

Convergent Synthesis of Fluorinated Dendrons Using the Mesylate Activation Route

Özgür Altan BOZDEMİR¹, Meltem DİLEK², Mehmet TUTAŞ^{1*}

¹*Department of Chemistry, Akdeniz University, Antalya-TURKEY*

²*Department of Chemistry, Afyon Kocatepe University, Afyon-TURKEY*
e-mail: tutas@akdeniz.edu.tr

Received 08.02.2007

In this paper we describe an alternative route for the preparation of dendrons bearing fluoro aryl functionalities at the periphery using mesylate activation. p-Fluorobenzyl bromide and perfluorobenzyl bromide were used to introduce the p-fluoro and perfluorobenzyl moieties at the periphery of dendrons. 3,5-Dihydroxybenzyl alcohol was used as the repeating unit of the dendrons. In this convergent approach, the Williamson ether synthesis technique was used as the generation enhancement step. Second generation mono- and perfluorobenzyl alcohol dendrons were obtained from active mesylate precursors. This mesylate activation method has the advantage of short reaction times in the subsequent steps and avoids chromatographic purification. Simple purification of these mesylate derivatives by crystallization is possible. Second generation dendrons were then built by repetition of the Williamson ether synthesis reaction of the mesylate derivatives, as described above. In this study it was shown that the mesylate activation route allows the preparation of second generation fluorinated dendrons with comparable yields to the bromide route, with reduced reaction times.

Introduction

Because of their unique structures and properties, interest in dendrimers has been increasing at an amazing rate.^{1–7} As other types of dendrimers, fluorinated dendrimers and dendrons are designed for several purposes. Fluorinated dendrimers and polymers are extensively used in the construction of low surface energy materials.^{8,9} Increased thermal stability, lipophobicity and hydrophobicity, and chemical resistance are the properties that permit the use of fluorinated dendrimers in major application areas, such as catalysis and material science.^{10–12} Several other applications have also been emerging in the literature.⁷ Fluorinated dendrimers can be used as nanoreactors,^{13,14} surfactants, and phase transfer catalysts in biphasic systems (water/supercritical fluids).^{12,15} Perfluorinated dendrimers are also used as electron transport materials for organic light emitting diodes in the field of material science.¹⁶ These results are triggering studies on this relatively slow developing branch of the dendrimer family. In addition, perfluorophenyl terminated polymers have properties that resemble the physical properties of both fluorinated polymers and fluorinated

*Corresponding author

dendrimers. These hyperbranched polymers have the advantages of these 2 classes (e.g., high solubility, low viscosity, hydrophobicity, lipophobicity, chemical resistance, and low cohesive forces). Therefore, fluorinated poly(aryl ether) dendrons are important building blocks for the construction of fluorinated dendrimers and hyperbranched polymers.

In the synthesis of fluorinated dendrons and dendrimers, the convergent approach developed by Frechet¹⁷ is used as the major route, and as a result of the simplicity and reliability of the method it was applied to construct monodisperse macromolecules by several other groups for a variety of applications.^{18–25} This procedure is based on the use of commercially available 3,5-dihydroxybenzyl alcohol as an AB₂ monomer. Yet, several drawbacks of the method are also known and different approaches have been developed to circumvent them.^{18,26}

The aim of this study was to apply the mesylate activation route to develop an easy procedure to prepare fluorinated poly(aryl ether) dendrons that have different generations.

Experimental

All the reagents were purchased from Merck, Fluka, or Sigma chemical companies, and were used as received. Acetone was dried with anhydrous K₂CO₃ and distilled. Column chromatography was carried out with Merck silica gel-60 (70-230 mesh). Preparative TLC plates were Merck aluminum sheets covered with silica gel 60 F₂₅₄. Elemental analyses were performed at Süleyman Demirel University, Isparta, Turkey. IR spectra were recorded on a Mattson/Unicam model 1000 FTIR as KBr pellets. ¹H- and ¹³C-NMR spectra were recorded on a Gemini Varian 200 50-MHz spectrometer or on a Bruker 500 125-MHz spectrometer. Atom Bombardment ZabSpec (FAB) mass spectrometry was used to determine the mass of the compounds. Melting points were measured on a Gallenkamp melting point apparatus.

