Convergent dendron approach using a phenol triallyl building block: synthesis of a phenol dendron containing 27 allyl termini

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A successful convergent dendron synthesis is achieved using a phenol triallyl (AB$_3$) building block by a sequence of reactions consisting of hydrosilylation-phenol protection. The key feature is the hydrosilylation using dimethylchloromethylsilane that avoids the side dehydrohalogenation previously found with linear branches containing β-hydrogens. The advantage of the AB$_3$ building block is the multiplication of the dendron branches by three at each generation, which allows the synthesis of the second-generation 27-allyl phenol dendron.

Since Vögtle' seminal report of the first iteration 25 years ago,[1] dendrimer syntheses have been achieved using a large variety of strategies and frameworks, and numerous potential application are forecast.[2–4] The divergent synthetic method has been the one used most because it is the easiest one to carry out, and also because it is the only one that can lead to large dendrimers even if defects cannot be discarded. The convergent method appeared in the early 90's with the reports of the groups of Frechet,[5] Miller[6] and Moore[7] and has been recently reviewed.[8] It is elegant, and its great advantages are that it can lead to pure dendrons that are bifunctional: they can be decorated on the periphery for a given function or property, and they still bear another functional group at the focal point for attachment onto a dendritic core, nanoparticle, polymer, surface, etc. Although dendrons have a limited size because their synthesis cannot be extended due to steric bulk around the focal point that needs be reactive, it is likely that they will play a key role in future nanotechnology involving molecular components. We have already shown that small dendrons bearing ferrocenylsilyl or amidoferrocenyl termini are efficient sensors for the dihydrogenophosphate anion when, as part of thiolate ligands, they are attached to gold nanoparticles.[9] So far, Fréchet's dendrons (AB$_2$ units) have been widely used in the literature, and AB$_3$ units are relatively scarce.[8] We now report another convergent dendron synthesis based on a phenoltriallyl building block up to the second generation, i.e. 27 allyl groups. This molecular brick has already been used to synthesize dendrimers, but these attempts of convergent syntheses of dendrons have so far been frustrated by side reactions.[10] Indeed the synthesis involved the nucleophilic substitution of the iodo group of the iodoalkyl branches by the phenol triallyl, but dehydrohalogenation became dominant. The present strategy prevents this side reaction by removing β-hydrogens on the termini.

Experimental section

Trichloro-trisilicium aryl sulfide 2

A mixture of triallyl sulfide dendron 1 (0.50 g, 1.93 mmol) and SiHMe$_2$(CH$_2$Cl) (0.945 g, 8.706 mmol, 1.1 mL), in Et$_2$O, was stirred for 48 h at ambient temperature. The solution was filtered on Celite, and the solvent was removed under vacuum. After column chromatography on silica gel with a mixture of pentane : Et$_2$O (95 : 5) as eluent, 2 was obtained as a colorless oil (1.020 g, 1.74 mmol, 90%). Elemental analysis calcd for C$_{26}$H$_{49}$Si$_3$Cl$_3$S: H 8.45, C 53.44; found: H 8.35, C 53.00%. ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.21 (s, C$_6$H$_4$, 4H); 2.72 (s, ClCH$_2$, 6H); 2.50 (s, SCH$_3$, 3H); 1.60 (m, CH$_2$, 6H); 1.06 (m, CH$_2$, 6H); 0.57 (m, SiCH$_2$, 6H); 0.05 (s, SiCH$_3$, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 143.3 (C$_q$, ArS); 140.0 (C$_q$, Ar); 127.4 (CH$_{Ar}$); 114.8 (CH$_{Ar}$); 43.1 (C$_q$–CH$_2$); 41.9 (CH$_2$); 30.2 (ClCH$_2$); 17.5 (CH$_2$CH$_2$Si); 15.9 (SCH$_3$); 14.2 (CH$_2$Si); −4.0 (SiMe).

Triiodo-trisilicium aryl sulfide 3

A mixture of 2 (0.500 g, 0.855 mmol) and, NaI (1.77 g, 12.8 mmol), in 2-butanone, was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et$_2$O (50 × 3 mL). This solution was washed with 3 × 50 mL of a saturated aqueous solution of Na$_2$S$_2$O$_3$. The solvent was removed under vacuum, which gave 3 as a yellow oil (0.624 g, 0.726 mmol 85%). Elemental analysis calcd for C$_{26}$H$_{49}$Si$_3$I$_3$S: H 5.75, C 36.37; found: H 5.55, C 35.82%. ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.21 (s, C$_6$H$_4$, 4H); 2.50 (s, SCH$_3$, 3H); 1.96 (s, ICH$_2$); 1.60 (m, CH$_2$, 6H); 1.06 (m, CH$_2$, 6H); 0.60 (m, SiCH$_2$, 6H); 0.09 (s, SiCH$_3$, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 143.1 (C$_q$, ArS); 140.6 (C$_q$, Ar); 127.5 (CH$_{Ar}$); 114.8 (CH$_{Ar}$); 43.1 (C$_q$–CH$_2$); 41.9 (CH$_2$); 17.5 (CH$_2$CH$_2$Si); 16.00 (SCH$_3$); 15.7 (CH$_2$Si); −3.39 (SiMe); −13.60 (CH$_2$I).

