Rapid synthesis of polyester dendrimers

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Aryl polyester dendrimers and dendrons have been prepared by using 'branched monomer strategies', in which the surface and the focal point of the multi-branched monomer have been protected with two different kinds of protective group. The protective group for the focal point was stable during deprotection of the surface. Different wedges could be attached to the multi-branched monomers to form large dendrons whilst active dendrons could be attached to different cores to form various dendrimers with different wedges and different cores.

Introduction

In the last 10 years, dendrimers, spherical polymers with a regular and highly symmetrical structure, have attracted extensive scientific interest because of their unusual architecture together with the many unusual properties associated with them which derive from their shape, numerous chain-ends and lack of chain-entanglement; there is also interest in their potential commercial utility.[1] Both the divergent approach developed by Tomalia and Newkome and the convergent method of Fréchet are successful synthetic methods in preparing 'well-defined' dendrimers.[2] However, these iterative synthetic approaches to even small dendrimers are tedious, often requiring chromatographic purification at every step of the growth process. This has created a demand for the rapid synthesis of dendrimers with a different core and different chain ends. Several accelerated approaches have been reported: *e.g.* a 'double-stage convergent growth approach' introduced by Wooley *et al*. for preparation of polyether dendrimers;[3] a 'two monomer approach' developed by Spindler *et al*. for the preparation of poly(ether-urethane) dendrimers;[4] 'branched-monomer approaches' used by Wooley *et al*. for the rapid synthesis of poly(ether-ester) dendrimers;[5] and an orthogonal coupling strategy used by Zeng *et al*. for preparation of large dendrons.[6]

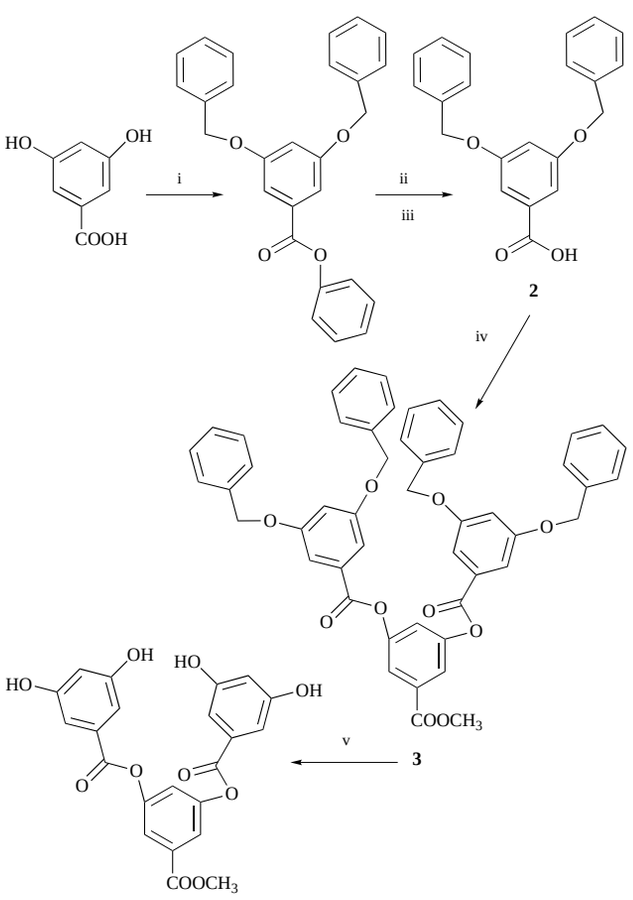
Hyperbranched polyesters (both random polymers and perfect dendrimers) have been prepared by several routes: (a) 'the methylsilyl ether–acid chloride approach',[7] (b) the 'acetate approach'[8] and (c) 'the hydroxy alkoxy ester approach';[9] these three are one-step approaches, which generate random hyperbranched polyesters of high molecular weight with a degree of branching of *ca*. 60%. (d) 'The convergent approach'[10] and (e) 'the divergent approach'[11] give rise to perfect polyester dendrimers.

