Activation of aryl ethers and aryl sulfides by the $Fe(\eta^5-C_5H_5)^+$ group for the synthesis of phenol dendrons and arene-centered poly-olefin dendrimers†

Valérie Sartor,[a] Sylvain Nlate,[a] Jean-Luc Fillaut,[a] Laurent Djakovitch,[a] Françoise Moulines,[a] Valérie Marvaud,[a] Frédéric Neveu,[a] Jean-Claude Blais,[b] Jean-François Létard[c] and Didier Astruc*[a]

[a] *Groupe de Chimie Supramoléculaire des Métaux de Transition, LCOO (CNRS UMR 5802), Université Bordeaux I, 33405 Talence cedex, France. E-mail: d.astruc@lcoo.u-bordeaux.fr*
[b] *Laboratoire de Chimie Structurale Organique et Biologique (CNRS EP 103), Université Paris VI, 4 Place Jussieu, 75252 Paris, France*
[c] *Laboratoire des Sciences Moléculaires, ICMCB (CNRS UPR 9048), Université Bordeaux I, 33608 Pessac, France*

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Organo-iron mediated syntheses of dendrons and dendrimers are described. The reaction of $[FeCp(\eta^6\text{-}p\text{-}EtOC_6H_4Me)][PF_6]$, **1**, with Bu^tOK or KOH and allyl bromide in THF gives both the triallylation of the acidic Me substituent and the heterolytic cleavage of the O–Me bond, which leads to the triallyl oxocyclohexadienyl complex $FeCp[\eta^5\text{-}p\text{-}(allyl)_3CC_6H_4{=}O]$, **2**. If excess Bu^tOK is added, the major compound obtained in this one-pot, eight-step reaction is the iron-free phenol derivative $p\text{-}(allyl)_3CC_6H_4OH$, **3**, in 50% yield. Surprisingly, the analogous aryl sulfide complexes $[FeCp(\eta^6\text{-}p\text{-}RSC_6H_4Me)][PF_6]$, **4a** (R = Me) and **4b** (R = Et), also give **3** [together with $(allyl)_3CC_6H_4SR$, **5**] by reaction with Bu^tOK and allyl bromide. The dendron **3** reacts with $1,3,5\text{-}C_6H_3[C(CH_2CH_2CH_2X)_3]_3$, **6**, giving the 27-allyl dendrimer **7** (first generation) whose purity, monitored by MALDI-TOF mass spectroscopy, is not as good when the reaction is performed with X = I (**6a**) as with X = mesylate (**6b**). Iteration of this divergent synthesis gives the 81-allyl dendrimer **10** (second generation) and ultimately the dendrimer **13** (third generation) with a theoretical number of 243 allyl groups. Protection and functionalization of **3** also allows to carry out convergent dendritic syntheses: reaction of **3** with the protected functional dendron $C_2H_5C(O)OC_6H_4C(CH_2CH_2CH_2I)_3$, **17**, followed by deprotection gives the phenol nona-allyl dendron $OHC_6H_4C[CH_2CH_2CH_2O\text{-}p\text{-}C_6H_4C(CH_2CH{=}CH_2)_3]_3$, **18**. Compound **18** reacts with the $1,3,5\text{-}C_6Me_3(CH_2Br)_3$ and $C_6(CH_2Br)_6$ cores to cleanly give the corresponding arene-centered 27-allyl and 54-allyl dendrimers **20** and **21**, as shown by the dominant molecular peaks in the MALDI-TOF mass spectra. Reaction of **17** with **18** followed by deprotection does not give the expected 27-allyl dendron, but (very selectively) a 19-allyl dendron **19** resulting from selective double branching and single dehydroiodation, which shows the limits of the convergent strategy.

Activation des éthers d'aryles et des sulfures d'aryle par le greffon $Fe(\eta^5-C_5H_5)^+$ pour la synthèse de dendrons phénoliques et de dendrimères à périphérie poly-oléfinique et possédant un coeur aromatique. Dans ce mémoire, nous décrivons la synthèse de dendrons et de dendrimères. La réaction de $[FeCp(\eta^6\text{-}p\text{-}EtOC_6H_4Me)][PF_6]$, **1**, avec Bu^tOK ou KOH et le bromure d'allyle produit à la fois la tri-allylation du substituant méthyle acide et la coupure hétérolytique de la liaison O–Me, conduisant au complexe tri-allyle $FeCp\eta^5\text{-}p\ \text{-}(allyl)_3CC_6H_4{=}O]$, **2**. Si on ajoute un excès de Bu^tOK, le principal composé obtenu, dans cette réaction en un seul pot pour huit étapes, est le dérivé phénolique décomplexé $p\text{-}(allyl)_3CC_6H_4OH$, **3**, avec un rendement de 50%. De façon apparemment surprenante, l'analogue soufré $[FeCp(\eta^6\text{-}p\text{-}RSC_6H_4Me)][PF_6]$, **4a** (R = Me) and **4b** (R = Et), donne aussi **3** [en même temps que $(allyl)_3CC_6H_4SR$, **5**] par réaction entre **1**, Bu^tOK et le bromure d'allyle. Le dendron **3** réagit avec $1,3,5\text{-}C_6H_3[C(CH_2CH_2CH_2X)_3]_3$, **6**, pour donner le dendrimère 27-allyle **7** ($1^{\text{ère}}$ génération). La pureté de **7**, déterminée par spectrométrie de masse MALDI-TOF, n'est pas aussi bonne quand la réaction est conduite avec X = I (**6a**) que quand elle est avec X = mésylate (**6b**). L'itération de cette synthèse divergente donne le dendrimère 81-allyle **10** (2^{nde} génération), et finalement le dendrimère **13** ($3^{\text{ème}}$ génération) comprenant un nombre théorique de 243 groupements allyles terminaux. La protection et la fonctionnalisation de **3** permet aussi de mener à bien des synthèse dendritiques convergentes: la réaction de **3** avec le dendron fonctionnel protégé $C_2H_5C(O)OC_6H_4C(CH_2CH_2CH_2I)_3$, **17**, suivie de déprotection, conduit au dendron nona-allyl phénol $OHC_6H_4C[CH_2CH_2CH_2O\text{-}p\text{-}C_6H_4C(CH_2CH{=}CH_2)_3]_3$, **18**. Ce composé **18** réagit avec les coeurs $1,3,5\text{-}C_6Me_3(CH_2Br)_3$ et $C_6(CH_2Br)_6$ pour donner proprement les dendrimères 27-allyle **20** et 54-allyle **21**, respectivement, comme l'indiquent les pics moléculaires dominant dans les spectres de masse MALDI-TOF. La réaction de **17** avec **18** suivie de déprotection ne conduit pas au dendron 27-allyle attendu, mais (très sélectivement) au dendron 19-allyle **19** résultant du double branchage sélectif et d'une dehydroiodation, ceci montrant la limite de la stratégie convergente.

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† Dedicated to Oliver Kahn, fully living in our memories as a generous friend and as an outstanding lecturer and scientist who pioneered the conceptual approach of molecular magnetism.

Electronic supplementary information (ESI) available: MALDI-TOF mass spectra of the 19-allyl dendron **19**, 27-allyl dendrimer **20**, 54-allyl dendrimer **21** and 81-allyl dendrimer **10**. See http://www.rsc.org/suppdata/nj/b0/b000370k/

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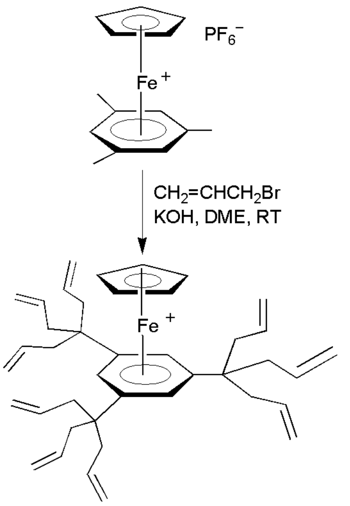
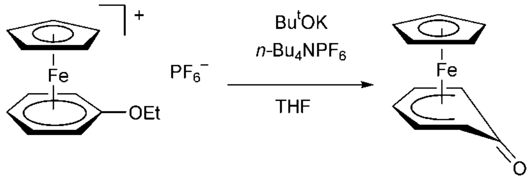
The temporary complexation of aromatics by 12-electron organo transition-metal fragments in robust 18-electron complexes such as [Cr(arene)(CO)$_3$], [Mn(arene)(CO)$_3$]$^+$ and [MCp(arene)]$^+$ (M = Fe or Ru) provides a powerful means to activate aromatics towards nucleophilic and deprotonation reactions.[1–5] This trend has been known and exploited for a long time, especially in the [Cr(arene)(CO)$_3$] series.[1–3] In the [MCp(arene)]$^+$ series, the activation is stronger than in the [Cr(arene)(CO)$_3$] one, however, which has led us to deprotonate such complexes bearing methyl substituents on the arene ligands.[6] Recent thermodynamics studies have indeed shown that the pK_a of these 18-electron complexes are lower by about 15 units than those of the free aromatics in DMSO.[7] Although stepwise deprotonation is known, we have recently been more concerned with the perfunctionalization of these complexes using a base (KOH or Bu^{t}OK) and a halide RX [R = alkyl, allyl, benzyl, *etc.*; X = Br or I, eqn. (1)].[6] This reaction consists in the iteration of deprotonation-alkylation sequences, yet it is different from catalysis, and represent an original way to activate ligands and synthesize dendritic cores.



(1)

The advantage of dendrons over dendrimers is that dendrons have a functional trunk whereas dendrimers do not, contrary to what etymology suggests.[8] Thus, dendrons can be attached to a variety of functional molecular and nanoscale materials. Therefore, it was of great interest for us to investigate an extension of the CpFe$^+$ induced aromatic perfunctionalization strategy to functional aromatics bearing methyl groups in order to synthesize dendrons, in addition to dendritic cores. Sometime ago, we disclosed the CpFe$^+$ induced heterolytic cleavage of the O–alkyl bond of phenylalkyl and diphenyl ether complexes, leading to oxocyclohexadienyl complexes [eqn. (2)], the deprotonated form of phenols.[9]



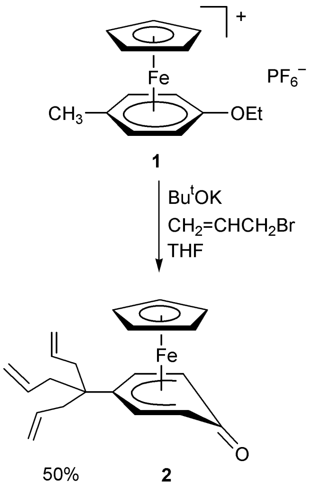
(2)

The next challenge was to perform both the perfunctionalization and heterolytic C–O cleavage reactions on the same arene ligand in a one-pot reaction, directly leading to a dendron. This goal has been successfully achieved and the results published in preliminary form;[10] it is the subject of the present article. Our new and apparently surprising finding of the reaction of the corresponding aryl sulfides is now included, together with the synthesis of new dendrimers such as a 54-allyl dendrimer resulting from the convergent method. These results are key steps in the context of our ongoing synthesis[11] and applications[12] of metallodendrimers.

Results

Heterolytic cleavage of the exo-cyclic O–C bond of aryl ether complexes in [FeCp(p-$CH_3C_6H_4OEt$)], 1

The yellow complex **1** is readily available[13] and can be synthesized in large quantities. It reacts with Bu^{t}OK and allyl bromide in THF to give the orange oxocyclohexadienyl complex **2** as a red oil in 50% yield after purification on a silica column. This reaction combines the heterolytic cleavage of the exocyclic O–C bond[9] and triallylation of the methyl group located in the para position[14] [eqn. (3)].

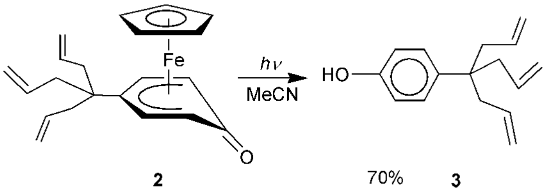


(3)

Other products found in minor amounts in this reaction are the decomplexation products resulting from partial reaction and/or decomplexation. Formation of **2** has been optimized by variation of the reaction temperature and time (see experimental section). First, Bu^{t}OK deprotonates the methyl group to give a deep red cyclohexadienyl complex, which is followed by the first allylation, then the two other deprotonation-allylation sequences follow before cleavage of the exocyclic O–C bond. This can be verified by protonation of the red intermediates, giving a yellow mixture of aryl ether allylated complexes of the type [FeCp{η^6-p-$EtOC_6H_4CH_{3-n}$(allyl)$_n$}][PF_6].

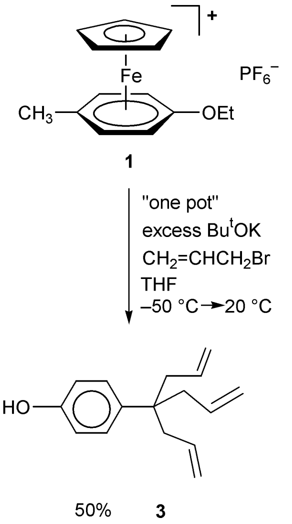
Synthesis of the triallyphenol dendron p-OHC_6H_4C(allyl)$_3$, 3

Compound **2** is decomplexed in acetonitrile using a Hg lamp,[15] which leads to the substitution of the arene ligand by three acetonitrile ligands in the cation; thus separation is facile, giving a 70% yield of p-OHC_6H_4C(allyl)$_3$, **3** a light brown solid [eqn. (4)].



(4)

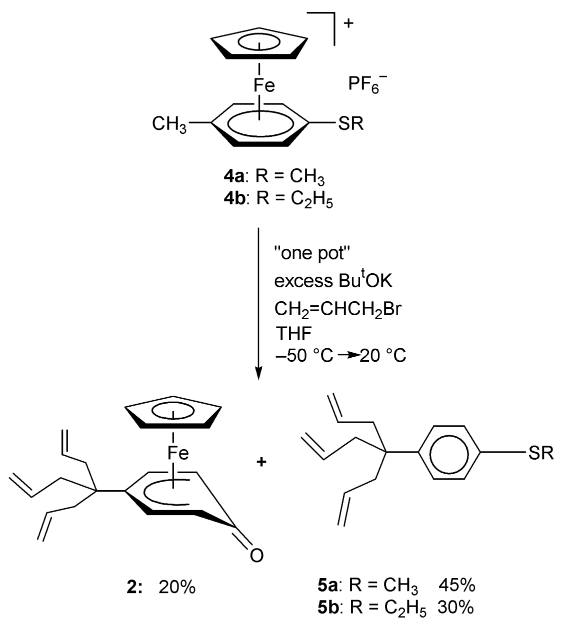
An alternative synthesis of **3**, which turns out to be more convenient than the above procedure, is the direct synthesis using the precursor **1** in a one-pot reaction. The procedure consists in using the same reactants as for the synthesis of **2** except that another portion of Bu^{t}OK is added at the end of the reaction in order to achieve decomplexation. This one-pot reaction produces **3** from **1** in 50% yield after purification using column chromatography [eqn. (5)]. Compound **3** is air-stable for a day but long-term storage must be carried out in the dark under an inert atmosphere, best in a refrigerator.



(5)

Cleavage reactions of thio aryl ethers using Bu^{t}OK

Aryl thiolate ligands are useful in bio-inorganic chemistry[16] and we wished to examine the possible extension of the reactions of eqns. (3) and (4) to the heterolytic cleavage of aryl sulfide π complexes analogous to **1**. These aryl sulfphide complexes, **4a** (R = CH_3) and **4b** (R = C_2H_5), are as easily available as the ether complexes by reactions of the corresponding alkyl aryl thiols with [FeCp(η^6-*p*-$ClC_6H_4CH_3$)] in the presence of Na_2CO_3.[6] The tentative S–C cleavage in **4** was investigated with both the methyl and ethyl aryl sulphide complexes. Optimization of the reaction time and temperature and search for the best alkyl group on sulfur led to the formation of **2** in 20% yield and the free aryl sulfide $CH_3SC_6H_4C(allyl)_3$, **5a**, in 45% yield. The formation of **5a** was expected, but that of **2** was not; it was checked twice by MALDI-TOF (matrix-assisted laser desorption ionization–time of flight)[17] mass spectroscopy, which showed its very clean formation by the presence of the molecular peak as the dominant peak; no peak was observed for the awaited sulfur analog [eqn. (6)]. The same reaction proceeded with the ethyl aryl ether complex, although the yields were lower.



