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Etienne Grau, Stefan Mecking. Polyterpenes by ring opening metathesis polymerization of caryophyllene and humulene. *Green Chemistry*, 2013, 15 (5), pp.1112-1115. 10.1039/c3gc40300a . hal-00915247

**HAL Id: hal-00915247**

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Submitted on 19 Nov 2019

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# Polyterpenes by Ring Opening Metathesis Polymerization of Caryophyllene and Humulene

Etienne Grau<sup>a</sup> and Stefan Mecking<sup>\*a</sup>

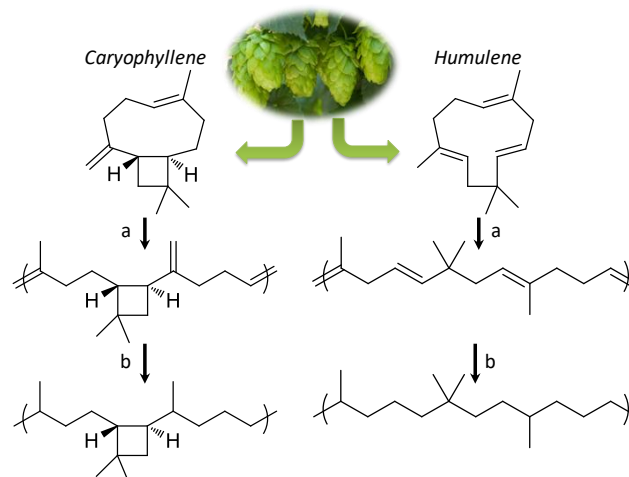
5 Ring opening metathesis polymerization of the natural sesquiterpenes caryophyllene and humulene, optionally complemented by exhaustive post-polymerization hydrogenation, yields non-crosslinked linear polymers with unprecedented microstructures reflecting the specific scaffolds of the feedstocks and low glass transition temperatures in the range from -15 to -50 °C.

Polymers with their myriad functions are indispensable to any modern technology. Today, their production is largely based on fossil fuels. In view of their limited range, other sources are desirable on the long term. Beyond such considerations, renewable resources are also attractive as they can contain unique chemical structures. Thus, carbohydrates,<sup>1</sup> fatty acids<sup>2</sup> or terpenes<sup>3</sup> contain a wealth of different structural elements. Particularly terpenes and terpenoids feature thousands of different scaffolds.<sup>4</sup> However, except for pinene, limonene and myrcene, there are few examples of other terpenes<sup>5</sup> used for polymerization. To translate the structural elements of a given renewable resource into useful materials properties, appropriate synthetic methods are required.

Caryophyllene and humulene are among the most abundant and cheaper sesquiterpenes. They are found in many plants and fungi.<sup>6</sup> For example, > 10<sup>5</sup> tons of clove oil<sup>7</sup> are produced annually by the clove tree *Eugenia caryophyllata* (*Syzygium aromaticum*). It contains 7-12% of caryophyllene and 1-4% of humulene. Another potential source is hop oil, with up to 25% of caryophyllene and 45% of humulene.<sup>8</sup>

Concerning the utilization of caryophyllene or humulene as a source of polymers, ill-defined polymeric materials have only been obtained from such sesquiterpenes as undesired side-products during episulfidation.<sup>9</sup> The unsaturated cyclic nature of caryophyllene and humulene in principal offers itself for ring opening metathesis polymerization (ROMP).<sup>10-13</sup> Thus, (-)-*trans*-caryophyllene (or  $\beta$ -caryophyllene) features a cyclobutane ring fused in a *trans* fashion to a nine-membered ring containing a 1,5-diene with the intra-ring double bond in *E* arrangement. Humulene, (1*E*,5*E*,8*E*)-1,4,4,8-tetramethylcycloundeca-1,5,8-triene, possess an eleven-membered ring with all three double bonds in a *trans* arrangement. The ROMP of such motifs is unusual, and there are only few reports of ROMP of nine- and eleven-membered rings, namely of the parent unsubstituted cyclononene or cycloundecene.<sup>14</sup> There is also only scarce evidence of ROMP of 1-methyl-substituted cycloalkenes.<sup>15</sup>

We now report on the reactivity of caryophyllene and humulene in metathesis polymerization, and properties and the reactivity of the polymers obtained (Scheme 1).

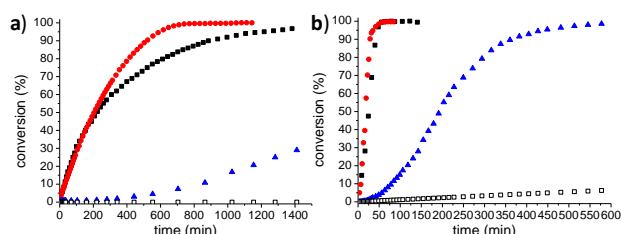


**Scheme 1.** Synthesis of poly(caryophyllene) and poly(hydrocaryophyllene), left, and poly(humulene) and poly(hydrohumulene), right. a: ROMP of the sesquiterpene; b: post-polymerization hydrogenation.

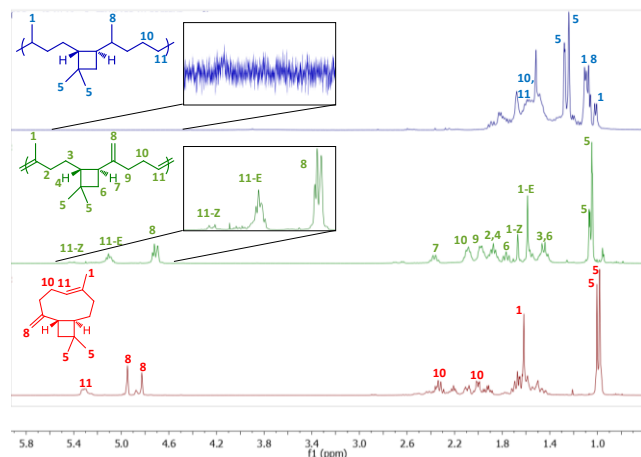
Five catalyst precursors differing in the nature of the active species and the initiation reactivity were screened for their behaviour towards caryophyllene, namely [(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh] (1), [(PCy<sub>3</sub>)( $\eta$ -C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Mes<sub>2</sub>)Cl<sub>2</sub>Ru=CHPh] (2), [(3-BrPyr)( $\eta$ -C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Mes<sub>2</sub>)Cl<sub>2</sub>Ru=CHPh] (3), [(PCy<sub>3</sub>)Cl<sub>2</sub>Ru=CH(*o*-iOPr-Ph)] (4) and [(PCy<sub>3</sub>)( $\eta$ -C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Mes<sub>2</sub>)Cl<sub>2</sub>Ru=CH(*o*-iOPr-Ph)] (5). Reactions were run at 25 °C over a prolonged period of a week in order to ensure a maximum conversion (Table S1). Polycaryophyllene can be produced in good yield with catalyst precursors 2, 3 and 5. With 1<sup>st</sup> generation metathesis catalysts (1 and 4), no polymer was obtained whatever the catalyst/monomer ratio.<sup>16</sup> For 2<sup>nd</sup> generation catalysts (2 and 5), the yield of the polymerization drastically decreased with lower catalyst loading, likely due to deactivation/decomposition of the catalyst. By contrast, with 3 complete conversion could be achieved even at a low catalyst loading of 0.04 mol-%.

The progress of polymerizations over time with the different catalyst precursors was also followed by <sup>1</sup>H NMR from monitoring of the =CHR, =CH<sub>2</sub> and CH<sub>3</sub> resonances (Figure 1a). Catalyst precursor 3 appears to be most active for ROMP of caryophyllene, with total conversion reached in less than 12 hours. 2 initially polymerizes with a similar rate. This levels off after ca. 4 hours, however, indicating catalyst deactivation. Indeed, with 2<sup>nd</sup> generation catalysts (2 and 5), ruthenium black is formed during the polymerization. This was not observed with 3. ROMP with 5 has a very long induction time and the conversion starts only after 5 hours at a lower rate. The *E/Z* selectivity of metathesis appears to be dependent on the catalyst, with 2 55% of *E* configured product was obtained, vs. 63% with 5 and 87% with 3. However, this

had no observable impact on the polymers  $T_g$  (vide infra).



**Fig. 1** ROMP kinetics of caryophyllene (a) and humulene (b) with ruthenium alkylidenes **1** (□), **2** (■), **3** (●) and **5** (▲). Determined by  $^1\text{H}$  NMR spectroscopy from the  $=\text{CHR}$ ,  $=\text{CH}_2$  and  $\text{CH}_3$  resonances at  $25^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  with a catalyst/monomer ratio of 1/125.



**Fig. 2**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectra of caryophyllene (bottom), polycaryophyllene (center) and poly(hydrocaryophyllene) (top, in  $\text{C}_2\text{D}_2\text{Cl}_4$ ). Insets: details of the range between 5.6 and 4.6 ppm.

During polymerization, the *exocyclic* methylene group does not react to any observable extent. Thus, the ratio between  $=\text{CHR}$  and  $=\text{CH}_2$  proton remains constant during the polymerization. Also, the polymers formed are entirely soluble which confirms that no cross-linking occurred. The polycaryophyllene microstructure depicted in Figure 1 was confirmed by comprehensive  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis (Figure 2 and Electronic Supplementary Information, ESI). Only six olefinic  $^{13}\text{C}$  resonances are observed for the polycaryophyllene, confirming that neither head-head nor tail-tail propagation nor cross-linking occur to an observable extent during the ROMP. The observed lack of reactivity of the vinylidene bond towards metathesis can be related to the high steric demand induced by the cyclobutane ring and the fact that the HOMO is mainly located on the other double bond. Finally, the intact cyclobutane ring present in the polymer is evidenced by its characteristic resonances at  $[(\delta\text{-}^1\text{H}) \text{ ppm}/(\delta\text{-}^{13}\text{C}) \text{ ppm}]$   $\text{HC-C}=\text{CH}_2$  [2.37/41.74],  $-\text{CH}_2\text{-CH}$  [1.87/48.69],  $\text{CH}_2$  [1.77/39.83] and [1.45/39.83], and  $\text{CMe}_2$  [-/33.85]. The number average molecular weights ( $M_n$ ) of the polycaryophyllene obtained with **3** were in the range of 1.7 to  $2.0 \times 10^4 \text{ g mol}^{-1}$ . Molecular weight distribution of  $M_w/M_n$  1.8 - 1.9 point to a well-behaved nature of the polymerization reaction, and to chain transfer, presumably by back-biting, determining molecular weights. The latter is in-line with the

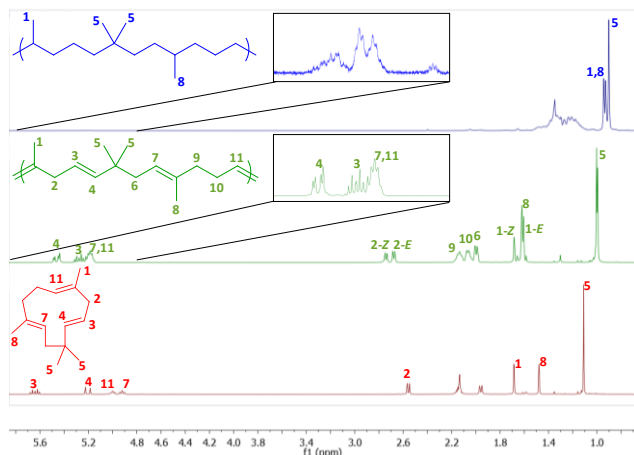
observed formation of several polymer chains per catalyst precursor molecule, as calculated from polymer molecular weights and catalyst loading. The polycaryophyllene obtained is a colorless, sticky and viscous material. DSC reveals a glass transition around  $T_g = -32^\circ\text{C}$ .

The two different types of double bonds in polycaryophyllene may undergo undesired cleavage reactions, cross-linking or rearrangements upon storage or in applications. To this end, post-polymerization hydrogenation was studied. Exposure to 50 bar of  $\text{H}_2$  at  $80^\circ\text{C}$  in the presence of a standard Pd/C catalyst (1/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  solvent) resulted in virtually complete conversion as evidenced by the absence of any olefinic  $^1\text{H}$  and  $^{13}\text{C}$  resonances (Figure 2 and ESI). This corresponds to a degree of hydrogenation  $> 99.5\%$ . In  $^1\text{H}$  NMR spectra four new doublets, corresponding to  $\text{CH}_3\text{-CH}$  motifs resulting from the hydrogenation of the double bonds, appear at 1.10, 1.08, 1.06 and 1.00 ppm (respectively 19.90, 27.69, 17.28 and 16.56 ppm in  $^{13}\text{C}$  NMR spectra). For one of the new stereocenters resulting from the reduction of the  $\text{C}=\text{CH}_2$  motifs a high ratio of 1/10 of the two stereoisomers is observed, compared to a 1/2 ratio for the other newly formed stereocenter. This high stereoselectivity can be understood in that the chiral center of the cyclobutane ring significantly impacts the hydrogenation pathways of the adjacent vinylidene unit. Notably, the cyclobutane ring is not affected by the hydrogenation procedure.<sup>17</sup>  $^1\text{H}$ - $^{13}\text{C}$  HSQC demonstrated the presence of six additional CH carbon atoms, which agrees with the expected structure. Hydrogenation results in an increase of the  $T_g$  to ca.  $-16^\circ\text{C}$ .

Based on the aforementioned findings, polymerization of humulene was performed with **3** (Table S2). A colorless sticky materials was obtained in high yield even at a low catalyst loading (0.04 mol-%).  $M_n$  amounted to  $3.0 \times 10^4 \text{ g mol}^{-1}$  typically, with  $M_w/M_n \approx 2$ . DSC showed a  $T_g$  around  $-48^\circ\text{C}$ .

Microstructure analysis of the polymer indicates that the ROMP occurs only on one of the three different double bonds of the humulene starting material (Scheme 1 and Fig. 3). The two other double bonds strictly retain their *E* configuration in the polymer, while a 60/40 *E/Z* ratio is observed for the reacted double bond. Moreover, only one new  $^{13}\text{C}$  NMR resonance arises for a methyl in  $\alpha$  position to a *Z* double bond (23.37 ppm vs. 16.24, 16.18 and 15.95 ppm). The methylene group adjacent to two double bonds is also strongly affected by the *E/Z* configurational change ( $[(\delta\text{-}^1\text{H}) \text{ ppm}/(\delta\text{-}^{13}\text{C}) \text{ ppm}]$ ): [2.74/35.48] for *Z* and [2.67/43.27] for *E*. This indicates that the trisubstituted double bond adjacent to this methylene unit undergoes ROMP. The unreactivity of the disubstituted olefin can be understood in that the two methyl substituents in  $\beta$  position generate a high steric constraint. However, the sterical constraints at the two trisubstituted double bonds appear to be similar. DFT studies provide an insight into the origin of the different reactivity observed. The HOMO of humulene is located mainly on the reacting double bond and is high in energy ( $+23 \text{ kJ mol}^{-1}$  compared to the occupied orbital located on the other trisubstituted double bond) due to two anti-bonding  $\pi\text{-}\pi$  interactions with the other double bonds (cf. ESI). Monitoring of humulene ROMP over time shows that the polymerization is faster compared to

caryophyllene polymerization under the same conditions (Figure 1b). Complete conversion is achieved in one hour using **2** or **3** as a catalyst precursor, and in ten hours with **5**.<sup>18</sup> Notably, ROMP of humulene also occurs with **1**. However, the reaction is slow and after 12 hours the conversion is 10%.



**Fig. 3** <sup>1</sup>H NMR spectra of humulene (bottom), polyhumulene (center) and poly(hydrohumulene) (top). Insets: details of the range between 5.7 and 4.8 ppm. Spectra recorded at 400 MHz in CDCl<sub>3</sub> (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) and 120°C for poly(hydrohumulene).

Hydrogenation of the polyhumulene under the same conditions as for polycaryophyllene resulted in a degree of hydrogenation of 98.3 % (Fig. 3). A new <sup>1</sup>H doublet resonance arises from the CH<sub>3</sub>-CH motif resulting from the hydrogenation of the trisubstituted double bonds, with  $\delta = 0.93$  ppm (19.86, 19.82 and 19.77 ppm in <sup>13</sup>C NMR).<sup>19</sup> DSC of polyhydrohumulene reveals a T<sub>g</sub> around -44°C.

The novel polymers obtained are soft materials with a low T<sub>g</sub>. This renders them attractive for film formation and coatings. An established environmentally friendly route to polymer coatings and films is their generation from aqueous polymer dispersions. To this end, preliminary studies showed that ROMP of caryophyllene as well as the hydrogenation step could also be performed in aqueous emulsion using mini- or microemulsion techniques,<sup>20</sup> without any additional organic solvents. For example, a solution of **3** in 3 mL of caryophyllene and 0.4 mL of hexadecane hydrophobe was ultrasonicated with 30 mL of an aqueous SDS solution (13.3 g L<sup>-1</sup>). Polymerization afforded a dispersion of particles with an average size of typically *ca.* 200 nm and a polydispersity of 0.1-0.3. NMR spectroscopy confirmed that the polymer produced is similar to the one produced in bulk. Also, molecular weights are comparable (M<sub>n</sub> = 2.0 × 10<sup>4</sup> g mol<sup>-1</sup> and M<sub>w</sub>/M<sub>n</sub> = 1.9).

## Conclusions

In conclusion, polymers can be obtained by ROMP of naturally occurring terpenes. Namely, the readily available sesquiterpenes caryophyllene and humulene can be polymerized with appropriate ruthenium alkylidenes. Their nine- and eleven-membered rings, respectively, are opened with selective reaction of only one of the different types of

double bonds present. This results in non-crosslinked polymers with a well-defined microstructure. These polymers as well as their fully saturated analogues are soft materials characterized by a glass transition in the range from -15 to -50 °C. This renders them attractive for environmentally friendly hydrophobic films and coatings based on renewable resources. To this end, aqueous dispersions are accessible by ROMP in emulsion as demonstrated for caryophyllene.

## Notes and references

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**Electronic Supporting Information**

# **Polyterpenes by Ring Opening Metathesis Polymerization of Caryophyllene and Humulene**

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## Experimental section

All chemicals were handled under argon atmosphere using standard Schlenk or glovebox techniques. Caryophyllene with a purity grade of 80% and 98.5% and humulene with a purity grade of  $\geq 96\%$  were purchased from Aldrich and were used as received. Metathesis catalysts ( $[(PCy_3)_2Cl_2Ru=CHPh]$ ,  $[(PCy_3)(\eta-C-C_3H_4N_2Mes_2)Cl_2Ru=CHPh]$ ,  $[(3-BrPyr)(\eta-C-C_3H_4N_2Mes_2)Cl_2Ru=CHPh]$ ,  $[(PCy_3)Cl_2Ru=CH(o-iOPr-Ph)]$  and  $[(PCy_3)(\eta-C-C_3H_4N_2Mes_2)Cl_2Ru=CH(o-iOPr-Ph)]$ ) were purchased from Aldrich and were used as received. Palladium on activated charcoal (10% Pd basis), sodium dodecyl sulfate, pentanol and hexadecane were purchased from Aldrich and was used as received.

### *Characterizations*

Molecular weights distributions were determined by size exclusion chromatography (SEC) using a Polymer Laboratories PL-GPC 50 instrument equipped with a refractive index and a UV/vis detector (columns: PLgel 5 $\mu$ m MIXED-C) in THF at 40°C against polystyrene standards.

Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating rate of 30 K/min from -150°C to 160°C. Two successive heating and cooling of the samples were performed. We have considered data obtained during the second heats.

GC analysis was carried out on a Perkin Elmer Clarus 500 GC system equipped with a Perkin Elmer Elite-5 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m, 5% diphenyl - 95% dimethyl polysiloxane) using flame ionization detection. Helium of 99.995% purity was used as the carrier gas. The initial temperature of 90°C was kept for one minute, and the column was then heated at a rate of 30 K min<sup>-1</sup> to 280°C, and kept isothermal at this temperature for 8 min (injector temperature 300°C; detector temperature 280°C).

High-resolution liquid NMR spectroscopy was carried out at 25°C with a Bruker Avance III 400 equipped with a BBFO plus probe or a Varian Unity Inova 400 equipped with aNUC/switchable mode – 5 mm “direct detection” probe. Chemical shift values ( $\delta$ ) were given in ppm in reference to the solvent signals. The identity of polymers and detailed NMR assignments were established by 2D NMR experiments ( $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC) in addition to 1D NMR experiments. Acquired data was processed and analyzed using MestReNova software.

DFT calculations were done using GAUSSIAN09 with the B3PW91 hybrid functional and a high quality 6-311++G(d) basis set. Molden are use to plot the molecular orbitals of caryophyllene and humulene.



### *ROMP of caryophyllene*

In a schlenk, given amounts of metathesis catalyst and then 5 mL of 80% caryophyllene were added under argon. The schlenk was mechanical stirred at 25°C for 1 week. Then the viscous polymer was dissolved in chloroform and filtered over celite to remove ruthenium black. The polymer was then vacuum dried. Up to 4.5 g of a sticky viscous colorless polymer was obtained. At low catalyst loading (0.04 mol%) a colorless polymer is obtained after several washing step (otherwise the product is greenish due to catalyst residue). NMR of the polymer was reported Fig S7-S11

### *Hydrogenation of polycaryophyllene*

100 mg of polycaryophyllene was dissolved under argon in a schlenk in 10 mL of a 1/1 v/v mixture of CH<sub>2</sub>Cl<sub>2</sub>/MeOH. Then 20 mg of palladium on activated charcoal was added to the solution. The mixture was introduced through cannula into a 22 mL stainless steel pressure reactor equipped with a glass insert. Temperature regulation was provided by a contact thermometer integrated into a heating block. Mixing was performed with a magnetic stirring bar. A static pressure of 50 bar of H<sub>2</sub> was applied and the mixture stirred at 80°C for 2 days. After cooling down to room temperature, the pressure was released and the crude reaction mixture was dissolved in toluene. Palladium catalyst was removed by filtration and the polymer was then dried under vacuum. 95 mg of a sticky viscous colorless polymer was obtained. NMR of the polymer was reported Fig S22-S25.

### *Kinetics ROMP of caryophyllene*

In a NMR tube, a metathesis catalyst and 98.5% caryophyllene 1/125 mixture was solubilized in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR spectra were recorded at regular time intervals to

follow the kinetic of the caryophyllene ROMP. Integrals of =CH<sub>2</sub>, =CHR and CH<sub>3</sub> signals were used to determined the polymerization kinetic.

#### *Hydrogenation of caryophyllene*

2 g of caryophyllene was dissolved under argon in a schlenk in 10 mL of MeOH. Then 20 mg of palladium on activated charcoal was added to the solution. The mixture was introduced through cannula into a 22 mL stainless steel pressure reactor equipped with a glass insert. Temperature regulation was provided by a contact thermometer integrated into a heating block. Mixing was performed with a magnetic stirring bar. A static pressure of 50 bar of H<sub>2</sub> was applied and the mixture was stirred at 80°C for 2 days. After cooling down to room temperature, the pressure was released and the crude reaction mixture was dissolved in toluene. Palladium catalyst was removed by filtration and the product was then dried under vacuum. 1.9 g of a colorless oil was obtained. NMR of the oil was reported Fig S26-S30.

#### *ROMP of humulene*

In a schlenk, given amounts of metathesis catalyst, then 0.5 mL of humulene were added under argon. The schlenk was mechanical stirred at 25°C for 1 week. The viscous polymer was dissolved in chloroform and filtered over celite to remove ruthenium black. The polymer was precipitated in methanol and the vacuum dried. Up to 480 mg of a sticky viscous colorless polymer was obtained. At low catalyst loading (0.04 mol%) a colorless polymer is obtained after several washing step (otherwise the product is greenish due to catalyst residue). NMR of the polymer was reported Fig S38-S42,

#### *Hydrogenation of polyhumulene*

500 mg of polycaryophyllene was dissolved under argon in a schlenk in 10 mL of a CH<sub>2</sub>Cl<sub>2</sub>. Then 20 mg of palladium on activated charcoal was added to the solution. The mixture was

introduced through cannula into a 22 mL stainless steel pressure reactor equipped with a glass insert. Temperature regulation was provided by a contact thermometer integrated into a heating block. Mixing was performed with a magnetic stirring bar. A static pressure of 50 bar of H<sub>2</sub> was applied and the mixture stirred at 80°C for 2 days. After cooling down to room temperature, the pressure was released and the crude reaction mixture was dissolved in toluene. Palladium catalyst was removed by filtration and the polymer was then dried under vacuum. 450 mg of a sticky viscous colorless polymer was obtained. NMR of the polymer was reported Fig S52-S55

*ROMP of caryophyllene and hydrogenation procedure in miniemulsion*

In a schlenk a given amount of metathesis catalyst was dissolved in a mixture of 3 mL of 80% caryophyllene and 0,4 mL of hexadecane. In a other schlenk 0,4 g of SDS was dissolved in 30 mL of distilled water. This solution was introduced through a cannula into the first schlenk. Then the mixture was sonicated under argon in a glass bath for 10 min. DLS of the initial dispersion was taken, the polymerization was performed at 25°C for 1 week. After 1 week, 0.5 mL of ethyl vinyl ether was added to quench the metathesis catalyst. 10 mL of this latex was introduced through cannula into a 22 mL stainless steel pressure reactor equipped with a glass insert. A static pressure of 50 bar of H<sub>2</sub> was applied and the mixture was stirred at 50°C for 2 days. After cooling down to room temperature, the pressure was released and the latex was recovered.

*ROMP of caryophyllene and hydrogenation procedure in microemulsion*

In a schlenk a given amount of metathesis catalyst was dissolved in a mixture of 1 mL of 80% caryophyllene and 2 mL of pentanol. In another schlenk 4 g of SDS was dissolved in 30 mL of distilled water. This solution was introduced through a cannula into the first schlenk.