We now describe a rapid synthesis of uniform polyester dendrimers using the 'branched monomer strategy', which reduces the reaction and separation steps, and is suitable for the synthesis of large polyester dendrimers with various cores and chain ends.

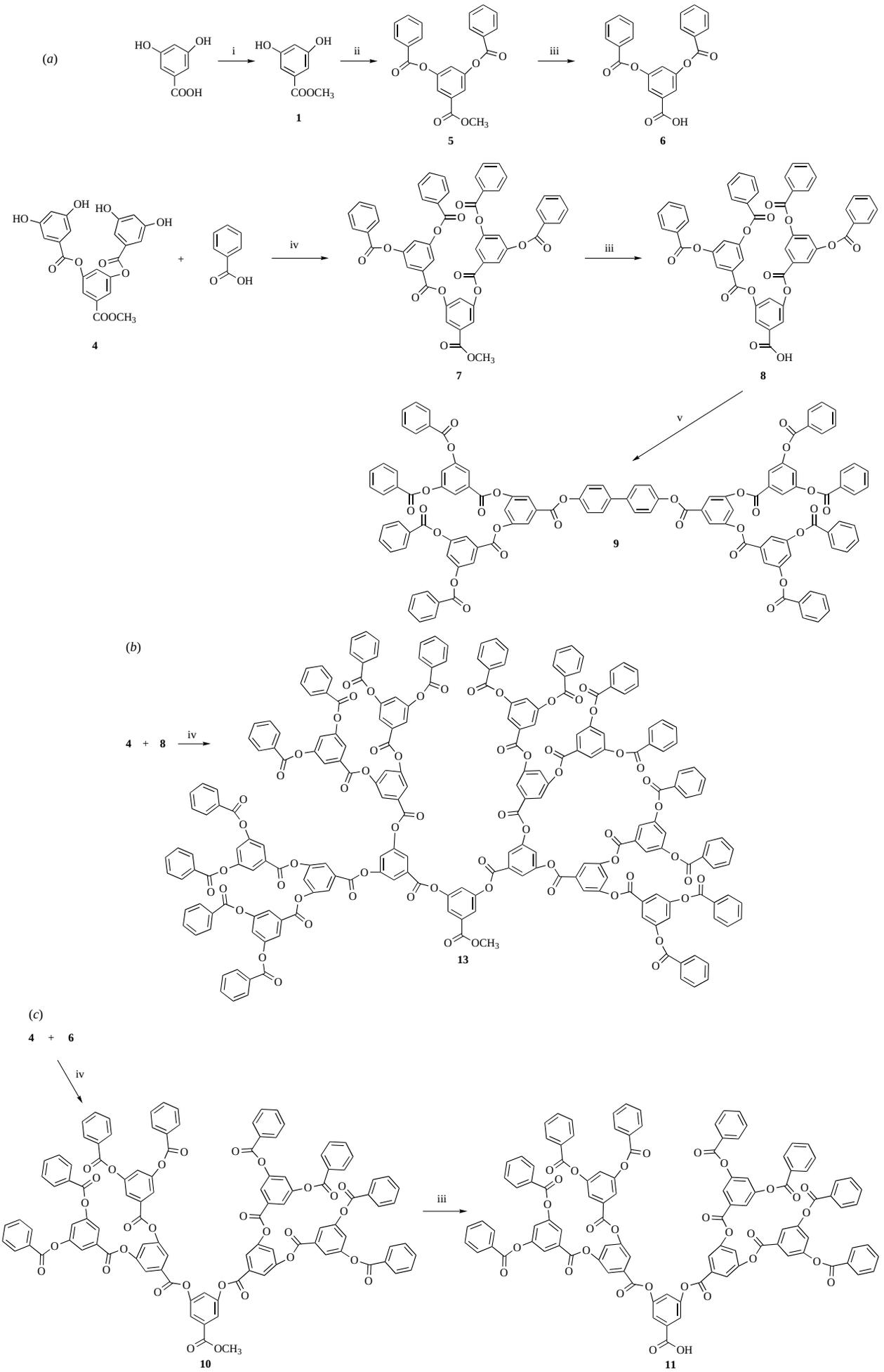
Results and discussion

Synthetic route

The synthesis of 'well defined dendrimers' demands the use of either the divergent or convergent approach. The former starts from a polyfunctional reactive core, which is used to initiate dendritic growth. Since the radially grown interior layers carry on their outer surface a very large number of reactive functional groups, it is difficult to ensure that all the surface functional groups react at every step and proceed with regular growth.