# Supporting Information to:

# Ni(II) and Co(II) bis(acetylacetonato) complexes for alkene/vinylsilane silylation and silicone crosslinking

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## 1. NMR identification of starting materials

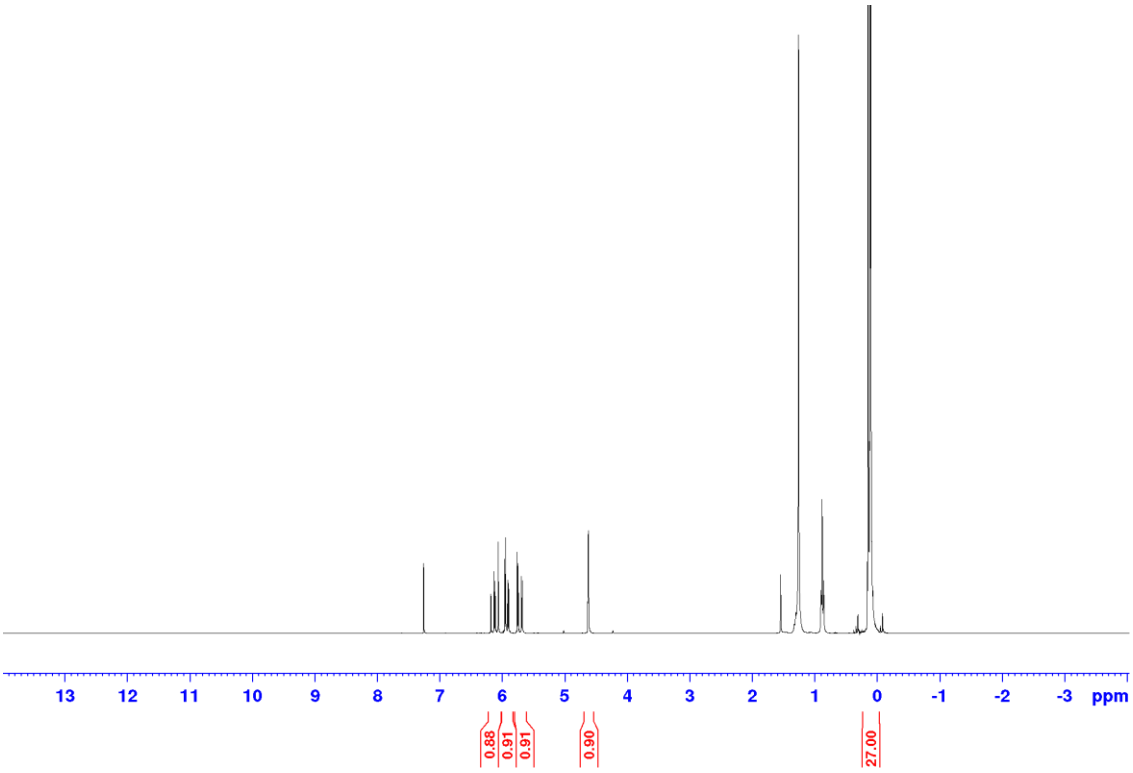



**Figure S1 – $^{1}$H NMR spectrum in $CDCl_3$– dvtms + MD'M + dodecane (full spectrum)**

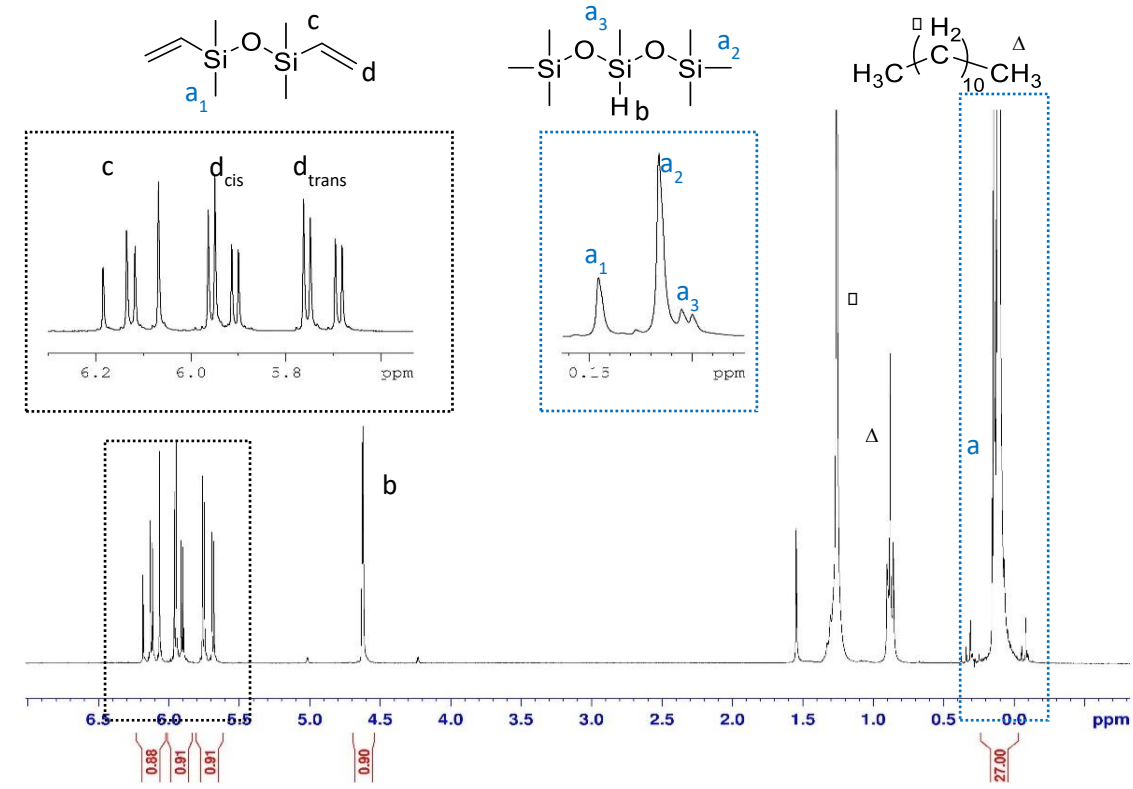



**Figure S2 – $^{1}$H NMR identification in $CDCl_3$– dvtms + MD'M + dodecane**

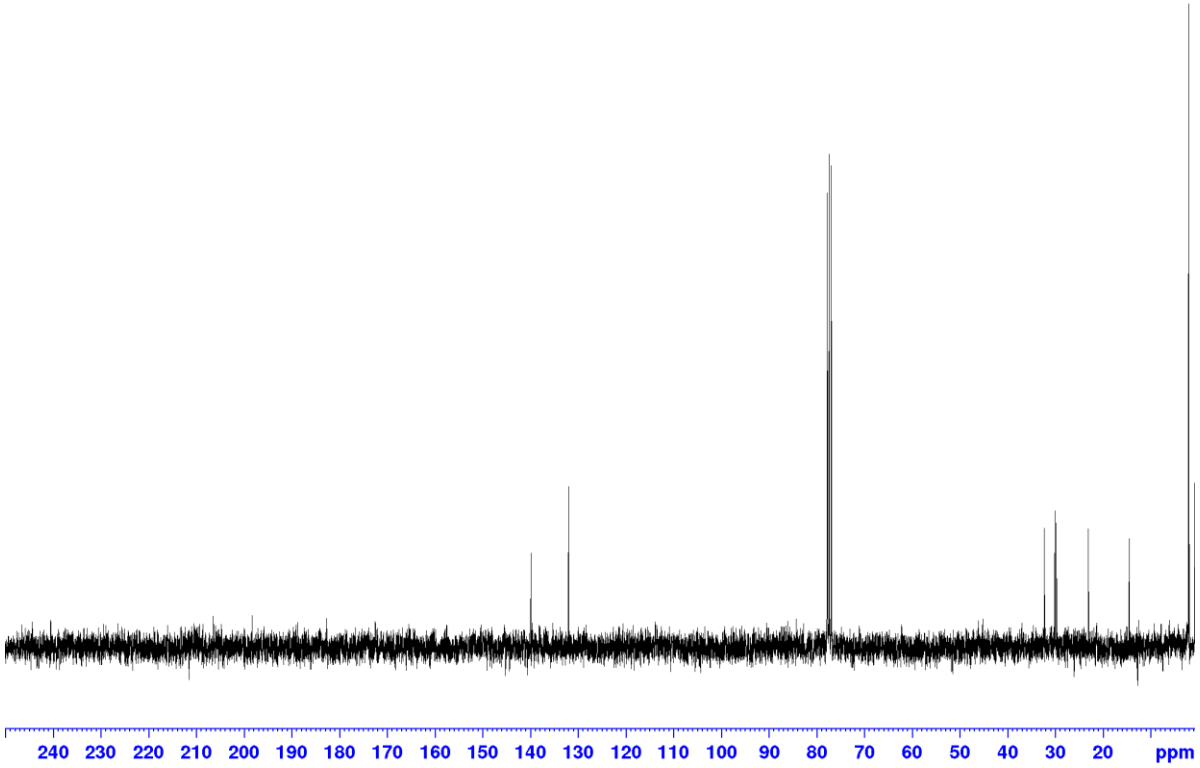



**Figure S3 – $^{13}C$ NMR spectrum in $CDCl_3$– dvtms + MD'M + dodecane (full spectrum)**

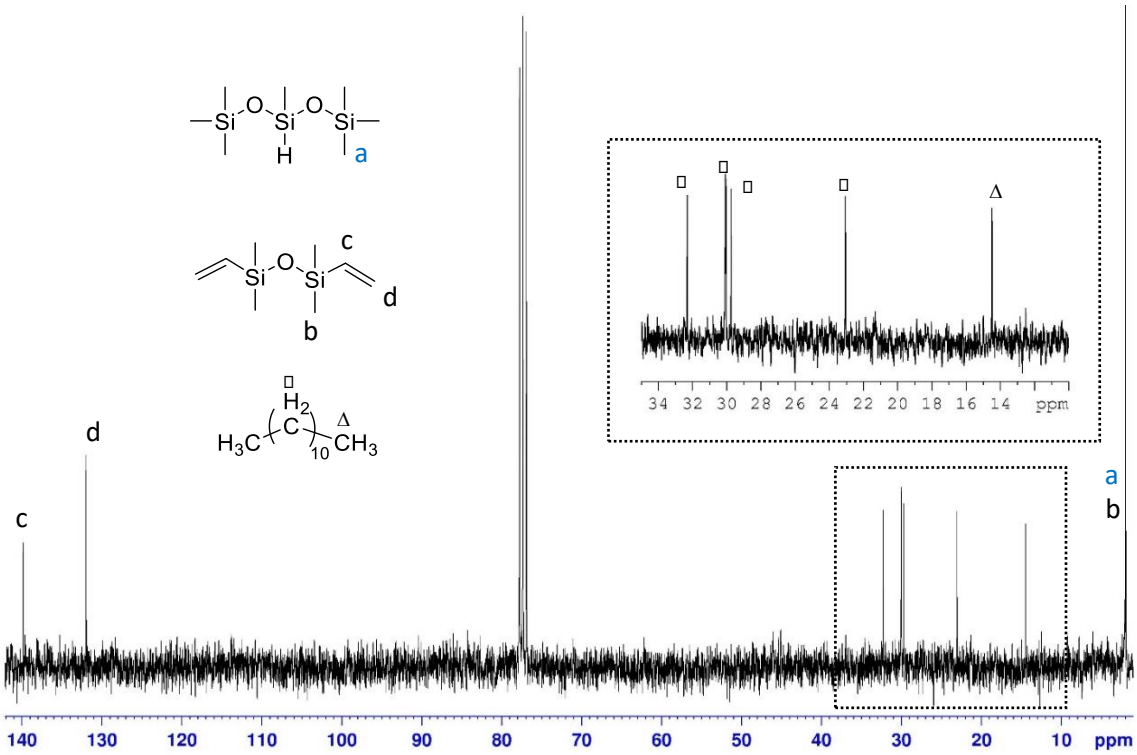



**Figure S4 – $^{13}C$ NMR identification in $CDCl_3$– dvtms + MD'M + dodecane**

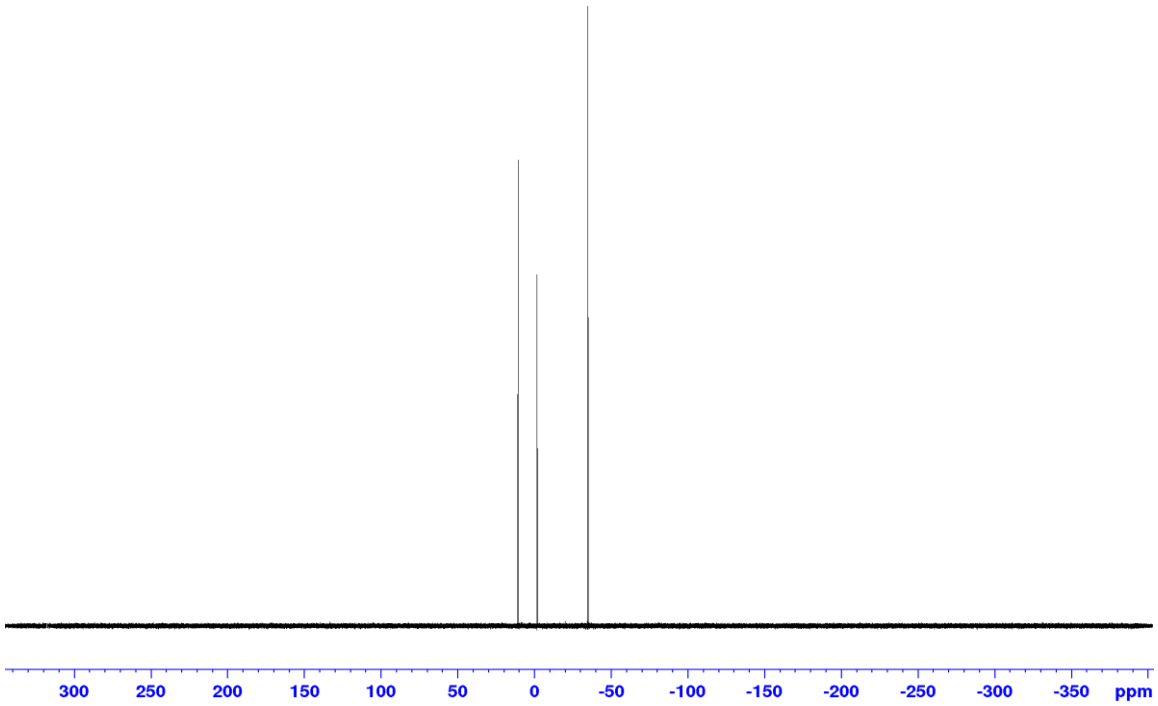



**Figure S5 – {$^{1}$H}-$^{29}$Si INEPT (decoupled $^{1}$H) NMR spectrum in MCH d14– dvtms + MD'M + dodecane (full spectrum)**

