

Supporting Information for:

Rhodium-Catalyzed Asymmetric Synthesis of β -Branched Esters from Allylic Amines

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A. General Information

General Experimental Procedures: All reactions were carried out in flame-dried (or oven-dried at 140 °C for at least 2 h) glassware under an atmosphere of nitrogen unless otherwise indicated. Nitrogen was dried using a drying tube equipped with Drierite™ unless otherwise noted. Air- and moisture-sensitive reagents were handled in a nitrogen-filled glovebox (working oxygen level ~ 0.1 ppm; working water level ~ 0.1 ppm). Column chromatography was performed with silica gel from Grace Davison Discovery Sciences (35-75 μm) with a column mixed as a slurry with the eluent and was packed, rinsed, and run under air pressure. Analytical thin-layer chromatography (TLC) was performed on precoated glass silica gel plates (by EMD Chemicals Inc.) with F-254 indicator. Visualization was either by short wave (254 nm) ultraviolet light, or by staining with potassium permanganate followed by brief heating on a hot plate or by a heat gun. Distillations were performed using a 3 cm shortpath column under reduced pressure or by using a Hickman still at ambient pressure.

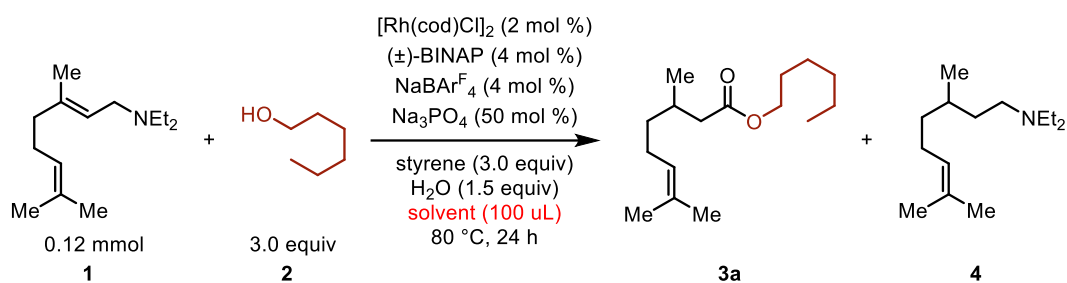
Instrumentation: ¹H NMR and ¹³C NMR were recorded on a Varian Unity 400/500 MHz (100/125 MHz respectively for ¹³C) spectrometer, a VXR-500 MHz spectrometer, or a Bruker 500 MHz spectrometer equipped with a CryoProbe. Spectra were referenced using either CDCl₃ as solvent (unless otherwise noted) with the residual solvent peak as the internal standard (¹H NMR: δ 7.26 ppm, ¹³C NMR: δ 77.16 ppm for CDCl₃). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet,) d (doublet,) t (triplet,) q (quartet,) p (pentet,) m (multiplet,) and br (broad). Coupling constants, *J*, are reported in Hertz and integration is provided, along with assignments, as indicated. Analysis by Gas Chromatography-Mass Spectrometry (GC-MS) was performed using a Shimadzu GC-2010 Plus Gas chromatograph fitted with a Shimadzu GCMS-QP2010 SE mass spectrometer using electron impact (EI) ionization after analytes traveled through a SHRXI-5MS- 30m x 0.25 mm x 0.25 μm column using a helium carrier gas. Data are reported in the form of *m/z* (intensity relative to base peak = 100). Gas Chromatography (GC) was performed on a Shimadzu GC-2010 Plus gas chromatograph with SHRXI-MS- 15m x 0.25 mm x 0.25 μm column with nitrogen carrier gas and a flame ionization detector (FID). Enantiomeric ratios were measured *via* High Performance Liquid Chromatography (HPLC) using a Shimadzu Prominence HPLC system with SPD-M20A UV/VIS Photodiode array detector. Low-resolution Mass Spectrometry and High Resolution Mass Spectrometry were performed in the Department of Chemistry at

University of Illinois at Urbana-Champaign. The glove box, MBraun LABmaster sp, was maintained under nitrogen atmosphere.

Materials: Solvents used for extraction and column chromatography were reagent grade and used as received. Reaction solvents tetrahydrofuran (Fisher, unstabilized HPLC ACS grade), diethyl ether (Fisher, BHT stabilized ACS grade), methylene chloride (Fisher, unstabilized HPLC grade), dimethoxyethane (Fisher, certified ACS), toluene (Fisher, optima ACS grade), 1,4-dioxane (Fisher, certified ACS), acetonitrile (Fisher, HPLC grade), and hexanes (Fisher, ACS HPLC grade) were dried on a Pure Process Technology Glass Contour Solvent Purification System using activated Stainless Steel columns while following manufacture's recommendations for solvent preparation and dispensation unless otherwise noted. All alcohols were distilled and degassed by the freeze-pump-thaw method, and were stored under an atmosphere of nitrogen in glove box before use.

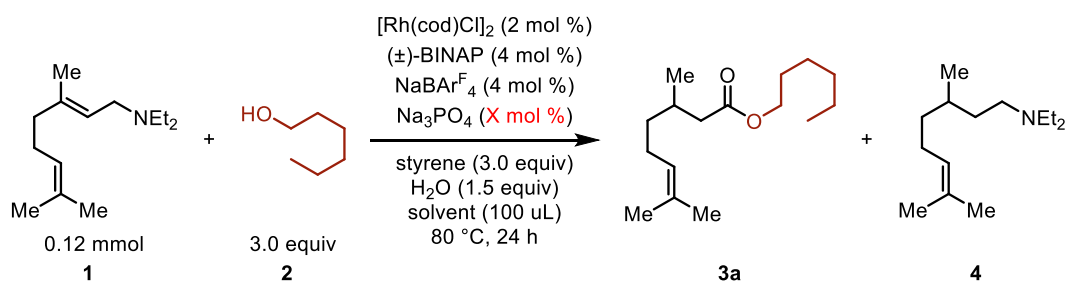
B. Select Optimization Results

Table SI: Ethereal Solvents for Esterification of Allylic Amines



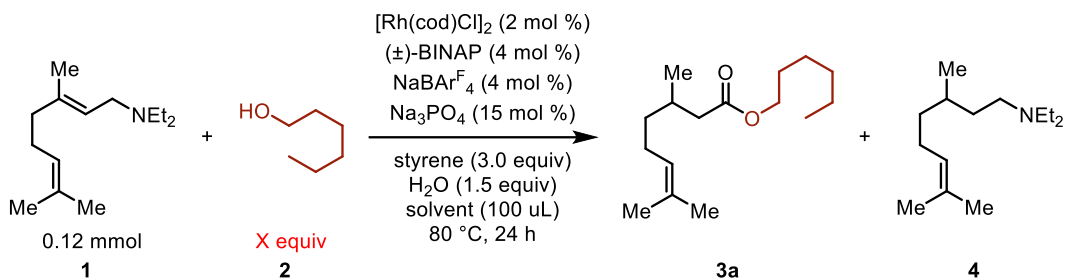
Entry	Solvent	3a % yield (GC)	4 % yield (GC)
1	DME	96	2
2	Et ₂ O	85	25
3	THF	83	13
4	1,4-dioxane	75	26

Table SII: Base Loading Screen for Esterification of Allylic Amines



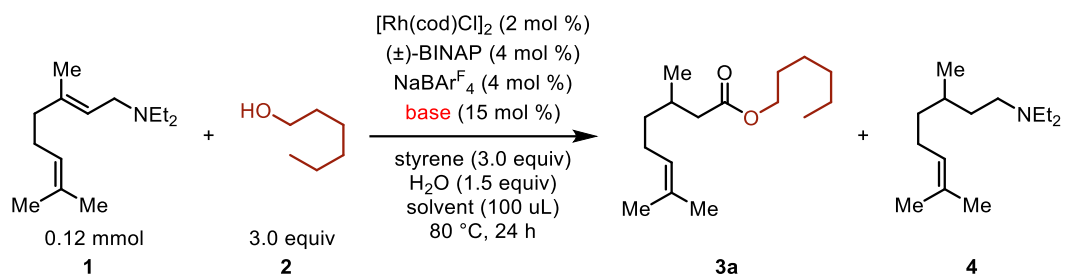
Entry	Base loading (mol %)	3a % yield (GC)	4 % yield (GC)
1	0	49	28
2	5	63	25
3	15	83	10
4	50	89	8
5	100	90	7

Table SIII: Nucleophile Equivalence Screen for Esterification of Allylic Amines



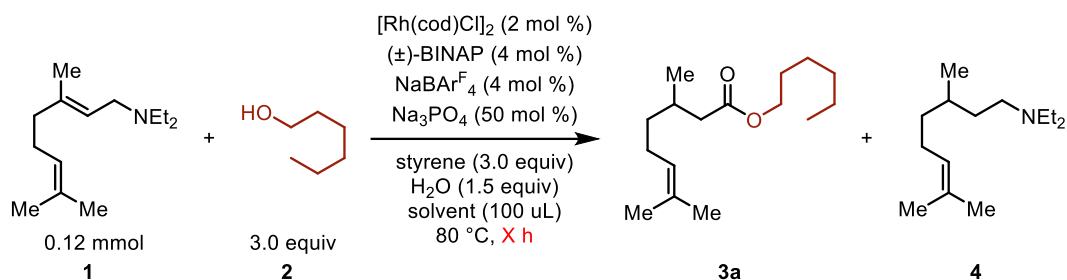
Entry	2 (X equiv)	3a % yield (GC)	4 % yield (GC)
1	1.0	49	17
2	1.5	71	10
3	2.0	82	13
4	3.0	89	6

Table SIV: Base Screen for Esterification of Allylic Amines



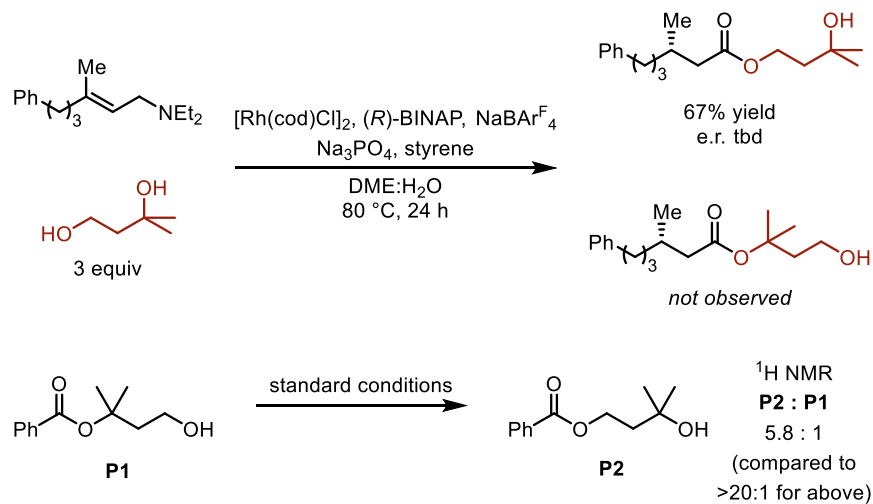
Entry	Base	3a % yield (GC)	4 % yield (GC)
1	Na ₃ PO ₄	84	8
2	K ₃ PO ₄	26	5
3	K ₂ CO ₃	49	5
4	NaH ₂ PO ₄	20	19
5	Na ₂ HPO ₄	55	29
6	Li ₃ PO ₄	54	30

Table SV: Time Screen for Esterification of Allylic Amines



Entry	Time (h)	3a % yield (GC)
1	0.08	2
2	0.17	3
3	0.33	6
4	0.67	9
5	1	15
6	2	22
7	4	45
8	6	46
9	12	70
10	24	91

Scheme SI: 1° vs. 3° Alcohol Competition Study



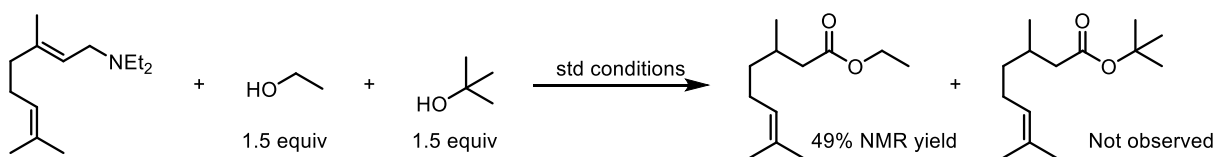
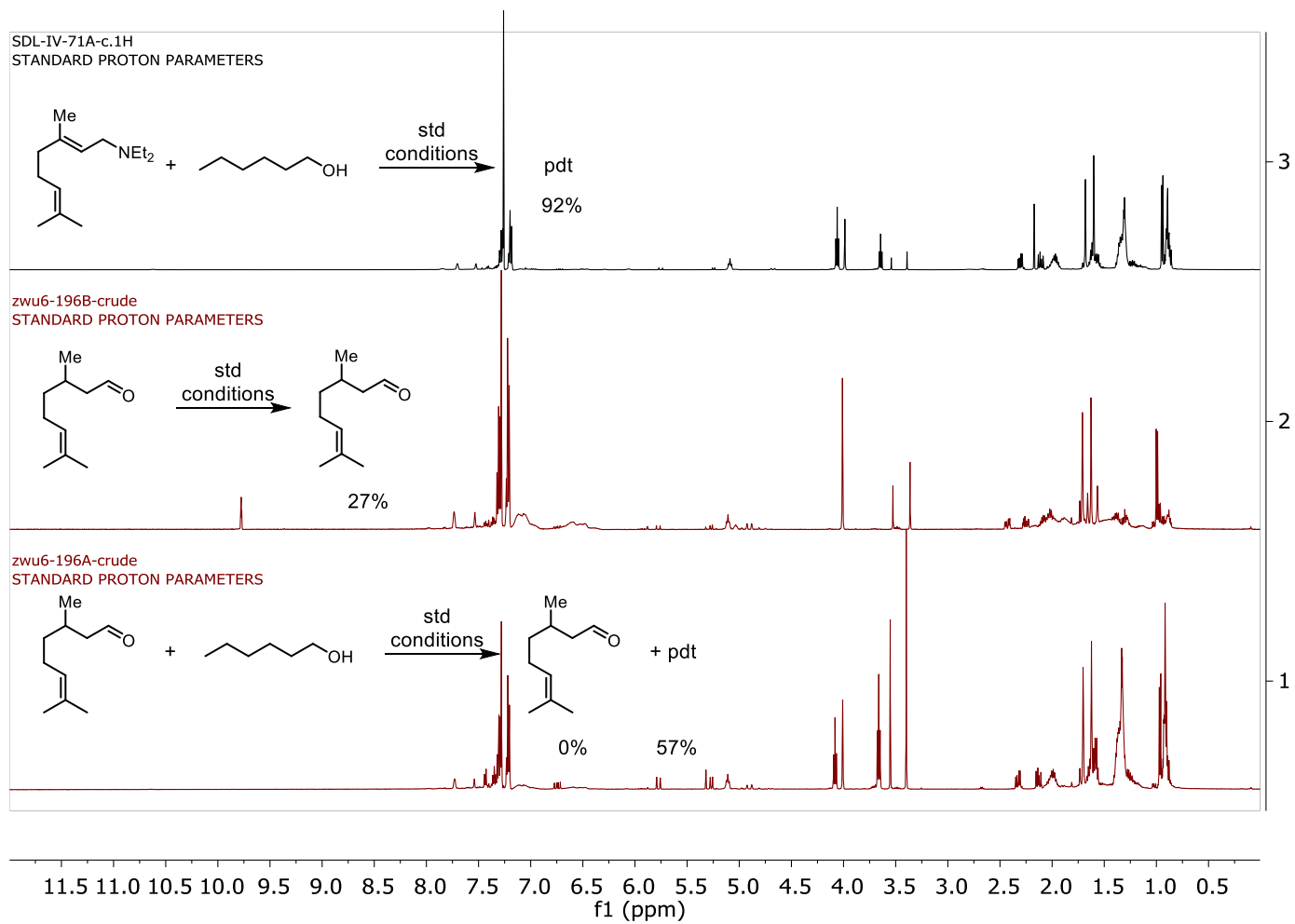
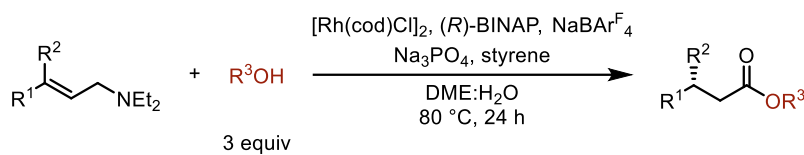


Figure SI: Crude NMR analysis of aldehyde vs. allylic amine as substrate

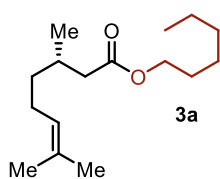


C. Experimental Procedure, Isolation, and Characterization

General procedure for Rh-catalyzed isomerization and esterification of allylic amines with alcohols.



General procedure: Under atmosphere of nitrogen, [Rh(cod)Cl]₂ (1.2 mg, 0.0024 mmol, 2.0 mol %), (R)-BINAP (3.0 mg, 0.0048 mmol, 4.0 mol %), NaBARF₄ (4.3 mg, 0.0048 mmol, 4.0 mol %), and Na₃PO₄ (9.8 mg, 0.060 mmol, 50 mol %) were added to a 4-mL vial equipped with a stir bar. Allylic amine **1** (25.1 mg, 0.12 mmol, 1.0 equiv) was then added to the reaction vial followed by addition of 1-hexanol **2** (45 μL, 0.36 mmol, 3.0 equiv), styrene (42 μL, 0.36 mmol, 3.0 equiv), and dimethoxyethane (0.100 mL, 0.120 M). The vial was then sealed with a plastic cap fitted with a PTFE-lined septum and removed from the glovebox. H₂O (10.0 μL, 0.18 mmol, 1.5 equiv) was added to the reaction mixed *via* syringe through the septum. The reaction vial was placed on a hot plate with stirring at 80 °C for 24 h. The reaction vial was cooled to room temperature followed by the addition of diphenylmethane (10.0 μL) as an internal standard for analysis of the crude reaction mixture. The crude reaction mixture was diluted with methylene chloride prior to analysis. Celite was added to the reaction mixture which was then concentrated *in vacuo* and purified directly *via* flash column chromatography without further work-up procedures.



Hexyl (S)-3,7-dimethyloct-6-enoate C₁₆H₃₀O₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% Et₂O/DCM)/Hex. R_f = 0.07

26.3 mg of inseparable mixture of product (**3a**) and hydrogenated product (**3a'**) in a ratio of 8:1. Corrected MW = 254.65 g/mol. **3a** (76%); **3a'** (10%).

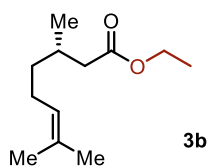
¹H NMR (500 MHz, CDCl₃) δ 5.09 (t, *J* = 7.1 Hz, 1H), 4.06 (t, *J* = 6.7 Hz, 2H), 2.30 (dd, *J* = 14.6, 5.9 Hz, 1H), 2.11 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.06 – 1.90 (m, 3H), 1.68 (s, 3H), 1.61 (d, *J* = 7.8 Hz, 4H), 1.40 – 1.13 (m, 9H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.93 – 0.85 (m, 4H).

Note: Integration values are higher than expected due to partial hydrogenation of the final product.

^{13}C NMR (126 MHz, CDCl_3) δ 173.54 (**3a**), 131.65 (**3a**), 124.45 (**3a**), 64.49 (**3a**), 42.16 (**3a'**), 42.06 (**3a**), 39.22 (**3a'**), 37.10 (**3a'**), 36.94 (**3a**), 31.59 (**3a**), 30.58 (**3a'**), 30.23 (**3a**), 28.79 (**3a**), 28.08 (**3a'**), 25.86 (**3a**), 25.78 (**3a**), 25.58 (**3a**), 24.80 (**3a'**), 22.81 (**3a'**), 22.70 (**3a**), 19.90 (**3a'**), 19.78 (**3a**), 17.79 (**3a**), 14.15 (**3a**).

HRMS: (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{16}\text{H}_{31}\text{O}_2$, 255.2324; found, 255.2327.

IR: ν 2936, 2927, 2858, 1735 cm^{-1} .



Ethyl (S)-3,7-dimethyloct-6-enoate $\text{C}_{12}\text{H}_{22}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.08$

16.2 mg of inseparable mixture of product (**3b**) and hydrogenated product (**3b'**) in a ratio of 7:1. Corrected MW = 198.55 g/mol. **3b (60%)**; **3b' (8%)**.

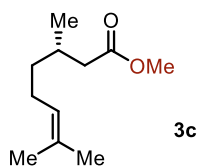
^1H NMR (500 MHz, CDCl_3) δ 5.09 (tdt, $J = 7.1, 2.8, 1.4$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.30 (dd, $J = 14.6, 6.0$ Hz, 1H), 2.10 (dd, $J = 14.6, 8.2$ Hz, 1H), 2.05 – 1.90 (m, 3H), 1.68 (d, $J = 1.3$ Hz, 3H), 1.60 (s, 3H), 1.40 – 1.11 (m, 7H), 0.94 (d, $J = 6.7$ Hz, 3H), 0.86 (dd, $J = 6.6, 0.9$ Hz, 1H) (**3b'**).

Note: Integration values are higher than expected due to partial hydrogenation of the final product.

^{13}C NMR (126 MHz, CDCl_3) δ 173.44 (**3b**), 131.67 (**3b**), 124.45 (**3b**), 60.24 (**3b**), 42.13 (**3b'**), 42.02 (**3b**), 39.21 (**3b'**), 37.11 (**3b'**), 36.94 (**3b**), 30.55 (**3b'**), 30.20 (**3b**), 29.86 (**3b'**), 28.07 (**3b'**), 25.86 (**3b**), 25.58 (**3b**), 24.79 (**3b'**), 22.81 (**3b'**), 22.72 (**3b'**), 19.89 (**3b'**), 19.76 (**3b**), 17.79 (**3b**), 14.44 (**3b**).

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{12}\text{H}_{22}\text{O}_2$, 197.1542; found, 197.1541.

IR: ν 2960, 2861, 2851, 1733 cm^{-1} .



Methyl (S)-3,7-dimethyloct-6-enoate $\text{C}_{11}\text{H}_{20}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.9$

15.9 mg of inseparable mixture of product (**3c**) and hydrogenated product (**3c'**) in a ratio of 6:1. Corrected MW = 184.54 g/mol. **3c (62%)**; **3c' (9%)**.

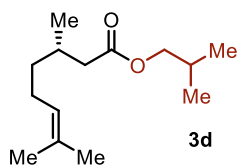
¹H NMR (500 MHz, CDCl₃) δ 5.09 (ddq, *J* = 8.5, 5.7, 1.4 Hz, 1H), 3.67 (s, 3H), 2.32 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.12 (dd, *J* = 14.7, 8.3 Hz, 1H), 2.06 – 1.91 (m, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.60 (s, 3H), 1.39 – 1.12 (m, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.0 Hz, 1H) (**3c'**).

Note: Integration values are inflated due to presence of the hydrogenated product.

¹³C NMR (126 MHz, CDCl₃) δ 173.88 (**3c**), 131.71 (**3c**), 124.41 (**3c**), 51.52 (**3c**), 41.86 (**3c'**), 41.75 (**3c**), 39.19 (**3c'**), 37.11 (**3c'**), 36.93 (**3c**), 30.53 (**3c'**), 30.20 (**3c**), 28.07 (**3c'**), 25.86 (**3c**), 25.58 (**3c**), 24.80 (**3c'**), 22.81 (**3c'**), 22.72 (**3c'**), 19.91 (**3c'**), 19.78 (**3c**), 17.79 (**3c**).

HRMS (EI-TOF) *m/z*: [M] calculated for C₁₁H₂₀O₂, 184.14633; found, 184.14651.

IR: ν 2956, 2920, 2852, 1739 cm⁻¹.



Isobutyl (S)-3,7-dimethyloct-6-enoate C₁₄H₂₆O₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% Et₂O/DCM)/Hex. R_f = 0.08

22.3 mg of inseparable mixture of product (**3d**) and hydrogenated product (**3d'**) in a ratio of 14:1. Corrected MW = 226.50 g/mol. **3d** (76%); **3d'** (6%).

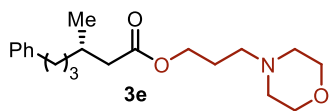
¹H NMR (500 MHz, CDCl₃) δ 5.09 (tp, *J* = 7.1, 1.4 Hz, 1H), 3.85 (dd, *J* = 6.7, 1.0 Hz, 2H), 2.32 (dd, *J* = 14.6, 6.0 Hz, 1H), 2.12 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.07 – 1.85 (m, 4H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.60 (s, 3H), 1.42 – 1.11 (m, 4H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H), 0.86 (dd, *J* = 6.6, 0.8 Hz, 1H).

Note: Integration values are higher than expected due to partial hydrogenation of the final product.

¹³C NMR (126 MHz, CDCl₃) δ 173.53 (**3d**), 131.67 (**3d**), 124.44 (**3d**), 70.52 (**3d**), 42.15 (**3d'**), 42.06 (**3d**), 39.22 (**3d'**), 37.12 (**3d'**), 36.94 (**3d**), 30.59 (**3d'**), 30.21 (**3d**), 28.08 (**3d'**), 27.88 (**3d**), 25.86 (**3d**), 25.58 (**3d**), 24.80 (**3d'**), 22.81 (**3d'**), 22.72 (**3d'**), 19.92 (**3d'**), 19.80 (**3d**), 19.28 (**3d**), 17.79 (**3d**).

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₄H₂₆O₂, 249.1831; found, 249.1835.

IR: ν 2961, 2916, 2875, 2850, 1735 cm⁻¹



3-morpholinopropyl (S)-3-methyl-6-phenylhexanoate C₂₀H₃₁NO₃

Isolation: 100 g basic alumina + 6 g H₂O, dry load on celite. Eluent: 2.5% Et₂O/DCM.

R_f = 0.25

28.4 mg (**3e**); 71% yield.

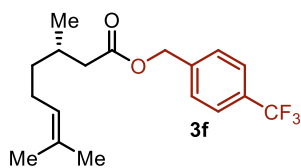
¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.15 (m, 3H), 4.12 (t, *J* = 6.6 Hz, 2H), 3.70 (t, *J* = 4.7 Hz, 4H), 2.59 (td, *J* = 8.5, 6.8, 4.0 Hz, 2H), 2.45 – 2.37 (m, 5H), 2.29 (dd, *J* = 14.7, 6.0 Hz, 1H), 2.11 (dd, *J* = 14.7, 8.1 Hz, 1H), 1.98 (dq, *J* = 14.0, 7.7, 7.2 Hz, 1H), 1.80 (dt, *J* = 13.7, 6.6 Hz, 2H), 1.69 – 1.55 (m, 3H), 1.41 – 1.33 (m, 1H), 1.29 – 1.20 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.40, 142.64, 128.50, 128.42, 125.84, 67.14, 62.67, 55.59, 53.85, 41.98, 36.48, 36.17, 30.45, 28.99, 26.02, 19.85.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₀H₃₂NO₃, 334.2382; found, 334.2394.

IR: ν 2941, 2919, 2849, 2809, 1732, 1118 cm⁻¹.

[α]_D²² = -4.6945 (*C* = 1.340, CHCl₃)



4-(trifluoromethyl)benzyl (S)-3,7-dimethyloct-6-enoate C₁₈H₂₃F₃O₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% Et₂O/DCM)/Hex. R_f = 0.1

23.2 mg of inseparable mixture of product (**3f**) and hydrogenated product (**3f'**) in a ratio of 7:1.

Corrected MW = 328.64 g/mol. **Product yield (51%)**; byproduct yield (8%).

¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 2H), 5.06 (ddt, *J* = 8.5, 5.8, 1.4 Hz, 1H), 2.38 (dd, *J* = 14.8, 5.9 Hz, 1H), 2.19 (dd, *J* = 14.8, 8.1 Hz, 1H), 1.98 (tq, *J* = 14.2, 7.6, 7.0 Hz, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.56 – 1.42 (m, 1H), 1.35 (ddt, *J* = 12.5, 9.5, 6.1 Hz, 1H), 1.30 – 1.06 (m, 2H), 0.95 (dd, *J* = 6.7, 0.9 Hz, 3H), 0.85 (dd, *J* = 6.5, 0.8 Hz, 1H) (**3f'**).

Note: integration values are inflated due to presence of hydrogenated byproduct.

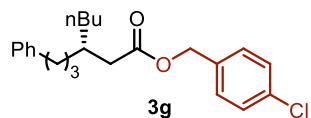
¹³C NMR (126 MHz, CDCl₃) δ 173.01 (**3f**), 140.28 (**3f**), 131.79 (**3f**), 130.47 (q, *J* = 32.6 Hz) (**3f**), 128.29 (**3f**), 125.65 (q, *J* = 3.8 Hz) (**3f**), 124.27 (**3f**), 124.16 (q, *J* = 272.1 Hz) (**3f**), 65.20 (**3f**), 41.92 (**3f'**), 41.82 (**3f**), 39.17

(3f'), 37.05 (3f'), 36.88 (3f), 30.59 (3f'), 30.22 (3f), 28.05 (3f'), 25.84 (3f), 25.54 (3f), 24.77 (3f'), 22.79 (3f'), 22.70 (3f'), 19.92 (3f'), 19.79 (3f), 17.79 (3f).

¹⁹F NMR (471 MHz, CDCl₃) δ -62.65.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₈H₂₃F₃O₂, 351.1548; found, 351.1545.

IR: ν 2959, 2918, 2855, 1738 cm⁻¹.



4-chlorobenzyl (S)-3-(3-phenylpropyl)heptanoate C₂₃H₂₉ClO₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20%

(5% Et₂O/DCM)/Hex. R_f = 0.11

37.6 mg (3g); 84% yield.

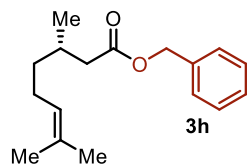
¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.24 (m, 6H), 7.20 – 7.13 (m, 3H), 5.05 (s, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.28 (dd, *J* = 6.9, 2.3 Hz, 2H), 1.89 (hept, *J* = 6.2 Hz, 1H), 1.59 (p, *J* = 8.0 Hz, 2H), 1.40 – 1.15 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.36, 142.63, 134.79, 134.22, 129.82, 128.86, 128.49, 128.41, 125.84, 65.33, 39.28, 36.27, 35.16, 33.70, 33.66, 28.86, 28.59, 23.03, 14.19.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₃H₂₉ClO₂, 395.1754; found, 395.1759.

IR: ν 2945, 2926, 2856, 1733 cm⁻¹.

[α]_D²³ = -1.1200 (*C* = 0.750, CHCl₃)



Benzyl (S)-3,7-dimethyloct-6-enoate C₁₇H₂₄O₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% Et₂O/DCM)/Hex. R_f = 0.1

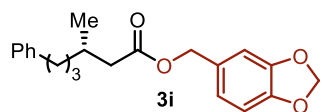
25.0 mg (3h); 80% yield

¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.29 (m, 5H), 5.12 (s, 2H), 5.07 (tdq, *J* = 7.0, 2.8, 1.3 Hz, 1H), 2.37 (dd, *J* = 14.7, 6.0 Hz, 1H), 2.17 (dd, *J* = 14.8, 8.2 Hz, 1H), 2.05 – 1.90 (m, 3H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.59 (s, 3H), 1.35 (dddd, *J* = 13.4, 9.5, 6.5, 5.8 Hz, 1H), 1.22 (dddd, *J* = 13.6, 9.3, 7.9, 6.2 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.22, 136.29, 131.69, 128.68, 128.34, 128.29, 124.39, 66.18, 41.95, 36.91, 30.22, 25.86, 25.55, 19.77, 17.79.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{17}\text{H}_{24}\text{O}_2$, 283.1674; found, 283.1667.

IR: ν 2957, 2925, 2855, 1730 cm^{-1} .



Benzo[d][1,3]dioxol-5-ylmethyl (S)-3-methyl-6-phenylhexanoate $\text{C}_{21}\text{H}_{24}\text{O}_4$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 30%

(5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. R_f = 0.15

24.5 mg (**3i**); 60% yield.

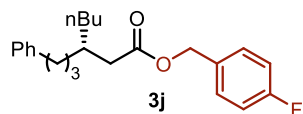
^1H NMR (500 MHz, CDCl_3) δ 7.27 (m, 2H), 7.20 – 7.13 (m, 3H), 6.84 – 6.75 (m, 3H), 5.96 (s, 2H), 5.00 (s, 2H), 2.62 – 2.52 (m, 2H), 2.32 (dd, J = 14.8, 6.2 Hz, 1H), 2.15 (dd, J = 14.7, 8.0 Hz, 1H), 1.99 (tq, J = 13.6, 7.0 Hz, 1H), 1.70 – 1.54 (m, 2H), 1.36 (ddt, J = 13.4, 10.9, 5.6 Hz, 1H), 1.28 – 1.19 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.18, 147.92, 147.71, 142.66, 130.03, 128.50, 128.41, 125.82, 122.40, 109.18, 108.37, 101.29, 66.16, 41.97, 36.43, 36.16, 30.48, 28.97, 19.86.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{21}\text{H}_{24}\text{O}_4$, 363.1586; found, 363.1584.

IR: ν 2920, 2852, 1731, 1243, 1039 cm^{-1} .

$[\alpha]_{\text{D}}^{23}$ = -3.5958 (C = 1.580, CHCl_3)



4-fluorobenzyl (S)-3-(3-phenylpropyl)heptanoate $\text{C}_{23}\text{H}_{29}\text{FO}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20%

(5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. R_f = 0.11

34.2 mg (**3j**); 80% yield.

^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.26 (m, 4H), 7.20 – 7.13 (m, 3H), 7.06 – 7.01 (m, 2H), 5.05 (s, 2H), 2.55 (t, J = 7.8 Hz, 2H), 2.27 (dd, J = 6.9, 2.1 Hz, 2H), 1.89 (hept, J = 6.2 Hz, 1H), 1.59 (p, J = 8.0 Hz, 2H), 1.40 – 1.16 (m, 8H), 0.85 (t, J = 6.9 Hz, 3H).

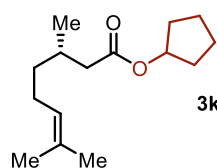
^{13}C NMR (126 MHz, CDCl_3) δ 173.41, 162.75 (d, $J = 246.7$ Hz), 142.65, 132.14 (d, $J = 3.3$ Hz), 130.42 (d, $J = 8.35$ Hz), 128.45 (d, $J = 10.0$ Hz), 125.83, 115.58 (d, $J = 21.6$ Hz), 65.44, 39.32, 36.27, 35.16, 33.71, 33.66, 28.85, 28.59, 23.03, 14.19.

^{19}F NMR (471 MHz, CDCl_3) δ -113.79.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{23}\text{H}_{29}\text{FO}_2$, 379.2049; found, 379.2057.

IR: ν 2945, 2928, 2857, 1734 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -1.3800$ ($C = 1.40$, CHCl_3)



Cyclopentyl (S)-3,7-dimethyloct-6-enoate $\text{C}_{15}\text{H}_{26}\text{O}_2$

3k Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.1$

21.5 mg of inseparable mixture of product (**3k**) and hydrogenated product (**3k'**) in a ratio of 8:1. Corrected MW = 238.61 g/mol. **3k** (66%); **3k'** (9%).

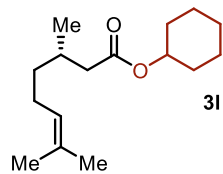
^1H NMR (500 MHz, CDCl_3) δ 5.16 (tt, $J = 5.7, 2.7$ Hz, 1H), 5.09 (dddd, $J = 7.1, 5.7, 2.9, 1.5$ Hz, 1H), 2.26 (dd, $J = 14.4, 6.1$ Hz, 1H), 2.07 (dd, $J = 14.5, 8.1$ Hz, 1H), 2.04 – 1.79 (m, 5H), 1.76 – 1.63 (m, 7H), 1.63 – 1.52 (m, 5H), 1.39 – 1.11 (m, 4H), 0.94 (d, $J = 6.7$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 1H) (**3k'**).

Note: Integration values are inflated due to presence of the hydrogenated product.

^{13}C NMR (126 MHz, CDCl_3) δ 173.25 (**3k**), 131.64 (**3k**), 124.48 (**3k**), 42.39 (**3k'**), 42.30 (**3k**), 39.24 (**3k'**), 37.09 (**3k'**), 36.92 (**3k**), 32.85 (**3k**), 32.81 (**3k**), 30.63 (**3k'**), 30.26 (**3k**), 28.08 (**3k'**), 25.86 (**3k**), 25.57 (**3k**), 24.78 (**3k'**), 23.87 (**3k**), 22.81 (**3k'**), 22.73 (**3k'**), 19.87 (**3k'**), 19.74 (**3k**), 17.79 (**3k**).

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{15}\text{H}_{26}\text{O}_2$, 237.1855; found, 237.1846.

IR: ν 2957, 2918, 2856, 2849, 1729 cm^{-1} .



Cyclohexyl (S)-3,7-dimethyloct-6-enoate $\text{C}_{16}\text{H}_{28}\text{O}_2$

3l Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.1$

19.1 mg of inseparable mixture of product (**31**) and hydrogenated product (**31'**) in a ratio of 8:1.

Corrected MW = 252.62 g/mol. **31** (**56%**); **31'** (7%).

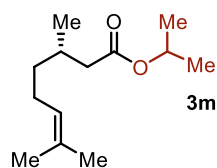
¹H NMR (500 MHz, CDCl₃) δ 5.09 (ddt, *J* = 7.2, 5.7, 1.5 Hz, 1H), 4.77 (tt, *J* = 8.9, 3.8 Hz, 1H), 2.28 (dd, *J* = 14.4, 6.1 Hz, 1H), 2.09 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.05 – 1.91 (m, 3H), 1.88 – 1.78 (m, 2H), 1.77 – 1.69 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58 – 1.50 (m, 2H), 1.46 – 1.11 (m, 9H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 1H) (**31'**).

Note: Integration values are higher than expected due to partial hydrogenation of the final product.

¹³C NMR (126 MHz, CDCl₃) δ 172.86 (**31**), 131.59 (**31**), 124.47 (**31**), 72.38 (**31**), 42.46 (**31'**), 42.37 (**31**), 39.21 (**31'**), 37.07 (**31'**), 36.90 (**31**), 31.84 (**31**), 31.80 (**31**), 30.64 (**31'**), 30.27 (**31**), 28.04 (**31'**), 25.83 (**31**), 25.55 (**31**), 24.76 (**31'**), 23.90 (**31**), 22.78 (**31'**), 22.70 (**31'**), 19.81 (**31'**), 19.69 (**31**), 17.77 (**31**).

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₆H₂₈O₂, 251.2011; found, 251.2017.

IR: ν 2930, 2859, 1730 cm⁻¹.



Isopropyl (*S*)-3,7-dimethyloct-6-enoate C₁₃H₂₄O₂

3m

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% Et₂O/DCM)/Hex. R_f = 0.7

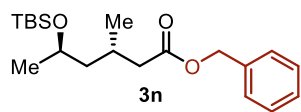
11.0 mg of inseparable mixture of product (**3m**) and hydrogenated product (**3m'**) in a ratio of 6:1. Corrected MW = 212.60 g/mol. **3m** (**37%**); **3m'** (6%).

¹H NMR (500 MHz, CDCl₃) δ 5.09 (tdt, *J* = 7.1, 2.9, 1.4 Hz, 1H), 5.01 (hept, *J* = 6.3 Hz, 1H), 2.27 (dd, *J* = 14.5, 6.0 Hz, 1H), 2.07 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.04 – 1.92 (m, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.60 (s, 3H), 1.39 – 1.27 (m, 3H), 1.23 (d, *J* = 6.3 Hz, 6H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 1H) (**3m'**).

Note: Integration values are inflated due to presence of the hydrogenated product.

¹³C NMR (126 MHz, CDCl₃) δ 172.96 (**3m**), 131.63 (**3m**), 124.49 (**3m**), 67.43 (**3m**), 42.45 (**3m**), 42.35 (**3m**), 39.23 (**3m'**), 37.10 (**3m'**), 36.94 (**3m**), 30.61 (**3m'**), 30.26 (**3m**), 29.86 (**3m'**), 28.07 (**3m'**), 25.86 (**3m**), 25.57 (**3m**), 24.78 (**3m'**), 22.81 (**3m'**), 22.73 (**3m'**), 22.05 (**3m**), 22.02 (**3m**), 19.83 (**3m'**), 19.71 (**3m**), 17.79 (**3m**).

IR: ν 2962, 2920, 2854, 1731 cm⁻¹.



Benzyl (3*S*,5*R*)-5-((tert-butyldimethylsilyloxy)-3-methylhexanoate C₂₀H₃₄O₃Si

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20%

(5% Et₂O/DCM)/Hex. R_f = 0.1

28.2 mg (**3n**); 67% yield.

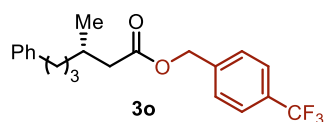
¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.28 (m, 5H), 5.11 (dd, *J* = 22.5, 12.4 Hz, 2H), 3.86 (dddt, *J* = 7.9, 5.9, 4.6, 1.9 Hz, 1H), 2.36 (q, *J* = 9.2 Hz, 1H), 2.22 – 2.11 (m, 2H), 1.48 (ddd, *J* = 13.2, 8.6, 4.4 Hz, 1H), 1.18 (dq, *J* = 13.7, 4.3 Hz, 1H), 1.11 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.87 (s, 9H), 0.04 (d, *J* = 4.0 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 172.94, 136.30, 128.66, 128.32, 128.25, 66.39, 66.15, 46.84, 42.65, 27.22, 26.03, 24.57, 19.77, 18.22, -3.95, -4.66.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₀H₃₄O₃Si, 373.2175; found, 373.2170.

IR: ν 2955, 2929, 2896, 2856, 1736, 1255, 1155, 1065, 835, 774 cm⁻¹.

[α]_D²³ = -12.4766 (*C* = 1.270, CHCl₃)



4-(trifluoromethyl)benzyl (S)-3-methyl-6-phenylhexanoate C₂₁H₂₃F₃O₂

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20%

(5% Et₂O/DCM)/Hex. R_f = 0.09

28.0 mg (**3o**); 64% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.20 – 7.13 (m, 3H), 5.15 (s, 2H), 2.64 – 2.52 (m, 2H), 2.37 (dd, *J* = 14.8, 6.1 Hz, 1H), 2.19 (dd, *J* = 14.9, 8.0 Hz, 1H), 2.01 (ddt, *J* = 20.4, 13.7, 6.8 Hz, 1H), 1.72 – 1.54 (m, 2H), 1.37 (ddt, *J* = 13.3, 10.8, 5.6 Hz, 1H), 1.25 (dddd, *J* = 13.3, 10.5, 7.7, 5.4 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

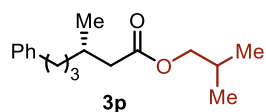
¹³C NMR (126 MHz, CDCl₃) δ 172.97, 142.57, 140.25, 130.48 (q, *J* = 32.5 Hz), 128.49, 128.43, 128.30, 125.86, 125.66 (q, *J* = 3.82 Hz), 124.16 (q, *J* = 272.18 Hz), 65.21, 41.81, 36.42, 36.14, 30.47, 28.95, 19.87.

¹⁹F NMR (471 MHz, CDCl₃) δ -62.64.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₁H₂₃F₃O₂, 387.1548; found, 387.1546.

IR: ν 2927, 2851, 1736, 1323, 1124, 1067 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -3.0616$ ($C = 1.320$, CHCl_3)



Isobutyl (S)-3-methyl-6-phenylhexanoate $\text{C}_{17}\text{H}_{26}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5%

$\text{Et}_2\text{O}/\text{DCM})/\text{Hex}$. $R_f = 0.08$

26.8 mg (**3p**); 85% yield.

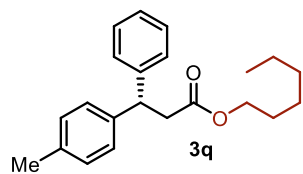
^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 3.84 (d, $J = 6.7$ Hz, 2H), 2.66 – 2.53 (m, 2H), 2.30 (dd, $J = 14.6, 6.1$ Hz, 1H), 2.12 (dd, $J = 14.6, 8.0$ Hz, 1H), 1.99 (dq, $J = 14.0, 7.7, 7.2$ Hz, 1H), 1.91 (dp, $J = 13.4, 6.7$ Hz, 1H), 1.72 – 1.55 (m, 2H), 1.38 (ddt, $J = 13.4, 11.0, 5.6$ Hz, 1H), 1.25 (dtt, $J = 10.5, 7.8, 5.4$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 3H), 0.93 (d, $J = 6.7$ Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 173.49, 142.69, 128.51, 128.41, 125.82, 70.52, 42.06, 36.48, 36.20, 30.48, 29.02, 27.87, 19.86, 19.28.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{17}\text{H}_{26}\text{O}_2$, 285.1831; found, 285.1827.

IR: ν 2959, 2931, 2873, 1733 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -5.9194$ ($C = 1.265$, CHCl_3)



hexyl 3-phenyl-3-(p-tolyl)propanoate $\text{C}_{22}\text{H}_{28}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% $\text{Et}_2\text{O}/\text{DCM})/\text{Hex}$. $R_f = 0.12$

32.7 mg (**3q**); 84% yield.

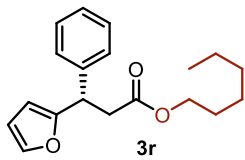
^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.20 (m, 4H), 7.17 (tt, $J = 7.0, 1.8$ Hz, 1H), 7.13 (td, $J = 8.2, 2.1$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 4.51 (t, $J = 8.1$ Hz, 1H), 3.96 (t, $J = 6.6$ Hz, 2H), 3.03 (d, $J = 8.1$ Hz, 2H), 2.29 (s, 3H), 1.46 (p, $J = 6.8$ Hz, 2H), 1.36 – 1.14 (m, 6H), 0.87 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.12, 143.90, 140.67, 136.16, 129.36, 128.65, 127.76, 127.66, 126.57, 64.77, 46.89, 41.09, 31.55, 28.66, 25.63, 22.66, 21.13, 14.17.

HRMS (ESI-TOF) m/z : $[M+H^+]$ calculated for $C_{22}H_{28}O_2$, 325.2168; found, 325.2169.

IR: ν 2937, 2925, 2857, 1732 cm^{-1} .

$[\alpha]_D^{23} = -1.5571$ ($C = 2.240$, $CHCl_3$)



Hexyl (S)-3-(furan-2-yl)-3-phenylpropanoate $C_{19}H_{24}O_3$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 30% (5% Et_2O/DCM)/Hex. $R_f = 0.1$

20.9 mg (**3r**); 58%

yield.

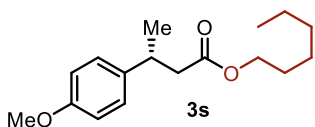
1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 6.28 (dt, $J = 3.0, 1.4$ Hz, 1H), 6.05 (dt, $J = 3.1, 1.0$ Hz, 1H), 4.55 (t, $J = 7.9$ Hz, 1H), 4.00 (t, $J = 6.7$ Hz, 2H), 3.09 (dd, $J = 15.5, 7.9$ Hz, 1H), 2.90 (dd, $J = 15.5, 7.9$ Hz, 1H), 1.53 – 1.47 (m, 2H), 1.33 – 1.19 (m, 6H), 0.88 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.60, 156.40, 141.82, 141.30, 128.73, 127.87, 127.16, 110.22, 105.83, 64.92, 41.61, 39.97, 31.54, 28.65, 25.63, 22.67, 14.16.

HRMS (ESI-TOF) m/z : $[M+H^+]$ calculated for $C_{19}H_{24}O_3$, 323.1623; found, 323.1623.

IR: ν 2956, 2922, 2852, 1733, 1154 cm^{-1} .

$[\alpha]_D^{23} = +41.8023$ ($C = 2.030$, $CHCl_3$)



Hexyl (R)-3-(4-methoxyphenyl)butanoate $C_{17}H_{26}O_3$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 30% (5% Et_2O/DCM)/Hex. $R_f = 0.2$

23.4 mg (**3s**); 70% yield.

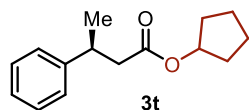
1H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 6.85 – 6.81 (m, 2H), 4.00 (t, $J = 6.7$ Hz, 2H), 3.78 (s, 3H), 3.23 (h, $J = 7.2$ Hz, 1H), 2.57 (dd, $J = 14.9, 7.3$ Hz, 1H), 2.51 (dd, $J = 14.9, 8.0$ Hz, 1H), 1.57 – 1.49 (m, 2H), 1.32 – 1.20 (m, 9H), 0.88 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.71, 158.20, 138.01, 127.80, 113.97, 64.62, 55.37, 43.42, 35.94, 31.57, 28.72, 25.70, 22.67, 22.22, 14.16.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{17}\text{H}_{26}\text{O}_3$, 301.1780; found, 301.1781.

IR: ν 2956, 2927, 2857, 1732, 1514, 1247 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -18.6362$ ($C = 1.270$, CHCl_3)



Cyclopentyl (*R*)-3-phenylbutanoate $\text{C}_{15}\text{H}_{20}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 30% (5%

$\text{Et}_2\text{O}/\text{DCM})/\text{Hex}$. $R_f = 0.12$

17.8 mg (**3t**); 64% yield

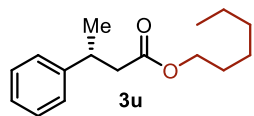
^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 5.09 (tt, $J = 6.1, 2.9$ Hz, 1H), 3.25 (h, $J = 7.2$ Hz, 1H), 2.58 (dd, $J = 14.8, 7.4$ Hz, 1H), 2.51 (dd, $J = 14.8, 7.9$ Hz, 1H), 1.81 – 1.71 (m, 2H), 1.66 – 1.47 (m, 6H), 1.29 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.35, 145.87, 128.56, 126.93, 126.49, 43.37, 36.86, 32.73, 32.71, 23.81, 22.12.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{15}\text{H}_{20}\text{O}_2$, 255.1361; found, 255.1362.

IR: ν 2962, 2919, 2873, 2850, 1728 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -18.2237$ ($C = 1.490$, CHCl_3)



Hexyl (*R*)-3-phenylbutanoate $\text{C}_{16}\text{H}_{24}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5%

$\text{Et}_2\text{O}/\text{DCM})/\text{Hex}$. $R_f = 0.9$

21.8 mg (**3u**); 73% yield.

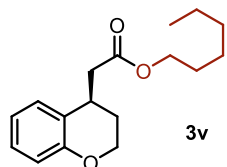
^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.01 (t, $J = 6.7$ Hz, 2H), 3.28 (h, $J = 7.1$ Hz, 1H), 2.62 (dd, $J = 15.0, 7.0$ Hz, 1H), 2.54 (dd, $J = 15.0, 8.1$ Hz, 1H), 1.57 – 1.50 (m, 2H), 1.32 – 1.22 (m, 9H), 0.88 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.64, 145.90, 128.61, 126.89, 126.52, 64.65, 43.16, 36.71, 31.56, 28.71, 25.69, 22.67, 22.04, 14.16.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{16}\text{H}_{24}\text{O}_2$, 271.1674; found, 271.1685.

IR: ν 2956, 2930, 2858, 1733, 1165 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -18.1065$ ($C = 1.340$, CHCl_3)



Hexyl (R)-2-(chroman-4-yl)acetate $\text{C}_{17}\text{H}_{24}\text{O}_3$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 30% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.1$

21.6 mg (**3v**); 65% yield.

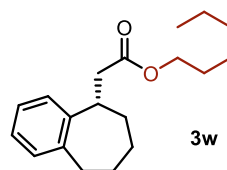
^1H NMR (500 MHz, CDCl_3) δ 7.14 – 7.08 (m, 2H), 6.86 (td, $J = 7.5, 1.3$ Hz, 1H), 6.80 (dd, $J = 8.1, 1.3$ Hz, 1H), 4.23 – 4.14 (m, 2H), 4.12 (td, $J = 6.8, 0.9$ Hz, 2H), 3.36 (dq, $J = 10.3, 5.2$ Hz, 1H), 2.80 (dd, $J = 15.5, 4.8$ Hz, 1H), 2.53 (dd, $J = 15.5, 10.0$ Hz, 1H), 2.16 (dddd, $J = 14.3, 8.7, 5.8, 4.2$ Hz, 1H), 1.85 (dtd, $J = 14.0, 5.4, 3.2$ Hz, 1H), 1.64 (dq, $J = 8.1, 6.7$ Hz, 2H), 1.39 – 1.23 (m, 6H), 0.90 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.39, 154.69, 128.86, 127.97, 124.75, 120.54, 117.21, 64.99, 63.34, 41.55, 31.56, 30.68, 28.74, 27.52, 25.75, 22.69, 14.15.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}^+]$ calculated for $\text{C}_{17}\text{H}_{24}\text{O}_3$, 299.1623; found, 299.1633.

IR: ν 2938, 2926, 2857, 1731, 1224, 1162 cm^{-1} .

$[\alpha]_{\text{D}}^{23} = -5.9385$ ($C = 1.800$, CHCl_3)



Hexyl (S)-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)acetate $\text{C}_{19}\text{H}_{28}\text{O}_2$

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 10% (5% $\text{Et}_2\text{O}/\text{DCM}$)/Hex. $R_f = 0.1$

29.1 mg (**3w**); 84% yield.

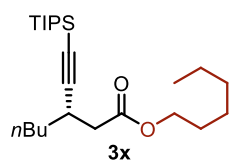
¹H NMR (500 MHz, CDCl₃) δ 7.17 – 7.04 (m, 4H), 4.06 (t, *J* = 6.7 Hz, 2H), 3.52 – 3.43 (m, 1H), 2.95 – 2.87 (m, 1H), 2.86 – 2.82 (m, 1H), 2.80 (dd, *J* = 15.1, 6.7 Hz, 1H), 2.70 (dd, *J* = 15.1, 8.9 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.83 – 1.69 (m, 3H), 1.65 – 1.47 (m, 4H), 1.38 – 1.19 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.08, 144.07, 142.71, 129.87, 126.37, 126.24, 64.71, 40.82, 38.84, 36.17, 33.51, 31.56, 29.86, 28.74, 27.95, 25.73, 22.69, 14.15.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₉H₂₈O₂, 289.2168; found, 289.2161.

IR: ν 2922, 2853, 1733 cm⁻¹.

[α]_D²³ = +10.8212 (*C* = 1.160, CHCl₃)



Hexyl (S)-3-((triisopropylsilyl)ethynyl)heptanoate C₂₄H₄₆O₂Si

Isolation: 60 mL silica gel, dry load on celite. Load column with DCM. Eluent: 20% (5% Et₂O/DCM)/Hex. **R_f** = 0.3

33.3 mg (3x); 70% yield

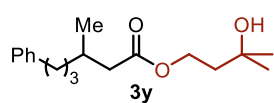
¹H NMR (500 MHz, CDCl₃) δ 4.07 (td, *J* = 6.8, 1.6 Hz, 2H), 2.94 – 2.84 (m, 1H), 2.53 (dd, *J* = 15.2, 7.7 Hz, 1H), 2.43 (dd, *J* = 15.2, 7.2 Hz, 1H), 1.61 (dt, *J* = 8.3, 6.8 Hz, 2H), 1.55 – 1.39 (m, 5H), 1.39 – 1.24 (m, 9H), 1.06 – 1.03 (m, 18H), 1.01 – 0.97 (m, 1H), 0.89 (td, *J* = 7.2, 2.7 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 171.84, 110.62, 81.66, 64.88, 40.74, 34.47, 31.61, 29.49, 29.42, 28.74, 25.77, 22.69, 22.49, 18.75, 14.16, 14.14, 11.37.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₄H₄₇O₂Si, 395.3345; found, 395.3353.

IR: ν 2929, 2864, 2167, 1739, 1463, 1162 cm⁻¹.

[α]_D²² = 0.3253 (*C* = 1.750, CHCl₃)



3-hydroxy-3-methylbutyl (S)-3-methyl-6-phenylhexanoate C₁₈H₂₈O₃

Isolation: 60 mL silica gel, dry load on celite. Eluent: (10% to 20%) EtOAc/Hex. **R_f** = 0.3

26.0 mg (3y); 74% yield.

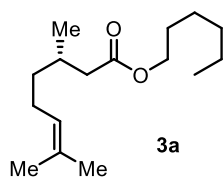
¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.15 (m, 3H), 4.24 (t, *J* = 6.9 Hz, 2H), 2.59 (ddd, *J* = 8.4, 6.8, 3.7 Hz, 2H), 2.29 (dd, *J* = 14.7, 6.0 Hz, 1H), 2.11 (dd, *J* = 14.8, 8.1 Hz, 1H), 1.98 (dq, *J* = 14.0, 7.2 Hz, 1H), 1.82 (t, *J* = 6.8 Hz, 2H), 1.72 – 1.56 (m, 2H), 1.56 – 1.53 (m, 2H), 1.37 (ddt, *J* = 13.4, 10.8, 5.6 Hz, 1H), 1.26 (s, 6H), 0.94 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 173.30, 142.64, 128.51, 128.42, 125.83, 70.21, 61.37, 42.05, 41.73, 36.45, 36.16, 30.43, 29.79, 28.98, 19.86.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₈H₂₈O₃Na, 315.1936; found, 315.1929.

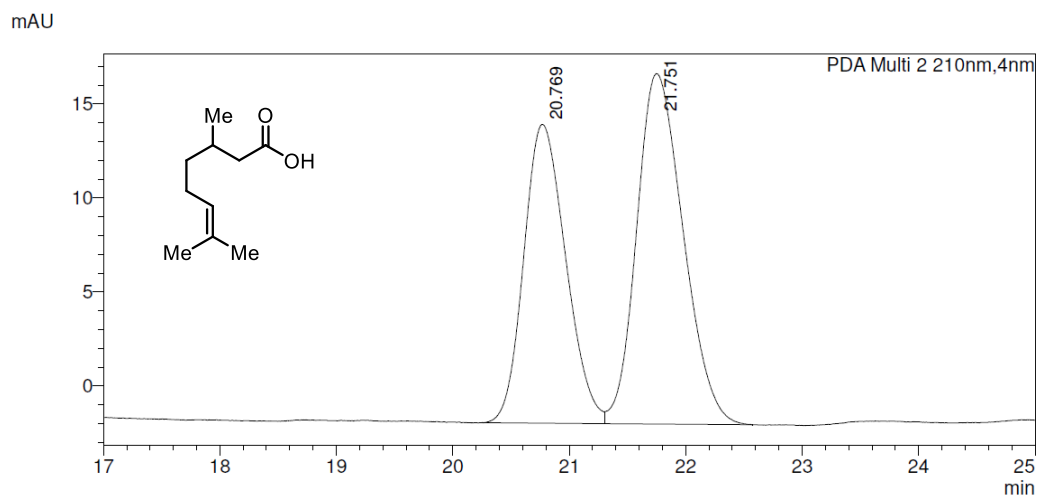
IR: ν 3442 (br), 2966, 2930, 2855, 1732, 1148 cm⁻¹.