[12] In the 'convergent approach' growth is initiated at the periphery of the dendrimer, each step then occurring only at the focal point of the growing dendrimer. The latter approach avoids the problem encountered in the former in which the



Scheme 1 Synthetic route of the multibranched monomer. *Reagents and conditions*: i, $NaHCO_3$, BnCl, DMF, N_2, 110 °C, 5 h; ii, KOH, methanol, H_2O, reflux, 3 h; iii, HCl; iv, methyl 3,5-dihydroxybenzoate (compound **1**), DPTS, DCC, CH_2Cl_2, 24 h; v, Pd–C, H_2, THF, 48 h.


(a)
i
ii
iii
1
5
6
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(b)
4 + 8
iv
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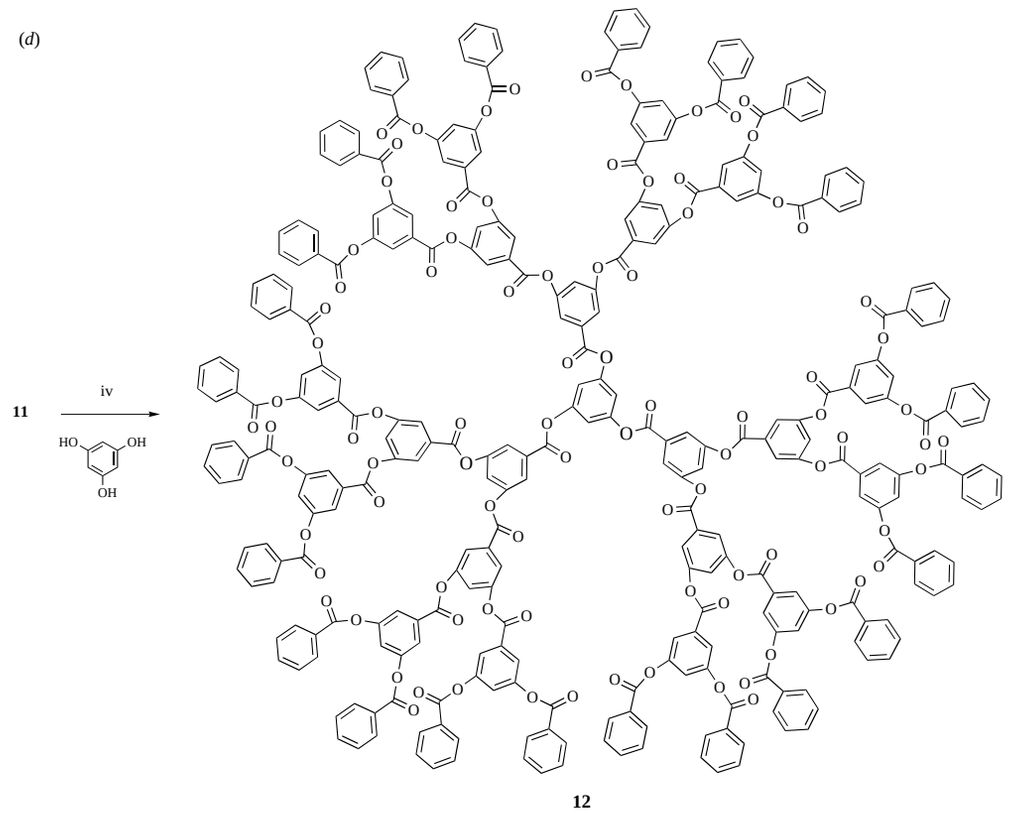
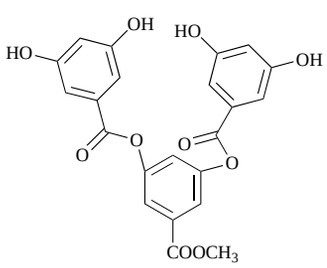
(c)
4 + 6
iv
iii
10
11



