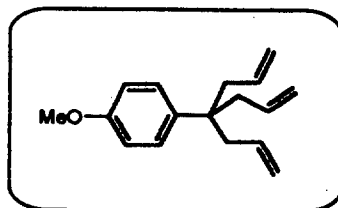


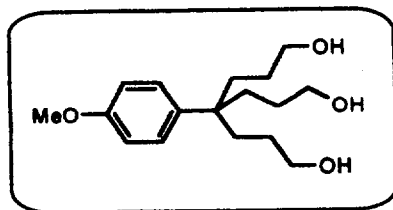
15) *p*-(1,1-di-(2-proprenyl)-3-butenyl)methoxybenzene, 12
(or in short *p*-triallylmethyl-methoxybenzene, 12)



Triallylmethylphenol 3 (1.9g, 8.32 mmol), methyl iodide (4 mL, 30 mmol), KOH (3.6g, 64 mmol) and 7 mL DMSO are introduced under nitrogen into a Schlenk tube. The reaction mixture is stirred for two hours at room temperature in the dark, then the excess of methyl iodide is removed under vacuum, the residue is extracted with 3 x 20 mL ether, this solution is washed with Na₂S₂O₃ and dried over sodium sulfate. This gives 12 as a light-brown oil (1.80g, 7.44 mmol, 90% yield).

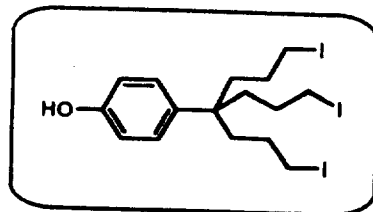
¹H RMN (CDCl₃) δ 7.20 and 6.85 (m, CH_{arom}, 4H); 5.68-5.55 (m, CHCH₂, 9H); 5.07-5 (m, CHCH₂, 18H); 3.78 (s, CH₃O, 3H); 2.44 (d, CH₂, 18H). ¹³C RMN (CDCl₃) δ 156.10 (C_{quat} aromO); 137.29 (C_{quat} aromC); 134.22 (CHCH₂); 127.23 (CH_{arom}CO); 117.08 (CHCH₂); 112.21 (CH_{arom}C); 54.78 (CH₃); 42.25 (C_{quat}-CH₂); 41.54 (CH₂). Anal. Calcd for C₁₇H₂₂O : C 84.25 ; H 9.15. Found C 83.84 ; H 9.05.

16) *p*-(1,1-di-(3-hydroxypropyl)-4-hydroxybutyl)methoxybenzene, 13



The hydroboration-oxidation of **12** (1.8g, 7.43 mmol) is carried out as described above in **8**) for the synthesis of the 27-alcohol from the olefinic precursor. This gives **13** as a colorless oil (1.9g, 6.4 mmol, 86% yield).

^1H RMN (CDCl_3) δ 7.22 and 6.9 (m, C_6H_4 , 4H); 3.74 (s, CH_3O , 3H); 3.47 (m, CH_2OH , 6H); 1.70 (m, $\text{CH}_2\text{CH}_2\text{OH}$, 6H); 1.3 (m, $\text{CH}_2\text{C}_{\text{quat}}$, 6H). ^{13}C RMN (CDCl_3) δ 156.76 ($\text{C}_{\text{quat arom OH}}$); 137.32 ($\text{C}_{\text{quat arom C}}$); 127.75 (CH_{arom}); 114.80 (CH_{arom}); 63.24 (CH_3); 53.41 (CH_2O); 42.37 ($\text{C}_{\text{quat-CH}_2}$); 34.58 ($\text{C}_{\text{quat CH}_2}$); 27.89 ($\text{CH}_2\text{CH}_2\text{O}$). Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4$: C 68.89; H 9.52. Found C 68.9; H 8.67.

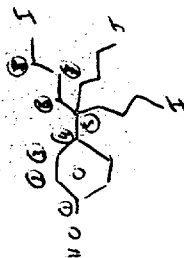
17) *p*-(1,1-di(3-iodopropyl)-4-iodobutyl)phenol 14

The triol dendron **13** (1.5g, 5.06 mmol), 5mL of anhydrous MeCN, then dry NaI (6g, 40 mmol) and freshly distilled SiMe₃Cl (5mL, 39 mmol) are successively introduced into a Schlenk tube under nitrogen. The closed reaction medium is left for two days at 80°C in the dark, then the solvent is removed under vacuum and the residue is extracted with 2 x 100mL ether, the ether solution is washed with an aqueous solution saturated with Na₂S₂O₃, dried over sodium sulfate and filtered. The solvent is removed under vacuum, which gives **13** as a pale-yellow oil (3g, 4.90 mmol, 97%).

