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Fast and Scalable Route to Aryl Polyallyl Dendrons and Dendrimers

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4-(4-methoxyphenyl)hepta-1,6-dien-4-ol 2b: Under an inert atmosphere, a solution of ethyl-4-methoxybenzoate (55.5 mmol, 10 g, 9 mL) in 20 mL diethyl ether cooled to 0 °C, was added to a Schlenk tube of allyl magnesium bromide 1M in diethyl ether (138 mmol, 138 mL) at 0°C. The green colour of the reaction mixture changed immediately and a white precipitate is formed. After 5 minutes stirring, a solution of NH₄Cl 5M (100 mL) was added to the reaction mixture, and the product was extracted with diethyl ether (3 x 40 mL), and dried over Na₂SO₄. The solvent was removed under vacuum and the product purified by chromatography on a silica-gel column with a pentane/diethyl ether mixture (7:3) to provide 2b as a colourless oil (52.5 mmol, 11.5 g, 95%). ¹H NMR (CDCl₃, 250 MHz): δ (ppm) 7.31 (d, 2H, Ph-H), 6.87 (d, 2H, Ph-H), 5.62 (m, 2H, CH=CH₂), 5.11 (m, 4H, CH=CH₂), 3.80 (s, 3H, CH₃), 2.67 (dd, 2H, CH₂), 2.49 (dd, 2H, CH₂). ¹³C NMR (CDCl₃, 63 MHz,): δ (ppm) 158.2 (C₉, Ph-O), 137.9 (C₉, Ph), 133.6 (CH-CH₂), 126.5 (CH, Ph), 113.4 (CH, Ph), 118.9 (CH-CH₂), 74.8 (C-OH), 55.1 (CH₃), 46.8 (CH₂). Anal. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 77.10; H, 8.47.

4-methoxy-triallylmethylphenyl 2c: In a Schlenk tube of allyl trimethylsilane (250 mmol, 39.5 mL) in 40 mL CH₂Cl₂, cooled to −78°C, was added a solution of BF₃ 1M in Et₂O (250 mmol, 250 mL). Then, CH₂Cl₂ (40 mL) solution of 2b (50 mmol, 11 g) also cooled to −78°C was added to the reaction mixture. The colourless mixture changed immediately to orange. After 5 minutes stirring, the cooled bath was removed and the solvent evaporated under vacuum. Then, 50 mL of Et₂O and 50 mL of H₂O were added to the mixture. The product was extracted with Et₂O (40 mL x 2) and dried over Na₂SO₄. The solvent was removed under vacuum and the product purified by chromatography on a silica-gel column with a pentane/diethyl ether mixture (95:5) to provide 2c as a colourless oil (47.5 mmol, 11.5 g, 95%). ¹H NMR (CDCl₃, 250 MHz): δ (ppm) 7.23 (d, 2H, Ph-H), 6.86 (d, 2H, Ph-H), 5.56 (m,
3H, CH=CH₂), 5.02 (m, 6H, CH=CH₂), 3.80 (s, 3H, CH₃), 2.43 (d, 6H, CH₂). ¹³C NMR (CDCl₃, 63 MHz): δ (ppm) 157.4 (C₉, Ph-O), 137.7 (C₉, Ph), 134.6 (CH=CH₂), 127.6 (CH, Ph), 117.5 (CH=CH₂), 113.3 (CH, Ph), 55.1 (CH₃), 42.6 (CH₂), 41.9 (C-CH₂). Anal. Calcd for C₁₇H₂₂O: C, 84.25; H, 9.15. Found: C, 84.05; H, 9.20.

4-triallylmethylphenol dendron 2.⁴¹¹ A mixture of 2c (45 mmol, 10.9g) and (n-Bu)₄NI (54 mmol, 19.9g) in 30 mL of CH₂Cl₂, was cooled to –78°C. Then, a solution of BCl₃ 1M in hexane (56 mmol, 56 mL) was slowly added to the reaction mixture. After 12 hours stirring, 49 mL of H₂O was added to the mixture followed by 118 mL of HCl 6N. The product was extracted with Et₂O (30 mL x 3) and the organic layer washed with a solution (20 mL) of Na₂S₂O₃ and dried over Na₂SO₄. The solvent was removed under vacuum and the product purified by chromatography on a silica-gel column with a petroleum ether/diethyl ether mixture (9:1) to provide 2 as a colourless oil (43.2 mmol, 9.86 g, 96%).

