

## **Supplementary information I**

### **Low Toxic, Thermoresponsive Dendrimers Based on Oligoethylene Glycols with Sharp and Fully Reversible Phase Transitions**

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## Experiment Details

**Materials.** Compounds **1a**, **1c**, **2a** and **2c** were synthesized according to our previous reports.<sup>16</sup> Linear PEG ( $M_n = 5600$ ) was purchased from Aldrich. B16F1 cells (mouse melanoma) and HaCat cells (human keratinocyte) were obtained from the American Type Culture Collection (Manassas, VA). Cells were cultured in Dulbecco's modified Eagle's medium supplemented with 10% FBS and antibiotics (Life Science, Grand Island, NY), and maintained in sub-confluency. Cell Counting Kit-8 (CCK-8) was purchased from Probiol GmbH (Munich, Germany). Dichloromethane (DCM) was distilled from  $\text{CaH}_2$  for drying. Other reagents and solvents were purchased at reagent grade and used without further purification. All reactions were run under a nitrogen atmosphere. Macherey-Nagel pre-coated TLC plates (silica gel 60 G/UV<sub>254</sub>, 0.25 mm) were used for thin-layer chromatography (TLC) analysis. Silica gel 60 M (Macherey-Nagel, 0.04–0.063 mm, 230–400 mesh) was used as the stationary phase for column chromatography.

**Instrumentation.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz) spectrometers, and chemical shifts are reported as  $\delta$  values (ppm) relative to internal  $\text{Me}_4\text{Si}$ . High resolution MALDI-TOF-MS analyses were performed by the MS service of the Laboratorium für Organische Chemie, ETH Zürich, on IonSpec Ultra instruments. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. UV/vis turbidity measurements were carried out for the lower critical solution temperature (LCST) determination on a Varian Cary 100 Bio UV/vis spectrophotometer equipped with a thermostatically regulated bath. Solutions of the dendrimers in de-ionized water (with concentration from 0.05 wt % to 2 wt %) were filtered with a 0.45  $\mu\text{m}$  filter before adding into a cuvette (path length 1 cm), which was placed in the spectrophotometer and heated or cooled at a rate of 0.2  $^\circ\text{C}\cdot\text{min}^{-1}$ . The absorptions of the solution at  $\lambda = 500$  nm were recorded. Dynamic Light Scattering (DLS) measurements were performed with a Zetasizer Nano instrument (Malvern, UK) using a light scattering apparatus equipped with a He-Ne (633 nm) laser (accurate measurement range 0.6 nm–6  $\mu\text{m}$ ). The measurements were made at the scattering angle of  $\theta = 173^\circ$  ("backscattering" detection). Solutions of the dendrimers in de-ionized water (0.25 wt %) were filtered with a 0.45  $\mu\text{m}$  filter prior to use. The hydrodynamic diameters ( $D_h$ ) were calculated according to the volume size distribution. Optical micrographs were recorded on a Leica DMRX instrument (objective lens  $\times 50$ ) equipped with a halogen-lamp and a color CCD camera (Leica DFC480) connected to an imaging and processing system. A hot-stage from Mettler (model FP82TM) was used. The dendrimer solutions (0.25 wt %) were sealed inside a concavity slide and the aggregation process was recorded every second with heating and cooling rates of 0.5  $^\circ\text{C}\cdot\text{min}^{-1}$ . Recording program for the movie of the thermoresponsive aggregation (heating and cooling) processes: heating from 35 to 37  $^\circ\text{C}$ , 0.5  $^\circ\text{C}\cdot\text{min}^{-1}$ , and then cooling from 37 to 35  $^\circ\text{C}$ , 0.5  $^\circ\text{C}\cdot\text{min}^{-1}$ . The total recording time is 8 minutes. The movie was compressed into 36 seconds with Windows Movie Maker. The Atom Force Microscopy (AFM) measurements were carried out on a Nanoscope<sup>®</sup> IIIa Multi Mode Scanning probe microscope (from Digital Instruments, San Diego, CA) operated in the tapping mode with an "E" scanner (scan range 10  $\mu\text{m}$   $\times$  10  $\mu\text{m}$ ) at room temperature in air. Olympus silicon OMCL-AC160TS cantilevers

(from Atomic Force F&E GmbH, Mannheim, Germany) were used with a resonance frequency between 200 and 400 kHz and a spring constant around 42 N/m.

**General procedure for synthesis of G1 benzyl chloride (A).** SOCl<sub>2</sub> (6.45 mmol) in DCM (5 mL) was added dropwise into the solution of benzyl alcohol (1.29 mmol) and DMAP (2.57 mmol) in DCM (20 mL). The mixture was stirred at r.t. for 4 h. After being successively washed with saturated NaHCO<sub>3</sub> and brine, the organic phase was dried over MgSO<sub>4</sub>. Purification by column chromatography with DCM/MeOH (20:1 then 10:1, v/v) afforded the product as colorless oil.

**General procedure for synthesis of G2 benzyl chloride (B).** SOCl<sub>2</sub> (5.80 mmol) in DCM (4 mL) was added dropwise into the solution of benzyl alcohol (0.29 mmol) and DMAP (1.74 mmol) in DCM (20 mL). The mixture was stirred at r.t. for 4 h. After being successively washed with saturated NaHCO<sub>3</sub> and brine, the organic phase was dried over MgSO<sub>4</sub>. Purification by column chromatography with DCM/MeOH (20:1 then 10:1, v/v) afforded the product as colorless oil.

**General procedure for synthesis of G1 dendrimer (C).** A mixture of THPE (0.20 mmol), benzyl chloride (0.65 mmol), KI (0.13 mmol), and potassium carbonate (2.00 mmol) in dry DMF (30 mL) was stirred at 80 °C over 24 h. After removal of DMF *in vacuo*, the residue was dissolved in DCM and washed sequentially with saturated NaHCO<sub>3</sub> and brine. After drying over MgSO<sub>4</sub>, purification by column chromatography with DCM/MeOH (20:1, v/v) afforded dendrimer G1 as a colorless oil.

**General procedure for synthesis of G2 dendrimer (D).** A mixture of THPE (0.097 mmol), benzyl chloride (0.43 mmol), KI (0.32 mmol) and cesium carbonate (1.94 mmol) in dry DMF (30 mL) was stirred at 80 °C over 48 h. After removal of DMF *in vacuo*, the residue was dissolved in DCM and washed sequentially with saturated NaHCO<sub>3</sub> and brine. After drying over MgSO<sub>4</sub>, purification by column chromatography with DCM/MeOH (10:1, v/v) afforded dendrimer G2 as a colorless oil.

**3,4,5-Tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl chloride (1b).** According to general procedure A from SOCl<sub>2</sub> (0.77 g, 6.45 mmol), DCM (5 mL), **1a** (0.82 g, 1.29 mmol), DMAP (0.31 g, 2.57 mmol) and DCM (20 mL), **1b** was yielded as colorless oil (0.71 g, 84%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.16–1.19 (m, 9H, CH<sub>3</sub>), 3.47–3.69 (m, 30H, CH<sub>2</sub>), 3.76 (t, 2H, CH<sub>2</sub>), 3.84 (t, 4H, CH<sub>2</sub>), 4.12 (t, 2H, CH<sub>2</sub>), 4.16 (t, 4H, CH<sub>2</sub>), 4.54 (s, 2H, CH<sub>2</sub>), 6.66 (s, 2H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 15.40, 47.17, 66.80, 69.20, 70.05, 70.22, 70.84, 70.94, 71.03, 71.15, 72.73, 108.30, 133.26, 138.76, 153.08. MS: *m/z* calcd, 654.34; found, 677.3285 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>31</sub>H<sub>55</sub>O<sub>12</sub>Cl, 655.22: C, 56.83; H, 8.46. Found: C, 56.82; H, 8.39.

**3,4,5-Tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyl chloride (1d).** According to general procedure A from SOCl<sub>2</sub> (2.00 g, 16.81 mmol), DCM (5 mL), **1c** (2.00 g, 3.36 mmol), DMAP (0.8 g, 6.55 mmol) and DCM (40 mL), **1d** was yielded as a colorless oil (1.70 g, 82%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 3.33 (s, 9H, CH<sub>3</sub>), 3.49–3.51 (m, 6H, CH<sub>2</sub>), 3.59–3.70 (m, 18H, CH<sub>2</sub>), 3.76 (t, 2H, CH<sub>2</sub>), 3.84 (t, 4H, CH<sub>2</sub>), 4.12 (t, 2H, CH<sub>2</sub>), 4.16 (t, 4H, CH<sub>2</sub>), 4.53 (s, 2H, CH<sub>2</sub>), 6.65 (s, 2H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 46.91, 58.74, 68.96, 69.80, 70.54, 70.56, 70.59, 70.68, 70.90, 72.05, 72.48, 108.05, 133.00, 138.52, 152.83. MS: *m/z* calcd, 612.29; found, 635.2816 [M + Na]<sup>+</sup>.

Elemental analysis (%) calcd for C<sub>28</sub>H<sub>49</sub>O<sub>12</sub>Cl, 613.14: C, 54.85; H, 8.05. Found: C, 54.56; H, 7.91.

