# Supporting Information for:

# N-heterocyclic carbenes - catalysts for the preparation of polyhedral silsesquioxanes

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**General remarks:** The chemicals were purchased from Aldrich (solvents, organic compounds), ABCR (silicon compounds) and Wacker (Silres603). Solvents for the preparation of free carbenes and PSS preparation were freshly distilled from Na/benzophenone under nitrogen and degassed using standard techniques.
The structure of products was determined by FT-IR and $^{29}$Si NMR. FT-IR spectra were measured on a Bruker IFS 66/S using a transmission technique (solutions containing the dissolved resin were dip-coated on a silicon wafer, rapidly dried in stream of cold nitrogen, and immediately spectra-recorded); the spectra of solid products were measured by the KBr pellet technique.
TMS was used as internal standard for all liquid NMR measurements ($\delta_{TMS}$ = 0 ppm, for $^{1}$H, $^{13}$C and $^{29}$Si). $^{29}$Si NMR spectra of reaction mixtures with a $D_2O$ insert lock were recorded at 25° C on a Varian Unity INOVA 300 MHz Upgrade spectrometer equipped with a 5 mm 1H/19F/X PFG ATB Broadband Probe. Experiments were accelerated by use of the relaxant $Cr(acac)_3$, which was added to the sample in a 0.01 M concentration. Recovery time dropped to only 5 s (33 ° pulse).
The poorly soluble phenyl PSSs could be effectively measured only by $^{29}$Si MAS NMR experiments, which were performed on the same NMR instrument equipped with a 5 mm MagicAngle Probe for VT CP/MAS. Sodium salt of 3-(trimethylsilyl)-propylsulfonic acid (DSS) was used as an external standard.

**Preparation of carbenes:** Carbenes were prepared according to published methods:
**1a)** 1,3-di-tert-butylimidazol-2-ilydene by tBuOK deprotonation[S1] of 1,3-di-tert-butylimidazolium chloride[S2] in THF,

**1b)** 1,3-di-1-adamantylimidazol-2-ilydene by tBuOK deprotonation[S3] of 1,3-bis-(1-adamantyl)imidazolium chloride[S4] in THF,

**1c)** 1,3-di-(2,6-isopropylphenyl)imidazol-2-ylidene by tBuOK deprotonation of 1,3-di(2,6-isopropylphenyl)imidazolium chloride in THF,

**1d)** 1,3-dimesitylimidazol-2-ilydene by tBuOK deprotonation[S5] of 1,3-dimesitylimidazolium chloride[S6] in THF,

**2)** 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene by vacuum pyrolysis of 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazoline.[S7]

The silver complexes of carbenes:

**3a)** bis-(1,3-dimethylimidazol-2-ilydene)silver(I) dichloroargentate(I) was prepared according to published procedure,

**3b)** bis-(3-methyl-1-propyl-imidazol-2-ilydene)silver(I) dichloroargentate(I):
$^{1}$H NMR (CHLOROFORM-d ,303MHz): δ = 7.19 (d, *J*=1.7 Hz, 1 H), 7.16 (d, *J*=1.8 Hz, 1 H), 4.10 (t, *J*=7.2 Hz, 2 H), 3.88 (s, 3 H), 1.79 - 1.95 (m, 2 H), 0.95 ppm (t, *J*=7.3 Hz, 3 H).
$^{13}$C NMR (CHLOROFORM-d ,76MHz): δ = 179.2, 122.5, 120.5, 53.4, 38.8, 24.8, 11.1 ppm.

**3c)** bis-(1-butyl-3-methylimidazol-2-ilydene)silver(I) dichloroargentate(I):
$^{1}$H NMR (CHLOROFORM-d ,303MHz): δ = 7.18 (d, *J*=1.7 Hz, 1 H), 7.15 (d, *J*=1.8 Hz, 1 H), 4.13 (t, *J*=7.2 Hz, 2 H), 3.87 (s, 3 H), 1.75 - 1.88 (m, 2 H), 1.35 (m, 2 H), 0.95 ppm (br. t, *J*=7.2 Hz, 3 H). $^{13}$C NMR (CHLOROFORM-d ,76MHz): δ = 179.2, 122.6, 121.3, 51.6, 38.8, 33.5, 19.6, 13.6 ppm.

3b and 3c were prepared from 1,3-dimethylimidazolium chloride, 1-butyl-3-methyl-imidazolium or 3-methyl-1-propyl-imidazolium chloride, following the reported procedure for 1-ethyl-3-methyl imidazol-2-ilydene compound.[S8] The starting ionic compounds were prepared via alkylation of 1-methylimidazole with propyl/butyl chloride in toluene, followed by purification with ethyl acetate.

**3d)** bis-(1,3-di(2,6-diisopropylphenyl)imidazol-2-ilydene)silver(I) dichloroargentate(I) was prepared was prepared according to published procedure,

**3e)** bis-(1,3-dimesitylimidazol-2-ilydene)silver(I) dichloroargentate(I) was prepared according to published procedure,

**Preparation of silicon compounds:**
The commercial resin Silres 603 was used as a phenyl prepolymer. (The PhP, but of different constitution, could be prepared by acidic hydrolysis of phenyltrimethoxysilane.[S9]) Silres 603 contained about 3% per weight of OH groups, which is approximately 1 OH group per 2 silicon atoms. It could be estimated from the $^{29}$Si NMR that the resin is composed of almost equal amounts of $T^2$ and $T^3$ siloxane units.

The isobutltrimethoxysilane (iBuTMOS) and isooctyltrimethoxysilane (iOcTMOS) hydrolizates were prepared by dissolution of 0.021 mol of each compound in 15 ml of 2:1 mixture of MeOH: AcMe and the subsequent addition of 1.13 g of water and 0.23 g of 0.1 M HCl and stirring at RT for 3 days. The solvents were removed in vacuum and the resulting oil was analysed by NMR, which showed that majority was composed of $T^1$ and $T^2$ siloxane units with a minor part of $T^3$ (no $T^0$).

Octa(isobutylsilsesquioxane)[S9] and octa(3-chloropropylsilsesquioxane)[S10] were prepared according to published procedures.

