Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Thermoresponsive dynamic covalent dendronized polymers

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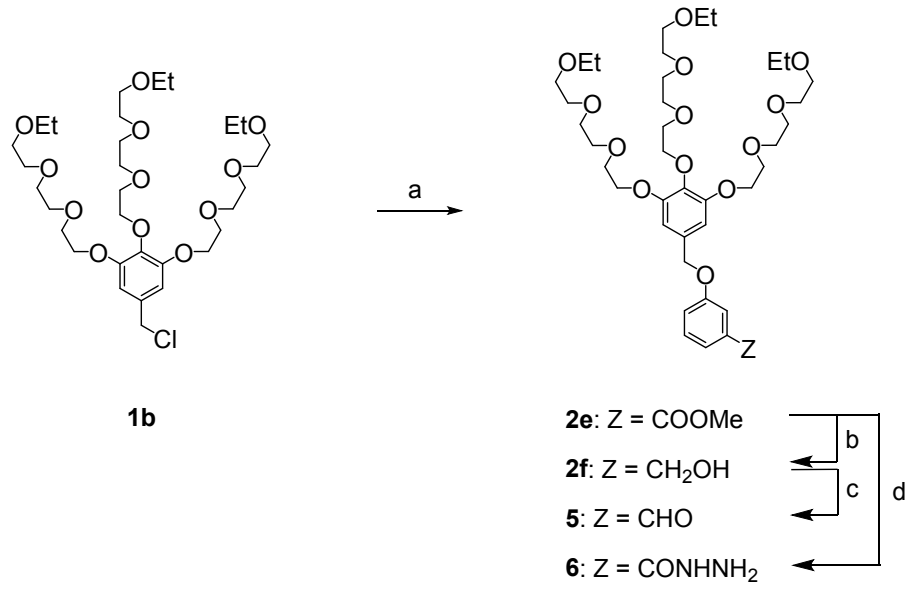
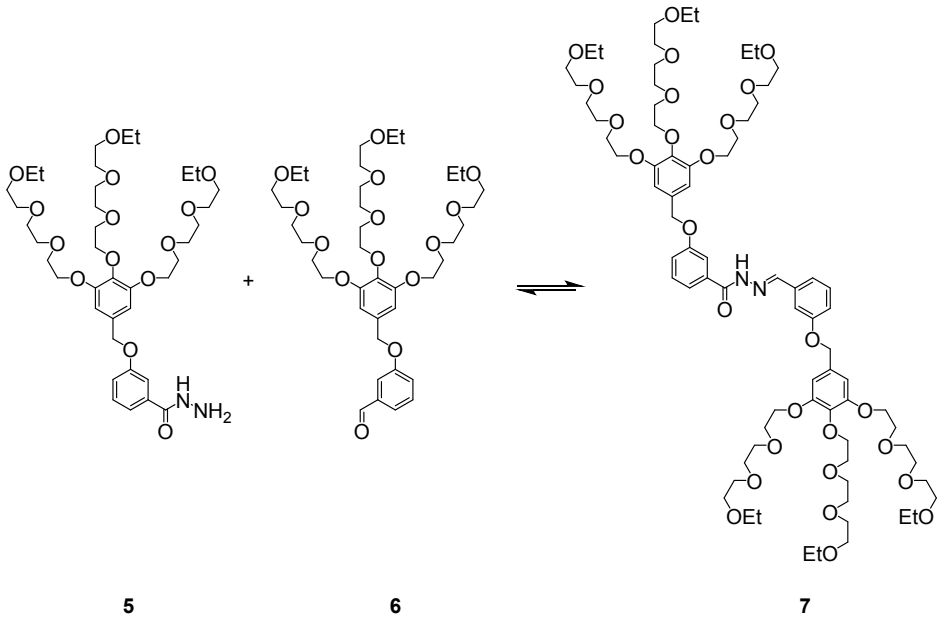


Scheme S1 Synthetic procedures for the model compounds. Reagents and conditions: (a) Methyl 3-hydroxybenzoate, KI, K_2CO_3, DMF, 80 °C (**2e**: 66%); (b)$LiAlH_4$, THF, -5 °C to 25 °C (**2f**: > 99%);(c) PCC, DCM, 0 °C to 25 °C (**5**: 65%); (d) hydrazine hydrate, MeOH (**6**: > 99%).



5 **6** **7**

Scheme S2 Dimerization reaction of model system between **5** and **6**.

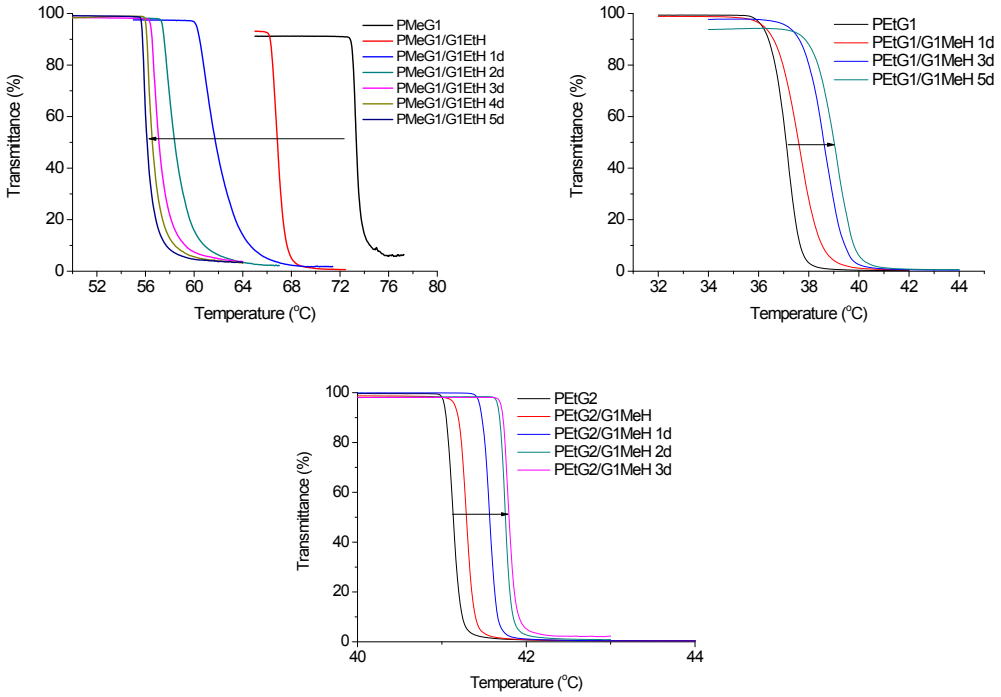


Fig. S1 Plots of transmittance *vs* temperature for 0.25 wt % buffer solutions (pH = 1.6) of a) **PMeG1** after addition of **G1EtH**, b) **PEtG1** after addition of **G1MeH** and c) **PEtG2** after addition of **G1MeH**. Heating rate = 0.2 $^{o}C \cdot min^{-1}$.

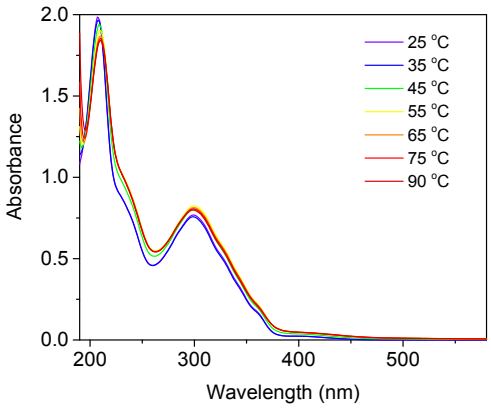


Fig. S2 UV/vis spectra of aqueous solutions of **PEtG1** at different temperatures, [**PEtG1**] = 39 $\mu g \cdot mL^{-1}$.

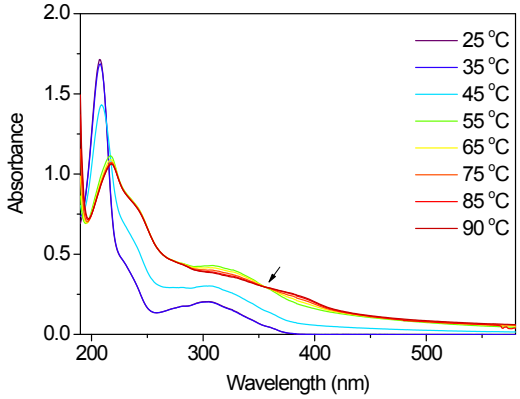


Fig. S3 UV/vis spectra of aqueous solutions of **PEtG2** and $CuSO_4$ at different temperatures, [-C=N-]: [Cu^{2+}] = 1:1, [**PEtG2**] = 25.5 μg·mL^{-1}.

Compound 2e. According to general procedure A from Methyl 3-hydroxybenzoate (0.30 g, 1.97 mmol), **1b** (1.1 g, 1.79 mmol), KI (0.20 g, 1.20 mmol), K_2CO_3 (0.74 g, 5.35 mmol) and dry DMF, **2e** was yielded as a yellow oil (0.86 g, 66%). ^{1}H NMR ($CDCl_3$): δ = 1.21-1.24 (m, 9H, CH_3), 3.51-3.56 (m, 6H, CH_2), 3.59-3.62 (m, 6H, CH_2), 3.66-3.69 (m, 12H, CH_2), 3.80 (br, 6H, CH_2), 3.82 (br, 2H, CH_2), 3.88 (br, 4H, CH_2), 3.94 (s, 3H, OCH_3), 4.16-4.19 (m, 6H, CH_2), 5.01 (s, 2H, CH_2), 6.70 (s, 2H, CH), 7.16-7.18 (d, 1H, CH), 7.37 (t, 1H, CH), 7.65-7.68 (m, 2H, CH).

Compound 2f. According to general procedure B from $LiAlH_4$ (0.04 g, 1.05 mmol), **2e** (0.59 g, 0.81 mmol) and dry THF, **2f** was yielded as a bright yellow oil (0.57 g, > 99%).

