Supporting Information

Combined Cu^{I}-Catalysed Alkyne-Azide Cycloaddition and Furan-Maleimide Diels-Alder "Click" Chemistry Approach to Thermoresponsive Dendrimers

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Diels-Alder "click" reaction of G1 13 and $MaAc_2$

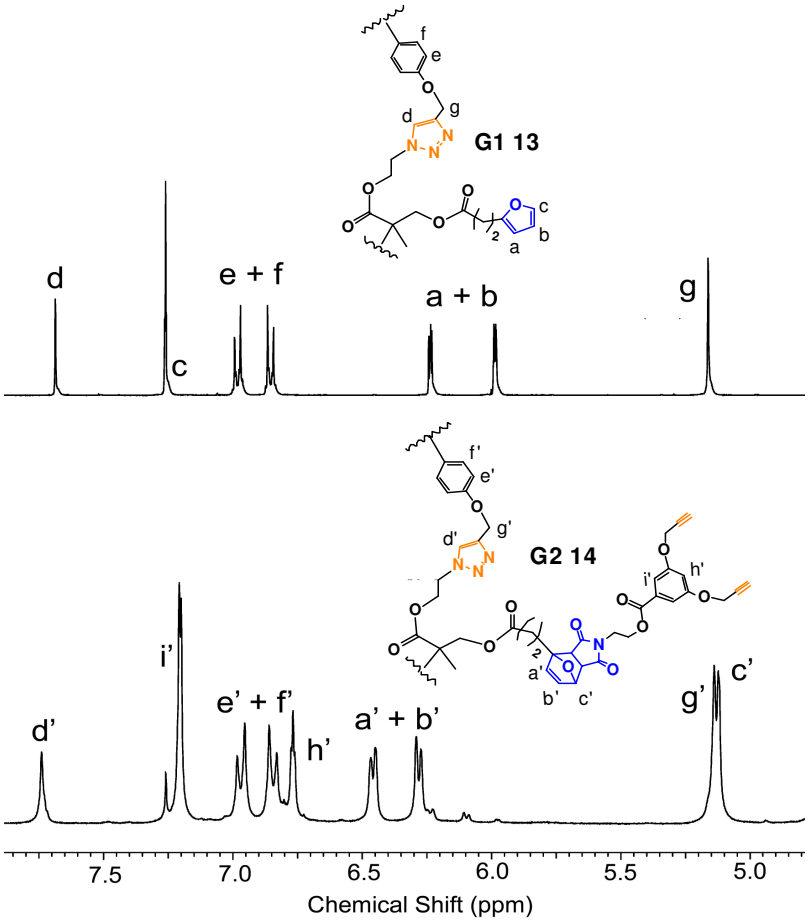
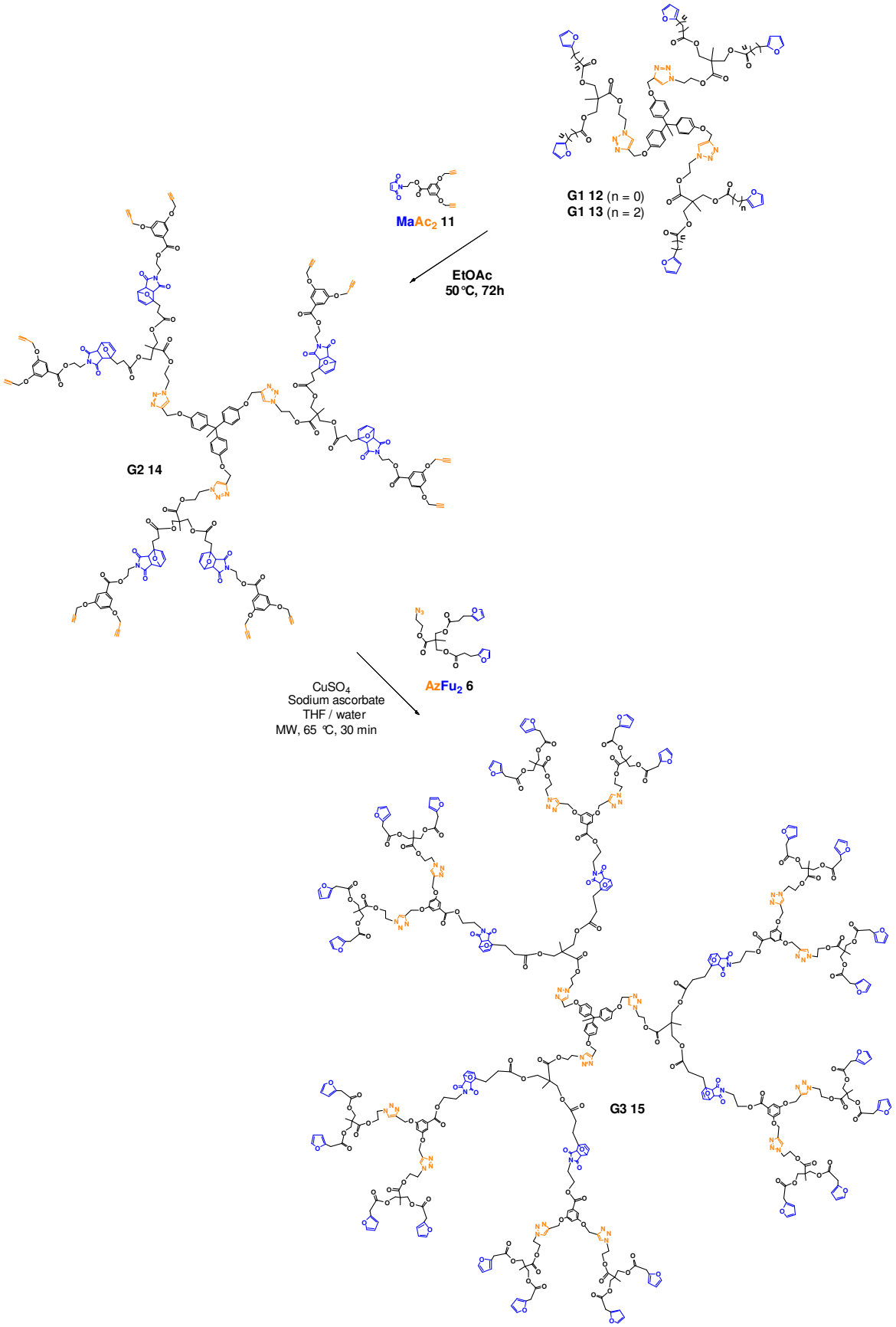