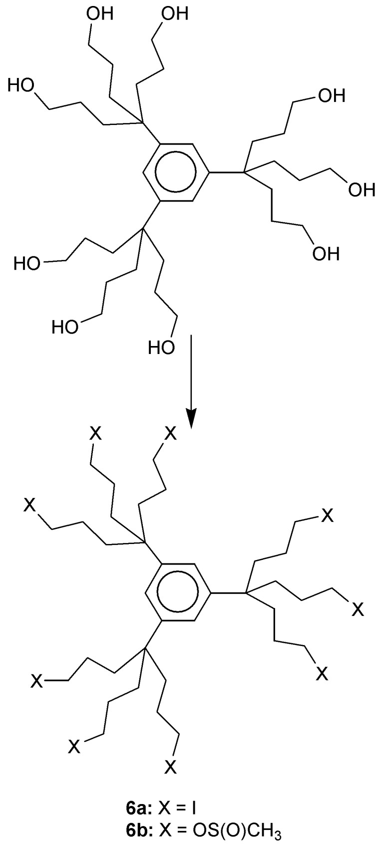
(6)

Divergent dendrimer syntheses using the dendron 3

The nonafunctional dendritic cores **6a** (X = I) and **6b** (X = mesylate) are available by nona-allylation of [FeCp(η^6-mesitylene)][PF_6] with KOH and allyl bromide,[14] followed by photolytic decomplexation,[15] regioselective hydroboration[18] and oxidation of the nonaborane[18] to the nona-ol[14] and subsequent functionalization. First, **6a** is synthesized as follows. Reaction of the nona-ol dendritic core with $SiMe_3Cl$ in THF in the presence of Et_3N provided the nona-trimethylsilyl dendritic core, which was converted *in situ* to the nona-iodo dendrimer **6a** by reaction with NaI [eqn. (7)].[19,20]

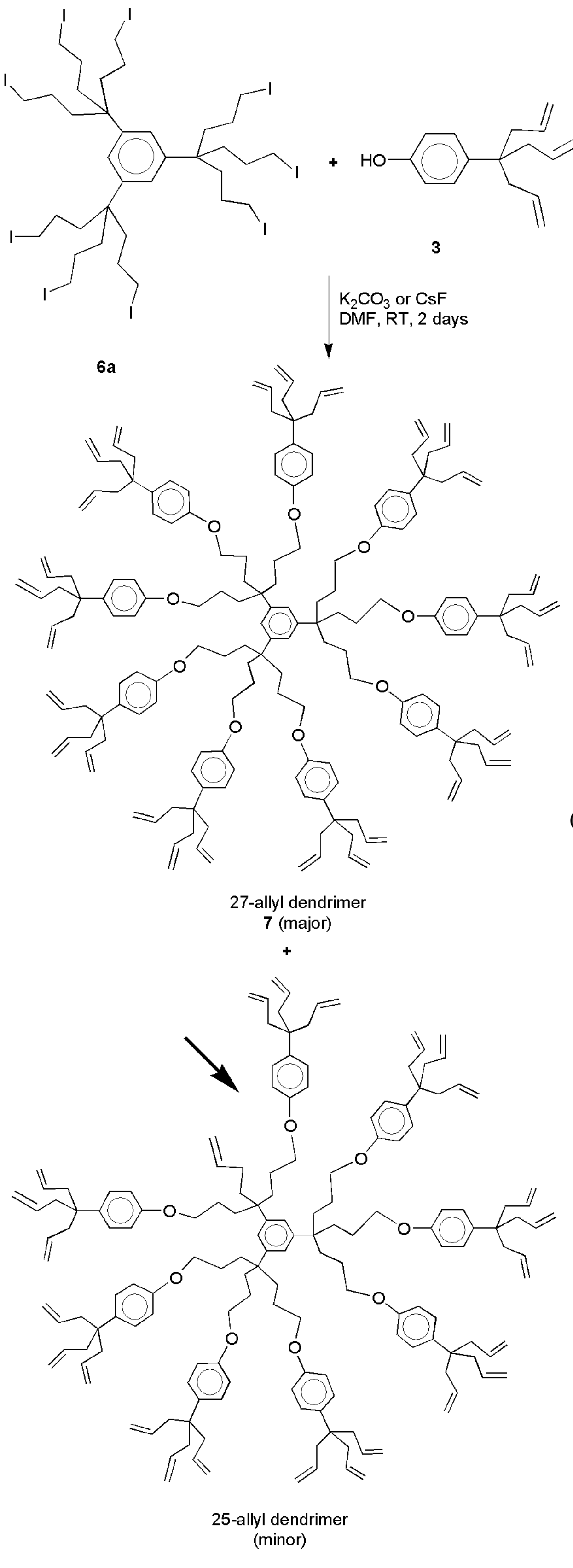
The MALDI-TOF mass spectrum of **6a** shows the successive loss of all the iodo atoms, and is therefore of little value to determine the purity of **6a**. In ^{1}H NMR, the terminal methylene carbon peak undergoes only a slight shift from 3.4 ppm for the nona-ol (CD_3OD) to 3.1 ppm for **6a** ($CDCl_3$). The reaction is best characterized with ^{13}C NMR by the replacement of the signal of the primary alcohol carbon at 63.7 ppm in the nona-ol by the upfield signal of the carbon attached to the iodo atom at 8.0 ppm in **6a** (see experimental section), which shows that it is quantitative.

Williamson-type coupling reaction[21] of the nona-iodo core **6a** with the dendron **3** was first tested using tertiobutylphenol, which has the advantages of being commercially available and having no olefin group, unlike **3**. In this way, the side dehydroiodation reaction leading to the formation of olefin termini can be monitored by ^{1}H NMR, because the downfield olefin signals are easily observable. The parameters potentially influencing the substitution-elimination competition[21,22] were varied using this model reaction. The results were that room temperature was preferred to higher temperatures, that the nature of the base (CsF *vs.* K_2CO_3) had little influence,[23] and that small amounts of elimination products were always



(7)

detected by ^{1}H NMR. Reaction of **6a** with **3** in DMF at room temperature in the presence of K_2CO_3 yielded the 27-allyl dendrimer **7** in 44% yield after chromatographic purification. The ^{1}H and ^{13}C NMR spectra of **7** are very clean, and the MALDI-TOF mass spectrum shows that the molecular peak $[M + Na]^+$ at 2559 dominates; an important peak corresponding to the octa-substituted dendrimer with dehydroiodation of the non-substituted branch and a small peak corresponding to the hepta-substituted dendrimer are also found. Thus, although the major dendrimer formed is the 27-allyl dendrimer, the 25-allyl dendrimer is also formed in good amounts and the 23-allyl dendrimer is formed in small amounts [eqn. (8)]. If the intensity of the peaks in the mass spectrum reflects the respective amounts, the Williamson coupling is achieved to an extent of 95% whereas elimination reaches about 5%, which is too much for further dendritic construction.



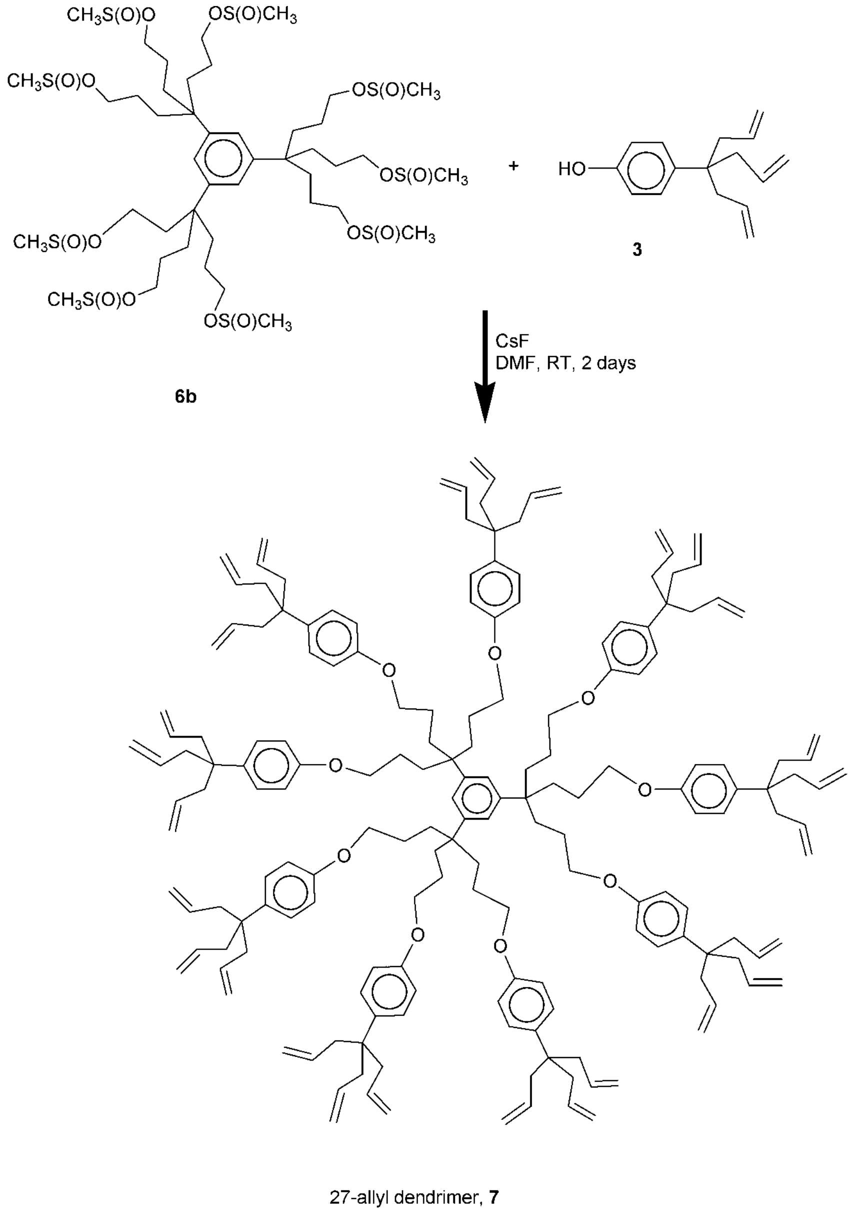
(8)

In order to prepare a purer 27-allyl dendrimer, we then switched to the nona-mesylate dendritic core **6b** in order to eliminate the side dehydrohalogenation reaction as much as possible. Indeed, Kellog *et al.* reported that the use of mesylate as a leaving group for substitution by propionic acid with cesium carboxylate in DMF did not give any elimination product.[24a] Such a preference was already noted in the construction of polyether dendrimers.[24b,c] Reaction of the nona-ol with chloromethylsulfonate in pyridine[25] gives a 95% yield of the nona-mesylate dendritic core **6b** as a colorless oil that is best stored at −25 °C. The completion of the reaction is characterized by the shift of the signals of the terminal methylene in $CDCl_3$ from 3.4 (CH_2OH) to 4.1 (CH_2OSO_2Me) in ^{1}H NMR and from 63.7 to 70.1 in ^{13}C NMR. Reaction of **6b** with the model tertiobutylphenol led to the total absence of signals due to olefinic protons in the ^{1}H NMR observations, indicating that elimination, if any, is occurring in lower amounts than the observation threshold in ^{1}H NMR. Reaction of **6b** with **3** in DMF in the presence of CsF produces the 27-allyl dendrimer as a colorless oil in 27% yield after chromatographic purification [eqn. (9)].

The ^{1}H and ^{13}C NMR spectra are exactly identical to those of **7** obtained from **6a** as above. The MALDI-TOF mass spectrum shows the molecular peaks $[M + Na]^+$ at 2559 and $[M + K]^+$ at 2575 with only a tiny peak at 2331 corresponding to octa-substitution and dehydromesylation of one branch. The proportion of dehydromesylation can be estimated to be of the order of 1%. In the crude reaction product, some hydroxymethyl termini were detected. Indeed, the very facile hydrolysis of the mesylate group to the hydroxy group is known.[26] Dendrimers containing this impurity were removed during the chromatographic purification, but their formation reaches 30%, which consequently leads to lower yields of **7** than when starting from the polyiodoalkyl precursor. Attempts to mesylate these residual hydroxy groups and condense them again with **3** were not successful, possibly because of steric inhibition and hydrophobicity of the dendritic cavity around the reaction site.

The dendrimer **7** synthesized from **6b** was used for further syntheses. Thus, regioselective hydroboration of **7** was carried out using disiamylborane ($HBsiam_2$) and the 27-borane dendrimer was oxidized to the 27-alcohol dendrimer **8**, a white solid, using H_2O_2 in basic medium [eqn. (10)]. The MALDI-TOF mass spectrum of **8** shows only the molecular peaks $[M + Na]^+$ at 3045.11 and $[M + K]^+$ at 3061.06, as well as a trace of 25-ol at ($[M + Na]^+$ at 2779.74 and $[M + K]^+$ at 2795.88) as expected from the purity of the precursor (Fig. 1).

Reaction of **8** with $SiMe_3Cl$ in the presence of Et_3N was carried out in THF instead of MeCN, because **8** is not soluble in MeCN, leading to the 27-alkoxytrimethylsilane intermediate,[27] which was converted *in situ* to the 27-iodo dendrimer by reaction with NaI in the presence of $SiMe_3Cl$ in MeCN after removing THF.[28] The 27-iodo dendrimer **9a**, a pale yellow solid, was obtained in 43% yield. Reaction of **8** with chloromethylsulfonate gave the 27-mesylate dendrimer **9b** as a colorless oil in 92% yield. Reaction of **9b** with **3** proceeds as for the first generation and gives the 81-allyl dendrimer **10** as a colorless oil in 71% yield after chromatographic separation [eqn. (11)]. The MALDI-TOF mass spectrum does not show the molecular peak, but many peaks corresponding to lack of substitution and deshydroiodation are observed. On the other hand, reaction of **9b** with **3** as for the first generation gives **10**



(9)

