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New simple convergent synthetic method for benzyl aryl ether dendritic structures

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Abstract—Phenolic benzyl aryl ether based dendrons with an ester periphery are easily prepared by convergent strategy through hydroxy substituted methyl benzoates and easily attainable benzoyl protected 3,5-bis(bromomethyl)phenol. The dendrons obtained can afford dendronized styrenes. © 2001 Elsevier Science Ltd. All rights reserved.

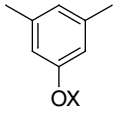
1. Introduction

Synthesis of dendritic polymers is a field under continuous expansion, because of the multiplicity of structures which can be attained, architectures of the resulting materials, variety of synthetic strategies, and especially because of the numerous applications of dendrimers as slow releasing systems, photophysical and electrochemical devices, or liquid crystals.[1–8] The panorama of these applications is widened up when dendritic structures are grafted to polymeric chains.[9–15] In general terms dendrimers include a core, a branching structure and a periphery. Physico-chemical properties, and hence applications, depend on the nature of these three basic constituents. A variety of branching structures have been developed, including those based on trivalent elements, namely, nitrogen, boron or phosphorus, tetravalent elements, such as silicon, germanium or bismuth,[5] besides the multiple possibilities offered by the tetravalent carbon atom. Among the widely used structures, benzene rings constitute flat polyvalent building blocks, and aryl and benzyl ethers and esters are found as the structural base of numerous dendrimers and dendritic polymers.

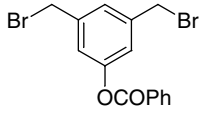
In order to have dendrimers that may find application for concentration of low polar organic matter in water, we needed structures sufficiently stable to long term hydrolytic, oxidative and photolytic processes. The benzyl aryl ether type of wedge structures described by Fréchet seemed a convenient start,[16] but we felt that a new approach could be introduced in order to employ handier materials and to simplify the synthetic procedure, by shortening the number of conversions and avoiding the frequently troublesome quantitative deprotonation of alcohols. We wanted to avoid ester reductions as well, although this implied introduction of a benzylic bromination instead.

2. Results and discussion

The synthetic strategy in the present approach is entirely convergent. The basic building block is the doubly bis(bromomethyl)phenyl benzoate **3**, which can be easily prepared from the handy 3,5-dimethylphenol **1** by protection of the phenolic hydroxyl group with benzoyl chloride, to give the benzoate **2**. Bromination of the latter with NBS leads to the bis(bromomethyl)phenyl benzoate **3** which, although obtained in pure form only in moderate to low yield (36%),† has proved shelf stable for months in its crystalline form. Ether bonds may be most easily formed by substitution of the benzylic bromine by a phenol, under the mild conditions, well established by Fréchet, with potassium carbonate as base, acetone as solvent and 18-crown-6 as phase transfer catalyst.[16] Methanolytic deprotection of the phenolic oxygen with a catalytic amount of sodium methoxide then allows isolation of the dendron. The same procedure can be carried out again in order to obtain a dendron of a higher generation. For the periphery we have employed two



1; X = H
2; X = COPh



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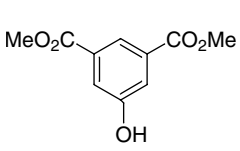
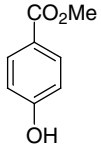


4a



4b

Keywords: dendrimers; ethers; phenols; esters; polymers.

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† Improvement of the procedure has not been attempted.

