Supporting Information for

Re-workable Polyhydroxyurethane Films with Reversible Acetal Networks Obtained from Multi-functional Six-membered Cyclic Carbonates

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Experimental

1. Characterization

^{1}H and ^{13}C NMR spectra were recorded with a JEOL ECS-400 NMR spectrometer operating at 400 MHz using a tetramethylsilane (TMS) as an internal reference. Fourier Transfer Infra-red (FT-IR) spectroscopy was conducted with a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR instrument. Matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF MS) was carried out with a Shimazu Biotech AXIMA Confidence on the reflectron mode. Samples were dissolved in THF containing sodium triacetate and 1,8,9-trihydroxyanthracene (dithranol) as a matrix. Size exclusion column chromatography (SEC) were performed with a Tosoh HLC-8320GPC using DMF as eluents operating at a flow rate of 0.5 mL min^{-1}. Number averaged molecular mass (M_n), Weight averaged molecular mass (M_w) and polydispersity (M_w/M_n) were determined from SEC traces using polystyrene standards. PAHU films were fabricated by gradual drying of monomer solutions under ambient atmosphere using a Sanso Vacuum Drying Oven SVD10P (width, 20 cm; depth, 25 cm; height, 20 cm). Stress-strain (S-S) curves of these films were measured with a Shimazu EZ Test EZ-LX with an operation rate of 50 mm min^{-1}. PAHU films were cut to dumbbell-shaped plates with a Super dumbbell cuter (DUMBBELL Co., Ltd) and subjected to the measurements according to JISK6251-7. Tensile strength at a fracture point (σ_f) and elongation at a fracture point (ε_f) of the sample films were analyzed with a TRAPEZIUM X software. The tensile tests were performed 3-5 times and then mechanical parameters were averaged.

2. Reagents

Di(trimethylolpropane) (DTMP) was obtained from Aldrich Co., Ltd. Dipentaerythritol (DPE), trimethylolpropane (TMP), 1,3-dibromopropane, neopentylglycol, *p*-toluenesulfonyl chloride (TsCl), vanillin, , diphenyl carbonate (DPC), and 1,3-diaminopropane (DAP) were purchased from Tokyo Chemical Industry Co., Ltd. benzaldehyde, *p*-toluenesulfonate monohydrate ($TsOH{\cdot}H_2O$), benzyl chloride (BzCl), dehydrated pyridine (Py), trimethylamine (NEt_3) magnesium chloride ($MgCl_2$) were obtained from Wako Pure Chemical Co., Ltd. These reagents were used without any purification. DTMPC was synthesized from DTMP with 4 equiv. DPC according to the method that we previously reported.[1] Other reagents and solvents were used without any purification.

3. Syntheses

3-1. Synthesis of Ph-DTMP

DTMP 50.0 g (200 mmol) were dissolved in MeOH (200 mL). To the solution, benzaldehyde 5.3 g (50 mmol) and $TsOH{\cdot}H_2O$ 500 mg (2.63 mmol, 5.3 mol% per CHO group) were added and the mixture was stirred at 50°C overnight. For neutralization, $NaHCO_3$ 336 mg (4.00 mmol) was added in the mixture and then stirred at ambient temperature for 30 min. After drying, the resulting solids were dispersed in EtOAc and then insoluble parts were removed by suction filtration. The filtrates were washed three times with water and the organic layer was dried with anhydrous Na_2SO_4. After the solution was concentrated, the resulting solids were purified by silica gel column chromatography (*n*-hexane/EtOAc volume ratio of 1/1). Ph-DTMP including two isomers (**cis-Ph-DTMP** and **trans-Ph-DTMP**) were obtained as white solids in 12.3 g (72.7%) yields. These isomers were able to be isolated by reprecipitation from n-hexane/EtOAc or silica gel column chromatography.

cis-Ph-DTMP: ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.37-7.31 (m, 5.0H, phenyl), 5.38 (s, 1H, Ph-C<u>H</u>-), 4.16 (t, 2H, *J* = 5.4 Hz, -OH), 3.90 (d, 2H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.56 (d, 2H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.55 (s, 4H, 2H, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 3.25 (d, 4H, *J* = 4.8Hz, HO-C<u>H</u>$_2$-), 3.22 (s, 2H, HO-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 1.23 (q, 2H, *J* = 7.5 Hz, HO-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 1.13 (q, 2H, *J* = 7.7 Hz, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 0.79-0.74 (m, 6H, -CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 138.1, 129.0, 128.3, 126.0 (phenyl), 102.0 (Ph-<u>C</u>H-), 74.8, 72.8, 71.0, 66.2 (-CH$_2$-O-), 43.1 (HO-CH$_2$-<u>C</u>-CH$_2$-CH$_3$), 36.7 (Ph-CH-O-CH$_2$-<u>C</u>-CH$_2$-CH$_3$), 24.4, 23.1 (CH$_3$-C<u>H</u>$_2$-), 7.6, 6.9 (CH$_3$-). IR (ATR): ν = 3300 (m; ν(O-H)), 2966-2857 (w; ν(C-H)), 1454-1388 (m; δ(C-C) of phenyl), 1105-1024 (m; ν(C-O) of ether and acetal), 748 (s; δ(C-H) of phenyl), 700 cm^{-1} (s; δ(C=C) of phenyl).

trans-Ph-DTMP: ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.42-7.34 (m, 5H, phenyl), 5.40 (s, 1H, Ph-C<u>H</u>-), 4.21 (t, 2H, *J* = 5.2 Hz, -OH), 3.81 (q, 4H, *J* = 10 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.27 (d, 4H, *J* = 5.6 Hz, HO-C<u>H</u>$_2$-), 3.14 (s, 2H, HO-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 3.07 (s, 2H, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 1.73 (q, 2H, *J* = 7.5 Hz, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 1.24 (q, 2H, *J* = 7.5 Hz, HO-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 0.87 (t, 3H, *J* = 7.6 Hz, Ph-CH-O-CH$_2$-C-CH$_2$-C<u>H</u>$_3$), 0.79 (t, 3H, *J* = 7.6 Hz, HO-CH$_2$-C-CH$_2$-C<u>H</u>$_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 138.9, 128.7, 128.2, 126.3 (phenyl), 101.1 (Ph-<u>C</u>H-O-), 72.1, 71.7, 61.7 (-CH$_2$-O-), 43.7 (HO-CH$_2$-<u>C</u>-), 36.8 (-<u>C</u>-CH$_2$-O-CH-Ph), 23.3, 22.1 (CH$_3$-C<u>H</u>$_2$-), 8.1, 7.8 (CH$_3$-).

3-2. Synthesis of cis-Ph-DTMPC

cis-Ph-DTMP 1.98 g (5.84 mmol) and DPC 6.43 g (30 mmol) were dissolved in DMAc (4 mL). To the solution, $MgCl_2$ 28 mg (0.29 mmol) was added and then the mixture was stirred at 100°C for 21 h. After purification by silica gel column chromatography at *n*-hexane/EtOAc volume ratio of 1/1, **cis-Ph-DTMPC** was obtained as a white solid. Yield: 1.95 g (91.4%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38-7.33 (m, 5.0H, phenyl), 5.40 (s, 1H, Ph-C<u>H</u>-), 4.34 (d, 2H, *J* = 11 Hz, -CH$_2$-OC(=O)-), 4.15 (d, 2H, *J* = 11 Hz, -CH$_2$-OC(=O)-), 4.04 (d, 2H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.75 (s, 2H, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 3.64 (d, 2H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.48 (s, 2H, -CH$_2$-O-C<u>H</u>$_2$-C-CH$_2$-OC(=O)-), 1.54 (q, 2H, *J* = 7.2 Hz, -OC(=O)O-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 1.24 (q, 2H, *J* = 7.5 Hz, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-CH$_3$), 0.93 (t, 3H, *J* = 7.6 Hz, -OC(=O)O-CH$_2$-C-CH$_2$-C<u>H</u>$_3$), 0.87 (t, 3H, *J* = 8.0 Hz, Ph-CH-O-CH$_2$-C-CH$_2$-C<u>H</u>$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.7 (C=O), 138.3, 129.1, 128.4, 126.1 (phenyl), 102.1 (Ph-<u>C</u>H-), 73.0, 72.8, 71.0, 70.3 (-CH$_2$-O-), 36.9, 35.7 (-<u>C</u>-CH$_2$-CH$_3$), 24.3, 23.7 (CH$_3$-<u>C</u>H$_2$-), 7.6, 7.0 (CH$_3$-). IR (ATR): ν = 2965-2854 (w; ν(C-H)), 1748 (s; ν(C=O)), 1469-1385 (m; δ(C-C) of phenyl), 1171, 1098 (m; ν(C-O) of ether and acetal), 760 (s; δ(C-H) of phenyl), 699 cm^{-1} (s; δ(C=C) of phenyl).

3-3. Synthesis of cis-Ph-DTMP-Bz$_2$

cis-Ph-DTMP 3.38 g (10.0 mmol) and dehydrated pyridine 2.37 g (30.0 mmol) were dissolved in CH_2Cl_2 (25 mL) and the solution was cooled at 0°C in an ice bath. To the solution, BzCl 3.34 g (23.8 mmol, 1.2 equiv. per OH group) was added and the reaction mixture was stirred at ambient temperature for 5 h. After that, the mixture was washed twice with $NaHCO_3$ aq. (pH = ca. 8, 100 mL) followed by with water (100 mL). The organic layer was dried with anhydrous Na_2SO_4 and then the solvents were removed by rotary evaporator. The resulting liquids were purified by silica gel column chromatography (*n*-hexane/EtOAc volume ratio of 3/1) and **cis-Ph-DTMP-Bz$_2$** was obtained as a colorless liquid with a quantitative yield (5.70 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03-8.01 (m, 4H, phenyl), 7.56-7.53 (m, 2H, phenyl), 7.43-7.31 (m, 9H, phenyl), 5.37 (s, 1H, Ph-C<u>H</u>-), 4.44-4.38 (m, 4H, BzO-C<u>H</u>$_2$-), 4.06 (d, 4H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$-), 3.75 (s, 2H, Ph-CH-O-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 3.60 (s, 2H, BzO-CH$_2$-C-C<u>H</u>$_2$-O-CH$_2$-), 3.59 (d, 2H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$-), 1.68 (q, 2H, *J* = 7.8 Hz, BzO-CH$_2$-C-C<u>H</u>$_2$-

CH_3), 1.23 (q, 2H, *J* = 7.6 Hz, Ph-CH-O-CH_2-C-C$\underline{H}_2$-CH_3), 1.00 (t, 3H, *J* = 7.4 Hz, BzO-CH_2-C-CH_2-C$\underline{H}_3$), 0.77 (t, 3H, *J* = 7.4 Hz, Ph-CH-O-CH_2-C-CH_2-C$\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.4 (C=O of Bz), 138.4-126.0 (phenyl), 101.9 (Ph-$\underline{C}$H-O-), 72.8, 71.4, 70.7, 65.4 (-CH_2-O-), 42.3 (BzO-CH_2-$\underline{C}$-), 36.8 (Ph-CH-O-CH_2-$\underline{C}$-), 24.2, 23.7 (CH_3-$\underline{C}H_2$-), 7.7, 6.9 (CH_3-). IR (ATR): ν = 2966-2848 (w; ν(C-H)), 1716 (s; ν(C=O)), 1451-1381 (m; δ(C-C) of aromatic), 1264 (s; ν(COO), 1098 (s; ν(C-O) of ether and acetal), 707 cm^{-1} (s; δ(C=C) of phenyl).

3-4. Synthesis of DTMP-Bz$_2$

cis-Ph-DTMP-Bz$_2$ 1.17 g (2.14 mmol), neopentylglycol 2.23 g (21.4 mmol) and TsOH·H_2O 50 mg (0.26 mmol, 12 mol% per acetal structure) were dissolved in MeOH 10 mL and the mixture was stirred at 50°C for 11 h. After the removal of MeOH, CH_2Cl_2 (100 mL) was added to give homogeneous solutions. The solutions were washed three times with water (100 mL) and then the organic layer was dried with anhydrous Na_2SO_4. After the organic layer was concentrated, the resulting liquids were purified by silica gel column chromatography (*n*-hexane/EtOAc volume ratio of 1/1). **DTMP-Bz$_2$** was obtained as a colorless liquid. Yield: 886 mg (90.3%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.02 (d, 4H, *J* = 7.2 Hz, phenyl), 7.57 (t, 2H, *J* = 7.2 Hz, phenyl), 7.44 (t, 4H, *J* = 7.8 Hz, phenyl), 4.41 (q, 4H, *J* = 11 Hz, BzO-C$\underline{H}_2$-), 3.65 (dd, 4H, *J* =29, 11 Hz, HO-C$\underline{H}_2$-), 3.41 (s, 4H, -CH_2-O-CH_2-), 2.70 (br, 2H, HO-), 1.64 (q, 2H, *J* = 7.6 Hz, BzO-CH_2-C-C$\underline{H}_2$-CH_3), 1.27(q, 2H, *J* = 7.6 Hz, HO-CH_2-C-C$\underline{H}_2$-CH_3), 1.01 (t, 3H, *J* = 7.6 Hz, BzO-CH_2-C-CH_2-C$\underline{H}_3$), 0.80 (t, 3H, *J* = 7.6 Hz, HO-CH_2-C-CH_2-C$\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.4 (C=O of Bz), 133.2, 129.8, 129.6, 128.5 (phenyl), 72.9, 70.8, 66.4, 64.7 (-CH_2-O-), 43.1, 42.6 (-$\underline{C}$-CH_2-CH_3), 23.3, 23.1 (-C$\underline{H}_2$-CH_3), 7.5 (-CH_3). IR (ATR): ν = 3405 (m; ν(O-H)), 2963-2878 (w; ν(C-H)), 1716 (s; ν(C=O)), 1265 (s; ν(COO)), 1107 (m; ν(C-O) of ether and alcohol), 708 cm^{-1} (s; δ(C-H) of aromatic).

3-5. Synthesis of multi-functional tosylates[2]

Tri-OTs: TMP 13.4 g (100 mmol) was dissolved in mixed solvent of CH_2Cl_2 (220 mL) and NEt_3 90.5 g (894 mmol). To the solution, TsCl 68.6 g (360 mmol) was slowly added at 0°C in an ice bath and then the mixture was stirred at ambient temperature for several days. After organic solvents were removed by rotary evaporator, the black oils were added in mixed solvents of 250 mM HCl aq. (1500 mL) and MeOH (300 mL). The resulting precipitates were collected by suction filtration and the solids were washed thoroughly with water followed by MeOH. After drying, **Tri-OTs** was obtained as white solids. Yield: 75.9%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 (d, 6H, *J* = 8.4 Hz, phenyl), 7.36 (d, 6H, *J* = 8.0 Hz, phenyl), 3.76 (s, 6H, TsO-C$\underline{H}_2$-), 2.47 (s, 9H, CH_3- of Ts), 1.36 (q, 2H, *J* = 7.5 Hz, CH_3-C$\underline{H}_2$-), 0.64 (t, 3H, *J* = 7.4 Hz, C$\underline{H}_3$-CH_2-).13C NMR (100 MHz, $CDCl_3$, δ): 145.5, 131.9, 130.2, 128.1 (phenyl), 67.8 (TsO-$\underline{C}H_2$-) , 42.0 (TsO-CH_2-$\underline{C}$-), 21.9 (CH_3- of Ts), 21.7 (CH_3-$\underline{C}H_2$-), 6.7 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 2975 (w; ν(C-H) of methylene), 1356, 1174 (s; ν(S=O)), 997-809 cm^{-1} (s; ν(S-O-C)).

Tetra-OTs: Yield: 96.9%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.73 (d, 8H, *J* = 8.4 Hz, phenyl), 7.35 (d, 8H, *J* = 7.6 Hz, phenyl), 3.79-3.74 (m, 8H, TsO-C$\underline{H}_2$-), 3.11 (s, 4H, -CH_2-O-CH_2-), 2.46 (s, 12H, CH_3- of Ts), 1.26 (q, 4H, *J* = 7.5 Hz, CH_3-C$\underline{H}_2$-), 0.63 (t, 6H, *J* = 7.4 Hz, C$\underline{H}_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.3, 132.4, 130.1, 128.1 (phenyl), 69.7 (-CH_2-O-CH_2-), 69.2 (TsO-$\underline{C}H_2$-), 42.5 (TsO-CH_2-$\underline{C}$-), 22.1 (CH_3- of Ts), 21.8 (CH_3-$\underline{C}H_2$-), 7.1 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 2966-2880 (w; ν(C-H) of methylene), 1356, 1172 (s; ν(S=O)), 1095 (m; ν(C-O) of ether), 954- 810 cm^{-1} (s; ν(S-O-C)).

Hexa-OTs: Yield: 17.61 g (95.0%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 (d, 12H, *J* = 8.4 Hz, phenyl), 7.36 (d, 12H, *J* = 8.0 Hz, phenyl), 3.81 (s, 12H, TsO-CH_2-), 3.17 (s, 4H, -CH_2-O-CH_2-), 2.46 (s, 18H, CH_3-). ^{13}C NMR (100 MHz,

$CDCl_3$, δ): 145.5, 131.8, 130.1, 128.0 (phenyl), 67.9 (-CH_2-O-CH_2-), 66.6 (TsO-$\underline{C}H_2$-), 43.7 (TsO-CH_2-$\underline{C}$-), 21.7 (CH_3-). IR (ATR): ν = 2953-2853 (w; ν(C-H) of methylene), 1359, 1173 (s; ν(S=O)), 1095 (m; ν(C-O) of ether), 965-785 cm^{-1} (s; ν(S-O-C)).

3-6. Synthesis of Multi-functional aldehydes[2]

Tri-Van: To DMF (20 mL) were added **Tri-OTs** 3.60 g (6.00 mmol), vanillin 4.11 g (27.0 mmol, 1.5 equiv. per OTs group) and K_2CO_3 4.90 g (35.5 mmol). The mixture was stirred at 100°C for 3 days and then DMF was removed by vacuum pump. The resulting solids were added in $CHCl_3$ (100 mL) and the mixture was washed three times with water (100 mL) followed by saturated NaCl aq. (100 mL). The organic layer was dried with anhydrous Na_2SO_4 and then concentrated by rotary evaporator. The resulting brown solids were purified by silica gel column chromatography ($CHCl_3$/EtOAc volume ratio of 20/1). **Tri-Van** was obtained as a pale yellow solid. Yield: 67.3%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.78 (s, 3H, -CHO), 7.48 (dd, 3H, *J* = 8.2, 1.8 Hz, phenyl), 7.31 (d, 3H, *J* = 2.0 Hz, phenyl), 7.21 (d, 3H, *J* = 8.4 Hz, phenyl), 4.17 (s, 6H, -O-CH_2-), 3.72 (s, 9H, CH_3-O-), 1.75 (q, 2H, *J* = 7.6 Hz, CH_3-$\underline{C}H_2$-), 0.93 (t, 3H, *J* = 7.4 Hz, CH_3-CH_2-). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 191.9 (-CHO), 154.0, 150.0, 130.5, 126.4, 113.4, 110.5 (phenyl), 69.0 (-O-CH_2-), 56.3 (CH_3-O-), 43.5 (-O-CH_2-$\underline{C}$-), 23.0 (CH_3-$\underline{C}H_2$-), 7.9 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 2963-2831 (w; ν(C-H) of methylene), 2723 (w; ν(C-H) of aldehyde), 1679 (s; ν(C=O)), 1585, 1508 (s; ν(C=C) of aromatic), 1263, 1132, 1024 (s; ν(C-O)), 807 (m; δ(C-H) of aromatic), 730 cm^{-1} (m; δ(C=C) of aromatic).

Tetra-Van: Yield: 50.0%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.81 (s, 4H, -CHO), 7.35-7.32 (m, 8H, phenyl), 6.87 (d, 4H, *J* = 7.6 Hz, phenyl), 4.08-4.02 (m, 8H, PhO-$\underline{C}H_2$-), 3.80 (s, 12H, CH_3-O-), 3.61 (s, 4H, -CH_2-O-CH_2-), 1.70 (q, 2H, *J* = 7.6 Hz, CH_3-$\underline{C}H_2$-), 0.89 (t, 3H, *J* = 7.4 Hz, $\underline{C}H_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 191.0 (-CHO), 154.4, 150.2, 130.2, 126.6, 112.0, 109.6 (phenyl), 71.0 (-CH_2-O-CH_2-), 69.5 (PhO-$\underline{C}H_2$-), 56.0 (CH_3-O-), 43.5 (CH_3-CH_2-$\underline{C}$-), 23.3 (CH_3-$\underline{C}H_2$-), 7.7 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 2961-2830 (w; ν(C-H) of methylene), 2719 (w; ν(C-H) of aldehyde), 1678 (s; ν(C=O)), 1584, 1508 (s; ν(C=C) of aromatic), 1263, 1133, 1024 (s; ν(C-O)), 808, 781 (m; δ(C-H) of aromatic), 729 cm^{-1} (m; δ(C=C) of aromatic).

Hexa-Van: Yield: 1.28 g (60.3%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.80 (s, 6H, -CHO), 7.32-7.29 (m, 12H, phenyl), 6.85 (d, 6H, *J* = 8 .0 Hz, phenyl), 4.30 (s, 12H, PhO-$\underline{C}H_2$-), 3.96 (s, 4H, -CH_2-O-CH_2-), 3.77 (s, 18H, CH_3-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 190.7 (-CHO), 153.8, 150.0, 130.4, 126.3, 112.2, 109.4 (phenyl), 69.7 (-CH_2-O-CH_2-), 67.8 (PhO-$\underline{C}H_2$-), 55.8 (-CH_3), 45.6 (-CH_2-O-CH_2-$\underline{C}$-). IR (ATR): ν = 2934-2827 (w; ν(C-H) of methylene), 2718 (w; ν(C-H) of aldehyde), 1677 (s; ν(C=O)), 1584, 1507 (s; ν(C=C) of aromatic), 1261, 1132, 1022 (s; ν(C-O)), 806, 780 (m; δ(C-H) of aromatic), 728 cm^{-1} (m; δ(C=C) of aromatic).

3-7. Synthesis of multi-functional polyols protected by Bz groups[3]

Tri-DTMP-Bz_2: **Tri-Van** 2.81 g (5.23 mmol), **DTMP-Bz_2** 10.8 g (23.5 mmol, 1.5 equiv. per aldehyde group) and TsOH·H_2O 150 mg (0.79 mmol, 5 mol% per aldehyde group) were dissolved in CH_2Cl_2 (20 mL). To the solution, anhydrous $MgSO_4$ 20.0 g (166 mmol) was added and then the mixture was stirred at 40°C for 2 days. After that, the mixture was added slowly in cold water (200 mL) containing $NaHCO_3$ 67 mg (0.8 mmol) and insoluble parts were extracted with CH_2Cl_2 (200 mL). The organic layer was washed three times with water (200 mL) and dried with anhydrous Na_2SO_4. After the evaporation of solvents, the resulting solids were purified by reprecipitation from $CHCl_3$/MeOH mixed solvents to afford **Tri-DTMP-Bz_2** as a colorless solid. Yield: 86.2%. ^{1}H

NMR (400 MHz, $CDCl_3$, δ): 7.97-7.92 (m, 12H, Bz), 7.66-7.42 (m, 6H, Bz), 7.52-7.42 (m, 12H, Bz), 6.96-6.84 (m, 9H, vanillin), 5.30 (s, 2.2H, Ph-C<u>H</u>- of cis-form), 5.23 (s, 0.7H, Ph-C<u>H</u>- of trans-form), 4.36-4.29 (m, 12H, BzO-C<u>H</u>$_2$-), 4.03 (s, 6H, PhO-C<u>H</u>$_2$-), 3.89 (d, 4.5H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.78-3.68 (m, 3.1H, Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.65-3.12 (m, 13.3H, CH_3-O- and Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.54-3.50 (m, 9.0H, Ph-CH-O-C<u>H</u>$_2$- of cis-form and BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.44 (s, 1.6H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 3.10 (s, 1.5H, BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.71-1.56 (m, 9.4H, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form, CH_3-C<u>H</u>$_2$-C-CH_2-OBz and CH_3-C<u>H</u>$_2$- of TMP core), 1.18-1.08 (m, 4.6H, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.95-0.90 (m, 12H, C<u>H</u>$_3$-CH_2-C-CH_2-OBz and C<u>H</u>$_3$-CH_2- of TMP core), 0.77-0.65 (m, 9H, C<u>H</u>$_3$-CH_2-C-CH_2-O-CH-Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.0 (C=O),149.1, 133.8, 132.4, 130.0, 129.7, 129.3, 119.0, 114.6, 110.5 (phenyl), 100.9 (Ph-<u>C</u>H-), 72.5, 71.8, 70.0 (-CH_2-O-), 56.0 (CH_3-O-), 42.4, 37.1, 36.7 (CH_3-CH_2-<u>C</u>-), 24.2, 23.7 (CH_3-<u>C</u>H_2-), 8.0, 7.2 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 2961-2852 (w; ν(C-H) of methylene), 1717 (s; ν(C=O)), 1516, 1450 (w; ν(C=C) of aromatic), 1262, 1096 (s; ν(C-O)), 708 cm^{-1} (s; δ(C=C) of aromatic).

