

928 (M^+), 893 ($M^+ - Cl$), 844 ($M^+ - 3 CO$), 809 ($M^+ - 3 CO - Cl$), 499, 454, 426, 307.

Rhenium complex **7**: Under argon, $[Re(CO)_5Cl]$ (27.3 mg, 0.075 mmol) was dissolved in anhydrous toluene (10 mL). At 60 °C, **5** (47 mg, 0.075 mmol) was added in a countercurrent of argon and the reaction mixture heated to 80 °C for 15 h. The cooled solution was filtered, washed with toluene (1 mL), suspended in ether, filtered, and dried in a high vacuum to give **7** (66 mg, 0.071 mmol, 94%) as a yellow powder. 1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.04 (s, 1H, CH(6')), 8.88 (d, 1H, CH(6)), 8.21 (dd, 1H, CH(4')), 8.17 (d, 1H, CH(3')), 8.08 (dd, 1H, CH(3)), 7.86 (dd, 1H, CH(4)), 7.22 (m, 2H, CH(7,8)), 7.12 (m, 2H, CH(7,8)), 6.96 (m, 2H, CH(7,8)), 6.90–6.78 (m, 10H, CH(7,8)), 6.00 (quint., 1H, CHO), 4.54 (s, 2H, CH(9)), 3.99 (s, 2H, CH_2COO), 3.06 (t, d, 2H, CH_2), 2.85 (dd, 2H, CH_2), 2.52 (s, 3H, CH_3); MS (FAB): m/z : 928 (M^+), 893 ($M^+ - Cl$), 844 ($M^+ - 3 CO$), 499 ($M^+ - 1$), 471, 454, 307.

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Polycationic Dendrimers**

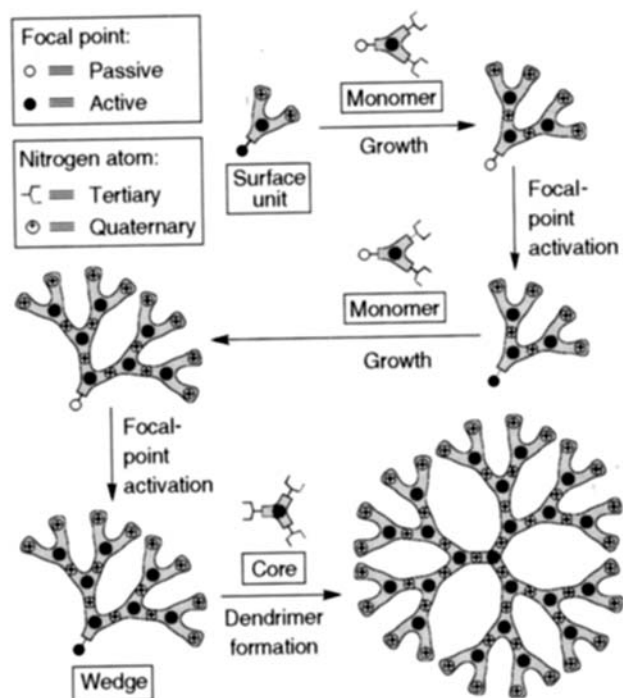
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Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

Dendritic molecules^[1] carrying multiple cationic sites are—unlike their polyanionic counterparts^[2]—still very rare.^[3] The catalytic activity of a dendrimer coated with quaternary ammonium centers on its surface has been investigated,^[4] and a series of dendrimers in which the core and branch points are either ammonium^[5] or phosphonium sites^[6] have been reported. However, the potential applications of dendrimers might be hindered by the low yields of their syntheses.

We are interested in creating dendritic microenvironments, in which a wide range of different chemical reactions can be carried out.^[7] It is not unlikely that dendrimers with cavities that are splattered with positive charges and yet largely lipophilic should be able to bind simultaneously counterions—in the shape of reactive nucleophiles^[8]—and organic substrates.^[9]

Here we present a particularly attractive and efficient convergent approach (Scheme 1) to gram quantities of



Scheme 1. Schematic representation of the convergent approach to the synthesis of a third-generation polycationic dendrimer with quaternary ammonium linkages.