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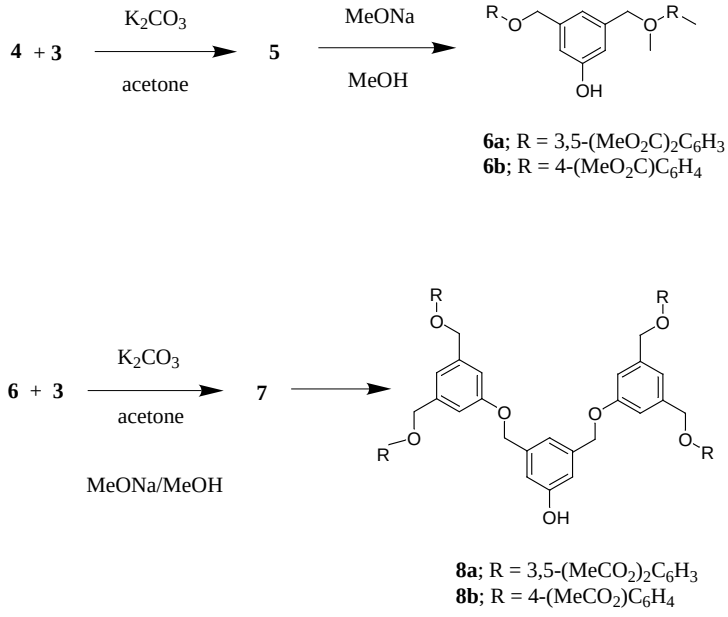
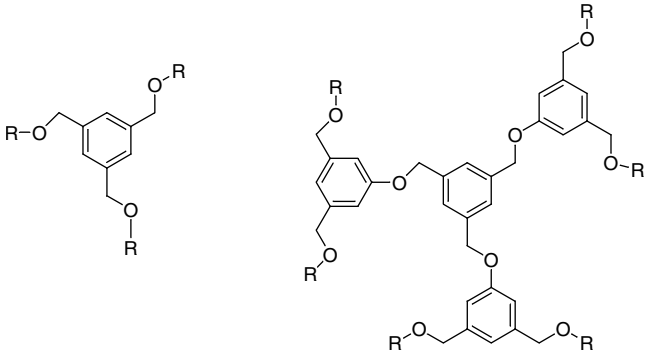


Scheme 1.

commercially available phenolic carboxylic acid methyl esters **4** (Scheme 1).

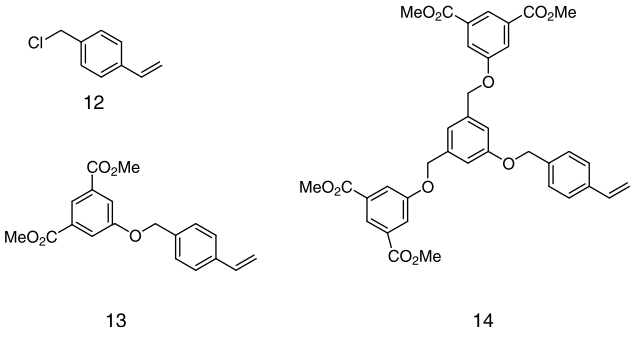
Thus, reaction of the phenolic methyl esters **4** with the dibromo benzoate **3** gave the first generation dendrons **5**, which were deprotected by alkaline methanolysis to afford the phenolic dendrons **6**. These were purified by precipitation from solution in dichloromethane by careful addition of hexane. Purification of the protected dendron **5a** was first attempted, but it was found that purification after removal of the benzoyl rest sample was easier and spectroscopically pure (^{1}H and ^{13}C NMR and MS) dendrons **6a** and **6b** were obtained in 84 and 73% yields, respectively. These dendrons were allowed to react similarly with the bis(bromomethyl)phenyl benzoate **3** to give the second generation dendrons **7** and **8** in spectroscopically pure forms in 63 and 50% yields, for **8a** and **8b**, respectively.



10 **11**

R = 3,5-(MeO$_2$C)$_2$C$_6$H$_3$

Synthesis of dendrimers with the rather small 1,3,5-trimethylbenzene as a core was essayed. The dimethoxycarbonyl phenol **4a** gave dendrimer **10** in 94% yield on reaction with tris-bromomethylbenzene **9**. The first generation dendron **6a** reacted as well with the tribromo mesitylene **9**[17] and dendrimer **11** was obtained in a 93% yield. Again NMR and MS spectra were in agreement with the assigned structures. However, the reaction failed for the second-generation dendron **8a**.



