



Chemical Characterization of Residual Fuel Hydrocarbons in Soils at the Santa Susana Field Laboratory

Environmental Remediation Services for Environmental Compliance for Area IV

FINAL REPORT

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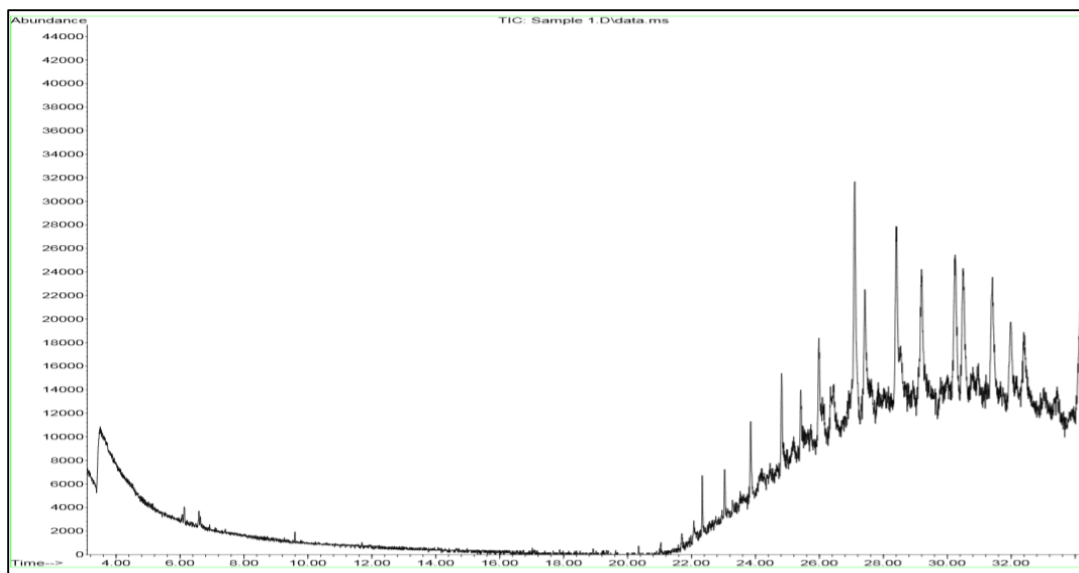
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Executive Summary

Five soil samples were collected from Area IV of the former Santa Susana Field Laboratory (SSFL) and analyzed using gas chromatography/mass spectroscopy (GC/MS) to determine the chemical constituents of the material being characterized as total petroleum hydrocarbon (TPH). One objective of this study was to determine to what extent natural organic material (NOM) contributes to the TPH signal. Another objective was to investigate the use of silica gel cleanup as a method to remove polar NOM before TPH analysis to provide a more accurate measure of actual petroleum hydrocarbons. A third issue which ended up being addressed in this study was the inherent difficulties of accurately measuring TPH at low levels.

Results of the GC/MS spectral analyses suggest that the contamination of Area IV soils being characterized as TPH consists of high molecular weight hydrocarbons, suggestive of residual-range oil (RRO). These hydrocarbons are mostly highly-branched and cyclic hydrocarbons which are known to be slow to biodegrade. PAHs are also present in the soils, as well as some heterocyclic compounds. Many of the branched hydrocarbons and PAHs are partially oxidized. Also detected in the soil samples were organic acids such as oleic acid and oxalic acid, suggestive of NOM. This NOM fraction accounted for about 5 to 8% of the total TPH.

Silica gel cleanup by EMAX Laboratory removed 5 to 40% of the TPH in the five soil samples. Mixed results were obtained in the Cal Poly lab, with silica gel cleanup actually increasing the TPH for three of the five samples. GC/MS analysis showed that silica gel cleanup removed some of the polar organic compounds, but not all of them. Thus, the silica gel approach may underestimate the contribution of NOM to TPH measurement. PAHs and large branched hydrocarbons were not removed by the silica gel cleanup.

An important observation during this study is that it is difficult to accurately quantify TPH at the very low soil TPH concentrations of the Area IV soils used in this study (100 to 300 mg/kg). TPH concentrations of soil samples sent to two different contract laboratories as part of the earlier bioremediation study differed by nearly an order of magnitude. Reliable TPH measurement near background TPH levels or near the 5 mg/kg look-up table value for Area IV would be nearly impossible. At these very low TPH concentrations several factors can significantly impact the calculation of TPH concentrations from GC data, making the calculated concentrations unreliable. TPH concentrations are calculated by integrating the area under numerous overlapping peaks, and thus a baseline has to be drawn underneath the peaks for the integration. Drifting baselines, non-zero signal at the end of the elution time, and non-zero blanks all can make the calculation of TPH inaccurate at low TPH concentrations.

The look-up table value published by the DTSC for TPH is 5 mg/kg, which is 20 times lower than any state standard for RRO, and 1,000 times lower than typical values used by many states. Most states have now started using risk-based clean-up goals. It is beyond the scope of this study to argue for a change in clean-up goals, however, this study has demonstrated that there are clear technical problems with measuring TPH concentrations at such low levels.

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1.0 Introduction

Cal Poly recently completed three soil treatability studies to support remediation efforts for contaminated soil in Area IV of the former Santa Susana Field Laboratory (SSFL). The purpose of these studies was to determine the viability of using *in-situ* remediation techniques, such as bioremediation, phytoremediation and/or natural attenuation to reduce contaminant concentrations and thus reduce the volume of soil needing to be excavated and hauled off-site. In the process of conducting this research, Cal Poly researchers noted difficulties accurately measuring total petroleum hydrocarbon (TPH) concentrations at the very low levels specified by the Department of Toxic Substances and Control (DTSC) for cleanup goals and also discovered the presence of natural organic material (NOM) in the soil samples which was inadvertently contributing to TPH quantification. To address these issues, Cal Poly was given the charge to investigate the chemical composition of the material in the soil being quantified as TPH, and test methods such as silica gel cleanup for providing more accurate TPH measurement.

Possible anomalies in the measurement of TPH were elucidated in the analysis of the final soil samples for a bioremediation microcosm experiment which was part of the bioremediation study. Initial soil samples collected during this experiment and those collected after 126 days of incubation were analyzed for TPH by EMAX, an EPA-certified contract laboratory. Final samples collected after 244 days of incubation were analyzed for TPH by a different contract laboratory – Lancaster Laboratory. TPH concentrations reported by Lancaster Laboratory were 5 to 10 times higher than those reported by EMAX for earlier samples. Both laboratories use an EPA-approved method for gas chromatographic (GC) analysis. Since such an increase in TPH concentration didn't make sense, additional final samples were then analyzed by EMAX, and the TPH concentrations were reported to be similar to those measured earlier. This suggested that different lab techniques may be resulting in widely different measurements of TPH. In the current research, possible reasons for these discrepancies were explored, such as GC integration problems caused by drifting baselines and interference from the presence of NOM. Ordinarily these problems are not expected to be significant, but at the very low TPH concentrations of the samples from Area IV, these problems may have significantly impacted the analysis of TPH.

Another interesting finding at the end of the bioremediation study was the identification of natural oils, such as oleic acid and palmitic acid, in a soil sample from the end of the soil microcosm experiment. A preliminary chemical analysis using gas chromatography/mass spectrometry (GC/MS) indicated significant amounts of natural organic material (NOM) which is likely to be counted as total petroleum hydrocarbon (TPH) and/or extractable fuel hydrocarbons (EFH) in standard tests for petroleum hydrocarbons. From the GC/MS analysis of one of the final bioremediation soil samples, the larger peaks in the chromatogram were associated with organic acids, while the smaller peaks were attributed to weathered petroleum hydrocarbons (Figure 1-1). The interference from NOM could potentially result in reported TPH/EFH soil concentrations higher than that attributable to hydrocarbons from petroleum-based

origins. It is therefore important to 1) understand the actual composition of the material thought to be petroleum hydrocarbons so that clean-up goals can be set accordingly, and 2) develop analytical methods to independently quantitate petroleum hydrocarbons with minimal interference from NOM in the soil.

A common method to remove polar organic compounds from soil extracts prior to TPH analyses is a cleanup procedure using silica gel fractionation. However, it is not certain if this method is accurate for removing NOM (Muji and Jonker, 2009). Thus, another objective of this study was to investigate the use of silica gel cleanup for Area IV soils, specifically to determine if this methods effectively removes NOM before TPH analysis.

To address the issues described above, a series of laboratory investigations of soils from SSFL were conducted. TPH quantitation methods were tested and chemical composition was investigated for five fresh soil samples collected from Area IV to provide representative samples for testing the relative quantities of TPH and NOM in the soil. Cal Poly researchers worked with CDM Smith staff to identify the five sites for soil collection. The specific objectives listed below were addressed by this research:

1. Characterize chemical constituents in the five soil samples using GC/MS to analyze for NOM, as well as hydrocarbons and PAHs.
2. Quantify NOM relative to petroleum hydrocarbons.
3. Evaluate the standard silica gel cleanup protocol to separate NOM from petroleum hydrocarbons – determine if silica gel cleanup removes the NOM in Area IV soils and leaves intact the petroleum hydrocarbons and PAHs.
4. Interpret site-wide TPH/EFH analytical results with silica gel prep.

This study also examined the look-up table values for TPH set by the DTSC in terms of the technical feasibility of accurate TPH measurement at these low concentrations. The DTSC created a lookup table with cleanup goals for each of the soil contaminants at Area IV, and set a lookup table value for TPH of 5 mg/kg for the C15-C20 equivalent carbon range. However, the DSTC stated that “for locations where TPH is the sole contaminant, a cleanup strategy will be considered based on the findings of the soil treatability study” (DTSC 2013). One of the objectives of this follow-on study is therefore to make conclusions regarding the measurement of TPH which may inform future clean-up standards for TPH at Area IV.

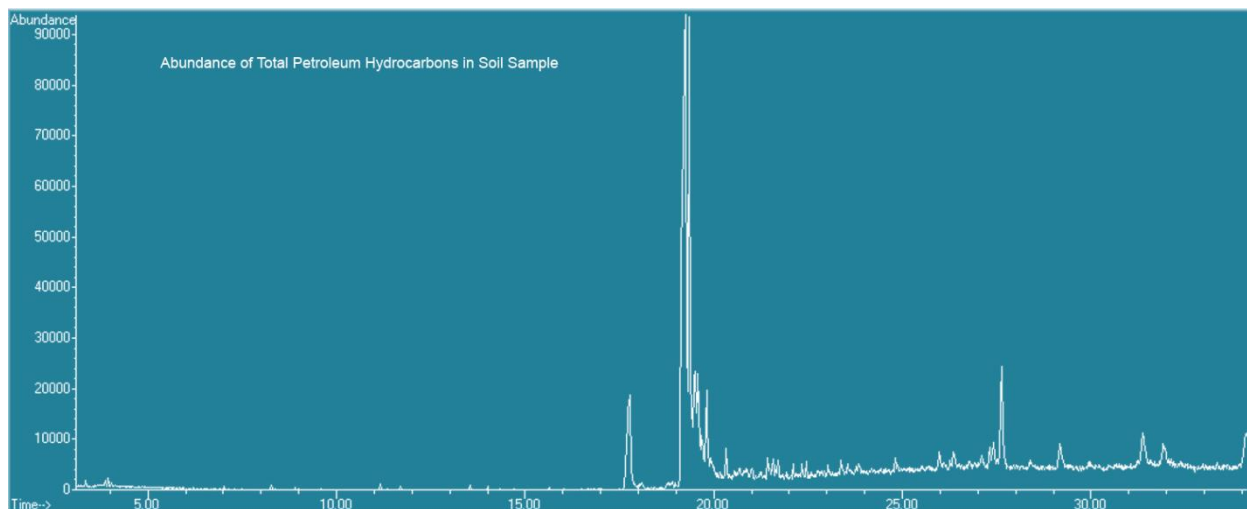


Figure 1-1. Analysis of a soil sample from the end of the bioremediation microcosm experiment in the soil treatability study.

2.0 Background

2.1 Regulatory TPH clean-up levels

The USEPA originally exempted petroleum hydrocarbons from CERCLA regulation, and as a result states developed their own requirements for clean-up levels. These requirements were usually presented as concentration of TPH, and ranged from 10 to over 10,000 mg TPH/kg soil (TPHCWG, 1998). The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was formed in 1993 based on this observation that widely different clean-up requirements were being used by states at sites that were contaminated with petroleum compounds. The TPHCWG members recognized that these numerical standards were not based on scientific assessment of risk, and therefore recommended a new approach utilizing appropriate fraction-specific toxicity data. More recently, the State of Alaska conducted a survey of all 50 states and Canada and found that most states were by then using risk-based cleanup levels, but still found a wide range of TPH cleanup levels (ADEC 2013). For residual range oil (RRO), which is typical of SSFL soil contamination, the cleanup levels varied from 99 mg/kg (Texas) to 10,000 mg/kg (Utah). In comparison, the look-up table value established by the DTSC for Area IV at SSFL is only 5 mg/kg for TPH in the C15-C20 equivalent carbon range (DTSC 2011). However, as stated above, the DTSC noted that the final cleanup strategy should be based on the findings of the soil treatability study. In this final phase of the soil treatability studies, it is thus important to determine if the 5 mg/kg cleanup level can be measured accurately.

2.2 GC/MS analysis of petroleum hydrocarbons

TPH is most often measured using gas chromatography with a flame ionization detector (GC/FID). However, gas chromatography with a mass spectrometer detector was used in the present study to provide more detailed identification of specific compounds in the unresolved complex mixture typically observed for petroleum compounds in Area IV soils. The MS detector allows for identification of specific compounds by comparison of mass spectra to a library of 250,000 specific compounds. However, mass spectroscopy has some limitations, and it should be used with caution for identification of compounds in complex mixtures such as petroleum products (TPHCWG, 1998). It should also be noted that GC/FID is better for quantifying TPH than GC/MS because the response of an FID is proportional to the mass of hydrocarbon present regardless of the type of hydrocarbon (e.g., aromatic, aliphatic or olefin). In contrast, the MS detector may have different responses for different types of hydrocarbon compounds (TPHCWG, 1998). In this study, the GC/MS was primarily used for diagnostic purposes to roughly characterize the residual “TPH” and determine if some of the compounds eluting with the TPH are actually natural organic material.

2.3 Silica gel treatment to remove lipids

An important limitation of the standard method for measuring TPH is that the entire chromatogram of the unresolved complex mixture is integrated, and thus non-petroleum hydrocarbons, such as soil or sediment organic matter (i.e., degradation products of plants and animals), or lipids may be inadvertently included in the measurement of TPH. If not properly removed, these compounds can cause an overestimation of TPH concentrations, as they will contribute to the overall detector response by FID or MS. Therefore, “appropriate sample clean-up is of great importance when determining TPH concentrations in environmental matrixes” (Mujis and Jonker, 2009). The most common cleanup technique used on extracts for TPH analyses is silica-gel cleanup using EPA Method SW-846 3630 (TPHCWG, 1998). Mujis and Jonker (2009) evaluated this silica gel cleanup method and found 84% TPH recovery and 59% removal of lipids from Dutch sediment samples.

3.0 Methodology

3.1 Soil collection

Fresh soil samples were collected from five locations of Area IV at the SSFL site (Table 3-1). Soil sample collection was conducted by Hazardous Waste Operations and Emergency Response (HAZWOPER)-certified field personnel per 29 CFR 1910.120. Soils were collected with decontaminated stainless steel instruments. Splits of each sample were sent to Cal Poly and EMAX Laboratory.

Table 3-1. Legend for soil sample identification

Soil Sample Number	Sample ID
1	5D-612
2	5D-885
3	01-BE-B
4	02-LS-C
5	18-B-A

3.2 Extraction and TPH analytical methods

Extraction:

The TPH extraction protocol was adapted from EPA Standard Method #3550. Ten to 25-g samples of each soil sample were placed in a 100-mL sample bottle. Approximately 30 mL of methylene chloride (MeCl) was added to the sample bottle containing the soil, and the sample was sonicated for 3 min at 60,000 Hz using a Sonifier 250 (Branson Ultrasonics Corp., Danbury, Connecticut). Sodium sulfate (Na₂SO₄) was added to a 24-cm (diameter) 802 Fluted Grade Whatman Inc. filter mounted in a glass funnel to remove water from the extracts. Na₂SO₄ was also added directly to the sample bottle. The extract was poured through the fluted filter and then through a Millipore API 04200 glass fiber filter into a test tube. Another 25 mL of MeCl was added to the soil sample. This additional solvent was then sonicated and filtered as described above and added to the previous 25 mL of MeCl for a total extract volume of 50 mL.

Each sample extract was transferred to a Turbovap® tube and concentrated using a Turbovap® nitrogen evaporation system in a room temperature (20 - 25°C) water bath to an approximate volume of 2 mL. The sample was transferred into a 10-mL graduated cylinder, and the volume was brought up to 5 mL with additional MeCl. These extracts were poured into two GC vials with crimp caps for GC analysis.

GC/MS analysis:

Samples from each extract were run through an Agilent Technologies 6890N Gas Chromatograph (splitless inlet) with an Agilent 5975B inert Mass Selective Detector. A 50-m fused silica column 250- μ m in diameter was used (Agilent Catalog #19091S-433) in the chromatograph. Samples were automatically loaded using an Agilent 7683B Series Injector capable of holding eight GC vials, two solvent vials, and a waste vial. The sample injection volume was 2 μ L from a 10- μ L syringe. To ensure no samples were cross-contaminated, the injector was programmed to rinse the syringe twice with methylene chloride before taking sample extract from the GC vial. The temperature ramped from 45°C to 275°C at a rate of 12°C per minute and was then held at 275°C for the remainder of the 34-min run. The GC front inlet was pressurized to 12.26 psi at a temperature of 200°C. Helium was used as the carrier gas.

Each chromatogram was integrated over the appropriate range of elution times, and the resulting area was used to calculate the TPH concentration in the solvent extract using a calibration curve derived from known standards.

Standard curves:

Calibration curves were prepared using SAE-30 motor oil, because the apparent equivalent carbon range matched that of the soil sample extracts. For the motor oil standards, 0.0250 g of SAE 30 motor oil was weighed out in a small beaker and rinsed into a 50-mL volumetric flask using MeCl. The flask was then filled to volume with methylene chloride, for a final solution with 5000-mg/L motor oil in MeCl. Standard dilutions were then prepared from the 5000-mg/L stock solution. A sample calibration curve is shown in Figure 3-1.

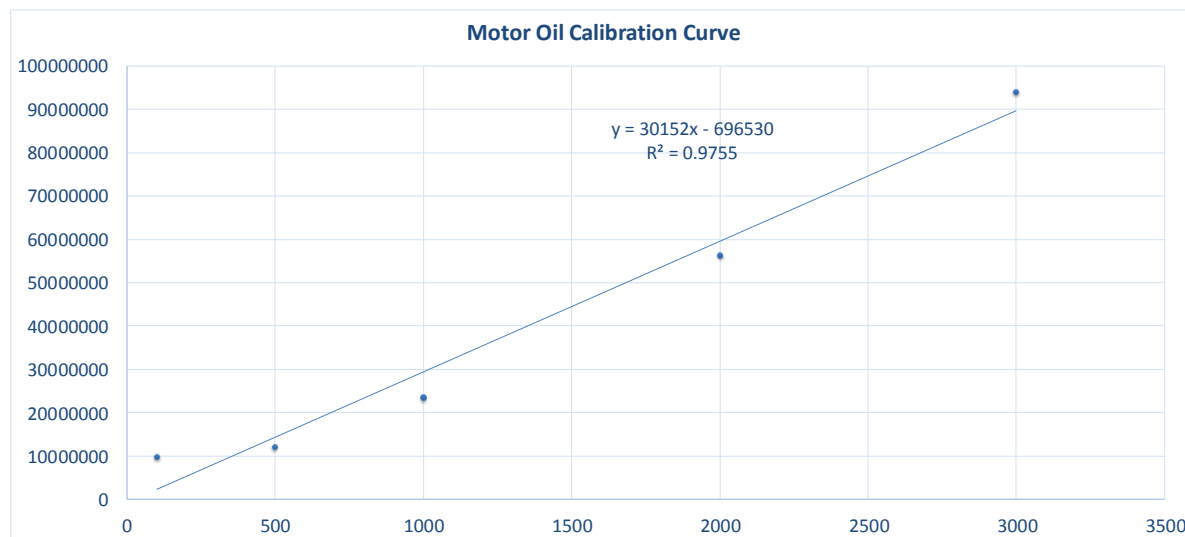


Figure 3-1. Sample calibration curve for TPH measurement in MeCl extracts.

3.3 Silica gel technique

The MeCl extracts from each soil sample (before concentrating) were run on a silica gel column as a preparatory method to remove polar compounds. Chromatographic-grade silica gel (100-200 mesh, Fisher Scientific S817-1) was baked overnight at 130°C and placed in a 10 in x 10.5 mm ID glass chromatographic column (Ace Glass, Inc 5906-05). After rinsing the column with MeCl, it was filled with MeCl and a glass wool plug was pushed into the bottom with a glass rod. The column was packed with 11.0 g $\pm$ 0.1 g of activated silica gel as a slurry. The slurry was created by adding approximately 5 mL of methylene chloride. The slurry was transferred, with rinsing, into the column containing glass wool. The sample in MeCl was poured through the column, and the eluent collected in a glass flask. The sample was carefully transferred to a Turbovap® tube and concentrated using a Turbovap® nitrogen evaporation system in a room temperature (20 - 25°C) water bath to an approximate volume of 2 mL. The sample was transferred into a 10-mL graduated cylinder, and the volume was brought to 5 mL with additional MeCl. The samples were stored in the freezer and analyzed by GC/MS as described above.

4.0 Results

4.1 TPH analysis of five soil samples

Results of TPH analyses for duplicate soil samples in the Cal Poly Lab by GC/MS are compared to TPH results reported by EMAX using GC/FID in Table 4-1 (detailed results from EMAX are in Appendix A). High variability was observed between the Cal Poly duplicate analyses, with relative standard deviations ranging from 13 to 82%. The variation between Cal Poly TPH results and those of EMAX was even greater, with percent differences ranging from -5% to +256%. Note that the difference between TPH concentrations previously measured by Lancaster Laboratories (another commercial laboratory) and EMAX (as described in Section 2.4) were much greater than the differences between TPH concentrations measured by Cal Poly and EMAX. For Sample 1, the TPH concentration measured by EMAX was non-detect, but it was 56 and 208 mg/kg for replicate analyses at Cal Poly conducted on two different soil aliquots of Sample 1.

The high variability in measured TPH concentrations may be attributed to soil heterogeneity as well as inherent difficulties of measuring such low TPH concentrations. Soil Sample 1 contained small rocks about 2-8 mm in size, and the presence of these rocks could result in soil aliquots with varying amounts of fine soil for which TPH concentrations are expected to be highest. Also, what appeared to be small tar balls had been previously observed in bulk soil collected for the bioremediation and phytoremediation soil treatability studies. These small tar balls would be expected to cause large differences in TPH concentrations measured for samples containing tar balls vs. sample aliquots with no tar balls.

Several difficulties were encountered during the GC quantification of TPH at the low soil concentrations of these samples. First, the petroleum compounds appear to be of very high molecular weight, in the residual range oil (RRO) range (see for example Figure 4-1A below). Since the equivalent carbon range was so high, the baseline of the GC did not return to zero at the end of each run. This makes it very difficult to decide where to set the baseline for integration of total peak area for the unresolved peaks in the chromatogram. Second, the detector signal for the solvent (methylene chloride) was significant, causing a wide solvent shoulder extending 10 to 15 minutes into the chromatogram. Third, solvent blanks often exhibited peak areas similar to those of the low concentration samples and the low-concentration standards. Fourth, the r-squared for the standard curve was only about 0.97, which is lower than the value of 0.99 typically observed for standards with higher concentrations. At higher TPH concentrations all of these effects would be insignificant, but at very low TPH concentrations these effects could result in poor reproducibility and possibly even anomalous results.

**Table 4.1. TPH results from Cal Poly Lab (GC/MS)
compared to TPH results of EMAX commercial laboratory**

Sample Number	Sample ID	TPH Concentration (mg/kg)						Difference between Cal Poly and EMAX (%)
		EMAX	Cal Poly Lab					
			Rep 1	Rep 2	Average	Std. Dev.	Rel. Std. Dev. (%)	
1	5D-612	ND	208	56	132	108	82	+ ∞
2	5D-885	50	212	41	127	121	95	+154
3	01-BE-B	170	147	176	161	21	13	-5
4	02-LS-C	17	34	87	60	37	62	+256
5	18-B-A	190	219	316	268	69	26	+41

4.2 Effect of silica gel cleanup on TPH concentrations

Chromatograms for GC/MS analysis of the five soil samples with and without silica gel cleanup are shown in Appendix B, Figures B-1 through B-5. There were no obvious specific peaks removed by the silica gel clean-up in these chromatograms. However, a more detailed analysis of peaks associated with NOM is given below in Section 4.3.

TPH concentrations measured with and without silica gel cleanup are shown in Table 4.1. For the EMAX analyses, the TPH concentrations were 5 to 40% lower after silica gel cleanup. This suggests that polar NOM may have been removed by the silica gel cleanup method, but this is difficult to prove based on the Cal Poly chromatograms in Figures 4-1 through 4-5. For the Cal Poly analyses, the silica gel cleanup gave mixed results, with somewhat higher TPH concentrations observed after silica gel cleanup for 3 out of the 5 samples. One Cal Poly sample was the same with and without silica gel cleanup, and one sample decreased in TPH concentration after silica gel cleanup.

Table 4.2. Effect of silica gel cleanup on measured TPH concentrations by EMAX and Cal Poly

Soil Sample	Soil Sample Location	TPH Concentration (mg/kg)			
		EMAX Results		Cal Poly Results	
		Before Silica	After Silica	Before Silica	After Silica
1	5D-612	-	-	208	209
2	5D-885	50	43	212	99
3	5B- 01-BE-B	170	150	147	168
4	5B-02-LS-C	17	10	34	101
5	5B-18-CB-A	190	180	219	262

4.3 Identification and quantification of NOM and petroleum compounds

Specific compounds eluting in the GC analyses of the soil samples with and without silica gel cleanup were identified using their MS spectra. The Agilent GC/MS software has a library of 250,000 compounds used to match mass spectra to the peaks identified in the chromatograms. The software provides an estimate of the probability of a good match between the compounds eluting from the GC column and the stored model compounds in the library. A summary of the compounds observed in each chromatogram is given in Table 4-3, and chemical structures of 64 different potential compounds are shown in Appendix C along with their mass spectra. Match probabilities are shown in Table 4.3. It is important to remember that the mass spectra are not necessarily perfect matches for specific compounds, but this analysis provides a general snapshot of the types of compounds detected in the soil samples which are being counted as part of the “TPH.”

Many of the compounds identified by their mass spectra were highly branched and cyclic hydrocarbons (Appendix C, Figures C- 13, 30, 33, 34, 39-42, 44, 45, 56-58, 60, 61 and 63). Such compounds are typical of RRO because these hydrocarbons are resistant to biodegradation. A variety of PAHs were also identified by their mass spectra (Appendix C, Figures C- 3, 12, 15-17, 20-22, 25, 26, 37 and 52). Many of the hydrocarbons identified were partially oxidized (Appendix C, Figures C- 2, 5, 14, 18, 19, 23, 24, 27-29, 31, 43, 62 and 64). There were also organic acids identified, such as n-decanoic acid (Figure C-35), stearic acid (Figure C-48), and oleic acid (Figure C-49). These organic acids could be naturally-occurring organic compounds from plant sources (NOM) or degradation products of hydrocarbons. Other oxidized compounds observed which could be considered NOM include nonanal (Figure C-46) and an oxalic acid derivative (Figure C-50). There were also some heterocyclic compounds identified (Figures C- 4, 6, 8, 51, 53 and 54), but these were relatively rare. A couple of silicon-based compounds were observed (Figures C- 9-11) which may be coming from the column packing.

From the summary of compounds found in Table 4.3, it can be seen that only a few compounds, such as oleic acid, were removed by the silica gel cleanup. Oxalic acid derivatives were partially removed by the silica gel cleanup. PAHs and branched/cyclic hydrocarbons were not removed by the silica gel cleanup. It can be cautiously concluded that the silica gel cleanup removes part of the NOM, but not all of it, and that compounds typically associated with TPH, such as hydrocarbons and PAHs are not removed.

The quantitative contribution of NOM to the total TPH measured was estimated by integrating peaks of compounds thought to be NOM. About 3 to 8% of the TPH was attributed to NOM using this method (Table 4.4). For Soil Samples 1-3, the silica gel cleanup did not reduce the contributions of NOM, but for Soil Samples 4 and 5 all of the NOM appeared to be removed by the silica gel cleanup.

Table 4-3. Summary of common compounds identified in soil extracts using mass spectroscopy – with and without silica gel cleanup. Figure numbers refer to mass spectra and chemical structures shown in Appendix C.

Sample 1, no Silica Gel Prep				Sample 1, Silica Cleanup			
Elution Time	Compound	Concentration (mg/kg)	Probability (%)	Elution Time	Compound	Concentration (mg/kg)	Probability (%)
22.33	Sulfurous Acid/Oxalic Acid	5.64	8.5	6.14	Cyclopentane	1.73	55
23.04, 23.85	Oxalic Acid	6.67	30	6.64	Branched Cyclohexane (Figure C-33)	0.32	26.3
25.41	Large oxidized compound (Figures C-58, C-62)	6.03	35	7.3, 8.89, 10.2	Branched Heptane (Figures C-39, 40, 63)	3.38	55
27.1	28-Nor-1 7B(H)-hopane	9.12	53.3	22.33	Oxalic Acid	0.81	15
27.42	Large Organic Compound, Cl poss (Figure C-59)	6.66	10	23.85	Branched Tetracontane/ Oxalic Acid	1.06	6/ 3.62
28.4-32.4	Large Cyclic Organics, Cl & Br poss (Figure C-57)	46.53	5 to 10	25.4	Large Oxidized Organic (Figures 58, 62)	0.85	50
				27.1	28-Nor-1 7B(H)-hopane	3.29	15
				27.4	Heptacosane	2.52	16
Sample 2, no Silica Gel Prep				Sample 2, Silica Cleanup			
Elution Time	Compound	Concentration (mg/kg)	Probability (%)	Elution Time	Compound	Concentration (mg/kg)	Probability (%)
6.6	C8H17N2O (Figure C-6)	7.32	91.8	7.3	Branched Heptane (Figures C-39, 40, 63)	7.93	35
9.59	Decamethyl Cyclopentasiloxane	7.25	63.1	9.59	Quinolinedione	6.00	79
28.1	Oxalic Acid	10.43	50	22.35, 24.7, 27.4	Oxalic Acid	7.13	30
29.48	Bacchotricuneatinc	7.39	50				
23.5-30	Piperidinone	10.73	10 to 25				
Sample 3, no Silica Gel Prep				Sample 3, Silica Cleanup			
Elution Time	Compound	Concentration (mg/kg)	Probability (%)	Elution Time	Compound	Concentration (mg/kg)	Probability (%)
9.59	Chloro ethanol acetate	8.17	25	7.3, 8.89, 10.2, 11.4	Branched Heptane	7.81	55
18.67	Cyclic Octatomic Sulfur	8.32	98.3	18.67	Cyclic Octatomic Sulfur	5.68	97
18.81, 19.24	Pyrene	11.12	65	18.81, 19.24	Pyrene/ Fluoranthene	9.98	50
21.65-21.75	PAHs	10.55	50	21.65-21.75	PAHs (Figures C-3, 15, 16, 17, 20, etc.)	10.86	75
24.0-25.1	Benzo-k-fluoranthene	11.13	33	24-25.1	Benzo-k-Fluoranthene	10.18	35
26.5-28.5	oxalic acid/octadecanoic acid	13.50	10 to 20				
Sample 4, no Silica Gel Prep				Sample 4, Silica Cleanup			
Elution Time	Compound	Concentration (mg/kg)	Probability (%)	Elution Time	Compound	Concentration (mg/kg)	Probability (%)
21.69	2,4,6,8 Tetramethyl-Undecene	3.79	44.4	7.29	Heptane, 2,2,4,6,6-pentamethyl	8.96	42.3
22.34	Oleic Acid	3.92	9.71	7.87, 8.18	Methylene Chloride	6.07	80
24	Benzo-e-pyrene	3.88	34.2	8.89, 10.19, 11.4	Dimethyl Heptane	6.74	30.6
24.71, 24.85, 25.11	Benzo-k-fluoranthene/Perylene	5.25	30.5	17.08	Phthalic Acid	5.88	~40
28.4-30.22	Benzo-ghi-perylene	6.20	65.6- 77.1	17.87- 17.9	Ethaneperoxic Acid	5.85	76.2
				22.33	Hexylundecylester Sulfurous Acid	6.00	49- 54.5
				23.99-25.11	Benzo-k-fluoranthene	17.44	75.5
				29.0-30.2	Benzo-ghi-perylene	11.23	67.8
				26.5-27.1	Cyclic hydroxy-ethyl compound	7.26	50
Sample 5, no Silica Gel Prep				Sample 5, Silica Cleanup			
Elution Time	Compound	Concentration (mg/kg)	Probability (%)	Elution Time	Compound	Concentration (mg/kg)	Probability (%)
16.47	Fluorene	7.70	56	7.3	Branched Heptane (Figures 39, 40, 63)	7.96	36.7
18.82, 19.24	Fluoranthene/Pyrene	13.79	50	16.47	Fluorene	6.13	54
21.65, 21.71	Triphenylene (PAHs)	23.24	40	18.82, 19.24	Pyrene/ fluoranthene	9.58	50
24- 25.1	Benzo-k-fluoranthene	28.86	20	21.65-21.75	PAHs (Figures 3, 15, 16, 17, 20, etc.)	21.57	40
29- 30.2	Benzo-ghi-pyrylene	9.99	60- 70	24, 24.7, 24.85	Benzo-k-fluoranthene	23.43	50
				29- 30.2	Benzo-ghi-perylene	9.18	60- 70

**Table 4.4. Estimated Contribution of NOM to Measured TPH
of the Soil Samples With and Without Silica Gel Cleanup.**

Soil Sample	Without Silica Cleanup		With Silica Cleanup	
	Concentration NOM (mg/kg)	Percent of TPH	Concentration NOM (mg/kg)	Percent of TPH
1	9.3	4.03	9.0	4.02
2	16.8	6.89	9.0	7.14
3	9.1	4.95	6.6	3.45
4	4.0	7.94	0.0	0
5	7.4	2.93	0.0	0

4.4 Site-wide implications

Important implications of this study which are applicable to interpretation of site-wide TPH soil concentrations can be drawn from the results of the silica gel cleanup investigation and the general problems identified for TPH analysis of Area IV soils with low TPH concentrations. Results of this study show that the silica gel cleanup is an appropriate tool for increasing the accuracy of TPH measurements. Even more significant are the findings that accurate measurement of TPH concentrations is very difficult at low concentrations.

The silica gel cleanup used by EMAX for many TPH analyses site-wide can significantly lower TPH concentrations. Based on the GC/MS analyses reported here, this cleanup technique is appropriate because it appears to remove only polar organic compounds and not PAHs or petroleum hydrocarbons. Further, these results suggest that the removal of such polar compounds may not be complete, and therefore actual TPH concentrations should be even lower than those determined with the silica gel cleanup.

The GC/MS chromatograms show that the residual petroleum compounds in Area IV soils exhibit very high molecular weight consistent with residual-range organics (RRO). The RRO is similar to asphalt (bitumen). Such high molecular weight material gives GC signals outside the normal C-8 to C-40 equivalent carbon range, and this complicates TPH measurement because it is difficult to integrate the total unresolved complex mixture when the final signal is not zero – this is because it is difficult to decide what background level to use for an integrating baseline. See for example the chromatogram for Sample 1 (Appendix B, Figure B-1A) which shows a relatively high GC signal at the end of the GC run.

Setting TPH clean-up levels near background levels is problematic because of the inherent difficulties of measuring TPH concentrations near background concentrations. At these low TPH concentrations, effects such as drifting baselines, TPH in sample blanks, and solvent fronts become significant. These effects are ordinarily insignificant when measuring higher TPH concentrations. As described in Section 2.1, clean-up levels for RRO in the U.S. vary from

99 mg/kg in Texas to 10,000 mg/kg in Utah (ADEC 2013). States typically set their cleanup goals at 5,000 mg/kg for soils. Thus, the look-up table values for TPH at Area IV are about 20 times lower than the lowest state standard and 1,000 times lower than typical values.

Another observation from the bioremediation study is that the petroleum compounds sometimes appear to be concentrated in small tar balls in the soil as opposed to homogeneously dispersed in the soil. Such tar balls were observed in the bulk soil collected from Area IV for the bioremediation study using laboratory microcosms as well as the phytoremediation study. The presence of these tar balls would be expected to cause high variability of TPH measurements because one subsample may contain a tar ball while another does not.

5.0 Conclusions

The GC/MS spectral analyses suggest that the remaining TPH contamination of Area IV soils consists of high molecular weight hydrocarbons as expected for RRO or asphalt. These hydrocarbons are mostly highly-branched and cyclic hydrocarbons which are known to be slow to biodegrade. PAHs are also present in the soils, as well as some heterocyclic compounds. Many of the branched hydrocarbons and PAHs appeared to be partially oxidized. Also detected in the soil samples were organic acids such as oleic acid and oxalic acid, suggestive of NOM. Such compounds also can be degradation products of hydrocarbon biodegradation. This NOM fraction accounted for about 5 to 8% of the total TPH. NOM appeared to account for a larger fraction of the TPH in our preliminary analysis of a soil from the bioremediation microcosm experiment.

Silica gel cleanup by EMAX Laboratory removed 5 to 40% of the TPH in the five soil samples. Mixed results were obtained in the Cal Poly lab, with silica gel cleanup actually increasing the TPH for three of the five samples. The silica gel cleanup was found to remove some of the polar organic compounds, but not all of them. Thus, the silica gel approach may underestimate the contribution of NOM to TPH measurement. PAHs and large branched hydrocarbons were not removed by the silica gel cleanup.