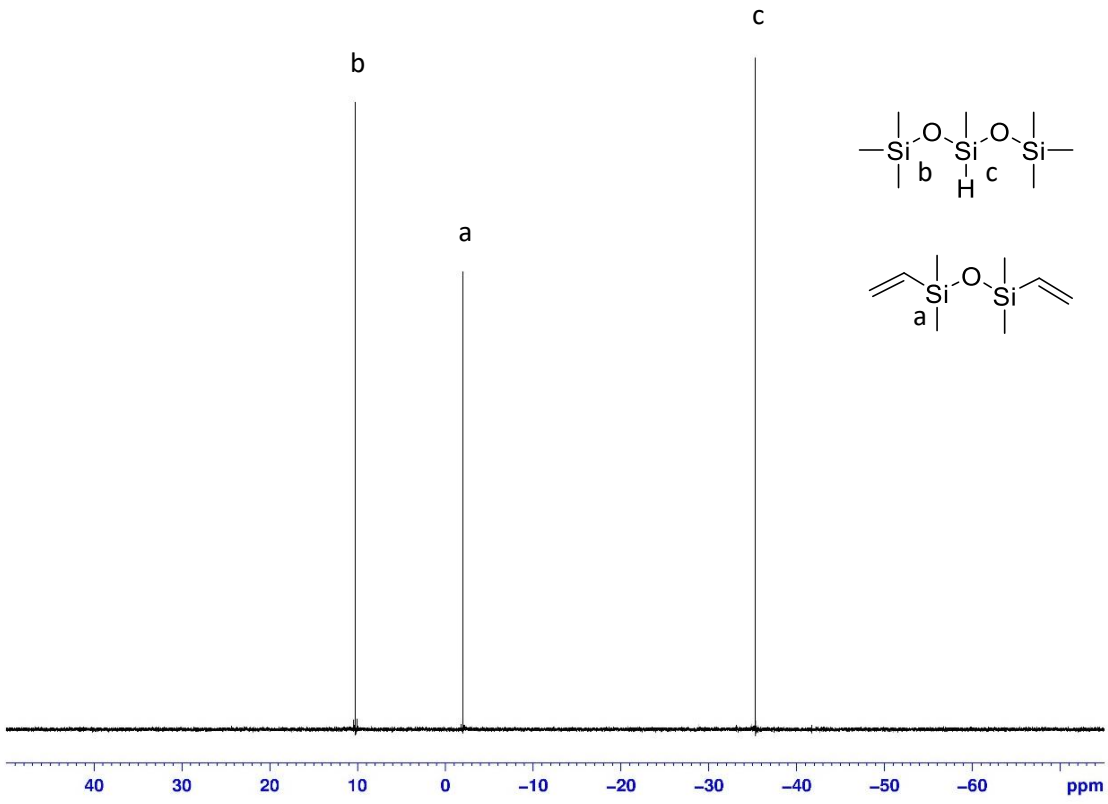



**Figure S6 – {$^{1}$H}-$^{29}$Si INEPT (decoupled $^{1}$H) NMR identification in MCH d14– dvtms + MD'M + dodecane**

## 2. Reactivity of $Ni(tmhd)_2$ with MD'M or dvtms

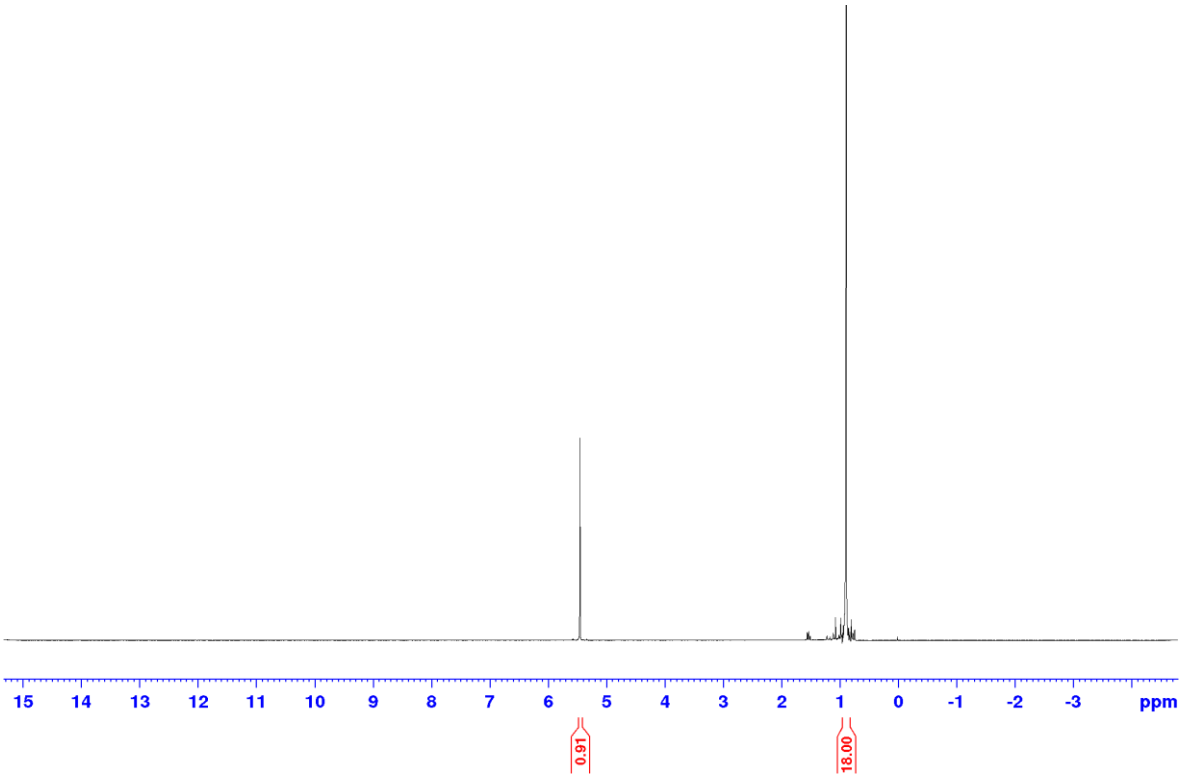



**Figure S7 – $^1H$ NMR spectrum in MCH d14 of $Ni(tmhd)_2$ (full spectrum)**

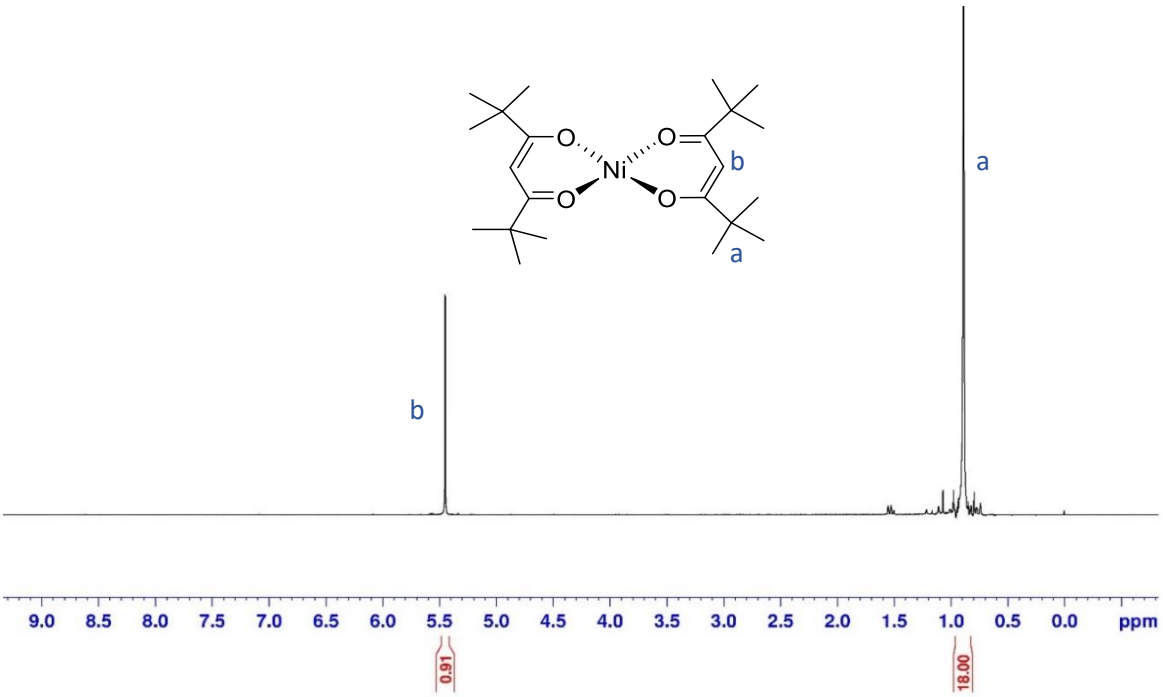



**Figure S8 – $^1H$ NMR identification in MCH d14 of $Ni(tmhd)_2$**

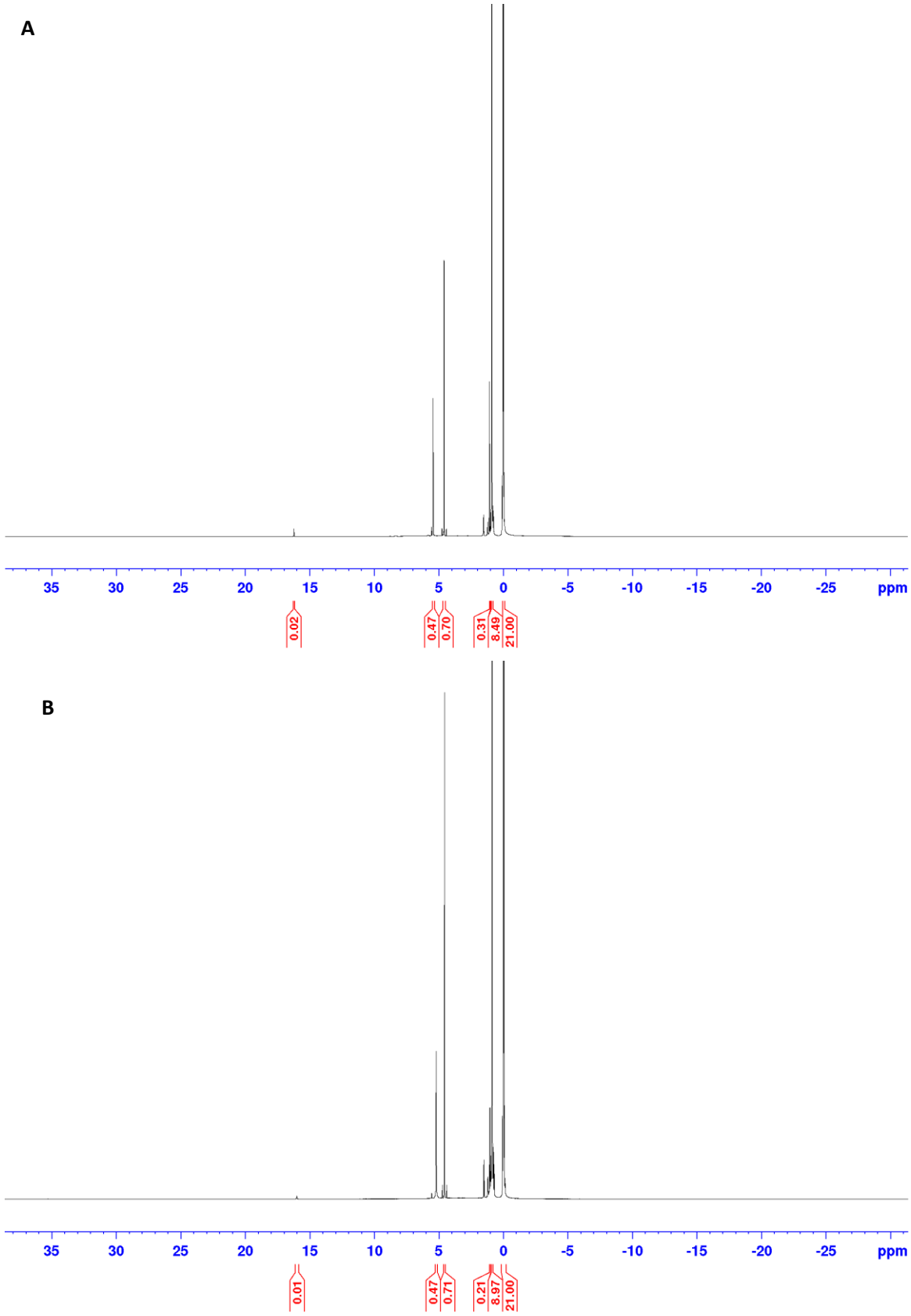



**Figure S9 – $^{1}$H NMR spectra in MCH d14 of Ni(tmhd)$_2$ mixed with MD'M at 25 °C (A) and at 90 °C (B) (full spectra)**

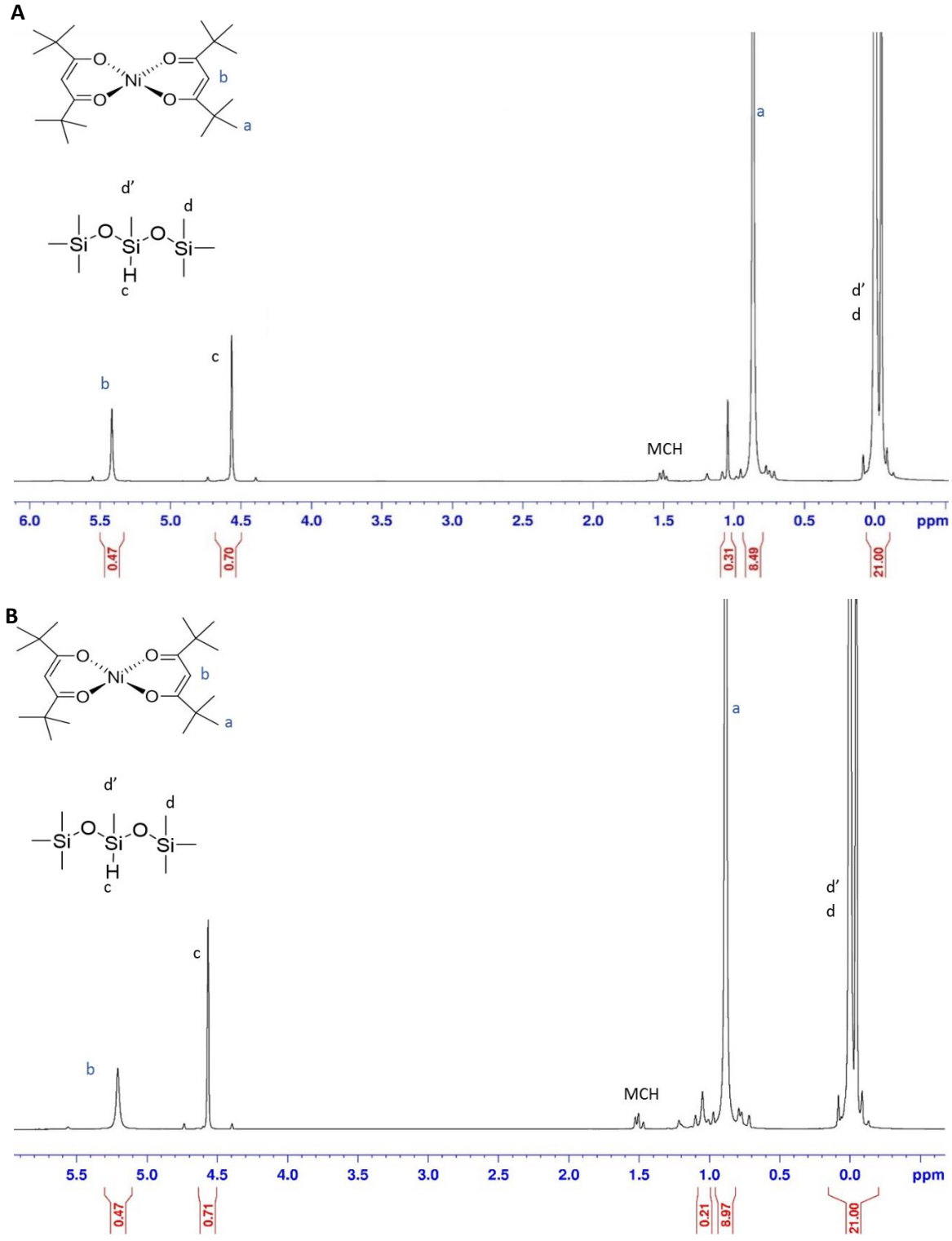



**Figure S10 – $^{1}$H NMR identification in MCH d14 of Ni(tmhd)$_2$ mixed with MD'M at 25 °C (A) and at 90 °C (B)**

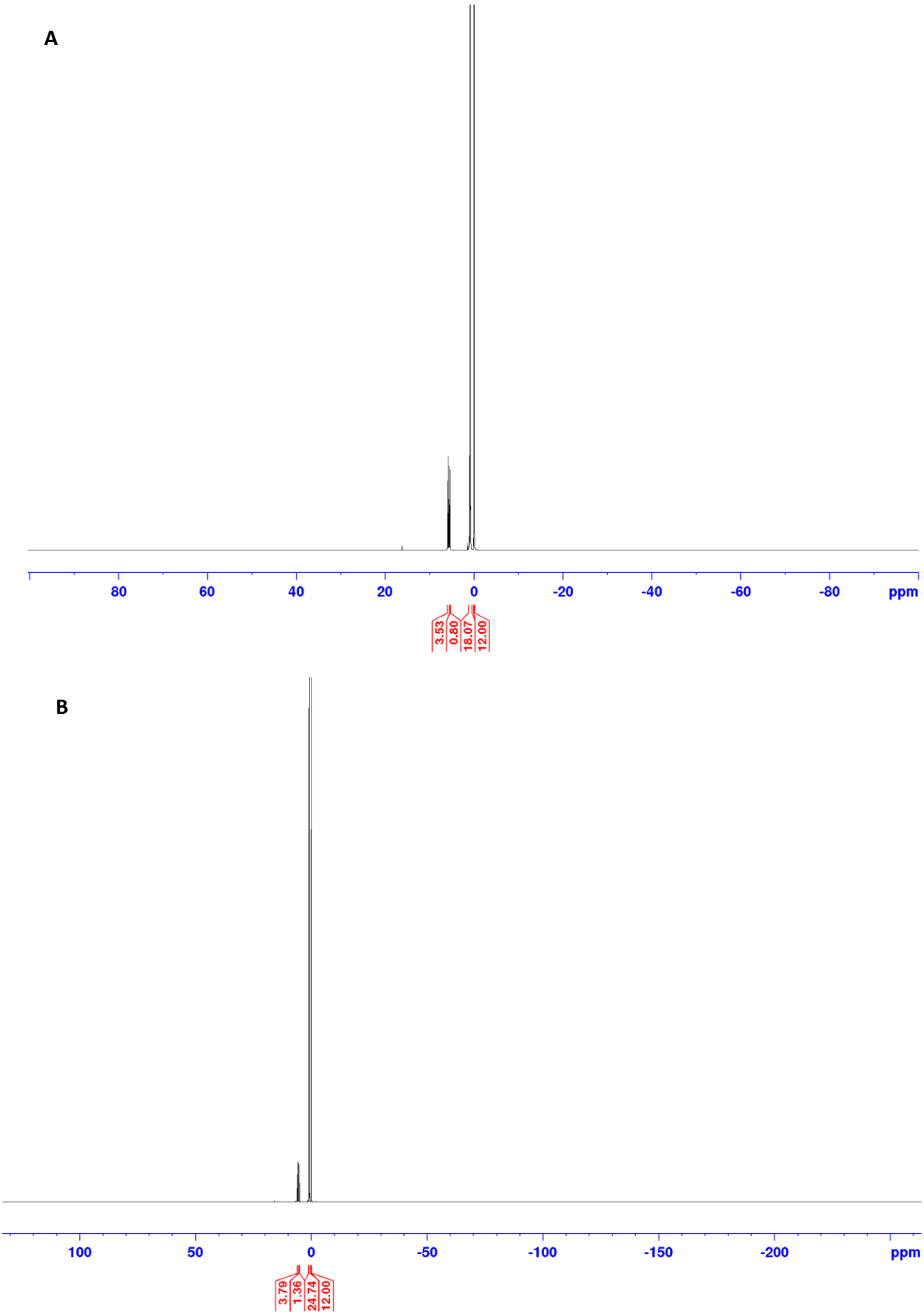



**Figure S11 – $^{1}$H NMR spectra in MCH d14 of Ni(tmhd)$_2$ mixed with dvtms at 25 °C (A) and at 90 °C (B) (full spectra)**