9-allyl-trisilicium aryl sulfide 5

A mixture of triallylmethylphenol 4 (0.598 g, 2.620 mmol) and K$_2$CO$_3$ (0.413g, 2.990 mmol), in 20 mL DMF, was stirred for 30 min at ambient temperature. The triiodo-trisilicium aryl sulfide 3 (0.500 g, 0.582 mmol) in solution in 5 mL DMF was added, and the reaction mixture was stirred at 80 °C 48 h. The solvent was removed under vacuum and the product was extracted with Et$_2$O. The organic layer was washed several times with water in order to remove DMF, then dried over

sodium sulfate, filtered and evaporated under vacuum. After column chromatography on silica gel using a mixture of pentane : Et$_2$O (9 : 1) as the eluent, **5** was obtained as a colorless oil (0.410 g, 0.353 mmol, 60%). Elemental analysis calcd for C$_{74}$H$_{106}$Si$_3$O$_3$S: H 9.21, C 76.62; found: H 9.23, C 76.52%. MALDI TOF mass spectrum, m/z: 1160.04 [M]$^+$ (calcd 1159.98). ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.19 (d, C$_6$H$_4$, 10H); 6.84 (d, C$_6$H$_4$, 6H); 5.54 (m, CH$_2$=CH, 9H); 5.00 (m, CH$_2$=CH, 18H); 3.49 (s, CH$_2$O, 6H); 2.45 (s, SCH$_3$, 3H); 2.43 (d, CH$_2$=CH–CH$_2$, 18H); 1.66 (m broad, CH$_2$, 6H); 1.20 (m broad, CH$_2$, 6H); 0.61 (m broad, CH$_2$, 6H); 0.05 (s, SiMe, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 159.41 (C$_q$, ArO); 145.00 (C$_q$, ArS); 137. 25 (C$_q$, Ar); 134.78 (CH$_2$=CH); 134.62 (C$_q$, Ar); 127.46 (CH$_{Ar}$); 127.09 (CH$_{Ar}$); 117.43 (CH$_2$=CH); 114.64 (CH$_{Ar}$); 113.55 (CH$_{Ar}$); 60.15 (CH$_2$O); 43.53 (C$_q$–CH$_2$); 42.65 (C$_q$–CH$_2$); 42.01 (CH$_2$); 17.70 (CH$_2$); 16.01 (SCH$_3$); 14.64 (CH$_2$); −4.56 (SiMe).

Trichloro-trisilicium phenol dendron 6

A mixture of triallyl dendron **4** (1 g, 4.380 mmol) and SiH-Me$_2$(CH$_2$Cl) (2.279 g, 24.091 mmol, 1.2 mL), in Et$_2$O, was stirred for 48 h at ambient temperature. The solution was filtered on Celite, and the solvent was removed under vacuum. After column chromatography on silica gel with a mixture of pentane : Et$_2$O (95 : 5) as eluent, **6** was obtained as a colorless oil (2.209 g, 3.985 mmol, 91%). Elemental analysis calcd for C$_{25}$H$_{47}$Si$_3$Cl$_3$O: H 8.55, C 54.18; found: H 8.35, C 54.62%. ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.12 (d, C$_6$H$_4$, 2H); 6.76 (d, C$_6$H$_4$, 2H); 4.65 (s, OH, 1H); 2.72 (s, ClCH$_2$, 6H); 1.60 (m, CH$_2$, 6H); 1.06 (m, CH$_2$, 6H); 0.57 (m, SiCH$_2$, 6H); 0.05 (s, SiCH$_3$, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 155.0 (C$_q$, ArO); 140.0 (C$_q$, Ar); 127.5 (CH$_{Ar}$); 114.8 (CH$_{Ar}$); 43.1 (C$_q$–CH$_2$); 41.9 (CH$_2$); 30.5 (ClCH$_2$); 17.5 (CH$_2$CH$_2$Si); 14.5 (CH$_2$Si); −4.1 (SiMe).