Scheme 2(a)–(d) A multi-branched monomer used as a building block to synthesize aryl polyester dendrons and dendrimers. *Reagents and conditions:* i, methanol, H_2SO_4, N_2, reflux, 10 h; ii, CH_2Cl_2, pyridine, benzoyl chloride, 10 h; iii, NaI, $AlCl_3$, CH_3CN, reflux, 12 h; iv, DMF, DPTS, DCC, 20 h; v, 4,4′-biphenol, CH_2Cl_2, DPTS, DCC, 20 h.

growth reactions were incomplete. Thus, the 'convergent method' is better suited to the synthesis of defect-free 'well defined dendrimers'. Nevertheless, since such syntheses are tedious, with protection–deprotection and column chromatography usually necessary at each step we have designed and synthesized an AB_4 monomer (see structure) which we have



The chemical structure of the multi-branched monomer

used to prepare well defined aryl polyester dendrimers and dendrons. In this process there is growth of two generations in one step with the avoidance of incomplete reactions. The multi-branched monomer was prepared by the process illustrated in Scheme 1 in which each reaction step was of high yield and giving rise to easily separable products. Initially, we designed and synthesized compound **3**, which has two kinds of protective groups: the benzyl groups at the periphery and the methyl group at the focal point. Removal of the former gives the multi-branched monomer **4** whilst removal of the latter gives a two-generation mono-dendron. Unfortunately, the ether linkages in compound **4** are unstable to the reaction conditions used to remove the methyl group. The multi-branched monomer **4** can react with benzoic acid to give the second generation dendron (G_2-CO_2Me, **7**) or with G_1-CO_2H to give the third generation dendron. The methyl ester terminal dendrons can be deprotected by refluxing with $AlCl_3$–NaI in acetonitrile to give the corresponding dendrons with a terminal carboxyl. The carboxyl terminal dendrons can be attached to the multibranched monomer or a core to give a large dendron (G4-CO_2Me, **13**, or a dendrimer, **12**). The process is shown in Scheme 2(*a*)–(*d*).

Synthesis

Methyl 3,5-dihydroxybenzoate and 3,5-dibenzyloxybenzoic acid were used to obtain the multi-branched monomer **4**. Compound **3** could be obtained in high yield (91%) by reaction of methyl 3,5-dihydroxybenzoate with 3,5-dibenzyloxybenzoic acid in a recently developed esterification.[13] The multi-branched monomer **4** could also be obtained in high yield by ready removal of the benzyl group in compound **3** in THF solution under an atmosphere of H_2 in the presence of Pd–C catalyst. Wedges bearing different surface functional groups can react with the multi-branched monomer to form different mono-dendrons with a methyl ester group at the focal point. The methyl ester can be selectively deprotected in the presence of aromatic esters. Active mono-dendrons (Gn-COOH) can be obtained in good yield by refluxing the methyl ester terminal mono-dendrons with $AlCl_3$ and NaI[14] in acetonitrile, and no side reaction was observed. The mole ratios of methyl ester dendrons with $AlCl_3$ and NaI are 1:1.5:4.5 in order to ensure complete reaction of the methyl ester. Since the multi-branched monomer and phloroglucinol are poorly soluble in dichloromethane, DMF was selected as the reaction medium instead. A large dendron or a dendrimer could be obtained by reaction of Gn-COOH with the multi-branched monomer (**4**) or a core (phloroglucinol) in DMF in the presence of DTPS and DCC. All the compounds larger than G_2 were purified by chromatography on a silica gel column.