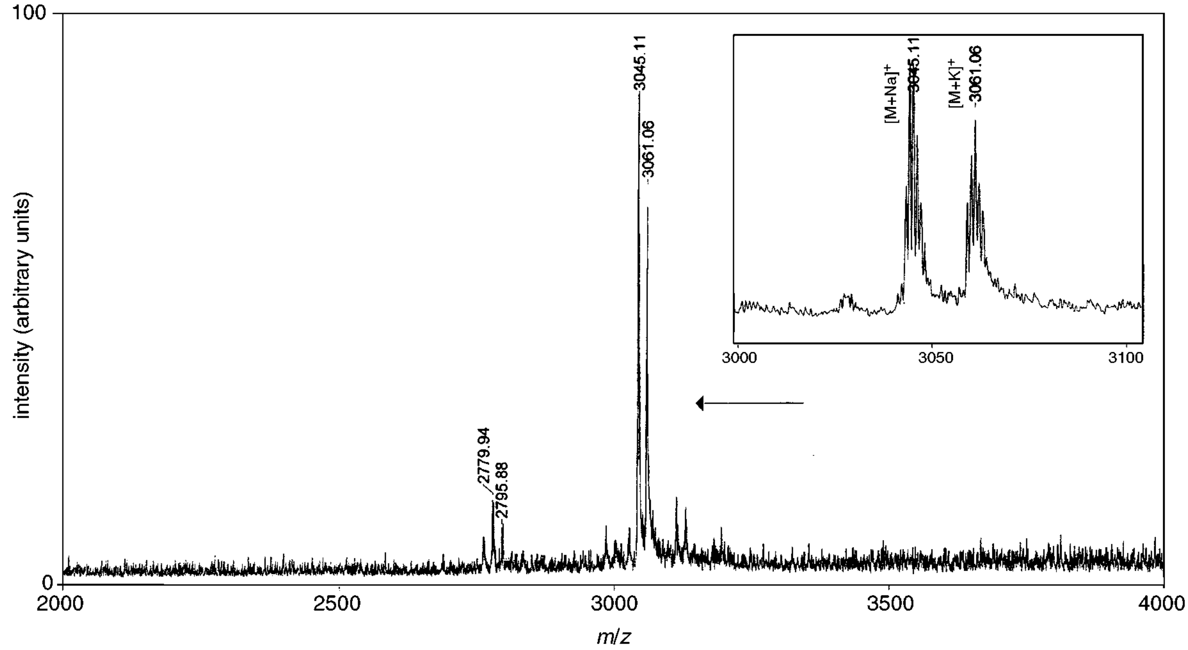
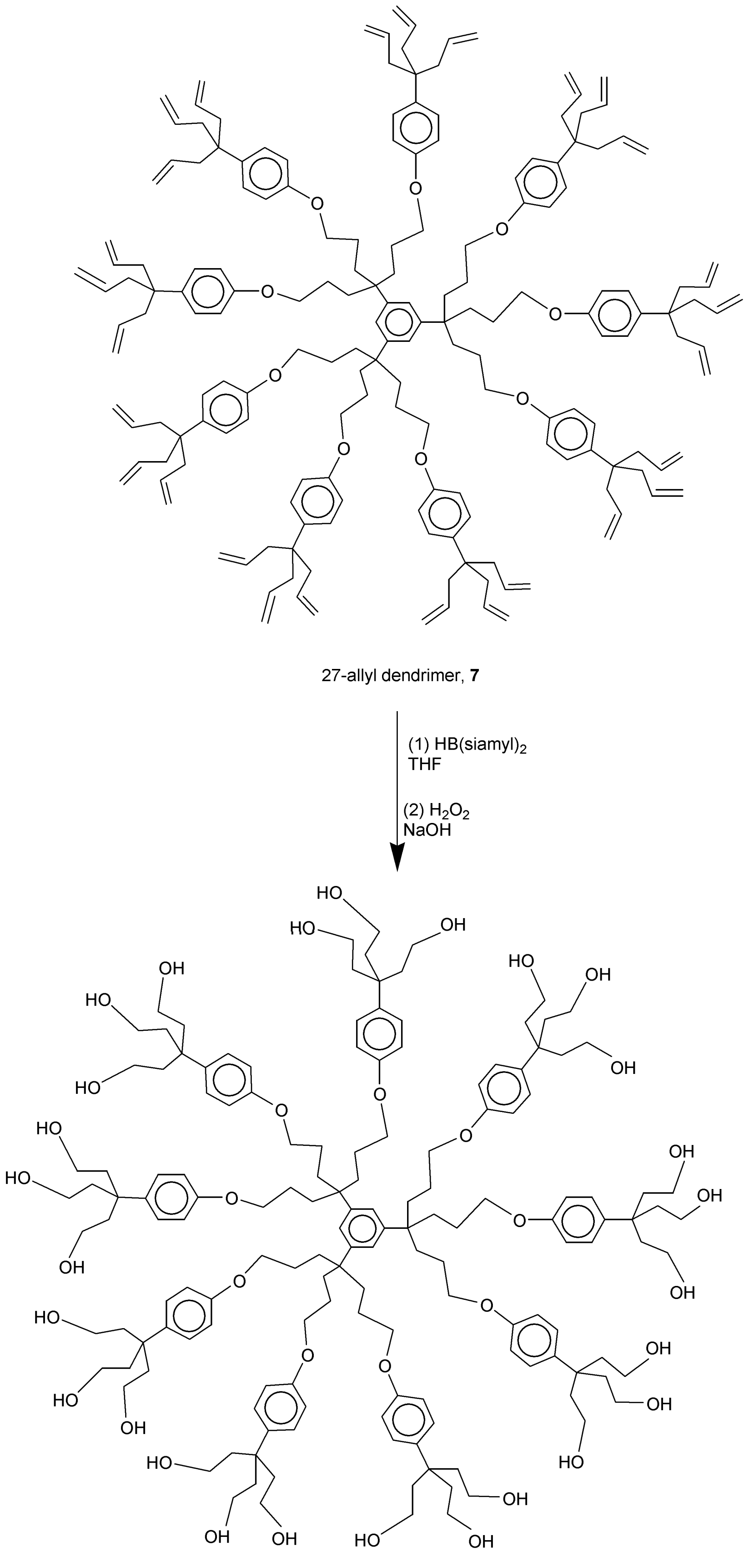


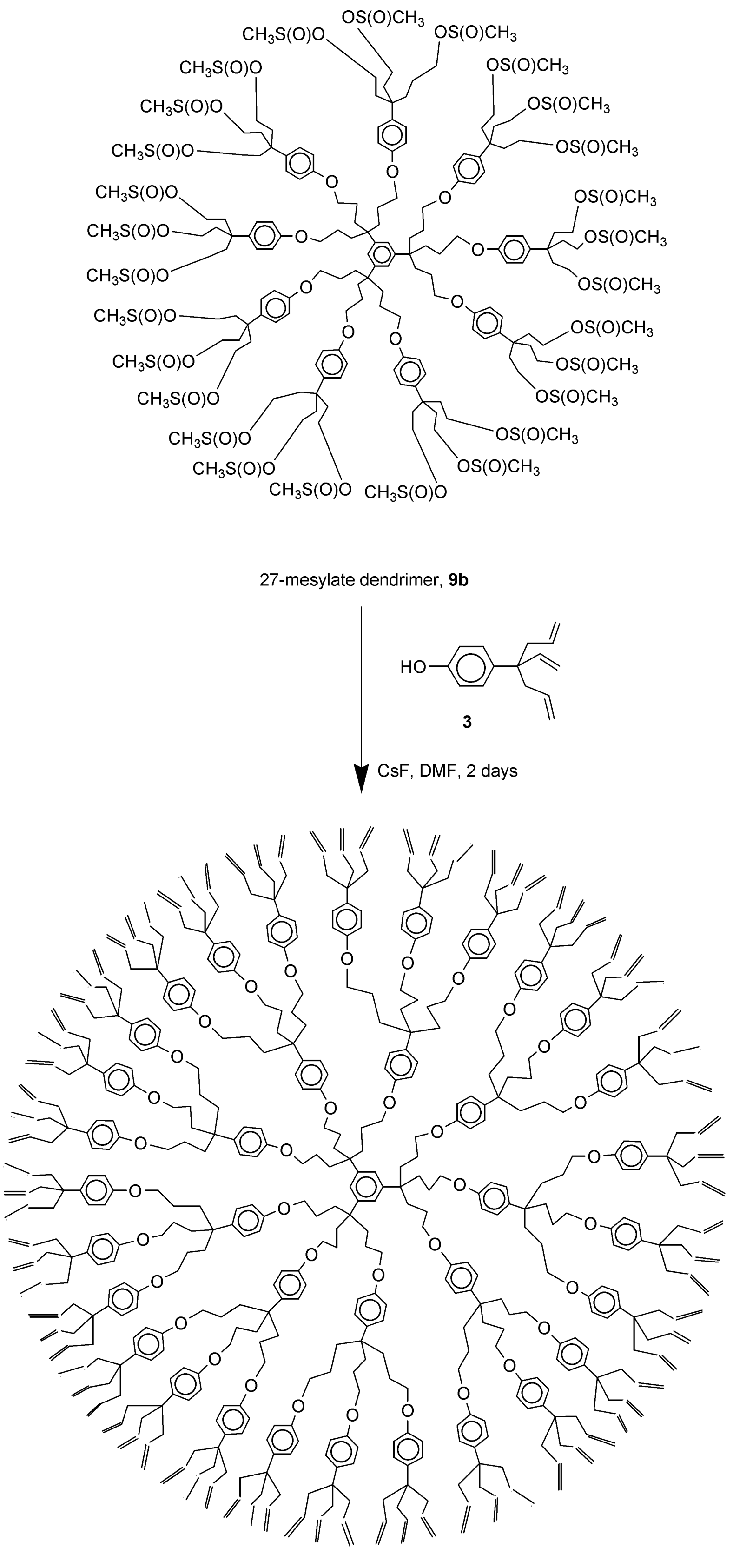
Fig. 1 MALDI-TOF mass spectrum of the 27-alcohol dendrimer **8** (molecular peaks M + Na^+ at 3047.73 and M + K^+ at 3063.74).



27-allyl dendrimer, **7**

27-alcohol dendrimer, **8**

(10)

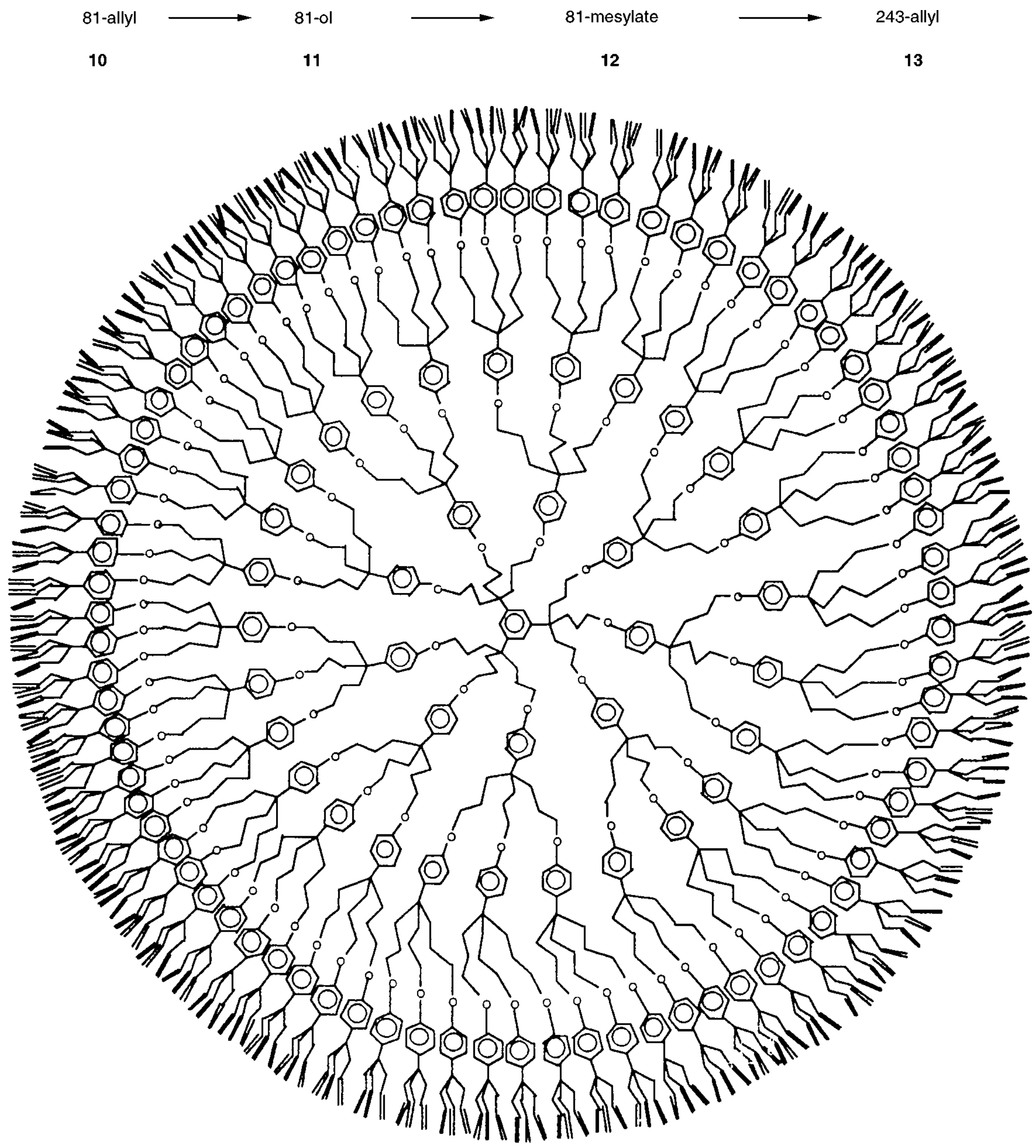


27-mesylate dendrimer, **9b**

3

81-allyl dendrimer, **10**

(11)



243-allyl

13

Scheme 1

in 6.4% yield after repeated chomatographic separation. The mass spectrum of this sample of **10** shows the molecular peak as the dominant peak $[M + Na]^+$ at 8723.38. Less intense peaks corresponding to the lack of one to nine dendrons and deshydromesylation are also observed.

Finally, hydroboration of this sample of **10** followed by oxidation of the 81-borane dendrimer as for the preceding generation gave the 81-ol dendrimer **11** in 53% yield as a white powder, and reaction of chloromethylsulfonate with **11** as above gave the 81-mesylate dendrimer **12** as a colorless oil in 85% yield. Reaction of **12** with **3** gave the 243-allyl dendrimer **13** (Scheme 1) in 11% yield after chromatographic separation. This reaction was monitored in ^{1}H NMR by the disappearance of the signals due to the CH_2OSO_2Me group at 3 and 2.3 ppm and the appearance of the signals of the olefin protons downfield near 5.6 and 5 ppm. The mass spectrum of **13** could not be obtained, possibly due to polydispersity. However, a clear ^{13}C NMR spectrum was recorded with the expected signals corresponding to the surface groups, those of the mesylate groups having totally disappeared (Fig. 2).

Convergent syntheses of dendrons and dendrimers using the dendron 3

Heterobifunctionalization and protection of the triallyl phenol dendron **3** has been achieved in order to carry out convergent dendrimer syntheses. First, the phenol group of **3** is protected by methylation using methyl iodide in DMSO[29] giving **14**, then the methyl aryl ether is functionalized by regioselective hydroboration using disiamylborane and oxidation of the triborane by H_2O_2 in basic aqueous medium,[18] which gives the protected triol **15**. Reaction of **15** with Me_3SiCl and NaI[19,31] leads to both iodation of the branch termini and deprotection of the phenol, giving **16**. Protection of the phenol group of **16** is achieved by propionylation using propionyl iodide in the presence of diisopropylethylamine,[31] giving the protected functional dendron **17** (Scheme 2). Tentative propionylation using propionyl chloride leads to partial chlorination of the branches and must be discarded.[32] Reaction of **17** with **3** followed by deprotection using K_2CO_3 successfully leads to the nona-allyl dendron **18** [eqn. (12)].

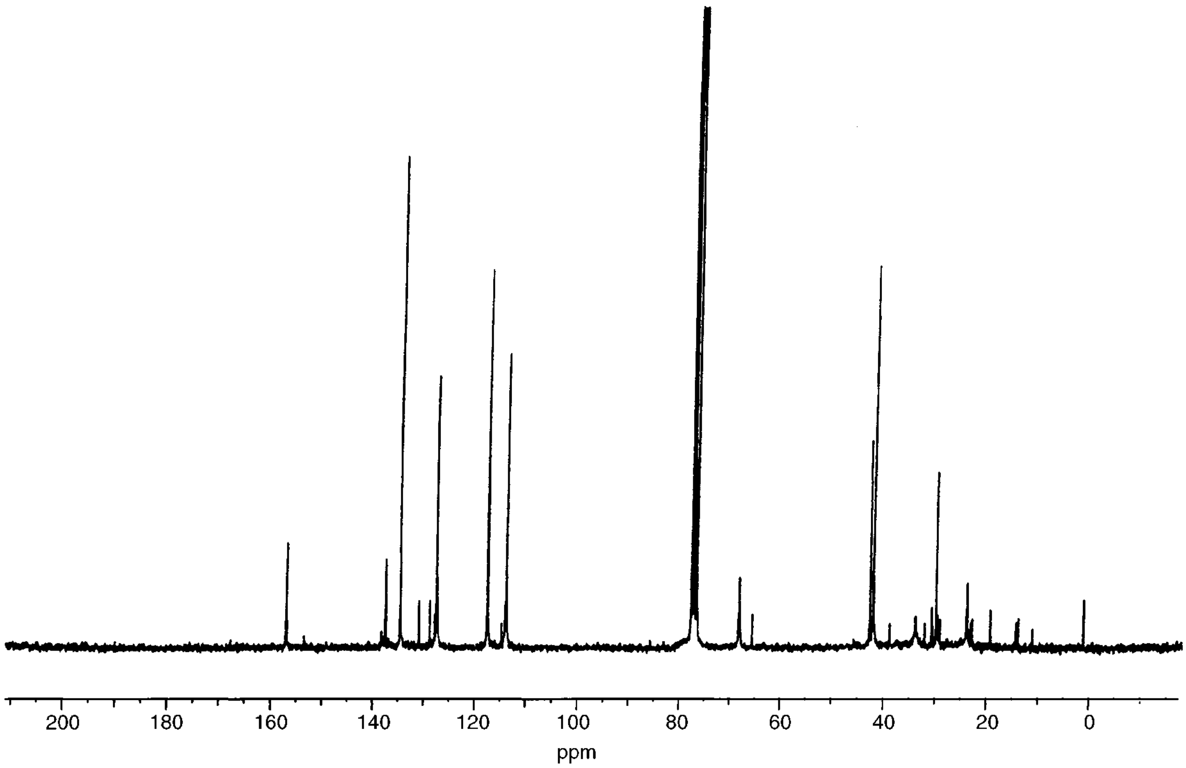
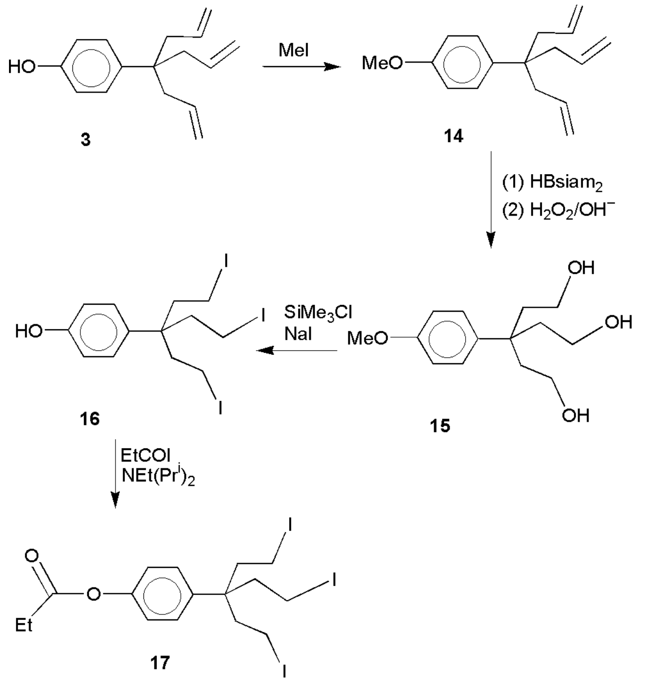


