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Zhonghua Xiang<sup>a b c</sup> & Derong Cao<sup>a</sup>

<sup>a</sup> College of Chemistry, South China University of Technology, Guangzhou, China

<sup>b</sup> Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, China

<sup>c</sup> Graduate School of Chinese Academy of Sciences, Beijing, China

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## Synthesis of Dendritic Phenol Ether Derivatives with a Naphthalene Core

Zhonghua Xiang<sup>1,2,3</sup> and Derong Cao<sup>1</sup>

<sup>1</sup>College of Chemistry, South China University of Technology,  
Guangzhou, China

<sup>2</sup>Guangzhou Institute of Chemistry, Chinese Academy of Sciences,  
Guangzhou, China

<sup>3</sup>Graduate School of Chinese Academy of Sciences, Beijing, China

**Abstract:** A series of dendritic phenol ether derivatives with a naphthalene core were synthesized by the Williamson reaction as a coupling reaction between 1-hydroxy-methylnaphthalene and polyether-based dendritic fragments in the presence of phase-transfer catalyst and alkali. The modified method for chlorination of dendritic benzyl alcohol was also developed using PPh<sub>3</sub> and CCl<sub>4</sub> as reagents and CH<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub> as solvent.

**Keywords:** Chlorination, dendrimer, naphthalene, Williamson reaction

### INTRODUCTION

Uniform (monodisperse) dendrimers represent the connecting link between organic compounds with low molecular masses and polymers, and they are distinguished by a number of special properties.<sup>[1]</sup> Recently, in the dendrimer series we studied some antenna systems of anthracenes substituted in the 9,10-position with Fréchet dendrons. Irradiation in the near-UV region (400 nm  $\geq \lambda \geq$  300 nm) of an approximately 10<sup>-3</sup> M solution of the dendrimers with both arms in benzene led to the quantitative [4 $\pi$  + 4 $\pi$ ] cycloaddition reaction between the benzene ring and anthracene ring.<sup>[2]</sup> The unusual photodimerization can be explained by an aggregation of the dendrimers in solution.

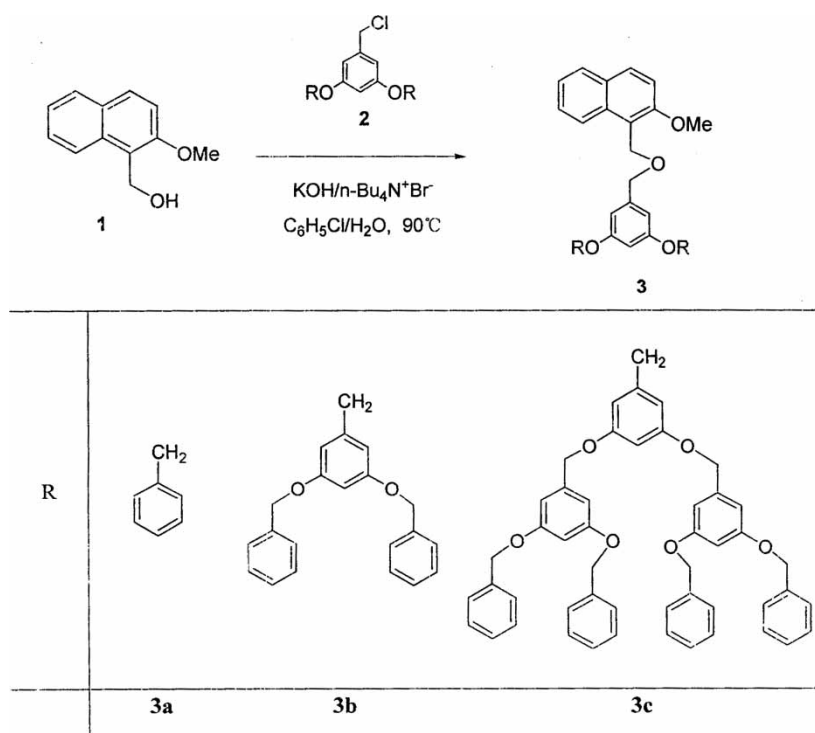
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Address correspondence to Derong Cao, College of Chemistry, South China University of Technology, Guangzhou 510640, China. E-mail: drcao@scut.edu.cn

Naphthalene linked with 3,5-dialkoxy benzene via  $-\text{CH}_2\text{OCH}_2-$  exhibited also an unusual intramolecular photocycloaddition reaction to the polycyclic compound in the diluted solutions under UV irradiation.<sup>[3]</sup> The quantitative process is completely reversible by heating or under UV irradiation. Its applications in materials science seem to be particularly promising in the field of optical switching processes or data storage systems.<sup>[4]</sup> To further study the influencing factors of the reaction, a series of dendrimers containing naphthalene as a core and benzene rings as side chains were synthesized by the reaction of 1-hydroxymethylnaphthalene **1** and the 3,5-dialkoxybenzylchloride **2a–c**. The nucleophilic substitution of the halogen atoms in **2a–c** with 1-hydroxymethylnaphthalene in an alkaline medium under phase-transfer conditions provided yields of the dendrimers **3a–c** between 31% and 67% (Scheme 1).