The polymerization was performed at 25°C for 1 week. After 1 week, 0.5 mL of ethyl vinyl ether was added to quench the metathesis catalyst. 10 mL of this latex was introduced through cannula into a 22 mL stainless steel pressure reactor equipped with a glass insert. A static pressure of 50 bar of H<sub>2</sub> was applied and the mixture was stirred at 50°C for 2 days. After cooling to room temperature, the pressure was released and the latex was recovered.

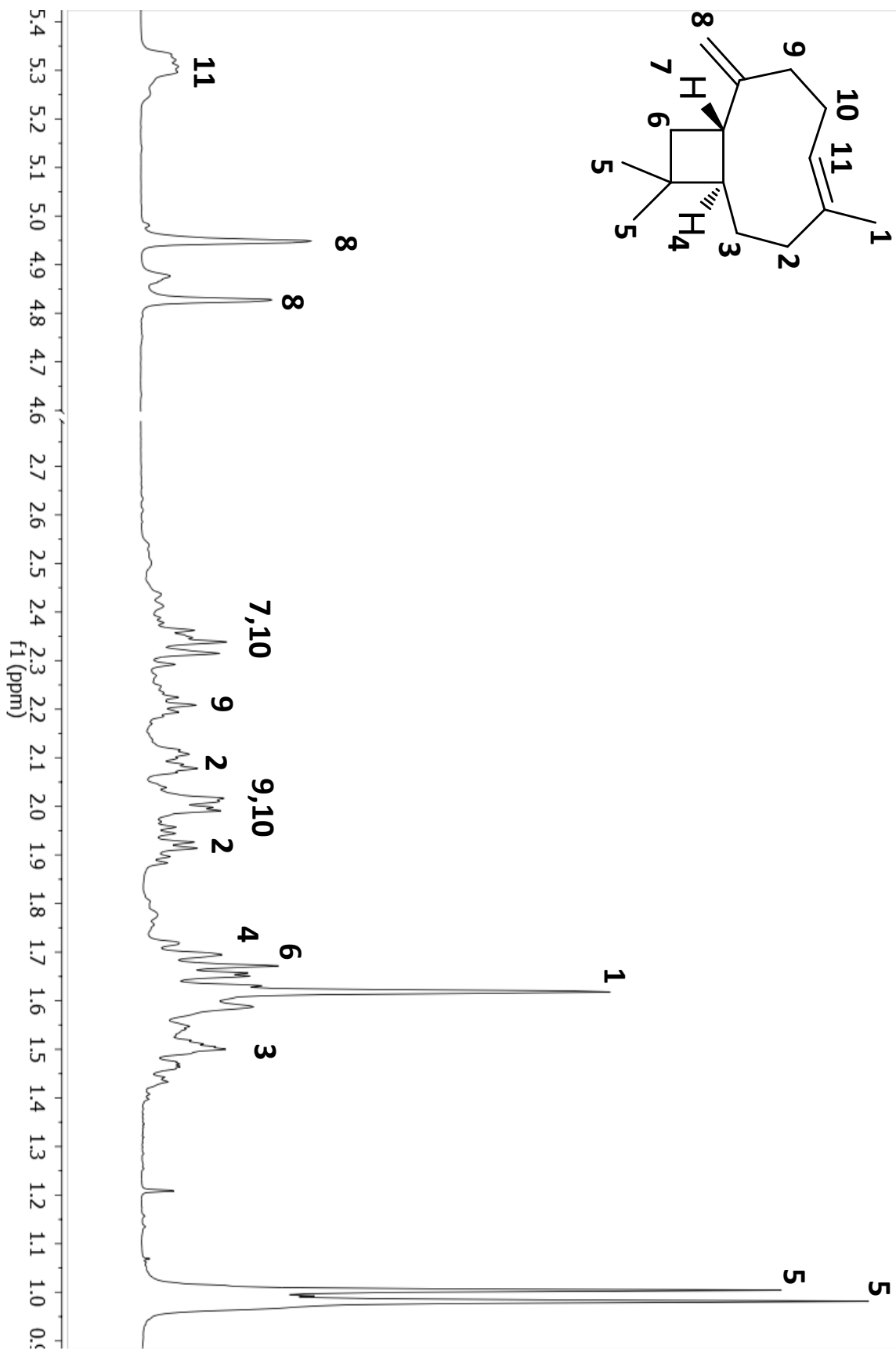
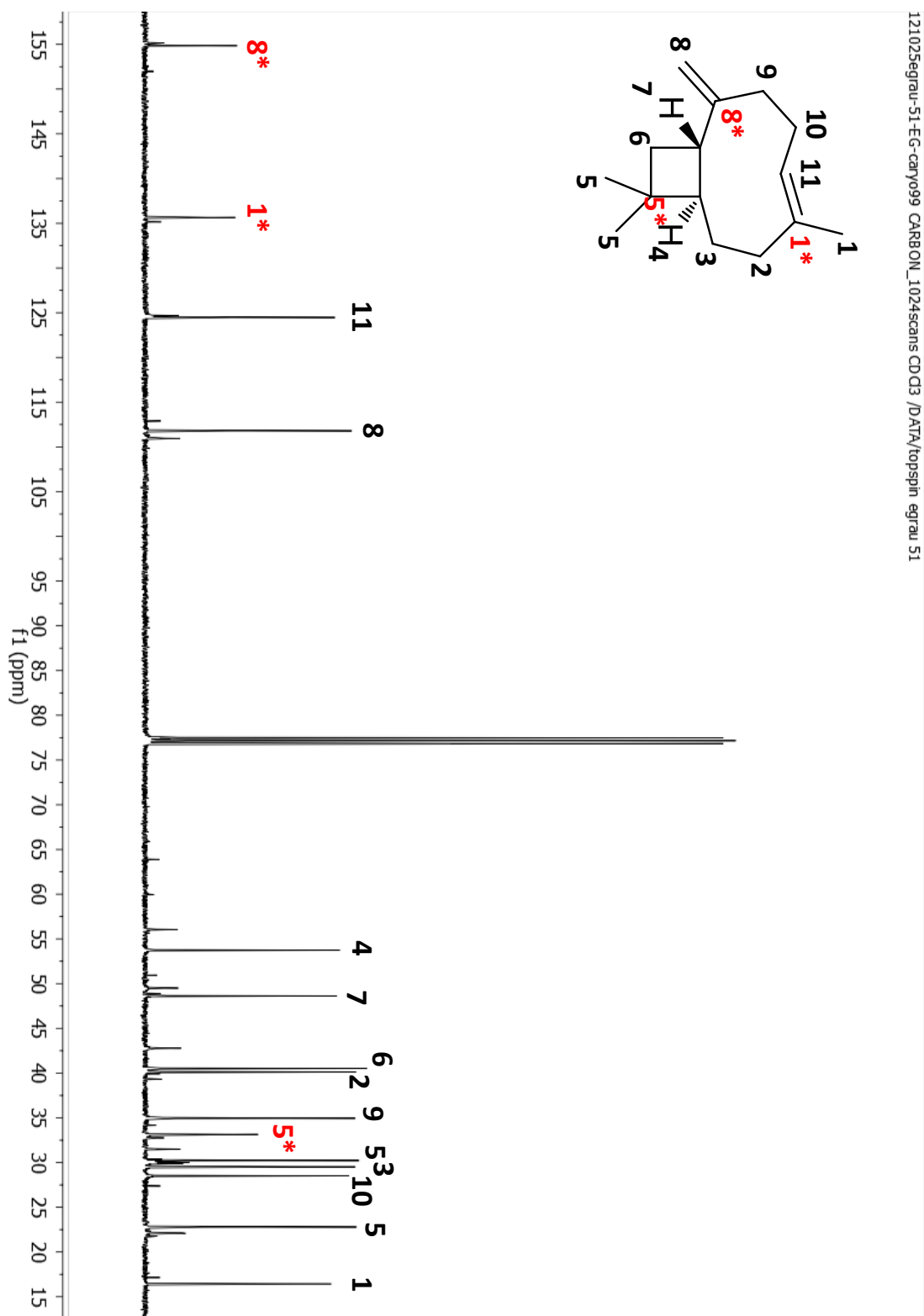


Figure S1: <sup>1</sup>H NMR spectrum of caryophyllene in CDCl<sub>3</sub>.



It should be mention that the additional signal correspond the minor conformer of caryophyllene  $\beta\beta$  see ref 6.

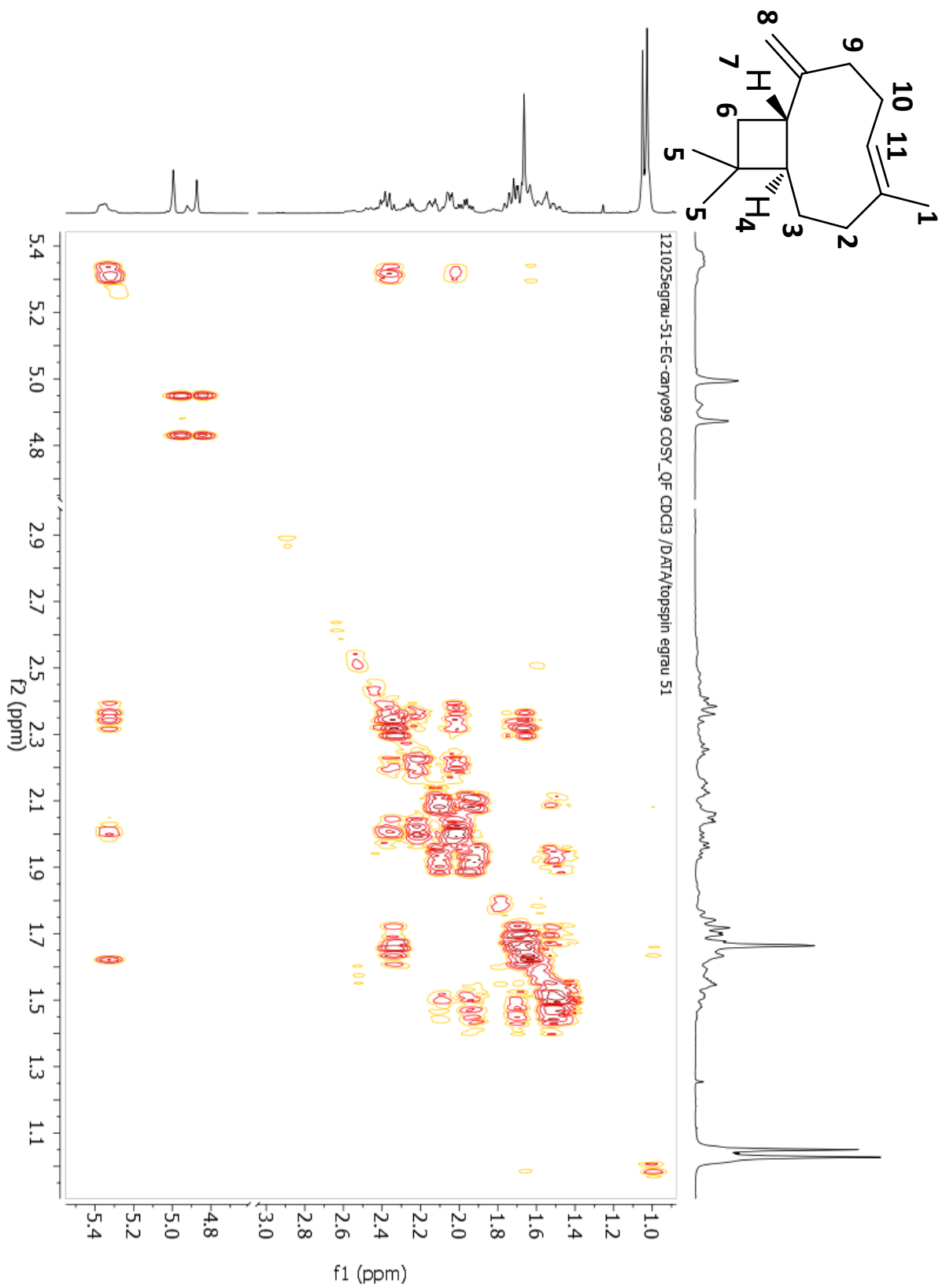


Figure S3:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of caryophyllene in  $\text{CDCl}_3$ .

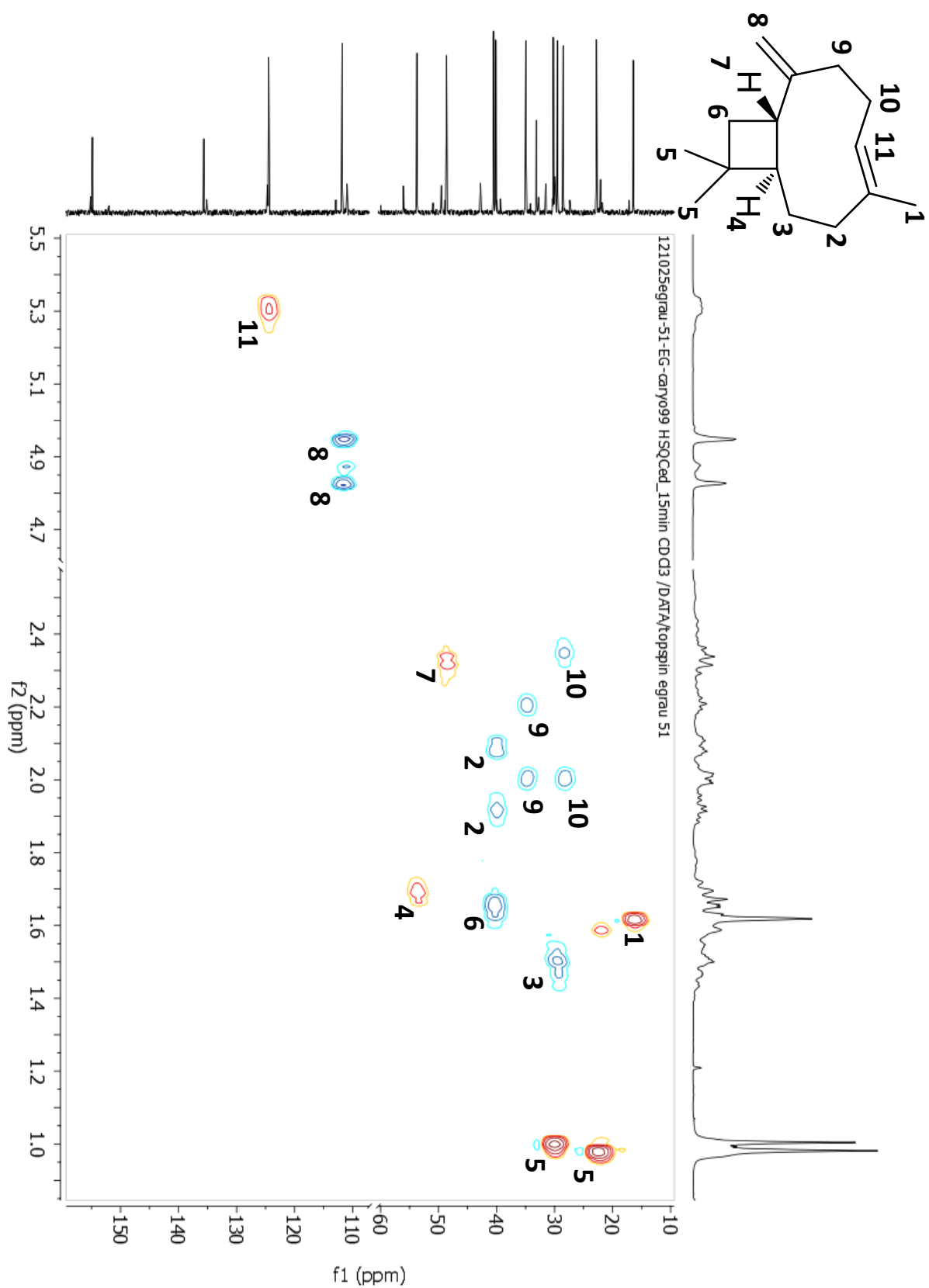


Figure S4:  $^1\text{H}$ - $^{13}\text{C}$ HSQC NMR spectrum of caryophyllene in  $\text{CDCl}_3$ .



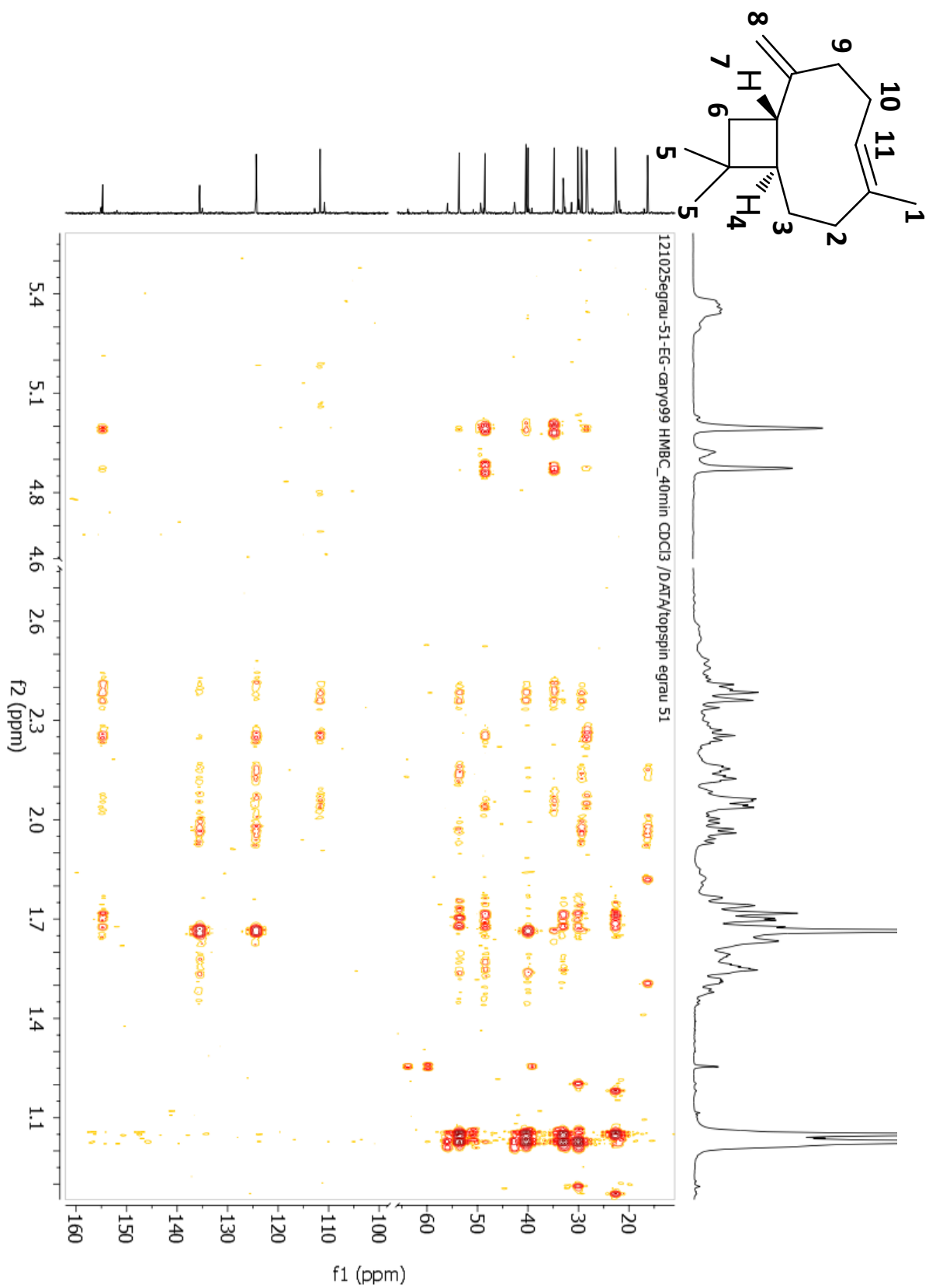


Figure S5:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of caryophyllene in  $\text{CDCl}_3$ .

**Table S1** ROMP of caryophyllene with different catalyst loading.<sup>a</sup>

Catalyst\ Monomer	1/500			1/1000			1/2500		
	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>
<b>1</b>	-	-	-	-	-	-	-	-	-
<b>2</b>	95%	18.1	1.8	33%	7.5	1.8	6%	3.0	2.0
<b>3</b>	100%	19.0	1.8	96%	17.4	1.8	98%	20.0	1.9
<b>4</b>	-	-	-	-	-	-	-	-	-
<b>5</b>	86%	14.3	1.8	73%	11.0	1.8	20%	7.6	1.7

a: Polymerizations performed at 25°C in bulk during 1 week under argon. b: Conversions in % were determined using <sup>1</sup>H NMR. c: M<sub>n</sub> in kg/mol and molecular weight distribution (Đ=M<sub>w</sub>/M<sub>n</sub>) as determined by SEC in THF vs. polystyrene standards.

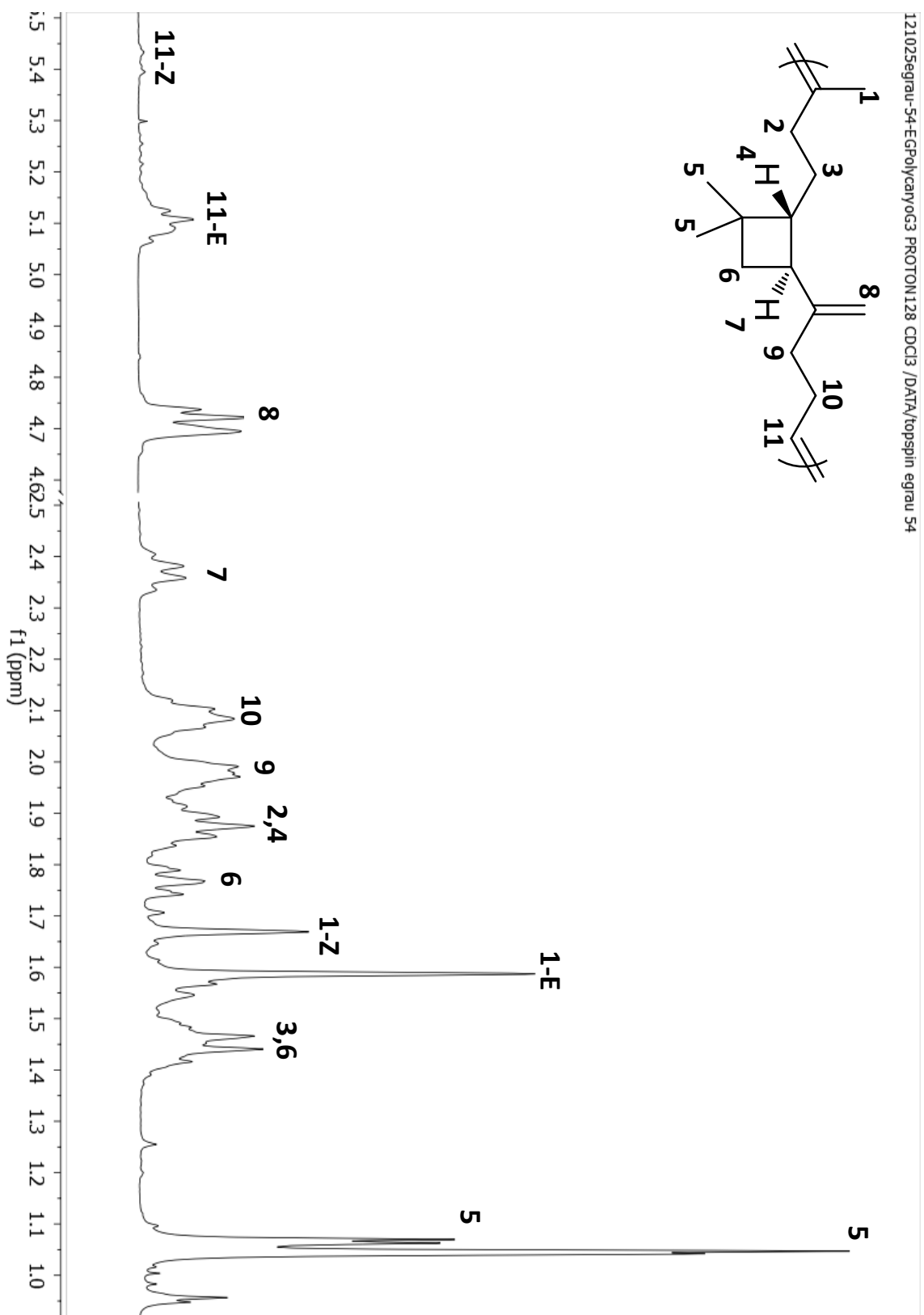


Figure S6:  $^1\text{H}$  NMR spectrum of polycaryophyllene in  $\text{CDCl}_3$ .