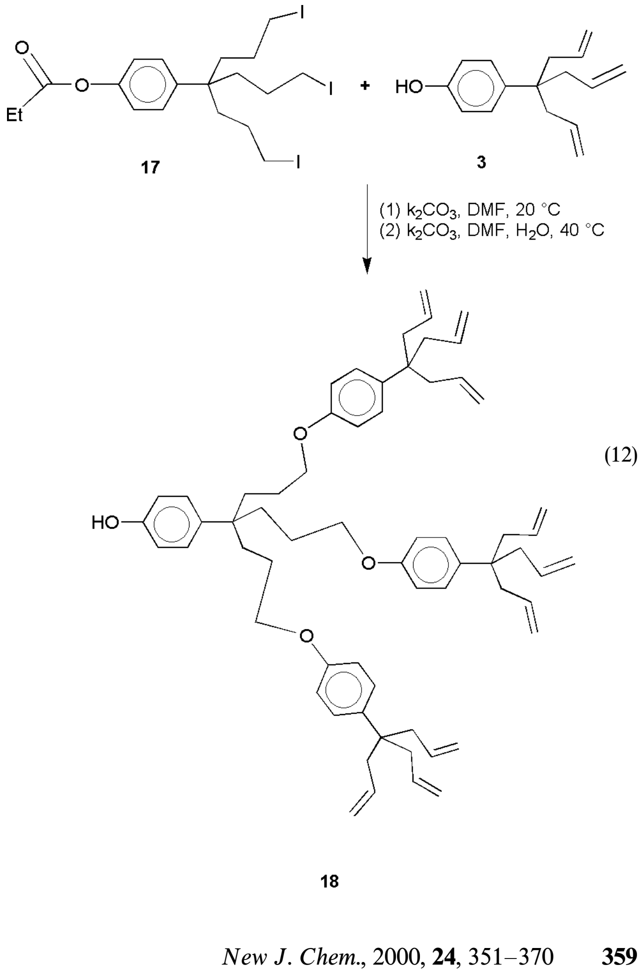
Fig. 2 $[^1H]^{13}C$ NMR spectrum of the 243-allyl dendrimer 13 in $CDCl_3$ solution (Bruker AC 250 FT, 62.9 MHz). The solvent triplet (CD) is noted around $\delta = 77$ *vs.* $SiMe_4$. For assignments, see Experimental section.

Continuation of the convergent strategy was attempted by reaction of the dendron **18** with the protected phenol triodo derivative **17** in the presence of K_2CO_3, followed by deprotection using K_2CO_3 at higher temperature. The clean ^1H and ^{13}C NMR spectra are in full agreement with the formation of the expected phenol 27-allyl dendron. The MALDI-TOF mass spectrum shows a unique molecular peak $[M + Na]^+$ at 2077.7, however, corresponding to the very selective substitution of two iodides by two dendrons and dehydroiodation of the third branch. Thus, the phenol derivative formed, **19**, has only 19 allyl branches (Scheme 3); it is obtained as a light brown oil in 25% yield after chromatographic separation.

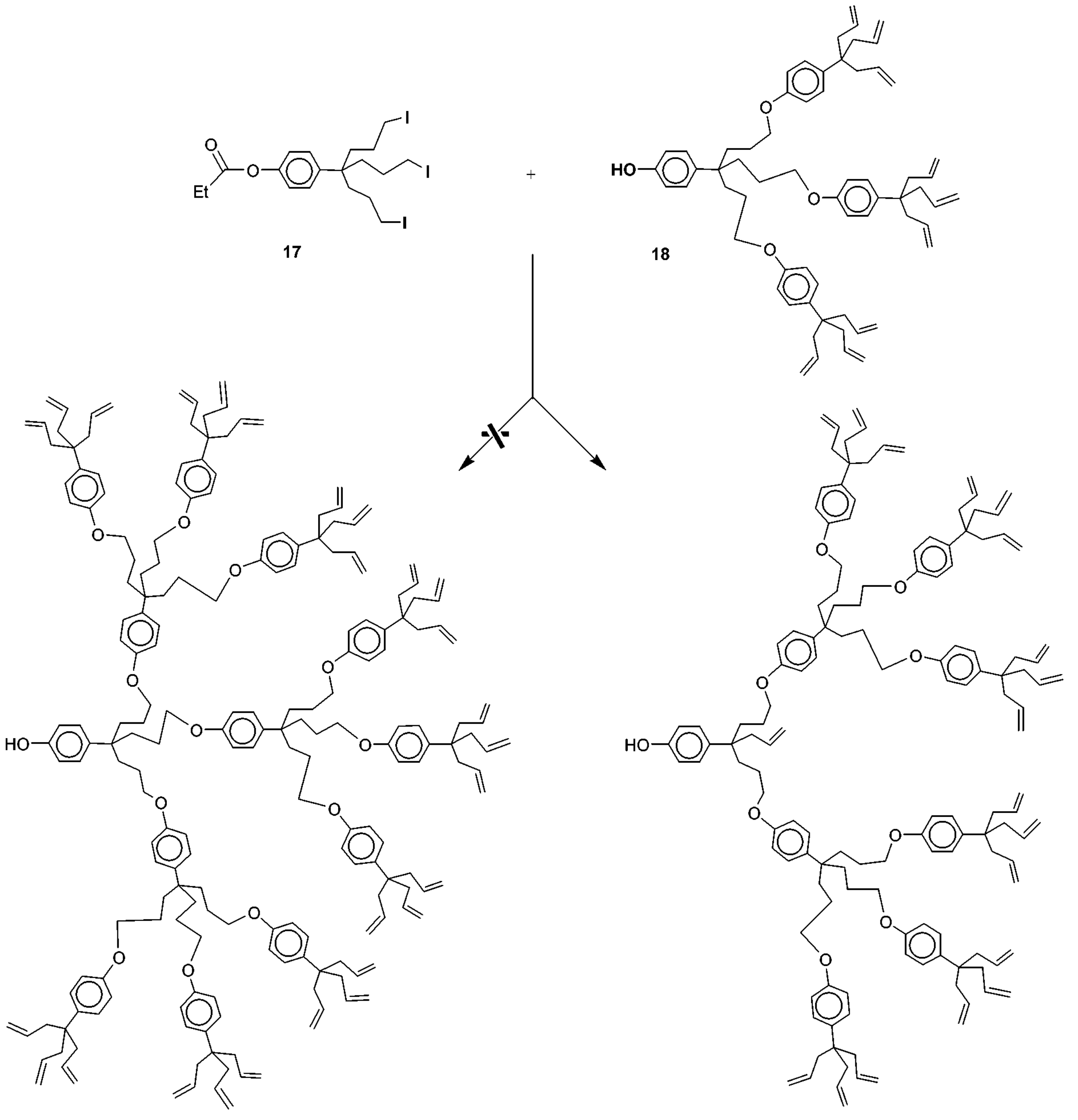


Scheme 2

The dendron **18** also reacts with 1,3,5-tribromomesitylene in the presence of K_2CO_3 to give the 27-allyl dendrimer **20** as a light brown oil in 30% yield (non-optimized) after chromatographic purification. The reaction is selective and complete as indicated by the MALDI-TOF mass spectrum showing the



(12)



17

18

19

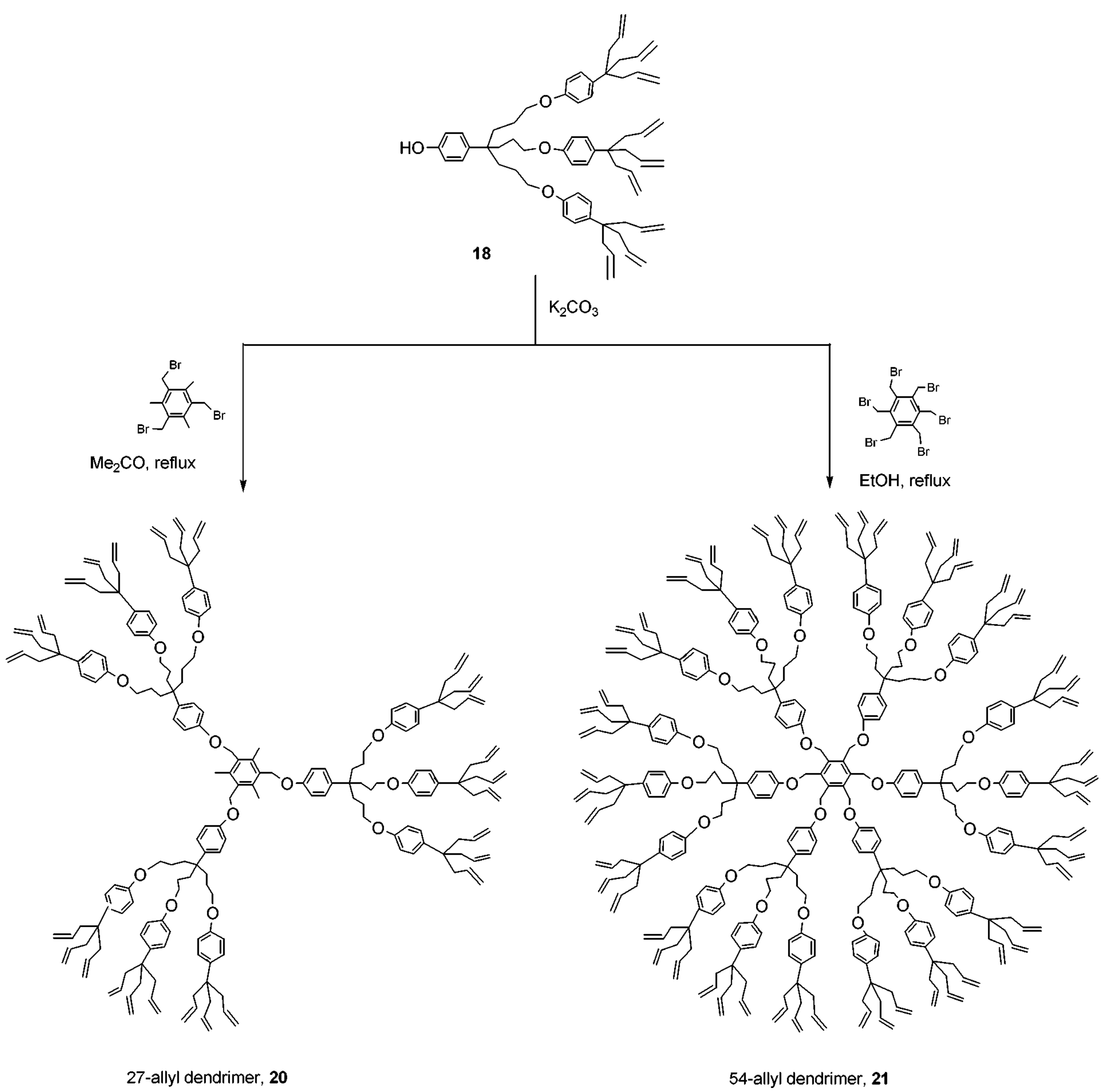
Scheme 3

molecular peak $[M + K]^+$ as the only significant peak at 2936.95. Finally, **18** reacts with hexakis(bromomethyl)benzene in the same way to give the 54-allyl dendrimer **21** as a white crystalline solid in 83% yield after chromatography (Scheme 4); **21** was characterized by its molecular peak appearing as the main peak in the MALDI-TOF mass spectrum.

Discussion

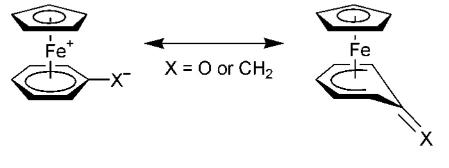
Formation of the triallylphenol dendrons 2 and 3

Heterolytic cleavage of exocyclic carbon–oxygen bonds is known from a previous study with aryl ether ligands lacking methyl groups,[9] and is also known in other ligands and metals[33,34] and even in the absence of metal under drastic conditions.[35] Oxocyclohexadienyl or phenate complexes resulting from exocyclic O–C cleavage have been known for a long time, being easily formed by deprotonation of phenol complexes.[36] The use of such phenol π complexes would not be appropriate here because their deprotonation to phenate π complexes would be a dead end. On the other hand, the alkyl group on the oxygen atom protects it during the three deprotonation-allylation sequences. Yet its bond to the oxygen atom is fragile enough to be cleaved thereafter, while the iron–arene bond is still resistant. Synthesis of the tridendate oxocyclohexadienyl complex **2** thus requires these seven steps to proceed in a precise order in a one-pot reaction. Deprotonation of a methyl arene substituent[37,38] by Bu^{t}OK is followed by allylation of the deep red methylenecyclohexadienyl intermediate to generate a yellow cationic arene complex, whose structure only differs from that of the starting complex by the substitution of an allyl group for a benzylic hydrogen atom. The monosubstituted allyl complex cannot be isolated in pure form because it is deprotonated *in situ* by the methylenecyclohexadienyl intermediate, and double substitution by allyl groups is always observed in minor amounts, even if only one equivalent of Bu^{t}OK is used. Such methylenecyclohexadienyl intermediates have been isolated and their structure is known.[37,38] The structure of the deprotonated species can be described by two mesomers: a dominant methylenecyclohexadienyl form and a zwitterionic form with a minor contribution[9] (Chart 1).

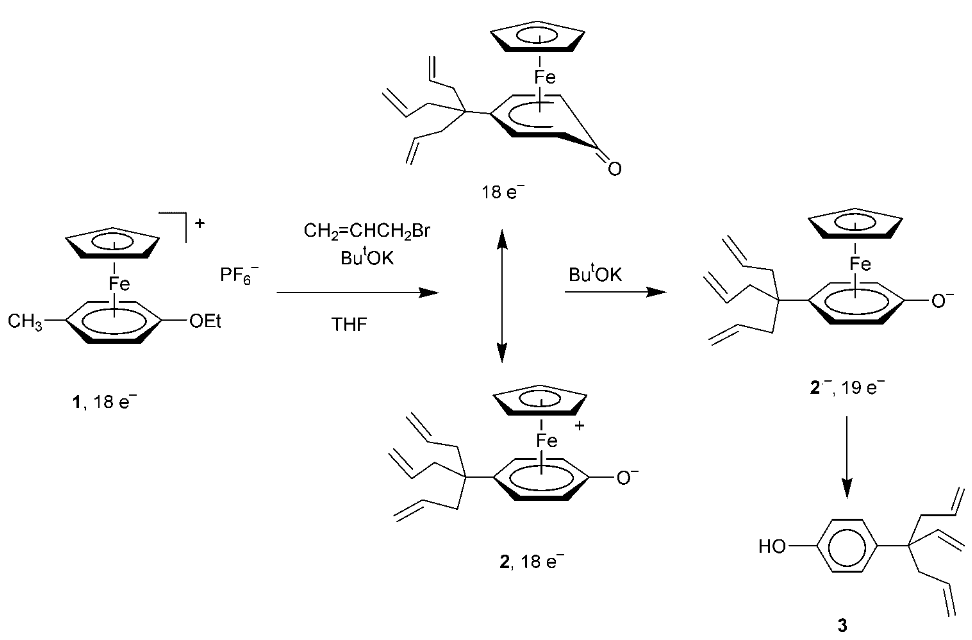


Scheme 4

The fact that two tautomers rather than two mesomers should be considered cannot be discarded, although we prefer the mesomer description in the absence of evidence for two species on the infrared time scale of 10^{13} s^{-1}. Two other analogous deprotonation-allylation sequences must proceed before heterolytic cleavage of the exocyclic O–C of the aryl ether complex by Bu^{t}OK. Therefore, the reaction mixture is kept at low temperature each of the three times that Bu^{t}OK is added in the course of the synthesis. Once the O–C bond has been cleaved, it is no longer possible to deprotonate the ligand because the oxocyclohexadienyl complex formed is neutral, thus no longer acidic. Minor amounts of reaction products analogous to **2** and containing only two allyl substituents are sometimes formed, and can be eliminated during the chromatographic purification. Their formation results from the fact that the third deprotonation-allylation sequence is much slower than the first two because of steric inhibition due to the allyl substituents. The synthesis of **3** proceeds analogously to that of **2**, but also requires one more step: the cleavage of the iron–arene bond by Bu^{t}OK. This last step does not occur at low temperature, but only more slowly at room temperature in the presence of excess Bu^{t}OK added at the very end of the reaction. We know that electron-rich anions such as Bu^{t}OK can transfer an electron to 18-electron organo iron cations of the $[FeCp(\eta^6\text{-arene})]^+$ type to produce unstable 19-electron intermediates, which decompose. The decomposition of such 19-electron species occurs because the 19th electron occupies an antibonding e_1^* orbital, which destabilizes the metal–arene bond,[38] especially when the arene bears a heteroatom in an exocyclic position and long alkyl chains,[39] which is the case for **2** (Scheme 5).



