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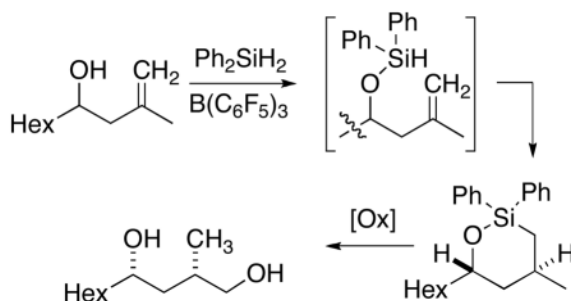
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B(C₆F₅)₃-promoted tandem silylation and intramolecular hydrosilylation: diastereoselective synthesis of oxasilinanes and oxasilepanes

 Roman Shchepin[†], Chunping Xu[†], and Patrick Dussault^{*}

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Abstract



B(C₆F₅)₃ promotes regio- and stereoselective cyclizations of unsaturated alkoxy silanes to generate oxasilinanes and oxasilepanes. The same products are available directly from alkenols via tandem silylation and hydrosilylation.

Intramolecular hydrosilylation of alkenes is an important transformation in organic synthesis.¹ Initially investigated for unsaturated silanes,² the methodology is now often applied to unsaturated alkoxy- and aminosilanes,³ where stereospecific oxidative cleavage of the newly formed C-Si bond enables stereodefined synthesis of diols and aminoalcohols.^{4,5} The majority of examples involve metal-catalyzed 5-*endo* or 5-*exo* ring closures, although six-membered cyclizations have been reported.^{1,3,6} We now report regio- and stereoselective formation of oxasilinanes and oxasilepanes via formation and cyclization of unsaturated alkoxy silanes in the presence of a nonmetal catalyst.

In the course of investigations into the influence of Lewis acids on the ozonolysis of unsaturated silanes, we found that addition of B(C₆F₅)₃ to a solution of unsaturated alkoxy silane **1-Pr** resulted in regioselective formation of oxasilinane **2-Pr** with high 3,5-*trans* diastereoselectivity (Table 1).^{7,8} The cyclization proceeded efficiently at -78 °C or RT and in the presence of either stoichiometric or catalytic B(C₆F₅)₃. Cyclization was also observed for the dimethylsilyl ether (not shown),⁹ but the hydrolytic instability of this class of reactants led us to abandon this thread following the discovery of the tandem cyclizations discussed later.

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Supporting Information Available. Details regarding preparation and characterization of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The cyclization, apparently the first intramolecular example of a known intermolecular hydrosilylation,¹⁰ was investigated further using alkoxy silanes prepared as illustrated in Scheme 1. 6-*Endo* cyclization onto an α -substituted styrene (**3-Pr**) proceeded slowly but in high yield and with high *trans* selectivity (Scheme 2). Cyclization onto a cyclobutene (**5-Pr**) proceeded much more slowly through a 6-*endo* pathway to furnish a modest yield of the *cis*-fused adducts (**6-Pr**) as a 5:1 mixture of sidechain epimers. A bishomoallyl substrate, **7-Pr**, reacted very slowly through a 6-*exo* pathway to furnish a *trans*-3,6-disubstituted-2-oxa-1-silinanane (**8-Pr**).

$B(C_6F_5)_3$ also catalyzes the reductive silylation of alcohols,¹¹ and we became intrigued by the possibility of tandem silylation/hydrosilylation (Table 2). $B(C_6F_5)_3$ -promoted reaction of alkenol **1** with stoichiometric Et_2SiH_2 or Ph_2SiH_2 generated oxasilinanes **2-Et** or **2-Ph** with very similar regio- and stereoselection as observed in the stepwise cyclizations. Although alcohols **3** and **5** decomposed under the tandem conditions, cyclohexenol **9** reacted to selectively furnish the 3,5-*trans* diastereomer of *cis*-fused octahydrobenzooxasilinanes **10-Et** and **10-Ph**; the lower yield for the Et_2SiH_2 reaction is likely related to undesired reductive deoxygenations (vide infra). Alkenol **11**, which generates an intermediate siloxane capable of undergoing cyclization through electronically comparable 5-*exo* or 6-*endo* pathways, reacted only through the latter. Bishomoallyl alcohol **13** underwent selective reaction through a 7-*endo* pathway to furnish oxasilepane **14-Et** as a 62:38 *cis/trans* mixture.

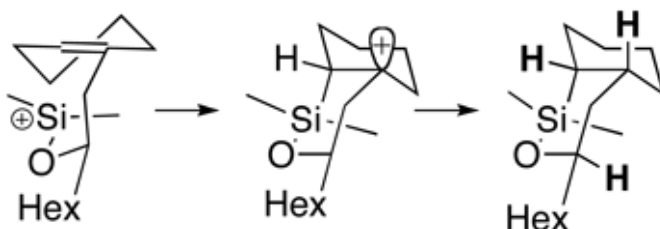
Reactions employing Et_2SiH_2 often furnished a significant amount of byproducts appearing to result from alcohol deoxygenation.¹² For example, reaction of benzylic alcohol **15** produced oxasilane **16-Et** along with a byproduct identified as a disiloxane on the basis of mass spectrometry and oxidative desilylation (Scheme 3).^{13,14} Application of the one-pot conditions to allylic alcohol **17** resulted only in rapid formation of the diethyl silyl ether. In general, reactions employing Ph_2SiH_2 proceeded more slowly but generated fewer byproducts; this can be seen, for example in the formation of **10-Et** vs. **10-Ph** (Table 2). The exception was cyclobutene **5**, where decomposition was observed for either silane.

Oxidative desilylation of the hindered siloxanes was initially attempted under Tamao conditions (KF, $KHCO_3$, aq. H_2O_2 , MeOH/THF).⁵ However, as illustrated in Scheme 4, the oxidations were found to proceed in higher yield using a procedure developed by Woerpel (*t*-BuOOH, CsOH \cdot H₂O, *n*-Bu₄NF, DMF).⁵ The stereochemistry of diols **1915** and **2116** was determined by comparison with literature reports, establishing (**14-Et**) or confirming (**16-Et**) the stereochemistry of cyclizations.

The cyclizations, clearly related to intermolecular $B(C_6F_5)_3$ -mediated hydrosilylations,¹⁰ and potentially related to cyclizations of unsaturated silanes in the presence of triphenylmethyl cation,¹⁷ almost certainly involve electrophilic attack on an alkene by a silylium-like species derived from interaction of $B(C_6F_5)_3$ with the Si-H (Scheme 5).^{18,19} Reduction of the resulting carbocation by the hydridoboron species would furnish the cyclized product and regenerate the Lewis acid catalyst. The selective formation of 3,5-*trans*-disubstituted oxasilinanes can be rationalized by hyperconjugation of the newly formed C-Si bond with the carbocation,²⁰ with the resulting conformation dictating approach of the hydride. Analogous stereoselectivity has been observed in formation of siloxanes through hydrogen atom delivery to carbon-centered radicals.²¹

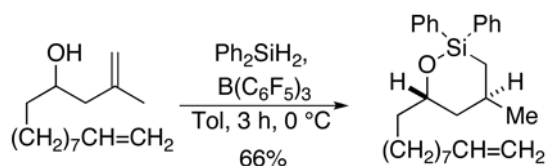
Although 5-*exo* cyclizations are well-established for Pt- or Rh-catalyzed hydrosilylations,^{1,3} we observed selective 6-*endo* vs. 5-*exo* cyclization with a substrate where either mode would proceed via a secondary carbocation (Table 2, substrate **11**). We also observed very different rates for 6-*exo* and 6-*endo* cyclizations involving electronically similar carbocation intermediates (**7-Pr** vs. **1-Pr**). These results point to the importance of interactions between

the alkene and the developing silylium-like species. The *cis* selectivity observed for six-membered ring annulations, which complements results from metal-catalyzed cyclizations, 1:3:22 presumably reflects stereoelectronic requirements for trapping of the β -silyl cations. 23 The stereoselectivity of sidechain introduction results from cyclization through the low-energy conformer of a chair-like transition state (eq 1).



(1)

Several lines of evidence indicate that the tandem reactions and stepwise processes involve a common hydrosilylation step. Both processes proceed with nearly identical regio- and diastereoselectivity. Furthermore, dialkylsilyl ethers are observed (TLC) as intermediates in some of the slower reactions, and become the only product when cyclization is disfavored, as for allylic alcohol **17** (Scheme 3). Finally, a diene substrate reacts selectively across the homoallyl alcohol (eq 2).



(2)

The formation of deoxygenated byproducts is observed mainly in the tandem reactions. The chemoselective deoxygenation of unhindered alcohols by trialkylsilane and $B(C_6F_5)_3$ has been postulated to involve attack of a silylium ate complex on intermediate silyl ethers,¹² suggesting the deoxygenations observed here result from intermolecular reductions directly competing with cyclization.

Overall, the transformation provides a new method for the regio- and stereoselective synthesis of cyclic siloxanes and derived diols. Given that $B(C_6F_5)_3$ has been reported to catalyze the hydrosilylation of ketones and aldehydes,²³ it is likely the method could be extended to allow the synthesis of oxasilacycles from unsaturated aldehydes and ketones.

Supplementary Material

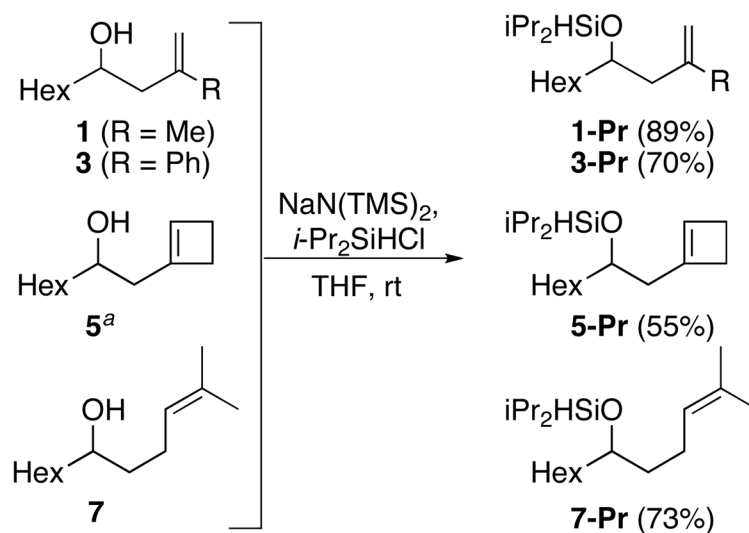
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Acknowledgments

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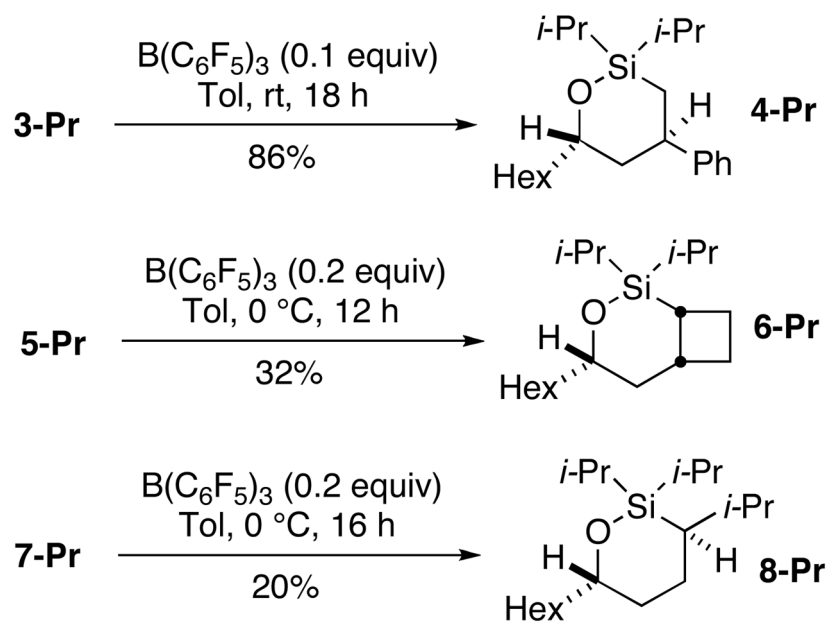


^aInseparable 3:1 mixture with 1-chloro-1-alkylcyclobutane

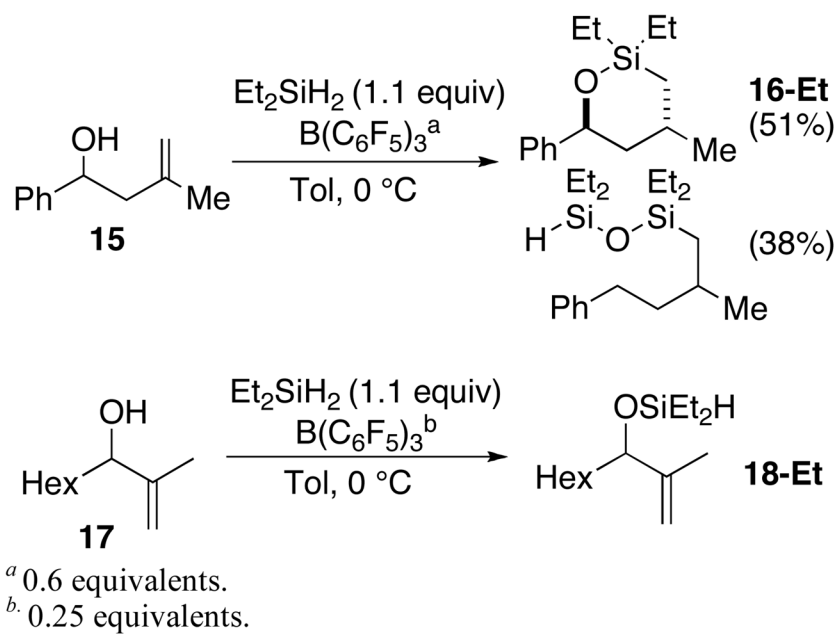
Scheme 1.

Preparation of alkoxy silanes

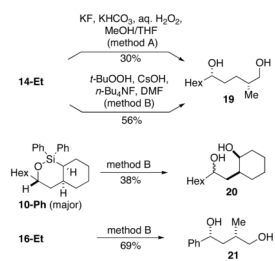
^aInseparable 3:1 mixture with 1-chloro-1-alkylcyclobutane



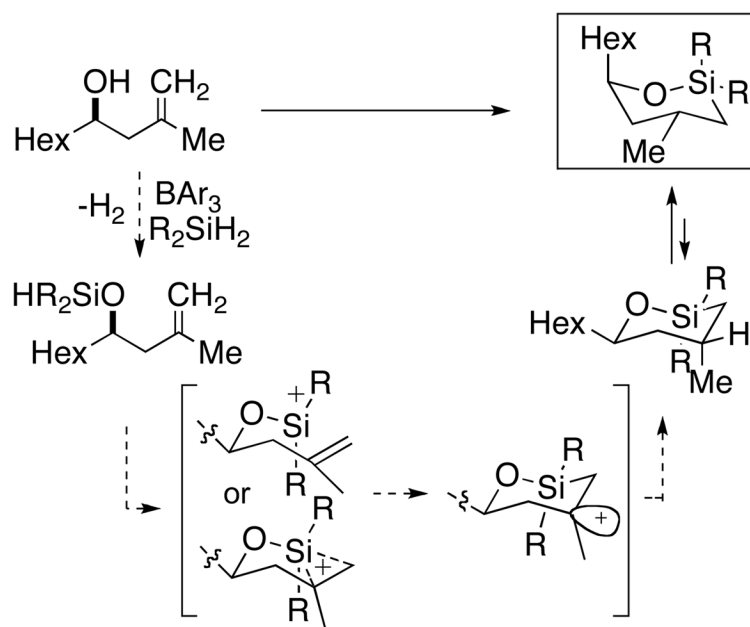
Scheme 2.
Additional cyclizations



Scheme 3.
Byproduct formation
^a 0.6 equivalents.
^b 0.25 equivalents.



Scheme 4.
Oxidative desilylation



Scheme 5.
Proposed mechanism

Table 1

Cyclization of **1-Pr**^a

BAr ₃ (equiv)	temp (°C) ^b	t (h)	yield (%)	trans %
1.0	-78	< 0.1	82	nd
0.4	rt	< 0.1	88	nd
0.1	-78	< 0.1	93	nd
0.07	rt	< 0.1	84	94 ^c

^aPrepared as illustrated in Scheme 1.

^bFinal temperature; reactants mixed at -78 °C.

^c5% of the *cis*-diastereomer isolated.

Table 2

Tandem silylation/hydrosilylation

subs	n	R ¹ , R ²	X	t (h)	prod	yield	trans % ^a
1	1	Me, H	Et	0.1	2-Et	47 %	>90
1	1	Me, H	Ph	0.15	2-Ph	80 %	>90
3	1	Ph, H	Ph	-	-	-	decomp
5	1	(CH ₂) ₂	Ph	-	-	-	decomp
9	1	(CH ₂) ₄	Et	0.5	10-Et ^b	39 %	90
9	1	(CH ₂) ₄	Ph	1	10-Ph ^b	73 %	84
11 ^c	1	H, Me	Et	0.1	12-Et	16 %	60
11 ^c	1	H, Me	Ph	1	12-Ph	24 %	~1:1
13	2	H, Me	Et	0.1	14-Et	73 %	38

^a 3,5 stereochemistry;^b cis ring fusion; see Scheme 3 for structure of 10-Ph.^c 3,3:1 mixture of E/Z isomers.

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Supporting Information - Experimental Procedures

<u>General Experimental Procedures:</u>	<u>2</u>
<u>Alcohol precursors</u>	<u>2</u>
2-Methyldec-1-en-4-ol (1):	2
2-Phenyldec-1-en-4-ol (3):	3
1-Cyclobutenyloctan-2-ol (5):	3
2-Methyl-2-dodecen-6-ol (7):	3
1-Cyclohexenyloctan-2-ol (9):	3
Undec-2-en-5-ol (11):	3
2-Methylundec-1-en-5-ol (13):	4
3-Methyl-1-phenylbut-3-en-1-ol (15):	4
2-Methylnon-1-en-3-ol (17):	4
<u>Diisopropylsilyl ethers</u>	<u>4</u>
Diisopropyl-(2-methyldec-1-en-4-oxy)silane (1-Pr):	4
Diisopropyl-(2-phenyldec-1-en-4-oxy) silane (3-Pr):	4
Diisopropyl-(1-cyclobutenyloctyl-2-oxy)silane (5-Pr):	5
Diisopropyl-(2-methyl-2-dodecen-6-oxy)silane (7-Pr):	5
<u>B(C₆F₅)₃-catalyzed cyclizations of diisopropylsilyl ethers (illustrated for 1-Pr)</u>	<u>5</u>
(<i>trans</i>)-1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane (<i>trans</i> - 2-Pr) and <i>cis</i> - 2-Pr	6
(<i>trans</i>)- 1,1-Diisopropyl-3-hexyl-5-phenyl-2,1-oxasilinane (<i>trans</i> - 4-Pr):	7
(3 α ,5 α ,6 α), (3 β ,5 α ,6 α)-1,1-Diisopropyl-3-hexyl-2-oxa-1-sila[4.2.0] bicyclooctane (6-Pr):	7
(<i>trans</i>)-1,1-Diisopropyl-3-hexyl-6-isopropyl-2,1-oxasilinane (8-Pr):	8
<u>B(C₆F₅)₃-catalyzed tandem silylation/hydrosilylation (general procedure)</u>	<u>8</u>
1,1-Diethyl-3-hexyl-5-methyl-2,1-oxasilinane (2-Et):	9
1,1-Diphenyl-3-hexyl-5-methyl-2,1-oxasilinane (2-Ph):	9
(3 β ,5 α ,6 α) and (3 α ,5 α ,6 α)-2,1-Benzoxasilin, octahydro-1,1-diethyl-3-hexyl (10-Et)	9
(3 β ,5 α ,6 α)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3 β ,5 α ,6 α)- 10-Ph) and (3 α , 5 α ,6 α)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3 α , 5 α ,6 α)- 10-Ph)	10
(3,6- <i>trans</i>) and (3,6- <i>cis</i>)-1,1-Diethyl-3-hexyl-6-methyl-2,1-oxasilinane (<i>trans</i> - 12-Et and (<i>cis</i>)- 12-Et)	11
(3,6- <i>trans</i>) and (3,6- <i>cis</i>)-1,1-Diphenyl-3-hexyl-6-methyl-2,1-oxasilinane (<i>trans</i> - 12-Ph and (<i>cis</i>)- 12-Ph):	12
(3,6- <i>trans</i>) and (3,6- <i>cis</i>)- 1,1-Diethyl-3-hexyl-6-methyl-2-oxa-1-silepane	

(<i>trans</i> - and <i>cis</i> - 14-Et).	12
(3,5- <i>trans</i>)- 1,1-Diethyl-5-methyl-3-phenyl-2,1-oxasilinane (16-Et):	13
Diethyl (2-methylnon-1-en-3-oxy)silane (18-Et):	
<u>Oxidative Desilylation:</u>	13
(Tamao oxidation) 2-Methylundecane-1,5-diol (19):	14
(Woerpel oxidation) 2-(2-Hydroxyoctyl)-cyclohexanol (20):	14
3-Methyl-1-phenyl-1,4-butanediol (21)	15
<u>References</u>	15

General Experimental Procedures:

Tetrahydrofuran (THF) was distilled from Na/Ph₂CO under N₂. Dichloromethane (CH₂Cl₂) was distilled from CaH₂. Stock solutions of B(C₆H₅)₃ were prepared either by: A) Transferring a freshly opened commercial sample (typically 1.0 g) into a oven-dried flask under N₂ followed by dissolution (0.2 M) in freshly distilled (Na/Ph₂CO) toluene; or B) Working inside a glove box under inert atmosphere, dividing a 1.0 g commercial sample of B(C₆F₅)₃ into individual vials (ca. 200 mg/vial). The vials were removed from the glove box to prepare stock solutions in toluene (0.2 M) that were used immediately and then discarded.ⁱ B(C₆H₅)₃ dissolves completely in toluene at 0.2M; the solubility of the hydrate is significantly lower. All other reagents and solvents were used as purchased unless otherwise noted. Thin layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates; developed plates were visualized with a hand-held UV lamp and/or by staining with one of the following: 1% ceric sulfate and 10% ammonium molybdate in 10% H₂SO₄ (general stain, after charring) or 1% aq. KMnO₄ (for alkenes). Analytical and preparative HPLC were performed on a 4.6 mm x 25 cm Si column (5 μm) or 21.4 mm x 25 cm Si column (8 μm); both employed RI detection. NMR spectra were recorded at 400 MHz (¹H) or 100 MHz (¹³C) in CDCl₃ unless otherwise indicated. ¹H NMR signals are reported as: [chemical shift (multiplicity, integration, J couplings in Hz, other information). Infrared spectra were recorded as neat films (ZnSe crystal or NaCl plates) with selected absorbances reported in wave numbers (cm⁻¹). High resolution mass spectrometry was conducted at the Nebraska Center for Mass Spectrometry.

Preparation of Alcohols:

2-Methyldec-1-en-4-ol (1): Into a 0 °C solution of heptanal (3.5 mL, 25 mmol) in THF (10 mL) was added dropwise a solution of 2-methylallyl magnesium chloride in THF (50 mL, nominally 0.5 M). After 20 min, the reaction was quenched with water (20 mL), acidified with conc. HCl (~

3 mL) and extracted with 10% EA/Hex (250 mL x 2). The combined extracts were sequentially washed with 10% aq. HCl and water. A standard workup and purification (5% EA/Hex) furnished 3.53 g (82%) of a compound with spectral properties matching literature reports.ⁱⁱ

2-Phenyldec-1-en-4-ol (3)ⁱⁱⁱ was prepared by ene reaction of heptanal with α -methylstyrene by the procedure of Snider:^{iv} ^1H δ 7.44-7.41 (2H); 7.38-7.33 (2H); 7.32-7.27 (2H); 5.43 (d, 1H, 1.6); 5.18 (bs, 1H); 3.66 (m, 1H), 2.84 (ddd, 1H, 14, 4, 1; AB with 2.67), 2.67 (dd, 1H, 14, 9); 1.69 (d, 1H, 3); 1.4-1.5 (3H), 1.2-1.3 (6 H), 0.88 (t, 3H, 6.5); ^{13}C δ 145.5, 140.5, 128.4, 127.7, 126.2, 115.2, 69.4, 43.8, 37.0, 31.8, 29.3, 25.6, 22.6, 14.1; IR 3368 (s, b); 2927, 2856, 1626, 1444, 898, 705 cm^{-1} ; HRFAB MS calc. For $\text{C}_{16}\text{H}_{24}\text{OLi}$ ($\text{M}+\text{Li}$)⁺: 239.1984; found 239.1984.

1-Cyclobutenyloctan-2-ol (5) was prepared from methylenecyclobutane (1.0 g, 15 mmol) and heptanal (2.7 mL, 1.3 equiv) by a similar procedure as for **3** to afford 0.99 g of alcohol **5** as an inseparable 3:1 mixture with 1-chlorocyclobutyl-2-octanol. The spectra of the product ($R_f = 0.3$, 10% EA) matched a literature report.^v

2-Methyl-2-dodecen-6-ol (7) was prepared (1.39 g, 71%) by reaction of the Grignard reagent derived from 5-bromo-2-methyl-2-pentene (2.0 mL, 15 mmol) with a slight excess of heptanal: $R_f = 0.4$ (5% EA/hex); ^1H δ 5.14 (bt, 1H, 6); 3.60 (m, 1H); 2.09 (m, 2H); 1.69 (bs, 3H); 1.63 (bs, 3H); 1.55-1.38 (6H); 1.35-1.23 (6H); 0.89 (t, 3H, 7); ^{13}C δ 132.0; 124.2; 71.8; 37.5, 37.3, 31.8, 29.4, 25.7, 25.6, 24.4, 22.6, 17.6, 14.1; IR: 3377 (b, s, OH); 3328, 2924, 2855, 1454, 1377 cm^{-1} ; 2928, 2864, 2092, 1463, 1379, 1056, 1001, 837 cm^{-1} ; HRFAB calculated for $\text{C}_{13}\text{H}_{25}\text{O}$ ($\text{M}-\text{H}$)⁺: 197.1905; found 197.1912 (-5.4 ppm); M^+ also observed at 196.1813.

1-Cyclohexenyloctan-2-ol (9) was prepared from the reaction of heptanal (1.12 mL, 8.0 mmol), methylenecyclohexane (1.12 mL, 10 mol) and Me_2AlCl (12 mL, nominally 1 M solution in hexanes) by a similar procedure as for **3**. The product (1.23 g, 73%) displayed spectra consistent with literature reports.^{vi} $R_f = 0.4$ (10% EA/Hex)

(E,Z)-Undec-2-en-5-ol (11) was prepared (1.17 g, 86%) from prop-1-enylmagnesium bromide (24 mL, nominally 0.5M in THF), epoxyoctane (1.2 mL, 8 mmol) and CuI (0.152g, 0.8 mmol).

The product was a 3.3:1 mixture of *E*- and *Z*-isomers based upon integration of the ^1H signals at δ 1.64 and 1.69 ppm. Spectral properties matched literature reports.^{vii} $R_f=0.4$ (10% EA/Hex).

2-Methylundec-1-en-5-ol (13)^{viii} was prepared (1.45 g, 98%) from 2-methylallyl magnesium chloride (24 mL, nominally 0.5M in THF), 2-hexyloxirane (1.2 mL, 8 mmol) and CuI(0.152g, 0.8 mmol) by a similar manner as **15**. $R_f=0.3$ (10% EA/Hex).

3-Methyl-1-phenylbut-3-en-1-ol (15) was prepared (1.30 g, quant.) from reaction of benzaldehyde (0.85 mL, 8.0 mmol) and 2-methylallyl magnesium chloride (20.8 mL, nominally 0.5M in THF) by a procedure similar to that applied for **1**. Spectral properties matched a literature report.^{ix} $R_f=0.3$ (10% EA/Hex)

2-Methylnon-1-en-3-ol (17)^x was prepared (1.05 g, 84%) from heptanal (1.12 mL, 8.00 mmol) and allylmagnesium chloride (20.8 mL, nominally 0.5M solution in THF) by a similar procedure as used for **1**. $R_f=0.2$ (10% EA/Hex). Spectral properties matched a literature report.

Alkoxysilanes:

Diisopropyl(2-methyldec-1-en-4-oxy)silane (1-Pr)

Into a THF (15 mL) solution of 2-methyldec-1-en-4-ol (0.724 g, 4.30 mmol) was added sodium bis(trimethylsilyl)amide (4.3 mL, nominally 2M) followed by $\text{SiClH}(i\text{-Pr})_2$ (1.1 mL). After 4 h the reaction was quenched with brine and extracted with hexane (2 x 200 mL). The combined organic extracts were concentrated *in vacuo* and the residue was purified by flash chromatography in hexane to afford 1.09 g (89%) of the silyl ether: $R_f=0.4$ (hexane); ^1H (600 MHz) δ 4.78 (app. s, 1H), 4.78(app. s, 1H), 4.21(s, 1H), 3.85(p, 1H, 5.7), 2.27(dd, 6 and 13.2), 2.17(dd, 1H, 7.2 and 13.2), 1.75(s, 3H), 1.43 (m, 10H), 1.05(m, 12H), 0.95(m, 2H), 0.90(t, 3H, 6.0); ^{13}C (150 MHz) δ 142.9, 112.8, 73.0, 45.7, 36.7, 31.9, 29.4, 25.2, 22.9, 22.6, 17.60, 17.57, 17.46, 14.1, 12.73, 12.71; IR 2927, 2862, 2097, 1642, 1463, 1377 cm^{-1} . HRMS (CI) calc. for $\text{C}_{17}\text{H}_{35}\text{OSi}$ (M-H)⁺: 283.2457; found 283.2469 (4.2 ppm); M⁺ (284.2543) observed in lower abundance.

Diisopropyl-(2-phenyldec-1-en-4-oxy)silane (3-Pr) was prepared (0.435 g, 70%) from alcohol **3** (0.428 g, 1.8 mmol) by a procedure similar to that applied to the synthesis of **1-Pr**: $R_f = 0.9$ (5% EA/hex); ^1H δ 7.42 (bd, 2H, 8), 7.34 (bt, 2H, 8), 7.72 (app tt, 1H, 8, 1); 5.32 (d, 1H, 1.6), 5.13 (bs, 1H); 4.18 (bt, 1H, 1.6), 3.76 (m, 1H), 2.81 (ddd, 1H, 14, 5.8, 1); 2.64 (ddd, 1H, 14, 6.4, 1); 1.55-1.36 (3H), 1.33-1.18 (7H); 1.04-0.98 (12H, overlapping Me doublets); 0.98 -0.91 (m, 2H); 0.88 (t, 3H, 6.4); ^{13}C δ 145.7, 141.2, 128.2, 127.3, 126.3, 114.9, 72.9, 43.2, 36.5, 31.8, 29.4, 24.9, 22.6, 17.54, 17.48, 14.41, 14.07, 12.64, 12.61; IR: 3031, 2954, 2865, 3095, 1462, 1254 cm^{-1} ; HRFAB Calc. For $\text{C}_{22}\text{H}_{37}\text{OSi}$ (M-H) $^+$: 345.2613; found 345.2605 (2.5 ppm).

Diisopropyl(1-cyclobutenyloctyl-2-oxy)silane (5-Pr) was prepared in 55% yield (485 mg) from **5** (546 mg, estimated 2.25 mmol based upon purity) by a similar procedure as for **1-Pr**: $R_f = 0.3$ (hexane); ^1H δ 5.72 (s, 1H); 4.20 (s, 1H); 3.81 (apparent pentet, 1H, 5-6); 2.45 (m, 2H), 2.35 (bs, 2H); 2.22 (m, 2H); 1.5-1.23 (10H); 1.07-1.02 (12H, isopropyl groups); 1.02-0.95 (2H); 0.895 (t, 3H, 6.5); ^{13}C δ 147.3, 129.3, 73.1, 38.8, 36.9, 32.0, 31.9, 29.4, 27.0, 25.3, 22.6, 17.6, 17.5, 17.4, 14.1, 12.7; IR 2926, 2864, 2089, 1462, 1055, 837 cm^{-1} ; HRFAB Calc. For $\text{C}_{18}\text{H}_{35}\text{OSi}$ (M-H) $^+$: 295.2457; found 295.2452 (1.7 ppm).

Diisopropyl-(2-methyl-2-dodecen-6-oxy)silane (7-Pr) was prepared (0.707g, 73%) from alcohol **7** (617 mg, 3.1 mmol) by a similar procedure as for **1-Pr**: $R_f = 0.3$ (hexane); ^1H δ 5.12 (bt, 1H, 6-7), 4.21 (s, 1H), 3.69 (pentet, 1H, 6.4); 2.08 & 1.98 (ABXY, 2H), 1.69 (s, 3H); 1.62 (s, 3H); 1.53-1.45 (4H), 1.35-1.25 (8H), 1.08-1.02 (12H, isopropyl), 1.02-0.95 (2H); 0.90 (t, 3H, 6); ^{13}C δ 131.4, 124.5, 74.3, 36.9, 36.8, 31.9, 29.5, 25.7, 25.3, 24.0, 22.6, 17.64, 17.59, 17.5, 14.1, 12.7; IR 2929, 2864, 2088, 1463, 1377, 1063, 1002, 841, 800 cm^{-1} ; HRFAB Calc. For $\text{C}_{19}\text{H}_{39}\text{OSi}$ (M-H) $^+$: 311.2770; found 311.2773 (1.0 ppm).

