Electronic Supplementary Material (ESI) for Polymer Chemistry.

‘One-pot’ sequential deprotection/functionalisation of linear-dendritic hybrid polymers using a xanthate mediated thiol/Michael addition.

Electronic Supporting Information

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Materials and Methods

Materials

2,2-Dimethoxypropane, potassium ethyl xanthogenate, butylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), benzyl acrylate, 2,2-bis(hydroxylmethyl)propanoic acid, oligo(ethylene glycol) methyl ether acrylate (M_n = 480 g/mol), butyl acrylate, *t*-butyl methacrylate, copper(I) chloride, isopropanol, 2,2`-bipyridine, dichloromethane (anhydrous) and p-toluenesulfonic acid monohydrate were purchased from Sigma Aldrich and were used without further purification. 2-(Dimethylamino)ethyl acrylate, 2-bromoacetic acid, pyridine (anhydrous), 4-dimethylaminopyridine (DMAP), hydroxyethyl acrylate and N,N′-dicyclohexylcarbodiimide (DCC) were purchased from Alfa Aesar and were used without further purification. para-Toluene sulfonyl ethanol (TSe) was purchased from Fluorochem. Dimethylaminopyridinium *p*-toluenesulfonate (DPTS) was prepared using literature procedures.[1] HPLC grade dichloromethane, acetone, hexane and ethyl acetate were supplied by Fisher Scientfic. Analytical TLC was performed on commercial Merck plates coated with silica gel. Flash chromatography was performed using a Grace Reveleris flash system with 80 g Silica Reveleris flash cartridges.

Analysis

Nuclear magnetic resonance (NMR) spectra were collected using a Bruker Avance 400 MHz. ^{1}H Spectra were recorded at 400 MHz and ^{13}C spectra were recorded at 100 MHz. $CDCl_3$ and CD_3OD containing tetramethylsilane (TMS) purchased from Goss Scientific were used as NMR solvents. Chemical shifts (δ) are reported in parts per million (ppm) and TMS was used as an internal standard for both ^{1}H and ^{13}C spectra. Electrospray mass spectrometry data was obtained using a MicroMass LCT mass spectrometer using electron ionisation and direct infusion syringe pump sampling. All samples were diluted with methanol. Elemental analyses were recorded in the Microanalytical Laboratory at the University of Liverpool. Size exclusion chromatography (SEC) was carried out using a Malvern Viscotek GPC Max connected to a Viscotek 270 Light Scattering detector, Viscometer and Refractive index (RI) triple detection system. HPLC grade tetrahydrofuran THF (Fisher) containing 2% triethylamine (Sigma Aldrich) was used as the eluent, with a flow rate of 1mL/min. SEC Columns were mixed bed columns supplied by Viscotek. The column oven was set at 35 °C. The obtained spectra were analyzed using Malvern OmiSec software calibrated by a universal calibration calculation relative to a narrow linear polystyrene standard (105k). Matrix-assisted laser desorption/ionization - time of flight mass spectrometry (MALDI-TOF) sample solutions were prepared with a 2 mg/ml concentration in THF. Matrix solution was prepared at a concentration of 10mg/ml in THF and a 1mg/ml NA counter ion solution was prepared. 5 µl of sample solution, 20 µl of matrix solution and 1.5 µl of counter ion was added to a eppendorf sample tube and homogenized. Solution was deposited on a stainless steel sample plate and the solvent allowed to evaporate. Spectrum acquisitions were conducted on a Bruker UltraFlex MALDI-TOF with SCOUT-MTP Ion Source (Bruker Daltonics, Bremen) equipped with a N_2-laser (337nm), a grid less ion source and reflector design. All spectra were acquired using a reflector-positive method with an acceleration voltage of 25 kV and a reflector voltage of 26,3 kV. The detector mass range was set to exclude everything under 1000 Da in order to exclude high intensity peaks from the lower mass range. A total of 1000 shots were performed per sample and the laser intensity was set to the lowest possible value for acquisition of high resolution spectra. The instrument was calibrated using SpheriCalTM calibrants purchased from Polymer Factory Sweden AB. The obtained spectra were analyzed with FlexAnalysis Bruker Daltonics, Bremen, version 2.2.

Synthesis

Isopropylidene-2,2-bis(methoxy)propionic Acid (2). This compound was prepared by the procedure reported by Ihre et al.[2] Spectroscopic data agreed with those reported.

Isopropylidene-2,2-bis(methoxy)propionic Anhydride (3). This compound was prepared from **2** according to the procedure reported by Malkoch et al.[3] Spectroscopic data agreed with those reported.

General esterification procedure for divergent dendron growth, Acet-G_1-TSe (5). Isopropylidene-2,2-bis(oxymethyl)propionic anhydride **3** (21.47 g, 65 mmol, 1.3 equiv.), para-toluene sulfonyl ethanol **4** (10.0 g, 50 mmol, 1 equiv.) and 4-dimethylaminopyridine (DMAP) (1.22 g, 10 mmol, 0.2 equiv.)

were dissolved in 20 mL (5 equiv./OH-group) of anhydrous pyridine and 60 mL (1:3 ratio of Pyridine:CH_2Cl_2 (v/v)) of anhydrous CH_2Cl_2 under a nitrogen atmosphere. After stirring at ambient temperature for 16 hours, the solution was monitored using TLC to confirm the loss of the starting alcohol. Following this, approximately 20 mL of water was added and stirred at ambient temperature for an additional 2 hours to quench the excess anhydride. The product was isolated by diluting the mixture with CH_2Cl_2 (500 mL) and washing with 1 M $NaHSO_4$ (3 x 250 mL), 1M $NaHCO_3$ (3 x 250 mL), and brine (1 x 250 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. Residual solvent was removed under high vacuum overnight. Purification by liquid chromatography on silica was not required for the isolation of **5**. Yield: 17.20 g, colourless viscous oil, (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 2.46 (s, 3H), 3.46 (t, *J* = 6.2 Hz, 2H), 3.56 (d, *J* = 11.9 Hz, 2H), 4.07 (d, *J* = 11.9 Hz, 2H), 4.46 (t, *J* = 6.2 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.23, 21.67, 22.14, 25.09, 41.84, 55.06, 57.98, 65.79, 98.11, 128.17, 130.12, 136.07, 145.22, 173.78. Calcd: $[MNa]^+$ ($C_{17}H_{24}NaO_6S$) = 379.12 Da. Found: ESI-MS: $[MNa]^+$ = 379.10 Da. Anal. Calcd for $C_{17}H_{24}O_6S$: C, 57.28; H, 6.79; S, 9.00. Found: C, 57.31; H, 6.72; S, 8.89.

General deprotection procedure for removal of acetonide protecting groups, OH_2-G_1-TSe (6). Eight spatulas of DOWEX 50W-X2 was added to a solution of Acet-G_1-TSe 5 (17.20 g, 48.3 mmol, 1 equiv.) in 400 mL of methanol. The mixture was stirred at 50 °C for 3 hours, and the deprotection followed using TLC until total disappearance of the starting material resulted. Once complete, the resin was filtered off and the solution evaporated to dryness. Residual solvent was removed under high vacuum overnight. Yield: 14.83 g, white crystals, (97%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.03 (s, 3H), 2.45 (s, 3H), 3.49-3.57 (dd, 4H), 3.59 (t, *J* = 5.9 Hz, 2H), 4.40 (t, *J* = 5.8 Hz, 2H), 7.47 (d, 2H), 7.83 (d, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.07, 21.61, 51.58, 55.90, 58.93, 65.66, 129.30, 131.22, 137.76, 146.71, 175.89. Calcd: $[MNa]^+$ ($C_{14}H_{20}NaO_6S$) = 339.10 Da. Found: ESI-MS: $[MNa]^+$ = 339.10 Da. Anal. Calcd for $C_{14}H_{20}O_6S$: C, 53.15; H, 6.37; S, 10.14. Found: C, 53.31; H, 6.34; S, 10.01.

$Acet_2$-G_2-TSe (7). Acet-G_1-TSe 6 (14.73 g, 46.56 mmol, 1 equiv.), DMAP (2.56 g, 20.95 mmol, 0.45 equiv.), **3** (46.15 g, 139.68 mmol, 3 equiv.), 38 mL pyridine and 114 mL CH_2Cl_2 were reacted according to the general esterification procedure, resulting in a viscous colourless oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (30:70) increasing the polarity to EtOAc:hexane (50:50). Yield: 26.35 g, colourless viscous oil, (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 6H), 1.17 (s, 3H), 1.34 (s, 6H), 1.42 (s, 6H), 2.46 (s, 3H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.62 (d, *J* = 11.9 Hz, 4H), 4.13 (d, *J* = 11.9 Hz, 4H), 4.17-4.23 (m, 4H), 4.45 (t, *J* = 6.2 Hz, 2H), 7.39 (d, 2H), 7.80 (d, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.37, 18.46, 21.60, 21.65, 25.63, 42.10, 46.69, 54.88, 58.28, 65.07, 65.98, 66.01, 98.13, 128.11, 130.15, 136.24, 145.24, 172.04, 173.50. Calcd: $[MNa]^+$ ($C_{30}H_{44}NaO_{12}S$) = 651.25 Da. Found: ESI-MS: $[MNa]^+$ = 651.20 Da. Anal. Calcd for $C_{30}H_{44}O_{12}S$: C, 57.31; H, 7.05; S, 5.10. Found: C, 57.36; H, 6.99; S, 4.95.

OH_4-G_2-TSe (8). $Acet_2$-G_2-TSe 7 (25.26 g, 40.18 mmol, 1 equiv), five spatulas of DOWEX 50W-X2 and 500 mL methanol was reacted according to the general deprotection procedure. Yield: 20.72 g, white crystals, (94%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.15 (s, 9H), 2.49 (s, 3H), 3.53-3.77 (m, 10H), 4.08 (d, *J* = 11.2 Hz, 2H), 4.14 (d, *J* = 11.2 Hz, 2H), 4.46 (t, *J* = 5.7 Hz, 2H), 7.50 (d, 2H), 7.85 (d, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.25, 17.81, 21.61, 47.61, 51.77, 55.77, 59.62, 65.80, 66.10, 129.26, 131.28, 137.85, 146.68, 173.67, 175.80. Calcd: $[MNa]^+$ ($C_{24}H_{36}NaO_{12}S$) = 571.18 Da. Found: ESI-MS: $[MNa]^+$ = 571.20 Da. Anal. Calcd for $C_{24}H_{36}O_{12}S$: C, 52.54; H, 6.61; S, 5.84. Found: C, 52.60; H, 6.54; S, 5.77.

$Acet_4$-G_3-TSe (9). OH_4-G_2-TSe 8 (20.64 g, 33 mmol, 1 equiv.), DMAP (2.44 g, 20 mmol, 0.62 equiv.), **3** (65.41 g, 198 mmol, 6 equiv.), 53 mL pyridine and 160 mL CH_2Cl_2 were reacted according to the general esterification procedure, resulting in a viscous colourless oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (30:70) increasing the polarity to EtOAc:hexane (60:40). Yield: 37.87 g, colourless viscous oil, (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 12H), 1.18 (s, 3H), 1.27 (s, 6H), 1.35 (s, 12H), 1.42 (s, 12H), 2.46 (s, 3H), 3.47 (t, *J* = 6.0 Hz, 2H), 3.62 (d, *J* = 12.1 Hz, 8H) 4.08-4.49 (m, 20H), 4.48 (t, *J* = 6.0 Hz, 2H), 7.39 (d, 2H), 7.82 (d, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.25, 17.68, 18.50, 21.67, 21.96, 25.30, 42.05, 46.53, 46.85, 54.74, 58.38, 64.90, 65.76, 65.93, 65.98, 98.11, 128.12, 130.14, 136.26, 145.18, 171.67, 171.83, 173.53. Calcd: $[MNa]^+$ ($C_{56}H_{84}NaO_{24}S$) = 1195.50 Da. Found: ESI-MS: $[MNa]^+$ = 1195.50 Da. Anal. Calcd for $C_{56}H_{84}O_{24}S$: C, 57.32; H, 7.22; S, 2.73. Found: C, 58.01; H, 7.20; S, 2.72.

OH_8-G_3-TSe (10). $Acet_4$-G_3-TSe 9 (37.60 g, 32.05 mmol, 1 equiv), five spatulas of DOWEX 50W-X2 and 500 mL methanol was reacted according to the general deprotection procedure. Yield: 31.56 g, white crystals, (97%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.17 (s, 15H), 1.30 (s, 3H), 2.50 (s, 3H), 3.56-3.73 (m, 18H), 4.14-4.38 (m, 12H), 4.50 (t, *J* = 5.5 Hz, 2H), 7.51 (d, 2H), 7.88 (d, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ = 13.70, 17.71, 18.23, 21.66, 47.74, 47.89, 51.80, 55.68, 59.82, 65.79, 66.15, 67.05, 129.29, 131.28, 137.88, 146.71, 173.33, 173.70, 175.89. Calcd: $[MNa]^+$ ($C_{44}H_{68}NaO_{24}S$) = 1035.37 Da. Found: ESI-MS: $[MNa]^+$ = 1035.40 Da. Anal. Calcd for $C_{44}H_{68}O_{24}S$: C, 52.17; H, 6.77; S, 3.17. Found: C, 52.16; H, 6.61; S, 3.15.