Although **2** is not strictly an arene complex, the arene contribution to the mesomers is indicated by the reduction potential[9b] (-2.3 V *vs.* $FeCp_2{}^{+/0}$ in DMF), which is accessible although it is more negative that those of the regular cationic arene complexes[38] (-1.7 V *vs.* $FeCp_2{}^{+/0}$ in DMF). We believe that, after electron transfer, the reduced form $\mathbf{2}^-$ is a true, although very unstable, 19-electron complex of phenate.[40] The reaction conditions of eqn. (4) and Scheme 5 avoid this reduction before the seven other steps. Thus the eight steps of this one-pot synthesis occur in the right order as indicated in the overall mechanism represented in Scheme 6. The ion-pairing and salt effects (*i.e.*, counteranion in Scheme 5) are



Scheme 5

very influential factors, which have been investigated in the case of the same reaction with the ethoxybenzene complex[9b,c] [eqn. (2)].

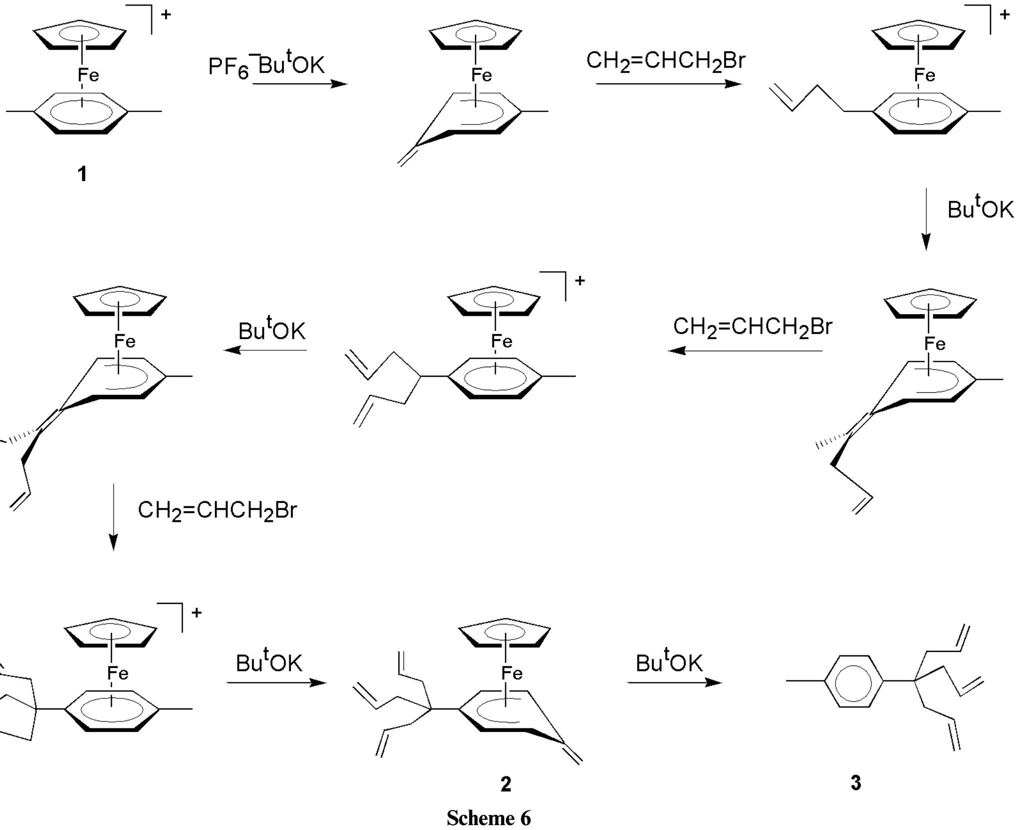
The formation of **3** from the aryl sulfide complexes **4a** and **4b** may appear as a rather surprising feature. The formation of **5** in large amounts in this reaction indicates that the exocyclic S–C bond is resistant to cleavage in the iron complex, thus the 7th step of Scheme 6 is skipped. This is confirmed by the absence of any aryl thiol formation and, instead, by the formation of **3**. It is known that thioalkyl groups are excellent leaving groups in the nucleophilic aromatic substitution of electron-poor aromatics.[41] Thus Bu^{t}O$^-$ plays the role of the incoming nucleophile in the reaction with **4**, then the classic O–C cleavage by Bu^{t}OK can occur as for **1** (Scheme 7).

We know that the O–C cleavage reaction is general with aryl alkyl ether complexes and even in diaryl ether complexes. It is also probable that, in the reaction of **1** (Scheme 5), allylation of **2** by allyl bromide occurs *in situ* and is followed by cleavage by Bu^{t}OK to re-form **2**. Thus, **1** is presumably a catalyst for the alkylation of allyl bromide by Bu^{t}OK, although investigation of turnovers have not been carried out (Scheme 8).

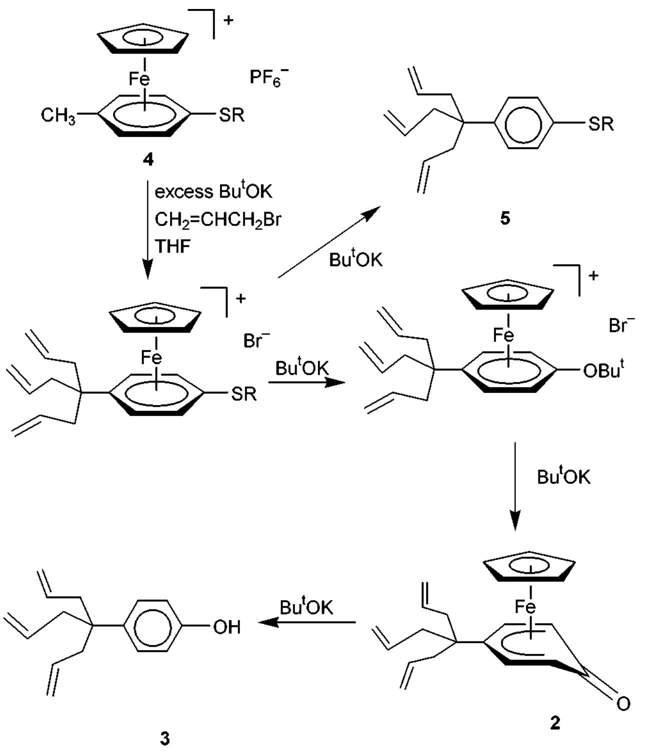
In summary, the best route to **3** is the one-pot eight-step procedure from **1**, Bu^{t}OK, allyl bromide and THF, which is very convenient.

Divergent and convergent dendrimer syntheses

The methods of dendrimer synthesis in molecular chemistry are quite varied.[8,42–54] They are divergent[42–46] or convergent[42,47,48] or can result from mixing both types. The divergent technique is most often used because it can lead to

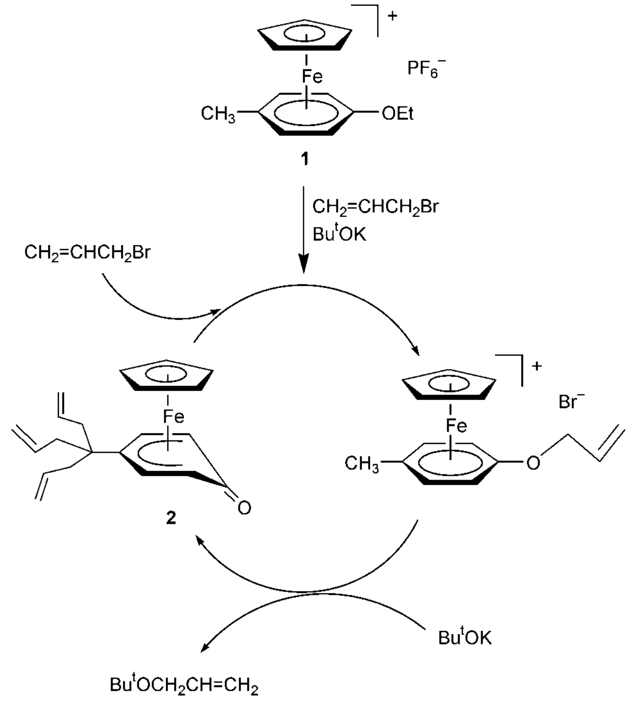


Scheme 6



Scheme 7

the formation of large dendrimers, but it is marred by impurities, which become more and more important as the generation number increases. The convergent method provides clean dendrimers for the low generations, but cannot be applied to the synthesis of large dendrimers because of the increasing steric bulk at the branching points. After Achar and Puddephatt's dendrimer syntheses astutely using oxidative addition on platinum centers,[54] the present dendrimer synthesis strategy is the second one to use organo transition-metal chemistry. The growth of the dendrimer is fast and large dendrimers are synthesized in only a very few generations. All the problems noted above are typically met in the present work however, as exemplified by the decreased dendrimer purity met in the divergent strategy from **7** (1st generation, 27-allyl) to **10** (2nd generation, 81-allyl) and **13** (3rd generation, 223-allyl), and the failure to synthesize the 27-allyl phenol dendron (Scheme 3) in the convergent strategy. The interest in the divergent strategy lies both in the synthesis of pure dendrimer of modest size (**7**) and in the relatively fast synthesis of the dendrimer **13** with a theoretical number of 243 branches. This construction is summarized in Scheme 9.



Scheme 8

Although this strategy gives the 81- and 243-allyl dendrimers **10** and **13** in low yields if the mesylate route is required, the related routes in which dehydroiodation is not available, such as the synthesis of the 54-allyl dendrimer **21**, give dendrimers as crystalline compounds with excellent purity and high yields. Efforts along this line to synthesize large quantities of dendrimers are ongoing in our laboratories. Except perhaps for **21**, the elemental analyses were not correct for the large dendrimers from 27- to 243-allyl. This problem is classic: it is now well known that solvent molecules and various guest molecules are very difficult to remove from dendrimer samples, even after several days under vacuum, which often leads to frustrating attempts to carry out successful elemental analyses.[55] This feature emphasizes even more the considerable assistance of MALDI-TOF mass spectroscopy in their characterization (see also the spectra in the Electronic Supplementary Information). The lack of success in obtaining a MALDI-TOF mass spectrum for **13** argues in favor of a polydisperse dendrimer[56] in spite of its satisfactory ^{1}H and ^{13}C NMR spectra (see Fig. 2). The increasing bulk around the reaction sites at the termini of the branches as the generation number increases is probably a limiting factor to synthesizing the 243-allyl dendrimer by the divergent route. An indication of this problem is represented by the molecular models of the 27-, 81- and 243-allyl dendrimers (Fig. 3). These models do not give conformational information. In particular, they do not address the problem of the location of the termini (at the periphery[57] or turning inside[58]). The overall bulk is clearly apparent, however.

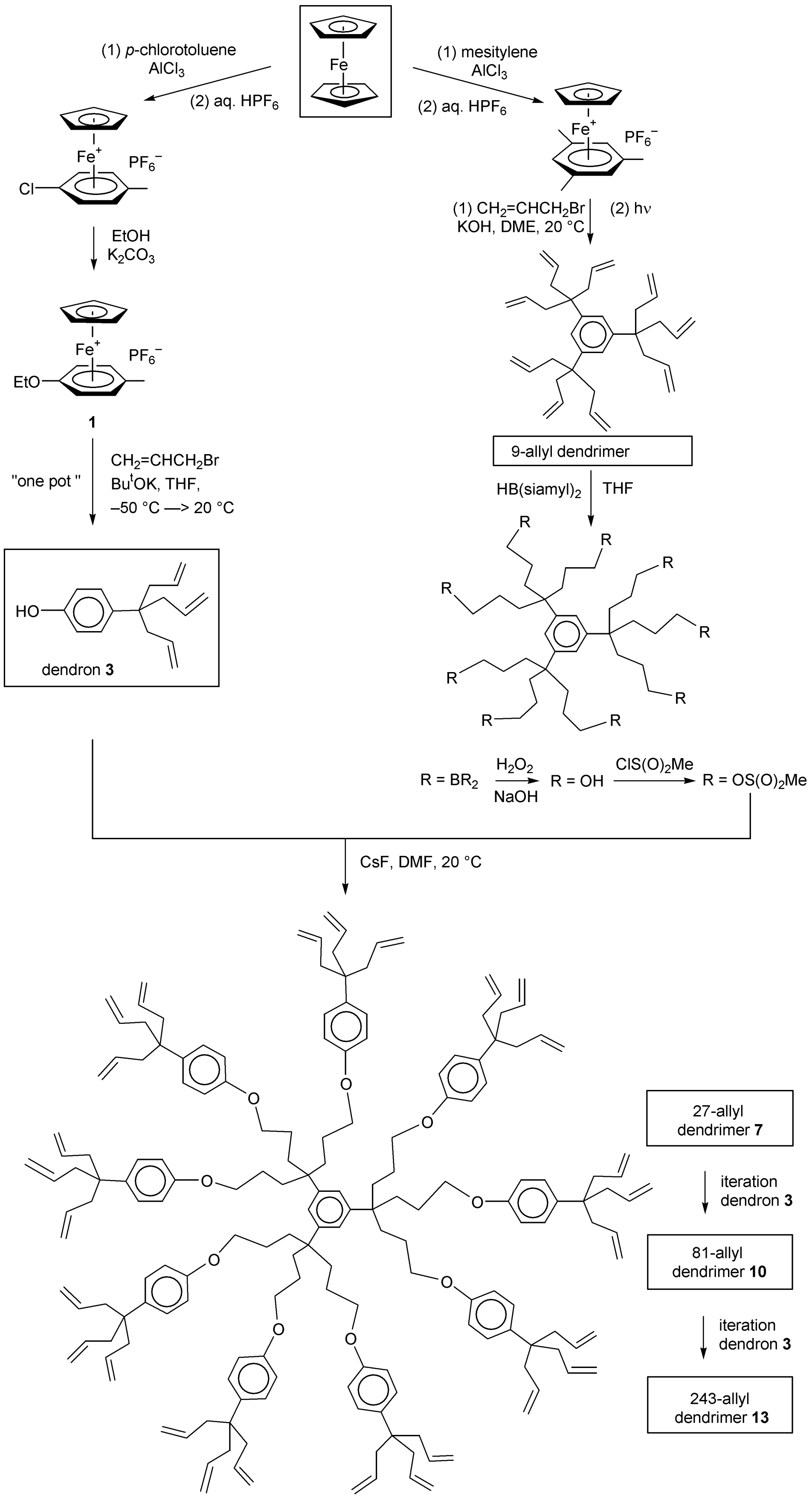
The design and practical synthesis of the tridentate dendron **3** has several advantages: (*i*) it allows one to carry out both the divergent and convergent strategies; (*ii*) it involves a rapid dendritic growth since the number of branches is multiplied by three, whereas most dendrimer syntheses only double the number of branches at each generation; (*iii*) the branches of the dendron are relatively long, which avoids steric problems at least for the first generations; (*iv*) it can be functionalized in different ways on both the phenol and olefin sides; (*v*) its synthesis in reasonable yields from a cheap starting material, which can be easily synthesized on a scale of several hundred grams, is now available from the present study in a one-pot procedure; (*vi*) the convergent route leads to a clean nona-allyl phenol dendron **18**, which is used as a building block for the one-step clean synthesis of dendrimers of moderate size, as exemplified by the synthesis of the 54-allyl dendrimer **21**.[59]

Conclusions

1. The first organo iron strategy for the construction of dendrimers and dendrons has been successfully developed using an original synergy between two modes of activation of aromatics by the electron-withdrawing cation CpFe$^+$: the enhanced acidity of the benzylic protons and the nucleophilic cleavage of the O–C bond of aryl ether complexes.