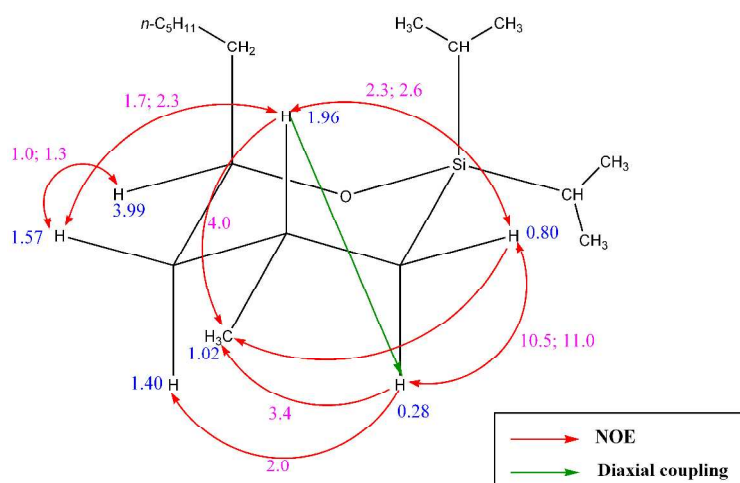
General Procedure for intramolecular hydrosilylation (illustrated for **1-Pr**). To an anhydrous toluene solution (6 mL) of **1-Pr** (0.285g, 1.00 mmol), either at -78, 0 °C, or rt, was added $\text{B}(\text{C}_6\text{F}_5)_3$. The amount of catalyst ranged from 0.1 to 1.0 eq, as a 0.2M solution in toluene. After the reaction was complete (TLC), the reaction was quenched with sat. aq. NaHCO_3 (5 mL) and the resulting mixture extracted with hexane (2 X 100 mL). The combined organic layers were concentrated *in vacuo* and the residue was purified by flash chromatography (hexane) to afford

trans-**2-Pr** (236 mg, 83%) followed by a small amount of *cis*-**2-Pr** (18 mg, 6%). Analysis of the crude reaction mixtures by GC/MS generally found 91-95% of the *trans* isomer; the minor (syn) byproduct eluted first on GC. Both diastereomers displayed a predominant fragment at *m/z* 241, [M-*i*Pr]⁺. The stereochemistry was assigned based upon the relative strength of nOe transfer in the *trans* and *cis* isomers (see Scheme below), and by the magnitude of the axial/axial and axial/equatorial couplings for ³J₅₋₆ couplings. The stereochemical assignment was supported by a correlation of the ³J_H of the minor (*cis*) byproduct with a literature report for similar molecules

xi

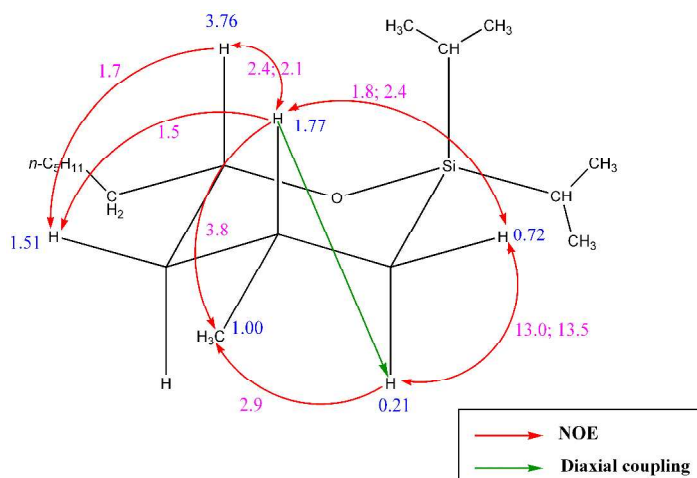
(3,5-*trans*)- **1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane** (*trans*-**2-Pr**)

R_f = 0.2 (hexane); ¹H δ 3.99(m, 1H), 1.96(m, 1H), 1.57(m, 1H), 1.38(m 11H), 0.99(m, 12H), 0.95(m, 4H), 0.88[m, 4H, includes 0.89(t, 3H, 6.8), and peak at 0.90], 0.80(ddd, 1H, J₁=1.6, J₂=4.8, J₃=14.8), 0.28(dd, 1H, 10.4 and 14.8); ¹³C δ 72.0, 41.3, 37.5, 31.9, 29.4, 26.3, 26.1, 23.8, 22.6, 17.28, 17.27; 17.19, 17.16, 15.1, 14.1, 13.7, 13.1; IR (2942, 2931, 2864, 1464 cm⁻¹; HRFABMS (3-NBA) calc. for C₁₄H₂₉OSi [M-(*i*-Pr)⁺]: 241.1988; found 241.1992 (1.7 ppm). Diaxial couplings and nOe excitations are summarized in the accompanying graphic.



(3,5-*cis*)- **1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane** (*cis*-**2-Pr**):

R_f = 0.4 (hexane); ¹H δ 3.76(m, 1H), 1.77(m, 1H), 1.51(d of q., 1H, 2 and 13.6), 1.38(m 11H), 1.04-0.94 [m, 15H, peak at 1.00 (d, 6.5) visible nOe upon irradiation at 0.21], 0.89[m, 5H,



includes 0.89(t, 3H, 6.8), and other peaks], 0.72(ddd, 1H, $J_1=2.4$, $J_2=4.0$, $J_3=14.4$), 0.21(dd, 1H, 12.8 and 14.4); ^{13}C δ 74.6, 44.3, 39.1, 31.9, 29.7, 29.4, 27.5, 25.3, 22.7, 17.71, 17.68, 17.14, 17.10, 15.7, 14.1, 13.1, 12.3; IR identical to *anti*-**2-Pr**. Diaxial couplings and nOe excitations are summarized in the accompanying graphic.

The ^1H NMR spectra of *cis*-3,5-disubstituted 2,1-oxasilacyclohexanes display H_3 (axial) as a ddd between 3.45 and 3.7 ppm and with individual coupling constants of up to 11 Hz.¹¹ The same work found the ^2J coupling for H_6/H_6' to be 14 Hz, and the axial/axial and equatorial/axial $^3\text{J}_{5-6}$ couplings to be 13.3 and 3.5 Hz, respectively. These values agree closely with our observations for *cis*-**2-Pr**.

(3,5-*trans*)- 1,1-Diisopropyl-3-hexyl-5-phenyl-2,1-oxasilinane (*trans*-4-Pr):

By a procedure similar to that described for **1-Pr**, cyclization of silane **3-Pr** (0.299 g, 0.862 mmol) furnished 0.257 g (86% yield) of **4-Pr**: $R_f = 0.3$ (5% EA/hex); ^1H δ 7.34 (t, 2H, 7.5); 7.27 (bd, 2H, 7.5); 7.22 (bd, 1H, 7.5); 4.16 (m, 1H); 3.05 (bt, 1H, 12.5), 1.96 (near dt, 12, 6; on same CH_2 as 1.75); 1.77 (m, 1H, on same CH_2 as 1.55); 1.75 (m, 1H, on same CH_2 as 1.96); 1.55 (m, 1H, on same CH_2 as 1.78), 1.5 (m, 1H, on same CH_2 as peak buried at 1.32), 1.4-1.26 (7H, includes portion of CH_2 shared with 1.5 as well as three CH_2 -related spin systems), 1.12 (d, 3H, 7), 1.10 (3H, obscured), 1.09 (d, 3H, 7), 1.02 (6H, broad s), 0.98 (m, 1H, part of CH_2 with 0.90); 0.92 (t, 3H, 7), 0.90 (partially obscured dd, 20, 14). Through-space (nOe) correlations: Excitation of 4.16: collapses 1.96 to dt (6,14) as H_4 equatorial); enhances 1.77, 1.75, 1.5, 1.32; Excitation of 3.05 enhances 7.27, 1.77, 1.5, (shows evidence of direct coupling to 1.96); enhances d at 1.11, 1.09, and m/bs at 1.00 and 0.08; enhances methyl at 0.89? ^{13}C 149.8, 128.5, 126.4, 125.9, 73.0, 40.7, 37.0, 34.4, 31.9, 29.4, 26.5, 22.7, 17.34, 17.27, 17.21, 17.16, 15.7, 14.1, 13.9, 13.0; HR-FAB calcd. $\text{C}_{22}\text{H}_{38}\text{OSi}$ (M-H)⁺: 345.2613; found: 345.2605 (2.5 ppm)

1,1-Diisopropyl-3-hexyl-2-oxa-1-sila[4.2.0] bicyclooctane (6-Pr) was prepared (65 mg, 32%) as a separable mixture of diastereomers by cyclization of **5-Pr** (200 mg, 0.67 mmol).

Diastereomer 1 ($3\alpha, 5\alpha, 6\alpha$); 54 mg; $R_f = 0.3$ (hexane); ^1H δ 3.58 (m, 1H, methine, cross speaks to spin system centered on 1.5 ppm); 2.51 (m, 1H, methine, coupled to 2.38, 1.95, 1.57); 2.38 (apparent pentet, 1H, part of methylene, coupled to 2.51, 1.99, 1.95, 1.68, 1.57); 1.99 (m, 1H, methine); 1.95 (m, 1H, part of methylene); 1.68 (dd, 1H, 13, 6); 1.57 (m, 1H); 1.55-1.25 (11H);

1.04-9.97 (12H, 4 Me in isopropyl); 0.898 (t, 3H, 6.4), 0.88 (m, 1H), noE from 3.58 reveals as apparent pentet); ^{13}C δ 73.18, 29.17, 38.61, 36.28, 21.97, 30.92, 29.41, 25.32, 26.69, 21.96, 18.57, 17.64, 17.53, 17.47, 17.07, 14.12, 13.44, 12.99; IR 2926, 2802, 1463, 1131, 1040, 882 cm^{-1} .

Diastereomer 2 (3 β ,5 α ,6 α): 11.6 mg; R_f = 0.2 (hexane); ^1H δ 4.11 (m or apparent heptet, 1H); 2.825 (m, 1H; coupled into 2.2, 1.92, 1.47; correlates with methine C at 32.6 ppm); 2.24 (m, 1H; correlates with methylene C at 26 ppm), 2.13 (m, 1H, correlates with methylene at 26 ppm), 2.06 (m, 1H, correlates with methylene at 20 ppm), 1.92 (m, 2H correlates with methylene at 26 and methine at 17); 1.47 (m, 4H), 1.4-1.25 (9H), 1.15-1.05 (1H); 1.07 (m, 3H), 1.03 (app d, 3H, 6.4), 0.997 (d, 3H, 6.7); 0.94 (d, 3H, 6.7); 0.83 (m, 1H); ^{13}C δ 69.55, 38.79, 37.78, 32.64, 31.97, 29.44, 26.28, 25.71, 22.68, 20.07, 17.53, 17.43, 17.33, 17.13, 16.24, 14.10, 13.18, 13.12; IR 2927, 2803, 1464, 1092, 993, 882 cm^{-1} ; HRMS calcd. for $\text{C}_{18}\text{H}_{35}\text{OSi}$ (M-H) $^+$: 295.2457; found: 295.2456 (6.4 ppm).

(*trans*) **1,1-Diisopropyl-3-hexyl-6-isopropyl-2,1-oxasilinane (8-Pr)** was prepared (87 mg, 20% yield) from from **7-Pr** (419 mg, 1.34 mmol) by a similar procedure (0.2 equiv $\text{B}(\text{C}_6\text{F}_5)_3$) as for **2-Pr**, except that the reaction was warmed to 0 $^\circ$ C and held at that temperature for 16 h. Following a careful flash chromatography to remove a large amount of byproduct, the product was isolated as a single product by NMR and GC/MS: R_f = 0.5 (hexane); ^1H δ 3.68 (m, 1H; C3-axial), 2.05 (dtd, 1H, 12.8, 5, 2.4; H_5 -*eq*, HMQC shows relationships to 1.35; COSY shows couplings to H_5 -axial, H_4 -axial, H_6); 1.69 (m, 2H; 1H includes H_4 -axial; linked by COSY to H_4 -*eq* at 1.15); 1H is CH of C_6 sidechain, with correlations to C_6 and sidechain methylenes); 1.5-1.25 (9H, includes: 1.35 m for H_5 -axial; multiple spin systems from sidechain CH_2 groups); 1.15 (m, 1H, C_4 -*eq*); 1.11 (d, 3H, 6-7, iPrSi); 1.09 (d, 3H, 6-7, iPrSi); 1.10 (m, 1H, CH), 1.05 (d, 3H, ~7, iPrSi); 1.00 (d, 3H, ~7, iPrSi); 0.96 and 0.93 (each d, 3H, J ~6.5, Me_2CHC_6); 0.89 (t, 3H, 4-5, Me); 0.63 (ddd, 13, 9, 5, H_6 , COSY to iPrCH at 1.7); GC-MS: single major peak at 28.17 min (269, [M-iPr]); ^{13}C δ 74.6, 39.2, 36.4, 32.2, 31.6, 29.6, 28.8, 27.6, 25.7, 24.8, 22.9, 22.0, 19.8, 18.6, 18.1, 17.8, 14.4, 13.8, 13.1; IR 2927, 2865 (s); 1464, 1382, 1068 cm^{-1} ; HRFAB calc for $\text{C}_{19}\text{H}_{39}\text{OSi}$ (M-H) $^+$: 311.2770; found 311.2783 (3.9 ppm); (M+H) $^+$ at 312.2818 also observed.

General procedure for tandem silylation/hydrosilylation: Into a solution of unsaturated alcohol (typically 1 mmol) in 6 mL anhydrous toluene was added diethylsilane or diphenylsilane (1.2 mmol). The solution was cooled to 0 °C and B(C₆F₅)₃ was added (typically 0.1-0.5 equiv) from a 0.2-0.3 M stock solution in anhydrous toluene, resulting in vigorous bubbling. Once the alkene had largely disappeared (TLC), the reaction was quenched with 10% aq. NaHCO₃ (30 mL). The resulting mixture was extracted with hexane (2 x 50 mL) and the crude products were purified by flash or column chromatography.

(3,5-*trans*)-1,1-Diethyl-3-hexyl-5-methyl-1-oxa-2-silane (2-Et)

Using the tandem procedure described above, alcohol **1** (0.34 g, 2.0 mmol) was reacted with diethylsilane (0.33 mL, 2.6 mmol). TLC indicated that the reaction was completed within 5 minutes. Column chromatography using 0-5% EA/hex as the eluting solvent afforded 0.24g (47%) of the silacyclohexane. A small portion of the product was purified by semi-preparative HPLC (21 x 250mm, 5 mL/minute of 1% EA/hex): R_f = 0.58 (5% EA/hex); ¹H δ 3.93-3.99(1H), 1.98-2.06(1H), 1.55-1.59(1H), 1.36-1.50(4H), 1.27(7H, m), 1.01(3H, d, 6.7), 0.94(3H, t, 6.4), 0.94(3H, t, 7.9), 0.88(3H, t, 6.8), 0.72(1H, ddd, 1.4, 4.6, 14.5), 0.57(4H, q, 7.5), 0.33(1H, dd, 10, 14.5); ¹³C δ 72.0, 41.4, 37.3, 31.9, 29.4, 26.3, 25.7, 24.1, 22.6, 17.7, 14.1, 7.6, 6.9, 6.7, 6.5; IR: 2953, 2925, 2874, 1458, 1413, 1156, 1047, 1003, 762 cm⁻¹. HR-FABMS calcd. for C₁₅H₃₂O:[M+H]⁺: 257.2301; Found: 257.2300

(3,5-*trans*)-1,1-Diphenyl-3-hexyl-5-methyl-1-oxa-2-silane (2-Ph) was prepared (0.59 g, 84%) from alcohol **1** (0.34 g, 2.0 mmol) and diphenylsilane (0.41 mL, 2.2 mmol) using the tandem procedure described above. The reaction was conducted for 10 min and the crude product was purified by gradient flash chromatography (0-5% EA/hex). A small portion of the product was purified by semi-preparative HPLC (21x250 mm, 5 mL/min of 1% EA/hex). The major product was assigned by comparison with **1-Pr**: R_f = 0.23 (2% EA/hex); ¹H δ 7.51-7.61(5H), 7.30-7.42(5H), 4.16-4.21(1H), 2.24-2.28(1H), 1.27-1.63(15H), 1.03(3H, d, 6.8), 0.87(3H, t, 6.8), 0.79-0.95(2H); ¹³C δ 137.26, 137.24, 134.2, 134.1, 129.63, 129.57, 127.78, 127.73, 72.2, 41.6, 37.5, 31.8, 29.2, 26.1, 25.0, 24.8, 22.6, 19.0, 14.1; IR: 3068, 3049, 3000, 2954, 2925, 2856, 1454, 1428, 1151, 1116, 1041, 997, 821, 756, 731, 699 cm⁻¹; HR FABMS calcd. for C₂₃H₃₃OSi [MH]⁺: 353.2307; found: 353.2300 (1.7 ppm).

(3 β ,5 α ,6 α) and (3 α ,5 α ,6 α) **2,1-Benzoxasilin, octahydro-1,1-diethyl-3-hexyl (10-Et)**: Using the tandem procedure described above, alcohol **9** (0.21g, 1.00 mmol) was reacted with diethylsilane (0.17 mL, 1.3 mmol) for 30 min, to furnish, after standard workup and chromatography, 0.11 g (39%) of the oxasilane. A small portion of the product was purified by semi-preparative HPLC (21x250 mm, 5 mL/min of 1% EA/hex) to furnish a 5:1 mixture of C₃ epimers. Traces of several minor components were visible (RI detection) just before elution of the major product: R_f = 0.34 (2% EA/hex); ¹H δ 3.87(1H, m), 1.95-1.99(1H), 1.61-1.78(3H), 1.27-1.52(17H), 1.13(1H, q, 5.2), 0.97(3H, t, 8.0), 0.95(3H, t, 8.0), 0.88(3H, t, 6.8), 0.69-0.78(1H), 0.55-0.66(3H). ¹³C δ 70.0, 38.6, 38.1, 33.5, 31.9, 31.5, 29.4, 26.0, 25.4, 25.0, 24.7, 24.5, 22.7, 14.1, 6.8, 6.7, 6.2; IR: 2852, 1459, 1413, 1377, 1237, 1187, 1127, 1097, 1059, 1004, 972, 934, 802, 724 cm⁻¹; MS: HR-FAB: calcd. for C₁₈H₃₆O:[M-H]⁺: 295.2456; found: 295.2448. The stereochemistry of the major product was assigned in analogy with **10-Ph** (below) and by the chemical shifts for the axial H₃-axial (3.7 ppm) in the trans/cis isomer (major) vs. the equatorial H₃ (3.9 ppm) in the cis/cis isomer (minor).

(3 β ,5 α ,6 α) and (3 α ,5 α ,6 α)-**2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl (10-Ph)**

Using the tandem procedure described above, alkenol **9** (0.22g, 1.1 mmol) was reacted with diphenylsilane (0.21 mL, 1.1 mmol) for 1 h, to furnish, after standard workup and a gradient flash chromatography (0-5% EA/hex), 0.30 g (73%) of the cyclic oxasilane as a 1:5 mixture (NMR) of the *cis/cis* and *trans/cis* isomers, differing in the stereochemistry at C₃. R_f = 0.50 (2% EA/hex); HR FABMS calc. for C₂₆H₃₇OSi [MH]⁺: 393.2613; found: 393.2629 (3.8 ppm). A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min of 1% EA/hex); the minor product eluted first.

cis/cis (3 α ,5 α ,6 α)- (minor) ¹H δ 7.65-7.69(2H), 7.49-7.51(2H), 7.28-7.45(6H), 3.84-3.89(1H; COSY correlation with spin systems at δ 2.1, 1.96; weak correlation with δ 1.5; nOe observed to 2.1 and 1.2); 2.05-2.10(1H, correlates only with δ 1.96), 1.93-1.99(1H, correlates with δ 3.9, 2.05, 1.2), 1.42-1.71(12H), 1.19-1.39(10H), 1.2 (1H, obscured t or dd, correlates with 1.97, 1.7); 0.90(3H, t, 6.8); ¹³C δ 135.6, 134.5, 134.3, 129.6, 129.5, 127.9, 127.5, 74.7, 38.8, 35.3, 34.5, 33.5, 32.0, 29.4, 27.9, 25.4, 22.9, 22.7, 22.3, 21.2, 14.2; IR 3068, 3048, 3000, 2925, 2855,

1447, 1428, 1142, 1116, 1092, 1055, 1009, 970, 924, 801, 736, 710, 699 cm^{-1} . HRFAB calc. for $\text{C}_{26}\text{H}_{37}\text{OSi}(\text{MH})^+$: 393.2613; found: 393.2629 (3.8 ppm).

trans,cis ($3\beta,5\alpha,6\alpha$) (major) ^1H δ 7.65 (m, 2H; nOe to 1.7), 7.55 (2H; modest nOe to 4.3), 7.31-7.41(6H), 4.31(1H, m, H_3 ; correlates with 1.6, 1.5; significant noE to d 7.7, 2.1; this proton appears to be significantly deshielded by the edge of the neighboring arene; this assumption is supported by the observation of mutual nOes involving the arene as well as by MM2 calculations; 2.20 (m, 1H; COSY crosspeaks wth 2.1, 1.5-1.6; nOE to 1.73, 1.5, 1.4), 2.07 (ddd, 1H, J values estimated as 13-14, 8, 3-4; COSY with 2.2, 1.5; nOE to peaks at d 4.3, 1.4), 1.83(m, 1H; correlates to 1.45; nOe with d 1.5, 1.3), 1.73(dt, 1H; weak COSY with 1.83; nOE to 2.2, 1.5), 1.17-1.48(20H), 0.87(3H, t, 6.8); ^{13}C δ 137.8, 136.7, 134.6, 134.3, 134.2, 129.5, 129.3, 127.8, 127.7, 127.6, 72.4, 37.7, 37.6, 32.6, 31.8, 29.5, 29.3, 26.1, 25.3, 24.8, 24.5, 24.0, 22.6, 14.1; IR 3068, 3048, 3022, 2999, 2920, 2851, 1590, 1486, 1447, 1428, 1376, 1187, 1114, 1057, 997, 938, 916, 821, 801, 772, 699 cm^{-1} .

(3,6-*trans* and 3,6-*cis*- **1,1-Diethyl-3-hexyl-6-methyl-2-oxa-1-silane** (*trans*- and *cis*-**12-Et**):

Using the tandem procedure describe above, alkenol **11** (0.34 g, 2.0 mmol) was reacted with Et_2SiH_2 (0.33 mL, 2.6 mmol) for 5 minutes to furnish, following standard workup and chromatography (0-5% EA/hex), a 2.7: 1 mixture of *trans*- and *cis*-**12-Et** (81.9 mg, 16%): $R_f = 0.41$ (2% EA/hex); HREIMS calc. for $\text{C}_{15}\text{H}_{31}\text{OSi}(\text{M-H})^+$: 255.2244; found 255.2142 (0.9 ppm). A small portion of the product was purified by semi-preparative HPLC (21 x 250 mm, 5 mL/min 1% EA/hex); the major (*trans*) and minor (*cis*) isomers elute at 16 and 17 min, respectively. The assignment of *cis*- and *trans* oxasilanes was based upon the upfield ^1H chemical shift for the axial H_3 .

trans-**12**: ^1H δ 3.60-3.65(1H), 1.83-1.89(1H), 1.61-1.66(1H), 1.20-1.47(12H), 0.99(3H, t, 7.9), 0.98(3H, t, 7.9), 0.91(3H, t, 6.8), 0.88(3H, t, J-6.8), 0.49-0.84(4H); ^{13}C δ 74.5, 38.7, 35.8, 32.7, 31.9, 29.4, 25.5, 22.7, 17.5, 15.7, 14.1, 6.7, 5.0, 1.7; IR 2954, 2927, 2876, 2858, 1461, 1377, 1236, 1087, 1042, 1014, 836, 724 cm^{-1} .

cis-**12**: ^1H δ 3.70-3.76(1H), 1.82-1.90(1H), 1.62-1.69(1H), 1.24-1.56(14H), 1.02(3H, d, 7.6), 0.97(3H, t, 7.9), 0.96(3H, t, 7.9), 0.88(3H, t, 6.8), 0.51-0.74(4H); ^{13}C δ 74.2, 38.1, 31.9, 30.8, 29.8, 29.3, 25.8, 22.7, 15.0, 14.4, 14.1, 6.8, 6.3, 4.2, 4.1; IR 2953, 2927, 2874, 1460, 1413, 1377, 1235, 1161, 1138, 1088, 1044, 1005 cm^{-1} .

(*trans*) and (*cis*)- **1,1-Diphenyl-3-hexyl-6-methyl-1-oxa-2-silacyclohexane** (*trans*- and *cis*-**12-Ph**). Using the tandem procedure described above, alcohol **11** (0.34g, 2.0 mmol) was reacted with Ph₂SiH₂ (0.41 mL, 2.2 mmol) for 1 h. The crude products were subjected to column chromatography using 0-5% EA/hex as the eluting solvent to afford 0.17g (24%) of the oxasilacyclohexane. A small portion of the product was further purified by semi-preparative HPLC (21x250mm, 1% EA/hexane, 5 mL/min), which partially resolved the major and minor isomers. The predominant isomer was assigned as *trans* on the basis of the 3.85 ppm chemical shift for the axial H₃: R_f =0.32 (2% EA/hex); ¹H (mixture of diastereomers) δ 7.65-7.68(m), 7.53-7.55(m), 7.30-7.44(m) 4.02-4.07(m), 3.85-3.90(m), 1.94-2.04(m), 1.78-1.86(m), 1.39-1.74(m), 1.13(d, 3H, 7.2), 1.07(d, 3H, 8), 0.87-0.92(m); ¹³C (mixture of two diastereomers) δ 136.0, 135.1, 134.5, 134.4, 134.3, 129.8, 129.6, 129.5, 127.9, 127.8, 127.7, 127.6, 75.8, 74.8, 38.8, 38.6, 35.9, 32.3, 31.9, 30.2, 30.1, 29.39, 29.36, 25.5, 25.4, 22.7, 19.4, 16.3, 15.3, 14.1, 13.9; IR: 3069, 3048, 2927, 2857, 1457, 1428, 1117, 1042, 987, 933, 736, 700 cm⁻¹; HRFAB calc. for C₂₃H₂₃OSi (M+H)⁺: 353.2300; found: 353.2293 (2.1 ppm).

(3,6-*trans*) and (3,6-*cis*)-**1,1-Diethyl-3-hexyl-6-methyl-2-oxa-1-silapane** (*trans*- and *cis*-**14-Et**). Using the tandem procedure described above, alcohol **13** (0.360 g, 1.95 mmol) was reacted with diethylsilane (0.28 mL, 2.2 mmol) for 5 min, to furnish, following standard workup and chromatography, 0.29 g (55%) of a 38:62 mixture of 3,6-*trans*- and 3,6-*cis*-oxasilacycloheptanes accompanied by 0.16 g of an unknown side product. A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min 1% EA/hex); the major and minor diastereomers eluting at 17.0 and 18.0 min, respectively: R_f = 0.2 (hexane); IR: 2982, 2953, 2925, 2874, 1461, 1377, 1237, 1090, 1007, 850, 757 cm⁻¹; HREIMS calcd. for C₁₆H₃₄OSi:[M-C₂H₅]⁺: 241.1764; found: 241.1986.

Diastereomer I (*trans*, minor): ¹H δ 3.59 (td, 1H, 8.6, 4), 1.73(m, 3H), 1.26-1.48(11H), 1.08 (m, 1H), 0.99(3H, d, 6.6), 0.95(3H, t, 7.9), 0.94(3H, t, 7.9), 0.88(3H, t, 6.8), 0.69 (dt, 1H, 15, 2) 1H), 0.48-0.63(5H). ¹³C δ 75.0, 39.9, 39.3, 38.4, 32.0, 31.0, 29.3, 28.8, 26.1, 23.3, 22.7, 14.1, 7.00, 6.8, 6.1, 5.9

Diastereomer 2 ((*cis*, major): ^1H δ 3.76 (m, 1H), 1.96 (m, 1H), 1.34-1.73(17H), 1.01(3H, d, 6.7), 0.94(6H, t, 7.9), 0.88(3H, t, 6.8), 0.73 (m,1H), 0.51-0.63(5H). ^{13}C δ 73.8, 38.4, 35.2, 34.6, 31.9, 29.44, 29.37, 26.2, 25.6, 22.7, 22.1, 14.1, 7.3, 6.9, 6.8, 6.3

(*trans*-)-**1,1-Diethyl-5-methyl-3-phenyl-2-oxa-1-silane** (*trans*-**16-Et**) was prepared as a single diastereomer from **15** (0.32g, 2.0 mmol) and Et_2SiH_2 (0.33 mL, 2.6 mmol) using procedure “B” described above except that the reaction temperature was held between 5 and 10 °C. The product was assigned as the *trans*-isomer in analogy with **2-Pr**; this was confirmed by a correlation via diol **21** (vida infra). The crude product was purified by column chromatography (0-5% EA/Hex) to furnish 0.25 g of a diethylsiloxysiloxane byproduct followed by 0.25 g (51%) **16-Et**, predominantly as the *trans* diastereomer. A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min of 1% EA/hex).

16-Et: R_f = 0.2 (hexane) or 0.4 in 5% EA/hex); ^1H δ 7.24-7.28(1H), 7.34-7.40(4H), 5.19(1H, dd, 3.9, 7.5), 2.19 (m, 1H), 1.85(1H, ddd, 14.1, 7.5, 3), 1.73(1H, ddd, 14.1, 7.1, 4), 1.17(3H, d, 6.9), 1.05(3H, t, 7.9), 1.05(3H, t, 7.9), 0.94(1H, dd, 5.7, 12.2), 0.74(2H, q, 7.9), 0.69(2H, q, 7.9), 0.55(1H, dd, 7.0, 14.7); ^{13}C δ 145.7, 128.1, 126.6, 125.4, 71.9, 43.7, 25.0, 23.5, 16.5, 8.0, 7.3, 6.7, 6.6; IR: 3087, 3063, 3028, 2953, 2874, 1494, 1453, 1412, 1377, 1354, 1236, 1207, 1137, 1088, 1066, 1005, 907, 853, 809, 737, 699 cm^{-1} ; HR-FABMS calcd. for $\text{C}_{15}\text{H}_{24}\text{OSi}$: $[\text{M}-\text{H}]^+$: 247.1517; found: 247.1527.

Byproduct: R_f = 0.8 in 5% EA/hex. The byproduct displayed major ions at 343 (M-H) $^+$ and 189 (M- Si(Et) $_2$ OSi(Et) $_2$ H) $^+$ in the GC/MS spectra, and was tentatively assigned as 1,1-diethyl-1-(diethylsiloxy)-2-methyl-4-phenylbutyl silane. This assignment was supported by the lack of a carbinol HC and the presence of silane (4.5 ppm, narrow pentet) and multiple Et_2Si spin systems (1.1-0.87 for methyl groups; 0.7-0.45 for ethyl) in a complicated ^1H NMR spectrum. ^{13}C : 143.1, 128.4, 128.3, 125.5, 42.7, 33.7, 28.6, 22.9, 22.8, 7.4, 7.3, 7.1, 6.8, 6.6. Oxidative cleavage (Tamao oxidation, below) furnished 2-methyl-4-phenyl-1-butanol: xii R_f = 0.3 (20% EA/hex); ^1H δ 7.30 (app t, 2H, 7); 7.22-7.18 (3H); 3.54 (dd, 1H, ABX, 10.8, 6); 3.48 (dd, 1H, ABX, 10.8 6.4); 2.73 (ddd, ABXY, 1H, 13.6, 10, 5.6); 2.62 (ddd, ABXY, 13.6, 10, 6); 1.79 (m, 1H); 1.68 (apparent hextet, 1H, 6-7); 1.58 (1H, bs, OH); 1.46 (m, 1H); 1.008 (d, 3H, 7.2). IR (ATR crystal) 3346 (s, broad), 2926, 2873, 1454, 1037 cm^{-1} ; HREI: calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: $[\text{M}]^+$ 164.1204; Found: 164.1204 (1.6 ppm).

Diethyl (2-methylnon-1-en-3-oxy) silane (18-Et): Attempted one-pot reaction of 2-methyl non-1-en-3-ol (**17**, 0.22 g, 1.4 mmol) with diethylsilane (0.20 mL, 1.1 equiv) and $B(C_6F_5)_3$ (0.2 g, n toluene, ~0.4 mmol) as described for the synthesis of **2-Et** furnished the corresponding diethylsilyl ether, **18-Et** as an inseparable mixture with small amounts of one or more siloxanes: $R_f = 0.8$ (hexane); 1H : δ 4.85 (bs, 1H); 4.75 (bs, 1H); 4.51 (app pentet, 2.4, residual diethylsilane); 4.16 (t, 1H, 6.4); 1.68 (s, 3H); 1.45 (s, 0.7H, residual Si-H); 1.5 (m, 2H), 1.33-1.18 (8H); 1.0 - 0.92 (19 H, including some silane); 0.88 (t, 3H); 0.62 (dq, 4H, 7, 2); 0.53 (m, 8H, residual silane and siloxane); ^{13}C : δ 147.4; 110.49; 76.71, 36.02, 31.9, 29.4, 25.5, 22.7, 17.1, 14.1, 7.47, 7.24, 6.97, 6.64, 6.61, 6.55; IR 2954, 2116, 1450 cm^{-1} . HRMS was attempted but gave no recognizable fragments.

Oxidation to diols

Tamao oxidation^{xiii} (illustrated for (2R*,5S*)-2-methylundecane-1,5-diol (19): 135 mg (0.50 mmol) of **14-Et** was reacted with KF (0.058 g, 2 eq), $KHCO_3$ (0.100 g, 2 eq), 30% H_2O_2 (1 mL, 20 eq, ca. 9M in H_2O) in MeOH/THF for 48 h to afford 0.030 g (30%) of diol **19** as an inseparable mixture of diastereomers. $R_f = 0.2$ (30% EA/hex); 1H δ 3.58 (m, 1H); 3.47 (t, 2H, 6; or bd, 1H, ~6, depending upon sample concentration), 2.3 (broad, 2H, varies with concentration); 0.89 (app t, 3H, 8); 0.857 (app t, 3H, 8); 1.8-1.2 (15H); 0.85-0.92 (6H); ^{13}C δ 72.4, 72.0, 67.8, 67.6, 37.53, 37.49, 35.8, 35.3, 34.3, 34.0, 31.8, 29.3, 28.9, 28.6, 25.7, 25.6, 22.6, 20.8, 16.8, 16.4, 14.1; The major diastereomer was assigned as 2R*,5S* based upon comparison with ^{13}C data reported for a similar diol (major: 71.8, 67.8 ppm; minor 72.3, 67.6 ppm.^{xiv} IR 3330 (b, OH), 2926, 2856, 1458, 1030 cm^{-1} ; HRFAB calc. For $C_{12}H_{27}O_2$ $[MH]^+$: 203.2011; found: 203.2014 (1.3 ppm).

Oxidation of 88 mg (0.33 mmol) of the major (2nd eluting isomer) of **14-Et** using the Woerpel procedure described below afforded 36.8 mg (56%) of **19**. Spectral details were identical to those reported above.

Woerpel oxidation:^{xv} 2-(2-Hydroxyoctyl)-cyclohexanol (20): To a solution of *tert*-butyl hydroperoxide (0.73 mL, 5-6M in decane) in 3 mL DMF at 0 $^{\circ}C$ was added cesium hydroxide

(0.52g, 3.1 mmol). The reaction mixture was allowed to warm to 25 °C, whereupon a solution of oxasilane **10-Ph** (0.10g, 0.26 mmol) in 2 mL DMF was added dropwise. After 10 minutes, tetrabutylammonium fluoride (1.3 mL, 1M in THF) was added. The reaction solution was stirred at RT for 2 h and then quenched with 10 mL of 10% aq. sodium bisulfite. The mixture was extracted with ether (2 x 20 mL) and the combined organic layers were dried and concentrated. The residue was subject to column chromatography using 40% EA/hex as eluting solvent to afford 22.8 mg (38%) of diol **20**: R_f = 0.50 (50% EA/hex); IR (same except where noted): 3329-31, 2927-8, 2856, 1450, 1071 (diast 2), 1039 (diast 1), 976 cm^{-1} ; HRMS calc. for $\text{C}_{14}\text{H}_{29}\text{O}_2$ (MH)⁺: 229.2168; found: 229.2159 (3.5 ppm).

Diastereomer 1: ^1H δ 3.95(1H, m), 3.73-3.78(1H), 2.19(2H, s), 1.65-1.72(4H), 1.48-1.61(3H), 1.29-1.47(14H), 0.88(3H, t, 6.6) ^{13}C δ 69.2, 69.1, 40.0, 38.1, 38.0, 33.1, 31.8, 29.3, 27.1, 25.8, 25.4, 22.6, 20.5, 14.1

Diastereomer 2: ^1H δ 3.90-3.93(1H), 3.65-3.70(1H), 1.72-1.75(1H), 1.25-1.61(18H), 0.88(3H, t, 6.6); ^{13}C δ 70.9, 70.0, 39.4, 39.1, 38.7, 32.4, 31.8, 29.3, 28.2, 25.6, 24.3, 22.6, 21.4, 14.1 MS:

(1R*,3S*) 3-Methyl-1-phenyl-1,4-butanediol (21) was prepared in 69% by oxidation of oxasilane **16-Et** using the Woerpel procedure described above: R_f = 0.2 (40% EA/hex); The product was assigned by comparison with literature reports.^{xvi} R_f = 0.2 (40% EA/hex); ^1H δ 4.89 (dd, 1H, 7.6, 4.7); 3.57 (dd, ABX, 1H, 10.4, 4.4); 3.52 (dd, ABX, 1H, 10.4, 6.4); 1.9-1.7 (3-4H, includes both ABX and a multiplet); 0.97 (d, 3H, 6.8); ^{13}C δ 144.7, 128.4, 127.4, 125.8, 71.8, 67.9, 43.5, 32.2, 17.2.