$Acet_8$-G_4-TSe (11). OH_8-G_3-TSe 10 (3.67 g, 3.62 mmol, 1 equiv.), DMAP (0.71 g, 5.80 mmol, 1.6 equiv.), **3** (14.35 g, 43.44 mmol, 12 equiv.), 12 mL pyridine and 24 mL CH_2Cl_2 were reacted according to the general esterification procedure, resulting in a viscous colourless oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (30:70) increasing the polarity to EtOAc:hexane (70:30). Yield: 6.67 g, colourless viscous oil, (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 24H), 1.20-1.30 (m, 21H), 1.34 (s, 24H), 1.41 (s, 24H), 2.46 (s, 3H), 3.47 (t, *J* = 6.0 Hz, 2H), 3.62 (d, *J* = 12.1 Hz, 16H), 4.14 (d, *J* = 12.1 Hz, 16H) 4.17-4.38 (m, 28H), 4.48 (t, *J* = 6.0 Hz, 2H), 7.40 (d, 2H), 7.82 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.13, 17.49, 17.68, 18.49, 21.66, 22.00, 25.26, 42.02, 46.56, 46.68, 46.81, 54.70, 58.38, 64.80, 65.53, 65.91, 65.96, 66.22, 98.08, 128.10, 130.13, 136.36, 145.14, 171.41, 171.54, 171.85, 173.48. Calcd: $[MNa]^+$ ($C_{108}H_{164}NaO_{48}S$) = 2284.0 Da, $[M+2Na]^{2+}$ ($C_{108}H_{164}Na_2O_{48}S$) = 1153.5 Da. Found: ESI-MS: $[MNa]^+$ = 2284.10 Da, $[M+2Na]^{2+}$ = 1153.5 Da. Found: MALDI-TOF MS: $[MNa]^+$ = 2283.81 Da. Anal. Calcd for $C_{108}H_{164}O_{48}S$: C, 57.33; H, 7.31; S, 1.42. Found: C, 57.27; H, 7.19; S, 1.35.

OH_{16}-G_4-TSe (12). $Acet_8$-G_4-TSe 11 (6.25 g, 2.76 mmol, 1 equiv), three spatulas of DOWEX 50W-X2 and 100 mL methanol was reacted according to the general deprotection procedure. Yield: 5.28 g, white crystals, (98%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.11 (s, 24H), 1.16 (s, 3H), 1.26 (s, 18H), 2.44 (s, 3H), 3.50-3.70 (m, 34H), 4.08-4.37 (m, 28H), 4.50 (t, 2H), 7.46 (d, 2H), 7.83 (d, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.34, 17.74, 18.08, 18.31, 21.71, 47.77, 47.91, 48.36, 51.79, 55.70, 59.86, 65.81, 66.14, 67.08, 67.41, 129.32, 131.31, 137.90, 146.70, 173.27, 173.78, 175.89. Calcd: $[MNa]^+$ ($C_{84}H_{132}NaO_{48}S$) = 1963.75 Da, $[M+2Na]^{2+}$ ($C_{84}H_{132}Na_2O_{48}S$) = 993.37 Da. Found: ESI-MS: $[MNa]^+$ = 1963.80 Da, $[M+2Na]^{2+}$ = 993.4 Da. Anal. Calcd for $C_{84}H_{132}O_{48}S$: C, 51.95; H, 6.85; S, 1.65. Found: C, 51.36; H, 6.80; S, 1.69.

2-((Ethoxycarbonothioyl)thio)acetic acid (13). This compound was prepared by the procedure reported by Auty et al.[4] Spectroscopic data agreed with those reported.

2-((Ethoxycarbonothioyl)thio)acetic anhydride (14). 2-((Ethoxycarbonothioyl)thio)acetic acid 13 (19.11 g, 106 mmol, 1 equiv.) was dissolved in 100 mL CH_2Cl_2. N,N′-Dicyclohexylcarbodiimide (DCC) (10.94 g, 53.01 mmol, 0.5 equiv.) was added to the mixture, and stirring continued at ambient temperature for 24 hrs. The reaction was monitored by ^{13}C NMR. Determination of reaction completion resulted by the appearance of the anhydride carbonyl carbon at 163 ppm and the disappearance of the acid carbonyl carbon at 174 ppm. The Dicyclohexylurea (DCU) byproduct was removed by filtration, and the solvent evaporated. Yield: 18.91 g, pale yellow solid, (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.1 Hz, 6H) 4.07 (s, 4H), 4.66 (q, *J* = 7.1 Hz, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.73, 38.59, 71.28, 163.11, 211.42

Xan_2-G_1-TSe (15). This compound was prepared from **13** according to the procedure reported by Auty et al.[4] Spectroscopic data agreed with those reported.

Xan_4-G_2-TSe (16). This compound was prepared from **13** according to the procedure reported by Auty et al.[4] Spectroscopic data agreed with those reported.

General procedure for functionalisation with Xanthate surface groups using anhydride chemistry, Xan_8-G_3-TSe (17). OH_8-G_3-TSe 10 (5.17 g, 5.10 mmol, 1 equiv.) and DMAP (1.0 g, 8.16 mmol, 1.6 equiv.) were dissolved in 25 mL of anhydrous pyridine. After cooling the mixture in an ice bath, 2-((Ethoxycarbonothioyl)thio)acetic anhydride 14 (18.17 g, 53.05 mmol, 10.4 equiv.) in 50 mL of anhydrous CH_2Cl_2 was added slowly under a nitrogen atmosphere. After stirring at ambient temperature for 16 hours, approximately 10 mL of water was added and stirred at ambient temperature for an additional 3 hours to quench the excess anhydride. The product was isolated by diluting the mixture with CH_2Cl_2 (250 mL) and washing with 1 M $NaHSO_4$ (3 x 150 mL), 1M $NaHCO_3$ (3 x 150 mL), and

brine (1 x 150 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness resulting in a viscous dark orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (15:85) increasing the polarity to EtOAc:hexane (50:50). Residual solvent was removed under high vacuum overnight. Yield: 8.95 g, orange viscous oil, (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.30 (m, 21H), 1.42 (t, *J* = 7.2 Hz, 24H), 2.47 (s, 3H), 3.47 (t, *J* = 5.8 Hz, 2H), 3.94 (s, 16H), 4.16-4.36 (m, 28H), 4.49 (t, *J* = 5.8 Hz, 2H), 4.63 (t, *J* = 7.2 Hz, 16H) 7.40 (d, 2H), 7.81 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.77, 17.28, 17.63, 17.86, 21.72, 37.73, 46.35, 46.51, 46.75, 54.73, 58.39, 65.46, 66.22, 70.89, 128.10, 130.18, 136.28, 145.21, 167.43, 171.48, 171.63, 171.69, 212.63. Calcd: $[MNa]^+$ ($C_{84}H_{116}NaO_{40}S_{17}$) = 2331.22 Da. Found: MALDI-TOF MS: $[MNa]^+$ = 2331.42 Da. Anal. Calcd for $C_{84}H_{116}O_{40}S_{17}$: C, 43.66; H, 5.06; S, 23.59. Found: C, 44.01; H, 5.04; S, 23.86.

Xan_{16}-G_4-TSe (18). OH_{16}-G_4-TSe 12 (3.81 g, 1.96 mmol, 1 equiv.), DMAP (1.56 g, 12.74 mmol, 6.5 equiv.), 14 (16.13 g, 47.10 mmol, 24 equiv.), 13 mL pyridine and 40 mL CH_2Cl_2 were reacted according to the general xanthate anhydride functionalisation procedure, resulting in a viscous dark orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (20:80) increasing the polarity to EtOAc:hexane (60:40). Yield: 6.69 g, dark orange viscous oil, (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21-1.34 (m, 45H), 1.42 (t, *J* = 7.0 Hz, 48H), 2.47 (s, 3H), 3.48 (t, *J* = 5.2 Hz, 2H) 3.94 (s, 32H), 4.27 (m, 60H), 4.49 (t, *J* = 5.2 Hz, 2H), 4.63 (t, *J* = 7.0 Hz, 32H), 7.41 (d, 2H), 7.80 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.78, 17.22, 17.53, 17.64, 17.87, 21.73, 37.73 46.32, 46.66, 46.72, 54.68, 58.40, 65.28, 65.80, 66.19, 66.19, 66.50, 70.90, 128.07, 130.19, 136.39, 145.18, 167.43, 171.40, 171.51, 171.67, 212.63. Calcd: $[MNa]^+$ ($C_{164}H_{228}NaO_{80}S_{33}$) = 4555.45 Da. Found: MALDI-TOF MS: $[MNa]^+$ = 4555.85 Da. Anal. Calcd for $C_{164}H_{228}O_{80}S_{33}$: C, 43.41; H, 5.06; S, 23.32. Found: C, 43.84; H, 5.07; S, 23.26.

Xan_2-G_1-COOH (19). This compound was prepared from **15** according to the procedure reported by Auty et al.[3] Spectroscopic data agreed with those reported.

Xan_4-G_2-COOH (20). This compound was prepared from **16** according to the procedure reported by Auty et al.[3] Spectroscopic data agreed with those reported.

General procedure for deprotection of para-toluene sulfonyl ester (TSe) Xan_8-G_3-COOH (21). Xan_8-G_3-TSe 17 (7.21 g, 3.12 mmol, 1 equiv.) was dissolved in 70 mL of anhydrous CH_2Cl_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.61 mL, 4.06 mmol, 1.3 equiv.) added dropwise to the mixture. The reaction was left stirring under a nitrogen atmosphere at ambient temperature for 16 hours and monitored until completion by TLC (60:40 hexane:ethyl acetate). The product was isolated by diluting the mixture with CH_2Cl_2 (100 mL) and washing with 1 M $NaHSO_4$ (2 x 100 mL) and brine (1 x 100 mL. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The product was precipitated twice into hexanes:ethyl acetate (9:1). Residual solvent was removed under high vacuum overnight. Yield: 4.97 g, orange viscous oil, (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 12H), 1.29 (s, 6H), 1.35 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 24H), 3.95 (s, 16H), 4.28 (m, 28H), 4.64 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.77, 17.48, 17.72, 17.90, 37.50, 46.20, 46.33, 46.80, 65.58, 66.26, 66.72, 70.92, 167.69, 171.49, 171.67, 173.18, 212.61. Calcd: $[MNa]^+$ ($C_{75}H_{106}NaO_{38}S_{16}$) = 2149.18 Da. Found: MALDI TOF MS: $[MNa]^+$ = 2149.10 Da. Anal. Calcd for $C_{75}H_{106}O_{38}S_{16}$: C, 42.32; H, 5.02; S, 24.10. Found: C, 42.69; H, 5.02; S, 23.86.

Xan_{16}-G_4-COOH (22). Xan_{16}-G_4-TSe 18 (6.44 g, 1.42 mmol, 1 equiv.), DBU (0.277mL, 1.85 mmol, 1.3 equiv.) and 50 mL CH_2Cl_2 were reacted according to the general procedure for deprotection of para-toluene sulfonyl ester (TSe) resulting in a viscous dark orange oil that was precipitated twice into hexanes:ethyl acetate (9:1). Yield: 5.25 g, orange viscous oil, (85%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.36 (m, 45H), 1.42 (t, *J* = 7.20 Hz, 48H), 3.95 (s, 32H), 4.11-4.44 (m, 60H), 4.63 (t, *J* = 7.20 Hz, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.79, 17.48, 17.59, 17.65, 17.87, 37.74, 46.30, 46.35, 46.67, 46.72, 65.43, 65.92, 66.21, 66.82, 66.50, 70.92, 167.53, 171.39, 171.45, 171.85, 172.98, 212.63. Calcd: $[MK]^+$ ($C_{155}H_{218}KO_{78}S_{32}$) = 4389.38 Da. Found: MALDI-TOF MS: $[MK]^+$ = 4393.83 Da. Anal. Calcd for $C_{155}H_{218}O_{78}S_{32}$: C, 42.74; H, 5.04; S, 23.56. Found: C, 42.99; H, 5.01; S, 23.38.

