Supporting Information

A Unified Approach to Substituted Allenoates via Pd-Catalyzed β-Hydride Elimination of (*E*)-Enol Triflates

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General Information

All catalytic reactions were performed under nitrogen and monitored by TLC and/or LC/MS analysis. TLC analysis was performed on Silica Gel 60, aluminum-backed TCL plates. LC/MS analysis was performed on an Agilent 1200 Series LC/MS equipped with a ZORBAX Eclipse XDB-C18 analytical column from Agilent (4.6 x 150 m, 5 μm, Part #: 993967-902) attached to 6130 series single-quad mass spectrometer with a multimode ion source capable of both low-resolution ESI and APCI (positive and negative ionization). Column chromatography was performed using 230-400 Mesh silica gel. ^{1}H and ^{13}C NMR analyses were performed on a Varian Unity INOVA 500 MHz, Bruker AVIII 500 MHz, a Varian Mercury 300 MHz, or a Bruker AVIII 300 MHz NMR. All reagents and solvents were purchased from commercial sources without further purification. β-keto ester derivatives that were not commercially available were synthesized using standard alkylation techniques.

General procedures

General procedure for the synthesis of mono-substituted allenoates from (E)-enol triflates

To scintillation vial equipped with a magnetic stir bar was added the (*E)*-enol triflate (1 equiv.). The reaction vial was capped and purged with N_2 for 15 min. *i*PrOAc (0.2 M) was added to the flask, followed by Hunig's base (3 equiv.) The reaction was stirred at 50 ^{o}C and upon completion (as judged by TLC) the reaction was allowed to reach room temperature and was diluted with hexanes. White solids appeared and were filtered off. The filtrate was concentrated under reduced pressure. Purification was performed using a silica gel column, eluting with a gradient from 100% hexanes to 5% EtOAc/hexanes.

Detailed procedure for the synthesis of di-substituted allenoate 4f on a 1mmol scale

To a scintillation vial equipped with a magnetic stir bar was added $Pd_2(dba)_3 \bullet CHCl_3$ (1 mol%, 0.01 mmol, 0.010 g). The reaction vial was capped and purged with N_2 for 15 min. 0.4 ml of a 0.1 M solution of $P(O\textit{i}Pr)_3$ (4 mol%, 0.04 mmol) in *i*PrOAc (0.2 M) were added to the vial by syringe, followed by an additional 2 ml of *i*PrOAc (0.2 M) and the resulting solution was stirred at 50 ^{o}C for 20 min. Next, the (*E*)-enol triflate (1 equiv., 1 mmol, 0.396 g) was added as a solution in the remaining 2.4 ml of *i*PrOAc (0.2 M) followed by Hunig's base (3 equiv., 3 mmol, 0.522 ml). The reaction was stirred at 50 ^{o}C for 6 hrs and upon completion (as judged by TLC), the reaction was allowed to reach room temperature and was diluted with hexanes. White solids appeared and were filtered off. The filtrate was concentrated under reduced pressure. The crude yellow oil was purified using a silica gel column, eluting with 5% EtOAc/hexanes to obtain the desired allenoate **4f**.

General procedure for the synthesis of di-substituted allenoates from (E)-enol triflates

To a scintillation vial equipped with a magnetic stir bar was added $Pd_2(dba)_3 \bullet CHCl_3$ (1 mol%). The reaction vial was capped and purged with N_2 for 15 min. *i*PrOAc (0.2 M) and $P(O\textit{i}Pr)_3$ (4 mol%) were added to the vial and the resulting solution was stirred at 50 ^{o}C

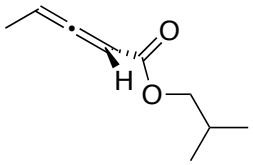
for 20 min. Then, the (*E*)-enol triflate (1 equiv.) was added followed by Hunig's base (3 equiv.) The reaction was stirred at 50 ^{o}C and upon completion (as judged by TLC), the reaction was allowed to reach room temperature and was diluted with hexanes. White solids appeared and were filtered off. The filtrate was concentrated under reduced pressure. Purification was performed using a silica gel column, eluting with 5% EtOAc/hexanes.

General procedure for the synthesis of tri- and tetra-substituted allenoates from (E)-enol triflates

To a scintillation vial equipped with a magnetic stir bar was added $Pd_2(dba)_3$•$CHCl_3$ (1 mol%). The reaction vial was capped and purged with N_2 for 15 min. *i*PrOAc (0.2 M) and $P(OPh)_3$ (4 mol%) were added to the vial and the resulting solution was stirred at 70 ^{o}C for 20 min. Then, the (*E*)-enol triflate (1 equiv.) was added followed by Hunig's base (3 equiv.) The reaction was stirred at 70 ^{o}C and upon completion (as judged by TLC), the reaction was allowed to reach room temperature and was diluted with hexanes. White solids appeared and were filtered off. The filtrate was concentrated under reduced pressure. Purification was performed using a silica gel column, eluting with 5% EtOAc/hexanes.

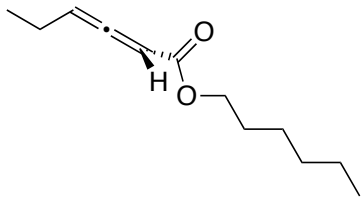
Characterization Data:

Isobutyl-penta-2,3-dienoate (4a)



Synthesized allenoate resulted in a colorless oil, isolated yield: 67% (run 1= 0.100 g, 1 mmol, run 2= 0.106 g, 1 mmol). **4a:5a**= 11:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4a**: δ 0.94 (d, *J* = 6.7 Hz, 6H), 1.78 (dd, *J* = 7.1, 3.4 Hz, 3H), 1.96 (hept, *J* = 13.4, 6.7 Hz, 1H), 3.92 (m, 2H), 5.57 (m, 2H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5a**: δ 1.83 (t, *J* = 2.6 Hz), 3.23 (q, *J* = 2.6 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4a**: δ 12.92, 19.19, 27.94, 70.97, 87.80, 90.26, 166.46, 213.18. HRMS (APCI+, m/z): calcd. For $C_9H_{14}O_2$, $[M+H^+]^+$: 155.1067; found: 155.1061.

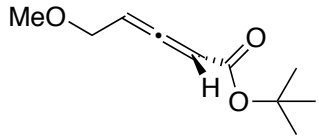
Hexyl-hexa-2,3-dienoate (4b)



Synthesized allenoate resulted in a light yellow oil, isolated yield: 68% (run 1= 0.149 g, 1 mmol, run 2= 0.118 g, 1 mmol). **4b:5b**=17:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4b**: δ 0.88 (m, 4H), 1.06 (t, *J* = 7.4 Hz, 3H), 1.33 (m, 6H), 1.63 (p, *J* = 6.9 Hz, 3H), 2.14 (m, 2H), , 4.11 (qt, *J* = 10.8, 6.7 Hz, 2H), 5.59 (dt, *J* = 6.3, 3.3 Hz, 1H), 5.65 (q, *J* = 6.4 Hz,

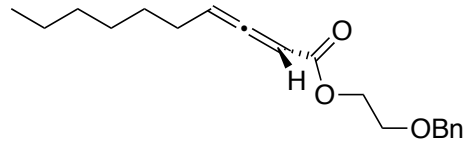
1H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5b**: δ 1.12 (t, *J* = 7.5 Hz), 1.85 (m), 2.19 (dt, *J* = 7.5, 2.4 Hz), 3.22 (t, *J* = 2.4 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4b**: δ 13.20, 14.09, 20.98, 22.66, 25.69, 28.74, 31.55, 65.04, 88.99, 97.13, 166.50, 212.27. HRMS (APCI+, m/z): calcd. For $C_{12}H_{20}O_2$, $[M+H^+]^+$: 197.1536; found: 197.1543.

<u>*tert*-Butyl-5-methoxypenta-2,3-dienoate (4c)</u>



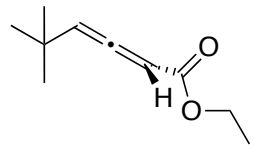
Synthesized alkyne resulted in a yellow oil, isolated yield: 62% (run 1= 0.126 g, 1 mmol, run 2= 0.103 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4c**: δ 1.47 (s, 9H), 3.37 (s, 3H), 4.08 (m, 2H), 5.61 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4c**: δ 28.24, 57.80, 68.88, 81.29, 90.83, 92.49, 164.90, 212.08. HRMS (APCI+, m/z): calcd. For $C_{10}H_{16}O_3$, $[M+Na^+]^+$: 207.0992; found: 207.0990.

<u>2-(benzyloxy)ethyl-deca-2,3-dienoate (4d)</u>



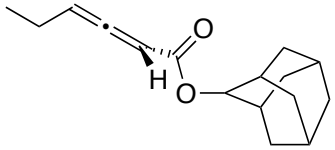
Synthesized allenoate resulted in a yellow oil, isolated yield: 61% (run 1= 0.190 g, 1mmol, run 2= 0.175 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4d**: δ 0.76 (t, *J* = 6.9 Hz, 3H), 1.18 (m, 8H), 1.34 (m, 2H), 2.01 (tt, *J* = 7.5, 5.3 Hz, 2H), 3.58 (t, 2H), 4.20 (t, 2H), 4.45 (s, 2H), 5.51 (m, 2H), 7.17 (m, 1H), 7.22 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4d**: δ 14.15, 22.67, 27.57, 28.74, 31.65, 64.08, 68.04, 73.26, 88.12, 95.66, 127.75, 128.50, 138.11, 166.28, 212.71. HRMS (APCI+, m/z): calcd. For $C_{19}H_{26}O_3$, $[M+H^+]^+$: 303.1955; found: 303.1964.

<u>Ethyl-5,5-dimethyl-hexa-2,3-dienoate (4e)</u>[1]



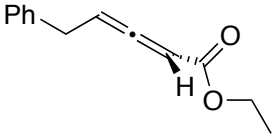
Synthesized allenoate resulted in a colorless oil, isolated yield: 79% (run 1=0.133 g, 1 mmol, run 2= 0.130 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4e**: δ 1.11 (s, 9H), 1.27 (td, *J* = 7.1, 2.6 Hz, 3H), 4.18 (m, 2H), 5.61 (qd, *J* = 6.1, 2.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4e**: δ 14.35, 30.14, 32.77, 60.77, 89.84, 106.88, 166.25, 210.62. HRMS (APCI+, m/z): calcd. For $C_{10}H_{16}O_2$, $[M+H^+]^+$: 169.1223; found: 169.1225.

Adamantan-2-yl-hexa-2,3-dienoate (4f)[2]



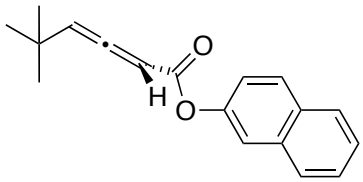
Synthesized allenoate resulted in a yellow oil, isolated yield: 75% (run 1= 0.185 g, 1 mmol, run 2= 0.187 g, 1 mmol). ^{1}H NMR (300 MHz, Chloroform-*d*) for **4f**: δ 1.06 (t, *J* = 7.4 Hz, 3H), 1.66 (m, 8H), 2.14 (m, 14H), 5.50 (dt, *J* = 6.3, 3.2 Hz, 1H), 5.61 (q, *J* = 6.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4f**: δ 13.42, 21.08, 31.02, 36.40, 41.52, 80.86, 90.61, 96.89, 165.44, 211.84. HRMS (APCI+, m/z): calcd. For $C_{16}H_{22}O_2$, $[M+H^+]^+$: 247.1693; found: 247.1685.

Ethyl-5-phenylpenta-2,3-dienoate (4g)[3]



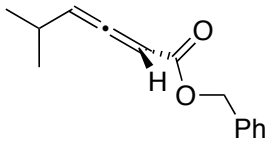
Synthesized allenoate resulted in a yellow oil, isolated yield: 69% (run 1= 0.141 g, 1 mmol, run 2= 0.136 g, 1 mmol). **4g:5g**= 10:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4g**: δ 1.31 (t, *J* = 7.1 Hz, 3H), 3.47 (m, 2H), 4.20 (m, 2H), 5.61 (dt, *J* = 6.2, 2.6 Hz, 1H), 5.76 (td, *J* = 7.5, 6.1 Hz, 1H), 7.29 (m, 5H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5g**: δ 3.32 (t, *J* = 2.5 Hz), 3.63 (t, *J* = 2.6 Hz). ^{13}C NMR (75 MHz, Chloroform-*d*) for **4g**: δ 14.36, 34.28, 60.96, 88.74, 94.84, 126.73, 128.63, 138.77, 166.06, 212.88. HRMS (APCI+, m/z): calcd. For $C_{13}H_{14}O_2$, $[M+H^+]^+$: 203.1067; found: 203.1071.

Naphthalen-2-yl-5,5-dimethylhexa-2,3-dienoate (4h)



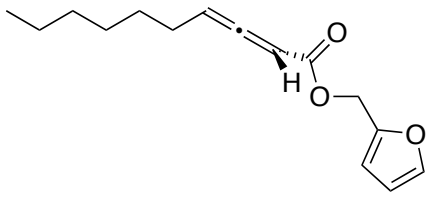
Synthesized allenoate resulted in an off-white solid, isolated yield: 86% (run 1= 0.214 g, 1 mmol, run 2= 0.195 g, 0.8 mmol). **4h:5h**= 21:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4h**: δ 1.20 (s, 9H), 5.76 (d, *J* = 6.0 Hz, 1H), 5.88 (d, *J* = 6.1 Hz, 1H), 7.29 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.48 (dddd, *J* = 14.8, 8.2, 6.9, 1.5 Hz, 2H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.84 (m, 3H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5h**: δ 1.13 (s), 2.30 (s), 3.55 (s). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 30.19, 33.01, 89.44, 107.46, 118.58, 121.29, 125.74, 126.62, 129.42, 131.55, 133.92, 148.78, 164.93, 211.85. HRMS (APCI+, m/z): calcd. For $C_{18}H_{18}O_2$, $[M+H^+]^+$: 267.1380; found: 267.1374.

Benzyl-5-methyl-hexa-2,3-dienoate (4i)[4]



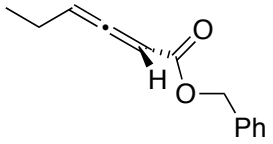
Synthesized allenoate resulted in a yellow oil, isolated yield: 88% (run 1= 0.188 g, 1 mmol, run 2= 0.190 g, 1 mmol). **4i:5i**= 23:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4i**: δ 1.0840 (d, *J* = 6.8, 1.2 Hz, 6H), 2.4815 (m, 1H), 5.1871 (m, 2H), 5.6630 (m, 2H), 7.3493 (m, 5H). %. ^{1}H NMR (500 MHz, Chloroform-*d*) for **5i**: 1.1649 (d, *J* = 6.9 Hz), 3.2970 (d, *J* = 2.2 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4i**: δ 22.34, 27.83, 66.49, 89.23, 102.80, 128.08, 128.22, 128.62, 136.26, 166.20, 211.77. HRMS (APCI+, m/z): calcd. For $C_{14}H_{16}O_2$, $[M+H^+]^+$: 217.1223; found: 217.1219.

Furan-2-ylmethyl-deca-2,3-dienoate (4j)



Synthesized allenoate resulted in a light yellow oil, isolated yield: 69% (run 1= 0.163 g, 1 mmol, run 2= 0.176 g, 1mmol). **4j:5j**= 11:1. ^{1}H NMR (300 MHz, Chloroform-*d*) for **4j**: δ 0.90 (t, *J* = 6.7 Hz, 3H), 1.36 (m, 6H), 2.14 (m, 2H), 5.13 (s, 2H), 5.63 (m, 2H), 6.40 (m, 2H), 7.43 (s, 1H). ^{1}H NMR (300 MHz, Chloroform-*d*) for **5j**: δ 3.29 (t, *J* = 2.5 Hz). ^{13}C NMR (75 MHz, Chloroform-*d*) for **4j**: δ 14.18, 22.66, 27.53, 28.69, 31.65, 58.40, 87.91, 95.81, 110.72, 143.27, 149.68, 165.99, 212.85. HRMS (APCI+, m/z): calcd. For $C_{15}H_{20}O_3$, $[M+Na^+]^+$: 271.1305; found: 271.1297.

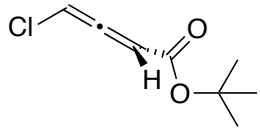
Benzyl-hexa-2,3-dienoate (4k)



Synthesized allenoate resulted in a light yellow oil, isolated yield: 79% (run 1= 0.151 g, 1 mmol, run 2= 0.166g, 1 mmol). **4k:5k**= 10:1 ^{1}H NMR (300 MHz, Chloroform-*d*) for **4k**: δ 1.08 (t, *J* = 7.4 Hz, 3H), 2.16 (m, 2H), 5.18 (m, 2H), 5.68 (m, 2H), 7.36 (m, 5H). ^{1}H NMR (300 MHz, Chloroform-*d*) for **5k**: δ 1.14 (t, *J* = 7.5 Hz), 3.30 (t, *J* = 2.5 Hz). ^{13}C NMR (75 MHz, Chloroform-*d*) for **4k**: δ 13.19, 20.94, 66.51, 88.76, 97.40, 128.22,

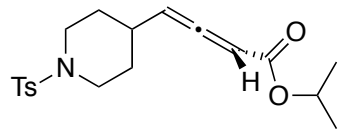
128.61, 136.20, 166.22, 212.60. HRMS (APCI+, m/z): calcd. For $C_{13}H_{14}O_2$, $[M+H^+]^+$: 203.1067; found: 203.1064.

Tert-butyl-4-chlorobuta-2,3-dienoate (4l)



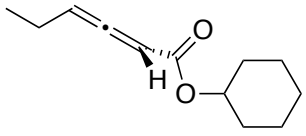
Synthesized allenoate resulted in an orange oil, isolated yield: 66% (run 1= 0.119 g, 1 mmol, run 2= 0.120 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4l**: δ 1.49 (s, 9H), 5.85 (d, *J* = 5.8 Hz, 1H), 6.40 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4l**: δ 28.14, 82.31, 92.43, 97.64, 162.67, 210.88. HRMS (APCI+, m/z): calcd. For C_9H_8, $[M+H^+]^+$:175.0520; found: not found.

Isopropyl-4-(1-tosylpiperidin-4-yl)buta-2,3-dienoate (4m)



Synthesized allenoate resulted in an off-white solid, isolated yield: 87% (run 1= 0.103 g, 0.33 mmol, run 2= 0.315 g, 1 mmol). **4m:5m**= 11:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4m**: δ 1.2190 (m, 6H), 1.5296 (m, 2H), 1.8227 (m, 2H), 2.1012 (dt, *J* = 10.1, 3.7 Hz, 1H), 2.3729 (dt, *J* = 11.7, 2.6 Hz, 2H), 2.4138 (s, 3H), 3.6754 (m, 2H), 4.9952 (m, 1H), 5.5572 (m, 2H), 7.3031 (d, *J* = 8.0 Hz, 2H), 7.6189 (d, *J* = 8.3 Hz, 2H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5m**: δ 2.7646 (ddd, *J* = 11.9, 8.4, 3.2 Hz), 3.1255 (d, *J* = 2.2 Hz), 3.3211 (ddd, *J* = 11.2, 6.7, 3.5 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4m**: δ 21.90, 26.35, 31.09, 33.95, 44.57, 45.80, 68.37, 90.36, 98.88, 127.76, 129.72, 133.37, 143.58, 16535, 211.48. HRMS (APCI+, m/z): calcd. For C_9H_8, $[M+H^+]^+$:364.1577; found:364.1563.

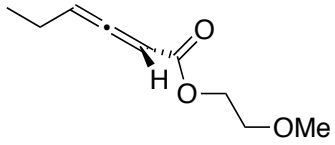
Cyclohexyl-hexa-2,3-dienoate (4n)



Synthesized allenoate resulted in a light yellow oil, isolated yield: 78% (run 1= 0.151 g, 1 mmol, run 2= 0.150 g, 1mmol). **4n:5n**= 46:1. ^{1}H NMR (300 MHz, Chloroform-*d*) for **4n**: δ 1.05 (t, *J* = 7.4 Hz, 3H), 1.40 (m, 6H), 1.75 (m, 4H), 2.13 (pd, *J* = 7.2, 3.2 Hz, 2H), 4.79 (tt, *J* = 8.7, 3.8 Hz, 1H), 5.56 (dt, *J* = 6.3, 3.3 Hz, 1H), 5.64 (q, *J* = 6.3 Hz, 1H). ^{1}H NMR (300 MHz, Chloroform-*d*) for **5n**: δ 3.19 (t, *J* = 2.5 Hz). ^{13}C NMR (75 MHz, Chlo-

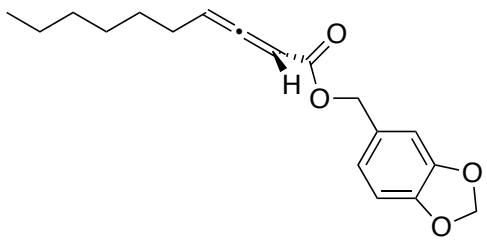
roform-*d*) δ 13.22, 20.96, 23.73, 25.54, 31.65, 72.88, 89.39, 97.02, 165.85, 212.14. HRMS (APCI+, m/z): calcd. For $C_{12}H_{18}O_2$, $[M+H^+]^+$: 195.1380; found: 195.1372.

2-methoxyethyl-hexa-2,3-dienoate (4o)



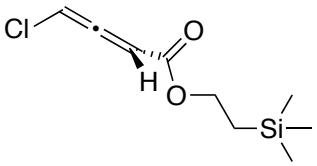
Synthesized allenoate resulted in a light yellow oil, isolated yield: 75% (run 1= 0.124 g, 1 mmol, run 2= 0.130 g, 1 mmol). **4o:5o**= 33:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4o**: δ 1.0573 (td, *J* = 7.4, 0.8 Hz, 3H), 2.1429 (m, 2H), 3.3828 (d, *J* = 0.8 Hz, 3H), 3.6106 (m, 2H), 4.2724 (qd, *J* = 4.1, 2.5 Hz, 2H), 5.6650 (m, 2H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5o**: δ 3.2820 (t, *J* = 2.4 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4o**: δ 13.18, 20.93, 59.14, 63.98, 70.59, 88.71, 97.44, 166.39, 212.60. HRMS (APCI+, m/z): calcd. For $C_9H_{14}O_3$, $[M+H^+]^+$: 171.1016; found: 171.1009.

Benzo[d][1,3]dioxol-5-ylmethyl-hexa-2,3-dienoate (4p)



Synthesized allenoate resulted in a yellow oil, isolated yield: 55% (run 1= 0.190 g, 1 mmol, run 2= 0.143 g, 1 mmol). **4p:5p**= 18:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4p**: δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.29 (m, 6H), 1.44 (m, 2H), 2.12 (m, 2H), 5.07 (d, *J* = 2.9 Hz, 2H), 5.60 (m, 2H), 5.96 (s, 2H), 6.78 (d, 1H), 6.85 (m, 2H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5p**: δ 3.27 (t, *J* = 2.5 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 14.20, 22.70, 27.62, 28.86, 31.69, 66.54, 88.18, 95.74, 101.28, 108.33, 109.09, 122.24, 130.04, 147.92, 166.23, 212.78. HRMS (APCI+, m/z): calcd. For $C_{18}H_{22}O_4$, $[M+Na^+]^+$: 325.1410; found: 325.1414.

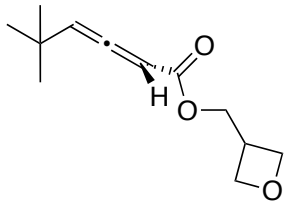
2-(trimethylsilyl)ethyl-4-chlorobuta-2,3-dienoate (4q)



Synthesized allenoate resulted in an orange oil, isolated yield: 48% (run 1= 0.113 g, 1 mmol, run 2= 0.095 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4q**: δ 0.05 (s,

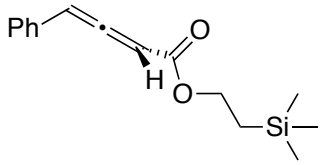
9H), 1.04 (m, 2H), 4.28 (m, 2H), 5.93 (d, J = 5.8 Hz, 1H), 6.43 (d, J = 5.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4q**: δ 1.32, 17.40, 64.15, 92.73, 96.16, 163.67, 211.34. HRMS (APCI+, m/z): calcd. For $C_9H_{15}O_2ClSi$, $[M+Na^+]^+$: 241.0422; found: 241.0420.

Oxetan-3-ylmethyl-5,5-dimethylhexa-2,3-dienoate (4r)



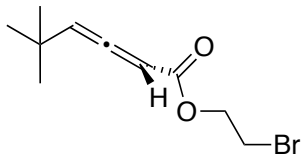
Synthesized allenoate resulted in a colorless oil, isolated yield: 65% (run 1= 0.141 g, 1 mmol, run 2= 0.126 g, 0.84 mmol). ^{1}H NMR (300 MHz, Chloroform-*d*) for **4r**: δ 1.11 (s, 9H), 1.34 (s, 3H), 4.15 (d, J = 11.1 Hz, 1H), 4.26 (m, 1H), 4.36 (d, J = 5.9 Hz, 2H), 4.53 (dd, J = 6.0, 2.6 Hz, 2H), 5.62 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4r**: δ 21.35, 30.11, 32.80, 39.40, 68.94, 79.67, 89.42, 106.96, 166.35, 210.97. HRMS (APCI+, m/z): calcd. For $C_{13}H_{20}O_3$, $[M+H^+]^+$: 225.1485; found: 225.1491.

2-(trimethylsilyl)ethyl-4-phenylbuta-2,3-dienoate (4s)



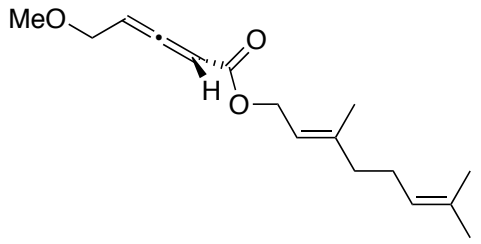
Synthesized allenoate resulted in a yellow oil, isolated yield: 80% (run 1= 0.207 g, 1 mmol, run 2= 0.205 g, 1 mmol). **4s:5s**= 6:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4s**: δ 0.0269 (s, 9H), 1.0297 (m, 2H), 4.2710 (td, J = 8.4, 1.6 Hz, 2H), 6.0051 (d, J = 6.4 Hz, 1H), 6.6120 (d, J = 6.4 Hz, 1H), 7.3107 (m, 5H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5s**: δ 0.0613 (s), 3.4891 (s), 7.4437 (dd, J = 6.8, 3.0 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4s**: δ 1.49, 17.31, 63.39, 92.08, 98.63, 127.51, 128.06, 128.82, 131.24, 131.76, 165.19, 214.53. HRMS (APCI+, m/z): calcd. For $C_{15}H_{20}O_2Si$, $[M+Na^+]^+$: 283.1125; found: 283.1123.

2-bromoethyl-5,5-dimethylhexa-2,3-dienoate (4t)



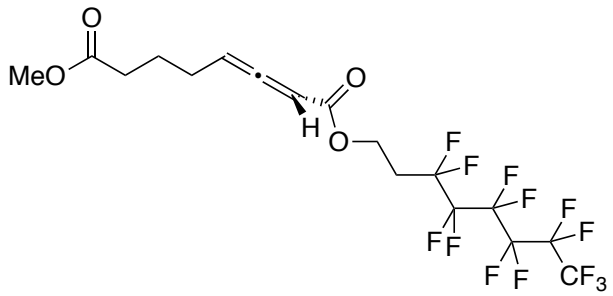
Synthesized allenoate resulted in a colorless oil, isolated yield: 41% (run 1= 0.096 g, 1 mmol, run 2= 0.100 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4t**: δ 1.12 (s, 9H), 3.52 (t, *J* = 6.1 Hz, 2H), 4.43 (ddt, *J* = 50.8, 12.1, 6.2 Hz, 2H), 5.63 (m, *J* = 1.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4t**: δ 28.80, 30.11, 32.87, 64.11, 89.18, 107.15, 165.81, 211.21. HRMS (APCI+, m/z): calcd. For $C_{10}H_{15}O_2Br$, $[M+H^+]^+$: 247.0328; found: 247.0331.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl-5-methoxypenta-2,3-dienoate (4u)



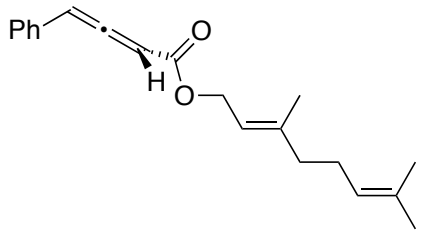
Synthesized allenoate resulted in a yellow oil, isolated yield: 61% (run 1= 0.145 g, 1 mmol, run 2= 0.182 g, 1 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **4u**: δ 1.60 (s, 3H), 1.69 (d, *J* = 12.0 Hz, 6H), 2.07 (m, 4H), 3.37 (s, 3H), 4.08 (qdd, *J* = 12.3, 6.6, 2.6 Hz, 2H), 4.66 (d, *J* = 7.0 Hz, 2H), 5.08 (m, 1H), 5.35 (m, 1H), 5.69 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4u**: δ 16.64, 17.83, 25.81, 26.45, 39.69, 57.93, 62.09, 68.79, 89.34, 92.88, 118.33, 123.88, 131.98, 142.55, 165.66, 212.51. HRMS (APCI+, m/z): calcd. For $C_{16}H_{24}O_3$, $[M+Na^+]^+$: 287.1618; found: 287.1626.

8-methyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)octa-2,3-dienedioate (4v)



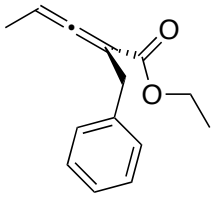
Synthesized allenoate resulted in a yellow oil, isolated yield: 55% (run 1= 0.162 g, 0.68 mmol, run 2= 0.140 g, 0.50 mmol). **4v:5v**= 4:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4v**: δ 1.80 (dddd, *J* = 12.9, 9.8, 6.2, 2.9 Hz, 2H), 2.18 (qd, *J* = 7.0, 3.3 Hz, 2H), 2.37 (td, *J* = 7.4, 2.5 Hz, 2H), 2.46 (m, 4H), 3.65 (s, 3H), 4.42 (m, 2H), 5.60 (m, 2H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5v**: δ 2.26 (ddd, *J* = 6.8, 4.5, 2.4 Hz), 3.2508 (t). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4v**: δ 18.30, 23.85, 23.92, 25.94, 26.89, 30.74, 33.06, 51.59, 56.76, 57.36, 71.95, 83.00, 88.13, 94.88, 165.66, 168.55, 173.70, 213.02. HRMS (APCI+, m/z): calcd. For $C_{17}H_{15}O_4F_{13}$, $[M+H^+]^+$: 531.0836; found: 531.0845.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl-4-phenylbuta-2,3-dienoate (4w)



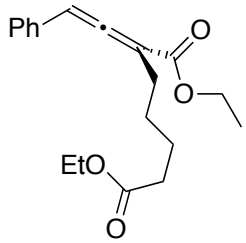
Synthesized allenoate resulted in a yellow oil, isolated yield: 80% (run 1= 0.235 g, 1 mmol, run 2= 0.240 g, 1 mmol). **4w:5w**= 7:1. ^{1}H NMR (500 MHz, Chloroform-*d*) for **4w**: δ 1.5923 (m, 3H), 1.7096 (m, 6H), 2.0887 (m, 4H), 4.7153 (dd, *J* = 7.1, 2.1 Hz, 2H), 5.0995 (m, 1H), 5.3852 (m, 1H), 6.0528 (d, *J* = 6.4 Hz, 1H), 6.6483 (d, *J* = 6.4 Hz, 1H), 7.3235 (m, 5H). ^{1}H NMR (500 MHz, Chloroform-*d*) for **5w**: δ 3.5335 (s), 7.4648 (dd, *J* = 6.7, 3.0 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*) for **4w**: δ 16.67, 17.83, 25.80, 26.44, 39.68, 62.24, 92.08, 98.86, 118.38, 123.89, 127.67, 128.22, 128.33, 131.36, 131.95, 142.51, 165.21, 214.79. HRMS (APCI+, m/z): calcd. For $C_{20}H_{24}O_2$, $[M+Na^+]^+$: 319.1669; found: 319.1666.

Ethyl-2benzylpenta-2,3-dienoate (10a)



Synthesized allenoate resulted in a colorless oil, isolated yield: 56% (run 1= 0.060 g, 0.5 mmol, run 2= 0.062 g, 0.5 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **10a**: δ 1.27 (t, *J* = 7.1 Hz, 3H), 1.71 (d, *J* = 7.3 Hz, 2H), 3.57 (qd, *J* = 15.0, 2.2 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 5.46 (qt, *J* = 7.2, 2.1 Hz, 1H), 7.26 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **10a**: δ 13.20, 14.40, 35.55, 61.05, 90.21, 100.29, 126.31, 128.31, 129.00, 139.70, 167.38, 211.36. HRMS (APCI+, m/z): calcd. For $C_{14}H_{16}O_2$, $[M+H^+]^+$: 217.1223; found: 217.1214.

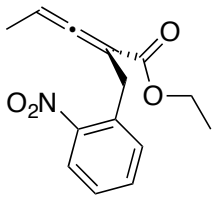
diethyl-2-(2-phenylvinylidene)heptanedioate (10b)



Synthesized allenoate resulted in a yellow oil, isolated yield: 85% (run 1= 0.280 g, 1 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) for **10b**: δ 1.22 (t, 6H), 1.36 (m, 2H), 1.49 (m, 2H), 1.59 (m, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 2.35 (qd, *J* = 6.8, 2.9 Hz, 2H), 4.08 (q, *J*

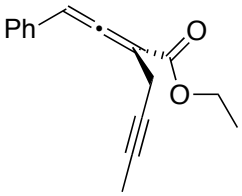
= 7.1 Hz, 2H), 4.19 (qd, *J* = 7.1, 1.7 Hz, 2H), 6.50 (t, *J* = 2.9 Hz, 1H), 7.27 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) for **10b**: δ 14.37, 24.85, 27.81, 28.84, 34.39, 60.29, 61.21, 98.51, 104.47, 127.33, 127.77, 128.92, 132.70, 166.85, 173.82, 212.10. HRMS (APCI+, m/z): calcd. For $C_{18}H_{22}O_4$, $[M+H^+]^+$: 303.1591; found: 303.1578.