Tetra-DTMP-Bz$_2$: Yield: 74.4%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.94-7.88 (m, 16H, Bz), 7.62-7.53 (m, 8H, Bz), 7.48-7.38 (m, 16H, Bz), 6.83-6.67 (m, 12H, vanillin), 5.24 (s, 2.9H, Ph-C<u>H</u>- of cis-form), 5.27 (s, 1.0H, Ph-C<u>H</u>- of trans-form), 4.31-4.25 (m, 16H, BzO-C<u>H</u>$_2$-), 3.87-3.81 (m, 14.0H, PhO-C<u>H</u>$_2$- and Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.75-3.64 (m, 6.0H, Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.61-3.58 (m, 17.7H, CH_3-O- and Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.50-3.47 (m, 12.1H, Ph-CH-O-C<u>H</u>$_2$- of cis-form and BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.42-3.40 (m, 6.3H, -CH_2-O-CH_2- of DTMP core and Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 3.06 (s, 2.0H, BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.64 (q, 2.2H, *J* = 7.1 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.56-1.48 (m, 12H , CH_3-C<u>H</u>$_2$-C-CH_2-OBz and CH_3-C<u>H</u>$_2$- of DTMP core), 1.07 (q, 6.0H, *J* = 7.3 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.91-0.86 (m, 12H, C<u>H</u>$_3$-CH_2-C-CH_2-OBz), 0.78-0.61 (m, 18H, C<u>H</u>$_3$-CH_2-C-CH_2-O-CH-Ph and CH_3-CH_2- of DTMP core). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.5 (C=O), 149.8, 133.2, 133.1, 130.1, 129.6, 128.6, 118.9, 110.5 (phenyl), 101.9 (Ph-<u>C</u>H-), 72.9, 72.1, 71.5, 70.8, 70.1, 65.5 (-CH_2-O-), 56.3 (CH_3-O-), 42.3, 36.8 (CH_3-CH_2-<u>C</u>-),24.3, 23.7 (CH_3-<u>C</u>H_2-), 7.8, 7.0 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 2963-2858 (w; ν(C-H) of methylene), 1716 (s; ν(C=O)), 1515, 1450 (w; ν(C=C) of aromatic), 1265, 1096 (s; ν(C-O)), 707 cm^{-1} (s; δ(C=C) of aromatic).

Hexa-DTMP-Bz$_2$: Yield: 5.14 g (85.7%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.96-7.90 (m, 24H, Bz), 7.64-7.54 (m, 12H, Bz), 7.50-7.39 (m, 24H, Bz), 6.85-6.66 (m, 18H, vanillin), 5.25 (s, 4.3H, Ph-C<u>H</u>- of cis-form), 5.21 (s, 1.6H, Ph-C<u>H</u>- of trans-form), 4.30 (s, 24H, BzO-C<u>H</u>$_2$-), 4.05 (s, 12H, PhO-C<u>H</u>$_2$-), 3.88 (d, 9.2H, *J* = 10 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.78-3.66 (m, 10.6H, Ph-CH-O-C<u>H</u>$_2$- of tans-form and -CH_2-O-CH_2- of DPE), 3.61-3.57 (m, 27H, CH_3-O- and Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.51-3.49 (m, 17.7H, Ph-CH-O-CH_2- of cis-form and BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.42 (s, 3.1H, BzO-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 3.08 (s, 3.0H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.66 (q, 3.0H, *J* = 7.6 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.56 (q, 12H, *J* = 6.7 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-OBz), 1.09 (q, 9.0H, *J* = 6.8 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.93-0.88 (m, 18H, C<u>H</u>$_3$-CH_2-C-CH_2-OBz), 0.76-0.63 (m, 18H, C<u>H</u>$_3$-CH_2-C-CH_2-O-CH-Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.3 (C=O), 149.6, 149.5, 133.1, 133.0, 131.4, 130.0, 129.5, 128.4, 118.8, 113.9, 110.2 (phenyl), 101.8, 101.6 (Ph-<u>C</u>H-), 72.7, 71.9, 71.4, 70.7, 68.6, 65.4 (-CH_2-O-), 56.0 (CH_3-O-), 42.2, 37.0, 36.7 (-O-CH_2-<u>C</u>-), 24.2, 23.7 (CH_3-<u>C</u>H_2-), 7.7, 6.8 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 2966-2854 (w; ν(C-H) of methylene), 1717 (s; ν(C=O)), 1517, 1451 (w; ν(C=C) of aromatic), 1265, 1100 (s; ν(C-O)), 710 cm^{-1} (s; δ(C=C) of aromatic).

3-8. Synthesis of multi-functional DTMPs

Tri-DTMP: **Tri-DTMP-Bz$_2$** 8.09 g (4.35 mmol) was dissolved in THF (100 mL). To the solution, MeOH (100 mL) was added and then NaOH 5.2 g (130 mmol) dissolving in water (20 mL) was added. The mixture was stirred at ambient temperature for 1-2 days. After evaporation of the solvents, the mixture was dispersed in water (200 mL) and then extracted with CH_2Cl_2 (250 mL). The organic layer was washed three times with water (250 mL) and then dried with anhydrous Na_2SO_4. After concentration, **Tri-DTMP** was obtained as a pale yellow solid. Yield: > 99%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.97-6.89 (m, 9H, phenyl), 5.32 (s, 2.1H, Ph-C$\underline{H}$- of cis-form), 5.31 (s, 0.9H, Ph-C$\underline{H}$- of trans-form), 4.24-4.19 (m, 6H, HO-), 4.04 (s, 6H, PhO-C$\underline{H_2}$-), 3.91 (d, 4.6H, *J* = 11 Hz, Ph-CH-O-C$\underline{H_2}$- of cis-form), 3.82-3.74 (m, 3.3H, Ph-CH-O-C$\underline{H_2}$- of trans-form), 3.67 (s, 9H, CH_3-O-), 3.56-3.53 (m, 8.7H, Ph-CH-O-C$\underline{H_2}$- of cis-form and Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.28-3.24 (m, 15.5H, HO-C$\underline{H_2}$- and HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.13 (s, 1.5H, Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 3.05 (s, 1.4H, HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 1.71 (q, 3.5H, *J* = 7.6 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of trans-form and CH_3-C$\underline{H_2}$- of TMP core), 1.28-1.21 (m, 6H, CH_3-C$\underline{H_2}$-C-CH_2-OH), 1.14 (q, 4.7H, *J* = 7.5 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of cis-form), 0.94-0.76 (m, 21H, C$\underline{H_3}$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.3, 149.1, 132.5, 119.2, 114.0, 111.0 (phenyl), 101.3 (Ph-$\underline{C}$H-), 72.3, 71.9, 70.6, 62.2, 62.0 (-CH_2-O-), 56.3 (CH_3-O-), 44.0, 36.7 (CH_3-CH_2-$\underline{C}$-), 24.4, 22.5 (CH_3-$\underline{C}H_2$-), 8.1, 7.3 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 3405 (w; ν(O-H)), 2962-2857 (w; ν(C-H) of methylene), 1515, 1463 (w; ν(C=C) of aromatic), 1263, 1096, 1019 cm^{-1} (s; ν(C-O)).

Tetra-DTMP: Yield: >99%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.91-6.77 (m, 12H, phenyl), 5.30 (s, 3.9H, Ph-C$\underline{H}$-), 4.21 (s, 8H, HO-), 3.91 (d, 6.0H, *J* = 11 Hz, Ph-CH-O-C$\underline{H_2}$- of cis-form), 3.85-3.74 (m, 12.1H, Ph-CH-O-C$\underline{H_2}$- of trans-form and PhO-C$\underline{H_2}$-), 3.67-3.66 (m, 12H, CH_3-O-), 3.56-3.54 (m, 11.7H, Ph-CH-O-C$\underline{H_2}$- of cis-form and Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.45 (s, 4H, -CH_2-O-CH_2- of DTMP core), 3.28-3.24 (m, 21.7H, HO-C$\underline{H_2}$- and HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.14 (s, 2.0H, Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 3.06 (s, 2.1H, HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 1.72 (q, 2.1H, *J* = 7.2 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of trans-form), 1.52 (q, 4H, *J* = 6.9 Hz, CH_3-C$\underline{H_2}$- of DTMP core), 1.28-1.22 (m, 8H, CH_3-C$\underline{H_2}$-C-CH_2-OH), 1.15 (q, 5.9H, *J* = 7.5 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of cis-form), 0.88-0.76 (m, 30H, C$\underline{H_3}$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.0, 131.9, 118.9, 113.3, 110.6 (phenyl), 101.0 (Ph-$\underline{C}$H-), 72.5, 72.0, 71.6, 70.3, 61.9 (-CH_2-O-), 55.9 (CH_3-O-), 43.7, 36.3 (CH_3-CH_2-$\underline{C}$-), 24.1, 23.4, 22.2 (CH_3-$\underline{C}H_2$-), 7.8 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 3405 (w; ν(O-H)), 2962-2858 (w; ν(C-H) of methylene), 1517, 1460 (w; ν(C=C) of aromatic), 1263, 1097 cm^{-1} (s; ν(C-O)).

Hexa-DTMP: Yield: 3.21 g (96.9%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.90-6.75 (m, 18H, phenyl), 5.29 (s, 5.9H, Ph-C$\underline{H}$-), 4.21-4.17 (m, 12H, HO-), 4.06 (s, 12H, PhO-C$\underline{H_2}$-), 3.92 (d, 8.9H, *J* = 11 Hz, Ph-CH-O-C$\underline{H_2}$- of cis-form), 3.84-3.70 (m, 10.6H, Ph-CH-O-C$\underline{H_2}$- of trans-form and -CH_2-O-CH_2- of DPE core), 3.64-3.63 (m, 17.5H, CH_3-O-), 3.57-3.54 (m, 17.6H, Ph-CH-O-C$\underline{H_2}$- of cis-form and Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.29-3.24 (m, 31.9H, HO-C$\underline{H_2}$- and HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of cis-form), 3.14 (s, 3.2H, Ph-CH-O-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 3.06 (s, 3.1H, HO-CH_2-C-C$\underline{H_2}$-O-CH_2- of trans-form), 1.73 (q, 3.2H, *J* = 7.2 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of trans-form), 1.25 (q, 12H, *J* = 7.6 Hz, CH_3-C$\underline{H_2}$-C-CH_2-OH), 1.15 (q, 9.0H, *J* = 7.2 Hz, CH_3-C$\underline{H_2}$-C-CH_2-O-CH-Ph of cis-form), 0.89-0.77 (m, 36H, C$\underline{H_3}$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.0, 132.1, 118.9, 113.7, 110.5 (phenyl), 101.0 (Ph-$\underline{C}$H-), 72.0, 71.6, 70.2, 61.9 (-CH_2-O-), 55.9 (CH_3-O-), 43.7, 36.3 (CH_3-CH_2-$\underline{C}$-), 24.1, 22.2 (CH_3-$\underline{C}H_2$-), 7.8, 7.0 ($\underline{C}H_3$-CH_2-). IR (ATR): ν = 3396 (w; ν(O-H)), 2960-2858 (w; ν(C-H) of methylene), 1516, 1462 (w; ν(C=C) of aromatic), 1264, 1098 cm^{-1} (s; ν(C-O)).

3-9. Synthesis of multi-functional DTMP-based 6-CCs

Tri-DTMPC: **Tri-DTMP** 5.10 g (4.13 mmol), DPC 10.6 g (49.6 mmol, 4 equiv. per 1,3-diol structure) and $MgCl_2$ 118 mg (1.24 mmol, 10 mol% per 1,3-diol structure) were dissolved in DMF (40 mL). The mixture was stirred at 100°C overnight and then DMF was removed under reduced pressure. The resulting solids were dissolved in CH_2Cl_2 (200 mL) and washed three times with water (200 mL) and then dried with anhydrous Na_2SO_4. After concentration, the resulting solids were purified by silica gel column chromatography (eluents: $CHCl_3$/EtOAc = 10/1 to $CHCl_3$/MeOH = 10/1 by Vol.). **Tri-DTMPC** was obtained as a white solid. Yield: 94.2%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.97-6.89 (m, 9H, phenyl), 5.33 (s, 2.9H, Ph-C<u>H</u>-), 4.27-4.19 (q, 12H, *J* = 11 Hz, -OC(=O)O-CH_2-), 4.04 (s, 6H, PhO-C<u>H</u>$_2$-), 3.91 (d, 4.6H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.83-3.74 (m, 3.1H, Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.68-3.67 (m, 9H, CH_3-O-), 3.63 (s, 4.3H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.56 (d, 4.4H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.42 (s, 4.2H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.13 (s, 1.4H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.71 (q, 3.5H, *J* = 7.3 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form and CH_3-C<u>H</u>$_2$- of TMP core), 1.41-1.35 (m, 6H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-CH_3), 1.15 (q, 4.6H, *J* = 7.5 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.94-0.75 (m, 21H, C<u>H</u>$_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.1, 148.8, 148.1, 132.1, 118.8, 113.6, 110.5 (phenyl and C=O), 101.0 (Ph-<u>C</u>H-), 72.6, 71.8, 70.0, (-CH_2-O-), 56.0 (CH_3-O-), 43.2, 36.4, 35.0 (CH_3-CH_2-<u>C</u>-), 23.8, 23.0 (CH_3-<u>C</u>H$_2$-), 7.4, 7.0 (<u>C</u>H$_3$-CH_2-). IR (ATR): ν = 2964-2858 (w; ν(C-H) of methylene), 1748 (s; ν(C=O)), 1515, 1466 (w; ν(C=C) of aromatic), 1264, 1165, 1096, 1025 cm^{-1} (s; ν(C-O)).

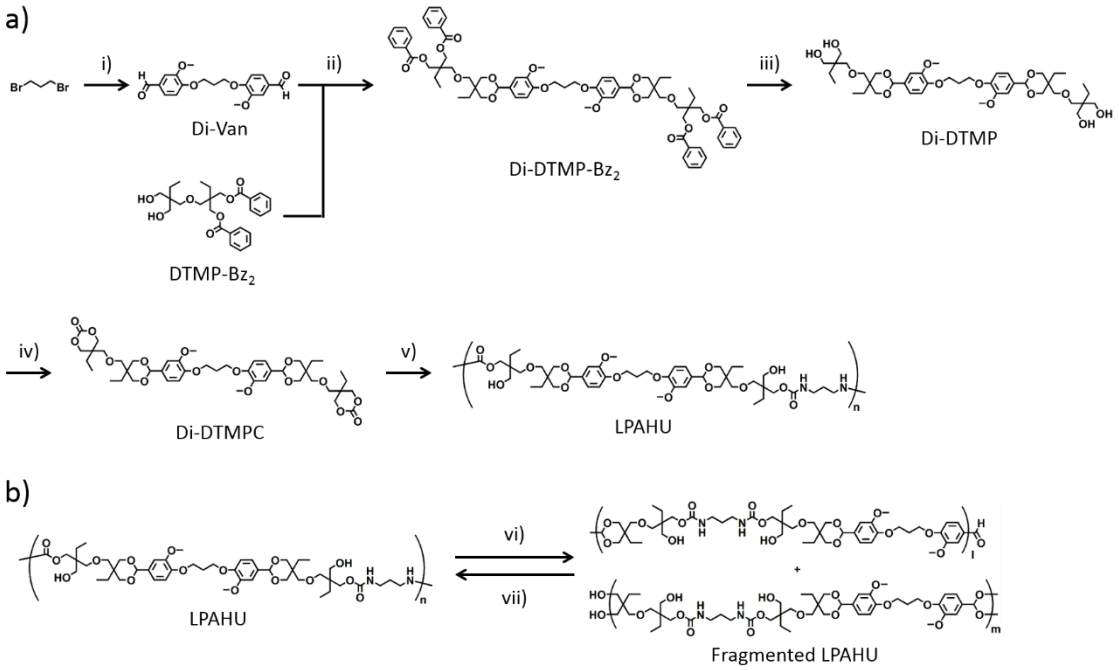
Tetra-DTMPC: Yield: 94.0%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.91-6.80 (m, 12H, phenyl), 5.32 (s, 3.9H, Ph-C<u>H</u>-), 4.27-4.19 (q, 16H, *J* = 10 Hz, -OC(=O)O-CH_2-), 3.92 (d, 6.1H, *J* = 11 Hz, Ph-CH-O-CH_2- of cis-form), 3.86-3.75 (m, 12.3H, PhO-C<u>H</u>$_2$- and Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.68-3.67 (m, 11.7H, CH_3-O-), 3.63 (s, 6.0H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.57 (d, 6.2H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.45 (s, 4H, -CH_2-O-CH_2- of DTMP core), 3.42 (s, 6.0H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.33 (s, 1.9H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 3.14 (s, 2.1H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.72 (q, 2.1H, *J* = 7.6 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.52 (q, 4H, *J* = 6.7 Hz, CH_3-C<u>H</u>$_2$- of DTMP core), 1.39 (q, 8H, *J* = 7.5 Hz, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-CH_3), 1.16 (q, 5.9H, *J* = 7.5 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.88-0.76 (m, 30H, C<u>H</u>$_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.0, 148.0, 131.1, 118.8, 113.3, 110.5 (phenyl and C=O), 100.9 (Ph-<u>C</u>H-), 72.5, 71.8, 70.0, (-CH_2-O-), 56.0 (CH_3-O-), 43.2, 36.4, 35.0 (CH_3-CH_2-<u>C</u>-), 23.8, 23.0 (CH_3-<u>C</u>H$_2$-), 7.3, 7.0 (<u>C</u>H$_3$-CH_2-). IR (ATR): ν = 2964-2858 (w; ν(C-H) of methylene), 1749 (s; ν(C=O)), 1515, 1464 (w; ν(C=C) of aromatic), 1263, 1165, 1098, 1024 cm-1 (s; ν(C-O)).

Hexa-DTMPC: Yield: 3.13 g (94.1%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.89-6.76 (m, 18H, phenyl), 5.30 (s, 5.8H, Ph-C<u>H</u>-), 4.26-4.19 (m, 24H, -OC(=O)O-CH_2-), 4.06 (br, 12H, PhO-C<u>H</u>$_2$-), 3.92 (d, 9.0H, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.85-3.74 (m, 6.5H, Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.69-3.63 (m, 29.7H, CH_3-O-, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form and -CH_2-O-CH_2- of DPE core), 3.58-3.55(d, 9.3H, *J* = 11 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.41 (s, 8.9H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.14 (s, 2.9H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 1.73 (q, 3.0H, *J* = 7.2 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.38 (q, 12H, *J* = 7.5 Hz, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-CH_3), 1.16 (q, 9.0H, *J* = 7.3 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.88-0.76 (m, 36H, C<u>H</u>$_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.0, 148.7, 148.1, 132.1, 117.0, 113.6, 110.5 (phenyl and C=O), 101.0 (Ph-<u>C</u>H-), 72.6, 71.8, 70.0, (-CH_2-O-), 55.9 (CH_3-O-), 36.4, 35.0 (CH_3-CH_2-<u>C</u>-), 23.8, 23.0 (CH_3-<u>C</u>H$_2$-), 7.4, 7.0 (<u>C</u>H$_3$-CH_2-). IR (ATR): ν =2965-2852 (w; ν(C-H) of methylene), 1749 (s; ν(C=O)), 1515, 1463 (w; ν(C=C) of aromatic), 1262, 1163, 1097, 1021 cm-1 (s; ν(C-O)).

3-10. Synthesis of linear poly(acetal-hydroxyurethane) (LPAHU)

LPAHU was synthesized by the polyaddition of Di-functional DTMP-based 6-CC (**Di-DTMPC**) and DAP. **Di-DTMPC** was synthesized by the procedure similar to multi-functional 6-Cs. The synthetic route to **LPAHU** was shown in Scheme S1.

Scheme S1. a) Synthetic route to di-functional DTMP-based 6-CC (**Di-DTMPC**) under phosgene-free conditions and linear PAHU (**LPAHU**). b) Reversible fragmentation/extension reaction of **LPAHU** under acidic conditions.



i) Vanillin, K_2CO_3, DMF, 100°C, 2 d. vi) TsOH, CH_2Cl_2, 40°C, 2 d. vii) NaOH, THF/MeOH. r.t., overnight viii) DPC, $MgCl_2$, DMF, 100°C, overnight. v) 1.1 equiv. DAP, DMF, r. t., 3-5 d. vi) TsOH· H_2O, DMF, 50°C, 1 h. vii) drying, 50°C, reduced pressure.

3-10-1. Synthesis of Di-Van

1,3-dibromopropane 2.02 g (10.0 mmol) and vanillin 3.65 g (24.0 mmol, 2.4 equiv.) were dissolved in DMF (25 mL). To the solution, K_2CO_3 2.7 g (20 mmol) was added and then the mixture was stirred at 100°C for 22 h. After the mixture was concentrated, the solids were dissolved in CH_2Cl_2 (150 mL). The solution was washed three times with water (200 mL) and then dried with anhydrous Na_2SO_4. After the organic layer was concentrated, the resulting solids were purified by reprecipitation from CH_2Cl_2/MeOH. **Di-Van** was obtained as a white solid. Yield: 3.12 g (90.7%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.80 (s, 2H, CHO), 7.51 (d, 2H, *J* = 8.0 Hz, phenyl), 7.35 (d, 2H, *J* = 2.0 Hz, phenyl), 7.18 (d, 2H, *J* = 8.4 Hz, phenyl), 4.21 (t, 4H, *J* = 6.2 Hz, PhO-C$\underline{H}_2$-), 3.79 (s, 6H, CH_3-), 2.22 (qui, 2H, *J* = 6.2 Hz, -CH_2-C$\underline{H}_2$-CH_2-). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 192.0 (-CHO), 153.8, 149.8, 130.2, 126.6, 112.7, 110.1 (phenyl), 65.6 (PhO-$\underline{C}H_2$-), 56.1 (-CH_3), 28.9 (-CH_2-$\underline{C}H_2$-CH_2-). IR (ATR): ν = 2953-2874 (w; ν(C-H) of methylene), 2720 (w; ν(C-H) of aldehyde), 1679 (s; ν(C=O)), 1585, 1509 (s; ν(C=C) of aromatic), 1262, 1133, 1025 (s; ν(C-O)), 818 (m; δ(C-H) of aromatic), 730 cm^{-1} (m; δ(C=C) of aromatic).

3-10-2. Synthesis of Di-DTMP-Bz_2

Di-Van 3.00 g (8.71 mmol), **DTMP-Bz_2** 12.0 g (26.1 mmol, 1.5 equiv. per aldehyde group) and $TsOH \cdot H_2O$ 165 mg (0.867 mmol, 0.05 equiv. per aldehyde group) were dissolved in CH_2Cl_2 (20 mL). To the solution, anhydrous $MgSO_4$ ca. 20 g was added and then the mixture was stirred at 40°C for 2 days. After cooled to ambient temperature, the mixture was added slowly in cold water (200 mL) containing $NaHCO_3$ 73 mg (087 mmol) and then extracted with CH_2Cl_2 (200 mL). The organic layer was washed three times with water (200 mL) and then dried with anhydrous Na_2SO_4. After the crude products were purified by reprecipitation from $CHCl_3$/MeOH, **Di-DTMP-Bz_2** was obtained as a white solid. Yield: 9.65 g (90.5%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.92 (t, 8H, *J* = 8.4 Hz, benzyl), 7.63-7.57 (m, 4H, benzyl), 7.49-7.41 (m, 8H, benzyl), 6.92-6.82 (m, 6H, vanillin), 5.28 (s, 1.5H, Ph-C<u>H</u>- of cis-form), 5.22 (s, 0.5H, Ph-C<u>H</u>- of trans-form), 4.29 (t, 8H, *J* = 12 Hz, BzO-C<u>H_2</u>-), 4.05 (t, *J* = 6.0 Hz, PhO-C<u>H_2</u>-), 3.86 (d, 3.2H, *J* = 11 Hz, Ph-CH-O-C<u>H_2</u>- of cis-form), 3.78-3.64 (m, 8.3H, Ph-CH-O-C<u>H_2</u>- of trans-form and CH_3-O-), 3.61 (s, 2.8H, Ph-CH-O-CH_2-C-C<u>H_2</u>-O-CH_2- of cis-form), 3.52-3.48 (m, 9.0H, Ph-CH-O-C<u>H_2</u>- of cis-form and BzO-CH_2-C-C<u>H_2</u>-O-CH_2- of cis-form), 3.41 (s, 1.1H, Ph-CH-O-CH_2-C-C<u>H_2</u>-O-CH_2- of trans-form), 3.08 (s, 1.0H, BzO-CH_2-C-C<u>H_2</u>-O-CH_2- of trans-form), 2.10 (m, 2H, -CH_2-C<u>H_2</u>-CH_2-), 1.65 (q, 1.0H, *J* = 7.5 Hz, CH_3-C<u>H_2</u>-C-CH_2-O-CH-Ph of trans-form), 1.57 (q, 4H, *J* = 7.3 Hz, CH_3-C<u>H_2</u>-C-CH_2-OBz), 1.08 (q, 3.0H, *J* = 7.5 Hz, CH_3-C<u>H_2</u>-C-CH_2-O-CH-Ph of cis-form), 0.90 (t, 6H, *J* = 7.6 Hz, C<u>H_3</u>-CH_2-C-CH_2-OBz), 0.75-0.62 (m, 6H, C<u>H_3</u>-CH_2-C-CH_2-O-CH-Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 165.7 (C=O),148.7, 148.2, 133.5, 131.7, 129.7, 129.3, 129.0, 128.9, 118.6, 112.8, 110.2 (phenyl), 100.9 (Ph-<u>C</u>H-), 71.8, 70.3, 65.2, 65.1 (-CH_2-O-), 55.6 (CH_3-O-), 42.0, 36.4 (CH_3-CH_2-<u>C</u>-), 28.9 (-CH_2-<u>C</u>H_2-CH_2-), 23.9, 23.3 (CH_3-<u>C</u>H_2-), 7.7, 6.9 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 2966-2856 (w; ν(C-H) of methylene), 1710 (s; ν(C=O)), 1521, 1451 (w; ν(C=C) of aromatic), 1264, 1105, 1024 (s; ν(C-O)), 709 cm^{-1} (s; δ(C=C) of aromatic).