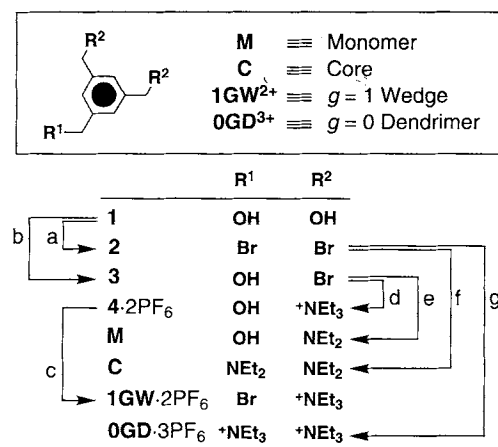
polycationic wedges and dendrimers.^[10] The core and branching points are based on a mesitylene framework. Generation growth is achieved by using the high-yielding Menshutkin reaction, in which the growing dendritic wedge bearing a reactive benzylic CH_2Br group at the focal point is attached to the benzylic CH_2NEt_2 functionalities in a monomer unit, thereby producing new cationic sites.^[11] The larger “passive” wedge is isolated, and the new benzylic CH_2OH group then converted into the reactive CH_2Br group to afford a larger “active” wedge. The series of first-, second-, and third-generation wedges are incorporated into the corresponding dendrimers by allowing the active wedges to react with the core, namely, 1,3,5-tris(diethylaminomethyl)benzene (**C**). To ensure that the Menshutkin reaction is high-yielding, the amines (i. e., the monomer **M** and the core **C**) must be of extremely high purity. As new cationic sites are created, the “soft” PF_6^- anion is introduced to aid the solubility of the positively charged macromolecules in organic solvents.

The synthesis^[12] of the monomer **M**, the core **C**, the first-generation ($g=1$) wedge **1GW**·2 PF_6 , and the zero-generation ($g=0$) dendrimer **0GD**·3 PF_6 are summarized in Scheme 2. 1,3,5-Tris(bromomethyl)benzene (**2**), which was obtained by bromination of 1,3,5-tris(hydroxymethyl)benzene^[13] (**1**) with three equivalents of Ph_3P/CBr_4 in THF, was treated with an excess of Et_2NH to give the core **C** (97% yield). Reaction of **1** with two equivalents of Ph_3P/CBr_4 in THF afforded 3,5-bis(bromomethyl)phenylmethanol (**3**, 55% yield), which was converted into the monomer **M** (86% yield) by treatment with excess Et_2NH . Reaction of **3** with excess Et_3N yielded **4**·2Br quantitatively. After counterion exchange with NH_4PF_6/H_2O to produce **4**·2 PF_6 , the CH_2OH group in **4**²⁺ was converted into a CH_2Br group with $HBr/HOAc$ to afford, after counterion exchange, the wedge **1GW**·2 PF_6 ($g=1$, 89% yield). Successive treatment of **2** with an excess of NEt_3 and NH_4PF_6 yielded the dendrimer