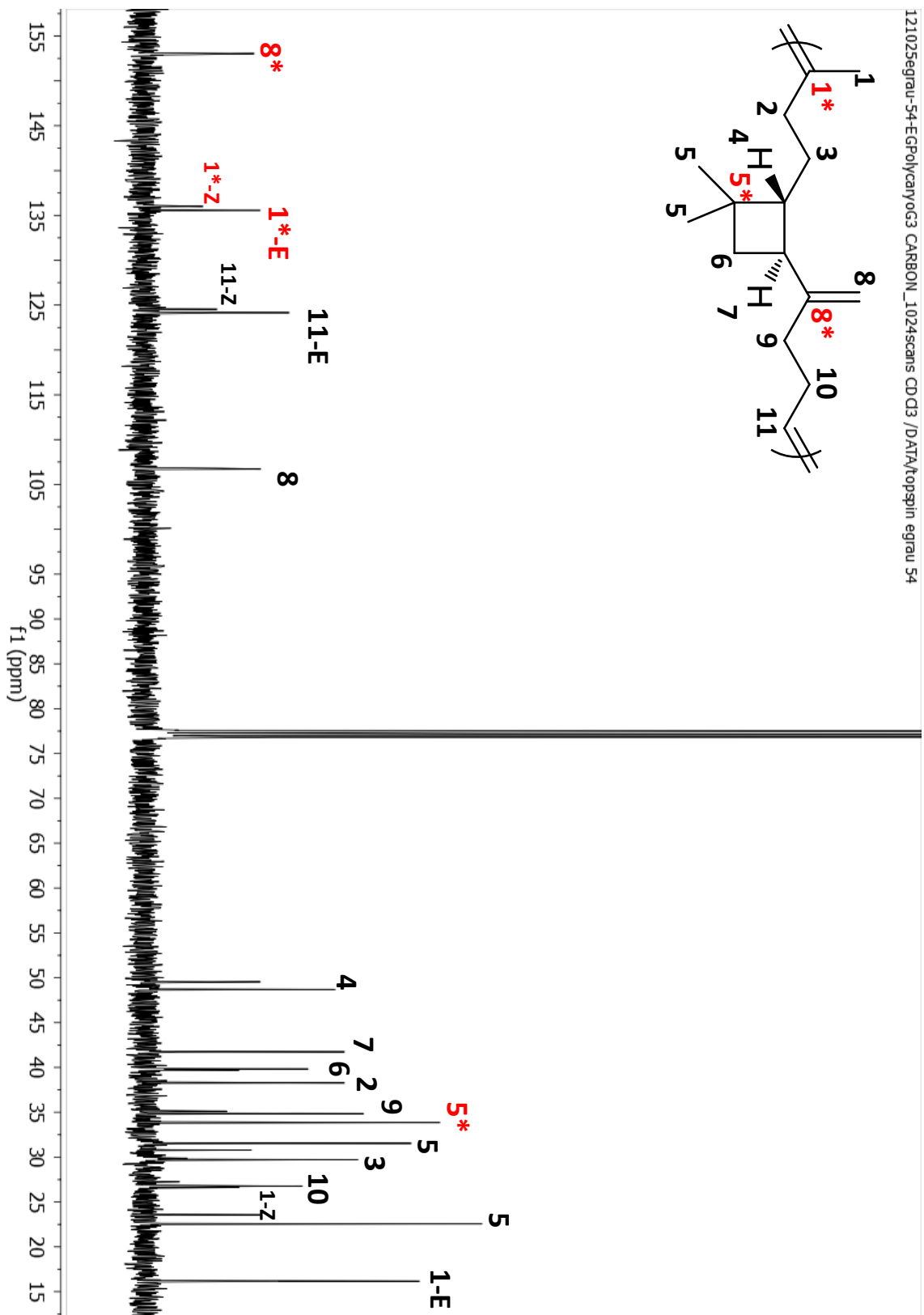


Figure S7:  $^{13}\text{C}$  NMR spectrum of polycaryophyllene in  $\text{CDCl}_3$ .

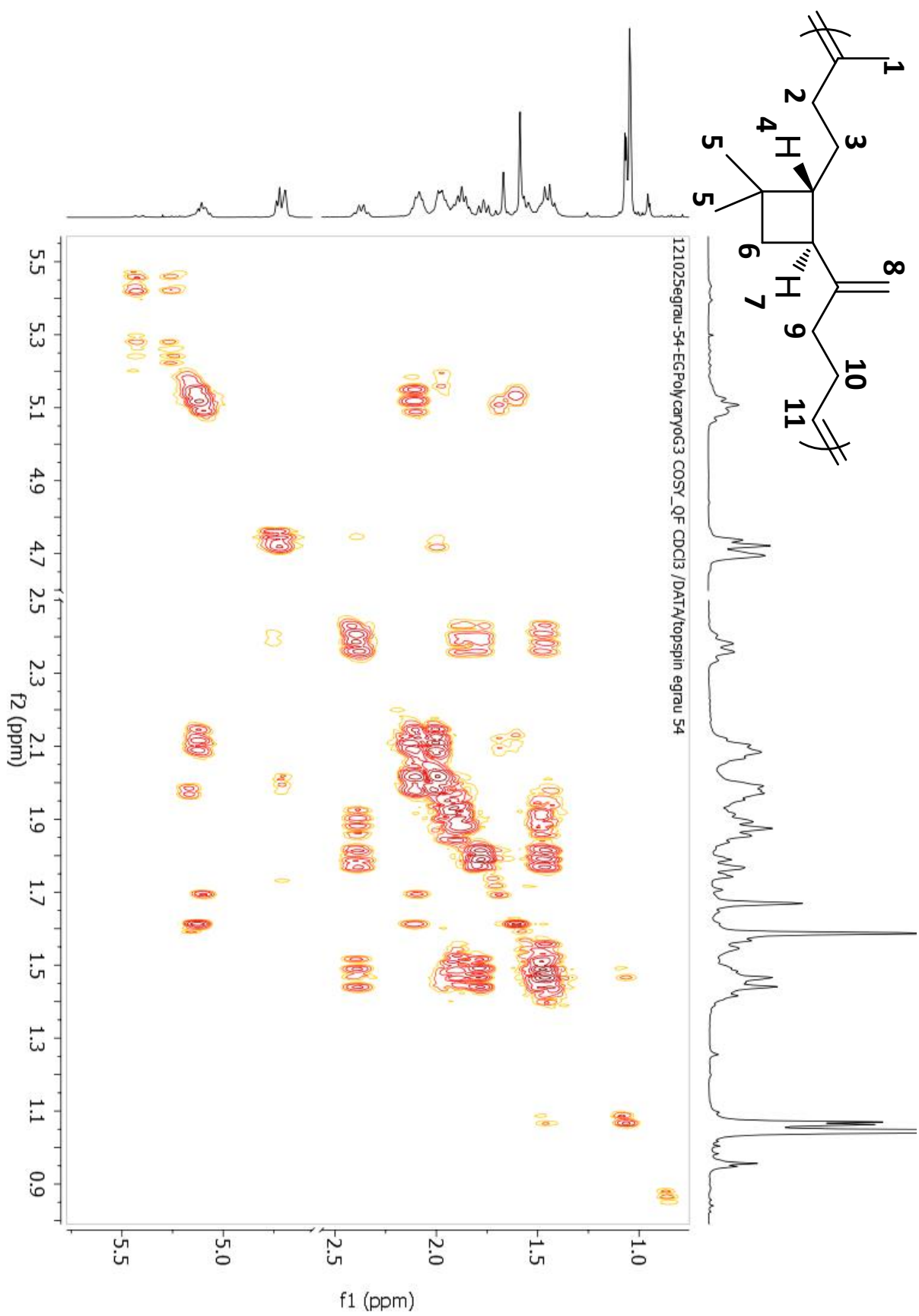


Figure S8:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of polycaryophyllene in  $\text{CDCl}_3$ .

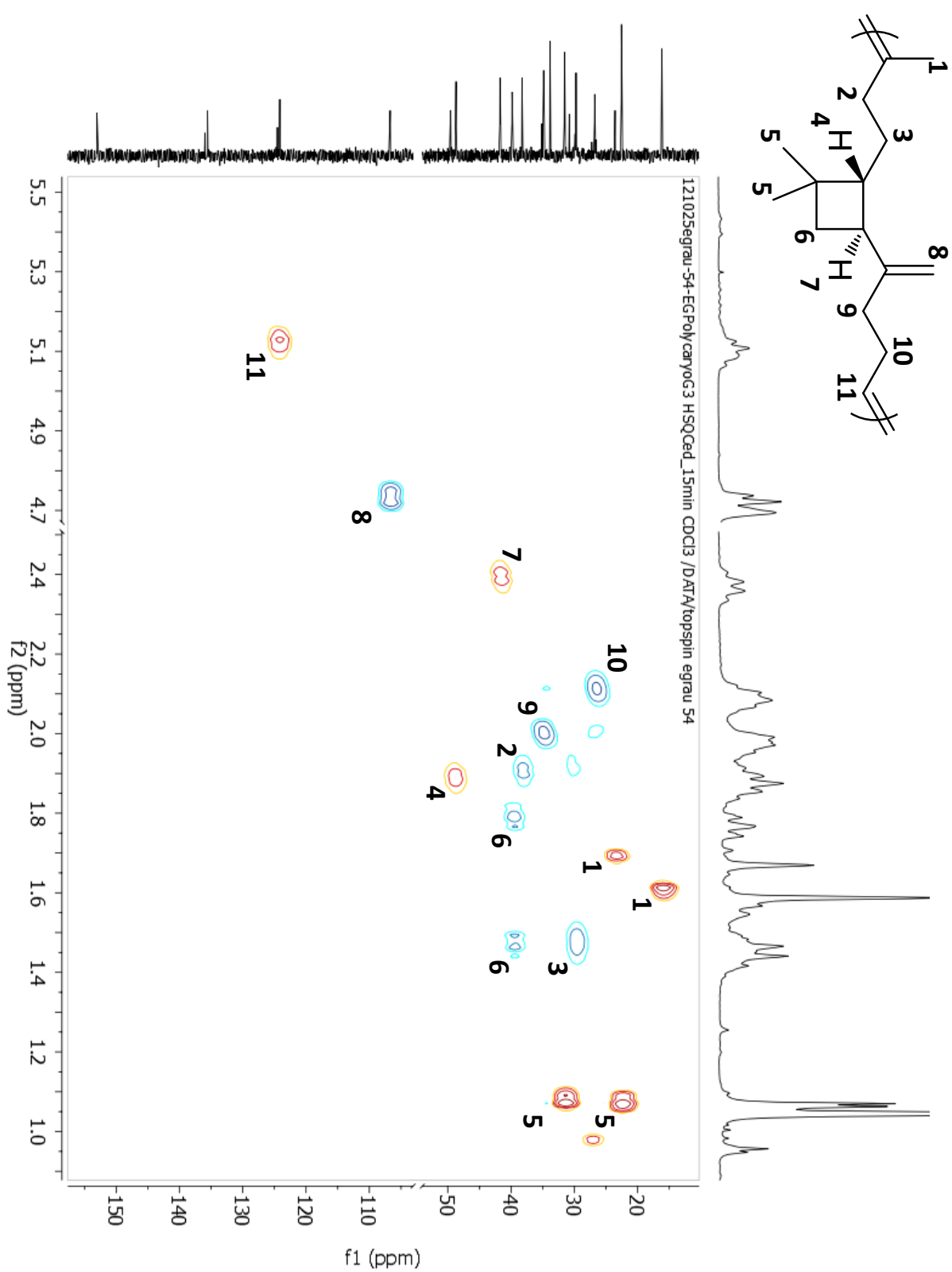


Figure S9:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of polycaryophyllene in  $\text{CDCl}_3$ .

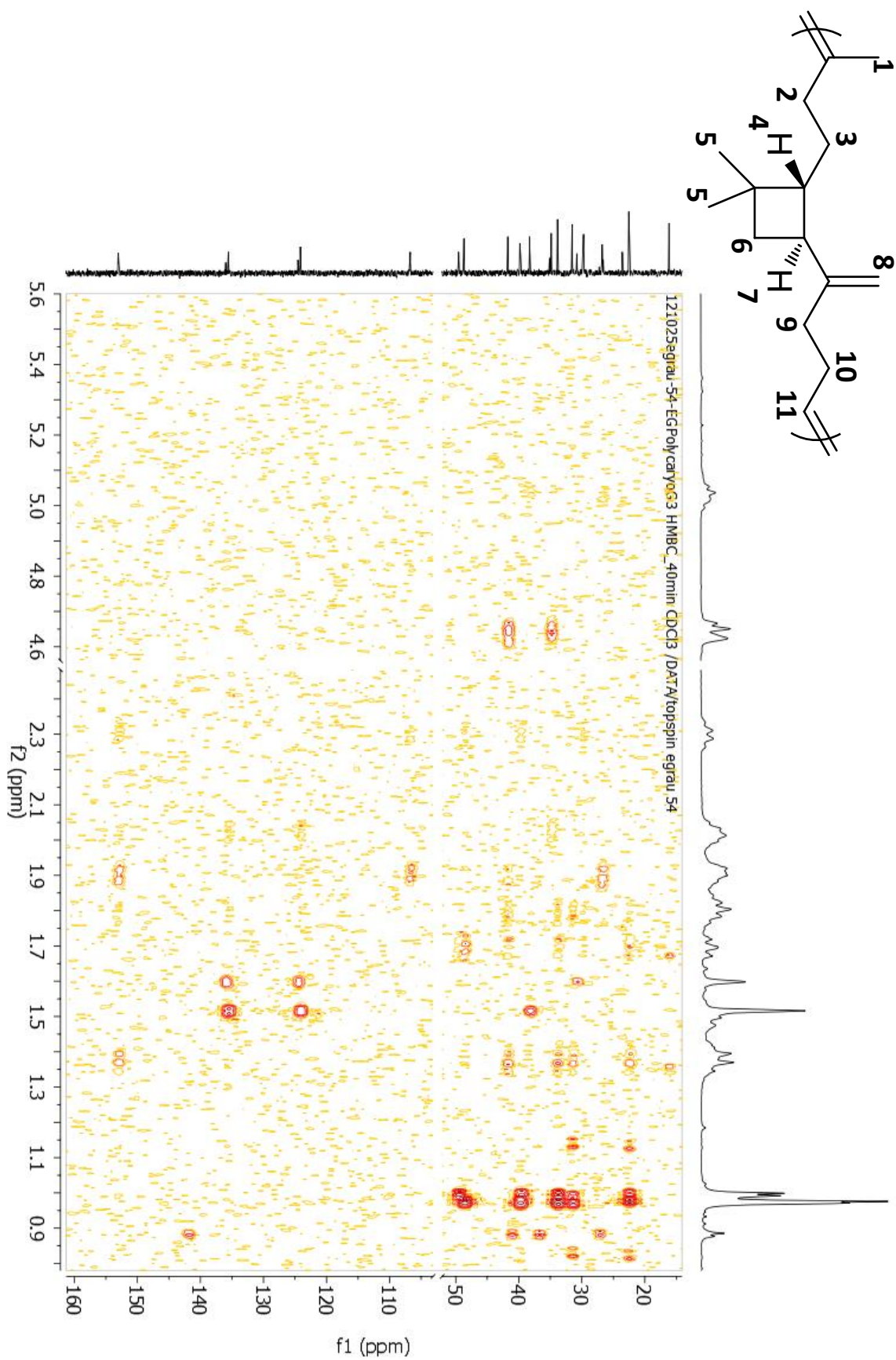


Figure S10:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of polycaryophyllene in  $\text{CDCl}_3$ .

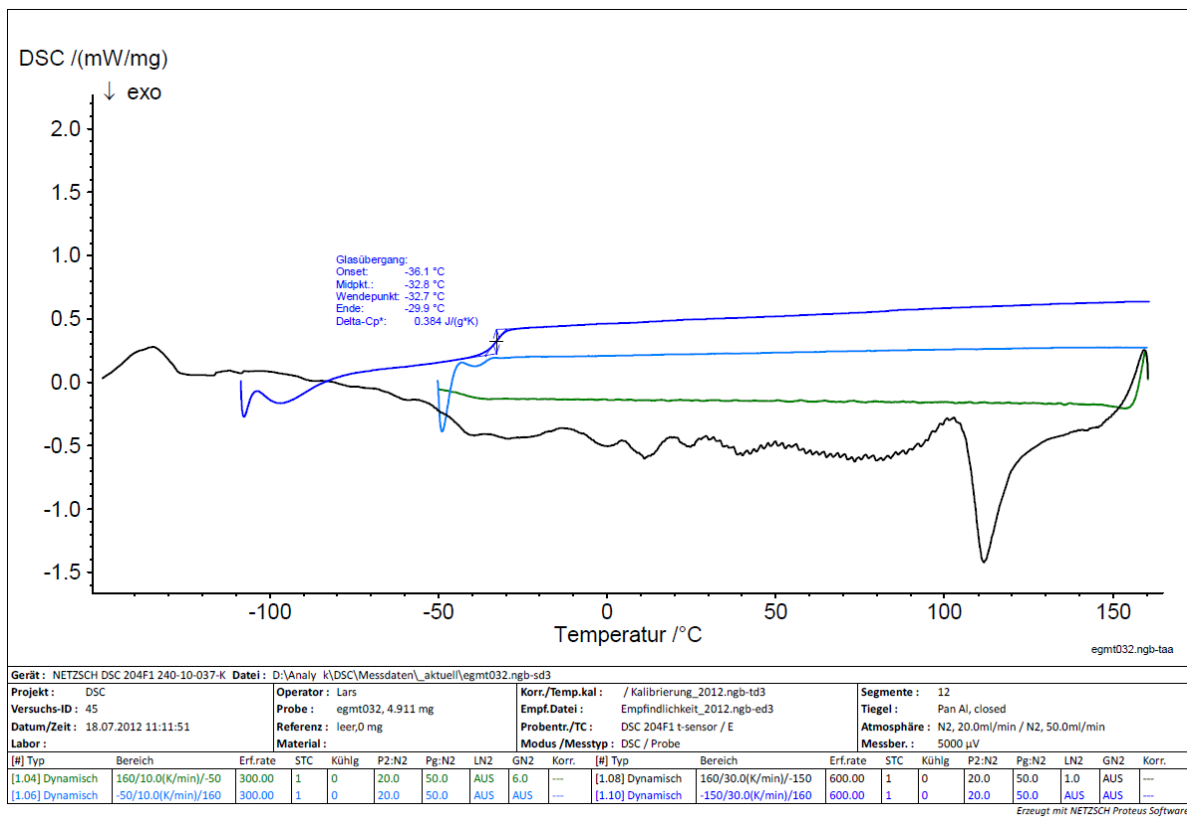


Figure S11: DSC trace of polycaryophyllene. In green 1<sup>st</sup> cooling at -10K/min from 160°C to -50°C, in pale blue 2<sup>nd</sup> heating at 10K/min up to 160°C then 2<sup>nd</sup> cooling in black at -30K/min down to -150°C finally 3<sup>rd</sup> heating in blue at 30K/min up to 160°C.



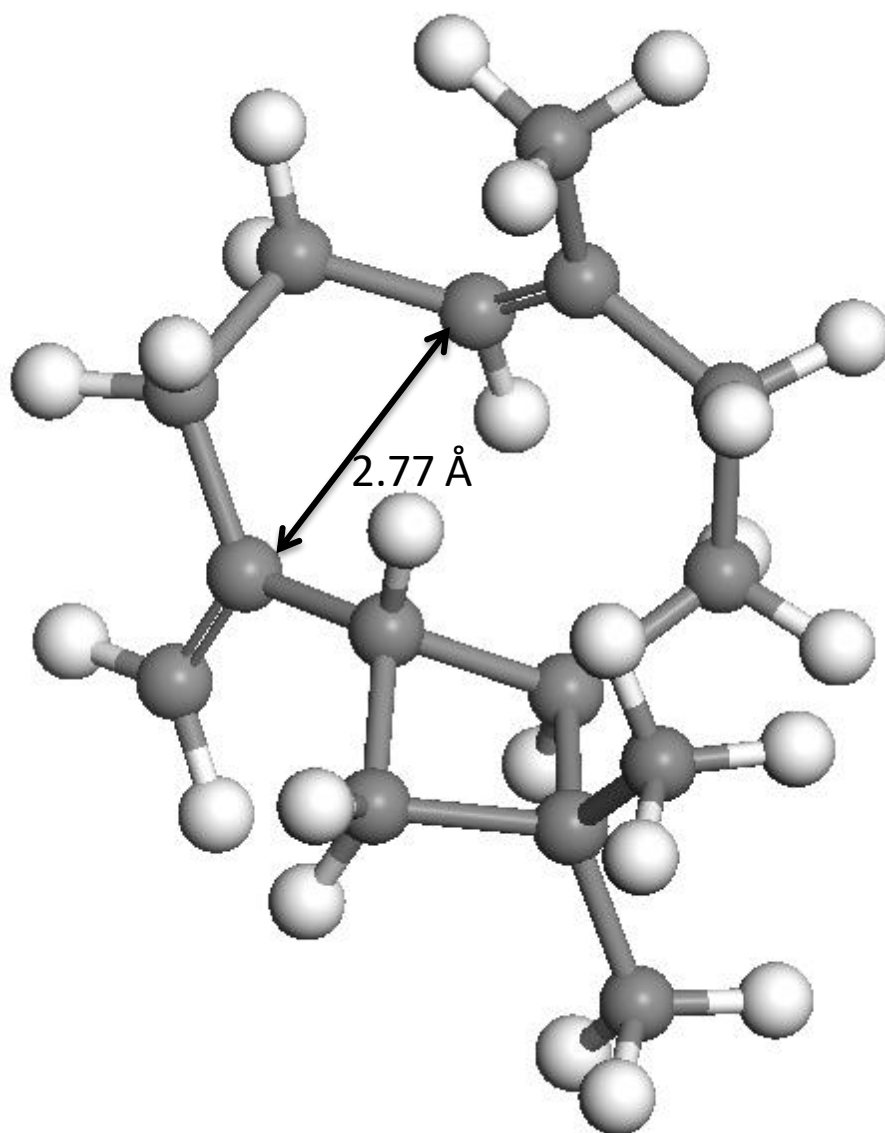


Figure S12: 3D view of caryophyllene calculated using GAUSSIAN09 with the B3PW91 hybrid functional and a high quality 6-311++G(d) basis set.

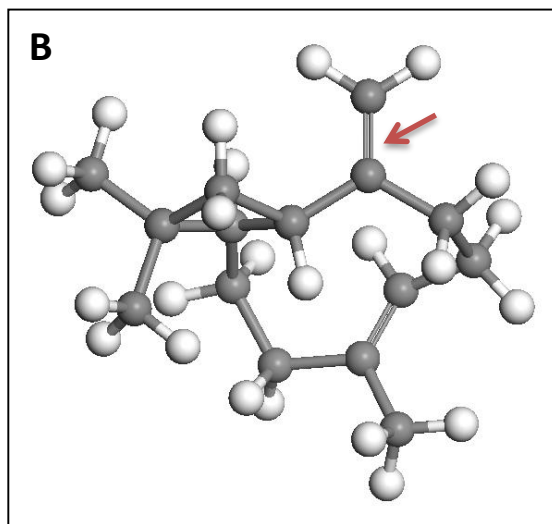
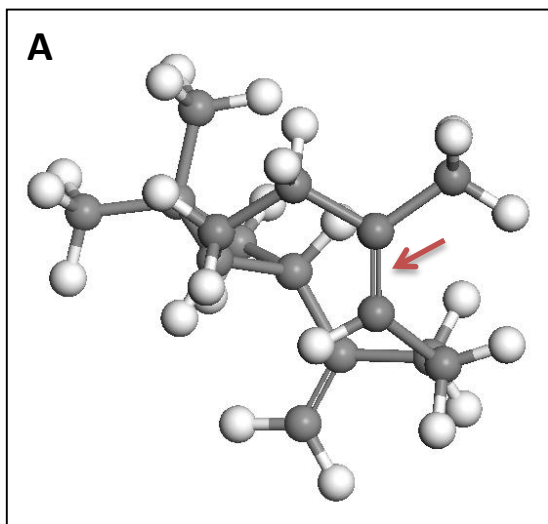
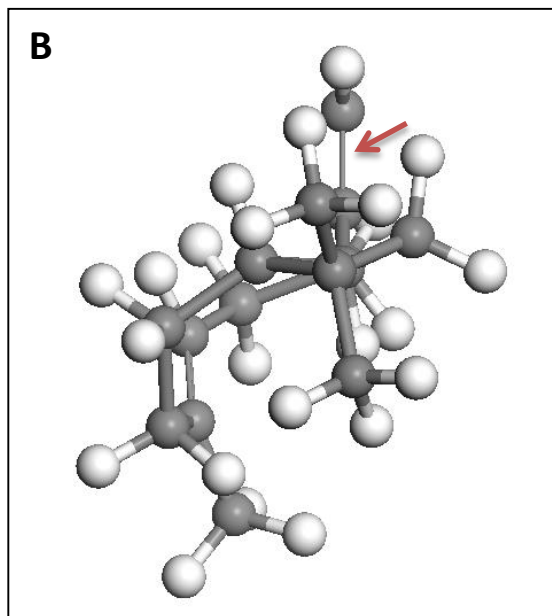
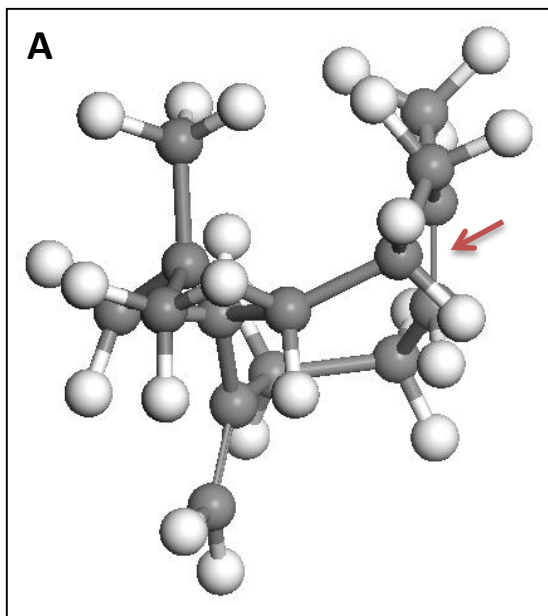
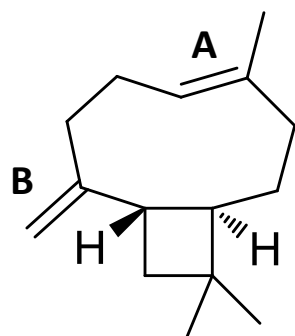


Figure S13: 3D side and top views of caryophyllene with for each double bonds (red arrow indicated the double bond position).

