Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Alkene-assisted *cis*-to-*trans* isomerization of polyunsaturated alkenes

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I. Derivation of the formula for the extent of *trans* isomerization in skipped poly-alkenes.

Let's say that we have n molecules in our mixture and m double bonds in each molecule. Combined ^{1}H and ^{13}C NMR spectroscopic data allows us to determine following parameters:

- a, the fraction of *bis*-allylic positions in our mixture that are surrounded by two *trans* bonds.
- b, the fraction of *bis*-allylic positions in our mixture that are surrounded by one *trans* and one *cis* double bonds.
- c, the fraction of *mono*-allylic positions in our mixture that are next to *trans* bonds.

Besides, m is known but n is not known and may be very large. We need to find the fraction of *trans*-bonds t given a, b, c, and m.

We will represent the sample as a $n \times m$ matrix M where each entry corresponds to a bond and each row to a molecule. Let also 0 represent a *cis*-bond and 1 - a *trans*-bond. We will use dot products of *columns* of the matrix M to find t.

Let x_i be the i-th column of M for each $i = 1, \ldots, m$ and let e be the vector of dimension n all of whose entries are 1. Further, let A be the total number of *bis*-allylic positions with *trans-trans* bonds, let B be the total number of *bis*-allylic positions with *cis-trans* bonds, let C be the total number of *mono*-allylic positions by *trans*-bonds, and let T be the total number of *trans*-bonds, i.e.,

$$a = \frac{A}{n(m-1)}, \qquad b = \frac{B}{n(m-1)}, \qquad c = \frac{C}{2n}, \qquad t = \frac{T}{mn}$$

Then, since we only have ones and zeroes in M, the dot product $e \cdot x_i$ is exactly the number of ones in x_i and total number of *trans*-bonds in our mixture is

$$T = e \cdot \sum_{i=1}^{m} x_i$$

In a similar manner, we have

$$C = e \cdot (x_1 + x_m),$$

$$A = \sum_{i=1}^{m-1} x_i \cdot x_{i+1},$$

$$B = \sum_{i=1}^{m-1} (e - x_i) \cdot x_{i+1} + \sum_{i=1}^{m-1} x_i \cdot (e - x_{i+1}) = e \cdot \left(x_1 + 2\sum_{i=2}^{m-1} x_i + x_m \right) - 2\sum_{i=1}^{m-1} x_i \cdot x_{i+1}$$

$$= 2e \cdot \sum_{i=1}^{m} x_i - e \cdot (x_1 + x_m) - 2\sum_{i=1}^{m-1} x_i \cdot x_{i+1}$$

Therefore, we get $B = 2T - C - 2A$, or, equivalently, $T = A + \frac{B}{2} + \frac{C}{2}$. Finally,

$$t = \frac{T}{mn} = \frac{A}{mn} + \frac{B}{2mn} + \frac{C}{2mn} = \frac{2(m-1)a + (m-1)b + 2c}{2m}$$

II. Expanded Table 1 from the manuscript.

Parameters presented in the table:

- a, the fraction of *bis*-allylic positions in the mixture that are surrounded by two *trans* bonds.
- b, the fraction of *bis*-allylic positions in the mixture that are surrounded by one *trans* and one *cis* double bonds.
- c, the fraction of *mono*-allylic positions in the mixture that are next to *trans* bonds.
- t, the extent of *trans* isomerization (% of *trans* bonds in the mixture).

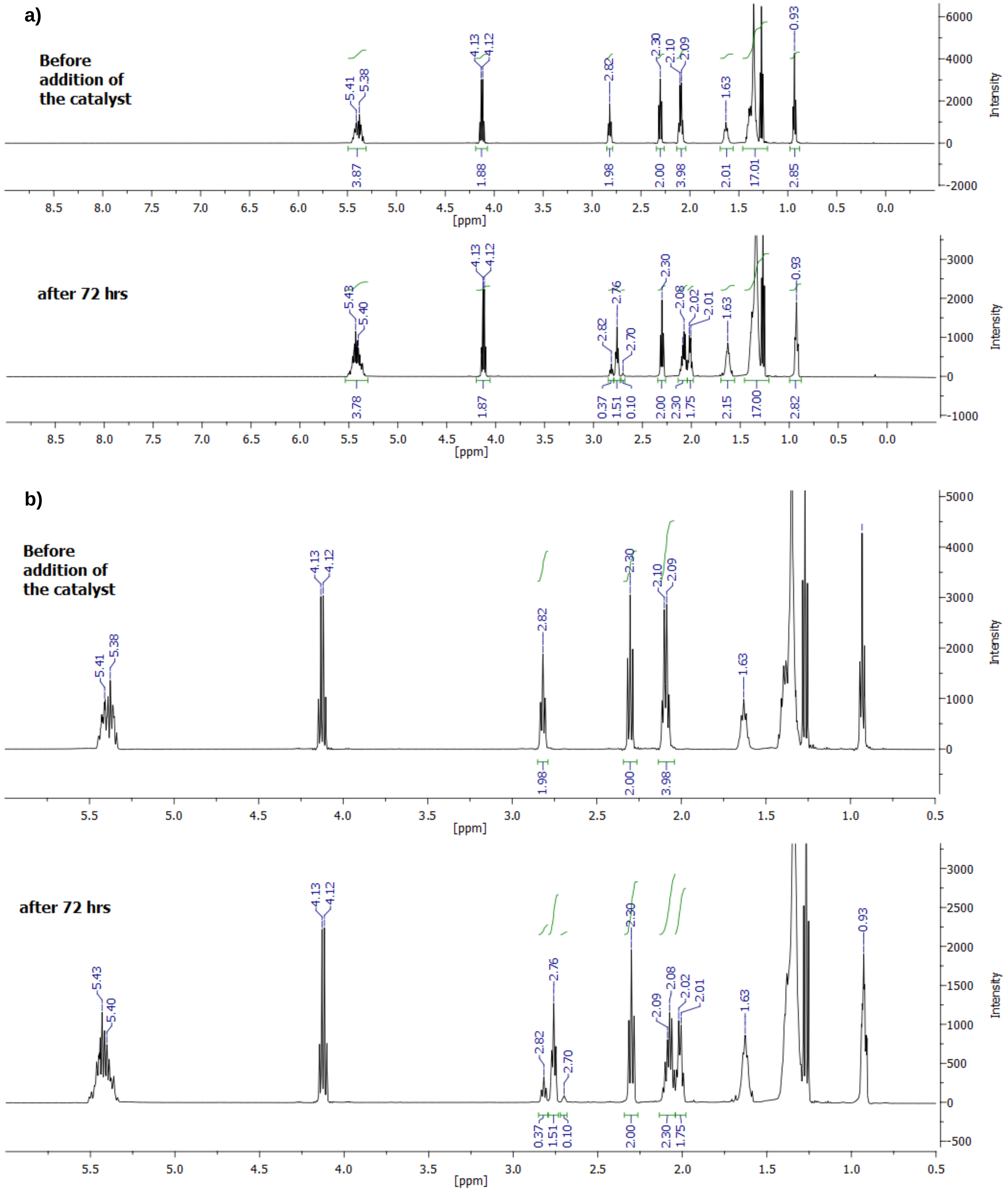
	Substrate	Cat. %	Time, h	^{1}H NMR data			^{13}C NMR data			mean parameters			
				a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*t*
1	**E-Lin**	1	72	5	76	43				5	76	43	43
2	**E-Lnn**	1	4	0	80	78	0	78	75	0	79	77	52
3	**A-Lnn**	1	24	1	49	48				1	49	48	32
4	**O-Lnn**	1	24	4	80	81	3	82	84	4	81	83	57
5	**H-Lnn**	1	24	0	78	77	0	78	78	0	78	78	52
6	**E-Ara**	2	18	24	n.d.	n.d.	25	67	75	25	67	75	63
7	**E-DHA**	3	18	33	n.d.	n.d.	34	58	73	34	58	73	65
8	**A-DHA**	3	24	31	n.d.	n.d.	31	47	58	31	47	58	55
9	**O-DHA**	3	24	29	n.d.	n.d.	31	65	78	30	65	78	65
10	**H-DHA**	3	8	34	n.d.	n.d.	36	59	79	35	59	79	67
11	**E-Lin**	1	24	1	54	28				1	54	28	28
12	**E-Lin-d_4**	1	24	2	28	16				2	28	16	16
13	**T-Lnn**	3	18	0	73	72	0	73	74	0	73	73	49
14	**POLY**	1[a]	24	n.a.	n.a.	n.d.	n.a.	n.a.	80	n.a.	n.a.	80	80
15	**M-Ole**	5[b]	48	n.a.	n.a.	38	n.a.	n.a.	37[c]	n.a.	n.a.	37	37

n.d. = not determined due to peak overlap; n.a. = not available due to absence of such position in the substrate; [a]With respect to the repeating unit. [b]Reaction was carried in acetone-d_6 and was heated to 60 ˚C. [c]Formation of positional isomers.

III. Isomerization of E-Lin with complex 1 in DCM-d$_2$ at r.t. (entry 1, Table 1)

Figure S1: ^{1}H NMR spectra (500 MHz, DCM-d$_2$) of reaction mixture: a) full spectra; b) sections of ^{1}H-NMR spectra (expanded between 6.0–0.5 ppm) for greater clarity.*

**From this point on, all ^{1}H NMR spectra will be presented in a similar fashion due to the appearance of all significant spectral information within the specified range.*



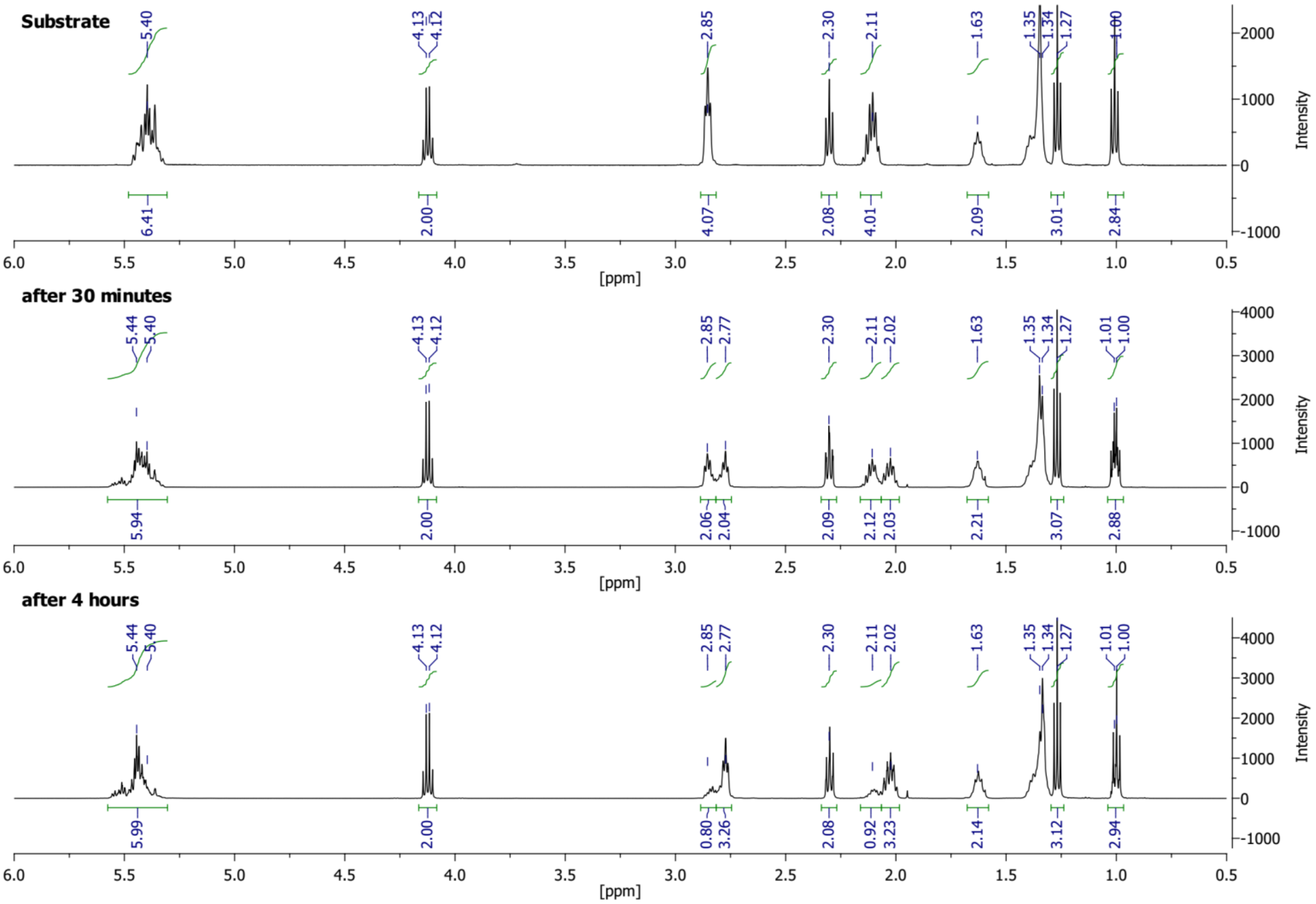
^{1}H NMR spectrum of **E-Lin** consists of three key elements: vinylic protons that resonate as a multiplet at 5.32-5.45 ppm, *bis*-allylic protons that occur as a triplet at 2.82 ppm and *mono*-allylic protons – as a quartet at 2.07-2.12 ppm (Figure S1). Addition of complex **1** to the solution of **E-Lin** in DCM-d_2 initiates *cis*-to-*trans* isomerization of substrate's double bonds that, in turn, results in several changes of ^{1}H NMR spectra that follow the characteristic trend of such process. First of all, while the vinylic multiplet at 5.32-5.45 ppm partially decreases in size another multiplet appears on its low-frequency side at 5.39-5.50 ppm indicating partial isomerization of *cis*-double bonds to *trans*.

Protons of allylic positions that are surrounded by newly formed *trans*-double bonds should resonate upfield to original peaks on proton spectra. Indeed, a new multiplet appears at 1.98-2.04 ppm indicating *mono*-allylic protons by newly formed *trans*-double bonds. Integration shows that after 24 hours of reaction time just about 1 *mono*-allylic proton out of 4 (about 28%) has a *trans*-double bond next to it (labelled as "*E*-*mono*-allylic" for subsequent discussion). After 72 hours the fraction of *E*-*mono*-allylic protons reaches 43%.

Likewise, two new triplets are formed for *bis*-allylic protons at 2.76 and 2.70 ppm. However, when reaction reaches equilibrium after 72 hours the peak at 2.70 ppm represents not more than 5% of all *bis*-allylic protons. The fact that this peak occurs exactly where *bis*-allylic protons of ethyl linolelaidate (*trans*,*trans*-9,12-octadecadienoate) resonate suggests that in general only one of two double bonds in **E-Lin** is isomerized. *Cis*-to-*trans* isomerization of either double bond in **E-Lin** forms a *bis*-allylic position surrounded by one *cis*-double bond and one *trans*-double bond. Such position resonates at 2.76 ppm: exactly between the original *bis*-allylic position surrounded by two *cis*-double bonds (labelled as "(*Z*,*Z*)-*bis*-allylic" for subsequent discussion) and the *bis*-allylic position surrounded by two *trans*-double bonds (labelled as "(*E*,*E*)-*bis*-allylic" for subsequent discussion). Such *bis*-allylic position represents either *cis*,*trans*- or *trans*,*cis*-system (labelled as "(*E*,*Z*)/(*Z*,*E*)-*bis*-allylic" for subsequent discussion) and reaction mixture most probably consists of both isomers. Integration of this newly formed peak at 2.76 ppm after 24 hours of reaction time indicates that the fraction of (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions in the reaction mixture reaches 54%, and after 72 hours the percentage of such positions in the equilibrium mixture equals 76%. Combined evidence suggest that the resulting equilibrium mixture is mostly composed of (*E*,*Z*)- and (*Z*,*E*)-**E-Lin** isomers with traces of (*E*,*E*)-**E-Lin** isomer. Such mixture composition contains 43% of *trans*-double bonds.

IV. Isomerization of E-Lnn with complex 1 in DCM-d_2 at r.t. (entry 2, Table 1)

Figure S2: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Key elements of ^{1}H NMR spectrum of **E-Lnn** are as follows: vinylic protons resonate as a multiplet at 5.33-5.46 ppm, *bis*-allylic protons occur as a triplet at 2.85 ppm and *mono*-allylic protons – as a multiplet at 2.08-2.15 ppm (Figure S2). Similar to *cis*-to-*trans* isomerization of **E-Lin**, addition of complex **1** to the solution of **E-Lnn** results in partial reduction of original vinylic and allylic peaks followed by appearing of a new multiplet at 5.48-5.56 ppm, a triplet at 2.77 ppm and a multiplet at 1.99-2.07 ppm. Based on peak integration around 80% of *bis*-allylic positions and around 78% of *mono*-allylic positions are converted into new configurations by the time the equilibrium is established. The fact that only one new triplet at 2.77 ppm could be observed for *bis*-allylic protons suggests that no (*E*,*E*)-*bis*-allylic positions were formed. Further evidence for this theory could be obtained from the analysis of ^{13}C NMR spectra.

Figure S3b illustrates selected sections of ^{13}C NMR spectra of pure **E-Lnn** and equilibrium mixture after 4 hours of reaction time. *Mono*-allylic carbon atoms of **E-Lnn** occur as two singlets at 27.16 and 20.50 ppm and its *bis*-allylic carbon atoms - as two singlets at 25.55 and 25.46 ppm. In a course of *cis*-to-*trans* isomerization of **E-Lnn** all four original peaks for allylic carbons diminish in size while several new peaks appear at 32.48, 30.38-30.26 and 25.52 ppm.

Examination of ^{13}C NMR data for all 8 possible geometric isomers of **E-Lnn** from the literature[1] indicates that as one double bond next to allylic carbon atom changes its configuration from *cis* to *trans* its carbon resonance is shifted downfield by approximately 5 ppm. These are the cases of *E*-*mono*-allylic and (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms. When both double bonds around *bis*-allylic carbon atom obtain *trans*-configuration its chemical shift appears downfield by about 10 ppm as in the case of (*E*,*E*)-*bis*-allylic carbon atoms.