2-Hydroxyethyl 2-bromoisobutyrate (23) – Ethylene glycol (272 mL, 4.85 mol, 50 equiv.) and triethylamine (28 mL, 200 mmol, 2 equiv.) were dissolved in 100 mL of dry tetrahydrofuran. Using an ice bath to cool the vessel, α-Bromoisobutyryl bromide (12 mL, 97.1 mmol, 1 equiv.) was added slowly, dropwise, to the mixture over 30 minutes. The reaction was left stirring under a nitrogen atmosphere at ambient temperature for 16 hours. The product was isolated by pouring the crude mixture

into distilled water (800 mL) and extracting the aqueous phase with CH_2Cl_2 (6 x 100 mL). The combined organic layers were washed with 1M HCl (pH 4) (2 x 300mL), dried over $MgSO_4$ and evaporated to dryness. Residual solvent was removed under high vacuum overnight. Yield: 15.64 g, pale yellow oil, (76%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 6H), 3.88 (m, *J* = 4.7 Hz, 2H), 4.32 (m, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.70, 55.79, 60.89, 67.41, 171.94. Calcd: $[MNH_4]^+$ ($C_6H_{15}BrNO_3$) = 228.02 Da. Found: CI MS: $[MNH_4]^+$ = 228.02 Da. Anal. Calcd for $C_6H_{11}BrO_3$: C, 34.14; H, 5.25. Found: C, 34.63; H, 5.30.

General procedure for focal point modification to α-bromoisobutyrate moiety Xan_2-G_1-BiB (24). Xan_2-G_1-COOH 19 (8.25 g, 18 mmol, 1 equiv.), 2-Hydroxyethyl 2-bromo-2-methylpropanoate 23 (5.70 g, 27 mmol, 1.5 equiv.), and DPTS (1.06 g, 3.6 mmol, 0.2 equiv.) were dissolved in 80 mL of anhydrous CH_2Cl_2 under a nitrogen atmosphere. N,N′′-Dicyclohexylcarbodiimide (DCC) (7.43 g, 36 mmol, 2 equiv.) was added to the mixture in a small volume of CH_2Cl_2, and stirring continued at ambient temperature for 16 hrs. The product was isolated by diluting the mixture with CH_2Cl_2 (150 mL), washed with H_2O (2 x 100 mL) and brine (1 x 100 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness resulting in a viscous dark orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (10:90) increasing the polarity to EtOAc:hexane (30:70). Residual solvent was removed under high vacuum overnight. Yield: 6.39 g, yellow viscous oil, (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 6H), 1.94 (s, 6H), 3.93 (s, 4H), 4.28 (d, *J* = 11.1 Hz, 2H), 4.35 (d, *J* = 11.1 Hz, 2H), 4.40 (s, 4H), 4.64 (q, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.76, 17.86, 30.66, 37.75, 46.26, 55.32, 62.72, 63.34, 66.28, 70.90, 167.42, 171.41, 172.06, 212.58. Calcd: $[MNa]^+$ ($C_{21}H_{31}BrNaO_{10}S_4$) = 673.0 Da. Found: ESI-MS: $[MNa]^+$ = 673.0 Da. Anal. Calcd for $C_{21}H_{31}BrO_{10}S_4$: C, 38.71; H, 4.80; S, 19.68. Found: C, 39.99; H, 4.86; S, 19.37.

Xan_4-G_2-BiB (25) – Xan_4-G_2-COOH 20 (6.52 g, 6.42 mmol, 1 equiv.), 2-Hydroxyethyl 2-bromo-2-methylpropanoate 23 (2.03 g, 9.63 mmol, 1.5 equiv.), DPTS (0.38 g, 1.28 mmol, 0.2 equiv.), DCC (2.65 g, 12.84 mmol, 2 equiv.) in 60 mL of anhydrous CH_2Cl_2 were reacted according to the general procedure for focal point modification resulting in a viscous orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (20:80) increasing the polarity to EtOAc:hexane (60:40). Yield: 4.53 g, yellow viscous oil, (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 6H), 1.29 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 12H), 1.94 (s, 6H), 3.96 (s, 8H), 4.19-4.36 (m, 12H), 4.36-4.49 (m, 4H), 4.64 (q, *J* = 7.1 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.75, 17.65, 17.87, 30.67, 37.73, 46.36, 46.67, 55.38, 62.90, 63.25, 65.66, 66.25, 70.88, 167.43, 171.37, 171.66, 171.86, 212.62. Calcd: $[MNa]^+$ ($C_{41}H_{59}BrNaO_{12}S_8$) = 1229.04 Da. Found: ESI-MS: $[MNa]^+$ = 1229.17 Da. Anal. Calcd for $C_{41}H_{59}BrO_{20}S_8$: C, 40.75; H, 4.92; S, 21.23. Found: C, 43.22; H, 5.20; S, 21.13.

Xan_8-G_3-BiB (26) – Xan_8-G_3-COOH 21 (4.670 g, 2.21 mmol, 1 equiv.), 2-Hydroxyethyl 2-bromo-2-methylpropanoate 23 (0.466 g, 2.21 mmol, 1.0 equiv.), DPTS (2.43 g, 2.43 mmol, 1.1 equiv.), DCC (0.501 g, 2.43 mmol, 1.1 equiv.) in 30 mL of anhydrous CH_2Cl_2 were reacted according to the general procedure for focal point modification resulting in a viscous orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (10:90) increasing the polarity to EtOAc:hexane (50:50). Yield: 2.91 g, yellow viscous oil, (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22-1.34 (m, 21H), 1.42 (t, *J* = 7.2 Hz, 24H), 1.94 (s, 6H), 3.95 (s, 16H), 4.17-4.51 (m, 32H), 4.63 (t, *J* = 7.2 Hz, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.76, 17.52, 17.63, 17.86, 30.64, 46.31, 46.57, 46.73, 55.48, 62.95, 63.22, 65.38, 66.18, 70.89, 167.42, 171.34, 171.44, 171.66, 171.76, 212.64. Calcd: $[MNa]^+$ ($C_{81}H_{115}NaO_{40}S_{16}$) = 2341.16 Da. Found: MALDI TOF MS: $[MNa]^+$ = 2341.36 Da. Anal. Calcd for $C_{81}H_{115}BrO_{40}S_{16}$: C, 41.90; H, 4.99; S, 22.10. Found: C, 42.75; H, 5.02; S, 22.29.

Xan_{16}-G_4-BiB (27) – Xan_{16}-G_4-COOH 22 (2.073 g, 0.476 mmol, 1 equiv.), 2-Hydroxyethyl 2-bromo-2-methylpropanoate 23 (0.10 g, 0.476 mmol, 1.0 equiv.), DPTS (0.154 g, 0.524 mmol, 1.1 equiv.), DCC (0.108 g, 0.524 mmol, 1.1 equiv.) in 10 mL of anhydrous CH_2Cl_2 were reacted according to the general procedure for focal point modification resulting in a viscous orange oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (10:90) increasing the polarity to EtOAc:hexane (50:50). Yield: 1.46 g, orange viscous oil, (67%). δ = 1.22-1.34 (m, 45H), 1.42 (t, *J* = 7.20 Hz, 48H), 1.94 (6H, s), 3.95 (s, 32H), 4.17-4.47 (m, 64H), 4.63 (t, *J* = 7.20 Hz, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.78, 17.54, 17.64, 17.88, 30.66, 37.73, 46.30, 46.62, 46.66, 46.71, 60.41, 65.25, 65.76, 66.17, 66.47, 70.90, 167.42, 171.18, 171.28, 171.35, 171.47, 171.66, 212.63. Calcd: $[MNa]^+$ ($C_{161}H_{227}BrNaO_{80}S_{32}$) = 4565.38 Da. Found: MALDI-TOF MS: $[M+Na]^+$ = 4567.19 Da.

Morpholino propanyl acrylate (39) – Morpholio propan-2-ol (5 g, 34.44 mmol, 1 equiv.), triethylamine (6.24 mL, 44.77 mmol, 1.3 equiv.) and a catalytic amount of DMAP were dissolved in 40 mL CH_2Cl_2. After cooling the mixture in an ice bath, acryloyl chloride (3.64 mL, 44.77 mmol, 1.3 equiv.) was added slowly, dropwise, to the mixture using a dropping funnel. The mixture turned orange on addition of acryloyl chloride. The ice bath was removed after 1 hour, and the mixture was left stirring at ambient temperature for 16 hours. After filtration to remove the salts, the product was isolated by diluting the mixture with CH_2Cl_2 (100mL) and washing with 1M $NaHCO_3$ (3 x 100mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. Yield: 5.10 g, dark orange oil, (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, *J* = 6.1 Hz, 1H), 2.32-2.59 (m, 6H), 3.66 (t, *J* = 4.7 Hz, 4H), 5.16 (m, 1H), 5.80 (dd, *J* = 1.6 Hz, 10.4 Hz, 1H), 6.10 (dd, *J* = 10.4 Hz, 17.2 Hz, 1H), 6.38 (dd, *J* = 1.6 Hz, 17.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.46, 54.05, 63.37, 67.03, 68.00, 128.93, 130.42, 165.71.

Model atom transfer radical polymerisation (ATRP) of tertiary butyl methacrylate (tBuMA) using ethyl 2-bromoisobutyrate (EBiB) in the presence of 13 – Target DP_n = 50 monomer units for the primary chains, EBiB (0.028 g, 0.141 mmol, 1 equiv.), tBuMA (1 g, 7.03 mmol, 50 equiv.), bpy (0.044 g, 0.282 mmol, 2 equiv.), 13 (0.025 g, 0.141 mmol, 1 equiv.) and 2 drops of anisole were placed into a 10 mL round-bottomed flask. IPA/H_2O (92.5/7.5 v/v) was added to the flask (50% wt% based on tBuMA) and the solution was stirred and deoxygenated using a nitrogen purge for 10 minutes. Cu(I)Cl (0.014 g, 0.141 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 40 °C. The reaction was terminated when conversion reached >99%, indicated by ^{1}H NMR after 16 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumina column to remove the catalytic system, and precipitated twice into cold (-78 °C) pet ether (30-40). After drying the precipitated sample overnight under high vacuum to remove residual solvents, the polymer was obtained as a white solid.

A**tom transfer radical polymerisation (ATRP) of tertiary butyl methacrylate (*t*-BuMA) in IPA/H_2O with Xan_2-G_1-BiB (24) or Xan_4-G_2-BiB (25) xanthate initiators –** In a typical synthesis, targeting DP_n = 50 monomer units for the primary chains, 24 (0.4581 g, 0.703 mmol, 1 equiv.), tBuMA (5 g, 35.16 mmol, 50 equiv.), bpy (0.220 g, 1.406 mmol, 2 equiv.) and 2 drops of anisole were placed into a 50 mL round-bottomed flask. IPA/H_2O (92.5/7.5 v/v) was added to the flask (50 wt% based on tBuMA) and the solution was stirred and deoxygenated using a nitrogen purge for 10 minutes. Cu(I)Cl (0.070 g, 0.703 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 40 °C. The reaction was terminated when conversion reached >90%, indicated by ^{1}H NMR after 8 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumni column to remove the catalytic system, and precipitated twice into cold (-78 °C) hexane. After drying the precipitated sample overnight under high vacuum to remove residual solvents, the polymer was obtained as a white solid.

A**tom transfer radical polymerisation (ATRP) of tertiary butyl methacrylate (tBuMA) in acetone with 24, 25, 26, or 27 xanthate initiators -** In a typical synthesis, targeting DP_n = 50 monomer units for the primary chains, 27 (0.653 g, 0.2812 mmol, 1 equiv.), tBuMA (2 g, 14.06 mmol, 50 equiv.), bpy (0.088 g, 0.5624 mmol, 2 equiv.) and 2 drops of anisole were placed into a 50 mL round-bottomed flask. Acetone was added to the flask (50% wt% based on ^{t}BuMA) (i.e. 2 g ^{t}BuMA = 2 g (2.53 mL) acetone) and the solution was stirred and deoxygenated using a nitrogen purge for 10 minutes. Cu(I)Cl (0.070 g, 0.703 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 50 °C. Care was taken to ensure that the vessel was sealed thoroughly to ensure the acetone did not evaporate. The reaction was terminated when conversion reached >94%, indicated by ^{1}H NMR after 28 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumni column to remove the catalytic system and precipitated twice into cold (-78 °C) hexane. After drying the precipitated sample overnight under high vacuum to remove residual solvents, the polymer was obtained as a white solid.

General Procedure for one-pot deprotection and Michael addition of the linear dendritic hybrids – In a typical synthesis, the xanthate functional linear dendritic hybrids (0.1 g) was dissolved in 1 mL of anhydrous THF and deoxygenated using a nitrogen purge for 10 minutes. *n*-Butyl amine (2.5 molar excess relative to each xanthate group on the hybrid) was added and the solution stirred at ambient temperature for 1.5 hours. The functional acrylate (5.0 molar excess relative to each thiol) was added, deoxygenated using a nitrogen purge for 2 minutes, and left stirring overnight at ambient temperature. The functionalised polymer hybrid was obtained by precipitation of the mixture into cold (-78 °C)

hexane. Precipitated samples were dried overnight by high vacuum and freeze dried to remove residual solvents.