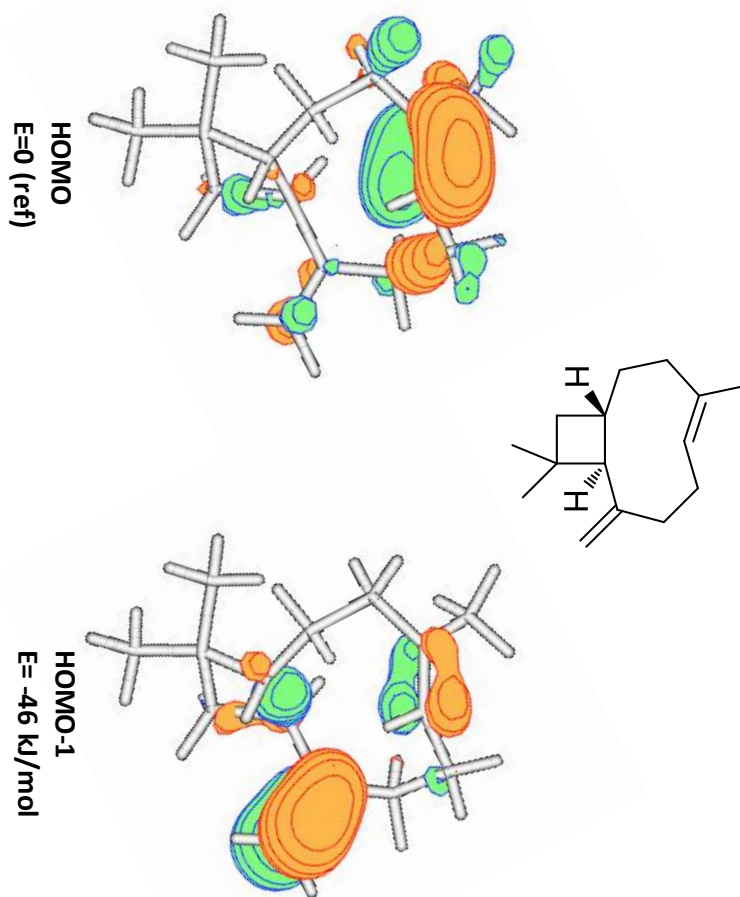


Figure S14: 3D views of HOMO and HOMO-1 of caryophyllene.

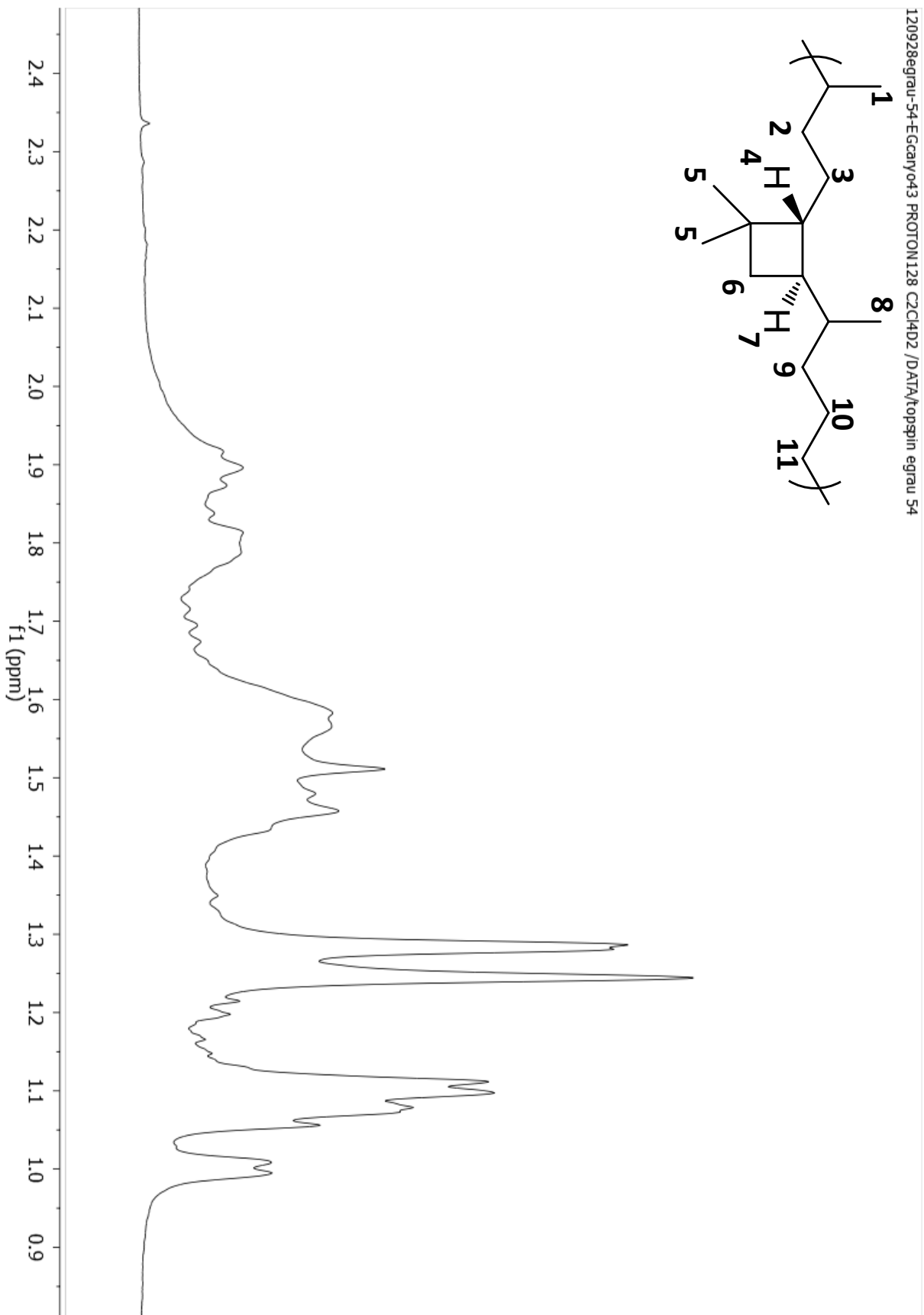


Figure S15: <sup>1</sup>H NMR spectrum of poly(hydrocaryophyllene) in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.

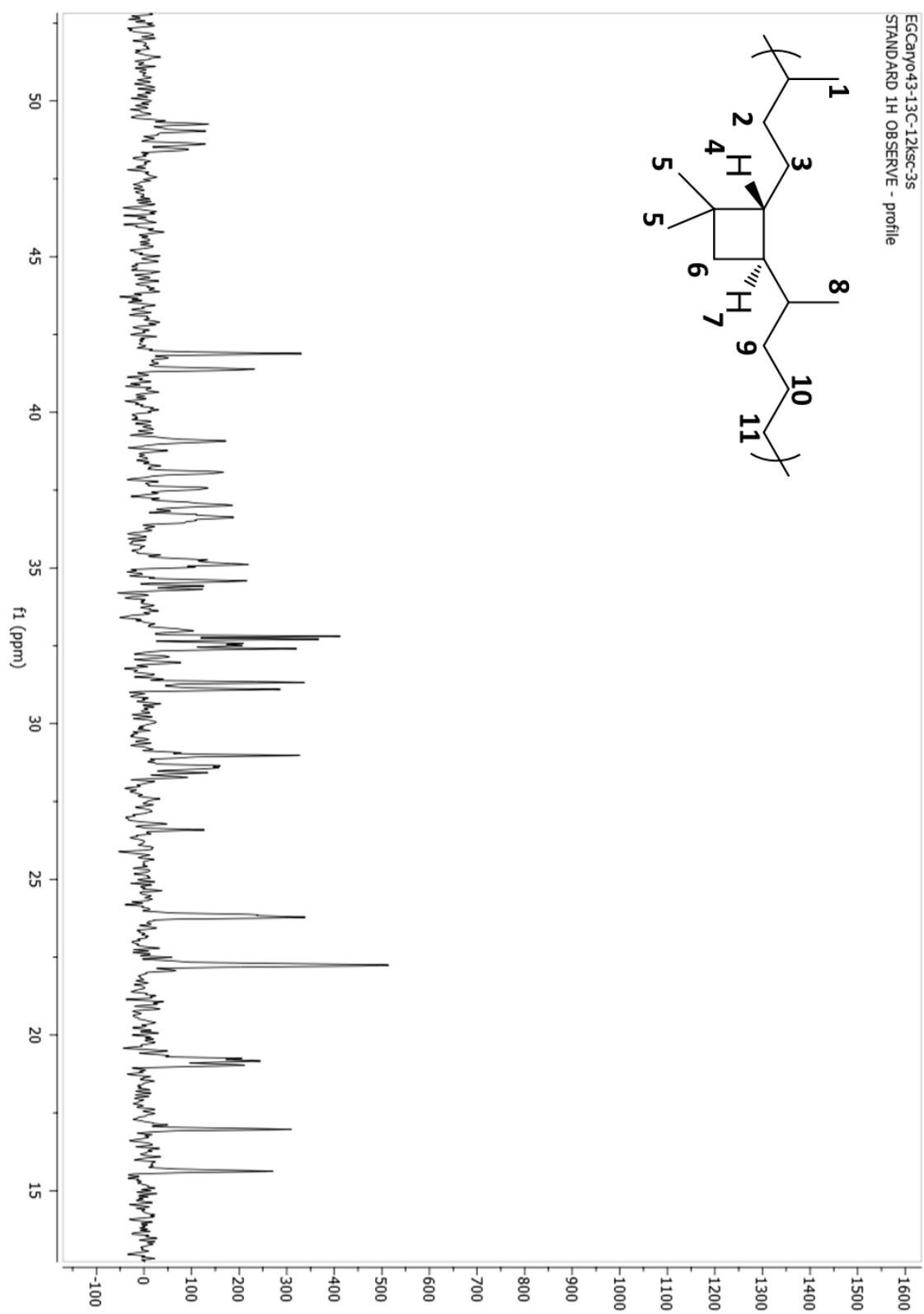


Figure S16:  $^{13}\text{C}$  NMR spectrum of poly(hydrocaryophyllene) in  $\text{C}_2\text{D}_2\text{Cl}_4$ .

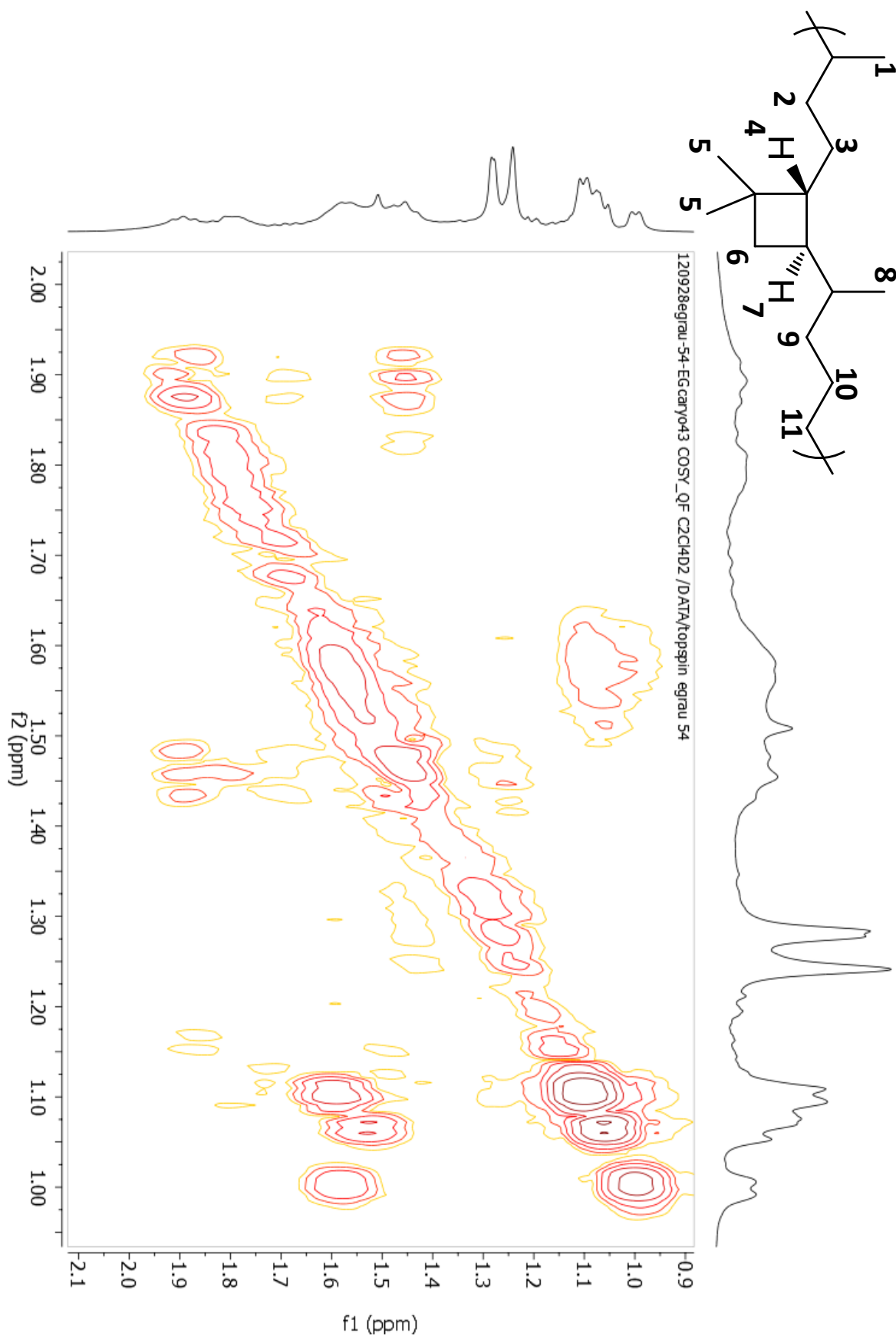


Figure S17:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of poly(hydrocaryophyllene) in  $\text{C}_2\text{D}_2\text{Cl}_4$ .

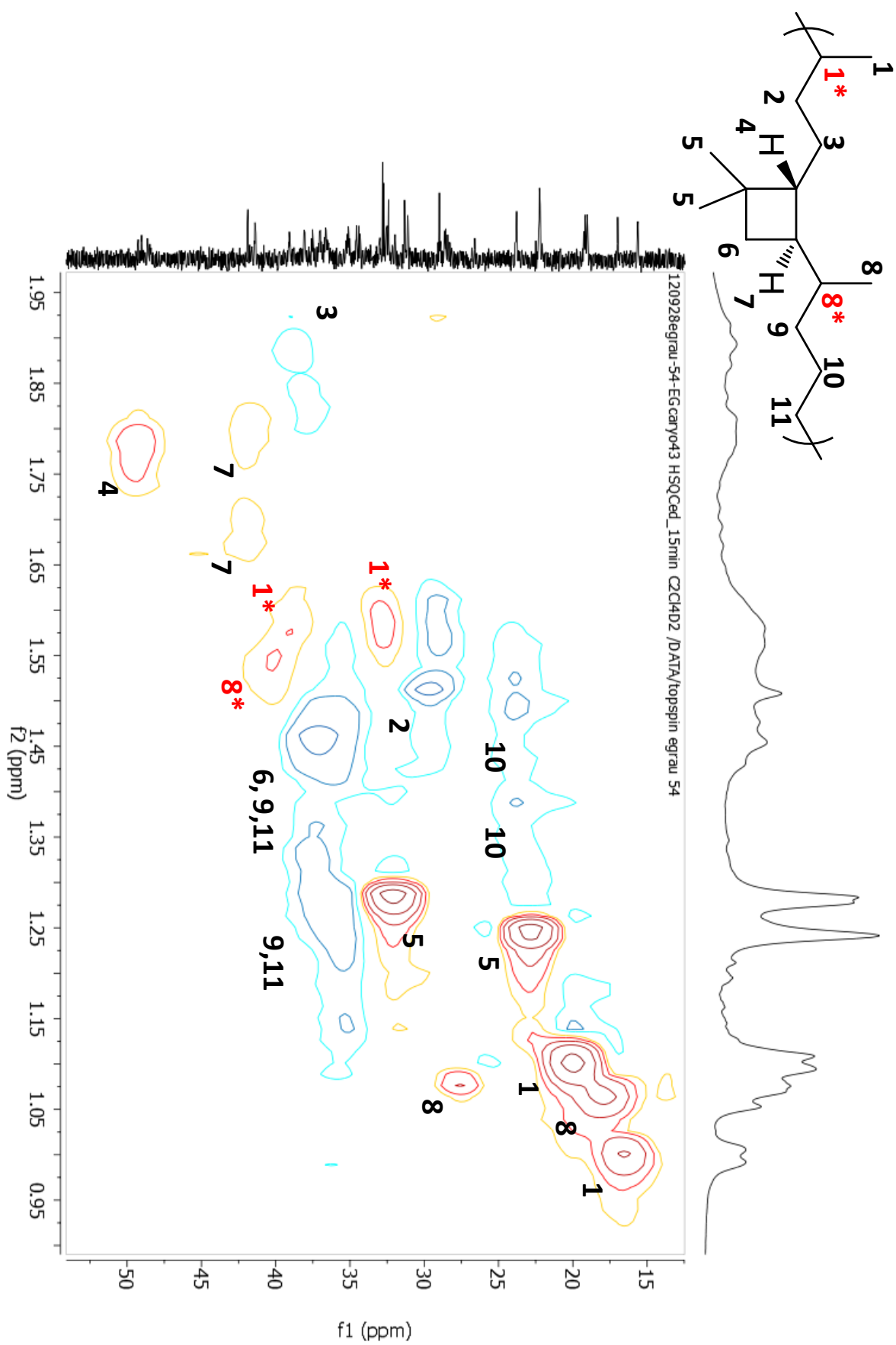


Figure S18:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of poly(hydrocaryophyllene) in  $\text{C}_2\text{D}_2\text{Cl}_4$ .

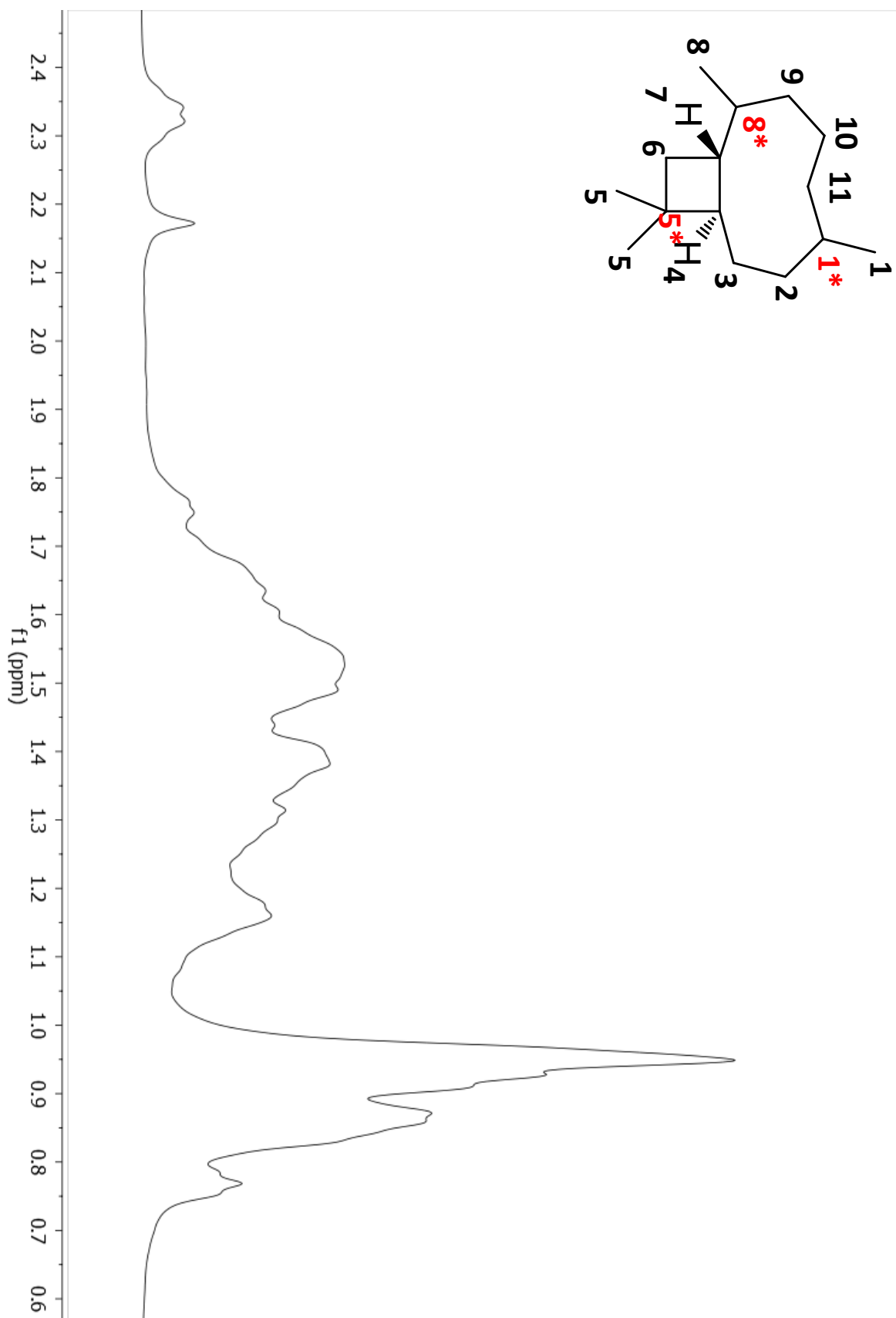


Figure S19: <sup>1</sup>H NMR spectrum of hydrocaryophyllene in CDCl<sub>3</sub>.



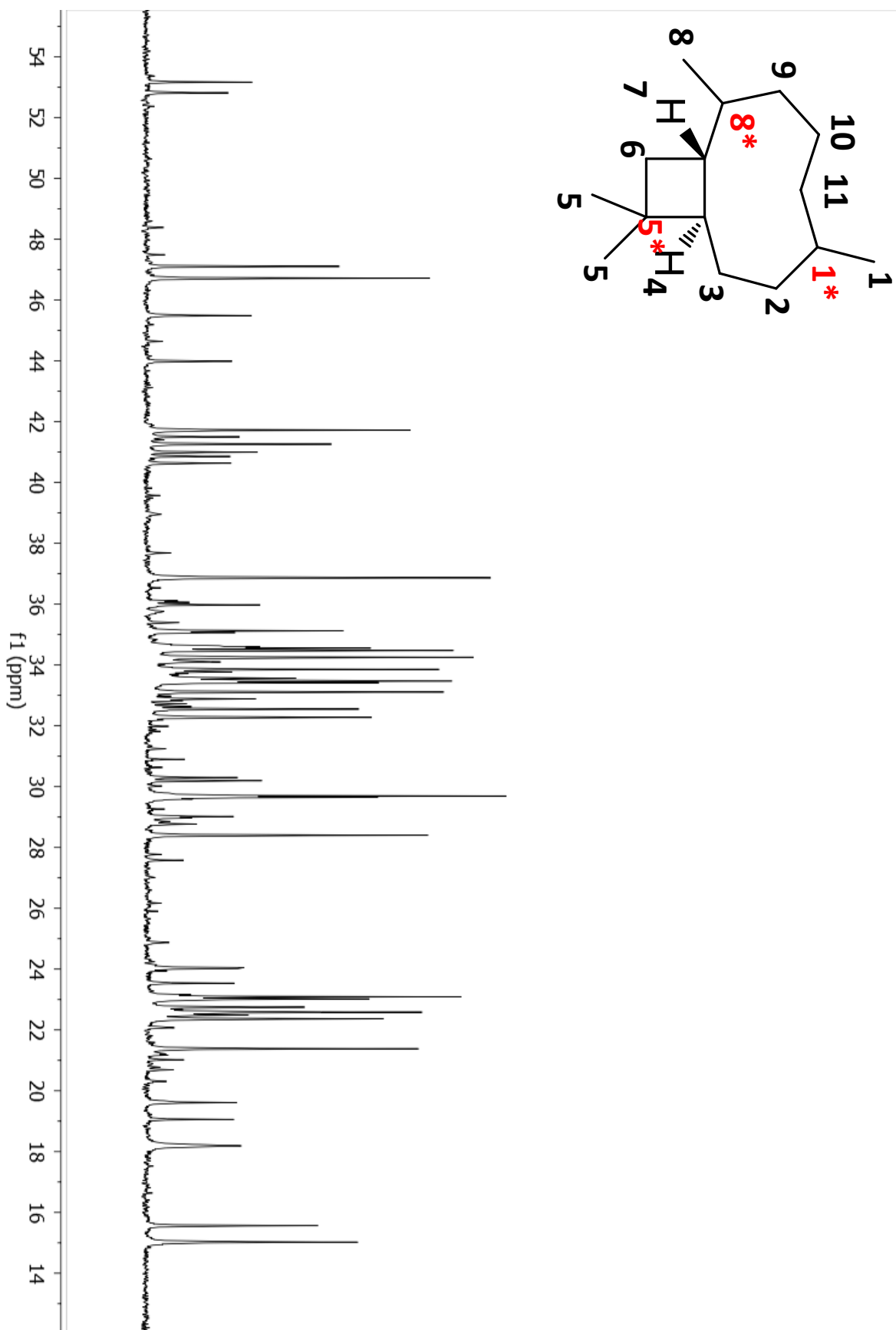


Figure S20:  $^{13}\text{C}$  NMR spectrum of hydrocaryophyllene in  $\text{CDCl}_3$ .