D. HPLC Traces of Isolated Esters

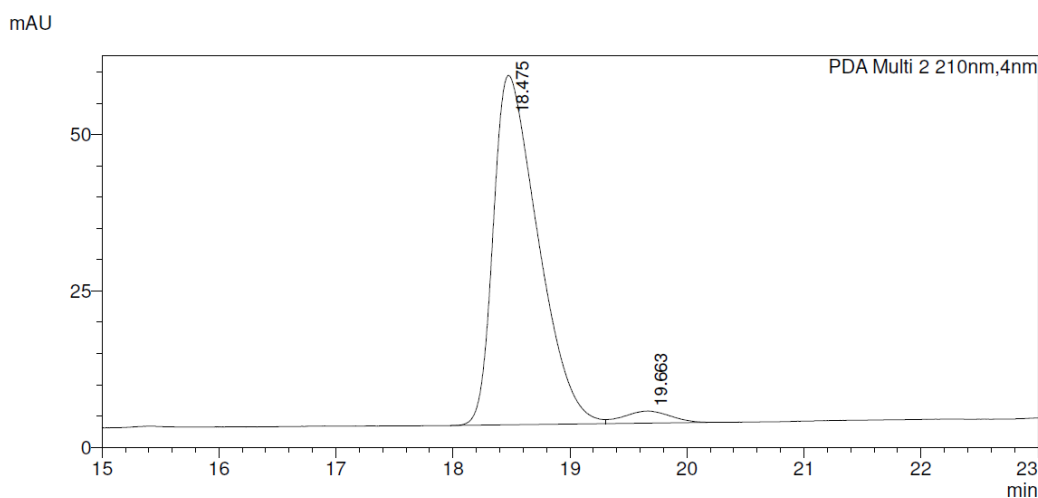


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-

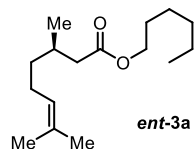
3, 96.5:3.5 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

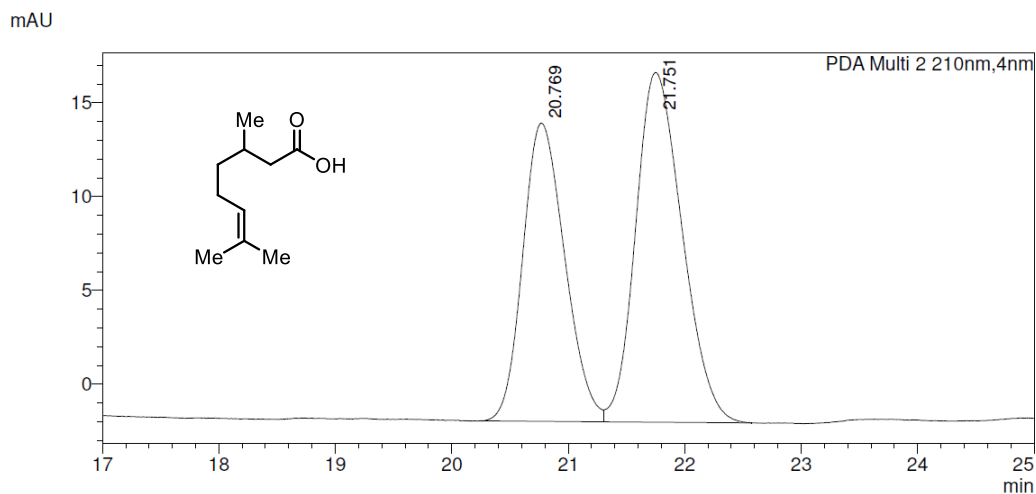


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.475	1482133	96.509	55810	96.665
2	19.663	53606	3.491	1926	3.335
Total		1535739	100.000	57736	100.000

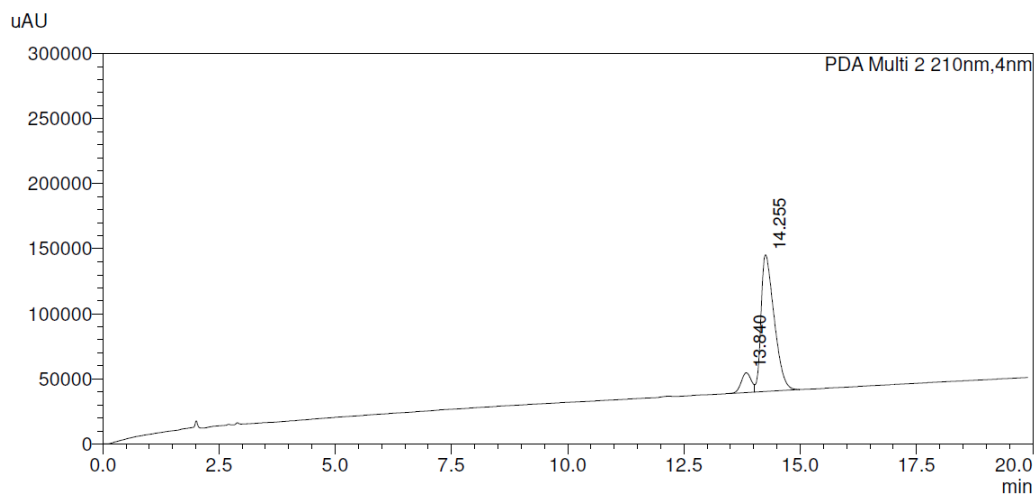


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

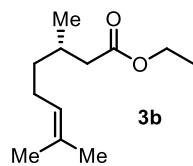
90.0:10.0 e.r. (95.9:4.1 e.s.)



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

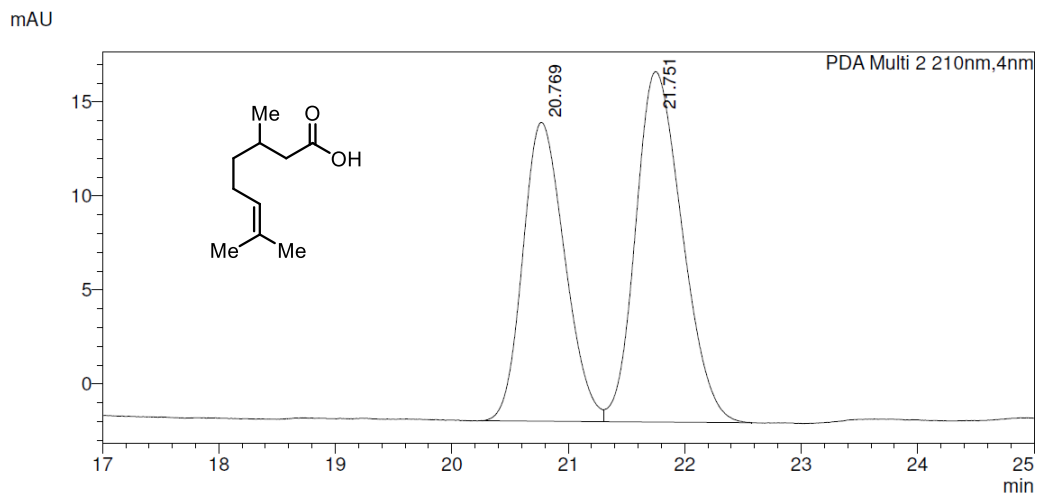


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.840	228917	15171	12.623	9.982
2	14.255	2064322	105013	87.377	90.018
Total		2293239	120183	100.000	100.000

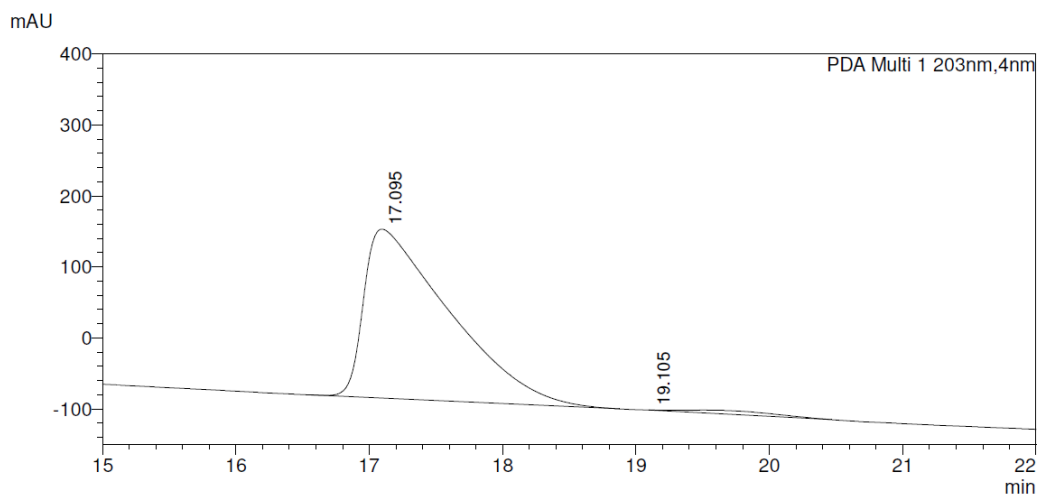


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

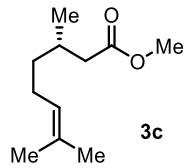
97.9:2.1 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

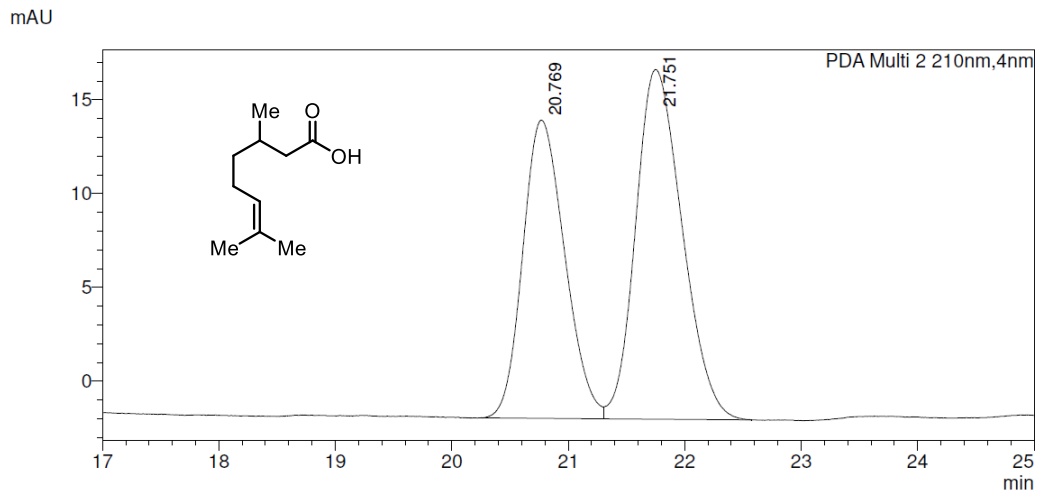


PDA Ch1 203nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.095	10613495	97.874	237961	99.976
2	19.105	230590	2.126	57	0.024
Total		10844085	100.000	238018	100.000

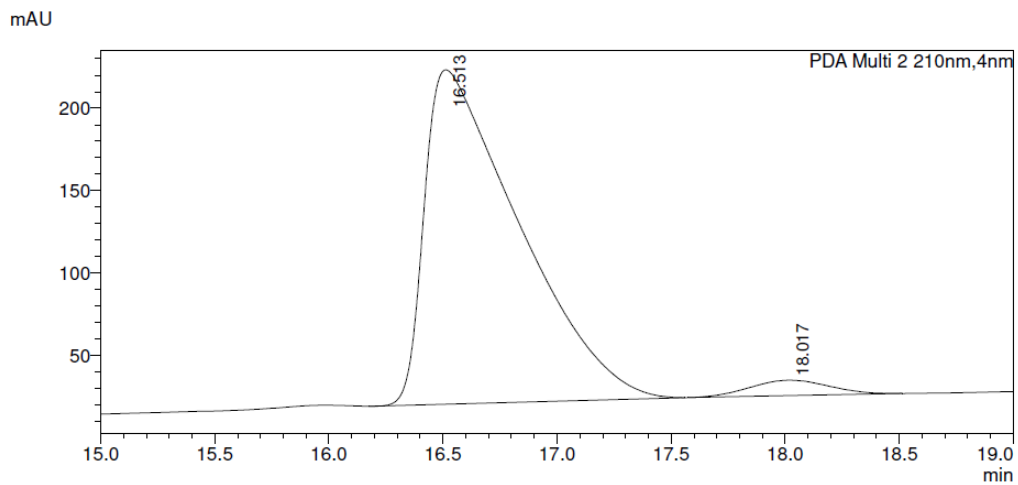


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3

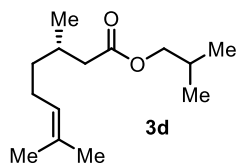
96.2 : 3.8 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

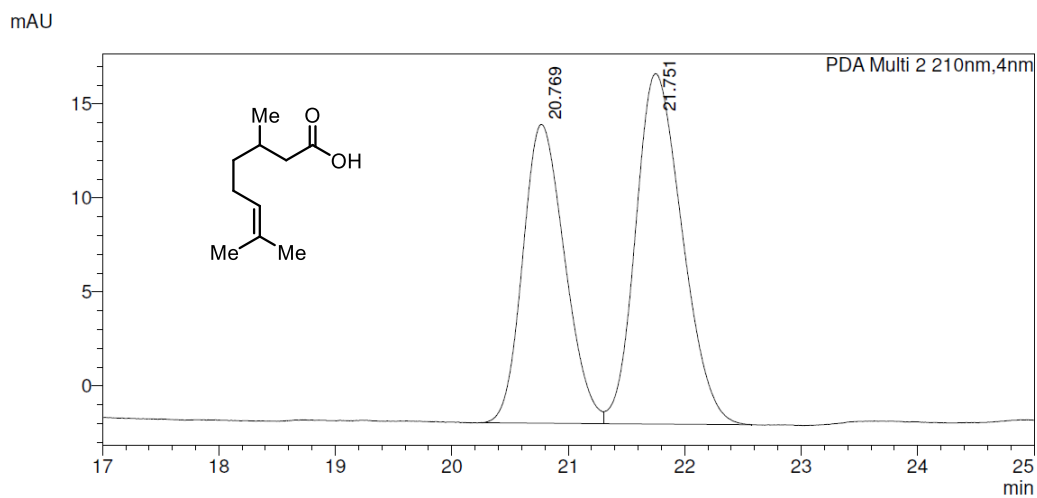


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	16.513	5831210	96.244	202690	95.560
2	18.017	227589	3.756	9418	4.440
Total		6058798	100.000	212108	100.000

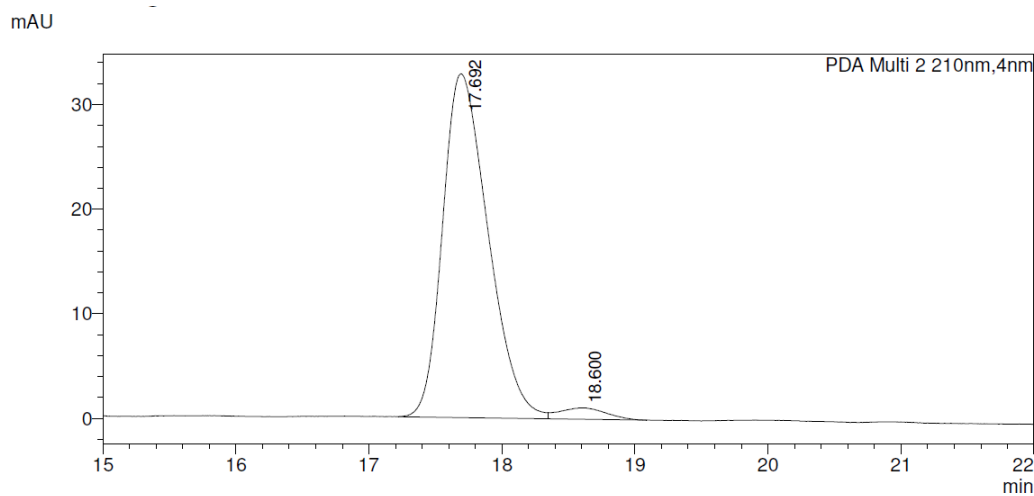


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

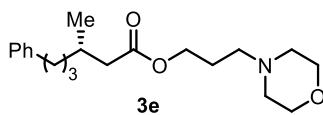
96.7:3.3 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

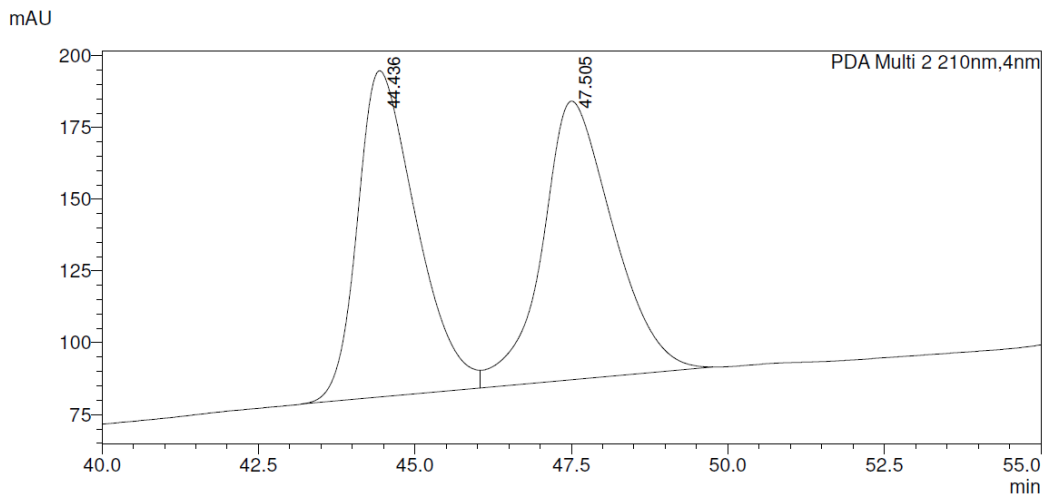


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.692	780574	96.700	32842	96.818
2	18.600	26636	3.300	1079	3.182
Total		807210	100.000	33921	100.000

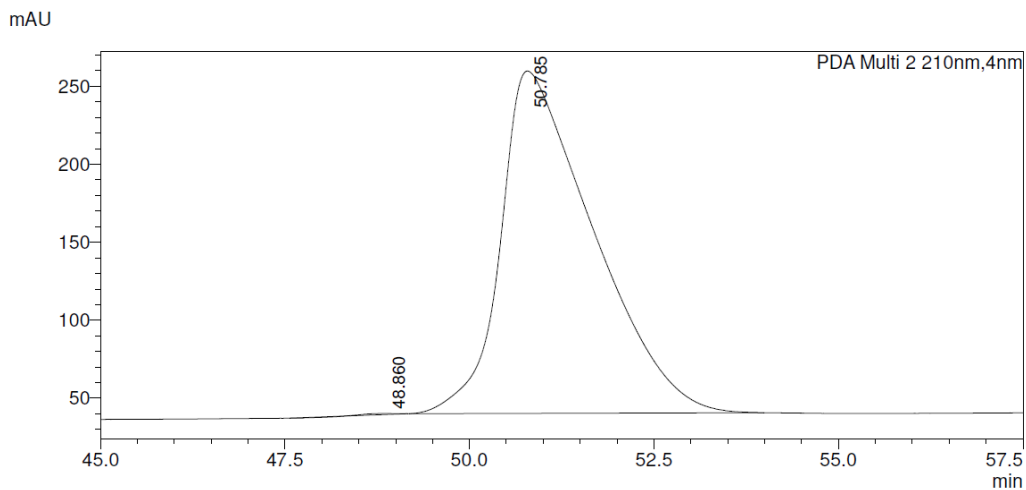


1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3% IPA/Hex, 0.8 mL/min, CHIRALPAK IA-3

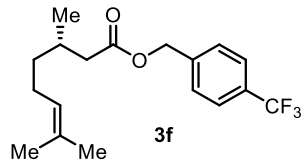
99.9 : 0.1 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	44.436	7434789	49.190	113601	53.930
2	47.505	7679628	50.810	97046	46.070
Total		15114417	100.000	210647	100.000

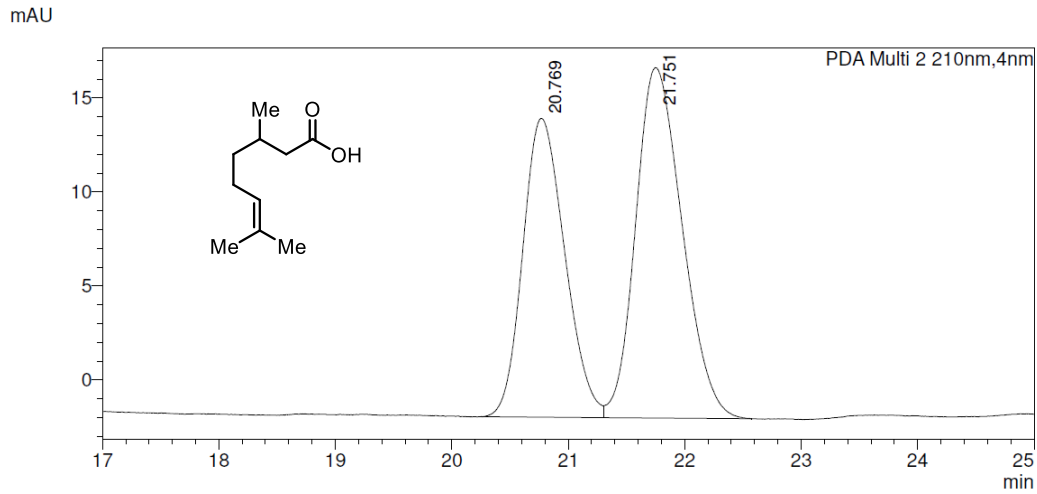


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	48.860	16343	0.085	706	0.321
2	50.785	19233423	99.915	219562	99.679
Total		19249766	100.000	220268	100.000

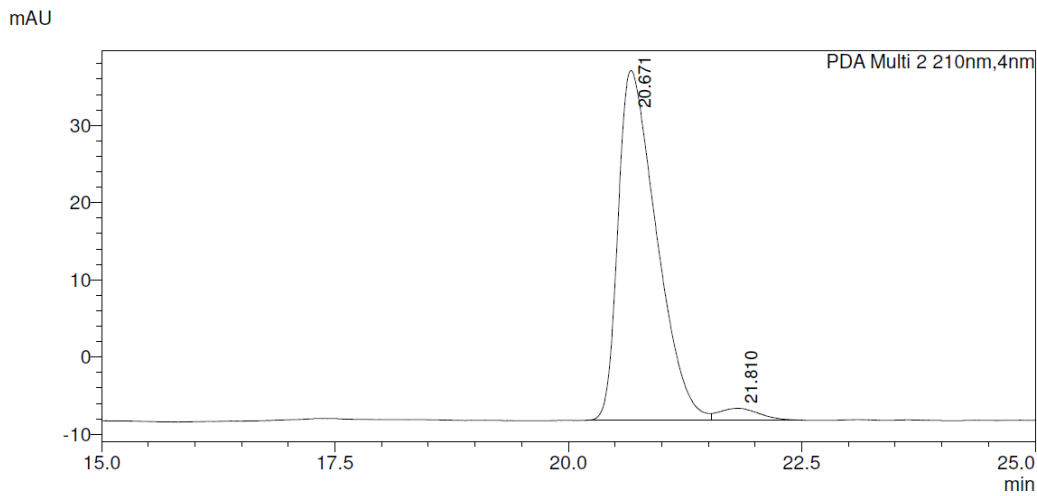


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

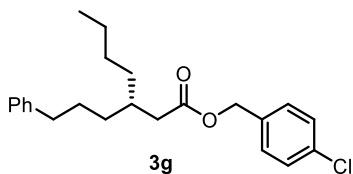
96.5:3.5 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

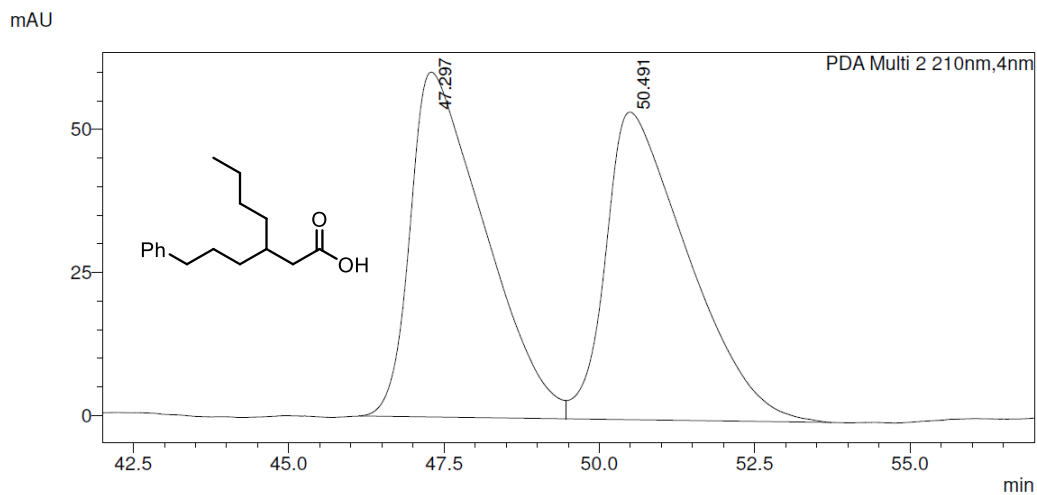


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.671	1295084	96.489	45343	96.675
2	21.810	47130	3.511	1559	3.325
Total		1342214	100.000	46902	100.000

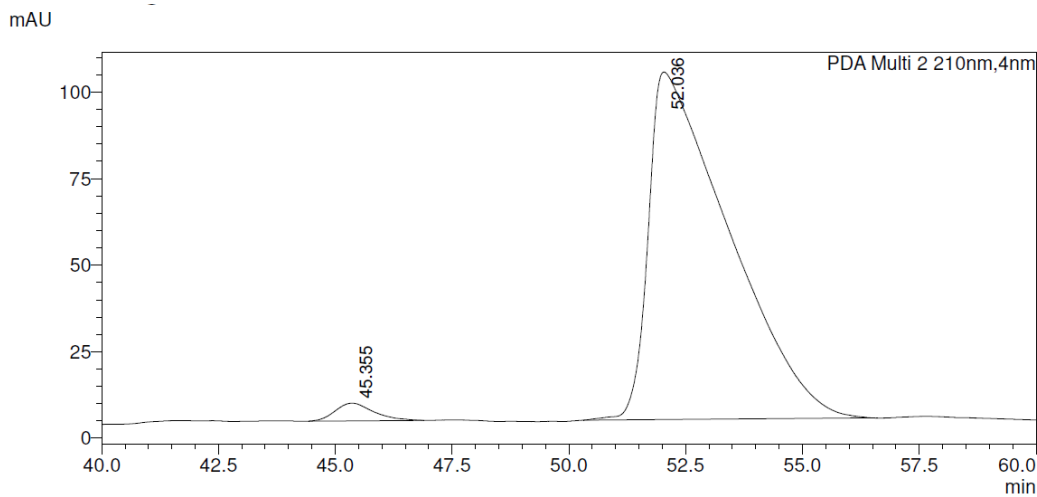


Saponified to carboxylic acid, **97.6:2.4 e.r.**

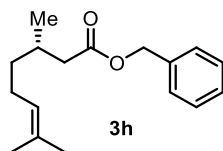
60%[1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex]/40%Hex, CHIRALPAK IA-3



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	47.297	5024968	50.244	60259	52.849
2	50.491	4976235	49.756	53763	47.151
Total		10001202	100.000	114022	100.000

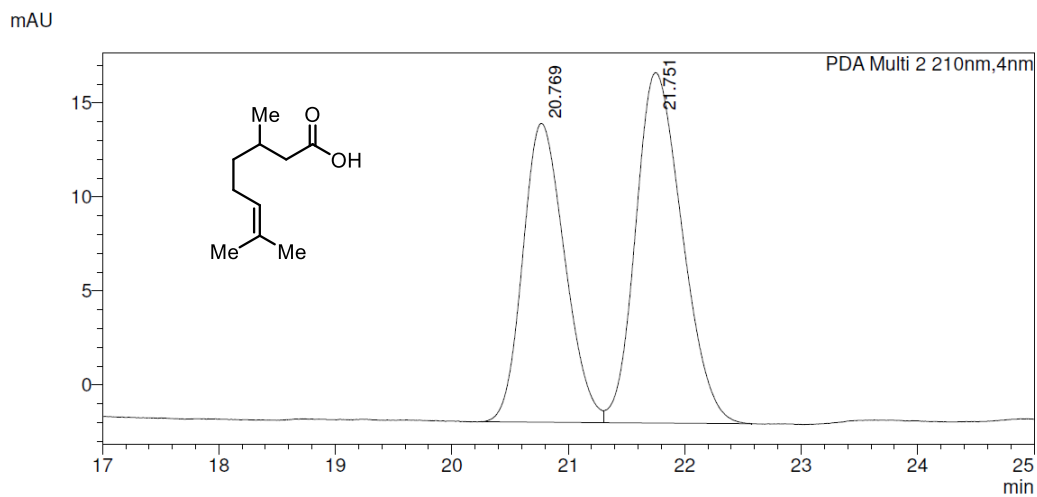


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	45.355	292202	2.375	5121	4.858
2	52.036	12013123	97.625	100287	95.142
Total		12305325	100.000	105408	100.000

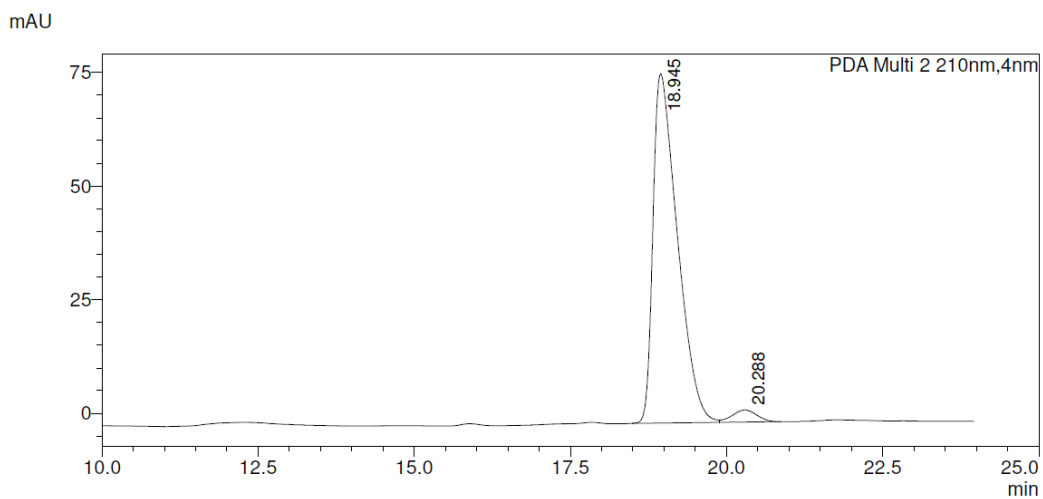


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

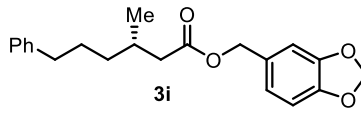
96.6:3.4 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

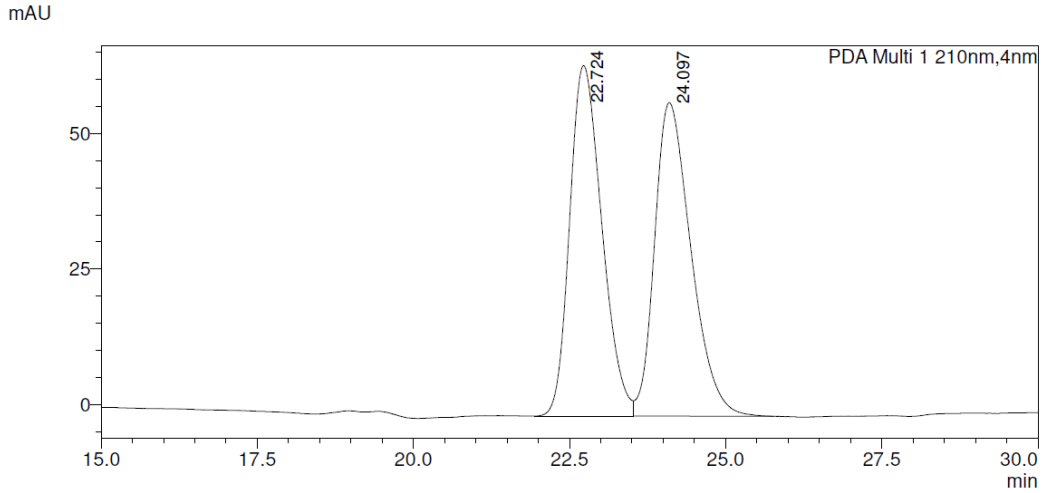


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.945	2087235	96.620	76769	96.643
2	20.288	73026	3.380	2667	3.357
Total		2160261	100.000	79436	100.000

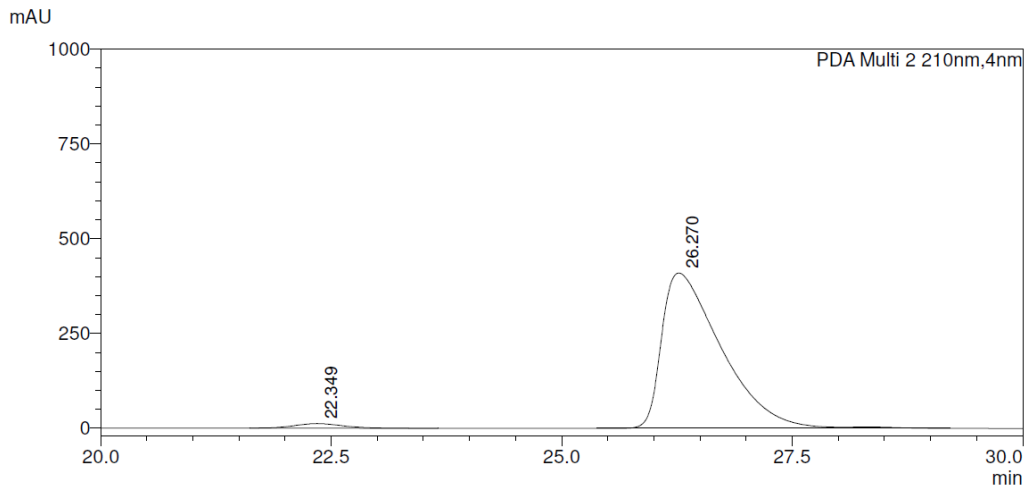


2.5%(0.2%TFA/0.1%DEA/5%EtOH/Hex)97.5%Hex, CHIRALPAK IC-3

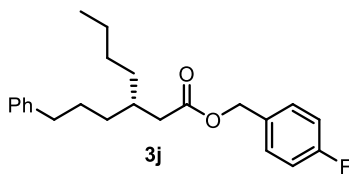
97.7:2.3 e.r.



PDA Ch1 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	22.724	2320117	49.725	64589	52.785
2	24.097	2345734	50.275	57773	47.215
Total		4665851	100.000	122362	100.000

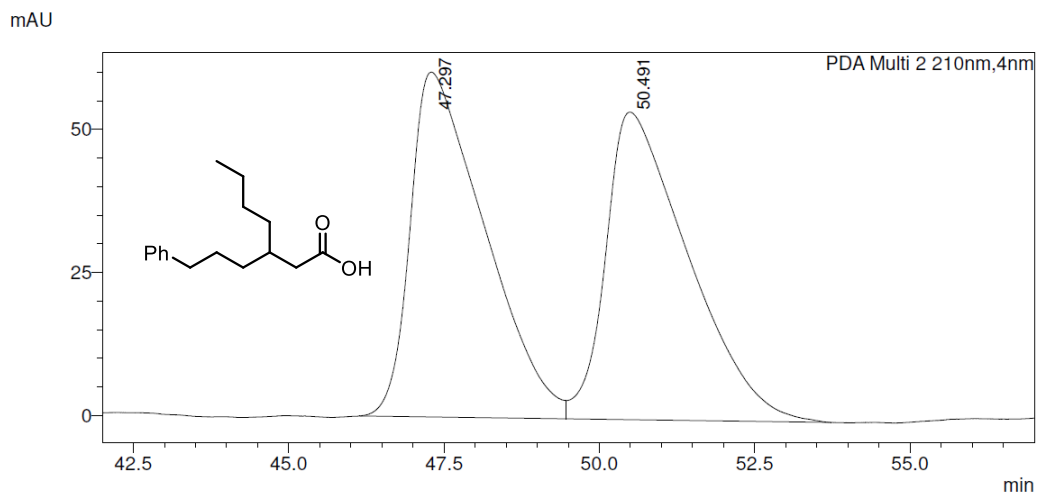


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	22.349	429953	2.271	11863	2.813
2	26.270	18499587	97.729	409831	97.187
Total		18929540	100.000	421694	100.000

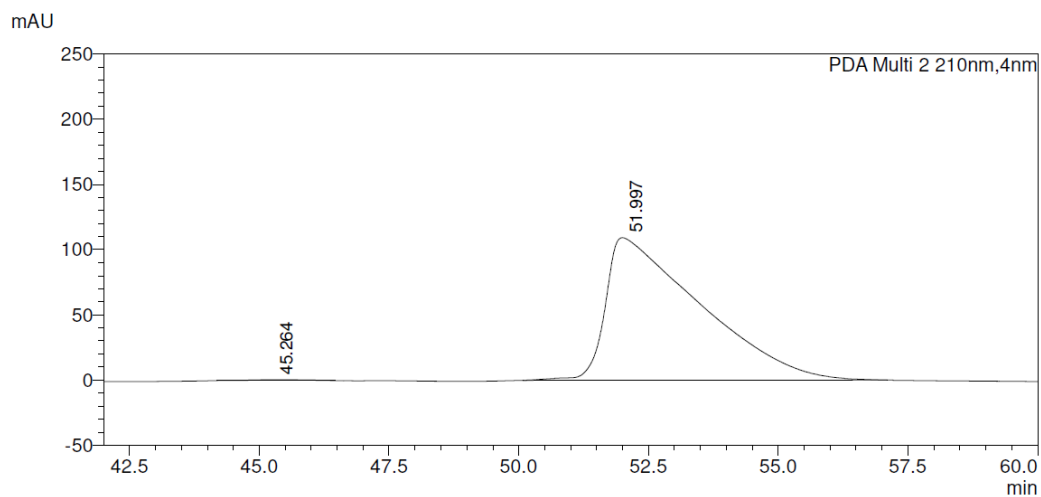


Saponified to carboxylic acid, **99.7:0.3 e.r.**

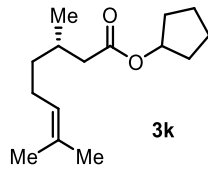
60%[1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex]/40%Hex, CHIRALPAK IA-3



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	47.297	5024968	50.244	60259	52.849
2	50.491	4976235	49.756	53763	47.151
Total		10001202	100.000	114022	100.000

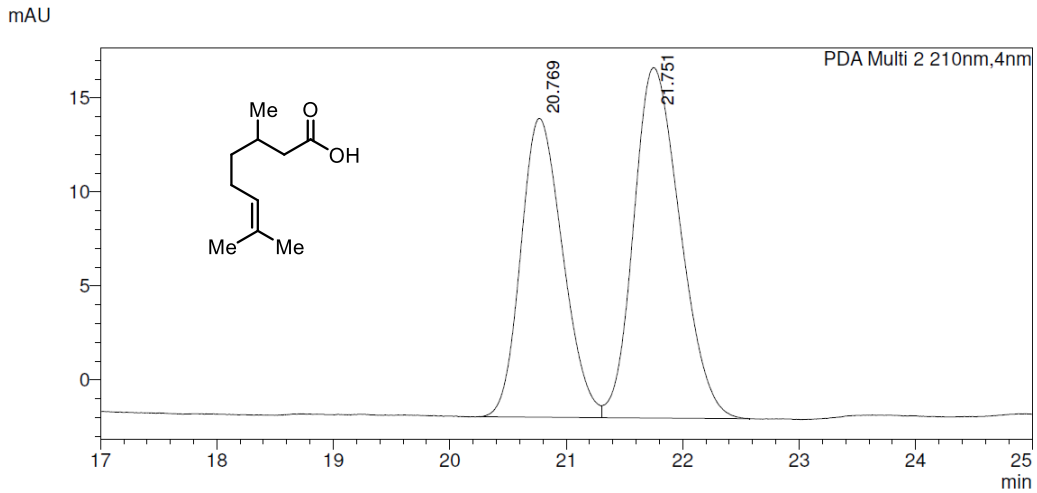


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	45.264	44358	0.320	596	0.542
2	51.997	13838175	99.680	109311	99.458
Total		13882534	100.000	109907	100.000

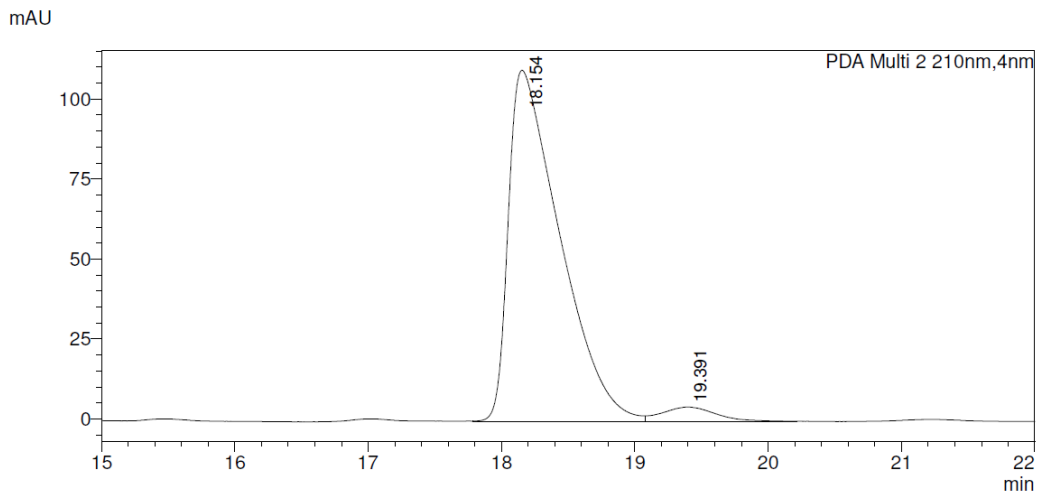


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

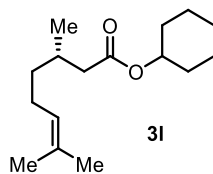
96.1:3.9 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

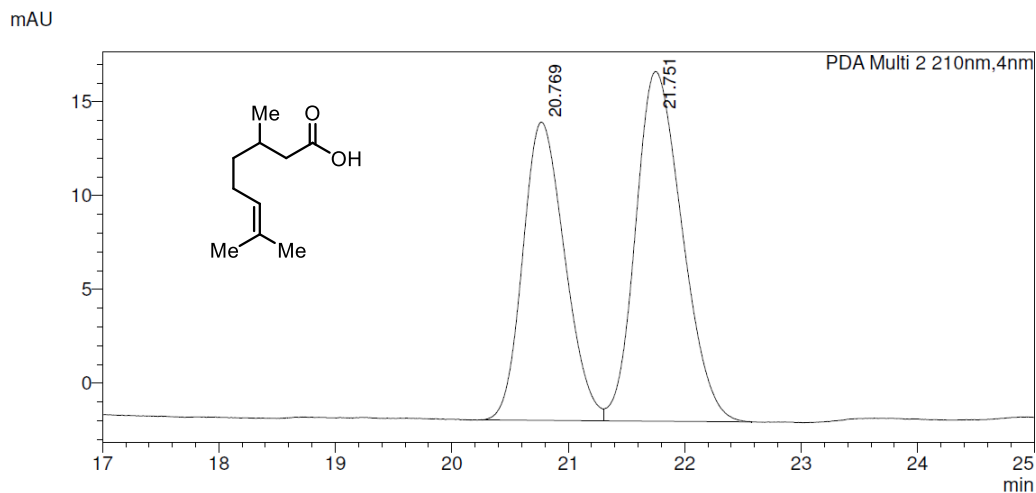


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.154	2940043	95.988	109630	96.128
2	19.391	122869	4.012	4415	3.872
Total		3062912	100.000	114045	100.000

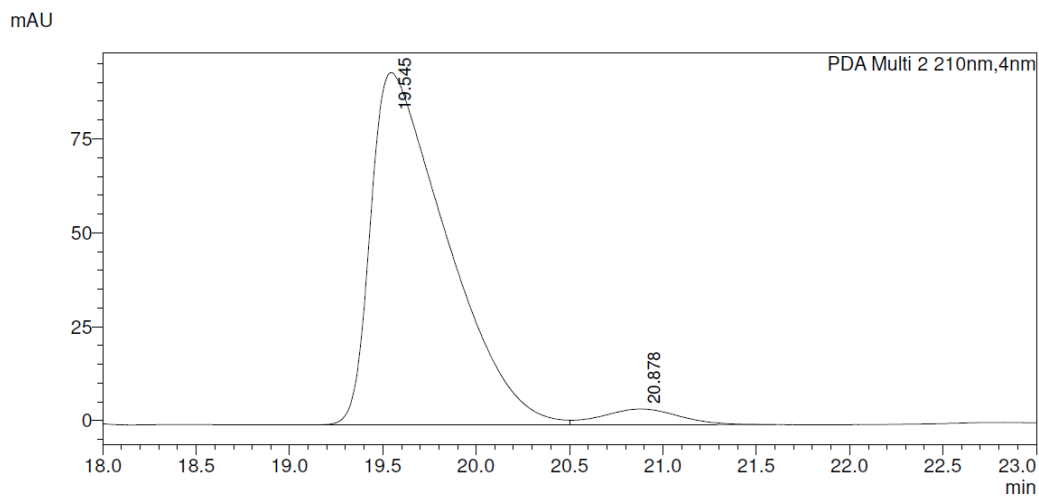


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

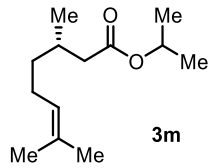
95.7:4.3 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

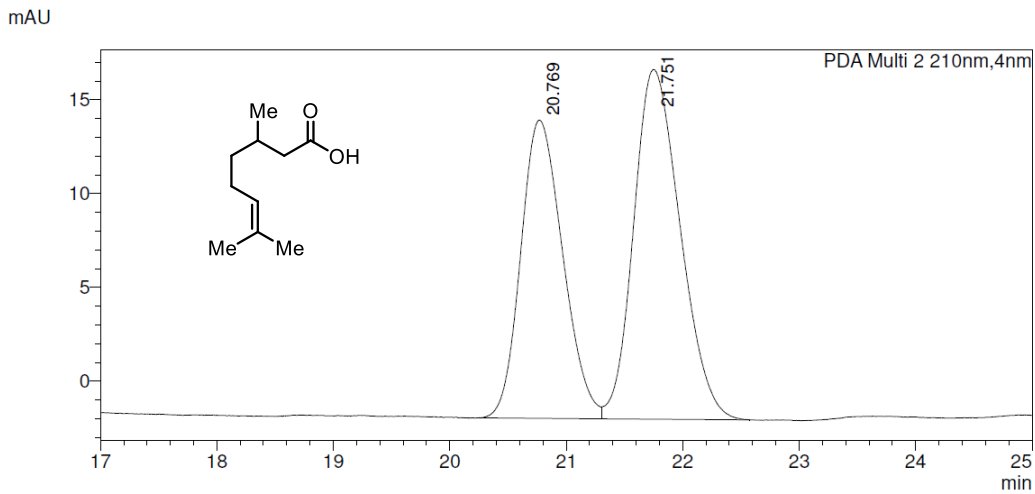


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	19.545	2656751	95.657	93715	95.698
2	20.878	120620	4.343	4213	4.302
Total		2777371	100.000	97928	100.000

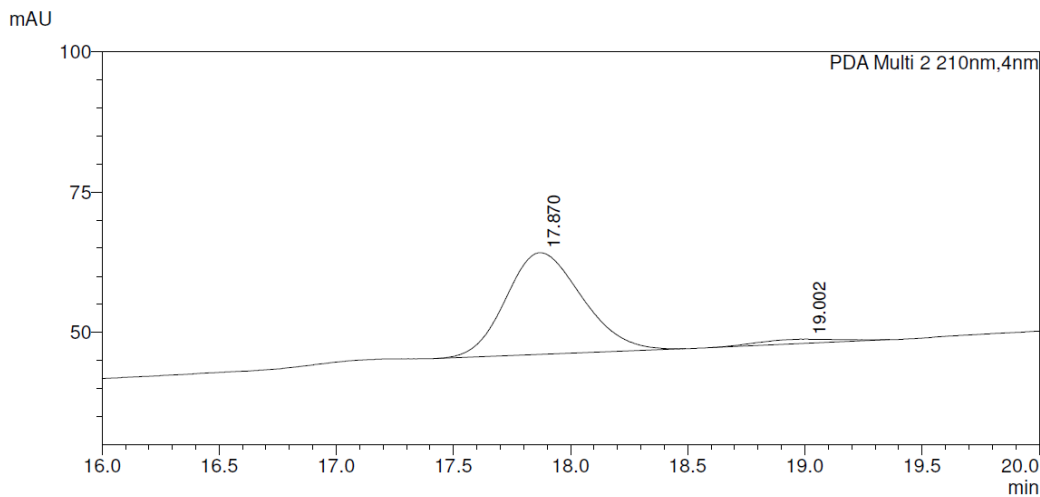


Saponified to citronellic acid, 1%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3,

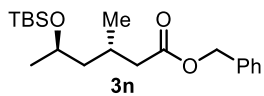
95.5 : 4.5 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.769	398717	43.456	15904	46.029
2	21.751	518801	56.544	18649	53.971
Total		917518	100.000	34553	100.000

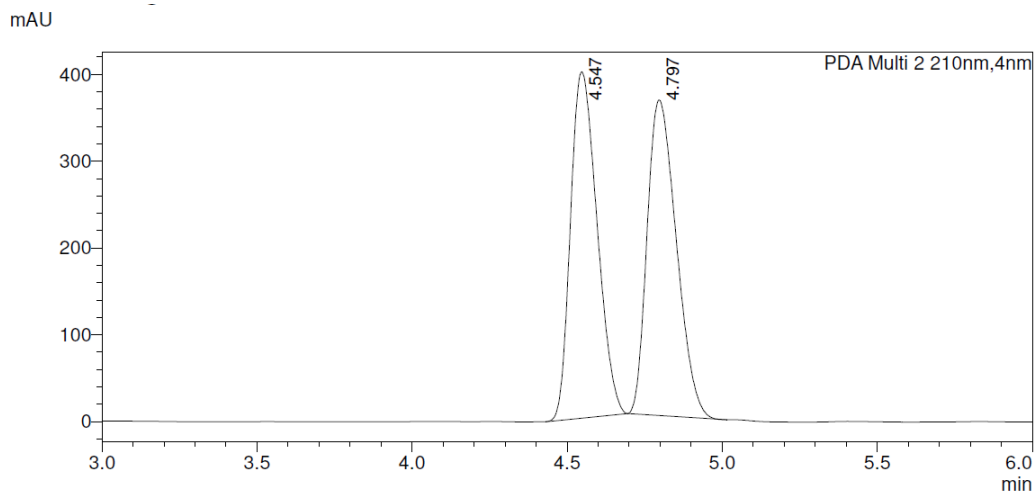


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.870	410456	95.490	18116	95.979
2	19.002	19385	4.510	759	4.021
Total		429842	100.000	18875	100.000



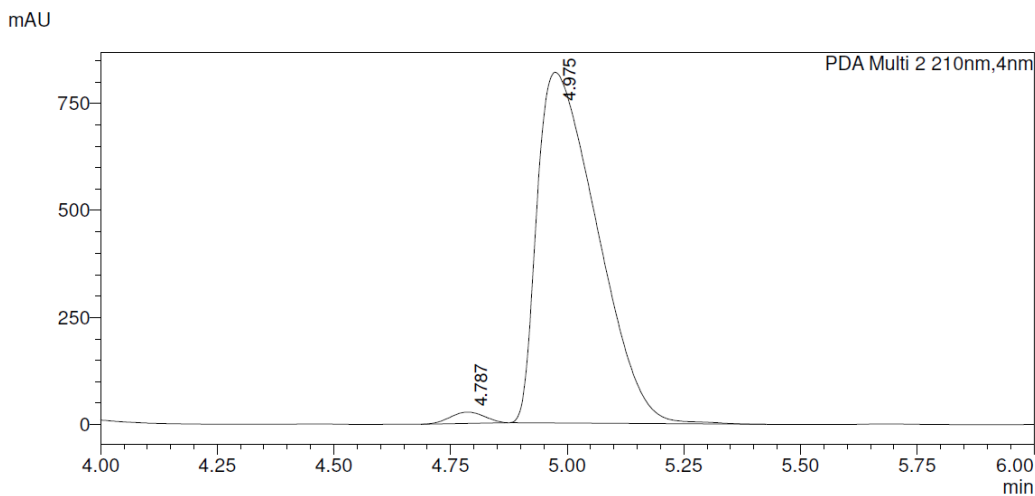
0.5%(0.2%TFA/0.1%DEA/5%THF/Hex)/0.3%IPA/Hex, CHIRALPAK IC-3

98.2:1.8 e.r.



