

Supporting Information

Dendrimeric Tectons in Halogen Bonding-Based Crystal Engineering

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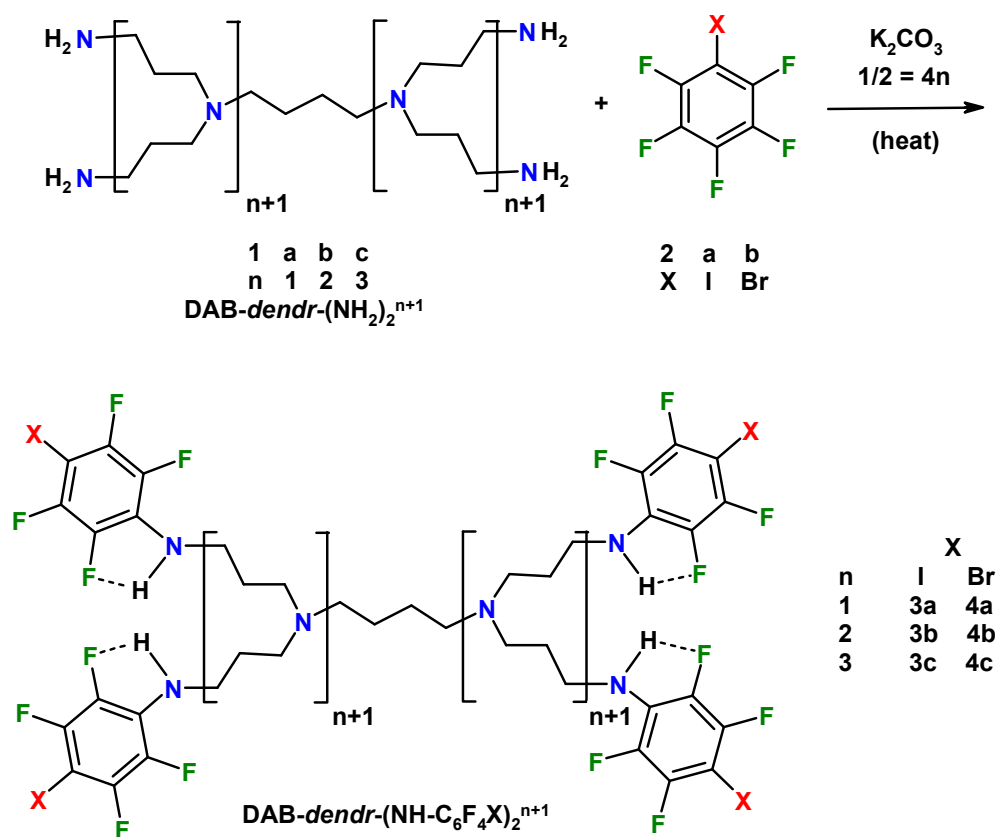
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Scheme 2.



DAB-dendr-(NH-C₆F₄I)₂² C₄₀H₃₆N₆F₁₆I₄ 3a

White solid, mp = 100-103 °C; 68% yield; IR $\nu_{\max}$ = 3424, 3165, 2953, 2823, 1640, 1524, 1488, 1149, 947, 796 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 5.03 (4 H, br s, NH), 3.47 (8 H, m, NH-CH₂), 2.53 (8 H, t, J = 6.4 Hz, CH₂-N), 2.42 (4 H, m, CH₂-N), 1.75 (8 H, quintet, J = 6.4 Hz, CH₂-CH₂-NH), 1.45 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 147.3 (dm, $^1J_{C,F}$ = 241 Hz, C_{ar}), 136.9 (dm, $^1J_{C,F}$ = 241 Hz, C_{ar}), 128.7 (m, C_{ar}-N), 54.1 (CH₂-N), 53.8 (t, $^2J_{C,F}$ = 28.3 Hz, C_{ar}-I), 52.5 (CH₂-N), 45.1 (t, $^4J_{C,F}$ = 4.3 Hz, CH₂-NH), 27.1 (N-CH₂-CH₂-CH₂-N), 24.9 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -158.2 (8 F, d, $^3J_{F,F}$ = 18 Hz, CF-CN), -124.5 (8 F, d, $^3J_{F,F}$ = 18 Hz, CF-CI); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ -168.3 (4 F, br t, $^3J_{F,F}$ = 22 Hz) and -155.6 (4 F, br t, $^3J_{F,F}$ = 20 Hz) CF-CF-CI and/or CF-CF-CN, -156.6 (4 F, br d, $^3J_{F,F}$ = 21 Hz) and -115.3 (4F, br d, $^3J_{F,F}$ = 24 Hz) CF-CN and/or CF-CI; MS (ESI) m/z 1413 (M+H⁺) isotope cluster.

DAB-dendr-(NH-C₆F₄Br)₂² C₄₀H₃₆N₆F₁₆Br₄ 4a

White solid, mp = 85-87 °C; 74% yield; IR $\nu_{\max}$ = 3423, 3220, 2954, 2822, 1640, 1518, 1494, 1154, 956, 821 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 4.89 (4 H, br s, NH), 3.45 (8 H, m, NH-CH₂), 2.55 (8 H, m, CH₂-N), 2.44 (4 H, m, CH₂-N), 1.76 (8 H, quintet, J = 6.3 Hz, CH₂-CH₂-NH), 1.46 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 145.3 (dm, $^1J_{C,F}$ = 243 Hz, C_{ar}), 137.2 (dm, $^1J_{C,F}$ = 241 Hz, C_{ar}), 127.8 (m, C_{ar}-N), 84.5 (t, $^2J_{C,F}$ = 23.5 Hz, C_{ar}-Br), 54.2 (CH₂-N), 52.6 (CH₂-N), 45.2 (t, $^4J_{C,F}$ = 4.2 Hz, CH₂-NH), 27.2 (N-CH₂-CH₂-CH₂-N), 24.9 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -158.4 (8 F, d, $^3J_{F,F}$ = 18 Hz, CF-CN), -136.2 (8 F, d, $^3J_{F,F}$ = 18 Hz, CF-CBr); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ -170.2 (4 F, br t, $^3J_{F,F}$ = 23 Hz) and -157.4 (4 F, br t, $^3J_{F,F}$ = 20 Hz) CF-CF-CBr and/or CF-CF-CN, -158.2 (4 F, br d, $^3J_{F,F}$ = 21 Hz) and -130.9 (4 F, br d, $^3J_{F,F}$ = 23 Hz) CF-CN and/or CF-CBr. MS (ESI) m/z 1225 (M+H⁺) most abundant peak of the isotope cluster of title compound.