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B(C₆F₅)₃-promoted tandem silylation and intramolecular hydrosilylation: diastereoselective synthesis of oxasilinanes and oxasilepanes

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Supporting Information: ¹H and ¹³C NMR spectra

Alcohols	pages
2-Methyldec-1-en-4-ol (1): ¹ H, ¹³ C	3-4
2-Phenyldec-1-en-4-ol (3): ¹ H, ¹³ C	5-6
1-Cyclobutenyloctan-2-ol (5): ¹ H, ¹³ C	7-8
2-Methyl-2-dodecen-6-ol (7): ¹ H, ¹³ C	9-10
1-Cyclohexenyloctan-2-ol (9): ¹ H, ¹³ C	11-12
(<i>E,Z</i>)-Undec-2-en-5-ol (11): ¹ H, ¹³ C	13-14
2-Methylundec-1-en-5-ol (13): ¹ H, ¹³ C	15-16
3-Methyl-1-phenylbut-3-en-1-ol (15): ¹ H, ¹³ C	17-18
2-Methylnon-1-en-3-ol (17): ¹ H, ¹³ C	19-20

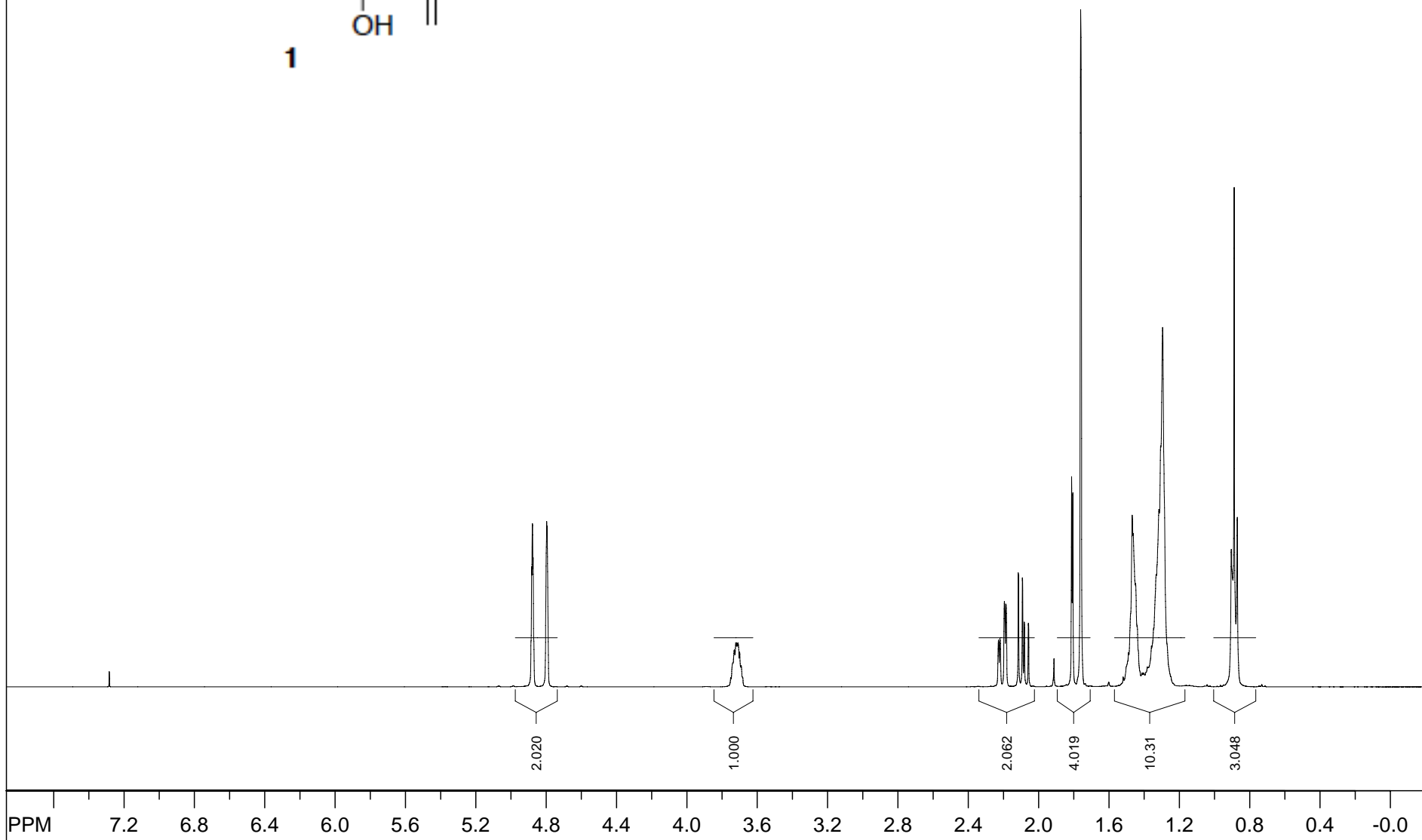
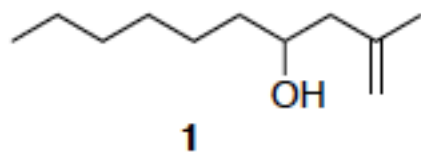
Alkoxysilanes	pages
Diisopropyl-(2-methyldec-1-en-4-oxy)silane (1Pr): ¹ H, ¹³ C	21-22
Diisopropyl-(2-phenyldec-1-en-4-oxy) silane (3-Pr): ¹ H, ¹³ C	23-24
Diisopropyl-(1-cyclobutenyloctyl-3-oxy)silane (5-Pr): ¹ H, ¹³ C	25-26
Diethyl-(2-methylnon-1-en-3-oxy) silane (18-Et): ¹ H, ¹³ C	27-28

Cyclic Siloxanes	pages
(<i>trans</i>)-1,1-Diethyl-3-hexyl-5-methyl-2,1-oxasilinane (<i>trans</i> - 2-Et): ¹ H, ¹³ C	29-30
(<i>trans</i>)-1,1-Diphenyl-3-hexyl-5-methyl-2,1-oxasilinane (<i>trans</i> - 2-Ph): ¹ H, ¹³ C	31-32
(<i>trans</i>)-1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane (<i>trans</i> - 2-Pr): ¹ H, ¹³ C	33-34
(<i>trans</i>)-1,1-Diisopropyl-3-hexyl-5-phenyl-2,1-oxasilinane (<i>trans</i> - 4-Pr): ¹ H, ¹³ C	35-36
1,1-Diisopropyl-3-hexyl-2-oxa-1-sila[4.2.0] bicyclooctane (6-Pr):	
(<i>3α,5α,6α</i>)- 6-Pr : ¹ H, ¹³ C	37-38
(<i>3β,5α,6α</i>)- 6-Pr : ¹ H, ¹³ C	39-40
(<i>trans</i>)-1,1-Diisopropyl-3-hexyl-6-isopropyl-2,1-oxasilinane (<i>trans</i> - 8-Pr): ¹ H, ¹³ C	41-42
2,1-Benzoxasilin, octahydro-1,1-diethyl-3-hexyl (10-Et)	
(<i>3β,5α,6α</i>) and (<i>3α,5α,6α</i>)- 10Et : ¹ H, ¹³ C	43-44
(<i>3β,5α,6α</i>)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl (10-Ph)	
(<i>3β,5α,6α</i>)-(10-Ph): ¹ H, ¹³ C	45-46
(<i>3α,5α,6α</i>)-(10-Ph): ¹ H, ¹³ C	47-48
(<i>trans</i>)-1,1-Diethyl-3-hexyl-6-methyl-2,1-oxasilinane (12-Et): ¹ H, ¹³ C	49-50

(<i>trans</i>)-1,1-Diphenyl-3-hexyl-6-methyl-2,1-oxasilinane (12-Ph): ^1H , ^{13}C	51-52
1,1-Diethyl-3-hexyl-6-methyl-2-oxa-1-silepane (14-Et): (<i>trans</i>)- 14-Et : ^1H	53
(<i>cis</i>)- 14-Et : ^1H , ^{13}C (mixture)	54-55
(3,5- <i>trans</i>)-1,1-Diethyl-5-methyl-3-phenyl-2,1-oxasilinane (16-Et): ^1H , ^{13}C	56-57

<u>Diols</u>	<u>pages</u>
2-Methylundecane-1,5-diol (19): ^1H , ^{13}C	58-59
2-(2-Hydroxyoctyl)-cyclohexanol (20): diastereomer 1: ^1H , ^{13}C	60-61
diastereomer 2: ^1H , ^{13}C	62-63
3-Methyl-1-phenyl-1,4-butanediol (21): ^1H , ^{13}C	64-65

SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\More spectra\cx-6-24\1\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

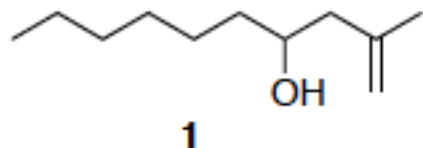
freq. of 0 ppm: 400.130000 MHz

processed size: 32768 complex points

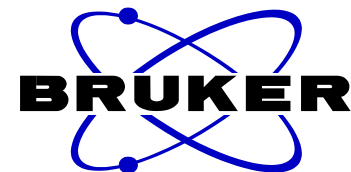
LB: 0.300 GB: 0.0000

Hz/cm: 129.722 ppm/cm: 0.32420

13C



143.08
 113.59
 77.52
 77.20
 76.88
 68.81
 46.39
 37.30
 32.01
 29.54
 25.87
 22.79
 22.56
 14.26



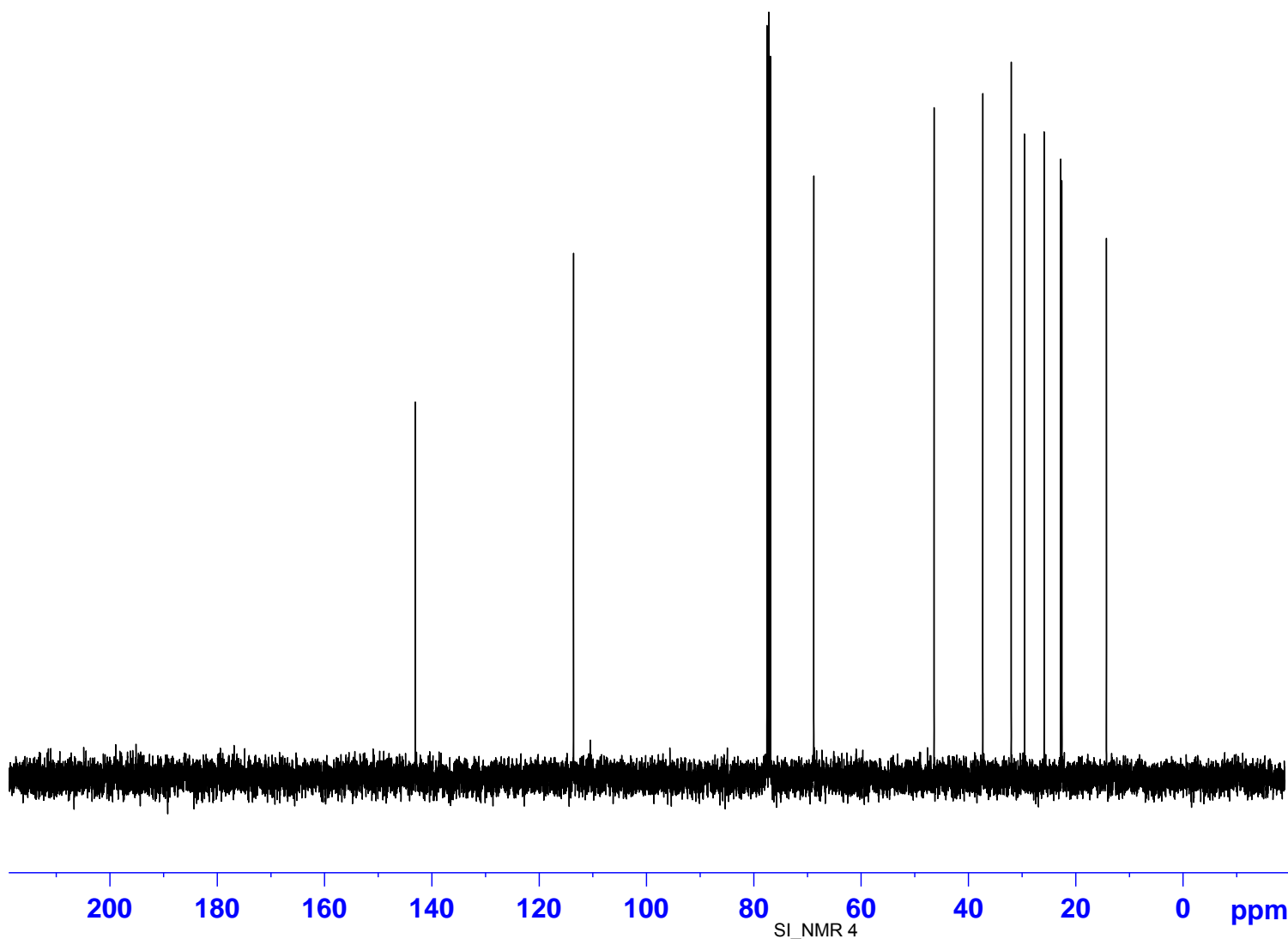
Current Data Parameters
 NAME cx-6-24
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20100805
 Time 16.44
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 33
 DS 4
 SWH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 812.7
 DW 20.850 usec
 DE 6.50 usec
 TE 295.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

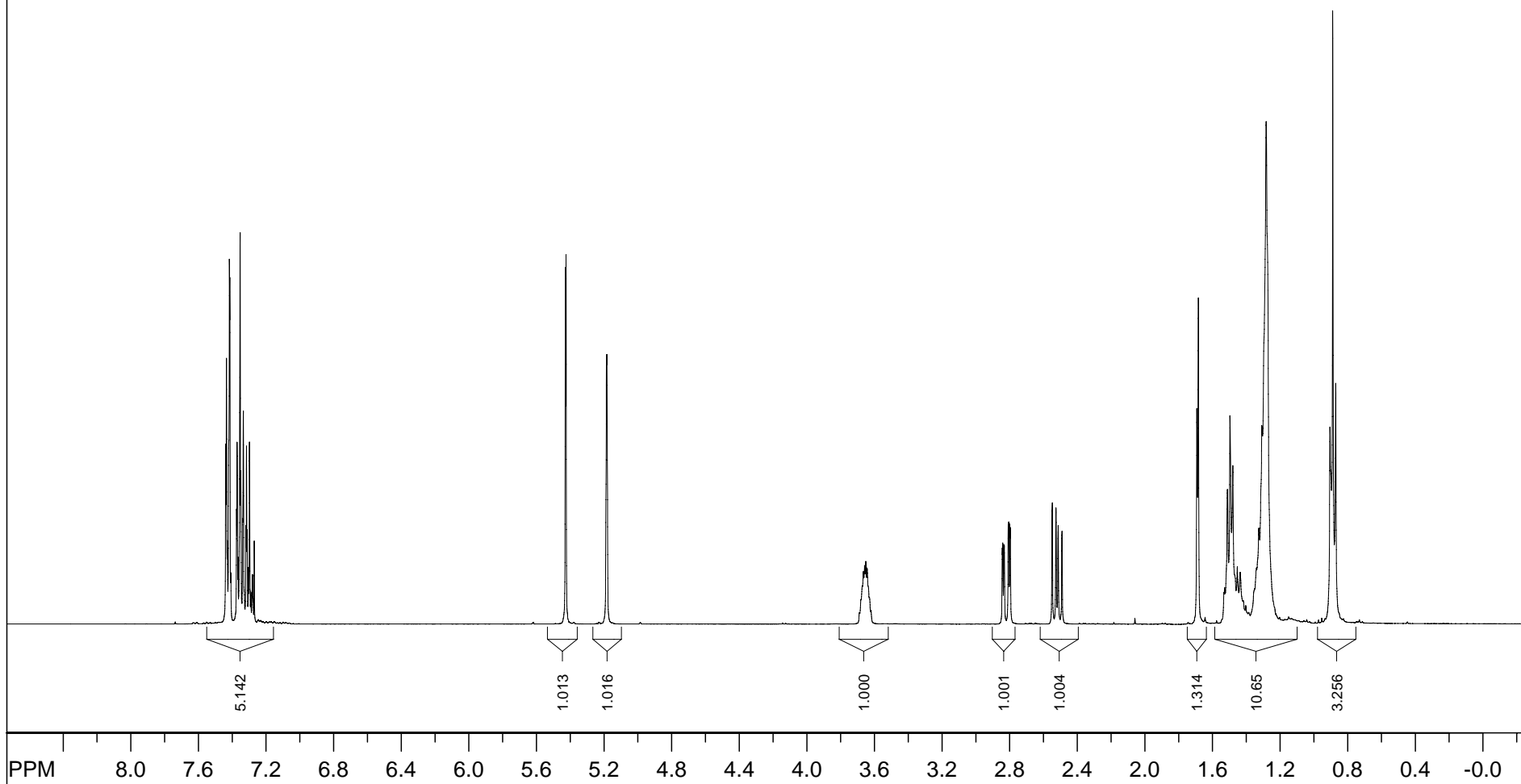
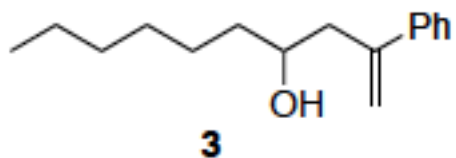
==== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.50 dB
 SFO1 100.6228298 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 70.00 usec
 PL2 -3.35 dB
 PL12 13.34 dB
 PL13 13.34 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127525 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-431\fid expt: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

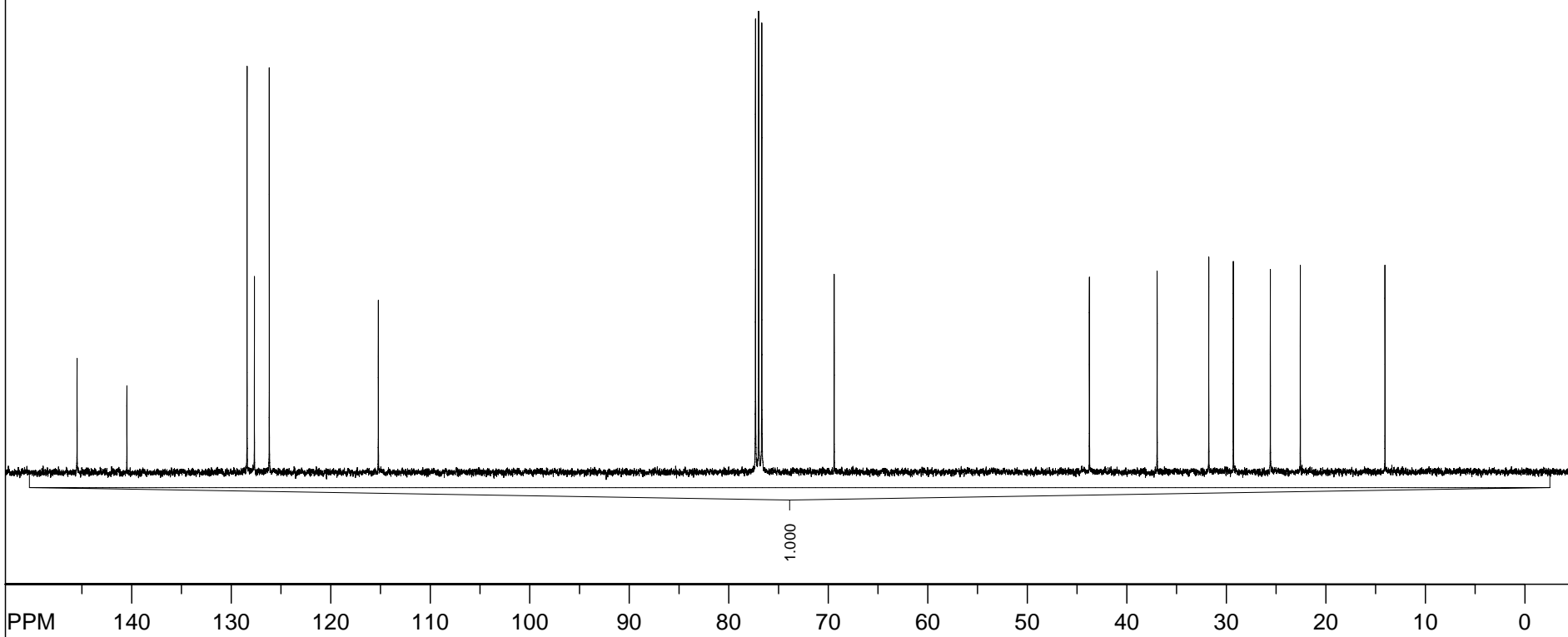
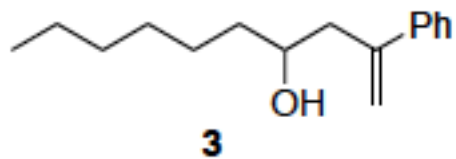
freq. of 0 ppm: 400.130006 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 144.396 ppm/cm: 0.36087

Spi 100.612775 MHz



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-43\2\fid exp: <zggp30>

transmitter freq.: 100.622830 MHz

time domain size: 65536 points

width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt

number of scans: 388

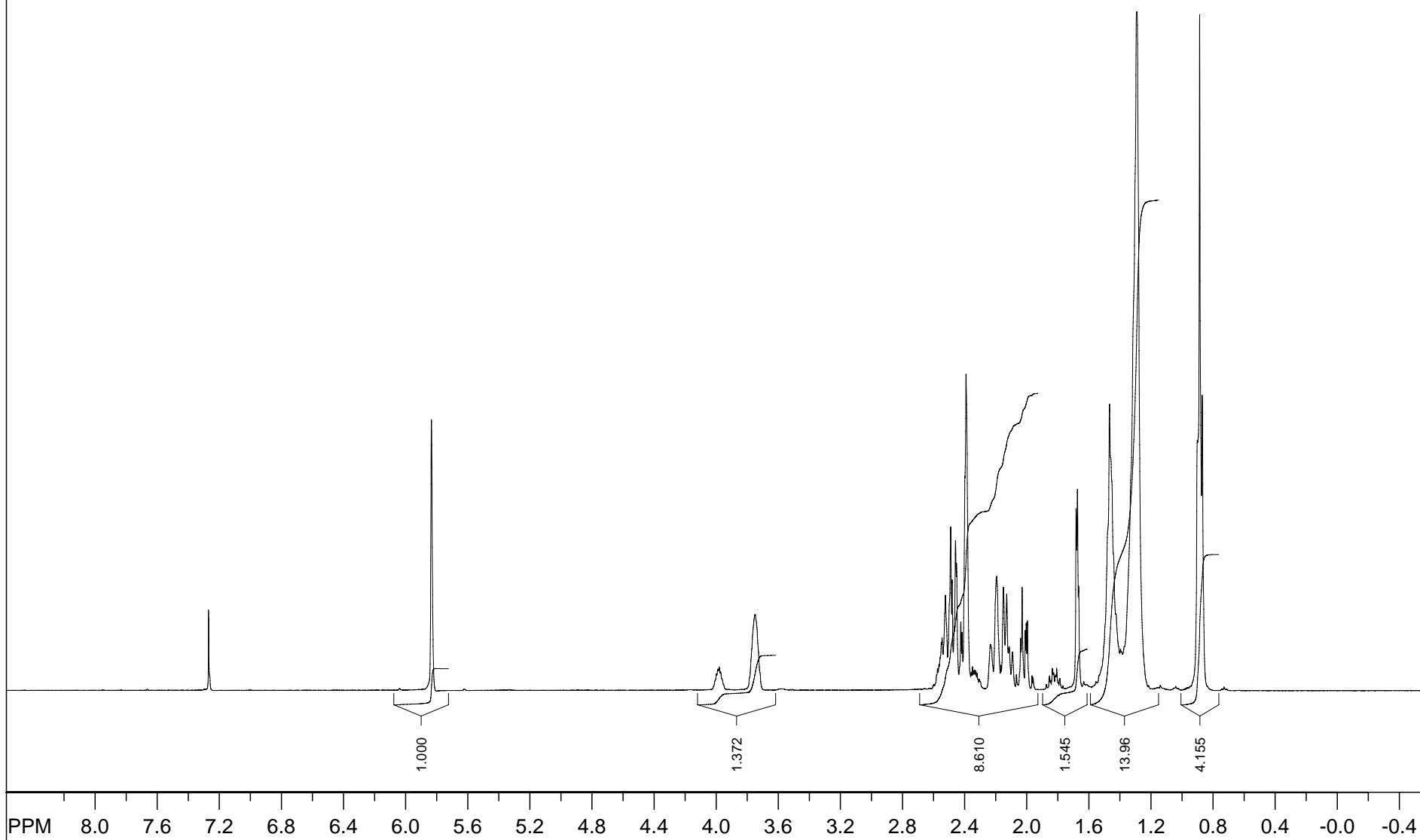
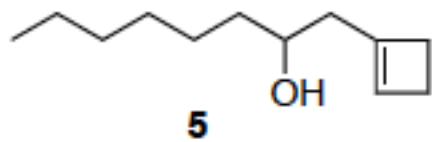
freq. of 0 ppm: 100.612775 MHz

processed size: 65536 complex points

LB: 1.000 GB: 0.0000

Hz/cm: 636.391 ppm/cm: 6.32451

SpinW



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-62\1\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

freq. of 0 ppm: 400.130006 MHz

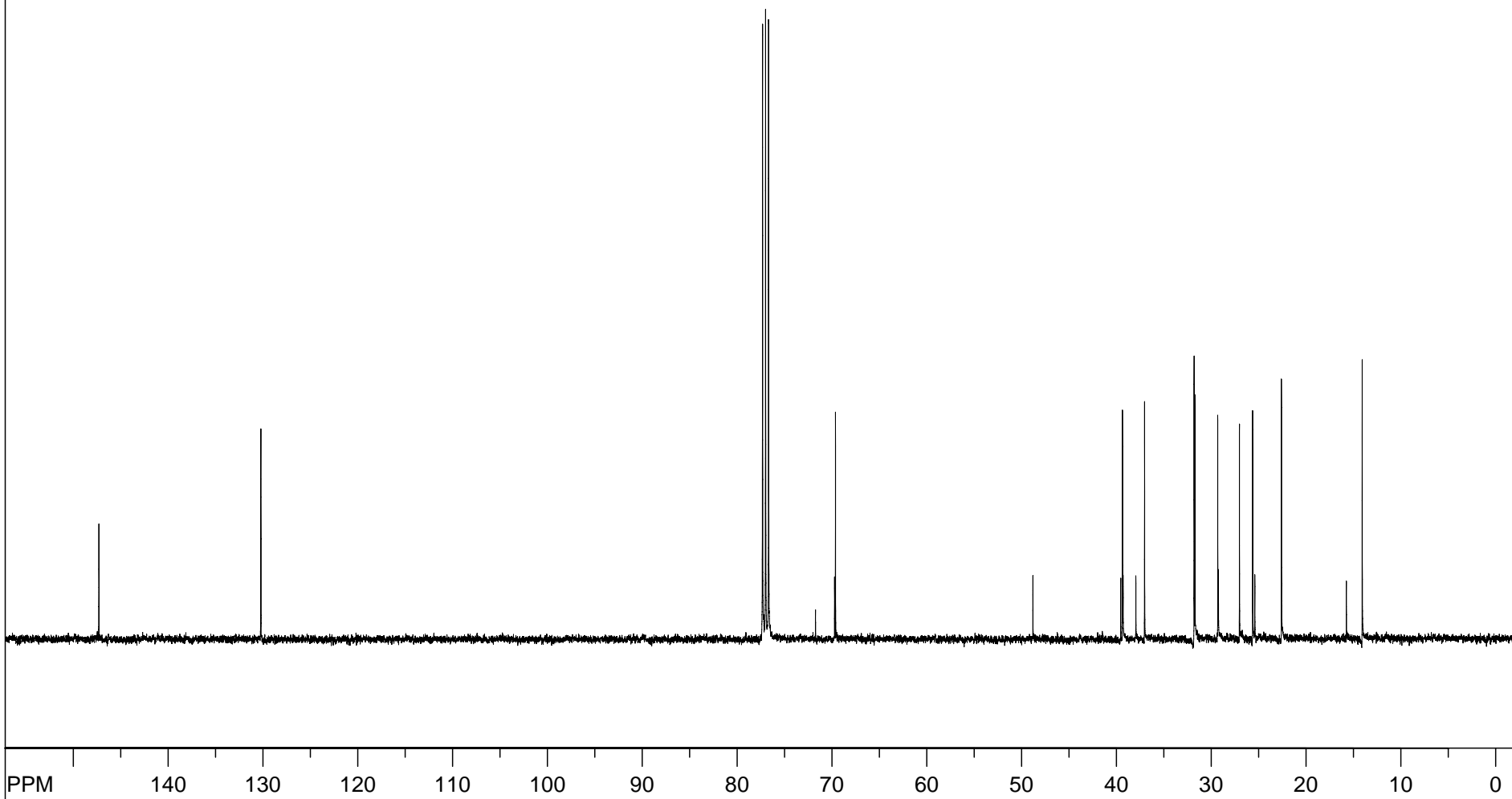
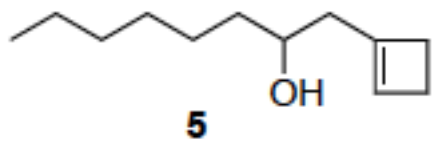
processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 146.733 ppm/cm: 0.36671

SI_NMR 7

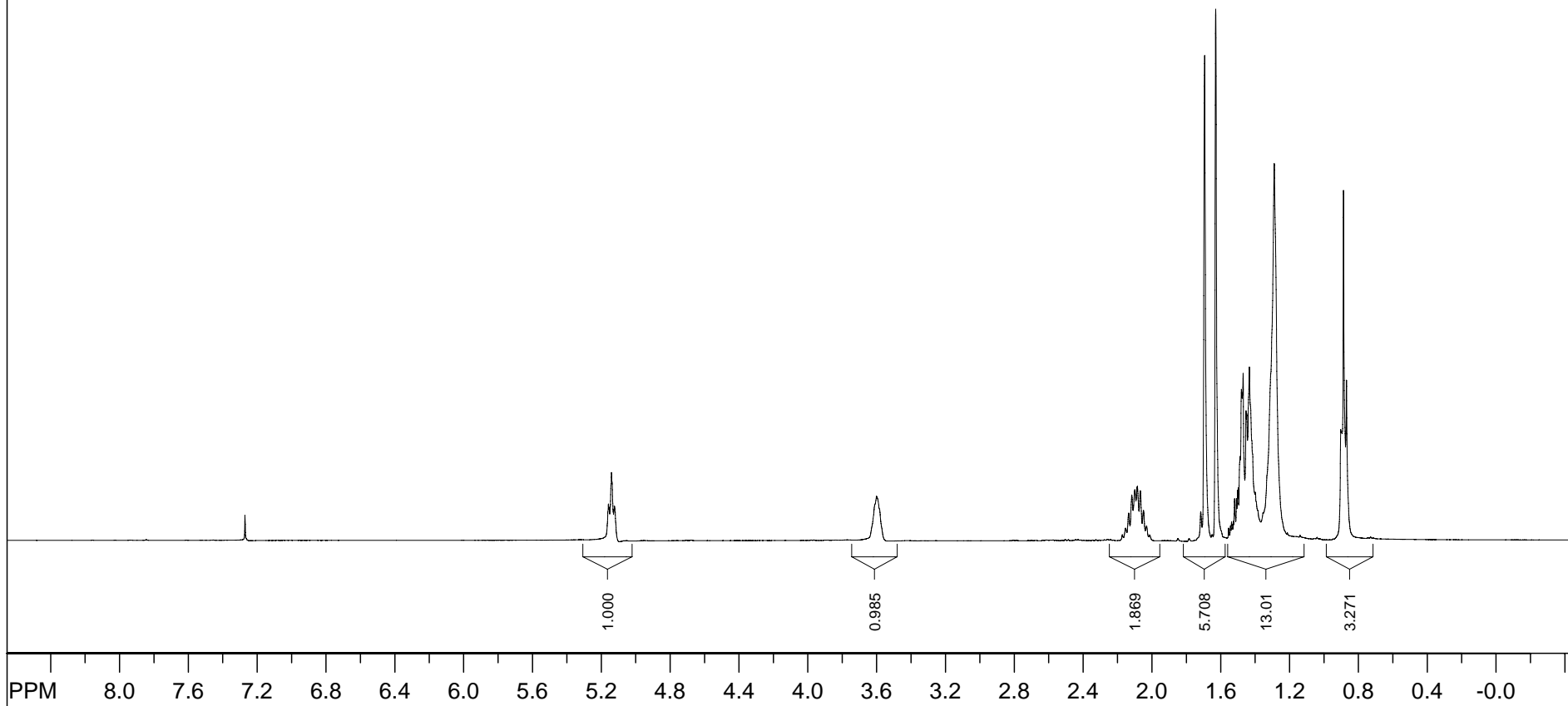
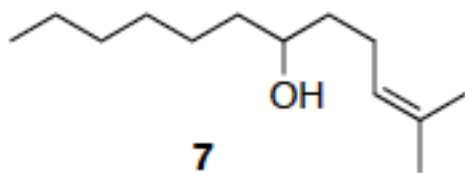
Sp



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-62\2\fid exp: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 562

freq. of 0 ppm: 100.612773 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.0000
Hz/cm: 644.008 ppm/cm: 6.40022

SpinWo



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-68\1\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

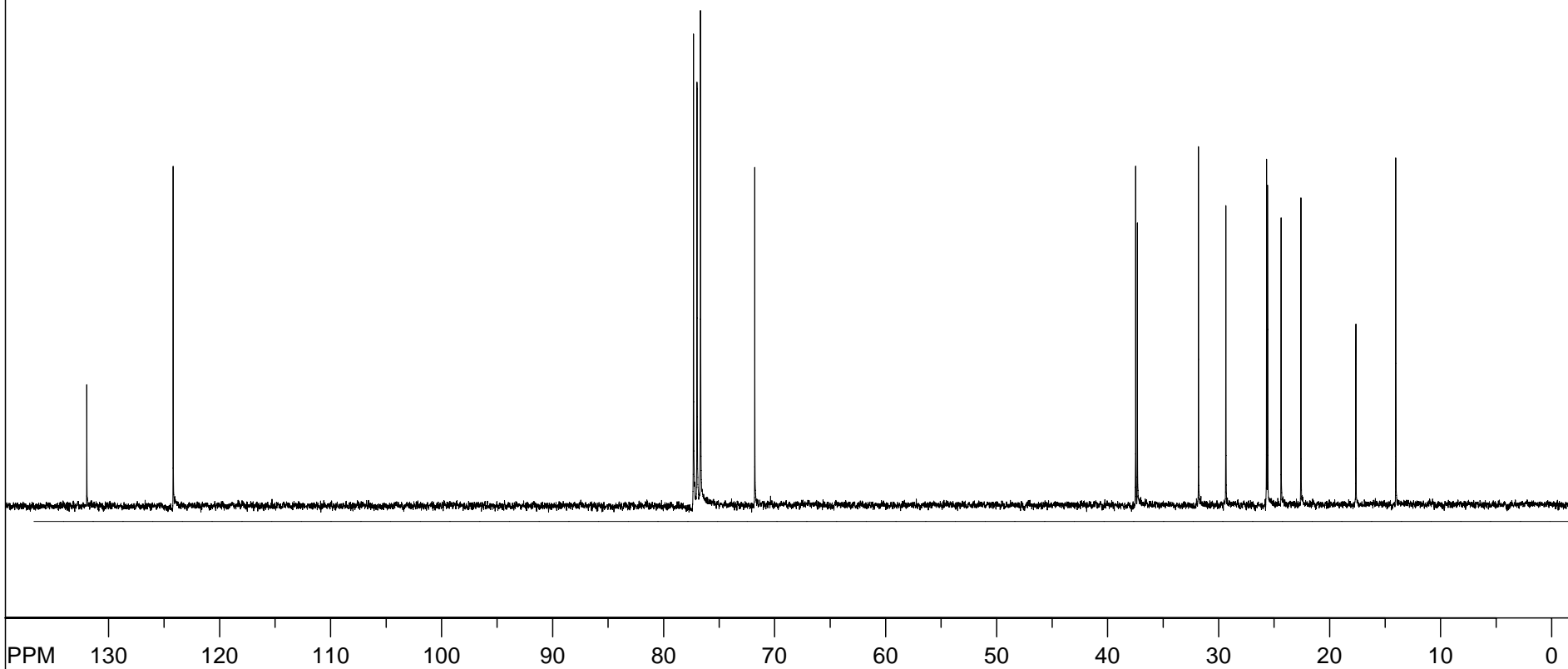
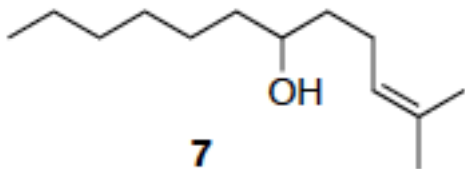
freq. of 0 ppm: 400.130005 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 146.214 ppm/cm: 0.36541