12 **13** **14**

We were interested as well in the preparation of dendritic polystyrenes, as Percec has stressed the effect of self-assembly on the acceleration, control and self-encapsulation of the radical polymerization of styrenic monodendrons.[9–13] When the phenolic esters **4a** and **6a** were allowed to react with 4-chloromethylstyrene **12** the substituted phenoxymethylstyrenes **13** and **14** were obtained as crystalline compounds in 71 and 35% yields, respectively. Polymerization of the former (0.7–1 mol L^{-1}) with AIBN (0.03–0.05 mol L^{-1}) in THF for 48 h under argon atmosphere reached a yield of 72–87%. The polymer was characterized by ^{1}H NMR, size exclusion chromatography (SEC) with polystyrene standard, and differential scanning calorimetry (DSC). Thus, number-average molecular weights ($\bar{M}_n$) from 1.3 to 3.2×10^4 and glass transition temperatures (T_g) ranging from 82 to 88°C were obtained.

The second phenoxymethylstyrene **14** underwent polymerization under uncontrolled conditions, affording an insoluble vitreous material. Controlled polymerization of phenoxymethylstyrene **14** and more detailed study of the polymerization of compound **13** will be published elsewhere.

3. Conclusions

In conclusion, benzyl, phenyl ether based dendrons with a methyl ester periphery can be easily prepared, at least up to the second generation, according to a convergent strategy with 3,5-bis(bromomethyl)phenol and phenolic methylcarboxylic esters as basic synthons.

4. Experimental

4.1. General

IR spectra were recorded as KBr discs with a Perkin–Elmer 1750 FTIR spectrophotometer. NMR spectra were recorded with Brucker 300 or Varian Unity (300 MHz) instruments using $CDCl_3$ as solvent and TMS as internal reference, unless otherwise stated. Mass spectra were determined with a VG AutoSpec spectrometer. Melting points are uncorrected and were measured with a Reichert apparatus. Bulb-to-bulb distillations were carried out with a Büchi GKR-50 apparatus and given boiling points stand for the temperature of the furnace. Acetone was distilled from anhydrous K_2CO_3. Acetone containing 18-crown-6 (1 mg mL^{-1}) was stored over 3 Å molecular sieves. Methanol was distilled from Mg and stored over 3 Å molecular sieves. NBS was crystallized from hot water**.** Centrifugation was performed with an ALC centrifugette 4206 model (15 min, 5000 rpm). Pyridine was dried over CaH_2. All other reagents were purchased from Aldrich or Fluka and used without further purification.

All reactions were carried under argon atmosphere and with the standard precautions for exclusion of moisture. Evaporation of solvents was carried out under vacuum with a rotatory evaporator and a water bath at 40°C.

4.1.1. 3,5-Dimethylphenyl benzoate 2. 3,5-Dimethylphenol (5.28 g; 40 mmol) was added portionwise to stirred pyridine (10 mL) at 0°C and the solution stirred for 10 min. Benzoyl chloride (5.62 g; 40 mmol) was added dropwise under stirring and the mixture was allowed to warm up to room temperature and stirred for 3 h. The mixture was poured into ice water and extracted with diethyl ether. The organic layer was washed with cold 2 M HCl, water and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil of almost pure product. Bulb-to-bulb distillation (178–181°C, 0.1 mmHg) gave 3,5-dimethylphenyl benzoate **2** as a light yellow oil (7.13 g; 31.6 mmol; 73%) (lit.[18] mp 55°C). ν_{max} 1737 (CO), 1618, 1591 (Ar), 1261 (C–O) and 707 cm^{-1} (Ar–H); δ_H 8.31 (2H, d, J=7.8 Hz, H-2′), 7.67 (1H, t, J=7.5 Hz, H-4′), 7.55 (2H, t, J=7.7 Hz, H-3′), 6.98 (1H, s, H-4), 6.95 (2H, s, H-2) and 2.43 (6H, s, Ar–CH_3) ppm; δ_C 165.81, 151.42, 139.78, 133.99, 130.61, 130.23, 129.05, 128.13, 119.84 and 21.76 ppm.