DAB-dendr-(NH-C₆F₄I)₂³ C₈₈H₈₈N₁₄F₃₂I₈ 3b

Yellow oil; 65% yield; IR $\nu_{\max}$ = 3428, 2948, 2816, 1637, 1513, 1486, 1147, 947, 906, 800, 730 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 5.07 (8 H, br s, NH), 3.47 (16 H, m, NH-CH₂), 2.53 (20 H, m, N-CH₂-CH₂-CH₂-NH, N-CH₂-CH₂-CH₂-N), 2.41 (16 H, m, N-CH₂-CH₂-CH₂-N, CH₂-CH₂-N), 1.75 (16 H, quintet, J = 5.9 Hz, CH₂-CH₂-NH), 1.61 (8 H, m, N-CH₂-CH₂-CH₂-N), 1.34 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 147.3 (dm, $^1J_{C,F}$ = 241 Hz, C_{ar}), 136.9 (dm, $^1J_{C,F}$ = 242 Hz, C_{ar}), 128.7 (m, C_{ar}-N), 53.8 (t, $^2J_{C,F}$ = 28.3 Hz, C_{ar}-I), 52.4 (CH₂-N), 52.1 (CH₂-N), 51.9 (CH₂-N), 45.1 (t, $^4J_{C,F}$ = 4.2 Hz, CH₂-NH), 27.1 (N-CH₂-CH₂-CH₂-N), 24.1 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -158.1 (16 F, d, $^3J_{F,F}$ = 19.9 Hz, CF-CN), -124.3 (16 F, d, $^3J_{F,F}$ = 19.9 Hz, CF-CI); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ -168.4 (8 F, br t, $^3J_{F,F}$ = 23 Hz) and -155.6 (8 F, br t, $^3J_{F,F}$ = 20 Hz) CF-CF-CI and/or CF-CF-CN, -156.7 (8 F, br d, $^3J_{F,F}$ = 18 Hz) and -115.3 (8 F, br d, $^3J_{F,F}$ = 24 Hz) CF-CN and/or CF-CI. MS (ESI) m/z 2965-2966 (M+H⁺) isotope cluster.

DAB-dendr-(NH-C₆F₄Br)₂³ C₈₈H₈₈N₁₄F₃₂Br₈ 4b

Brown oil; 74% yield; IR $\nu_{\max}$ = 3423, 3220, 2950, 2817, 1640, 1492, 1151, 951, 823 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 4.90 (8 H, br s, NH), 3.46 (16 H, m, NH-CH₂), 2.54 (20 H, m, N-CH₂-CH₂-CH₂-NH, N-CH₂-CH₂-CH₂-N), 2.43 (16 H, m, N-CH₂-CH₂-CH₂-N, CH₂-CH₂-N), 1.76 (16 H, quintet, J = 5.9 Hz, CH₂-CH₂-NH), 1.61

(8 H, m, N-CH₂-CH₂-CH₂-N), 1.35 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 145.2 (dm, ¹J_{C,F} = 243, C_{ar}), 136.5 (dm, ¹J_{C,F} = 241 Hz, C_{ar}), 127.8 (m, C_{ar}-N), 84.2 (t, ²J_{C,F} = 23.5 Hz, C_{ar}-Br), 52.4 (CH₂-N), 52.1 (CH₂-N), 51.9 (CH₂-N), 45.1 (t, ⁴J_{C,F} = 4.2 Hz, CH₂-NH), 27.1 (N-CH₂-CH₂-CH₂-N), 24.2 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -159.1 (16 F, d, ³J_{F,F} = 18.9 Hz, CF-CN), -137.0 (16 F, d, ³J_{F,F} = 18.9 Hz, CF-CBr); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ -170.0 (8 F, m) and -157.4 (8 F, br t, ³J_{F,F} = 21 Hz) CF-CF-CBr and/or CF-CF-CN, -158.1 (8 F, br d, ³J_{F,F} = 20 Hz) and -130.8 (8 F, br d, ³J_{F,F} = 18 Hz) CF-CN and/or CF-CBr. MS (ESI) m/z 2589 (M + H⁺) most abundant peak of the isotope cluster of title compound.

DAB-dendr-(NH-C₆F₄I)₂⁴ C₁₈₄H₁₉₂N₃₀F₆₄I₁₆ 3c

Yellow oil; 50% yield. ¹H NMR (250 MHz, CDCl₃): δ 5.10 (16 H, br s, NH), 3.46 (32 H, m, NH-CH₂), 2.52 (56 H, m, N-CH₂-CH₂-CH₂-NH, N-CH₂-CH₂-CH₂-N), 2.40 (28 H, m, N-CH₂-CH₂-CH₂-N, CH₂-CH₂-N), 1.75 (32 H, quintet, *J* = 5.9 Hz, CH₂-CH₂-NH), 1.58 (24 H, m, N-CH₂-CH₂-CH₂-N), 1.25 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 147.3 (dm, ¹J_{C,F} = 240 Hz, C_{ar}), 136.9 (dm, ¹J_{C,F} = 242 Hz, C_{ar}), 128.8 (m, C_{ar}-N), 53.8 (t, ²J_{C,F} = 28.4 Hz, C_{ar}-I), 52.5 (CH₂-N), 52.2 (CH₂-N), 51.9 (CH₂-N), 45.1 (t, ⁴J_{C,F} = 4.2, CH₂-NH), 27.1 (N-CH₂-CH₂-CH₂-N), 24.1 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -157.9 (32 F, d, ³J_{F,F} = 19.0 Hz, CF-CN), -124.3 (32 F, d, ³J_{F,F} = 19.0 Hz, CF-CI); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ; -168.4 (16 F, m) and -155.6 (16 F, m) CF-CF-CI and/or CF-CF-CN, -156.7 (16 F, br d, ³J_{F,F} = 18 Hz), -115.3 (16 F, br d, ³J_{F,F} = 25 Hz) CF-CN and/or CF-CI. MS (ESI) m/z 2024 (M+3H)³⁺ isotope cluster not resolved.

DAB-dendr-(NH-C₆F₄Br)₂⁴ C₁₈₄H₁₉₂N₃₀F₆₄Br₁₆ 4c

Brown oil; 45% yield. ¹H NMR (250 MHz, CDCl₃): δ 5.03 (16 H, br s, NH), 3.44 (32 H, m, NH-CH₂), 2.54 (56 H, m, N-CH₂-CH₂-CH₂-NH, N-CH₂-CH₂-CH₂-N), 2.44 (28 H, m, N-CH₂-CH₂-CH₂-N, CH₂-CH₂-N), 1.93-1.42 (56 H, m, CH₂-CH₂-N), 1.30 (4 H, m, N-CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 145.3 (dm, ¹J_{C,F} = 243 Hz, C_{ar}), 136.6 (dm, ¹J_{C,F} = 241 Hz, C_{ar}), 127.8 (m, C_{ar}-N), 84.3 (t, ²J_{C,F} = 23.5 Hz, C_{ar}-Br), 52.5 (CH₂-N), 52.1 (CH₂-N), 51.9 (CH₂-N), 45.1 (t, ⁴J_{C,F} = 4.2 Hz, CH₂-NH), 27.1 (N-CH₂-CH₂-CH₂-N), 24.1 (N-CH₂-CH₂-CH₂-CH₂-N). ¹⁹F NMR (235 MHz, CDCl₃), *para* isomer: δ -159.1 (32 F, d, ³J_{F,F} = 18.3 Hz, CF-CN), -137.1 (32 F, d, ³J_{F,F} = 18.3 Hz, CF-CBr); ¹⁹F NMR (235 MHz, CDCl₃), *ortho* isomer: δ -170.2 (16 F, br t, ³J_{F,F} = 24 Hz) and -157.4 (16 F, br t, ³J_{F,F} = 21 Hz) CF-CF-CBr and/or CF-CF-CN, -158.2 (16 F, br d, ³J_{F,F} = 15 Hz) and -130.9 (16 F, br d, ³J_{F,F} = 23 Hz) CF-CN and/or CF-CBr. MS (ESI) m/z 2660 (M+2H)²⁺ isotope cluster not resolved.