Characterization

The aryl polyester dendrimers or dendrons obtained were characterized spectroscopically (IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS and GPC *etc.*). ^{1}H NMR spectroscopy proved to be an efficient method for characterization of the 'well defined' dendrimers. In the ^{1}H NMR spectra, the resonance for exterior phenyl groups occur at 7.5–7.7 ppm, the resonance for

interior aromatic protons occur at 7.8–8.3 ppm and methoxy group hydrogens occur at 3.94 ppm. The characteristic resonance of a methoxy group at 3.94 ppm disappeared when a G_3-CO_2Me was converted into the corresponding G_3-COOH. The integration data for these groups also confirmed the structures of the dendrimers. In the ^{13}C NMR spectra of Gn-CO_2CH_3 dendrimers, the resonance occurring at 162.6–165.2 ppm was attributed to C=O whilst the resonance occurring at 120.1–151.6 ppm was attributed to aromatic carbon atoms and that at 52.54 ppm to OCH_3.

Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) was successful for the characterization of dendrimers. There are three peaks (1839.8, 1854.0, 1880.0) in the MALDI-MS spectra of the dendrimers G_3-CO_2CH_3 (*m* 1817.5), which are maybe attributed to $M^+ + Na$, $M^+ + K$ and $M^+ + Cu$. There was only one peak (1825.7) in the MALDI-MS spectrum of the dendrimer G_3-CO_2H (*m* 1803.6), which is maybe attributed to $M^+ + Na$. The peak at 3773.0 Dalton in the MALDI-MS spectrum of the dendrimer G_4-CO_2CH_3 (*m* 3739.4) is probably attributable to $M^+ + K$.

The purity of the compounds was confirmed by IR, ^1H NMR, ^{13}C NMR, mass spectrometry, microanalysis and gel-permeation chromatography (GPC). The GPC results of compounds **10**, **12** and **13**, indicate that they are free of impurities, and their molecular weights are of narrow distribution. The retention times (t_r) for dendrimers **12**, **13** and **10** are 5.845, 5.865 and 6.327 min, respectively. Dendrimer **12** has the highest molecular weight, so its retention time is the shortest, dendrimer **10** has the lowest molecular weight, so its retention time is the longest.

In summary, the branched monomer **4** can be used as a building block to prepare dendrimers with a variety of peripheral functional groups and functional cores. In such compounds, the peripheral functional groups of the dendrimer should be inert under the reaction conditions used to remove the protective groups at the focal point of the mono-dendrons. This branched monomer can be used to synthesize rapidly many kinds of large polyester dendrimers with different wedges and cores.

Experimental

^1H NMR were recorded with $CDCl_3$ solutions on a Varian 400 (400 MHz) or a Varian 80 (80 MHz) spectrometer using TMS proton signal as an internal standard. IR spectra were recorded on an ISF-66V spectrometer as thin films on KBr plates. Molecular weight of the compounds was measured on an LD 11700-TOF MS mass spectrometer. Gel-permeation chromatography was carried out on a HSG-15H chromatograph connected to a UV detector. Acetonitrile was distilled from CaH_2, CH_2Cl_2 from P_2O_5, and THF from sodium before use. Anhydrous sodium iodide was prepared by heating NaI·$2H_2O$ under an N_2 atmosphere to remove water and stored with P_2O_5. DPTS (4-*N*,*N*-dimethylaminopyridinium toluene-*p*-sulfonate) was prepared by adopting the method proposed by J. Moore *et al.*[13] The other reagents were all analytical grade and used without further purification. Compounds **1** and **2** were synthesized according to the literature procedure.[12]