**3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl chloride (2b).** According to general procedure B from SOCl<sub>2</sub> (0.69 g, 5.80 mmol), DCM (4 mL), **2a** (0.70 g, 0.29 mmol), DMAP (0.21 g, 1.74 mmol) and DCM (20 mL), **2b** was yielded as a colorless oil (0.51 g, 72%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.19–1.23 (m, 27H, CH<sub>3</sub>), 3.48–3.74 (m, 114H, CH<sub>2</sub>), 3.79 (t, 8H, CH<sub>2</sub>), 3.85–3.88 (m, 16H, CH<sub>2</sub>), 4.12–4.18 (m, 24H, CH<sub>2</sub>), 4.47 (s, 6H, CH<sub>2</sub>), 4.56 (s, 2H, CH<sub>2</sub>), 6.63 (s, 6H, CH), 6.69 (s, 2H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 15.15, 46.90, 66.54, 68.82, 68.90, 68.93, 69.66, 69.79, 69.84, 69.97, 70.58, 70.68, 70.70, 70.76, 70.77, 70.88, 72.43, 73.20, 106.83, 107.90, 134.18, 137.62, 152.72, 152.82, 152.83. MS: *m/z* calcd, 2425.33; found, 2448.312 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>118</sub>H<sub>205</sub>O<sub>48</sub>Cl, 2427.34: C, 58.39; H, 8.51. Found: C, 58.29; H, 8.38.

**3,4,5-Tris(2-(2-(2-(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyl-oxy)ethoxy)ethoxy)ethoxy)benzyl chloride (2d).** According to general procedure B from SOCl<sub>2</sub> (1.53 g, 12.88 mmol), DCM (5 mL), **2c** (1.47 g, 0.64 mmol), DMAP (0.47 g, 3.86 mmol) and DCM (30 mL), **2d** was yielded as a colorless oil (1.10 g, 74%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 3.33–3.34 (m, 27H, CH<sub>3</sub>), 3.49–3.52 (m, 18H, CH<sub>2</sub>), 3.58–3.69 (m, 78H, CH<sub>2</sub>), 3.75 (t, 8H, CH<sub>2</sub>), 3.82–3.83 (m, 16H, CH<sub>2</sub>), 4.10 (t, 8H, CH<sub>2</sub>), 4.13–4.16 (m, 16H, CH<sub>2</sub>), 4.44 (s, 6H, CH<sub>2</sub>), 4.53 (s, 2H, CH<sub>2</sub>), 6.59 (s, 6H, CH), 6.65 (s, 2H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 47.16, 59.00, 69.06, 69.17, 69.91, 70.06, 70.09, 70.79, 70.81, 70.93, 70.95, 71.12, 72.30, 72.68, 73.45, 107.05, 108.33, 134.43, 137.87, 138.73, 152.97, 153.06. MS: *m/z* calcd, 2299.19; found, 2322.174 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>109</sub>H<sub>187</sub>O<sub>48</sub>Cl, 2301.10: C, 56.89; H, 8.19. Found: C, 55.91; H, 8.01.

**5,5',5''-(4,4',4''-(ethane-1,1,1-triyl)tris(benzene-4,1-diyl))tris(oxy)tris(methylene)tris(1,2,3-tris(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzene) (Et-G1).** According to general procedure C from 1, 1, 1-Tris(4-hydroxy-phenyl)ethane (85.8 mg, 0.28 mmol), **2c** (0.6 g, 0.92 mmol), KI (28.8 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (387.0 mg, 2.80 mmol) and dry DMF (40 mL), **Et-G1** was yielded as a colorless oil (0.53 g, 88%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.16–1.20 (m, 27H, CH<sub>3</sub>), 2.08–2.11 (m, 3H, CH<sub>3</sub>), 3.46–3.68 (m, 90H, CH<sub>2</sub>), 3.76–3.77 (m, 6H, CH<sub>2</sub>), 3.83–3.84 (m, 12H, CH<sub>2</sub>), 4.12–4.16 (m, 18H, CH<sub>2</sub>), 4.93 (s, 4H, CH<sub>2</sub>), 4.96 (s, 2H, CH<sub>2</sub>), 6.66–6.74 (m, 6H, CH), 6.84–6.88 (m, 6H, CH), 6.99–7.03 (m, 6H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 15.15, 30.71, 50.70, 50.78, 66.55, 68.85, 68.91, 69.79, 69.83, 69.97, 70.13, 70.20, 70.59, 70.69, 70.75, 70.77, 70.85, 70.89, 72.47, 106.81, 106.95, 114.02, 114.21, 114.66, 129.73, 132.77, 132.84, 137.93, 138.05, 142.21, 142.36, 152.83, 152.88, 156.83, 157.01. MS: *m/z* calcd, 2161.21; found, 2184.206 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>113</sub>H<sub>180</sub>O<sub>39</sub>, 2162.64: C, 62.76; H, 8.39. Found: C, 62.75; H, 8.21.

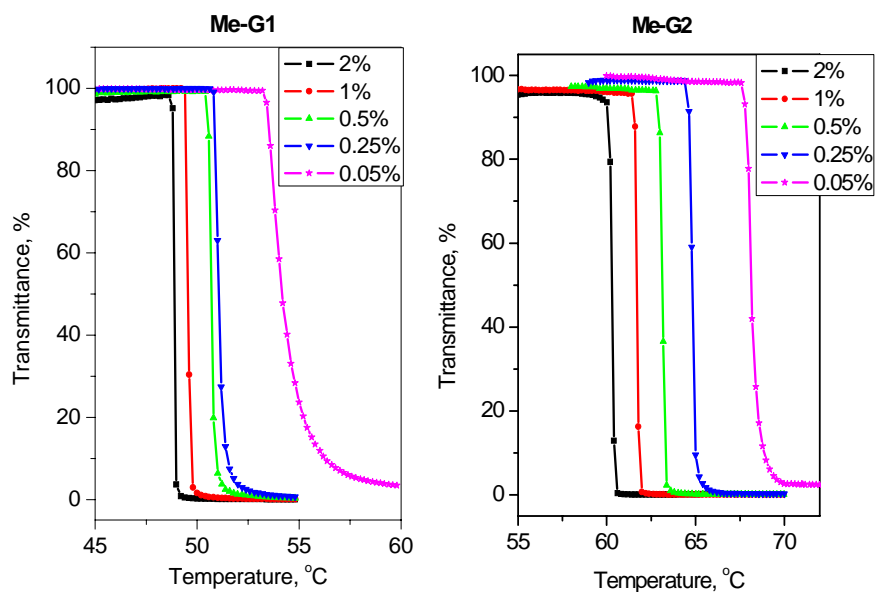
**5,5',5''-(4,4',4''-(ethane-1,1,1-triyl)tris(benzene-4,1-diyl))tris(oxy)tris(methylene)tris(1,2,3-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene) (Me-G1).** According to general procedure C from 1, 1, 1-Tris(4-hydroxy-phenyl)ethane (60.6 mg, 0.20 mmol), **2e** (0.40 g, 0.65 mmol), KI (20.8 mg, 0.13 mmol), and K<sub>2</sub>CO<sub>3</sub> (276.4 mg, 2.00 mmol) in dry DMF (30 mL), **Me-G1** was yielded as a colorless oil (0.36 g, 90%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.08–2.17 (m, 3H, CH<sub>3</sub>), 3.33–3.34 (m, 27H, CH<sub>3</sub>), 3.49–3.69 (m, 72H, CH<sub>2</sub>), 3.76–3.78 (m, 6H, CH<sub>2</sub>), 3.81–3.85 (m, 12H, CH<sub>2</sub>), 4.12–4.17 (m, 18H,

CH<sub>2</sub>), 4.93 (s, 4H, CH<sub>2</sub>), 4.96 (s, 2H, CH<sub>2</sub>), 6.66–6.70 (m, 6H, CH), 6.84–6.88 (m, 6H, CH), 6.99–7.03 (m, 6H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 30.58, 50.70, 50.78, 58.74, 68.85, 68.91, 69.79, 69.82, 70.13, 70.20, 70.52, 70.55, 70.68, 70.85, 70.88, 72.04, 72.44, 72.47, 106.81, 106.95, 114.03, 114.20, 114.64, 129.72, 132.78, 132.85, 137.91, 138.03, 142.21, 142.35, 152.83, 152.87, 156.83, 157.01. MS: *m/z* calcd, 2035.07; found, 2058.063 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>104</sub>H<sub>162</sub>O<sub>39</sub>, 2036.40: C, 61.34; H, 8.02. Found: C, 61.07; H, 7.87.