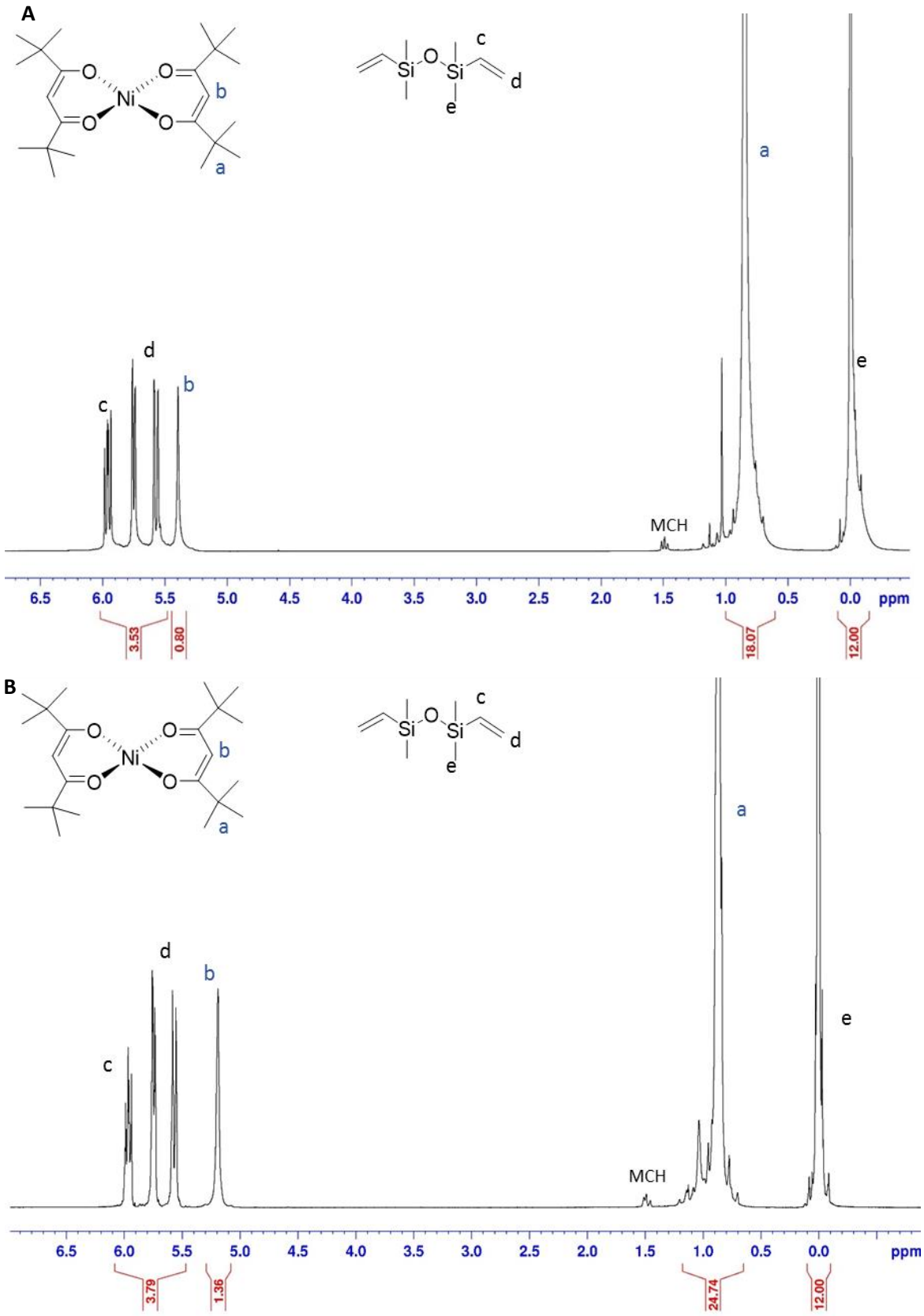



**Figure S12 – $^{1}$H NMR spectra in MCH d14 of Ni(tmhd)$_2$ mixed with dvtms at 25 °C (A) and at 90 °C (B)**

## 3. NMR identification of reaction products between dvtms and MD'M catalyzed by $Ni(tmhd)_2$

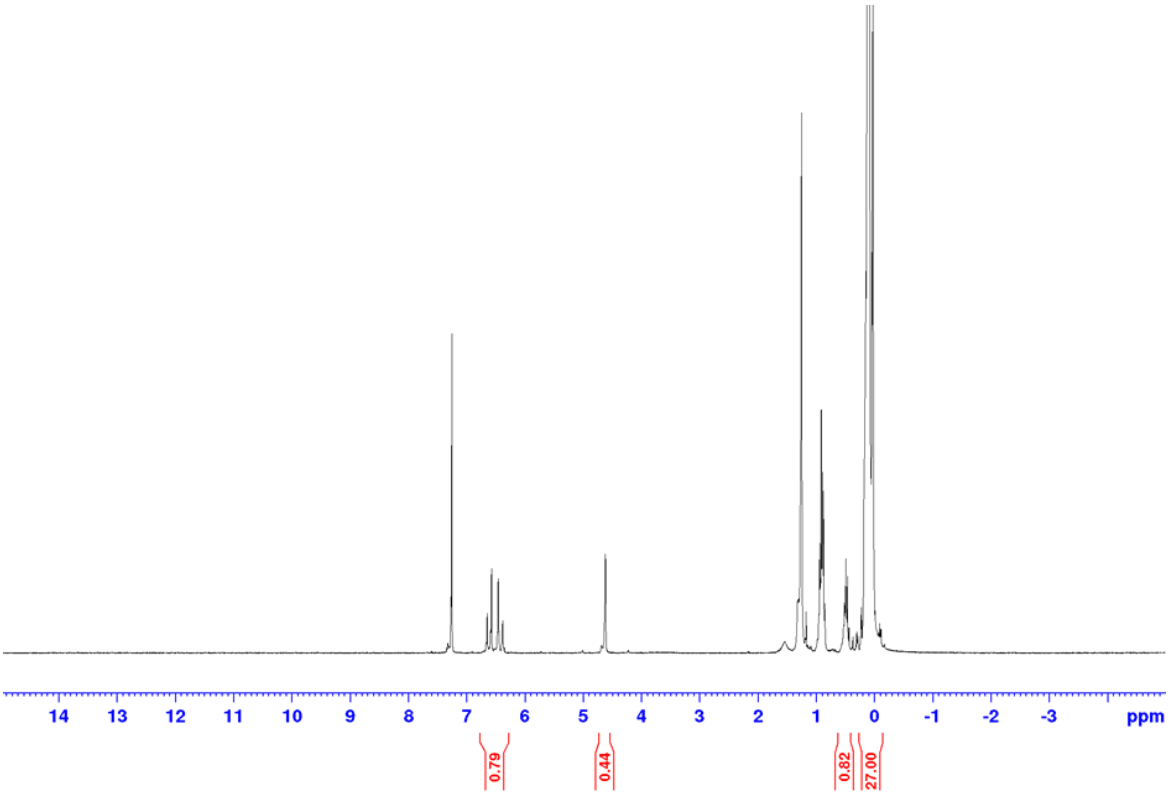



**Figure S13 – $^1H$ NMR spectrum in $CDCl_3$ for the reaction between dvtms and MD'M catalyzed by $Ni(tmhd)_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat) (full spectrum)**

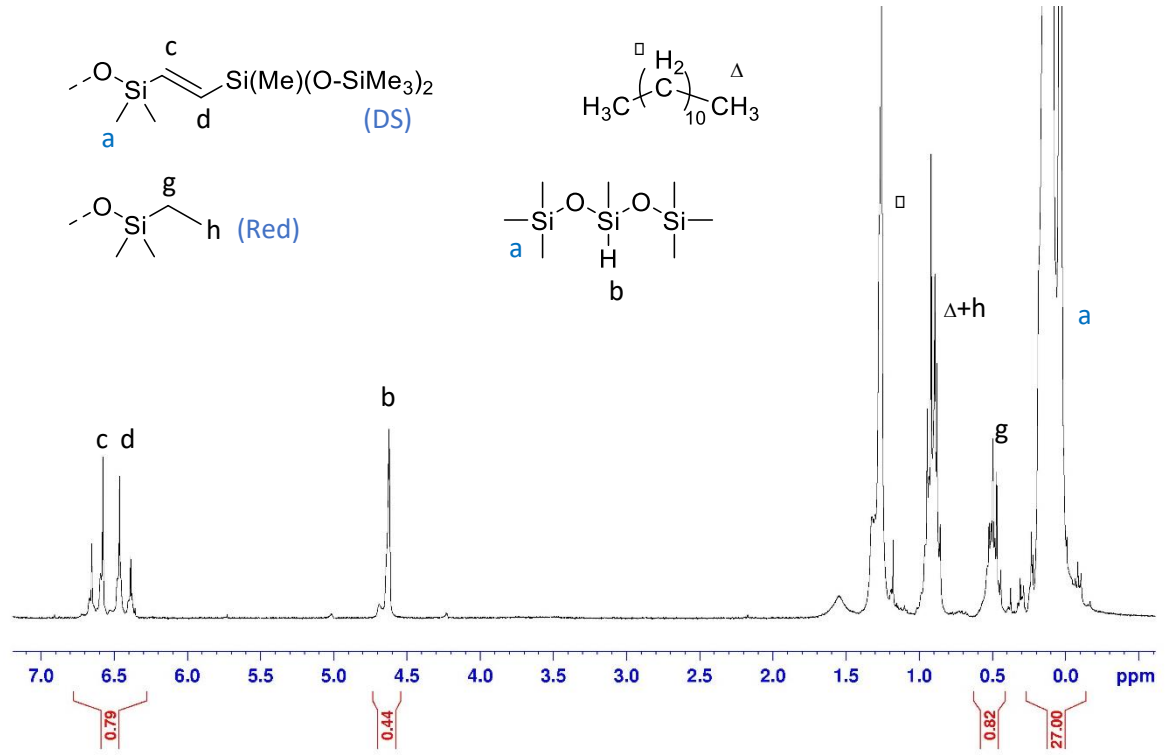



**Figure S14 – $^1H$ NMR spectrum in $CDCl_3$ for the reaction between dvtms and MD'M catalyzed by $Ni(tmhd)_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat)**

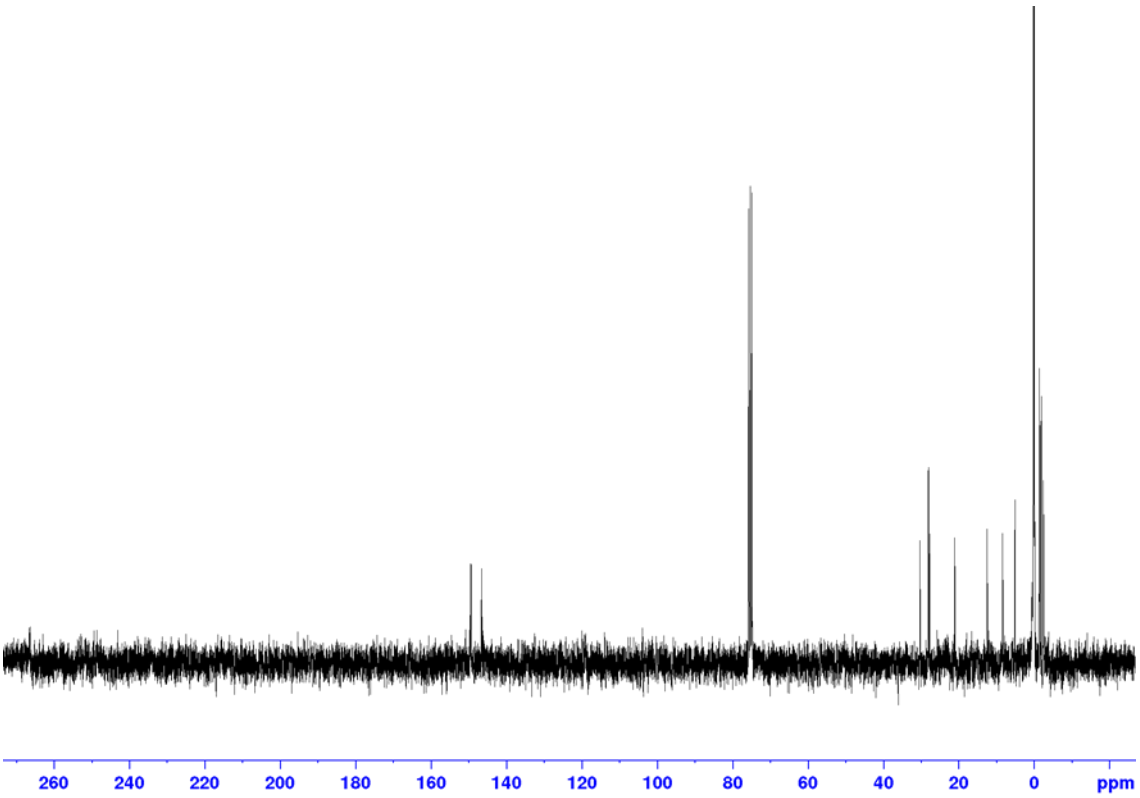



**Figure S15 – $^{13}C$ NMR spectrum in $CDCl_3$ for the reaction between dvtms and MD'M catalyzed by $Ni(tmhd)_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat) (full spectrum)**

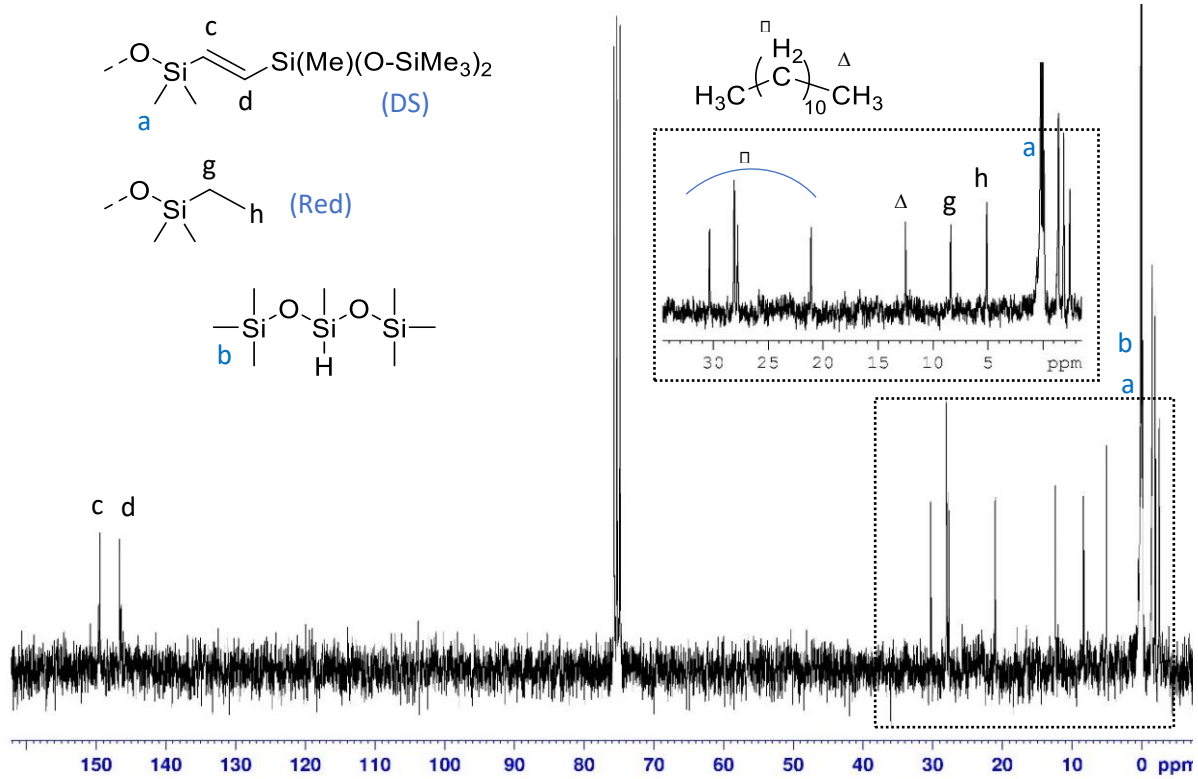



**Figure S16 – $^{13}C$ NMR spectrum in $CDCl_3$ for the reaction between dvtms and MD'M catalyzed by $Ni(tmhd)_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat)**

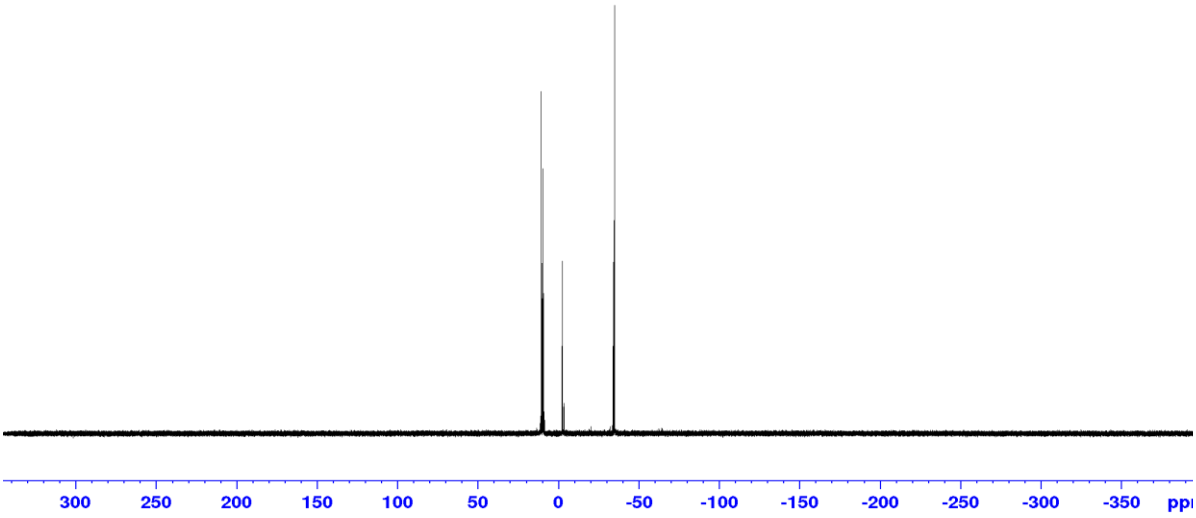



**Figure S17 – $^{29}$Si NMR spectrum in MCH d14 for the reaction between dvtms and MD'M catalyzed by Ni(tmhd)$_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat) (full spectrum)**

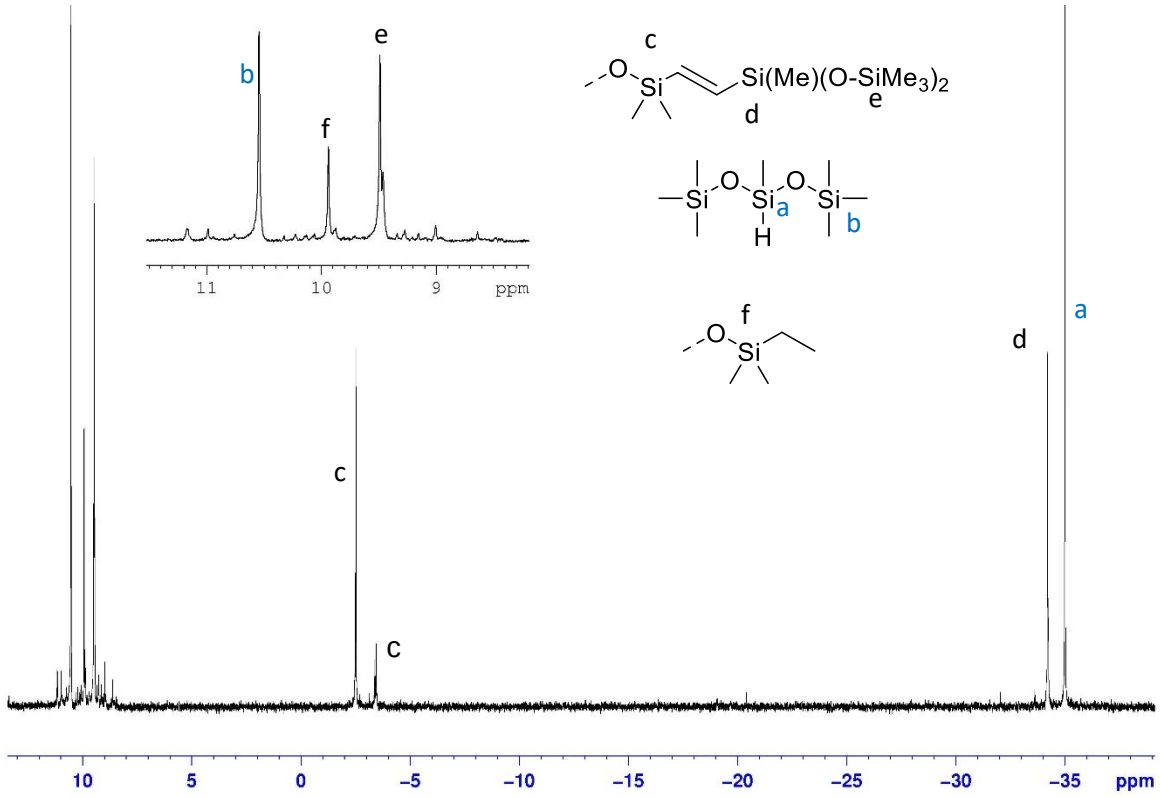



**Figure S18 – $^{29}$Si NMR spectrum in MCH d14 for the reaction between dvtms and MD'M catalyzed by Ni(tmhd)$_2$ (t = 24 h, T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat)**

## 4. $^{1}$H NMR kinetics of the reaction between dvtms and MD'M catalyzed by Ni(tmhd)$_2$

The NMR tube with all the reactants in MCH d14 (dvtms and MD'M catalyzed by Ni(tmhd)$_2$, 0.5 %mol cata, ratio SiH:SiVi = 1, neat) was introduced in the spectrometer at 20°C (room temperature) and shimmed. As the reaction will start only at 90 °C, the tube was heat, under rotation (to avoid any temperature gradient and simulate an agitation), at 50 °C then 70 °C. At each temperature step, the probe was shimmed when all the temperature was stabilized (especially the shim coil temperature) and NMR spectra were recorded to ensure that no reaction occurs. Then, always under rotation, the temperature was set at 90°C, wait until the shim coil temperature stabilized, shimmed and the kinetics started to be recorded. The process was quick enough to ensure that the first spectrum recorded at 90°C is identical to the ones recorded at 20 °C, 50 °C and 70 °C (the reaction did not start).