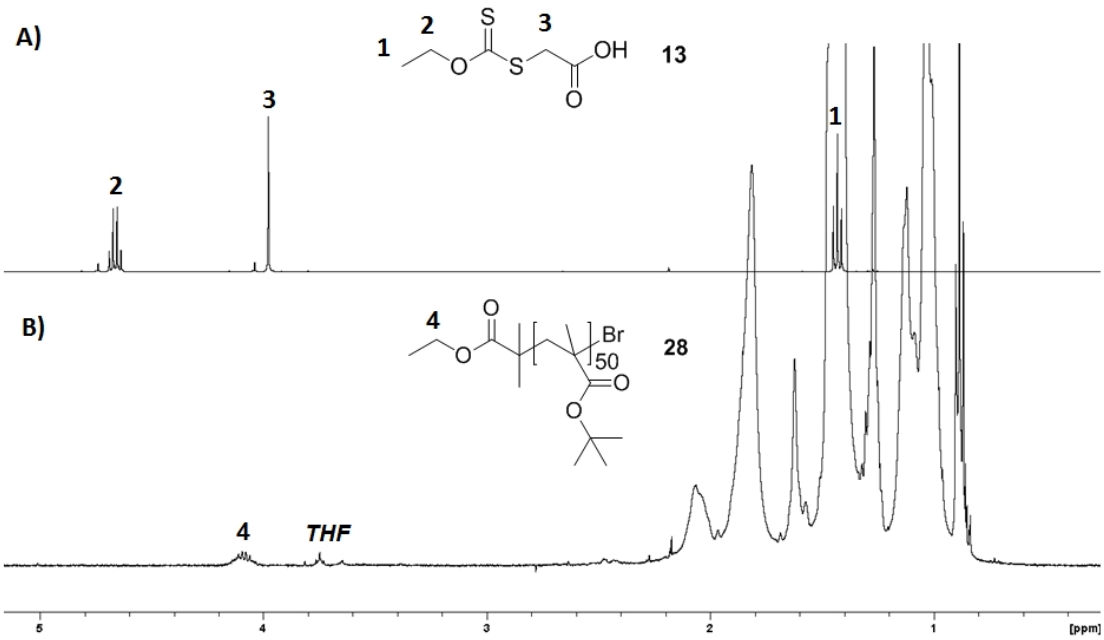

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) overlay of A) Xanthate moiety, **13**; B) Polymer, **28**

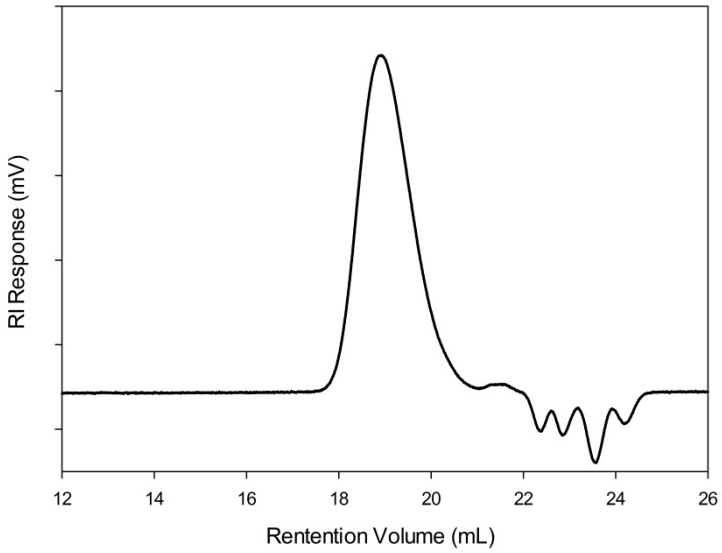

Figure S2. Triple detection size exclusion chromatography (Refractive index) of polymer **28** (THF eluent).