Ethyl-2-(2-nitrobenzyl)penta-2,3-dienoate (10c)



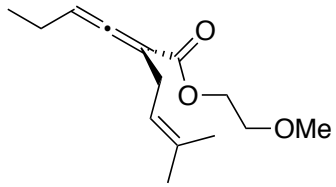
Synthesized allenoate resulted in a yellow oil, isolated yield: 38% (run 1= 0.112 g, 1 mmol, run 2= 0.043 g, 0.53 mmol). H NMR (300 MHz, Chloroform-*d*) for **10c**: δ 1.25 (t, *J* = 7.1 Hz, 3H), 1.58 (d, *J* = 7.3 Hz, 3H), 3.93 (qd, *J* = 15.4, 2.9 Hz, 2H), 4.17 (td, *J* = 7.1, 0.7 Hz, 2H), 5.37 (dt, *J* = 7.3, 2.9 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.51 (m, 1H), 7.91 (dd, *J* = 7.8, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) for **10c**: δ 12.93, 14.36, 32.72, 61.25, 91.41, 98.85, 124.77, 127.65, 132.58, 132.94, 134.32, 149.53, 166.89, 210.80. HRMS (APCI+, m/z): calcd. For $C_{14}H_{15}NO_4$, $[M+H^+]^+$: 262.1074; found: 262.1063.

ethyl-2-(2-phenylvinylidene)hex-4-ynoate (10d)



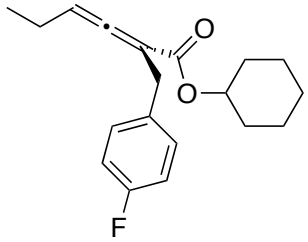
Synthesized allenoate resulted in a yellow oil, isolated yield: 68% (run 1= 0.153 g, 0.94 mmol). ^{1}H NMR (300 MHz, Chloroform-*d*) for **10d**: δ 1.28 (t, *J* = 7.1 Hz, 3H), 1.74 (t, *J* = 2.6 Hz, 3H), 3.28 (m, 2H), 4.25 (qd, *J* = 7.1, 3.1 Hz, 2H), 6.67 (t, *J* = 3.0 Hz, 1H), 7.36 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) for **10d**: δ 3.57, 14.33, 19.88, 61.46, 75.09, 78.01, 99.79, 101.83, 127.60, 127.95, 128.86, 132.22, 165.95, 212.44. HRMS (APCI+, m/z): calcd. For $C_{16}H_{16}O_2$, $[M+H^+]^+$: 241.1223; found: 241.1214.

2-methoxyethyl (*S*)-2-(3-methylbut-2-en-1-yl)hexa-2,3-dienoate (10e)



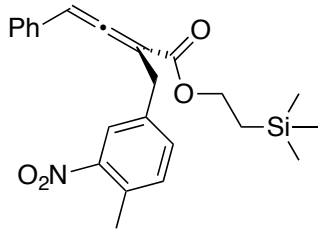
Synthesized allenoate resulted in a light yellow oil, isolated yield: 65% (run 1= 0.155 g, 1 mmol, run 2= 0.073 g, 0.48 mmol). ^{1}H NMR (300 MHz, Chloroform-*d*) for **10e**: δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.66 (d, *J* = 20.5, 1.3 Hz, 6H), 2.11 (dd, *J* = 7.4, 6.5 Hz, 2H), 2.92 (m, 2H), 3.38 (s, 3H), 3.61 (t, *J* = 4.9 Hz, 2H), 4.27 (td, *J* = 4.6, 2.6 Hz, 2H), 5.16 (tt, *J* = 7.2, 1.4 Hz, 1H), 5.58 (tt, *J* = 6.4, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) for **10e**: δ 13.35, 17.93, 21.49, 25.77, 27.65, 59.16, 64.10, 70.60, 97.18, 100.64, 121.06, 133.35, 167.76, 210.11. HRMS (APCI+, m/z): calcd. For $C_{14}H_{22}O_3$, $[M+H^+]^+$: 239.1642; found: 239.1634.

Cyclohexyl-2-(4-fluorobenzyl)hexa-2,3-dienoate (10f)



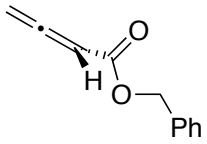
Synthesized allenoate resulted in a light yellow oil, isolated yield: 51% (run 1= 0.154 g, 1 mmol, run 2= 0.126 g, 0.81 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **10f**: δ 0.96 (t, *J* = 7.4 Hz, 3H), 1.40 (m, 6H), 1.67 (m, 2H), 1.77 (m, 2H), 2.03 (q, *J* = 7.1 Hz, 2H), 3.52 (m, 2H), 4.80 (tt, *J* = 8.3, 3.8 Hz, 1H), 5.52 (tt, *J* = 6.4, 2.5 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 7.17 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **10f**: δ 13.36, 21.43, 23.55, 25.62, 31.58, 31.58, 34.77, 72.95, 97.18, 101.84, 114.94, 115.11, 130.43, 130.49, 135.43, 160.67, 162.61, 166.79, 210.44. HRMS (APCI+, m/z): calcd. For $C_{19}H_{23}FO_2$, $[M+H^+]^+$: 303.1755; found: 303.1744.

2-(trimethylsilyl)ethyl-2-(4-methyl-3-nitrobenzyl)-4-phenylbuta-2,3-dienoate (10g)



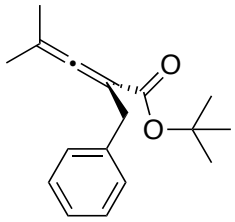
Synthesized allenoate resulted in a yellow oil, isolated yield: 73% (run 1= 0.125 g, 0.42 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) for **10g**: δ 0.01 (s, 9H), 1.00 (m, 2H), 2.54 (s, 3H), 3.74 (m, 2H), 4.27 (m, 2H), 6.56 (t, *J* = 2.2 Hz, 1H), 7.29 (m, 7H), 7.92 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) for **10g**: δ 1.36, 17.44, 20.72, 35.53, 64.01, 99.22, 103.40, 125.10, 127.47, 127.49, 128.24, 129.02, 131.83, 133.43, 134.00, 145.16, 166.31, 213.13. HRMS (APCI+, m/z): calcd. For $C_{23}H_{27}NO_4Si$, $[M+Na^+]^+$: 432.1602; found: 432.1598.

benzyl buta-2,3-dienoate (12)[4,5]



Synthesized allenoate resulted in a colorless oil, isolated yield: 87% (run 1= 0.081 g, 0.5 mmol, run 2= 0.280 g, 2 mmol). ^{1}H NMR (300 MHz, Chloroform-*d*) for **12**: δ 5.20 (s, 2H), 5.24 (d, *J* = 6.5 Hz, 2H), 5.69 (t, *J* = 6.5 Hz, 1H), 7.37 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) for **12**: δ 66.78, 79.57, 88.00, 128.27, 128.35, 128.67, 136.00, 165.69, 216.15. HRMS (APCI+, m/z): calcd. For $C_{11}H_{10}O_2$, $[M+H^+]^+$: 175.0754; found: 175.0750.

***tert*-butyl 2-benzyl-4-methylpenta-2,3-dienoate (14)**



Synthesized allenoate resulted in a colorless oil, isolated yield: 75% (run 1= 0.086 g, 0.5 mmol, run 2= 0.065 g, 0.36 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) for **14**: δ 1.40 (s, 9H), 1.67 (s, 6H), 3.47 (s, 2H), 7.19 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) for **14**: δ 19.51, 28.22, 35.92, 80.49, 99.56, 100.00, 126.01, 128.14, 128.89, 140.29, 166.92, 208.70. HRMS (APCI+, m/z): calcd. For $C_{17}H_{22}O_2$, $[M+Na^+]^+$: 281.1512; found: 281.1501.

References:

1) Li, C. -Y.; Zhu, B. H.; Ye, L. –W.; Jing, Q.; Sun, Z. –L.; Tang, Y.; Shen, Q. *Tetrahedron Lett.* **2007**, *63*, 8046.

2) Crouch, I. T.; Neff, R. K; Frantz, D. E. *J. Am. Chem. Soc.* **2013**, *135,* 4970.

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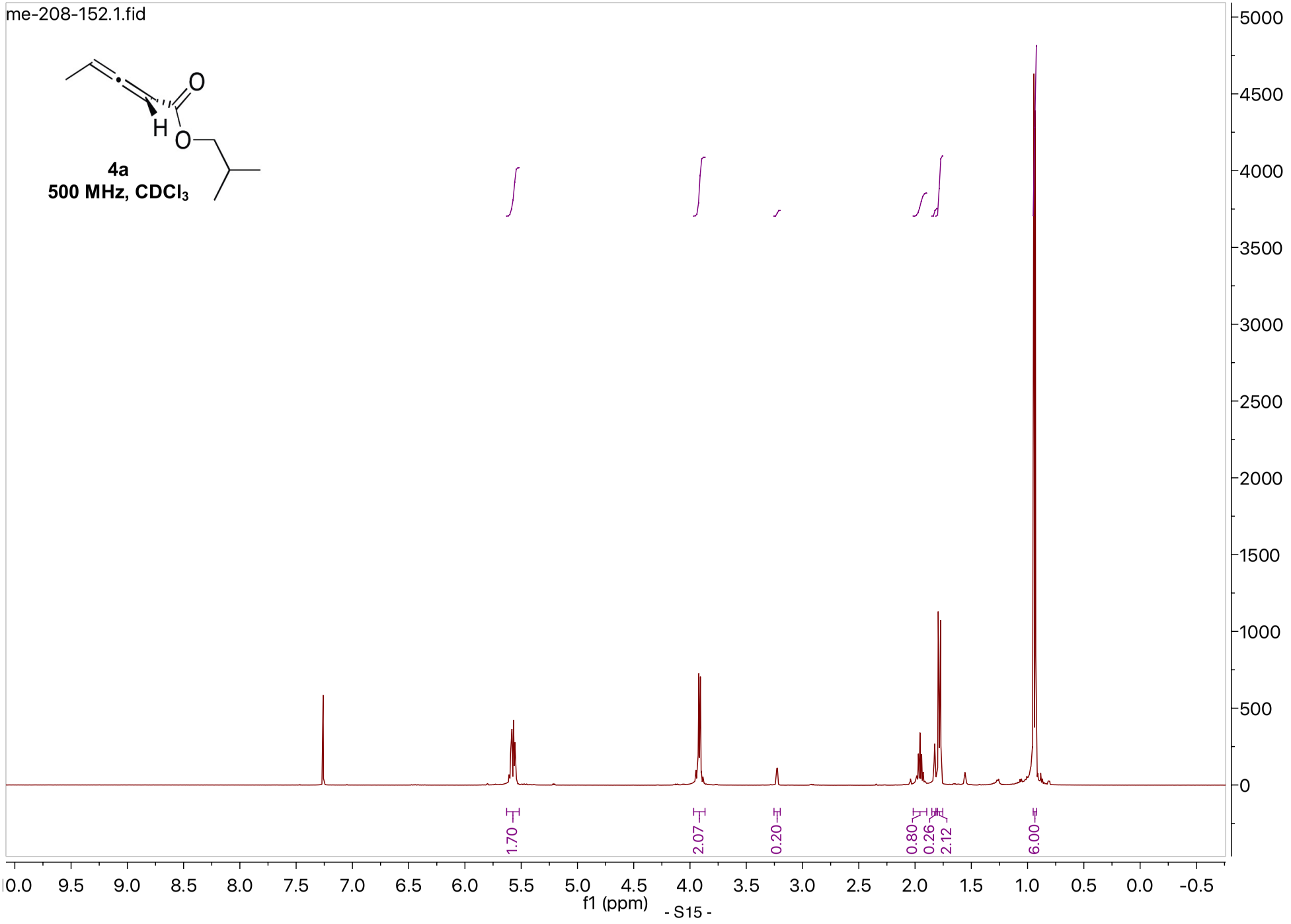
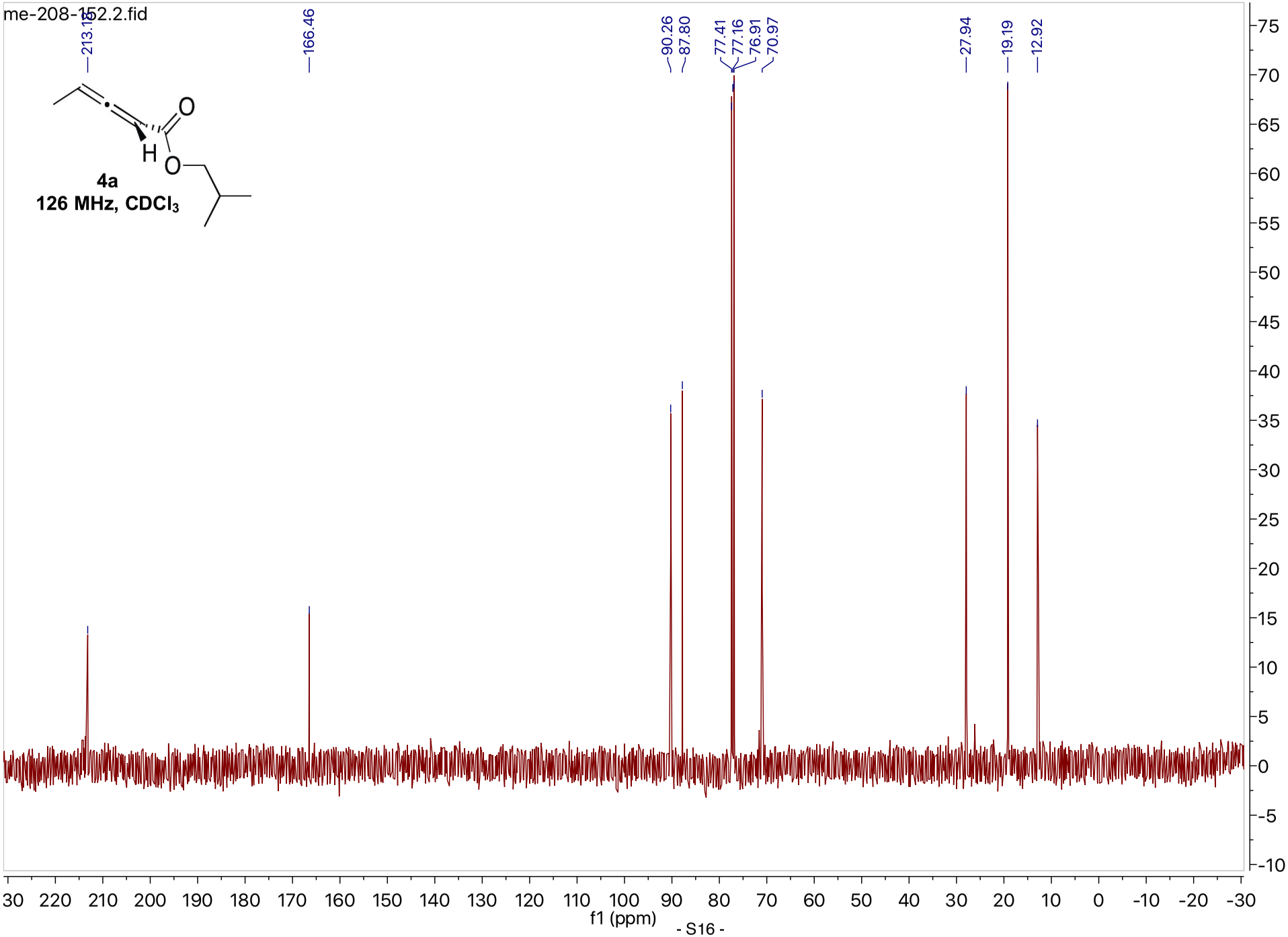
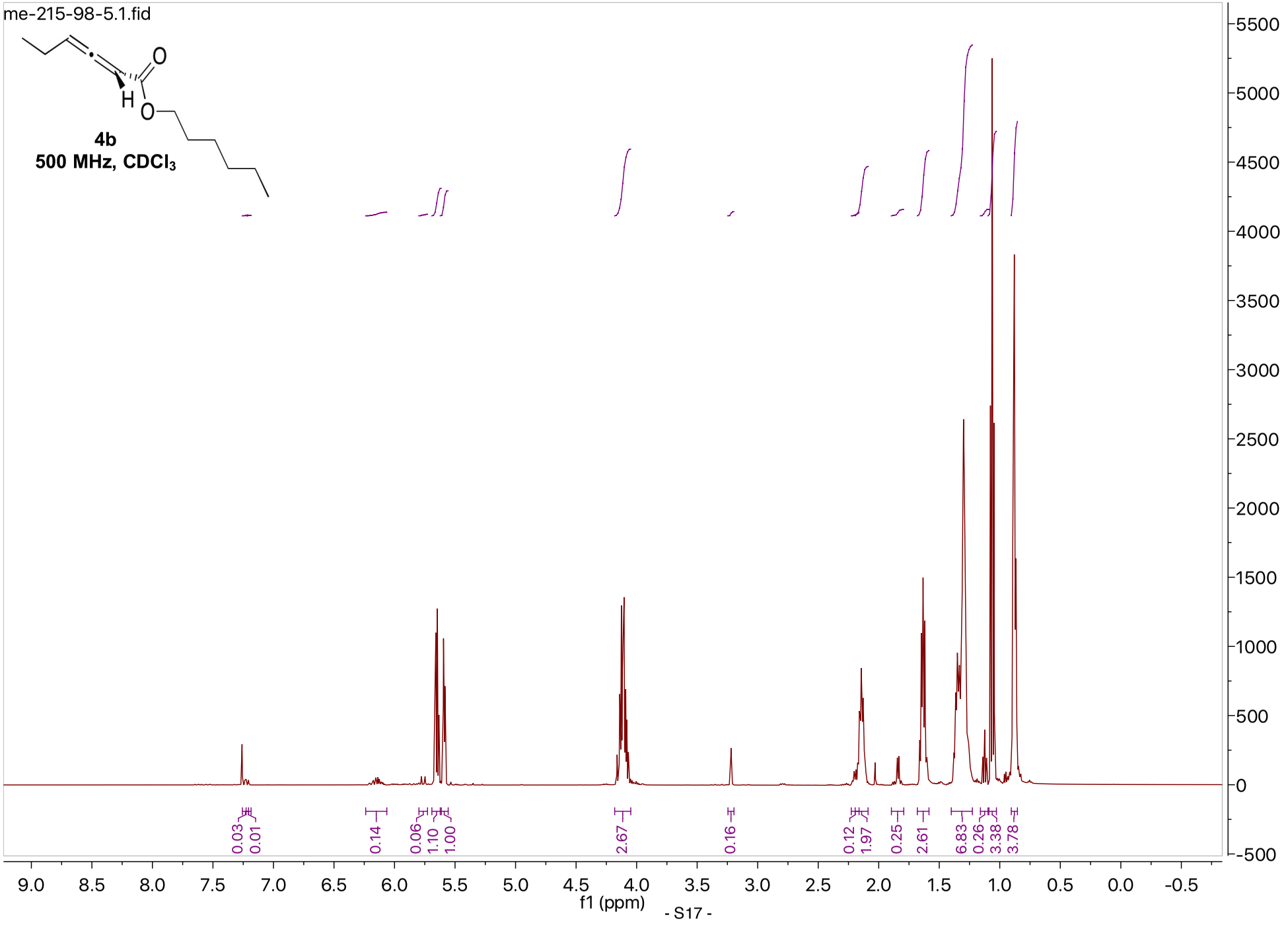
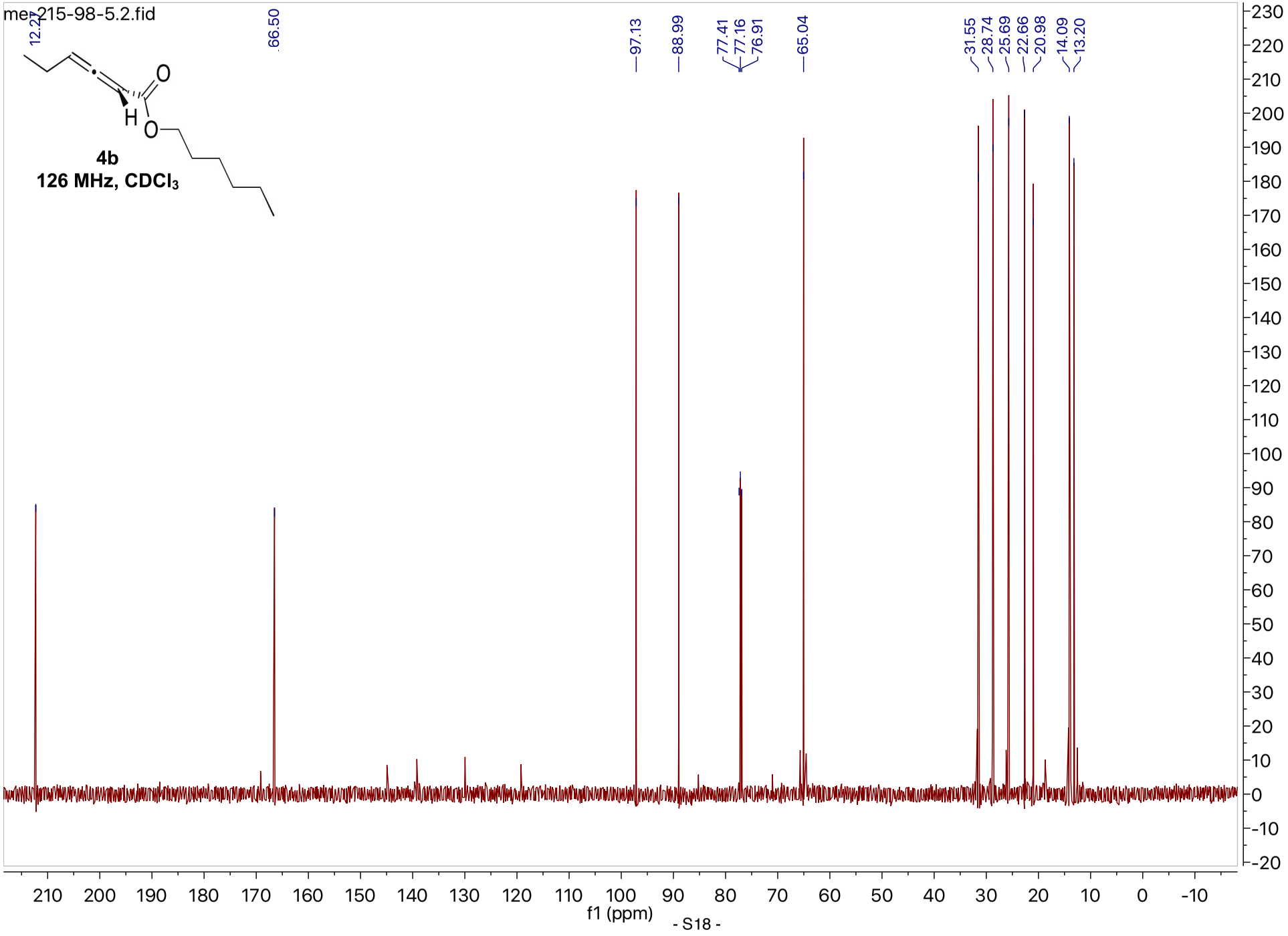
4) Lang, R. W.; Hansen, H. –J. *Org. Synth.* **1984**, *62,* 202.

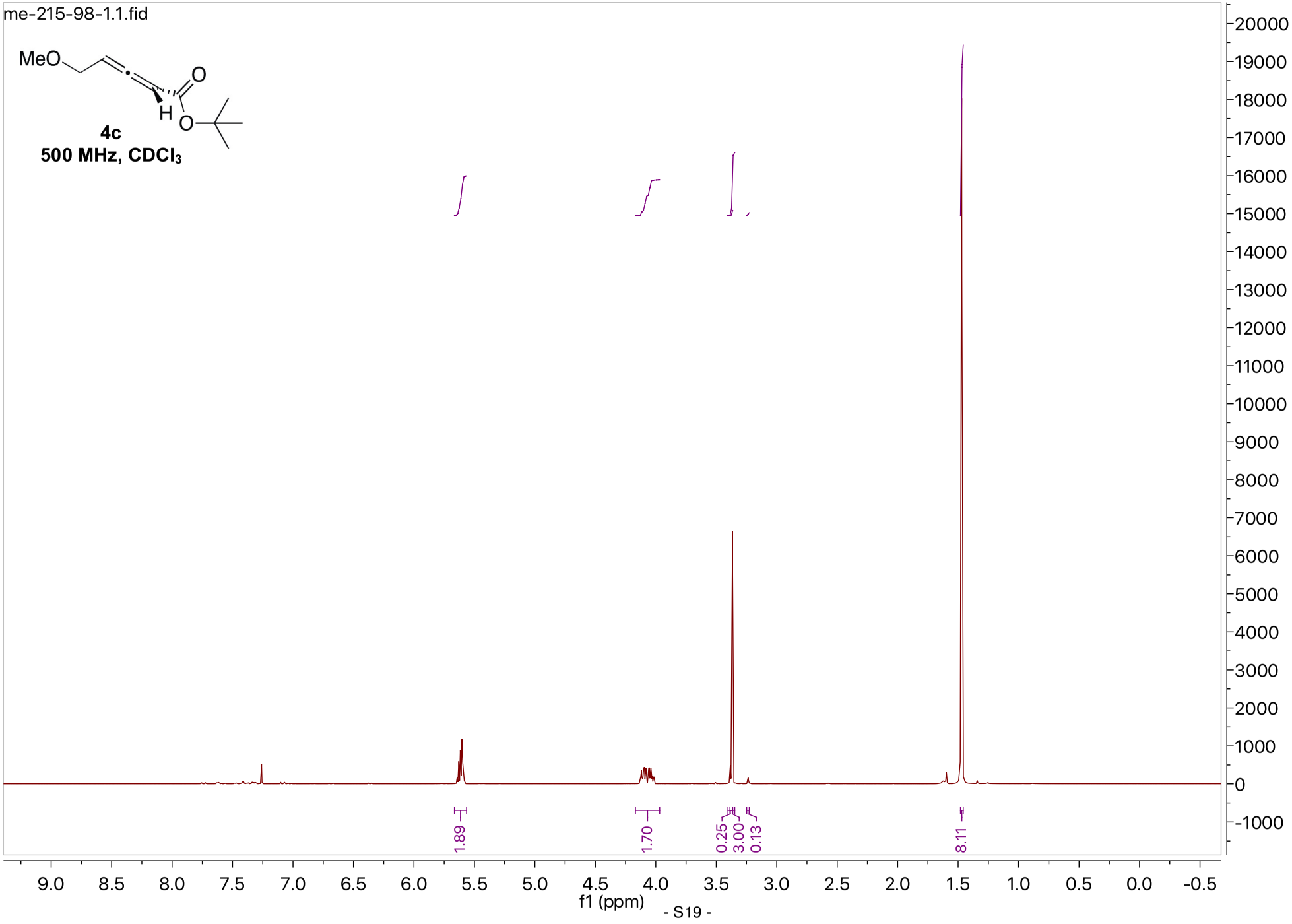
5) Rout, L.; Harned, A. M. *Chem. Eur. J.* **2009**, *15,* 12926.

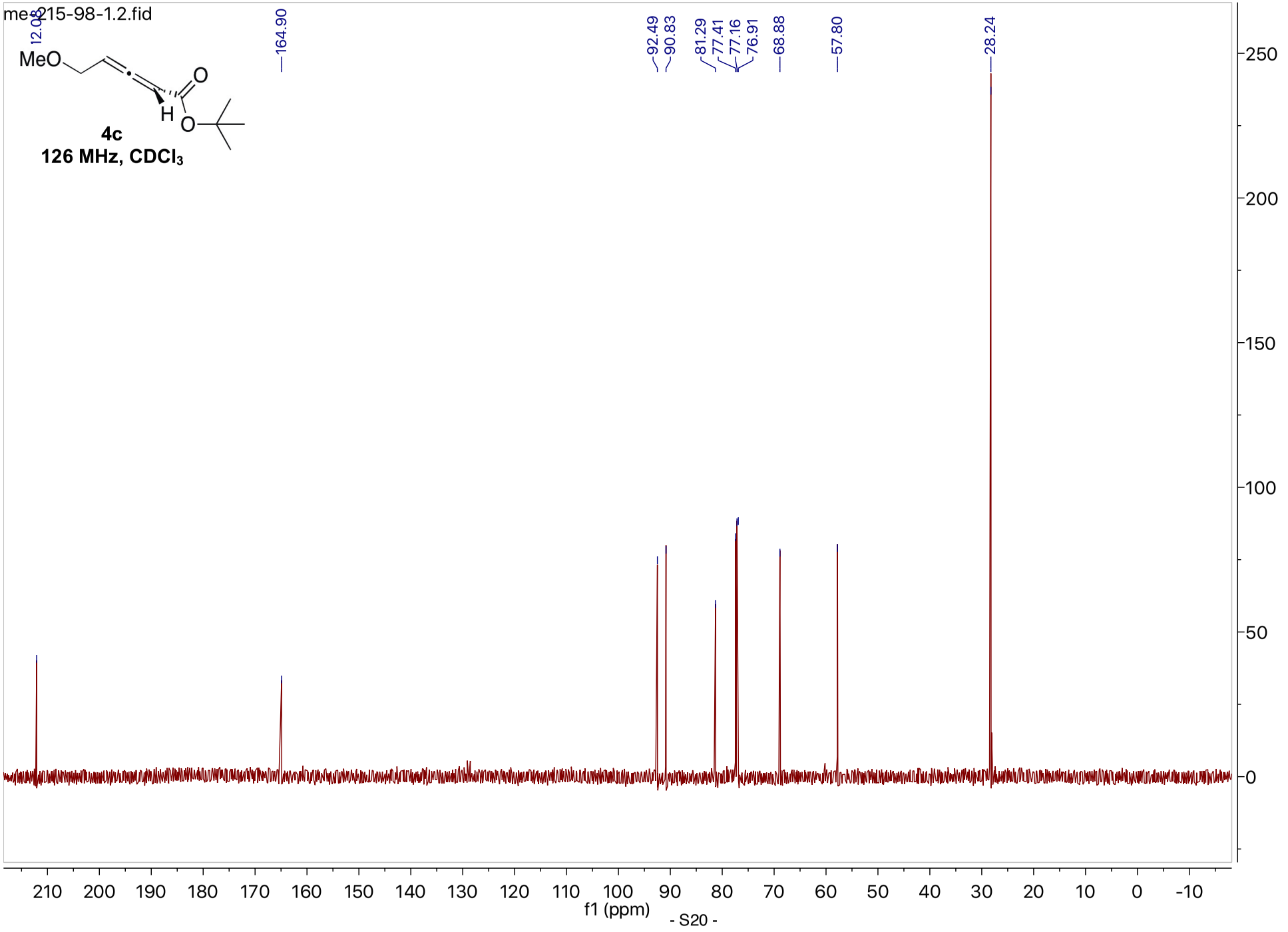

me-208-152.1.fid
O
H
O
4a
500 MHz, CDCl3
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.70
2.07
0.20
0.80
0.26
2.12
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

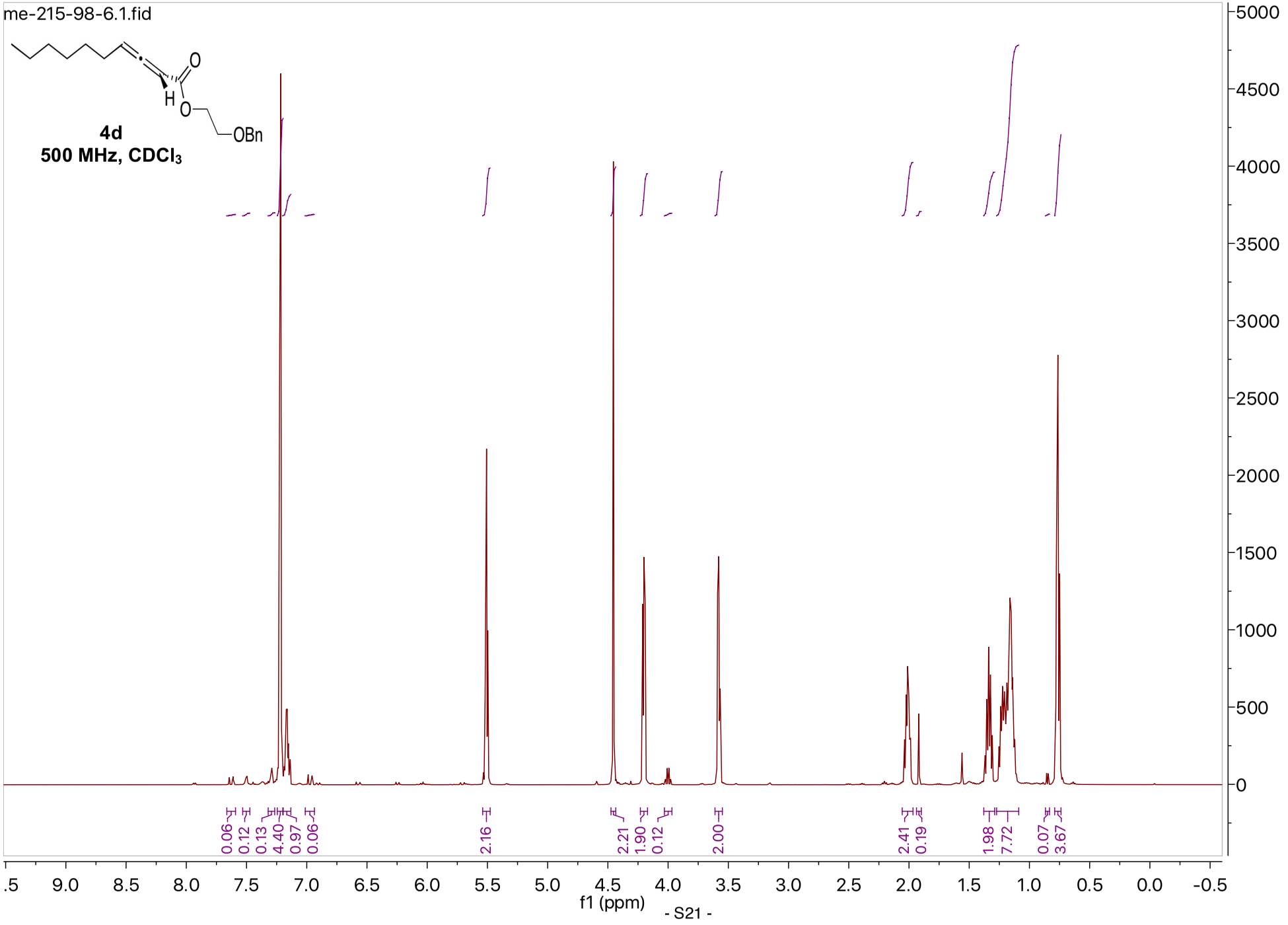

me-208-152.2.fid
213.15
166.46
90.26
87.80
77.41
77.16
76.91
70.97
27.94
19.19
12.92
O
H
O
4a
126 MHz, CDCl3
f1 (ppm)