Figure S1. ^{1}H NMR ($CDCl_3$) of the **G1 13** and **G2 14** dendrimers showing the changes upon Diels-Alder cycloaddition of the furyl moieties with **$MaAc_2$ 11**.

Scheme S1. Synthesis of **G2 14** and **G3 15** dendrimers.



Characterization of Dendrimers

G1 12 : (yield = 64%, MW reactor) ^{1}H NMR ($CDCl_3$, 400 MHz) : 1.30 (s, 9H, COCC*H*$_3$), 2.06 (s, 3H, C*H*$_3$), 4.44 (d, *J* = 11 Hz, 6H, CC*H*$_2$O), 4.49 (d, *J* = 11 Hz, 6H, CC*H*$_2$O), 4.56 (m, 6H, CHNC*H*$_2$C*H*$_2$), 4.63 (m, 6H, CHNC*H*$_2$C*H*$_2$), 5.11 (s, 6H, ArOC*H*$_2$), 6.51 (dd, *J* = 4, 2 Hz, 6H, C*H*$_{fur}$), 6.83 (d, *J* = 9 Hz, 6H, Ar*H*), 6.95 (d, *J* = 9 Hz, 6H, Ar*H*), 7.13 (d, *J* = 3 Hz, 6H, C*H*$_{fur}$), 7.54 (s, 6H, C*H*$_{fur}$O), 7.74 (s, 3H, NC*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz) : 17.8, 30.8, 46.9, 49.0, 50.7, 61.3, 63.4, 65.5, 112.1, 113.9, 118.8, 123.6, 129.7, 142.2, 143.9, 144.6, 146.9, 156.3, 158.0, 172.1; ESI-MS : *m/z* 1616.5 ([M+Na]$^+$), 1594.5 ([M+H]$^+$).