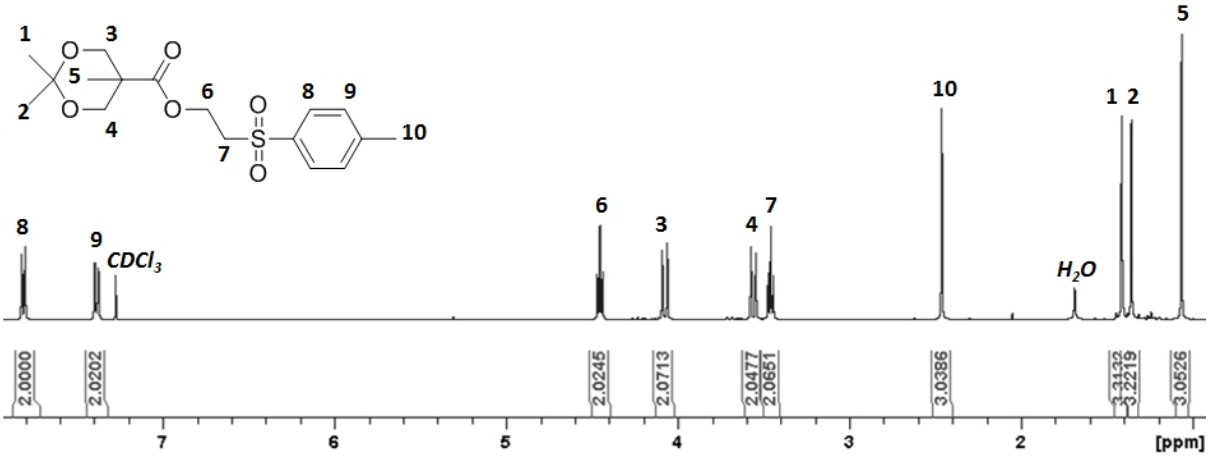

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of **Acet-G_1-TSe, 5**

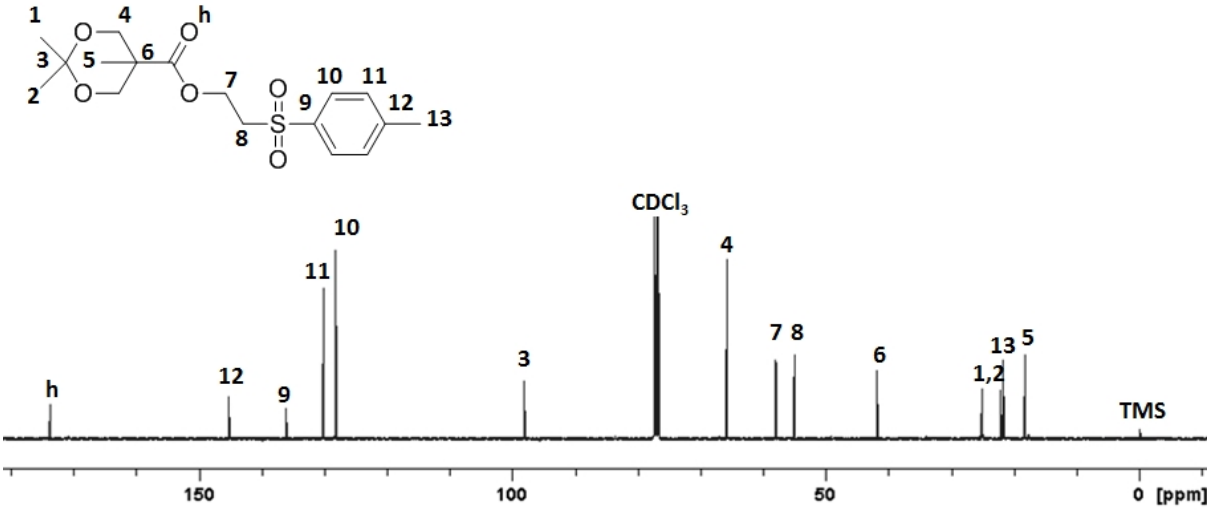

Figure S4. ^{13}C NMR (400 MHz, $CDCl_3$) of **Acet-G_1-TSe, 5**

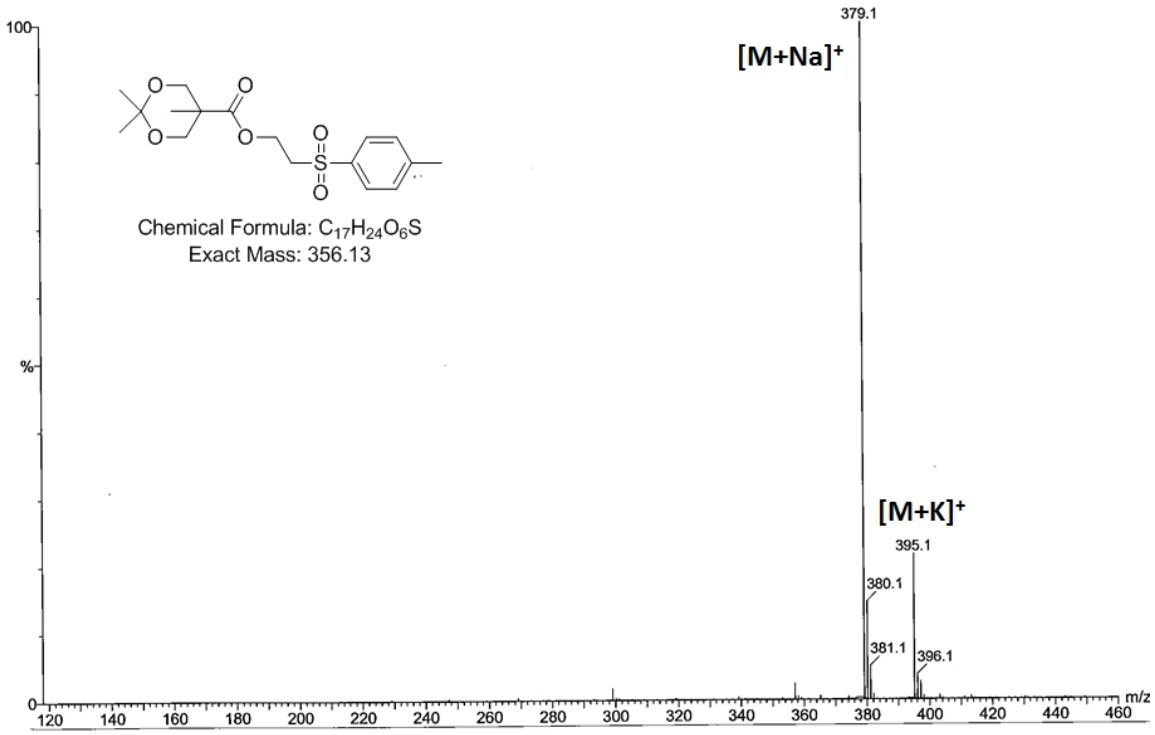

Figure S5. ESI-MS (MeOH) of **Acet-G_1-TSe, 5**

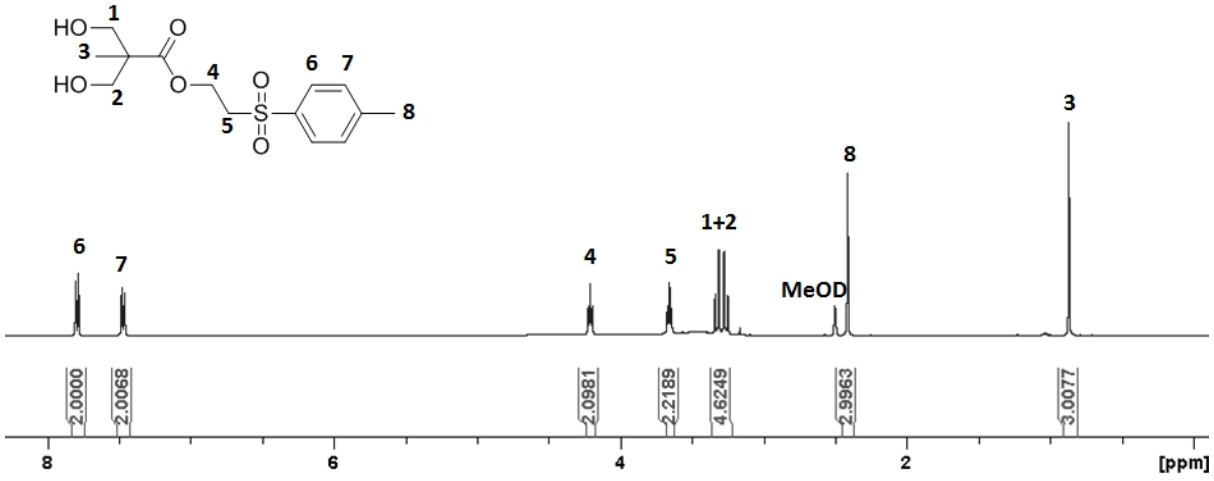

Figure S6. ^{1}H NMR (400 MHz, MeOD) of **OH_2-G_1-TSe, 6**

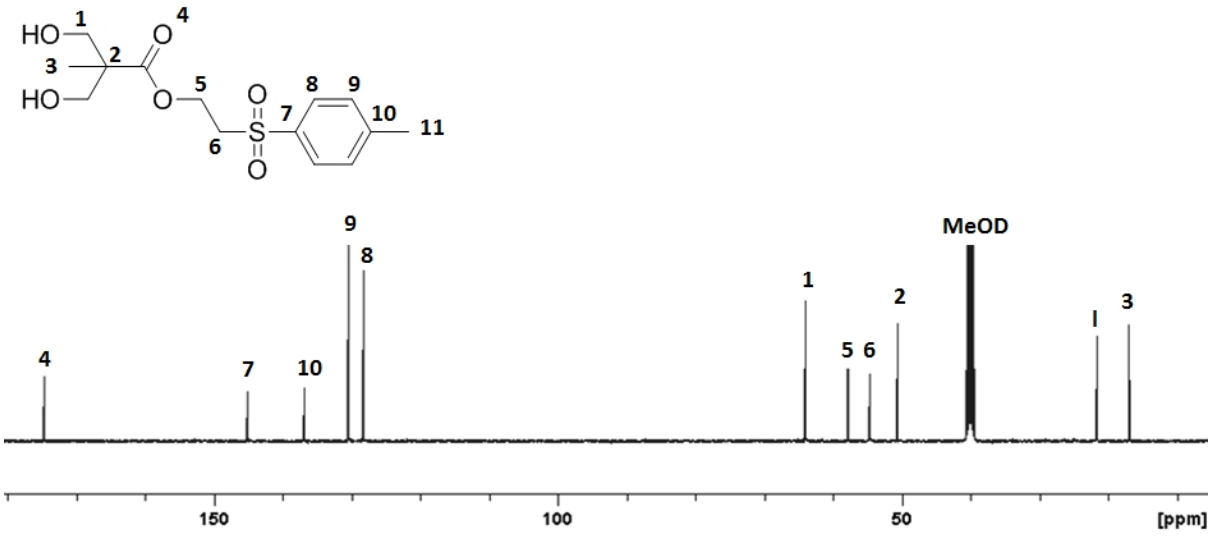

Figure S7. ^{13}C NMR (400 MHz, MeOD) of **OH_2-G_1-TSe, 6**

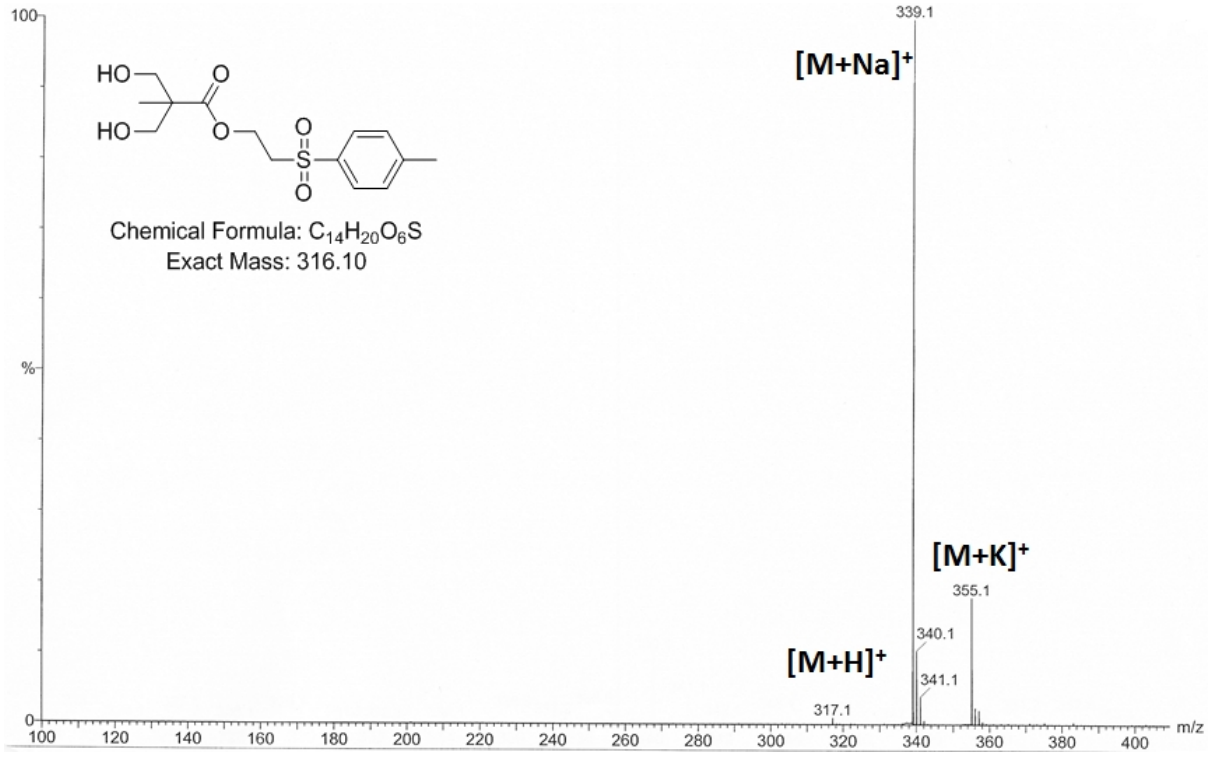

Figure S8. ESI-MS (MeOH) of **OH_2-G_1-TSe, 6**

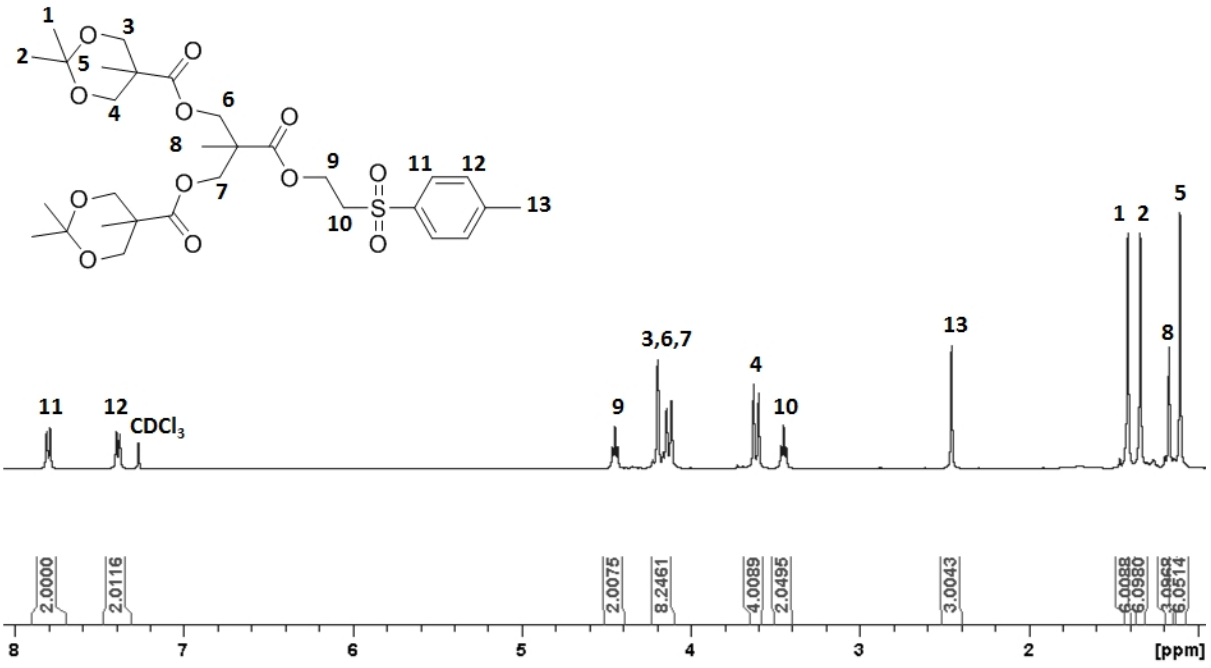

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of **Acet$_2$-G$_2$-TSe, 7**