An important observation during this study is that it is difficult to accurately quantify TPH at the very low soil TPH concentrations of the Area IV soils used in this study (100 to 300 mg/kg). Reliable TPH measurement near background TPH levels or near the 5 mg/kg look-up table value for Area IV would be nearly impossible. At these very low TPH concentrations several factors can significantly impact the calculation of TPH concentrations from GC data, making the calculated concentrations unreliable. TPH concentrations are calculated by integrating the area under numerous overlapping peaks, and thus a baseline has to be drawn underneath the peaks for the integration. Drifting baselines, non-zero signal at the end of the elution time, and non-zero blanks all can make the calculation of TPH inaccurate at low TPH concentrations. At higher TPH concentrations, these effects become much less significant.

The look-up table value published by the DTSC for TPH is 5 mg/kg, which is 20 times lower than any state standard for RRO, and 1,000 times lower than typical values used by many states. Most states have now gone to risk-based clean-up goals (ADEC, 2011). It is beyond the scope of this study to argue for a change in clean-up goals, however, this study has demonstrated that there are clearly technical problems with measuring TPH concentrations at such low levels.

6.0 References

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Appendix A: Detailed EMAX TPH results for five soil samples showing equivalent carbon ranges.

All analyses conducted on April 22, 2015.

Table A-1: EMAX results for TPH analyses without silica gel clean-up

Soil Sample ID	Percent moisture	Silica Cleanup?	Equivalent Carbon Range	TPH Concentration (mg/kg)
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	(C12-C14)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	(C15-C20)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	(C21-C30)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	(C30-C40)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	(C8-C11)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	NO	TOTAL (C8-C40)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	(C12-C14)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	(C15-C20)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	(C21-C30)	13
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	(C30-C40)	37
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	(C8-C11)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	NO	TOTAL (C8-C40)	50
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	(C12-C14)	
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	(C15-C20)	2.9
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	(C21-C30)	77
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	(C30-C40)	91
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	(C8-C11)	
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	NO	TOTAL (C8-C40)	170
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	(C12-C14)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	(C15-C20)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	(C21-C30)	4
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	(C30-C40)	13
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	(C8-C11)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	NO	TOTAL (C8-C40)	17
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	(C12-C14)	
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	(C15-C20)	7.8
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	(C21-C30)	100
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	(C30-C40)	83
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	(C8-C11)	
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	NO	TOTAL (C8-C40)	190

Table A-2: EMAX results for TPH analyses with silica gel clean-up

Soil Sample ID	Percent moisture	Silica Cleanup?	Equivalent Carbon Range	TPH Concentration (mg/kg)
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	(C12-C14)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	(C15-C20)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	(C21-C30)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	(C30-C40)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	(C8-C11)	
SSFL-EFH-SO-612-SA5D-0.5-1.0	7.7	YES	TOTAL (C8-C40)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	(C12-C14)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	(C15-C20)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	(C21-C30)	21
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	(C30-C40)	22
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	(C8-C11)	
SSFL-EFH-SO-885-SA5D-0.5-1.0	4.7	YES	TOTAL (C8-C40)	43
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	(C12-C14)	
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	(C15-C20)	
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	(C21-C30)	73
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	(C30-C40)	73
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	(C8-C11)	
SSFL-EFH-SO-01-BE-B-SA5B-0.5-1.0	3.4	YES	TOTAL (C8-C40)	150
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	(C12-C14)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	(C15-C20)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	(C21-C30)	3.3
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	(C30-C40)	6.9
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	(C8-C11)	
SSFL-EFH-SO-02-LS-C-SA5B-0.5-1.0	8.1	YES	TOTAL (C8-C40)	10
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	(C12-C14)	
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	(C15-C20)	7.2
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	(C21-C30)	82
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	(C30-C40)	86
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	(C8-C11)	
SSFL-EFH-SO-18-CB-A-SA5B-0.5-1.0	2.9	YES	TOTAL (C8-C40)	180

Appendix B. Cal Poly chromatograms of soil extracts with and without silica gel cleanup

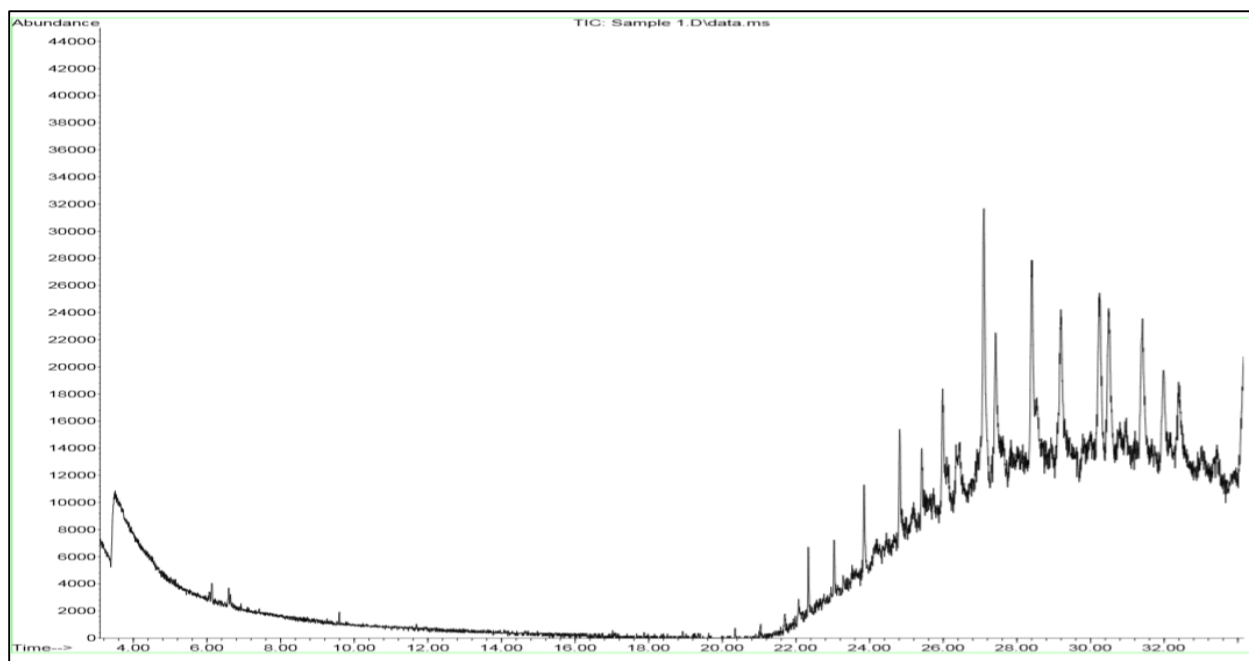


Figure B-1A: Sample 1 (5D-612) with no silica gel prep.

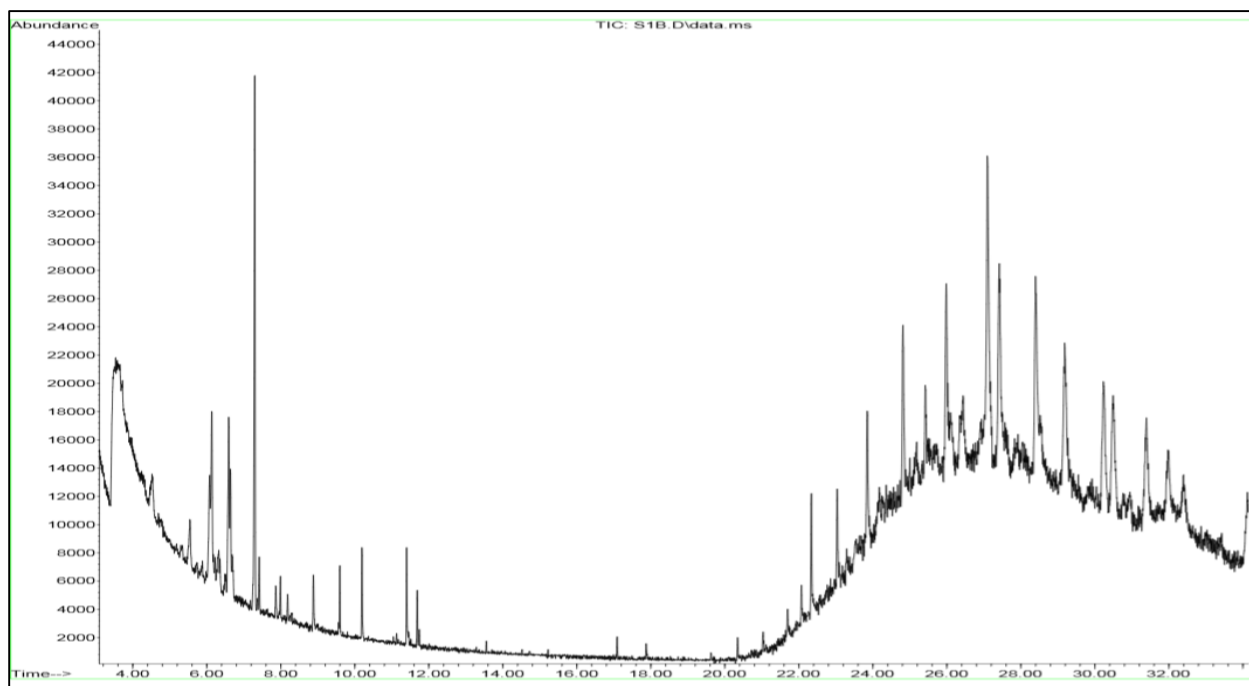


Figure B-1B: Sample 1 (5D-612) with silica gel prep.

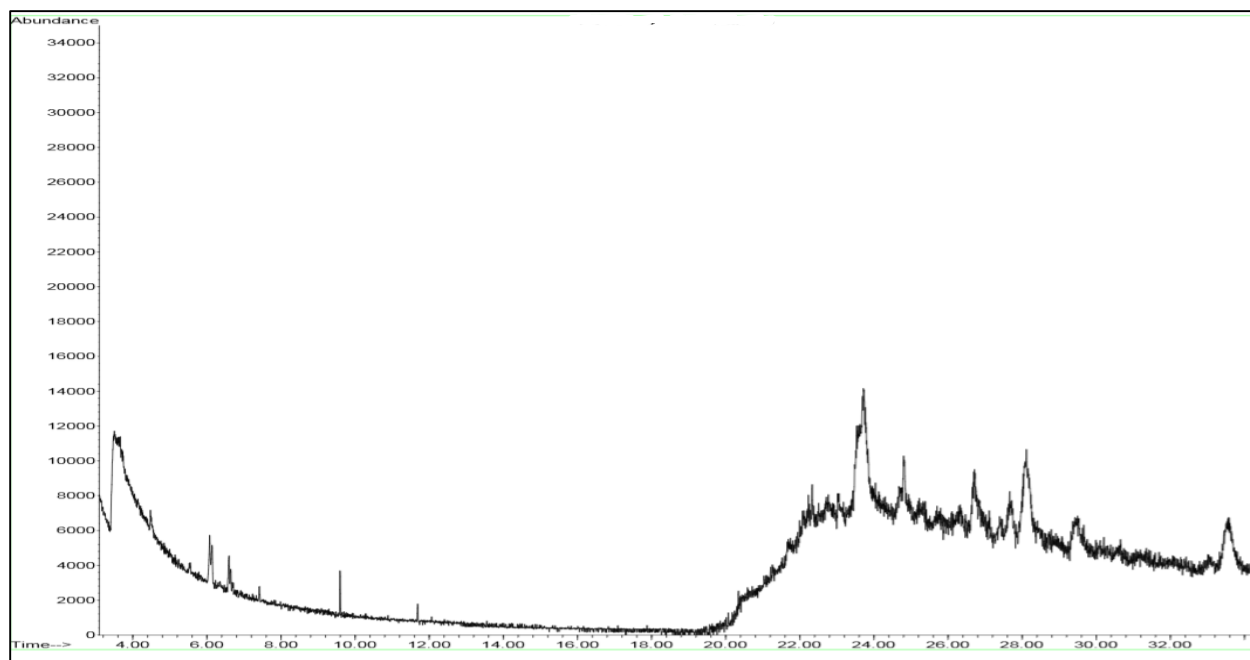


Figure B-2A: Sample 2 (5D-885) without silica gel prep.

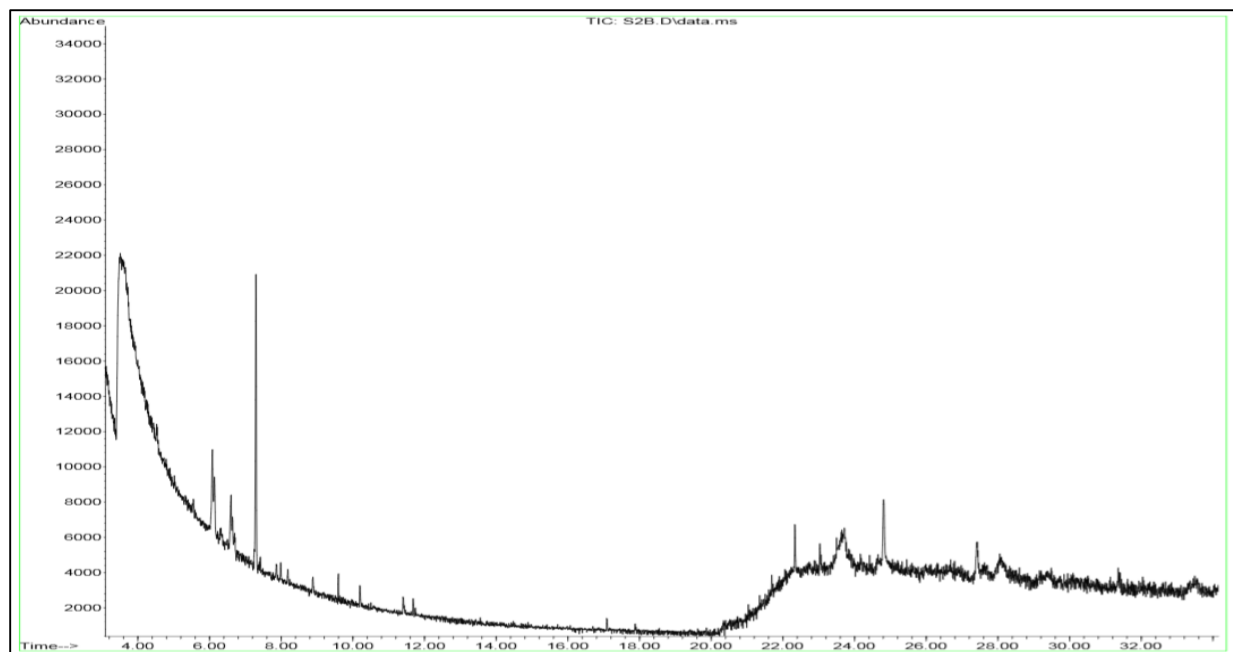


Figure B-2B: Sample 2 (5D-885) with silica gel prep.

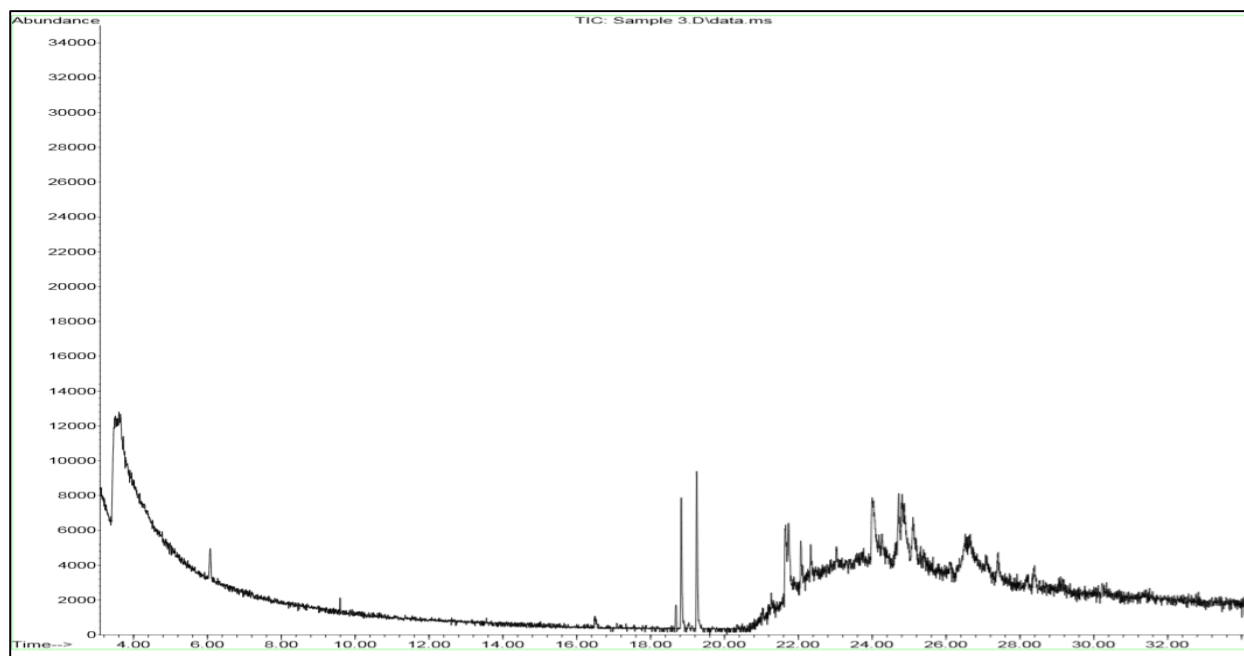


Figure B-3A: Sample 3 (01-BE-B) without silica gel prep.

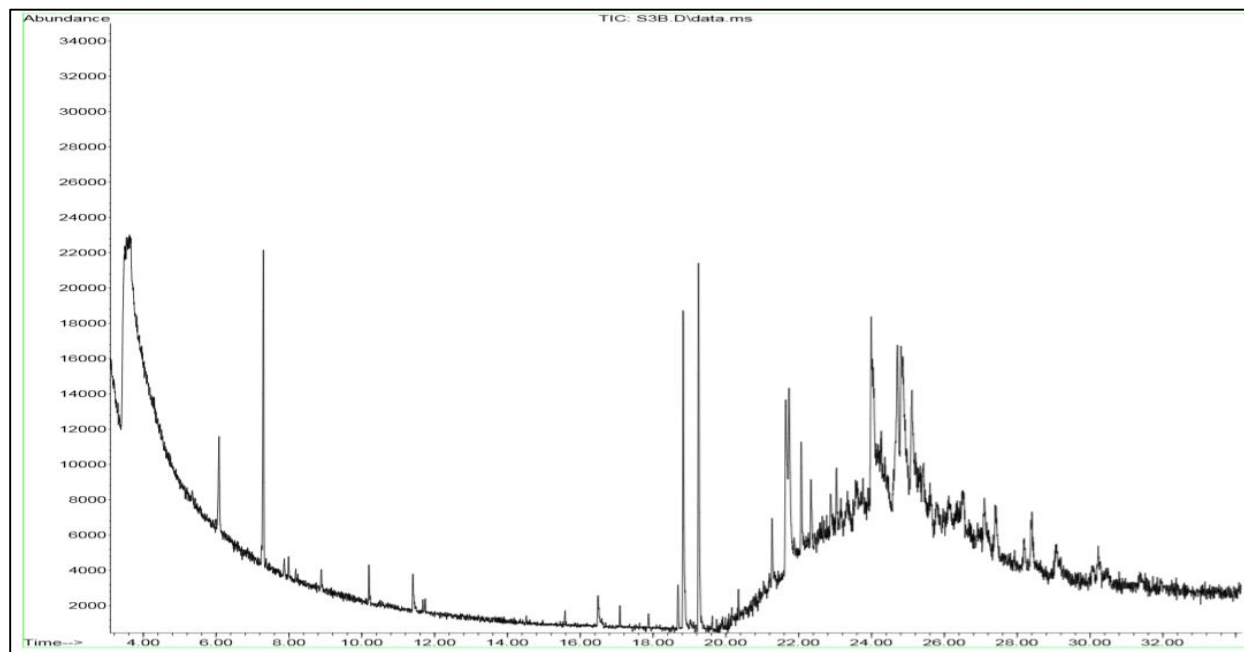


Figure B-3B: Sample 3 (01-BE-B) with silica gel prep.

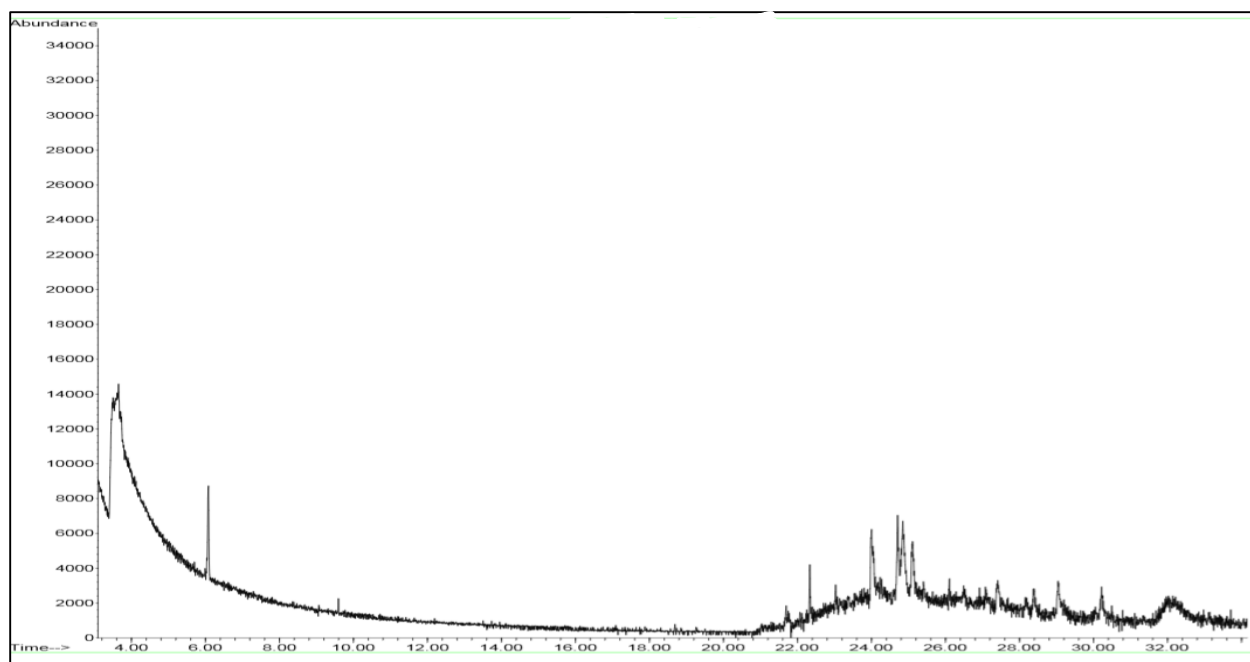


Figure B-4A: Sample 4 (02-LS-C) without silica gel prep.

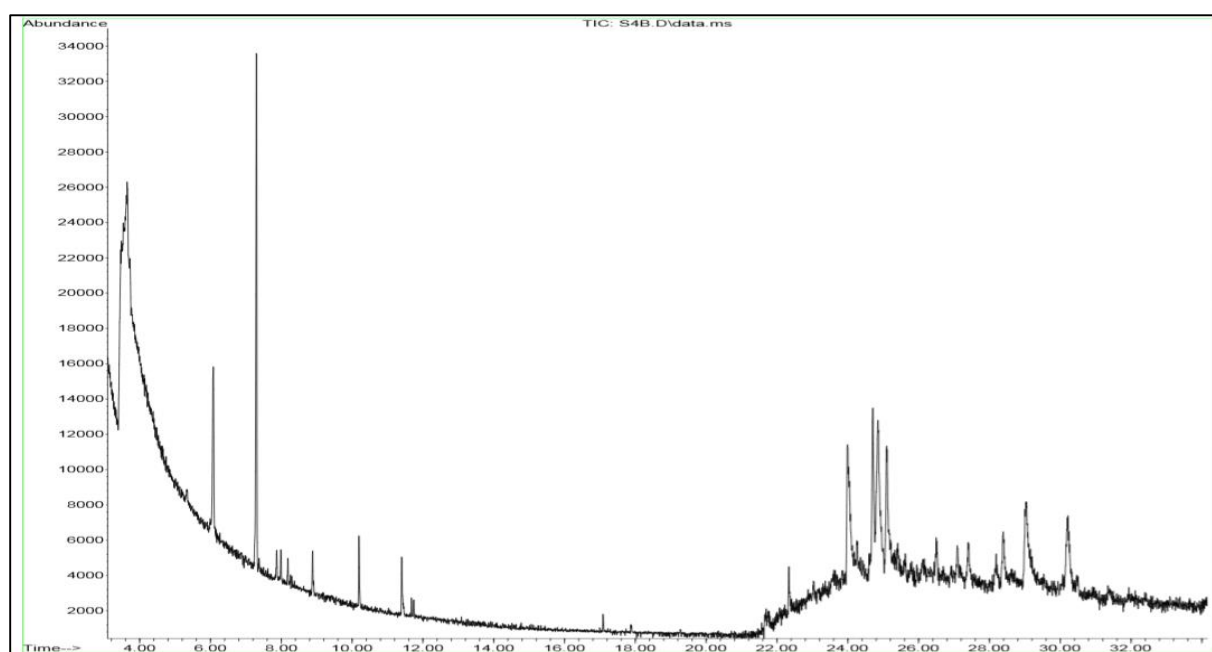


Figure B-4B: Sample 4 (02-LS-C) with silica gel prep.

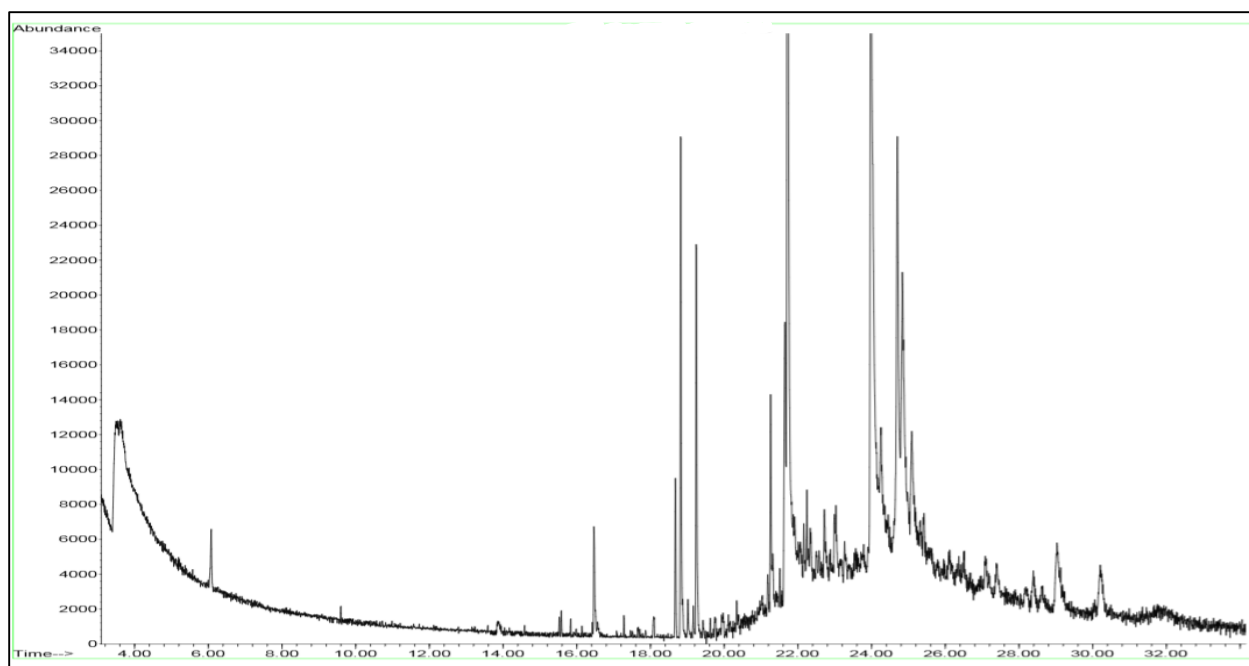


Figure B-5A: Sample 5 (18-B-A) without silica gel prep.

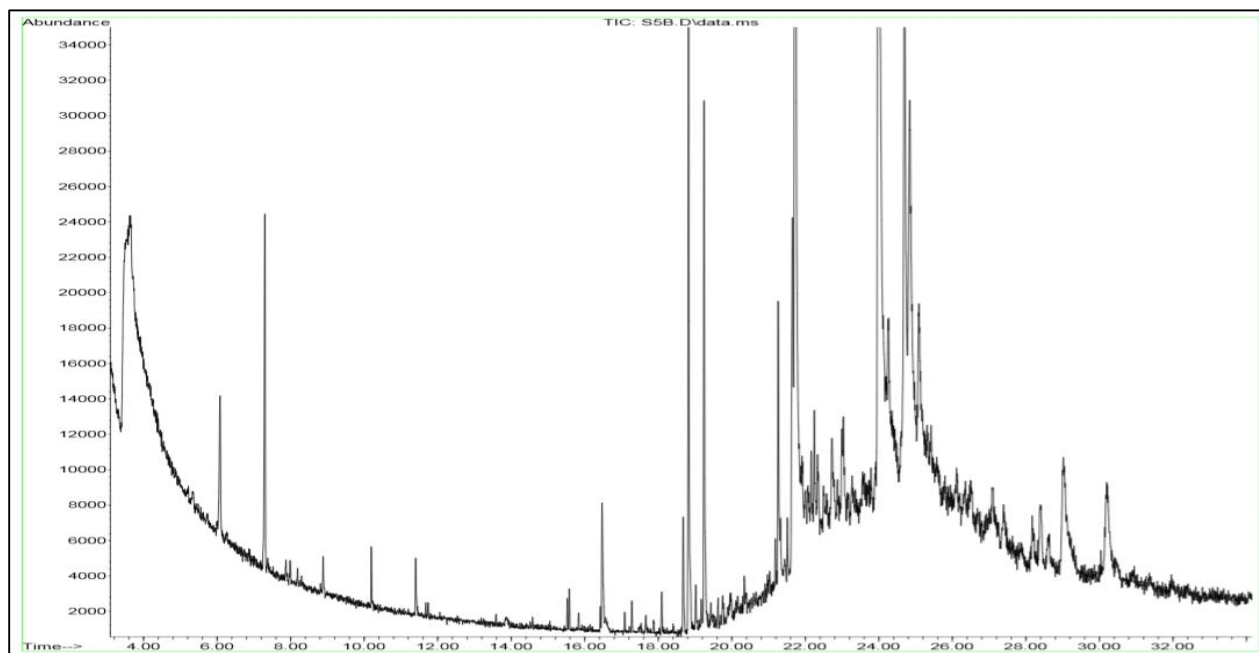


Figure B-5B: Sample 5 (18-B-A) with silica gel prep.

Appendix C. Mass spectral identification of specific compounds in the soil samples.