Table 2. Shifts of CF=CX signals in ^{19}F NMR spectra of 3a-c, 4a-c on pyridine addition.

Different amounts of excess pyridine were added to a 0.005 M solution of dendrimers **3a-c** and **4a-c** in CDCl_3 (CFCl_3 as internal standard). The upfield shifts ($\Delta\delta$ (ppm) = $\delta(\text{pure dendrimer}) - \delta(\text{dendrimer in the presence of pyridine})$) for the CF=CX signals are reported in Table 2, while the CF-CF=CX shift changes, if any, were negligible. The amount of added pyridine changed with the generation (*e.g.* 50 equivalents for generation 1, 100 equivalents for generation 2, 200 equivalents for generation 3) so that the ratio between iodine atoms number and pyridine nitrogen atoms number (namely the ratio between XB-donor and XB-acceptor sites) was either 2/25 or 2/10 in all the experiments.

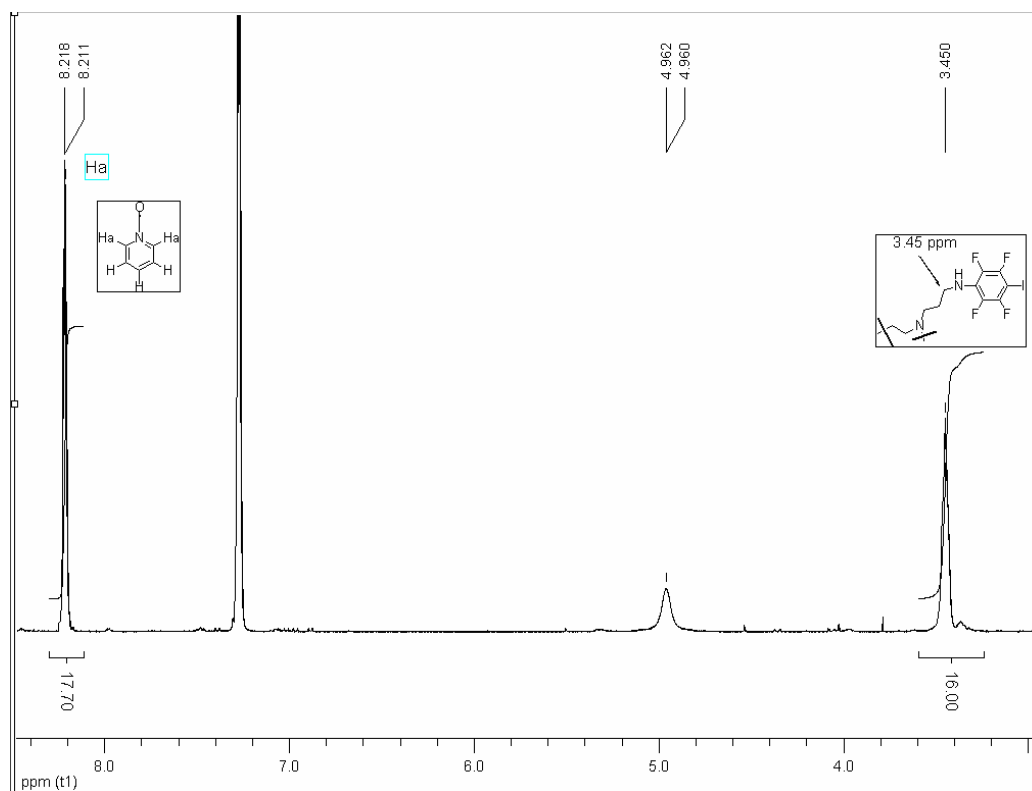
Dendrimer	I/N ratio	$\Delta\delta$ (ppm)
3a	2/25	0.05
3a	2/10	0.02
3b	2/25	0.06
3b	2/10	0.03
3c	2/25	0.09
3c	2/10	0.04
4a	2/25	0.03
4b	2/25	0.04
4c	2/25	0.05

Table 3.

	3a	7
I ₁	74.611	84.194
I ₂	53.722	66.276
I ₃	31.388	25.902
I _{av}	53.240	58.791
N3...N7	2.837(2) Å	2.870(3) Å
C1-C2-N3-C4	82.3(2) °	175.5(2) °
C2-N3-C4-C5	-154.8(2) °	68.1(3) °
N3-C4-C5-C6	69.2(3) °	67.7(3) °
C4-C5-C6-N7	-60.4(4) °	-61.8(5) °
C5-C6-N7-C8	-172.4(2) °	171.6(2) °
C1-C2-N3-C14	-153.2(2) °	58.0(2) °
C2-N3-C14-C15	80.5(2) °	59.7(2) °
N3-C14-C15-C16	173.1(2) °	-164.9(2) °
C14-C15-C16-N17	-168.4(2) °	-177.6(2) °
C15-C16-N17-C18	-70.3(4) °	-146.3(2) °
I1...F6[3/2-x,1/2+y,1/2-z]	3.120(2) Å	
I2...F4[2-x,1-y,1-z]	3.266(2) Å	
F1...H7	2.22 Å	
F4...H6B	2.42 Å	
F5...H17	2.19 Å	
F8...H16B	2.28 Å	
F8...H17[3/2-x,1/2+y,1/2-z]	2.52 Å	
I1...N35[x,1+y,z]		2.943(3) Å
C11-I1...N35[x,1+y,z]		172.71(10) °
I2...N26[1/2-X,-3/2+Y,1/2-Z]		2.838(3) Å
C11-I2...N26[x,1+y,z]		177.61(10) °
F1...H7		2.42 Å
F4...H6B		2.29 Å
F5...H17		2.34 Å
F8...H24[1/2-x,-1/2+y,1/2-z]		2.45 Å
Centroid A		C8,C9,C10,C11,C12,C13
Centroid B		C18,C19,C20,C21,C22,C23
Centroid C		C24,C25,N26,C27,C28,C29
Centroid D		C32,C33,C34,N35,C36,C37
D...C		3.810 Å
C...B		3.646 Å
B...A'		3.716 Å
A'...A		3.857 Å