3,5-Bis[(4-fluorobenzyl)oxy]benzyl alcohol (3)

A mixture of p-fluorobenzyl bromide (**1**) (1.375 g, 7.3 mmol), 3,5-dihydroxybenzyl alcohol (**2**) (0.5 g, 3.6 mmol), K₂CO₃ (1.232 g, 8.9 mmol), and 18-crown-6 (0.189 g, 0.71 mmol) in dry acetone (50 mL) was refluxed for 2 days under a nitrogen atmosphere. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined extracts were dried (MgSO₄) and evaporated, and the residue was chromatographed on silica gel with diethyl ether/hexane (7:3) as the eluent to give the product (0.9 g, 70% yield). mp 79-80 °C; found: C, 70.70; H, 5.06. Anal. calcd. for C₂₁H₁₈O₃F₂: C, 71.8; H, 5.05. IR: $\nu = 3334, 2975, 2924, 2847, 1618, 1516, 1468, 1388, 1311, 1260, 1183, 1081, 1030, 850 \text{ cm}^{-1}$. ¹H-NMR (200 MHz-CDCl₃): $\delta = 1.83$ (OH), 4.64 (s, 2 H ArCH₂OH), 4.99 (s, 4 H 4-F-ArCH₂O), 6.51 (t, 1 H, $J = 2.3$ Hz), 6.62 (d, 2 H $J = 2.2$ Hz), 7.03-7.43 (m, 8 H 4-F-Ar). ¹³C-NMR (50 MHz-CDCl₃): $\delta = 67.2$ (ArCH₂OH), 71.6 (4-F-ArCH₂O), 145.5, 108.1, 162.1, 103.7 (ArC₁, C₂, C₃, C₄), 134.7, 131.0, 117.4 (d, ³J_{C-F} = 22 Hz), 164.6 (¹J_{C-F} = 245 Hz) (4-F-Ar C₁, C₂, C₃, C₄). Mass = 356 m/z.

3,5-Bis[(4-fluorobenzyl)oxy]benzyl methanesulfonate (4)

To a mixture of 3,5-bis[(4-fluorobenzyl)oxy]benzyl alcohol (**3**) (1 g, 2.81 mmol) and NEt₃ (1.42 g, 14.05 mmol) in dry dichloromethane (25 mL) was added methanesulfonyl chloride (1.29 g, 14.05 mmol) over 15

min at $-10\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. After stirring for 1 h at $-10\text{ }^{\circ}\text{C}$, the reaction mixture was poured into a mixture of crushed ice (50 mL) and concentrated HCl (5 mL). The dichloromethane layer was separated and washed with saturated NaHCO_3 and dried (MgSO_4). After evaporation of the solvent, the crude product was crystallized from diethyl ether to yield the mesylate derivative (1.04 g, 85% yield). mp $70\text{--}71\text{ }^{\circ}\text{C}$; found: C, 60.80; H, 4.60; S, 7.37. Anal. calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_5\text{SF}_2$: C, 60.83; H, 4.61; S, 7.37. IR: $\nu = 2920, 2862, 1607, 1515, 1378, 1352, 1355, 1168\text{ cm}^{-1}$. $^1\text{H-NMR}$ (200 MHz- CDCl_3): $\delta = 2.91$ (s, 3H, CH_3), 5.00 (s, 2H $\text{ArCH}_2\text{OSO}_2\text{CH}_3$), 5.16 (s, 4H ArCH_2O), 6.60 (t, 1H $J = 2.1$ Hz), 6.64 (d, 2 H $J = 2.2$ Hz), 7.04-7.44 (m, 8 H 4-F-Ar). $^{13}\text{C-NMR}$ (50 MHz- CDCl_3): $\delta = 38.4$ (CH_3), 69.6 ($\text{ArCH}_2\text{OSO}_2\text{CH}_3$), 71.2 (4-F- ArCH_2O), 135.7, 107.7, 160.1, 102.4 ($\text{ArC}_1, \text{C}_2, \text{C}_3, \text{C}_4$), 132.2, 128.3, 115.6 (d, $^3J_{\text{C-F}} = 22$ Hz), 163.7 ($^1J_{\text{C-F}} = 258$ Hz) (4-F- $\text{ArC}_1, \text{C}_2, \text{C}_3, \text{C}_4$). Mass: 434 m/z.