Compound 5. According to general procedure C from PCC (0.23 g, 1.07 mmol), **2b** (0.57 g, 0.81 mmol) and dry DCM, **5** was yielded as a bright yellow oil (0.37 g, 65%). ^{1}H NMR ($CDCl_3$): δ = 1.20-1.24 (m, 9H, CH_3), 3.51-3.57 (m, 6H, CH_2), 3.59-3.62 (m, 6H, CH_2), 3.66-3.69 (m, 12H, CH_2), 3.74-3.76 (m, 6H, CH_2), 3.82 (t, 2H, CH_2), 3.87 (t, 4H, CH_2), 4.16-4.20 (m, 6H, CH_2), 5.03 (s, 2H, CH_2), 6.70 (s, 2H, CH), 7.25-7.27 (m, 1H, CH), 7.47-7.52 (m, 3H, CH), 10.00 (s,1H, HC=O).

Compound 6. According to general procedure D from **2e** (0.29 g, 0.40 mmol), hydrazine hydrate (0.90 mL, 22.04 mmol) and anhydrous MeOH, **6** was yielded as a bright yellow solid (0.29 g, > 99%). ^{1}H NMR (DMSO-d_6): δ = 1.01-1.08 (m, 9H, CH_3), 3.36-3.40 (m, 6H, CH_2), 3.42-3.45 (m, 6H, CH_2), 3.48-3.52 (m, 12H, CH_2), 3.55-3.58 (m, 6H, CH_2), 3.65 (t, 2H, CH_2), 3.72 (t, 4H, CH_2) , 4.00 (t, 2H, CH_2), 4.08 (t, 4H, CH_2), 4.57 (br, 2H, NH_2), 5.03 (s, 2H, CH_2), 6.79 (s, 2H, CH), 7.13-7.16 (m, 1H, CH), 7.35-7.38 (m, 1H, CH), 7.41-7.43 (m, 1H, CH), 7.46-7.47 (m, 1H, CH), 9.77 (s, 1H, NH).

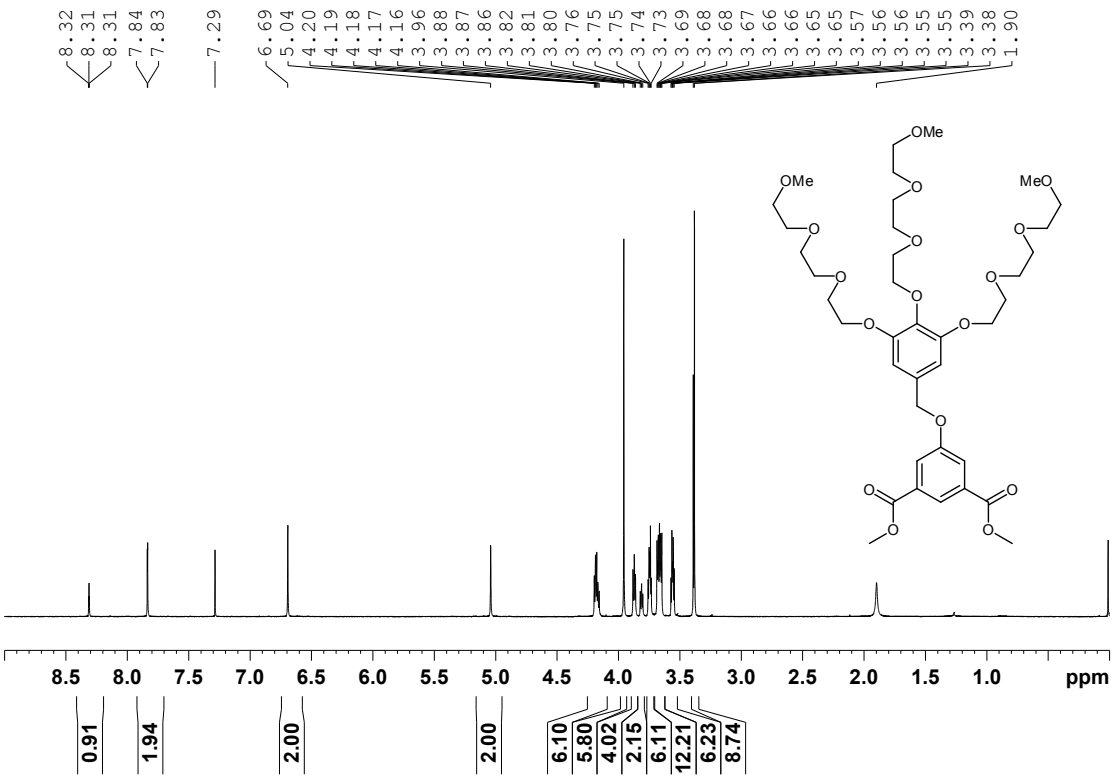


Fig. S4 ^{1}H NMR spectrum of **2a** in $CDCl_3$.

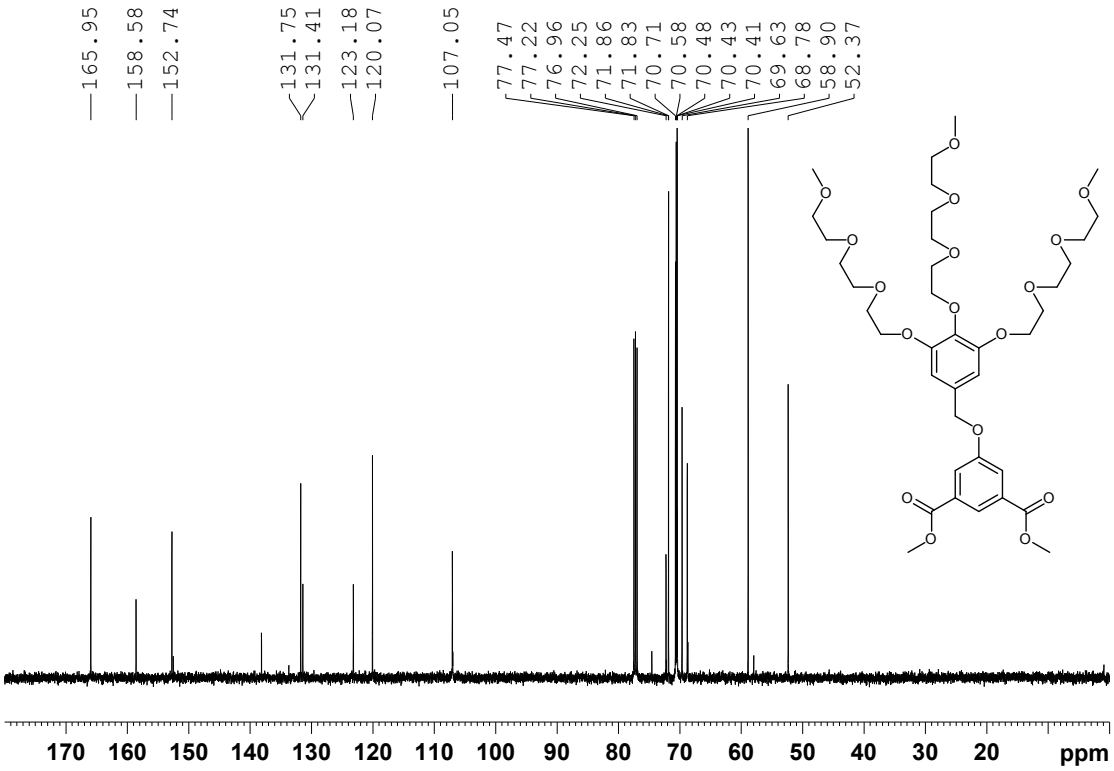


Fig. S5 ^{13}C NMR spectrum of **2a** in $CDCl_3$.

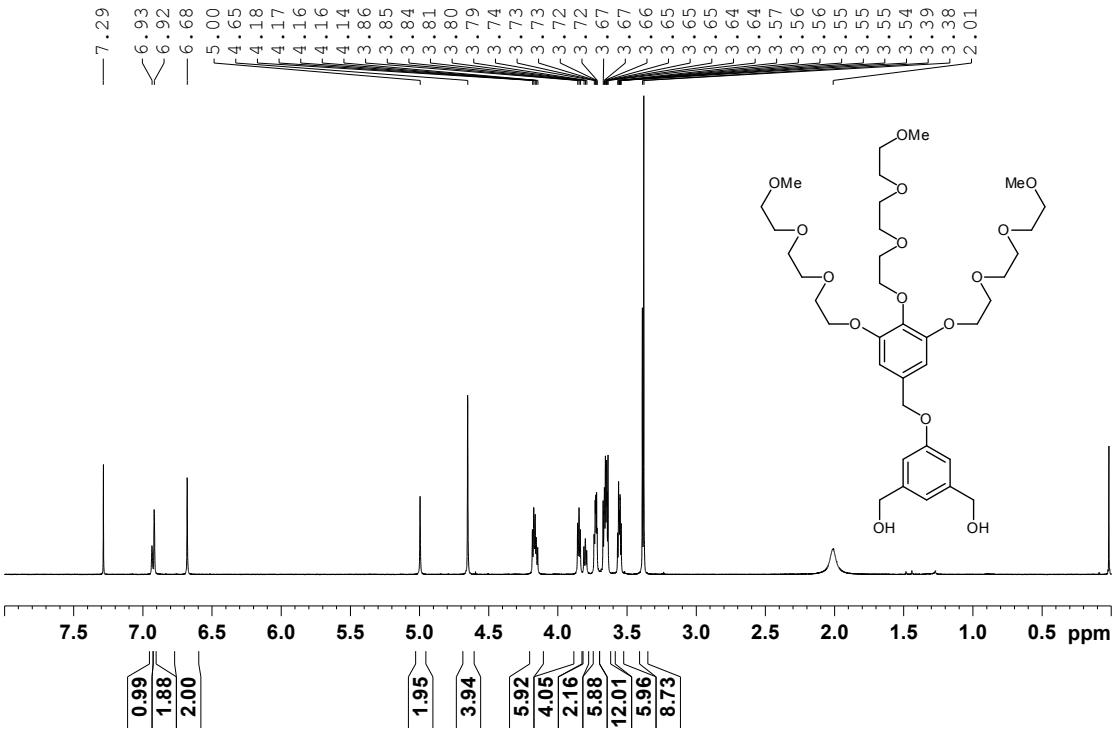


Fig. S6 ^{13}C NMR spectrum of **2b** in $CDCl_3$.

