Concave Reagents, 45. 2,6-Di-tert-butylpyridine-Loaded Dendrimers and Their Use in Vinyl Triflate Synthesis

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Dedicated to Prof. Dr. Bernd Giese on the occasion of his 65th birthday

Abstract: 2,6-Di-tert-butyl-pyridine (DTBP) has been connected with dendrons and dendrimers of the Fréchet type. Four dendrimers, both first and second generation derivatives have been synthesized and used as non-nucleophilic, recyclable bases in the formation of cyclohexenyl-1-triflate from cyclohexanone.

Keywords: steric hindrance, dendrimers, triflate, base catalysis, recycling

Palladium-catalyzed cross-coupling reactions (e.g., Suzuki, Stille, Heck, Sonogashira) have become more and more important in organic synthesis. 2,3 Besides halogenated compounds, aryl, and vinyl triflates are also valuable starting materials. A one step synthesis of vinyl triflates developed by Stang 4 requires 2,6-di-tert-butylpyridine (DTBP, 2a) or its 4-methyl derivative 2b as a sterically hindered, non-nucleophilic base (Figure 1). With triflic anhydride (Tf2O), standard bases like pyridine form salts such as 1 and thus lead to heterogeneous reaction mixtures. When using nucleophilic tertiary bases such as pyridine, the triflated quarternary ions such as 1 become the triflating agents, while the use of DTBPs 2 leaves Tf2O as the triflating agent. 5

Figure 1

Using DTBP 2b as base, 4 cyclohexenyl-1-triflate (4) can be synthesized in 76% yield starting from cyclohexanone (3) and Tf2O (Scheme 1).

In this reaction, the base 2b has to be used in at least equimolar quantities, and it is expensive. Therefore a polymer-bound version 2c had been developed 6 but disappointingly, a lower yield (57%) and the formation of a dimeric side product 16 (Scheme 5) were observed (18%).

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the bromide 13 using tetrabromomethane and triphenylphosphine (Scheme 4).

This dendron 13 was then reacted with core molecules, the diphenol 8 and the triphenol 9, using conditions as discussed for the first-generation dendrimers. Thus, two second-generation dendrimers 14 and 15 could be synthesized in 63% and 58% yield, respectively (Scheme 5).

These second-generation dendrimers 14 and 15 carry up to twelve DTBP units on their surface and possess a molecular weight of up to 3845 g/mol which was verified by MALDI-MS. The dendrimers could be isolated in 100 mg batches. Spectroscopy as well as microanalyses showed no inclusion of solvent.

**Application in Vinyl Triflate Synthesis**

To test the ability of the DTBP-loaded dendrimers 10, 11, 14, and 15 to act as shielded bases, the synthesis of cyclohexyl-1-triflate (4) from cyclohexanone (3) and Tf$_2$O was carried out as described in the literature. Table 1 compares the yields of 4 when different DTBPs were used, including the dendrimers 10, 11, 14, and 15.

In contrast to the polymer 2c, DTBP 2b and all dendritic DTBPs 10, 11, 14, and 15 produced the vinyl triflates 4 in 70–76% yield, and no dimeric side product 16 was found. The dendritic DTBPs 10, 11, 14, and 15 could be recovered in yields of up to 90% (see Experimental, Table 2). Thus they offer an alternative to the single use of expensive 2b, and in contrast to the polymer bound DTBP 2c, they give the desired triflate 4 in yields comparable to 2b.

Melting points were determined on a Büchi hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Paragon FT-IR-spectrometer. $^1$H NMR spectra were recorded in CDCl$_3$ or CCl$_4$ solutions on Bruker AC 200 (200 MHz) and AM 300 (300 MHz) spectrometers with TMS as internal standard. $^{13}$C NMR spectra were recorded at 50 MHz or 75 MHz on a Bruker AC 200 or AM 300 with CDC$_3$ or CCl$_4$ as solvent using the TMS carbon signal as internal standard. Mass spectra (EI or CI) were obtained on a Finnigan MAT 44S. MALDI spectra were recorded on a Bruker Biflex III instrument. Analytical TLC was performed on commercial Merck plates coated with silica gel GF$_{254}$ (0.25 mm thick). Column chromatography was performed on silica gel, Merck Kieselgel (0.063–0.2 mm). Size-exclusion chromatography (GPC) was carried out with a Waters 510 HPLC pump and a Waters 486 tunable UV-detector; data analysis was performed with Millennium 2000 soft-
ware; column was from MZ laboratories (300 × 8 mm; pore size: 500 Å) with THF as solvent. Elemental analyses were carried out on VarioEl, Elementaranalysensysteme GmbH. 2,6-Di-tert-butyl-4-methylpyridine (2b) was synthesized according to the literature.13 All other starting materials were purchased and used without further purification.