3,5-Bis[(3,5-Bis[(4-fluorobenzyl)oxy]benzyl)oxy]benzyl alcohol (5)

A mixture of 3,5-bis[(4-fluorobenzyl)oxy]benzyl methanesulfonate (**4**) (0.134 g, 0.33 mmol), 3,5-dihydroxybenzyl alcohol (**2**) (0.023 g, 0.16 mmol), K_2CO_3 (0.0339 g, 0.33 mmol), and 18-crown-6 (0.0087 g, 0.033 mmol) in dry acetone (50 mL) was refluxed overnight under a nitrogen atmosphere. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (3×50 mL). The combined extracts were dried (MgSO_4), the solvent was evaporated, and the residue was chromatographed on silica gel with dichloromethane/diethyl ether (20:1) as the eluent to give the desired product (0.098 g, 75% yield). mp $96\text{--}97\text{ }^{\circ}\text{C}$; found: C, 72.05; H, 4.90; Anal. calcd. for $\text{C}_{49}\text{H}_{40}\text{O}_7\text{F}_4$: C, 72.05; H, 4.93. IR: $\nu = 3417, 3072, 2923, 2873, 1600, 1511, 1452, 1375, 1322, 1224, 1153, 1054, 1016, 827\text{ cm}^{-1}$. $^1\text{H-NMR}$ (200 MHz- CDCl_3): $\delta = 4.47$ (s, 2 H ArCH_2OH), 4.82 (s, 4 H ArCH_2O), 4.84 (s, 8 H 4-F- ArCH_2O), 6.35 (t, 1 H $J = 2.1$ Hz), 6.38 (t, 2 H $J = 2.2$ Hz), 6.45 (d, 2 H $J = 2.1$ Hz), 6.50 (d, 4 H $J = 2.1$ Hz), 6.9-7.2 (m, 16 H 4-F-Ar). $^{13}\text{C-NMR}$ (50 MHz- CDCl_3): $\delta = 65.2$ (ArCH_2OH), 69.4 (4-F- ArCH_2O), 69.8 (ArCH_2O), 143.5, 105.7, 160.0, 101.3 ($\text{Ar}(\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4)\text{CH}_2\text{OH}$), 139.4, 106.3, 160.0, 101.5 ($\text{Ar}(\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4)\text{CH}_2\text{O}$), 132.4, 129.3, 115.5 (d, $^3J_{\text{C-F}} = 21.5$ Hz), 162.4 ($^1J_{\text{C-F}} = 249$ Hz) (4-F-Ar $\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4$). Mass: 816 m/z.

3,5-Bis[(perfluorobenzyl)oxy]benzyl alcohol (7)

A mixture of perfluorobenzyl bromide (**6**) (1.96 g, 7.5 mmol) and 3,5-dihydroxybenzyl alcohol (**2**) (0.5 g, 3.6 mmol) was allowed to react with K_2CO_3 (1.084 g, 7.9 mmol) and 18-crown-6 (0.095 g, 0.35 mmol) in dry acetone (80 mL) under a nitrogen atmosphere. After 3 days, the solvent was evaporated and water (100 mL) was added to the residue. After extraction with dichloromethane (3×100 mL) the combined extracts were dried (MgSO_4) and evaporated, and the residue was chromatographed on silica gel with dichloromethane/hexane (1:1) as the eluent to give the product (1.35 g, 75% yield). mp $98\text{--}99\text{ }^{\circ}\text{C}$; found: C, 50.4; H, 2.08. Anal. calcd. for $\text{C}_{21}\text{H}_{10}\text{O}_3\text{F}_{10}$: C, 50.37; H, 2.01. IR: $\nu = 3416, 2976, 2920, 1658, 1604, 1504, 1446, 1395, 1316, 1290, 1164, 1056, 971, 945, 841, 712\text{ cm}^{-1}$. $^1\text{H-NMR}$ (200 MHz- CDCl_3): $\delta = 4.53$ (s, 2 H ArCH_2OH), 4.93 (s, 4 H $\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 6.34 (t, 1 H $J = 2$ Hz), 6.58 (d, 2 H $J = 2$ Hz). $^{13}\text{C-NMR}$ (50 MHz- CDCl_3): $\delta = 57.6$ ($\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 65.0 (ArCH_2O), 144.0, 106.3, 159.8, 101.4 ($\text{ArC}_1, \text{C}_2, \text{C}_3, \text{C}_4$), 107.5, 137.5 (d of m $^1J_{\text{C-F}} = 250$ Hz), 141.5 (d of m $^1J_{\text{C-F}} = 250$ Hz), 145.5 (d of m $^1J_{\text{C-F}} = 250$ Hz) ($\text{C}_6\text{F}_5\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4$). Mass: 500 m/z.