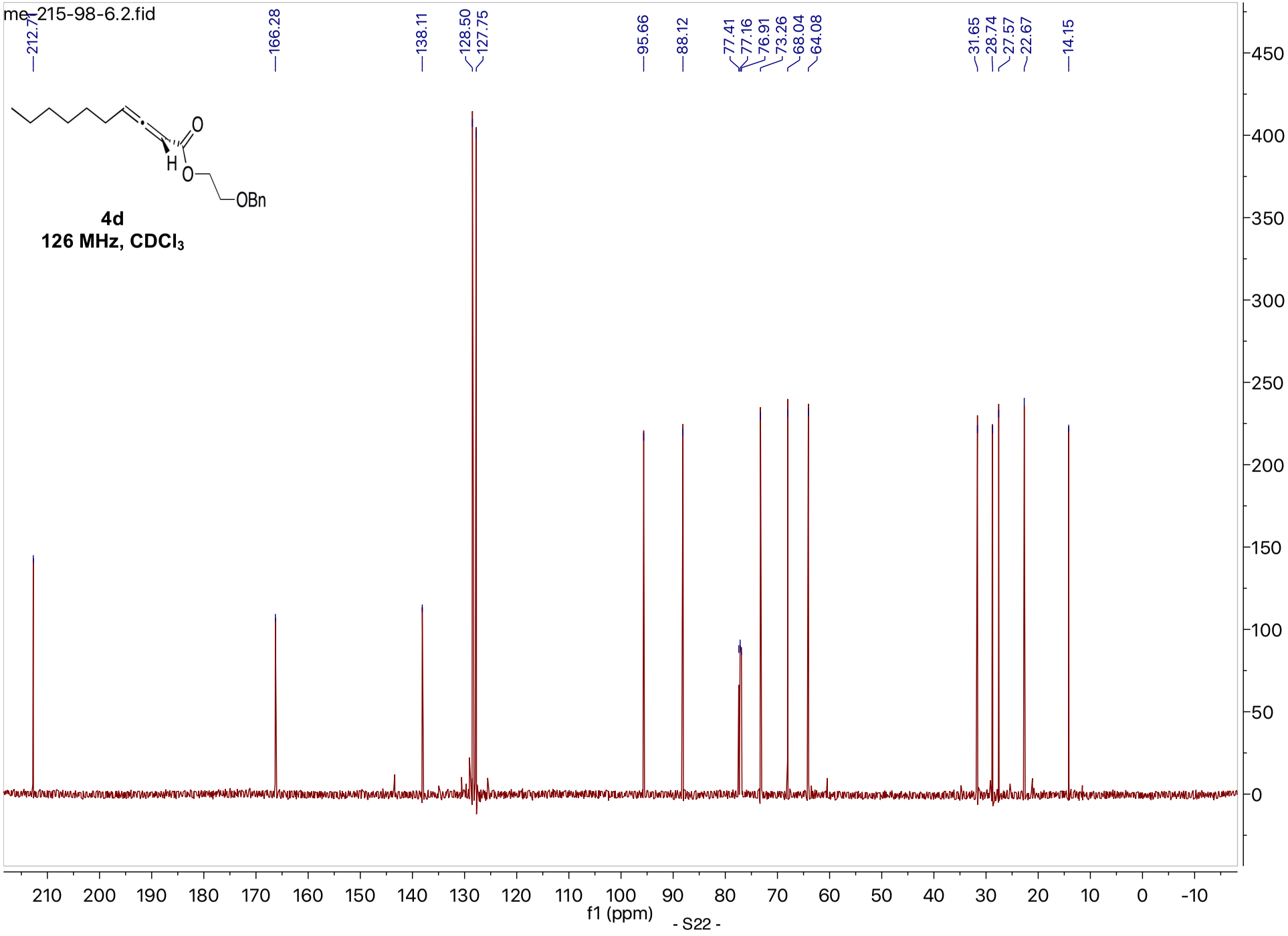

me-215-98-5.1.fid
O
H
O
4b
500 MHz, CDCl3
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0.03
0.01
0.14
0.06
1.10
1.00
2.67
0.16
0.12
1.97
0.25
2.61
6.83
0.26
3.38
3.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


mer-215-98-5.2.fid
12.22
66.50
97.13
88.99
77.41
77.16
76.91
65.04
31.55
28.74
25.69
22.66
20.98
14.09
13.20
O
H
O
4b
126 MHz, CDCl3
f1 (ppm)

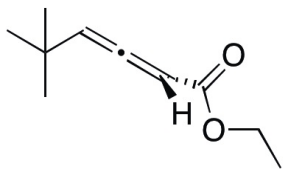

me-215-98-1.1.fid
MeO
O
H
O
4c
500 MHz, CDCl3
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.89
1.70
0.25
3.00
0.13
8.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


mes-215-98-1.2.fid
12.02
MeO
O
H
O
4c
126 MHz, CDCl3
164.90
92.49
90.83
81.29
77.41
77.16
76.91
68.88
57.80
28.24
250
200
150
100
50
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)


me-215-98-6.1.fid
4d
500 MHz, CDCl3
O
H
O
OBn
0.06
0.12
0.13
4.40
0.97
0.06
2.16
2.21
1.90
0.12
2.00
2.41
0.19
1.98
7.72
0.07
3.67
f1 (ppm)

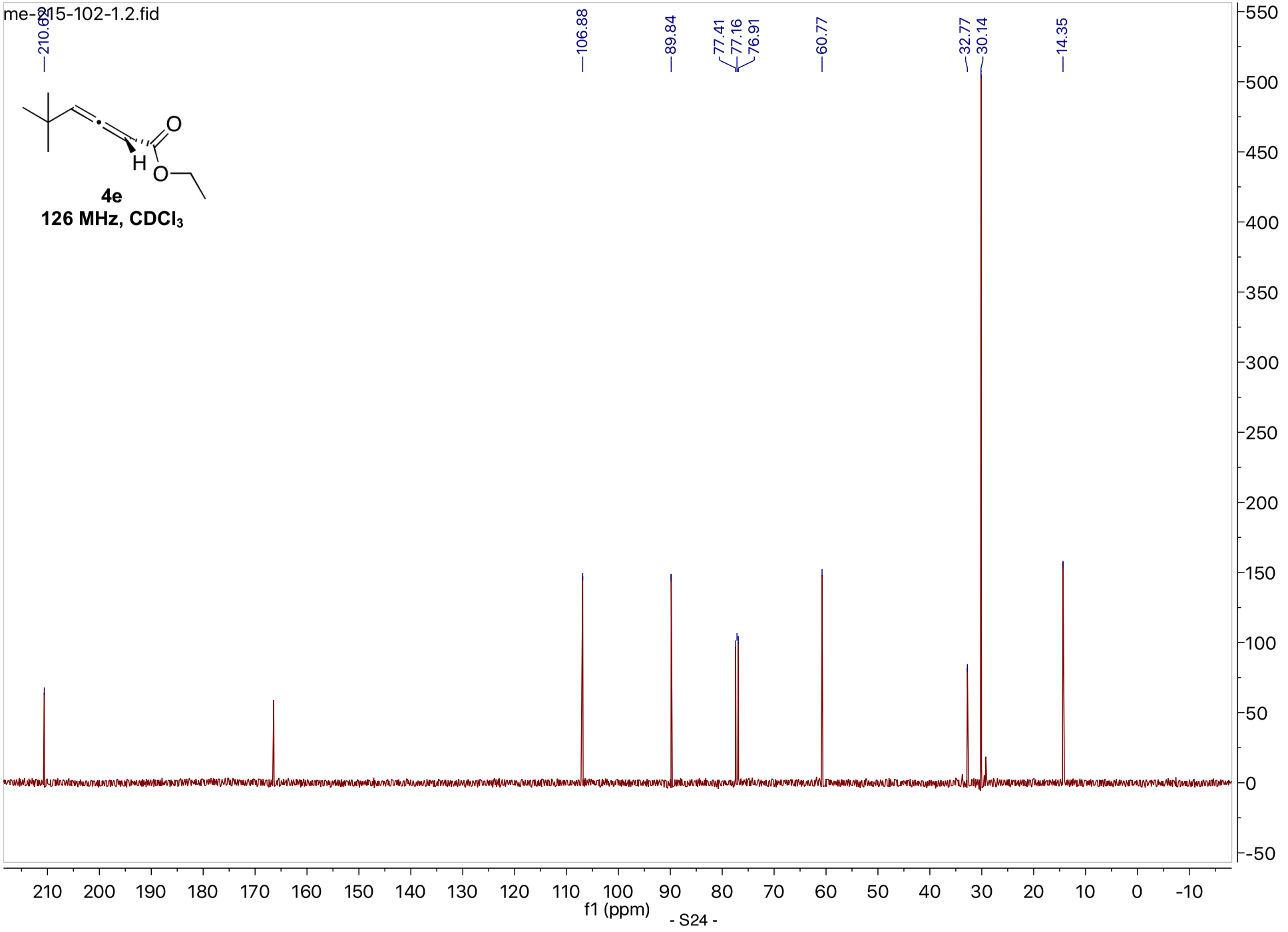

me-215-98-6.2.fid
212.71
166.28
138.11
128.50
127.75
95.66
88.12
77.41
77.16
76.91
73.26
68.04
64.08
31.65
28.74
27.57
22.67
14.15
O
H
O
OBn
4d
126 MHz, CDCl3
450
400
350
300
250
200
150
100
50
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

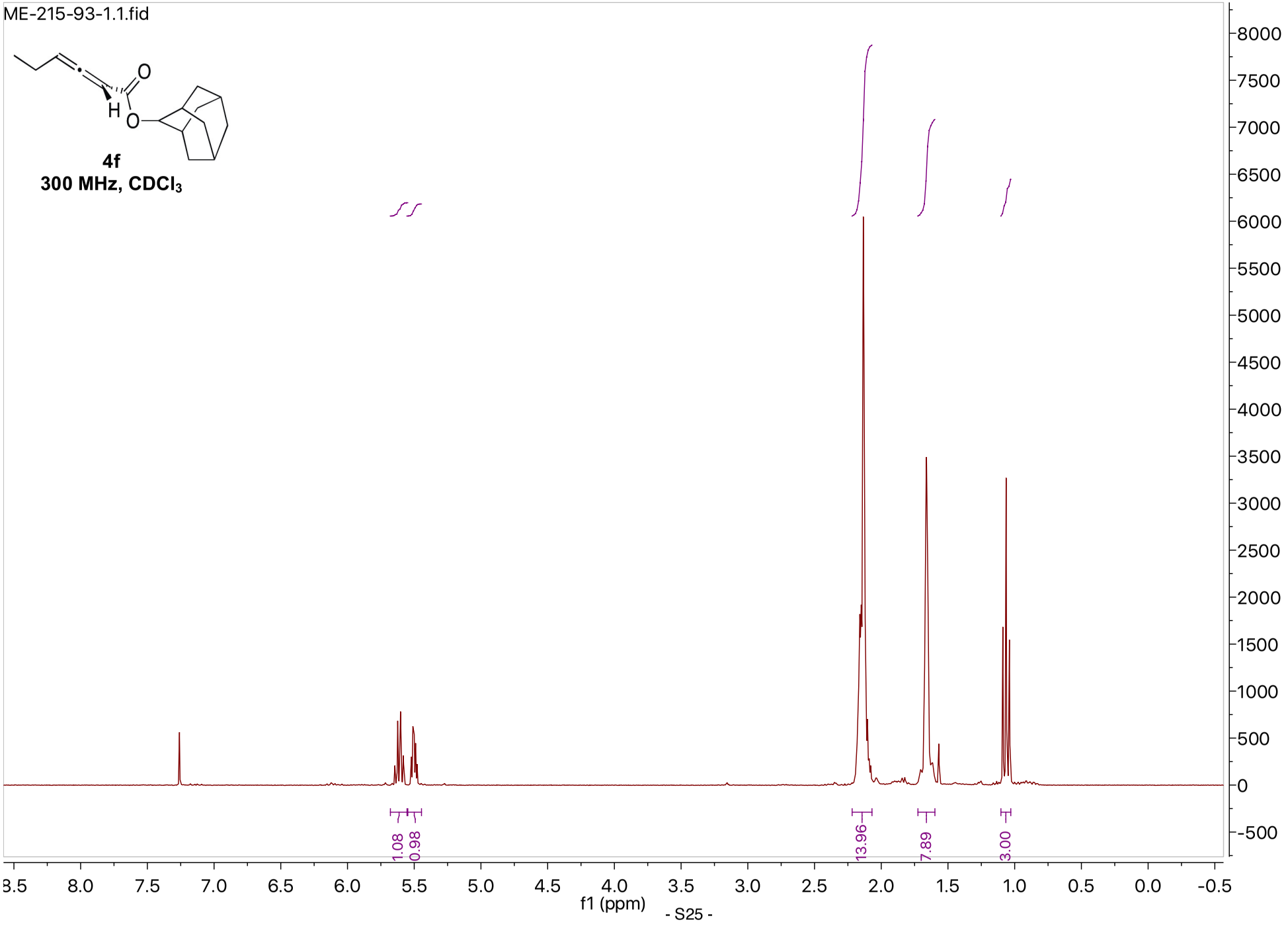
me-208-154

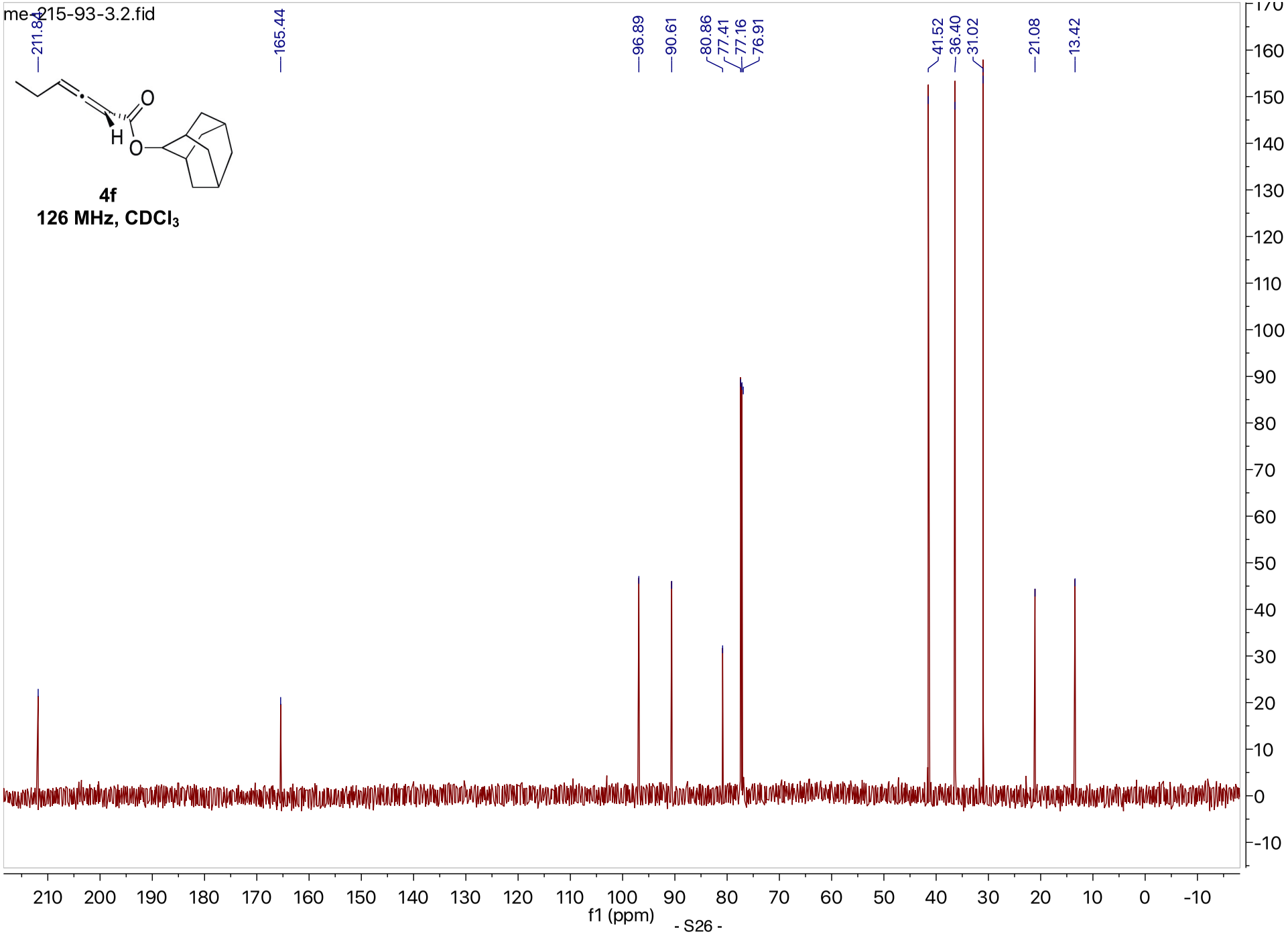


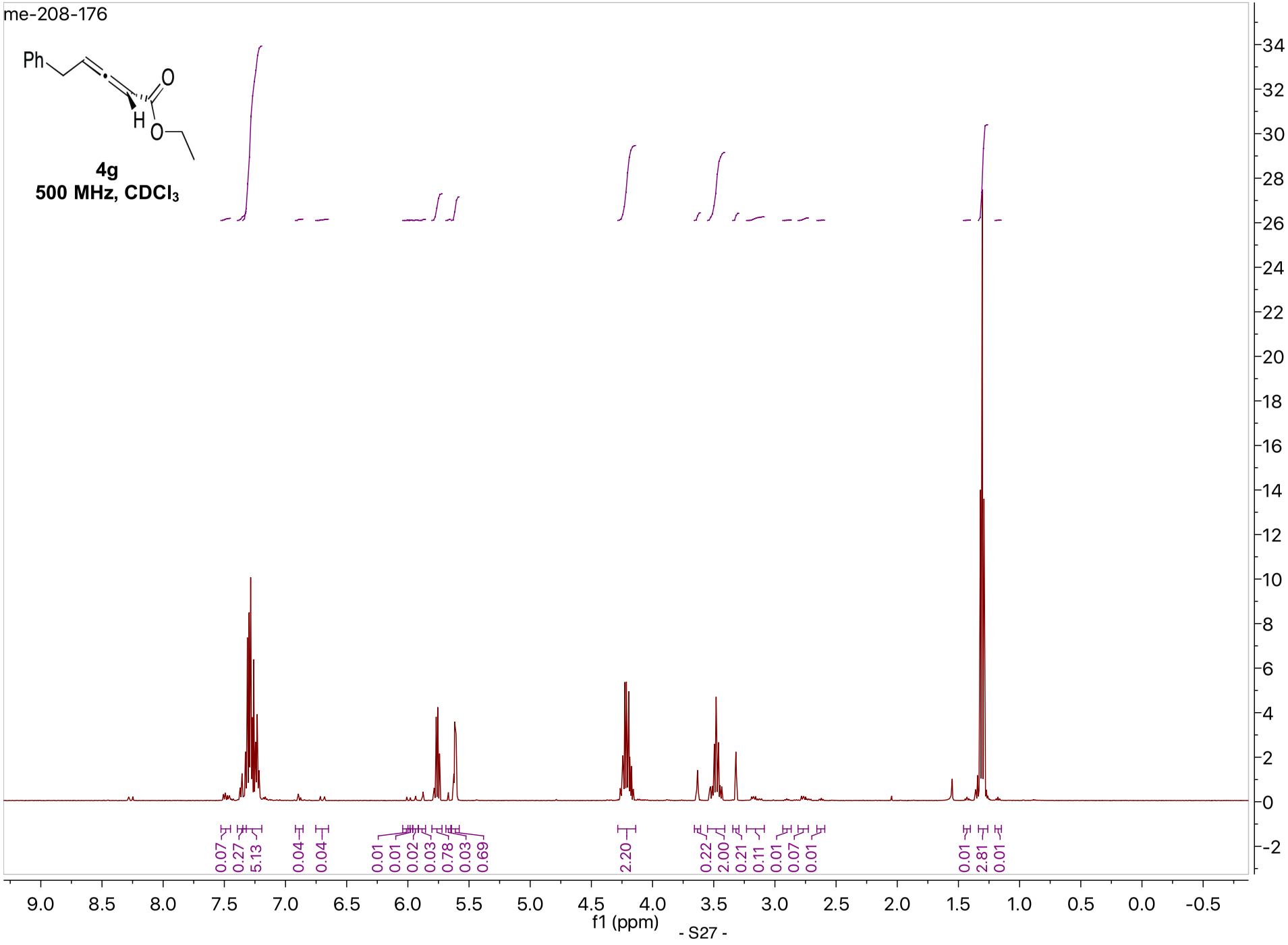
4e

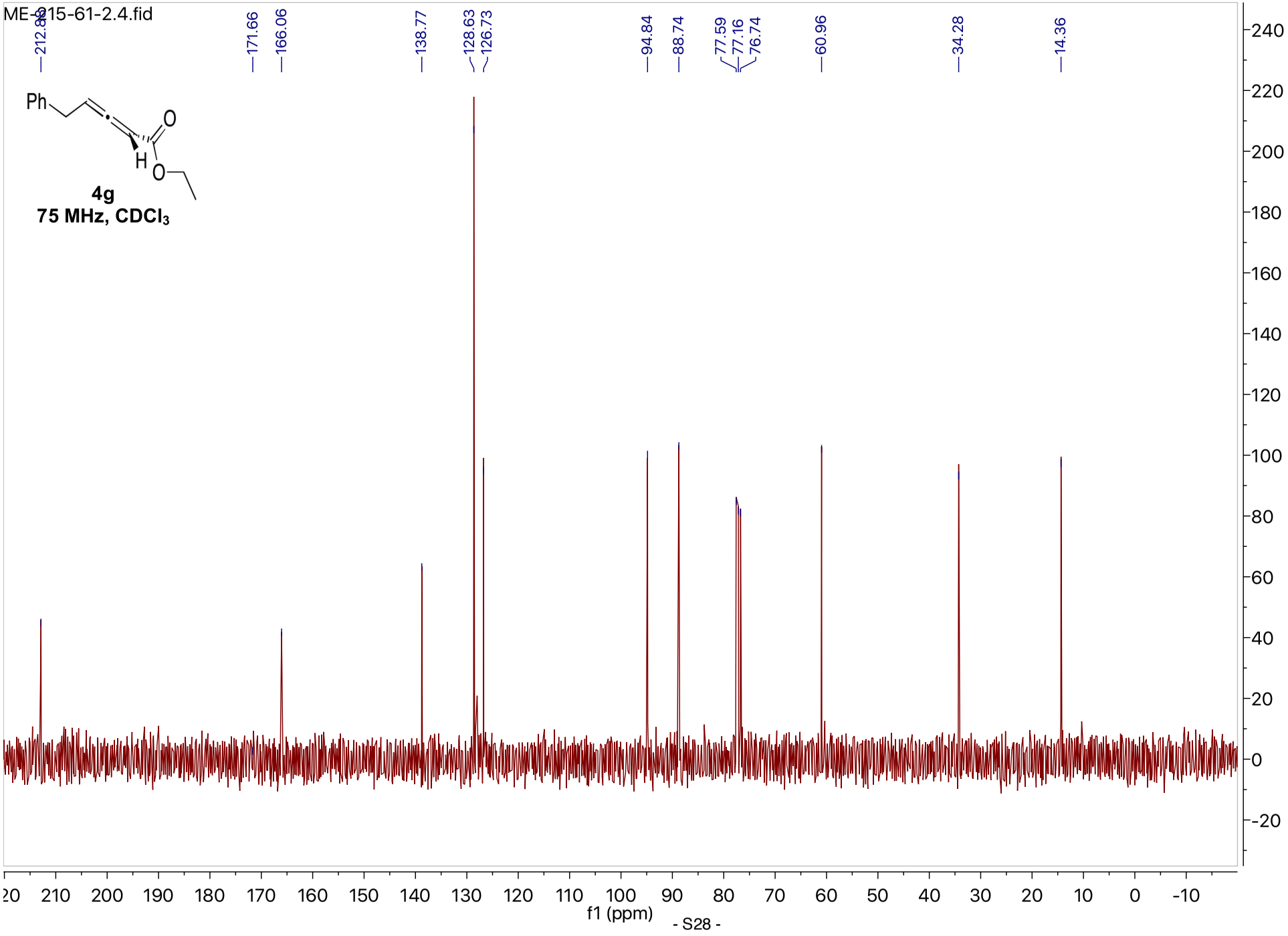
500 MHz, $CDCl_3$


me-215-102-1.2.fid
210.61
106.88
89.84
77.41
77.16
76.91
60.77
32.77
30.14
14.35
O
H
O
4e
126 MHz, CDCl3
550
500
450
400
350
300
250
200
150
100
50
0
-50
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)

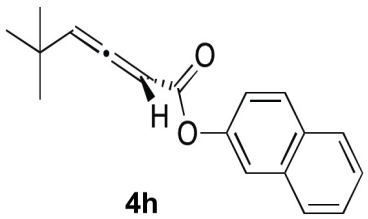

ME-215-93-1.1.fid
O
H
O
4f
300 MHz, CDCl3
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1.08
0.98
13.96
7.89
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


me-215-93-3.2.fid
211.84
165.44
96.89
90.61
80.86
77.41
77.16
76.91
41.52
36.40
31.02
21.08
13.42
O
H
O
4f
126 MHz, CDCl3
f1 (ppm)

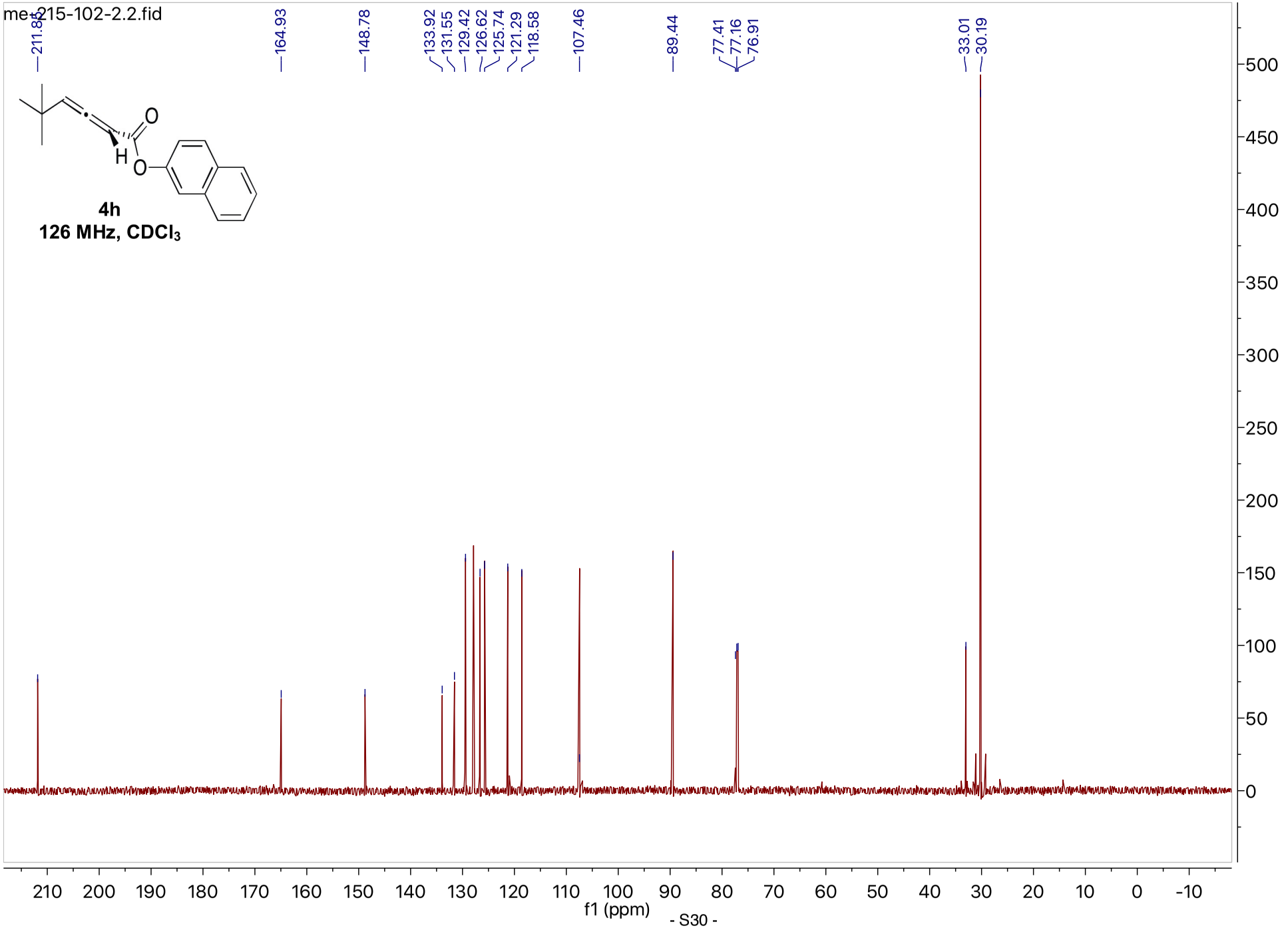

me-208-176
Ph
O
H
O
4g
500 MHz, CDCl3
0.07
0.27
5.13
0.04
0.04
0.01
0.01
0.02
0.03
0.78
0.03
0.69
2.20
0.22
2.00
0.21
0.11
0.01
0.07
0.01
0.01
2.81
0.01
f1 (ppm)

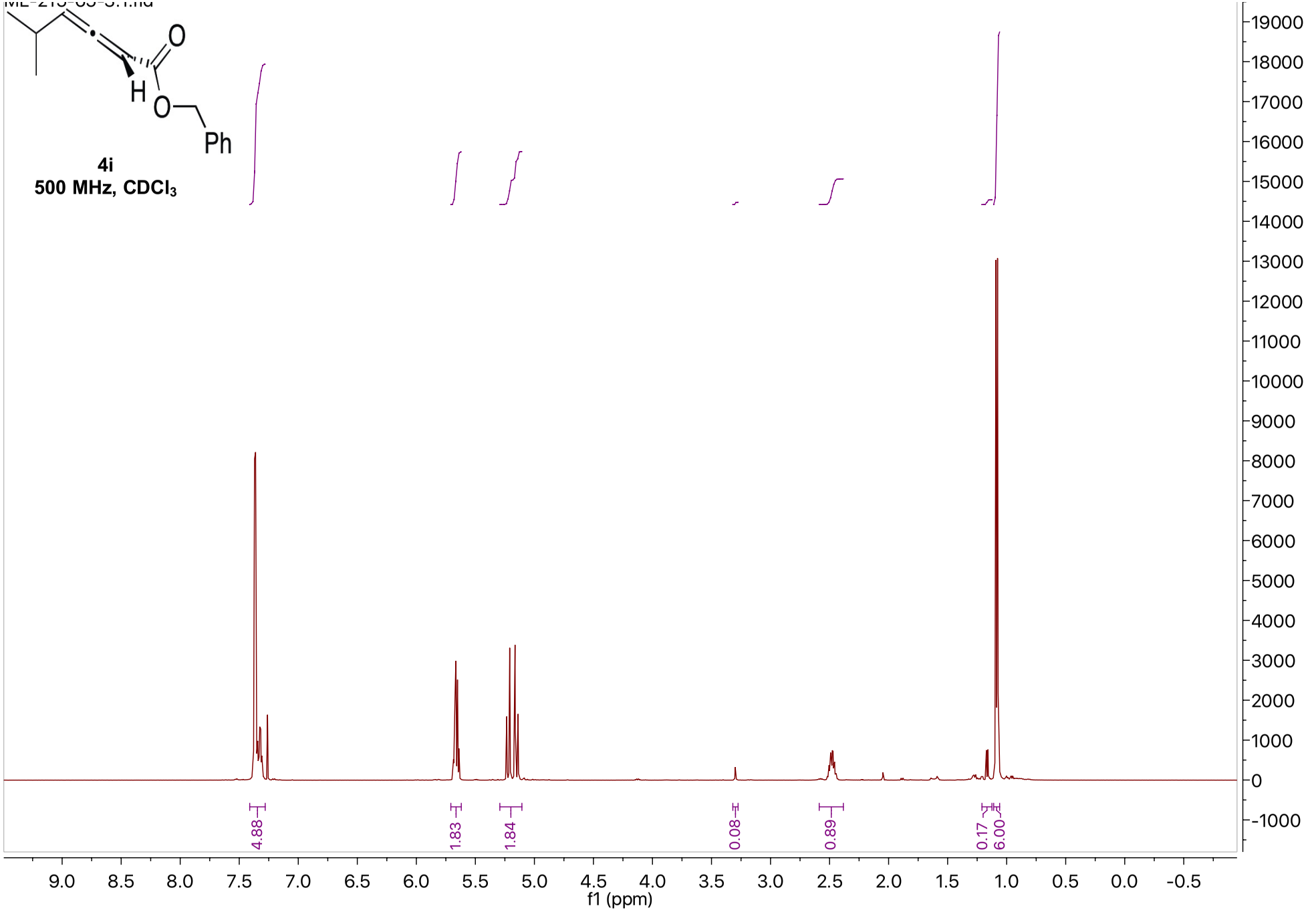

ME-215-61-2.4.fid
212.86
171.66
166.06
138.77
128.63
126.73
94.84
88.74
77.59
77.16
76.74
60.96
34.28
14.36
Ph
O
H
O
4g
75 MHz, CDCl3
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