**The procedures for preparing PSS compounds:**

**Preparation of $Ph_8T_8$:** Either toluene or benzene can be used for the preparation of this compound; since the latter is highly toxic, the use of toluene is preferred. Into a 25 ml round-bottom flask, 15 ml of freshly distilled and degassed toluene (benzene), a stirring bar and 21 mmol of silsesquioxane resin (Silres 603) were placed and stirred until the siloxane was completely dissolved. Then 0.25 mmol of carbene was added under nitrogen and refluxed for 48 hours under nitrogen. The white solid product was filtered off and thoroughly washed with fresh toluene, acetone and finally with methanol and dried in a vacuum oven. The product thus obtained was recrystallized in the following manner: the crude product was dissolved in dichloromethane, filtered and the solvent then removed by slow evaporation in a fume hood and all residue was analyzed. This was necessary to obtain clear NMR data. The spectral properties correspond to those previously reported.[S9] $Ph_8T_8$: $^{29}$Si MAS NMR (DSS): -77.70 ppm.

**Preparation of $Ph_{12}T_{12}$:** Into a 25 ml round-bottom flask, 15 ml of freshly distilled and degassed THF, a stirring bar and 21 mmol of silsesquioxane resin (Silres 603) were placed and stirred until the siloxane was completely dissolved. Then 0.25 mmol of carbene was added under nitrogen and refluxed for 7 days under nitrogen. The white solid product was filtered off and thoroughly washed with fresh THF toluene, acetone and finally with methanol, and dried in a vacuum oven. The spectral properties correspond to those previously reported.[S9] $Ph_{12}T_{12}$: $^{29}$Si MAS NMR (DSS): -77.53 and -80.45 ppm.

**Preparation of PSS from hydrolyzates:** The oily hydrolyzates of iBuTMS and iOcTMS were dissolved in 15 ml of freshly distilled and degassed THF with the aid of a magnetic stirrer. A solution of free 1,3-di-1-adamantylimidazol-2-ilydene in THF (1/4 mmol) was then added and mixture then refluxed for 48 hours under nitrogen. The solution was examined with NMR and IR. The chemical shifts found in the reaction mixtures were:
$iBu_8T_8$: $^{29}$Si NMR (THF, $Cr(acac)_3$, TMS): -67.79 ppm, 67 %,
$iBu_{10}T_{10}$: $^{29}$Si NMR (THF, $Cr(acac)_3$, TMS): -69.95 ppm, 33 %.

$iOc_8T_8$: $^{29}$Si NMR (THF, $Cr(acac)_3$, TMS): -68.12 ppm, 80 %,
$iOc_{10}T_{10}$: $^{29}$Si NMR (THF, $Cr(acac)_3$, TMS): -70.20 ppm, 20%.

**Reactivity of carbenes with PSS:** In 15 ml of freshly distilled THF, 1.29 g of octa(3-chloropropylsilsesquioxane) and 1.09 g of octa(isobutylsilsesquioxane) were dissolved and 0.25mmol of free 1,3-dis-1-adamantylimidazol-2-ilydene in THF was added to this mixture and the mixture refluxed for 48 hours under nitrogen. The resulting solution was examined with NMR and IR. According to the work of Marsmann[S11], signals in the region -67.30 – -67.44 ppm can be attributed to $iBu_2ClP_6T_8$ (the iBu groups on the diagonal of the same face) and $iBu_3ClP_5T_8$ (the iBu groups on the same face), the signal on - 67.78 ppm is the remaining $iBu_8T_8$, the group of signals between -68.78 – -69.40 ppm are $T_{10}$ signals and the signal at – 69.07 represents $ClP_{10}T_{10}$, signals between -71.02 to – 71.37 ppm correspond to $T_{12}$ signals; the signal at -71.29 ppm represents $ClP_{12}T_{12}$.

**Reeferences:**


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**Fig 1:** The $^{1}H$ NMR spectra of bis-(3-methyl-1-propyl-imidazol-2-ilydene)silver(I) dichloroargentate(I).