3,5-Bis[(perfluorobenzyl)oxy]benzyl methanesulfonate (8)

To a mixture of 3,5-bis[(perfluorobenzyl)oxy]benzyl alcohol (**7**) (0.3 g; 0.6 mmol) and NEt_3 (0.3 g, 3 mmol) in dry dichloromethane (25 mL) was added methanesulfonyl chloride (0.275 g; 2.4 mmol) over 15 min at $-10\text{ }^\circ\text{C}$ under a nitrogen atmosphere. After stirring for 1 h at $-10\text{ }^\circ\text{C}$, the reaction mixture was poured into a mixture of crushed ice (50 mL) and concentrated HCl (5 mL). The dichloromethane layer was separated, washed with saturated NaHCO_3 , and dried (MgSO_4). After evaporation of the solvent, the crude product was crystallized from diethyl ether to give the product (**8**) (0.28 g, 82% yield). mp $80\text{--}81\text{ }^\circ\text{C}$; IR: $\nu = 2920, 2869, 1604, 1515, 1375, 1354, 1171\text{ cm}^{-1}$. $^1\text{H-NMR}$ (500 MHz- CDCl_3): $\delta = 2.91$ (s, 3H, CH_3), 5.01 (s, 2H $\text{ArCH}_2\text{OSO}_2\text{CH}_3$), 5.16 (s, 4H $\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 6.51 (t, 1H $J = 2.2$ Hz), 6.61 (d, 2 H $J = 2.2$ Hz). $^{13}\text{C-NMR}$ (125 MHz- CDCl_3): $\delta = 39.3$ (CH_3), 57.8 ($\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 70.6 ($\text{ArCH}_2\text{OSO}_2$), 136.1, 108.0, 159.6, 102.8 ($\text{ArC}_1, \text{C}_2, \text{C}_3, \text{C}_4$), 109.6, 137.6 (d of m $^1J_{\text{C-F}} = 252$ Hz), 141.9 (d of m $^1J_{\text{C-F}} = 254$ Hz), 145.7 (d of m $^1J_{\text{C-F}} = 246$ Hz) ($\text{C}_6\text{F}_5\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4$).

3,5-Bis[(3,5-Bis[(perfluorobenzyl)oxy]benzyl)oxy]benzyl alcohol (9)

A mixture of 3,5-bis[(perfluorobenzyl)oxy]benzyl methanesulfonate (**8**) (0.15 g, 0.26 mmol), 3,5-dihydroxybenzyl alcohol (**2**) (0.017 g, 0.12 mmol), K_2CO_3 (0.025 g, 0.18 mmol), and 18-crown-6 (0.0087 g, 0.033 mmol) in dry acetone (80 mL) was refluxed overnight under a nitrogen atmosphere. The reaction mixture was poured into water (100 mL) and extracted with dichloromethane (3×50 mL). The combined extracts were dried (MgSO_4), the solvent was evaporated, and the residue was chromatographed on silica gel with dichloromethane/diethyl ether (20:1) as the eluent to give the desired product (**9**) (0.08 g, 60% yield). mp $96\text{--}97\text{ }^\circ\text{C}$. IR: $\nu = 3500, 2967, 2865, 1658, 1598, 1523, 1504, 1457, 1380, 1311, 1290, 1162, 1058, 975, 641, 740\text{ cm}^{-1}$. $^1\text{H-NMR}$ (500 MHz- CDCl_3): $\delta = 4.53$ (s, 2 H ArCH_2OH), 4.86 (s, 4 H ArCH_2O), 5.1 (s, 8 H $\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 6.34-6.51 (m, 9 H Ar). $^{13}\text{C-NMR}$ (125 MHz- CDCl_3): $\delta = 57.7$ ($\text{C}_6\text{F}_5\text{CH}_2\text{O}$), 66.1 (ArCH_2OH), 69.9 (ArCH_2O), 143.4, 106.8, 159.5, 102.2 ($\text{Ar}(\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4)\text{CH}_2\text{OH}$), 139.0, 107.0, 159.9, 102.5 ($\text{Ar}(\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4)\text{CH}_2\text{O}$), 109.6, 137.7 (d of m $^1J_{\text{C-F}} = 250$ Hz), 141.3 (d of m $^1J_{\text{C-F}} = 265$ Hz), 145.9 (d of m $^1J_{\text{C-F}} = 250$ Hz) ($\text{C}_6\text{F}_5\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4$).