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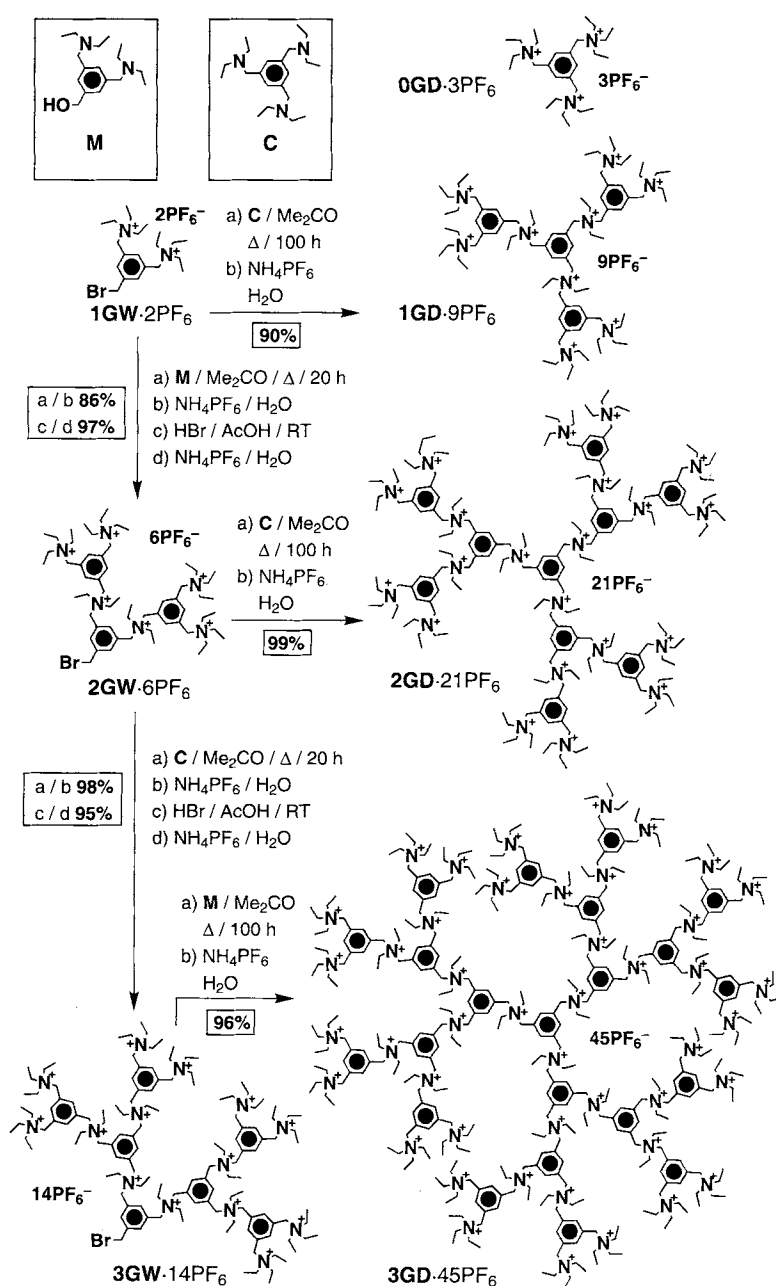


Scheme 2. Synthesis of the key building blocks—namely, the monomer **M**, the core **C**, the first-generation wedge **1GW**·2PF₆ (*g* = 1), and the zero-generation dendrimer **0GD**·3PF₆ (*g* = 0)—from 1,3,5-tris(hydroxymethyl)benzene (**1**). a) 45% HBr in AcOH, 20 °C, 46 h, 98%; b) CBr₄/PPh₃/THF, 20 °C, 2 h, 55%; c) 1. 45% HBr in AcOH, 20 °C, 20 h; 2. NH₄PF₆/H₂O, 100%; d) Et₃N/Me₂CO/MeOH, 20 °C, 2 h, 100%; e) Et₃NH, 20 °C, 4 h, 86%; f) Et₃NH/Et₂O, 20 °C, 23 h, 97%; g) Et₃N/MeOH, 20 °C, 2 h, 49%.

0GD·3PF₆ (*g* = 0, 67% yield), which is stable^[14] upon heating in CD₃SOCD₃ at 100 °C in the presence of about ten equivalents of NaOMe.