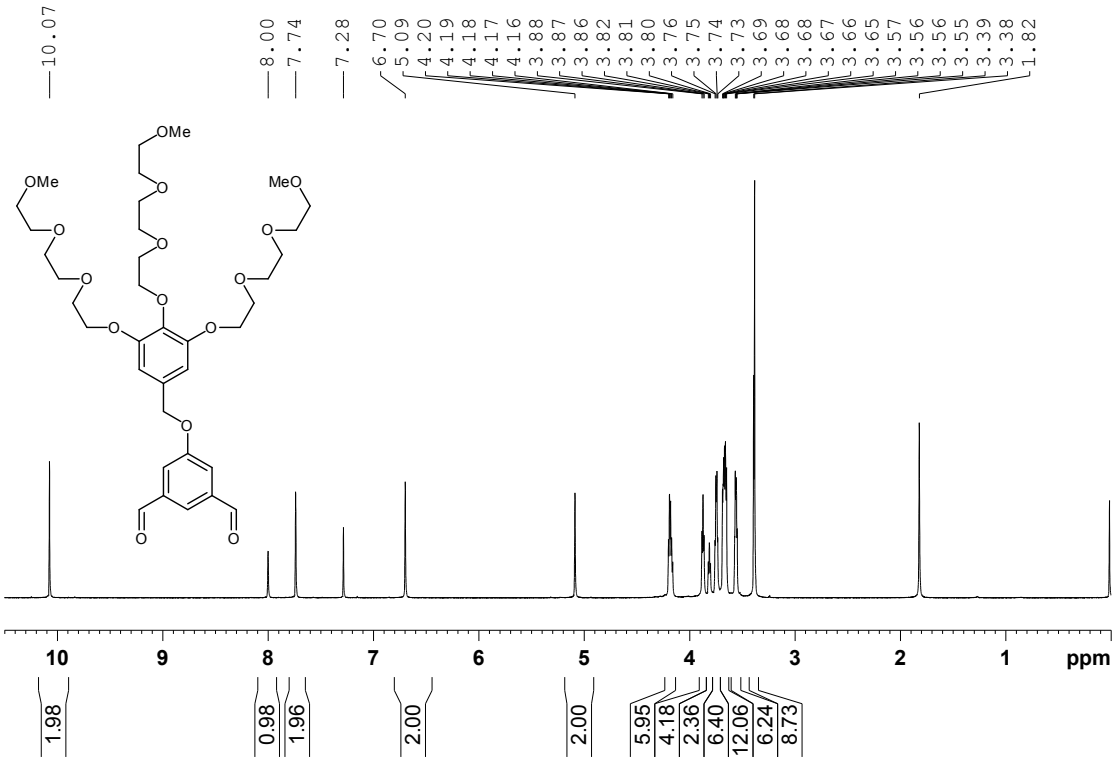


Fig. S7 ^{1}H NMR spectrum of **G1MeA** in $CDCl_3$.

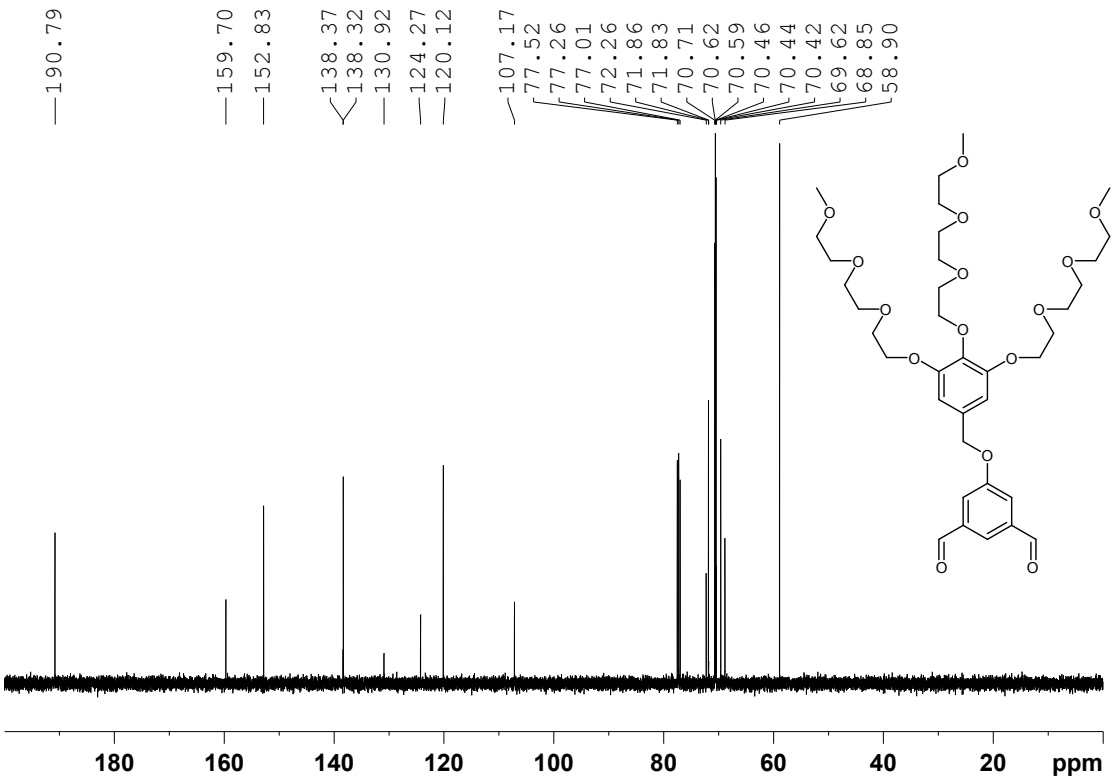


Fig. S8 ^{13}C NMR spectrum of **G1MeA** in $CDCl_3$.

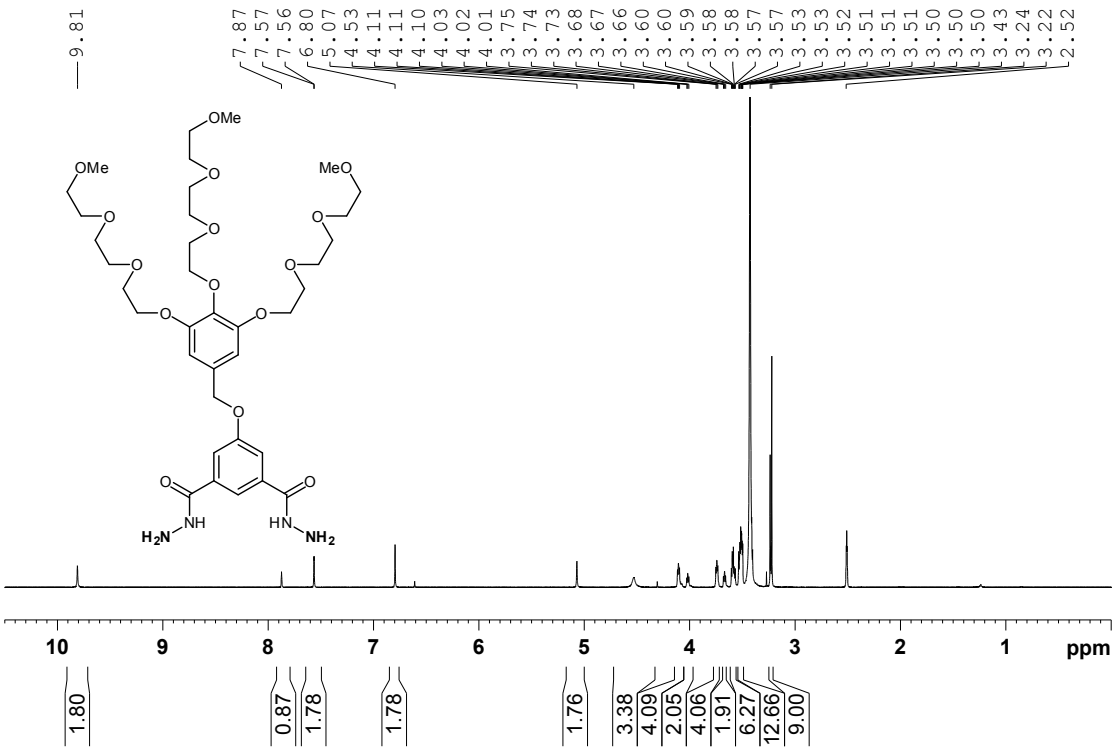


Fig. S9 ^{1}H NMR spectrum of **G1MeH** in DMSO-d_6.

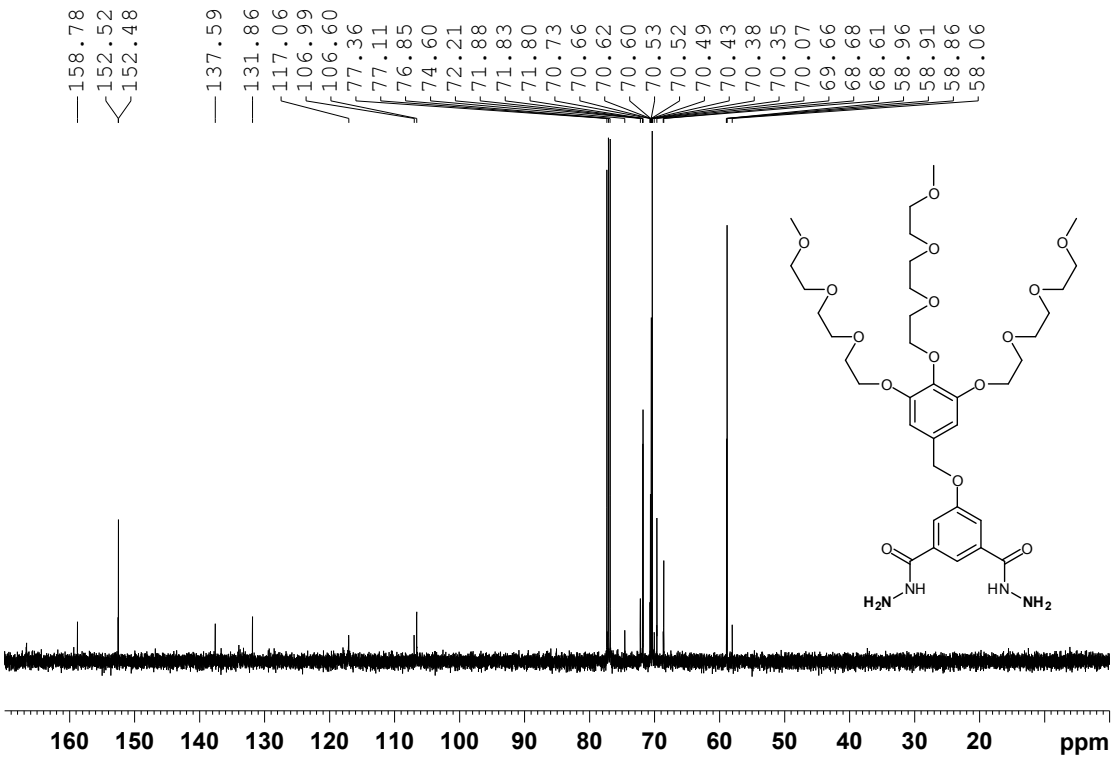


Fig. S10 ^{13}C NMR spectrum of **G1MeH** in $CDCl_3$.

