Supporting Information

Cascade Reaction of *α*-Aryl Vinyl and Propargyl Sulfonium Salts with Carbon Nucleophiles: Synthesis of Functionalized Benzyl and Homoallyl Thioethers

Vilas M. Awchar[a] and Sundarababu Baskaran[a*]

[a]Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

E-mail: sbhaskar@iitm.ac.in

Table of Contents **Page No.**

1. General information S2
2. Preparation of starting materials S2
3. Optimization studies S3
4. General procedures S5
   a. General procedure for the synthesis of benzyl thioethers
   b. General procedure for the synthesis of homoallyl thioethers
   c. General procedure for one-pot synthesis of benzyl thioethers
5. Single crystal and structure refinement of **3g** S6
6. Characterization data S7
7. References S24
8. NMR spectra S25

1. General Information

All the solvents were distilled prior to use. Dry solvents were prepared according to the standard procedures. All other reagents were used as received from either Aldrich or Lancaster chemical companies. Reactions requiring an inert atmosphere were carried out under an argon atmosphere. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. ^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in ppm from tetramethylsilane in the case of $CDCl_3$ as an internal standard. ^{13}C NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling. As an internal standard, chemical shifts were reported in ppm from the residual solvent. The high-resolution mass spectra (HRMS) were performed on a Micromass Q-TOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were recorded using Bruker-AXS Kappa CCD-Diffractometer with graphite-monochromator MoKα radiation (λ=0.7107 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F2 (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used. Acme (India) silica gel (100-200 mesh) was used for column chromatography.

2. Preparation of starting materials

a) Preparation of sulfonium salts:

Vinyl sulfonium tetraphenylborates **1a-1d** were prepared according to the literature[1,2] Propargyl sulfonium salts **4a-4c** were prepared according to the literature.[3,4]

b) Preparation of C-nucleophiles:

Compounds **2a-2r** were prepared according to the literature.[5-11]

3. Optimisation studies

a) Screening of base:

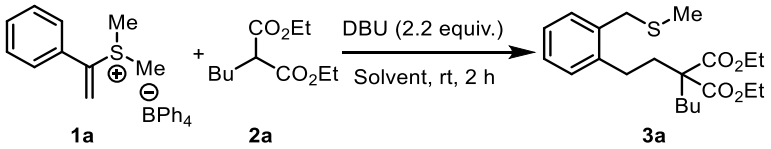
1a 2a 3a

Table 1. Optimization of reaction condition for 1a with 2a: using various bases[a]

Entry	Base	Equiv.	Yield (%)[b]
1	DBU	2.0	73
2	*t*BuOK	2.0	64
3	NaH	2.0	61
4	Et_3N	2.0	NR[c]
5	**DBU**	**2.2**	**76**
6	DBU	2.5	74

[a]Reaction conditions, vinyl sulfonium salt (0.5 mmol, 1.0 equiv.), C-nucleophile (0.55 mmol, 1.1 equiv.) and base dissolved in CH_3CN (2.0 mL) at rt for 2 h. [b]Isolated yield, [c]No reaction.

b) Screening of solvents:



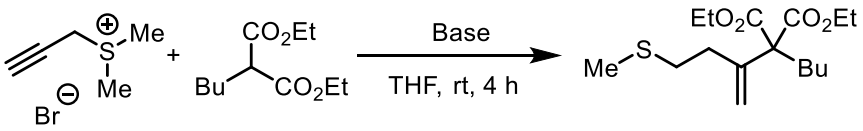
1a 2a 3a

Table 2. Optimization of reaction condition for 1a with 2a: using various solvents[a]

Entry	Solvent	Yield (%)[b]
1	THF	70
2	DCM	71
3	DCE	68
4	**MeCN**	**76**
5	PhMe	67
6	DMF	65
7	DMSO	61

[a]Reaction conditions, vinyl sulfonium salt (0.5 mmol, 1.0 equiv.), C-nucleophile (0.55 mmol, 1.1 equiv.) and DBU (1.1 mmol, 2.2 equiv.), dissolved in solvent (2.0 mL) at rt for 2 h. [b]Isolated yield.

c) Screening of base:



4a **2a** **5a**

Table 3. Optimization of reaction condition for 4a with 2a: using various bases[a]

Entry	Base	Equiv.	Yield (%)[b]
1	DBU	2.0	NR[c]
2	Cs_2CO_3	2.0	18
3	NaOEt	2.0	30
4	*t*BuOK	2.0	32
5	**NaH**	**2.0**	**86**

[a]Reaction conditions, proargyl sulfonium salt (1.0 mmol, 1.0 equiv.), C-nucleophile (1.0 mmol, 1.0 equiv.) and base dissolved in THF (4.0 mL) at rt for 4 h. [b]Isolated yield, [c]No reaction

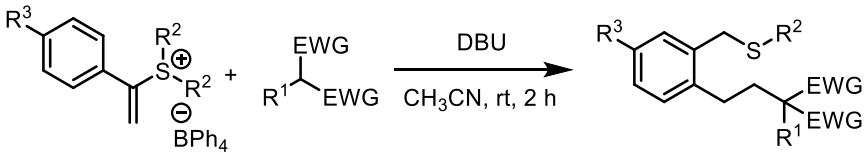
Table 4. Conversion of styrene to benzyl thioether: Multistep reaction versus one-pot reaction.

Entry	Product	Multistep Overall Yield (%)	One-pot Reaction Yield (%)[a]
1	**3a**	57	58
2	**3f**	46	45
3	**3j**	48	51
4	**3k**	51	47
5	**3o**	45	43
6	**3s**	47	48

[a]Isolated yield

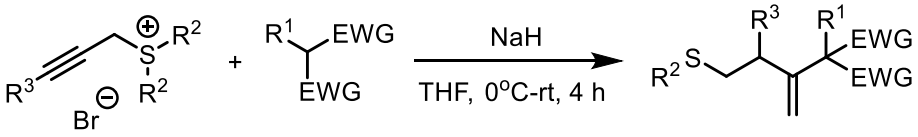
4. General Procedures

a. General Procedure A: Synthesis of benzyl thioethers



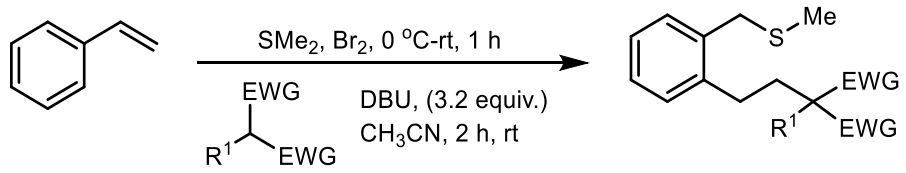
To a solution of vinyl sulfonium salt (1.0 equiv.) in dry MeCN (4 mL/mmol) at rt under N_2 atm. was added C-nucleophiles (1.1 equiv.) and DBU (2.2 equiv.) and the resultant reaction mixture was stirred for 2h at rt. After completion, the reaction mixture was quenched with a saturated solution of NH_4Cl and extracted with DCM (20 mL/mmol × 3). The combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel.

b. General Procedure B: Synthesis of homoallyl thioethers



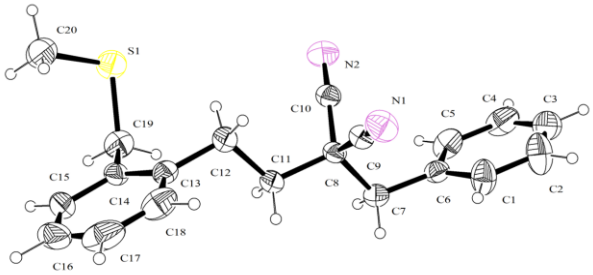
To a suspension of sodium hydride (oil-free, 2.0 equiv.) in THF (4 mL/mmol) at 0 °C, propargyl sulfonium salt (1.0 equiv.) was added. The mixture was stirred for 10 min, and then C-nucleophile (1.0 equiv.) was added dropwise at 0 °C under N_2 atm. After addition, the resultant mixture was stirred at room temperature for 4 h. After completion of the reaction, the mixture was quenched with a saturated NH_4Cl solution and extracted with ethyl acetate (20 mL/mmol × 3). The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure and the crude product was purified using column chromatography over silica gel.

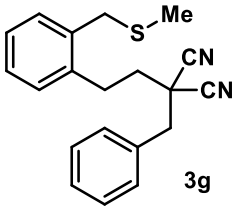
c. General Procedure C: One-pot synthesis of benzyl thioethers



To a solution of bromine (1.0 equiv.) in dry MeCN (2 mL/mmol) at 0 °C under N_2 atm, dimethyl sulfide (3.5 equiv.) was added dropwise over a period of 5 min, resulting in the formation of a yellow precipitate. The yellow reaction mixture was stirred at 0 °C for 10 min, and then a styrene derivative (2.0 equiv.) was added dropwise over a period of 5 min. The homogeneous reaction mixture was allowed to warm to room temperature, resulting in the precipitation of the sulfonium bromide. After 30 minutes, the mother liquor was removed using a syringe, and the reaction mixture was charged with acetonitrile (4 mL/mmol) followed by C-nucleophile (1.1 equiv.) and DBU (3.2 equiv.). The resulting mixture was stirred for another 2 h at room temperature, quenched with a saturated NH_4Cl solution, and extracted with DCM (20 mL/mmol × 3). The combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography.

5. Crystal data and structure refinement of 3g

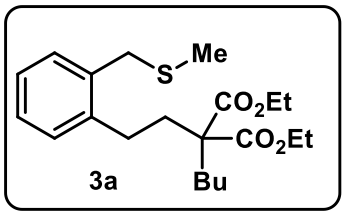




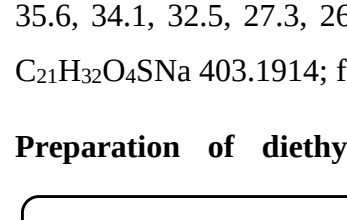
CCDC	2270405
Empirical formula	$C_{20}H_{20}N_2S$
Formula weight	320.44 g/mol
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 5.7116(3) Å α = 90° b = 9.0628(5) Å β = 92.604(3)° c = 34.5624(19) Å γ = 90°
Volume	1787.21(17) $Å^3$
Z, Calculated density	4, 1.191 g/cm^3
Absorption coefficient	0.182 mm^{-1}

6. Characterisation Data

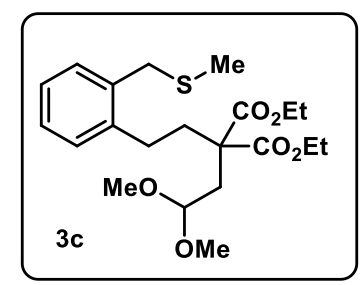
Preparation of diethyl 2-butyl-2-(2-((methylthio)methyl) phenyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2a** (118 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol) was carried out using the general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as eluent, and the pure product **3a** was obtained in (144 mg, 76%) as a colourless oil; **IR (neat):** 2959, 2869, 1725, 1492, 1464, 1255, 1204, 1031, 861, 742, 673 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.13 (m, 4H), 4.22 (q, *J* = 7.2 Hz, 4H), 3.69 (s, 2H), 2.64-2.59 (m, 2H), 2.18-2.13 (m, 2H), 2.03 (s, 3H), 2.01-1.97 (m, 2H), 1.41-1.31 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.24-1.18 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.6, 140.1, 135.5, 130.2, 129.8, 127.4, 126.0, 61.1, 57.6, 35.6, 34.1, 32.5, 27.3, 26.2, 22.9, 15.2, 14.1, 13.9; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{21}H_{32}O_4SNa$ 403.1914; found 403.1914.



Preparation of diethyl 2-benzyl-2-(2-((methylthio)methyl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2b** (137 mg, 0.55 mmol), and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as eluent, and the pure product **3b** was obtained (145 mg, 72%) as a colourless oil; **IR (neat):** 2989, 2931, 1736, 1485, 1268, 1192, 1101, 842, 740, 694 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 3H), 7.17-7.10 (m, 6H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.62 (s, 2H), 3.36 (s, 2H), 2.73-2.69 (m, 2H), 2.08-2.03 (m, 2H), 1.99 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.2, 139.9, 136.1, 135.6, 130.2, 129.9, 129.7, 128.3, 127.5, 127.0, 126.1, 61.4, 58.9, 38.7, 35.5, 33.6, 27.4, 15.2, 14.1; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{24}H_{31}O_4S$ 415.1938; found 415.1938.

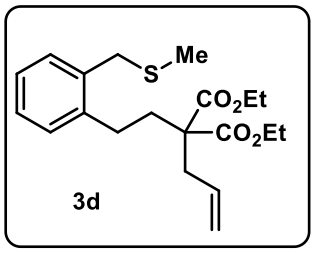


Preparation of diethyl 2-(2,2-dimethoxyethyl)-2-(2-((methylthio)methyl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2c** (136 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The

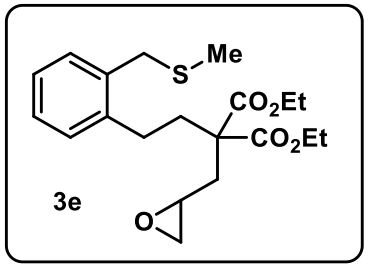


crude product was purified by column chromatography over silica gel, using 20% EtOAc in hexane as the eluent, and the pure product **3c** was obtained (131 mg, 64%) as a colourless oil; **IR (neat):** 2926, 2854, 1731, 1460, 1365, 1187, 1051, 1051, 966, 864, 745 cm^{-1}; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.15 (m, 4H), 4.50 (t, *J* = 5.3 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 3.69 (s, 2H), 3.32 (s, 6H), 2.63-2.59 (m, 2H), 2.35 (d, *J* = 5.3 Hz, 2H), 2.24-2.19 (m, 2H), 2.0 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.1, 139.9, 135.5, 130.2, 129.8, 127.5, 126.1, 102.1, 61.3, 55.4, 53.5, 35.8, 35.5, 34.6, 27.3, 15.2, 14.0; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{21}H_{32}O_6SNa$ 435.1812; found 435.1819.

Preparation of diethyl 2-allyl-2-(2-((methylthio)methyl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2d** (110 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3d** was obtained (127 mg, 70%) as a colourless oil; **IR (neat):** 3072, 2979, 2917, 1725, 1638, 1440, 1368, 1202, 1019, 919, 856, 745, 673 cm^{-1}; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 4H),5.77-5.66 (m, 1H), 5.21-5.12 (m, 2H), 4.22 (q, *J* = 7.0 Hz, 4H), 3.68 (s, 2H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.65-2.61 (m, 2H), 2.16-2.11 (m, 2H), 2.01 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.1, 139.9, 135.5, 132.5, 130.2, 129.8, 127.4, 126.1, 119.0, 61.3, 57.3, 37.3, 35.5, 34.1, 27.1, 15.2, 14.1; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{20}H_{29}O_4S$ 365.1781; found 365.1782.

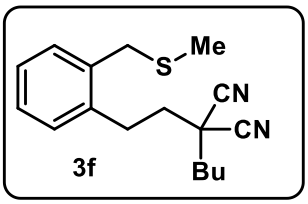


Preparation of diethyl 2-(2-((methylthio)methyl)phenethyl)-2-(oxiran-2-ylmethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2e** (118 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 30% EtOAc in hexane as the eluent, and the pure product **3e** was obtained (131 mg, 69%) as a colourless oil; **IR (neat):** 2982, 2933, 1727, 1446, 1238, 1206,1092, 1022, 924, 859, 750, 671, 698 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.18 (m, 3H), 7.15-7.12 (m, 1H), 4.28-4.23 (m, 4H), 3.74 (d, *J* = 13.1 Hz, 1H), 3.69 (d, *J* = 13.1 Hz, 1H), 3.02-3.00 (m, 1H), 2.77-2.70 (m, 2H), 2.62-2.55 (m, 1H), 2.50-2.48 (m, 1H), 2.37-2.33 (m, 1H), 2.31-2.28 (m, 2H), 2.10-2.06 (m, 1H), 2.02 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 6H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$)

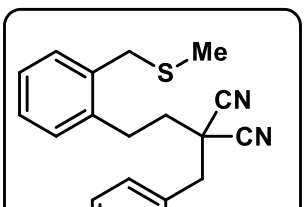


δ 171.0, 171.0, 139.8, 135.6, 130.2. 129.9, 127.5. 126.1, 61.6, 61.5, 56.7, 48.5, 46.6, 36.3, 35.5, 35.0, 27.4, 15.2, 14.0; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{20}H_{28}O_5SNa$ 403.1550; found 403.1552.

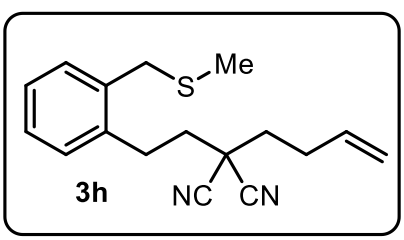
Preparation of 2-butyl-2-(2-((methylthio)methyl)phenethyl)malononitrile: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2f** (67 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **3f** was obtained (88 mg, 62%) as a pale yellow oil; **IR (neat):** 2942, 1454, 1212, 1360, 1052, 752cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 4H), 3.73 (s, 2H), 3.09-3.05 (m, 2H), 2.32-2.27 (m, 2H), 2.09 (s, 3H), 2.00-1.96 (m, 2H), 1.73-1.65 (m, 2H), 1.49-1.40 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 137.3, 135.6, 130.8, 130.0, 129.9, 127.9, 126.9, 115.6, 39.2, 37.7, 37.5, 36.2, 28.6, 27.6, 22.0, 15.6, 13.6; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{17}H_{22}N_2SNa$ 309.1396; found 309.1392.



Preparation of 2-benzyl-2-(2-((methylthio)methyl)phenethyl)malononitrile: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2g** (85 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **3g** was obtained (89 mg, 56%) as a white solid. melting point 88-90 ºC; **IR (neat):** 3022**,** 2923, 2359, 2324, 1711, 1486, 1449, 1085, 748, 699 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (s, 5H), 7.18-7.10 (m, 4H), 3.64 (s, 2H), 3.18 (s, 2H), 3.05-3.01 (m, 2H), 2.28-2.23 (m, 2H), 1.98 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 136.1, 134.7, 130.8, 129.7, 129.2, 128.9, 127.9, 127.7, 126.8, 125.9, 114.1, 42.3, 38.3, 37.9, 35.1, 27.7, 14.6; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{20}H_{20}N_2SNa$ 343.1239; found 343.1240.

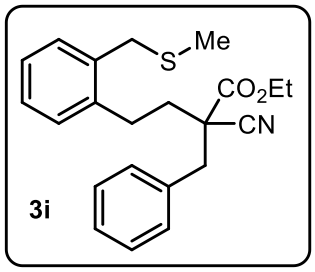


Preparation of 2-(but-3-en-1-yl)-2-(2-((methylthio)methyl)phenethyl)malononitrile: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2h** (66 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by



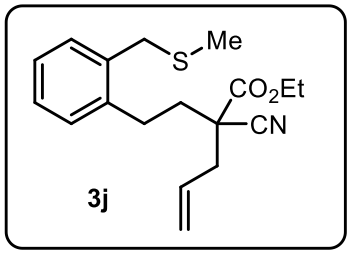
column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3h** was obtained (92 mg, 65%) as a pale yellow oil; **IR (neat):** 3017, 2975, 2925, 2248, 1718, 1646, 1496, 1442, 1307, 1241 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 4H), 5.87-5.77 (m, 1H), 5.20-5.10 (m, 2H), 3.73 (s, 2H), 3.09-3.05 (m, 2H), 2.50-2.44 (m, 2H), 2.34-2.30 (m, 2H), 2.10-2.05 (m, 5H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 137.2, 135.6, 134.5, 130.8, 129.9, 127.9, 127.0, 117.4, 115.3, 39.3, 37.3, 36.9, 36.2, 29.7, 28.6, 15.6; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{17}H_{20}N_2SNa$ 307.1239; found 307.1245.

Preparation of ethyl 2-benzyl-2-cyano-4-(2-((methylthio)methyl)phenyl)butanoate: The



reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2i** (111 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3i** was obtained (123 mg, 67%) as a pale yellow oil; **IR (neat):** 3055, 2989, 1739, 1697, 1489, 1446, 1369, 1227, 1099, 1045, 1024, 745, 701 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 5H), 7.21-7.17 (m, 4H), 4.23-4.14 (m, 2H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.66 (d, *J* = 12.9 Hz, 1H), 3.22 (d, *J* =13.5Hz, 1H), 3.10 (d, *J* = 13.4Hz, 1H), 2.99 (td, *J* = 13, 4.5 Hz, 1H), 2.77 (td, *J* = 12.9, 4.8 Hz, 1H), 2.34 (td, *J* = 13.2, 4.8, Hz, 1H), 2.14 (td, *J* = 13, 4.6 Hz, 1H), 2.04 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 168.4, 138.3, 135.7, 134.0, 130.5, 129.9, 129.9, 128.5, 127.9, 127.6, 126.6, 118.8, 62.8, 51.5, 43.3, 38.7, 35.8, 28.6, 15.5, 13.9; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{22}H_{25}NO_2SNa$ 390.1498; found 390.1497.

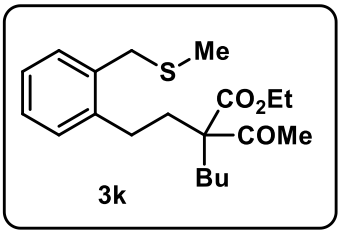
Preparation of ethyl 2-cyano-2-(2-((methylthio)methyl)phenethyl)pent-4-enoate: The



reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2j** (84 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3j** was obtained (154 mg, 64%) as a pale yellow oil; **IR (neat):** 2997, 2934, 1740, 1444, 1301, 1227, 1039, 994, 860, 771, 697 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15-7.06 (m, 4H), 5.81-5.72 (m, 1H), 5.19-5.16 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.66 (d, *J* = 12.9 Hz, 1H), 3.60 (d, *J* = 12.9 Hz, 1H), 2.89 (td, *J* = 13, 4.5 Hz, 1H), 2.69 (td, *J* = 12.9, 4.8 Hz, 1H), 2.62 (dd, *J* = 13.5, 7.2 Hz, 1H),2.51 (dd, *J* = 13.8, 7.2 Hz, 1H),2.16 (td, *J* = 13.1, 4.9 Hz, 1H),

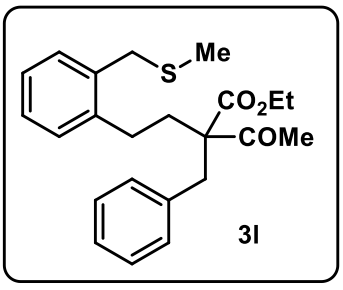
2.03 (td, *J* = 12.9, 4.5 Hz, 1H), 1.99 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 168.3, 138.3, 135.7, 130.4, 129.9, 127.6, 126.5, 120.9, 118.7, 62.8, 49.5, 41.4, 38.0, 35.8, 28.4, 15.5, 14.1; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{18}H_{24}NO_2S$ 318.1522; found 318.1520.

Preparation of ethyl 2-acetyl-2-(2-((methylthio)methyl)phenethyl)hexanoate: The



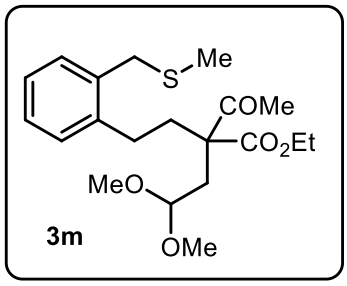
reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2k** (102 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3k** was obtained (119 mg, 68%) as a colourless oil; **IR (neat):** 2959, 2871, 1711, 1455, 1359, 1248, 1160, 1019, 862, 745 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21-7.12 (m, 4H), 4.29-4.19 (m, 2H), 3.71 (d, *J* = 12.9 Hz, 1H), 3.66 (d, *J* = 12.9 Hz, 1H), 2.58-247 (m, 2H), 2.22-2.15 (m, 4H), 2.08 (td, *J* = 13.0, 5.1 Hz, 1H), 2.03 (s, 3H), 1.98 (td, *J* = 11.0, 5.1 Hz, 2H), 1.39-1.32 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.32-1.06 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 3H), **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 205.3, 172.4, 140.0, 135.5, 130.2, 129.7, 127.5, 126.0, 63.4, 61.3, 35.7, 33.0, 31.5, 27.1, 26.8, 26.0, 23.0, 15.3, 14.1, 13.9: **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{20}H_{30}O_3SNa$ 373.1808; found 373.1808.

Preparation of ethyl 2-acetyl-2-benzyl-4-(2-((methylthio)methyl)phenyl)butanoate: The

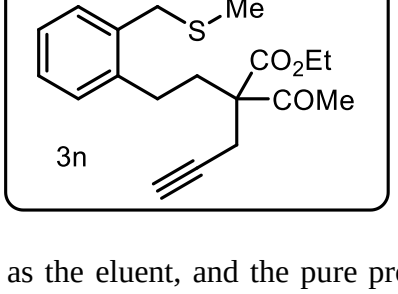


reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2l** (121 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3l** was obtained (134 mg, 70%) as a pale yellow oil; **IR (neat):** 2950, 1716, 1552, 1438, 1357, 1168, 1025, 856, 725 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.21 (m, 3H), 7.19-7.08 (m, 6H), 4.27-4.17 (m, 2H), 3.62 (d, *J* = 13 Hz, 1H), 3.57 (d, *J* =13.1 Hz, 1H), 3.33 (d, *J* = 14.3 Hz, 1H), 3.29 (d, *J* = 14.3 Hz, 1H), 2.66 (td, *J* = 14, 5.4 Hz, 1H), 2.57 (td, *J* = 12.7, 5.4 Hz, 1H), 2.81 (s, 3H), 2.12 (td, *J* = 14.1, 5.2 Hz, 1H), 2.06 (td, *J* = 14, 5.2 Hz, 1H), 1.99 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 205.1, 171.9, 139.8, 136.2, 135.5, 130.3, 129.8, 129.6, 128.4, 127.5, 127.0, 126.1, 64.7, 61.5, 38.0, 35.7, 33.3, 27.6, 27.0, 15.2, 14.0; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{23}H_{29}O_3S$ 385.1832; found 385.1831.

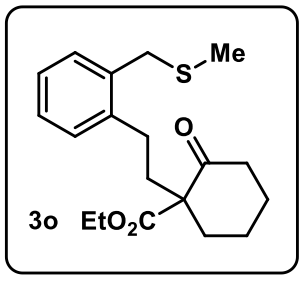
Preparation of ethyl 2-acetyl-4,4-dimethoxy-2-(2-((methylthio)methyl)phenethyl)butanoate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2m** (119 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 20% EtOAc in hexane as the eluent, and the pure product **3m** was obtained (128 mg, 67%) as a pale yellow oil; **IR (neat):** 2982, 2942, 2828, 1714, 1489, 1442, 1352, 1189, 1122, 1050, 962, 768, 745 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 4H), 4.42 (t, *J* = 5.1 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.72(d, *J* = 12.8 Hz, 1H), 3.66(d, *J* = 12.8 Hz, 1H), 3.32 (s, 3H), 3.30 (s, 3H), 2.61-2.48 (m, 2H), 2.40-2.32 (m, 2H), 2.31-2.24 (m, 1H), 2.19 (s, 3H), 2.15-2.07 (m, 1H), 2.03 (s, 3H),1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 204.5, 171.9, 139.8, 135.5, 130.3, 129.7, 127.5, 126.1, 102.3, 61.5, 61.2, 54.2, 53.4, 35.7, 35.6, 33.8, 27.1, 26.8, 15.3, 14.0; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{20}H_{30}O_5SNa$ 405.1706; found 405.1705.



Preparation of ethyl 2-acetyl-2-(2-((methylthio)methyl)phenethyl)pent-4-ynoate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2n** (92 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3n** was obtained (104 mg, 63%) as a colourless oil; **IR (neat):** 3301, 3284, 1439, 1358, 1191, 1100, 977, 857, 748, 671 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 4H), 4.29-4.28 (m, 2H), 3.74 (d, *J* = 13.0 Hz, 1H), 3.68 (d, *J* = 13.0 Hz, 1H), 2.91 (qd, *J* = 17.5, 2.6 Hz, 2H), 2.65-2.50 (m, 2H), 2.41 (td, *J* = 13.8, 5.0 Hz, 1H), 2.30-2.26 (m, 1H), 2.23 (s, 3H), 2.07 (t, *J* = 2.6 Hz, 1H), 2.03 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 203.1, 170.7, 139.6, 135.5, 130.3, 129.9, 127.5, 126.2, 79.1, 71.7, 62.6, 61.9, 35.7, 33.1, 27.0, 26.5, 21.7, 15.3, 14.1; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{19}H_{24}O_3SNa$ 355.1338; found 355.1335.

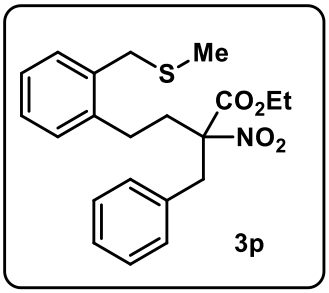


Preparation of ethyl 1-(2-((methylthio)methyl)phenethyl)-2-oxocyclohexane-1-carboxylate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2o** (94



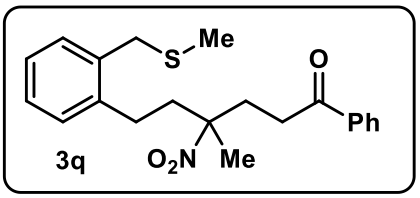
mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **3o** was obtained (102 mg, 61%) as a yellow oil; **IR (neat):** 2935, 2862, 1711, 1443, 1234, 1182, 1016, 742 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.17 (m, 3H), 7.15-7.10 (m, 1H), 4.31-4.22 (m, 2H), 3.79 (d, *J* =13 Hz, 1H), 3.73 (d, *J* =13 Hz, 1H), 2.74 (td, *J* = 13.1, 4.4 Hz, 1H), 2.60-2.45 (m, 4H), 2.11 (td, *J* = 13.4, 4.4 Hz, 1H), 2.05 (s, 3H), 1.83 (td, *J* = 13.3, 4.8 Hz, 1H), 1.81-1.61 (m, 4H), 1.55 (td, *J* = 13.2, 4.4 Hz, 1H), 1.31 (t, *J* =7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 208.0, 172.0, 140.4, 135.6, 130.2, 129.8, 127.4, 126.0, 61.3, 60.8, 41.1, 36.6, 36.4, 35.6, 27.6, 22.6, 15.3, 14.2; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{19}H_{26}O_3SNa$ 357.1495; found 357.1491.

Preparation of ethyl 2-benzyl-4-(2-((methylthio)methyl)phenyl)-2-nitrobutanoate: The



reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2p** (122 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3p** was obtained (108 mg, 56%) as a yellow oil; **IR (neat):** 2976, 1743, 1551, 1489, 1359, 1251, 1193, 1094, 850, 742 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 3H), 7.19-7.10 (m, 6H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.71-3.57 (m, 4H), 2.78-2.72 (m, 2H), 2.38-2.34 (m, 2H), 2.00 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 166.5, 138.3, 135.6, 133.0, 130.5, 129.8, 129.7, 128.8, 127.9, 127.7, 126.5, 96.3, 63.0, 40.2, 35.7, 34.5, 26.7, 15.3, 13.9; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{21}H_{25}NO_4SNa$ 410.1397; found 410.1404.

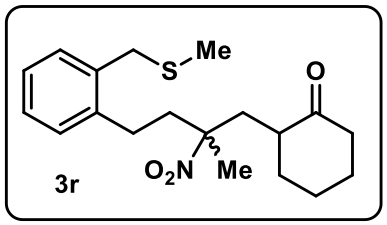
Preparation of 4-methyl-6-(2-((methylthio)methyl)phenyl)-4-nitro-1-phenylhexan-1-one:



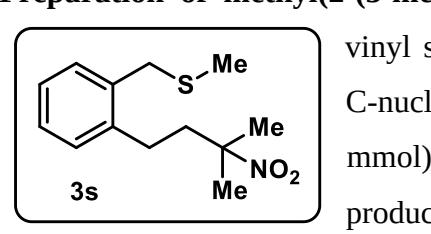
The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2q** (113 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **3q** was obtained (113 mg, 61%) as a pale yellow oil; **IR (neat):** 2961, 2909, 1690, 1545, 1466, 1355, 1043, 836, 743 cm^{-1} **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.25-7.13 (m, 4H), 3.72-3.61 (m, 2H), 3.06-3.00 (m, 2H), 2.76 (td, *J* = 13.0, 4.8 Hz, 1H), 2.63 (td, *J* = 12.9, 4.2 Hz, 1H), 2.57-

2.49 (m, 1H), 2.46-2.32 (m, 2H),2.17 (td, *J* = 13.1, 4.8 Hz, 1H), 2.03 (s, 3H), 1.70 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 198.0, 138.8, 136.4, 135.5, 133.4, 130.5, 129.8, 128.7, 128.0, 127.7, 126.4, 90.8, 41.4, 36.0, 33.6, 33.0, 26.9, 22.1, 15.5; **HRMS** (ESI) m/z: [M+ Na]$^+$ calcd for $C_{21}H_{25}NO_3SNa$ 394.1447; found 394.1446.

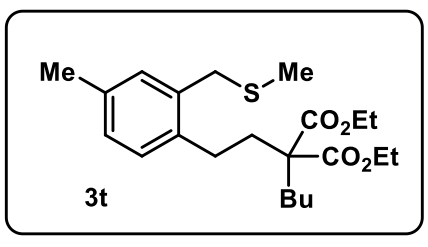
Preparation of 2-(2-methyl-4-(2-((methylthio)methyl)phenyl)-2-nitrobutyl)cyclohexan-1-one: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (242 mg, 0.5 mmol) with C-nucleophile **2r** (101 mg, 0.55 mmol), and DBU (168 mg, 1.1 mmol) was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 30% EtOAc in hexane as the eluent, and the pure product **3r** was obtained (117 mg, 67%) as a yellow oil; **IR (neat):** 2942, 2855, 1708, 1598, 1489, 1444, 1390, 1350, 1134, 1067, 977, 850, 748, cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.18 (m, 2H), 7.16-7.11 (m, 2H), 3.73-3.62 (m, 2H), 2.91 (dd, *J* = 14.8, 5.4 Hz, 0.4H), 2.76-2.68 (m, 1.6H), 2.63-2.51 (m, 1H), 2.48-2.41(m, 1.5H), 2.37-2.25 (m, 3H), 2.12-2.02 (m, 6H), 2.00-1.99 (m, 0.5H), 1.88-1.82 (m, 2H), 1.66-1.61 (m, 2H), 1.52 (s, 2H), 1.47-1.36 (m, 1H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 210.9, 210.5, 139.2, 138.2, 135.5, 130.4, 129.8, 129.8, 127.6, 126.3, 126.3, 91.4, 90.7, 47.0, 46.6, 42.8, 42.2, 42.0, 39.5, 38.7, 37.9, 36.4, 36.3, 35.9, 28.2, 28.0, 27.0, 26.8, 25.5, 25.4, 23.6, 21.1, 15.4; **HRMS** (ESI) m/z: [M+ Na]$^+$ calcd for $C_{19}H_{27}NO_3SNa$ 272.1604; found 272.1610.



Preparation of methyl(2-(3-methyl-3-nitrobutyl)benzyl)sulfane: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1a** (300 mg, 0.62 mmol) with C-nucleophile **2s** (60 mg, 0.68 mmol) and DBU (207 mg, 1.36 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3s** was obtained (95 mg, 61%) as a yellow oil; **IR (neat):** 2981, 2927, 1538, 1446, 1357, 1241, 1052, 968, 852, 755 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 2H), 7.16-7.14 (m, 2H), 3.68 (s, 2H), 2.68-2.64 (m, 2H), 2.23-2.20 (m, 2H), 2.05 (s, 3H), 1.67 (s, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 139.0, 135.5, 130.4, 129.7, 127.6, 126.3, 88.0, 42.4, 35.9, 27.1, 25.9, 15.4; **HRMS** (ESI) m/z: [M+ Na]$^+$ calcd for $C_{13}H_{19}NO_2SNa$ 276.1029; found 276.1035.

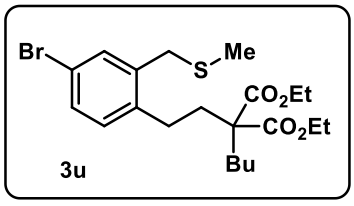


Preparation of diethyl 2-butyl-2-(4-methyl-2-((methylthio)methyl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate



1b (250 mg, 0.5 mmol) with C-nucleophile **2a** (119 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3t** was obtained (140 mg, 70%) as a colourless oil; **IR (neat):** 2967, 2923, 2867, 1729, 1502, 1461, 1367, 1260, 1196, 1054, 1024, 861, 827, 735 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06–6.99 (m, 3H), 4.21 (q, *J* = 7.2 Hz, 4H), 3.66 (s, 2H), 2.58-2.54 (m, 2H), 2.29 (s, 3H), 2.15-2.10 (m, 2H), 2.03 (s, 3H), 2.00-1.95 (m, 2H), 1.40-1.31 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.24-1.17 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.7, 136.9, 135.5, 135.3, 130.8, 129.7, 128.2, 61.1, 57.6, 35.6, 34.2, 32.5, 26.9, 26.2, 22.9, 20.9, 15.3, 14.1, 13.9; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{22}H_{35}O_4S$ 395.2251; found 395.2257.

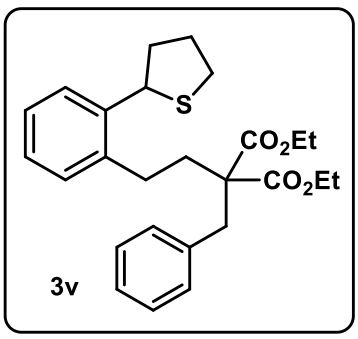
Preparation of diethyl 2-(4-bromo-2-((methylthio)methyl)phenethyl)-2-butylmalonate:



3u

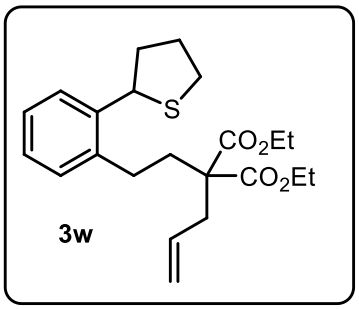
The reaction of α-aryl vinyl sulfonium tetraphenylborate **1c** (282 mg, 0.5 mmol) with C-nucleophile **2a** (119 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3u** was obtained (157 mg, 68%) as a colourless oil; **IR (neat):** 2962**,** 1728, 1473, 1374, 1252, 1195, 1024, 871, 820, 735 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.64 (s, 2H), 2.58-2.34 (m, 2H), 2.12-2.08 (m, 2H), 2.03 (s, 3H), 1.99-1.94 (m, 2H), 1.38-1.32 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H), 1.22-1.16 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.5, 139.1, 137.9, 132.7, 131.4, 130.4, 119.6, 61.2, 57.5, 35.2, 34.0, 32.6, 27.0, 26.2, 22.9, 15.3, 14.1, 13.8; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{21}H_{31}BrO_4SNa$ 481.1019; found 481.1019.

Preparation of diethyl 2-benzyl-2-(2-(tetrahydrothiophen-2-yl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1d** (255 mg, 0.5 mmol) with C-nucleophile **2b** (137 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3v** was obtained (132 mg, 60%)



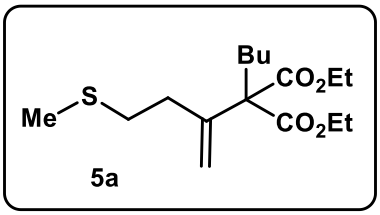
3v

as a colourless oil; **IR (neat):** 3066, 2940, 2882, 1725, 1597, 1452, 1176, 1019, 864, 739, 701 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.28-7.18 (m, 3H), 7.16-7.10 (m, 4H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.63 (t, *J* = 7.1 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 3.35 (s, 2H), 3.20-3.12 (m, 1H), 3.00-2.96 (m, 1H), 2.79-2.67 (m, 1H), 2.65-2.57 (m, 1H), 2.26-2.21 (m, 2H), 2.09-2.03 (m, 2H), 1.98-1.86 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.1, 140.6, 139.1, 136.0, 129.9, 129.3, 128.3, 127.4, 127.0, 126.9, 126.7, 61.4, 58.9, 47.6, 39.7, 38.7, 34.1, 33.4, 31.1, 28.0, 14.1; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{32}O_4SNa$ 463.1914; found 463.1926.



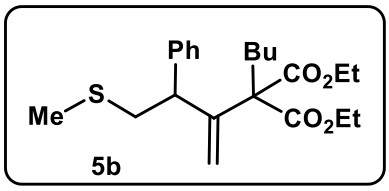
Preparation of diethyl 2-allyl-2-(2-(tetrahydrothiophen-2-yl)phenethyl)malonate: The reaction of α-aryl vinyl sulfonium tetraphenylborate **1d** (255 mg, 0.5 mmol) with C-nucleophile **2b** (110 mg, 0.55 mmol) and DBU (168 mg, 1.1 mmol), was carried out using general procedure **A**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **3w** was obtained (121 mg, 62%) as a colourless oil; **IR (neat):** 2980, 2863, 1731, 1641, 1442, 1369, 1262, 1176, 1097, 1022, 922, 855, 752 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.6 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H),7.07 (d, *J* = 7.5 Hz, 1H), 5.75-5.62 (m, 1H), 5.21-5.12 (m, 2H), 4.70 (t, *J* = 7.9 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 4H), 3.18-3.13 (m, 1H), 3.01-2.97 (m, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.66-2.53 (m, 2H), 2.34-2.27 (m, 2H), 2.16-2.05 (m, 2H), 2.02-1.90 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 171.0, 140.5, 139.2, 132.5, 129.4, 127.4, 126.9, 126.7, 119.0, 61.3, 57.3, 47.6, 39.8, 37.3, 34.5, 33.4, 31.1, 27.7, 14.1; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{31}O_4S$ 391.1938; found 391.1937.

Preparation of diethyl 2-butyl-2-(4-(methylthio)but-1-en-2-yl)malonate: The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol with C-nucleophile **2a** (216 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **5a** was obtained (272 mg, 86%) as a pale yellow oil; **IR (neat):** 2959, 2920, 1728, 1635, 1460, 1240, 1199, 1111, 1033, 905, 862 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.22 (s, 1H), 5.16 (s, 1H), 4.21-4.17 (m, 4H), 2.67-2.64 (m, 2H), 2.41-2.37 (m, 2H), 2.13 (s, 3H), 2.02-2.01 (m, 2H), 1.31-1.25 (m, 10H), 0.90-0.88 (m, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.2, 144.1,

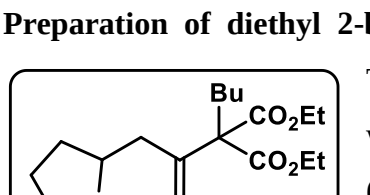


114.5, 63.9, 61.2, 33.8, 33.3, 33.0, 27.0, 23.0, 15.5, 14.0, 13.8; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{16}H_{28}O_4SNa$ 339.1601; found 339.1607.

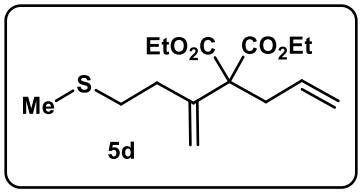
Preparation of diethyl 2-butyl-2-(4-(methylthio)-3-phenylbut-1-en-2-yl)malonate: The reaction of propargyl sulfonium salt **4b** (257 mg, 1.0 mmol) with C-nucleophile **2a** (216 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **5b** was obtained (180 mg, 46%) as a yellow oil; **IR (neat):** 2962, 2865, 1723, 1632, 1449, 1242, 1193, 1117, 1033, 916, 864, 699 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.19-7.16 (m, 1H), 5.67 (s, 1H), 5.51 (s, 1H), 4.09-4.01 (m, 1H), 3.92-3.86 (m, 2H), 3.85-3.77 (m, 1H), 3.60 (dd, *J* = 9.2, 5.7 Hz, 1H), 3.02 (dd, *J* = 12.9, 5.6 Hz, 1H), 2.79 (dd, *J* = 12.8, 9.4 Hz, 1H), 2.04-1.89 (m, 5H), 1.29-1.11 (m, 7H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 6.1 Hz, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.9, 146.3, 141.9, 128.2, 127.9, 126.6, 116.2, 64.1, 60.9, 60.9, 48.4, 42.9, 33.8, 26.8, 22.8, 16.2, 13.8, 13.7; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{22}H_{33}O_4S$ 393.2094; found 393.2094.



Preparation of diethyl 2-butyl-2-(3-(tetrahydrothiophen-2-yl)prop-1-en-2-yl)malonate: The reaction of propargyl sulfonium salt **4c** (207 mg, 1.0 mmol) with C-nucleophile **2a** (216 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **5c** was obtained (277 mg, 81%) as a pale yellow oil; **IR (neat):** 2952, 2868, 1725, 1635, 1466, 1368, 1242, 1205, 1036, 905, 862 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.26 (s, 1H), 5.21 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 3.62-3.55 (m, 1H), 2.90-2.80 (m, 2H), 2.51 (dd, *J* = 16.4, 6.1 Hz, 1H), 2.33 (dd, , *J* = 16.4, 7.8 Hz, 1H), 2.14-1.96 (m, 4H), 1.92-1.85 (m, 1H), 1.64-1.55 (m, 1H), 1.34-1.24 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 170.3, 143.7, 114.8, 63.7, 61.2, 61.1, 46.6, 40.9, 37.0, 33.9, 32.2, 30.1, 26.9, 23.0, 14.0, 13.8; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{18}H_{30}O_4SNa$ 365.1757; found 365.1752.

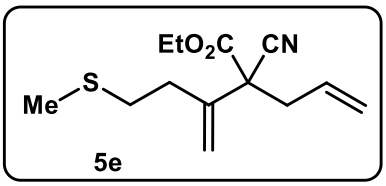


Preparation of diethyl 2-allyl-2-(4-(methylthio)but-1-en-2-yl)malonate: The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol) with C-nucleophile **2d** (200 mg, 1.0 mmol) and sodium hydride (48

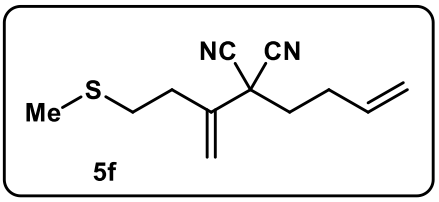


mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 5% EtOAc in hexane as the eluent, and the pure product **5d** was obtained (234 mg, 78%) as a colourless oil; **IR (neat):** 3080, 2979, 2914, 1731, 1635, 1440, 1288, 1045, 914, 862 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88-5.80 (m, 1H), 5.21 (s, 1H), 5.18 (s, 1H), 5.11-5.04 (m, 2H), 4.1-4.19 (m, 4H), 2.82-2.80 (m, 2H), 2.67-2.64 (m, 2H), 2.43-2.39 (m, 2H), 2.11 (s, 3H), 1.28-1.25 (m, 6H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 169.7, 144.0, 133.6, 118.1, 114.8, 64.0, 61.4, 38.7, 33.3, 33.1, 15.5, 13.9; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{15}H_{24}O_4SNa$ 323.1288 found 323.1291.

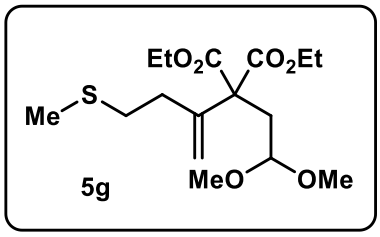
Preparation of ethyl 2-cyano-2-(4-(methylthio)but-1-en-2-yl)pent-4-enoate: The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol) with C-nucleophile **2j** (153 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **5e** was obtained (187 mg, 74%) as a colourless oil; **IR (neat):** 3083, 2982, 2917, 2851, 1743, 1644, 1440, 1222, 916, 853 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.83-5.73 (m, 1H), 5.49 (s, 1H), 5.30-5.25 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.87 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.71-2.64 (m, 3H), 2.44-2.41 (m, 2H), 2.13 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 166.6, 140.4, 130.6, 121.0, 117.6, 116.0, 63.2, 54.9, 39.4, 32.5, 31.9, 15.6, 13.9; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{13}H_{20}NO_2S$ 254.1209; found 254.1211.



Preparation of 2-butyl-2-(4-(methylthio)but-1-en-2-yl)malononitrile: The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol) with C-nucleophile **2h** (120 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 10% EtOAc in hexane as the eluent, and the pure product **5f** was obtained (147 mg, 67%) as a yellow oil; **IR (neat):** 2959, 2926, 2868, 1644, 1457, 1434, 1374, 1240, 1123, 1019, 922 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.69 (s, 1H), 5.38 (s, 1H), 5.17-5.10 (m, 2H), 2.76-2.72 (m, 2H), 2.52-2.49 (m, 2H), 2.40-2.33 (m, 2H), 2.17-2.12 (m, 5H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 137.9, 134.2, 117.5, 117.4, 114.4, 43.0, 37.0, 32.4, 31.0, 29.4, 15.7; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{12}H_{16}N_2SNa$ 243.0926; found 243.0929.



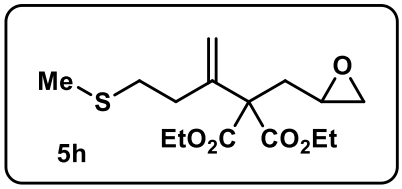
Preparation of diethyl 2-(2,2-dimethoxyethyl)-2-(4-(methylthio)but-1-en-2-yl)malonate:



5g

The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol) with C-nucleophile **2c** (248 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 20% EtOAc in hexane as the eluent, and the pure product **5g** was obtained (247 mg, 71%) as a pale yellow oil; **IR (neat):** 2982, 1727, 1447, 1290, 1179, 1096, 1032, 911 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.32 (s, 1H), 5.19 (s, 1H), 4.55 (t, *J* = 5.0 Hz, 1H); 4.22-4.15 (m, 4H), 3.29 (s, 6H), 2.67-2.64 (m, 2H), 2.45-2.42 (m, 2H), 2.37 (d, *J* = 4.2 Hz, 2H), 2.11 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$) δ 169.6, 144.0, 115.0, 102.2, 61.4, 61.1, 53.4, 37.9, 33.5, 33.2, 15.5, 13.9; **HRMS** (ESI) m/z: $[M+ Na]^+$ calcd for $C_{16}H_{28}O_6SNa$ 371.1499; found 371.1496.

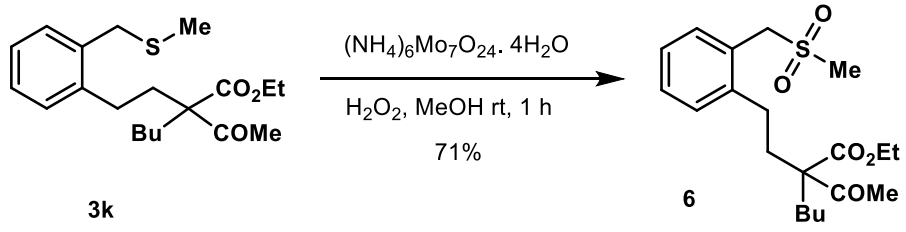
Preparation of diethyl 2-(4-(methylthio)but-1-en-2-yl)-2-(oxiran-2-ylmethyl)malonate:



5h

The reaction of propargyl sulfonium salt **4a** (181 mg, 1.0 mmol) with C-nucleophile **2e** (216 mg, 1.0 mmol) and sodium hydride (48 mg, 2.0 mmol), was carried out using general procedure **B**. The crude product was purified by column chromatography over silica gel, using 20% EtOAc in hexane as the eluent, and the pure product **5h** was obtained (240 mg, 76%) as a pale yellow oil; **IR (neat):** 2982, 2912, 1721, 1634, 1446, 1257, 1204, 1110, 1078, 1048, 922 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.22 (s, 2H), 4.27-4.20 (m, 4H), 3.16-3.12 (m, 1H), 2.74 (t, *J* = 5.0 Hz, 1H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.48-2.42 (m, 3H), 2.32 (dd, *J* = 14.5, 5 Hz, 1H), 2.20 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.12-2.12 (m, 3H), 1.28 (td, *J* = 7.1, 1.6 Hz, 6H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 169.7, 169.6, 144.1, 114.8, 62.6, 61.7, 61.7, 48.9, 47.3, 37.5, 33.3, 33.1, 15.5, 13.9; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{15}H_{25}O_5S$ 317.1417; found 317.1421.

Procedure for oxidation of benzyl thioether 3k to sulfone 6 using ammonium heptamolybdate:

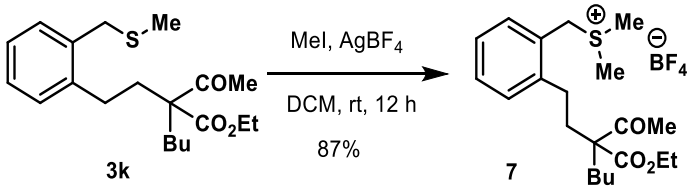


3k

6

Following the literature procedure,[12] the oxidation of benzyl thioether **3k** to sulfone **6** was achieved: A mixture of benzyl thioether **3k** (1 mmol, 0.35 g), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.123 g, 10 mol%) and 30% aq. H_2O_2 (4 mmol 0.48 g) in CH_3OH (3 mL) was stirred at room temperature. Upon completion of the reaction, as indicated by TLC, the methanol was removed under reduced pressure, and the crude mixture was diluted with ether and washed with aq. $NaHCO_3$ solution. The organic layer was washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Then crude product was purified by column chromatography over silica gel, using 30% EtOAc in hexane as the eluent, and the pure product **6** was obtained (272 mg, 81%) as a white solid; melting point 88-90 ^oC; **IR (neat):** 3455, 2952, 2862, 1701, 1460, 1356, 1182, 1036, 963, 859, 768 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.33-7.29 (m, 1H), 7.27-7.22 (m, 2H), 4.53 (d, *J* = 14 Hz, 1H), 4.41 (d, *J* = 14 Hz, 1H), 4.32-4.22 (m, 2H), 2.88 (s, 3H), 2.66 (td, *J* = 14, 4.6 Hz, 1H), 2.56 (td, *J* = 13, 5 Hz, 1H), 2.20 (s, 3H), 2.09 (td, *J* = 13.8, 4.5 Hz, 1H), 2.04-1.89 (m, 3H), 1.38-1.27 (m, 5H), 1.25-1.14 (m, 1H), 1.13-1.02 (m, 1H), 0.90 (t, *J* = 7.24 Hz, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.8, 172.4, 141.9, 132.0, 130.2, 129.4, 126.8, 126.0, 63.3, 61.5, 57.5, 40.0, 33.6, 32.7, 28.3, 27.1, 26.1, 23.0, 14.1, 13.8; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{31}O_5S$ 383.1887; found 383.1885.

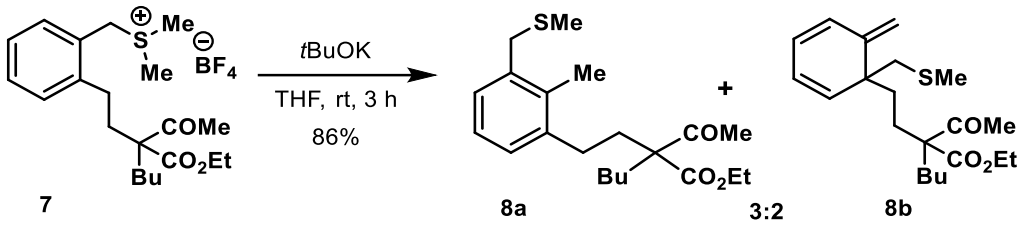
Procedure for methylation of 3k using methyl iodide and silver tetrafluoroborate:



Following the literature procedure,[13] methylation of **3k** to sulfonium salt **7** was achieved: To aa solution of benzyl thioether **3k** (1 mmol, 0.35 g) in DCM (6 mL) was added iodomethane (2 mmol, 0.284 g) followed by silver tetrafluoroborate (1 mmol, 0.195 g) and the resultant mixture was stirred at room temperature under N_2 in dark. After completion of the reaction, the mixture was filtered over a pad of Celite, and the filter cake was washed with DCM. The combined filtrate was removed in vacuo to afford the desired product **7** (0.392 g, 87%) as a viscous colourless oil. **IR (neat):** 2949, 2868, 1704, 1428, 1359, 1045, 859, 777, 696, 649 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 4.95 (d, *J* = 12.7 Hz, 1H), 4.81 (d, *J* = 12.7 Hz, 1H), 4.34-4.20 (m, 2H), 3.08 (s, 3H), 3.03 (s, 3H), 2.63-2.48 (m, 2H), 2.24 (s, 3H), 2.04-2.18 (m, 4H), 1.34-1.30 (m, 5H), 1.24-1.13 (m, 1H), 1.11-1.03 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C**

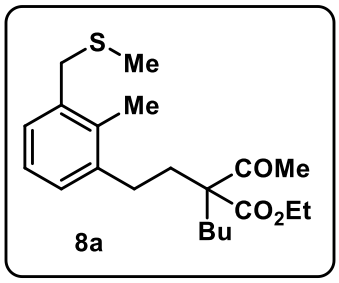
{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.0, 172.4, 141.6, 132.7, 130.8, 130.7, 127.7, 125.6, 63.2, 61.6, 45.6, 34.5, 34.1, 29.0, 27.4, 26.2, 24.3, 24.0, 22.9, 14.1, 13.7; **HRMS** (ESI) m/z: [M+ H-BF_4]$^+$ calcd for $C_{21}H_{34}O_3S$ 366.2218; found 366.2212.

Procedure for Thia-Sommelet-Hauser rearrangement of sulfonium salt 7.



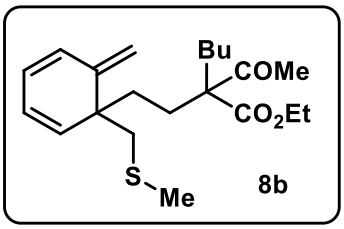
To the of solution Sulfonium salt **7** (1 mmol, 0.452 g) in THF (3 mL) was added potassium *tert*-butoxide (1 mmol, 0.112 g), and the resultant mixture was stirred at room temperature under N_2. Upon completion of the reaction, as indicated by TLC, the crude mixture was quenched with a saturated solution of NH_4Cl and then extracted with ethyl acetate (3x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified using column chromatography over silica gel using 5% EtOAc in hexane as the eluent, and the pure product **8a** and **8b** was obtained (0.313 g, 86%) as a colourless oil.

IR (neat): 2961, 2875, 1708, 1459, 1359, 1245, 1168, 1026, 793, 742 cm^{-1}; **^{1}H NMR** (400



MHz, $CDCl_3$) δ 7.08-7.01 (m, 3H), 4.26-4.19 (m, 2H), 3.68 (s, 2H), 2.50-2.31 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 2.14-2.07 (m, 1H), 2.03 (s, 3H), 2.00-1.93 (m, 3H), 1.35 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20-1.05 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.2, 172.5, 140.5, 136.2, 134.4, 128.3, 128.1, 125.4, 63.4, 61.2, 37.1, 32.3, 31.3, 28.6, 26.7, 26.0, 23.0, 15.3, 14.3, 14.1, 13.8; **HRMS** (ESI) m/z: [M+ H]$^+$ calcd for $C_{21}H_{33}O_3S$ 365.2145; found 365.2158.

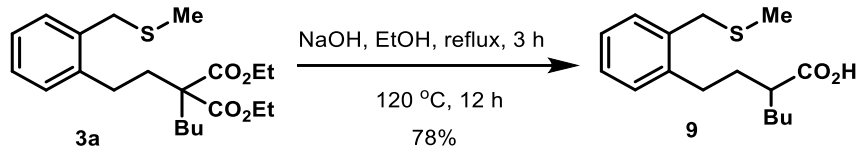
IR (neat): 2956**,** 2923, 2868, 1701, 1460, 1359, 1254, 1196, 1022, 754 cm^{-1}; **^{1}H NMR** (400



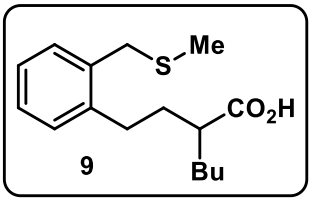
MHz, $CDCl_3$) δ 6.19 (d, *J* = 9.2 Hz, 1H), 6.11 (dd, *J* = 9.2, 5.6 Hz, 1H), 5.89-5.85 (m, 1H), 5.57-5.53 (m, 1H), 5.27 (s, 1H), 4.98 (d, *J* = 8.8 Hz, 1H), 4.26-4.12 (m, 2H), 2.60 (d, *J* = 12.5 Hz, 1H), 2.54-2.50 (m, 1H), 2.08-2.06 (m, 6H), 1.86-1.70 (m, 3H), 1.65-1.57 (m, 1H), 1.42-1.20 (m, 5H), 1.24-1.22 (m, 2H), 1.02-0.95 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 205.3, 172.5, 172.5,

148.0, 147.7, 134.6, 134.6, 129.6, 129.4, 124.1, 123.9, 122.9, 122.7, 114.6, 114.3, 63.1, 61.1, 50.2, 50.2, 45.8, 45.8, 37.3, 37.1, 30.8, 30.7, 26.6, 26.4, 26.4, 25.8, 22.9, 17.9, 14.1; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{33}O_3S$ 365.2145; found 365.2142.

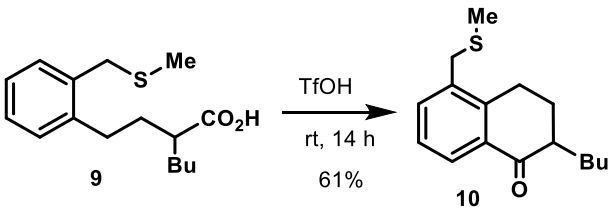
Procedure for base hydrolysis of 3a, followed by decarboxylation



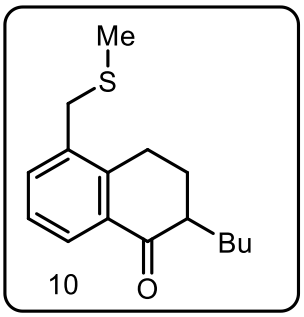
Following the modified literature procedure,[14] hydrolysis of **3a**, followed by decarboxylation to acid **9** was achieved: To a solution of compound **3a** (0.76 g, 2 mmol) in EtOH was added aq. solution of NaOH (2 M) and the resultant mixture was heated to reflux for 3 h. The EtOH was evaporated under reduced pressure, and the resulting aqueous layer was extracted with ethyl acetate. The aqueous phase was acidified to pH ~1 using 3 M HCl and extracted with ethyl acetate. Then, combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was to be heated at 120 °C with stirring for 12 h. After cooling, the reaction mixture to room temperature was diluted with ethyl acetate, dried over anhydrous Mg_2SO_4, and evaporated. The crude product was purified by column chromatography over silica gel using 30% EtOAc in hexane as the eluent to afford the carboxylic acid **9** (0.436 g, 78%) as a colourless oil. **IR (neat):** 3490, 3053, 2959, 2065, 1701, 1636, 1452, 1264, 751, 708 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.14 (m, 4H), 3.75-3.66 (m, 2H), 2.79-2.70 (m, 2H), 2.48 (s, 1H), 2.0-1.96 (m, 4H), 1.80-1.70 (m, 2H), 1.57 (s, 1H), 1.33 (s, 4H), 0.89 (s, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.8, 140.2, 135.5, 130.2, 129.7, 127.4, 126.0, 45.4, 35.8, 33.4, 31.9, 30.3, 29.4, 22.6, 15.4, 13.9; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{24}O_2SNa$ 303.1389; found 303.1393.



Procedure for intramolecular Friedel-Craft acylation of carboxylic acid 9



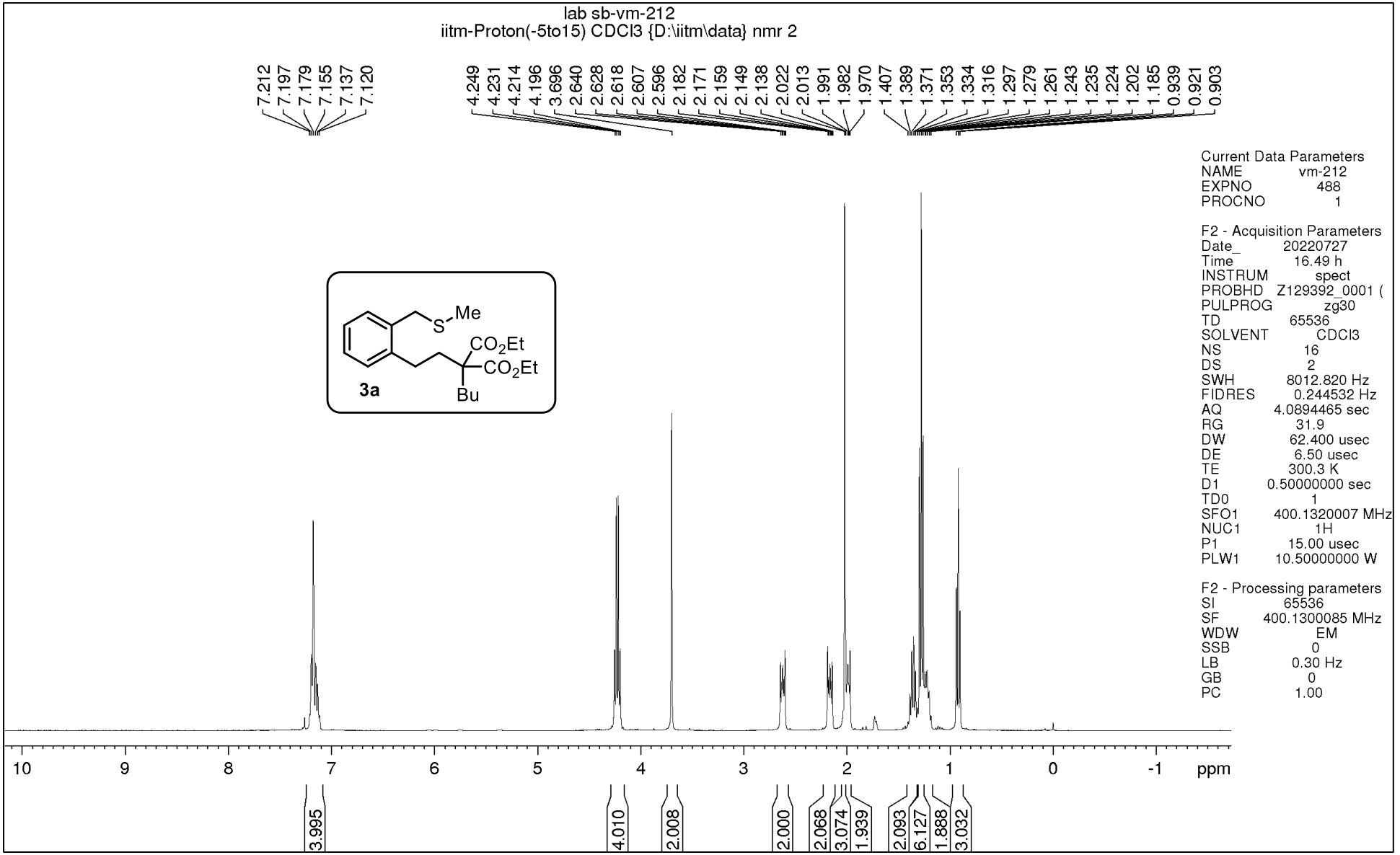
Following the literature procedure,[15] intramolecular Friedel-Craft acylation of carboxylic acid



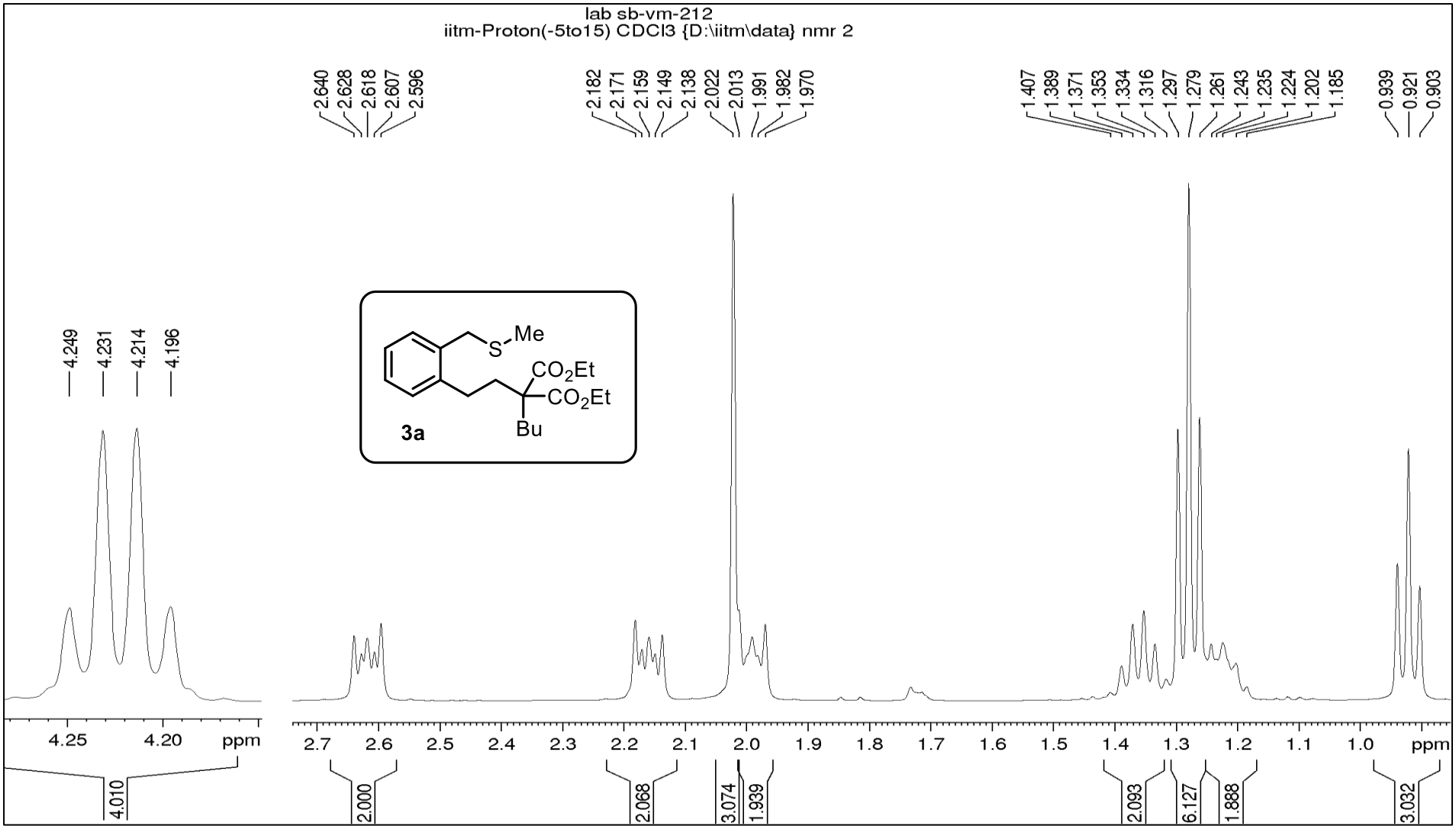
9 to α-tetralone derivative **10** was achieved: The carboxylic acid **9** (280 mg, 1.0 mmol) and triflic acid (1.0 ml) were stirred at room temperature under N_2. Upon completion of the reaction, as indicated by TLC. The reaction mixture was poured into ice water and extracted with ethyl acetate, and organic layer was washed with aq. $NaHCO_3$, and brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography over silica gel using 10% EtOAc in hexane as an eluent to afford the compound **10** (185 mg, 61%) as a colourless oil; **IR (neat):** 2917, 2854, 1681, 1589, 1457, 1225, 902, 742 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H),7.34 (d, *J* = 7.2 Hz, 1H), 7.26-7.22 (m, 1H), 3.71 (t, *J* = 14.2 Hz, 2H), 3.16-3.12 (m, 1H), 3.00-2.92 (m, 1H), 2.48-2.46 (m, 1H), 2.29-2.24 (m, 1H), 2.03 (s, 3H), 1.92-1.88 (m, 2H), 1.48-1.35 (m, 5H), 0.93-0.92 (m, 3H), **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 200.5, 142.3, 135,6, 134.3, 133.5, 126.7, 125.9, 46.8, 35.8, 29.2, 29.0, 27.5, 24.6, 22.8, 15.3, 14.0; **HRMS** (ESI) m/z: $[M+ H]^+$ calcd for $C_{16}H_{23}OS$ 263.1464; found 263.1461.