Wedge growth (Scheme 3) as far as the third-generation wedge (*g* = 3, **3GW**¹⁴⁺) was achieved by a repetitive sequence of steps: a) successive Menshutkin reactions between **M** and wedges **1GW**·2PF₆ (*g* = 1) and **2GW**·6PF₆ (*g* = 2) in Me₂CO, b) subsequent counterion exchange, c) treatment of the benzylic alcohol functionality with HBr/HOAc to give the benzylic bromide, and d) counterion exchange with aqueous NH₄PF₆. All the steps proceeded with better than 90% yields. Dendrimers **1GD**·9PF₆ (*g* = 1), **2GD**·21PF₆ (*g* = 2), and **3GD**·45PF₆ (*g* = 3) with 9, 21, and 45 cationic sites, respectively, were synthesized in yields of 90, 99, and 96% by allowing the core **C** to react with the wedges **1GW**·2PF₆, **2GW**·6PF₆, and **3GW**·14PF₆ in turn in Me₂CO to effect the three necessary Menshutkin reactions followed by counterion exchange. They are all stable white solids which decompose without melting above 200 °C; they are very soluble in organic solvents such as Me₂CO, DMF, DMSO, MeNO₂, and MeOH. The constitutions and purities of all the wedges and dendrimers were established by LSI mass spectrometry, ¹H and ¹³C NMR spectroscopy, and elemental analysis. The LSI mass spectra of **1GW**·2PF₆, **2GW**·6PF₆, **3GW**·14PF₆, **0GD**·3PF₆, and **1GD**·9PF₆ display peaks at *m/z* = 543, 1706, 4027, 710, and 2451, respectively, corresponding to [M - PF₆]⁺. **2GD**·21PF₆ and **3GD**·45PF₆ do not exhibit [M - PF₆]⁺ ions, possibly as a result of their highly charged character.

An extremely efficient synthetic route to polycationic dendrimers has been established. There is every reason to believe that further growth of the dendrimers beyond the third generation will be possible using, for example a “double-stage” approach.^[15] This simple and very high-yielding synthetic methodology for constructing monodisperse macro-



Scheme 3. Synthesis of up to third-generation dendrimers and wedges from the monomer **M**, the core **C**, and the first-generation wedge **1GW**·2PF₆.

molecular polyelectrolytes, whose solubility can be influenced by the nature of the counterions, has important implications when it comes, for example, to investigating interfacial phenomena and devising new analytical procedures^[16] and catalytic processes.

Experimental Section

3: m.p. 94–95 °C; MS(EI): *m/z* = 294 [M⁺], 213 [M⁺ - Br], 134 [M⁺ - 2Br]; ¹H NMR (CDCl₃, 300 MHz): δ = 1.80 (br s, 1H), 4.45 (s, 4H), 4.68 (s, 2H), 7.32 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ = 32.7, 64.4, 127.3, 128.7, 138.6, 142.2; elemental analysis calcd for C₉H₁₀Br₂O: C 36.77, H 3.43; found: C 36.85, H 3.32.

C: b.p. 129 °C (0.40 torr); MS (EI): *m/z* = 333 [M⁺]; ¹H NMR (CDCl₃, 300 MHz): δ = 1.02 (t, 18H, *J* = 7 Hz), 2.49 (q, 12H, *J* = 7 Hz), 3.53 (s, 6H), 7.14 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ = 11.7, 46.6, 57.4, 128.0, 139.3; elemental analysis calcd for C₂₁H₃₀N₃: C 75.62, H 11.78, N 12.60; found: C 75.50, H 11.86, N 12.86.

M: b.p. 129 °C (0.10 torr); MS (EI): *m/z* = 278 [M⁺]; ¹H NMR (CDCl₃, 300 MHz): δ = 1.02 (t, 12H, *J* = 7 Hz), 2.49 (q, 8H, *J* = 7 Hz), 3.53 (s, 4H), 4.63 (s, 2H),

7.15–7.22 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 11.4, 46.5, 57.3, 64.7, 126.1, 128.8, 139.5, 141.2$; elemental analysis calcd for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}$: C 73.33, H 10.86, N 10.06; found: C 73.40, H 10.86, N 9.92.

4· 2PF_6^- : m.p. 185–187 °C (decomp); MS (LSI): m/z : 481 [$M^+ - \text{PF}_6^-$]; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.31$ (t, 18H, $J = 7$ Hz), 3.17 (q, 12H, $J = 7$ Hz), 4.49 (s, 4H), 4.60 (d, 2H, $J = 6$ Hz), 5.46 (t, 1H, $J = 6$ Hz), 7.40 (s, 1H), 7.56 (s, 2H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 52.0, 58.9, 62.0, 128.4, 132.0, 134.5, 144.4$; elemental analysis calcd for $\text{C}_{21}\text{H}_{40}\text{F}_{12}\text{N}_2\text{O}_2$: C 40.26, H 6.44, N 4.47; found: C 40.32, H 6.39, N 4.34.