4-(6-methoxynaphthyl)-hepta-1,6-dien-4-ol 3b: This compounds was obtained according to the procedure described above for 2b, but from ethyl-6-methoxy-2-naphthoate 3a. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with petroleum ether/diethyl ether mixture (95:5) to provide 3b as a colourless oil. Yield: 14.2g, 95%. ¹H NMR (CDCl₃, 250 MHz): δ (ppm) 7.81 (s, 1H, Naph-H), 7.73 (d, 2H, Naph-H), 7.45 (d, 1H, Naph-H), 7.45 (d, 1H, Naph-H), 7.15 (d, 2H, Naph-H), 7.13 (s, 1H, Naph-H), 5.60 (m, 2H, CH=CH₂), 5.09 (m, 4H, CH=CH₂), 3.92 (s, 3H, CH₃), 2.78 (dd, 2H, CH₂), 2.58 (dd, 2H, CH₂). ¹³C NMR (CDCl₃, 63 MHz): δ (ppm) 157.6 (C₉, Naph-O), 140.8 (C₉, Naph), 133.4 (CH-CH₂), 133.2 (C₉, Naph), 129.6 (CH, Naph), 126.7 (CH, Naph), 124.2 (CH, Naph), 123.9 (CH, Naph), 119.2 (CH-CH₂), 118.8 (CH, Naph), 105.4 (CH, Naph), 75.1 (C-OH), 55.3 (CH₃), 46.8 (CH₂). MS (EI, 70 eV) m/z (%): 291 (17) [M+Na]+, 269 (17) [MH]+, 251 (53), 227 (100). Anal. Calcd for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.47; H, 7.50.

6-methoxy-2-triallylmethylnaphthalene 3c: This compounds was obtained according to the procedure described above for 2c, but from 4-(6-methoxynaphthyl)-hepta-1,6-dien-4-ol 3b. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with petroleum ether/diethyl ether mixture (95:5) to provide 3c as a white solid. Yield: 13.9g, 90%. ¹H NMR (CDCl₃, 250 MHz): δ (ppm) 7.71 (d and s, 2H, Naph-H),
Anal. Calcd for C129.6H7N
Yield: column 4-(6-bromonaphthyl)hepta-1,6-dien-4-ol for C125.3132.8NMR Naph, with the described 2-triallylmethyl-6-naphthol. 

CH125.3132.8NMR Naph, 63 MHz): δ (ppm) 157.5 (Cq, Naph-O), 140.9 (Cq, Naph), 134.6 (CH-CH2), 132.7 (Cq, Naph), 129.6 (CH, Naph), 128.7 (CH, Naph), 126.6 (CH, Naph), 125.7 (CH, Naph), 125.2 (CH, Naph), 118.6 (CH, Naph), 117.6 (CH-CH2), 105.4 (CH, Naph), 55.3 (CH3), 43.3 (C-CH2), 41.7 (CH2). MS (EI, 70 eV) m/z (%) 293 (24) [MH]+, 251 (100), 209 (25). Anal. Calcd for C21H24O: C, 86.26; H, 8.27. Found: C, 85.27; H, 8.41.

2-triallylmethyl-6-naphthol 3: This compounds was obtained according to the procedure described above for 2, but from 6-methoxy-2-triallylmethylnaphthalene 3c. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with a petroleum ether/diethyl ether mixture (9:1) to provide 3 as a white solid. Yield: 12.2g, 92%. 1H NMR (CDCl3, 250 MHz): δ (ppm) 7.70-7.06 (m, 4H, Naph-H), 7.12-7.06 (m, 2H, Naph-H), 5.56 (m, 3H, CH=CH2), 5.01 (m, 7H, OH and CH=CH2), 2.55 (d, 6H, CH2). 13C NMR (CDCl3, 63 MHz): δ (ppm) 153.2 (Cq, Naph), 140.9 (Cq, Naph), 134.6 (CH-CH2), 132.8 (Cq, Naph), 130.0 (CH, Naph), 128.7 (Cq, Naph), 126.2 (CH, Naph), 125.9 (CH, Naph), 125.3 (CH, Naph), 117.7 (CH=CH2), 117.6 (CH, Naph), 109.1 (CH, Naph), 43.3 (CH2), 41.7 (CH2). MS (EI, 70 eV) m/z (%) 279 (17) [MH]+, 259 (13), 237 (100), 209 (12). Anal. Calcd for C26H22O: C, 86.29; H, 7.97. Found: C, 85.50; H, 8.01.

