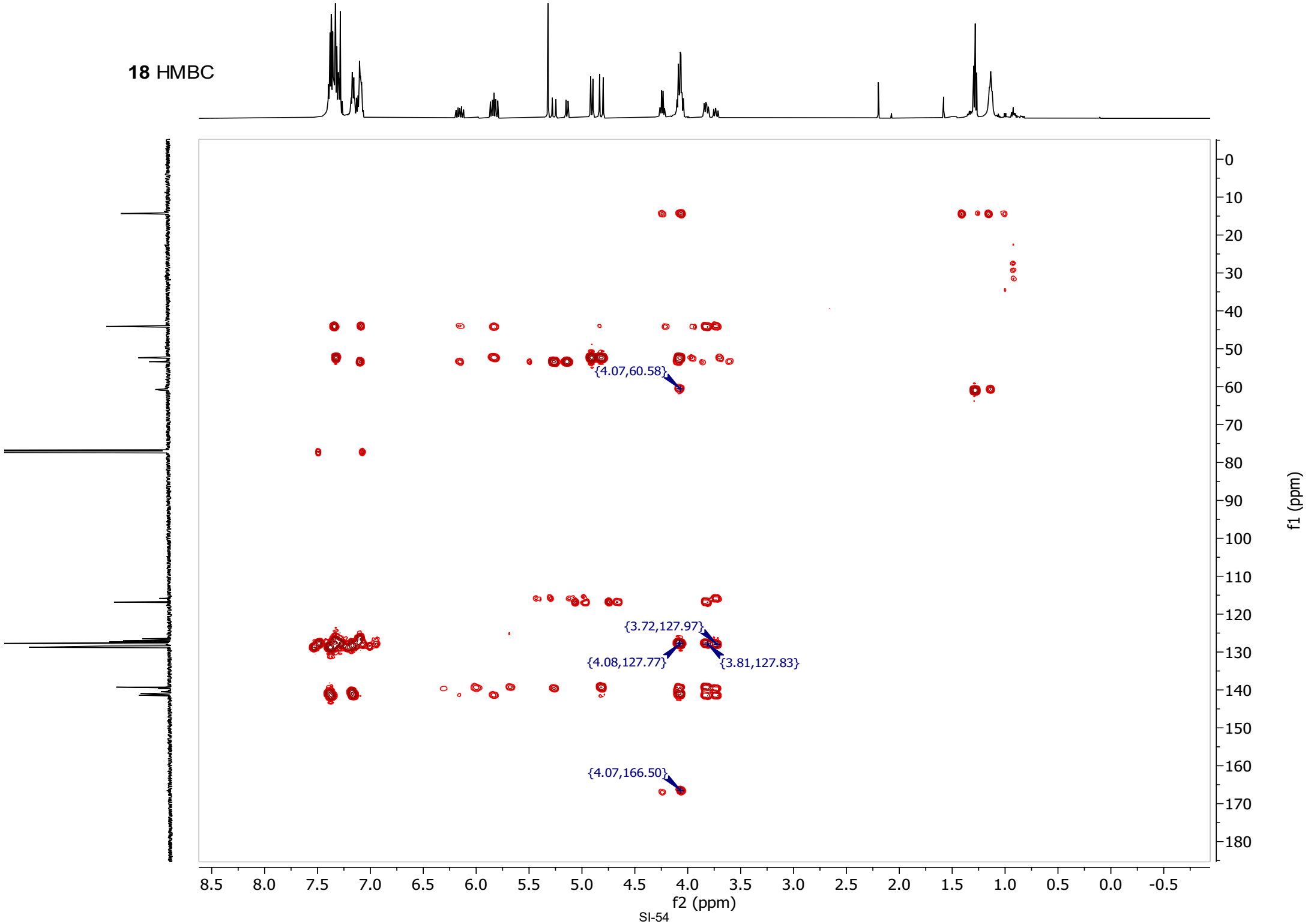

7.37
7.36
7.35
7.34
7.34
7.33
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
4.25
4.23
4.22
4.21
4.03
4.01
4.00
2.81
2.80
2.80
2.79
2.01
2.01
2.00
1.28
1.26
1.25
0.94
0.92
0.91
-0.00 TMS
O
O
CH
N+
N-
H3C
17
4.96
2.00
0.97
1.98
0.98
3.28
f1 (ppm)