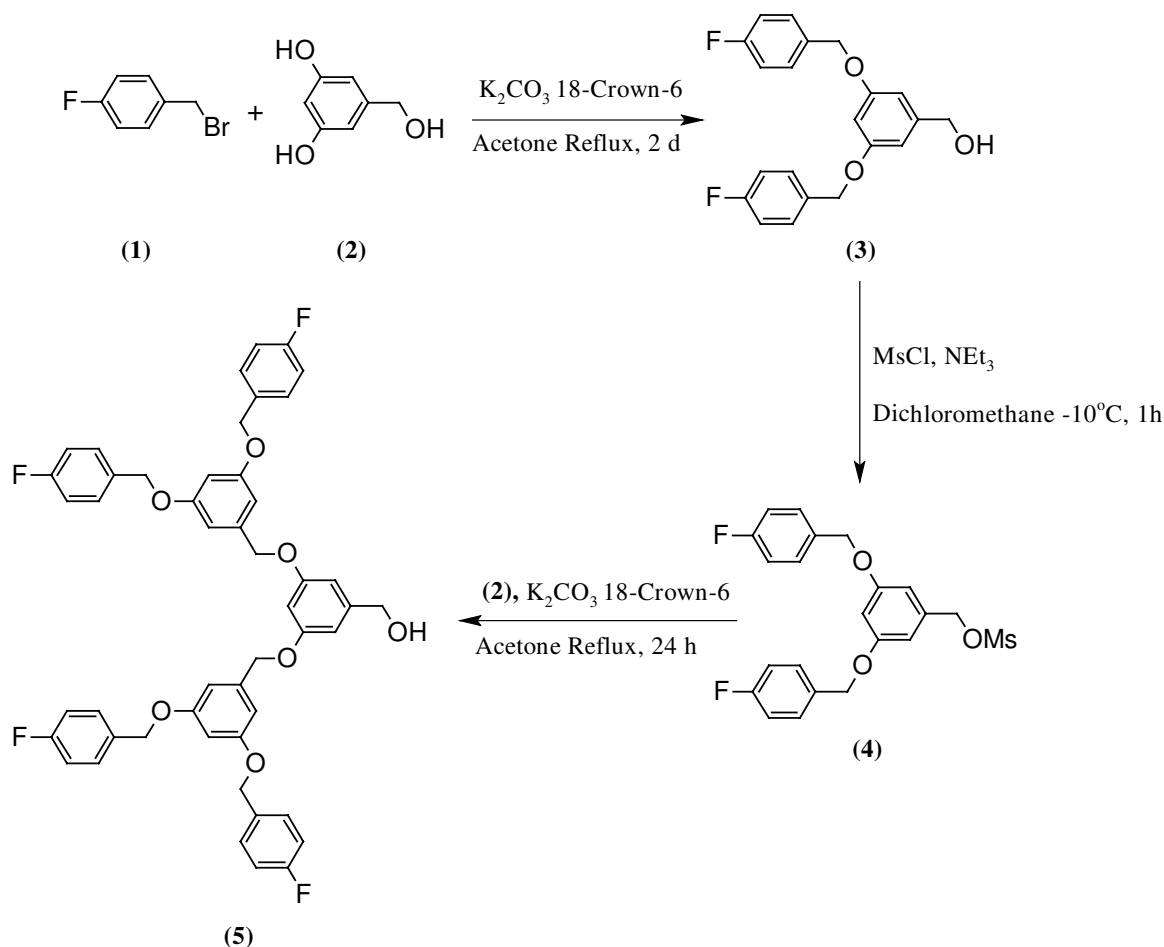
Results and Discussion

The Fréchet type convergent approach in dendrimer synthesis is the most frequently used procedure. In this method the activation of benzylic alcohols to prepare poly(aryl ether) bromides utilizes $\text{PPh}_3/\text{CBr}_4$.¹⁷ Disadvantages of this procedure are the high cost and the column chromatographic separation necessary for the purification of the first and higher generation benzyl bromide dendrons. In addition, reported yields of these compounds are not always easy to produce and great care is necessary, especially with higher generation bromides.¹⁸

In the synthesis of the first and second generation fluorinated dendrons the same drawbacks are encountered. Therefore, we used the mesylate activation route¹⁸ as an alternative to the bromide route.²⁷ Mesylates were prepared from the corresponding benzylic alcohols using methanesulfonyl chloride in the presence of an excess amount of NEt_3 . As usual, the reaction was carried out at $-10\text{ }^\circ\text{C}$ to prevent chloride by-product-forming side reactions. The apparent advantages of the mesylate route over the bromide route

in the synthesis of mono- and perfluorinated dendrons are reduced reaction times and simple purification of first and second generation mesylate dendrons by crystallization; therefore, chromatographic separations can be avoided.

