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Design and synthesis of readily degradable acyloxysilane dendrimers

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ABSTRACT

Two types of dendrimers with AB_2 branching, one with acyloxysilanes at the branching position (V type) and the other at the non-branching position (Y type), were synthesized using hydrosilylation with chlorosilanes followed by heterofunctional condensation with olefin-functional carboxylic acids, and examined as readily degradable template materials. The V type dendrimer was much more susceptible to ligand redistribution with chlorosilanes during preparation, whereas the Y type was less. The acyloxysilane linkages in these dendrimers could be cleaved readily by alcoholysis or hydrolysis on demand, making for suitable templates.

1. Introduction

Cleavable or degradable dendritic structures (including dendrimers, dendrons, and hyper-branched polymers) have been explored for various applications, such as drug and gene delivery,[1] release of fragrances and flavors,[2] generation of materials with microcavities,[3] and molecular imprinting,[4] in which these structures function as a 'covalent reservoir.[5] Ideally, the degradation of these structures should be tunable, and occur on demand under relatively mild conditions. The degradation conditions need to be orthogonal to reactions employed in the synthesis of the structures.

To date, most degradation reactions rely on hydrolyzable linkages, typically carbonyl based, including esters,[6] amides,[5] and carbamates.[7] Often, harsh degradation conditions are needed, such as treatment with strong base or strong acid, which preclude the incorporation of some functional groups and place restrictions on reactions for dendrimer synthesis or modification. For example, we previously found that the conditions needed for degradation of carbamate dendrimers limited the cross-linking methods that could be used in dendrimer modification.[8] Milder, anhydrous degradation reactions would permit incorporation of functional groups and synthetic methods that have not been previously accessible.

We investigated the use of acyloxysilane bonds, $R_3Si{-}O{-}(C{=}O){-}R$, in the construction of degradable dendrimer backbones. Also known as silyl esters, these bonds are appealing for degradable templates since they have been shown to cleave easily by alcoholysis and hydrolysis.[9,10] These reactions are quantitative, and the reactivity can be tuned by changing the substituent groups, through increasing steric bulk or different electronic contributions. Acyloxysilanes are susceptible to nucleophilic attack at either the Si or the C=O, depending on the nucleophile.[11] In addition, redistribution of silicon substituents, which commonly includes R, H, Cl, or OR (alkoxy, silanol, siloxy) substituents, has been observed that can be initiated by thermolysis or catalysis.[12] Such exchange of chlorosilanes and acyloxysilanes depends on steric and electronic effects at both silicon centers.[13]

Here, we report positioning the acyloxysilane bonds at branching (V type) and non-branching (Y type) silicon in the preparation of easily degradable dendrimers, in order to determine the versatility and/or limitations of each. Dendrimer generation growth was accomplished using a two-step process: platinum-catalyzed hydrosilylation with chlorosilanes and heterofunctional condensation at the chlorosilanes with olefinic carboxylic acid monomers in the presence of amine base, a strategy similar to the preparation of a variety of carbosilane-based dendrimers[14] and alkoxysilane dendrimers.[15] This two-step process was chosen to minimize self-termination events, such as cyclization.

2. Results and discussion

2.1. Acyloxysilane dendrimer synthesis strategy

In V type acyloxysilane dendrimers (Scheme 1), branching occurs at the silyl ester Si. Thus, a branching monomeric building unit was used that possessed one hydride and two chloro groups (e.g., dichlorosilane), with the fourth ligand at Si reserved for tuning selectivity and reactivity. Generation growth was accomplished by hydrosilylation of the branching monomeric unit with the previous

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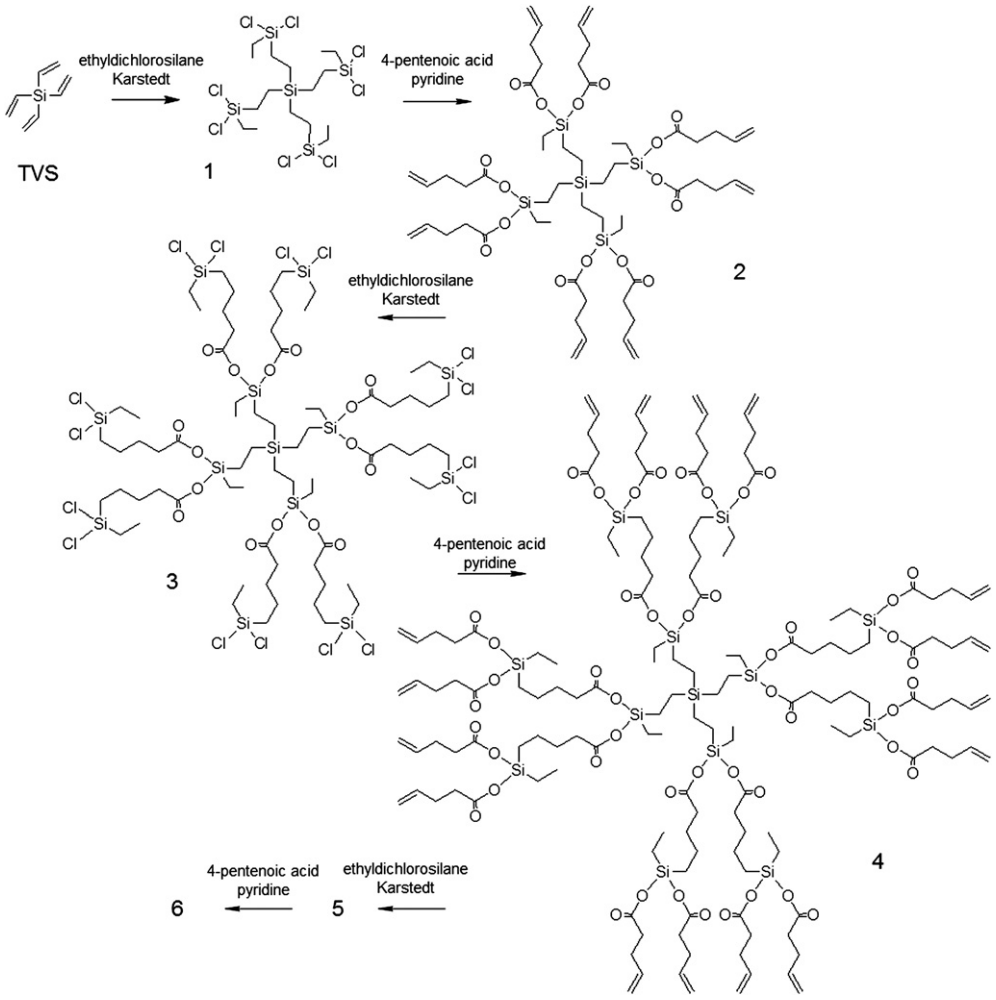