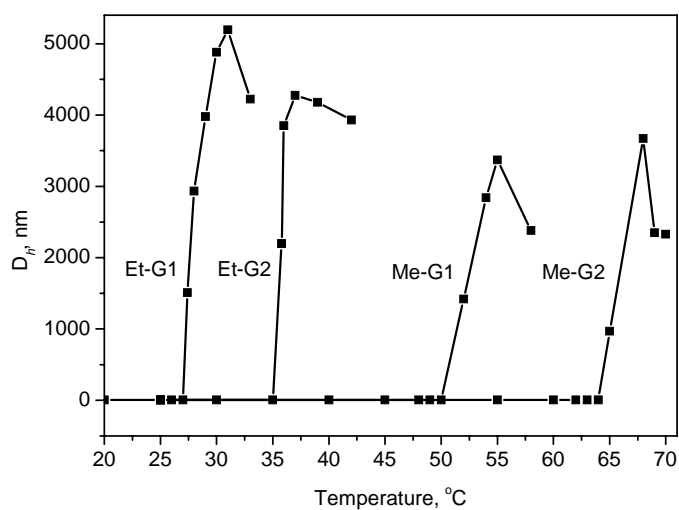
**Et-G2.** According to general procedure D from 1, 1, 1-Tris(4-hydroxy-phenyl)ethane (5.5 mg, 0.018 mmol), **3c** (200.0 g, 0.082 mmol), KI (9.6 mg, 0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (117.3 mg, 0.36 mmol) and dry DMF (20 mL), **Et-G2** was yielded as a colorless oil (0.10 g, 74%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.18–1.23 (m, 81H, CH<sub>3</sub>), 2.14 (s, 3H, CH<sub>3</sub>), 3.45–3.88 (m, 414H, CH<sub>2</sub>), 4.12–4.19 (m, 72H, CH<sub>2</sub>), 4.47 (s, 18H, CH<sub>2</sub>), 4.95 (s, 6H, CH<sub>2</sub>), 6.63 (s, 18H, CH), 6.73 (s, 6H, CH), 6.93 (d, 6H, CH), 7.06 (d, 6H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.60, 15.01, 60.57, 66.39, 68.71, 69.53, 69.71, 69.82, 70.09, 44, 70.54, 70.56, 70.61, 70.63, 70.74, 72.30, 72.37, 73.04, 106.72, 106.88, 70113.87, 129.61, 132.57, 134.05, 137.00, 137.55, 142.08, 152.59, 152.74, 156.90. MS: *m/z* calcd, 7474.18; found, 7506.85 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>374</sub>H<sub>630</sub>O<sub>147</sub>, 7479.00: C, 60.06; H, 8.49. Found: C, 59.59; H, 8.24.

**Me-G2.** According to general procedure D from 1, 1, 1-Tris(4-hydroxy-phenyl)ethane (29.7 mg, 0.097 mmol), **3e** (1.00 g, 0.43 mmol), KI (51.2 mg, 0.32 mmol), Cs<sub>2</sub>CO<sub>3</sub> (632.1 mg, 1.94 mmol) and dry DMF (30 mL), **Me-G2** was yielded as a colorless oil (0.5 g, 73%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.14 (s, 3H, CH<sub>3</sub>), 3.36–3.37 (m, 81H, CH<sub>3</sub>), 3.53–3.87 (m, 360H, CH<sub>2</sub>), 4.12–4.19 (m, 72H, CH<sub>2</sub>), 4.46 (s, 18H, CH<sub>2</sub>), 4.95 (s, 6H, CH<sub>2</sub>), 6.62 (s, 18H, CH), 6.73 (s, 6H, CH), 6.93 (d, 6H, CH), 7.06 (d, 6H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 58.59, 68.70, 68.79, 69.53, 69.70, 70.09, 70.38, 70.40, 70.42, 70.53, 70.55, 70.72, 71.90, 72.28, 72.37, 73.04, 106.72, 106.88, 113.84, 129.62, 132.58, 134.05, 137.53, 137.95, 142.08, 152.58, 152.73, 156.94. MS: *m/z* calcd, 7095.76; found, 7125.62 [M + Na]<sup>+</sup>. Elemental analysis (%) calcd for C<sub>347</sub>H<sub>576</sub>O<sub>147</sub>, 7100.28: C, 58.70; H, 8.18. Found: C, 58.44; H, 8.06.

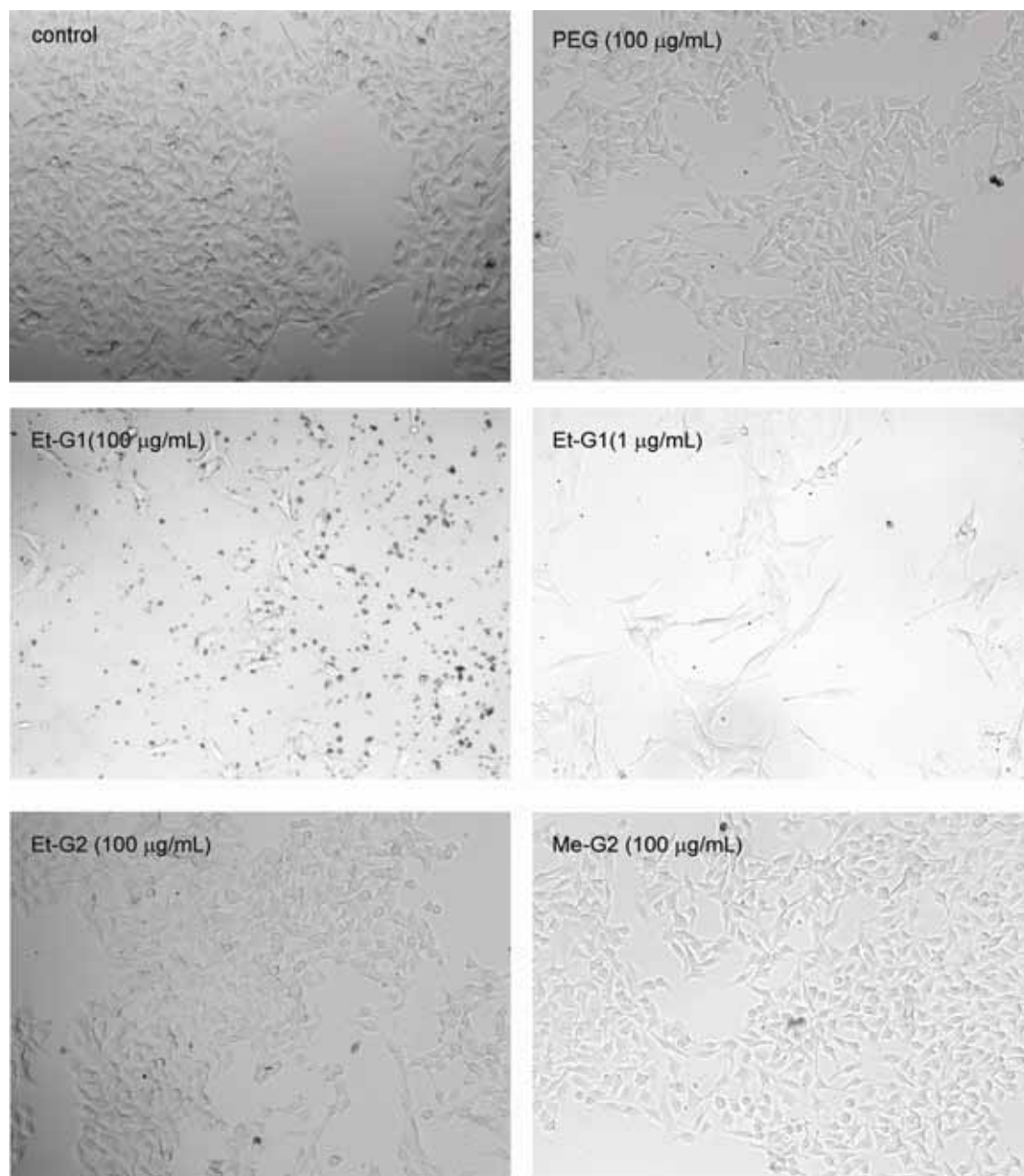
**In vitro cytotoxicity:** Cytotoxicity of dendrimers to B16F1 and HaCat cell lines was determined by cell counting kit-8 (CCK-8) assay. These cells were seeded in two 96 well tissue culture plates, respectively, at a concentration of 1000 cells/well in 100 μL culture medium. The cells were cultured overnight at 37 °C in a humidified atmosphere of 5% CO<sub>2</sub>. Then the cells were incubated with different concentrations of PEG or dendrimers aqueous solution (2 μL) for 48 h. 10 μL of a CCK-8 solution was added to each well and the cells were incubated for another 3 h in a tissue culture incubator. The absorbance was then measured at 450 nm using a microplate reader. The viability of cells exposed to dendrimers was expressed relative to vehicle-treated control cells.



**Figure S1.** Plots of transmittance vs temperature for aqueous solutions of **Me-G1** and **Me-G2** at different concentrations.