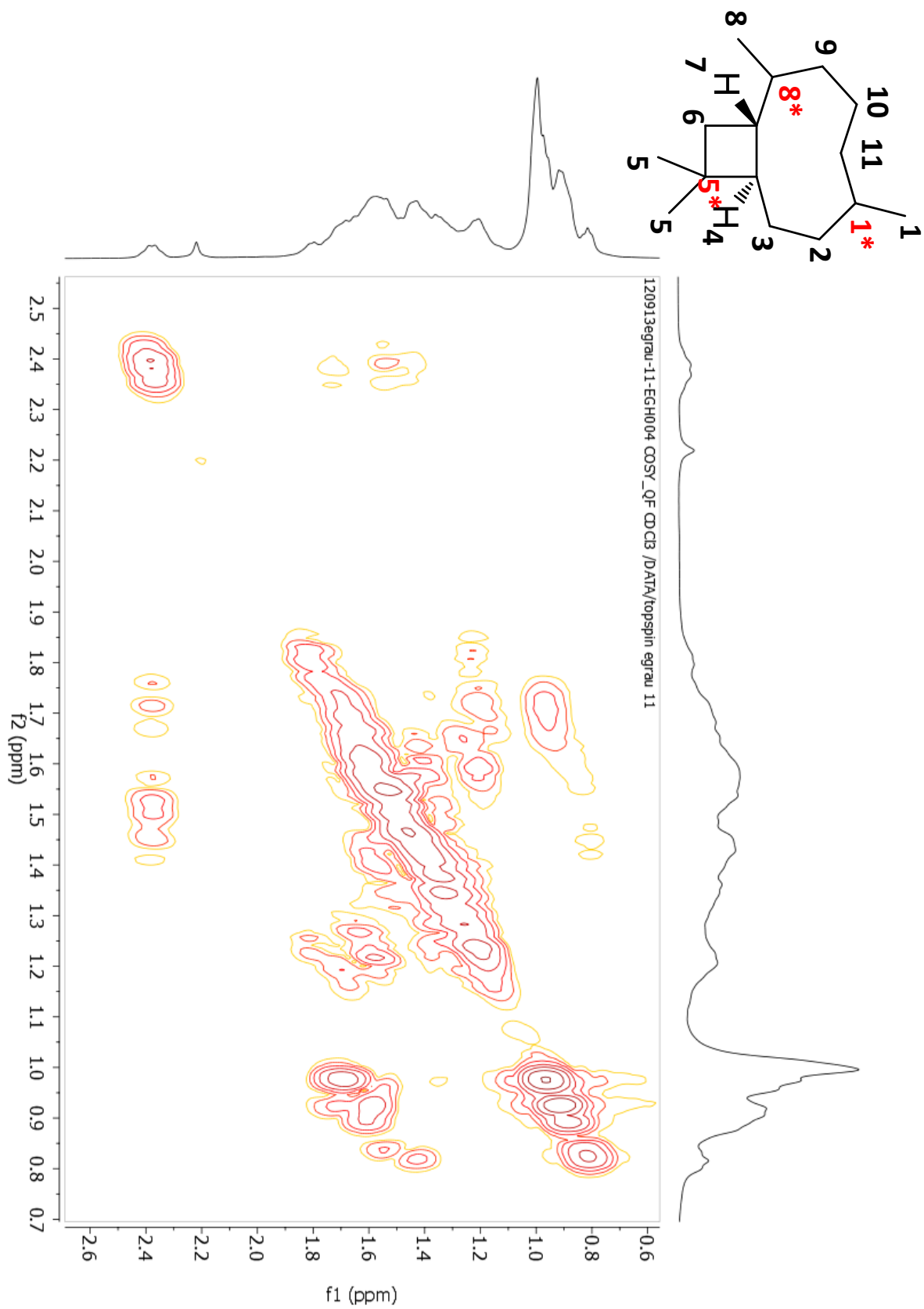


Figure S21:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of hydrocaryophyllene in  $\text{CDCl}_3$ .

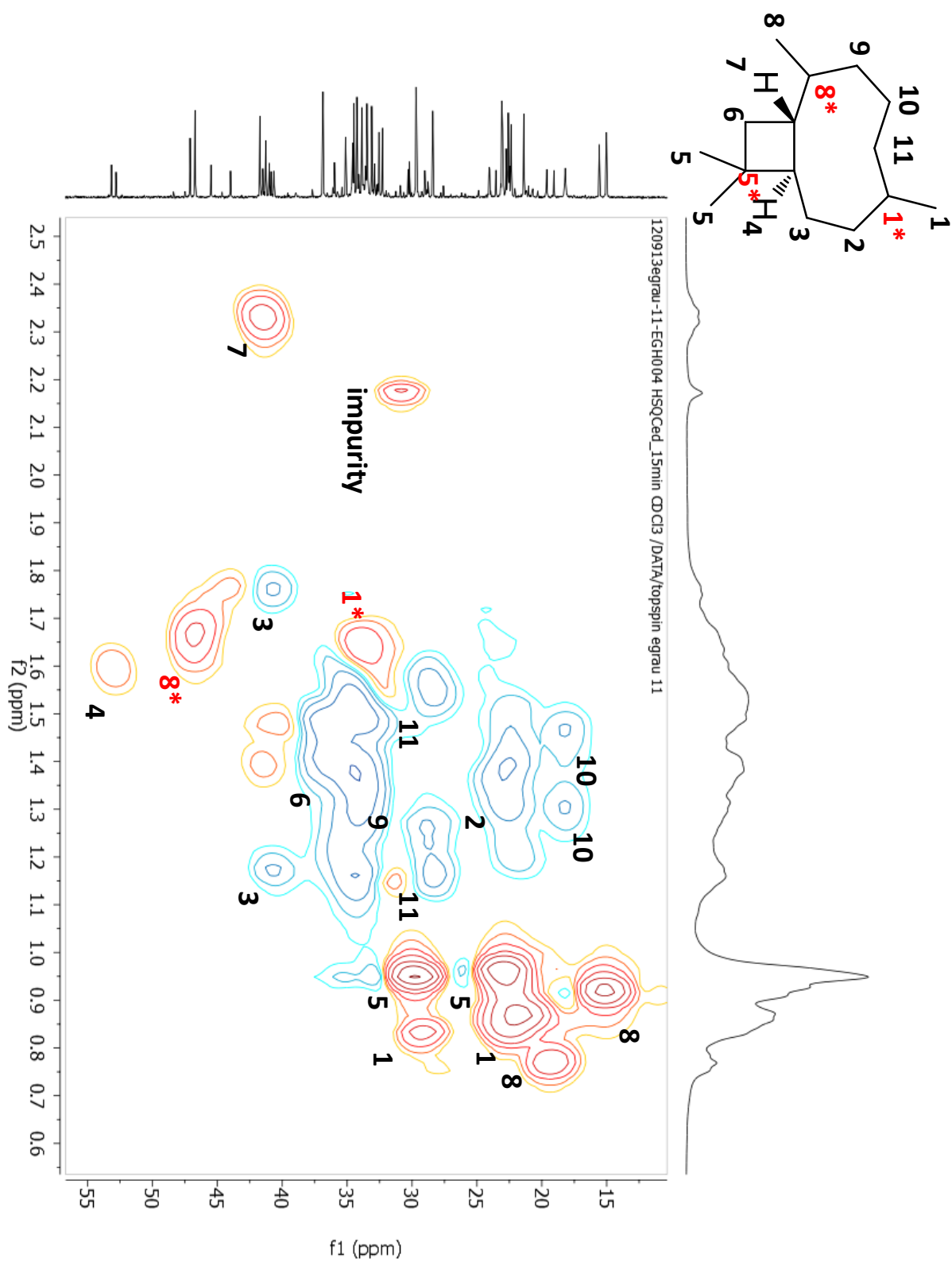


Figure S22:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of hydrocaryophyllene in  $\text{CDCl}_3$ .

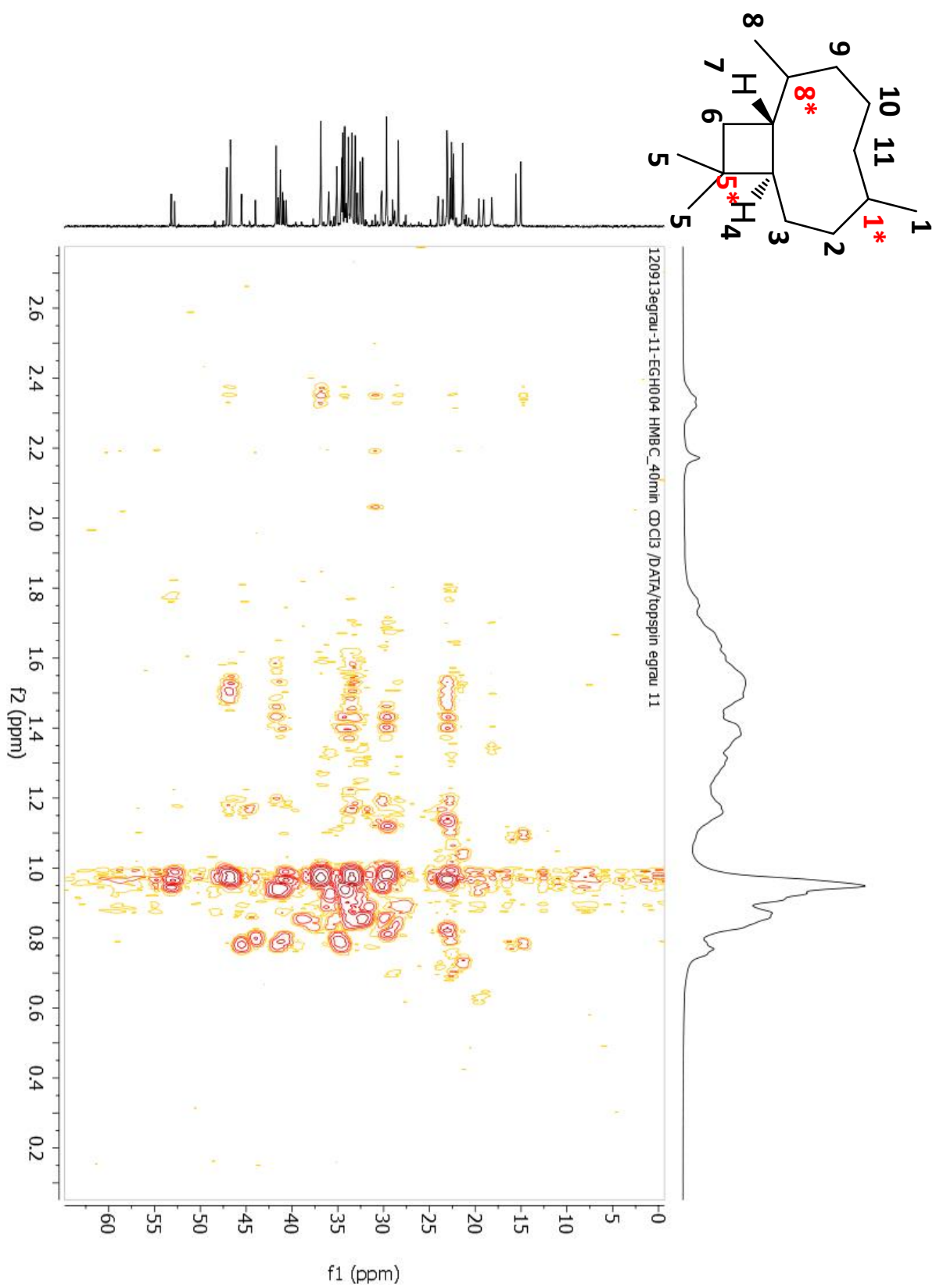


Figure S23:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of hydrocaryophyllene in  $\text{CDCl}_3$ .

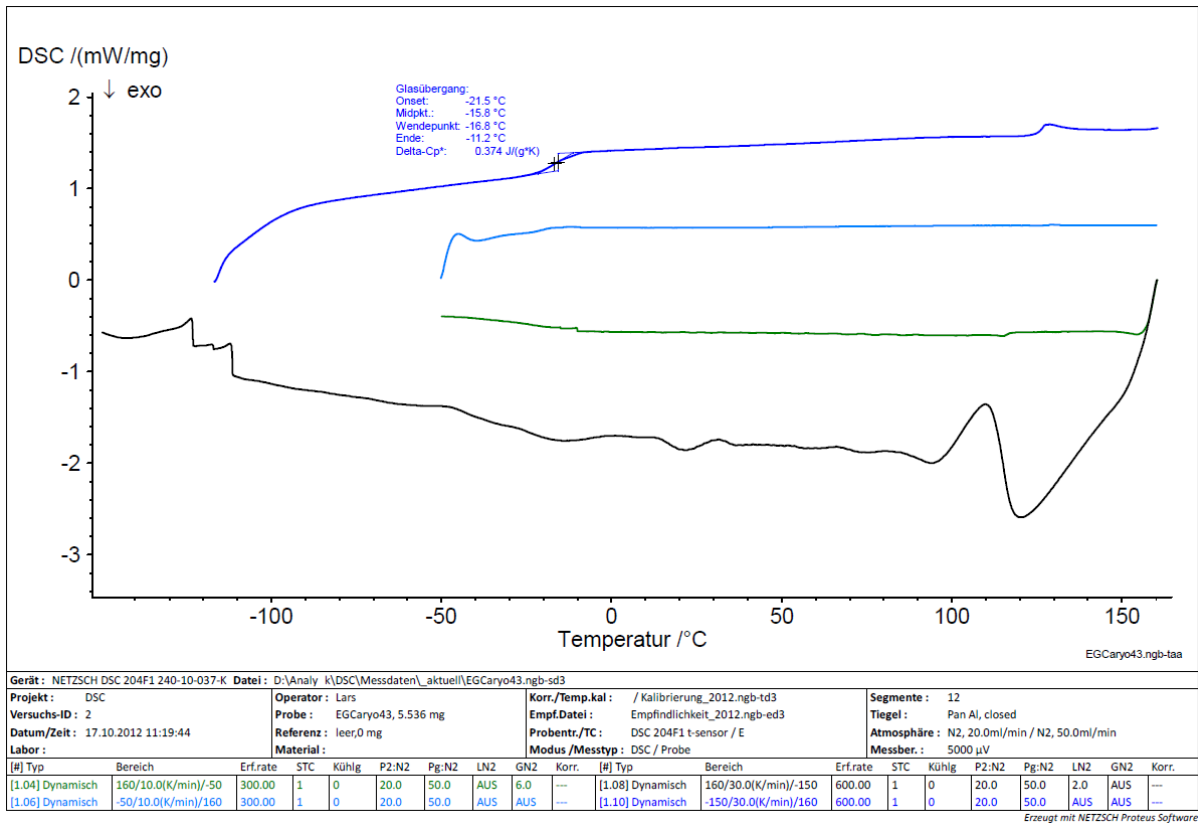


Figure S24: DSC trace of poly(hydrocaryophyllene). In green 1<sup>st</sup> cooling at -10K/min from 160°C to -50°C, in pale blue 2<sup>nd</sup> heating at 10K/min up to 160°C then 2<sup>nd</sup> cooling in black at -30K/min down to -150°C finally 3<sup>rd</sup> heating in blue at 30K/min up to 160°C.

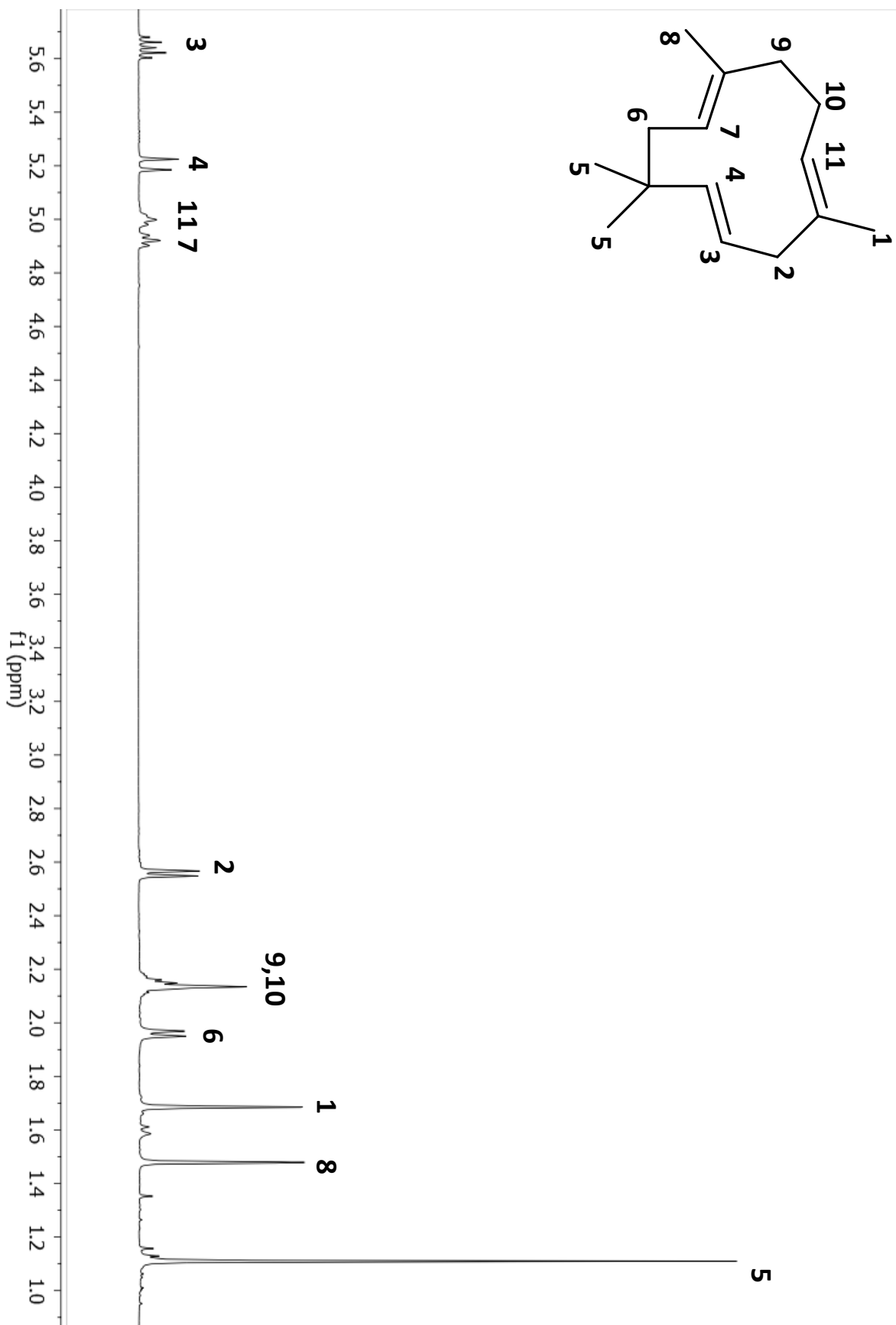


Figure S25: <sup>1</sup>H NMR spectrum of humulene in CDCl<sub>3</sub>.

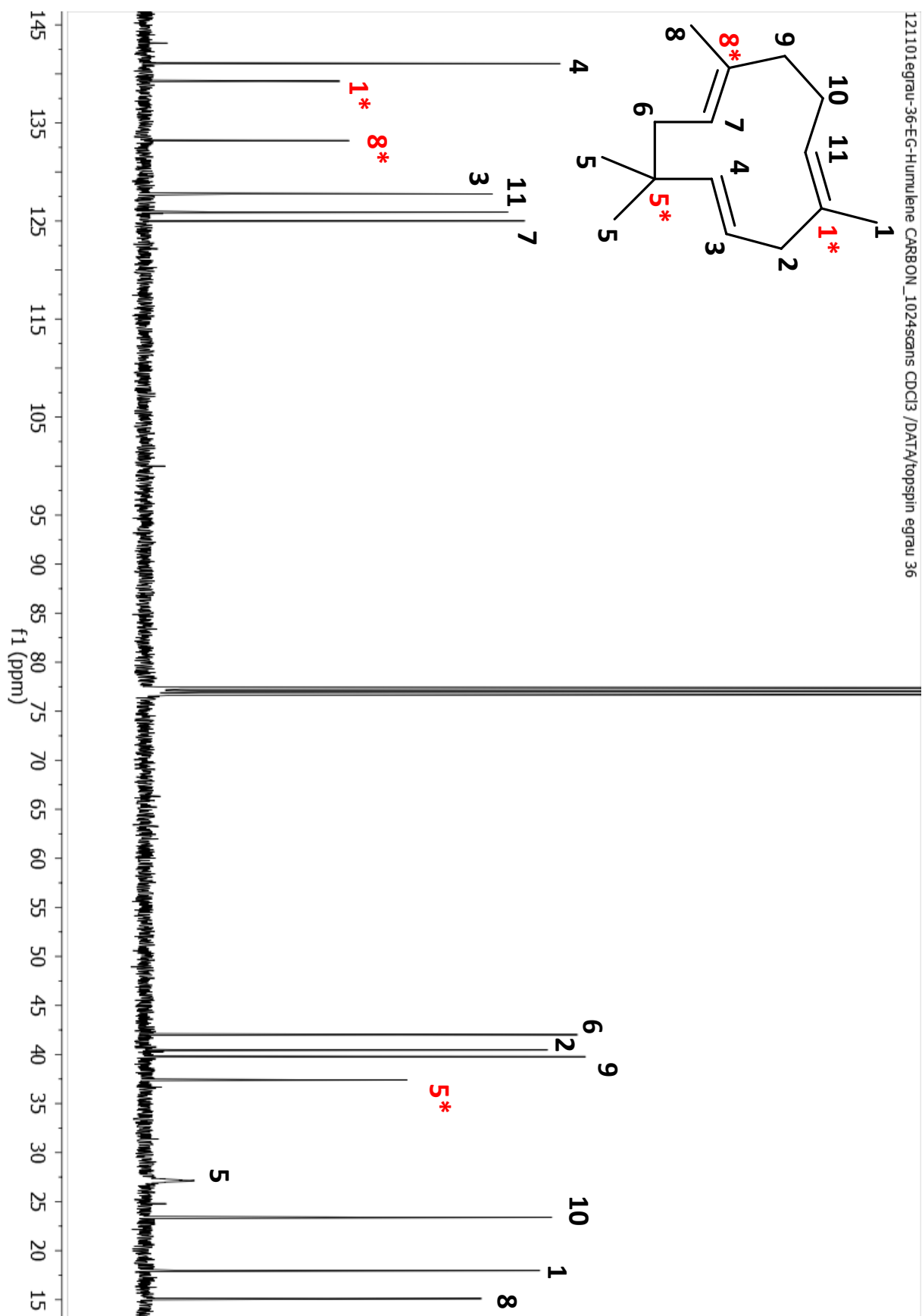


Figure S26:  $^{13}\text{C}$  NMR spectrum of humulene in  $\text{CDCl}_3$ .

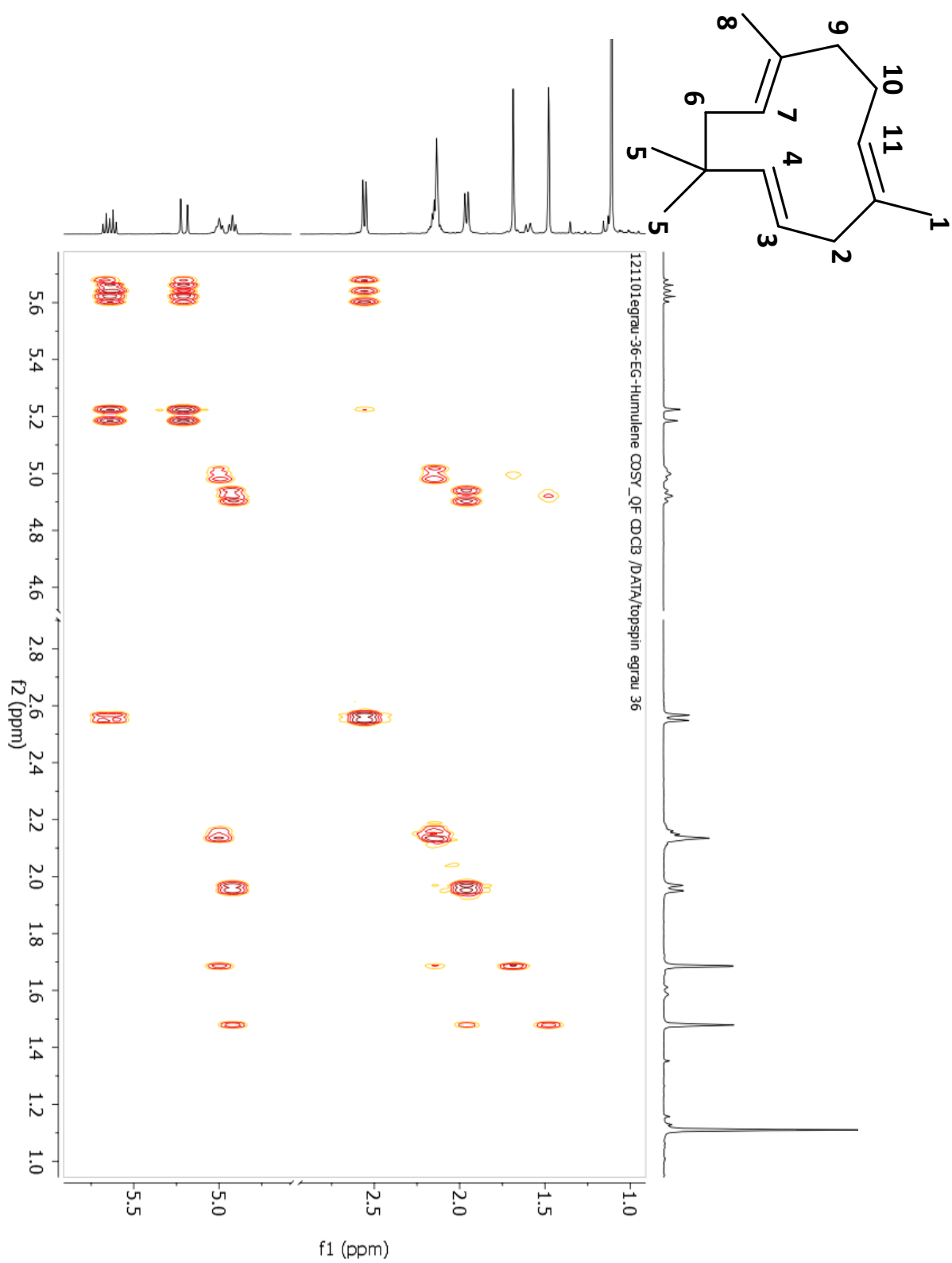


Figure S27: <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of humulene in CDCl<sub>3</sub>.