2. The triallyl phenol dendron **3** is synthesized in 50% overall yield in a one-pot eight-step synthesis from [FeCp(η^6-p-MeC$_6$H$_4$OEt)][PF$_6$], **1**, a cheap starting material easily available on a scale of several hundred grams.

3. The cationic aryl sulfide iron complexes **4** analogous to **1** do not undergo S–C cleavage by reaction with Bu^{t}OK and allyl bromide, but **3** and the metal-free triallyl aryl sulfide **5** are formed; the apparently surprising formation of **3** is accounted for by a nucleophilic aromatic substitution of the


Fe
(1) p-chlorotoluene
AlCl3
(2) aq. HPF6
(1) mesitylene
AlCl3
(2) aq. HPF6
Fe+
PF6−
Cl
EtOH
K2CO3
EtO
1
"one pot"
CH2=CHCH2Br
BuᵗOK, THF,
–50 °C —> 20 °C
HO
dendron 3
(1) CH2=CHCH2Br
KOH, DME, 20 °C
(2) hν
9-allyl dendrimer
HB(siamyl)2
THF
R
R = BR2
H2O2
NaOH
R = OH
ClS(O)2Me
R = OS(O)2Me
CsF, DMF, 20 °C
O
27-allyl dendrimer 7
iteration dendron 3
81-allyl dendrimer 10
iteration dendron 3
243-allyl dendrimer 13

Scheme 9

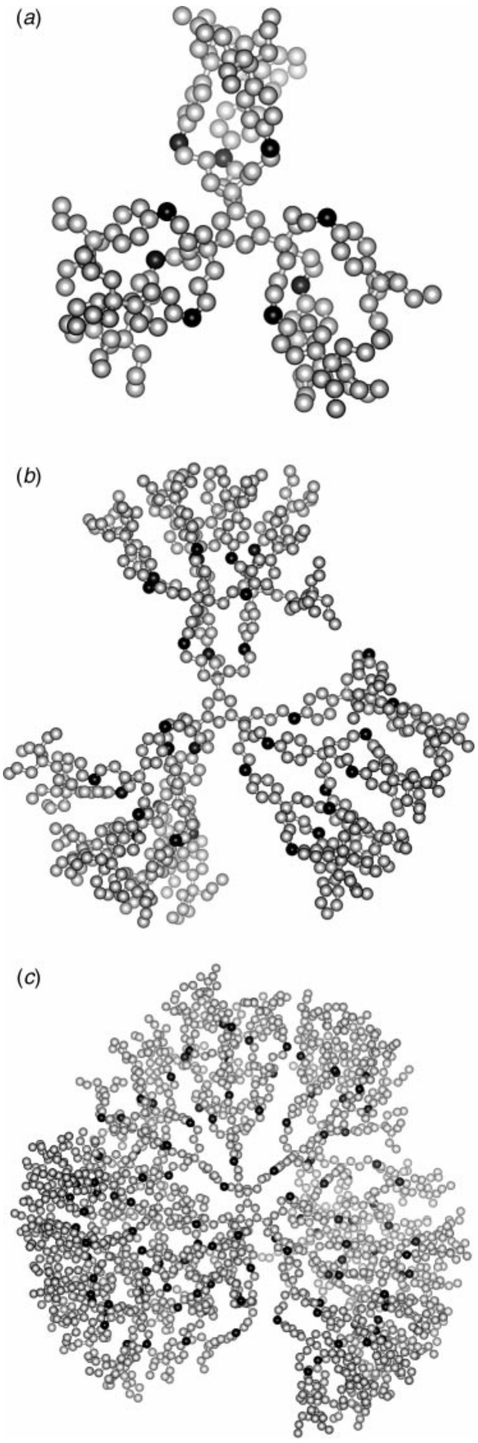


Fig. 3 Molecular modeling (Cerius program) of the (*a*) 27-allyl dendrimer 7, (*b*) 81-allyl dendrimer 10 and (*c*) 243-allyl dendrimer 13.

thioalkyl group by Bu^tO^-, followed by the classic O–C cleavage.

4. Functionalization of a nona-allyl dendritic core has led to the use of **3** as a building block for the rapid divergent dendrimer synthesis up to a theoretical number of 243 branches after only three generations.

5. A convergent strategy based on **3** has led to the clean synthesis of a nona-allylphenol dendron **18**, a very useful building block for clean, one-step synthesis of larger dendrimers such as the 54-allyl dendrimer **21**.

6. MALDI-TOF mass spectroscopy has been systematically used all along this work. It has helped to considerably improve the syntheses whereas ^1H and ^{13}C NMR brought comparatively much less accurate information. Finally, the dendrons or dendrimers **3** to **18** (except **13**) have been shown to have a good level of purity, their molecular peak being always dominant (see the Electronic Supplementary Information).

7. This study opens practical and powerful routes to further studies in dendritic and nanosized materials chemistry and their applications based on the dendrons **3** and **18**. Various strategies along these lines are presently ongoing in our laboratories.

Experimental

General

All reactions were carried out in an inert atmosphere in oven-dried or flamed glassware using Schlenk techniques and a Vacuum Atmosphere Company dry-lab. Reagent grade solvents used for the syntheses are dried and distilled prior to use: tetrahydrofuran (THF) is distilled over Na–benzophenone ketyl, then over CaH_2 ; 1,2-dimethoxyethane (DME) is distilled over Na–benzophenone ketyl (caution: THF and DME are not distilled to dryness); *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are distilled over CaH_2 immediately before use; pyridine is distilled over KOH immediately before use. All other chemicals are used as received.

^1H NMR spectra were recorded with a Bruker AC 250 FT (250 MHz) and a Bruker AC 200 FT (200 MHz), and ^{13}C NMR spectra were recorded with a Bruker AC 250 FT (62.9 MHz). All chemical shifts are reported in ppm with internal reference to tetramethylsilane or to the solvent. The elemental analyses were carried out at the CNRS center in Vernaison (France). All mass spectra were recorded using the MALDI-TOF technique on a Voyager Elite TOF mass spectrometer (Perspective Biosystems, Framingham, USA). One μL of an acetone solution of the matrix (2,5-dihydroxybenzoic acid) and analyte at concentrations of 0.1 M and 0.1 mM, respectively, was deposited on the target for MALDI analysis. $[FeCp(\eta^6\text{-}p\text{-}ClC_6H_4Me)]\text{-}[PF_6]$ and $[FeCp(\eta^6\text{-mesitylene})]\text{-}[PF_6]$, precursors of **2** and $[FeCp(\eta^6\text{-1,3,5-triallyl-methylbenzene})][PF_6]$,[14] respectively, are synthesized by ligand exchange between ferrocene and $p\text{-}ClC_6H_4Me$ in the presence of $AlCl_3$ and Al powder according to refs. 60 and 61, respectively, modified with improved yields according to ref. 62 (1 equiv. H_2O per ferrocene is added; the arene is used as solvent at reflux overnight). $[FeCp(\eta^6\text{-}p\text{-}EtOC_6H_4Me)][PF_6]$, **1**, is synthesized in essentially quantitative yield by reaction between $[FeCp(\eta^6\text{-}p\text{-}ClC_6H_4Me)][PF_6]$, Na_2CO_3 and ethanol (used as solvent at reflux overnight) according to ref. 13.

Syntheses

[FeCp(η^6-*p*-triallylmethylphenate)], 2 [eqn. (3)]. $[FeCp(\eta^6\text{-}p\text{-}EtOC_6H_4Me)][PF_6]$, **1** (see above),[6c,7] (5 g, 12.4 mmol) and Bu^tOK (12.6 g, 112.5 mmol) are introduced into a flamed three-necked flask under nitrogen, then 100 mL of freshly distilled THF is introduced by canula into this reaction mixture at −50 °C. After stirring 15 min., 20 mL (0.232 mmol) of cold allyl bromide is added. The reaction medium is stirred at ambient temperature in the dark for 2 days, Bu^tOK (12.6 g, 112.5 mmol) and allyl bromide (10 mL, 0.116 mmol) in 50 mL THF are introduced at −50 °C and the reaction mixture is stirred for 2 more days at ambient temperature in the dark. Bu^tOK (12.6 g, 112.5 mmol) and allyl bromide (5 mL, 0.058 mmol) in 10 mL THF are again added at −50 °C and the reaction mixture is stirred for an additional 2 days. Finally, Bu^tOK (9 g, 80 mmol) and allyl bromide (5 mL, 0.058 mmol) in 10 mL THF are added at −50 °C and the reaction mixture is allowed to stir for 2 more days under the same conditions. The solid residue is removed from the reaction mixture by filtration, the solvent of the filtrate is removed under vacuum, and the resulting solid residue is purified by chromatography on a neutral alumina column using methanol as the eluent, which gives a red oil (2.2 g, 6.2 mmol, 50% yield). ^{1}H NMR ($\mathrm{CD_3COCD_3}$) δ 5.75 (m, $\mathrm{CH_{arom}}$, 2H); 5.49 (m, $\mathrm{CH_{arom}}$, 2H); 5.06–4.97 (m, $\mathrm{C\mathit{H}CH_2}$ and $\mathrm{C_5H_5}$, 8H); 4.57 (m, $\mathrm{CHC\mathit{H}_2}$, 6H); 2.44 (m, $\mathrm{CH_2}$, 6H). ^{13}C NMR ($\mathrm{CD_3COCD_3}$) δ 154.89 ($\mathrm{C_{quat\,arom}O}$); 135.26 ($\mathrm{\mathit{C}HCH_2}$); 119.24 ($\mathrm{CH\mathit{C}H_2}$); 101.89 ($\mathrm{\mathit{C}_{quat\,arom}C}$); 84.18 ($\mathrm{\mathit{C}H_{arom}CO}$); 74.93 ($\mathrm{C_5H_5}$); 73.22 ($\mathrm{\mathit{C}H_{arom}C}$); 43.56 ($\mathrm{CH_2}$); 42.54 ($\mathrm{\mathit{C}_{quat}CH_2}$). Anal. calcd for $\mathrm{C_{21}H_{24}OFe, H_2O}$: C 68.83; H 7.16; C 8.74; Fe 15.28. Found C 68.82; H 7.20.

***p*-Triallylmethylphenol, 3, by photochemical decomplexation of 2 [eqn. (4)].** The complex **2** (2 g, 0.575 mmol) and 200 mL degassed MeCN are introduced under nitrogen into a Schlenk flask. The solution is irradiated for 12 h with a Hg vapor lamp, the solvent is removed under vacuum and the residue is dissolved in 200 mL ether. This solution is washed with 100 mL 6 N HCl, dried over sodium sulfate, filtered and the solvent is removed under vacuum. The residue is purified by chromatography on a silica column with pentane–ether (95 : 5) as the eluent, which yields **3** as a light brown solid (0.920 g, 0.40 mmol, 70% yield). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.18 and 6.83 (m, $\mathrm{CH_{arom}}$, 4H); 6.58 (m, OH, 1H); 5.68–5.55 (m, $\mathrm{C\mathit{H}CH_2}$, 9H); 5.07–5 (m, $\mathrm{CHC\mathit{H}_2}$, 18H); 2.44 (d, $\mathrm{CH_2}$, 18H). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 153.40 ($\mathrm{C_{quat\,arom}OH}$); 137.60 ($\mathrm{\mathit{C}_{quat\,arom}C}$); 134.56 ($\mathrm{\mathit{C}HCH_2}$); 127.73 ($\mathrm{\mathit{C}H_{arom}COH}$); 117.42 ($\mathrm{CH\mathit{C}H_2}$); 114.89 ($\mathrm{\mathit{C}H_{arom}C}$); 42.59 ($\mathrm{\mathit{C}_{quat}CH_2}$); 41.87 ($\mathrm{CH_2}$). Anal. calcd for $\mathrm{C_{16}H_{20}O}$: C 84.16; H 8.83; O 7.01. Found C 84.14; H 8.82.

***p*-Triallylmethylphenol, 3, by one-pot synthesis from [FeCp(η^6-*p*-EtOC$_6$H$_4$Me)][PF$_6$], 1 [eqn. (5)].** [FeCp(η^6-*p*-$\mathrm{EtOC_6H_4Me}$)][$\mathrm{PF_6}$], **1** (5 g, 12.4 mmol) and Bu^{t}OK (12.6 g, 112.5 mmol), are introduced into a flamed three-necked flask under Ar, then 100 mL of freshly distilled THF is introduced by canula into this reaction mixture at −50 °C. After stirring 15 min., cold allyl bromide (20 mL, 0.232 mmol) is added. The reaction medium is stirred at ambient temperature in the dark for 1 day, then Bu^{t}OK (12.6 g, 112.5 mmol) and allyl bromide (10 mL, 0.116 mmol) in 50 mL THF are introduced at −50 °C, and the reaction mixture is warmed to 25 °C over 3 h and stirred 1 more day at ambient temperature in the dark. Bu^{t}OK (12.6 g, 112.5 mmol) and allyl bromide (8 mL, 0.092 mmol) are again added at −50 °C and the reaction mixture is stirred for 1 more day. Finally, Bu^{t}OK (18.3 g, 163 mmol) is added in 80 mL THF at −50 °C and the reaction mixture is allowed to stir for 1 more day under the same conditions. The solvent is removed under vacuum and the solid residue is dissolved in 500 mL ether, this solution is washed with 100 mL 6 N HCl, dried over sodium sulfate and filtered. The solvent is removed under vacuum and the residue is chromatographed on a silica column using pentane–ether (95 : 5) as the eluent, which gives **3** as a light brown solid (1.71 g, 0.75 mmol, 60% yield).

Reaction of Bu^{t}OK and allyl bromide with [FeCp(η^6-*p*-MeC$_6$H$_4$SR)][PF$_6$], R = Me (4a) or Et (4b) eqn. (6)]. The reaction has been carried out as from **1**, and the organic derivatives **2** and **5** are separated by column chromatography. **2** is obtained in 20% yield with R = Me and 15% yield with R = Et. **5a** and **5b** are characterized as above. **5a** *p*-$\mathrm{MeSC_6H_4C(CH_2{-}CH{=}CH_2)_3}$]: 45% yield. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.23 (m, $\mathrm{CH_{arom}}$, 4H); 5.64–5.50 (m, $\mathrm{C\mathit{H}CH_2}$, 3H); 5.07–4.99 (m, $\mathrm{CHC\mathit{H}_2}$, 6H); 2.50 (s, $\mathrm{SCH_3}$, 3H); 2.43 (d, $\mathrm{C\mathit{H}_2CHCH_2}$, 6H). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 143.42 ($\mathrm{SC_{6\,quat}H_4}$); 135.40 ($\mathrm{CH_2\mathit{C}H}$); 134.42 ($\mathrm{C_{6\,quat}H_4}$); 127.29 ($\mathrm{CH_{arom}}$); 126.38 ($\mathrm{CH_{arom}}$); 117.73 ($\mathrm{CH\mathit{C}H_2}$); 43.30 ($\mathrm{\mathit{C}_{quat}CH_2}$); 41.81 ($\mathrm{\mathit{C}H_2CHCH_2}$); 15.89 ($\mathrm{SCH_3}$). Anal. calcd for $\mathrm{C_{17}H_{22}S}$: C 79.01; H 8.58. Found C 79.45; H 8.76. **5b** [*p*-$\mathrm{EtSC_6H_4C(CH_2{-}CH{=}CH_2)_3}$]: 58% yield. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.30–7.11 (m, $\mathrm{CH_{arom}}$, 4H); 5.66–5.45 (m, $\mathrm{C\mathit{H}CH_2}$, 3H); 5.05–4.97 99 (m, $\mathrm{CHC\mathit{H}_2}$, 6H); 2.93 (q, $\mathrm{SC\mathit{H}_2CH_3}$, 2H), 2.43 (d, $\mathrm{C\mathit{H}_2CHCH_2}$, 6H); 1.31 (t, $\mathrm{SCH_2C\mathit{H}_3}$, 3H,); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 143.50 ($\mathrm{SC_{6\,quat}H_4}$); 135.40 ($\mathrm{CH_2\mathit{C}H}$); 134.38 ($\mathrm{C_{6\,quat}H_4}$); 128.83 ($\mathrm{CH_{arom}}$); 127.29 ($\mathrm{CH_{arom}}$); 117.74 ($\mathrm{CH\mathit{C}H_2}$); 43.00 ($\mathrm{\mathit{C}_{quat}CH_2}$); 41.79 ($\mathrm{\mathit{C}H_2CHCH_2}$); 27.74 ($\mathrm{S\mathit{C}H_2CH_3}$); 14.45 ($\mathrm{SCH_2\mathit{C}H_3}$). Anal. calcd for $\mathrm{C_{18}H_{24}S}$: C 79.37; H 8.89. Found C 80.00; H 8.91. MS (EI) *m*/*z* (rel. int.): 272 (23) $[\mathrm{M}]^{+}$, 231 (100), 202 (6), 190 (33).