Scheme 1. Synthesis of V type acyloxysilane dendrimers by repeated cycles of catalyzed (Karstedt) hydrosilylation with dichloroethylsilane (half-generation dendrimers **1**, **3**, **5**), and condensation with 4-pentenoic acid in the presence of pyridine (full-generation dendrimers **2**, **4**, **6**).

generation to form the half generation, and full generation was completed by heterofunctional condensation with 4-pentenoic acid in the presence of pyridine, which promoted condensation and formed the byproduct pyridinium chloride, an easily removed salt. 4-Pentenoic acid was selected as the carboxylic acid monomer due to commercial availability and stability on storage.

For Y type acyloxysilane dendrimers (Scheme 2), branching occurs at Si atoms away from the silyl ester. Thus, two separate silicon centers are involved, which imparts more control on the steric bulk and provides an opportunity for further functionalization for specific applications. Generation growth was accomplished by hydrosilylation of chlorodimethylsilane, followed by heterocondensation with (diallylmethyl)silyl-4-butanoic acid **16**. The structure can be modified by varying the carbon chain length, increasing the branching to three, and varying the olefinic branch of the acid.

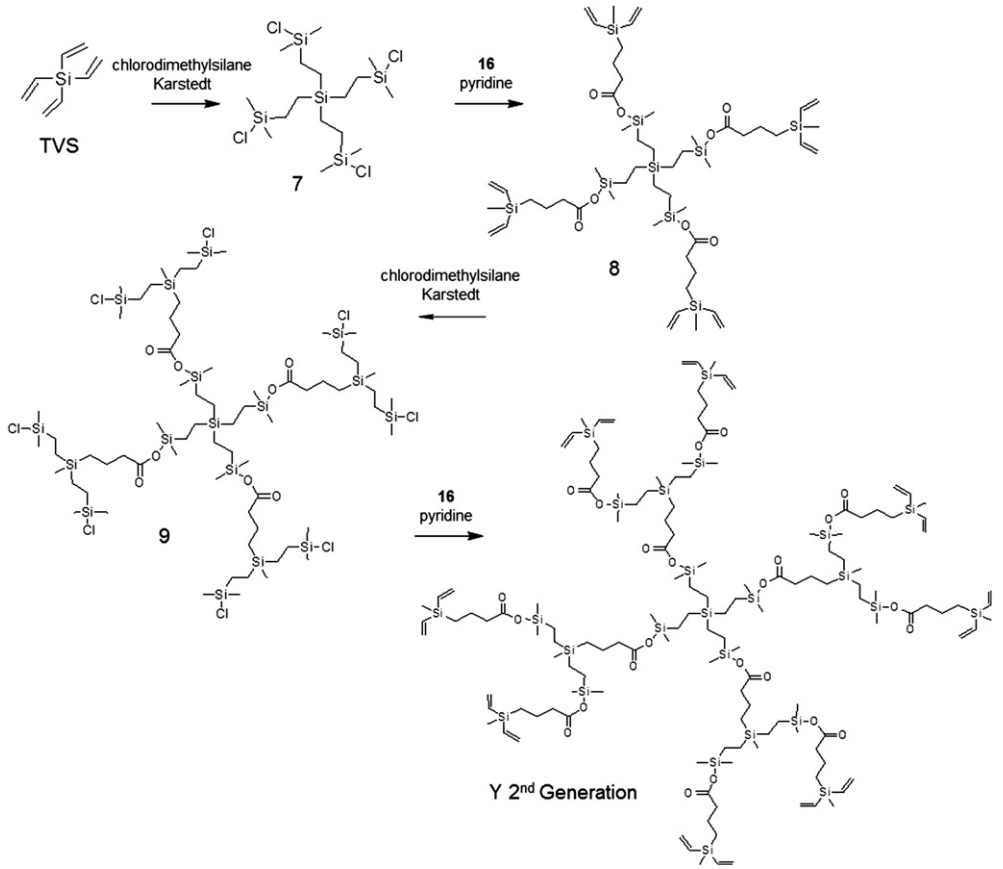
In both examples, tetravinylsilane was chosen to be the core, which has four olefins and tetrahedral symmetry. Hydrosilylation was performed with the Karstedt catalyst ($Pt(0)_2DVTMS_3$, divinyltetramethyldisiloxane) in tetrahydrofuran (THF). From its X-ray crystal structure, the Karstedt catalyst has both chelating and bridging divinyltetramethyldisiloxane ligands at the Pt centers prior to reaction (Fig. 1).[16]

2.2. V Type dendrimer synthesis

Half-generation dendrimer, **1**, was prepared by hydrosilylation of tetravinylsilane by dichloroethylsilane in the presence of the Karstedt catalyst in THF at 40 °C. ^{1}H NMR showed complete conversion of tetravinylsilane within 4 h. After purification by evacuation of volatile components, the resulting clear oil showed complete disappearance of vinyl olefin resonances in the high frequency region (δ 6.18 and 5.83 ppm) and the corresponding appearance of new resonances in the methylene region (δ 0.89 and 0.67 ppm) (Fig. S3). The product contained 85% **1** by β-addition and 15% of its isomer by α-addition. The competition between α- and β-hydrosilylation was both temperature- and solvent-dependent, and was shown to favor β-addition in THF at 40 °C, as reported by Seyferth and co-workers.[17] **1** was highly moisture sensitive and was kept under rigorous air-free conditions.