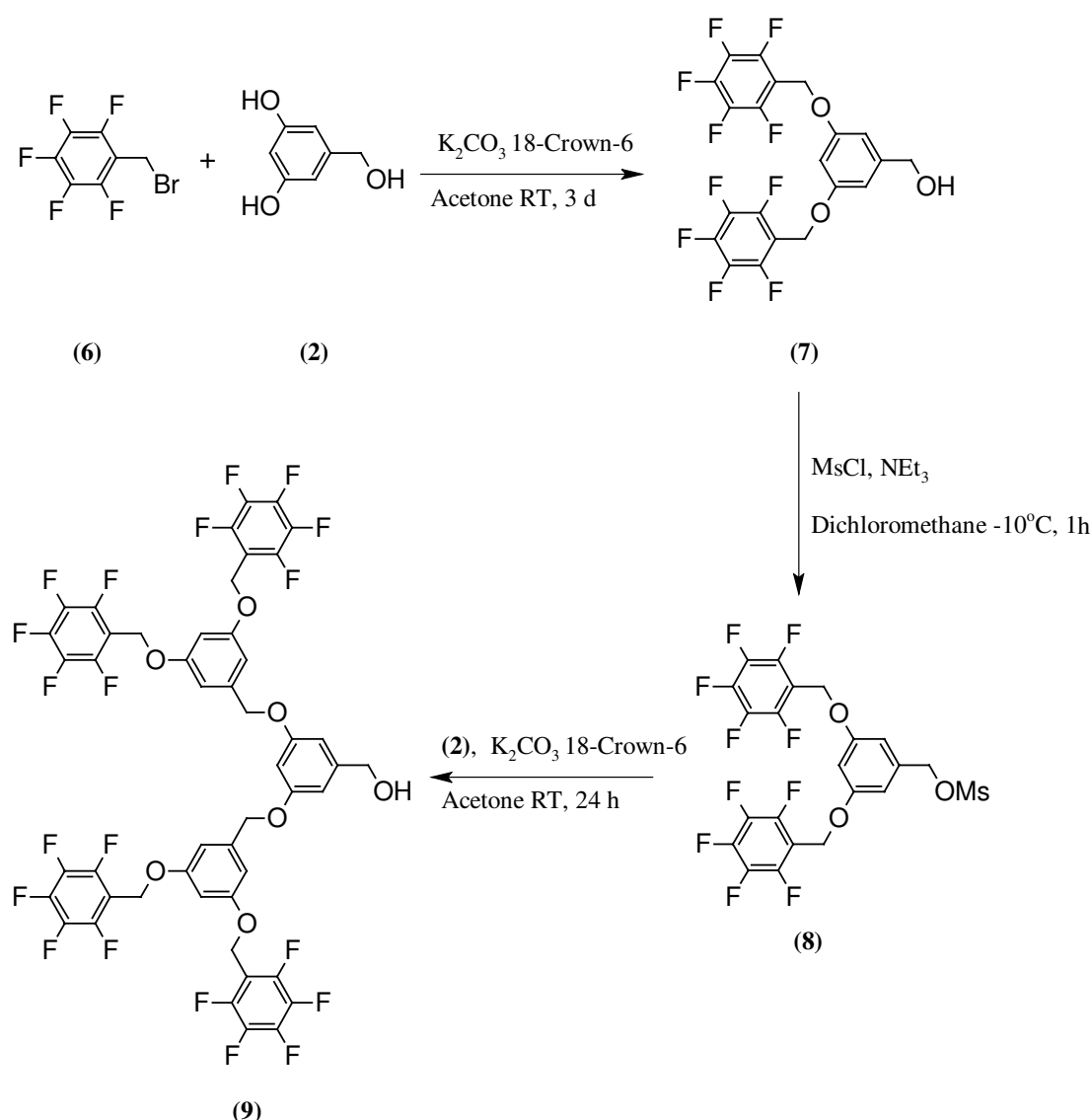
The synthesis of the first generation monofluorobenzyl alcohol dendron (**3**) starts from the reaction of 2 equivalents of 4-fluorobenzyl bromide (**1**) with one equivalent of 3,5-dihydroxybenzyl alcohol (**2**) in the presence of K_2CO_3 and 18-crown-6 in acetone at reflux temperature for 2 days in 70% yield after purification by silica gel column chromatography. This benzylic alcohol (**3**) was then activated for further generation enhancement with methanesulfonyl chloride in the presence of an excess of NEt_3 in dichloromethane at $-10\text{ }^\circ\text{C}$ for 1 h. The product, a first generation monofluorinated mesylate dendron (**4**), was simply purified by crystallization from diethyl ether in 85% yield. In the synthesis of the second generation monofluorinated dendron (**5**), reaction of 2 equivalents of this very active mesylate (**4**) with one equivalent of 3,5-dihydroxybenzyl alcohol (**2**) in acetone at reflux temperature was carried out and resulted in 75% yield after column chromatographic purification on silica gel. This mesylate activation route caused the reduction of reaction time from 2 days to overnight reflux (Scheme 1).