1GW· 2PF_6^- : **4**· 2PF_6^- (14.1 g, 22.4 mmol) was added to 45% HBr in HOAc (60 mL). The reaction mixture was stirred for 65 h before being concentrated under vacuum to yield a brown oil, which was treated with aqueous NH_4PF_6 to afford **1GW**· 2PF_6^- as a white solid (13.8 g, 20.0 mmol, 89%); m.p. 183–185 °C (decomp); MS (LSI): m/z : 543 [$M^+ - \text{PF}_6^-$]; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.31$ (t, 18H, $J = 7$ Hz), 3.17 (q, 12H, $J = 7$ Hz), 4.50 (s, 4H), 4.83 (s, 2H), 7.48 (s, 1H), 7.72 (s, 2H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 32.9, 52.0, 58.5, 129.1, 135.0, 136.1, 139.9$; elemental analysis calcd for $\text{C}_{21}\text{H}_{39}\text{BrF}_{12}\text{N}_2\text{P}_2$: C 36.59, H 5.70, N 4.06; found: C 36.33, H 5.50, N 3.88.

2GW· 6PF_6^- and **3GW**· 14PF_6^- : Wedge **1GW**· 2PF_6^- or **2GW**· 6PF_6^- and the monomer **M** (0.45 mol%) were heated at reflux in Me_2CO . After removal of the solvent under vacuum, the residue was treated with an excess of NH_4PF_6 in aqueous Me_2CO . The precipitated PF_6^- salts were isolated by filtration, washed with H_2O , and dried before being stirred with 45% HBr in HOAc at room temperature for 65 h. Concentration of the solution under vacuum afforded a brown oil, which was treated with aqueous NH_4PF_6 to yield the appropriate second- or third-generation wedge

2GW· 6PF_6^- : white solid (97% yield); decomposition without melting above 130 °C; MS (LSI): m/z : 1706 [$M^+ - \text{PF}_6^-$]; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.33$ (t, 36H, $J = 7$ Hz), 1.45 (t, 12H, $J = 7$ Hz), 3.19 (m, 32H), 4.53 (s, 8H), 4.66 (br s, 8H), 4.80 (s, 2H), 7.69 (s, 3H), 7.76 (s, 4H), 7.82 (s, 2H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 8.4, 32.6, 52.0, 52.7, 58.2, 60.3, 129.2, 129.3, 129.4, 135.6, 136.5, 138.2, 138.6, 140.0$; elemental analysis calcd for $\text{C}_{99}\text{H}_{107}\text{BrF}_{36}\text{N}_6\text{P}_6$: C 38.30, H 5.83, N 4.54; found: C 38.28, H 5.89, N 4.59.

3GW· 14PF_6^- : white solid (95% yield); decomposition without melting above 100 °C; MS (LSI): m/z : 4027 [$M^+ - \text{PF}_6^-$]; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.33$ (br s, 72H), 1.50 (m, 36H), 3.20 (br s, 72H), 4.52 (br s, 16H), 4.68 (br s, 24H), 4.80 (s, 2H), 7.60–7.95 (m, 21H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 8.4, 52.0, 52.7, 58.2, 59.8, 129.2, 129.5, 138.5, 139.0$; elemental analysis calcd for $\text{C}_{135}\text{H}_{243}\text{BrF}_{54}\text{N}_{14}\text{P}_{14}$: C 38.87, H 5.87, N 4.70; found: C 38.78, H 6.08, N 4.75.