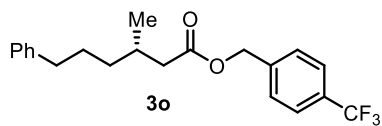
PDA Ch2 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	4.547	2373587	49.953	397759	52.286
2	4.797	2378047	50.047	362980	47.714
Total		4751634	100.000	760739	100.000



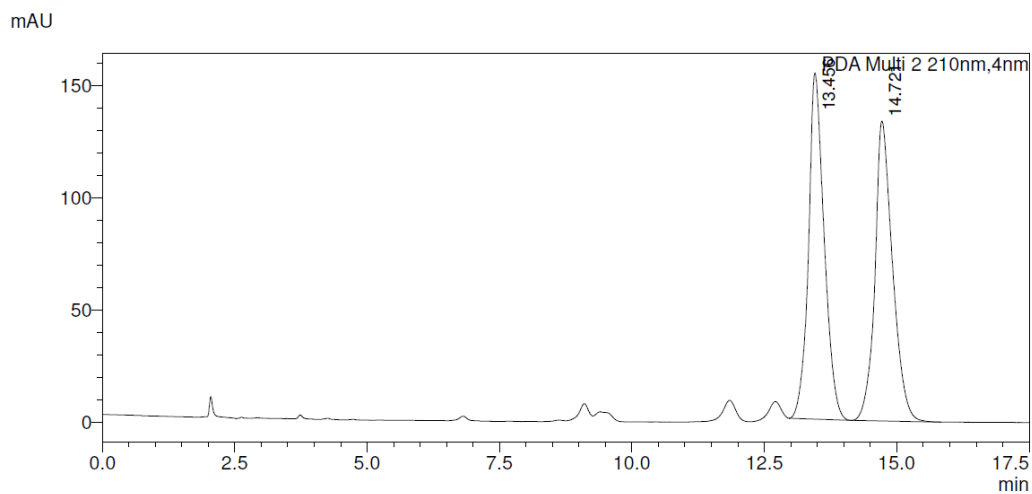
PDA Ch2 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	4.787	136020	1.825	26582	3.145
2	4.975	7318250	98.175	818552	96.855
Total		7454270	100.000	845134	100.000

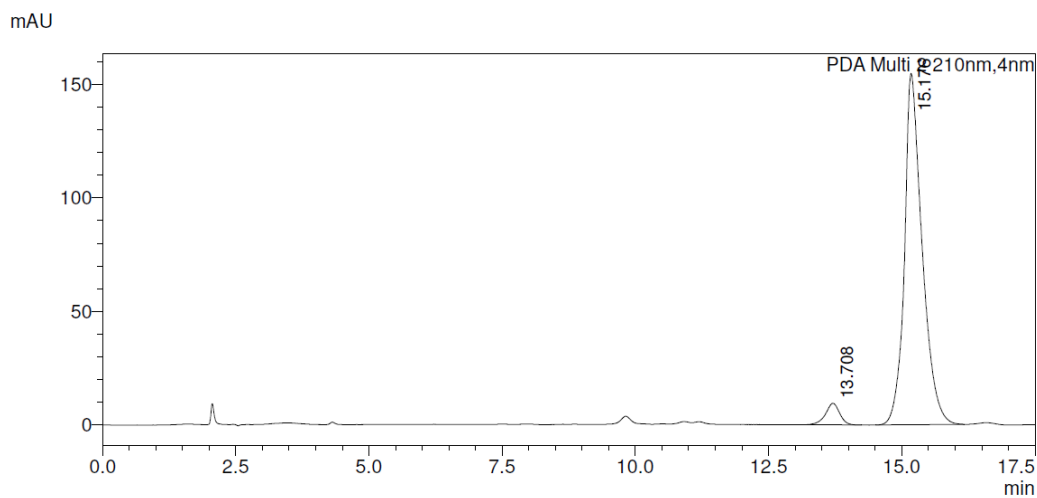


0.3%(0.2%TFA/0.1%DEA/5%EtOH/Hex)/99.7%Hex, CHIRALPAK IC-3

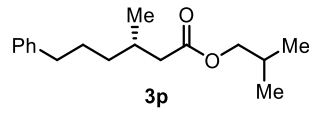
95.3:4.7 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.456	3185332	50.593	154362	53.576
2	14.721	3110651	49.407	133756	46.424
Total		6295984	100.000	288118	100.000

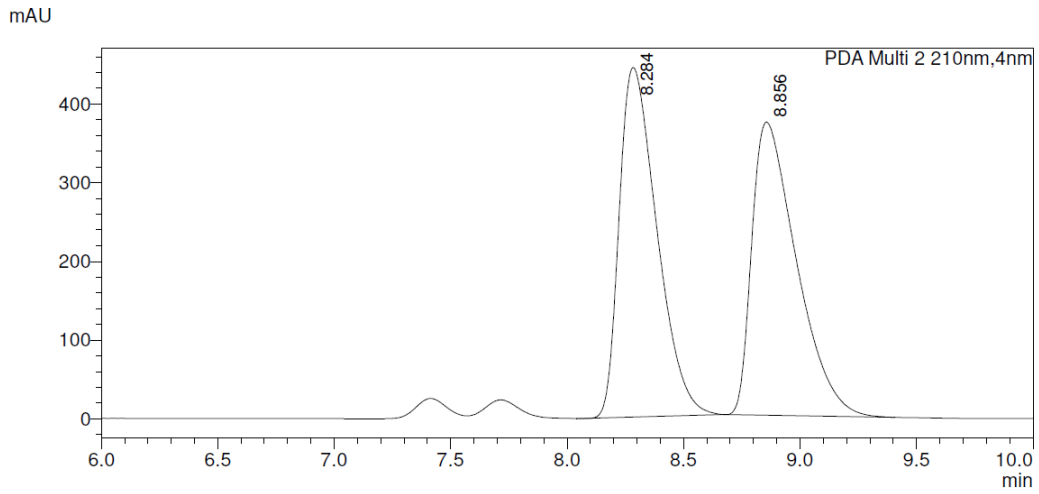


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.708	175854	4.684	9467	5.770
2	15.176	3578364	95.316	154600	94.230
Total		3754218	100.000	164068	100.000

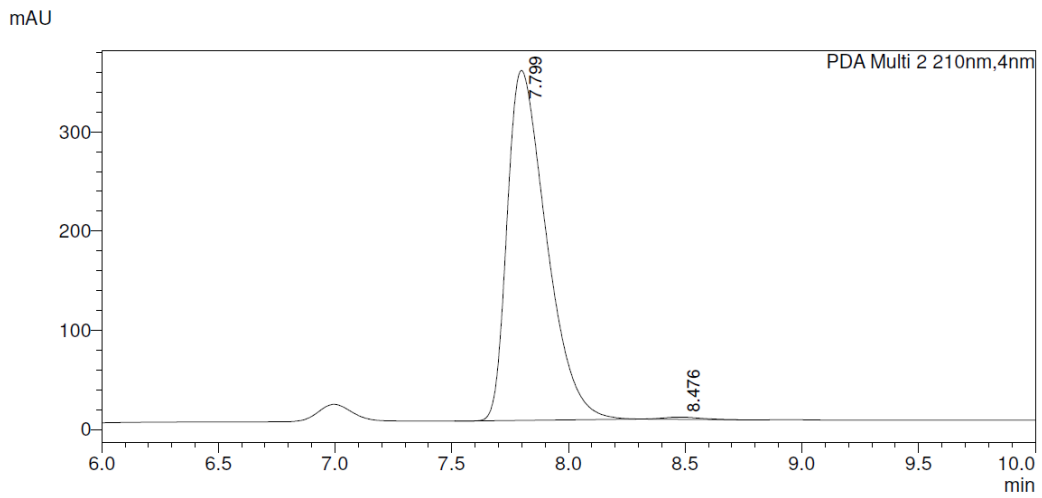


0.3%THF/Hex, CHIRALPAK IC-3

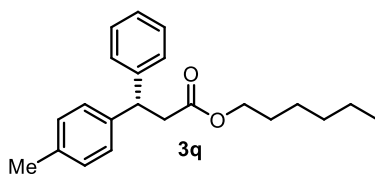
99.4:0.6 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.284	4997191	50.160	443719	54.389
2	8.856	4965409	49.840	372100	45.611
Total		9962600	100.000	815819	100.000

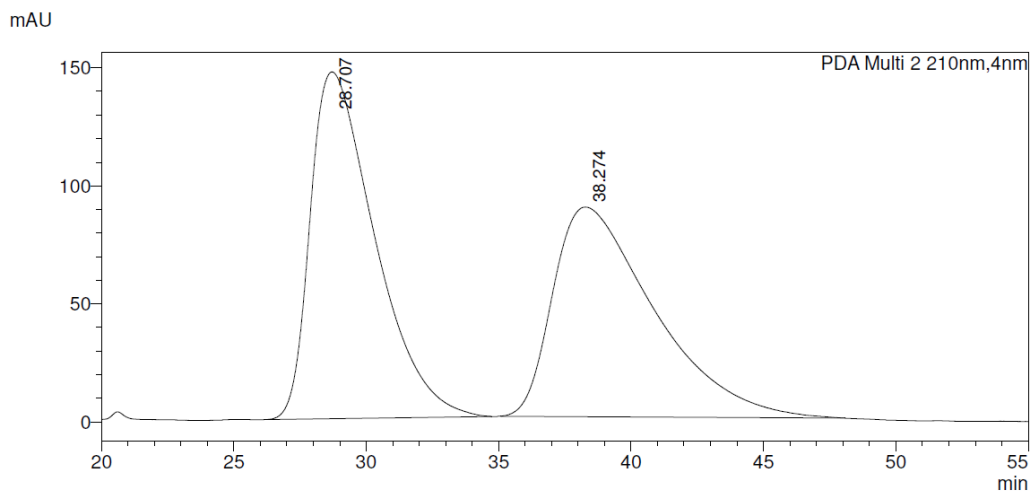


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.799	4124964	99.433	352563	99.399
2	8.476	23521	0.567	2133	0.601
Total		4148485	100.000	354696	100.000

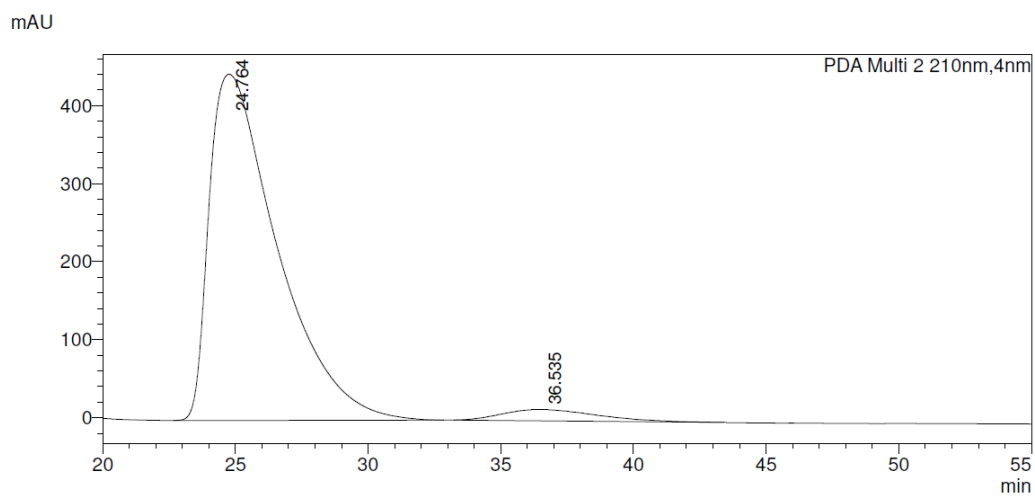


0.3%THF/Hex, 0.8 mL/min, CHIRALCEL OJ-H

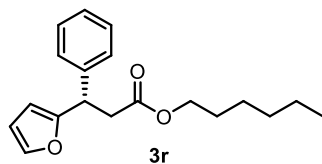
95.6:4.4 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	28.707	24896177	51.327	146884	62.319
2	38.274	23609238	48.673	88814	37.681
Total		48505415	100.000	235698	100.000

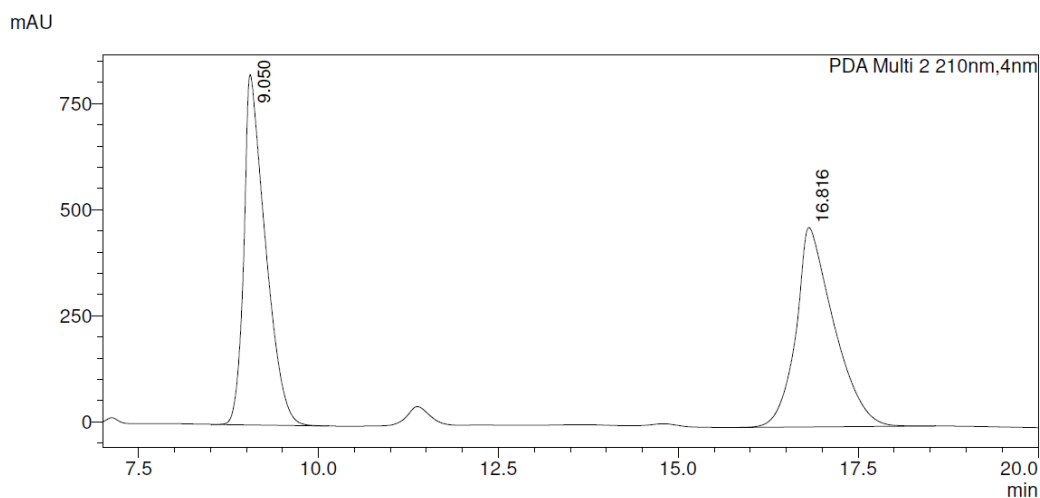


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	24.764	79183178	95.638	443657	96.817
2	36.535	3611696	4.362	14585	3.183
Total		82794873	100.000	458242	100.000

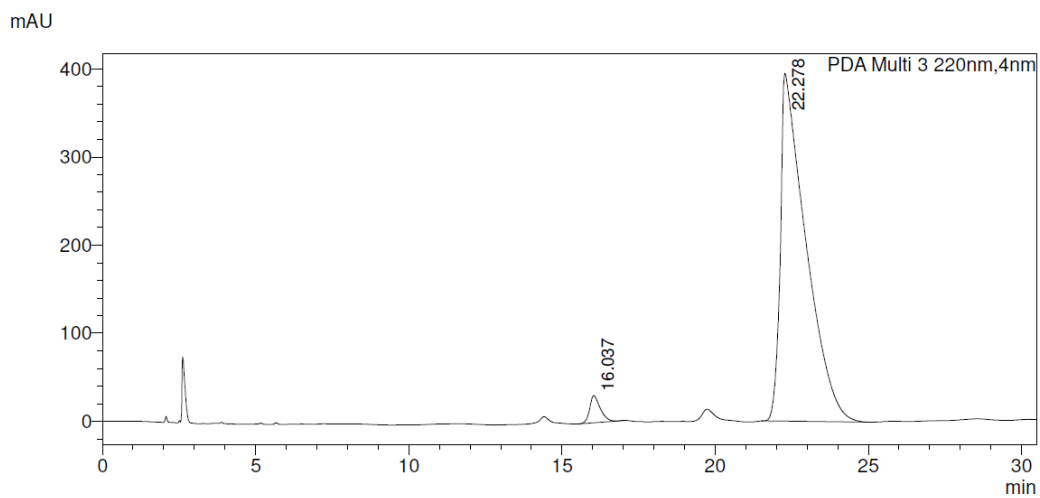


0.3%DCM/Hex, 1.0 mL/min, CHIRALPAK IB-3

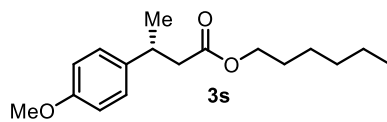
96.8 : 3.2 e.r.



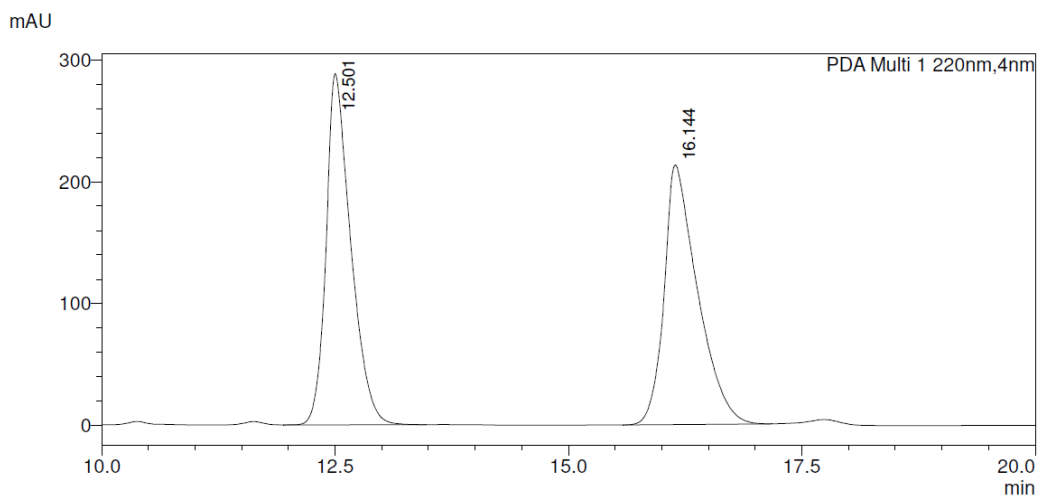
PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.050	17260464	49.973	824806	63.700
2	16.816	17279041	50.027	470024	36.300
Total		34539505	100.000	1294830	100.000



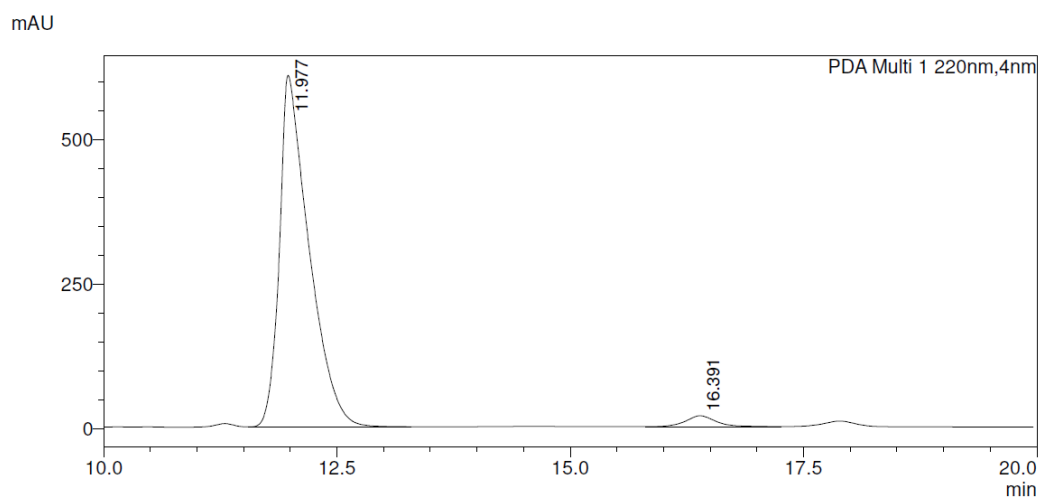
PDA Ch3 220nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	16.037	745059	3.158	30770	7.235
2	22.278	22847486	96.842	394514	92.765
Total		23592545	100.000	425284	100.000



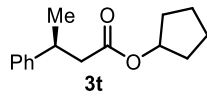
0.3%THF/Hex, 0.8 mL/min, CHIRALPAK IB-3, **97.0:3.0 e.r.**



PDA Ch1 220nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.501	5304998	49.932	287965	57.503
2	16.144	5319540	50.068	212819	42.497
Total		10624538	100.000	500784	100.000

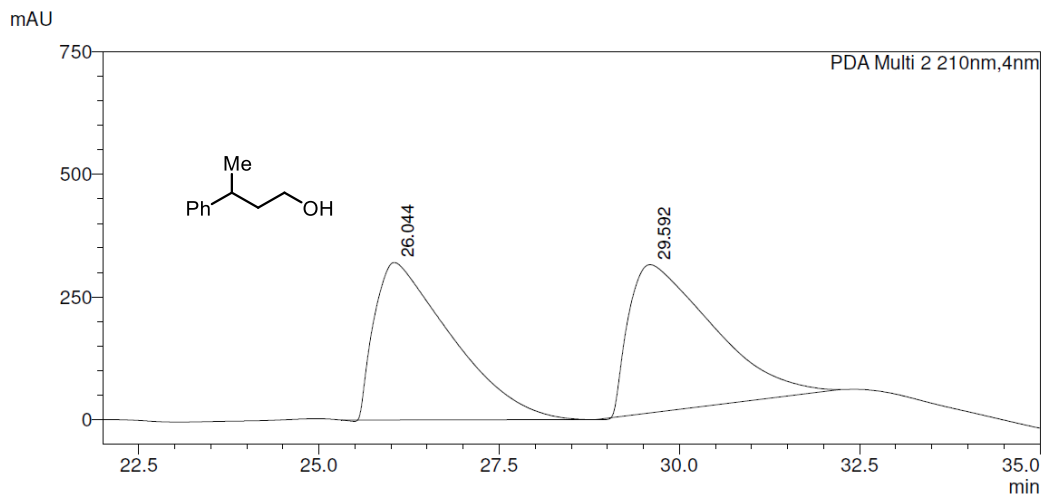


PDA Ch1 220nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.977	13436560	96.977	607738	97.015
2	16.391	418880	3.023	18700	2.985
Total		13855440	100.000	626438	100.000



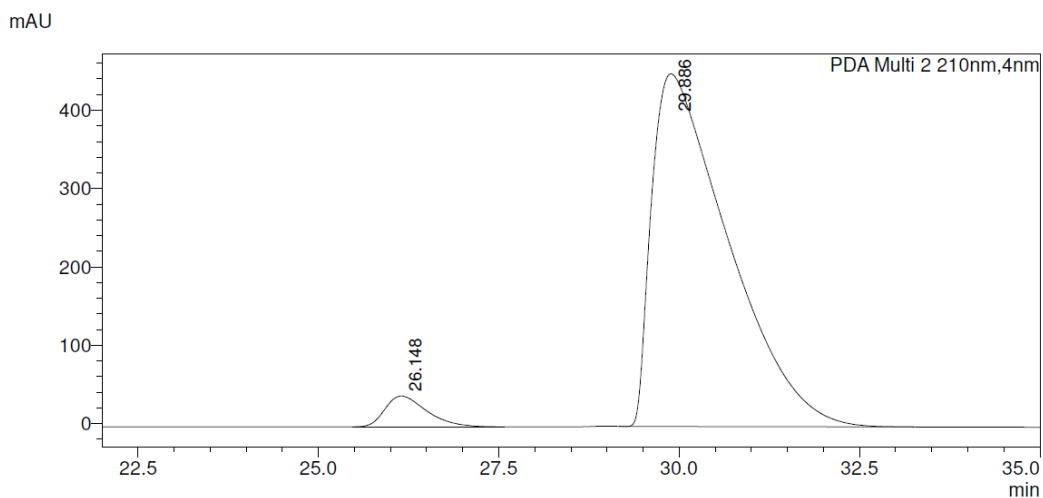
Reduced with LiAlH₄ to the 1° alcohol; **95.4 : 4.6 e.r.**

0.3%DCM/Hex, 1.0 mL/min, CHIRALCEL OJ-H



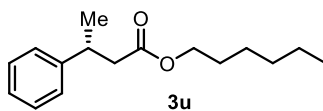
PDA Ch2 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	26.044	23869421	49.375	321168	51.492
2	29.592	24473977	50.625	302554	48.508
Total		48343398	100.000	623722	100.000



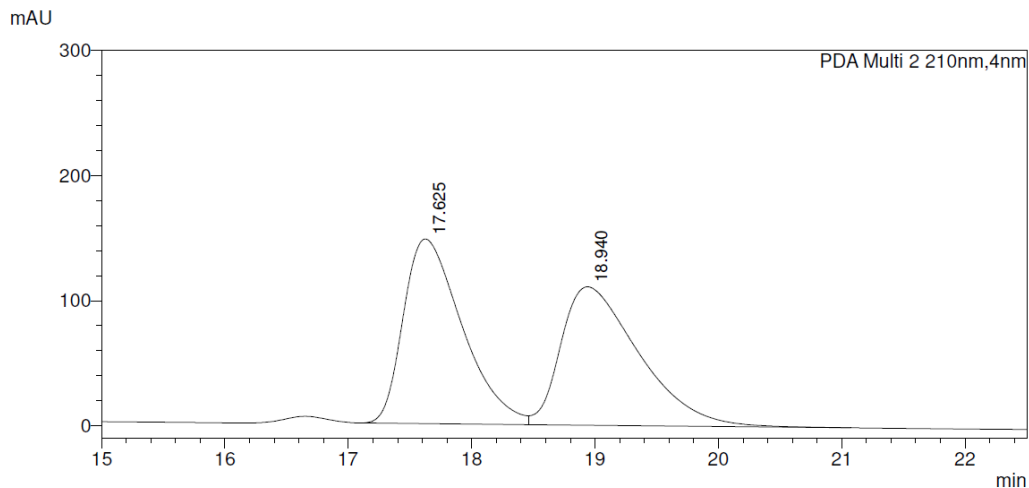
PDA Ch2 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	26.148	1584746	4.556	39335	8.041
2	29.886	33200155	95.444	449842	91.959
Total		34784902	100.000	489177	100.000

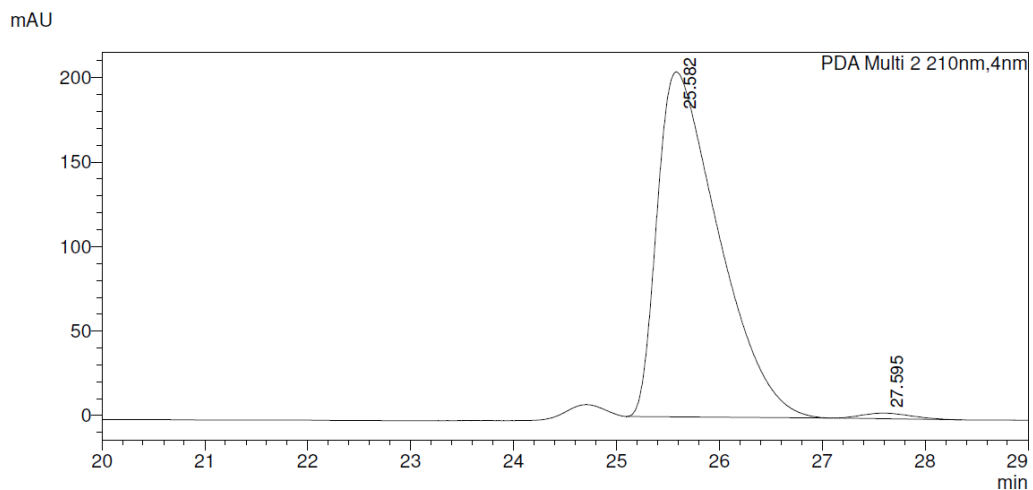


100% Hex, 0.5 mL/min, CHIRALPAK IA-3

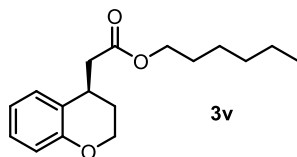
98.7 : 1.3 e.r.



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.625	4909128	50.203	147579	57.155
2	18.940	4869454	49.797	110628	42.845
Total		9778582	100.000	258207	100.000



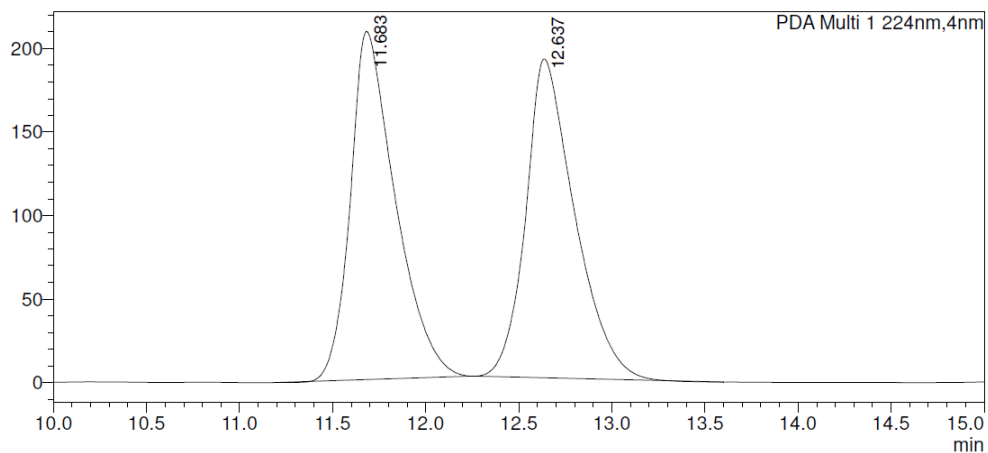
PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	25.582	8478555	98.700	204311	98.410
2	27.595	111648	1.300	3301	1.590
Total		8590203	100.000	207612	100.000



0.3%THF/Hex, 0.8 mL/min, CHIRALPAK IB-3

96.7:3.3 e.r.

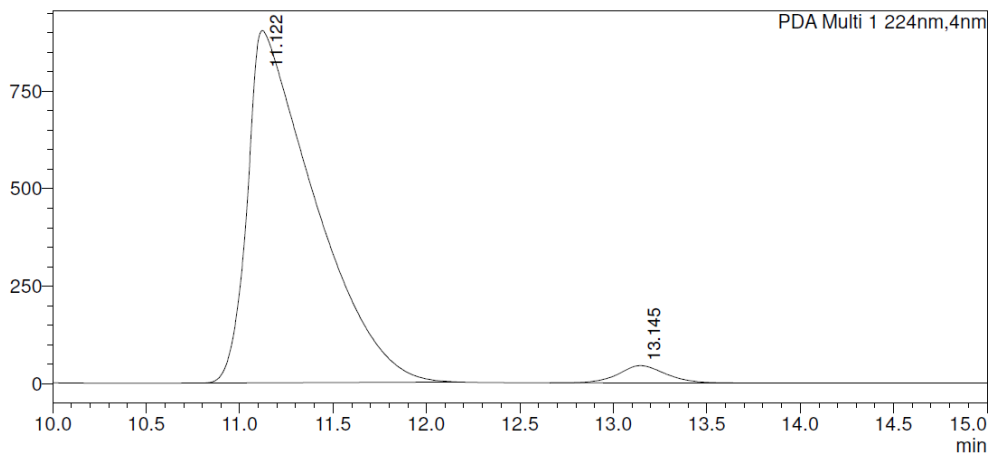
mAU



PDA Ch1 224nm

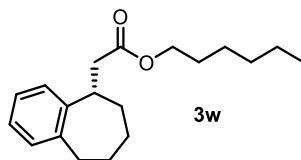
Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.683	3507435	50.079	208320	52.195
2	12.637	3496379	49.921	190801	47.805
Total		7003813	100.000	399121	100.000

mAU



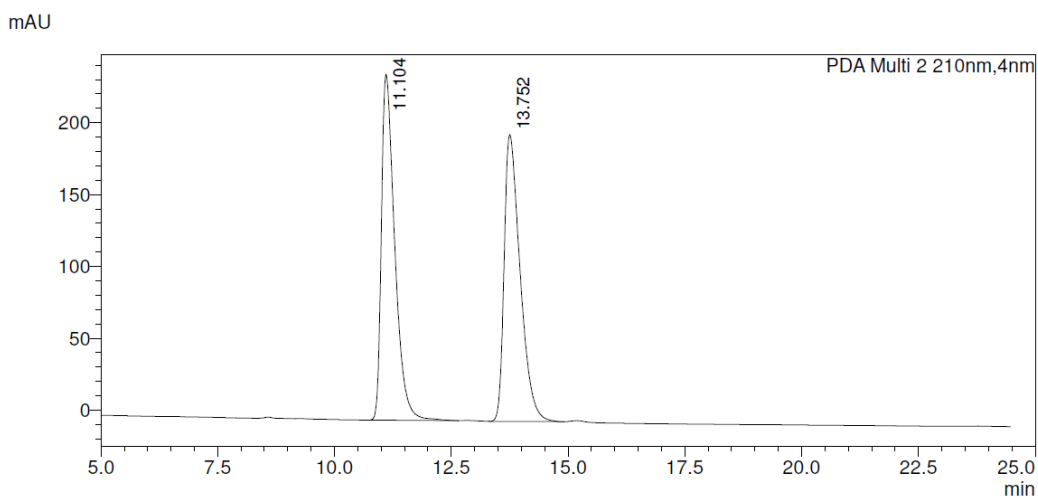
PDA Ch1 224nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.122	22729071	96.692	902909	95.315
2	13.145	777618	3.308	44379	4.685
Total		23506689	100.000	947288	100.000

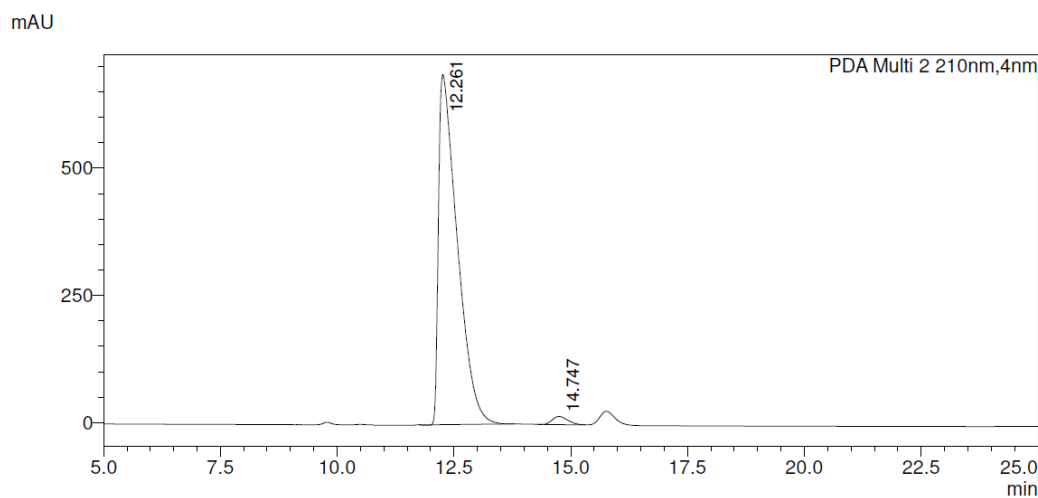


0.3%(95%hex, 5%EtOH, 0.2%TFA, 0.1%DEA), 99.7% hexanes, 0.8ml/min, CHIRALPAK IA-3

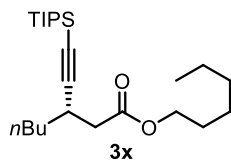
98.1:1.9 e.r.



PDA Ch2 210nm				
Peak#	Ret. Time	Area	Height	Area%
1	11.104	4786878	240525	50.223
2	13.752	4744335	199572	49.777
Total		9531213	440096	100.000

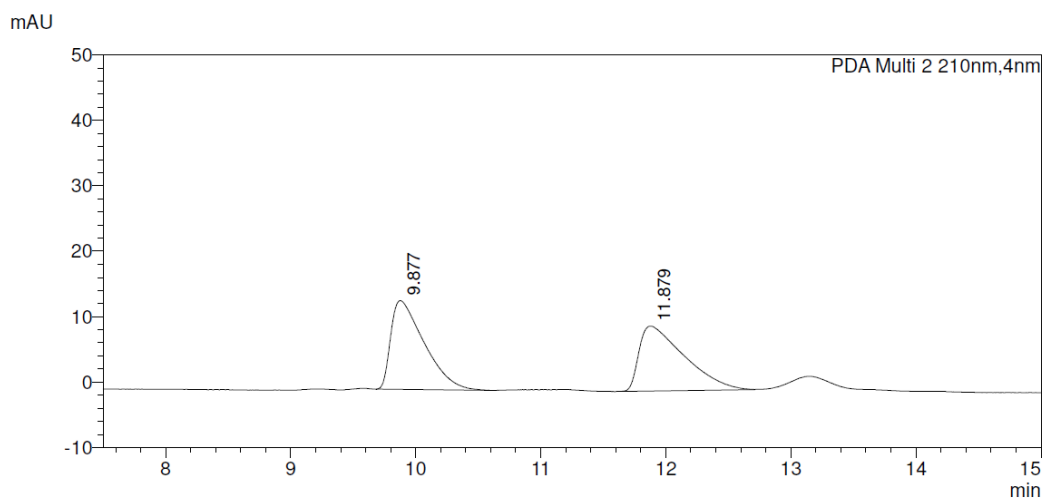


PDA Ch2 210nm				
Peak#	Ret. Time	Area	Height	Area%
1	12.261	19173915	688179	98.073
2	14.747	376728	16244	1.927
Total		19550644	704422	100.000

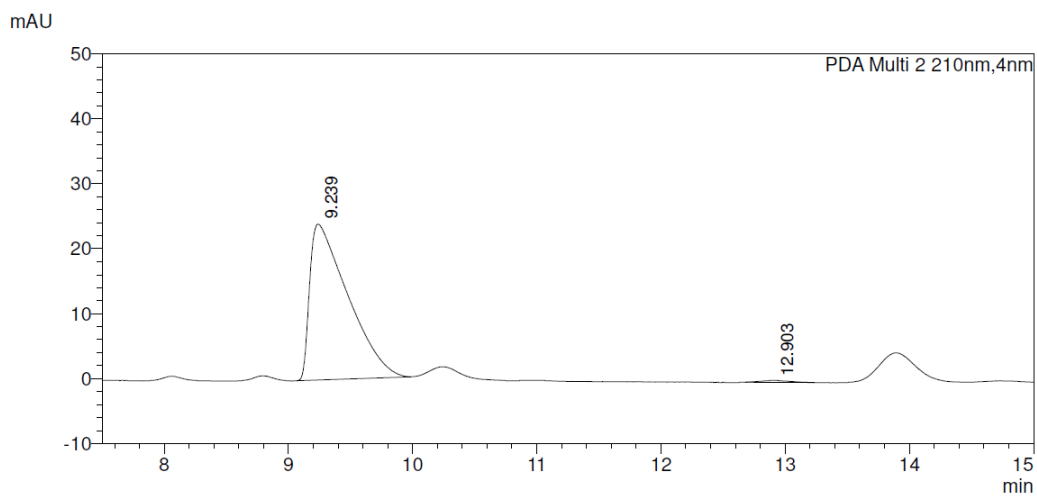


100% Hex, 1.0 mL/min, CHIRALPAK IC-3

99.1 : 0.9 e.r.

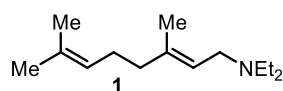


PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.877	252315	50.291	13580	57.771
2	11.879	249398	49.709	9927	42.229
Total		501713	100.000	23507	100.000



PDA Ch2 210nm					
Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.239	512507	99.094	23989	98.840
2	12.903	4688	0.906	281	1.160
Total		517194	100.000	24270	100.000

E. Allylic Amine Synthesis and Characterization

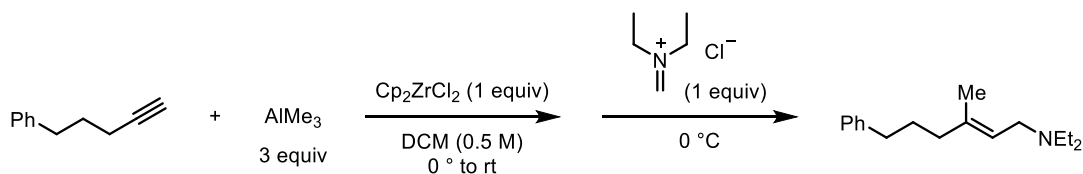


(E)-N,N-diethyl-3,7-dimethylocta-2,6-dien-1-amine

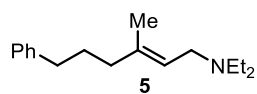
Synthesized according to literature precedent.¹

¹H NMR (500 MHz, CDCl₃) δ 5.28 – 5.21 (m, 1H), 5.08 (tt, *J* = 6.9, 1.5 Hz, 1H), 3.05 (d, *J* = 6.9 Hz, 2H), 2.51 (q, *J* = 7.2 Hz, 4H), 2.09 (q, *J* = 7.4 Hz, 2H), 2.05 – 1.99 (m, 2H), 1.67 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 137.73, 131.57, 124.38, 121.99, 50.71, 46.81, 39.99, 26.59, 25.85, 17.82, 16.44, 11.98.



(E)-N,N-diethyl-3-methyl-6-phenylhex-2-en-1-amine: Zirconocene dichloride (5.80 g, 20.0 mmol, 1.0 equiv) was added to a dry 250-mL round-bottomed flask under N₂ atmosphere followed by 40 mL dry methylene chloride. The mixture was cooled to 0 °C with stirring. Trimethylaluminum (2 M in Hexanes) (30 mL, 60.0 mmol, 3.0 equiv) was added slowly *via* syringe. The reaction mixture stirred at 0 °C for 10 min. The reaction mixture turned yellow after stirring. 5-phenyl-1-pentyne (3.0 mL, 20.0 mmol) was then added to the reaction mixture *via* syringe. After addition of the alkyne, the flask was warmed to rt and stirred overnight. The reaction flask was cooled to 0 °C followed by addition of *N*-ethyl-*N*-methyleneethaniminium chloride (2.42 g, 20 mmol, 1.0 equiv) in 10 mL dry methylene chloride (*N*-ethyl-*N*-methyleneethaniminium chloride solution was made in a N₂ glovebox). The reaction mixture stirred for an additional 2.5 h, after which it was quenched at 0 °C with sat. NH₄Cl. The crude reaction mixture was filtered over celite. The filtrate was dried with anhydrous Na₂SO₄, filtered, and the solvent was removed *in vacuo*. The crude oil was purified *via* flash column chromatography on silica gel with 1% MeOH/10% Et₂O/89% (3% NH₃/DCM). The product was then distilled at reduced pressure (106–108 °C at 0.176 Torr) to yield 1.45 g (33%) of a clear, colorless oil.

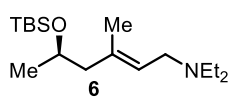


(E)-N,N-diethyl-3-methyl-6-phenylhex-2-en-1-amine C₁₇H₂₇N

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.15 (m, 3H), 5.29 (tq, *J* = 6.8, 1.3 Hz, 1H), 3.07 (d, *J* = 6.8 Hz, 2H), 2.61 – 2.56 (m, 2H), 2.51 (q, *J* = 7.2 Hz, 4H), 2.06 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.64 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 142.78, 137.61, 128.56, 128.39, 125.77, 122.18, 50.67, 46.85, 39.57, 35.65, 29.73, 16.42, 12.00.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₇H₂₈N, 246.2222; found, 246.2217.



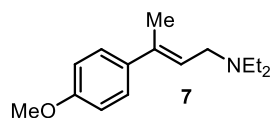
(R,E)-5-((tert-butyldimethylsilyloxy)-N,N-diethyl-3-methylhex-2-en-1-amine

C₁₇H₃₇NOSi

Synthesized according to literature precedent.¹

¹H NMR (500 MHz, CDCl₃) δ 5.28 (td, *J* = 6.6, 1.5 Hz, 1H), 3.93 (dt, *J* = 6.9, 5.9 Hz, 1H), 3.06 (d, *J* = 6.8 Hz, 2H), 2.51 (q, *J* = 7.1 Hz, 4H), 2.22 (dd, *J* = 13.1, 6.0 Hz, 1H), 2.06 (dd, *J* = 13.1, 6.8 Hz, 1H), 1.65 (s, 3H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 6H), 0.88 (s, 9H), 0.04 (d, *J* = 7.4 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 135.12, 124.68, 67.64, 50.67, 50.42, 46.86, 26.02, 23.57, 18.31, 17.16, 11.95, -4.40, -4.63.

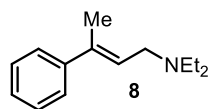


(E)-N,N-diethyl-3-(4-methoxyphenyl)but-2-en-1-amine C₁₅H₂₃NO

Synthesized according to literature precedent.¹

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.33 (m, 2H), 6.87 – 6.83 (m, 2H), 5.86 – 5.80 (m, 1H), 3.81 (s, 3H), 3.26 (dd, *J* = 6.7, 1.0 Hz, 2H), 2.58 (q, *J* = 7.1 Hz, 4H), 2.04 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 158.76, 136.23, 136.01, 126.80, 124.29, 113.68, 55.44, 51.53, 47.14, 16.24, 12.06.



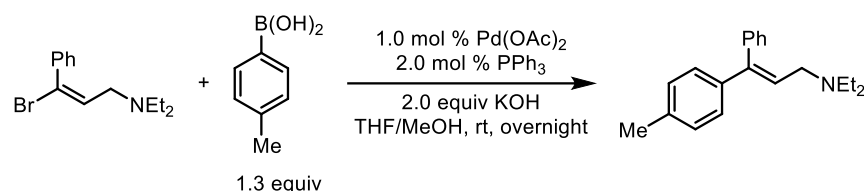
(E)-N,N-diethyl-3-phenylbut-2-en-1-amine C₁₄H₂₁N

Synthesized according to literature precedent.¹

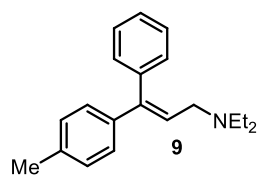
¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.39 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 5.91 (tq, *J* = 6.6, 1.4 Hz, 1H), 3.28 (dd, *J* = 6.6, 1.0 Hz, 2H), 2.58 (q, *J* = 7.2 Hz, 4H), 2.07 (d, *J* = 1.2 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 143.68, 136.65, 128.33, 126.92, 125.95, 125.79, 51.53, 47.19, 16.23, 12.08.

3,3-diaryl allylic diethylamine substrates were synthesized by the following method and the starting vinyl bromide was synthesized according to our previous report.¹



Procedure: A 50 mL round bottom flask was charged with a stir bar and 11 mg Pd(OAc)₂ (0.050 mmol, 1.0 mol %), 26 mg PPh₃ (0.10 mmol, 2.0 mol %), 0.560 g KOH (10 mmol, 2.0 equiv), starting material vinyl bromide (1.34g, 5 mmol, 1.0 equiv), 0.880 g 4-methyl boronic acid (6.5 mmol, 1.3 equiv) and 5 mL THF and 5 mL MeOH. The reaction was stirred at rt overnight followed by dilution with EtOAc, and washed by 1 N NaOH solution and brine. The organic layer was then dried over MgSO₄, concentrated *in vacuo*, purified by Al₂O₃ column chromatography: 200 g Al₂O₃ + 12 g H₂O, 30 : 1 hexanes/ EtOAc with 0.5% MeOH as eluent.



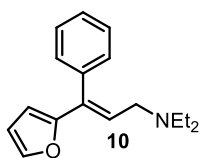
(E)-N,N-diethyl-3-phenyl-3-(p-tolyl)prop-2-en-1-amine C₂₀H₂₅N

Prepared according to the above procedure and isolated at 70% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.34 – 7.29 (m, 1H), 7.18 – 7.12 (m, 4H), 7.10 – 7.06 (m, 2H), 6.19 (t, *J* = 6.7 Hz, 1H), 3.15 (d, *J* = 6.8 Hz, 2H), 2.52 (q, *J* = 7.2 Hz, 4H), 2.32 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 143.24, 140.11, 139.65, 137.01, 129.97, 128.96, 128.21, 127.27, 127.15, 126.55, 51.86, 47.13, 21.20, 11.96.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₀H₂₆N, 280.2065; found, 280.2070.



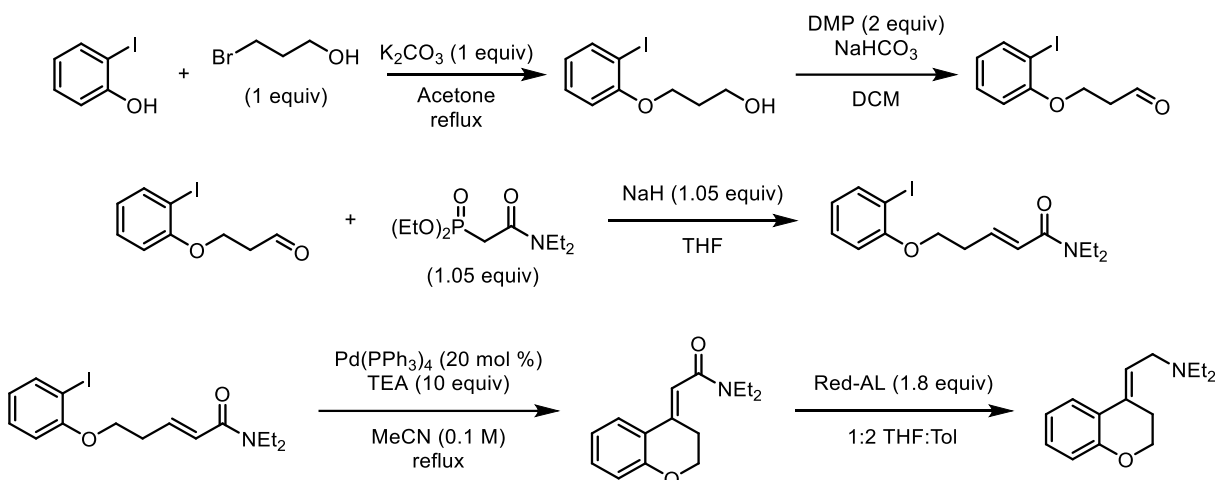
(E)-N,N-diethyl-3-(furan-2-yl)-3-phenylprop-2-en-1-amine C₁₇H₂₁NO

Prepared according to the above procedure and isolated at 69% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.32 (m, 4H), 7.25 – 7.22 (m, 2H), 6.40 (t, J = 7.0 Hz, 1H), 6.31 (dd, J = 3.3, 1.8 Hz, 1H), 5.80 (d, J = 3.3 Hz, 1H), 3.14 (d, J = 7.0 Hz, 2H), 2.52 (q, J = 7.1 Hz, 4H), 0.96 (t, J = 7.2 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 155.34, 142.06, 137.29, 133.58, 129.75, 128.25, 127.67, 124.13, 111.28, 108.14, 50.94, 47.02, 12.01.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₇H₂₂NO, 256.1701; found, 256.1706.



(E)-2-(chroman-4-ylidene)-N,N-diethylethan-1-amine: 2-iodophenol (4.4 g, 20 mmol), K₂CO₃ (2.8 g, 20 mmol, 1.0 equiv), 3-bromo-1-propanol (1.8 mL, 20 mmol, 1.0 equiv), and acetone (20 mL) were added to a dried 250-mL round-bottomed flask equipped with a stir bar. A reflux condenser, and the reaction mixture was stirred at reflux overnight. The reaction flask was then cooled to room temperature. The crude reaction mixture was washed with DI H₂O and extracted with EtOAc. The aqueous layer was back-extracted with methylene chloride. The combined organic layers were dried over MgSO₄. The mixture was filtered to remove solids, and the solvent was removed *in vacuo*. The crude product was used without further purification.

A 500-mL round-bottomed flask with stir bar (not dried) was charged with 3-(2-iodophenoxy)propan-1-ol (5.6 g, 20 mmol), NaHCO₃ (4 g, 47.6 mmol, 2.4 equiv), and wash bottle grade methylene chloride (100 mL).

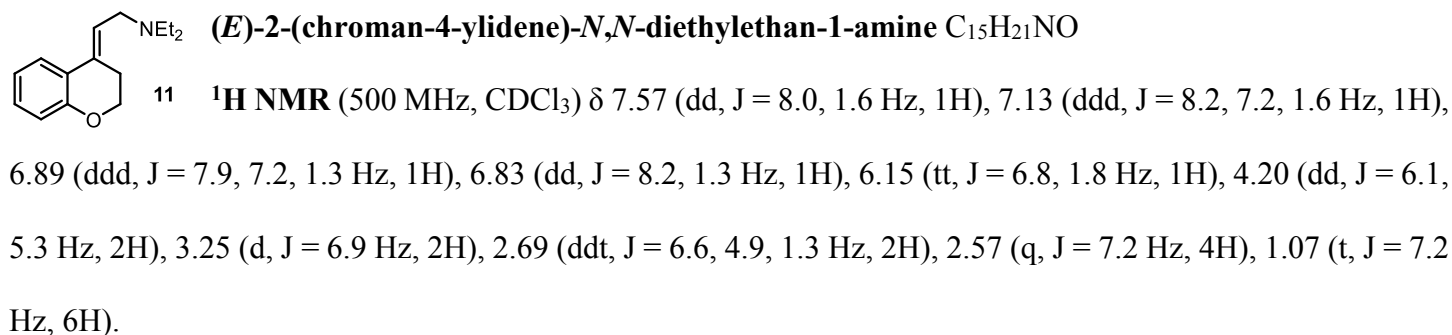
The reaction mixture was cooled to 0 °C with stirring. Dess-Martin periodinane (17 g, 40 mmol, 2.0 equiv) was added to the stirring reaction mixture in one portion, and the reaction continued stirring for 2.5 h. The reaction mixture was warmed to room temperature and filtered over a bed of celite. The filtrate was washed with sat. NaHCO₃. The combined aqueous layers were extracted with methylene chloride. The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. The crude product was purified *via* flash column chromatography over silica gel with 10% to 20% to 30% EtOAc/Hex. The product was obtained as an orange oil (4.2 g, 76% yield).

A 250-mL round-bottomed flask was equipped with a magnetic stir bar and dried. NaH (60% dispersion in mineral oil) (0.63 g, 15.75 mmol, 1.05 equiv) was added to the flask and then placed under N₂ atmosphere. Dry THF (25 mL) was added to the flask *via* syringe. The reaction flask was then cooled to 0 °C. **Diethyl (2-(diethylamino)-2-oxoethyl)phosphonate** was added dropwise *via* syringe. The reaction mixture was stirred until clear. **3-(2-iodophenoxy)propanal** was then added to the reaction flask and stirred overnight while slowly warming to room temperature. The reaction mixture was cooled to 0 °C and then quenched with sat. NH₄Cl. The solids were filtered and the filtrate was extracted with EtOAc. The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The crude oil was purified *via* silica gel flash column chromatography (10% to 50% EtOAc/Hex gradient).

A dry 250-mL 3-necked flask equipped with a stir bar was charged with Pd(PPh₃)₄ (1.2 g, 1 mmol, 0.20 equiv) under N₂ atmosphere. Triethylamine (7 mL, 50 mmol, 10 equiv), **(E)-N,N-diethyl-5-(2-iodophenoxy)pent-2-enamide** (1.9 g, 5 mmol), and MeCN (50 mL) were then added to the reaction flask sequentially *via* syringe. The flask was topped with a reflux condenser and heated to reflux overnight. The reaction mixture was then cooled to room temperature, and the solvent was removed *in vacuo*. The crude oil was washed with DI H₂O and extracted with methylene chloride. The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The crude oil was used without further purification.

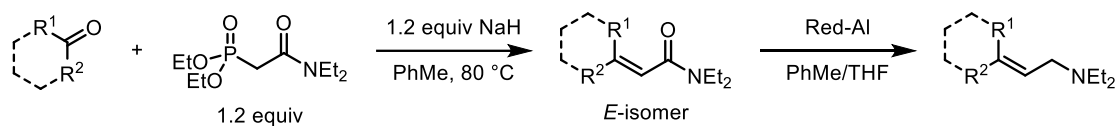
A dry 100-mL round-bottomed flask equipped with a stir bar was dried and placed under N₂ atmosphere. To the flask was added dry THF (4 mL) and dry toluene (8 mL) followed by **(E)-2-(chroman-4-ylidene)-N,N-diethylacetamide** (0.98 g, 4 mmol). The reaction solution was cooled to 0 °C. Red-AL (3.5 M in toluene) (2.4

mL, 7.2 mmol, 1.8 equiv) was added dropwise *via* syringe. The reaction flask was warmed to room temperature and stirred for 2.25 h. The reaction solution was cooled to 0 °C and quenched with NaOH (5 M aq.) The crude reaction mixture was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. The crude product was purified *via* silica gel flash column chromatography [1% MeOH/10% Et₂O/89% (3% to 7% NH₃ in DCM)]. The product was obtained in 0.583 g, 63%.



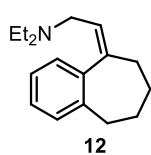
¹³C NMR (126 MHz, CDCl₃) δ 154.50, 130.23, 128.77, 124.11, 122.72, 120.94, 120.04, 117.59, 66.26, 50.55, 47.15, 26.26, 12.04.

The cyclic allylic diethylamine substrates 1k and 1m were synthesized by following method and the starting diethyl (2-(diethylamino)-2-oxoethyl) phosphonate was synthesized according to our previous report.¹



Olefination: A dry 100mL round-bottom flask was charged with a stir bar and 0.48g NaH (60 wt %, 12 mmol, 1.2 equiv), purged with nitrogen followed by the addition of 15 mL toluene. The flask was cooled to 0 °C, and diethyl (2-(diethylamino)-2-oxoethyl)phosphonate was added dropwise (2.8 mL, 12 mmol, 1.2 equiv). The reaction was stirred at 0 °C for 30 min until the solution become clear. The ketone was added dropwise (10 mmol, 1.0 equiv) to the reaction over 5 min, then warmed to 80 °C and stirred overnight. The reaction was quenched with sat. NH₄Cl solution, and the aqueous layer was extracted with DCM three times. The combined organic layers were dried over MgSO₄ and purified by silica column chromatography.

Reduction: A dry 20 mL round-bottom flask was charged with a stir bar, purged with N₂ three times, followed by the addition of unsaturated amide (4.0 mmol), dry THF (3 mL) and dry toluene (6 mL, V(tol)/V(THF)=2). The flask was then cooled in an ice bath, and RedAl solution (2.0 equiv, 3.5 M) was added dropwise. The reaction was stirred at 0 °C for 2 hours then warmed to rt for another 4 hours. The crude reaction was cooled in an ice bath and quenched by the addition of 10 mL 5 M NaOH solution and 20 mL toluene. After stirring for 30 minutes, the crude was transferred to a separatory funnel. Organic layer was separated, washed by 5 M NaOH solution twice, dried over MgSO₄, concentrated *in vacuo* and further purified by Al₂O₃ column chromatography.



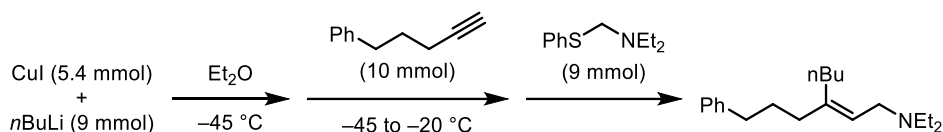
(Z)-N,N-diethyl-2-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)ethan-1-amine C₁₇H₂₅N

Prepared according to the above procedure and isolated at 25% overall yield.

¹H NMR (500 MHz, CDCl₃) δ 7.17 – 7.09 (m, 3H), 7.02 – 6.97 (m, 1H), 5.64 (t, J = 6.8 Hz, 1H), 3.00 (d, J = 6.8 Hz, 2H), 2.77 – 2.67 (m, 2H), 2.47 (q, J = 7.1 Hz, 4H), 2.33 – 2.24 (m, 2H), 1.85 (p, J = 5.9 Hz, 2H), 1.72 – 1.61 (m, 2H), 0.92 (t, J = 7.1 Hz, 6H).

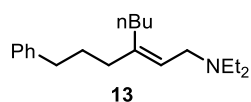
¹³C NMR (125 MHz, CDCl₃) δ 145.62, 141.73, 141.18, 129.12, 128.98, 126.92, 125.59, 124.99, 51.08, 46.81, 38.10, 36.63, 33.30, 27.87, 11.76.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₁₇H₂₆N, 244.2065; found, 244.2059.



(E)-N,N-diethyl-3-(3-phenylpropyl)hept-2-en-1-amine: CuI (1.1 g, 5.4 mmol, 0.54 equiv) and Et₂O (40 mL) were added to a dry 100-mL Schlenk flask equipped with a stir bar under atmosphere of N₂. The flask was cooled to –45 °C. *n*-butyl lithium (1.6 M in hexanes) (6 mL, 9 mmol, 0.9 equiv) was added to the reaction flask *via* syringe. The reaction mixture stirred at temperature for 30 min. 5-phenyl-1-pentyne was then added to the reaction mixture *via* syringe. The reaction was stirred at –45 °C for an additional 10 min after which it was warmed to –20 °C and stirred for an additional 2 h. The flask was then cooled to –45 °C, and *N*-ethyl-*N*-

((phenylthio)methyl)ethanamine was added to the reaction mixture *via* syringe. The flask was warmed to room temperature and allowed to stir overnight. The reaction mixture was then cooled to 0 °C and quenched with sat. NH₄Cl then NH₄OH (1 M aq.). The crude reaction mixture was filtered. The filtrate was extracted with EtOAc, dried over MgSO₄, and the solvent was removed *in vacuo*. The crude oil was dissolved in Et₂O and extracted with HCl (1 M) x3. The combined aqueous layers were basified with 10% NaOH (aq.) and extracted with methylene chloride. The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The crude oil was purified *via* basic alumina flash column chromatography (12 g DI H₂O in 300 g basic alumina; 1% to 10% MeOH/5% to 10% Et₂O/pet. ether). The product was purified again *via* silica gel flash column chromatography [1% MeOH/10% Et₂O/89%(1% to 7% NH₃ in DCM)]. The product was collected as a colorless oil in 21% yield.

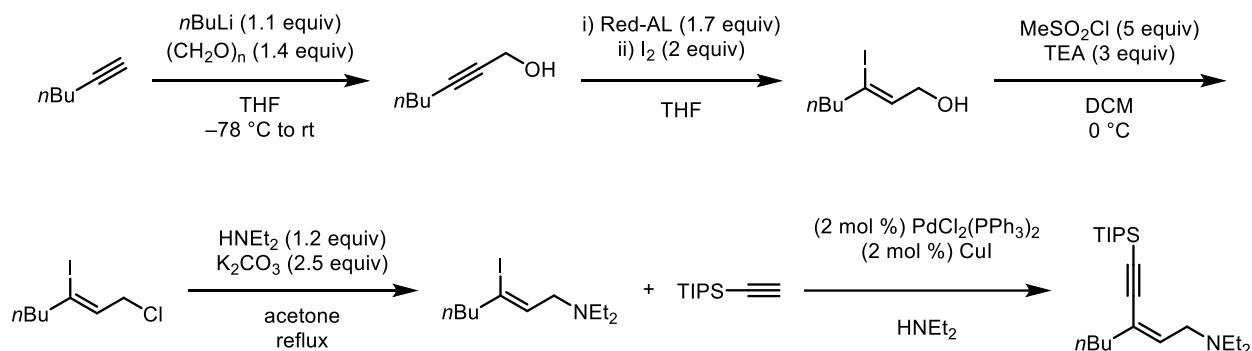


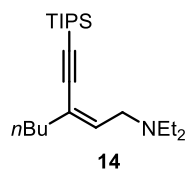
(E)-N,N-diethyl-3-(3-phenylpropyl)hept-2-en-1-amine C₂₀H₃₃N

¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 5.26 (t, J = 6.7 Hz, 1H), 3.07 (d, J = 6.7 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.51 (q, J = 7.1 Hz, 4H), 2.09 – 2.00 (m, 4H), 1.78 – 1.69 (m, 2H), 1.35 – 1.24 (m, 4H), 1.03 (t, J = 7.1 Hz, 6H), 0.90 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 142.83, 141.97, 128.55, 128.39, 125.77, 122.43, 50.49, 46.87, 36.76, 35.81, 30.90, 30.32, 30.02, 23.02, 14.20, 12.03.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₀H₃₄N, 288.2691; found, 288.2694.