G1 13 : (yield = 67%) ^{1}H NMR ($CDCl_3$, 400 MHz) : 0.96 (s, 9H, COCC*H*$_3$), 2.09 (s, 3H, C*H*$_3$), 2.63 (t, *J* = 8 Hz, 12H, C*H*$_2$C*H*$_2$fur), 2.91 (t, *J* = 8 Hz, 12H, C*H*$_2$C*H*$_2$fur), 4.10 (d, *J* = 7 Hz, 3H, CC*H*$_2$O), 4.13 (d, *J* = 7 Hz, 3H, CC*H*$_2$O), 4.14 (d, *J* = 11 Hz, 3H, CC*H*$_2$O), 4.19 (d, *J* = 11 Hz, 3H, CC*H*$_2$O), 4.49 (m, 6H, CHNC*H*$_2$C*H*$_2$), 4.59 (m, 6H, CHNC*H*$_2$C*H*$_2$), 5.16 (s, 6H, ArOC*H*$_2$), 5.99 (m, 6H, C*H*$_{fur}$), 6.24 (dd, *J* = 3, 2 Hz, 6H, C*H*$_{fur}$), 6.85 (d, *J* = 9 Hz, 6H, Ar*H*), 6.98 (d, *J* = 9 Hz, 6H, Ar*H*), 7.26 (m, 6H, C*H*$_{fur}$O), 7.69 (s, 3H, NC*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz) : 17.7, 23.4, 30.8, 32.5, 46.5, 48.9, 50.7, 62.0, 63.1, 65.3, 105.5, 110.3, 113.9, 123.4, 129.7, 141.3, 142.3, 144.7, 153.8, 156.4, 171.9, 172.2; ESI-MS : *m/z* 1785.6 ([M+Na]$^+$), 1762.5 ([M+H]$^+$).

G3 15 : (yield = 61%) ^{1}H NMR ($CDCl_3$, 400 MHz) : 1.12 (br s, 45H, C*H*$_3$), 2.00-3.00 (39H, C*H*$_3$+C*H*$_2$C*H*$_2$fur+NCOC*H*), 2.62 (br s, 48H, C*H*$_2$C*H*$_2$fur), 2.90 (br s, 48H, C*H*$_2$C*H*$_2$fur), 3.84 (br s, 12H, OCNC*H*$_2$C*H*$_2$), 4.16 (m, 60H, CC*H*$_2$O), 4.38 (br s, 12H, OCNC*H*$_2$C*H*$_2$), 4.40-4.70 (12H, CHNCH$_2$CH$_2$), 4.48 (br s, 24H, CHNC*H*$_2$C*H*$_2$), 4.59 (br s, 24H, CHNC*H*$_2$C*H*$_2$), 5.00-5.30 (36H, ArOC*H*$_2$+ C*H*$_{fur}$O), 5.98 (br s, 24H, C*H*$_{fur}$), 6.23 (br s, 30H, C*H*$_{fur}$), 6.40 (br s, 6H, C*H*$_{fur}$), 6.80 (br s, 6H, Ar*H*), 6.84 (d, *J* = 8 Hz, 6H, Ar*H*), 6.95 (m, 6H, Ar*H*), 7.22 (s, 12H, Ar*H*), 7.26 (br s, 24H, C*H*$_{fur}$O), 7.76 (br s, 15H, NC*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz) : 17.7, 23.4, 24.7, 29.6, 29.8, 34.3, 37.9, 46.5, 49.1, 50.6, 61.9, 63.0, 65.3, 80.7, 90.9, 105.5, 107.4, 108.9, 110.3, 114.0, 123.9, 129.8, 131.9, 132.7, 135.8, 141.4, 143.9, 153.9, 156.4, 159.3, 165.8, 171.9, 172.2, 174.7, 175.9; MALDI-TOF-MS : *m/z* 1254.5 ([dendron fragment+Li]$^+$), 1768.8 ([**G1**+Li]$^+$).