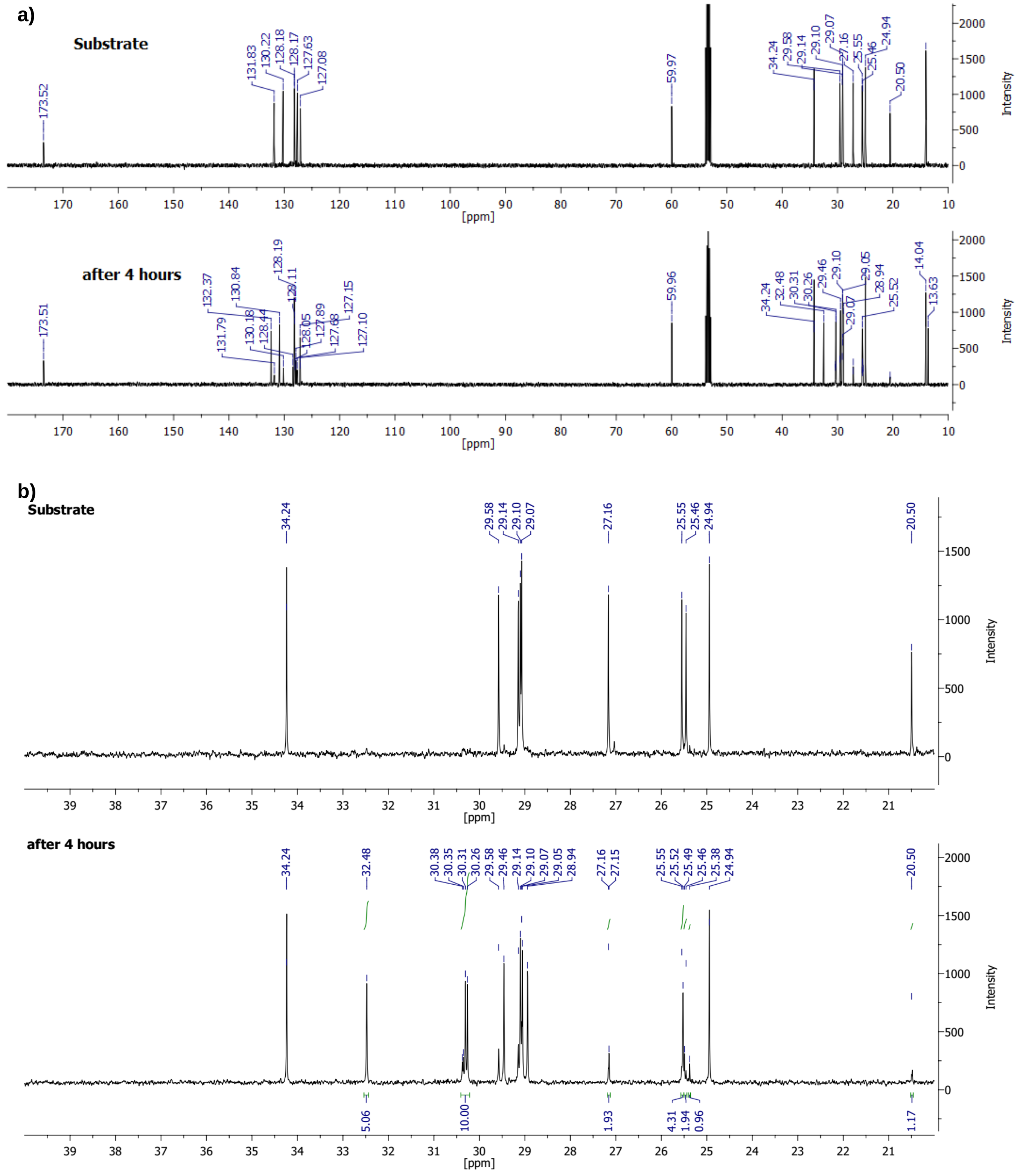
Following this logic, it can be clearly seen that by the time the equilibrium is established two singlets for original *Z*-*mono*-allylic carbon atoms at 27.16 and 20.50 ppm are diminished in size while two new singlets have appeared for *E*-*mono*-allylic carbon atoms at 32.48 and 25.52 ppm, respectively. Integration of these peaks indicates that by the time the equilibrium is established around 75% of all *mono*-allylic positions have *trans*-double bonds beside them.

Meanwhile, while two singlets for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.55 and 25.46 ppm are diminished in size, only one set of new peaks about 5 ppm downfield from them could be observed: 30.38, 30.35, 30.31 and 30.26 ppm. These peaks indicate newly formed (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms. The fact that no new peaks were found in the 35-36 ppm range strongly suggests an absence of (*E*,*E*)-*bis*-allylic carbon atoms in the equilibrium mixture supporting our previous examination of ^{1}H NMR spectra. Integration of *bis*-allylic carbon atom peaks indicates that around 78% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions only. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 77% *E*-*mono*-allylic and 79% (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. Such mixture composition contains 52% of *trans*-double bonds.

It is strongly strongly believed that obtained equilibrium mixture is mainly composed of (*t*,*c*,*t*) (i.e. *trans,cis,trans* or *9E,12Z,15E*) isomer of **E-Lnn** and virtually has no (*t*,*t*,*t*), (*t*,*t*,*c*) or (*c*,*t*,*t*) isomers in it.

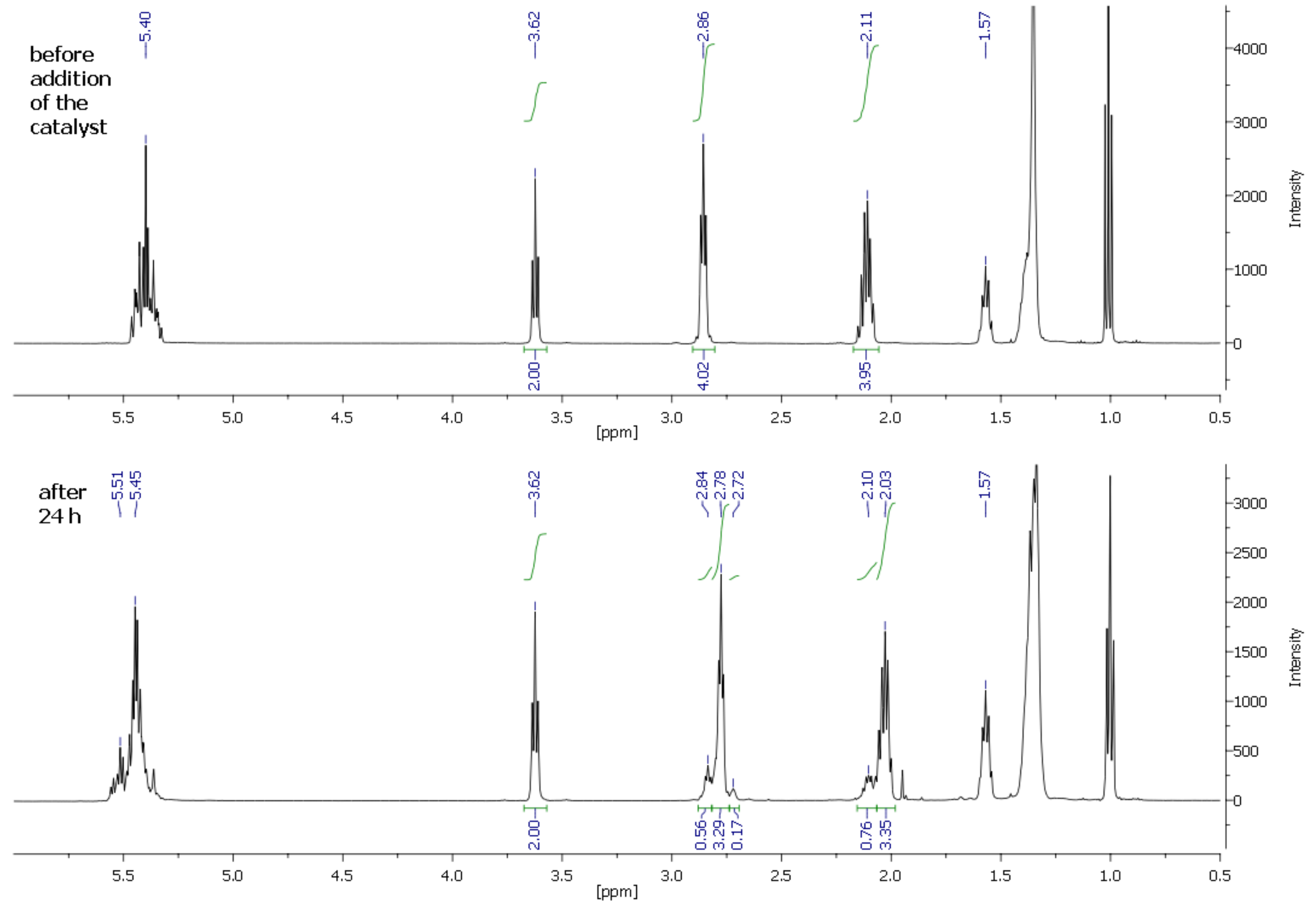
Figure S3: $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture. a) full spectra; b) sections of $^{13}C\{^{1}H\}$ NMR spectra (expanded between 40.0–20.0 ppm) for greater clarity.*

**From this point on, all* $^{13}C\{^{1}H\}$ *NMR spectra will be presented in a similar fashion because crucial spectral information discussed in text appears within the specified range.*



V. Isomerization of O-Lnn with complex 1 in DCM-d_2 at r.t. (entry 4, Table 1)

Figure S4: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Isomerization of alcohol **O-Lnn** with complex **1** resulted in the similar outcome as did its ester analogue **E-Lnn**. By the time the equilibrium was established about 80% of *bis*-allylic and 81% of *mono*-allylic positions were converted into new configurations. Also, due to the presence of a minor peak at 2.72 ppm there seems to be just a small amount of (*E*,*E*)-*bis*-allylic positions presented in the equilibrium mixture – about 4% (Figure S4). Further evidence for this theory could be obtained from the analysis of ^{13}C NMR spectra.

Figure S5: Sections of $^{13}C\{^1H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture.

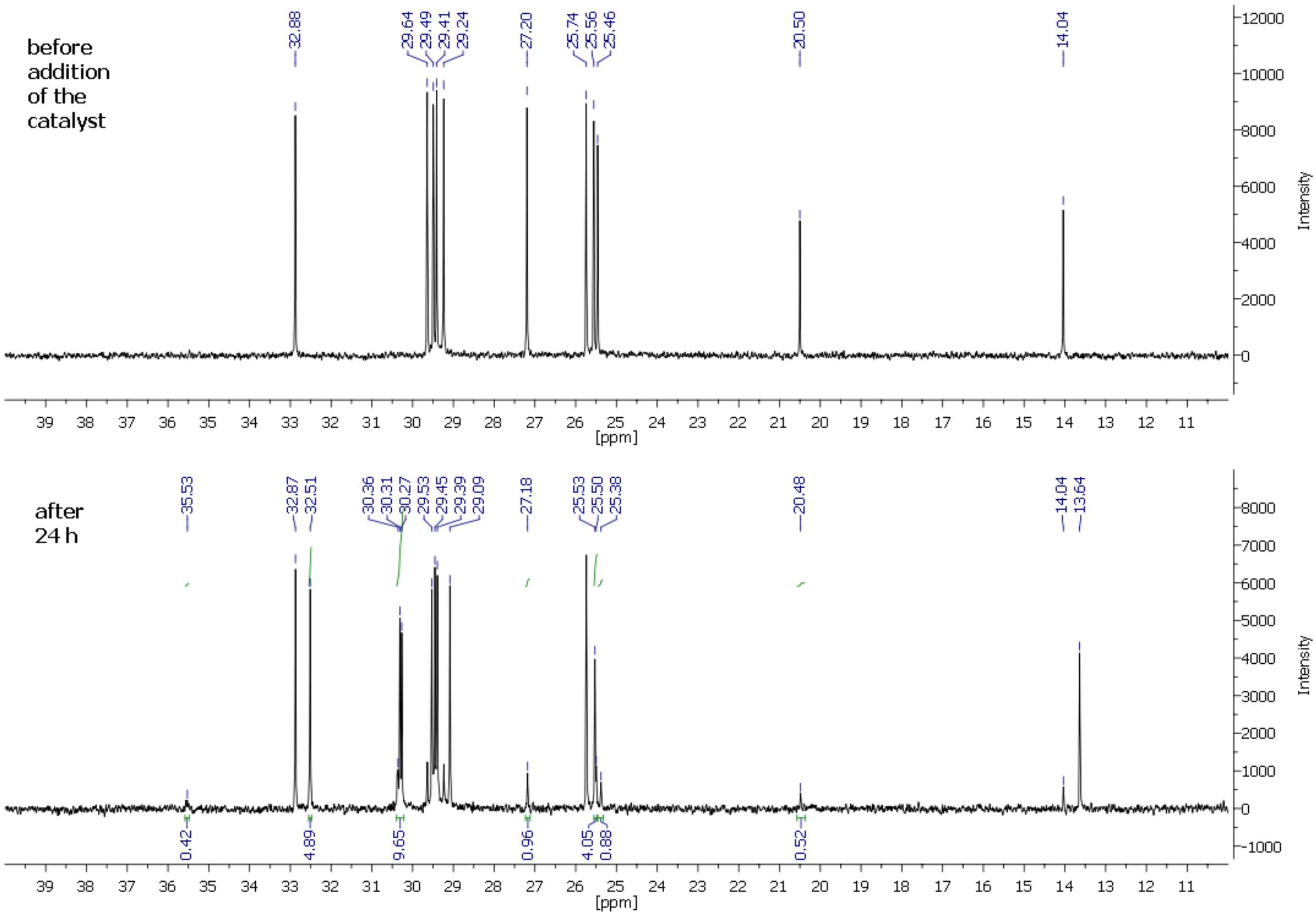
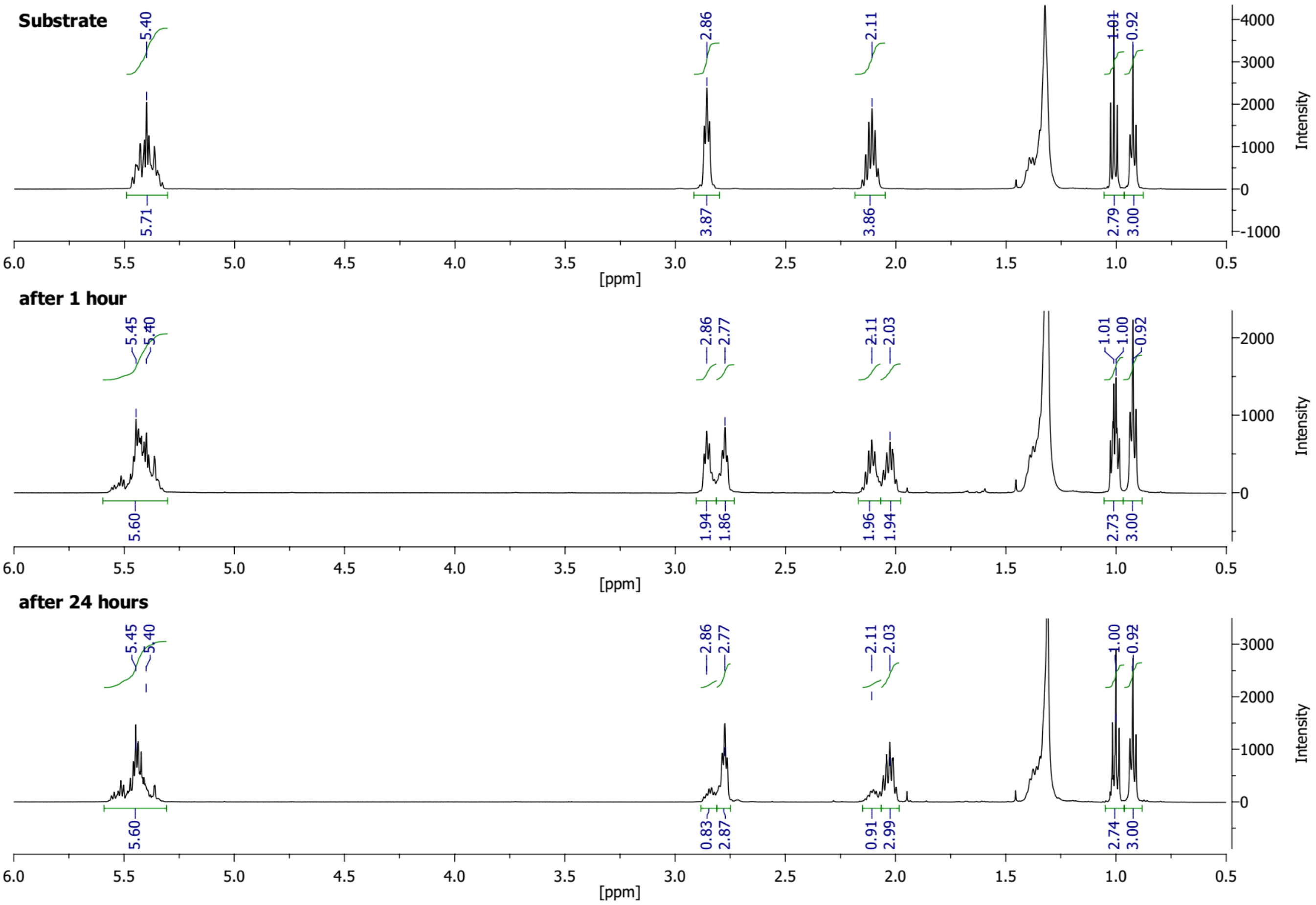


Figure S5 illustrates selected sections of ^{13}C NMR spectra of pure **O-Lnn** and equilibrium mixture after 24 hours of reaction time. Similar to the reaction of **E-Lnn**, in a course of *cis*-to-*trans* isomerization of **O-Lnn** two singlets for original *Z-mono*-allylic carbon atoms at 27.20 and 20.50 ppm are diminished in size while two new singlets have appeared for *E-mono*-allylic carbon atoms at 32.51 and 25.53 ppm. Integration of these peaks indicates that around 84% of all *mono*-allylic positions have *trans*-double bonds beside them. Meanwhile, two singlets for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.56 and 25.46 ppm are diminished in size producing one major set of new peaks about 5 ppm downfield from them: 30.36, 30.31 and 30.27 ppm. These peaks indicate formation of (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. A very small peak is observed at 35.53 ppm pointing at the minor presence of (*E*,*E*)-*bis*-allylic carbon atoms in the equilibrium mixture supporting our previous examination of ^1H NMR spectra. Integration of *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 82% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions, while about 3% - into (*E*,*E*)-*bis*-allylic positions. Averaging the parameters obtained from the examination of both ^1H and ^{13}C NMR spectra results is 83% *E-mono*-allylic, 81% (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic and 4% (*E*,*E*)-*bis*-allylic positions. Such mixture composition contains 57% of *trans*-double bonds.

Same as for **E-Lnn**, it is strongly believed that obtained equilibrium mixture is mainly composed of (*t,c,t*) isomer of **O-Lnn** and has just a minor amount of (*t,t,t*), (*t,t,c)* or (*c,t,t*) isomers in it.

VI. Isomerization of H-Lnn with complex 1 in DCM-d_2 at r.t. (entry 5, Table 1)

Figure S6: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Isomerization of hydrocarbon **H-Lnn** with complex **1** resulted in the similar outcome as for both **E-Lnn** and **O-Lnn**. By the time the equilibrium was established about 77% of *bis*-allylic and 78% of *mono*-allylic positions were converted into new configurations. Similar to reaction of **E-Lnn**, only one new triplet at 2.77 ppm could be observed for *bis*-allylic protons indicating that virtually no (*E*,*E*)-*bis*-allylic positions were formed in a course of *cis*-to-*trans* isomerization of **H-Lnn** (Figure S6). Further evidence for this theory could be obtained from the analysis of ^{13}C NMR spectra.

Figure S7: Sections of ^{13}C{^{1}H} NMR spectra (125.7 MHz, DCM-d$_2$) of substrate and reaction mixture.