Compound 3

A stirred solution of 3,5-dibenzyloxybenzoic acid (7.88 g, 23 mmol), methyl 3,5-dihydroxybenzoate (1.88 g, 11.2 mmol) and DPTS (1.2 g) in dry CH_2Cl_2 (60 ml) was cooled to 0 °C in an ice–water bath whilst DCC (5.5 g, 26 mmol) in CH_2Cl_2 (20 ml) was added dropwise to it. After this, the mixture was allowed to warm to room temperature and stirring was continued for 20 h. Dilute hydrochloric acid (20 ml) was added to the reaction mixture which was then stirred for 4 h. After this the resulting precipitate was filtered off and washed thoroughly with CH_2Cl_2. The oil layer, separated from the combined filtrate, was dried (Na_2SO_4) and evaporated to give the crude product. This was purified by chromatography eluting with $CHCl_3$ to give compound **3** (8.21 g, 91% yield based on methyl 3,5-dihydroxybenzoate), mp 140–142 °C (Found: C, 74.85; H, 4.90. Requires C, 74.92; H, 4.95%); ν_{max}/cm^{-1} 3100–2850, 1739.5, 1722.9, 1597.0, 143.8 and 1378.0; $\delta_H(CDCl_3)$ 7.84–7.39 (m, ArH), 5.09 (s, $PhCH_2OPh$) and 3.92 (s, CO_2CH_3); *m/z* (MALDI) 824.0 ($M^+ + Na$) and 839.6 ($M^+ + K$) (Calc. for $C_{50}H_{40}O_{10}$: 800.86).

Compound 4 (multi-branched monomer)

A solution of compound **3** (2.45 g, 3 mmol) in dry THF (20 ml) and 5% Pd–C (0.5 g) was stirred under an atmosphere of H_2 at room temperature for 48 h. The catalyst was then filtered off, and the filtrate was evaporated to dryness under reduced pressure to give compound **4** (95%) which was not further purified, mp 92–94 °C (Found: C, 59.84; H, 3.66. Requires C, 59.96; H, 3.63%); ν_{max}/cm^{-1} 3500–2500, 1718.0, 1599.2, 1450.3, 1304.6, 1211.8, 1140.9 and 1007.1; δ_H(DMSO) 7.02–7.78 (m, ArH) and 3.88 (s, CO_2CH_3); $\delta_C(CDCl_3)$ 165.66, 164.53, 158.90, 151.75, 131.73, 130.44, 120.19, 114.01, 113.32, 107.90 and 52.45; *m/z* (MALDI) 462.5 ($M^+ + Na$) (Calc. for $C_{22}H_{16}O_{10}$: 440.36).

Compound 5 (Methyl 3,5-benzoyloxybenzoate, G_1-CO_2CH_3)

Pyridine (2.5 ml) in CH_2Cl_2 (20 ml) was added to a solution of benzoyl chloride (3.92 g, 28 mmol) and methyl 3,5-dihydroxybenzoate (2.34 g, 14 mmol) in CH_2Cl_2 (30 ml) with stirring. The reaction mixture was stirred at room temperature for 10 h after which the resulting precipitate was filtered off and washed. The combined filtrates were then washed with dilute hydrochloric acid (20 ml) and water (20 ml), dried (Na_2SO_4) and evaporated to dryness. The crude product was recrystallized from cyclohexane–diethyl ether (7:3) to give compound **5** (4.2 g, 91.1%), mp 66 °C (Found: C, 70.11; H, 4.25. Requires C, 70.21; H, 4.26%); ν_{max}/cm^{-1} 3092, 3063, 3034, 2954, 2918, 2853, 1751, 1731, 1600 and 1444.6; $\delta_H(CDCl_3)$ 7.43–8.27 (m, ArH) and 3.94 (s, CO_2CH_3); $\delta_C(CDCl_3)$ 165.05, 163.20, 151.36, 133.98, 131.43, 130.27, 128.78, 121.45, 121.10, 120.48 and 52.49.