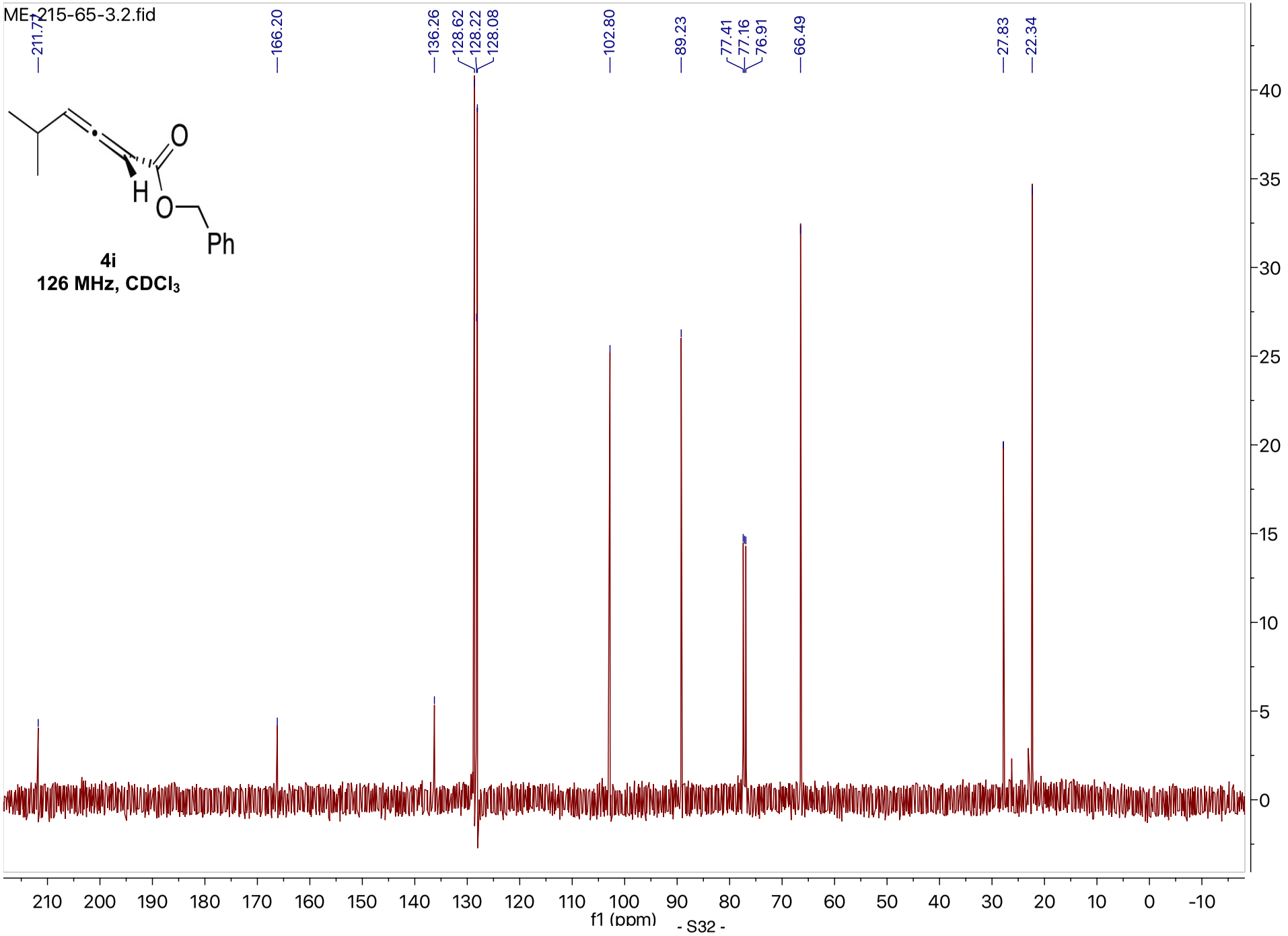
me-215-102-2.1.fid

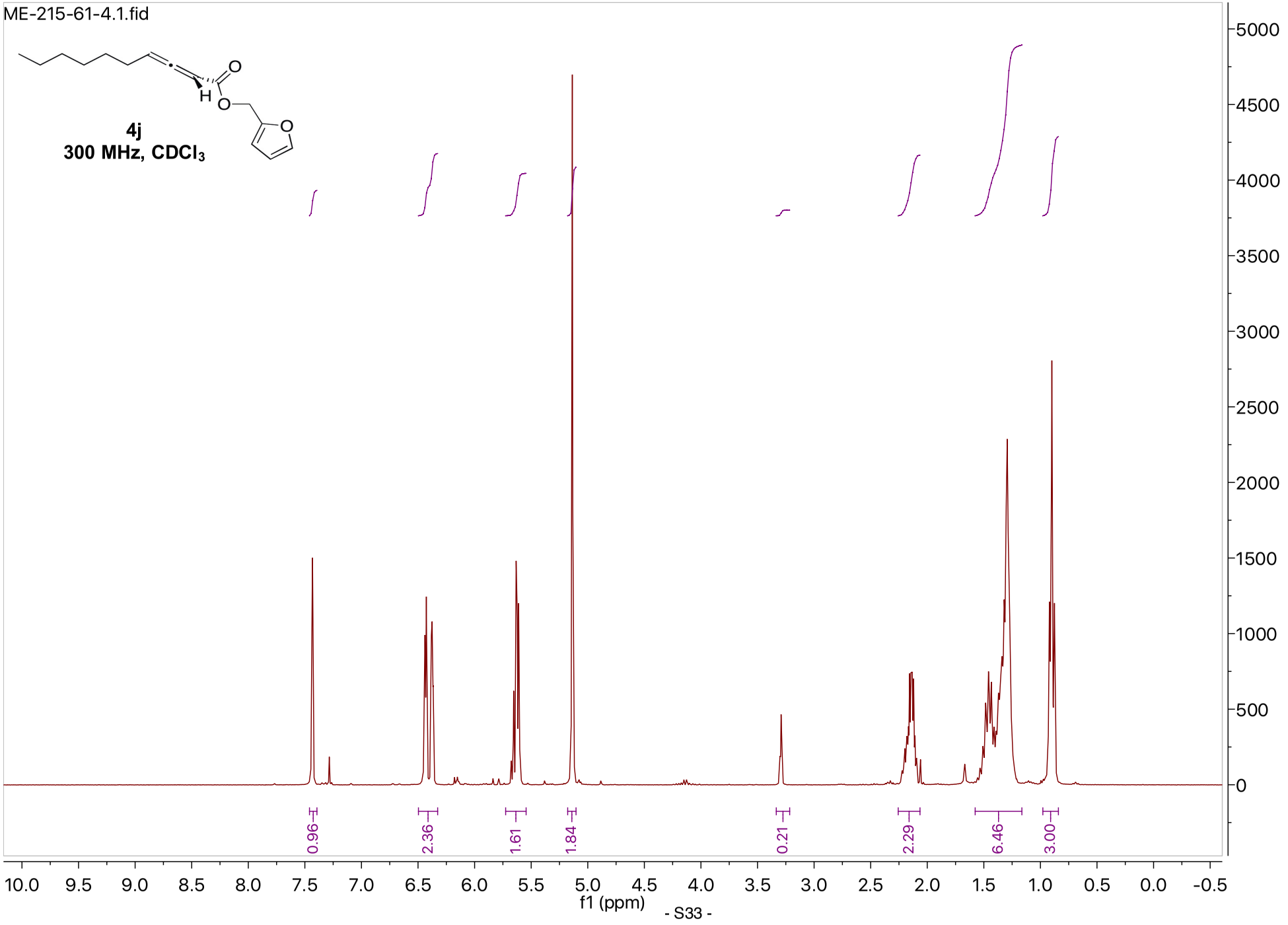


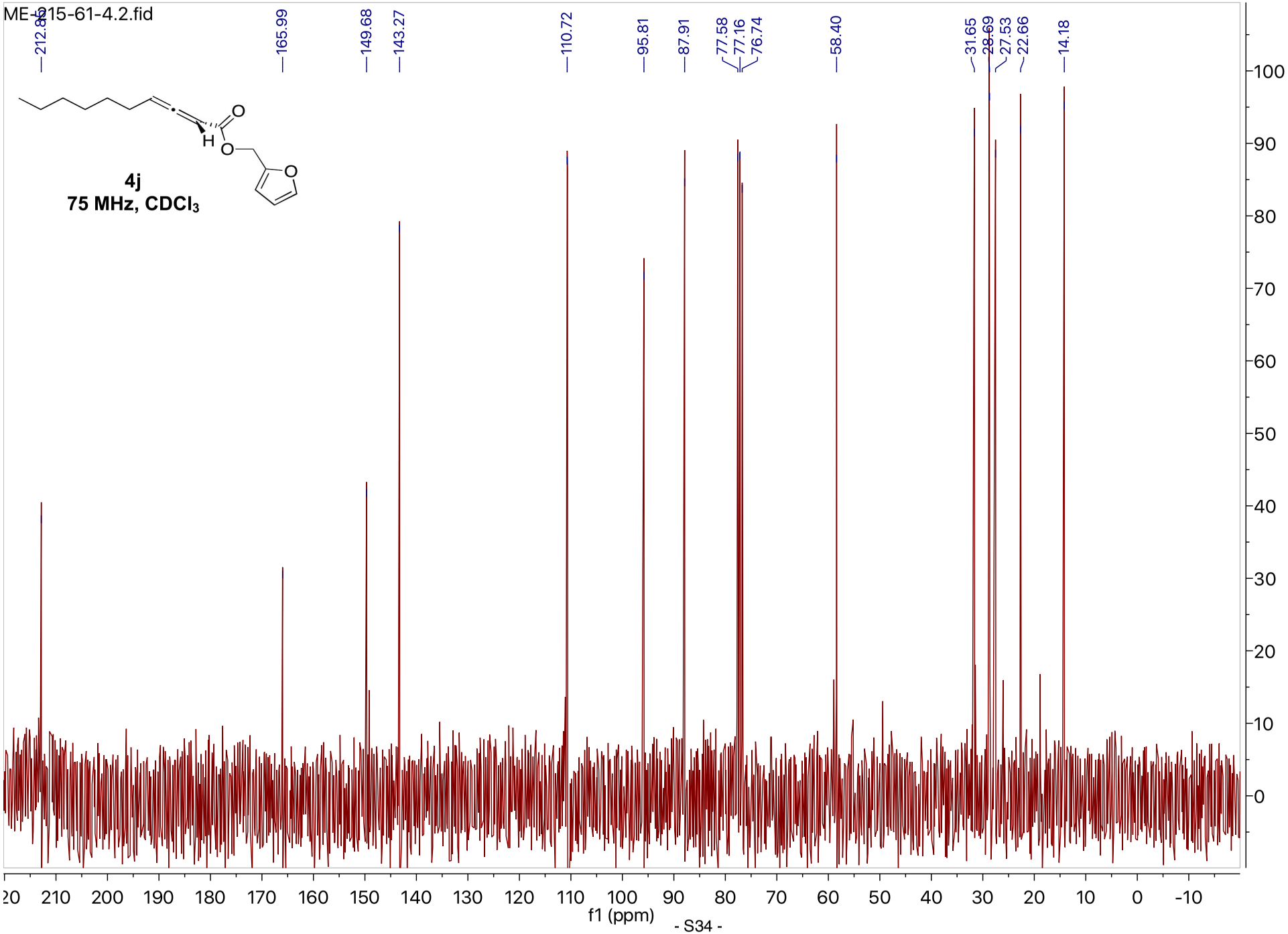
4h
500 MHz, $CDCl_3$

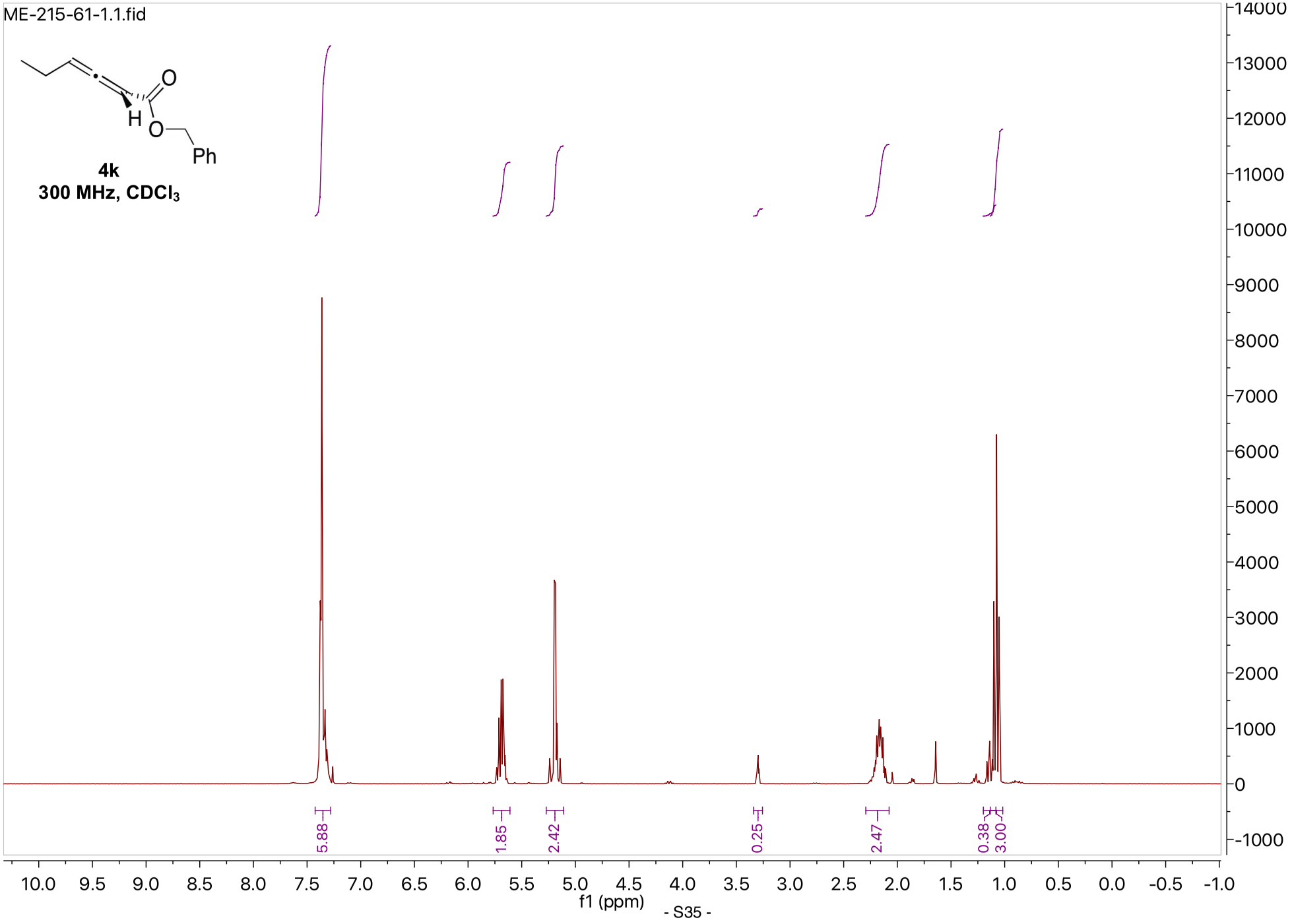

me-215-102-2.2.fid
211.85
164.93
148.78
133.92
131.55
129.42
126.62
125.74
121.29
118.58
107.46
89.44
77.41
77.16
76.91
33.01
30.19
O
H
O
4h
126 MHz, CDCl3
500
450
400
350
300
250
200
150
100
50
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

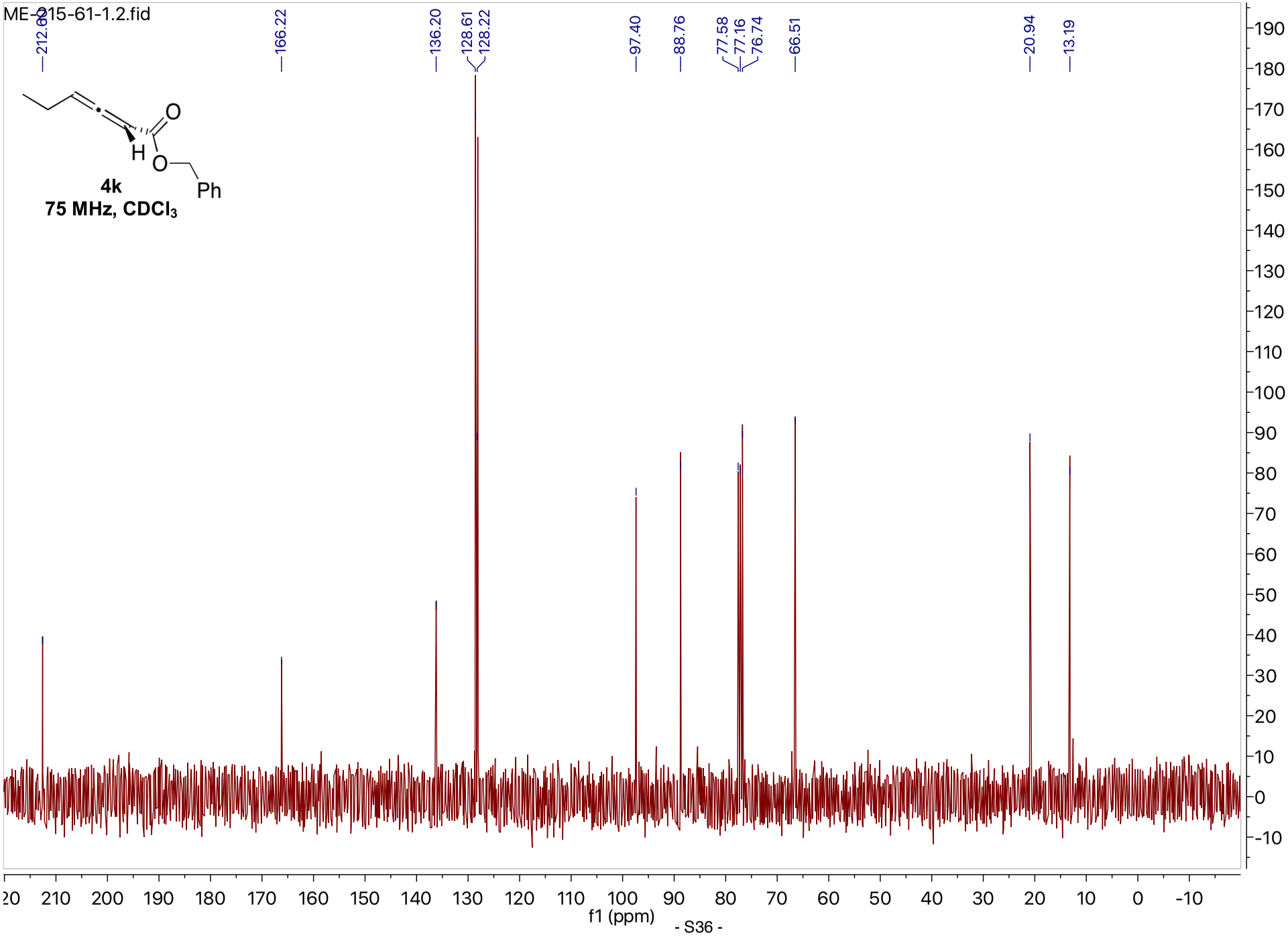

O
H
O
Ph
4i
500 MHz, CDCl3
4.88
1.83
1.84
0.08
0.89
0.17
6.00
f1 (ppm)

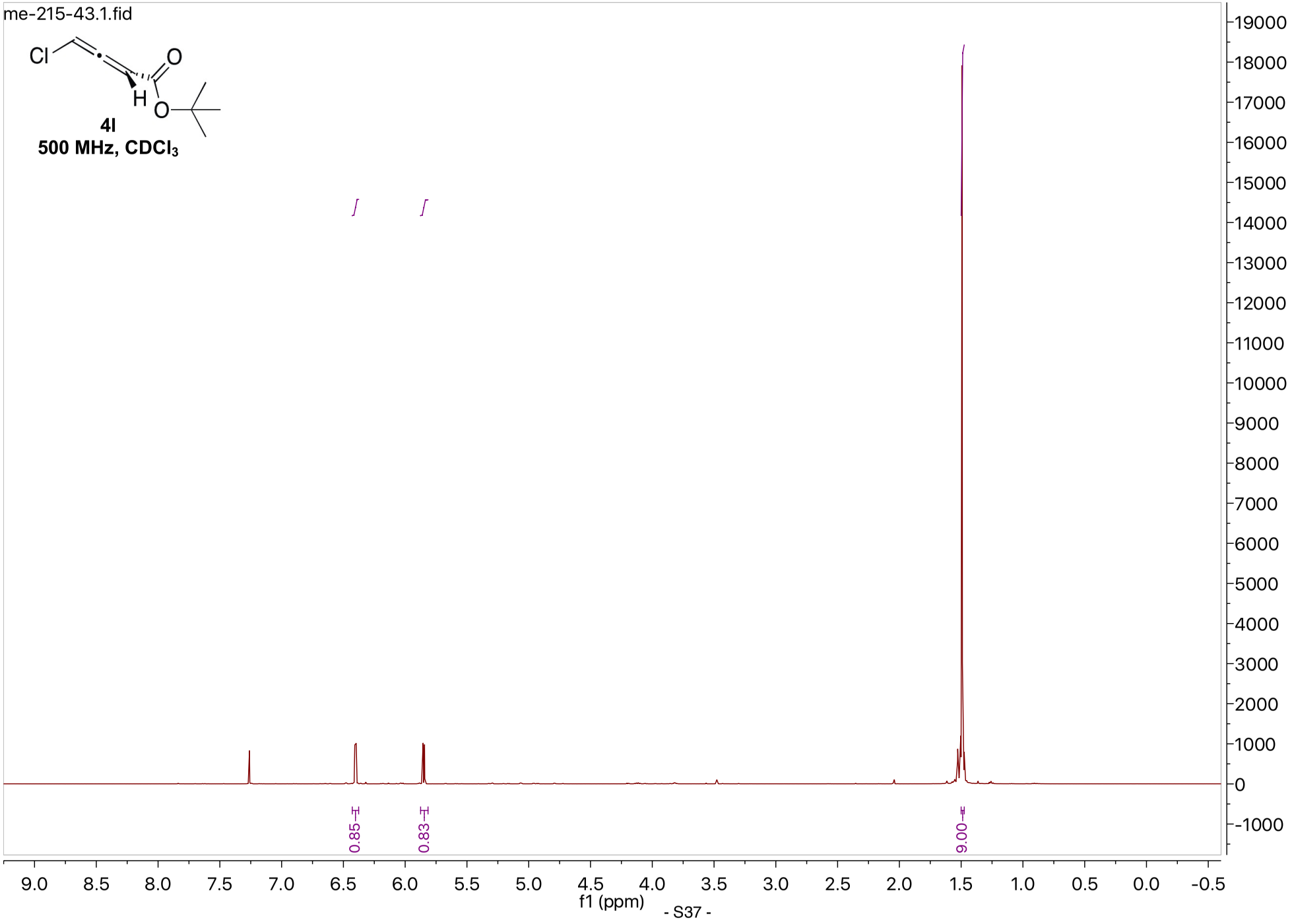

ME-215-65-3.2.fid
211.77
166.20
136.26
128.62
128.22
128.08
102.80
89.23
77.41
77.16
76.91
66.49
27.83
22.34
O
H
O
Ph
4i
126 MHz, CDCl3
40
35
30
25
20
15
10
5
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

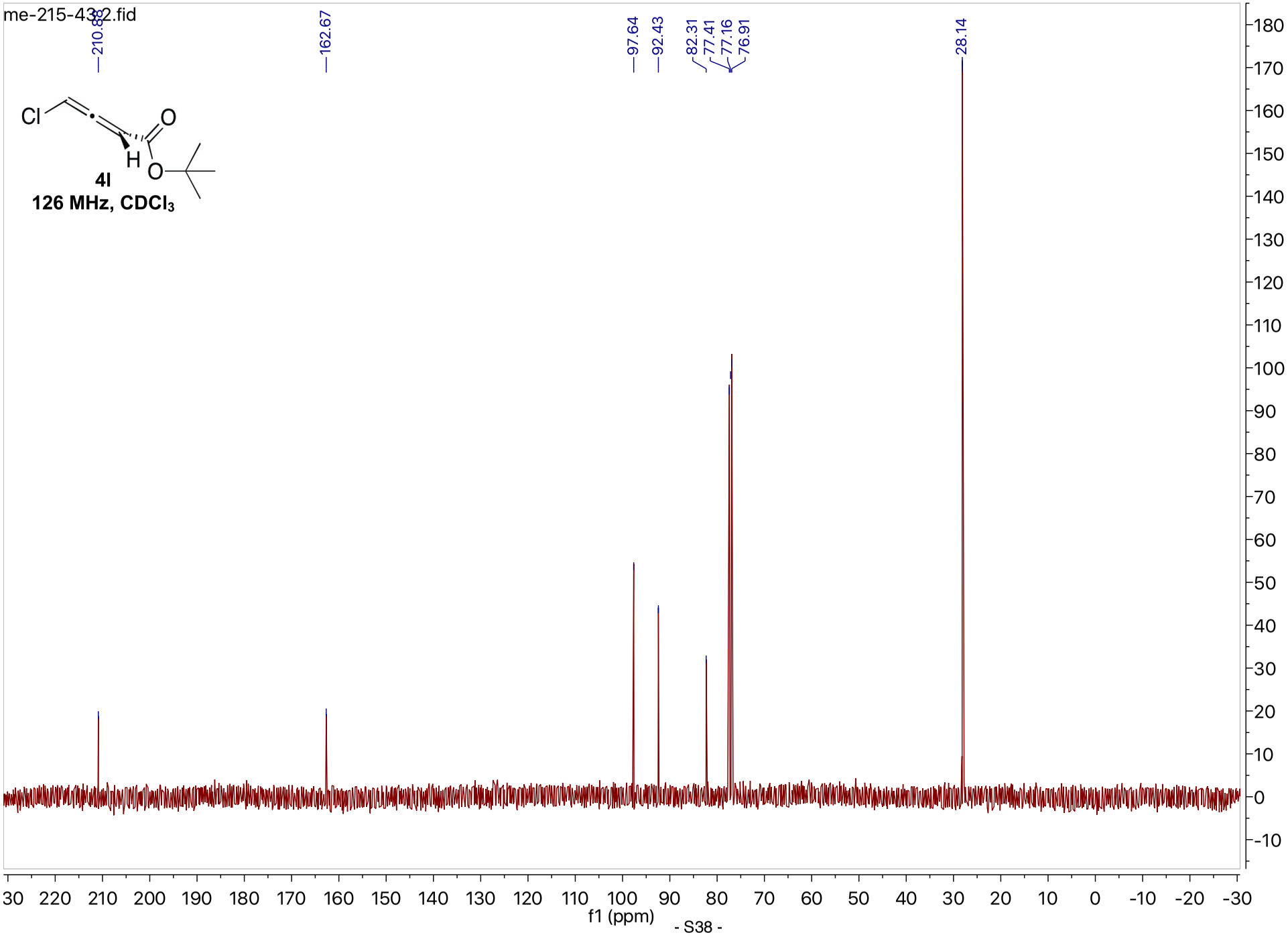

ME-215-61-4.1.fid
4j
300 MHz, CDCl3
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0.96
2.36
1.61
1.84
0.21
2.29
6.46
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ME-215-61-4.2.fid
212.85
165.99
149.68
143.27
110.72
95.81
87.91
77.58
77.16
76.74
58.40
31.65
28.69
27.53
22.66
14.18
4j
75 MHz, CDCl3
f1 (ppm)


ME-215-61-1.1.fid
O
H
O
Ph
4k
300 MHz, CDCl3
5.88
1.85
2.42
0.25
2.47
0.38
3.00
f1 (ppm)


ME-215-61-1.2.fid
212.62
166.22
136.20
128.61
128.22
97.40
88.76
77.58
77.16
76.74
66.51
20.94
13.19
O
H
O
Ph
4k
75 MHz, CDCl3
f1 (ppm)


me-215-43.1.fid
Cl
O
H
O
4l
500 MHz, CDCl3
0.85
0.83
9.00
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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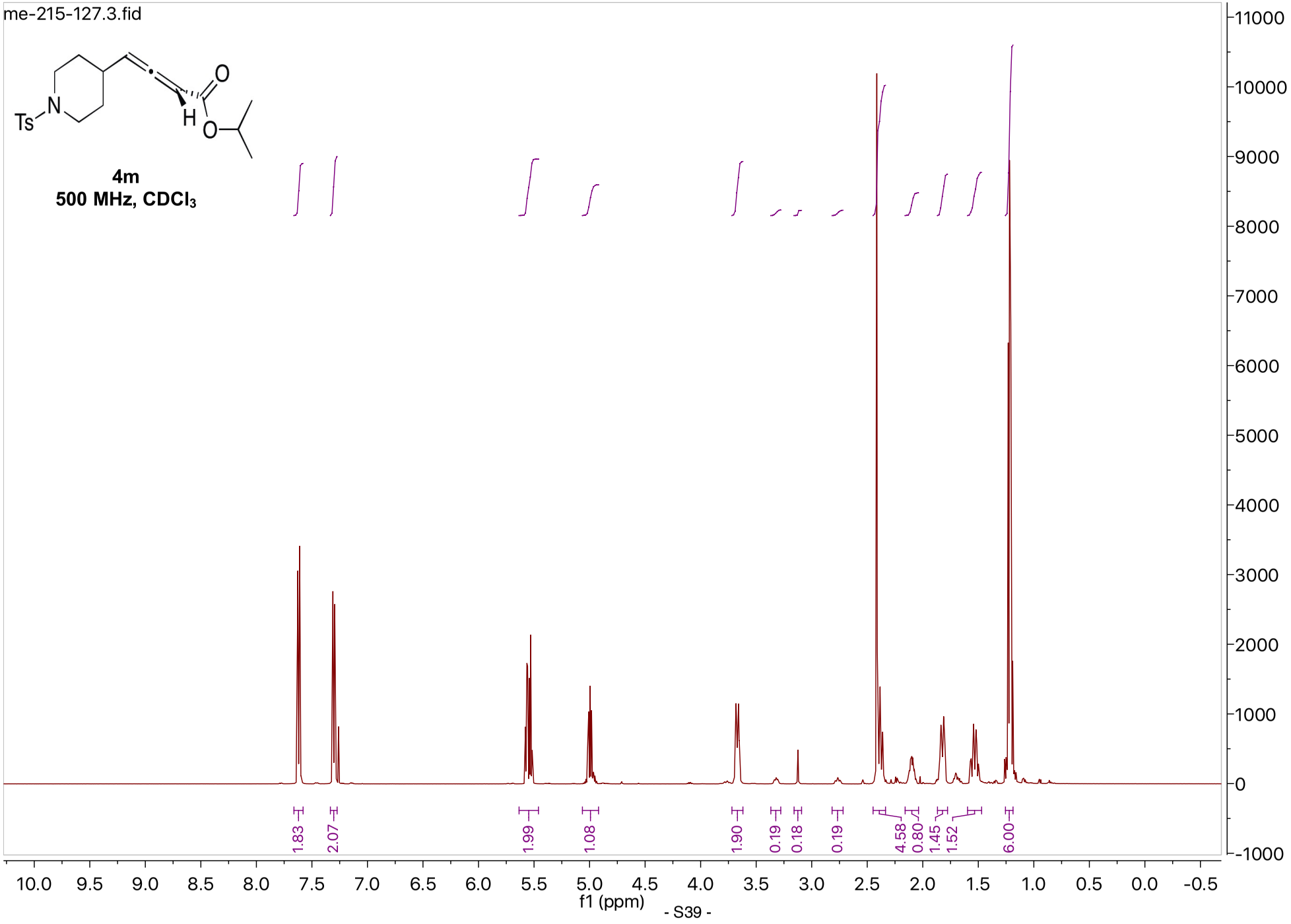
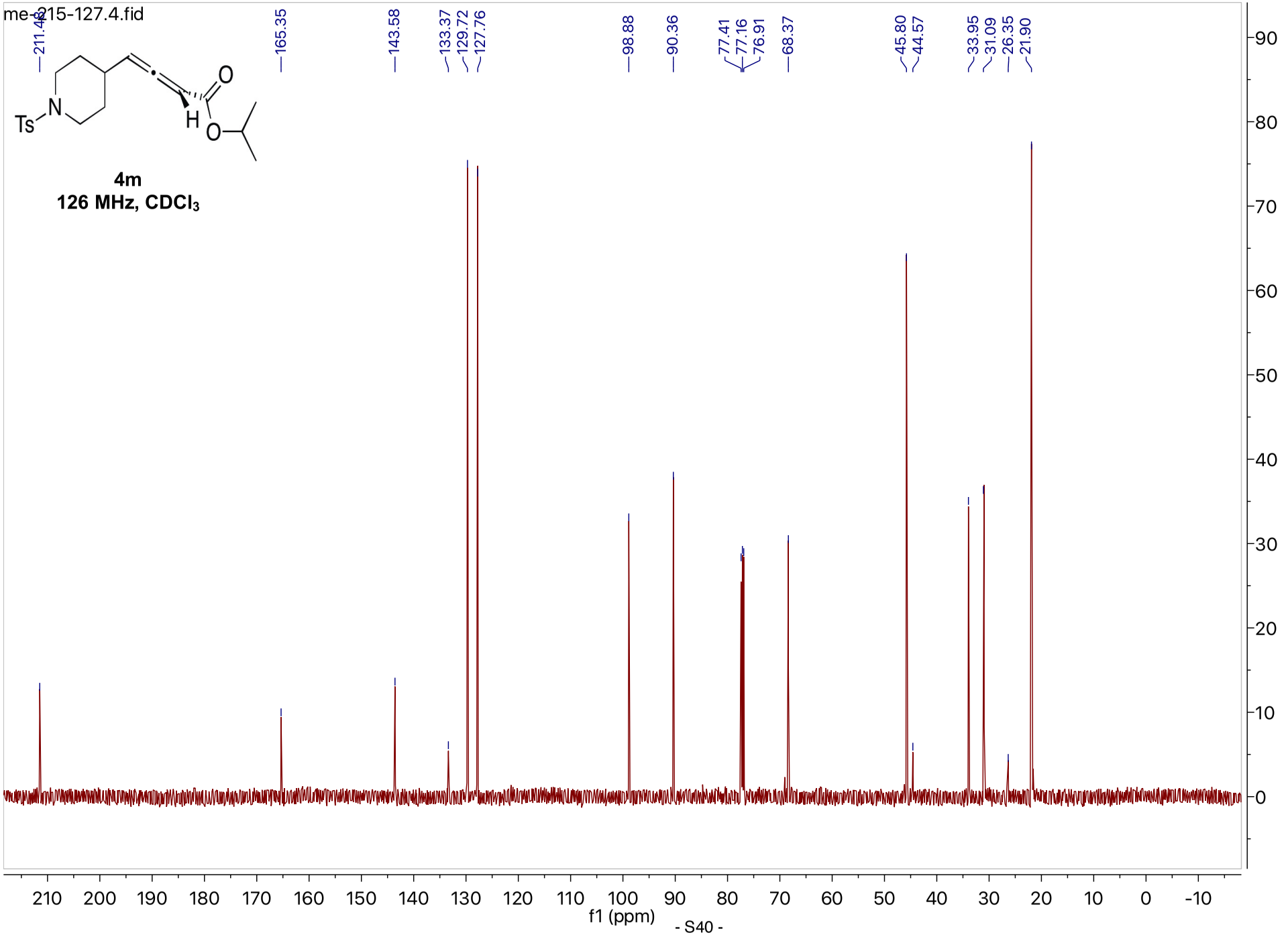
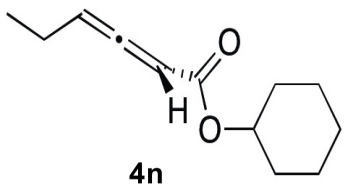
210.82
162.67
97.64
92.43
82.31
77.41
77.16
76.91
28.14
Cl
O
H
O
4l
126 MHz, CDCl3
f1 (ppm)


me-215-127.3.fid
Ts
N
H
O
O
4m
500 MHz, CDCl3
1.83
2.07
1.99
1.08
1.90
0.19
0.18
0.19
4.58
0.80
1.45
1.52
6.00
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