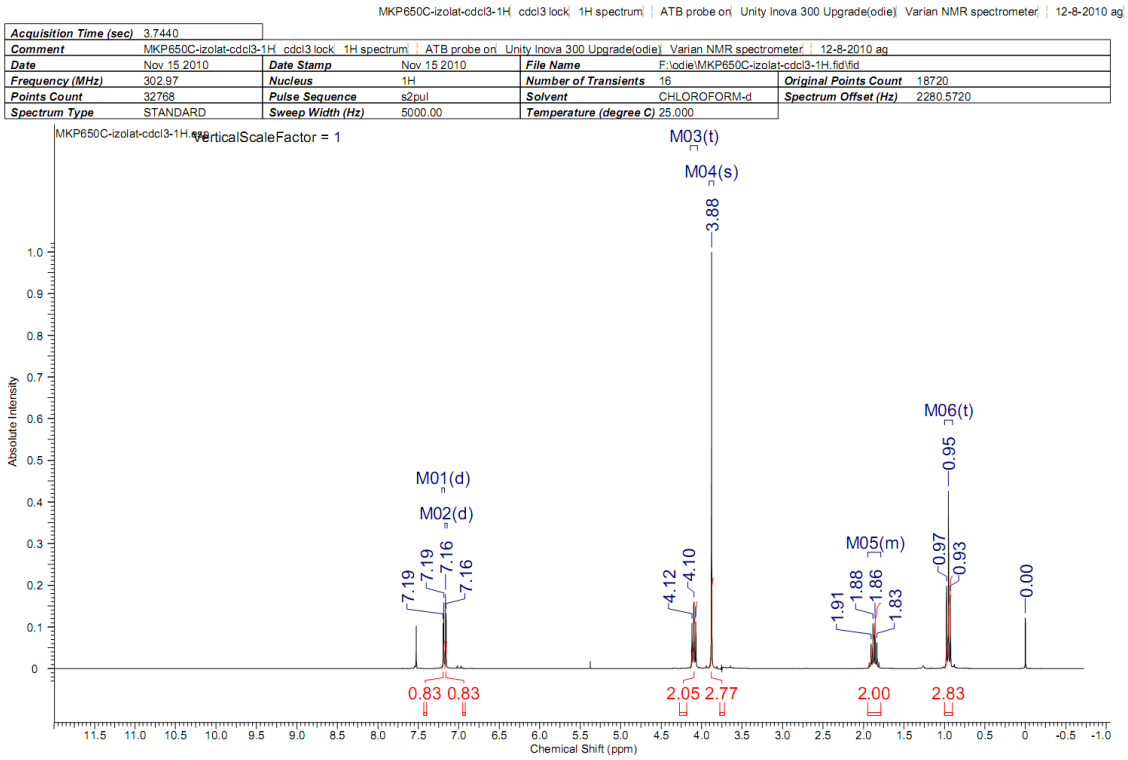


**Fig 2:** The $^{13}C$ NMR spectra of bis-(3-methyl-1-propyl-imidazol-2-ilydene)silver(I) dichloroargentate(I).

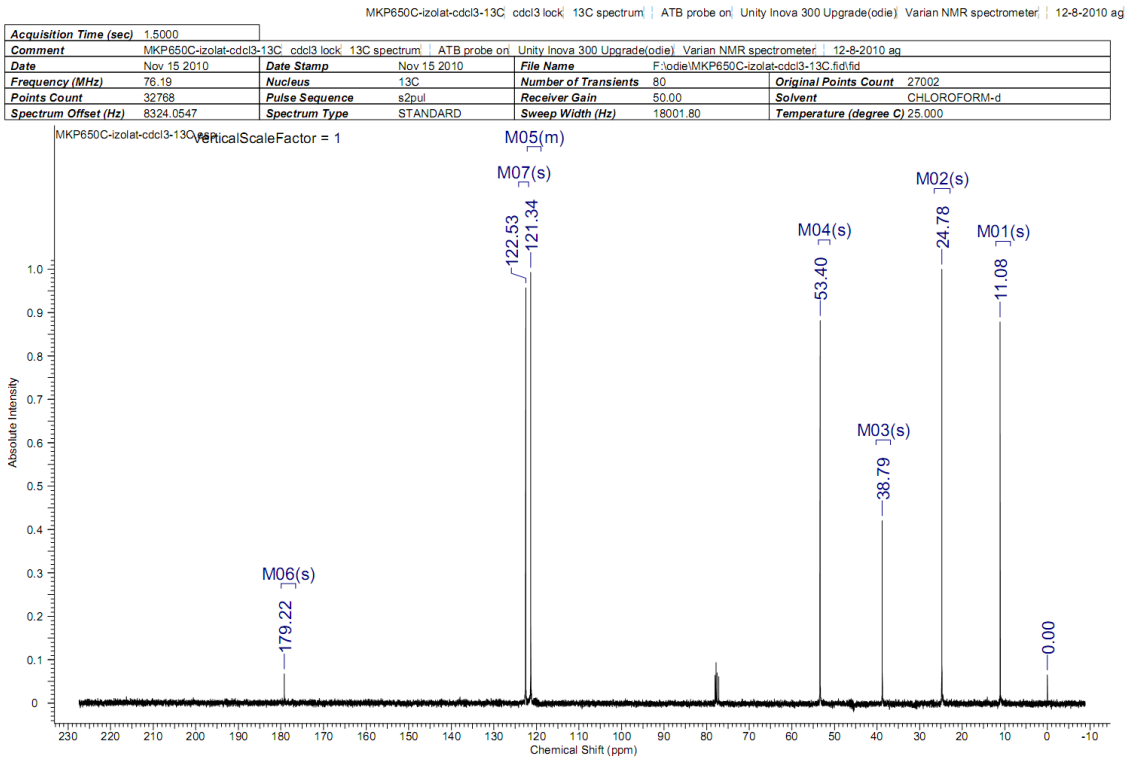

**Fig 3:** The $^{1}H$ NMR spectra of