## RESULTS AND DISCUSSION

Scheme 1 summarizes the preparation of the dendrimers with a naphthalene core, **3a–c**. A mixture of **1** and **2a–c** in chlorobenzene/ $\text{H}_2\text{O}$  under



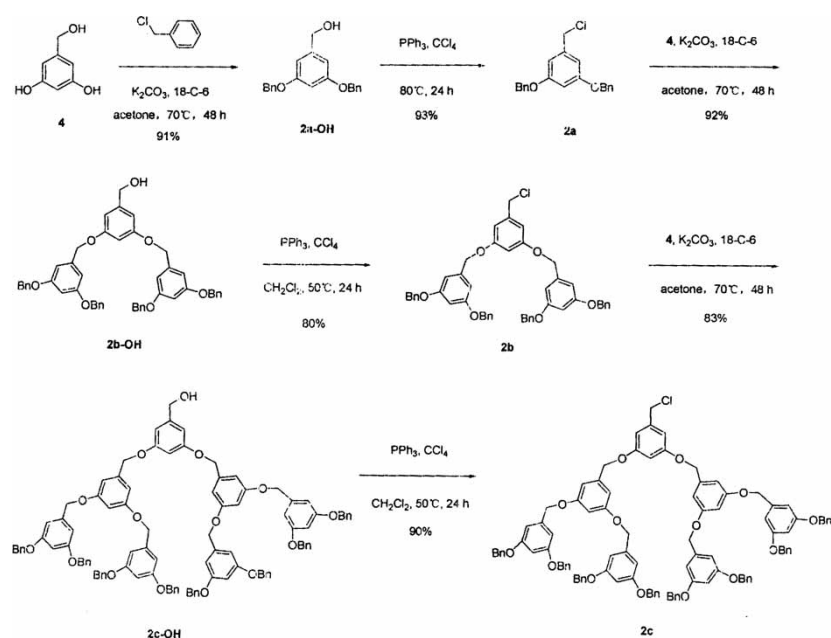
Scheme 1. Preparation of the dendrimers **3a–c**.

**Table 1.** Yield of **3b** at different temperature

Entry	Temperature (°C)	Reaction time (h)	Yield (%)
1	60	48	54
2	80	48	54
3	90	48	57

*n*-Bu<sub>4</sub>NBr as phase-transfer catalyst and KOH as alkaline yielded the dendrimers **3a–c**. An increase in dendron size makes the reaction less effective; for example, the yields of **2a** and **2c** were 67% and 31% respectively. To improve the yield of **3c**, we let the alcohol **1** three times excess than dendritic benzyl chlorides **2**, but it did not increase the yield. We studied the effect of temperature on the yield of **3b** (Table 1). The results showed that the influence of temperature is not remarkable, but the reaction rate is faster at a higher temperature.

Scheme 2 summarizes the preparation of the Fréchet-type dendritic fragments. The convergent synthesis of this dendrimer has been developed by Hawker and Fréchet and was successfully used by other groups to construct monodisperse macromolecules.<sup>[5]</sup> However, the drawbacks of the method are that (1) the growth of the dendritic wedges is time-consuming and (2) the reported yields of **2-Br** are not always easy to reproduce and

**Scheme 2.** Preparation of the dendritic fragments.

**Table 2.** Yield of **2b** in different solvents

Entry	Temperature (°C)	Reagents	Solvent	Yield (%)
1	rt	PPh <sub>3</sub> and CBr <sub>4</sub>	THF	62
2	80	PPh <sub>3</sub> and CCl <sub>4</sub>	CCl <sub>4</sub>	71
3	50	PPh <sub>3</sub> and CCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> /CCl <sub>4</sub>	80

great care is necessary, especially with the higher generation bromides. Several methods have been reported to avoid the difficult step of bromination.<sup>[6–8]</sup> In our hands, we synthesized 3,5-bis(benzyloxy)benzyl chloride **2a** using CCl<sub>4</sub> and PPh<sub>3</sub> in high yield (93%). Here CCl<sub>4</sub> is both reagent and solvent. Stimulated by the success of preparation of **2a**, we prepared **2b** in the same way. However, the yield of **2b** was not as high as **2a**. And we found that the mixture was heterogeneous in the end of the reaction. Also we synthesized **2b-Br** by following Fréchet's method, and the reported yield was hard to achieve.