4.1.2. 3,5-Bis(bromomethyl)phenyl benzoate 3. 3,5-Dimethylphenyl benzoate **2** (2.26 g; 10 mmol) was dissolved in CCl_4 (40 mL) and NBS (3.91 g; 22 mmol) and *tert*-butylperoxide (0.1 mL) were added. The mixture was heated under reflux for 24 h in the presence of light (160 W, 230 V). The reaction mixture was cooled to room temperature, the supernatant precipitate was filtered off and washed with CCl_4.The combined filtered solutions were evaporated to give a yellow solid material (3.91 g; 100%) of a crude, which crystallized from benzene–hexane as faint yellow needles of 3,5-bis(bromomethyl)phenyl benzoate **3** (1.38 g; 36%), mp 124–126°C. Found: C, 46.94; H, 3.22; Br, 41.36. $C_{15}H_{12}Br_2O_2$ requires: C, 46.91; H, 3.12; Br, 41.61%. ν_{max} 1741 (CO), 1597, 1450 (Ar) 1259 (C–O) and 698 cm^{-1}; δ_H 8.19 (2H, d, J=7.8 Hz, H-2′), 7.66 (1H, t, J=7.2 Hz, H-4′), 7.52 (2H, t, J=7.7 Hz, H-3′), 7.33 (1H, s, H-4), 7.23 (2H, s, H-2), and 4.48 (4H, s, Ar–CH_2Br) ppm; δ_C 164.81, 151.15, 139.8, 133.85, 130.19, 129.08, 128.65, 126.94, 122.41 and 31.95 ppm;

4.1.3. 1,3,5-Tris(bromomethyl)benzene 9. This was obtained from mesitylene and NBS by substantially the same procedure described by Vögtle,[17] as white needles (35%), mp 98–100°C (lit.[17] mp 94°C). ν_{max} 1636 (Ar), 1455, 1212, 704 cm^{-1} (Ar–H); δ_H 7.29 (3H, s Ar–H) and 4.37 (6H, s, ArCH_2Br) ppm; δ_C 139.45, 129.98 and 32.60 ppm.

4.1.4. 3,5-3,5-(Dimethoxycarbonylphenoxymethyl)phenyl benzoate 5a and 3,5-3,5-(dimethoxycarbonylphenoxymethyl)phenol 6a. A mixture of dimethyl 5- hydroxyisophthalate **4a** (1.26 g; 6 mmol), 3,5-bis(bromomethyl)phenyl benzoate **3** (1.15 g; 3 mmol), K_2CO_3 (1.28 g; 9.3 mmol) and 18-crown-6 (176 mg; 0.7 mmol) in acetone (90 mL) was heated under reflux and stirred vigorously for 24 h. The mixture was allowed to cool and the solvent evaporated to dryness. The residue was partitioned between water and dichloromethane and the aqueous layer was extracted with dichloromethane (3×20 mL) and the combined extracts dried. Evaporation of the solvent gave an amorphous white material (1.84 g; 95%), which was dissolved in dichloromethane. Centrifugation followed by precipitation of the solution with hexane gave the title compound in crude form as an amorphous white material (1.72 g; 89%). Found (MS, EI^+) 642.1726 $(M)^+$. $C_{35}H_{30}O_{12}$ requires 642.1737. ν_{max} 1728 (CO), 1596, 1456, 1434 (Ar), 1246 (C–O) and 756 cm^{-1} (Ar–H).