References

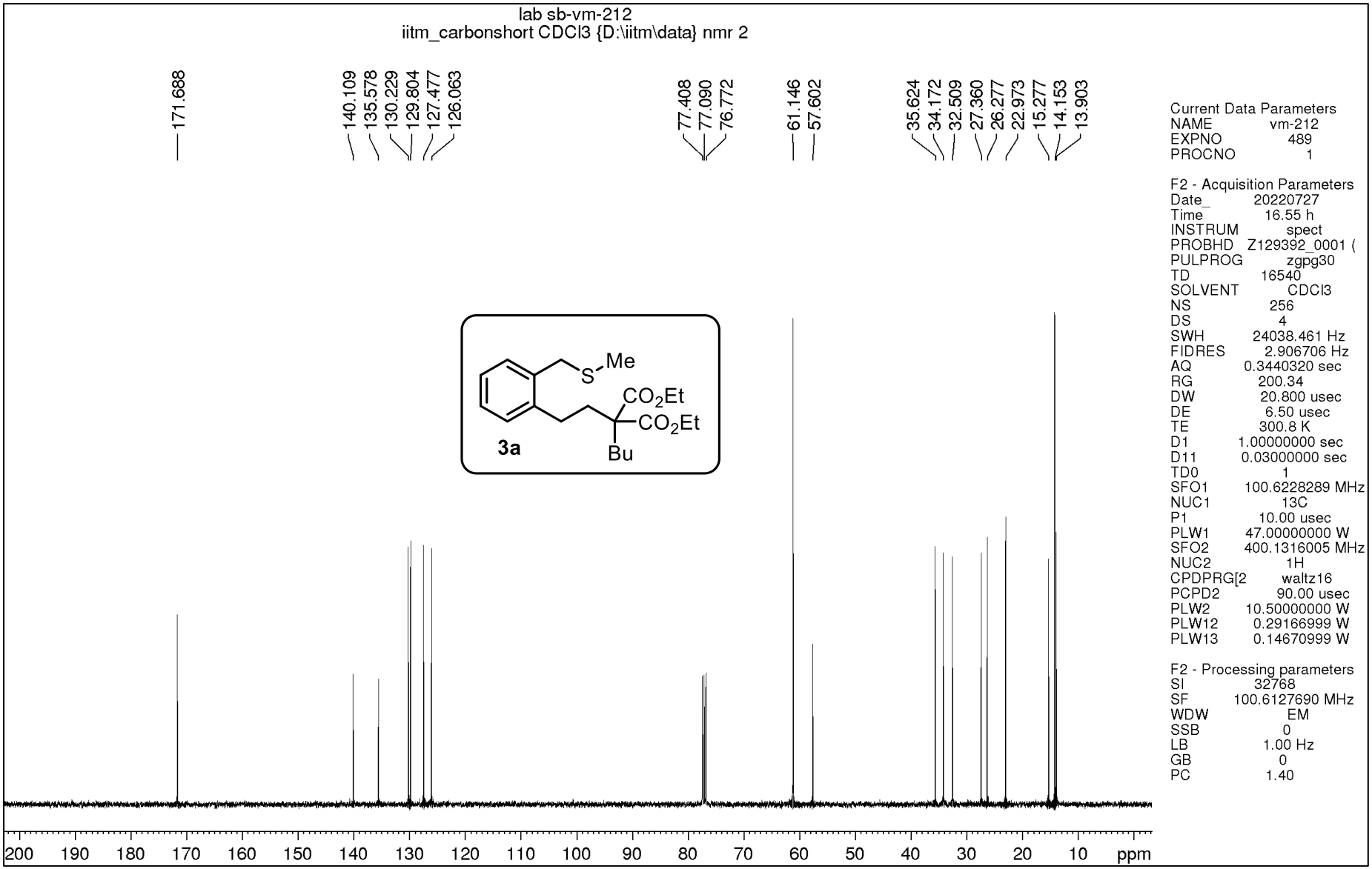
1) J. V. Matlock, S. P. Fritz, S. A. Harrison, D. M. Coe, E. M. McGarrigle, and V. K. Aggarwal, *J. Org. Chem.*, 2014, **79**, 10226-10239.
2) Z. H. Wang, L. W. Shen, K. X. Xie, Y. You, J. Q. Zhao, and W. C. Yuan, *Org. Lett*., 2020, **22**, 3114-3118.
3) F. Xia, Y. Q. Lu, P. Sun, Q. Y. Guo, Q. L. Shi, J. Z. Zhang and C. Qiu, *Org. Biomol. Chem.*, 2022, **20**, 8415-8419.
4) D. D. Chen, X. L. Hou and L. X. Dai, *Tetrahedron Lett.*, 2009, **50**, 6944-6946.
5) J. E. Beddow, S. G. Davies, K. B. Ling, P. M. Roberts, A. J. Russell, A. D. Smith and J. E. Thomson, *Org. Biomol. Chem.*, 2007, **5**, 2812-2825.
6) G. Nie, X. Huang, Z. Wang, D. Pan, J. Zhang and Y. Chi, *Org. Chem. Front.*, 2021, **8**, 5105-5111.
7) X. Dong, L. P. Xu, Y. Yang, Y. Liu, X. Li, Q. Liu, L. Zheng, F. Wang and H. Liu, *Org. Chem. Front.*, 2021, **8**, 6009-6018.
8) J. Halder, D. Das and S. Nanda, *Org. Biomol. Chem.*, 2018, **16**, 2549-2575.
9) Q. He, J. Liu, J. S. Lan, J. Ding, Y. Sun, Y. Fang, N. Jiang, Z. Yang, L. Sun, Y. Jin and S. S. Xie, *Bioorg. Chem.*, 2018, **81**, 512-528.
10) C. Sanna, C. L. Mesa, L. Mannina, P. Stano, S. Viel and A. Segre, *Langmuir*, 2006, **22**, 6031-6041.
11) J. H. Clark and D. G. Cork, *J. Chem. Soc., Chem. Commun.*, 1982, 635-636.
12) K. Jeyakumar, R. D. Chakravarthy and D. K. Chand, *Catal. Commun.*, 2009, **10**, 1948-1951.
13) K. Okada and M. Tanaka, *J. Chem. Soc., Perkin Trans. 1*, 2002, **1**, 2704-2711.
14) S. Y. Yan, Y. Q. Han, Q. J. Yao, X. L. Nie, L. Liu, *Angew. Chem. Int. Ed.*, 2018, **57**, 9093-9097.
15) G. K. S. Prakash, P. Yan, B. Török and G. A. Olah, *Catal. Lett.*, 2003, **87**, 109-112.