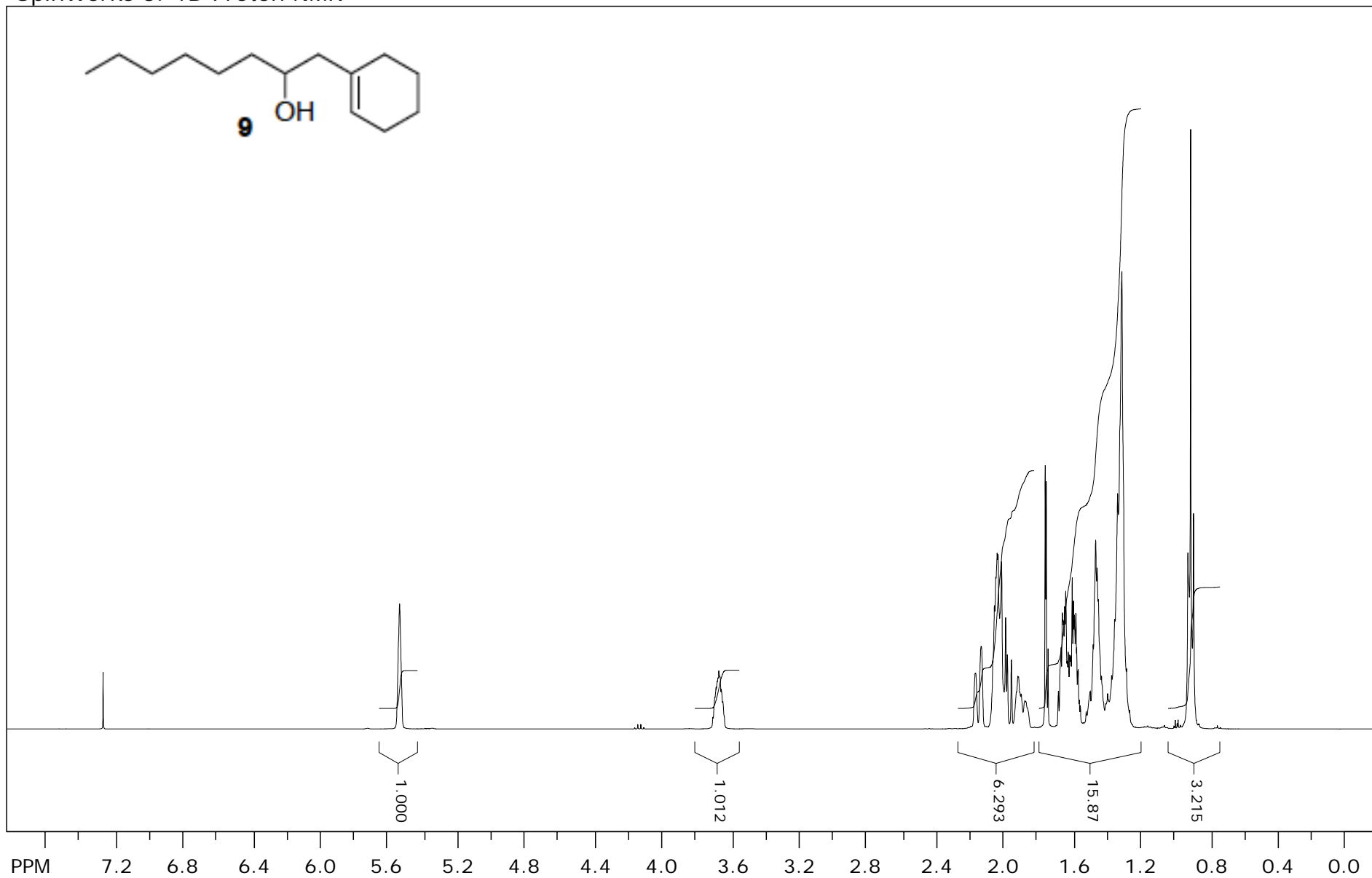
SpinW



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-68\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 486

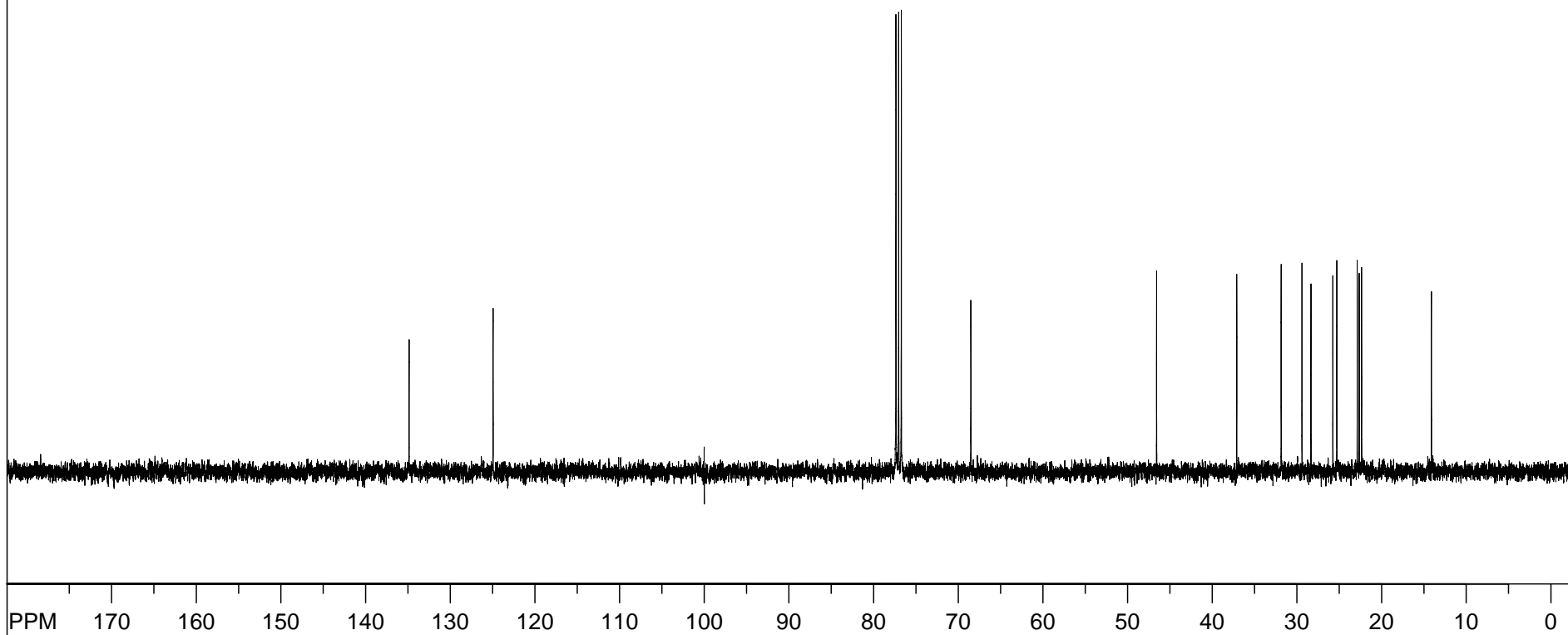
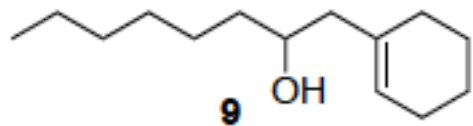
freq. of 0 ppm: 100.612772 MHz
processed size: 16384 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 569.912 ppm/cm: 5.66385

SpinWorks 3: 1D Proton NMR



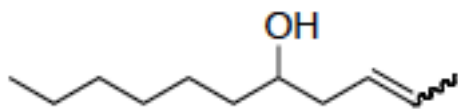
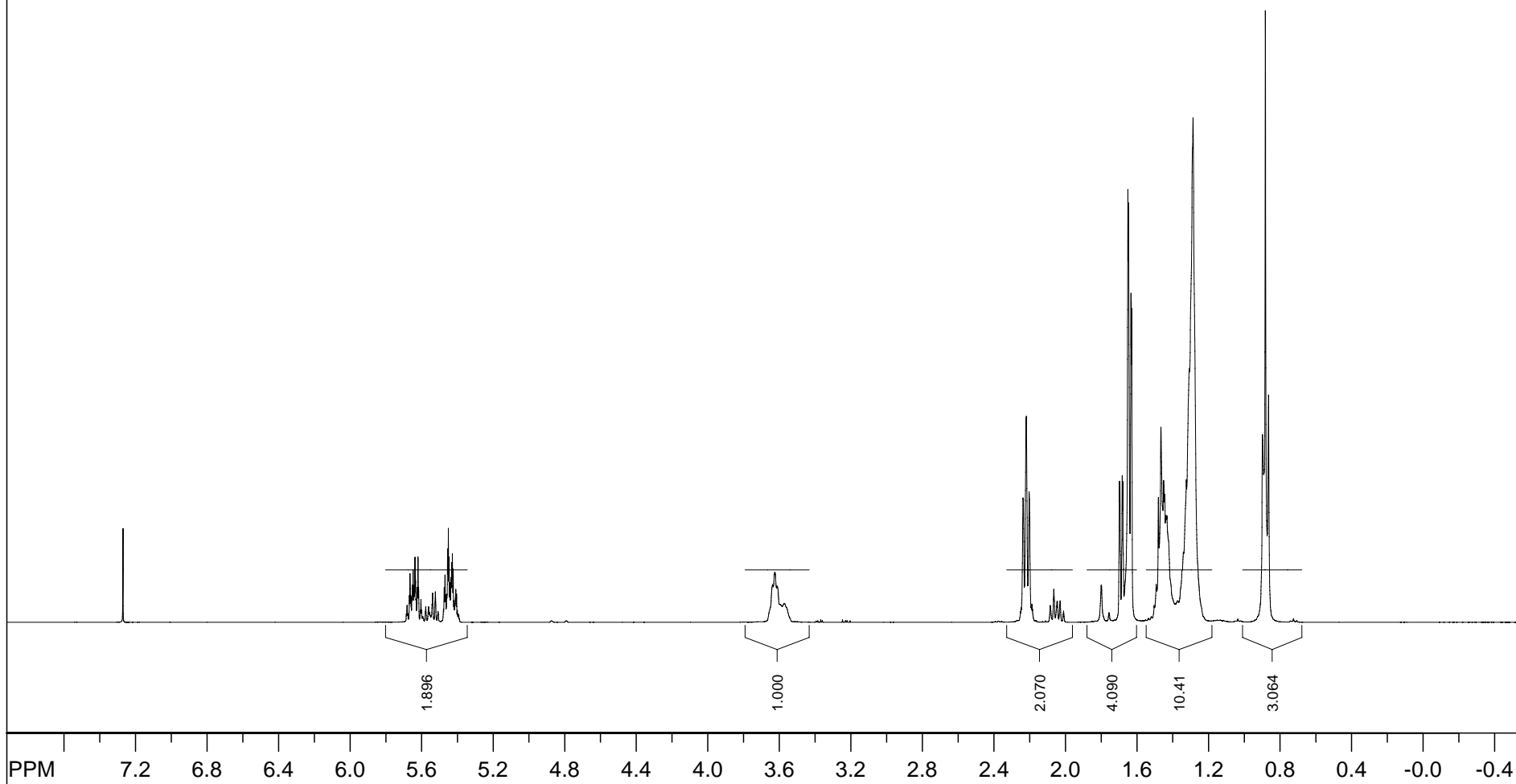
file: ...S_paper\More spectra\cx-6-23\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.6885 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 128.818 ppm/cm: 0.32194



file: D:\CX_RVS_paper\More spectra\cx-6-23\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 43

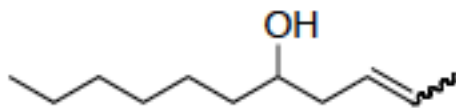
freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 747.188 ppm/cm: 7.42563

**11**

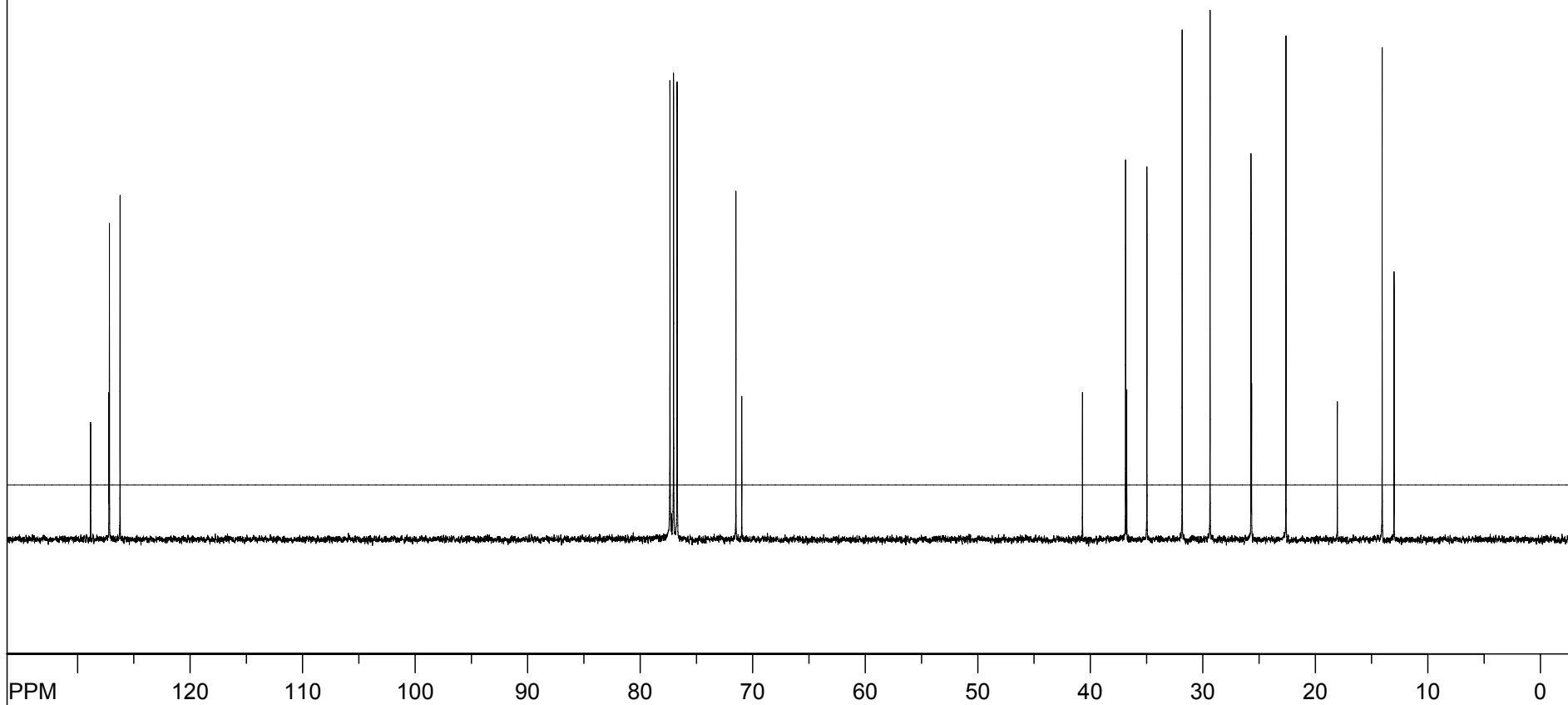
file: D:\Roman's\rvs-4-31\1\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130006 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 136.016 ppm/cm: 0.33993

SpinWorks 2.5: ¹³C NMR



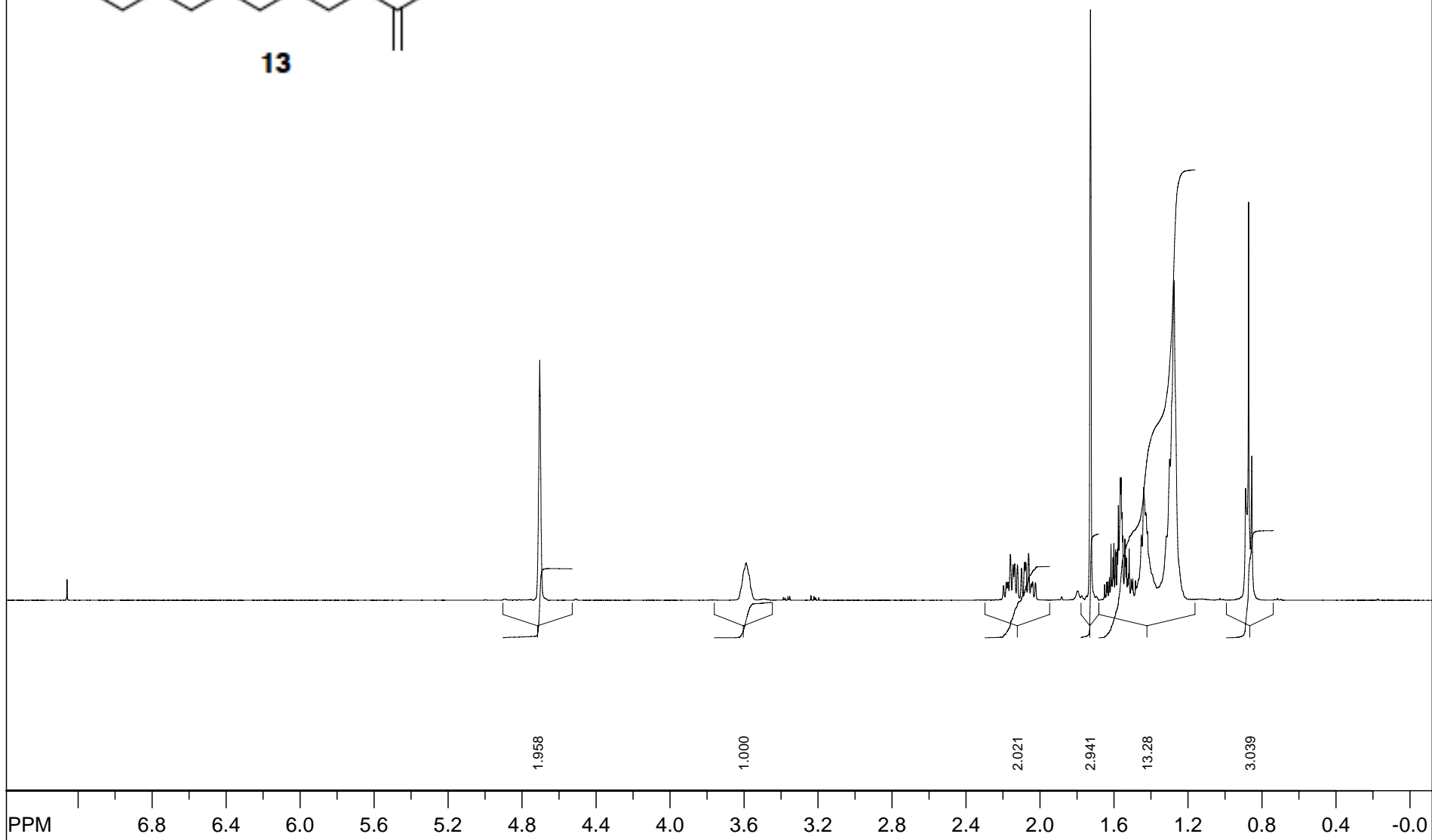
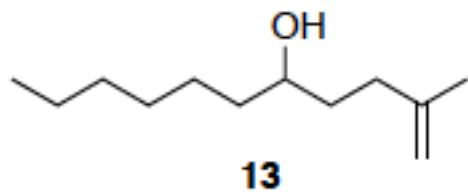
11



file: D:\Roman's\rvs-4-31\2\fid exp: <zgpg3
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 398

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 562.193 ppm/cm: 5.58714

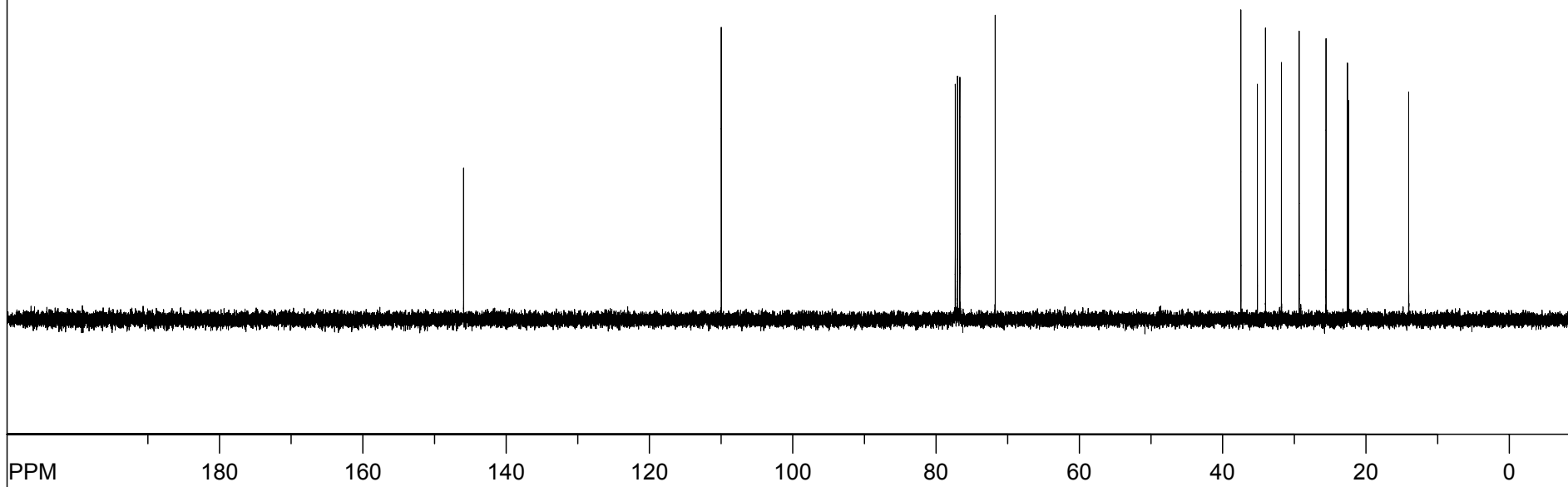
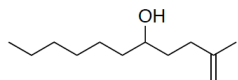
SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\More spectra\cx-6-19-sm\1\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 123.360 ppm/cm: 0.30830

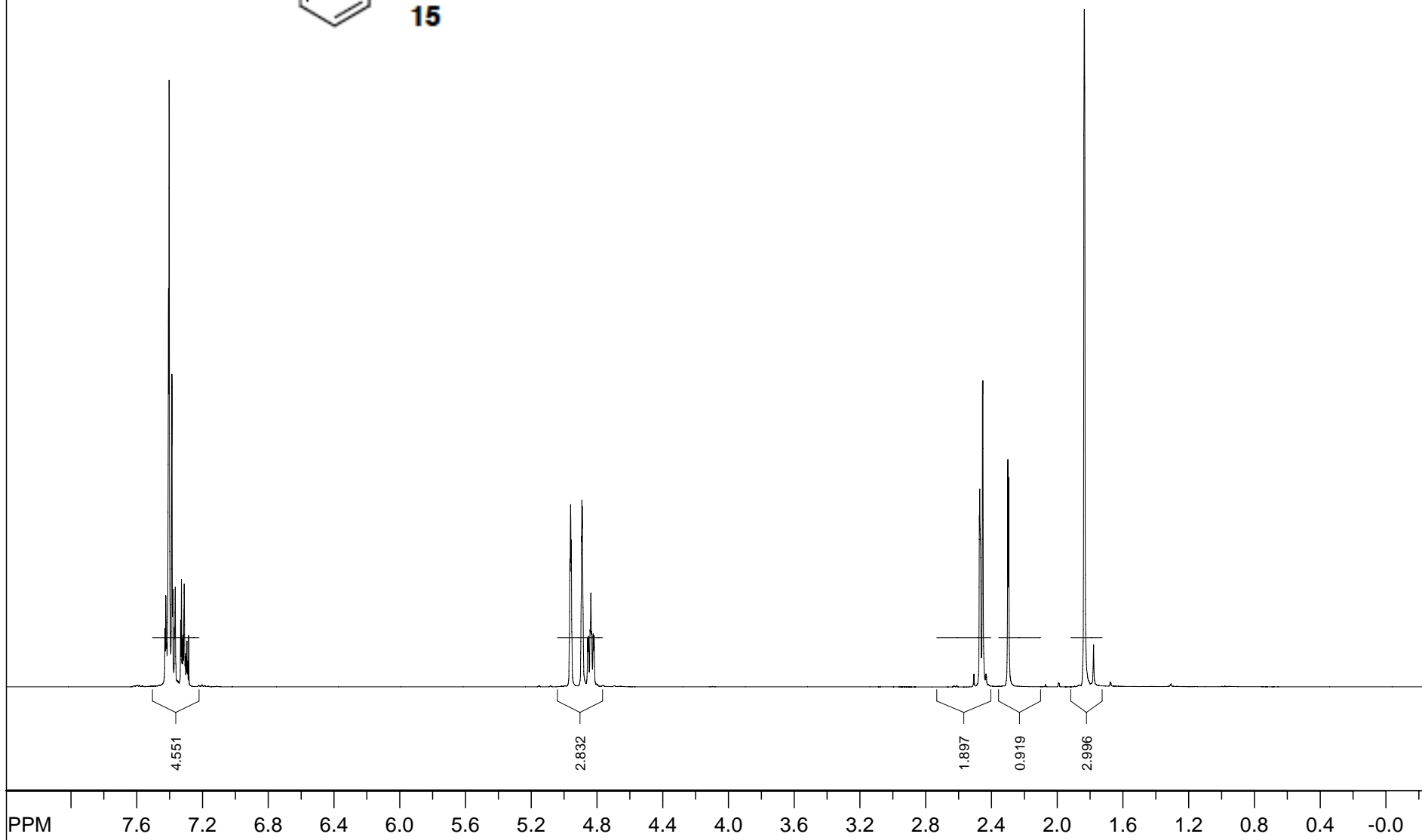
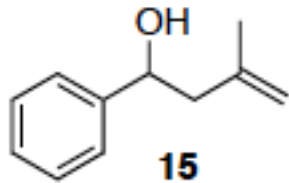
SpinWorks 2.5: ¹³C NMR



file: D:\CX_RVS_paper\More spectral\cx-6-19-sm\2\fid exp: <zggp30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 38

freq. of 0 ppm: 100.612774 MHz
processed size: 65536 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 882.914 ppm/cm: 8.77449

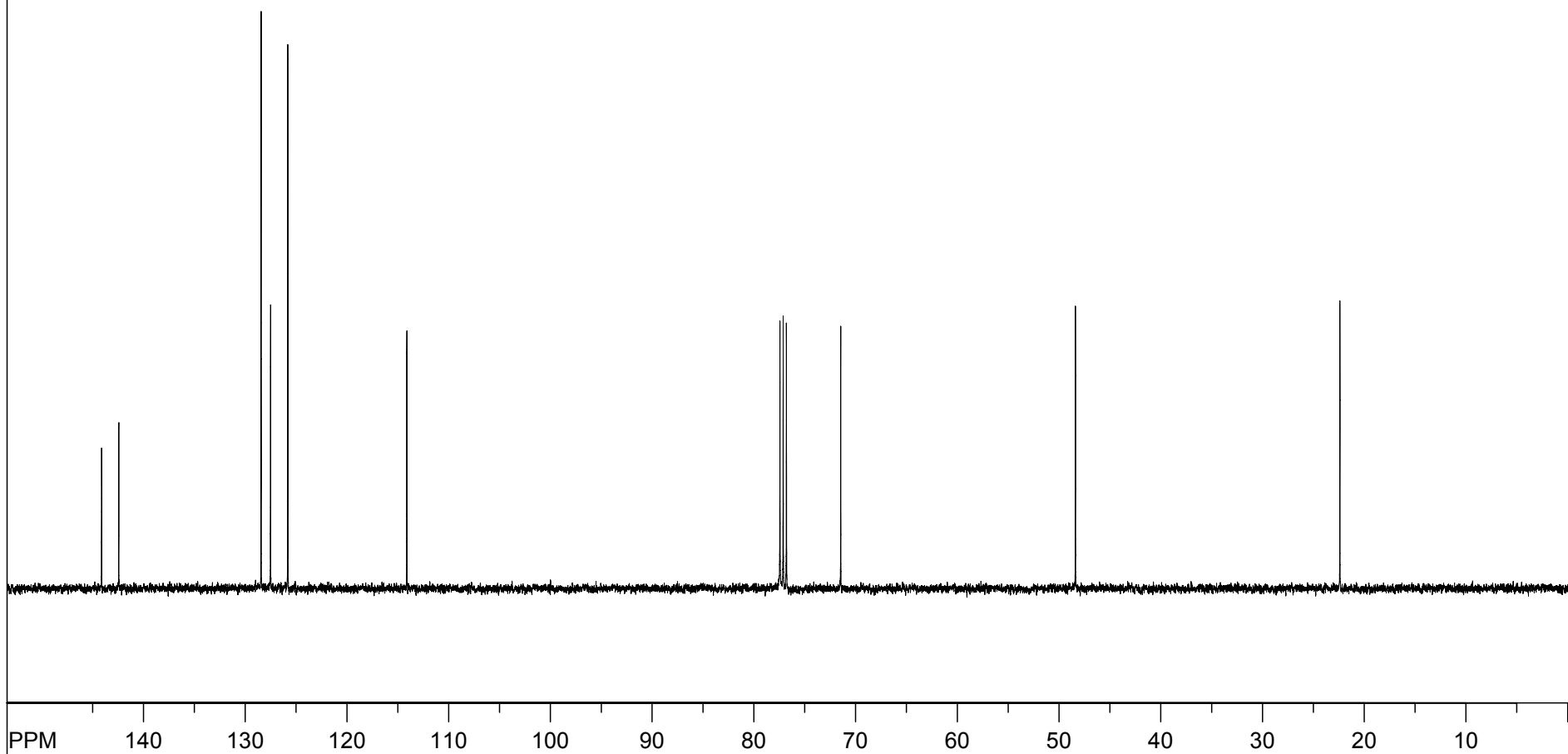
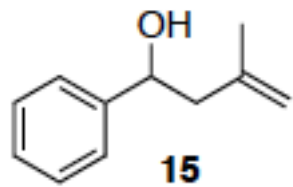
SpinWorks 2.5: 1D P



file: D:\Roman's\rvs-4-30\1\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 138.813 ppm/cm: 0.34692

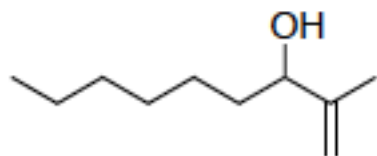
S



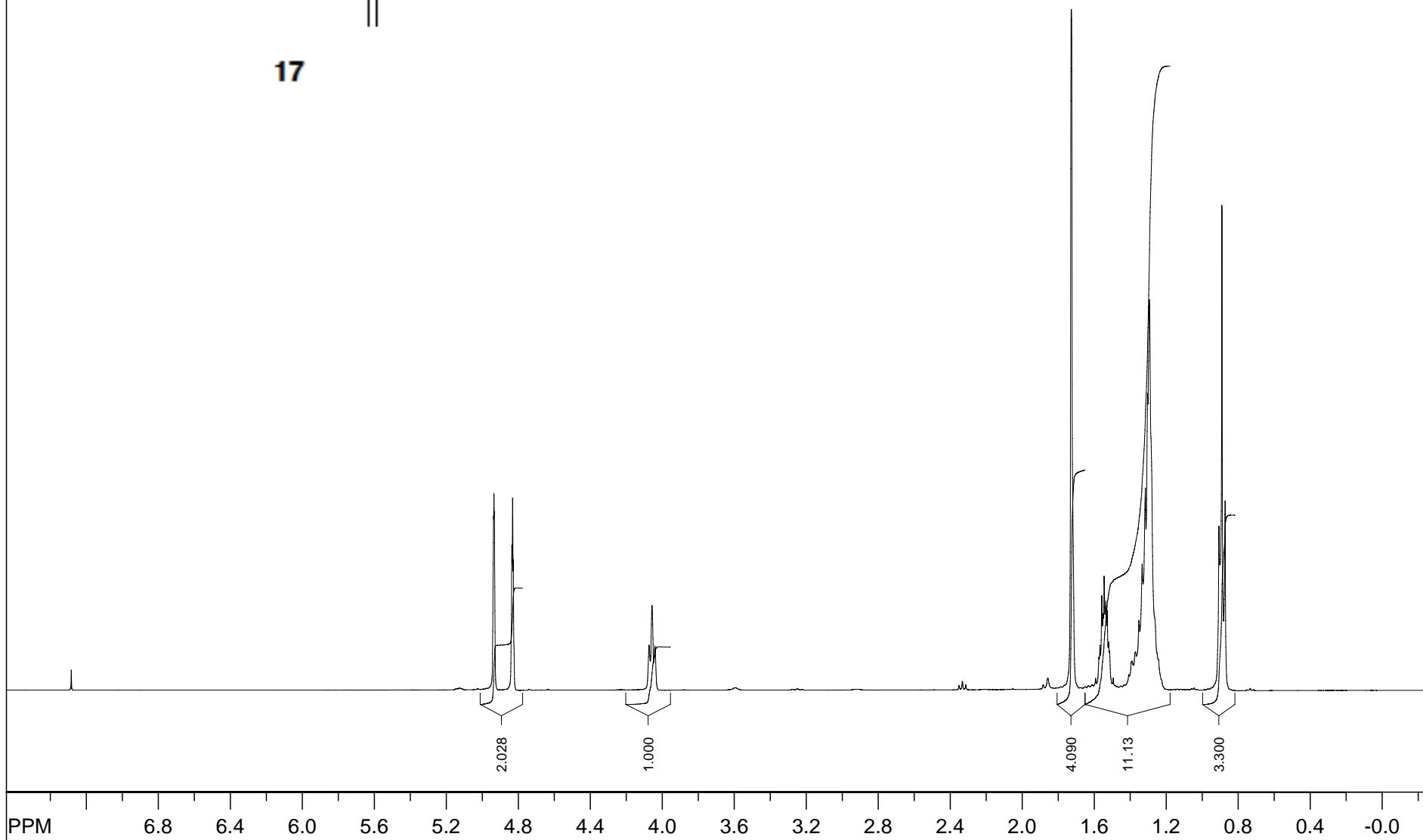
file: D:\Roman's\rvs-4-30\2\fid
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 77