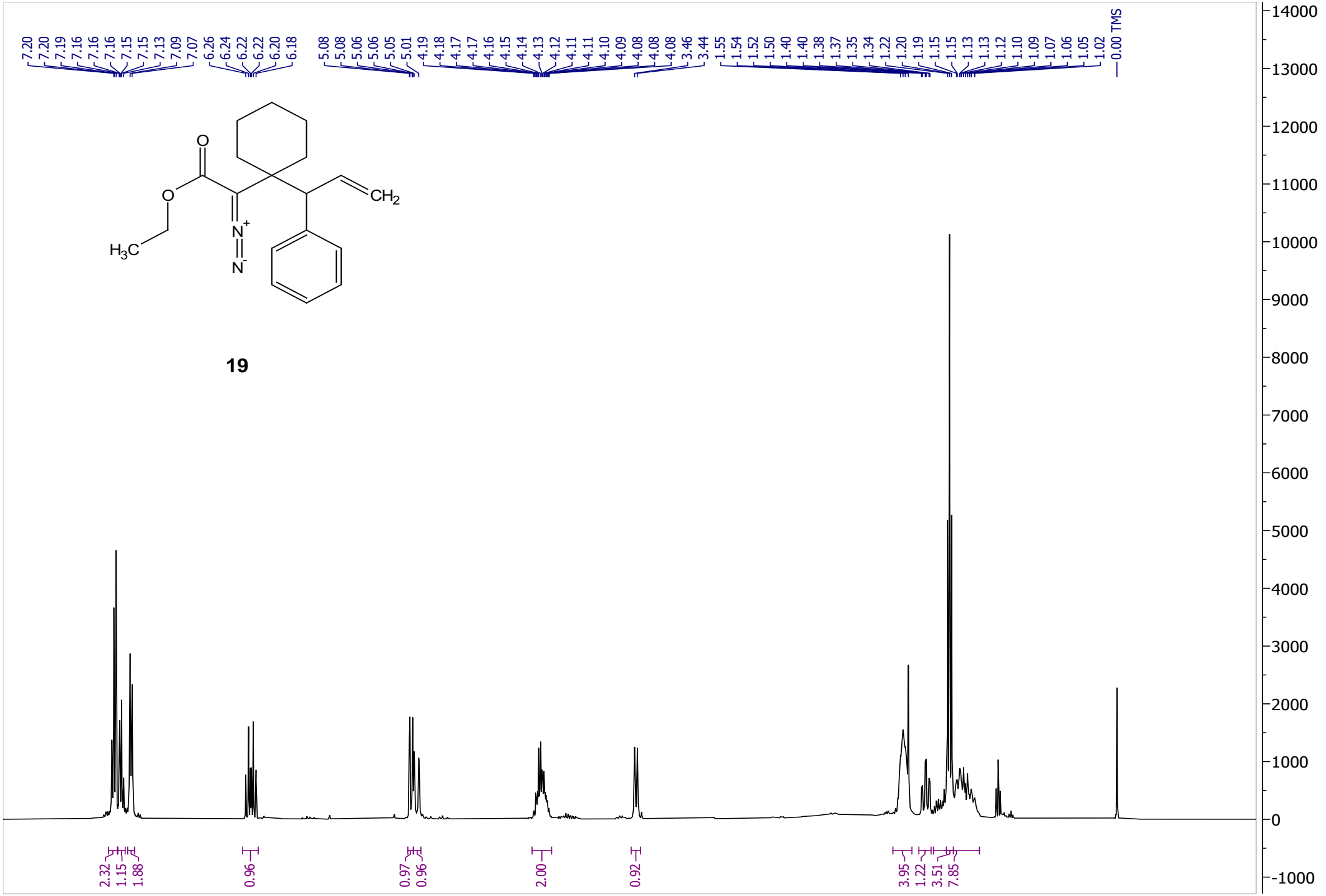

166.68
139.92
128.88
127.67
127.30
81.06
77.16 CDCl3
70.89
61.05
38.77
23.07
14.53
O
O
CH
N+
N-
H3C
17
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

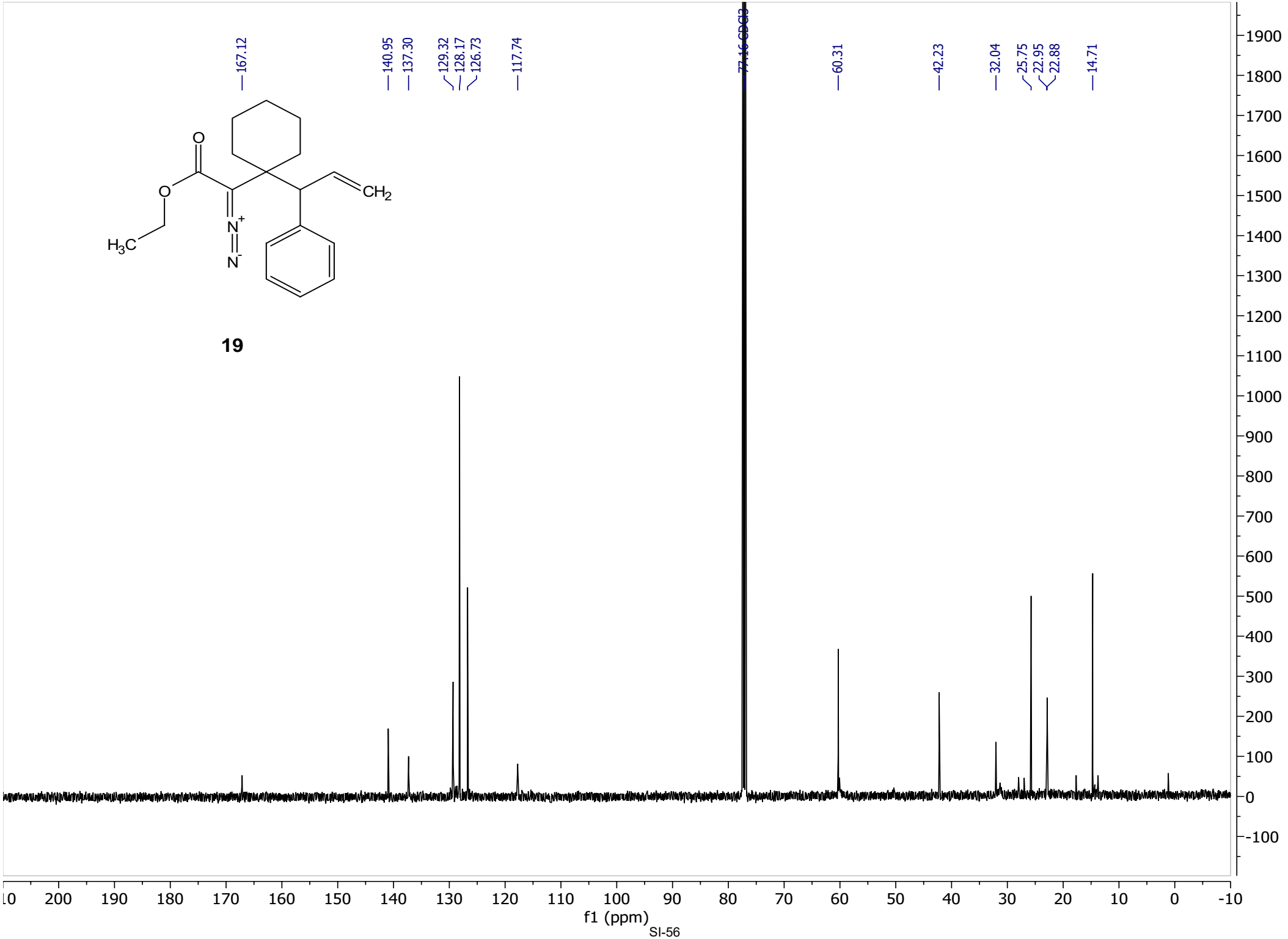

7.35 7.34 7.34 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.15 7.15 7.14 7.14 7.13 7.13 7.12 7.10 7.10 7.09 7.07 7.06 7.05 7.05 7.04 6.14 6.12 6.12 6.10 5.83 5.82 5.81 5.80 5.78 5.78 5.76 5.30 5.25 5.21 5.12 5.10 4.89 4.86 4.80 4.77 4.23 4.22 4.21 4.20 4.20 4.19 4.07 4.05 4.04 4.03 4.02 4.01 3.81 3.79 3.78 3.77 3.70 3.70 1.55 1.27 1.25 1.24 1.12 1.11 1.09 -0.00 TMS
O
O
CH2
H3C
N+
N-
18
11.35
4.40
0.65
1.01
0.55
0.50
0.94
0.99
1.01
3.27
0.98
0.57
1.66
2.60
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