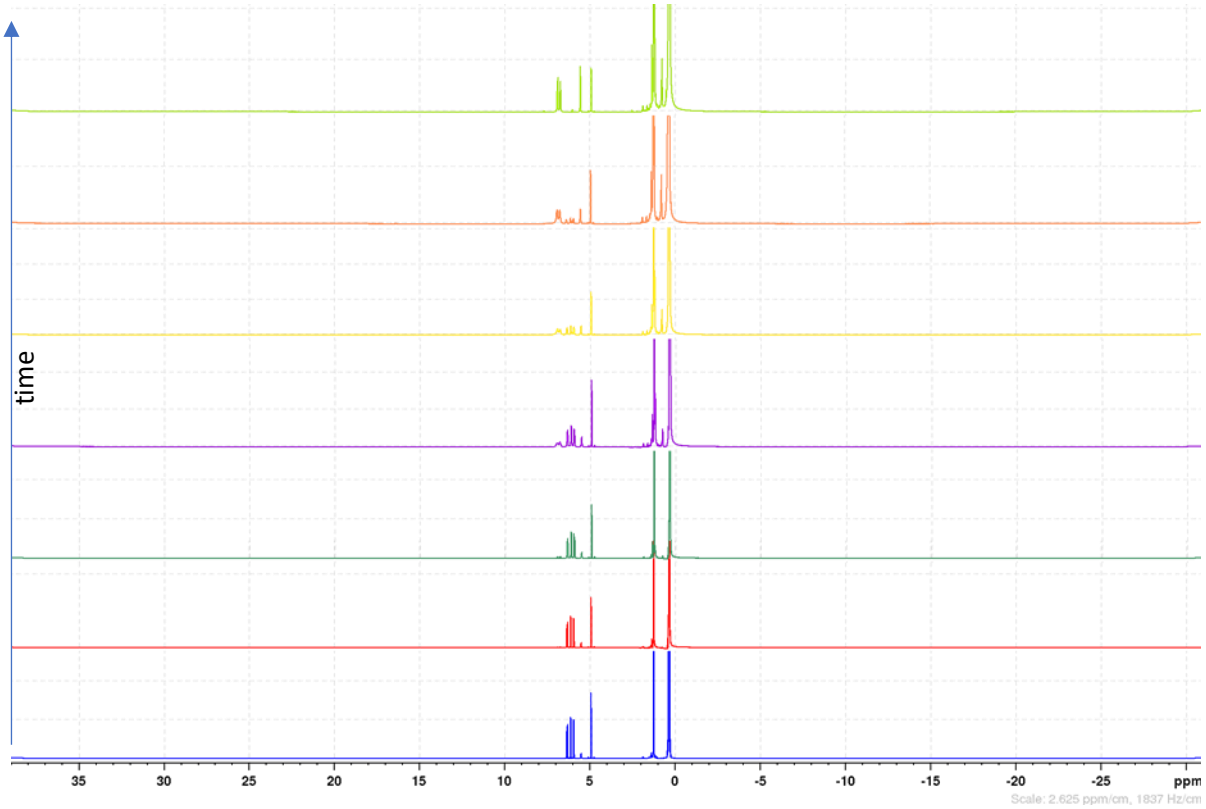



**Figure S19 – $^{1}$H NMR kinetic spectra in MCH d14 for the reaction between dvtms and MD'M catalyzed by Ni(tmhd)$_2$ – superposition in function of time (T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat) (full spectrum)**

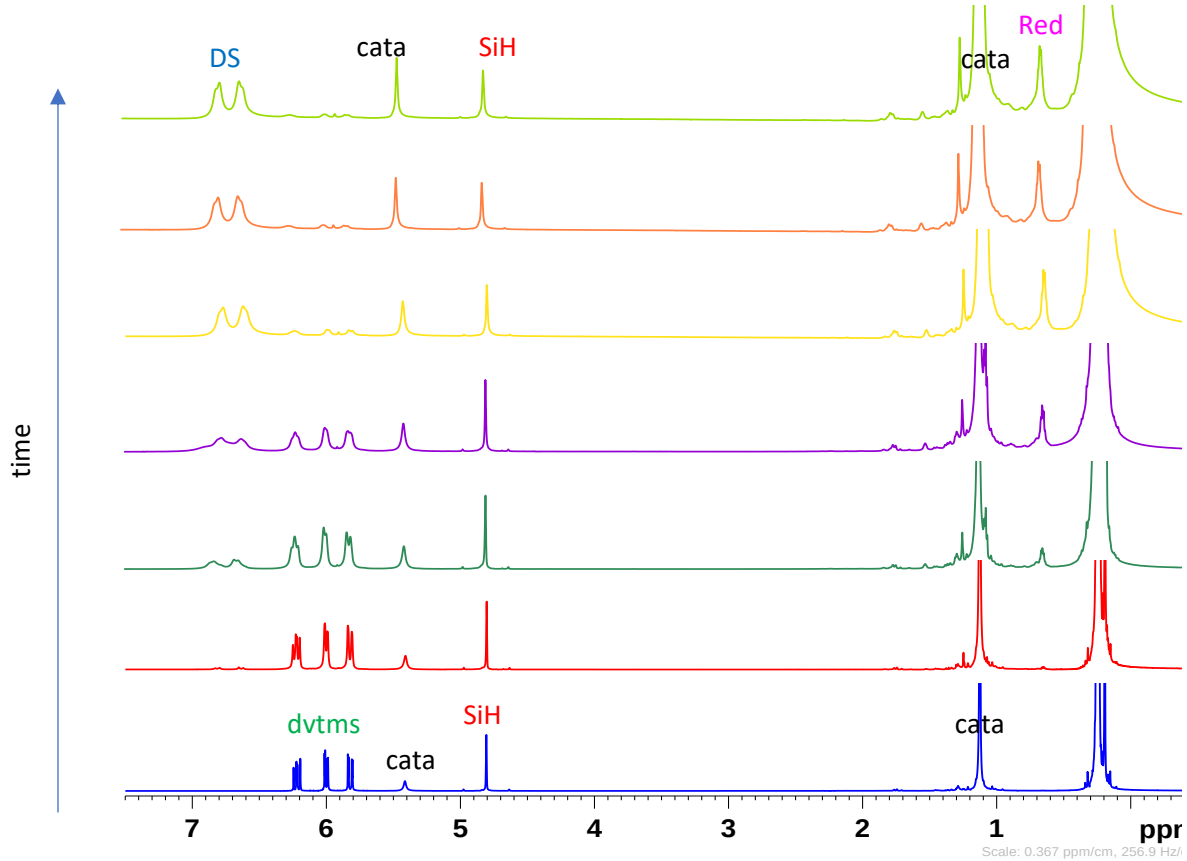
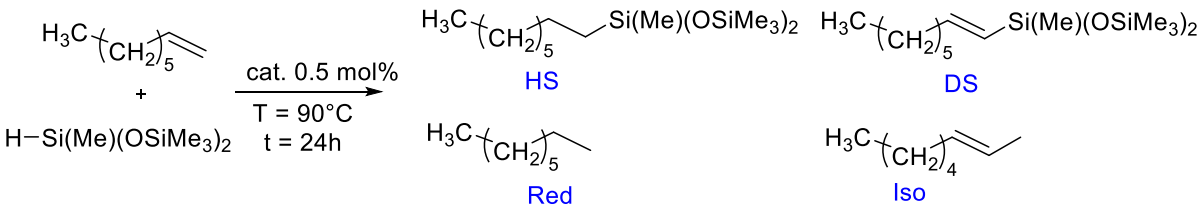



**Figure S20 – $^1$H NMR kinetic spectra in MCH d14 for the reaction between dvtms and MD'M catalyzed by Ni(tmhd)$_2$ – superposition in function of time (T = 90 °C, 0.5 %mol cata, ratio SiH:SiVi = 1, neat)**

## 5. Evaluation of catalytic activity for 1-octene silylation with MD'M depending of the different complexes

**Table S1 – Evaluation of catalytic activity for 1-octene hydrosilylation with MD'M**




| | | Conversion (%) | | Selectivity (%1-octene) | | | |
|---|---|---|---|---|---|---|---|
| *Entry* | *Catalyst* | MD'M | 1-octene | HS | DS | Red | Iso |
| 1 | $Ni(acac)_2$ | 7% | 32% | 21% | 5% | 5% | 70% |
| 2 | $Ni(tmhd)_2$ | 39% | 100% | 39% | 5% | 8% | 49% |
| 3 | $Co(acac)_2$ | 14% | 34% | 26% | 7% | 8% | 59% |
| 4 | $Co(tmhd)_2$ | 26% | 53% | 21% | 12% | 11% | 56% |

*Reaction conditions: 90°C, neat, 0.5mol%, ratio SiH/SiVi =1:1, 24h reaction time*

*Selectivities and Conversions were determined using a combination of NMR, GC-MS (for product identification) and GC for conversions.*

## 6. Thermal kinetics by DSC analysis

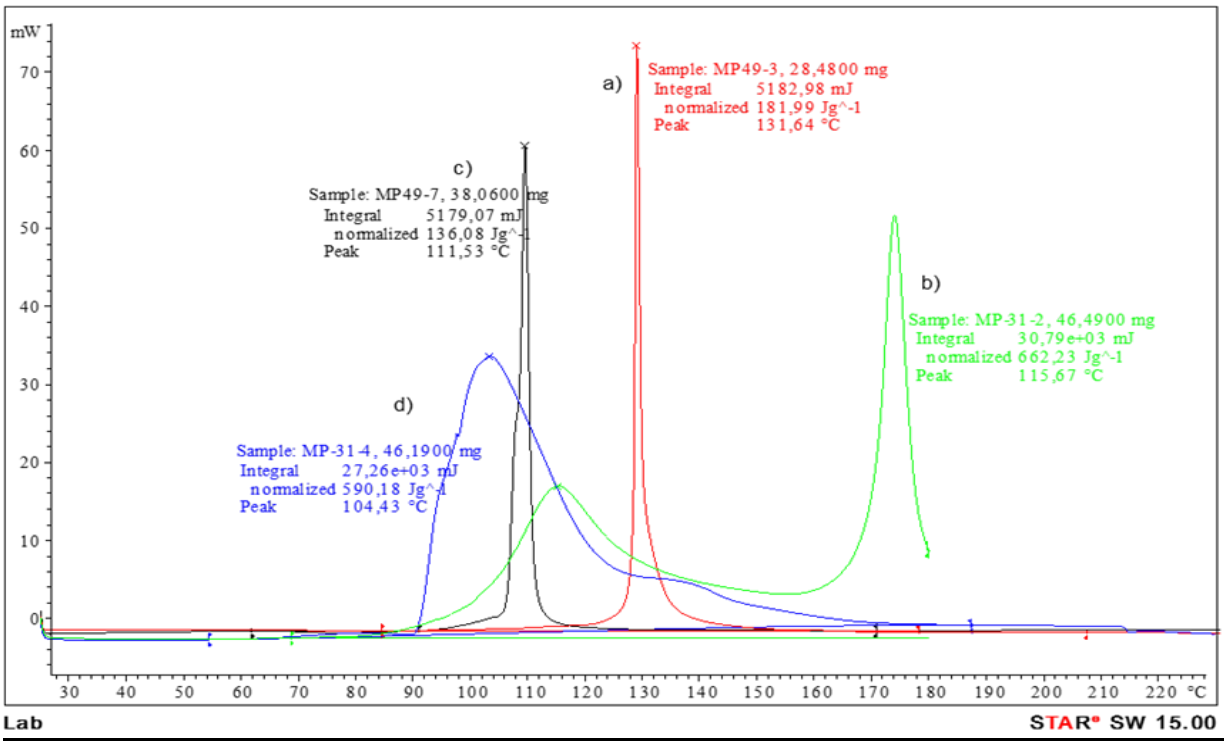



**Figure S21 – DSC thermograms of dvtms and poly-SiH PDMS oil crosslinking, a) $Ni(acac)_2$, b) $Ni(tmhd)_2$, c) $Co(acac)_2$ and d) $Co(tmhd)_2$. Reaction conditions: 8°C/min, 0.5 mol%, ratio SiH/SiVi =1:1**

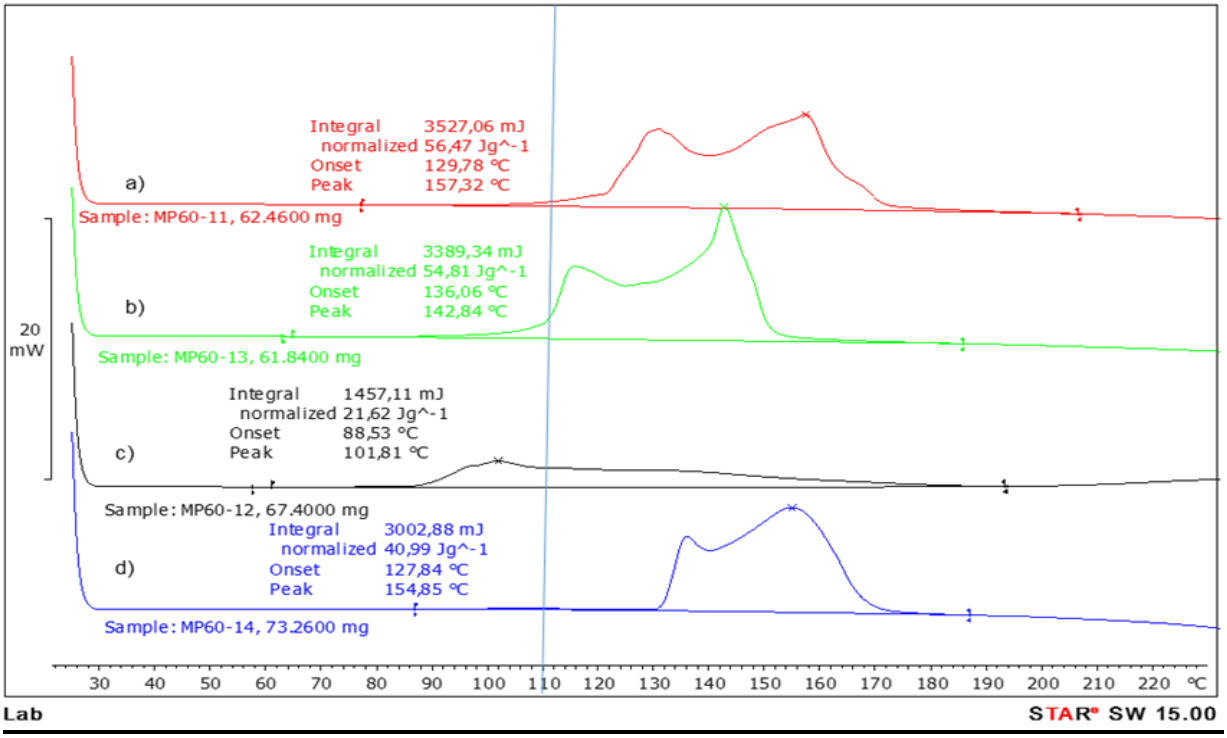
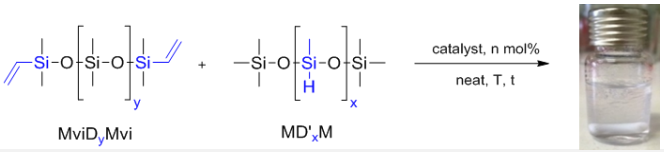



**Figure S22 – DSC thermograms of dvtms and poly-SiH PDMS oil crosslinking, a) $Ni(acac)_2$, b) $Ni(tmhd)_2$, c) $Co(acac)_2$ and d) $Co(tmhd)_2$. Reaction conditions: 8°C/min, 0.5 mol%, ratio SiH/SiVi =1:1**

## 7. $^{1}H$ and $^{13}C$ HR-MAS NMR studies of crosslinked silicone gels

First, network of crosslinked silicones are formed according to the conditions indicated in the Table S2.

**Table S2 – Conditions of catalytic tests for divinyl and poly-SiH silicone oils crosslinking**




MviD$_y$Mvi + MD'$_x$M

| Entry | *y* | *X* | *Catalyst* | Mol% | SiH:SiVi | T | SST |
|---|---|---|---|---|---|---|---|
| 1 | 20 | 50 | $Ni(acac)_2$ | 1 | 3 | 110 | 30 min |
| 2 | 20 | 50 | $Ni(tmhd)_2$ | 1 | 3 | 110 | 15 min |
| 3 | 20 | 50 | $Co(acac)_2$ | 1 | 3 | 110 | 25 min |
| 4 | 20 | 50 | $Co(tmhd)_2$ | 1 | 3 | 110 | 40 min |

After the SST, networks are allowed to return to ambient temperature. Then, samples were swelled 3h in $CDCl_3$ and introduced into 50-µL $ZrO_2$ rotors.

High-resolution magic angle spinning (HR MAS) NMR spectroscopy was recorded in a Bruker AVANCE III 400-MHz spectrometer with a 4-mm $^{1}H/^{13}C$ HR-MAS dual Probe at a spinning rate of 5 kHz at room temperature.

On the $^{1}H$ NMR spectra, when rotor were packed with “acac” complexes, three visible signals are attributed to spinning side bands (12.57, 17.22 and 17.40 ppm at 5kHz from the isotropic peaks). With “tmhd” complexes, two visible signals are attributed to spinning side bands (12.57 and 17.22 ppm). The spinning side bands are identified on the spectra with *

The spinning side bands were identified by recording the spectra at different field with two different spinning frequencies (at different spinning frequencies and different field, only the chemical of the spinning side bands will change)

On all the $^{13}C$ NMR spectra, the broad signal centered at 110.9 ppm is attributed to the background signal (probably due to PTFE insert, see *Macromolecules* **2001**, 34 (24), 8416–8418) while the signal at 50.9 ppm corresponds to a spinning side band.