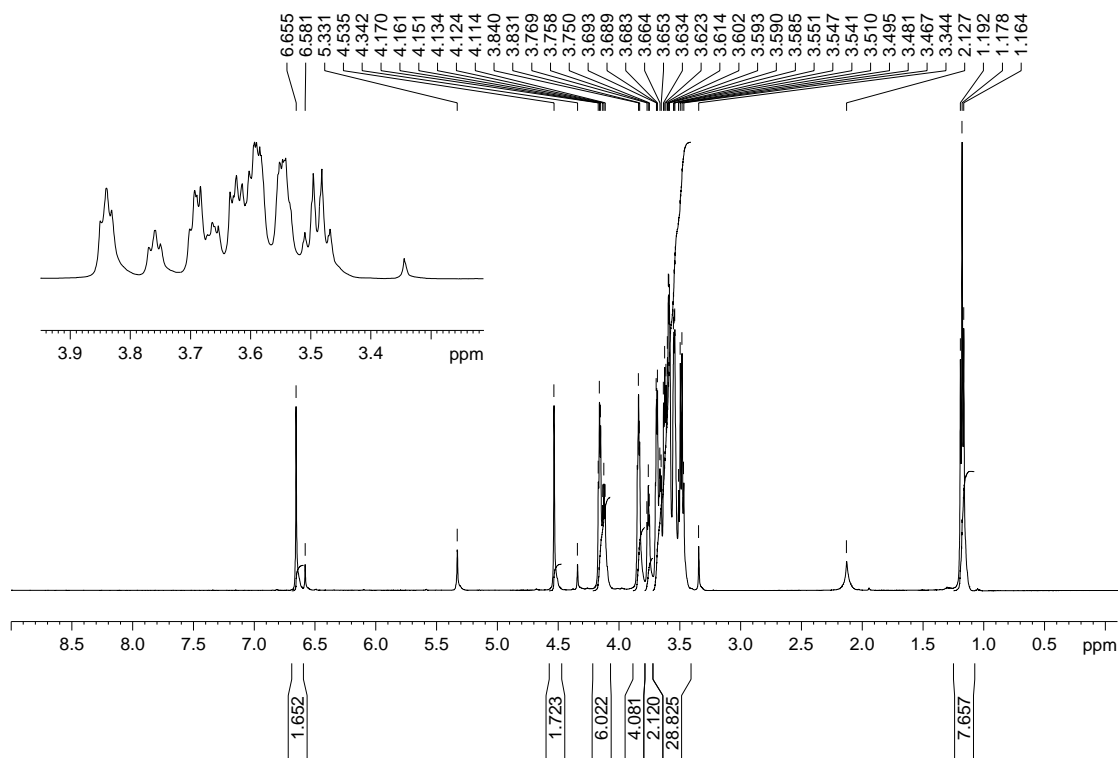


**Figure S2.** Plots of hydrodynamic diameters ( $D_h$ ) of the aggregates from **Et-G1**, **Et-G2**, **Me-G1** and **Me-G2** in aqueous solution as a function of temperature from DLS measurements

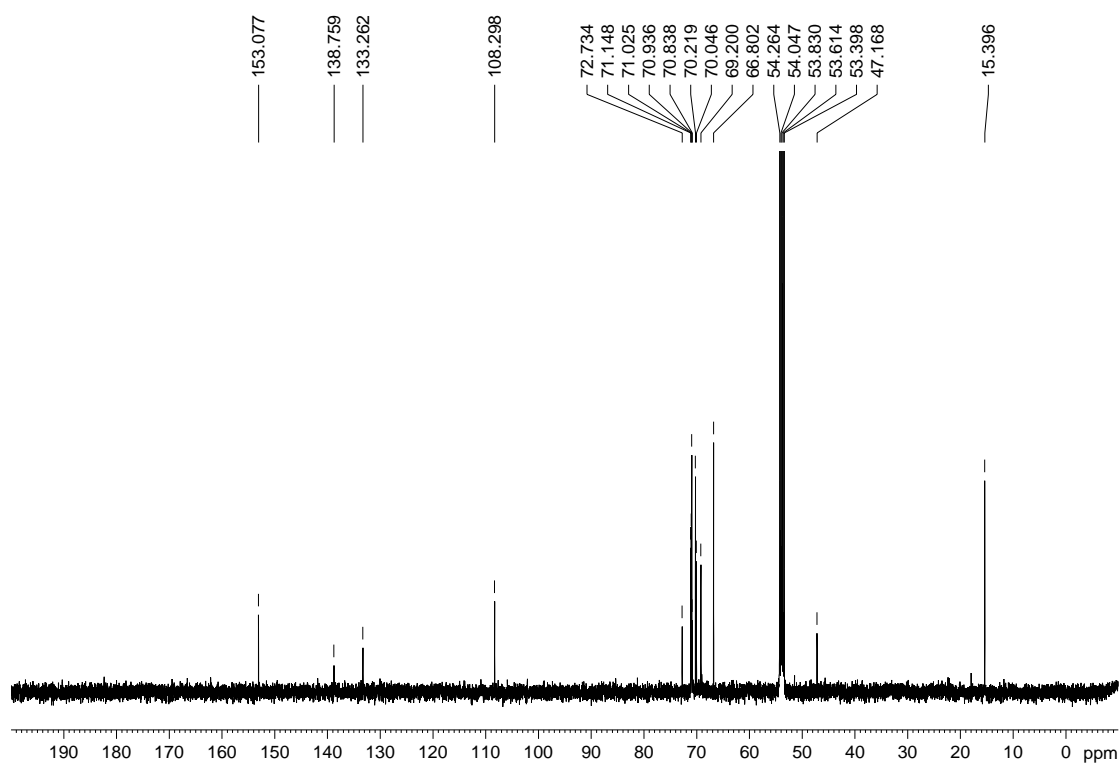


**Figure S3.** Microscopic images of B16F1 cells after incubation with untreated cells, PEG and dendrimer solutions at 37 °C for 48 h.