Triiodo-trisilicium phenol dendron 7

A mixture of **6** (2.178 g, 3.930 mmol) and, NaI (2.279 g, 58.945 mmol), in 2-butanone, was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et$_2$O (50 × 3 mL). This solution was washed with 3 × 50 mL of a saturated aqueous solution of Na$_2$S$_2$O$_3$. The solvent was removed under vacuum, which gave **7** as a yellow oil (3.234 g, 3.903 mmol, 99%). Elemental analysis calcd for C$_{25}$H$_{47}$Si$_3$I$_3$O: H 5.72, C 36.24; found: H 5.64, C 37.01%. ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.12 (d, C$_6$H$_4$, 2H); 6.76 (d, C$_6$H$_4$, 2H); 4.76 (s, OH, 1H); 1.94 (s, ICH$_2$, 6H); 1.60 (m, CH$_2$, 6H); 1.05 (m, CH$_2$, 6H); 0.58 (m, SiCH$_2$, 6H); 0.07 (s, SiCH$_3$, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 155.1 (C$_q$, ArO); 140.6 (C$_q$, Ar); 127.5 (CH$_{Ar}$); 114.8 (CH$_{Ar}$); 43.1 (C$_q$–CH$_2$); 41.9 (CH$_2$); 17.5 (CH$_2$CH$_2$Si); 15.7 (CH$_2$Si); −2.95 (SiMe); −13.1 (CH$_2$I).

Triiodo-trisilicium phenol propionate 8

13.35 mL (1.776 g, 9.655 mmol) of a fresh solution of C$_2$H$_5$COI, prepared by slowly adding 2.4 mL C$_2$H$_5$COCl to 5 g of Me$_3$SiI and 22.6 mL CH$_2$Cl$_2$, was added to a solution of **7** (2 g, 2.414 mmol) in 30 mL CH$_2$Cl$_2$. Then, NEt$_2$Pr^i (0.030 g, 0.214 mmol) was also added. The reaction mixture was stirred for 16 h at ambient temperature. After removal of the solvent under vacuum, the residue was extracted with CH$_2$Cl$_2$ (3 × 40 ml). The organic solution was washed with a saturated aqueous solution of sodium bicarbonate, then with an aqueous solution saturated with Na$_2$S$_2$O$_3$ and dried over sodium sulfate. After removing the solvent under vacuum, the protected phenol dendron **8** was obtained as an orange–yellow oil. Elemental analysis calcd for C$_{28}$H$_{51}$Si$_3$I$_3$O: H 5.92, C 36.72; found: H 5.72, C 36.21%. (1.943 g, 2.196 mmol, 91%). ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.24 (d, C$_6$H$_4$, 2H); 7.03 (d, C$_6$H$_4$,

2H); 2.59 (q, CH$_3$CH$_2$CO, 2H); 1.96 (s, ICH$_2$, 6H); 1.65 (m, CH$_2$, 6H); 1.05 (m, CH$_2$, 6H); 0.60 (m, SiCH$_2$, 6H); 0.08 (s, SiCH$_3$, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 175.8 (CO); 150.0 (C$_q$, ArO); 145.1 (C$_q$, Ar); 127.3 (CH$_{Ar}$); 120.8 (CH$_{Ar}$); 43.6 (C$_q$–CH$_2$); 41.8 (CH$_2$); 27.6 (CH$_2$); 17.6 (CH$_2$CH$_2$Si); 15.7 (CH$_2$Si); 9.1 (CH$_3$CH$_2$CO); −3.0 (SiMe); −13.1 (CH$_2$I).

### 9-Allyl-trisilicium phenol dendron 9

A mixture of triallylmethylphenol **9** (0.680 g, 2.978 mmol) and, K$_2$CO$_3$ (0.417 g, 2.978 mmol), in 20 mL DMF, was stirred for 30 min at ambient temperature. The protected triiodo-trisilicium phenol propionate **8** (0.440 g, 0.497 mmol) in solution in 5 mL DMF was added, and the reaction mixture was stirred at 80 °C for 48 h. Then 0.360 g K$_2$CO$_3$ and 0.600 mL water were added, and the reaction mixture was stirred at 80 °C for 24 h. The solvent was removed under vacuum and the product extracted with Et$_2$O. The organic layer was washed several times with water in order to remove DMF, then dried over sodium sulfate, filtered and evaporated under vacuum. After column chromatography on silica gel using a mixture of pentane : Et$_2$O (9 : 1) as the eluent, **9** was obtained as a colorless oil (0.380 g, 0.336 mmol, 68%). Elemental analysis calcd for C$_{73}$H$_{104}$Si$_3$O$_4$: H 9.28, C 77.60; found: H 9.31, C 77.09%. MALDI TOF mass spectrum, m/z: 1151.77 [M + Na]$^+$ (calcd 1152.87). ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.20 (d, C$_6$H$_4$, 6H); 7.09 (d, C$_6$H$_4$, 2H); 6.87 (d, C$_6$H$_4$, 6H); 6.67 (d, C$_6$H$_4$, 2H); 5.56 (m, CH$_2$=CH, 9H); 5.03 (m, CH$_2$=CH, 18H); 4.62 (s, OH, 1H); 3.52 (s, CH$_2$O, 6H); 2.43 (d, CH$_2$=CH–CH$_2$, 18H); 1.61 (m broad, CH$_2$, 6H); 1.14 (m broad, CH$_2$, 6H); 0.60 (m broad, CH$_2$, 6H); 0.06 (s, SiMe, 18H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 159.38 (C$_q$, ArO); 152.84 (C$_q$, ArO); 139.77 (C$_q$, Ar); 137.17 (C$_q$, Ar); 134.74 (CH$_2$=CH); 127.51 (CH$_{Ar}$); 127.40 (CH$_{Ar}$); 117.40 (CH$_2$=CH); 114.65 (CH$_{Ar}$); 113.52 (CH$_{Ar}$); 60.08 (CH$_2$O); 43.13 (C$_q$–CH$_2$); 42.60 (C$_q$–CH$_2$); 41.96 (CH$_2$); 17.63 (CH$_2$); 14.58 (CH$_2$); −4.61 (SiMe).