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 621.862 ppm/cm: 6.18013

SpinWc



17



file: D:\CX_RVS_paper\More spectra\cx-6-20-sm\1\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

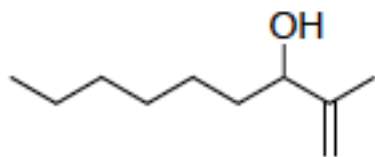
freq. of 0 ppm: 400.130000 MHz

processed size: 32768 complex points

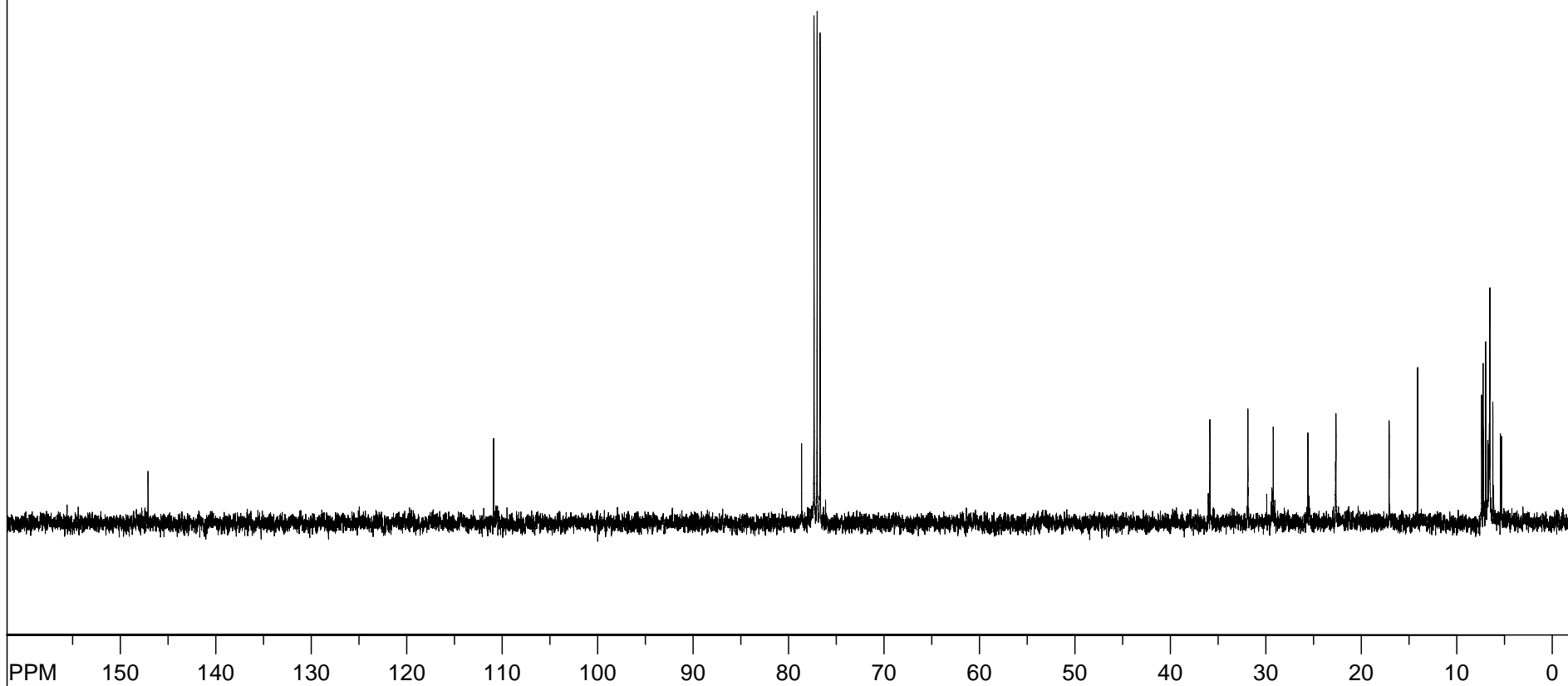
LB: 0.300 GB: 0.0000

Hz/cm: 126.996 ppm/cm: 0.31738

SpinWorks :



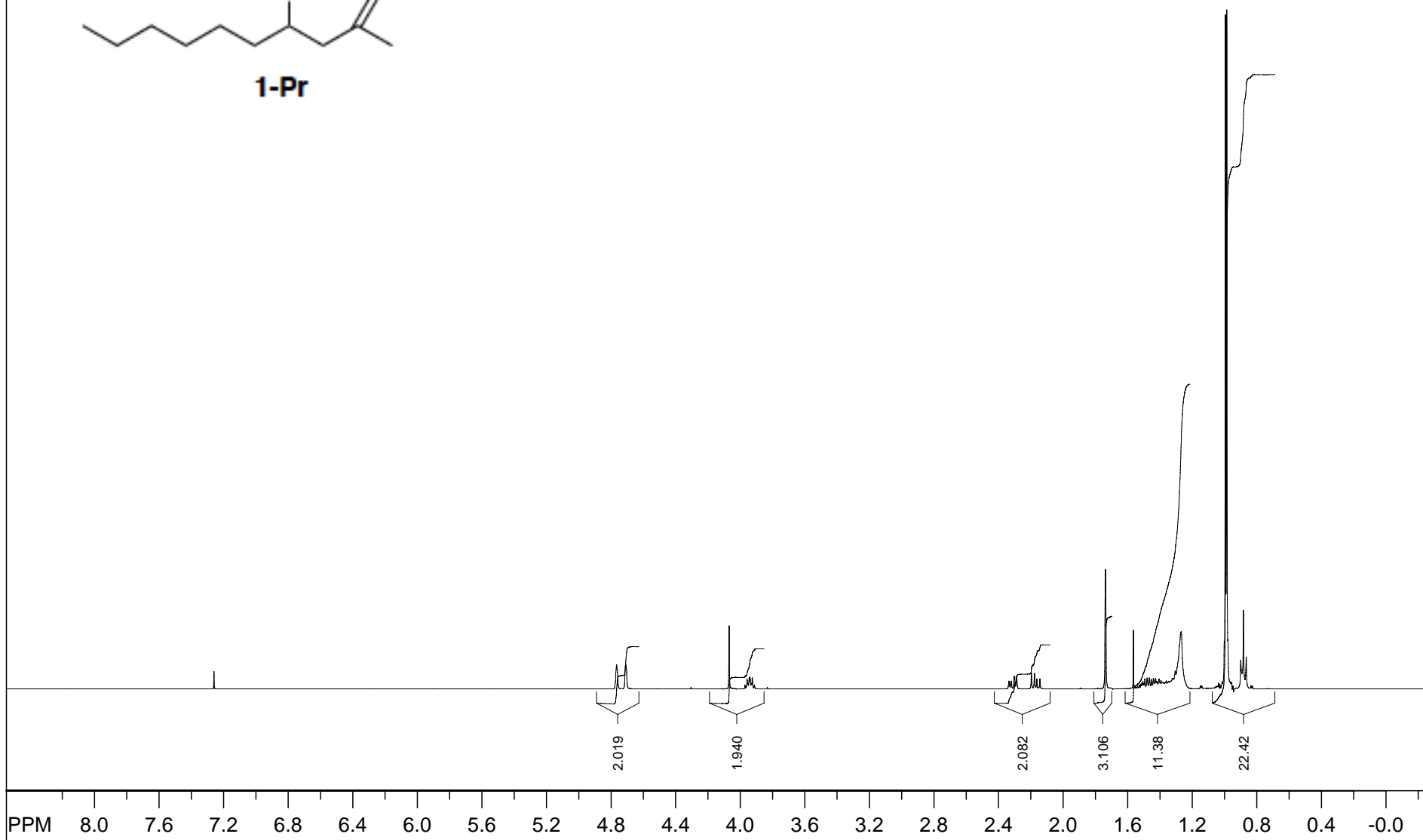
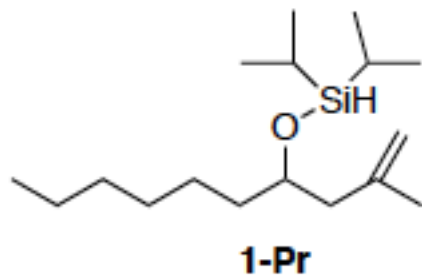
17



file: D:\CX_RVS_paper\More spectra\cx-6-20-crude\2\fid exp: <zpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 67

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 662.012 ppm/cm: 6.57915

Spin'



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-4-h11\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 32768 points

width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt

number of scans: 16

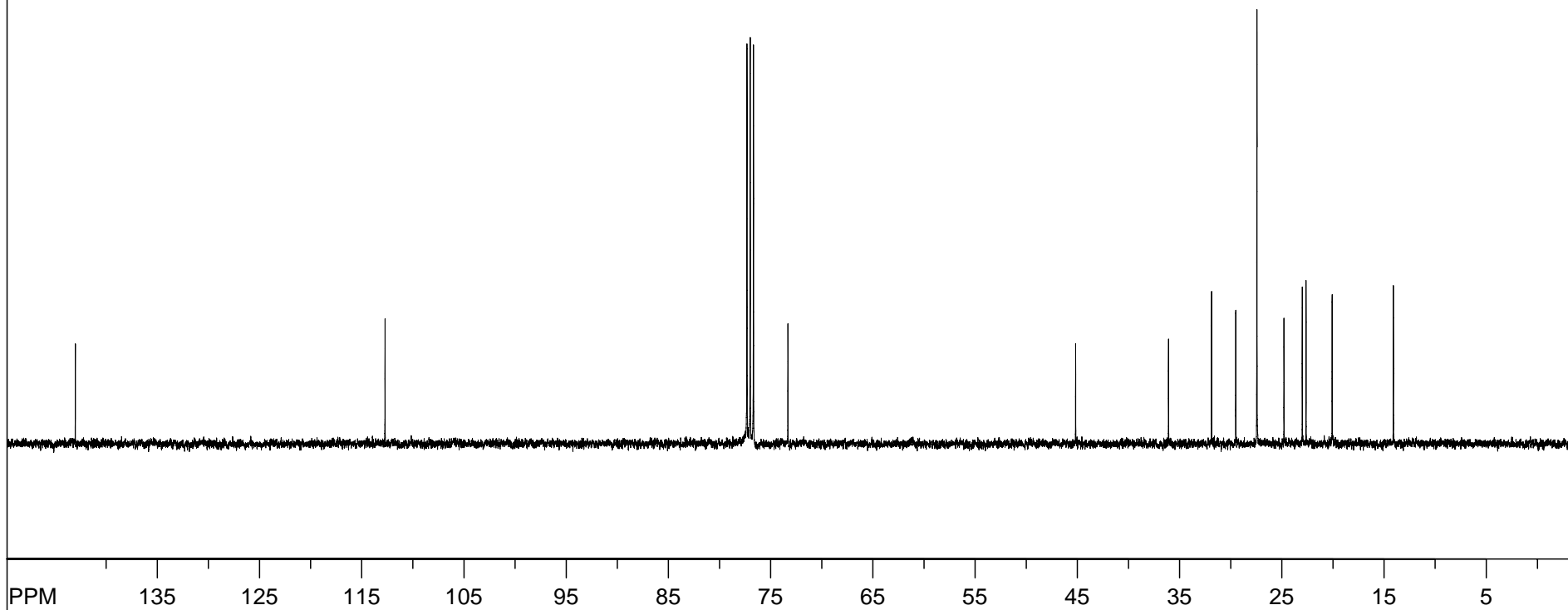
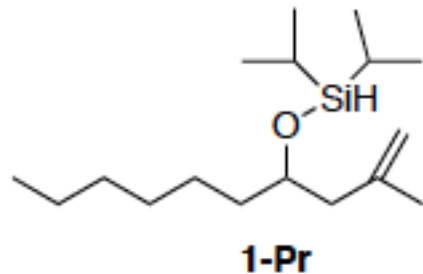
freq. of 0 ppm: 400.130009 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 141.280 ppm/cm: 0.35308

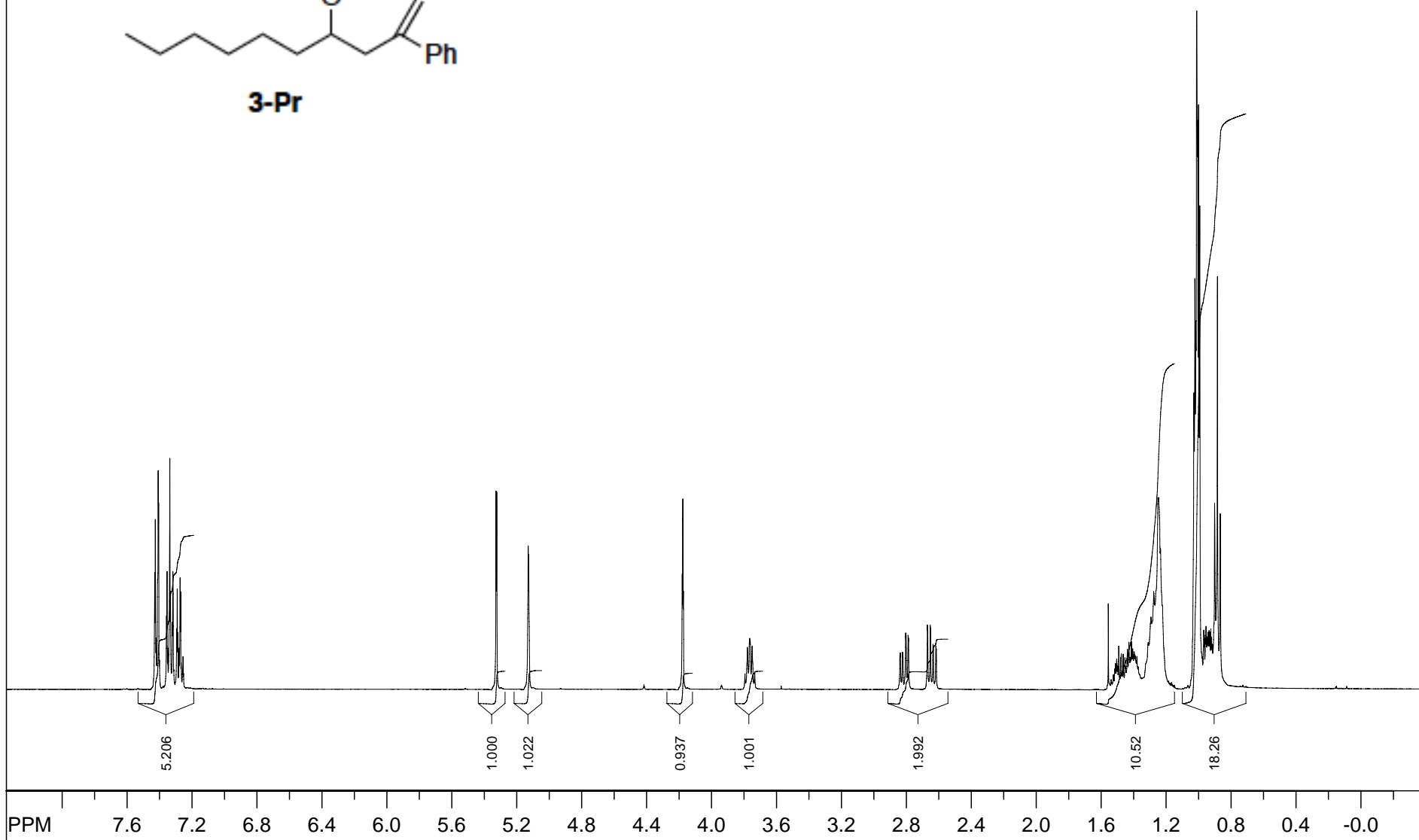
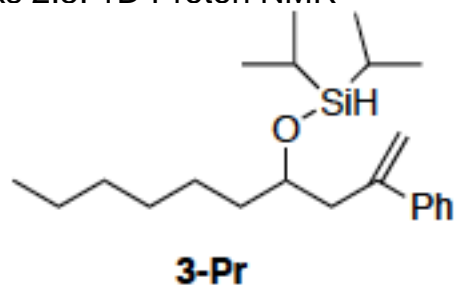
SpinWor



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-4-c13\1\fid_expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 162

freq. of 0 ppm: 100.612770 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 618.133 ppm/cm: 6.14307

SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-74\3\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

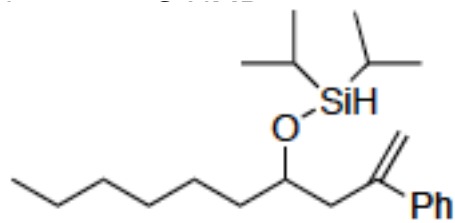
freq. of 0 ppm: 400.130006 MHz

processed size: 32768 complex points

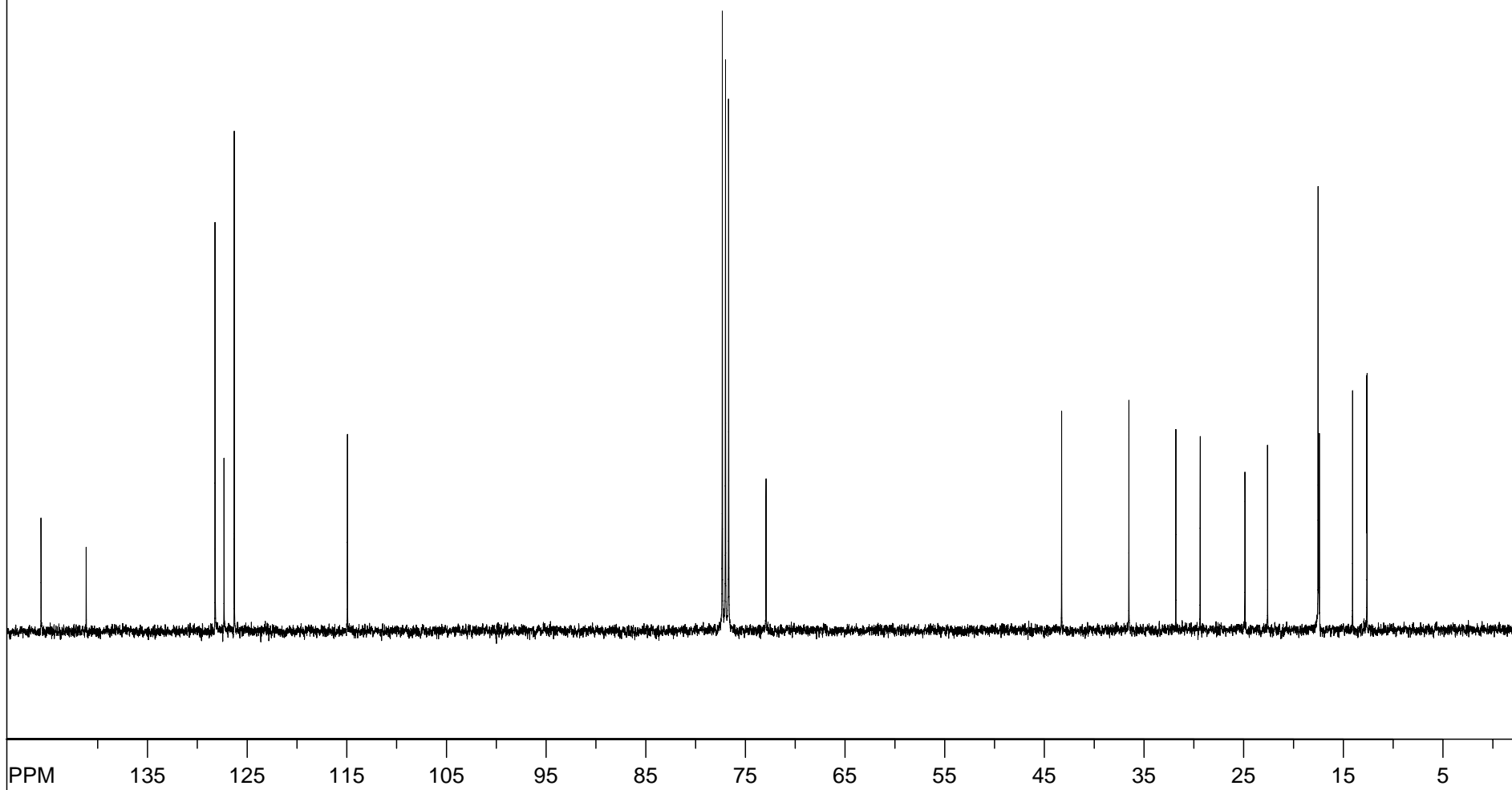
LB: 0.300 GB: 0.0000

Hz/cm: 140.241 ppm/cm: 0.35049

SpinWc



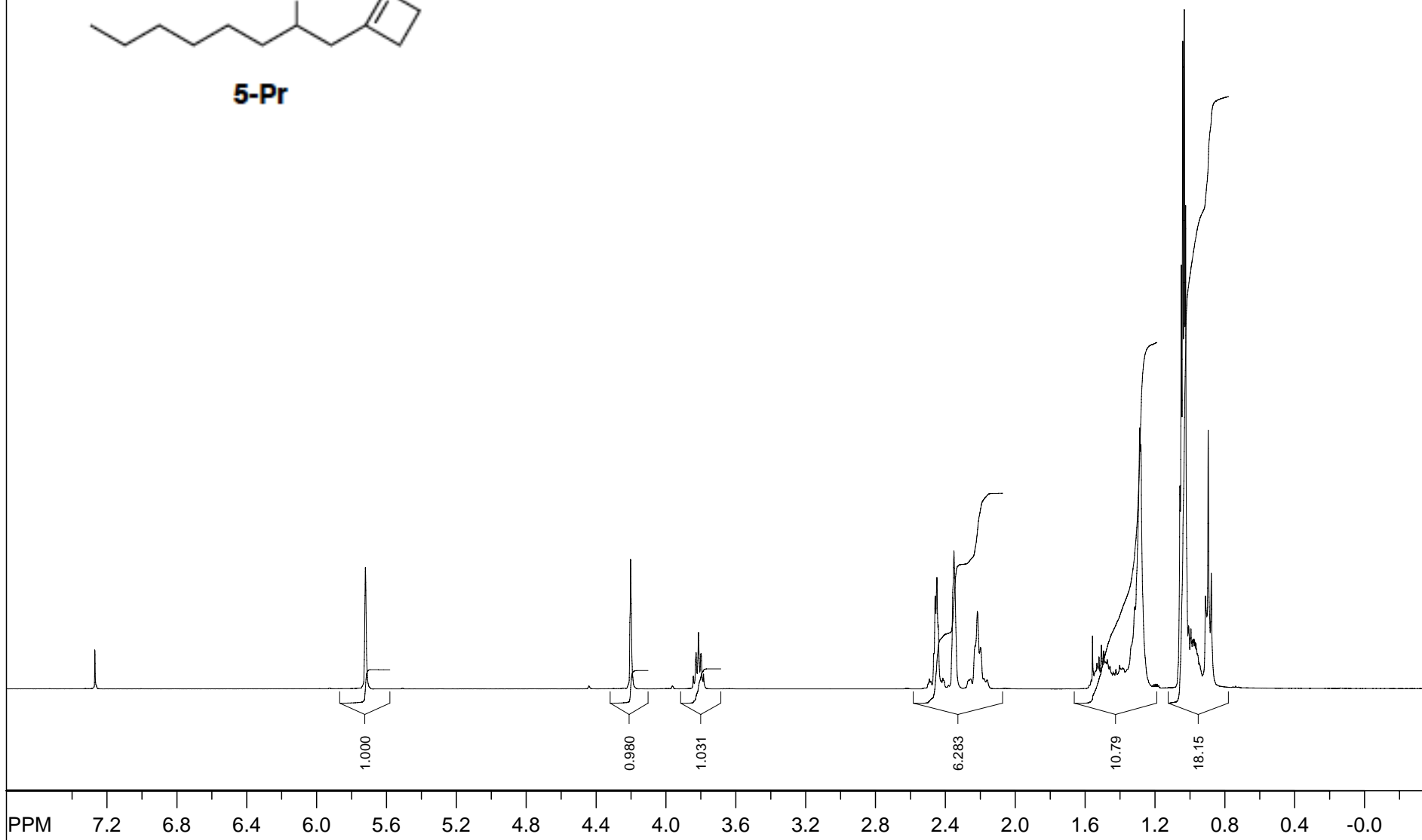
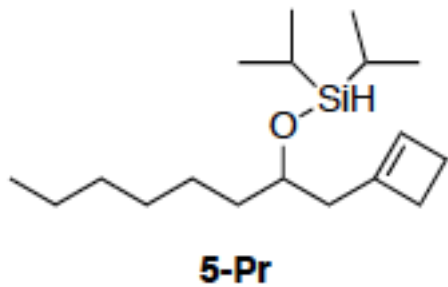
3-Pr



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-74\2\fid exp: <zggg30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 323

freq. of 0 ppm: 100.612771 MHz
processed size: 16384 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 612.154 ppm/cm: 6.08365

SpinW



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-67\1\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

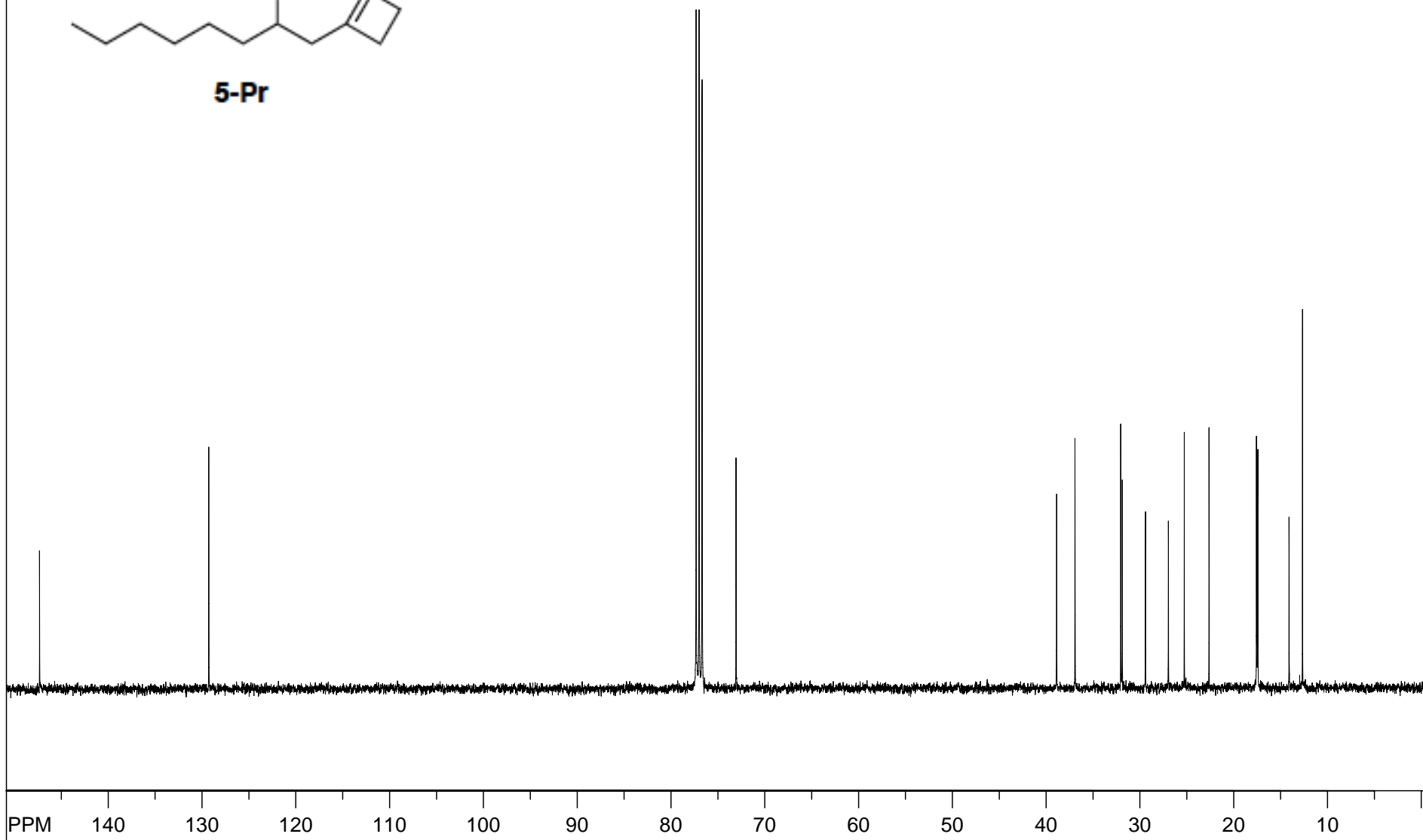
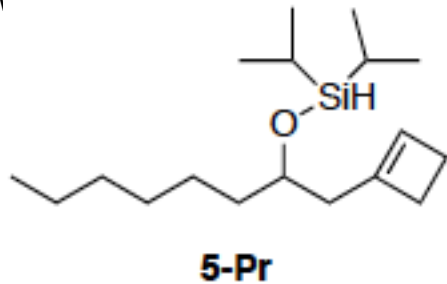
freq. of 0 ppm: 400.130006 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 130.632 ppm/cm: 0.32647

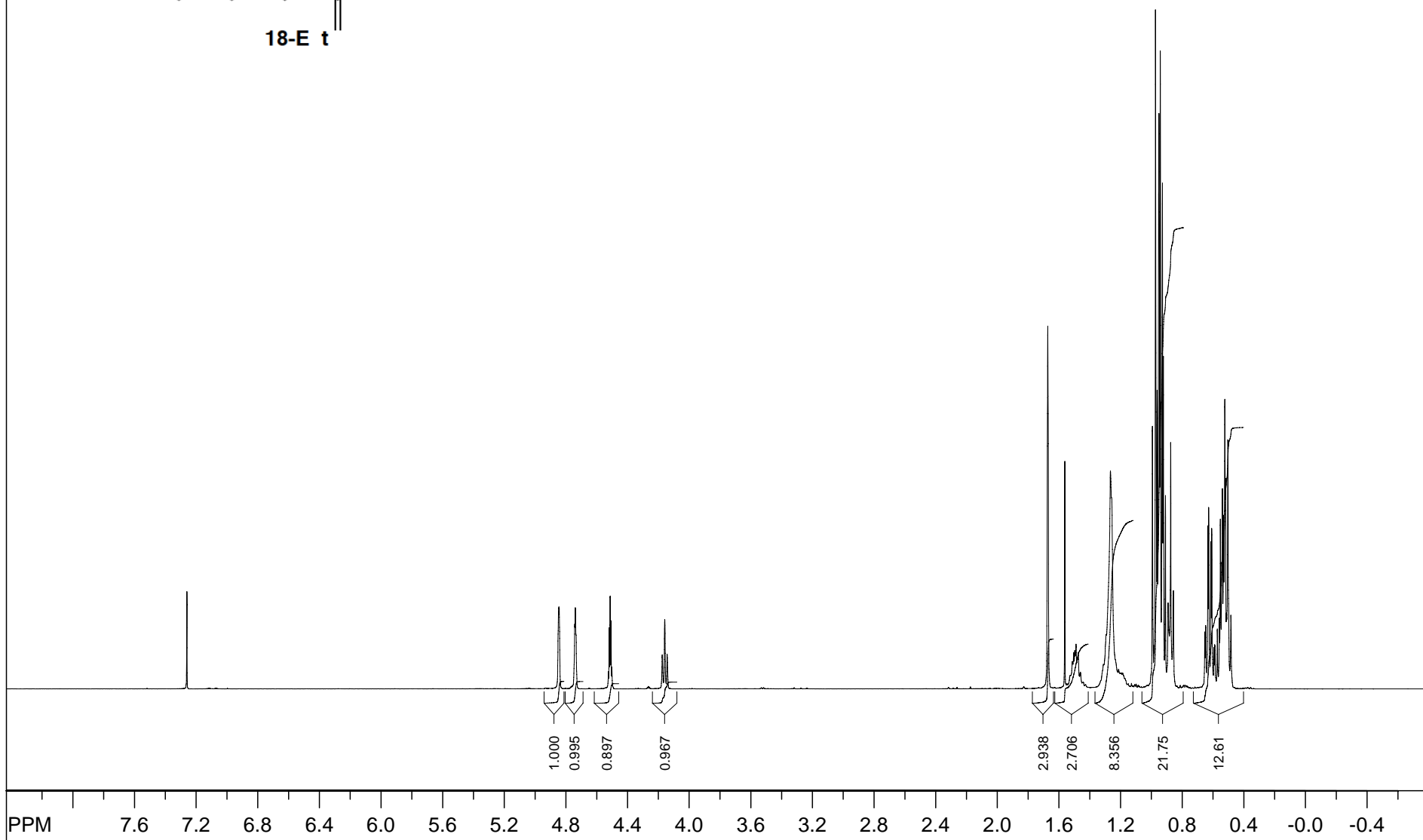
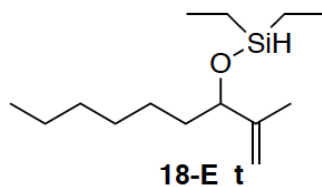
Spin\



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-672\fid exp: <zggp30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 645

freq. of 0 ppm: 100.612769 MHz
processed size: 16384 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 611.461 ppm/cm: 6.07676

SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\cx-6-20-f31\fid exp1: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

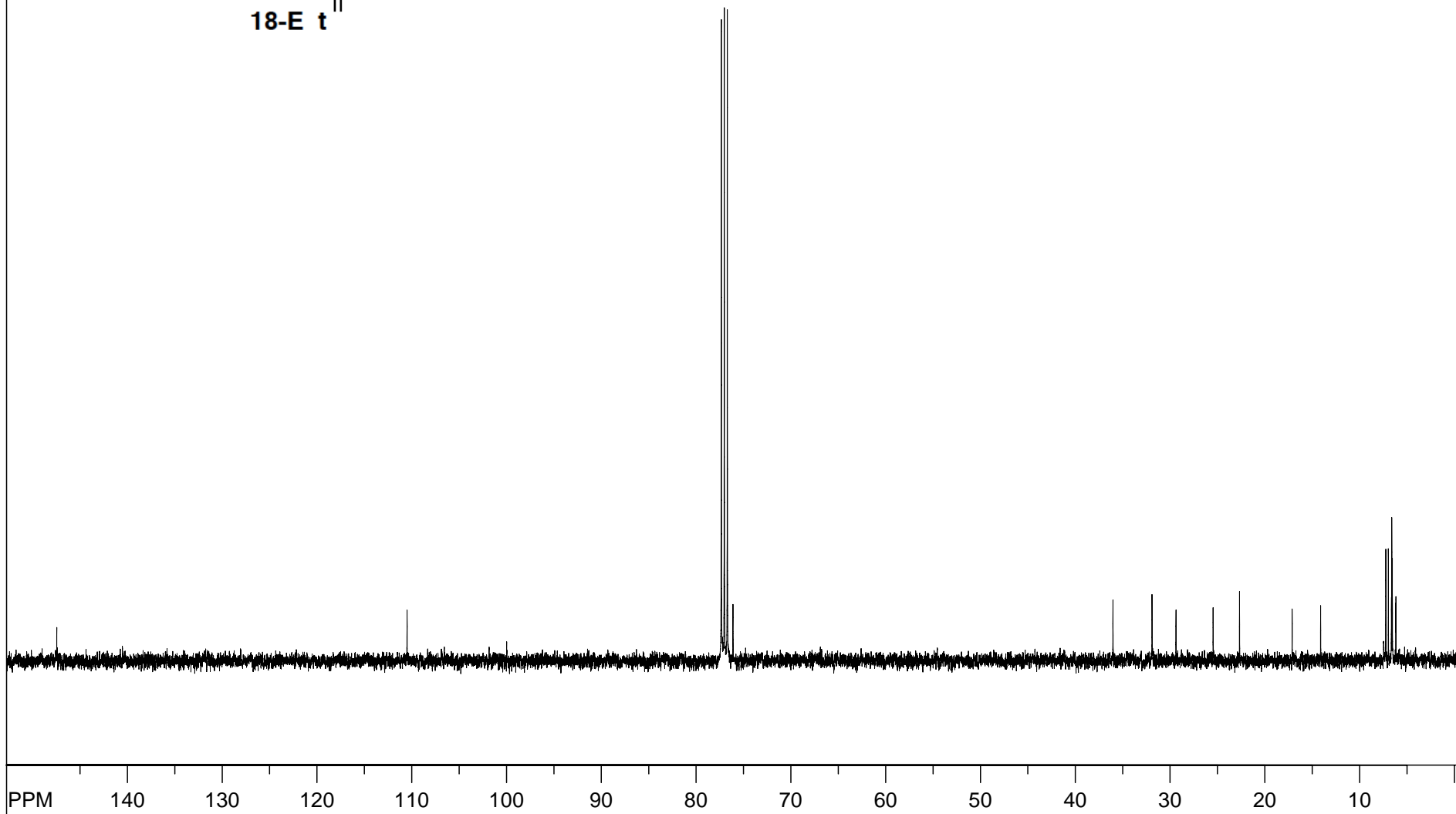
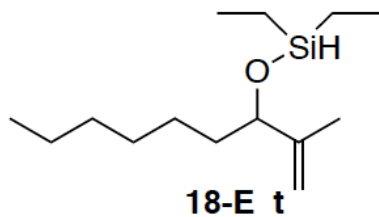
freq. of 0 ppm: 400.130010 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