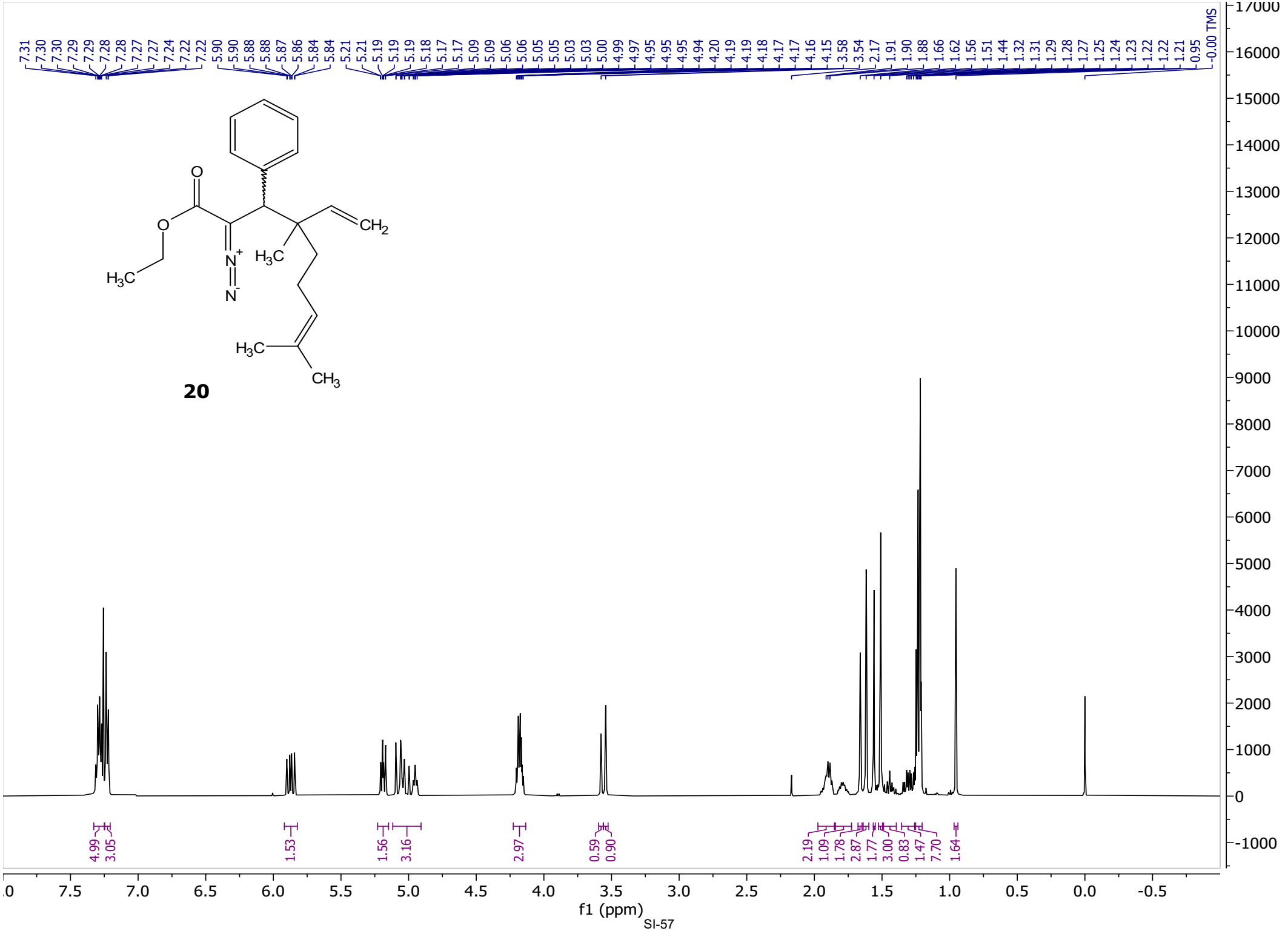

141.51
141.10
140.59
139.73
139.39
128.88
128.86
128.55
128.53
128.03
127.87
127.67
127.45
127.17
127.06
126.63
116.94
115.97
77.16 CDCl3
61.09
60.85
53.54
52.48
44.23
44.11
14.58
14.45
O
O
CH2
H3C
N+
N-
18
f1 (ppm)

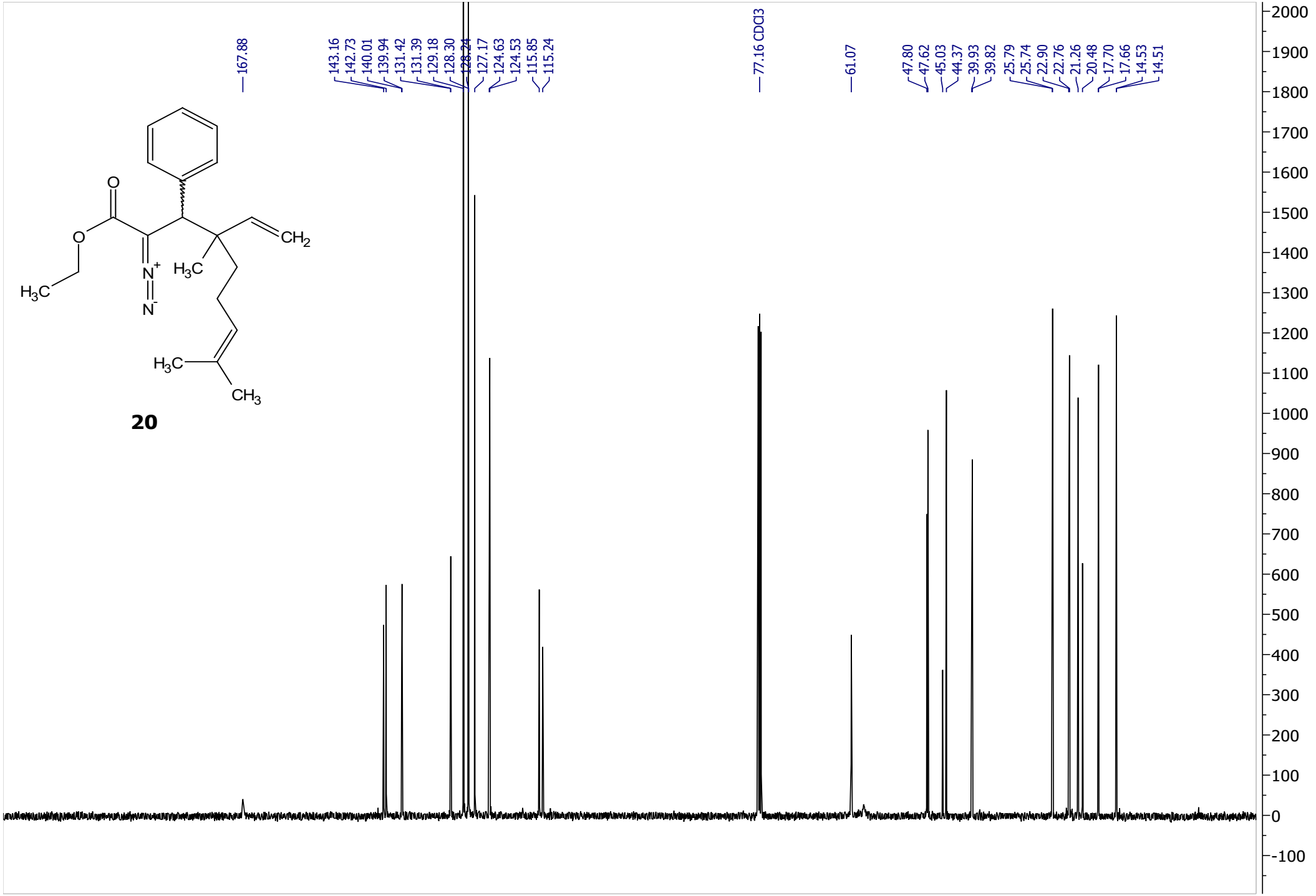

18 COSY
{4.21,1.28}
{4.03,1.13}
{4.25,1.28}
{4.23,1.28}
{5.81,3.82}
{6.15,3.73}
{5.84,3.81}
{4.05,3.82}
{4.09,3.72}
{4.09,3.81}
{5.84,4.92}
{5.81,4.84}
{6.16,5.26}
{6.13,5.25}
{6.18,5.25}
{6.11,5.25}
f2 (ppm)
f1 (ppm)