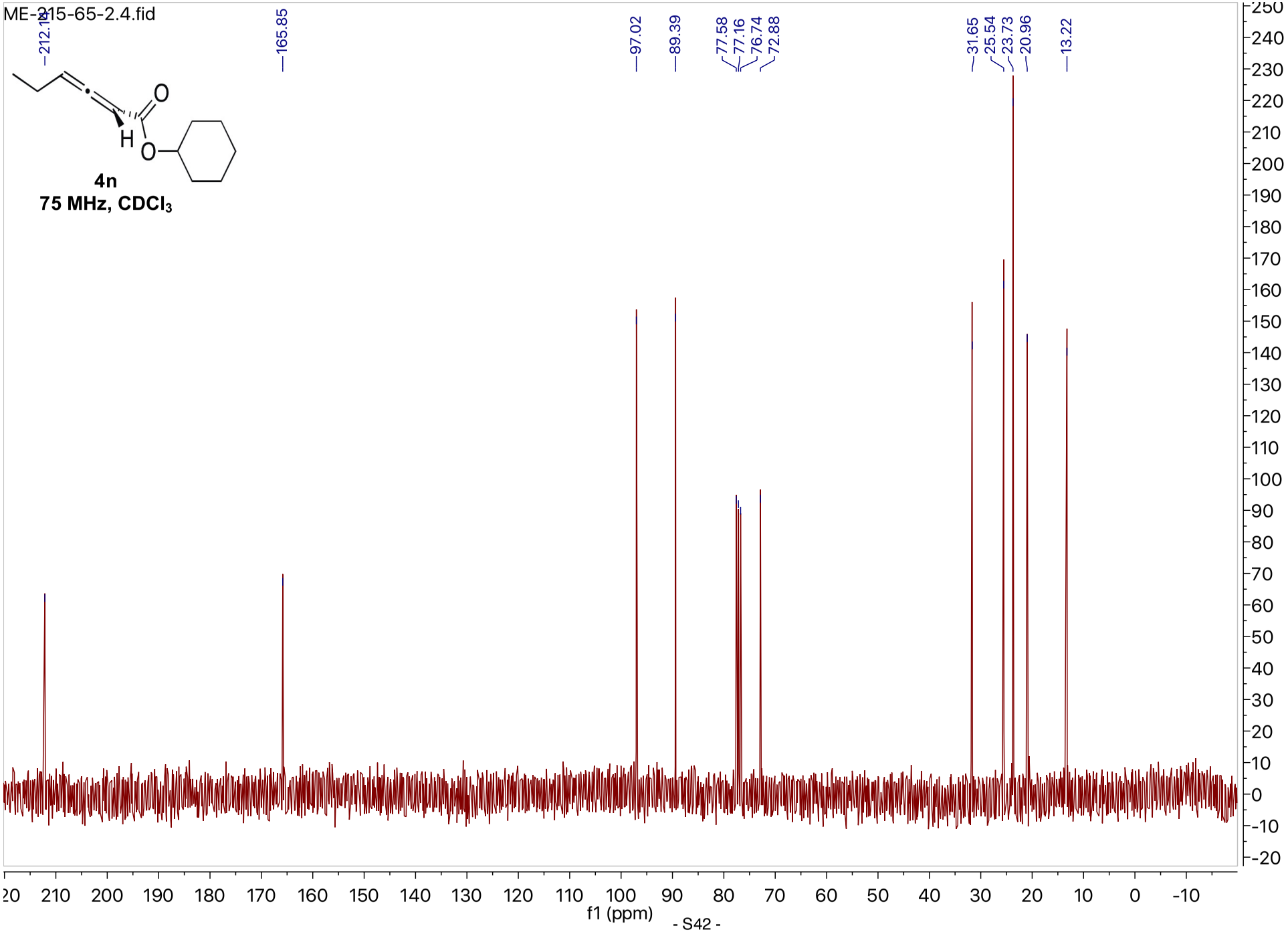

me-215-127.4.fid
211.46
165.35
143.58
133.37
129.72
127.76
98.88
90.36
77.41
77.16
76.91
68.37
45.80
44.57
33.95
31.09
26.35
21.90
Ts
N
H
O
O
4m
126 MHz, CDCl3
f1 (ppm)

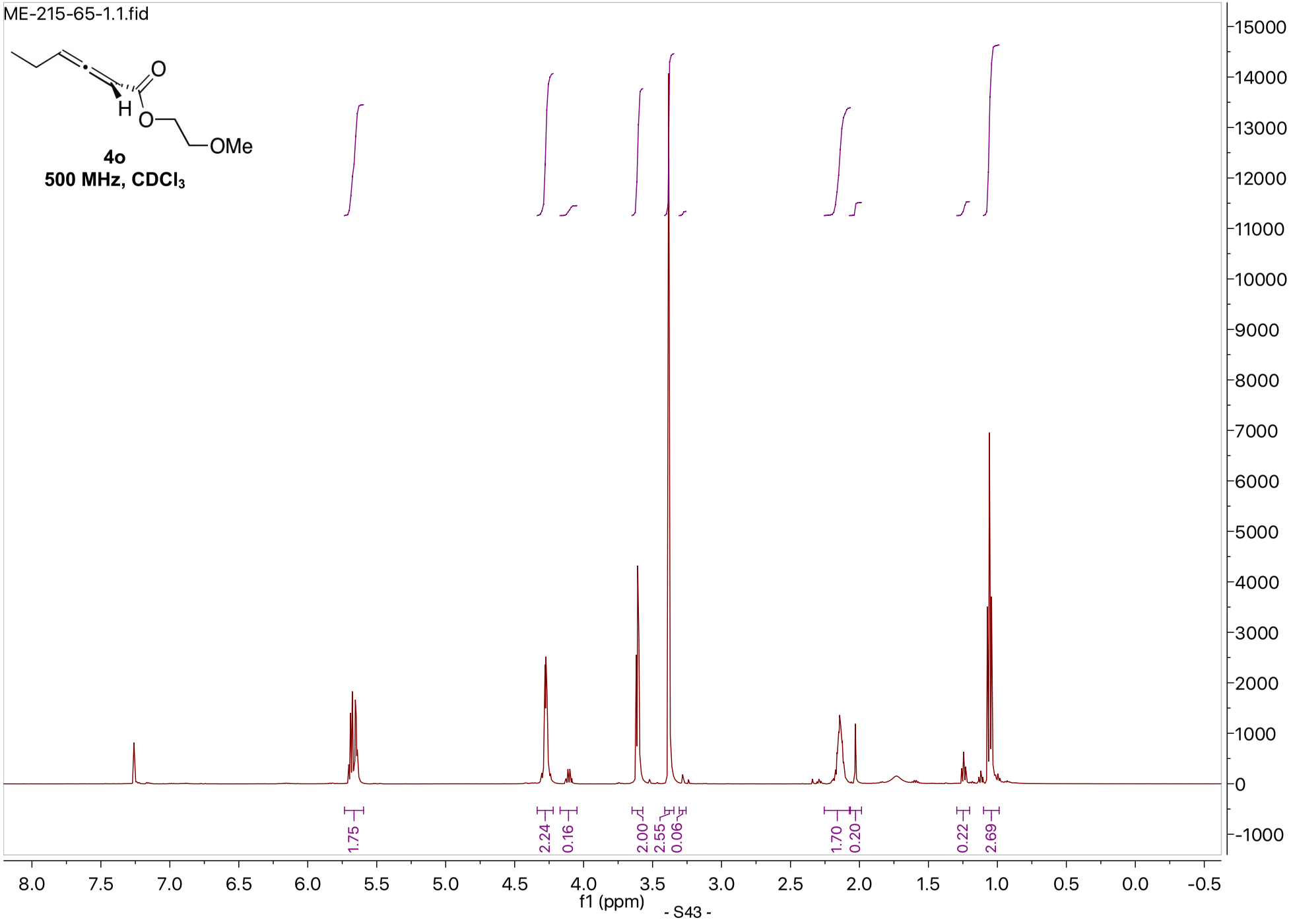
ME-215-65-2.3.fid



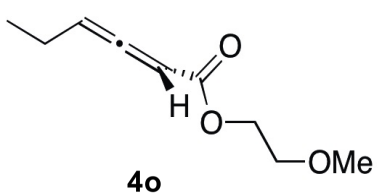
4n

300 MHz, $CDCl_3$


ME-215-65-2.4.fid
212.17
165.85
97.02
89.39
77.58
77.16
76.74
72.88
31.65
25.54
23.73
20.96
13.22
O
H
O
4n
75 MHz, CDCl3
f1 (ppm)

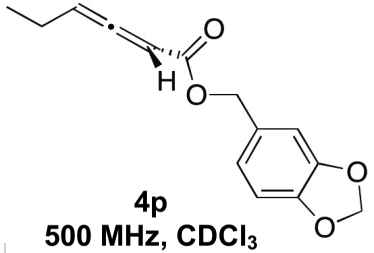

ME-215-65-1.1.fid
O
H
O
OMe
4o
500 MHz, CDCl3
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.75
2.24
0.16
2.00
2.55
0.06
1.70
0.20
0.22
2.69
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

ME-215-65-1.2.fid

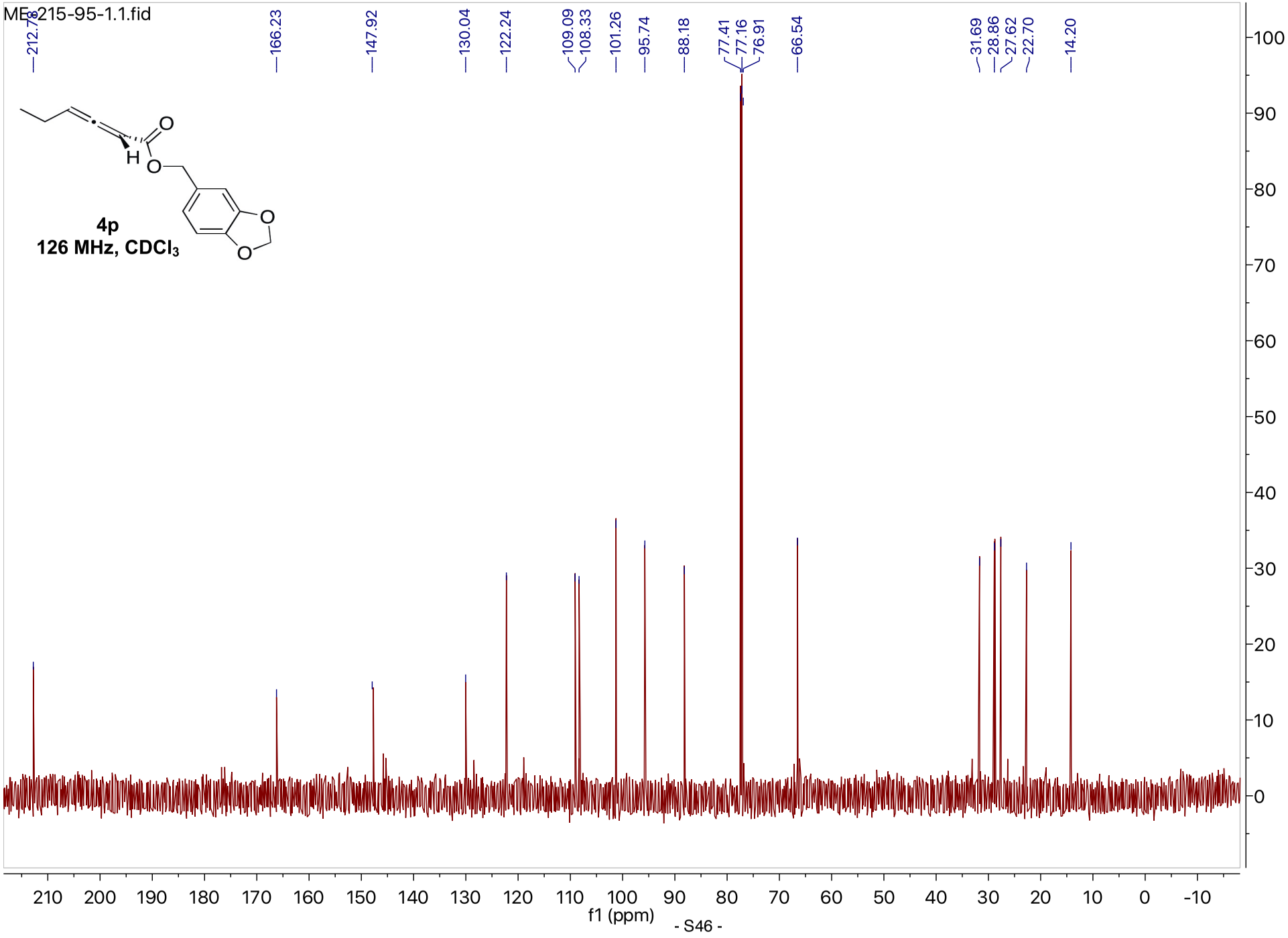


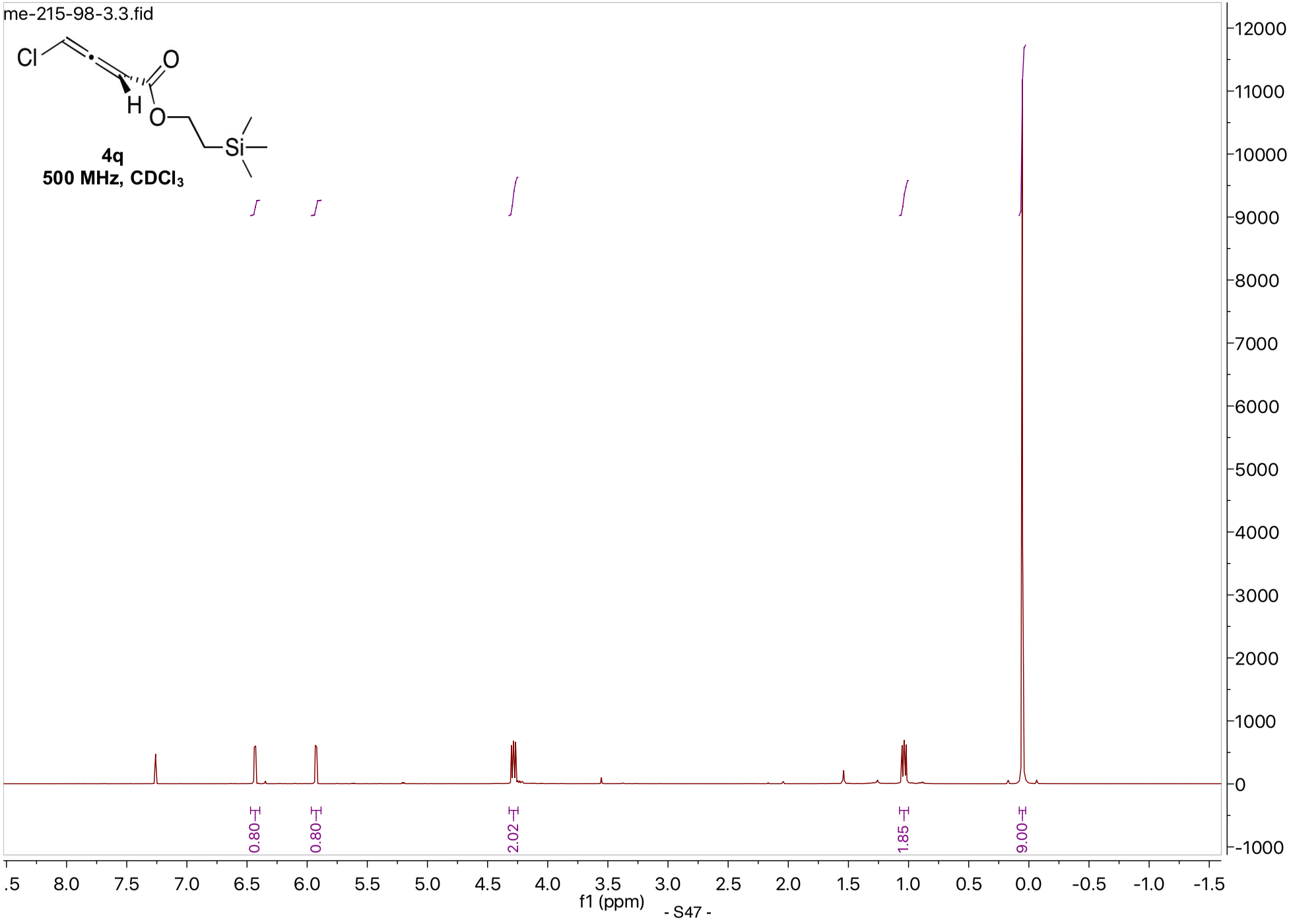
4o
126 MHz, $CDCl_3$

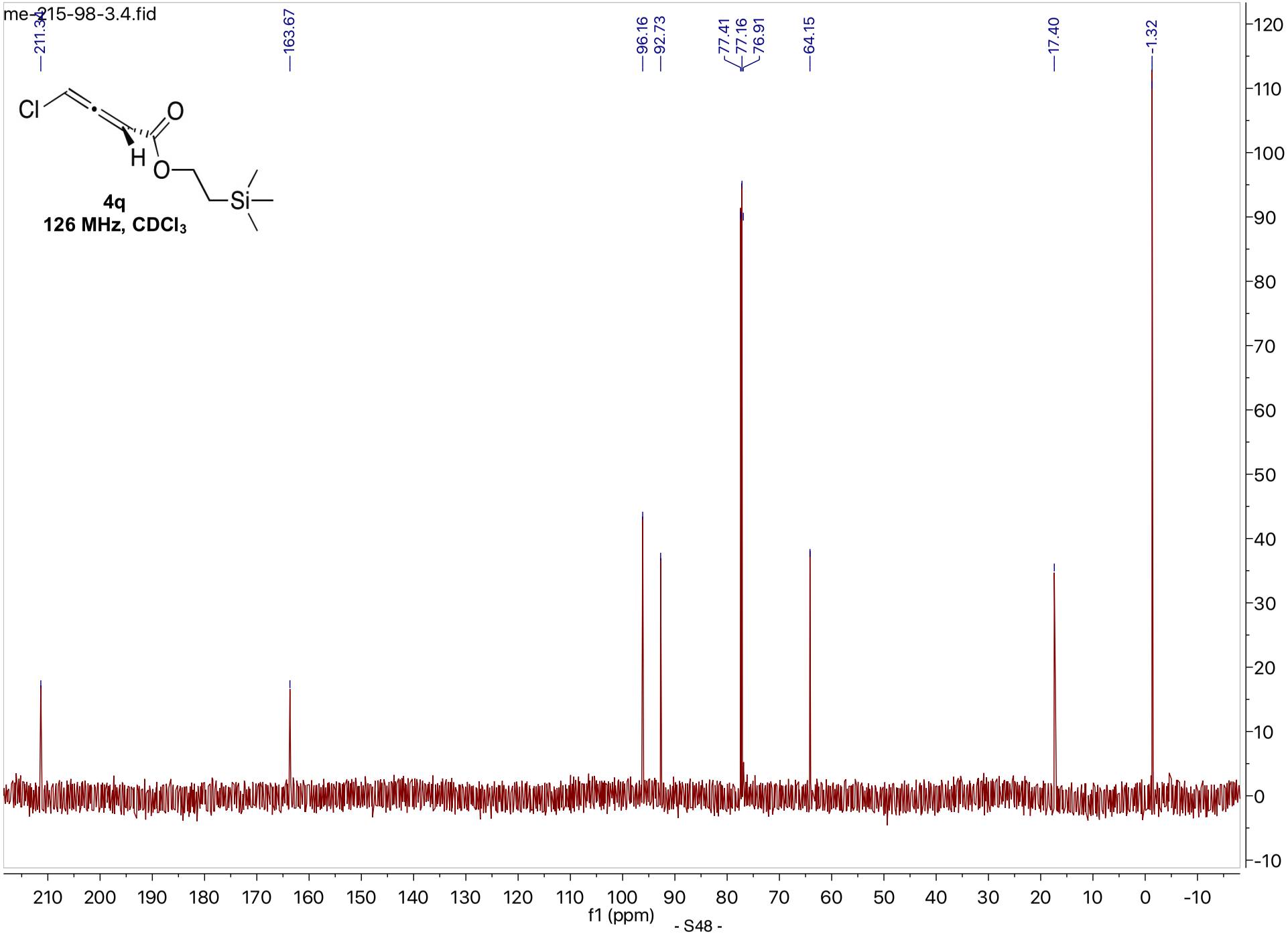
me-208-174

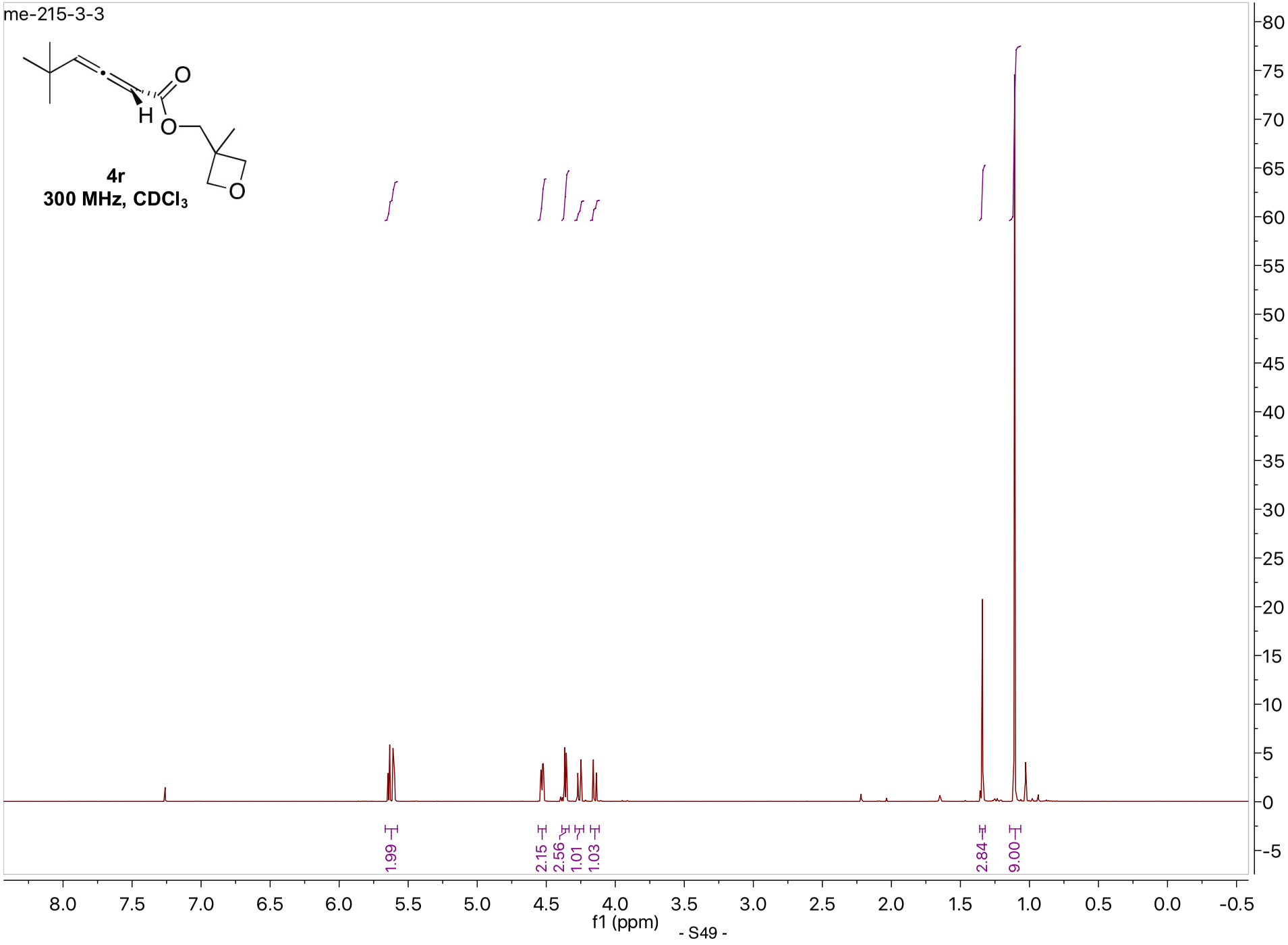


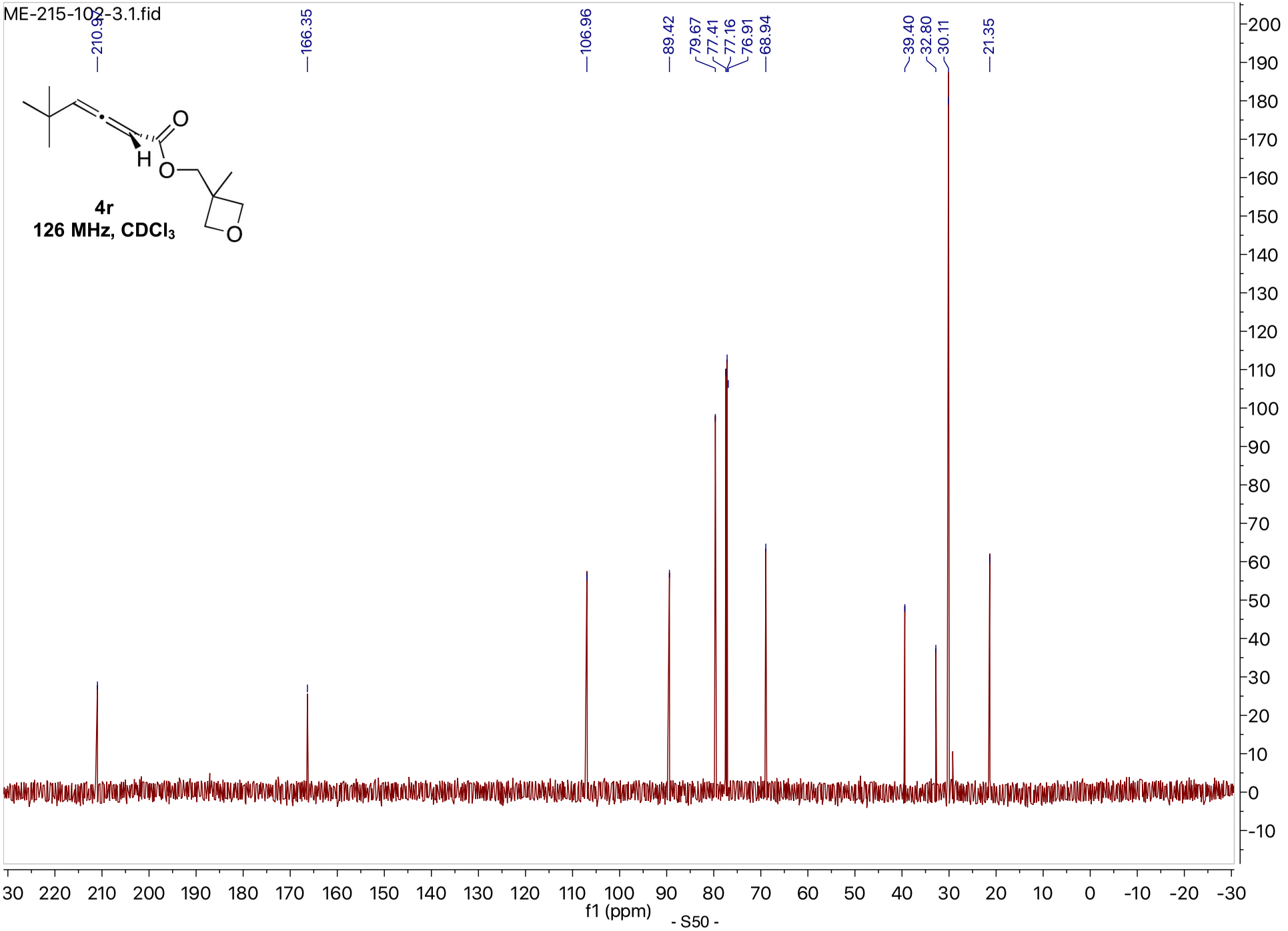
4p
500 MHz, $CDCl_3$


ME-215-95-1.1.fid
212.78
166.23
147.92
130.04
122.24
109.09
108.33
101.26
95.74
88.18
77.41
77.16
76.91
66.54
31.69
28.86
27.62
22.70
14.20
O
H
O
O
O
4p
126 MHz, CDCl3
f1 (ppm)

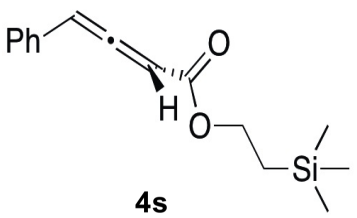

me-215-98-3.3.fid
Cl
O
H
O
Si
4q
500 MHz, CDCl3
0.80
0.80
2.02
1.85
9.00
f1 (ppm)


me-215-98-3.4.fid
211.34
163.67
96.16
92.73
77.41
77.16
76.91
64.15
17.40
1.32
Cl
O
H
O
Si
4q
126 MHz, CDCl3
f1 (ppm)


me-215-3-3
4r
300 MHz, CDCl3
1.99
2.15
2.56
1.01
1.03
2.84
9.00
f1 (ppm)

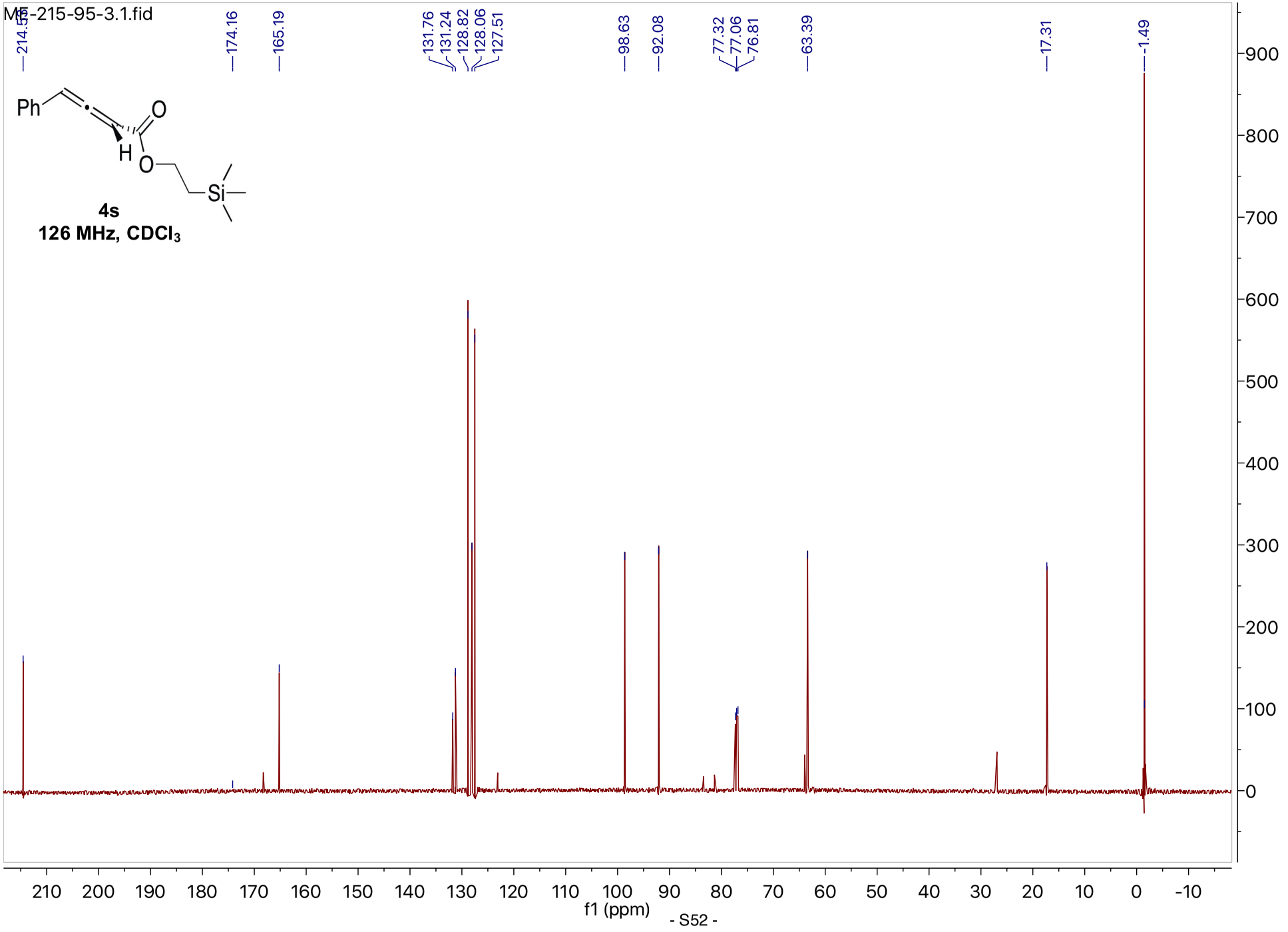

ME-215-102-3.1.fid
210.92
166.35
106.96
89.42
79.67
77.41
77.16
76.91
68.94
39.40
32.80
30.11
21.35
O
H
O
O
4r
126 MHz, CDCl3
f1 (ppm)