0GD· 3PF_6^- : Et_3N (5 mL) was added with constant stirring to a solution of **2** (0.13 g, 0.39 mmol) and NH_4PF_6 (0.15 g, 1.3 mmol) in Me_2CO (5 mL), and then the reaction was stirred for 3 h. The solution was filtered and dried over K_2CO_3 , and the solvent removed. The product was purified by recrystallization from Me_2CO /hexane to give **0GD**· 3PF_6^- (white solid, 67% yield); MS(EI): m/z : 710 [$M^+ - \text{PF}_6^-$]; ^1H NMR (CD_3COCD_3 , 300 MHz): $\delta = 1.56$ (t, 27H, $J = 7$ Hz), 3.51 (q, 18H, $J = 7$ Hz), 4.79 (s, 6H), 8.08 (s, 3H); ^{13}C NMR (CD_3COCD_3 , 75 MHz): $\delta = 8.0, 53.5, 59.9, 130.8, 139.6$.

1GD· 9PF_6^- , **2GD**· 21PF_6^- , and **3GD**· 45PF_6^- : Wedge **1GW**· 2PF_6^- , **2GW**· 6PF_6^- , or **3GW**· 14PF_6^- (3.1 equiv) and the core **C** were heated at reflux in Me_2CO for 100 h. The solution was then added to an excess of aqueous NH_4PF_6 , and the mixture stirred for 10 min. The resulting precipitate was filtered, washed with H_2O , and dried.

1GD· 9PF_6^- : white solid (90% yield); decomposition without melting above 200 °C; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.33$ (br s, 54H), 1.50 (br s, 18H), 3.18 (br s, 48H), 4.51 (br s, 12H), 4.68 (brs, 12H), 7.60–8.00 (m, 12H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 8.4, 52.0, 52.7, 58.1, 59.8, 129.2, 129.5, 138.4$; elemental analysis calcd for $\text{C}_{84}\text{H}_{156}\text{F}_{34}\text{N}_6\text{P}_6$: C 38.85, H 6.05, N 4.85; found: C 38.64, H 6.46, N 4.52.

2GD· 21PF_6^- : white solid (99% yield); decomposition without melting above 200 °C; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.33$ (br s, 108H), 1.47 (m, 54H), 3.19 (m, 108H), 4.53 (br s, 24H), 4.65 (br s, 36H), 7.60–8.00 (m, 30H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 8.4, 52.0, 52.7, 58.2, 60.2, 129.2, 129.3, 129.4, 138.2, 138.3, 138.4, 138.5$; elemental analysis calcd for $\text{C}_{198}\text{H}_{360}\text{F}_{126}\text{N}_{21}\text{P}_{21}$: C 39.12, H 5.97, N 4.84; found: C 39.12, H 5.84, N 4.92.

3GD· 45PF_6^- : white solid (96% yield); decomposition without melting above 200 °C; ^1H NMR (CD_3SOCD_3 , 300 MHz): $\delta = 1.33$ (br s, 216H), 1.51 (br s, 126H), 3.18 (br s, 228H), 4.52 (br s, 48H), 4.67 (br s, 84H), 7.70–7.90 (m, 66H); ^{13}C NMR (CD_3SOCD_3 , 75 MHz): $\delta = 7.4, 8.4, 52.0, 52.7, 58.2, 59.8, 129.2, 129.5, 138.4$; elemental analysis calcd for $\text{C}_{426}\text{H}_{768}\text{F}_{270}\text{N}_{45}\text{P}_{45}$: C 39.22, H 5.93, N 4.83; found: C 39.09, H 5.94, N 4.78.

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polyelectrolytes

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- The nomenclature employed for describing the wedges and dendrimers: a number (0, 1, 2, or 3) denoting the generation followed by the letter G for generation, and thereafter by the letter W or D for a wedge or a dendrimer, respectively.
- Although **1** is commercially available, it is convenient and economical to make on a 100-g scale. Esterification of 1,3,5-tribenzenecarboxylic acid (trimesic acid) with $\text{MeOH}/\text{H}_2\text{SO}_4$ followed by reduction of the triester affords 1,3,5-tris(hydroxymethyl)benzene in quantitative yield.
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