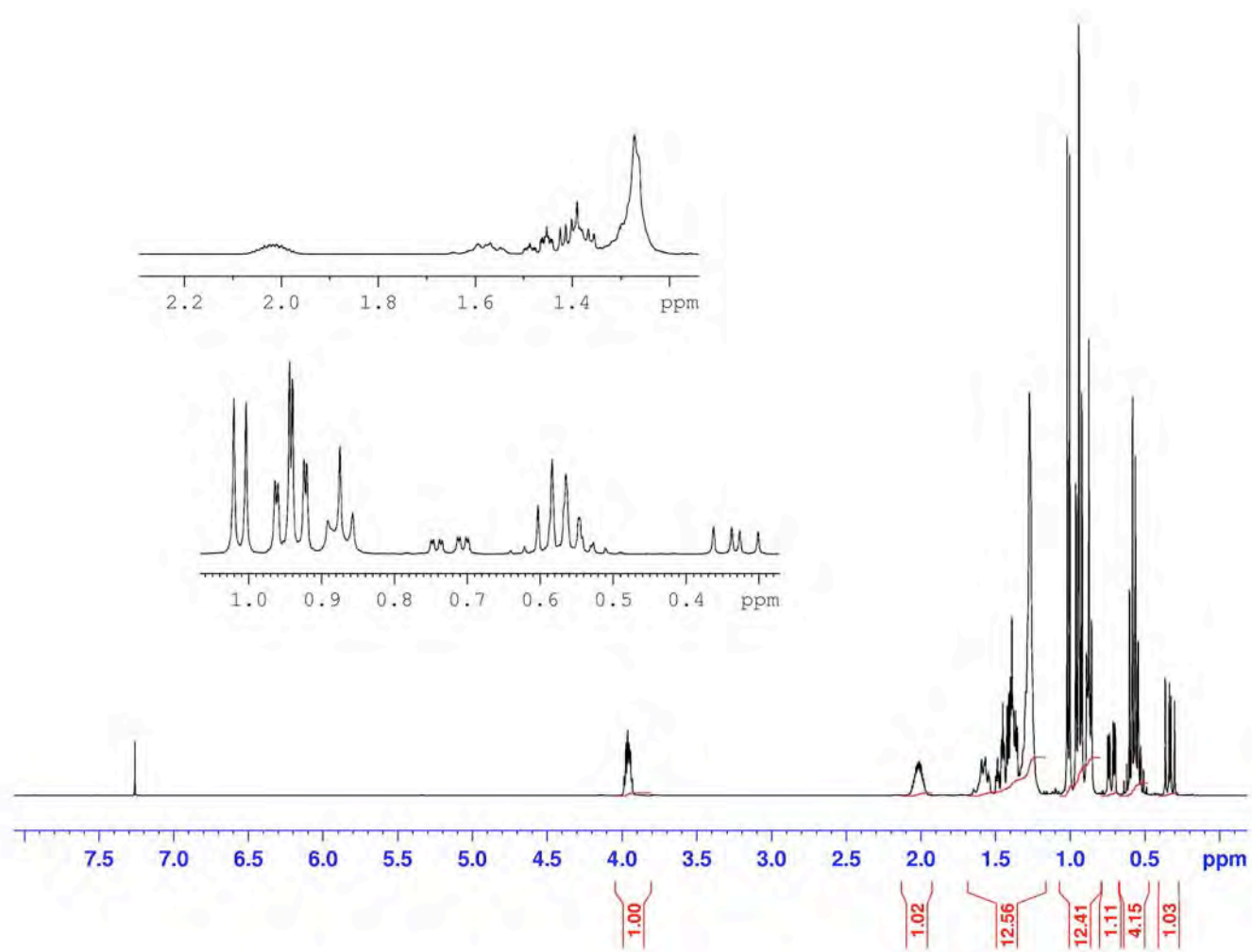
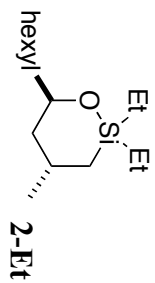
Hz/cm: 148.032 ppm/cm: 0.36996

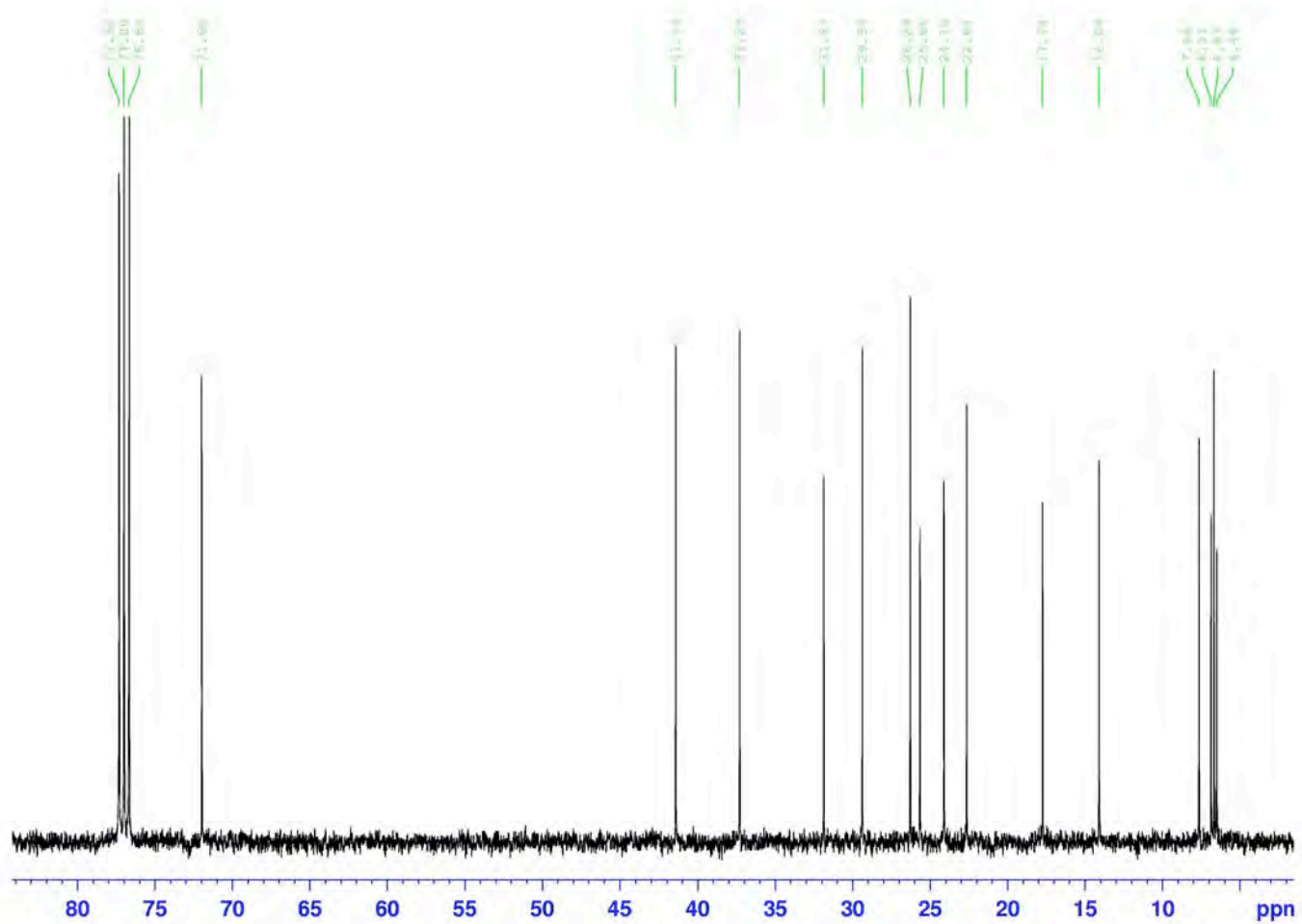
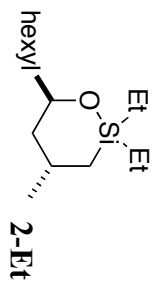
SpinWorks 2.5: ¹³C NMR

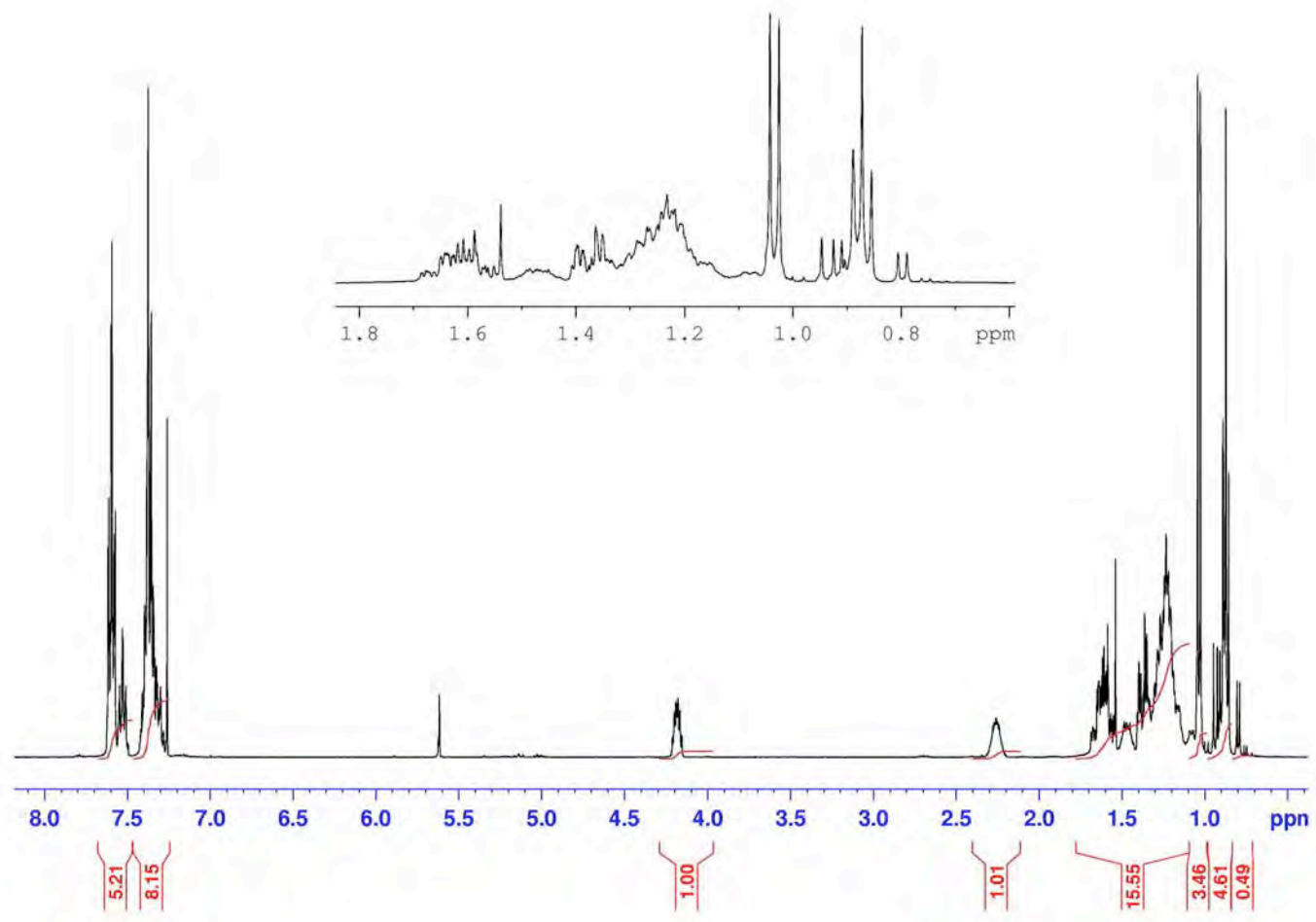
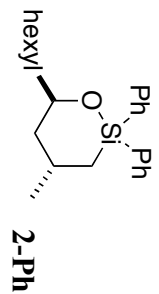


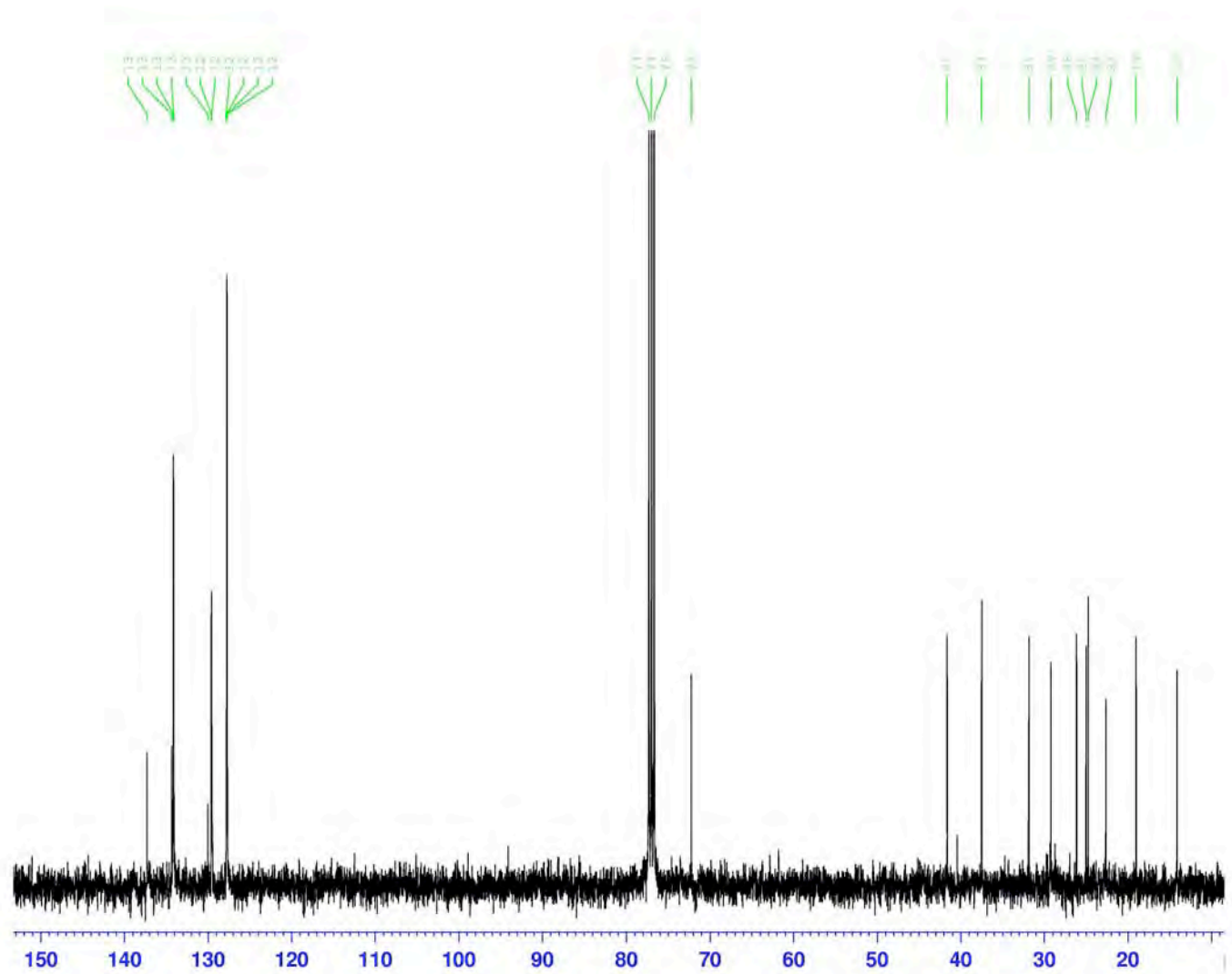
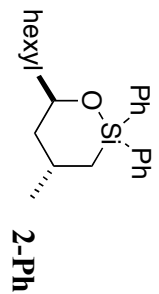
file: D:\CX_RVS_paper\Lost RVS-CX Spectra\cx-6-20-f3\2\fid exp: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 105

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 619.078 ppm/cm: 6.15247

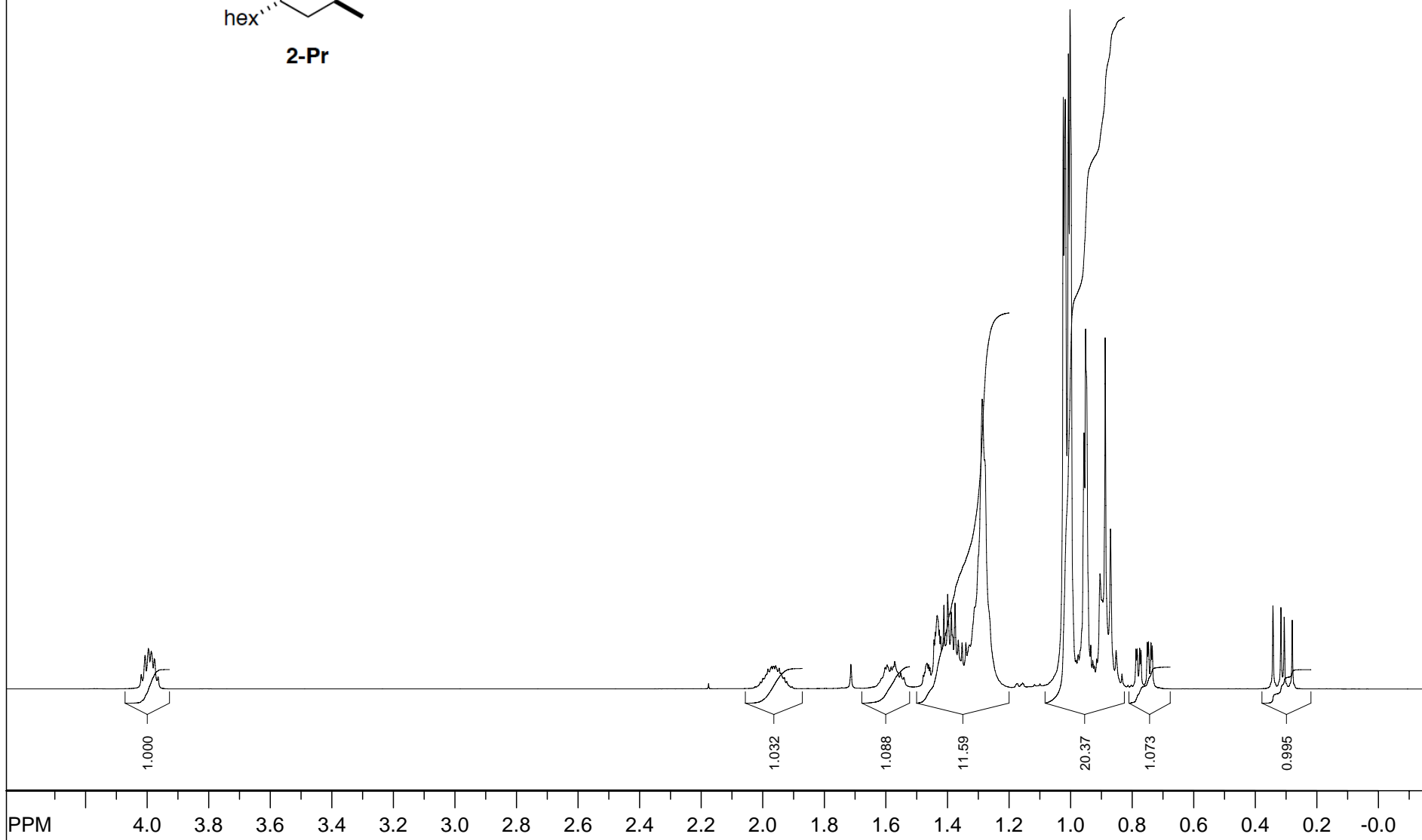
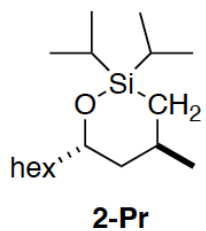






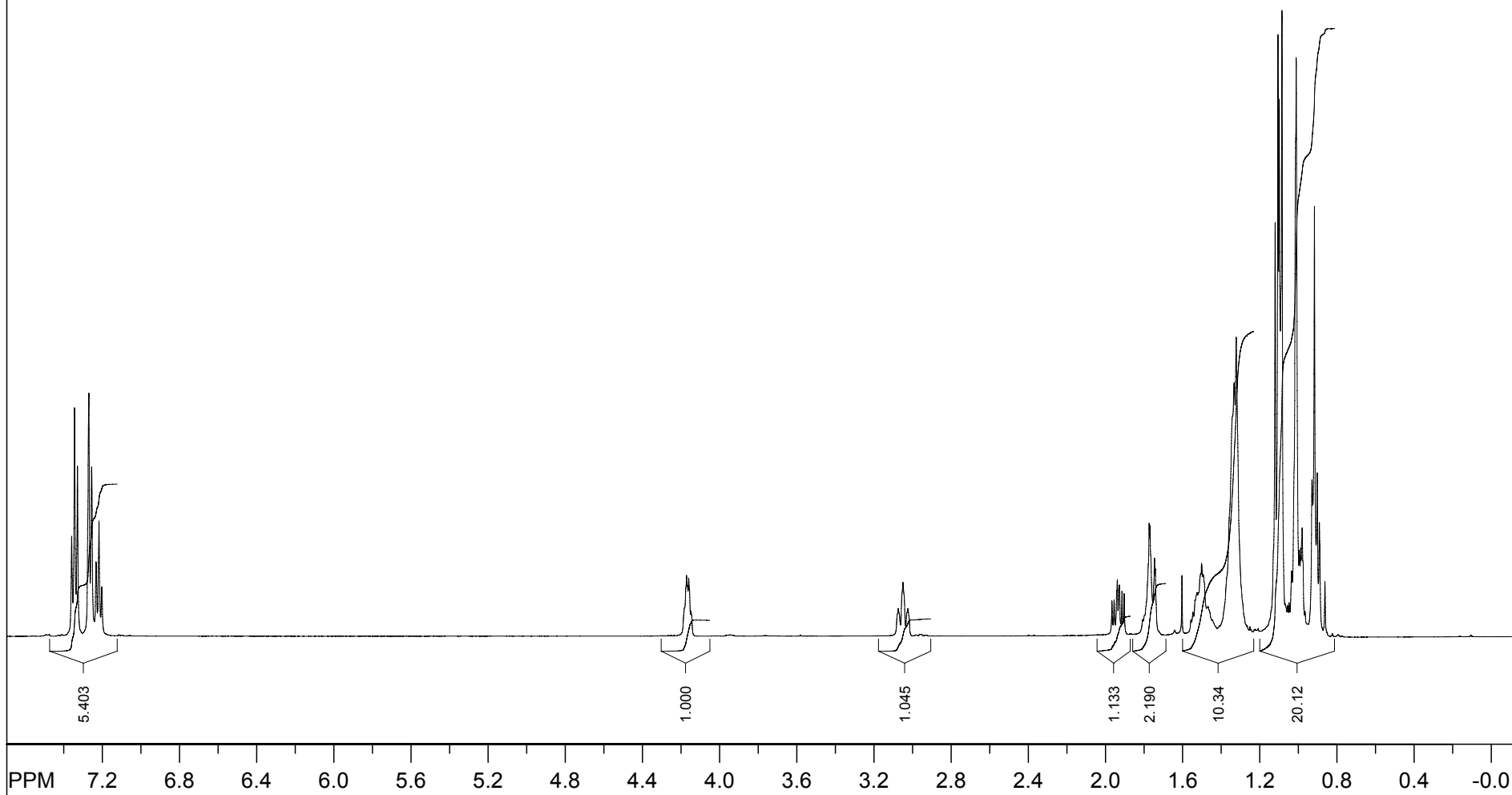
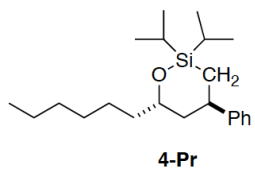


SpinWorks 2.5:



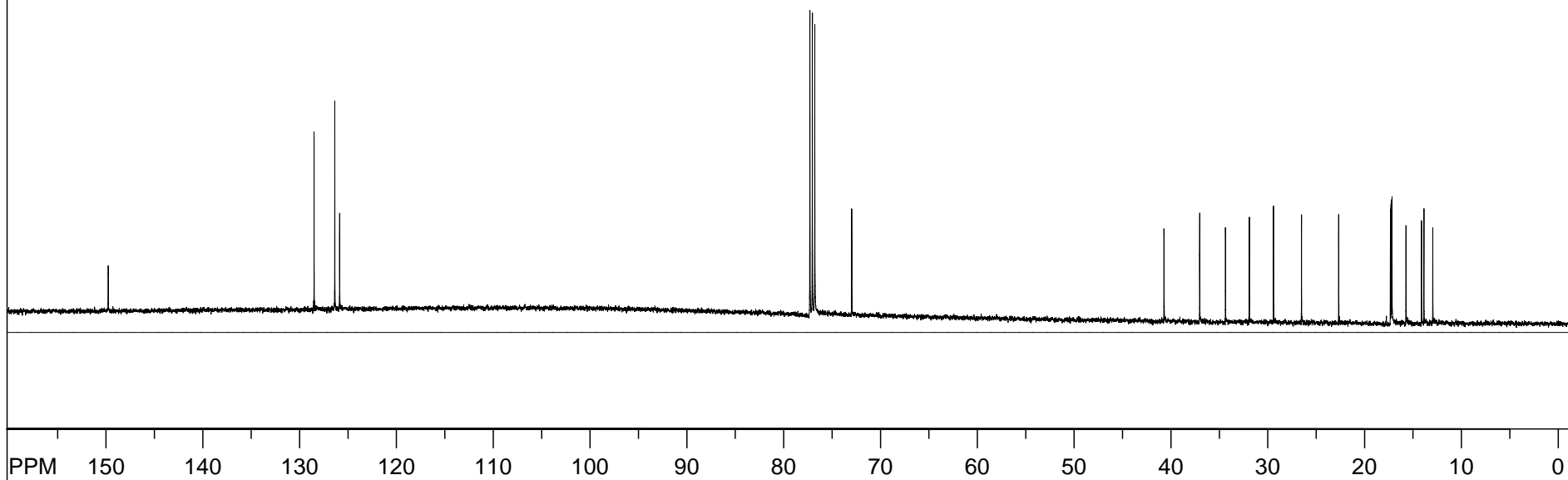
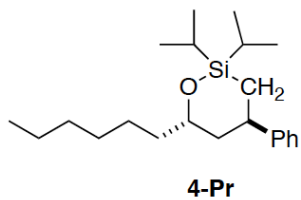
file: D:\CX_RVS_paper\rvs-4-21\1\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130006 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 74.120 ppm/cm: 0.18524



file: D:\CX_RVS_paper\rvs-4-78\1>
 transmitter freq.: 500.132001 MHz
 time domain size: 65536 points
 width: 5000.00 Hz = 9.997361 ppm = 0.076294 Hz/pt
 number of scans: 8

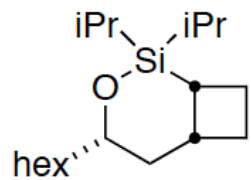
freq. of 0 ppm: 500.130005 MHz
 processed size: 32768 complex points
 LB: 0.300 GB: 0.0000
 Hz/cm: 157.019 ppm/cm: 0.31396



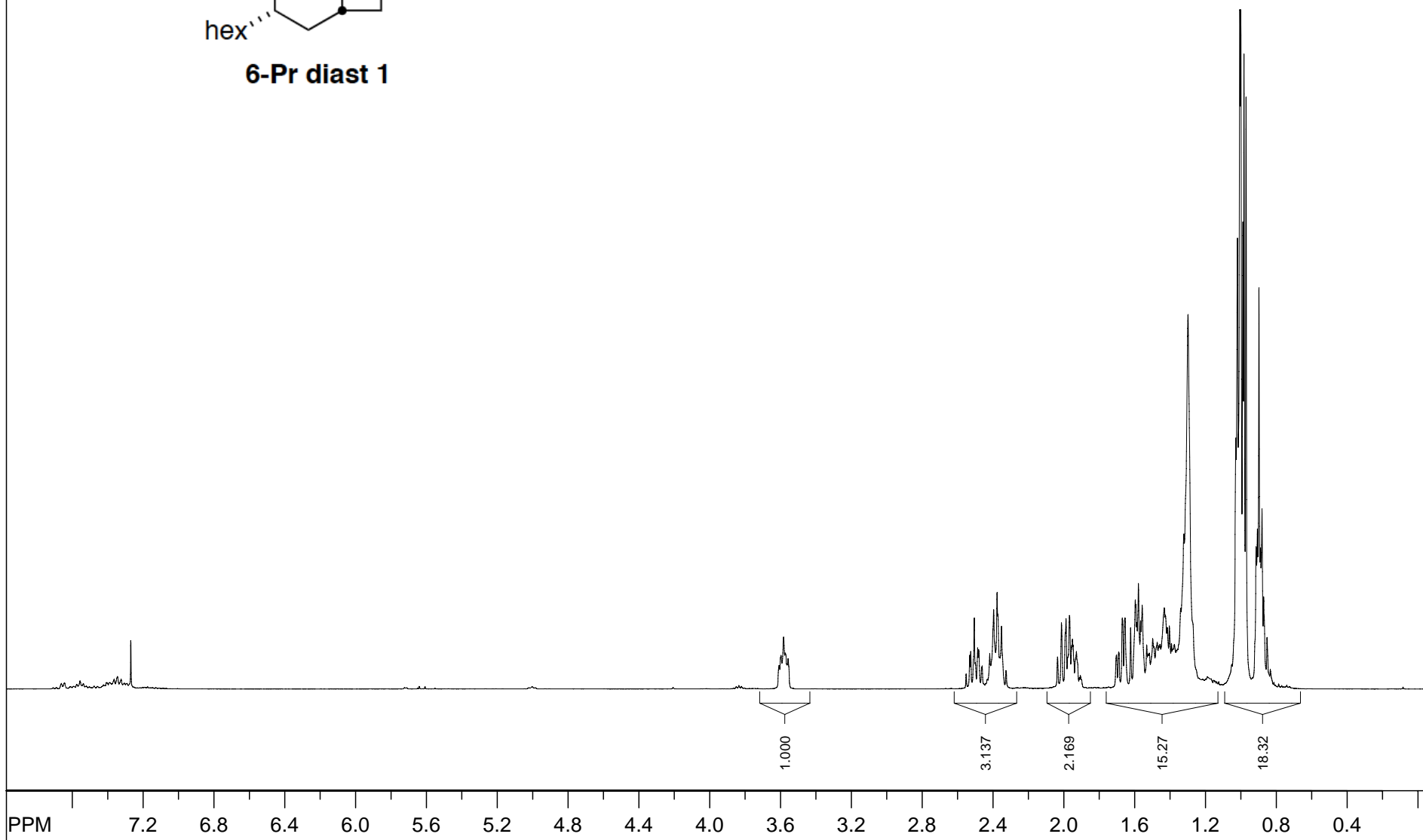
file: D:\CX_RVS_paper\rvs-4-78\2\fid exp: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 32768 points
width: 30030.03 Hz = 238.768729 ppm = 0.916444 Hz/pt
number of scans: 168

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 816.735 ppm/cm: 6.49386

SpinWorks 2.5: 1D Proton NMR



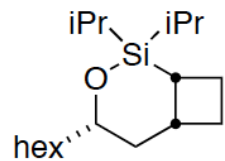
6-Pr diast 1



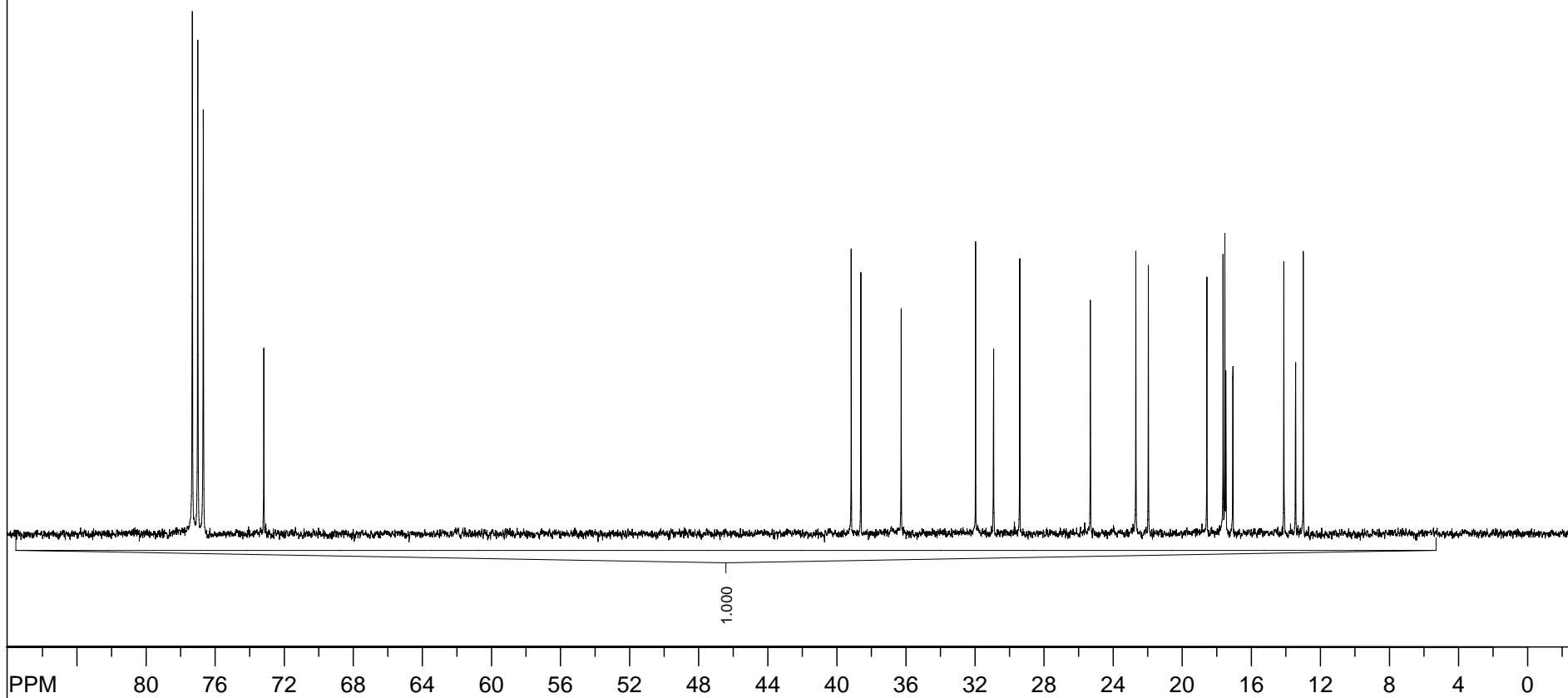
file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-211\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130005 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 128.814 ppm/cm: 0.32193