(Z)-N,N-diethyl-3-((triisopropylsilyl)ethynyl)hept-2-en-1-amine C₂₂H₄₃NSi

¹H NMR (500 MHz, CDCl₃) δ 5.79 (tt, J = 7.0, 1.2 Hz, 1H), 3.37 (dd, J = 7.0, 1.1 Hz, 2H), 2.54 (q, J = 7.2 Hz, 4H), 2.15 (td, J = 7.3, 1.1 Hz, 2H), 1.52 (p, J = 7.4 Hz, 2H), 1.31 (dq, J = 14.6,

7.3 Hz, 2H), 1.09 (s, 21H), 1.04 (t, J = 7.1 Hz, 6H), 0.89 (t, J = 7.3 Hz, 3H).

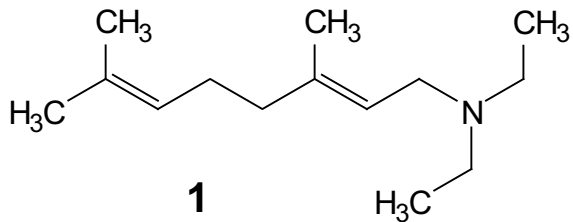
¹³C NMR (126 MHz, CDCl₃) δ 134.96, 126.05, 105.45, 95.60, 52.94, 47.14, 36.97, 30.47, 22.02, 18.81, 14.04, 12.06, 11.47.

HRMS (ESI-TOF) *m/z*: [M+H⁺] calculated for C₂₂H₄₄NSi, 350.3243; found, 350.3232.

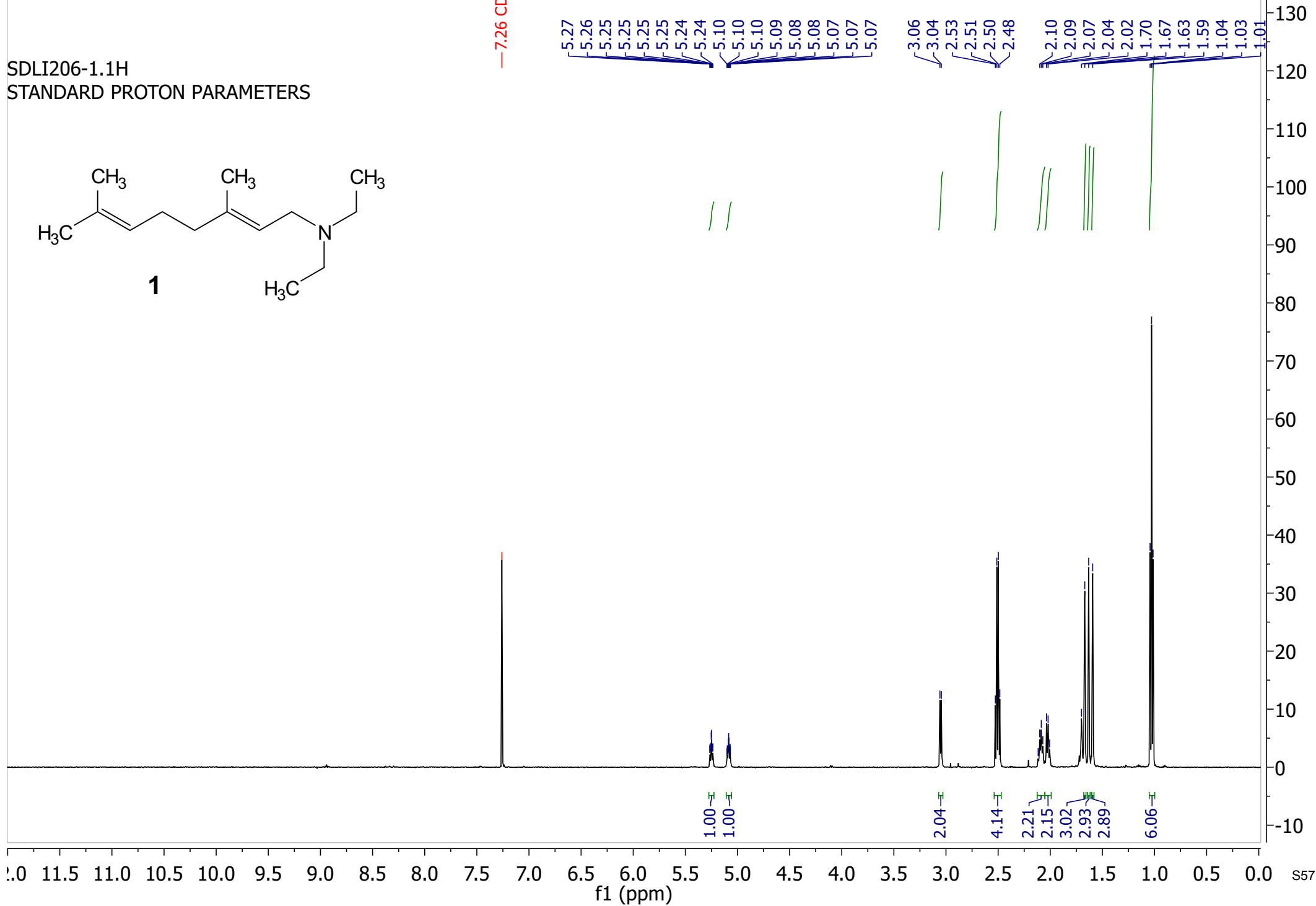
F. References

- (1) Wu, Z.; Laffoon, S. D.; Nguyen, T. T.; McAlpin, J. D.; Hull, K. L. *Angew. Chem. Int. Ed.* **2017**, *56*, 1371-1375.

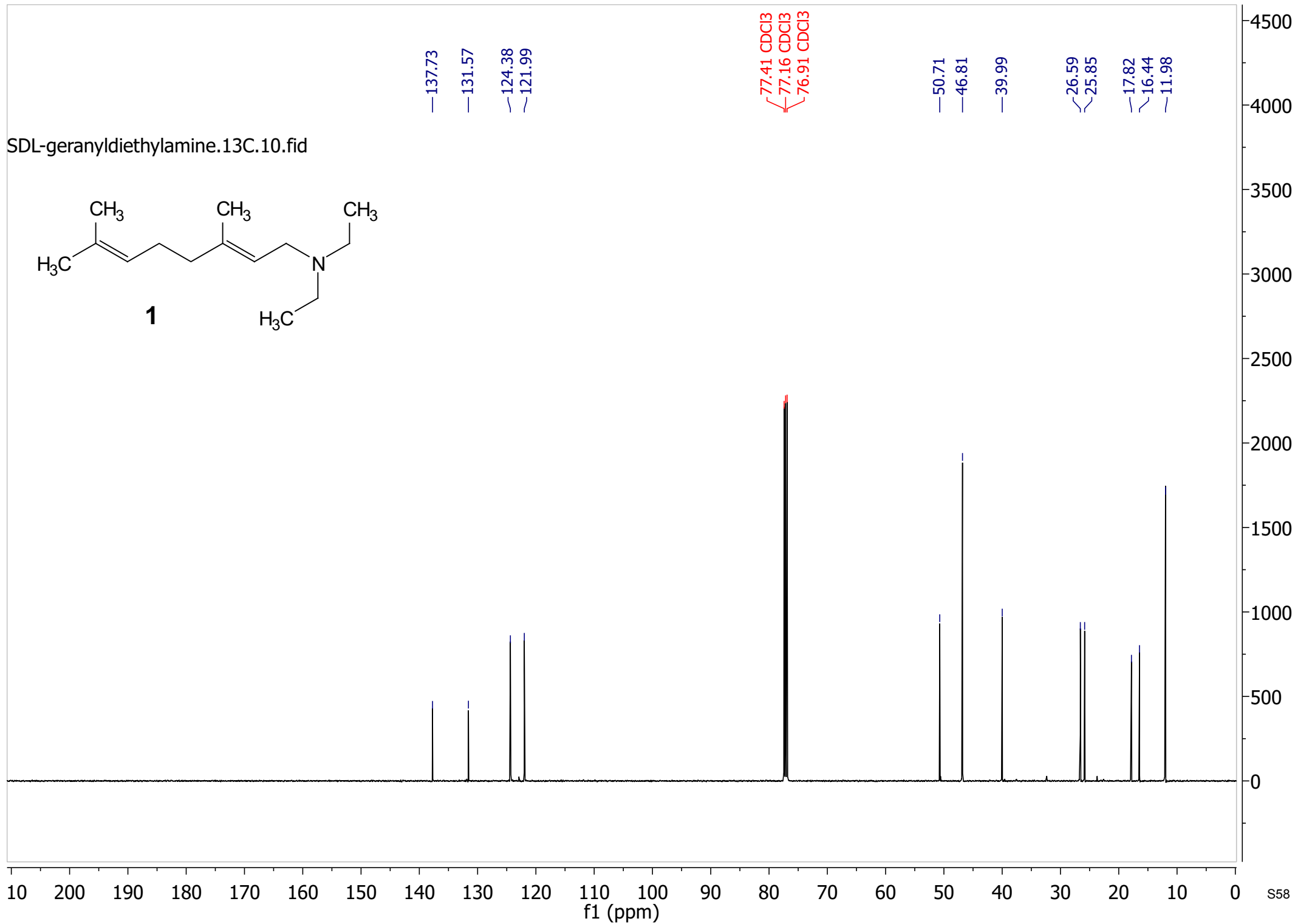
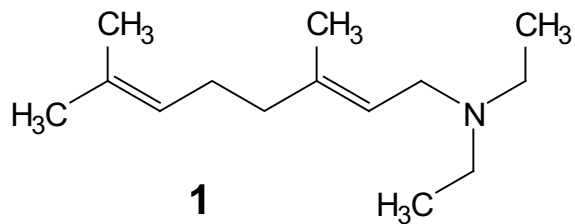
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STANDARD PROTON PARAMETERS



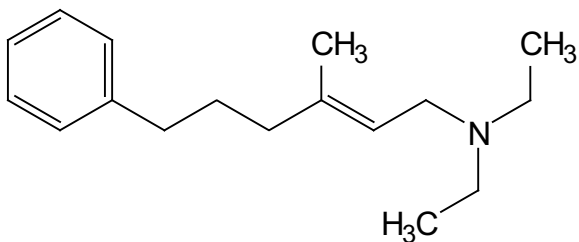
— 7.26 CDCl₃



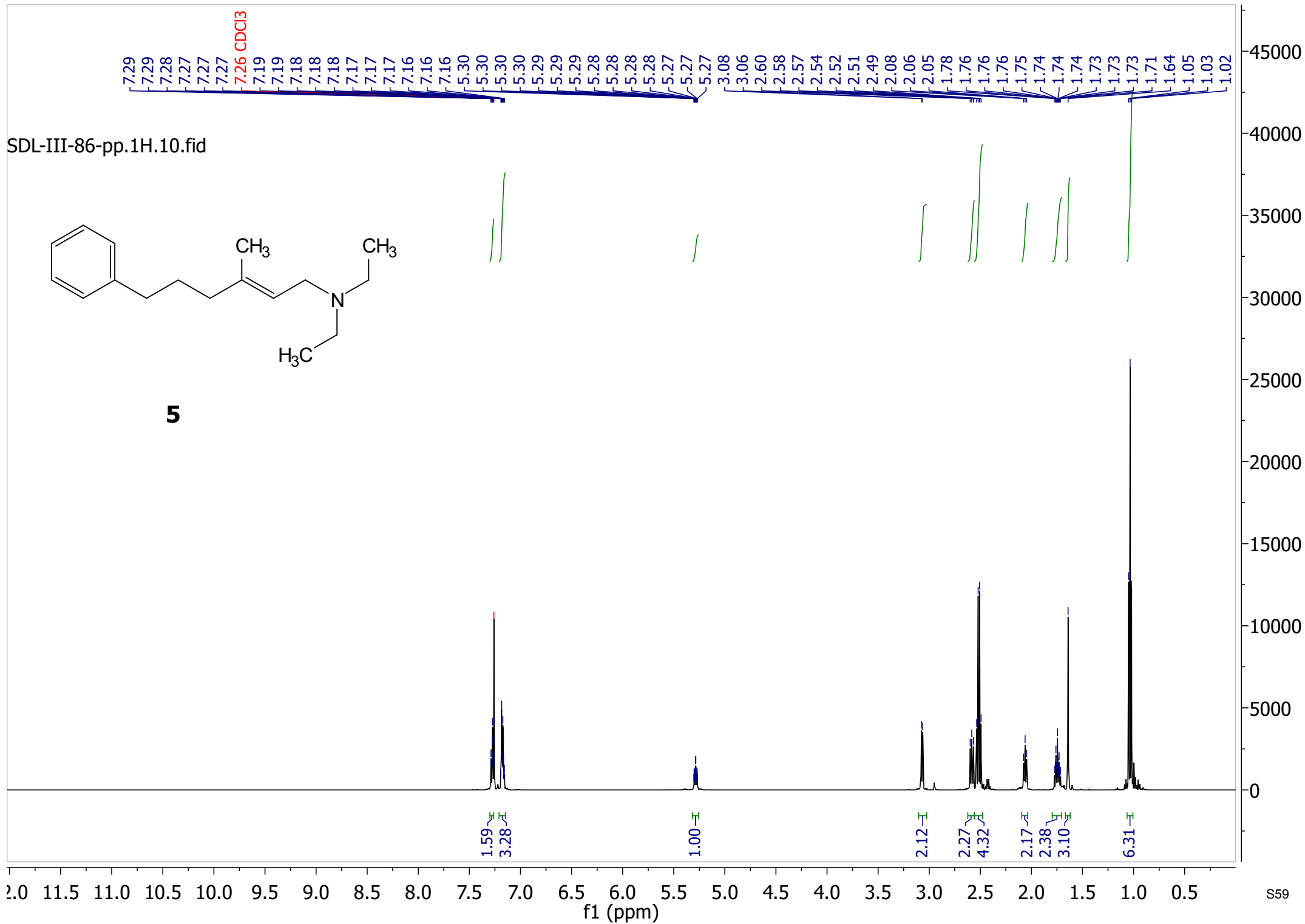
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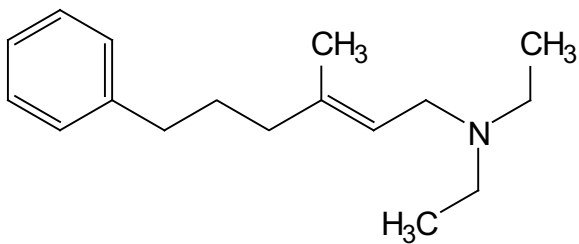
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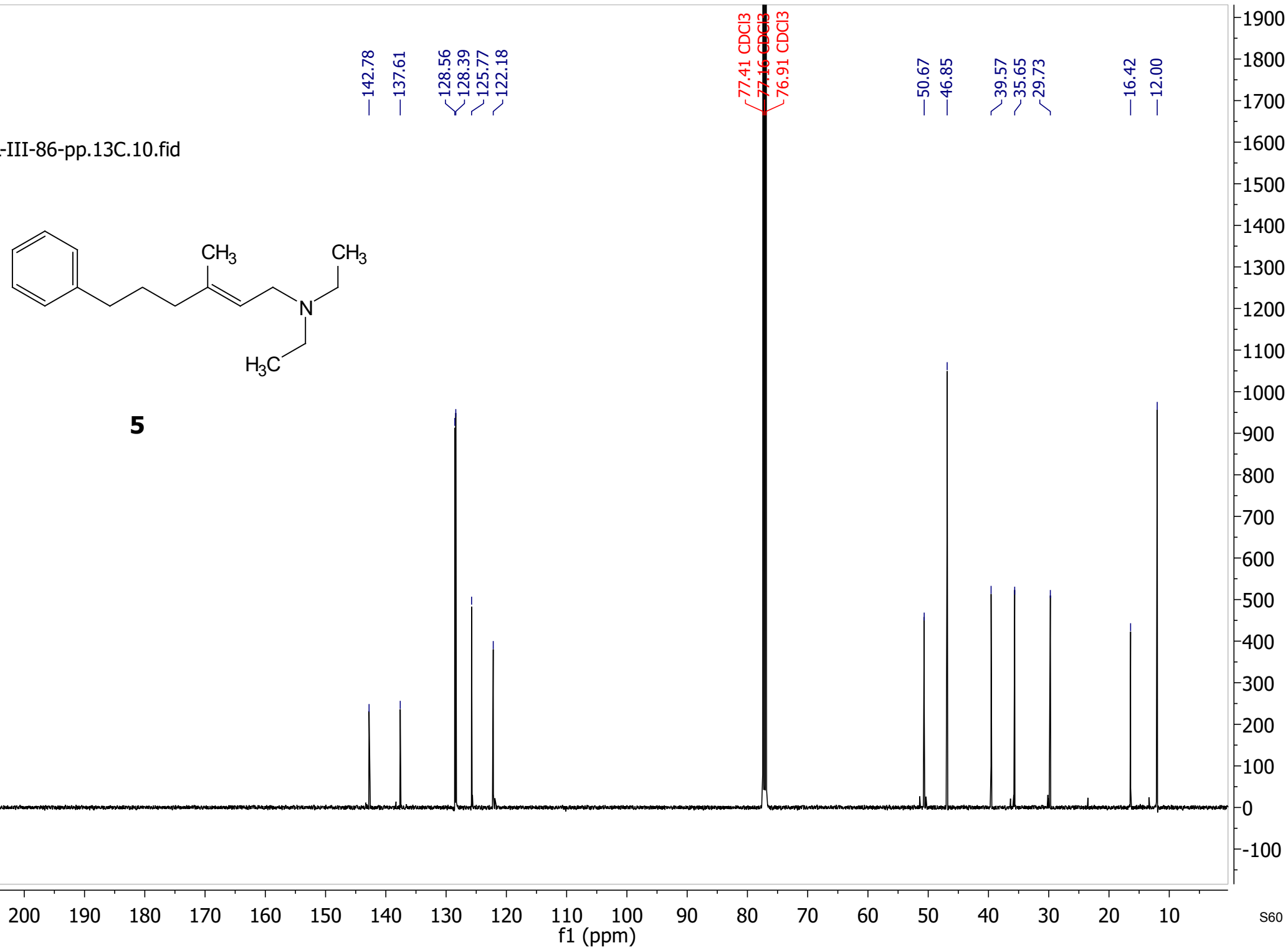
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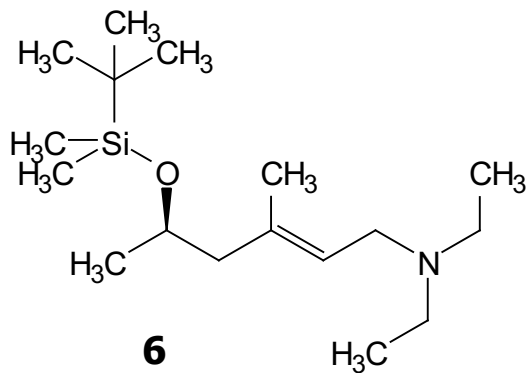
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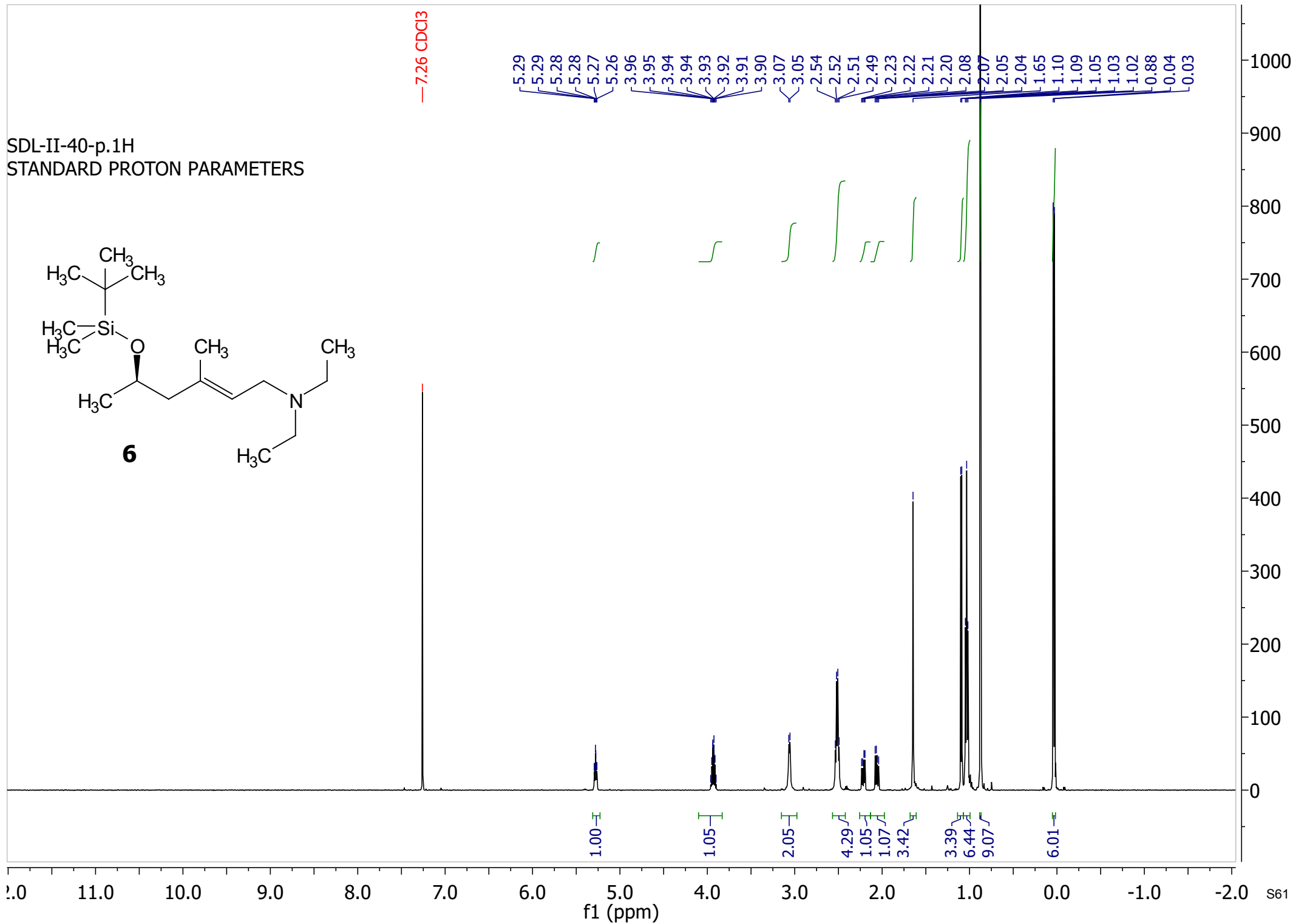
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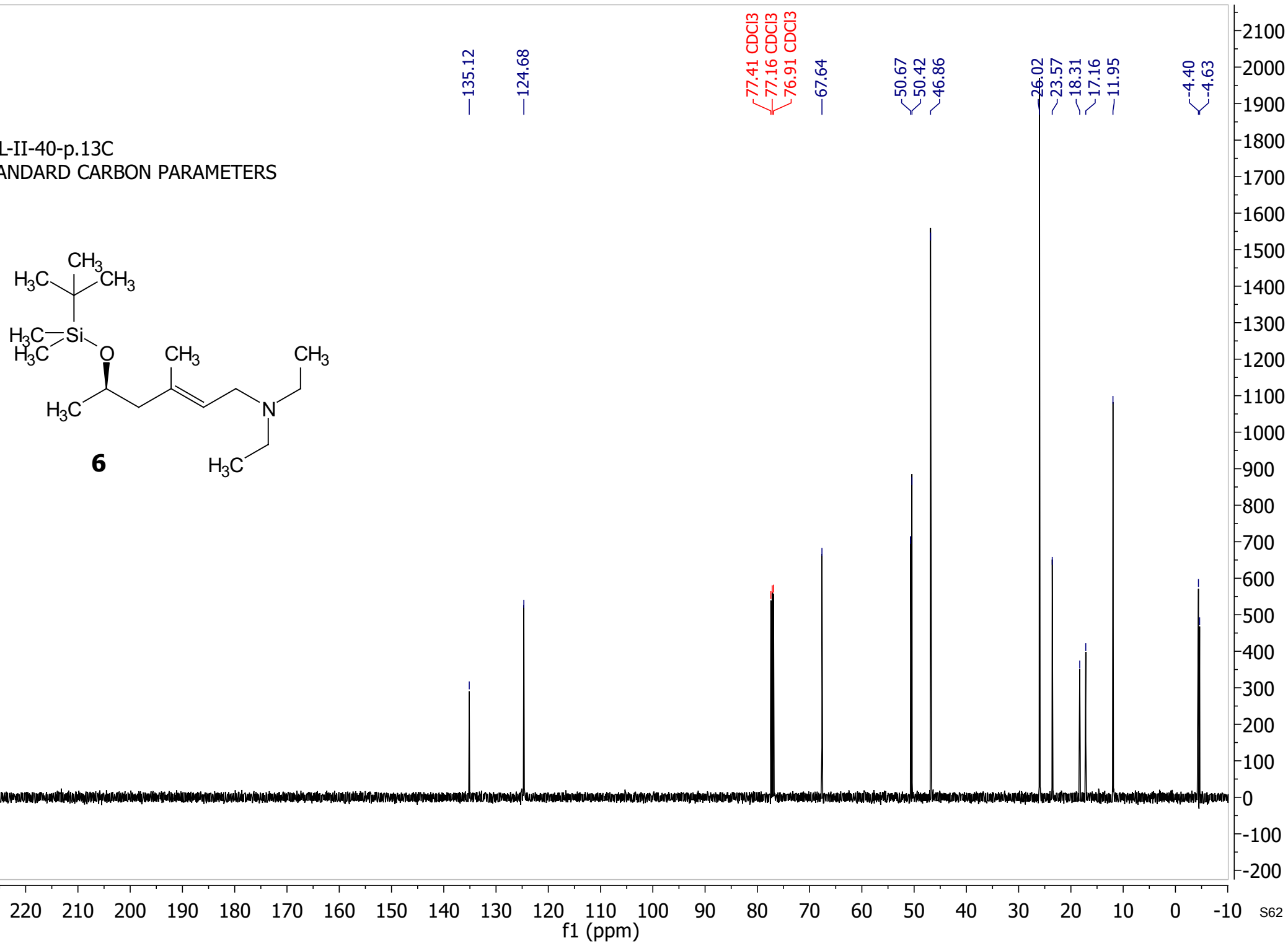
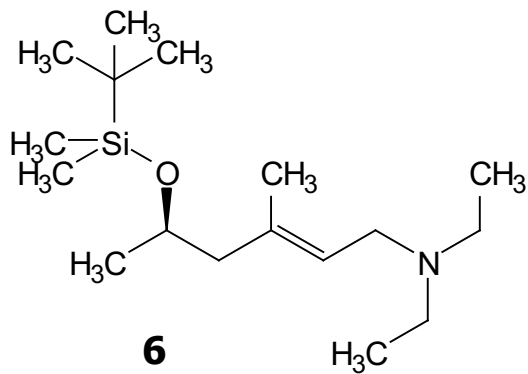
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STANDARD PROTON PARAMETERS



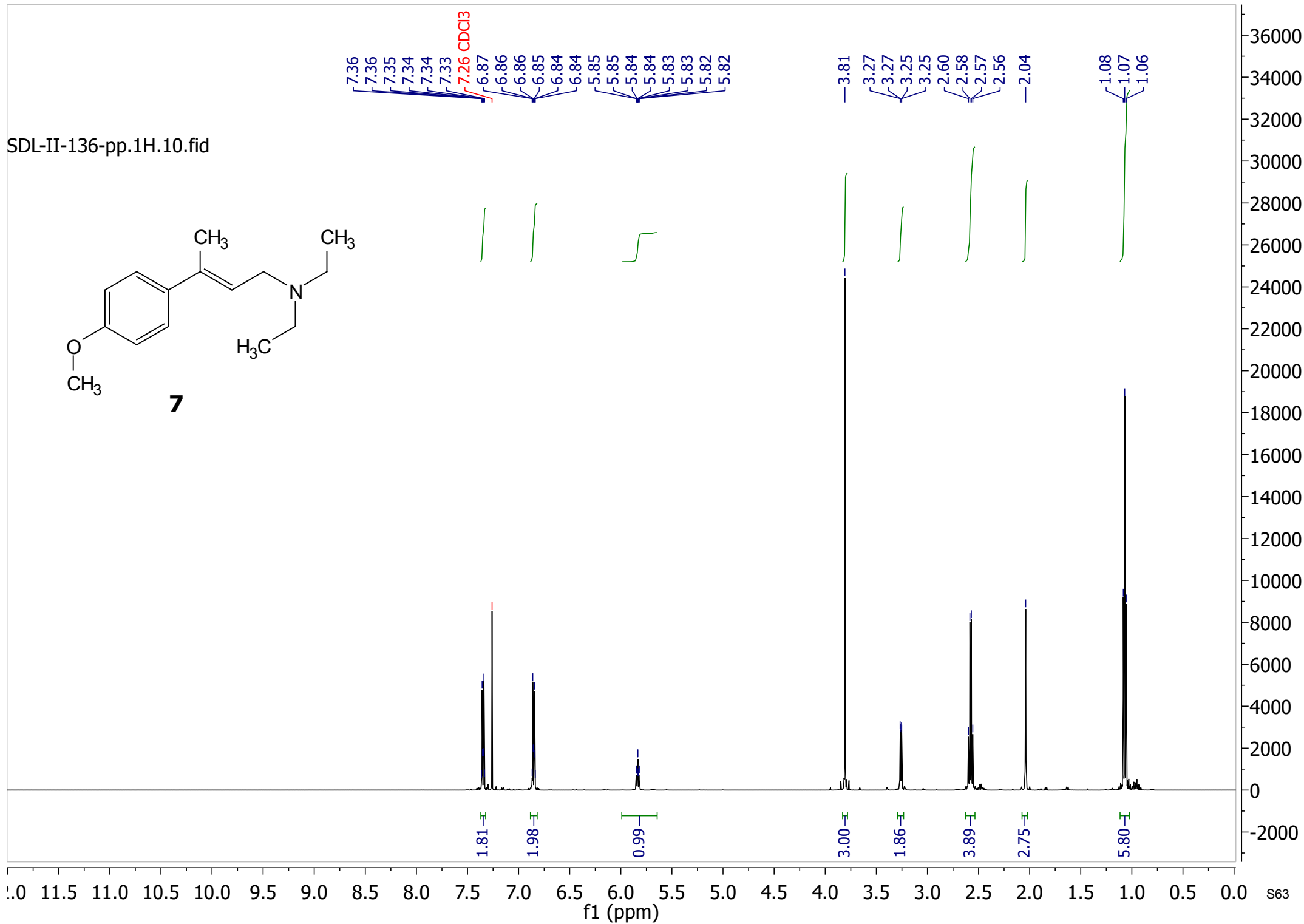
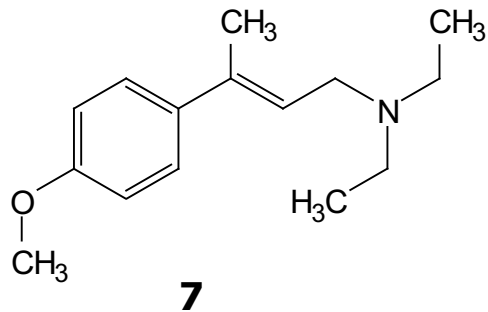
—7.26 CDCl₃



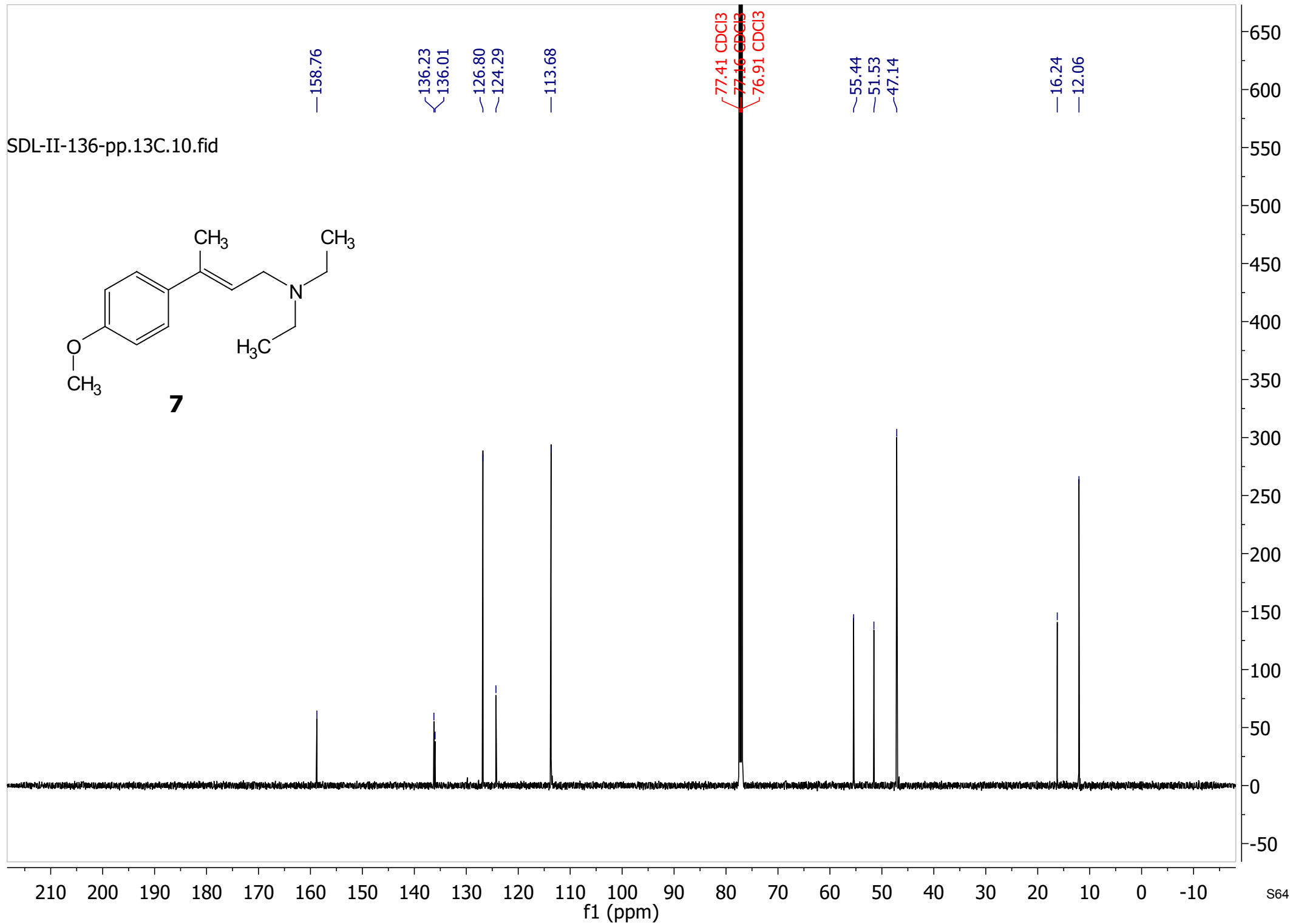
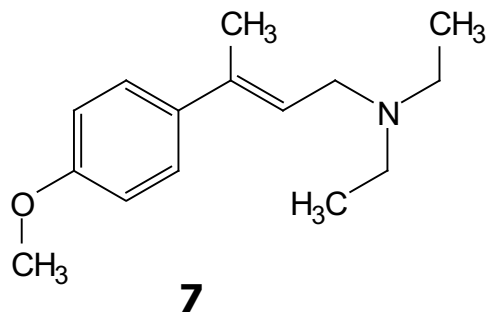
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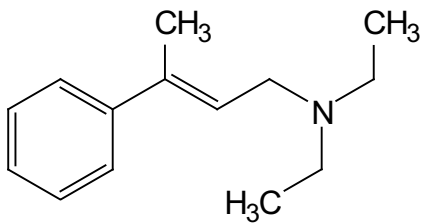
SDL-II-136-pp.1H.10.fid



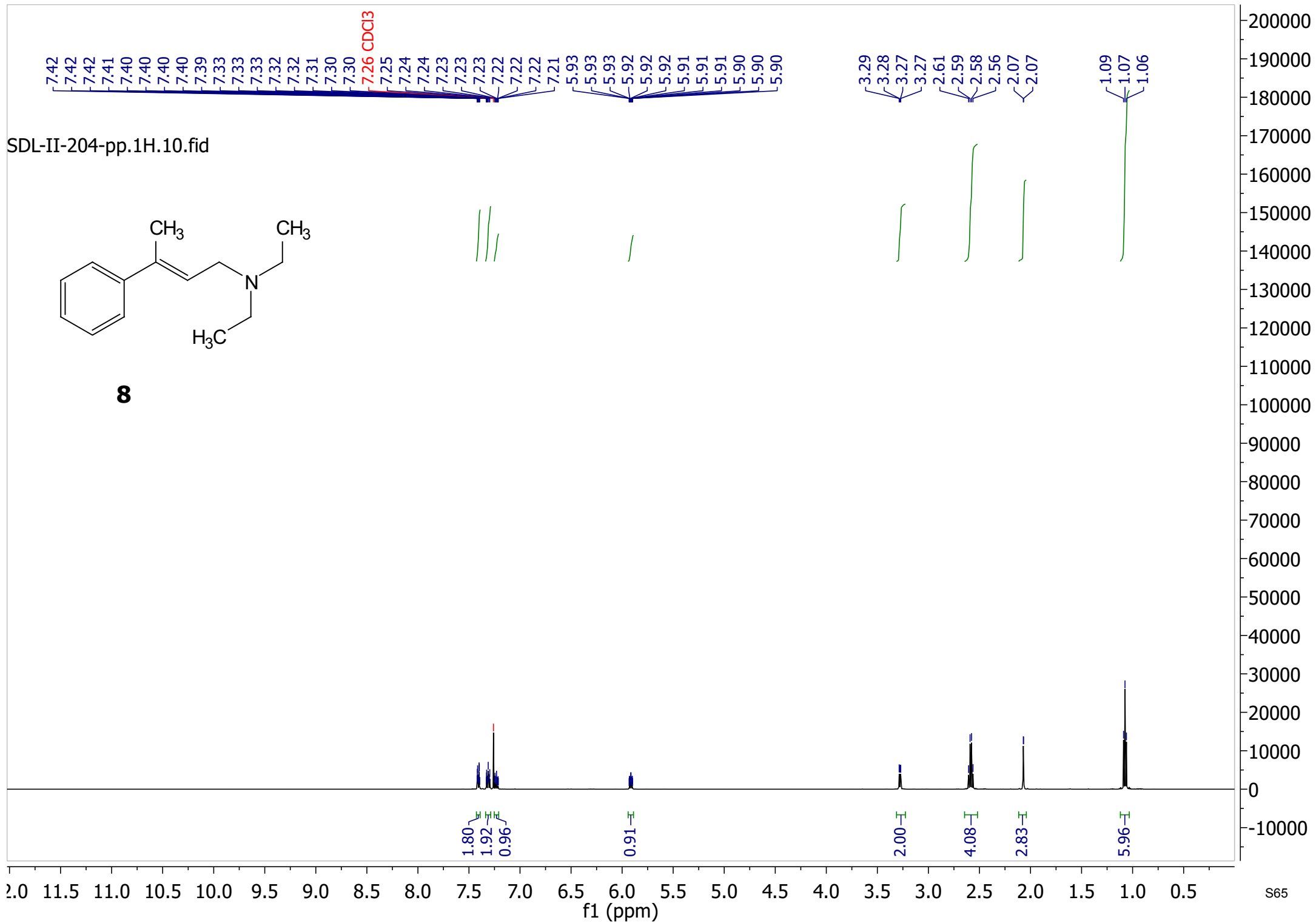
SDL-II-136-pp.13C.10.fid



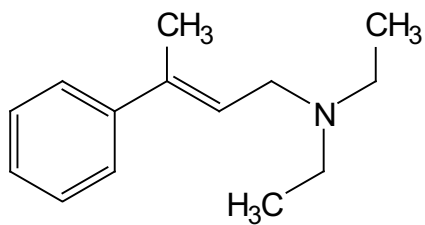
SDL-II-204-pp.1H.10.fid



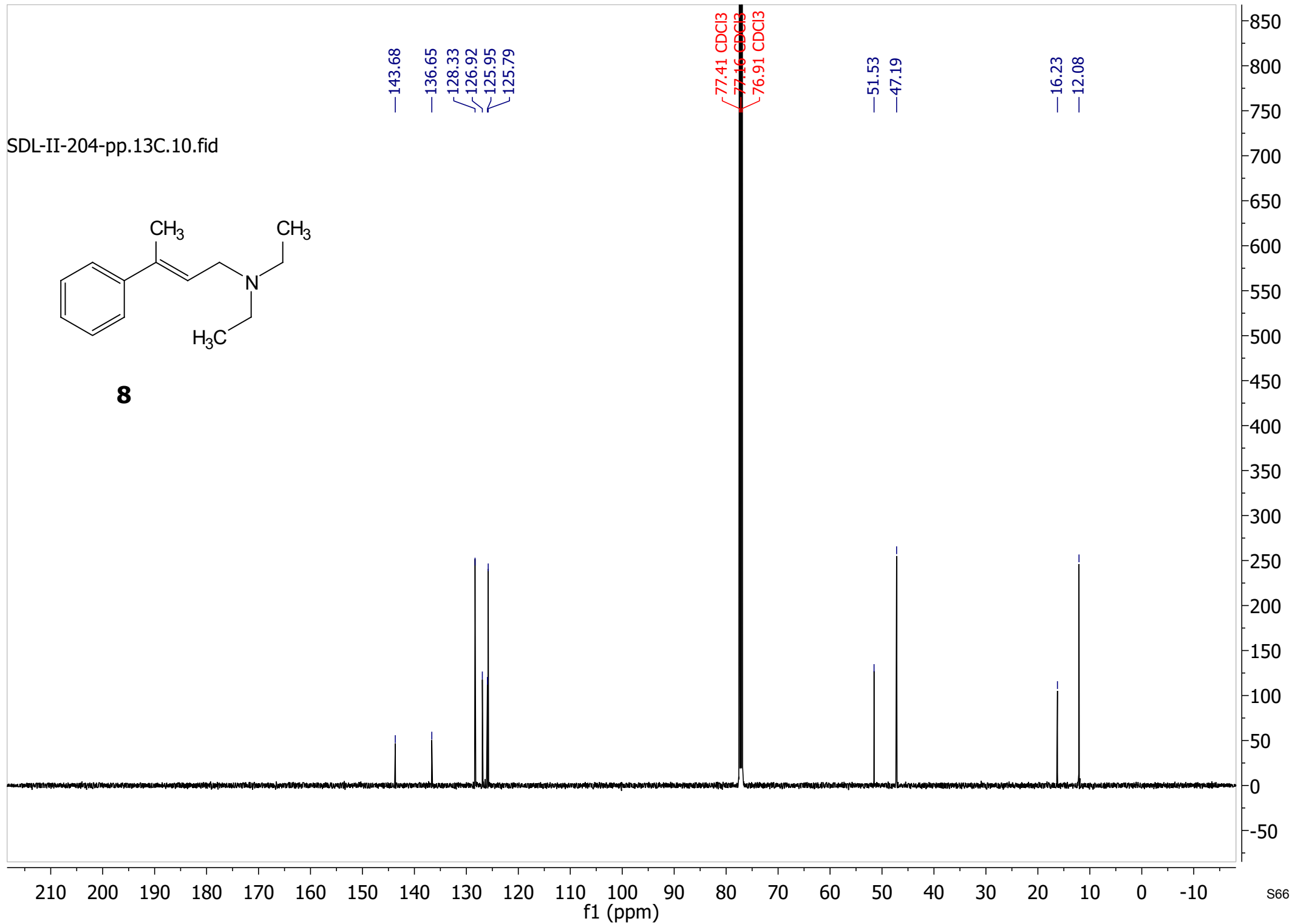
8



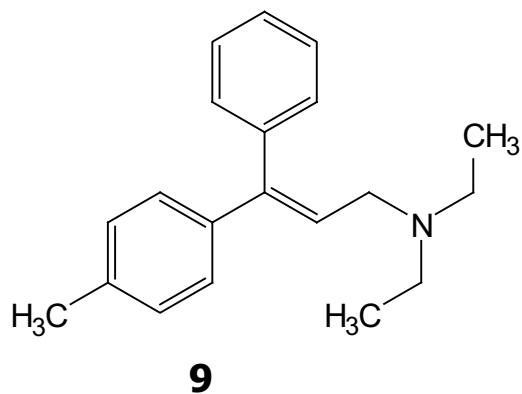
SDL-II-204-pp.13C.10.fid



8



zwu5-79-HNMR
STANDARD PROTON PARAMETERS



7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.26 CDCl3
7.17
7.16
7.16
7.15
7.15
7.15
7.15
7.15
7.14
7.13
7.13
7.08
7.08
7.08
7.07
7.07
7.07
7.07
6.21
6.19
6.18

3.16
3.14
2.55
2.53
2.52
2.50
2.32

0.98
0.96
0.95

1.92
1.02
3.84
1.90

0.99

2.00

4.12
2.91

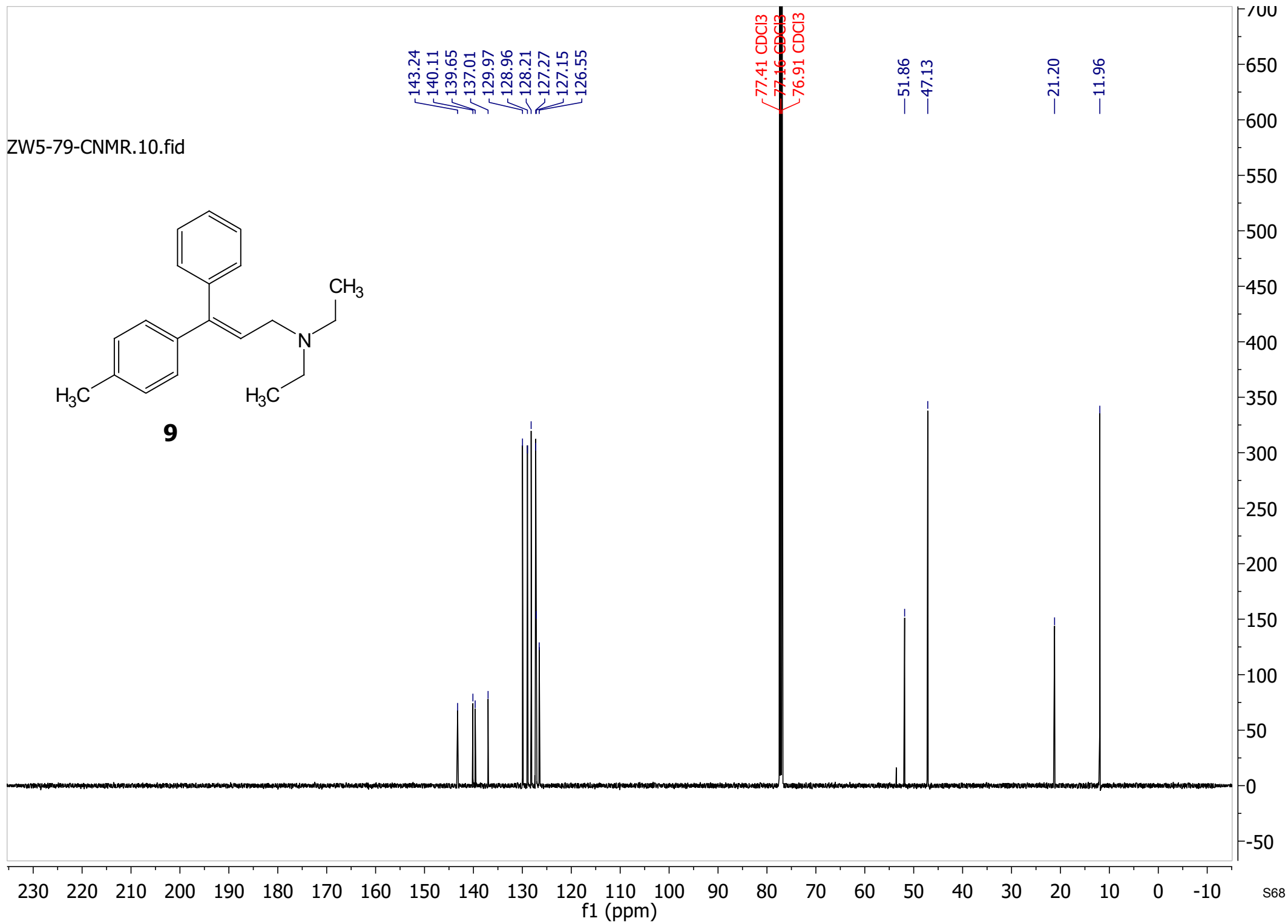
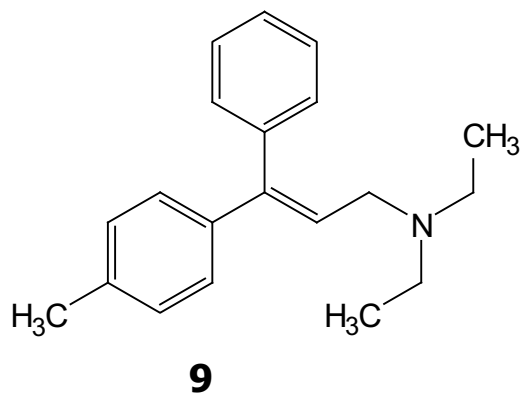
6.05

DCM

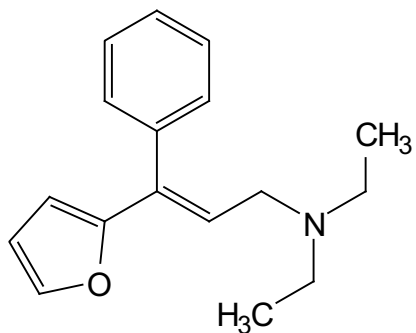
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

f1 (ppm)