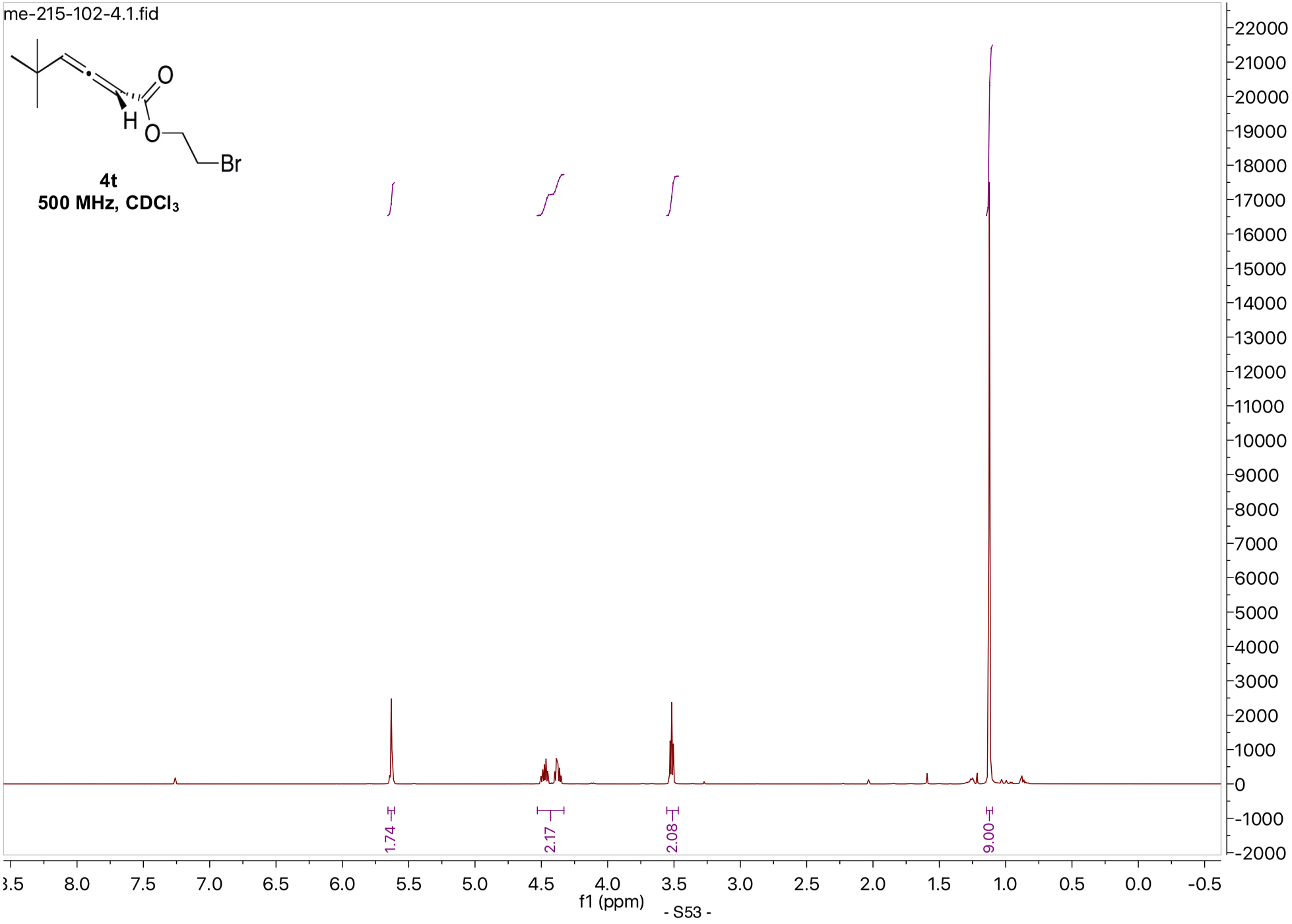
ME-222-14.1.fid

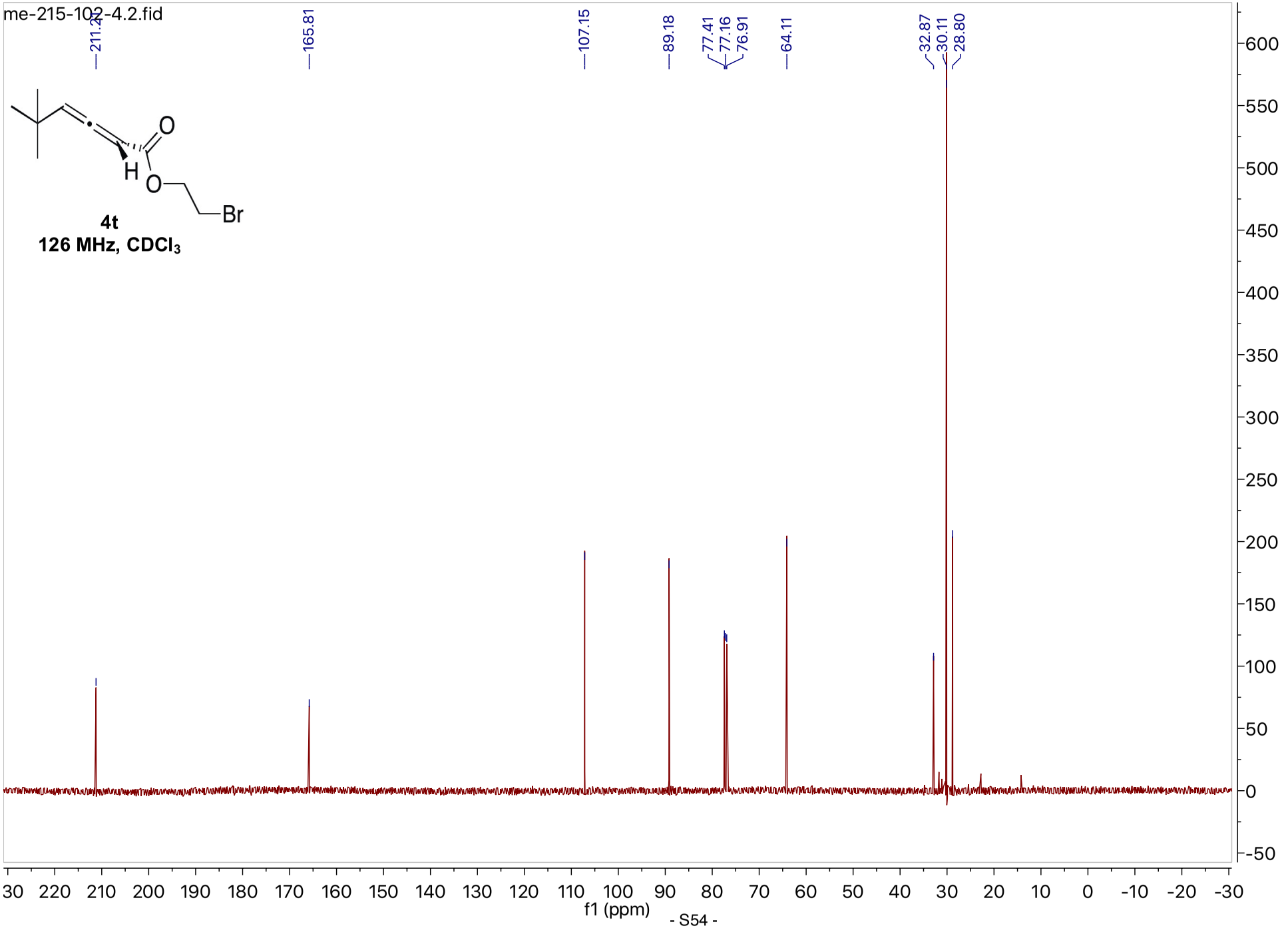


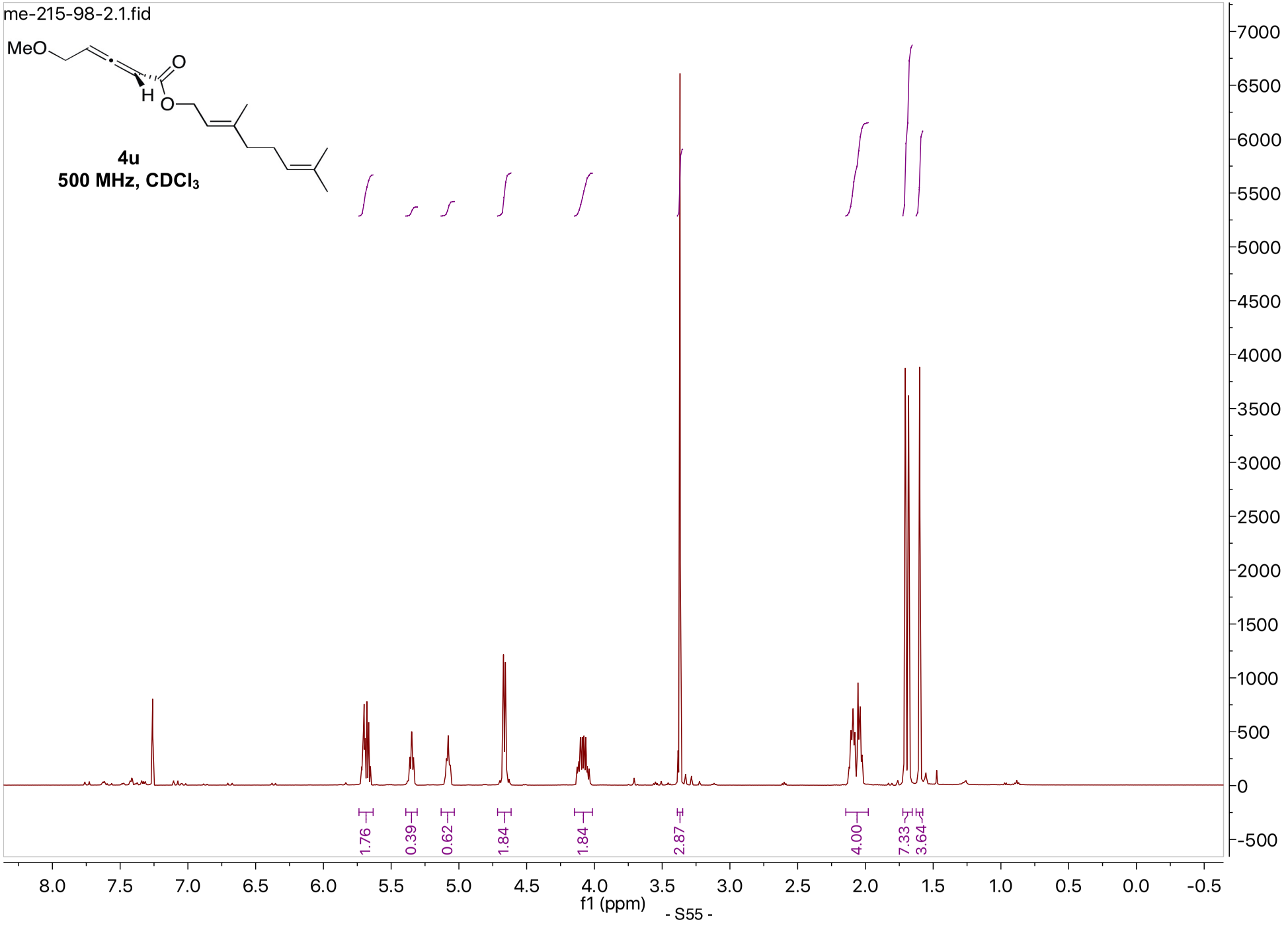
4s

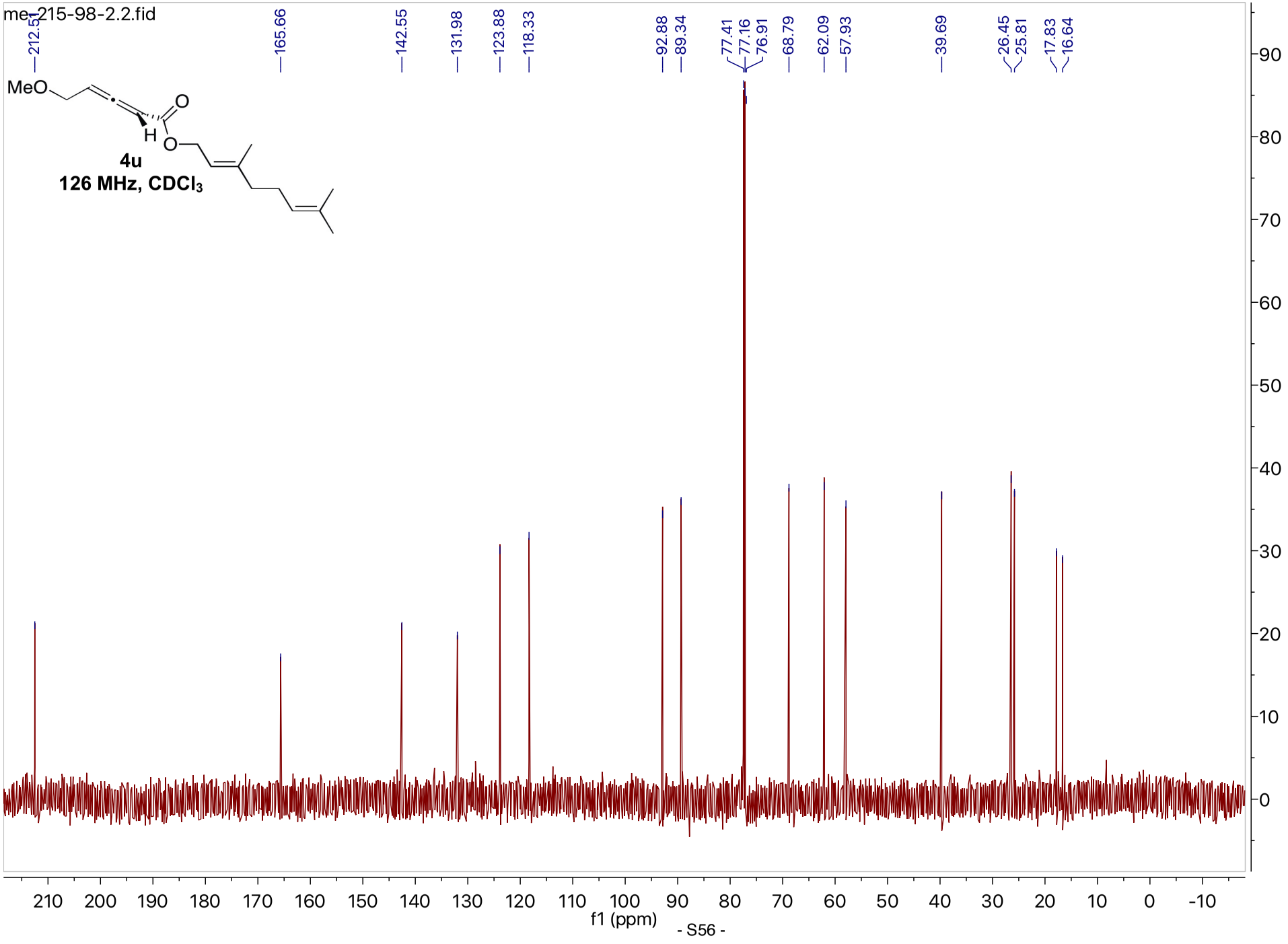
500 MHz, $CDCl_3$

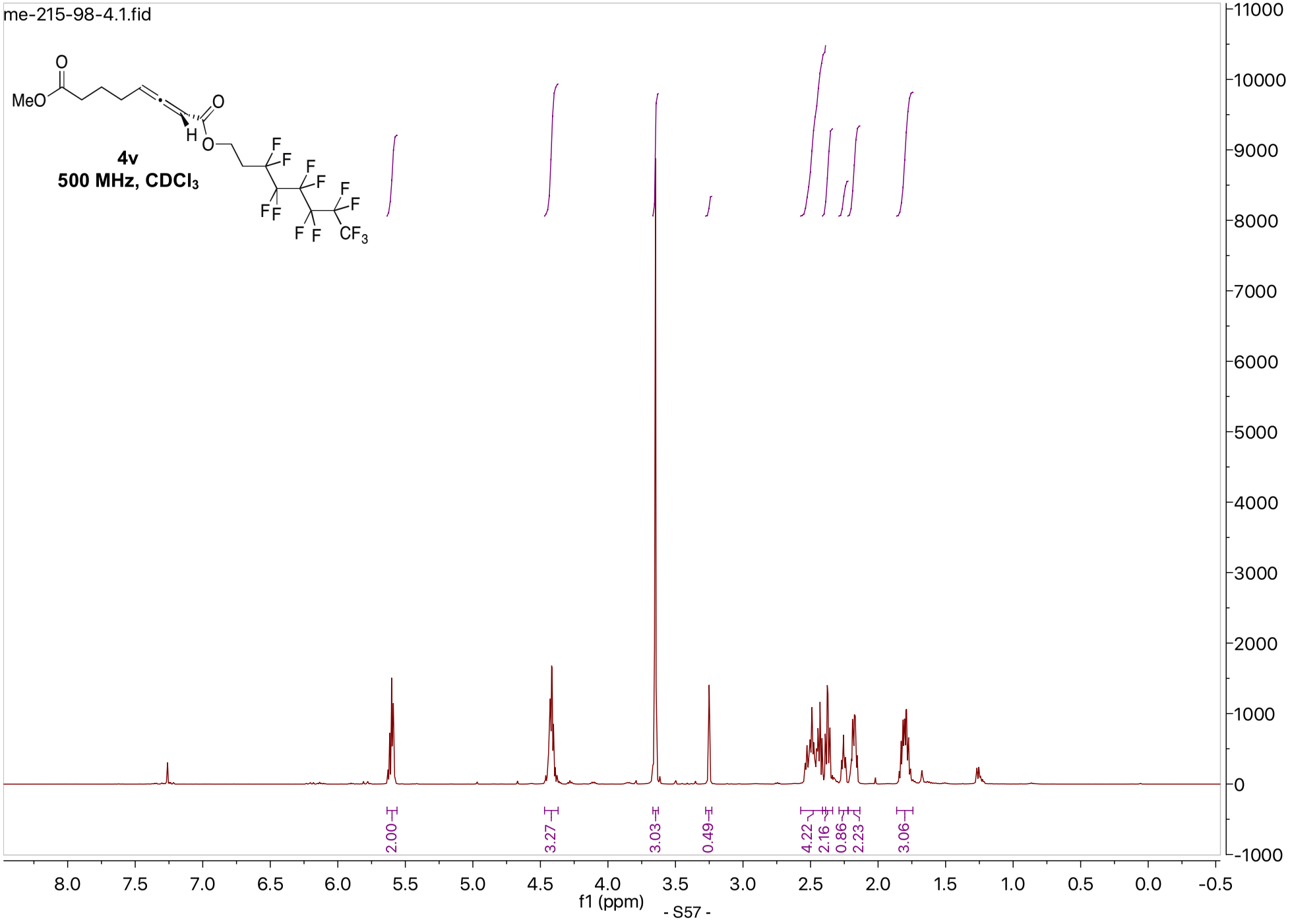

ME-215-95-3.1.fid
214.55
174.16
165.19
131.76
131.24
128.82
128.06
127.51
98.63
92.08
77.32
77.06
76.81
63.39
17.31
1.49
Ph
O
H
O
Si
4s
126 MHz, CDCl3
f1 (ppm)

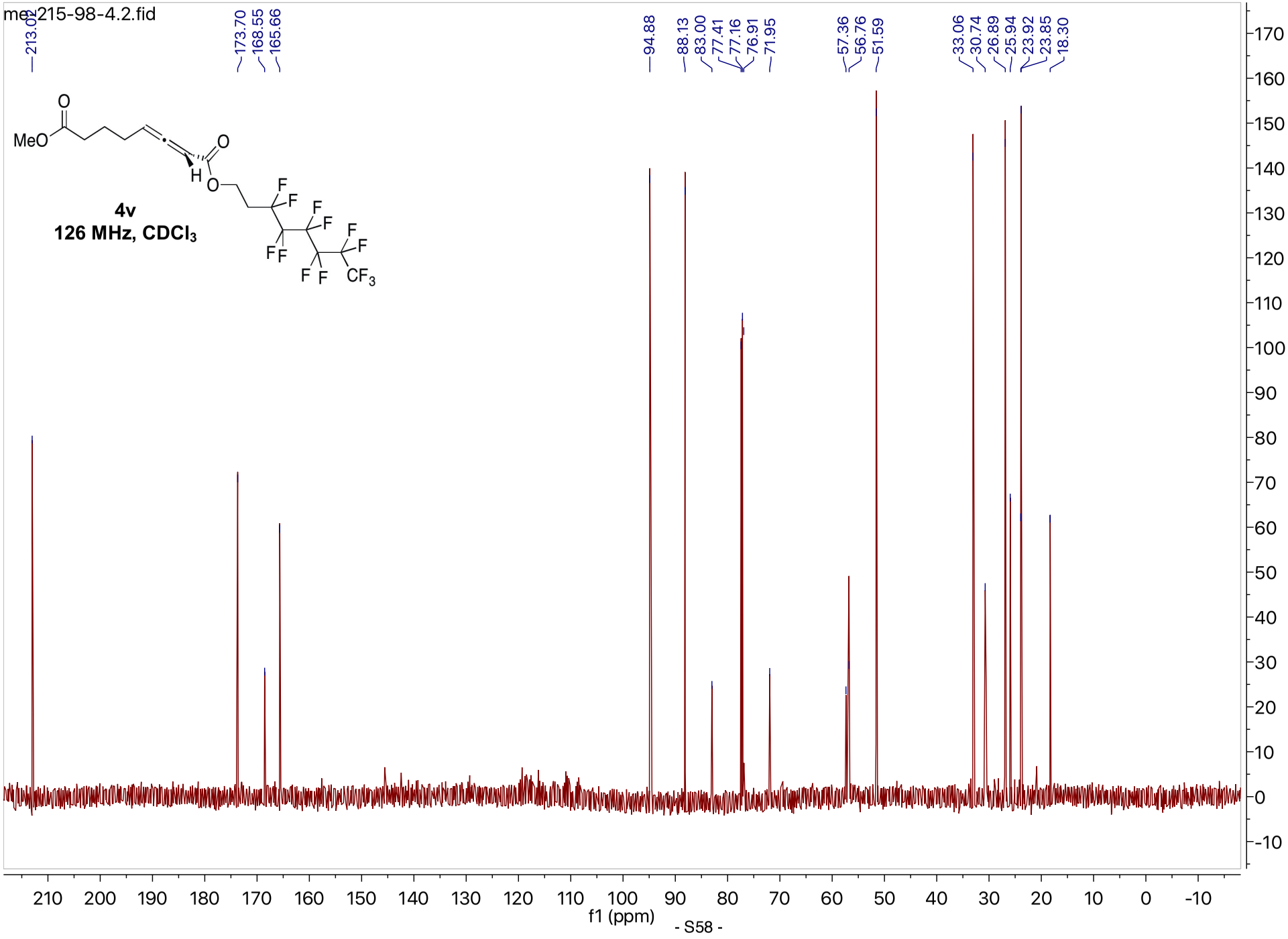

me-215-102-4.1.fid
O
H
O
Br
4t
500 MHz, CDCl3
1.74
2.17
2.08
9.00
f1 (ppm)

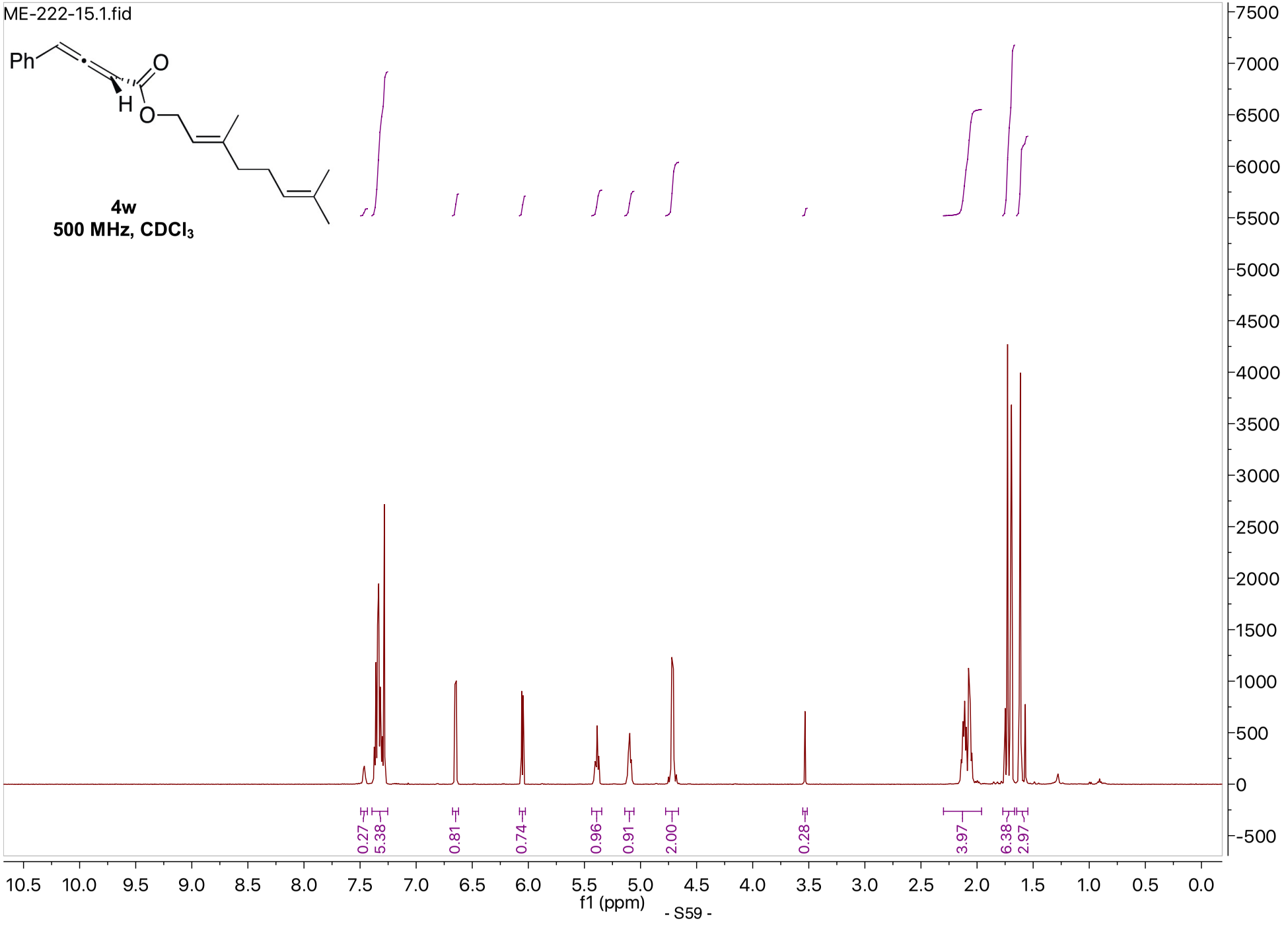

me-215-102-4.2.fid
211.27
165.81
107.15
89.18
77.41
77.16
76.91
64.11
32.87
30.11
28.80
O
H
O
Br
4t
126 MHz, CDCl3
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

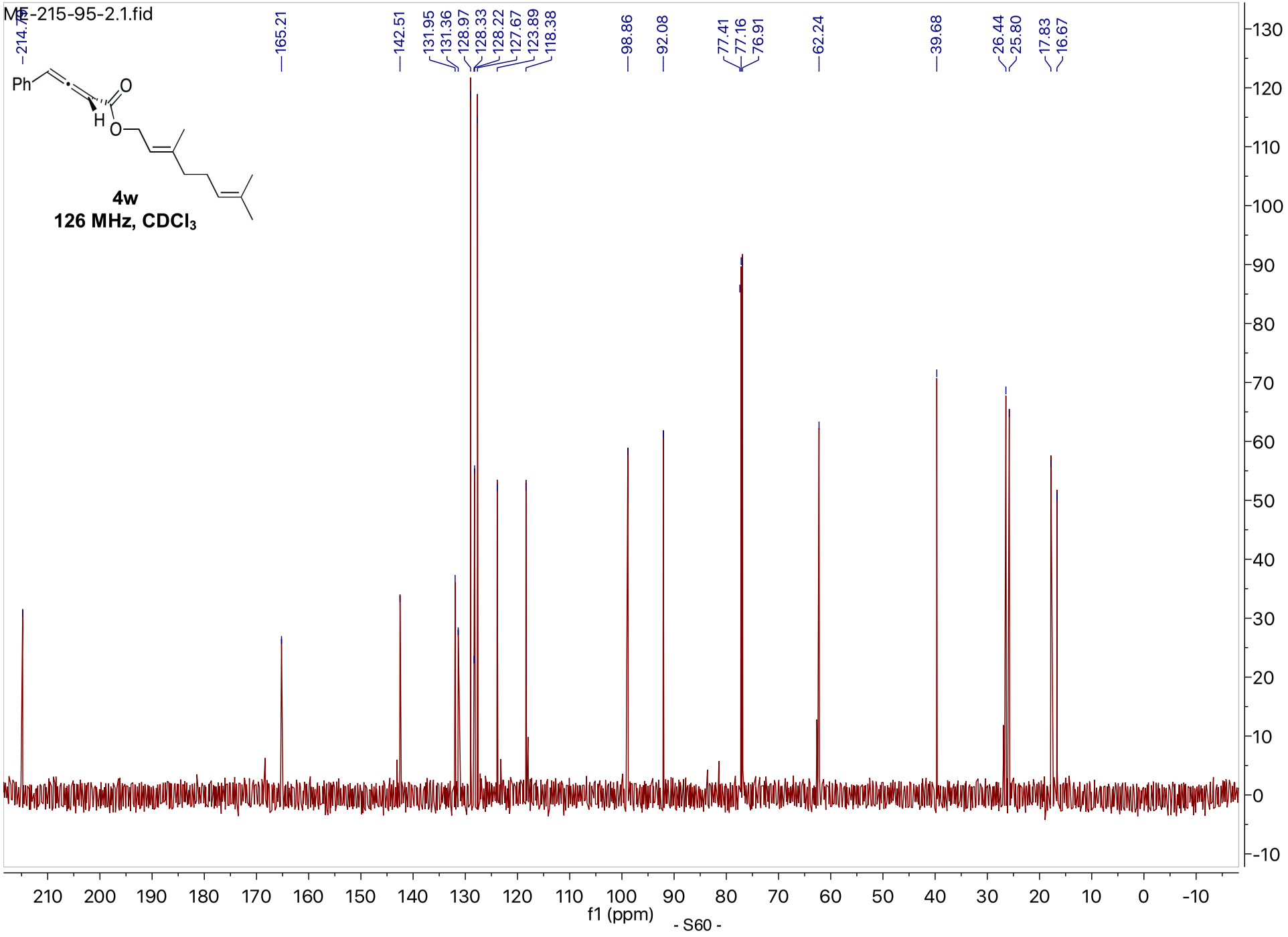

me-215-98-2.1.fid
MeO
O
H
O
4u
500 MHz, CDCl3
1.76
0.39
0.62
1.84
1.84
2.87
4.00
7.33
3.64
f1 (ppm)