Appendix: Compound Figures

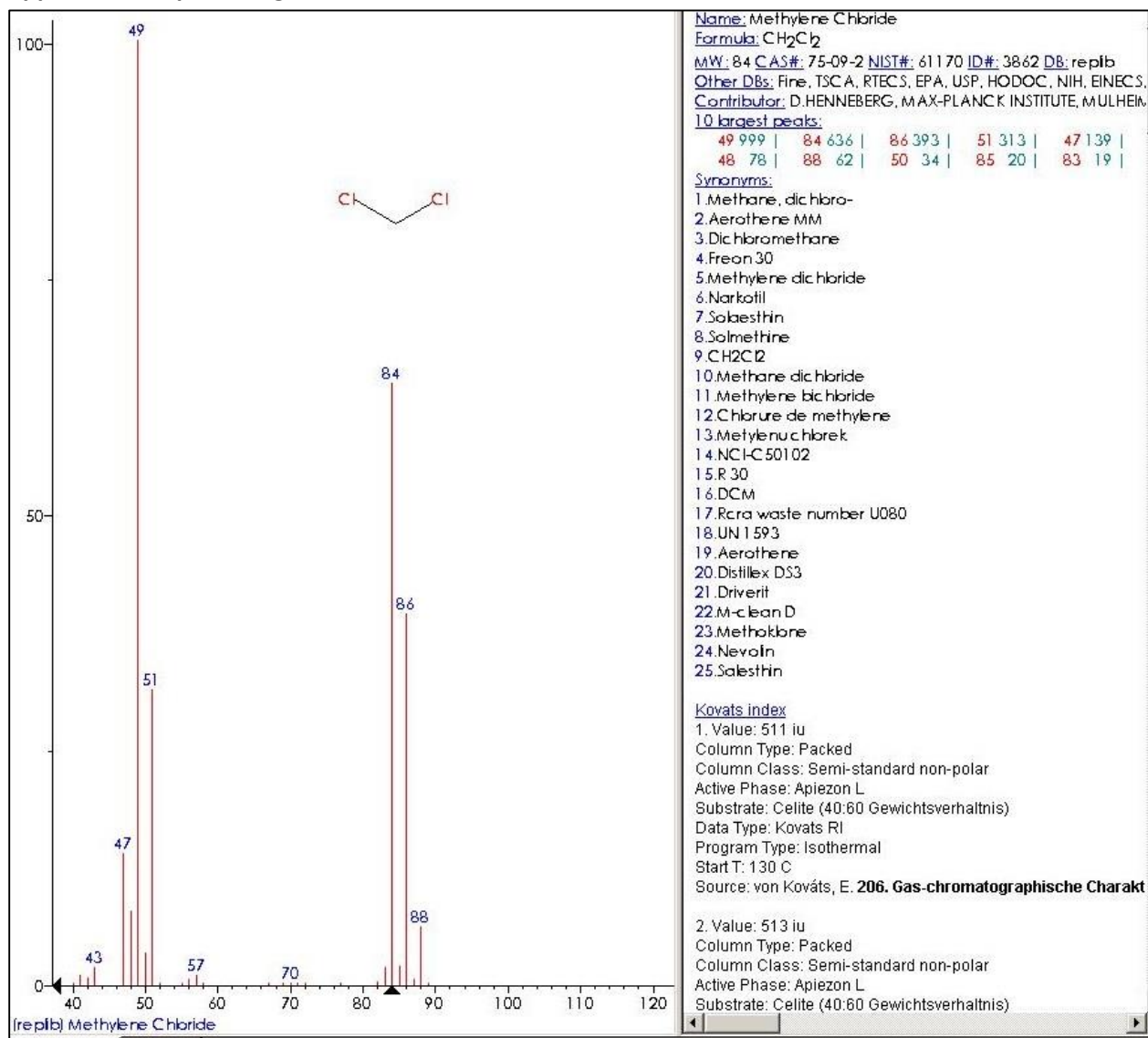


Figure C-1

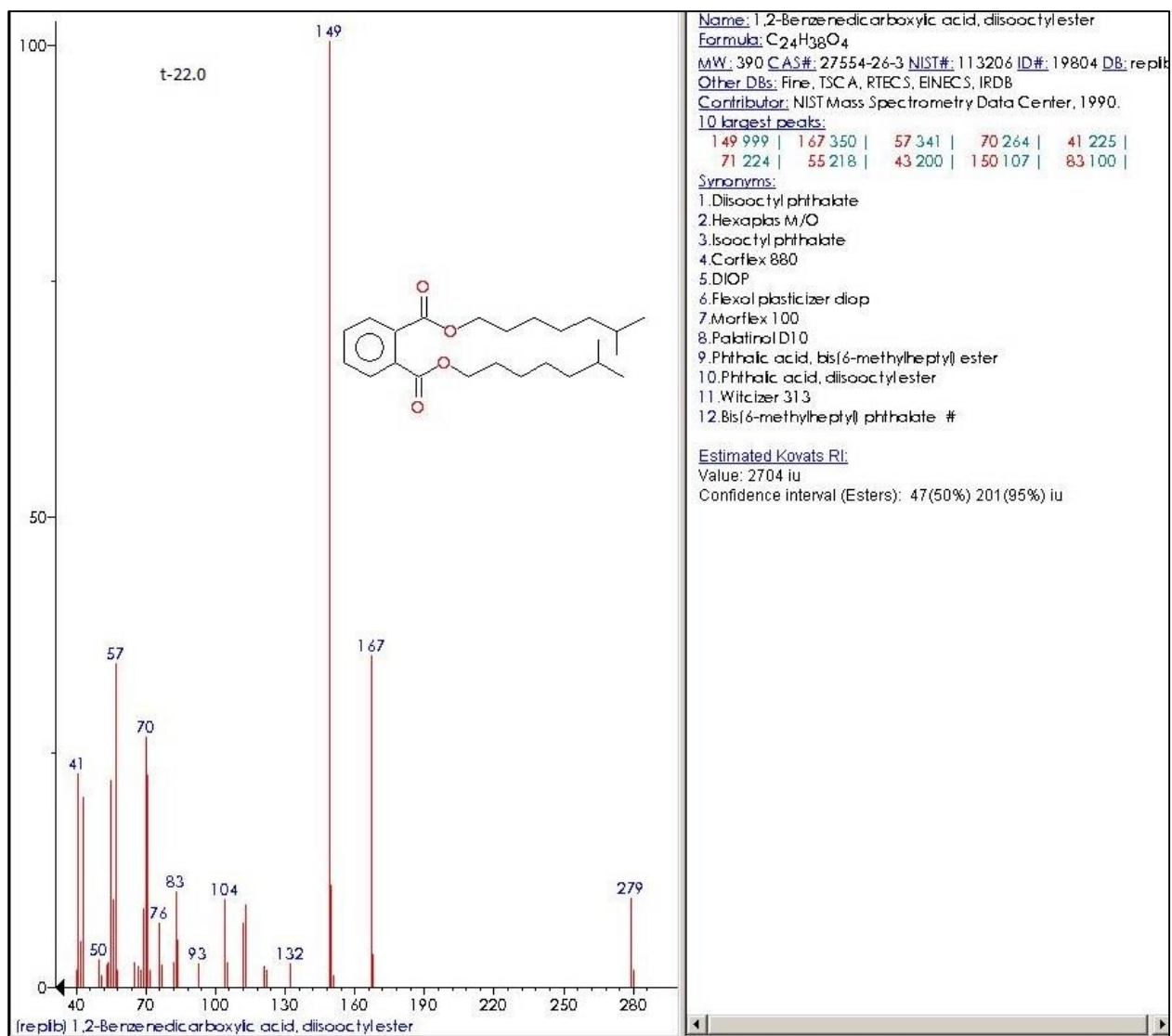


Figure C-2

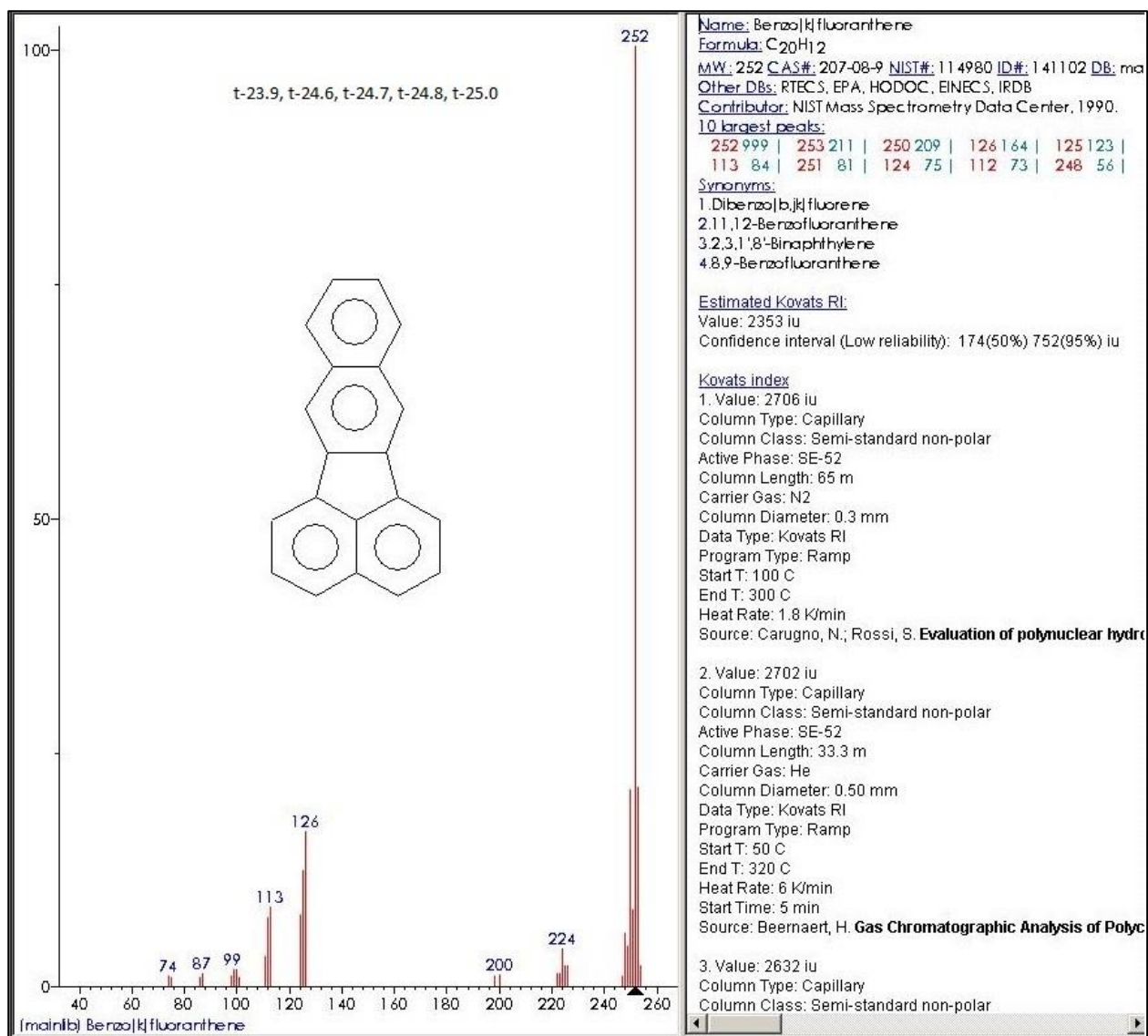


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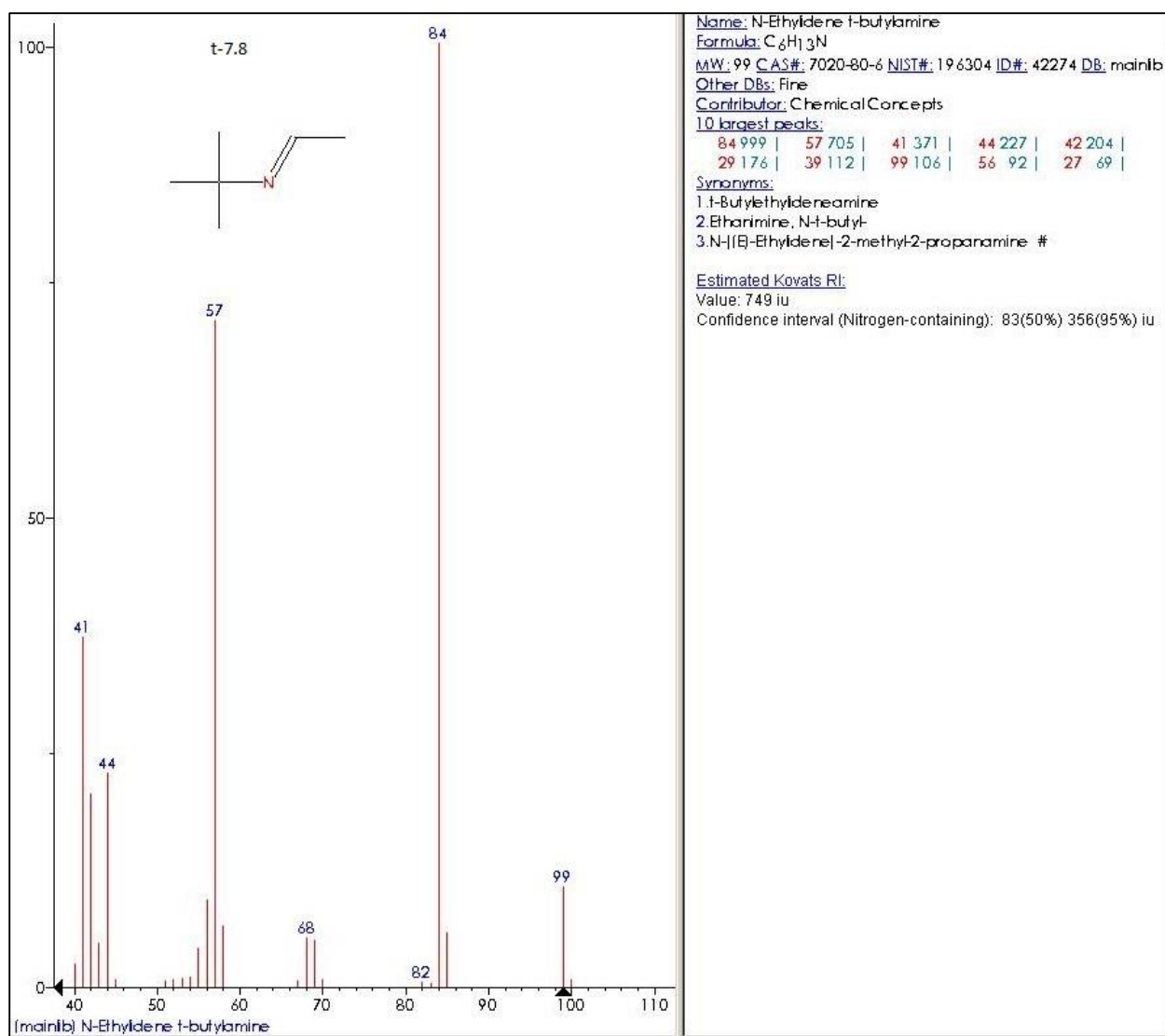