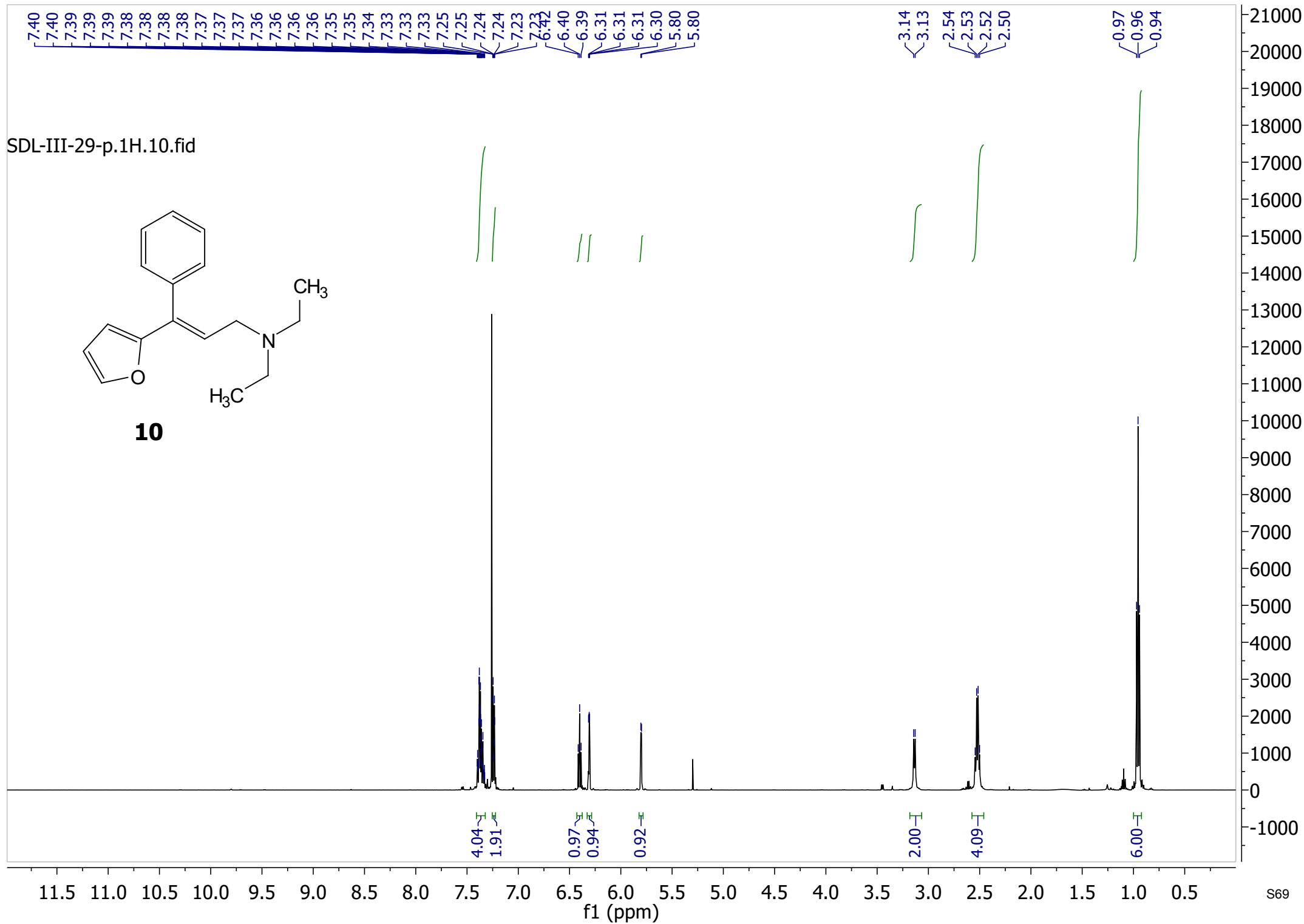
ZW5-79-CNMR.10.fid



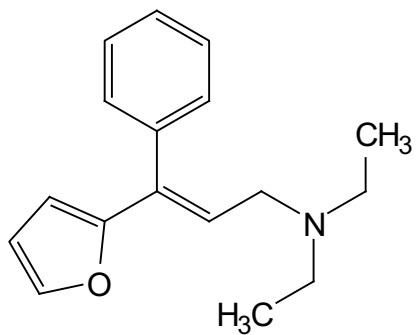
SDL-III-29-p.1H.10.fid



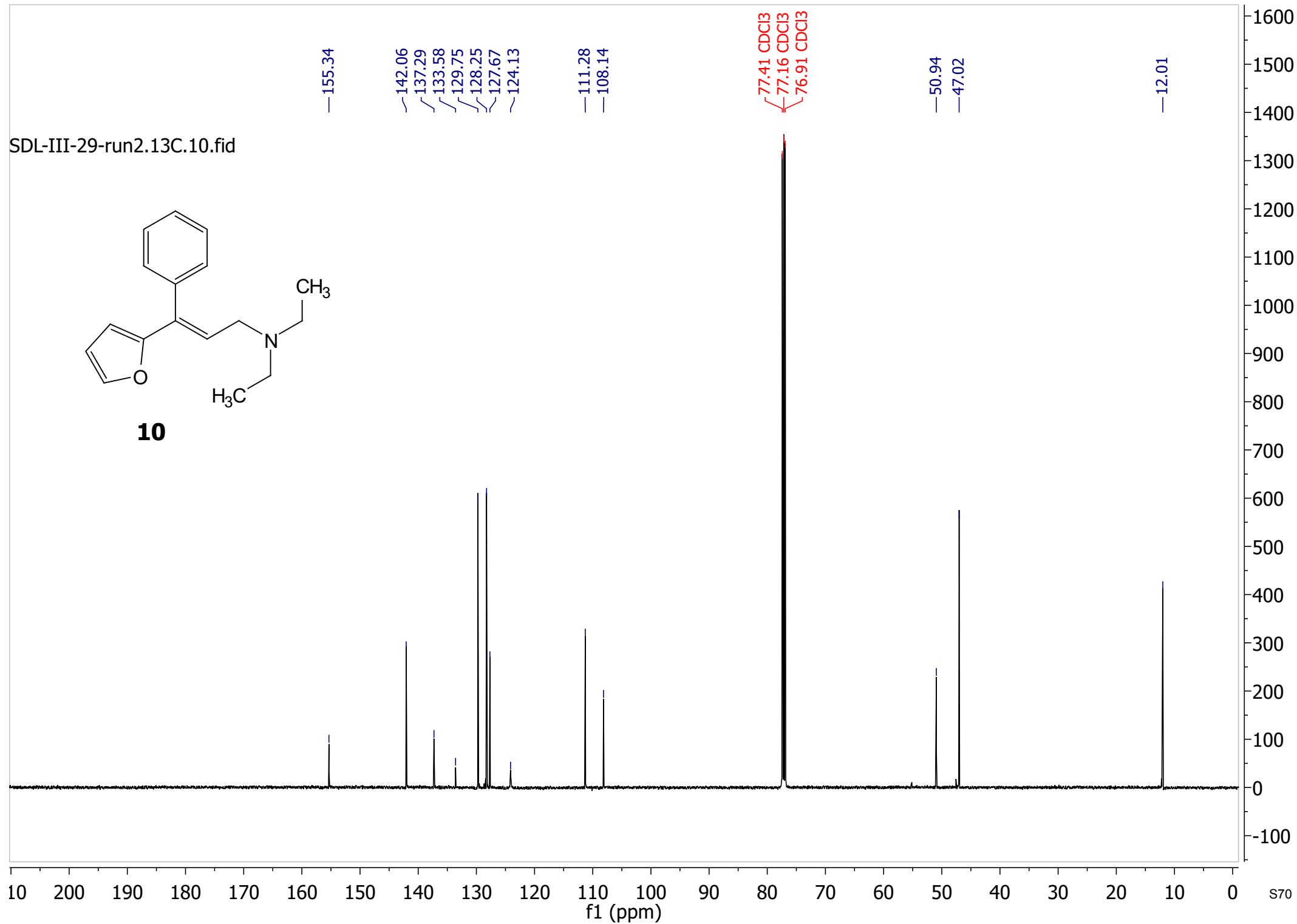
10



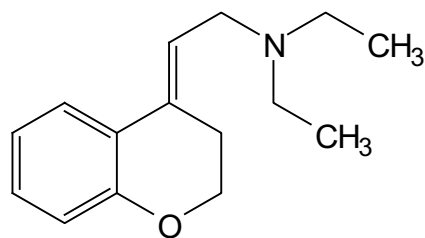
SDL-III-29-run2.13C.10.fid



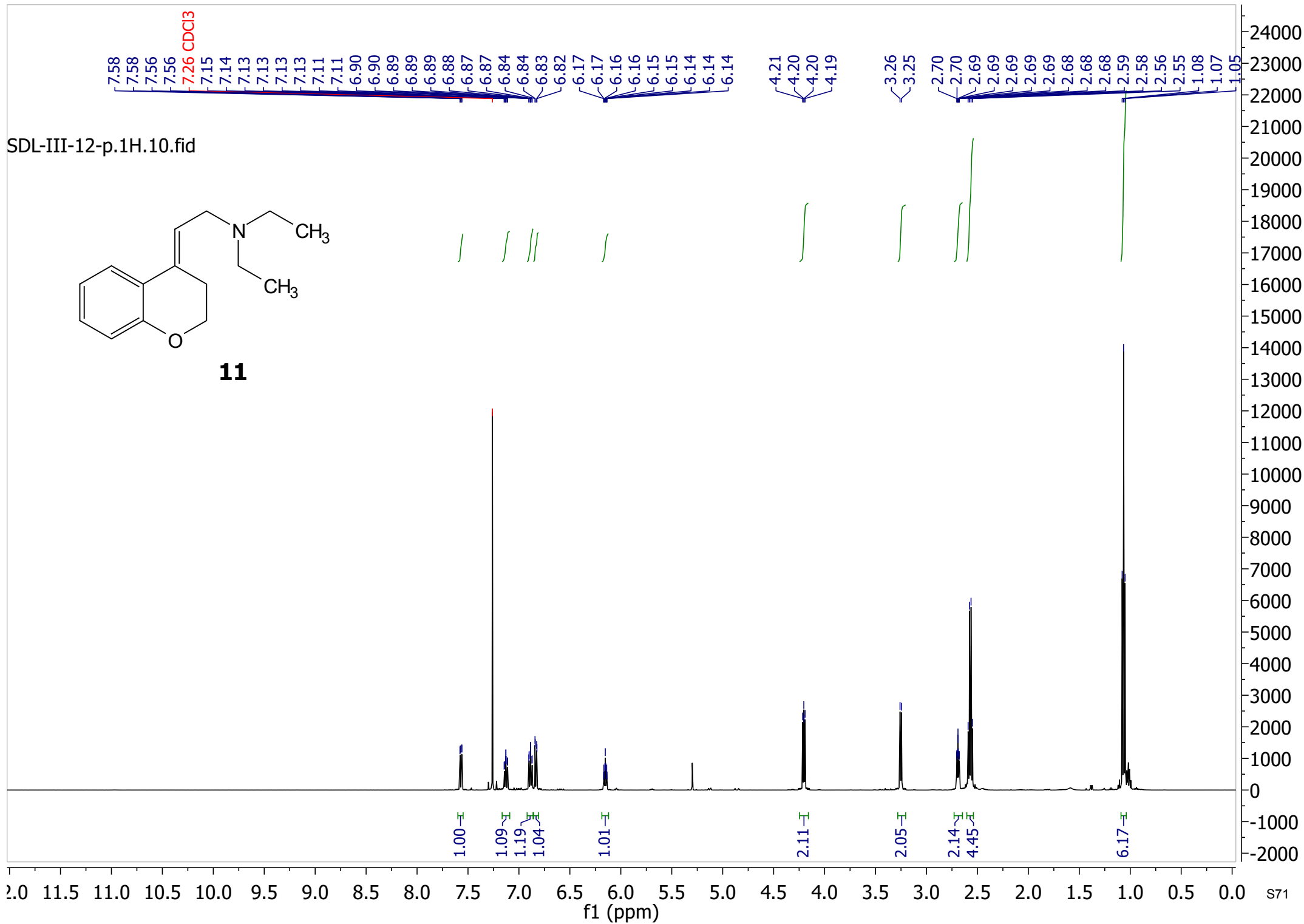
10



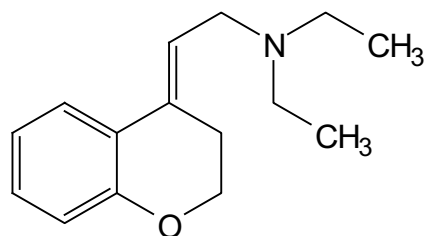
SDL-III-12-p.1H.10.fid



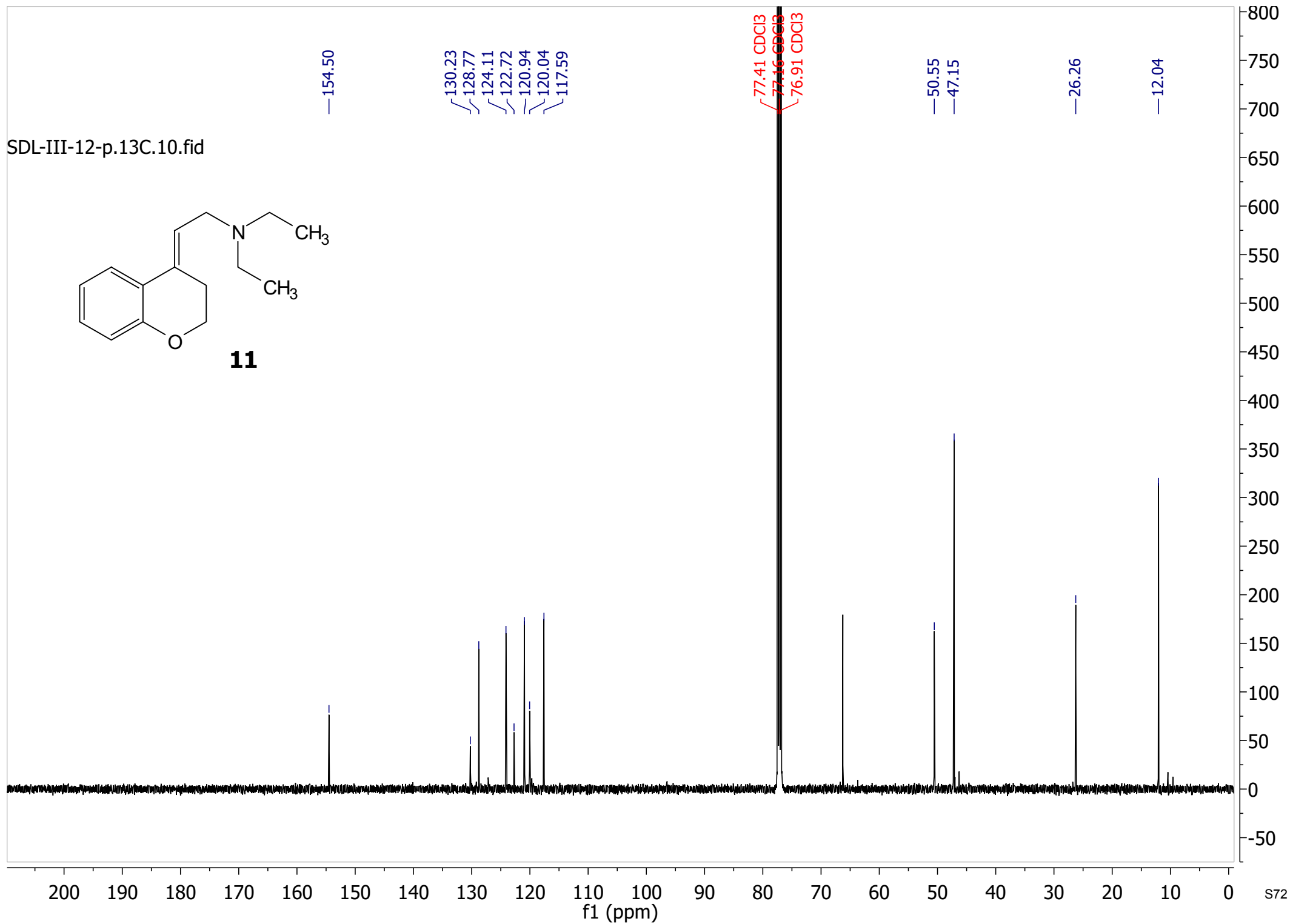
11

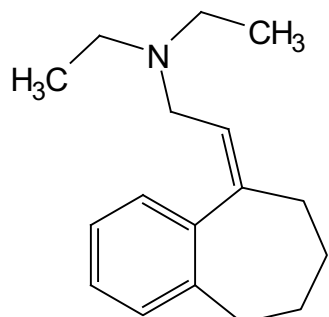


SDL-III-12-p.13C.10.fid



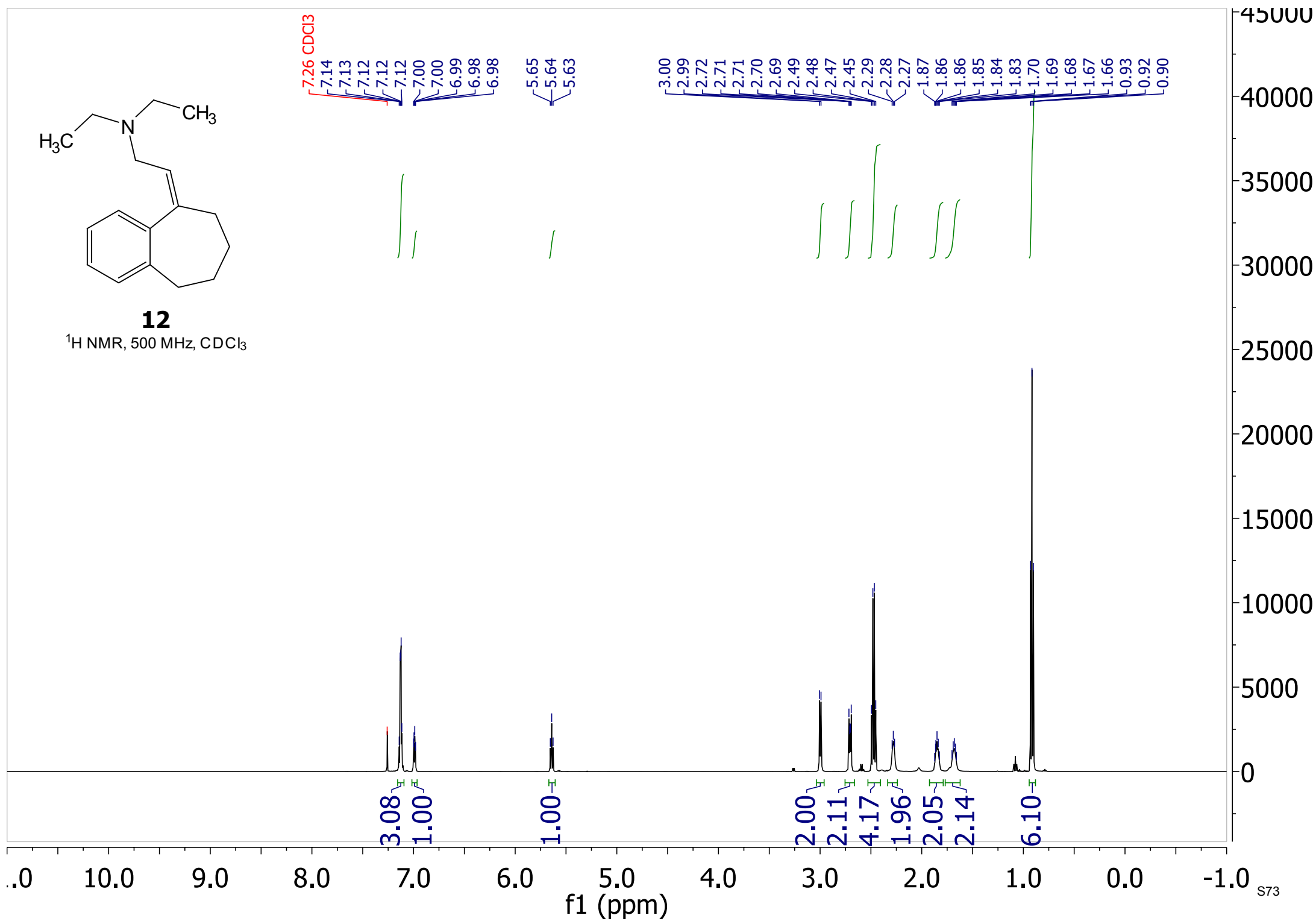
11

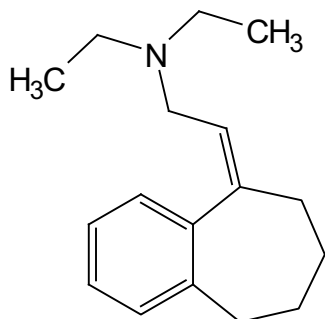




12

¹H NMR, 500 MHz, CDCl₃





12

¹³C NMR, 125 MHz, CDCl₃

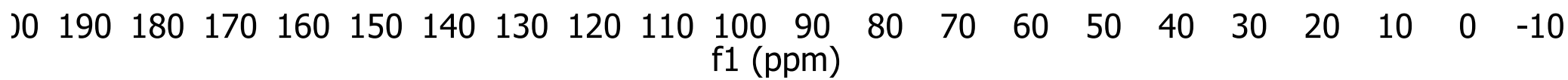
145.62
141.73
141.18
129.12
128.98
126.92
125.59
124.99

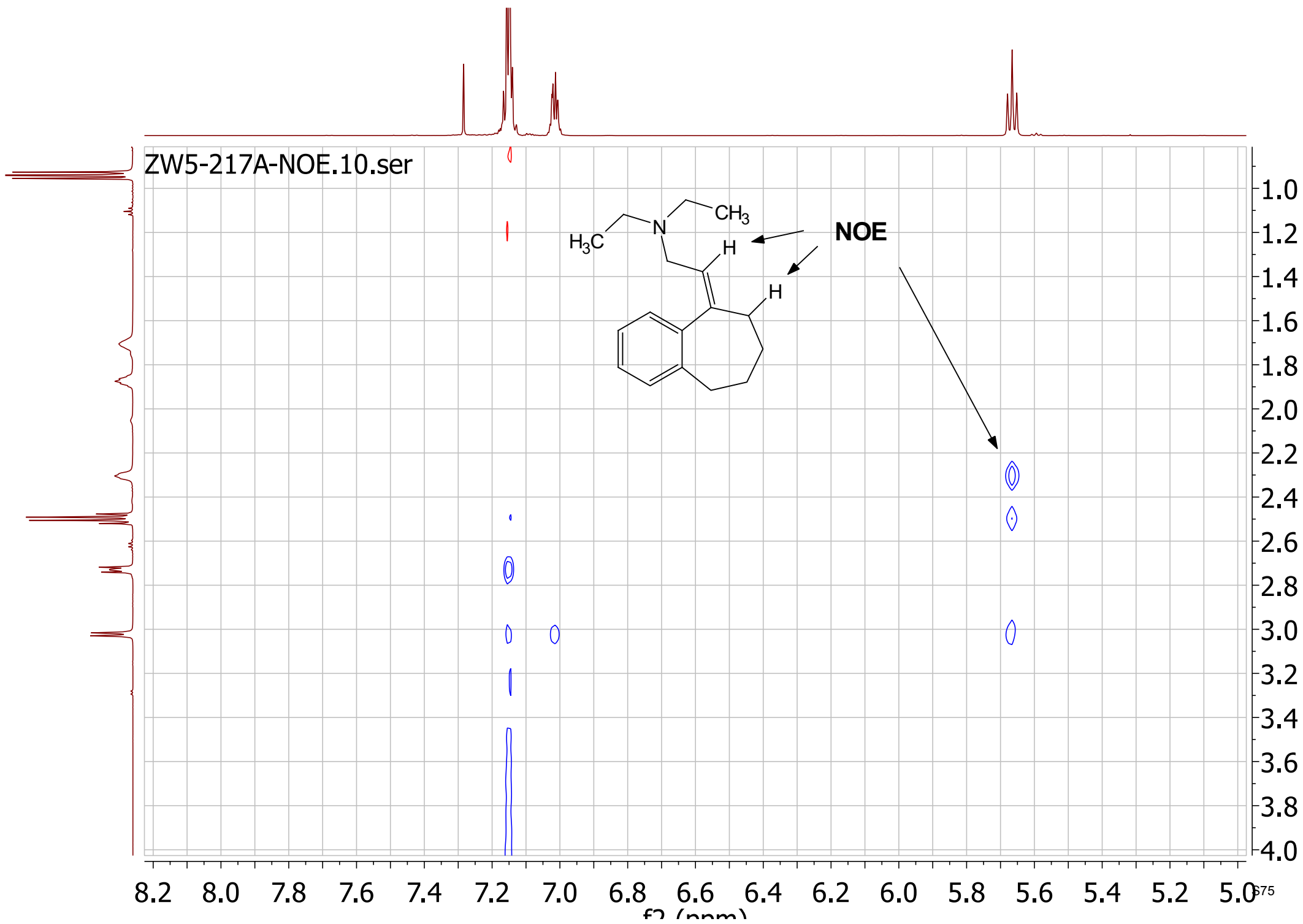
77.41 CDCl₃
77.16 CDCl₃
76.91 CDCl₃

51.08
46.81

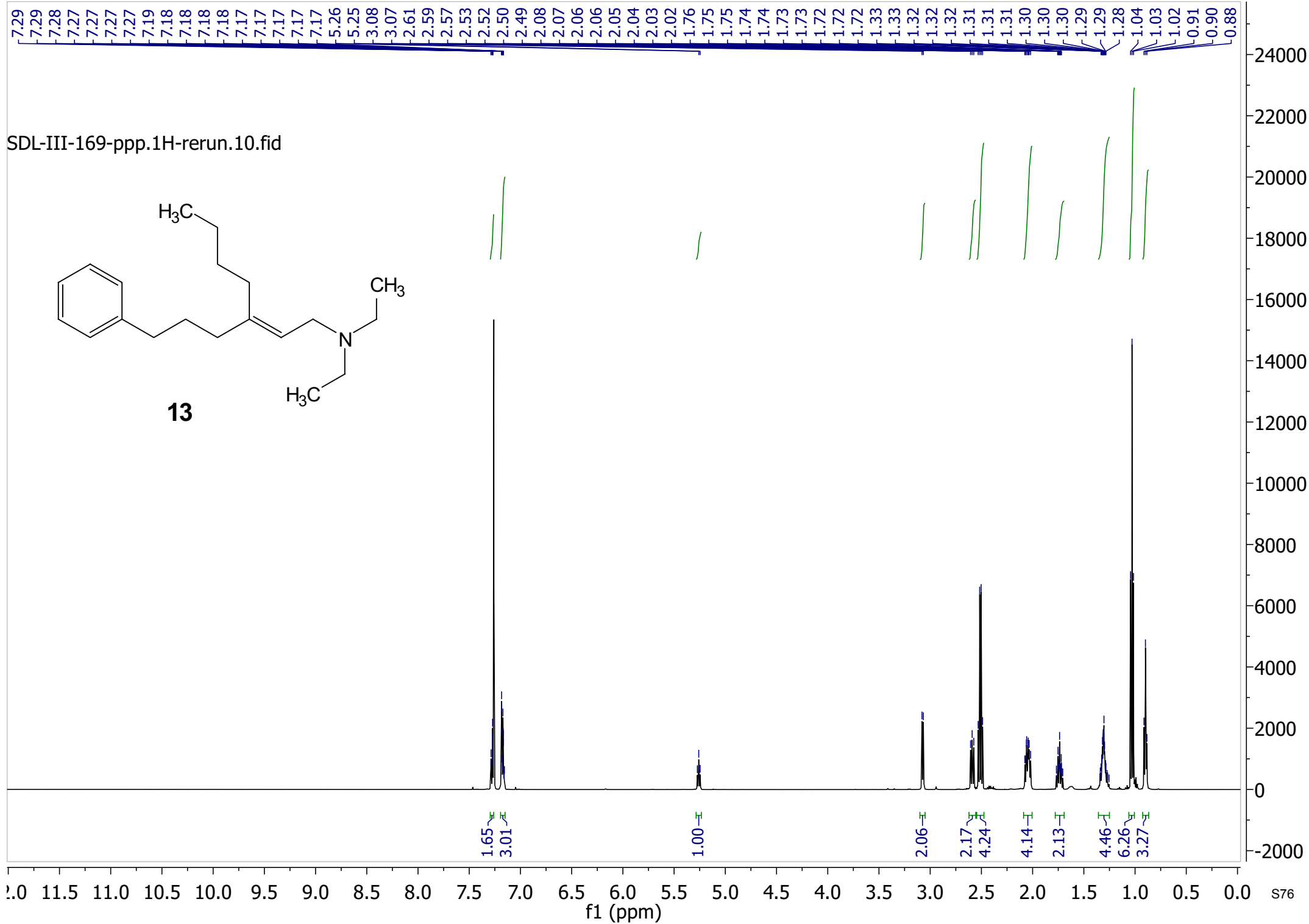
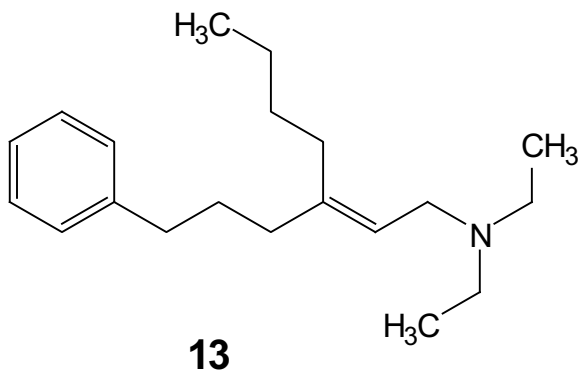
38.10
36.63
33.30
27.87

11.76

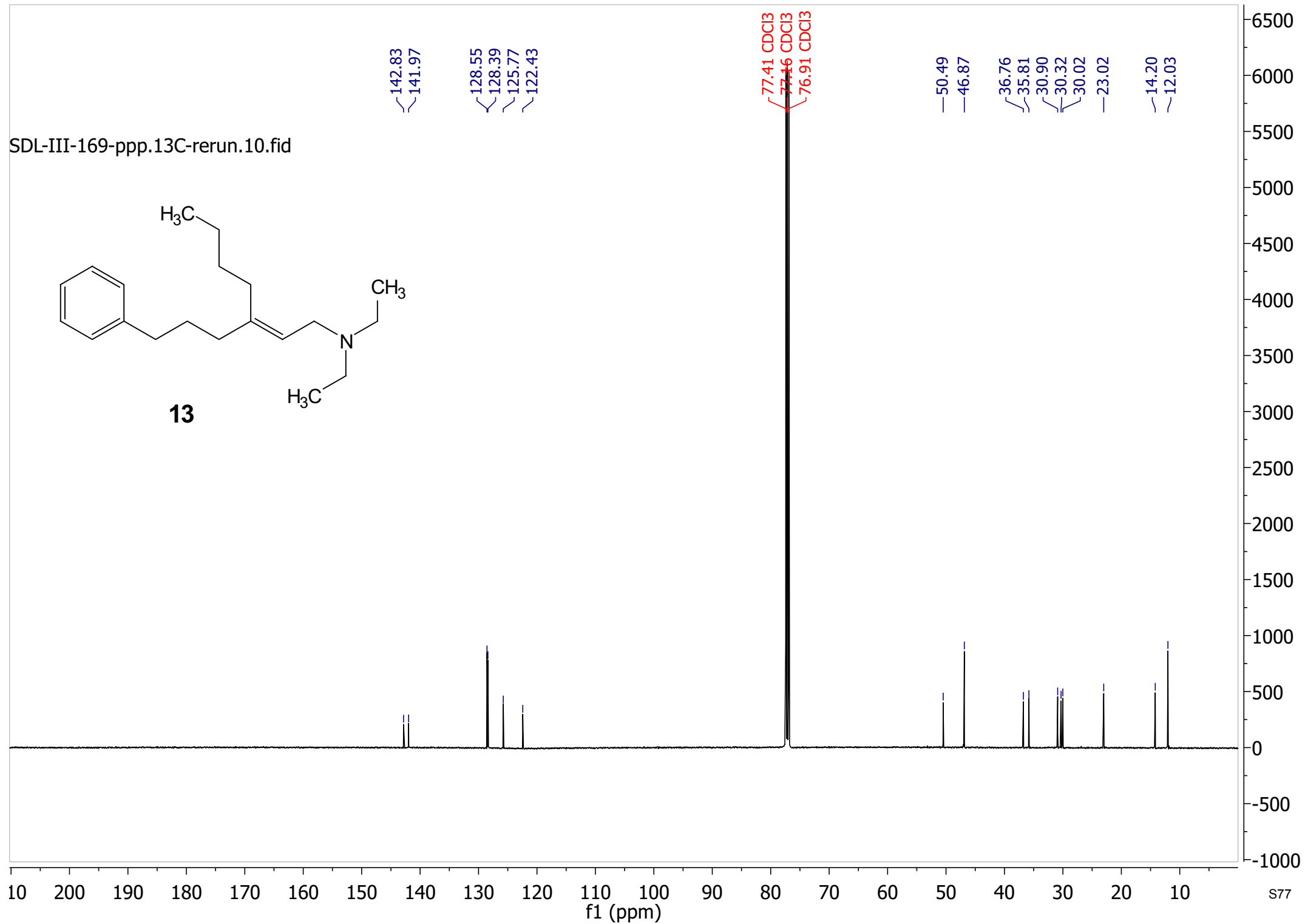
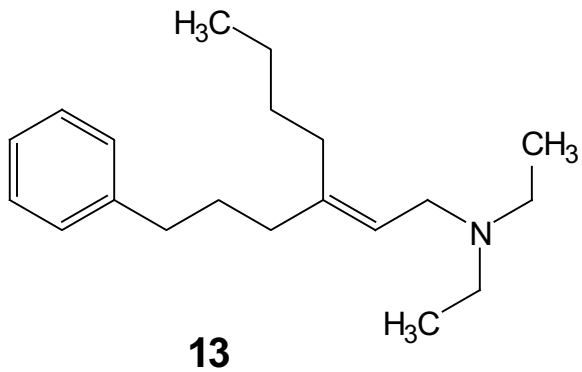




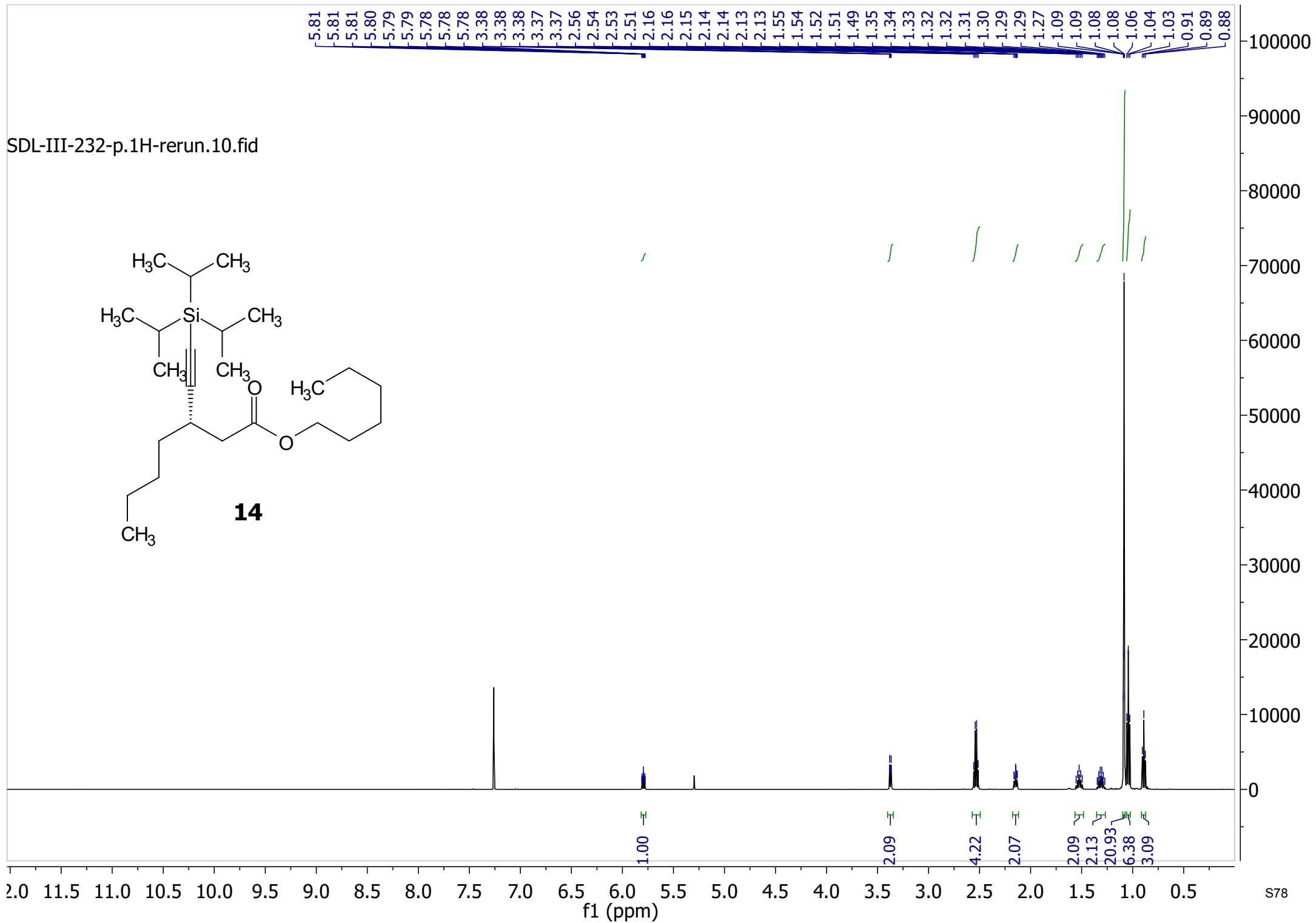
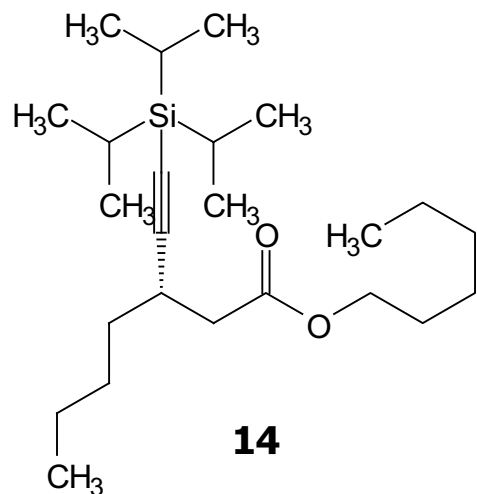
SDL-III-169-ppp.1H-rerun.10.fid



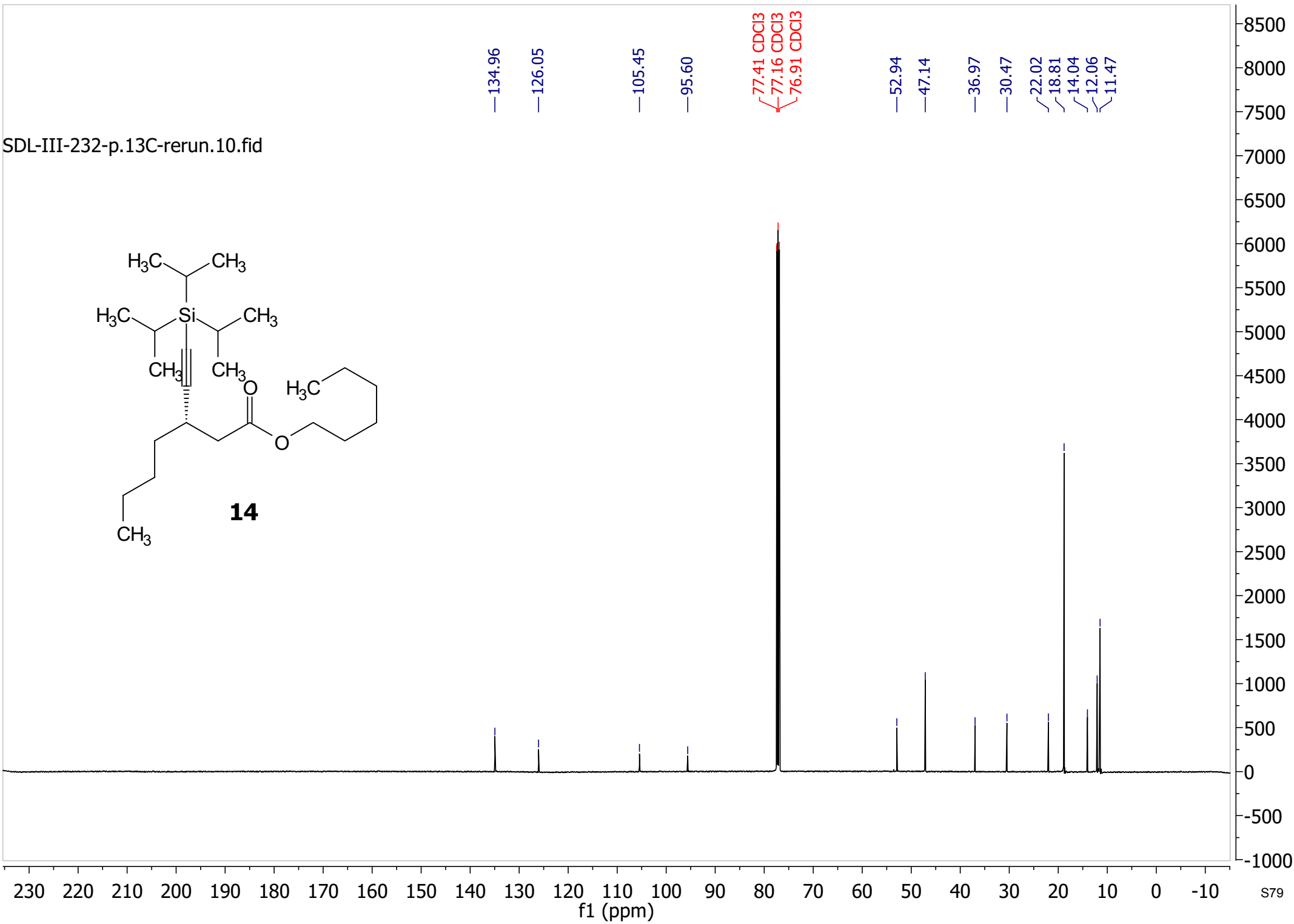
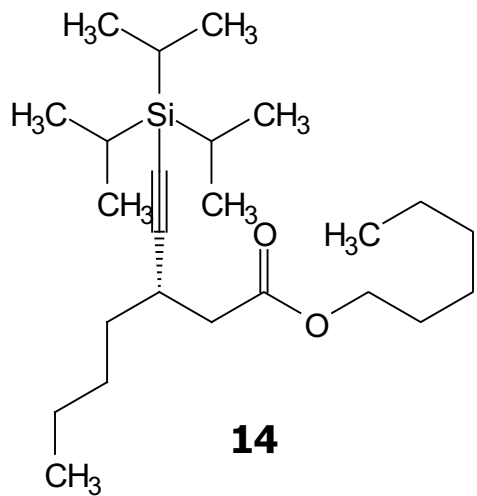
SDL-III-169-ppp.13C-rerun.10.fid



SDL-III-232-p.1H-rerun.10.fid

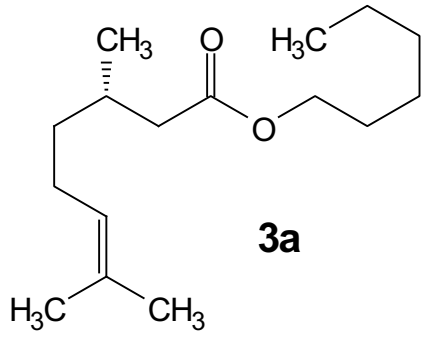


SDL-III-232-p.13C-rerun.10.fid

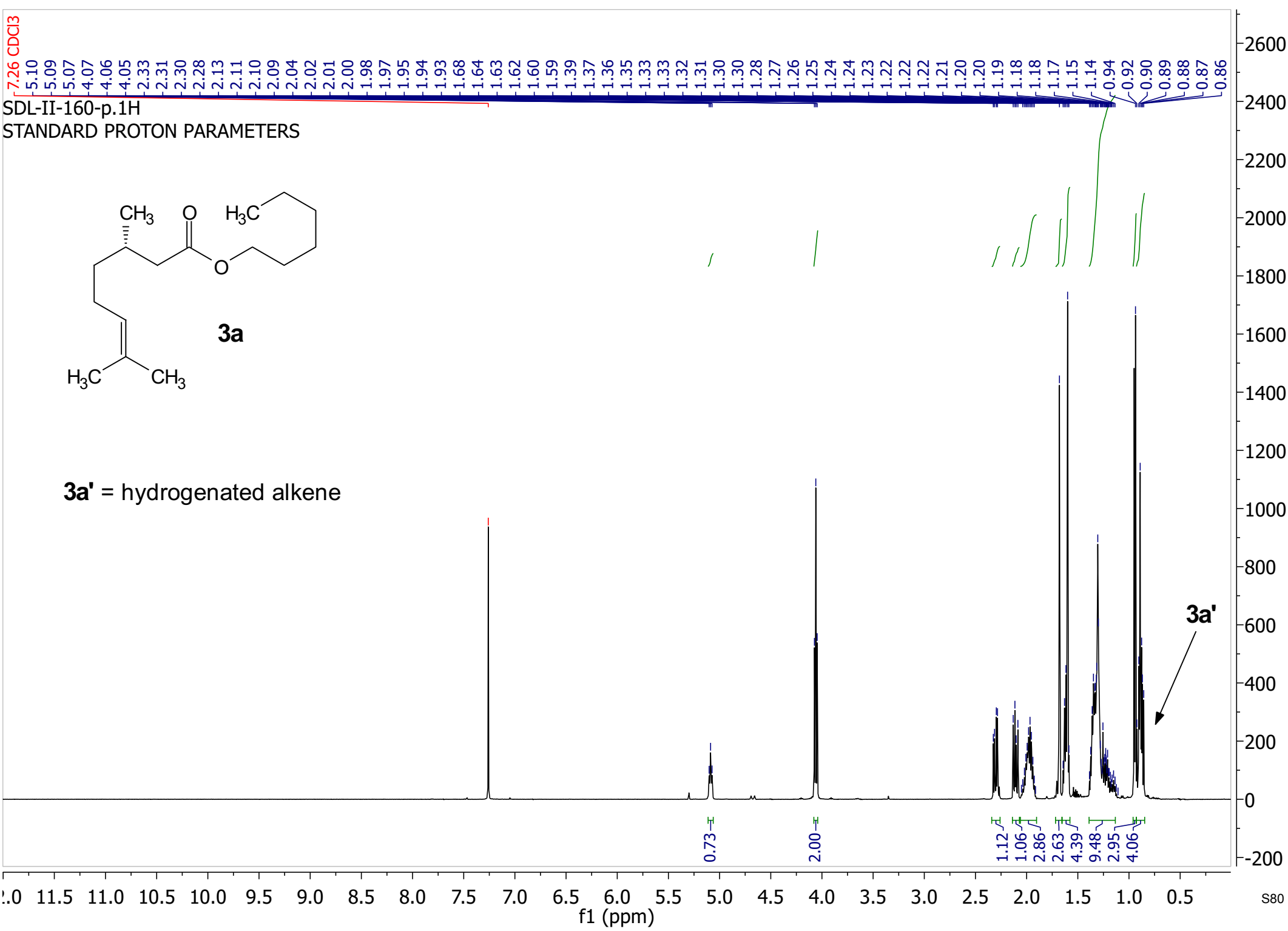


7.26 CDCl3
-5.10
-5.09
-5.07
-4.07
-4.06
-4.05
-2.33
-2.31
-2.30
-2.28
-2.13
-2.11
-2.10
-2.09
-2.04
-2.02
-2.01
-2.00
-1.98
-1.97
-1.95
-1.94
-1.93
-1.68
-1.64
-1.63
-1.62
-1.60
-1.59
-1.39
-1.37
-1.36
-1.35
-1.33
-1.33
-1.32
-1.31
-1.30
-1.30
-1.28
-1.27
-1.26
-1.25
-1.24
-1.24
-1.23
-1.22
-1.22
-1.22
-1.21
-1.20
-1.20
-1.19
-1.18
-1.18
-1.17
-1.15
-1.14
-0.94
-0.92
-0.90
-0.89
-0.88
-0.87
-0.86

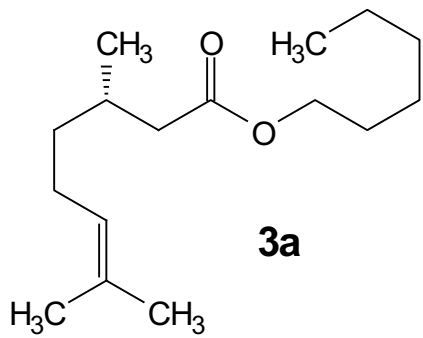
SDL-II-160-p.1H
STANDARD PROTON PARAMETERS



3a' = hydrogenated alkene



SDL-II-160-p.13C.10.fid



3a' = (hydrogenated alkene)

— 173.54

— 131.65

— 124.45

77.41 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

64.49

42.16 3a'

42.06

39.22 3a'

37.10 3a'

36.94

31.59

30.58 3a'

30.23

28.79

28.08 3a'

25.86

25.78

25.58

24.80 3a'

22.81 3a'

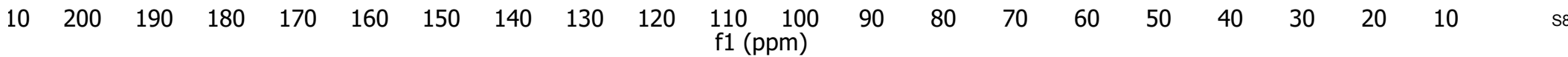
22.70

19.90 3a'

19.78

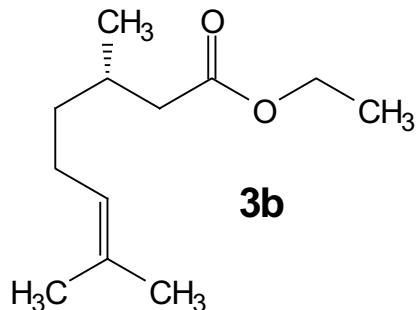
17.79

14.15

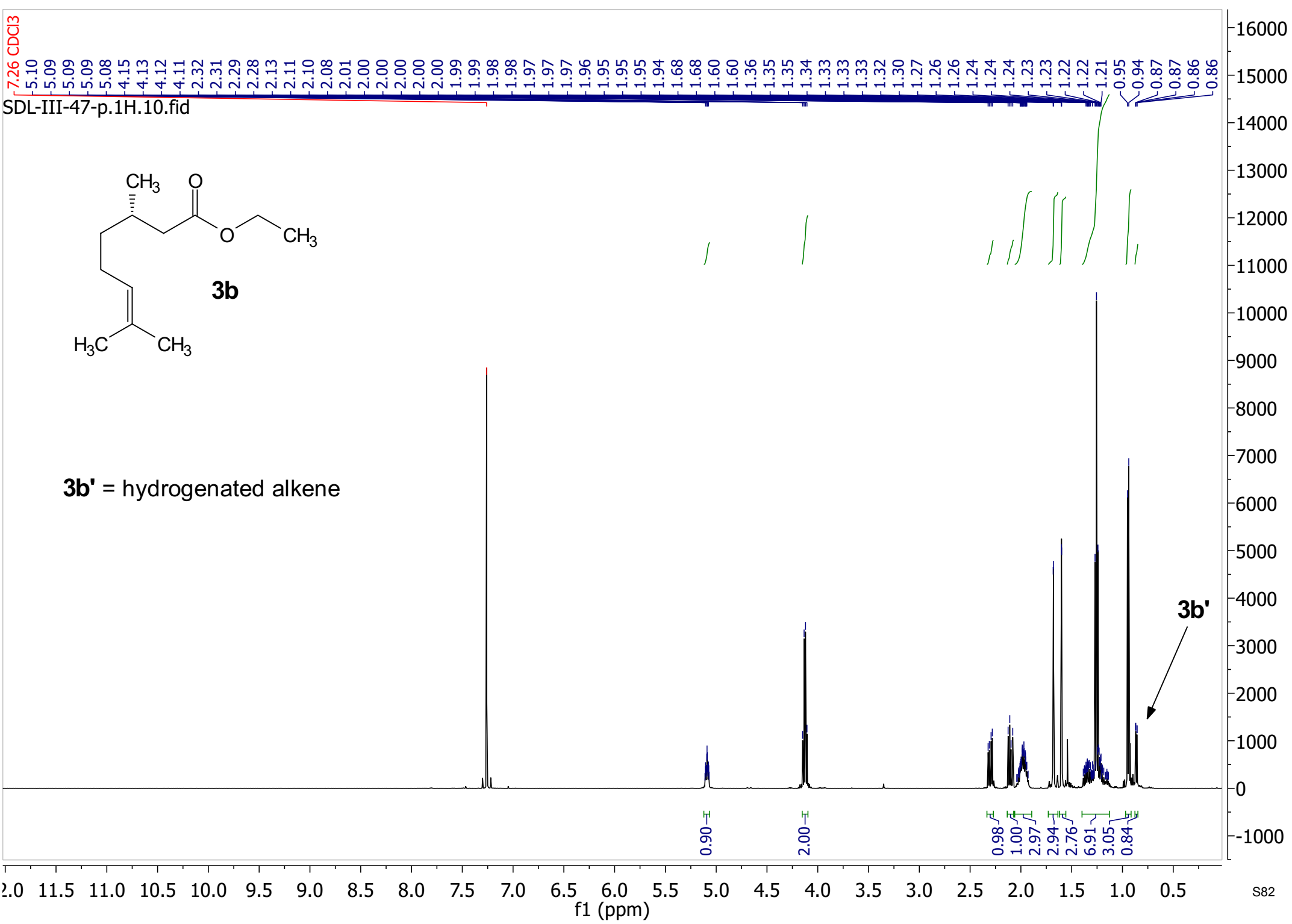


7.26 CDCl3
 5.10
 5.09
 5.09
 5.09
 5.08
 4.15
 4.13
 4.12
 4.11
 2.32
 2.31
 2.29
 2.28
 2.13
 2.11
 2.10
 2.08
 2.01
 2.00
 2.00
 2.00
 2.00
 2.00
 1.99
 1.99
 1.98
 1.98
 1.97
 1.97
 1.97
 1.96
 1.95
 1.95
 1.95
 1.94
 1.68
 1.68
 1.60
 1.60
 1.36
 1.35
 1.35
 1.34
 1.33
 1.33
 1.33
 1.32
 1.30
 1.27
 1.26
 1.26
 1.24
 1.24
 1.24
 1.23
 1.23
 1.22
 1.22
 1.21
 0.95
 0.94
 0.87
 0.87
 0.86
 0.86

SDL-III-47-p.1H.10.fid

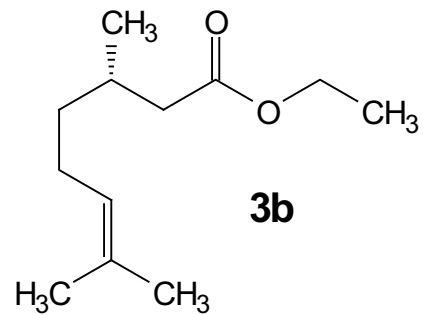


3b' = hydrogenated alkene

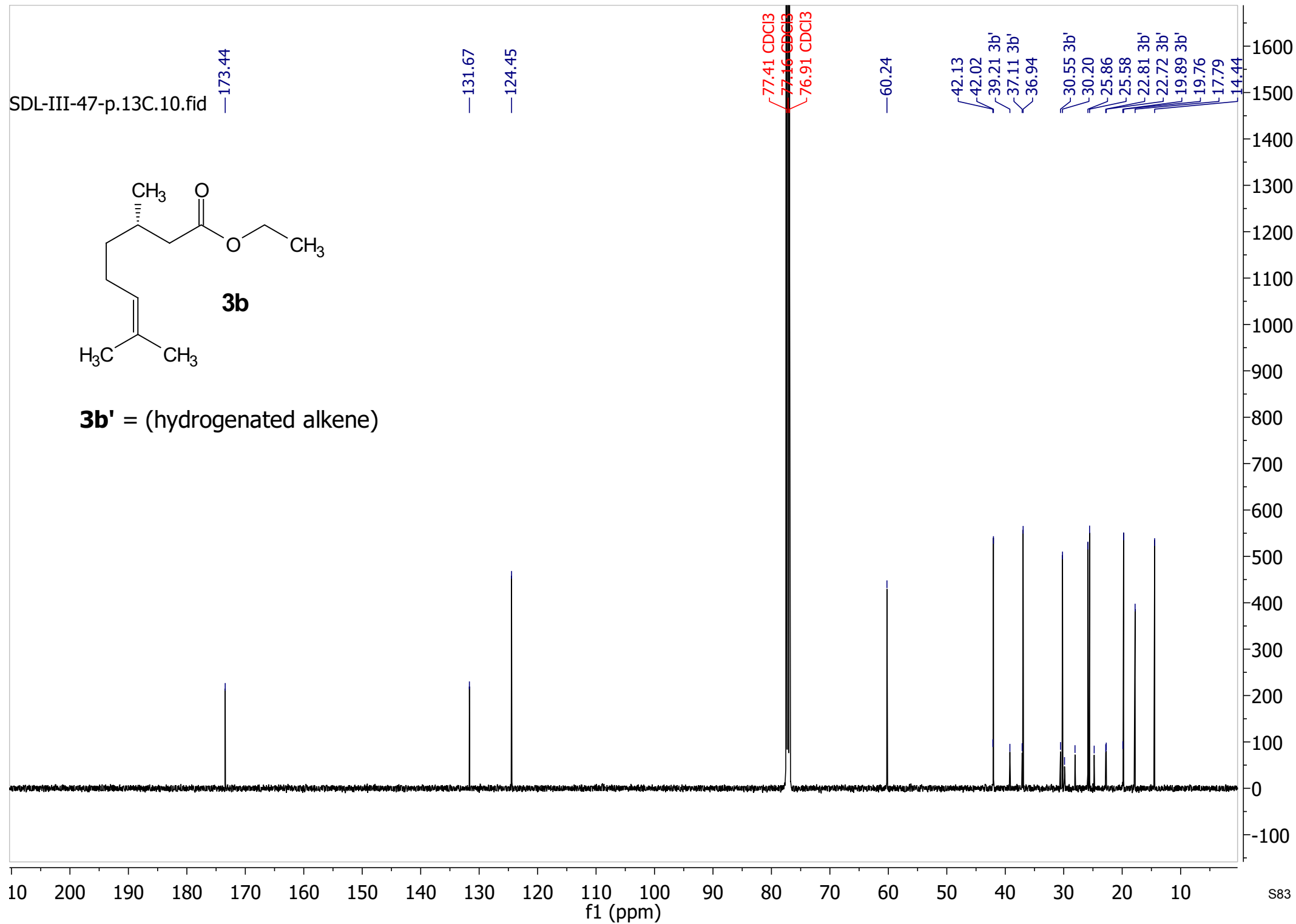


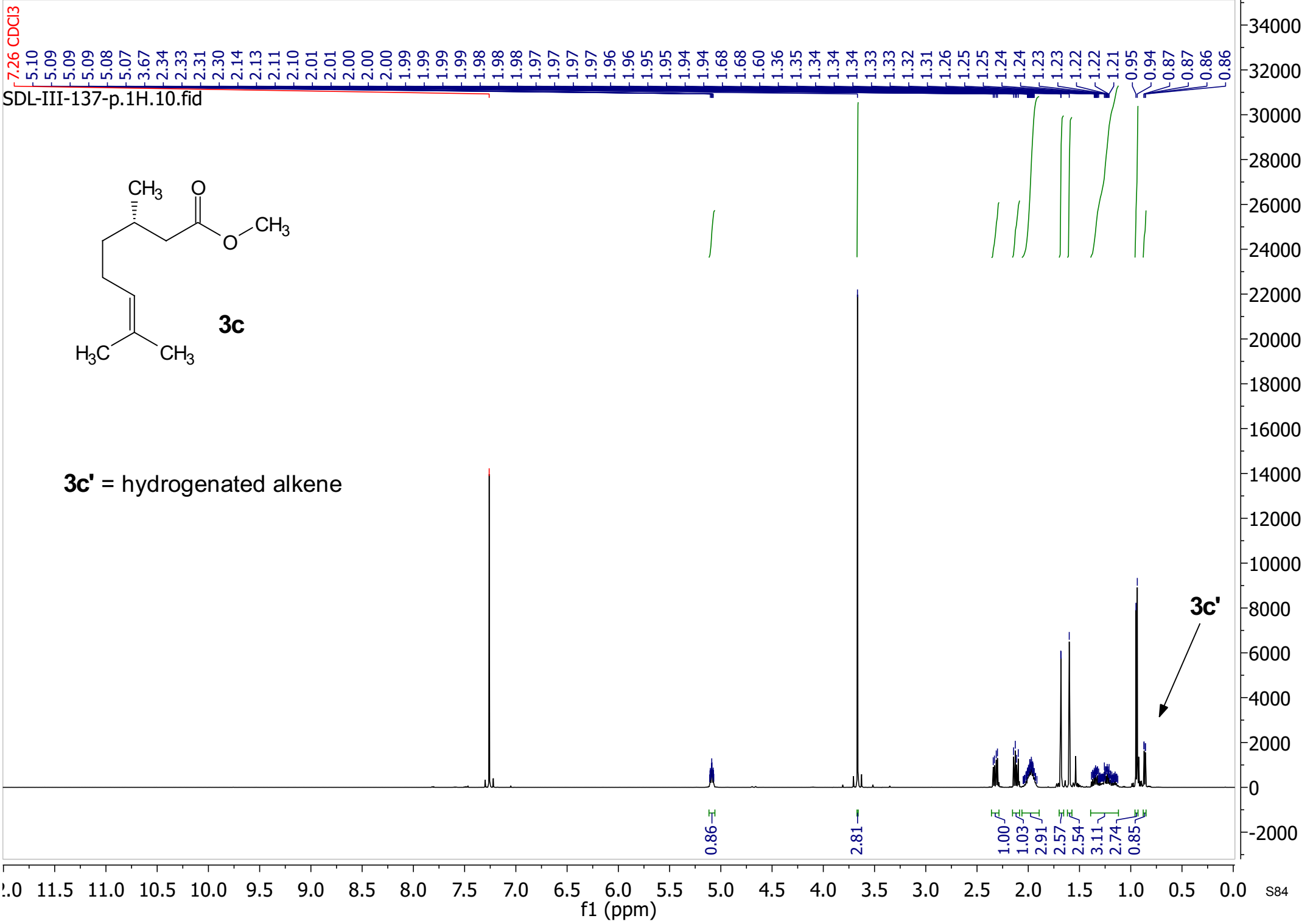
3b'

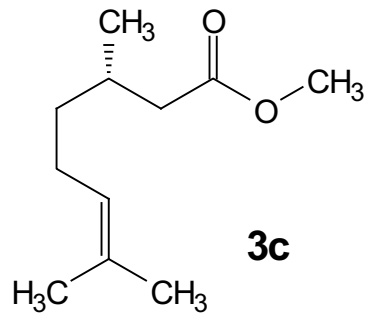
SDL-III-47-p.13C.10.fid



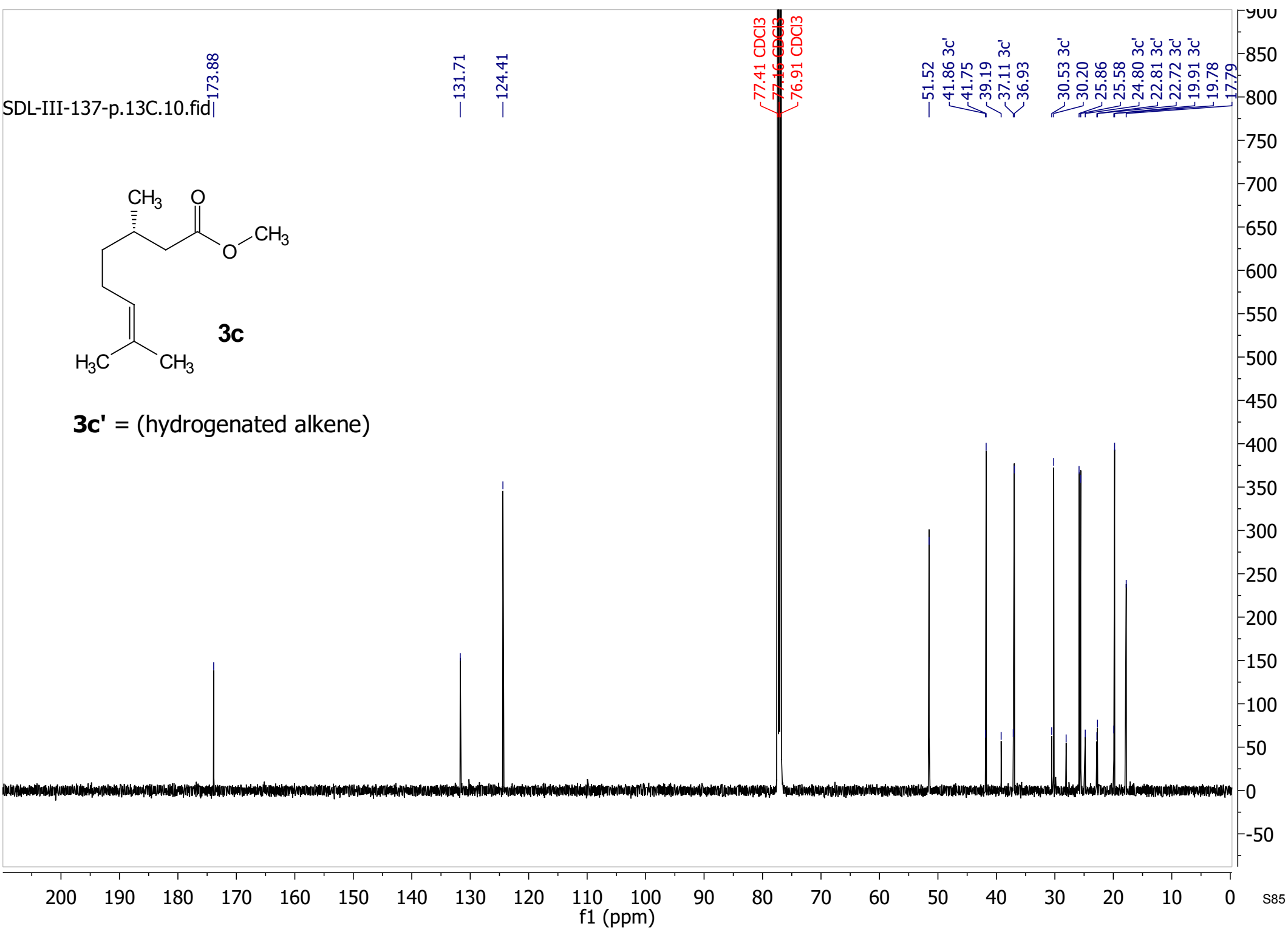
3b' = (hydrogenated alkene)