Nona-iodo core 6a [eqn. (7)]. The nona-ol core synthesized according to ref. 14 (1.17 g, 1.82 mmol) in 200 mL MeCN, then dry NaI (10 g, 66 mmol) and freshly distilled $\mathrm{SiMe_3Cl}$ (5 mL, 39 mmol) are successively introduced into a flamed Schlenk flask. This reaction mixture is stirred under nitrogen in the dark for 12 h at 80 °C. The solvent is then removed under vacuum, the residue is dissolved in 200 mL ether, this solution is washed with a saturated aqueous solution of $\mathrm{Na_2S_2O_3}$ and filtered, and the solvent is removed under vacuum. This gives **6a** as a pale yellow solid (2.64 g, 1.62 mmol, 89%). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.04 (s, $\mathrm{C_6H_3}$, 3H); 3.14 (m, $\mathrm{CH_2I}$, 18H); 1.81 (m, $\mathrm{C\mathit{H}_2CH_2I}$, 18H); 1.56 (m, $\mathrm{CH_2C_{quat}}$, 18H). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 145.51 ($\mathrm{C_{quat\,arom}}$); 121.98 ($\mathrm{CH_{arom}}$); 42.8 ($\mathrm{\mathit{C}_{quat}CH_2}$); 38.56 ($\mathrm{\mathit{C}H_2CH_2I}$); 27.79 ($\mathrm{\mathit{C}H_2C_{quat}}$); 8.5 ($\mathrm{CH_2I}$). Anal. calcd for $\mathrm{C_{36}H_{57}I_9}$: C 28.48; H 3.52; I 70. Found C 26.55; H 3.49.

Nona-mesylate core 6b [eqn. (7)]. The nona-ol (0.6 g, 0.934 mmol) in 7 mL anhydrous pyridine is introduced in a flamed Schlenk tube under an inert atmosphere. The solution is cooled to −5 °C, and chloromethylsulfonate (13 mL, 16 mmol) is slowly added to this solution over 1 h. The solution is stirred for 4 h at 0–2 °C. Ice (50 g) is added to this solution and iced 6 N HCl is added until pH 3 is reached. Extraction with 3 × 50 mL dichloromethane is followed by drying over sodium sulfate. After filtration and removal of the solvent under vacuum, the residue is washed with 50 mL cold pentane. The nona-mesylate **6b** is obtained in this way as a colorless oil and is stored at −25 °C (1.2 g, 0.89 mmol, 95% yield). ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.02 (s, $\mathrm{C_6H_3}$, 3H); 4.09 (m, $\mathrm{CH_2O}$, 18H); 2.93 (s, $\mathrm{CH_3}$, 27H); 1.72 (m, $\mathrm{C\mathit{H}_2CH_2\,O}$, 18H); 1.42 (m, $\mathrm{CH_2C_{quat}}$, 18H). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 145.12 ($\mathrm{C_{quat\,arom}}$); 121.99 ($\mathrm{CH_{arom}}$); 70.73 ($\mathrm{CH_2O}$); 42.36 ($\mathrm{\mathit{C}_{quat}CH_2}$); 36.91 ($\mathrm{CH_3}$); 33.62 ($\mathrm{\mathit{C}H_2CH_2O}$); 23.56 ($\mathrm{\mathit{C}H_2C_{quat}}$).

27-Allyl dendrimer 7 from the nona-iodo core 6a [eqn. (8)]. Triallylmethylphenol **3** (1.25 g, 5.5 mmol) in 10 mL of freshly distilled DMF and potassium carbonate (3.85 g, 27 mmol) are introduced into a flamed Schlenk tube under nitrogen and the reaction mixture is stirred for 30 min., then the nona-iodo core **6a** (0.5 g, 3.06 mmol) in 20 mL anhydrous DMF is progressively added. The reaction mixture is stirred for 3 days at room temperature, the organic derivative is extracted with 3 × 100 mL ether, the solution is dried over sodium sulfate, filtered, and the solvent is removed under vacuum. The product is purified by chromatography on a neutral alumina column using a pentane–ether mixture (98 : 2) as the eluent. This gives the 27-allyl dendrimer **7** as a colorless oil (0.342 g, 44%).

27-Allyl dendrimer 7 from the nona-mesylate core 6b [eqn. (9)]. Cesium fluoride (5.4 g, 36 mmol) is heated at 160 °C under vacuum for 3 h in a flamed Schlenk tube. Then, **3** (5.49 g, 24 mmol) is dissolved in 15 mL of freshly distilled DMF and this solution is added into the Schlenk tube under nitrogen. The mixture is stirred for 30 min., then the nona-mesylate **6b** (1.2 g, 0.89 mmol) in 15 mL anhydrous DMF is progressively added over 30 min. This reaction mixture is stirred for 3 days at room temperature under nitrogen. After extraction with 3 × 50 mL pentane, the organic layer is dried over sodium sulfate and filtered. The solvent is removed under vacuum and the residue is chromatographed on a neutral alumina column using a pentane–ether mixture (98 : 2), which gives **7** as a colorless oil (0.61 g, 0.24 mmol, 27%). ^{1}H NMR ($CDCl_3$) δ 7.32 (s, C_6H_3, 3H); 7.2 (d, C_6H_4, 18H); 6.8 (d, C_6H_4, 18H); 5.66–5.49 (m, $C\mathit{H}CH_2$, 27H); 5.06–4.99 (m, $CHC\mathit{H}_2$, 54H); 3.9 (m, CH_2O, 18H); 2.43 (d, $C\mathit{H}_2CHCH_2$, 54H); 1.97 (m, $CC\mathit{H}_2CH_2$, 18H); 1.67 (m, $C\mathit{H}_2CH_2O$, 18H). ^{13}C NMR ($CDCl_3$) δ 156.86 ($OC_{6\,\text{quat}}H_4$); 145.74 ($C_{6\,\text{quat}}H_3$); 137.48 ($C_{6\,\text{quat}}H_4$); 134.71 ($CH_2\mathit{C}H$); 127.67 (CH_{arom}); 122.44 (CH_{arom}); 117.59 ($CH\mathit{C}H_2$); 113.94 (C_6H_4); 68.24 (CH_2O); 43.17 ($\mathit{C}_{\text{quat}}CH_2$); 42.71 ($\mathit{C}_{\text{quat}}CH_2$); 42.03 ($\mathit{C}H_2CHCH_2$); 34.02 ($\mathit{C}H_2CH_2O$); 24.17 ($C\mathit{C}H_2CH_2$). MALDI-TOF MS: $[M + Na]^+$ 2558.88 (calcd 2558.80).

27-Alcohol dendrimer 8 [eqn. (10)]. The 27-alcohol is synthesized from the 27-allyl precursor **7** in the same way as the nona-ol according to ref. 6*a*. This procedure follows the hydroboration-oxidation by Brown *et al.*[63] A molar THF solution of BH_3 (127 mL, 127 mmol) is introduced into a flamed Schlenk tube under nitrogen and cooled to −15 °C. A 2 M THF solution of 2-methyl-2-butene (127 mL, 254 mmol) is cooled to −15 °C, then added into the Schlenk tube containing the BH_3 solution and the reaction mixture is kept at −12 °C for 2 h. The 27-allyl dendrimer **7** (0.800 g, 0.315 mmol) dissolved in 40 mL of freshly distilled THF is then added and the reaction mixture is stirred for one 1 day in the dark. Then, 30 mL degassed water, 30 mL 3 M NaOH and 45 mL 30% H_2O_2 are added. The reaction mixture is left for 15 h at 50 °C, the two phases are separated, the aqueous phase is saturated with potassium carbonate and extracted with 5 × 50 mL THF. The organic phases are gathered collected and dried over sodium sulfate, filtered, and concentrated to 30 mL under reduced pressure. The 27-alcohol dendrimer **8** is obtained by precipitation upon addition of 100 mL ether (0.800 g, 0.265 mmol, 84% yield). ^{1}H NMR (CD_3OD) δ 7.39 (s, C_6H_3, 3H); 7.21 and 6.77 (m, C_6H_4, 36H); 3.78 (m, CH_2OC_{arom}, 18H); 3.44 (m, $C\mathit{H}_2OH$, 54H); 1.95 (m, $CC\mathit{H}_2CH_2$, 72H); 1.64 (m, $CCH_2C\mathit{H}_2$, 72H). ^{13}C NMR (CD_3OD) δ 158.3 ($C_{\text{quat arom}}O$); 148.24 ($C_{\text{quat arom}}$); 140.25 ($C_{\text{quat arom}}$); 128.63 (CH_{arom}); 124.7 (CH_{arom}); 115.25 (CH_{arom}); 69.50 ($\mathit{C}H_2OC$); 63.71 (CH_2OH); 42.95 ($\mathit{C}_{\text{quat}}CH_2$); 42.88 ($\mathit{C}_{\text{quat}}CH_2$); 34.89 ($C\mathit{C}H_2CH_2$); 27.95 ($CH_2CH_2O$); 25.59 ($\mathit{C}H_2CH_2O$). MALDI-TOF MS $[M + Na]^+$ 3045.11; $[M + K]^+$ 3063.7 (calcd 3061.06).

27-Iodo dendrimer 9a. The 27-alcohol dendrimer **8** (0.338 g, 0.128 mmol) is dissolved in 30 mL of freshly distilled THF; this solution is introduced into a Schlenk tube under an inert atmosphere, then freshly distilled $SiMe_3Cl$ (4.4 mL, 22.7 mmol) and Et_3N (2.4 mL, 38.5 mmol) are added. The reaction mixture is stirred for 2 days at room temperature, then the solvent is removed under vacuum, the residue is dissolved in 10 mL of anhydrous MeCN; $SiMe_3Cl$ (2.2 mL, 11.3 mmol) and NaI (5.7 g, 38 mmol) are added. The solution is kept for one 1 day at 40 °C under nitrogen, then the solvent is removed under vacuum and the residue is extracted with 100 mL dichloromethane, this solution is washed with 3 × 50 mL of an aqueous solution saturated with $Na_2S_2O_3$ and dried over sodium sulfate. After filtration, the 27-iodo dendrimer **9a** is obtained as a pale yellow solid by precipitation from this solution upon addition of 200 mL ether (0.330 g, 0.055 mmol, 43% yield). ^{1}H NMR ($CDCl_3$) δ 7.40 (s, C_6H_3, 3H); 7.20 and 6.75 (m, C_6H_4, 36H); 3.78 (m, CH_2OC_{arom}, 18H); 3.1 (m, CH_2I, 54H); 1.92 (m, $CC\mathit{H}_2CH_2$, 72H); 1.60 (m, $CCH_2C\mathit{H}_2$, 72H). ^{13}C NMR ($CDCl_3$) δ 158.3 ($C_{\text{quat arom}}O$); 148.25 ($C_{\text{quat arom}}$); 140.27 ($C_{\text{quat arom}}$); 128.60 (CH_{arom}); 124.69 (CH_{arom}); 115.24 (CH_{arom}); 69.50 ($\mathit{C}H_2OC$); 42.94 ($\mathit{C}_{\text{quat}}CH_2$); 42.9 ($\mathit{C}_{\text{quat}}CH_2$); 34.9 ($C\mathit{C}H_2CH_2$); 27.96 ($\mathit{C}H_2CH_2O$); 25.28 ($CH_2\mathit{C}H_2O$); 7.6 ($CH_2I$).

27-Mesylate dendrimer 9b. The synthesis of **9b** from 0.800 g (0.264 mmol) **8** is effected according to the same procedure as that described above for the synthesis of **6b**, and yields **9b** as a colorless oil (1.2 g, 0.234 mmol, 92% yield). ^{1}H NMR ($CDCl_3$) δ 7.38 (s, C_6H_3, 3H); 7.20 and 6.77 (m, C_6H_4, 36H); 3.80 (m, CH_2OC_{arom}, 18H); 3.77 (m, CH_2OSO_2, 54H); 2.83 (m, SO_2CH_3, 81H); 1.94 (m, $CC\mathit{H}_2CH_2$, 72H); 1.63 (m, $CCH_2C\mathit{H}_2$, 72H). ^{13}C NMR ($CDCl_3$) δ 156.79 ($C_{\text{quat arom}}O$); 144.59 ($C_{\text{quat arom}}$); 136.42 ($C_{\text{quat arom}}$); 126.8 (CH_{arom}); 121.89 (CH_{arom}); 113.9 (CH_{arom}); 70.6 (CH_2SO_2); 67.87 ($\mathit{C}H_2OC$); 41.22 ($\mathit{C}_{\text{quat}}CH_2$); 36.76 ($SO_2CH_3$); 32.43 ($C\mathit{C}H_2CH_2$); 23.15 ($\mathit{C}H_2CH_2O$).

81-Allyl dendrimer 10 [eqn. (11)]. The 81-allyl dendrimer **10** is synthesized from the 27-iodo dendrimer **9a** (0.330 g, 0.0551 mmol) using 1.2 g (5.26 mmol) of triallylmethylphenol according to the same procedure as that described above for the synthesis of **7** from **6a**. The product is purified by chromatography on a neutral alumina column using a pentane–ether mixture (3 : 1) as the eluent, which gives **10** as a colorless oil (0.342 g, 0.0393 mmol, 71% yield of crude **10**, see text). Alternatively, **10** is synthesized from **9b** (0.343 g, 0.0668 mmol) according to the same procedure as that described above for the synthesis of **7** from **6b**. The product is purified by chromatography on neutral alumina columns using a pentane–ether mixture (3 : 1) as the eluent, which gives **10** as a colorless oil (0.030 g, 0.0035 mmol, 6.4% yield). ^{1}H NMR ($CDCl_3$) δ 7.2 and 6.8 (m, C_6H_4, 144H); 5.66–5.49 (m, $C\mathit{H}CH_2$, 81H); 5.06–4.99 (m, $CHC\mathit{H}_2$, 162H); 3.9 (m, CH_2O, 72H); 2.43 (d, $C\mathit{H}_2CHCH_2$, 162H); 1.97 (m, $CC\mathit{H}_2CH_2$, 72H); 1.67 (m, $C\mathit{H}_2CH_2O$, 72H). ^{13}C NMR ($CDCl_3$) δ 156.81 ($OC_{6\,\text{quat}}H_4$); 145.79 ($C_{6\,\text{quat}}H_3$); 137.46 ($C_{6\,\text{quat}}H_4$); 134.62 ($CH_2\mathit{C}H$); 127.52 (C_6H_4); 122.42 (C_6H_3); 117.44 ($CH\mathit{C}H_2$); 113.81 (C_6H_4); 68.12 (CH_2O); 43.17 ($\mathit{C}_{\text{quat}}CH_2$); 42.60 ($\mathit{C}_{\text{quat}}CH_2$); 41.91 ($\mathit{C}H_2CHCH_2$); 33.79 ($\mathit{C}H_2CH_2O$); 23.72 ($C\mathit{C}H_2CH_2$). MALDI-TOF MS: $[M + Na]^+$ 8723.38 (calcd 8723.91).

81-Alcohol dendrimer 11 (Scheme 1). The dendrimer **11** is synthesized from **10** (obtained from the 27-mesylate dendrimer) according the same procedure as that used for the syntheses of the nona-ol and 27-alcohol **8** (see above). From 0.18 g (0.020 mmol) of **10**, **11** is obtained as a white powder (108 mg, 0.0106 mmol, 53% yield). ^{1}H NMR (CD_3OD) δ 7.21 and 6.77 (m, C_6H_4, 144H); 3.78 (m, CH_2OC_{arom}, 72H); 3.44 (m, $C\mathit{H}_2OH$, 162H); 1.95 (m, $CC\mathit{H}_2CH_2$, 234H); 1.64 (m, $CCH_2C\mathit{H}_2$, 234H). ^{13}C NMR (CD_3OD) δ 157.99 ($C_{\text{quat arom}}O$); 140.04 ($C_{\text{quat arom}}$); 128.43 (CH_{arom}); 115.04 (CH_{arom}); 69.26 ($\mathit{C}H_2OC$); 63.5 (CH_2OH); 42.89 ($\mathit{C}_{\text{quat}}CH_2$); 42.66 ($\mathit{C}_{\text{quat}}CH_2$); 34.69 ($C\mathit{C}H_2CH_2$); 27.7 ($\mathit{C}H_2CH_2O$); 24.5 ($\mathit{C}H_2CH_2O$).