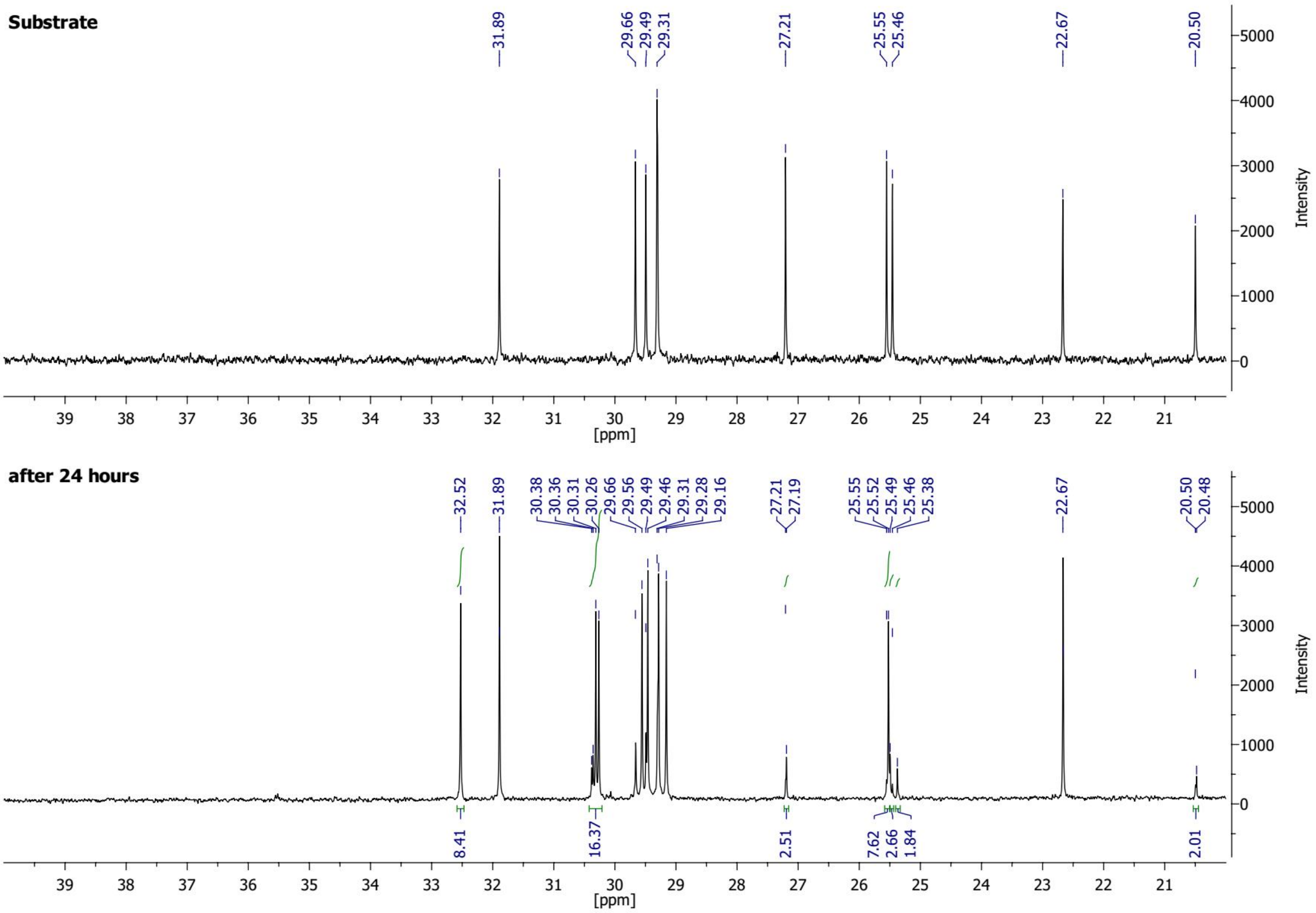


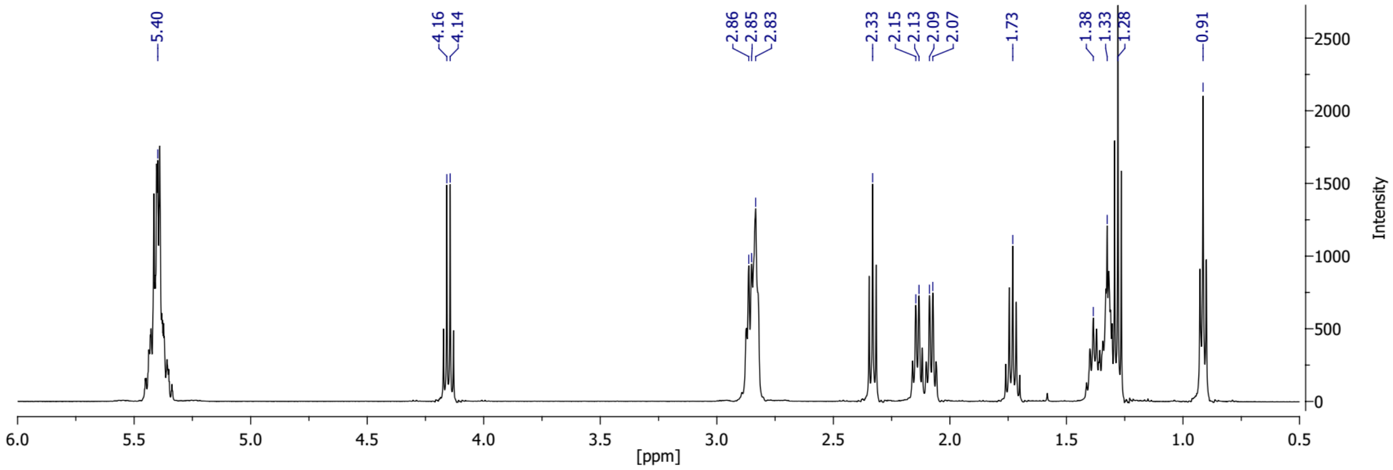
Figure S7 illustrates selected sections of ^{13}C NMR spectra of pure **H-Lnn** and equilibrium mixture after 24 hours of reaction time. Similar to reaction of **E-Lnn**, in a course of *cis*-to-*trans* isomerization of **H-Lnn** two singlets for original *Z*-*mono*-allylic carbon atoms at 27.21 and 20.50 ppm are diminished in size while two new singlets have appeared for *E*-*mono*-allylic carbon atoms at 32.52 and 25.52 ppm. Integration of these peaks indicates that around 78% of all *mono*-allylic positions have *trans*-double bonds beside them. Meanwhile, two singlets for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.55 and 25.46 ppm are diminished in size producing only one set of new peaks about 5 ppm downfield from them: 30.38, 30.36, 30.31 and 30.26 ppm. No new peaks were found in the 35-36 ppm range which strongly suggests absence of (*E*,*E*)-*bis*-allylic carbon atoms in the equilibrium mixture supporting our previous examination of ^{1}H NMR spectra. Integration of *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 78% of all (*Z*,*Z*)-*bis*-allylic positions were transformed only into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 78% *E*-*mono*-allylic and 78% (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. Such mixture composition contains 52% of *trans*-double bonds.

Same as for **E-Lnn**, it is strongly believed that obtained equilibrium mixture is mainly composed of (*t,c,t*) isomer of **H-Lnn** and virtually has no (*t,t,t*), (*t,t,c)* or (*c,t,t*) isomers in it.

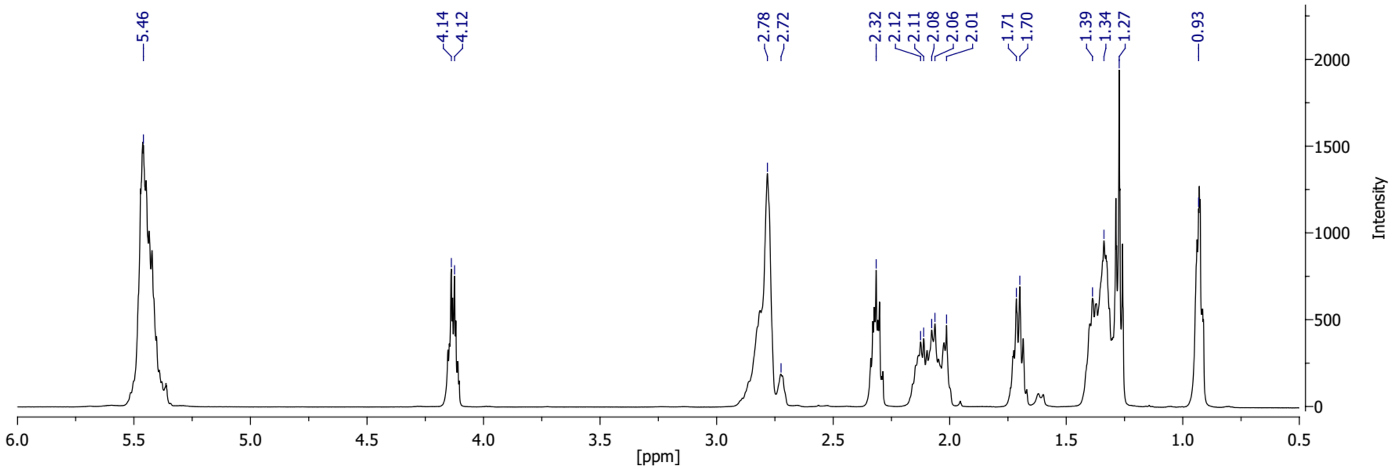
VII. Isomerization of E-Ara with complex 1 in DCM-d_2 at r.t. (entry 6, Table 1)

Figure S8: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.

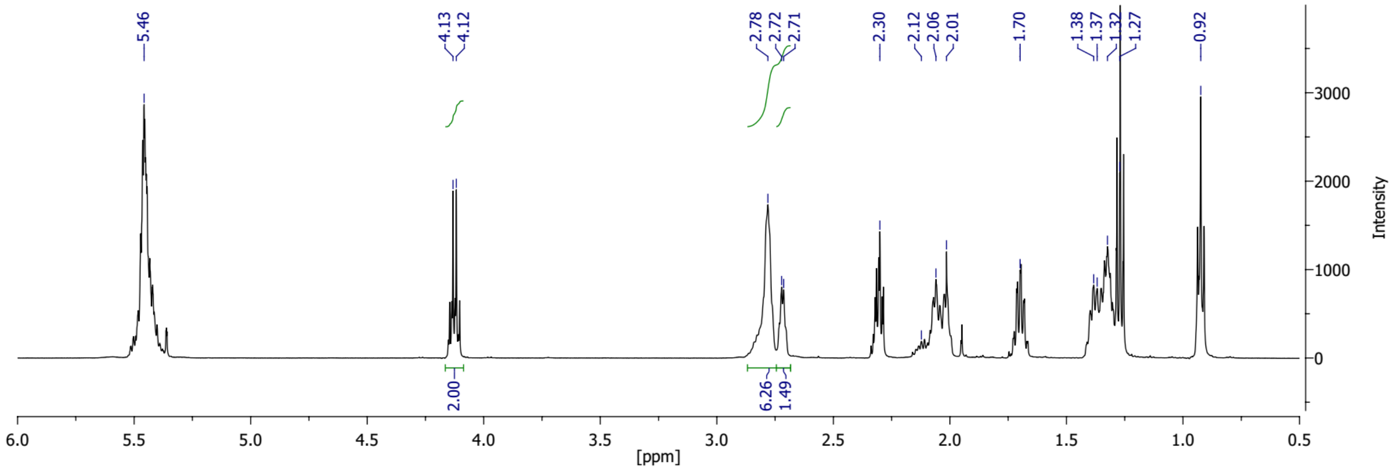
Substrate (^{1}H NMR in CDCl$_3$)



after 30 minutes



after 18 hours



Key elements of ^{1}H NMR spectrum of **E-Ara** are as follows: *bis*-allylic protons occur as several peaks at 2.80-2.89 ppm and *mono*-allylic protons – as a two quartets at 2.08 and 2.12 ppm (Figure S8). Addition of complex **1** to the solution of **E-Ara** results in diminishing of areas of original allylic peaks followed by appearing of a multiplet at 2.78 for (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic protons, a multiplet at 2.71 ppm for (*E*,*E*)-*bis*-allylic protons as well as two multiplets at 2.06 and 2.01 ppm for *E*-*mono*-allylic protons. It is impossible to estimate the extent of *cis*-to-*trans* isomerization of *mono*-allylic positions using ^{1}H NMR data due to severe peak overlapping. However, the fraction of (*E*,*E*)-*bis*-allylic positions in the equilibrium mixture can be estimated as about 24% of overall number of *bis*-allylic positions by integrating a multiplet at 2.71 ppm.

Figure S9: Sections of $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture.

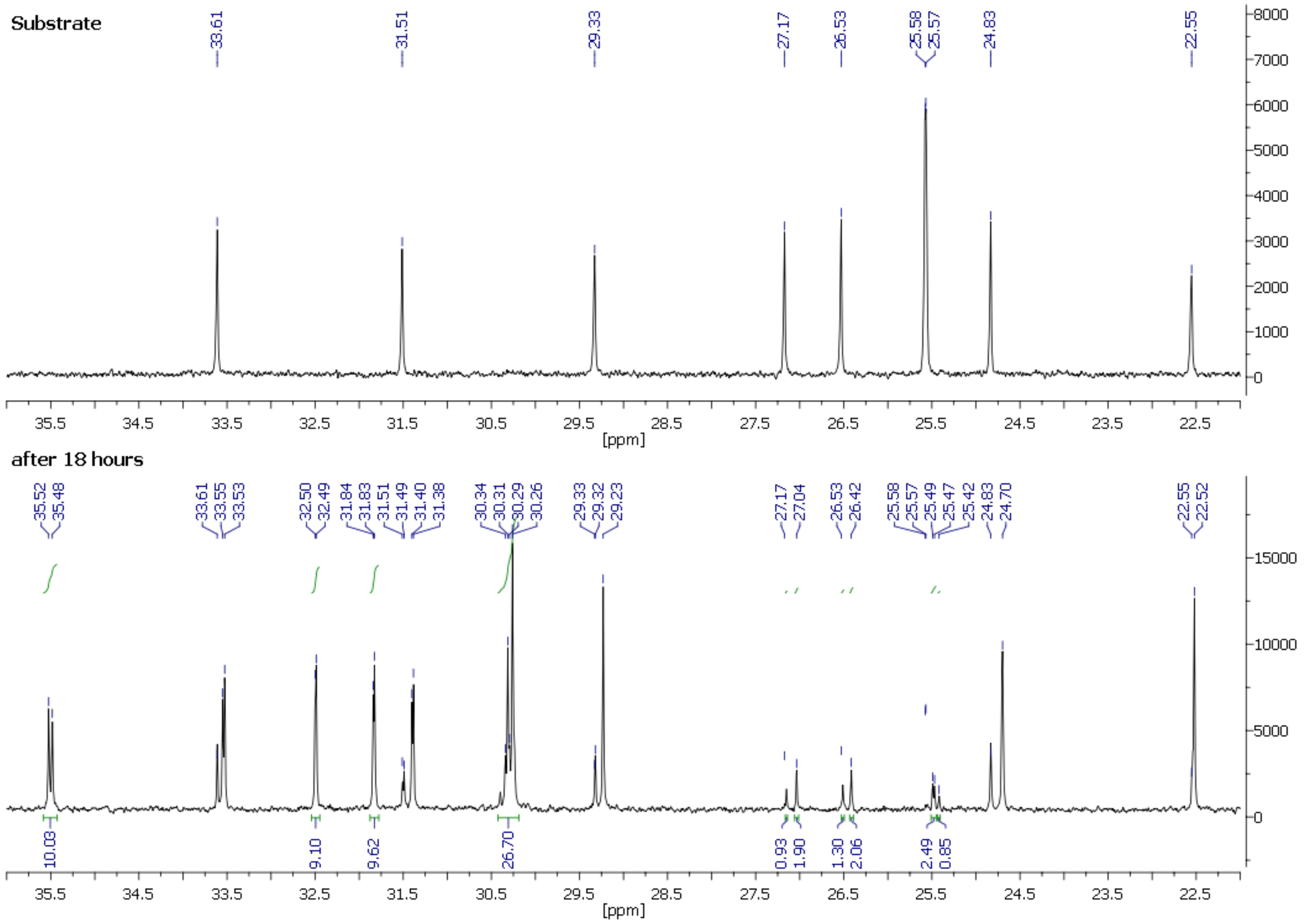
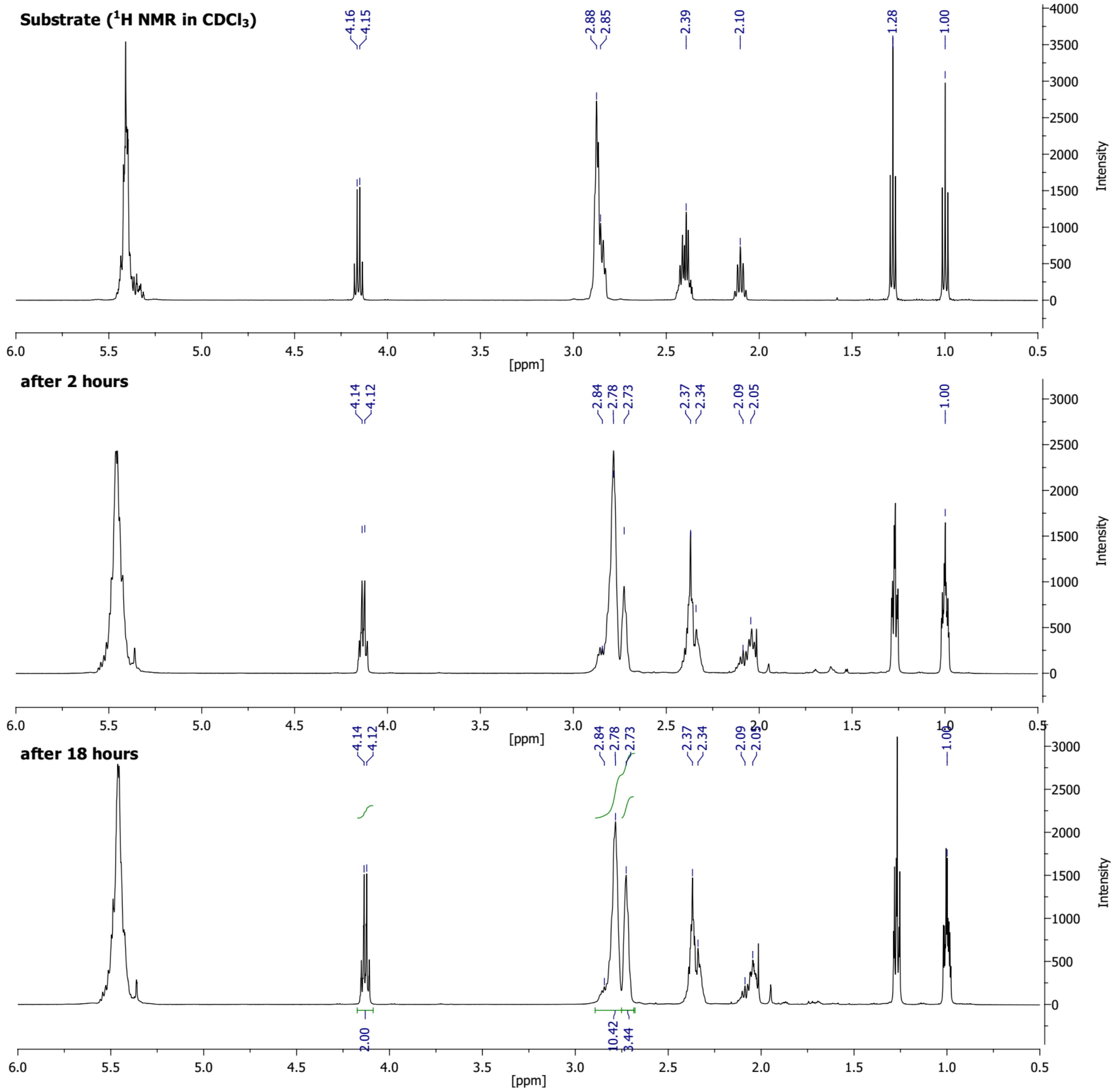


Figure S9 illustrates selected sections of ^{13}C NMR spectra of pure **E-Ara** and equilibrium mixture after 18 hours of reaction time. Similar to the reactions of *cis*-to-*trans* isomerization of **E-Lnn**, **O-Lnn** and **H-Lnn** described above, reaction between **E-Ara** and complex **1** results in diminished size of original *Z-mono*-allylic carbon atom peaks at 27.17 and 26.53 ppm followed by appearance of new sets of peaks at 32.49-32.50 and 31.83-31.84 ppm corresponding to *E-mono*-allylic carbon atoms. Integration of these peaks indicates that around 75% of all *mono*-allylic positions have *trans*-double bonds beside them in the equilibrium mixture. At the same time a set of peaks for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.57-25.58 ppm is also diminished in size. However, unlike the cases of **E-Lnn**, **O-Lnn** and **H-Lnn** described above, instead of mainly producing only a single set of peaks at 30.26-30.34 ppm corresponding to (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms, the formation of an intensive set of peaks is observed about 10 ppm downfield from original peaks. These new peaks at 35.48 and 35.52 ppm indicate the considerable presence of (*E*,*E*)-*bis*-allylic carbon atoms in the equilibrium mixture. Integration of *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 67% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions and 25% - into (*E*,*E*)-*bis*-allylic positions supporting our previous examination of ^{1}H NMR spectra. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 75% *E-mono*-allylic, 67% (*E*,*Z*)/(*Z*,*E*)- and 25% (*E*,*E*)-*bis*-allylic positions. Such mixture composition contains 63% of *trans*-double bonds.