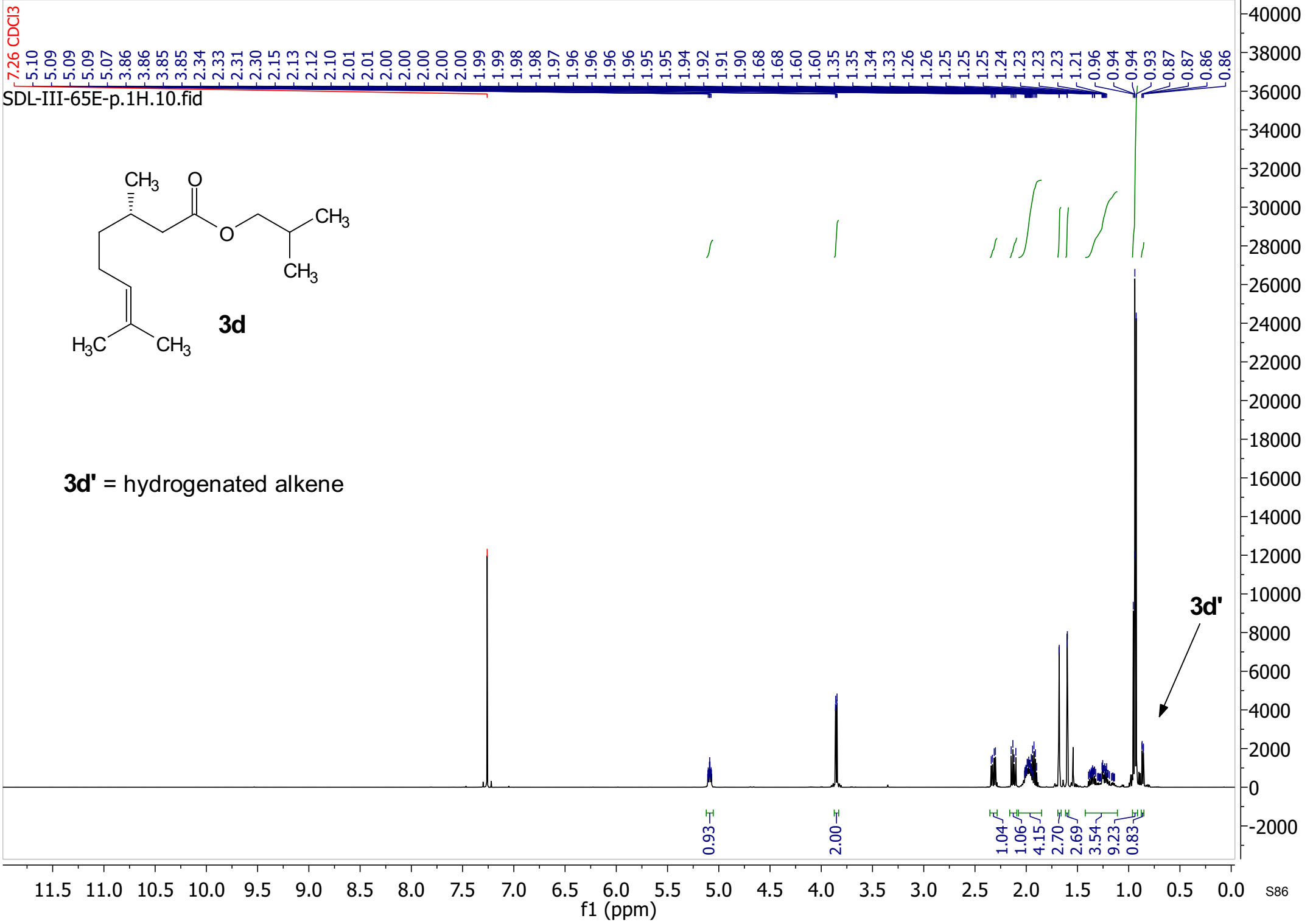


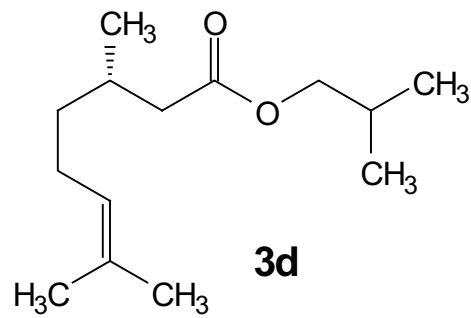




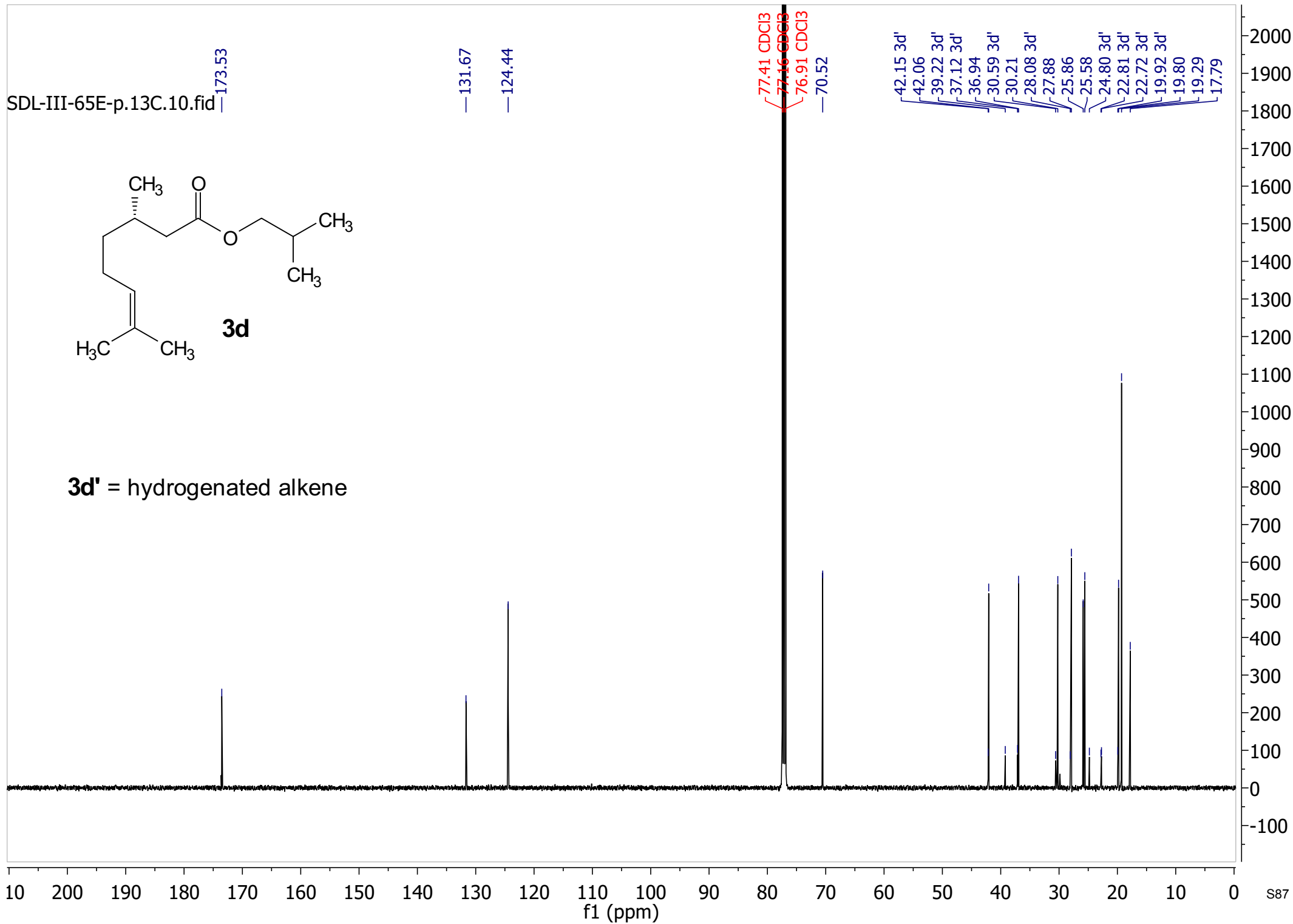
3c' = (hydrogenated alkene)

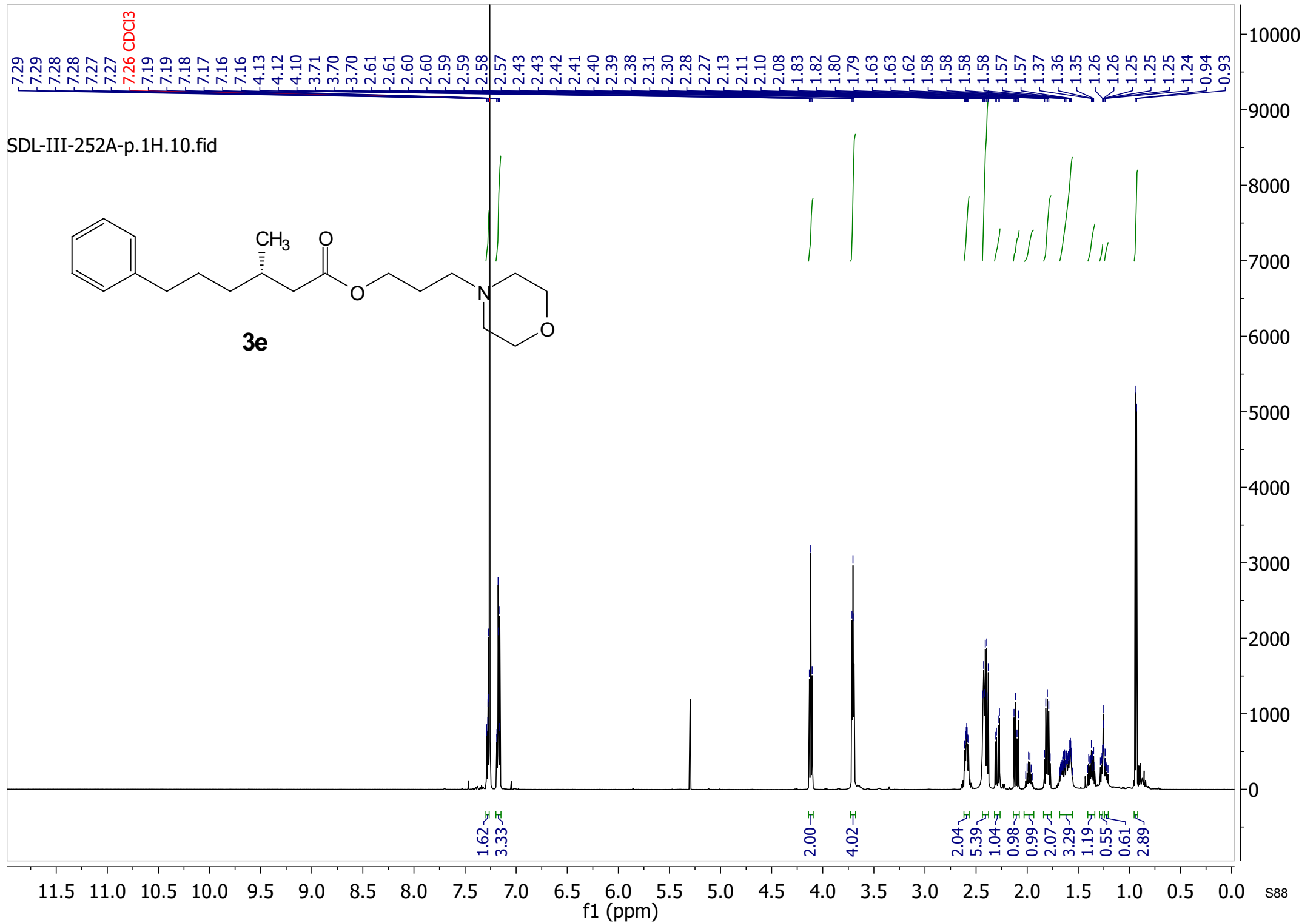




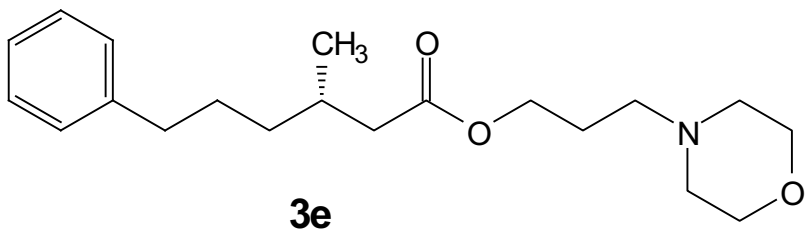


3d' = hydrogenated alkene





SDL-III-252A-p.13C.10.fid



—173.40

—142.64

—128.50

—128.42

—125.84

77.42 CDCl3

77.16 CDCl3

76.91 CDCl3

—67.14

—62.67

—55.59

—53.85

—41.98

—36.48

—36.17

—30.45

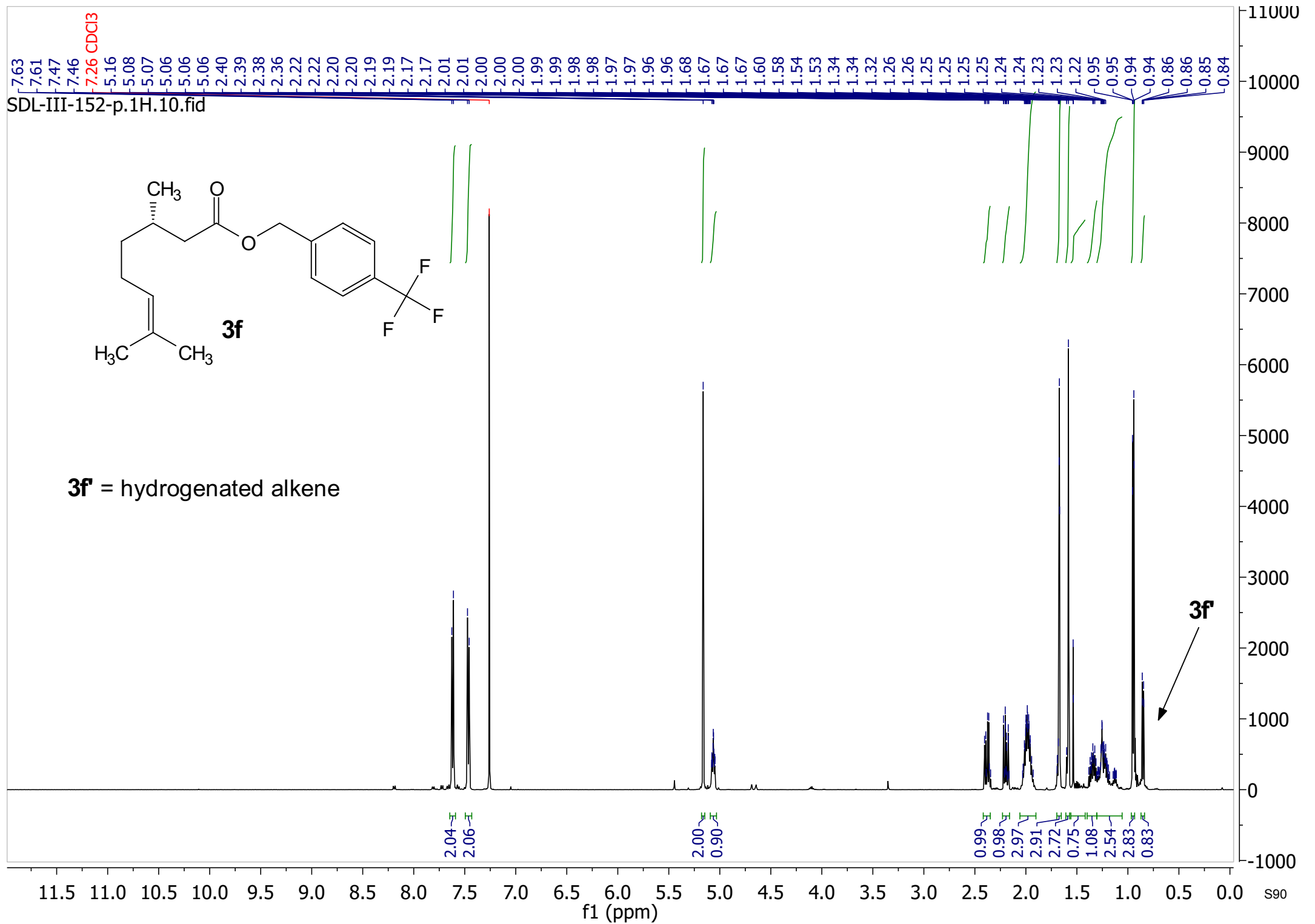
—28.99

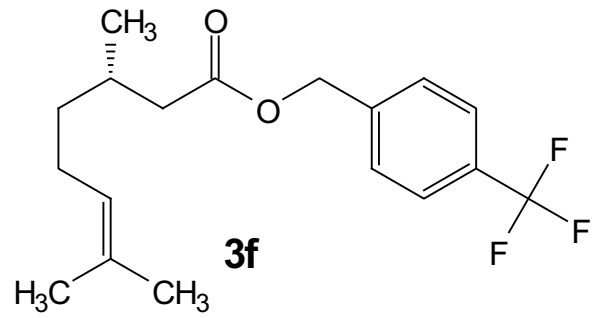
—26.02

—19.85

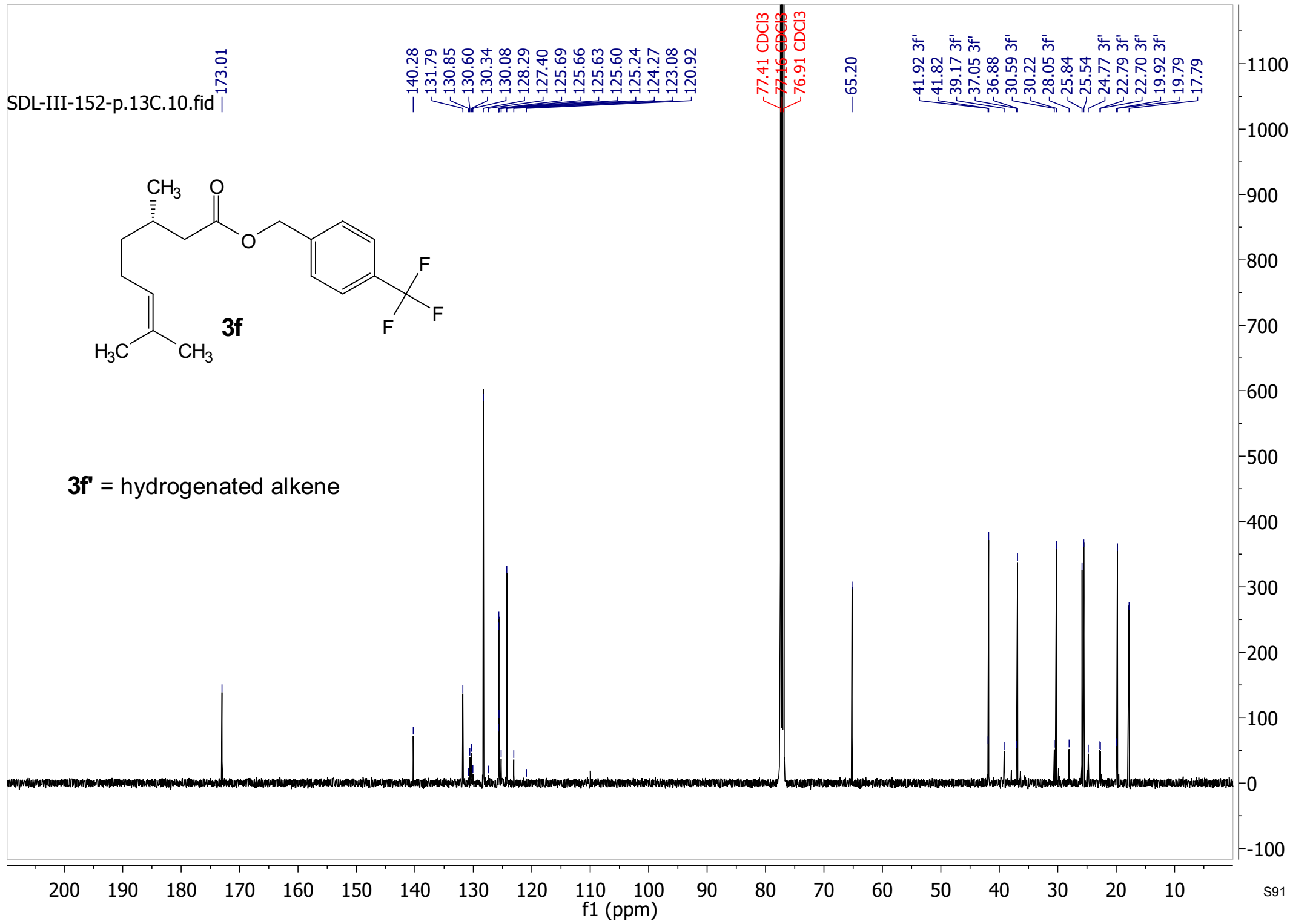
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

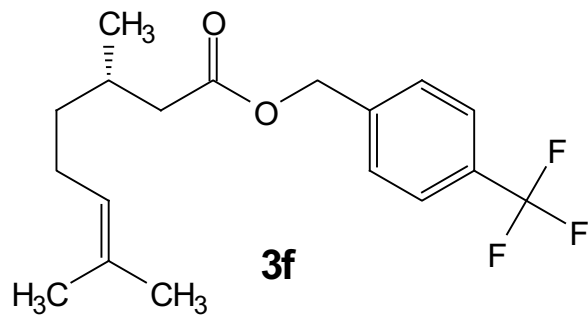




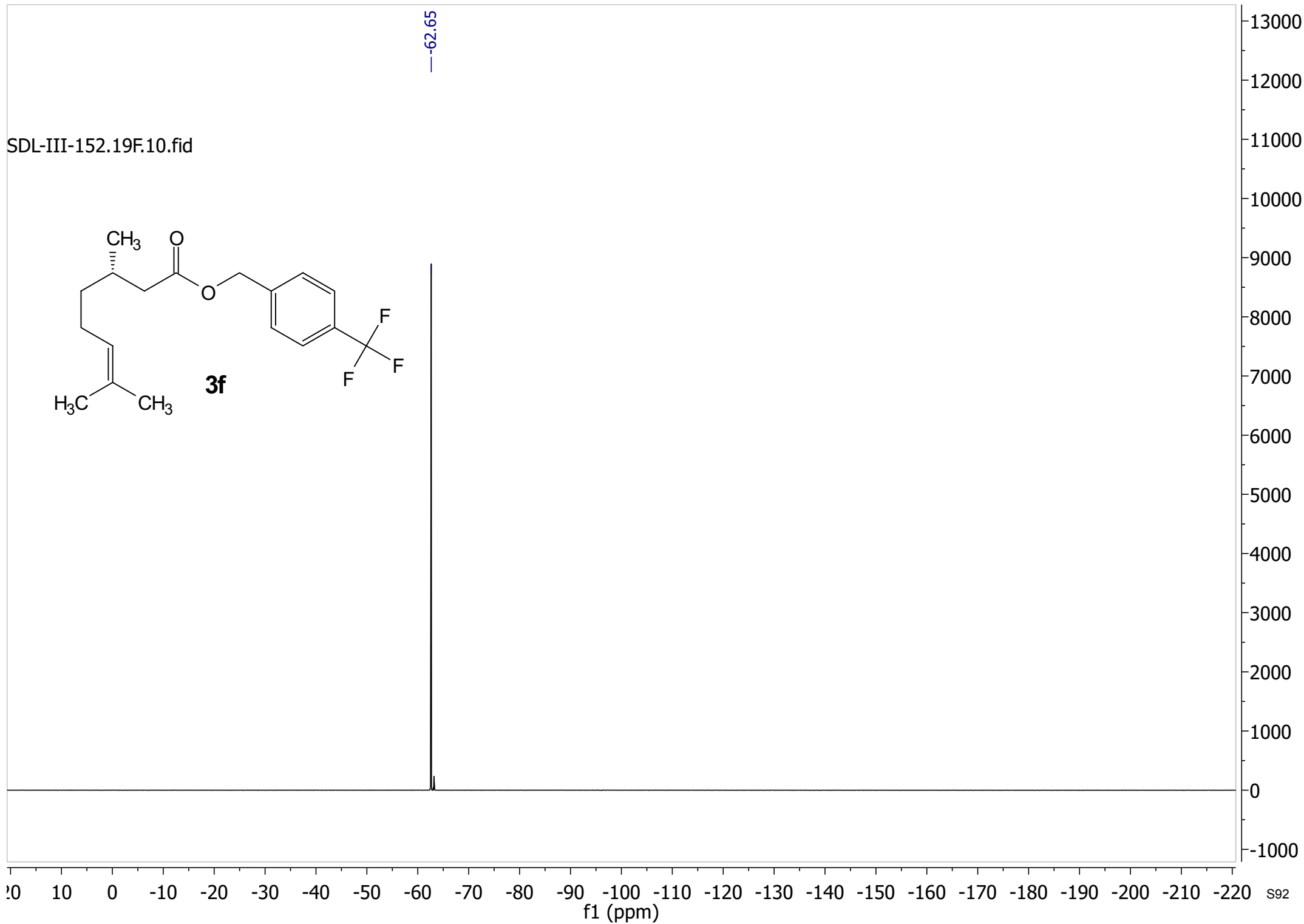
3f = hydrogenated alkene



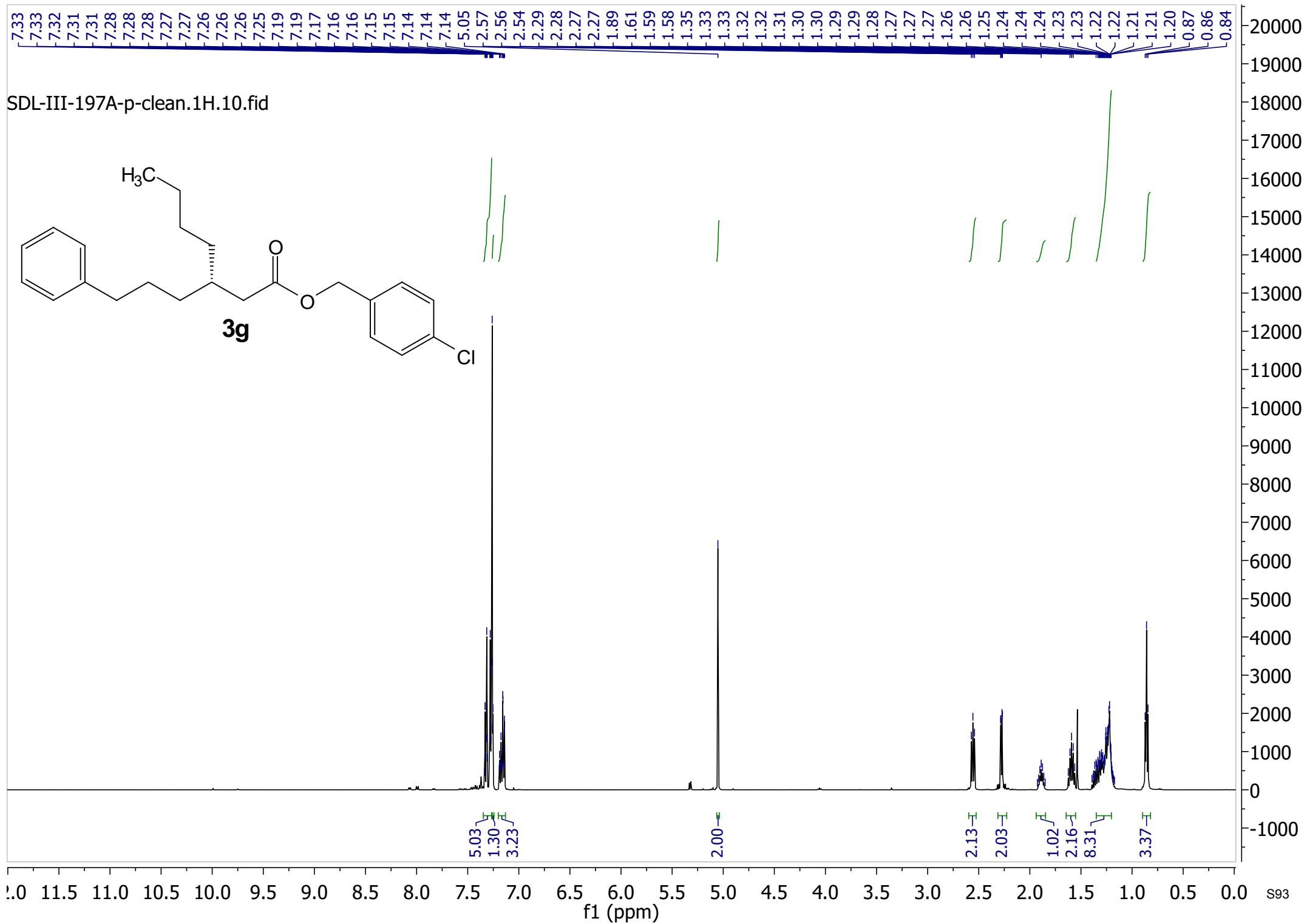
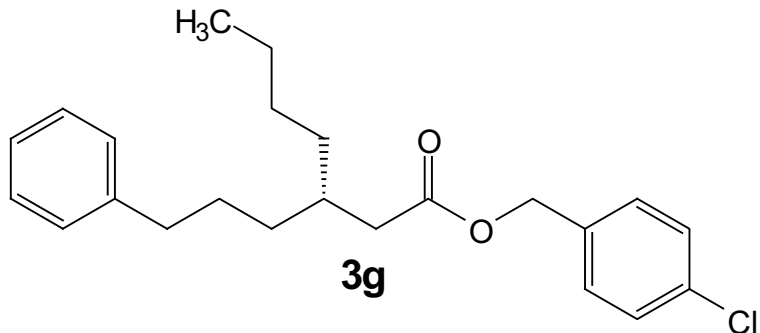
SDL-III-152.19F.10.fid



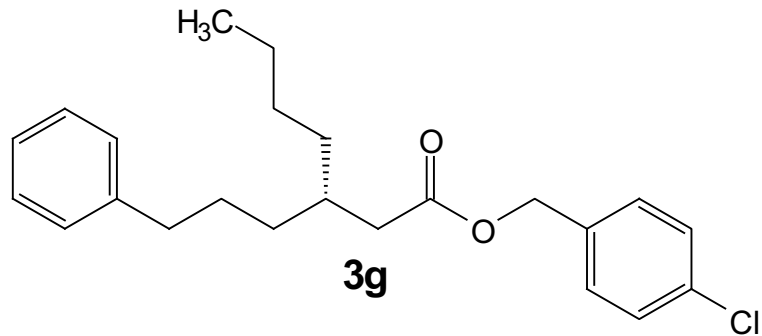
62.65



SDL-III-197A-p-clean.1H.10.fid



SDL-III-197A-p-clean.13C.10.fid



—173.36

—142.63

—134.79

—134.22

—129.82

—128.86

—128.49

—128.41

—125.84

77.41 CDCl₃

77.16 CDCl₃

76.91 CDCl₃

—65.33

39.28

36.27

35.16

33.70

33.66

28.86

28.59

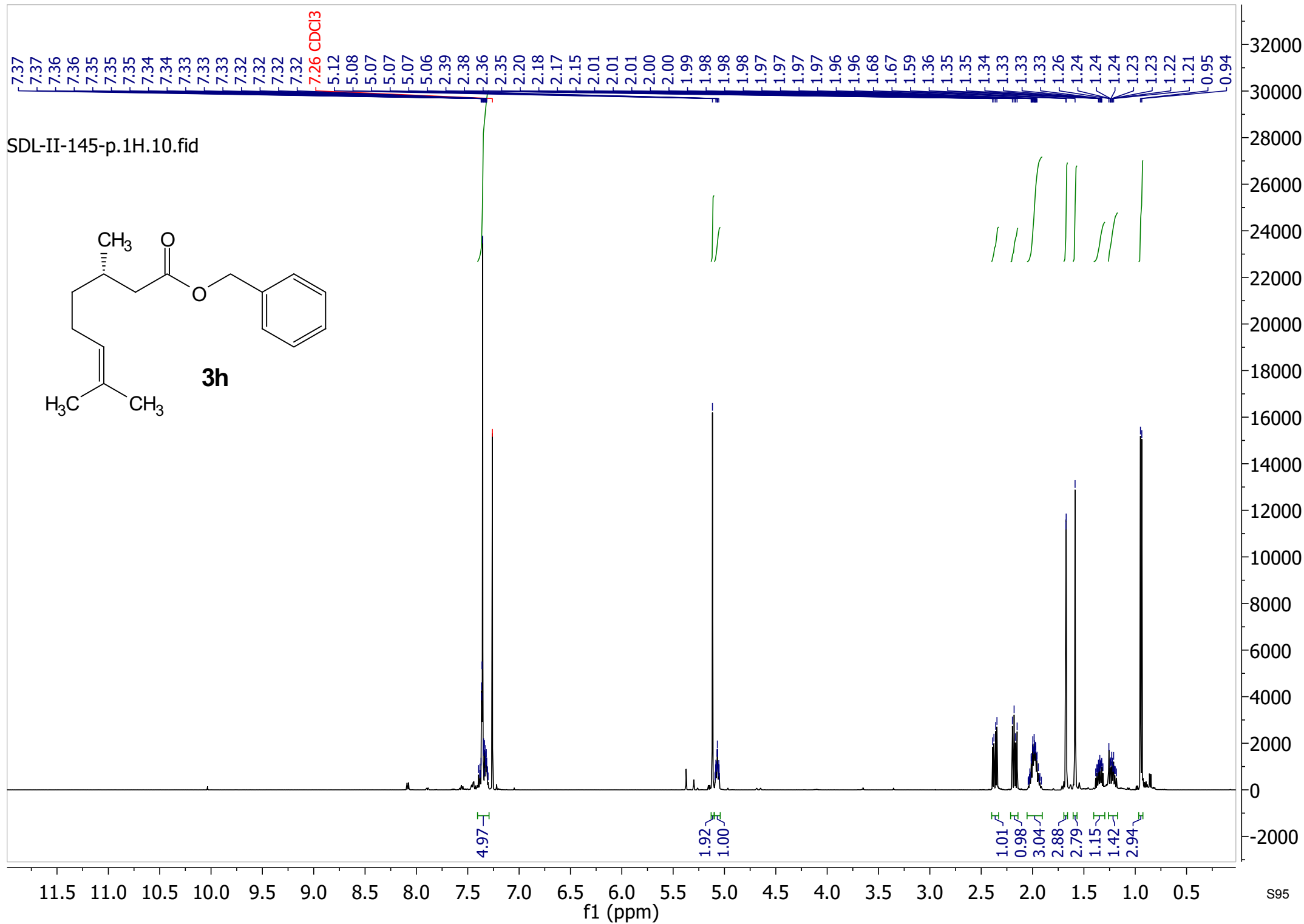
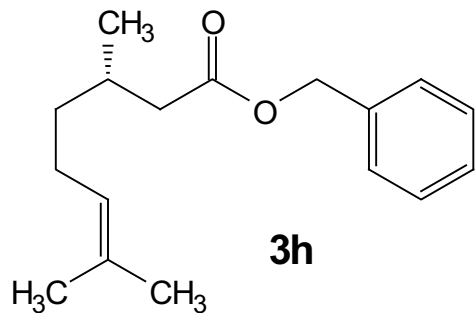
23.03

—14.19

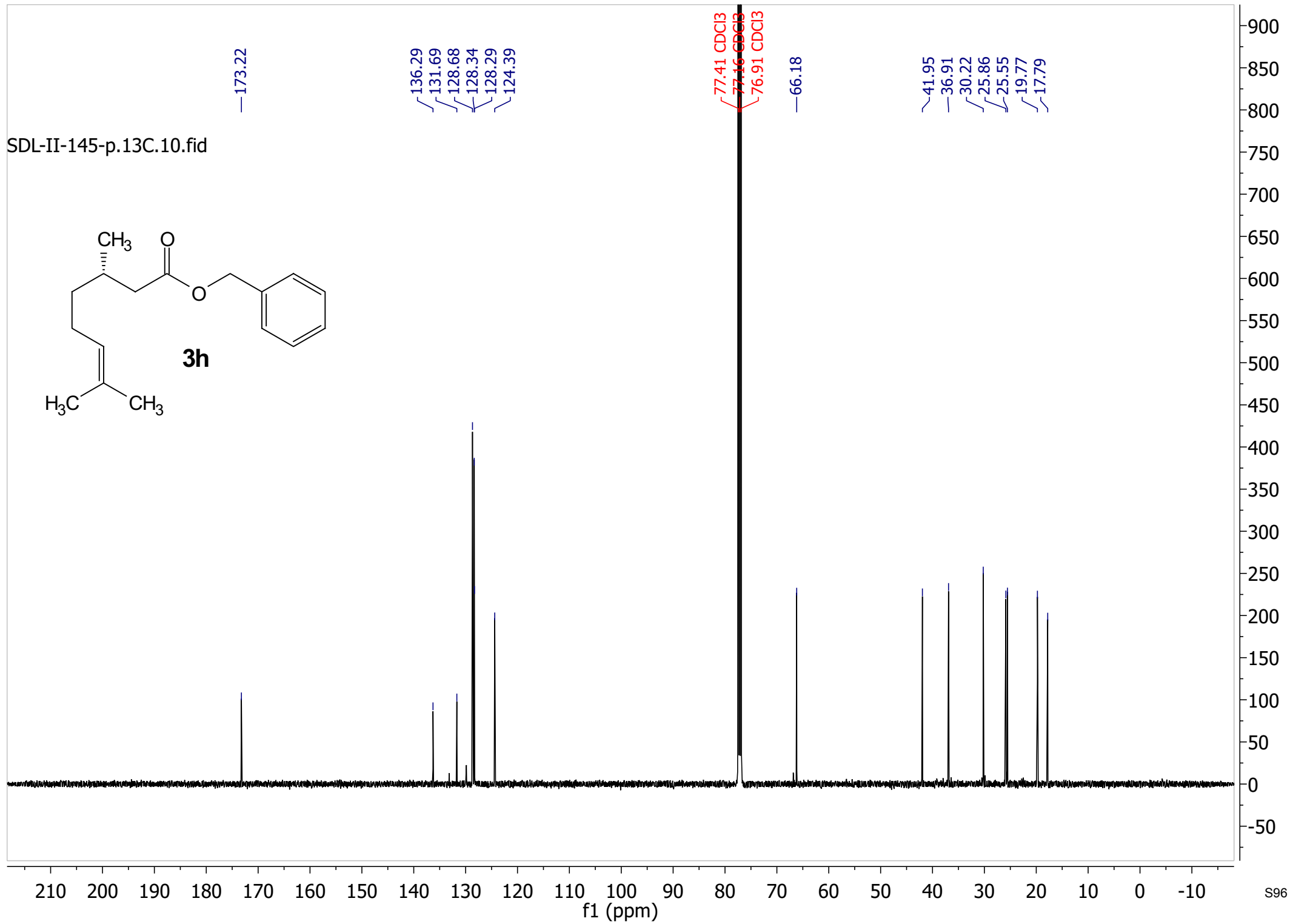
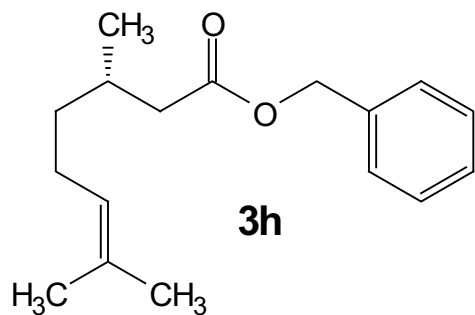
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

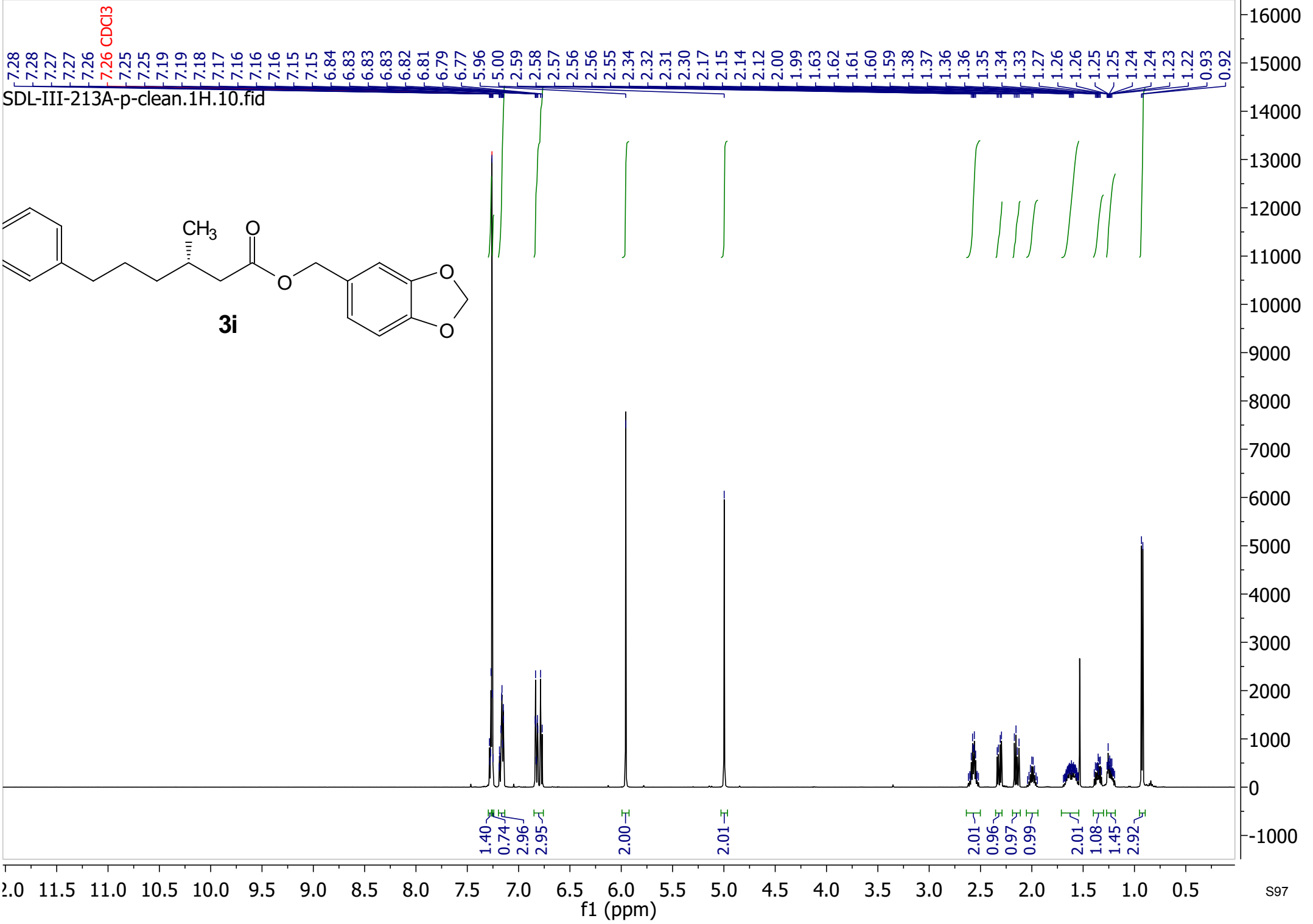
f1 (ppm)

SDL-II-145-p.1H.10.fid

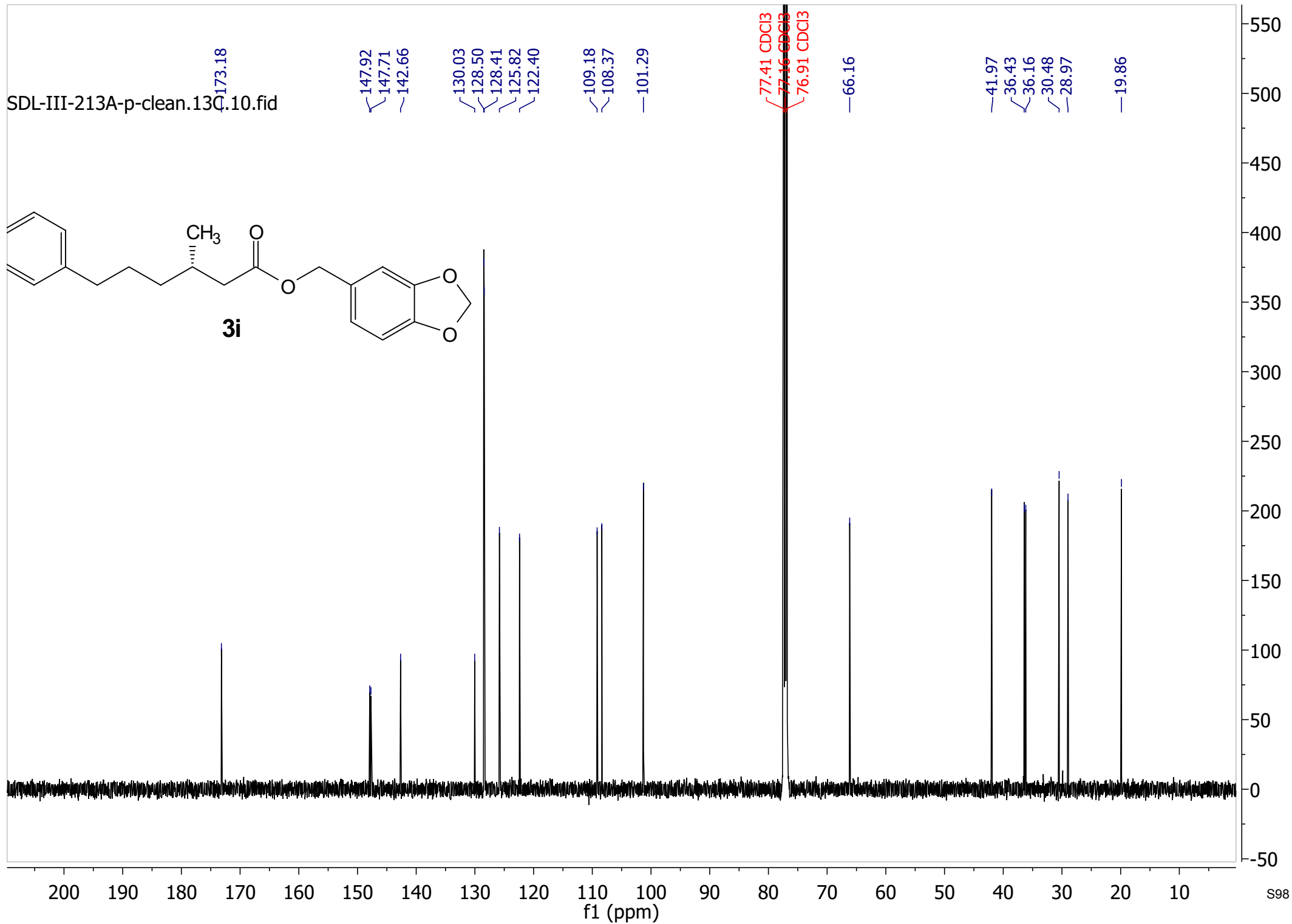
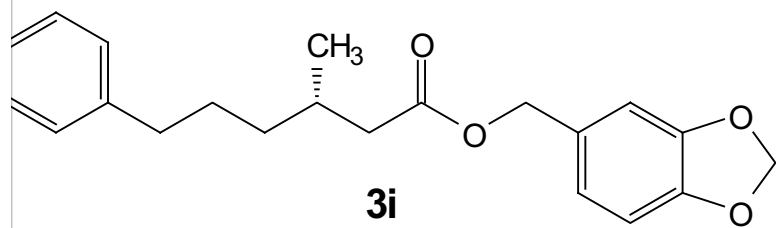


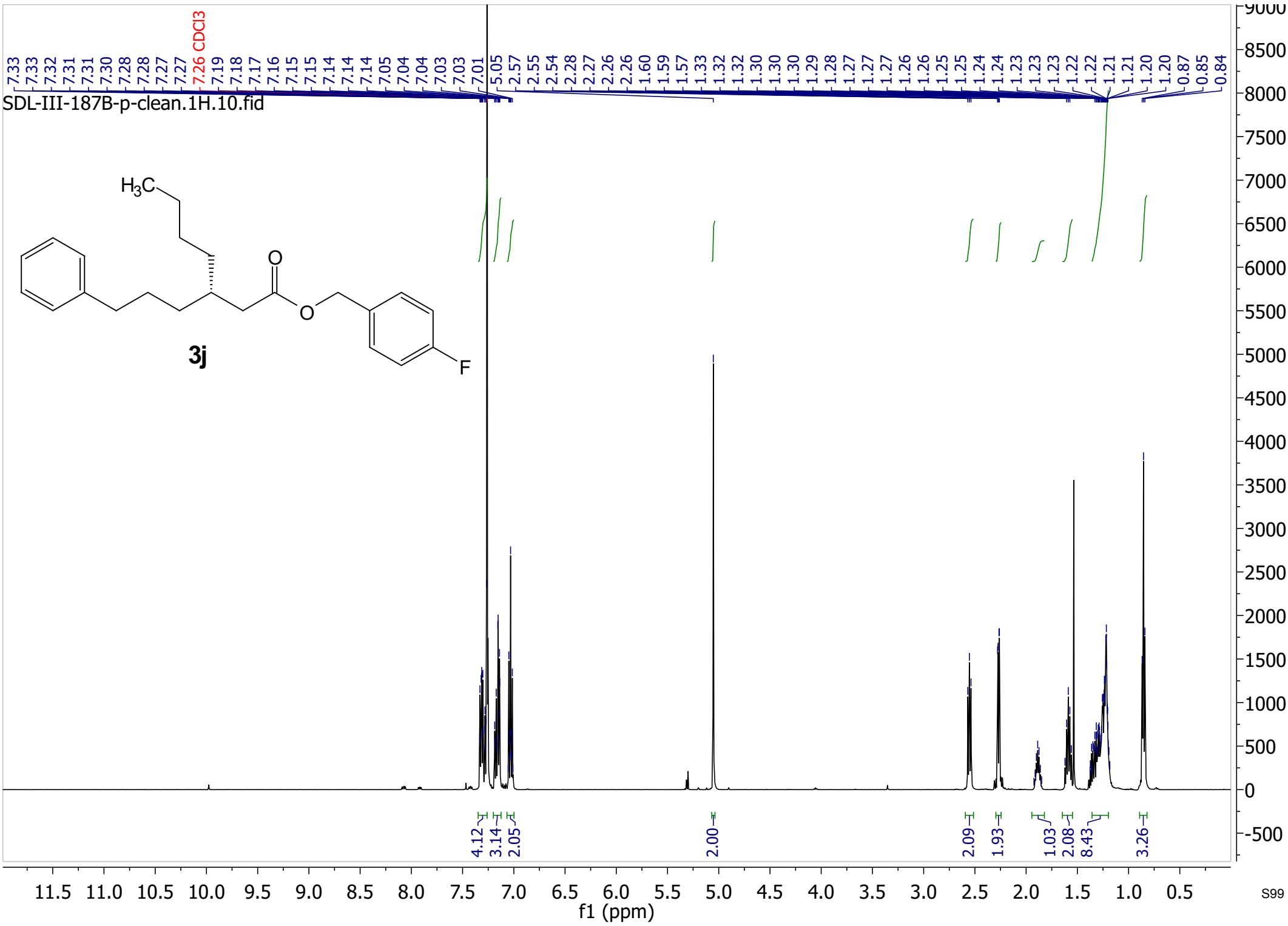
SDL-II-145-p.13C.10.fid



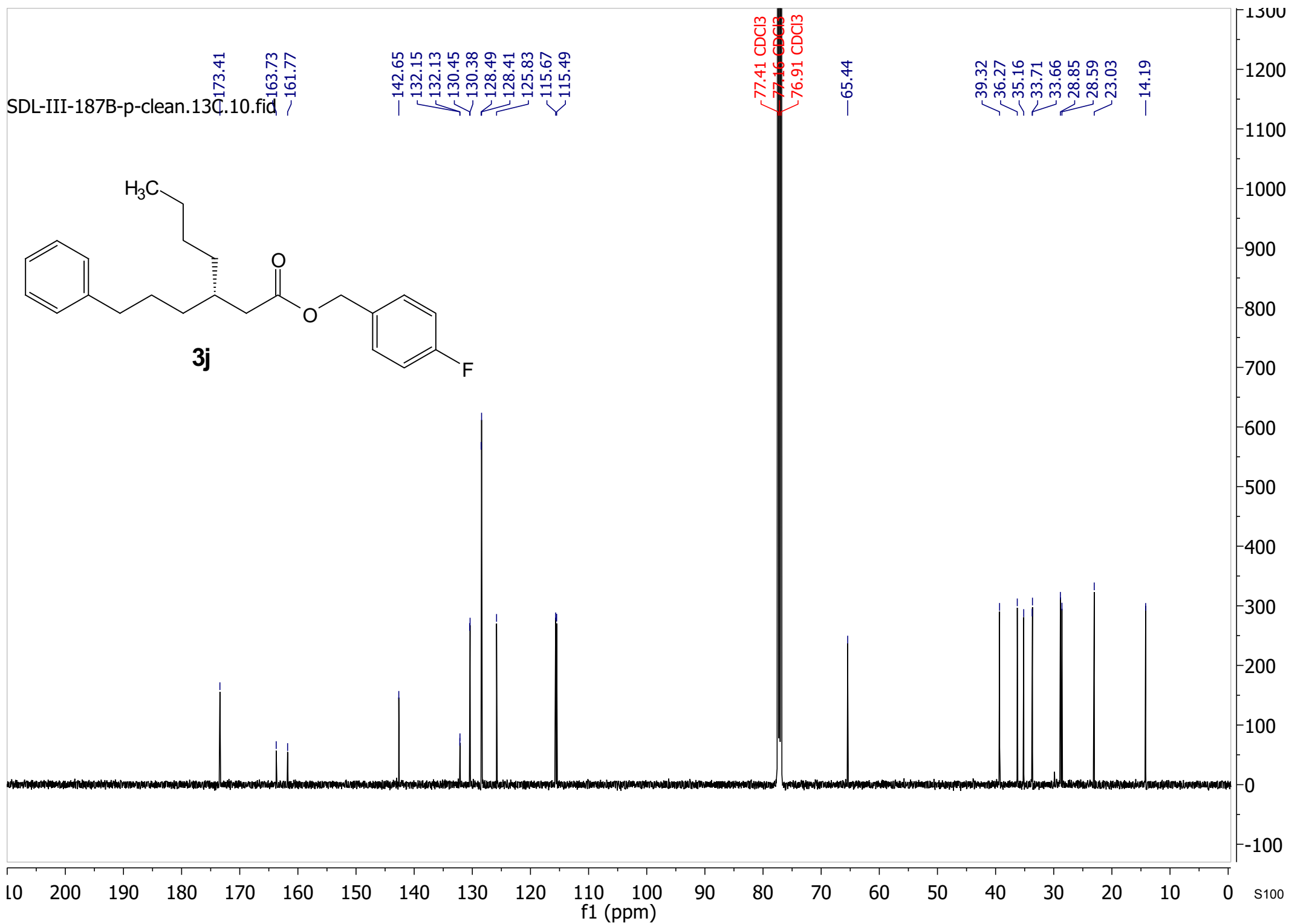
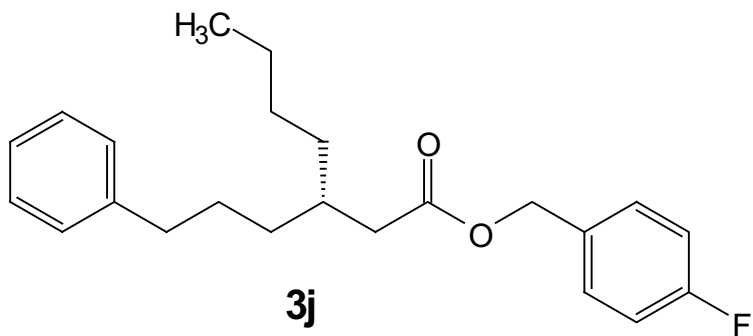