❖ $Ni(acac)_2$

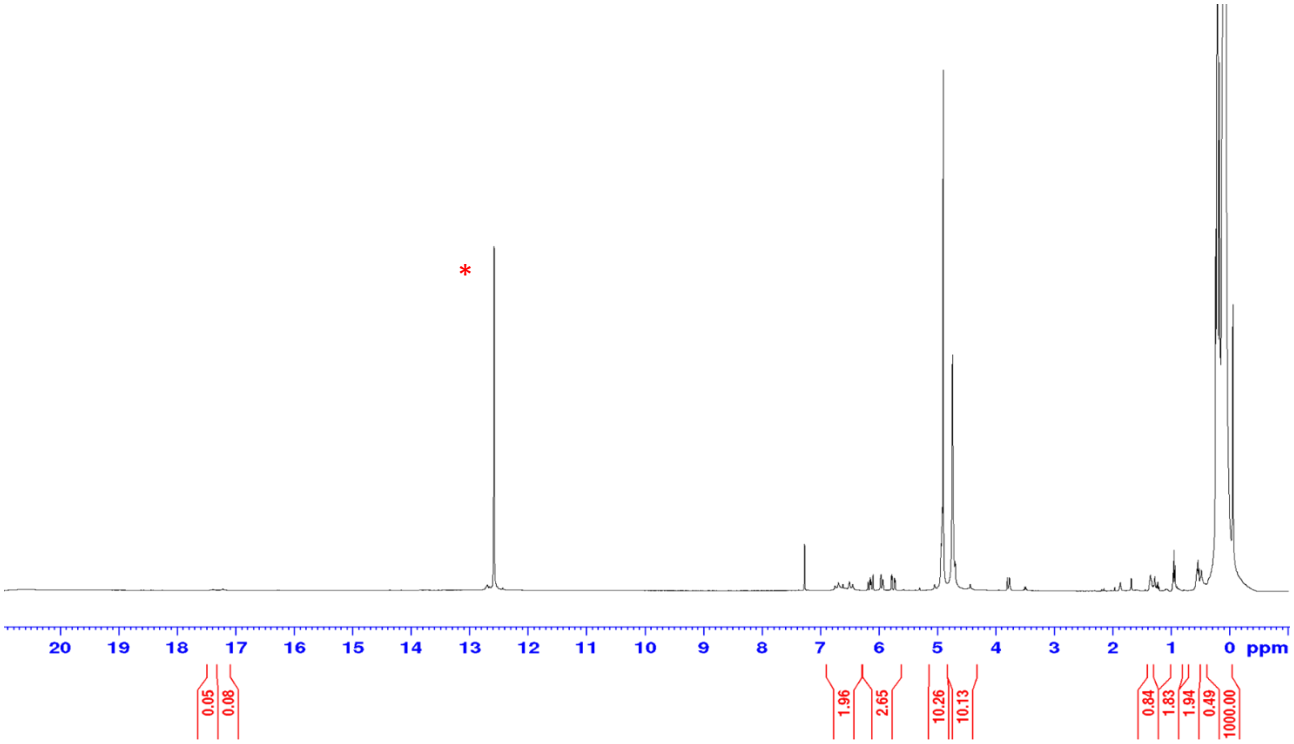



**Figure S23 – $^1H$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(acac)_2$ (full spectrum) * = spinning side bands**

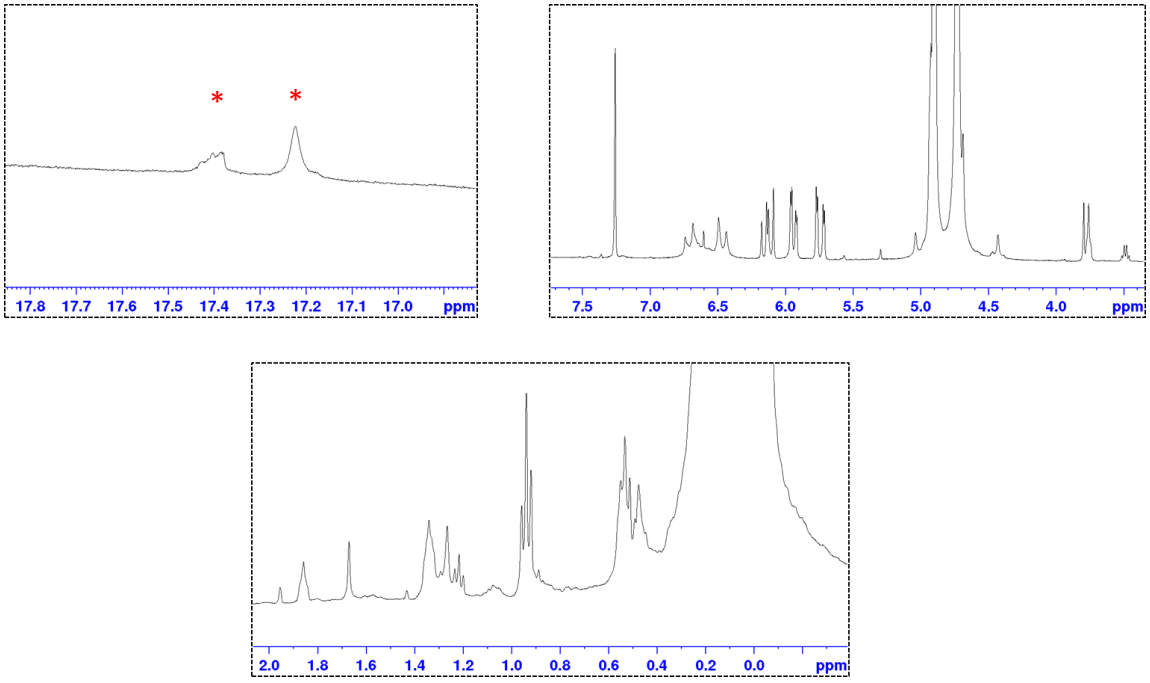



**Figure S24 – Focus on the different regions of interest of the $^1H$ HR-MAS NMR spectrum for the the crosslinked silicone gel obtained with $Ni(acac)_2$ ; * = spinning side bands**

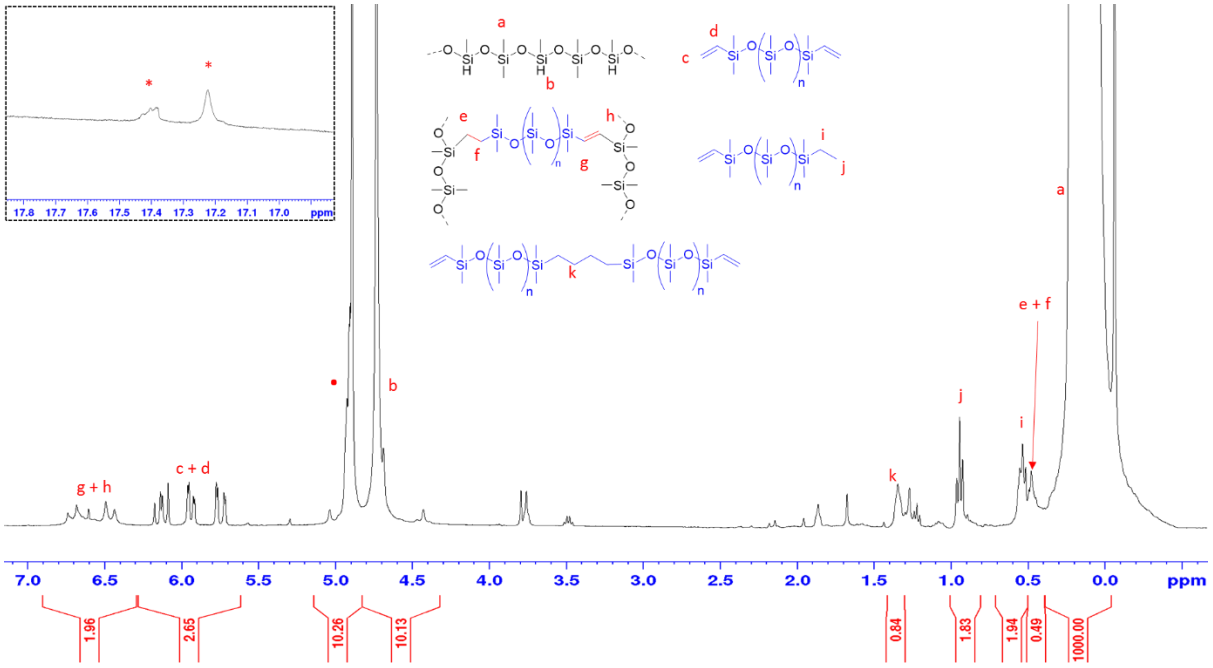



**Figure S25 – $^{1}$H HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(acac)_2$; * = spinning side bands**

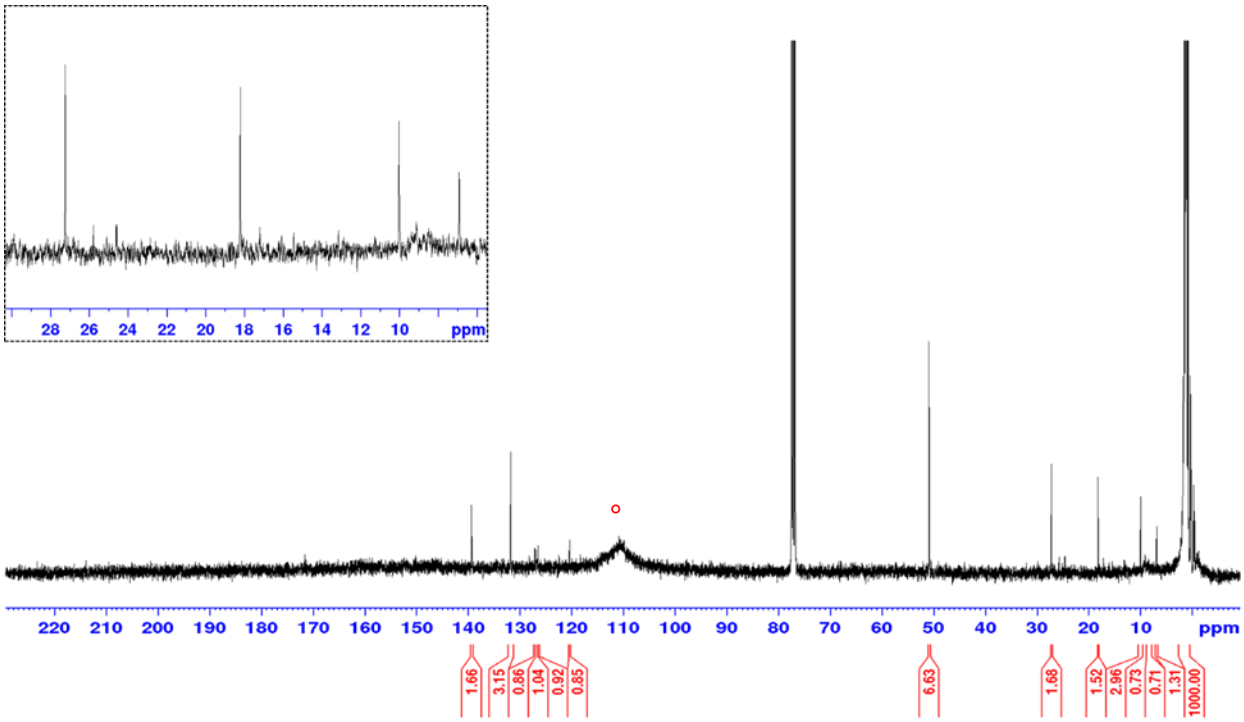



**Figure S26 – $^{13}$C HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(acac)_2$ (full spectrum) ° = background signal**

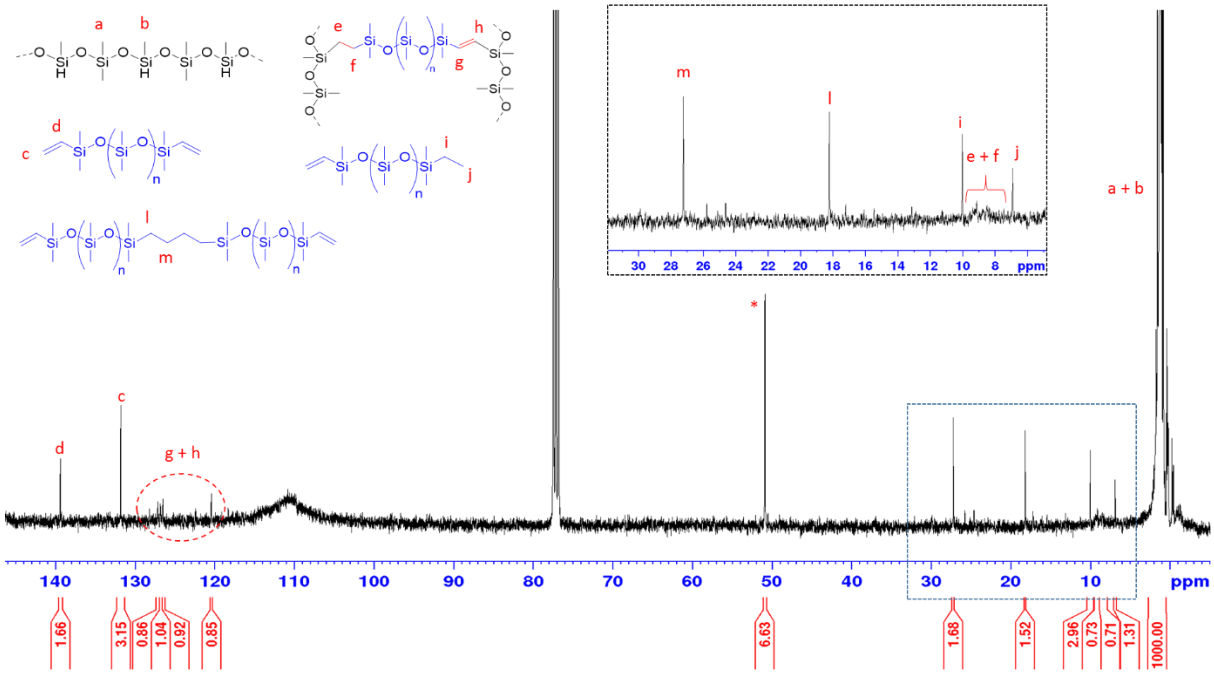



**Figure S27 – $^{13}C$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(acac)_2$ ; * = spinning side bands**

❖ $Ni(tmhd)_2$

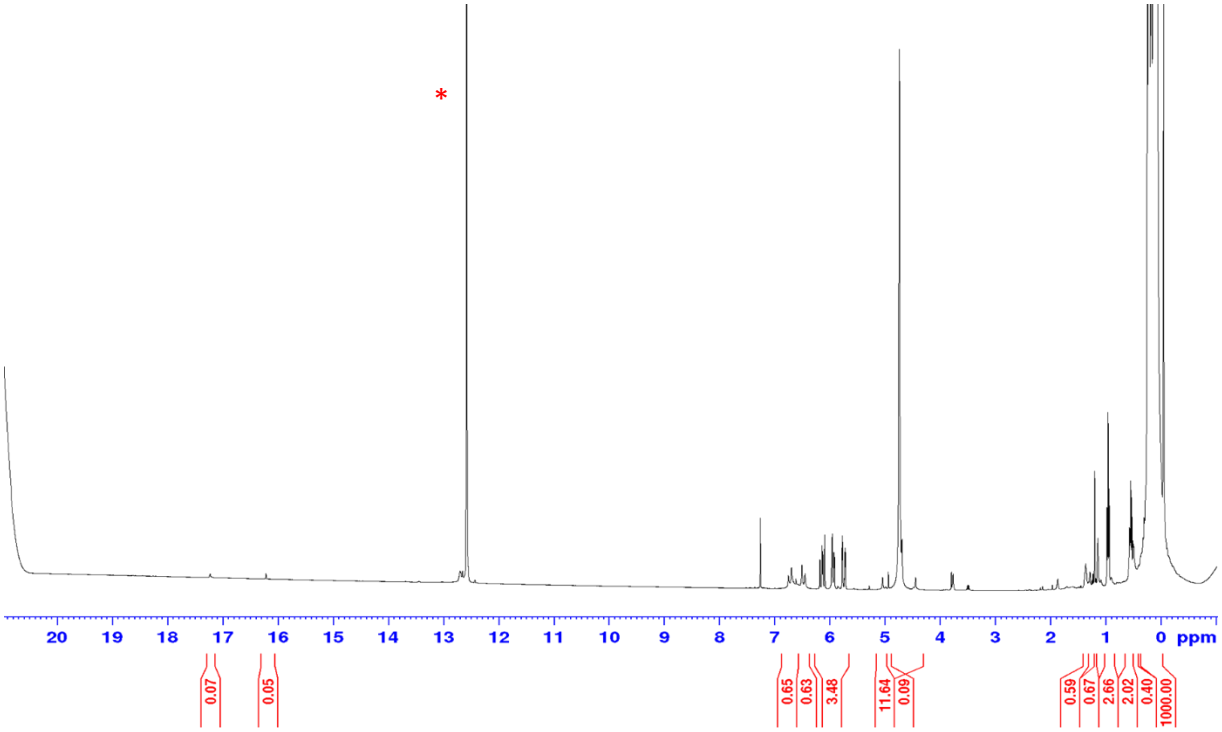



**Figure S28 – $^1H$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(tmhd)_2$ (full spectrum); * = spinning side bands**

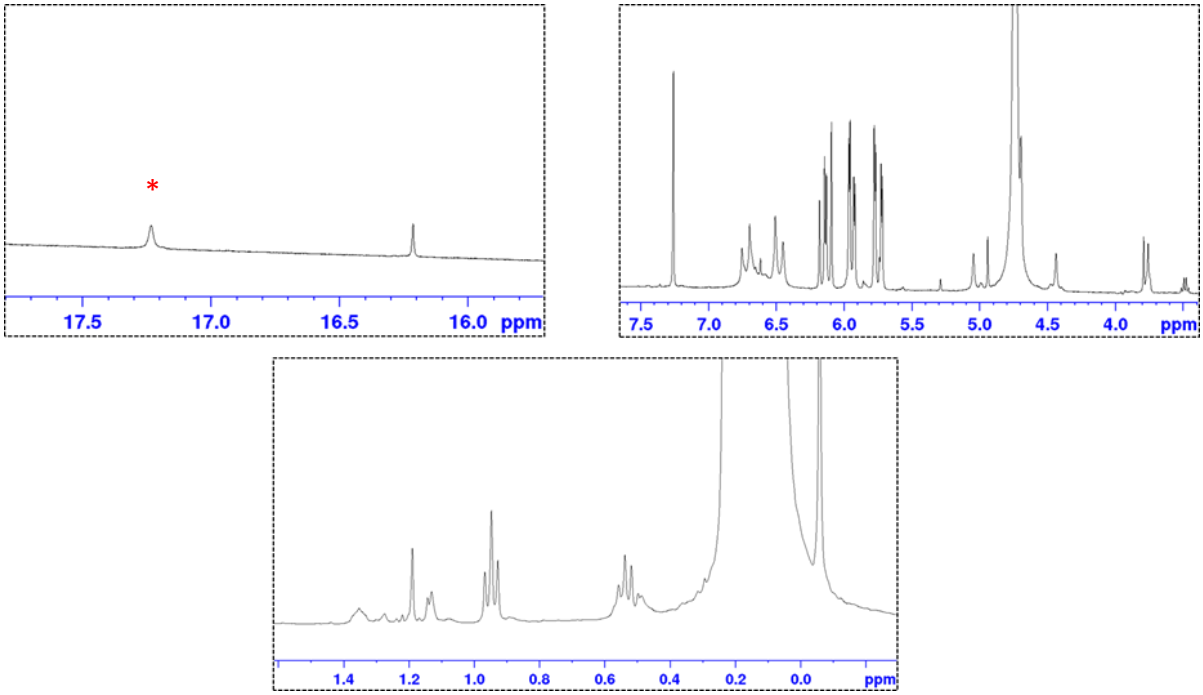



**Figure S29 – Focus on the different regions of interest of the $^1H$ HR-MAS NMR spectrum for the the crosslinked silicone gel obtained with $Ni(tmhd)_2$ ; * = spinning side bands**