Following the logic as for the cases of **E-Lnn**, **O-Lnn** and **H-Lnn**, it is believed that obtained equilibrium mixture is mainly composed of (*t*,*t*,*c*,*t*) and (*t*,*c*,*t*,*t*) isomers of **E-Ara**, i.e. one internal *cis*-double bond must remain intact.

VIII. Isomerization of E-DHA with complex 1 in DCM-d_2 at r.t. (entry 7, Table 1)

Figure S10: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.


Substrate (^{1}H NMR in CDCl$_3$)

after 2 hours

after 18 hours

Key elements of ^{1}H NMR spectrum of **E-DHA** are as follows: *bis*-allylic protons occur as several peaks at 2.81-2.88 ppm and *mono*-allylic protons – as a two multiplets at 2.09 and 2.37 ppm (Figure S10). Similar to the case of **E-Ara**, *cis*-to-*trans* isomerization of **E-DHA** results in diminishing of areas of original allylic peaks followed by appearing of a multiplet at 2.78 for (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic protons, a multiplet at 2.73 ppm for (*E*,*E*)-*bis*-allylic protons as well as two multiplets at 2.34 and 2.05 ppm for *E*-*mono*-allylic protons. It is impossible to estimate the extent of *cis*-to-*trans* isomerization of *mono*-allylic positions using ^{1}H NMR data due to severe peak overlapping. However, the amount (*E*,*E*)-*bis*-allylic positions in the equilibrium mixture can be estimated as about 33% of overall number of *bis*-allylic positions by integrating a multiplet at 2.73 ppm.

Figure S11: Sections of ^{13}C{^{1}H} NMR spectra (125.7 MHz, DCM-d$_2$) of substrate and reaction mixture.

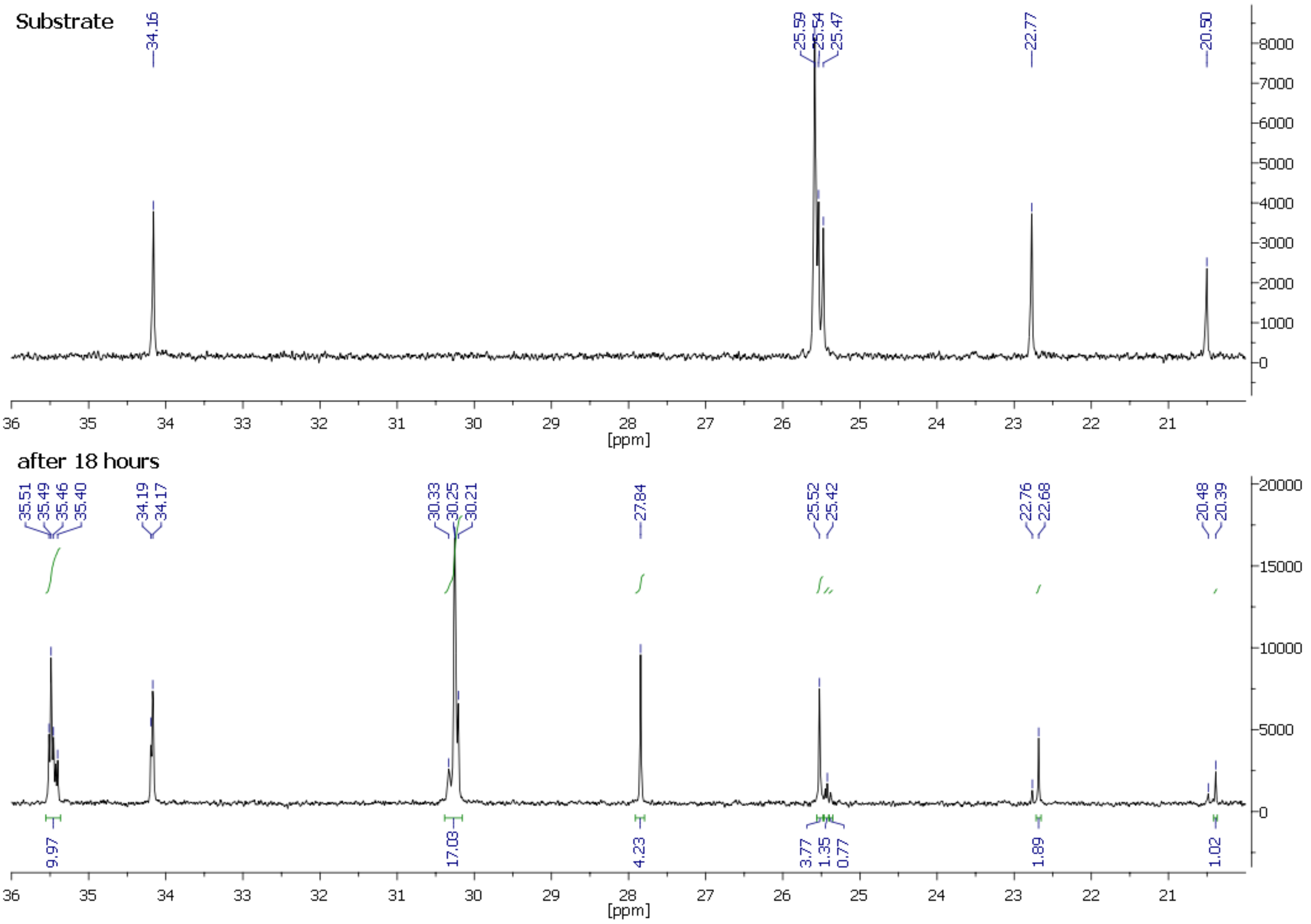
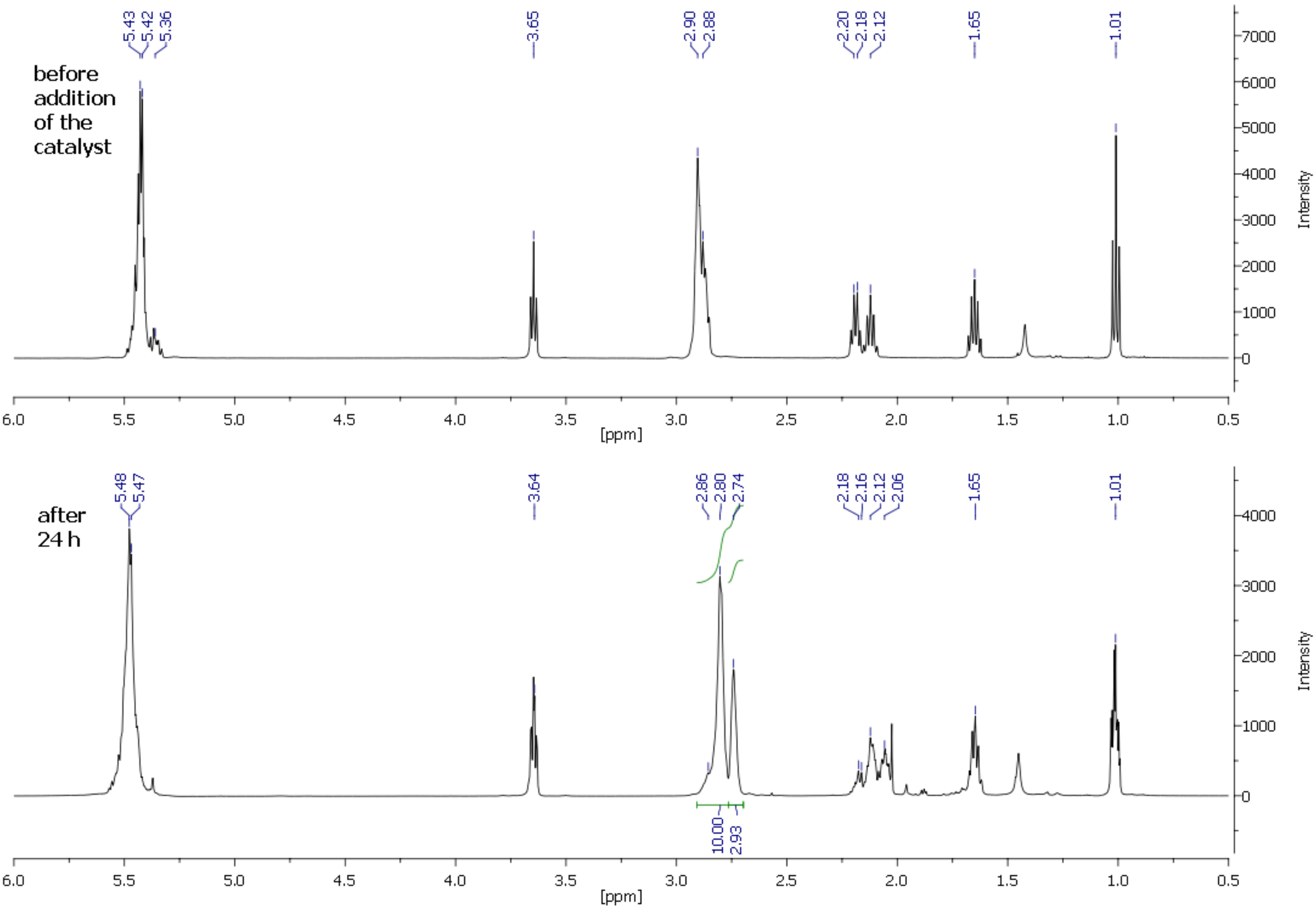


Figure S11 illustrates selected sections of ^{13}C NMR spectra of pure **E-DHA** and equilibrium mixture after 18 hours of reaction time. Reaction of *cis*-to-*trans* isomerization of **E-DHA** follows the same trend as **E-Ara**. Original *Z*-*mono*-allylic carbon atom peaks at 22.77 and 20.50 ppm are diminished in size and new peaks appear at 27.84 and 25.52 ppm corresponding to *E*-*mono*-allylic carbon atoms. Integration of these peaks indicates that around 73% of all *mono*-allylic positions have *trans*-double bonds beside them in the equilibrium mixture. At the same time a set of peaks for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.47- 25.59 ppm is also diminished in size while we observe one set of peaks at 30.21-30.33 ppm corresponding to (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms and another at 35.40-35.51 ppm indicating the presence of (*E*,*E*)-*bis*-allylic carbon atoms. Integration of all *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 58% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions and 34% - into (*E*,*E*)-*bis*-allylic positions supporting our previous examination of ^{1}H NMR spectra. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 73% *E*-*mono*-allylic, 58% (*E*,*Z*)/(*Z*,*E*)- and 34% (*E*,*E*)-*bis*-allylic positions. Such mixture composition contains 65% of *trans*-double bonds.

It is believed that obtained equilibrium mixture is mainly composed of isomers of **E-DHA** that have all their double bonds in the *trans*-configuration except of one of its inner ones: (*t*,*t*,*t*,*t*,*c*,*t*), (*t*,*t*,*t*,*c*,*t*,*t*), (*t*,*t*,*c*,*t*,*t*,*t*), and (*t*,*c*,*t*,*t*,*t*,*t*).

IX. Isomerization of O-DHA with complex 1 in DCM-d_2 at r.t. (entry 9, Table 1)

Figure S12: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Key elements of ^{1}H NMR spectrum of **O-DHA** are as follows: *bis*-allylic protons occur as several peaks at 2.82-2.96 ppm and *mono*-allylic protons – as a group of multiplets at 2.08-2.20 ppm (Figure S12). Similar to the cases of **E-Ara** and **E-DHA**, *cis*-to-*trans* isomerization of **O-DHA** results in diminishing of areas of original allylic peaks followed by appearing of a multiplet at 2.80 for (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic protons, a multiplet at 2.74 ppm for (*E*,*E*)-*bis*-allylic protons as well as a new set of multiplets at 2.02- 2.14 ppm for *E*-*mono*-allylic protons. It is impossible to estimate the extent of *cis*-to-*trans* isomerization of *mono*-allylic positions using ^{1}H NMR data due to severe peak overlapping. However, the amount (*E*,*E*)-*bis*-allylic positions in the equilibrium mixture can be estimated as about 29% of overall number of *bis*-allylic positions by integrating a multiplet at 2.74 ppm.

Figure S13: Sections of $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture.

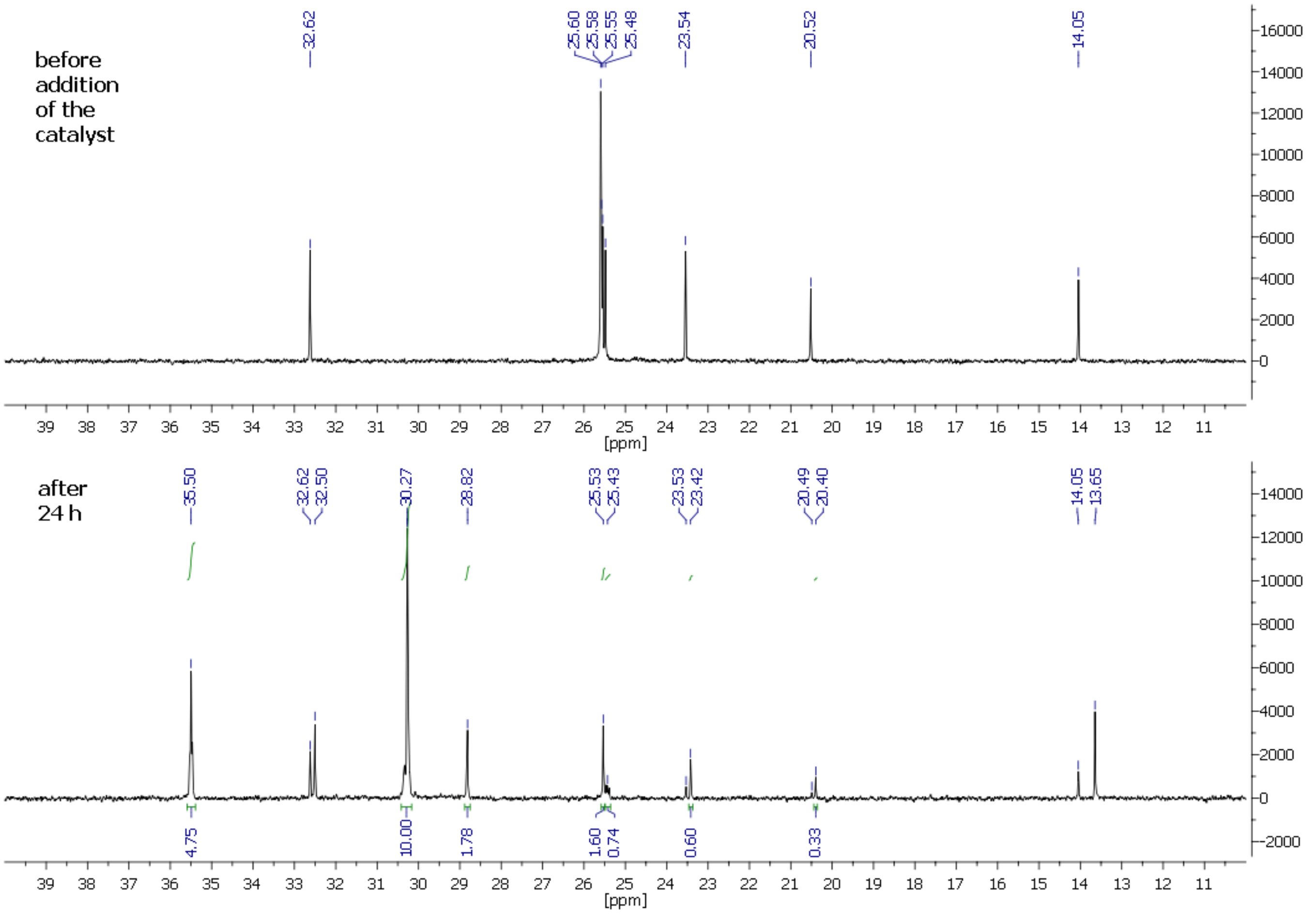
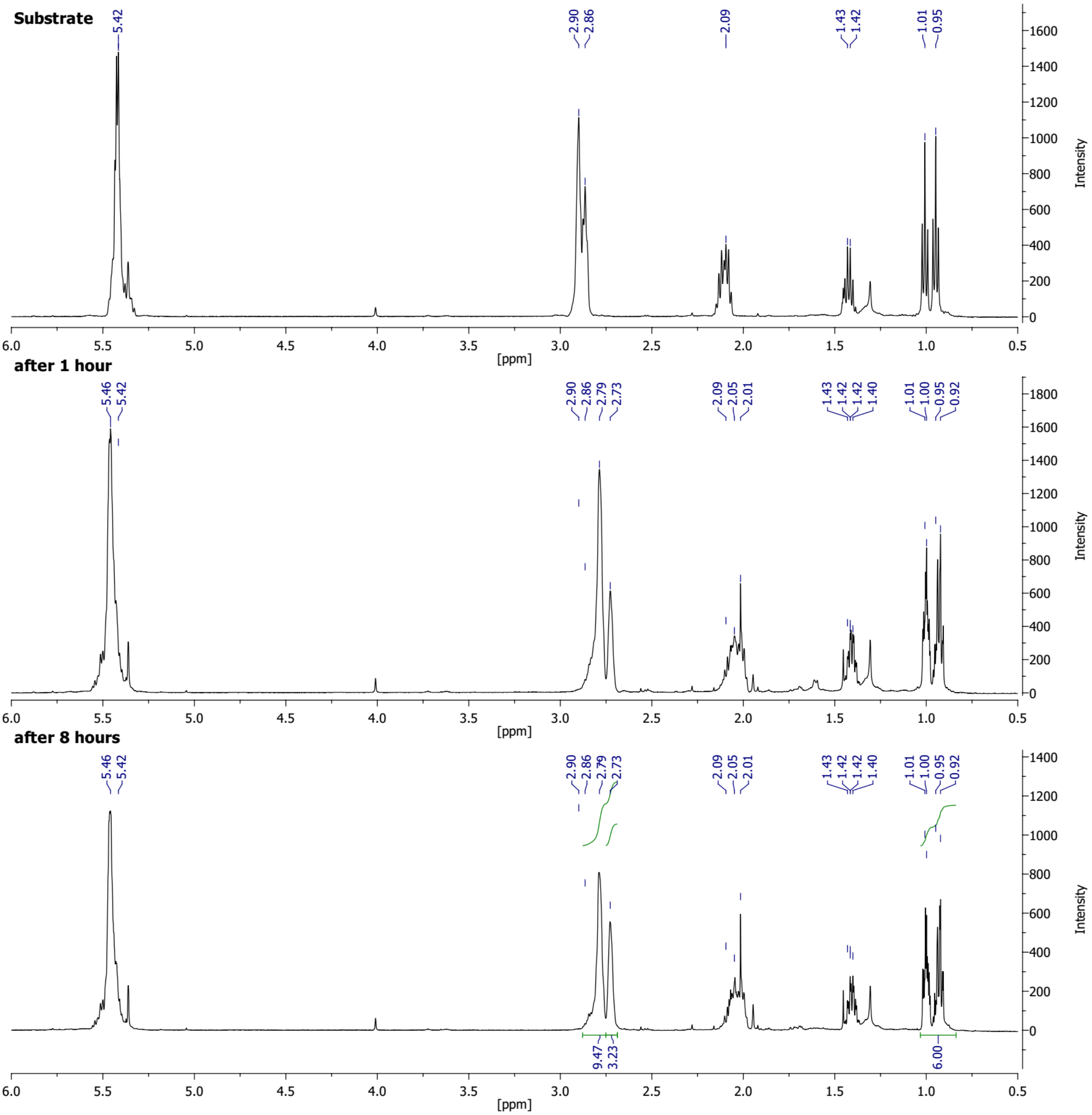