bis-(1-butyl-1-methyl-imidazol-2-ilydene)silver(I) dichloroargentate(I).

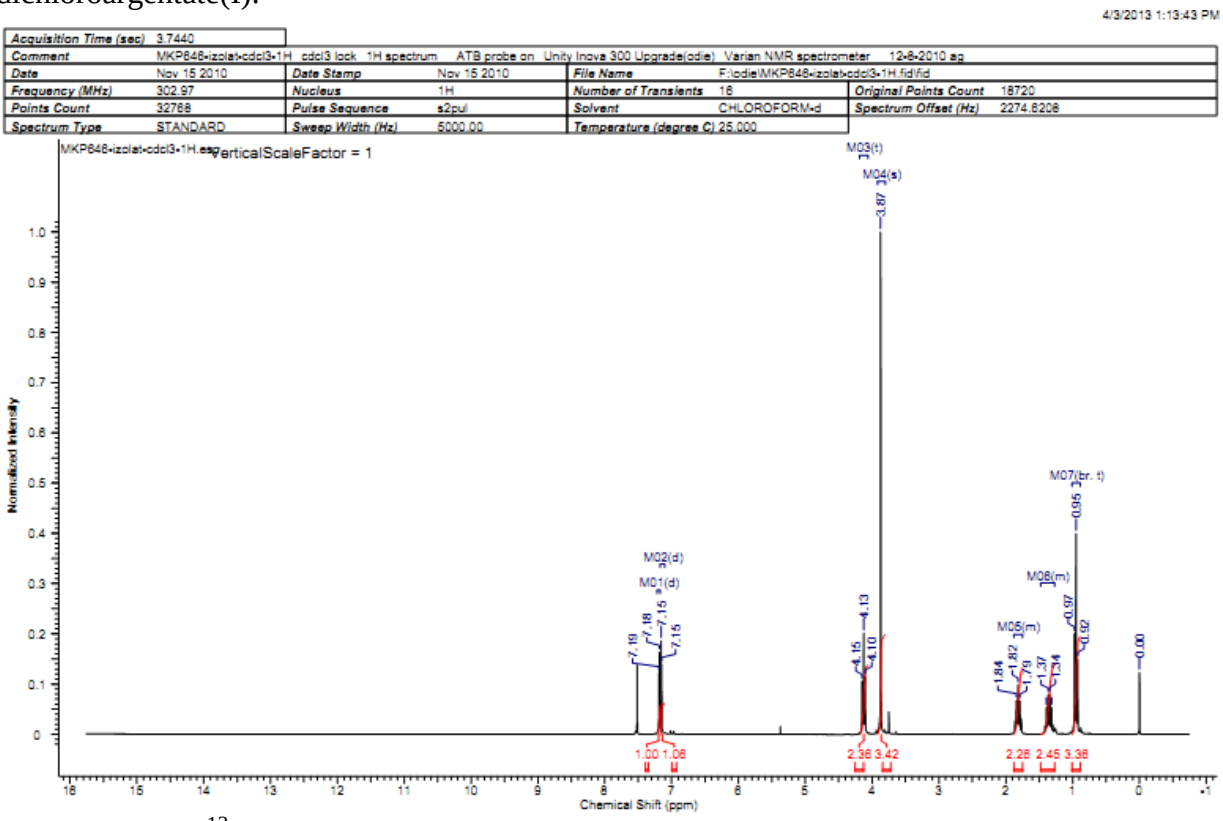


**Fig 4:** The $^{13}C$ NMR spectra of bis-(1-butyl-1-methyl-imidazol-2-ilydene)silver(I) dichloroargentate(I).

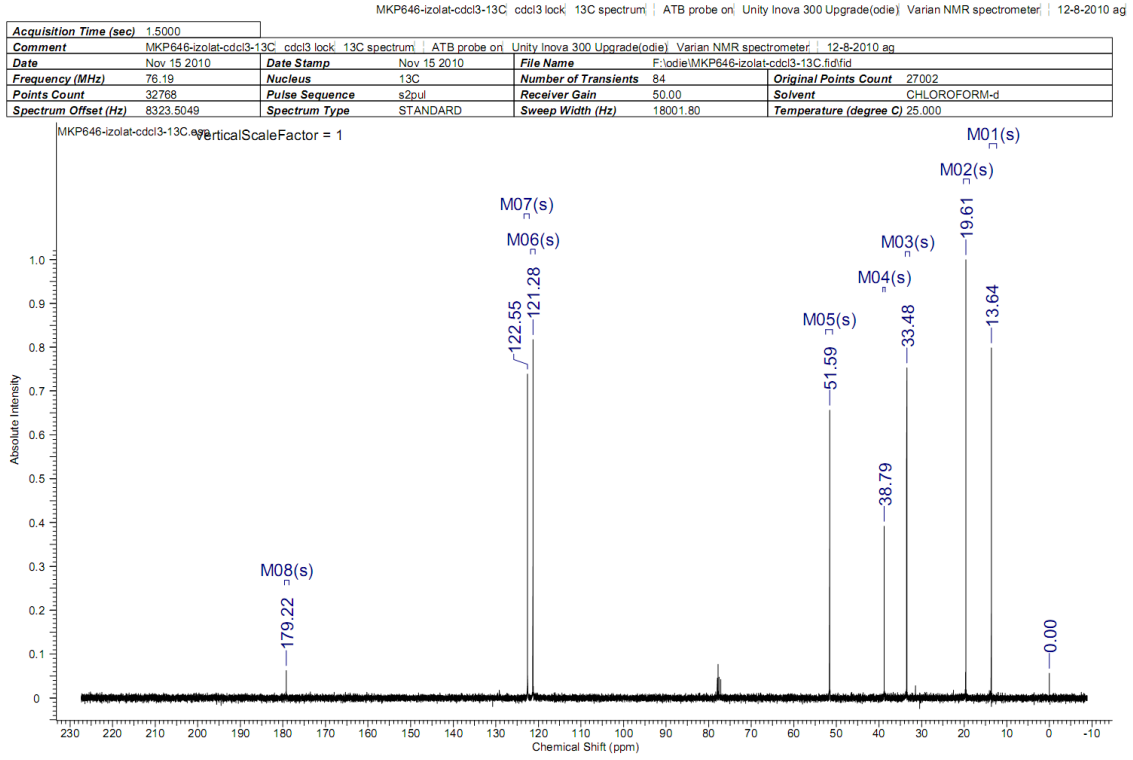