SpinWorks 2.5: ^{13}C NMR



6-Pr diast 1



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-2\fid exp: <zggp30>

transmitter freq.: 100.622830 MHz

time domain size: 32768 points

width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt

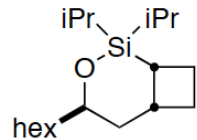
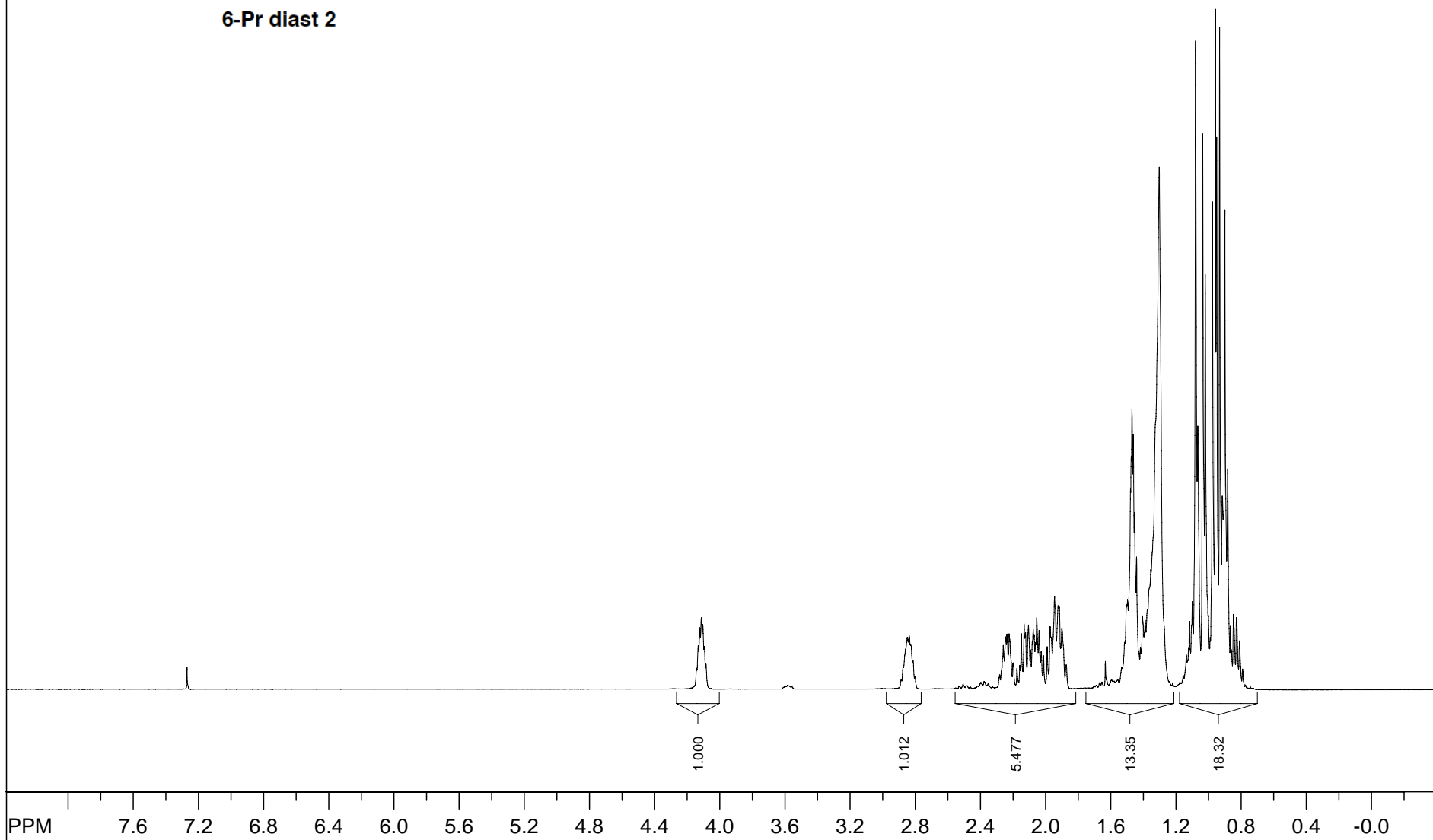
number of scans: 409

freq. of 0 ppm: 100.612769 MHz

processed size: 16384 complex points

LB: 1.000 GB: 0.0000

Hz/cm: 366.323 ppm/cm: 3.64055

**6-Pr diast 2**

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-11\fid exp: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

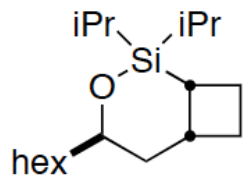
freq. of 0 ppm: 400.130005 MHz

processed size: 32768 complex points

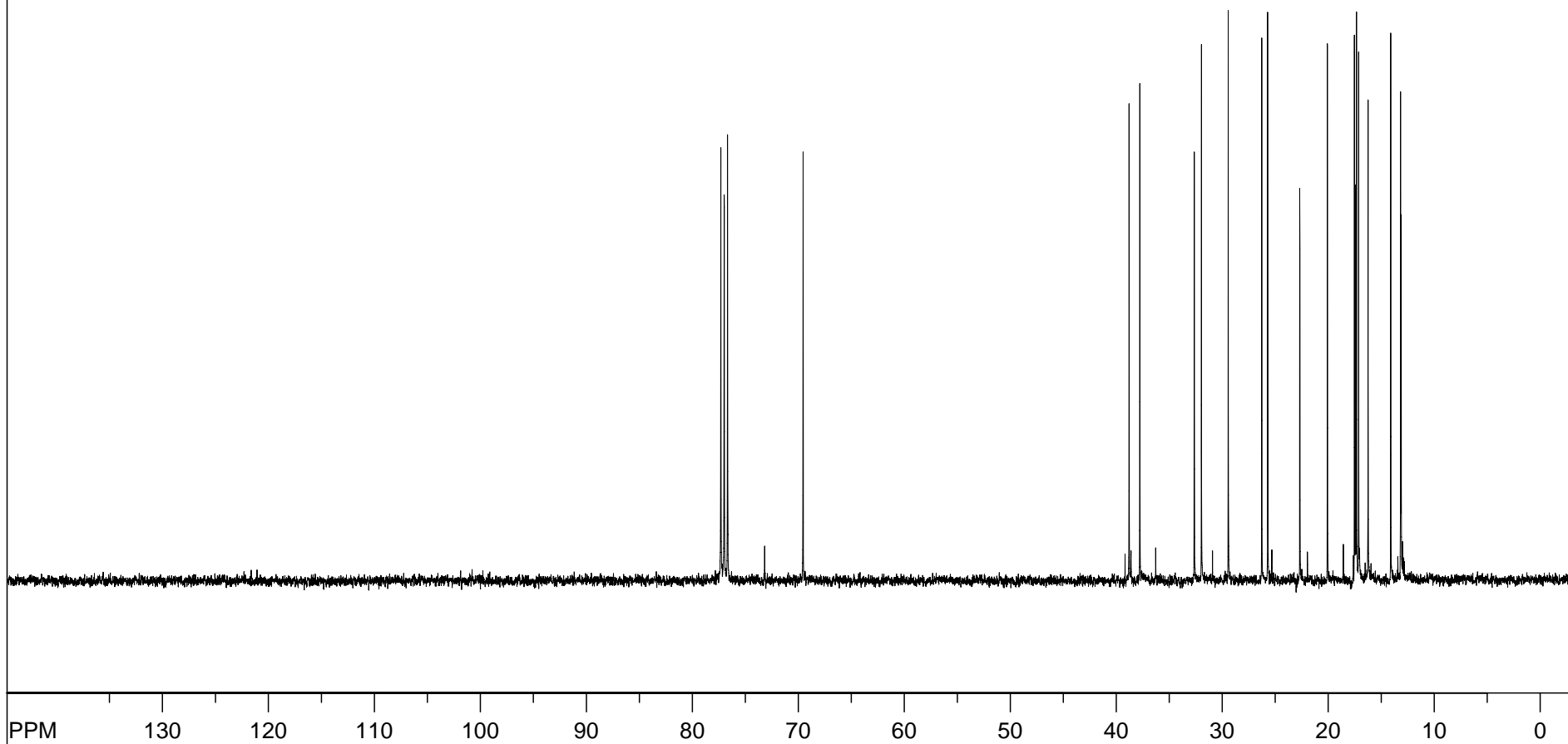
LB: 0.300 GB: 0.0000

Hz/cm: 141.279 ppm/cm: 0.35308

SpinWorks 2 5: 13C NMR

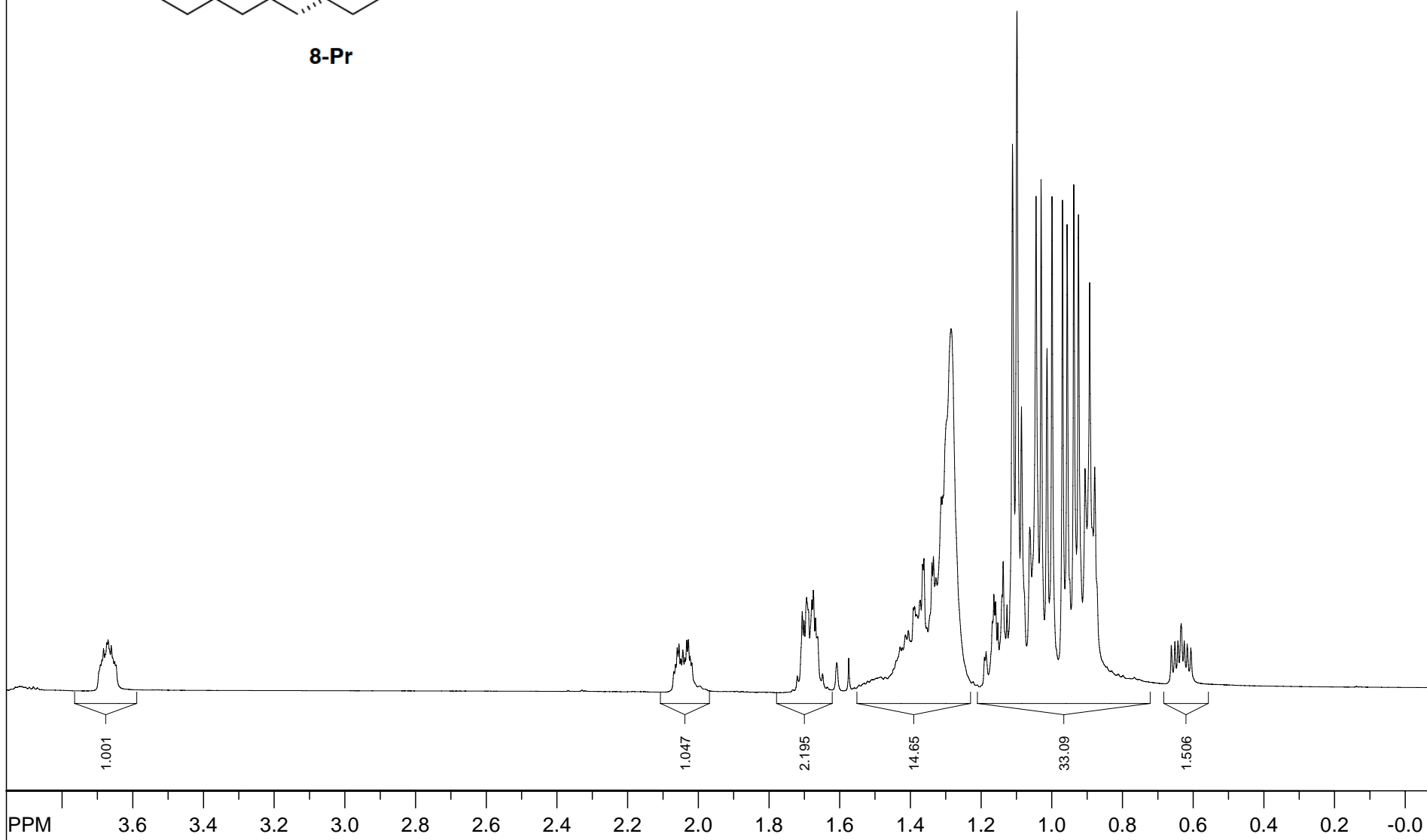
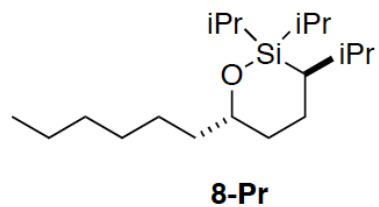


6-Pr diast 2



file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-12\fid exp: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 263

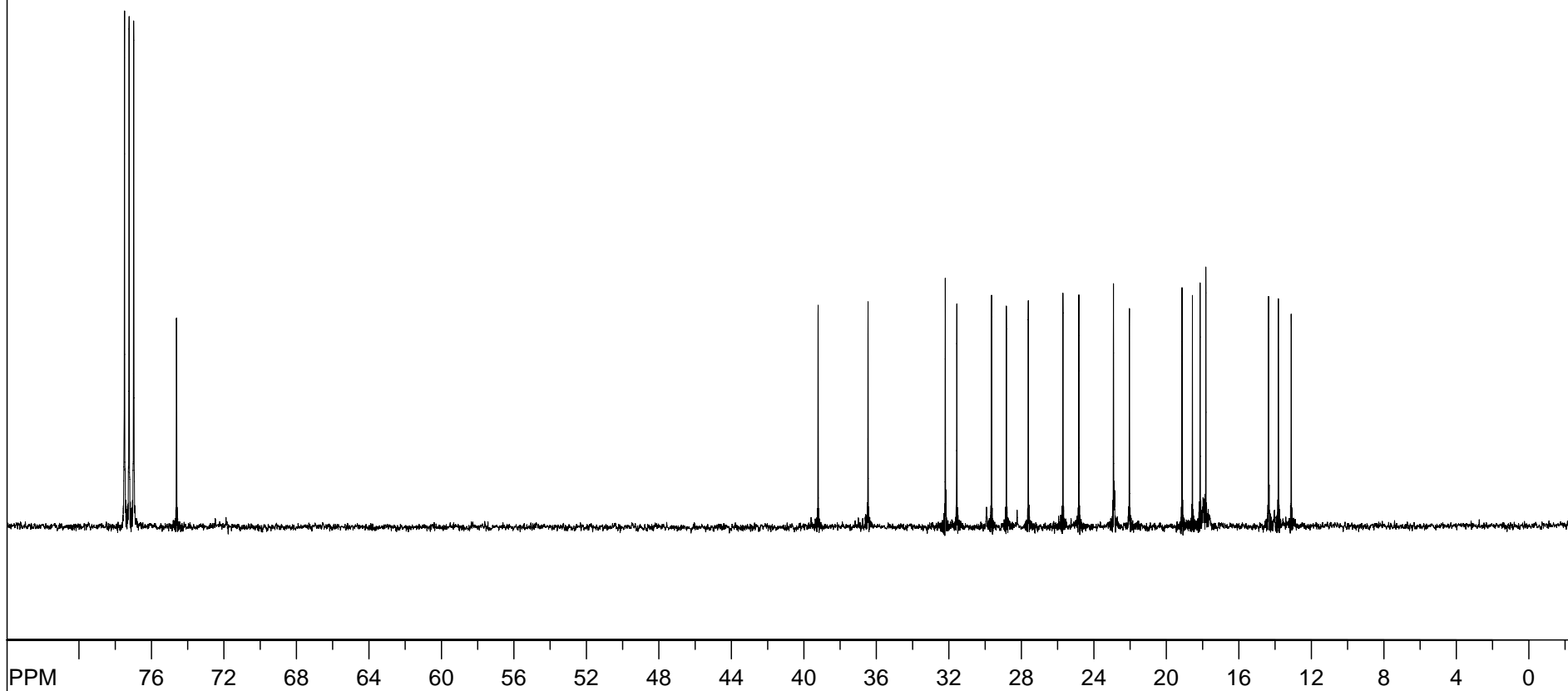
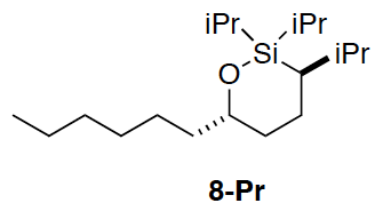
freq. of 0 ppm: 100.612769 MHz
processed size: 16384 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 596.919 ppm/cm: 5.93224



file: D:\CX_RVS_paper\rvs-4-76-1\1\fid exp: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16

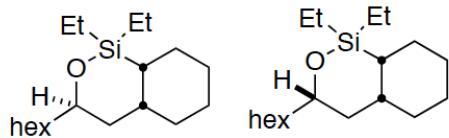
freq. of 0 ppm: 500.130008 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 80.537 ppm/cm: 0.16103

SpinWorks 2.5:

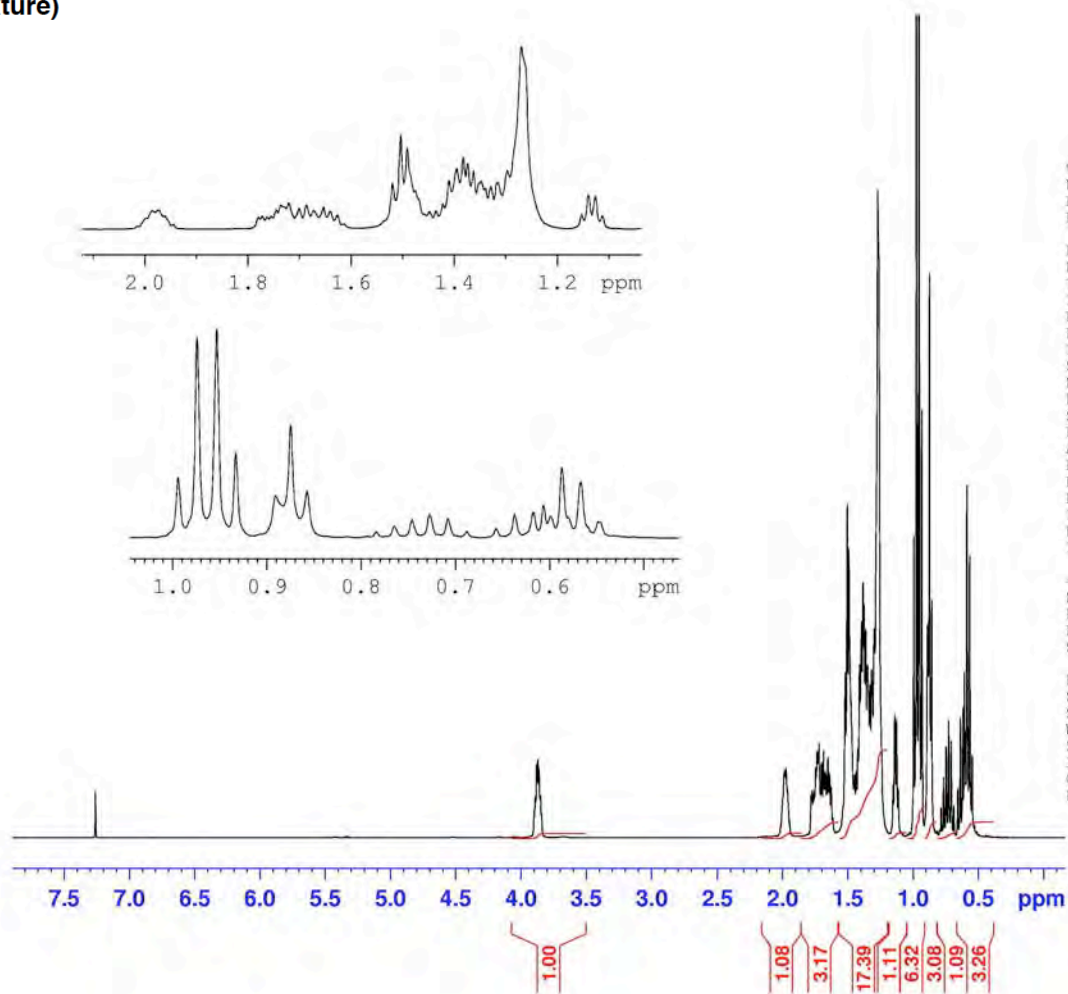


file: D:\CX_RVS_paper\rvs-4-76-1\6\fid exp: <zggp30>
transmitter freq.: 125.770364 MHz
time domain size: 16384 points
width: 30030.03 Hz = 238.768729 ppm = 1.832888 Hz/pt
number of scans: 256

freq. of 0 ppm: 125.757762 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 436.295 ppm/cm: 3.46898



10-Et (5:1 mixture)

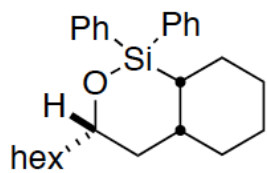


Current Data Parameters
 NAME cx-6-28-f2-hplc
 EXPNO 1
 PROCNO 1

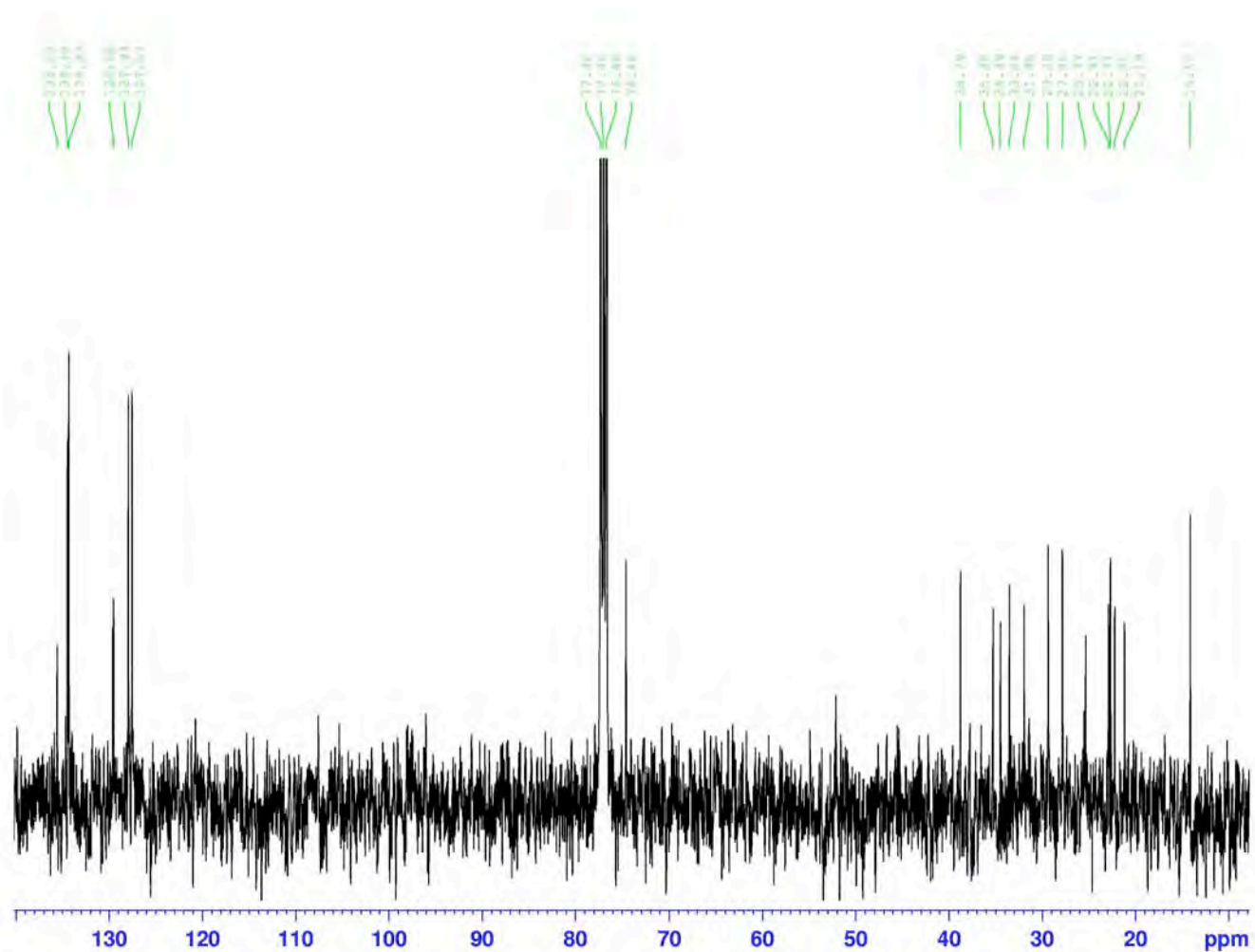
F2 - Acquisition Parameters
 Date_ 20061205
 Time 11.39
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 35.9
 DW 60.400 usec
 DE 6.00 usec
 TE 293.2 K
 D1 1.00000000 sec
 TD0 1

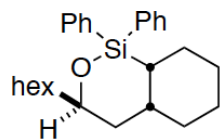
CHANNEL f1
 NUC1 1H
 P1 9.00 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300096 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40

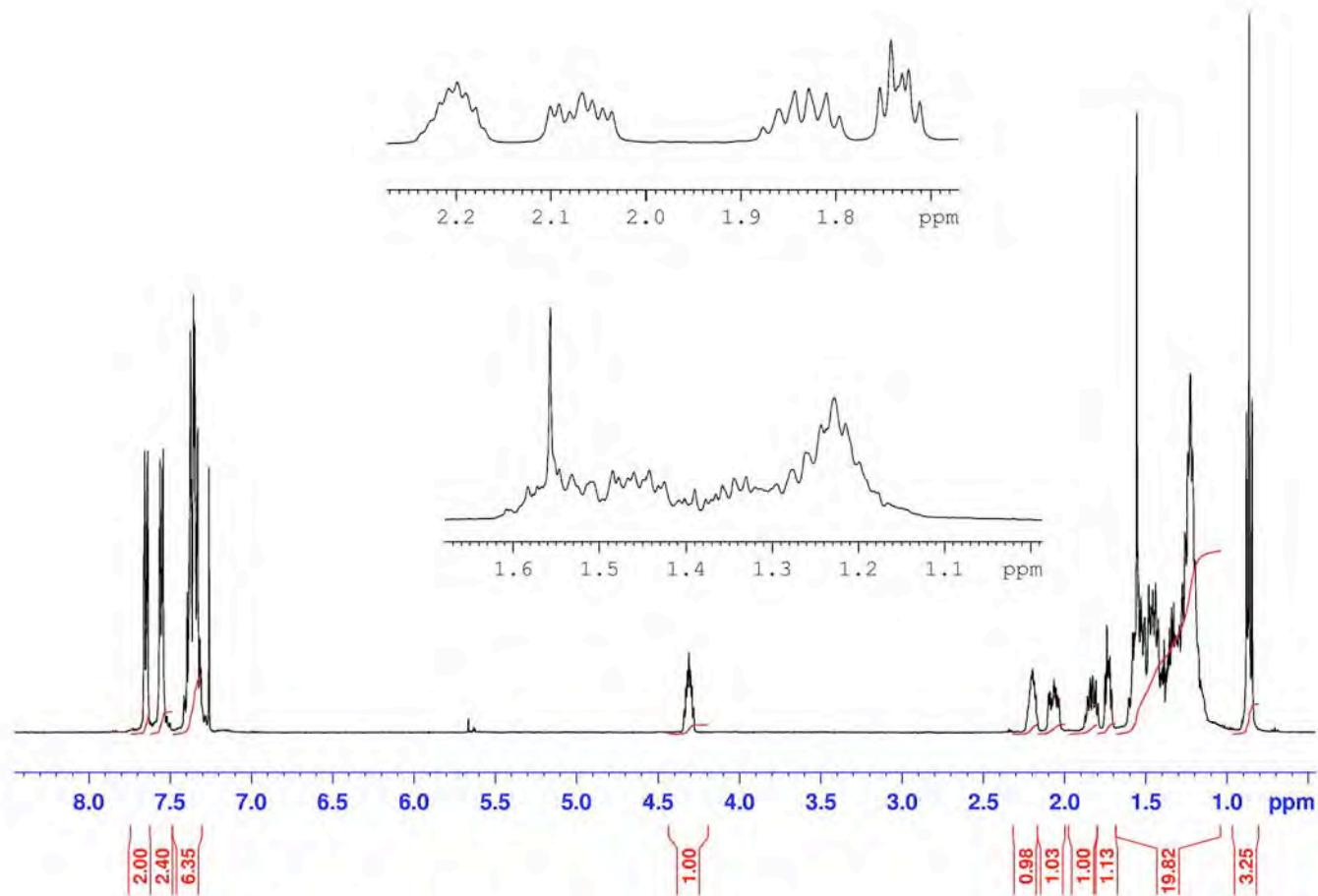


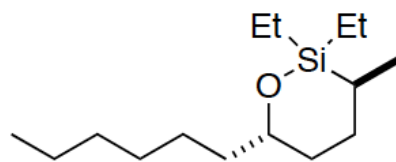
10-Ph diast 1 (minor)



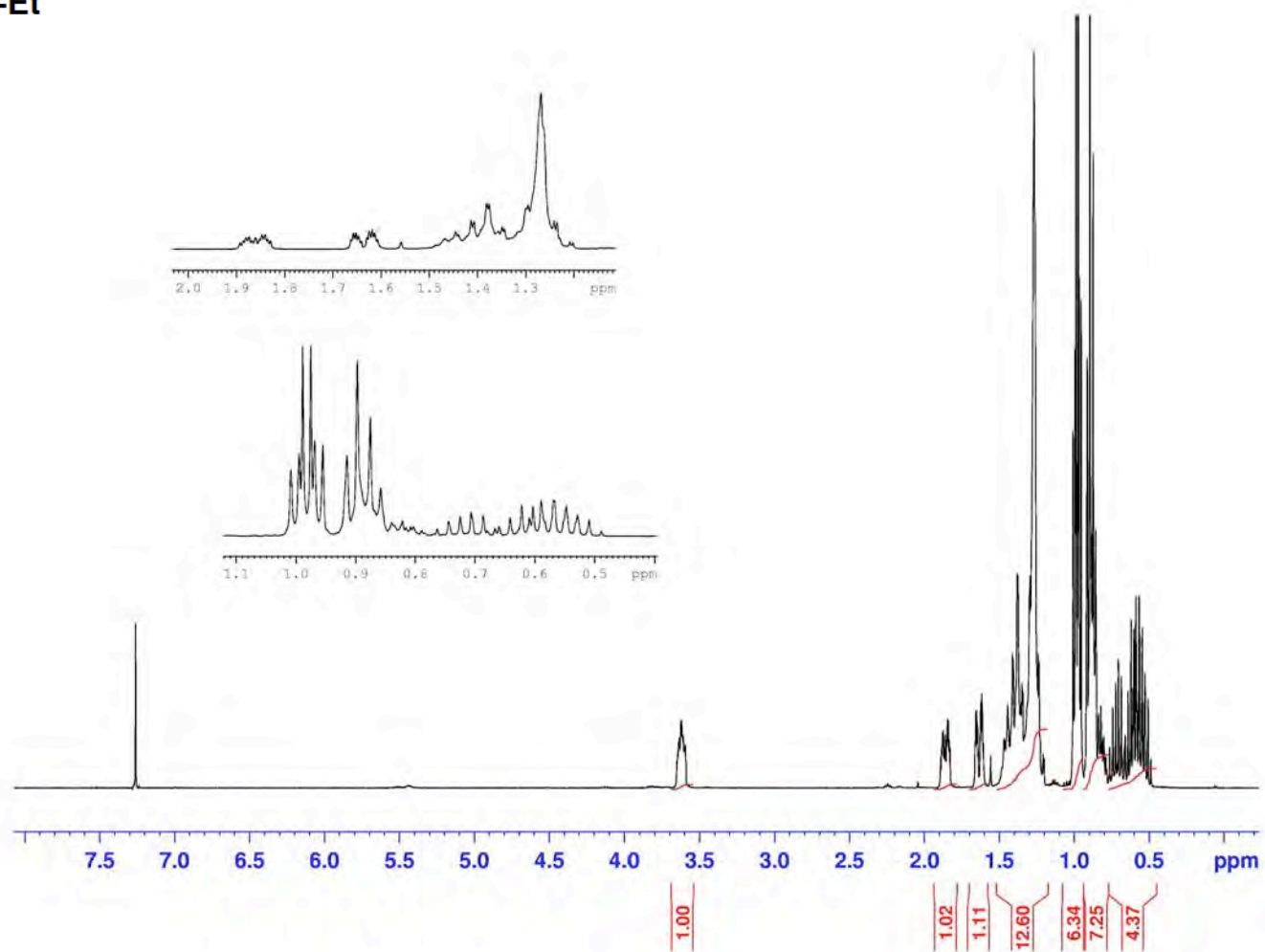


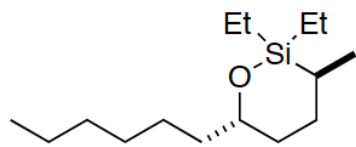
10-Ph diast 2 (major)