MALDI-TOF Analyses:

Dendrimers of generation 1 and 2 (**G1 12/G1 13** and **G2 14**) have all been characterized using a variety of techniques including ESI mass spectrometry. Under MALDI-TOF mass spectrometry conditions, the second and third generation dendrimers **G2 14** and **G3 15** undergo a retro-Diels-Alder reaction, and as expected, we observed peaks related to the retro-Diels-Alder products. For example, in the MALDI-TOF spectrum of **G3 15**, we observed a peak related to the mass of the released dendron, as well as a peak corresponding to the mass of **G1 13** (Figure **S2**).

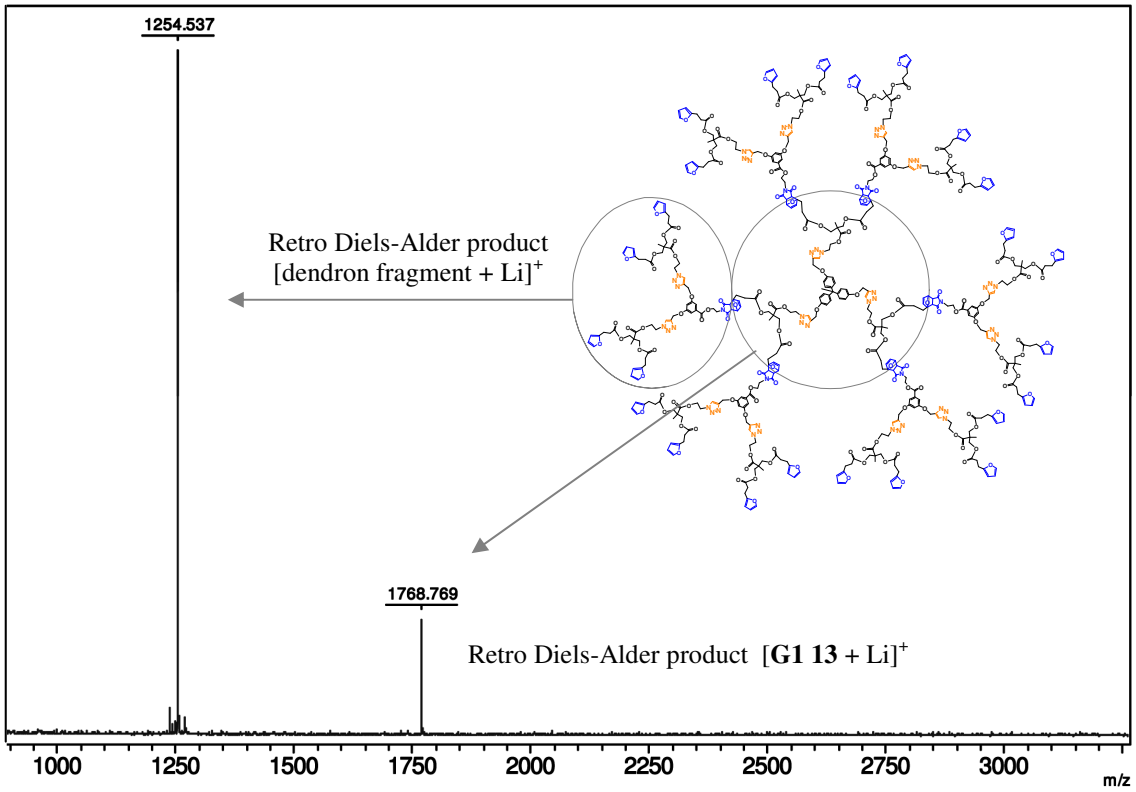
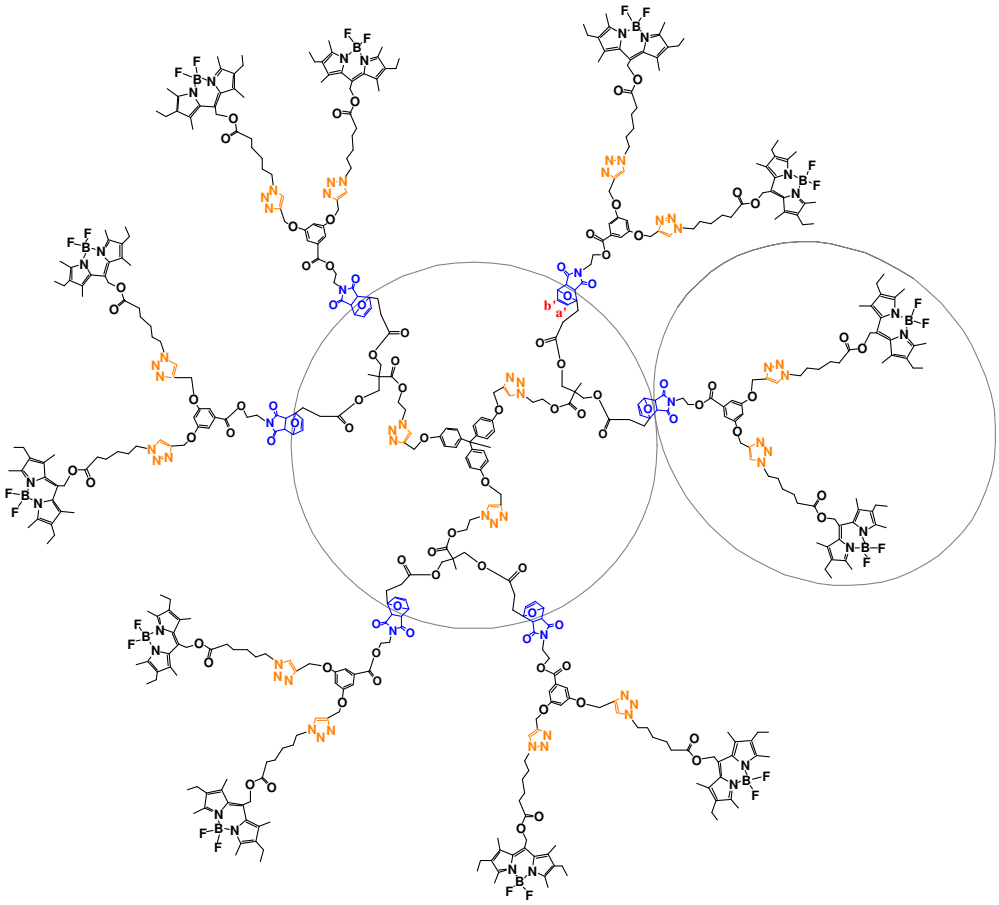


Figure **S2.** MALDI-TOF spectrum of the **G3** dendrimer.

Functionalization of the G2 Dendrimer with BODIPY



Under MALDI-TOF mass spectrometry conditions, this functionalized dendrimer also undergoes a retro-Diels-Alder reaction as described above for **G2 14** and **G3 15**. As expected, we observed peaks related to the retro Diels-Alder products (*m/z* 1768 ([**G1** + Li]$^+$), 1306 ([BODIPY-functonalized **G2 14** dendron fragment + Li]$^+$)). By FT-IR spectroscopy, the disapearance of the band due to the alkynyl moieties (2123 cm^{-1}) found in **G2 14** was also noted. The functionalized dendrimer was characterized using techniques including ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectroscopy (Figures **S3** and **S4**).