Preparation of first-generation dendrimer, **2**, was completed by condensation of **1** with 3 equiv of 4-penteneoic acid in anhydrous hexanes in the presence of 3 equiv of pyridine (per chlorosilane). The HCl–pyridine salt was removed by air-free filtration over a medium frit glass filter. Afterward, the residual 4-penteneoic acid was silylated with chlorotrimethylsilane to reduce the boiling point, again in the presence of excess pyridine as the base. After a second filtration of HCl–pyridine salts, all of the volatiles including the silylated 4-pentenoic acid were evacuated. It is important to exclude moisture during preparation, purification, analysis, and storage to avoid degradation of the acyloxysilane dendrimers.

These two synthesis steps were easily scalable, particularly the hydrosilylation reaction. The preparations of **3** and **4**, as well as higher generations, such as third-generation **6** (Fig. S2), could be carried out in a similar manner by repeating these two steps.



Scheme 2. Synthesis of Y type acyloxysilane dendrimer by repeated cycles of catalyzed (Karstedt) hydrosilylation with chlorodimethylsilane, followed by condensation with (diallylmethyl)silyl-4-butanoic acid **16** in the presence of pyridine.

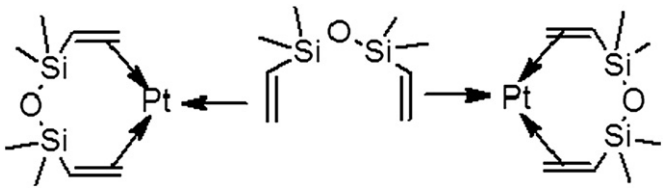


Fig. 1. Structure of Karstedt catalyst.

^{1}H NMR was not very useful in identifying ligand exchange or distinguishing products of α- and β-hydrosilylation. Fig. 2 shows the spectra for first (**2**), second (**4**), and third-generation (**6**) full-dendrimers. They all exhibited the common features of macromolecules, such as broad resonances and loss of splitting patterns. The major difference between **2** and **4** was the new methylene resonances at δ 1.60 and 1.40 ppm for **4**, due to hydrosilylation of the terminal olefin of **2**. The spectrum of the third-generation dendrimer (Fig. S1) was nearly identical to **4** except for the integrals of the resonances, consistent with expectation due to branching generations. The methylene protons of the core (δ 0.60 ppm and 0.45 ppm) were difficult to observe, due to the large number of protons of the ethylsilane groups at δ 1.00 ppm.

Ligand redistribution was encountered in generation growth hydrosilylation reactions in the preparation of **3** (1.5-generation) and **5** (2.5-generation). Detection of the extent of ligand redistribution immediately after reaction was difficult as further redistribution might have taken place during purification. For products after purification, redistribution could be readily detected with ^{29}Si NMR. Fig. 3 shows the spectrum of the purified product **3**,

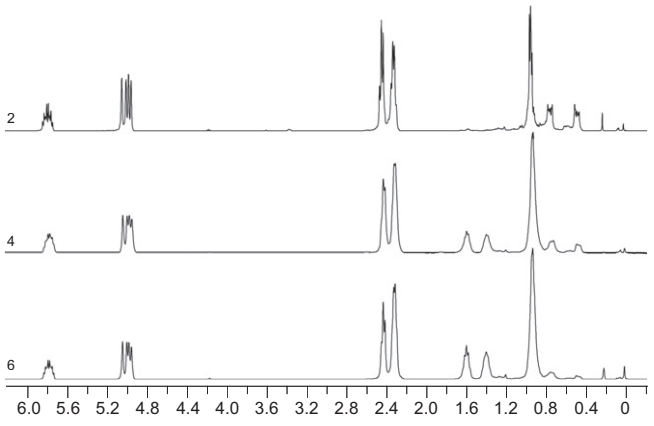


Fig. 2. ^{1}H NMR of V type dendrimers. Top to bottom: first- (**2**), second- (**4**), and third-generation dendrimers (**6**).

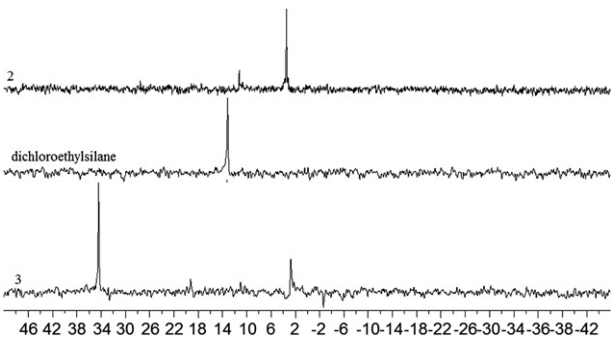


Fig. 3. ^{29}Si NMR of first-generation dendrimer (**2**), dichloroethylsilane (DCES), and the product in the preparation of 1.5-generation (**3**).

after evacuation of excess dichloroethylsilane and THF. For **2**, resonances were found at δ 11 ppm (core) and 3 ppm (geminal acyloxysilane), while dichloroethylsilane resonance was at 13 ppm. For the reaction product between these two, in addition to the expected resonances at δ 34, 11 and 3 ppm assigned to **3**, another resonance also appeared at δ 19 ppm, which was about halfway between the Si in dichlorosilanes and the dichlorosilyl groups in **3**. We assign this to Si in mixed acyloxychlorosilane species, with one chloro- and one acyloxy-substituent, which was formed by ligand redistribution. The resulting material contained defective dendrimers of **3**.

2.3. Ligand redistribution study

For the syntheses in Schemes 1 and 2, ligand exchange processes of interest were examined using model compound **10** and dichloroethylsilane (Fig. 4). Silane **10** mimics a segment of a V type dendrimer. In an NMR tube, **10** was dissolved in $CDCl_3$, dichloroethylsilane was added, and the reaction was monitored by ^{29}Si NMR. The ^{29}Si NMR resonance for **10** appeared at δ 5 ppm, and for dichloroethylsilane at δ 13 ppm. After 1 h, two new resonances were observed at δ 21 and −0.35 ppm, which were attributed to compounds **11** and **12**, respectively. After 24 h, the resonance of dichloroethylsilane disappeared, and another two new resonances appeared at δ 36 and −13.7 ppm, which were attributed to doubly exchanged products, dichlorodiethylsilane and **13**, respectively. Since **10** mimics the products of generation growth, condensation of a dichlorosilyl fragment with 4-pentenoic acid, the single exchange products would be the same as incomplete condensation, and double exchange products would reverse the condensation reaction.