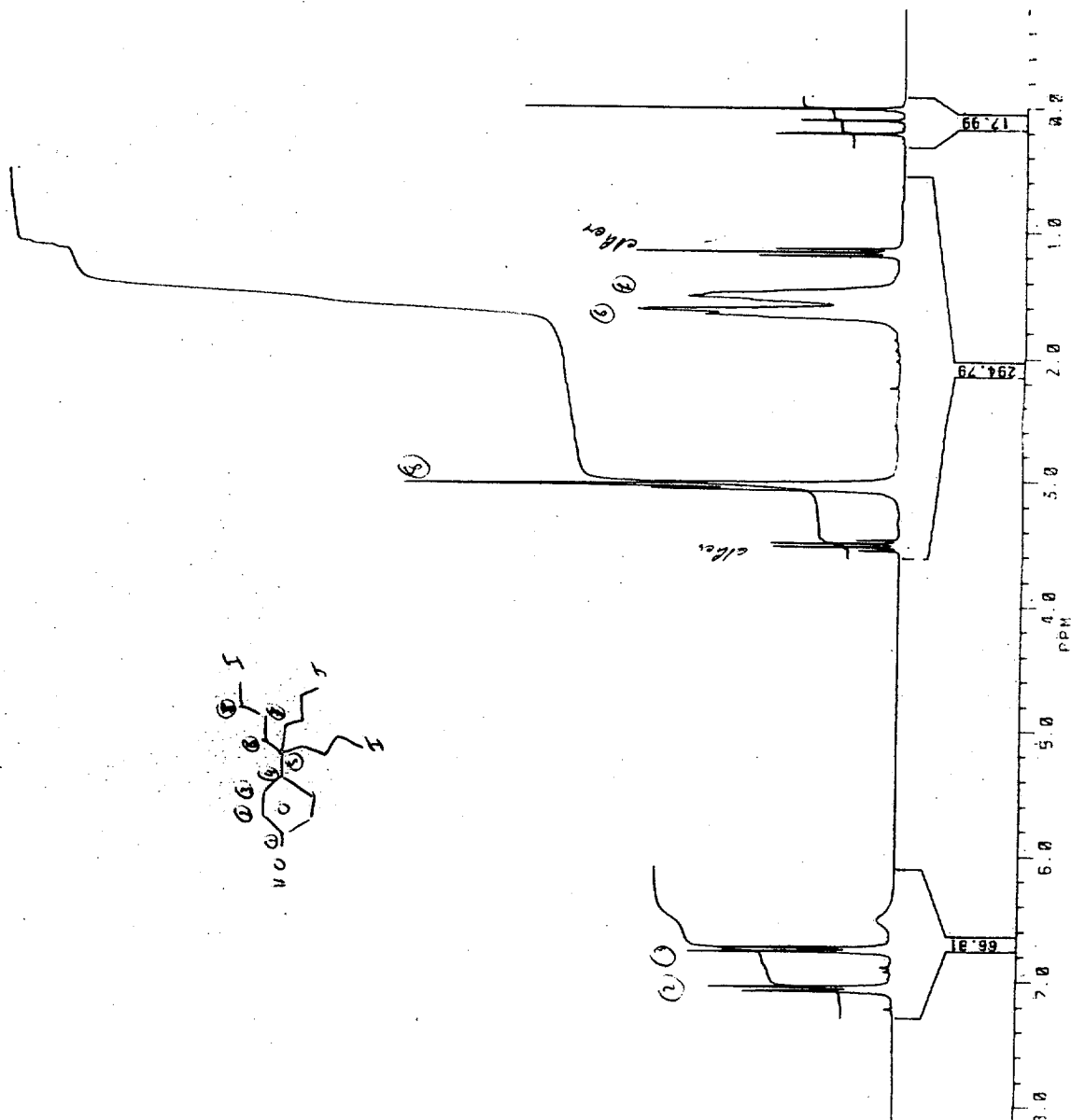
¹H RMN (CDCl₃) δ 7.10 and 6.81 (m, C₆H₄, 4H); 3.06 (t, CH₂I, 6H); 1.64 (m, CH₂CH₂I, 6H); 1.54 (m, CH₂C_{quat}, 6H). ¹³C RMN (CDCl₃) δ 153.76 (C_{quat arom}OH); 137.59 (C_{quat arom}C); 127.40 (CH_{arom}); 115.40 (CH_{arom}); 41.8 (C_{quat}-CH₂); 38.58 (CH₂CH₂I); 27.69 (CH₂C_{quat}); 8.45 (CH₂I). Anal. Calcd for C₁₆H₂₃I₃O : 31,55 ; H 3,31. Found C 30,85 ; H 3,03.

phenol trioxide ¹H NMR

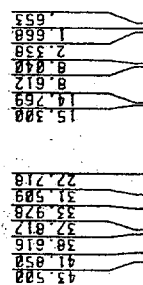
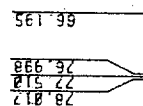
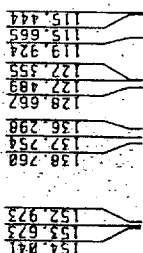
VS159



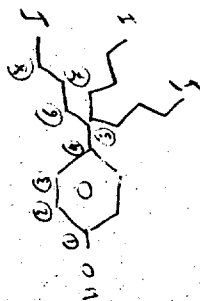
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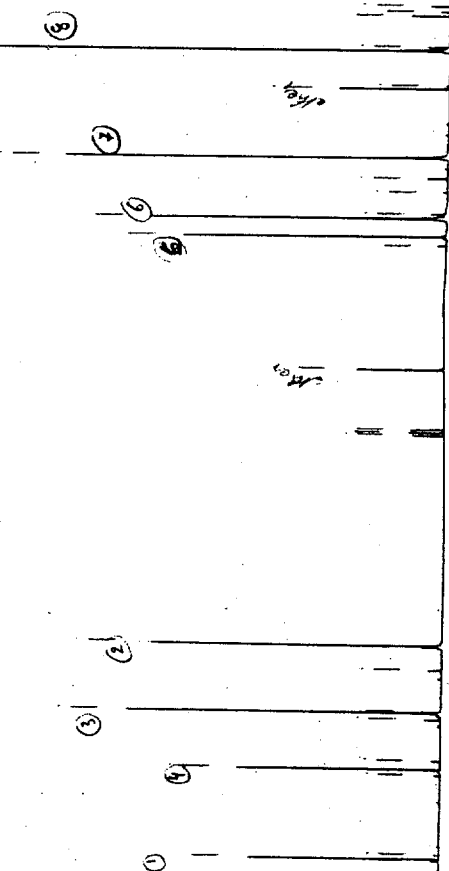
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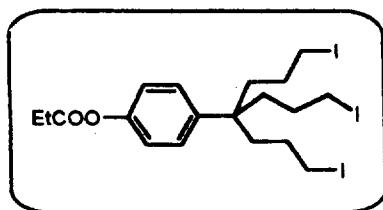