Table 1  Comparison of the Yields of Cyclohexenyl-1-triflate (4) in the Reaction of Cyclohexanone (3) with Tf₂O Using a Range of DTBPs as Bases

<table>
<thead>
<tr>
<th>Base</th>
<th>Yield of 4 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b (4-Me-DTBP)</td>
<td>70, 76₄</td>
</tr>
<tr>
<td>2c (polymeric DTBP)</td>
<td>57₅,a</td>
</tr>
<tr>
<td>10 (1st-generation, 4 DTBPs)</td>
<td>74</td>
</tr>
<tr>
<td>11 (1st-generation, 6 DTBPs)</td>
<td>72</td>
</tr>
<tr>
<td>14 (2nd-generation, 8 DTBPs)</td>
<td>74</td>
</tr>
<tr>
<td>15 (2nd-generation, 12 DTBPs)</td>
<td>75</td>
</tr>
</tbody>
</table>

₅ The dimer 16 was found in 18% yield besides the desired product 4.

Scheme 5

4-(Bromomethyl)-2,6-di-tert-butylpyrididine (2d)
NBS (3.6 g, 21 mmol) and AIBN (ca. 100 mg) were added to a solution of 2,6-di-tert-butyl-4-methylpyridine (2b, 4 g, 20 mmol) in anhyd CCl₄ (200 mL). The solution was heated to reflux for 4 h. During this time, AIBN (3 × ca. 100 mg) was added (after 1 h, 2 h, and 3 h). When all NBS had reacted and only succinimide was floating on the solution (there was no more insoluble NBS at the bottom of the reaction vessel), the solid was filtered off and the solvent was evaporated in vacuo. Distillation in vacuo gave 4 g (70%) of 2d as a colorless oily liquid.

Bp 68 °C/0.02 Torr (Lit.14 94 °C/2 Torr).
IR (KBr): 2957, 2921, 2865 (CH), 1599 (Ar), 1479, 1416, 1360, 1249, 1219, 1164, 853, 698, 674 cm⁻¹.
¹H NMR (CCl₄, 200 MHz): δ = 1.37 [s, 18 H, C(C₃H₃)], 4.35 (s, 2 H, ArCH₂Br), 7.08 (s, 2 H, PyH).
¹³C NMR (CCl₄, 50 MHz): δ = 30.4 [q, C(CH₃)], 37.8 [s, C(CH₃)], 140.9 [s, Py(C-5)].
MS (Cl, isobutane): m/z (%) = 284 (100) [M⁺ + 1], 282 [M⁺ + 1] (70), 204 (21), 100 (31).

Dendrons 6 and 12; General Procedure
A mixture of the (dendritic) benzylbromide 2d¹⁴ or 7 (2.1–2.4 equiv), 3,5-dihydroxybenzyl alcohol (5, 1.0 equiv), anhyd K₂CO₃ (2.5–3.0 equiv) and 18-C-6 (0.2–0.6 equiv) was heated to reflux under nitrogen in anhyd acetone (100 mL). The progress of the reaction was monitored by TLC, and the reaction was stopped after 4–8 d when no starting material could be detected, or when no further conversion could be detected.
After evaporation of the solvent, H2O (90 mL) and CH2Cl2 (30 mL) were added, and the aqueous layer was extracted with CH2Cl2 (3–5×20–100 mL). After drying with MgSO4 and evaporation of the solvent in vacuo, the crude product was purified by chromatography (200–500-fold excess of silica gel).