Figure C-4

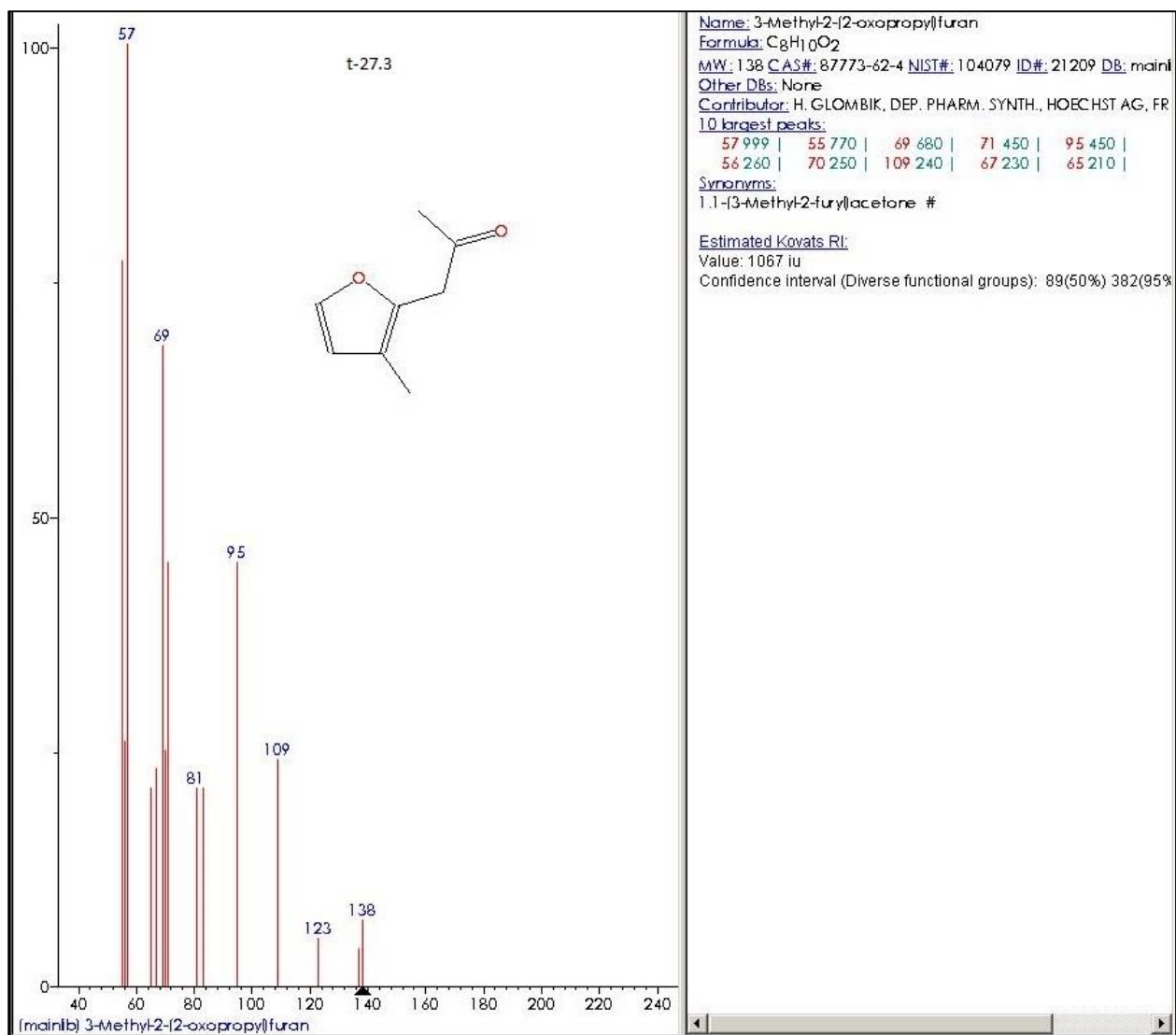


Figure C-5

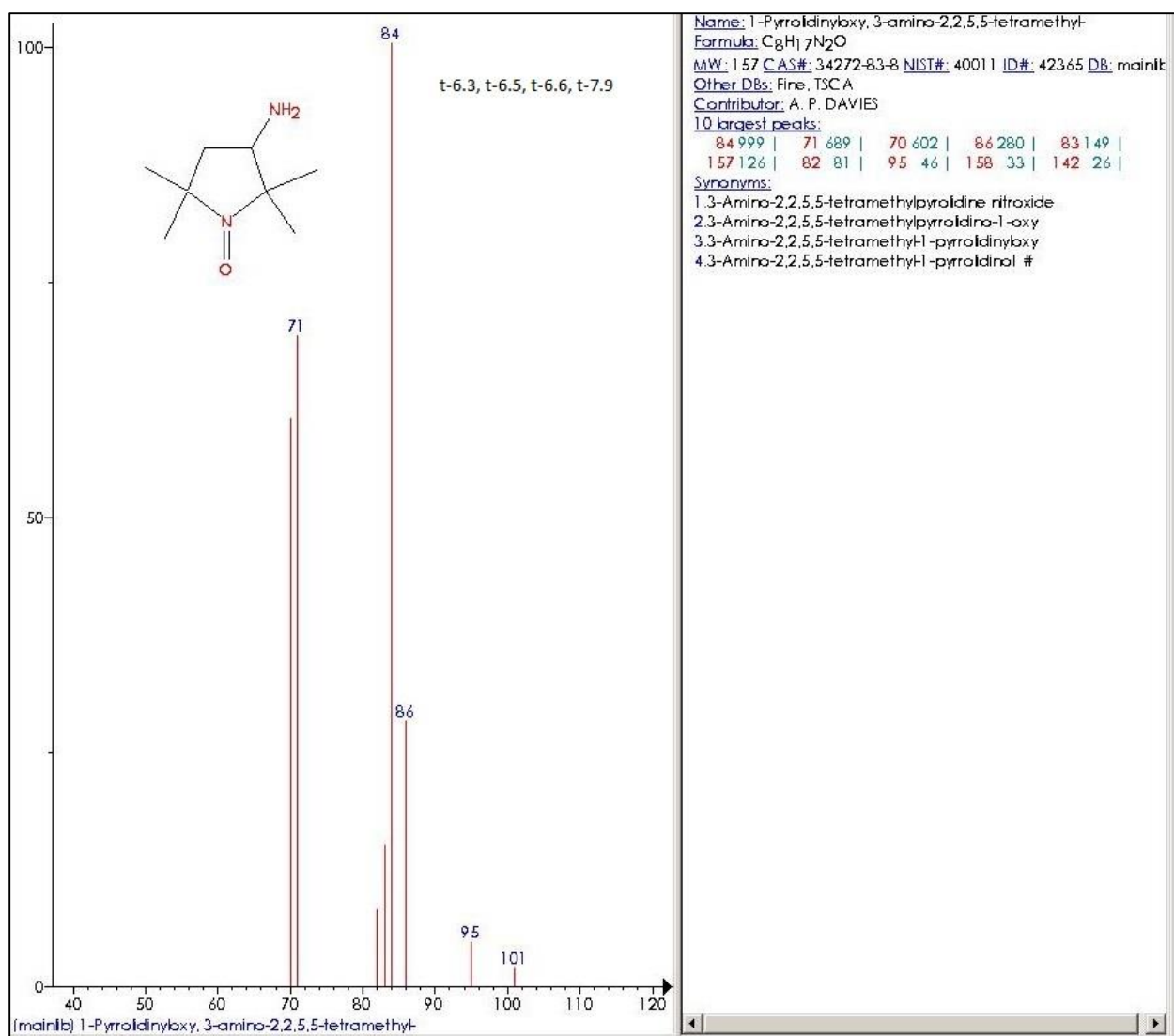


Figure C-6

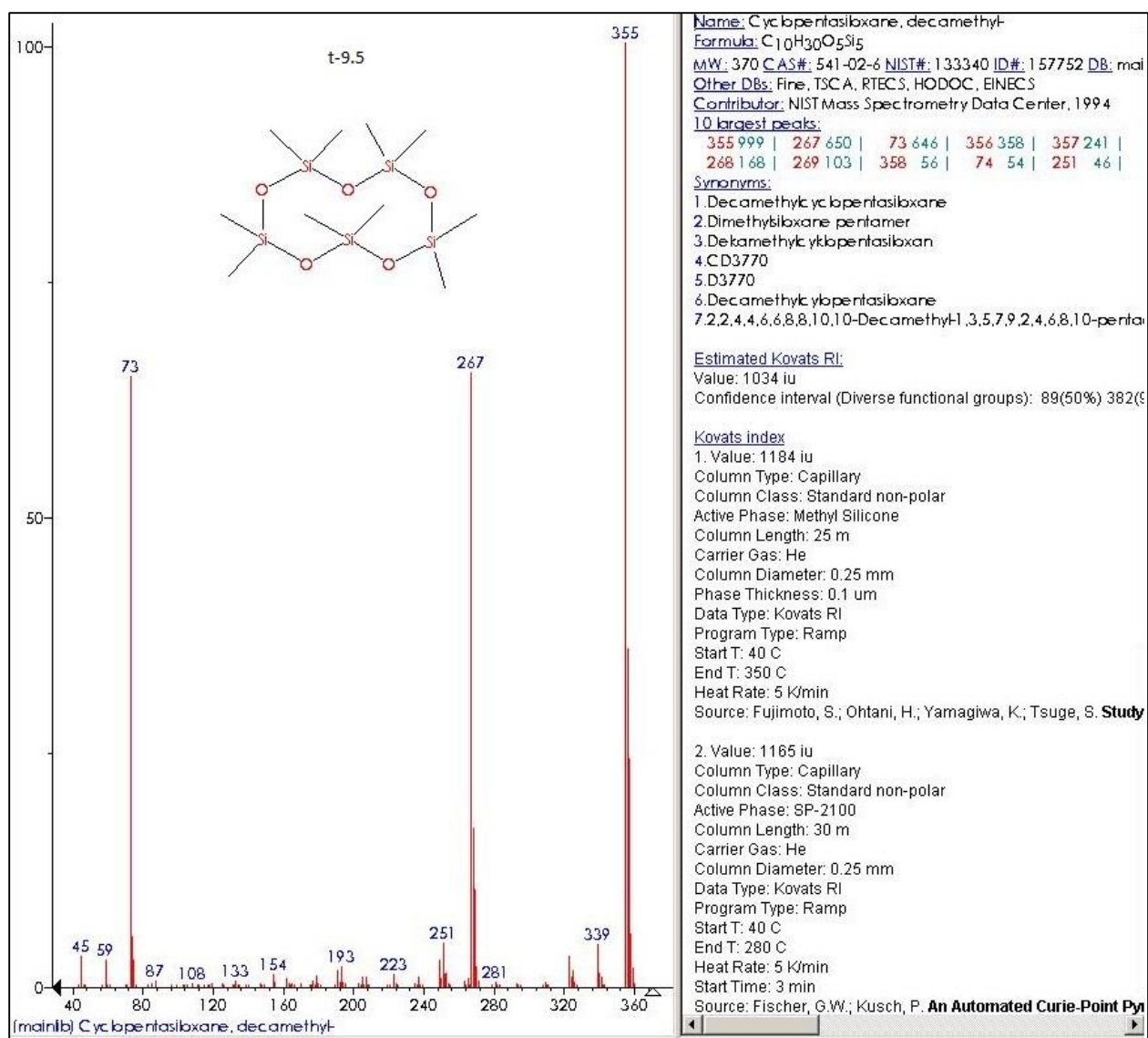


Figure C-7

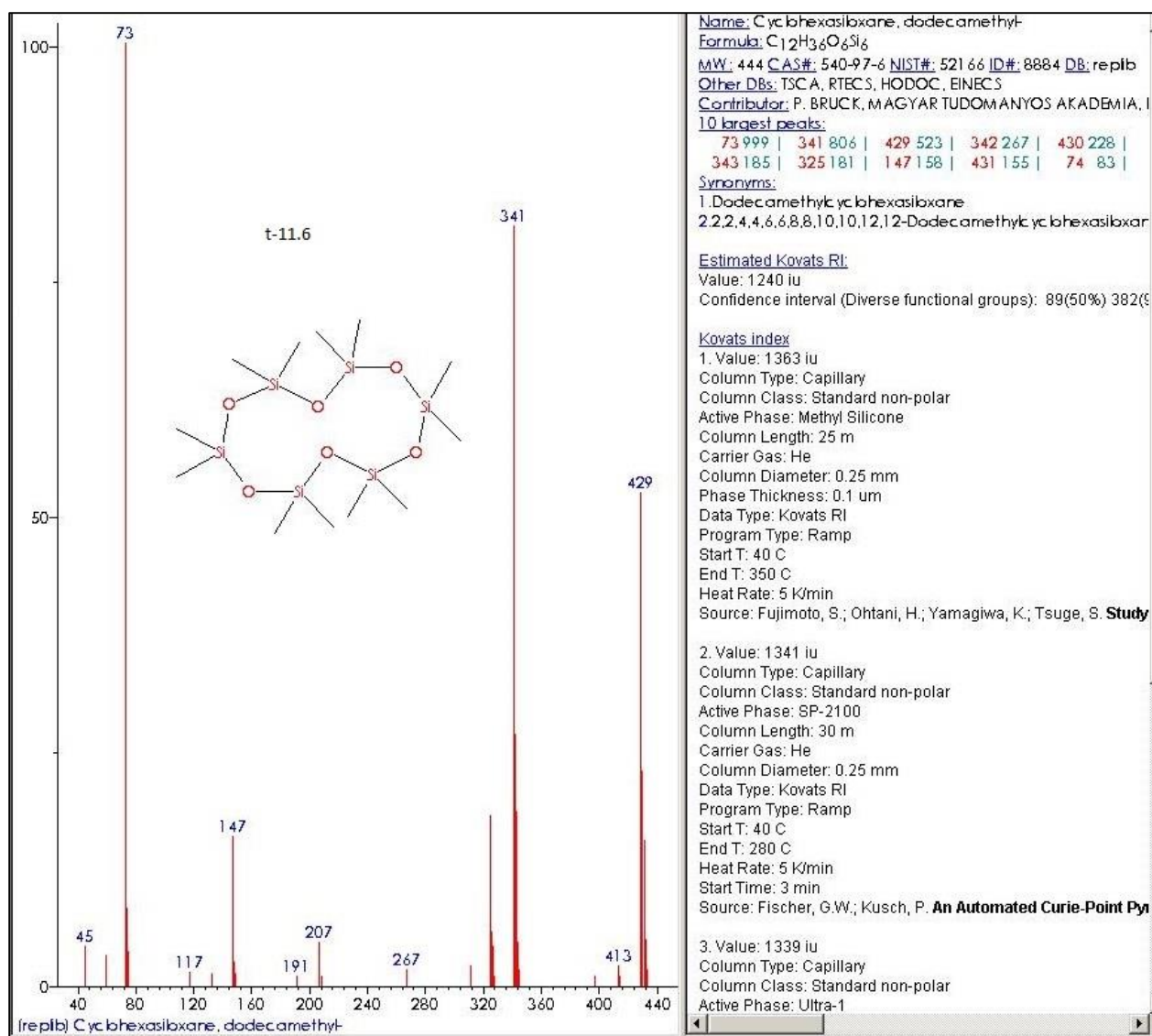


Figure C-9

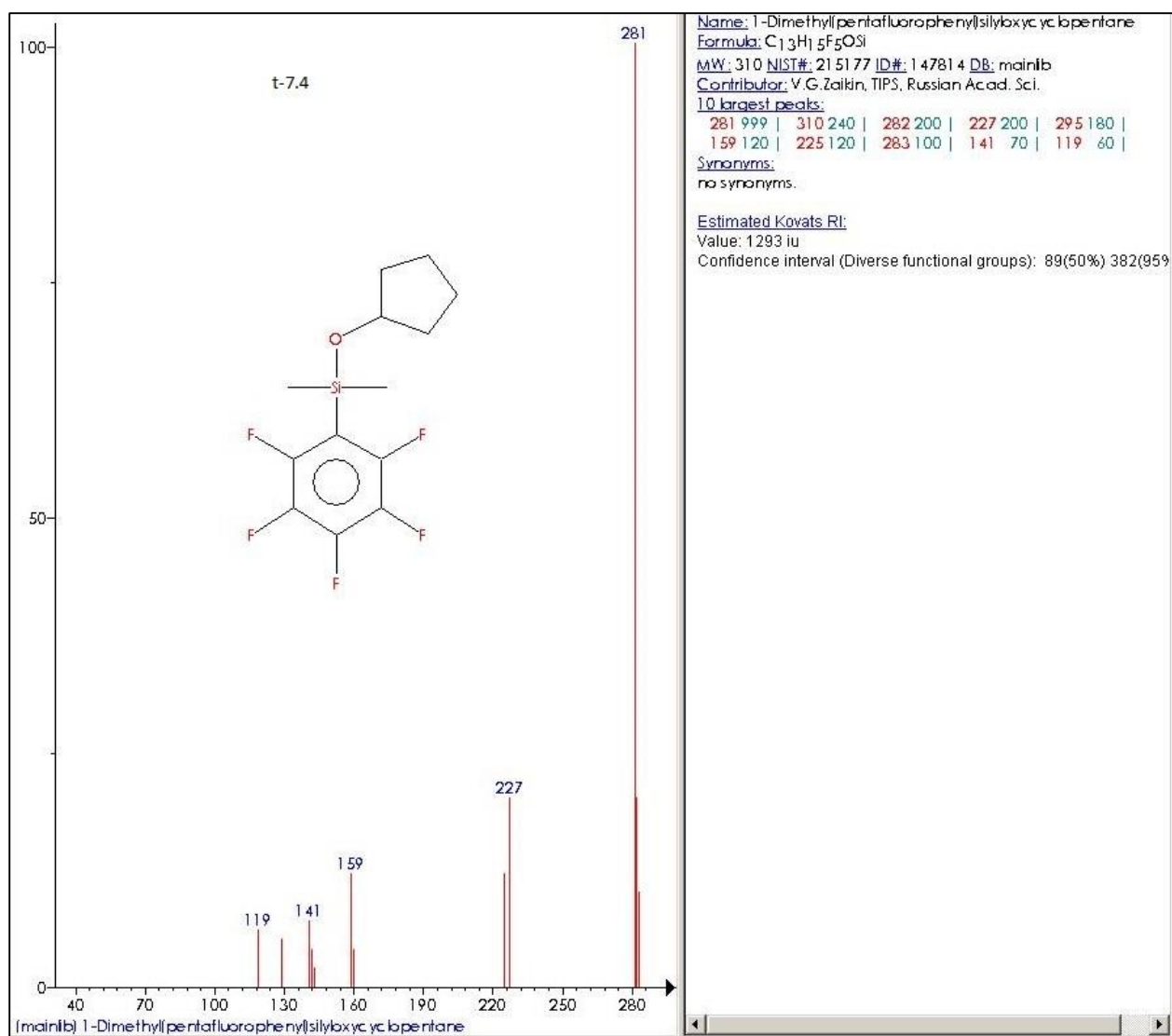


Figure C-10

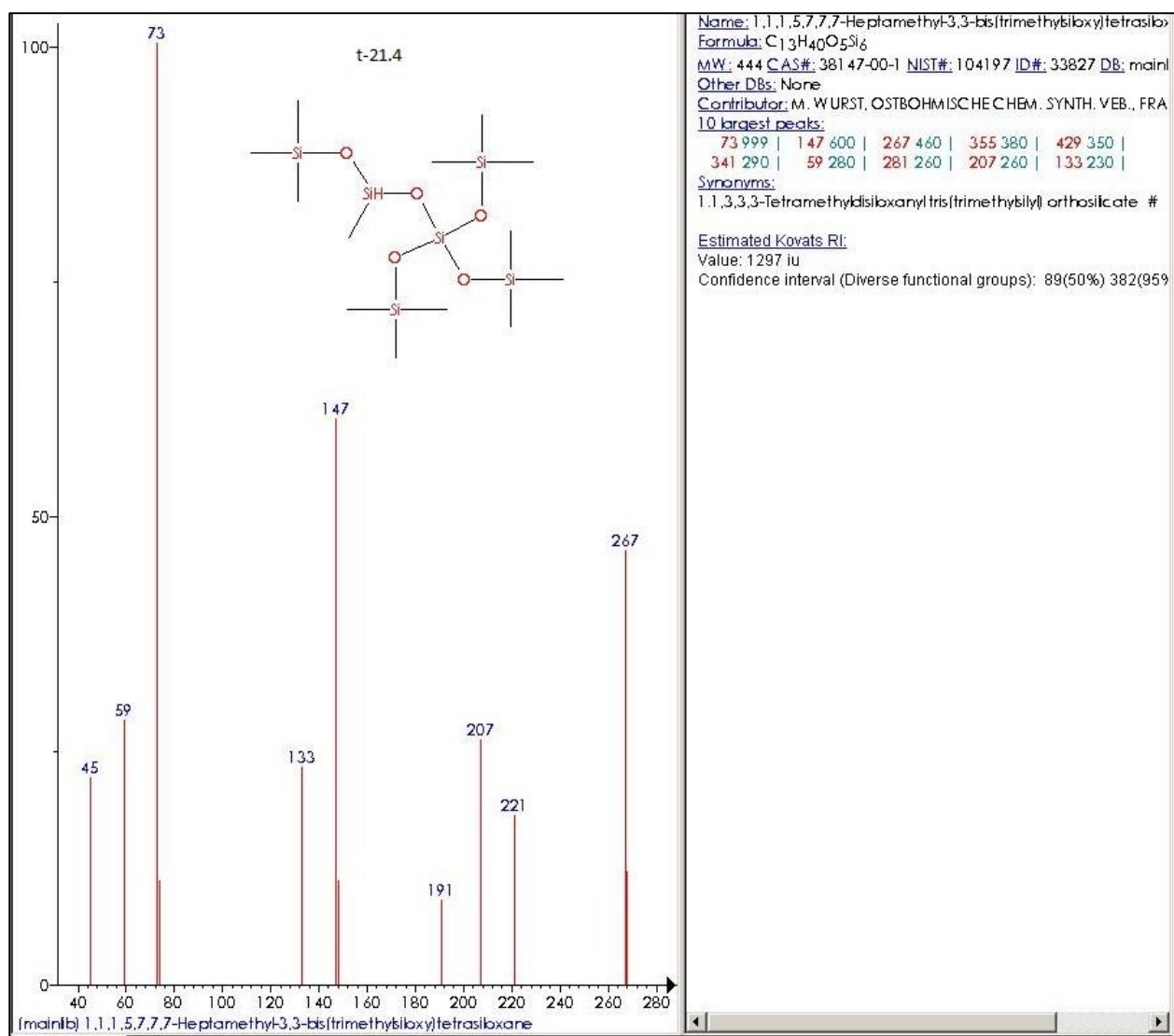


Figure C-11

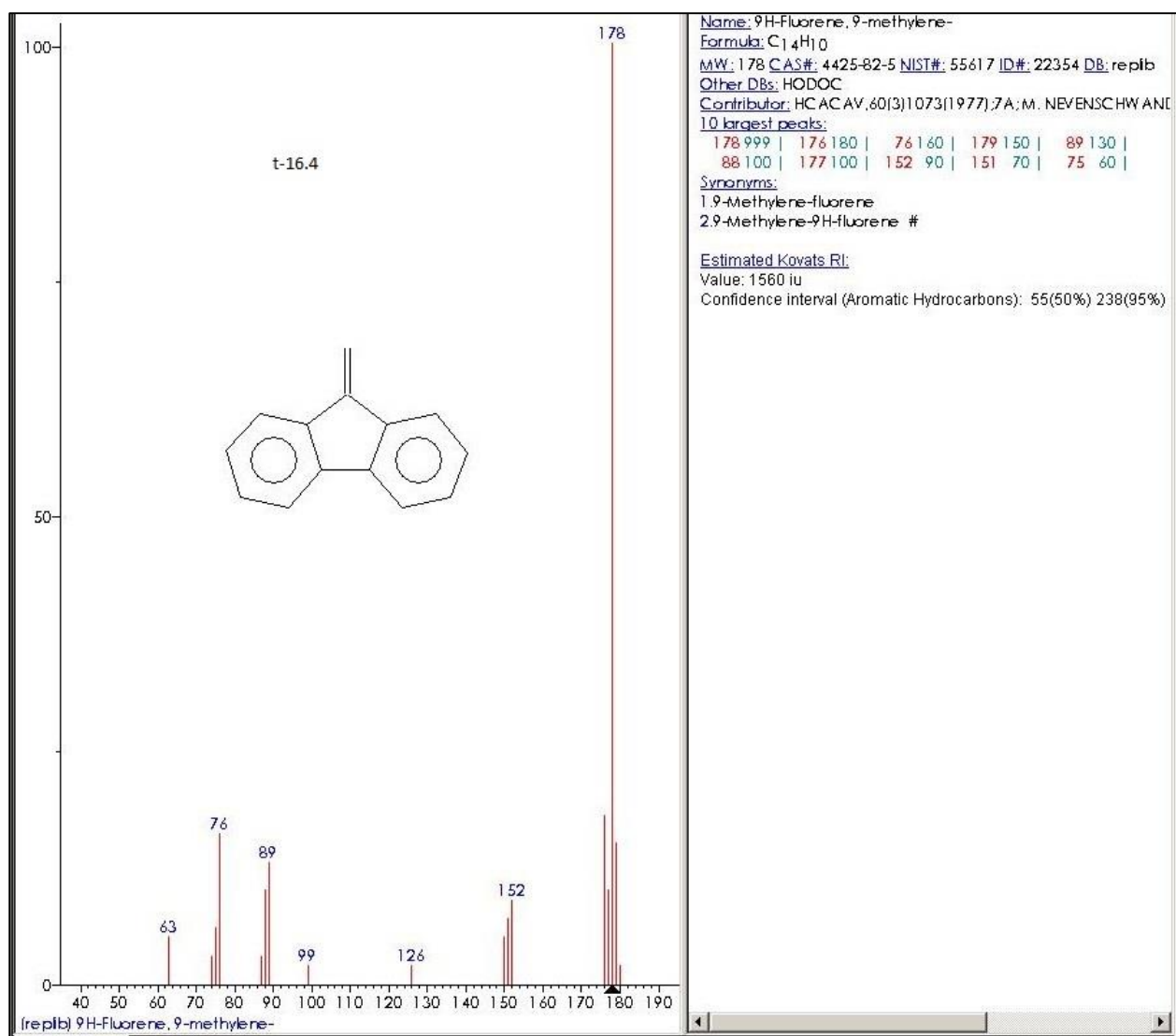


Figure C-12

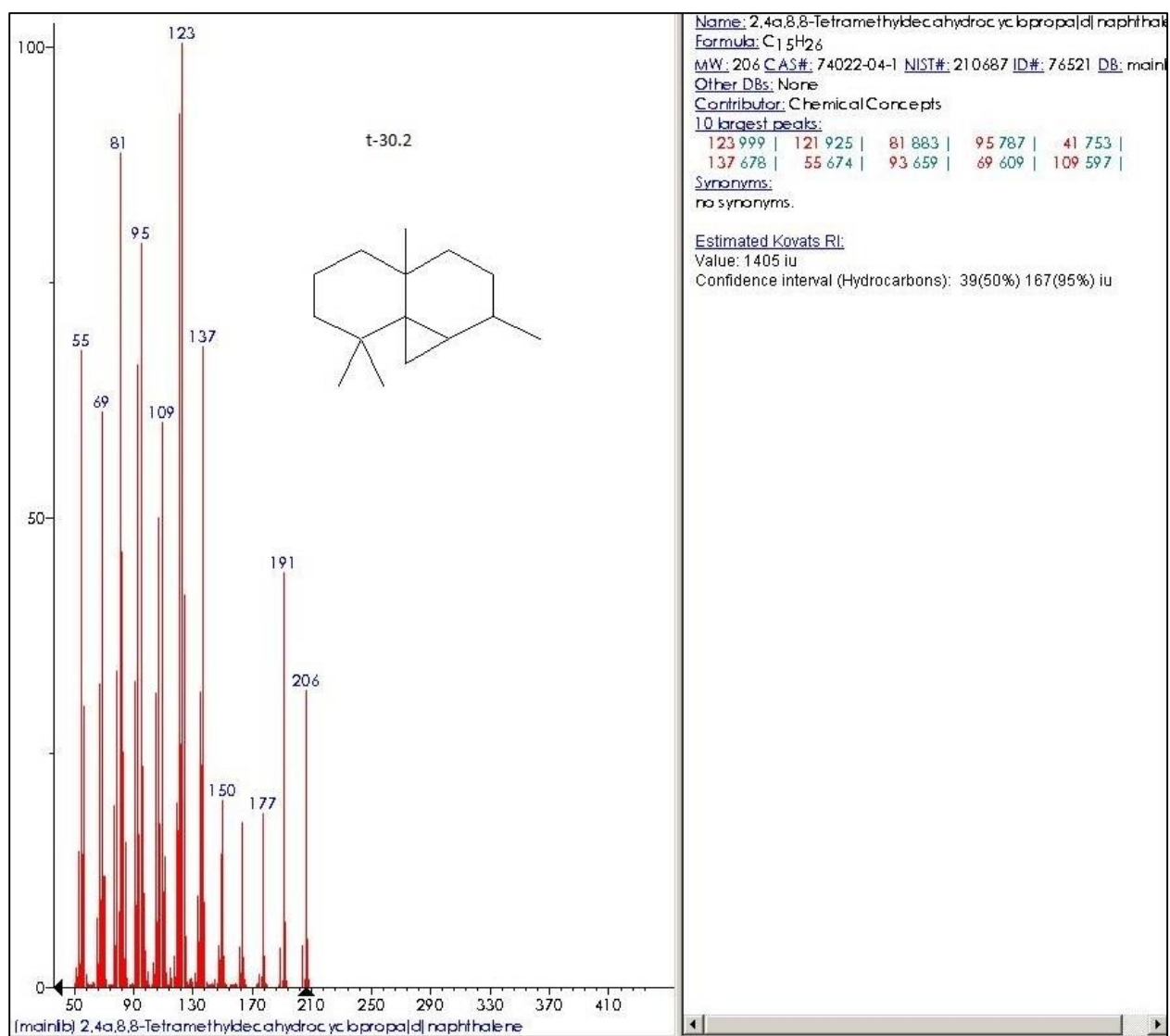


Figure C-13

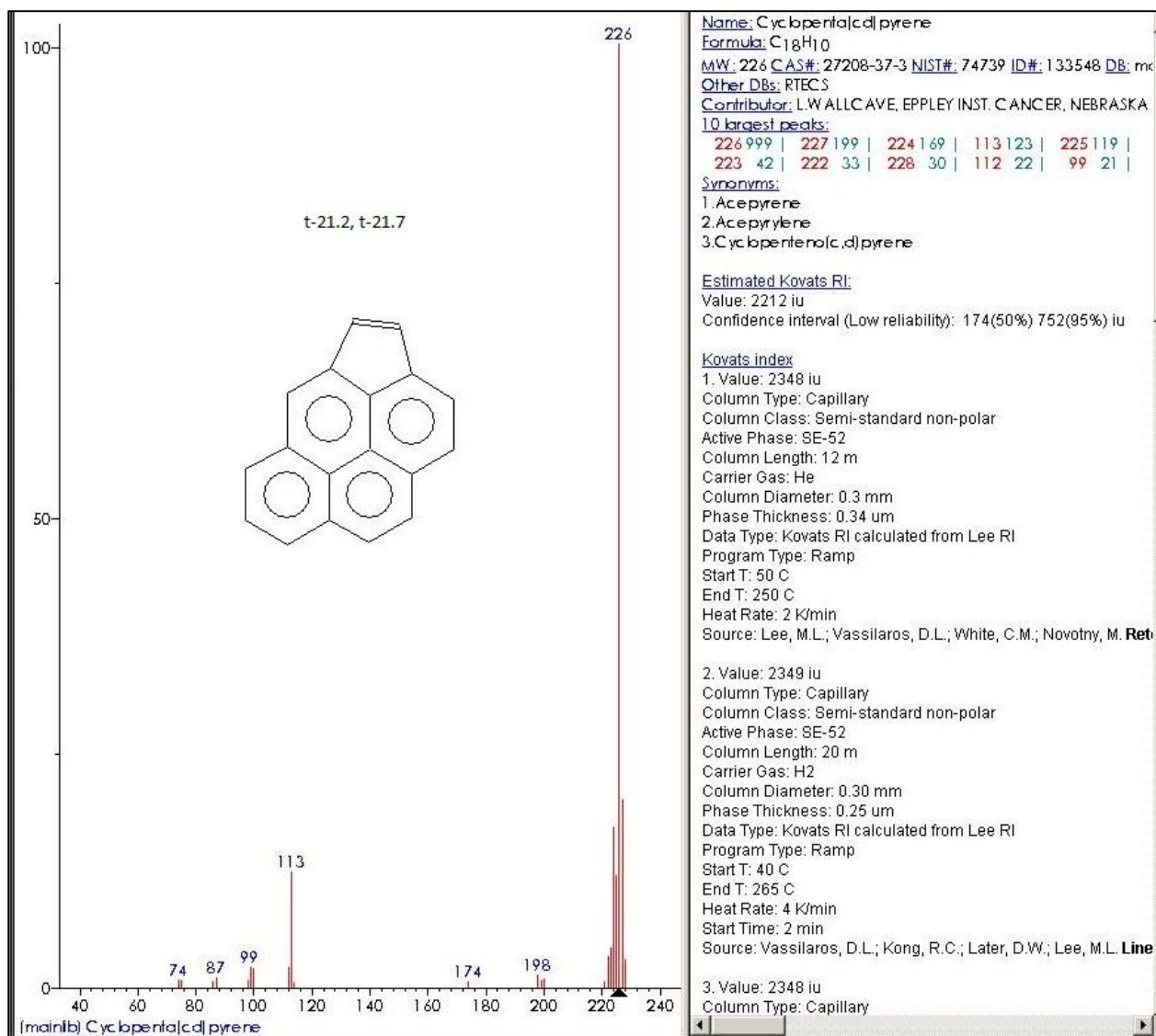


Figure C-15

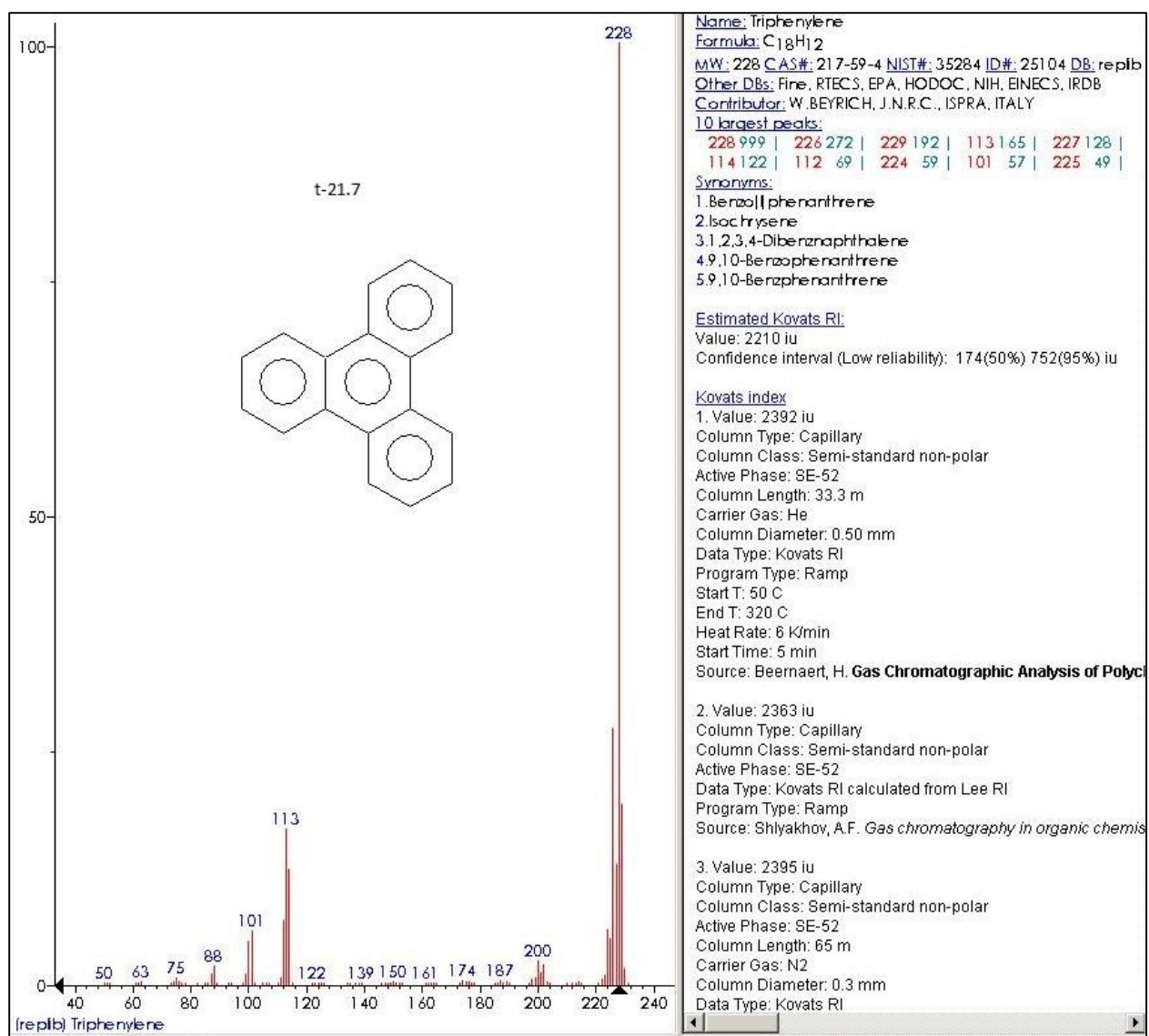


Figure C-16

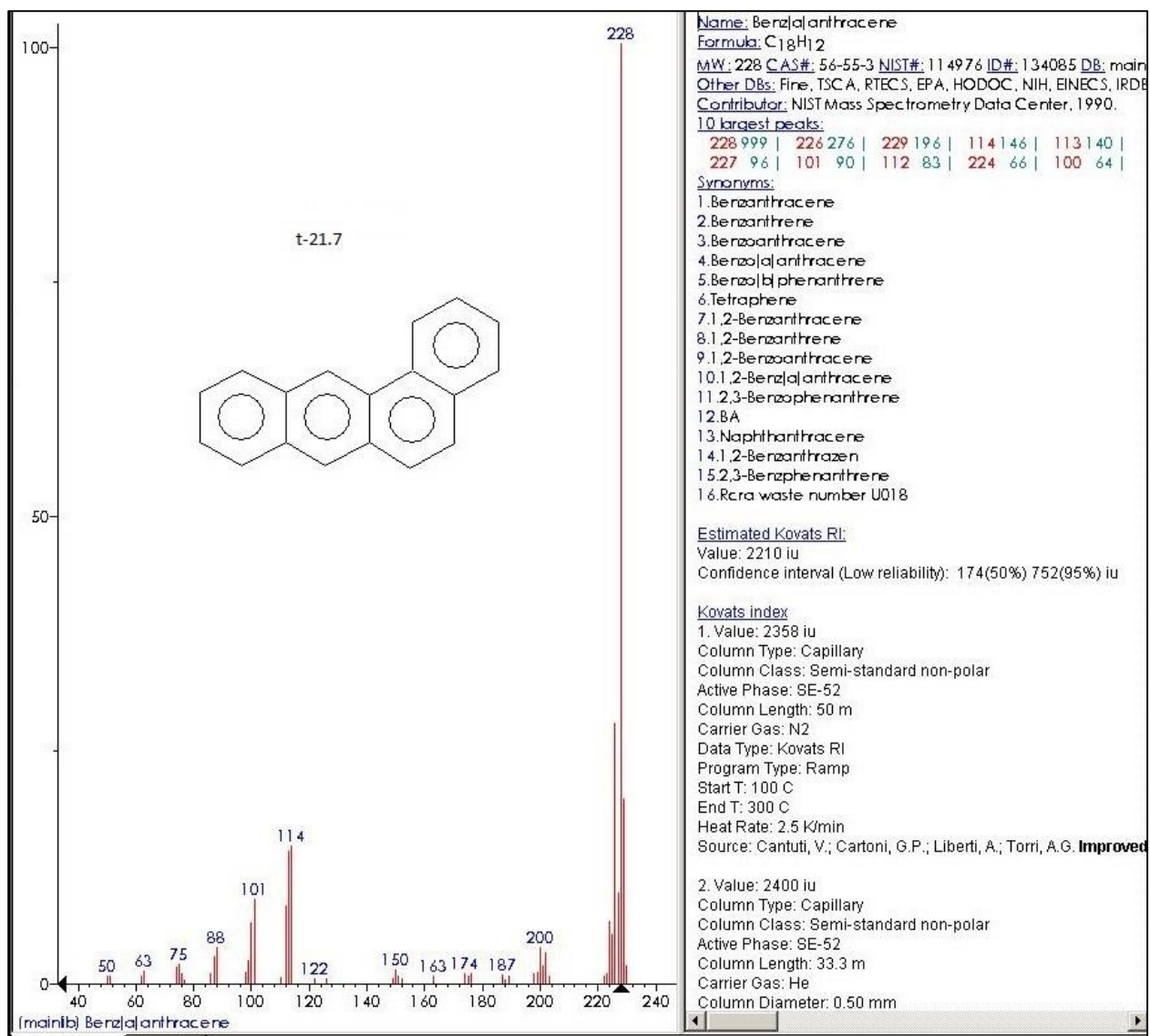


Figure C-17

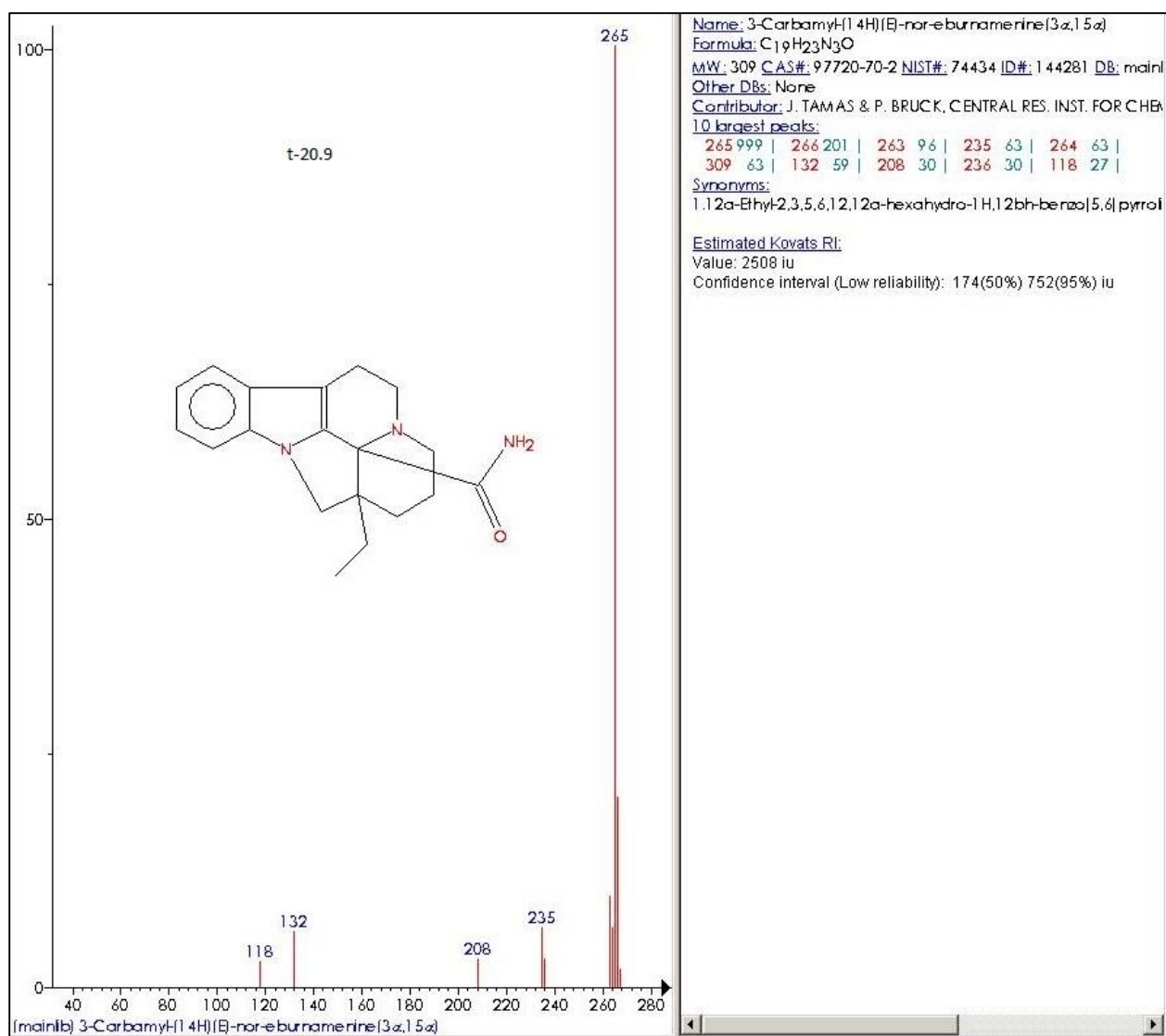


Figure C-18

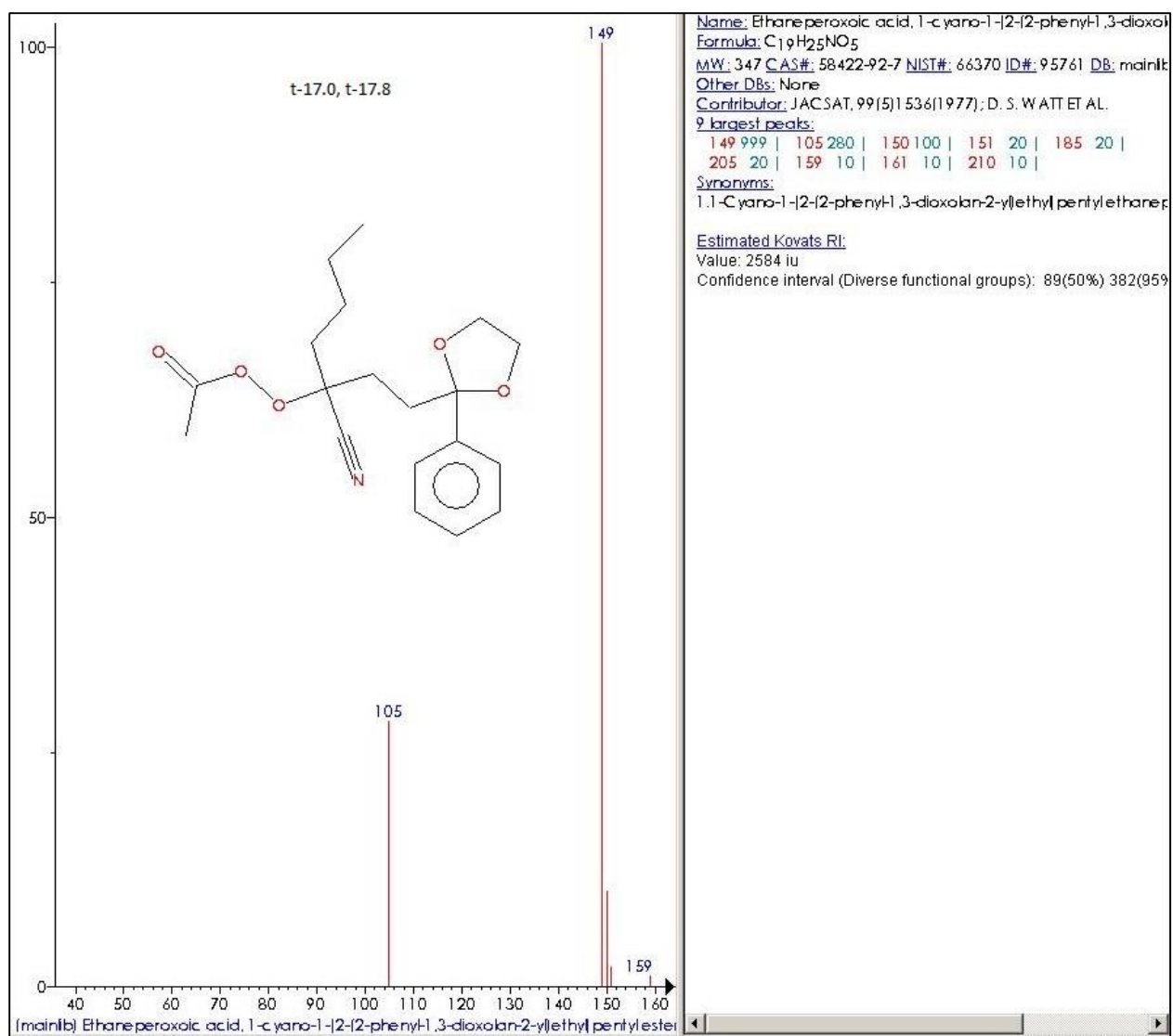


Figure C-19

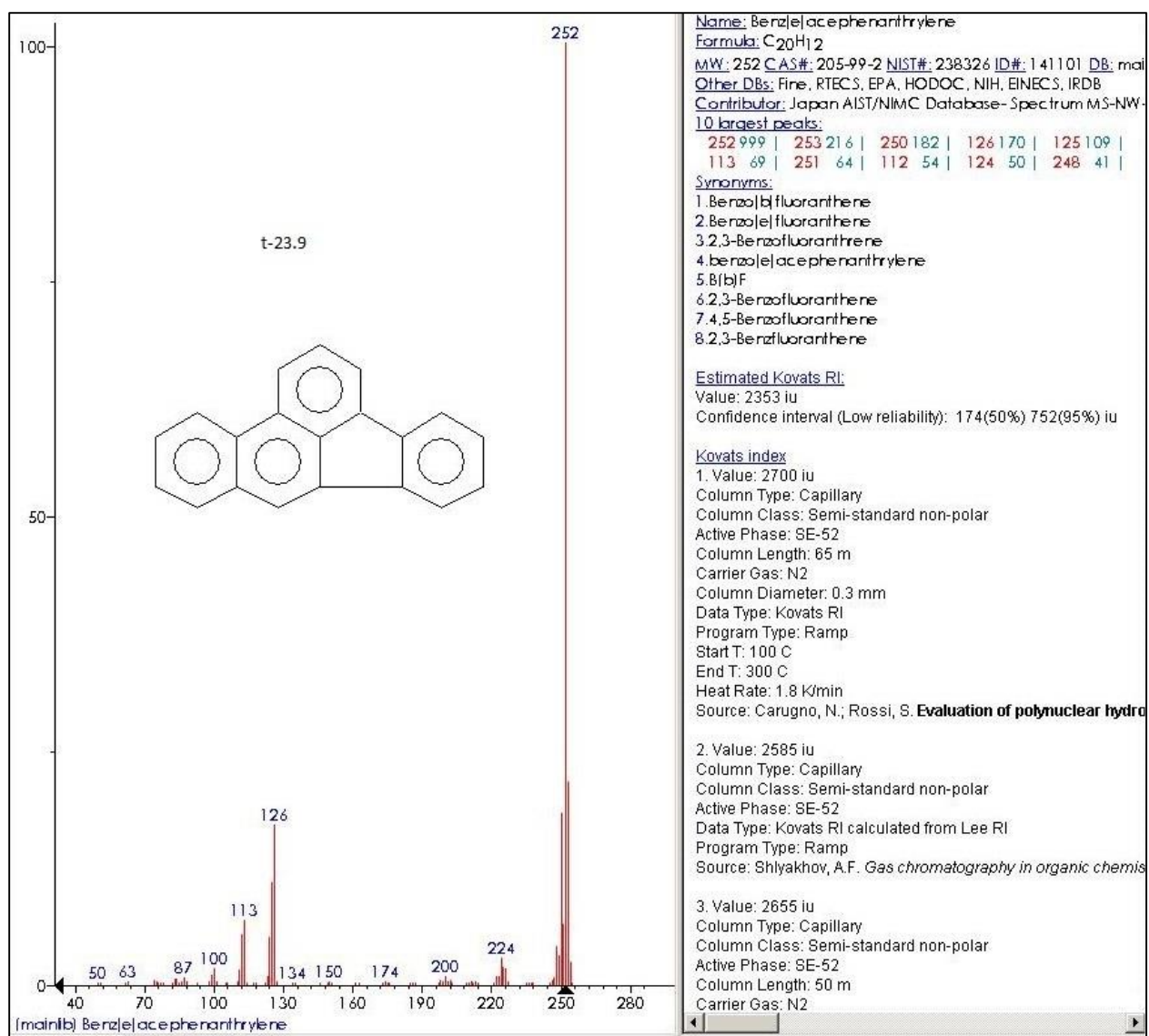


Figure C-20

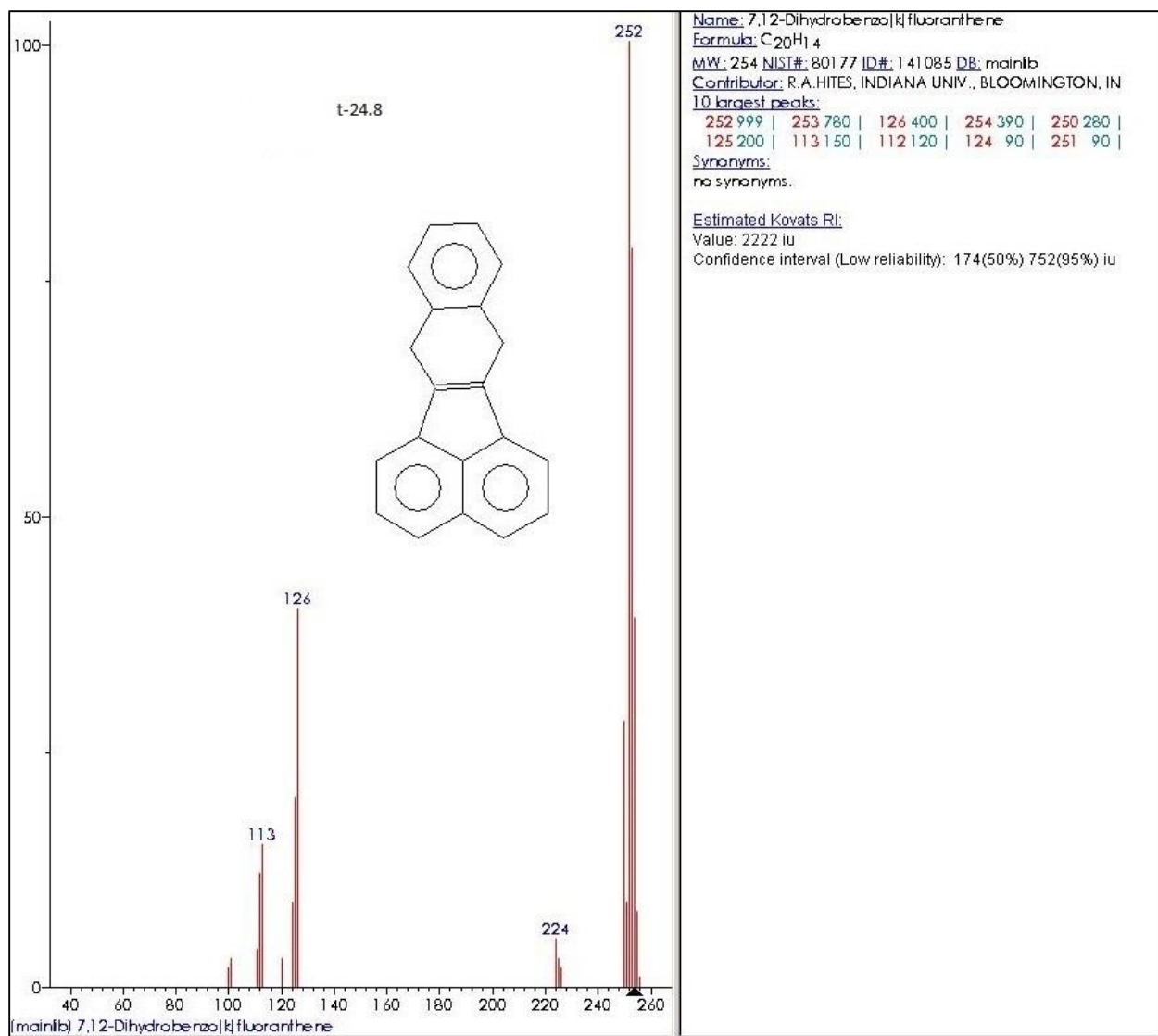


Figure C-21

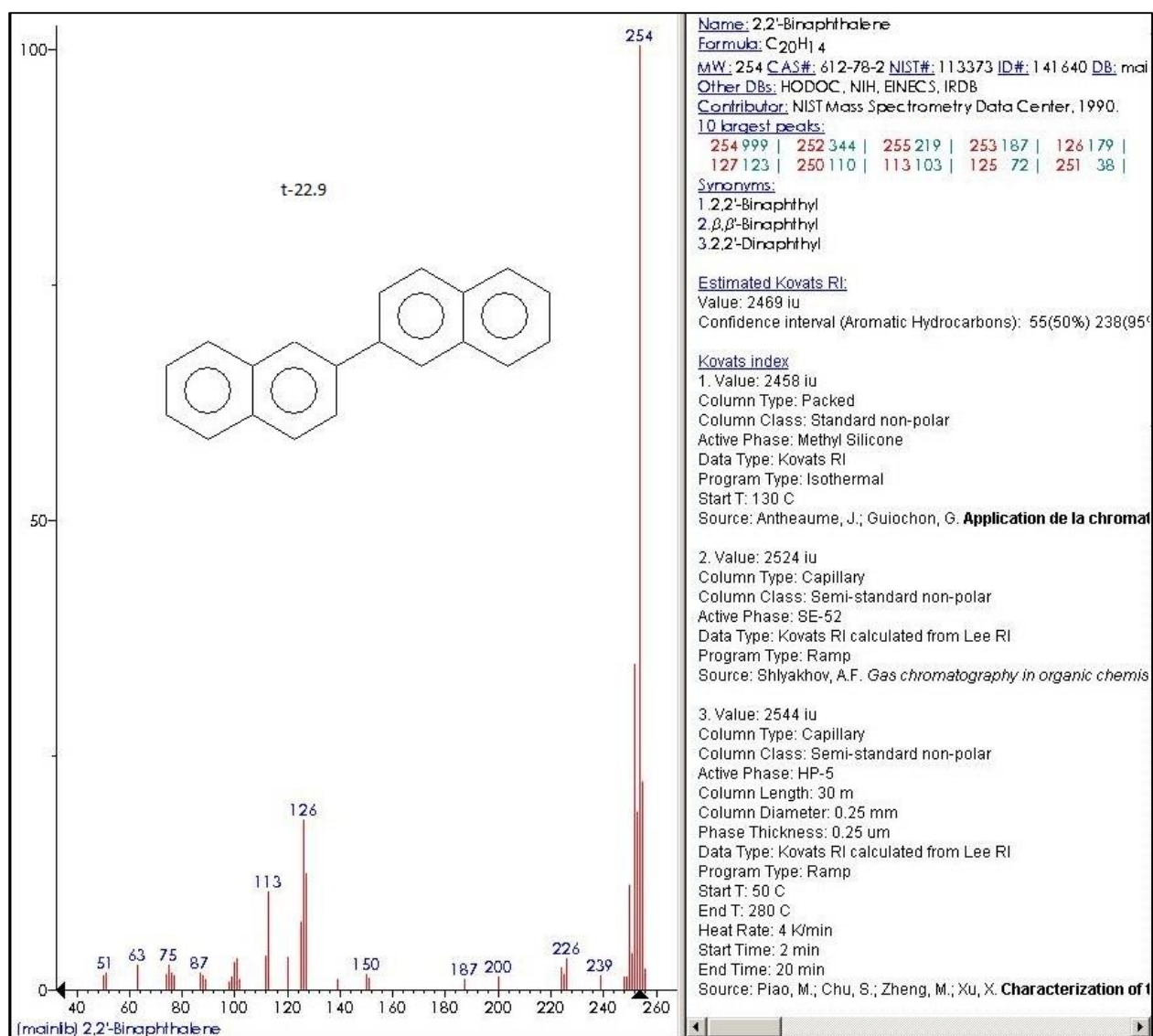


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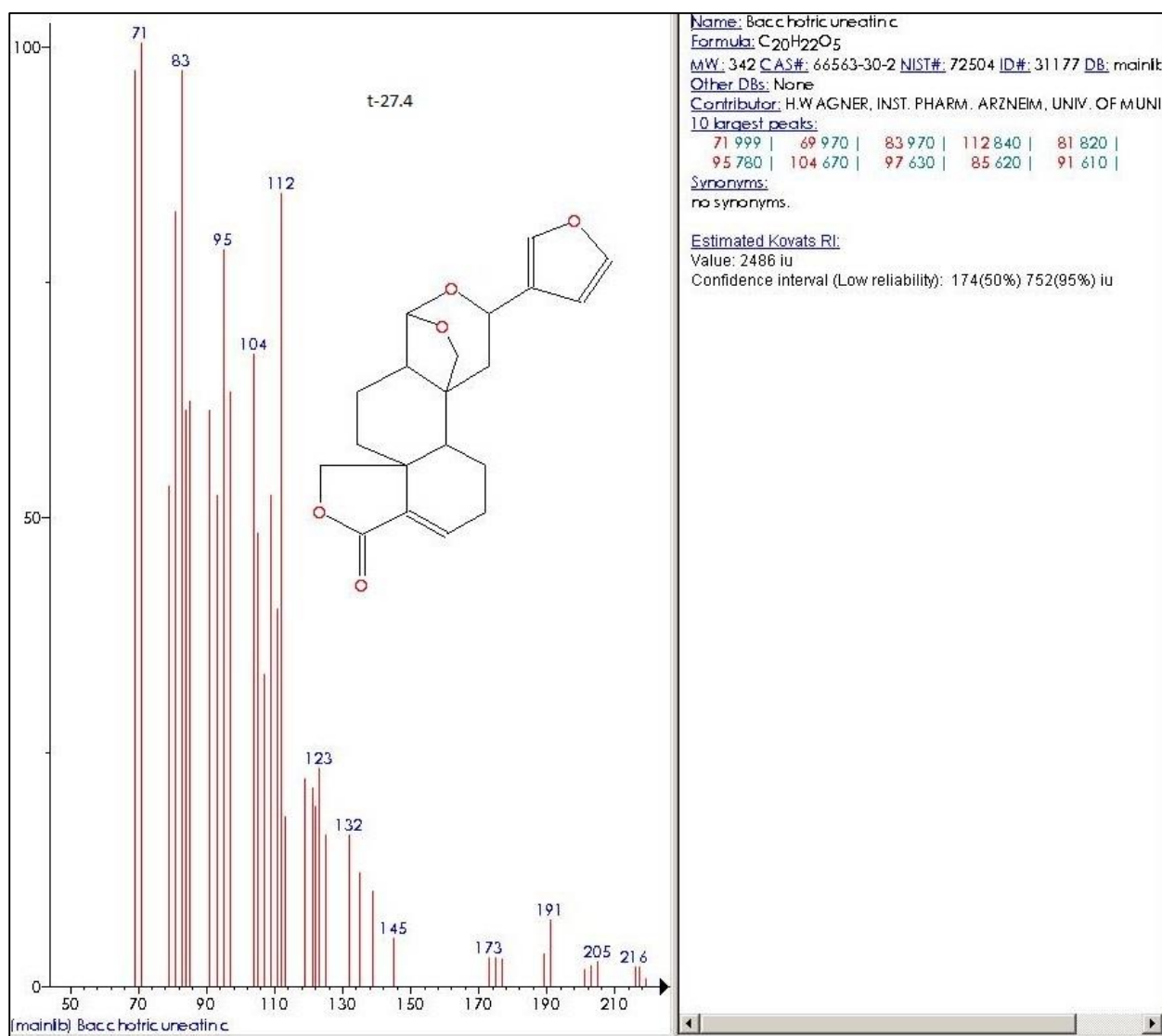


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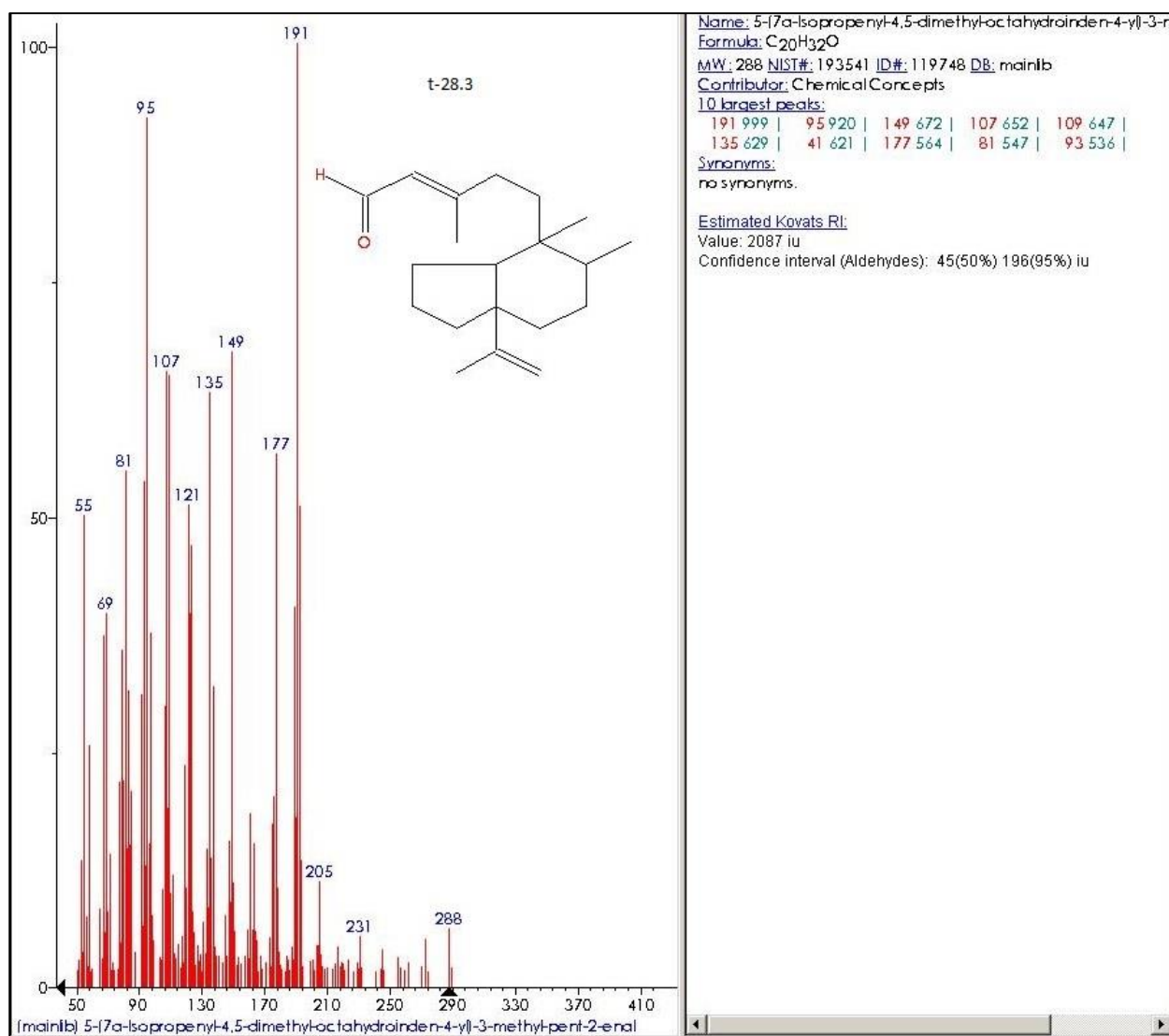