18 HMBC
{4.07,60.58}
{3.72,127.97}
{4.08,127.77}
{3.81,127.83}
{4.07,166.50}
f2 (ppm)
f1 (ppm)

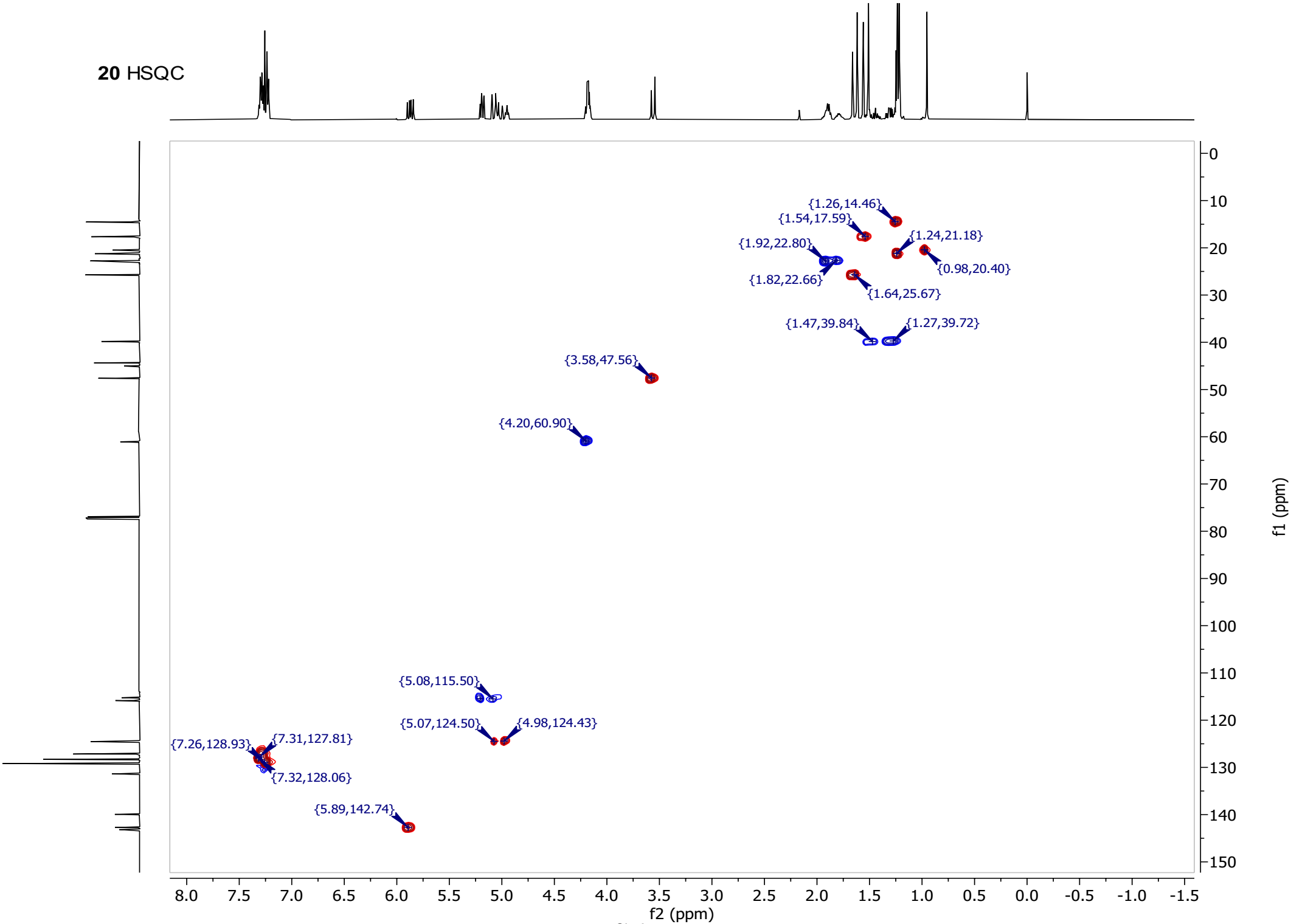

7.20 7.20 7.19 7.16 7.16 7.16 7.15 7.15 7.13 7.09 7.07 6.26 6.24 6.22 6.22 6.20 6.18 5.08 5.08 5.06 5.06 5.05 5.01 4.19 4.18 4.17 4.17 4.16 4.15 4.14 4.13 4.12 4.11 4.11 4.10 4.09 4.08 4.08 4.08 3.46 3.44 1.55 1.54 1.52 1.50 1.40 1.40 1.38 1.37 1.35 1.34 1.22 1.20 1.19 1.15 1.15 1.13 1.13 1.12 1.10 1.09 1.07 1.06 1.05 1.02 0.00 TMS
O
O
CH2
N+
N-
H3C
19
2.32 1.15 1.88 0.96 0.97 0.96 2.00 0.92 3.95 1.22 3.51 7.85
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