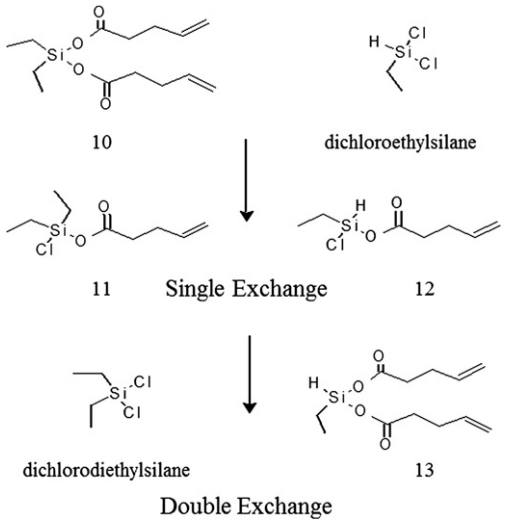
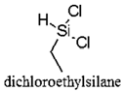
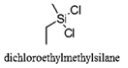
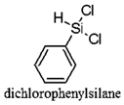
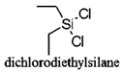
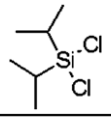


Fig. 4. Ligand exchange of **10** with dichloroethylsilane.

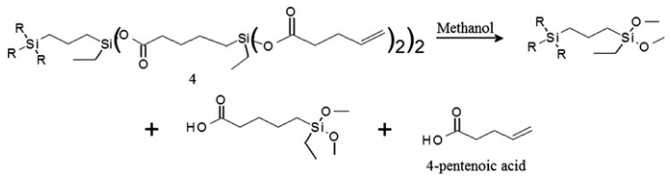
Additional experiments were conducted in order to gain a better insight into the extent of exchange during purification in the synthesis of V type dendrimer by examining ligand exchange between the first-generation dendrimer **2** and various dichlorosilanes without the Karstedt catalyst. The results are shown in Table 1. Under these conditions, dichloroethylsilane exchanged completely with **2**. Dichlorophenylsilane also exchanged rapidly with **2**, though only to 75% under the same conditions. Exchange was observed with dichlorodiorganyl silanes also, including dichloroethylmethylsilane and dichlorodiethylsilane. Only with dichlorodiisopropylsilane was there no observable exchange.

Table 1
Exchange of **2** with various dichlorosilanes. Compound **2** (0.050 mL) was dissolved in 0.380 mL of $CDCl_3$ followed by addition of 0.50 mL of respective dichlorosilanes, heated at 40 °C for 3 h

Dichlorosilane	% Exchanged	Dichlorosilane	% Exchanged
 dichloroethylsilane	100	 dichloroethylmethylsilane	25
 dichlorophenylsilane	75	 dichlorodiethylsilane	15
			0

2.4. V Type dendrimer degradation

V type dendrimers could be degraded under mild conditions by treatment with anhydrous methanol to form methoxysilanes and free carboxylic acids. Being less reactive or prone to gelation than silanols, methoxysilanes are preferred degradation products that are expected to be advantageous for post-synthetic functionalization. Degradation by methanolysis of both first and second-generation dendrimers, **2** and **4** (Scheme 3) occurred rapidly at room temperature. Only degradation at the silyl ester bond was observed. The degradation reactions could be monitored accurately by ^{13}C NMR. Although ^{1}H NMR contained analogous results, separate identification of methyl protons of methoxysilanes and methanol was difficult because of similar frequency shifts. The carbonyl carbons for dendrimer **4** were at δ 173 and 172 ppm, while 4-pentenoic acid was observed at δ 180 ppm. After methanolysis (Fig. 5), only two carbonyl resonances at δ 180 and 179 ppm were observed. The shifts to lower frequencies from those of **4** indicated replacement of the silyl ester bond with a less electron withdrawing substituent, as expected for methanolysis. No other products were detected.



Scheme 3. Degradation of **4** by methanolysis. R=dendrimer arms.

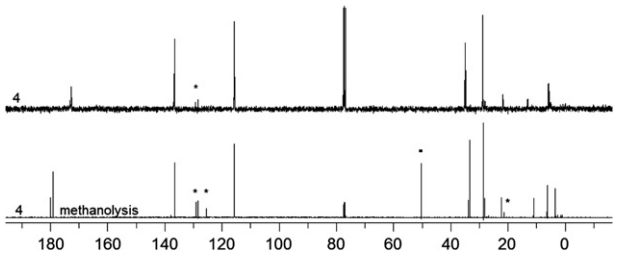
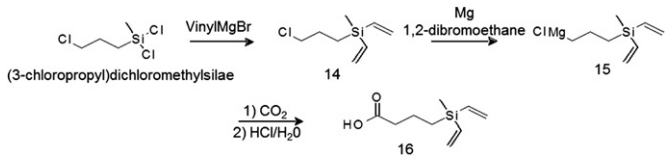


Fig. 5. ^{13}C NMR of **4** (top) and the product of methanolysis degradation (bottom) (*toluene, ■methanol).

2.5. Y Type dendrimer synthesis

The divinylsilyl acid used for branching was synthesized according to Scheme 4. (3-Chloropropyl)dichloromethylsilane was

used as the starting compound, although other molecules with different alkyl lengths or number of chlorosilane functional groups can be used for different dendrimer architectures. Grignard substitution of the chlorosilane was performed to introduce the olefin branches (step v). After purification, greater than 85% yield of product **14** was obtained. Then, the alkyl chloride moiety was activated with Mg to prepare a Grignard reagent, which was reacted with CO_2, and worked up with HCl to yield the branching carboxylic acid **16**.



Scheme 4. Synthesis of divinylsilyl carboxylic acid monomer **16** branching at chlorosilane, by Grignard substitution, followed by activation to Grignard, and then nucleophilic attack of CO_2.

Proton NMR of **14** showed vinyl resonances at δ 6.11 and 5.75 ppm and three methylene resonances at δ 1.80, 0.76, and 3.5 ppm (Fig. 6). For the divinyl acid **16**, the vinyl resonances remained and the three methylene resonances shifted to lower frequencies, especially the protons closest to chlorine, which shifted to δ 2.4 ppm. ^{13}C NMR of **16** showed the resonances of vinyls at δ 132 and 136 ppm, and the carbonyl carbon at δ 180 ppm, indicating that the free carboxylic acid form was present.