Figure S13 illustrates selected sections of ^{13}C NMR spectra of pure **O-DHA** and equilibrium mixture after 24 hours of reaction time. Reaction of *cis*-to-*trans* isomerization of **O-DHA** follows the same trend as **E-DHA**. Original *Z*-*mono*-allylic carbon atom peaks at 23.54 and 20.52 ppm are diminished in size and new peaks appear at 28.82 and 25.53 ppm corresponding to *E*-*mono*-allylic carbon atoms. Integration of these peaks indicates that around 78% of all *mono*-allylic positions have *trans*-double bonds beside them in the equilibrium mixture. At the same time a set of peaks for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.48- 25.60 ppm is also diminished in size while we observe one set of peaks at 30.27-30.34 ppm corresponding to (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms and another at 35.47-35.50 ppm indicating the presence of (*E*,*E*)-*bis*-allylic carbon atoms. Integration of all *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 65% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions and 31% - into (*E*,*E*)-*bis*-allylic positions supporting our previous examination of ^{1}H NMR spectra. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 78% *E*-*mono*-allylic, 65% (*E*,*Z*)/(*Z*,*E*)- and 31% (*E*,*E*)-*bis*-allylic positions. Such mixture composition contains 65% of *trans*-double bonds.

It is strongly believed that reaction of *cis*-to-*trans* isomerization of **O-DHA** produces similar equilibrium mixture as **E-DHA**.

X. Isomerization of H-DHA with complex 1 in DCM-d_2 at r.t. (entry 10, Table 1)

Figure S14: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Key elements of ^{1}H NMR spectrum of **H-DHA** are as follows: *bis*-allylic protons occur as several peaks at 2.86-2.90 ppm and *mono*-allylic protons – as a group of multiplets at 2.07-2.15 ppm (Figure S14). Similar to the cases of **E-DHA** and **O-DHA**, *cis*-to-*trans* isomerization of **H-DHA** results in diminishing of areas of original allylic peaks followed by appearing of a multiplet at 2.79 for (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic protons, a multiplet at 2.73 ppm for (*E*,*E*)-*bis*-allylic protons as well as a new set of multiplets at 1.98- 2.08 ppm for *E*-*mono*-allylic protons. It is impossible to estimate the extent of *cis*-to-*trans* isomerization of *mono*-allylic positions using ^{1}H NMR data due to severe peak overlapping. However, the amount (*E*,*E*)-*bis*-allylic positions in the equilibrium mixture can be estimated as about 34% of overall number of *bis*-allylic positions by integrating a multiplet at 2.73 ppm.

Figure S15: Sections of $^{13}C\{^1H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture.

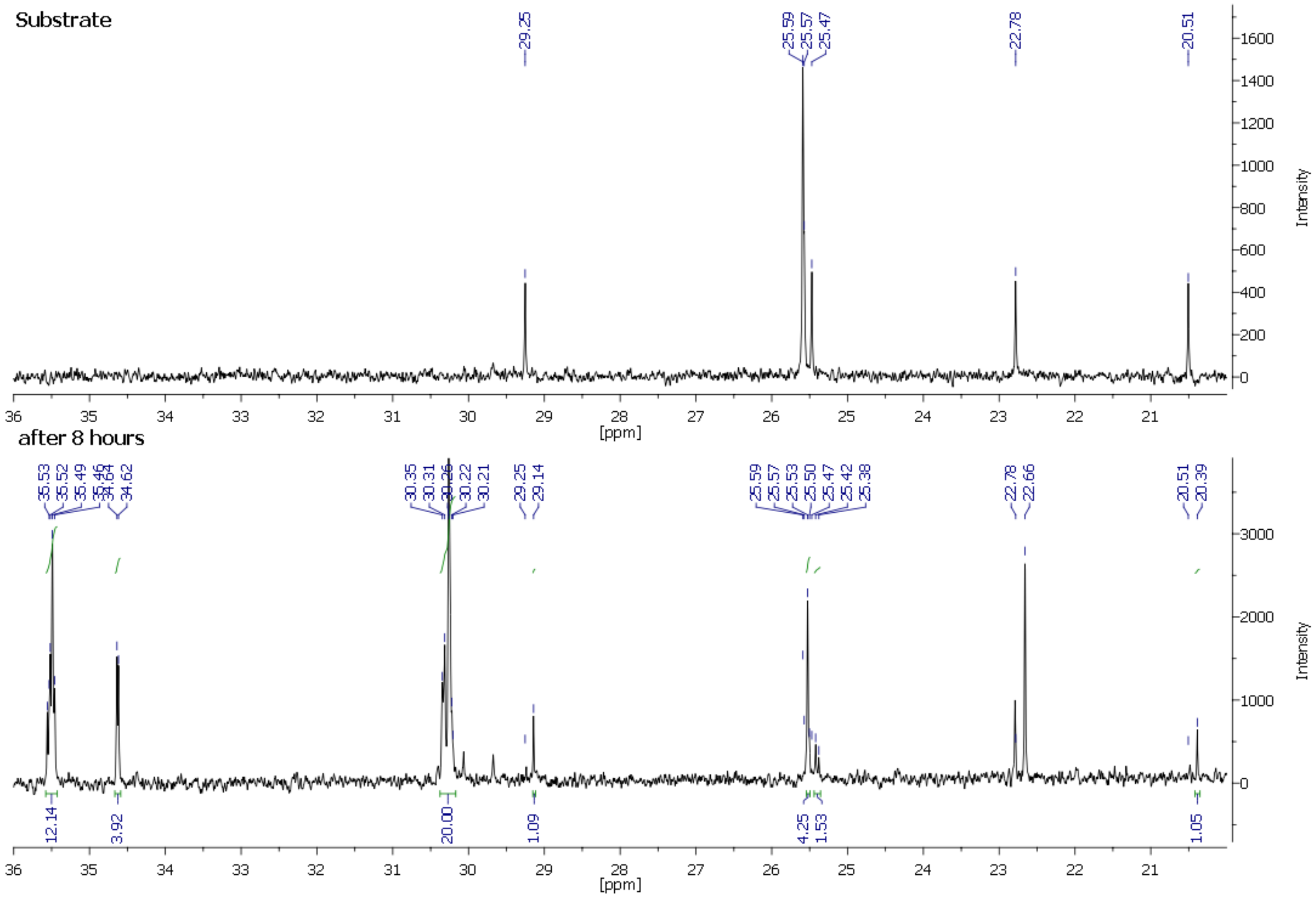
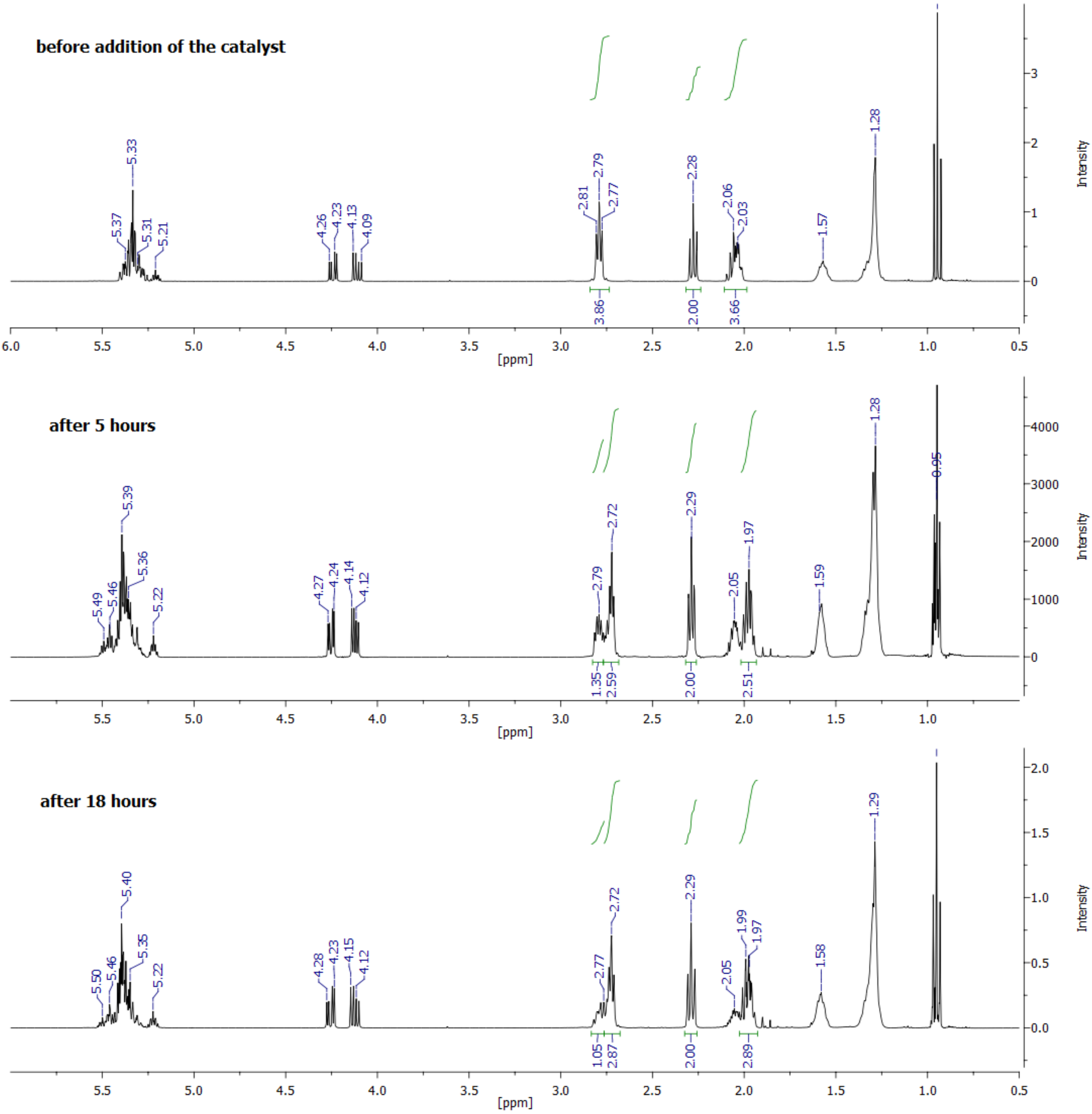


Figure S15 illustrates selected sections of ^{13}C NMR spectra of pure **H-DHA** and equilibrium mixture after 8 hours of reaction time. Reaction of *cis*-to-*trans* isomerization of **H-DHA** follows the same trend as **E-DHA** and **O-DHA**. Original *Z*-*mono*-allylic carbon atom peaks at 29.25 and 20.51 ppm are diminished in size and new peaks appear at 34.62-34.64 and 25.53 ppm corresponding to *E*-*mono*-allylic carbon atoms. Integration of these peaks indicates that around 79% of all *mono*-allylic positions have *trans*-double bonds beside them in the equilibrium mixture. At the same time a set of peaks for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.47- 25.59 ppm is also diminished in size while we observe one set of peaks at 30.21-30.35 ppm corresponding to (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic carbon atoms and another at 35.46-35.53 ppm indicating the presence of (*E*,*E*)-*bis*-allylic carbon atoms. Integration of all *bis*-allylic carbon atom peaks indicates that by the time the equilibrium is established around 59% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions and 36% - into (*E*,*E*)-*bis*-allylic positions supporting our previous examination of ^1H NMR spectra. Averaging the parameters obtained from the examination of both ^1H and ^{13}C NMR spectra results is 79% *E*-*mono*-allylic, 59% (*E*,*Z*)/(*Z*,*E*)- and 35% (*E*,*E*)-*bis*-allylic positions. Such mixture composition contains 67% of *trans*-double bonds.

It is strongly believed that reaction of *cis*-to-*trans* isomerization of **H-DHA** produces similar equilibrium mixture as **E-DHA** and **O-DHA**.

XI. Isomerization of T-Lnn with complex 1 in DCM-d_2 at r.t. (entry 13, Table 1)

Figure S16: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Isomerization of triglyceride **T-Lnn** with complex **1** resulted in the similar outcome as for its ester analogue **E-Lnn**. By the time the equilibrium was established about 73% of *bis*-allylic and 72% of *mono*-allylic positions were converted into new configurations (Figure S16).

Figure S17: Sections of $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of reaction mixture.

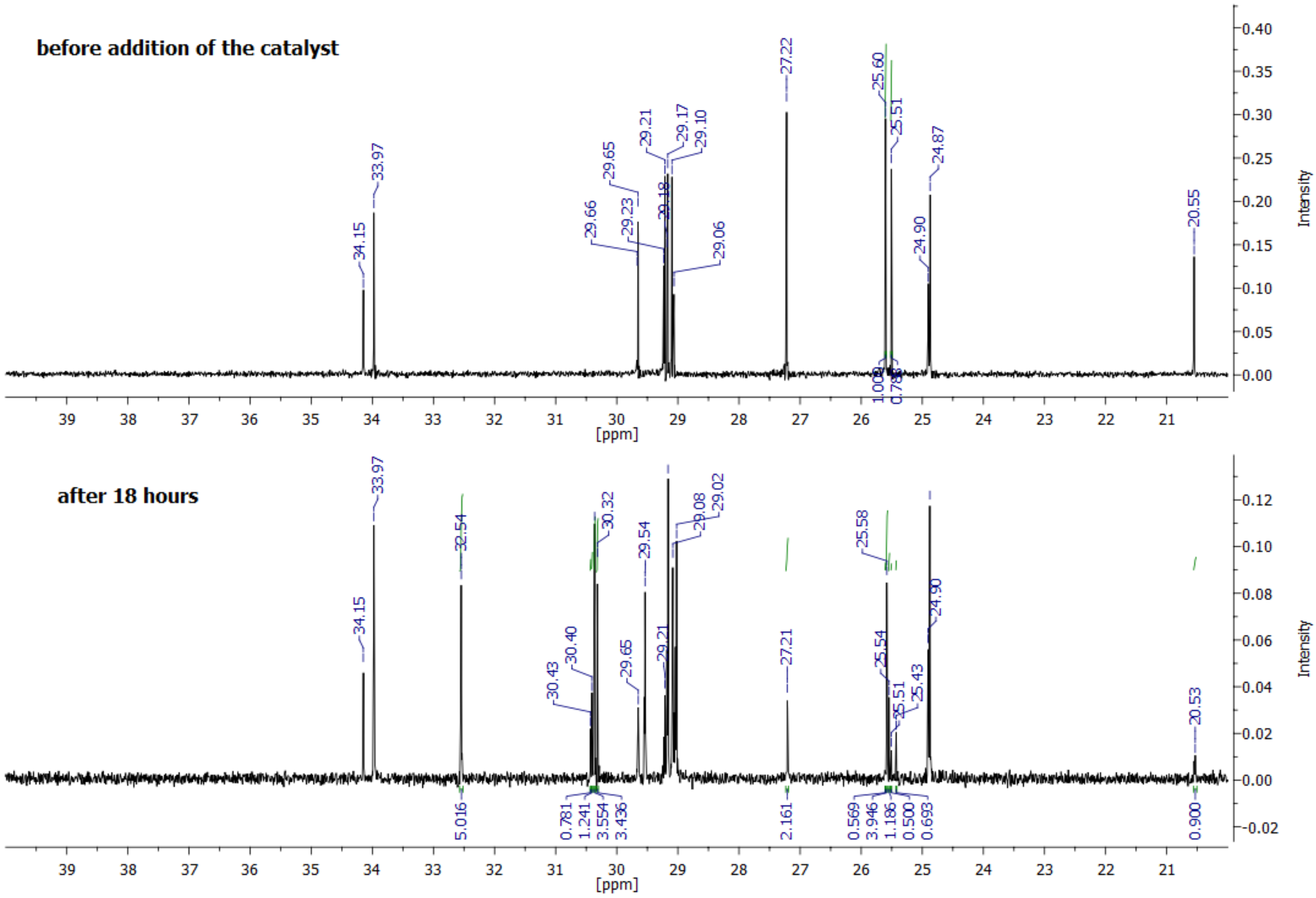
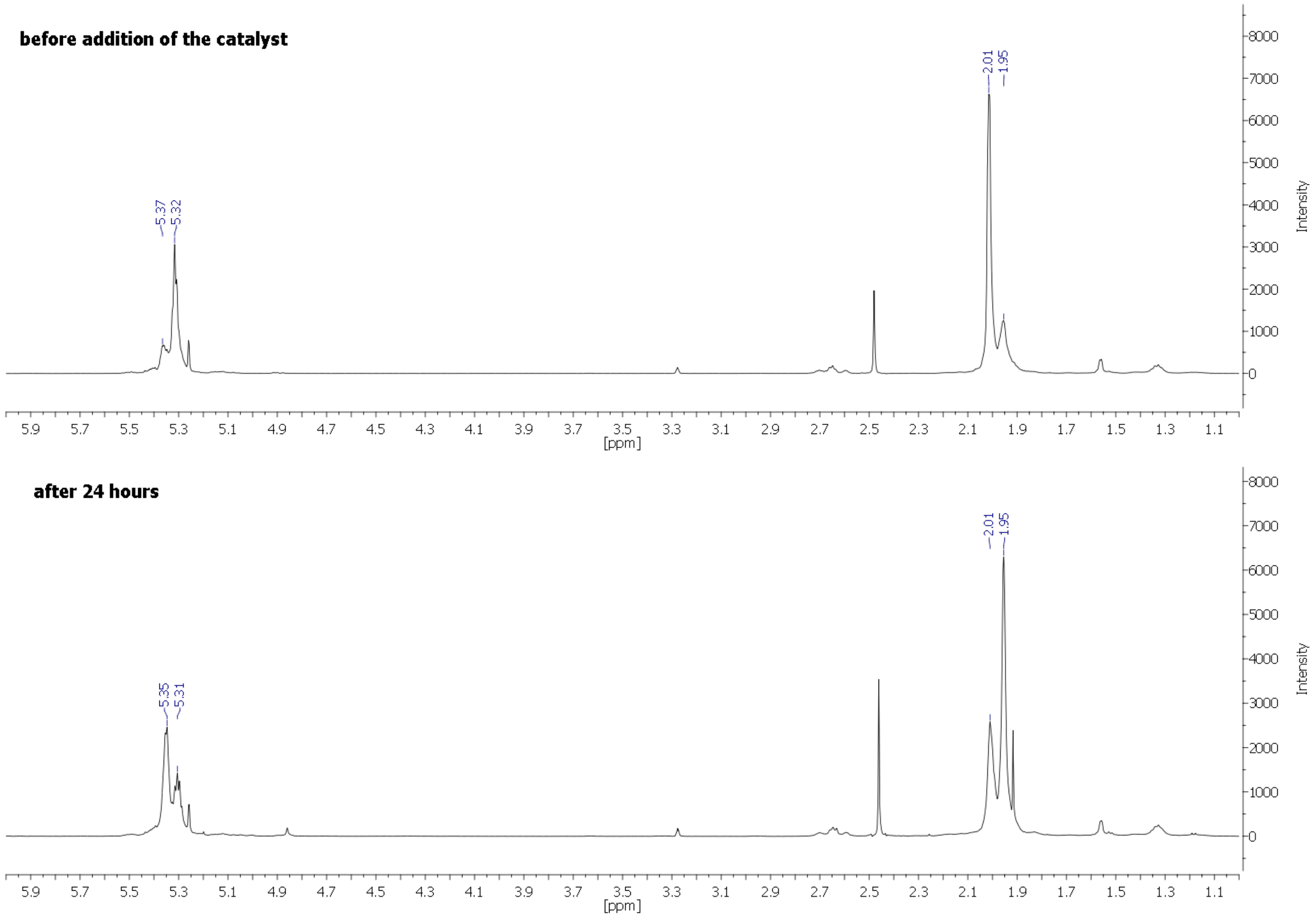