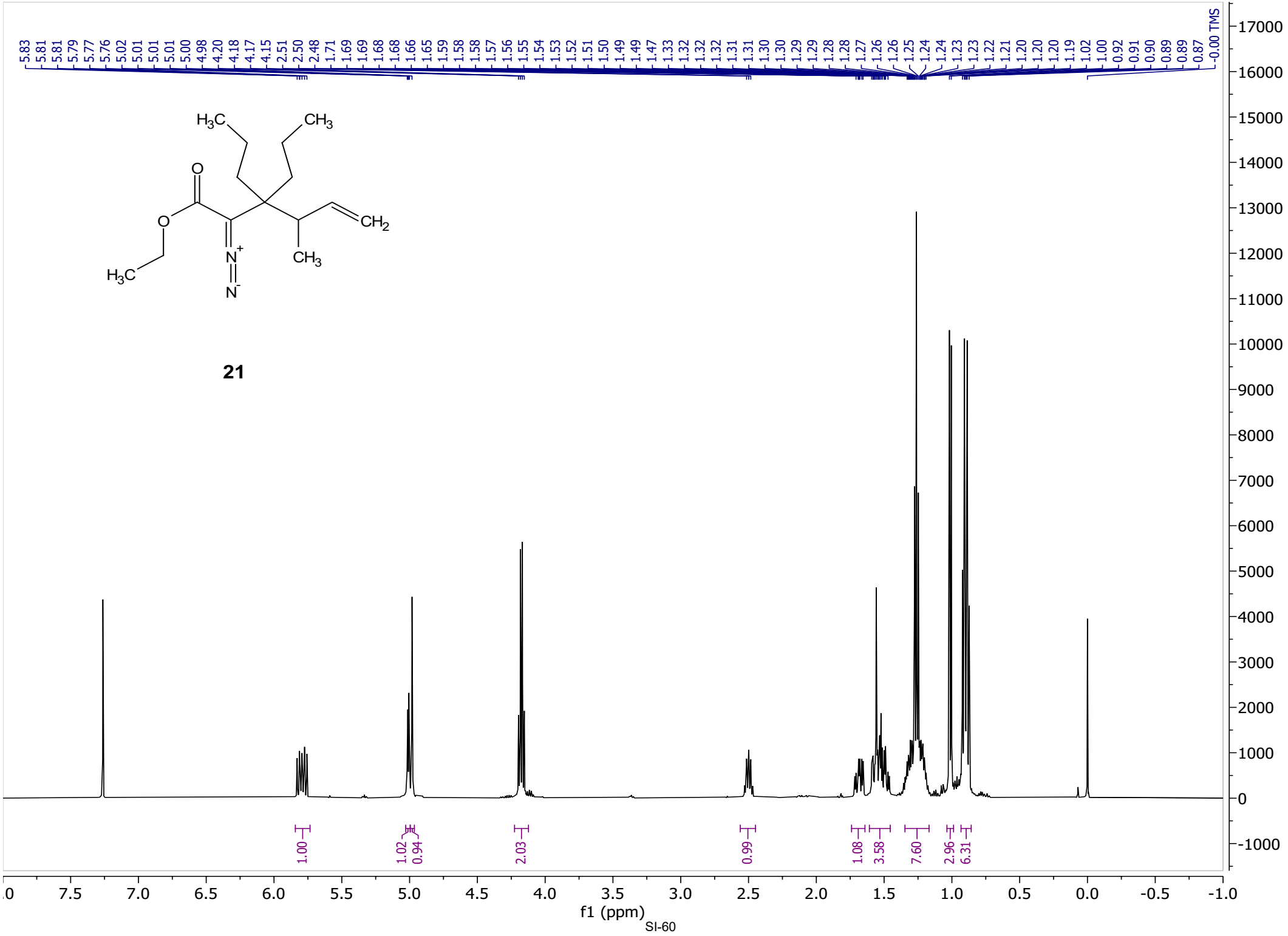

167.12
140.95
137.30
129.32
128.17
126.73
117.74
77.16 CDCl3
60.31
42.23
32.04
25.75
22.95
22.88
14.71
O
O
CH2
N+
N-
H3C
19
f1 (ppm)