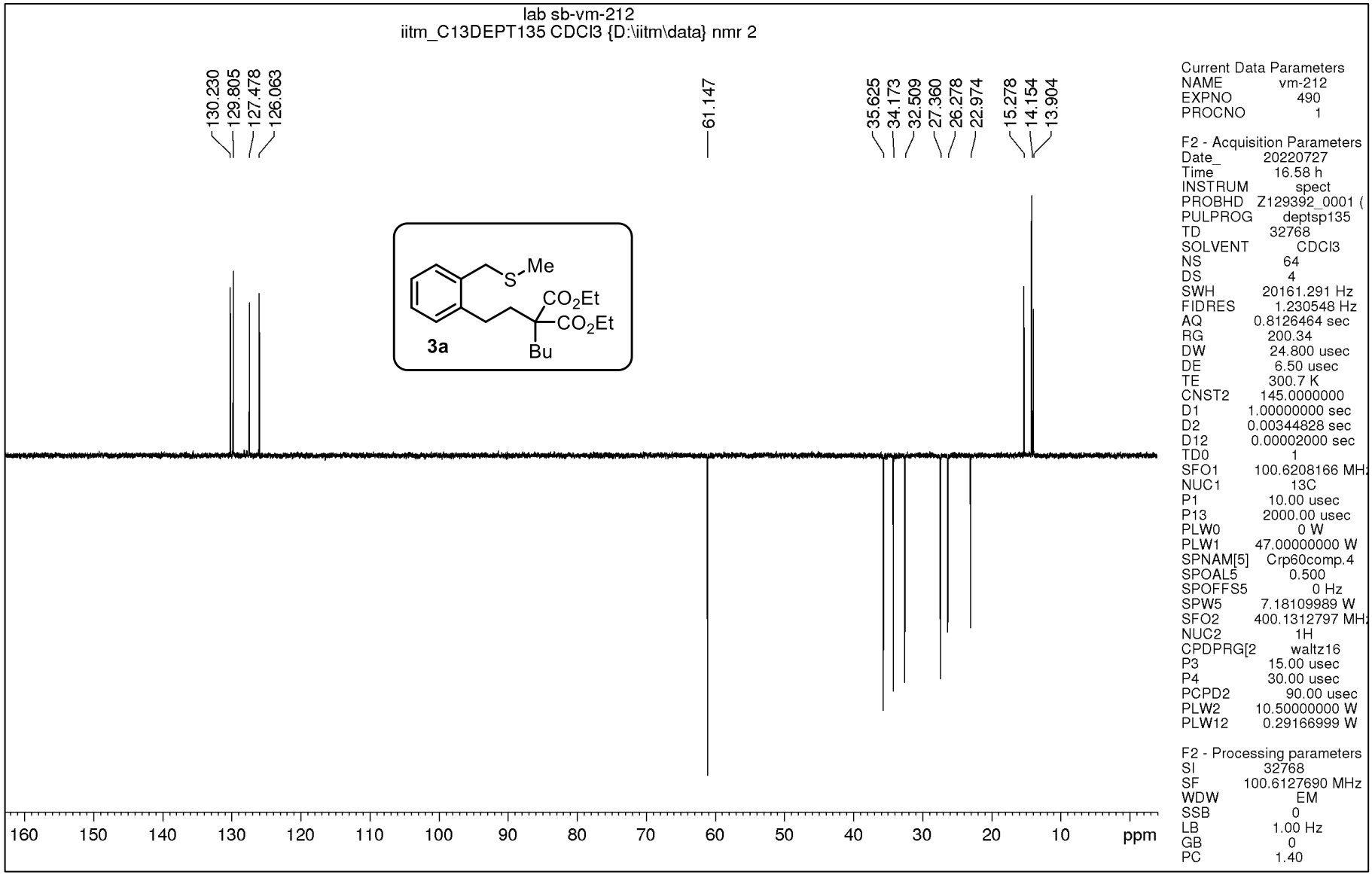
^{1}H NMR spectrum of compound 3a



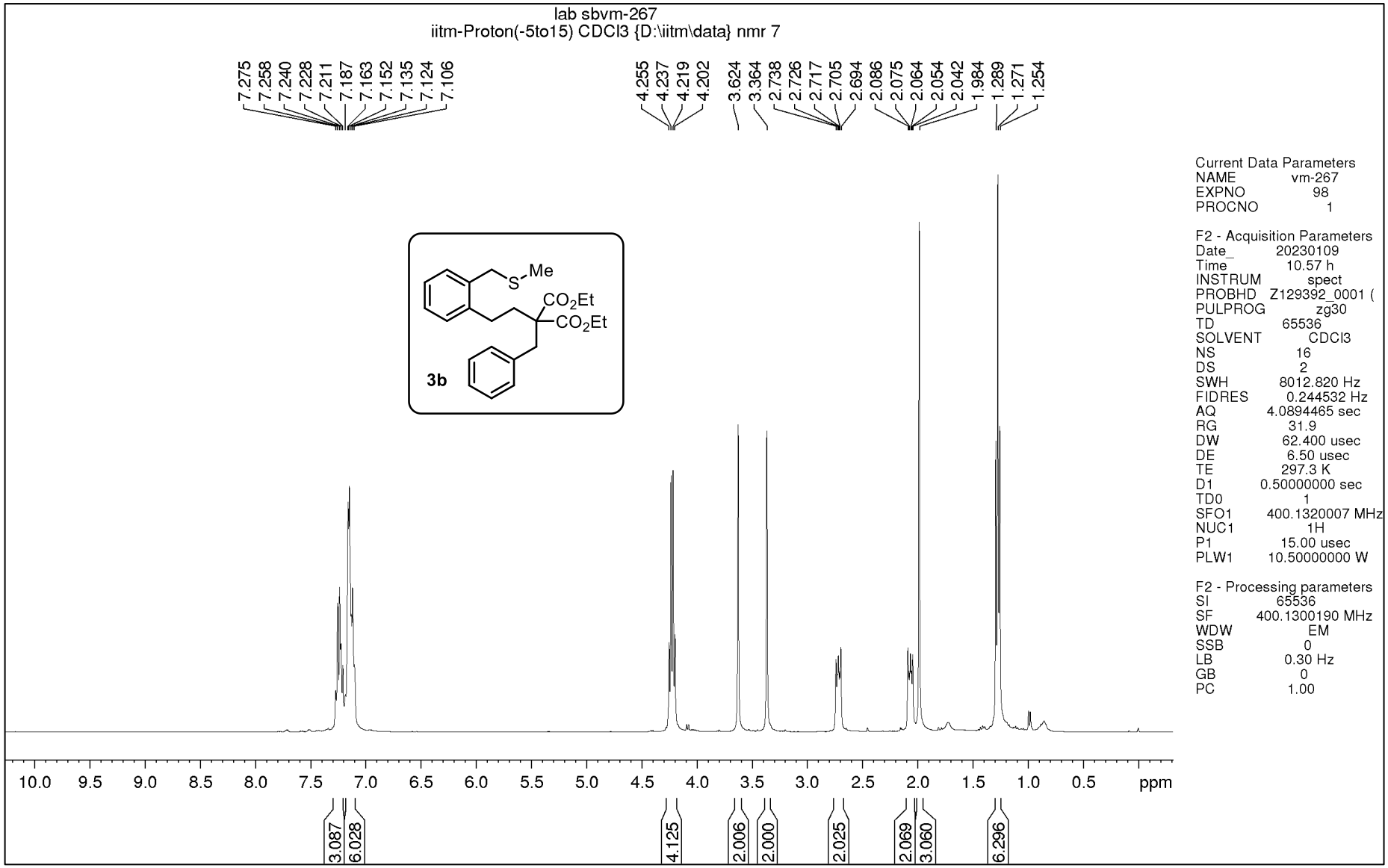
^{1}H NMR spectrum of compound 3a



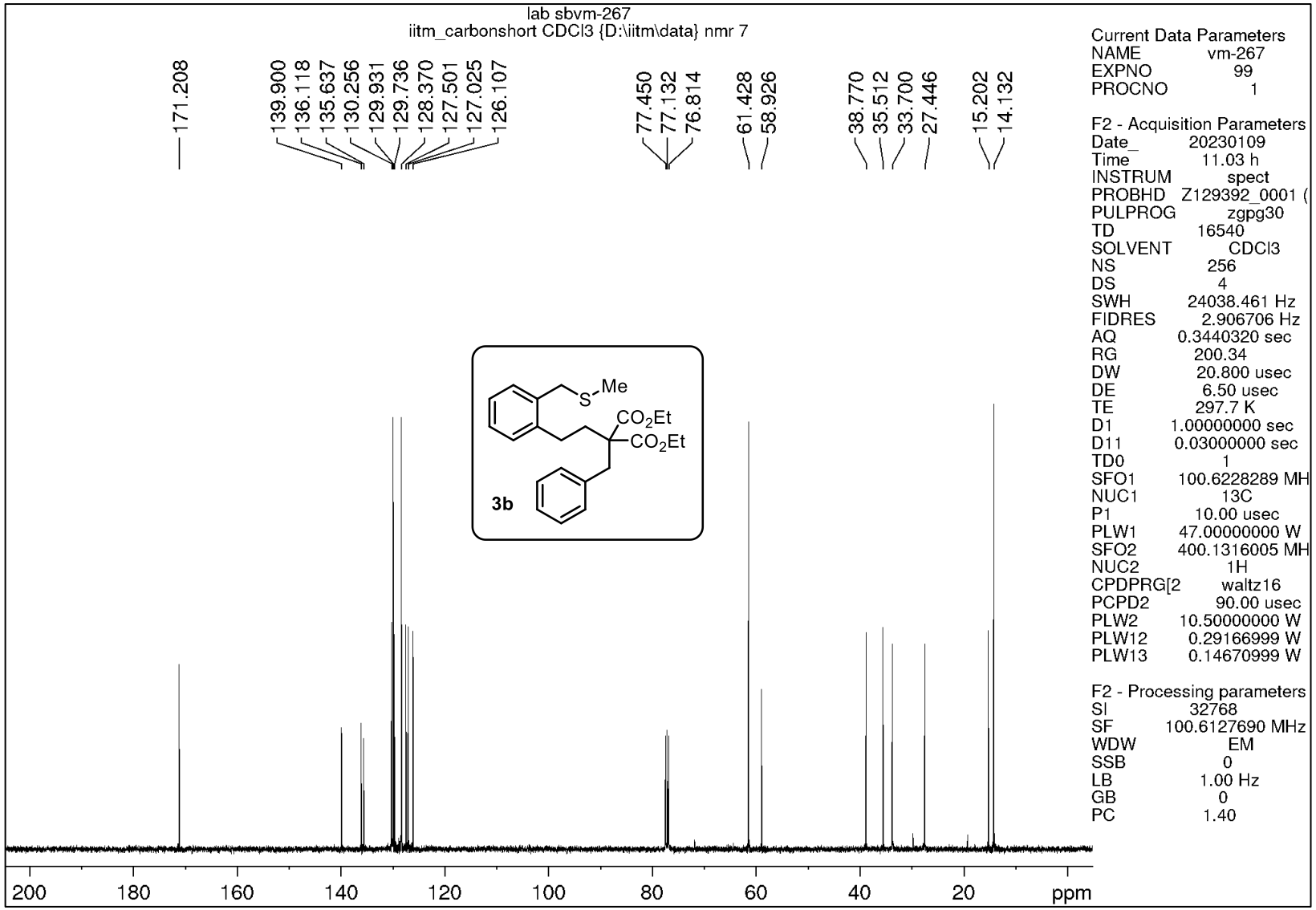
^{13}C NMR spectrum of compound 3a



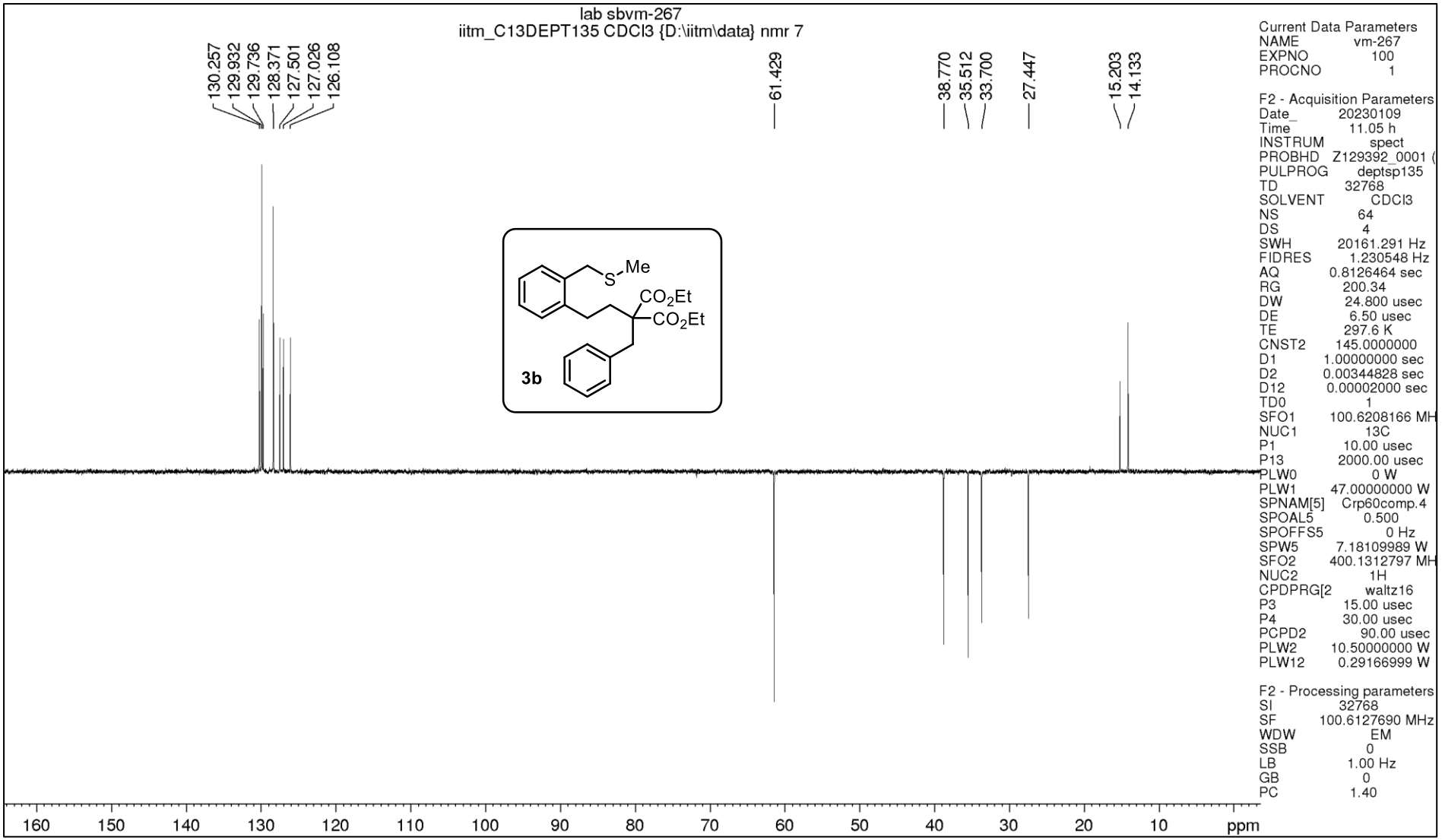
DEPT-135 NMR spectrum of compound 3a



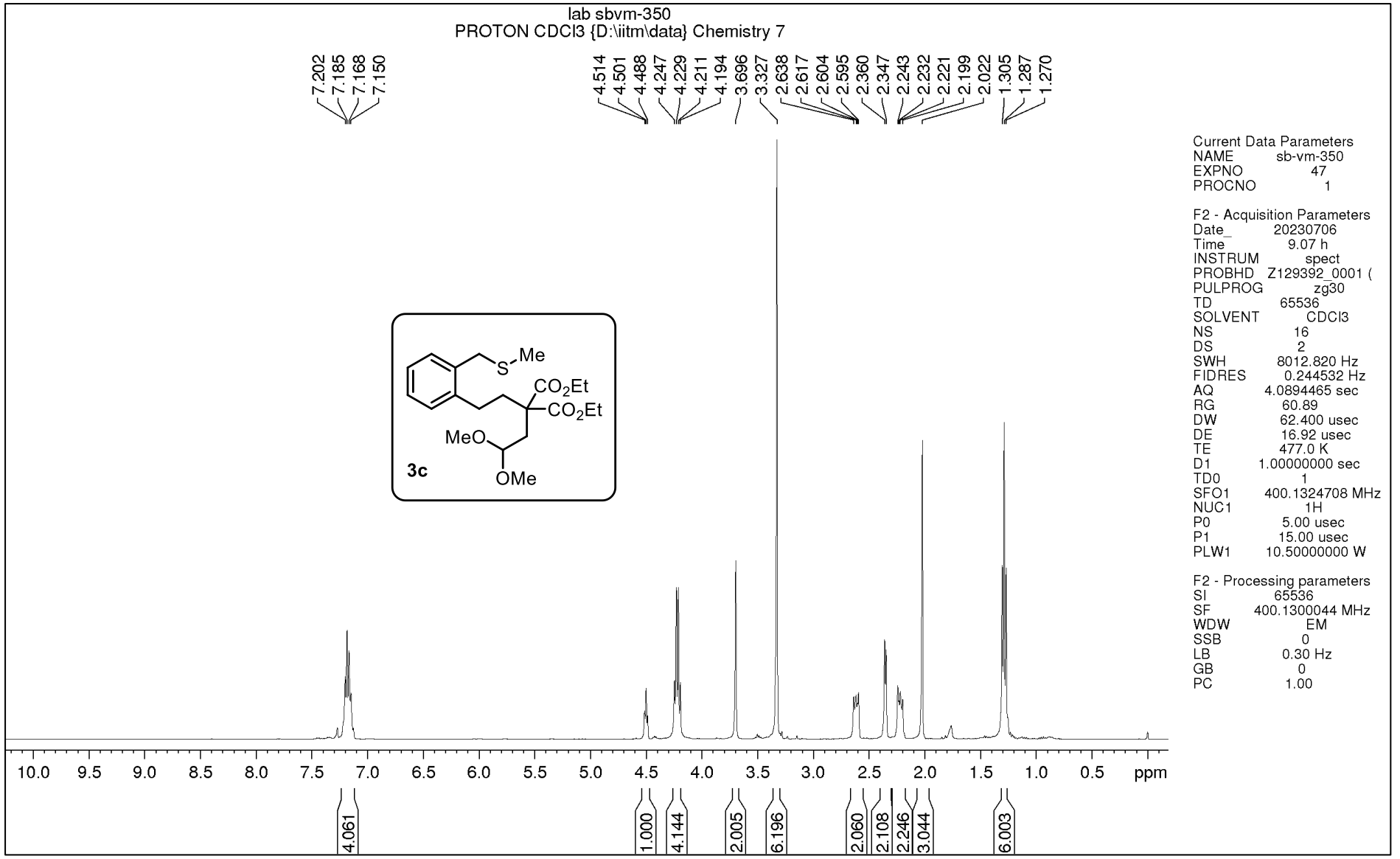
^{1}H NMR spectrum of compound 3b



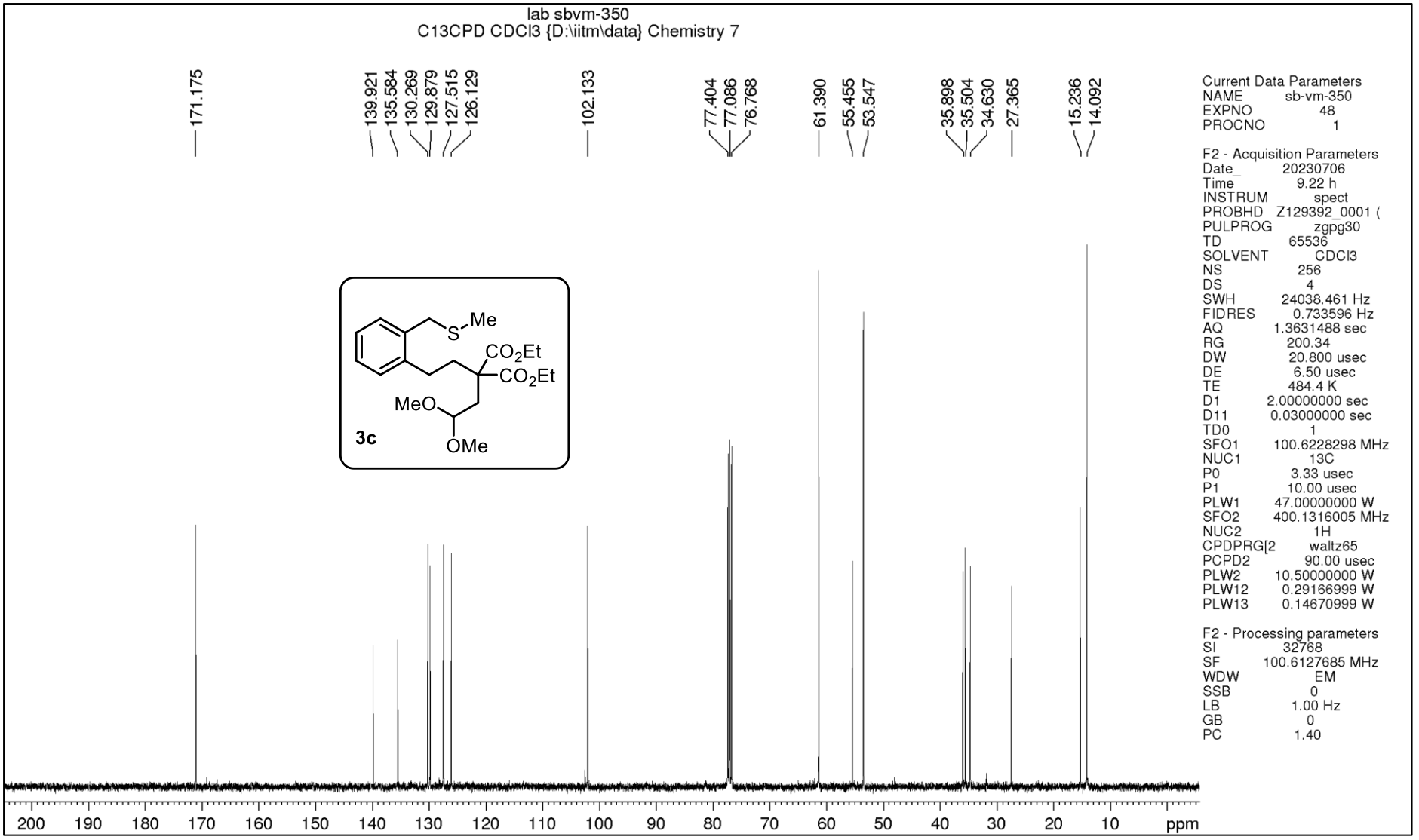
^{13}C NMR spectrum of compound 3b



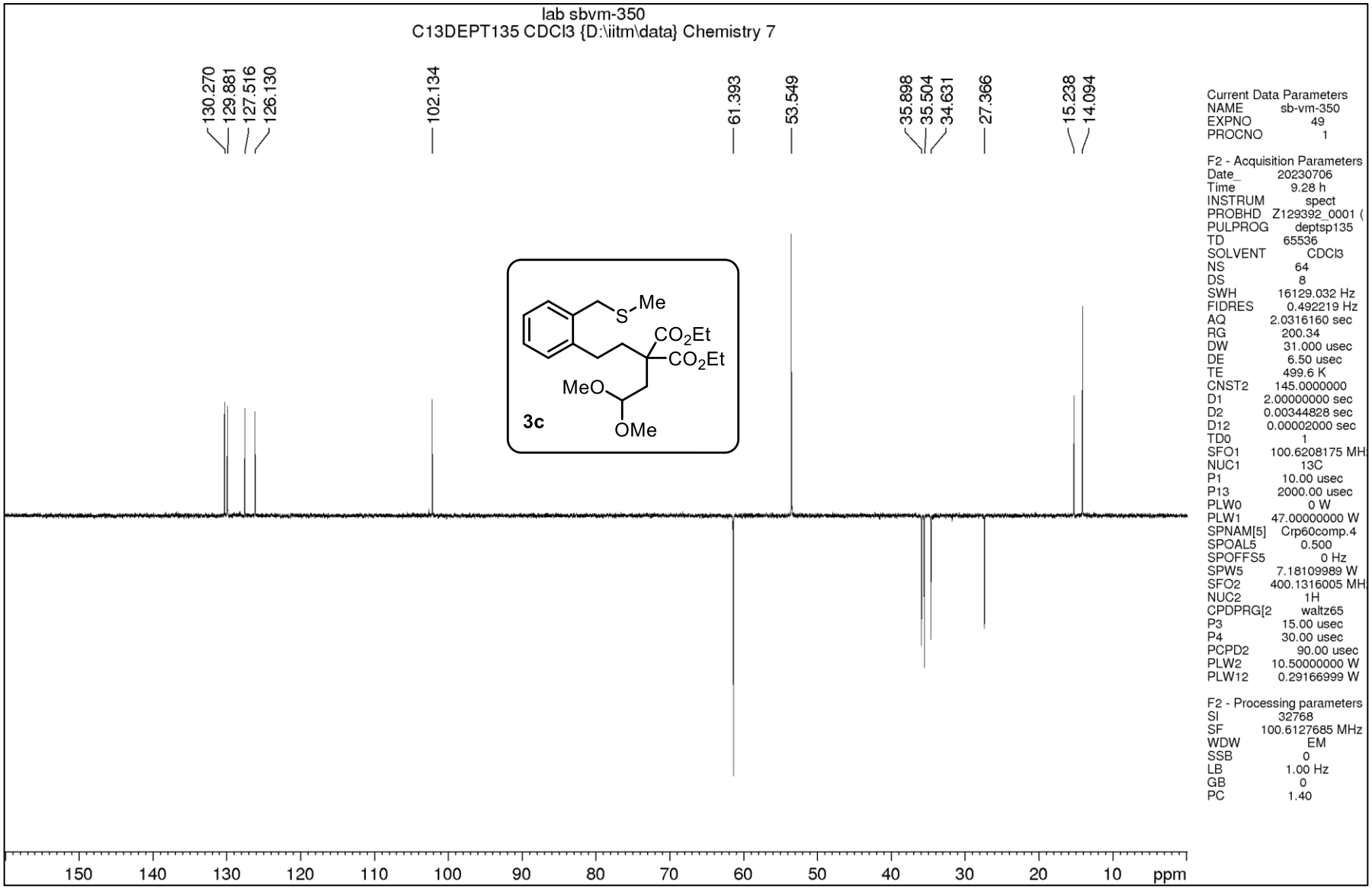
DEPT-135 NMR spectrum of compound 3b



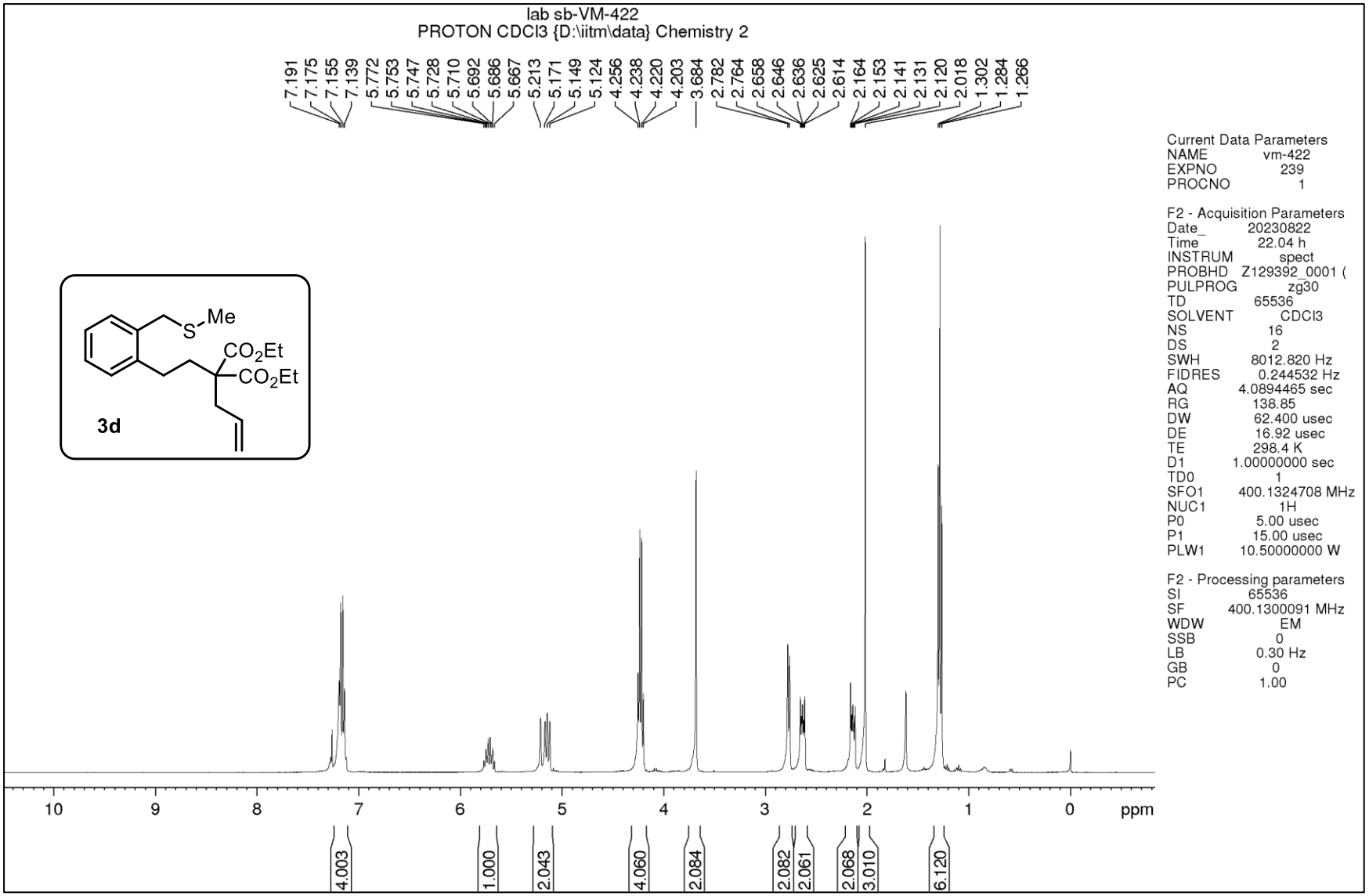
^{1}H NMR spectrum of compound 3c



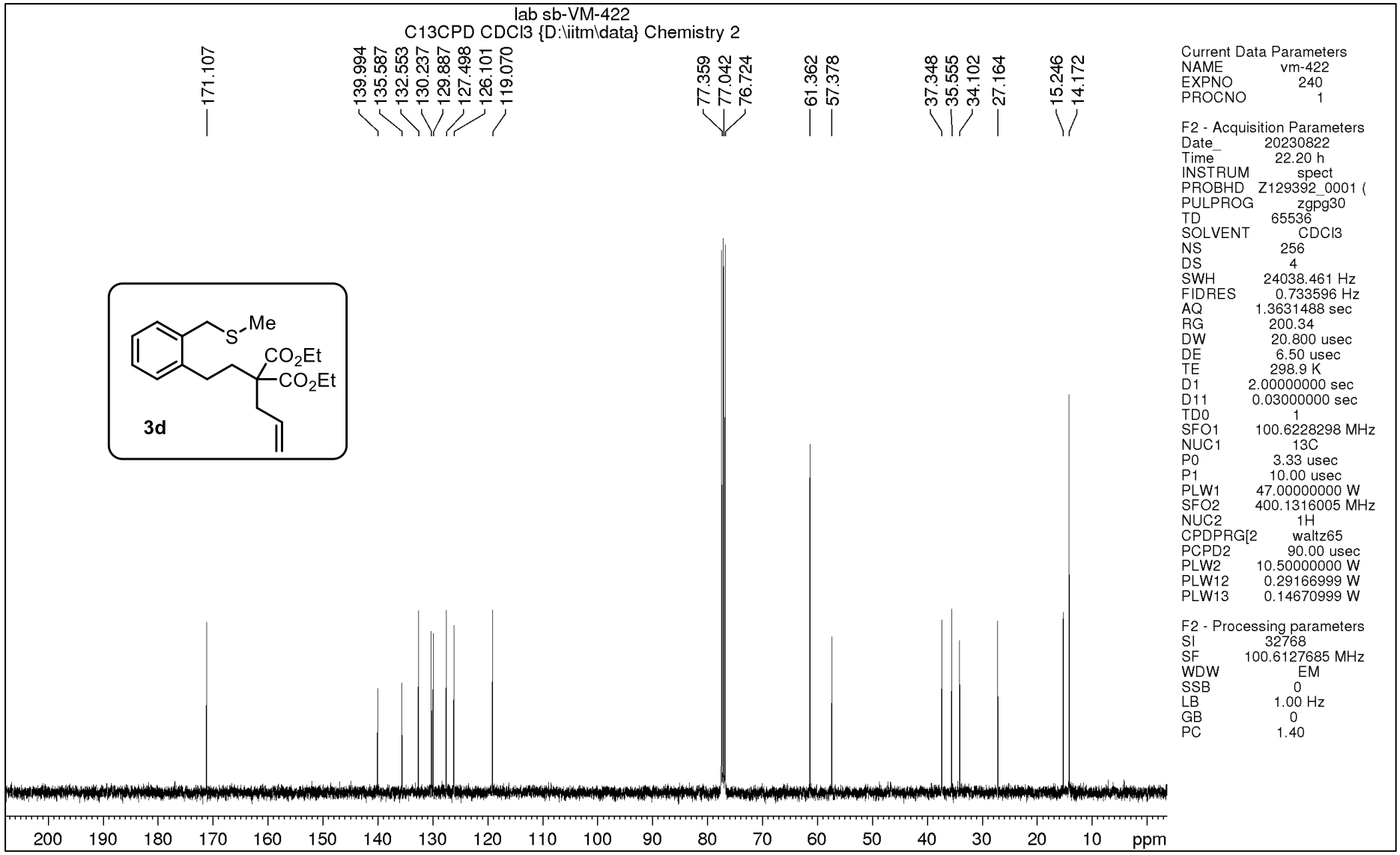
^{13}C NMR spectrum of compound 3c



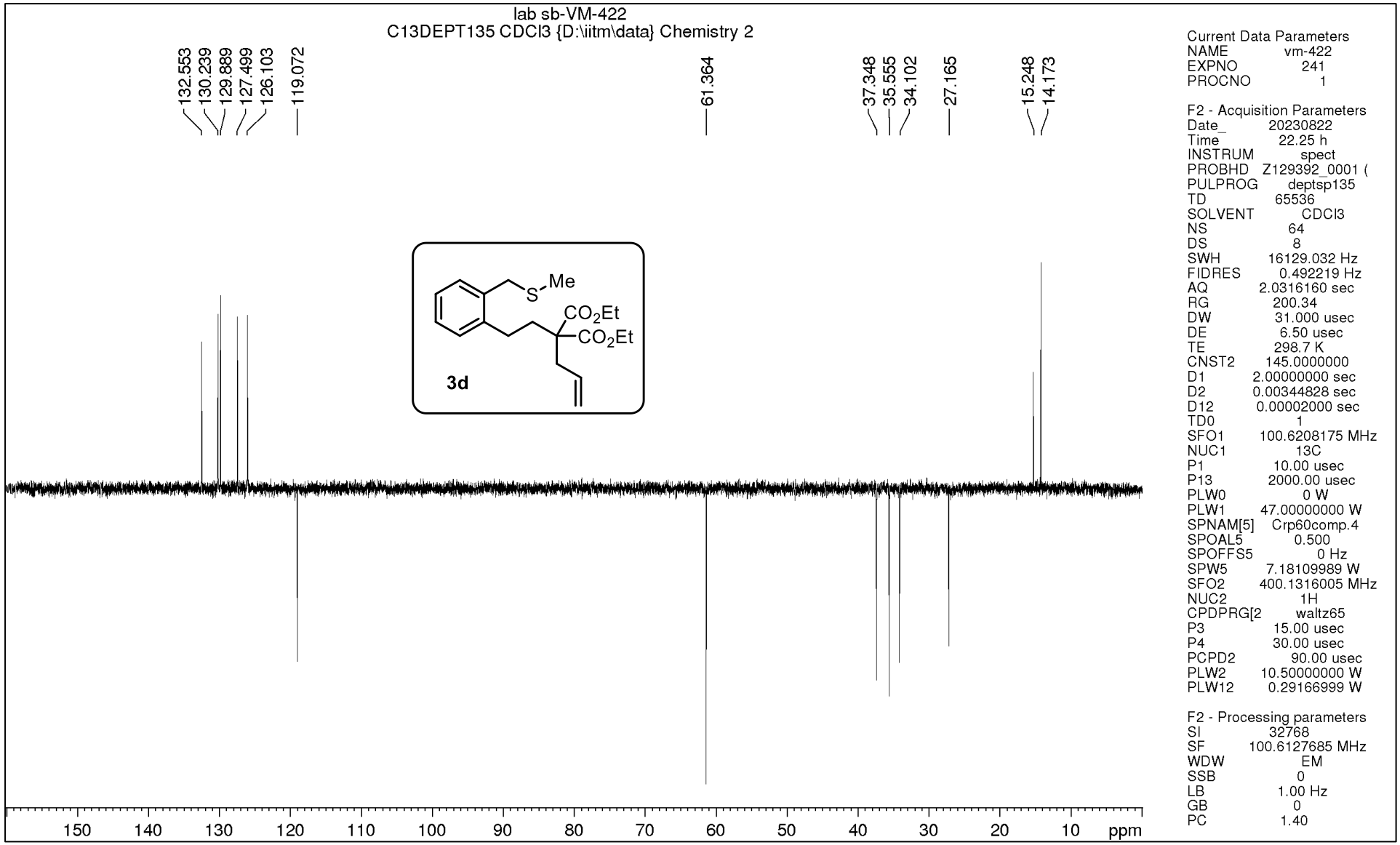
DEPT-135 NMR spectrum of compound 3c



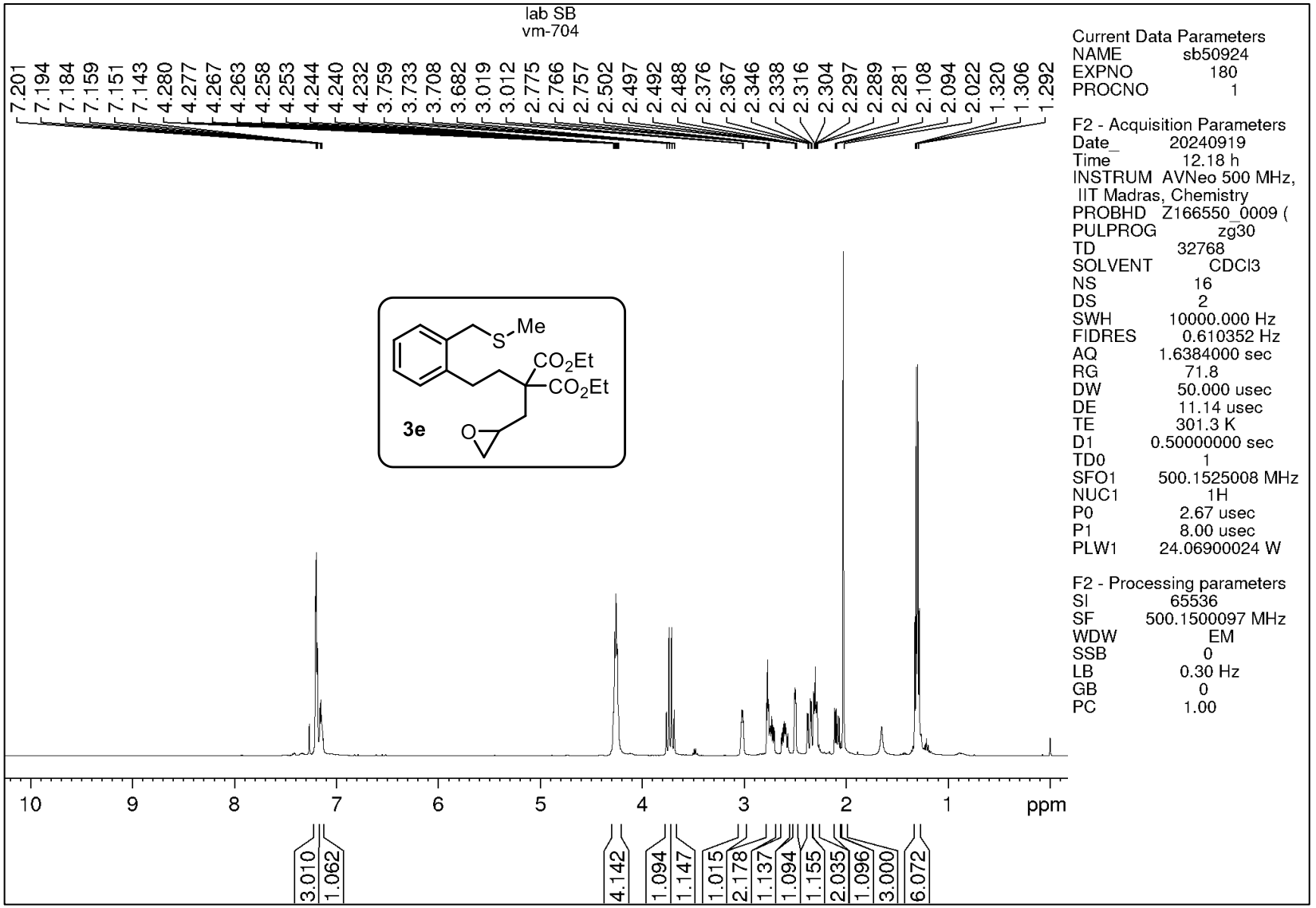
^{1}H NMR spectrum of compound 3d



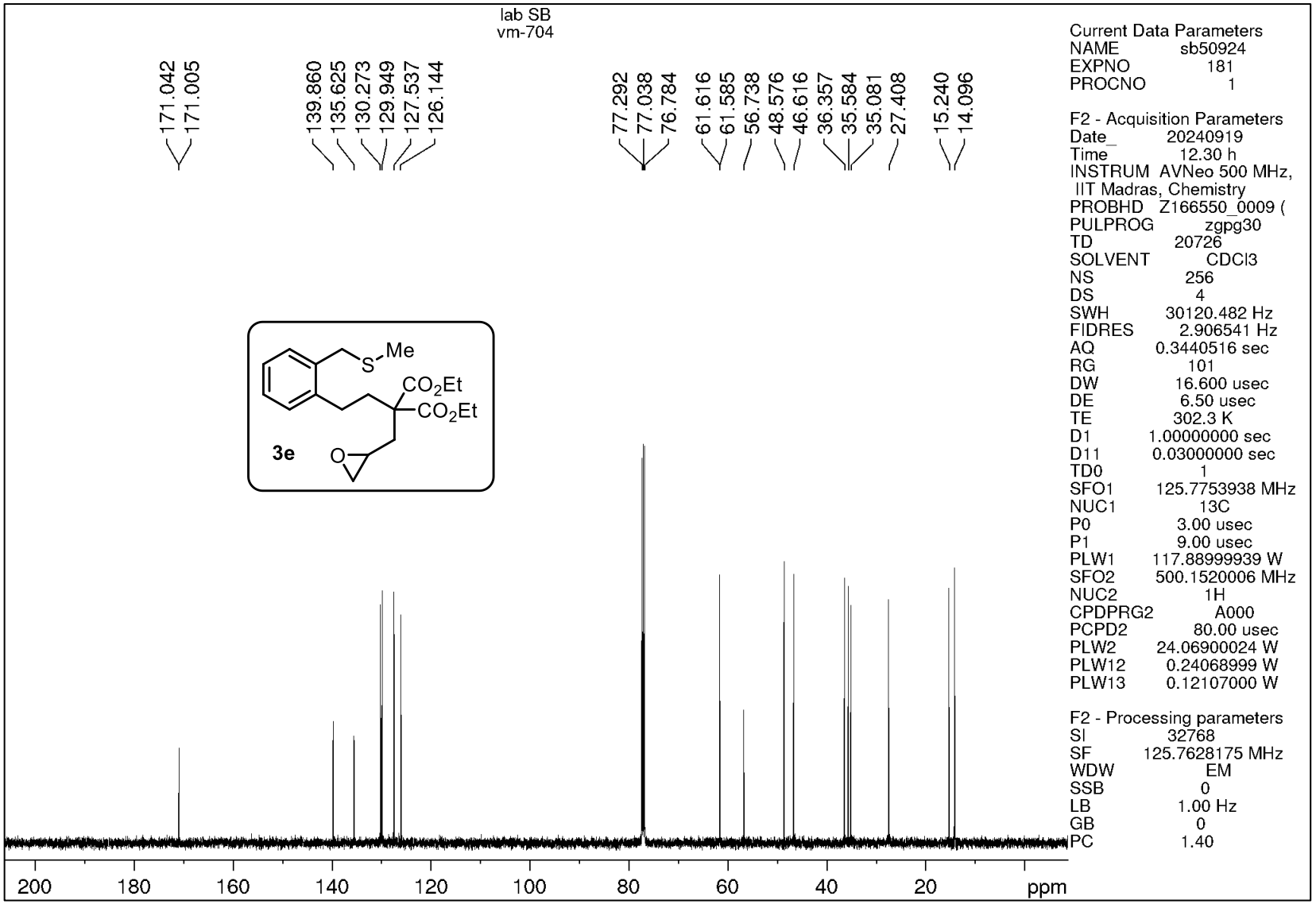
^{13}C NMR spectrum of compound 3d



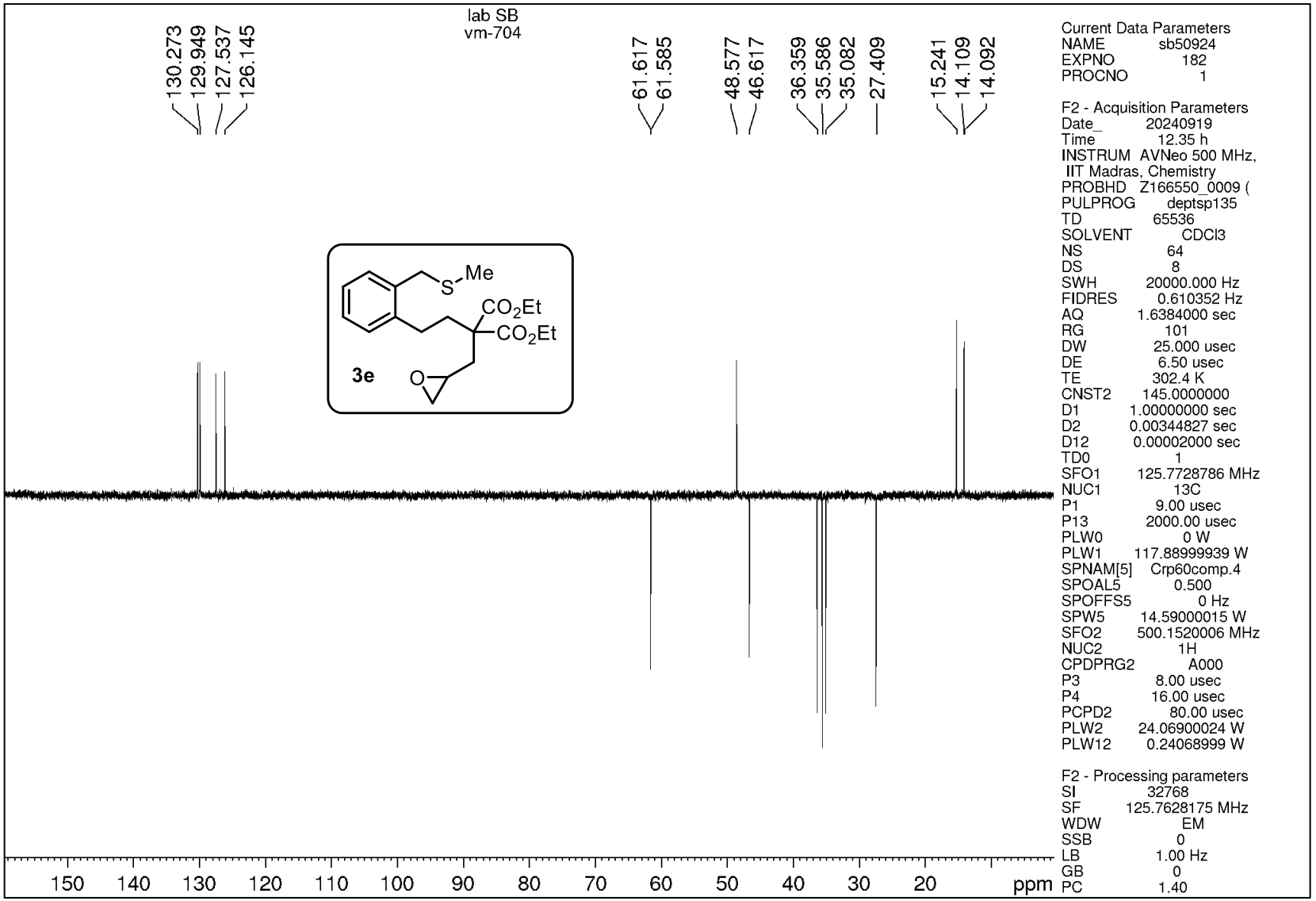
DEPT-135 NMR spectrum of compound 3d



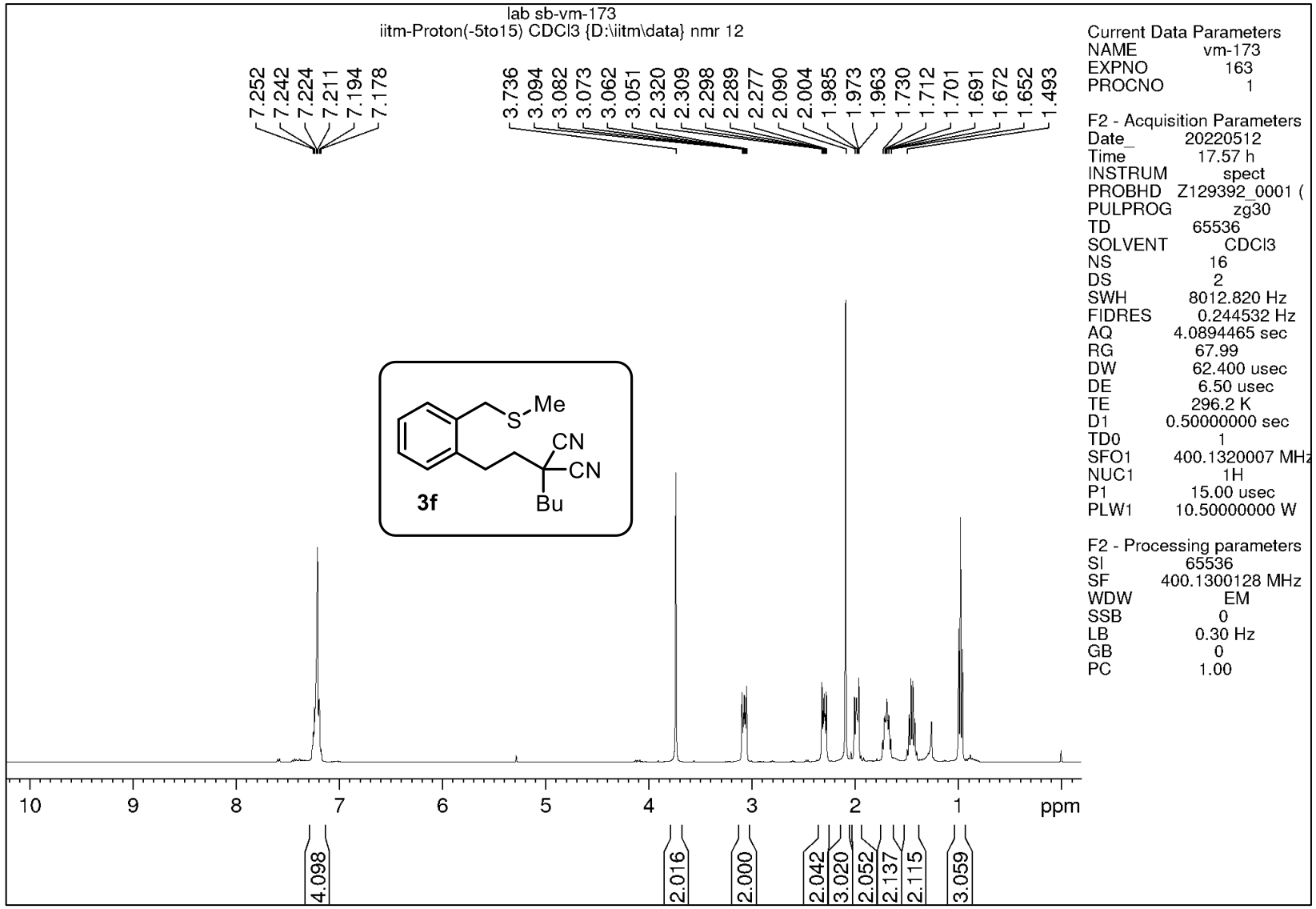
^{1}H NMR spectrum of compound 3e



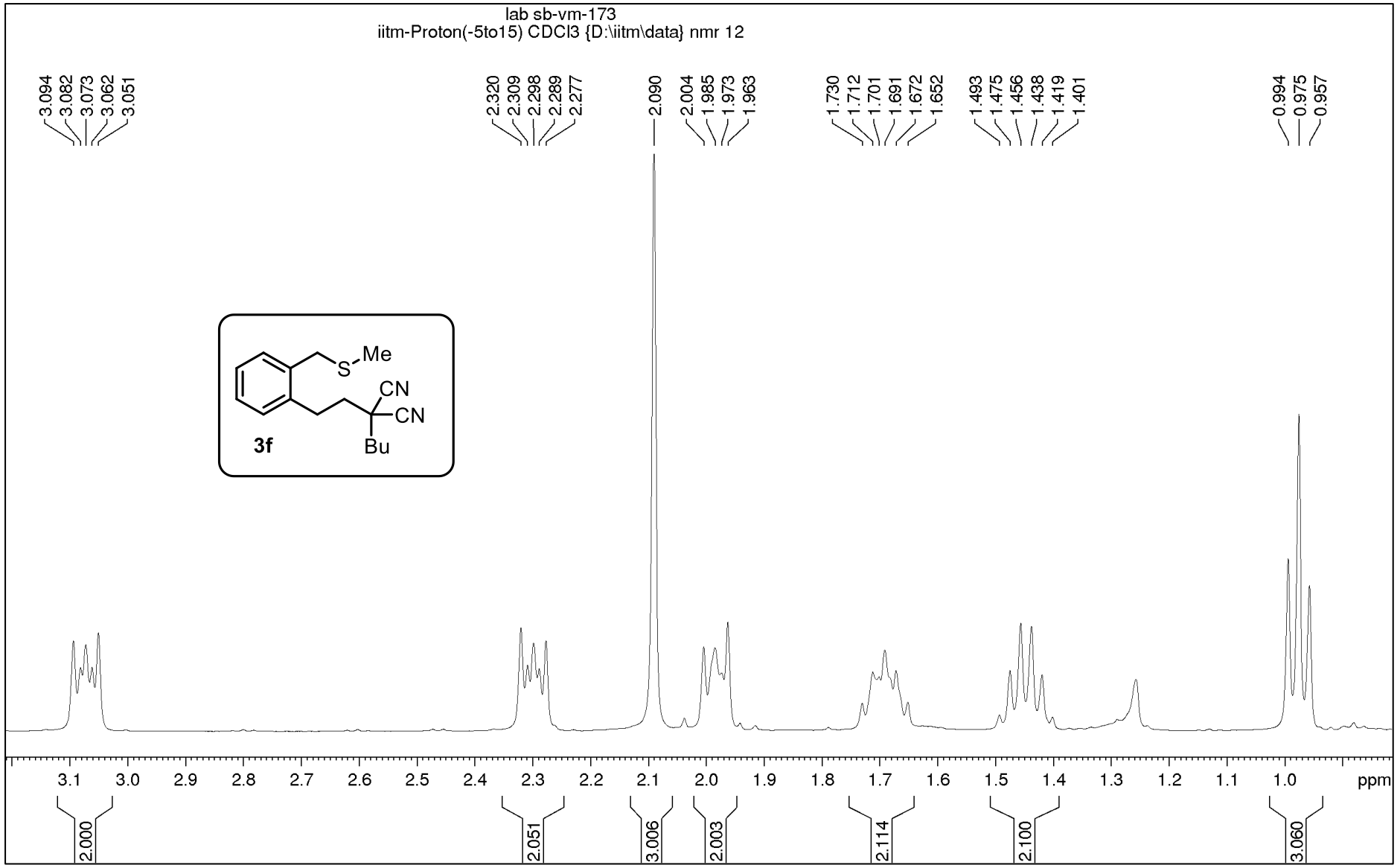
^{13}C NMR spectrum of compound 3e



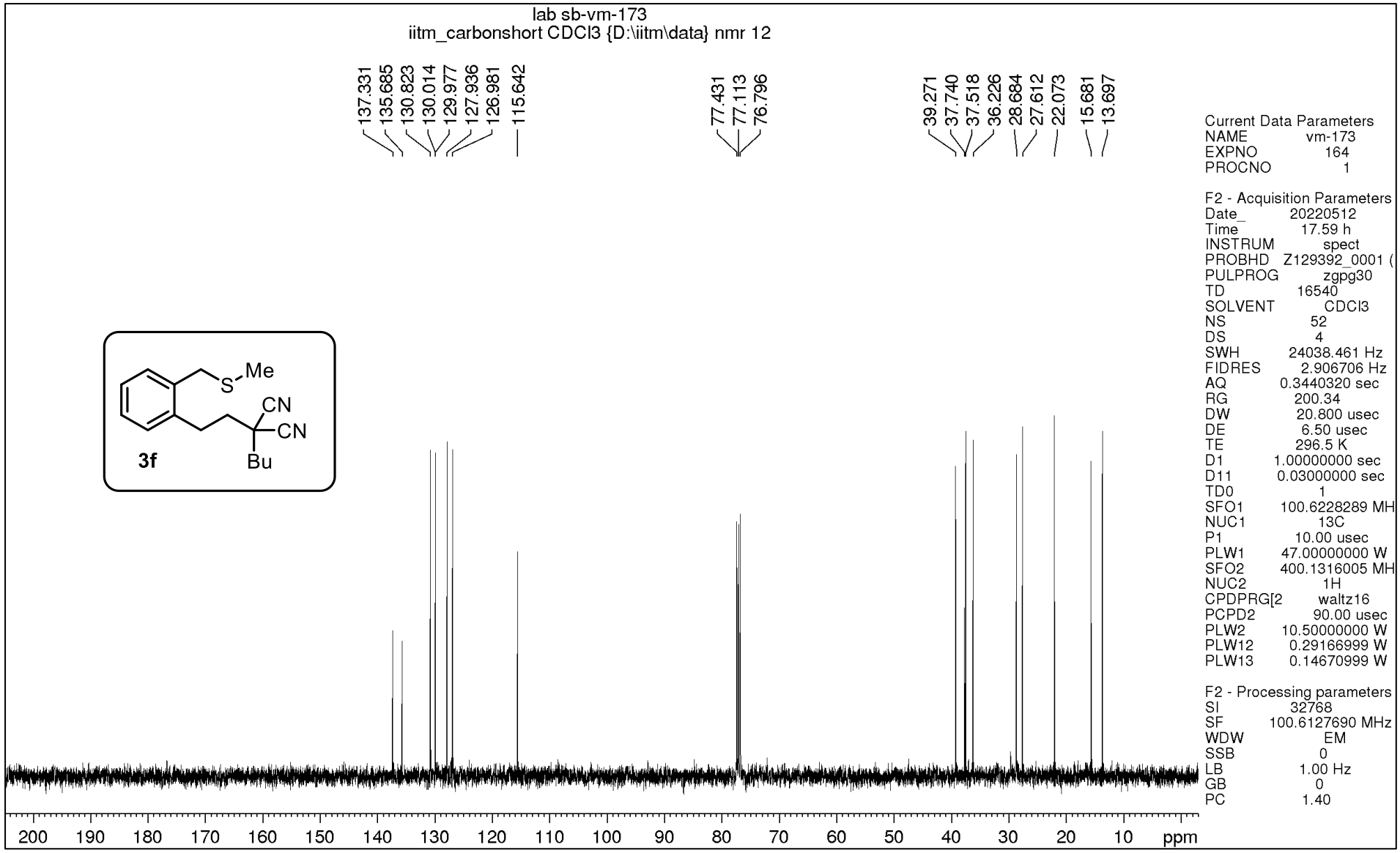
DEPT-135 NMR spectrum of compound 3e



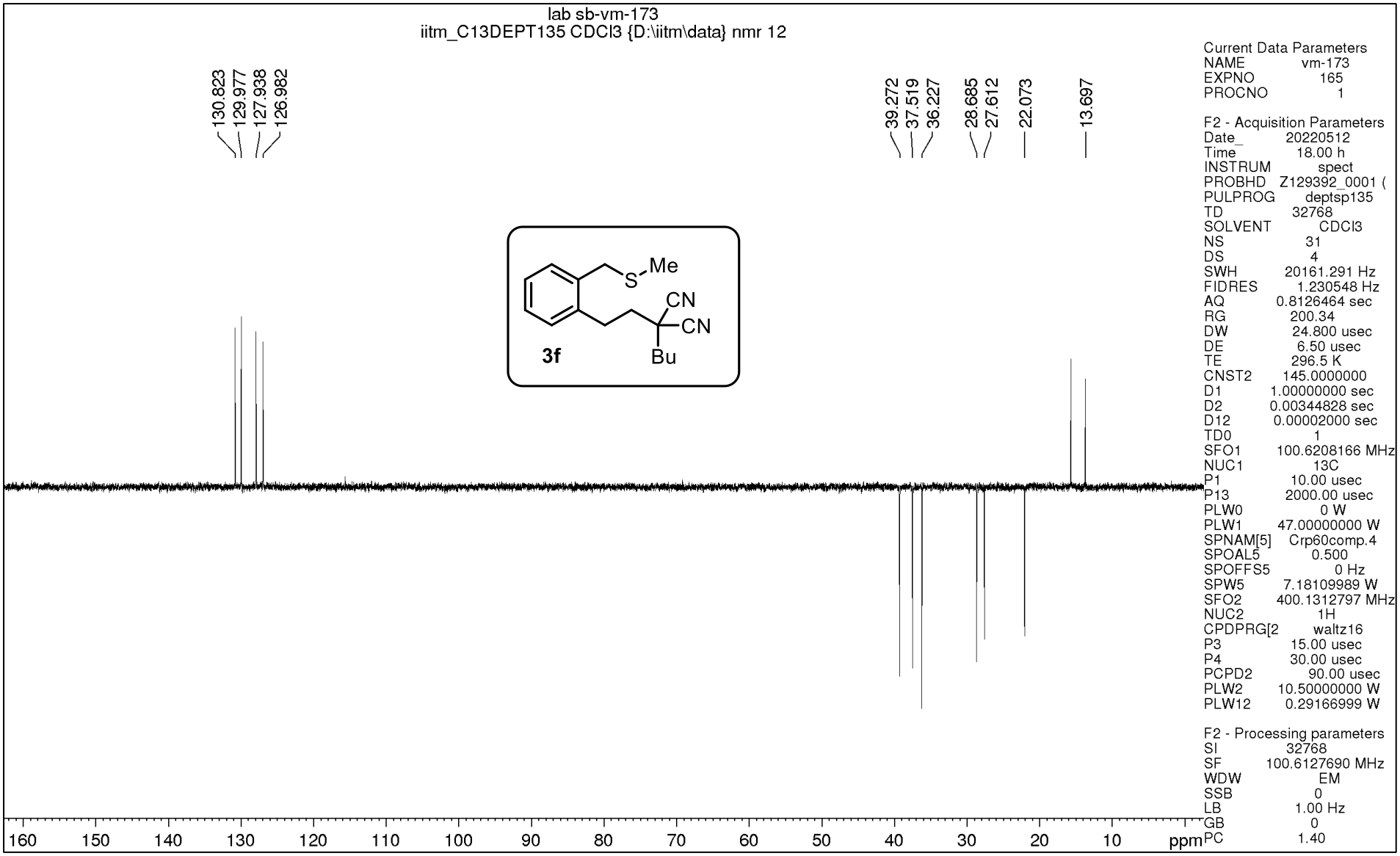
^{1}H NMR spectrum of compound 3f



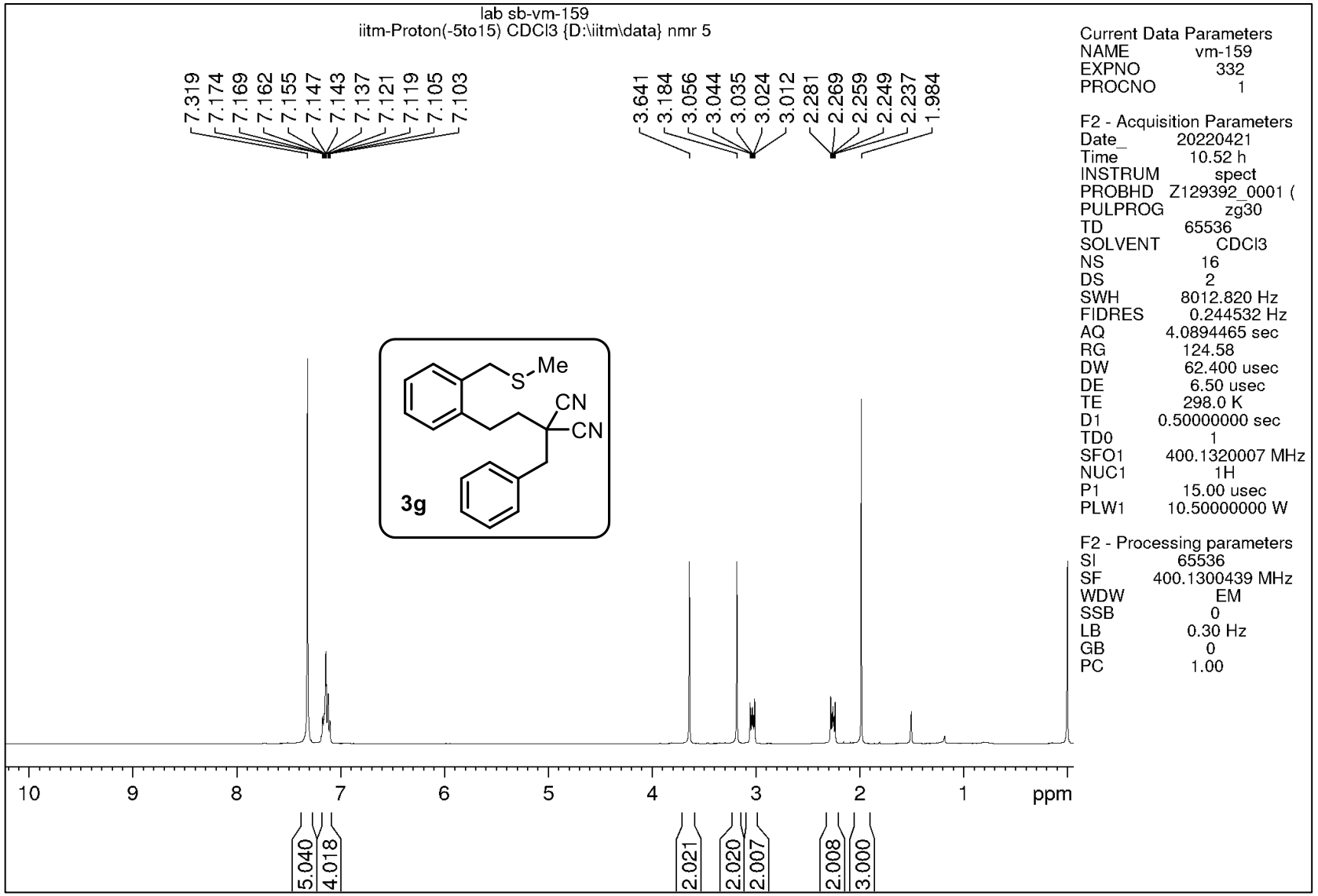
^{1}H NMR spectrum of compound 3f



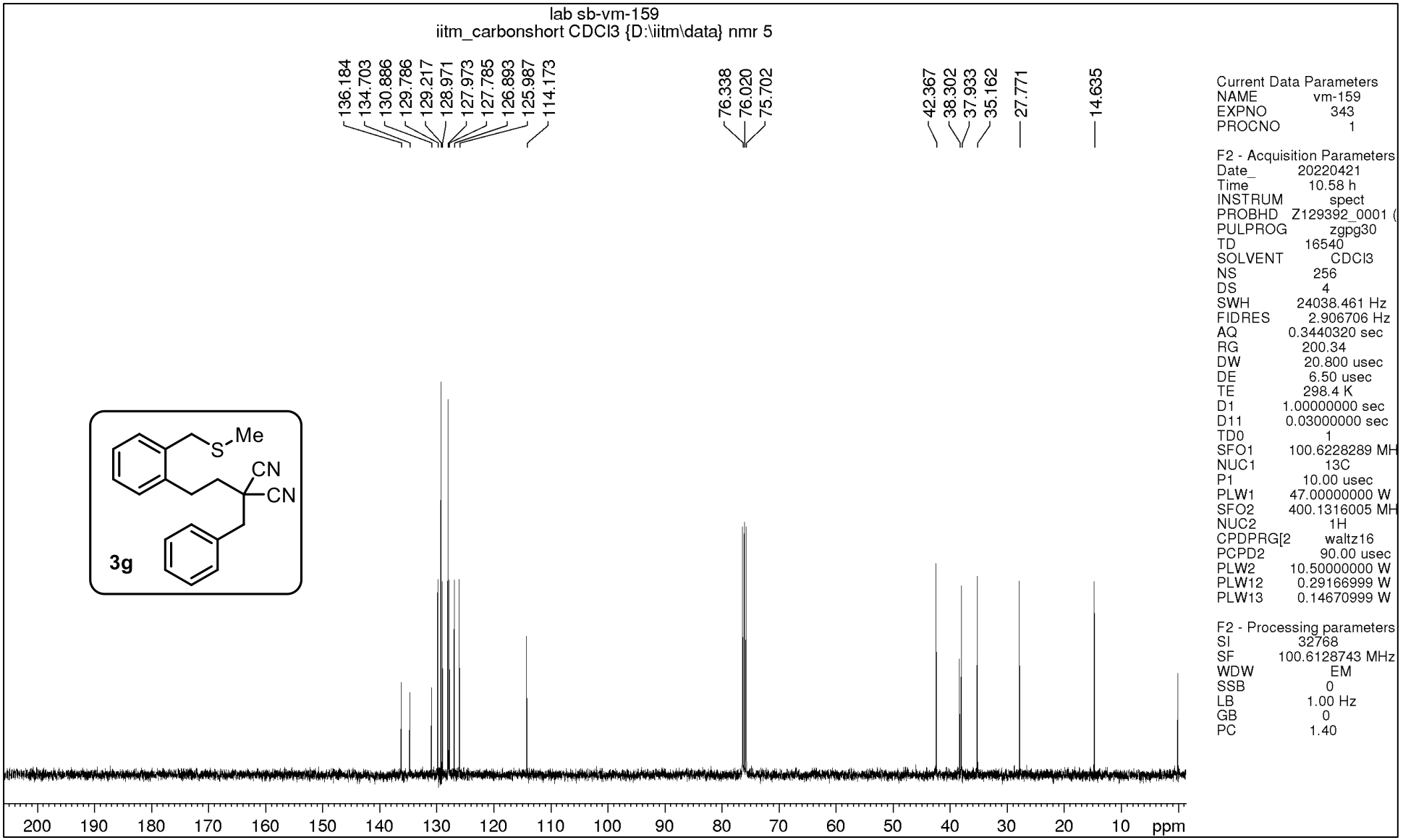
^{13}C NMR spectrum of compound 3f



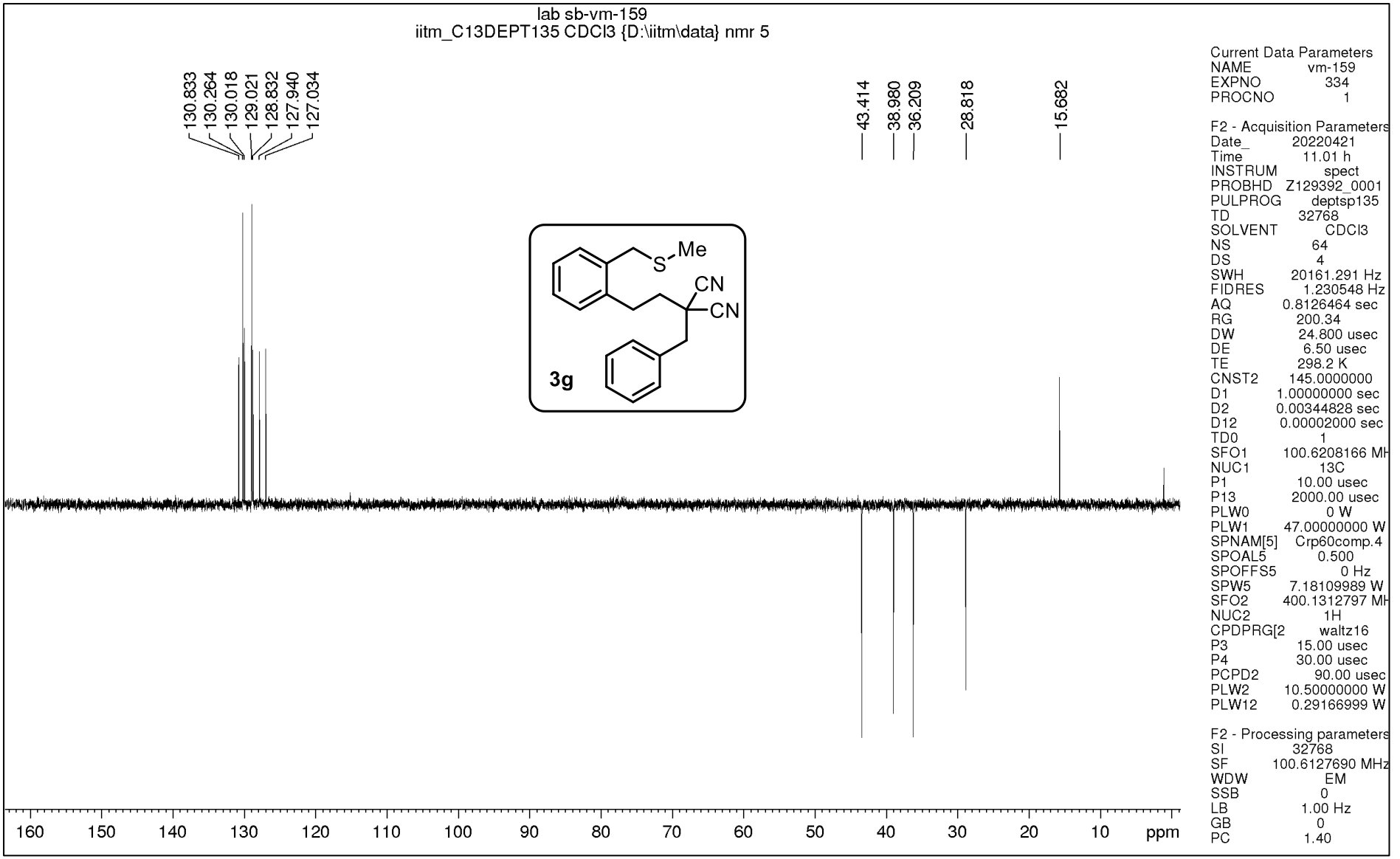
DEPT-135 NMR spectrum of compound 3f



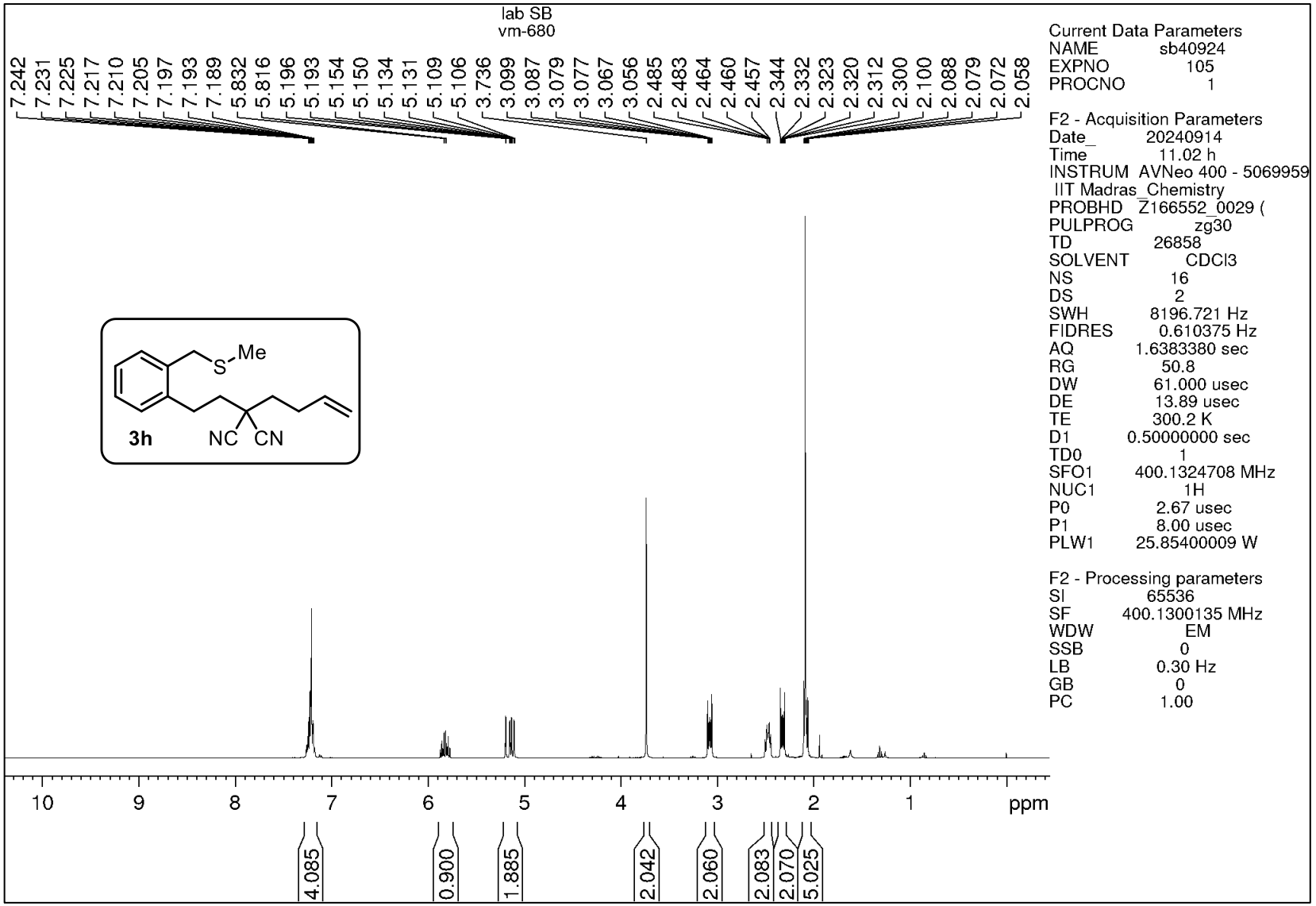
^{1}H NMR spectrum of compound 3g



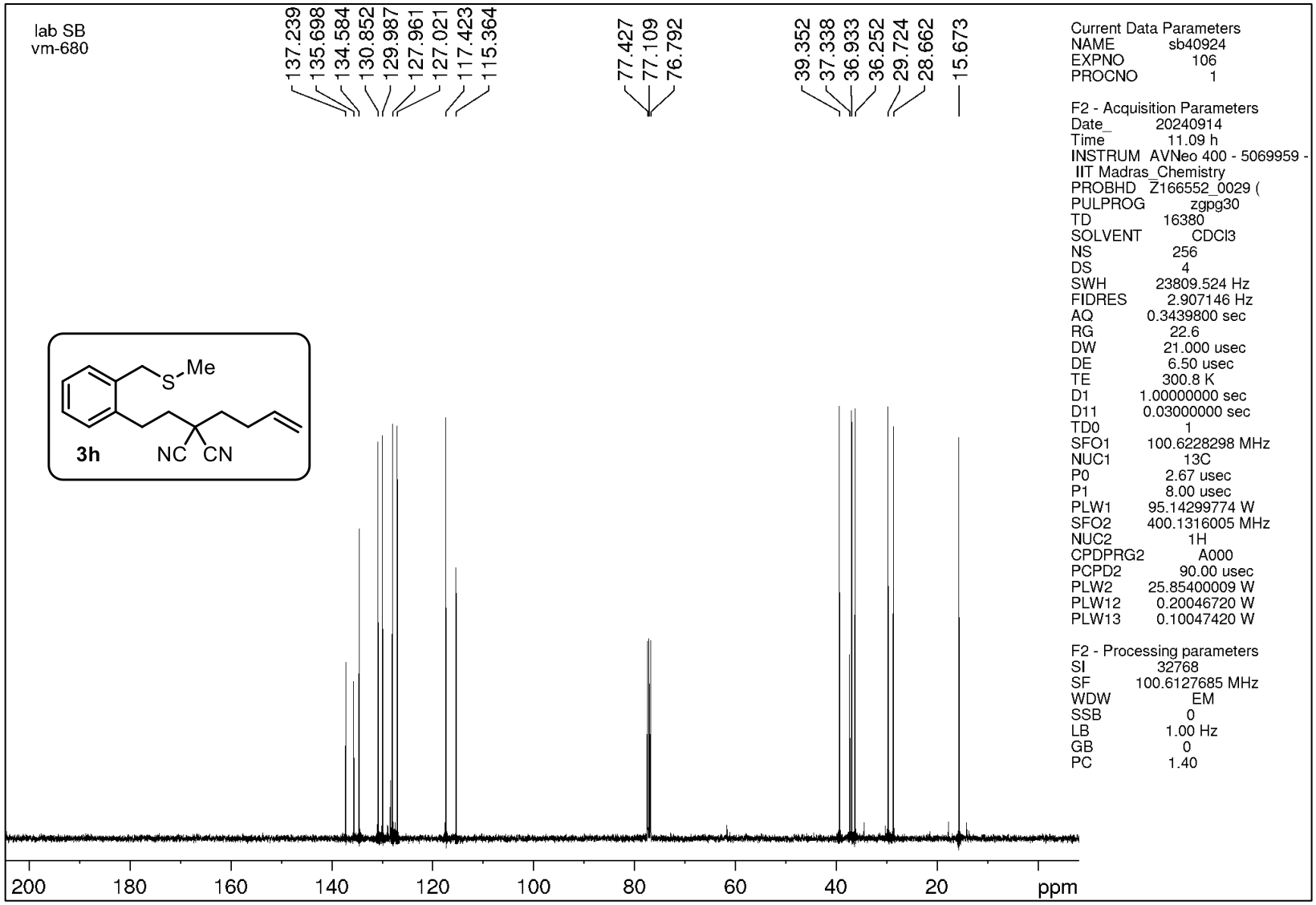