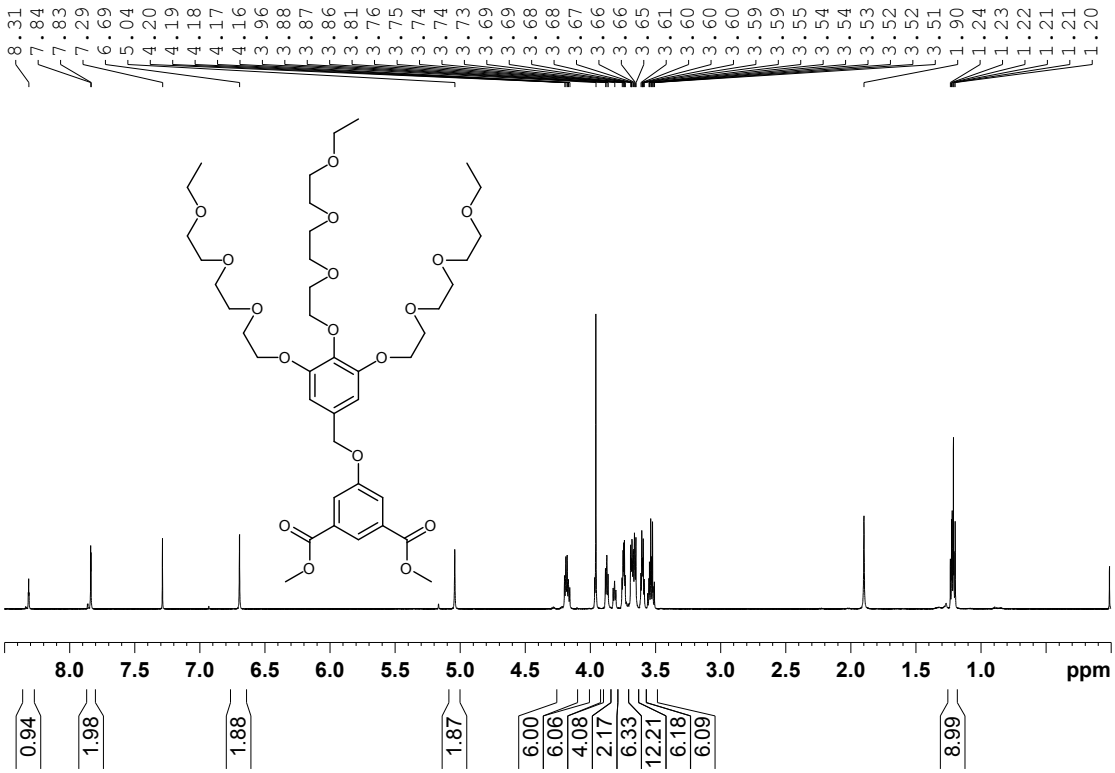


Fig. S11 ^{1}H NMR spectrum of **2c** in $CDCl_3$.

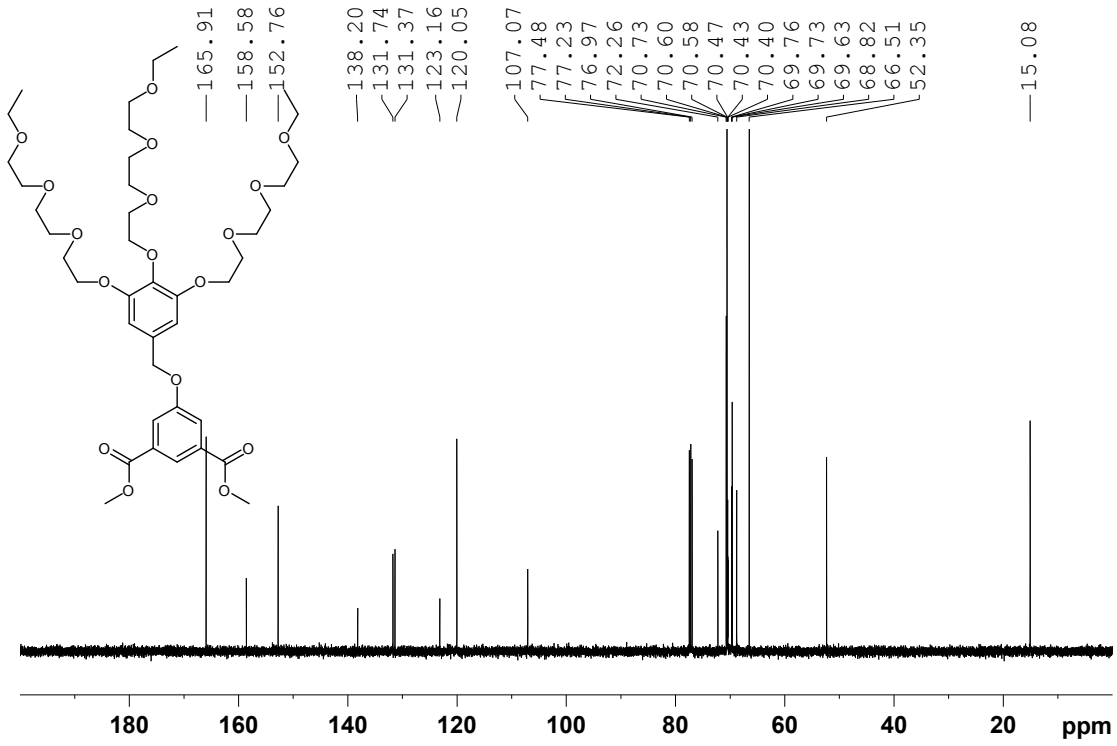


Fig. S12 ^{13}C NMR spectrum of **2c** in $CDCl_3$.

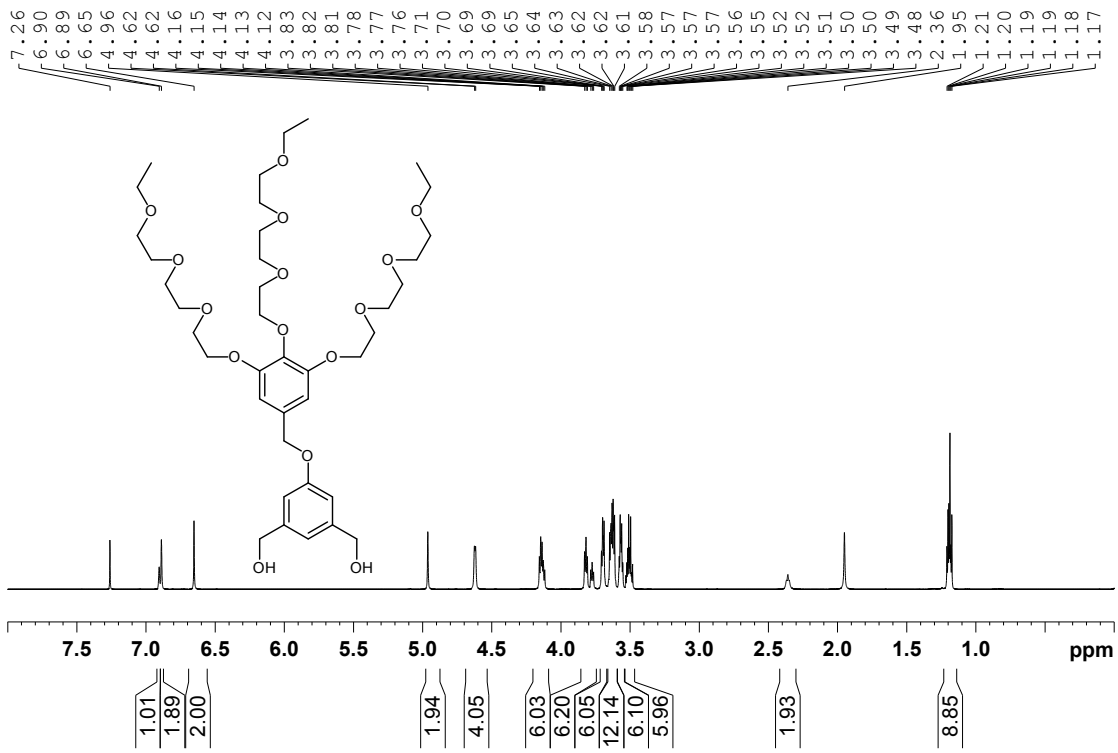


Fig. S13 ^{1}H NMR spectrum of **2d** in $CDCl_3$.