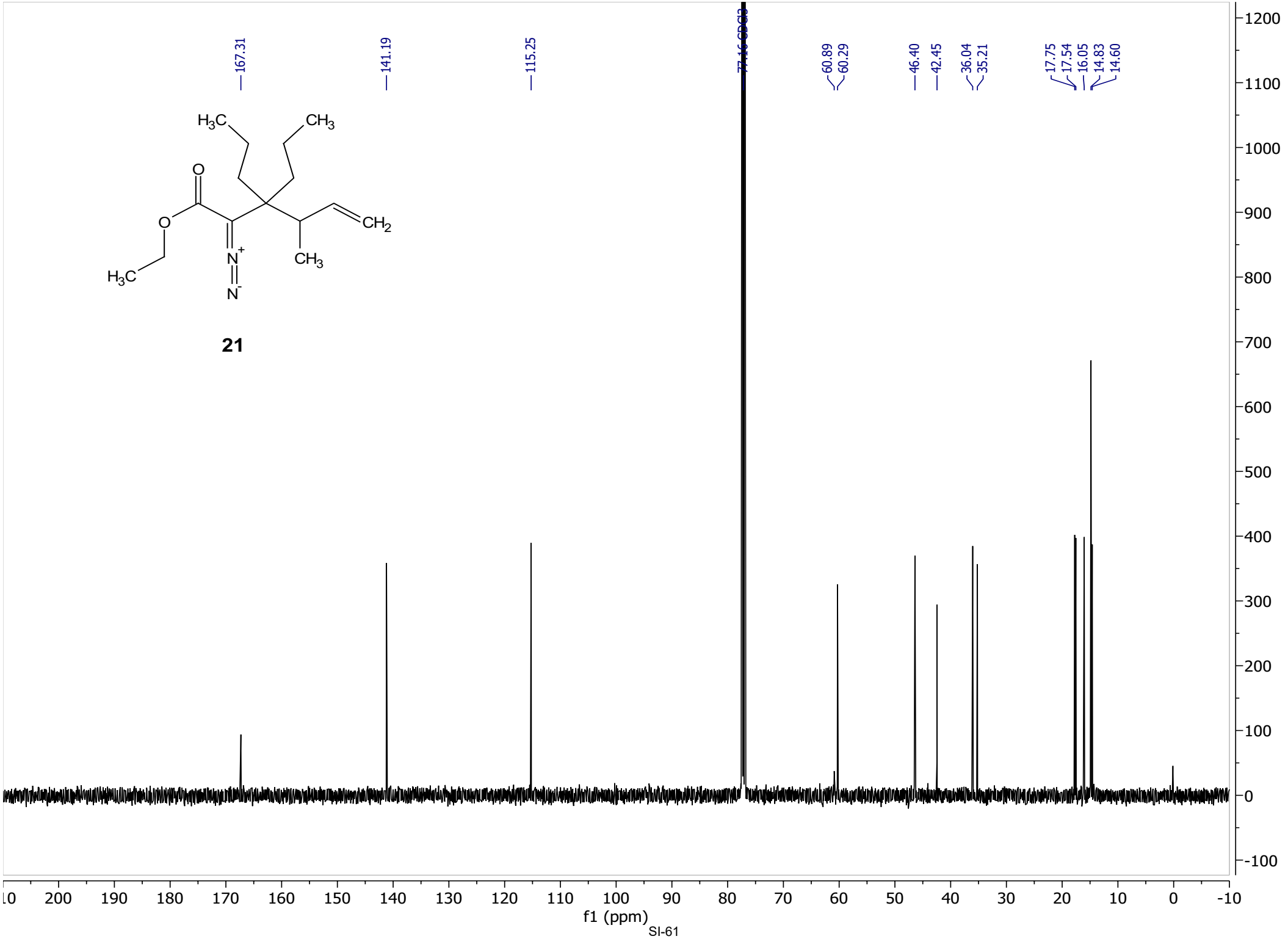

7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.24 7.22 7.22
5.90 5.90 5.88 5.88 5.87 5.86 5.84 5.84
5.21 5.21 5.19 5.19 5.19 5.18 5.17 5.17 5.09 5.09 5.06 5.06 5.05 5.05 5.03 5.03 5.00 4.99 4.97 4.95 4.95 4.95 4.94 4.20 4.19 4.19 4.18 4.17 4.17 4.16 4.15 3.58 3.54 2.17 1.91 1.90 1.88 1.66 1.62 1.56 1.51 1.44 1.32 1.31 1.29 1.28 1.27 1.25 1.24 1.23 1.22 1.22 1.21 0.95 -0.00 TMS
O
O
N+
N-
H3C
H3C
CH2
H3C
H3C
CH3
20
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
4.99 3.05 1.53 1.56 3.16 2.97 0.59 0.90 2.19 1.09 1.78 2.87 1.77 3.00 0.83 1.47 7.70 1.64
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

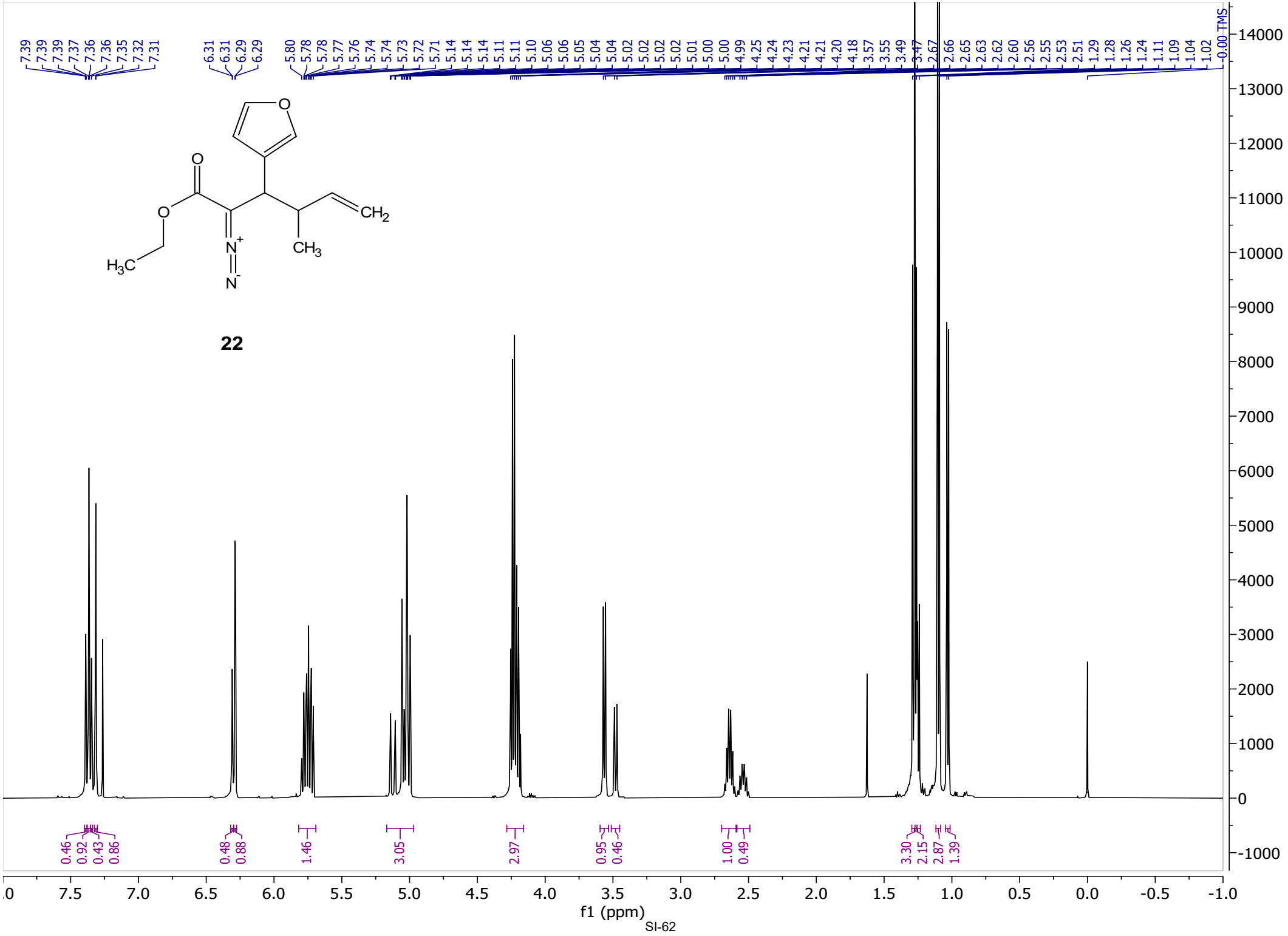

167.88
143.16
142.73
140.01
139.94
131.42
131.39
129.18
128.30
128.24
127.17
124.63
124.53
115.85
115.24
77.16 CDCl3
61.07
47.80
47.62
45.03
44.37
39.93
39.82
25.79
25.74
22.90
22.76
21.26
20.48
17.70
17.66
14.53
14.51
O
O
H3C
N+
N-
H3C
CH2
H3C
CH3
20
f1 (ppm)