Figure S17 illustrates selected sections of ^{13}C NMR spectra of pure **T-Lnn** and equilibrium mixture after 18 hours of reaction time. Similar to the reaction of **E-Lnn**, in a course of *cis*-to-*trans* isomerization of **T-Lnn** two singlets for original *Z*-*mono*-allylic carbon atoms at 27.22 and 20.55 ppm are diminished in size while two new singlets have appeared for *E*-*mono*-allylic carbon atoms at 32.54 and 25.58 ppm. Integration of these peaks indicates that around 74% of all *mono*-allylic positions have *trans*-double bonds beside them. Meanwhile, two singlets for original (*Z*,*Z*)-*bis*-allylic carbon atoms at 25.60 and 25.51 ppm are diminished in size producing one major set of new peaks about 5 ppm downfield from them: 30.43, 30.40, 30.36 and 30.32 ppm. These peaks indicate formation of (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. Integration of *bis*-allylic carbon atom peaks indicates that by the time the equilibrium was established around 73% of all (*Z*,*Z*)-*bis*-allylic positions were transformed into (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. No peaks are observed about 10 ppm downfield to singlets for original (*Z*,*Z*)-*bis*-allylic carbon atoms indicating that no (*E*,*E*)-*bis*-allylic carbon atoms are presented in the equilibrium mixture. Averaging the parameters obtained from the examination of both ^{1}H and ^{13}C NMR spectra results is 73% *E*-*mono*-allylic and 73% (*E*,*Z*)/(*Z*,*E*)-*bis*-allylic positions. Such mixture composition contains 49% of *trans*-double bonds.

Similar to **E-Lnn**, it is strongly believed that obtained equilibrium mixture is mainly composed of (*t*,*c*,*t*) isomer of **T-Lnn**.

XII. Isomerization of POLY with complex 1 in DCM-d_2 at r.t. (entry 14, Table 1)

Figure S18: ^{1}H NMR spectra (500 MHz, DCM-d_2) of reaction mixture.



Key elements of ^{1}H NMR spectrum of **POLY** are as follows: vinylic protons appear as a group of multiplets at 5.39-5.62 ppm and *mono*-allylic protons – as a group of multiplets at 1.91-2.05 ppm (Figure S18). C*is*-to-*trans* isomerization of **POLY** results in diminishing of areas of original allylic and vinylic peaks followed by appearance of multiplets at lower and higher frequencies to the original resonances, respectively. It is impossible to estimate the extent of *cis*-to-*trans* isomerization of **POLY** positions using ^{1}H NMR data due to severe peak overlapping. More data could be obtained from the analysis of ^{13}C NMR spectra.

Figure S19: Sections of $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and reaction mixture.

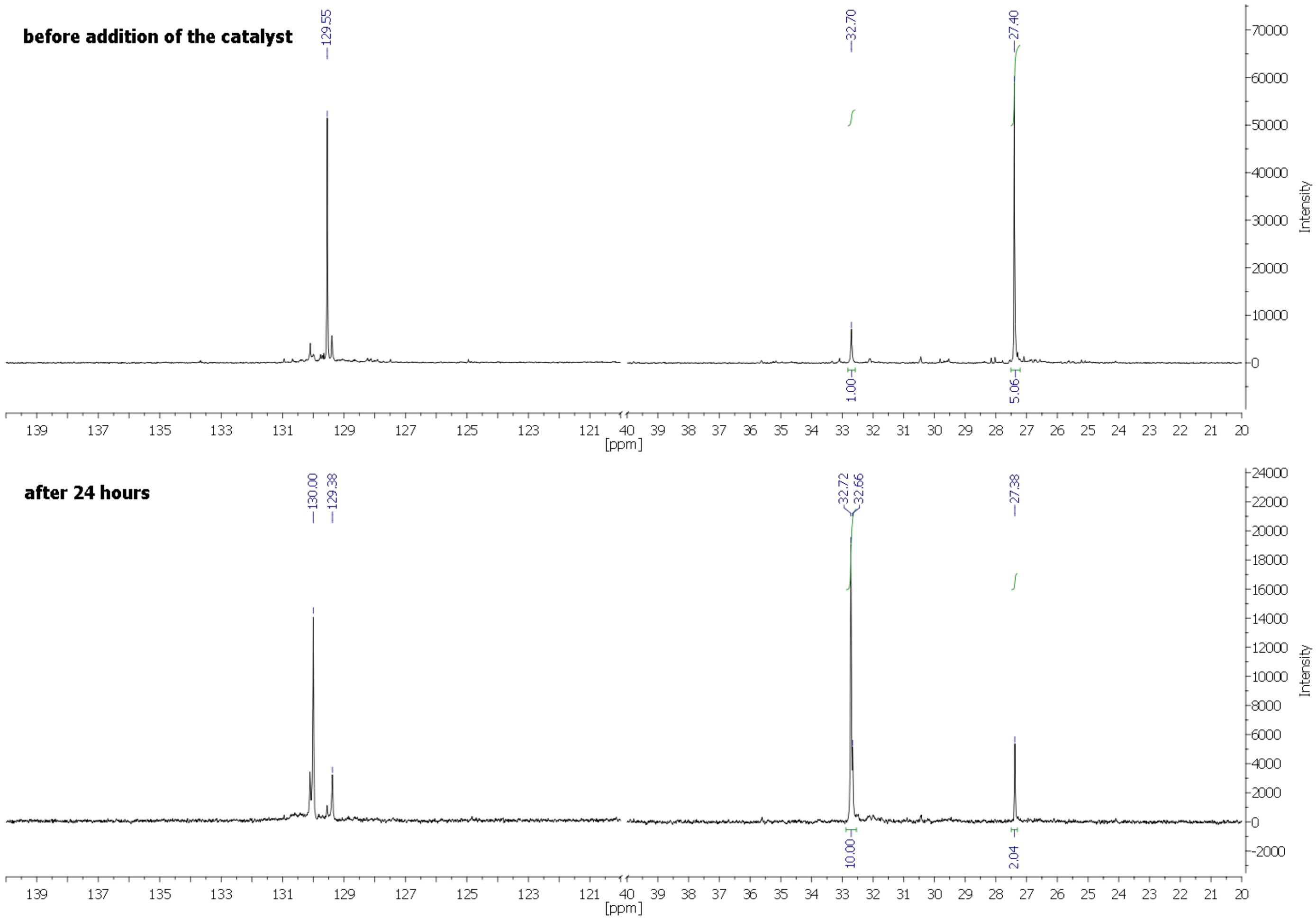
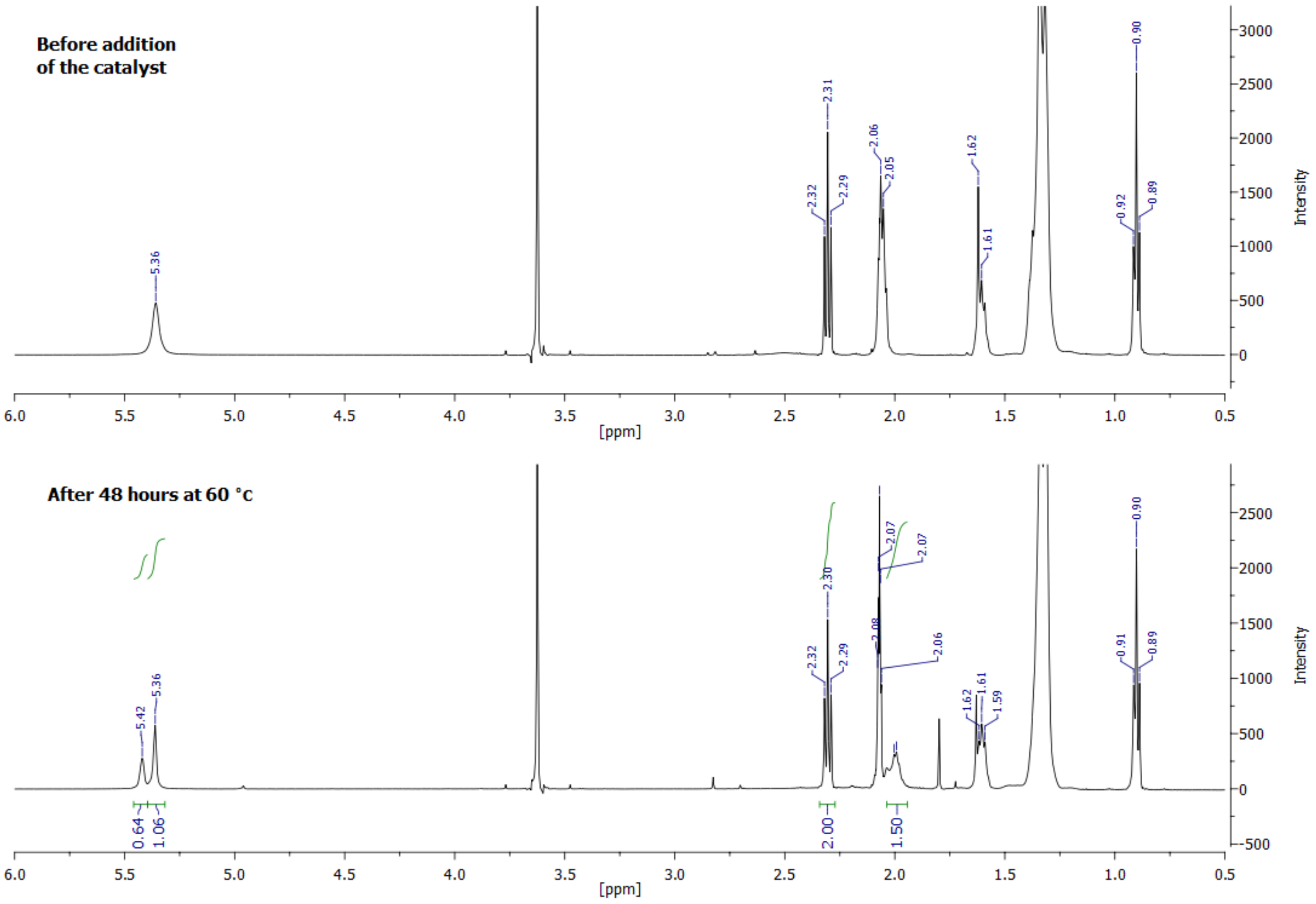


Figure S19 illustrates selected sections of ^{13}C NMR spectra of pure **POLY** and equilibrium mixture after 24 hours of reaction time. Reaction of *cis*-to-*trans* isomerization of **POLY** follows the same trend as was described before. Original *Z*-*mono*-allylic carbon atom peak at 27.40 ppm is diminished in size and new peak appears at 32.72 ppm corresponding to *E*-*mono*-allylic carbon atoms. Integration of these peaks indicates that around 80% of all *mono*-allylic positions have *trans*-double bonds beside them in the equilibrium mixture which means that about 80% of all double bonds in the substrate have been isomerized to *trans.*

XIII. Isomerization of M-Ole with complex 1 in acetone-d₆ at 60 ˚C (entry 15, Table 1)

Figure S20: ^{1}H NMR spectra (500 MHz, acetone-d$_6$) of reaction mixture.



Key elements of ^{1}H NMR spectrum of **M-Ole** are as follows: vinylic protons appear as a broadened peak at 5.30-5.42 ppm and *mono*-allylic protons – as a multiplet at 2.00-2.10 ppm (overlapping with acetone-d$_6$ residual peak; Figure S20). C*is*-to-*trans* isomerization of **M-Ole** results in diminishing of areas of original allylic and vinylic peaks followed by appearance of multiplets at lower and higher frequencies to the original resonances, respectively. Integration of these new peaks allowed us to estimate that around 38% of all *mono*-allylic positions in **M-Ole** have *trans*-double bonds beside them in the equilibrium mixture.

Figure S21: Sections of $^{13}C\{^{1}H\}$ NMR spectra (125.7 MHz, DCM-d_2) of substrate and isolated product mixture.

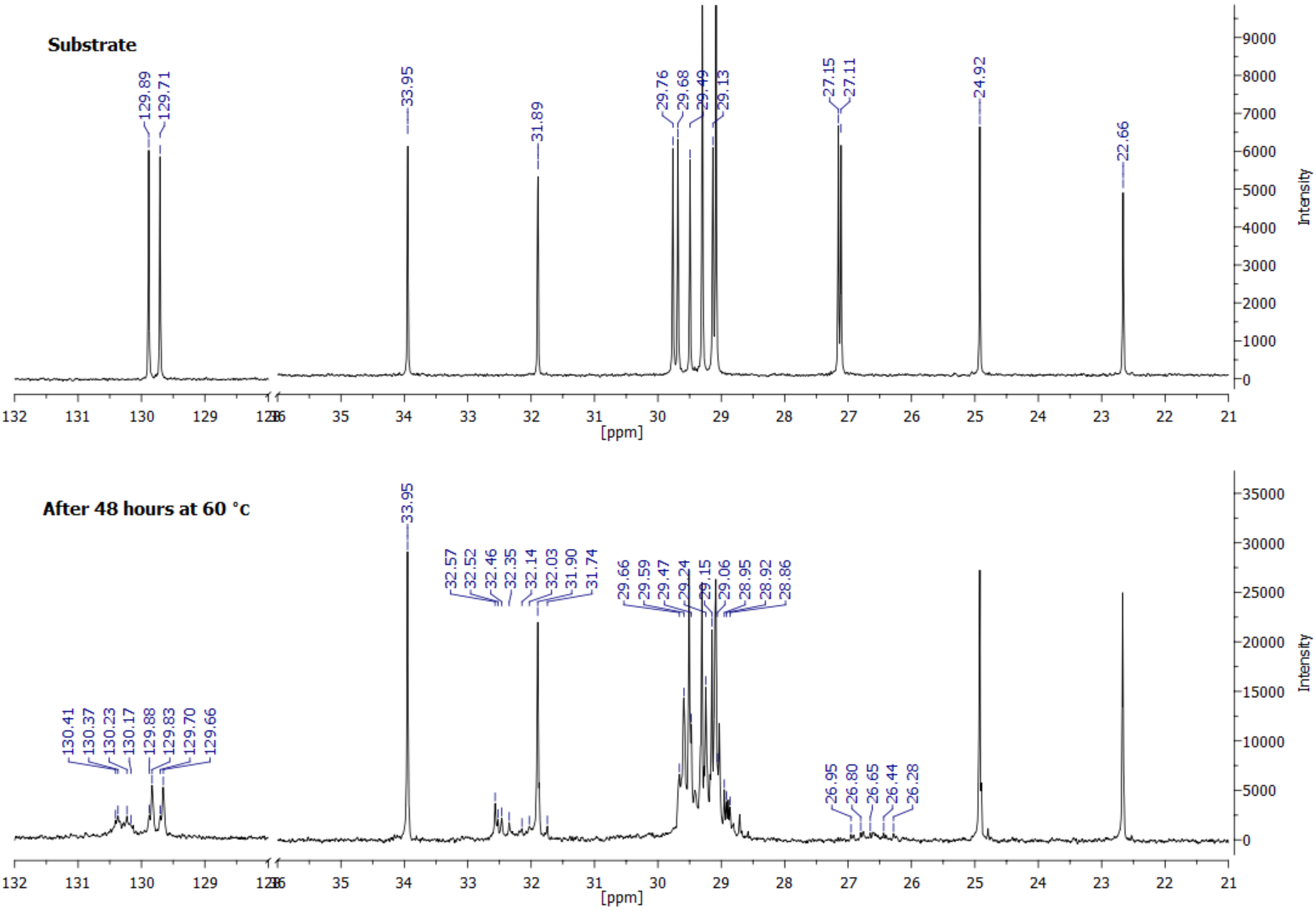


Figure S21 illustrates selected sections of ^{13}C NMR spectra of pure **M-Ole** and equilibrium mixture after 48 hours of reaction time. Reaction of *cis*-to-*trans* isomerization of **M-Ole** follows the similar trend as was described before. Original *Z*-*mono*-allylic carbon atom peaks at 27.15 and 27.11 ppm are diminished in size and new peaks corresponding to *E*-*mono*-allylic carbon atoms appear about 5 ppm downfield to them. However, here the similarity between *cis*-to-*trans* isomerization of **M-Ole** and other examples involving poly-alkenes discussed above ends. Instead of producing only a single pair of singlets for two *E*-*mono*-allylic carbon atoms about 5 ppm downfield to original peaks, a large group of peaks appears at 31.74-32.57 ppm. Meanwhile, instead of simply diminishing in size, two original singlets at 27.15 and 27.11 ppm completely transform into a large set of peaks at 26.28-26.95 ppm. Similar pattern could be observed for vinilyc peaks as well. In contrast to *cis*-to-*trans* isomerization of poly-alkenes, this unusual behaviour suggests that isomerization of **M-Ole** led to migration of its double bond along a carbon chain and formation of a complicated mixture of positional isomers.

XIV. Computational details.

Quantum chemical calculations were performed on the model substrate (x=n=1, R=R'=Me, Table 1) with the Gaussian09[2] program package by employing the B3LYP[3,4] functional. In all calculations, LANL2DZ basis set modified by Couty and Hall[5] was used for the ruthenium atom. Optimization of all stationary points was performed in the gas phase with the 6-31G** basis set employed for the alkene's carbon and hydrogen atoms, and 3-21G basis set for Cp and Cp* atoms.