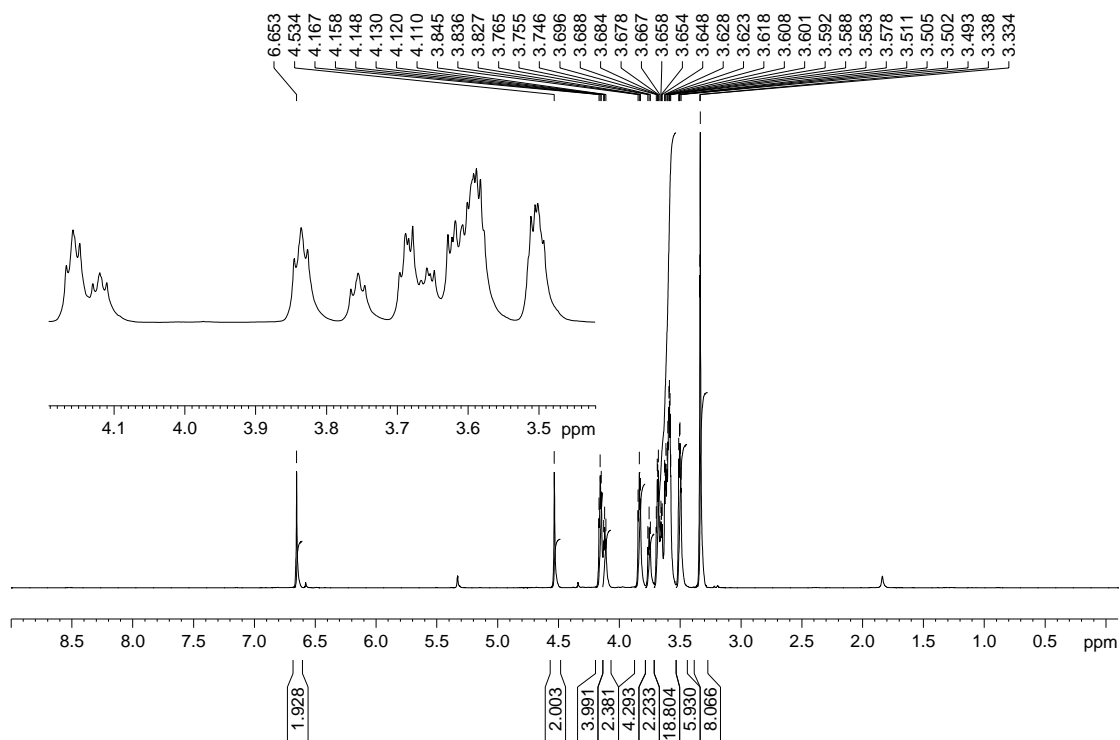




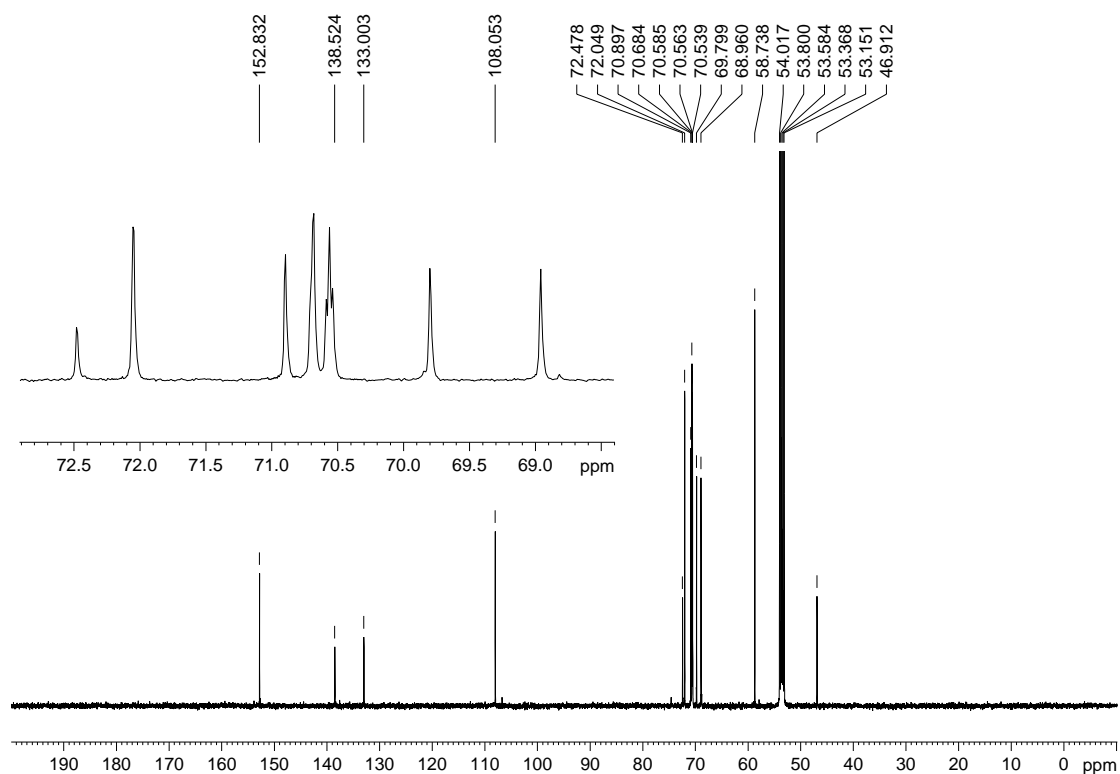
**Figure S4.** <sup>1</sup>H NMR spectrum of compound **1b** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S5.** <sup>13</sup>C NMR spectrum of compound **1b** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S6.** <sup>1</sup>H NMR spectrum of compound **1d** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S7.** <sup>13</sup>C NMR spectrum of compound **1d** in CD<sub>2</sub>Cl<sub>2</sub>.

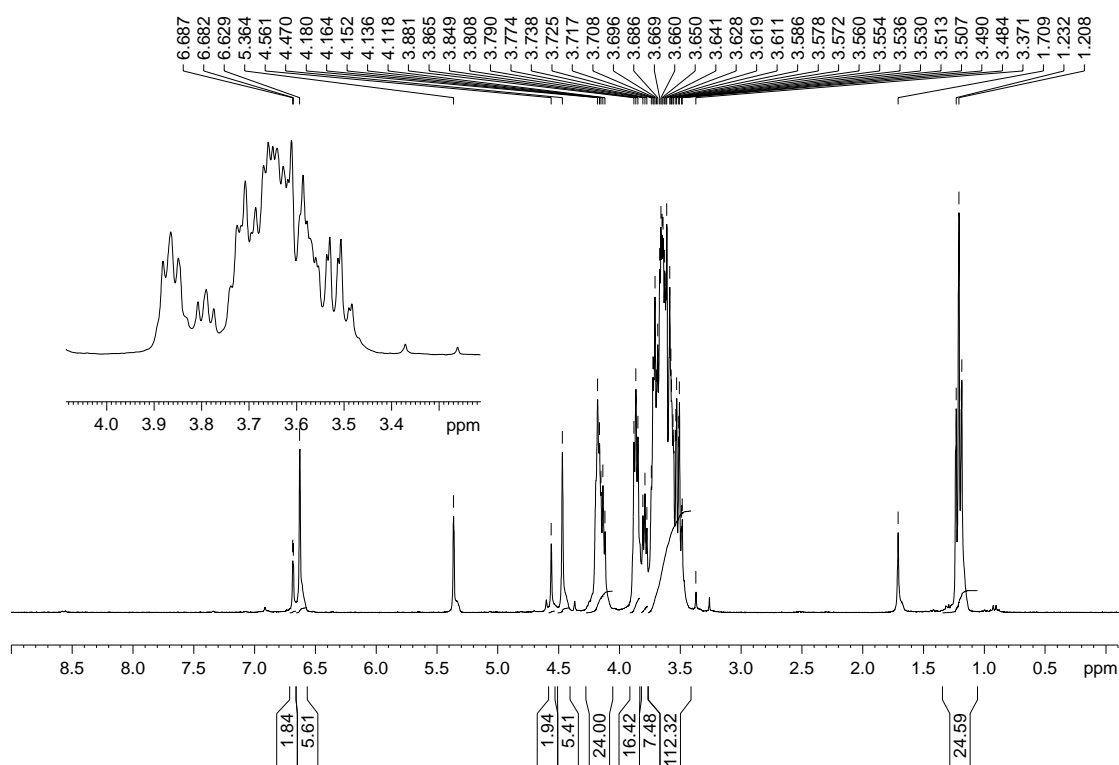


Figure S8. <sup>1</sup>H NMR spectrum of compound **2b** in CD<sub>2</sub>Cl<sub>2</sub>.

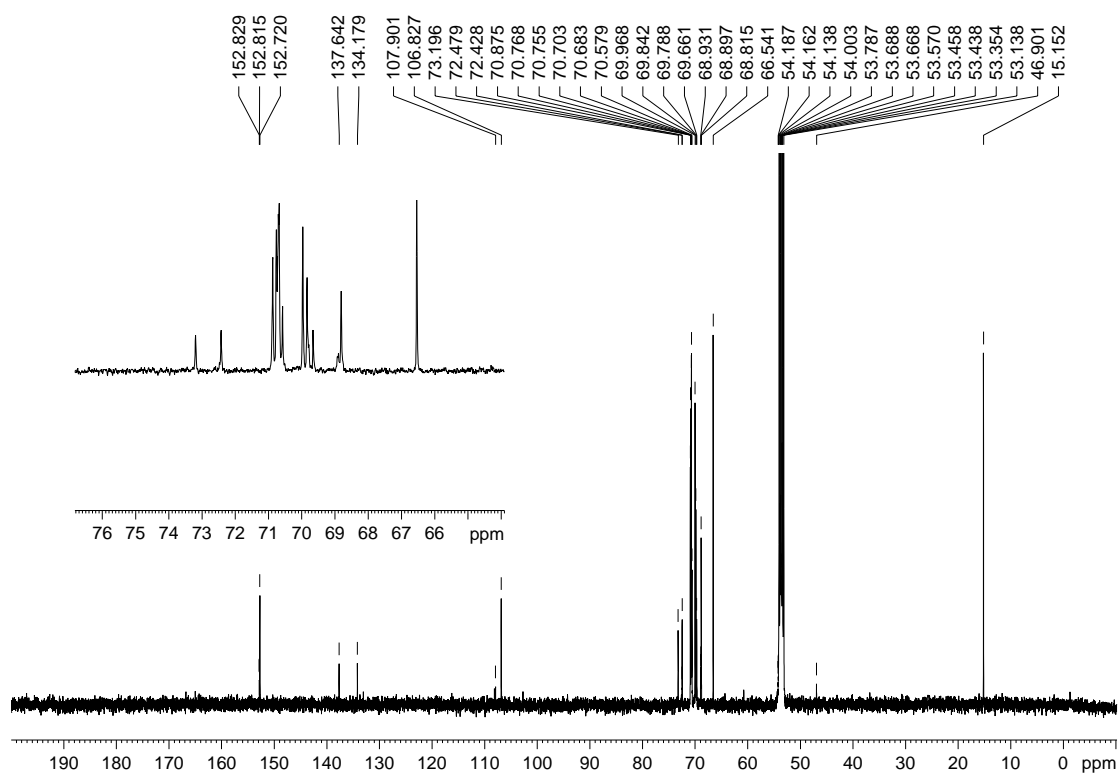
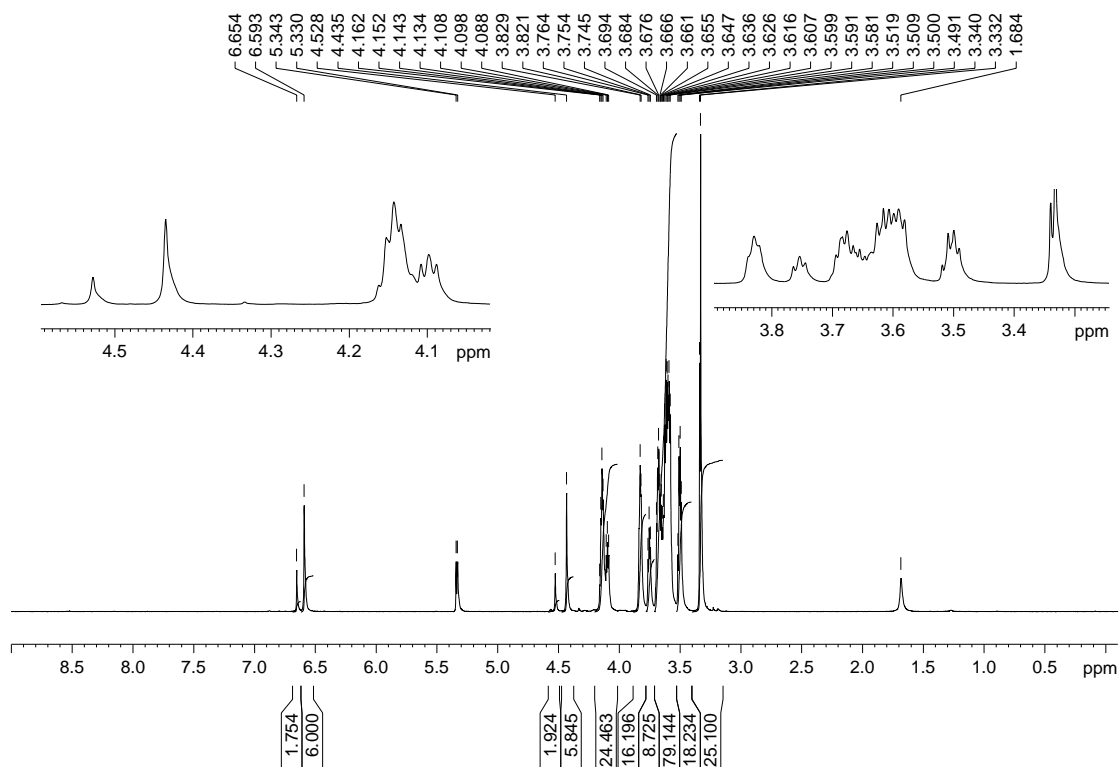
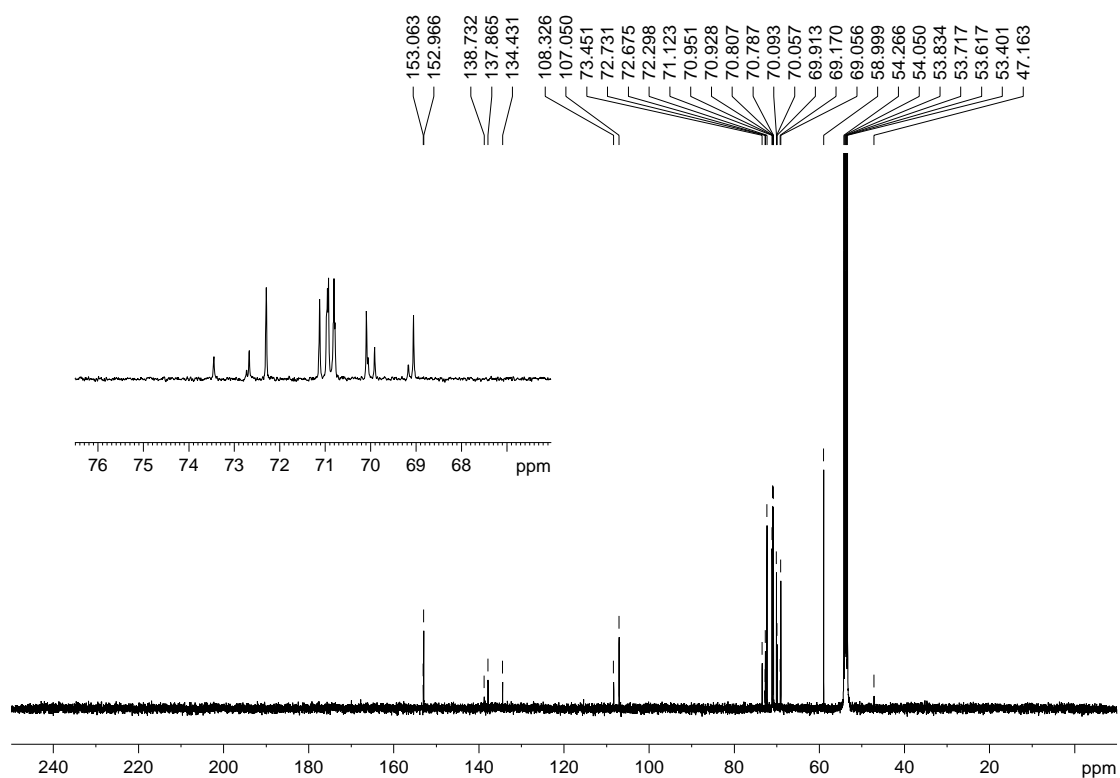