phenol triado 13 C NMR



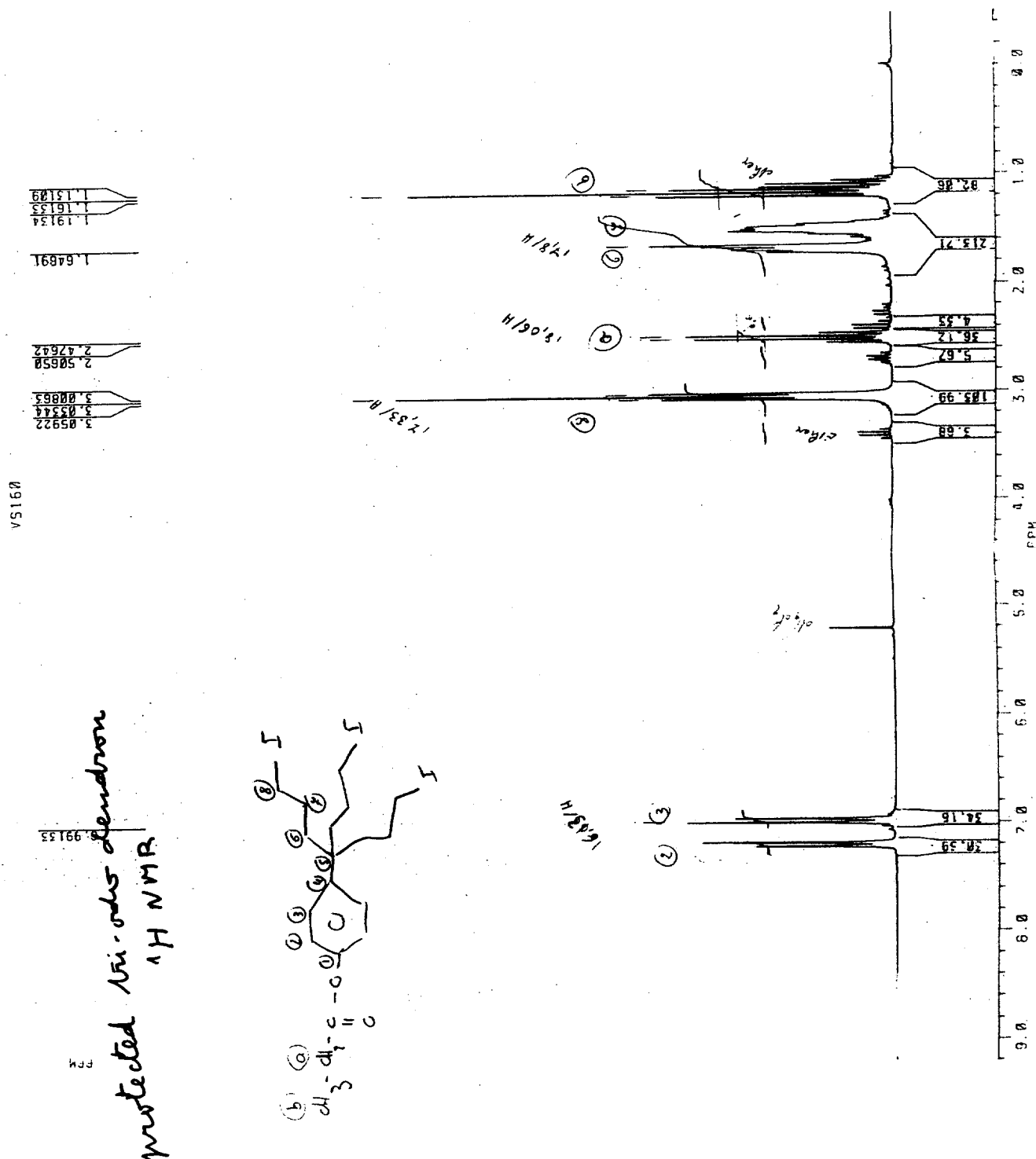
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18) *p*-(1,1-di(3-iodopropyl)-4-iodobutyl)phenolpropionate, 15

A solution of $\text{C}_2\text{H}_5\text{COI}$ is prepared by slowly adding 2.4 mL $\text{C}_2\text{H}_5\text{COCl}$ to 5g of Me_3SiI , stirring 15 min., then adding 22.6 mL dichloromethane. This solution is added into a Schlenk flask containing **14** (2.7g, 4.52 mmol) in 30 mL dichloromethane, then $\text{NEt}_2\text{-}i\text{-Pr}$ (0.84 mL, 4.83 mmol) is also added. The reaction mixture is stirred under nitrogen for 16 h, then extracted using 50 mL dichloromethane. The organic solution is washed with a saturated aqueous solution of sodium bicarbonate, then with an aqueous solution saturated with $\text{Na}_2\text{S}_2\text{O}_3$, and dried over sodium sulfate. After removing the solvent under vacuum, the product **15** is obtained as an orange oil (2.85g, 4.27 mmol, 94%).

^1H RMN (CDCl_3) δ 7.21 and 7.01 (m, C_6H_4 , 4H); 3.06 (t, CH_2I , 6H); 2.42 (q, $\text{CH}_3\text{CH}_2\text{CO}$, 2H); 1.71 (m, $\text{CH}_2\text{CH}_2\text{I}$, 6H); 1.58 (m, $\text{CH}_2\text{C}_{\text{quat}}$, 6H) 1.11 (t, $\text{CH}_3\text{CH}_2\text{CO}$, 3H). ^{13}C RMN (CDCl_3) δ 172.83 (CO); 148.93 ($\text{C}_{\text{quat arom CO}}$); 143.13 ($\text{C}_{\text{quat arom C}}$); 127.15 (CH_{arom}); 121.33 (CH_{arom}); 42.17 ($\text{C}_{\text{quat-CH}_2}$); 38.58 ($\text{CH}_2\text{CH}_2\text{I}$); 27.85 ($\text{CH}_3\text{CH}_2\text{CO}$); 27.5 ($\text{CH}_2\text{C}_{\text{quat}}$); 9.2 ($\text{CH}_3\text{CH}_2\text{CO}$); 7.84(CH_2I).