We considered that the low yield of the chlorination might be due to the heterogeneous system. It might be possible to improve the yield of **2b** by introducing some solvent to make the homogeneous mixture. CH<sub>2</sub>Cl<sub>2</sub> is a good choice. Table 2 showed that the yield increased when CH<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub> was used as the solvent. The yield of the higher generation **2c** was also desired (90%).

## EXPERIMENTAL

### General Procedure for the Synthesis of Dendritic Benzyl Alcohols **2-OH**

A mixture of the appropriate benzyl chloride (2.00 equiv), 3,5-dihydroxybenzyl alcohol (1.00 equiv), dried potassium carbonate (2.50 equiv), and 18-crown-6 (0.20 equiv) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool and filtrate. The residue was washed with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic liquids were then evaporated and dried. The crude product was purified as outlined in the following text.

### General Procedure for the Synthesis of Dendritic Benzyl Chlorides **2**

Triphenylphosphine was added to a mixture of the dendritic benzyl alcohol **2-OH** with appropriate amount solvent, and the mixture was heated at reflux and stirred under nitrogen for 24 h. For higher generation, a larger amount of triphenylphosphine was required. After the reaction was

completed, the reaction mixture was evaporated and dried. The crude product was purified as outlined in the following text.

Compound **2a-OH** was prepared from benzyl chloride. The residue was purified by flash chromatography with petroleum ether (bp 60–90 °C)/ethyl acetate (v/v, 4:1) as the eluent to give **2a-OH** as a white crystalline solid: yield 91%; mp 78–79 °C.

Compound **2a** was prepared from **2a-OH** (1.00 equiv) and triphenylphosphine (1.50 equiv) in CCl<sub>4</sub>. The residue was purified by flash chromatography with petroleum ether (bp 60–90 °C)/ethyl acetate (v/v, 10:1) as the eluent to give **2a** as a white crystalline solid: yield 93%; mp 72–74 °C.

Compound **2b-OH** was prepared from **2a**. The residue was purified by flash chromatography with petroleum ether (bp 60–90 °C)/ethyl acetate (v/v, 2:1) to give **2b-OH** as a white crystalline solid: yield 92%; mp 108–110 °C.

Compound **2b** was prepared from **2b-OH** (1.00 equiv) and triphenylphosphine (2.00 equiv) in CCl<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub> (v/v, 1:1). The residue was purified by flash chromatography with petroleum ether (bp 60–90 °C)/CH<sub>2</sub>Cl<sub>2</sub> (v/v, 2:1) to give **2b** as a white crystalline solid: yield 80%; mp 110–112 °C.

Compound **2c-OH** was prepared from **2b** and purified by flash chromatography with CH<sub>2</sub>Cl<sub>2</sub> as the eluent to give **2c-OH** as a colorless glass: yield 83%.

Compound **2c** was prepared from **2c-OH** (1.00 equiv) and triphenylphosphine (2.50 equiv) in CCl<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub> (v/v, 1:1). The residue was purified by flash chromatography with petroleum ether (bp 60–90 °C)/CH<sub>2</sub>Cl<sub>2</sub> (v/v, 1:2) as the eluent to give **2c** as a colorless glass: yield 90%.

### General Procedure for the Synthesis of the Dendrimers 3

A mixture of **1** (2-methoxy-1-naphthalenemethanol) (1.00 equiv), the corresponding benzyl chloride **2** (1.00 equiv), KOH (1.20 equiv), and n-Bu<sub>4</sub>NBr (0.05 equiv) in chlorobenzene and water (v/v, 30:1) was heated at 90 °C and stirred vigorously under nitrogen for 48 h. Then CH<sub>2</sub>Cl<sub>2</sub> and water were added to the mixture. The separated water layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were then evaporated and dried. The crude product was purified as outlined in the following text.

1-(Benzyloxymethyl)naphthalene **3a** was prepared from **2a** and purified by flash chromatography with petroleum ether (bp 60–90 °C)/ethyl acetate (v/v, 8:1) as the eluent to give **3a** as a white crystalline solid: mp 86–88 °C, yield 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.93 (s, 3H, OCH<sub>3</sub>), 4.55 (s, 2H, CH<sub>2</sub>), 4.97 (s, 4H, CH<sub>2</sub>), 5.06 (s, 2H, CH<sub>2</sub>), 6.52 (t, 1H, arom. H), 6.62 (d, 2H, arom. H), 7.25–7.48 (m, 13H, arom. H), 7.76–7.84 (m, 2H, arom. H), 8.10 (m, 1H, arom. H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 56.7, 62.2, 70.0, 71.9, 101.4, 106.7, 113.3, 118.6, 123.6, 124.0, 126.8, 127.5, 127.9, 128.2, 128.5, 129.2, 130.3, 133.8, 137.0, 141.4, 155.7, 159.9; MS (FD): *m/z* = 490 (M<sup>+</sup>•). Anal. calcd. for C<sub>33</sub>H<sub>30</sub>O<sub>4</sub> (490.59): C, 80.79; H, 6.16. Found: C, 80.69; H, 6.17.