^{13}C NMR spectrum of compound 3g



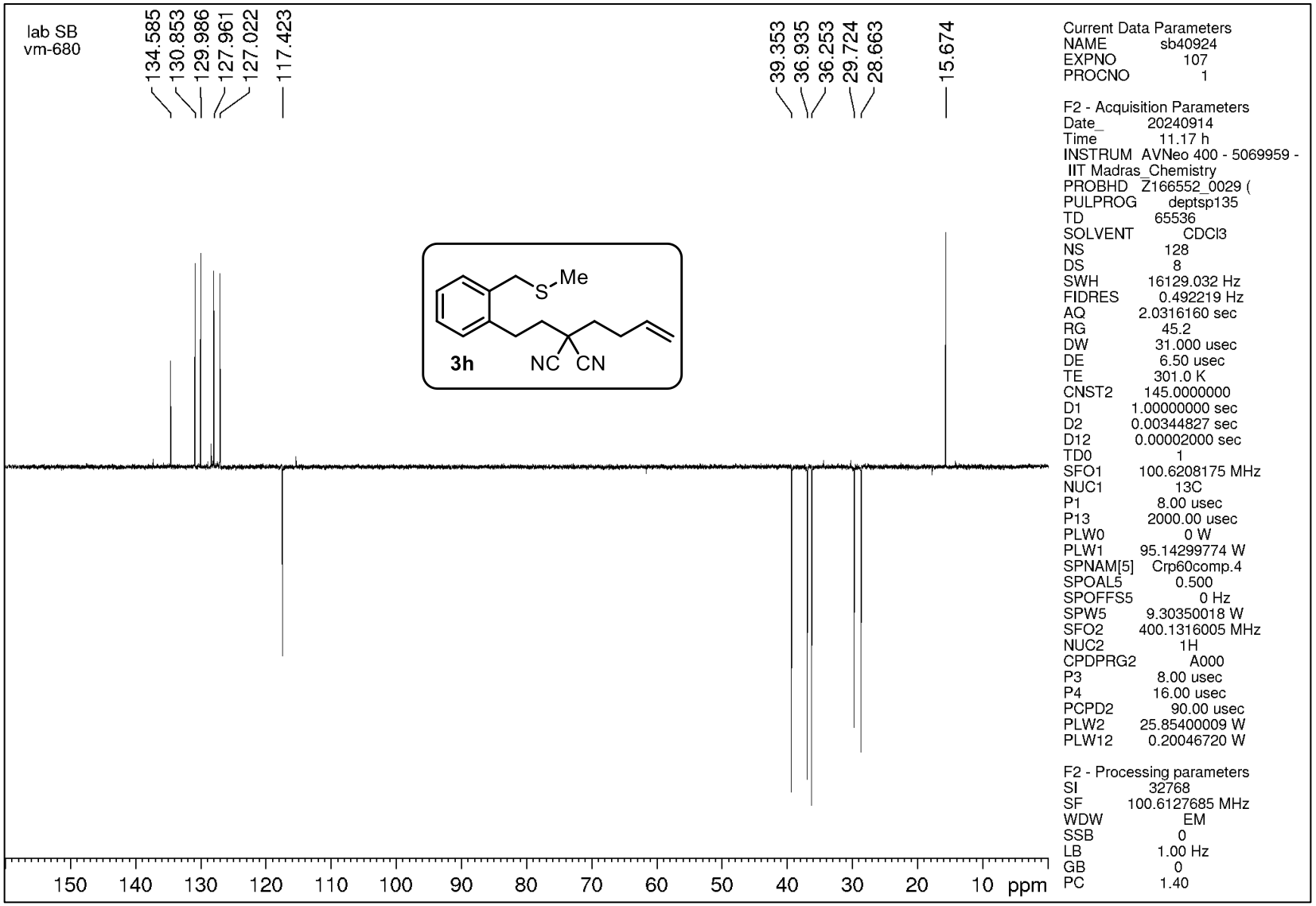
DEPT-135 NMR spectrum of compound 3g



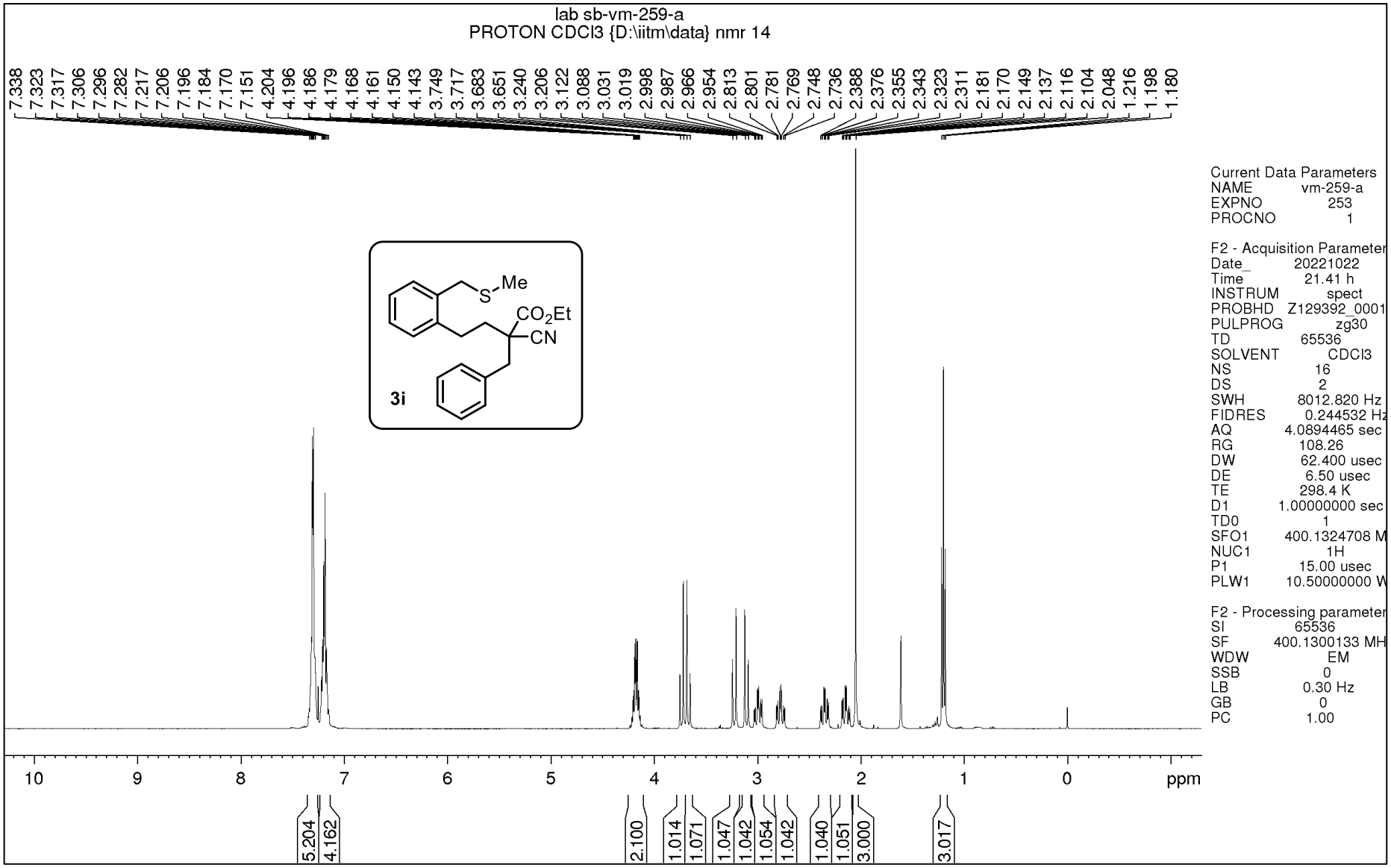
^{1}H NMR spectrum of compound 3h



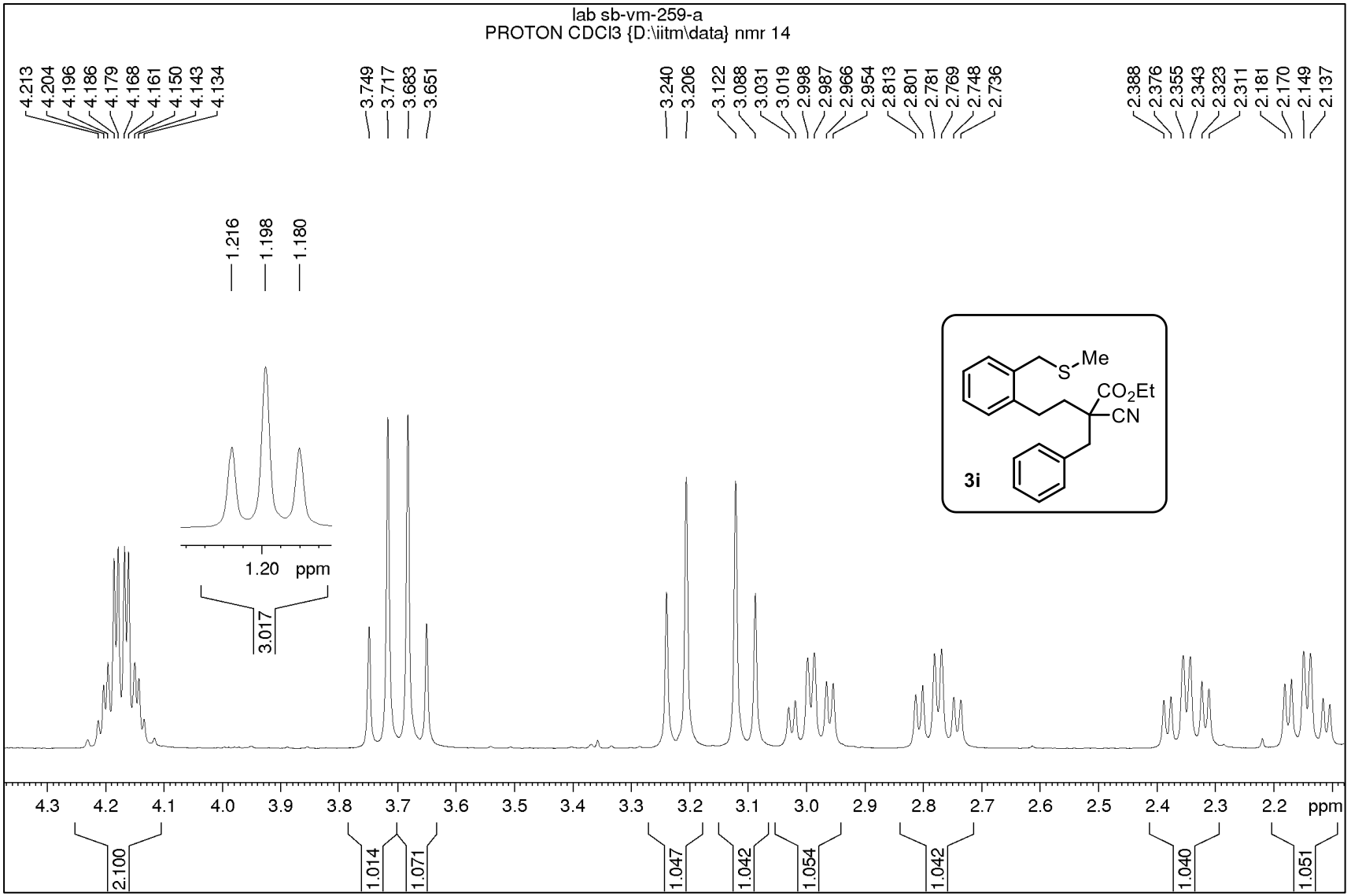
^{13}C NMR spectrum of compound 3h



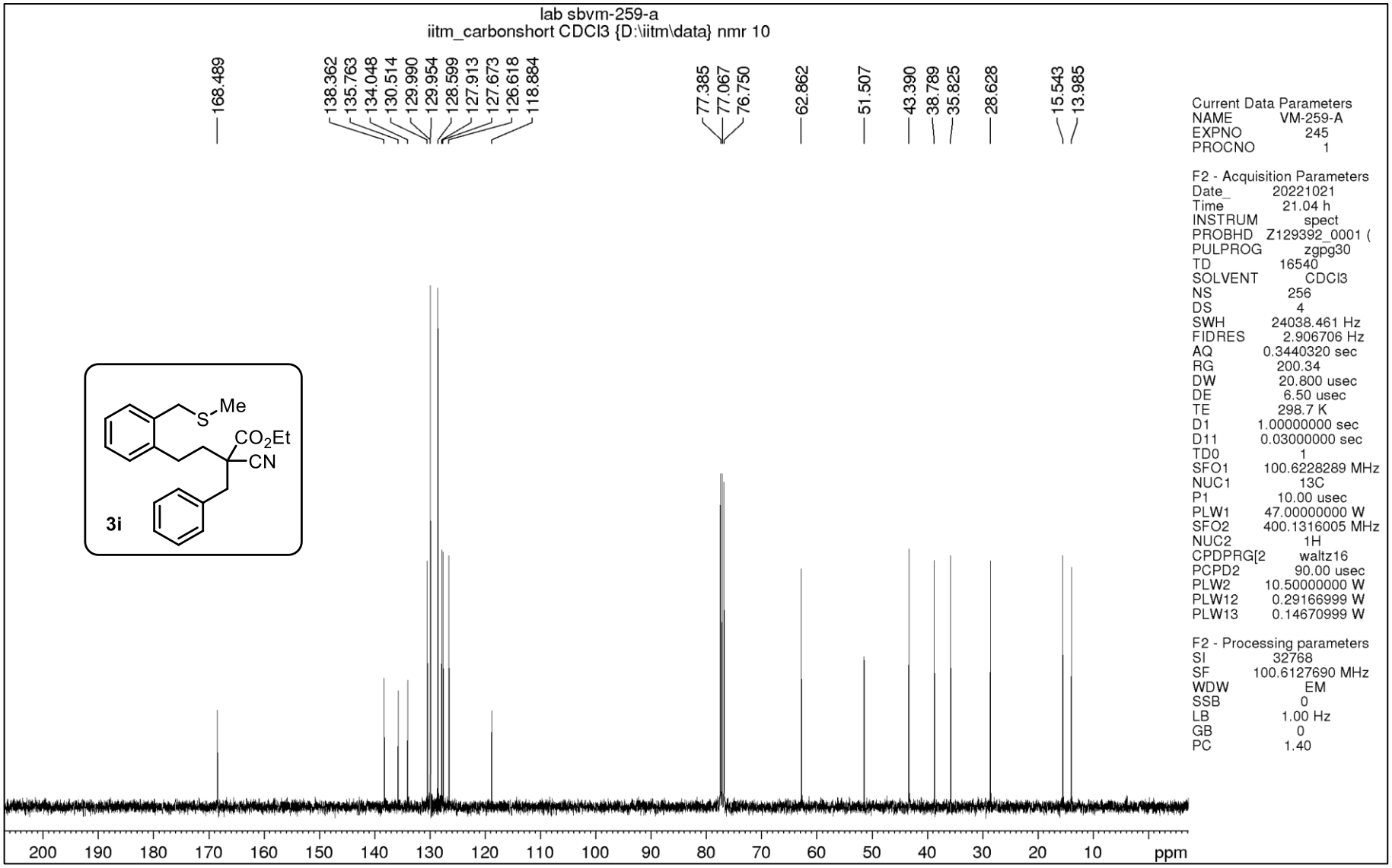
DEPT-135 NMR spectrum of compound 3h



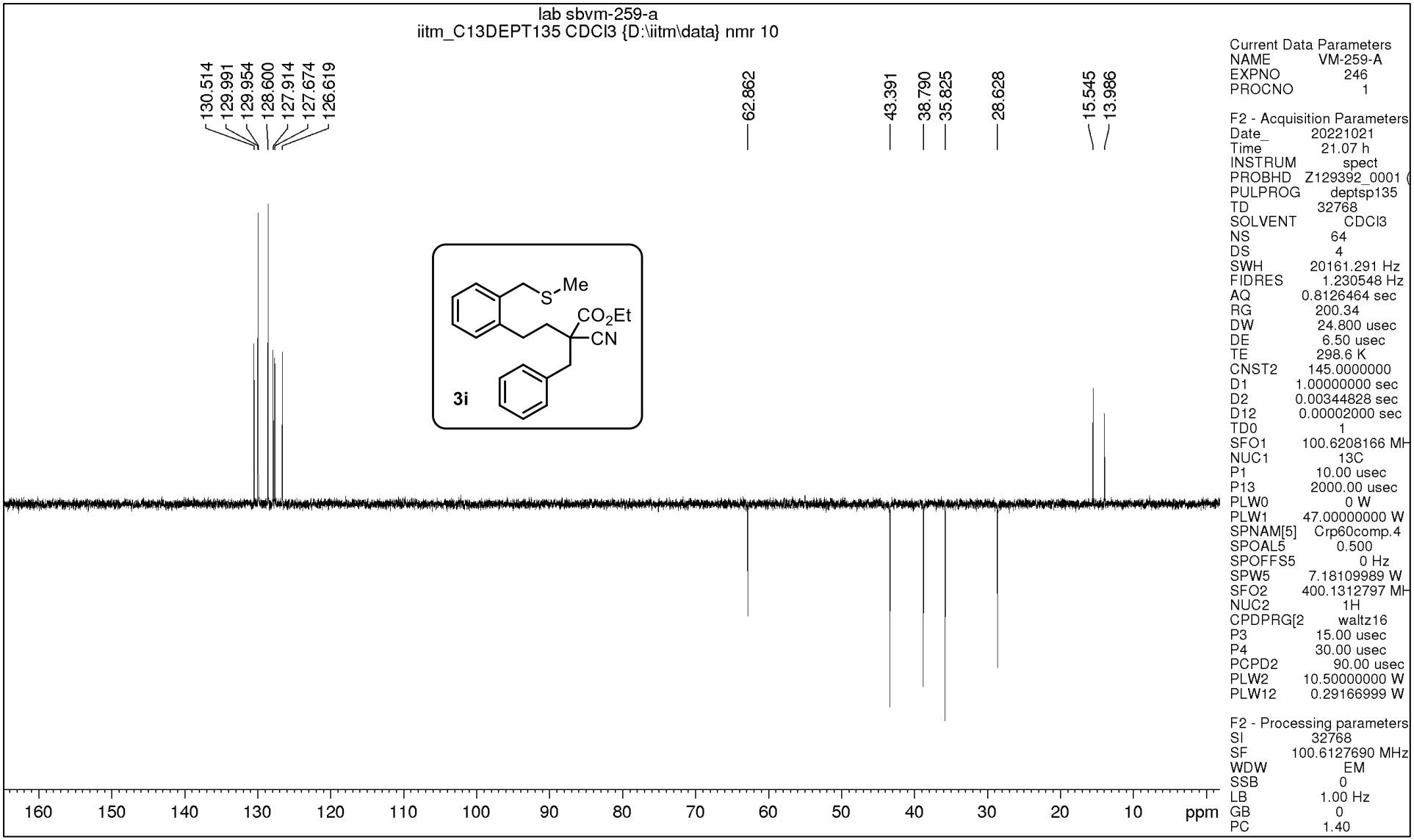
^{1}H NMR spectrum of compound 3i



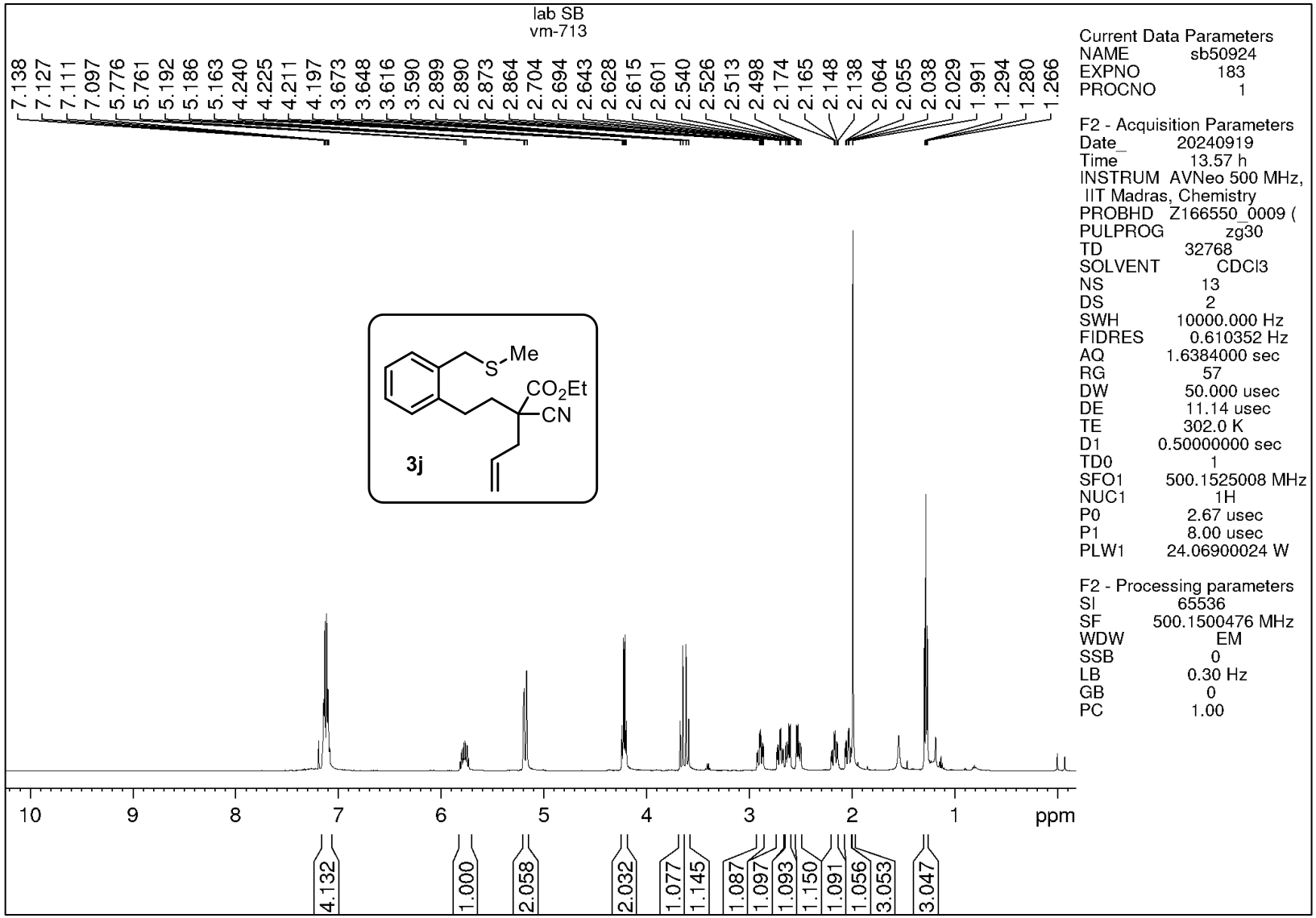
^{1}H NMR spectrum of compound 3i



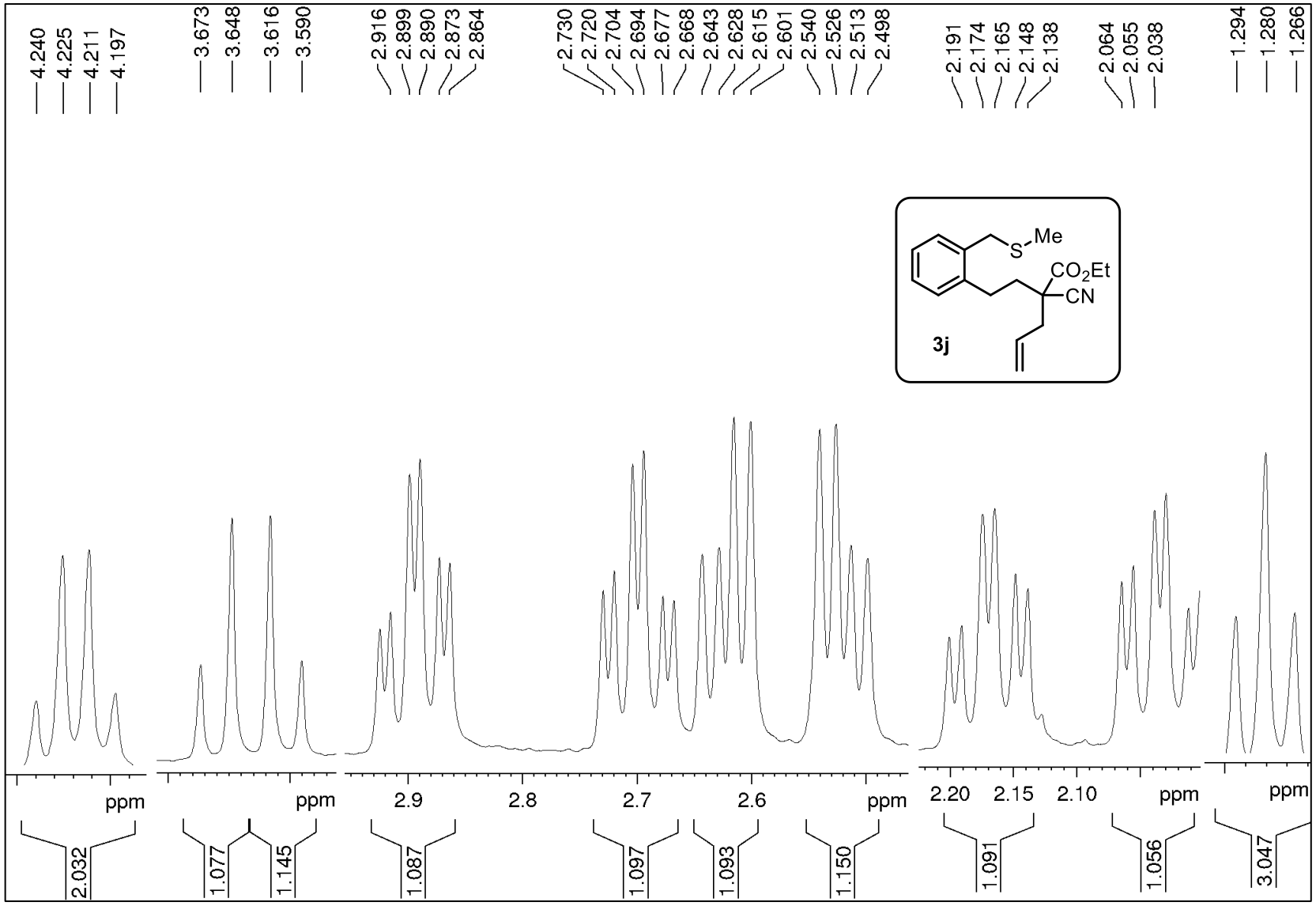
^{13}C NMR spectrum of compound 3i



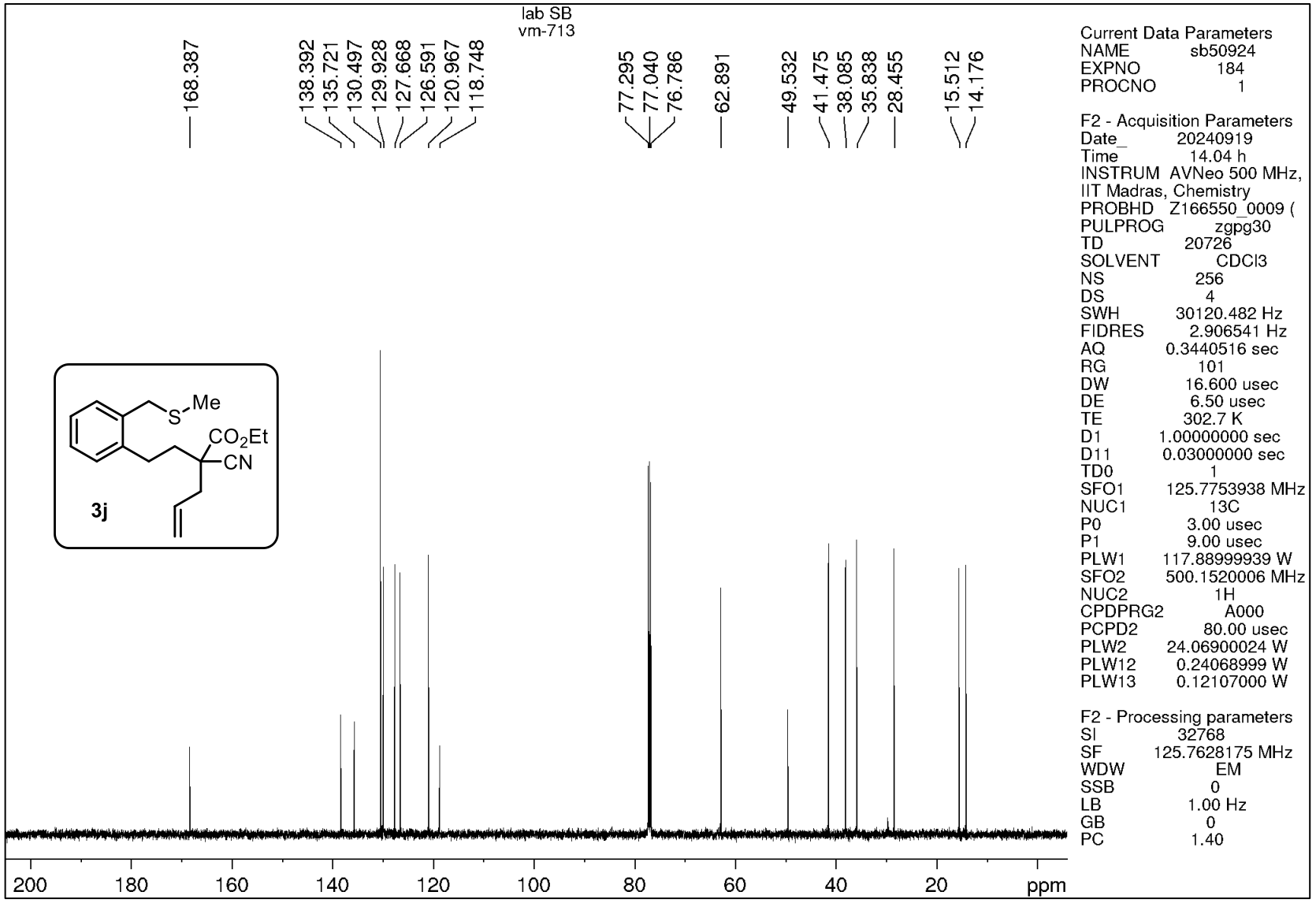
DEPT-135 NMR spectrum of compound 3i



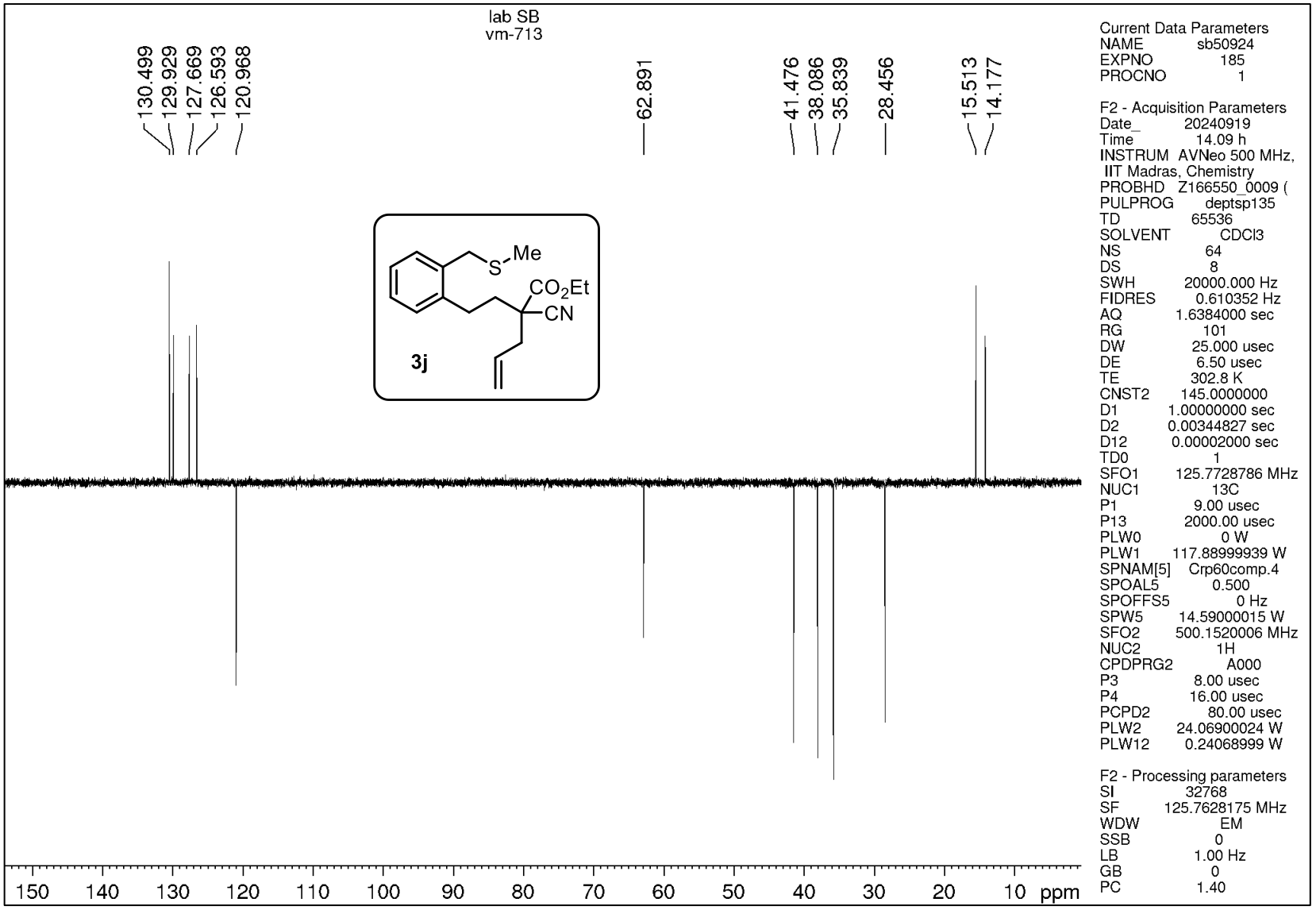
^{1}H NMR spectrum of compound 3j



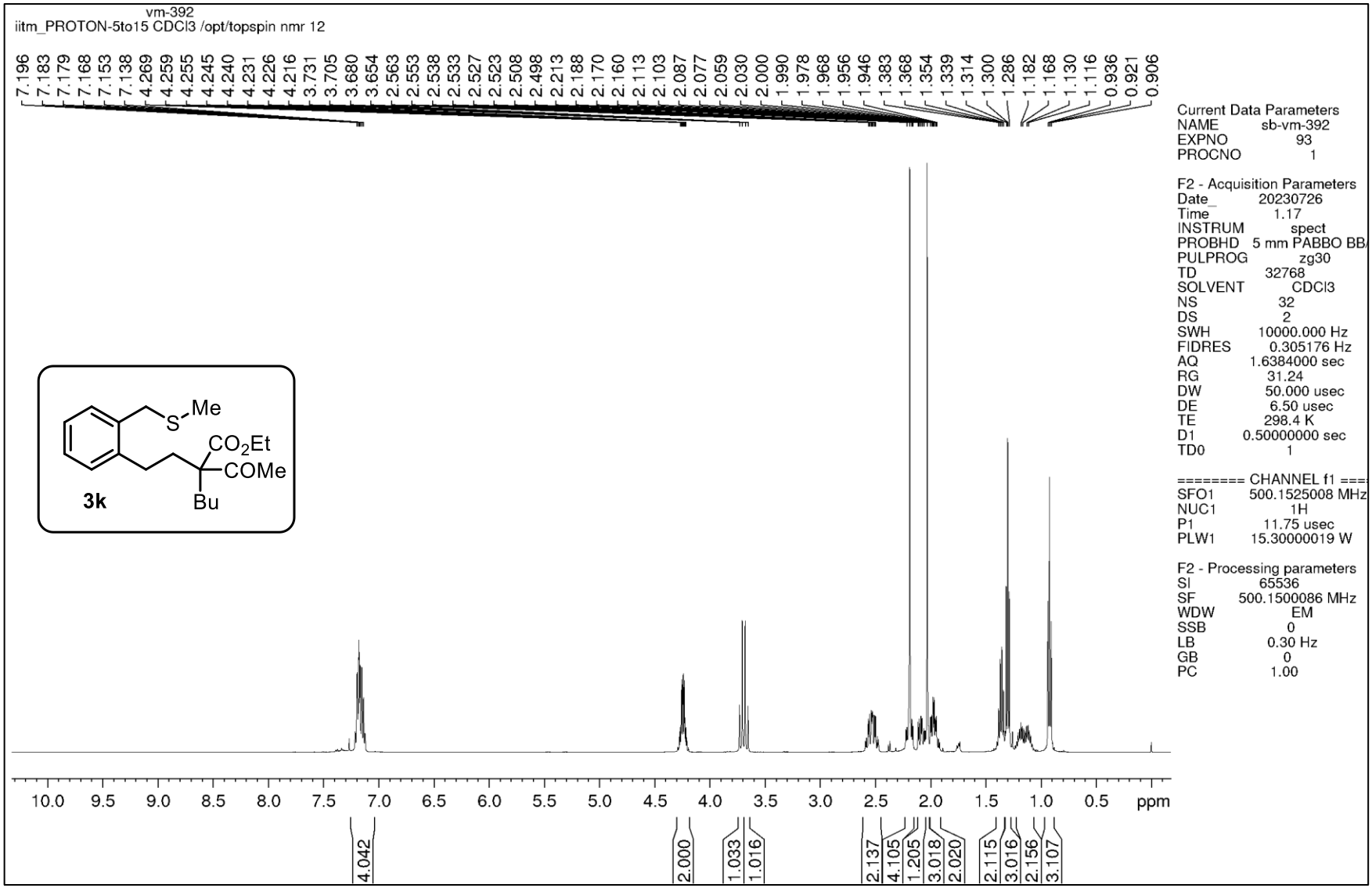
^{1}H NMR spectrum of compound 3j



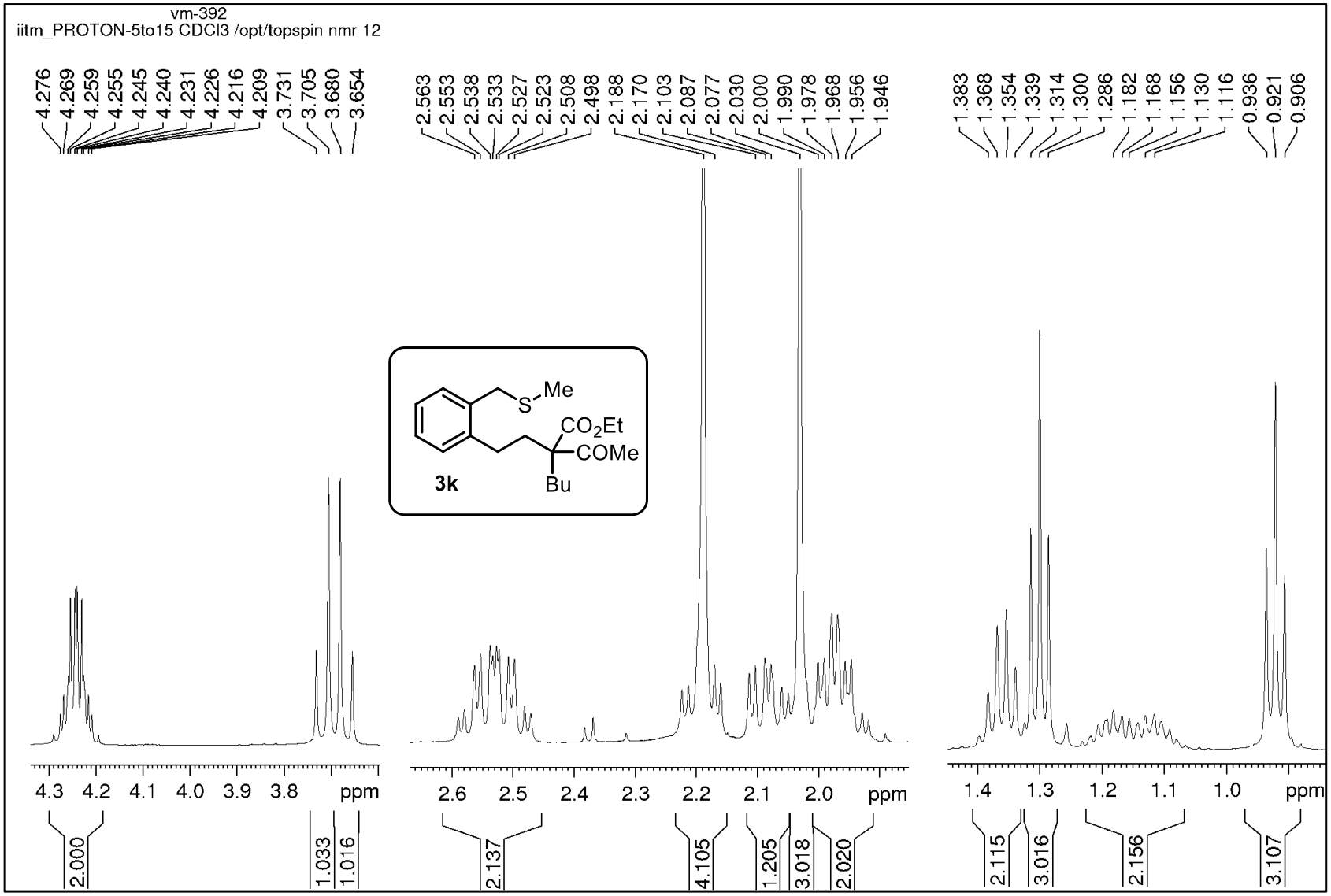
^{13}C NMR spectrum of compound 3j



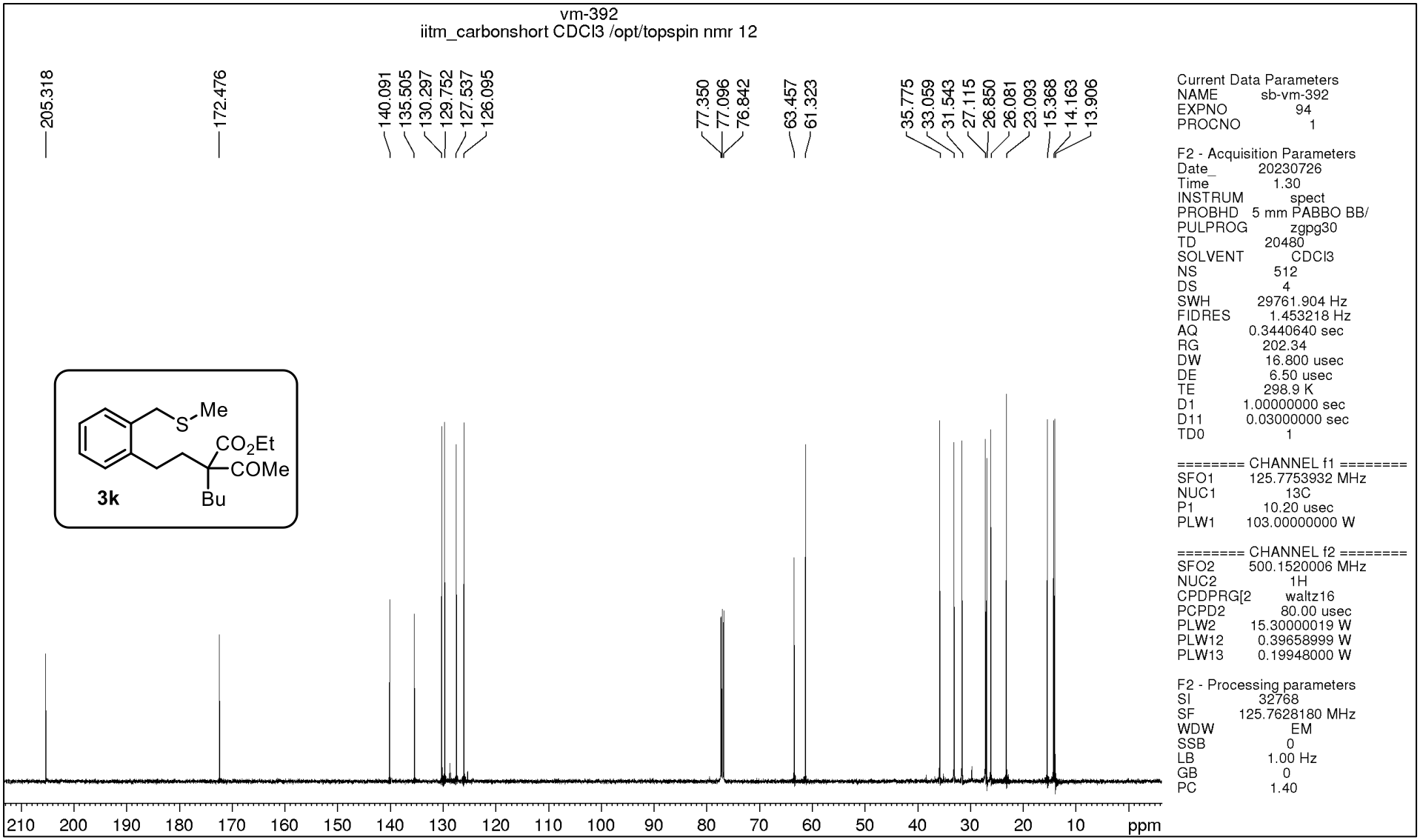
DEPT-135 NMR spectrum of compound 3j



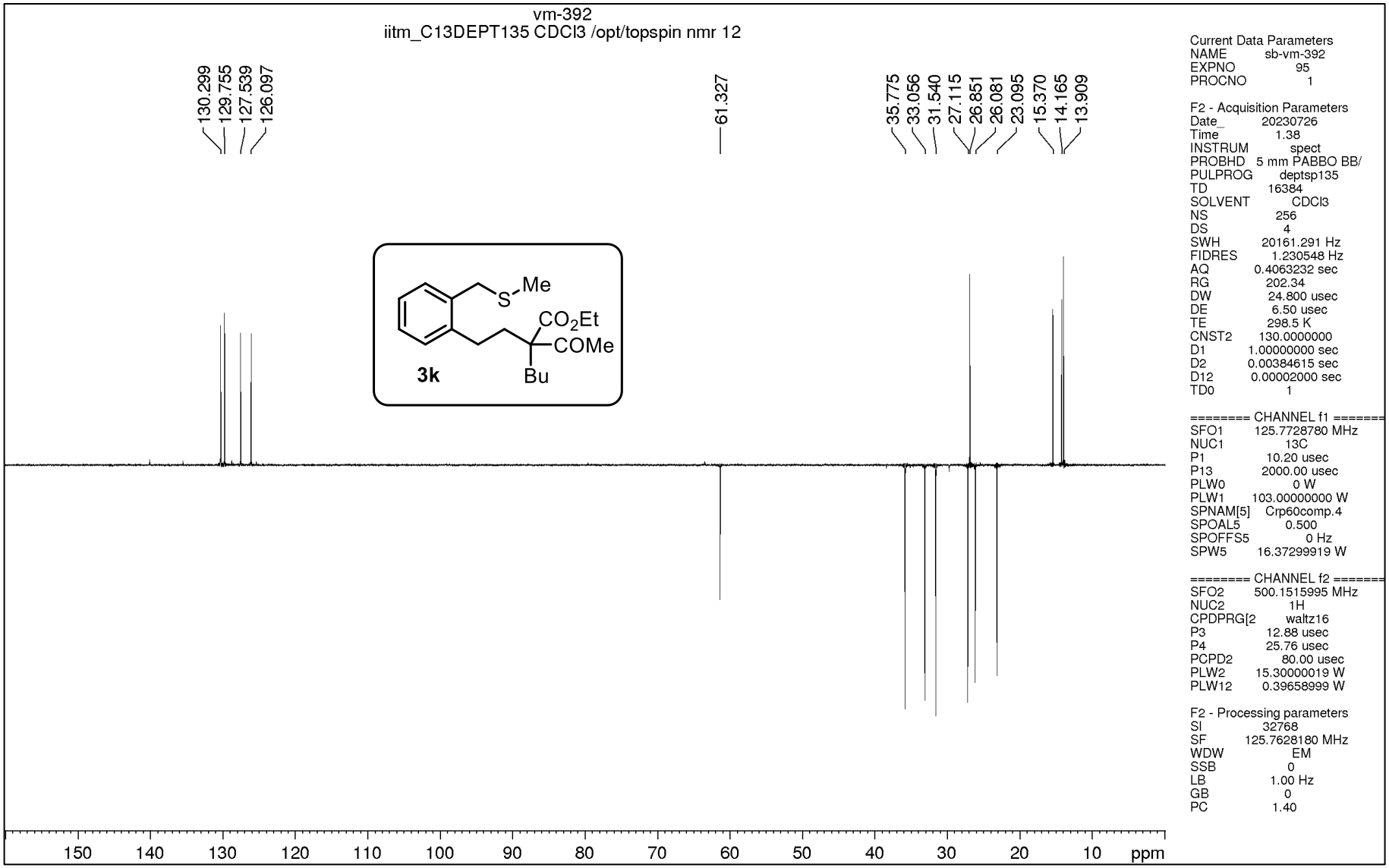
^{1}H NMR spectrum of compound 3k



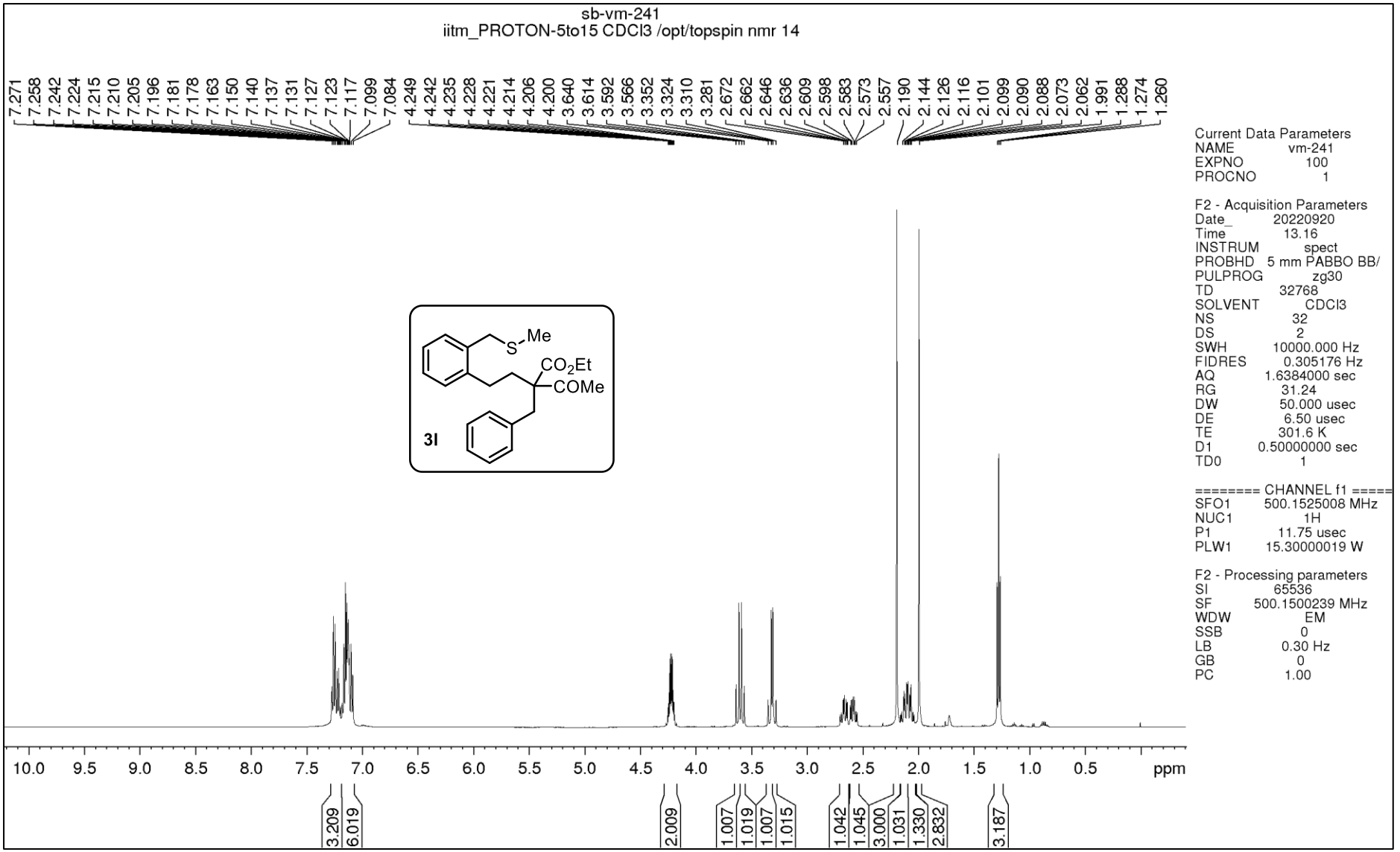
^{1}H NMR spectrum of compound 3k



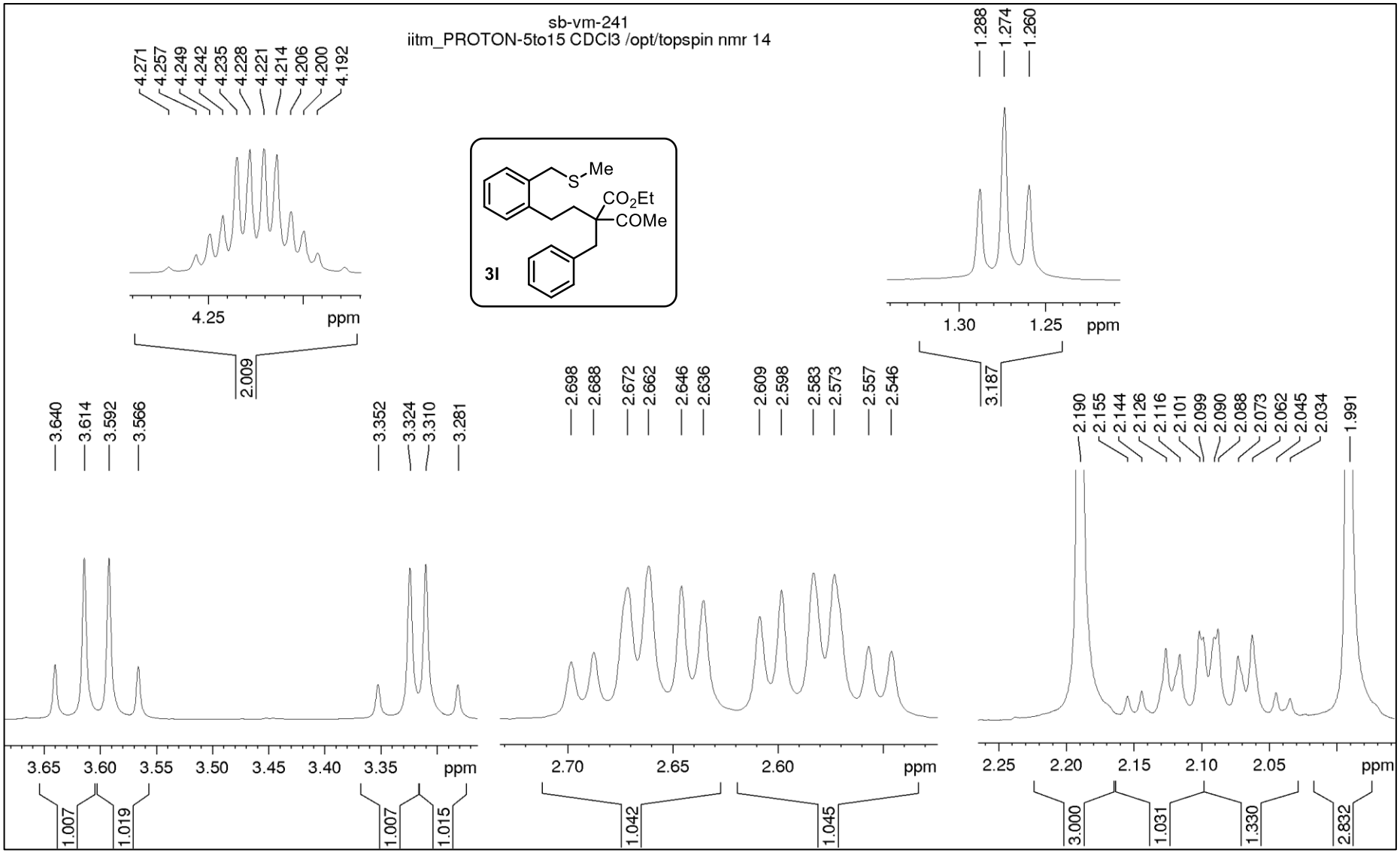
^{13}C NMR spectrum of compound 3k



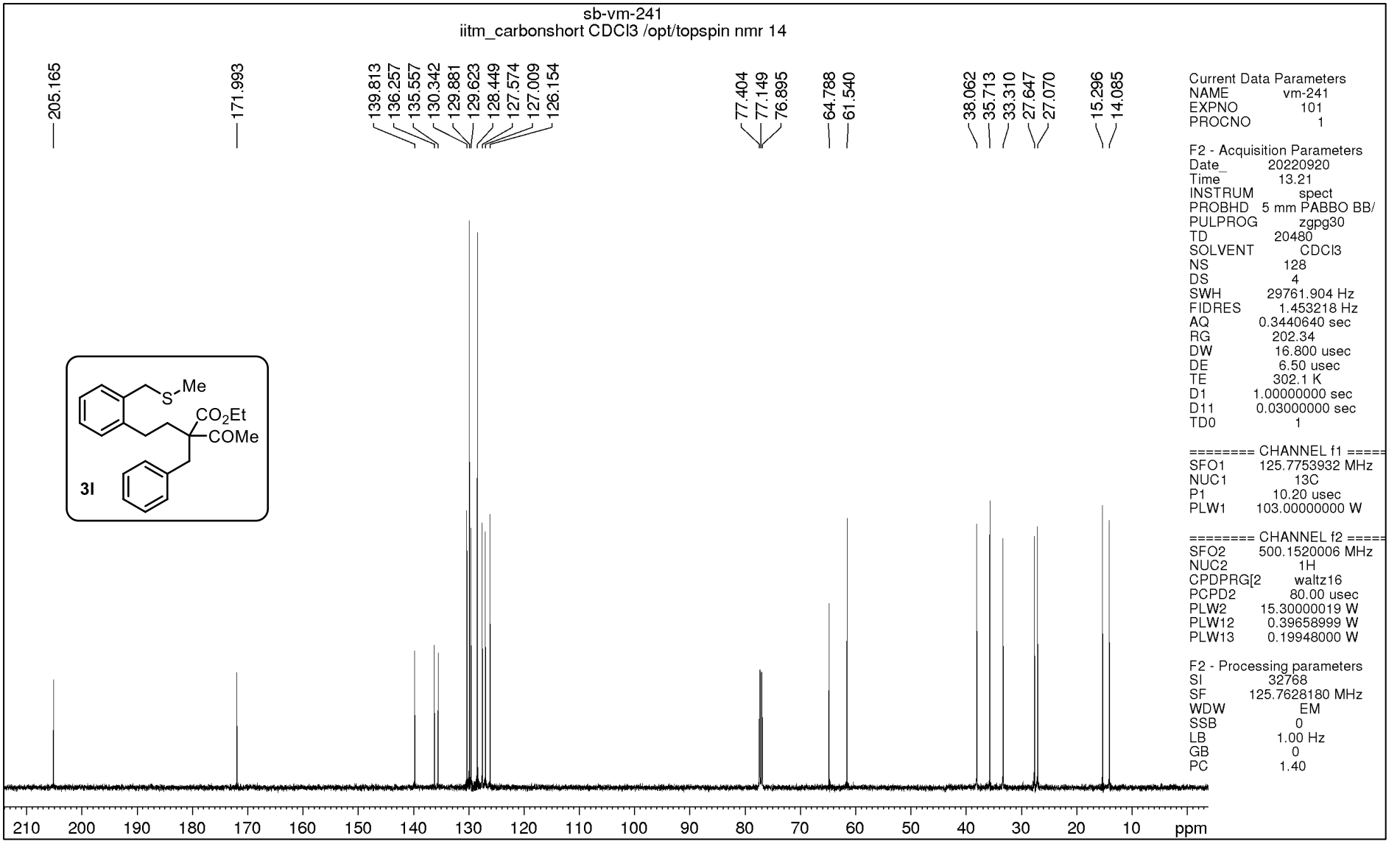
DEPT-135 NMR spectrum of compound 3k



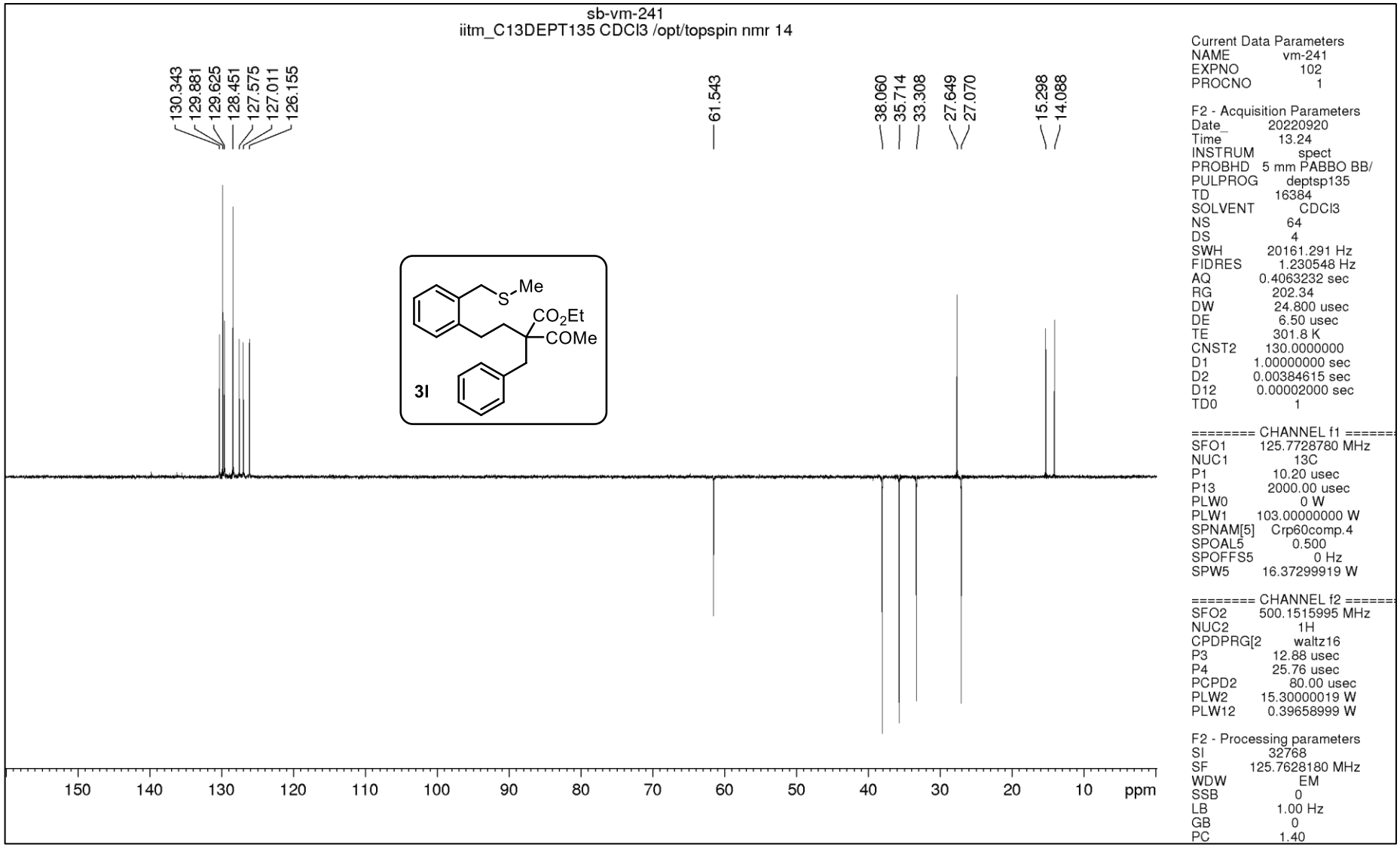
^{1}H NMR spectrum of compound 3l



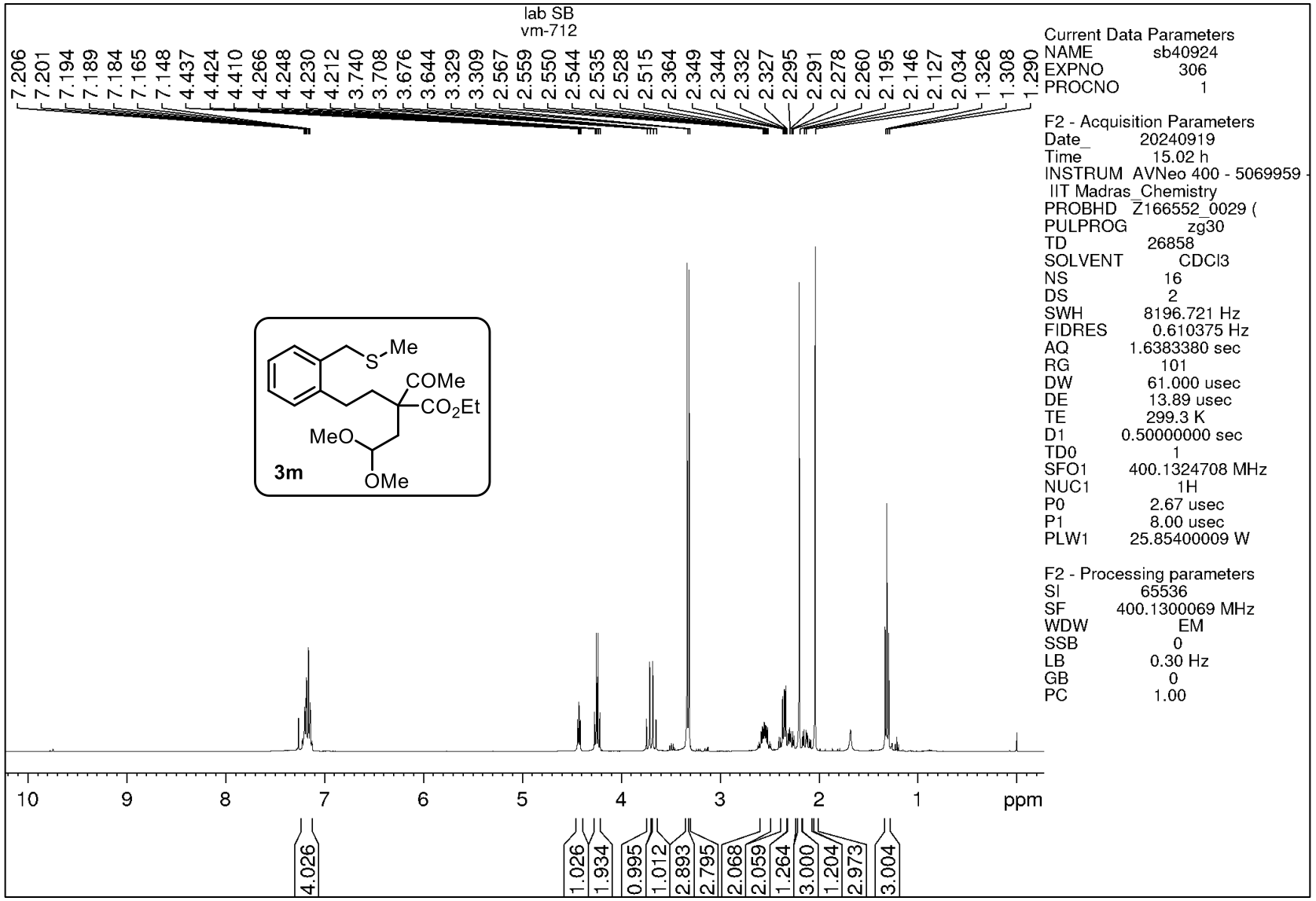
^{1}H NMR spectrum of compound 3l



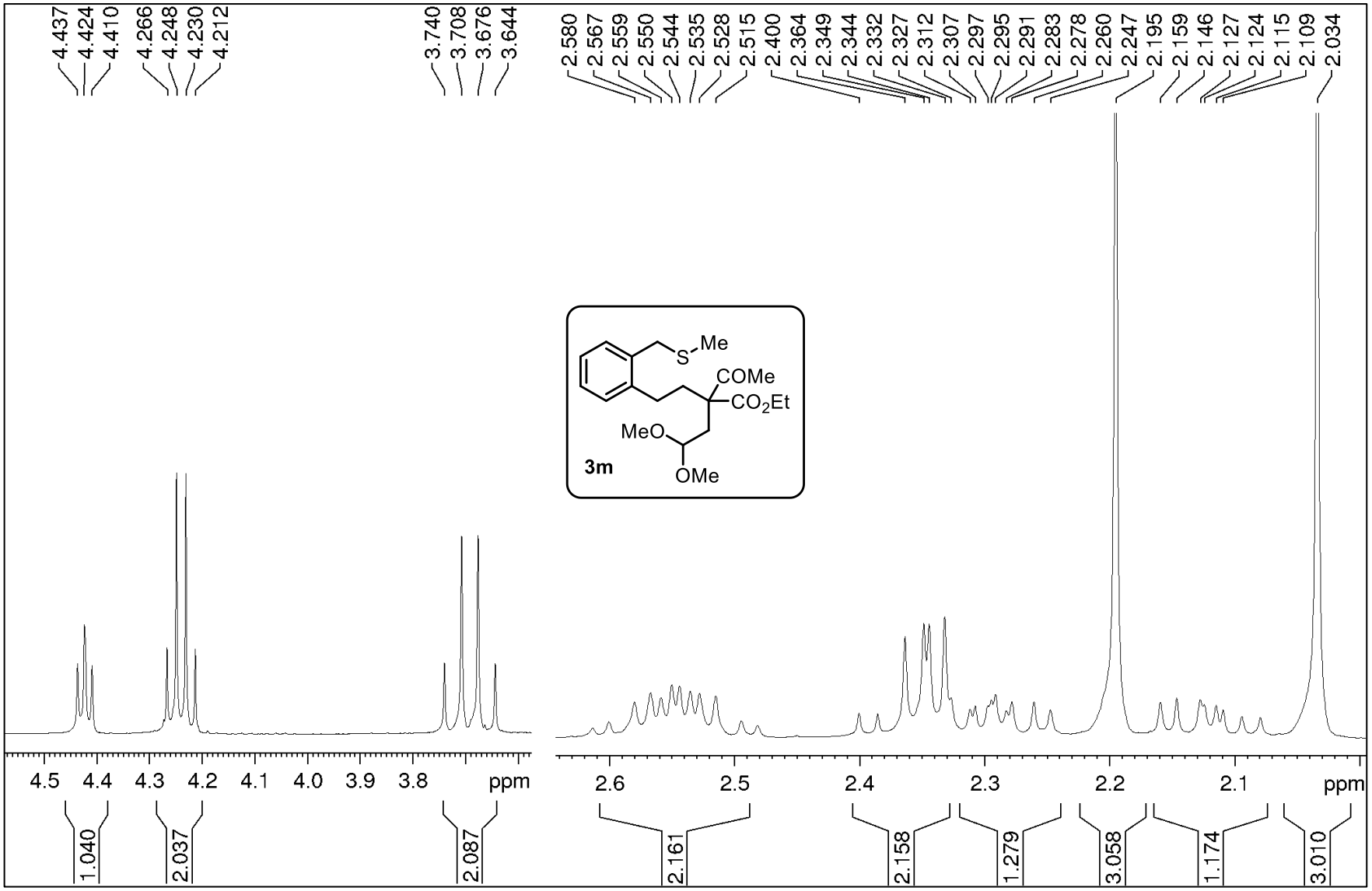
^{13}C NMR spectrum of compound 3l



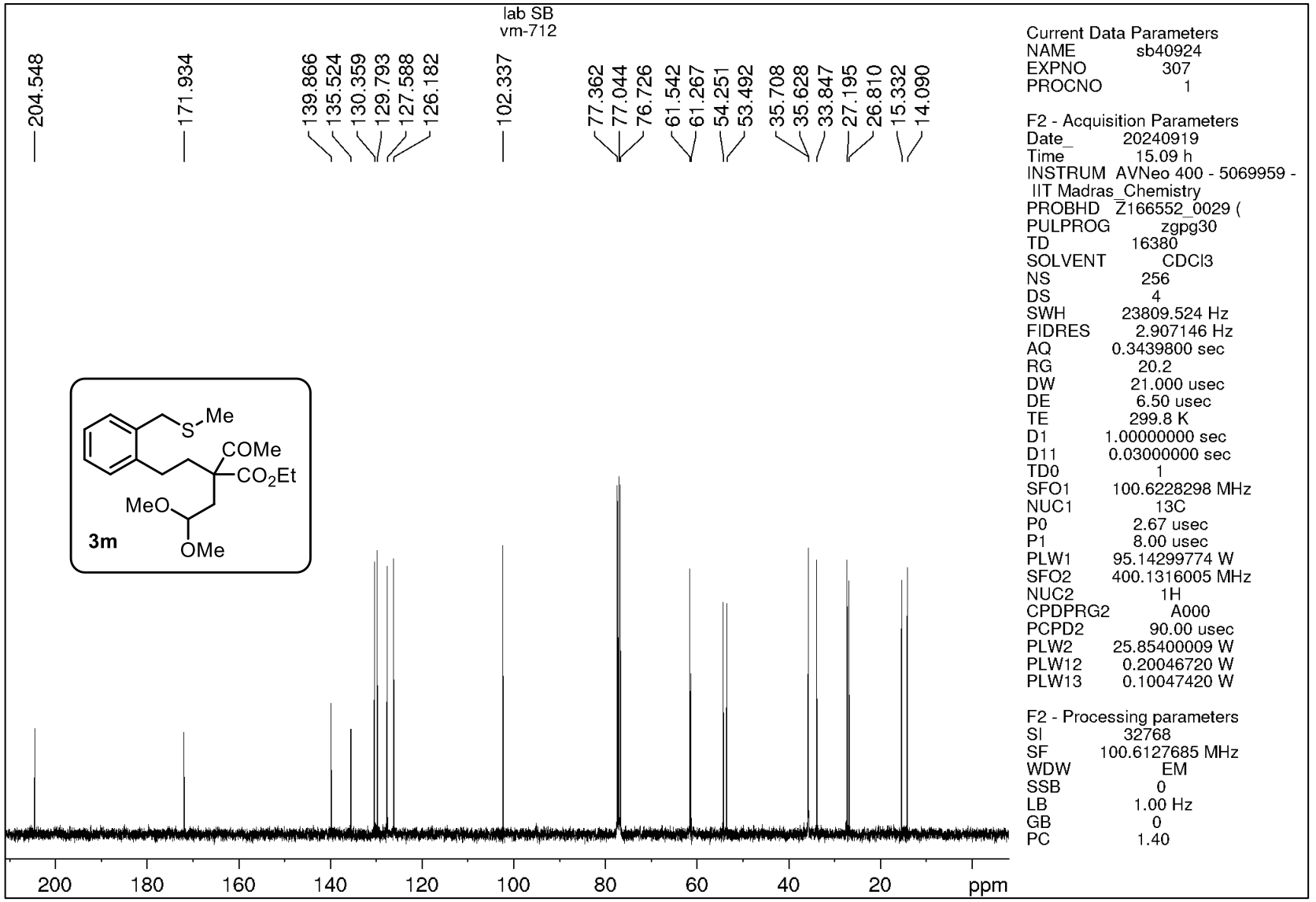
DEPT-135 NMR spectrum of compound 3l



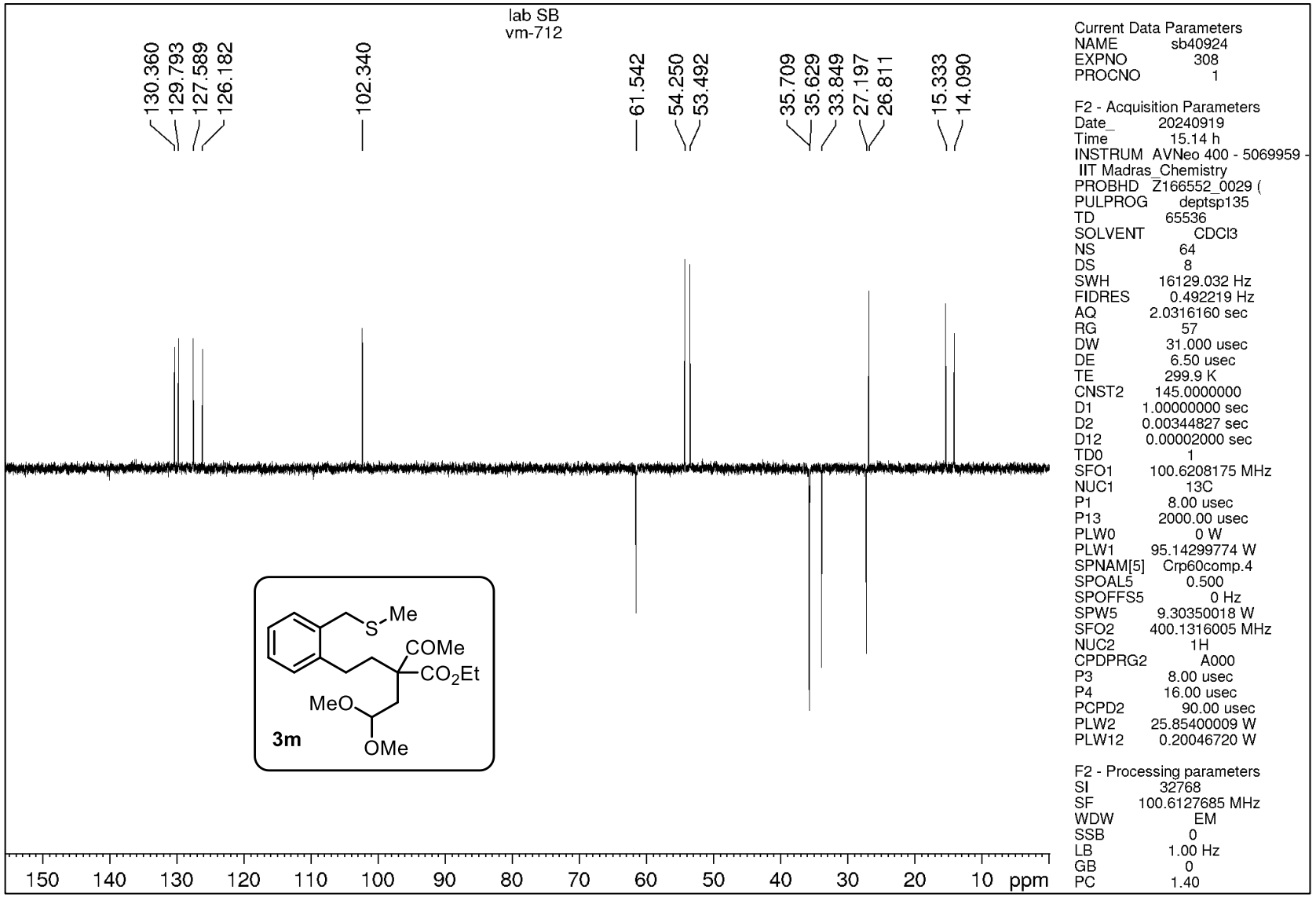
^{1}H NMR spectrum of compound 3m