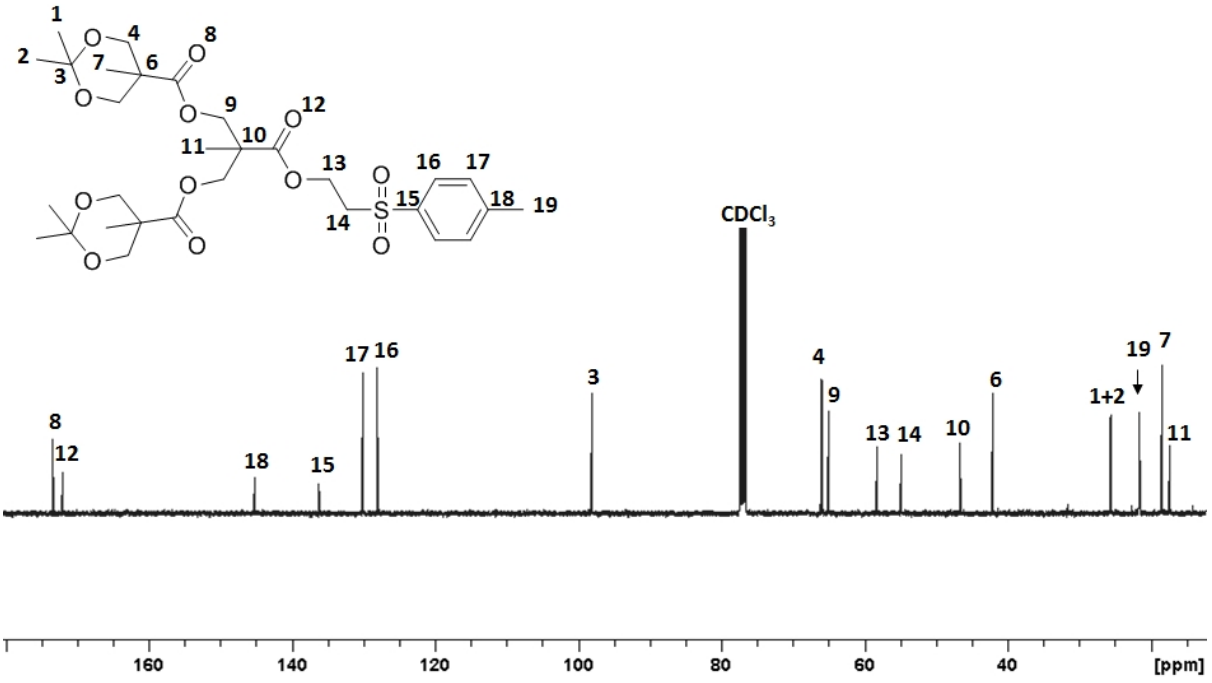

Figure S10. ^{13}C NMR (400 MHz, $CDCl_3$) of **Acet$_2$-G$_2$-TSe, 7**

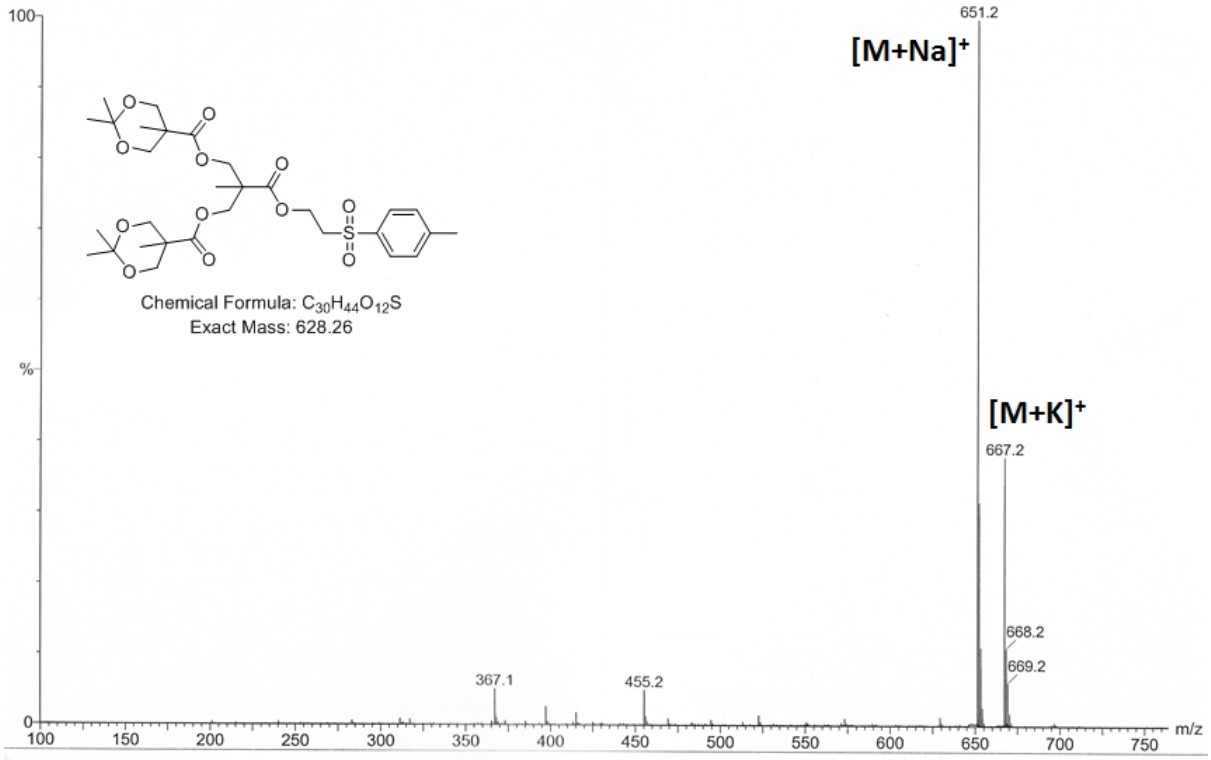

Figure S11. ESI-MS (MeOH) of **Acet$_2$-G$_2$-TSe, 7**

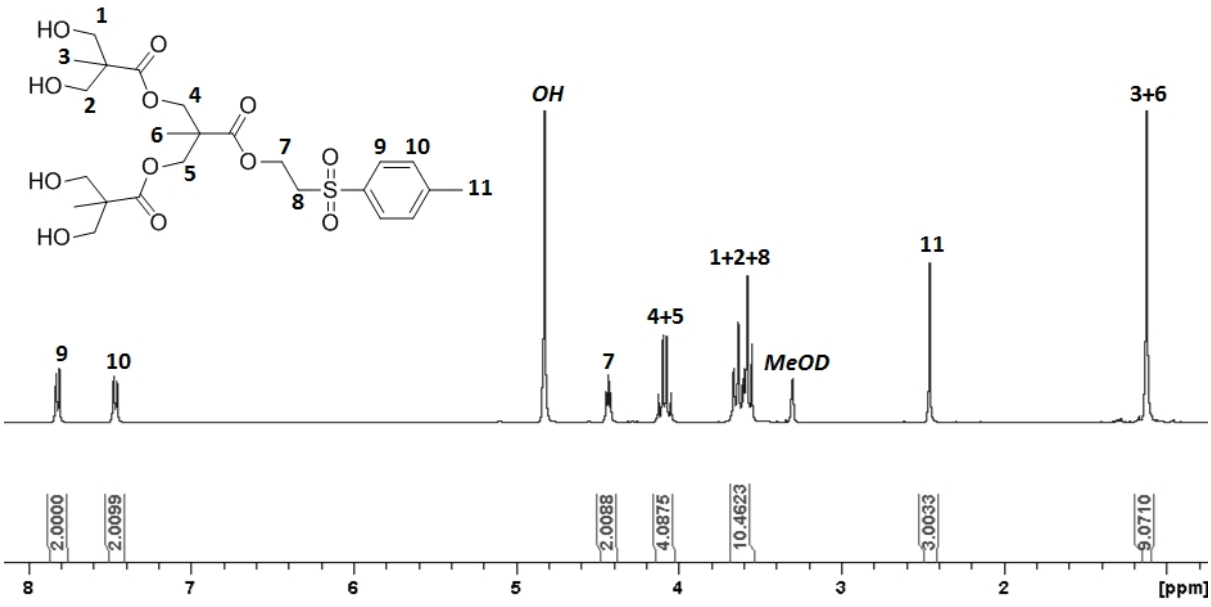

Figure S12. ^{1}H NMR (400 MHz, MeOD) of **OH$_4$-G$_2$-TSe, 8**

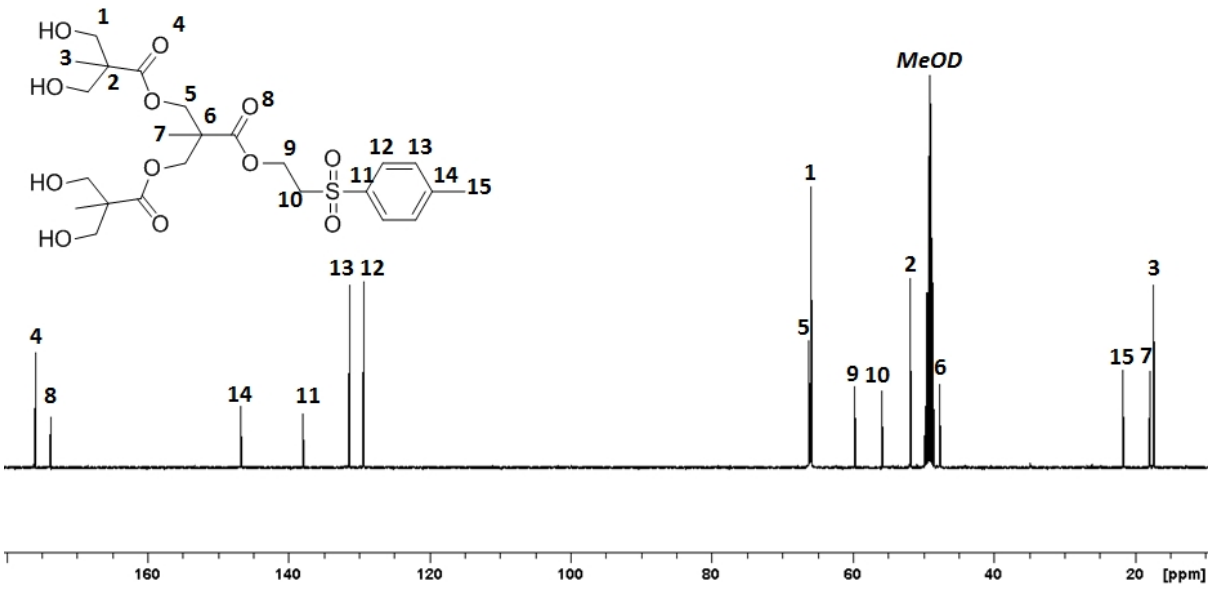

Figure S13. ^{13}C NMR (400 MHz, MeOD) of **OH_4-G_2-TSe, 8**

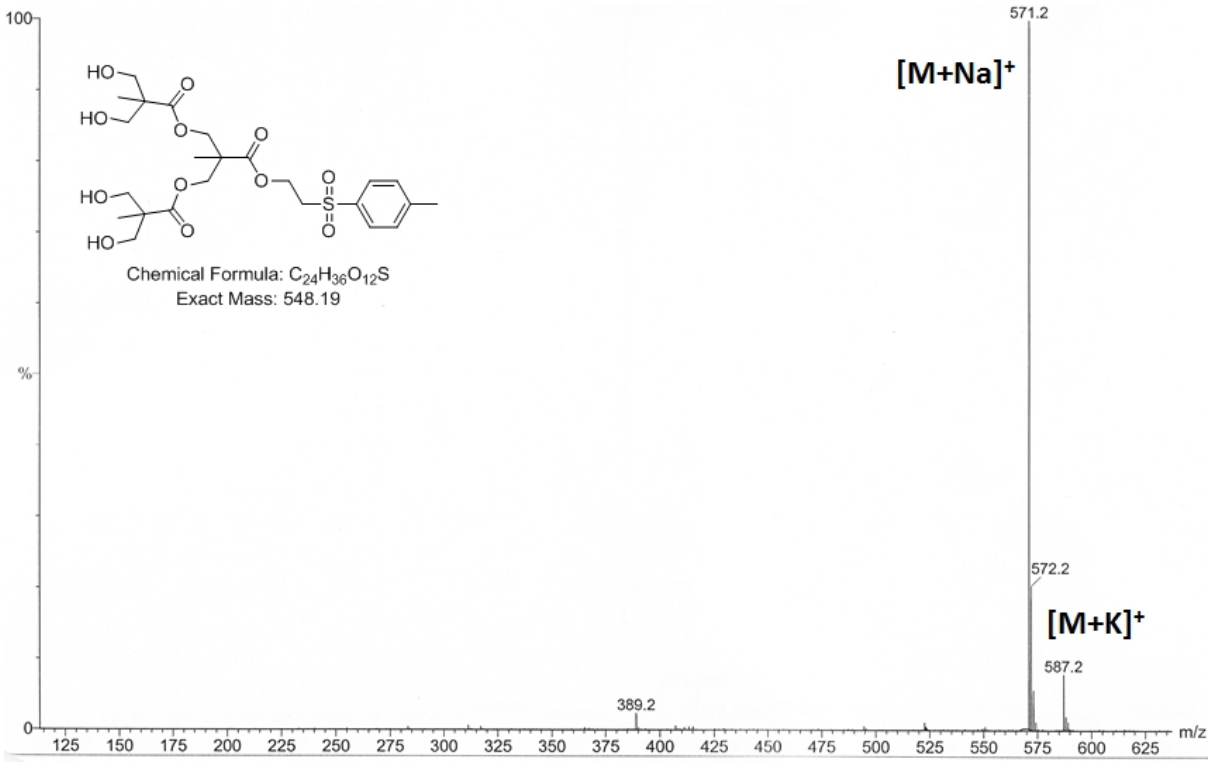

Figure S14. ESI-MS (MeOH) of **OH_4-G_2-TSe, 8**