Determination of the complexation properties of DAB-*dendr*-(NH-C₆F₄I)₂³ **3b**

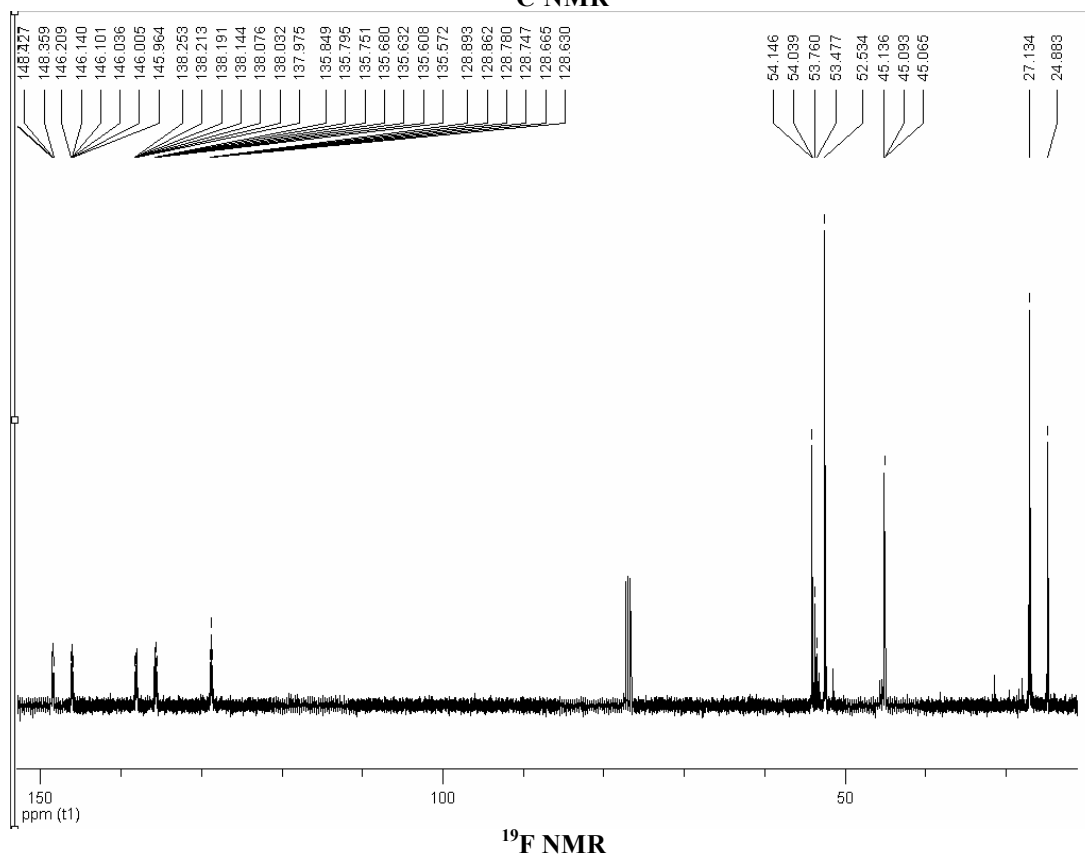
A dichloromethane solution of DAB-*dendr*-(NH-C₆F₄I)₂³ **3b** and pyridine *N*-oxide (molar ratio dendrimer : pyridine *N*-oxide = 1 : 800) is prepared. After partial evaporation of the solvent, a brownish oil separated from a yellowish liquid. The liquid was removed, the oil was washed with water and diluted in CDCl₃. After drying over anhydrous Na₂SO₄, the ¹H NMR was registered and showed a CH₂-NH-C₆F₄I / CH=CH-NO ratio (1/1.05) consistent with the binding of a pyridine *N*-oxide to any iodofluorobenzene residue of the dendrimer.



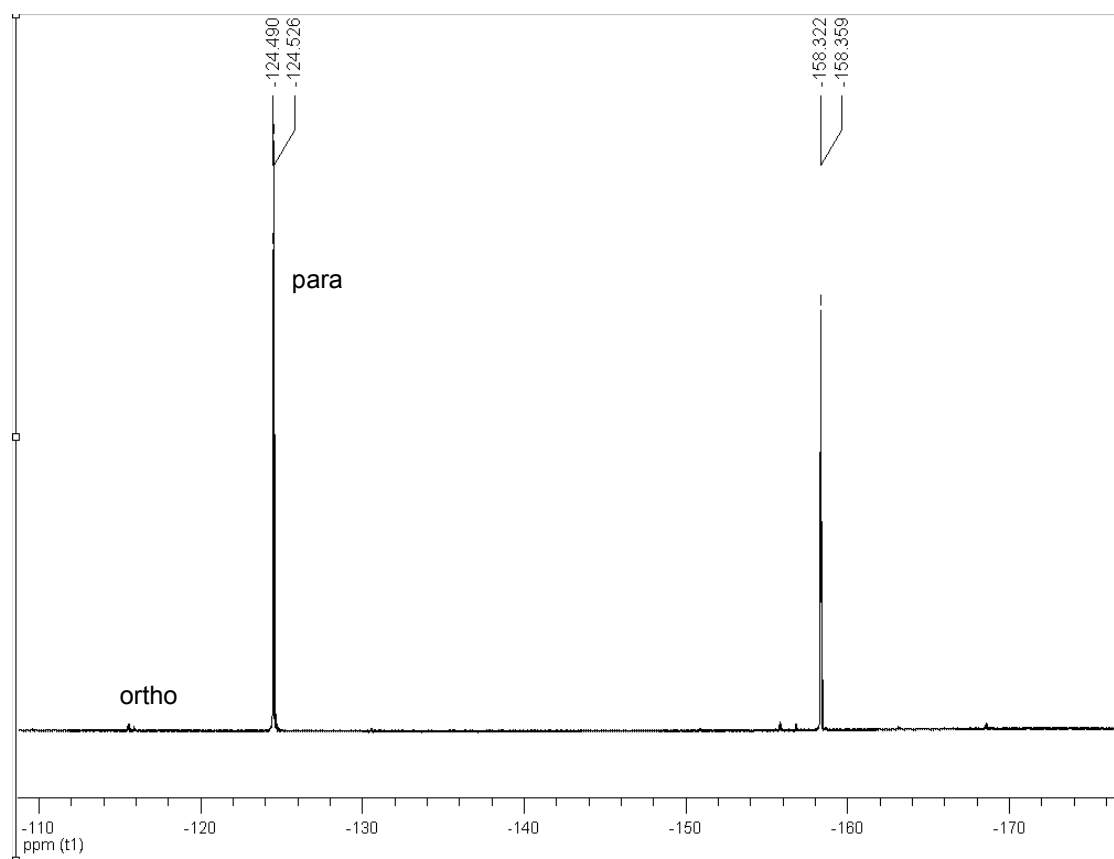
Similarly, a dichloromethane solution of DAB-*dendr*-(NH-C₆F₄I)₂⁴ **3c** and pyridine *N*-oxide (molar ratio dendrimer : pyridine *N*-oxide = 1 : 1600) was partially evaporated, the separated oil was removed and repeatedly washed with water. On ¹H NMR analysis of the residue, the CH₂-NH-C₆F₄I / CH=CH-NO ratio was 1.00:0.96, once again consistent with the binding of a pyridine *N*-oxide to any iodotetrafluorobenzene residue of the dendrimer.