Scheme 1

In contrast to the corresponding monofluoro counterparts, perfluorinated benzyl bromides are more sensitive to heat and, therefore, synthesis of these derivatives must be carried out at lower temperatures and require relatively long reaction times.^{27,28} In this mesylate activation method the synthesis of the

first generation perfluorinated dendron (**7**) was carried out with the reaction of 2 equivalents of perfluorobenzyl bromide (**6**) with one equivalent of 3,5-dihydroxybenzyl alcohol (**2**) in acetone in the presence of K_2CO_3 and 18-crown-6 at room temperature for 3 days in 75% yield, following purification by silica gel column chromatography. The corresponding mesylate (**8**) was obtained by the reaction of this product with methanesulfonyl chloride in the presence of NEt_3 in dichloromethane at $-10^\circ C$ and was purified by crystallization from diethyl ether in 82% yield. The second generation perfluorinated poly(aryl ether) dendron (**9**) was obtained by the reaction of 2 equivalents of the first generation perfluorinated mesylate with one equivalent of 3,5-dihydroxybenzyl alcohol (**2**) at reflux temperature in acetone in the presence of K_2CO_3 and 18-crown-6. After silica gel column chromatographic purification, the product was obtained in 60% yield (Scheme 2).



Scheme 2

As these results show, the mesylate activation route could be used in the synthesis of second generation mono- and perfluorinated poly(aryl ether) dendrons with comparable yields to the bromide route.

Purification of first generation active mesylate dendrons by simple crystallization is another advantage of this method, rendering large-scale synthesis possible.