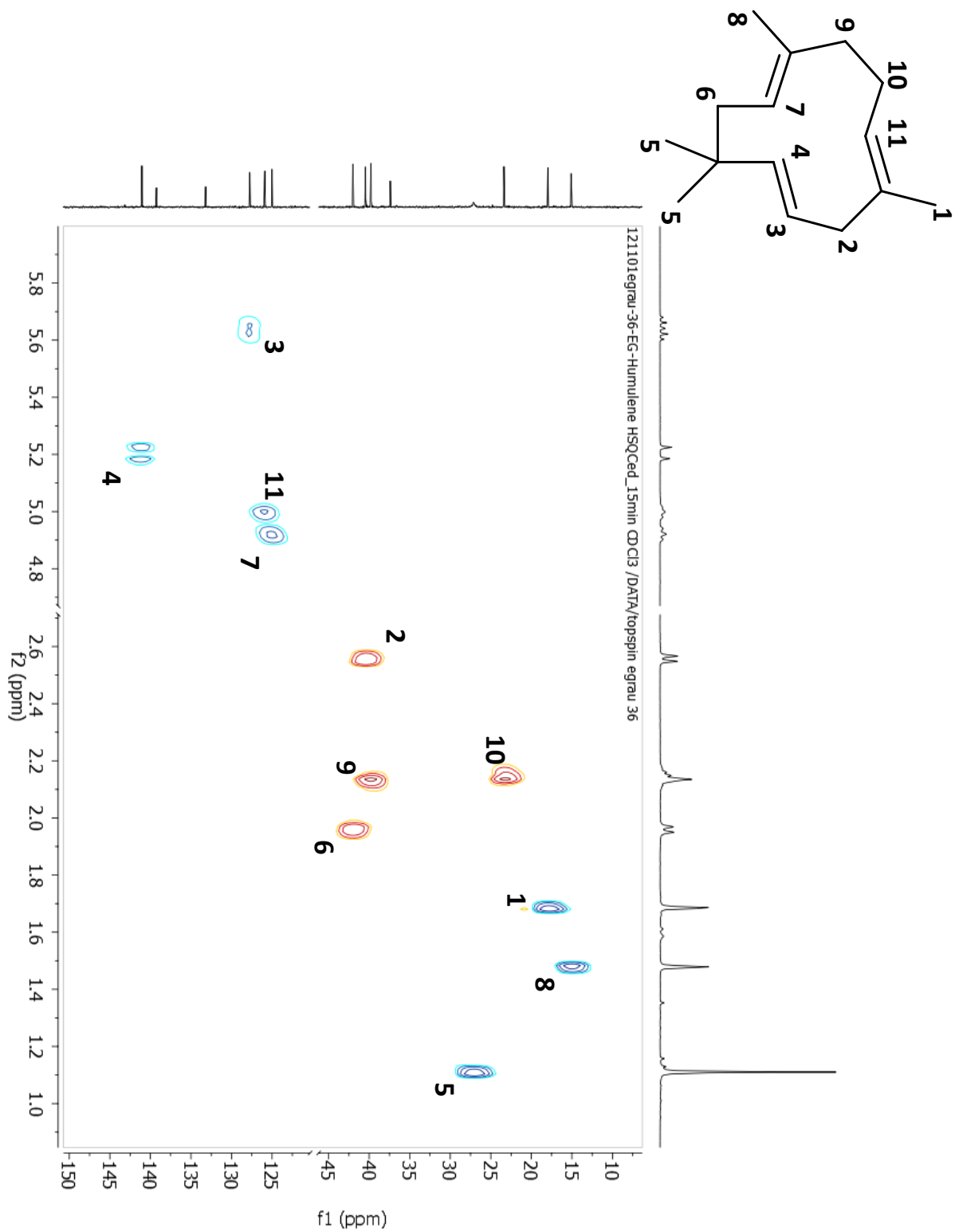


Figure S28:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of humulene in  $\text{CDCl}_3$ .

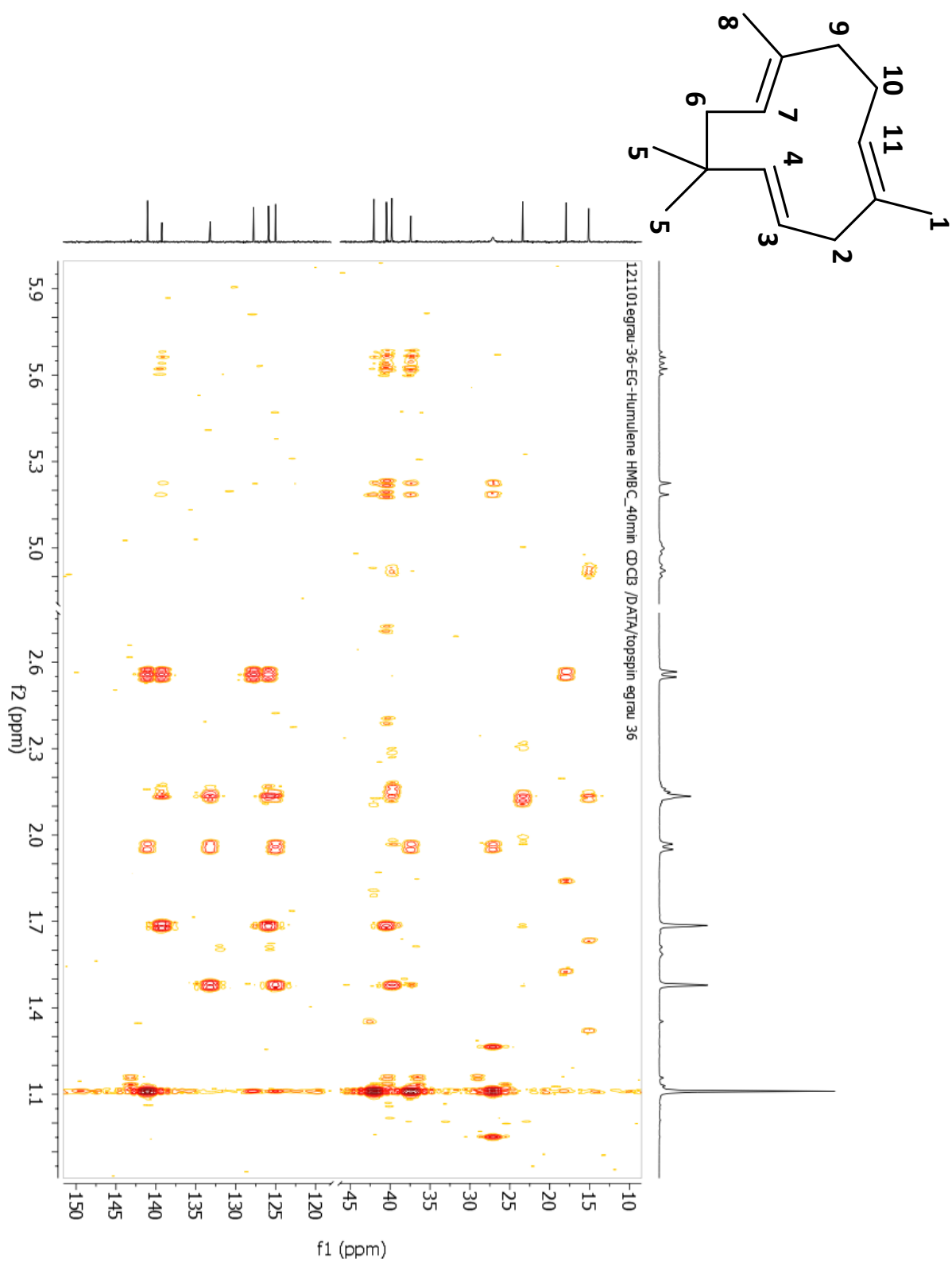


Figure S29:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of humulene in  $\text{CDCl}_3$ .

**Table S2** ROMP of humulene with different catalyst loading.<sup>a</sup>

Catalyst\ Monomer	1/500			1/1000			1/2500		
	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>	Conv <sup>b</sup>	Mn <sup>c</sup>	Đ <sup>c</sup>
<b>3</b>	100	36.0	2.1	93	32.8	1.8	81	33.5	1.9

a: Polymerizations performed at 25°C in bulk during 1 week under argon. b: Conversions in % were determined using <sup>1</sup>H NMR. c: M<sub>n</sub> in kg/mol and molecular weight distribution (Đ=M<sub>w</sub>/M<sub>n</sub>) as determined by SEC in THF vs. polystyrene standards.

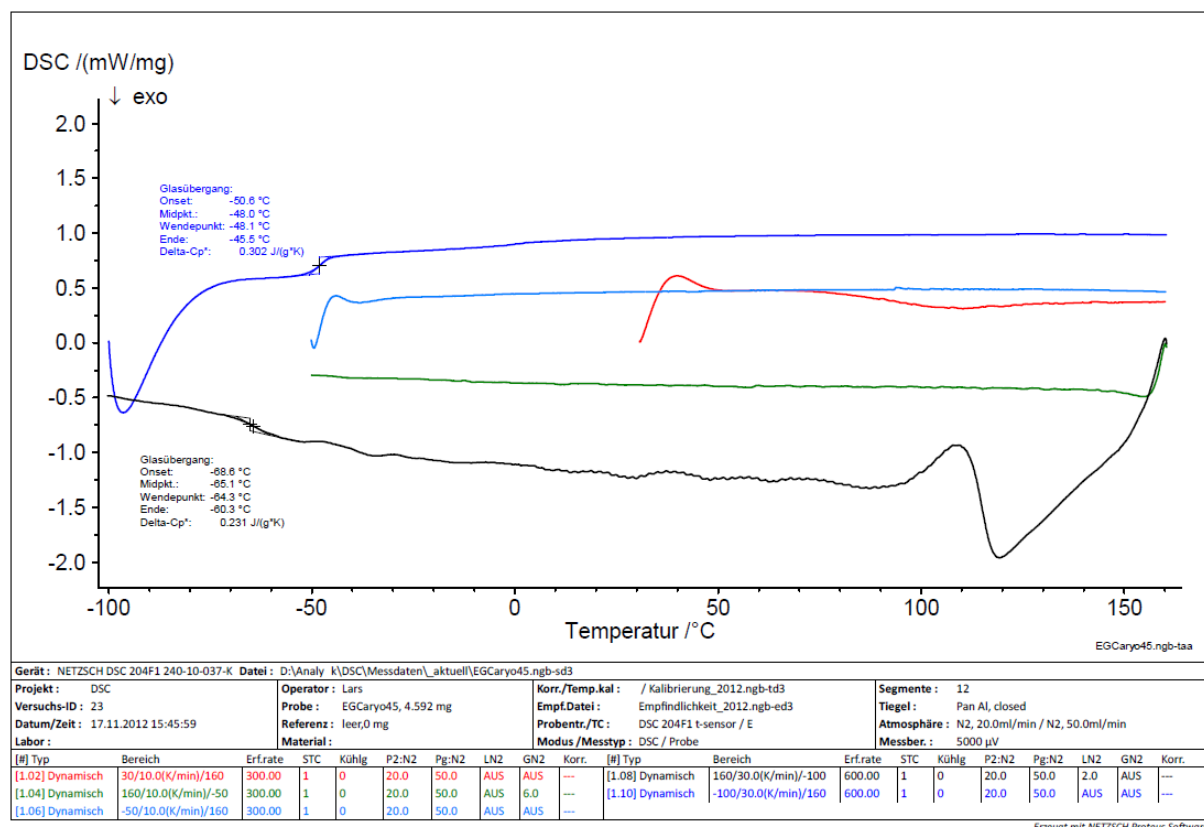


Figure S30: DSC trace of poly(humulene). In green 1<sup>st</sup> cooling at -10K/min from 160°C to -50°C, in pale blue 2<sup>nd</sup> heating at 10K/min up to 160°C then 2<sup>nd</sup> cooling in black at -30K/min down to -150°C finally 3<sup>rd</sup> heating in blue at 30K/min up to 160°C.

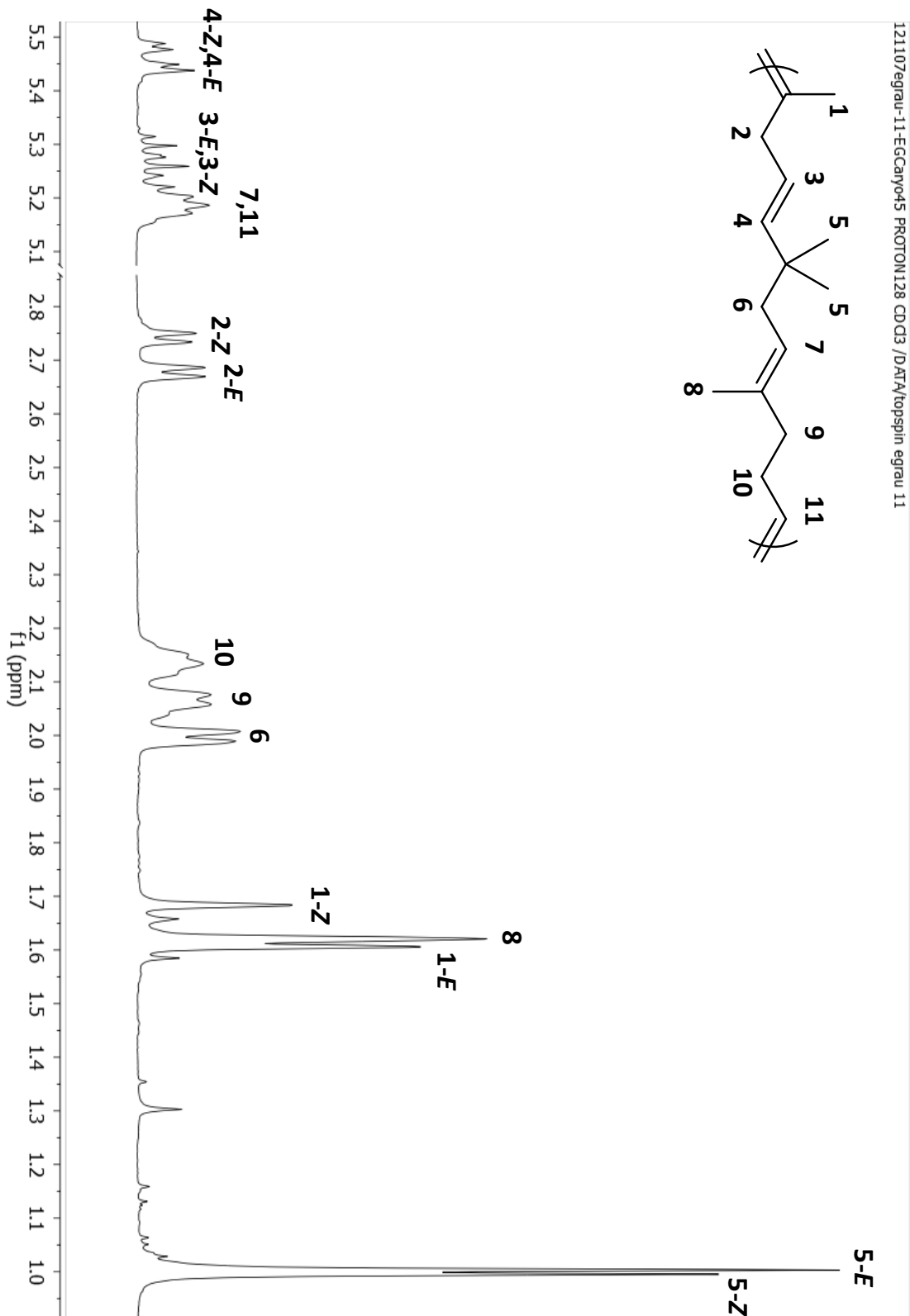


Figure S31: <sup>1</sup>H NMR spectrum of polyhumulene in CDCl<sub>3</sub>. *E/Z* means respectively that the repeating double bond is in *trans* or *cis* manner.

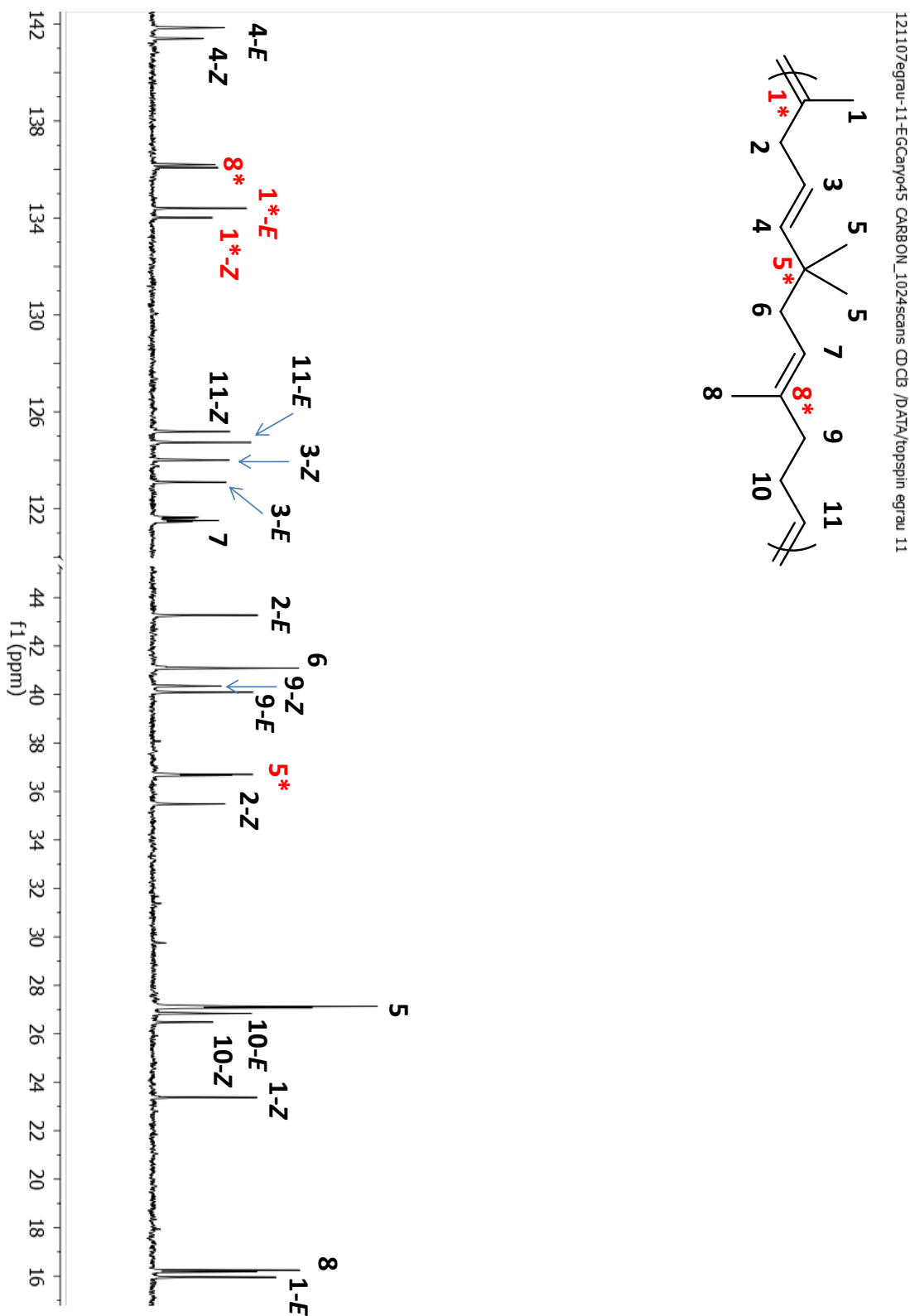


Figure S32:  $^{13}\text{C}$  NMR spectrum of polyhumulene in  $\text{CDCl}_3$ . *E/Z* means respectively that the repeating double bond is in *trans* or *cis* manner.

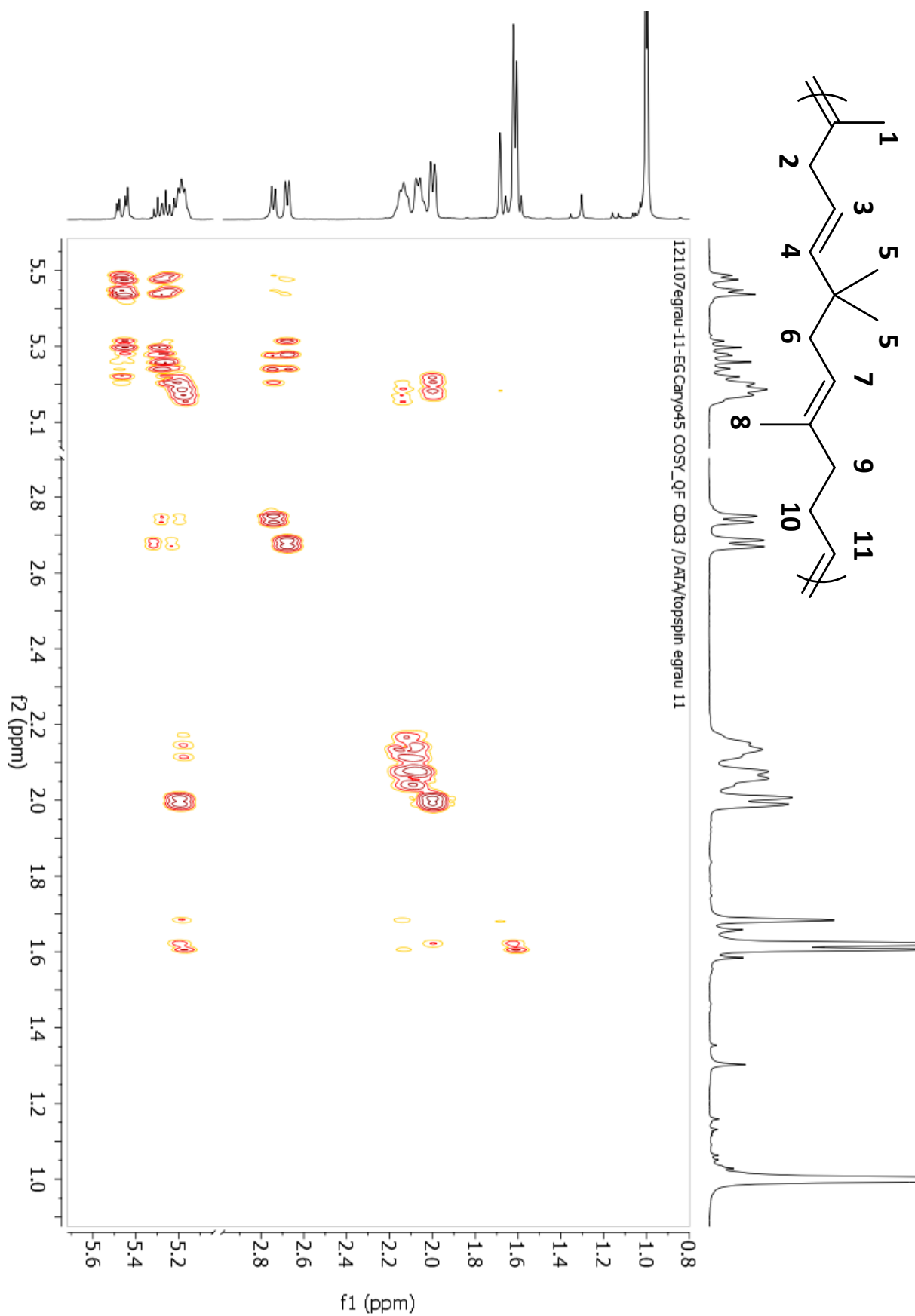


Figure S33:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of polyhumulene in  $\text{CDCl}_3$ . *E/Z* means respectively that the repeating double bond is in *trans* or *cis* manner.

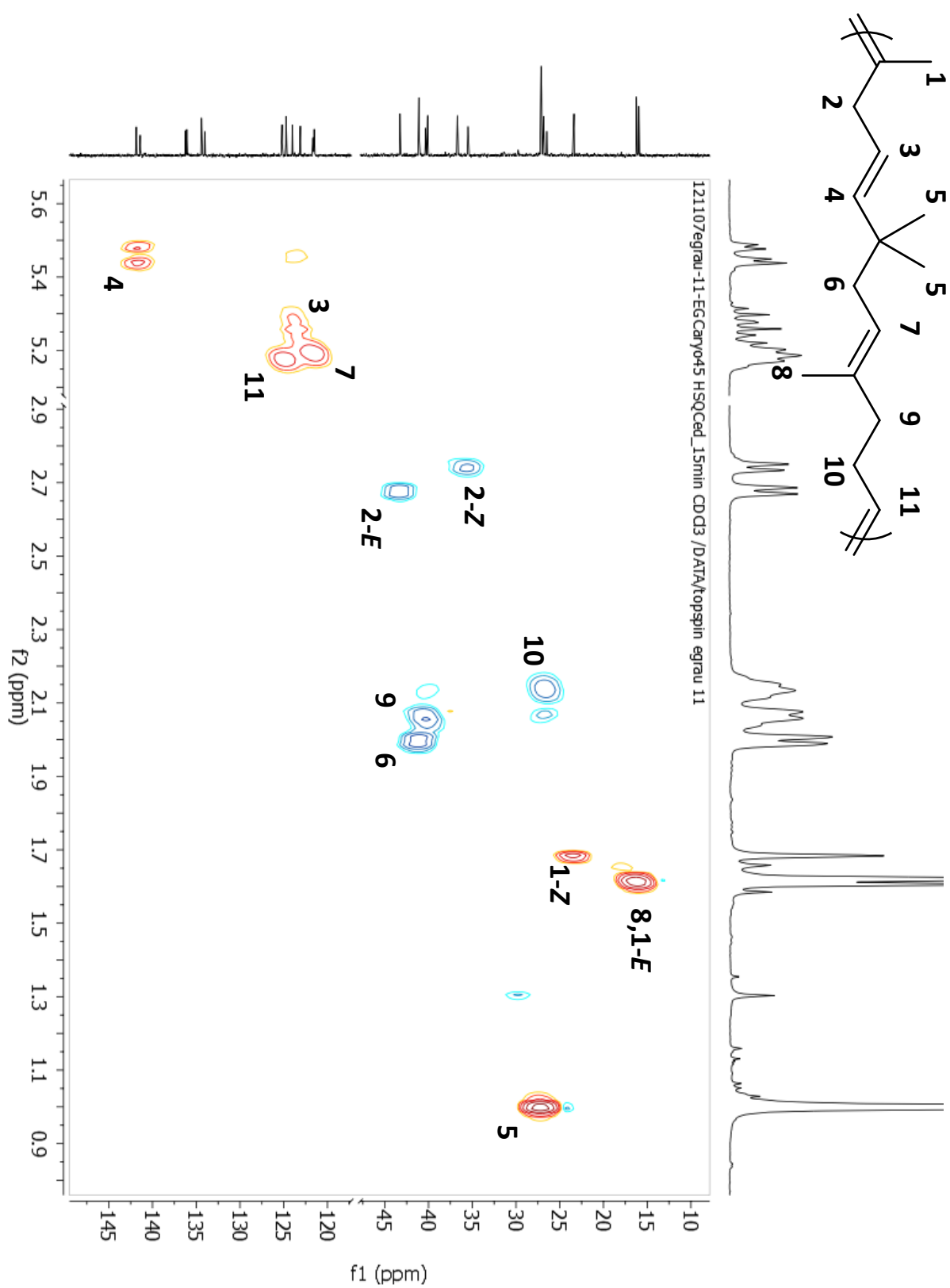


Figure S34:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of polyhumulene in  $\text{CDCl}_3$ . *E/Z* means respectively that the repeating double bond is in *trans* or *cis* manner.