SDL-III-213A-p-clean.13C.10.fid

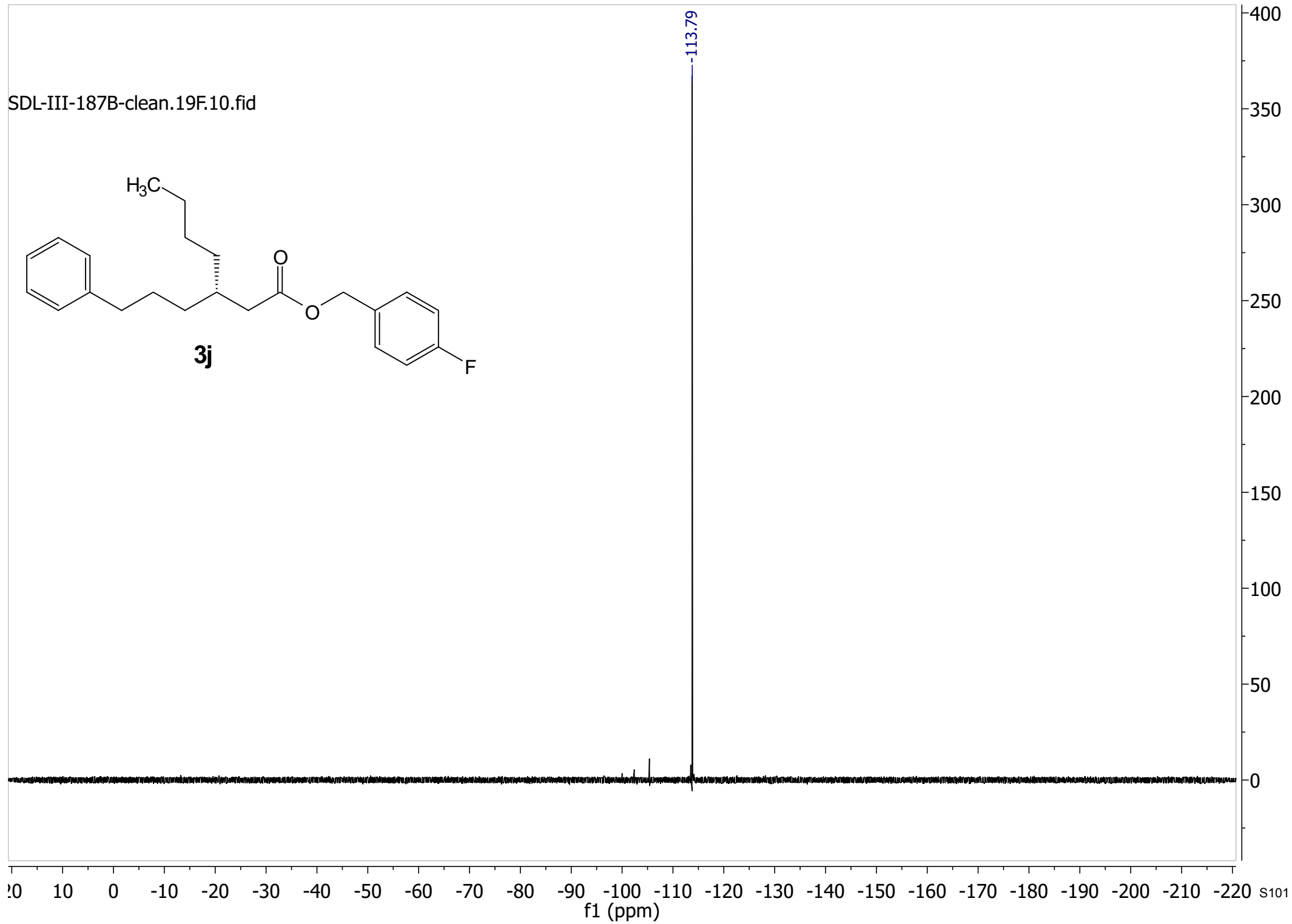
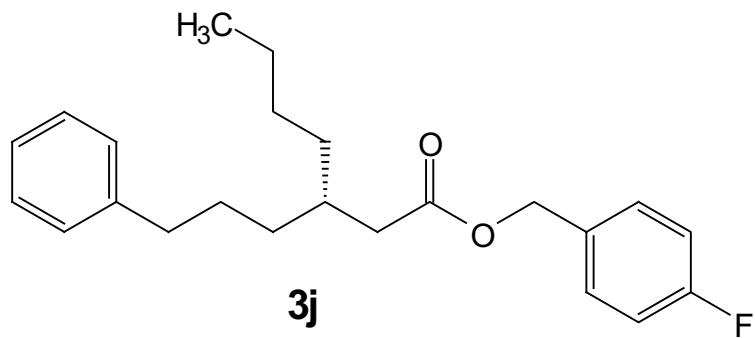


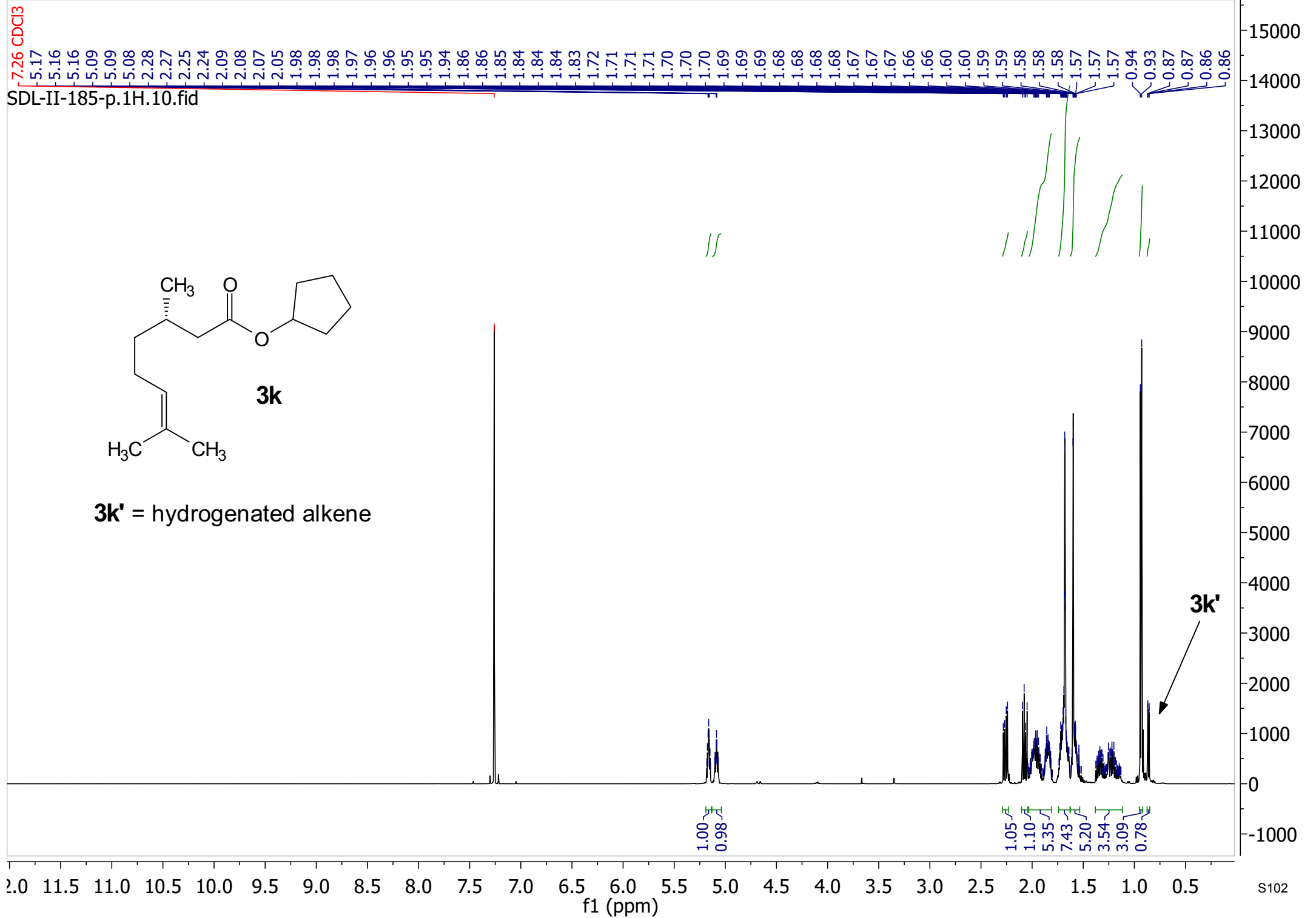


SDL-III-187B-p-clean.13C.10.fid

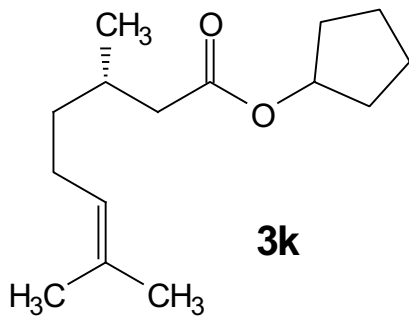


SDL-III-187B-clean.19F.10.fid





SDL-II-185-p.13C.10.fid



3k' = hydrogenated alkene

— 173.25

— 131.64

— 124.48

77.41 CDCl3

77.16 CDCl3

76.91 CDCl3

42.39 3k'

42.30

39.24 3k'

37.09 3k'

36.92

32.85

32.81

30.63 3k'

30.26

28.08 3k'

25.86

25.57

24.78 3k'

23.87

22.81 3k'

22.73 3k'

19.87 3k'

19.74

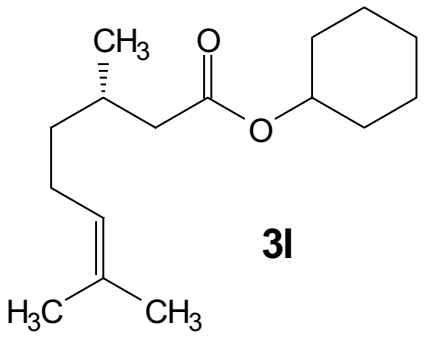
17.79

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 s103

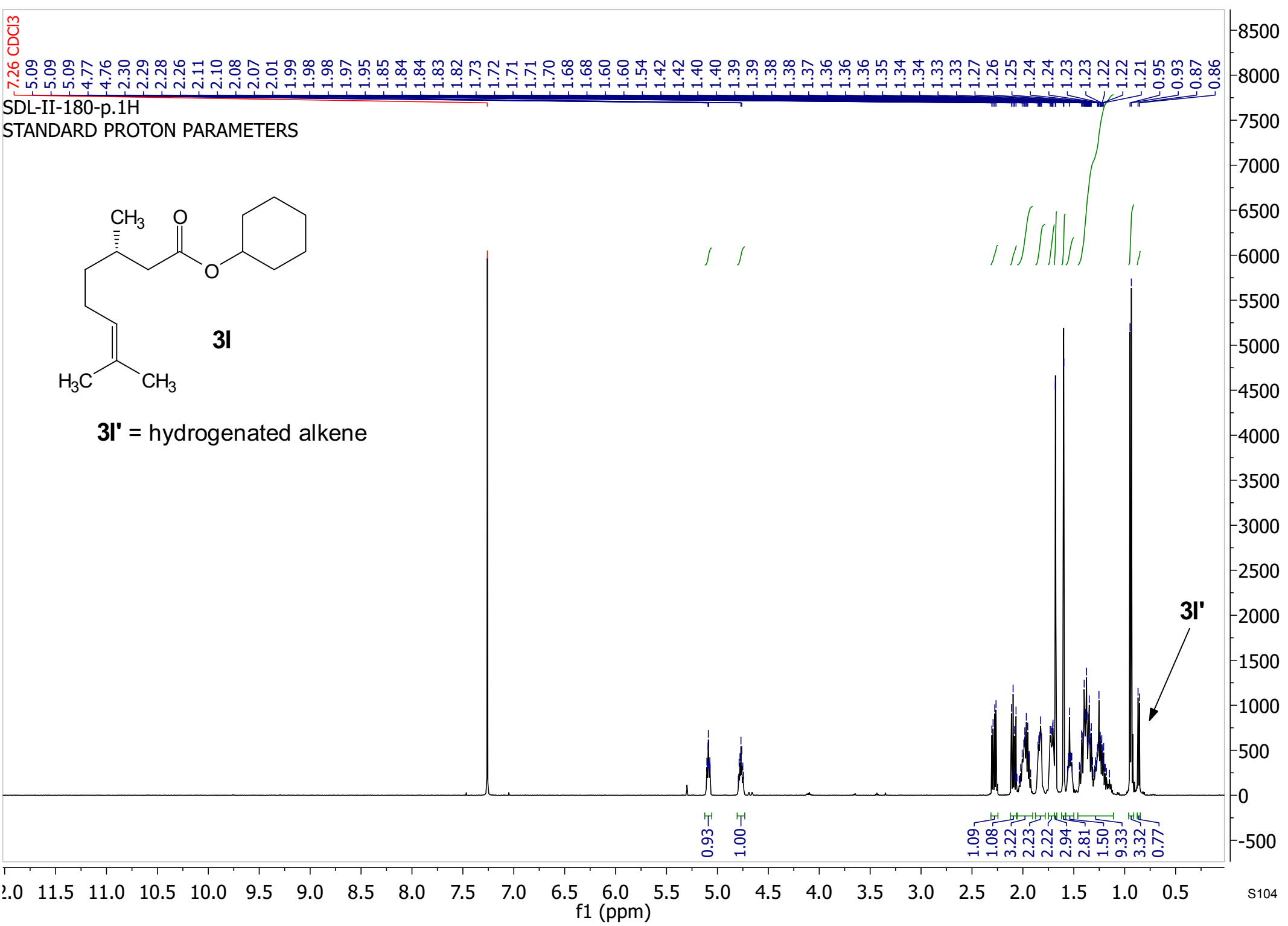
f1 (ppm)

7.26 CDCl3
 -5.09
 -5.09
 -5.09
 -4.77
 -4.76
 -2.30
 -2.29
 -2.28
 -2.26
 -2.11
 -2.10
 -2.08
 -2.07
 -2.01
 -1.99
 -1.98
 -1.98
 -1.97
 -1.95
 -1.85
 -1.84
 -1.84
 -1.83
 -1.82
 -1.73
 -1.72
 -1.71
 -1.71
 -1.70
 -1.68
 -1.68
 -1.60
 -1.60
 -1.54
 -1.42
 -1.42
 -1.40
 -1.40
 -1.39
 -1.39
 -1.38
 -1.38
 -1.37
 -1.36
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 -1.36
 -1.35
 -1.34
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 -1.33
 -1.27
 -1.26
 -1.25
 -1.24
 -1.24
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 -1.21
 -1.21
 -0.95
 -0.93
 -0.87
 -0.86

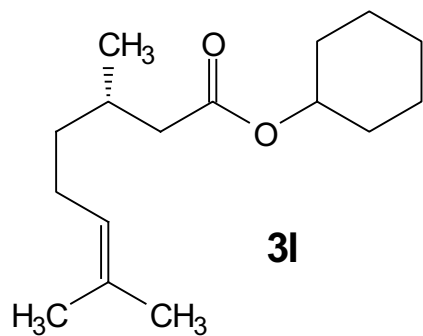
SDL-II-180-p.1H
 STANDARD PROTON PARAMETERS



3I' = hydrogenated alkene



SDL-II-180-p.13C.10.fid



3I' = hydrogenated alkene

— 172.89

— 131.62

— 124.50

77.41 CDCl3

77.16 CDCl3

76.91 CDCl3

72.41

42.49 3I'

42.40

39.24 3I'

37.10 3I'

36.93

31.87

31.83

30.67 3I'

30.30

28.07 3I'

25.86

25.58

24.79 3I'

23.93

22.81 3I'

22.73 3I'

19.84 3I'

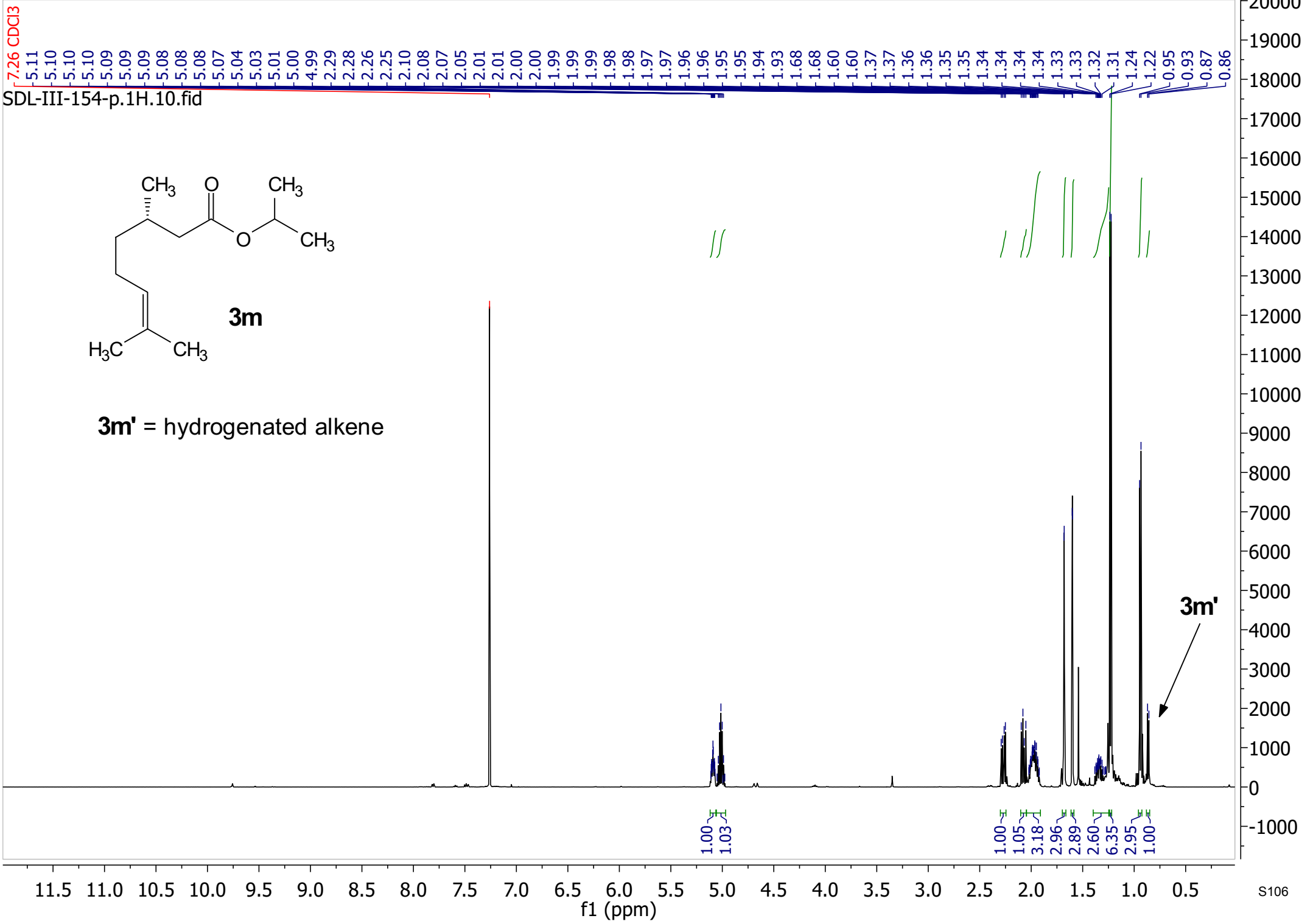
19.72

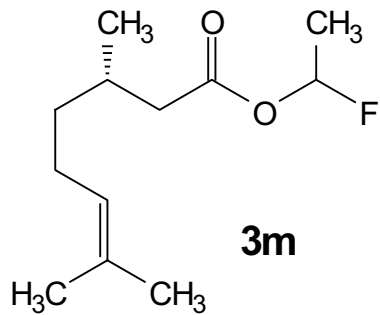
17.80

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

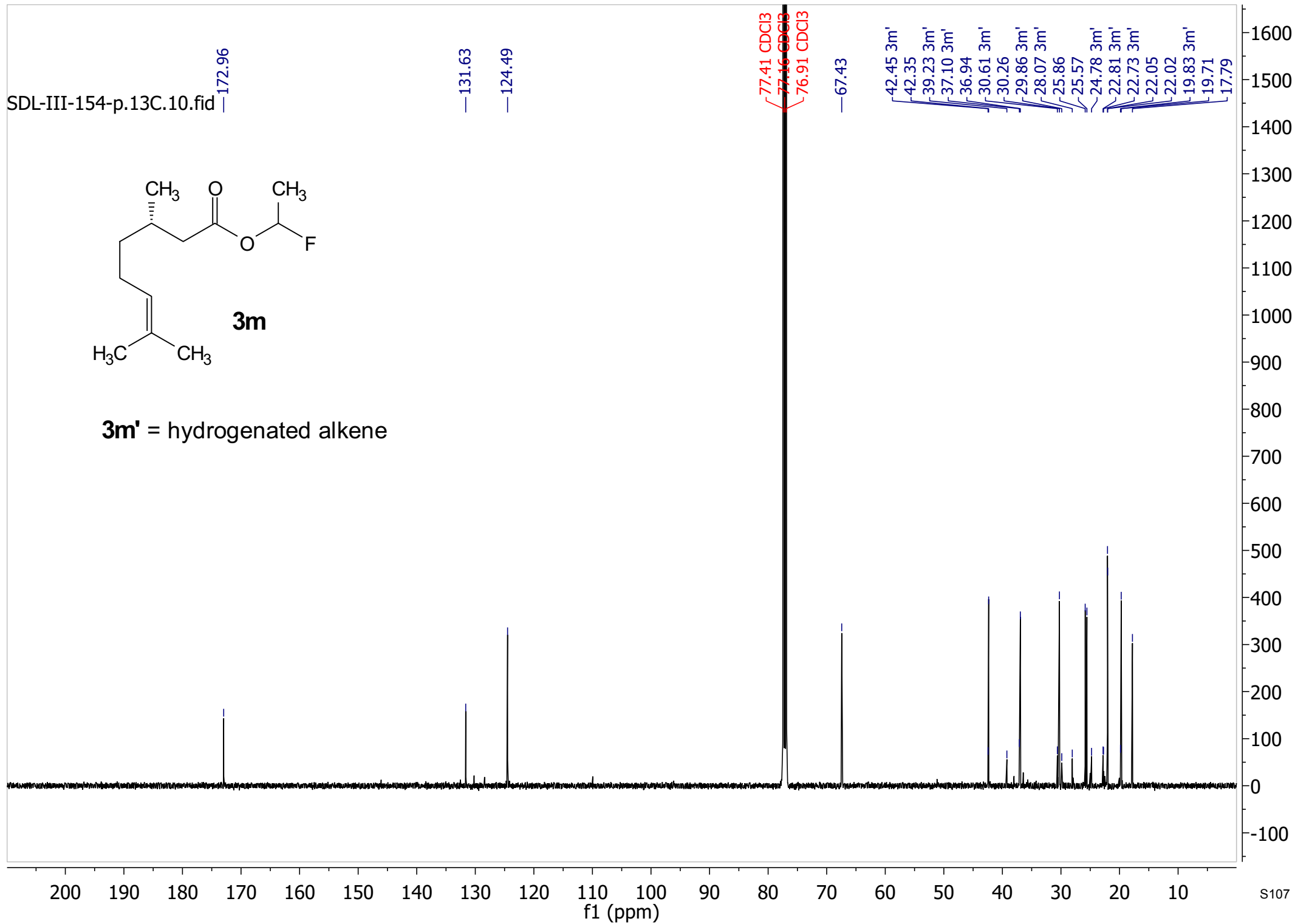
f1 (ppm)

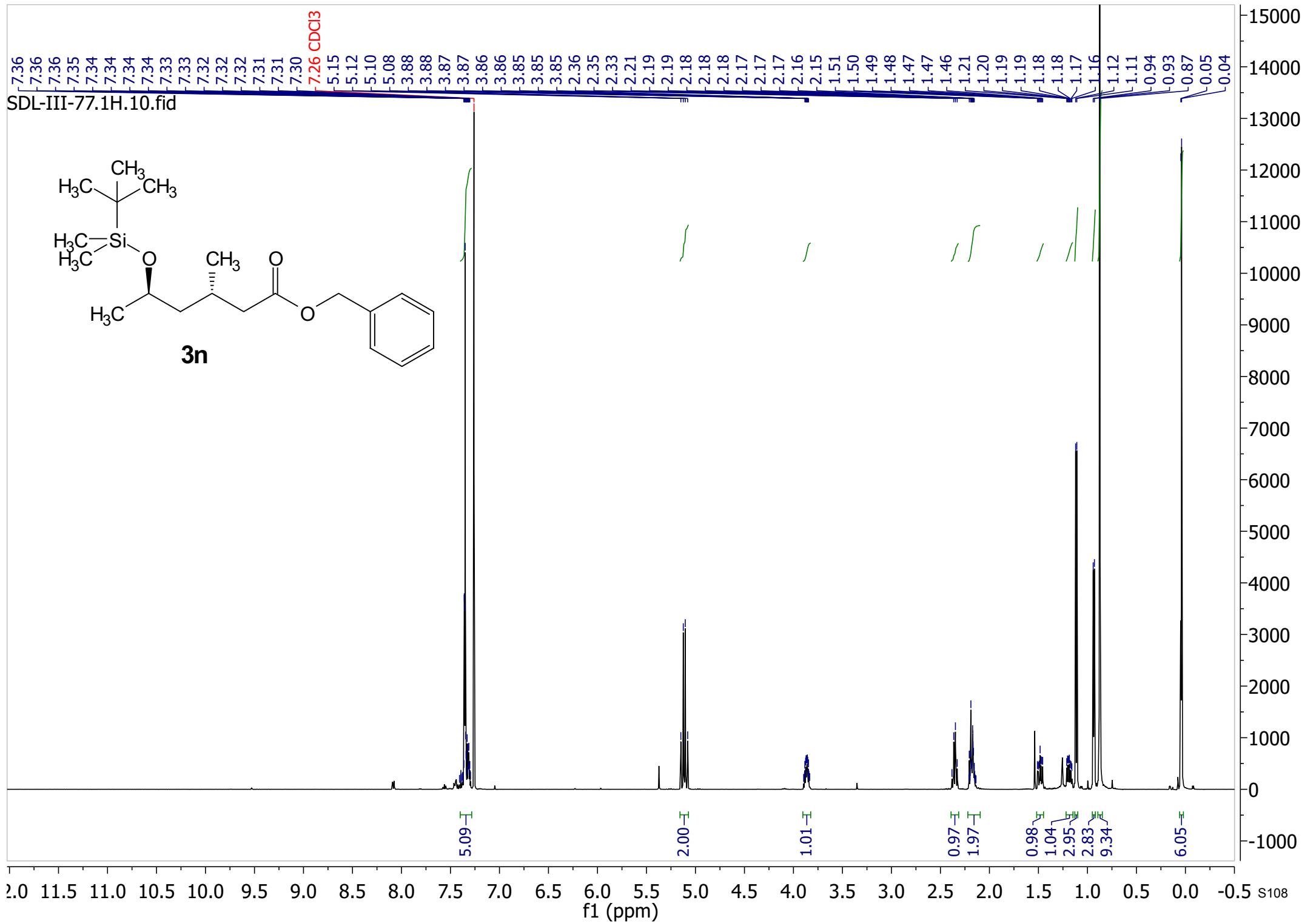
S105



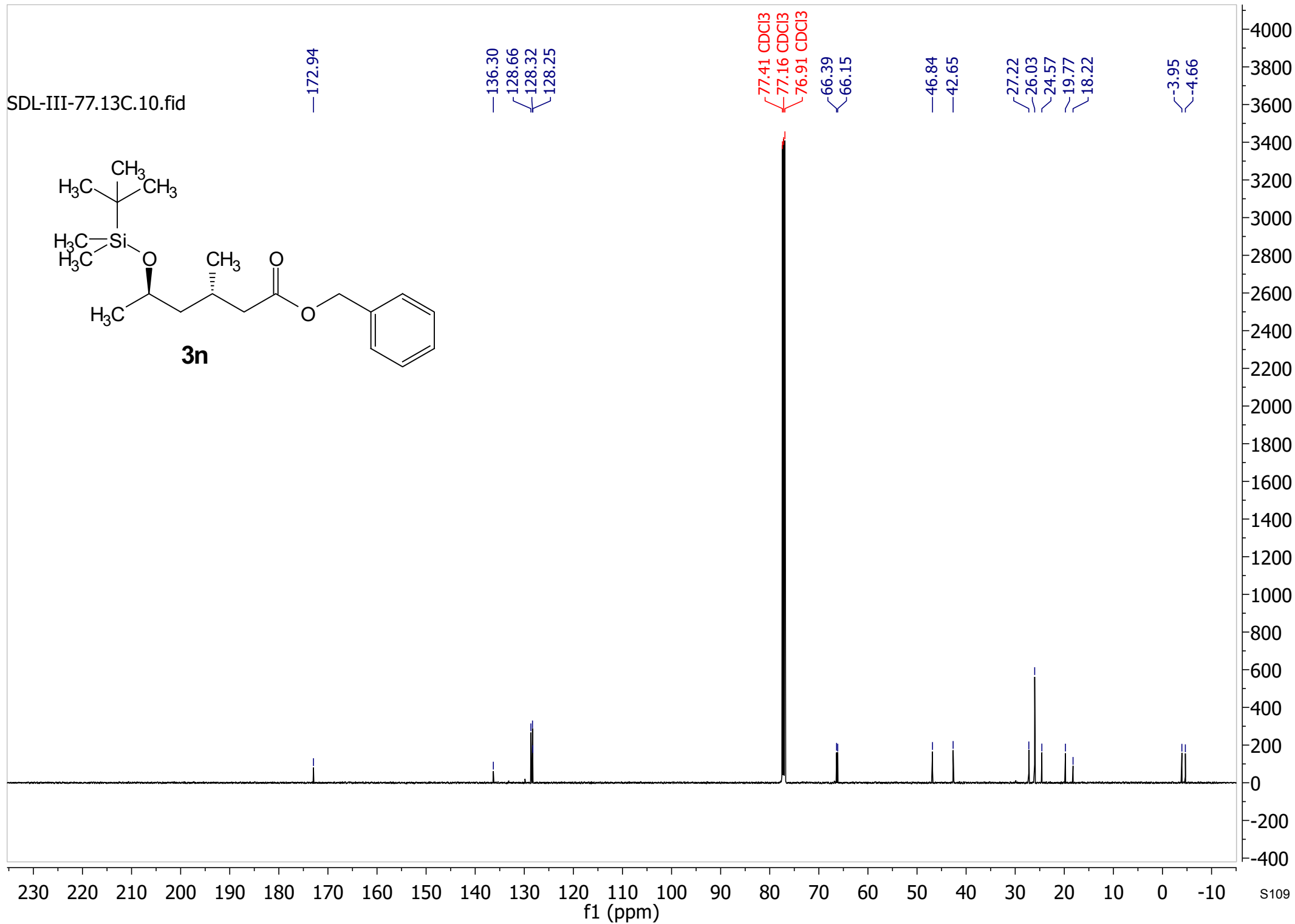
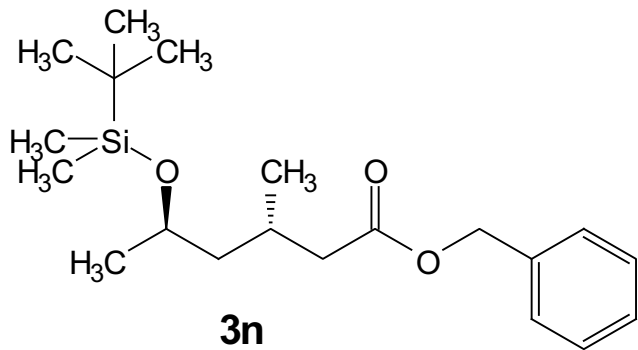


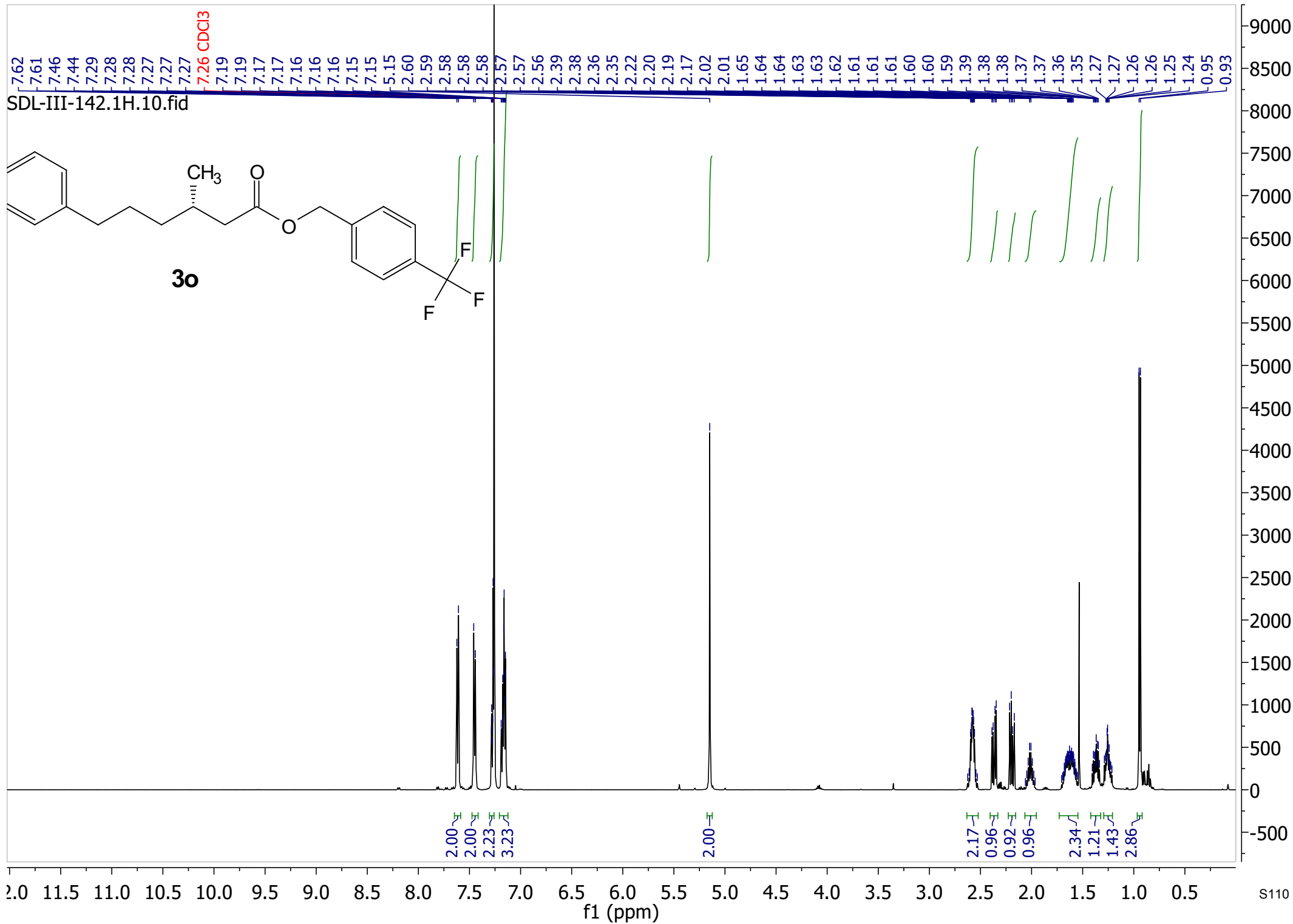
3m' = hydrogenated alkene



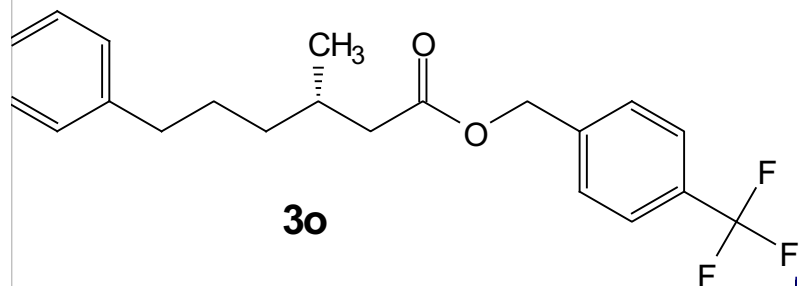


SDL-III-77.13C.10.fid





SDL-III-142.13C.10.fid



— 172.97

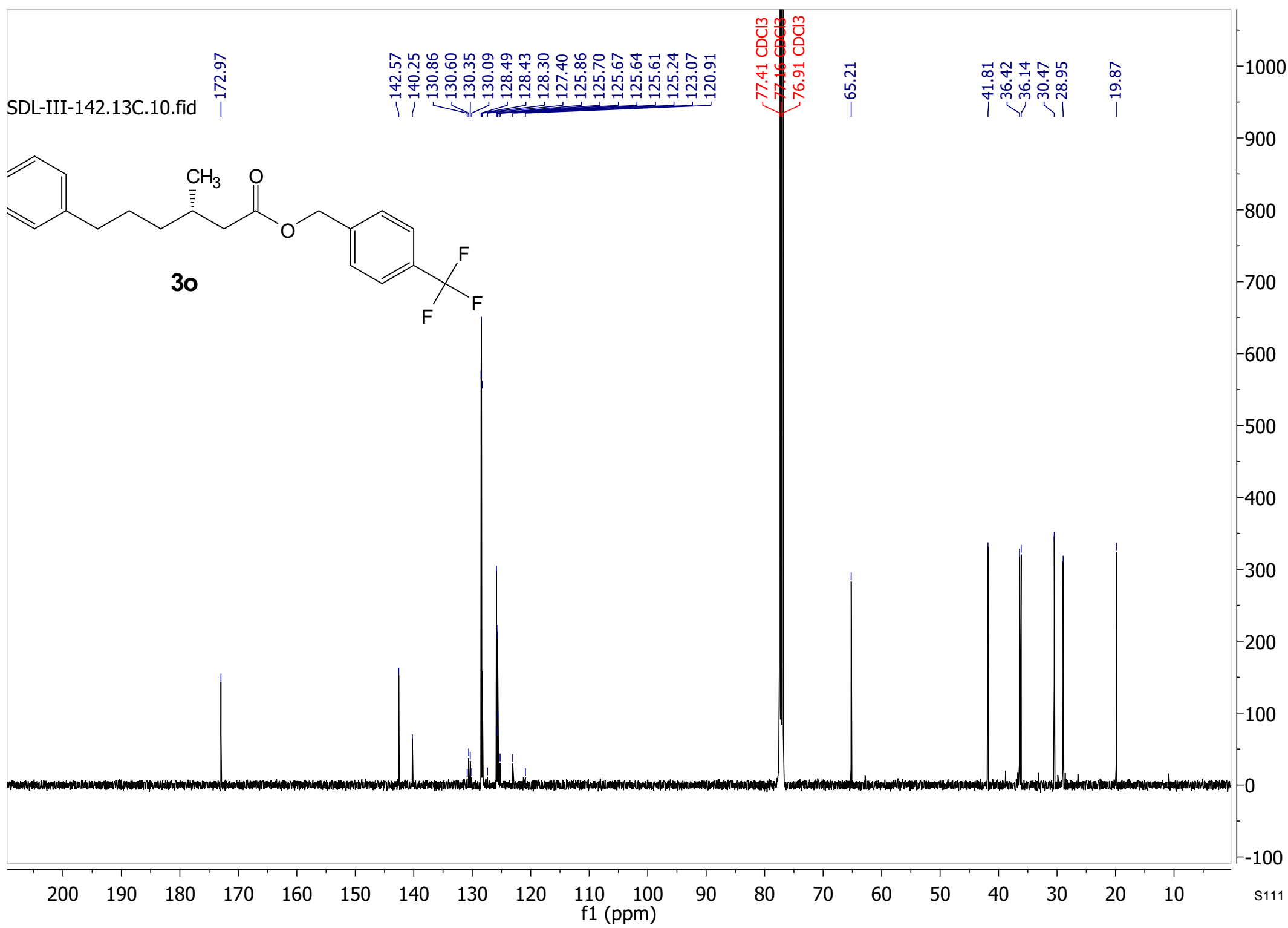
— 142.57
— 140.25
— 130.86
— 130.60
— 130.35
— 130.09
— 128.49
— 128.43
— 128.30
— 127.40
— 125.86
— 125.70
— 125.67
— 125.64
— 125.61
— 125.24
— 123.07
— 120.91

77.41 CDC13
77.16 CDC13
76.91 CDC13

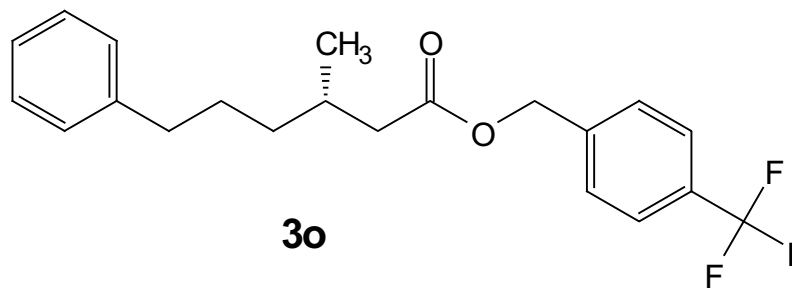
— 65.21

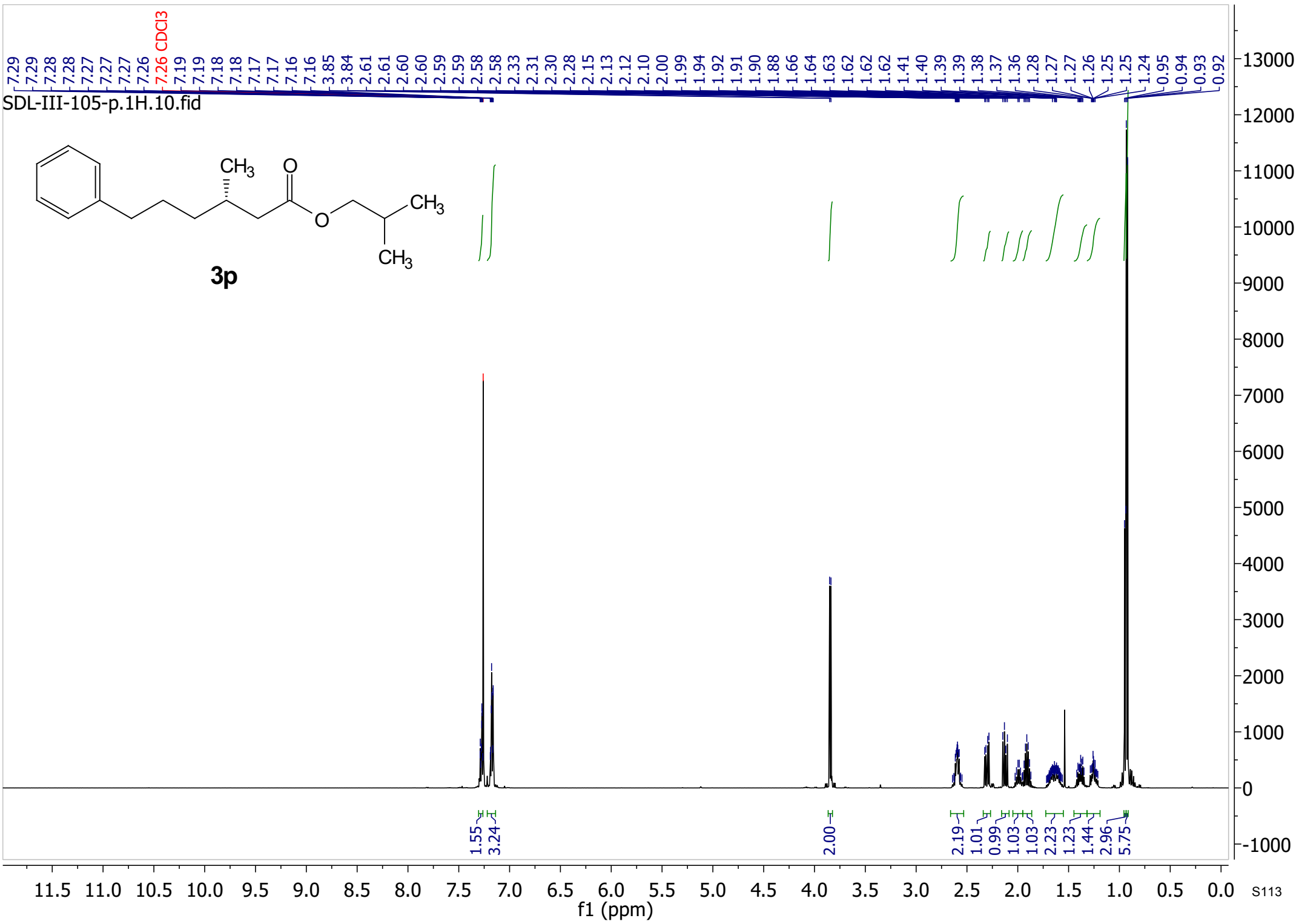
— 41.81
— 36.42
— 36.14
— 30.47
— 28.95

— 19.87

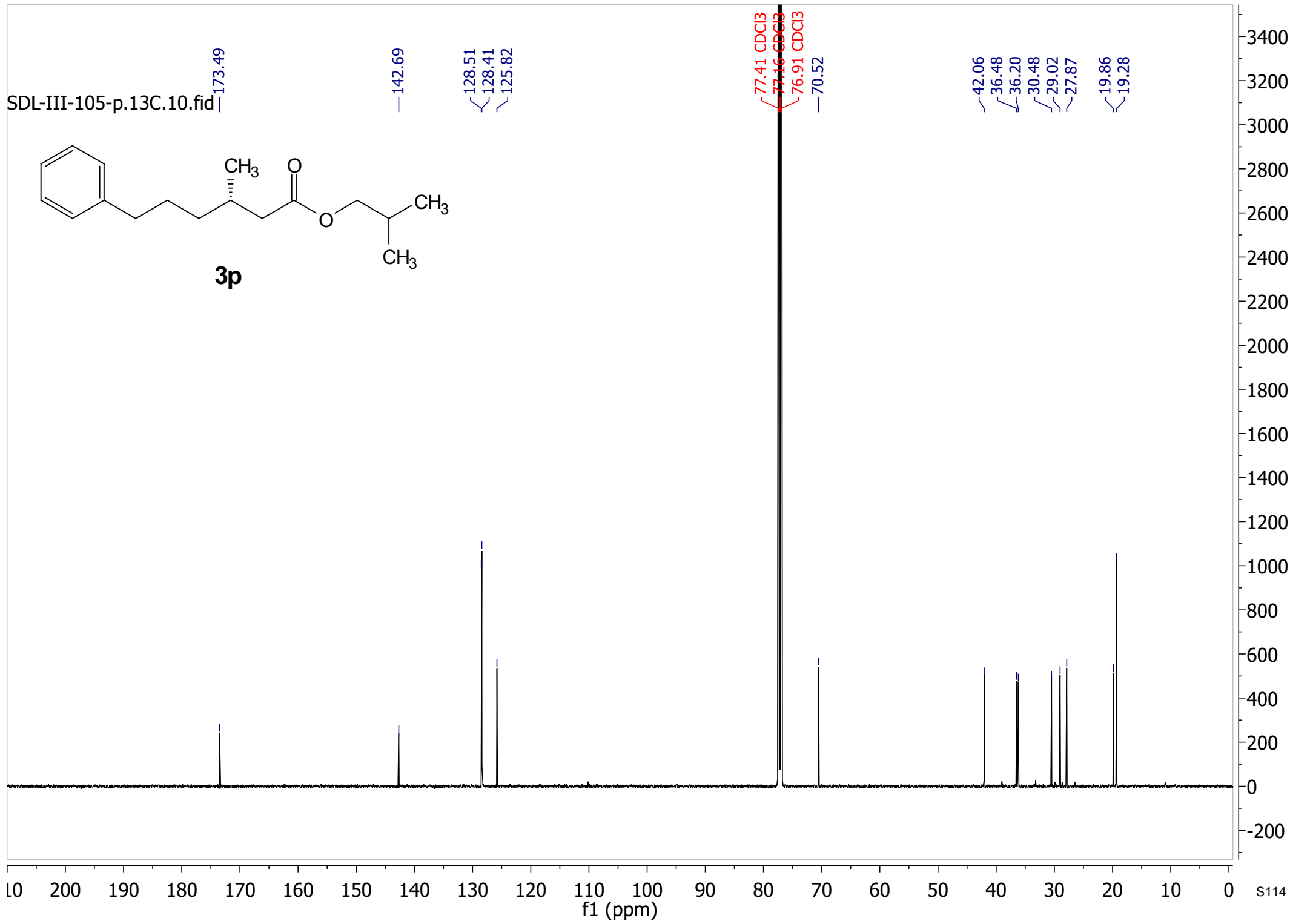
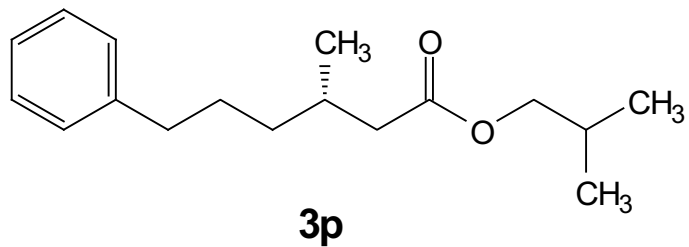


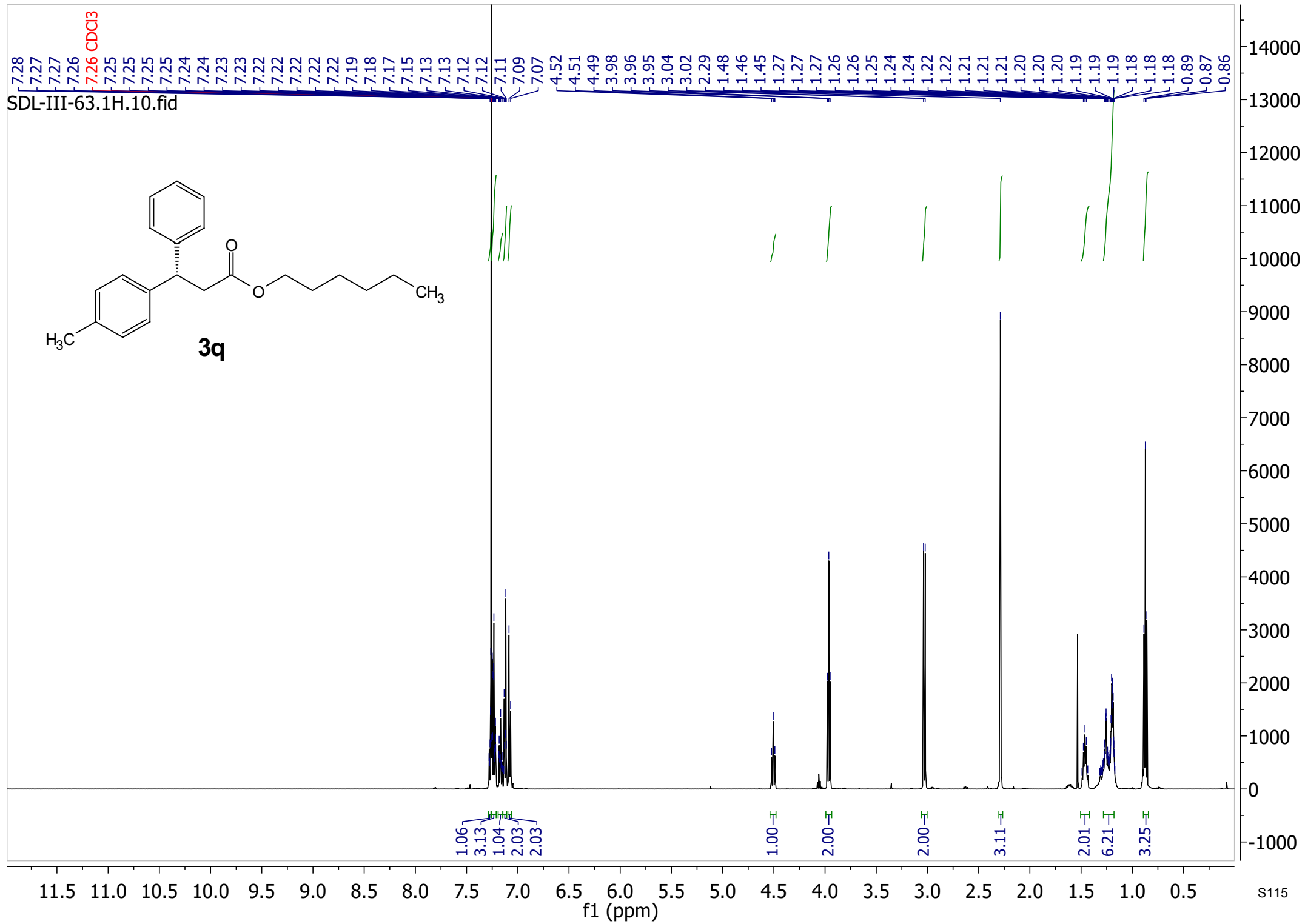
SDL-III-142.19F.10.fid



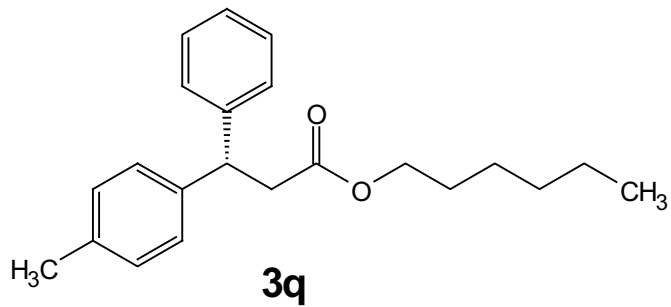


SDL-III-105-p.13C.10.fid





SDL-III-63.13C.10.fid



—172.12

—143.90

—140.67

—136.16

—129.36

—128.65

—127.76

—127.66

—126.57

77.41 CDC13

77.16 CDC13

76.91 CDC13

—64.77

—46.89

—41.09

—31.55

—28.66

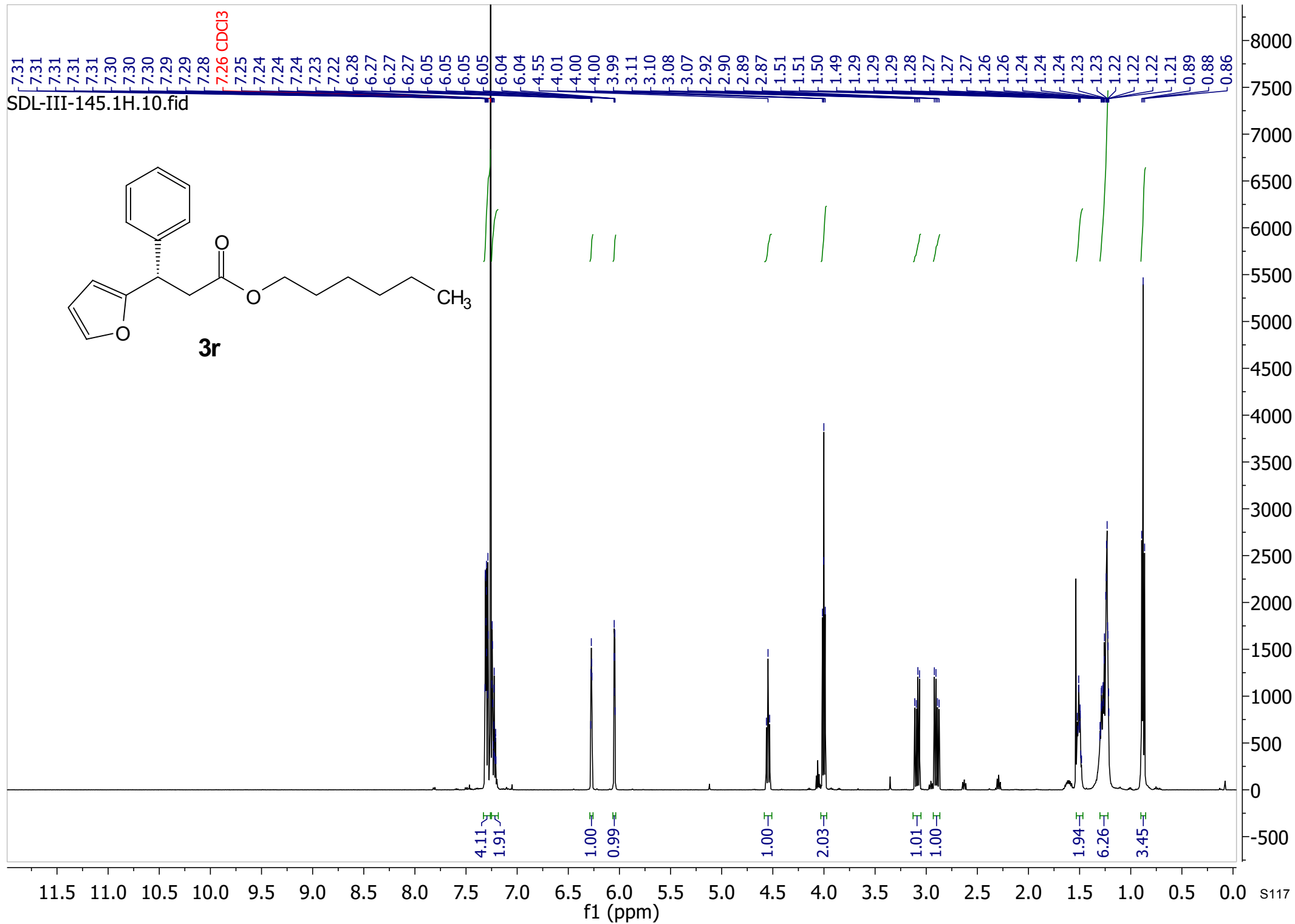
—25.63

—22.66

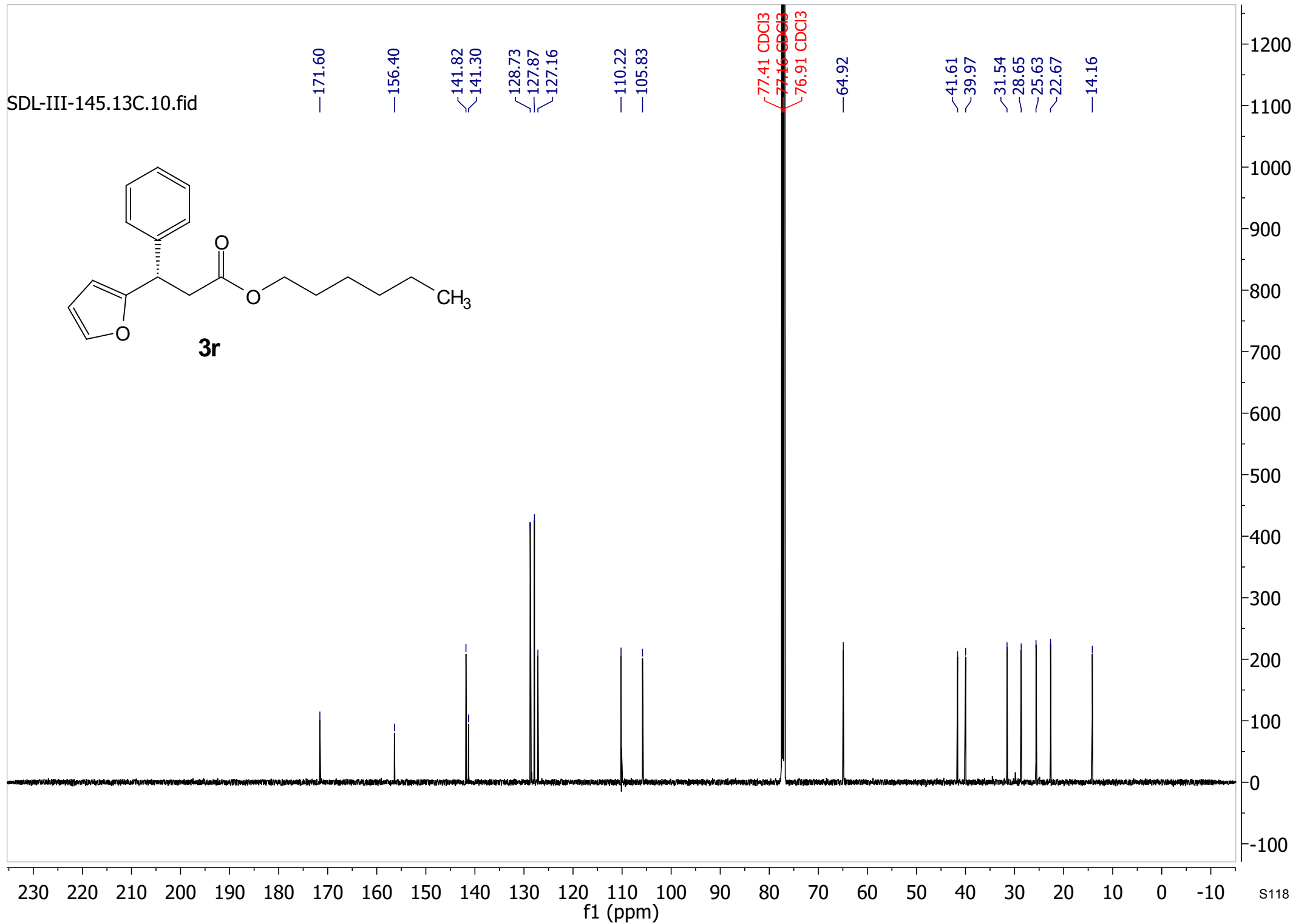
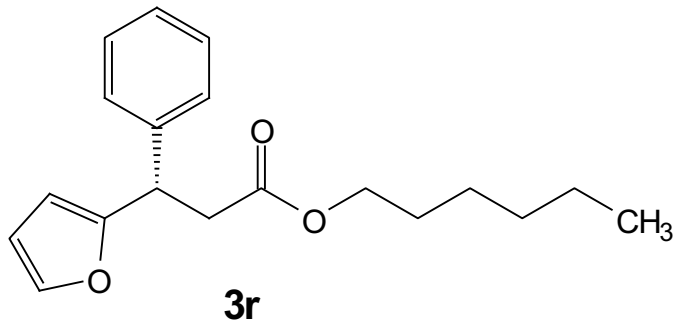
—21.13