Figure C-24

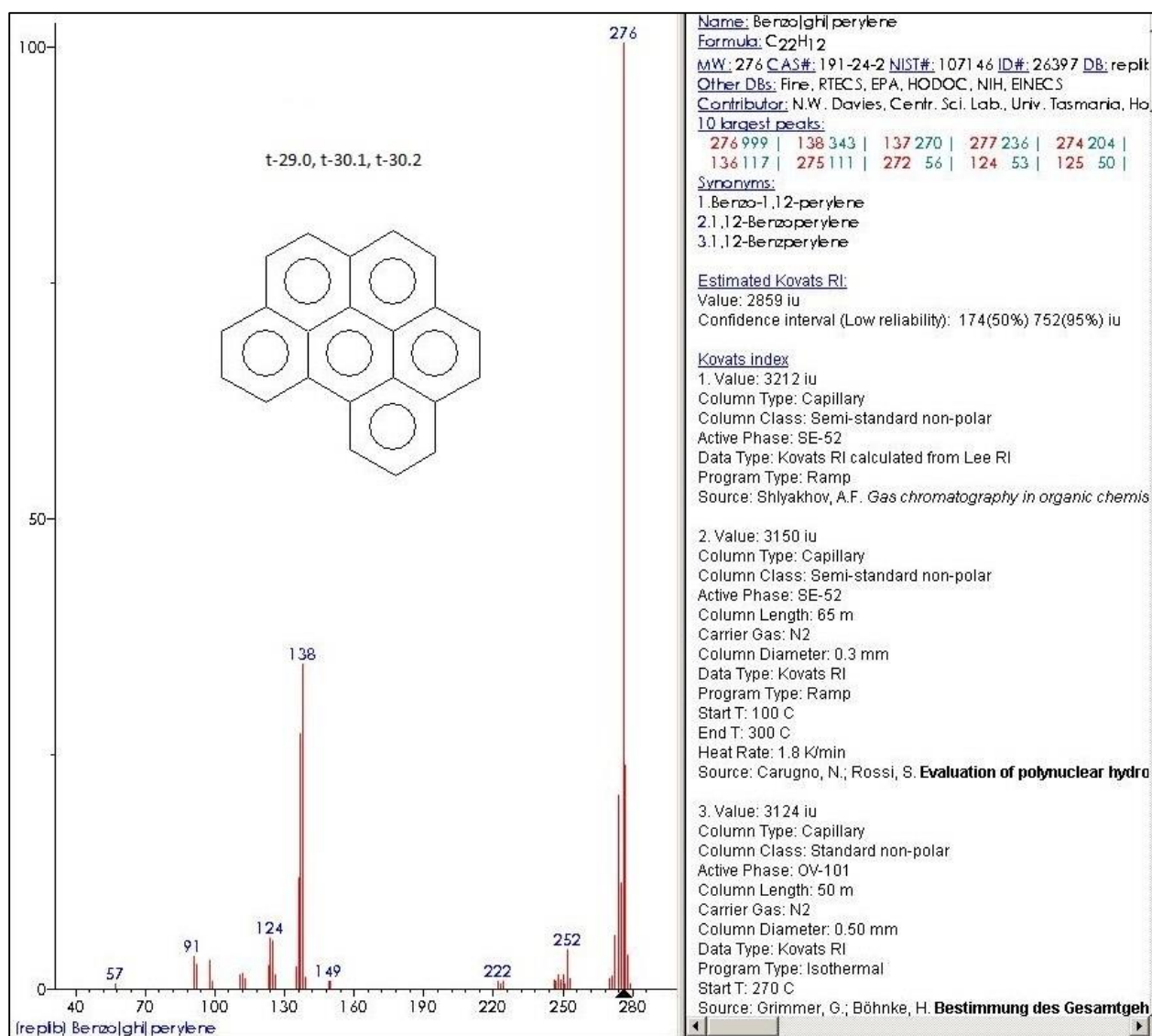


Figure C-25

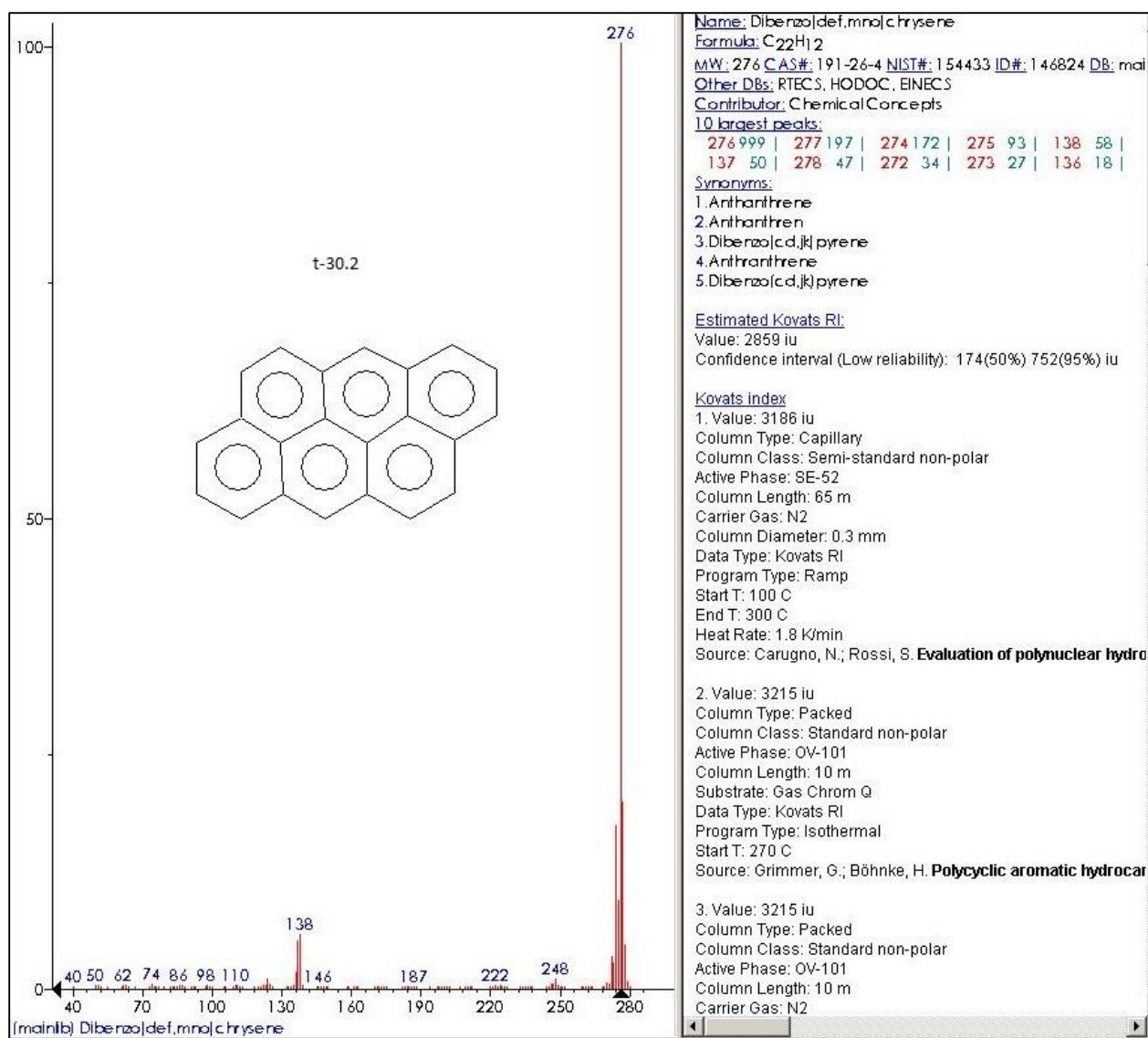


Figure C-26

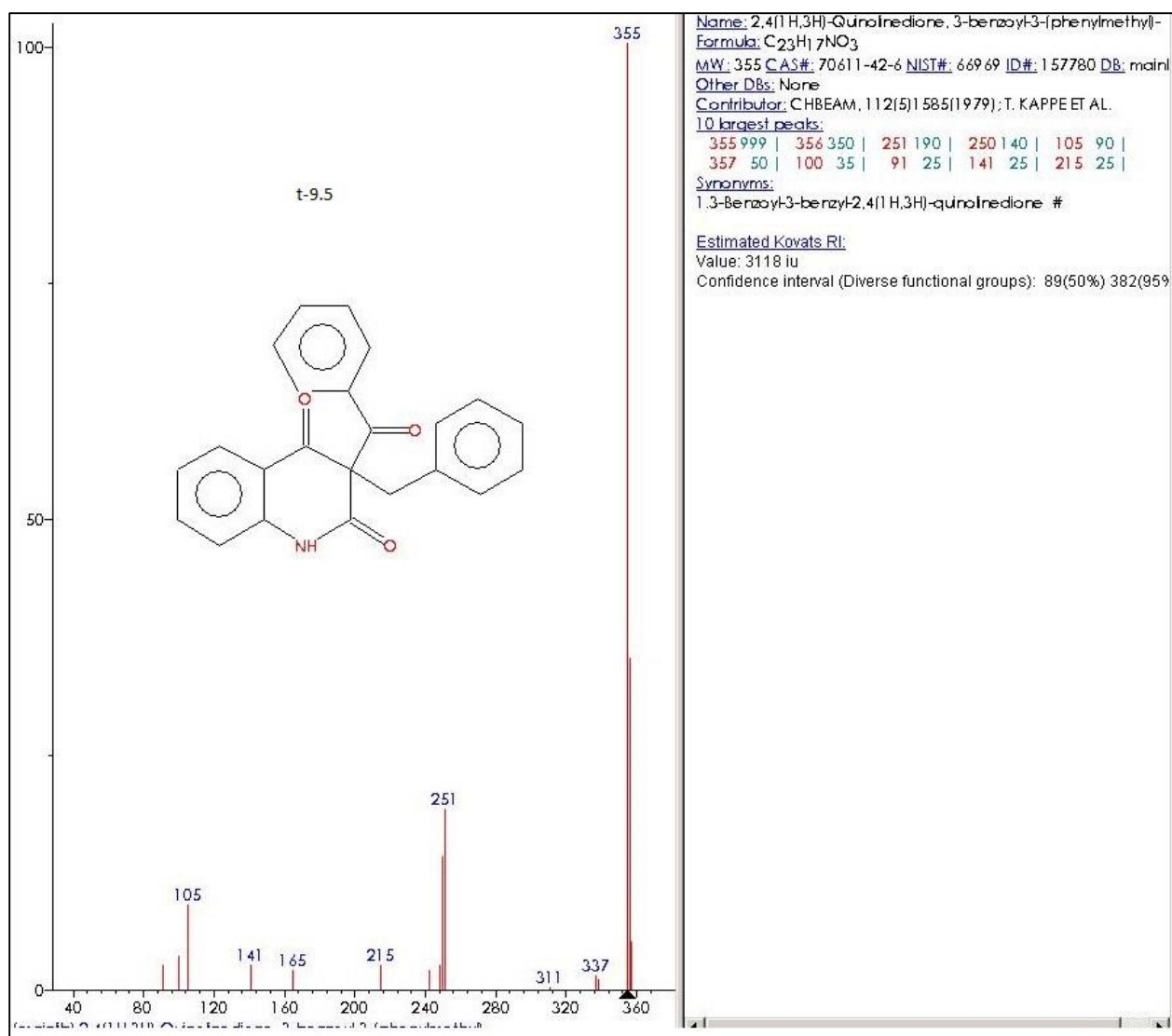


Figure C-27

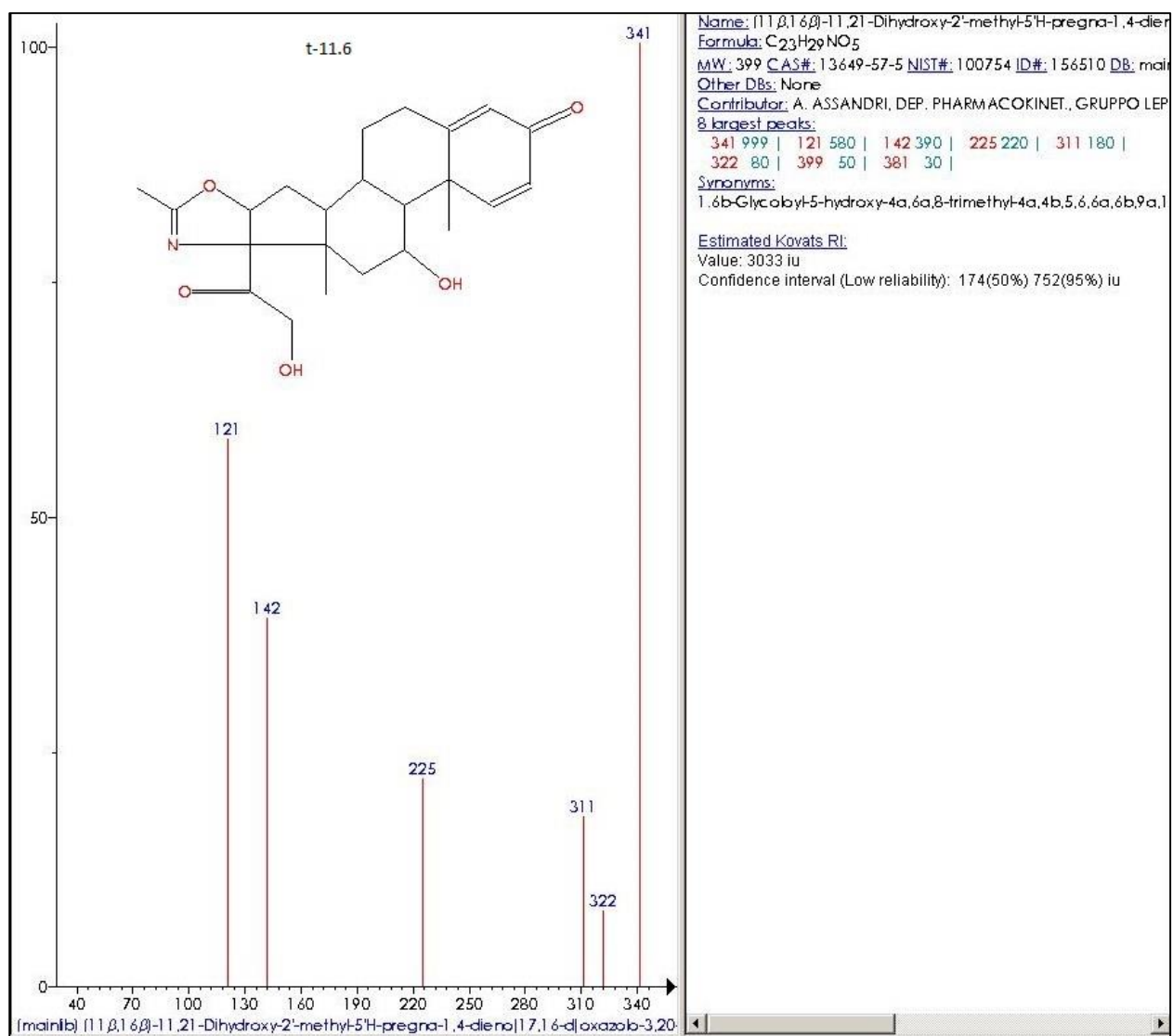


Figure C-28

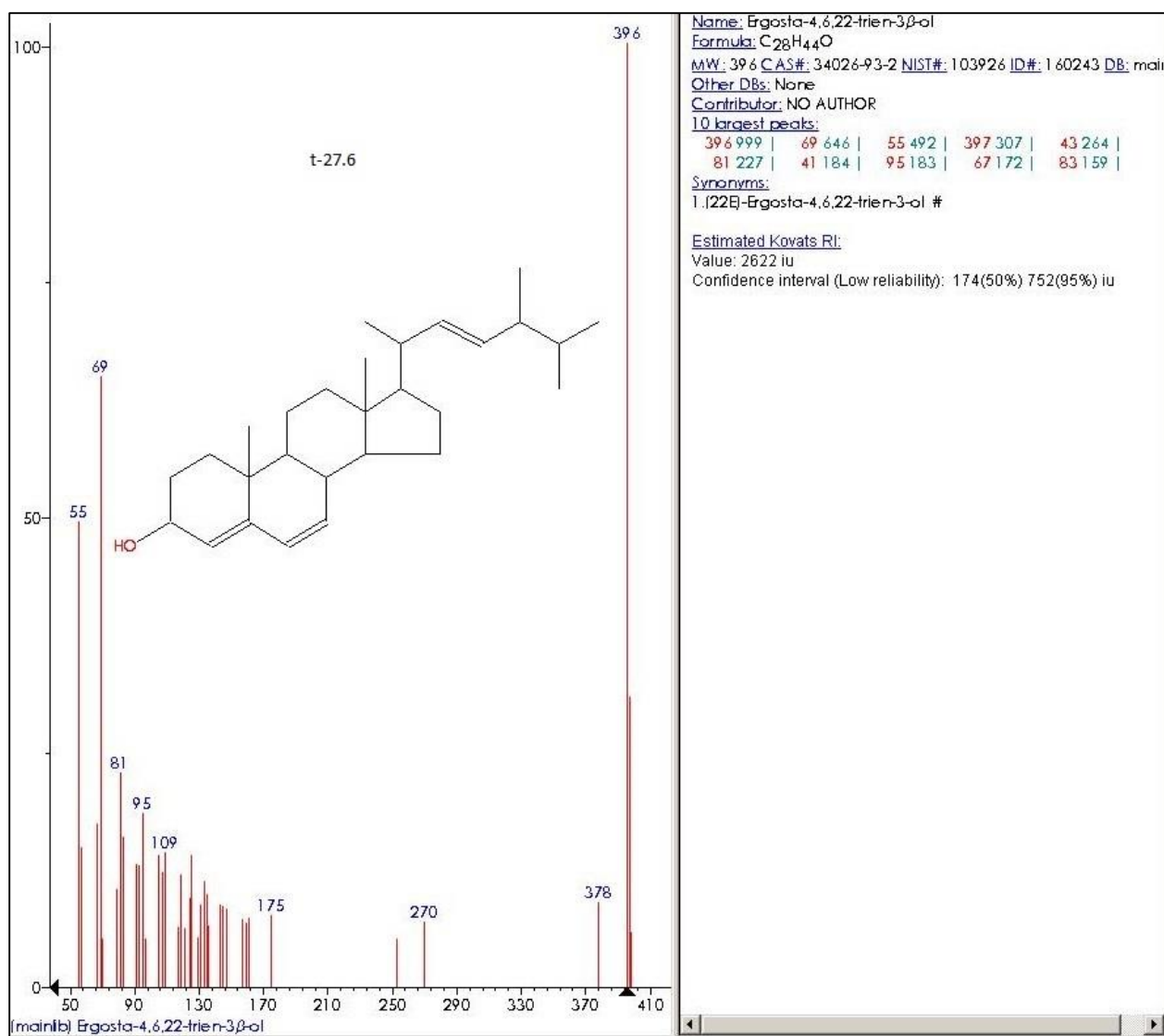


Figure C-29

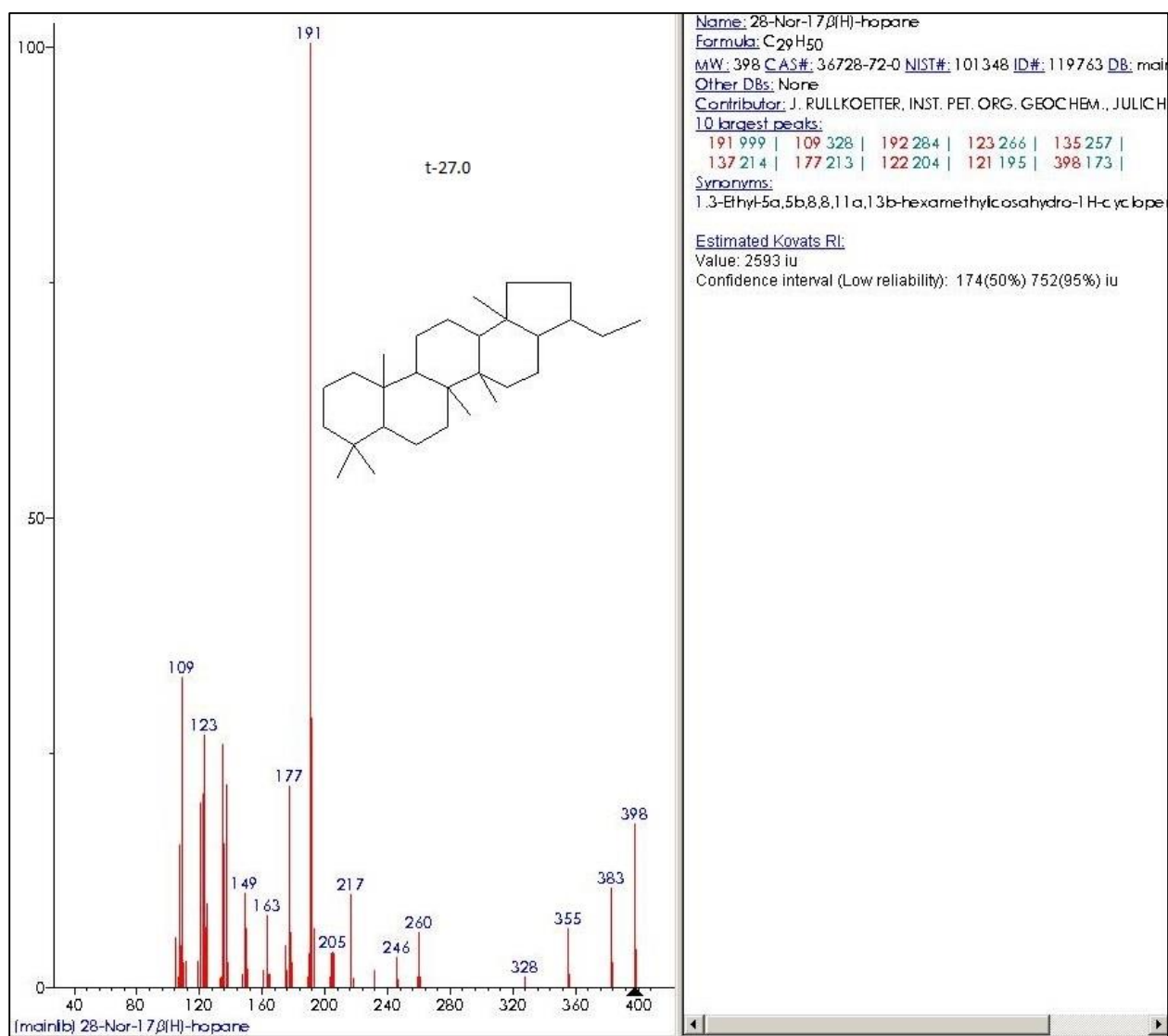


Figure C-30

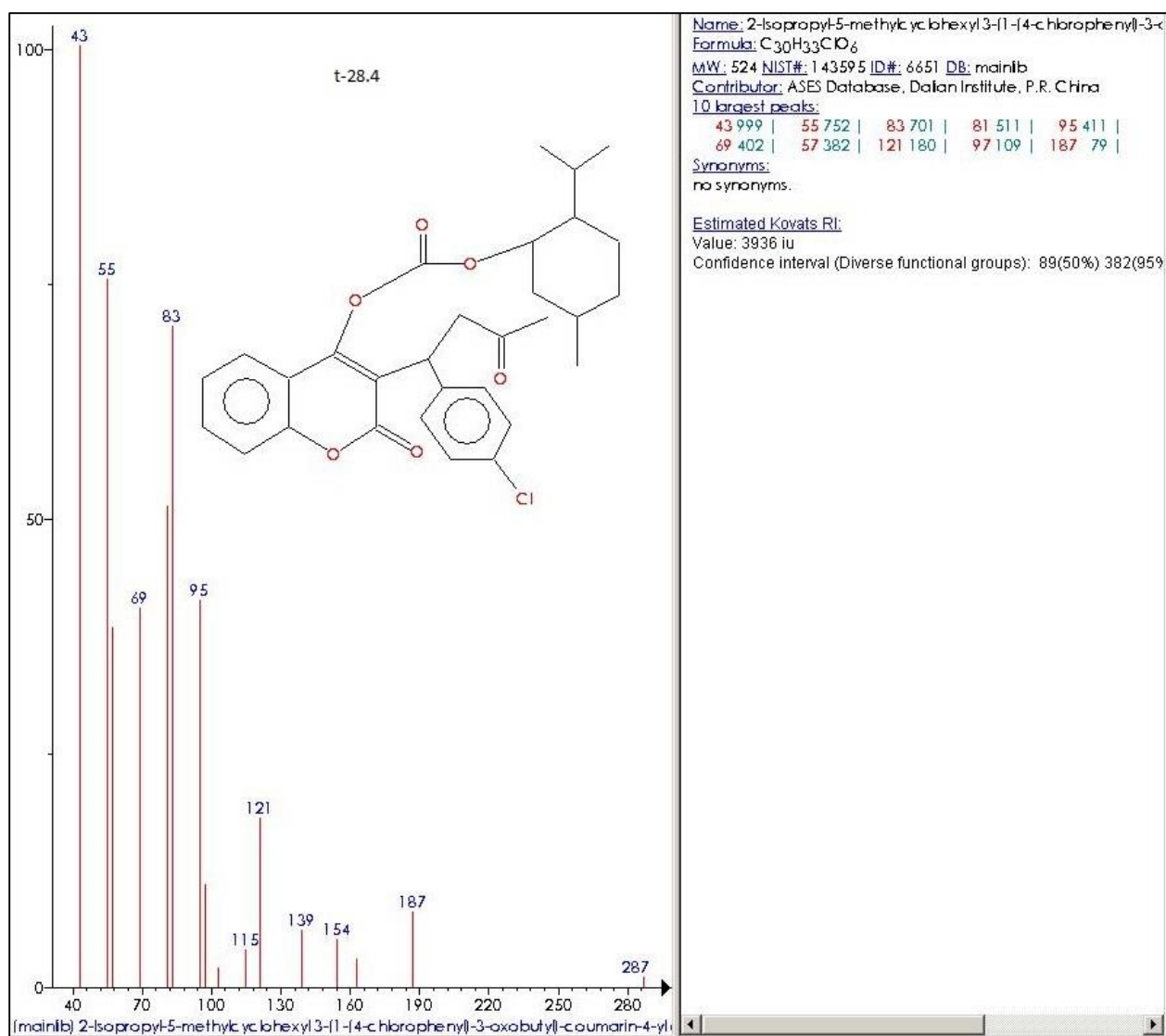


Figure C-31

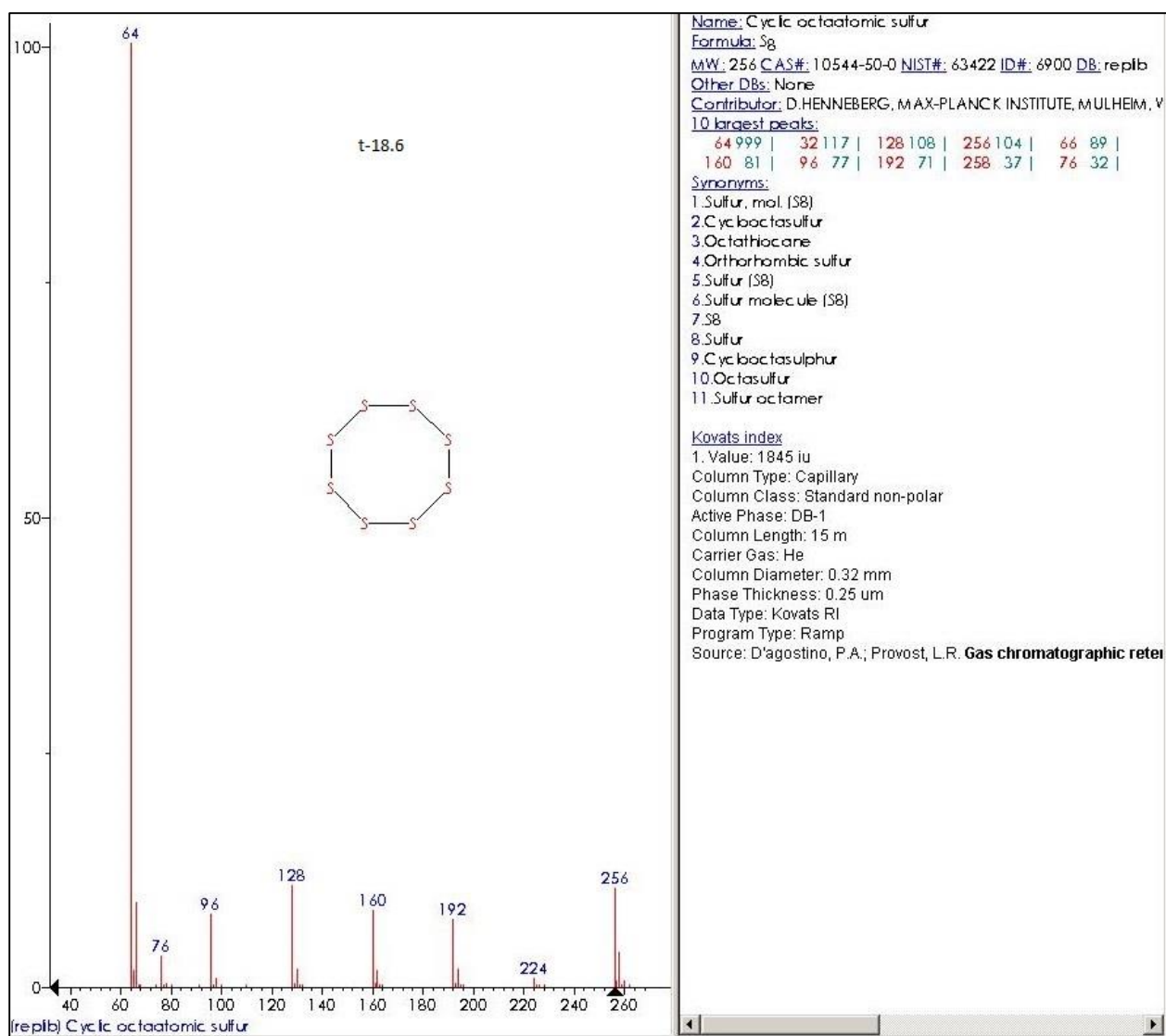


Figure C-32

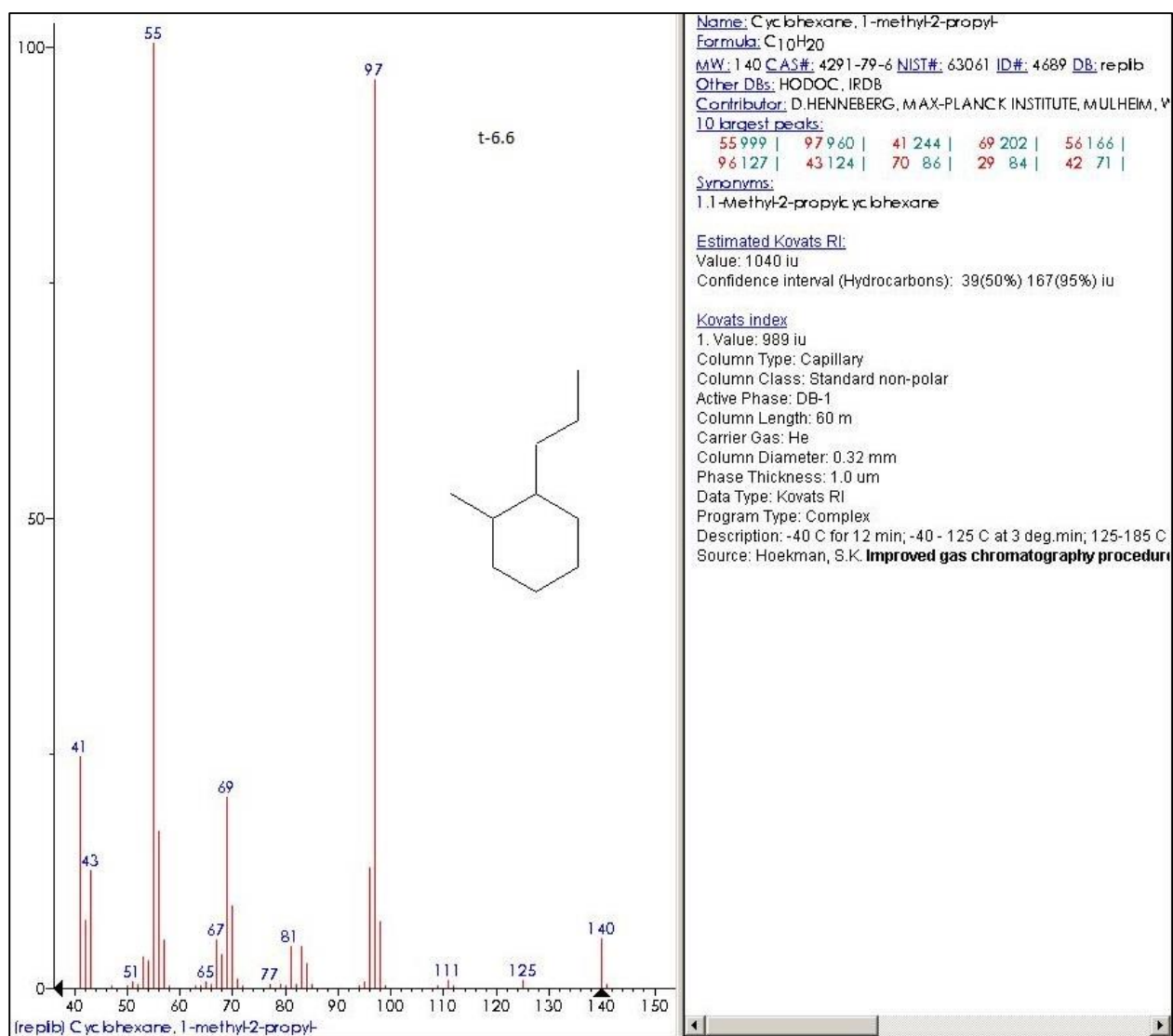


Figure C-33

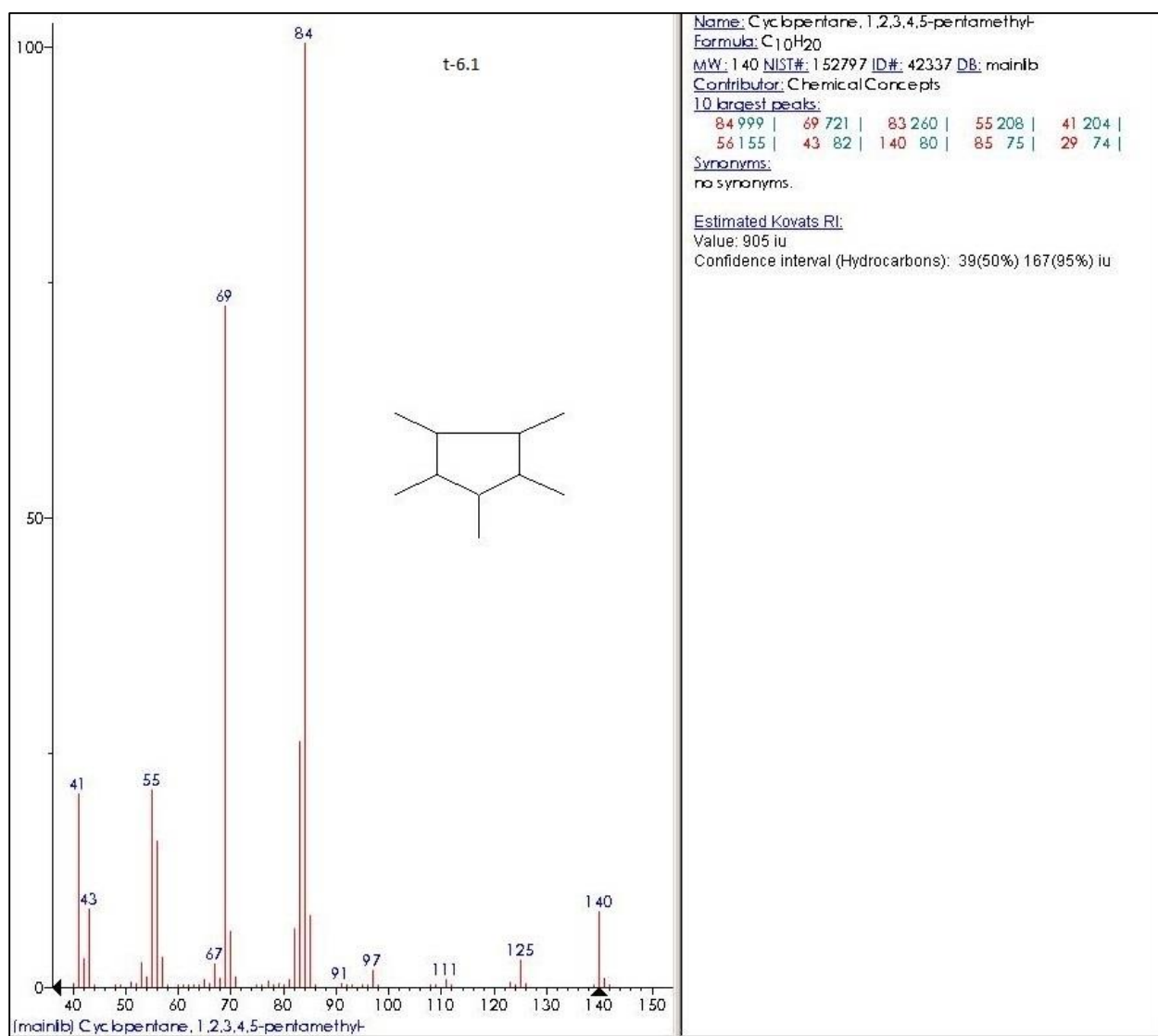