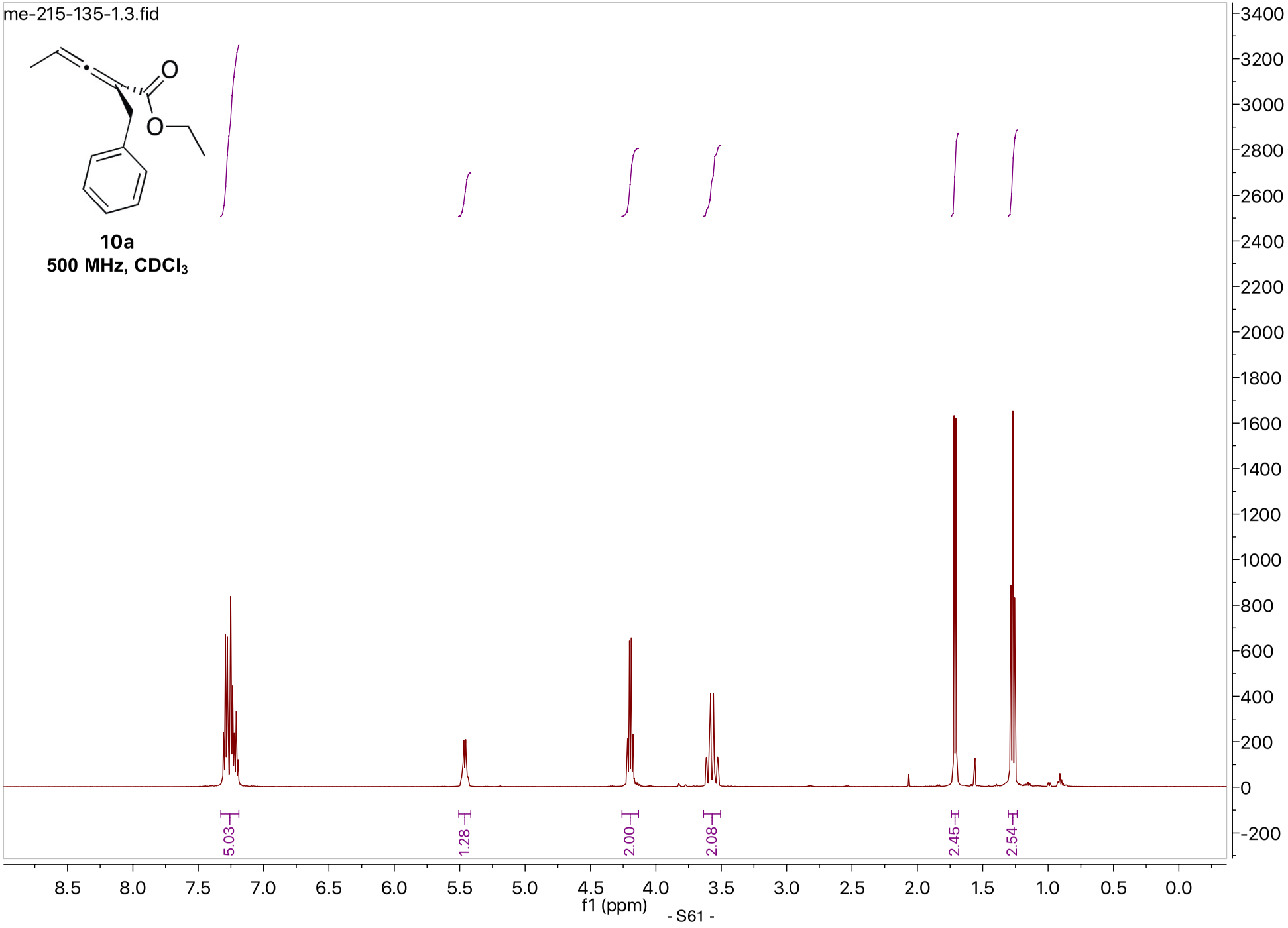

me-215-98-2.2.fid
212.51
165.66
142.55
131.98
123.88
118.33
92.88
89.34
77.41
77.16
76.91
68.79
62.09
57.93
39.69
26.45
25.81
17.83
16.64
MeO
O
H
O
4u
126 MHz, CDCl3
f1 (ppm)

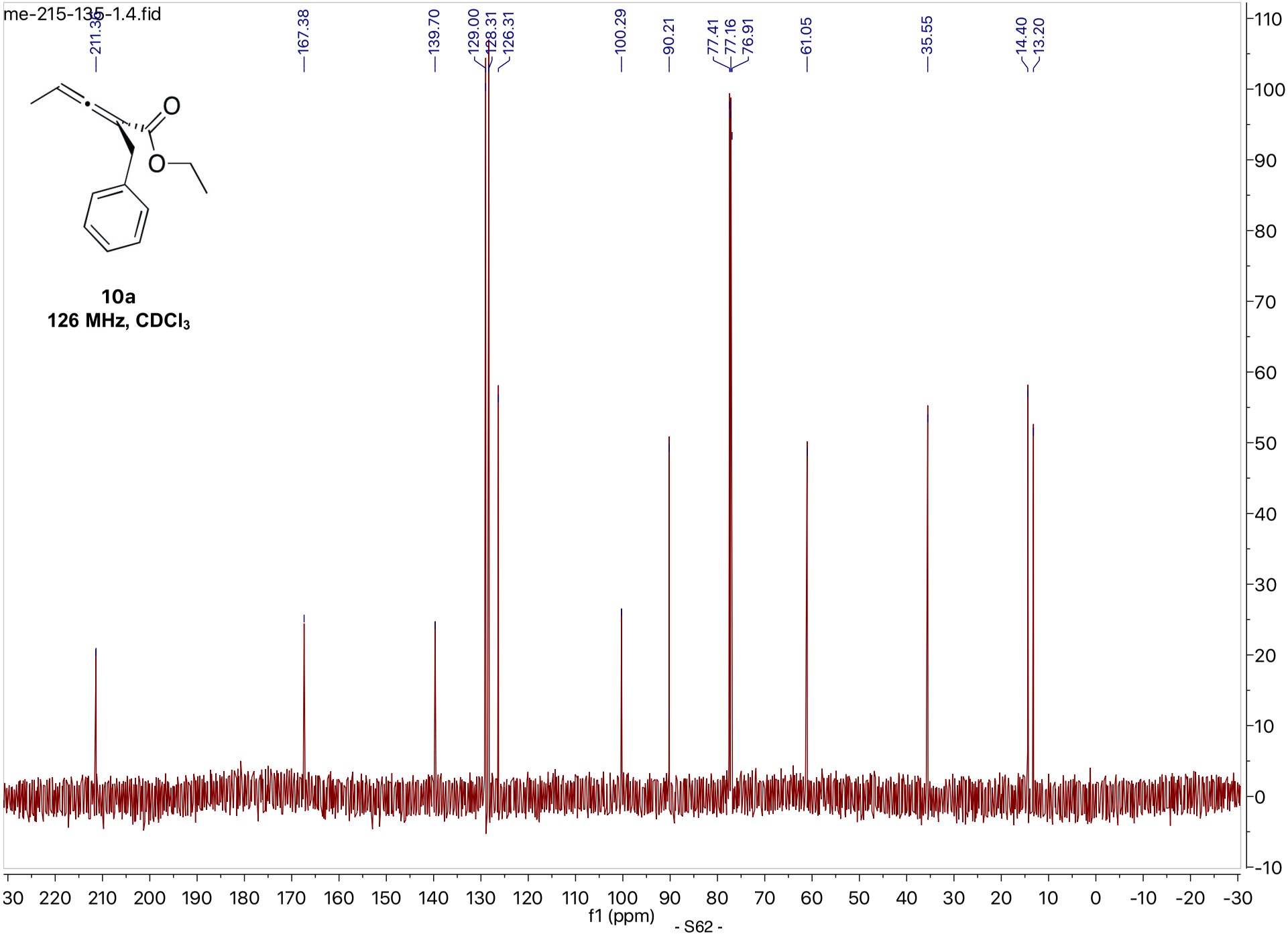

me-215-98-4.1.fid
MeO
O
O
H
O
F
F
F
F
F
F
F
F
F
F
CF3
4v
500 MHz, CDCl3
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.00
3.27
3.03
0.49
4.22
2.16
0.86
2.23
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

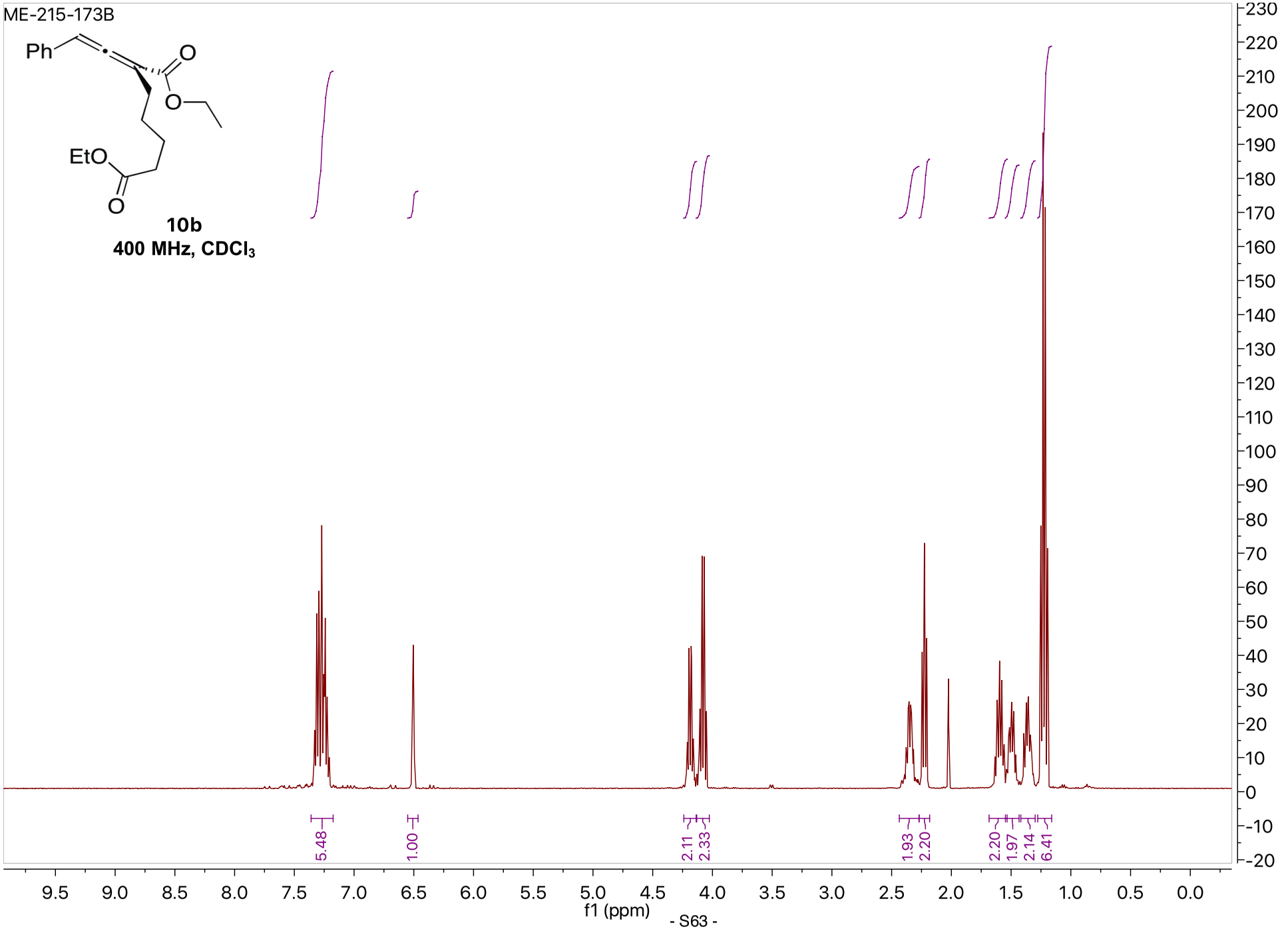

mez215-98-4.2.fid
213.02
173.70
168.55
165.66
94.88
88.13
83.00
77.41
77.16
76.91
71.95
57.36
56.76
51.59
33.06
30.74
26.89
25.94
23.92
23.85
18.30
MeO
O
O
H
O
F
F
F
F
F
F
F
F
F
F
CF3
4v
126 MHz, CDCl3
f1 (ppm)

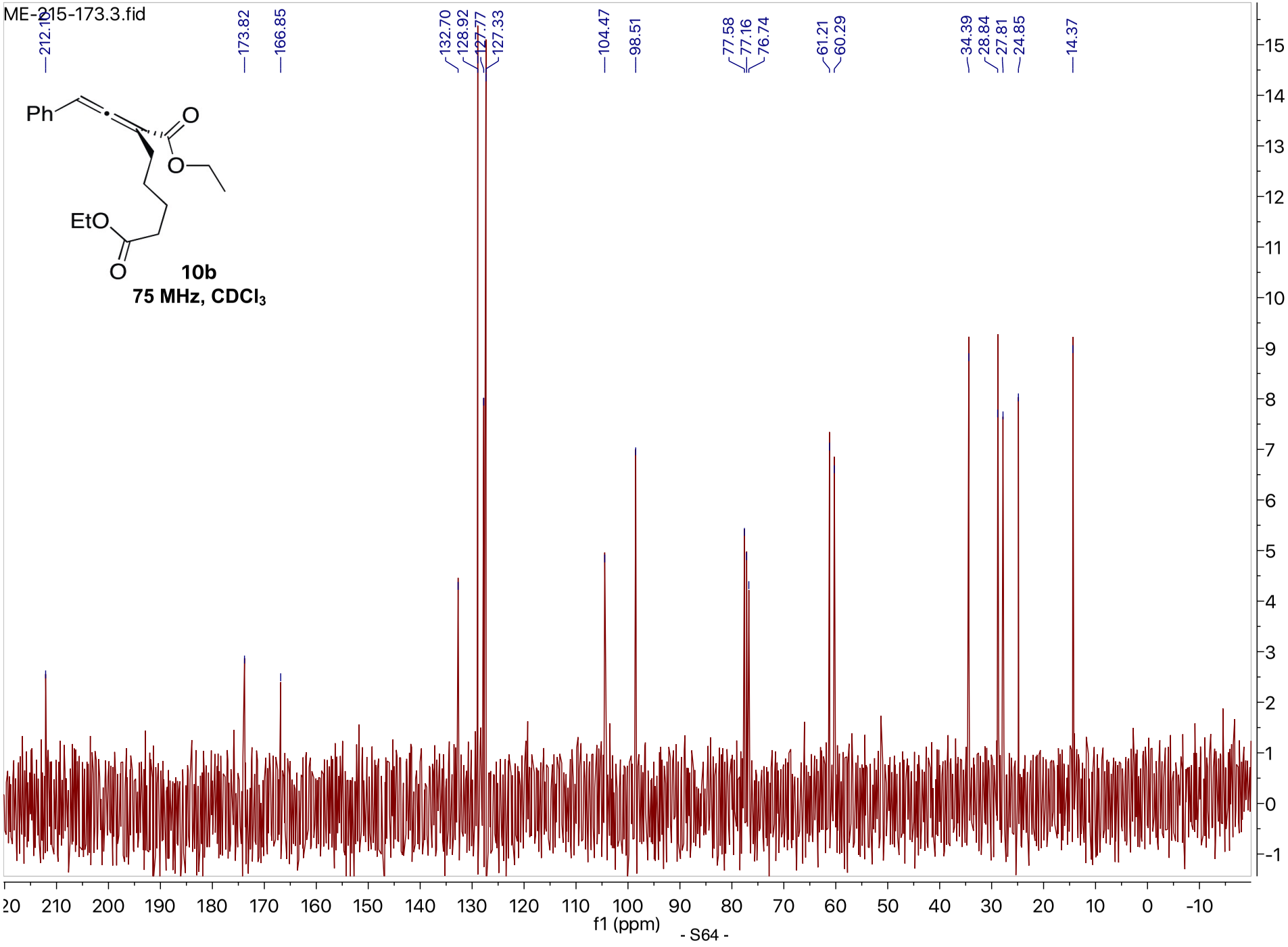

ME-222-15.1.fid
Ph
O
H
O
4w
500 MHz, CDCl3
0.27
5.38
0.81
0.74
0.96
0.91
2.00
0.28
3.97
6.38
2.97
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

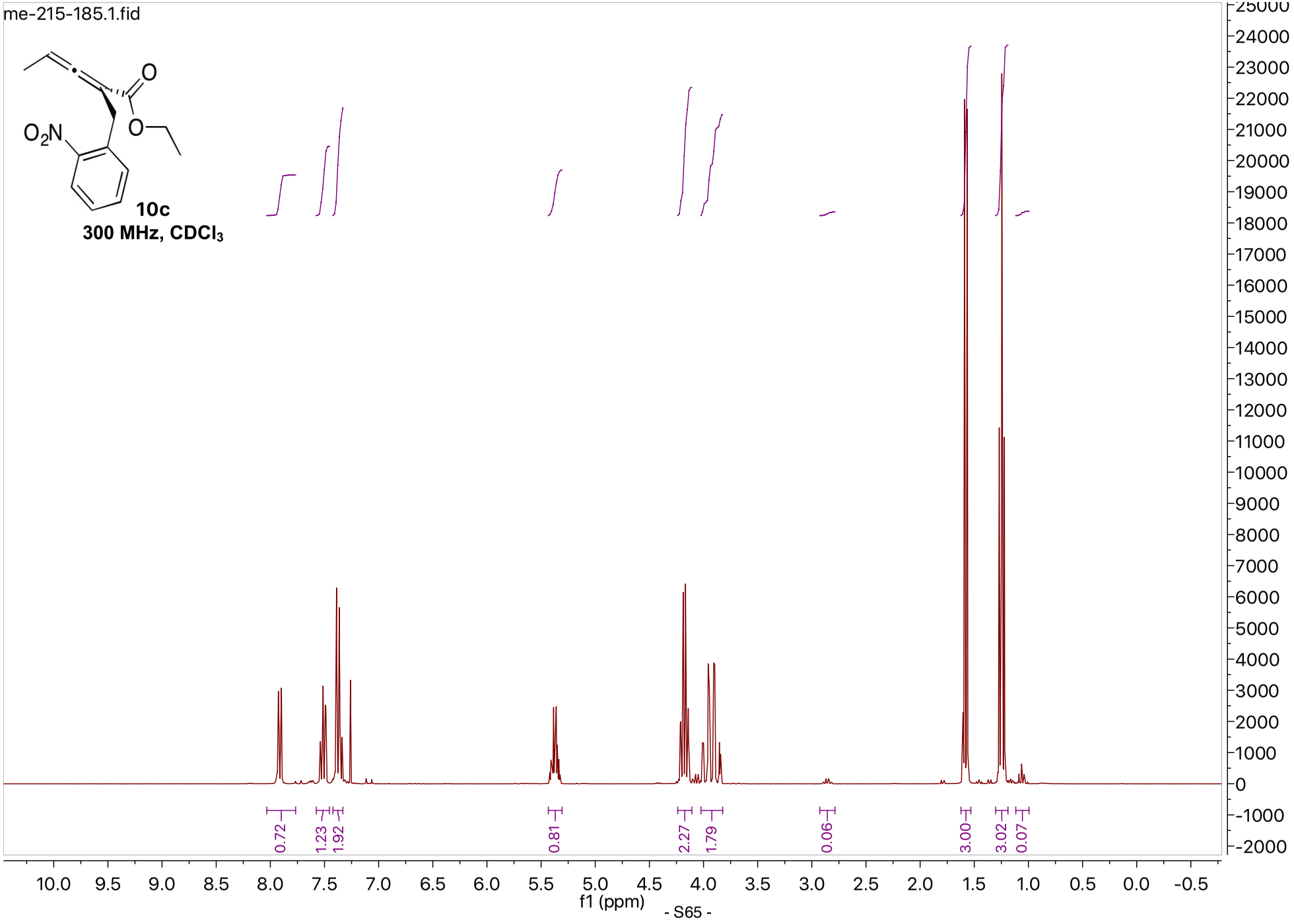

ME-215-95-2.1.fid
214.78
165.21
142.51
131.95
131.36
128.97
128.33
128.22
127.67
123.89
118.38
98.86
92.08
77.41
77.16
76.91
62.24
39.68
26.44
25.80
17.83
16.67
Ph
O
H
O
4w
126 MHz, CDCl3
f1 (ppm)

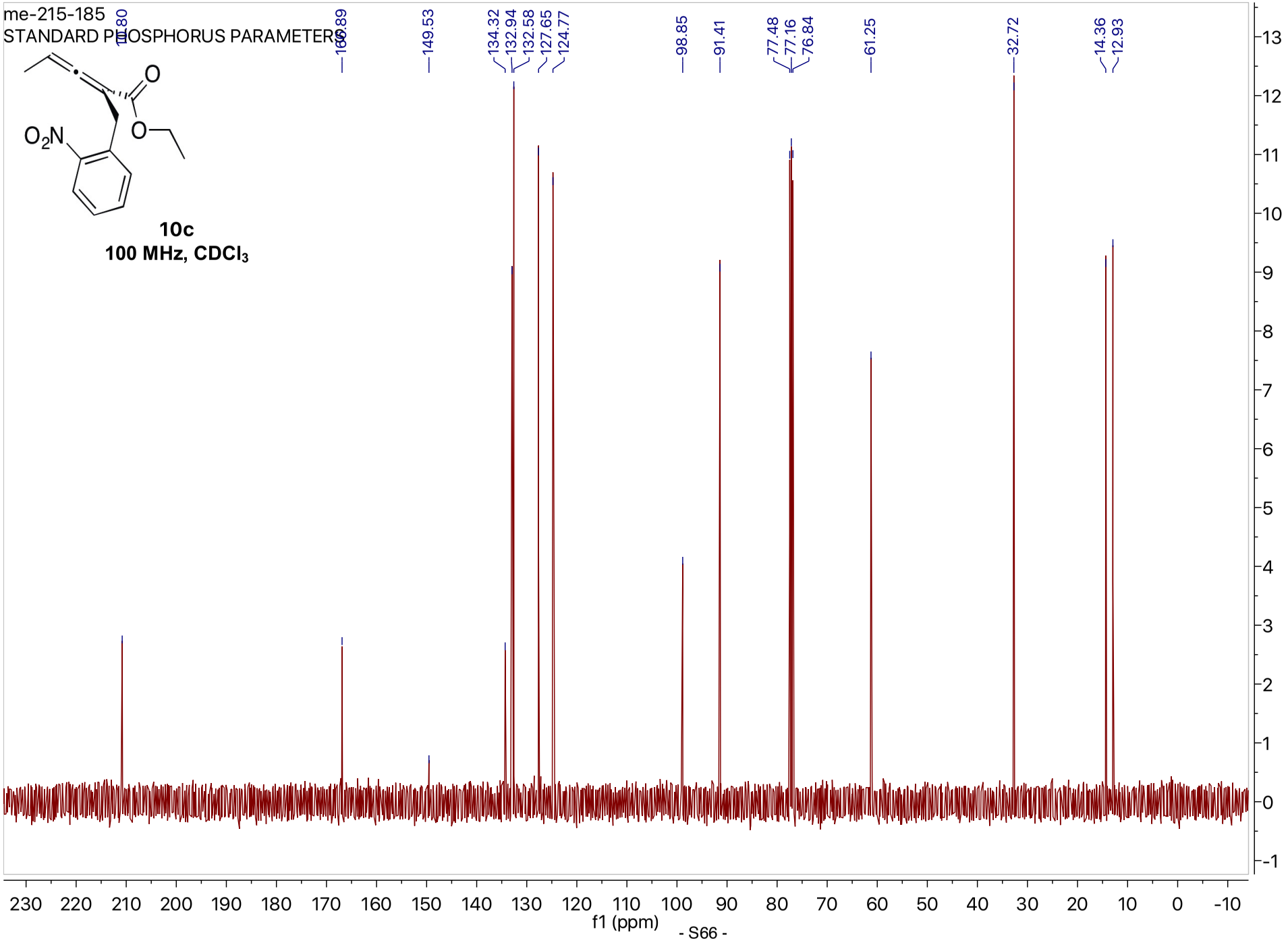

me-215-135-1.3.fid
O
O
10a
500 MHz, CDCl3
5.03
1.28
2.00
2.08
2.45
2.54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

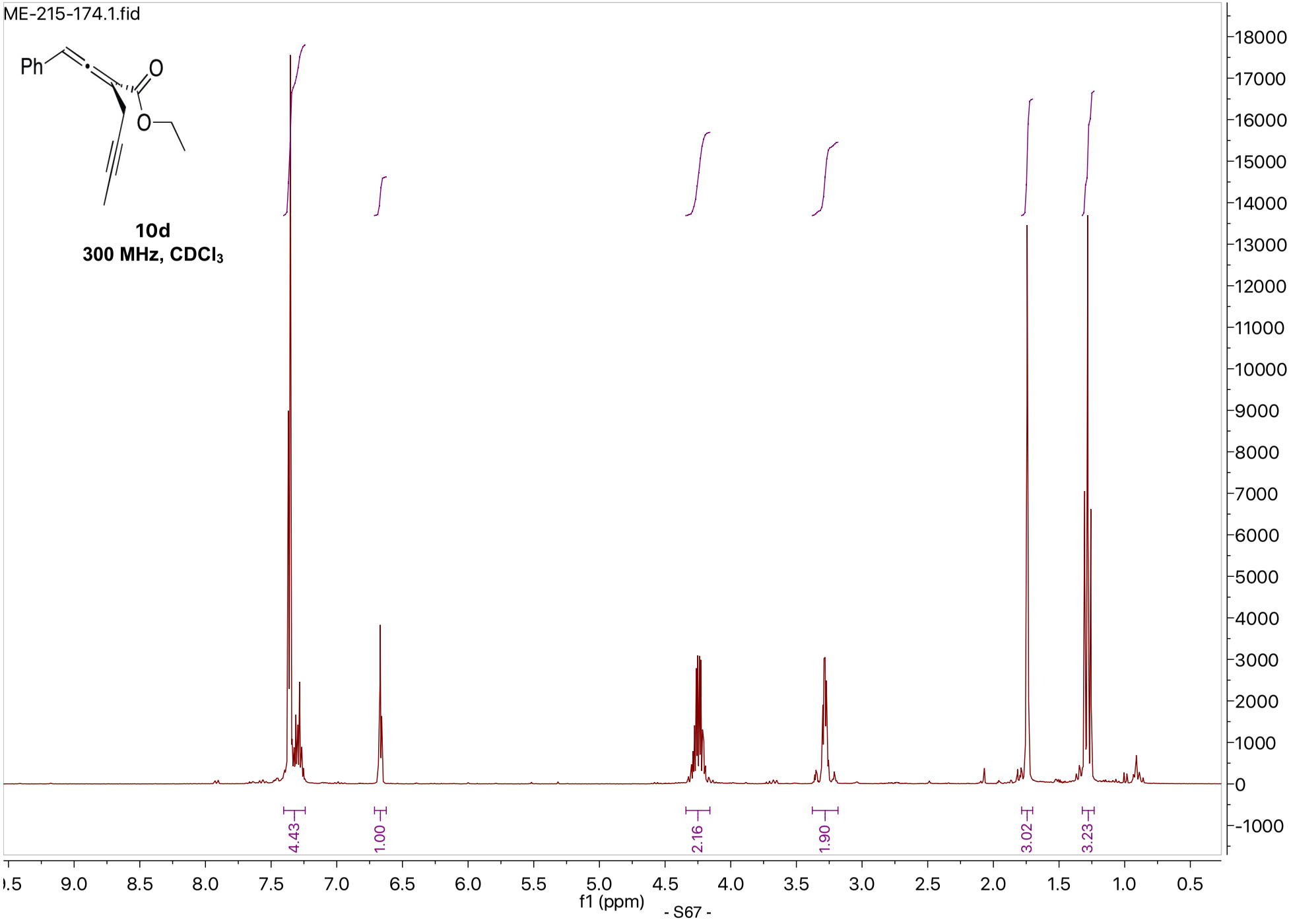

me-215-135-1.4.fid
211.36
167.38
139.70
129.00
128.31
126.31
100.29
90.21
77.41
77.16
76.91
61.05
35.55
14.40
13.20
O
O
10a
126 MHz, CDCl3
f1 (ppm)

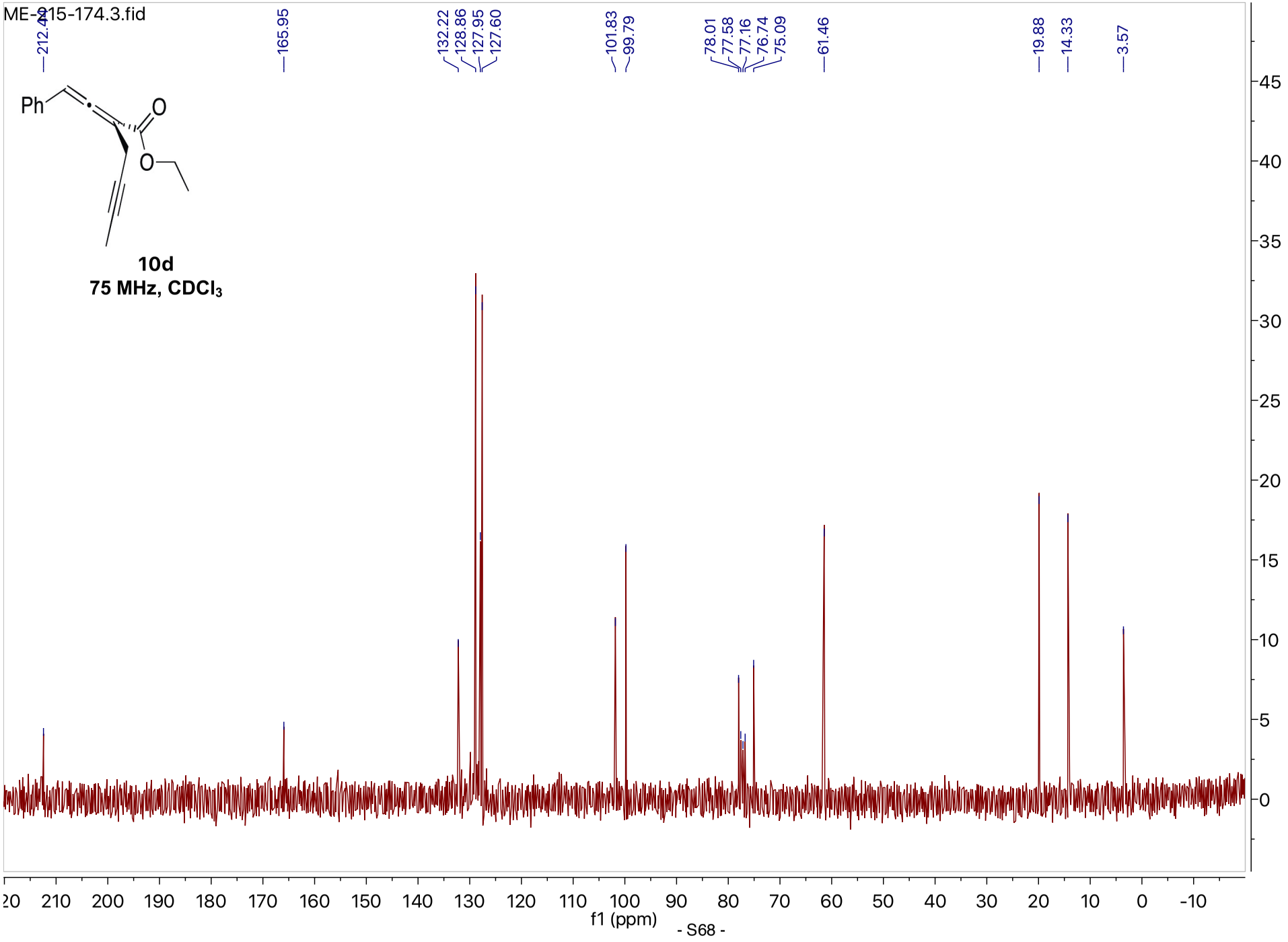

ME-215-173B
Ph
O
O
EtO
O
10b
400 MHz, CDCl3
5.48
1.00
2.11
2.33
1.93
2.20
2.20
1.97
2.14
6.41
f1 (ppm)

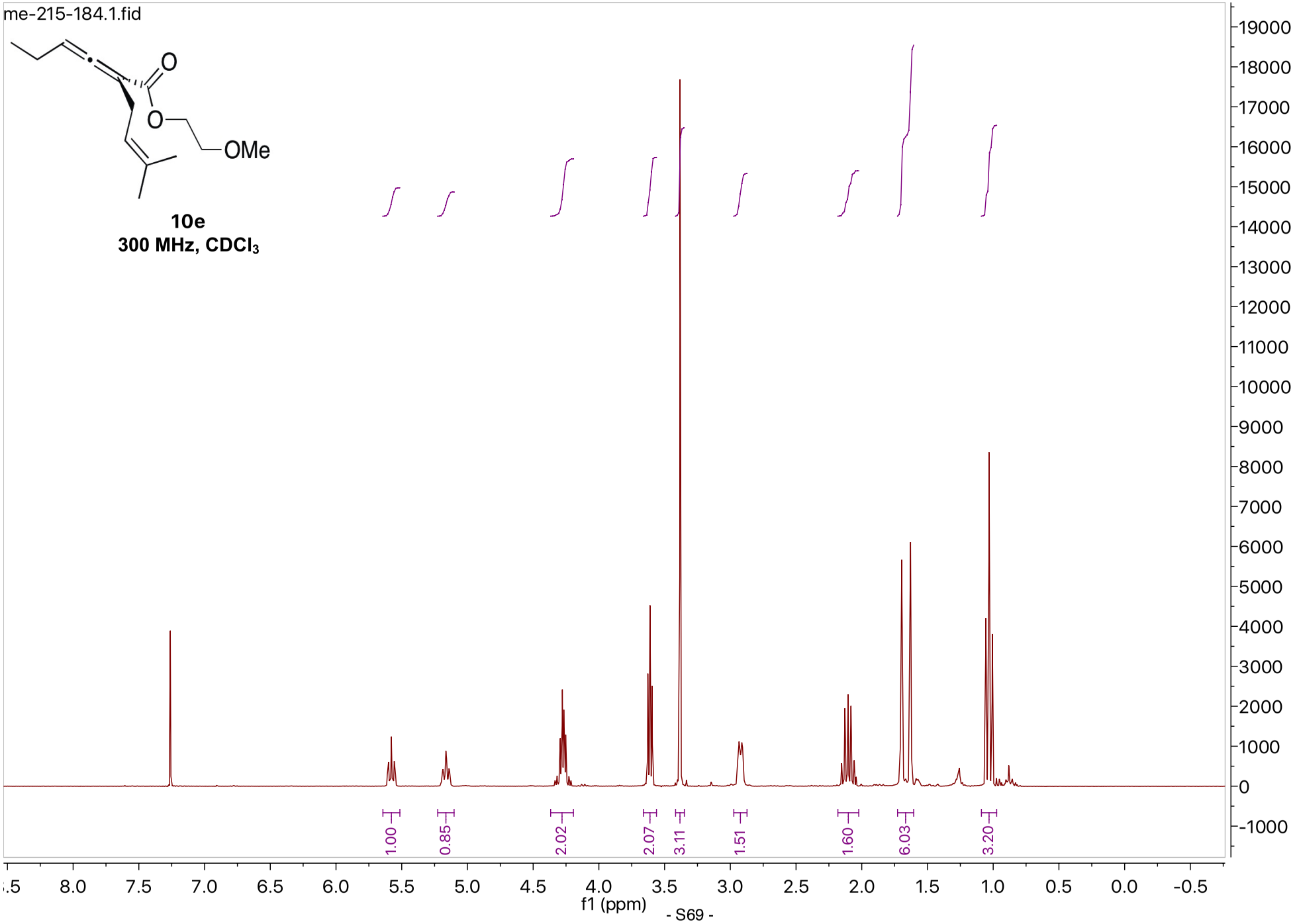

ME-215-173.3.fid
212.10
173.82
166.85
132.70
128.92
127.77
127.33
104.47
98.51
77.58
77.16
76.74
61.21
60.29
34.39
28.84
27.81
24.85
14.37
Ph
O
O
EtO
O
10b
75 MHz, CDCl3
f1 (ppm)