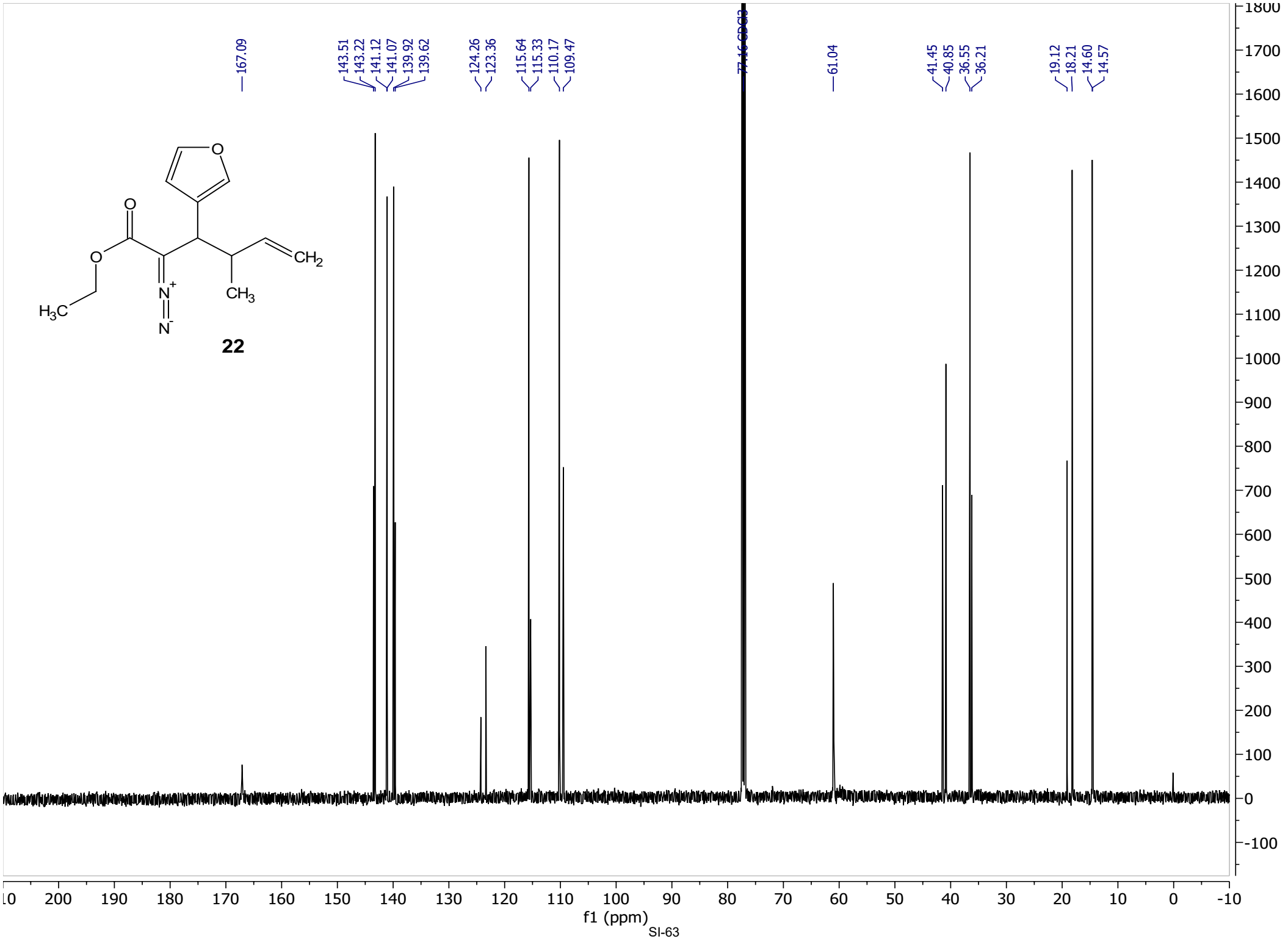
20 HSQC

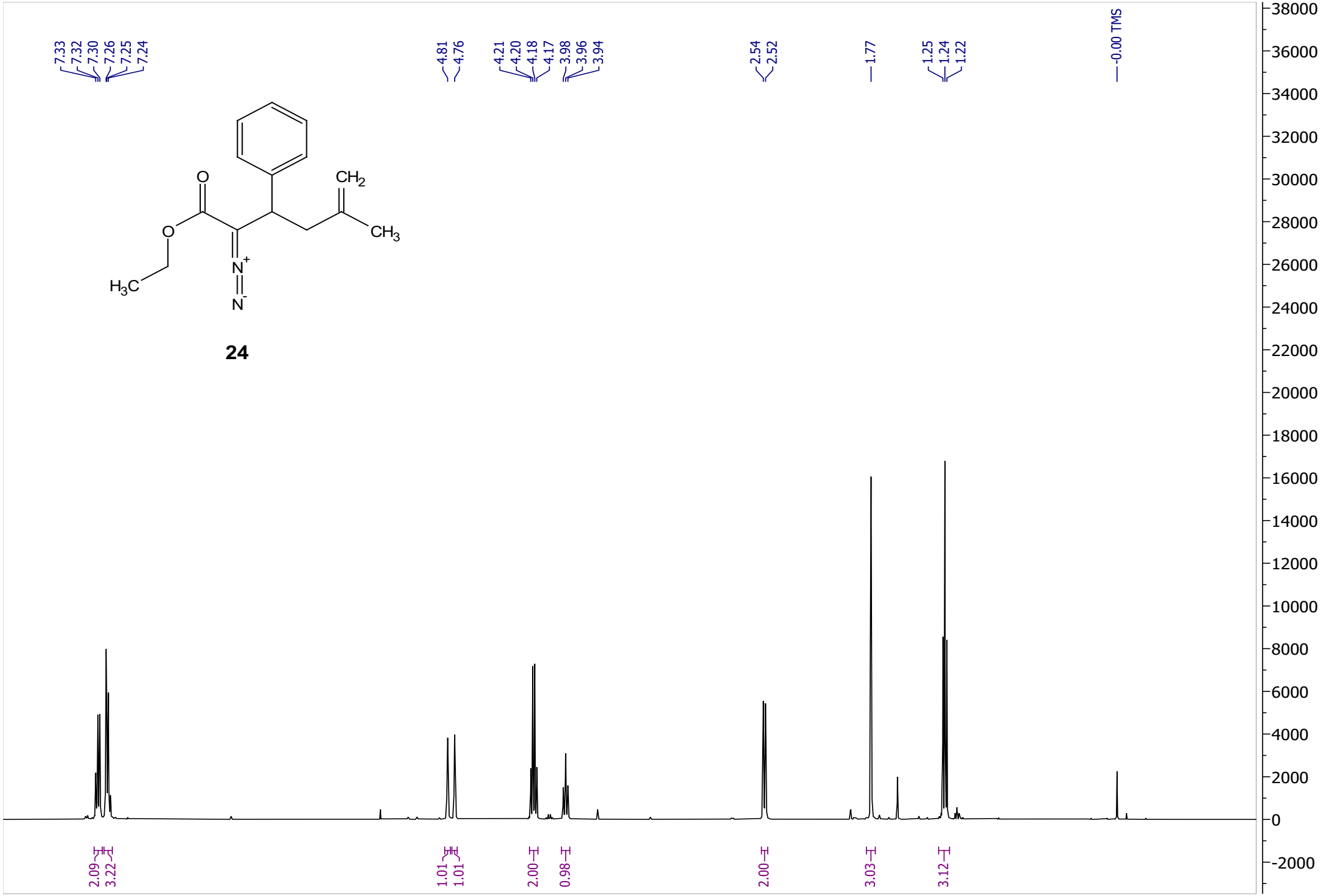

{1.26,14.46}
{1.54,17.59}
{1.24,21.18}
{1.92,22.80}
{0.98,20.40}
{1.82,22.66}
{1.64,25.67}
{1.47,39.84}
{1.27,39.72}
{3.58,47.56}
{4.20,60.90}
{5.08,115.50}
{5.07,124.50}
{4.98,124.43}
{7.26,128.93}
{7.31,127.81}
{7.32,128.06}
{5.89,142.74}
f2 (ppm)
f1 (ppm)