3-10-3. Synthesis of Di-DTMP

Di-DTMP-Bz_2 9.55 g (7.80 mmol) was dissolved in THF (60 mL). To the solution, MeOH (60 mL) and NaOH 6.4 g (10 mmol) dissolving in distilled water (20 mL) were added and then the mixture was stirred at ambient temperature for 18 h. After concentration, the resulting liquids were dissolved in CH_2Cl_2 (300 mL) and then washed three times with water (250 mL). The organic layer was dried with anhydrous Na_2SO_4 and then concentrated to afford **Di-DTMP** as colorless liquids. Yield: 5.65 g (89.5). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.96-6.90 (m, 6H, phenyl), 5.34 (s, 1.4H, Ph-C<u>H</u>- of cis-form), 5.32 (s, 0.5H, Ph-C<u>H</u>- of trans-form), 4.24-4.19 (m, 4H, OH), 4.09 (t, 4H, *J* = 6.0 Hz, PhO-C<u>H_2</u>-), 3.91 (d, 3.1H, *J* = 11 Hz, Ph-CH-O-C<u>H_2</u>- of cis-form), 3.79 (q, 2.2H, *J* = 12 Hz, Ph-CH-O-C<u>H_2</u>- of trans-form), 3.73 (s, 6H, CH_3-O-), 3.56-3.54 (m, 6.2H, Ph-CH-O-C<u>H_2</u>- of cis-form and Ph-CH-O-CH_2-C-C<u>H_2</u>-O-CH_2- of cis-form), 3.28-3.24 (m, 11H, HO-C<u>H_2</u>- and HO-CH_2-C-C<u>H_2</u>-O-CH_2- of cis-form), 3.13 (s, 0.9H, Ph-CH-O-CH_2-C-C<u>H_2</u>-O-CH_2- of trans-form), 3.06 (s, 1.0H, HO-CH_2-C-C<u>H_2</u>-O-CH_2- of trans-form), 2.13 (qui, 2H, *J* = 6.2 Hz, -CH_2-C<u>H_2</u>-CH_2-), 1.72 (q, 1.0H, *J* = 7.7 Hz, CH_3-C<u>H_2</u>-C-CH_2-O-CH-Ph of trans-form), 1.28-1.21 (m, 4H, CH_3-C<u>H_2</u>-C-CH_2-OH), 1.15 (3.1H, *J* = 7.5 Hz, CH_3-C<u>H_2</u>-C-CH_2-O-CH-Ph of cis-form), 0.88-0.76 (m, 12H, C<u>H_3</u>-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.8, 148.3, 131.8, 118.7, 112.8, 110.1 (phenyl), 101.0 (Ph-<u>C</u>H-), 72.0, 71.6, 65.2, 61.9 (-CH_2-O-), 55.7 (CH_3-O-), 43.7, 36.4 (CH_3-CH_2-<u>C</u>-), 29.0 (-CH_2-<u>C</u>H_2-CH_2-), 24.1, 22.2 (CH_3-<u>C</u>H_2-),7.8, 7.0 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 3405 (w; ν(O-H)), 2961-2855 (w; ν(C-H) of methylene), 1517, 1465 (w; ν(C=C) of aromatic), 1262, 1096, 1023 cm^{-1} (s; ν(C-O)).

3-10-4. Synthesis of Di-DTMPC

Di-DTMP 5.50 g (6.80 mmol) and DPC 11.7 g (54.4 mmol, 4 equiv. per 1,3-diol structure) were dissolved in DMF (65 mL). To the solution, $MgCl_2$ 130 mg (1.36 mmol, 0.1 equiv. per 1,3-diol structure) and then the mixture was stirred at 100°C for 14 h. After the removal of DMF, the resulting solids were dissolved in CH_2Cl_2 (150 mL) and washed three times with water (150 mL). After the drying with anhydrous Na_2SO_4, the pale yellow solids were purified by silica gel column chromatography (eluent, CH_2Cl_2/EtOAc volume ratio = 10/1 to 1/1). **Di-DTMPC** was obtained as a colorless liquid. Yield: 5.40 g (92.1%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.96-6.90 (m, 6H, phenyl), 5.35 (s, 2H, Ph-C<u>H</u>-), 4.24 (q, 8H, *J* = 10 Hz, -OC(=O)O-C<u>H</u>$_2$-), 4.09 (t, 4H, *J* = 6.2 Hz, PhO-C<u>H</u>$_2$-), 3.92 (d, 3.0H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.80 (q, 1.9H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.73 (s, 6H, CH_3-O-), 3.64 (s, 2.9H, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.57 (d, 3.2H, *J* = 12 Hz, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.43 (s, 2.9H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.13 (s, 0.9H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 2.13 (qui, 2H, *J* = 6.4 Hz, -CH_2-C<u>H</u>$_2$-CH_2-), 1.72 (q, 1.0H, *J* = 7.5 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.42-1.35 (m, 4H, -OC(=O)O-CH_2-C-C<u>H</u>$_2$-CH_3), 1.16 (q, 3.0H, *J* = 7.7 Hz, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.87-0.75 (m, 12H, C<u>H</u>$_3$-CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.8, 148.3, 148.1, 131.7, 118.7, 112.8, 110.1 (phenyl and C=O), 101.1 (Ph-<u>C</u>H-), 72.6, 71.8, 71.3, 70.5, 70.0, 65.2, (-CH_2-O-), 55.7 (CH_3-O-), 36.4, 35.0 (CH_3-CH_2-<u>C</u>-), 23.8, 23.0 (CH_3-<u>C</u>H_2-), 7.4, 7.0 (<u>C</u>H_3-CH_2-). IR (ATR): ν = 2966-2860 (w; ν(C-H) of methylene), 1748 (s; ν(C=O)), 1515, 1468 (w; ν(C=C) of aromatic), 1262, 1165, 1095, 1024 cm^{-1} (s; ν(C-O))

3-10-5. Synthesis of LPAHU[4]

Di-DTMPC 808 mg (0.94 mmol) and DAP 76.5 mg (1.03 mmol, 1.1 equiv.) were individually dissolved in DMF (1.0 mL). To the **Di-DTMPC** solution, the DAP solution was added and then the mixture was stirred at ambient temperature for 6 days. The mixture was added in water (100 mL) and the resulting precipitates were dissolved in CH_2Cl_2 (100 mL) and then organic layer was washed three times with water (100 mL). After the drying with anhydrous Na_2SO_4 and the evaporation of CH_2Cl_2, **LPAHU** was obtained as a white solid. Yield: 819 mg (92.6%). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.15-6.69 (m, 8H, phenyl and NH of urethane), 5.32 (s, 2H, Ph-C<u>H</u>-), 4.40 (br, 2H, OH), 4.17-4.08 (m, 4.2H, PhO-C<u>H</u>$_2$-), 3.89 (d, 3H, Ph-CH-O-C<u>H</u>$_2$- of cis-form), 3.81-3.72 (m, 12H, -NH-C(=O)O-C<u>H</u>$_2$-, CH_3-O- and Ph-CH-O-C<u>H</u>$_2$- of trans-form), 3.56-3.53 (m, 6H, Ph-CH-O-C<u>H</u>$_2$- of cis-form and -NH-C(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of cis-form), 3.28-3.25 (m, 4H, HO-C<u>H</u>$_2$- and residual MeOH), 3.14-2.93 (m, 6H, -C<u>H</u>$_2$-NH-, Ph-CH-O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form and -NH-C(=O)O-CH_2-C-C<u>H</u>$_2$-O-CH_2- of trans-form), 2.12 (br, -O-CH_2-C<u>H</u>$_2$-CH_2-), 1.72-1.50 (m, 3H, -NH-CH_2-C<u>H</u>$_2$- and CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of trans-form), 1.31-1.29 (m, 4H, -NH-C(=O)O-CH_2-C-C<u>H</u>$_2$-CH_3), 1.23-1.12 (m, CH_3-C<u>H</u>$_2$-C-CH_2-O-CH-Ph of cis-form), 0.86-0.73 (m, 12H, C<u>H</u>$_3$-CH_2-). IR (ATR): ν = 3350 (m; ν(O-H)), 2961-2856 (w; ν(C-H) of methylene), 1694 (s; ν(C=O)), 1514, 1463 (w; ν(C=C) of aromatic), 1261, 1096, 1028 cm^{-1} (s; ν(C-O)).

4. Fabrication of networked PAHU films

Multi-functional 6-CCs and DTMPC were dissolved in DMF (1.0 mL) at ambient temperature to prepare the carbonate monomer solution at different molar ratios (5, 10, 15 or 20 mol% multi-functional 6-CCs per total carbonate monomer (multi-functional 6-CCs + DTMPC)). To the solutions, DAP dissolved in DMF (1.0 mL) was added and then the mixtures ($[carbonate]_0$ = 0.5 M, $[6\text{-CC}]_0/[NH_2]_0$ = 1.0) were stirred at ambient temperature for ca. 5 min. After that, the solutions were poured in glass petri-dishes with 6.0 cm in diameter and allowed

to stand at 60°C overnight in an oven under ambient atmosphere. The resulting films were carefully removed and immersed in distilled water for purification. After drying under ambient atmosphere, the networked PAHU films were obtained.

5. Investigation of swelling properties of networked PAHU films

PAHU films cut to dumbbell-shaped plates (length, 3.5 cm) with a Super dumbbell cuter (DUMBBELL Co., Ltd) and immersed in H_2O, MeOH, acetone or DMF at ambient temperature for 24 h. After that, their lengths were measured before drying and then the ratio of these lengths were defined as swelling ratios (unit, %).

6. Investigation of fragmentation/extension properties of LPAHU

LPAHU 187 mg (0.20 unit mmol, acetal structure = ca. 0.4 mmol) and TsOH·H_2O 15 mg (0.08 mmol, 0.2 equiv. per acetal structure of **LPAHU**) were dissolved in DMF (1mL). To the solution, MeOH (4 mL) was added and the mixture was stirred at 60°C for ca. 1 h. The fraction of the mixture was analyzed by ^{1}H NMR spectroscopy and SEC measurements. After that, the mixture was concentrated and dried at 60°C under reduced pressure for ca. 1 h. The resulting sticky solids were analyzed by ^{1}H NMR spectroscopy and SEC measurements.

7. Investigation of crosslinking/de-crosslinking functions of networked PAHU films

To a 25 mL round-bottom flask were added PAHU films hashed, TsOH·H_2O (0.4 equiv. per acetal structure of the film), DMF (2 mL). By heating at 60°C for ca. 30 min, the films were dissolved in the solvents to give pale yellow solutions. The solutions were moved into glass petri-dishes in a diameter of 6.0 cm and then kept at 60°C overnight in an oven under ambient atmosphere. The resulting films were detached carefully from the dishes and immersed into water to remove residual DMF and TsOH. After drying under ambient atmosphere overnight, re-formed PAHU films were obtained. The de-crosslinking/re-crosslinking treatment was repeated 10 times and the re-formed film obtained in each cycle was characterized for their mechanical properties by tensile tests. In 2-10th processes, the re-formed films were readily able to be dissolved at the condition of TsOH·H_2O (0.2 equiv. per acetal structure).

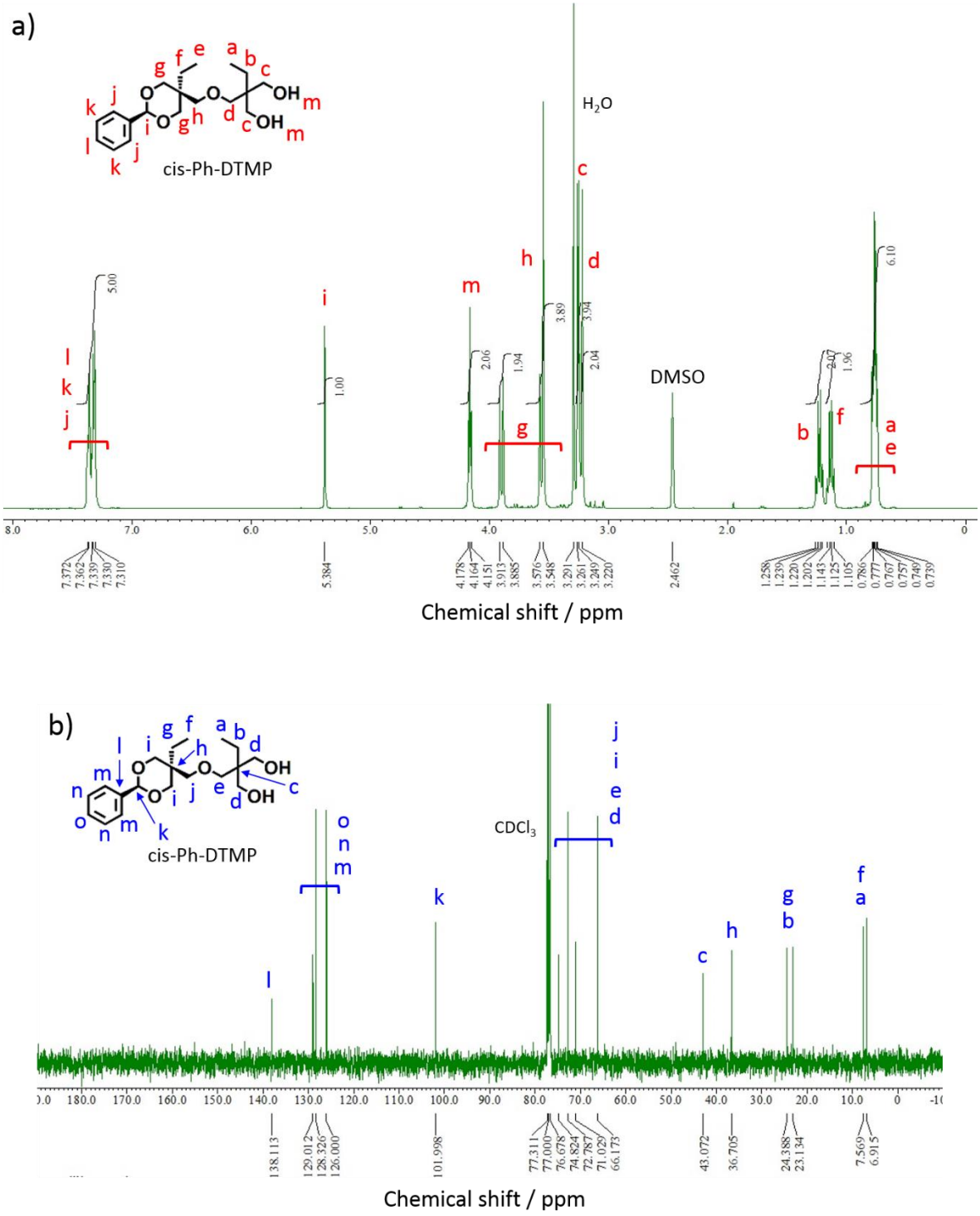


Figure S1. a) ^{1}H NMR and b) ^{13}C NMR spectra of **cis-Ph-DTMP** after purification. Solvent: DMSO-d_6 (^{1}H NMR) or $CDCl_3$ containing 0.03v/v% TMS (^{13}C NMR).

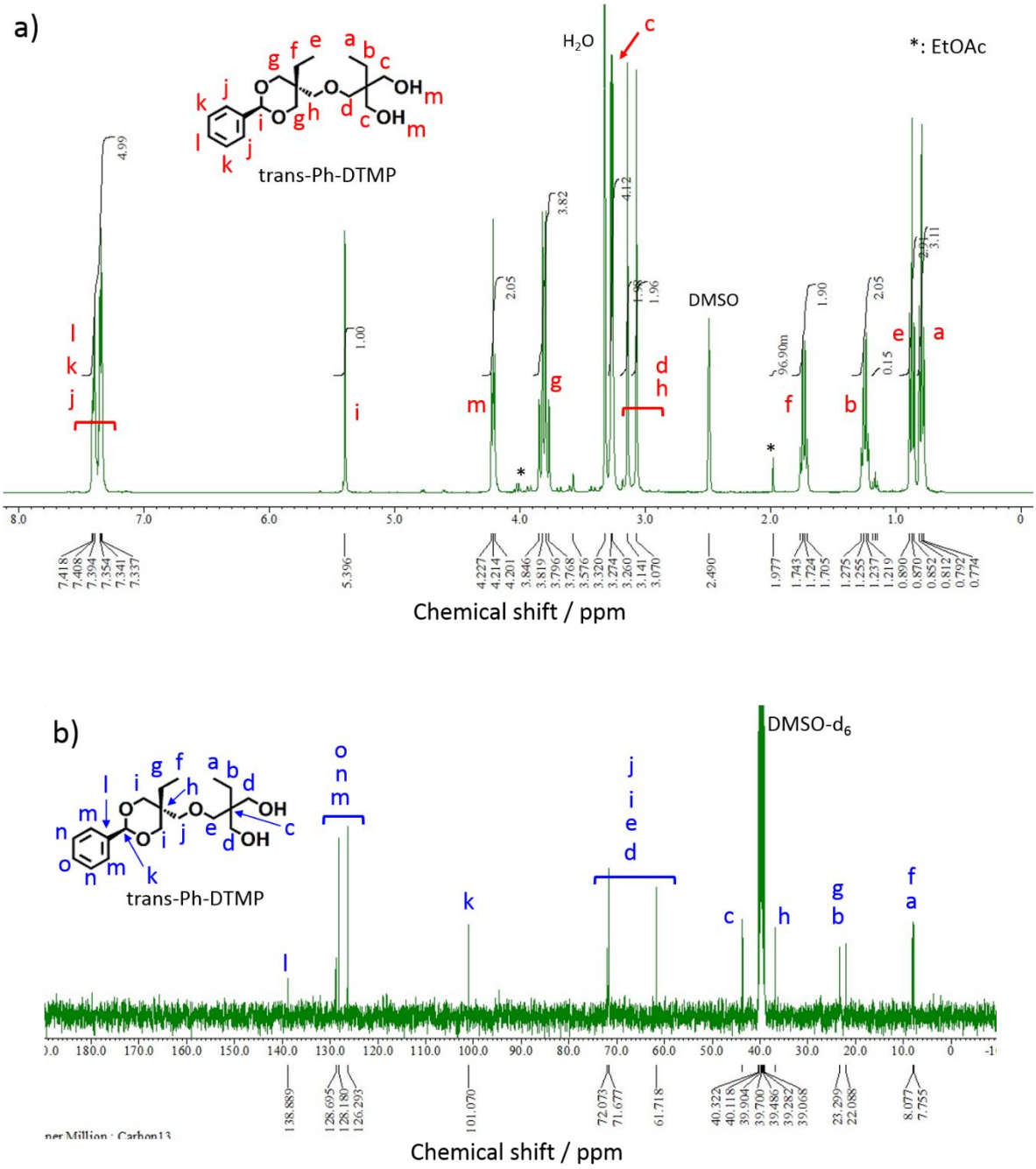


Figure S2. a) ^{1}H and b) ^{13}C NMR spectra of **trans-Ph-DTMP** after purification. Solvents: DMSO-d_6.

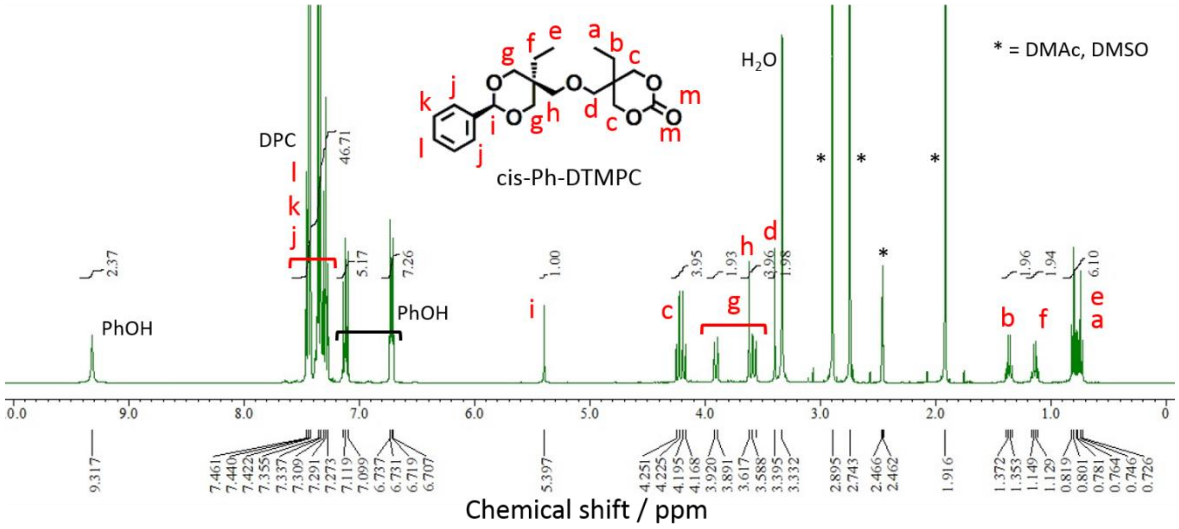


Figure S3. ^{1}H NMR spectrum of the DMAc solution of **cis-Ph-DTMP**, DPC and $MgCl_2$ after heating at 100 °C for 1 d. Solvent: DMSO-d_6.

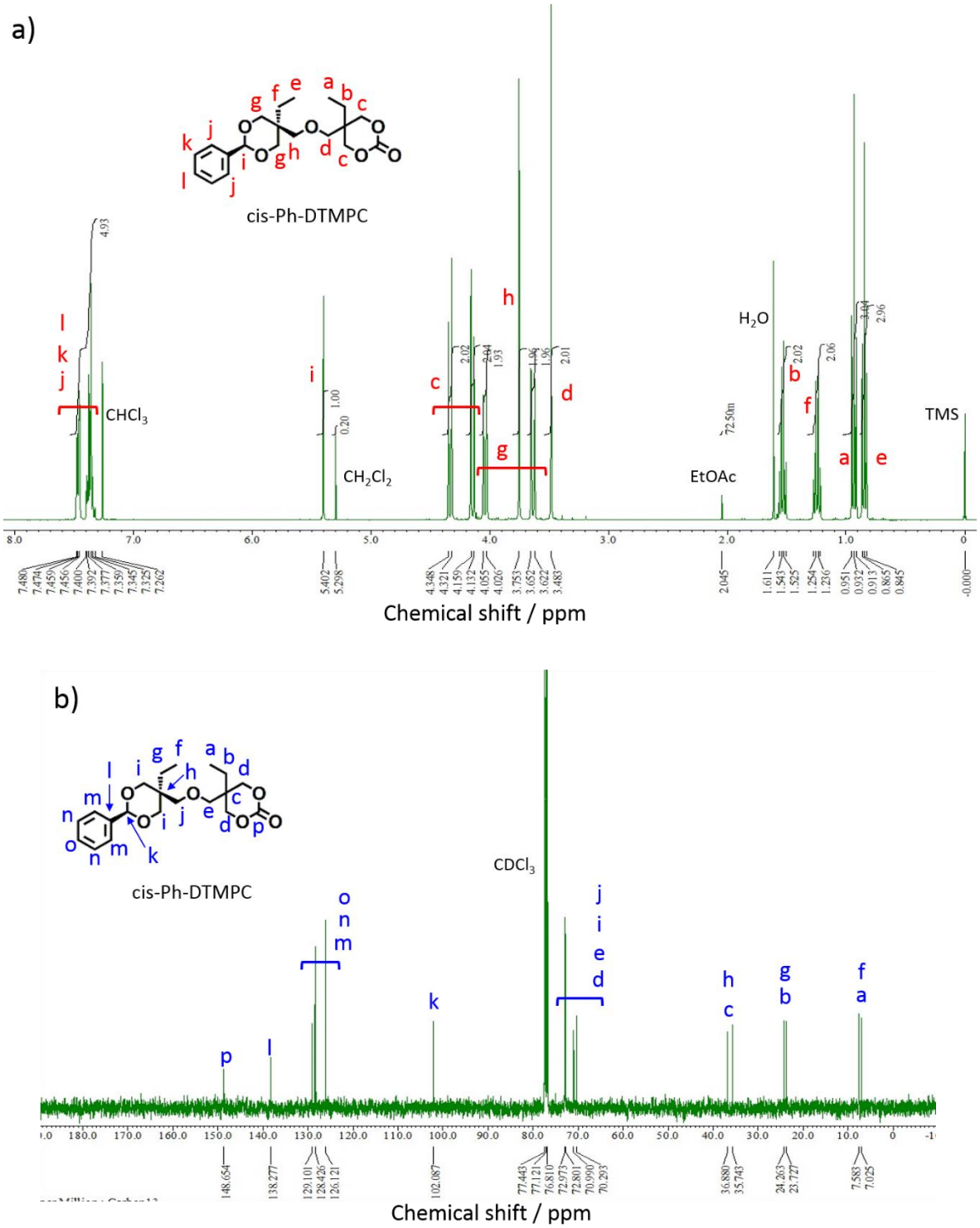


Figure S4. a) ^{1}H and b) ^{13}C NMR spectra of **cis-Ph-DTMPC** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