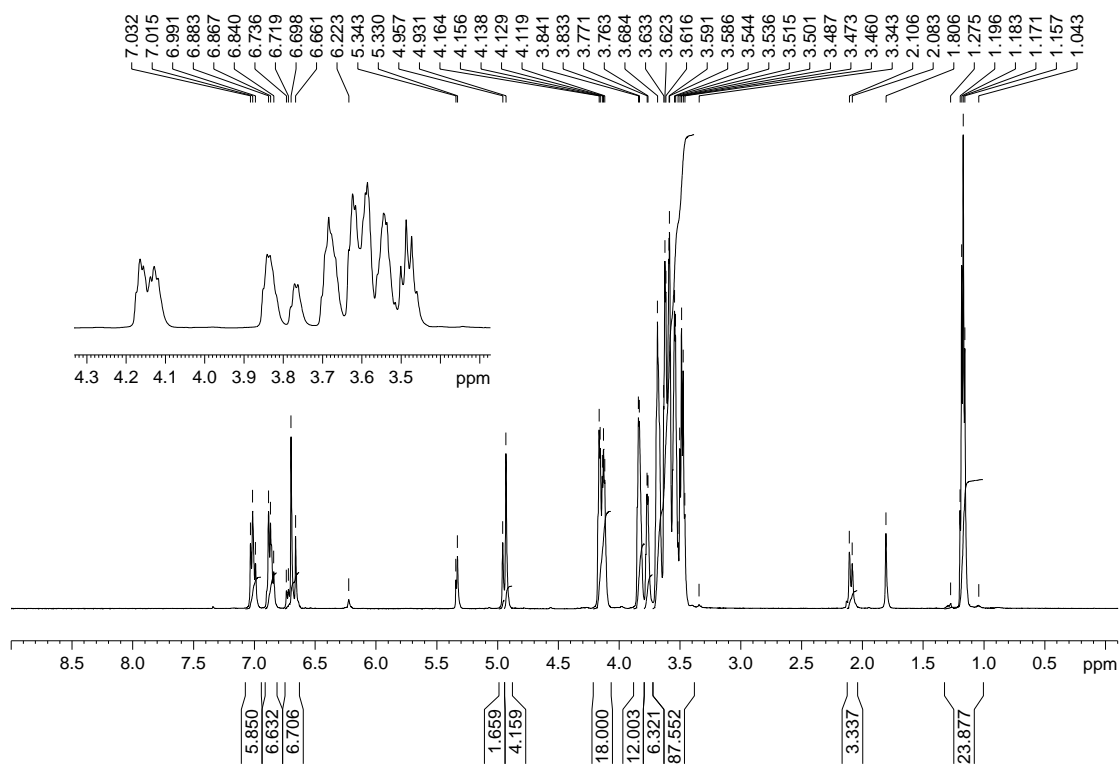
Figure S9. <sup>13</sup>C NMR spectrum of compound **2b** in CD<sub>2</sub>Cl<sub>2</sub>.



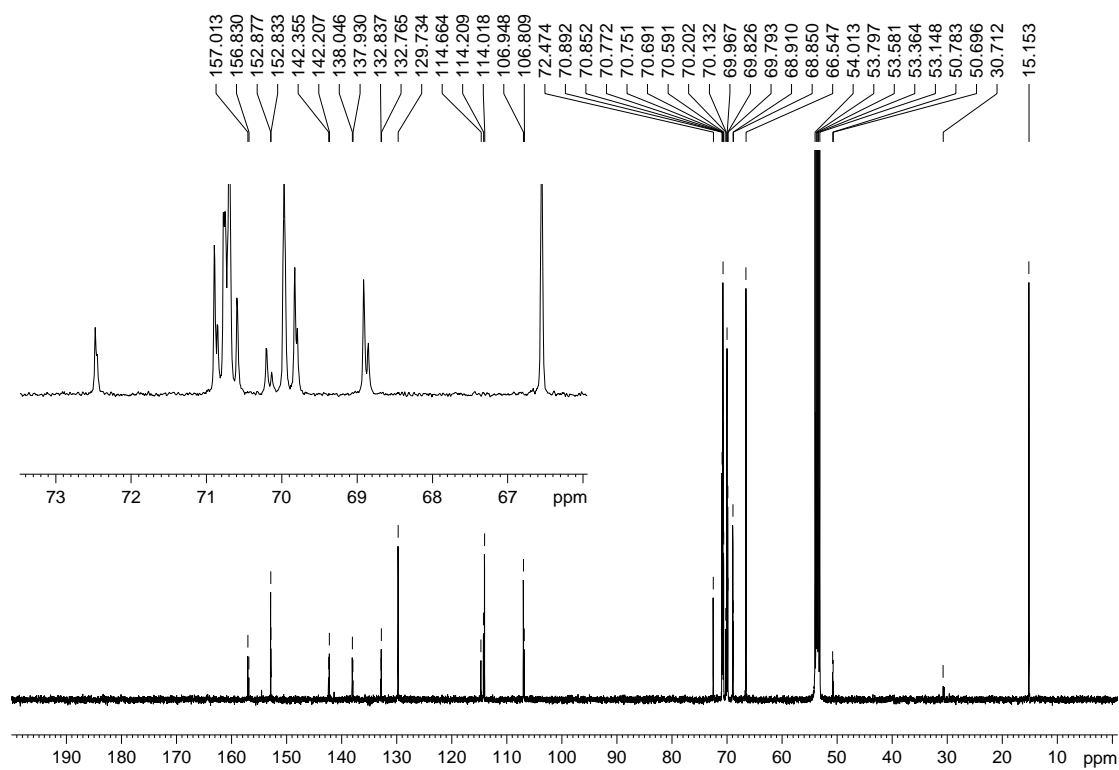
**Figure S10.** <sup>1</sup>H NMR spectrum of compound **2d** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S11.** <sup>13</sup>C NMR spectrum of compound **2d** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S12.** <sup>1</sup>H NMR spectrum of compound **Et-G1** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S13.** <sup>13</sup>C NMR spectrum of compound **Et-G1** in CD<sub>2</sub>Cl<sub>2</sub>.