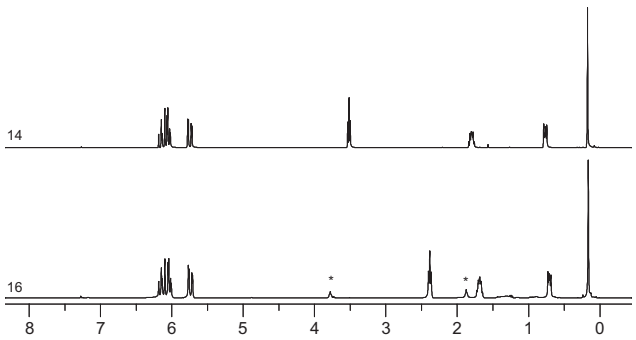


Fig. 6. ^{1}H NMR of product **14** (top) and carboxylic acid **16** (bottom). (*THF).

The Y type dendrimer was prepared with a divergent synthesis shown in Scheme 2, using tetravinylsilane as the core and **16** for branching. First, **7** was prepared by hydrosilylation with chlorodimethylsilane using the Karstedt catalyst. The reaction proceeded to completion readily, and **7** was purified by evacuation of volatiles. Then **7** was condensed with **16** in the presence of pyridine, and the reaction mixture was treated with chlorotrimethylsilane to cap the excess carboxylic acid. Pyridinium chloride salt was filtered under moisture-free conditions, and all volatiles were removed by evacuation to yield the first-generation dendrimer **8**. Complete removal of the excess divinylsilyl acid **16** was difficult, as the branching acid monomer remained high boiling, even when capped as a trimethylsilyl ester. Nevertheless, it could be accomplished by adding excess toluene and evacuation of volatiles multiple times. Successful synthesis of **7** was confirmed by multinuclear NMR analyses (Fig. 7). The ^{29}Si spectrum of **16** had a resonance at δ −12 ppm. The half-generation dendrimer **7** had two silicon resonances at δ 33 ppm (chlorosilane) and δ 10 ppm (core silicon). Condensation of **7** with **16** resulted in the new acyloxysilane in **8** with a resonance at δ 24 ppm, while the core remained at δ 10 ppm and the vinylsilicon of the acid remained at δ −12 ppm.

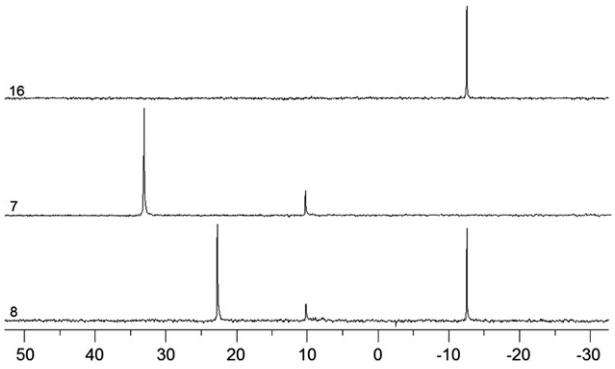


Fig. 7. ^{29}Si NMR of divinylsilyl carboxylic acid **16** (top), half-generation **7** (middle) and first-generation Y type dendrimer **8** (bottom).

Attempts to grow the next generation were not successful because hydrosilylation of **8** with chlorodimethylsilane to form the 1.5-generation dendrimer **9** could not be brought to completion. Although new methylene resonances were observed around δ 1.00 ppm, the vinyl resonances at δ 6.10 and 5.72 ppm were still observed. Increasing the temperature of hydrosilylation, addition of more catalyst precursor, or longer reaction times did not increase the yield of 1.5-generation dendrimer, which was estimated to be less than 10%. Even though the reaction was not complete, analysis indicated that no ligand redistribution had occurred during the hydrosilylation step. Nonetheless, improvement in this step is needed to bring the reaction to completion for the 1.5-generation synthesis, or an efficient purification method needs to be devised. Then, a purified **9** can be used to build the second-generation dendrimer.

3. Conclusion

Acyloxysilyl bonds can be incorporated into dendrimers or dendritic structures as an easily degradable bond. In principle, dendrimer growth can be achieved, using reactions such as hydrosilylation, without affecting the acyloxysilyl bond. However, the side reaction of ligand redistribution at the Si atom limits the generation growth process, since it results in loss of the acyloxysilyl bond from the dendritic structure and formation of a defective dendrimer. The ligand redistribution process can be minimized or even avoided by using a combination of substituent steric and electronic effects, and by designing the template dendrimer and product materials to avoid easily exchanged species. This was achieved with the Y type dendrimers with branching on the acid, where only single acyloxysilane and single chlorosilane are present. Nonetheless, the redistribution process restricts the types of dendrimer that may be synthesized with perfection.

Results of this study suggest that an acyloxysilyl bond is best applied as the final linkage before the ‘cargo’ in a degradable template. Since the cleavage of acyloxysilane bonds is facile even under mild conditions, the presence of a large variety of functional groups can be tolerated, such as those used in hydrosilylation and heterofunctional condensation for synthesis.

4. Experimental section

4.1. General

Solvents and chemicals were purchased (Aldrich Chemical) as well as the Karstedt catalyst (Gelest). All chemicals were used as supplied. Moisture-sensitive reagents were stored under N_2 in a glovebox (Vacuum Atmospheres), and reactions were performed with standard Schlenk techniques.