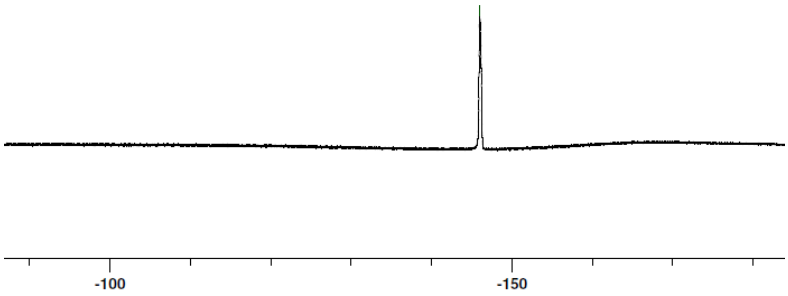


Figure **S3.** $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$) of the BODIPY functionalized dendrimer.

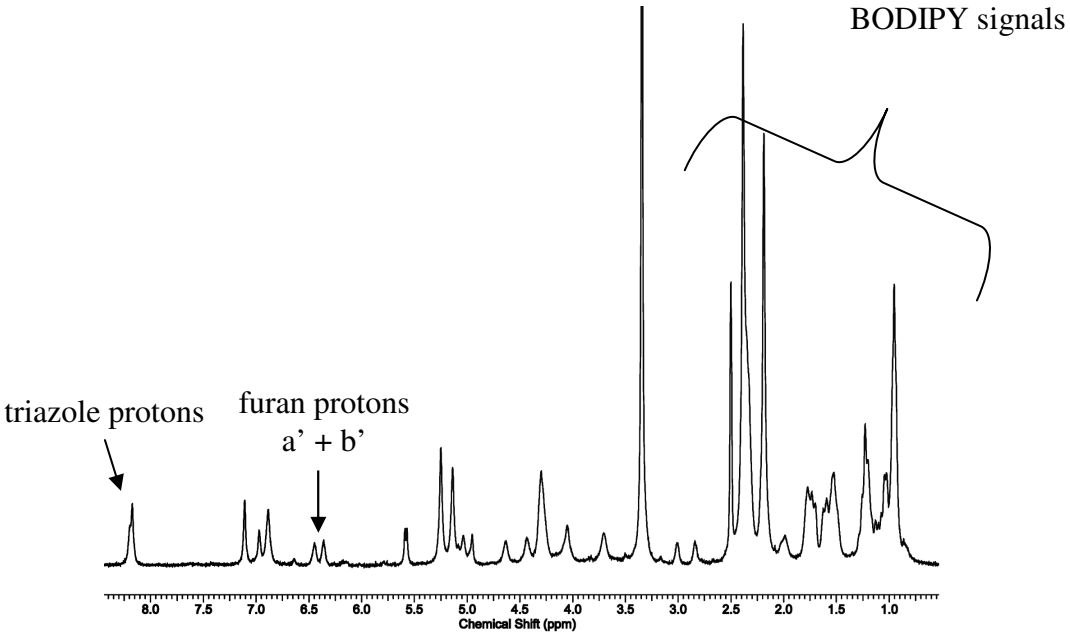


Figure **S4.** ^{1}H NMR (DMSO-d_6) of the BODIPY-functionalized **G2** dendrimer.