The above crude compound **5a** (128.4 mg; 0.2 mmol) was suspended in 1:1 benzene–methanol (10 mL), sodium methoxide (16.2 mg; 0.3 mmol) was added and the mixture heated under reflux for 30 min while monitored by TLC. The mixture was cooled to 0°C, acidified with aqueous acetic acid to pH 6, diluted with water (50 mL) and extracted with dichloromethane. The solution was washed with water, dried and the solvent evaporated. The resulting solid material was dissolved in dichloromethane and precipitated with hexane to give the compound 3,5-3,5-(dimethoxycarbonylphenoxymethyl)phenol **6a** as a white amorphous material (101.1 mg; 94%), mp 155–157°C. Found (MS, EI^+) 538.1460 $(M)^+$. $C_{28}H_{26}O_{11}$ requires 538.1475. ν_{max} 3402 (OH), 1728 (CO), 1596, 1456, 1434 (Ar), 1250 (C–O) and 756 cm^{-1} (Ar–H); δ_H 8.28 (2H, t, J=1.2 Hz, H-4′), 7.80 (4H, d, J=1.5 Hz, H-2′), 7.06 (1H, s, H-4), 6.91 (2H, s, H-2), 5.09 (4H, s, ArCH_2O) and 3.93 (12H, s, OCH_3) ppm; δ_C 166.37, 158.80, 156.61, 138.61, 131.97, 123.54, 120.33, 118.59, 114.31, 70.05 and 52.67 ppm.

4.1.5. 3,5-4-(Methoxycarbonylphenoxymethyl)phenyl

benzoate 5b and 3,5-4-(methoxycarbonylphenoxymethyl)phenol 6b By the same procedures as above, methyl *p*-hydroxybenzoate **4b** (1.21 g; 9 mmol), the bis-bromomethyl benzoate **3** (1.52 g; 4 mmol), anhydrous potassium carbonate (1.8 g; 13 mmol) and 18-crown-6 (100 mg; 0.4 mmol) in acetone (100 mL) heated under reflux for 24 h, work-up and precipitation from dichloromethane–hexane gave crude **5b** as an amorphous material (1.61 g; 73.5%).

As above, the latter material **5b** (1.61 g; 2.9 mmol), sodium methoxide (216 mg; 4 mmol) and methanol (40 mL), after heating for 0.5 h under reflux and work-up, gave 4-(methoxycarbonylphenoxymethyl)phenol **6b** (1.22 g; 99%) as a white amorphous material, mp 133–137°C. Found (MS, EI^+) 422.1218 $(M)^+$. $C_{24}H_{22}O_7$ requires 422.1365. ν_{max} 3364 (OH), 1719 (CO), 1596, 1456, 1434 (Ar), 1255 (C–O) and 847 cm^{-1} (Ar–H); δ_H 7.90 (4H, d, J=6.87 Hz, H-3′), 6.94 (1H, s, H-4), 6.87 (4H, d, J=6.9 Hz, H-2′), 6.82 (2H, s, H-2), 4.97 (4H, s, $ArCH_2O$) and 3.83 (6H, s, OCH_3) ppm; δ_C 167.35, 162.71, 156.90, 138.99, 132.04, 123.28, 118.43, 114.86, 114.34, 69.95 and 52.36 ppm.

4.1.6. 3,5-Bis-[3,5-3,5-(dimethoxycarbonylphenoxymethyl)-phenoxymethyl]phenyl benzoate 7a and 3,5-bis-[3,5-3,5-(dimethoxycarbonylphenoxymethyl)phenoxymethyl]-phenol 8a. A mixture of $(MeO_2C)_2$[G-1]–OH **6a** (0.59 g; 1.09 mmol), 3,5-bis(bromomethyl)phenyl benzoate **3** (0.21 g; 0.55 mmol), K_2CO_3 (0.22 g; 1.6 mmol), 18-crown-6 (0.05 g; 0.2 mmol) and acetone (50 mL) was heated under reflux for 41 h, while monitored by TLC. The mixture was cooled, the solvent partially evaporated, water added and the mixture stirred for 20 min. The white precipitate was filtered off and dried and purified by solution in dichloromethane and precipitation with hexane to obtain $(MeO_2C)_2$[G-2]–OCOPh **7a** as a white amorphous material (0.515 g; 73%). Found (MS, FAB^+) 1299.3690 $(M+H)^+$. $C_{71}H_{63}O_{24}$ requires 1299.3709. ν_{max} 1728 (CO), 1596, 1456, 1434 (Ar), 1246 (C–O) and 756 cm^{-1} (Ar–H).