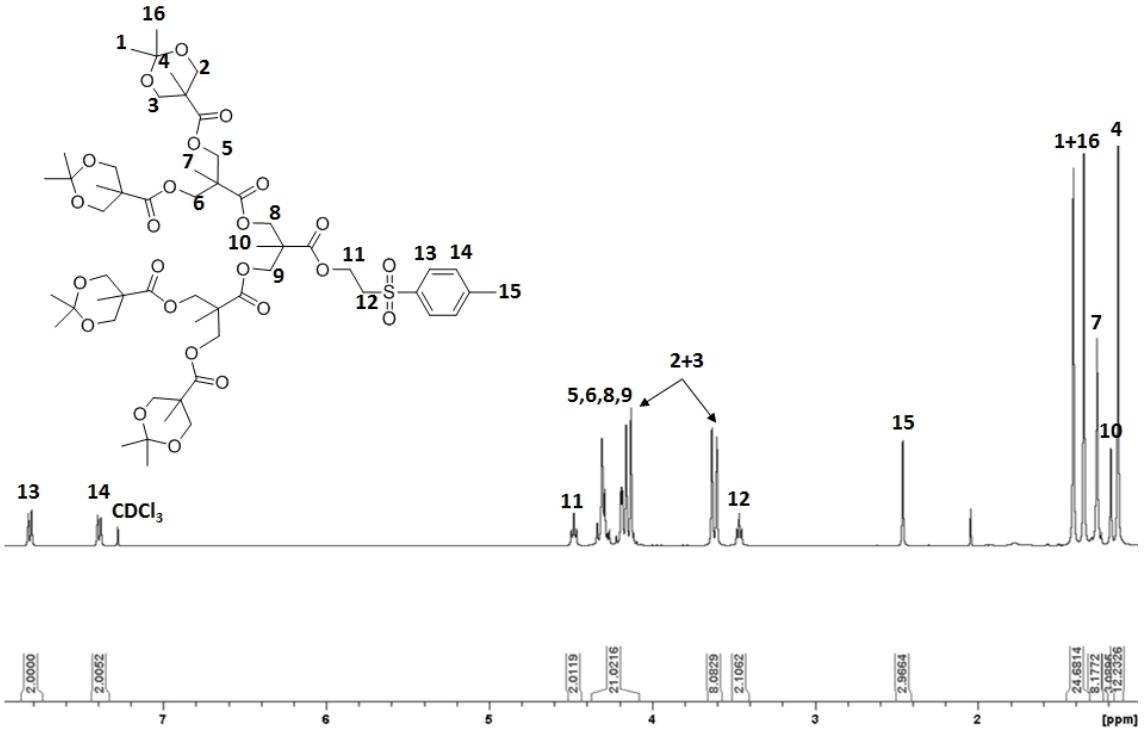

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Acet_4$-G_3-TSe, 9**

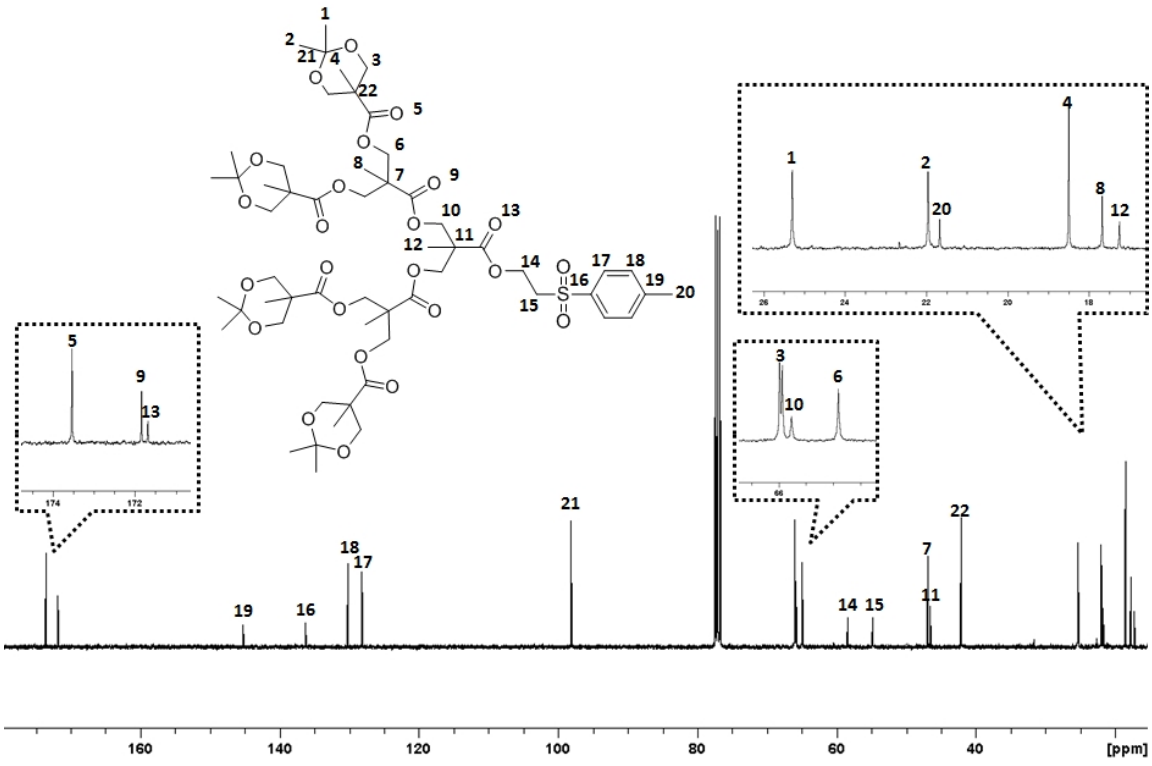

Figure S16. ^{13}C NMR (400 MHz, $CDCl_3$) of **$Acet_4$-G_3-TSe, 9**

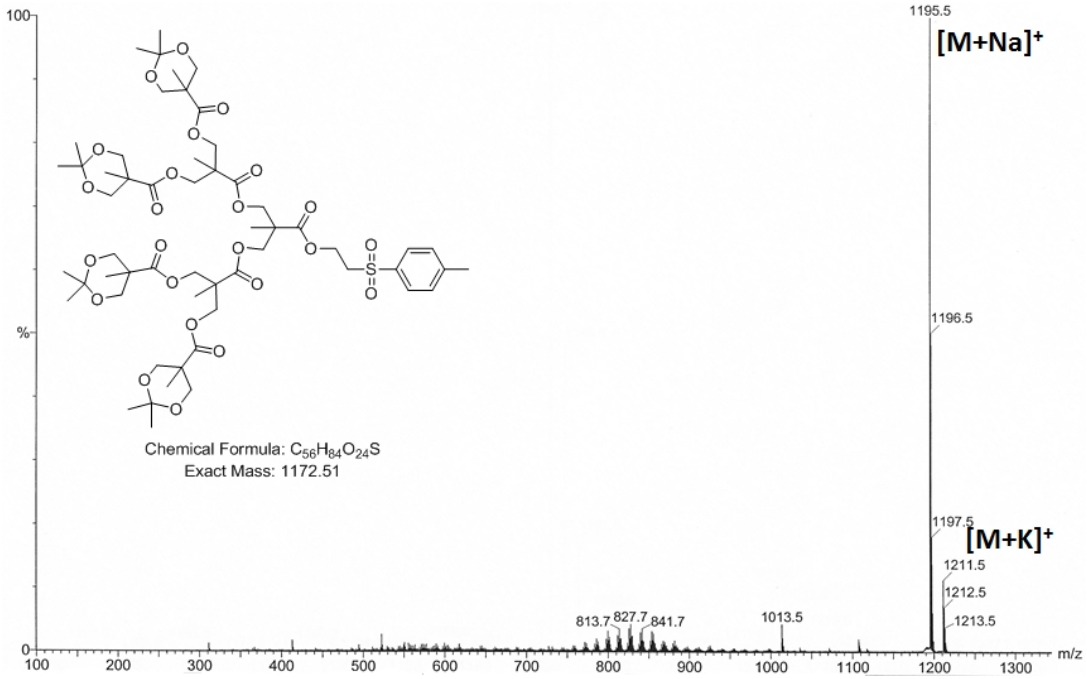

Figure S17. ESI-MS (MeOH) of **Acet$_4$-G$_3$-TSe, 9**

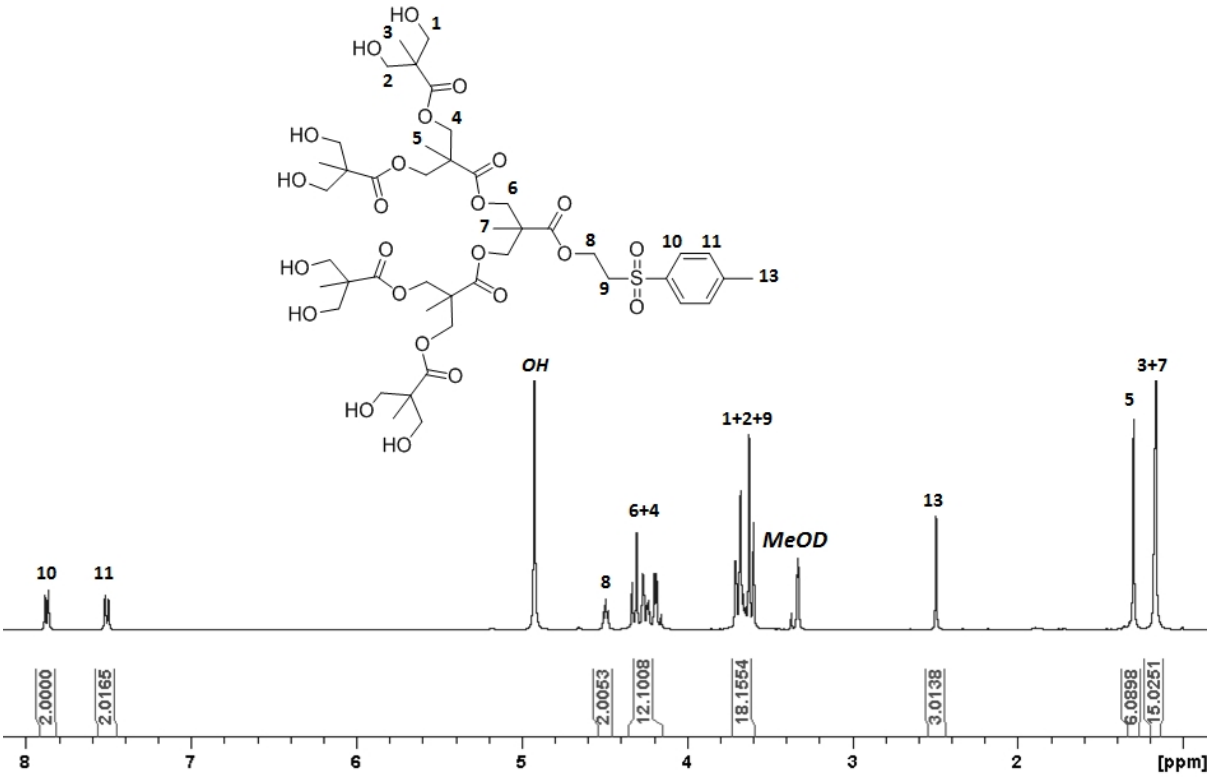

Figure S18. ^{1}H NMR (400 MHz, MeOD) of **OH$_8$-G$_3$-TSe, 10**

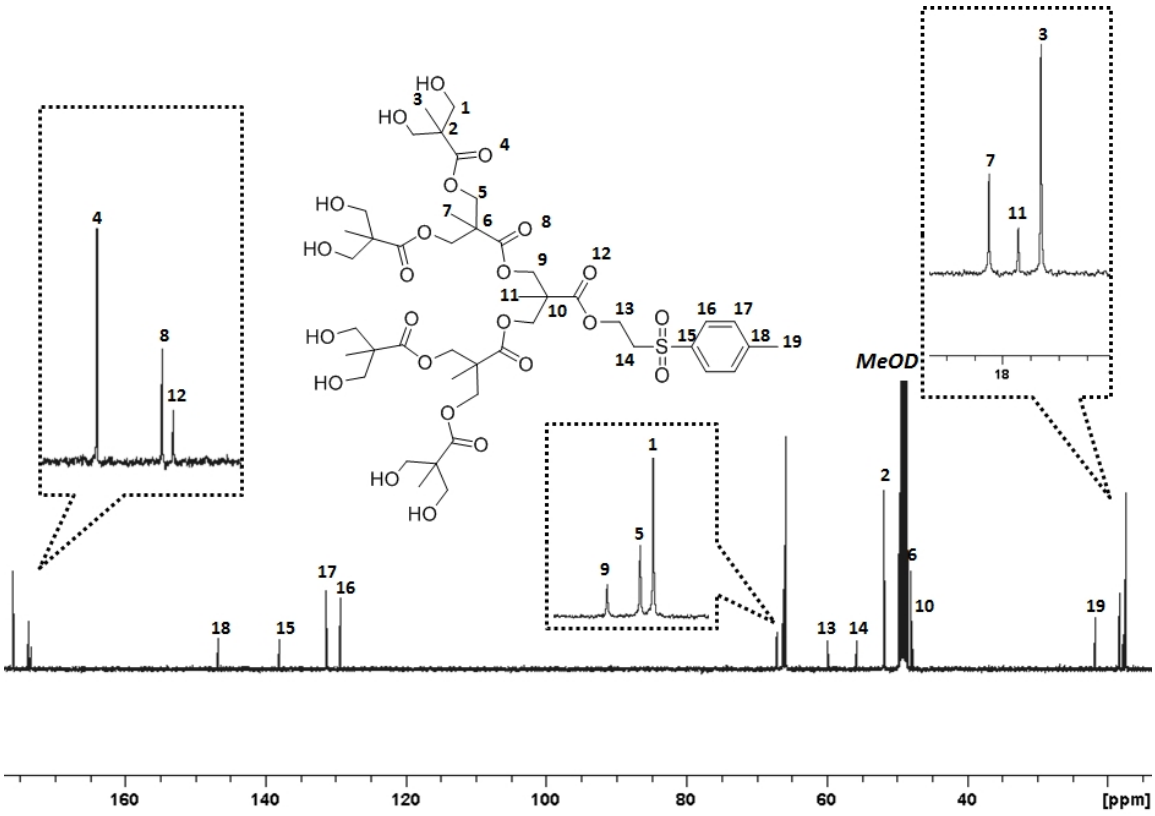

Figure S19. ^{13}C NMR (400 MHz, MeOD) of **OH_8-G_3-TSe, 10**