**Fig 5:** The $^{29}$Si NMR spectra of Silres 603.

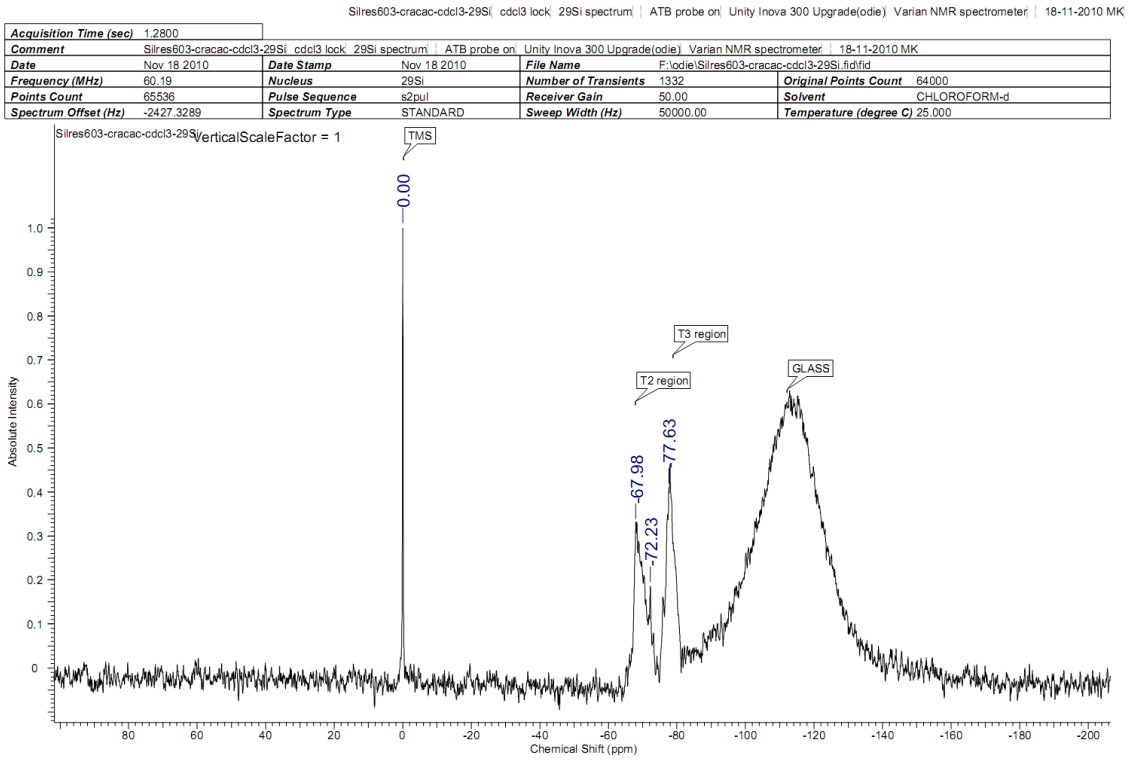


**Fig 6:** The $^{29}$Si NMR spectra of hydrolyzed isobutyltrimethoxysilane.

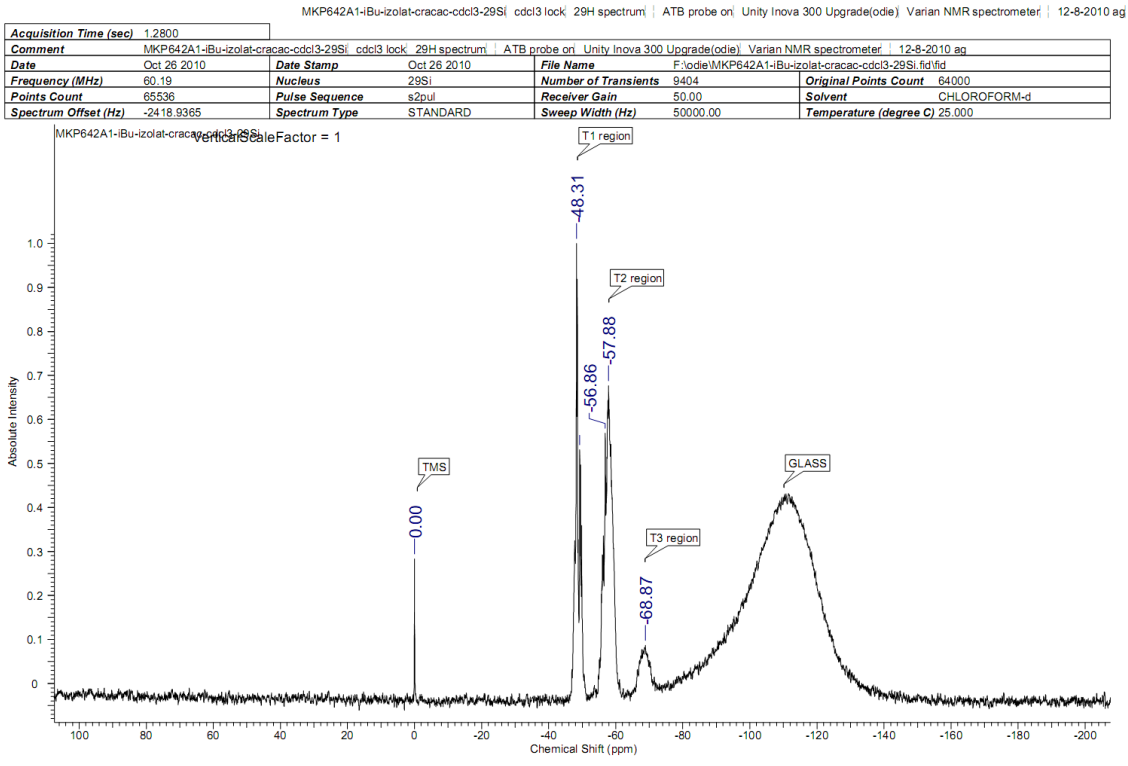