VSA160

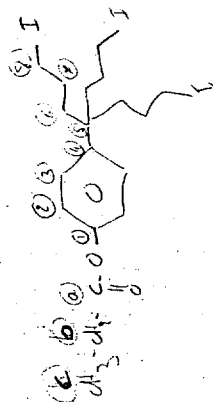
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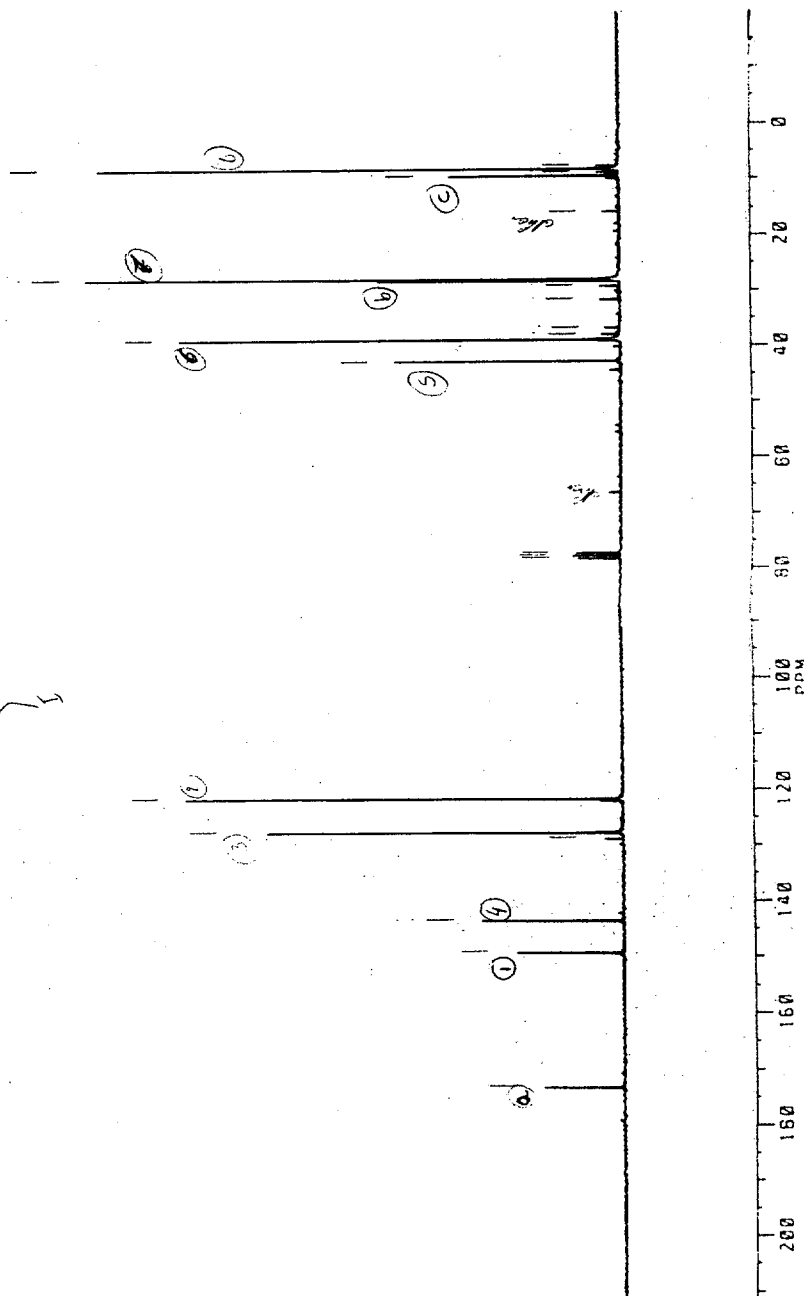
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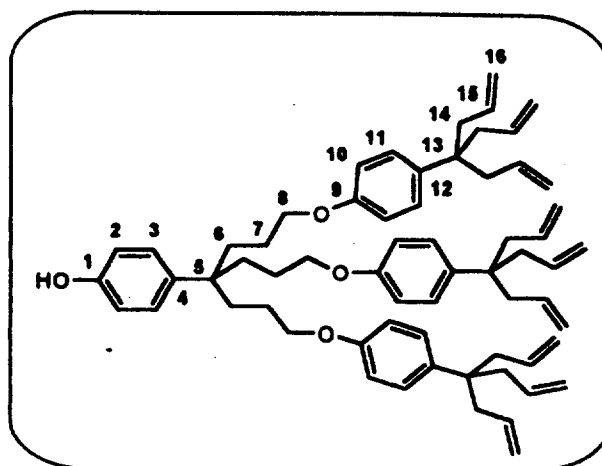
protected triols dendron
13C NMR



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19) 9-allyl phenate dendron 16



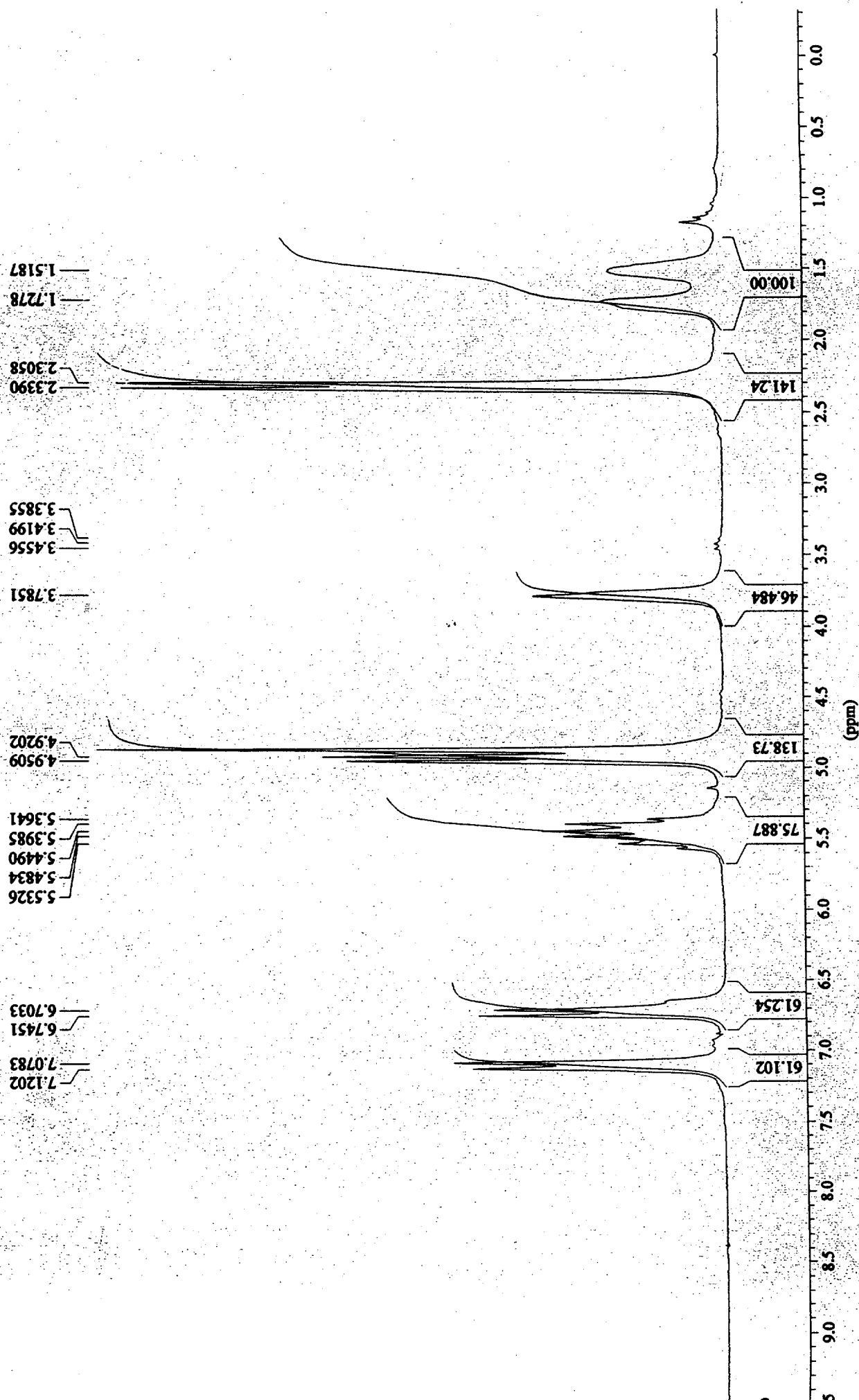
Triallylmethylphenol **3** (4.09g, 25 mmol) dissolved in 25 mL of freshly distilled DMF, then potassium carbonate (3.5g, 25 mmol) are introduced into a flamed Schlenk tube, and the mixture is stirred 30 min. under nitrogen at room temperature. The protected tri-iodo dendron **15** (2.85g, 4.26 mmol), dissolved in 10 mL of anhydrous DMF is slowly added, and the reaction mixture is stirred for two days at room temperature, then 3g potassium carbonate and 5 mL water are added, and the reaction mixture is stirred for 12h at 40°C. The product is extracted with 100mL ether, this solution is dried over sodium sulfate, then filtered and concentrated to 5mL. The product is purified by chromatography on a silica-gel column using pentane/ether (4/1) as the eluent. The 9-allyl phenate dendron **16** is obtained in this way as a light-brown oil (1.2g, 1.31 mmol, 30% yield).