Functionalization of the G2 Dendrimer with 3,5-dihydroxybenzyl moiety

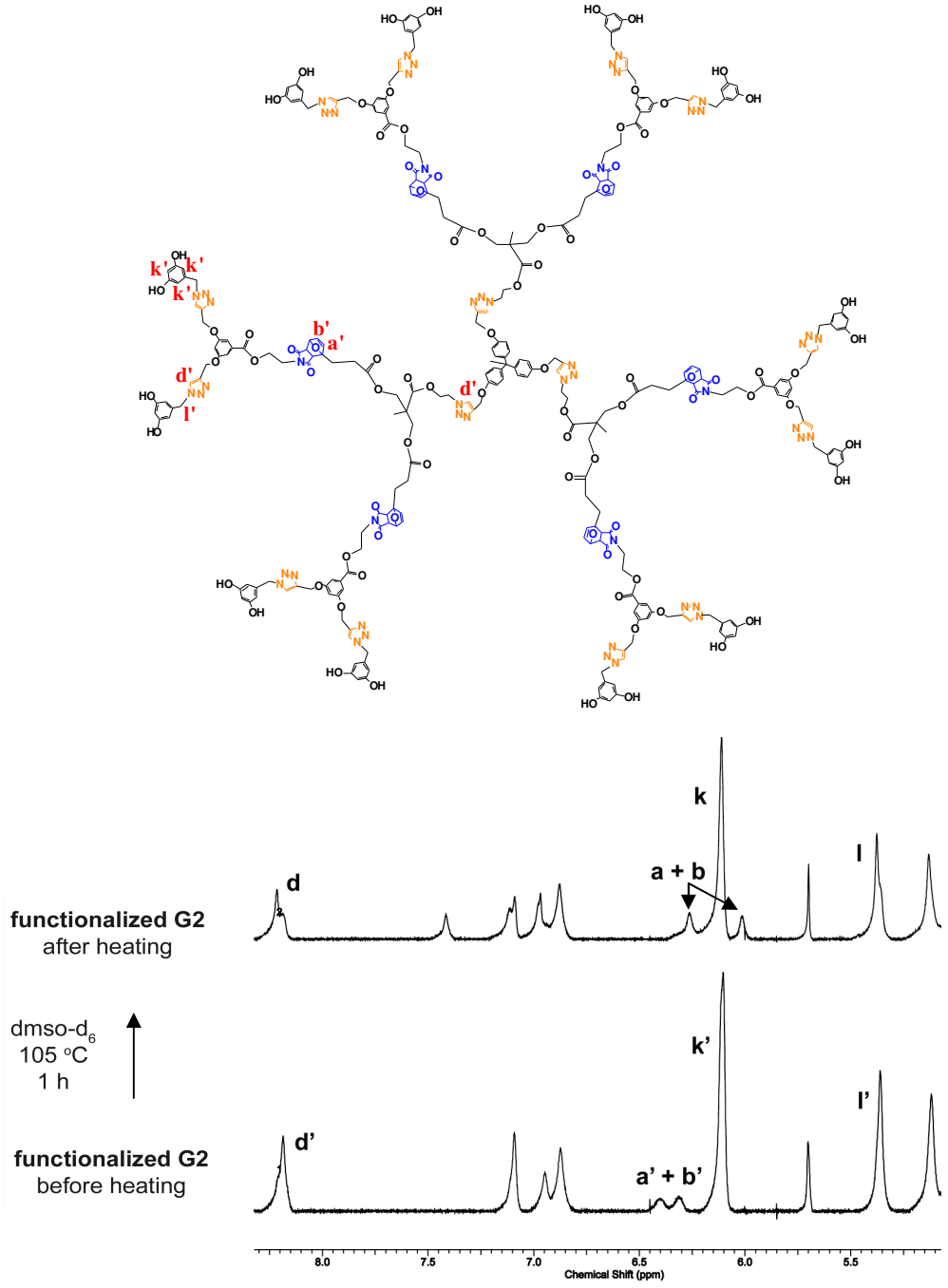


Figure **S5.** ^{1}H NMR (DMSO-d_6) of the DHBA-functionalized **G2** dendrimer and the changes noted before and after its retro Diels-Alder disassembly (performed in the NMR tube for 1h at 105 °C).