

## Synthesis of Novel Carbosilane Dendrimers with Myo-inositol Cores

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**Abstract:** The preparation of carbosilane dendrimers with cores of myo-inositol and the outmost periphery groups of allyl groups has been reported. By using alternate hydrosilylation and alkenylation reactions, the dendrimer have been carried up to the third generation with 48 allyl groups on the periphery.

**Keyword:** Carbosilane dendrimer, myo-inositol, divergent method, hydrosilylation, Grignard reagent.

Dendrimers are highly branched regular threedimensional monodispersed macromolecules with a branch occurring at each monomer unit. They are characterized by the presence of a large number of functional groups on the surface that results in solubility, viscosity, and thermal behaviors different from those of classical polymers. They are also characterized by the presence of internal cavities and different cores. They are widely used in molecular encapsulation, catalysis and polymerization initiators and synthesis of dendritic liquid crystalline polymers *etc.* because of their unique topology<sup>1</sup>. Silicon tetrachloride is used as a core in most cases to prepare carbosilane dendrimers<sup>2</sup>. Carbosilane dendrimers with other cores such as  $(\text{Me}(\text{CH}_2=\text{CH})\text{SiO})_4$  and  $((\text{CH}_2=\text{CHCH}_2\text{O})\text{Si}(\text{CH}_2)_2)$  have been reported by Chungkyun Kim *etc.*<sup>3</sup>.

In this paper we report a new type of carbosilane dendrimers with myo-inositol cores. Because myo-inositol is hydrophilic and some of its compounds serve as second messengers in molecular switches<sup>4</sup>, we expect it will lead to new characteristics to the dendrimers. For the synthesis of these dendrimers, we chose a divergent approach starting from hexa-O-allyl-myoinositol (**0G**). This compound was prepared in 52% isolated yield from the reaction of myo-inositol (compound **1**), NaH and allyl bromide in dry THF. Dendrimer layers were then added by alternating hydrosilylation and alkenylation with Grignard reagents<sup>4</sup> (**Scheme 1**). The hydrosilylation steps took 12-hour reaction period and the yields of products were nearly quantitative<sup>5</sup>. After the chlorosilyl-terminated intermediates were reacted with  $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ , dendrimers **1G**, **2G** and **3G** were obtained in 61%, 55% and 52% isolated yields, respectively<sup>6</sup>.

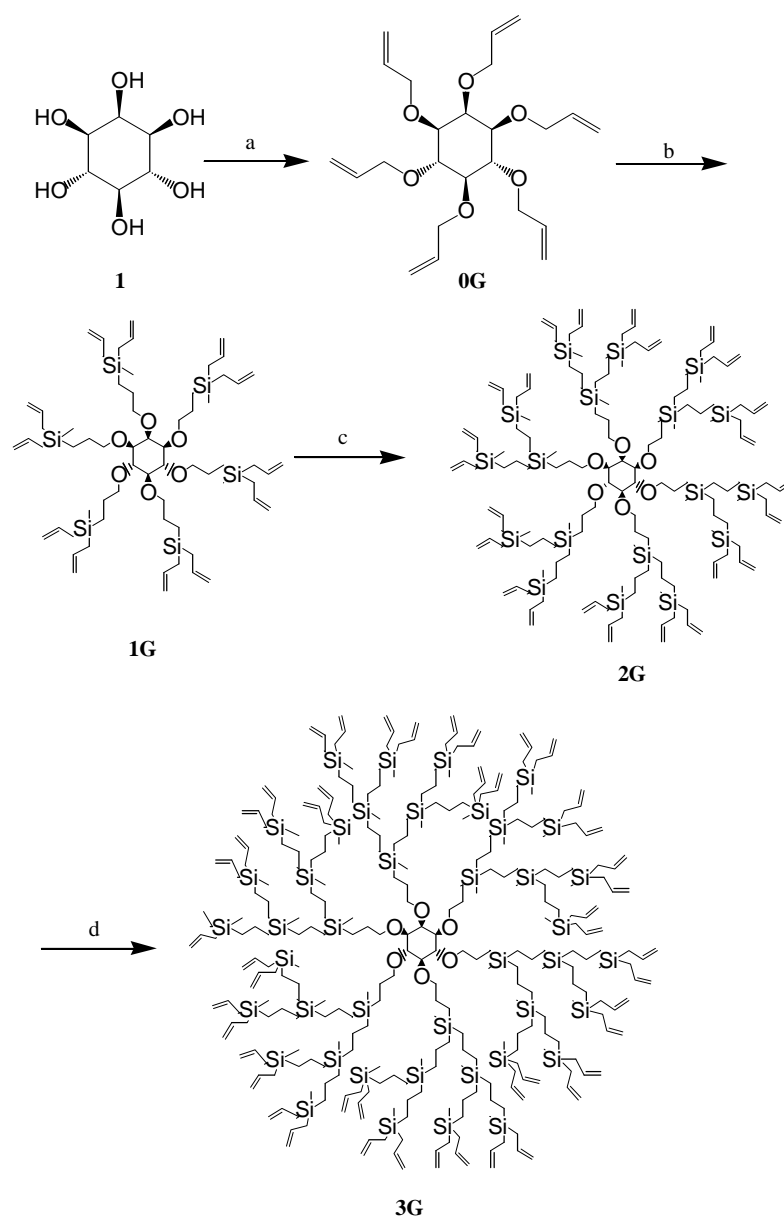
Compounds **1G**, **2G** and **3G** were characterized using IR and NMR spectroscopy

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and elemental analysis. In addition, molecular weights of these dendrimers were obtained using vapor pressure osmometry, and they were close to the theoretical values<sup>7-9</sup>. This showed that the dendrimers have perfect structures.