^1H RMN (CDCl_3) δ 7.18 and 6.83 (m, CH_{arom} , 16H); 5.68-5.55 (m, CHCH_2 , 9H); 5.07-5 (m, CHCH_2 , 18H); 3.9 (m, CH_2O , 6H); 2.44 (d, CH_2 , 18H); 1.9 (m, $\text{C}_{\text{quat}}\text{CH}_2$, 6H); 1.65 (m, CH_2CH_2 , 6H). ^{13}C RMN (CDCl_3) δ 156.87 ($\text{C}_{\text{quat arom O}}$); 153.55 ($\text{C}_{\text{quat arom OH}}$); 138.52 ($\text{C}_{\text{quat arom C}}$); 137.77 ($\text{C}_{\text{quat arom C}}$); 134.76 (CHCH_2); 127.91 ($\text{CH}_{\text{arom COH}}$); 127.73 ($\text{CH}_{\text{arom COH}}$); 117.63 (CHCH_2); 115.19 ($\text{CH}_{\text{arom C}}$); 114.35 ($\text{CH}_{\text{arom C}}$); 68.40 (CH_2O); 42.77 ($\text{C}_{\text{quat}}\text{-CH}_2$); 42.15 (CH_2CH); 33.87 ($\text{CH}_2\text{CH}_2\text{O}$); 23.81 (CCH_2CH_2). MALDI TOF-MS (Matrix 2,5-dihydroxybenzoic acid) : $[\text{m/z} + \text{Na}^+] = 935.6$

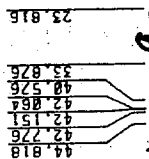
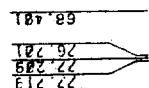
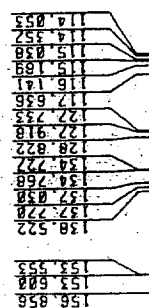
¹H NMR