81-Mesylate dendrimer 12 (Scheme 1). 12 is synthesized from **11** (0.60 g, 0.0059 mmol) according to the same procedure as that described above for **6b** and **9b**, which gives **12** as a colorless oil (0.082 g, 0.0050 mmol, 85% yield). ^{1}H NMR ($CDCl_3$) δ 7.3 and 6.7 (m, C_6H_4, 144H); 4.9 (m, CH_2OC_{arom}, 72H); 3 (m, CH_2OSO_2, 162H); 2.3 (m, SO_2CH_3, 243H); 1.7 (m, $CC\mathit{H}_2CH_2$, 234H); 1.3 (m, $CCH_2C\mathit{H}_2$, 234H). ^{13}C NMR ($CDCl_3$) δ 157.9 ($C_{\text{quat arom}}O$); 137.8 ($C_{\text{quat arom}}$); 127.6 (CH_{arom}); 114.1 (CH_{arom}); 70.6 (CH_2SO_2); 68.3 ($\mathit{C}H_2OC$); 41.6 ($\mathit{C}_{\text{quat}}CH_2$); 37.7 ($SO_2CH_3$); 32.4 ($C\mathit{C}H_2CH_2$); 23.9 ($\mathit{C}H_2CH_2O$).

243-Allyl dendrimer 13 (Scheme 1). 13 is synthesized from **12** (0.082 g, 0.005 mmol) and triallylmethyl phenol (0.327 g, 1.43 mmol) using the same procedure as that described above for the synthesis of the 27-allyl dendrimer **7**. **13** is separated by chromatography on a neutral alumina columns using a pentane–ether mixture (70 : 30) as the eluent, which gives **13** as a light brown oil (18 mg, 0.000 66 mmol, 11% yield). ^{1}H

NMR ($CDCl_3$) δ 7.22 and 6.79 (m, C_6H_4, 144H); 5.7–5.51 (m, CH_2CH_2, 81H); 5.04–4.99 (m, $CHCH_2$, 162H); 3.91 (m, CH_2O, 72H); 2.39 (d, CH_2CHCH_2, 162H); 1.95 (m, CCH_2CH_2, 72H); 1.65 (m, CH_2CH_2O, 72H). ^{13}C NMR ($CDCl_3$) δ 156.71 ($OC_{6\,quat}H_4$); 137.56 ($C_{6\,quat}H_4$); 134.61 (CH_2CH); 127.47 (C_6H_4); 117.30 ($CHCH_2$); 113.70 (C_6H_4); 68.09 (CH_2O); 43.15 ($C_{quat}CH_2$); 42.50 ($C_{quat}CH_2$); 42 (CH_2CHCH_2); 33.77 (CH_2CH_2O); 23.69 (CCH_2CH_2).

***p*-[1,1-Di(2-propenyl)-3-butenyl]methoxybenzene (or *p*-triallylmethyl-methoxybenzene), 14 (Scheme 2).** Triallylmethylphenol **3** (1.9 g, 8.32 mmol), methyl iodide (4 mL, 30 mmol), KOH (3.6 g, 64 mmol) and 7 mL DMSO are introduced under nitrogen into a Schlenk tube. The reaction mixture is stirred for 2 h at room temperature in the dark, then the excess of methyl iodide is removed under vacuum, the residue is extracted with 3 × 20 mL ether, this solution is washed with $Na_2S_2O_3$ and dried over sodium sulfate. This gives **14** as a light brown oil (1.80 g, 7.44 mmol, 90% yield). ^1H NMR ($CDCl_3$) δ 7.20 and 6.85 (m, CH_{arom}, 4H); 5.68–5.55 (m, $CHCH_2$, 9H); 5.07–5 (m, $CHCH_2$, 18H); 3.78 (s, CH_3O, 3H); 2.44 (d, CH_2, 18H). ^{13}C NMR ($CDCl_3$) δ 156.10 ($C_{quat\,arom}O$); 137.29 ($C_{quat\,arom}C$); 134.22 ($CHCH_2$); 127.23 ($CH_{arom}CO$); 117.08 ($CHCH_2$); 112.21 ($CH_{arom}C$); 54.78 (CH_3); 42.25 ($C_{quat}CH_2$); 41.54 (CH_2). Anal. calcd for $C_{17}H_{22}O$: C 84.25; H 9.15. Found C 83.84; H 9.05.

***p*-[1,1-Di(3-hydroxypropyl)-4-hydroxybutyl]methoxybenzene, 15 (Scheme 2).** The hydroboration-oxidation of **14** (1.8 g, 7.43 mmol) is carried out as described above for the synthesis of the 27-alcohol dendrimer **8** from the olefinic precursor. This gives **15** as a colorless oil (1.9 g, 6.4 mmol, 86% yield). ^1H NMR ($CDCl_3$) δ 7.22 and 6.9 (m, C_6H_4, 4H); 3.74 (s, CH_3O, 3H); 3.47 (m, CH_2OH, 6H); 1.70 (m, CH_2CH_2OH, 6H); 1.3 (m, CH_2C_{quat}, 6H). ^{13}C NMR ($CDCl_3$) δ 156.76 ($C_{quat\,arom}OH$); 137.32 ($C_{quat\,arom}C$); 127.75 (CH_{arom}); 114.80 (CH_{arom}); 63.24 (CH_3); 53.41 (CH_2O); 42.37 ($C_{quat}H_2$); 34.58 ($C_{quat}CH_2$); 27.89 (CH_2CH_2O). Anal. calcd for $C_{17}H_{28}O_4$: C 68.89; H 9.52. Found C 68.9; H 8.67.

***p*-[1,1-Di(3-iodopropyl)-4-iodobutyl]phenol, 16 (Scheme 2).** The triol dendron **15** (1.5 g, 5.06 mmol), 5 mL of anhydrous MeCN, then dry NaI (6 g, 40 mmol) and freshly distilled $SiMe_3Cl$ (5 mL, 39 mmol) are successively introduced into a Schlenk tube under nitrogen. The closed reaction medium is left for 2 days at 80 °C in the dark, then the solvent is removed under vacuum and the residue is extracted with 2 × 100 mL ether, the ether solution is washed with an aqueous solution saturated with $Na_2S_2O_3$, dried over sodium sulfate and filtered. The solvent is removed under vacuum, which gives **16** as a pale yellow oil (3 g, 4.90 mmol, 97%). ^1H NMR ($CDCl_3$) δ 7.10 and 6.81 (m, C_6H_4, 4H); 3.06 (t, CH_2I, 6H); 1.64 (m, CH_2CH_2I, 6H); 1.54 (m, CH_2C_{quat}, 6H). ^{13}C NMR ($CDCl_3$) δ 153.76 ($C_{quat\,arom}OH$); 137.59 ($C_{quat\,arom}C$); 127.40 (CH_{arom}); 115.40 (CH_{arom}); 41.8 ($C_{quat}CH_2$); 38.58 (CH_2CH_2I); 27.69 (CH_2C_{quat}); 8.45 (CH_2I). Anal. calcd for $C_{16}H_{23}I_3O$: C 31.55; H 3.31. Found C 30.85; H 3.03.

***sp*-[1,1-Di(3-iodopropyl)-4-iodobutyl]phenolpropionate, 17 (Scheme 2).** A solution of C_2H_5COI is prepared by slowly adding 2.4 mL C_2H_5COCl to 5 g of Me_3SiI, stirring 15 min., then adding 22.6 mL dichloromethane. This solution is added into a Schlenk flask containing **16** (2.7 g, 4.52 mmol) in 30 mL dichloromethane, then NEt_2Pr^i (0.84 mL, 4.83 mmol) is also added. The reaction mixture is stirred under nitrogen for 16 h, then extracted using 50 mL dichloromethane. The organic solution is washed with a saturated aqueous solution of sodium bicarbonate, then with an aqueous solution saturated with $Na_2S_2O_3$ and dried over sodium sulfate. After removing the solvent under vacuum, the product **17** is obtained as an orange oil (2.85 g, 4.27 mmol, 94%). ^1H NMR ($CDCl_3$) δ 7.21 and 7.01 (m, C_6H_4, 4H); 3.06 (t, CH_2I, 6H); 2.42 (q, CH_3CH_2CO, 2H); 1.71 (m, CH_2CH_2I, 6H); 1.58 (m, CH_2C_{quat}, 6H); 1.11 (t, CH_3CH_2CO, 3H). ^{13}C NMR ($CDCl_3$) δ 172.83 (CO); 148.93 ($C_{quat\,arom}CO$); 143.13 ($C_{quat\,arom}C$); 127.15 (CH_{arom}); 121.33 (CH_{arom}); 42.17 ($C_{quat}CH_2$); 38.58 (CH_2CH_2I); 27.85 (CH_3CH_2CO); 27.5 (CH_2C_{quat}); 9.2 (CH_3CH_2CO); 7.84 (CH_2I).

9-Allylphenol dendron 18 [eqn. (12)]. Triallylmethylphenol **3** (4.09 g, 25 mmol) dissolved in 25 mL of freshly distilled DMF, then potassium carbonate (3.5 g, 25 mmol) are introduced into a flamed Schlenk tube, and the mixture is stirred 30 min. under nitrogen at room temperature. The protected tri-iodo dendron **17** (2.85 g, 4.26 mmol), dissolved in 10 mL of anhydrous DMF, is slowly added, and the reaction mixture is stirred for 2 days at room temperature, then 3 g potassium carbonate and 5 mL water are added, and the reaction mixture is stirred for 12 h at 40 °C. The product is extracted with 100 mL ether, this solution is dried over sodium sulfate, then filtered and concentrated to 5 mL. The product is purified by chromatography on a silica-gel column using pentane–ether (4 : 1) as the eluent. The 9-allyl phenate dendron **18** is obtained in this way as a light brown oil (1.2 g, 1.31 mmol, 30% yield). ^1H NMR ($CDCl_3$) δ 7.18 and 6.83 (m, CH_{arom}, 16H); 5.68–5.55 (m, $CHCH_2$, 9H); 5.07–5 (m, $CHCH_2$, 18H); 3.9 (m, CH_2O, 6H); 2.44 (d, CH_2, 18H); 1.9 (m, $C_{quat}CH_2$, 6H); 1.65 (m, CH_2CH_2, 6H). ^{13}C NMR ($CDCl_3$) δ 156.87 ($C_{quat\,arom}O$); 153.55 ($C_{quat\,arom}OH$); 138.52 ($C_{quat\,arom}C$); 137.77 ($C_{quat\,arom}C$); 134.76 ($CHCH_2$); 127.91 ($CH_{arom}COH$); 127.73 ($CH_{arom}COH$); 117.63 ($CHCH_2$); 115.19 ($CH_{arom}C$); 114.35 ($CH_{arom}C$); 68.40 (CH_2O); 42.77 ($C_{quat}CH_2$); 42.15 (CH_2CH), 33.87 (CH_2CH_2O); 23.81 (CCH_2CH_2). MALDI-TOF MS: $[M + Na]^+$ 935.60 (calcd 936.33).

19-Allylphenol dendron 19 (Scheme 3). The dendron **19** is prepared from the nona-allyl phenol dendron **18** (0.750 g, 0.8 mmol), the protected tri-iodo dendron **17** (0.100 g, 0.15 mmol), potassium carbonate (0.120 g, 0.8 mmol) and 6 mL DMF using the procedure described above for the synthesis of the nona-allylphen dendron **18**. The reaction product **19** is purified by chromatography on a silica gel column using a pentane–ether mixture (4 : 1) as the eluent, which gives **19** as a light brown oil (0.110 g, 0.037 mmol, 25%). ^1H NMR ($CDCl_3$) δ 7.25 and 6.84 (m, CH_{arom}, 36H); 5.57 (m, $CHCH_2$, 19H); 5.06–4.99 (m, $CHCH_2$, 38H); 3.92 (m, CH_2O, 16H); 2.46 (d, CH_2, 38H); 1.87 (m, $C_{quat}CH_2$, 16H); 1.65 (m, CH_2CH_2, 16H). ^{13}C NMR ($CDCl_3$) δ 156.88 ($C_{quat\,arom}O$); 153.48 ($C_{quat\,arom}OH$); 138.61 ($C_{quat\,arom}C$); 137.77 ($C_{quat\,arom}C$); 134.71 ($CHCH_2$); 127.63 ($CH_{arom}COH$); 117.50 ($CHCH_2$); 115.04 ($CH_{arom}C$); 113.91 ($CH_{arom}C$); 68.24 (CH_2O); 42.7 ($C_{quat}CH_2$); 42.15 (CH_2CH), 33.83 (CH_2CH_2O); 23.78 (CCH_2CH_2). MALDI-TOF MS $[M + Na]^+$ 2077.70 (calcd 2078.02).

27-Allyl dendrimer 20 (Scheme 4). The synthesis of **20** from the nona-allylphenol dendron **18** (0.200 g, 0.218 mmol), 2,4,6-tris(bromomethyl)mesitylene (0.018 g, 0.004 56 mmol), potassium carbonate (0.045 g, 0.325 mmol) in 10 mL acetone is achieved according to the procedure described above for the synthesis of the 27-allyl dendrimer **7** from the nona-iodo core **6a**. The reaction product is purified by chromatography on a silica gel column using dichloromethane as the eluent, which gives **20** as a light brown oil (40 mg, 0.0138 mmol, 30% yield). ^1H NMR ($CDCl_3$) δ 7.24 and 6.82 (m, C_6H_4, 36H); 5.4 (m, $CHCH_2$, 27H); 4.98 (m, $CHCH_2$, 54H); 3.8 (m, CH_2O, 18H); 2.41 (s, CH_3, 9H); 2.38 (d, CH_2CHCH_2, 54H); 1.87 (m, CCH_2CH_2, 18H); 1.58 (m, CH_2CH_2O, 18H). ^{13}C NMR ($CDCl_3$) δ 156.87 ($OC_{6\,quat}H_4$); 137.56 ($C_{6\,quat}H_4$); 134.7 (CH_2CH); 127.63 (C_6H_4); 117.5 ($CHCH_2$); 113.85 (C_6H_4); 68.23 (CH_2O); 42.69 ($C_{quat}CH_2$); 41.97 (CH_2CHCH_2); 33.82

(CH_2CH_2O); 29.73 (CH_3); 23.77 (CCH_2CH_2). MALDI-TOF MS $[M + Na]^+$ 2919.05; $[M + K]^+$ 2935.96 (calcd $[M + Na]^+$ 2919.9; $[M + K]^+$ 2935.89).

54-Allyl dendrimer 21 (Scheme 4). An ethanol solution (10 mL) of the nona-allyl dendron **18** (0.380 g, 0.416 mmol) and K_2CO_3 (0.060 g, 0.428 mmol) was stirred at room temperature for 1 h in a flamed and deaerated Schlenk tube. Then, hexakishexabromomethylbenzene (0.040 g, 0.063 mmol) was added to the mixture, and the latter was heated at reflux for 2 days. After evaporation of the solvent under vacuum, the residue was dissolved in a Et_2O–H_2O mixture (50 mL : 50 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under vacuum. The crude product was purified by chromatography and obtained as a white solid in 83% yield (0.295 g, 0.052 mmol). ^1H NMR ($CDCl_3$) δ 7.18 (m, CH_{arom}, 48H); 6.80 (m, CH_{arom}, 48H); 5.52 (m, $CHCH_2$, 54H); 5.24 (s, $PhCH_2O$, 108H); 4.99 (m, $CHCH_2$, 108H); 3.80 (m, CH_2O, 36H); 2.41 (d, CH_2CHCH_2, 108H); 1.77 (m, CCH_2CH_2, 36H), 1.56 (m, CH_2CH_2O, 36H). ^{13}C NMR ($CDCl_3$): δ 156.87 ($OC_{6\,quat}H_4$); 156. ($OC_{6\,quat}H_4$); 139.22 ($C_{6\,quat}H_4$); 137.98 ($C_{6\,quat}H_4$); 137.55 ($C_{6\,quat}H_4$); 134.66 (CH_2CH); 127.58 (C_6H_4); 117.49 ($CHCH_2$); 114.49 (C_6H_4); 113.64 (C_6H_4); 68.15 (CH_2O); 63.68 (CH_2O); 42.65 ($C_{quat}CH_2$); 42.06 ($C_{quat}CH_2$), 41.95 (CH_2CHCH_2); 33.84 (CH_2CH_2O); 23.77 (CCH_2CH_2). MALDI-TOF MS: $[M + Na]^+$ 5654.1 (calcd 5653.3). Anal. calcd for $C_{396}H_{486}O_{24}$: C 84.47; H 8.71. Found C 83.47; H 8.66.

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