27-Allyl-9-siliciumphenol dendron 10

A mixture of 9-allyl-3-silicium phenol dendron **9** (0.500 g, 0.442 mmol) and, K$_2$CO$_3$ (0.070 g, 0.500 mmol), in 10 mL DMF, was stirred for 30 min. at ambient temperature. The protected tri-iododendron **8** (0.087 g, 0.098 mmol) in solution in 3 mL DMF was added, and the reaction mixture was stirred at 80 °C 72 h. Then, 0.052 g K$_2$CO$_3$ and 0.090 mL water were added, and the reaction mixture was stirred at 80 °C for 48 h. The solvent was removed under vacuum and the product was extracted with Et$_2$O. The organic layer was washed several times with water in order to remove DMF, then dried over sodium sulfate, filtered and evaporated under vacuum. After chromatography on silica gel using a mixture of pentane : Et$_2$O (9 : 1) as the eluent, **10** was obtained as a colorless oil (0.169 g, 0.044 mmol, 45%). Elemental analysis calcd for
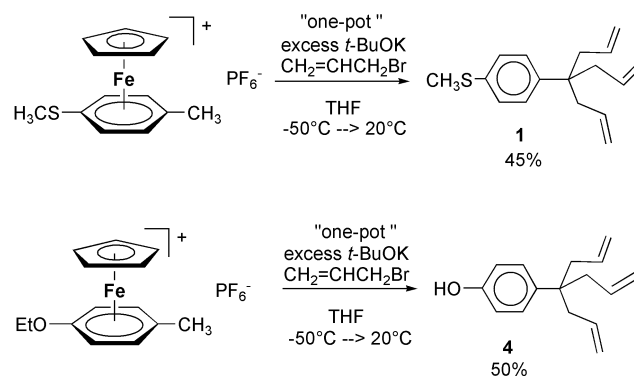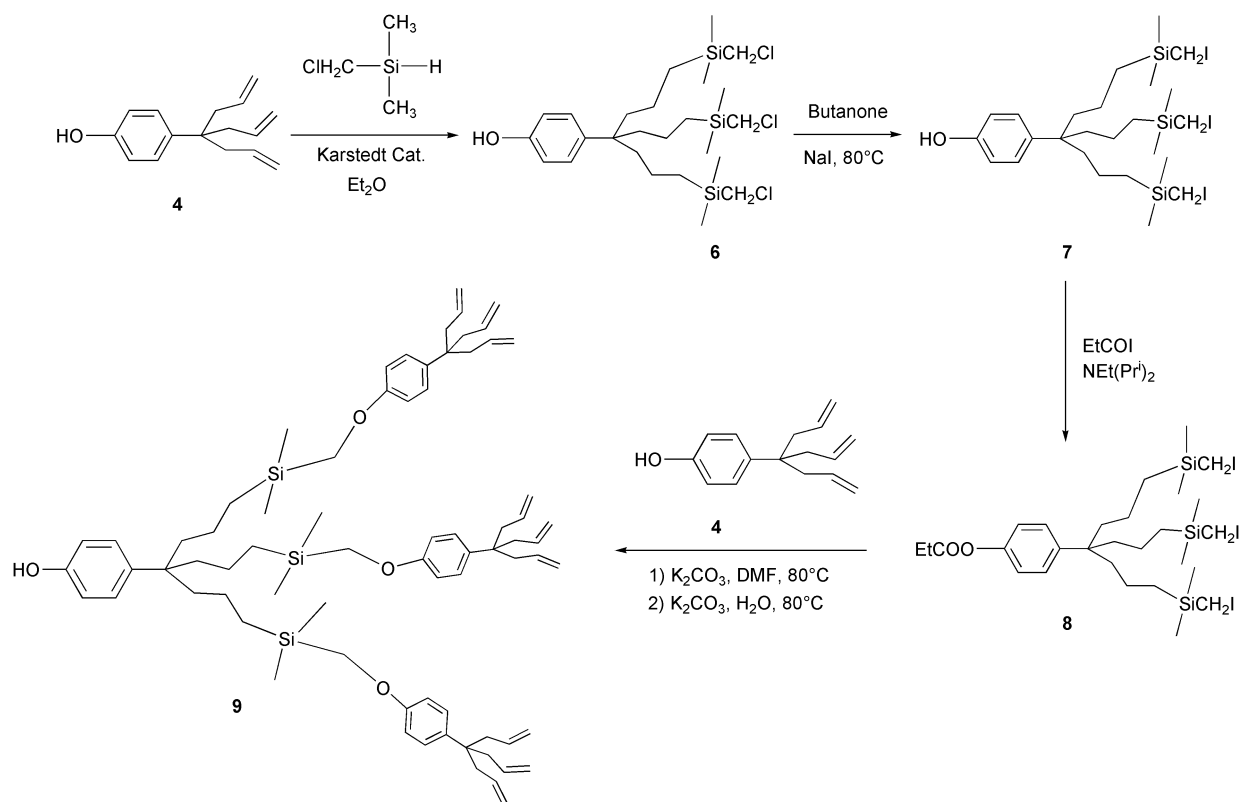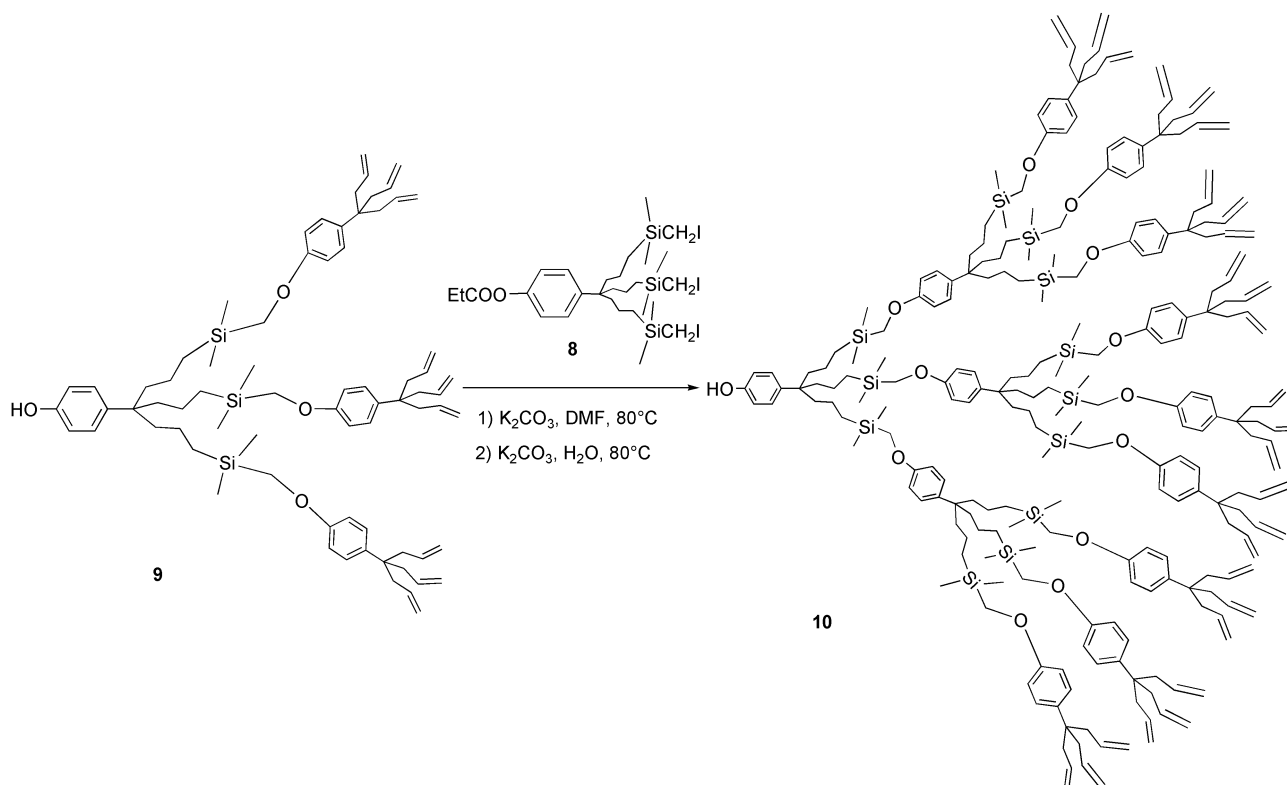