Pendron 9-allyl

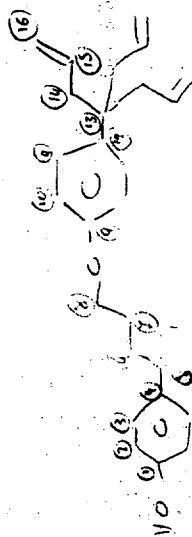
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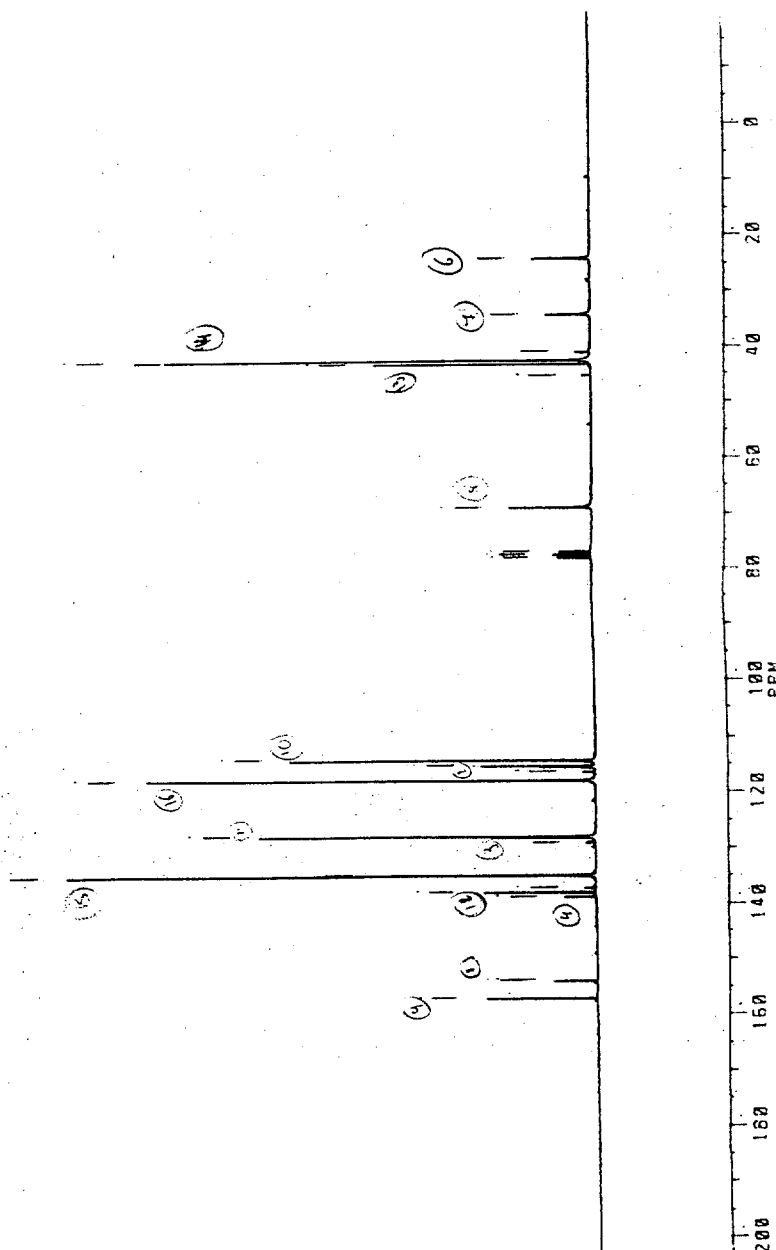
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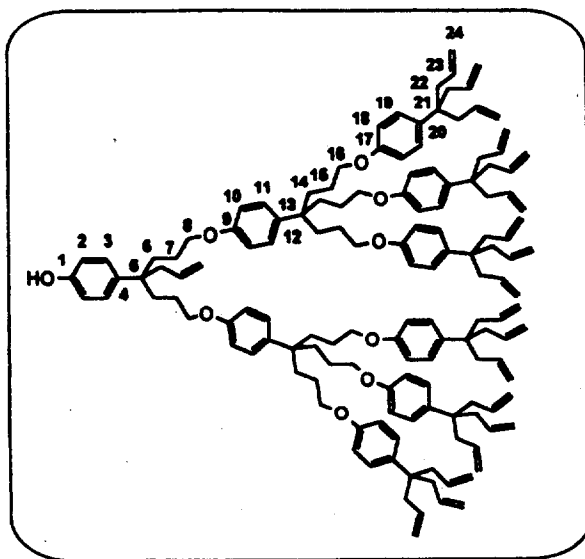
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20) 19-allylphenol dendron 17



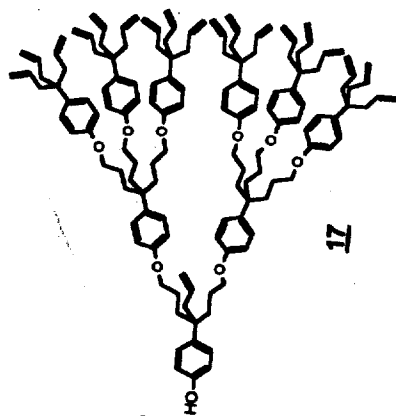
The 19-allylphenol dendron **17** is prepared from the nona-allyl phenol dendron **16** (0.750g, 0.8 mmol), the protected tri-iodo dendron **15** (0.100g, 0.15 mmol), potassium carbonate (0.120g, 0.8 mmol) and 6 mL DMF using the procedure described above in **19**) for the synthesis of the nona-allylphenate dendron **16**. The reaction product **17** is purified by chromatography on a silica-gel column using a pentane/ether mixture (4/1) as the eluent, which gives **17** as a light-brown oil (0.110g, 0.037 mmol, 25%).

^1H RMN (CDCl_3) δ 7.25 and 6.84 (m, CH_{arom} , 52H); 5.57 (m, CHCH_2 , 27H); 5.06–4.99 (m, CHCH_2 , 54H); 3.92 (m, CH_2O , 24H); 2.46 (d, CH_2 , 54H); 1.87 (m, $\text{C}_{\text{quat}}\text{CH}_2$, 24H); 1.65 (m, CH_2CH_2 , 24H). ^{13}C RMN (CDCl_3) δ 156.88 ($\text{C}_{\text{quat arom O}}$); 153.48 ($\text{C}_{\text{quat arom OH}}$); 138.61 ($\text{C}_{\text{quat arom C}}$); 137.77 ($\text{C}_{\text{quat arom C}}$); 134.71 (CHCH_2); 127.63 ($\text{CH}_{\text{arom COH}}$); 117.50 (CHCH_2); 115.04 ($\text{CH}_{\text{arom C}}$); 113.91 ($\text{CH}_{\text{arom C}}$); 68.24 (CH_2O); 42.7 ($\text{C}_{\text{quat}}\text{-CH}_2$); 42.15 (CH_2CH); 33.83 ($\text{CH}_2\text{CH}_2\text{O}$); 23.78 (CCH_2CH_2). MALDI TOF-MS (Matrix 2,5-dihydroxybenzoic acid): $[\text{m/z} + \text{Na}^+] = 2077.7$