**Fig 7:** The $^{29}$Si NMR spectra of hydrolyzed isooctyltrimethoxysilane.

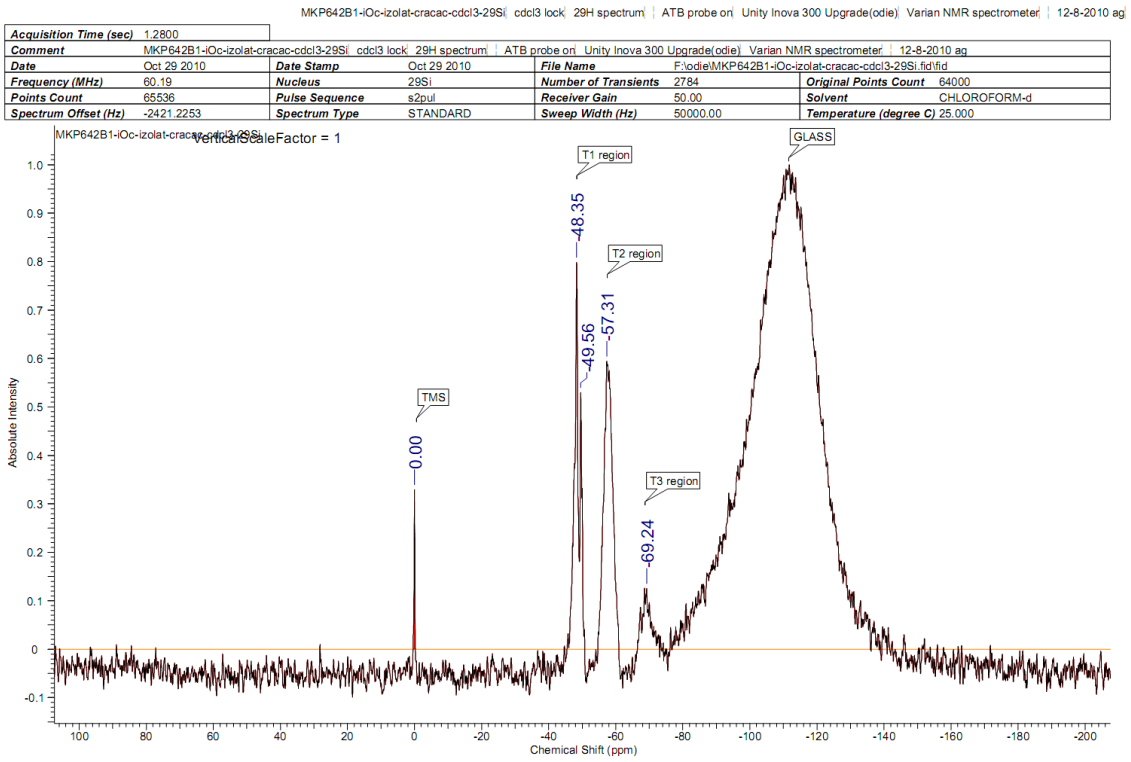


**Fig 8:** The $^{29}$Si NMR spectra of the starting mixture of octa(isobutylsilsesquioxane) and octa(3-chloropropylsilsesquioxane).