Species int1 and ts12 (see below) were also optimized in the presence of the solvent, DCM, which was incorporated through the polarizable continuum method (PCM) as implemented in the Gaussian suite of programs[6-8]. Due to the small differences between bond lengths of the structures optimized in the gas phase and in DCM, Table S1, all geometry optimizations were performed in the gas phase.

In order to obtain more reliable values for activation energies, single point energy calculations were performed on all optimized structures at the B2GP-PLYP[9,10]/6-311G**(C,H)-LANL2DZ(Ru) level in the presence of DCM, (see Figure S22).

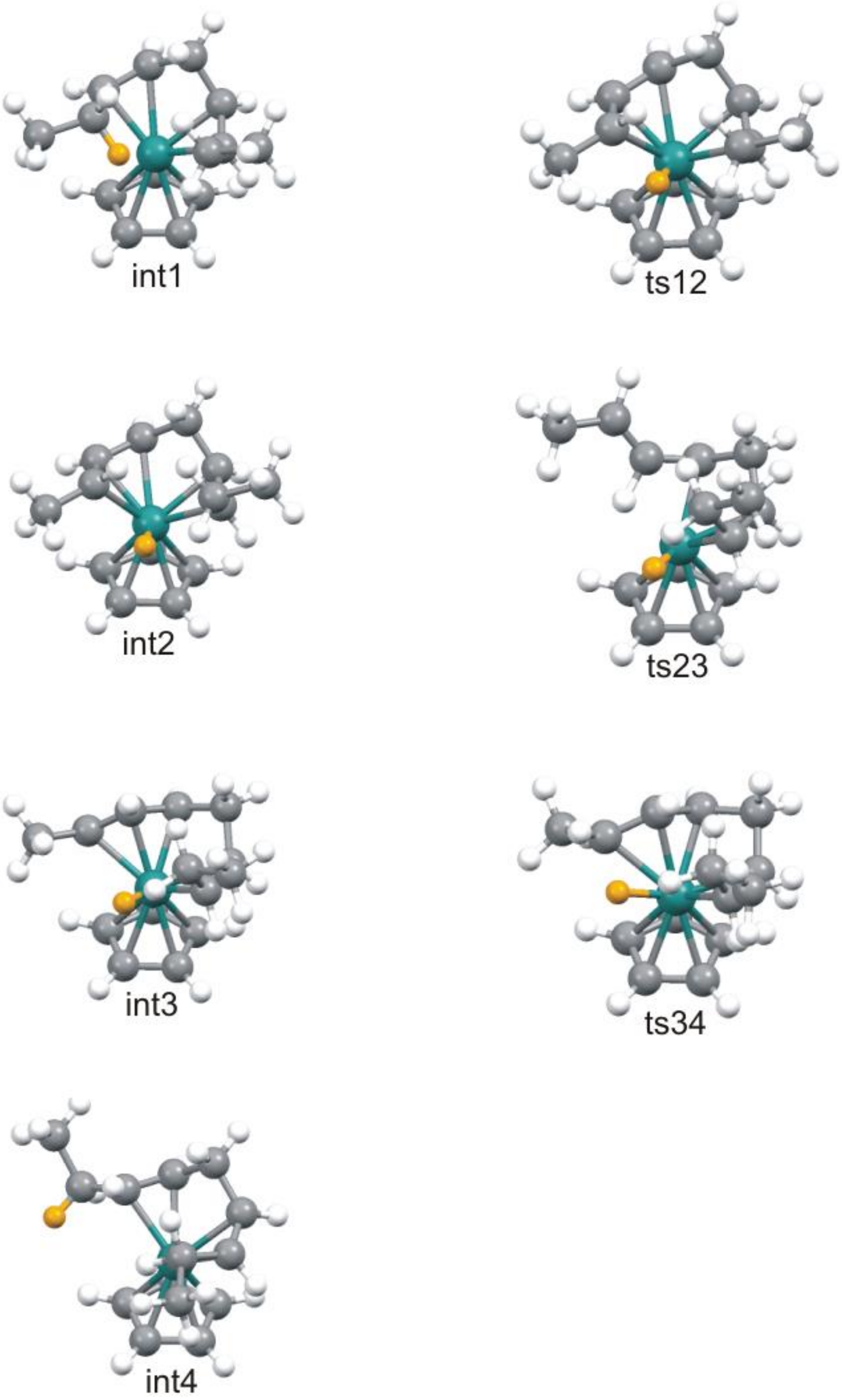
Table S1. Selected bond lengths (in Å) of species int1 and ts12 formed in a reaction with Cp*. DCM was used as a solvent.

	gas/PCM	
	int1	ts12
C29-Ru	2.312/2.304	2.348/2.336
C30-Ru	2.312/2.310	2.313/2.311
C32-Ru	2.363/2.361	2.320/2.321
C33-Ru	2.187/2.187	2.193/2.192
C34-Ru	2.481/2.480	2.308/2.306

Table S2. Energies of partially optimized structures (with respect to **int1**) for fixed C-H bond lengths obtained when one of the bis-allylic H atoms of **int1** was moved towards the lace at the Ru centre as observed in **int2**.

r(C-H) / Å	E / kcal/mol
1.092 (int1)	0.0
1.200	4.5
1.300	13.0
1.400	23.6
1.500	34.9
1.600	46.3
1.700	57.3

Figure S22: Optimized geometries of the key intermediates and transition states for cis-trans isomerization of a bis-olefin.



int1

ts12

int2

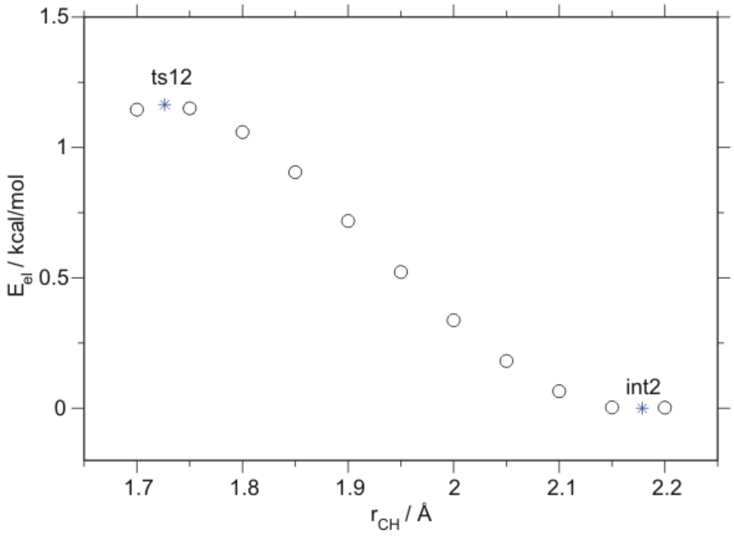
ts23

int3

ts34

int4

Figure S23: Electronic energy in kcal/mol (with respect to int2) computed at B3LYP/3-21G(Cp*)-6-31G**(alkene)-LANL2DZ(Ru) level along the reaction path from ts12 to int2 (reaction with Cp*). Partial optimization was performed for fixed C-H bond lengths. Blue stars represent stationary points.



Selected Cp*/Cp WBIs computed with the B3LYP functional and 3-21G(Cp*/Cp), 6-31G*(alkene) and LANL2DZ(Ru) basis sets.

	int1	ts12	int2	ts23	int3	ts34	int4
C29-Ru	0.383/0.401	0.369/0.384	0.348/0.365	0.345/0.357	0.370/0.385	0.433/0.445	0.397/0.414
C30-Ru	0.332/0.349	0.341/0.358	0.336/0.356	0.351/0.374	0.361/0.375	0.396/0.406	0.366/0.383
C32-Ru	0.338/0.363	0.423/0.438	0.435/0.448	**0.646/0.648**	0.522/0.525	0.483/0.499	0.325/0.349
C33-Ru	0.396/0.418	0.329/0.342	0.284/0.301	0.230/0.245	0.309/0.315	0.372/0.380	0.356/0.391
C34-Ru	0.180/0.213	0.407/0.420	0.472/0.476	0.052/0.047	0.464/0.468	0.320/0.326	0.011/0.011
C29-C30	1.473/1.452	1.462/1.445	1.468/1.448	1.451/1.431	1.438/1.424	1.425/1.417	1.454/1.428
C32-C33	1.460/1.430	1.357/1.343	1.335/1.326	**1.098/1.108**	1.257/1.256	1.339/1.331	1.506/1.469
C33-C34	1.041/1.049	1.223/1.224	1.296/1.287	**1.850/1.856**	1.339/1.331	1.183/1.178	1.022/1.020

NOTE: Labelling of atoms in the xyz files are not the same, but C29 is always refereed to the static carbon atom at the end of the alkene fragment.

Selected Cp*/Cp bond lengths in Å computed with the B3LYP functional and 3-21G(Cp*/Cp), 6-31G*(alkene) and LANL2DZ(Ru) basis sets.

	int1	ts12	int2	ts23	int3	ts34	int4
C29-Ru	2.312/2.313	2.348/2.347	2.373/2.368	2.374/2.376	2.368/2.364	2.324/2.326	2.183/2.175
C30-Ru	2.312/2.308	2.313/2.309	2.326/2.319	2.302/2.297	2.314/2.316	2.248/2.252	2.330/2.327
C32-Ru	2.363/2.353	2.320/2.317	2.320/2.317	**2.168/2.175**	2.228/2.236	2.217/2.218	2.335/2.316
C33-Ru	2.187/2.176	2.193/2.191	2.218/2.214	2.322/2.314	2.206/2.207	2.203/2/202	2.377/2.337
C34-Ru	2.481/2.443	2.308/2.309	2.296/2.299	3.597/3.587	2.306/2.312	2.318/2.323	3.383/3.316
C29-C30	1.392/1.393	1.391/1.392	1.389/1.391	1.392/1.394	1.396/1.397	1.405/1.405	1.393/1.395
C32-C33	1.392/1.395	1.407/1.408	1.410/1.411	**1.450/1.444**	1.421/1.421	1.410/1.410	1.383/1.388
C33-C34	1.495/1.491	1.433/1.432	1.416/1.416	**1.339/1.338**	1.407/1.407	1.446/1.447	1.509/1.512

Reaction with Cp*: optimized structures

int1:

44	0.039583	0.554855	0.418501
6	0.479381	0.018111	2.621428
6	1.675854	-0.144544	1.837447
6	1.403887	-1.155783	0.823560
6	0.038630	-1.609024	0.999780
6	-0.539578	-0.867857	2.104701
6	-1.887676	-1.120505	2.723402
6	-0.623176	-2.732170	0.252745
6	2.418666	-1.756012	-0.108396
6	3.013921	0.471654	2.140693
6	0.332680	0.924312	3.810693
1	0.973700	1.805599	3.721411
1	-0.701279	1.256294	3.937493
1	0.625473	0.386085	4.722348
1	-2.288344	-0.219426	3.196524
1	-1.805163	-1.895190	3.497037
1	-2.611111	-1.469287	1.980513
1	-1.704484	-2.583731	0.180848
1	-0.449502	-3.679947	0.779971
1	-0.219885	-2.831959	-0.758479
1	1.940295	-2.227912	-0.970951
1	2.993335	-2.528368	0.419870
1	3.128139	-1.006794	-0.472823
1	3.529836	-0.118368	2.909727
1	2.909816	1.494652	2.513972
1	3.655879	0.493549	1.255947
6	2.602439	3.942013	-1.548873
6	1.530151	3.272386	-0.667818
6	1.563175	1.766349	-0.829132
6	0.807800	1.003866	-1.715563
6	-0.520034	1.384653	-2.334486
6	-1.435055	0.584094	-1.427948
6	-1.994254	1.028107	-0.233157
6	-1.671454	2.351278	0.383865
6	-2.590307	2.775745	1.530425
1	-2.668927	1.989972	2.286250
1	-2.223609	3.683390	2.015696
1	-3.594323	2.980081	1.147338
1	-0.590561	2.327738	0.828297
1	-1.574098	3.142706	-0.364960
1	-2.757320	0.420047	0.244708
1	-1.729209	-0.402173	-1.777140
1	-0.720138	2.457768	-2.289793
1	-0.600888	1.069623	-3.377382
1	1.206062	0.047813	-2.043355
1	2.522035	1.330794	-0.556708
1	1.716578	3.531105	0.381082
1	0.549717	3.682927	-0.925593
1	3.604671	3.579115	-1.299507
1	2.425697	3.739979	-2.609641
1	2.593308	5.025930	-1.402599

ts12:

44	-0.071470	0.063937	0.029642
6	-0.108921	-0.066594	2.317121
6	1.263045	-0.001904	1.857137
6	1.525284	-1.205766	1.082143
6	0.319372	-1.986329	1.047530
6	-0.700667	-1.274671	1.796936
6	-0.758569	0.893829	3.274757
6	2.292416	1.000540	2.303199
6	2.866331	-1.615197	0.538686
6	0.160291	-3.352216	0.437913
6	-2.068759	-1.803134	2.132479
1	-2.781143	-0.991269	2.304105
1	-2.459175	-2.444569	1.336728
1	-2.020943	-2.404315	3.050048
1	-0.860520	-3.516517	0.080567
1	0.847329	-3.500728	-0.399473
1	0.377033	-4.121944	1.190596
1	2.767003	-2.355222	-0.260141
1	3.467876	-2.066414	1.338654
1	3.425125	-0.757814	0.150491
1	3.101740	1.096582	1.574078
1	2.738004	0.678532	3.253683
1	1.848867	1.988557	2.453753
1	-0.337671	1.897973	3.178267
1	-1.837853	0.954435	3.113057
1	-0.591746	0.553731	4.305414
6	-2.966395	1.818227	0.226686
6	-1.901318	1.268168	-0.695860
6	-1.948594	-0.108718	-1.090527
6	-1.002167	-0.680173	-1.960758
6	-0.080321	0.086884	-2.889988
6	1.101132	0.237637	-1.955961
6	1.427953	1.370536	-1.218497
6	1.085510	2.804213	-1.567090
6	2.212281	3.439494	-2.403856
1	-2.639637	2.734391	0.724012
1	-3.859904	2.062652	-0.359853
1	-3.254770	1.092757	0.991166
1	-1.551002	1.976761	-1.440251
1	-2.659204	-0.766635	-0.596583
1	-1.035724	-1.759661	-2.080162
1	0.164983	-0.486089	-3.787127
1	-0.504816	1.042354	-3.205859
1	1.759057	-0.625210	-1.905394
1	2.338273	1.285219	-0.628146
1	0.949289	3.384482	-0.648050
1	0.149263	2.872581	-2.128445
1	2.349115	2.911260	-3.352427
1	1.976911	4.483864	-2.627670
1	3.166072	3.419861	-1.866823
1	-0.501762	1.596211	0.260230

int2:

44	0.113600	-0.036756	-0.075292
6	-0.035655	0.018428	2.262211
6	1.360547	0.097717	1.862990
6	1.693863	-1.113092	1.160161
6	0.490249	-1.931572	1.088186
6	-0.564641	-1.231648	1.797127
6	-0.752479	1.021124	3.124486
6	2.330686	1.167447	2.283799
6	3.070025	-1.529964	0.720469
6	0.423817	-3.351309	0.595063
6	-1.935737	-1.779965	2.080969
1	1.836343	2.135206	2.409685
1	2.782636	0.898287	3.247730
1	3.140024	1.282252	1.557610
1	3.665295	-0.670854	0.400833
1	3.593622	-2.012011	1.556684
1	3.024196	-2.242293	-0.107066
1	1.120480	-3.519621	-0.230241
1	0.686141	-4.039000	1.409819
1	-0.581801	-3.610733	0.252276
1	-0.390213	2.037852	2.946065
1	-0.579538	0.789017	4.183879
1	-1.831781	1.002664	2.950620
1	-1.897877	-2.435454	2.960984
1	-2.313956	-2.374978	1.243873
1	-2.652405	-0.981626	2.292654
6	2.618135	1.327955	-1.826087
6	1.120725	1.291350	-1.653645
6	0.480240	2.070767	-0.660528
6	-0.909937	2.014599	-0.431761
6	-1.954517	1.539175	-1.423190
6	-2.018748	0.089545	-0.995591
6	-1.403752	-0.977339	-1.638129
6	-1.048840	-1.055882	-3.108490
6	-2.219690	-1.658391	-3.908408
1	-1.951146	-1.745720	-4.964954
1	-2.477026	-2.658761	-3.545694
1	-3.115000	-1.033248	-3.836213
1	-0.808060	-0.072090	-3.520420
1	-0.160737	-1.682005	-3.242181
1	-1.585328	-1.952454	-1.189280
1	-2.640158	-0.110592	-0.127492
1	-2.907234	2.057640	-1.292886
1	-1.636837	1.668860	-2.459651
1	-1.278520	2.497182	0.469525
1	1.093722	2.586377	0.074329
1	0.567857	1.075038	-2.560926
1	0.857185	-0.828499	-1.225611
1	2.891380	2.140482	-2.511087
1	3.135327	1.503673	-0.879269
1	2.995482	0.398469	-2.258919

ts23:

44	0.049423	0.084160	0.146247
6	-0.033280	0.289662	2.437882
6	1.340244	0.031331	2.076035
6	1.808207	1.124744	1.252053
6	0.717928	2.050879	1.075138
6	-0.439655	1.521806	1.790313
6	0.809311	3.408317	0.434419
6	-1.746751	2.235529	1.996538
6	-0.847648	-0.505517	3.421817
6	2.180482	-1.111621	2.573655
6	3.221488	1.310188	0.775473
1	3.834384	1.730518	1.583657
1	3.672612	0.359087	0.475716
1	3.270651	2.000411	-0.071077
1	1.481033	3.405996	-0.428673
1	1.200507	4.129964	1.164076
1	-0.170968	3.768793	0.111281
1	-2.021702	2.832072	1.121577
1	-1.669291	2.916642	2.854351
1	-2.556109	1.528837	2.198691
1	-1.918060	-0.400820	3.230591
1	-0.645103	-0.142940	4.438177
1	-0.594664	-1.567891	3.383711
1	1.571087	-1.998076	2.768412
1	2.673084	-0.827600	3.513124
1	2.959246	-1.377082	1.853506
6	-3.577769	-0.630626	-2.820988
6	-2.437582	-0.985878	-1.848107
6	-1.922674	0.262758	-1.163069
6	-0.940295	1.116306	-1.657758
6	0.106940	0.730523	-2.690308
6	1.103348	0.068223	-1.748013
6	0.956714	-1.342151	-1.445834
6	1.130894	-2.473521	-2.140391
6	0.866258	-3.863553	-1.652435
1	-4.402980	-0.130070	-2.304343
1	-3.976422	-1.537623	-3.284276
1	-3.230169	0.032778	-3.619337
1	-2.809815	-1.686819	-1.094132
1	-1.635242	-1.498394	-2.382874
1	-2.636449	0.720698	-0.480553
1	-0.956644	2.157363	-1.352669
1	0.526065	1.616087	-3.171875
1	-0.263546	0.059104	-3.470275
1	2.090380	0.517026	-1.656282
1	0.633197	-1.594842	-0.342952
1	1.529598	-2.377142	-3.150595
1	0.156630	-4.373448	-2.314465
1	1.785376	-4.460706	-1.663316
1	0.458344	-3.874833	-0.637329
1	-1.157744	-0.881317	0.540162

int3:

44	-0.038728	-0.107950	0.085177
6	0.057790	0.112133	2.380963
6	1.410708	-0.010819	1.888535
6	1.693544	1.139479	1.046009
6	0.521036	1.962487	1.012732
6	-0.501436	1.316441	1.824519
6	-0.591506	-0.778602	3.406297
6	2.420813	-1.012688	2.369939
6	3.033412	1.478984	0.453608
6	0.422267	3.334805	0.403636
6	-1.840814	1.904615	2.171986
1	-1.677740	-0.795682	3.288687
1	-0.226229	-1.805420	3.328308
1	-0.363051	-0.409169	4.414507
1	1.951325	-1.967823	2.619049
1	2.902807	-0.629948	3.279769
1	3.205967	-1.191067	1.630493
1	3.569763	0.584918	0.119838
1	3.660093	1.975125	1.206586
1	2.934709	2.159381	-0.397010
1	1.022015	3.417906	-0.507194
1	0.793127	4.081159	1.118866
1	-0.611289	3.599963	0.163860
1	-1.724704	2.623447	2.993963
1	-2.284532	2.440640	1.327085
1	-2.541575	1.132890	2.501221
6	-4.311383	-1.008658	-1.839575
6	-2.867630	-1.309968	-1.393785
6	-2.264783	-0.092255	-0.723237
6	-1.535177	0.919384	-1.349231
6	-0.747911	0.767577	-2.643841
6	0.518356	0.177444	-2.052579
6	0.530415	-1.208806	-1.739517
6	1.394730	-1.710258	-0.749434
6	1.375454	-3.155043	-0.335109
1	-4.342100	-0.196306	-2.572466
1	-4.938620	-0.719779	-0.990111
1	-4.758640	-1.895164	-2.297964
1	-2.285421	-1.622808	-2.264136
1	-2.872529	-2.152351	-0.695255
1	-2.813027	0.217924	0.164252
1	-1.584083	1.922040	-0.939315
1	-0.577217	1.734946	-3.118317
1	-1.225892	0.110274	-3.376234
1	1.440001	0.751877	-2.059366
1	-0.250292	-1.858197	-2.121691
1	2.333434	-1.184747	-0.591140
1	1.619370	-3.275566	0.722696
1	2.133846	-3.709091	-0.903263
1	0.402241	-3.616091	-0.520167
1	-0.836715	-1.424707	0.465303

ts34:

44	-0.043784	0.032895	0.090659
6	0.019382	-0.086887	2.380749
6	1.388326	-0.019930	1.876292
6	1.552012	1.232751	1.209944
6	0.285157	1.966982	1.324847
6	-0.632684	1.166665	2.072283
6	-0.520377	-1.139141	3.310590
6	2.458313	-1.046395	2.120137
6	2.834975	1.782189	0.645311
6	0.070393	3.389460	0.888564
6	-2.006621	1.577717	2.524501
1	-0.370783	-0.818593	4.350437
1	-1.591893	-1.302169	3.161912
1	-0.002814	-2.094260	3.187269
1	2.063577	-2.066269	2.070469
1	2.885036	-0.904665	3.121880
1	3.269664	-0.954302	1.393549
1	3.465492	0.985446	0.242248
1	3.398007	2.296031	1.435663
1	2.644547	2.501846	-0.154965
1	0.430014	4.072147	1.669808
1	0.620527	3.618320	-0.028996
1	-0.989552	3.607341	0.725532
1	-2.483408	2.252104	1.806677
1	-1.940194	2.107505	3.484035
1	-2.656328	0.710082	2.670692
6	1.548604	-3.511692	-2.627081
6	0.743317	-2.231136	-2.337573
6	0.692932	-1.963704	-0.842570
6	-0.385792	-2.188027	0.029561
6	-1.884981	-2.152095	-0.308267
6	-2.101016	-0.639372	-0.390797
6	-1.520477	-0.066561	-1.541560
6	-0.906066	1.233487	-1.695305
6	-0.480382	1.672941	-3.092096
1	1.095735	-4.382516	-2.143037
1	2.578338	-3.422704	-2.266063
1	1.587199	-3.704429	-3.703088
1	1.213927	-1.391047	-2.861494
1	-0.258359	-2.354688	-2.760400
1	1.670363	-2.086090	-0.378321
1	-0.159887	-2.512150	1.039068
1	-2.145343	-2.670484	-1.237824
1	-2.464458	-2.607448	0.496475
1	-2.781861	-0.116118	0.271691
1	-1.247680	-0.758207	-2.331278
1	-1.299724	2.049558	-1.093051
1	-1.366693	2.013678	-3.637892
1	-0.022852	0.855963	-3.655717
1	0.225849	2.505295	-3.049918
1	0.462459	0.918221	-1.256781

int4:

44	0.134988	-0.444206	0.129465
6	0.201392	-0.240906	2.361967
6	1.561896	-0.414432	1.893393
6	1.889850	0.728030	1.067657
6	0.747598	1.598058	1.005189
6	-0.314105	0.987440	1.793103
6	-0.504838	-1.114676	3.359582
6	2.525765	-1.474861	2.352236
6	3.226919	0.998647	0.438232
6	0.752605	2.991239	0.441010
6	-1.629056	1.625361	2.142848
1	-0.280158	-0.767192	4.377069
1	-1.589222	-1.079342	3.225133
1	-0.179684	-2.156417	3.284790
1	2.007092	-2.398025	2.626935
1	3.071579	-1.124543	3.238132
1	3.263211	-1.710948	1.579479
1	3.755425	0.070832	0.203015
1	3.852985	1.572366	1.135119
1	3.123532	1.583806	-0.479586
1	1.228257	3.672021	1.159835
1	1.314728	3.047589	-0.495895
1	-0.259092	3.356519	0.257793
1	-2.008124	2.239562	1.322094
1	-1.502164	2.276992	3.017801
1	-2.385181	0.875174	2.390859
6	2.448612	-2.606005	-1.685074
6	1.022605	-2.091600	-1.475769
6	0.345075	-2.585086	-0.239811
6	-1.020900	-2.462958	0.002723
6	-2.056086	-1.995890	-0.999697
6	-1.985811	-0.489491	-0.846097
6	-1.224727	0.330027	-1.660127
6	-1.459923	1.811327	-1.823474
6	-2.386581	2.089385	-3.022781
1	2.430740	-3.680858	-1.886911
1	3.063218	-2.437200	-0.796689
1	2.927529	-2.110409	-2.532787
1	1.122739	-0.921363	-1.434971
1	0.406578	-2.224433	-2.371167
1	0.960865	-3.097801	0.494015
1	-1.385745	-2.832882	0.956967
1	-1.819093	-2.311607	-2.020734
1	-3.047940	-2.384358	-0.756957
1	-2.667665	-0.037722	-0.129465
1	-0.740119	-0.137109	-2.518359
1	-1.907970	2.224922	-0.914513
1	-3.367874	1.626183	-2.881788
1	-1.960820	1.700680	-3.953620
1	-2.533583	3.165970	-3.148556
1	-0.508542	2.328513	-1.980826

Reaction with Cp: optimized structures

int1:

44	-0.066835	-0.037262	-0.013469
6	-0.011892	0.027064	2.304795
6	1.325406	0.014217	1.799022
6	1.500295	-1.216052	1.053987
6	0.267221	-1.955360	1.122502
6	-0.677337	-1.174893	1.881487
1	-1.678891	-1.472666	2.148715
1	0.092818	-2.933101	0.700284
1	2.415955	-1.556052	0.595102
1	2.081105	0.760293	1.985506
1	-0.450934	0.814423	2.899491
6	2.110287	3.422810	-2.292263
6	1.019989	2.695909	-1.480513
6	1.414378	1.255054	-1.231653
6	1.077649	0.148836	-2.009169
6	-0.110160	0.025740	-2.939169
6	-1.011683	-0.789570	-2.033383
6	-1.928413	-0.280466	-1.113712
6	-2.044111	1.169890	-0.788580
6	-3.250151	1.553825	0.069586
1	-3.321566	0.919832	0.957298
1	-3.189146	2.594893	0.394447
1	-4.168772	1.434654	-0.512134
1	-1.095495	1.524008	-0.175972
1	-1.949308	1.807077	-1.672395
1	-2.630914	-0.963724	-0.644416
1	-0.993396	-1.868064	-2.166016
1	-0.545951	0.989986	-3.209990
1	0.133251	-0.508165	-3.860116
1	1.743205	-0.710021	-2.004135
1	2.348352	1.155810	-0.681023
1	0.885289	3.209155	-0.521689
1	0.068857	2.766474	-2.015908
1	3.073166	3.401733	-1.772449
1	2.246764	2.962032	-3.275169
1	1.834092	4.470167	-2.442530

ts12:

44	0.015061	-0.036106	-0.033863
6	-0.005455	-0.016599	2.263287
6	1.357181	-0.015418	1.800324
6	1.586408	-1.266710	1.113800
6	0.373131	-2.019915	1.144602
6	-0.620516	-1.240507	1.839707
1	-0.474629	0.761524	2.845377
6	1.205680	2.595100	-1.773754
6	2.341711	3.164934	-2.645390
1	-2.522943	2.675117	0.526217
1	-3.762547	1.940808	-0.492570
1	-3.127549	1.049893	0.901178
1	-1.460921	1.800299	-1.604033
1	-2.573590	-0.892675	-0.613044

1	2.095491	0.743528	2.004283	1	-0.953049	-1.967468	-2.037892
1	2.524506	-1.592568	0.690841	1	0.249642	-0.798223	-3.813414
1	0.229944	-3.008330	0.735443	1	-0.404282	0.767174	-3.314353
1	-1.627657	-1.554873	2.065356	1	1.841196	-0.855524	-1.927509
6	-2.857952	1.731256	0.090646	1	2.441802	1.113248	-0.751653
6	-1.813253	1.132455	-0.823501	1	1.080347	3.226881	-0.888142
6	-1.861689	-0.262902	-1.140940	1	0.269324	2.644196	-2.337008
6	-0.915777	-0.883205	-1.979347	1	2.469836	2.583041	-3.563138
6	0.010067	-0.174843	-2.949393	1	2.119148	4.197989	-2.926430
6	1.190599	0.009672	-2.020778	1	3.295099	3.162817	-2.107840
6	1.532910	1.179304	-1.347837	1	-0.387510	1.509592	0.089626

int2:

44	-0.048335	0.025783	0.020506	6	-1.428884	-0.857529	-2.957533
6	-0.013154	-0.028369	2.375308	6	-2.677296	-1.378340	-3.696191
6	1.340137	0.010786	1.874930	1	-2.476879	-1.449128	-4.768760
6	1.563421	-1.174743	1.104580	1	-2.962495	-2.374333	-3.343222
6	0.332683	-1.933936	1.093486	1	-3.532831	-0.711192	-3.553704
6	-0.629095	-1.223020	1.898834	1	-1.162066	0.124339	-3.358089
1	-0.469288	0.706191	3.021372	1	-0.585407	-1.525041	-3.160510
1	2.075882	0.766930	2.101271	1	-1.894033	-1.782543	-1.031585
1	2.491861	-1.469004	0.640938	1	-2.803686	0.074759	0.133664
1	0.192289	-2.903966	0.643542	1	-3.034252	2.283213	-0.961124
1	-1.632610	-1.552441	2.121743	1	-1.848508	1.869248	-2.207773
6	2.424671	1.330562	-1.799645	1	-1.296656	2.590791	0.721249
6	0.936157	1.366797	-1.566529	1	1.050880	2.596322	0.206758
6	0.380220	2.131658	-0.512274	1	0.330746	1.212162	-2.453165
6	-0.998545	2.125660	-0.214476	1	0.574597	-0.698814	-1.235656
6	-2.115424	1.727081	-1.158957	1	2.711157	2.168944	-2.447034
6	-2.218322	0.271592	-0.760264	1	2.988071	1.417509	-0.867136
6	-1.693283	-0.804890	-1.467386	1	2.729640	0.411871	-2.305602

ts23:

44	0.001839	0.003606	-0.018023	6	-0.011364	-0.580043	-3.556816
6	-0.018274	-0.039038	2.226586	6	-1.160698	-1.429669	-3.999179
6	1.368866	-0.012312	1.808793	1	-1.444302	4.322799	-2.043630
6	1.641068	-1.231058	1.106715	1	-2.805782	4.145606	-0.926371
6	0.436503	-2.012763	1.084387	1	-3.026511	3.804710	-2.646244
6	-0.580840	-1.293405	1.795208	1	-2.861873	1.658796	-1.405701
1	-0.514320	0.702933	2.832607	1	-1.492991	1.827395	-2.491049
1	2.082602	0.763111	2.039786	1	-1.493462	2.347252	0.556030
1	2.590419	-1.527024	0.687946	1	0.873013	2.566532	0.469760
1	0.324369	-2.988983	0.638025	1	2.190268	2.537996	-1.551555
1	-1.584319	-1.638289	1.987578	1	0.753395	2.450137	-2.586127
6	-2.325691	3.716802	-1.811513	1	2.310265	0.107682	-1.519674
6	-1.951750	2.238425	-1.589131	1	-0.456080	-0.808768	-1.564158
6	-1.025630	2.111397	-0.398302	1	0.650636	-0.204106	-4.337128
6	0.362638	2.234098	-0.429167	1	-0.799999	-2.317396	-4.531178
6	1.216145	2.061529	-1.674841	1	-1.794097	-0.879782	-4.704637
6	1.323059	0.542970	-1.659051	1	-1.782161	-1.758225	-3.160916
6	0.303719	-0.256723	-2.297743	1	-1.584678	0.047600	-0.098441

int3:

44	-0.004149	-0.002206	-0.014177	6	-1.794485	1.443288	0.206505
6	-0.112452	-0.052293	2.305420	6	-1.631340	2.899687	0.532597
6	1.258888	0.112617	1.910763	1	2.055368	1.701336	-4.898624

6	1.641109	-1.052731	1.171909	1	3.080180	0.602660	-3.967848
6	0.512938	-1.961585	1.152549	1	1.635728	-0.014952	-4.784699
6	-0.562909	-1.344507	1.852323	1	0.186295	1.404540	-3.281622
1	-0.679677	0.641439	2.905955	1	1.617023	2.026572	-2.472913
1	1.890769	0.954813	2.143537	1	2.225189	-0.278319	-1.676320
1	2.622566	-1.250395	0.769311	1	0.673843	-2.076803	-1.696045
1	0.508611	-2.951883	0.724095	1	-1.216491	-0.418092	-3.441648
1	-1.533022	-1.777625	2.042554	1	-1.474964	-2.046230	-2.796316
6	2.043544	0.835960	-4.230310	1	-2.427521	-1.079187	-0.726813
6	1.203614	1.147408	-2.976242	1	-1.362076	1.601363	-1.897580
6	1.225020	-0.037486	-2.032744	1	-2.381832	0.861820	0.914220
6	0.322925	-1.103911	-2.024755	1	-2.619081	3.378747	0.542647
6	-1.102040	-1.049833	-2.556374	1	-1.004847	3.415398	-0.198632
6	-1.757941	-0.465386	-1.322043	1	-1.196623	3.043749	1.524912
6	-1.679543	0.936217	-1.101205	1	0.718584	1.367731	-0.321049

ts34:

44	0.004675	0.006191	0.004821	6	0.876846	2.035030	-0.715711
6	-0.012749	-0.047542	2.376591	6	1.828223	2.556959	-1.787416
6	1.332576	-0.017370	1.922665	1	-0.891368	-1.086541	-5.374005
6	1.580193	-1.222810	1.140487	1	-2.111753	-1.737379	-4.268903
6	0.370855	-1.966349	1.098381	1	-0.470098	-2.401920	-4.269987
6	-0.636518	-1.222014	1.832473	1	-1.204271	0.475831	-3.484970
1	-0.488805	0.688833	3.005921	1	0.427238	-0.194001	-3.460500
1	2.071503	0.729879	2.169576	1	-0.499266	-2.013829	-1.821566
1	2.524948	-1.516144	0.710871	1	-2.261832	-1.451974	-0.375682
1	0.229622	-2.924208	0.621812	1	-3.548087	0.539706	-0.301577
1	-1.641636	-1.556066	2.036413	1	-2.961947	1.081057	-1.876727
6	-1.052657	-1.480334	-4.366619	1	-1.768201	1.968040	0.765073
6	-0.630491	-0.439685	-3.312005	1	-0.682892	1.723079	-2.117131
6	-0.855615	-0.988756	-1.913784	1	1.107853	2.406171	0.280848
6	-1.887324	-0.661322	-1.017812	1	1.702924	3.642506	-1.860361
6	-2.652116	0.667580	-0.910725	1	1.621609	2.119498	-2.767204
6	-1.596914	1.525890	-0.210402	1	2.869488	2.356682	-1.526478
6	-0.519249	1.864362	-1.054323	1	1.322552	0.657781	-0.834424

int4:

44	-0.003992	0.053111	-0.038715	6	-2.930678	-1.313568	-0.790772
6	-0.061624	0.019945	2.280970	6	-4.053546	-1.561839	-1.816114
6	1.304460	-0.050563	1.838750	1	-0.748386	4.095033	0.274380
6	1.455165	-1.261558	1.071895	1	0.783167	3.435942	0.875383
6	0.174315	-1.913961	1.017630	1	0.742994	4.352498	-0.641651
6	-0.765489	-1.117678	1.777546	1	-0.806969	1.724456	-0.156424
1	-0.487979	0.806361	2.885978	1	-0.654316	2.521611	-1.713463
1	2.091169	0.640492	2.096901	1	2.095715	1.819522	-0.602676
1	2.370775	-1.629605	0.635411	1	2.126632	-0.086214	-2.080871
1	-0.027958	-2.867500	0.555700	1	-0.483623	0.954044	-3.300217
1	-1.796658	-1.362242	1.970861	1	0.454377	-0.451062	-3.815828
6	0.195446	3.634046	-0.024903	1	-0.524002	-1.864494	-2.052961
6	-0.042400	2.350279	-0.822173	1	-2.260471	0.626487	-1.579114
6	1.173750	1.538513	-1.104714	1	-3.365707	-0.885789	0.118467
6	1.192689	0.461981	-1.992302	1	-2.469084	-2.267609	-0.513444
6	0.074798	0.083734	-2.942547	1	-4.546164	-0.627067	-2.102333
6	-0.767591	-0.804439	-2.049675	1	-4.814272	-2.222445	-1.390970
6	-1.888051	-0.373547	-1.353621	1	-3.664785	-2.031705	-2.724554

XV. References.

1 H. Rakoff, E. A. Emken, *Chem. Phys. Lipids*, 1982, **31**, 215.

2 J. Frisch et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

3 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

4 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785.

5 M. Couty, M. B. Hall, *J. Comput. Chem.* 1996, **17**, 1359.

6 S. Miertuš, E. Scrocco and J. Tomasi *Chem. Phys.* 1981, **55**, 117.

7 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, **105**, 2999.

8 G. Scalmani, M. J. Frisch, *J. Chem. Phys.* 2010, **132**, 114110.

9 A. Karton, A. Tarnopolsky, J.-F. Lamère, G. C. Schatz and J. M. L. Martin, *J. Phys. Chem. A* 2008, **112**, 12868.

10 S. Kozuch, J. M. L. Martin, *J. Comp. Chem.* 2013, **34**, 2327.