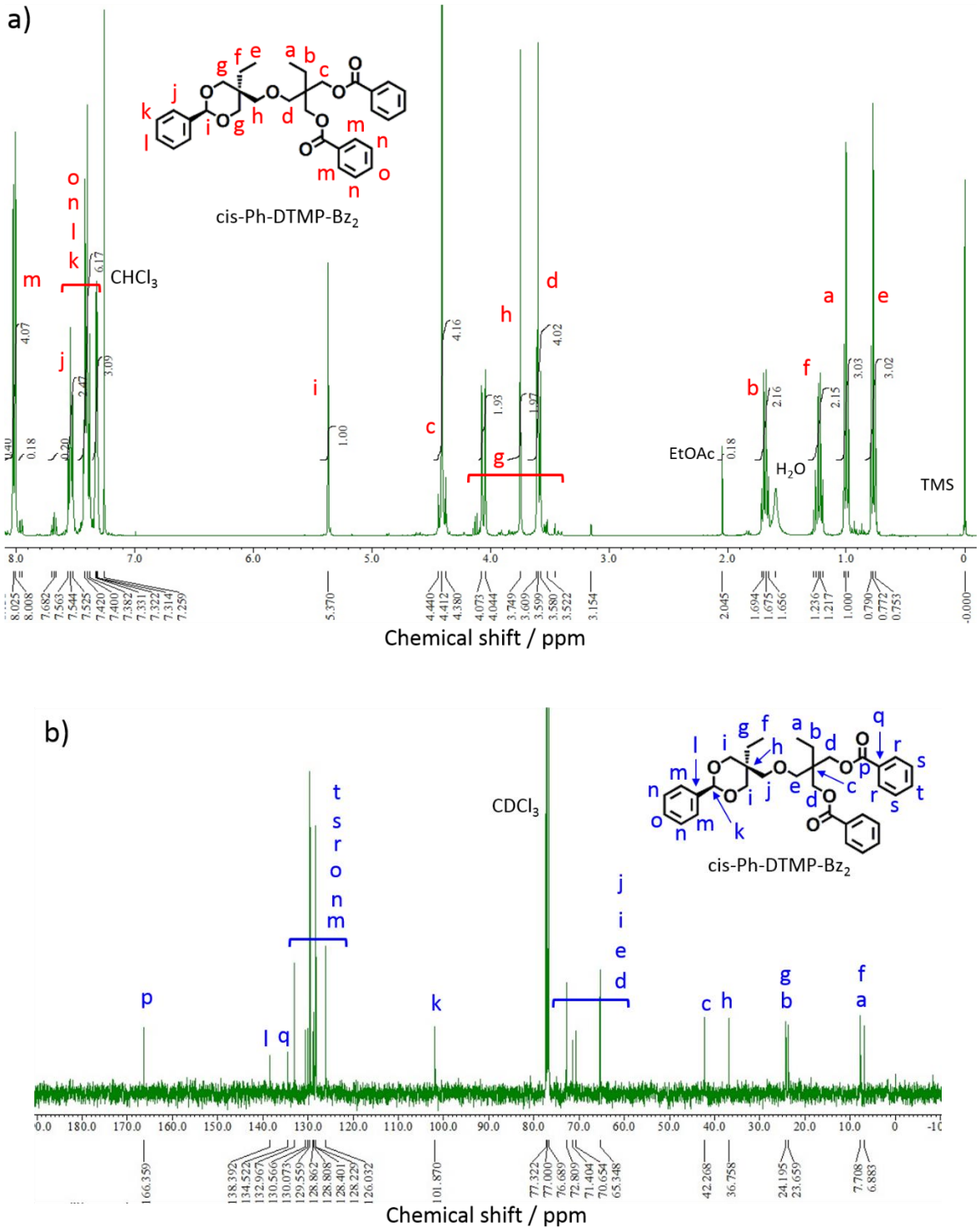


Figure S5. a) ^{1}H and b) ^{13}C NMR spectra of **cis-Ph-DTMP-Bz$_2$** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

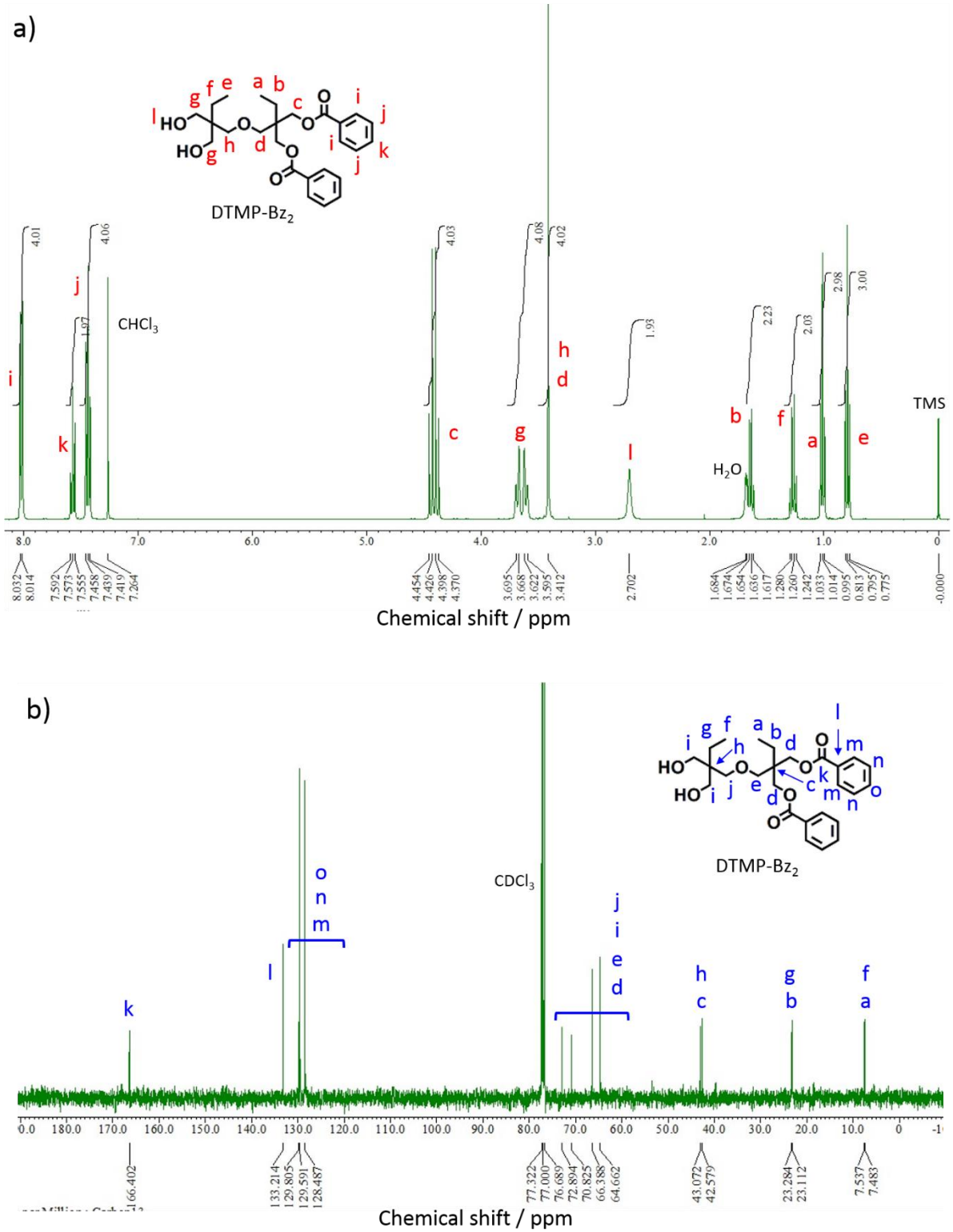


Figure S6. a) ^{1}H and b) ^{13}C NMR spectra of **DTMP-Bz$_2$** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

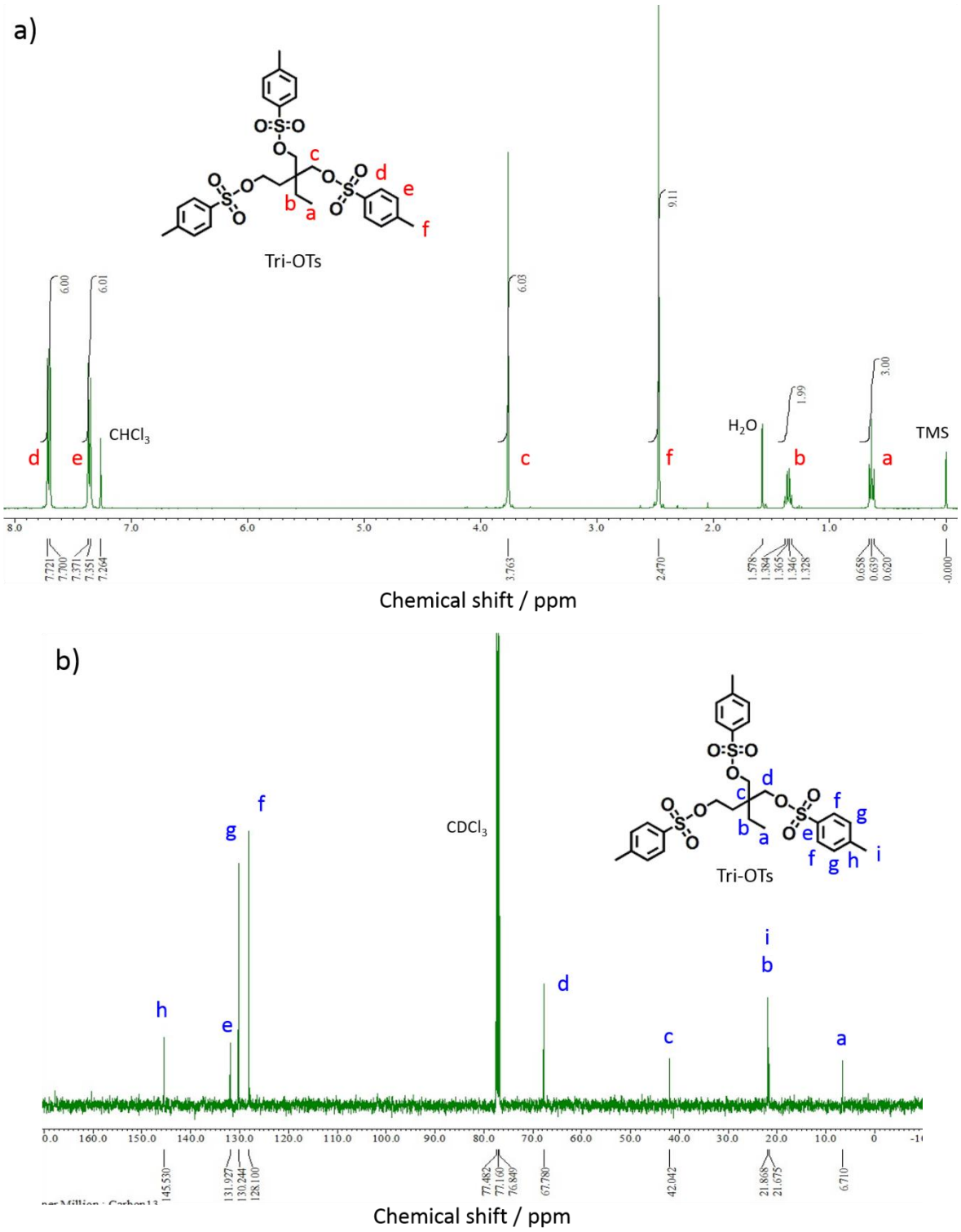


Figure S7. a) ^{1}H and b) ^{13}C NMR spectra of **Tri-OTs** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

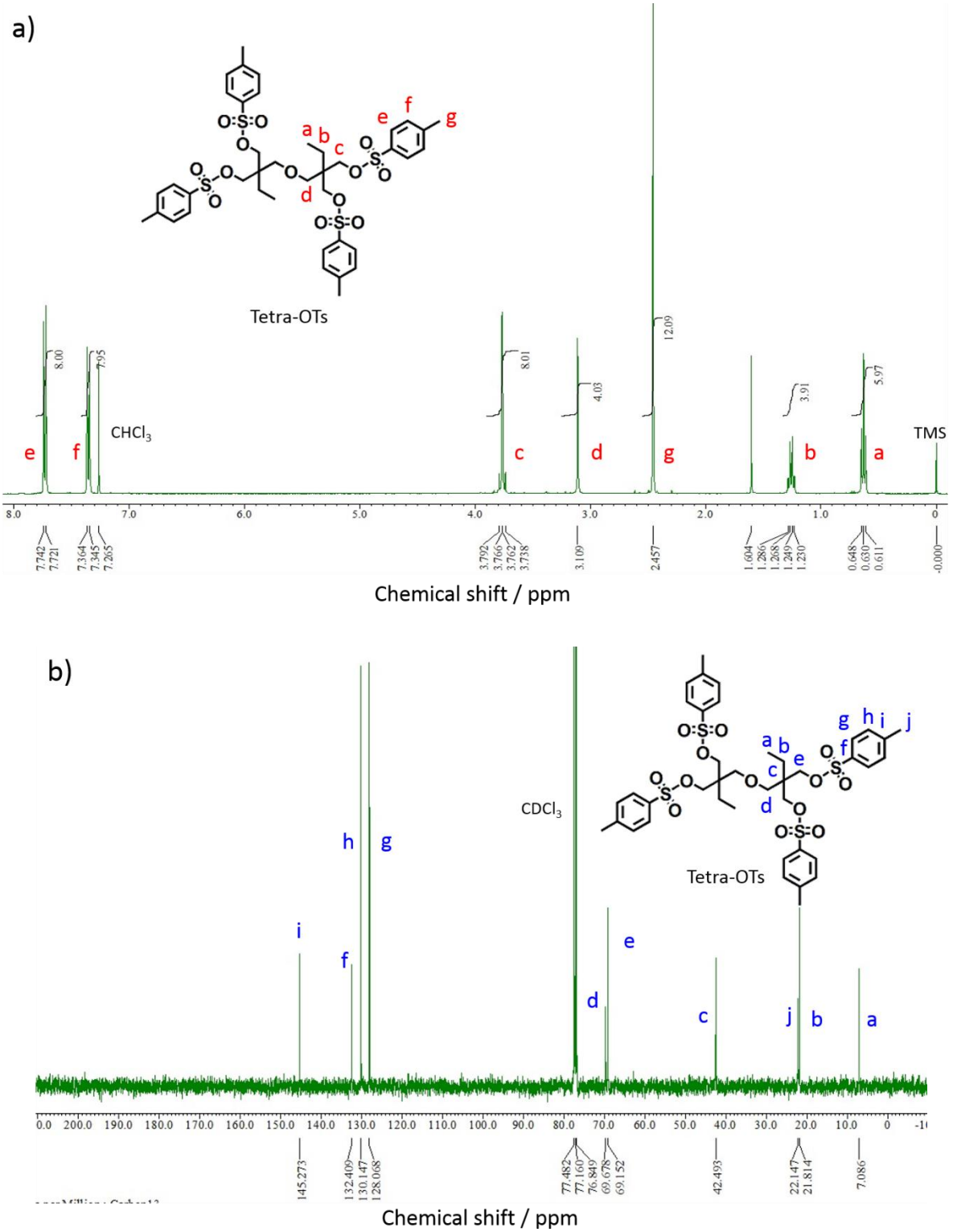


Figure S8. a) ^{1}H and b) ^{13}C NMR spectra of **Tetra-OTs** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

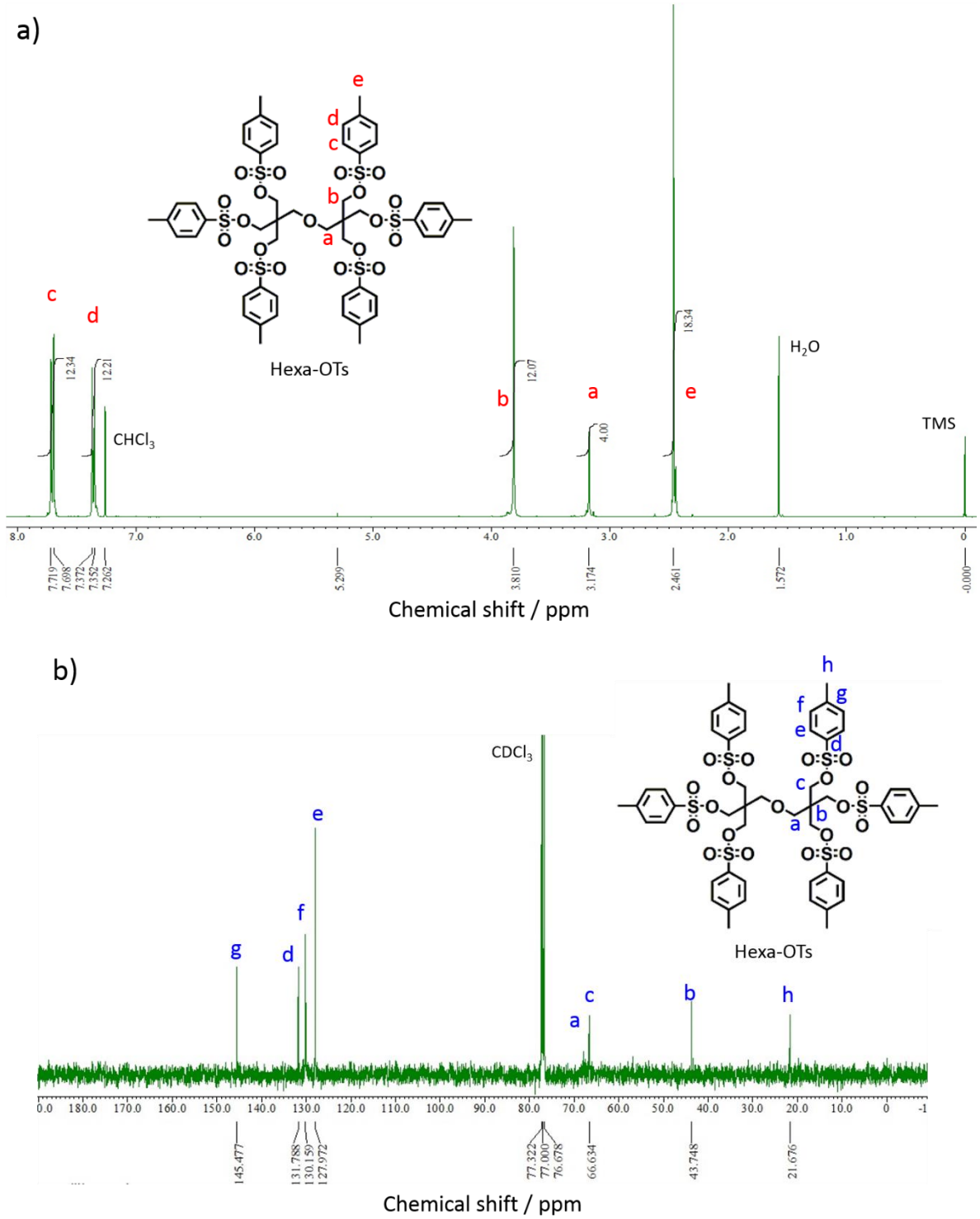


Figure S9. a) ^{1}H and b) ^{13}C NMR spectra of **Hexa-OTs** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS.

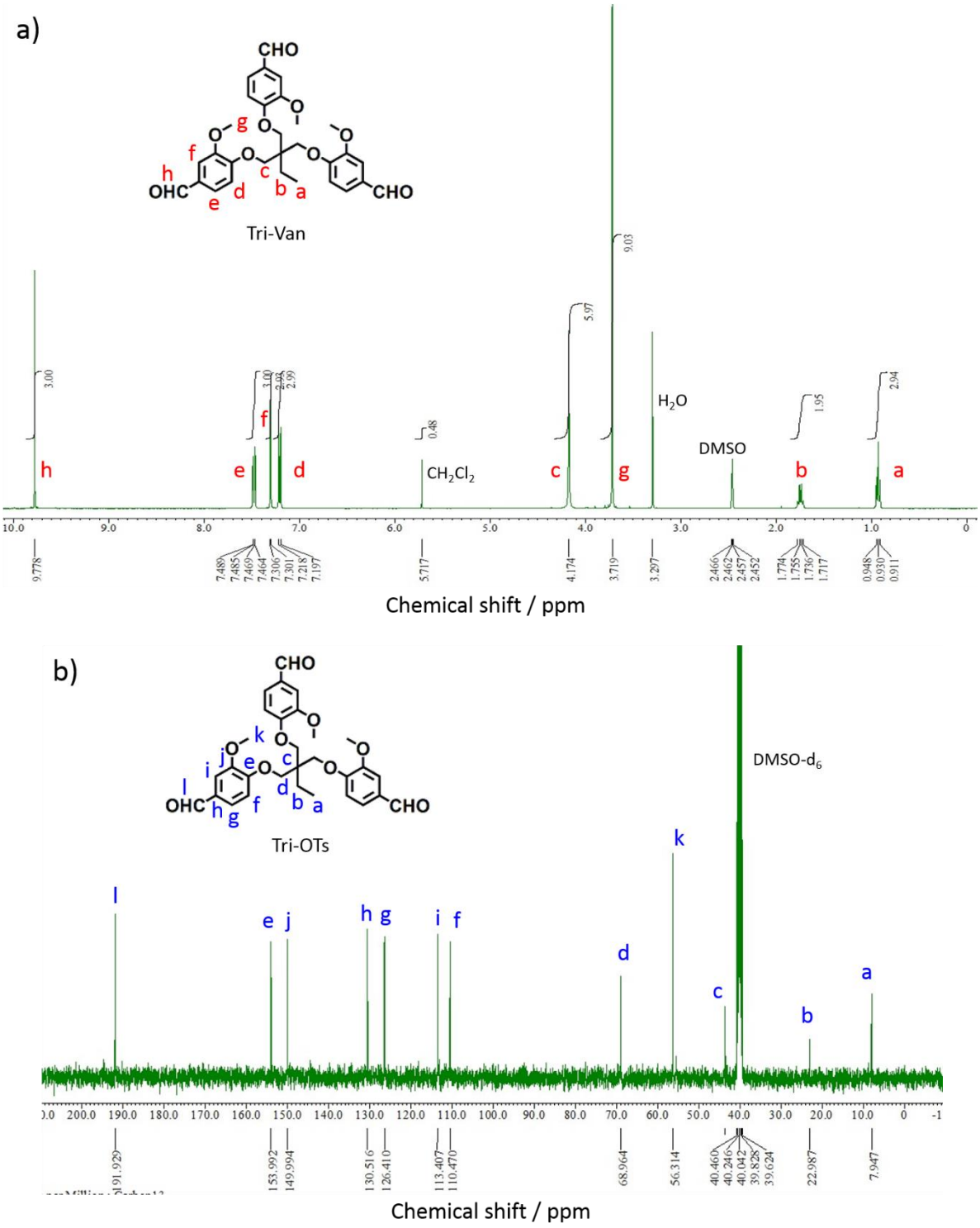


Figure S10. a) ^{1}H and b) ^{13}C NMR spectra of **Tri-Van** after purification. Solvents: DMSO-d_6.