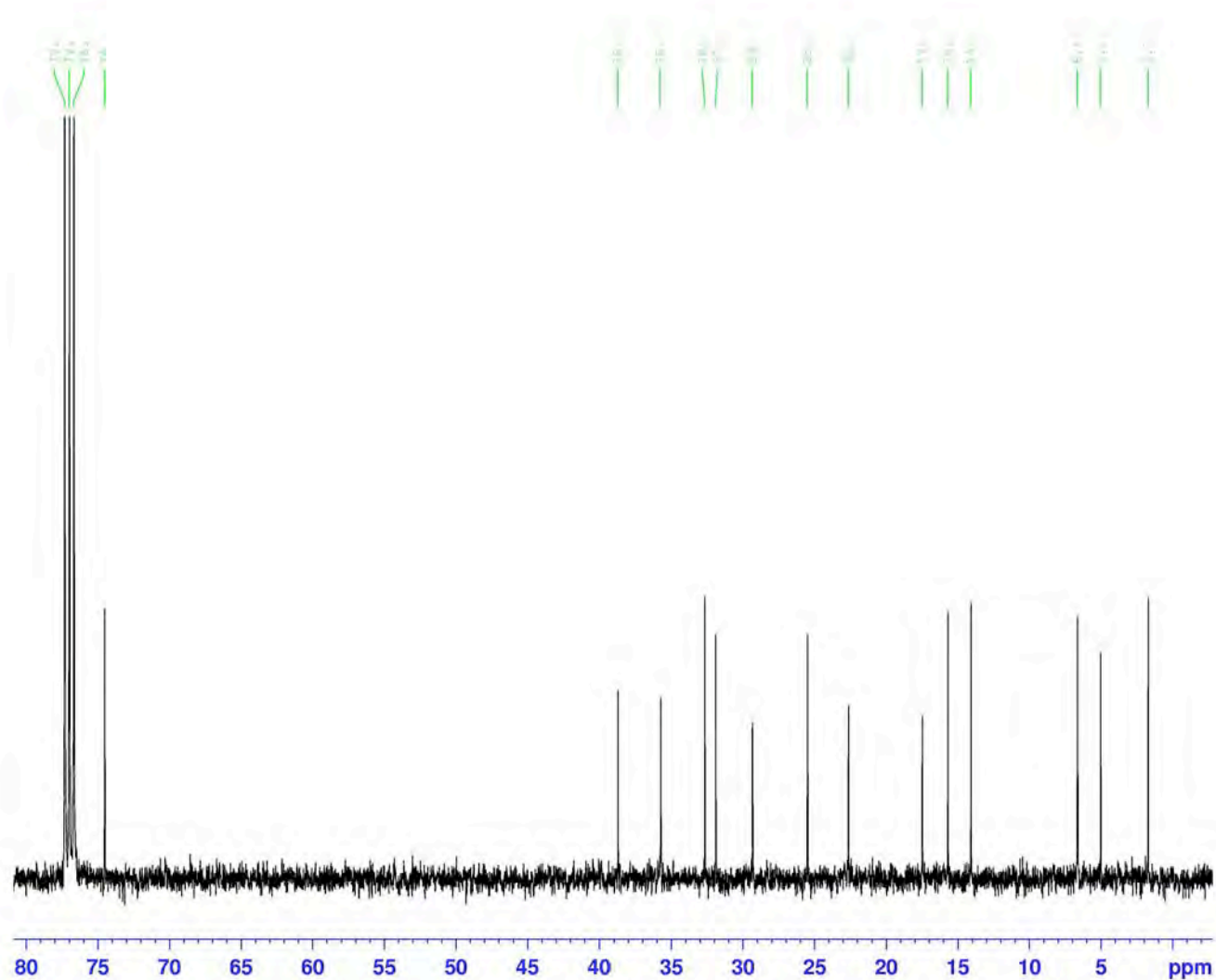


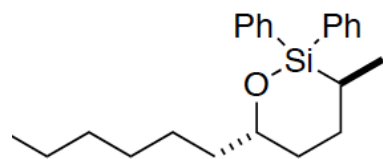
12-Et



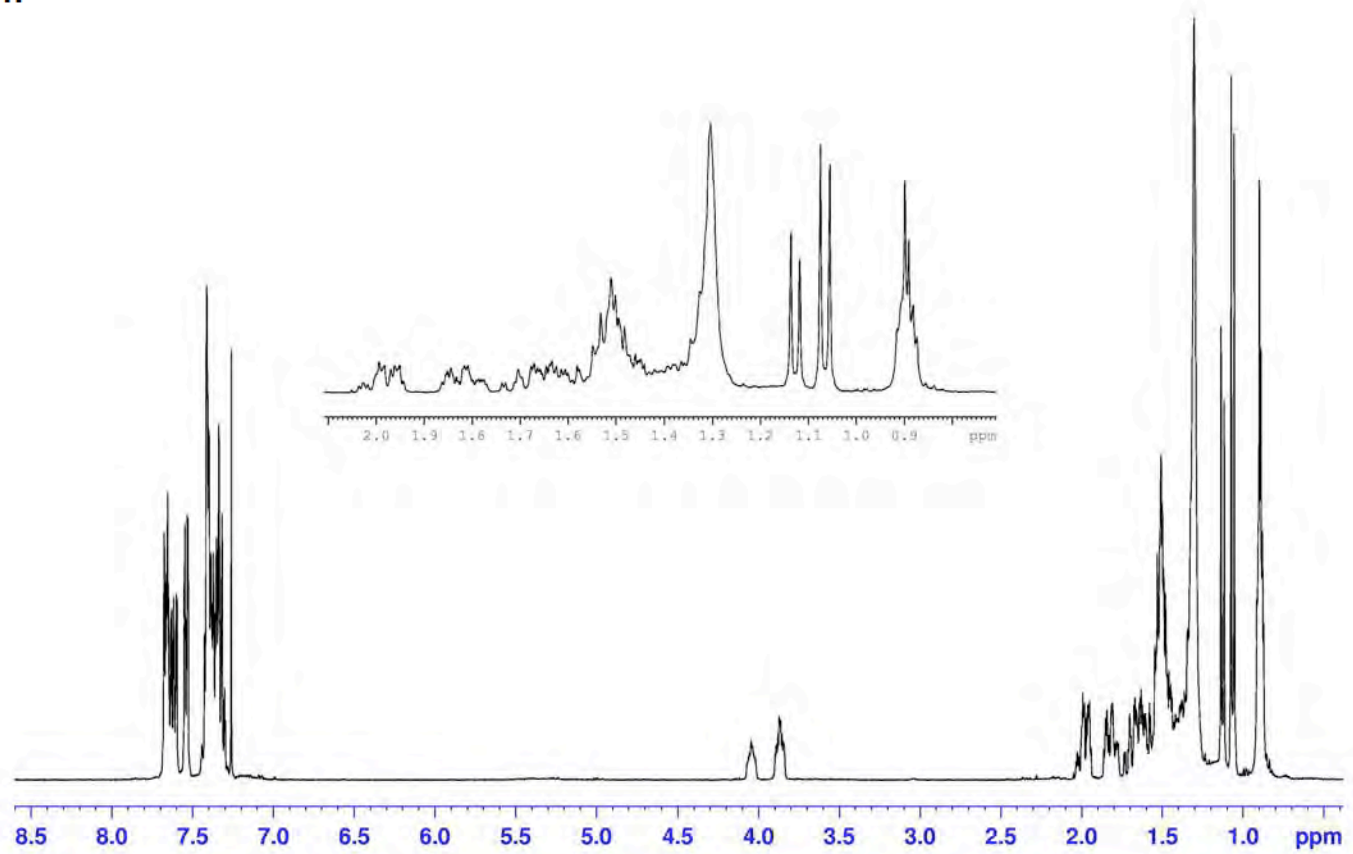


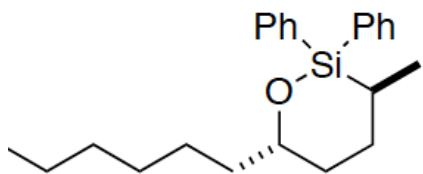
12-Et



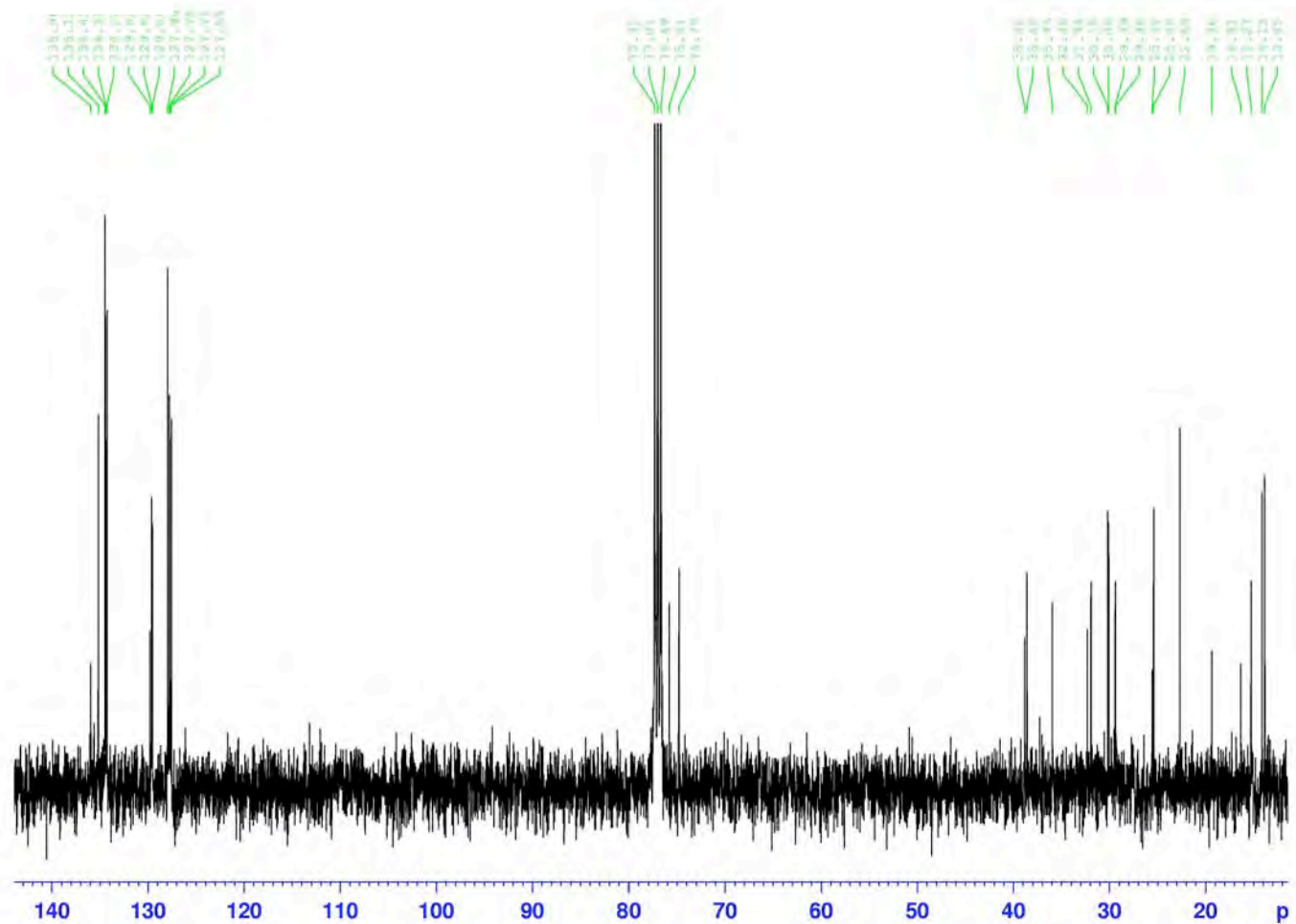


12-Ph

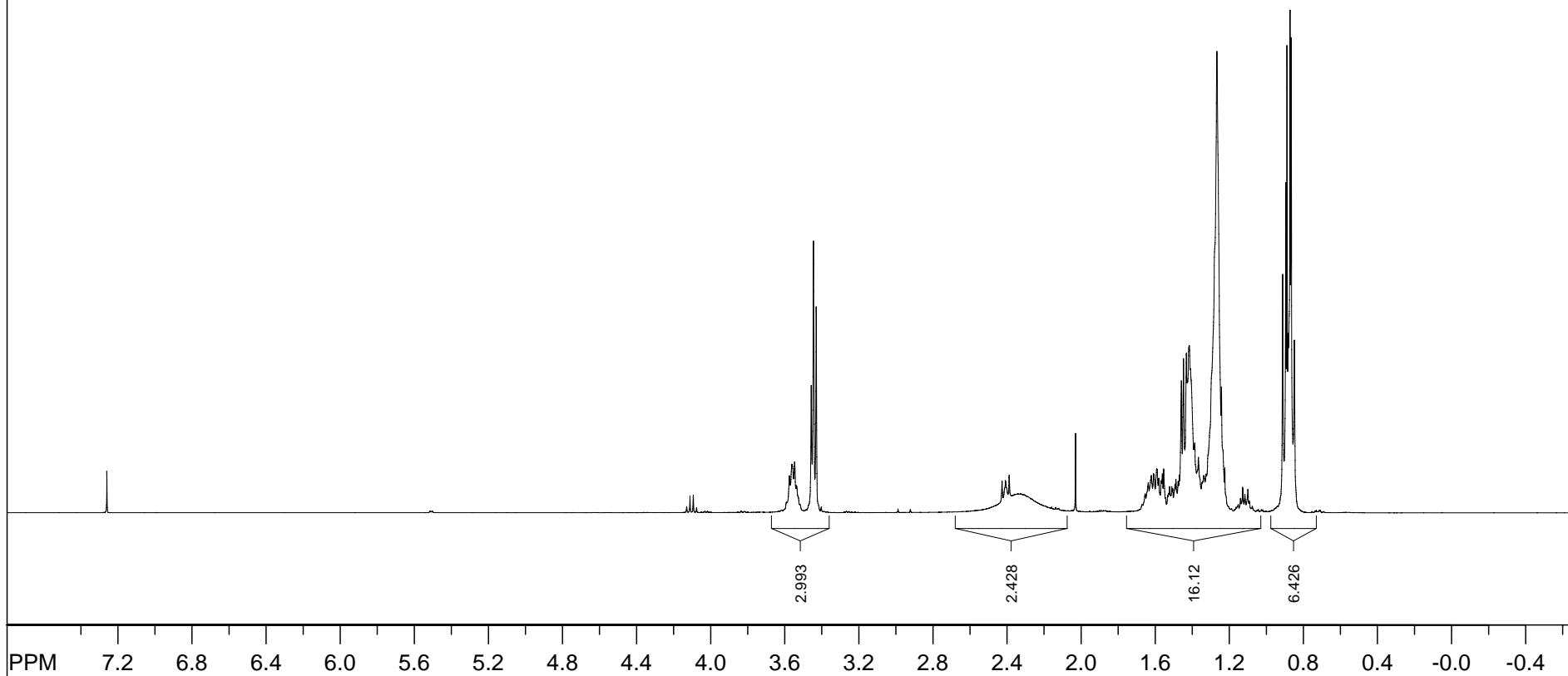
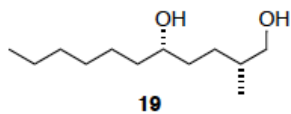




12-Ph



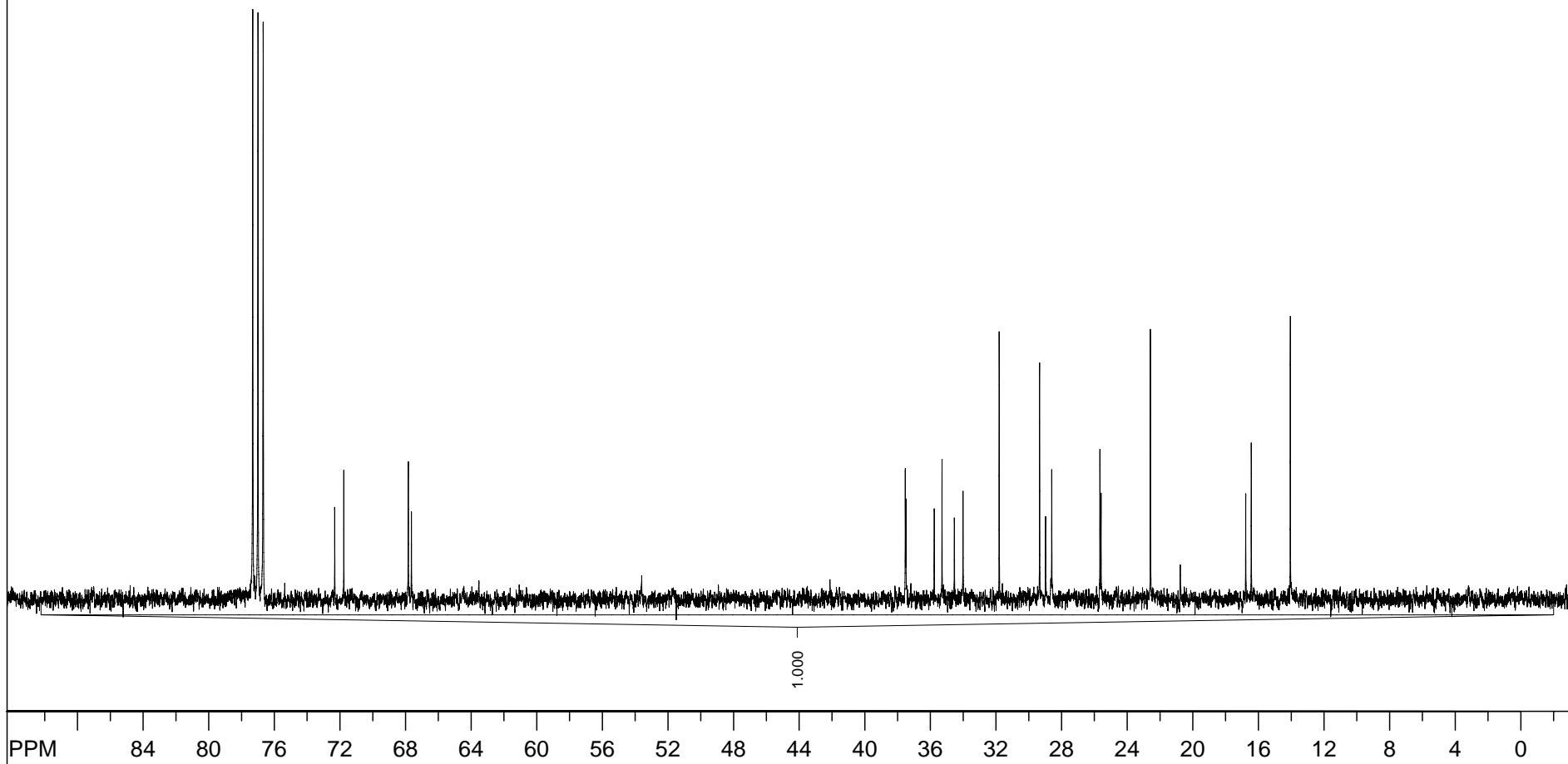
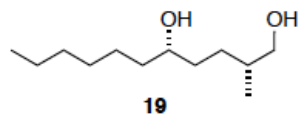
SpinWorks 2.5: 1D Proton NMR



file: D:\CX_RVS_paper\cx-6-42\1\fid exp: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

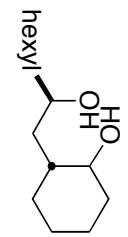
freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 135.826 ppm/cm: 0.33945

SpinWorks 2.5: 13C NMR

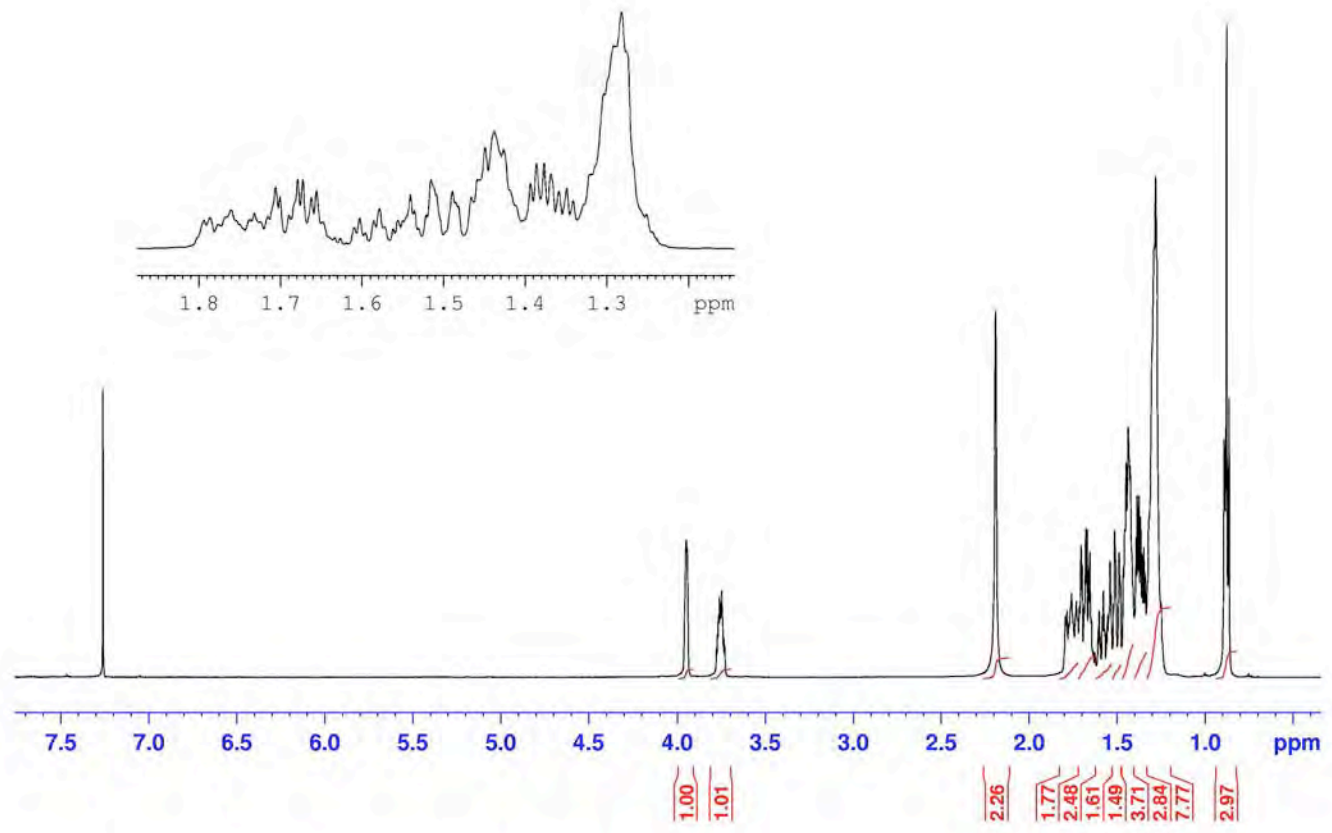


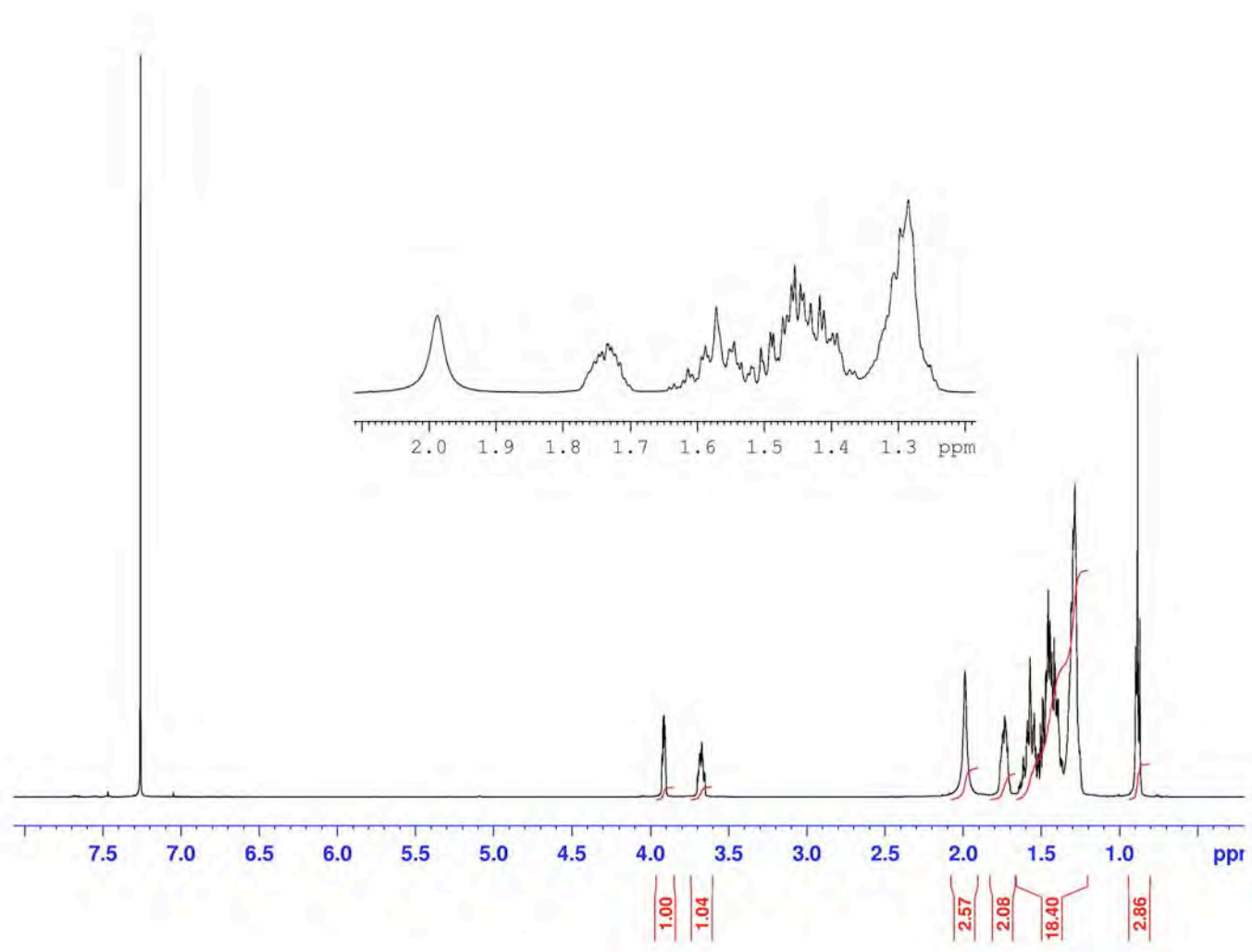
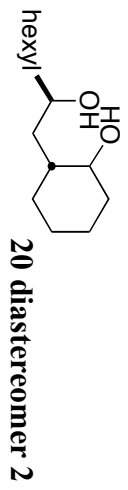
file: D:\CX_RVS_paper\cx-6-42\2\fid exp: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 67

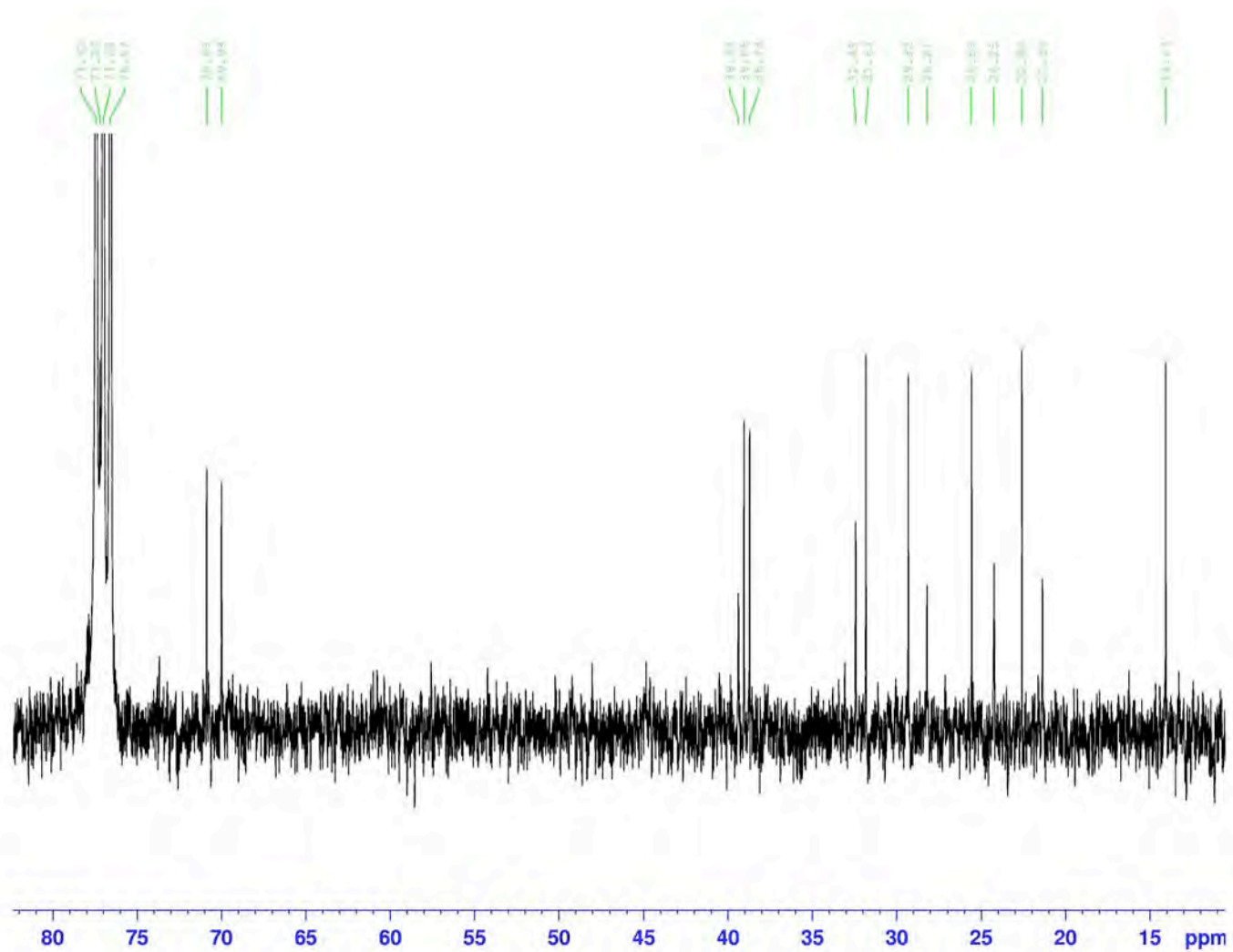
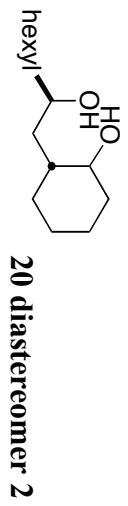
freq. of 0 ppm: 100.612775 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 385.712 ppm/cm: 3.83325

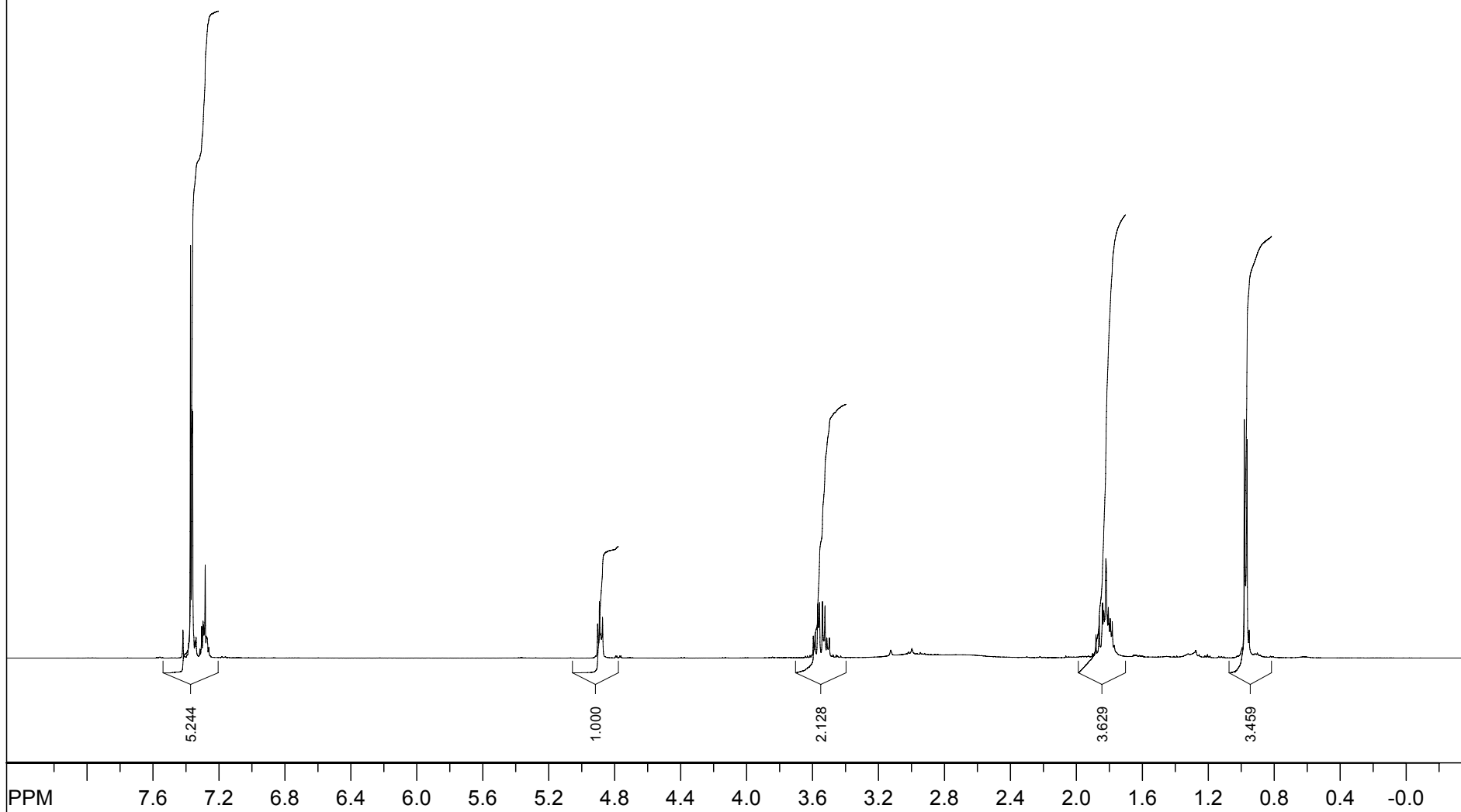
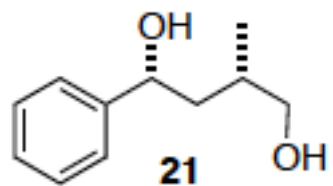


20-diastereomer 1









file: D:\CX_RVS_paper\More spectral\cx-6-25\1\fid expt: <zg30>

transmitter freq.: 400.132471 MHz

time domain size: 65536 points

width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt

number of scans: 16

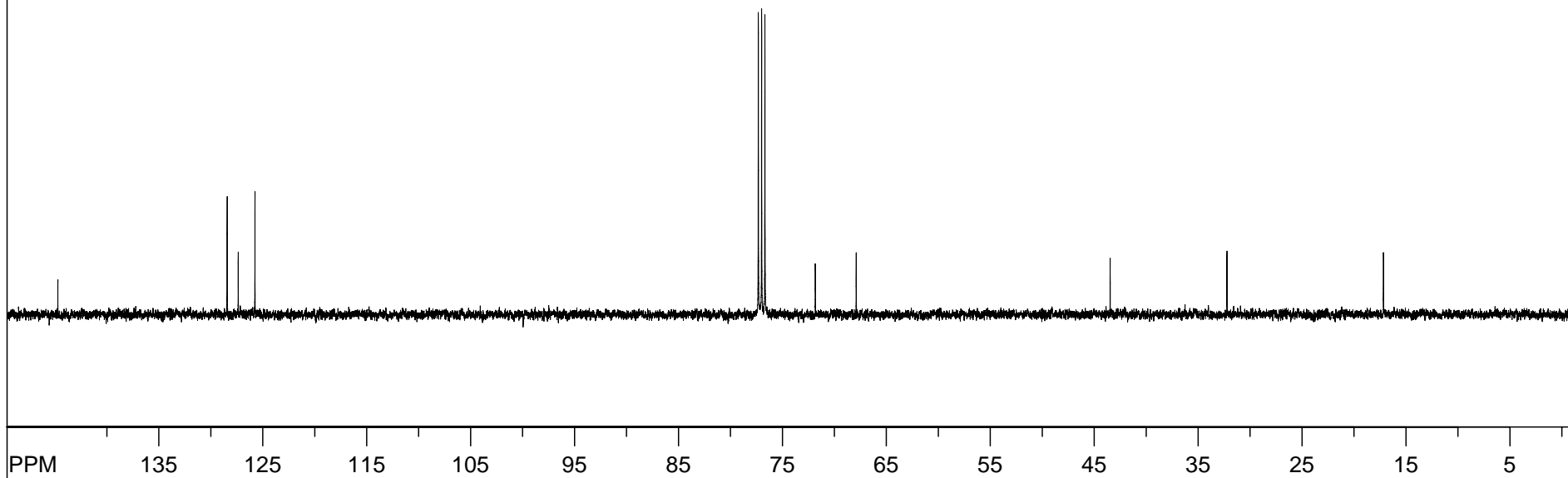
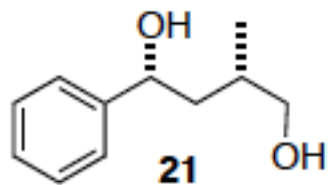
freq. of 0 ppm: 400.130000 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 142.318 ppm/cm: 0.35568

SpinWorks



file: D:\CX_RVS_paper\More spectra\cx-6-25\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 75

freq. of 0 ppm: 100.612774 MHz
processed size: 65536 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 608.691 ppm/cm: 6.04924