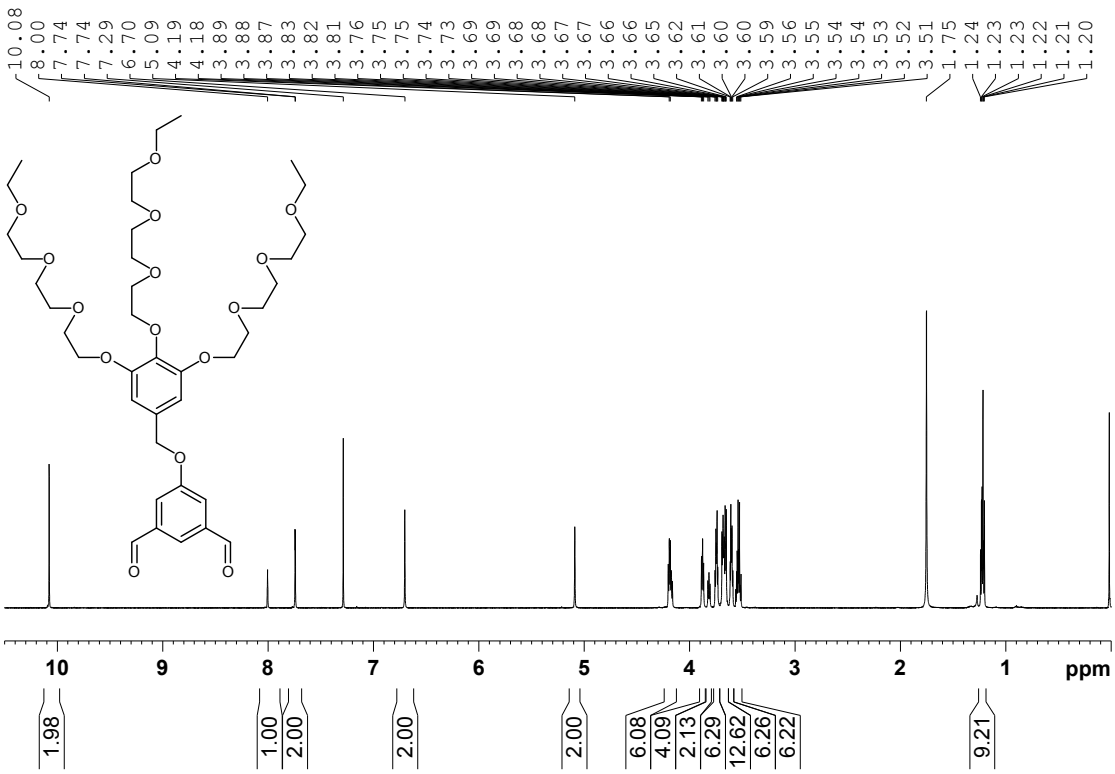


Fig. S14 ^{1}H NMR spectrum of **G1EtA** in $CDCl_3$.

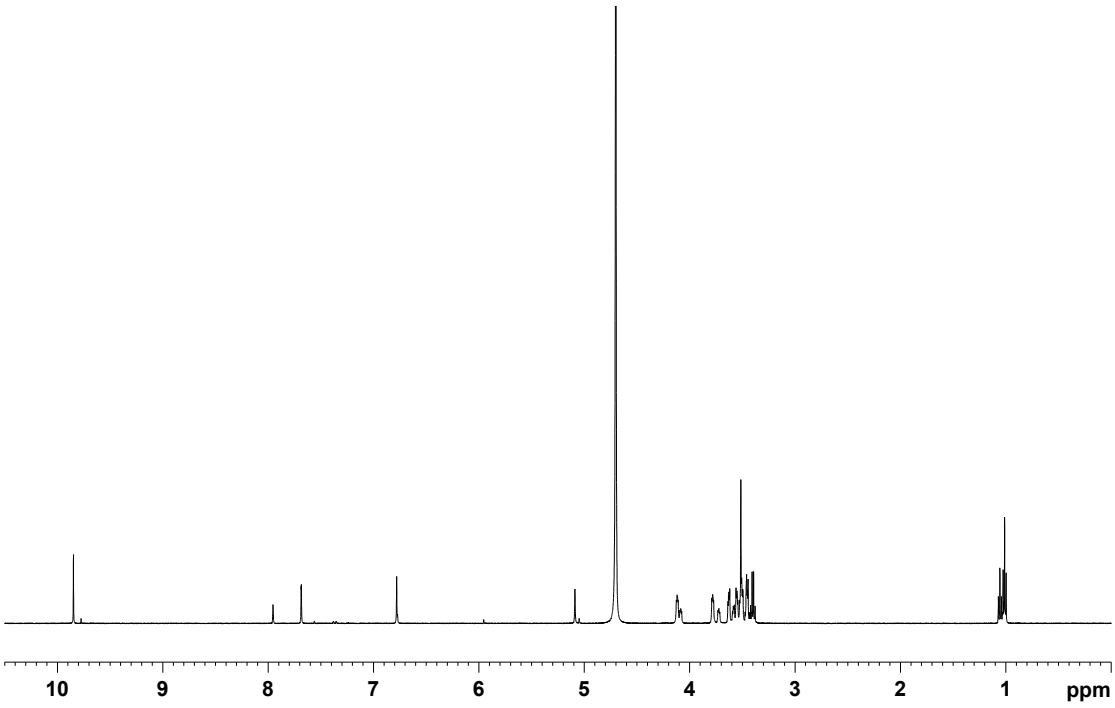


Fig. S15 ^{1}H NMR spectrum of **G1EtA** in D_2O.

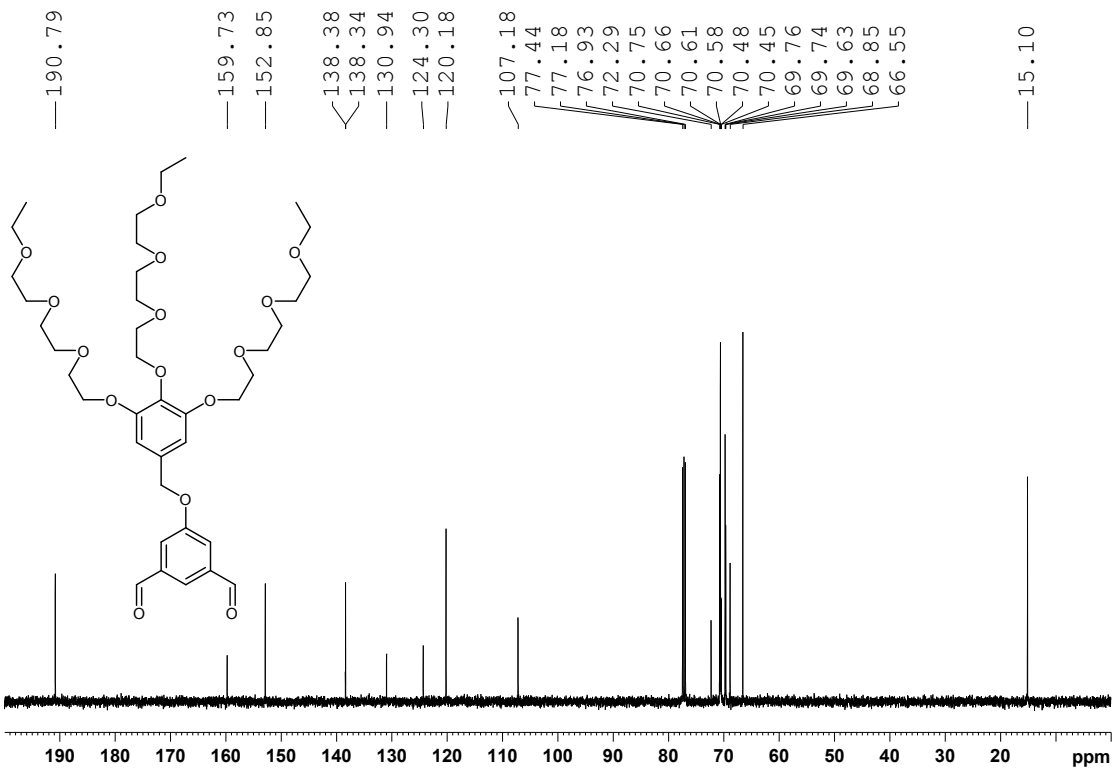


Fig. S16 ^{13}C NMR spectrum of **G1EtA** in $CDCl_3$.

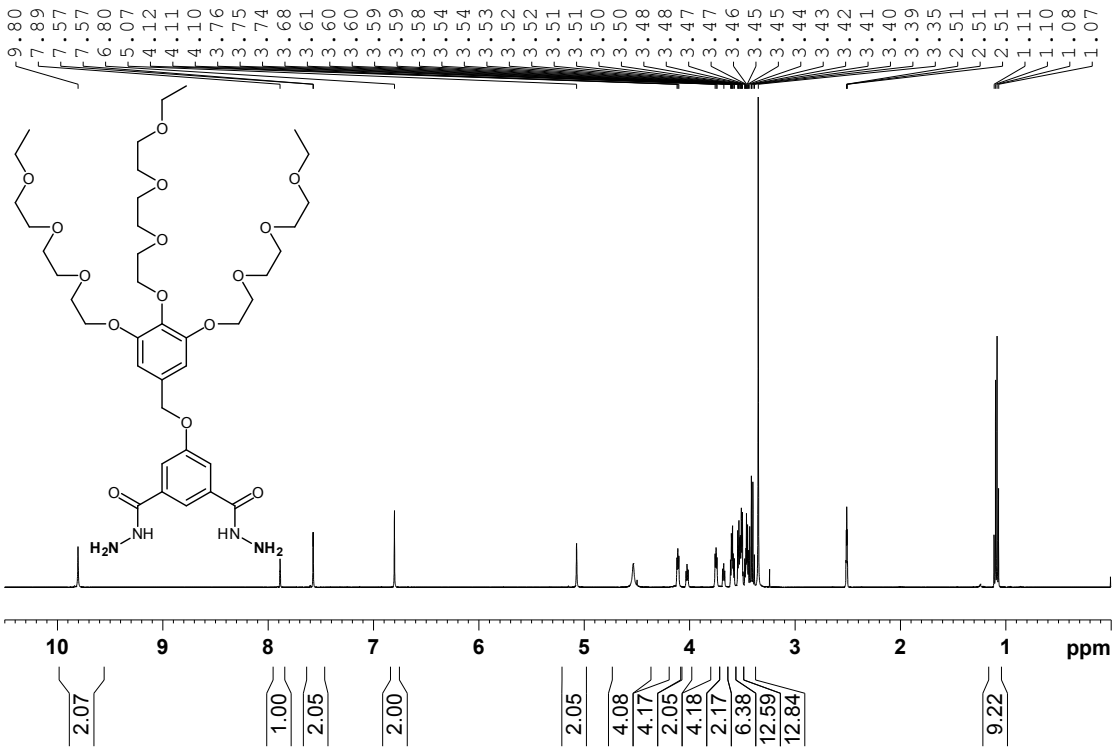


Fig. S17 ^{1}H NMR spectrum of **G1EtH** in DMSO-d_6.