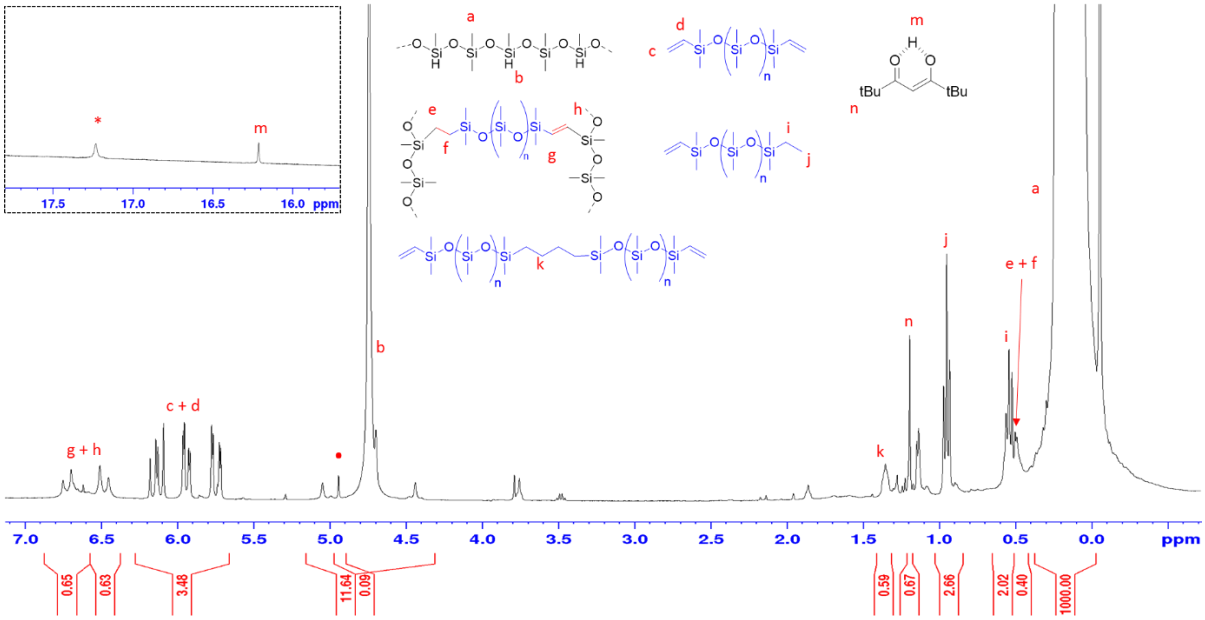



**Figure S30 – $^{1}$H HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(tmhd)_2$ ; * = spinning side bands**

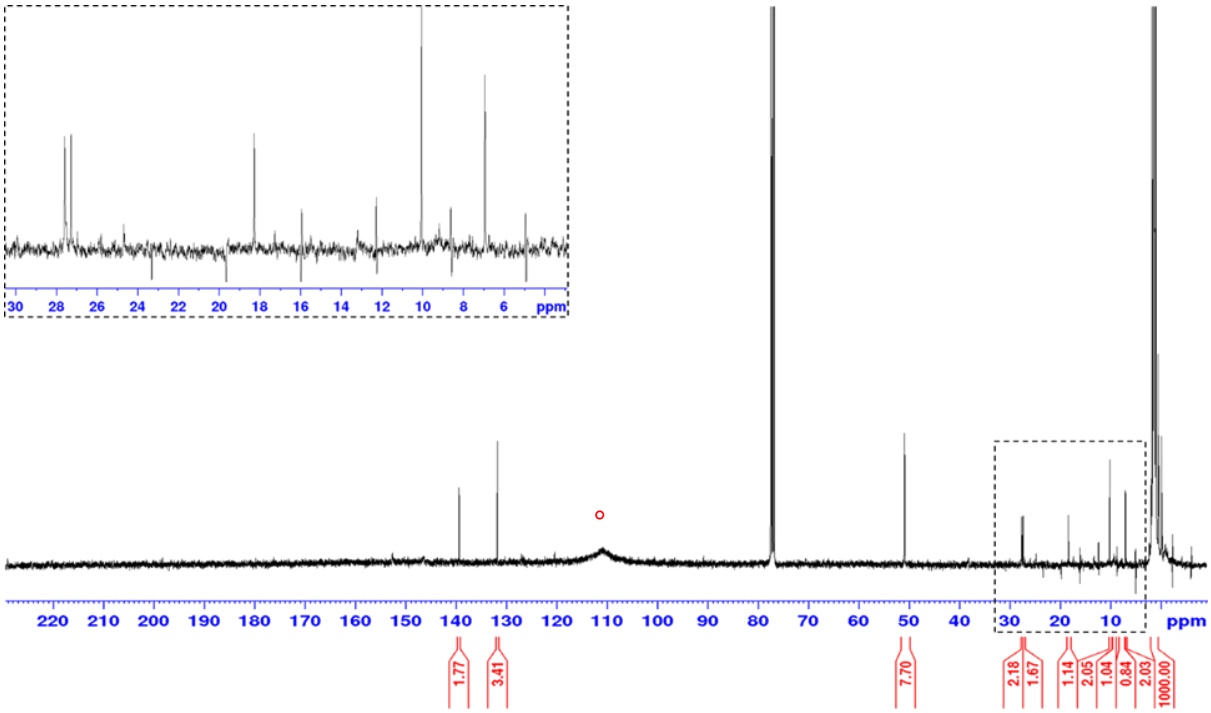



**Figure S31 – $^{13}$C HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(tmhd)_2$ (full spectrum) ° = background signal**

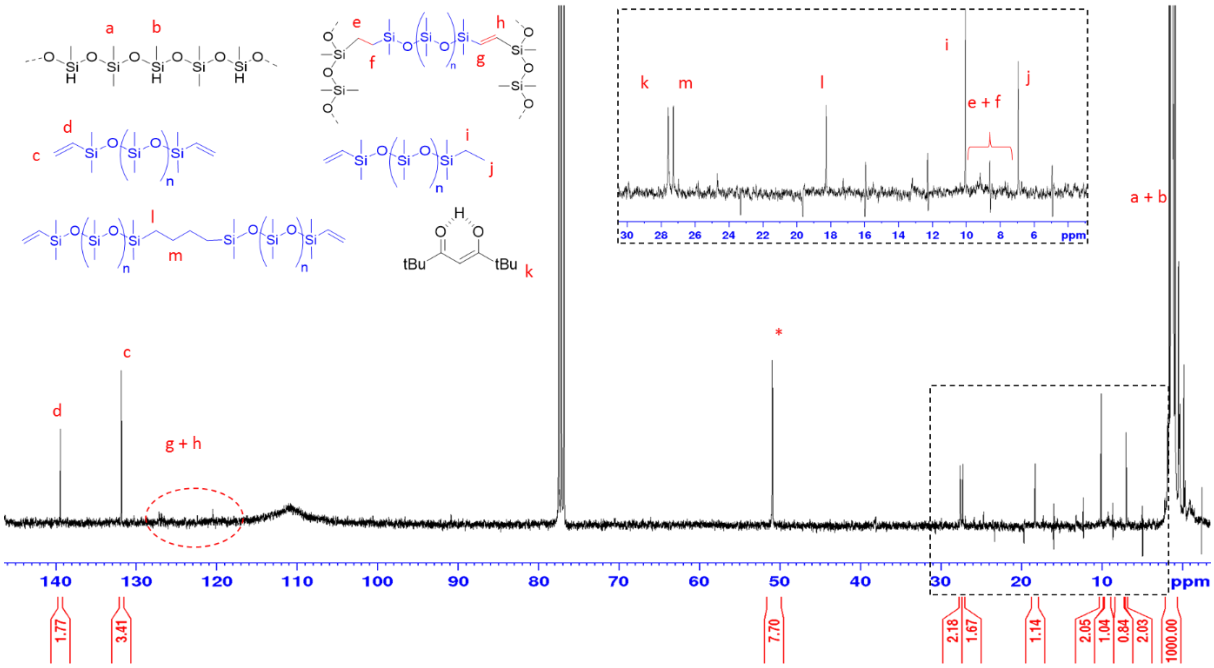



**Figure S32 – $^{13}$C HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Ni(tmhd)_2$ ; * = spinning side bands**

❖ $Co(acac)_2$

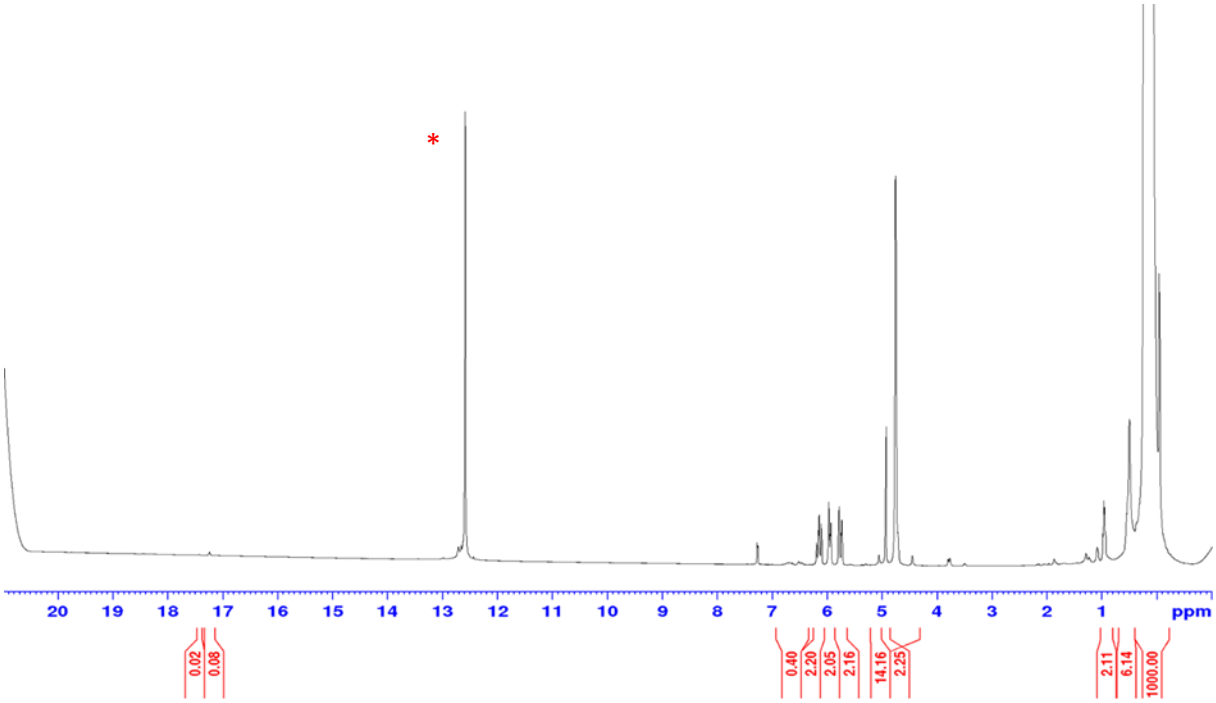



**Figure S33 – $^1$H HR-MAS NMR spectrum in CDCl3 for the crosslinked silicone gel obtained with $Co(acac)_2$ (full spectrum) ; * = spinning side bands**

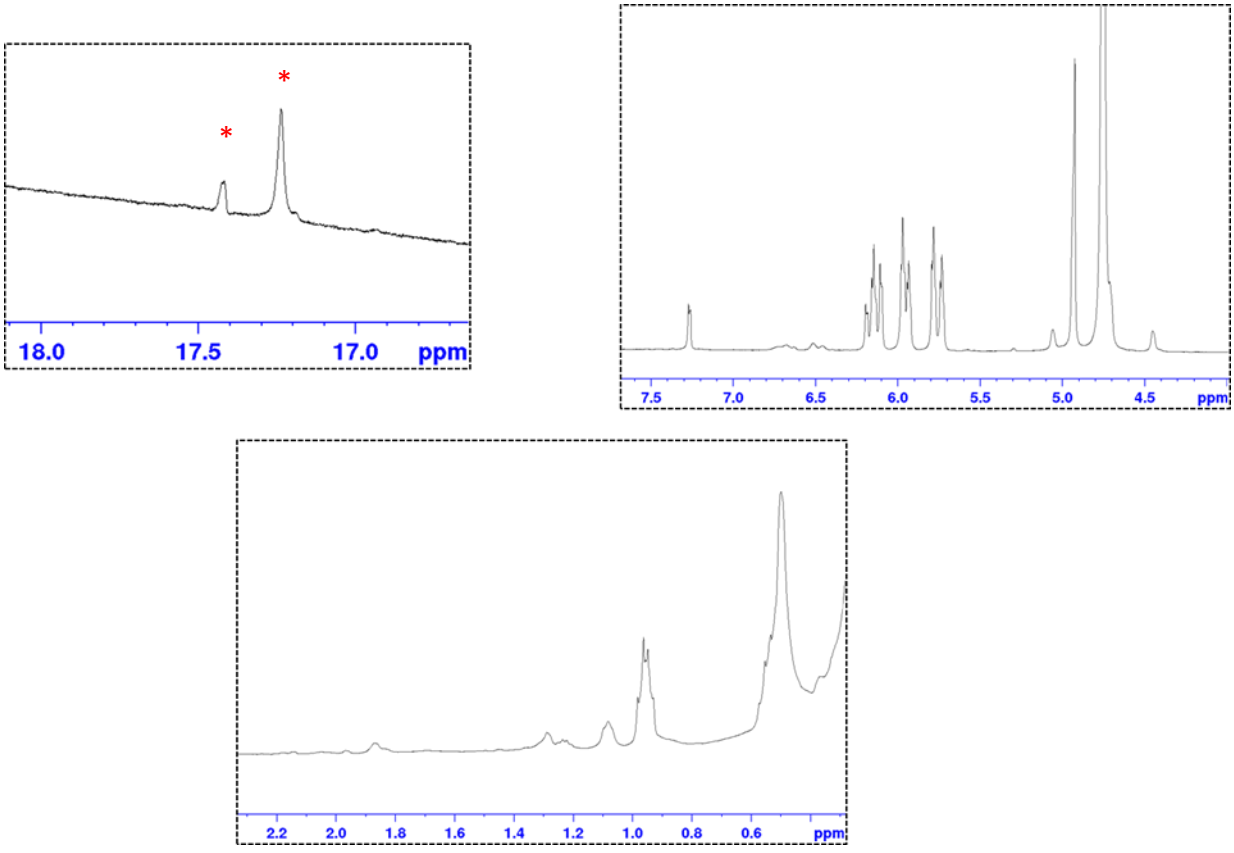



**Figure S34 – Focus on the different regions of interest of the $^1$H HR-MAS NMR spectrum for the the crosslinked silicone gel obtained with $Co(acac)_2$ ; * = spinning side bands**

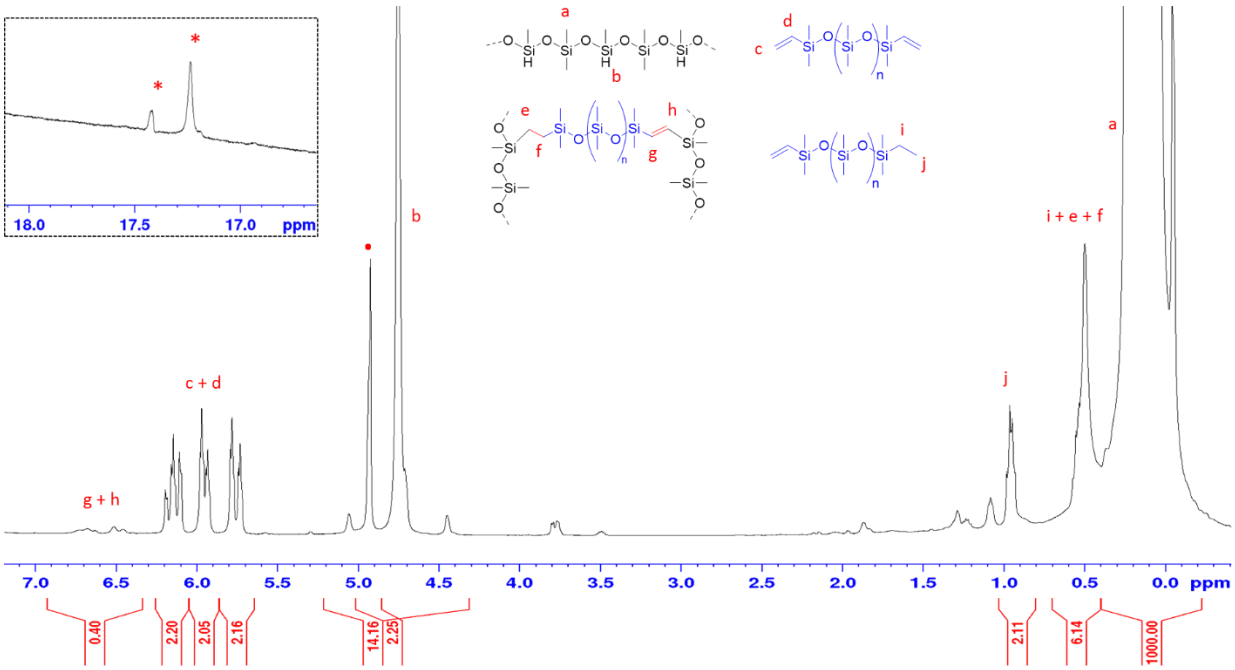



**Figure S35 – $^{1}$H HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(acac)_2$ ; * = spinning side bands**

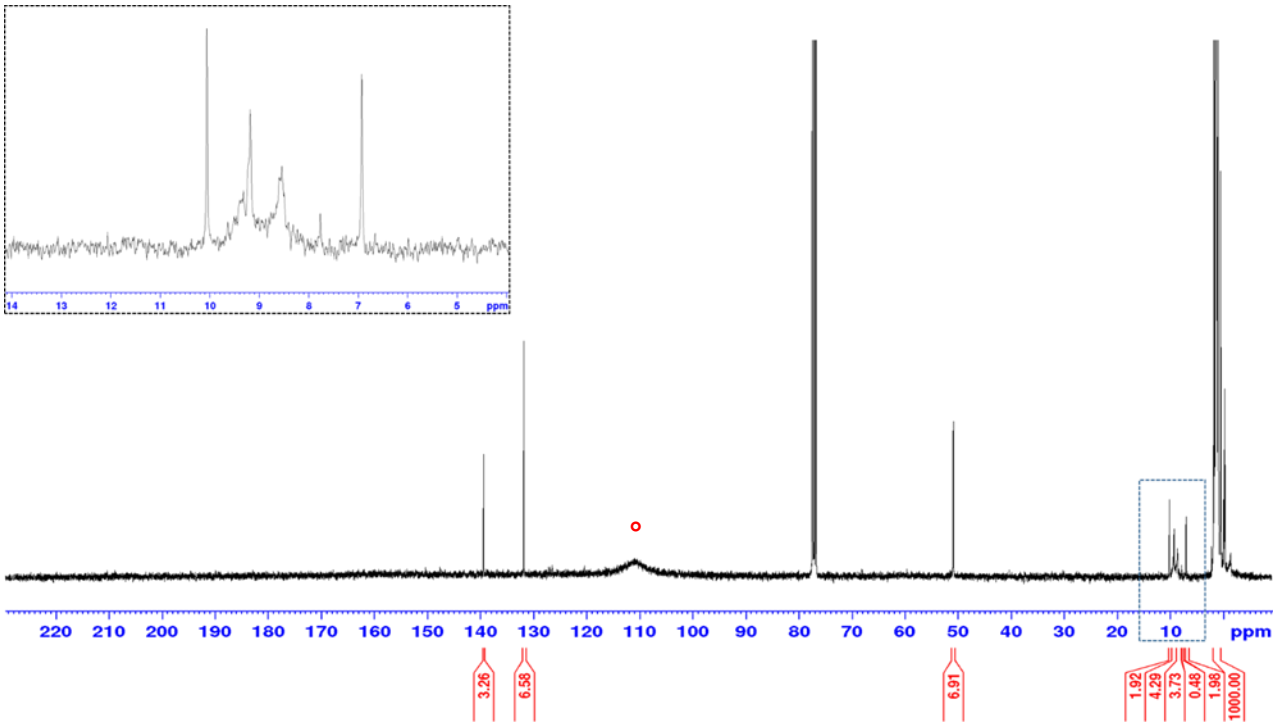



**Figure S36 – $^{13}$C NMR HR-MAS spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(acac)_2$ (full spectrum) ° = background signal**