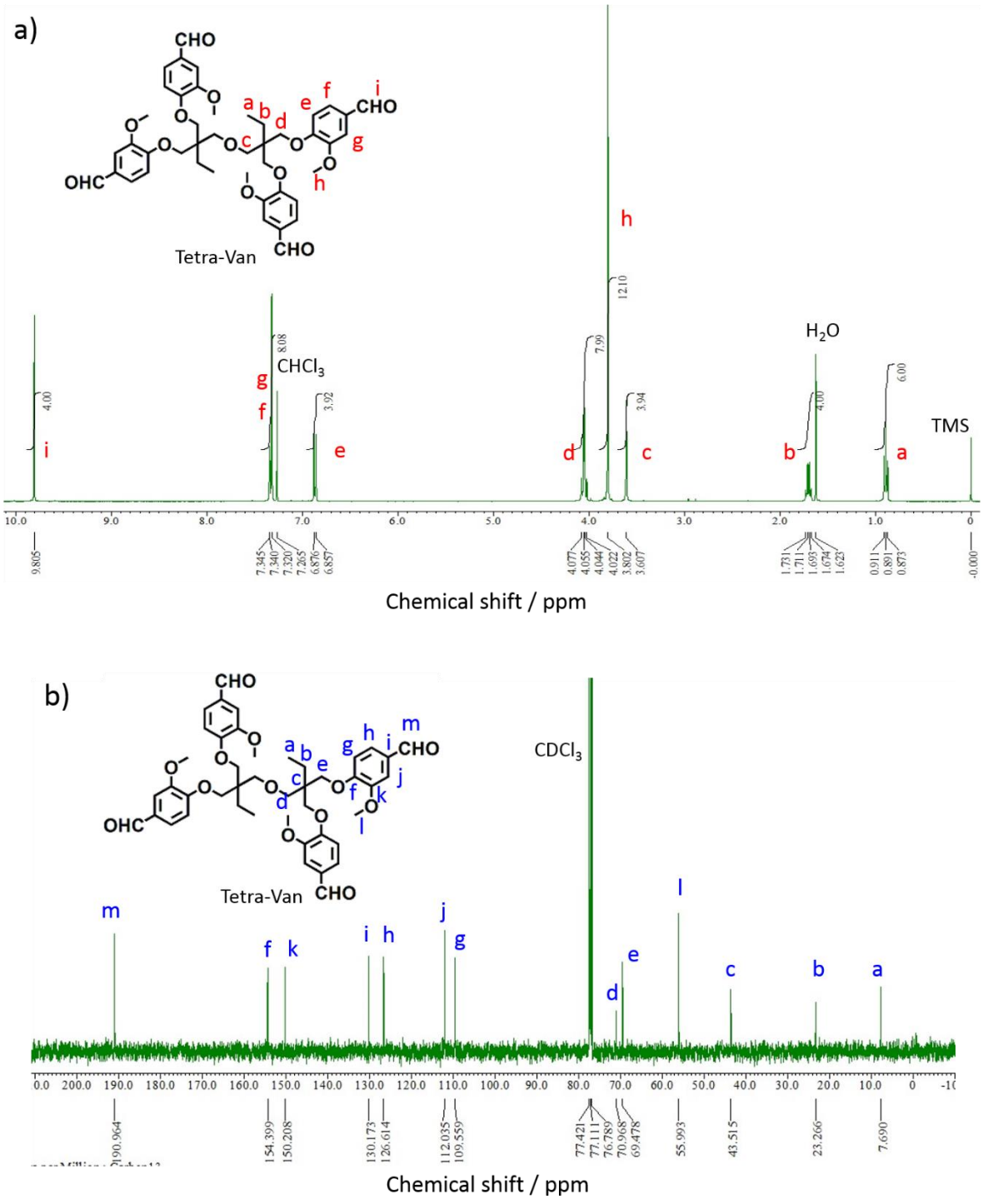


Figure S11. a) ^{1}H and b) ^{13}C NMR spectra of **Tetra-Van** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS

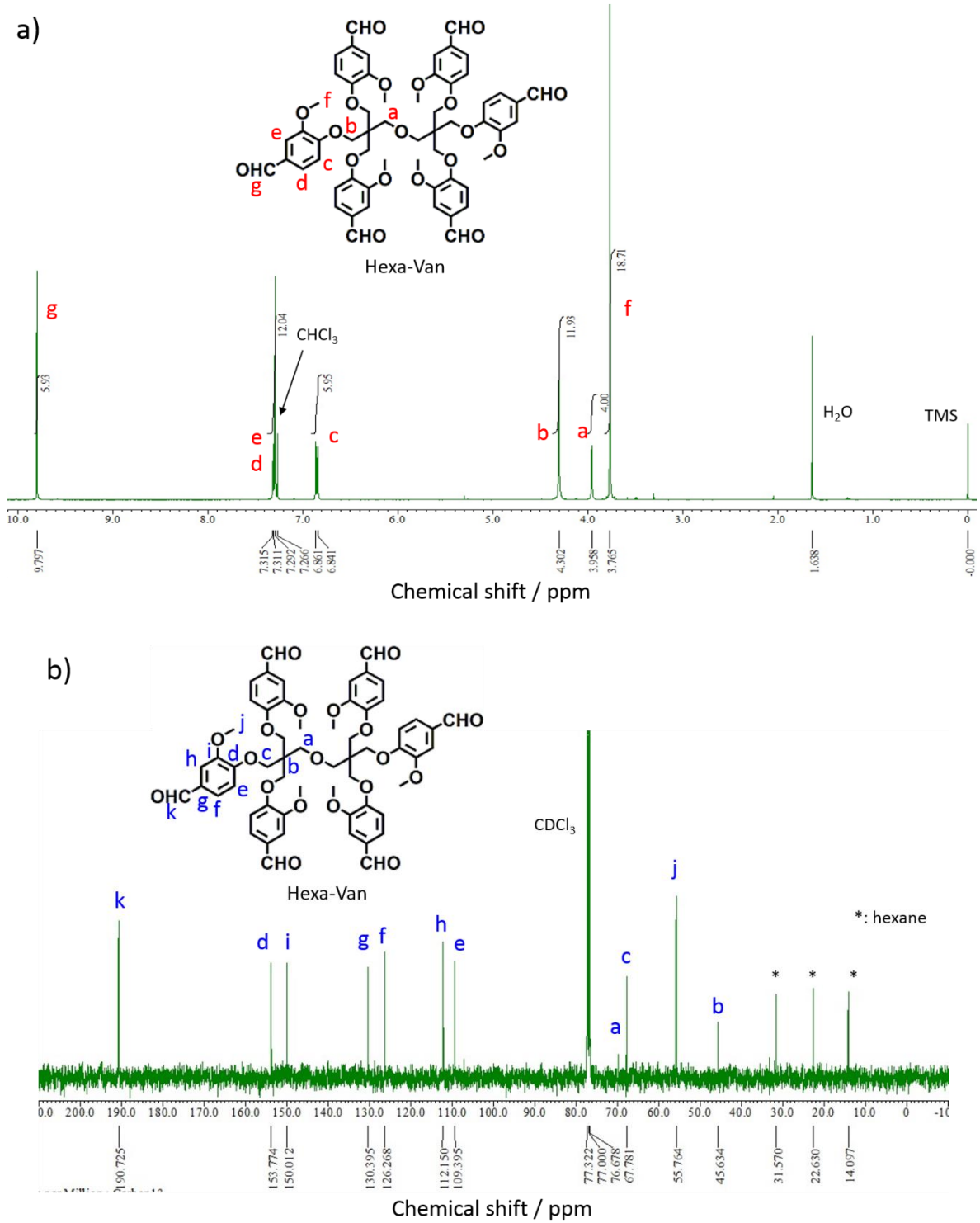


Figure S12. a) ^{1}H and b) ^{13}C NMR spectra of **Hexa-Van** after purification. Solvents: $CDCl_3$ containing 0.03v/v% TMS

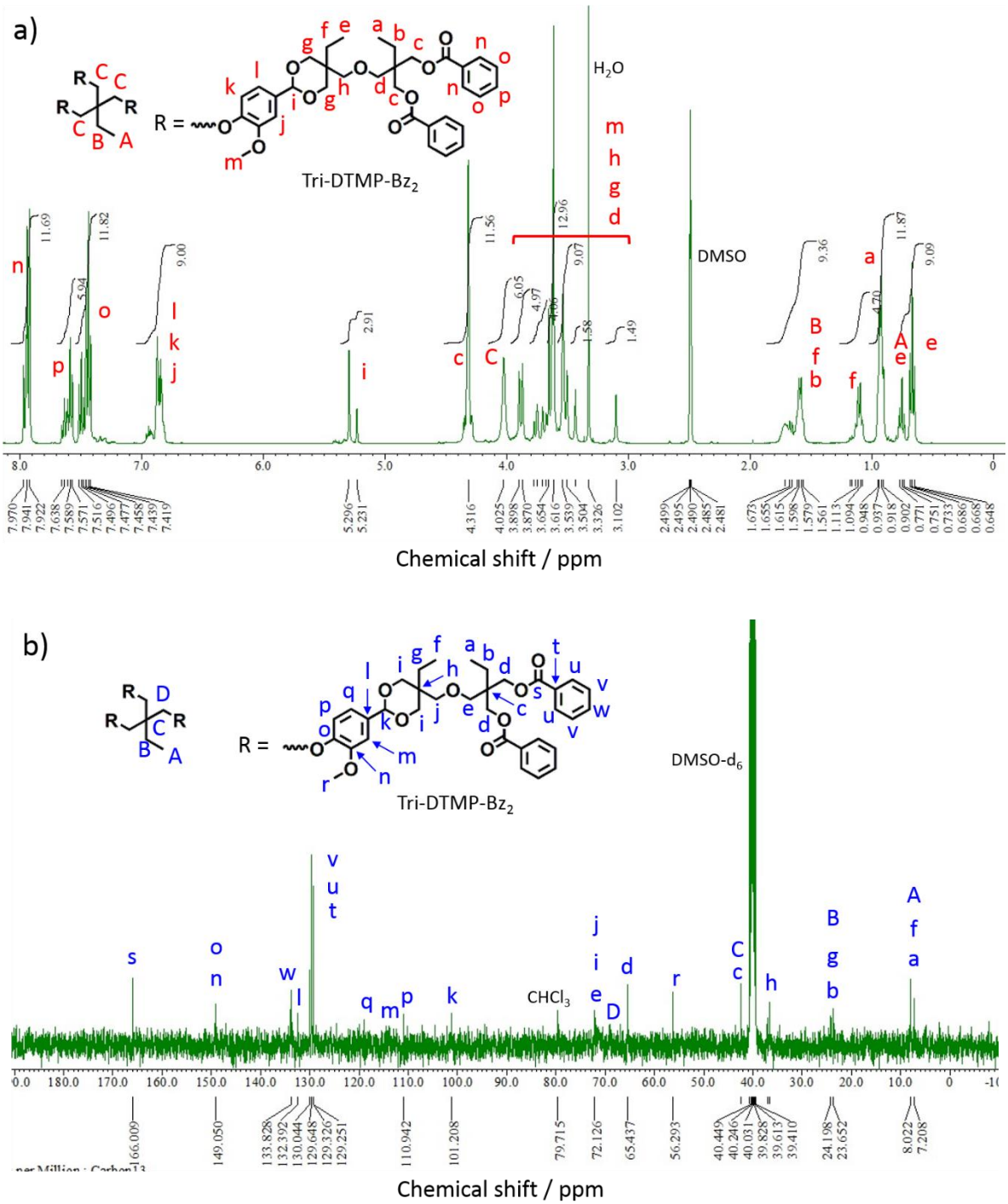


Figure S13. a) ^{1}H and b) ^{13}C NMR spectra of **Tri-DTMP-Bz$_2$** after purification. Solvents: DMSO-d$_6$.

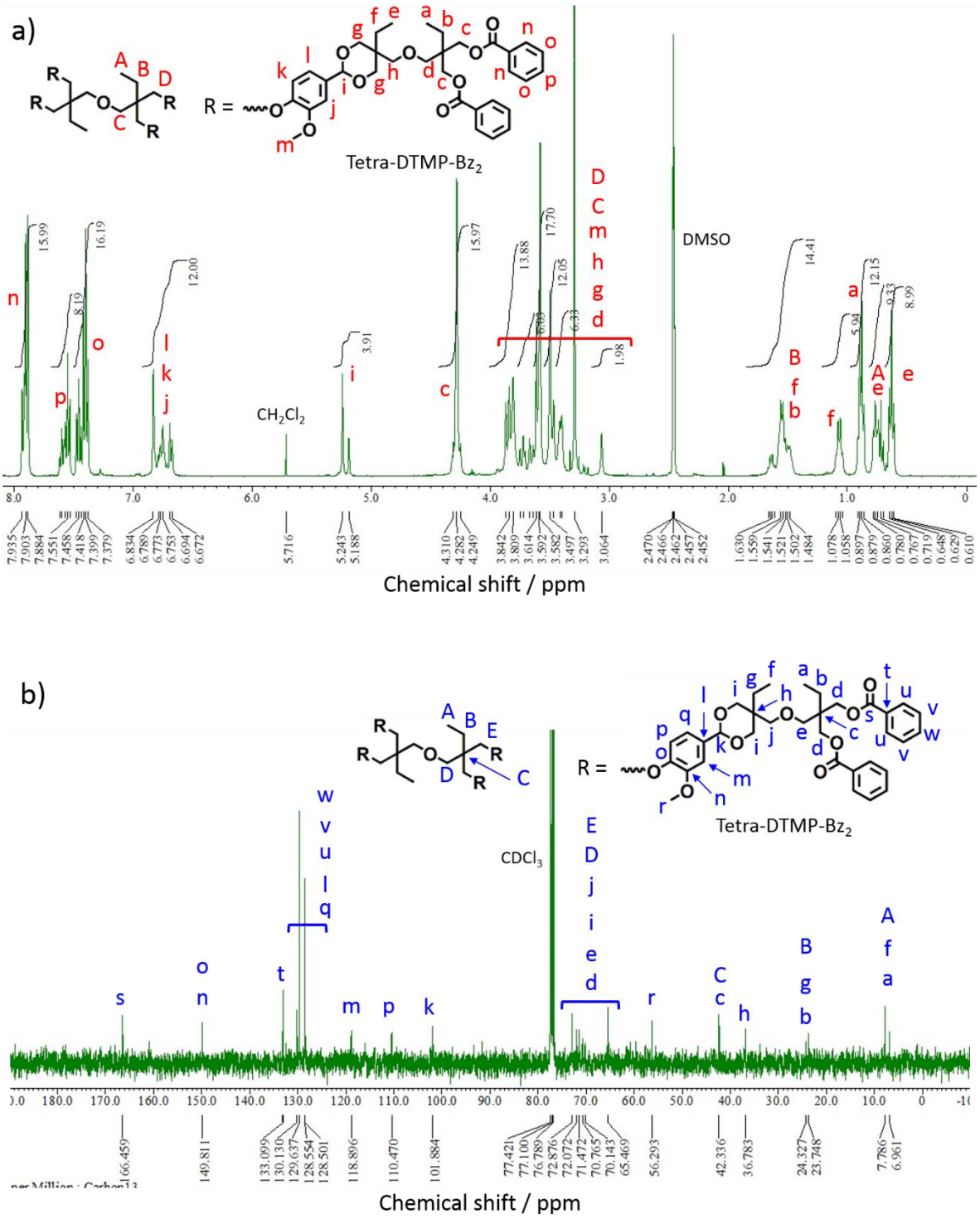


Figure S14. a) ^{1}H and b) ^{13}C NMR spectra of **Tetra-DTMP-Bz$_2$** after purification. Solvents: DMSO-d$_6$ (^{1}H NMR) or $CDCl_3$ containing 0.03v/v% TMS (^{13}C NMR).

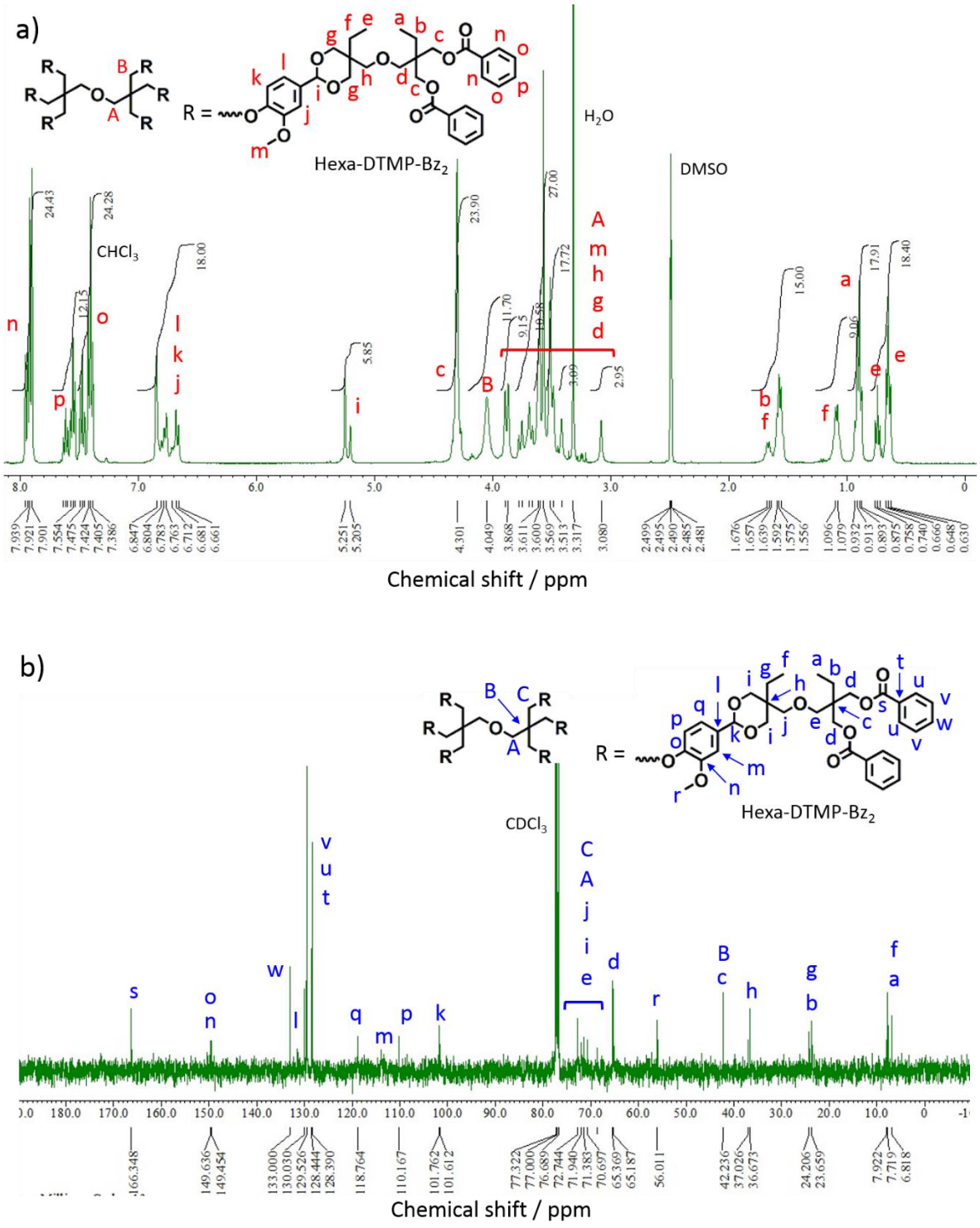


Figure S15. a) ^{1}H and b) ^{13}C NMR spectra of **Hexa-DTMP-Bz$_2$** after purification. Solvents: DMSO-d_6 (^{1}H NMR) or $CDCl_3$ containing 0.03v/v% TMS (^{13}C NMR).

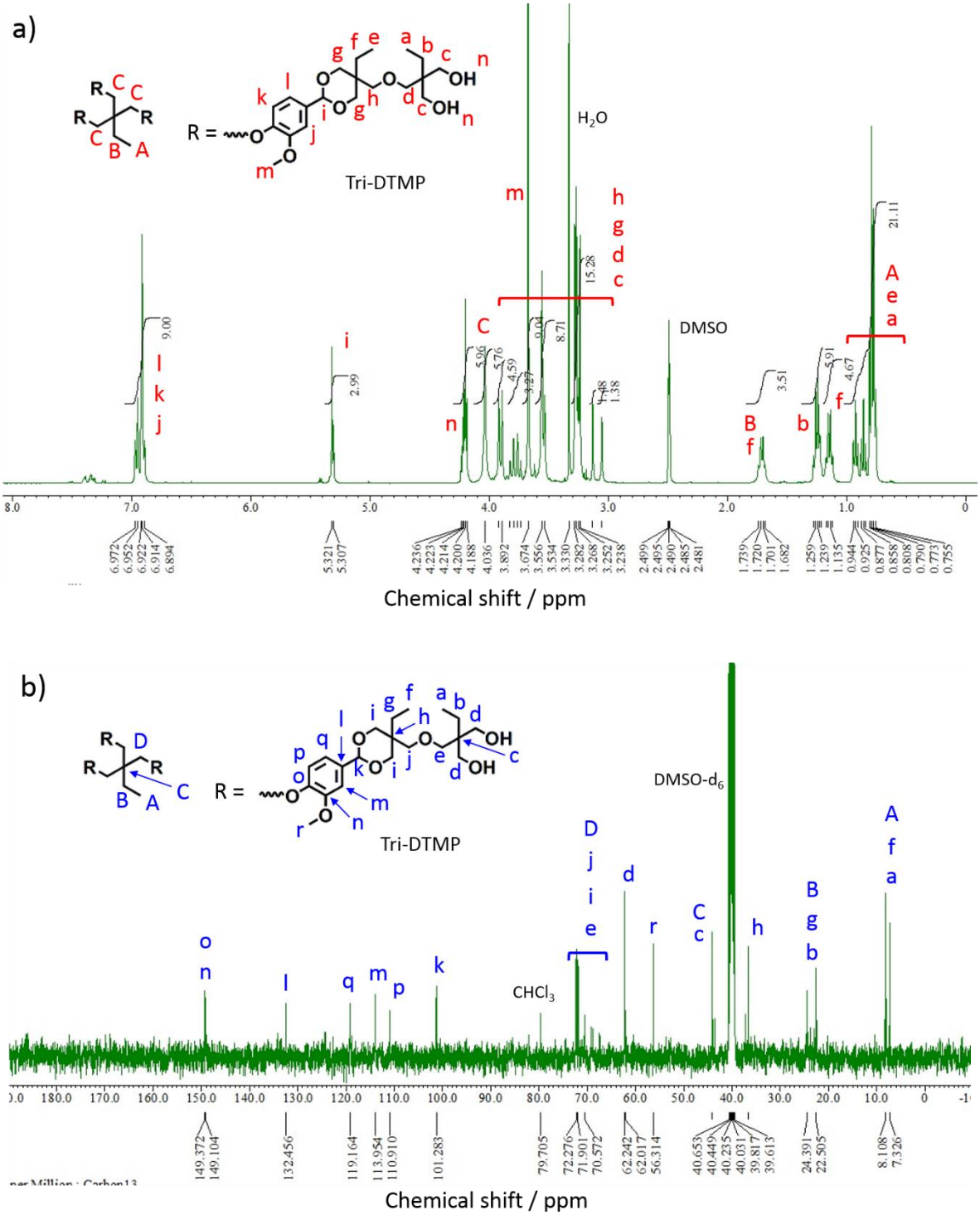


Figure S16. a) ^{1}H and b) ^{13}C NMR spectra of **Tri-DTMP** after purification. Solvents: DMSO-d_6.

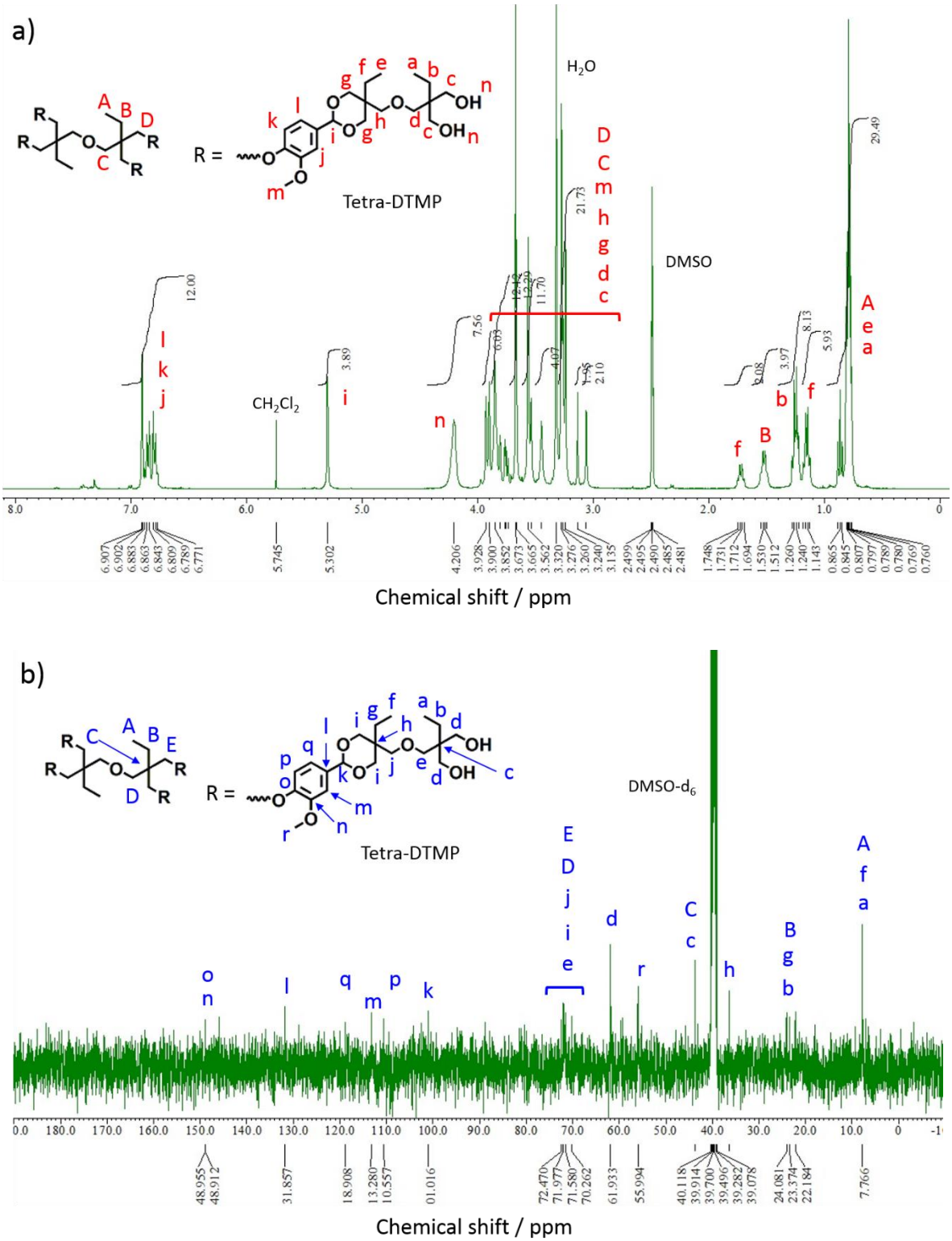


Figure S17. a) ^{1}H and b) ^{13}C NMR spectra of **Tetra-DTMP** after purification. Solvents: DMSO-d_6.