3,5-Bis[2,6-di-tert-butylypyridin-4-ylmethyl]benzyl Alcohol (6)

According to the general procedure, 4-(bromomethyl)2,6-di-tert-butylypyridine (2d, 650 mg, 2.28 mmol), 3,5-di-bromo-2,6-di-tert-butylpyridine (3, 155 mg, 1.11 mmol), anhyd K2CO3 (336 mg, 2.44 mmol), and 15–C-6 (58 mg, 0.20 mmol) were reacted for 3 d. Chromatography (cyclohexane–Et2O, 2:1, Rf 0.15) gave 247 mg (77%) of 6 as a colorless, glassy solid.

Mp 45–48 °C.

IR (KBr): 3434 (OH), 2959, 2865 (CH), 1597, 1477, 1360, 1255, 1202, 1166, 1070, 857 cm–1.

Found: C, 77.40; H, 8.72; N, 4.66.

1H NMR (300 MHz, CDCl3): δ = 1.38 [s, 36 H, C(CH3)3], 4.66 [s, 2 H, ArCH2OH], 4.98 [br s, 12 H, PyCH2Ar], 6.57 [m, (J = 2.2 Hz, 1 H, ArH)], 6.60 [t, (J = 2.2 Hz, 2 H, ArH)], 6.66 [m, (d, J = 2.2 Hz, 2 H, ArH)], 6.71 [d, (J = 2.2 Hz, 4 H, ArH)], 7.15 [br s, 8 H, PyH].

13C NMR (75 MHz, CDCl3): δ = 66.9 (t, ArCH2OH), 67.6, 70.1 (2 t, PyCH2Ar, ArCH2OAr), 101.3, 101.5, 105.6, 106.5, 113.7 [several d, ArCH], Py(C=3,5), 139.4 [s, Ar(C=C)], 143.5 [s, Ar(C=CH2OH)], 145.1 [s, Ar(C=Py), 160.1 [s, Ar(C=3,5)], 168.1 [s, Py(C=2,6)].

MS (EL 70 eV): m/z (%) = 1197 (43) [M+1], 992 (18), 620 (12), 598 (11), 529 (38), 203 (100), 189 (39).

Found: C, 77.40; H, 8.72; N, 4.66.

Dendrons 7 and 13; General Procedure

Dendritic benzylic alcohol 6 or 12 (1.0 equiv) was dissolved in as little freshly distilled, anhyd THF as necessary to give a clear solution. Under nitrogen, PPh3 (1.2–1.3 equiv) and CBr4 (1.2–1.3 equiv) were added, and the mixture was stirred at rt. The reaction was stopped when TLC showed no more starting material or the mixture turned yellow due to the formation of decomposition products; this usually took 15–200 min. If starting material could still be detected after 30 min by TLC, PPh3 (0.6 equiv) and CBr4 (0.6 equiv) were added and stirring was continued. The reaction was quenched by the addition of a large excess of H2O (ca. 30 mL), and the aqueous layer was extracted with CH2Cl2 (3–5×15–100 mL). The combined organic layer was dried with MgSO4, and after evaporation of the solvent, the crude product was purified by chromatography (200–500-fold excess of silica gel).

3,5-Bis[2,6-di-tert-butylypyridin-4-ylmethyl]benzyl Bromide (7)

According to the general procedure, 6 (2.6 g, 4.7 mmol), CBr4 (2.0 g, 6.0 mmol) and PPh3 (1.6 g, 6.0 mmol) were reacted for 30 min. Chromatography (CH2Cl2–EtOH, 15:1; Rf 0.85) gave 2.6 g (87%) of 7 as a slightly yellow, glassy solid.

Mp 47–50 °C.

IR (KBr): 2958, 2859 (C=H), 1593, 1570 (Ar), 1479, 1447, 1420, 1358, 1202, 1166, 1070, 859 cm–1.

1H NMR (300 MHz, CDCl3): δ = 1.36 [s, 36 H, C(CH3)3], 4.42 [s, 2 H, ArCH2Br], 5.03 [s, 4 H, PyCH2(O)Ar], 6.60 [d, (J = 2.2 Hz, 1 H, ArH)], 6.68 [d, (J = 2.2 Hz, 2 H, ArH)], 7.13 [s, 4 H, PyH].