Scheme 1



a. NaH, CH<sub>2</sub>=CHCH<sub>2</sub>Br, THF;

b, c, d. 1) MeSiHCl<sub>2</sub>, Karstedt catalyst, THF; 2) CH<sub>2</sub>=CHCH<sub>2</sub>MgBr, THF.

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5. General hydrosilylation procedure: 0G or 1G or 2G and methyldichlorosilane (approximately 1.5 molar equiv relative to the number of double bonds) were dissolved in THF, then 4 drops of Karstedt catalyst were added, the resulting solution was stirred under nitrogen at 50°C for 12 hours. All volatiles were then removed under reduced pressure, and the corresponding hydrosilylated product was obtained as thick colorless oil.
6. General alkenylation procedure: the intermediate prepared in hydrosilylation procedure was added dropwise into a newly made  $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ , the mixture was stirred under nitrogen at reflux for 24 hours. Then the mixture was cooled to room temperature and poured into ice-cold saturated aqueous  $\text{NH}_4\text{Cl}$ . The aqueous layer was extracted with  $\text{Et}_2\text{O}$ , and the combined organic layers were washed three times with water and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed on the rotary evaporator, the residue was chromatographed on silica gel using hexane/ $\text{EtOAc}$  as eluent, and the target dendrimer was obtained as colorless oil.
7. **1G**: clear colorless liquid,  $^1\text{H}$ NMR (90MHz,  $\text{CDCl}_3$ ,  $\delta$ ppm): 0.16 (s, 18H,  $\text{CH}_3$ ), 0.46-0.66(br, 12H,  $\text{SiCH}_2$ ), 1.27-1.52 (m, 12H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.61-1.82(d, 24H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 3.43-3.82 (s, 18H,  $>\text{CHO}$  and  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 4.65-4.90(m, 24H,  $\text{CH}_2=\text{CH}$ ), 5.50-5.98 (m, 12H,  $\text{CH}_2=\text{CH}$ ); IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3073( $\text{HC}=\text{C}$ ), 1629( $\text{C}=\text{C}$ ), 1251( $\text{Si}-\text{C}$ ), 1075( $\text{C}-\text{O}$ ). Anal Calcd. for  $\text{C}_{66}\text{H}_{120}\text{O}_6\text{Si}_6$ : C, 67.28; H, 10.27. Found: C, 67.02; H, 10.18. Mol wt (VPO): 1125 (calcd 1178).
8. **2G**: clear, colorless oil,  $^1\text{H}$ NMR (90MHz,  $\text{CDCl}_3$ ,  $\delta$ ppm): 0.14 (m, 54H,  $\text{CH}_3$ ), 0.48-0.66 (s, 54H,  $\text{SiCH}_2$ ), 1.27 (m, 36H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.52-1.61(d, 48H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 3.43-3.84 (d, 18H,  $>\text{CHO}$  and  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 4.77-4.94 (t, 48H,  $\text{CH}_2=\text{CH}$ ), 5.56-6.04 (br, 24H,  $\text{CH}_2=\text{CH}$ ). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3076( $\text{HC}=\text{C}$ ), 1630( $\text{C}=\text{C}$ ), 1254( $\text{Si}-\text{C}$ ), 1080( $\text{C}-\text{O}$ ). Anal Calcd. for  $\text{C}_{150}\text{H}_{288}\text{O}_6\text{Si}_{18}$ : C, 66.89; H, 10.78; Found: C, 66.75; H, 10.72. Mol wt (VPO): 2772 (calcd 2693).
9. **3G**: clear, colorless viscous oil,  $^1\text{H}$ NMR (90MHz,  $\text{CDCl}_3$ ,  $\delta$ ppm): 0.12 (m, 126H,  $\text{CH}_3$ ), 0.65-0.97 (s, 156H,  $\text{SiCH}_2$ ), 1.27 (m, 36H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.51-1.63(d, 96H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 3.42-3.64 (d, 18H,  $>\text{CHO}$  and  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 4.77-4.94 (t, 96H,  $\text{CH}_2=\text{CH}$ ), 5.55-5.94 (br, 48H,  $\text{CH}_2=\text{CH}$ ). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3075( $\text{HC}=\text{C}$ ), 1631( $\text{C}=\text{C}$ ), 1248( $\text{Si}-\text{C}$ ), 1082( $\text{C}-\text{O}$ ). Anal Calcd. for  $\text{C}_{318}\text{H}_{624}\text{O}_6\text{Si}_{42}$ : C, 66.73; H, 10.99; Found: C, 66.75; H, 10.72. Mol wt (VPO): 5631 (calcd 5724).

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