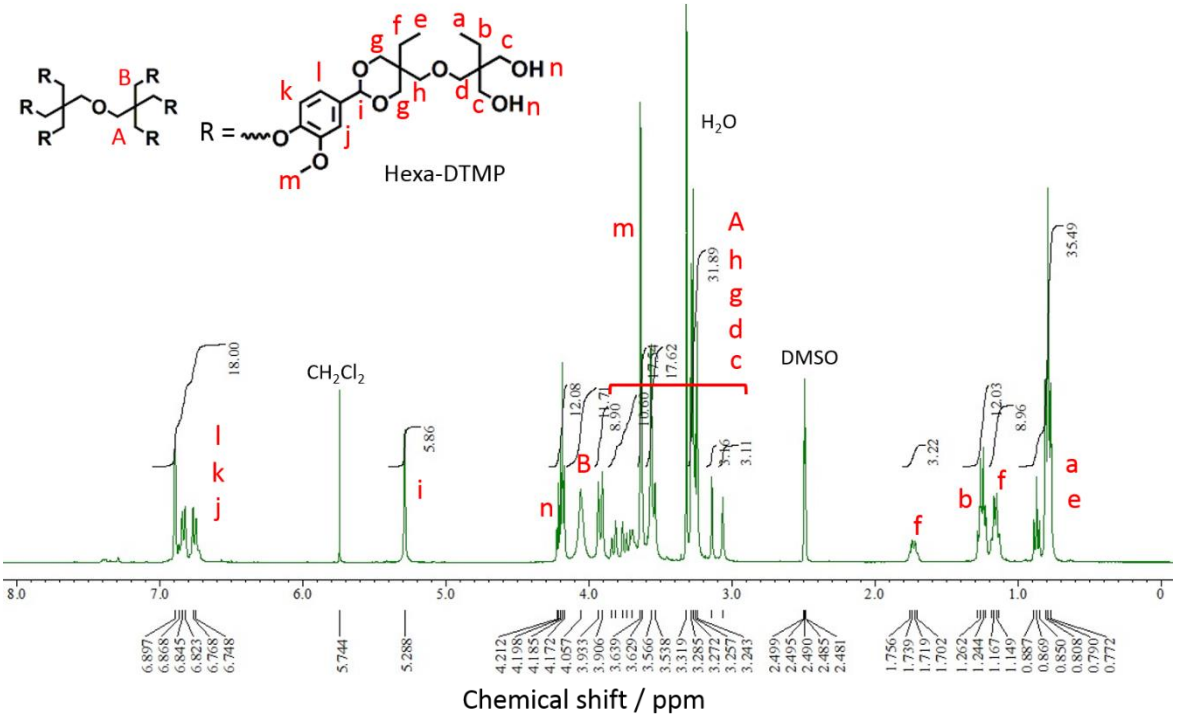


Figure S18. ^{1}H NMR spectrum of **Hexa-DTMP** after purification. Solvents: DMSO-d_6.

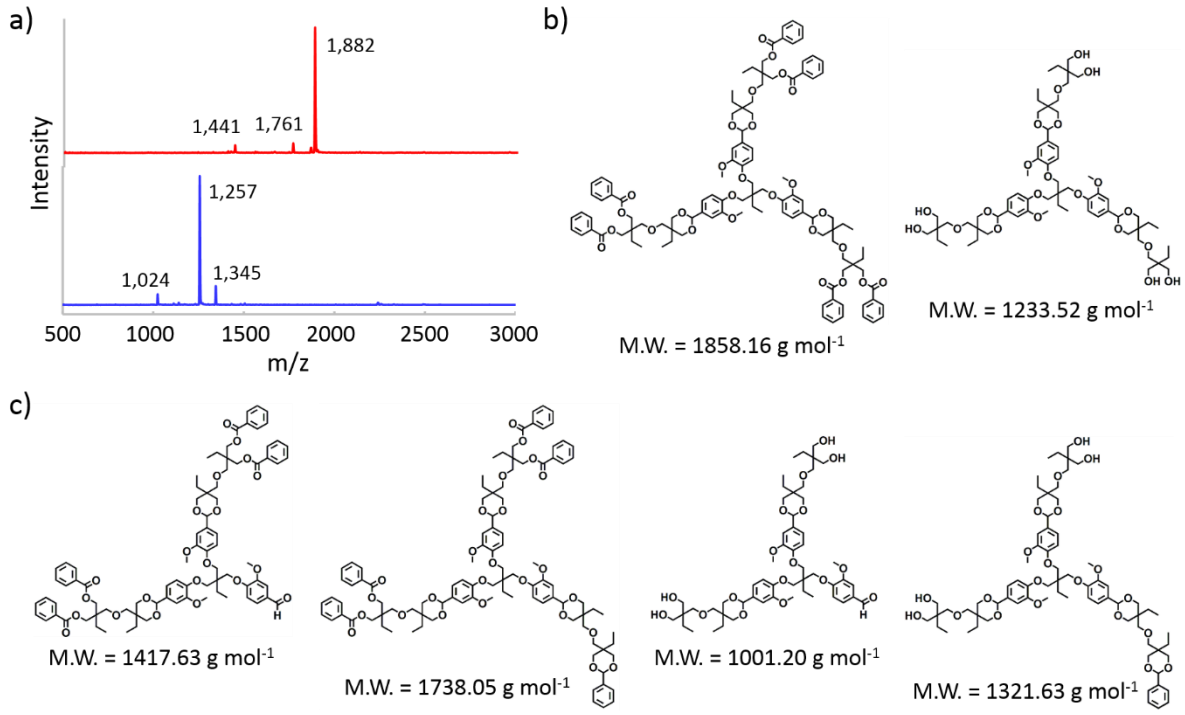


Figure S19. a) MALDI-TOF-mass spectra of **Tri-DTMP-Bz$_2$** (top) and **Tri-DTMP** (bottom) after purification. b) Chemical structures and molar weights of **Tri-DTMP-Bz$_2$** (left) and **Tri-DTMP** (right). c) Chemical structures and molar weights of the by-products included in **Tri-DTMP-Bz$_2$** and **Tri-DTMP**. The by-product with a M.W. of 1,322 g mol^{-1} was possibly produced from benzaldehyde or **Ph-DTMP** included in **DTMP-Bz$_2$** as impurities.

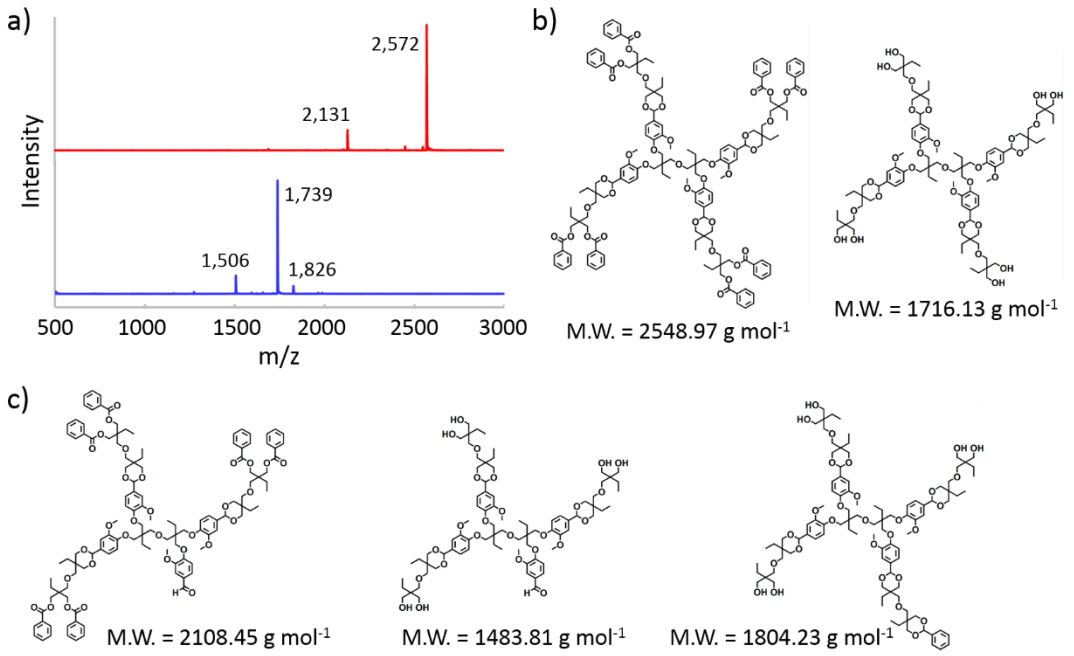


Figure S20. a) MALDI-TOF-mass spectra of **Tetra-DTMP-Bz$_2$** (top) and **Tetra-DTMP** (bottom) after purification. b) Chemical structures and M.W. of **Tetra-DTMP-Bz$_2$** (left) and **Tetra-DTMP** (right). c) Chemical structures and M.W. of the by-products included in **Tetra-DTMP-Bz$_2$** and **Tetra-DTMP**. The by-product with a M.W. of 1,804 g mol^{-1} was possibly produced from benzaldehyde or **Ph-DTMP** included in **DTMP-Bz$_2$** as impurities.

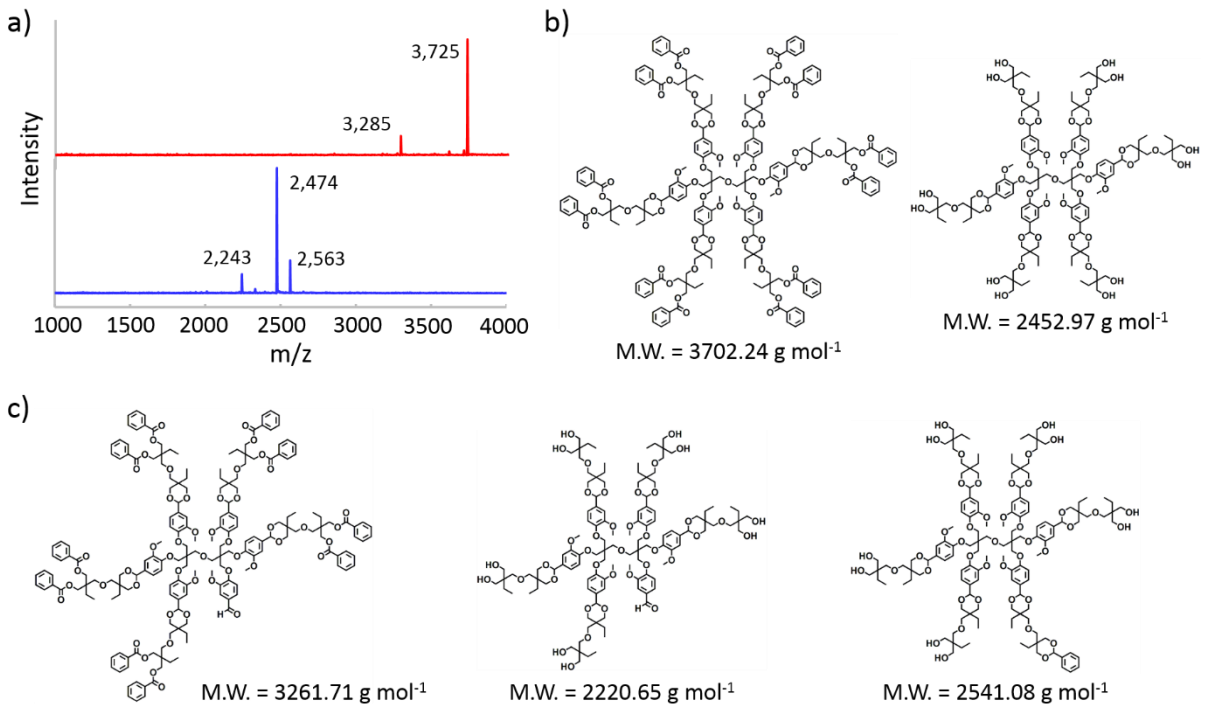


Figure S21. a) MALDI-TOF-mass spectra of **Hexa-DTMP-Bz$_2$** (top) and **Hexa-DTMP** (bottom) after purification. b) Chemical structures and M.W. of **Hexa-DTMP-Bz$_2$** (left) and **Hexa-DTMP** (right). c) Chemical structures and M.W. of the by-products included in **Hexa-DTMP-Bz$_2$** and **Hexa-DTMP**. The by-product with a M.W. of 2,541 g mol^{-1} was potentially produced from benzaldehyde or **Ph-DTMP** included in **DTMP-Bz$_2$** as impurities.

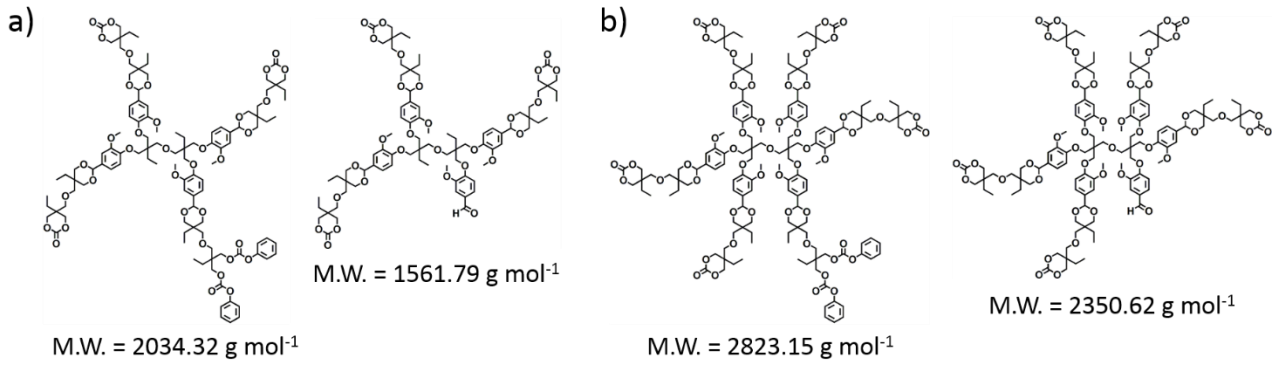


Figure S22. Chemical structures and M.W. of the by-products included in a) **Tetra-DTMP-Bz$_2$** and b) **Hexa-DTMP**.

Table S1. Analysis of the purity of multi-functional 6-CCs.

	acetal / %[a]	aldehyde groups / %[b]	6-CC structures / %[c]	bis(phenoxycarbonyl) groups / %[d]
Tri-DTMPC	97.3	2.7	96.6	3.4
Tetra-DTMPC	97.0	3.0	96.0	4.0
Hexa-DTMPC	97.5	2.5	96.2	3.8

[a] Molar fraction of acetal structures in multi-functional 6-CCs. [b] Molar fraction of residual aldehyde groups in multi-functional 6-CCs. [c] Molar fraction of 6-CC structures in multi-functional 6-CC. [d] Molar fraction of bis(phenoxycarbonyl) groups in multi-functional 6-CCs. These fractions were determined by ^{1}H NMR spectra of these multi-functional 6-CCs.

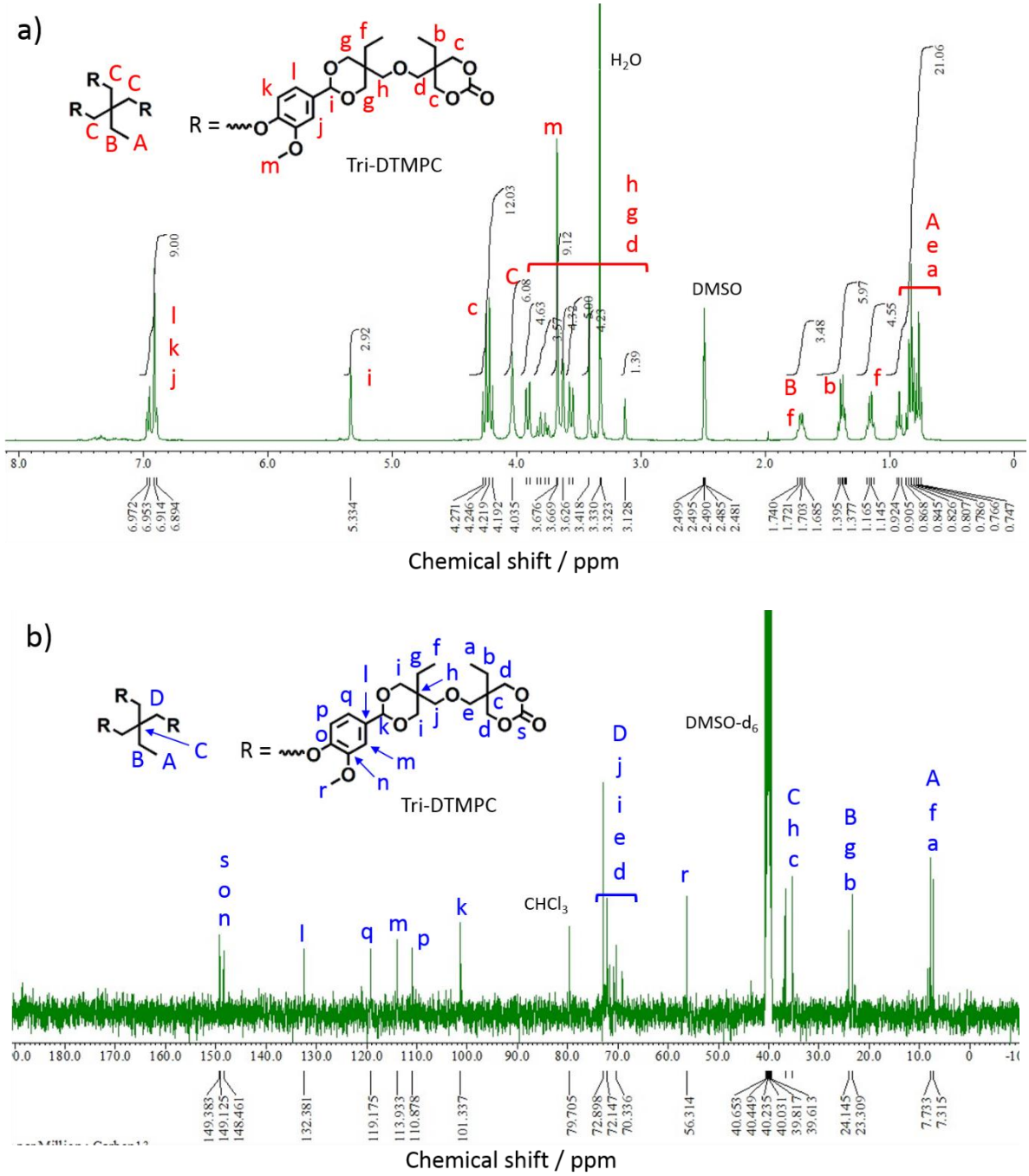


Figure S23. a) ^{1}H and b) ^{13}C NMR spectra of **Tri-DTMPC** after purification. Solvents: DMSO-d_6.

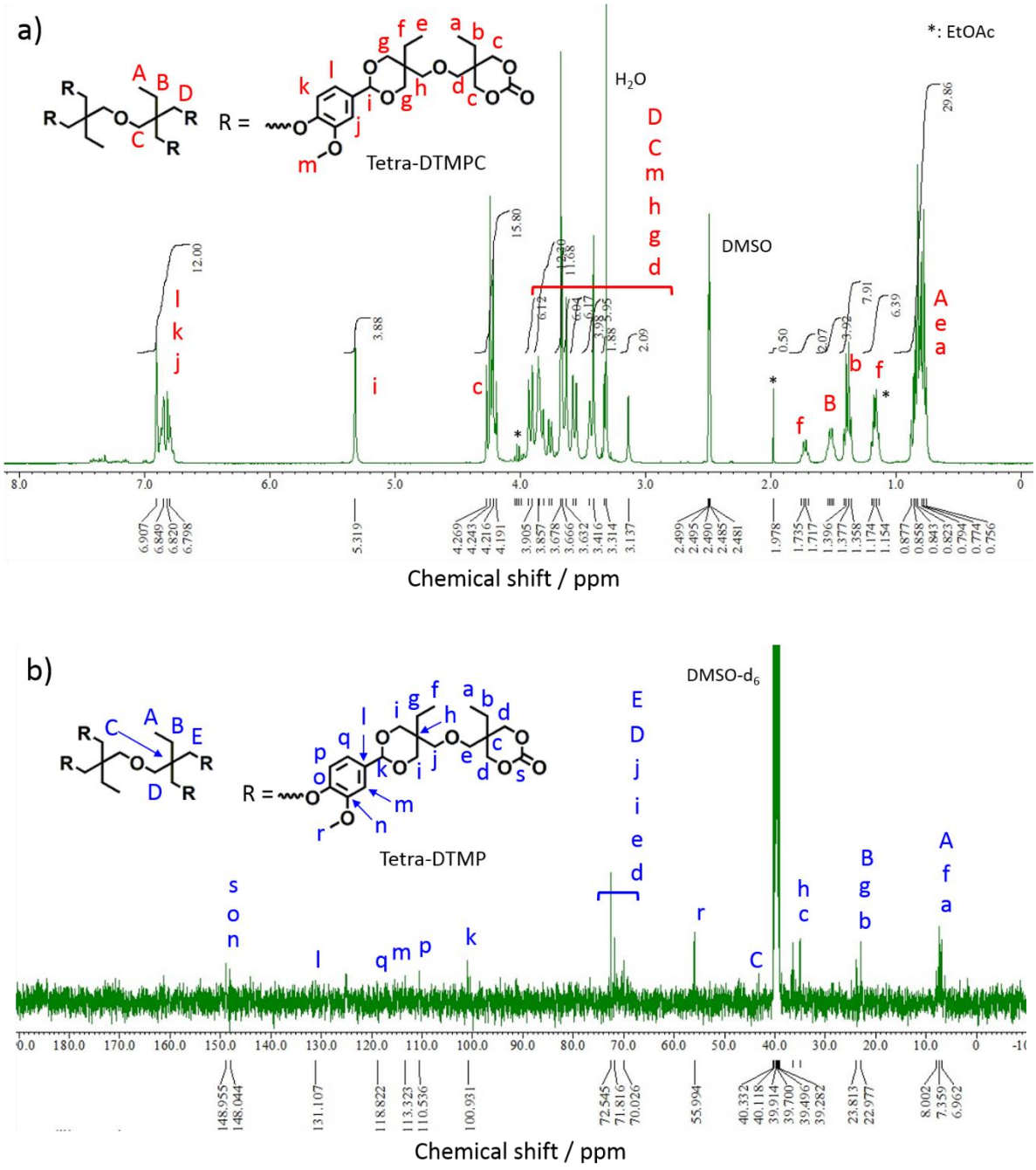


Figure S24. a) ^{1}H and b) ^{13}C NMR spectra o**f Tetra-DTMPC** after purification. Solvents: DMSO-d_6.

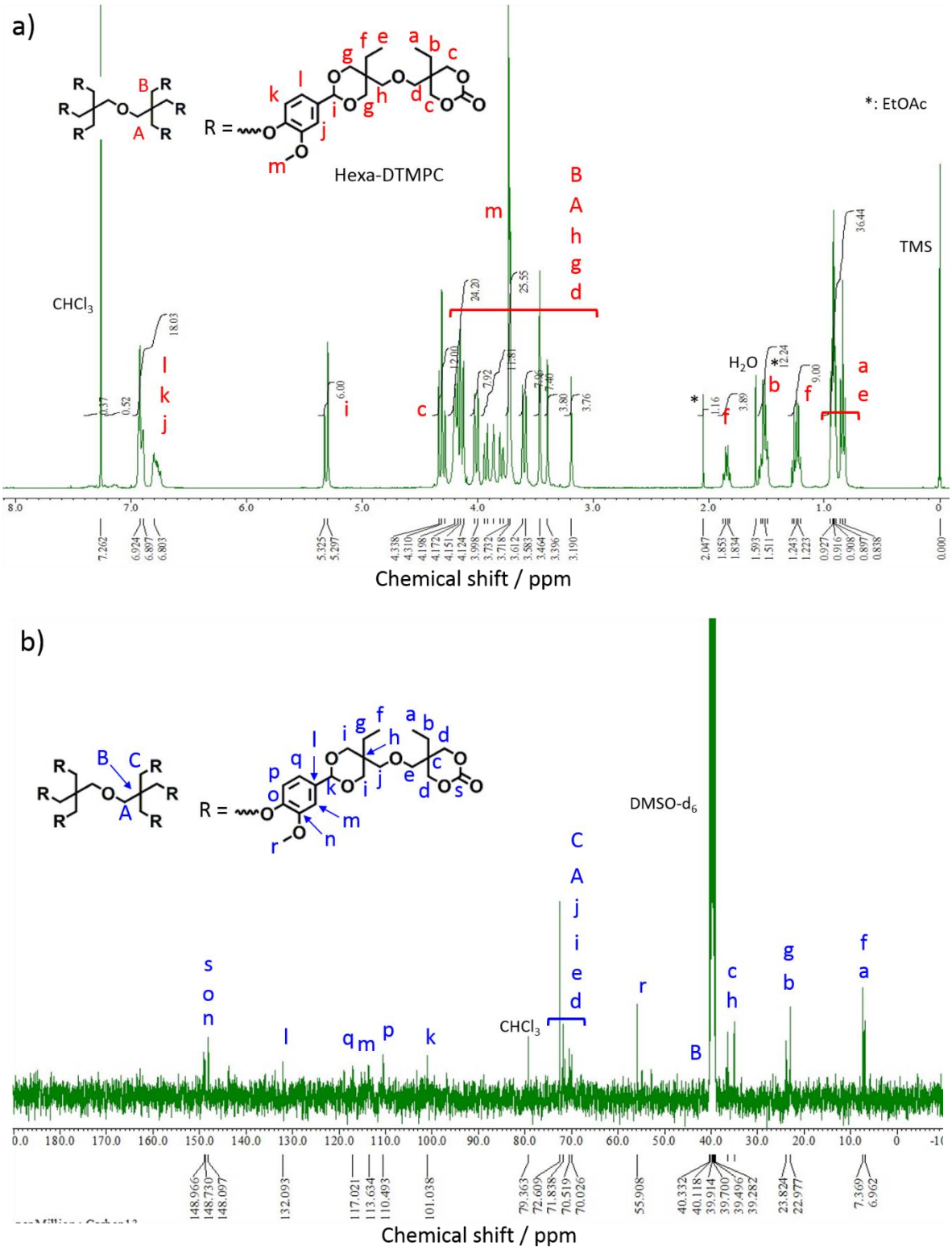


Figure S25. ^{1}H NMR spectrum of **Hexa-DTMPC** after purification (silica gel column chromatography and recrystallization from n-hexane/EtOAc). Solvents: $CDCl_3$ containing 0.03v/v% TMS (^{1}H NMR) and DMSO-d6 (^{13}C NMR).