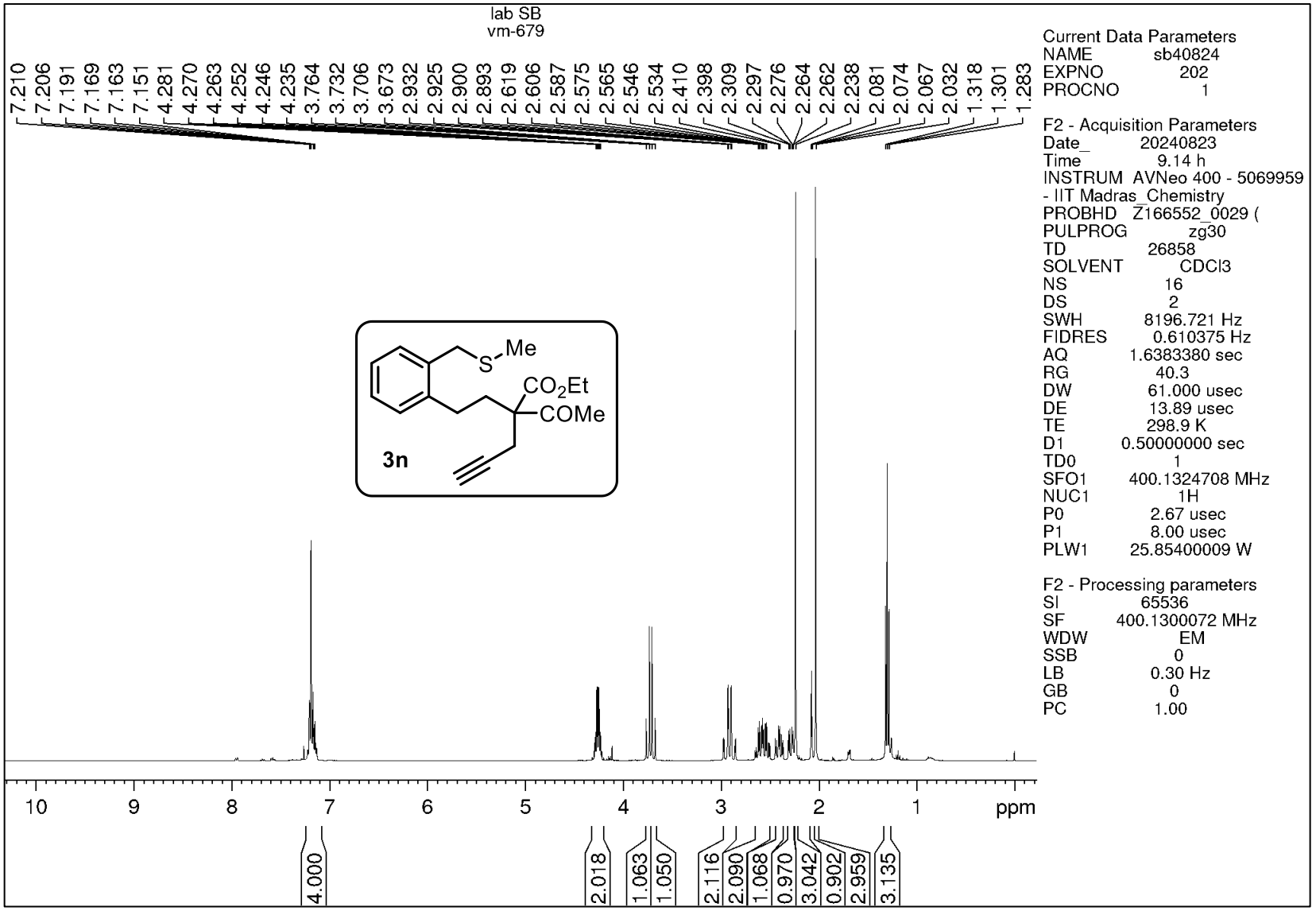
^{1}H NMR spectrum of compound 3m



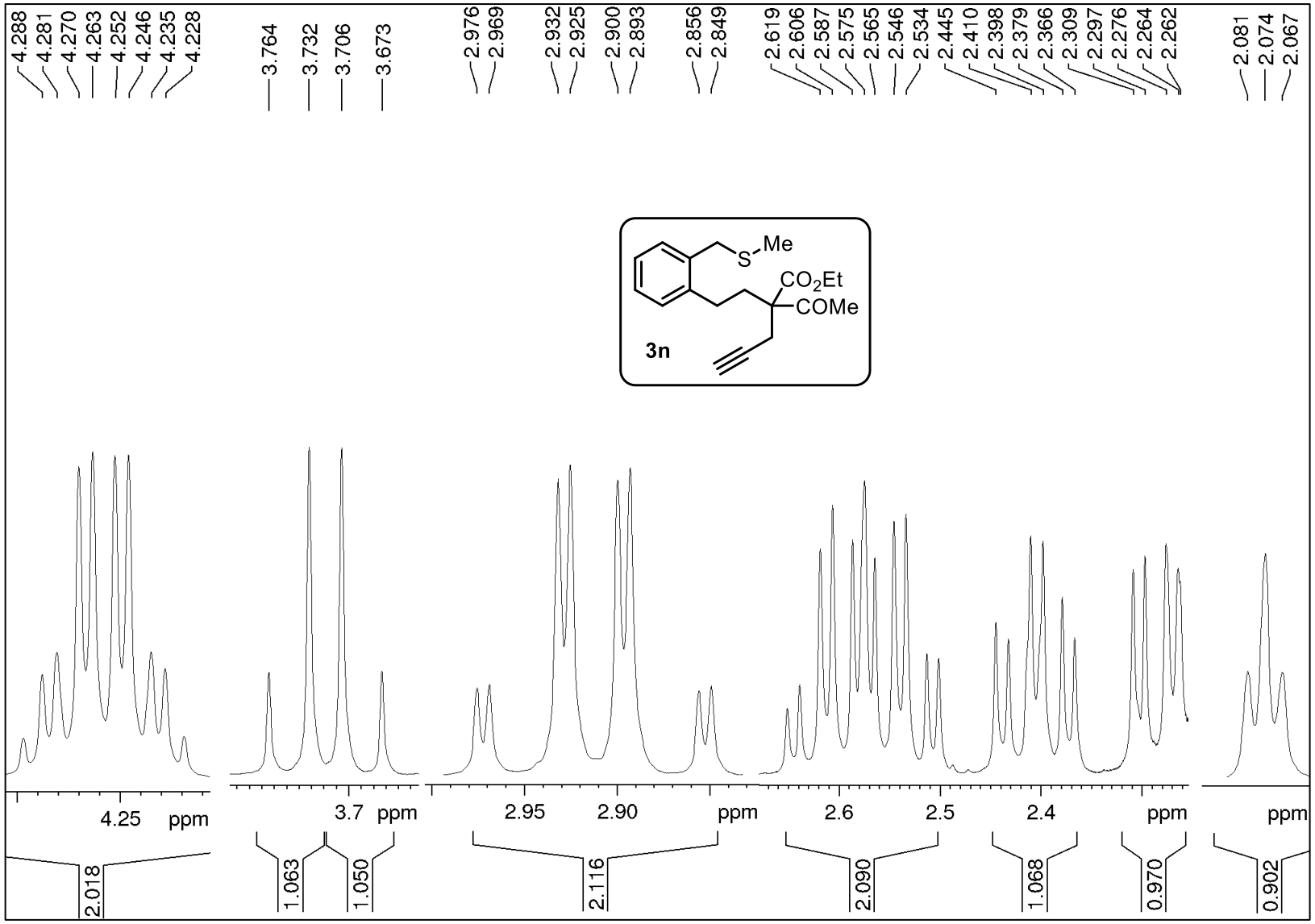
^{13}C NMR spectrum of compound 3m



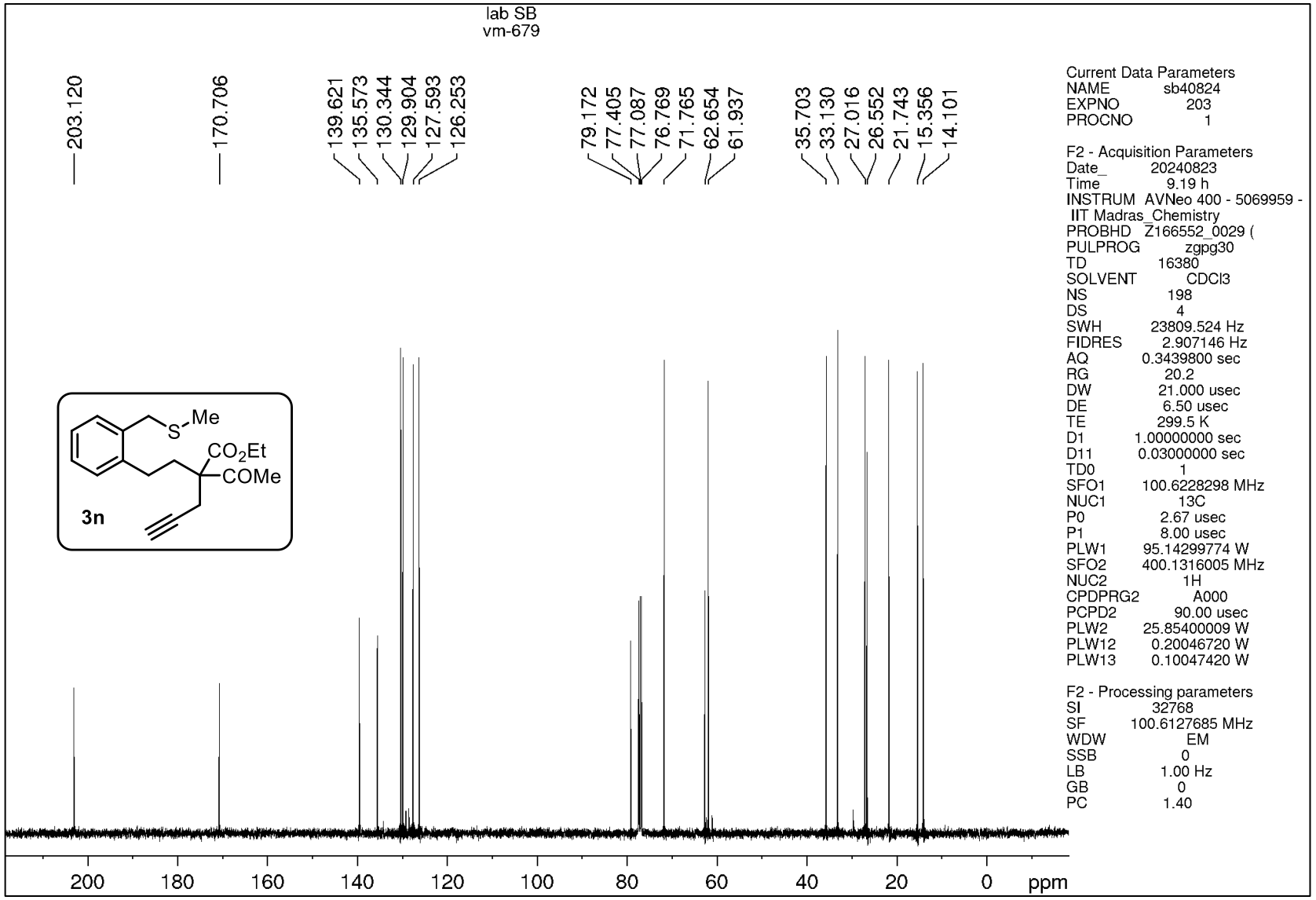
DEPT-135 NMR spectrum of compound 3m



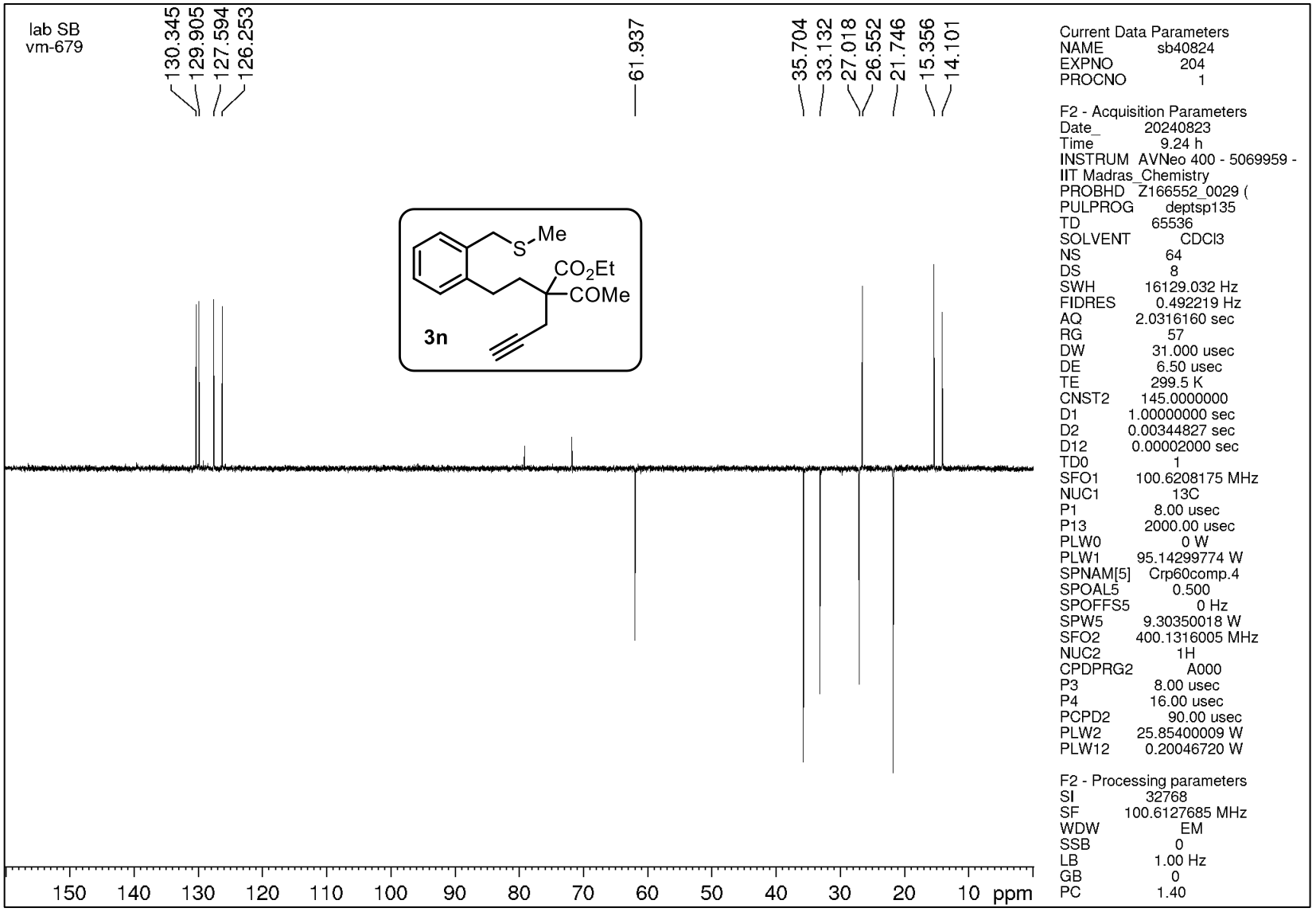
^{1}H NMR spectrum of compound 3n



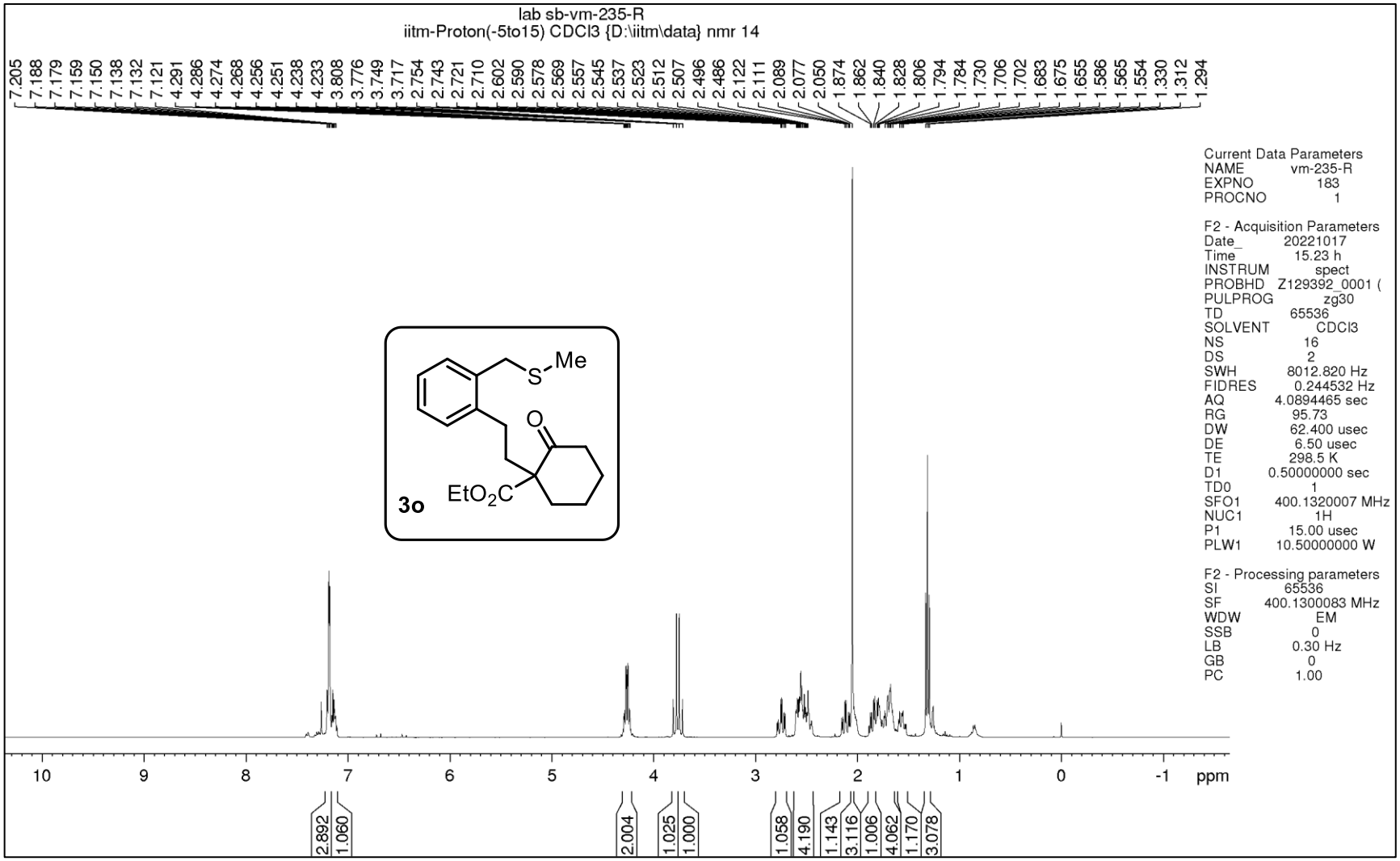
^{1}H NMR spectrum of compound 3n



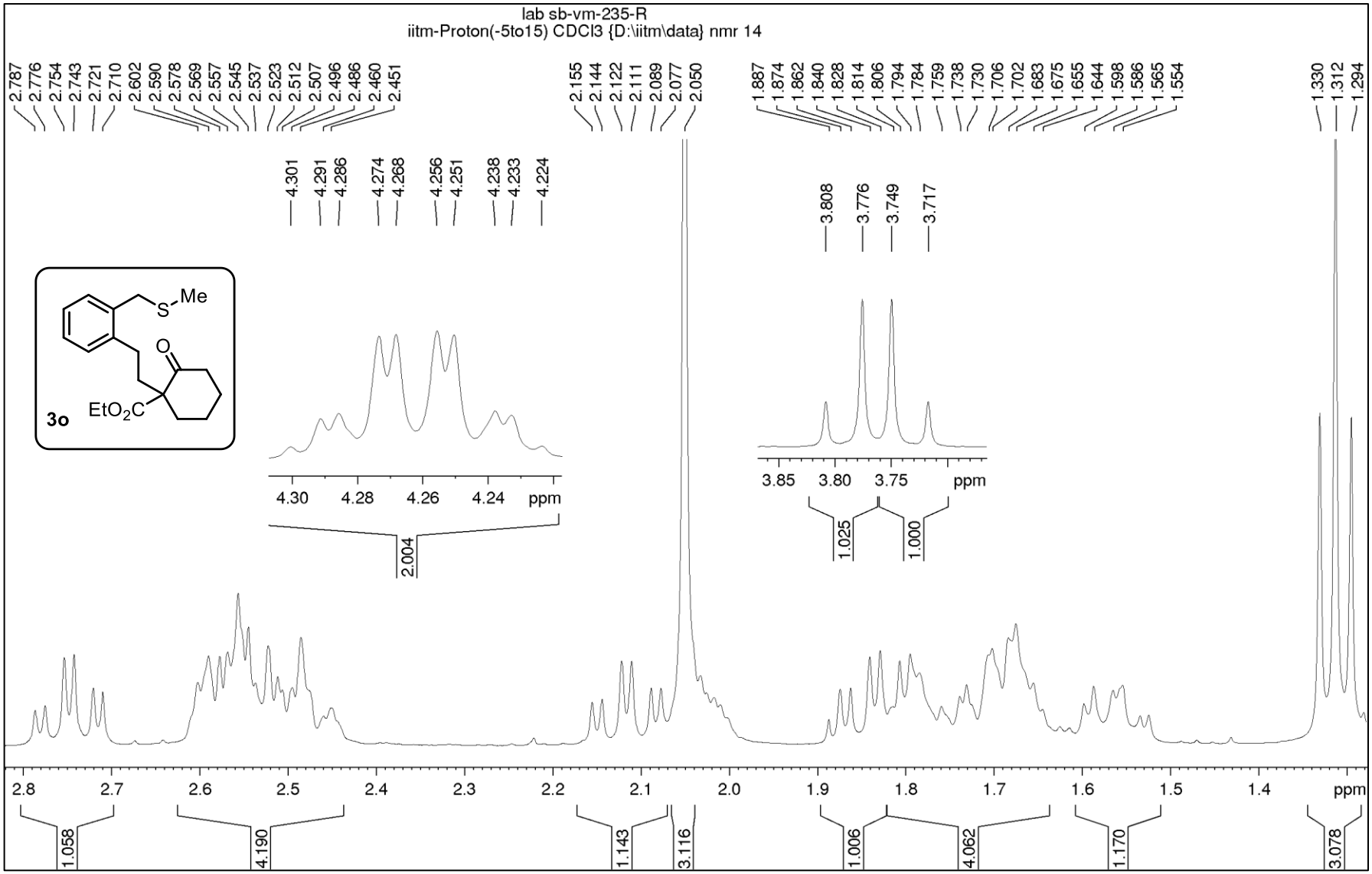
^{13}C NMR spectrum of compound 3n



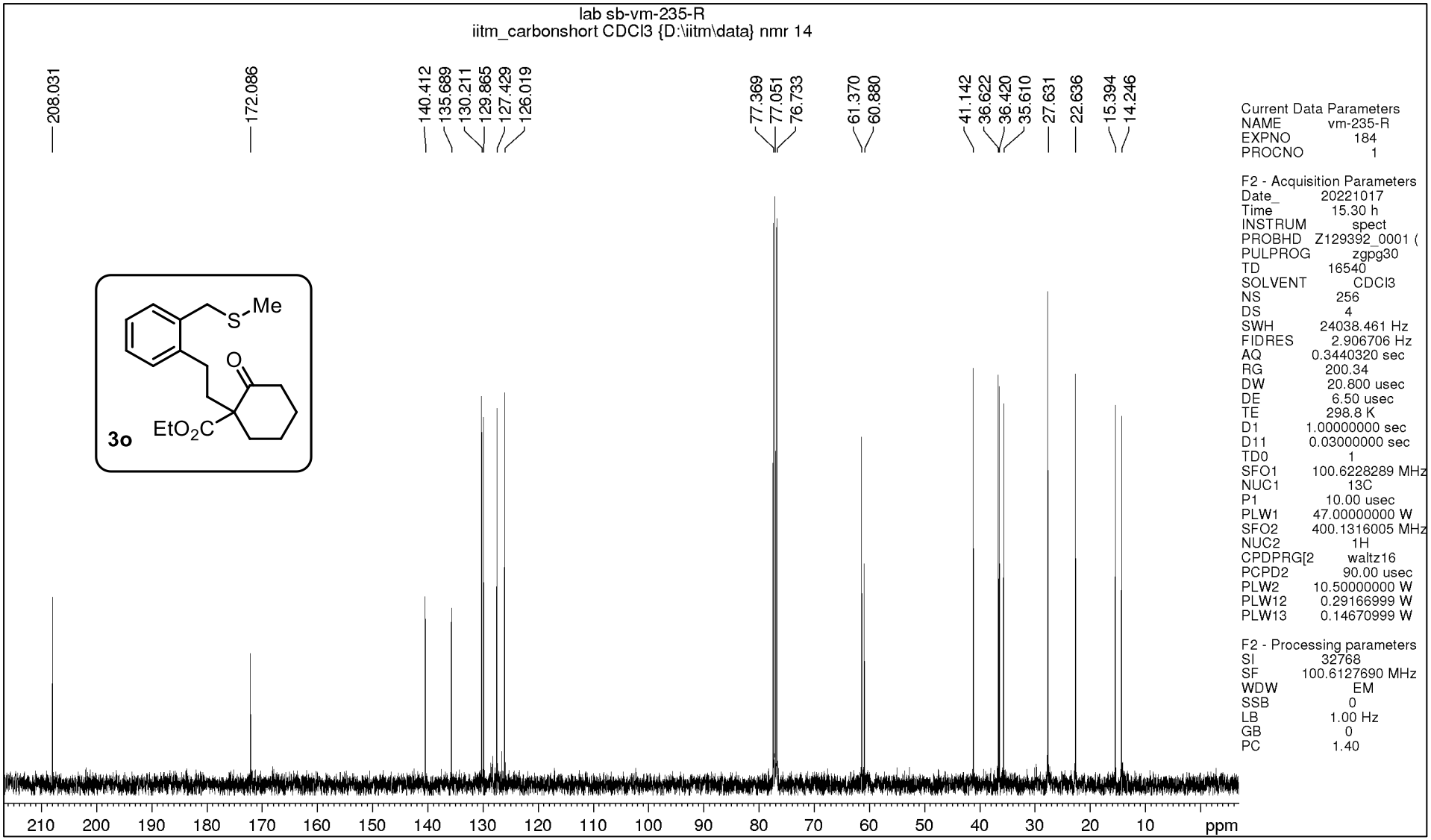
DEPT-135 NMR spectrum of compound 3n



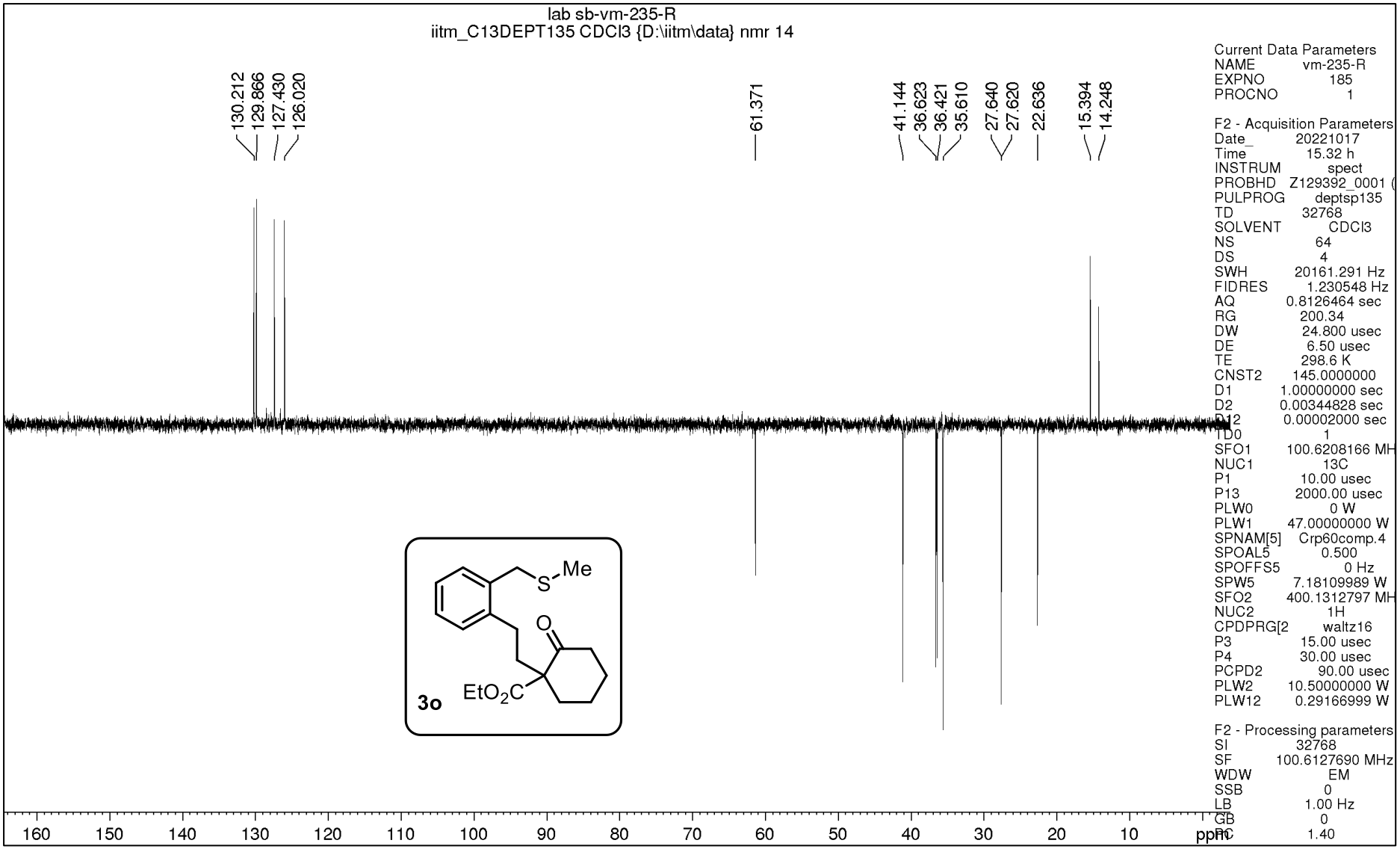
^{1}H NMR spectrum of compound 3o



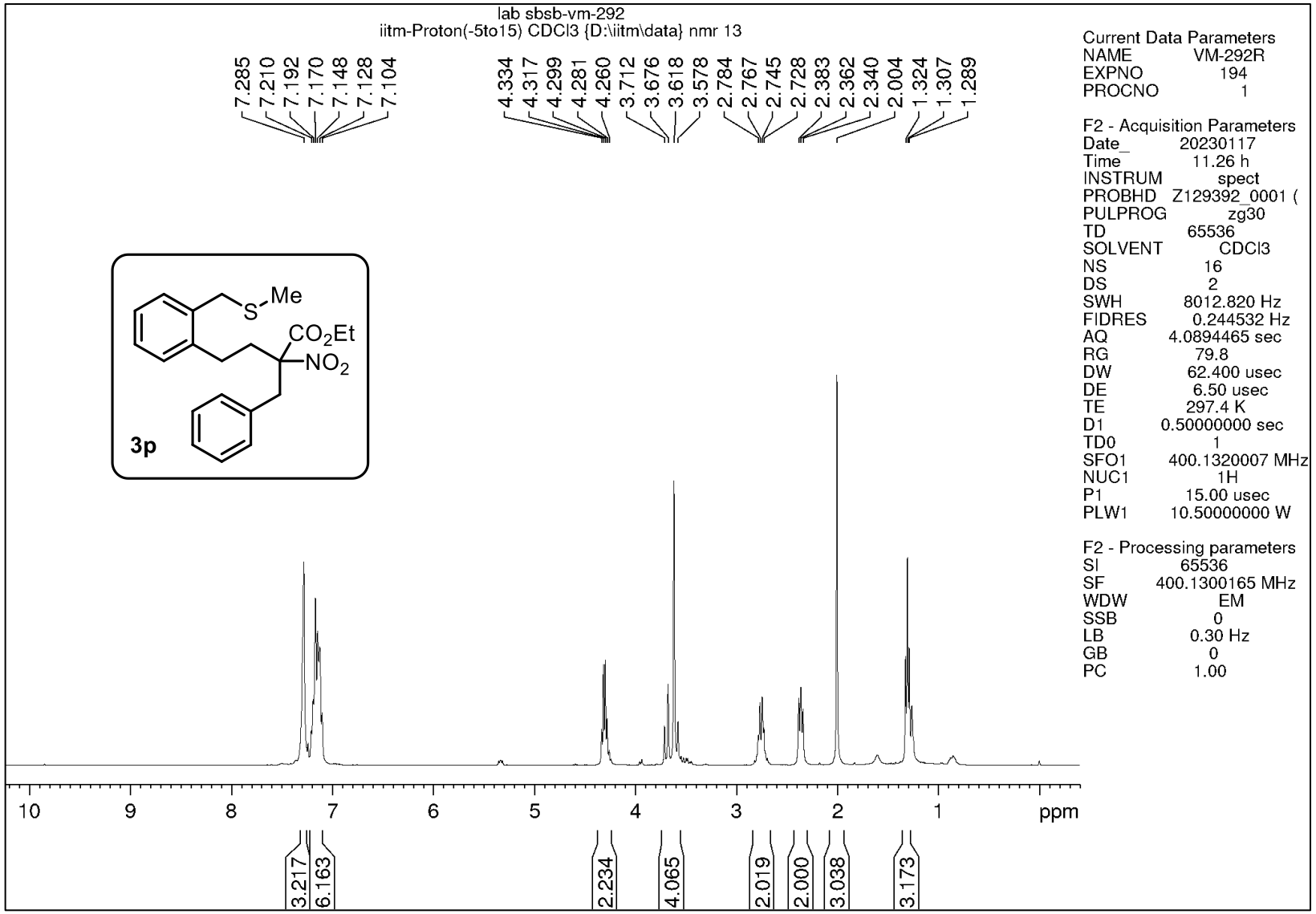
^{1}H NMR spectrum of compound 3o



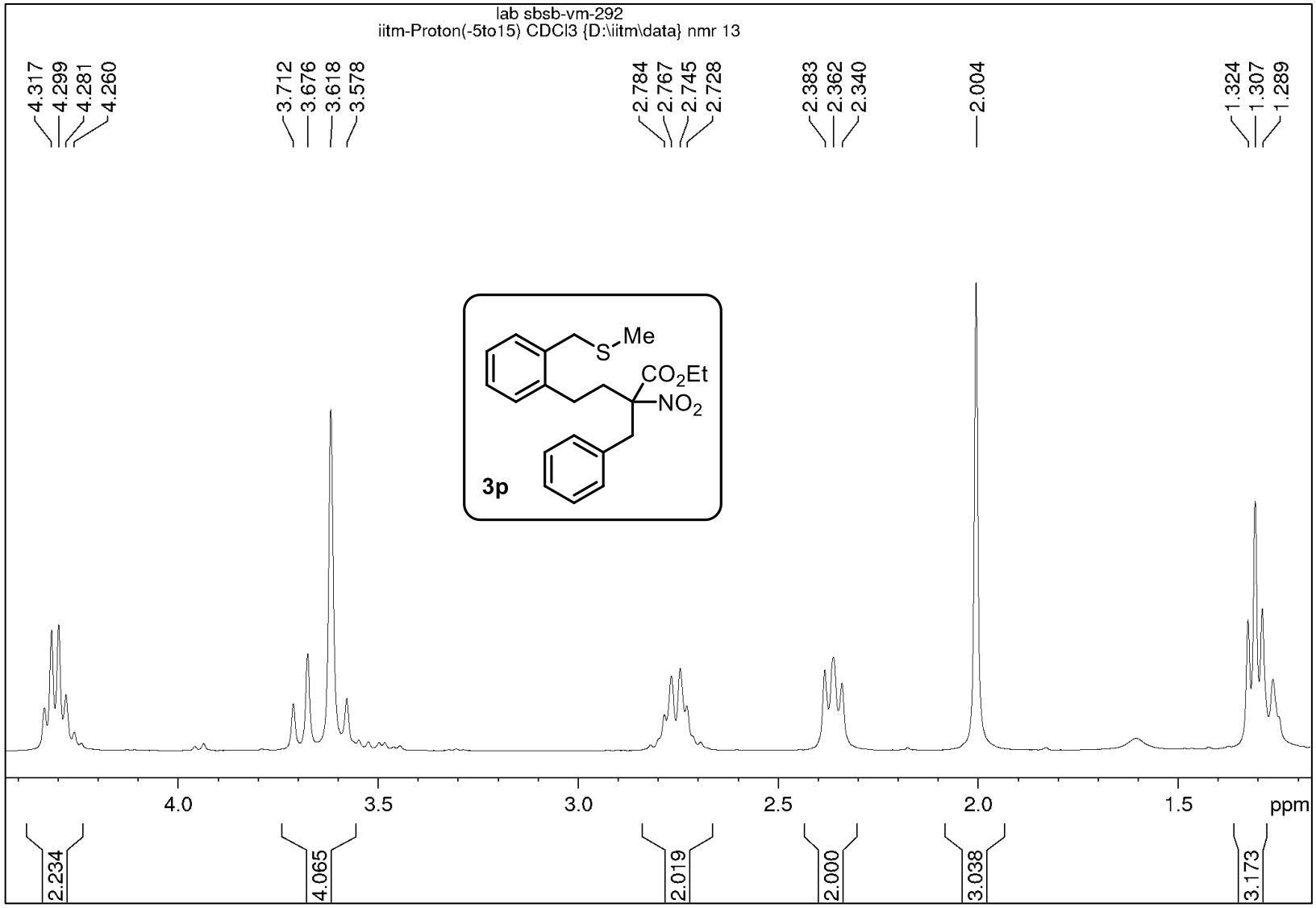
^{13}C NMR spectrum of compound 3o



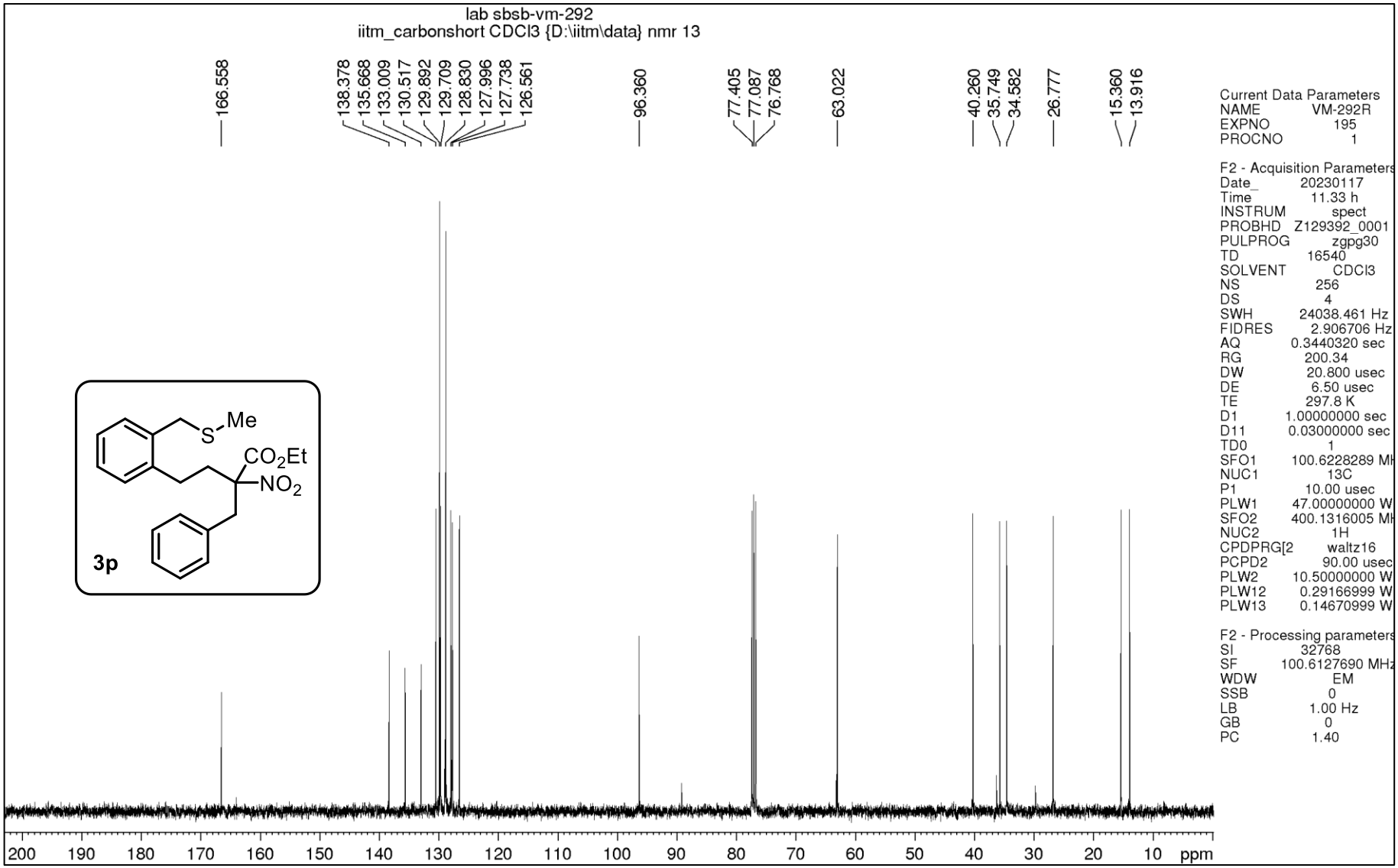
DEPT-135 NMR spectrum of compound 3o



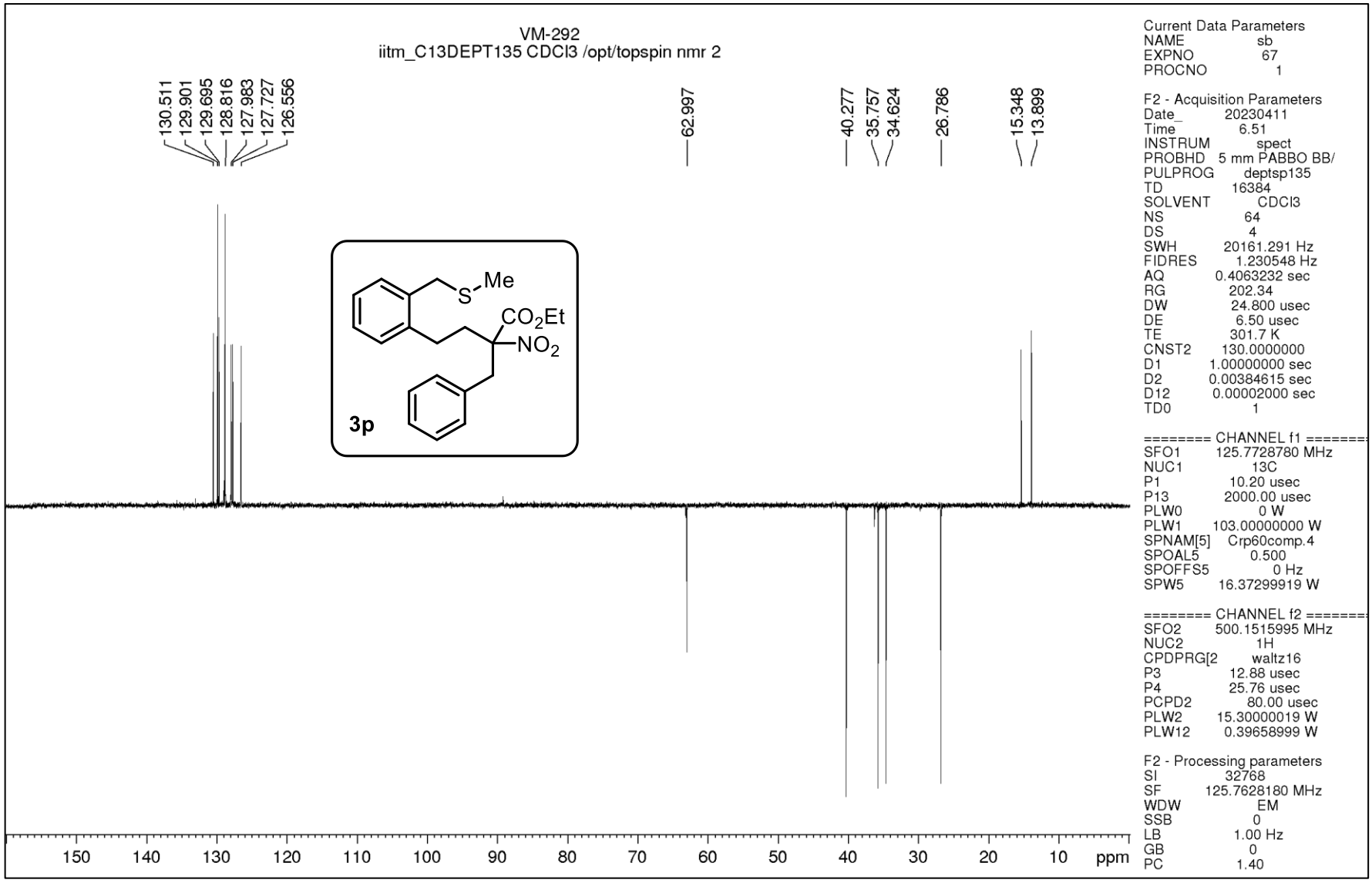
^{1}H NMR spectrum of compound 3p



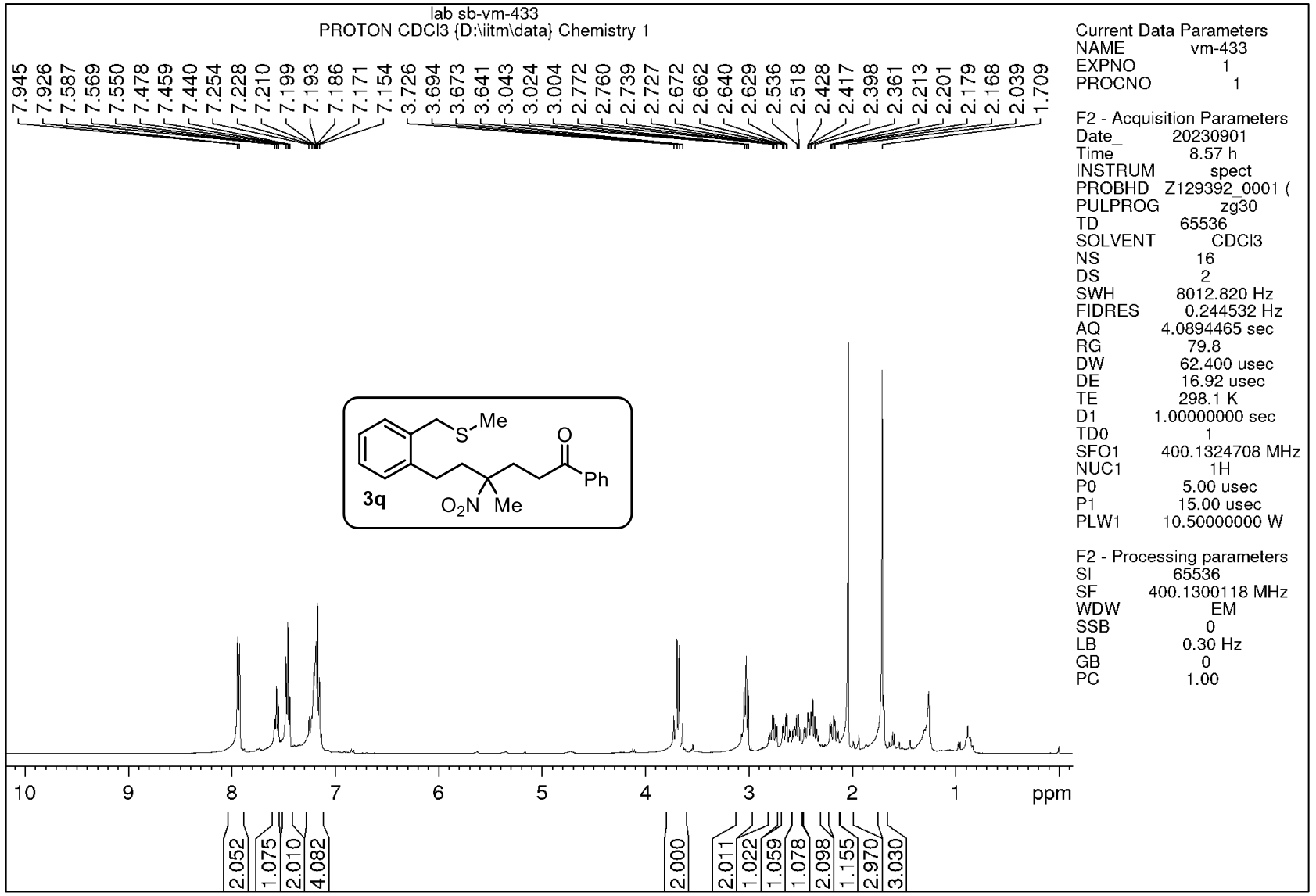
^{1}H NMR spectrum of compound 3p



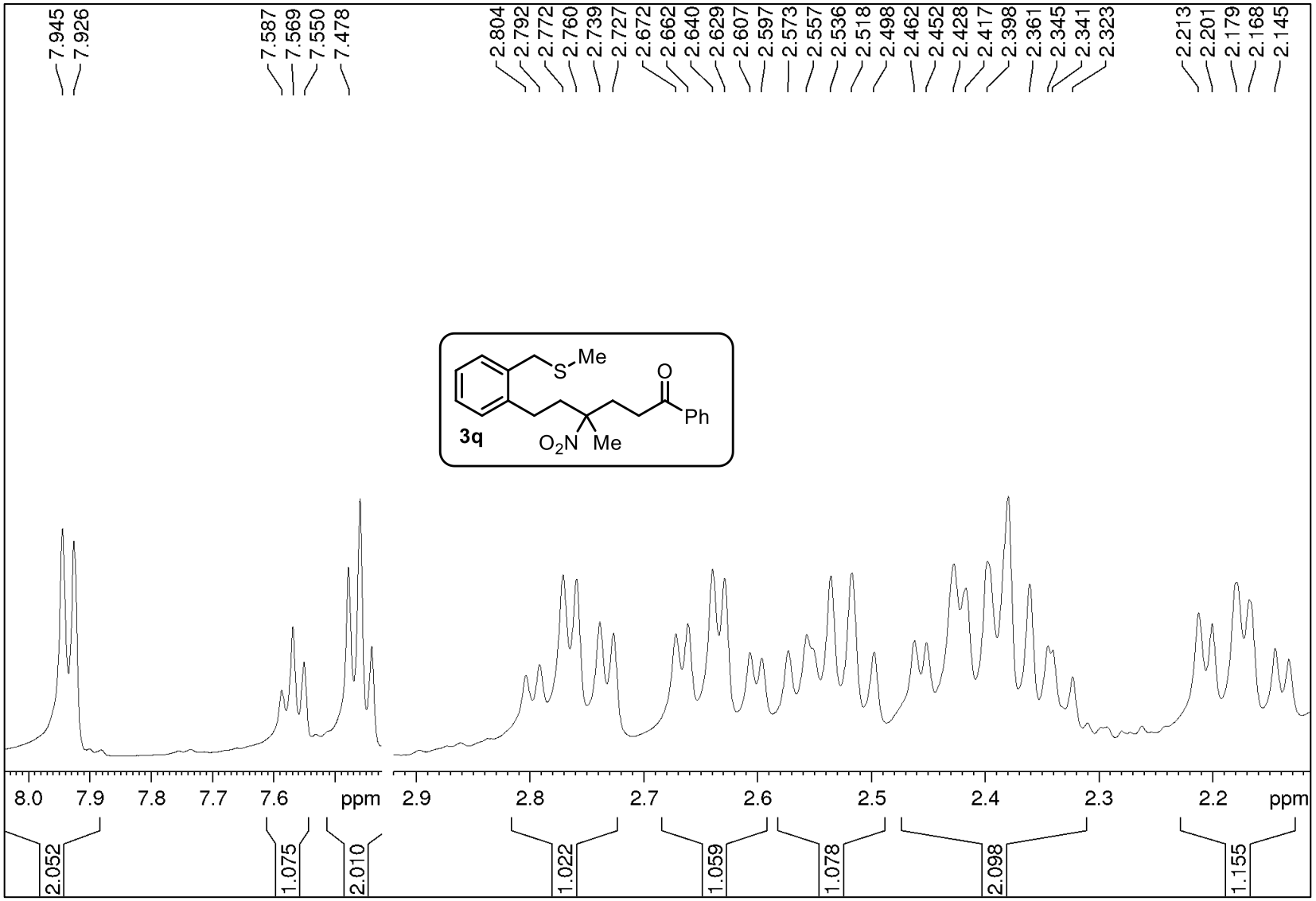
^{13}C NMR spectrum of compound 3p



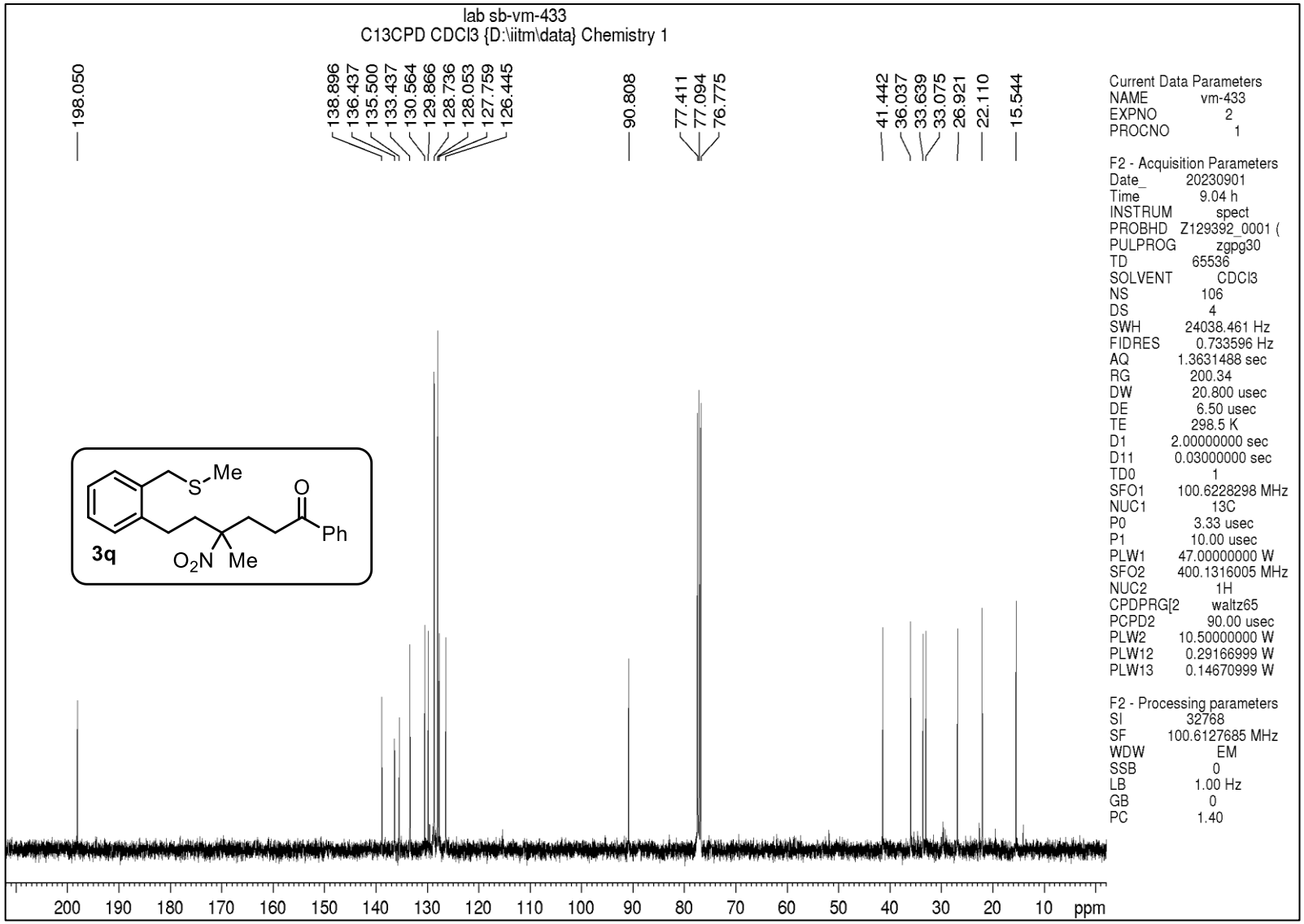
DEPT-135 NMR spectrum of compound 3p



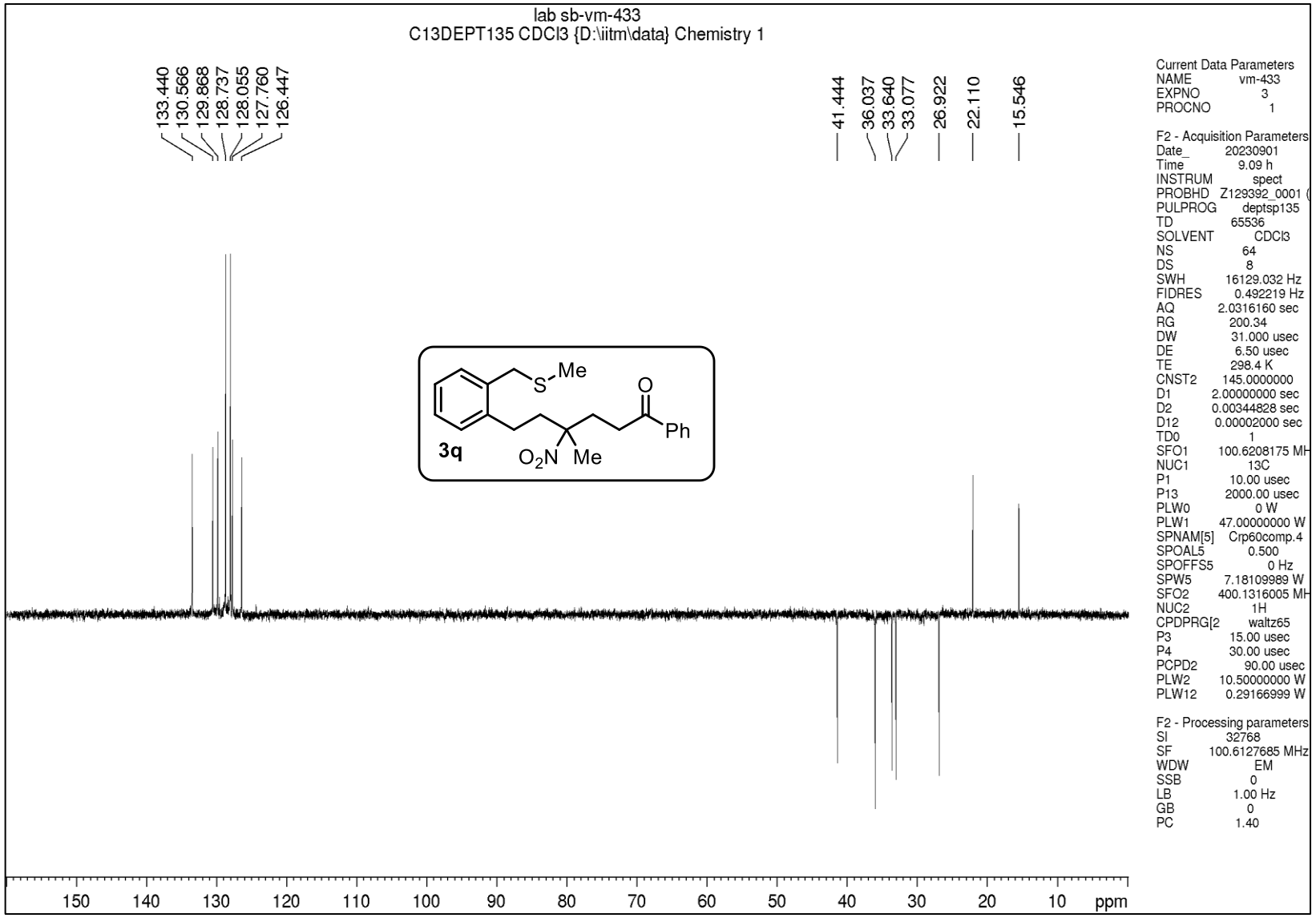
^{1}H NMR spectrum of compound 3q



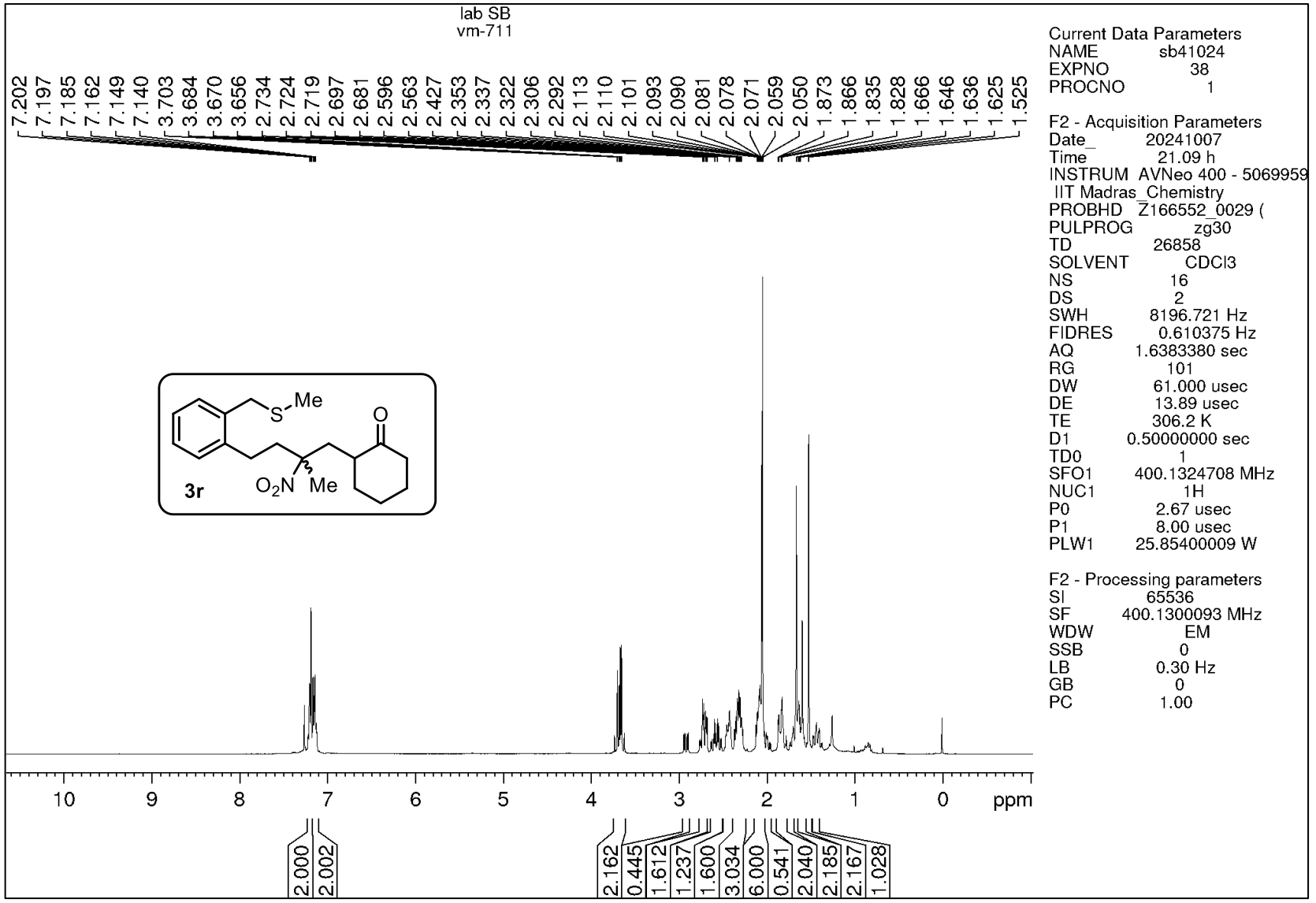
^{1}H NMR spectrum of compound 3q



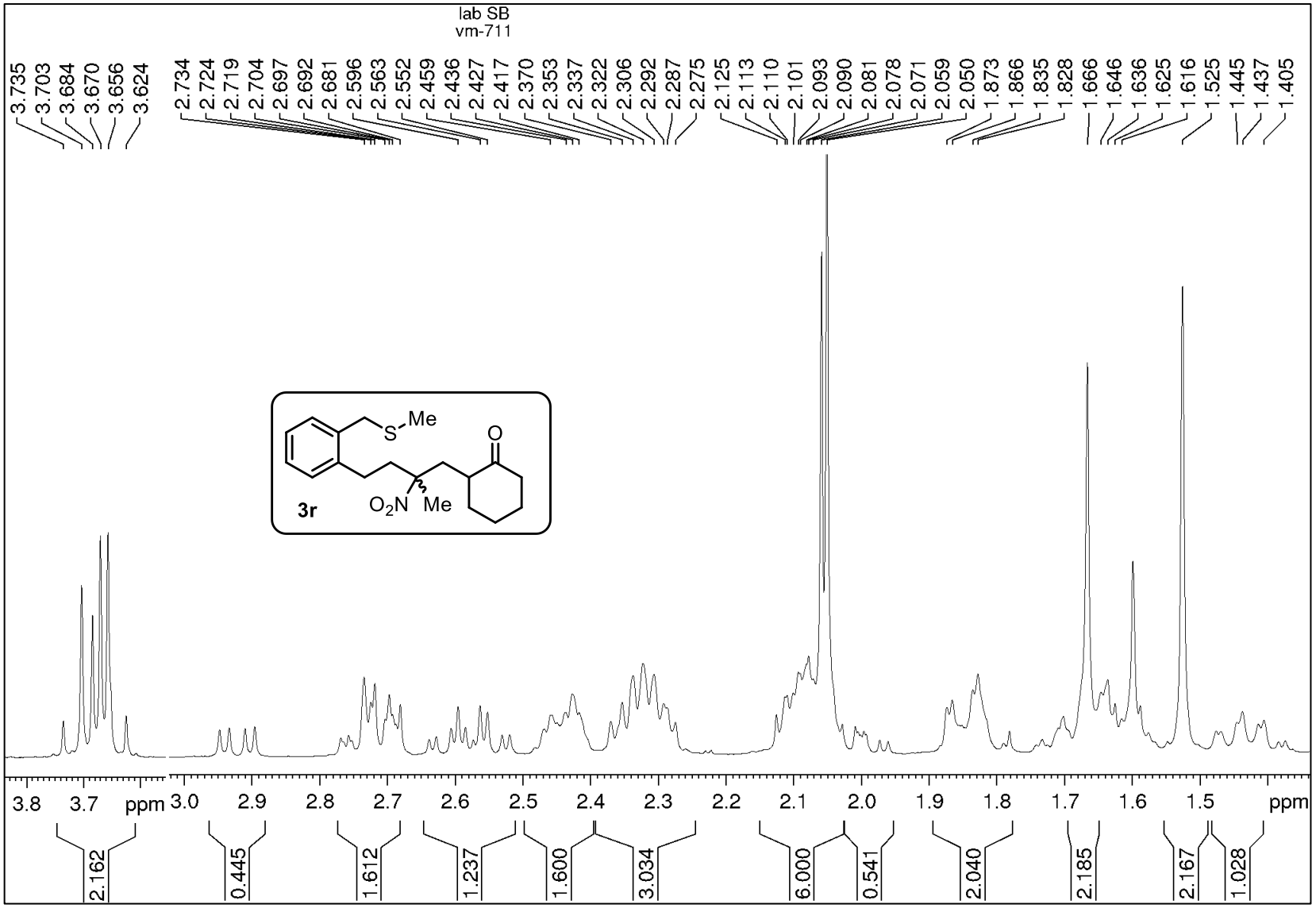
^{13}C NMR spectrum of compound 3q



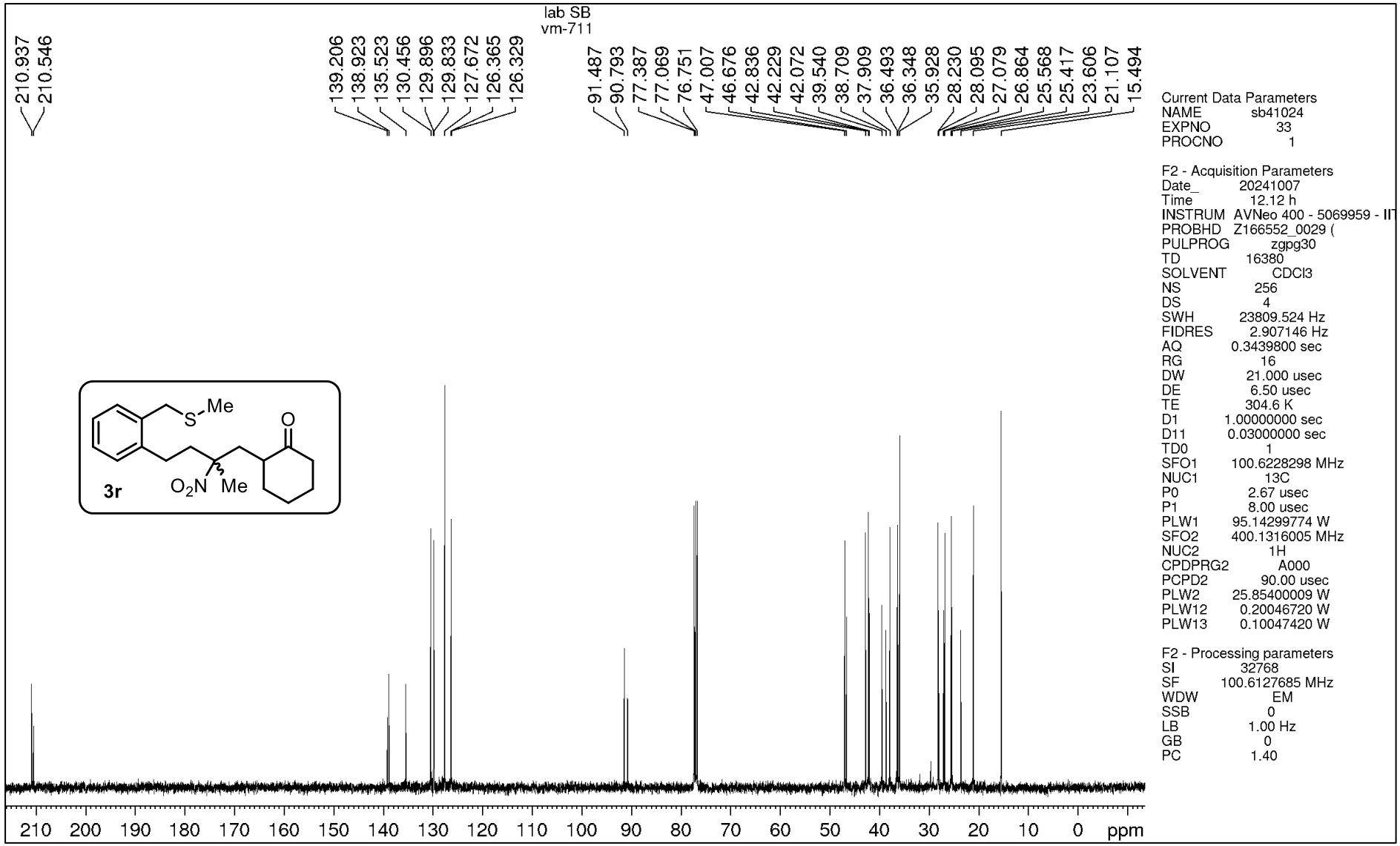
DEPT-135 NMR spectrum of compound 3q



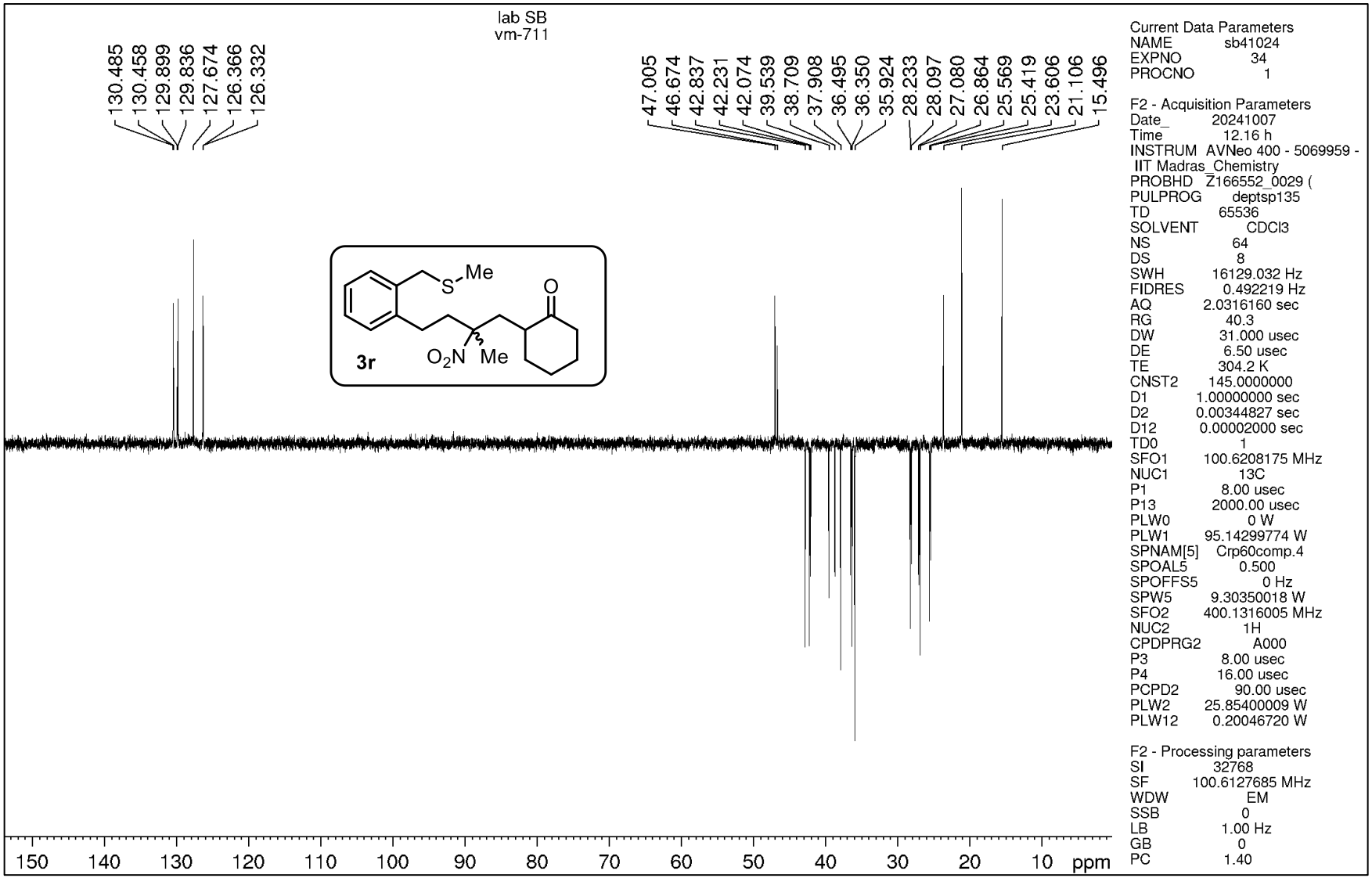
^{1}H NMR spectrum of compound 3r



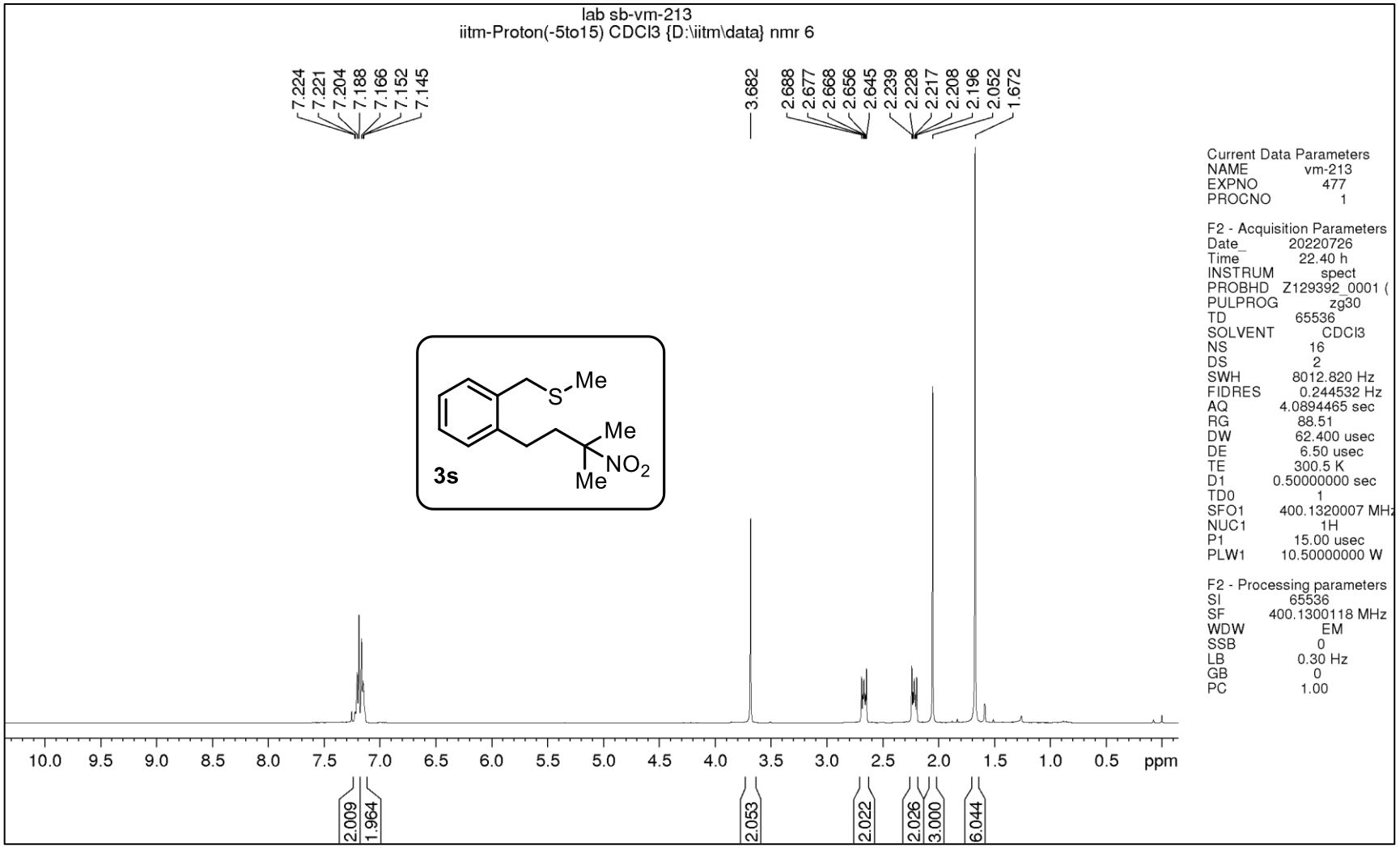
^{1}H NMR spectrum of compound 3r



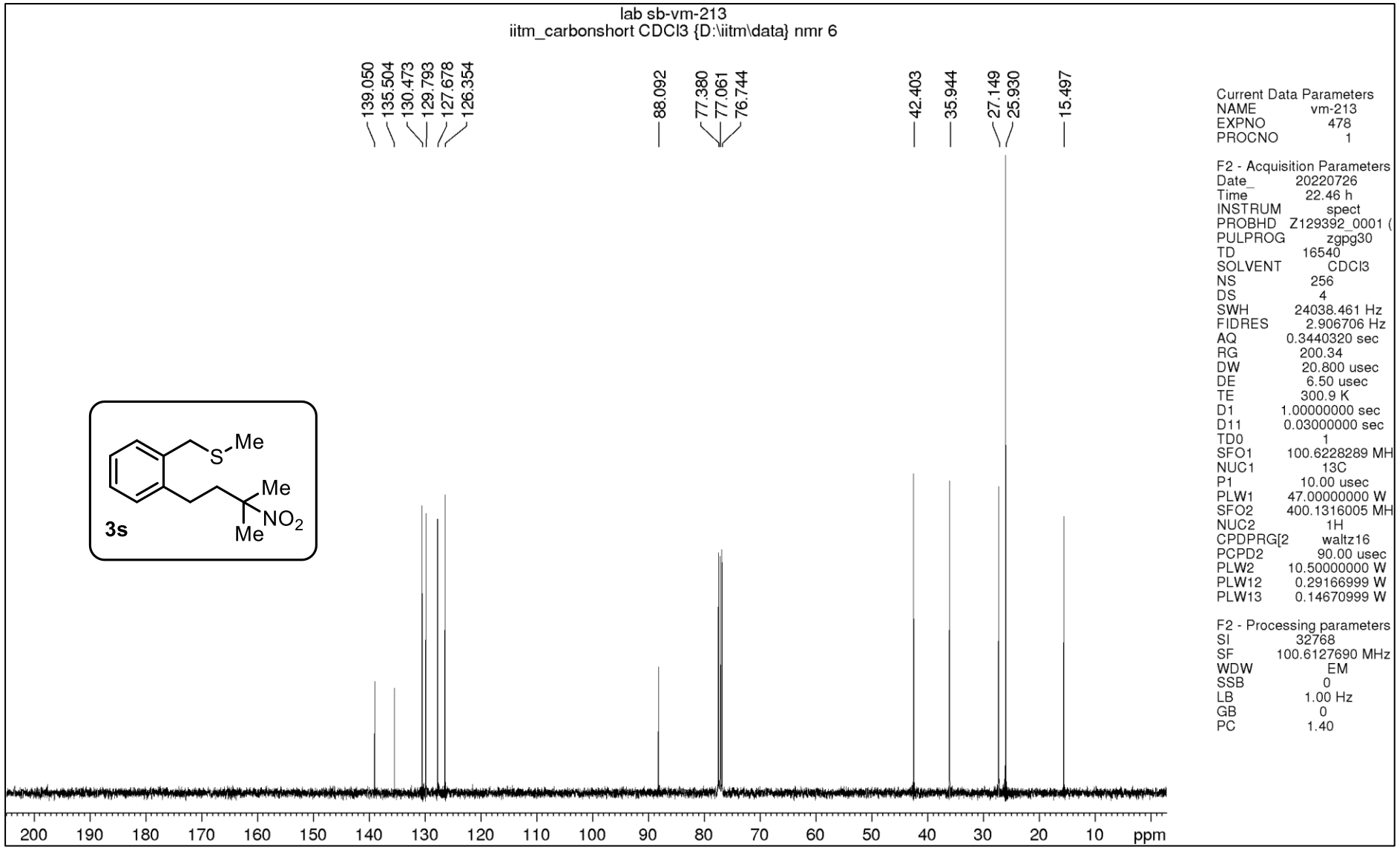
^{13}C NMR spectrum of compound 3r