^{19}F and ^{13}C NMR spectra of DAB-*dendr*-(NH-C₆F₄X)₂ⁿ⁺¹ (3a-c and 4a-c, X = I, Br and n = 1, 2, 3)

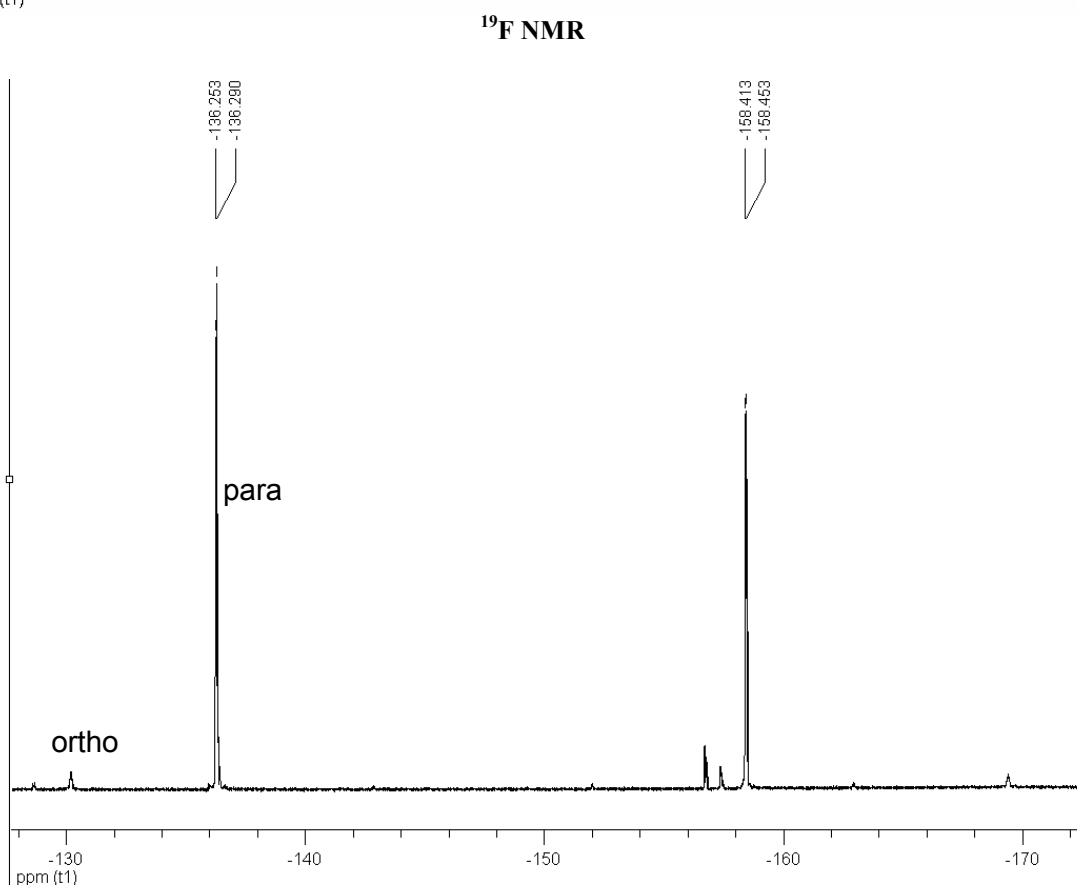
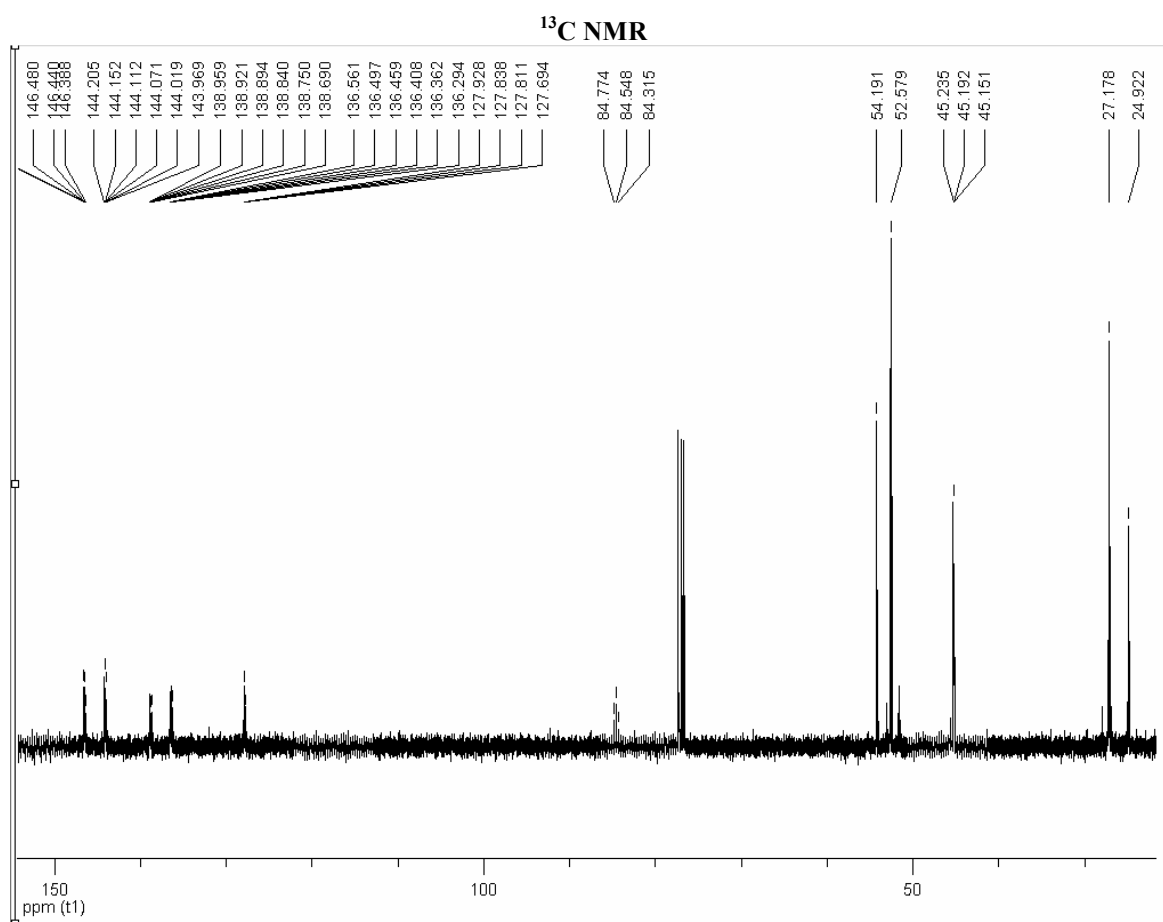
DAB-*dendr*-(NH-C₆F₄I)₂² 3a
 ^{13}C NMR