The above compound **7a** (800 mg; 0.62 mmol) was suspended in 1:1 benzene–methanol (50 mL), sodium methoxide (54 mg; 1 mmol) was added, the mixture was heated under reflux for 2 h while monitored by TLC, and then cooled to 0°C and acidified with aqueous acetic acid to pH 6. The precipitate (0.571 mg; 72%) was filtered off and dried and purified by solution in dichloromethane and precipitation with hexane to obtain 3,5-bis-[3,5-3,5-(dimethoxycarbonylphenoxymethyl)phenoxymethyl]phenyl **8a** (412 mg; 52%) as a white amorphous solid, mp 135°C. Found (MS, FAB^+) 1217.3290 $(M+Na)^+$, $C_{64}H_{58}O_{23}Na$ requires 1217.3266. ν_{max} 3431 (OH), 1724 (CO), 1596, 1456, 1434 (Ar), 1245 (C–O) and 757 cm^{-1} (Ar–H); δ_H 8.26 (4H, t, J=1.5 Hz, H-4″), 7.78 (8H, d, J=1.5 Hz, H-2″), 7.07 (2H, s, H-3′), 7.00 (5H, s, H-2′+H-4), 6.87 (2H, s, H-2), 5.09 (8H, s, $ArCH_2O$), 5.08 (4H, s, $ArCH_2O$) and 3.91 (24H, s, OCH_3) ppm; δ_C 166.34, 159.47, 158.79, 139.32, 138.49, 132.01, 123.53, 120.44, 118.75, 117.83, 113.58 (×2), 70.26, 69.97 and 52.70 ppm.

4.1.7. 3,5-Bis-[4-(methoxycarbonylphenoxymethyl)phenoxymethyl]phenyl benzoate 7b and 3,5-bis-[4-(methoxycarbonylphenoxymethyl)phenoxymethyl]phenol 8b. By the same procedures as above compound **6b** (1.26 g; 3 mmol), the bis-bromomethyl benzoate **3** (0.57 g; 1.5 mmol), anhydrous potassium carbonate (0.70 g; 5 mmol), 18-crown-6 (80 mg; 0.3 mmol) and acetone (80 mL), heating under reflux for 41 h and work-up gave an amorphous material (1.43 g), which was dissolved in dichloromethane and precipitated by addition of hexane to give the title compound **7b** (1.21 g; 76%) as a white amorphous material.

The latter material (0.80 g; 0.75 mmol), sodium methoxide (54 mg; 1 mmol), and 1:1 methanol–benzene (40 mL) heated under reflux for 2 h and work-up as above gave an amorphous material (548 mg; 76%), which was purified by dissolution/precipitation from dichloromethane–hexane to give 3,5-bis-[4-(methoxycarbonylphenoxymethyl)phenoxymethyl]phenol **8b** as a white amorphous material (475 mg; 66%), mp 139–142°C. Found (MS, FAB^+) 963.3230 $(M+1)^+$. $C_{56}H_{51}O_{15}$ requires 963.3228. ν_{max} 3403 (OH), 1713 (CO), 1510, 1434 (Ar), 1250 (C–O) and 847 cm^{-1} (Ar–H); δ_H 7.89 (8H, d, J=6.93 Hz, H-3″), 6.98 (2H, s, H-4′), 6.90 (4H, s, H-2′), 6.86 (8H, d, J=6.95 Hz, H-2″), 6.83 (1H, s, H-4), 6.76 (2H, s, H-2), 5.00 (8H, s, $ArCH_2O$), 4.94 (4H, s, $ArCH_2O$) and 3.80 (12H, s, OCH_3) ppm; δ_C 167.29, 162.65, 159.60, 156.92, 139.22, 138.81, 132.03, 123.32, 119.01, 118.35, 114.86, 114.30, 113.83, 70.05 and 52.34 ppm..