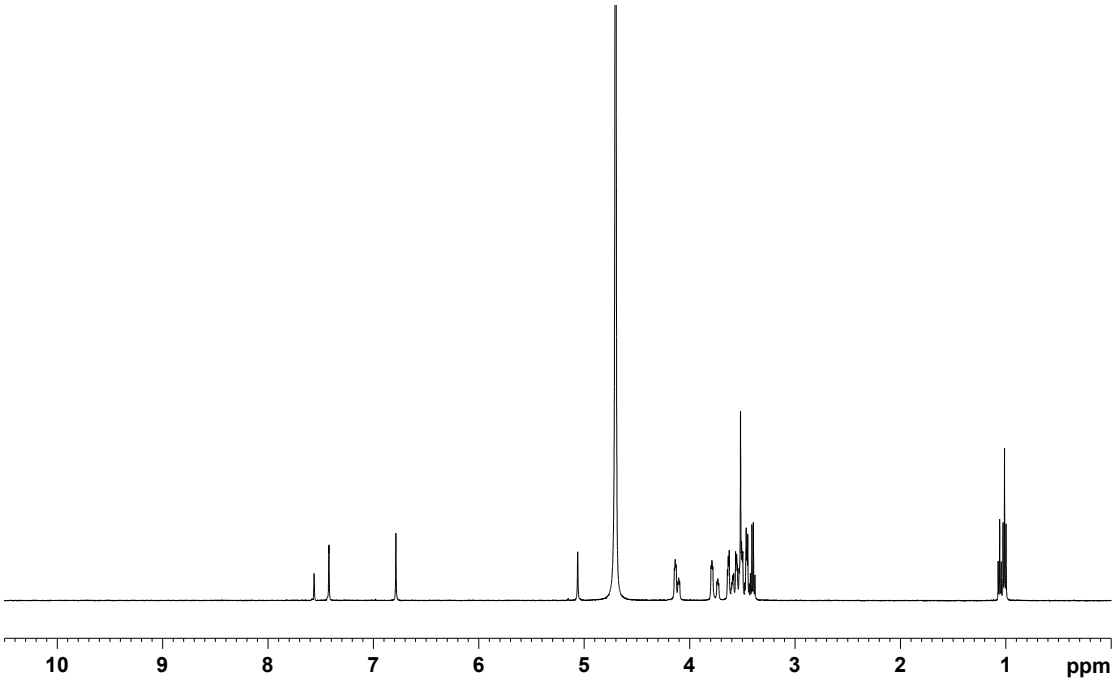


Fig. S18 ^{1}H NMR spectrum of **G1EtH** in D_2O.

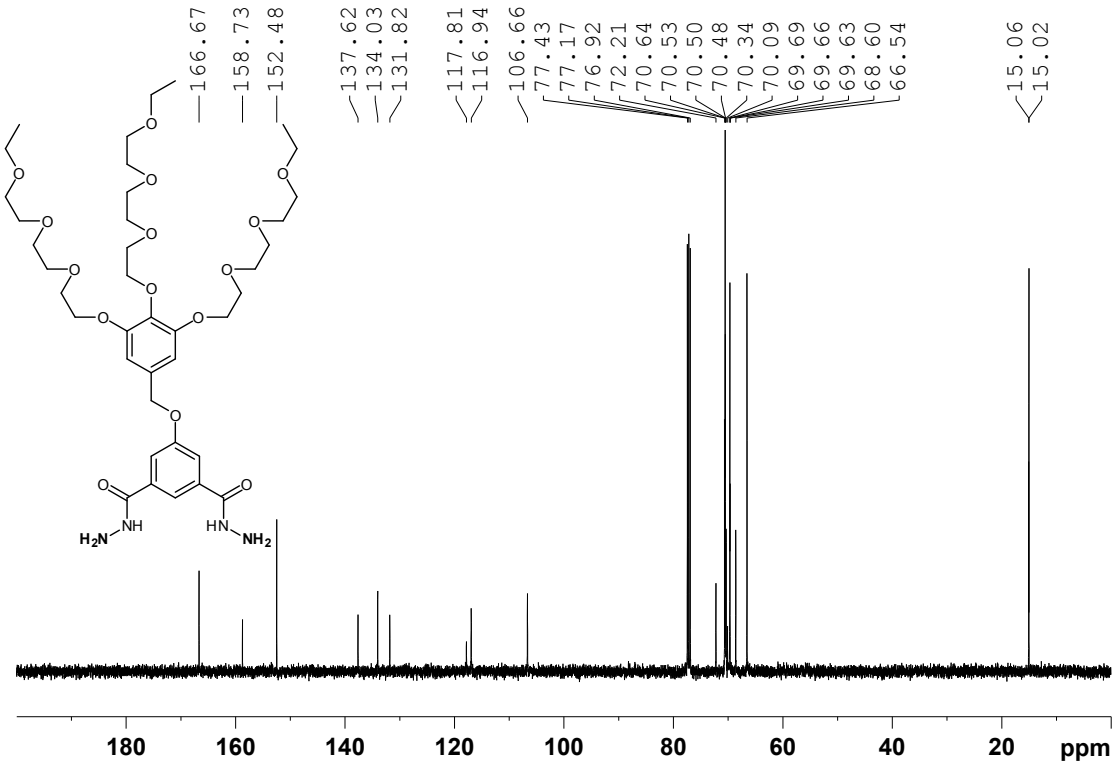


Fig. S19 ^{13}C NMR spectrum of **G1EtH** in $CDCl_3$.

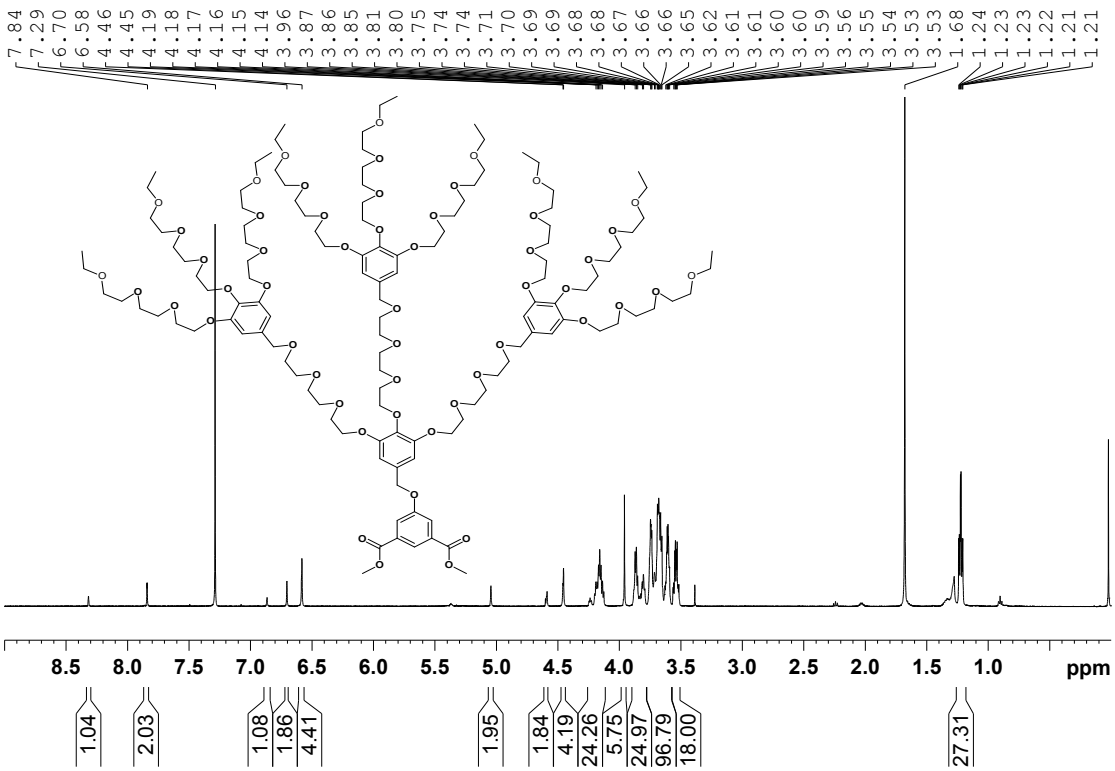


Fig. S20 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

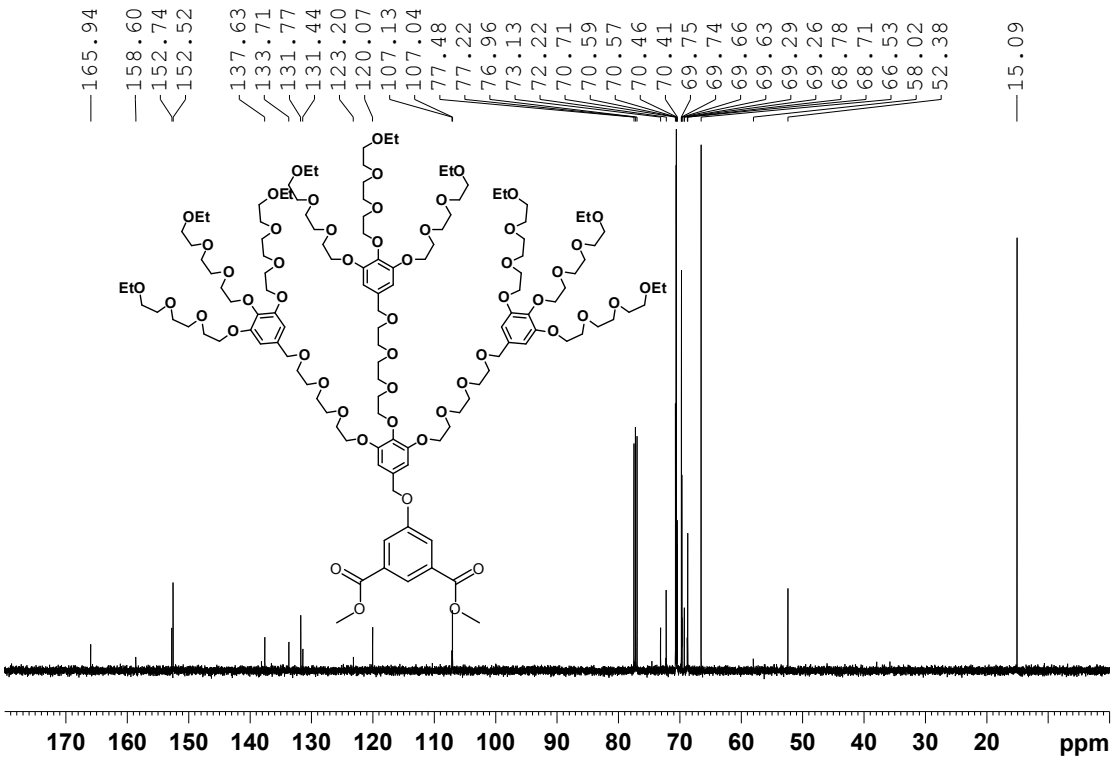


Fig. S21 ^{13}C NMR spectrum of **4a** in $CDCl_3$.