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Dendron 19-allyl

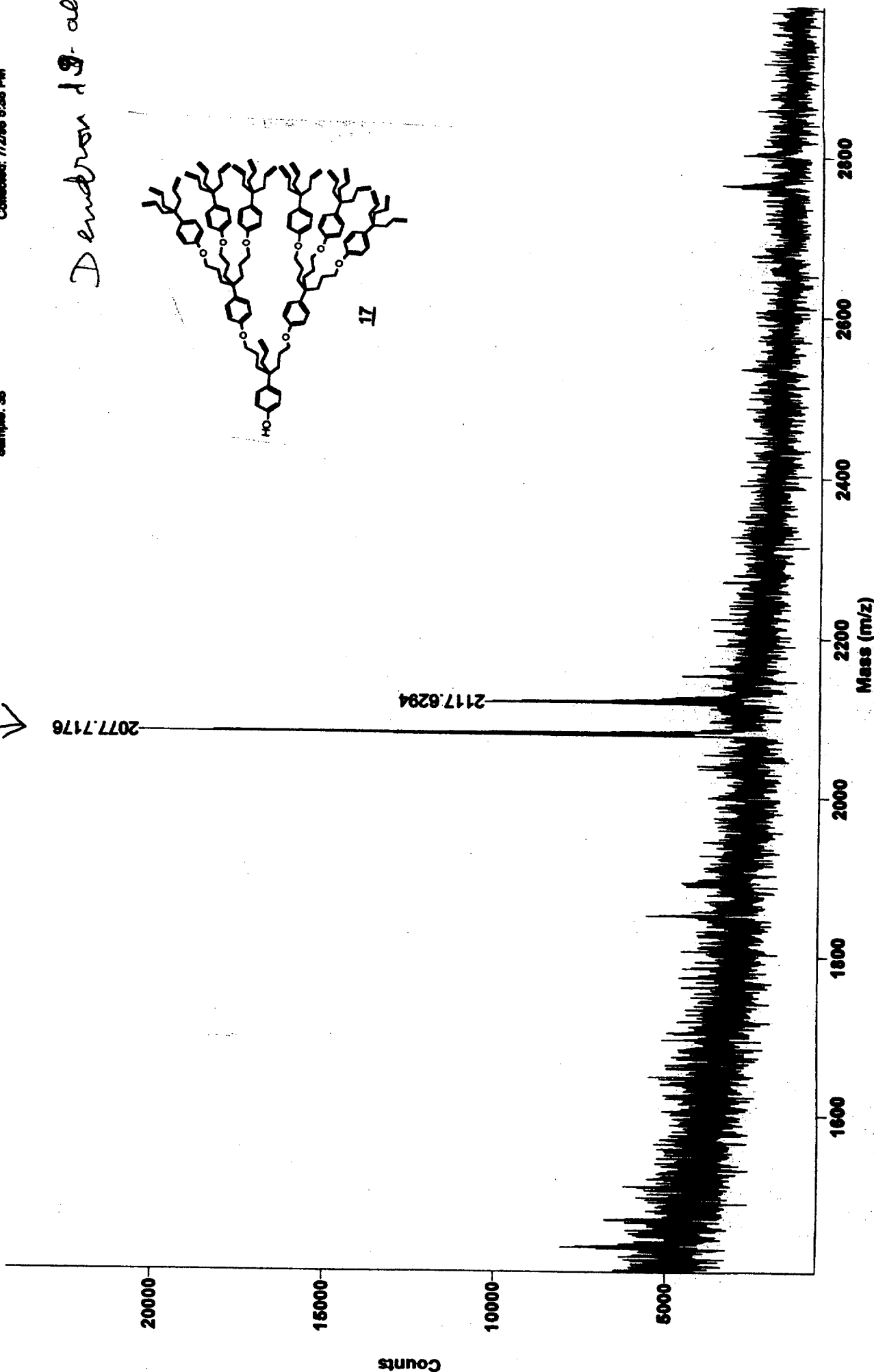


MN⁺



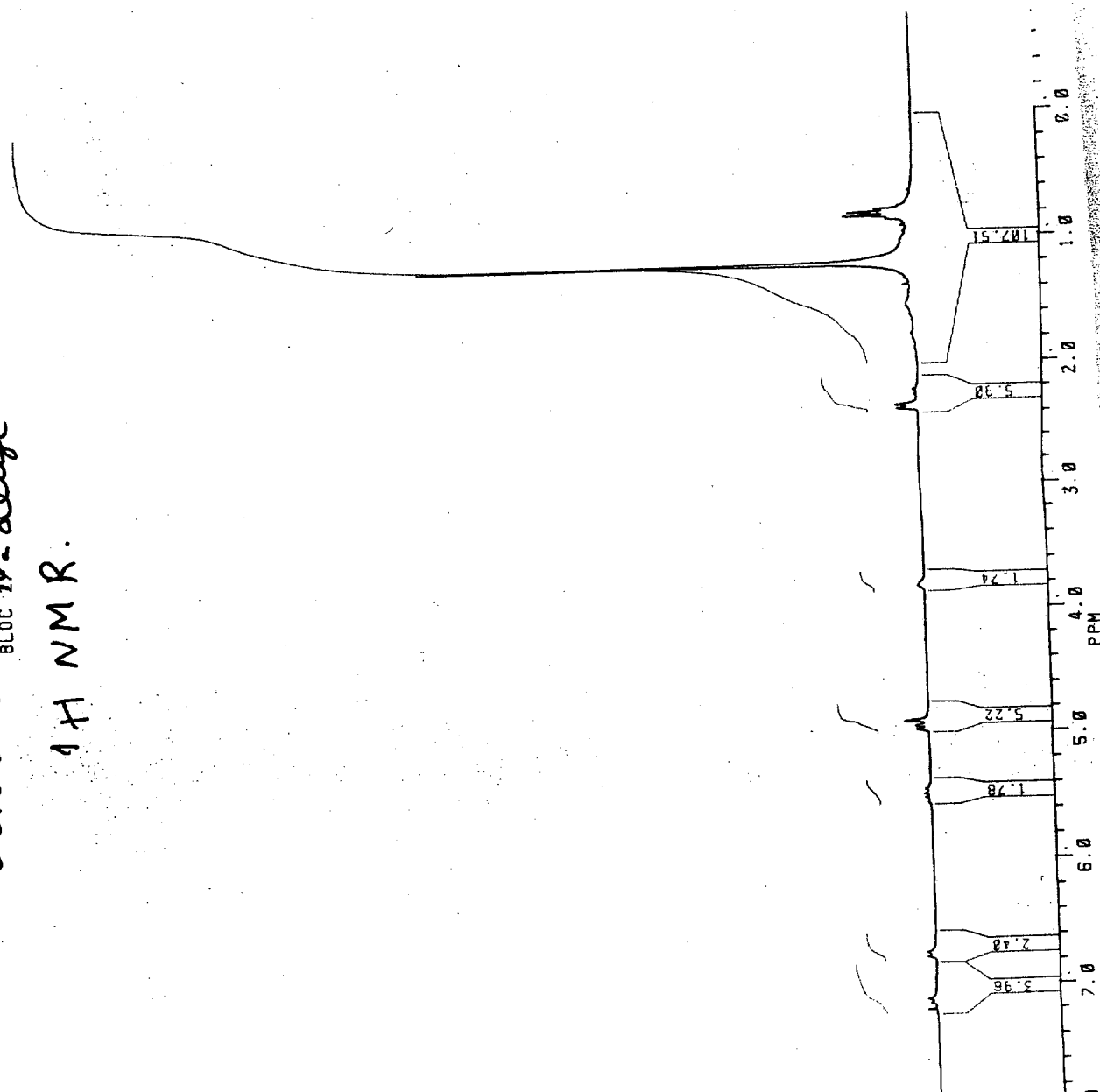
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dendron_{BLOC} 19-allyl
 1H NMR.