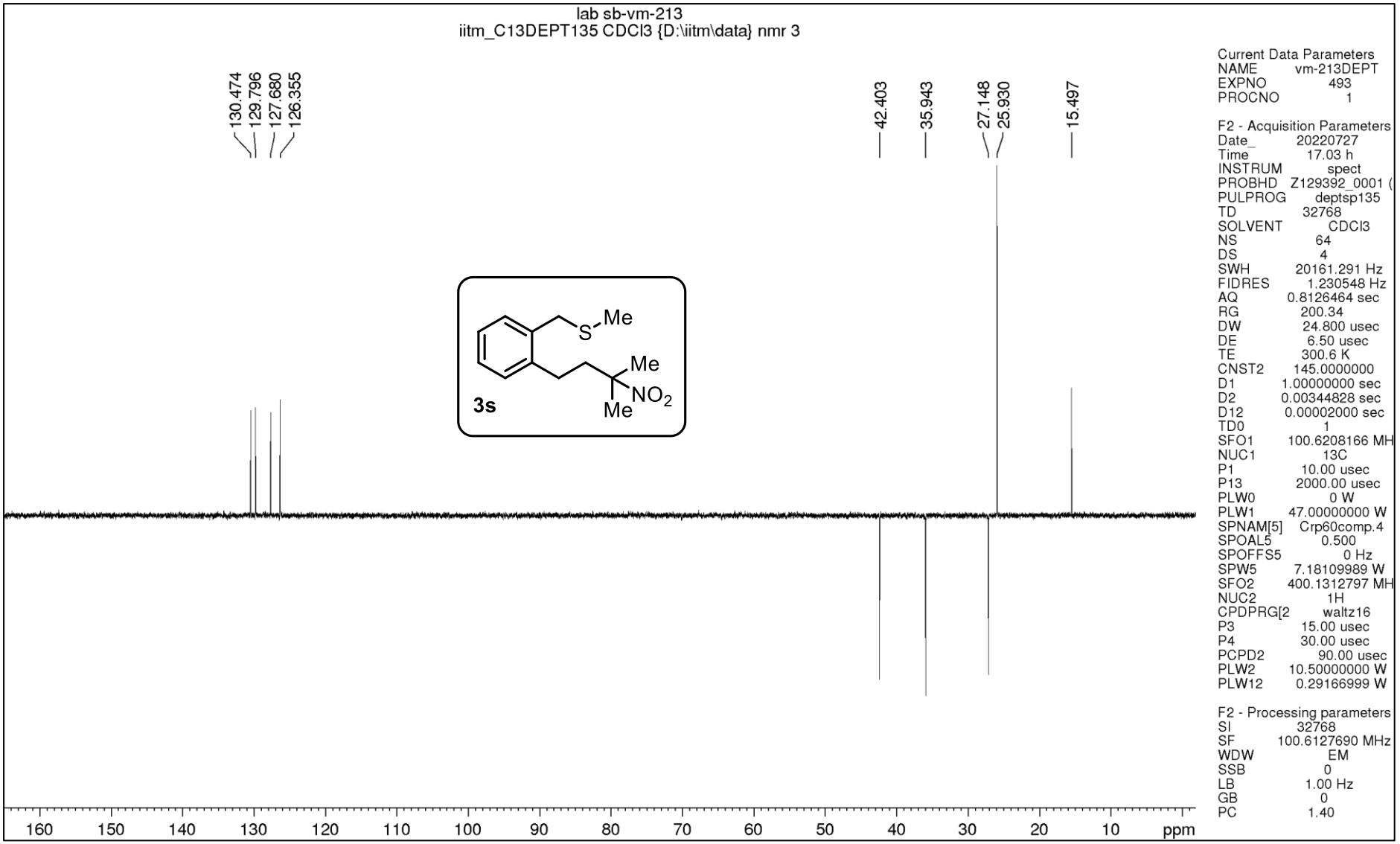
DEPT-135 NMR spectrum of compound 3r



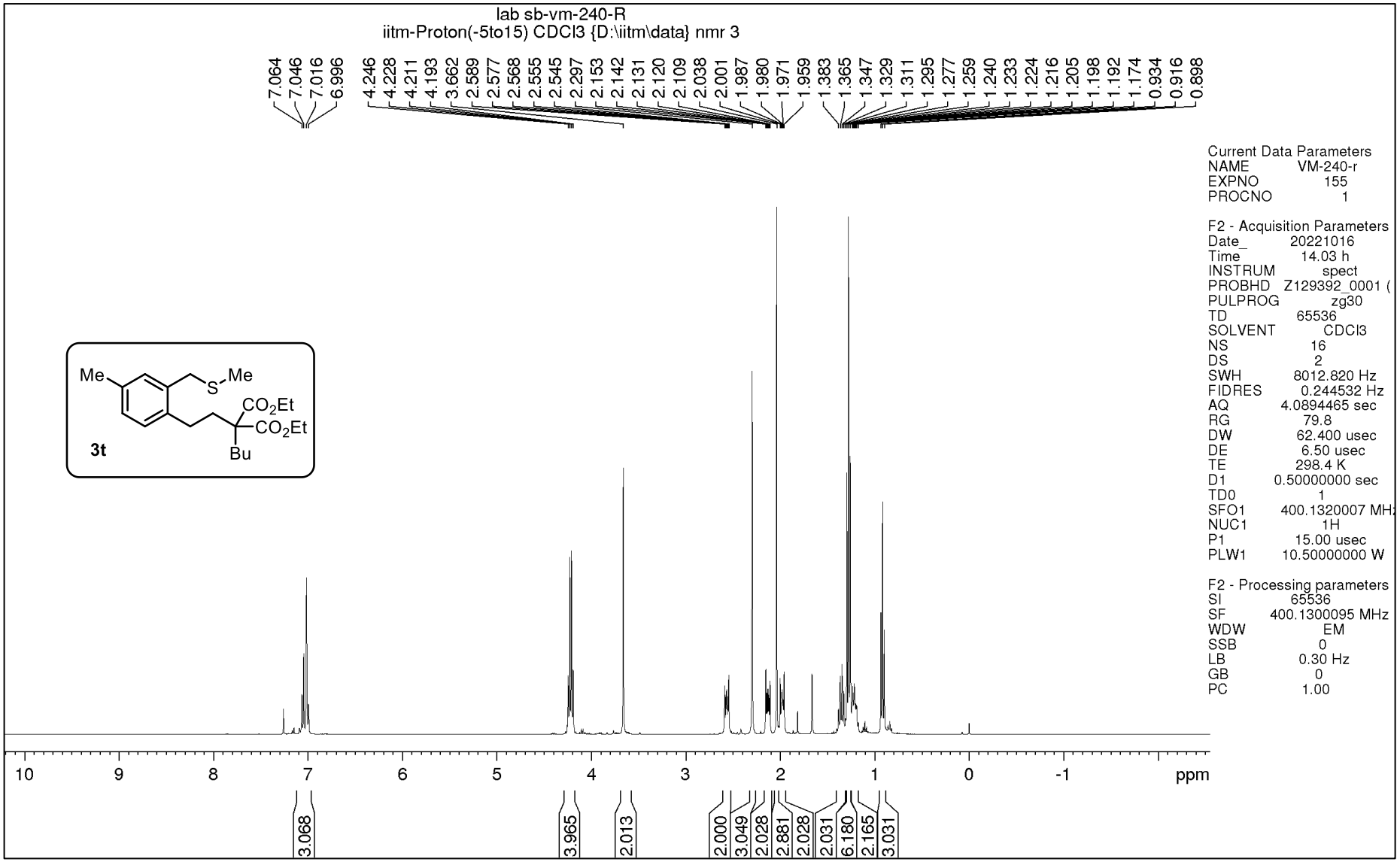
^{1}H NMR spectrum of compound 3s



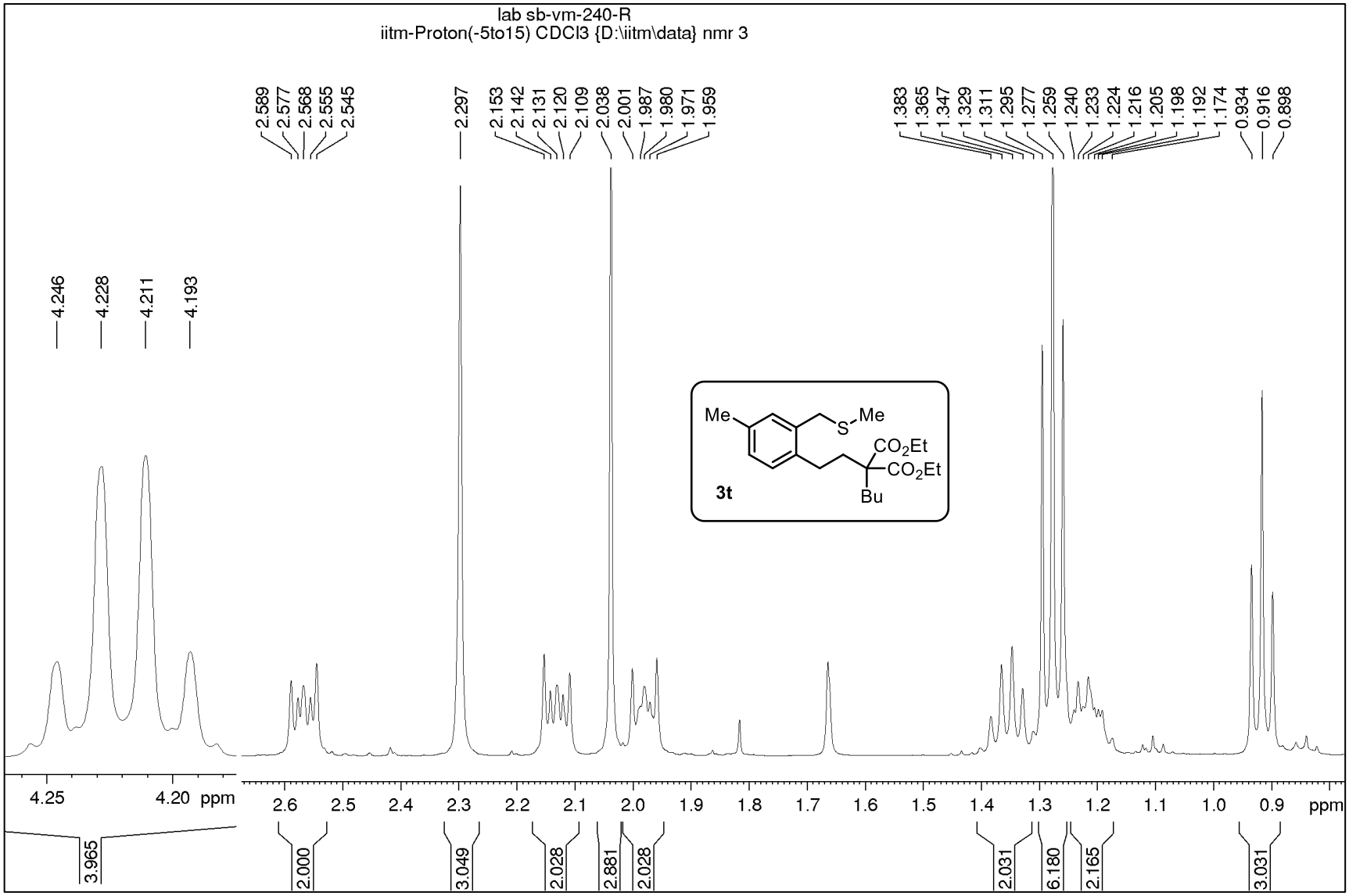
^{13}C NMR spectrum of compound 3s



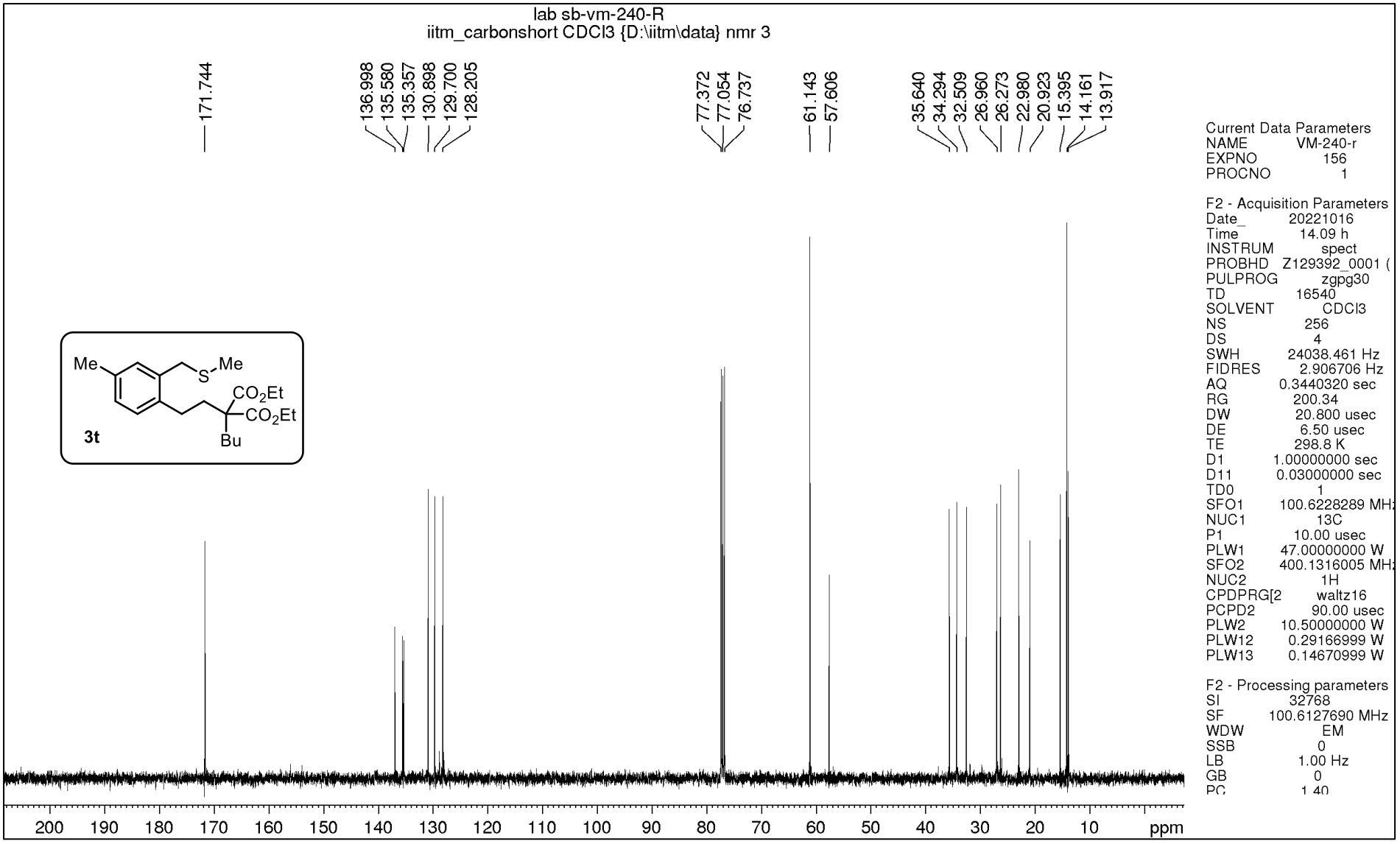
DEPT-135 NMR spectrum of compound 3s



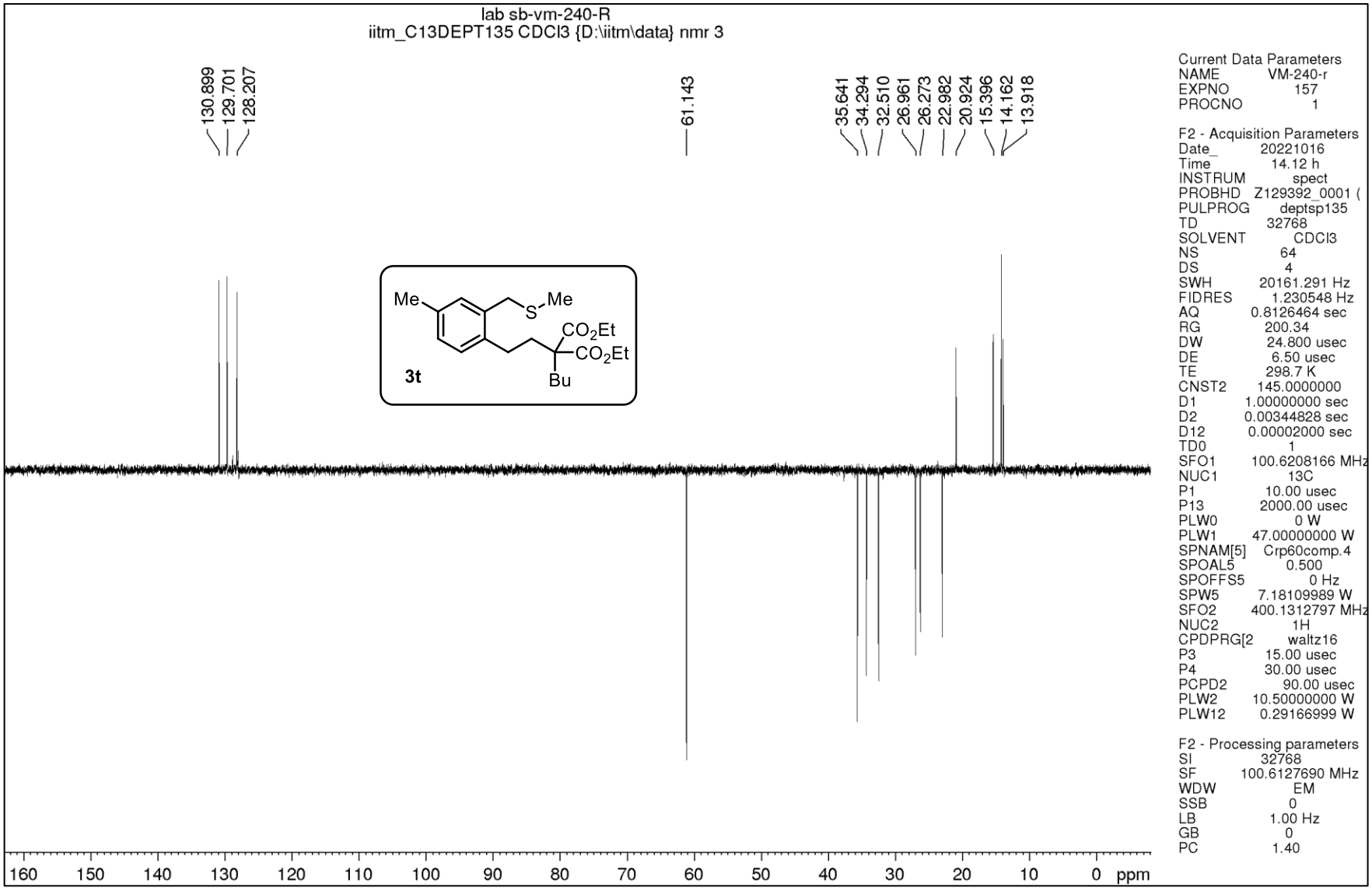
^{1}H NMR spectrum of compound 3t



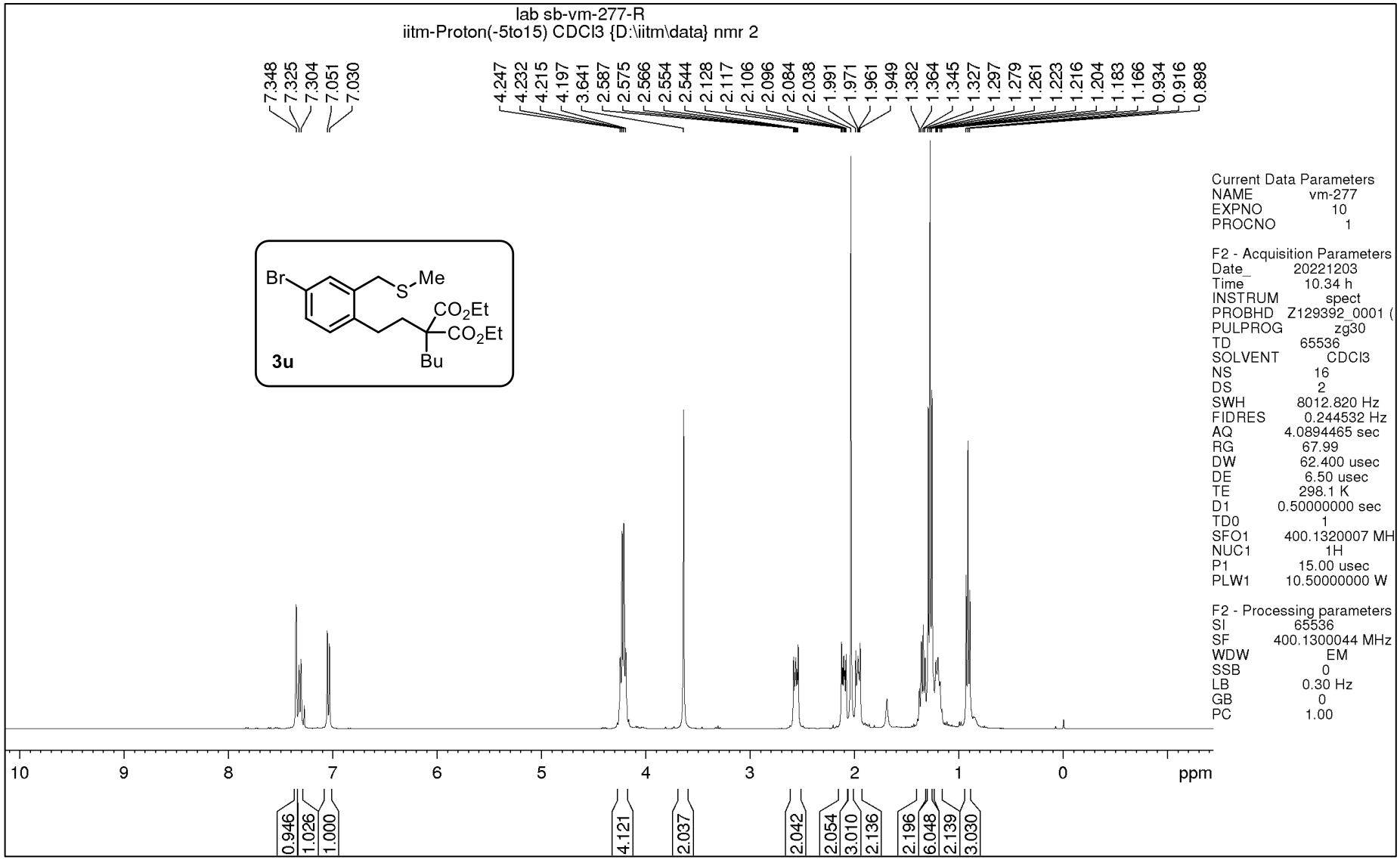
^{1}H NMR spectrum of compound 3t



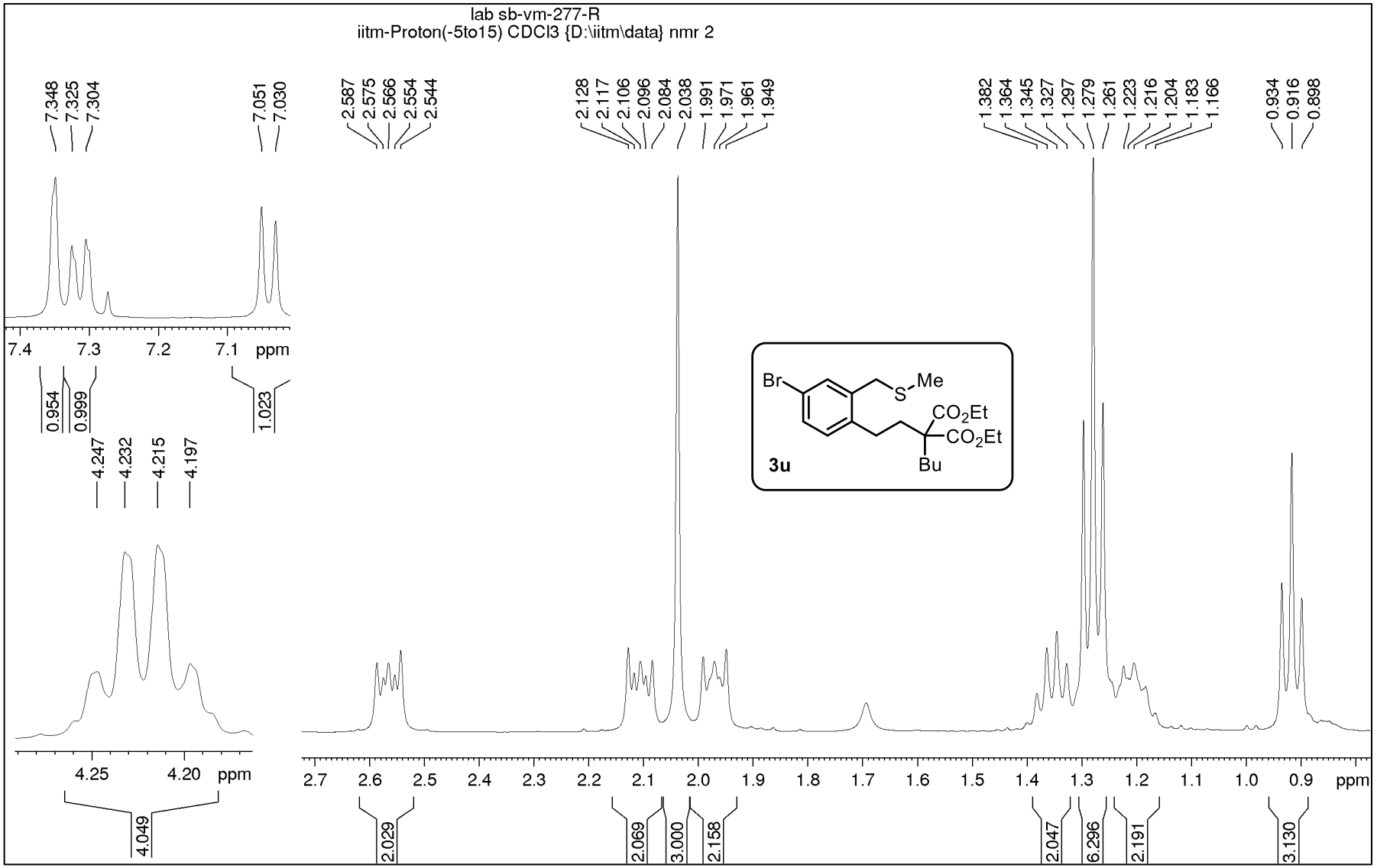
^{13}C NMR spectrum of compound 3t



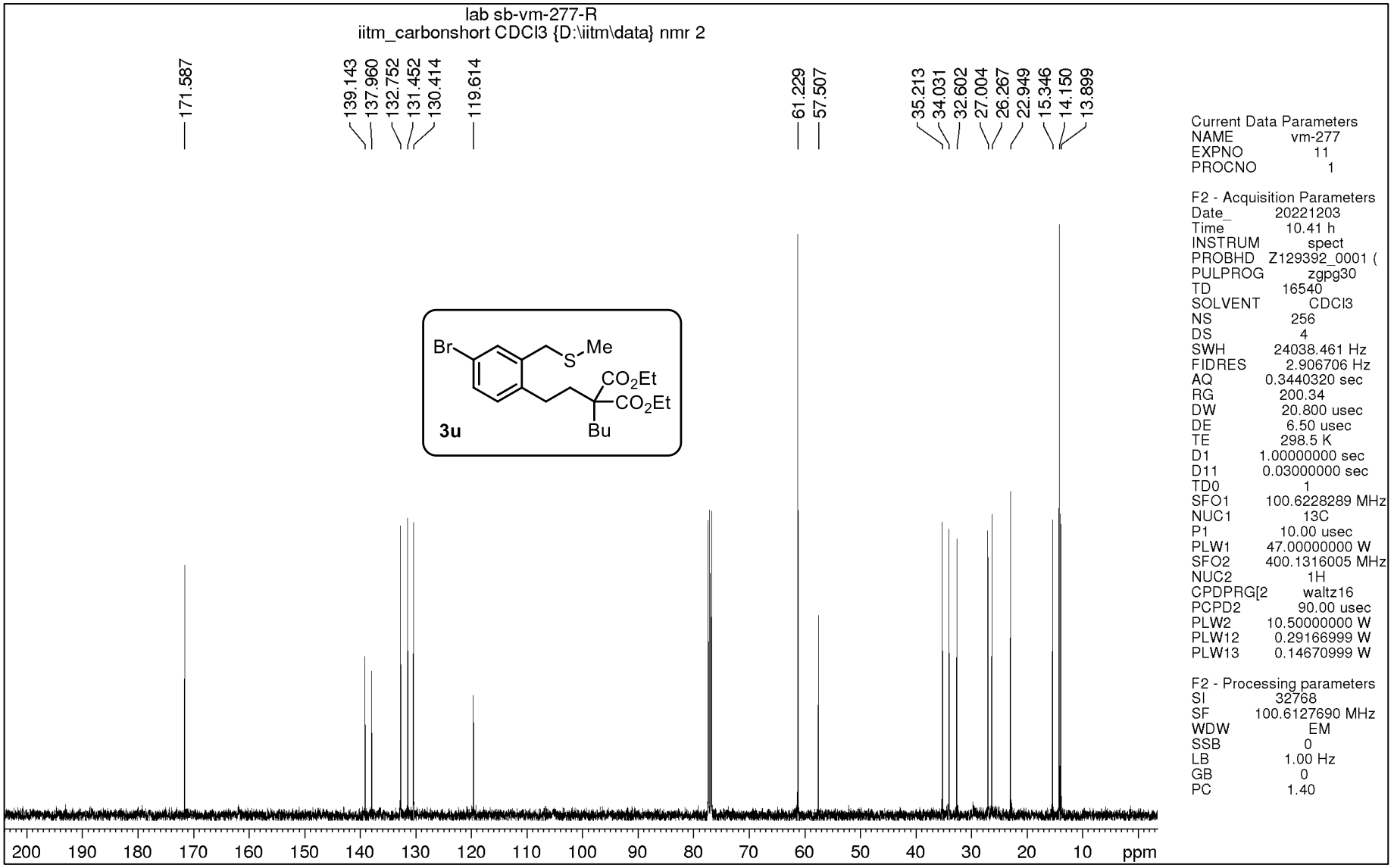
DEPT-135 NMR spectrum of compound 3t



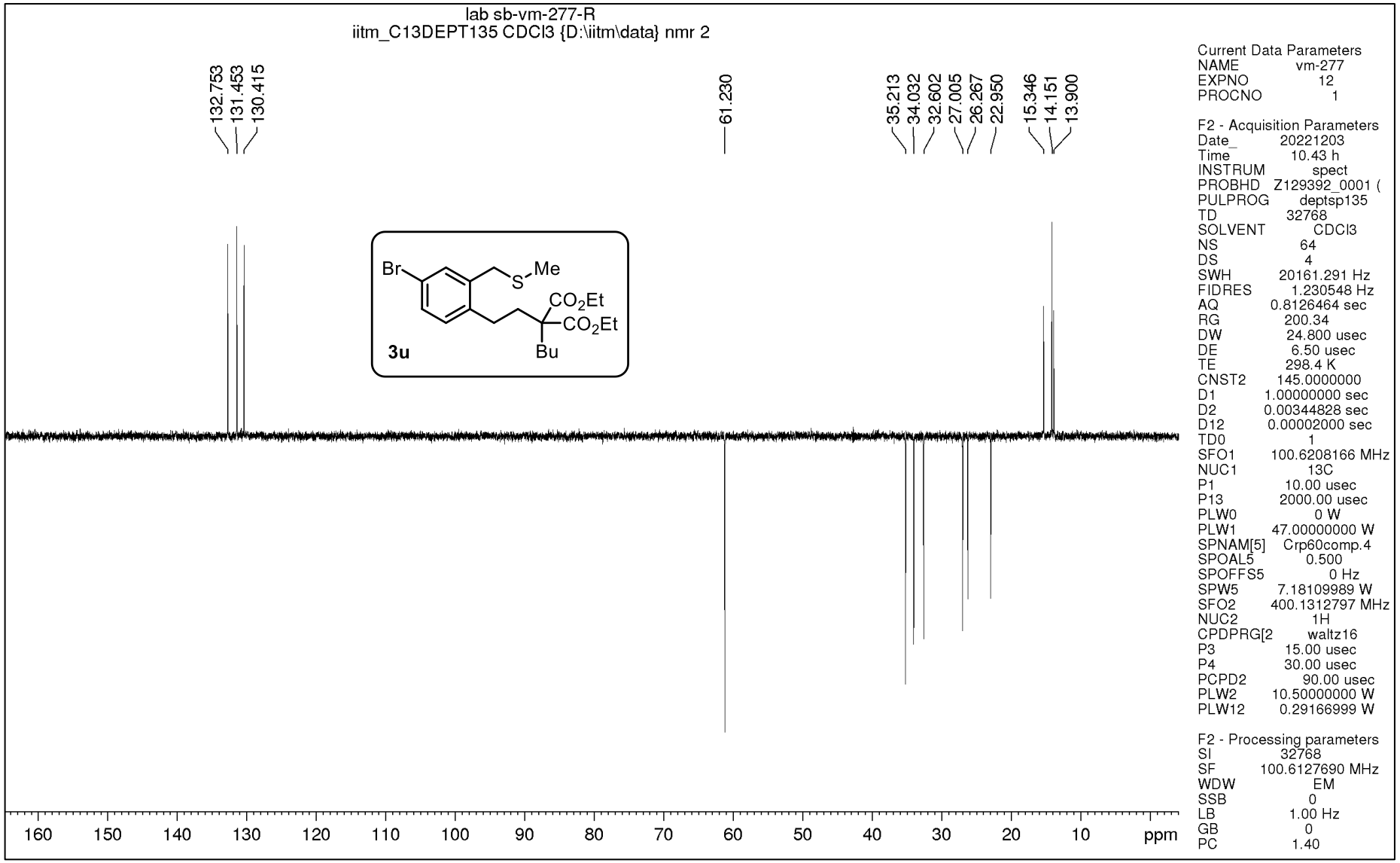
^{1}H NMR spectrum of compound 3u



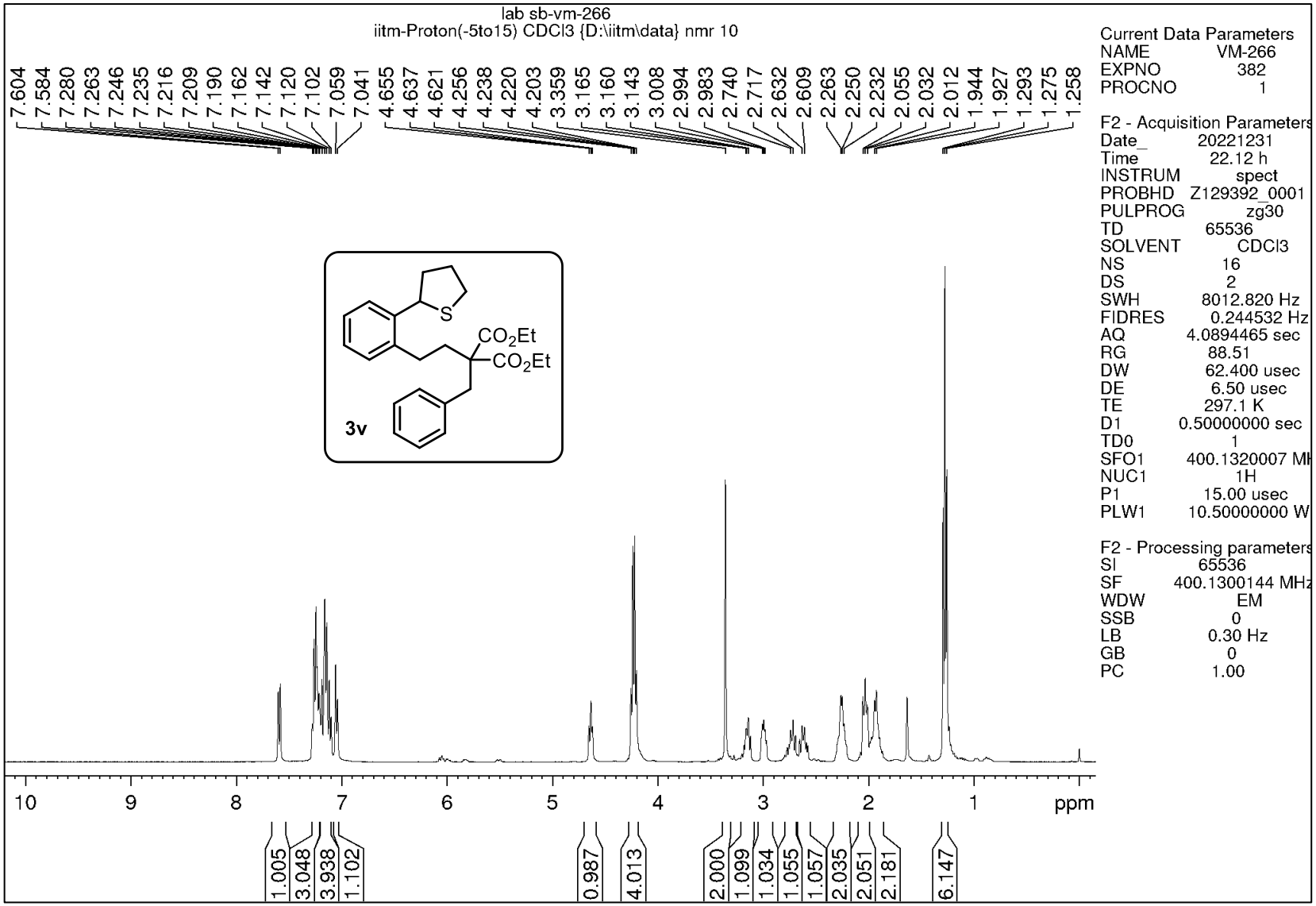
^{1}H NMR spectrum of compound 3u



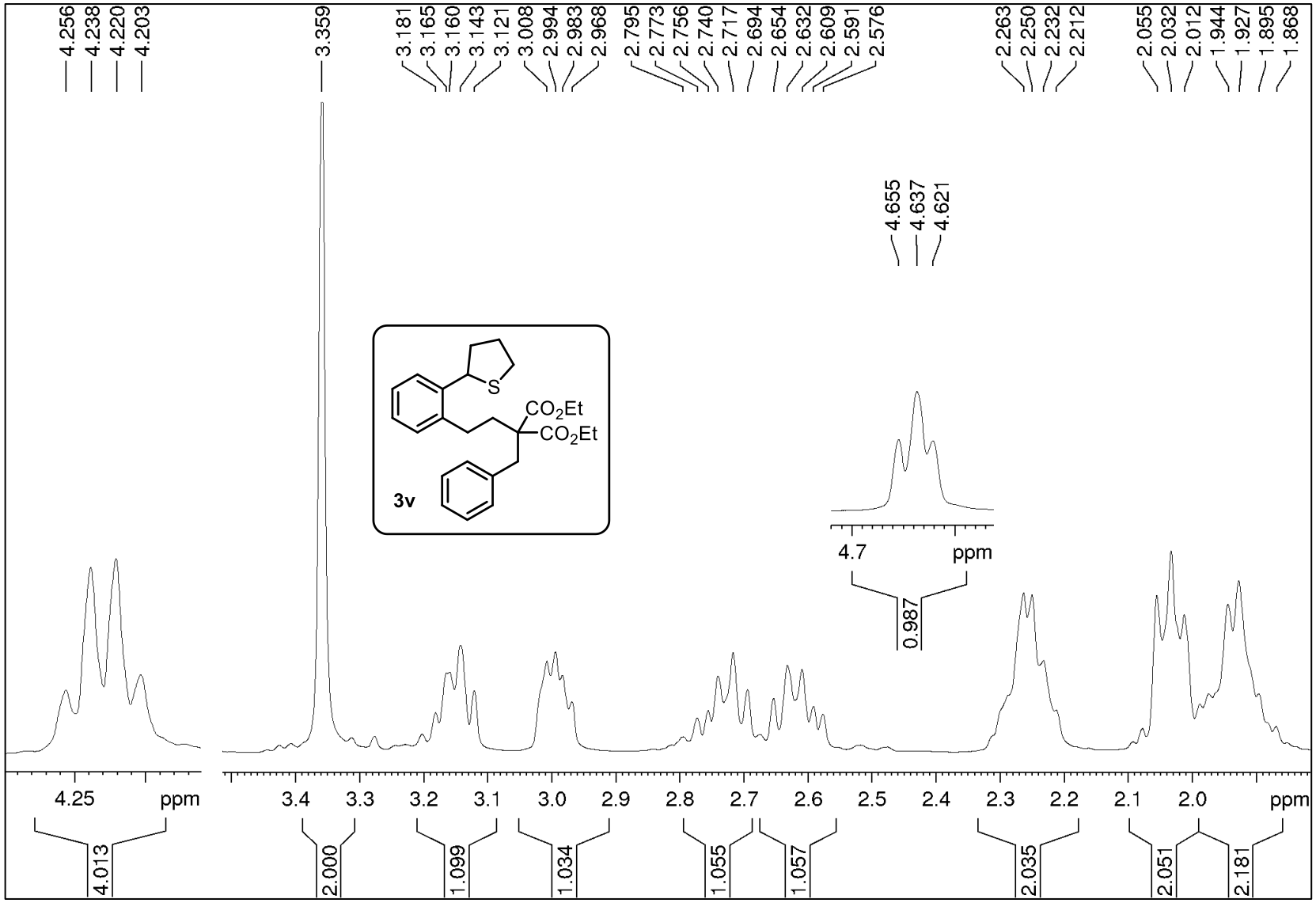
^{13}C NMR spectrum of compound 3u



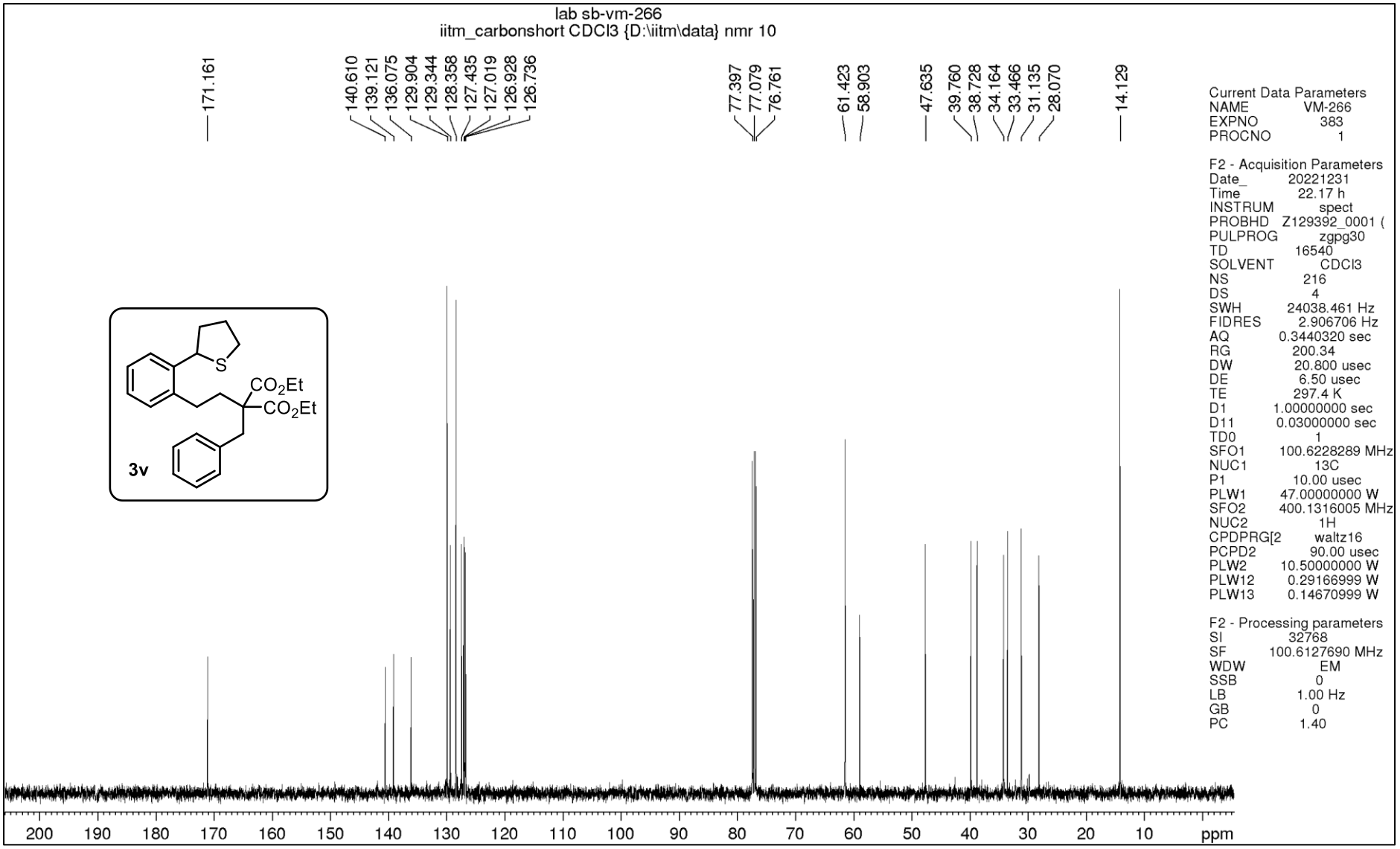
DEPT-135 NMR spectrum of compound 3u



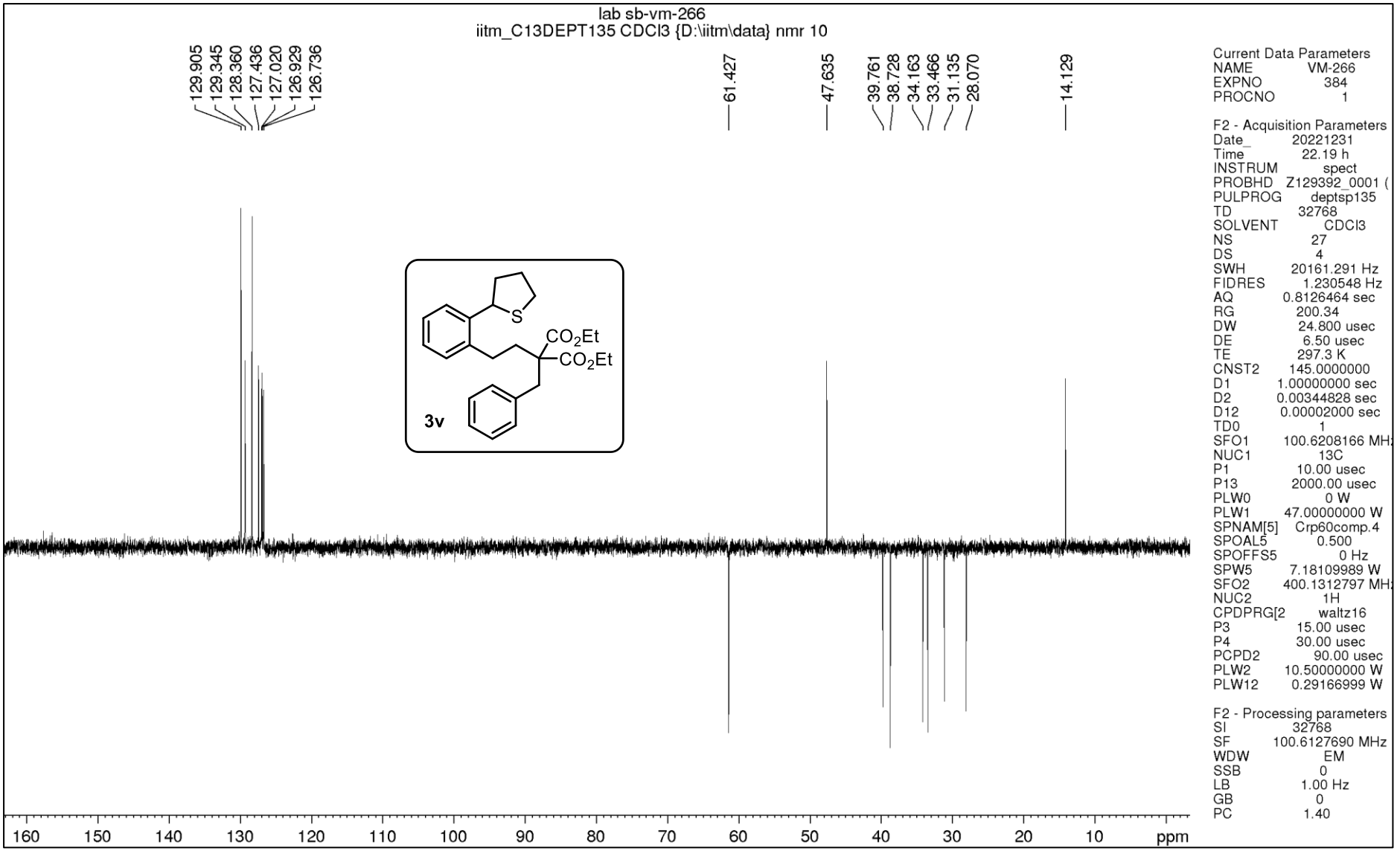
^{1}H NMR spectrum of compound 3v



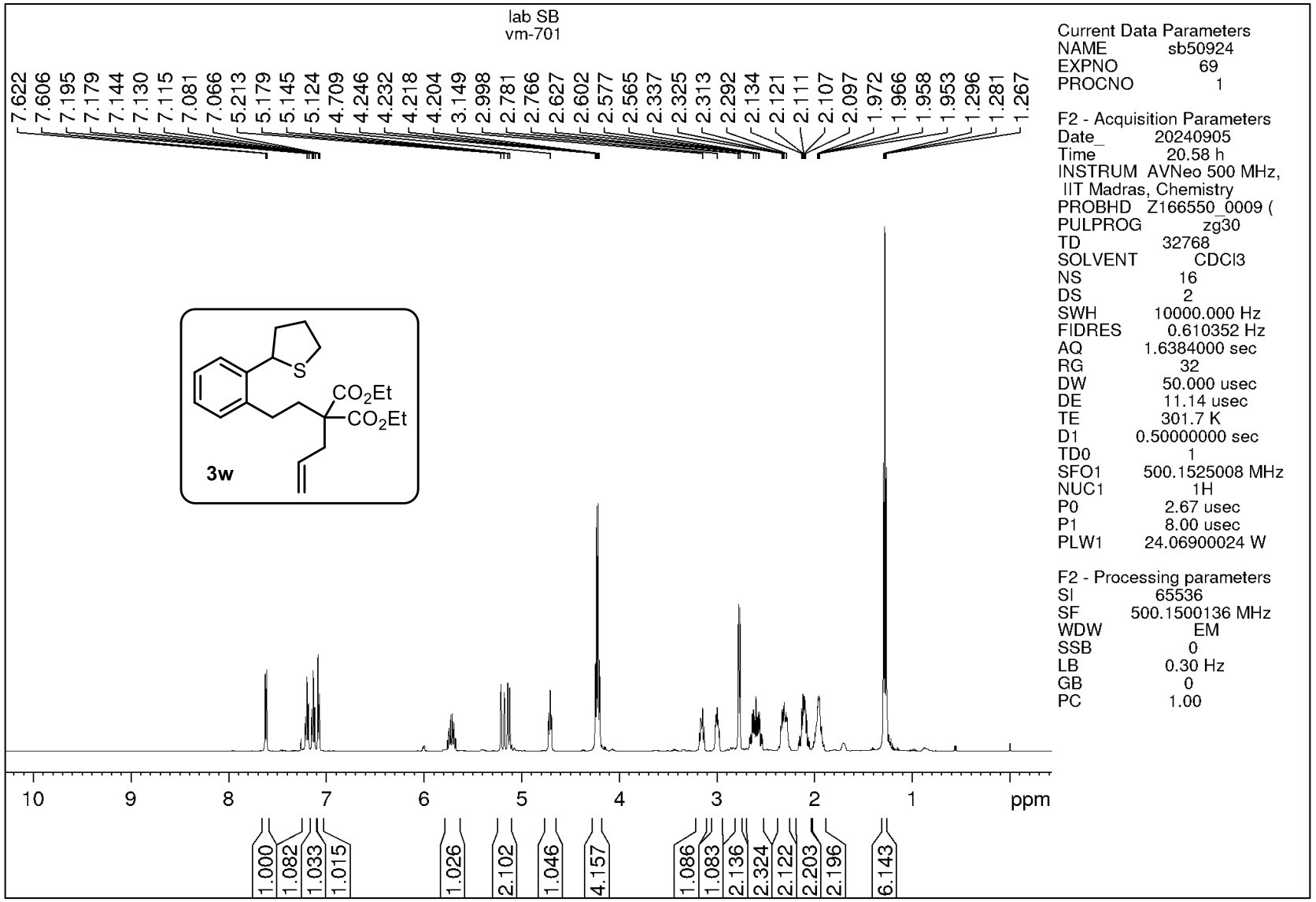
^{1}H NMR spectrum of compound 3v



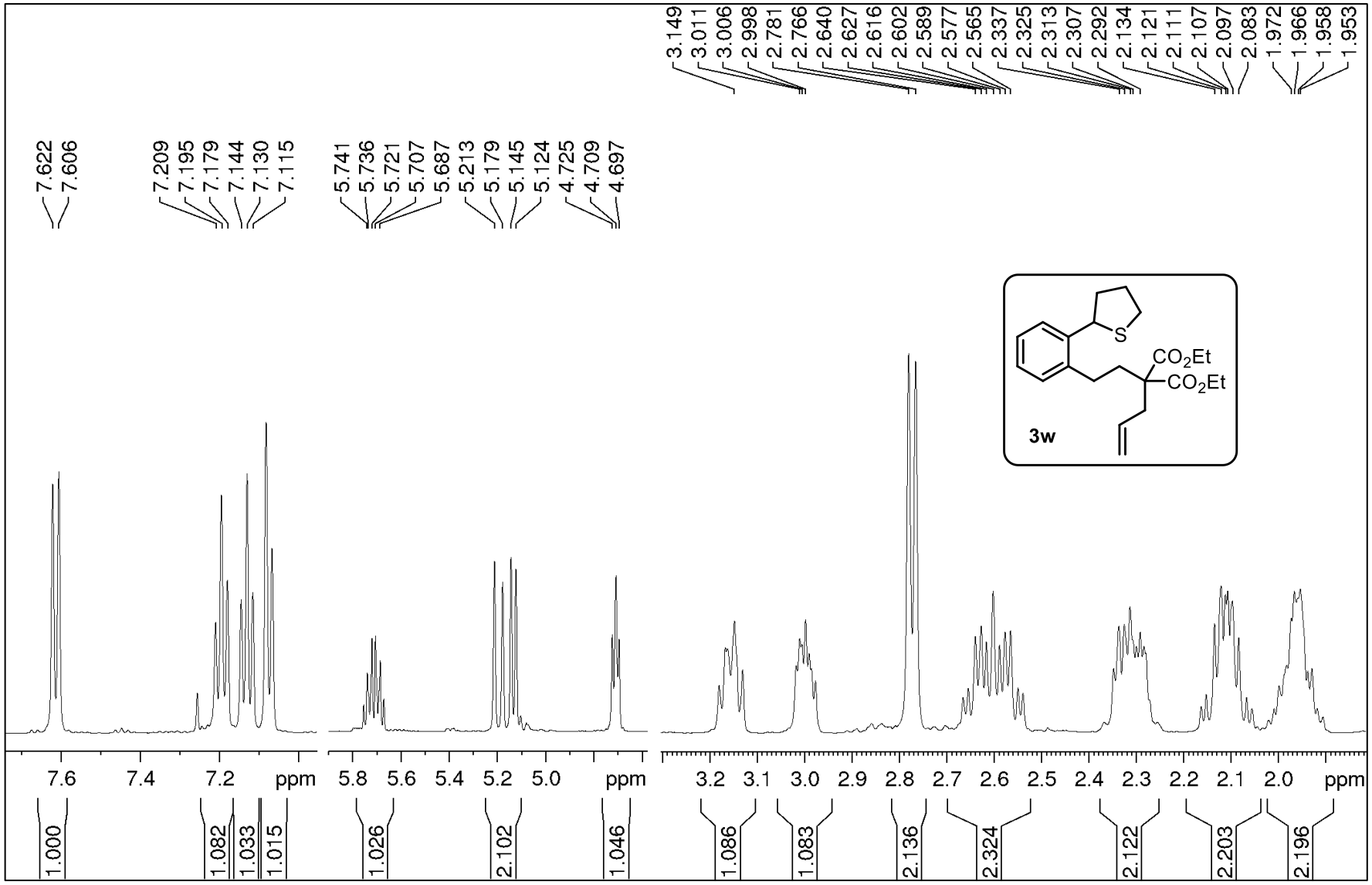
^{13}C NMR spectrum of compound 3v



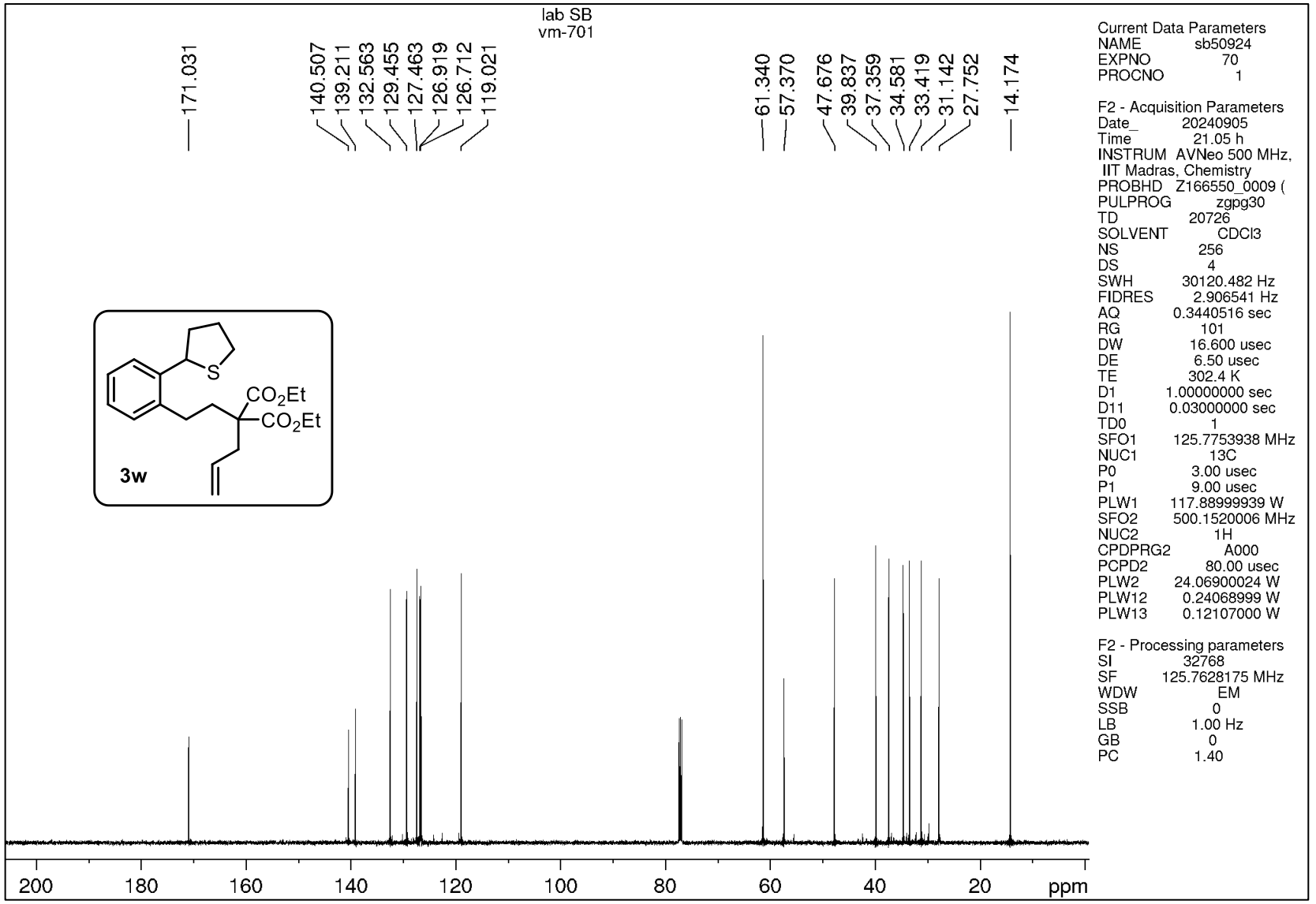
DEPT-135 NMR spectrum of compound 3v



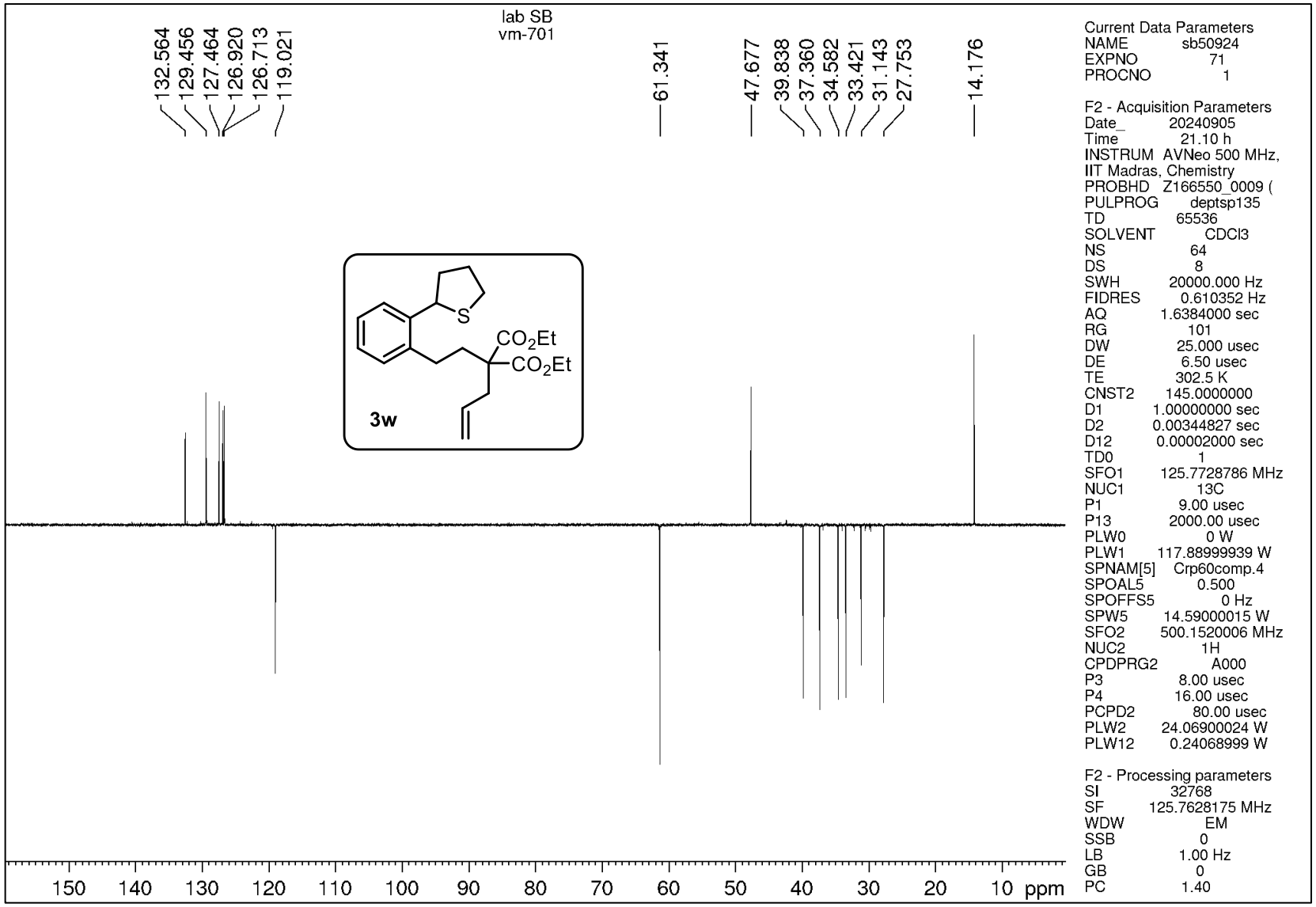
^{1}H NMR spectrum of compound 3w



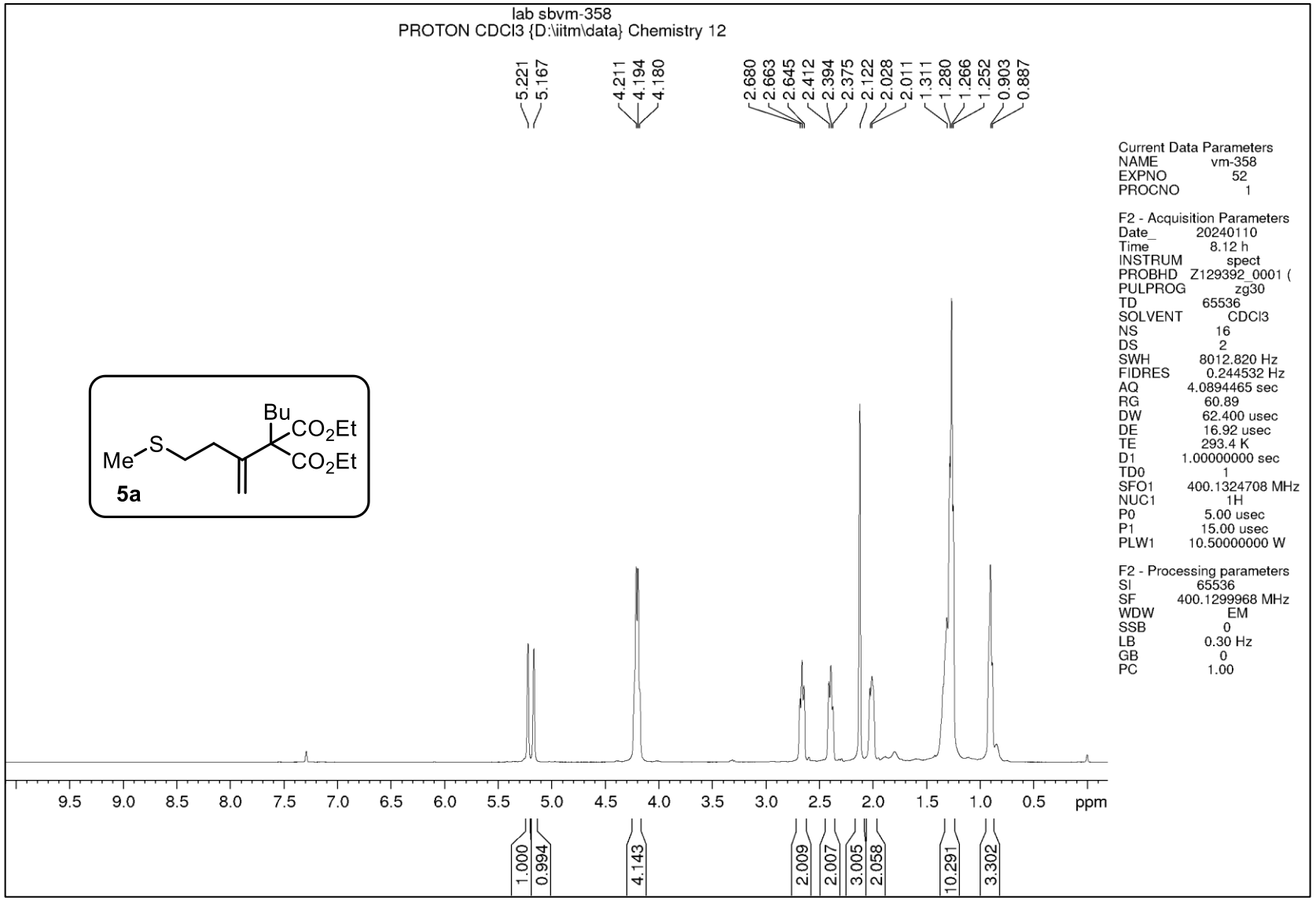
^{1}H NMR spectrum of compound 3w



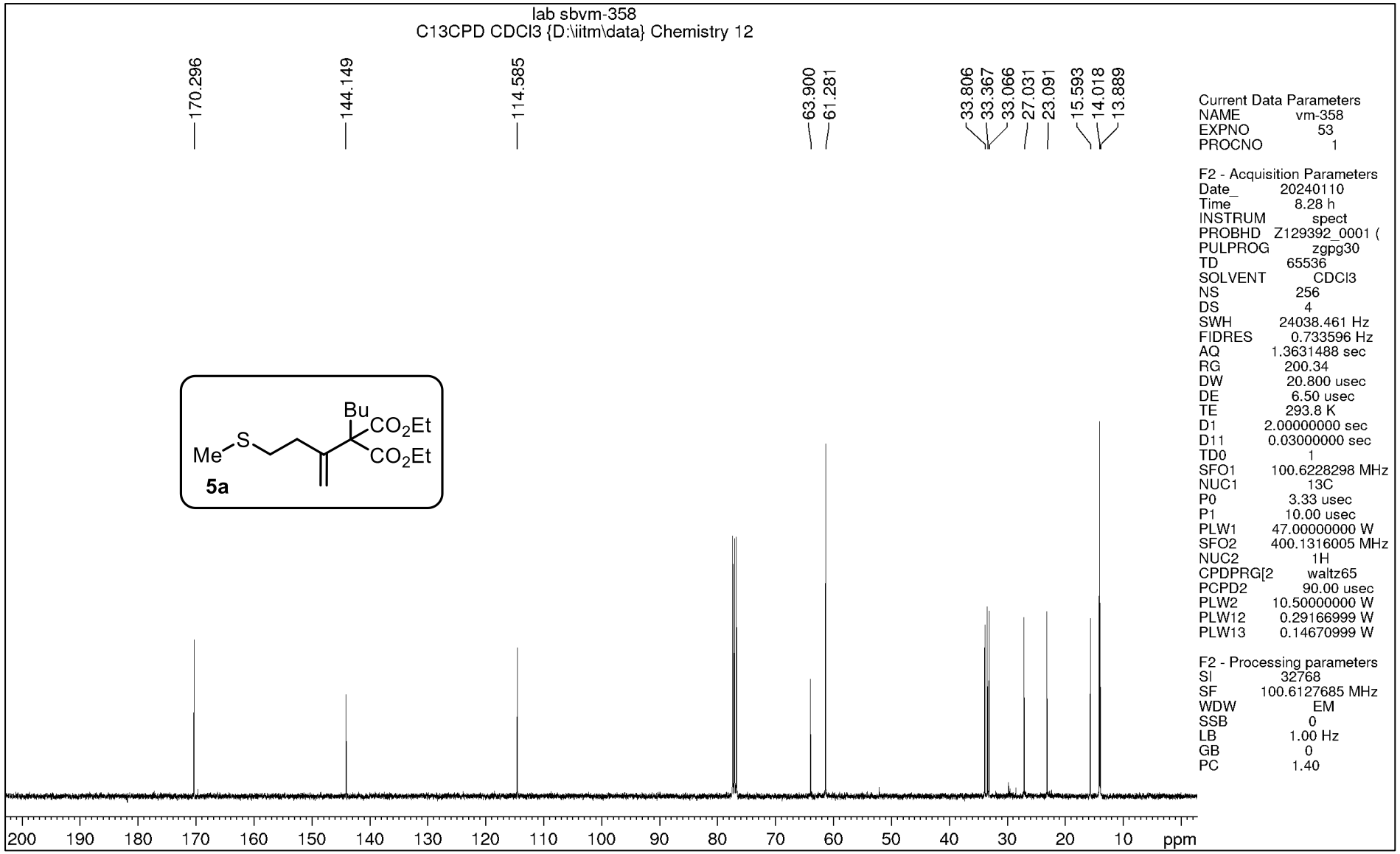
^{13}C NMR spectrum of compound 3w



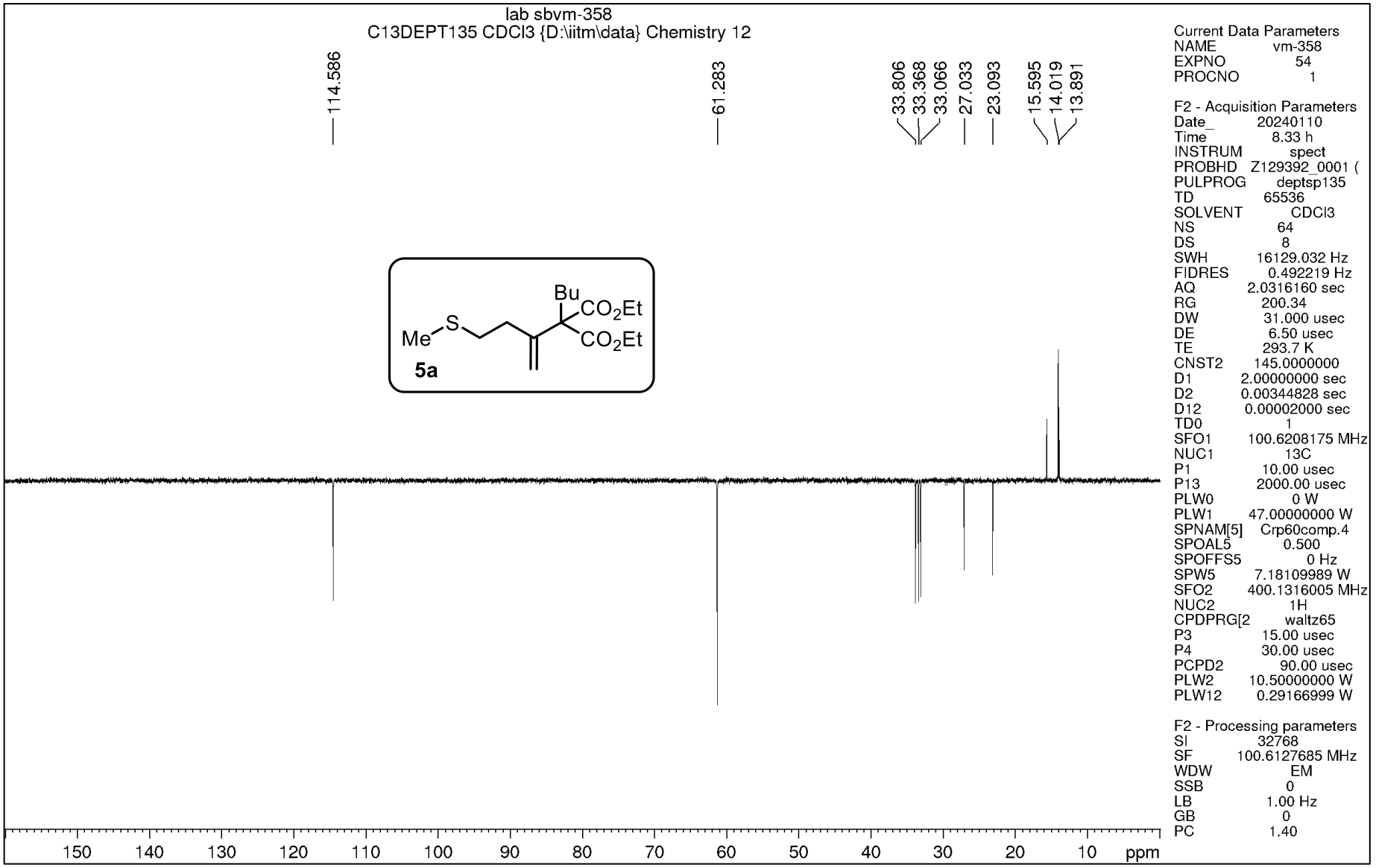
DEPT-135 NMR spectrum of compound 3w



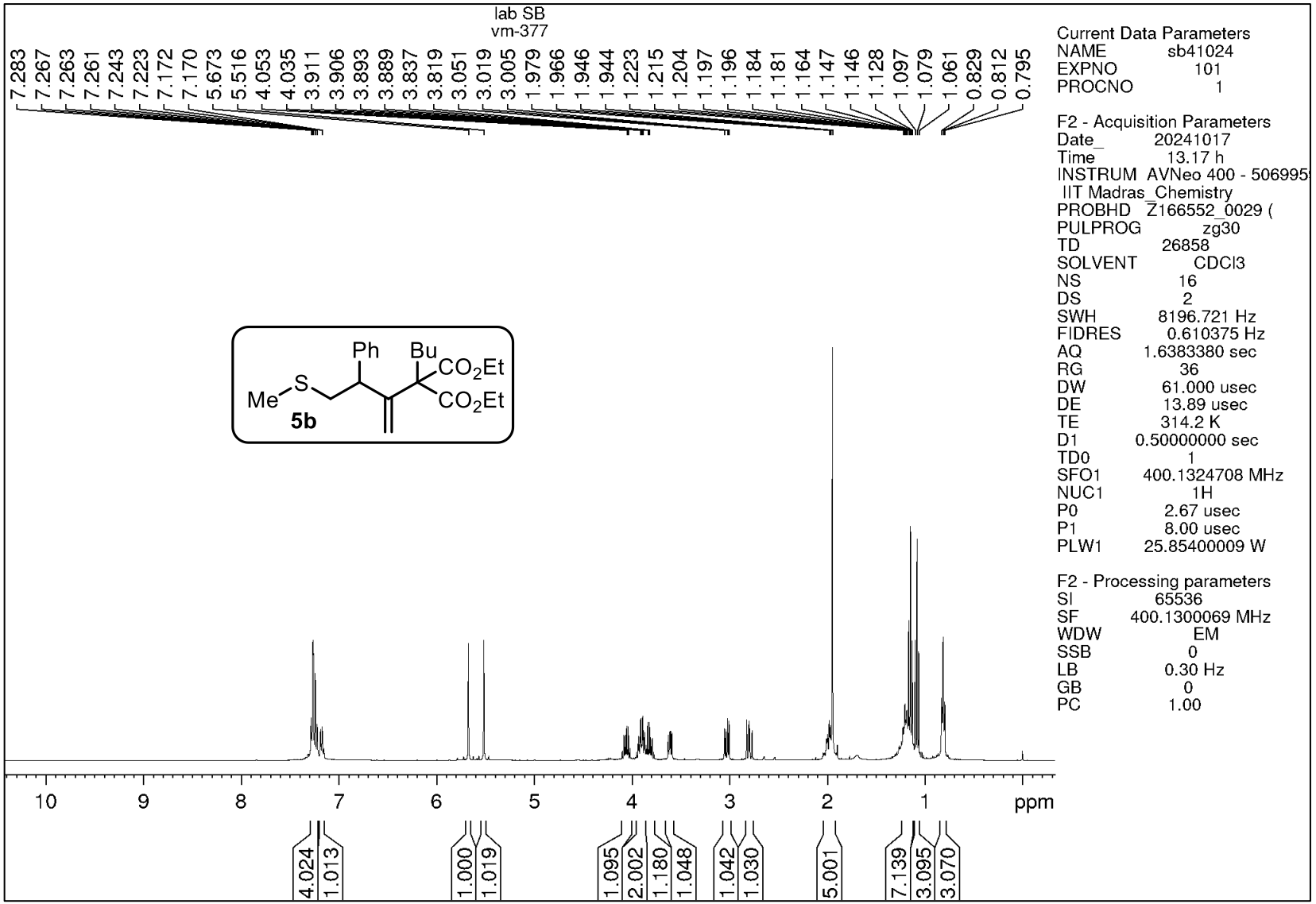
^{1}H NMR spectrum of compound 5a



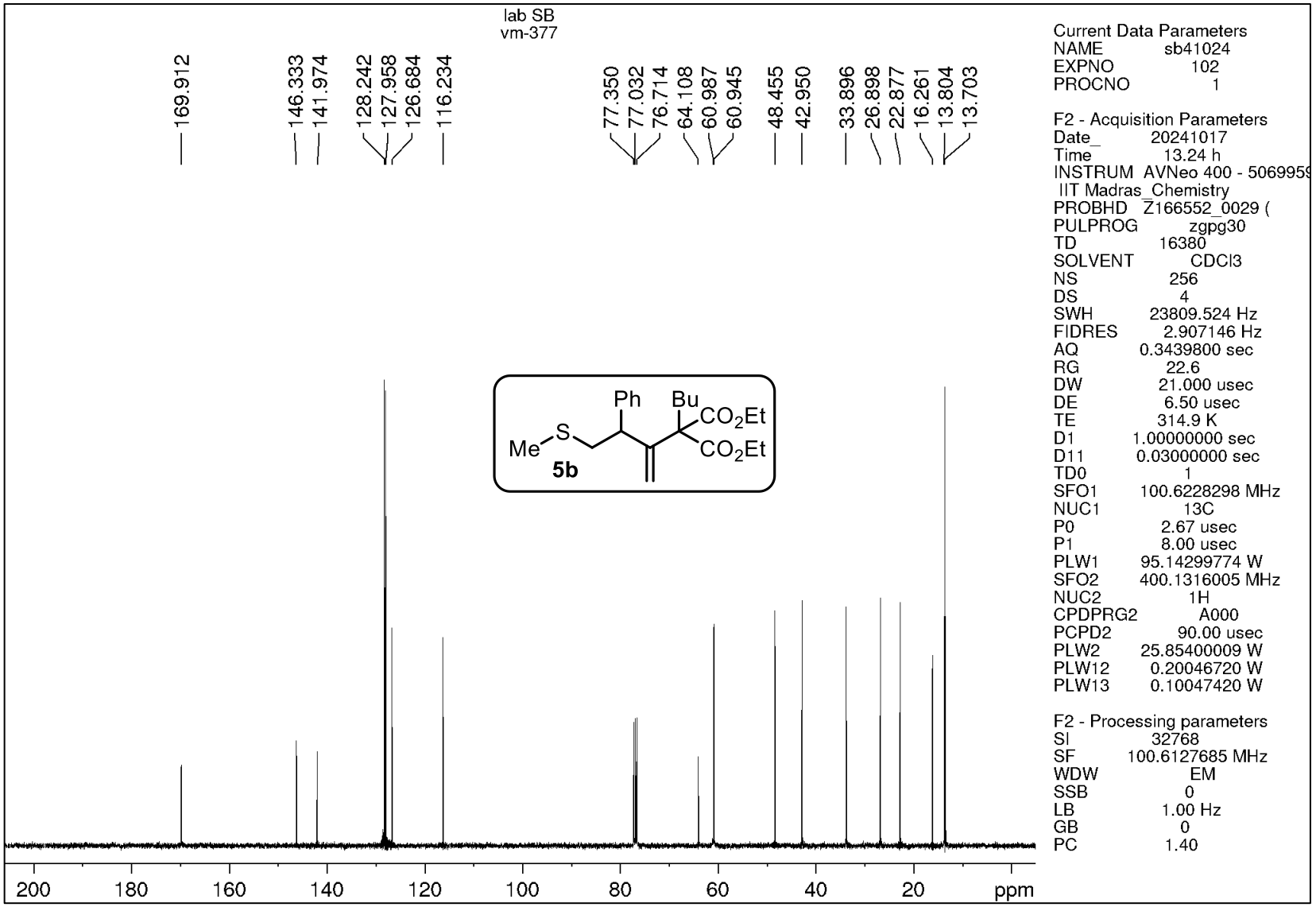