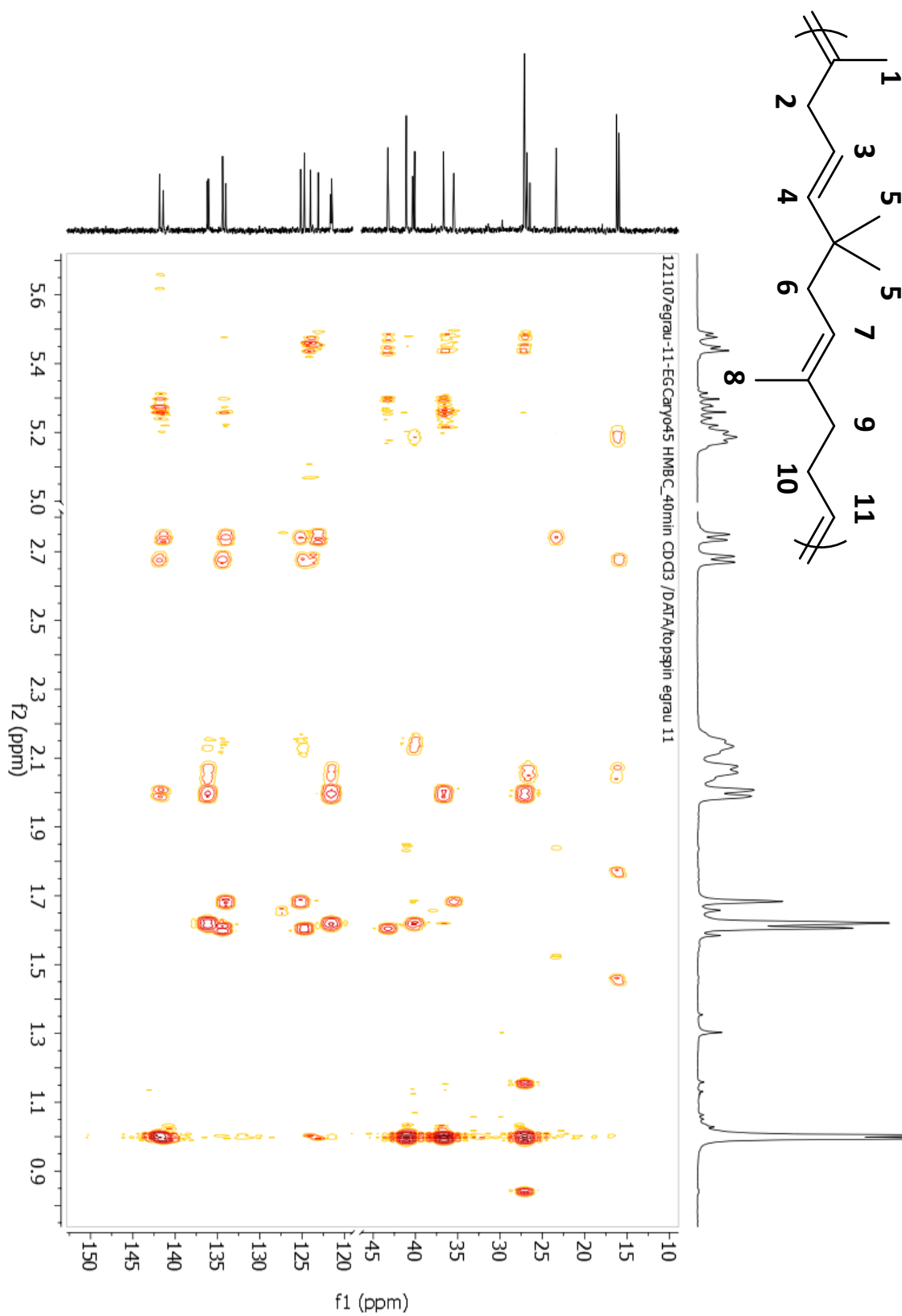


Figure S35:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of polyhumulene in  $\text{CDCl}_3$ . *E/Z* means respectively that the repeating double bond is in *trans* or *cis* manner.



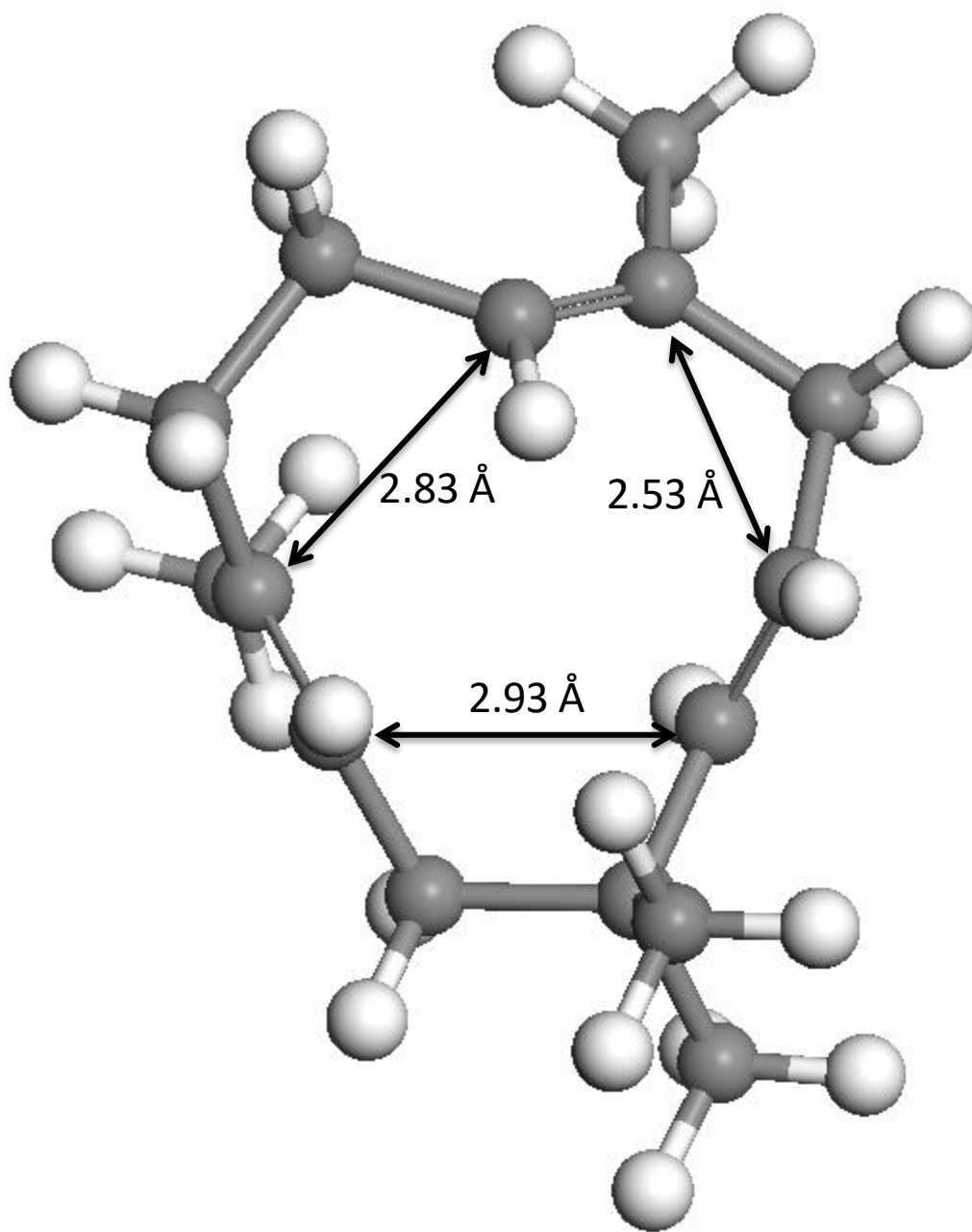


Figure S36: 3D view of humulene calculated using GAUSSIAN09 with the B3PW91 hybrid functional and a high quality 6-311++G(d) basis set.

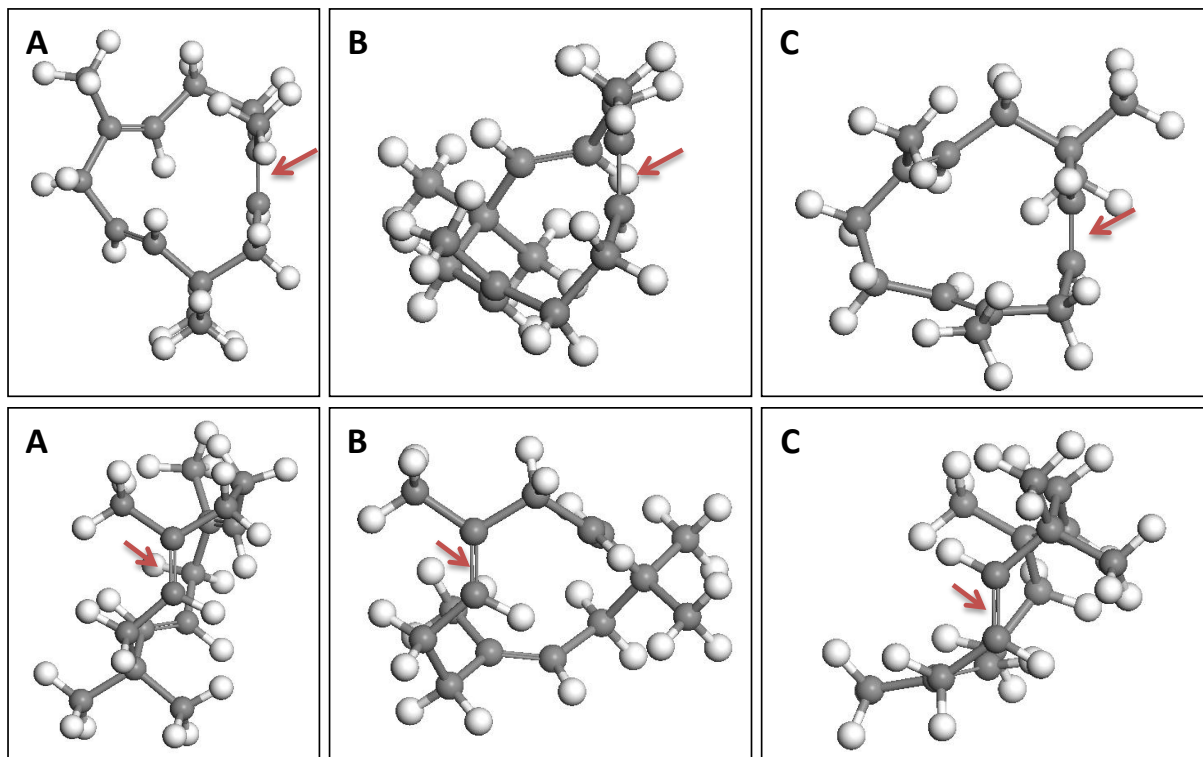
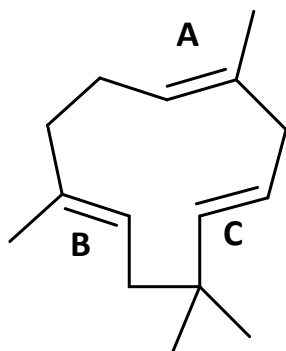


Figure S37: 3D side and top views of humulene for each double bonds (red arrow indicates the double bond position).

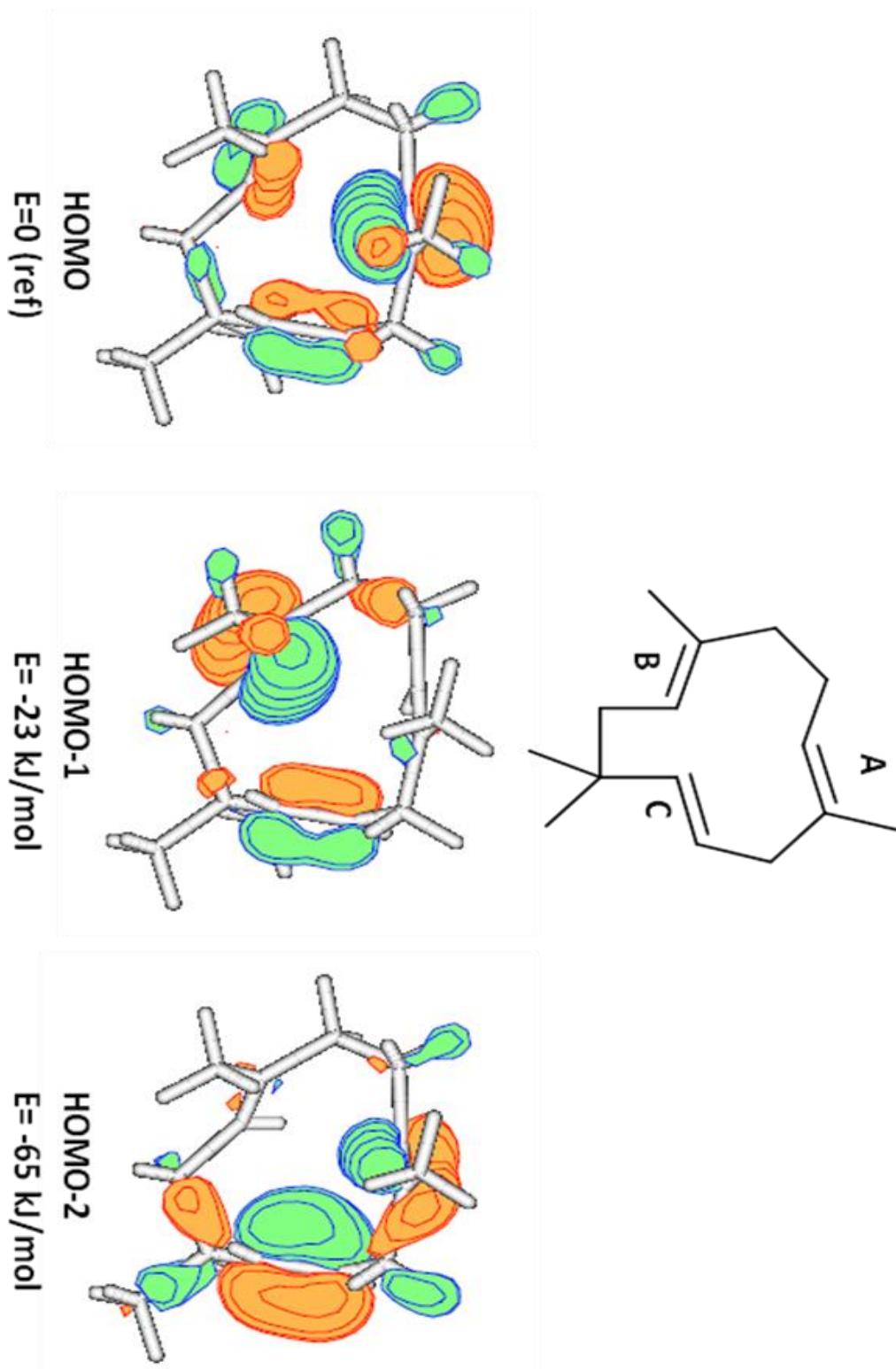


Figure S38: 3D views of HOMO, HOMO-1 and HOMO-2 of humulene.

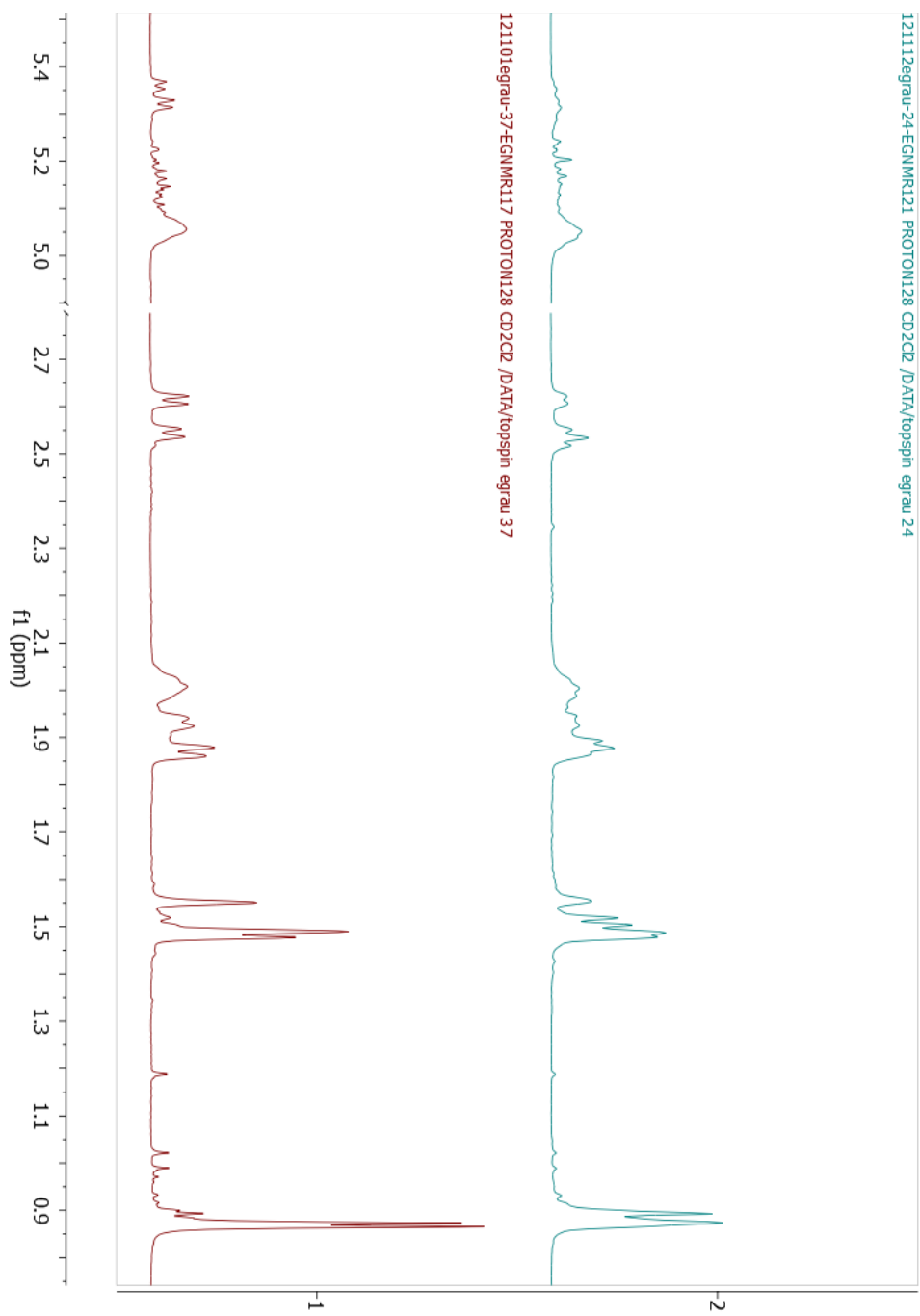


Figure S39:  $^1\text{H}$  NMR spectrum of polyhumulene in  $\text{CD}_2\text{Cl}_2$  obtained using **3** (in red) and **2** (in green)

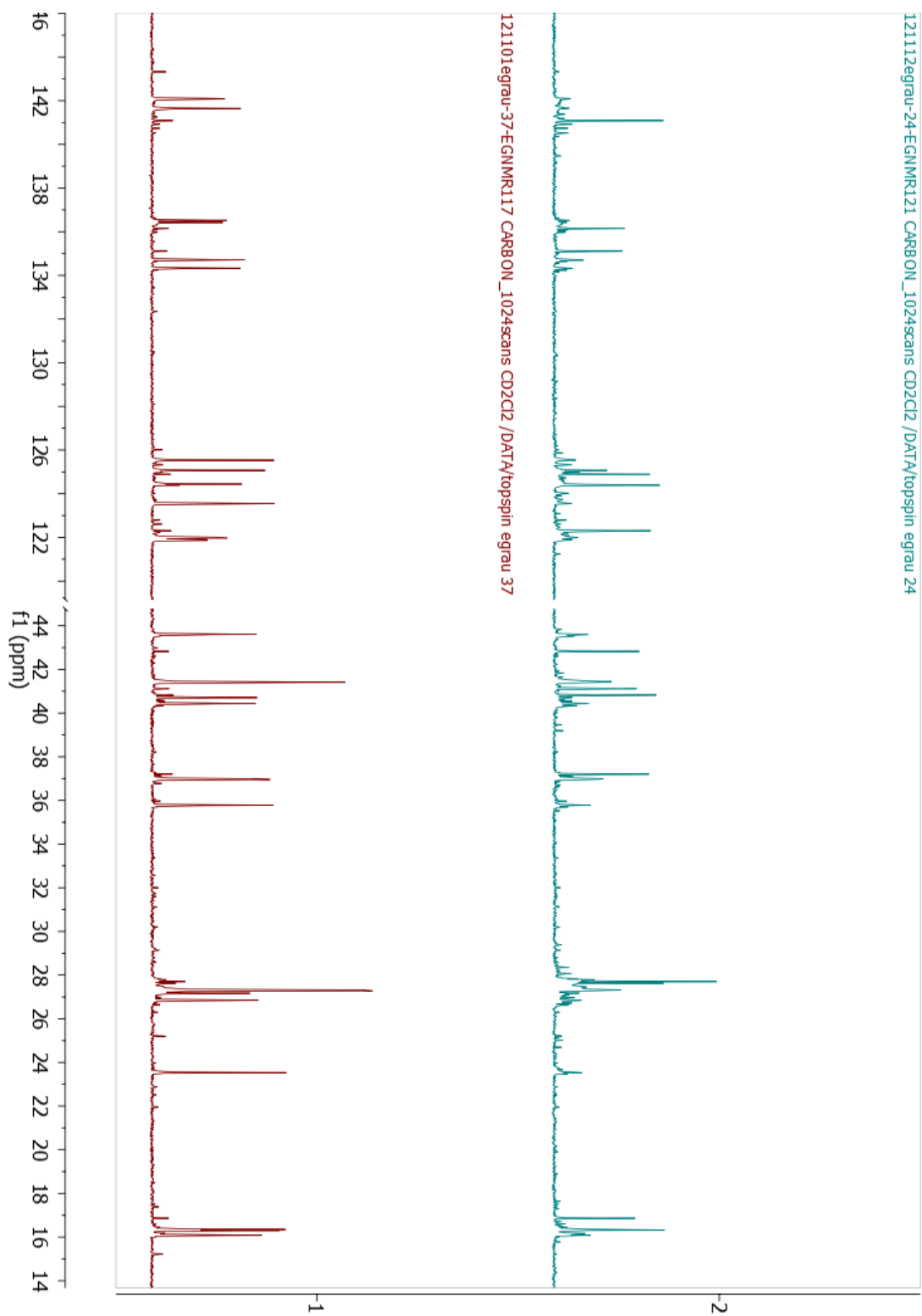


Figure S40:  $^{13}\text{C}$  NMR spectrum of polyhumulene in  $\text{CD}_2\text{Cl}_2$  obtained using **3** (in red) and **2** (in green)