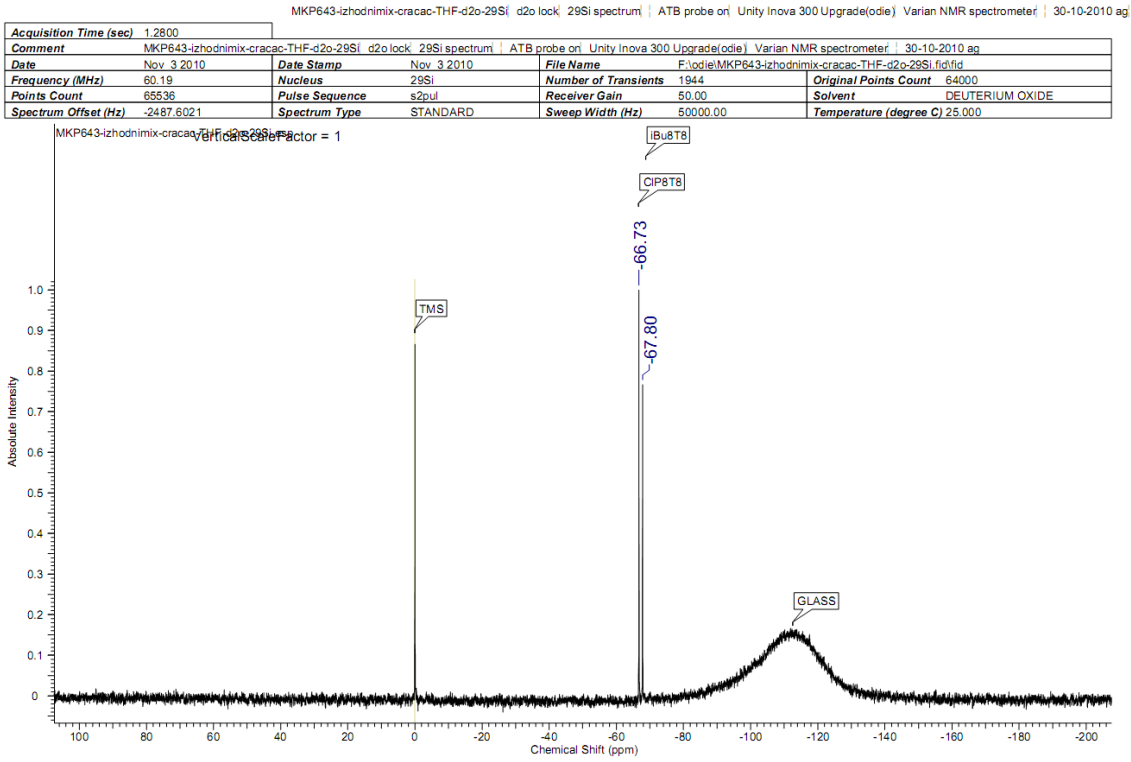

**Fig 9:** The $^{29}$Si MAS NMR spectra of octa(phenylsilsesquioxane).

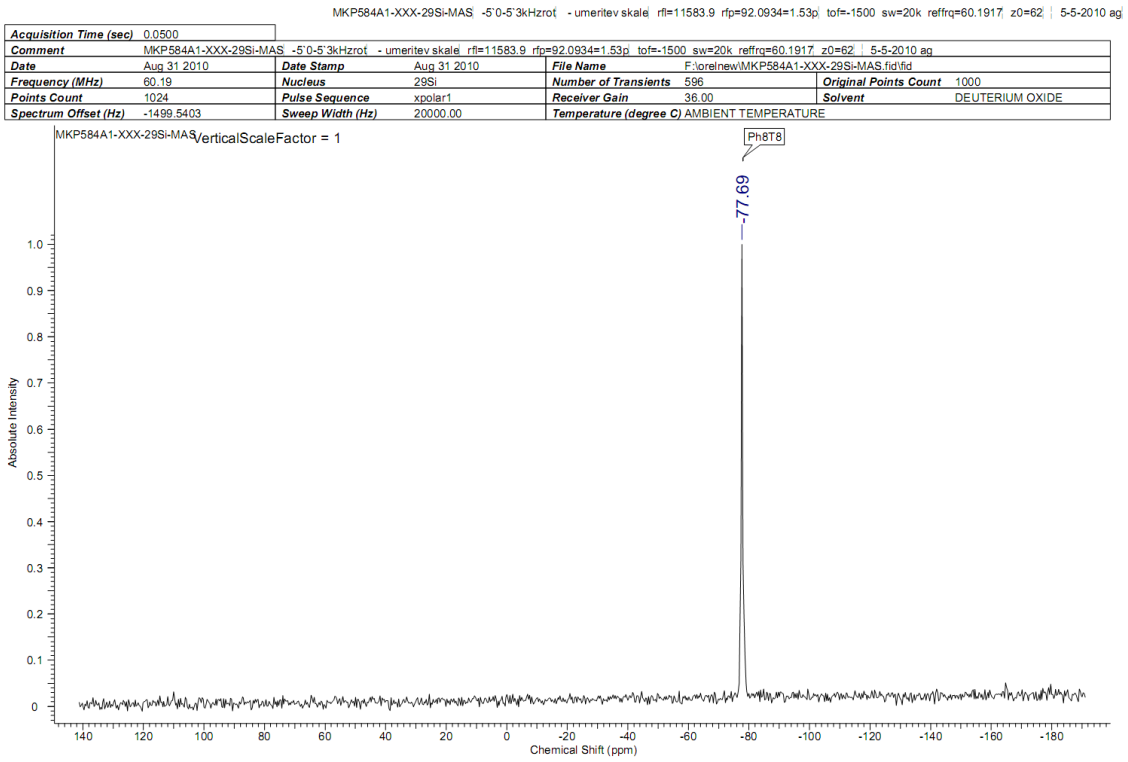


**Fig 10:** The $^{29}$Si MAS NMR spectra of dodeca(phenylsilsesquioxane).

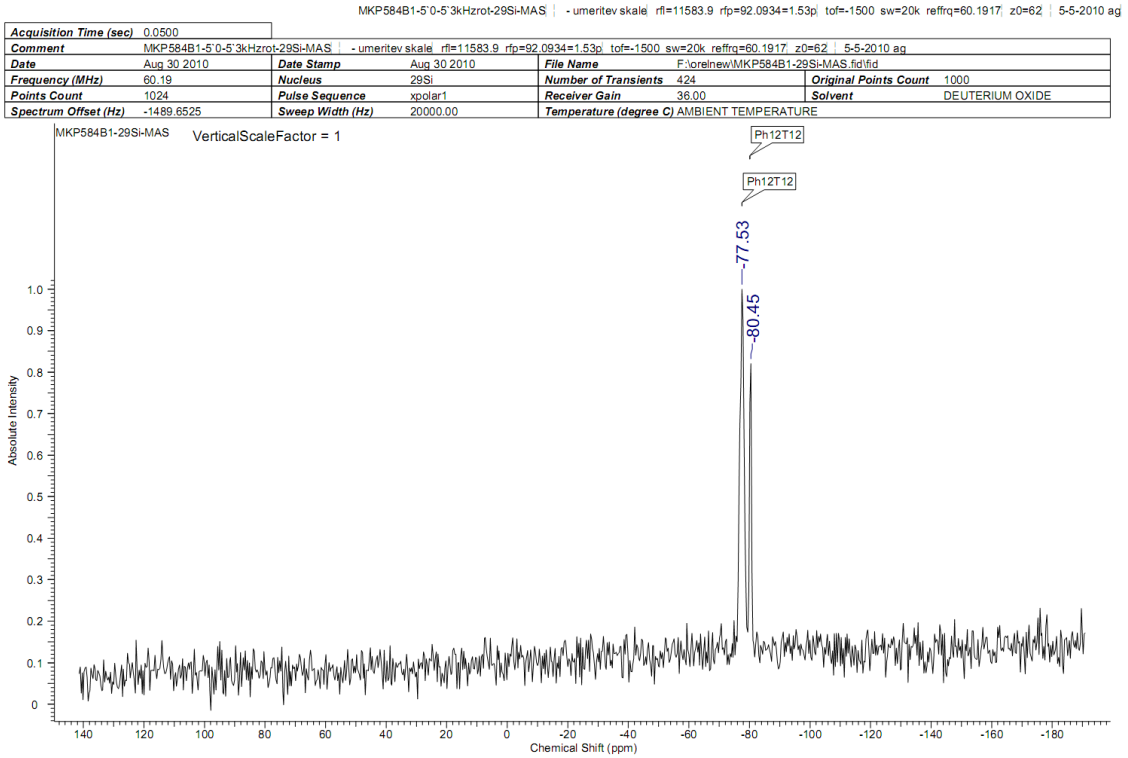

**Fig 11:** The $^{29}$Si NMR spectra of octa(isobutylsilsesquioxane) and deca(isobutylsilsesquioxane), produced by carbene action on hydrolyzate of isobutyltrimethoxysilane.