13C NMR (75 MHz, CDCl3): δ = 60.9 [q, C(CH3)3], 32.4 [s, C(CH3)3], 65.2 (t, ArCH2OH), 69.5 (t, PyCH2OAr), 101.2 [d, Ar(=CH)], 105.8 [d, Ar(=CH)], 113.7 [d, Py(=CH)], 143.6 [s, Ar(=C)], 145.2 [Py(=C)], 160.0 [Ar(=C)], 168.1 [s, Py(=C=O)].

MS (EL 70 eV): m/z (%) = 610 (100) [M+1], 608 (98) [M+2], 599 (17), 593 (18), 529 (36), 486 (13), 203 (70), 189 (74), 174 (16), 148 (14).

Found: C, 69.14; H, 8.05; N, 4.49.

Dendrimers 10 and 14; General Procedure

A mixture of dendritic benzylbromide 7 or 13 (2.2–2.3 equiv), 4,4′-dihydroxybiphenyl (8, 1.0 equiv), anhyd K2CO3 (3.0–3.3 equiv), and 18-C-6 (0.3–0.6 equiv) was dissolved in anhyd acetone (50 mL) and heated to reflux under nitrogen for 3–8 d, until no further conversion was observed by TLC. After cooling to rt. and evaporation of the solvent, the solid residue was dissolved in a threefold excess of H2O (30 mL) and CH2Cl2 (30 mL). The aqueous layer was extracted with...
CH₂Cl₂ (3–6 × 10 –50 mL). The combined organic layer was dried with MgSO₄, and after evaporation of the solvent, the crude product was purified by chromatography (300–500 fold excess of silica gel).

4,4′-Bis[3,5-bis(2,6-di-tert-butylpyridin-4-ylmethoxy)benzoxyl]biphenyl (10)

According to the general procedure, 7 (120 mg, 197 µmol), 4,4′-dihydroxybiphenyl (8, 17 mg, 94 µmol), anhyd K₂CO₃ (32.0 mg, 235 µmol), and 18-C-6 (8.0 mg, 28 µmol) were reacted for 6 d. Chromatography (cyclohexane–EtO, 5:1; Rf 0.35) gave 100 mg (81%) of 10 as a colorless, glassy solid.

Mp 60–65 °C.

IR (KBr): 2958, 2860 (CH), 1597, 1570 (Ar), 1497, 1456, 1418, 1359, 1280, 1213, 1163, 1058, 901, 858, 822 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 1.35 [s, 72 H, C(CH₃)₃], 5.01 (s, 8 H, PyCH₂OAr), 5.06 (s, 4 H, ArCH₂O–core), 6.61 (t, J = 2.2 Hz, 2 H, ArH), 6.74 (d, J = 2.2 Hz, 4 H, ArH), 7.01 (d, J = 8 Hz, 4 H, core–H), 7.15 (s, 8 H, Ar–H), 7.42 (d, J = 8 Hz, 4 H, core–H).

13C NMR (75 MHz, CDCl₃): δ = 30.1 [q, C(CH₃)₃], 37.7 [s, C(CH₃)₃], 69.6 (t, ArCH₂O–core), 69.9 (t, PyCH₂OAr), 102.2 (d, ArH), 106.6 (d, coreCH), 108.3 (d, ArCH), 113.3 (d, PyC–3,5), 129.7 (d, coreCH), 139.9 (s, Ar–C–1), 141.2 (s, core–C–1′), 145.0 (s, PyC–4), 156.8 (s, core–C–4′), 159.9 (s, Ar–C–3,5), 168.1 (s, PyC–2,6).

MS (EI, 70 eV): m/z (%) = 2454 (M⁺, 100), 2329 (M⁺ + 10), 2172 (M⁺ + 100), 1926 (M⁺ + 111), 1710 (M⁺ + 122), 1454 (M⁺ + 133), 1300 (M⁺ + 144), 1046 (M⁺ + 155), 800 (M⁺ + 166), 658 (M⁺ + 177), 516 (M⁺ + 188), 374 (M⁺ + 199), 232 (M⁺ + 210), 190 (M⁺ + 221), 148 (M⁺ + 232), 106 (M⁺ + 243), 74 (M⁺ + 254), 42 (M⁺ + 265), 31 (M⁺ + 276), 20 (M⁺ + 287), 9 (M⁺ + 298), 1 (M⁺ + 309).