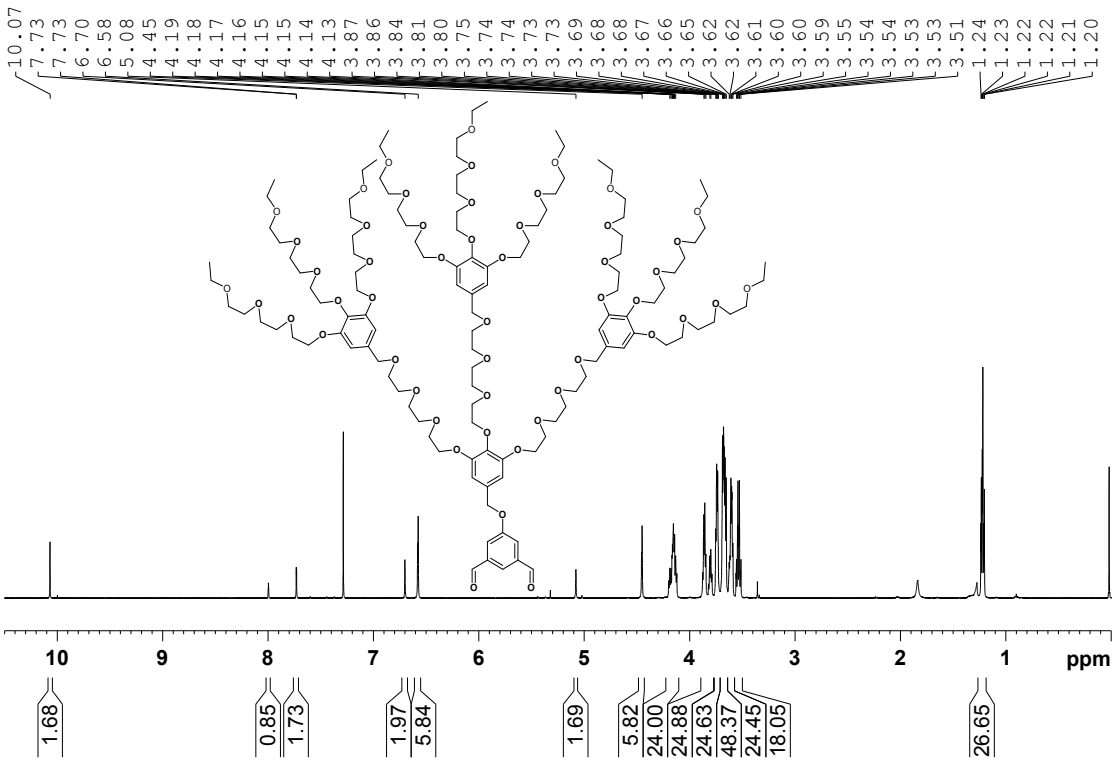


Fig. S22 ^{1}H NMR spectrum of **G2EtA** in $CDCl_3$.

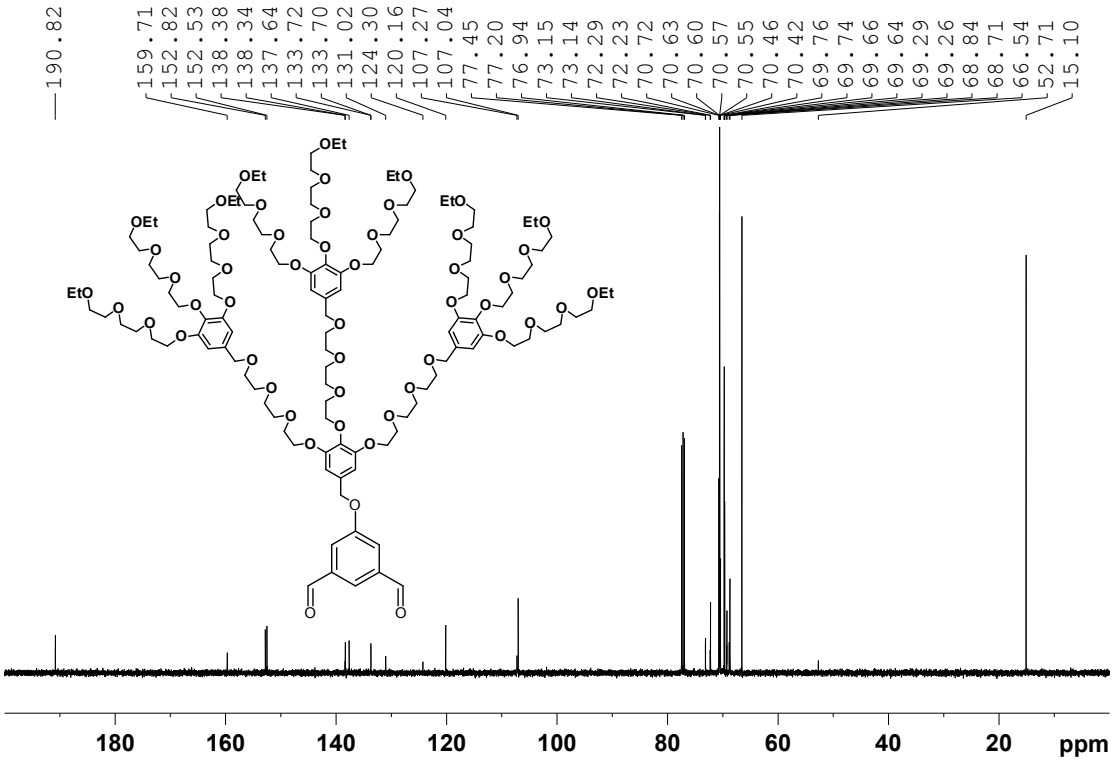


Fig. S23 ^{13}C NMR spectrum of **G2EtA** in $CDCl_3$.

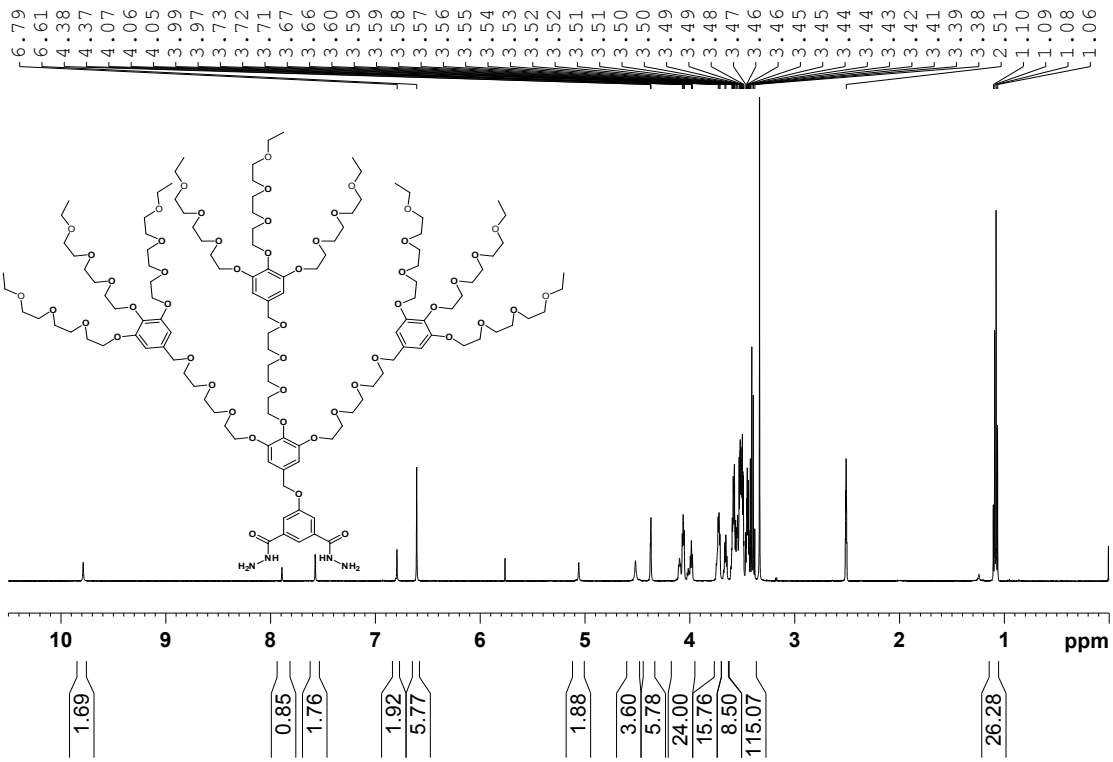


Fig. S24 ^{1}H NMR spectrum of **G2EtH** in DMSO-d_6.