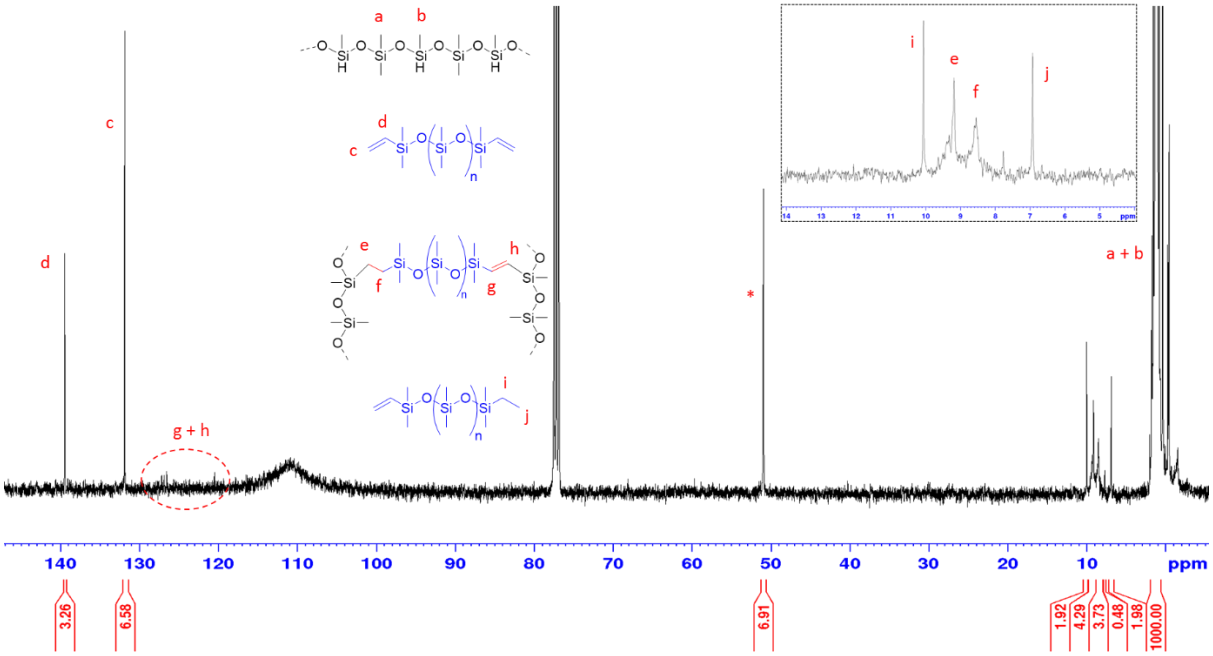



**Figure S37 – $^{13}C$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(acac)_2$ ; * = spinning side bands**

❖ $Co(tmhd)_2$

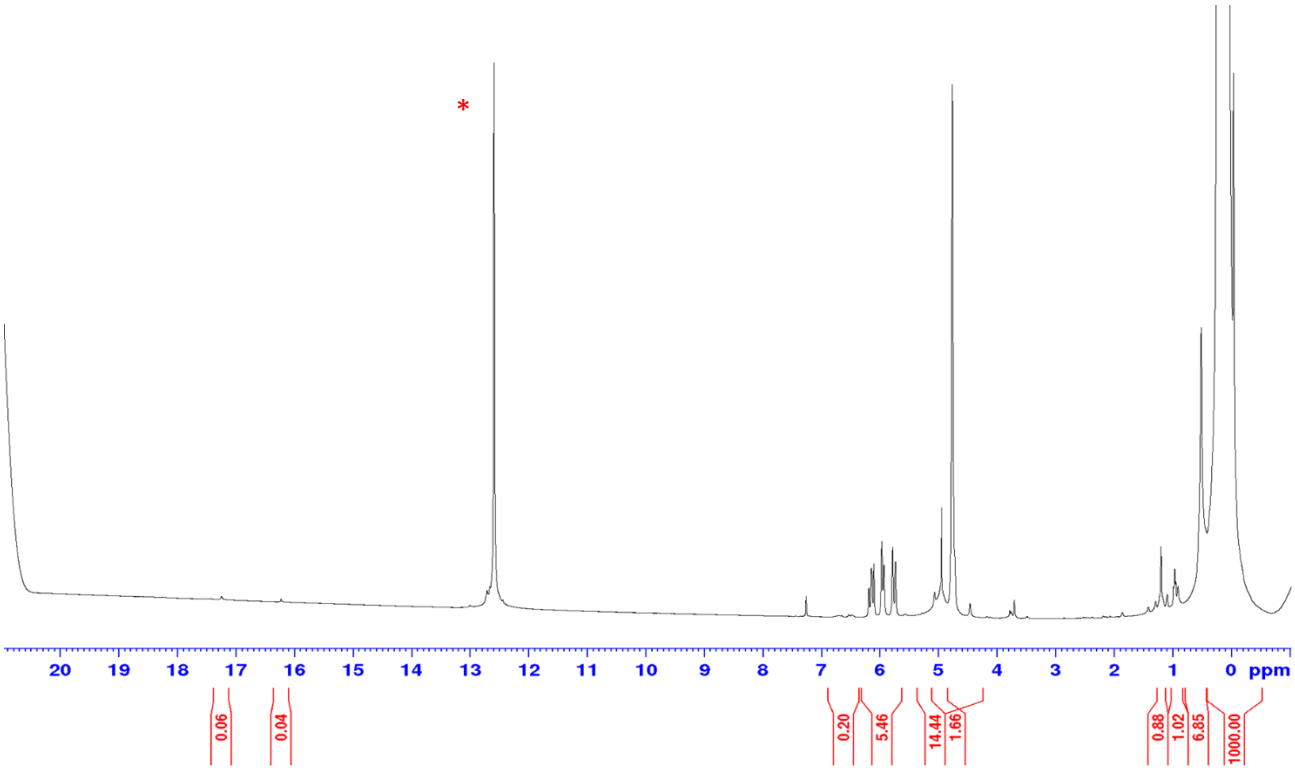



**Figure S38 – $^1H$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(tmhd)_2$ (full spectrum); * = spinning side bands**

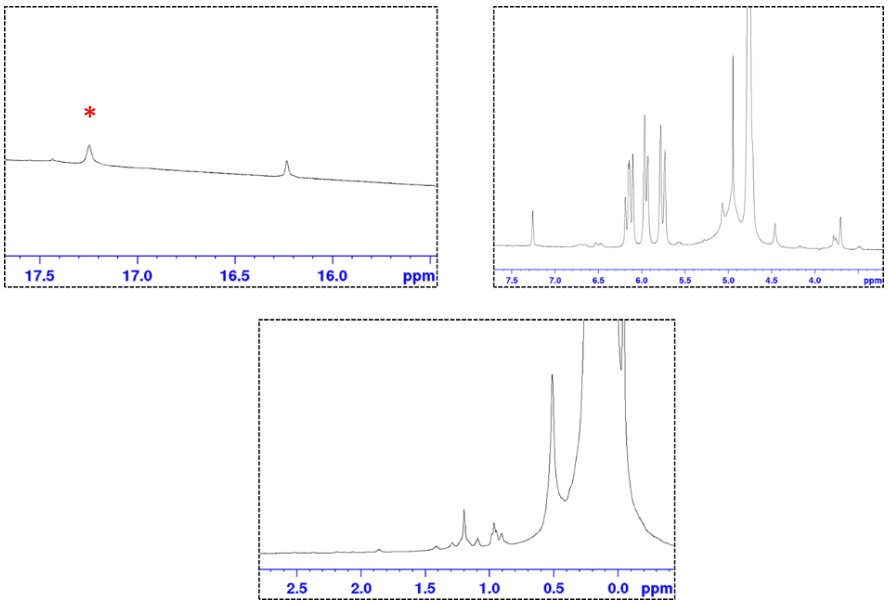



**Figure S39 – Focus on the different regions of interest of the $^1H$ HR-MAS NMR spectrum for the the crosslinked silicone gel obtained with $Co(tmhd)_2$ ; * = spinning side bands**

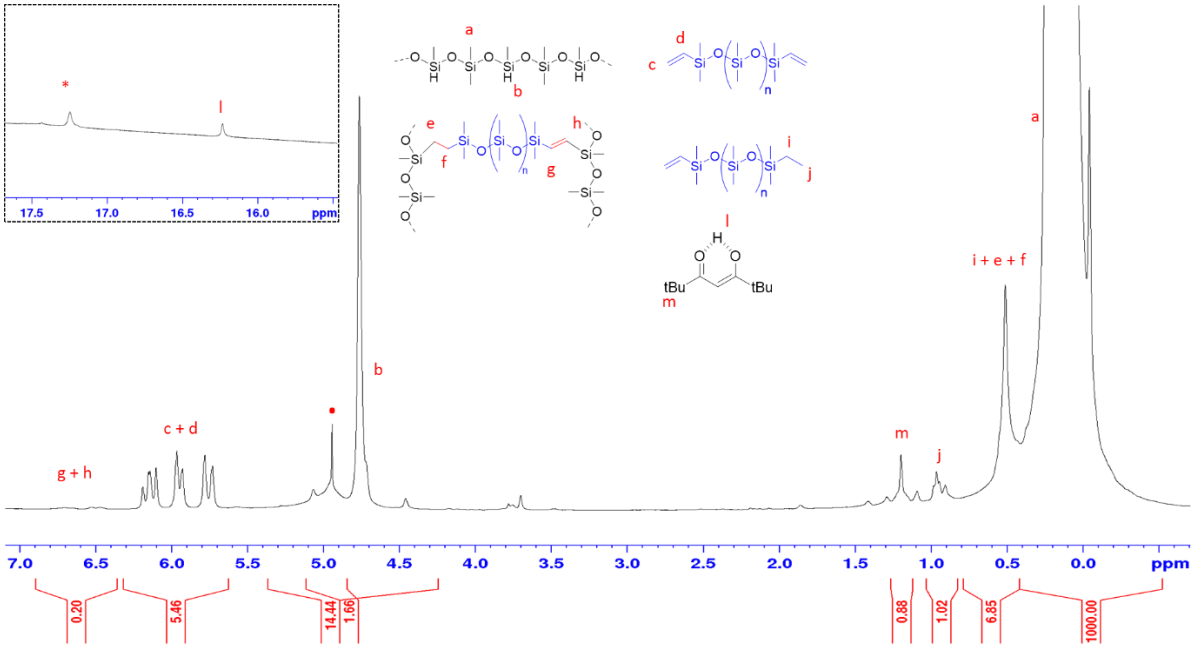



**Figure S40 – $^{1}$H HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(tmhd)_2$ ; * = spinning side bands**

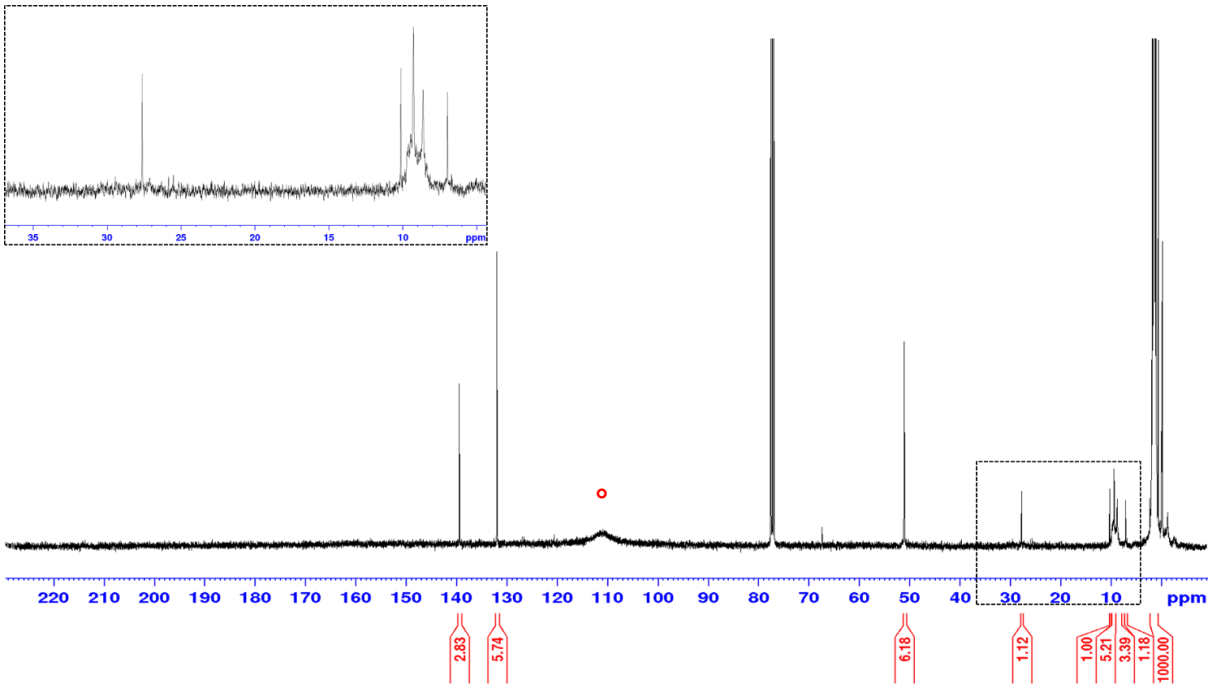



**Figure S41 – $^{13}$C HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(tmhd)_2$ (full spectrum) ° = background signal**

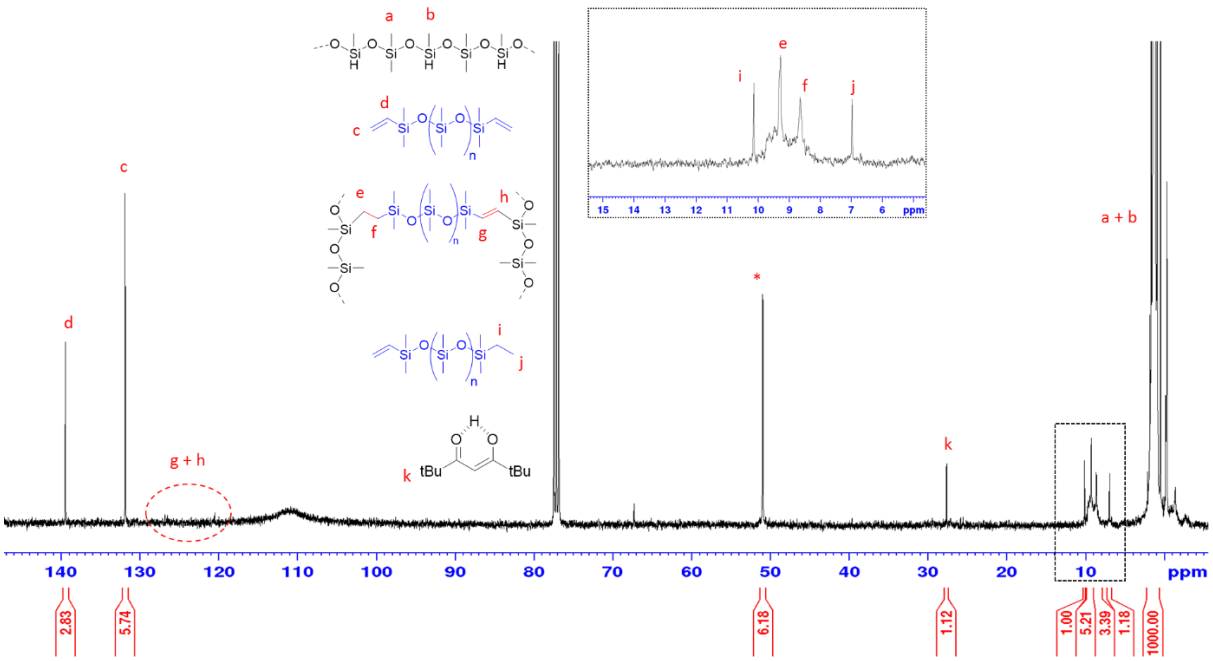



**Figure S42 – $^{13}C$ HR-MAS NMR spectrum in $CDCl_3$ for the crosslinked silicone gel obtained with $Co(tmhd)_2$ ; * = spinning side bands**