Figure C-34

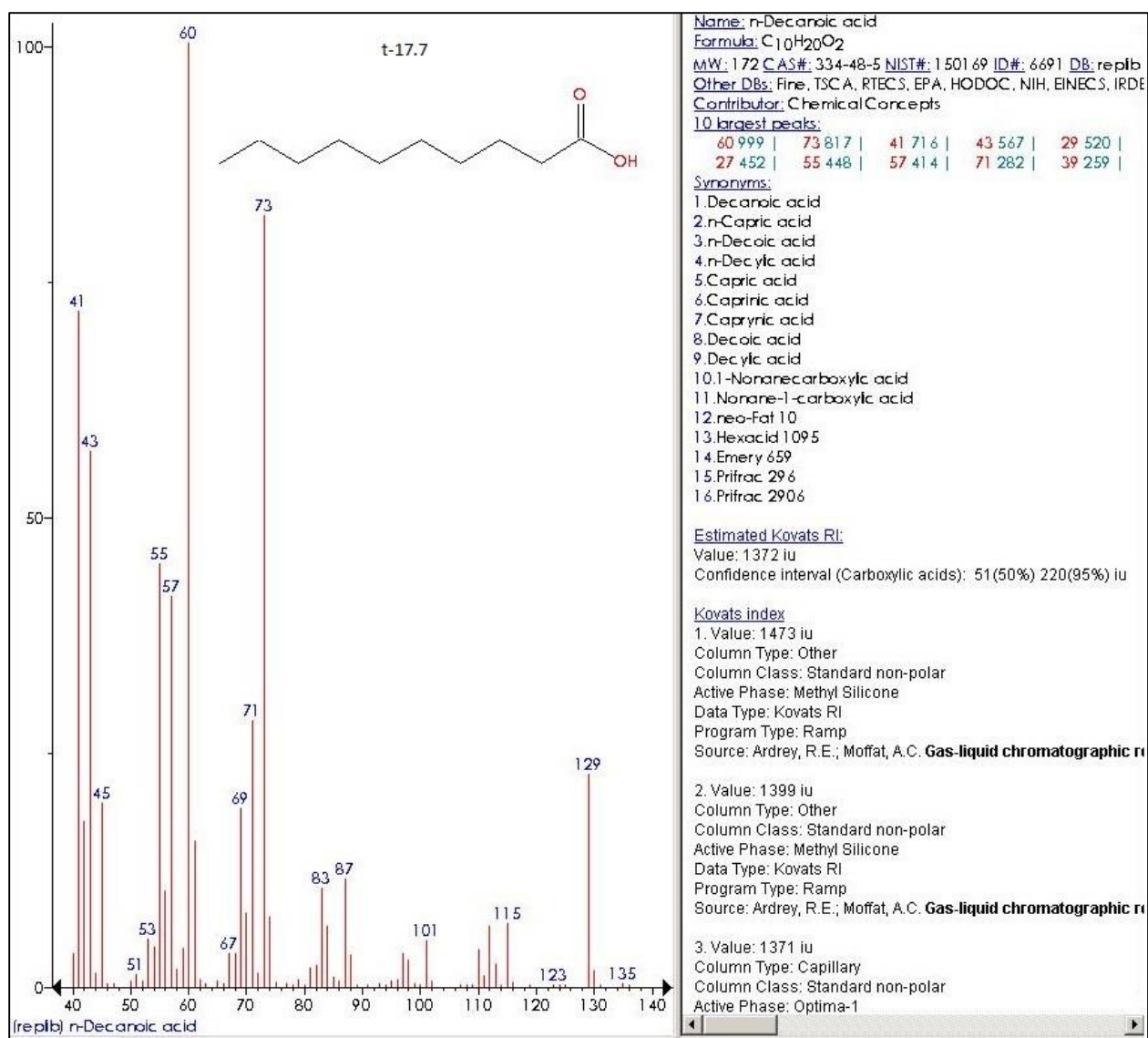


Figure C-35

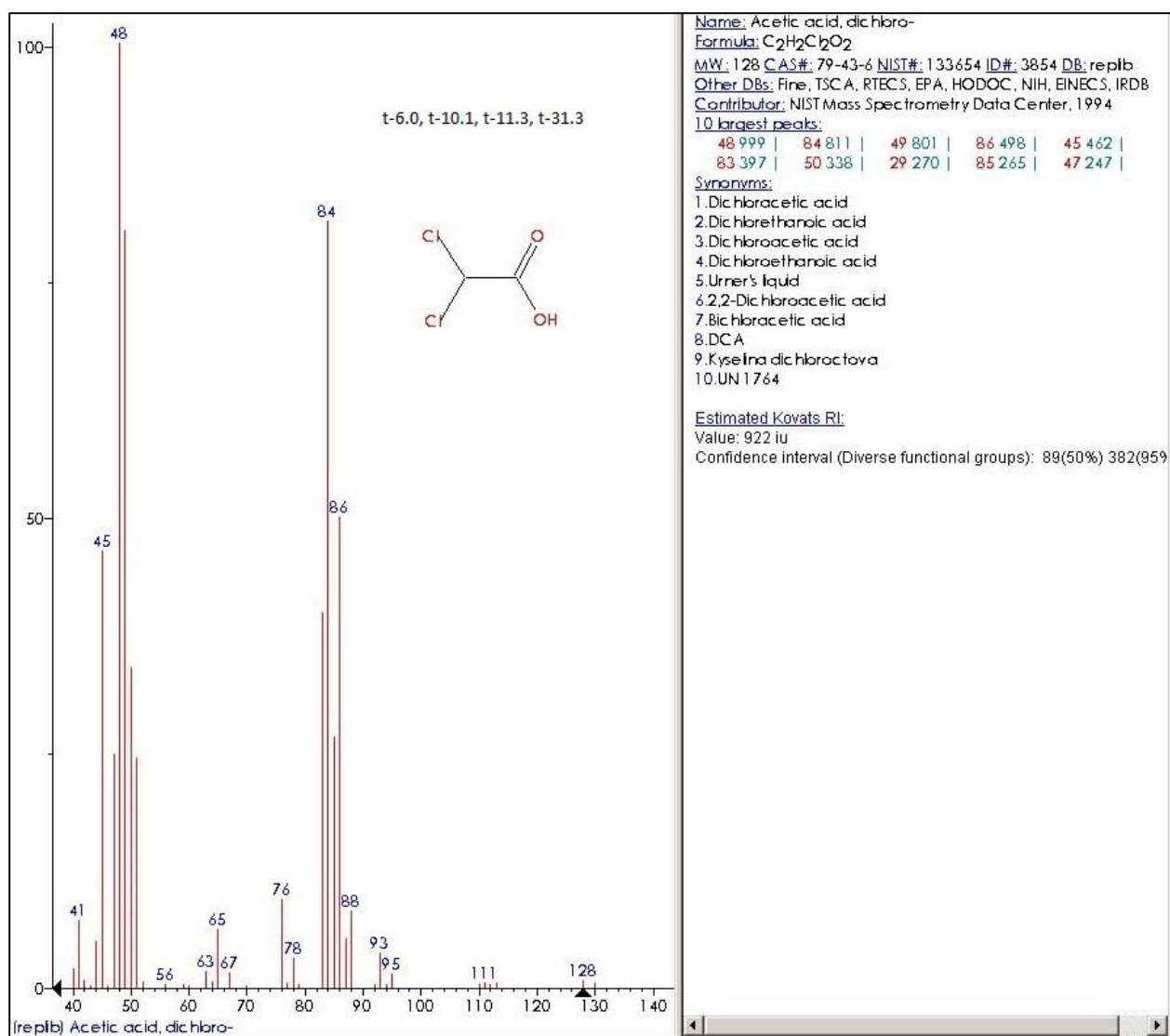


Figure C-36

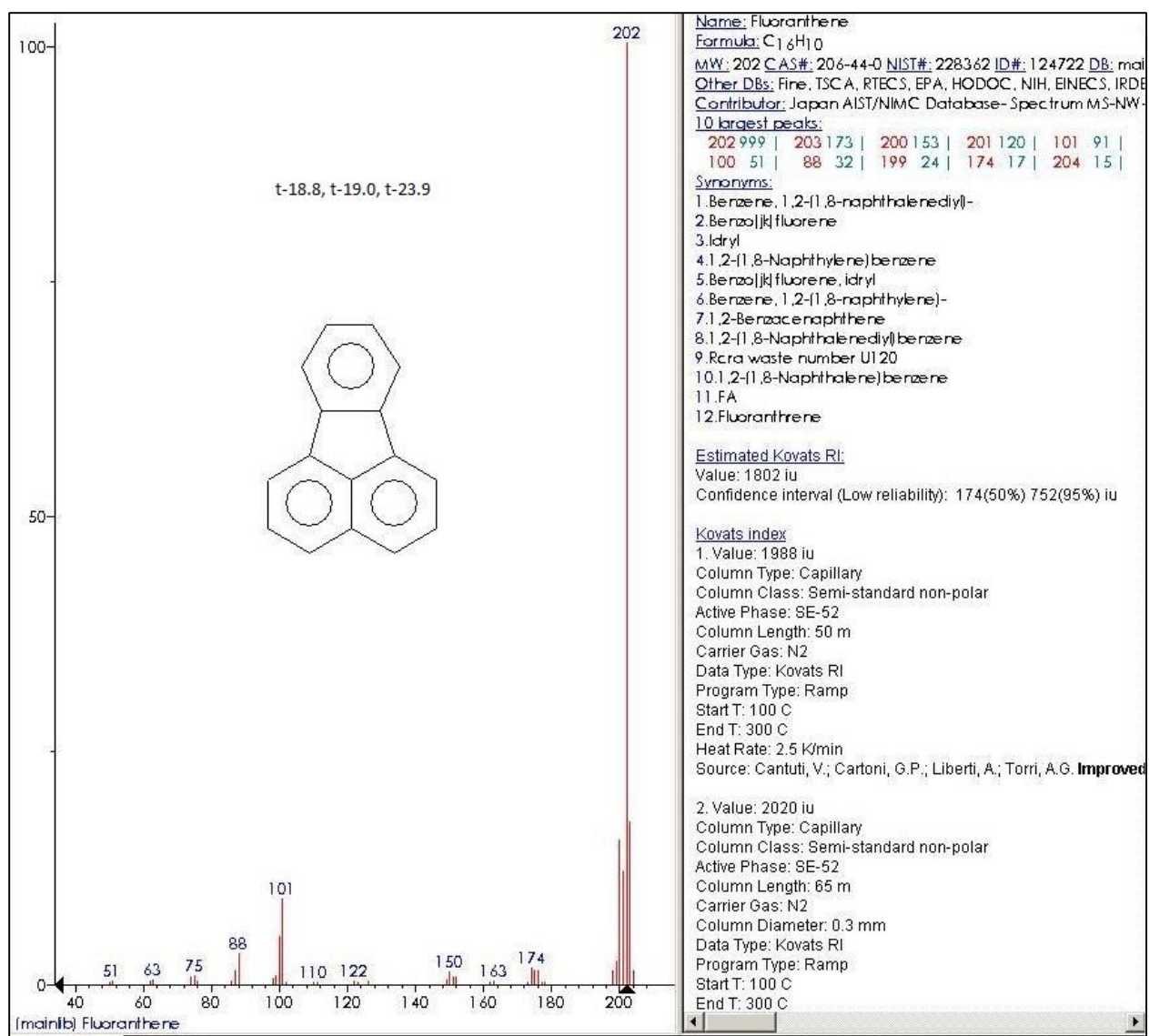


Figure C-37

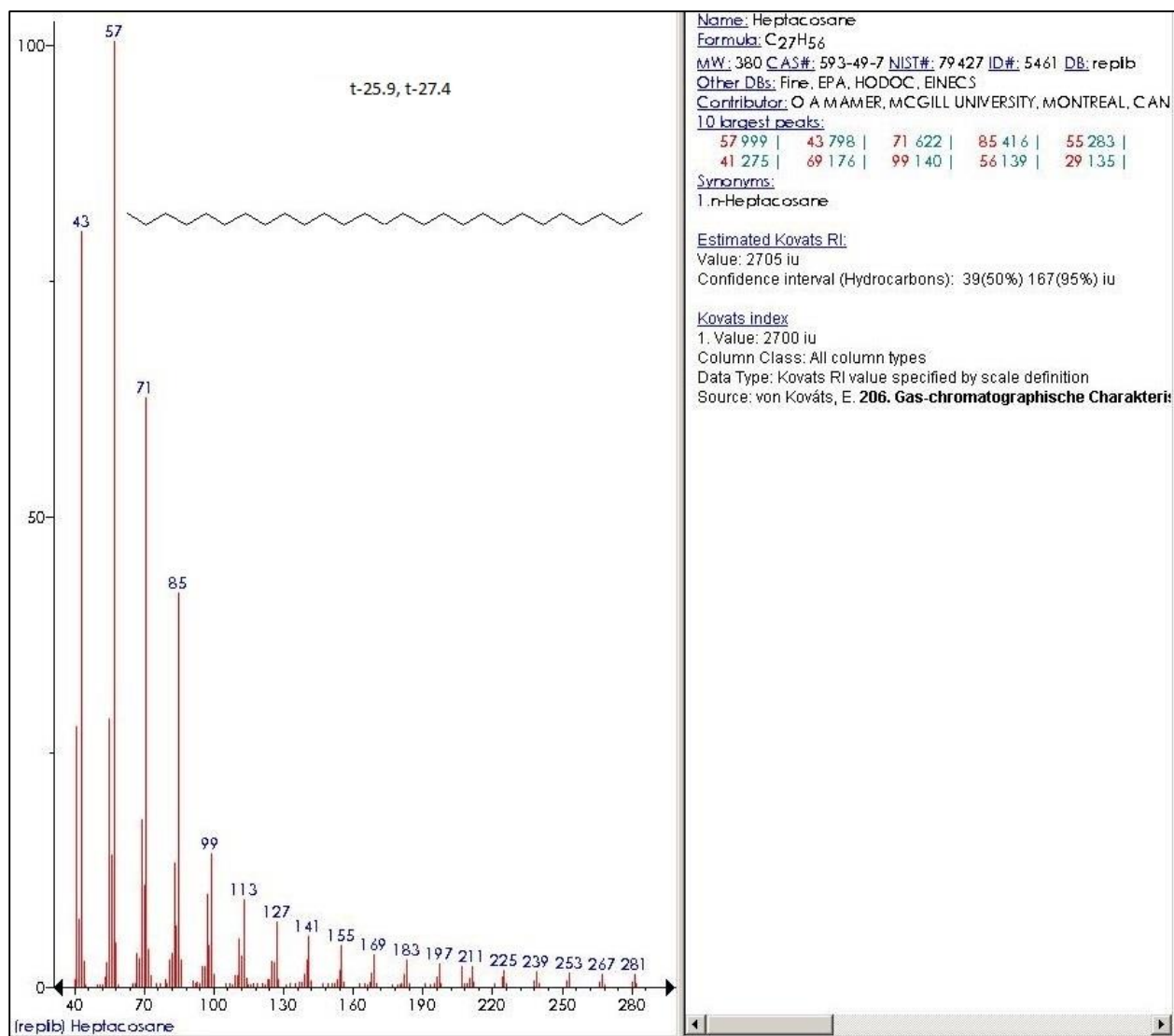


Figure C-38

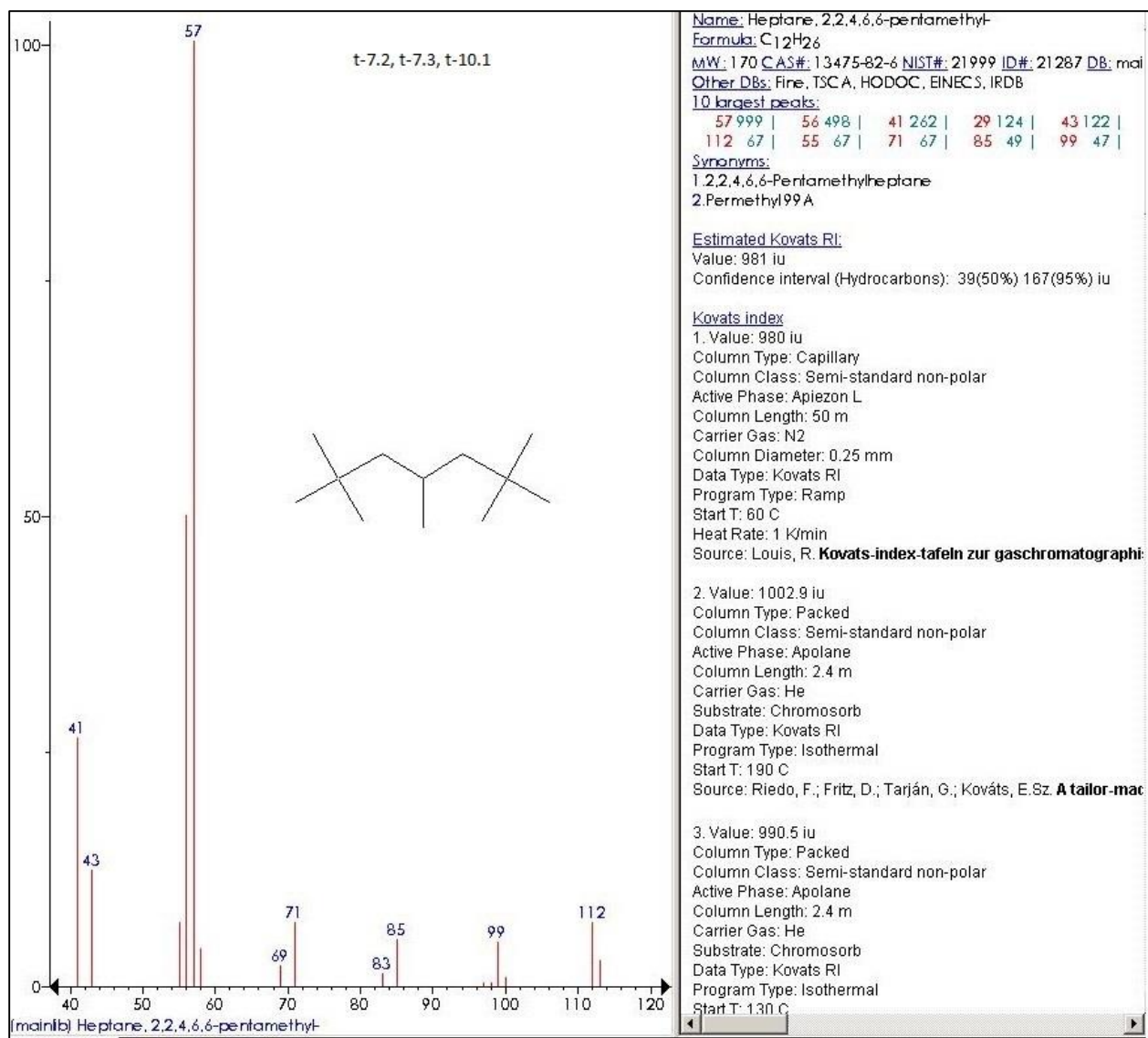


Figure C-39

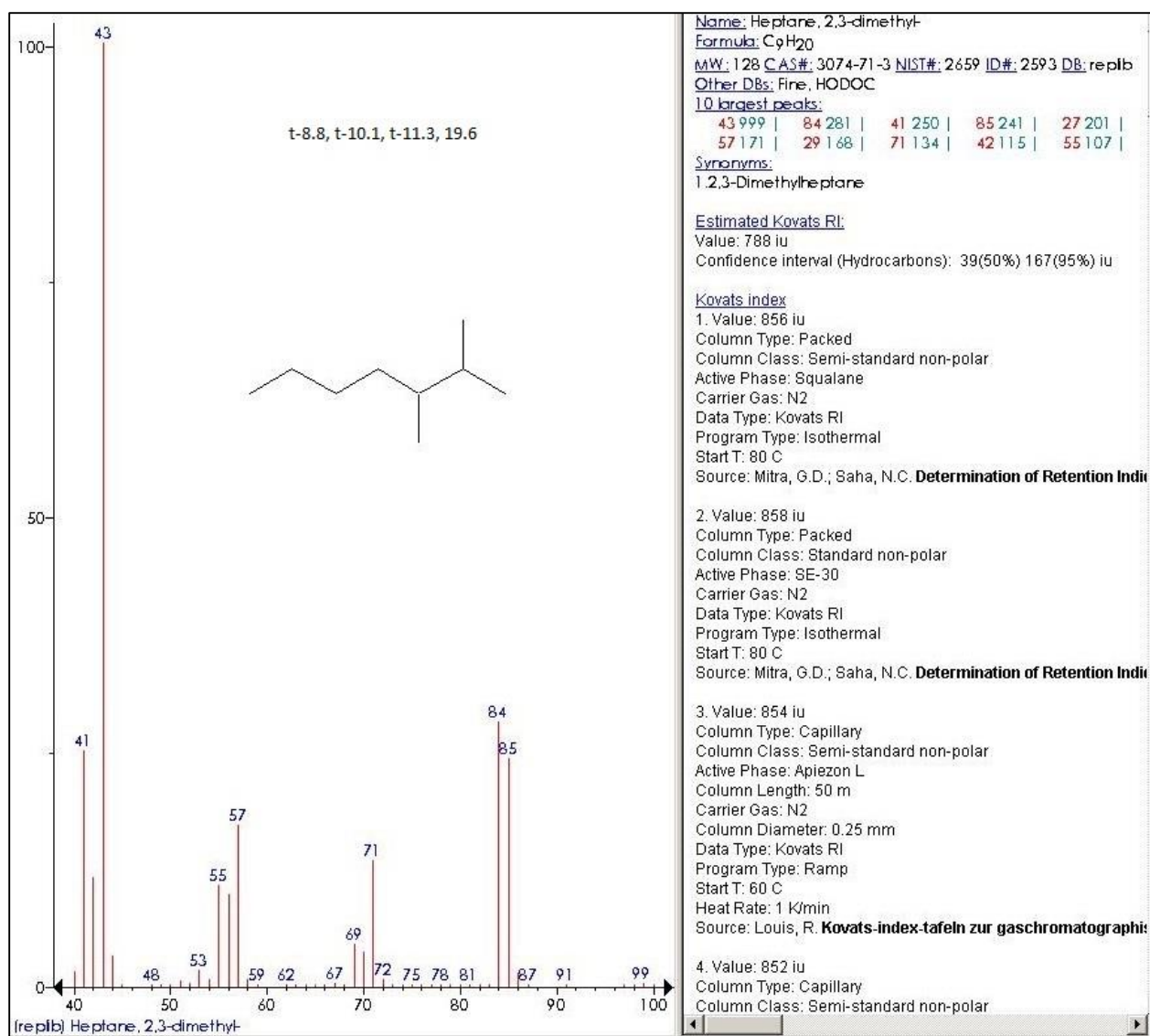


Figure C-40

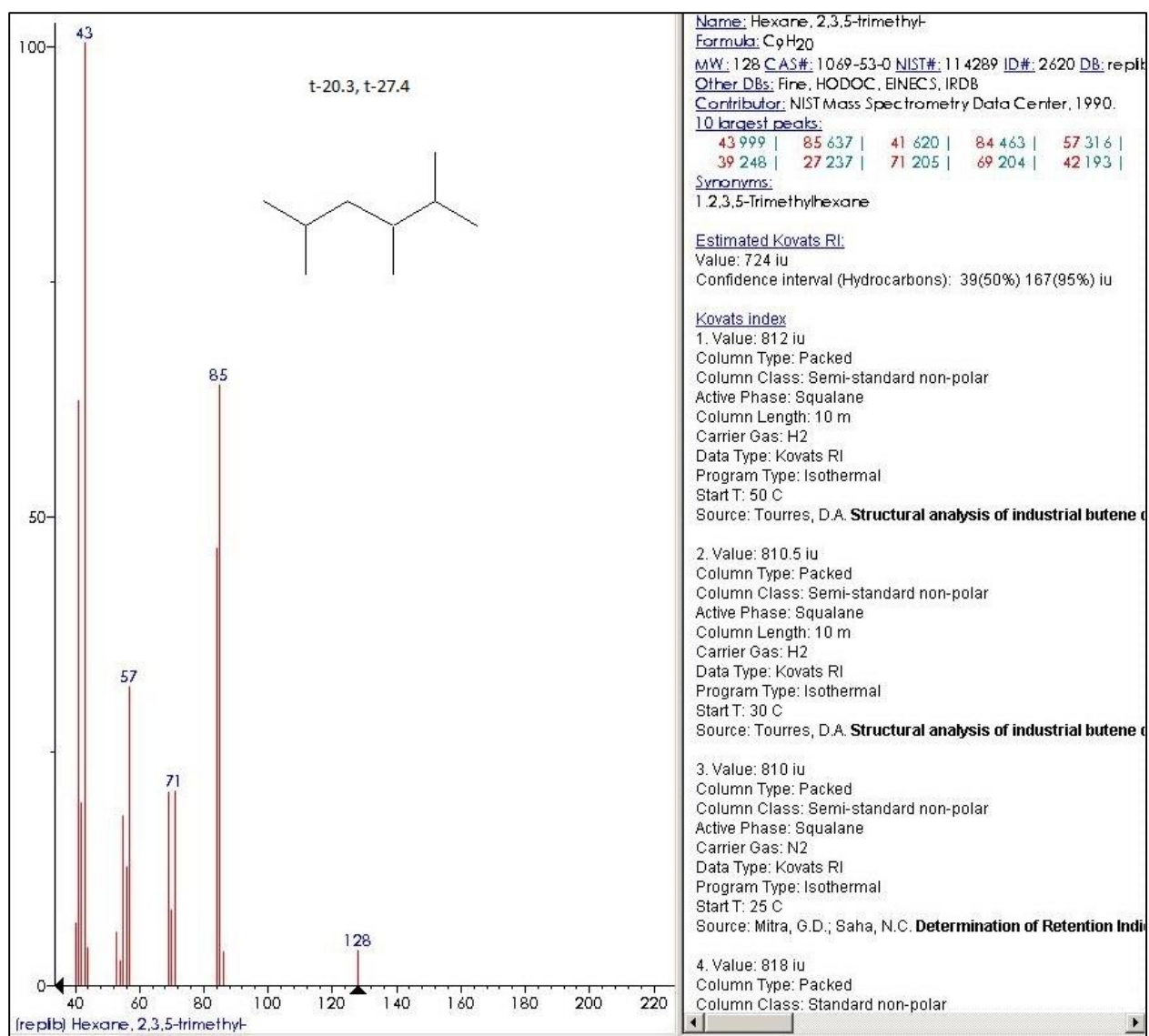


Figure C-41

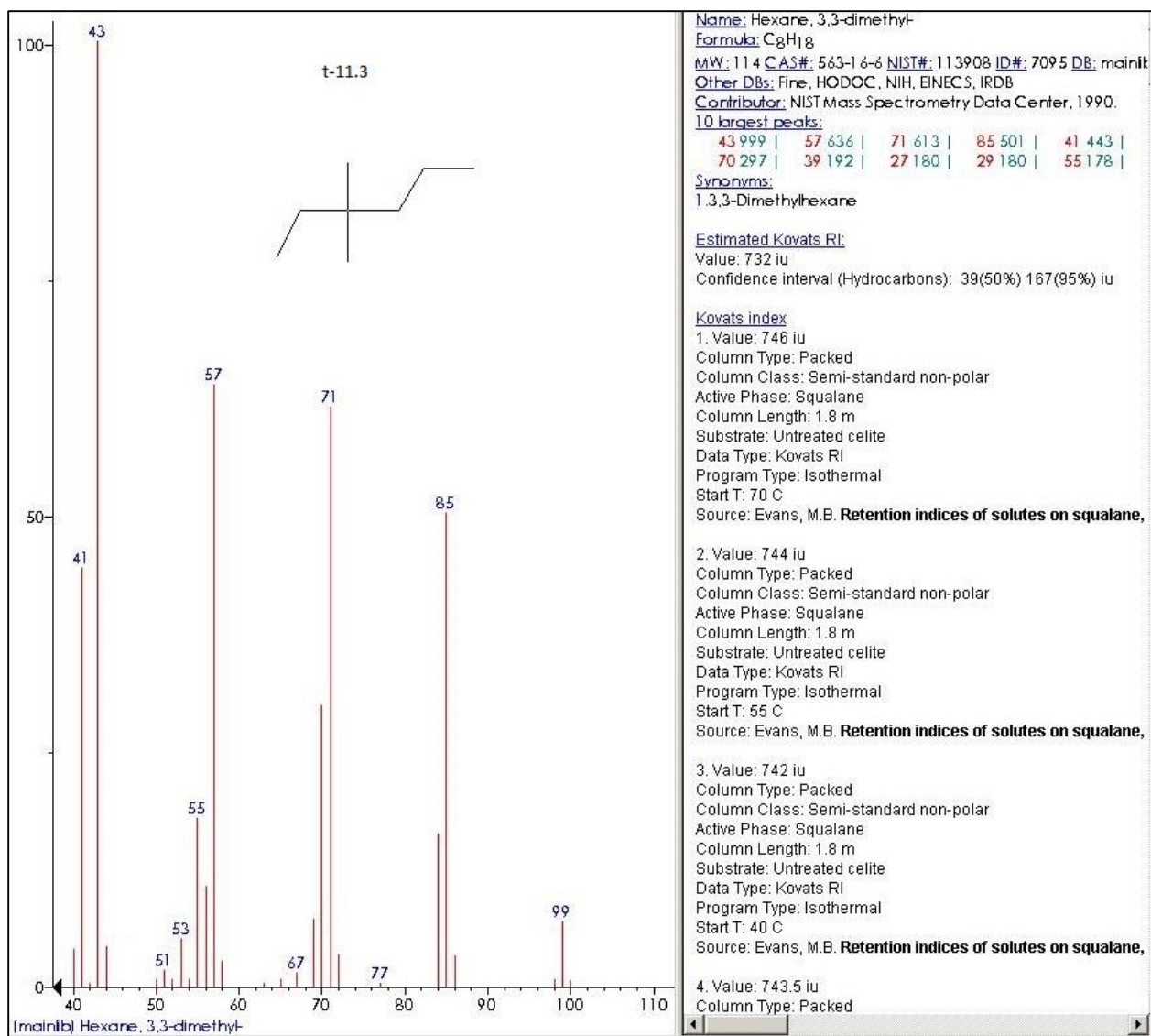


Figure C-42

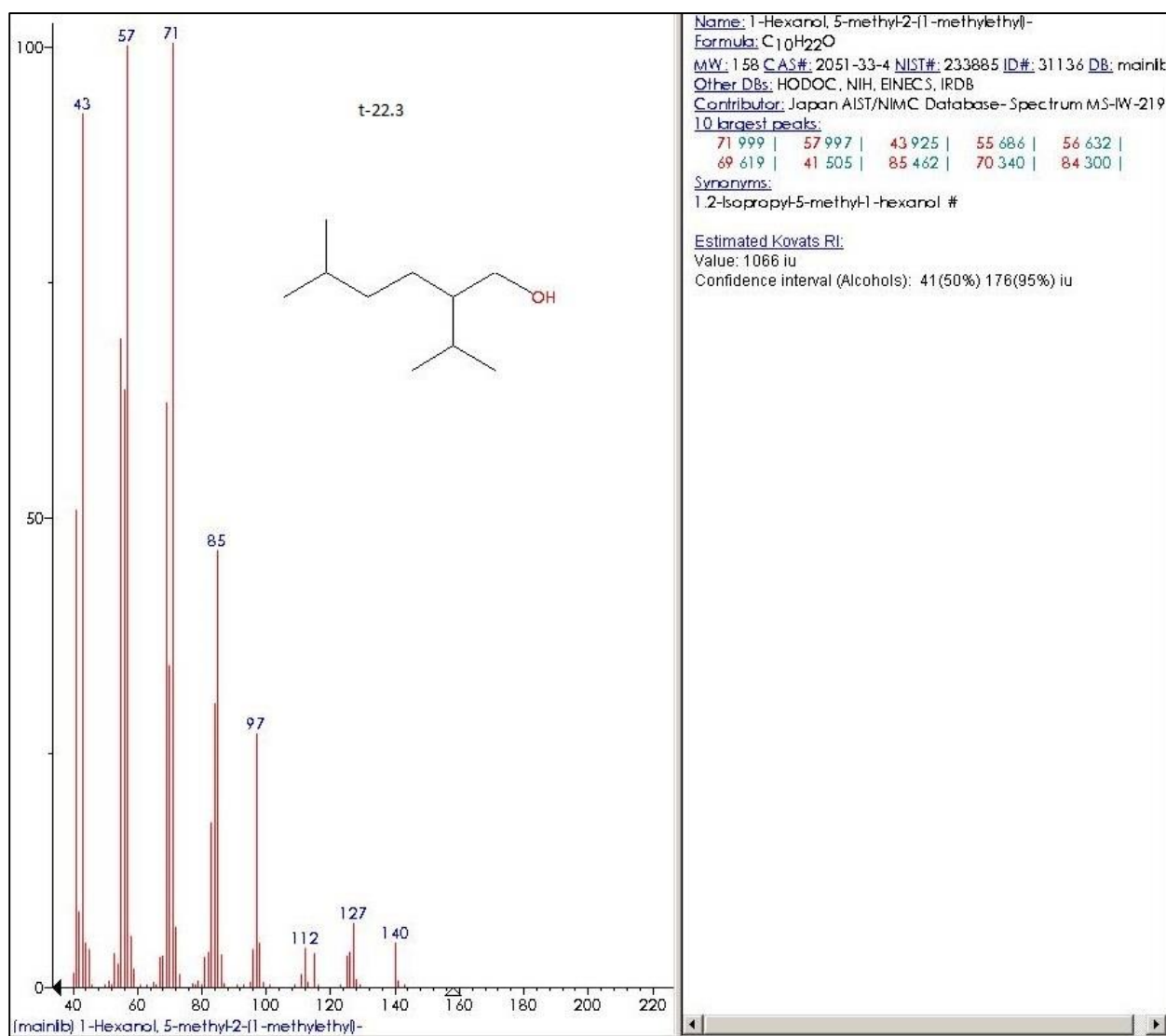


Figure C-43

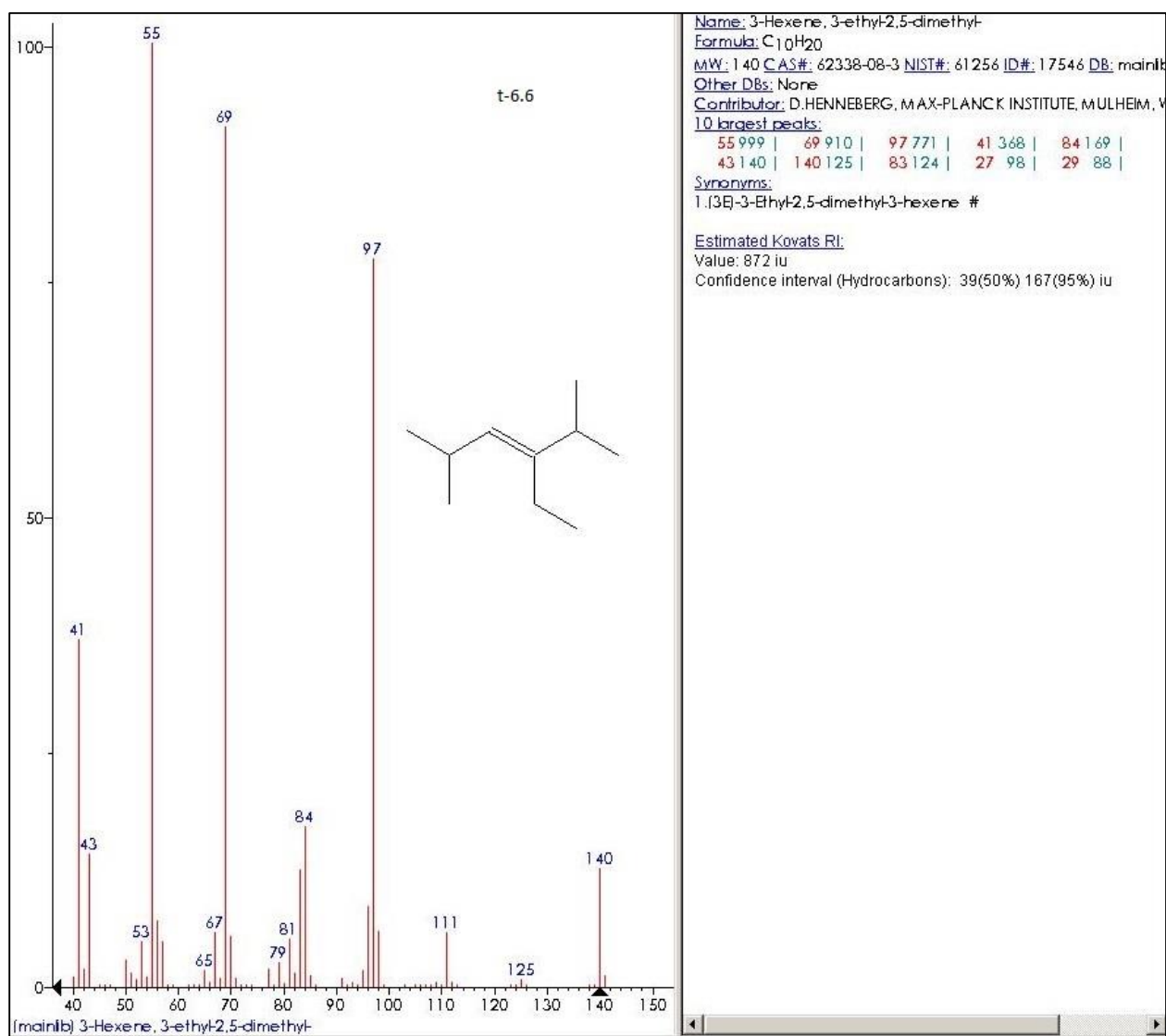