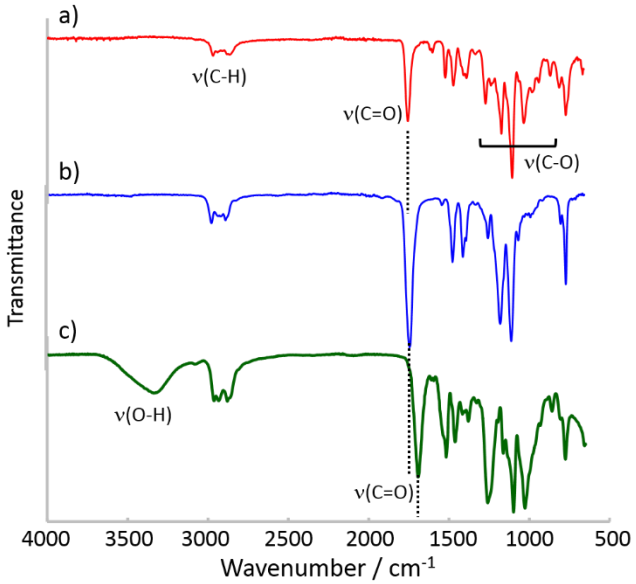


Figure S26. FT-IR spectra of a) **Hexa-DTMPC**, b) **DTMP** and c) **PAHU-Hexa-15.**

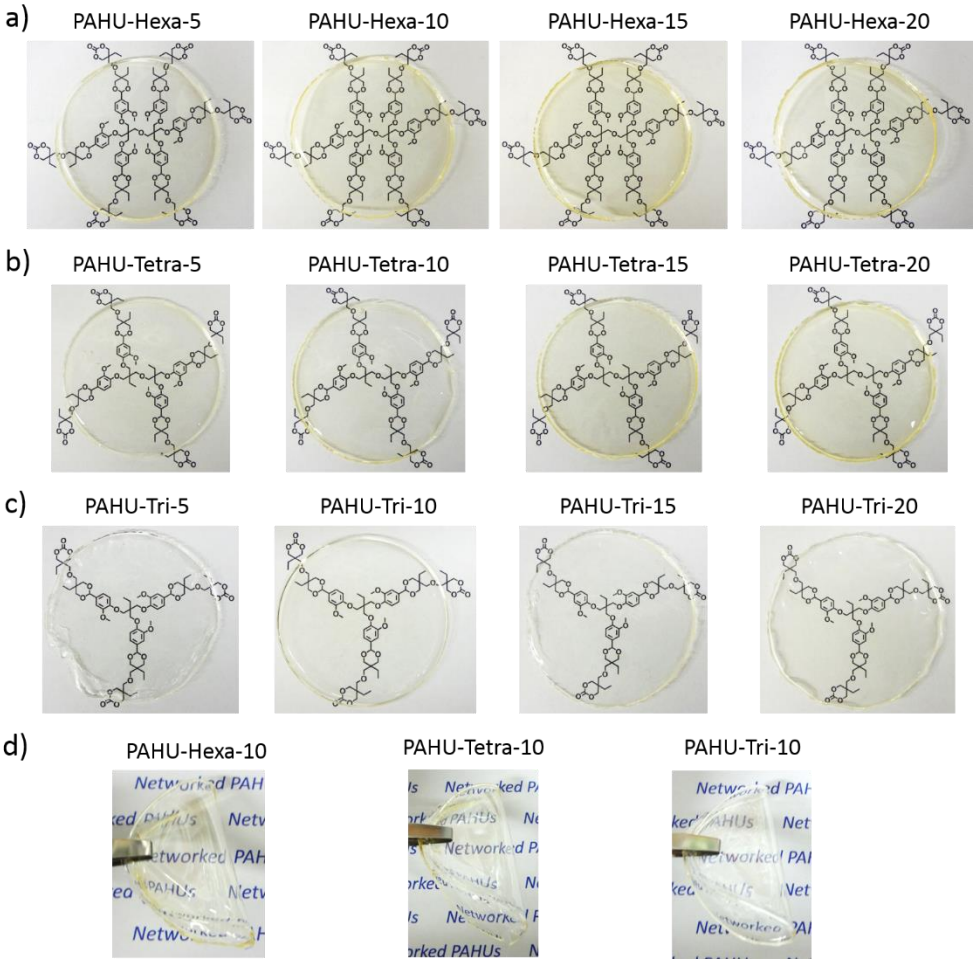


Figure S27. Photographs of networked PAHU films fabricated from multi-functional 6-CCs, **DTMPC** and DAP at different feed ratios. a) **PAHU-Hexa-n**. b) **PAHU-Tetra-n**. c) **PAHU-Tri-n** (n = 5, 10, 15 or 20). The molar fraction of multi-functional 6-CCs used are 5, 10, 15 or 20 mol% with respect to total carbonate monomers. d) Photographs of bent films prepared from different multi-functional 6-CCs.

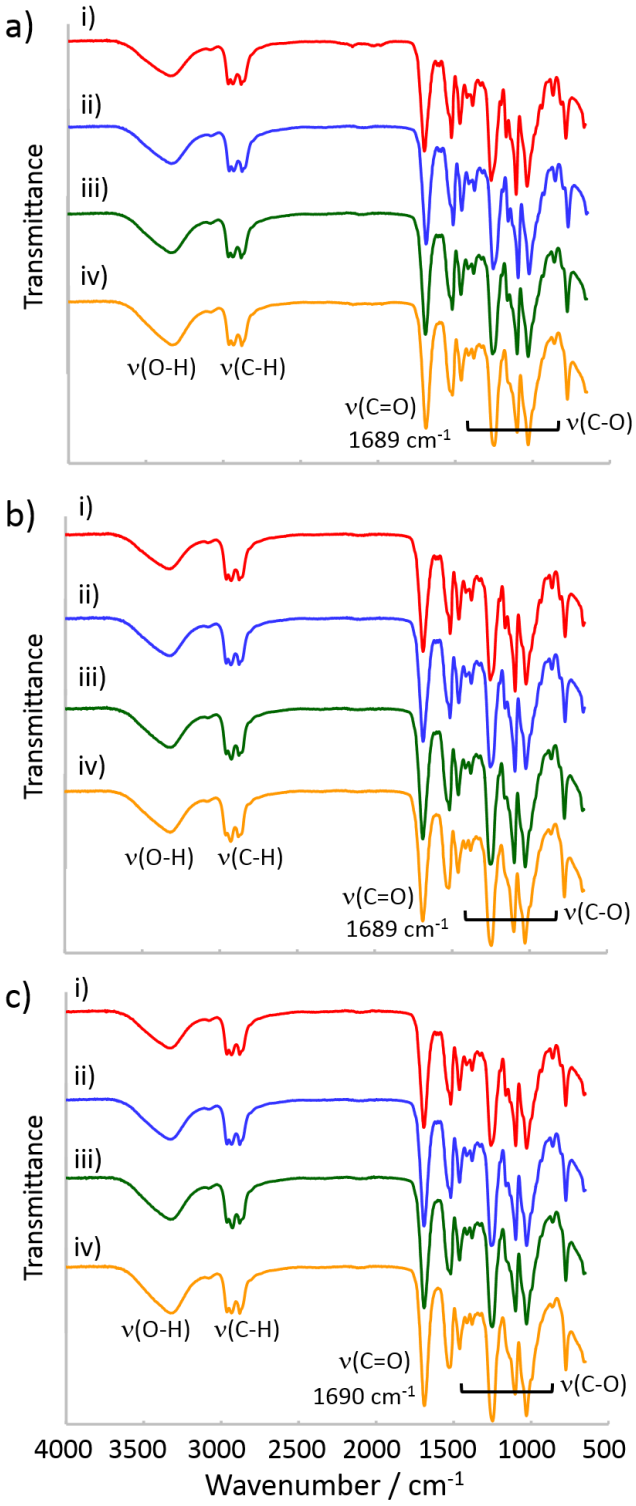


Figure S28. FT-IR spectra of networked PAHU films fabricated from different multi-functional 6-CCs, DTMPC and DAP at different feed ratios. a) **PAHU-Hexa-n.** b) **PAHU-Tetra-n**. c) **PAHU-Tri-n**. The molar fraction of multi-functional 6-CCs used are i) 5 mol% (n = 5), ii) 10 mol% (n = 10), iii) 15 mol% (n = 15), or iv) 20 mol% (n = 20).

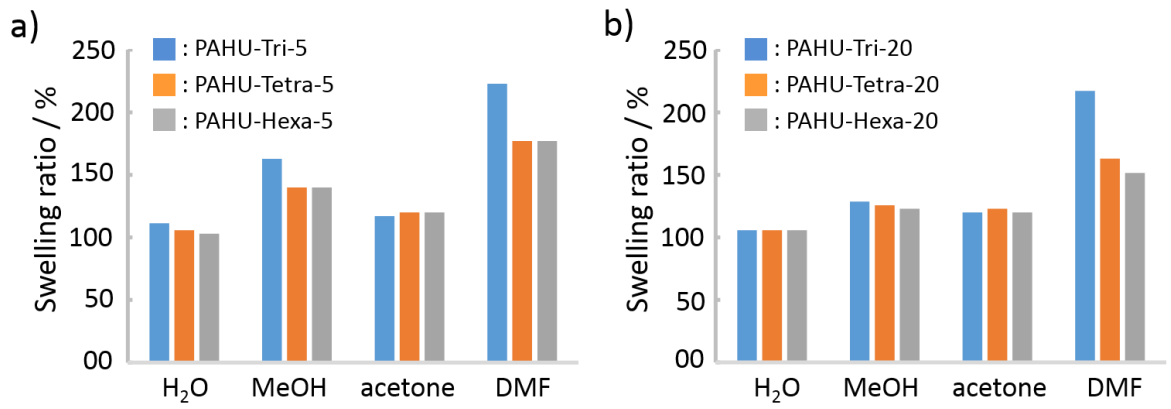


Figure S29. Swelling Properties of networked PAHU films in different solvents (H_2O, MeOH, acetone or DMF). Swelling ratios were calculated by the lengths of the films before/after immersion in solvents for 1day at room temperature. a) Networked PAHU films obtained using 5 mol% multi-functional 6-CCs. b) Networked PAHU films obtained using 20 mol% multi-functional 6-CCs. In these figures, a swelling ratio of 100% means no absorption of solvents (no swelling of the films).

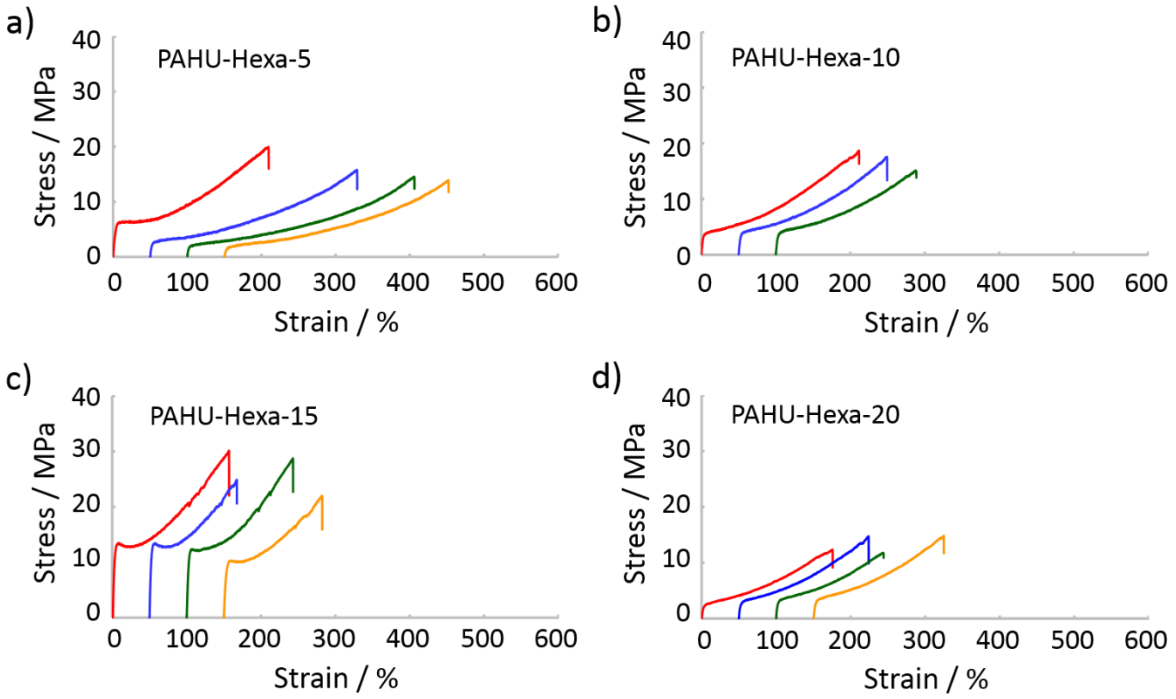


Figure S30. S-S curves of **PAHU-Hexa-n** fabricated at different **Hexa-DTMPC/DTMPC** feed ratios. a) **PAHU-Hexa-5**. b) **PAHU-Hexa-10**. c) **PAHU-Hexa-15**. d) **PAHU-Hexa-20**. Tensile tests were carried out 3 or 4 times.

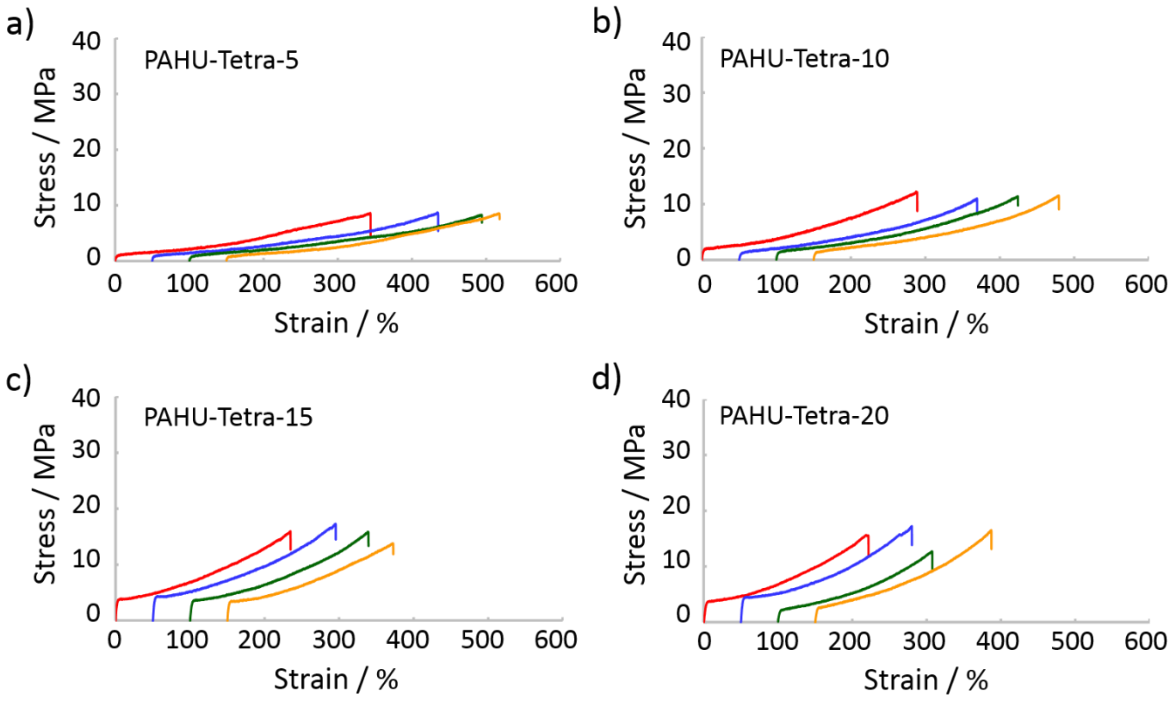


Figure S31. S-S curves of **PAHU-Tetra-n** fabricated at different **Tetra-DTMPC/DTMPC** feed ratios. a) **PAHU-Tetra-5**. b) **PAHU-Tetra-10**. c) **PAHU-Tetra-15**. d) **PAHU-Tetra-20**. Tensile tests were carried out 4 times.

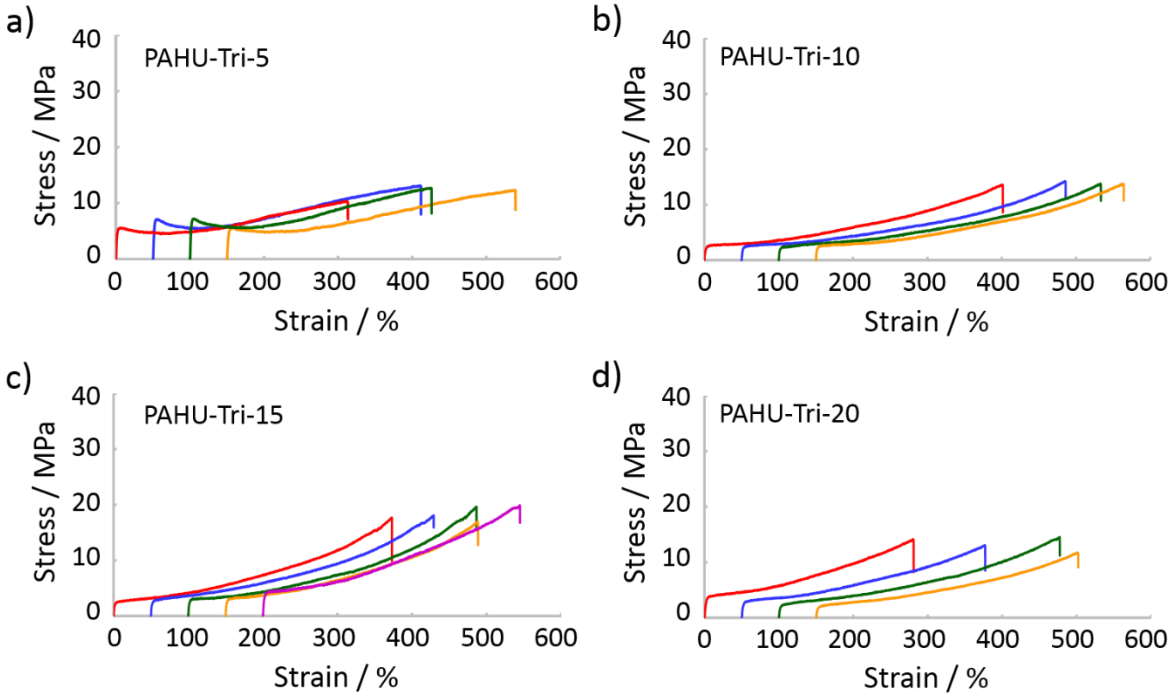


Figure S32. S-S curves of **PAHU-Tri-n** fabricated at different **Tri-DTMPC/DTMPC** feed ratios. a) **PAHU-Tri-5**. b) **PAHU-Tri-10**. c) **PAHU-Tri-15**. d) **PAHU-Tri-20** Tensile tests were carried out 4-5 times.

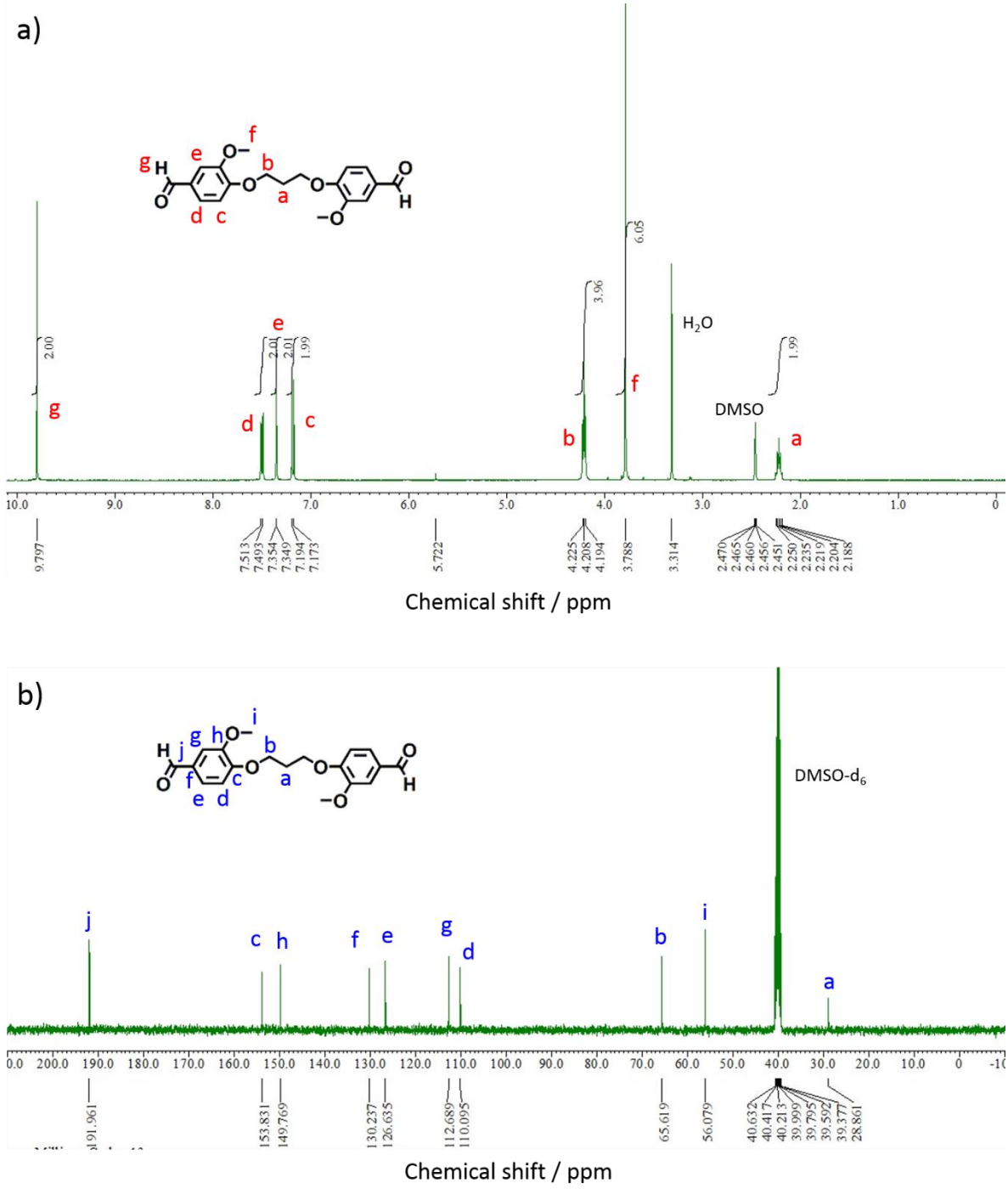
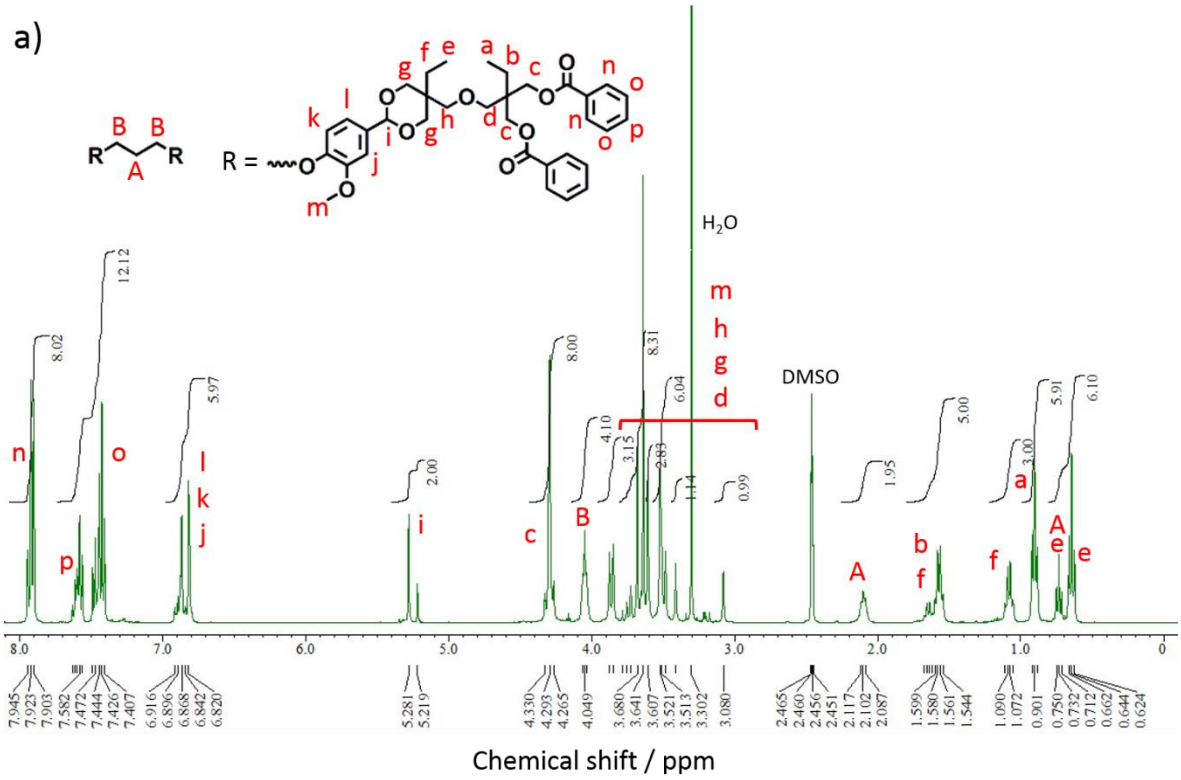


Figure S33. a) ^{1}H and b) ^{13}C NMR spectra of **Di-Van** after purification. Solvents: DMSO-d_6.