Scheme 1
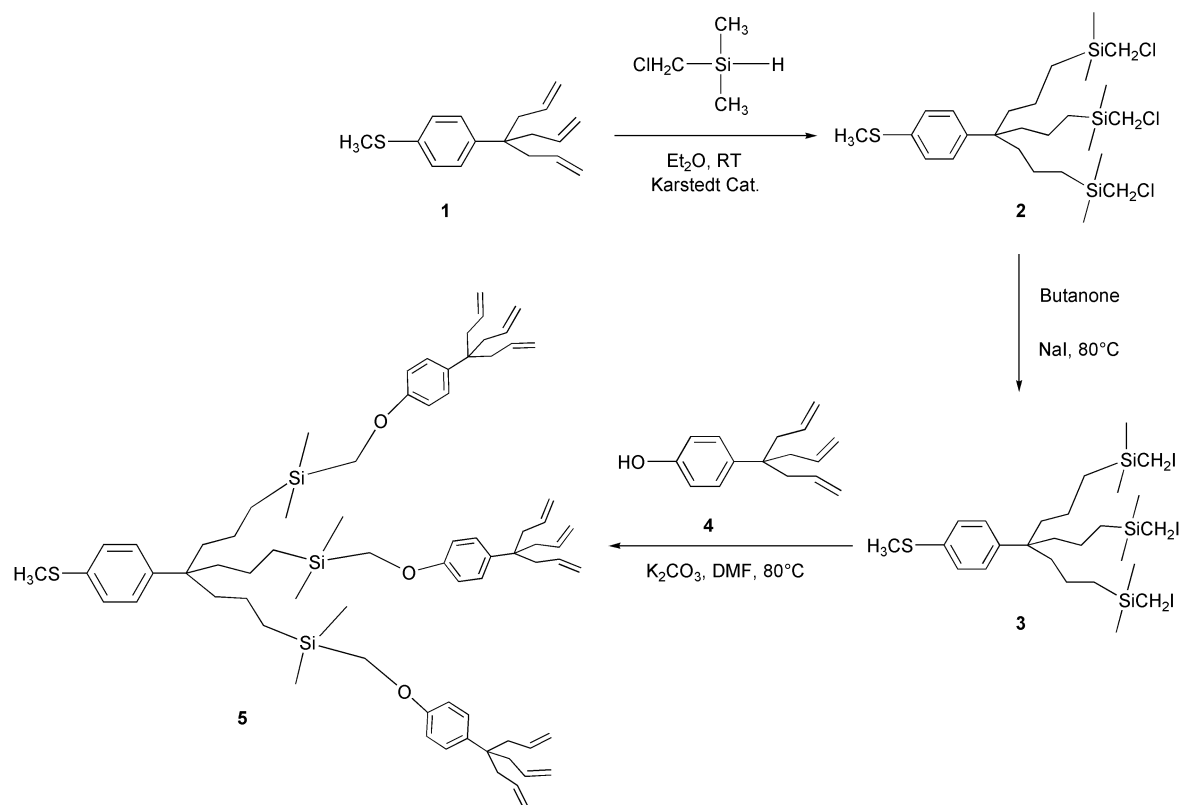
Scheme 2

$C_{244}H_{356}Si_{12}O_{13}$: H 9.36, C 76.43; found: H 9.54, C 75.72. MALDI TOF mass spectrum, m/z: 3856.37 $[M + Na]^+$ (calcd 3857.51). ^{1}H NMR (CDCl$_3$): δ_{ppm} 7.20 (d, C$_6$H$_4$, 24H); 7.01 (d, C$_6$H$_4$, 2H); 6.88 (d, C$_6$H$_4$, 24H); 6.67 (d, C$_6$H$_4$, 2H); 5.55 (m, CH$_2$=CH, 27H); 5.02 (m, CH$_2$=CH, 54H); 4.67 (s, OH, 1H); 3.51 (s, CH$_2$O, 6H); 2.43 (d, CH$_2$=CH–CH$_2$, 54H); 1.63 (m broad, CH$_2$, 18H); 1.15 (m broad, CH$_2$, 18H); 0.61 (m broad, CH$_2$, 18H); 0.06 (s, SiMe, 54H). ^{13}C NMR (CDCl$_3$): δ_{ppm} 159.27 (C$_q$, ArO); 159.00 (C$_q$, ArO); 139.08 (C$_q$, Ar); 137.07 (C$_q$, Ar); 134.63 (CH$_2$=CH); 127.30

Scheme 3

Scheme 4

(CH$_{Ar}$); 127.05 (CH$_{Ar}$); 117.32 (CH$_2$=CH); 113.40 (CH$_{Ar}$); 113.31 (CH$_{Ar}$); 60.02 (CH$_2$O); 42.92 (C$_q$–CH$_2$); 42.49 (C$_q$–CH$_2$); 41.86 (CH$_2$); 17.54 (CH$_2$) 14.43 (CH$_2$); −4.69 (SiMe).