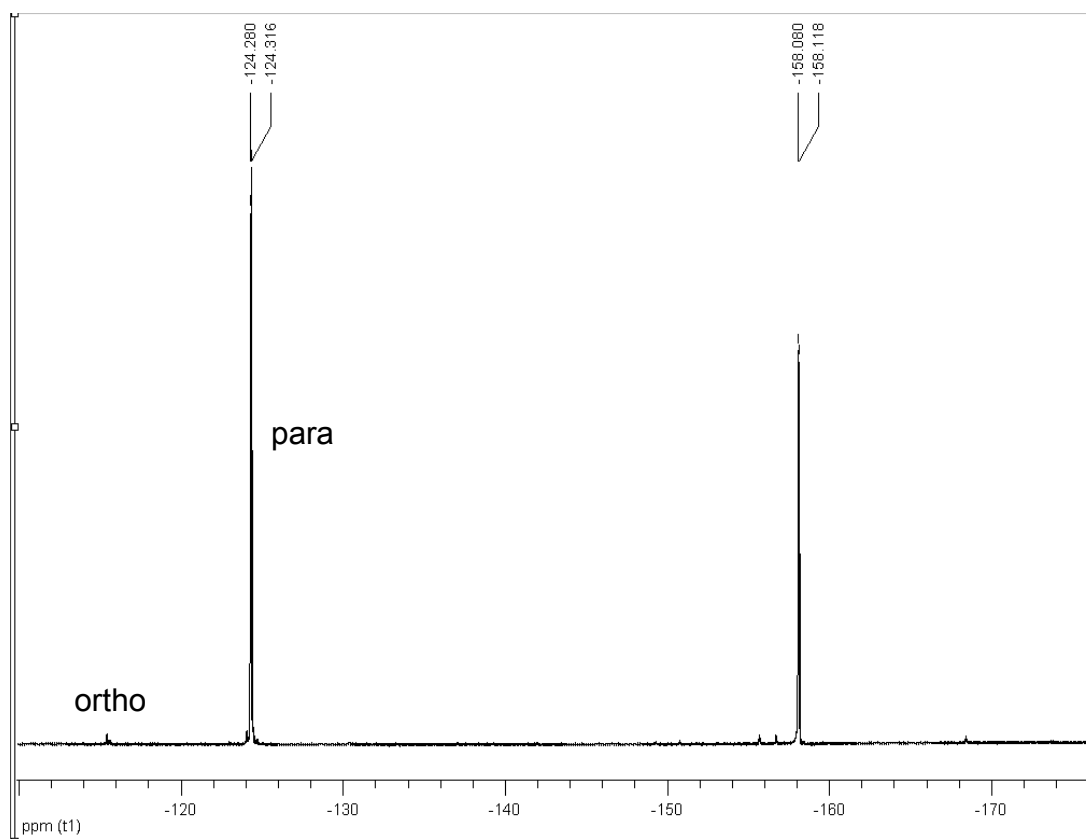
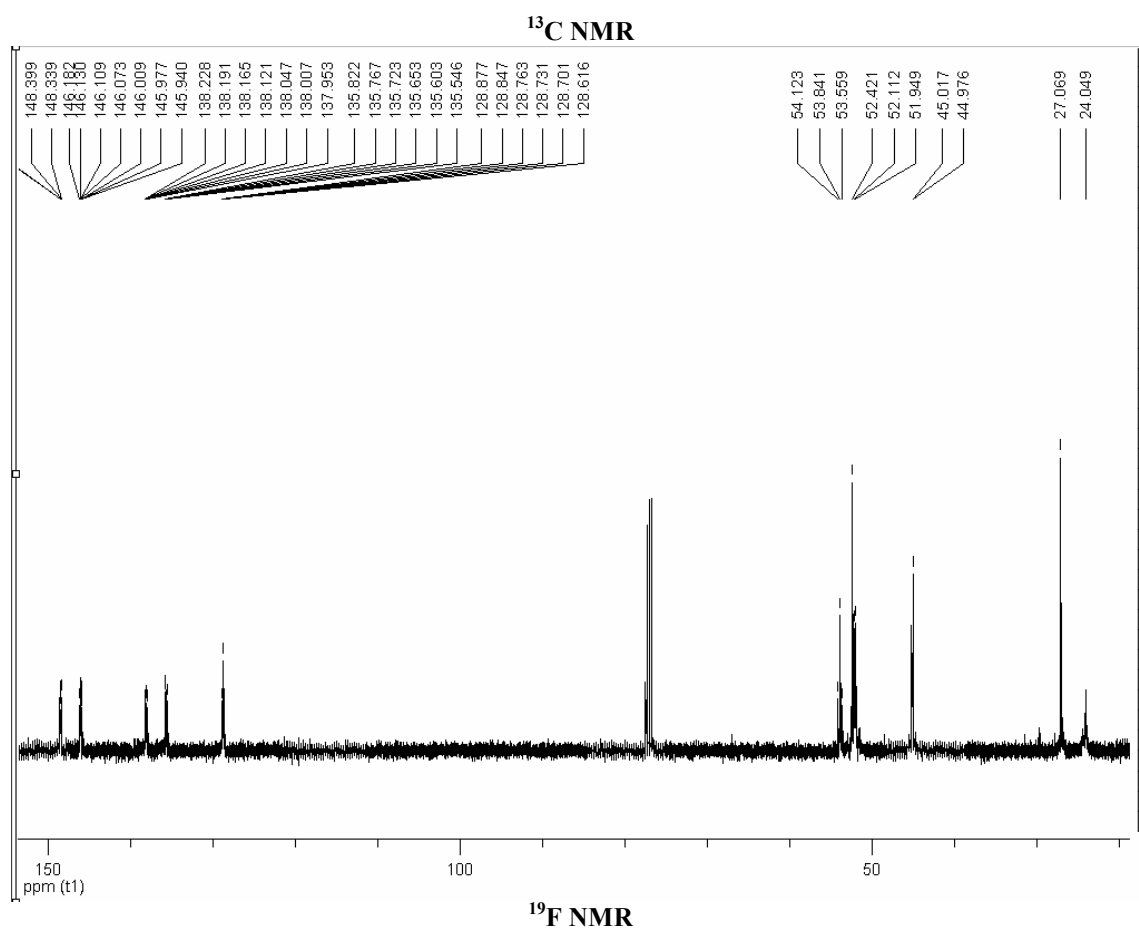
^{19}F NMR