Compound 6 (3,5-dibenzoyloxybenzoic acid, G_1-CO_2H)

A mixture of methyl 3,5-dibenzoyloxybenzoate (4 g, 10.6 mmol), NaI (4.8 g, 33 mmol) and $AlCl_3$ (1.59 g, 12 mmol) in dry acetonitrile (30 ml) was refluxed for 12 h. The reaction mixture was then cooled, poured into water, acidified with dilute hydrochloric acid and extracted with ethyl acetate (40 ml). The extract was washed with water, aqueous sodium thiosulfate and water, dried (Na_2SO_4) and evaporated on a water-bath. The resulting crude product was purified by chromatography eluting with cyclohexane–ethyl acetate (8:2) and then cyclohexane–ethyl acetate (5:5) to give compound **6** (3.4 g, 90.4%), mp 210–212 °C (Found: C, 69.56; H, 3.80. Requires C, 69.61; H, 3.86%); ν_{max}/cm^{-1} 3092, 3062, 3034, 1742, 1705 and 1593; $\delta_H(CDCl_3)$ 7.50–8.27 (m, ArH); $\delta_C(CDCl_3)$ 169.97, 164.56, 151.36, 133.99, 131.43, 130.28, 128.78, 128.69, 121.45 and 121.10.

Compound 7 (G_2-CO_2CH_3)

A mixture of compound **4** (0.44 g, 1 mmol), benzoic acid (0.5 g, 4.1 mmol) and DPTS (0.2 g) in dry DMF (15 ml) was cooled to 0 °C in an ice–water bath whilst DCC (1 g, 4.8 mmol) in DMF (10 ml) was added dropwise to it with stirring. The mixture was then allowed to warm to room temperature after which stirring was continued for 24 h. The resulting precipitate was filtered off and the filtrate was evaporated to dryness under reduced pressure. Dilute hydrochloric acid (20 ml) and CH_2Cl_2 (50 ml) were added to the residue which was then stirred for 4 h at room temperature. The resulting precipitate was filtered off and the organic layer was separated from the filtrate. It was then washed with water (30 ml), dried (Na_2SO_4) and evaporated to dryness on a water-bath. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to give compound **7** (0.72 g, 84.1%), mp 94–97 °C (Found: C, 70.48; H, 3.53.

Requires C, 70.03; H, 3.73%); ν_{max}/cm^{-1} 3092, 3062, 3034, 2954, 2925, 2853, 1741, 1596 and 1444.6; $\delta_H(CDCl_3)$ 7.43–8.28 (m, ArH) and 3.95 (s, CO_2CH_3).

Compound 8 (G_2-CO_2H)

Compound **8** was prepared by selective decomposition of compound **7** (2 g, 2.3 mmol) according to the reaction procedure described for the preparation of compound **6**. The crude product was purified by chromatography eluting with diethyl ether to give compound **8** as a colourless solid (1.6 g, 82.5%) (Found: C, 69.37; H, 3.77. Requires C, 69.77; H, 3.56%); ν_{max}/cm^{-1} 3250–2500, 1742, 1597 and 1444; $\delta_H(CDCl_3)$ 7.52–8.26 (m, ArH).

Compound 9

Compound **9** was prepared by reaction of compound **8** (100 mg, 0.12 mmol) with 4,4′-biphenol (10 mg, 0.05 mmol), the procedure followed being similar to that for the preparation of compound **3**. The crude product was purified by chromatography eluting with CH_2Cl_2 to give compound **9** as a colourless solid (91 mg, 91%) (Found: C, 71.43; H, 4.19. Requires C, 71.51; H, 4.23%); ν_{max}/cm^{-1} 3093, 3062, 1742 and 1597; $\delta_H(CDCl_3)$ 7.43–8.27 (m, ArH).

Compound 10 (G_3-CO_2CH_3)

Compound **10** was prepared by reaction of compounds **4** (0.335 g, 0.76 mmol) and **6** (1.156 g, 3.20 mmol), the procedure followed being similar to that for the preparation of compound **7**. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to give compound **10** as a colourless solid (1.2 g, 86.9%) (Found: C, 69.89; H, 3.50; $C_{105}H_{62}O_{30}$ requires C, 70.04; H, 3.52%); ν_{max}/cm^{-1} 3100–2850, 1742, 1597 and 1444; $\delta_H(CDCl_3)$ 7.43–8.27 (m, ArH) and 3.95 (s, CO_2CH_3); $\delta_C(CDCl_3)$ 165.05, 164.42, 162.78, 162.59, 151.50, 151.18, 150.90, 133.94, 132.47, 131.19, 130.85, 130.21, 128.62, 121.60, 121.07, 120.35, 120.08 and 52.47. *m/z* (MALDI) 1839.8 (M^+ + Na), 1855.6 (M^+ + K) and 1880.9 (possibly M^+ + Cu) (Calc. for $C_{106}H_{64}O_{30}$: 1817.5).