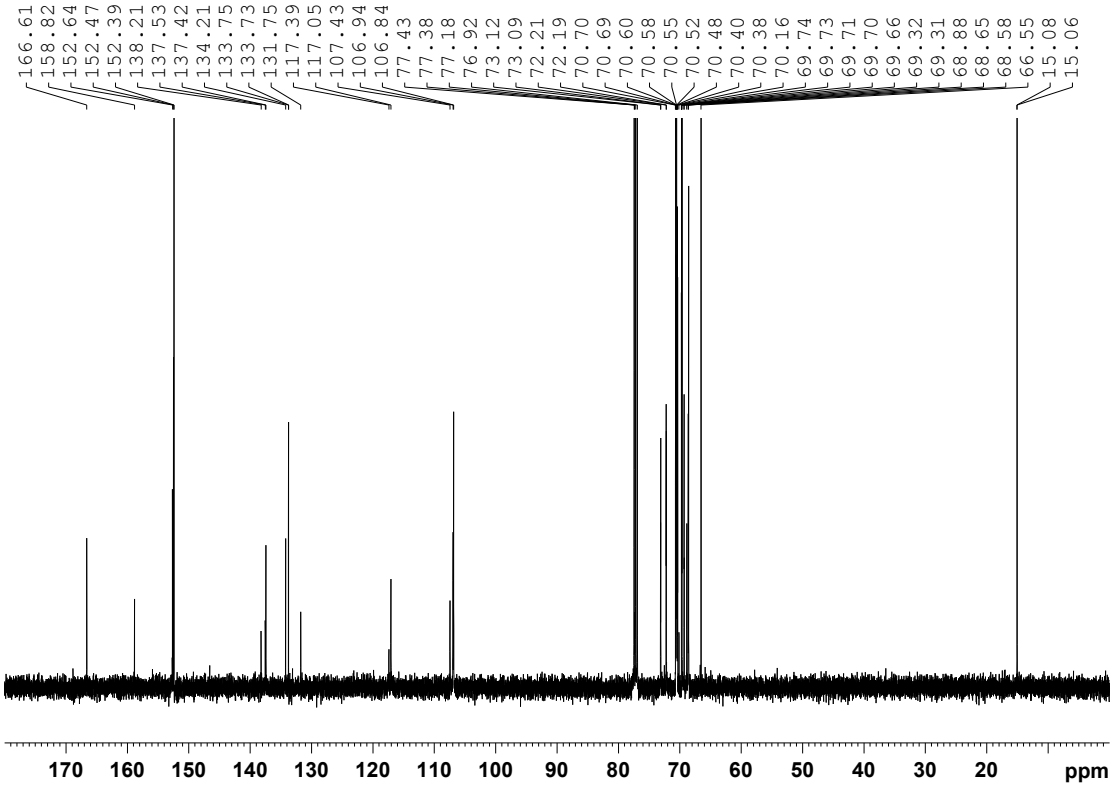


Fig. S25 ^{13}C NMR spectrum of **G2EtH** in $CDCl_3$.

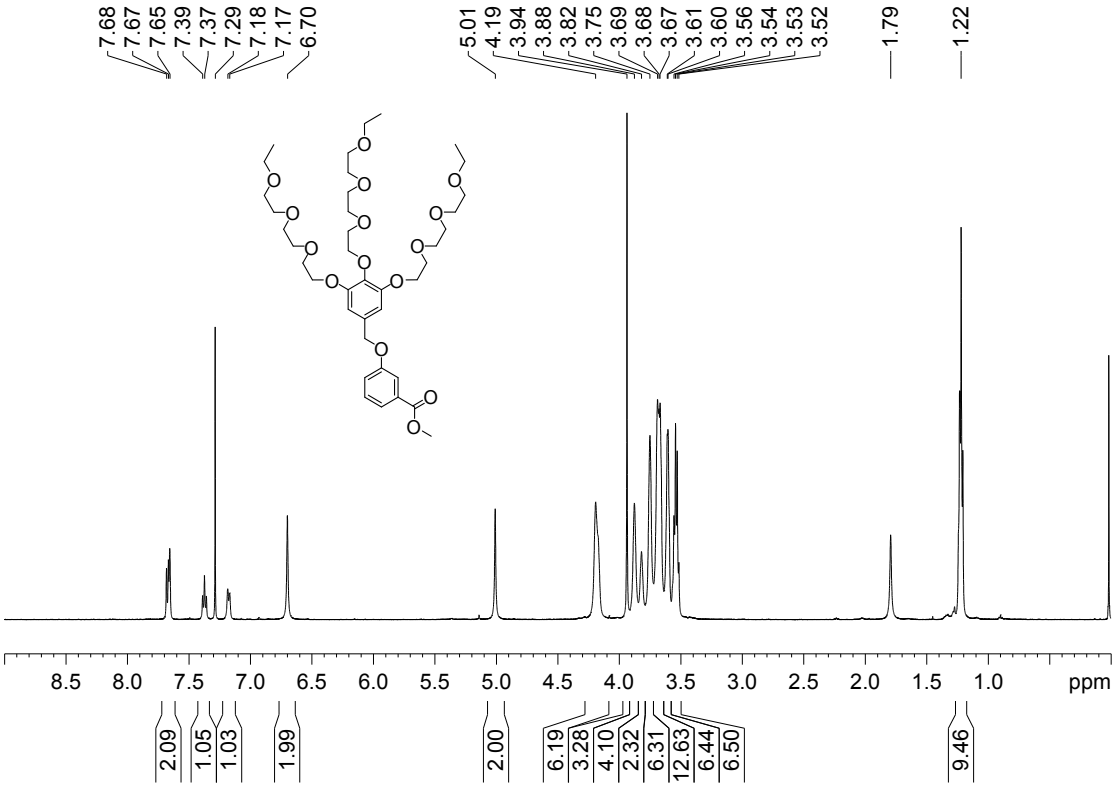


Fig. S26 ^{1}H NMR spectrum of **2e** in $CDCl_3$.

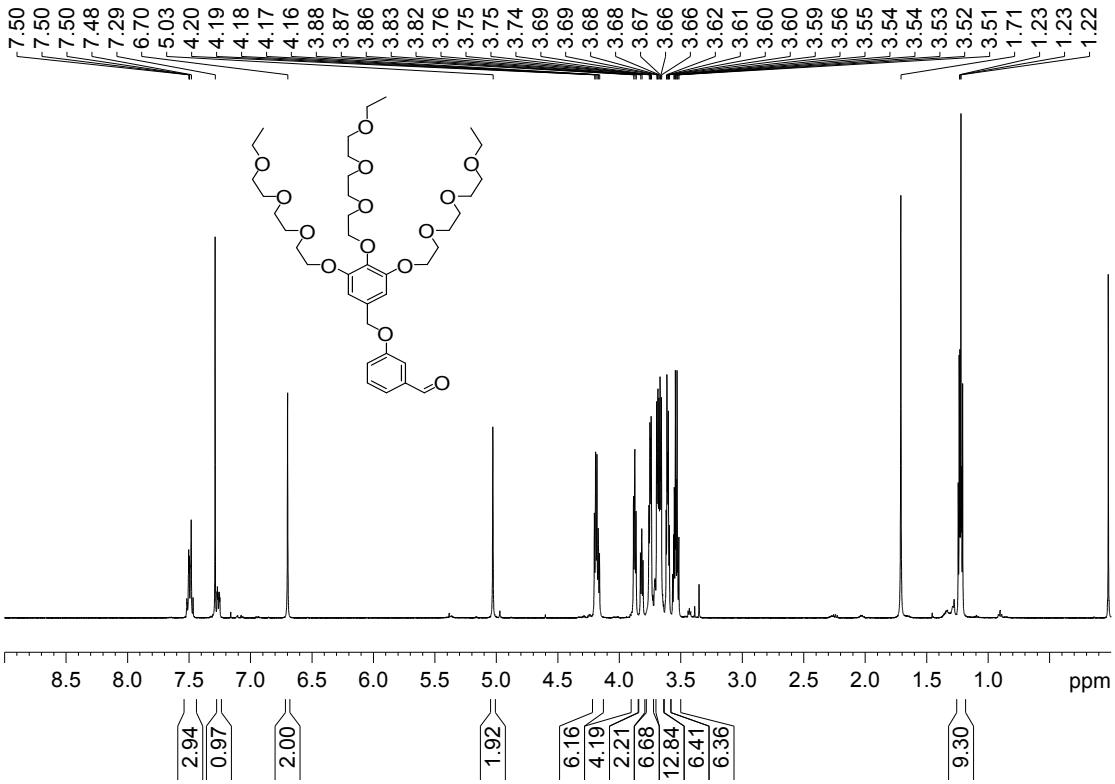


Fig. S27 ^{1}H NMR spectrum of **5** in $CDCl_3$.

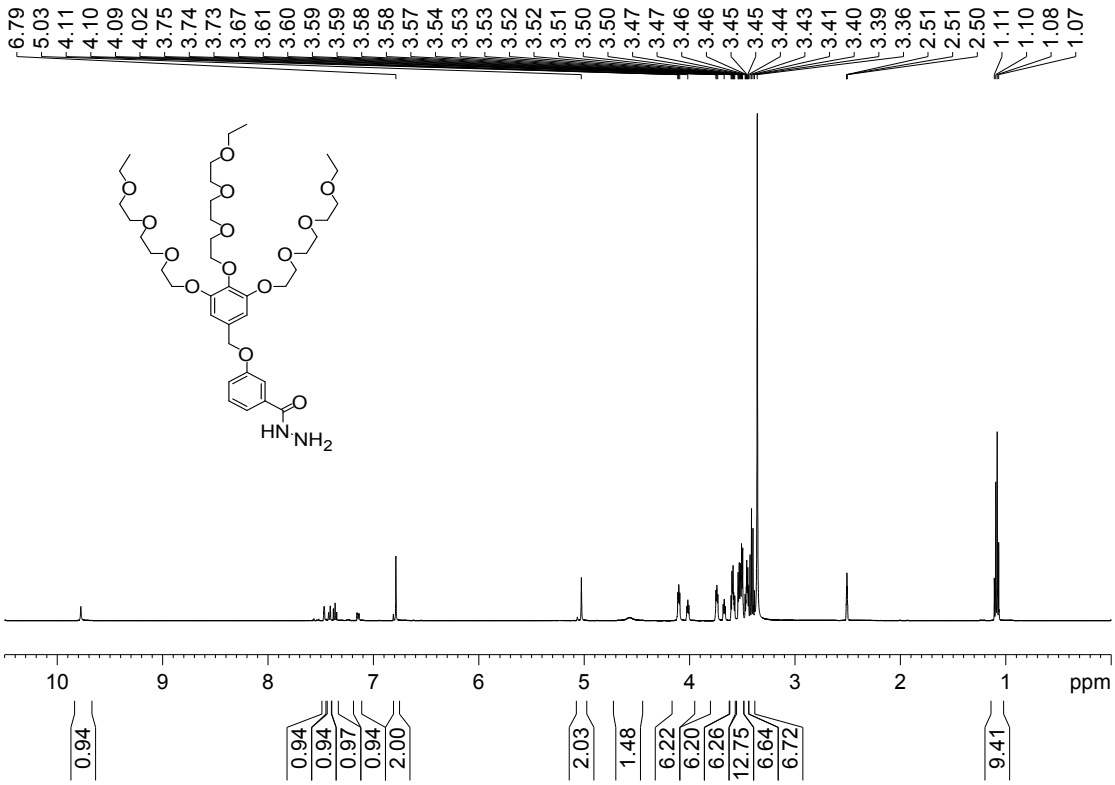


Fig. S28 ^{1}H NMR spectrum of **6** in DMSO-d_6.