1,1,1-Tris[3,5-bis(2,6-di-tetraethylbiphenyl-4-ylmethoxy)benzoxyl]phenylethane (15)

According to the general procedure, 13 (110 mg, 120 µmol), 1,1,1-tris(4-hydroxyphenyl)ethane (9, 11 mg, 36 µmol), anhyd K₂CO₃ (20 mg, 144 µmol), and 18-C-6 (8 mg, 18 µmol) were reacted for 8 d. Chromatography (cyclohexane–EtO, 4:1; Rf 0.8) gave 86 mg (58%) of 15 as a colorless glassy solid.

Mp 68–71 °C.

IR (KBr): 2958, 2923, 2861 (CH), 1597, 1570, 1497 (Ar), 1458, 1419, 1360, 1257, 1203, 1161, 1049, 856, 828, 770, 681 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 1.34 [s, 216 H, C(CH₃)₃], 2.06 (s, 3 H, core–C–4), 4.99 (br s, 42 H, ArCH₂O–core, ArCH₂OAr, PyCH₂OAr), 6.60 (m, (t, J = 2.2 Hz, 6 H, ArH), 6.73 (m, (d, J = 2.2 Hz, 12 H, ArH), 7.00 (d, J = 8 Hz, 4 H, core–H).

13C NMR (75 MHz, CDCl₃): δ = 30.1 [q, C(CH₃)₃], 37.8 [s, C(CH₃)₃], 69.6, 69.7 (2 t, ArCH₂O–core, ArCH₂OAr, PyCH₂OAr), 101.6, 106.6, 106.7, 113.8, 115.7, 127.7, 133.2 (several d, ArCH, core–CH, PyC–3,5), 139.3 (s, Ar–C–1), 141.3 (s, core–C–1′), 145.1 (s, PyC–4), 151.7 (s, core–C–4′), 160.0 (s, Ar–C–3,5), 168.1 (s, PyC–2,6).

MS (MALDI-TOF, THF, dithanol as matrix): m/z (%) = 3845 (M⁺, 100), 2875 (M⁺ + 10), 2016 (M⁺ + 122), 1275 (M⁺ + 144), 658 (M⁺ + 166), 422 (M⁺ + 188), 232 (M⁺ + 200), 148 (M⁺ + 221), 106 (M⁺ + 243), 94 (M⁺ + 254), 82 (M⁺ + 265), 70 (M⁺ + 276), 58 (M⁺ + 287), 46 (M⁺ + 298), 34 (M⁺ + 309), 22 (M⁺ + 320), 10 (M⁺ + 331).


Synthesis of Cyclohexenyl-1-trifluoromethylcarbene (4) from 2b

2,6-Di-tetraethylbiphenyl-4-methylpyridine (2b, 4.1 g, 20 mmol) was dissolved in anhyd CH₂Cl₂ (15 mL); cyclohexanone (3, 1.8 g, 18
mmol) and Tf2O (5.4 mg, 19 mmol) were added. The mixture was stirred at r.t. under argon for 24 h, towards the end of the reaction a precipitate formed. The solvent was evaporated in vacuo and the residue was dissolved in \( n \)-pentane (ca. 100 mL). The remaining solid was filtered off and washed several times with \( n \)-pentane (3 × 30 mL). The combined organic layer was washed with cold 1 N HCl (ca. 50 mL) and brine (ca. 50 mL). After drying with anhyd K2CO3, the solvent was evaporated in vacuo and the residue was distilled (70–72 °C/14 Torr; Lit.4,5 75–78 °C/15 Torr) yielding 3.0 g (70%, Lit.4,5 76%) of 4 as a colorless liquid in 98.5% purity by GC (column: Optima 1.25 m; temperature program: 5 min at 50 °C, 5 °C/min until 200 °C, 15 min at 200 °C, 20 °C/min until 250 °C, 20 min at 250 °C; cyclohexanone (3): \( t_f \) 4.6 min, cyclohexenyl-1-triflate 4: \( t_f \) 10.1 min, 2,6-di-tert-butyl-4-methylpyridine (2b): \( t_f \) 17.7 min, internal standard (\( n \)-hexadecane): \( t_f \) 26.1 min).