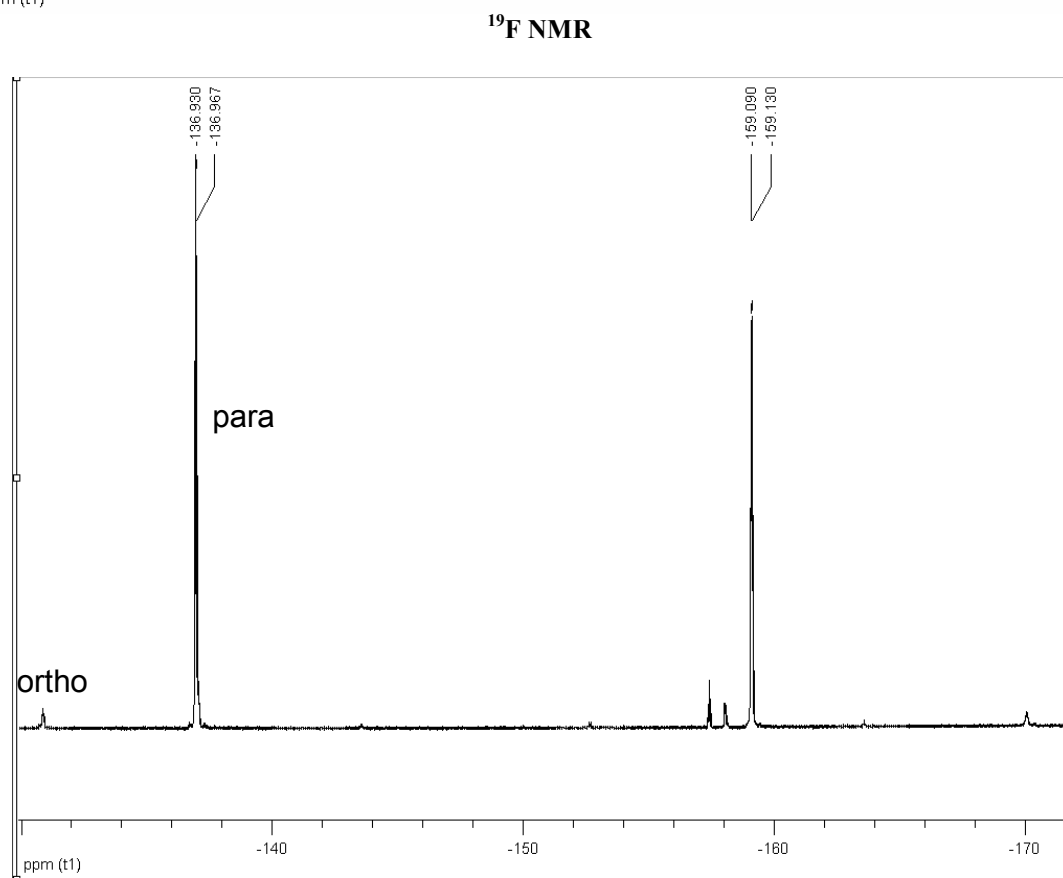
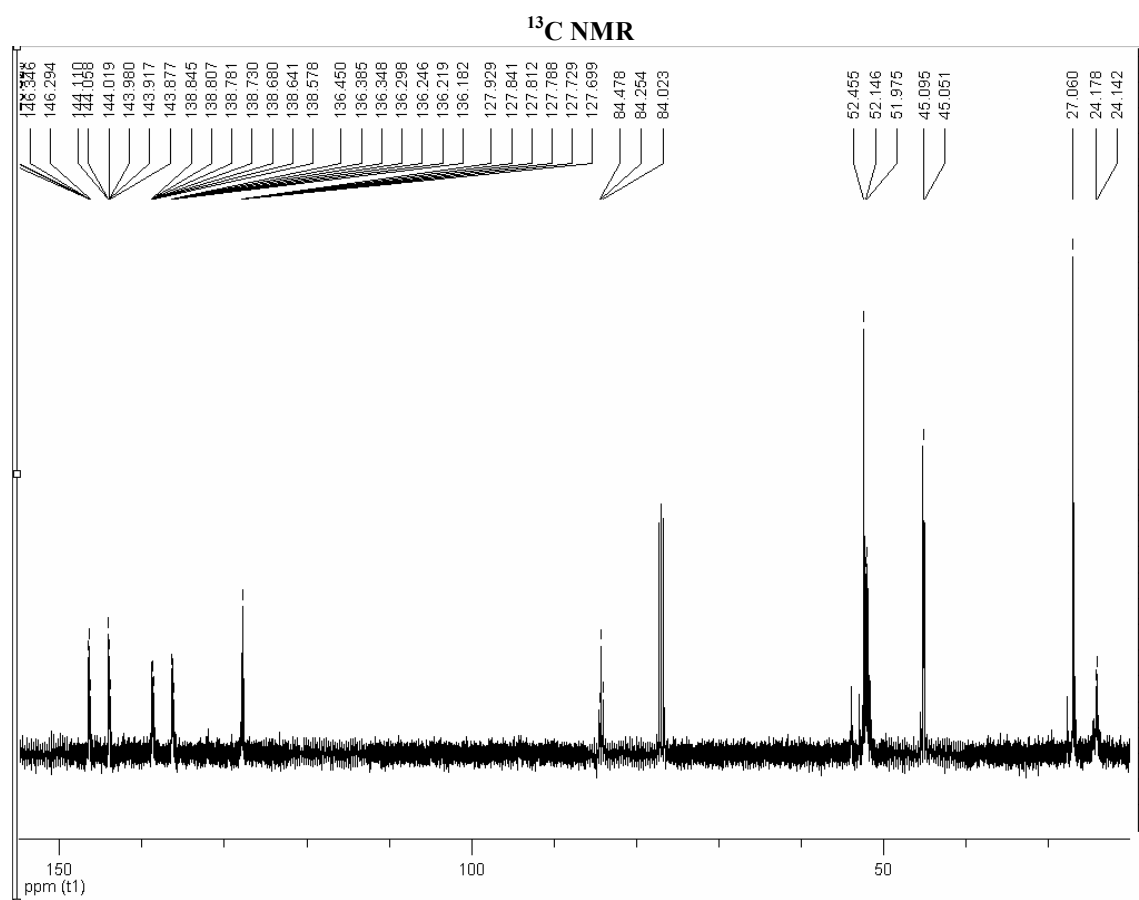
DAB-dendr-(NH-C₆F₄Br)₂² 4a