NMR spectra were acquired with a Varian Inova 400 MHz instrument in the Institute for Molecular Structure Education and Research Center at Northwestern University using the following parameters: ^{1}H: 400.14 MHz, 2 s recycle delay, internally referenced to solvent; ^{13}C: 100.63 MHz, ^{1}H decoupled, 2 s recycle delay, internally referenced to solvent; ^{29}Si: 79.50 MHz, 45 s recycle delay and externally referenced to tetramethylsilane in benzene-d_6 (C_6D_6). All chemical shifts are reported in ppm. ^{29}Si NMR RINEPT: Using a Refocused INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) pulse sequence with the following parameters $d1$=13 $d2$=0.0256 $d3$=0.0176.[18]

4.2. V Type dendrimer synthesis

*4.2.1. 0.5-Generation V dendrimer (**1**).* Tetravinylsilane (1 mmol, 0.167 mL, 0.134 g) was dissolved in anhydrous THF (10 mL), followed by the addition of Karstedt catalyst (0.010 mL, 2.1% Pt). Slowly, dichloroethylsilane (6 mmol, 0.711 mL, 0.774 g) was added to the reaction flask, which was then heated to 40 °C for 5 h. Excess silane and solvents were removed under reduced pressure, resulting in clear oil (1.35 g). ^{1}H NMR ($CDCl_3$): δ 1.09 (m, 20H), 0.90 (m, 8H), 0.67 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 12.42, 12.00, 6.36, 1.74. ^{29}Si NMR ($CDCl_3$): δ 35.28, 11.33. No useful MS or elemental analysis was obtained due to the high reactivity of silyl chloride with moisture.

*4.2.2. First-generation V dendrimer (**2**).* Product **1** (1.35 g) was dissolved in anhydrous hexanes (15 mL). Subsequently pyridine (30 mmol, 2.4 mL, 2.35 g) was syringed into the flask, followed by slow addition of 4-pentenoic acid (30 mmol, 3.0 mL, 2.94 g). The reaction was stirred, at room temperature for 1 h, then chlorotrimethylsilane (12 mmol, 1.5 mL, 1.30 g) was added, and stirring was continued for 15 min. The pyridinium chloride salts were removed by air-free filtration, and the captured salt was washed twice with anhydrous hexanes (10 mL). All the filtrates were combined, and the volatile components were removed under reduced pressure with gentle heating at 40 °C (2.15 g). ^{1}H NMR ($CDCl_3$): δ 5.83 (m, 8H), 5.05 (dd, J=17.2, 10.4 Hz, 16H), 2.48 (m, 16H), 2.36 (m, 16H), 1.02 (m, 20H), 0.80 (m, 8H), 0.54 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 172.12, 136.80, 116.00, 34.99, 29.05, 6.14, 5.55, 5.20, 1.80. ^{29}Si NMR ($CDCl_3$): δ 11.20, 3.40. LC/ESI-MS: m/z=1179 (theor. 1160). Anal. Calcd for $C_{56}H_{92}O_{16}Si_5$: C, 57.90; H, 7.98, found: C, 52.56; H, 8.06.

*4.2.3. 1.5-Generation V dendrimer (**3**).* Product **2** (1.16 g) was dissolved in toluene (10 mL), and Karstedt catalyst (0.010 mL, 2.1% Pt) was added. Subsequently dichloroethylsilane (14 mmol, 1.70 mL, 1.85 g) was added and the mixture was stirred for 15 min. Then the reaction mixture was heated to 40 °C and stirred for 4 h. All volatiles were removed under vacuum, leaving light yellow oil (2.16 g). ^{1}H NMR ($CDCl_3$): δ 2.42 (t, J=6.5 Hz, 16H), 1.71 (m, 16H), 1.58 (m, 16H), 1.10 (s, 40H), 1.00 (m, 16H), 0.80 (m, 8H), 0.60 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 172.79, 35.11, 27.83, 22.19, 19.60, 12.63, 6.42, 6.16, 5.58, 5.20, 1.32. ^{29}Si NMR ($CDCl_3$): δ 34.7, 19.6 (redistribution product), 11.4, 3.11. No useful MS or elemental analysis was obtained due to the high reactivity of silyl chloride with moisture.

*4.2.4. Second-generation V dendrimer (**4**).* Product **3** (1.00 g) was dissolved in toluene (20 mL). Then pyridine (30 mmol, 2.40 mL, 2.35 g) was added to the reaction flask, followed by 4-pentenoic acid (25 mmol, 2.50 mL, 2.45 g). The reaction was stirred for 3 h at room temperature when chlorotrimethylsilane (12 mmol, 1.50 mL, 1.30 g) was added. The pyridinium chloride salt was filtered on the air-free filtration apparatus, and washed with two portions hexane (10 mL). All volatiles were evacuated and then a fresh aliquot of toluene (6 mmol) was added and the system evacuated again. Product **4** was recovered as oil (1.28 g). ^{1}H NMR ($CDCl_3$): δ 5.83 (m, 16H), 5.05 (dd, J=17.4, 10.1 Hz, 32H), 2.46 (m, 32H), 2.37 (m, 48H), 1.65 (m, 16H), 1.45 (m, 16H), 1.00 (s, 76H), 0.80 (m, 8H), 0.54 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 173.2, 136.8, 115.7, 35.3, 35.0, 28.9, 28.8, 28.1, 21.8, 13.2, 6.19, 6.04, 5.92, 5.72, 5.10. ^{29}Si NMR ($CDCl_3$): δ 11.19, 3.87, 3.86. Anal. Calcd for $C_{152}H_{252}O_{48}Si_{13}$: C, 56.83; H, 7.91, found: C, 54.19; H, 7.90.

*4.2.5. 2.5-Generation V dendrimer (**5**).* Product **4** (1.28 g) was dissolved in toluene (12 mL), and Karstedt catalyst (0.015 mL, 2.1% Pt) was added. Dichloroethylsilane (28 mmol, 3.40 mL, 3.70 g) was added and the mixture was stirred for 15 min. Then the reaction mixture was heated to 40 °C and stirred for 4 h. All volatiles were removed under vacuum, leaving light yellow oil, **5** (2.60 g). ^{1}H NMR ($CDCl_3$): δ 2.33 (m, 48H), 1.65 (m, 48H), 1.50 (m, 48H), 1.04 (m, 120H), 1.00 (m, 48H), 0.76 (m, 8H), 0.54 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 173.0, 35.2, 27.6, 22.1, 19.7, 12.7, 6.26, 6.10, 5.94, 5.70. ^{29}Si NMR ($CDCl_3$): δ 34.7, 19.5 (redistribution product), 19.3 (redistribution product), 3.5, 3.0 (no core Si resonance observed). No useful MS or elemental analysis was obtained due to the high reactivity of silyl chloride with moisture.