Results and discussion

Dendritic growth has been carried out in parallel using the arylsulfide triallyl **1** and the phenol triallyl **4** that is an AB$_3$ unit for dendritic or hyperbranched polymer construction. The model **1** serves to test the divergent reaction of the allyl termini since it does not need protection. The compounds **1** and **4** have been reported, and are accessible by perallylation of the CpFe$^+$ complexes of the aryl ether and aryl sulfide respectively[10b,11] (Scheme 1).

The growing strategy is based on the hydrosilylation of the allyl branches using chloromethyldimethylsilane that has already been successfully used by Seyferth for dendrimer synthesis.[12] The chloromethyl termini are transformed into iodomethyl by reaction with sodium iodide in refluxing butanone, then nucleophilic substitution by phenol triallyl leads to the next generation. With **1**, these reactions can be carried out in a straightforward way without any protection (Scheme 2).

With the phenol triallyl brick, it is of course necessary to protect the phenol group during the dendron construction, *i.e.* this synthesis is now a real convergent strategy for the construction of a dendron that is ultimately deprotected either to react on a protected dendron or onto another framework. Thus, after introduction of the iodo groups on the branches, the phenol function is protected by the propionate before synthesis of the first generation nona-allyl dendron (Scheme 3). The protection allows the condensation of the phenol triallyl AB$_3$ unit, and later, of the phenol nona-allyl AB$_9$
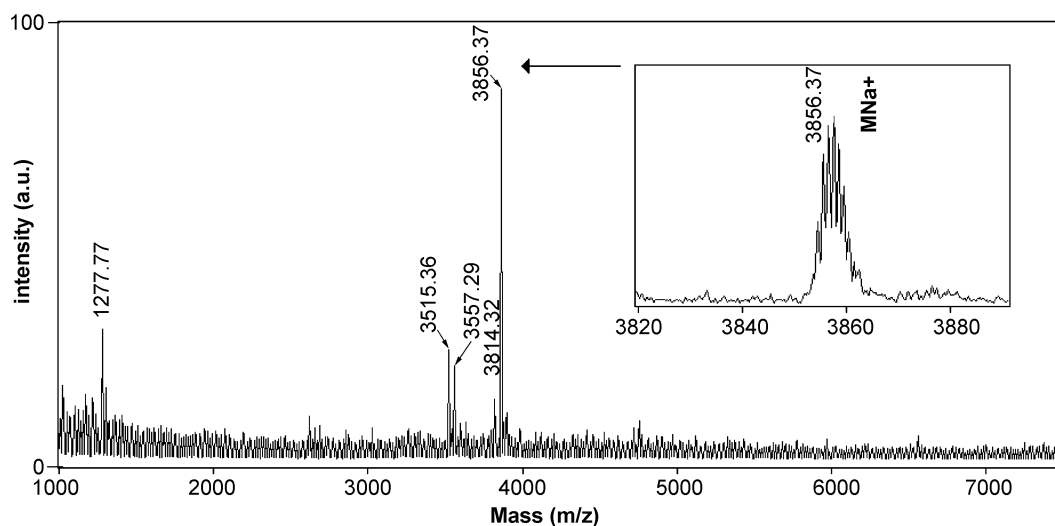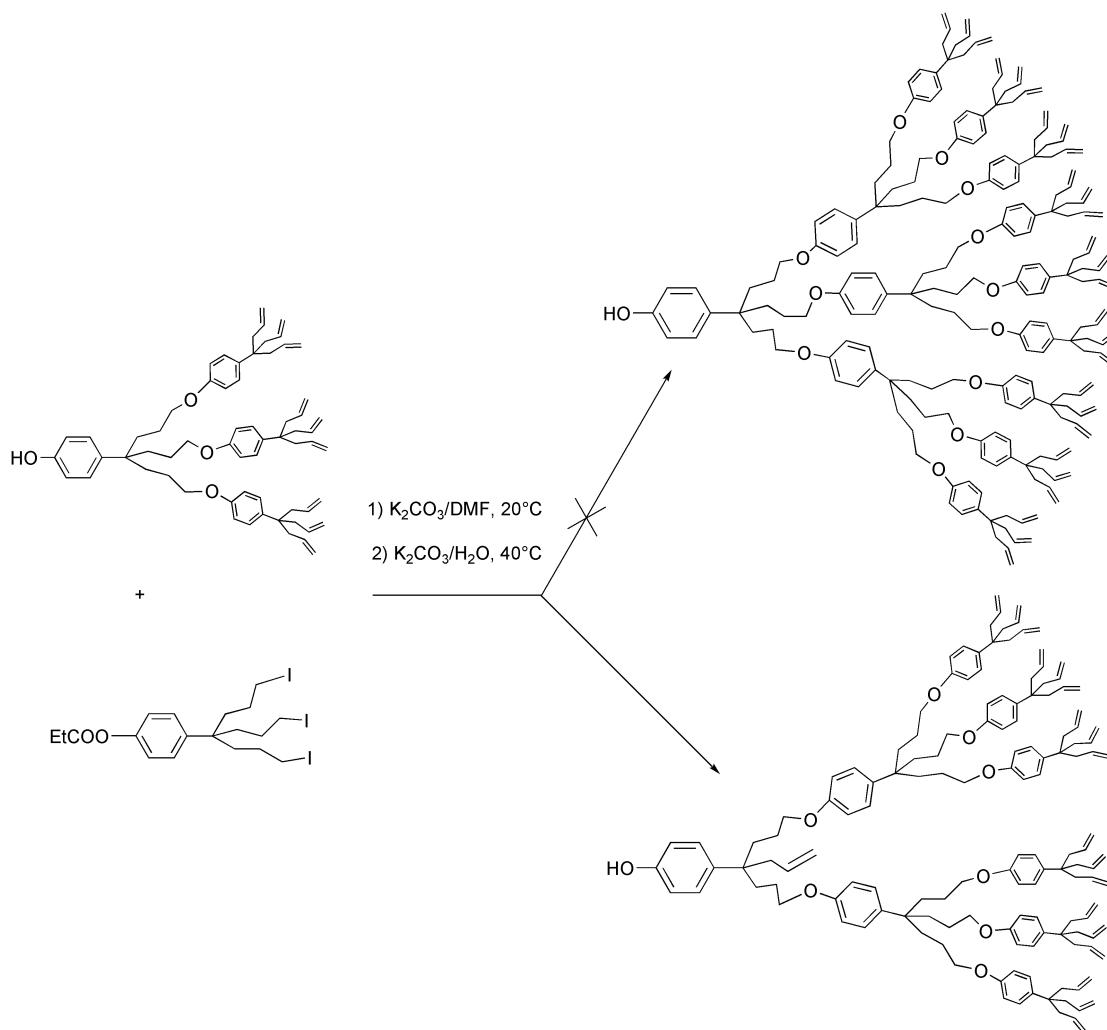