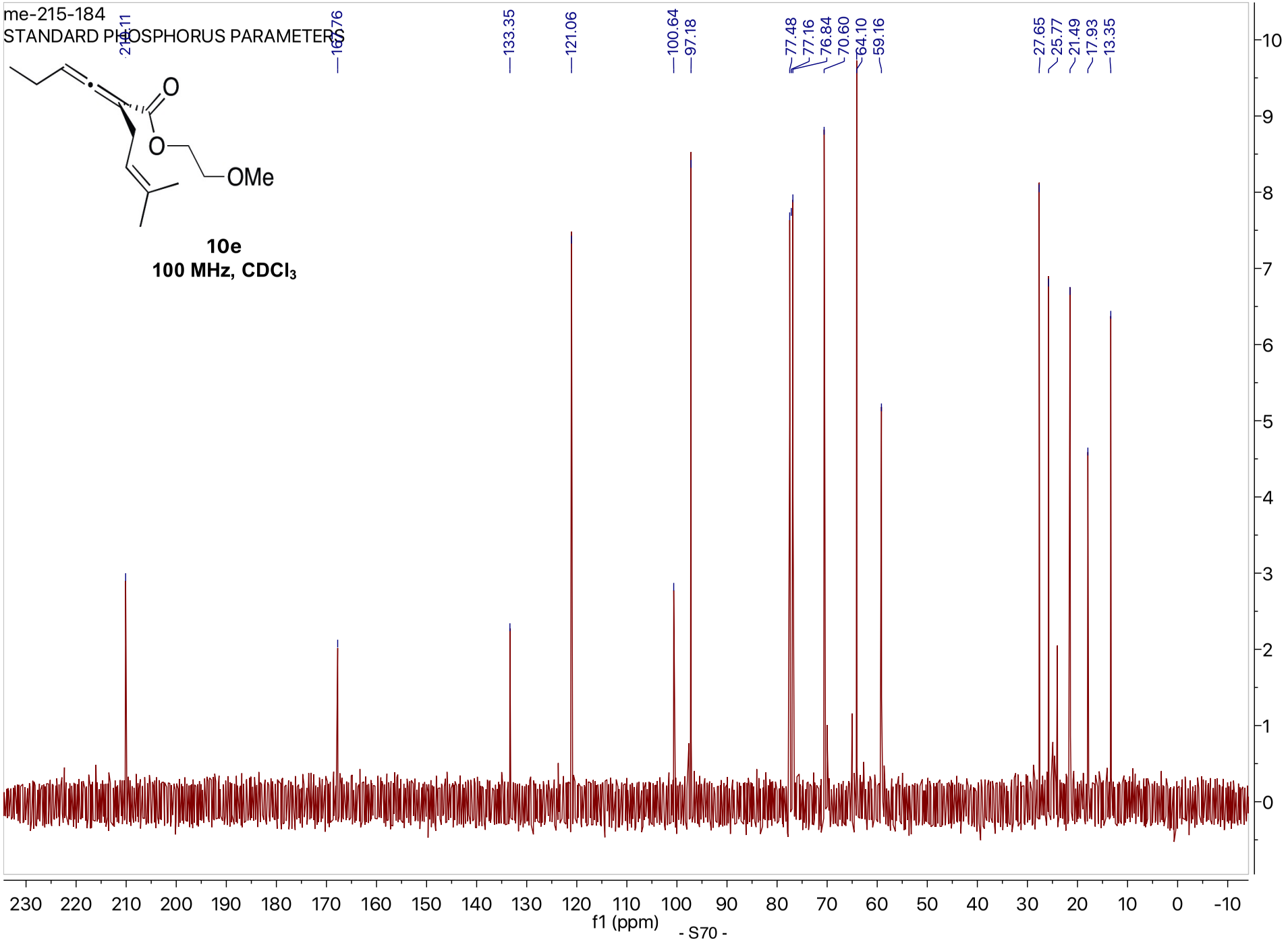

me-215-185.1.fid
O
O
O2N
10c
300 MHz, CDCl3
0.72
1.23
1.92
0.81
2.27
1.79
0.06
3.00
3.02
0.07
f1 (ppm)

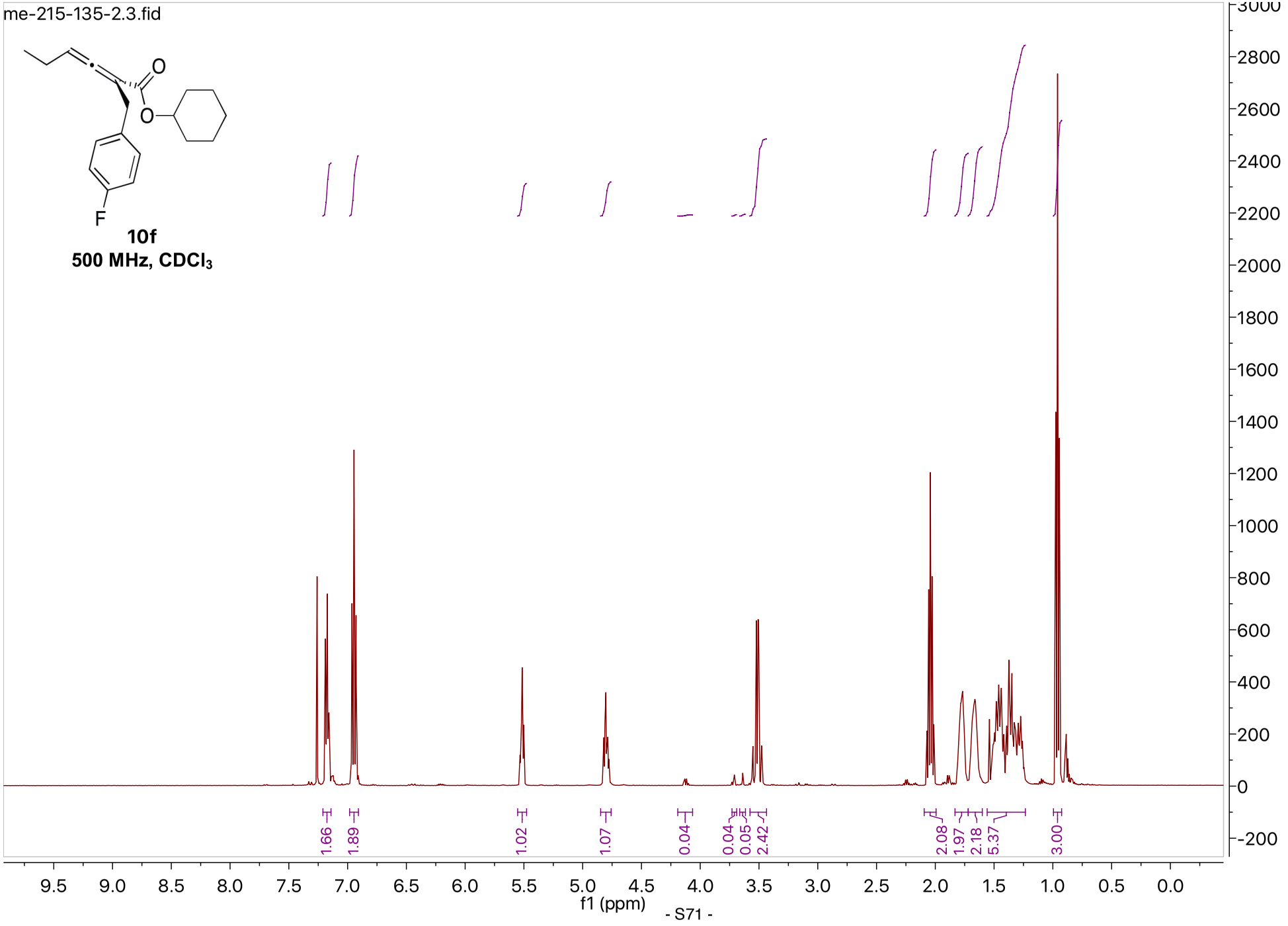

me-215-185
STANDARD PHOSPHORUS PARAMETERS
O2N
O
O
10c
100 MHz, CDCl3
168.80
166.89
149.53
134.32
132.94
132.58
127.65
124.77
98.85
91.41
77.48
77.16
76.84
61.25
32.72
14.36
12.93
f1 (ppm)

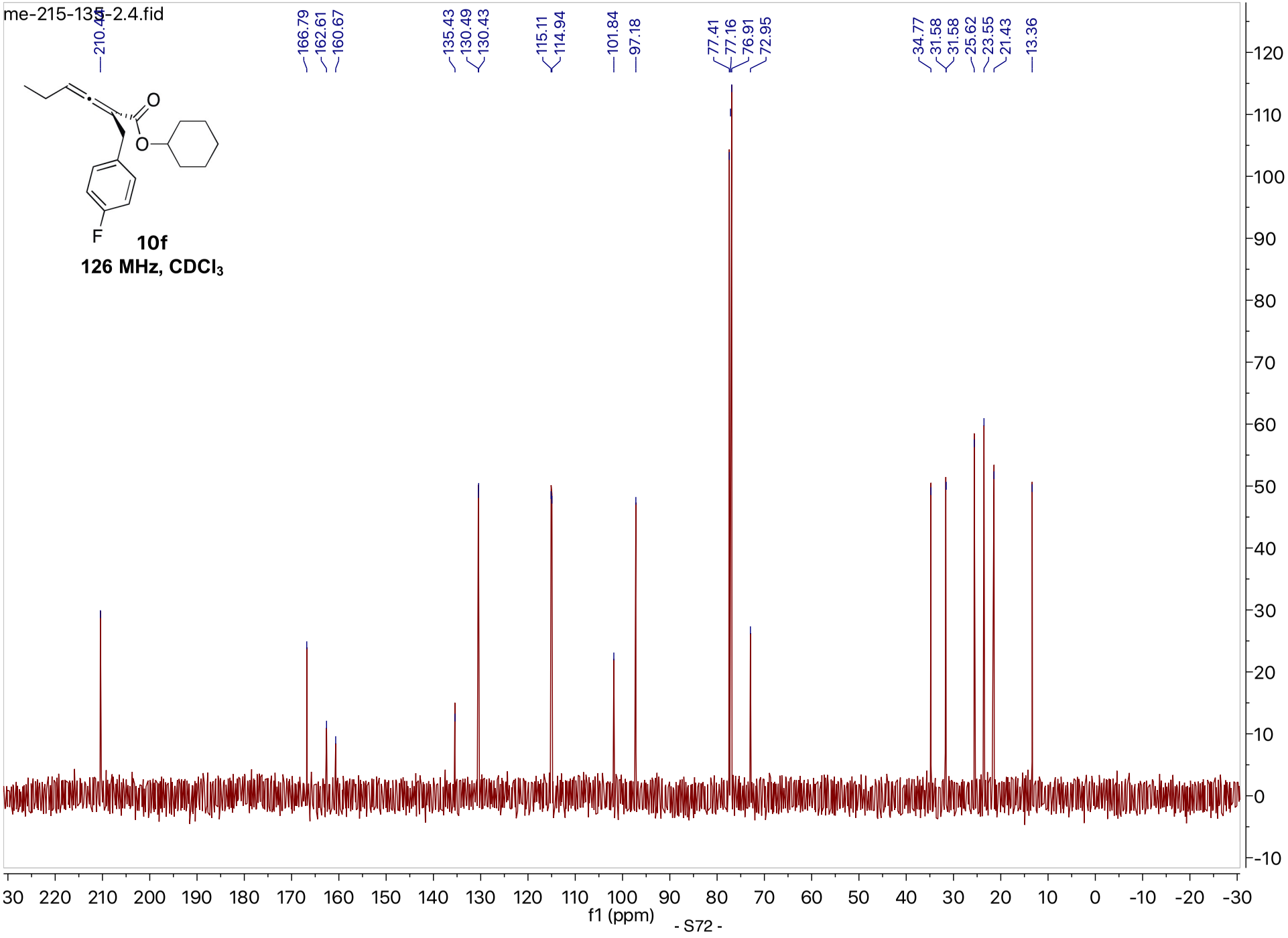

ME-215-174.1.fid
Ph
O
O
10d
300 MHz, CDCl3
4.43
1.00
2.16
1.90
3.02
3.23
f1 (ppm)

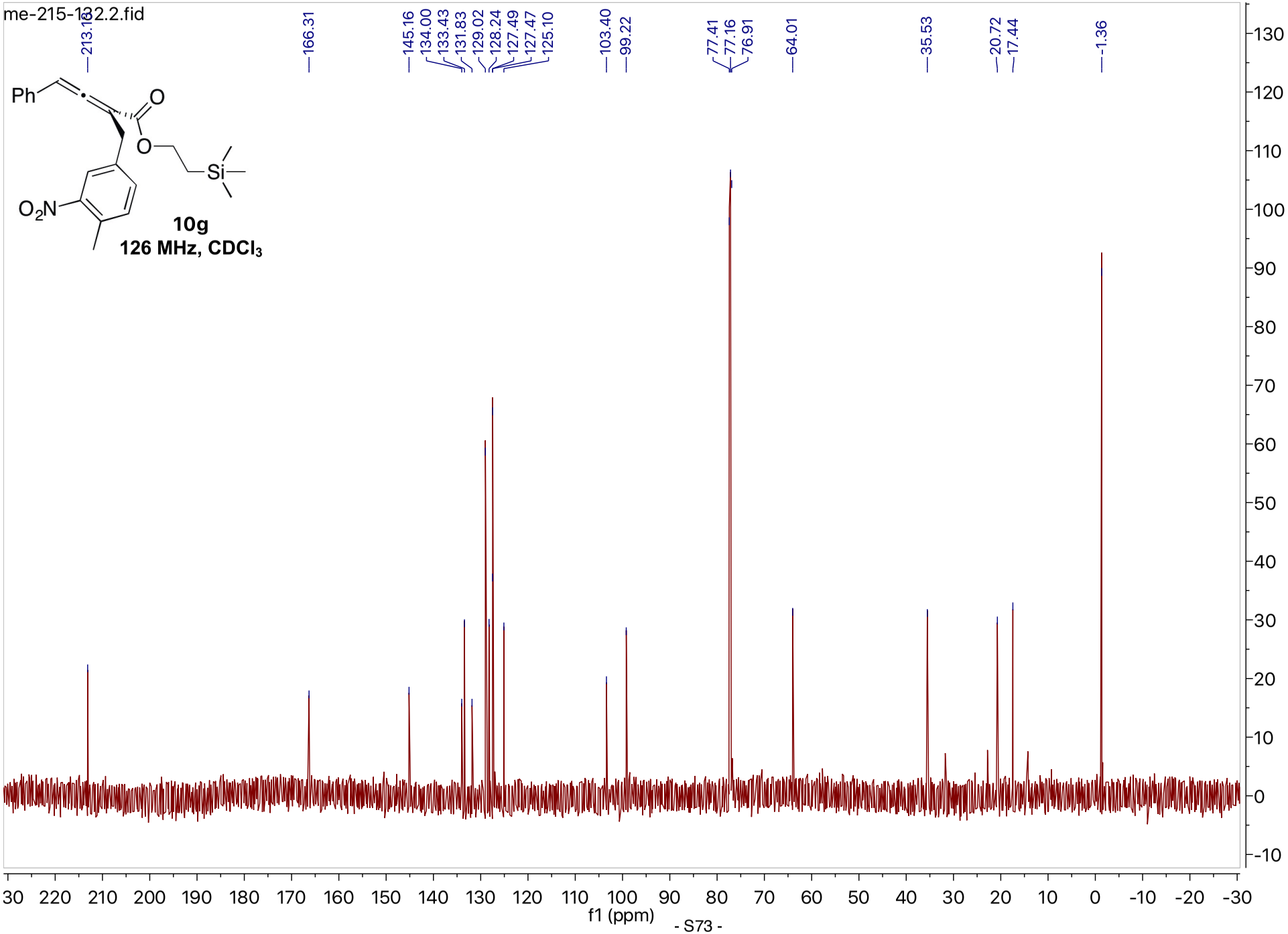

ME-215-174.3.fid
212.41
165.95
132.22
128.86
127.95
127.60
101.83
99.79
78.01
77.58
77.16
76.74
75.09
61.46
19.88
14.33
3.57
Ph
O
O
10d
75 MHz, CDCl3
f1 (ppm)

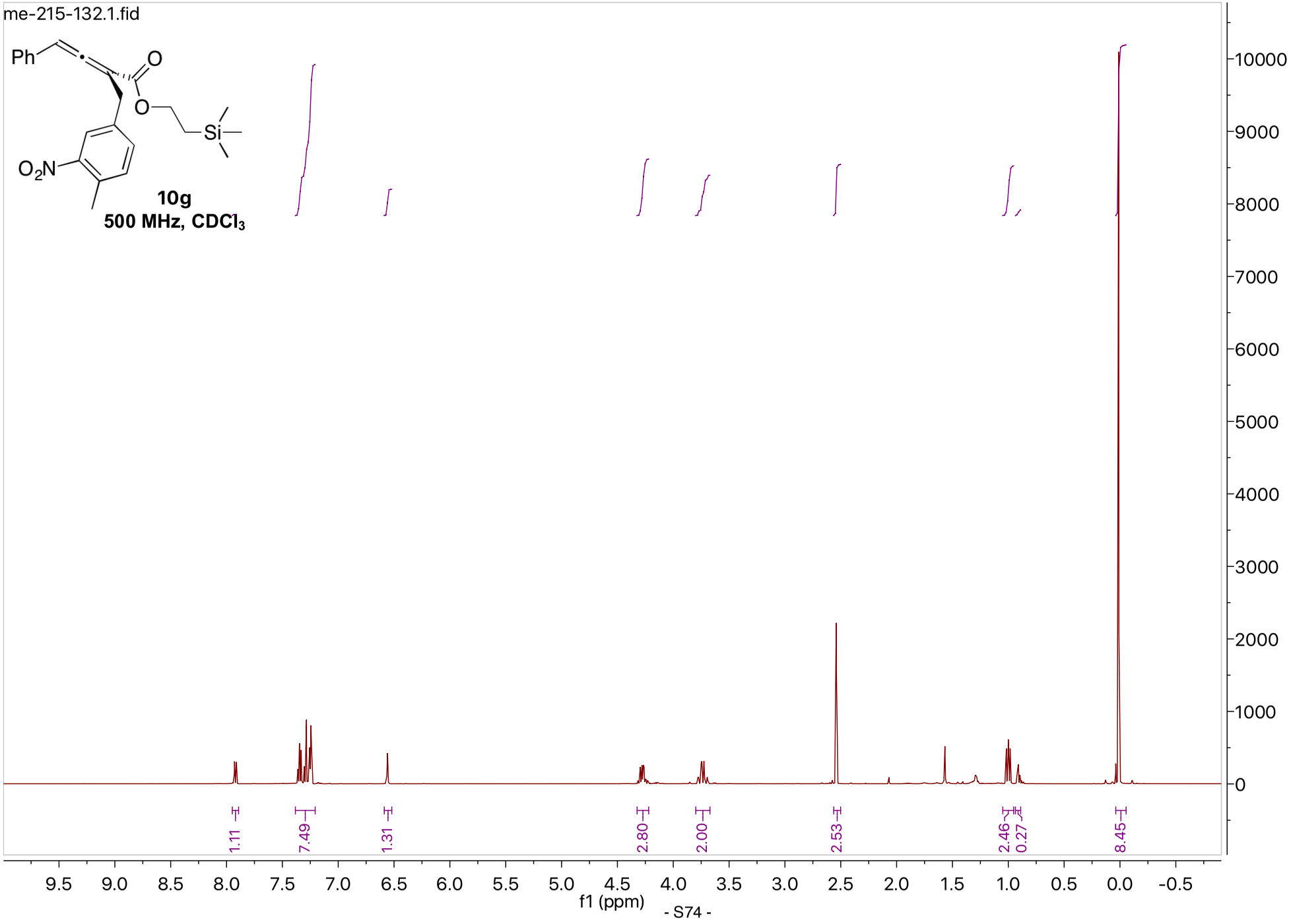

me-215-184.1.fid
O
O
OMe
10e
300 MHz, CDCl3
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
0.85
2.02
2.07
3.11
1.51
1.60
6.03
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

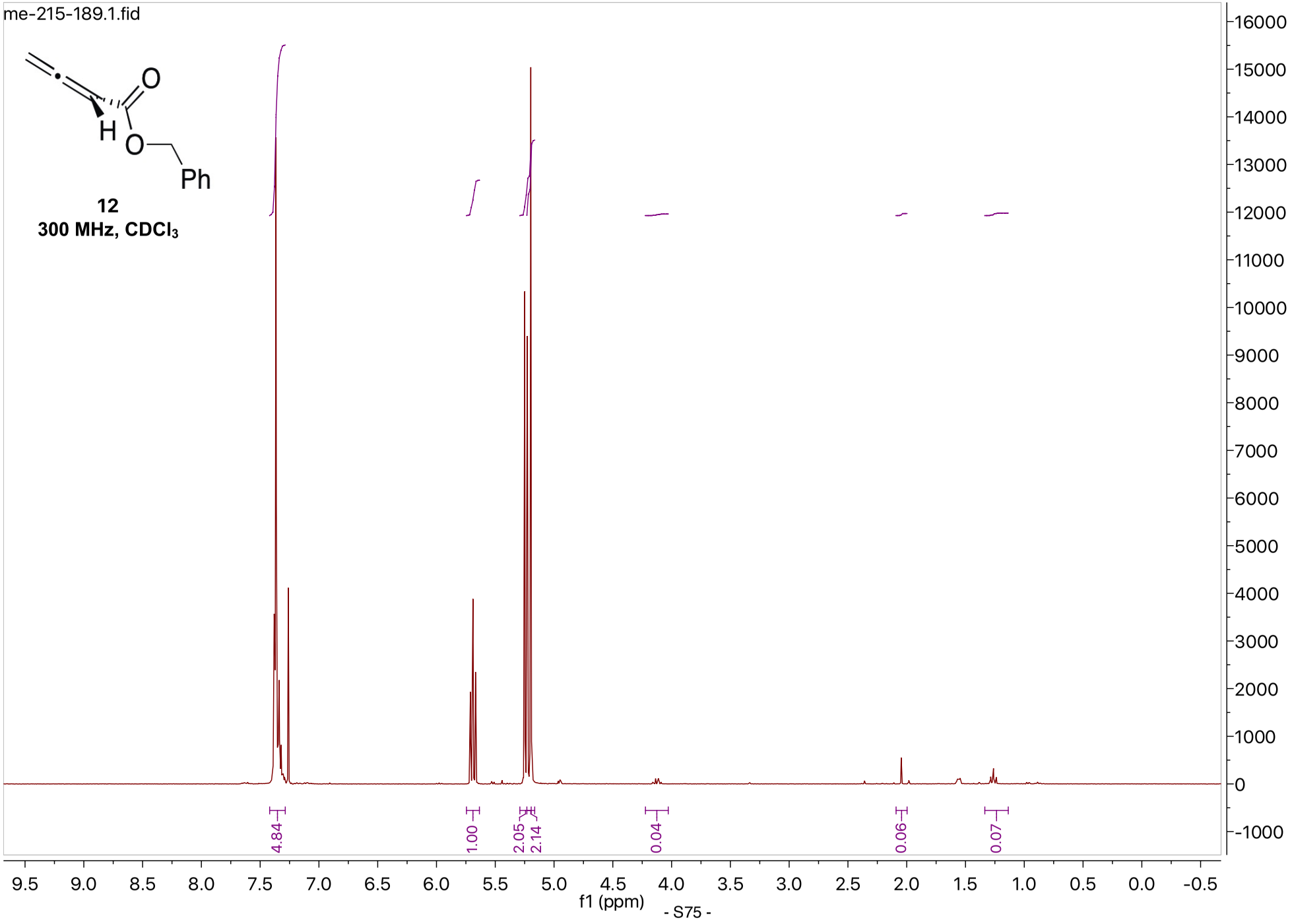

me-215-184
STANDARD PHOSPHORUS PARAMETERS
210.11
167.76
133.35
121.06
100.64
97.18
77.48
77.16
76.84
70.60
64.10
59.16
27.65
25.77
21.49
17.93
13.35
O
O
OMe
10e
100 MHz, CDCl3
f1 (ppm)

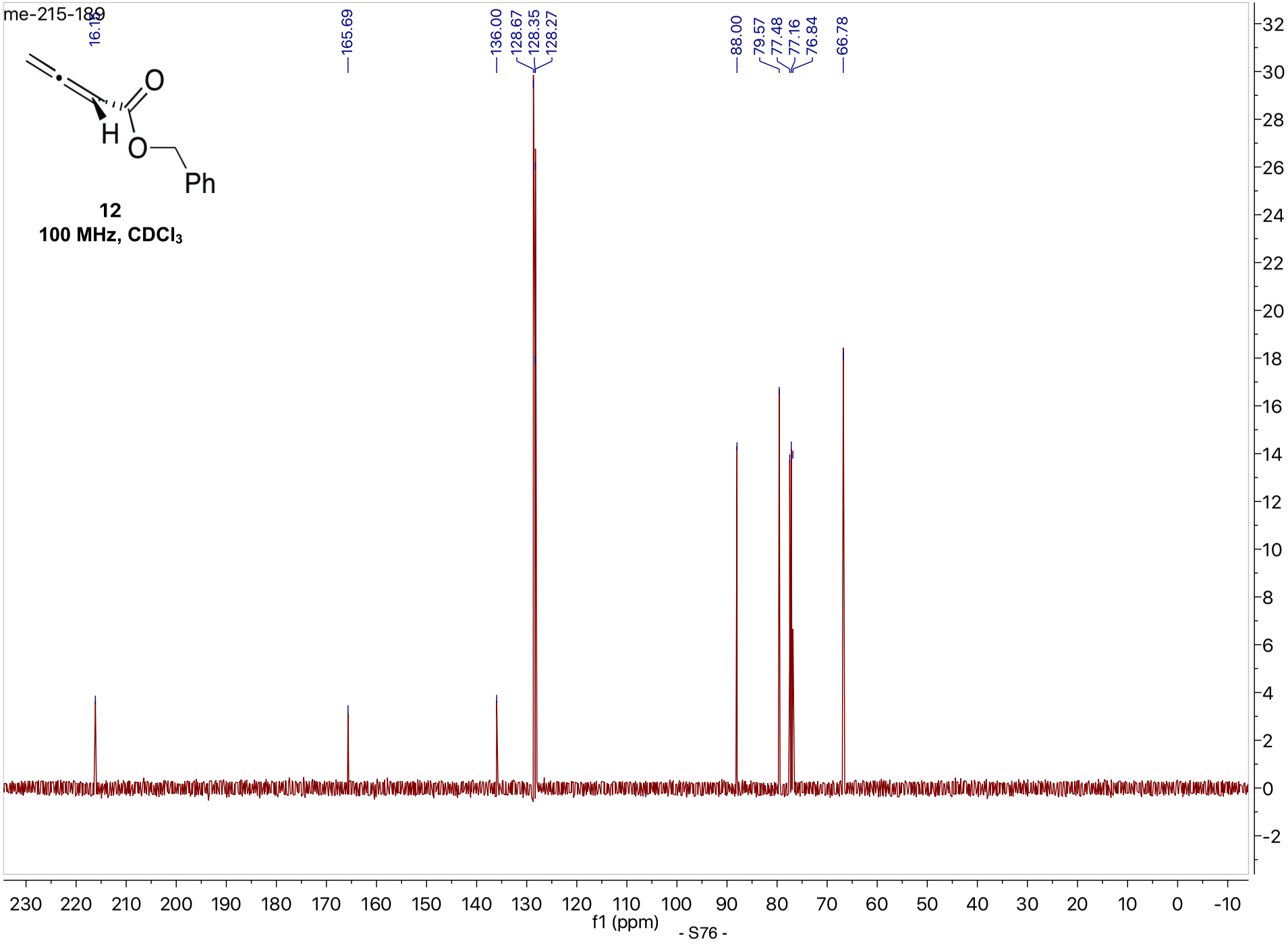

me-215-135-2.3.fid
O
O
F
10f
500 MHz, CDCl3
1.66
1.89
1.02
1.07
0.04
0.04
0.05
2.42
2.08
1.97
2.18
5.37
3.00
f1 (ppm)


me-215-135-2.4.fid
210.45
166.79
162.61
160.67
135.43
130.49
130.43
115.11
114.94
101.84
97.18
77.41
77.16
76.91
72.95
34.77
31.58
31.58
25.62
23.55
21.43
13.36
O
O
F
10f
126 MHz, CDCl3
f1 (ppm)

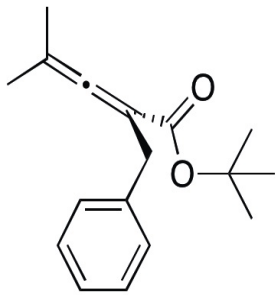

me-215-132.2.fid
213.16
166.31
145.16
134.00
133.43
131.83
129.02
128.24
127.49
127.47
125.10
103.40
99.22
77.41
77.16
76.91
64.01
35.53
20.72
17.44
-1.36
Ph
O
O
Si
O_2N
10g
126 MHz, $CDCl_3$
f1 (ppm)


me-215-132.1.fid
Ph
O
O
Si
O_2N
10g
500 MHz, $CDCl_3$
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.11
7.49
1.31
2.80
2.00
2.53
2.46
0.27
8.45
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


me-215-189.1.fid
O
H
O
Ph
12
300 MHz, CDCl3
4.84
1.00
2.05
2.14
0.04
0.06
0.07
f1 (ppm)

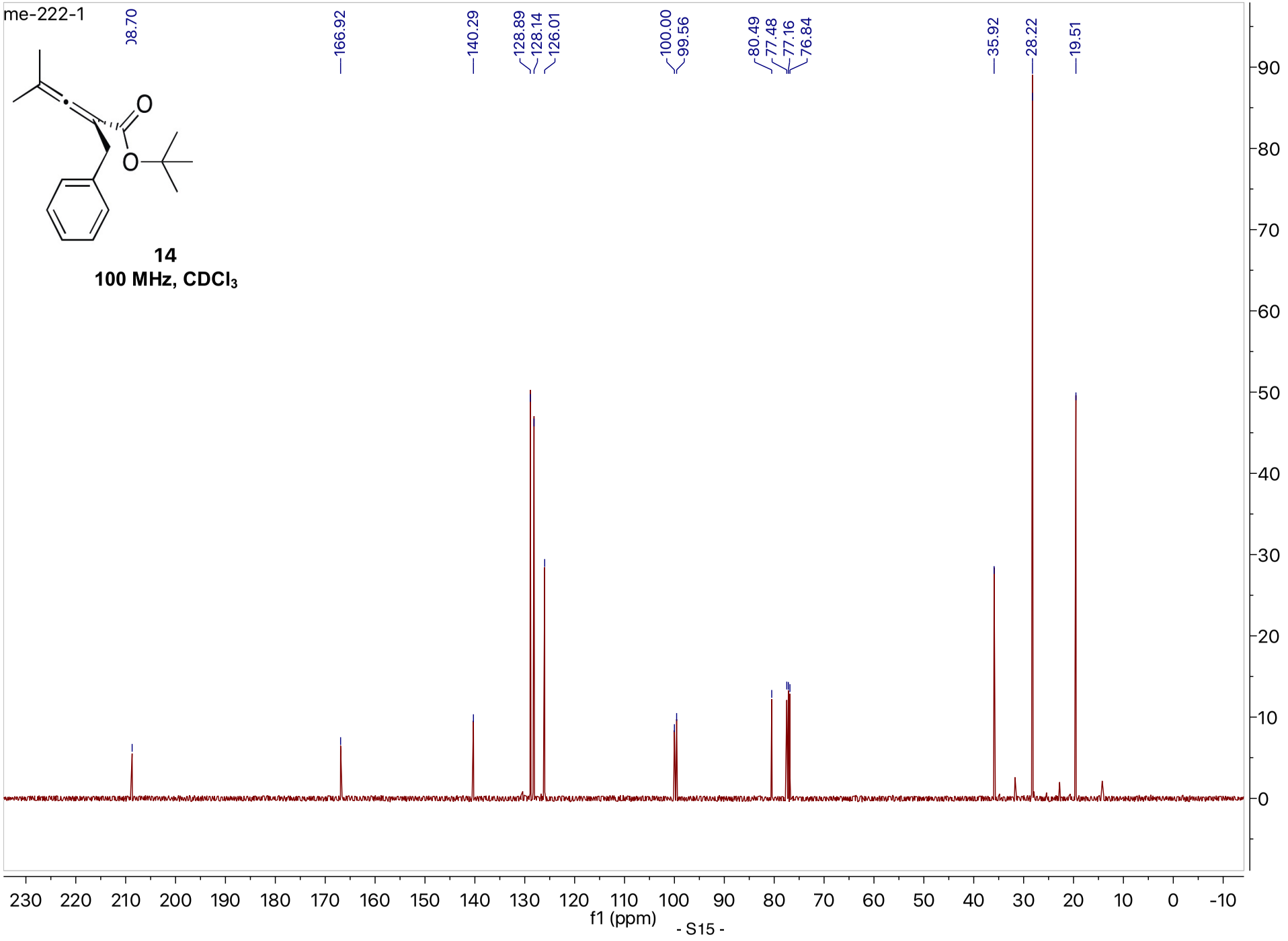

me-215-189
16.19
165.69
136.00
128.67
128.35
128.27
88.00
79.57
77.48
77.16
76.84
66.78
O
H
O
Ph
12
100 MHz, CDCl3
f1 (ppm)

me-222-1-proton



14

400 MHz, $CDCl_3$


me-222-1
208.70
166.92
140.29
128.89
128.14
126.01
100.00
99.56
80.49
77.48
77.16
76.84
35.92
28.22
19.51
O
O
14
100 MHz, CDCl3
f1 (ppm)