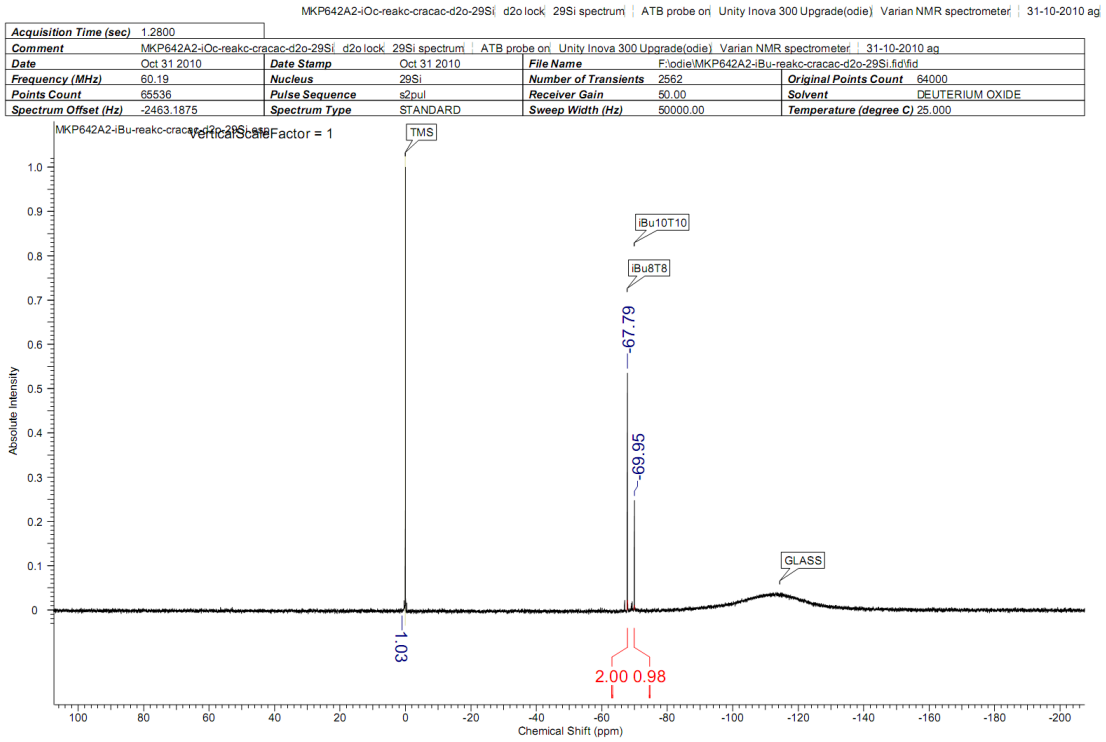


**Fig 12:** The $^{29}$Si NMR spectra of octa(isooctylsilsesquioxane) and deca(isooctylsilsesquioxane).

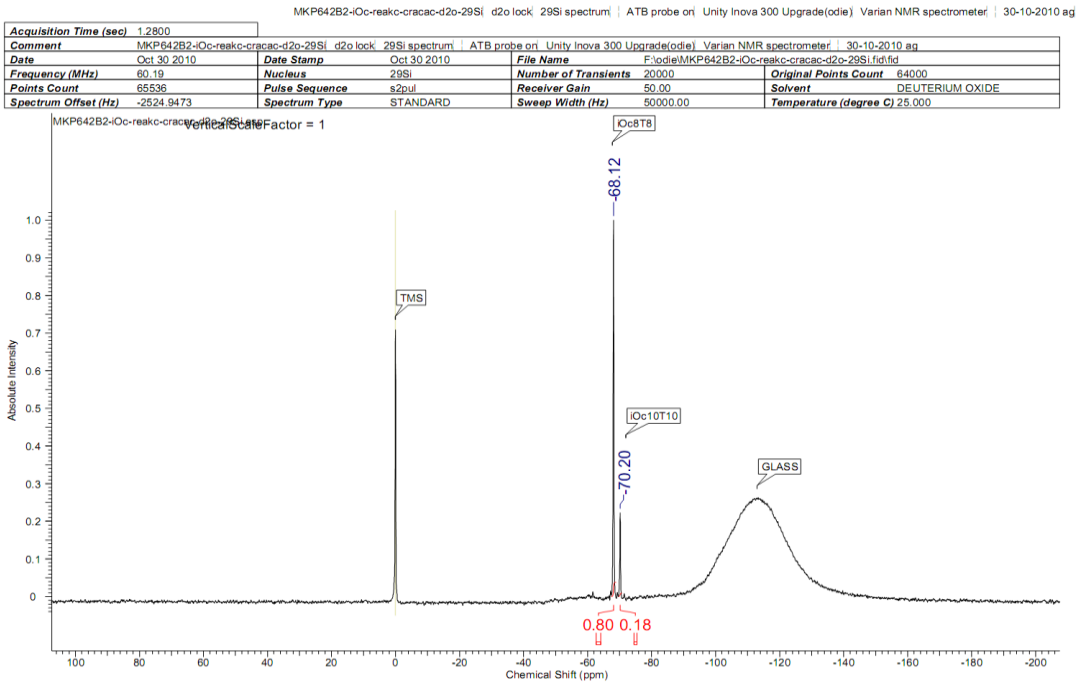

**Fig 13:** The $^{29}$Si NMR spectra of a mixture of various cages produced by refluxing octa(isobutylsilsesquioxane) and octa(3-chloropropylsilsesquioxane) with carbene in THF.

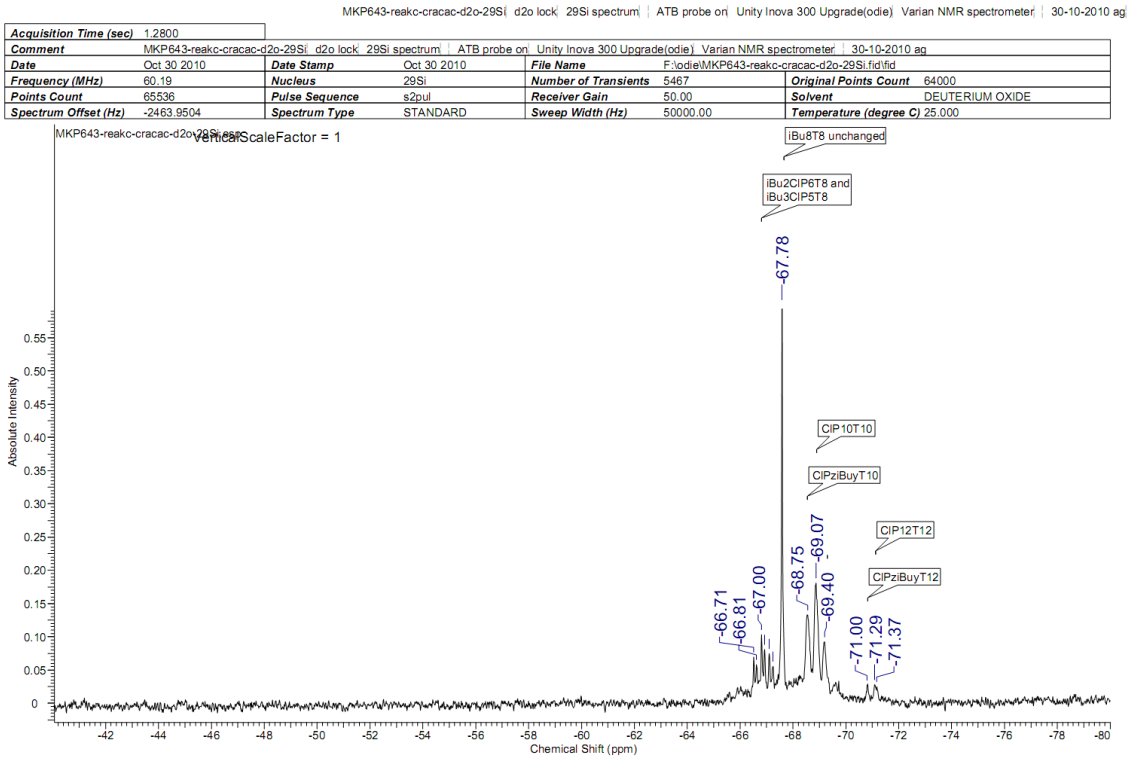


**Fig 14:** The $^{29}$Si NMR spectra of the reaction mixture obtained by refluxing the phenyl prepolymer with Ender's carbene in toluene.