\[ \text{MS (EI, 70 eV): } m/z = 230 (M^+) \]

**Synthesis of Cyclohexenyl-1-triflate (4) with a Range of DTBPs**

All reactions were carried out in 5 mL vials sealed with teflon septa. The reagents were added in the following sequence: 2b (1.1 equiv), or the analogous dendrimers 10, 11, 14, or 15 [calculated on a DTBP unit per of cyclohexanone (3), see Table 2], cyclohexanone (3, 10 mg, 100 mmol), anhyd CH2Cl2 (2 mL), Tf2O (30 mg, 106 mmol). The vial was flushed with argon and sealed, a needle connected to an argon balloon was pierced through the septum. The reaction was quenched with H2O (10 mL) and stirred for 10 min at r.t. The reaction was quenched with H2O (10 mL). After filtration, the residue was dissolved in CH2Cl2 (ca. 20 mL), filtered through basic Al2O3 which was washed with \( n \)-pentane (30 mL), the combined organic layer was washed with cold 1 N HCl (10 mL) and stirred for 10 min at r.t. The reaction was quenched with H2O (10 mL) and filtered. The aqueous layer was extracted with CH2Cl2 (3 × 30 mL), and the combined organic layer was dried with MgSO4. After evaporation of the solvent, the combined residues were stirred with a THF-i-PrNH solution (9:1, 5 mL) for 10 min at r.t. The reaction was quenched with H2O (10 mL) and filtered. The aqueous layer was extracted with CH2Cl2 (3 × 30 mL), the combined organic layer was dried with MgSO4, and the solvents were evaporated in vacuo. Thus 70–80% of the dendrimers 10, 11, 14, and 15 could be regenerated. Further material could be extracted from Al2O3 thus increasing the yield to 80–90% (Table 2).18

All dendrimer-fixed DTBPs 10, 11, 14, and 15 remained active in the triflate reaction over several reaction/evaporation cycles, however, a change of color from colorless to dark yellow slowly occurred. This is in accordance with the observation that the dendrimer-fixed DTBPs decomposed slowly when stored for months. In these cases, the purity of the yellow compounds was checked by GPC and GPC purification was carried out if necessary.

For better recovery of the dendrimer-fixed DTBPs, the reaction time was reduced to 5 h in order to avoid decomposition in the strong acidic medium.

**Table 2** Batch Sizes for the Syntheses of Cyclohexen-1-yl Triflate (4) from Cyclohexanone (3) with Tf2O

<table>
<thead>
<tr>
<th>DTBP Amount (mg)</th>
<th>( n )-C15H30 Yield (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>23 (110)</td>
<td>17.9</td>
</tr>
<tr>
<td>10</td>
<td>34 (27)</td>
<td>42</td>
</tr>
<tr>
<td>11</td>
<td>35 (18)</td>
<td>32</td>
</tr>
<tr>
<td>14</td>
<td>35 (14)</td>
<td>41</td>
</tr>
<tr>
<td>15</td>
<td>35 (9)</td>
<td>27</td>
</tr>
</tbody>
</table>

**Sources**

1. H NMR (200 MHz, CDCl3): \( \delta = 1.56 \) (m, 2 H), 1.73 (m, 2 H), 2.13 (m, 2 H), 2.29 (m, 2 H), 5.71 (m, 1 H).

**Synthesis 2005, No. 9, 1383–1388 © Thieme Stuttgart - New York**

**References**

14. As an intermediate, 2d has been described in the synthesis of 1,2-bis(2,6-di-tert-butylpyridy1)ethane: Hou, C. J.; Okamoto, Y. *J. Org. Chem.* 1982, 47, 1977.
15. Besides M* and M* + 1, a signal at 2219 [M* + 325] was detectable but did not match any fragments. Relative intensities did not change upon variation of the laser power. Possibly, impure dendrons have been used lacking one pyridine and one dihydroxybenzyl alcohol unit. In other batches using dendrons which had been purified by GPC, this impurity could be avoided.
16. As for 14, [M* + 325] signals could be detected (m/z = 3519), probably because the dendron contained the same impurity. Again, the impurity could be avoided when dendron 13 was purified by GPC.
18. Sometimes the material had to be purified by GPC which lowered the yield.