4-(6-bromonaphthyl)-hepta-1,6-dien-4-ol 4b: This compounds was obtained according to the procedure described above for 2b, but from methyl 6-bromo-2-naphthoate 4a. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with petroleum ether/diethyl ether mixture (95:5) to provide 4b as a colourless oil. Yield: 16.5g, 94%. 1H NMR (CDCl3, 250 MHz): δ (ppm) 7.98 (s, 1H, Naph-H), 7.86 (s, 1H, Naph-H), 7.72 (2xd, 2H, Naph-H), 7.53 (2xd, 2H, Naph-H), 5.61 (m, 2H, CH=CH2), 5.09 (m, 4H, CH=CH2), 2.78 (dd, 2H, CH2), 2.59 (dd, 2H, CH2). 13C NMR (CDCl3, 63 MHz): δ (ppm) 144.8 (Cq, Naph), 133.3 (Cq, Naph), 133.1 (CH-CH2), 131.6 (Cq, Naph), 129.9 (CH, Naph), 129.6 (CH, Naph), 129.5 (CH, Naph), 127.0 (CH, Naph), 124.8 (CH, Naph), 124.2 (CH, Naph), 119.7 (CH-CH2), 119.6 (CH, Naph), 75.3 (C-OH), 46.7 (CH2). MS (EI, 70 eV) m/z (%) 340 (6) [M+Na]+, 301 (33) [MH]+, 299 (32), 276 (49), 274 (51), 234 (100), 232 (399). Anal. Calcd for C17H17OBr: C, 64.37; H, 5.40. Found: C, 64.81; H, 5.43.
6-bromo-2-triallylmethylnaphthalene 4: This compound was obtained according to the procedure described above for 2c, but from 4-(6-bromonaphthyl)-hepta-1,6-dien-4-ol 4b. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with petroleum ether mixture to provide 4 as a colourless oil. Yield: 14.2g, 80%. 1H NMR (CDCl3, 250 MHz): δ (ppm) 7.96 (s, 1H, Naph-H), 7.74-7.50 (m, 5H, Naph-H), 5.53 (m, 3H, CH=CH2), 5.09 (m, 4H, CH=CH2), 2.78 (dd, 2H, CH2), 2.59 (dd, 2H, CH2). 13C NMR (CDCl3, 63 MHz): δ (ppm) 144.9 (Cq, Naph), 134.8 (Cq, Naph), 134.2 (CH-CH2), 132.8 (Cq, Naph), 131.6 (Cq, Naph), 129.8 (CH, Naph), 129.4 (CH, Naph), 129.2 (CH, Naph), 126.8 (CH, Naph), 126.2 (CH, Naph), 125.3 (CH, Naph), 117.3 (CH-CH2), 119.6 (CH, Naph), 75.3 (C-OH), 46.7 (CH2). Anal. Calcd for C20H24Br: C, 70.39; H, 6.20. Found: C, 70.23; H, 6.21.

Tetra-allyl dicarbinol 5b: This compound was obtained according to the procedure described above for 2b, but from diethyl terephthalate 5a. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with pentane/diethyl ether mixture (95:5) to provide 3b as yellow oil. Yield: 15.7g, 95%. 1H NMR (CDCl3, 250 MHz): δ (ppm) 7.33 (s, 4H, Ph-H), 5.56 (m, 4H, CH=CH2), 5.05 (m, 4H, CH=CH2), 2.66 (dd, 2H, CH2), 2.45 (dd, 2H, CH2), 2.32 (s, 1H, OH). 13C NMR (CDCl3, 63 MHz): δ (ppm) 144.4 (Cq, Ph), 133.8 (CH-CH2), 125.5 (CH, Ph), 119.4 (CH-CH2), 75.5 (C-OH), 47.0 (CH2). Anal. Calcd for C20H26O2: C, 80.50; H, 8.78. Found: C, 80.47; H, 8.79.