Figure C-44

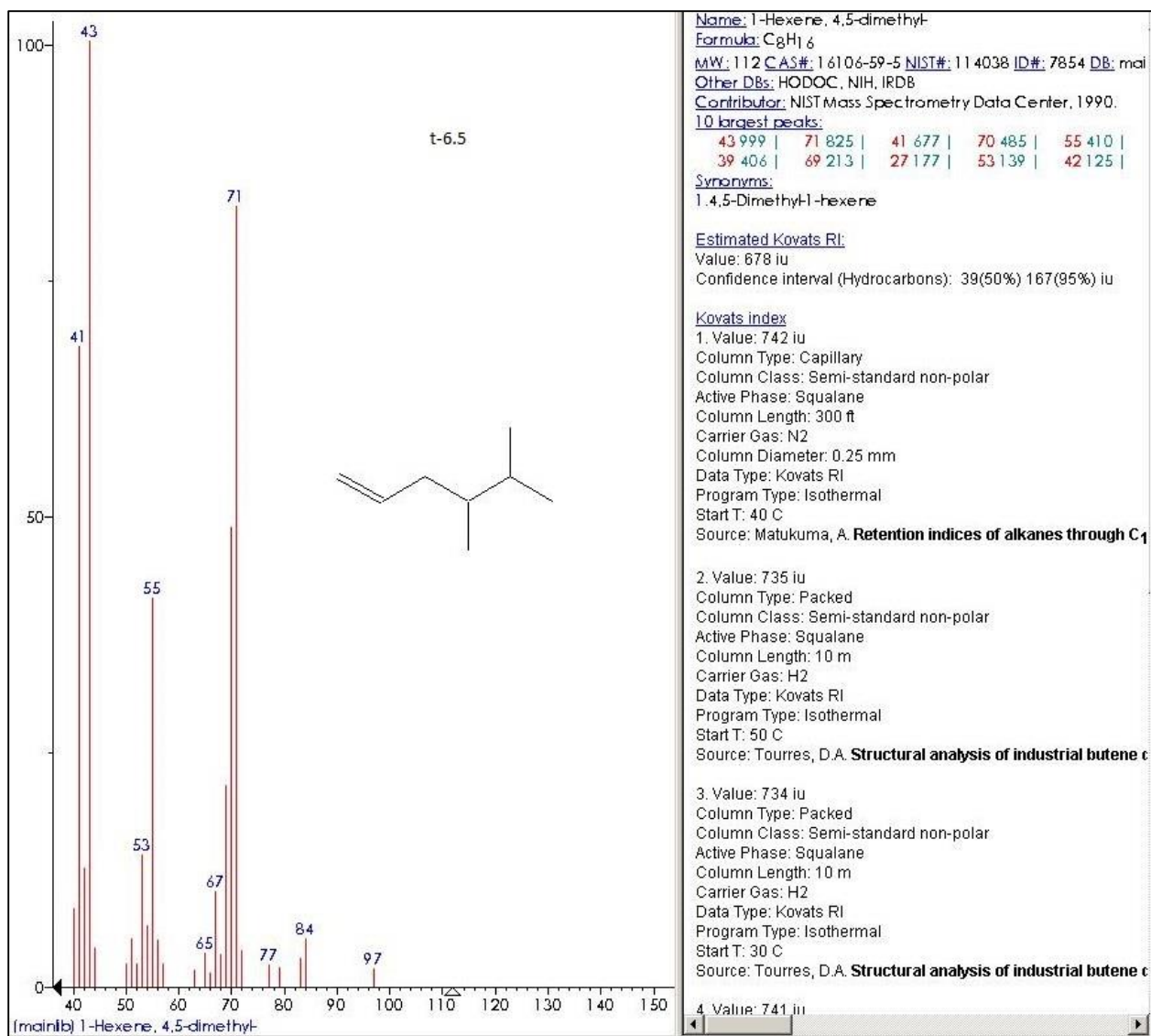


Figure C-45

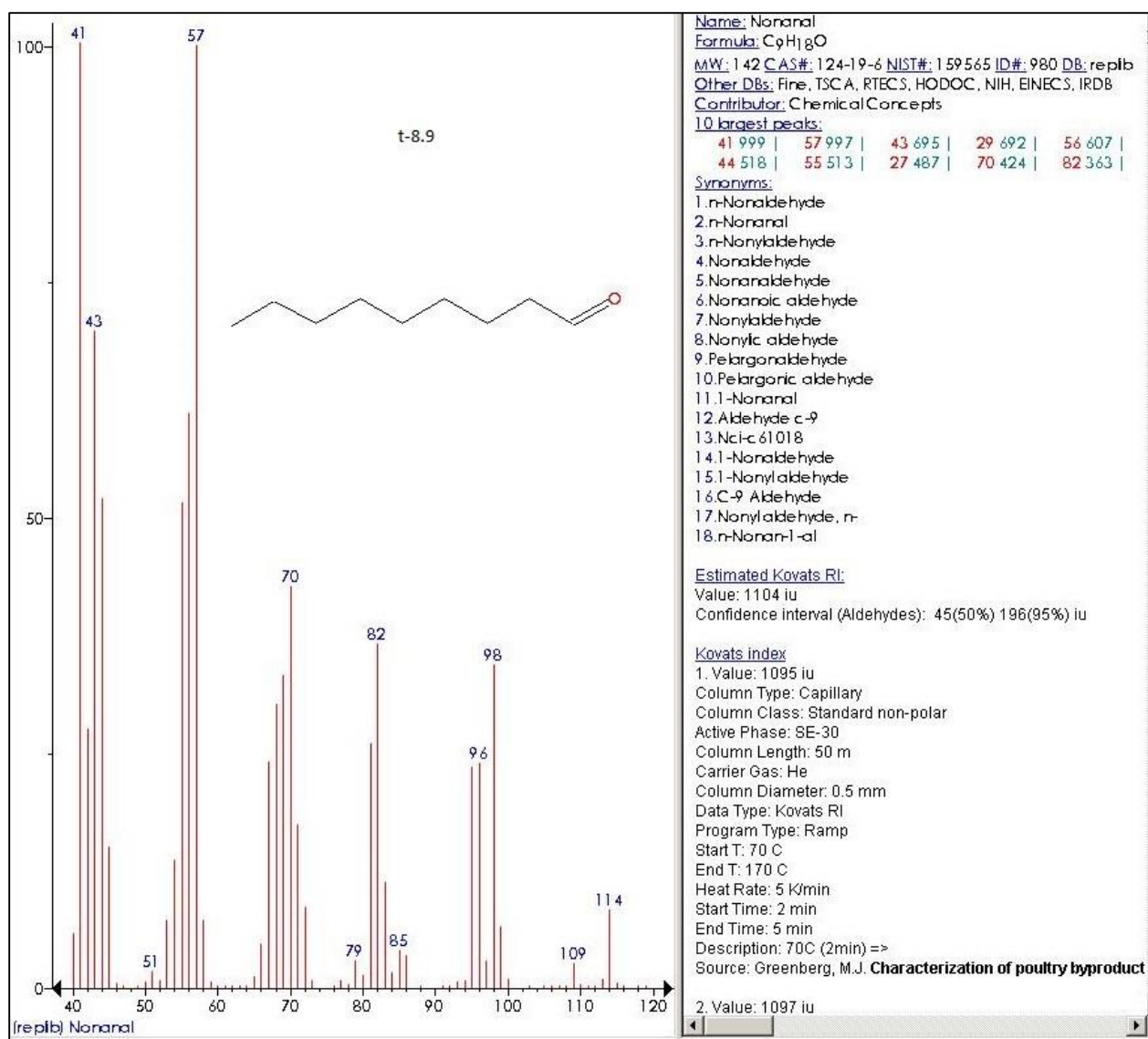


Figure C-46

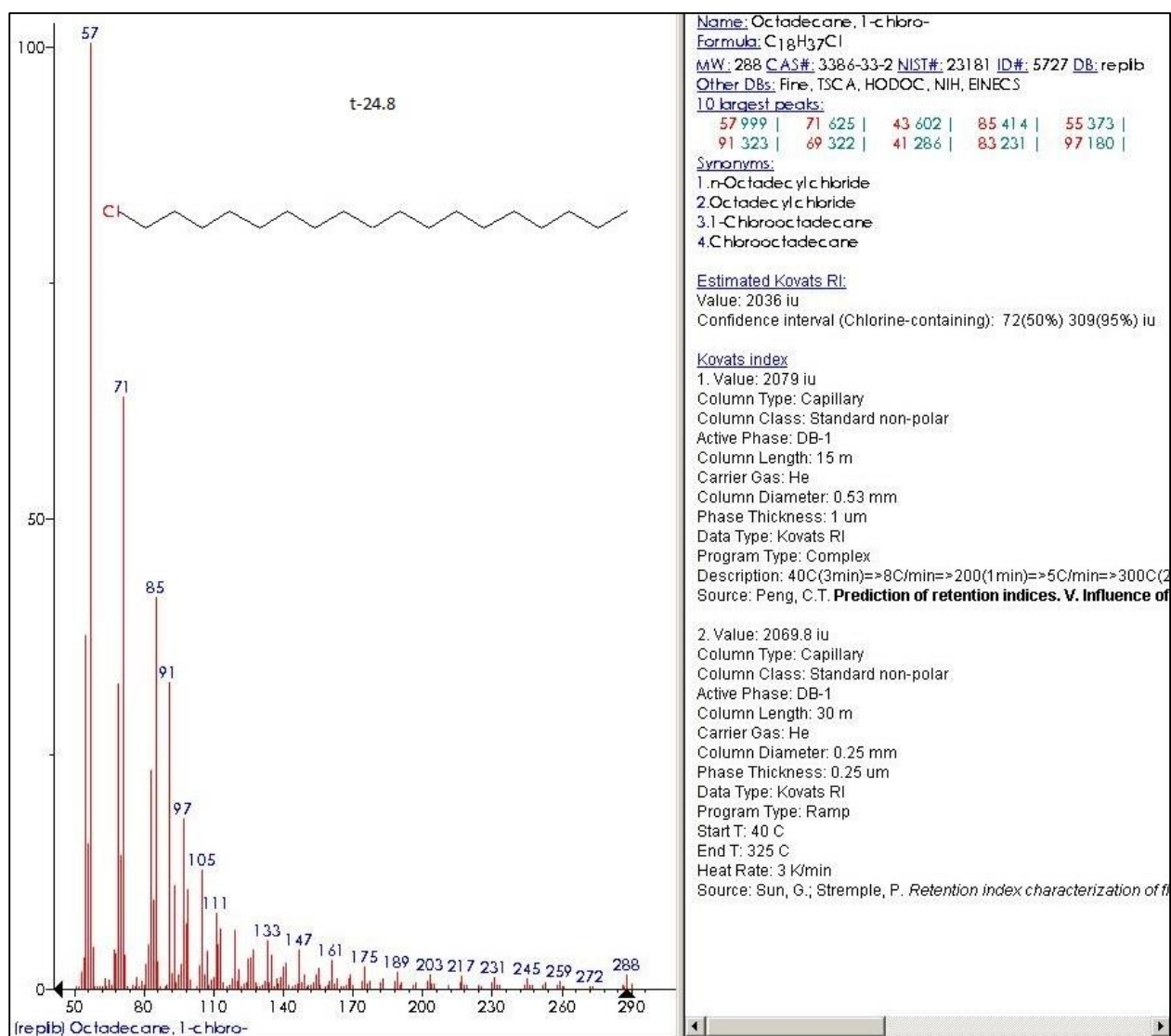


Figure C-47

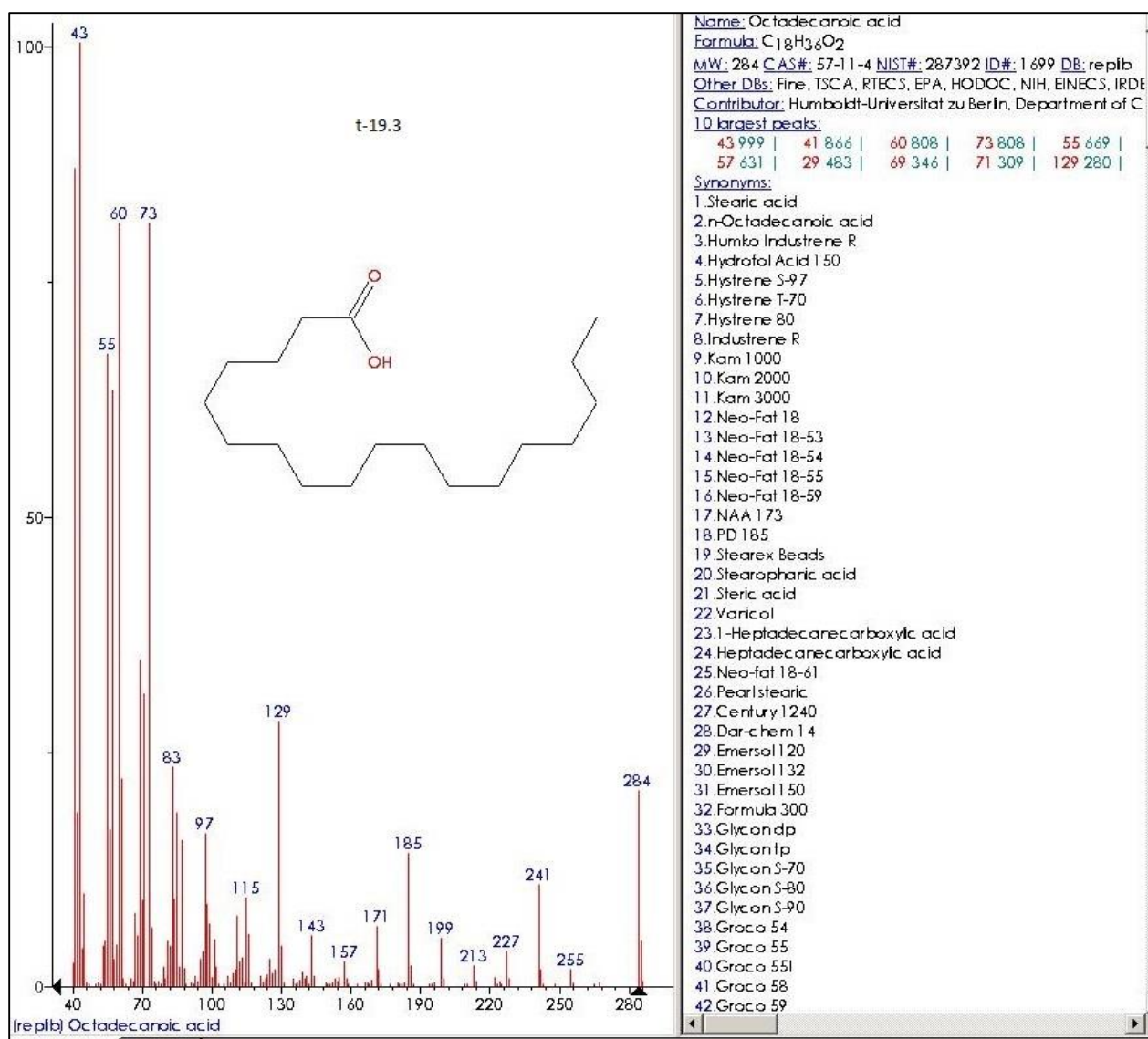


Figure C-48

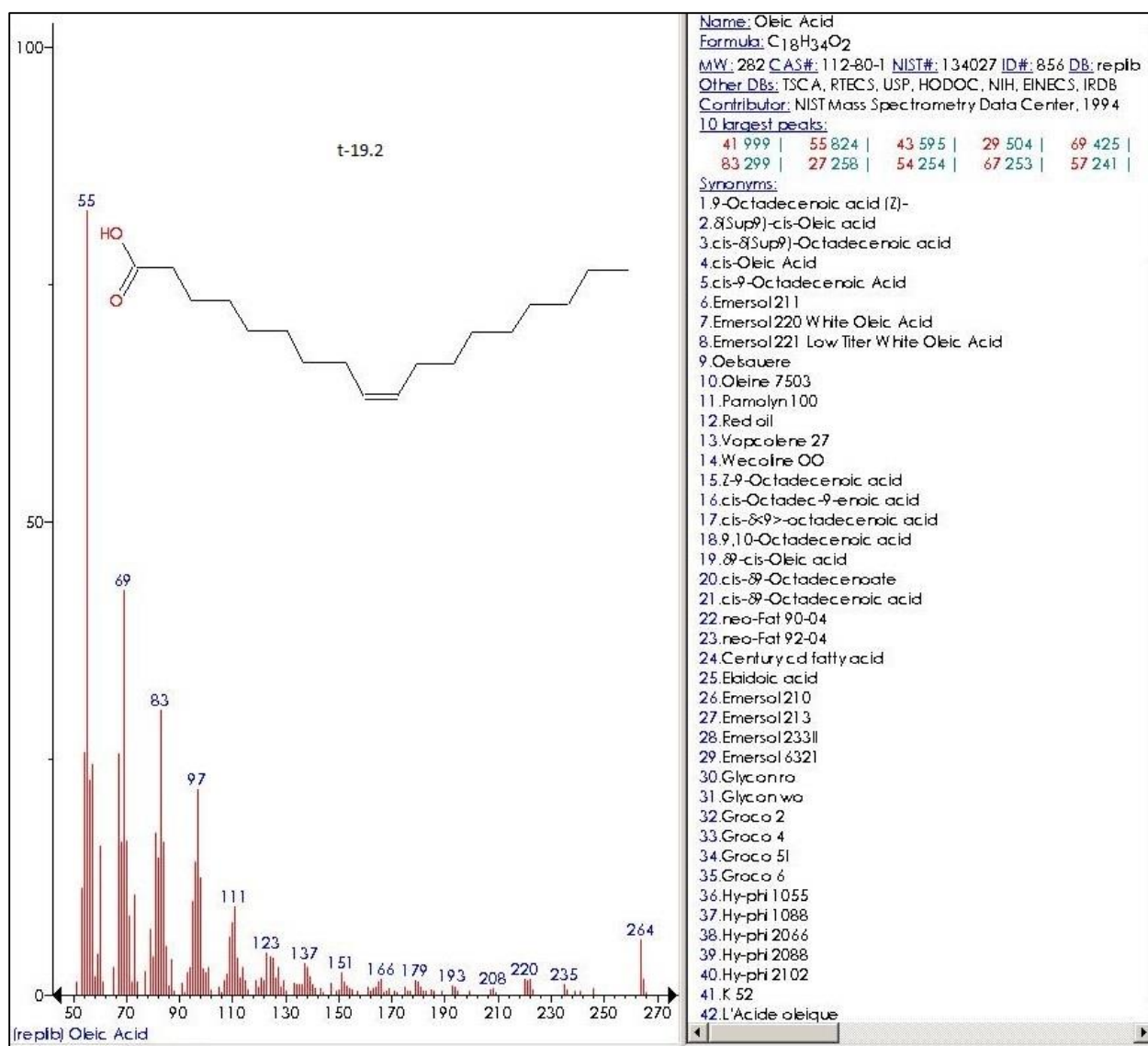


Figure C-49

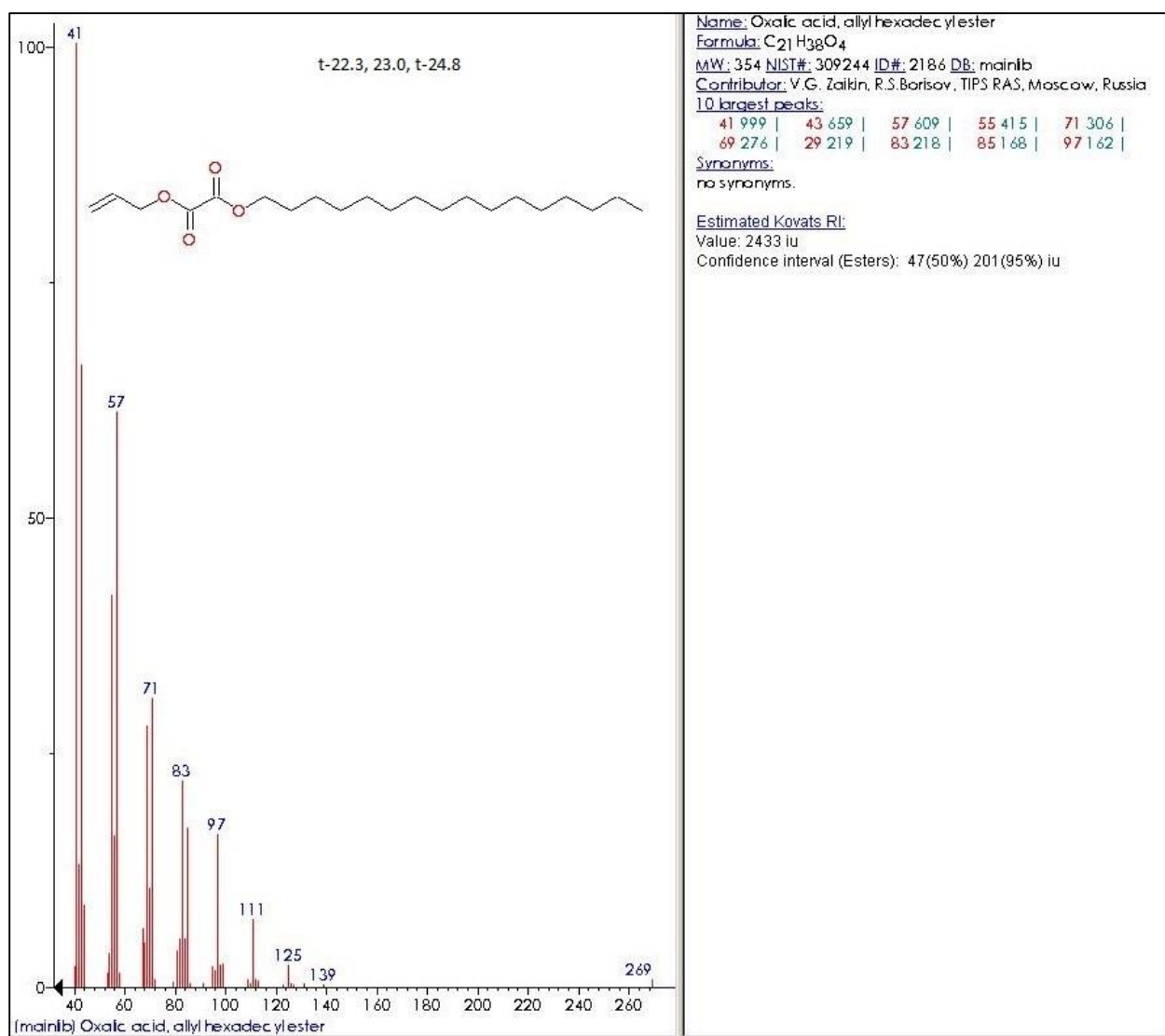


Figure C-50

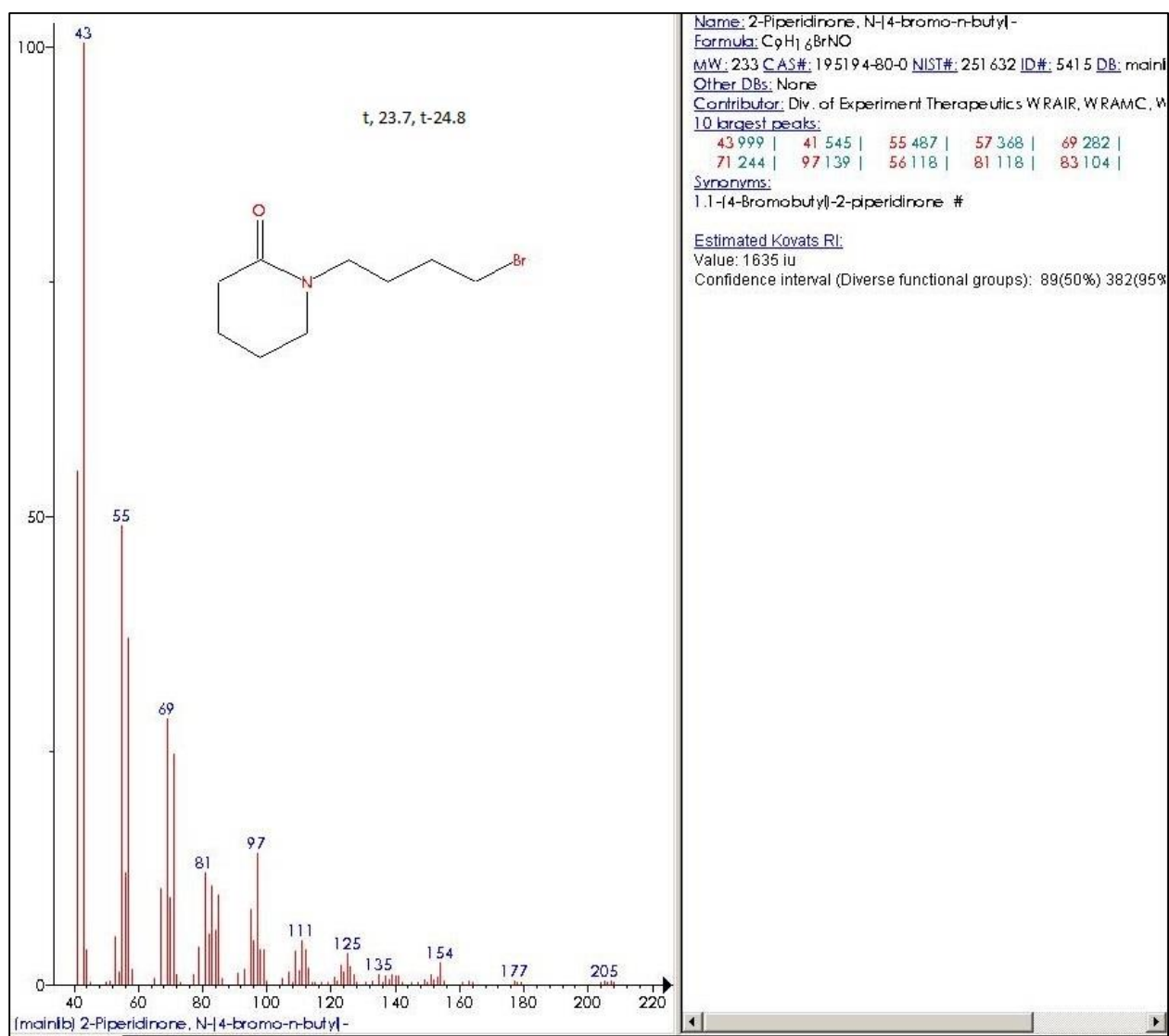


Figure C-51

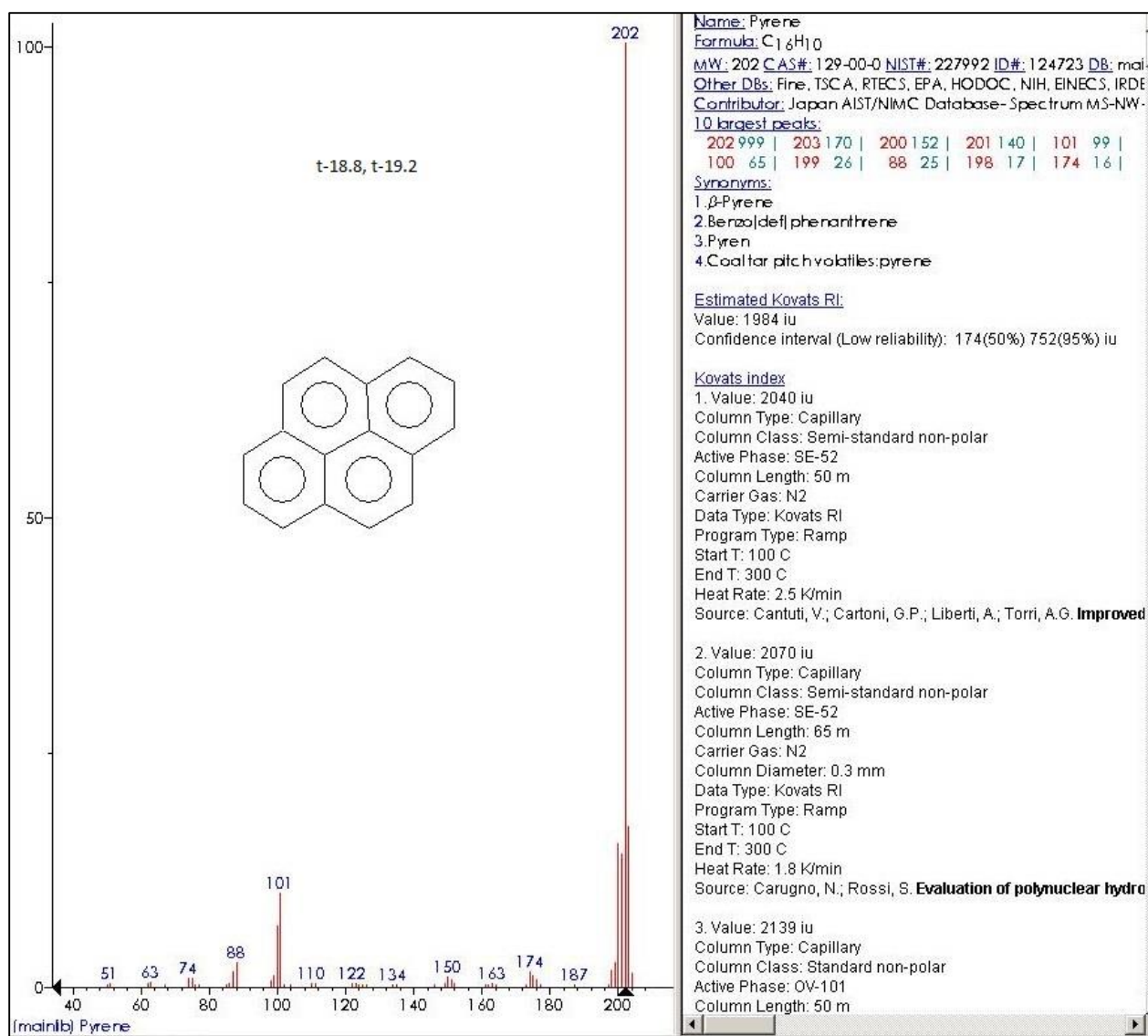


Figure C-52

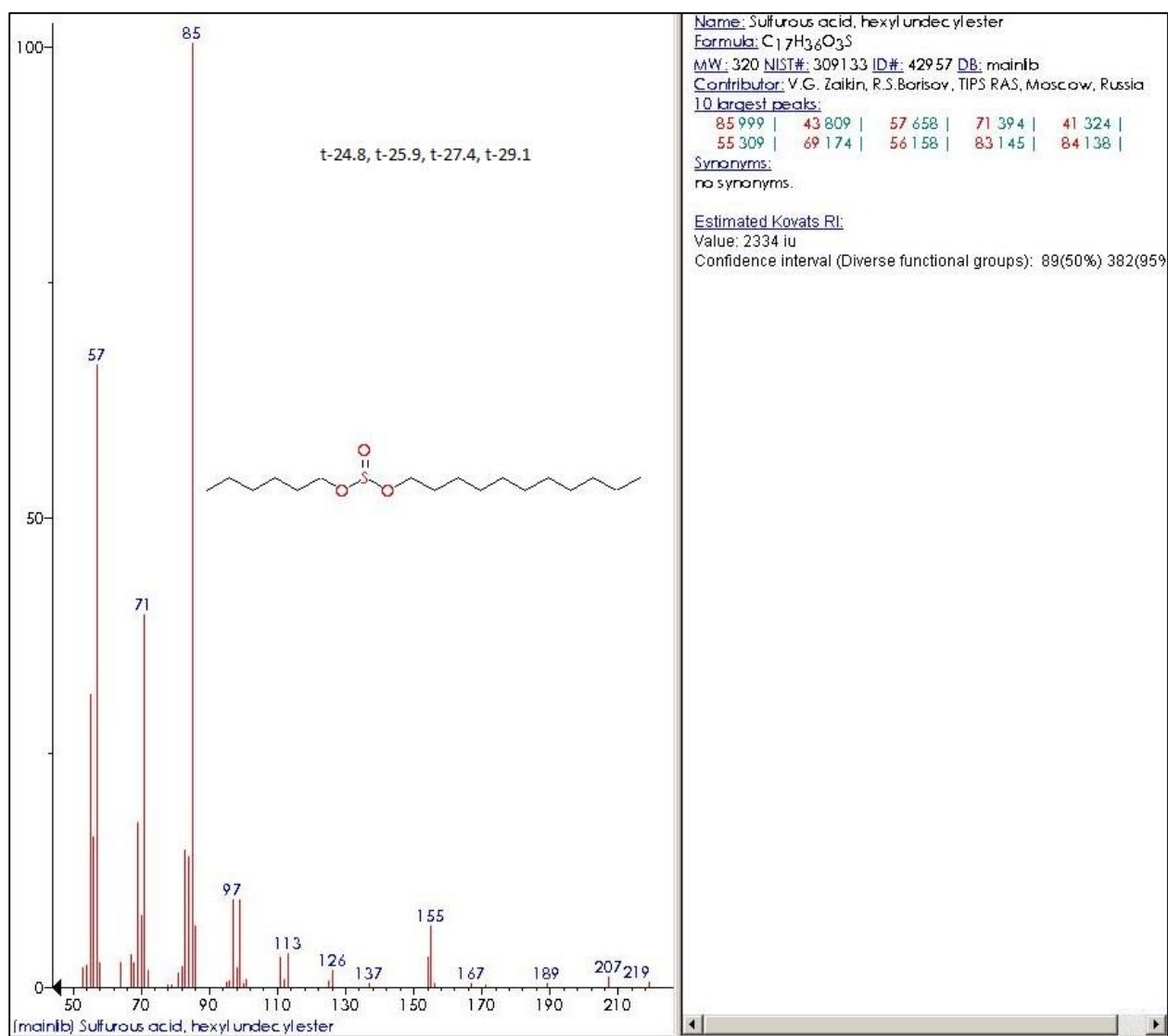


Figure C-53

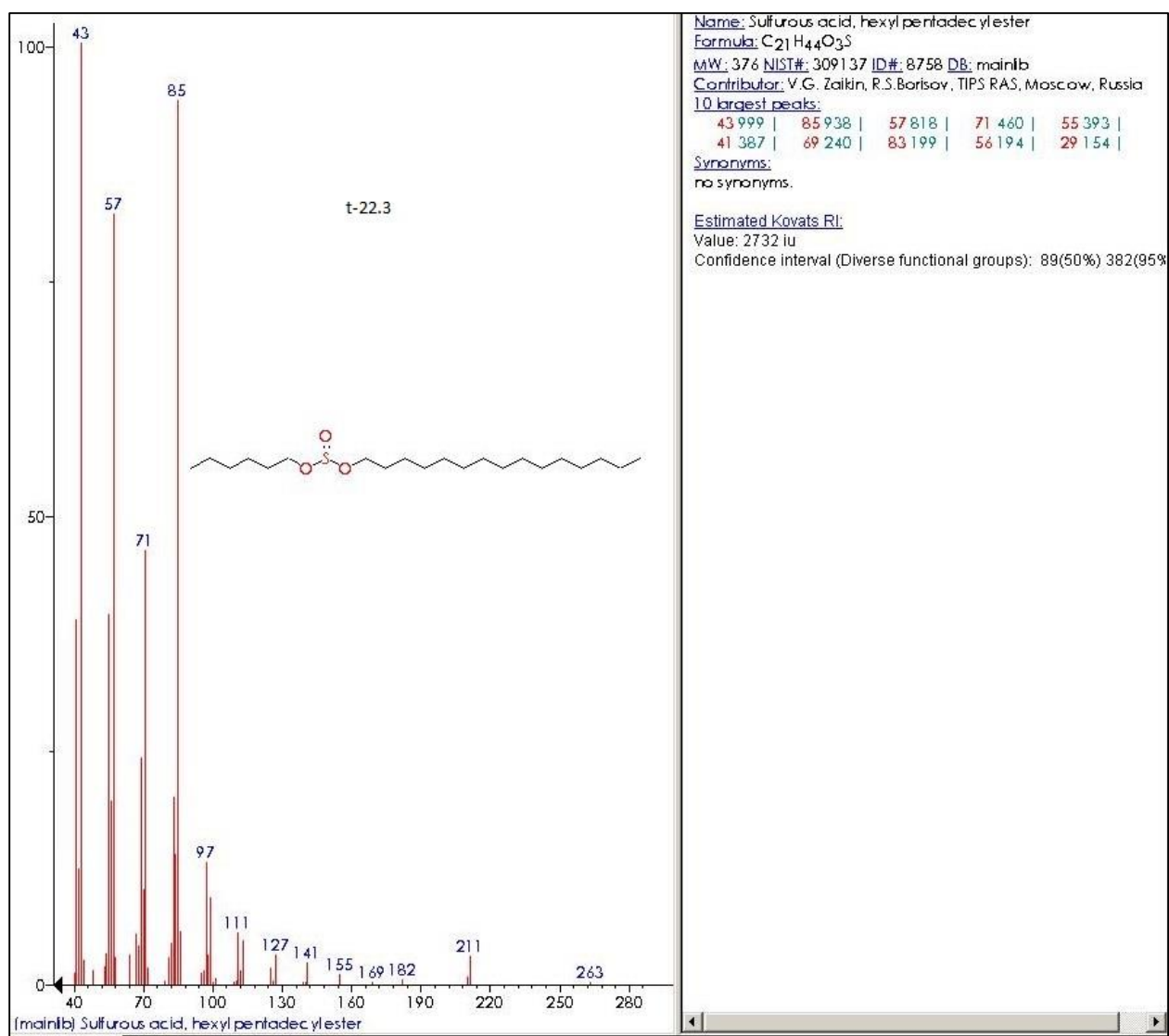