Compound 11 (G_3-CO_2H)

A mixture of compound **10** (1.2 g, 0.66 mmol), $AlCl_3$ (0.5 g, 3.7 mmol), NaI (1.7 g, 11.1 mmol) and acetonitrile (35 ml) was stirred and refluxed for 16 h. After this the reaction mixture was evaporated under reduced pressure and the residue was partitioned between dilute hydrochloric acid (30 ml) and CH_2Cl_2. The organic layer was separated and washed with water, aqueous sodium thiosulfate and water and then dried (Na_2SO_4) and evaporated to dryness on a water-bath. The crude product was purified by chromatography eluting with $CHCl_3$–THF–HOAc (7:3:0.001) to give compound **11** as a colourless solid (1.0 g, 84%) (Found: C, 69.84; H, 3.42; $C_{105}H_{62}O_{30}$ requires C, 69.92; H, 3.44%); ν_{max}/cm^{-1} 3250–2500, 1742, 1597 and 1444; $\delta_H(CDCl_3)$ 7.52–8.26 (m, ArH); $\delta_C(CDCl_3)$ 168.43, 164.53, 162.86, 162.63, 151.55, 151.23, 151.00, 134.02, 131.79, 131.23, 130.94, 130.31, 128.70, 121.70, 121.21 and 120.81; *m/z* (MALDI) 1825.7 (M^+ + Na) (Calc. for $C_{105}H_{62}O_{30}$: 1803.6).

Compound 12

Compound **12** was prepared by the reaction of compound **11** (300 mg, 0.17 mmol), phloroglucinol (6.3 mg, 0.05 mmol), DPTS (100 mg) and DCC (35 mg, 0.17 mmol) in DMF (40 ml). The procedure was similar to that described for the preparation of compound **7**. The crude product was purified by chromatography eluting with dichloromethane–ethyl acetate (100:1.4) to give pure compound **12** as a solid white foam (180 mg, 72%) (Found: C, 70.21; H, 3.32. Requires C, 70.36, H, 3.34%); ν_{max}/cm^{-1} 3100–2950, 1742, 1597 and 1444; $\delta_H(CDCl_3)$ 7.52–8.26 (m, ArH); $\delta_C(CDCl_3)$ 164.38, 162.73, 162.53, 162.34, 151.49, 151.18, 133.33, 131.10, 130.85, 130.21, 128.68, 128.61, 121.58 and 121.05.

Compound 13 (G_4-CO_2CH_3)

Compound **13** was prepared by reaction of compounds **8** (35.5 mg, 0.042 mmol) and **4** (4.4 mg, 0.010 mmol), DPTS (30 mg) and DCC (9.3 mg, 0.045 mmol) in DMF (30 ml). The procedure was similar to that described for the preparation of compound **7**. The crude product was purified by chromatography eluting with dichloromethane–ethyl acetate (100:1.2) to give pure compound **13** as a solid white foam (29.5 mg, 75%) (Found: C, 69.32; H, 3.40. Requires C, 69.47, H, 3.44%); ν_{max}/cm^{-1} 3100–2850, 1742, 1597 and 1444; $\delta_H(CDCl_3)$ 7.43–8.27 (m, ArH) and 3.95 (s, CO_2CH_3); $\delta_C(CDCl_3)$ 165.12, 164.49, 162.82, 162.62, 151.50, 151.12. 150.91, 134.06, 132.45, 131.24, 131.09, 130.87, 130.27, 128.67, 121.70, 121.23, 121.12, 120.66, 120.13 and 52.54; *m/z* (MALDI) 3773.0 (possibly M^+ + K) (Calc. for $C_{218}H_{128}O_{62}$ is 3739.4).

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