—14.17

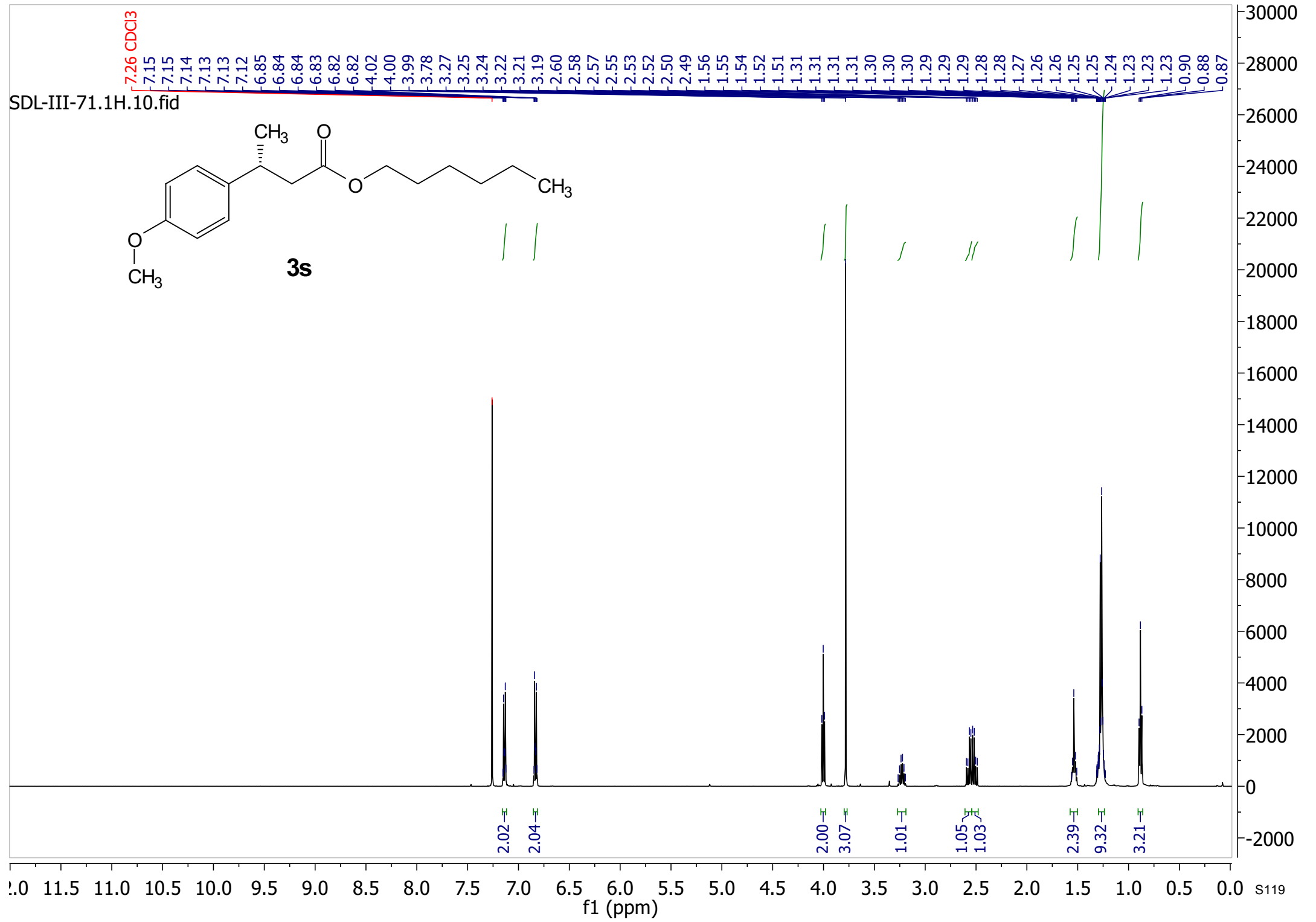
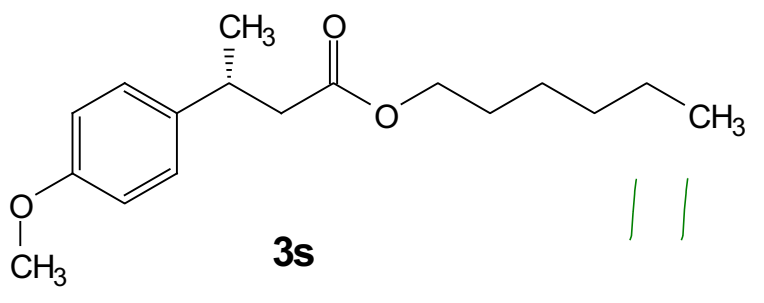
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm) s116



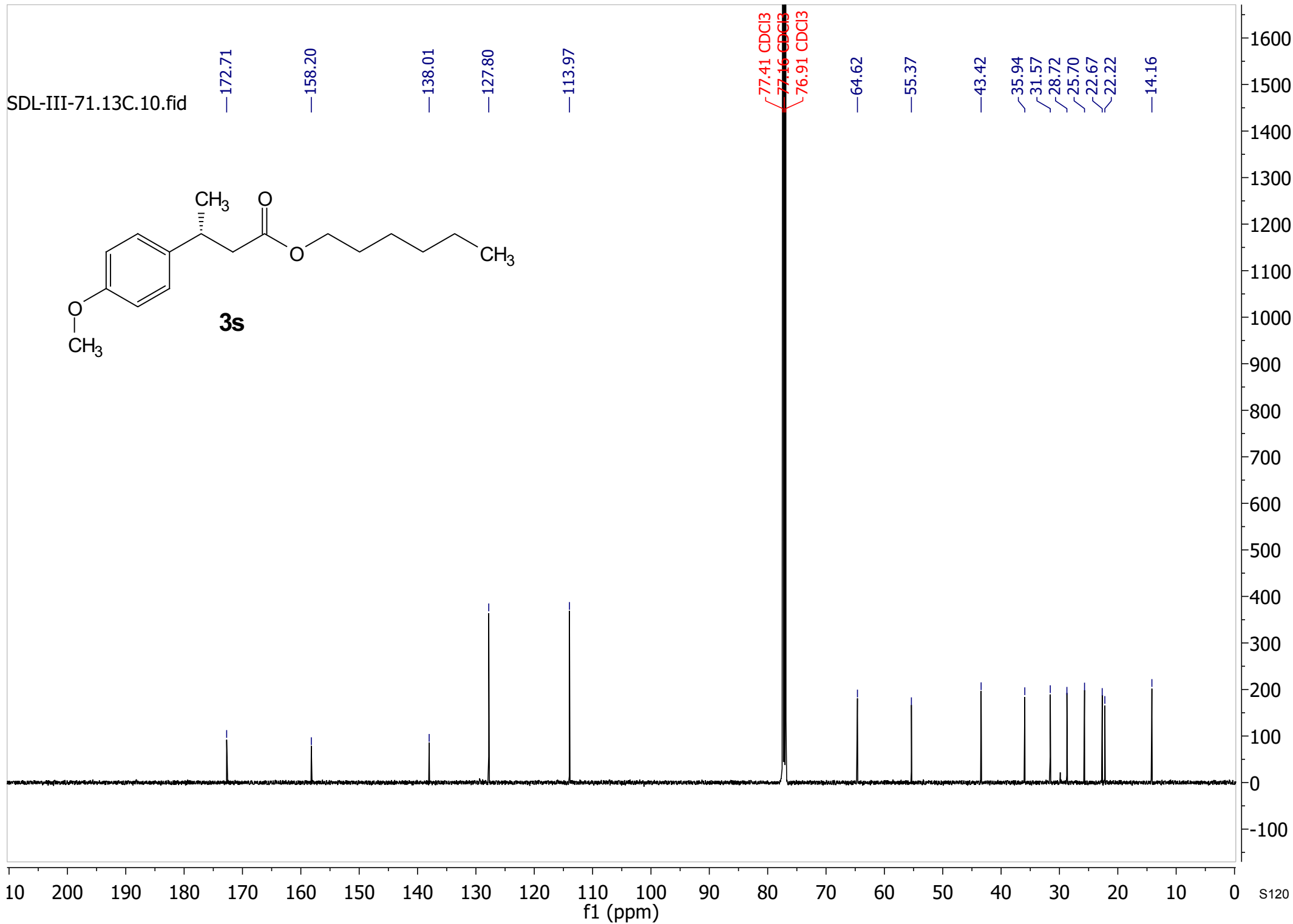
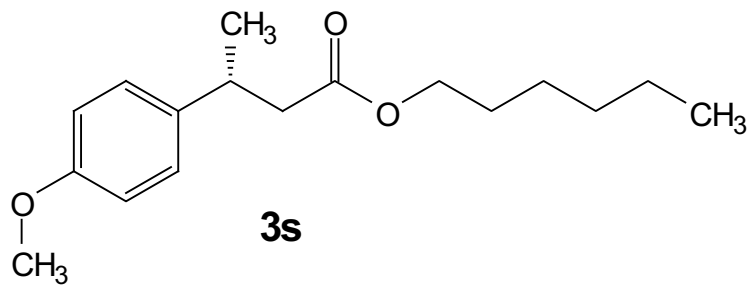
SDL-III-145.13C.10.fid



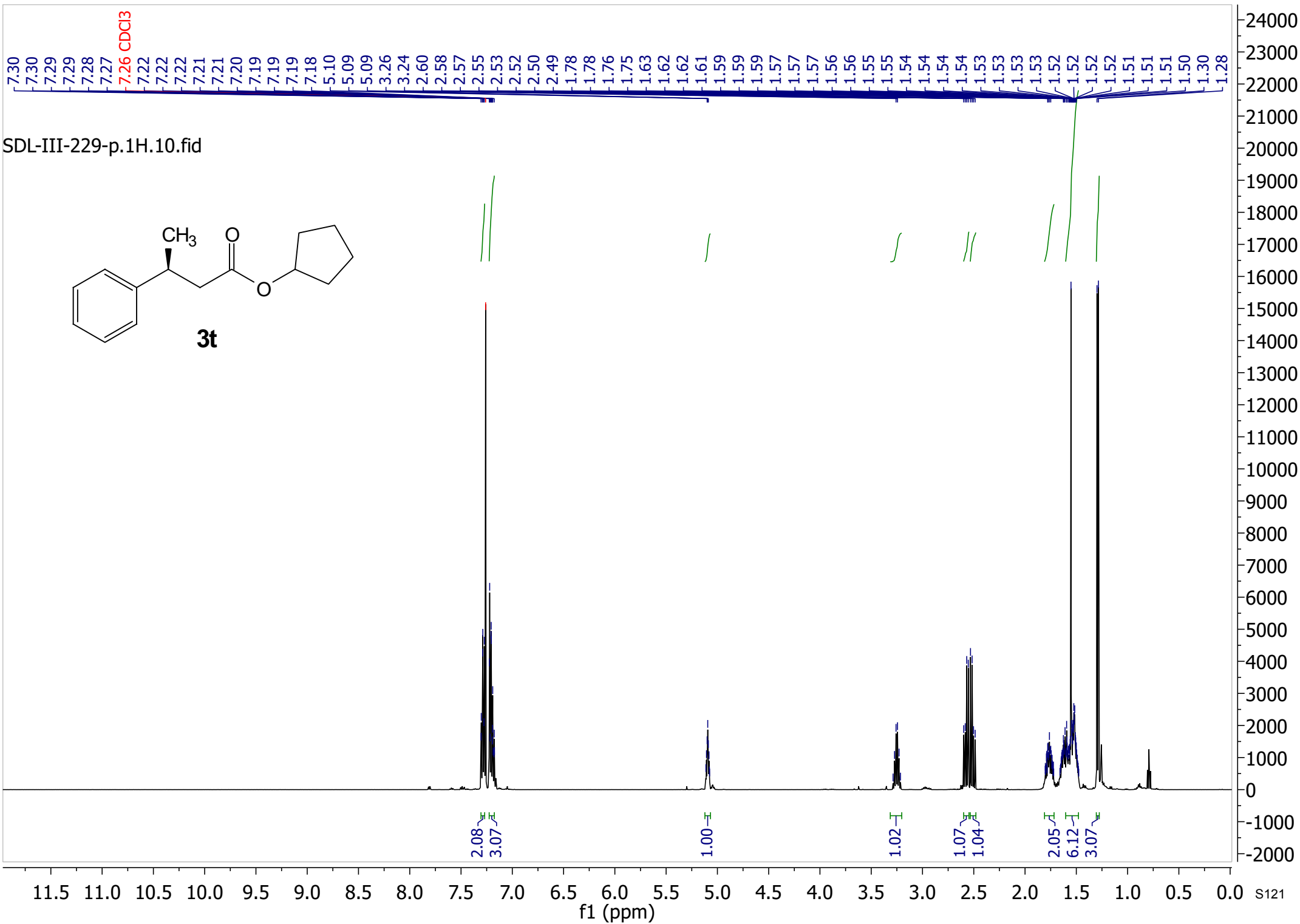
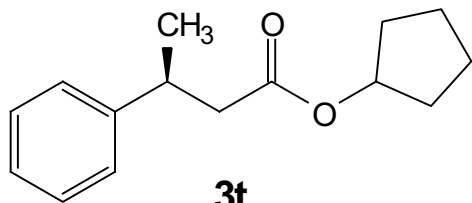
SDL-III-71.1H.10.fid



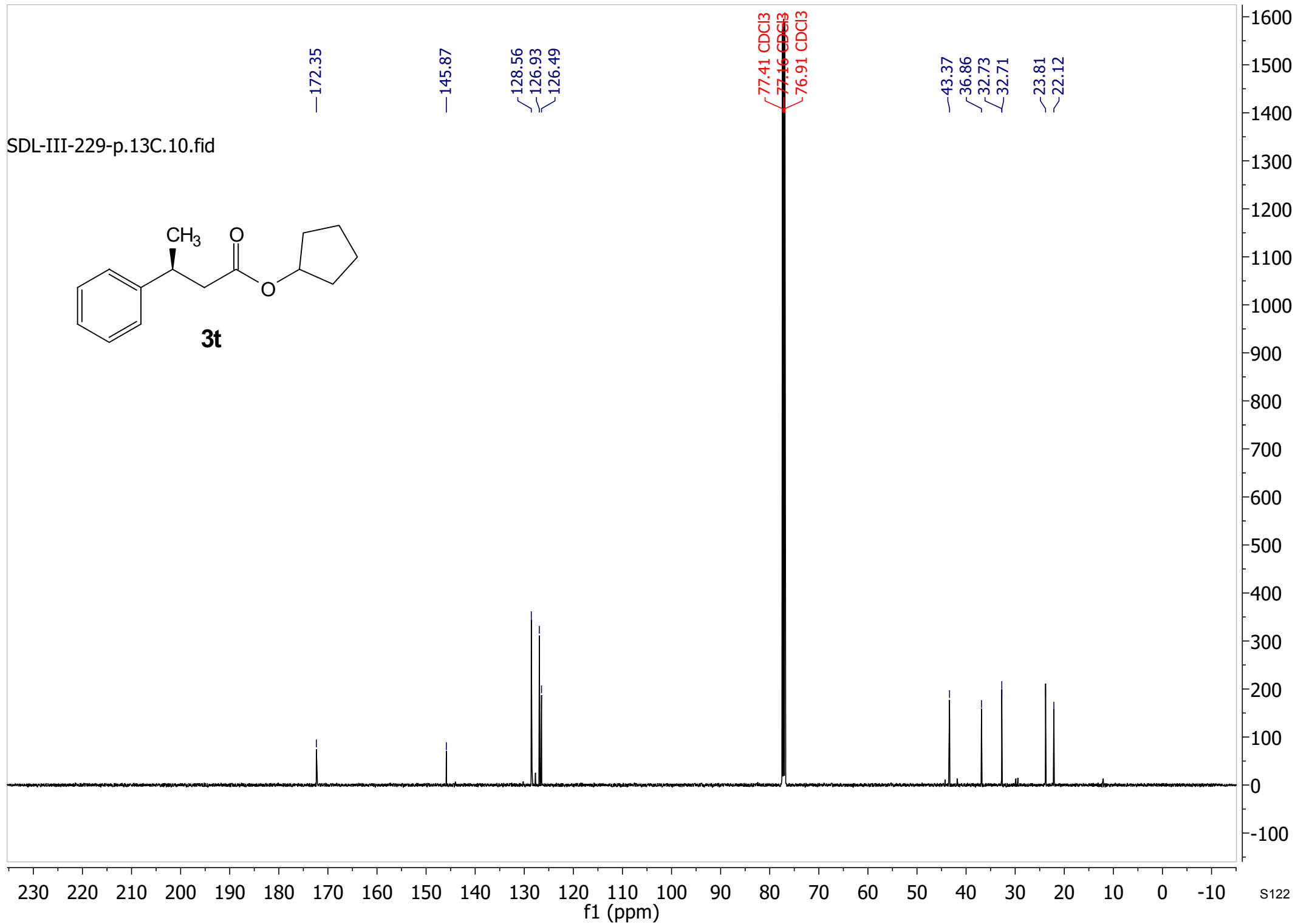
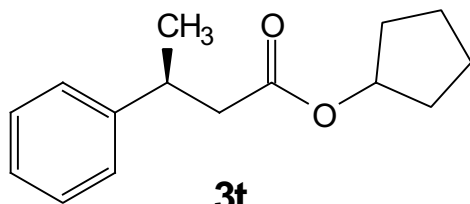
SDL-III-71.13C.10.fid

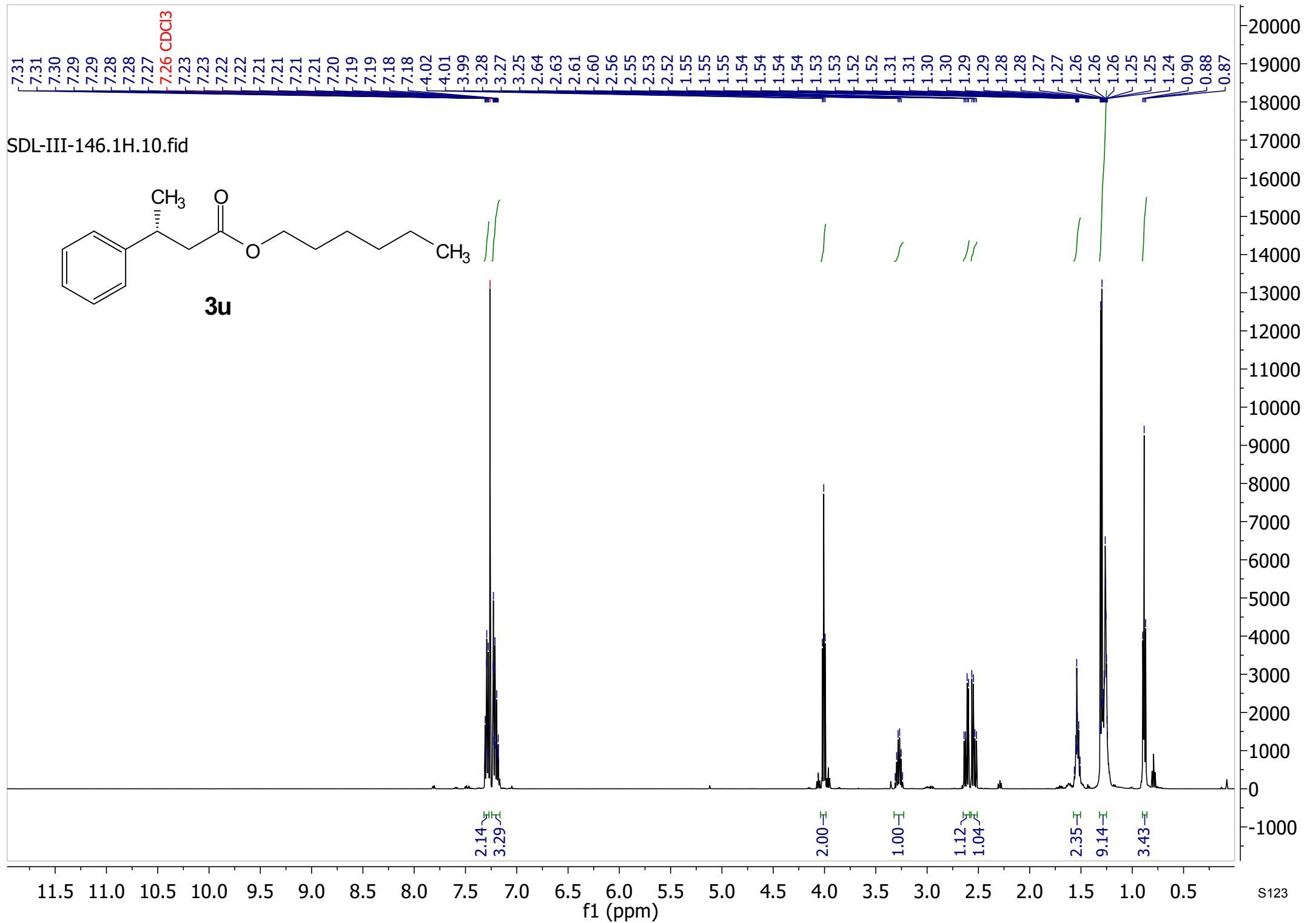


SDL-III-229-p.1H.10.fid

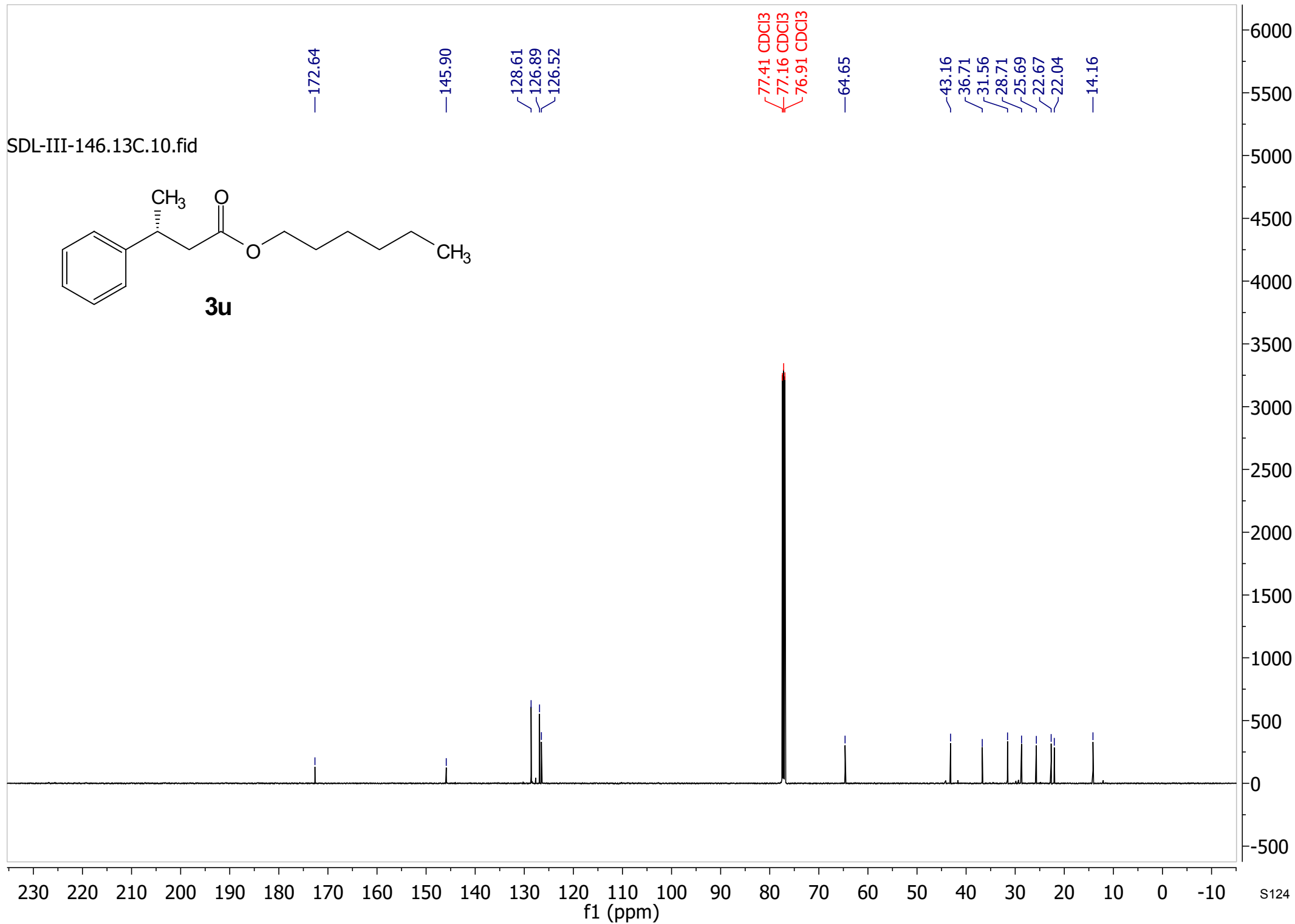
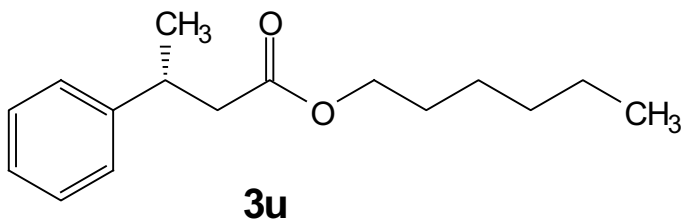


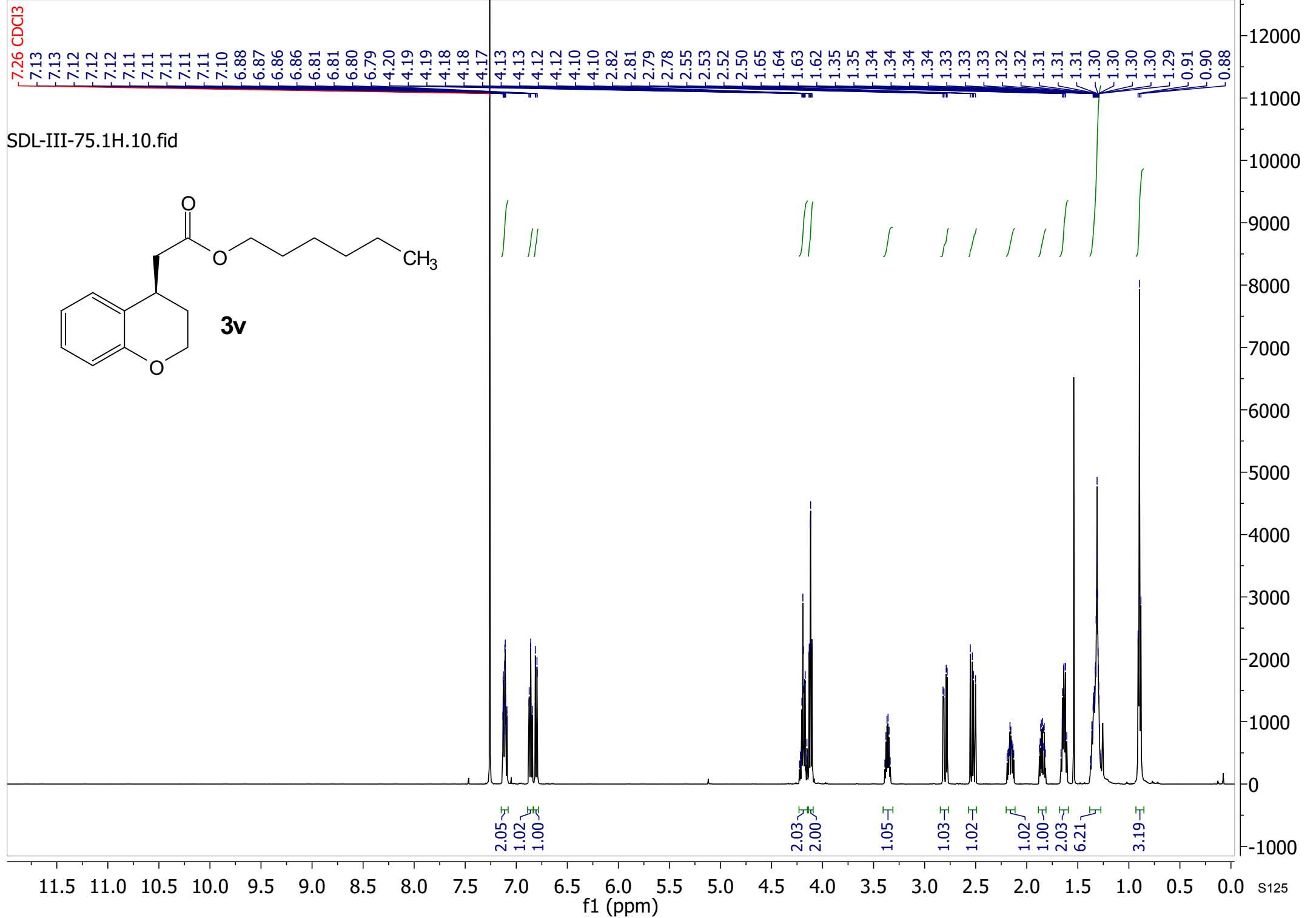
SDL-III-229-p.13C.10.fid



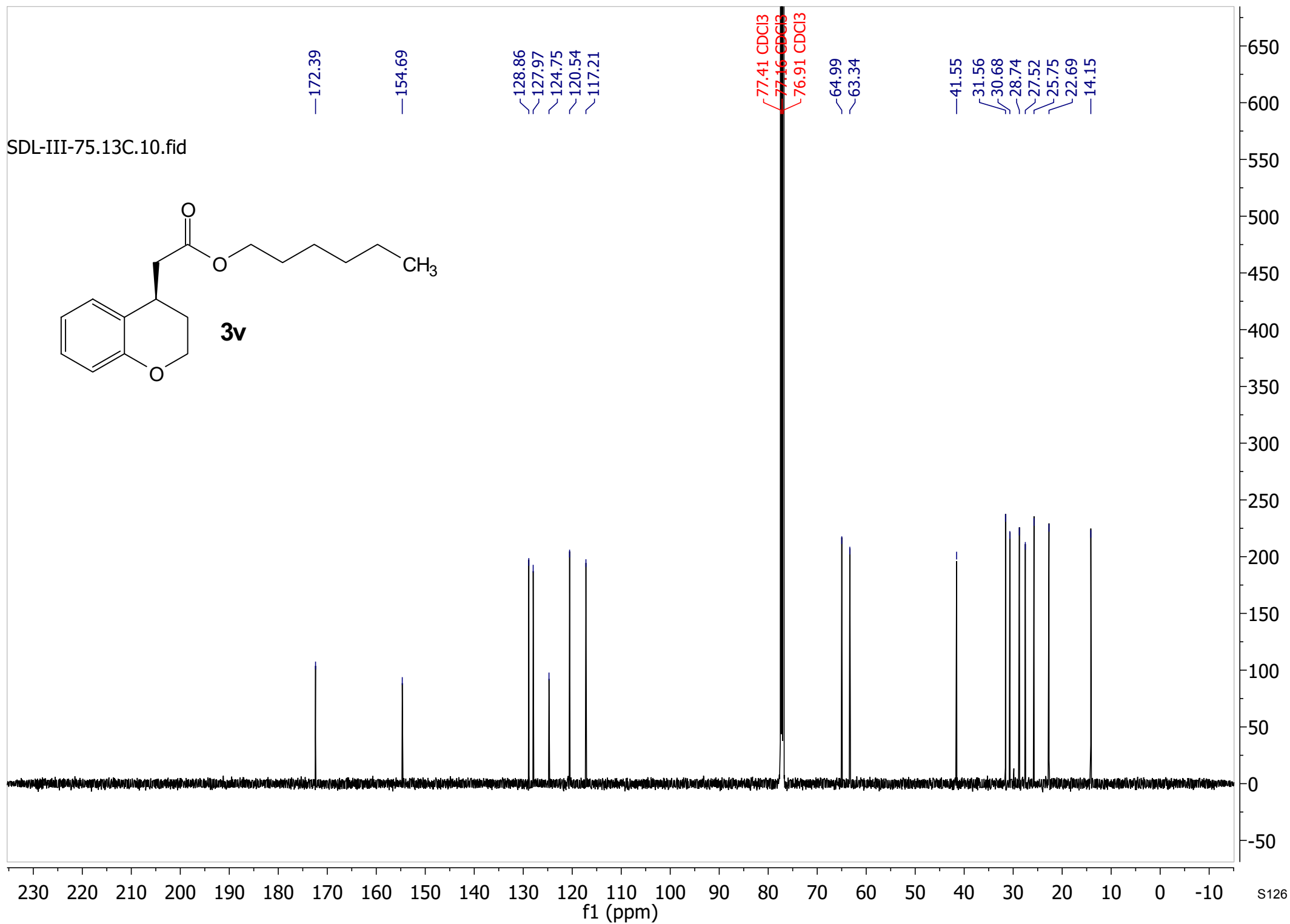
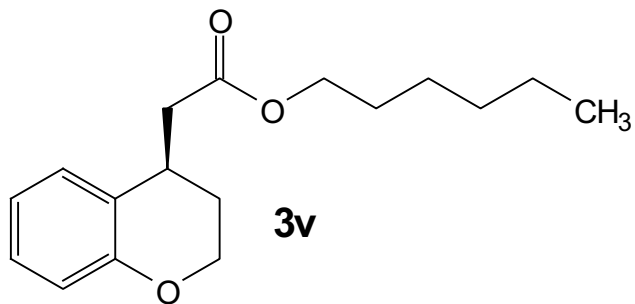


SDL-III-146.13C.10.fid



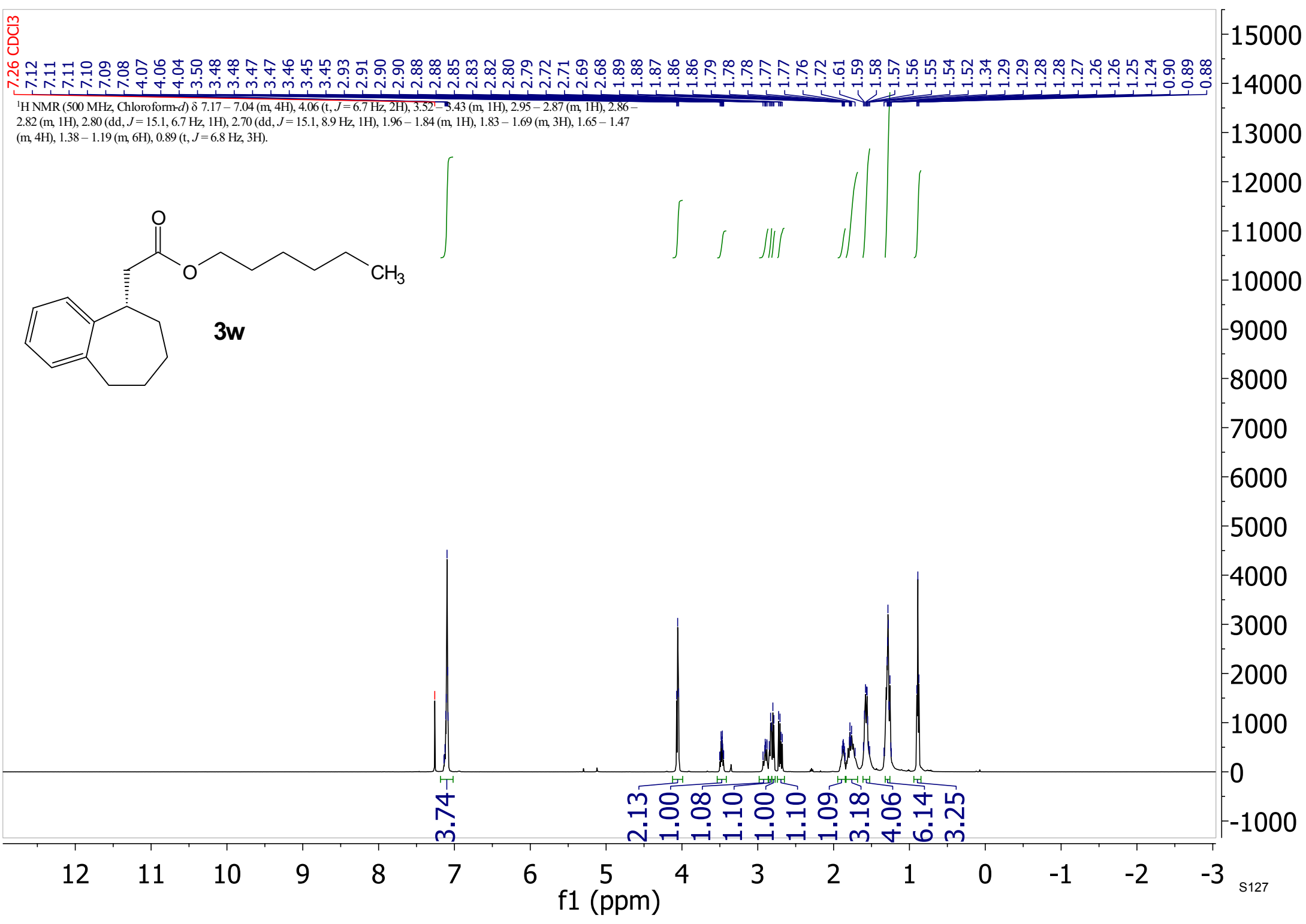
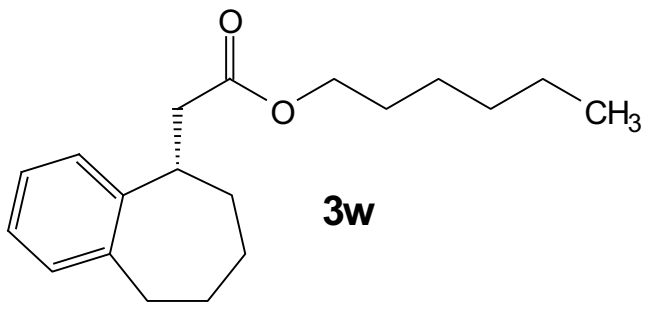


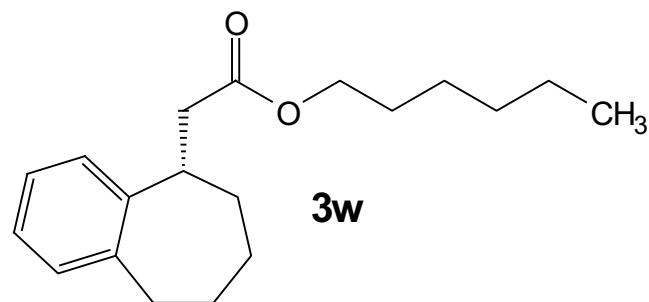
SDL-III-75.13C.10.fid



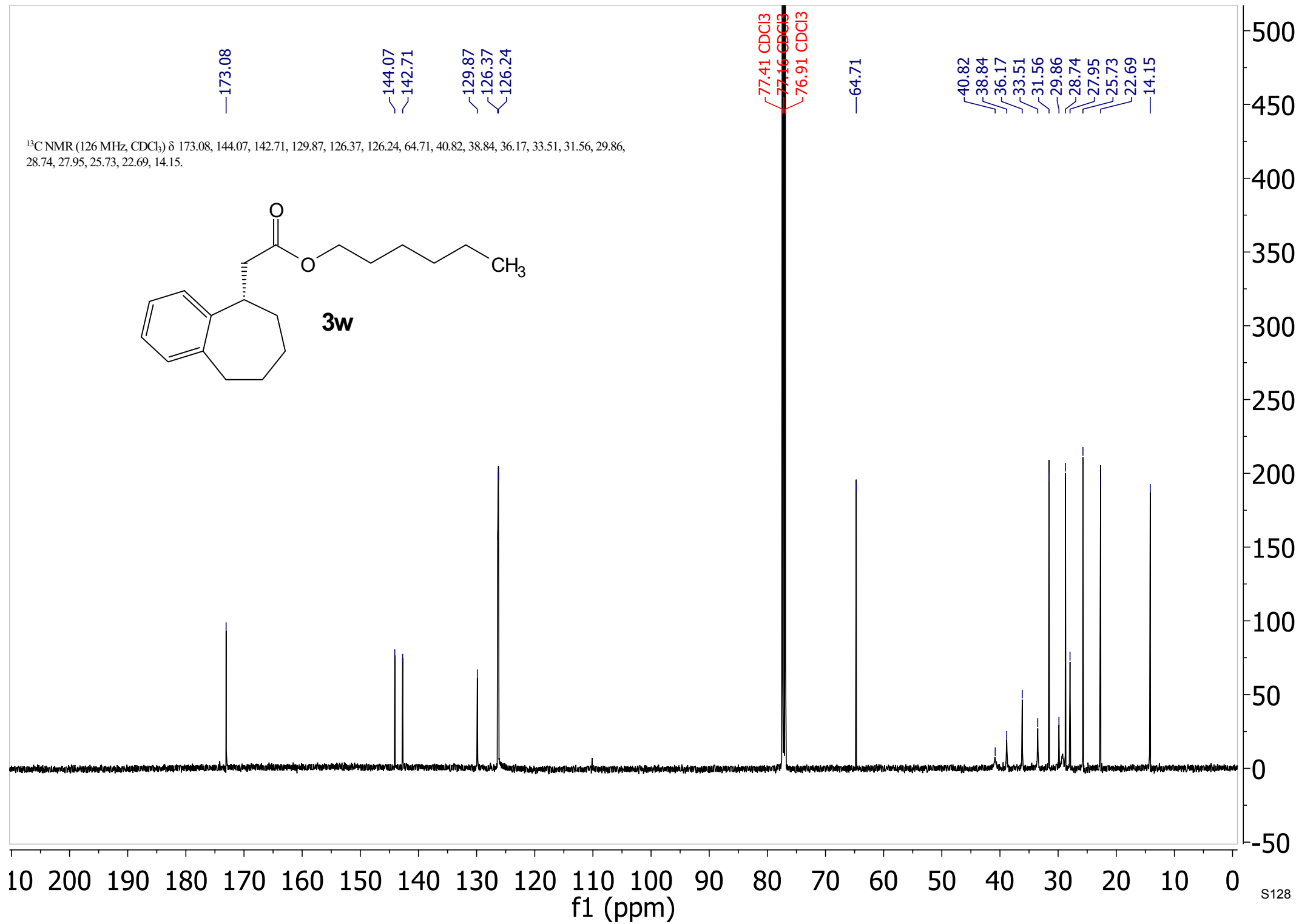
7.26 CDCl3

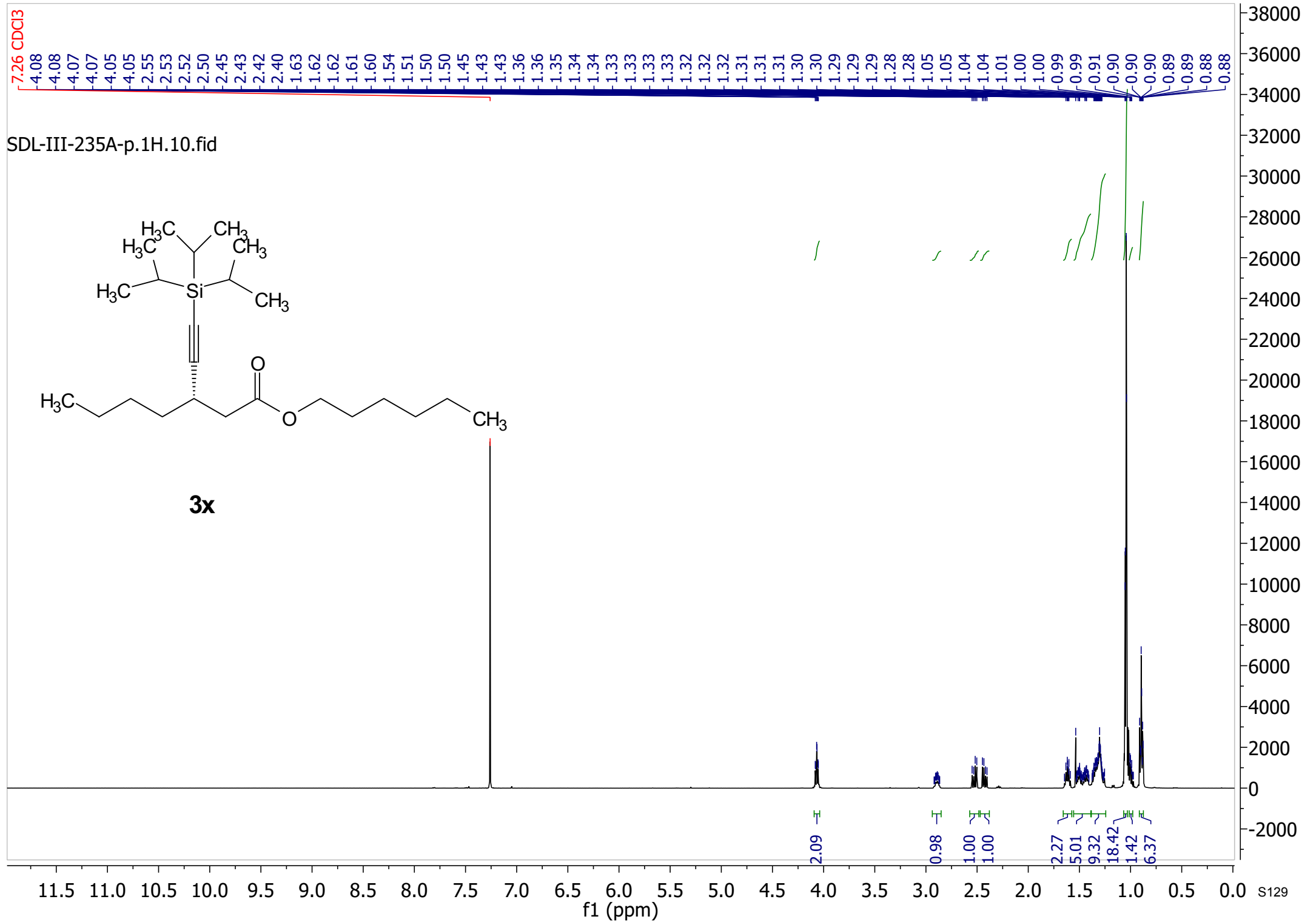
¹H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 7.04 (m, 4H), 4.06 (t, *J* = 6.7 Hz, 2H), 3.52 – 3.43 (m, 1H), 2.95 – 2.87 (m, 1H), 2.86 – 2.82 (m, 1H), 2.80 (dd, *J* = 15.1, 6.7 Hz, 1H), 2.70 (dd, *J* = 15.1, 8.9 Hz, 1H), 1.96 – 1.84 (m, 1H), 1.83 – 1.69 (m, 3H), 1.65 – 1.47 (m, 4H), 1.38 – 1.19 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H).



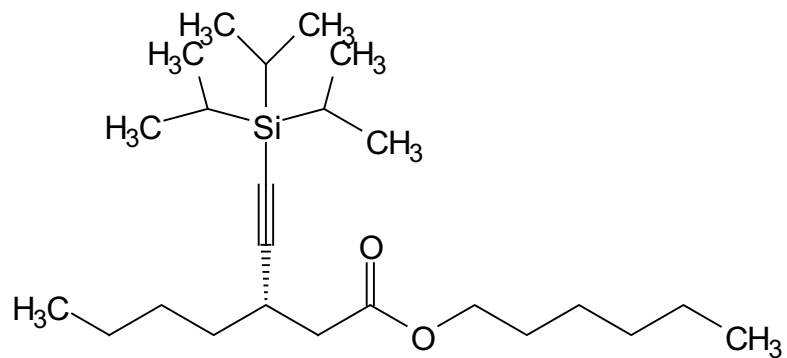


^{13}C NMR (126 MHz, CDCl_3) δ 173.08, 144.07, 142.71, 129.87, 126.37, 126.24, 64.71, 40.82, 38.84, 36.17, 33.51, 31.56, 29.86, 28.74, 27.95, 25.73, 22.69, 14.15.

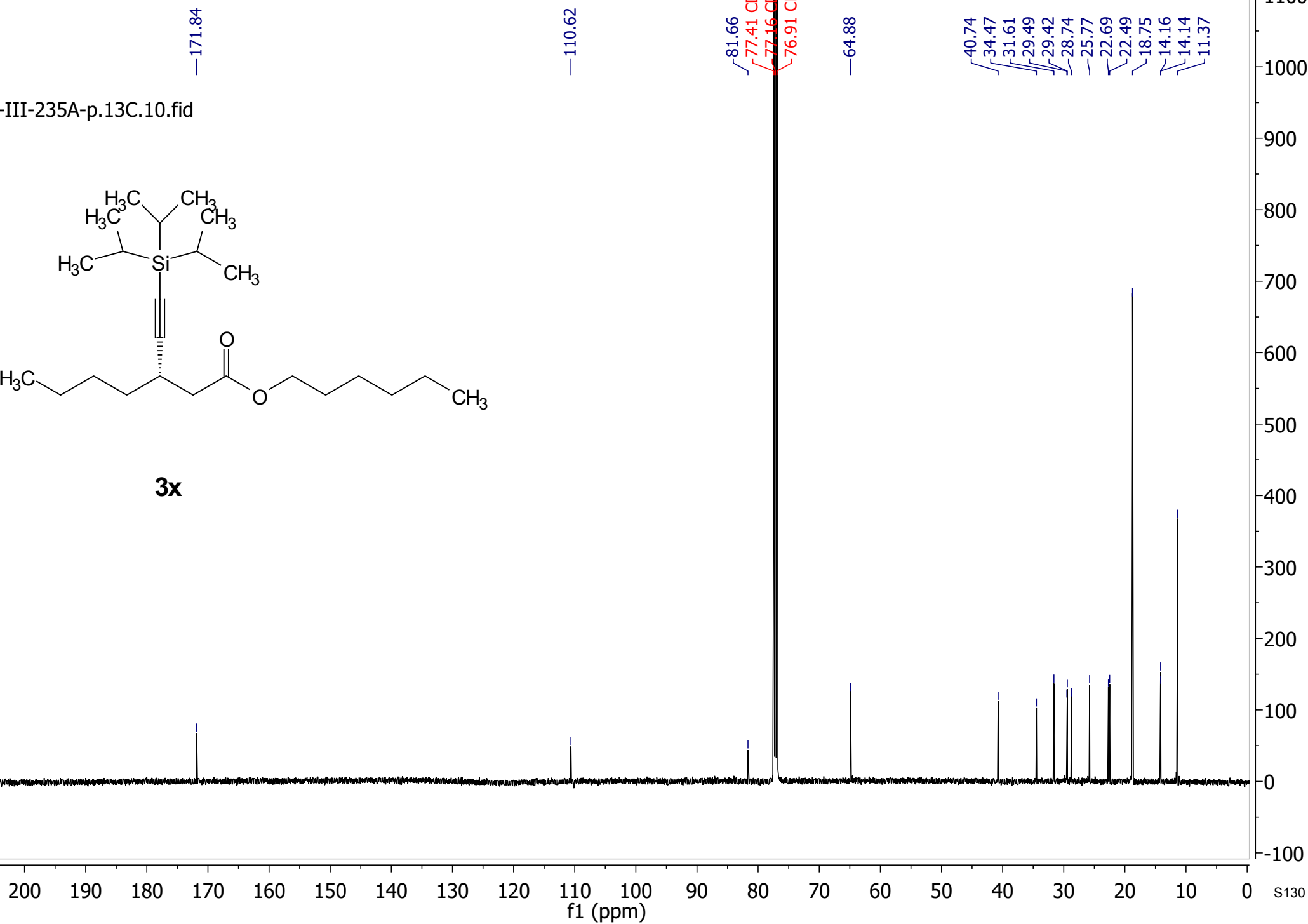


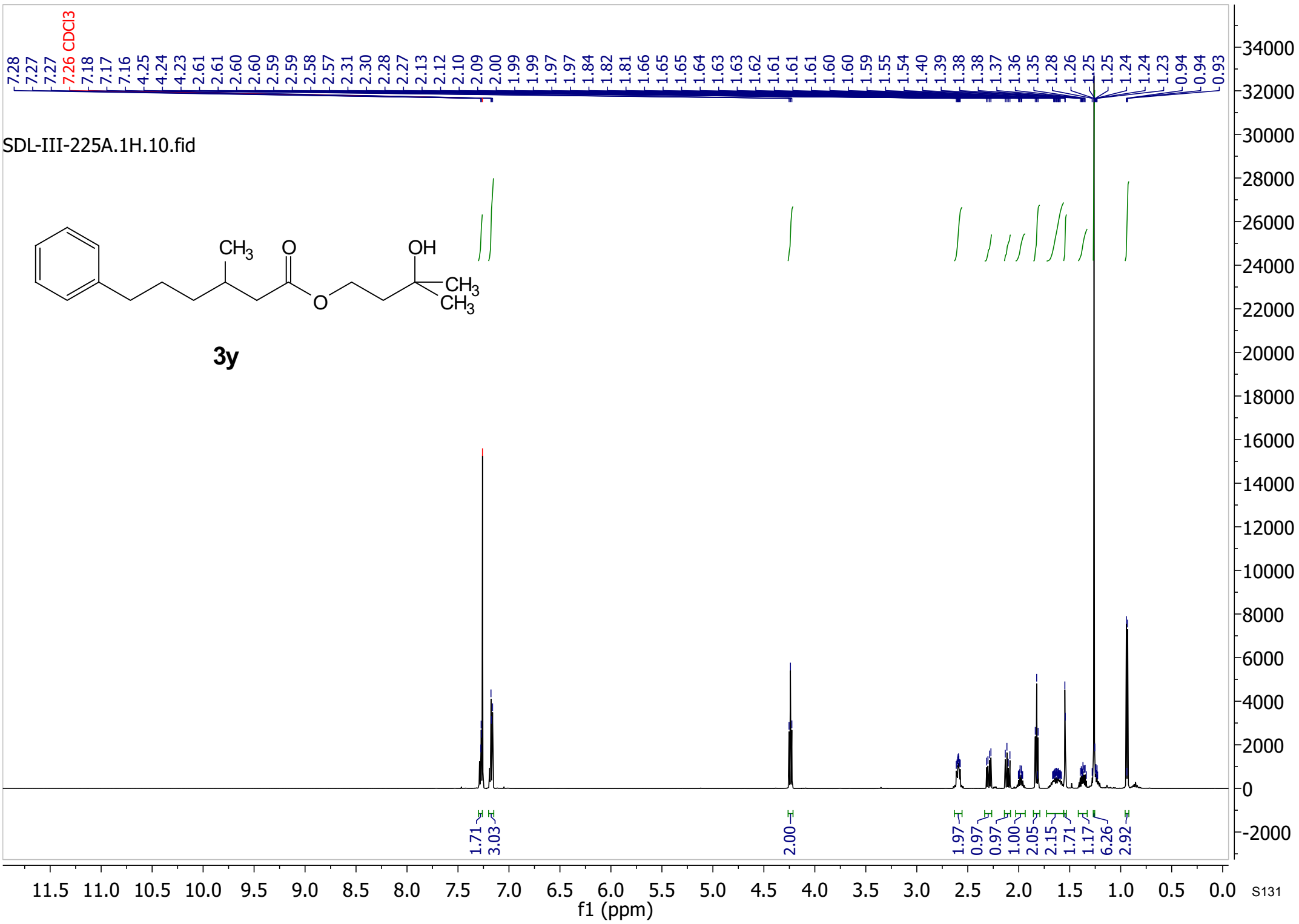


SDL-III-235A-p.13C.10.fid

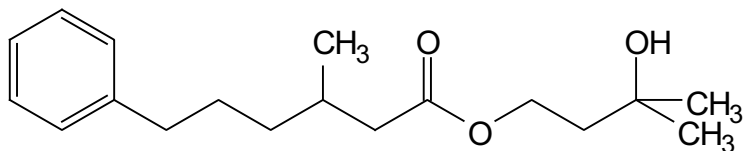


3x





SDL-III-225A.13C.10.fid



3y