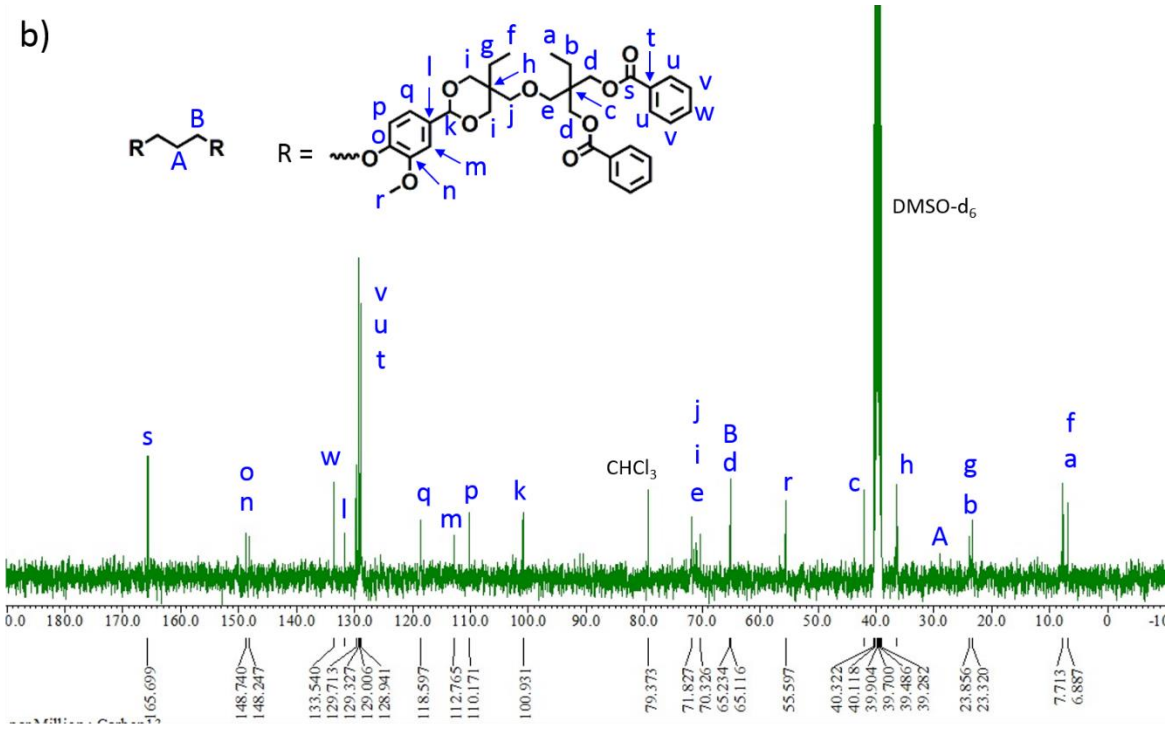


Figure S34. a) ^{1}H and b) ^{13}C NMR spectra of **Di-DTMP-Bz$_2$** after purification. Solvents: DMSO-d$_6$.

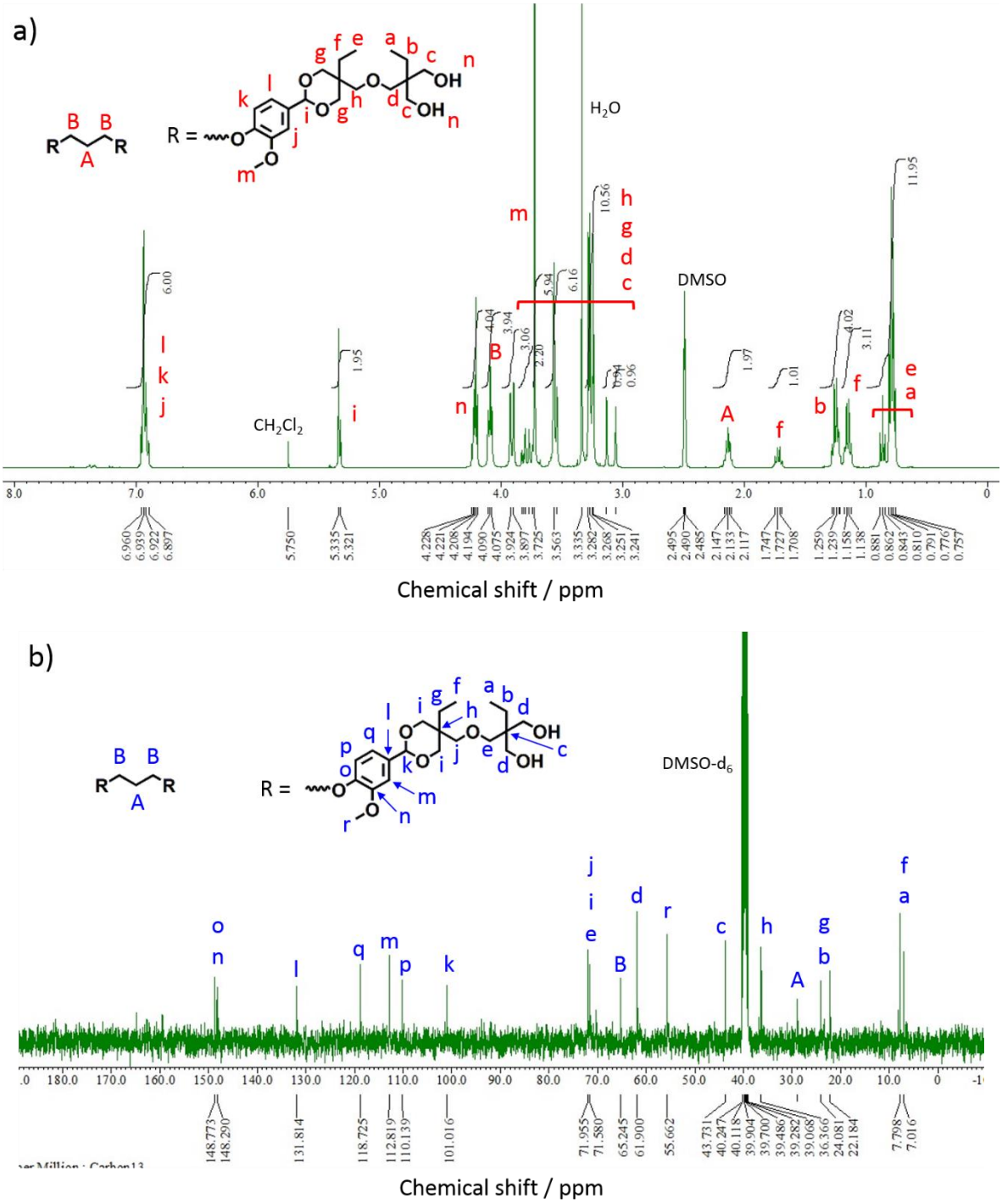


Figure S35. a) ^{1}H and b) ^{13}C NMR spectra of **Di-DTMP** after purification. Solvents: DMSO-d_6.

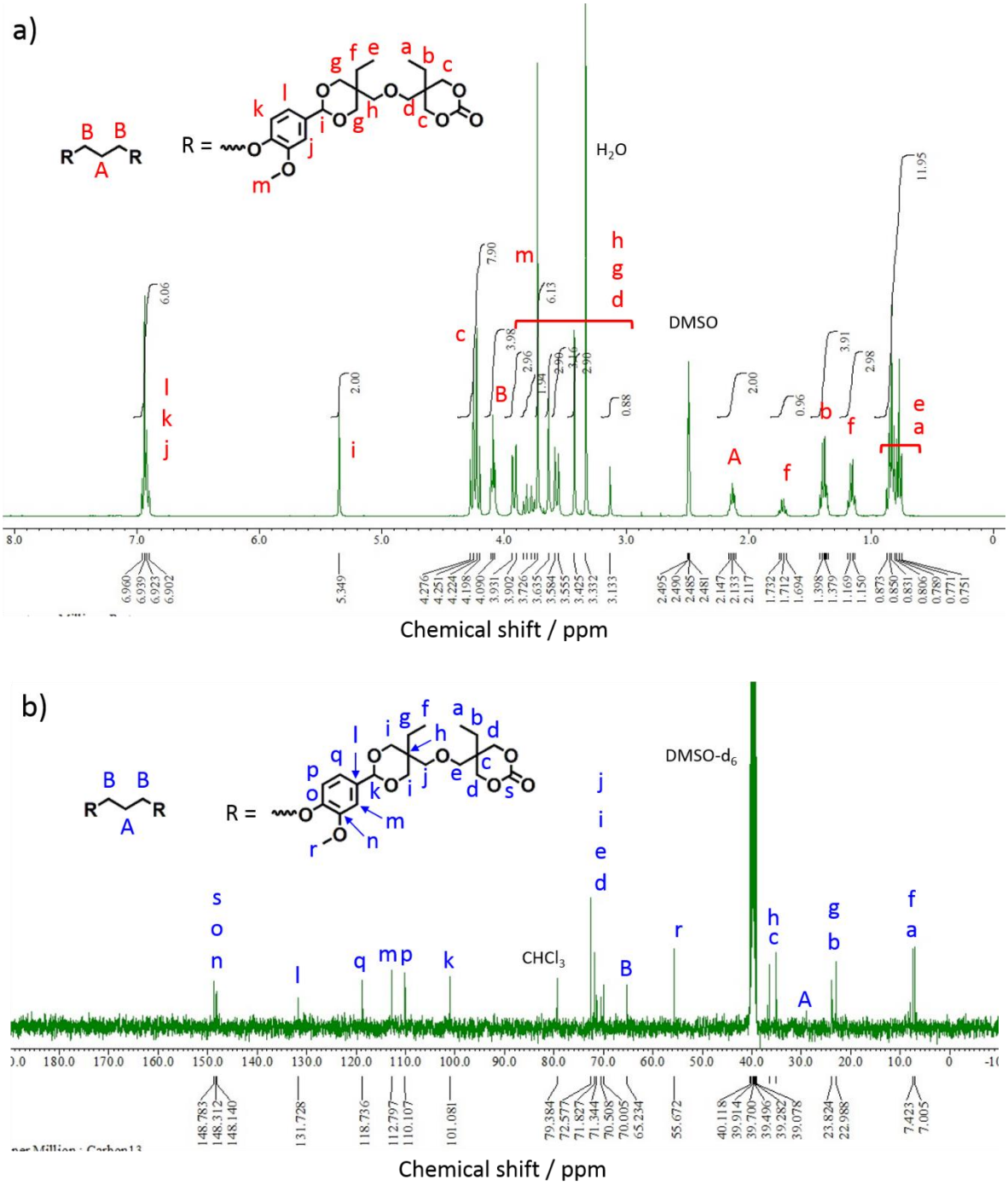


Figure S36. a) ^{1}H and b) ^{13}C NMR spectra of **Di-DTMPC** after purification. Solvents: DMSO-d_6.

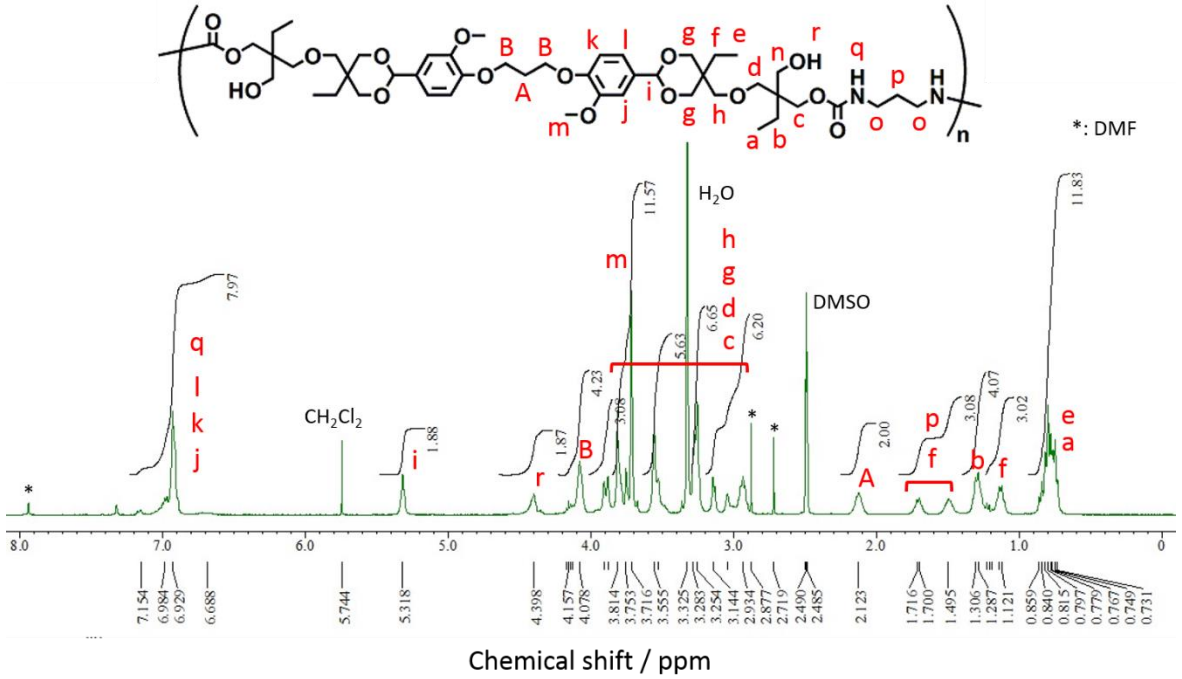


Figure S37. ^{1}H NMR spectrum of **LPAHU** after purification. Solvents: DMSO-d_6.

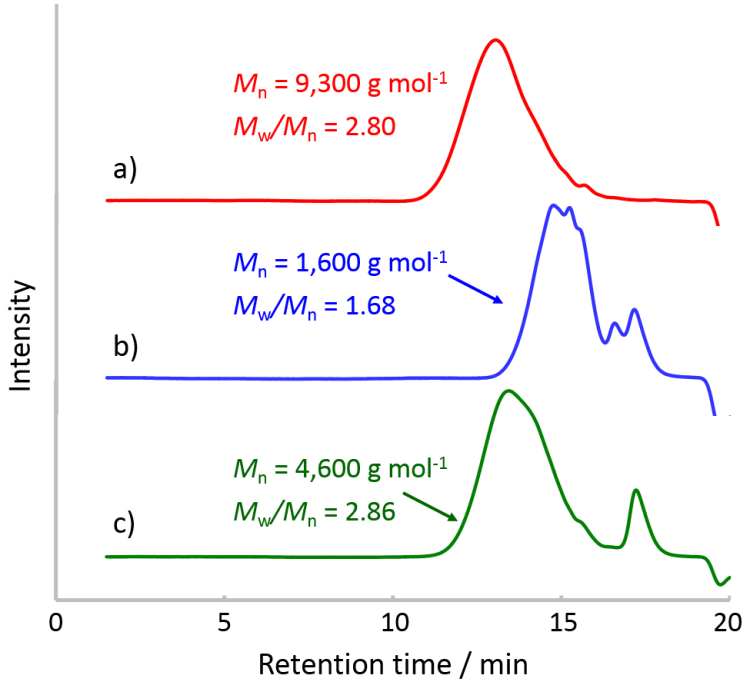


Figure S38. SEC traces of a) **LPAHU** before fragmentation, b) fragmented **LPAHU** after heating at 60°C in DMF containing TsOH monohydrate (0.2 equiv. per acetal structure), and c) partially-elongated **LPAHU** after the elimination of solvents by drying at 40°C under reduced pressure.

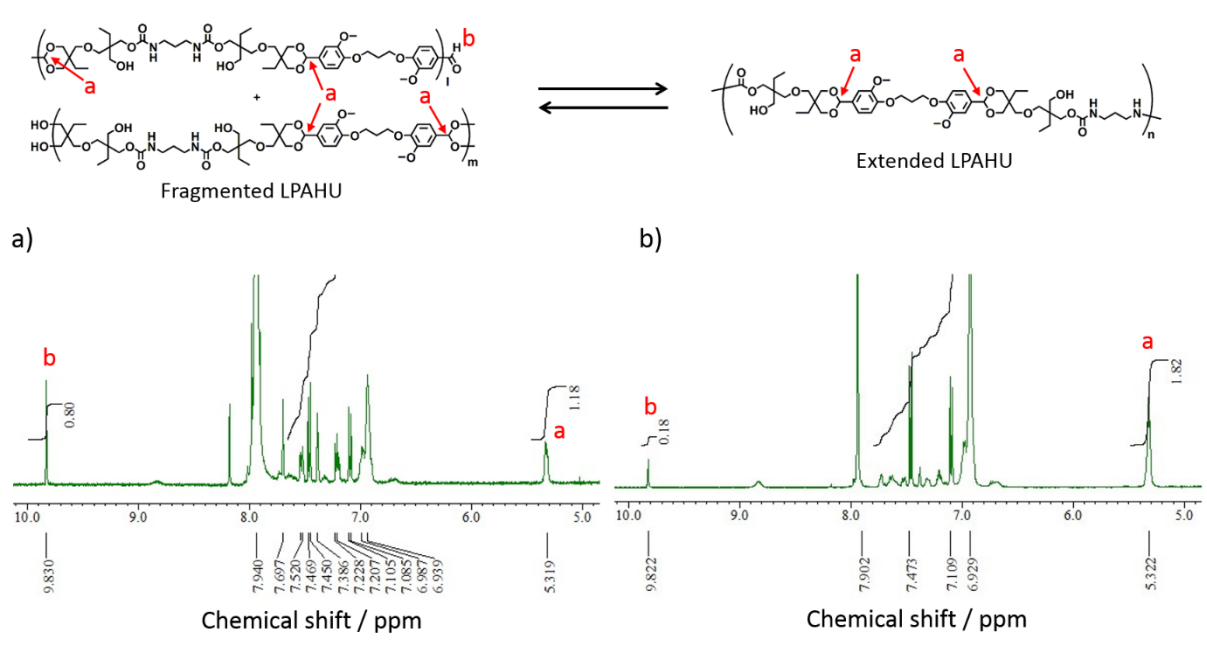


Figure S39. ^{1}H NMR spectra of a) fragmented **LPAHU** (after heating at 60°C in DMF solution containing TsOH monohydrate and b) partially-extended **LPAHU** (after the removal of the solvents by heating at 60°C under reduced pressure). Solvents: DMSO-d_6. Assignments of signals derived from acetal and aldehyde protons are shown in the spectra.

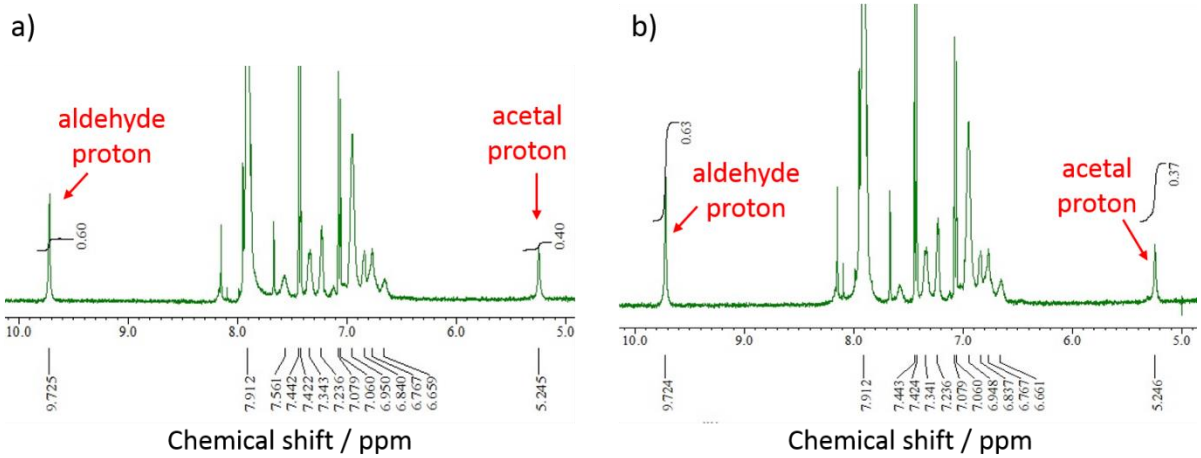


Figure S40. ^{1}H NMR spectra of partially-de-crosslinked **PAHU-Hexa-20** (after heating in DMF solution containing TsOH monohydrate) during a) 6th and b) 9th re-forming processes. Solvent: DMSO-d_6.

Table S2. Characterization of networked structures of **PAHU-Hexa-20** after de-crosslinking treatments by ^{1}H NMR spectroscopy.

	Re-workable process		
	1st	6th	9th
Proton ratio of the signal at 2.54 ppm [a]	097	1.09	1.14
Theoretical proton ratio of methylene protons adjacent to amino groups of DAP [b]	4.67	4.67	4.67
Remaining amino groups in **PAHU-Hexa-20 / %**	20.8	23.3	24.4

[a] Assigned to methylene protons adjacent to amino groups of DAP. The value is normalized by the total ratio of acetal and aldehyde protons. [b] Calculated using **Hexa-DTMPC**/DAP feed ratios. The value is normalized by the total ratio of acetal and aldehyde protons.

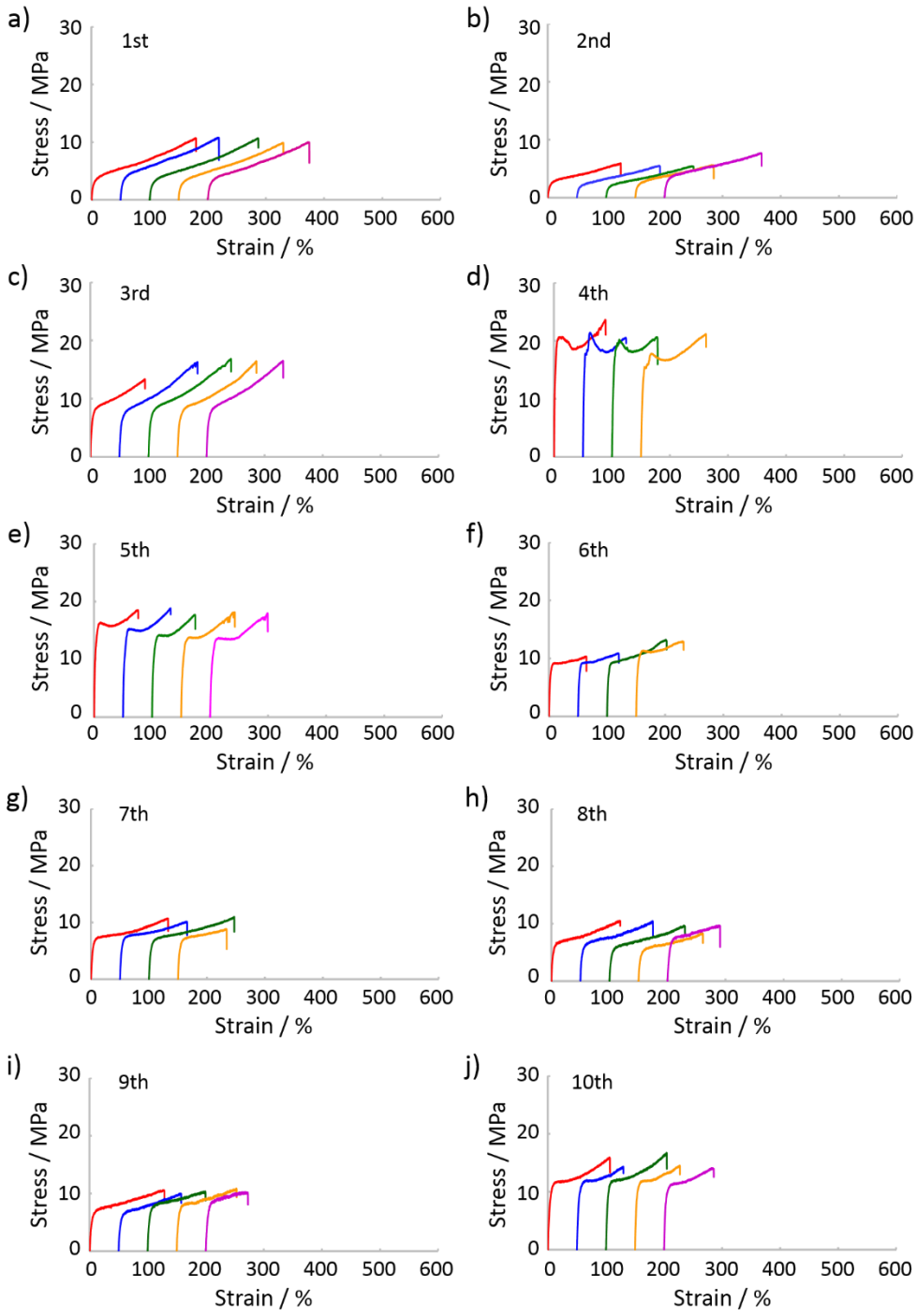


Figure S41. S-S curves of re-formed **PAHU-Hexa-20**. The re-formation treatment of the film was repeated 10 times. a) 1st, b) 2nd, c) 3rd, d) 4th, e) 5th, f) 6th, g) 7th, h) 8th, i) 9th, and j) 10th cycles. Tensile tests were carried out 4-5 times.

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