*4.2.6. Third-generation V dendrimer (**6**).* Product **5** (1.30 g) was dissolved in toluene (20 mL). Subsequently, pyridine (63 mmol, 5.0 mL, 4.89 g) was added to the reaction flask, followed by the addition of 4-pentenoic acid (50 mmol, 5.00 mL, 4.90 g). The reaction mixture was stirred for 3 h at room temperature, and then chlorotrimethylsilane (12 mmol, 1.50 mL, 1.30 g) was added. The pyridinium chloride salt was removed by air-free filtration, and washed with hexane (two portions, 10 mL). All volatiles were evacuated and then a fresh aliquot of toluene (6 mL) was added and the system evacuated again. The product third-generation dendrimer was recovered as oil (2.30 g). ^{1}H NMR ($CDCl_3$): δ 5.83 (m, 32H), 5.05 (dd, J=17.3, 10.1 Hz, 64H), 2.46 (m, 64H), 2.37 (m, 112), 1.65 (m, 48H), 1.45 (m, 48H), 1.00 (m, 188), 0.80 (m, 8H), 0.54 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 173.2, 136.8, 115.7, 35.3, 35.0, 28.9, 28.8, 28.1, 21.8, 13.2, 6.19, 6.04, 5.92, 5.72, 5.10. ^{29}Si NMR ($CDCl_3$): δ 3.48, 3.26 (the resonance of the core Si was not observed). Anal. Calcd for $C_{344}H_{572}O_{112}Si_{29}$: C, 56.49; H, 7.88, found: C, 57.40; H, 8.24.

*4.2.7. Degradation of dendrimers **2** and **4**.* Dendrimer **2** or **4** (0.100 mL) was dissolved in dichloromethane (2 mL). Then a sample of the mixture (0.100 mL) was injected into anhydrous methanol (1 mL). This sample was then dried under N_2, and dissolved in $CDCl_3$ (0.500 mL).

*4.2.7.1. Degradation of **2**.* ^{1}H NMR ($CDCl_3$): δ 9.14 (s, 8H), 5.86 (m, 8H), 5.06 (dd, J=17.3, 11.2 Hz, 16H), 2.47 (m, 16H), 2.40 (m, 16H), 1.00 (m, 20H), 0.65 (m, 8H), 0.54 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 179.0, 136.6, 115.8, 50.5, 33.5, 28.8, 6.80, 2.86. ^{29}Si NMR ($CDCl_3$): δ 10.5, −1.30, −11.2, −11.5.

*4.2.7.2. Degradation of **4**.* ^{1}H NMR ($CDCl_3$): δ 10.66 (s, 24H), 5.79 (m, 16H), 5.00 (dd, J=17.3, 11.2 Hz, 32H), 2.41 (m, 32H), 2.33 (m, 48H), 1.63 (m, 16H), 1.40 (m, 16H), 0.93 (t, J=8.0 Hz, 24H), 0.61 (m, 32H), 0.48 (s, 16H). ^{13}C NMR ($CDCl_3$): δ 180.3, 179.5, 136.5, 115.9, 33.9, 33.5, 28.7, 28.3, 22.5, 11.3, 6.48 3.66. ^{29}Si NMR ($CDCl_3$): δ −1.63, −1.76, −10.7.

4.3. Y Type dendrimer synthesis

*4.3.1. Divinyl(3-chloropropyl)methylsilane (**14**).* (3-Chloropropyl) dichloromethylsilane (25 mmol, 4.00 mL, 4.82 g) was dissolved in anhydrous THF (10 mL) and cooled to 0 °C in an ice bath. Then, vinylmagnesium bromide (55 mmol, 55.00 mL, 1 M THF solution) was added dropwise over 30 min. The reaction was allowed to warm to room temperature over 30 min, and excess Grignard reagent was neutralized with 1 M HCl (2 mL). Product **14** was

extracted from the aqueous layer with cyclohexane (three portions, 25 mL). The organics were collected and dried with sodium sulfate, filtered, and concentrated on a rotary-evaporator. The residual oil was distilled at (32 °C, evacuated and closed) (3.31 g, 76% yield). ^{1}H NMR ($CDCl_3$): δ 6.14 (dd, J=19.7, 14.8 Hz, 2H), 6.05 (dd, J=14.8, 4.4 Hz, 2H), 5.75 (dd, J=19.7, 4.4 Hz, 2H), 3.52 (t, J=7.0 Hz, 2H), 1.80 (m, 2H), 0.76 (m, 2H), 0.17 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 136.35, 133.64, 48.06, 27.63, 11.89, −5.23. ^{29}Si NMR ($CDCl_3$): δ −12.12. Anal. Calcd for $C_8H_{15}SiCl$: C, 55.00; H, 8.66, found: C, 55.49; H, 8.62.

*4.3.2. Divinyl(4-butanoate)methylsilane (**16**).* Magnesium turnings (17.7 mmol, 0.430 g) were added to a 3-neck flask equipped with a condenser, a stopcock to manifold, and a septum. The system was heated to 80 °C and evacuated for 30 min. Then anhydrous THF (10 mL) was injected and refluxed for 10 min. 1,2-Dibromoethane in THF (1.77 mmol, 0.200 mL, 10% solution) was introduced under reflux. Divinyl(3-chloropropyl)methylsilane **14** (16 mmol, 2.92 mL) was added over 20 min, maintaining reflux. The reaction was continuously refluxed for 30 min, until a dark brown-black solution resulted containing product **15**. CO_2 (340 mmol, 15.0 g) was frozen into a Schlenk flask from an anhydrous CO_2 tank. The THF Grignard solution, as prepared, was syringed onto the CO_2 and the mixture was warmed to room temperature. Sodium bicarbonate (5 mL, pH 10) solution was added and the mixture was washed with Et_2O (three portions, 25 mL). Finally, 1 M HCl solution was added until the aqueous phase pH reached 1, which allowed the acid **16** to be extracted with Et_2O (2.48 g, 85% yield). ^{1}H NMR ($CDCl_3$): δ 6.13 (dd, J=19.7, 14.8 Hz, 2H), 6.03 (dd, J=14.8, 4.4 Hz, 2H), 5.73 (dd, J=19.7, 4.4 Hz, 2H), 2.38 (t, J=7.3 Hz, 2H), 1.68 (m, 2H), 0.70 (m, 2H), 0.16 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 180.61, 136.59, 133.57, 37.85, 19.54, 13.98, −5.26. ^{29}Si NMR ($CDCl_3$): δ −12.26. HRMS (ESI) Calcd for $C_9H_{15}O_2Si$: 183.0847 ($M-H^-$), found: 183.0836.