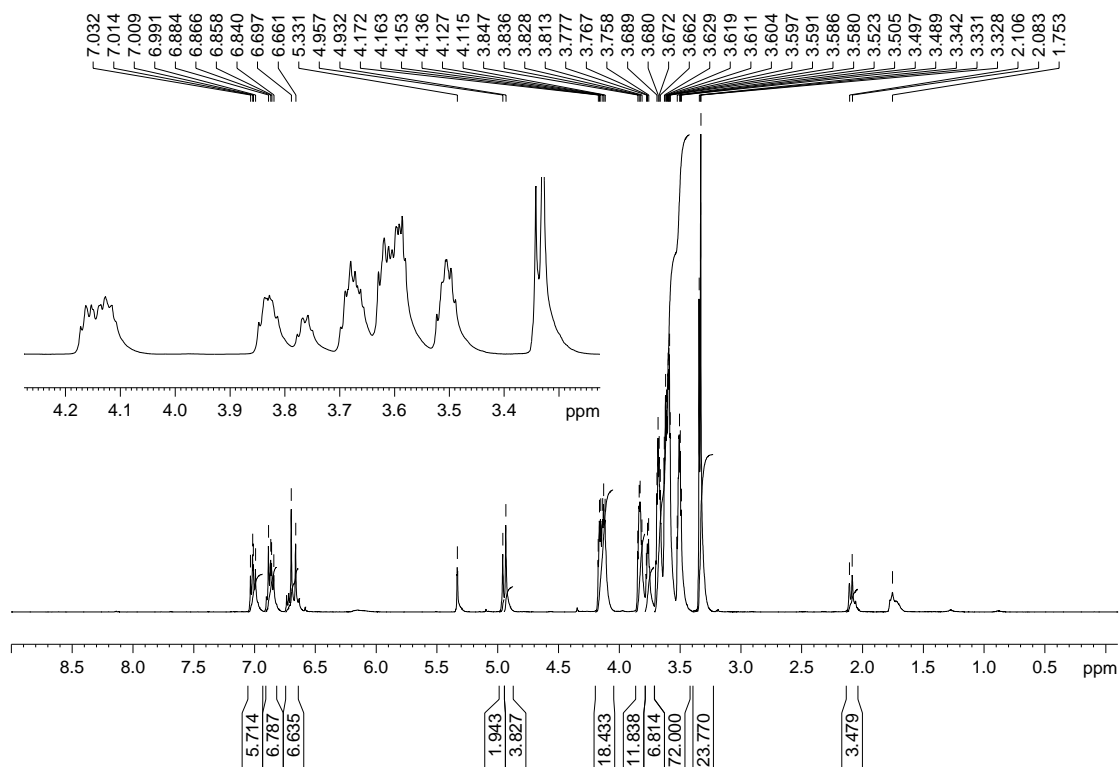


Figure S14. <sup>1</sup>H NMR spectrum of compound Me-G1 in CD<sub>2</sub>Cl<sub>2</sub>.

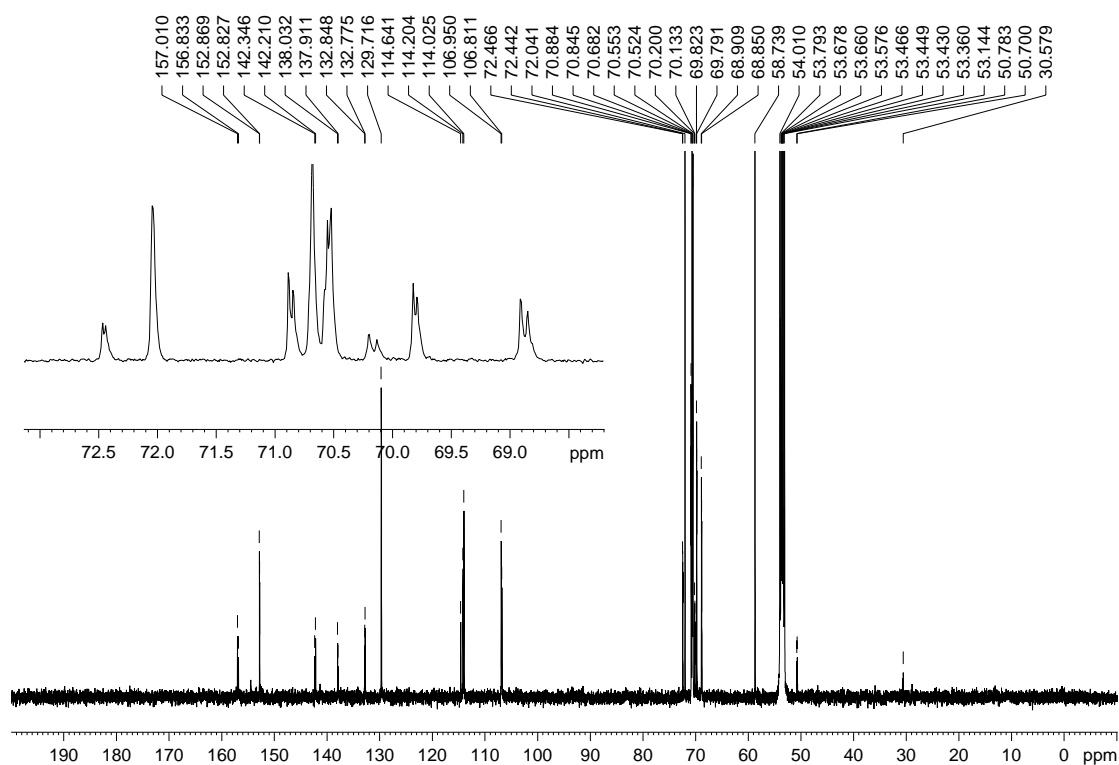


Figure S15. <sup>13</sup>C NMR spectrum of compound Me-G1 in CD<sub>2</sub>Cl<sub>2</sub>.

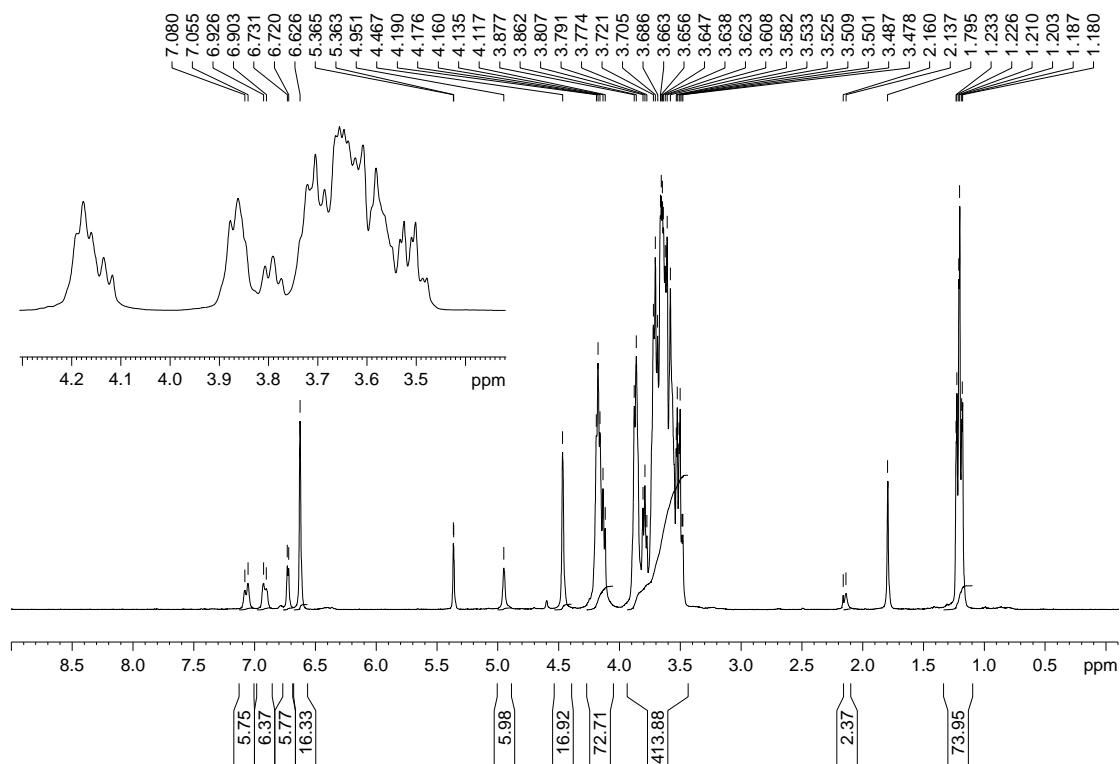


Figure S16. <sup>1</sup>H NMR spectrum of compound Et-G2 in CD<sub>2</sub>Cl<sub>2</sub>.