Hexa-allyl tricarbinol 6b: This compound was obtained according to the procedure described above for 2b, but from the readily obtained triethyl 1,3,5-benzenetricarboxylate 6a. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with pentane/diethyl ether mixture (70:30) to provide 6b as a white solid. Yield: 21.3g, 94%. 1H NMR (CDCl3, 250 MHz): δ (ppm) 7.23 (s, 3H, Ph-H), 5.53 (m, 6H, CH=CH2), 5.00 (m, 12H, CH=CH2), 2.63 (dd, 6H, CH2), 2.46 (dd, 6H, CH2), 2.32 (s, 1H, OH). 13C NMR (CDCl3, 63 MHz): δ (ppm) 145.6 (Cq, Ph), 133.8 (CH-CH2), 121.2 (CH, Ph), 119.3 (CH-CH2), 75.9 (C-OH), 47.3 (CH2). MALDI-TOF MS (408.58): 431.3 (M+ + Na). Anal. Calcd for C22H36O3: C, 79.37; H, 8.88. Found: C, 79.80; H, 8.72.

Hexa-allyl dendritic core 5:[19] In a Schlenk tube of allyl trimethylsilane (500 mmol, 79 mL) in 40 mL CH2Cl2, cooled to –78°C, was added a solution of BF3 1M in Et2O (500 mmol, 500 mL). Then, CH2Cl2 (50 mL) solution of 5b (52.7 mmol, 15.7 g) also cooled to –78°C was
added to the reaction mixture. After 12 hours stirring, the colour of the mixture changed from colourless to orange. The solvent was evaporated under vacuum, 50 mL of Et$_2$O and 50 mL of H$_2$O were added. The product was extracted with Et$_2$O (40 mL x 2) and dried over Na$_2$SO$_4$. The solvent was removed under vacuum and the product purified by chromatography on a silica-gel column with a pentane/diethyl ether mixture (95:5) to provide 5 as a colourless oil (15.8 mmol, 5.5 g, 30%). $\delta$ (ppm) 7.24 (s, 4H, Ph-H), 5.54 (m, 6H, CH=CH$_2$), 5.01 (m, 12H, CH=CH$_2$), 2.45 (d, 12H, CH$_2$). $^{13}$C NMR (CDCl$_3$, 63 MHz): $\delta$ (ppm) 144.6 (C$_q$, Ph), 134.6 (CH=CH$_2$), 126.3 (CH, Ph), 117.5 (CH-CH$_2$), 42.2 (CH$_2$). MS (EI, 70 eV) m/z (%) 345 (28) [M]+, 305 (100), 263 (79), 221 (64).

_Nona-allyl dendritic core 6:_\textsuperscript{[19]} In a Schlenk tube of allyl trimethylsilane (750 mmol, 118.5 mL) in 50 mL CH$_2$Cl$_2$, cooled to –78°C, was added a solution of BF$_3$ 1M in Et$_2$O (750 mmol, 750 mL). Then, CH$_2$Cl$_2$ (50 mL) solution of 6b (52.2 mmol, 21.3 g) also cooled to –78°C was added to the reaction mixture. After 12 hours stirring, the color of the mixture changed from colourless to orange. The solvent was evaporated under vacuum, and 50 mL of Et$_2$O as well as 50 mL of H$_2$O added successively. The product was extracted with Et$_2$O (30 mL x 2) and dried over Na$_2$SO$_4$. The solvent was removed under vacuum and the product purified by chromatography on a silica-gel column with a pentane/diethyl ether mixture (95:5) to provide 6 as a colourless oil (7.8 mmol, 3.8 g, 15%). $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ (ppm) 7.03 (s, 3H, Ph-H), 5.1 (m, 9H, CH=CH$_2$), 4.97 (m, 18H, CH=CH$_2$), 2.43 (d, 12H, CH$_2$). $^{13}$C NMR (CDCl$_3$, 63 MHz,): $\delta$ (ppm) 144.4 (C$_q$, Ph), 134.6 (CH=CH$_2$), 133.6 (CH, Ph), 122.8 (CH, Ph), 117.4 (CH=CH$_2$), 43.6 (C-CH$_2$). 41.8 (CH$_2$).