❖ Overlay of $^{1}H$ NMR HR-MAS spectra and $^{13}C$ NMR HR-MAS spectra

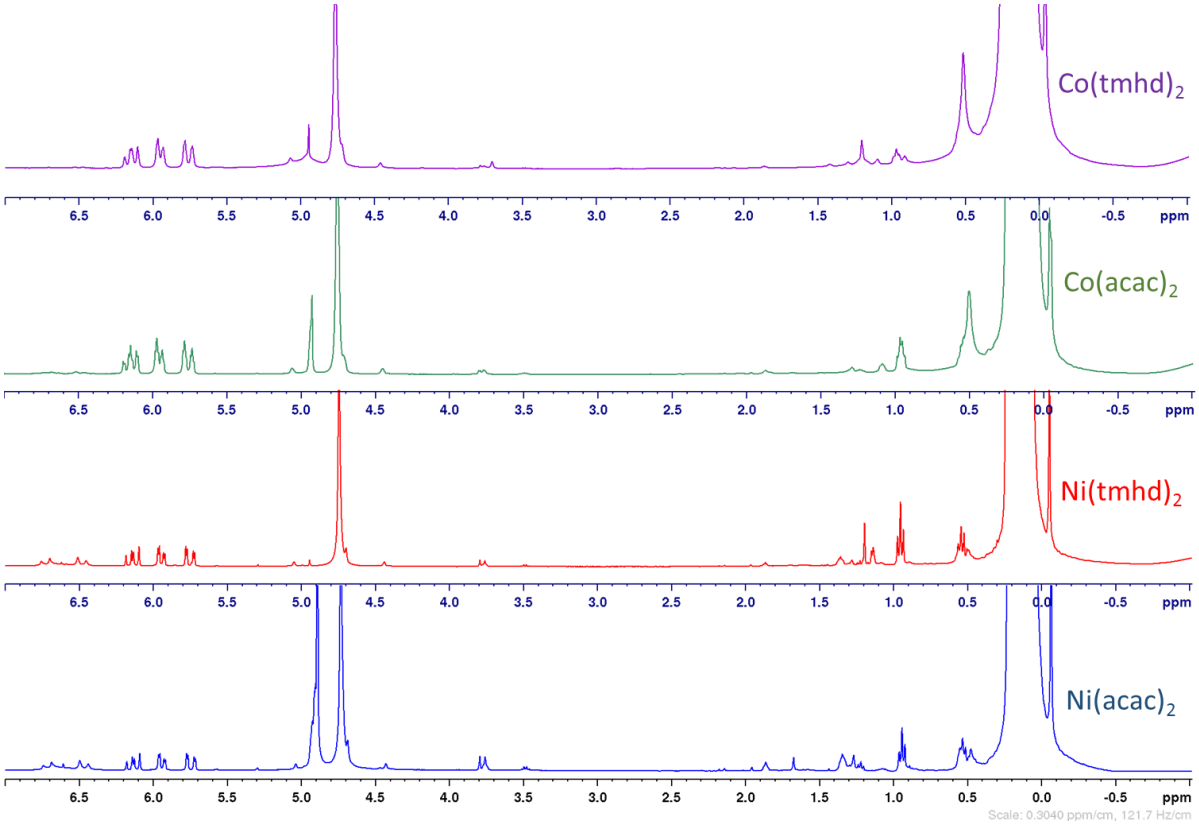



**Figure S43 – Overlay of $^{1}H$ HR-MAS NMR spectra in $CDCl_3$ for the crosslinked silicone gel obtained with the four catalysts**

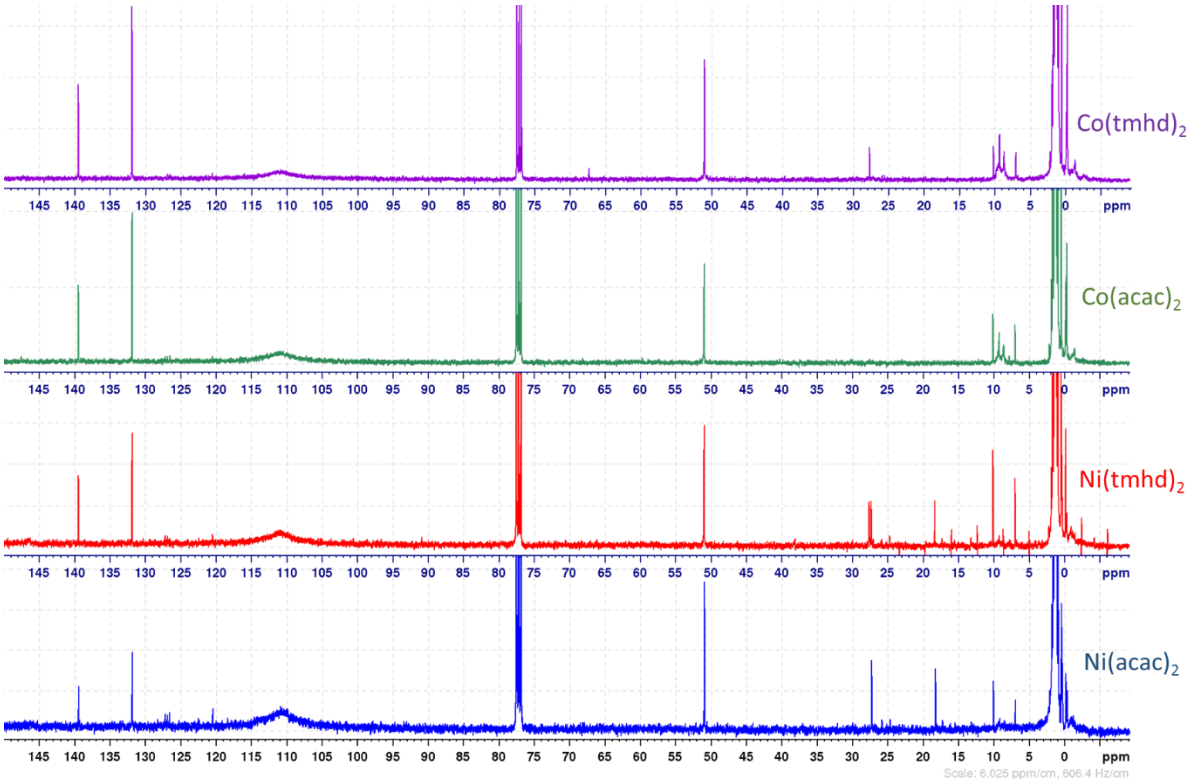



**Figure S44 – Overlay of $^{13}C$ HR-MAS NMR spectra in $CDCl_3$ for the crosslinked silicone gel obtained with the four catalysts**

## 8. Evaluation of selectivities of all catalysts for silicone crosslinking from HR-MAS NMR datas

The characteristic signals for enol forms of free tmhd- of the diketone ligands can be observed, at very low intensity, on $^{1}H$ NMR HR-MAS spectra (δ = 16.2 ppm for the acidic H, 1.2 ppm for the protons of the *tert*-butyl group) and on $^{13}C$ NMR HR-MAS spectra (δ = 27.7 ppm).

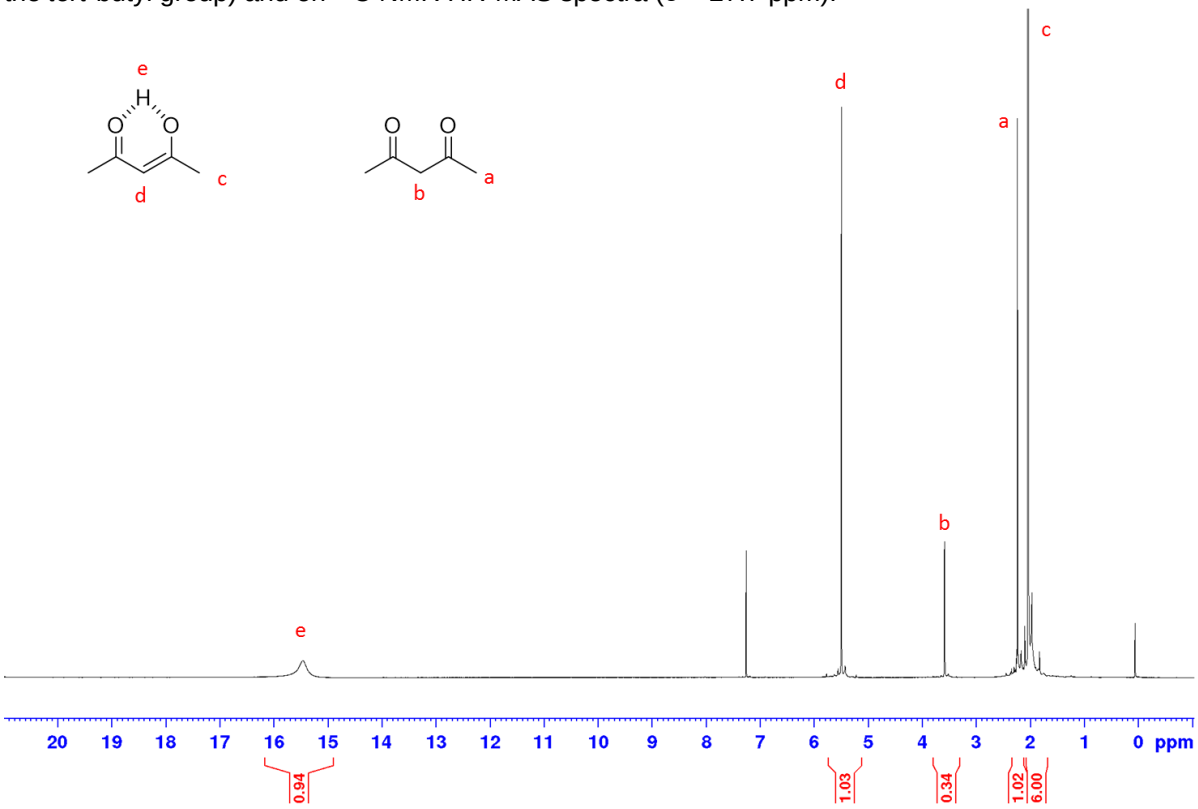



**Figure S45 – $^{1}H$ liquid NMR spectrum in $CDCl_3$ for acetylacetone (acac)**

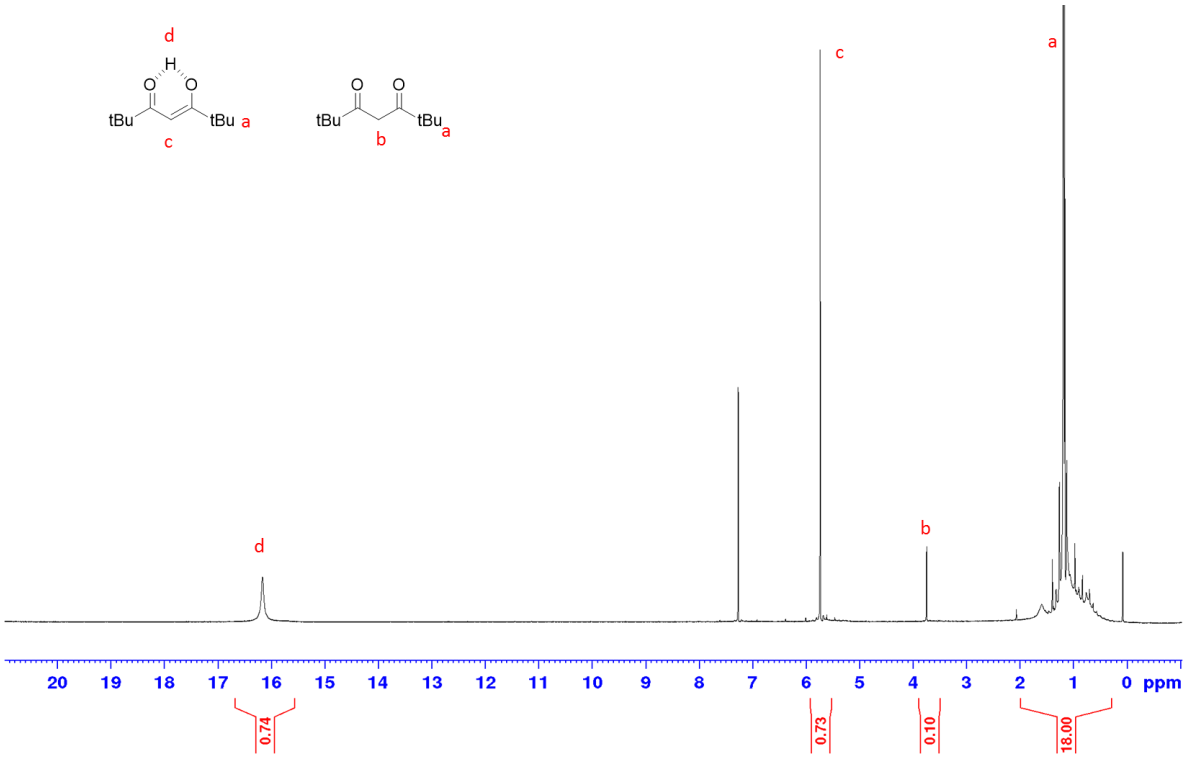



**Figure S46 – $^{1}H$ liquid NMR spectrum in $CDCl_3$ for 2,2,6,6-tetramethyl-3,5-heptanedione (tmhd)**

❖ $Ni(tmhd)_2$: Case Study

**$^1$H HR-MAS NMR**

For the selectivities determination, the signal integral (a) was set to 1000 and used as the reference signal, for all experiments.

**Table S3 – Evaluation of selectivities of $Ni(tmhd)_2$ for the silicone crosslinking**

| Product | Signals[a] | Integral value[a] | proton equivalent | Ratio[b] | Selectivity (%)[c] |
|---|---|---|---|---|---|
| HS | e+f | 0.4035 | 4 | 0.1008 | 5.6 |
| Red | J | 2.6646 | 3 | 0.8866 | 49.6 |
| Dim | K | 0.5873 | 4 | 0.1468 | 8.2 |
| DS | g+h | 1.3082 | 2 | 0.6541 | 36.6 |

[a] signals and integral values from the spectrum $^1$H NMR HR-MAS (Figure S30)
[b] Ratio = integral value / proton equivalent
[c] Selectivity = Ratio of product / sum of all ratios

**$^{13}$C HR-MAS NMR**

The $^{13}$C NMR signals (ex: Figure S32 & Figure S44) are rather qualitative than quantitative, because of the decoupling. This decoupling will lead to the NOE (Nuclear Overhauser Effect) and the signal will be increased depending on the number of protons around the carbon (linked but also close in space). This effect is difficult to predict as it depends on many parameters. Therefore, because of this effect, a decoupled $^{13}$C spectrum is inherently non-quantitative (and all spectra are decoupled). On the other hand, a comparative study between several spectra is possible. As a consequence, signals for **DS** products (g+h) might be underestimated, with an additional factor being the reduced mobility of this segment. The $^{13}$C NMR HR-MAS sequence here shows some limitations and even the thorough adjustments of d1 and d2 could prove insufficient to warrant quantitative analysis. However, in combination with $^1$H HR-MAS NMR, the comparison between Co and Ni, and both ligand sets is interesting. For a methodology perspective it is interesting to note that HR-MAS NMR spectroscopy is a powerful tool to readily observe the differences between so-called “model reactions” and actual crosslinking of silicones by silylation reactions. The global steric hindrance of the systems grealty influence the selectivities of the chosen (pre)catalysts based on **Co** and **Ni** and on the acetylacetonato-based scaffold.

❖ Comparison between all systems when using short (model compounds) or longer molecules (actual crosslinking substrates).

The table S4 below present the comparison between selectivities of the different systems with short and long molecules.

**Table S4 – Evaluation of selectivities depending to the catalyst and the longer of the molecules**

| Entry | *catalyst* | *Vinylsilane* | *-SiH* | Mol% | SiH:SiVi | T (°C) | Conv vinyl (%) | Conv -SiH (%) | Selectivities | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | **HS** | **SD** | **Red** | **Dim** |
| 1 | | $M^{Vi}D_{70}M^{Vi}$ | $MD'_{50}M$ | 1 | 3 | 110 | - | - | 6,4 | 51 | 31,6 | 11 |
| 2 | $Ni(acac)_2$ | Vpmds | MD'M | 0,5 | 1 | 90 | 52 | 100 | 0 | 45 | 40 | 15 |
| 3 | | Dvtms | MD'M | 0.5 | 1 | 90 | 53 | 100 | 0 | 53 | 47 | 0 |
| 4 | | $M^{Vi}D_{70}M^{Vi}$ | $MD'_{50}M$ | 1 | 3 | 110 | - | - | 5,6 | 36,6 | 49,6 | 8,2 |
| 5 | $Ni(tmhd)_2$ | Vpmds | MD'M | 0,5 | 1 | 90 | 47 | 100 | 0 | 43 | 43 | 14 |
| 6 | | Dvtms | MD'M | 0.5 | 1 | 90 | 52 | 100 | 0 | 52 | 48 | 0 |
| 7 | | $M^{Vi}D_{70}M^{Vi}$ | $MD'_{50}M$ | 1 | 3 | 110 | - | | Majority | Minority | Minority | 0 |
| 8 | $Co(acac)_2$ | Vpmds | MD'M | 0,5 | 1 | 90 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | | Dvtms | MD'M | 0.5 | 1 | 90 | 35 | 73 | 14 | 48 | 38 | 0 |
| 10 | | $M^{Vi}D_{70}M^{Vi}$ | $MD'_{50}M$ | 1 | 3 | 110 | - | - | Majority | Minority | Minority | 0 |
| 11 | $Co(tmhd)_2$ | Vpmds | MD'M | 0,5 | 1 | 90 | 30 | 45 | 70 | 15 | 15 | 0 |
| 12 | | Dvtms | MD'M | 0.5 | 1 | 90 | 35 | 72 | 14 | 48 | 38 | 0 |

For both Cobalt based systems, $Co(acac)_2$ and $Co(tmhd)_2$ (entry 5 and 7), we can see the formation of more HS products with the utilization of longer molecules compared to the results with smaller molecules (entry 6 and 8) thanks to their respective spectra $^1$H HR-MAS NMR (Figure S35 and Figure S40). No dimerization product is observed with these catalysts. **NB:** SST for crosslinking at 90°C of dvtms & $MD'_{50}M$ (1:1) with 0.5 mol% cat.: for $Ni(acac)_2$ and $Ni(tmhd)_2$ we observe SST of ~3h whereas for $Co(acac)_2$ it is 15min and for $Co(tmhd)_2$ about 40 min.

## 9. Miscellaneous

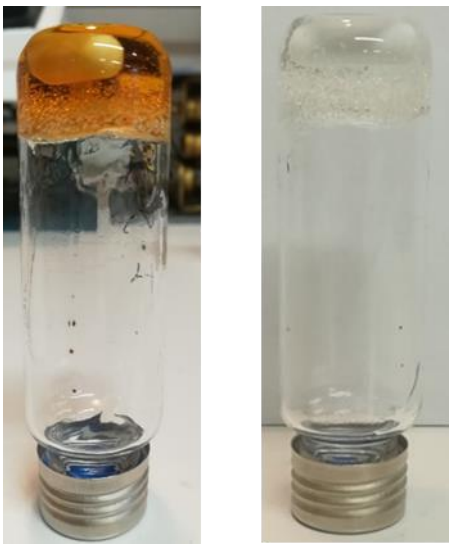


**Figure S47 – Crosslinked silicones by Ni(tmhd)$_2$ before prolonged air ($0_2$ and moisture) contact (left) and after (right)**

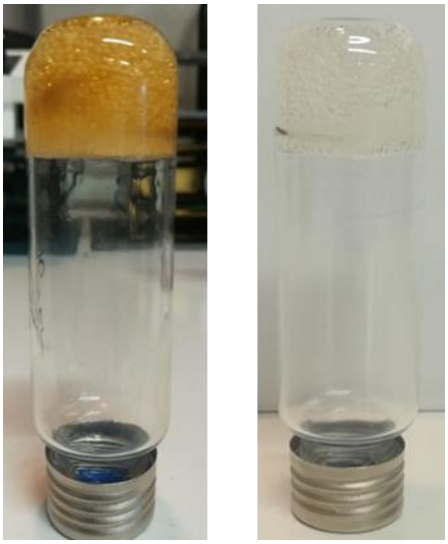


**Figure S48 – Crosslinked silicones by Ni(acac)$_2$ before prolonged air ($0_2$ and moisture) contact**

**Figure S49 – Crosslinked silicones by $Co(acac)_2$ before prolonged air ($0_2$ and moisture) contact (left) and after (right)**

**Figure S50 – Crosslinked silicones by $Co(tmhd)_2$ before prolonged air ($0_2$ and moisture) contact (left) and after (right)**