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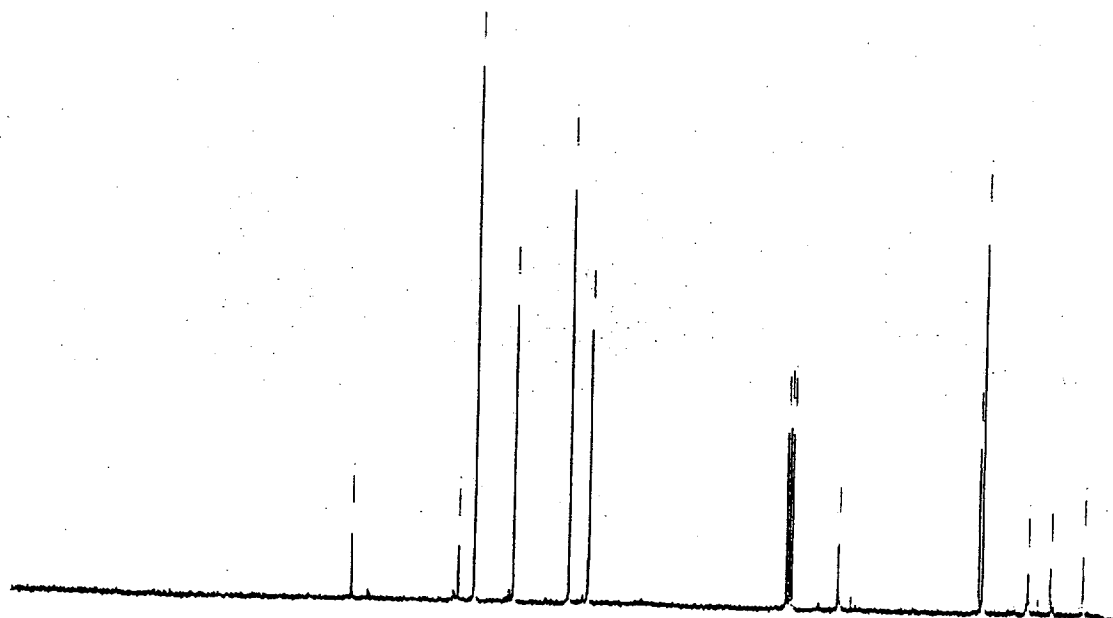
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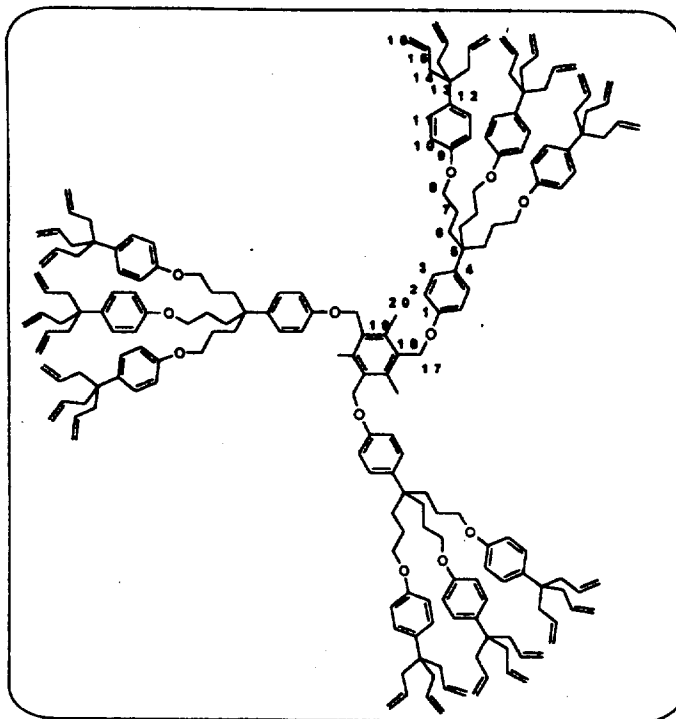
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¹³C NMR
dendron: bloc 19-allyl



21) 27-allyl 3C dendrimer 18



The synthesis of the 27-allyl 3C dendrimer **18** from the 9-allylphenol dendron **16** (0.200g, 0.218 mmol), 2,4,6-tris(bromomethyl)mesitylene (0.018g, 0.00456 mmol), potassium carbonate (0.045g, 0.325 mmol) in 10 mL acetone is achieved according to the procedure described above in 6) for the synthesis of the 27-allyl dendrimer **9** from the nona-iodo core **7**. The reaction product is purified by chromatography on a silica-gel column using dichloromethane as the eluent, which gives a light-brown oil (40 mg, 0.0138 mmol, 30% yield).

^1H RMN (CDCl_3) δ 7.24 and 6.82 (m, C_6H_4 , 36H); 5.4 (m, CHCH_2 , 27H); 4.98 (m, CHCH_2 , 54H); 3.8 (m, CH_2O , 18H); 2.41 (s, CH_3 , 9H); 2.38 (d, CH_2CHCH_2 , 54H); 1.87 (m, CCH_2CH_2 , 18H); 1.58 (m, $\text{CH}_2\text{CH}_2\text{O}$, 18H). ^{13}C RMN (CDCl_3) δ 156.87 ($\text{OC}_6\text{quatH}_4$); 137.56 (C_6quatH_4); 134.7 (CH_2CH); 127.63 (C_6H_4); 117.5 (CHCH_2); 113.85 (C_6H_4); 68.23 (CH_2O); 42.69 ($\text{C}_{\text{quat}}\text{CH}_2$); 41.97 (CH_2CHCH_2); 33.82 ($\text{CH}_2\text{CH}_2\text{O}$); 29.73 (CH_3); 23.77 (CCH_2CH_2). MALDI TOF-MS (Matrix 2,5-dihydroxybenzoic acid) : $[\text{m/z} + \text{Na}^+] = 2919$; $[\text{m/z} + \text{K}^+] = 2935.9$

UPMC - LCSOB

MALDI TOF Mass spectrum

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Savitsky-Golay Order = 2 Points = 19

convergent