Compound **3b** was prepared from **2b** and purified by flash chromatography with petroleum ether (bp 60–90 °C)/CH<sub>2</sub>Cl<sub>2</sub> (v/v, 1:2) as the eluent to give **3b** as a white crystalline solid: yield 57%, mp 100–102 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.91 (s, 3H, OCH<sub>3</sub>), 4.53 (s, 2H, CH<sub>2</sub>), 4.90 (s, 4H, CH<sub>2</sub>), 5.01 (s, 8H, CH<sub>2</sub>), 5.06 (s, 2H, CH<sub>2</sub>), 6.55–6.65 (m, 9H, arom. H), 7.30–7.41 (m, 22H, arom. H), 7.46 (m, 1H, arom. H), 7.75–7.81 (m, 2H, arom. H), 8.08 (m, 1H, arom. H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 56.7, 62.2, 69.9, 70.1, 71.9, 101.4, 101.5, 106.4, 106.7, 113.3, 118.5, 123.6, 123.9, 126.8, 127.5, 128.0, 128.2, 128.6, 129.2, 130.4, 133.8, 136.8, 139.4, 141.4, 155.7, 159.8, 160.1; MS (FAB): m/z = 915 (M<sup>+</sup> + 1), 171, 91. Anal. calcd. for C<sub>61</sub>H<sub>54</sub>O<sub>8</sub> (914.38): C, 80.06; H, 5.95. Found: C, 79.90; H, 5.74.

Compound **3c** was prepared from **2c** and purified by flash chromatography with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/ether (v/v/v, 300:150:1) as the eluent to give **3c** as a colorless glass: yield 31%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.89 (s, 3H, OCH<sub>3</sub>), 4.53 (s, 2H, CH<sub>2</sub>), 4.88 (s, 4H, CH<sub>2</sub>), 4.93 (s, 8H, CH<sub>2</sub>), 4.99 (s, 16H, CH<sub>2</sub>), 5.05 (s, 2H, CH<sub>2</sub>), 6.52–6.66 (m, 21H, arom. H), 7.28–7.40 (m, 42H, arom. H), 7.45 (t, 1H, arom. H), 7.72 (m, 1H, arom. H), 7.78 (m, 1H, arom. H), 8.08 (m, 1H, arom. H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 56.6, 62.2, 70.0, 70.1, 71.9, 101.3, 101.6, 106.4, 106.7, 113.2, 118.4, 123.6, 123.9, 126.8, 127.5, 128.0, 128.2, 128.5, 129.1, 130.3, 133.8, 136.7, 139.2, 139.4, 141.4, 155.6, 159.8, 160.0, 160.1 (the signals partially overlap in the <sup>13</sup>C NMR of data **3c**); MS (FAB): m/z = 1592, 154, 91. Anal. calcd. for C<sub>117</sub>H<sub>102</sub>O<sub>16</sub> (1762.72): C, 79.66; H, 5.83. Found: C, 79.60; H, 5.57.

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## REFERENCES

1. (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules*; Wiley-VCH: Weinheim, 1996; (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, 2001.
2. Cao, D.; Meier, H. The unusual photochemistry of dendrimers with an anthracene core. *Angew. Chem. Int. Ed.* **2001**, *40*, 186.
3. (a) Irie, M. Diarylethenes for memories and switches. *Chem. Rev.* **2000**, *100*, 1685; (b) Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyranes and spirooxazines for memories and switches. *Chem. Rev.* **2000**, *100*, 1741.
4. Cao, D.; Meier, H. Photochemical generation of benzene–naphthalene biplanemers. *Tetrahedron Lett.* **2005**, *46*, 4975.

5. Hawker, C. J.; Frechet, M. J. Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
6. Forier, B.; Dehaen, W. Alternative convergent and accelerated double-stage convergent approaches towards functionalized dendritic polyethers. *Tetrahedron* **1999**, *55*, 9829.
7. Balagurusamy, V. S. K.; Ungar, G.; Percec, V. Rational design of the first spherical supramolecular dendrimers self-organized in a novel thermotropic cubic liquid-crystalline phase and the determination of their shape by X-ray analysis. *J. Am. Chem. Soc.* **1997**, *119*, 1539.
8. Yamazaki, N.; Washio, I.; Shibasaki, Y.; Ueda, M. Facile synthesis of aryl ether dendrimer from unprotected AB<sub>2</sub> building blocks using thionyl chloride as an activating agent. *Org. Lett.* **2006**, *8*, 2321.