Figure C-54

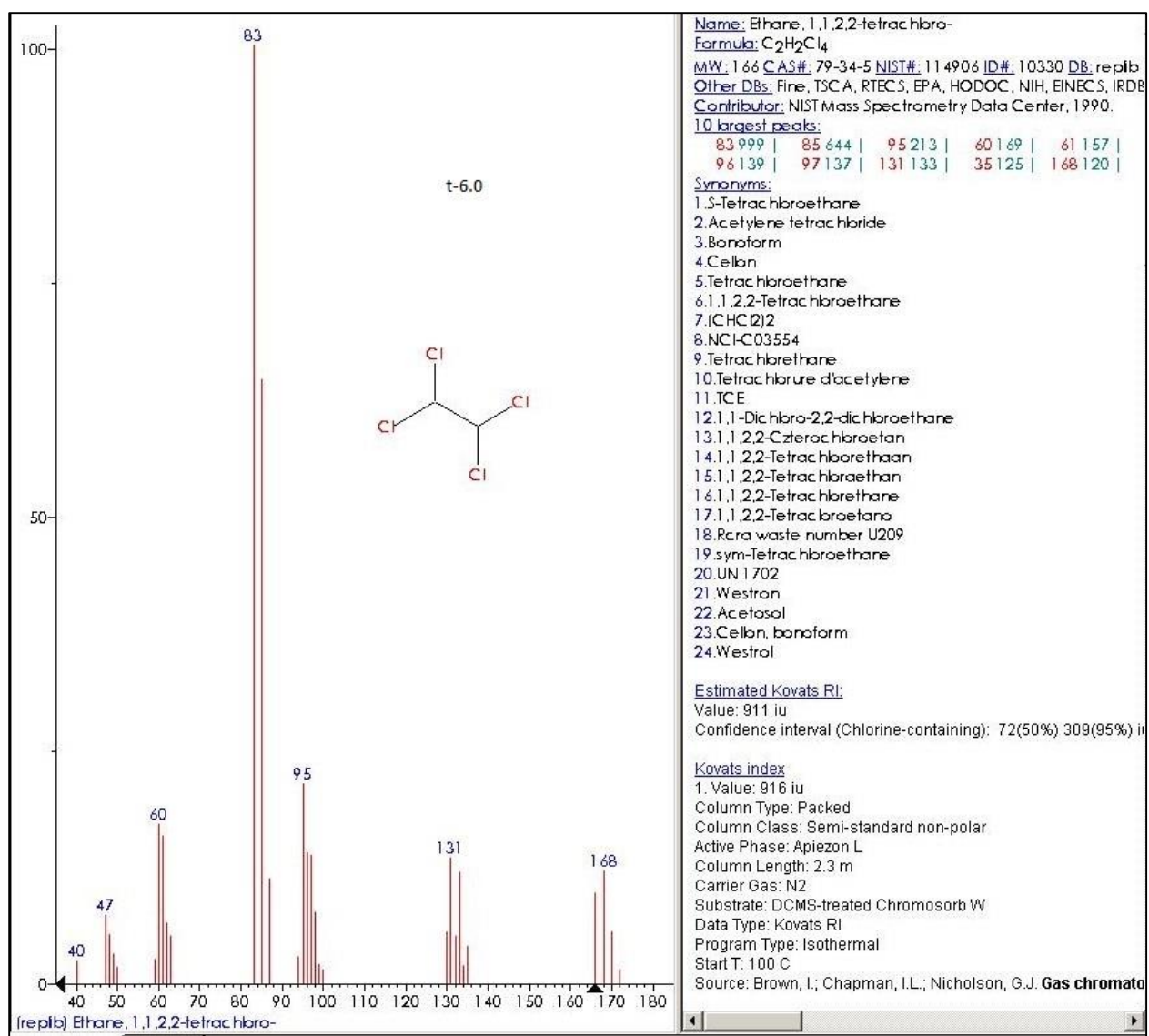


Figure C-55

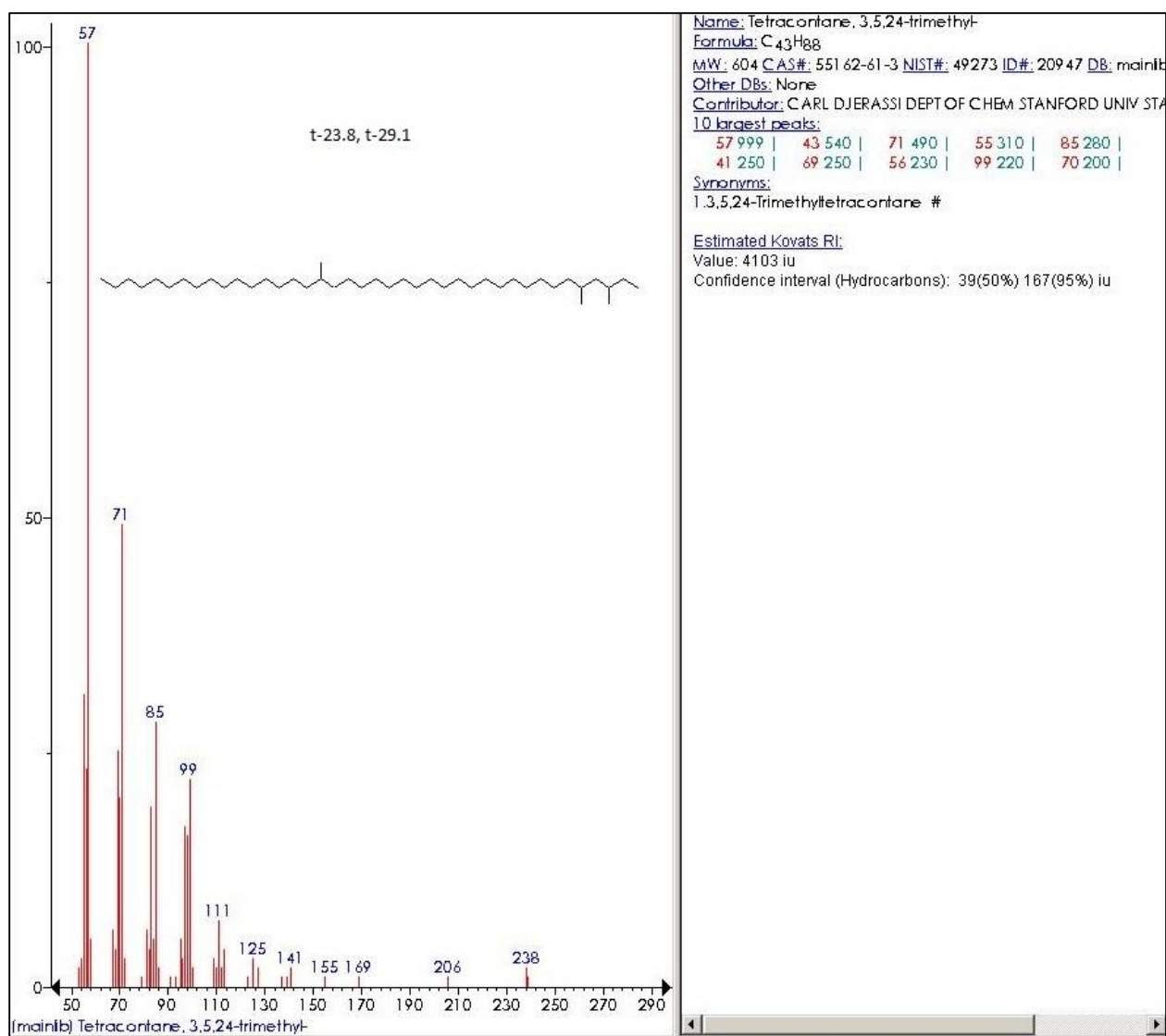


Figure C-56

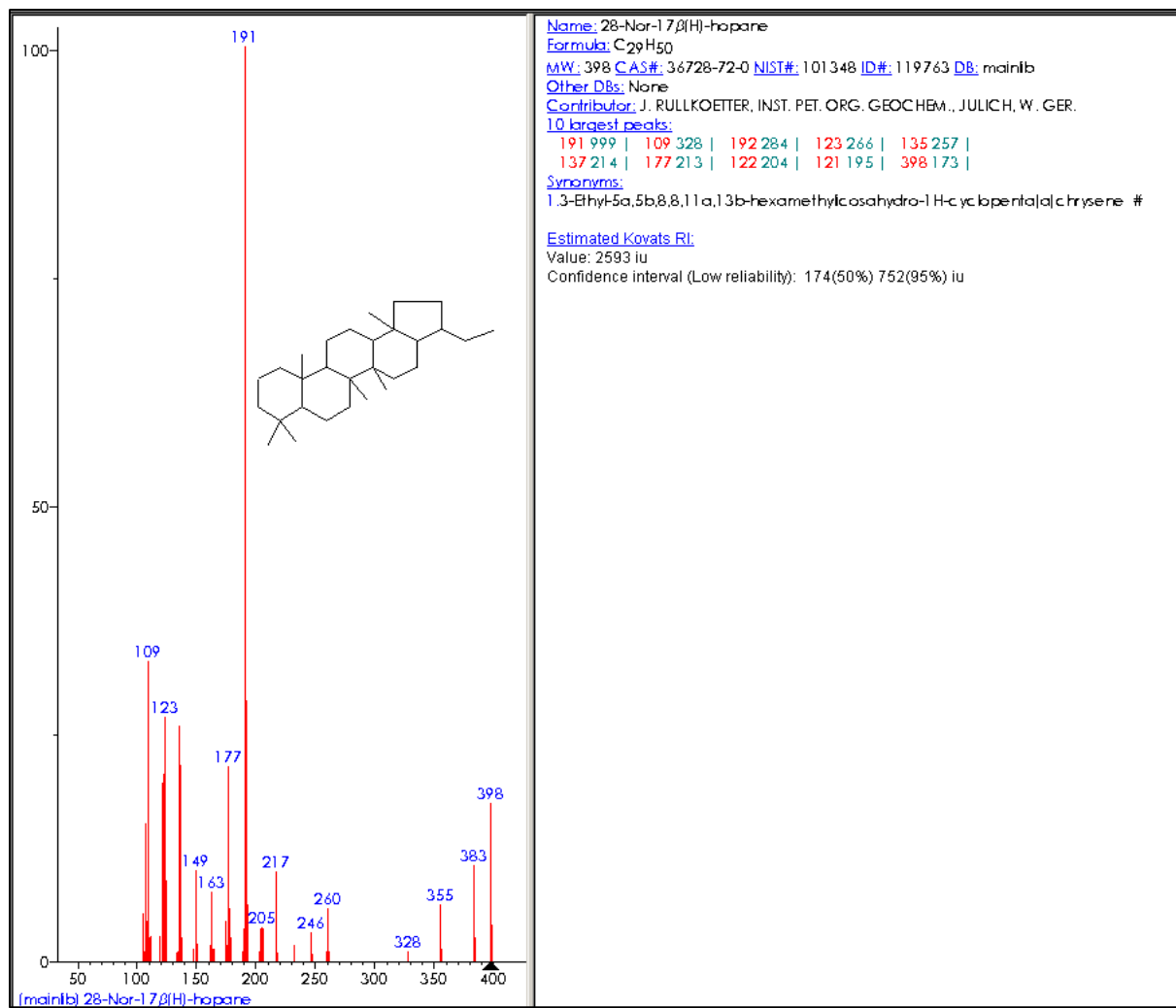
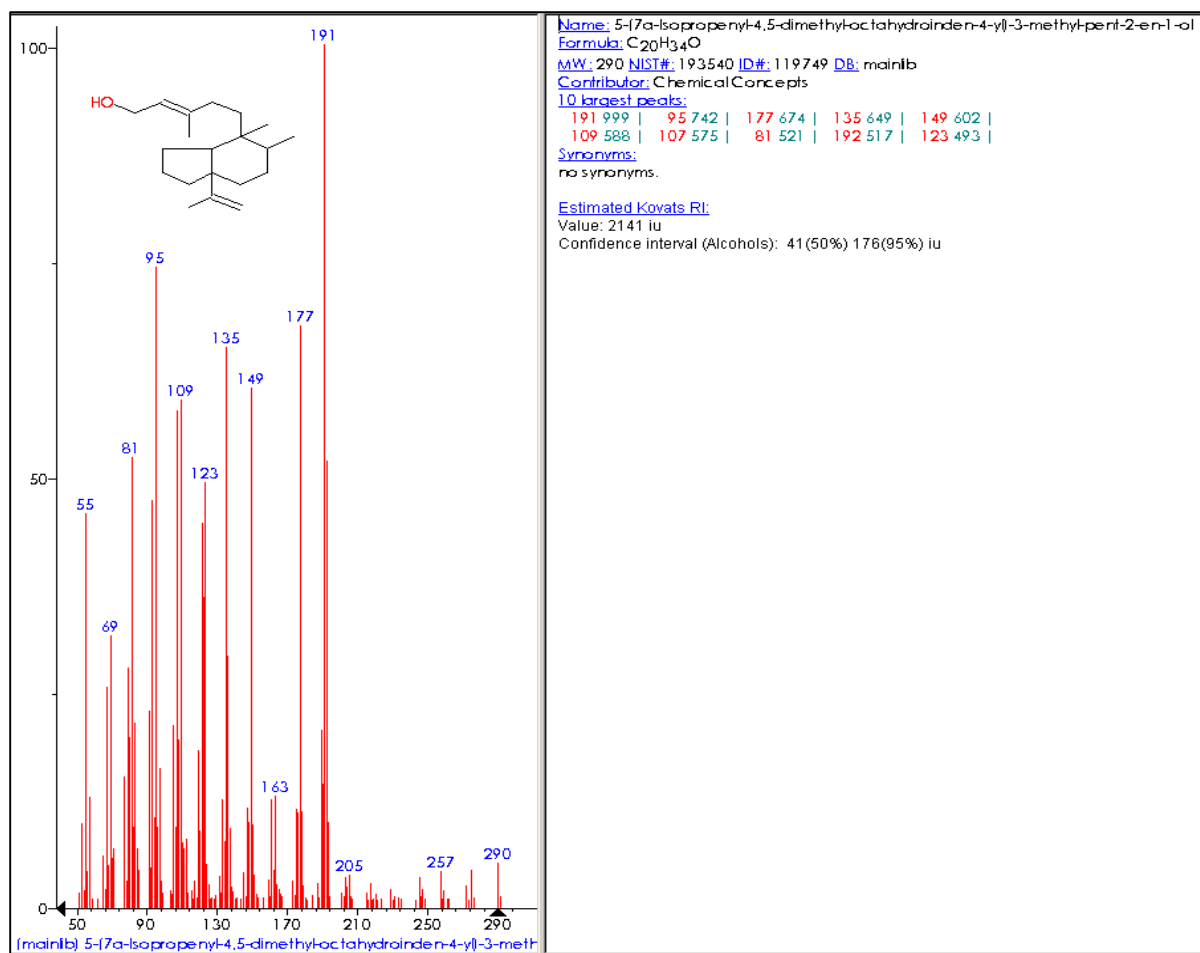


Figure C-57



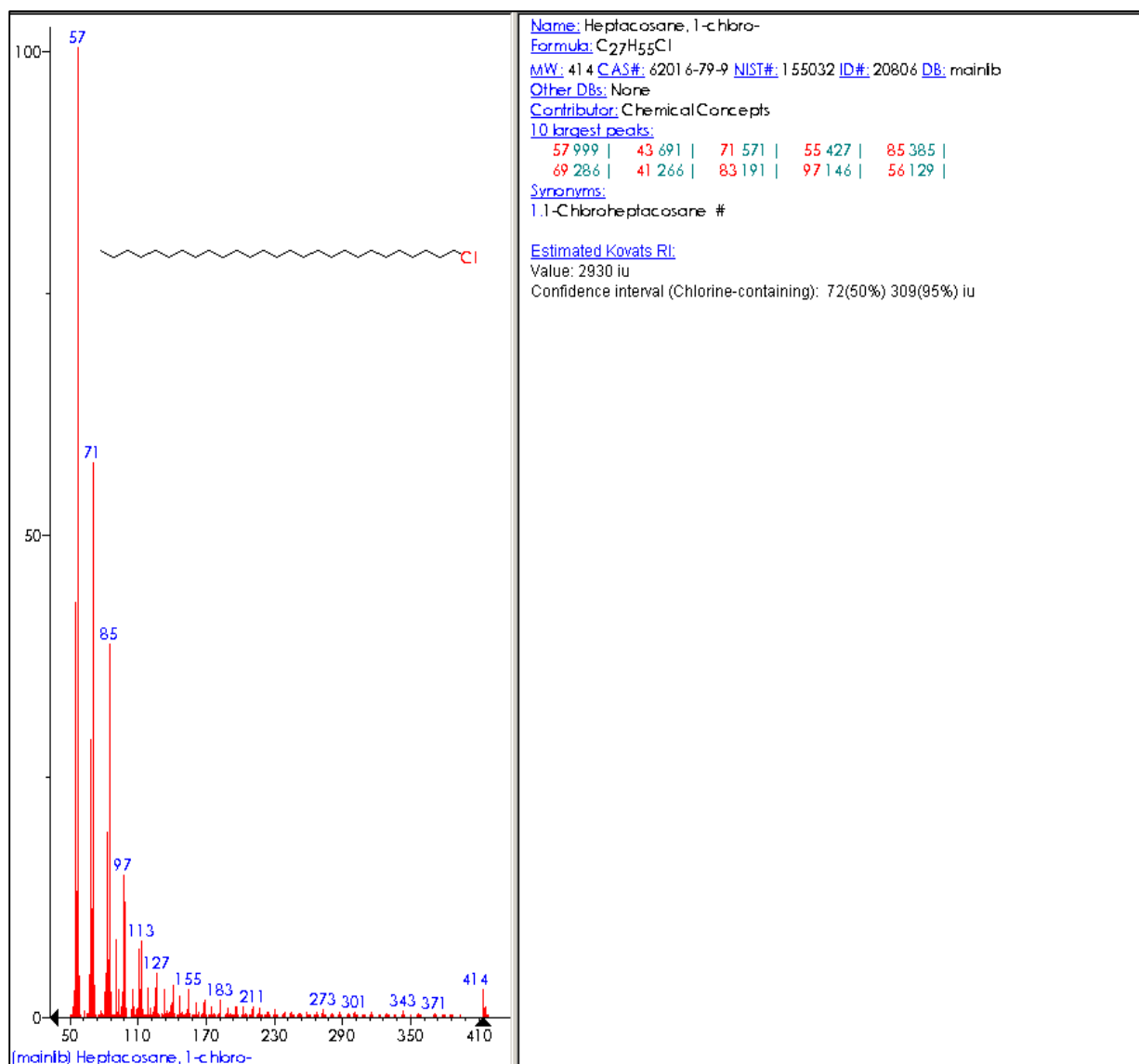


Figure C-59

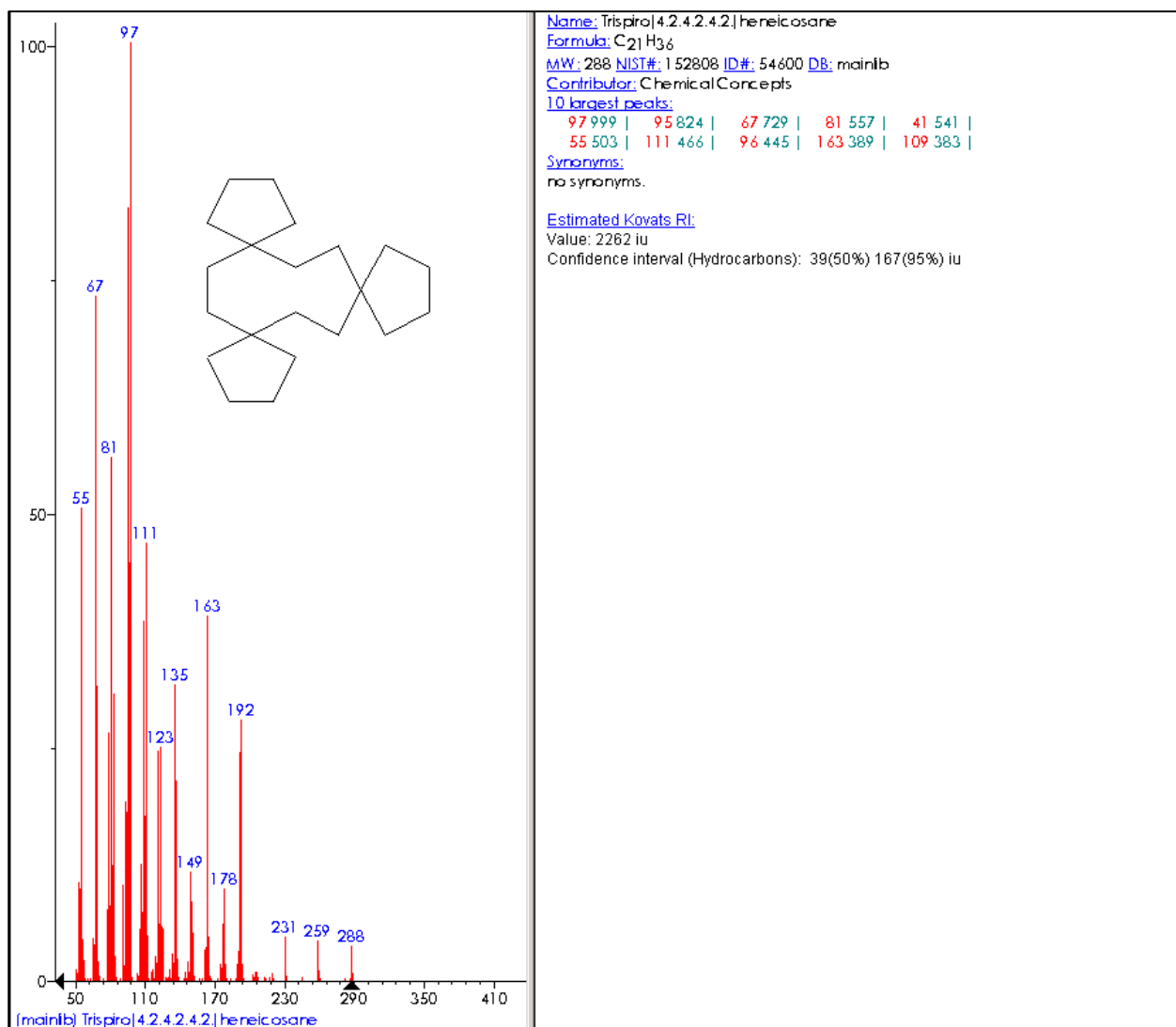


Figure C-60

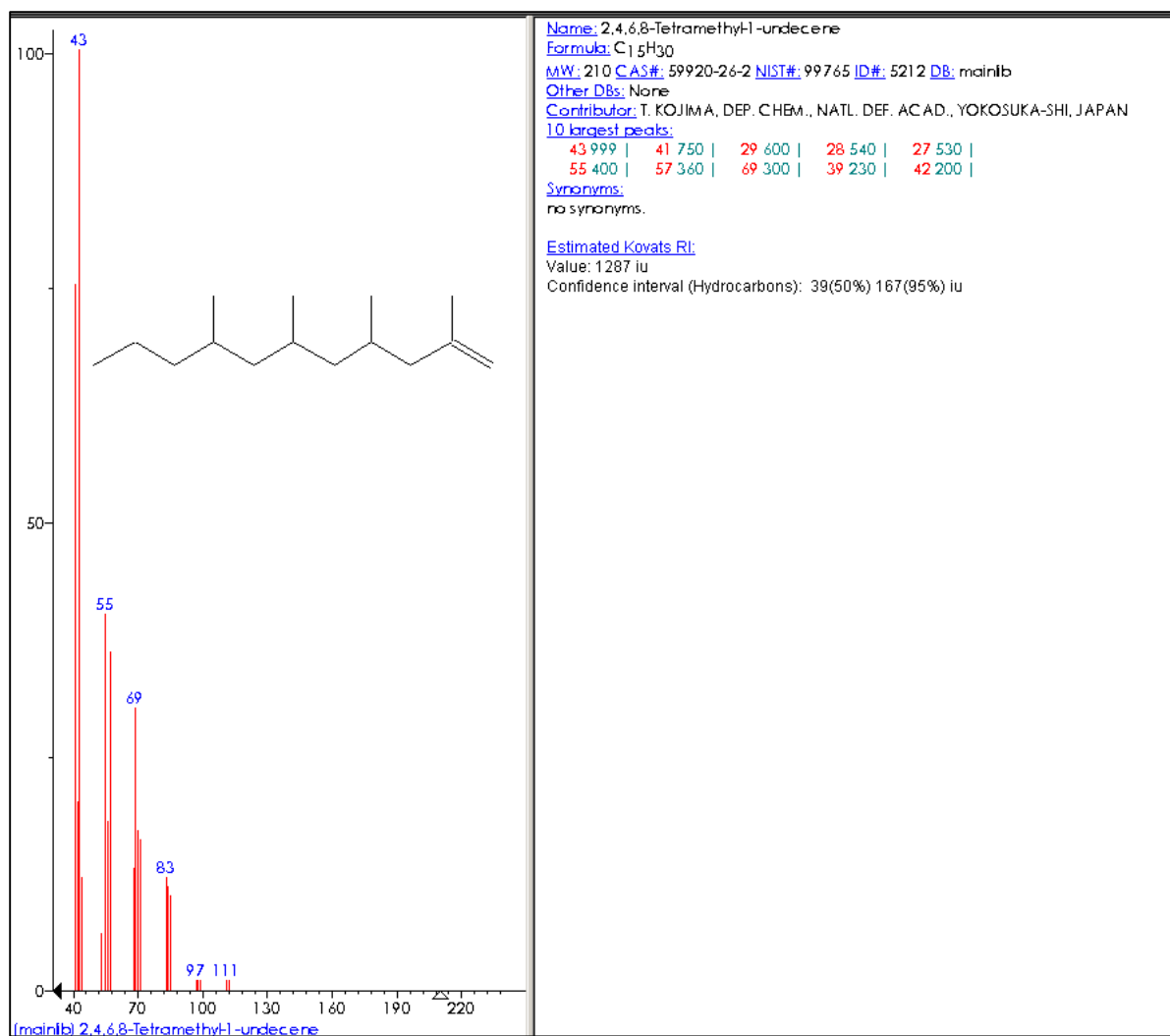


Figure C-61

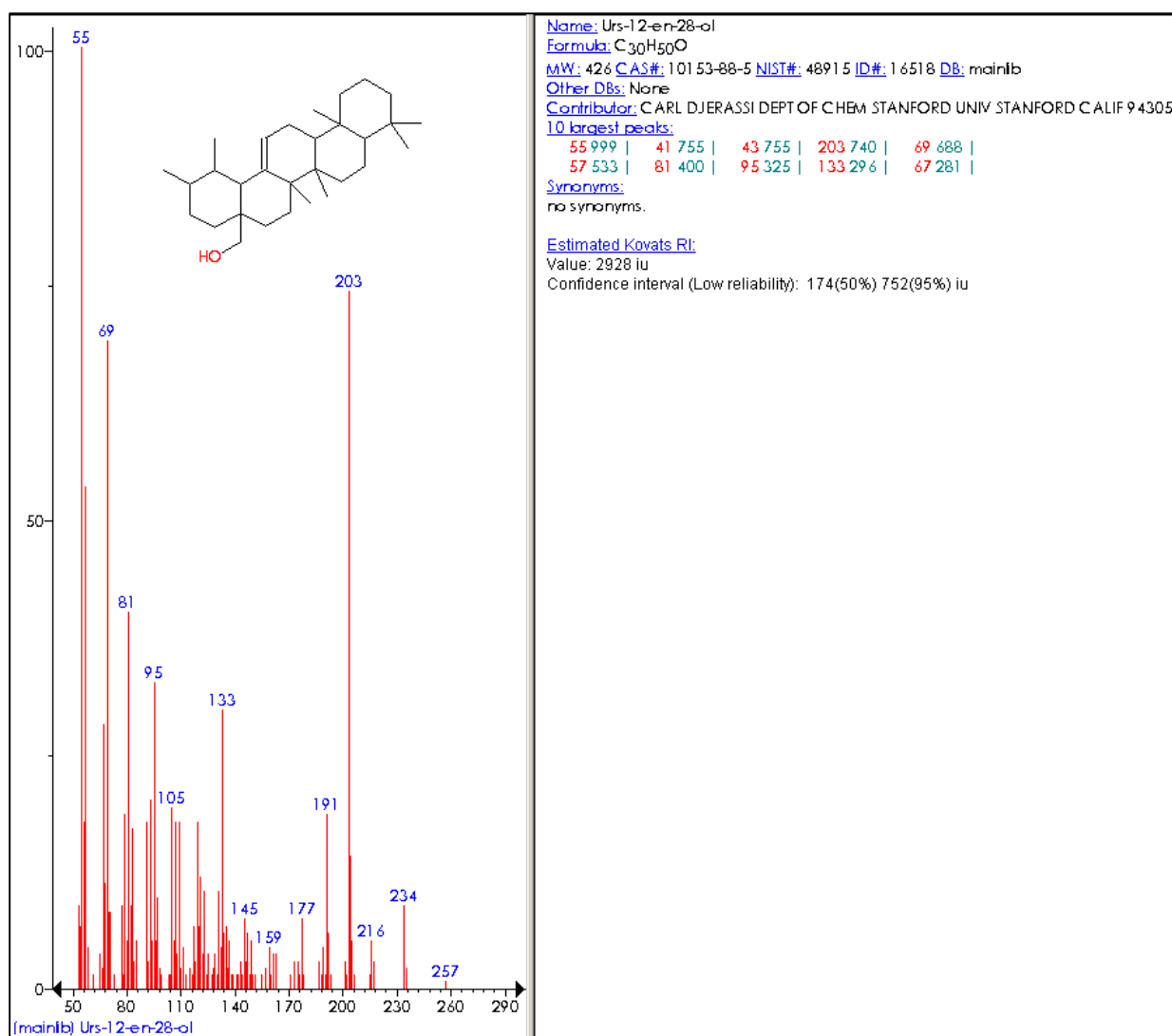


Figure C-62

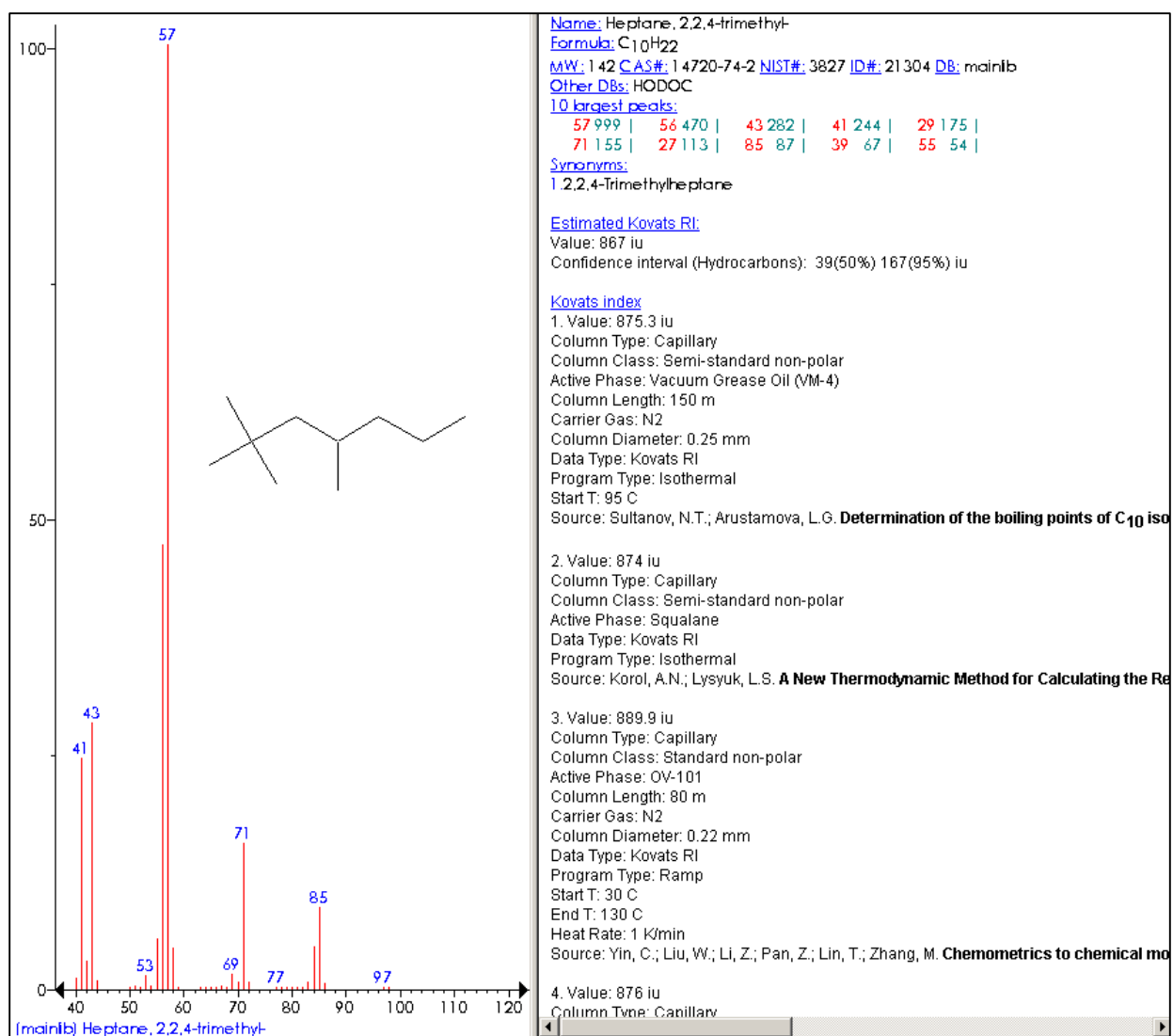


Figure C-63

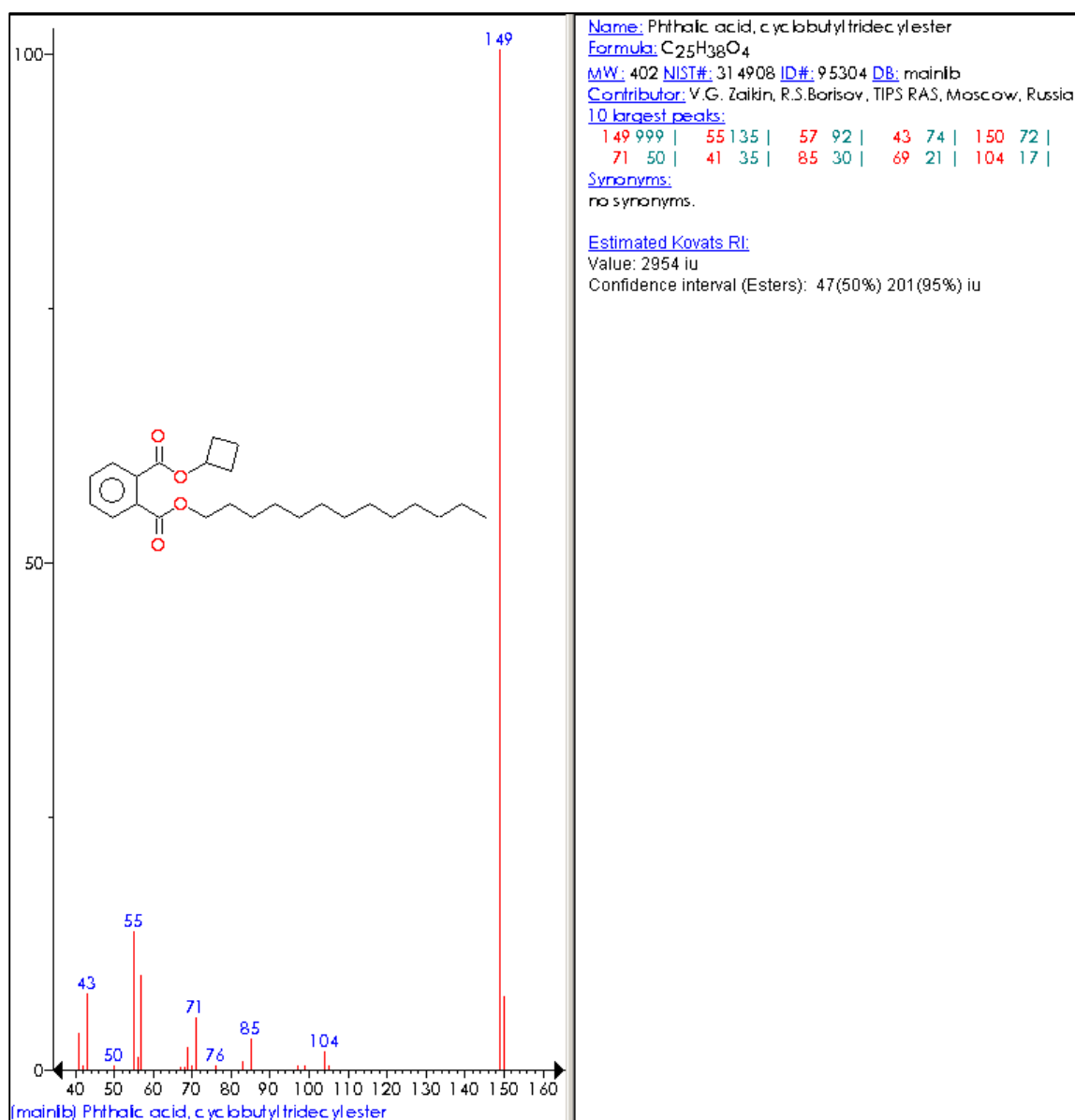


Figure C-64