DAB-dendr-(NH-C₆F₄I)₂³ 3b

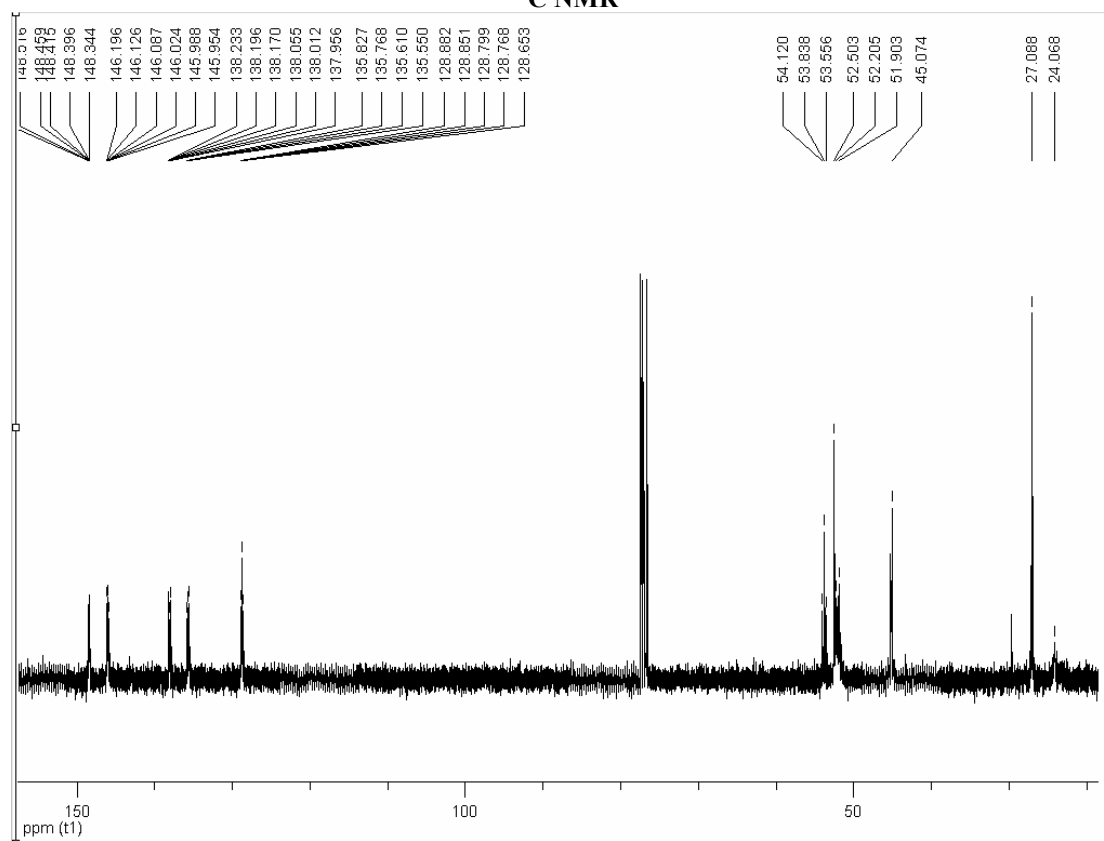


DAB-dendr-(NH-C₆F₄Br)₂³ 4b

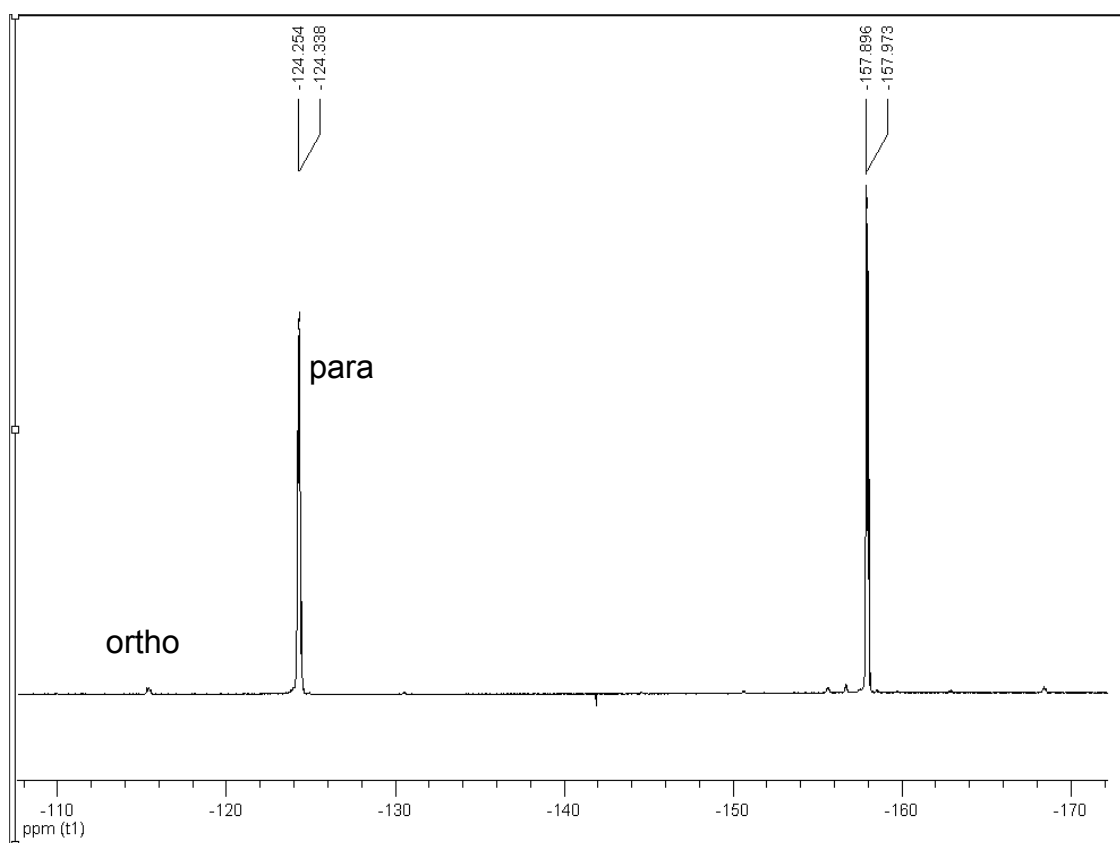


DAB-dendr-(NH-C₆F₄I)₂⁴ 3c

¹³C NMR

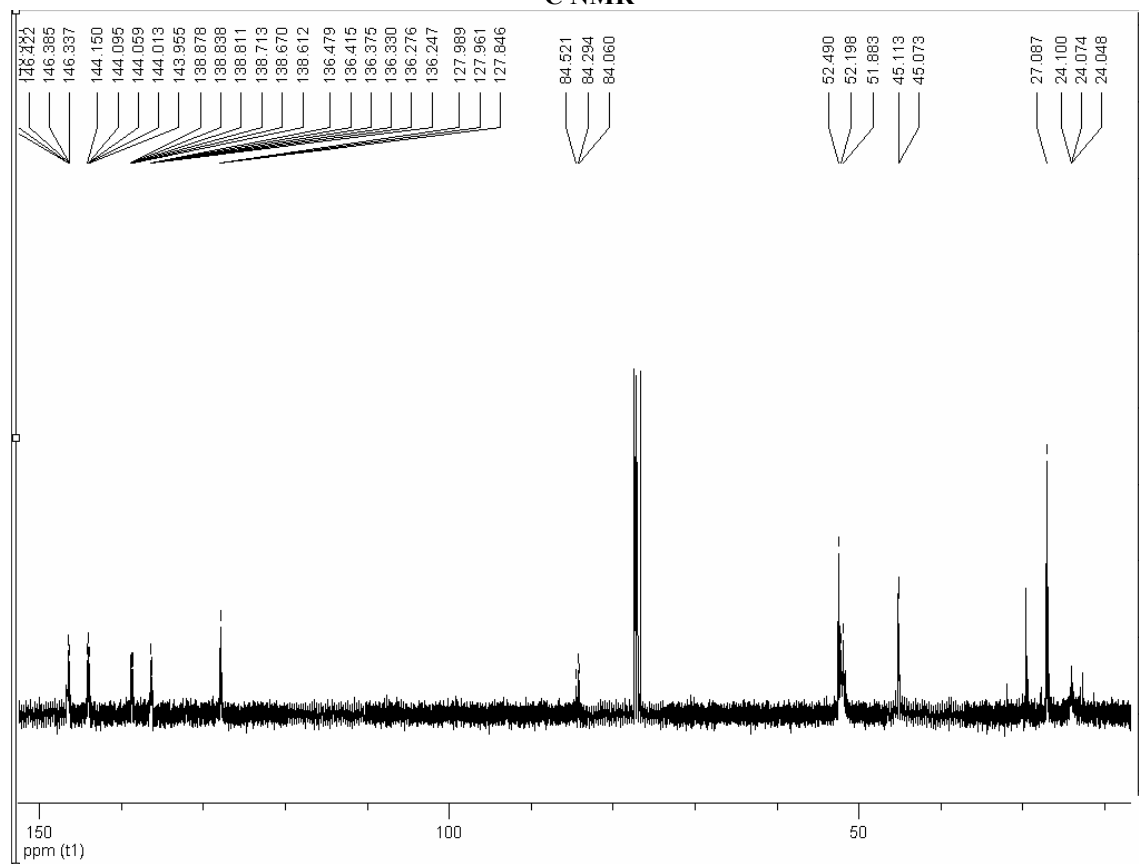


¹⁹F NMR



DAB-dendr-(NH-C₆F₄Br)₂⁴ 4c

¹³C NMR



¹⁹F NMR