Conclusion

The potential use of fluorinated materials in a wide variety of research and application areas increases the importance of fluorinated poly(aryl ether) dendrons as one of the major building blocks for the synthesis of dendrimers and hyperbranched polymers. In our study we applied the mesylate activation route as a reliable method for their synthesis with reduced reaction times without yield loss.

Acknowledgment

The authors thank the Akdeniz University Research Projects Management Unit.

References

1. D.A. Tomalia, A.M Naylor and W.A. Goddard III, **Angew. Chem. Int. Ed. Engl.** **29**, 138 (1990).
2. D.A. Tomalia and H.D. Durst, **Top. Curr. Chem.** **165**, 193 (1993).
3. G.R. Newkome, C.N. Moorefield and F. Vögtle, “**Dendritic Macromolecules: Concepts, Synthesis, Perspectives**”, Weinheim, VCH, Germany, 1996.
4. J.M.J. Frechet, **Science** **263**, 1710 (1994).
5. J.M.J. Frechet and D.A. Tomalia, “**Dendrimers and Other Dendritic Polymers**”, John Wiley and Sons, Chichester, 2001.
6. M. Aydinli, M.Tutaş, B. Atasoy and Ö.A. Bozdemir, **React. Funct. Polym.** **65**, 317 (2005).
7. A.M. Caminade, C.O. Turrin, P. Sutra and J.P. Majoral, **Curr. Opin. Colloid. In.** **8**, 282 (2003).
8. J. Wang, G. Mao, C.K. Ober and E.J. Kramer, **Macromolecules** **30**, 1906 (1997).
9. W. Wang, D.G. Castner and D.W. Grainger, **Supramol. Sci.** **4**, 83 (1997).
10. R.D. Chambers, “**Fluorine in Organic Chemistry**”, John Wiley and Sons, New York, 1973.
11. A.G. Bernake, M. Kramer, B. Olah and R. Haag, **Chem. Eur. J.** **10**, 2822 (2004).
12. A.J. Cooper, J.D. Londons, G. Wignall, J.B. McClain and J.S. Lin, **Nature** **389**, 368 (1997).
13. L.K. Yeung and R.M. Crooks, **Nano Lett.** **1**, 14 (2001).
14. R. Roesler, B.J.N. Har and W.E. Piers, **Organometallics** **21**, 4300 (2002).
15. E.L.V. Goetheer, M.W.P.L. Baars, L.J.P. van den Broeke, E.W. Meijer and J.T.F. Keurentjes, **Ind. Eng. Chem. Res.** **39**, 4363 (2000).
16. C. Pitois, R. Vestberg, M. Rodlert, E. Malmstrom, A. Hult and M. Lindgren, **Opt. Mater.** **21**, 499 (2003).
17. C.J. Hawker and J.M.J. Frechet, **J. Am. Chem. Soc.** **112**, 1638 (1990).
18. B. Forier and W. Dehaen, **Tetrahedron** **55**, 9829 (1999).
19. S.L. Gilat, A. Adronov and J.M.J. Frechet, **J. Org. Chem.** **64**, 7474 (1999).

20. J. Issberner, R. Mors, and F. Vögtle, **Angew. Chem. Int. Ed. Engl.** **33**, 2413 (1994).
21. D. Seebach, J.M. Lapierre, K. Skobridis and G. Greiveldinger, **Angew. Chem. Int. Ed. Engl.** **33**, 440 (1994).
22. A.L. Lehninger, D.L. Nelson and M.M. Cox, "**Principles of Biochemistry**", Worth Publishers, New York, 1993.
23. C. Devadoss, P. Bharathi and J.S. Moore, **J. Am. Chem. Soc.** **118**, 9635 (1996).
24. D.L. Jiang and T. Aida, **Nature** **388**, 454 (1997).
25. I. Gitsov and J.M.J. Frechet, **Macromolecules** **26**, 6536 (1993).
26. K.L. Wooley, C.J. Hawker and J.M.J. Frechet, **J. Am. Chem. Soc.** **113**, 4252 (1991).
27. A. Mueller, T. Kowalewski and K.L. Wooley, **Macromolecules** **31**, 776 (1998).
28. J.K. Gooden, M.L. Gross, A. Mueller, A.D. Stefanescu and K.L. Wooley, **J. Am. Chem. Soc.** **120**, 10180 (1998).