Fig. 1 MALDI-TOF mass spectrum of the 27-allyl dendron **10** (molecular peaks [M + Na]$^+$ at 3856.37).

Scheme 5

first-generation dendron. This convergent synthesis involving protection–deprotection has been carried out until the synthesis of the 27-allyl phenol that has been obtained in its deprotected form, *i.e.* as the second-generation dendron (Scheme 4). The first generation 9-allyl and second generation 27-allyl dendrons have been characterized by their standard spectroscopic and analytical data, but also especially by the prominent molecular peak in the MALDI TOF mass spectrum. In these mass spectra (see Fig. 1), impurities due to unfinished reactions are detected but are present only in relatively small amounts. The side peak at 3814.32 Dalton that is close to the molecular peak results from a small impurity corresponding to the phenoltriallyl AB$_3$ unit **4** in which one allyl group is missing (unfinished synthesis during the CpFe$^+$-induced allylation reaction). The second side peak at 3557.27 Dalton corresponds to a dendron in which the ninth tripod is missing (again uncompleted introduction of the phenoltriallyl group **4**). The third side peak at 3515.36 Dalton corresponds to the combination of both impurities (unfinished triallylation and unfinished introduction of the phenoltriallyl group **4**). The peak at 1277.77 Dalton corresponds to exactly one third of the molecular peak, and is thus attributed to this molecular peak with a tricationic charge (m/z with $z = 3$).

This successful synthesis of the 27-allyl dendron phenol contrasts with the preceding attempt using a triiodoalkyl phenol bearing hydrogens in the position β relative to the iodo group. In that case, nucleophilic substitution proceeded correctly for two of the branches because it was faster than dehydrohalogenation. A rather pure 19-allyl phenol dendron was obtained (as shown in Scheme 5), however, the third

nucleophilic substitution was considerably slowed down due to the steric bulk of the two other nearby covalently attached dendrons. Thus, dehydrohalogenation of the third iodoalkyl branch proceeded quantitatively (Scheme 5). With the new triiodoalkyl dendron, the lack of β positions inhibits the dehydrohalogenation reaction.

Conclusion

The arylsulfide **1** and phenol derivative **4** are easily available in relatively good yields in only three steps from *p*-chlorotoluene *via* CpFe$^+$-mediated synthesis. Thus, the chemistry reported here is easily carried out and should prove useful. The arylsulfide is a good model for the convergent synthesis from **4**. It is also a good model for the synthesis of aryl thiol dendrons that could bind gold nanoparticles and surfaces. The convergent synthesis of the 27-allyl phenol dendron from **4** was successful and proceeds in relatively good yields. Its advantage is that it multiplies the number of branches by three at each generation, allowing a very rapid growth up to 27 allyl branches in the second-generation dendron.

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