^{13}C NMR spectrum of compound 5a



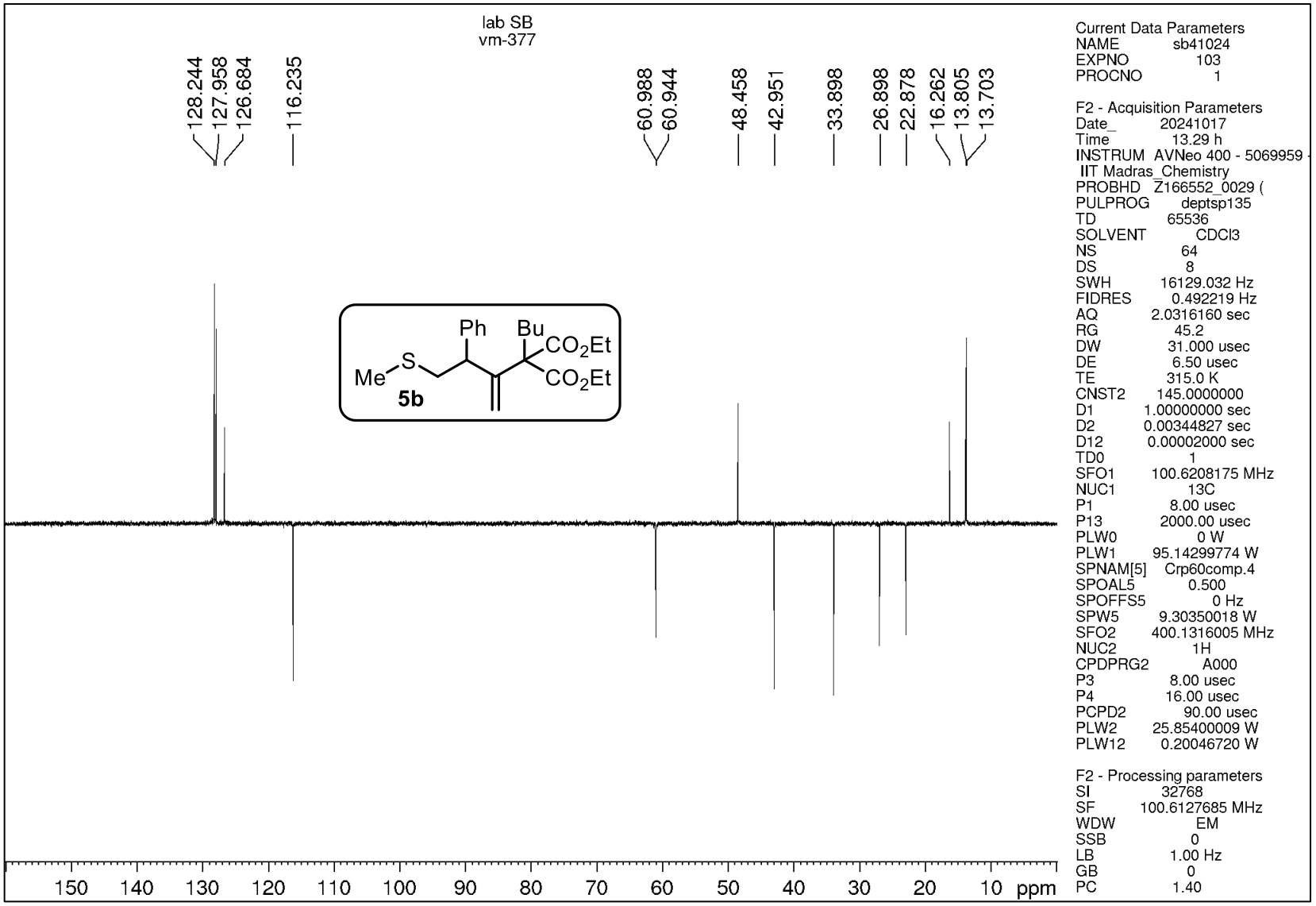
DEPT-135 NMR spectrum of compound 5a



^{1}H NMR spectrum of compound 5b

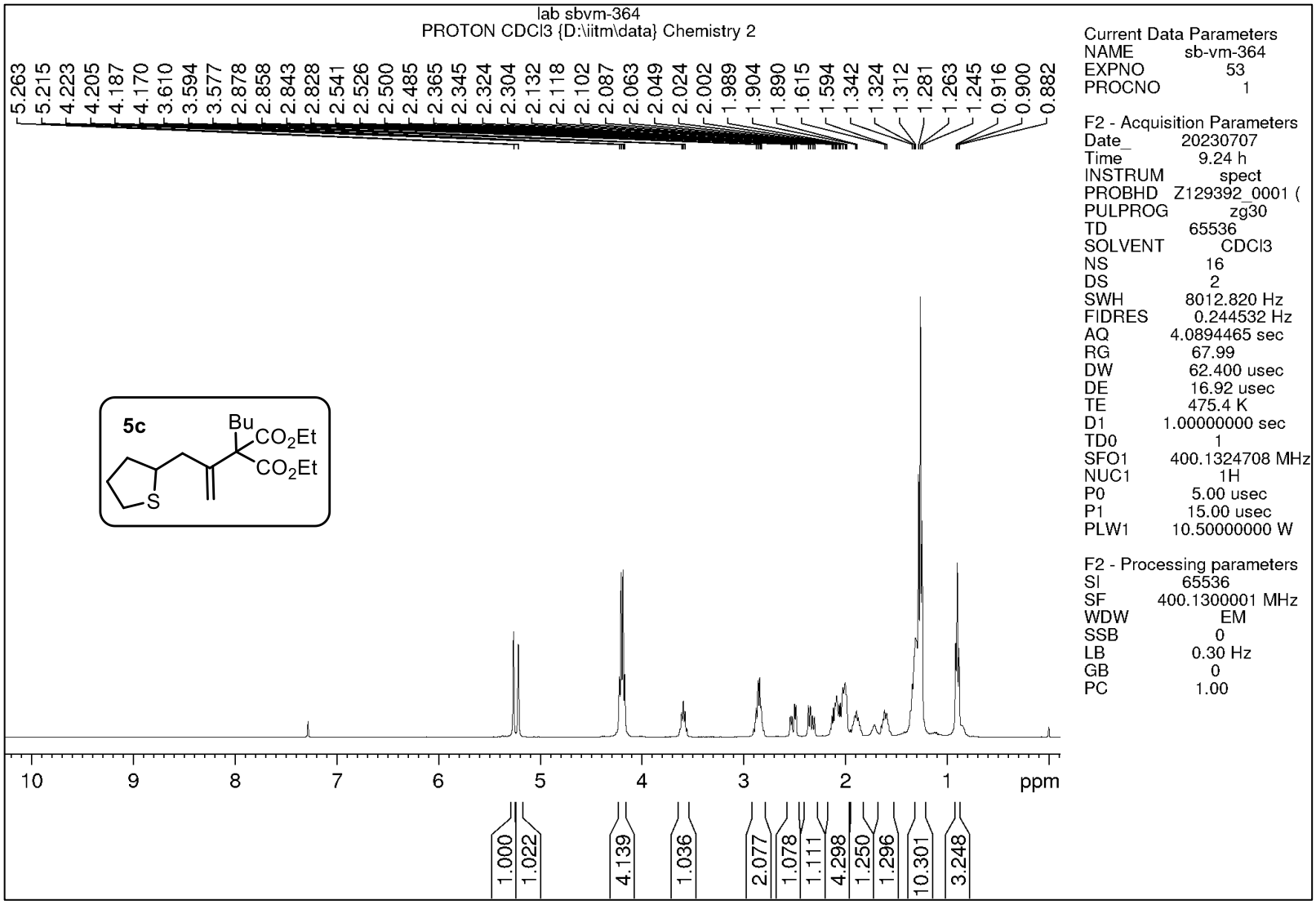


^{13}C NMR spectrum of compound 5b

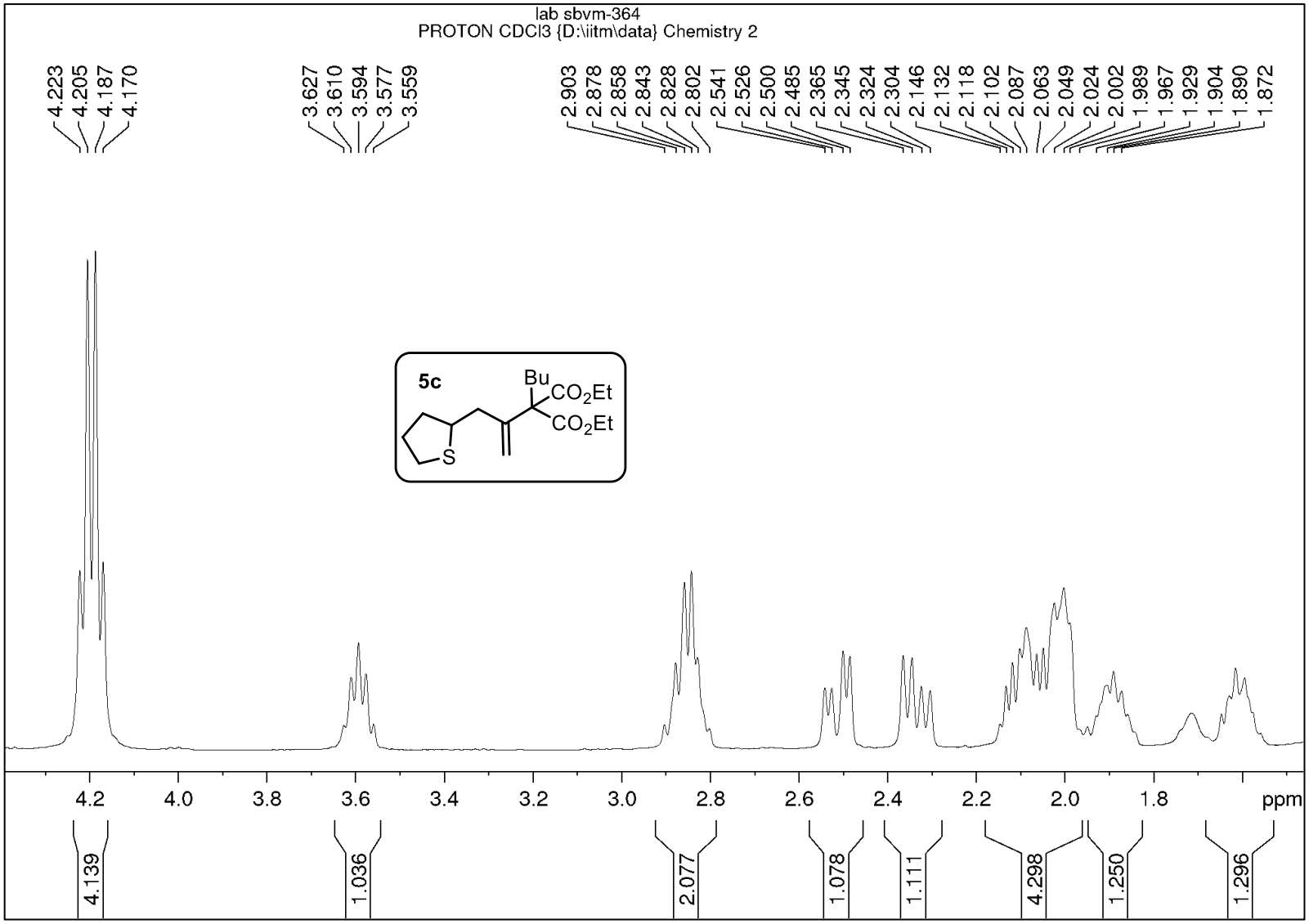


DEPT-135 NMR spectrum of compound 5b

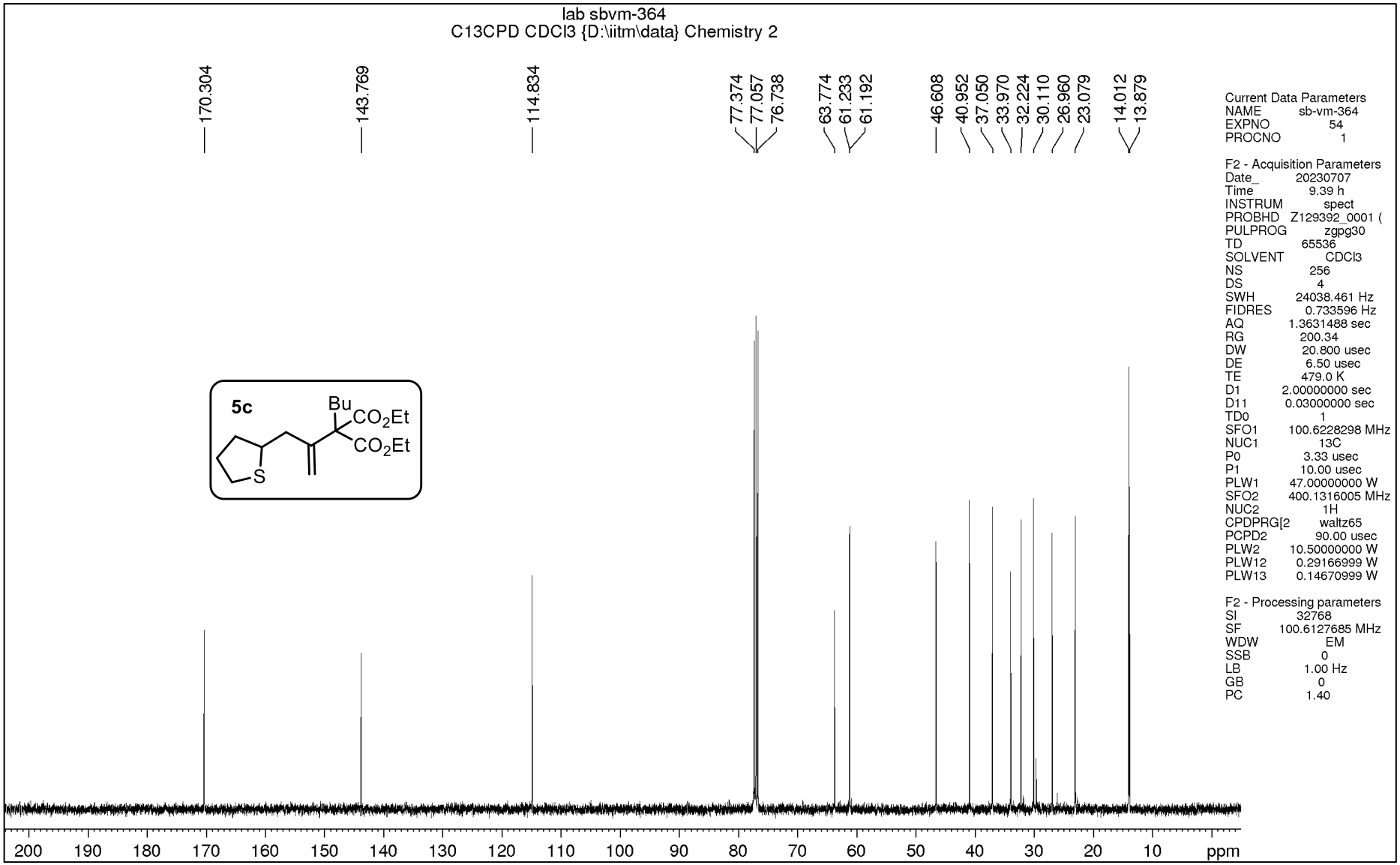
^{1}H NMR spectrum of compound 5c



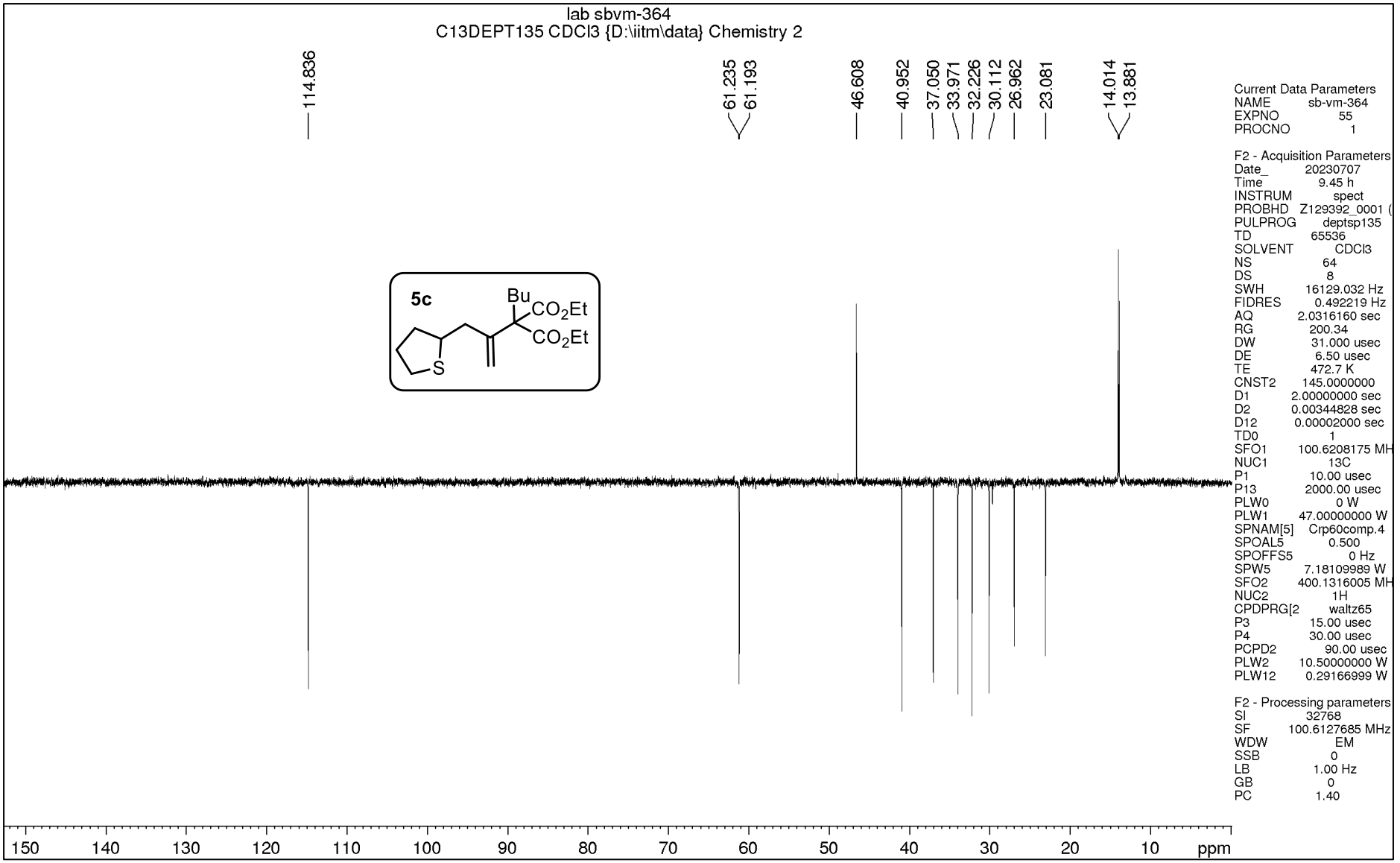
^{1}H NMR spectrum of compound 5c



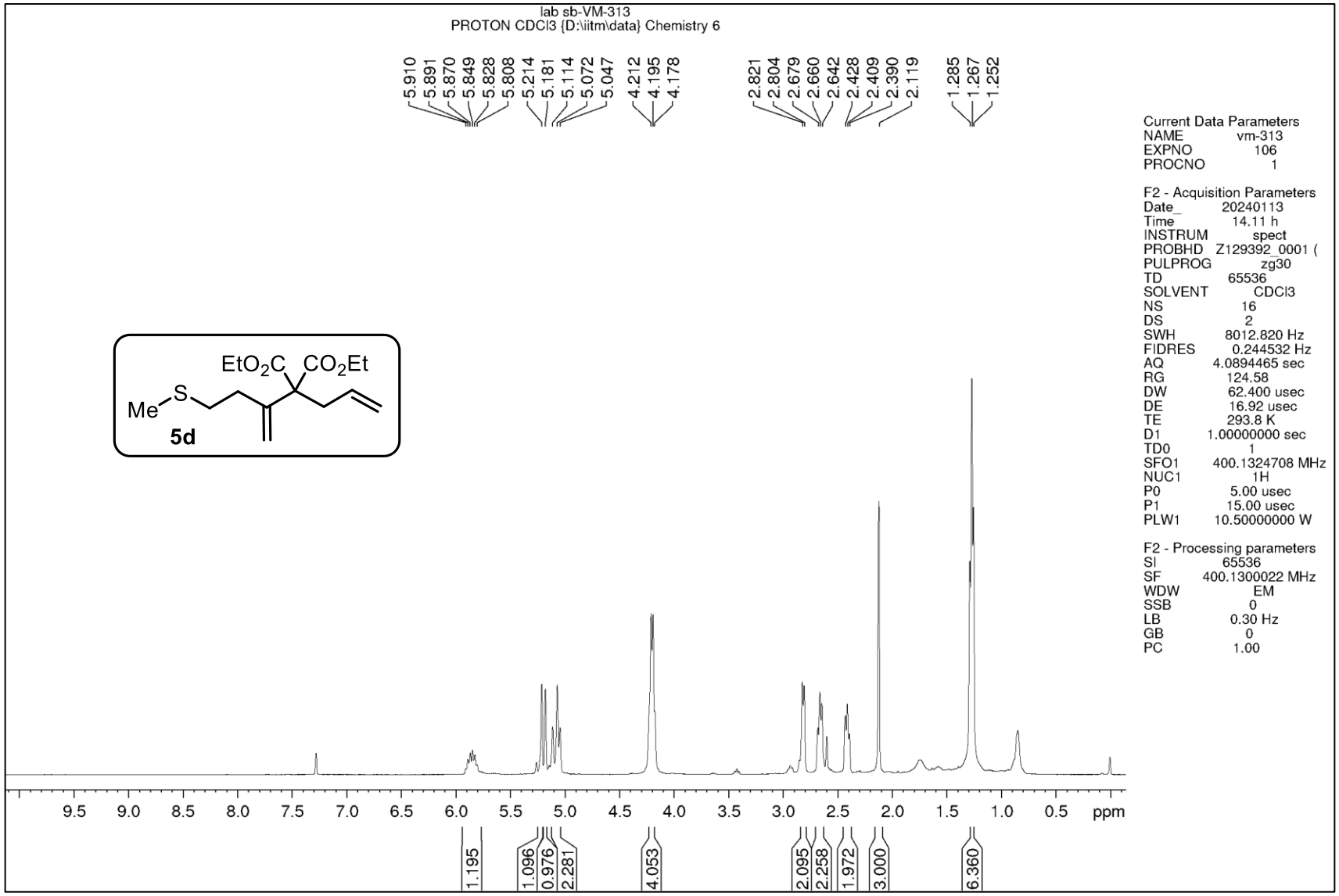
^{1}H NMR spectrum of compound 5c



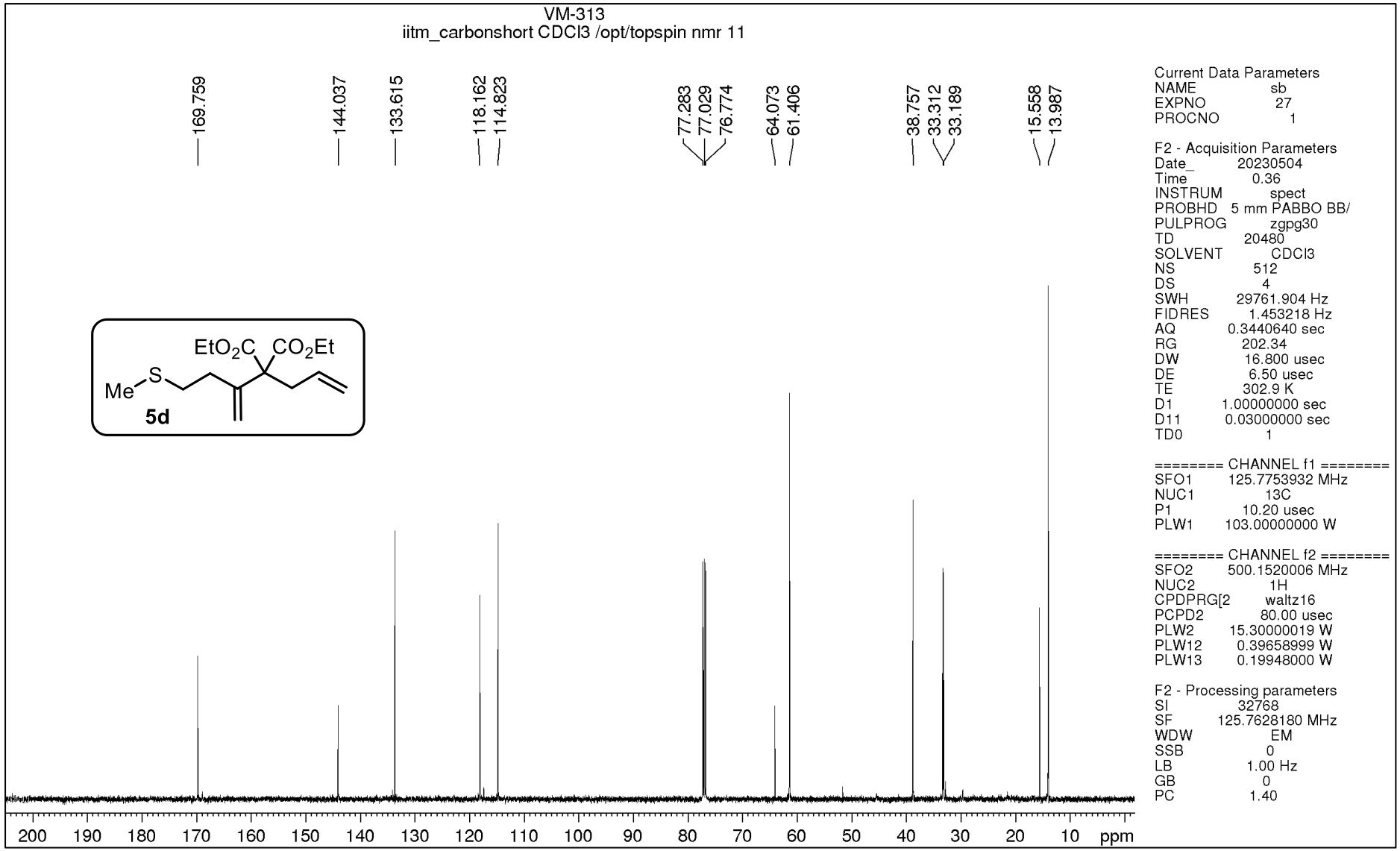
^{13}C NMR spectrum of compound 5c



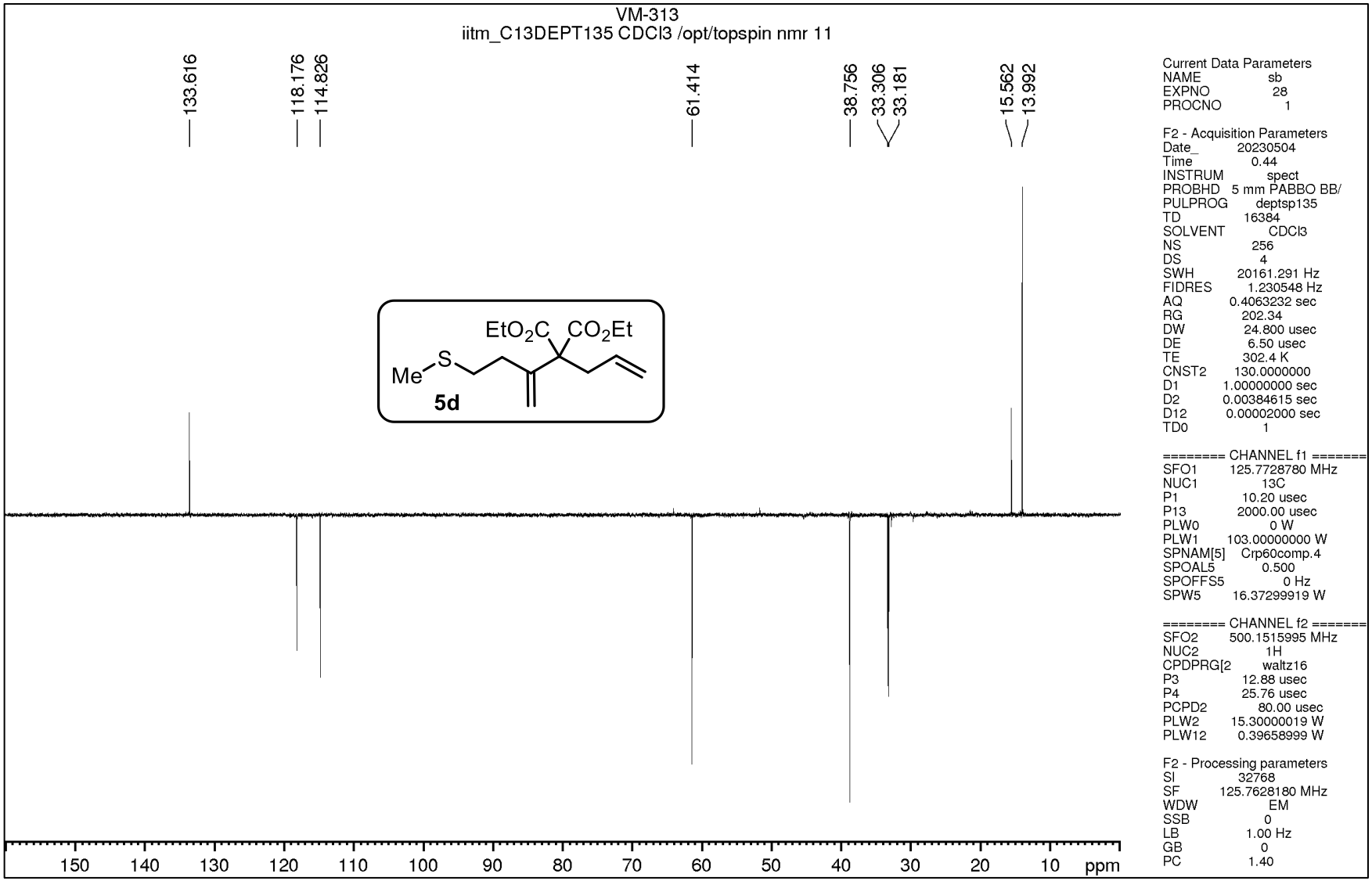
DEPT-135 NMR spectrum of compound 5c



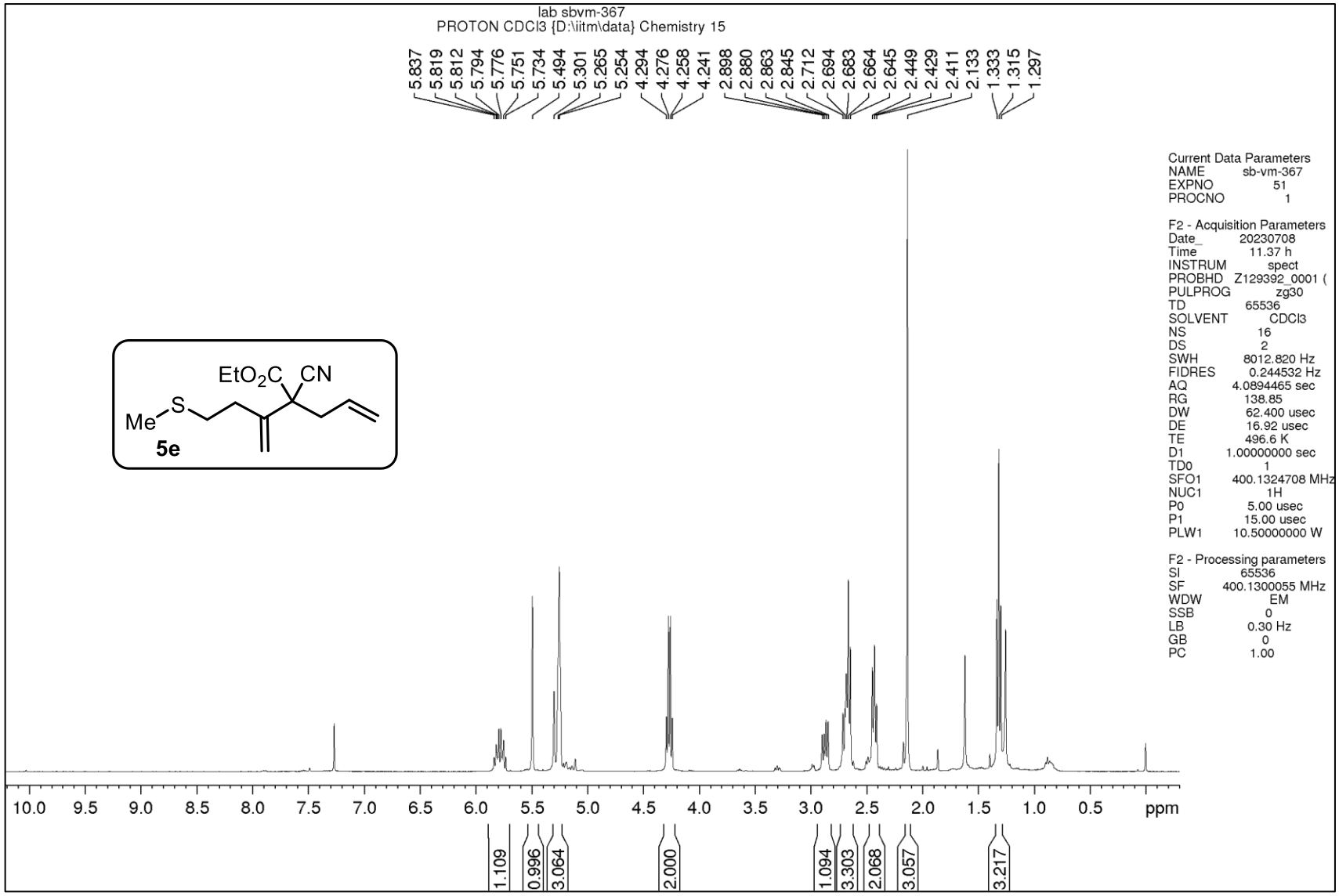
^{1}H NMR spectrum of compound 5d



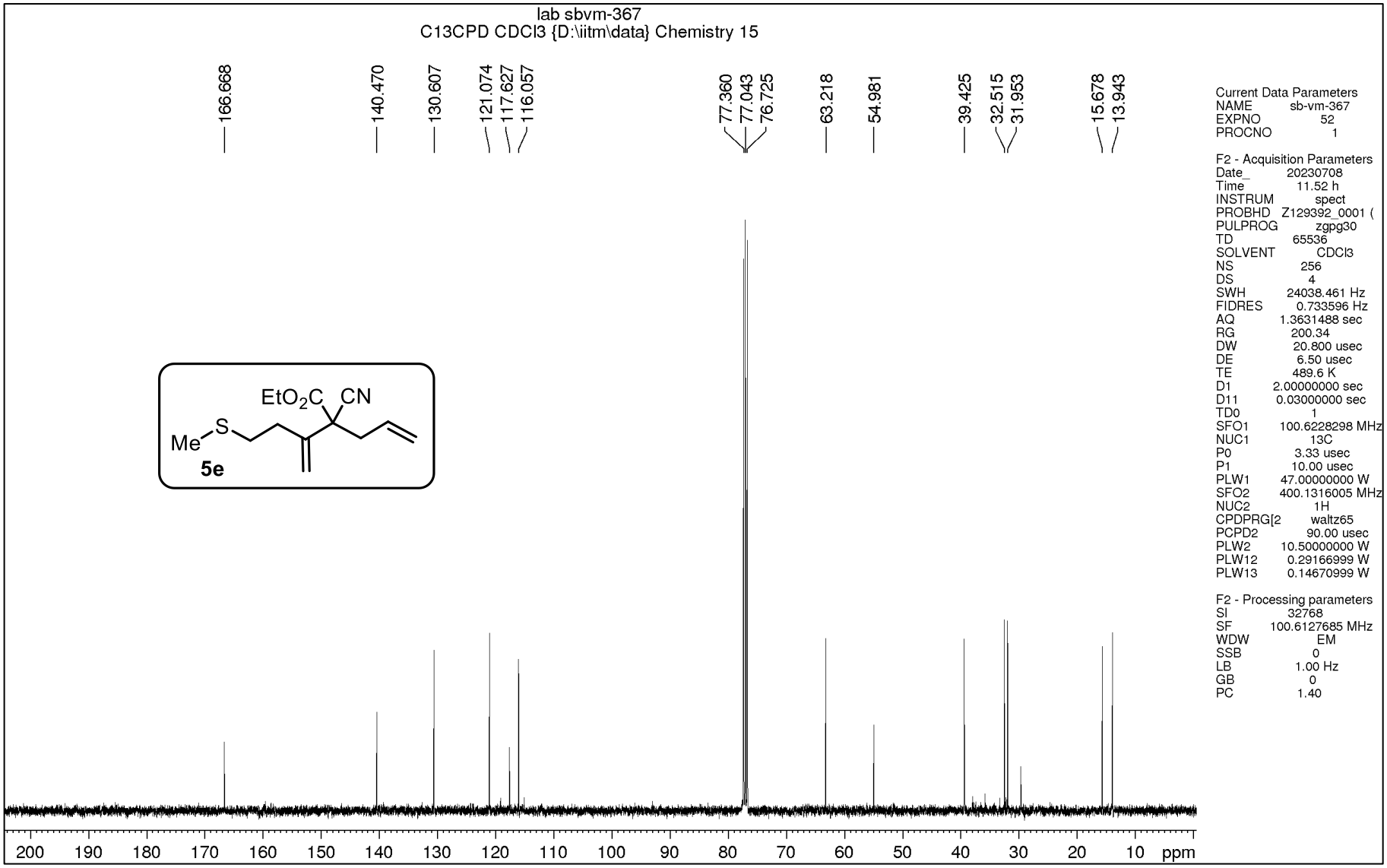
^{13}C NMR spectrum of compound 5d



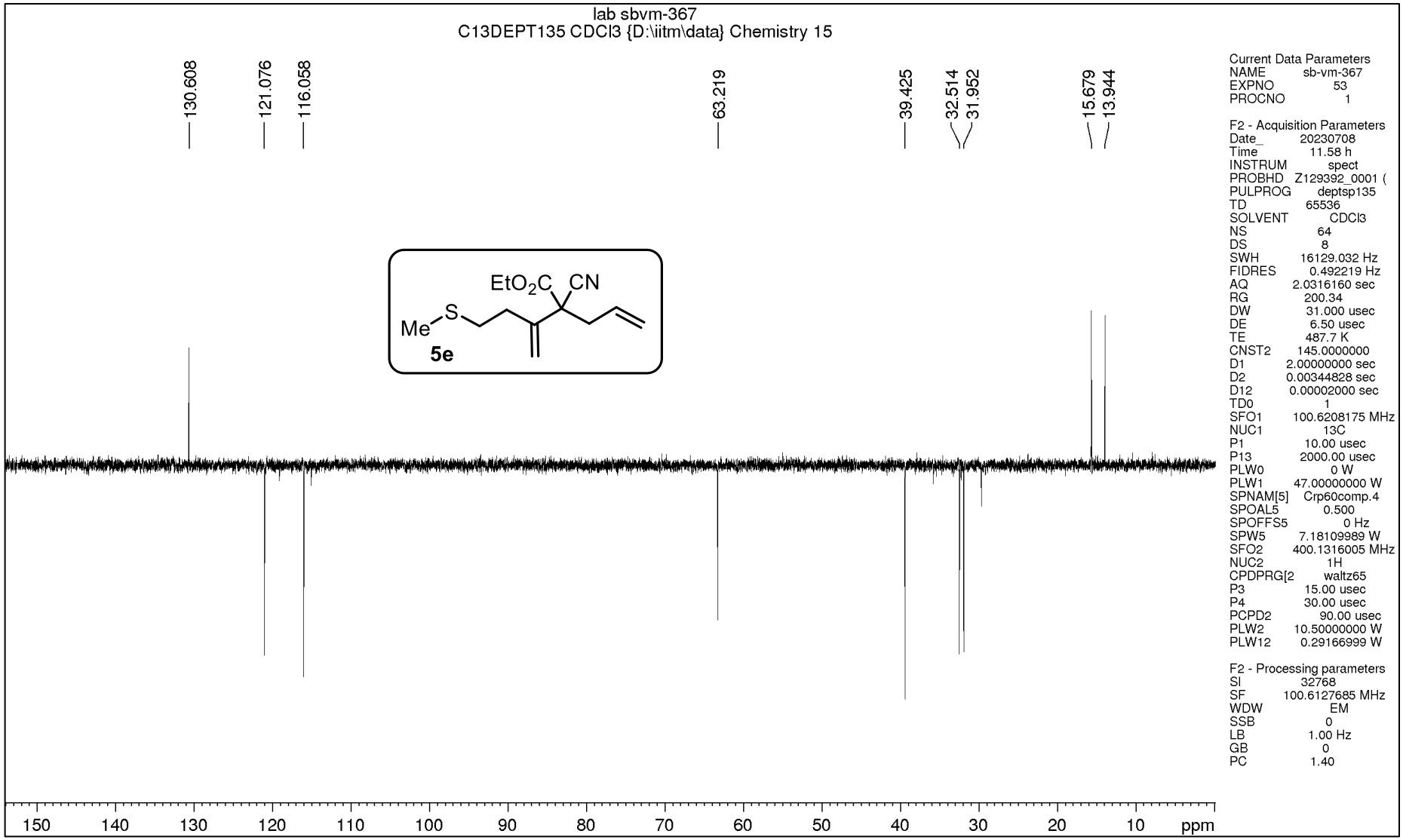
DEPT-135 NMR spectrum of compound 5d



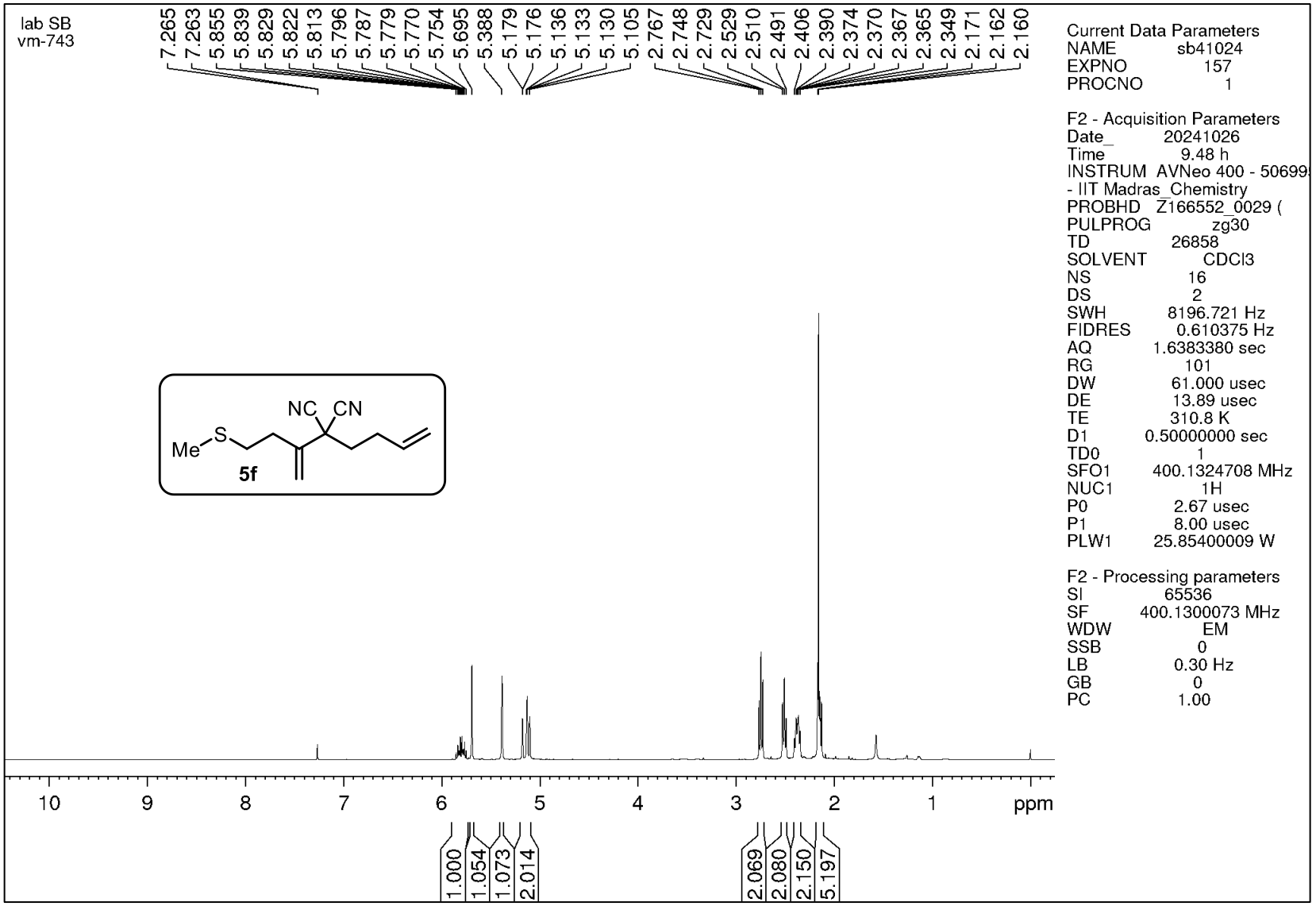
^{1}H NMR spectrum of compound 5e



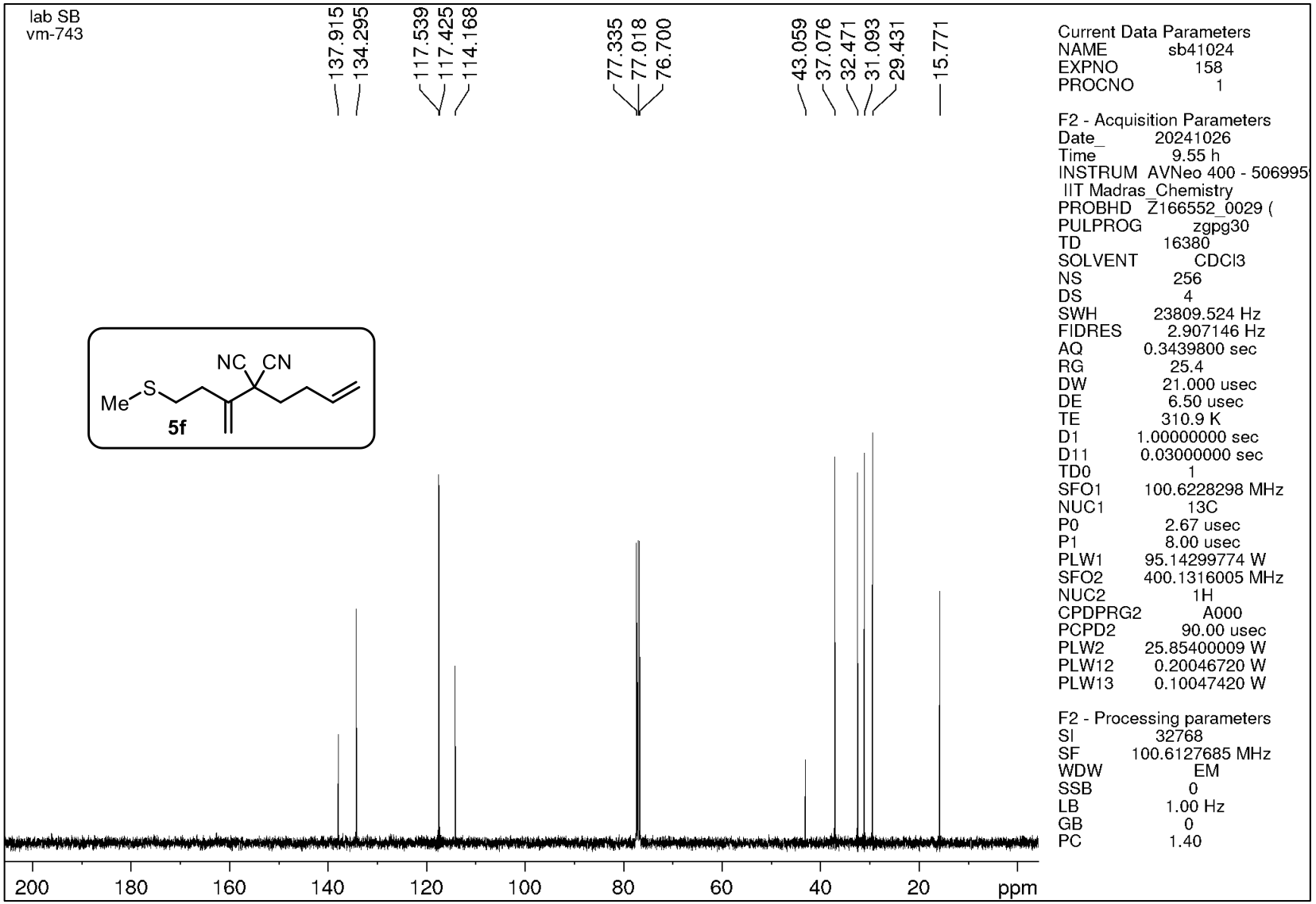
^{13}C NMR spectrum of compound 5e



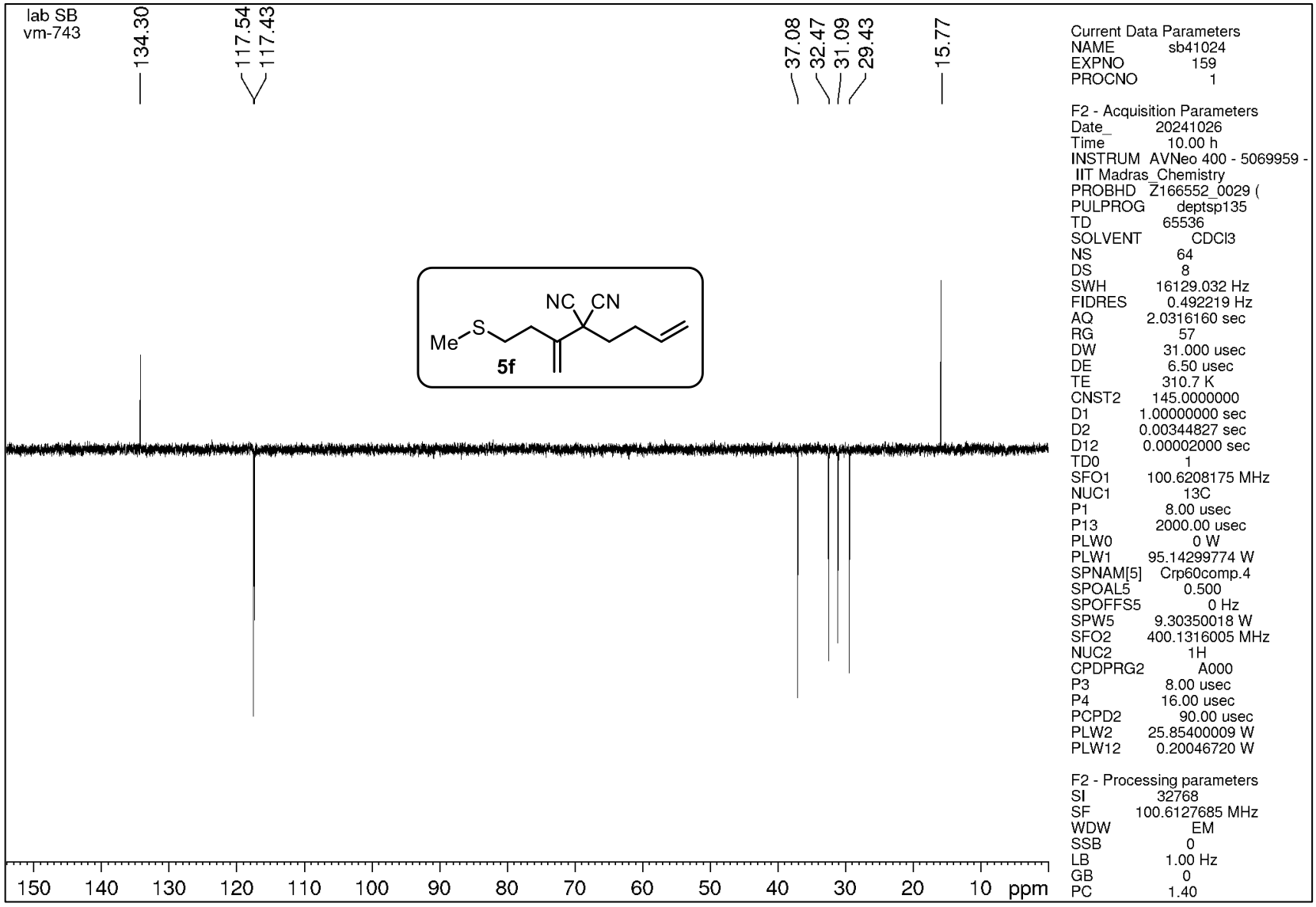
DEPT-135 NMR spectrum of compound 5e



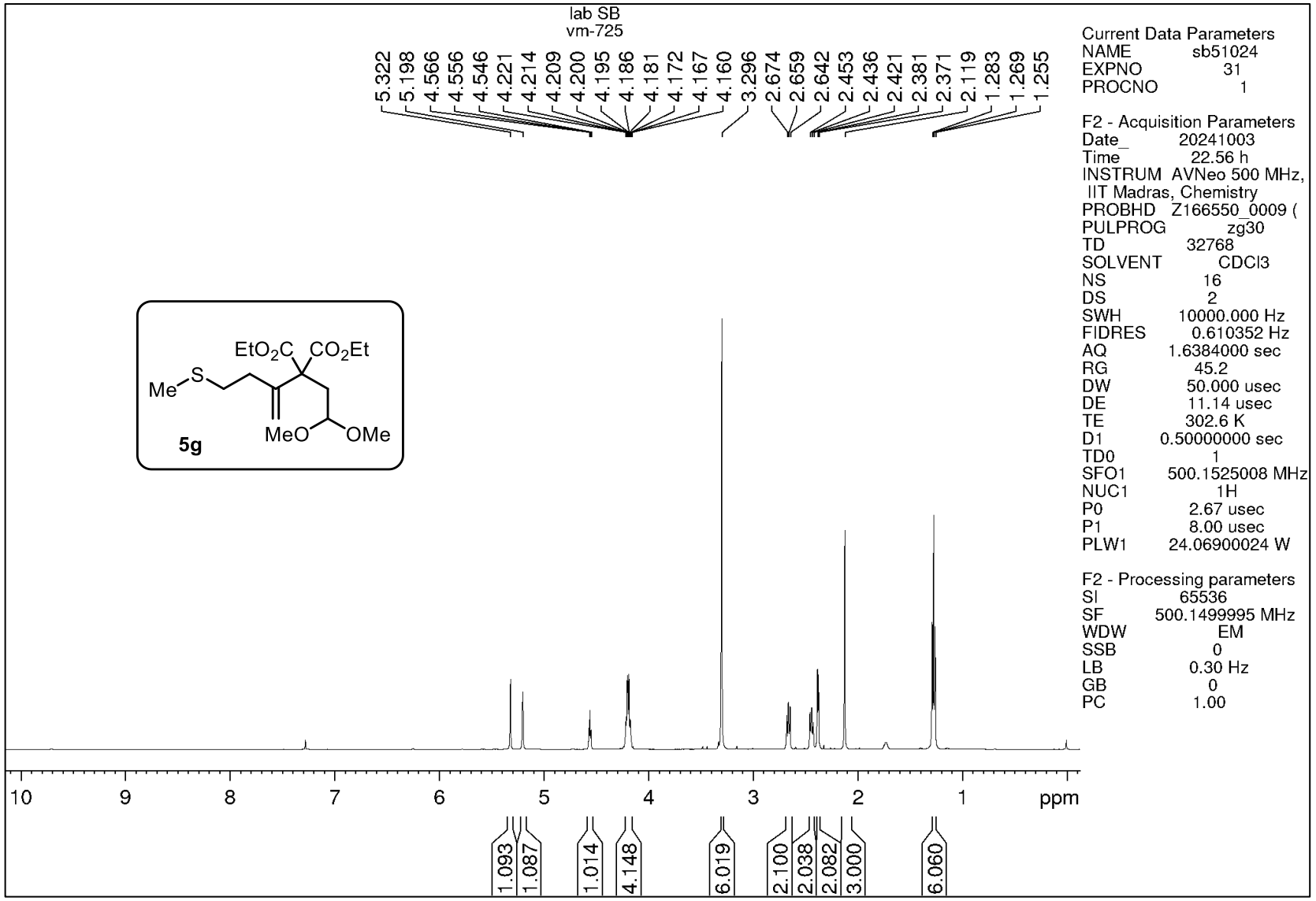
^{1}H NMR spectrum of compound 5f



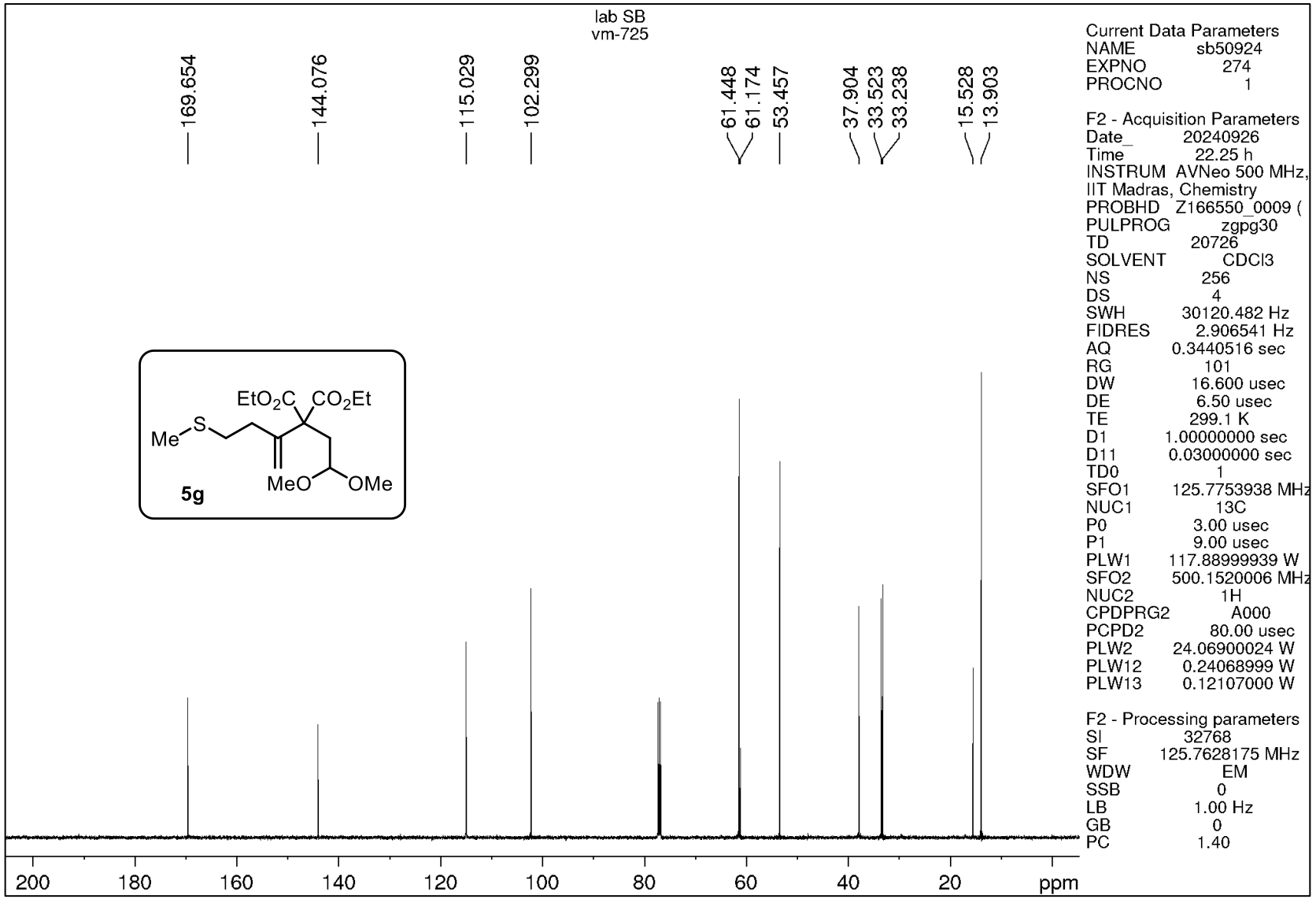
^{13}C NMR spectrum of compound 5f



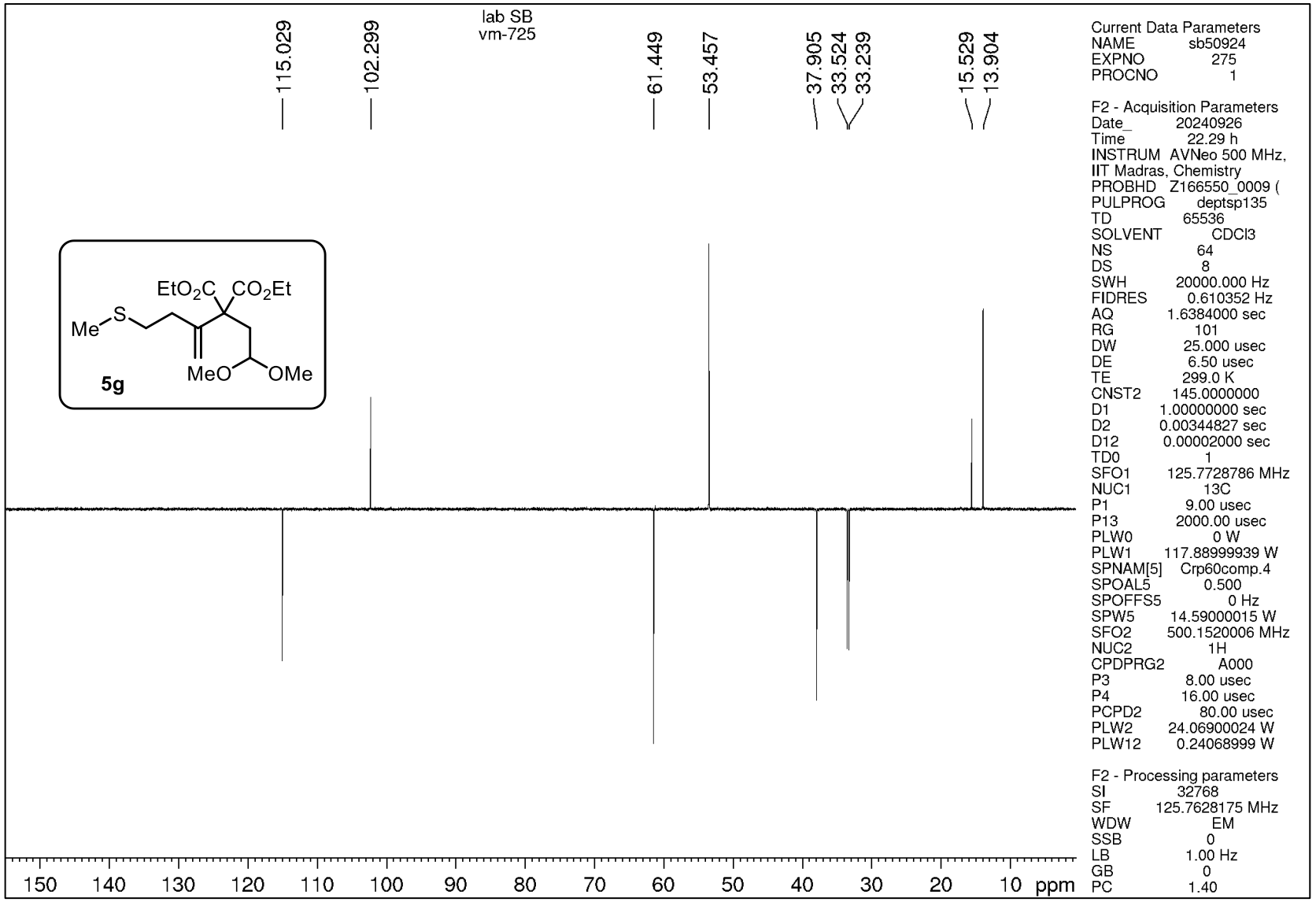
DEPT-135 NMR spectrum of compound 5f



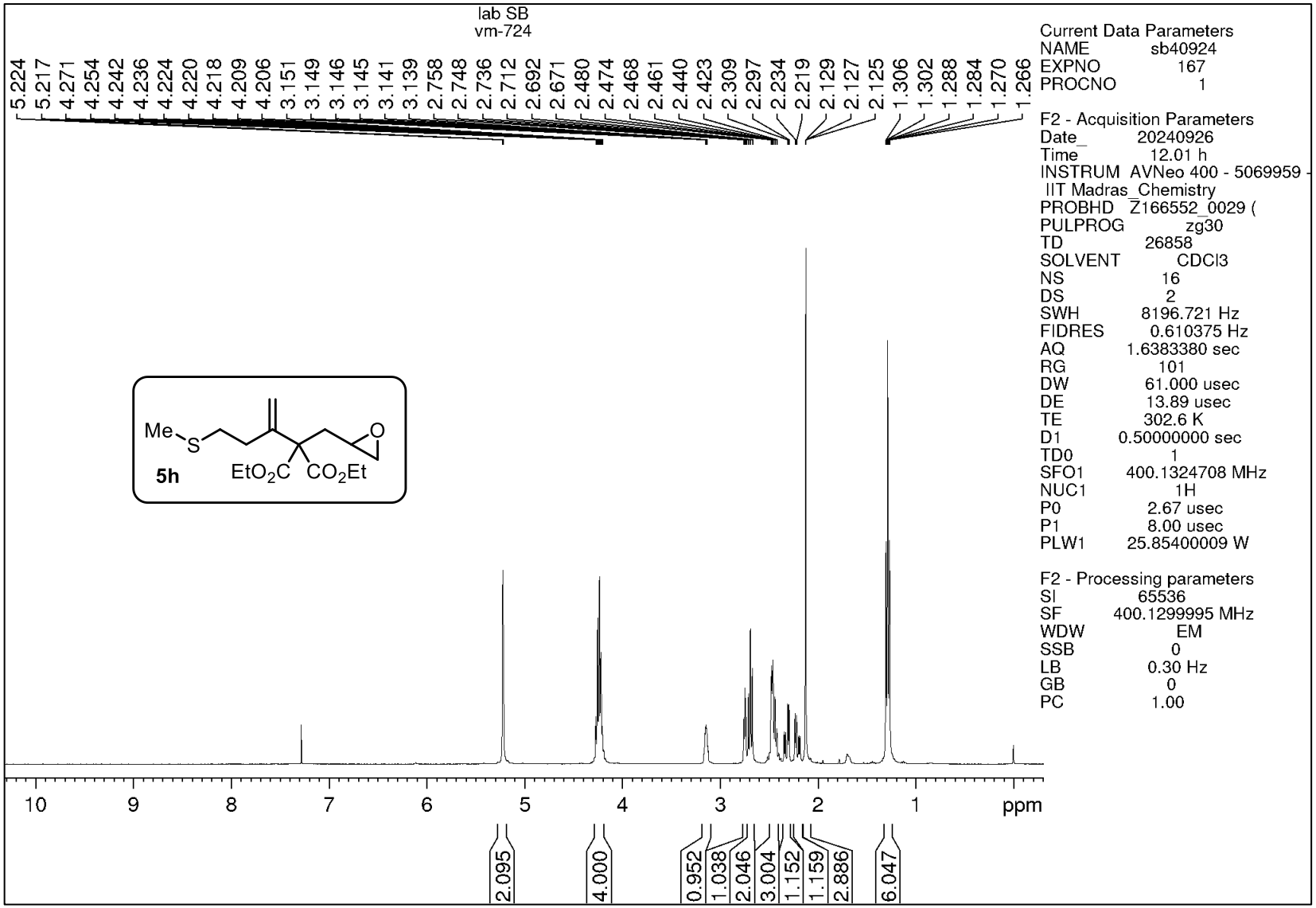
^{1}H NMR spectrum of compound 5g



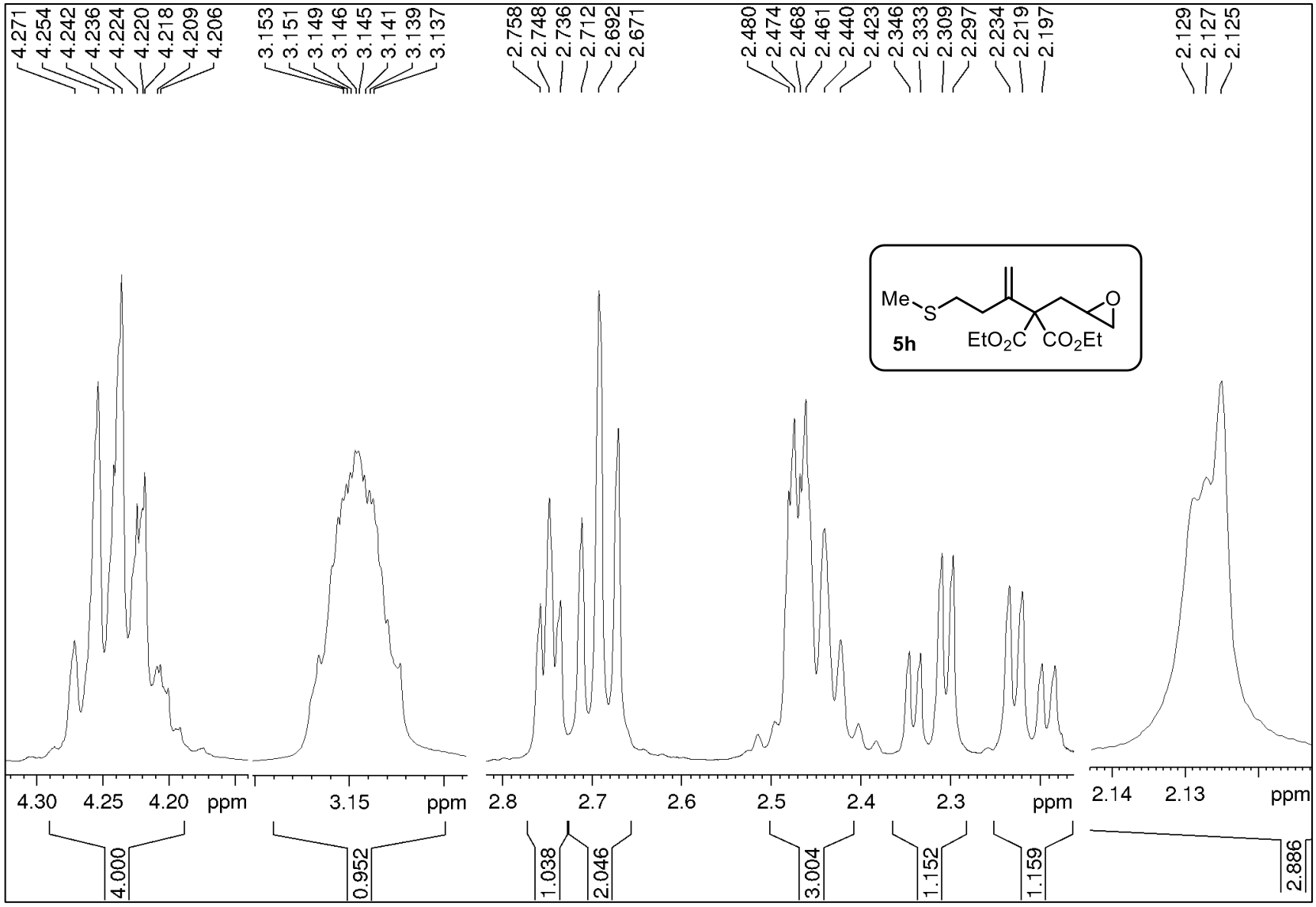
^{13}C NMR spectrum of compound 5g



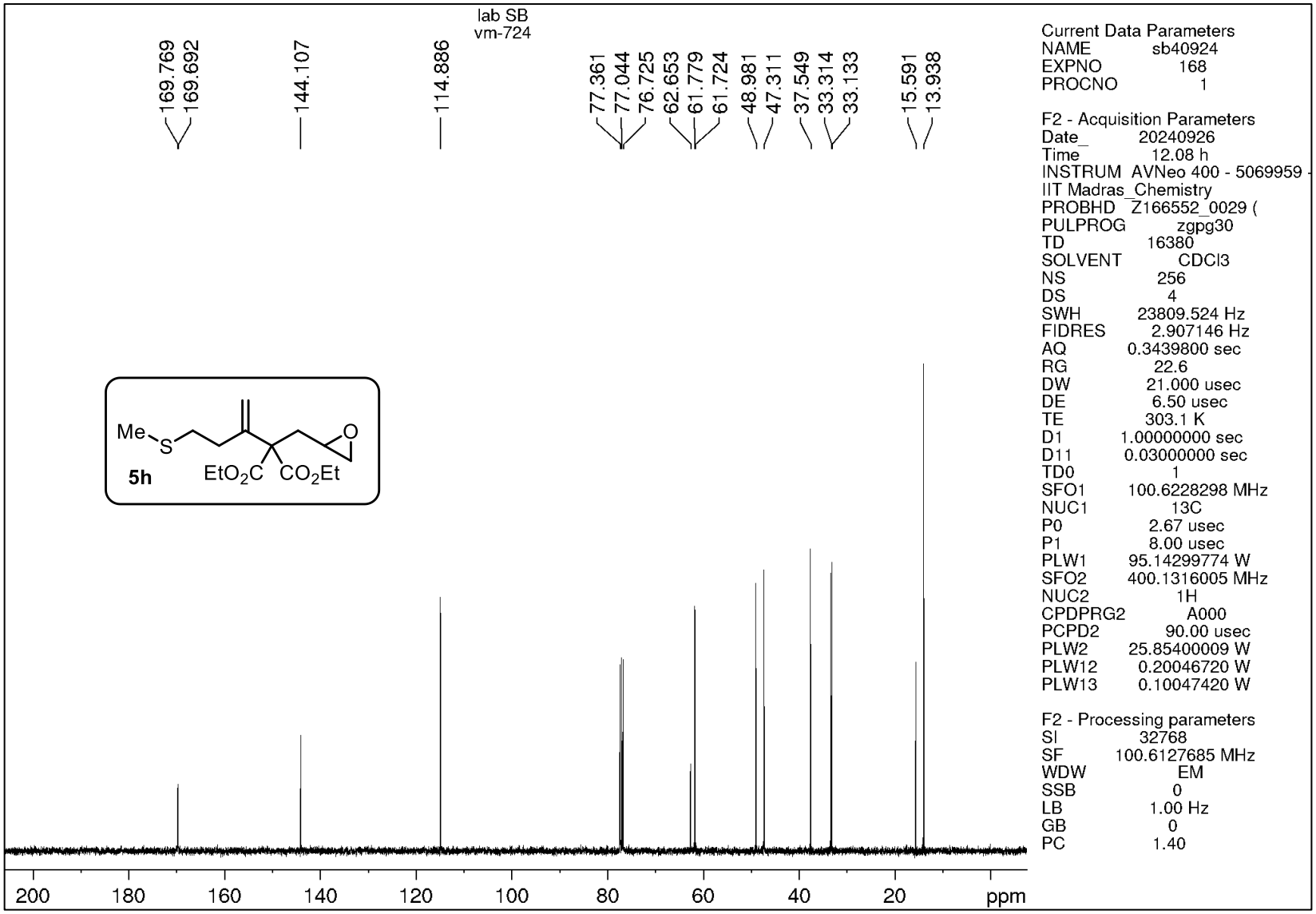
DEPT-135 NMR spectrum of compound 5g



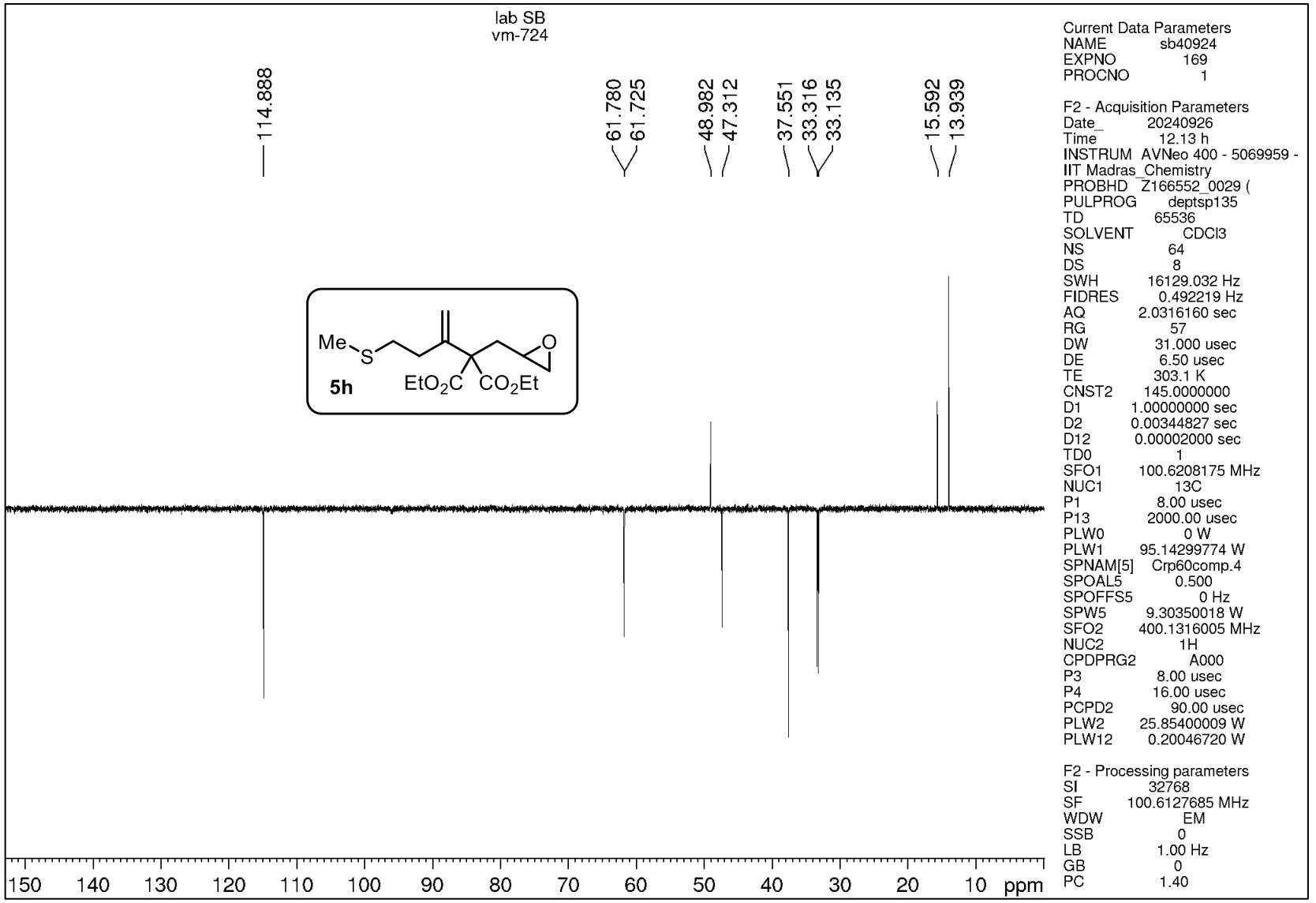