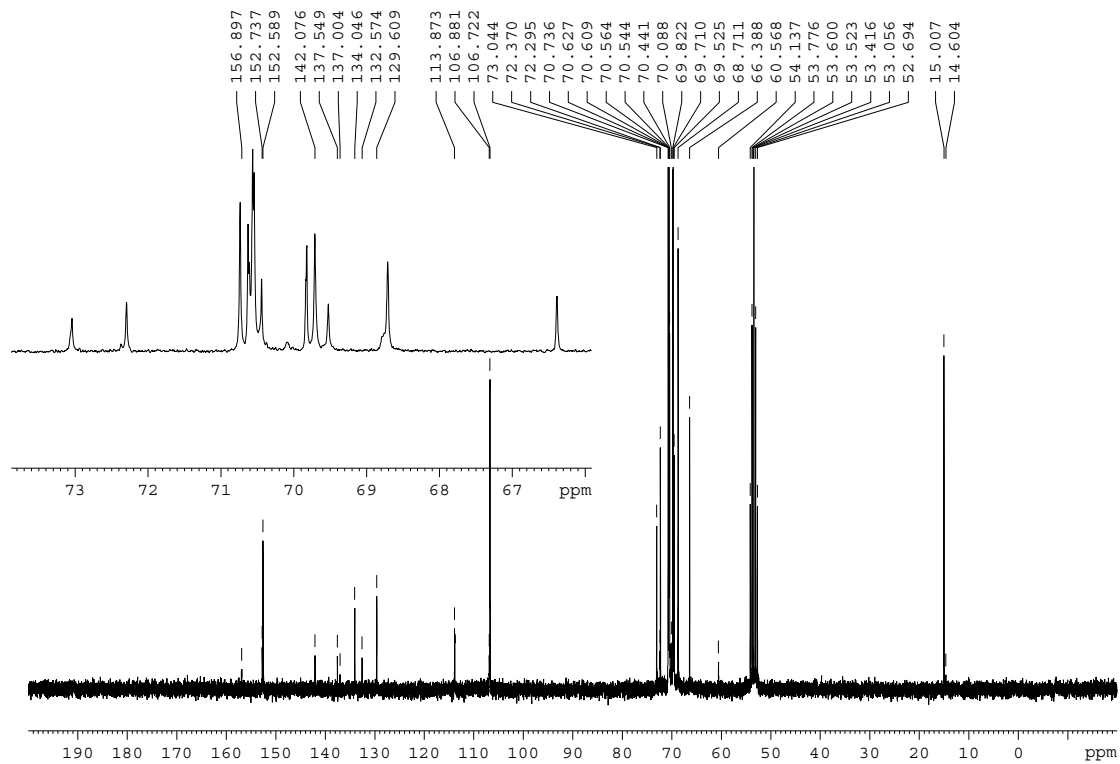


Figure S17. <sup>13</sup>C NMR spectrum of compound Et-G2 in CD<sub>2</sub>Cl<sub>2</sub>.

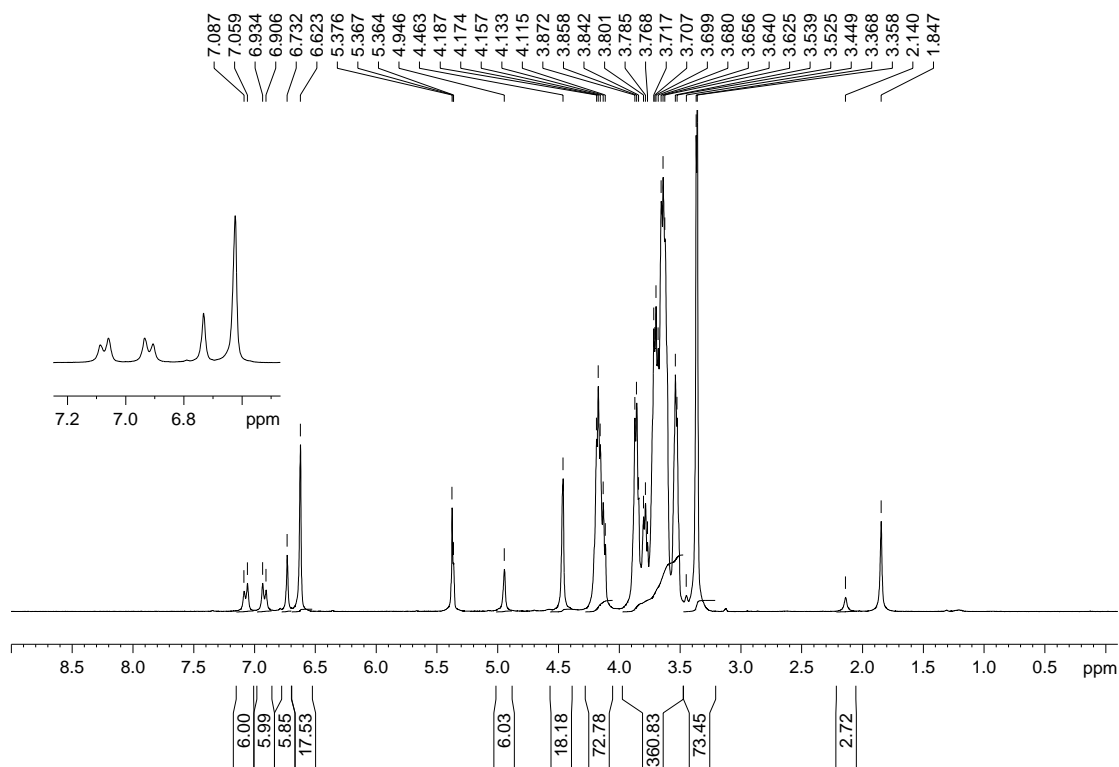


Figure S18. <sup>1</sup>H NMR spectrum of compound Me-G2 in CD<sub>2</sub>Cl<sub>2</sub>.

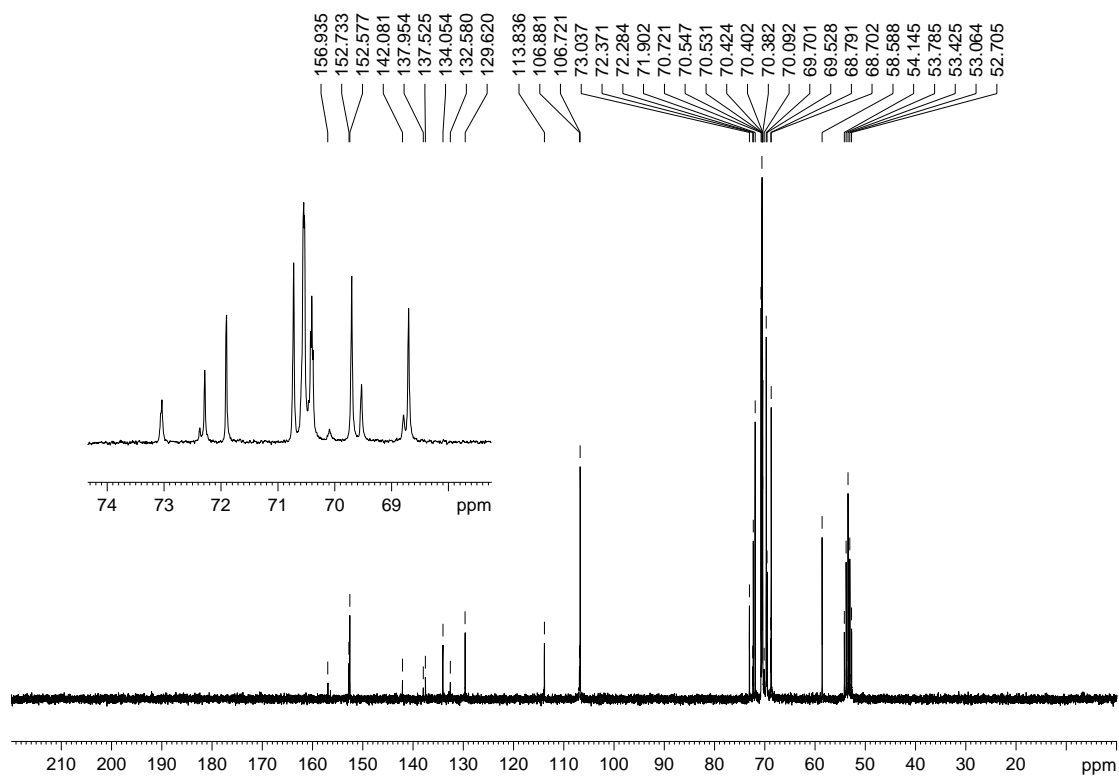


Figure S19. <sup>13</sup>C NMR spectrum of compound Me-G2 in CD<sub>2</sub>Cl<sub>2</sub>.