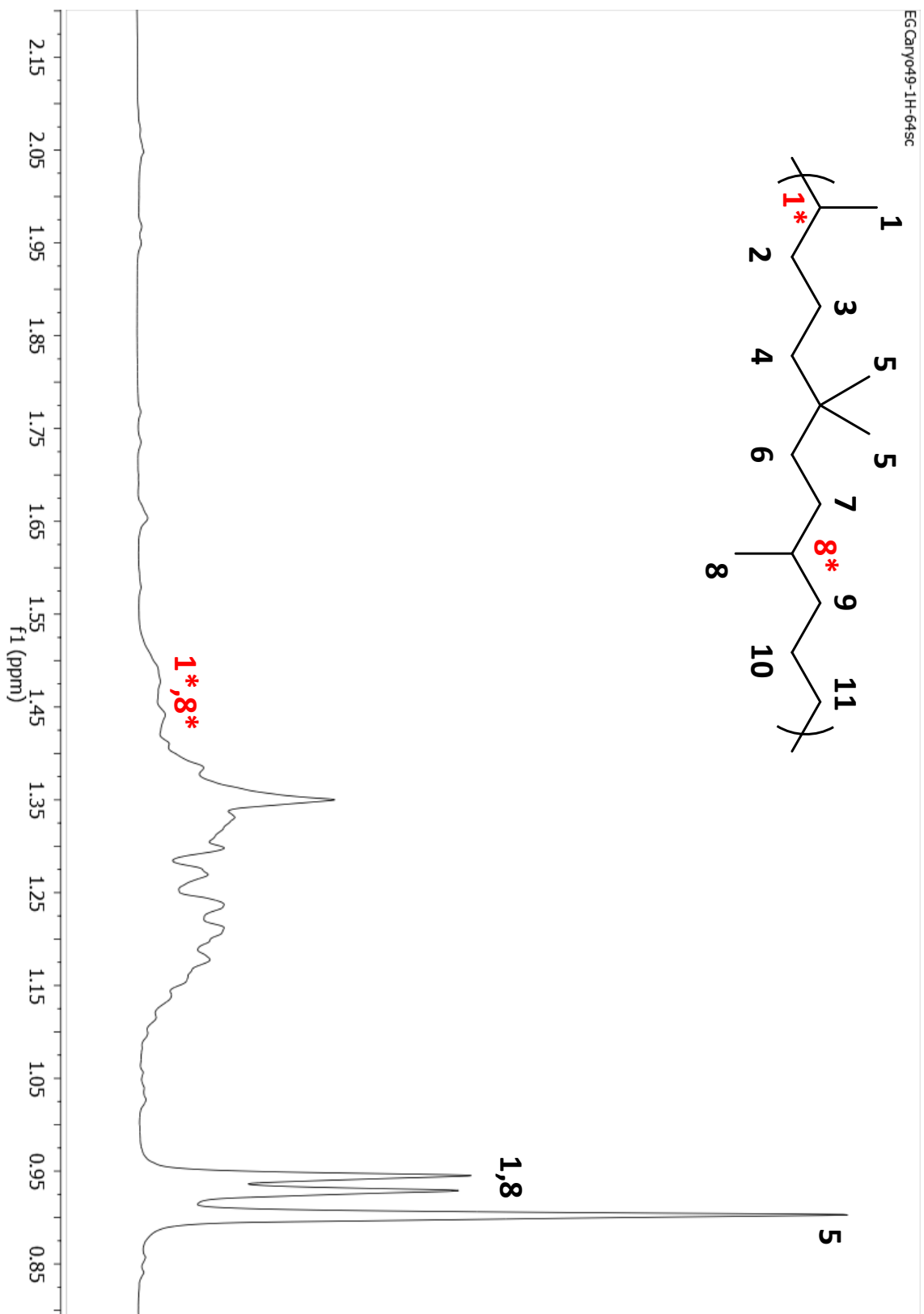


Figure S41:  $^1\text{H}$  NMR spectrum of polyhydrohumulene in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $120^\circ\text{C}$

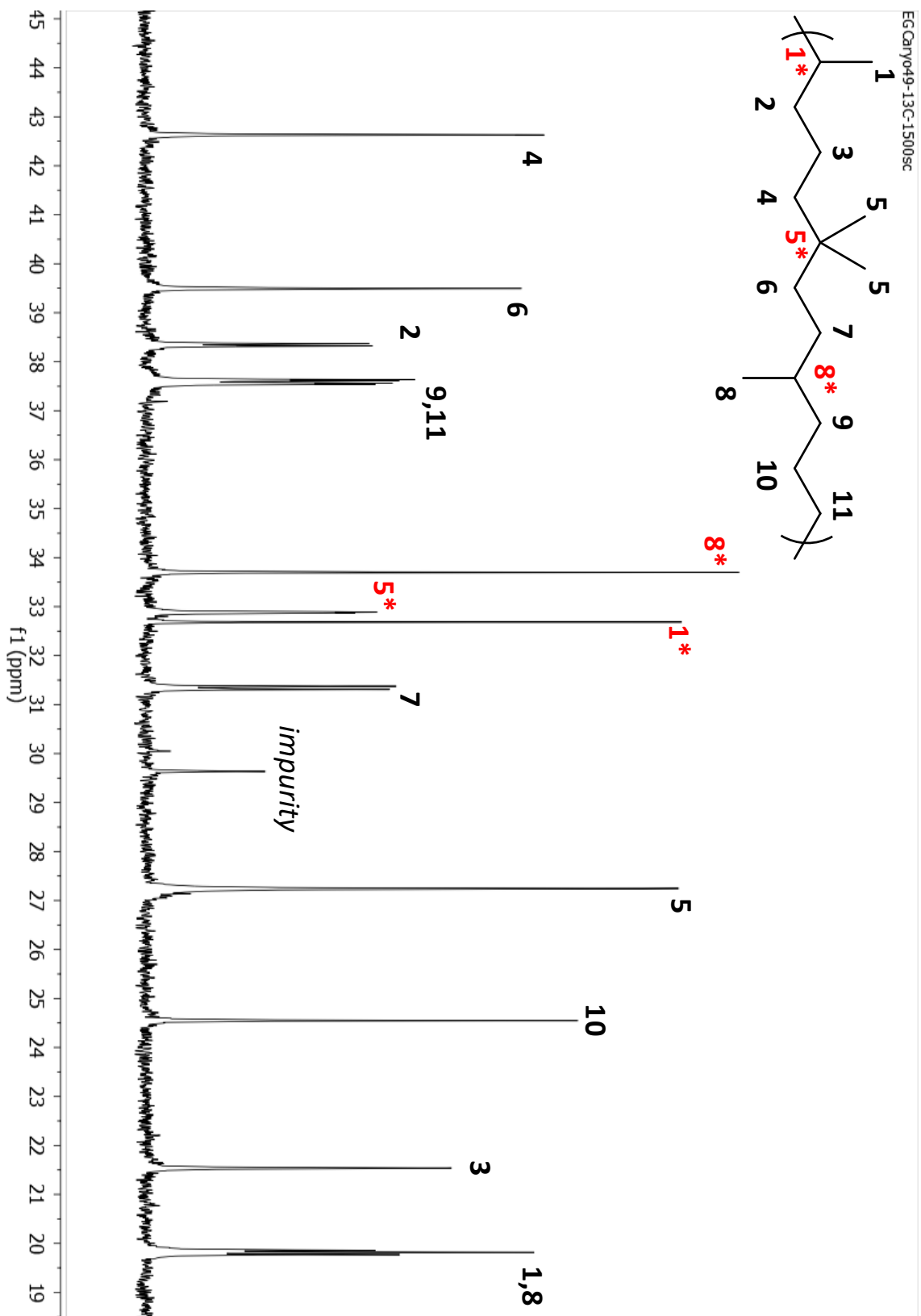


Figure S42:  $^{13}\text{C}$  NMR spectrum of polyhydrohumulene in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $120^\circ\text{C}$

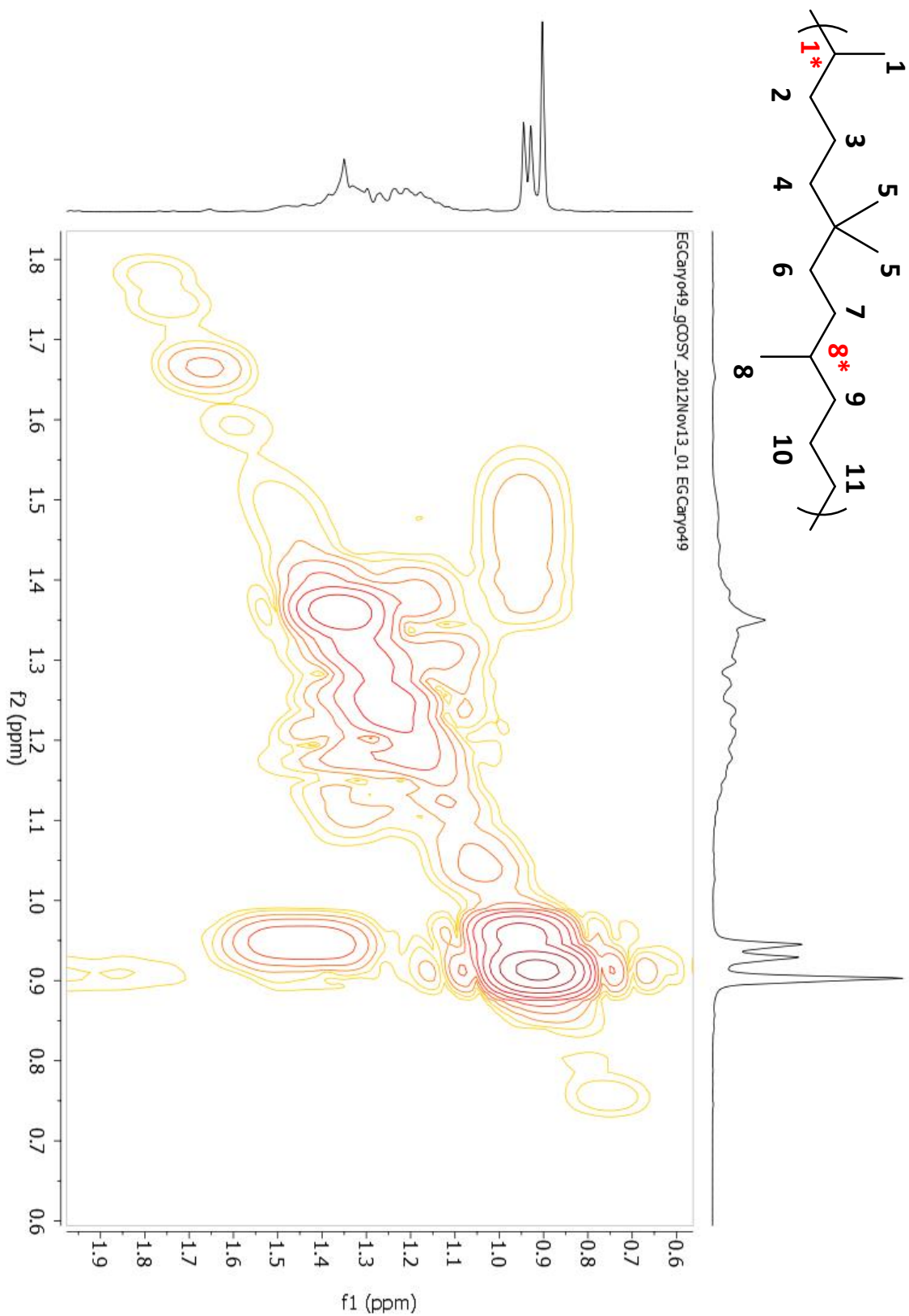


Figure S43:  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of polyhydrohumulene in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $120^\circ\text{C}$



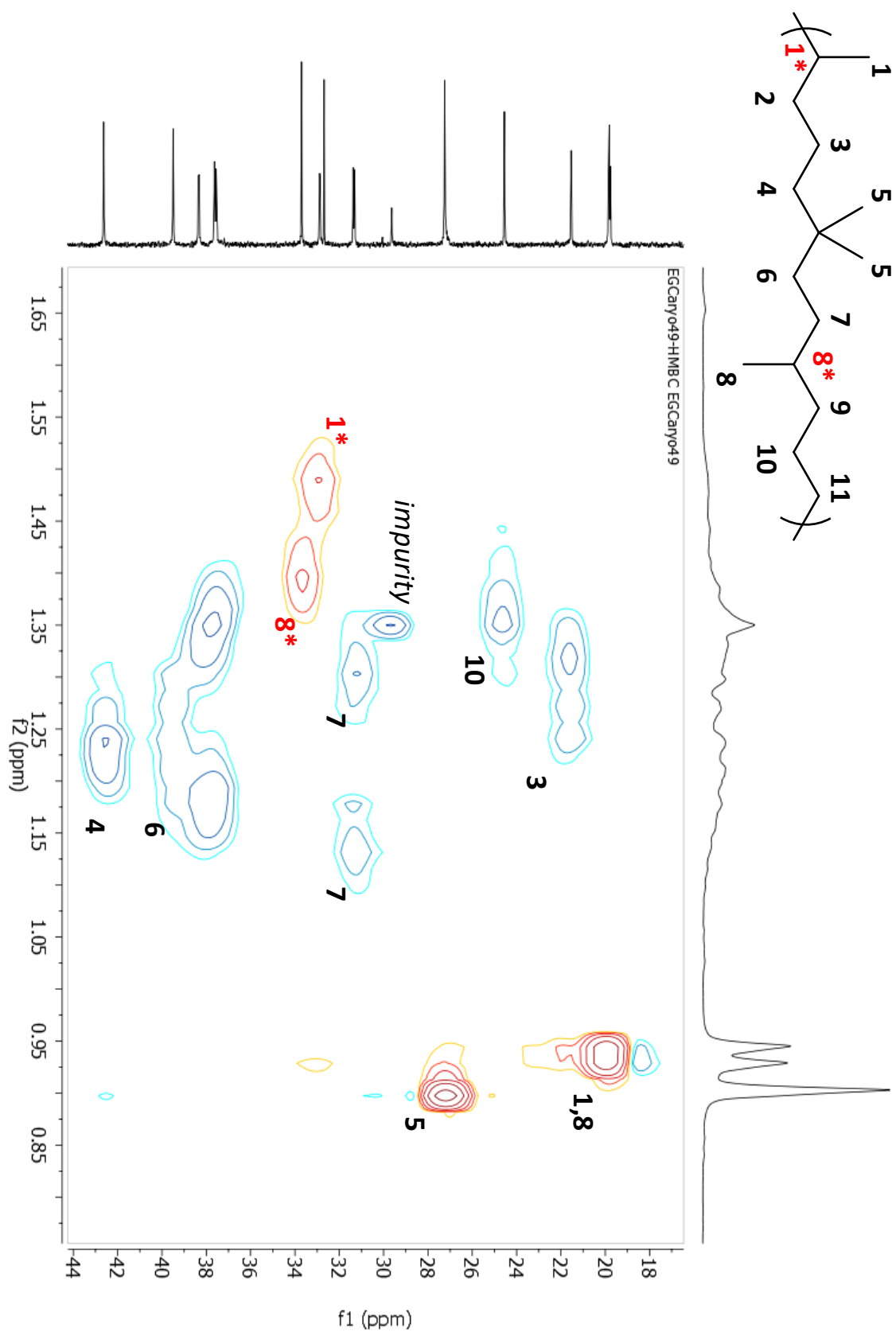


Figure S44:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of polyhydrohumulene in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $120^\circ\text{C}$

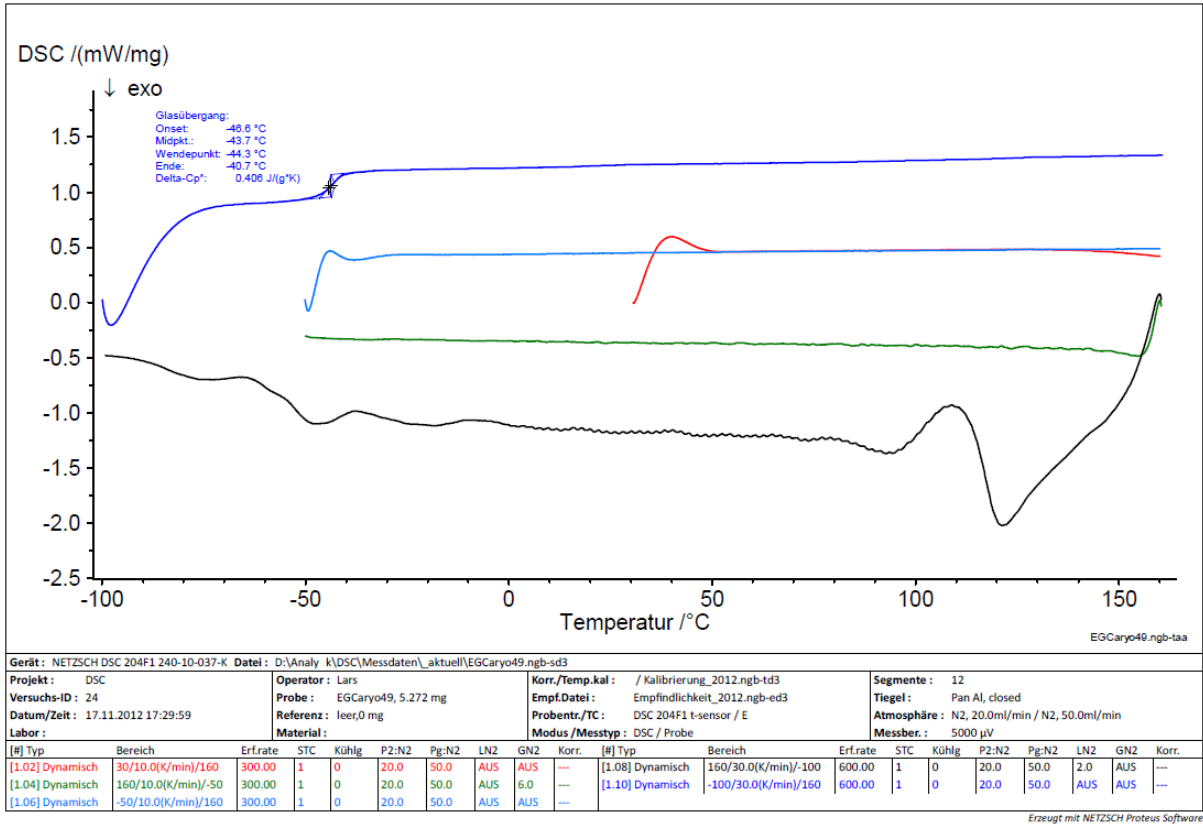


Figure S45: DSC trace of poly(hydrohumulene). In green 1<sup>st</sup> cooling at -10K/min from 160°C to -50°C, in pale blue 2<sup>nd</sup> heating at 10K/min up to 160°C then 2<sup>nd</sup> cooling in black at -30K/min down to -150°C finally 3<sup>rd</sup> heating in blue at 30K/min up to 160°C.

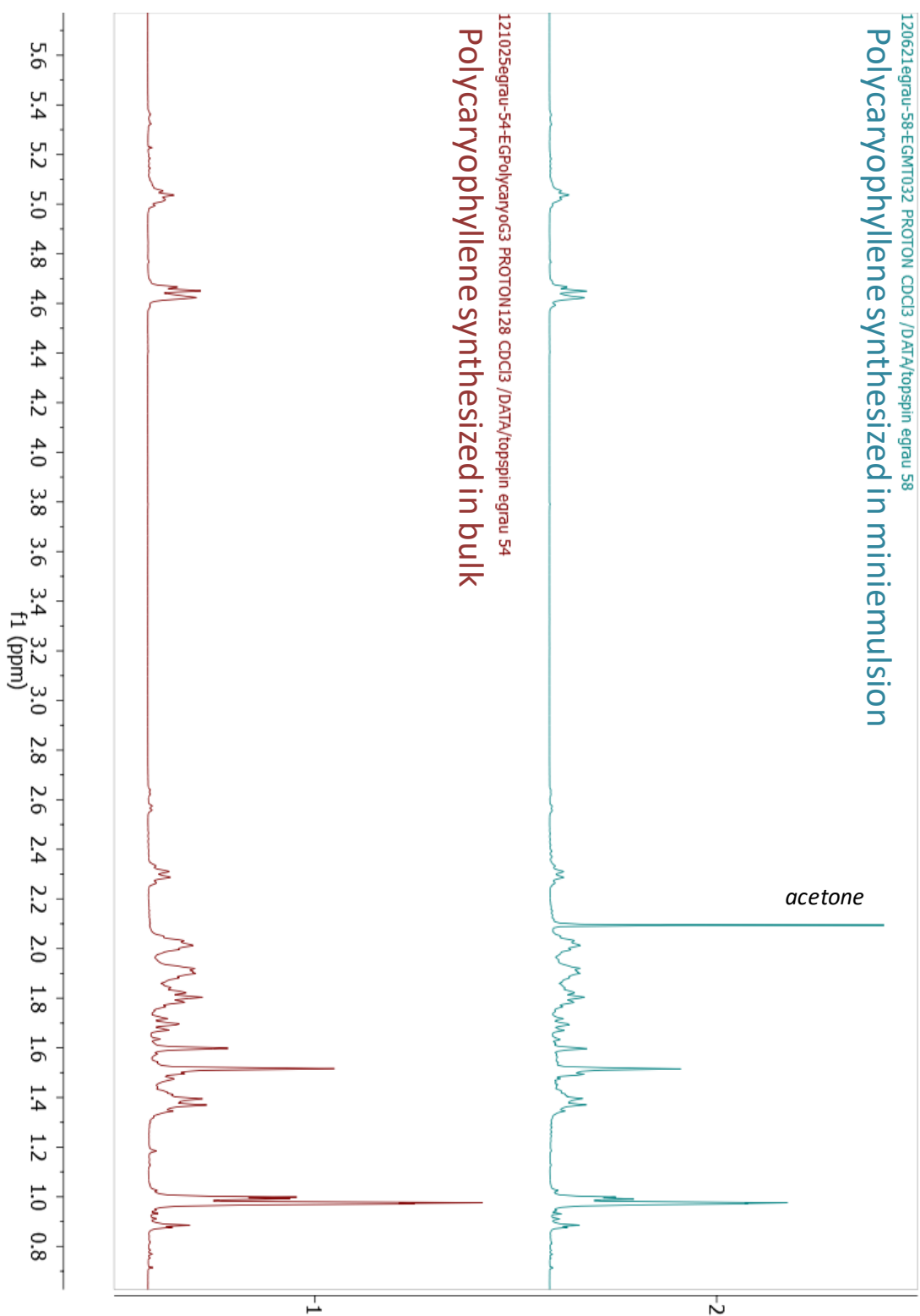


Figure S46: <sup>1</sup>H NMR spectrum of polycaryophyllene synthesized via miniemulsion in CDCl<sub>3</sub>.

**MW Averages**

Mp: 37404

Mn: 19998

Mv: 34498

Mw: 37348

Mz: 69633

Mz+1: 291391

PD: 1.8676

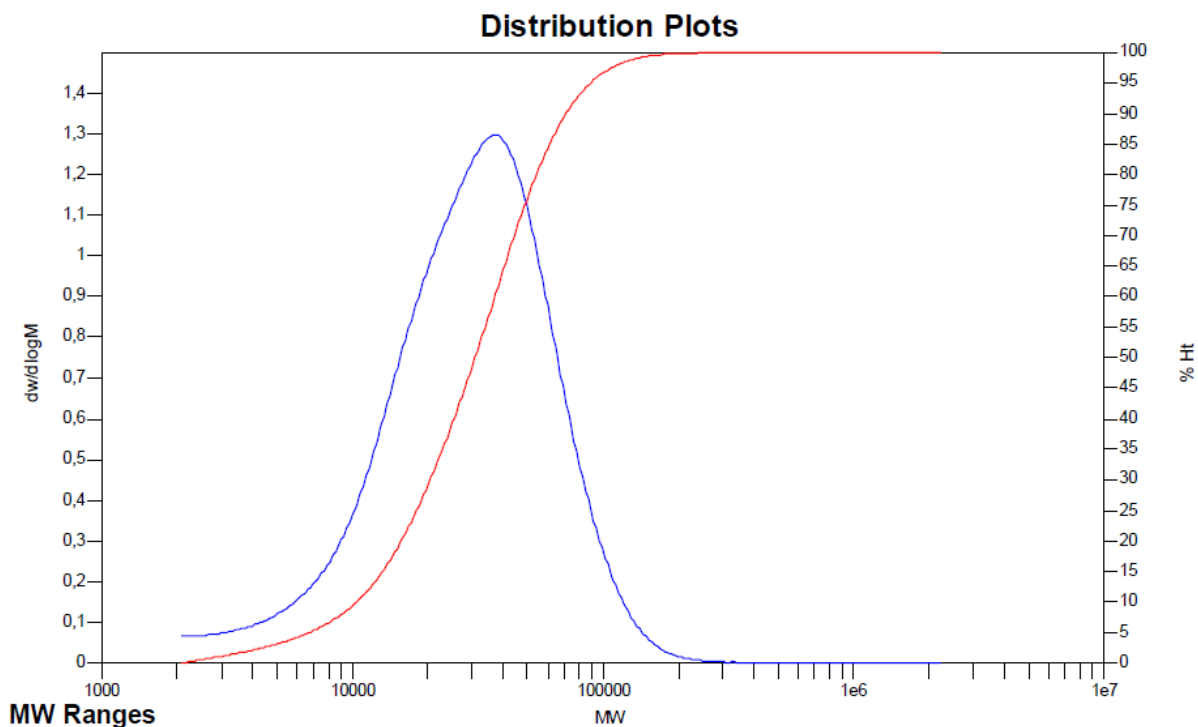


Figure S47: SEC curve of polycaryophyllene obtained by miniemulsion

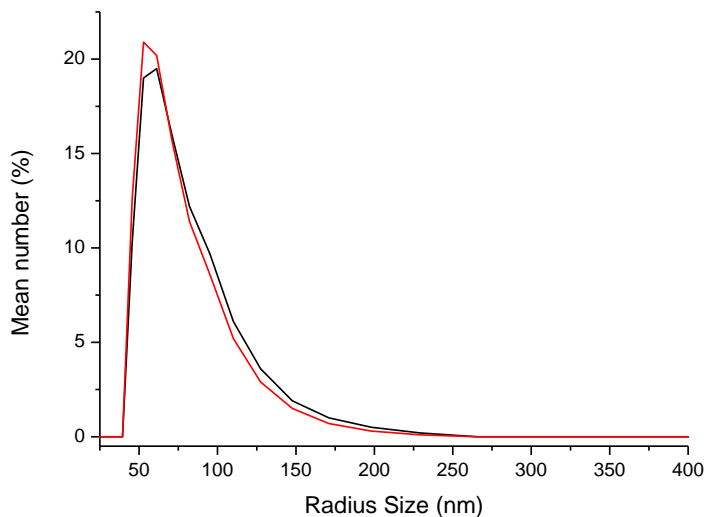


Figure S48: DLS curves of polycaryophyllene obtained by miniemulsion before (in black) and after hydrogenation (in red)