*4.3.3. 0.5-Generation Y dendrimer (**7**).* Tetravinylsilane (1 mmol, 0.167 mL, 0.134 g) was dissolved in anhydrous THF (10 mL). Karstedt catalyst solution (0.010 mL, 2.1% Pt) was added and the mixture was stirred for 2 min. Then chlorodimethylsilane (6 mmol, 0.666 mL, 0.568 g) was injected into the flask, which was stirred for 15 min while the mixture was heated to reflux from the heat of reaction. When the exotherm subsided, the flask was submerged into a 40 °C bath for 3 h. All volatiles were evacuated leaving a white semi-solid. No further purification was attempted with the reactive chlorosilane intermediates (0.51 g) ^{1}H NMR ($CDCl_3$): δ 0.66 (m, 8H), 0.57 (m, 8H), 0.40 (s, 24H). ^{13}C NMR ($CDCl_3$): δ 11.4, 2.2, 1.2. ^{29}Si NMR ($CDCl_3$): δ 33.1.

*4.3.4. First-generation Y dendrimer (**8**).* Product**7** (0.8 mmol) remaining in the reaction flask was dissolved toluene (10 mL), and then pyridine (5.5 mmol, 0.450 mL, 0.44 g) was added, followed by **16** (3.6 mmol, 0.670 g). The mixture was stirred for 1 h, and then chlorotrimethylsilane (1 mmol, 0.127 mL, 0.108 g) was injected and the reaction proceeded for another 15 min. The pyridinium chloride salt was air-free filtered and washed twice with toluene (two portions, 10 mL). All volatiles were evacuated. ^{1}H NMR indicated capped-**16** was present. The product was purified further by addition of toluene (25 mL) and evacuation to remove residual capped-**16**. Product **8** was recovered as clear oil (0.95 g) ^{1}H NMR ($CDCl_3$): δ 6.34 (dd, J=19.5, 14.6 Hz, 8H) 6.22 (dd, J=14.6 Hz. J=4.1 Hz, 8H), 5.92 (dd, J=19.5, 4.1 Hz, 8H), 2.54 (t, J=7.6 Hz, 8H), 1.84 (m, 8H), 0.87 (m, 8H), 0.79 (m, 8H), 0.67 (m, 8H), 0.47 (s, 24H), 0.35 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 174.3, 136.7, 133.5, 39.5, 19.7, 13.9, 8.2, 1.8, −2.2, −5.2. ^{29}Si NMR ($CDCl_3$): δ 23.2, 10.4, −12.8. Anal. Calcd for $C_{48}H_{100}O_8Si_9$: C, 54.53; H, 9.54, found: C, 57.70; H, 9.29.

*4.3.5. 1.5-Generation Y dendrimer (**9**).* Product **8** (0.300 mL) was dissolved in anhydrous THF (10 mL). Karstedt catalyst solution (0.015 mL, 2.1% Pt) was added and, after 3 min, dimethylchlorosilane (2.4 mmol, 0.266 mL, 0.227 g) was injected. After 15 min of stirring at room temperature, the reaction flask was heated to 40 °C and stirred for 3 h. All volatiles were evacuated at 40 °C, and multinuclear NMR analysis was performed on the residual brown (Pt agglomerates) oil **16**. About 30% conversion of olefins was accomplished under these conditions, by integral analysis to dendrimer arms (no internal standard).

4.4. Redistribution reactions

*4.4.1. Synthesis of diethylsilyldipentanoate (**10**).* Dichlorodiethylsilane (1 mmol, 0.150 mL) was dissolved in toluene (6 mL), to which pyridine (2.6 mmol, 0.260 mL, 0.54 g) and 4-pentenoic acid (2.5 mmol, 0.260 mL, 0.255 g) were added. The reaction was stirred for 30 min, and then chlorotrimethylsilane (2.5 mmol, 0.200 mL, 0.23 g) was added and stirred for 30 min. The pyridinium chloride salts were filtered under air-free conditions, and the volatile components were evacuated (0.278 g, 98% yield). ^{1}H NMR ($CDCl_3$): δ 5.80 (m, 2H), 5.00 (dd, 4H), 2.45 (m, 4H), 2.34 (m, 4H), 0.96 (m, overlapped ethyl, 10H). ^{13}C NMR ($CDCl_3$): δ 172.8, 136.7, 115.7, 34.9, 29.0, 5.92, 5.40. ^{29}Si NMR ($CDCl_3$): δ 5.28.

*4.4.2. Redistribution of **10** with dichloroethylsilane.* Product **10** (0.08 mL) was dissolved in $CDCl_3$ (0.750 mL) and dichloroethylsilane (0.020 mL) was added. The reaction was analyzed at 1 h by ^{29}Si NMR. It contained four resonances attributed to four different compounds, see Fig. 2, compound identified in parenthesis. ^{29}Si NMR ($CDCl_3$): δ 21.2 (**11**), 13.2 (dichloroethylsilane), 5.33 (**10**), −0.33 (**12**). At 24 h the solution was analyzed again, and was found to contain 6 resonances. The two additional peaks were found by ^{29}Si NMR ($CDCl_3$): δ 36.5 (dichlorodiethylsilane), −13.7 (**13**).

*4.4.3. Redistribution of **2** with various dichlorosilanes.* For all dichlorosilane redistribution tests an NMR tube $CDCl_3$ (0.380 mL) and **6** (0.050 mL) was prepared. Then, the individual dichlorosilanes (0.050 mL) were injected; one per NMR tube, and the NMR tube was heated for 3 h at 40 °C. Full multinuclear NMR was acquired. Silicon NME was most useful and a full ^{29}Si analysis appears in Fig. S1 of the Supplementary data.

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Supplementary data

The contents of Supplementary data include the following: (A) ^{29}Si NMR of ligand redistribution of first-generation V Type dendrimer (**2**) with various dichlorosialnes, (B) third-generation V Type dendrimer (**6**) figure and (C) FTIR of first-(**2**), second-(**4**), and third-generation (**6**) V Type dendrimers. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.07.068.

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