



# SYNTHESIS OF CARBOSILANE DENDRIMERS WITH AN AMINE-CONTAINING SHELL USING CuAAC

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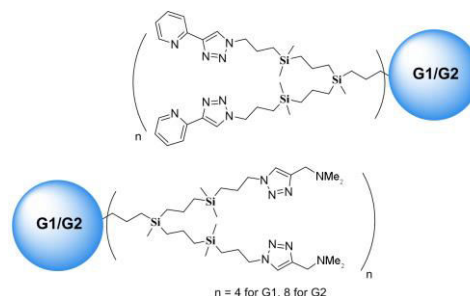
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## Abstract

A new synthetic approach to carbosilane dendrimers bearing amino-containing functional groups in the shell is proposed based on the Cu-catalyzed azide–alkyne cycloaddition. The structures of the resulting compounds are confirmed using <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy, as well as gel permeation chromatography.



**Key words:** carbosilane dendrimers, click reaction, azide–alkyne cycloaddition, *N,N*-dimethylpropargylamine, 2-ethynylpyridine.

## Introduction

Dendrimers with an amine shell are widely used for the delivery of biologically active molecules and DNA and for the creation of dendriplexes and various nanostructures [1–3].

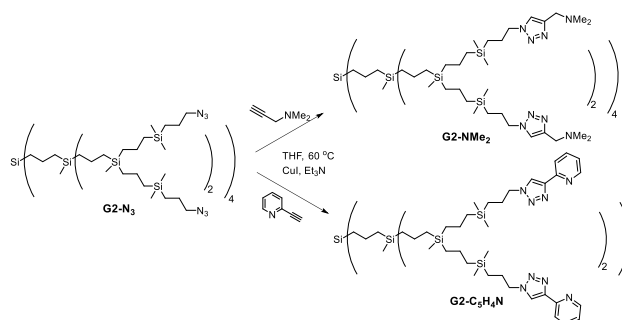
In turn, carbosilane dendrimers feature high chemical stability, inertness and hydrophobicity of the framework, while maintaining high reactivity of the functional groups and offering proper analytical control during the structure formation up to high generations [4, 5].

The hydrophobic internal framework of carbosilane dendrimers in combination with the amine shell opens up new ways of using carbosilane dendrimers for the delivery of drugs and genes, as well as for the coordination of metal ions [6].

## Results and discussion

In this work, a series of new carbosilane dendrimers with two types of the amine-containing functional shells, namely, dimethylamine (**G1-NMe<sub>2</sub>** and **G2-NMe<sub>2</sub>**) and pyridin-2-yl (**G1-C<sub>5</sub>H<sub>4</sub>N** and **G2-C<sub>5</sub>H<sub>4</sub>N**) were synthesized. The dendrimers were obtained by the copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction between the previously obtained first and second generation carbosilane dendrimers with an azidopropyl shell (**G1-N<sub>3</sub>**, **G2-N<sub>3</sub>**) [7] and *N,N*-dimethylpropargylamine or 2-ethynylpyridine (Scheme 1).

A combination of heterocyclic 1,2,3-triazole rings with the conjugated pyridine and dimethylamine chelating units enables the application of such structures for the coordination of transition metal ions, for example, for the stabilization of narrowly dispersed silver nanoparticles [8]. That is why 2-ethynylpyridine and 1,1-dimethylpropargylamine were chosen



**Scheme 1.** Synthesis of **G2-NMe<sub>2</sub>** and **G2-C<sub>5</sub>H<sub>4</sub>N**.

for the functionalization of the carbosilane dendrimers featuring an azide shell.

CuAAC was carried out in dry THF at 60 °C upon addition of 1 mol % of CuI. The reaction course was monitored using <sup>1</sup>H NMR spectroscopy by the disappearance of the signals of characteristic CH<sub>2</sub> groups at the azide moiety and the appearance of new ones, corresponding to the completion of CuAAC (Fig. 1). The structures of the compounds obtained were confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy for all the compounds and gel permeation chromatography (GPC) for **G1-C<sub>5</sub>H<sub>4</sub>N** and **G2-C<sub>5</sub>H<sub>4</sub>N** (see Figs. S1–S18 in the Electronic supplementary information (ESI)).

## Experimental section

### General remarks

The synthesis of the first and second generation carbosilane dendrimers with an azidopropyl shell was described earlier [7]. THF was dried by the standard procedure. 2-Ethynylpyridine,

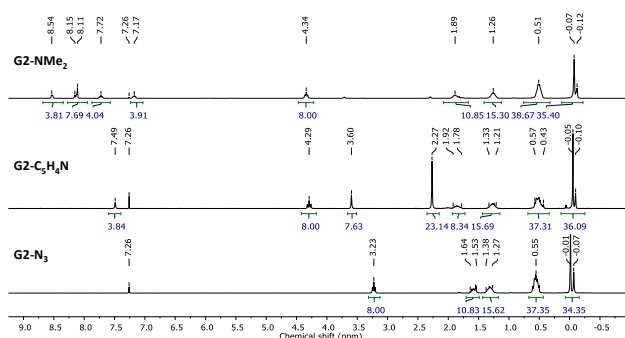


Figure 1.  $^1\text{H}$  NMR spectra of  $\text{G2-NMe}_2$ ,  $\text{G2-N}_3$ , and  $\text{G2-C}_5\text{H}_4\text{N}$ .

*N,N*-dimethylpropargylamine (98%, Sigma Aldrich), and  $\text{CuI}$  (Acros Organics) were purchased from commercial sources and used without further purification.

The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  spectra were recorded with a Bruker Avance 300 NMR spectrometer in  $\text{CDCl}_3$ ; chemical shifts were referenced relative to residual chloroform signal (7.26 ppm,  $^1\text{H}$ ).

The GPC analysis was performed on a Shimadzu chromatograph (Japan, Germany) using a RID-20A refractometer detector, Phenogel 5u 1000 Å column ( $300 \times 7.8$  mm), polystyrene standards, and THF as an eluent. The experiments were performed at 40 °C with the flow rate of 1 mL/s.

## Syntheses

**General procedure.** A mixture of the azide-terminated dendrimer, the acetylene substrate, 1 mol % of  $\text{CuI}$ , and the catalytic amount of  $\text{Et}_3\text{N}$  in THF was stirred at 60 °C for 6 h. The conversion was monitored using  $^1\text{H}$  NMR spectroscopy. The product was evacuated at 60 °C and 0.5 mbar.

The detailed synthetic procedure for each dendrimer is presented in the ESI.

## Conclusions

The first and second generation carbosilane dendrimers with the dimethylaminotriazole shell and carbosilane dendrimers with the triazole–pyridine shell were synthesized using the CuAAC reaction. The developed approach can be further used to obtain carbosilane dendrimers with a cationic shell for biomedical applications or for coordination of metal ions.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the synthetic procedures for the dendrimers; the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  spectra; the GPC curves. For ESI, see DOI: 10.32931/io2402a.

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