4.1.8. 1,3,5-Tris-(3,5-dimethoxycarbonyl)phenoxymethylbenzene 10. A mixture of 1,3,5-tris(bromomethyl)benzene **9** (120.8 mg; 33.7 mmol), dimethyl 5-hydroxyisophthalate **4a** (222.5 mg; 1.06–1.1 mmol), K_2CO_3 (143.5 mg; 1.07 mmol), 18-crown-6 (30 mg; 0.12 mmol) and acetone (30 mL) was stirred vigorously and heated under reflux under argon atmosphere for 24 h. The mixture was allowed to cool and the solvent evaporated to dryness; aqueous Na_2CO_3 was added to the residue, the mixture stirred for 10 min and the solid material filtered off, washed with water and dried under vacuum. The product was purified by precipitation with hexane from its solution in dichloromethane, and 1,3,5-tris-(3,5-dimethoxycarbonyl)phenoxymethylbenzene **10** was obtained as a white amorphous material (246 mg; 94%), mp 171°C. Found (MS, FAB^+) 745.2125, $(M+1)^+$. $C_{39}H_{37}O_{15}$ requires 745.2132. ν_{max} 1728 (CO), 1595 (Ar), 1434 (CH_3), 1244 (C–O) and 756 (Ar–H); δ_H 8.21 (3H, s, H-4′), 7.77 (6H, s, H-2′), 7.48 (3H, s, H-2), 5.15 (6H, s, $ArCH_2O$) and 3.87 (18H, s, CO_2CH_3) ppm; δ_C 166.43, 158.98, 137.64, 132.28, 126.67, 123.80, 120.47, 70.36 and 52.86 ppm.

4.1.9. 1,3,5-Tris-[3,5-3,5-(dimethoxycarbonyl)phenoxymethyl]benzene 11. A mixture of 1,3,5-tris(bromomethyl)-benzene (27.97 mg; 0.787 mmol), $(MeO_2C)_2$[G1]–OH (127 mg; 0.236 mmol), K_2CO_3 (33 mg; 2.4 mmol), 18-crown-6 (15 mg; 0.6 mmol) and acetone (15 mL) was stirred vigorously and heated under reflux for 48 h. The mixture was allowed to cool to rt and the solvent evaporated. The residue was dissolved in dichloromethane and water; the aqueous layer was washed twice with dichloromethane (2×20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated to give a white solid material (145 mg), which was dissolved in dichloromethane and precipitated with hexane to give

1,3,5-tris-[3,5-3,5-(dimethoxycarbonyl)phenoxymethyl]benzene. Found (MS, FAB$^+$) 1752 $(M+Na)^+$. 1729 $(M+1)^+$, $C_{93}H_{84}O_{33}Na$ requires 1752.66. $C_{93}H_{85}O_{33}$ requires 1730.68. ν_{max} 1724 (CO), 1596 (Ar), 1455, 1434, 1242 (C–O) and 757 (Ar–H); δ_H 8.41 (6H, d, J=1.3 Hz, H-4″), 7.94 (12H, d, J=1.4 Hz, H-2′′), 7.65 (3H, s, H-2), 7.19 (3H, s, H-4′), 7.04 (6H, s, H-2′), 5.28 (6H, s, $ArCH_2O$), 5.25 (12H, s, $Ar–CH_2O$) and 4.05 (36H, s, CO_2CH_3) ppm; δ_C 166.40, 159.66, 159.00, 138.61, 138.06, 132.24, 123.72, 120.47, 113.93, 70.42 and 52.82 ppm.