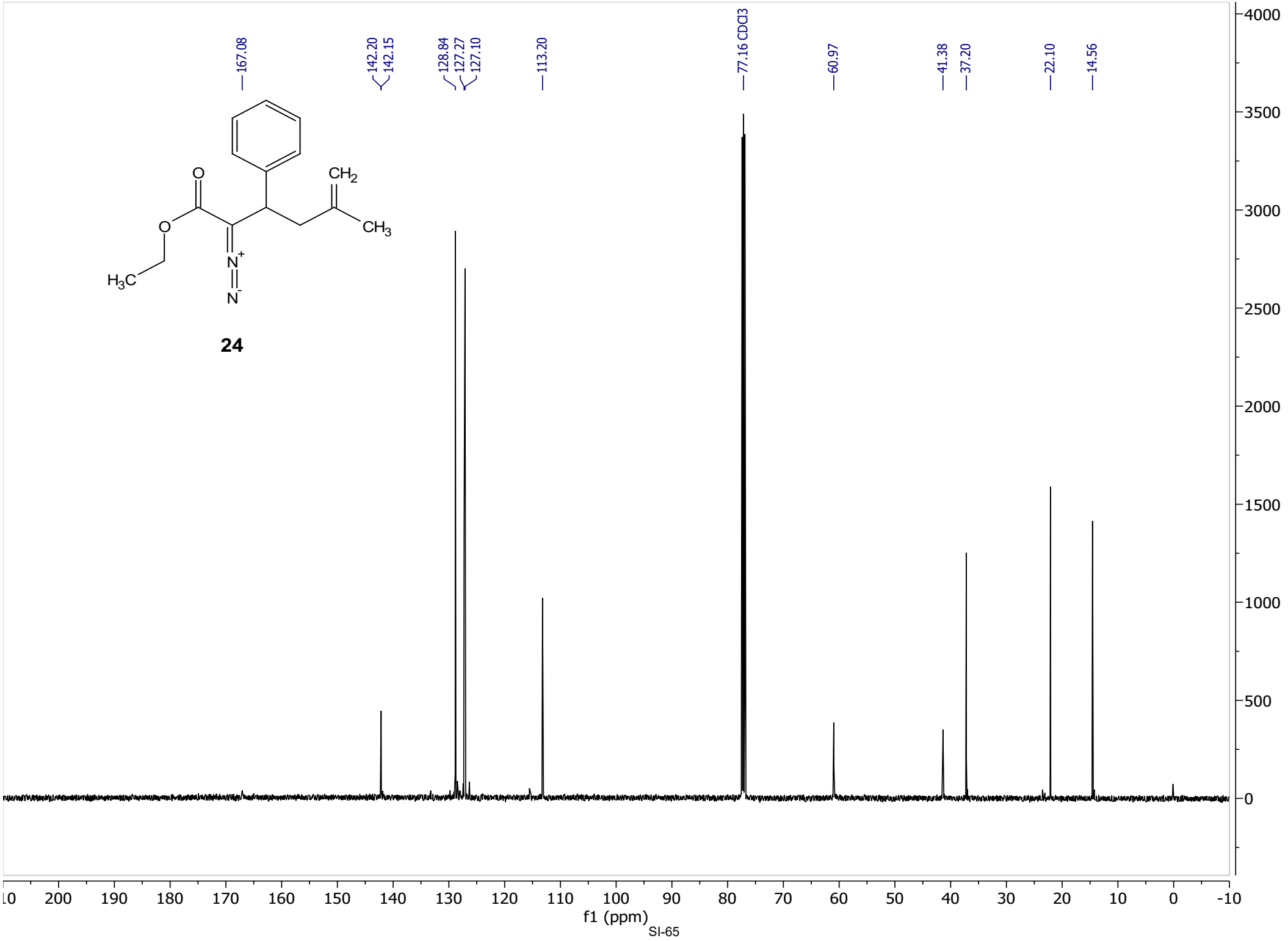

5.83 5.81 5.81 5.79 5.77 5.76 5.02 5.01 5.01 5.01 5.00 4.98 4.20 4.18 4.17 4.15 2.51 2.50 2.48 1.71 1.69 1.69 1.68 1.68 1.66 1.65 1.59 1.58 1.58 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.49 1.47 1.33 1.32 1.32 1.32 1.31 1.31 1.30 1.30 1.29 1.29 1.28 1.28 1.27 1.26 1.26 1.25 1.24 1.24 1.23 1.23 1.22 1.21 1.20 1.20 1.20 1.19 1.02 1.00 0.92 0.91 0.90 0.89 0.89 0.87 -0.00 TMS
H3C
CH3
O
O
CH2
N+
N-
CH3
H3C
21
1.00
1.02
0.94
2.03
0.99
1.08
3.58
7.60
2.96
6.31
f1 (ppm)


167.31
141.19
115.25
77.16 CDCl3
60.89
60.29
46.40
42.45
36.04
35.21
17.75
17.54
16.05
14.83
14.60
H3C
CH3
O
O
CH2
N+
N-
H3C
CH3
21
f1 (ppm)


7.39 7.39 7.39 7.37 7.36 7.36 7.35 7.32 7.31
6.31 6.31 6.29 6.29
5.80 5.78 5.78 5.77 5.76 5.74 5.74 5.73 5.72 5.71 5.14 5.14 5.14 5.11 5.11 5.10 5.06 5.06 5.05 5.04 5.04 5.02 5.02 5.02 5.02 5.01 5.00 5.00 4.99 4.25 4.24 4.23 4.21 4.21 4.20 4.18 3.57 3.55 3.49 3.47 2.67 2.66 2.65 2.63 2.62 2.60 2.56 2.55 2.53 2.51 1.29 1.28 1.26 1.24 1.11 1.09 1.04 1.02 0.00 TMS
O
O
O
CH2
N+
N-
CH3
H3C
22
0.46 0.92 0.43 0.86
0.48 0.88
1.46
3.05
2.97
0.95 0.46
1.00 0.49
3.30 2.15 2.87 1.39
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.09
143.51
143.22
141.12
141.07
139.92
139.62
124.26
123.36
115.64
115.33
110.17
109.47
77.16 CDCl3
61.04
41.45
40.85
36.55
36.21
19.12
18.21
14.60
14.57
O
O
O
CH2
CH3
N+
N-
H3C
22
f1 (ppm)


7.33
7.32
7.30
7.26
7.25
7.24
4.81
4.76
4.21
4.20
4.18
4.17
3.98
3.96
3.94
2.54
2.52
1.77
1.25
1.24
1.22
-0.00 TMS
O
O
CH2
CH3
N+
N-
H3C
24
2.09
3.22
1.01
1.01
2.00
0.98
2.00
3.03
3.12
f1 (ppm)


167.08
142.20
142.15
128.84
127.27
127.10
113.20
77.16 CDCl3
60.97
41.38
37.20
22.10
14.56
O
O
CH2
CH3
N+
N-
H3C
24
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)