^{1}H NMR spectrum of compound 5h



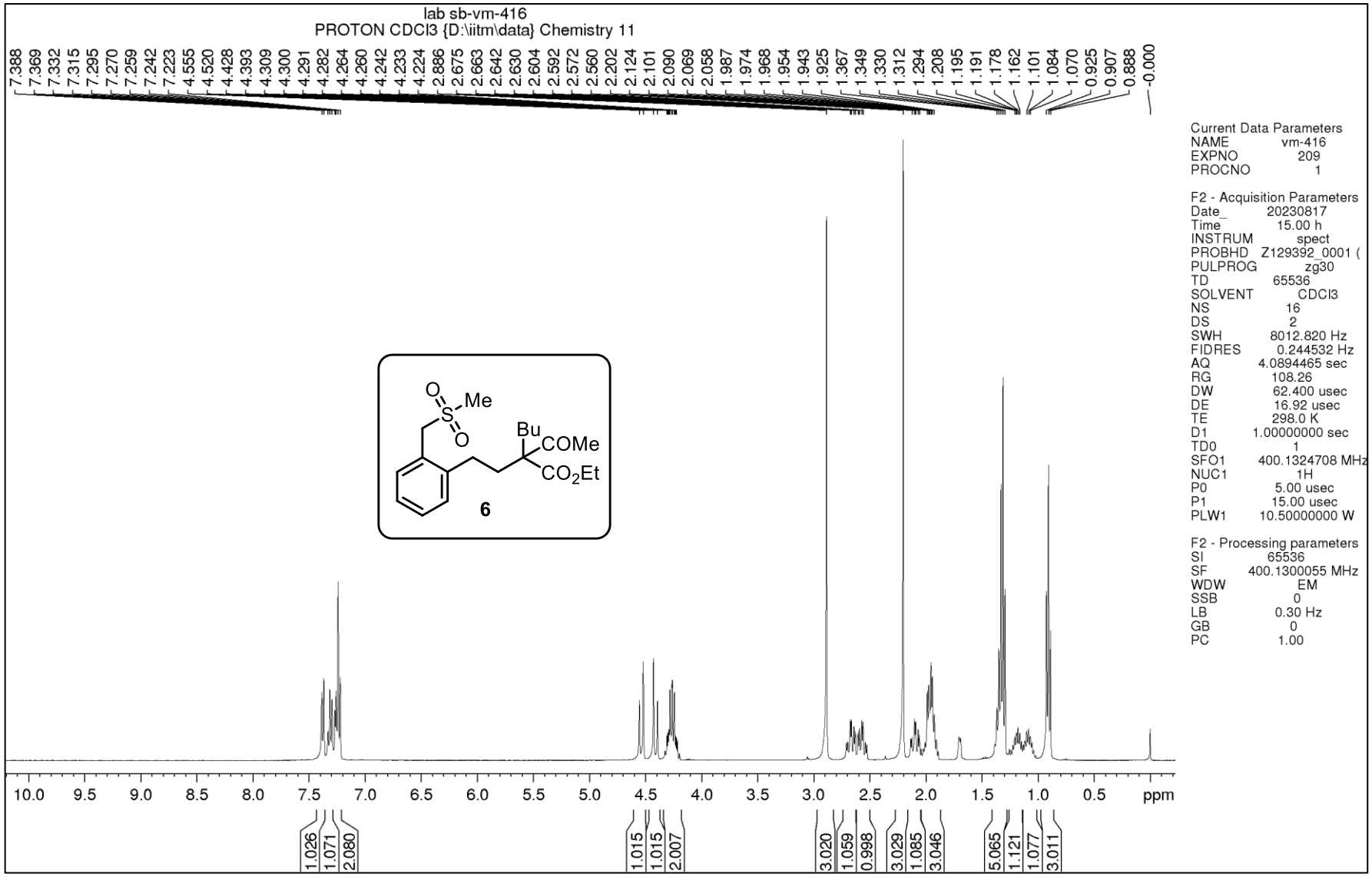
^{1}H NMR spectrum of compound 5h



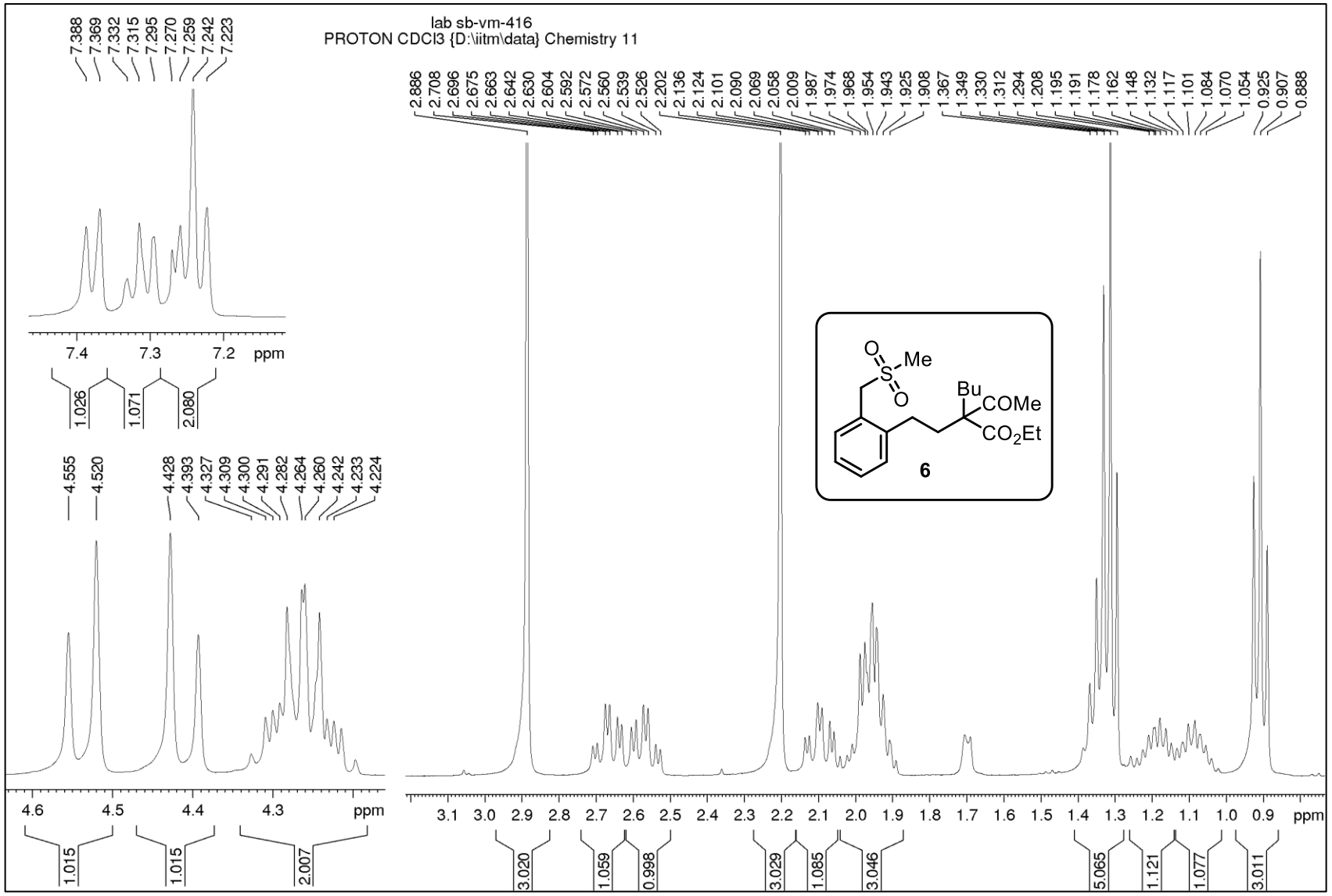
^{13}C NMR spectrum of compound 5h



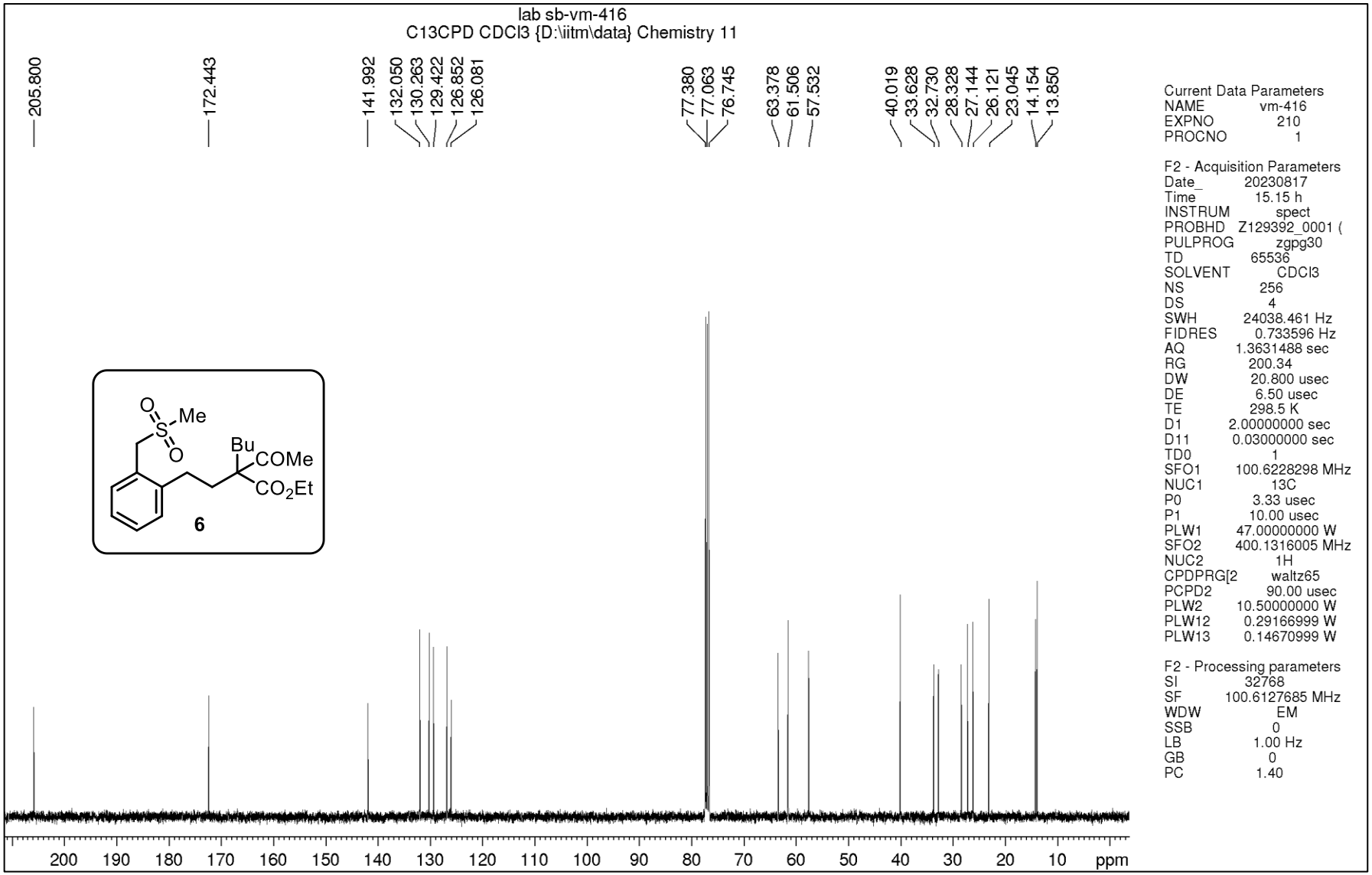
DEPT-135 NMR spectrum of compound 5h



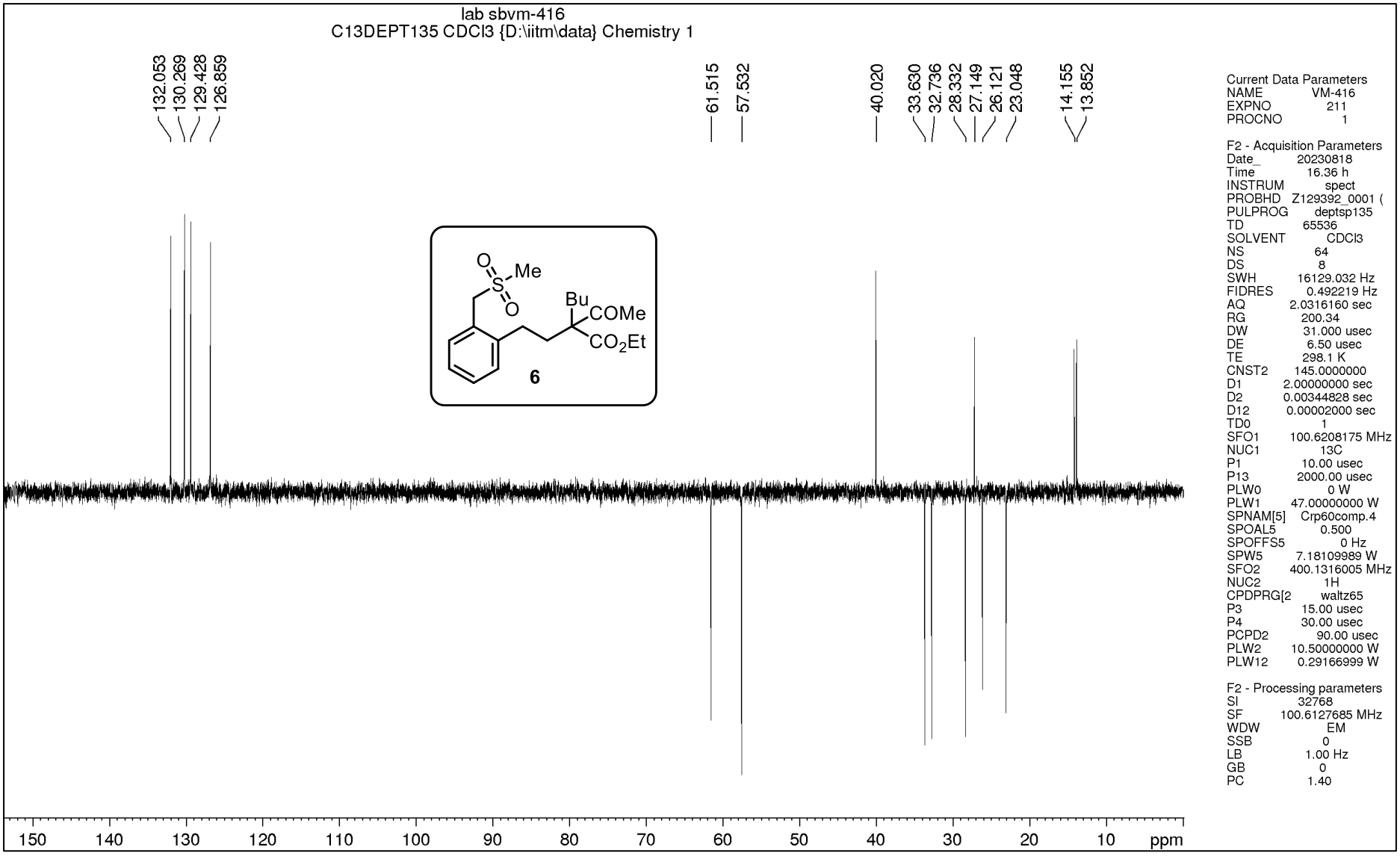
^{1}H NMR spectrum of compound 6



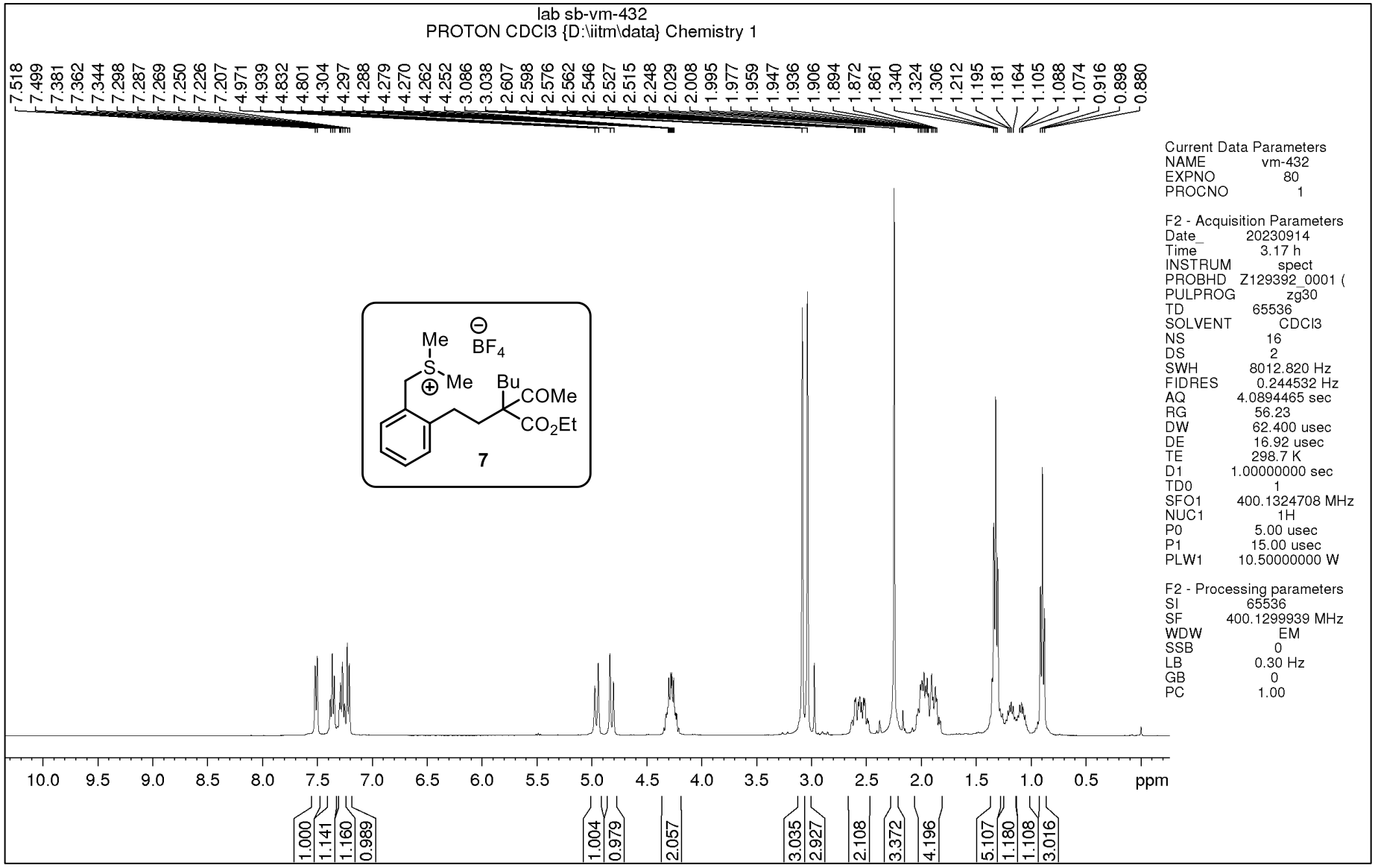
^{1}H NMR spectrum of compound 6



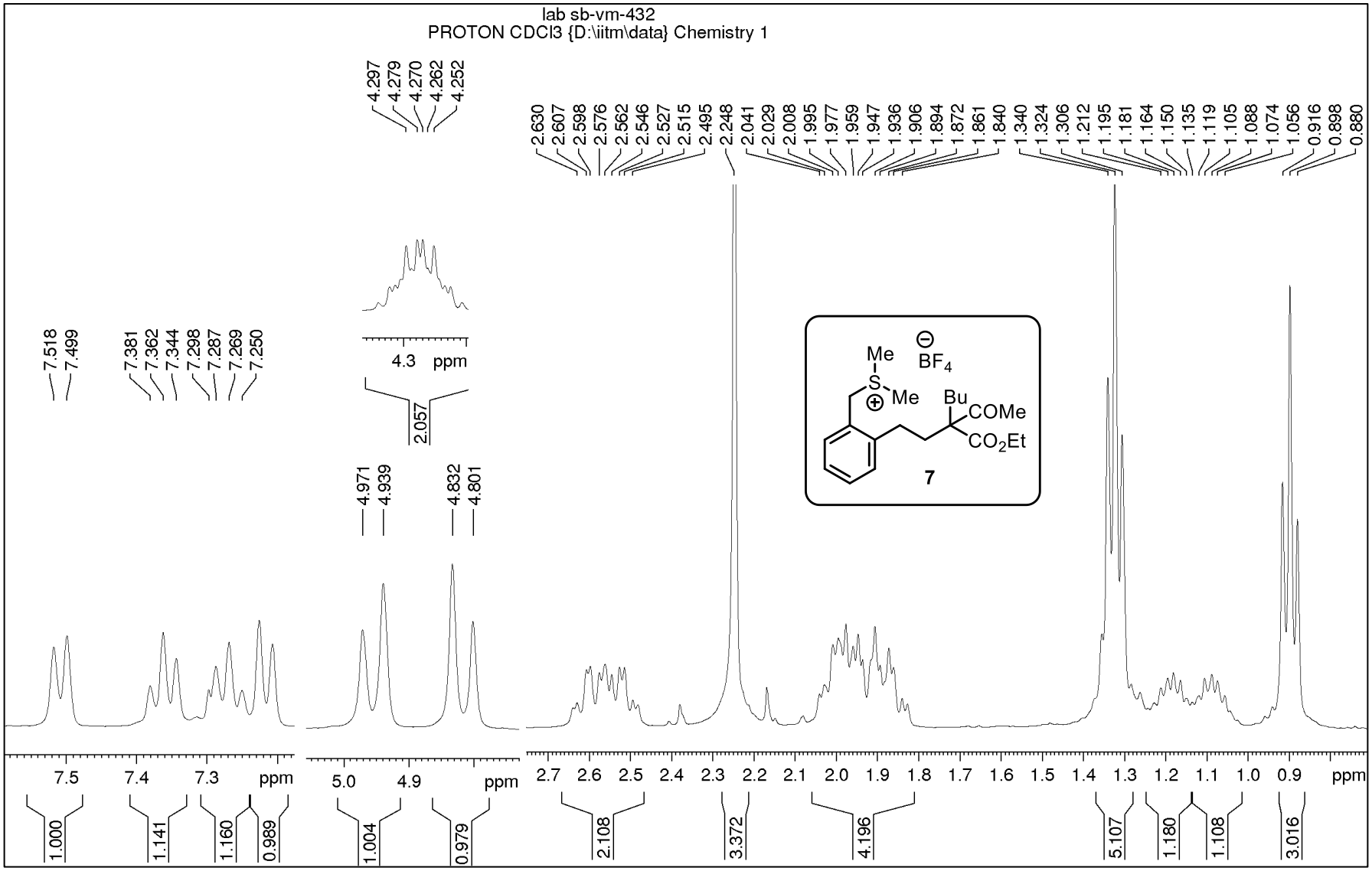
^{13}C NMR spectrum of compound 6



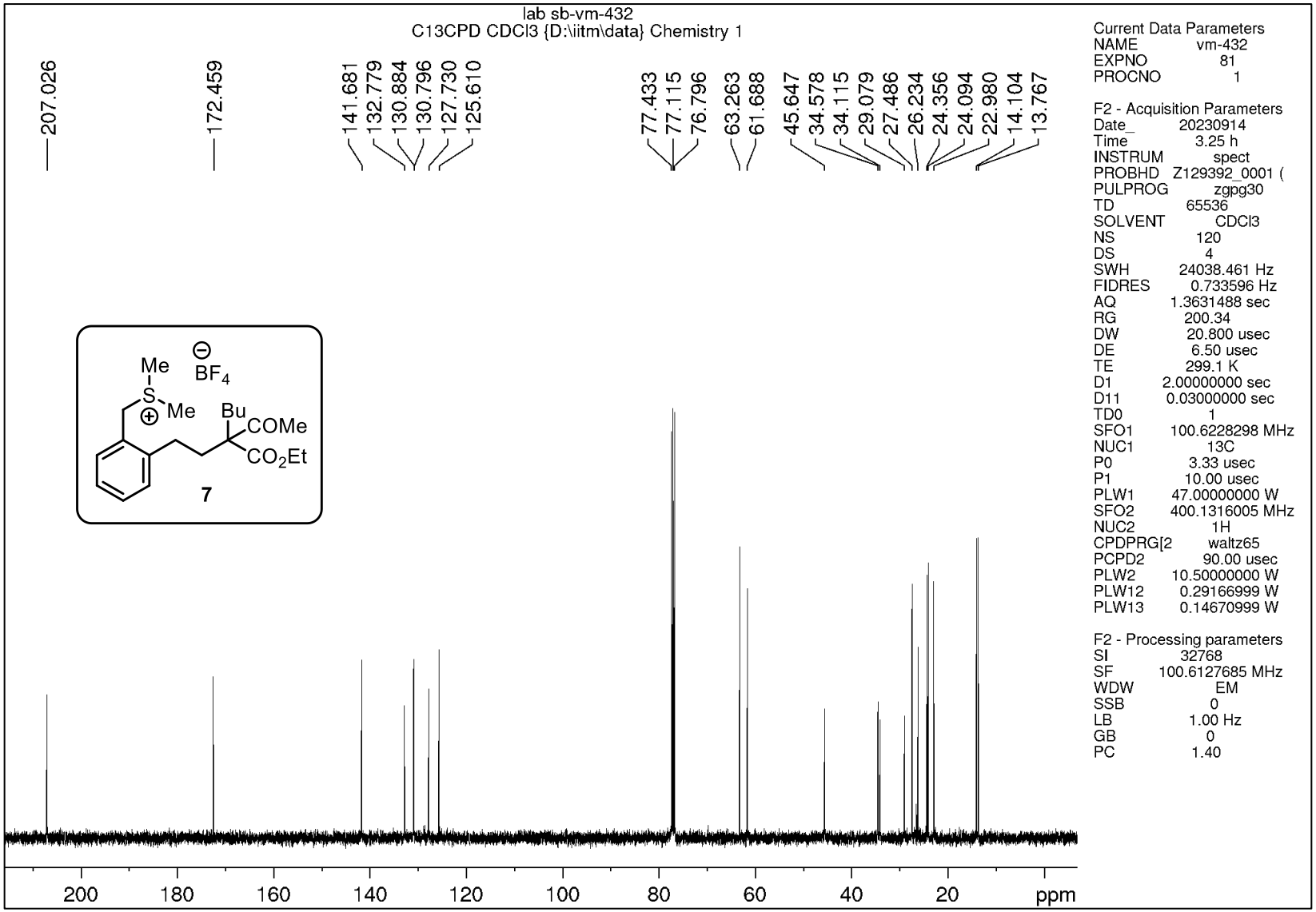
DEPT-135 NMR spectrum of compound 6



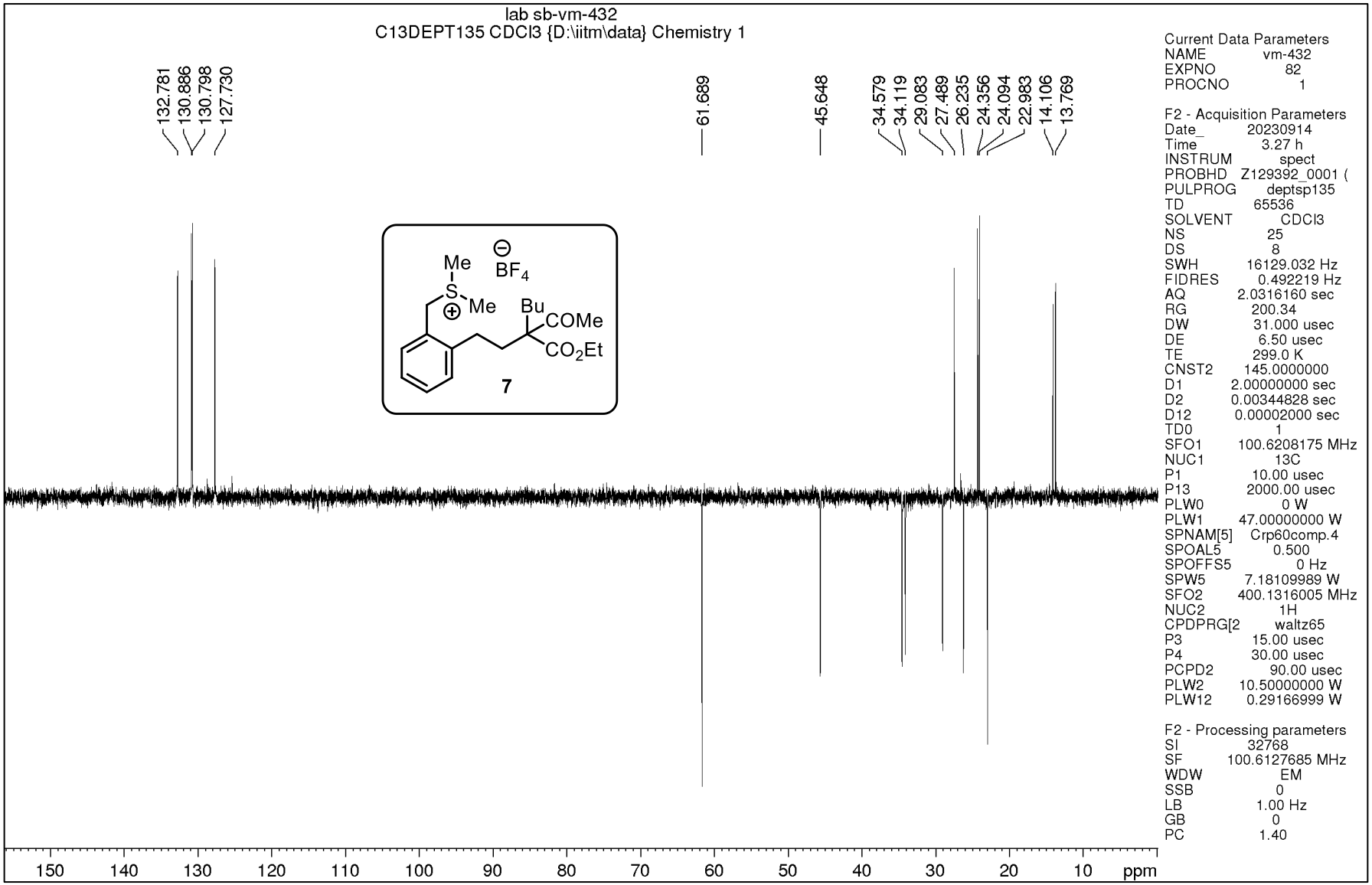
^{1}H NMR spectrum of compound 7



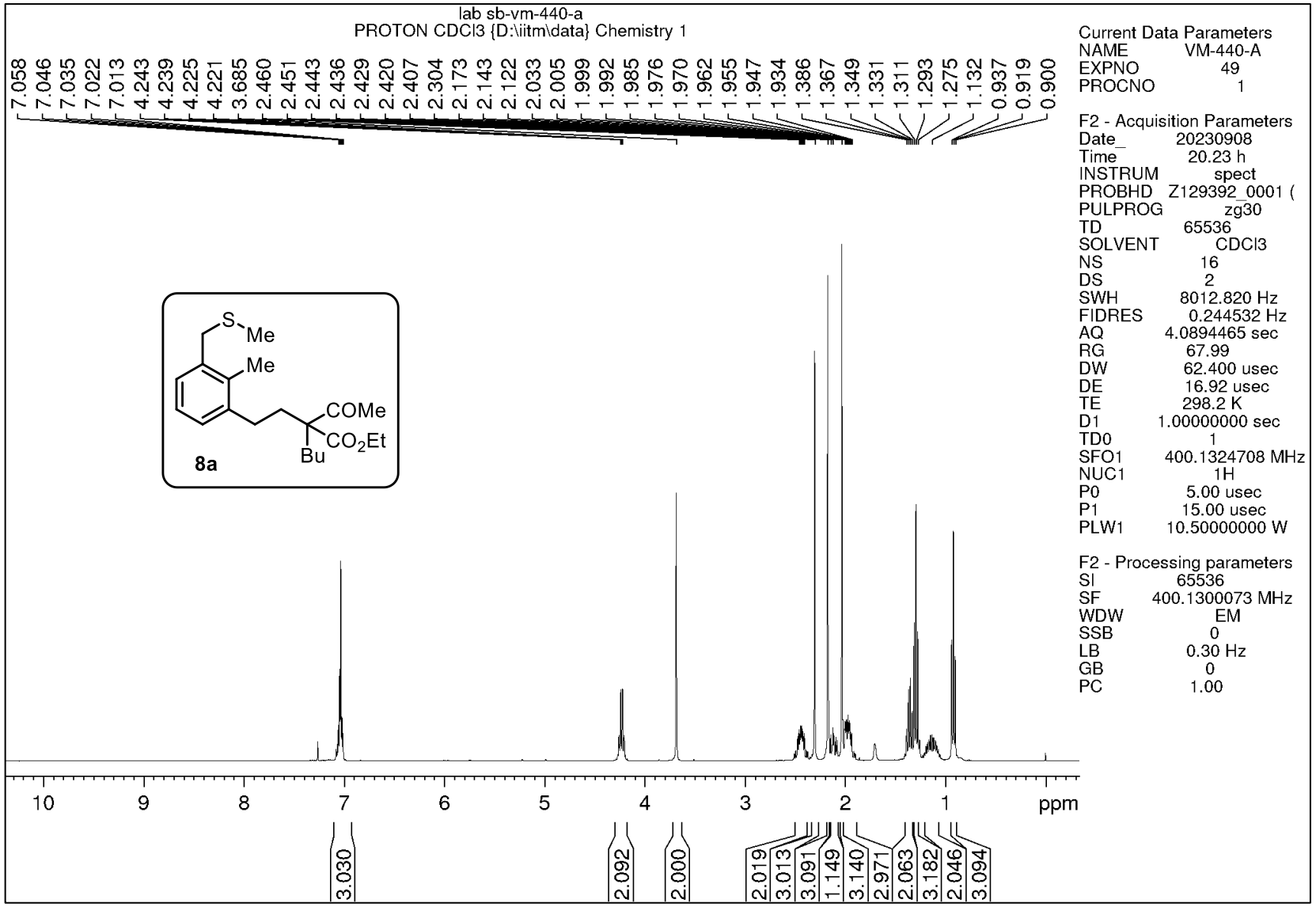
^{1}H NMR spectrum of compound 7



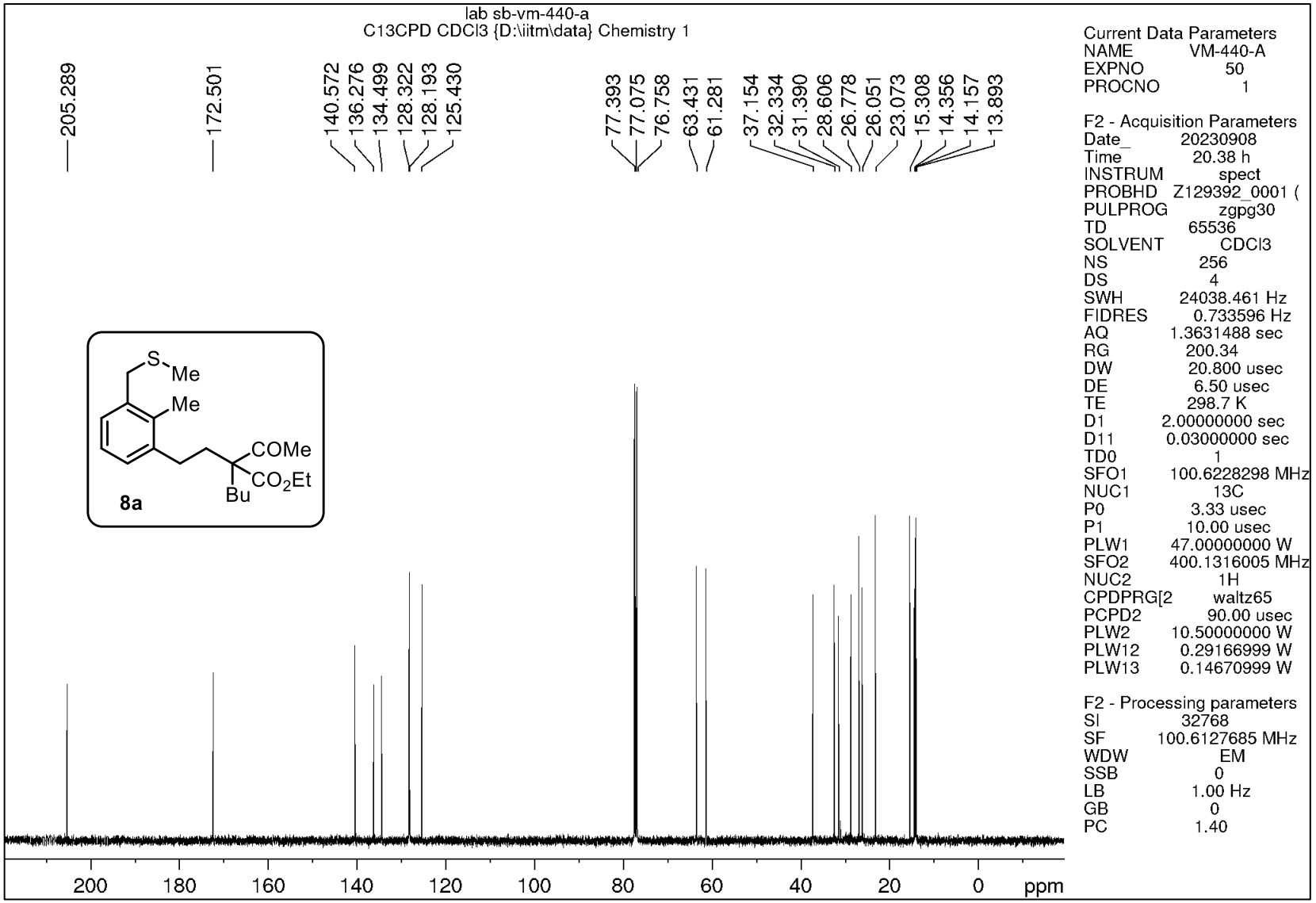
^{13}C NMR spectrum of compound 7



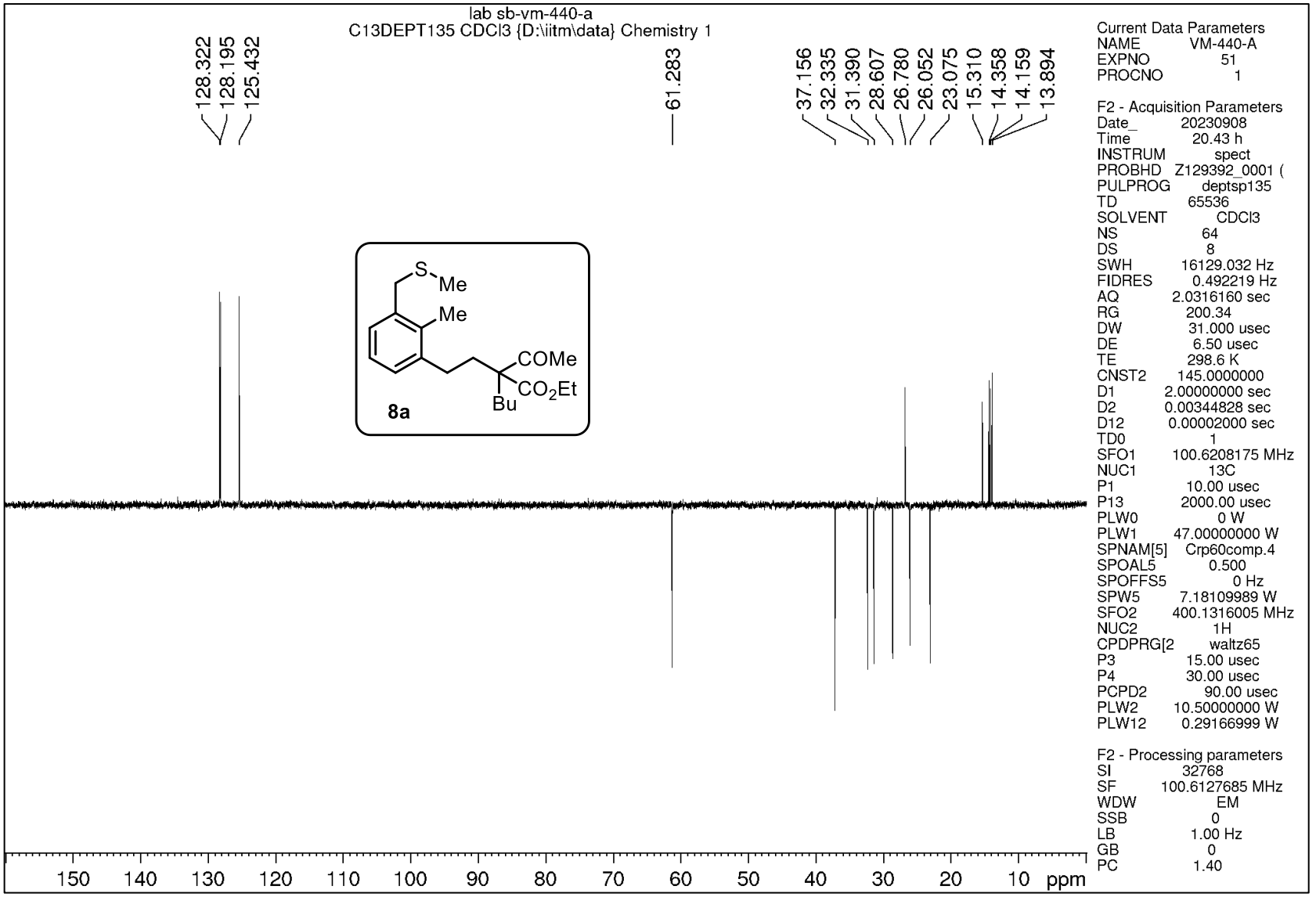
DEPT-135 NMR spectrum of compound 7



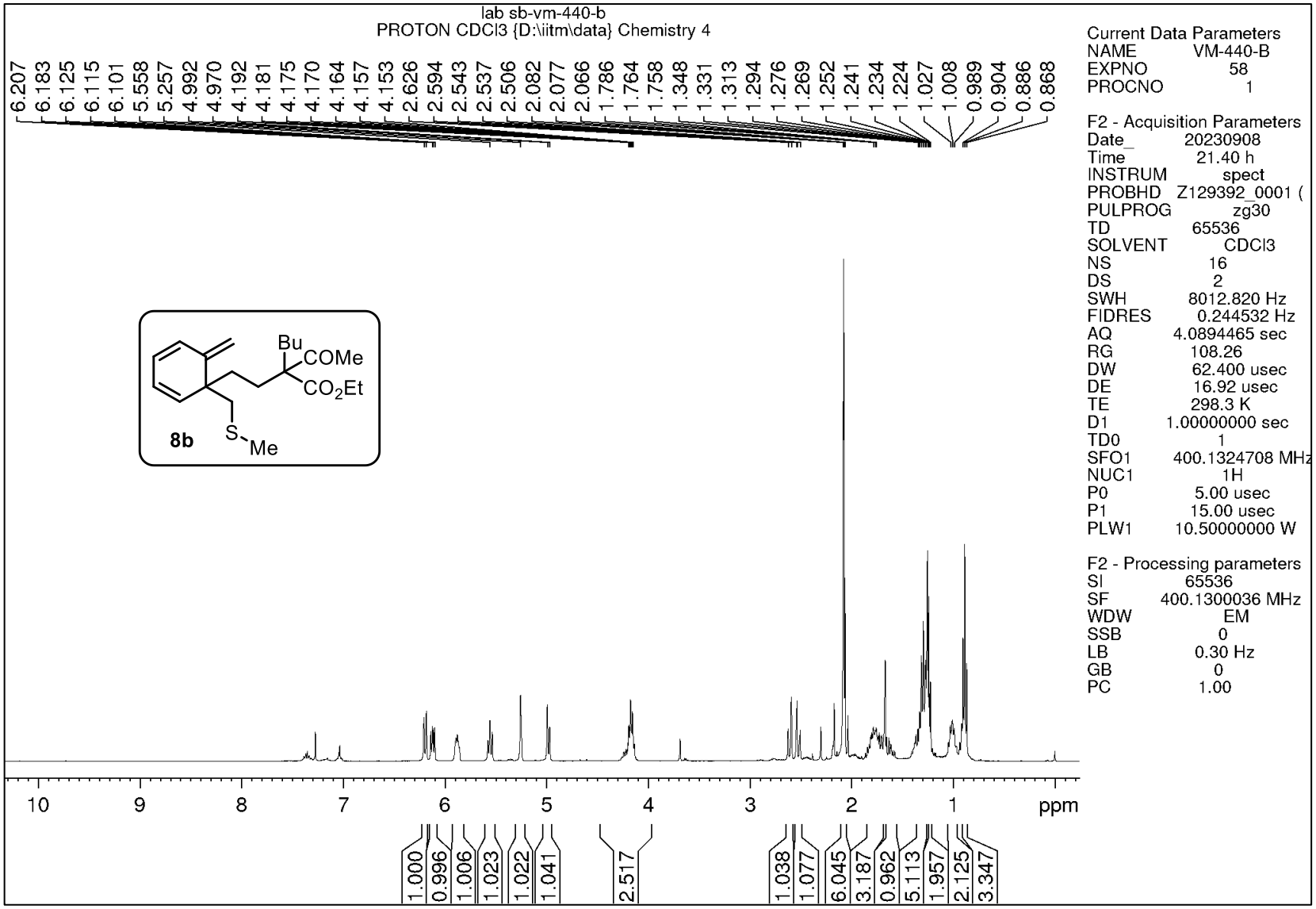
^{1}H NMR spectrum of compound 8a



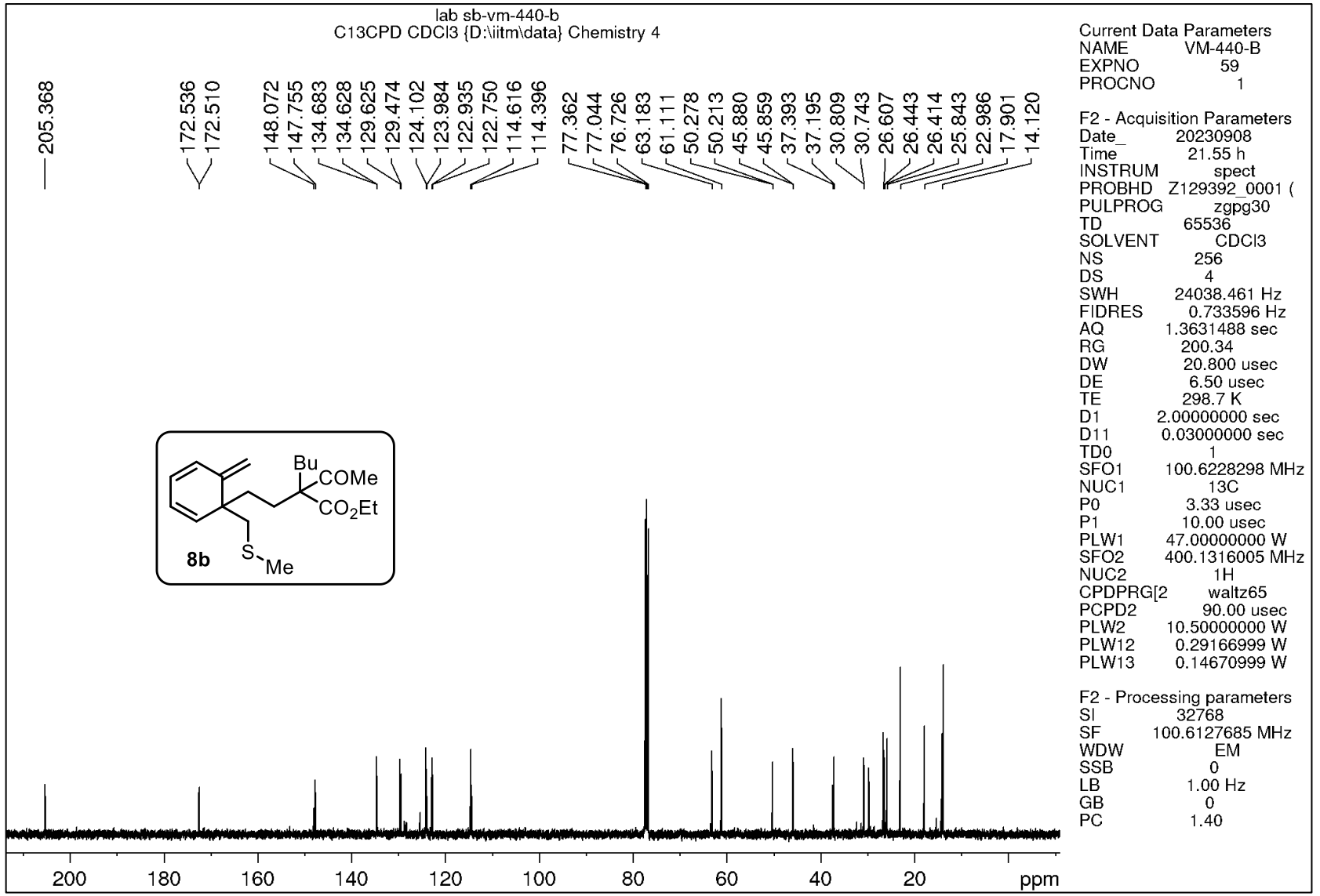
^{13}C NMR spectrum of compound 8a



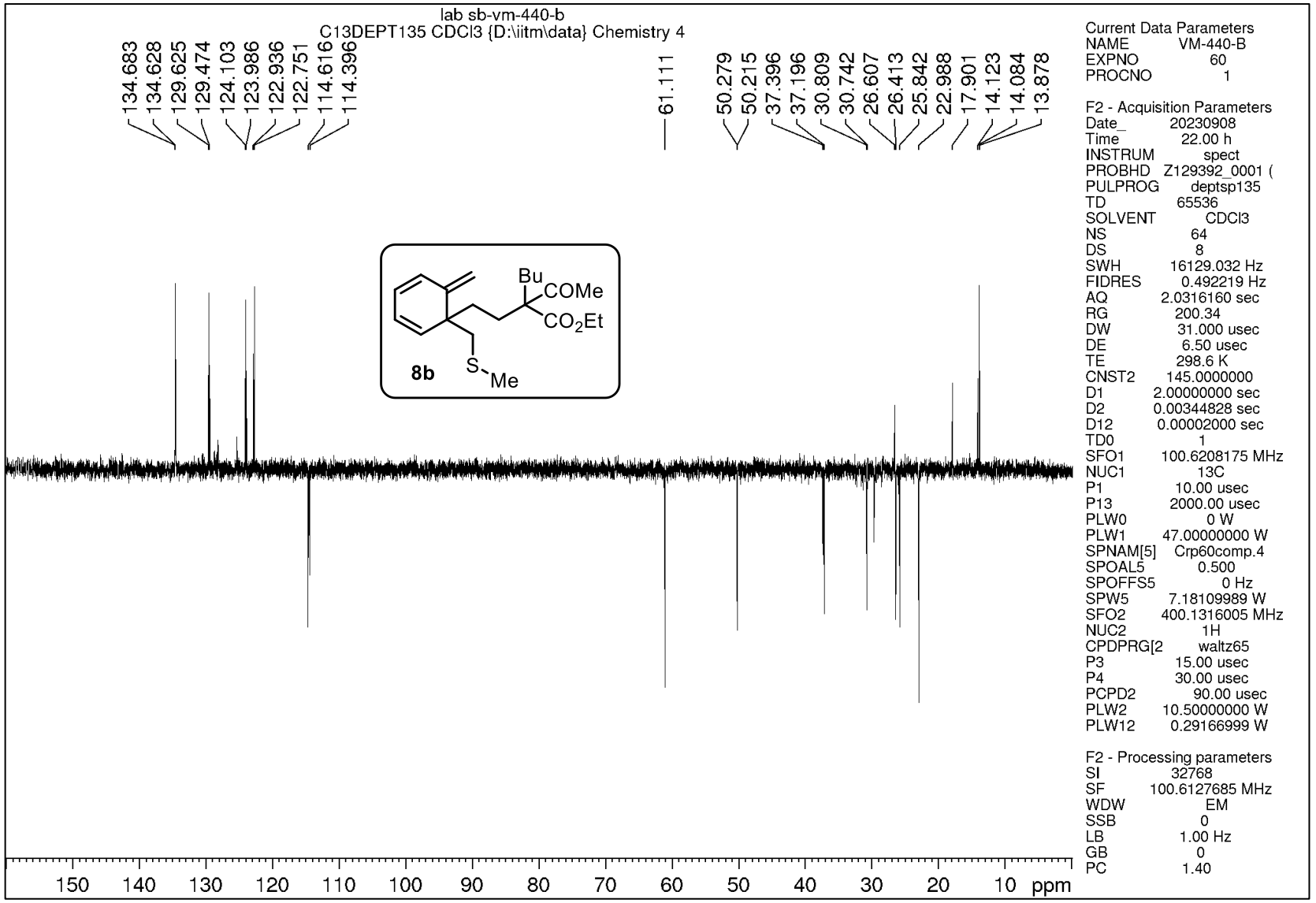
DEPT-135 NMR spectrum of compound 8a



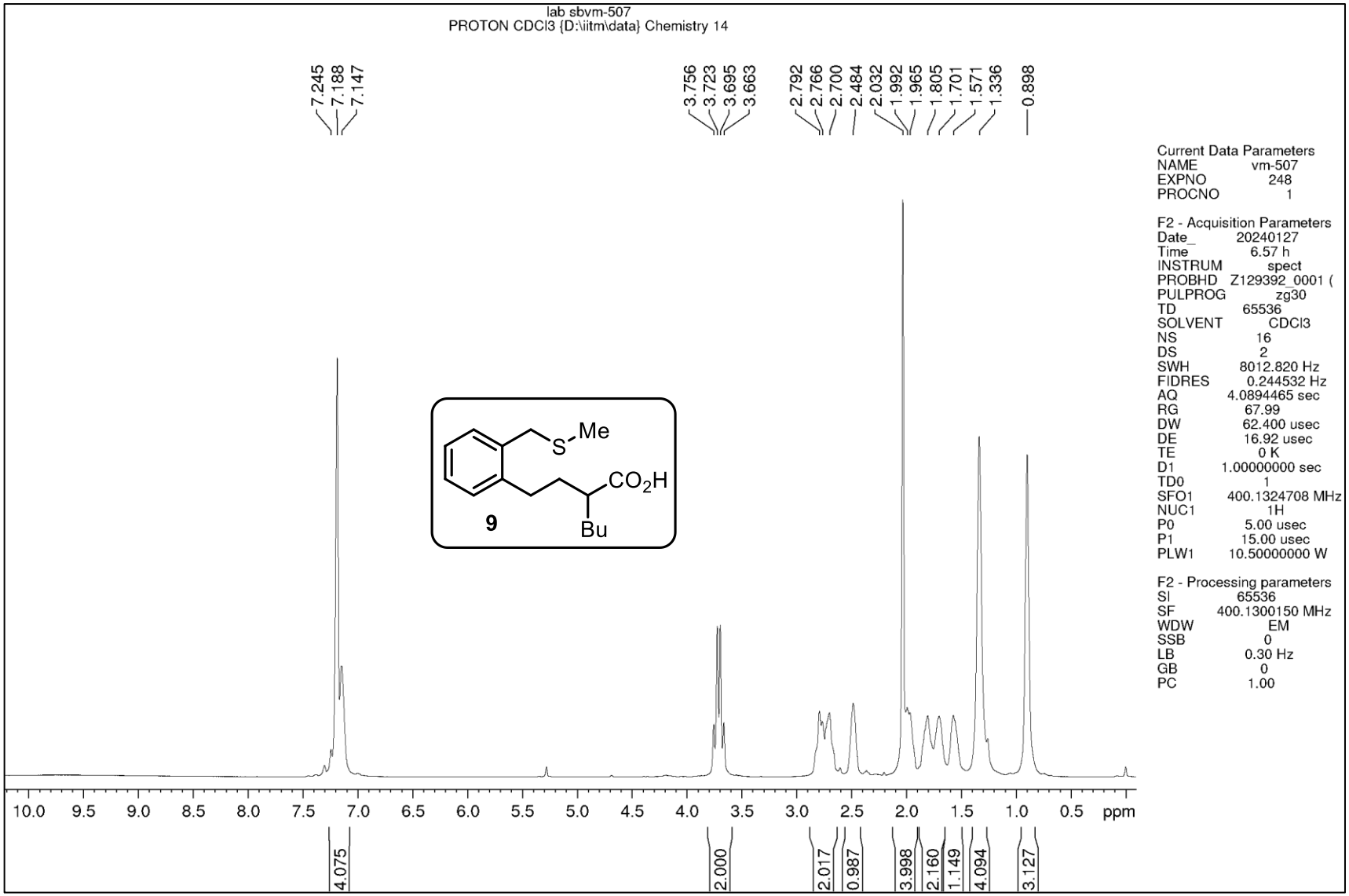
^{1}H NMR spectrum of compound 8b



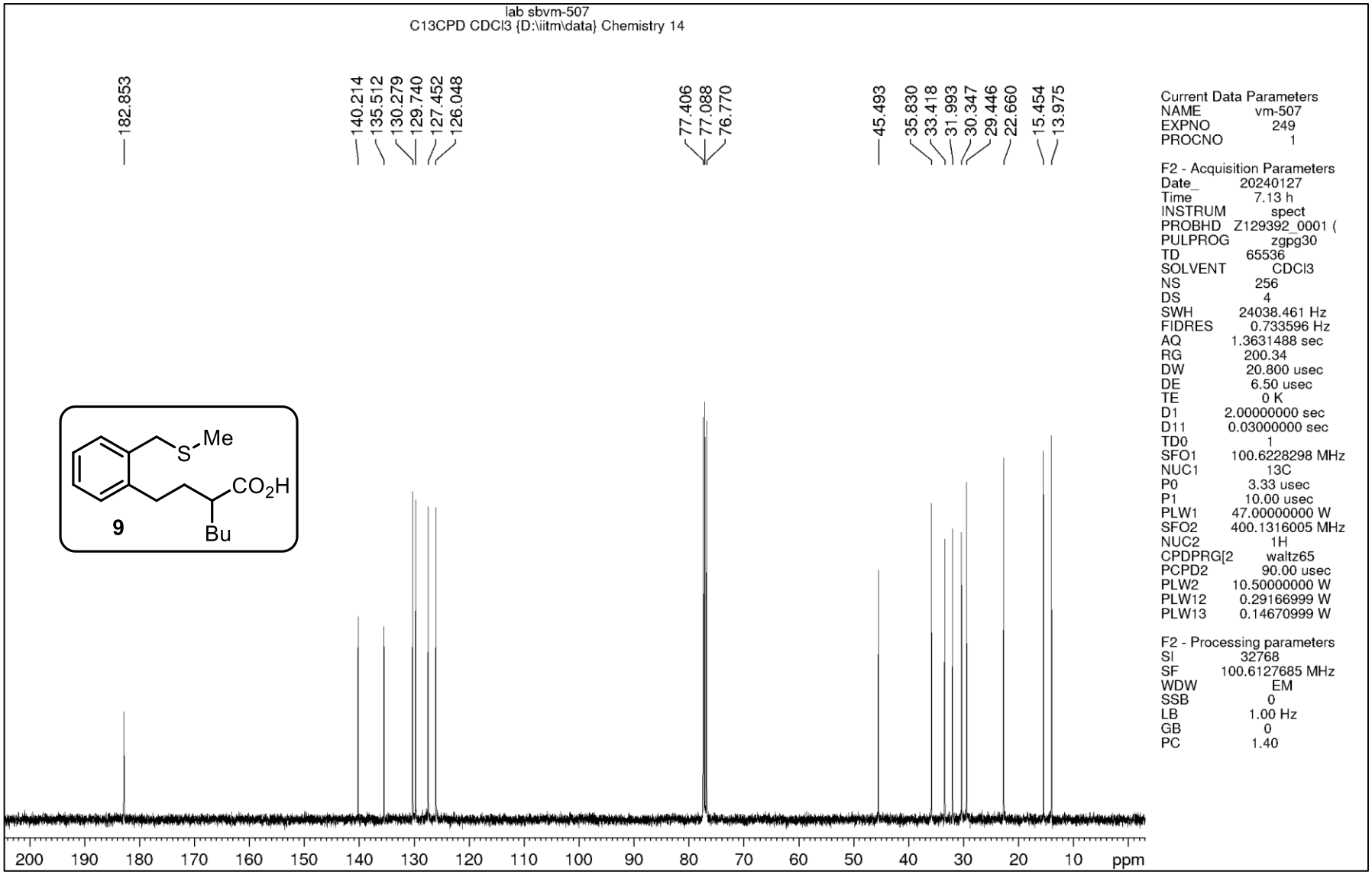
^{13}C NMR spectrum of compound 8b



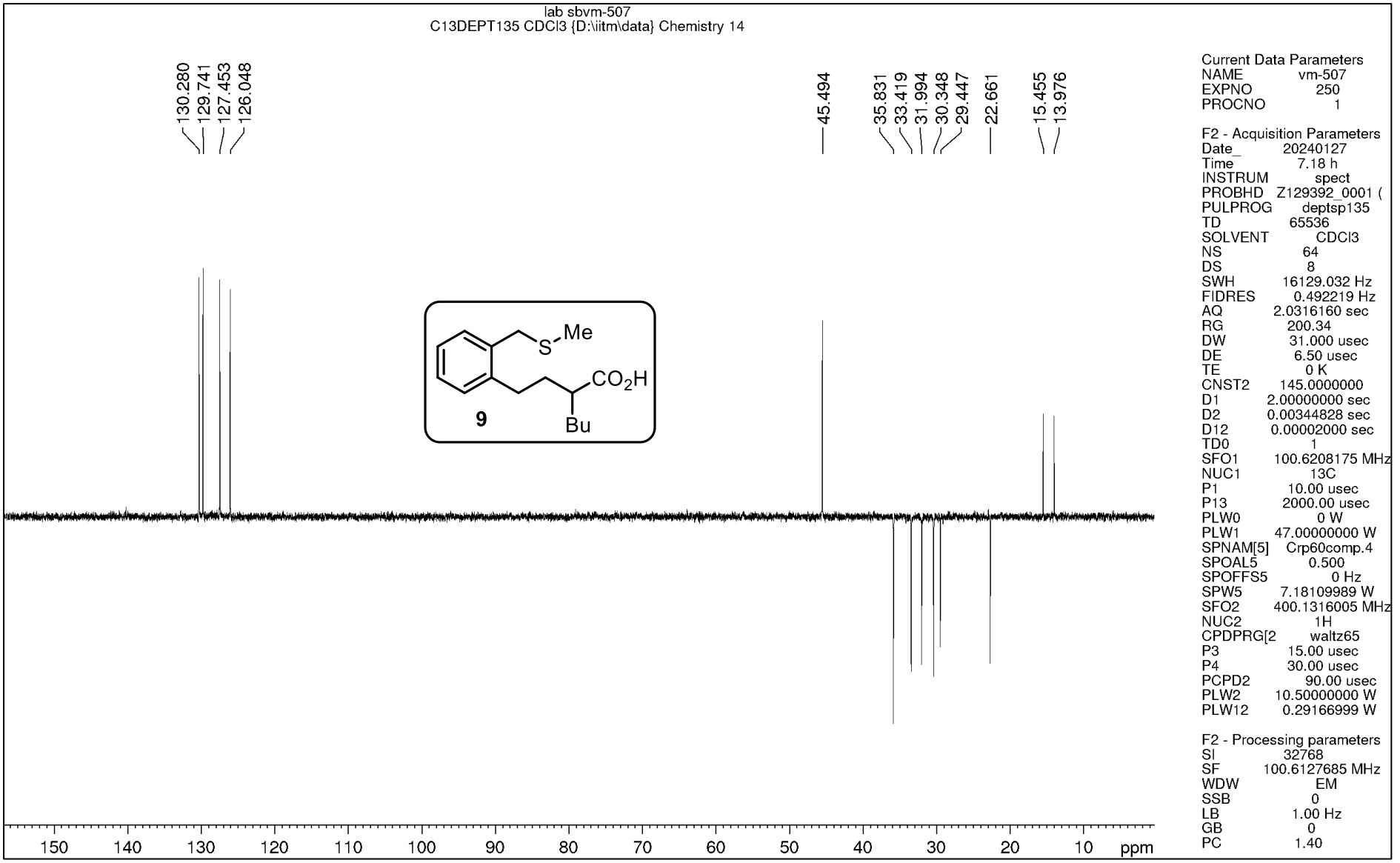
DEPT-135 NMR spectrum of compound 8b



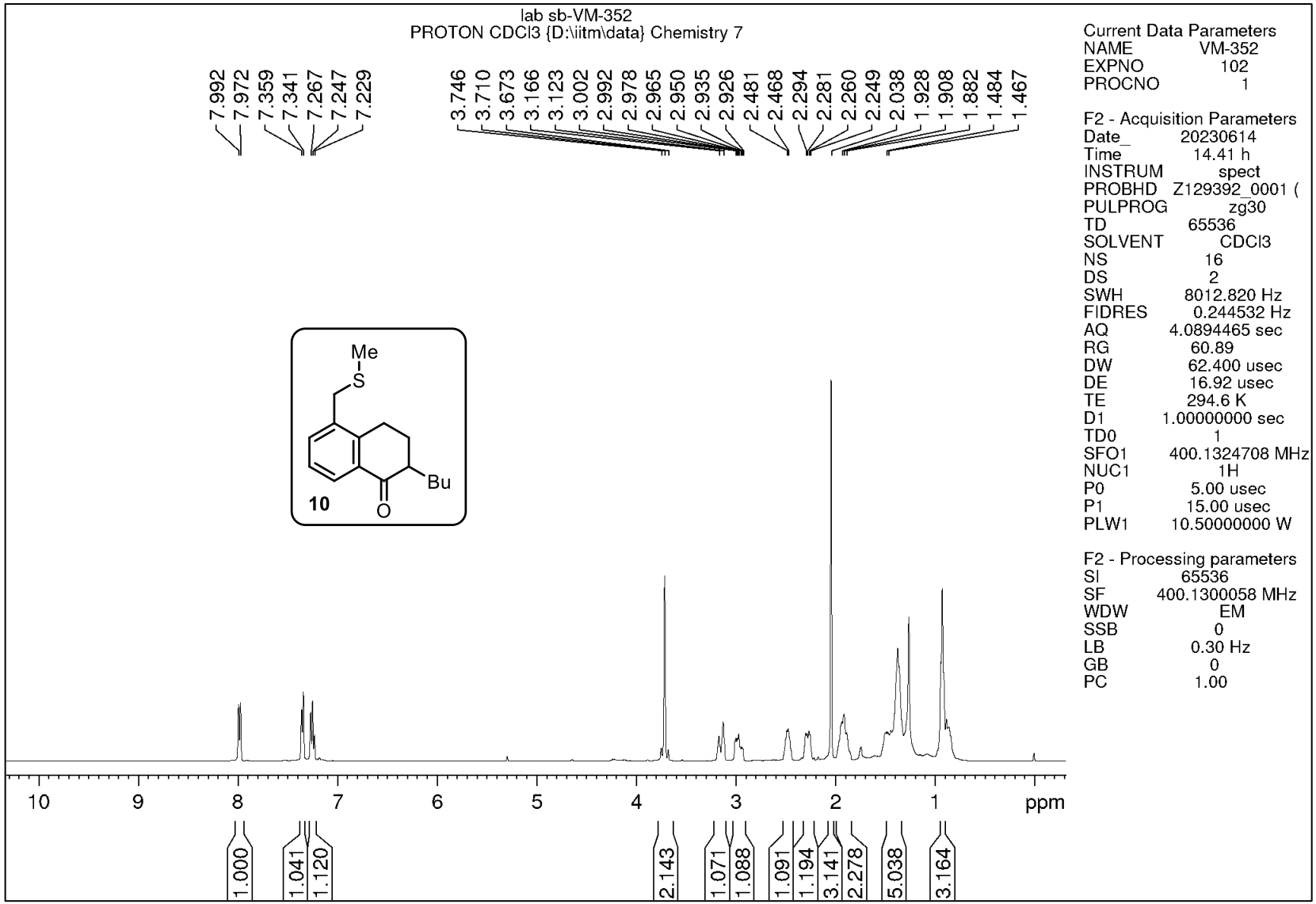
^{1}H NMR spectrum of compound 9



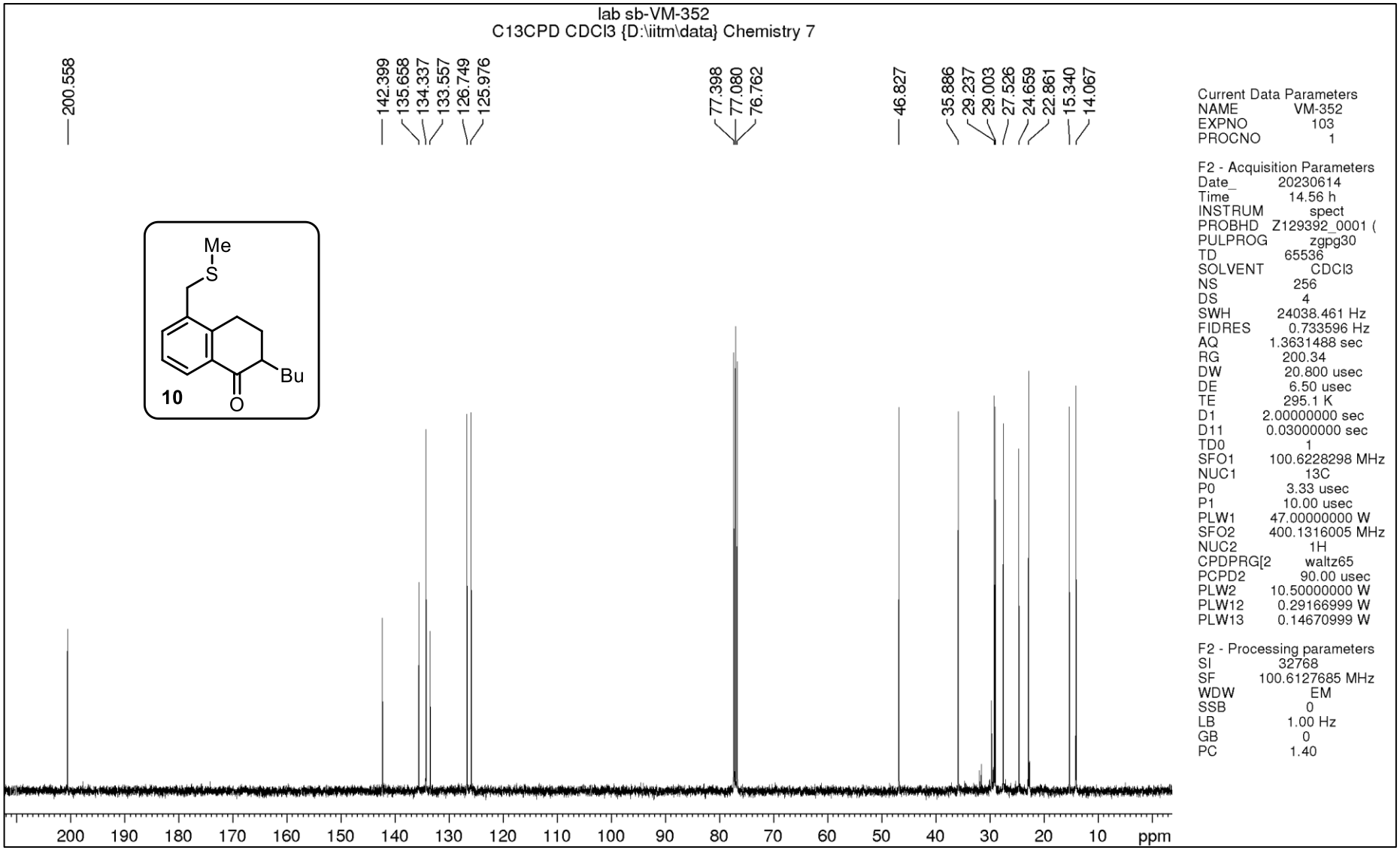
^{13}C NMR spectrum of compound 9



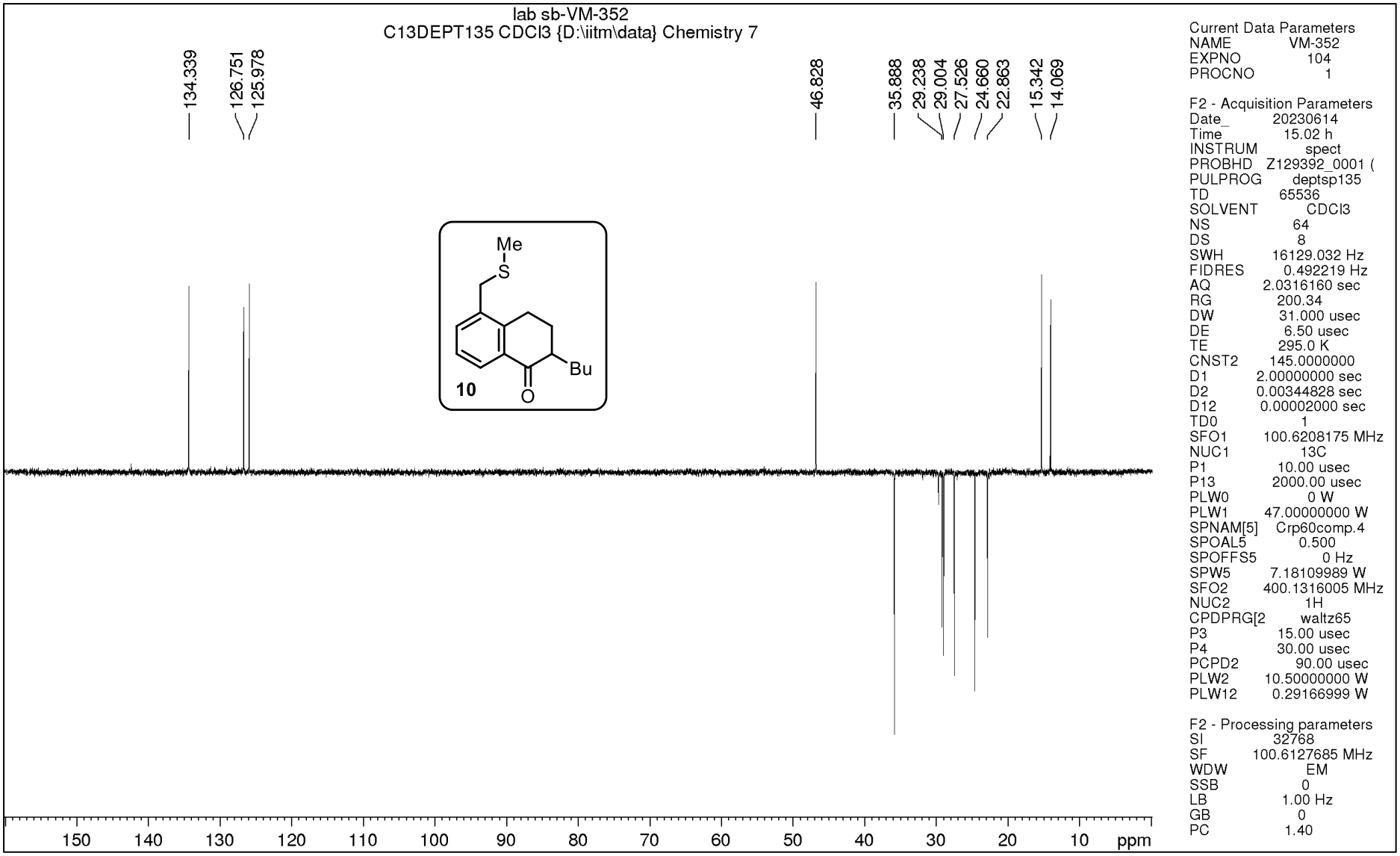
DEPT-135 NMR spectrum of compound 9



^{1}H NMR spectrum of compound 10



^{13}C NMR spectrum of compound 10



DEPT-135 NMR spectrum of compound 10