4.1.10. 4-(3,5-Dimethoxycarbonylphenoxymethyl)styrene 13. Dimethyl 5-hydroxyisophthalate **5** (0.63 g; 3.3 mmol), 4-vinylbenzyl chloride **12** (0.56 g; 3 mmol), K_2CO_3 (0.65 g; 4.7 mmol), 18-crown-6 (50 mg; 0.2 mmol) and acetone (50 mL) were heated under reflux for 48 h. The solvent was evaporated and the residue was dissolved in water and dichloromethane. The water layer was washed with dichloromethane. The combined organic fractions were dried (Na_2SO_4) and the solvent evaporated to give an almost pure white solid (0.96 g; 80%), which was crystallized from dichloromethane–hexane as white needles, mp 75–76%, of 4-(3,5-dimethoxycarbonylphenoxymethyl)styrene **13** (0.85 g; 71%). Found (MS, EI) 326.1151. Calculated for $C_{19}H_{18}O_5$ 326.1154. ν_{max} 1730 (CO), 1596 (C=C), 1441 (Me), 1250 (C–O), 1039, 1001 and 912 ($RCH=CH_2$), and 880 cm^{-1}; δ_H 8.22 (1H, t, J=1.5 Hz, H-4′), 7.76 (2H, d, J=1.4 Hz, H-2′), 7.37 (2H, d, J=6.3 Hz, H-3), 7.33 (2H, d, J=6.2 Hz, H-2), 6.66 (1H, dd, J=17.6 and 10.9 Hz, $Ar–CH=CH_2$), 5.70 (1H, dd, J=17.6 and 0.8 Hz, $Ar–CH=CH_2$), 5.20 (1H, dd, J=10.9 and 0.8 Hz, $Ar–CH=CH_2$), 5.06 (2H, s, $ArCH_2O$) and 3.86 (6H, s, OCH_3) ppm; δ_C 166.51, 159.12, 137.99, 136.72, 135.91, 132.19, 128.20, 126.90, 123.63, 120.57, 114.74, 70.60 and 52.86 ppm.

4.1.11. 4-[3,5-3,5-(Dimethoxycarbonylphenoxymethyl)]-phenoxymethylstyrene 14. The compound **6a** (1.51 g; 2.80 mmol), anhydrous potassium carbonate (0.69 g; 5 mmol), 18-crown-6 (121 mg; 0.46 mmol) and acetone (120 mL) were stirred at rt for 0.5 h. 4-Vinylbenzyl chloride (0.45 mL; 3.2 mmol) was added and the mixture heated under reflux for 48 h. The solvent was evaporated and the residue was partioned between water and dichloromethane (2×50 mL). The aqueous layer was extracted with dichloromethane (2×20 mL). The combined organic layers were washed with brine and dried (Na_2SO_4) and the solvent evaporated to give a white solid (2.76 g). A sample (1.07 g) was dissolved in dichloromethane and precipitated by addition of hexane to obtain 4-[3,5-3,5-(dimethoxycarbonylphenoxymethyl)]phenoxymethylstyrene **14** as a white amorphous solid (0.25 g; 35%), mp 113–115°C. Found (MS, EI$^+$) 654.2107 $(M)^+$. $C_{37}H_{34}O_{11}$ requires 654.2101. ν_{max} 1718 (CO); δ_H 8.28 (2H, t, J=1.2 Hz, H-4″), 7.81 (4H, d, J=1.2 Hz, H-2″), 7.41 and 7.37 (4H, AB, J=6 Hz, H-2 and H-3), 7.10 (1H, s, H-4′), 7.03 (2H, s, H-2′), 6.71 (1H, dd, J=13.2.6 and 8.1 Hz, $Ar–CH=CH_2$), 5.75 (1H, d, J=13.2 Hz, $Ar–CH=CH_2$), 5.32 (1H, d, J=8.1 Hz, $Ar–CH=CH_2$), 5.12 (4H, s, $ArCH_2O$), 5.07 (2H, s, $ArCH_2O$) and 3.93 (12H, s, OCH_3) ppm; δ_C 166.44, 159.74, 159.00, 138.55, 137.80, 136.78, 136.51, 132.23, 128.12, 126.83, 123.72, 120.48, 119.07, 114.56, 113.95, 70.42, 70.29 and 52.85.

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