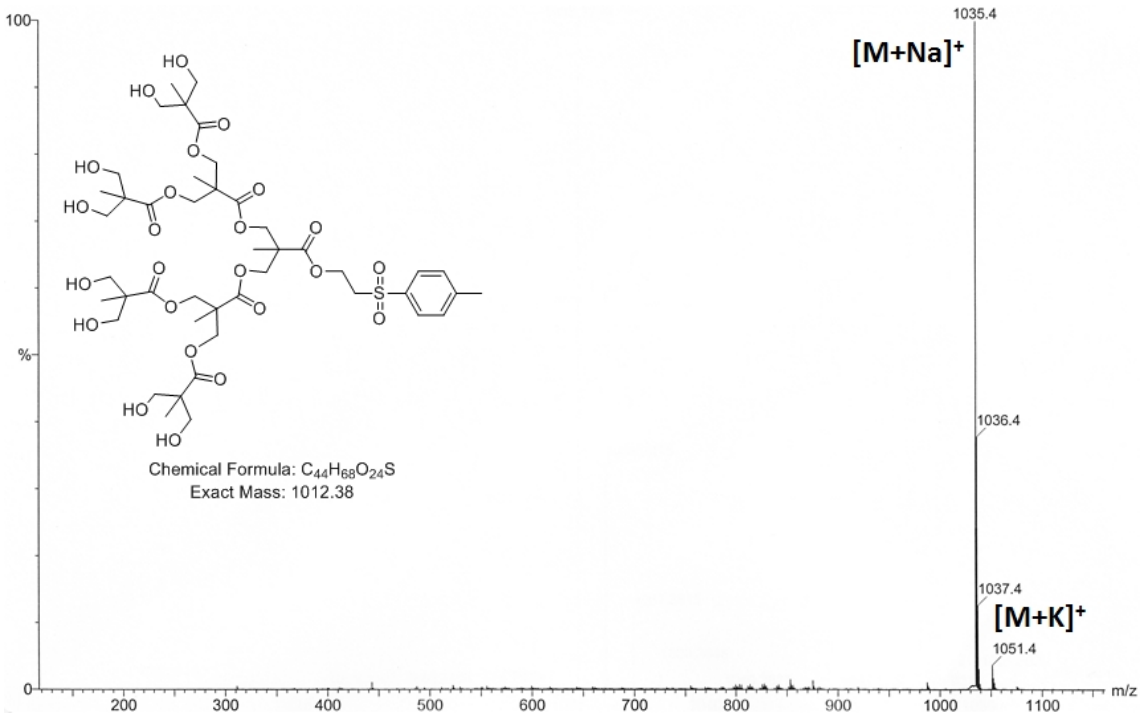

Figure S20. ESI-MS (MeOH) of **OH_8-G_3-TSe, 10**

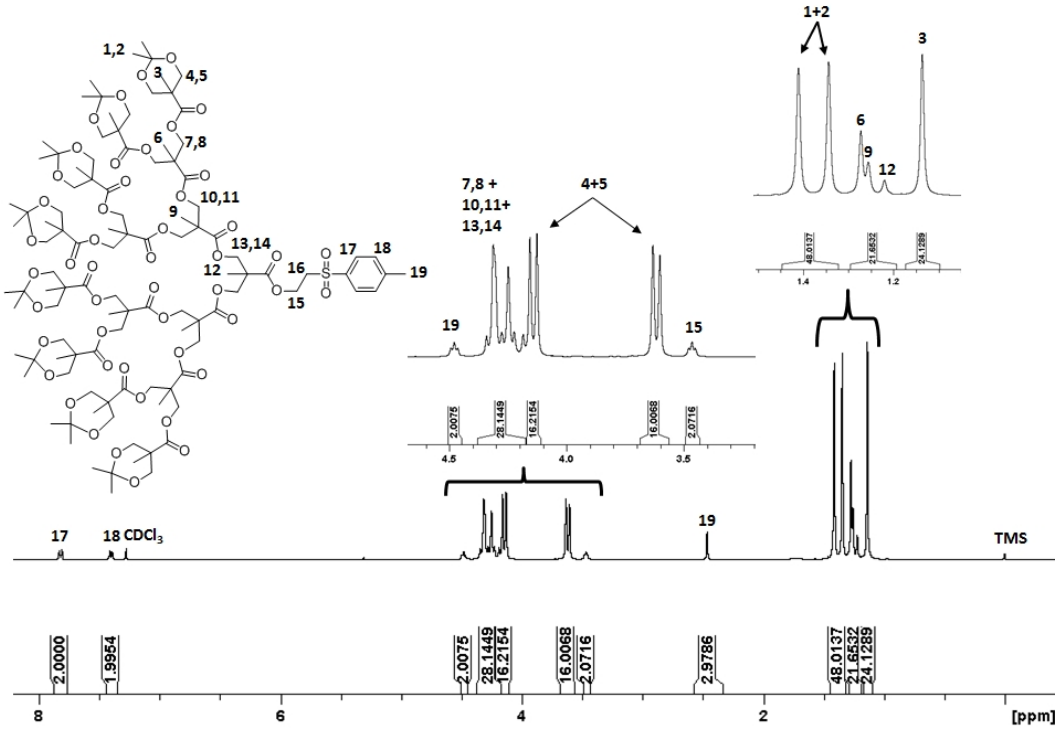

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of **Acet$_8$-G$_4$-TSe, 11**

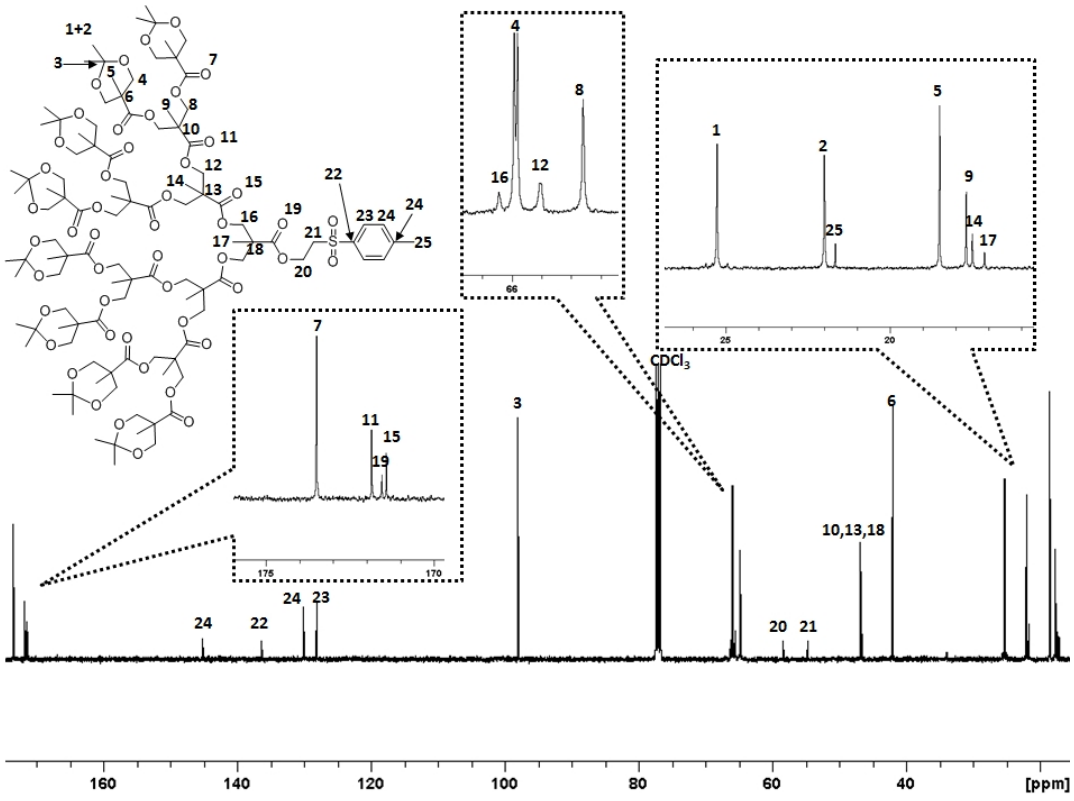

Figure S22. ^{13}C NMR (400 MHz, $CDCl_3$) of **Acet$_8$-G$_4$-TSe, 11**

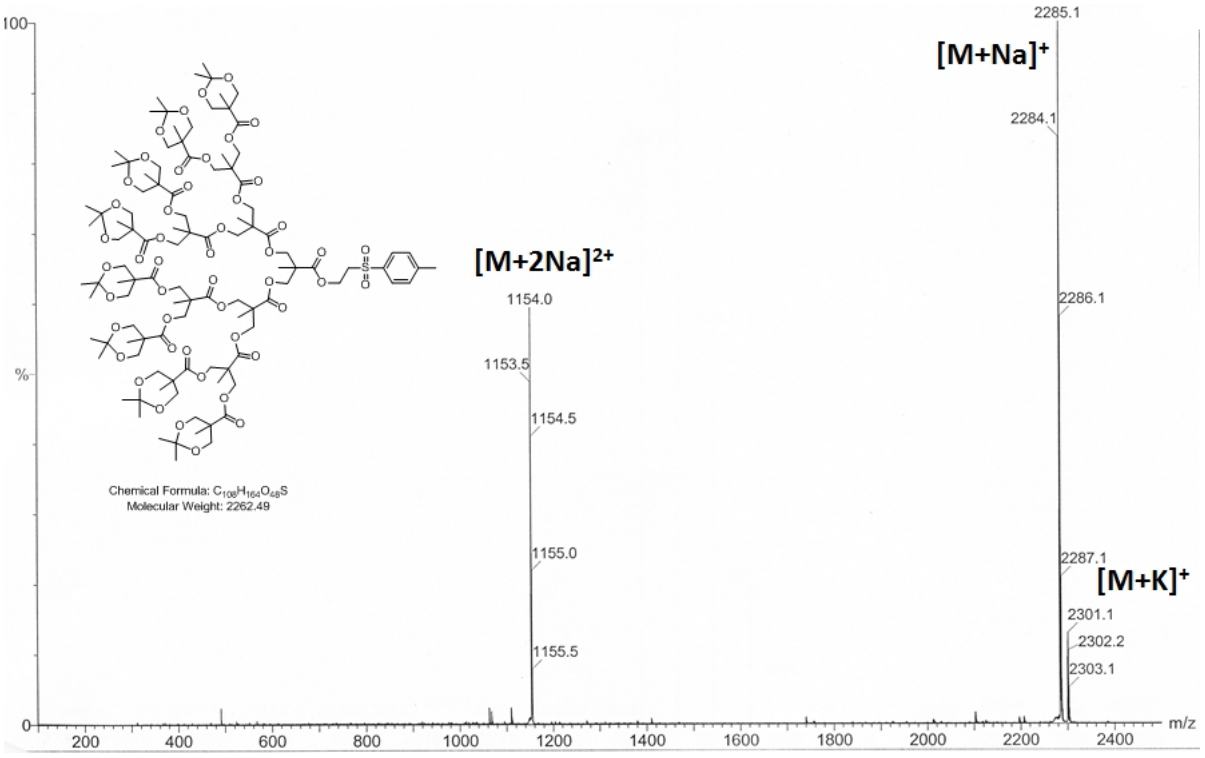

Figure S23. ESI-MS (MeOH) of **Acet$_8$-G$_4$-TSe, 11**

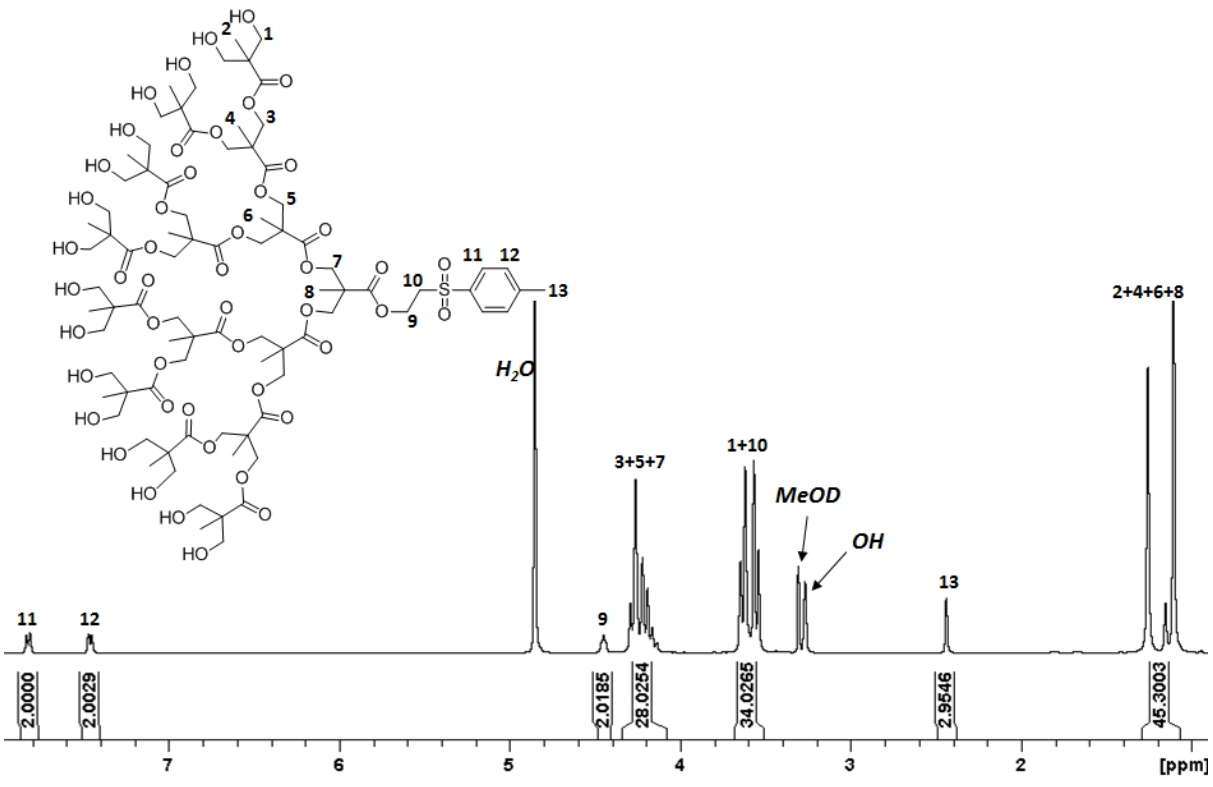

Figure S24. ^{1}H NMR (400 MHz, MeOD) of **OH$_{16}$-G$_4$-TSe, 12**

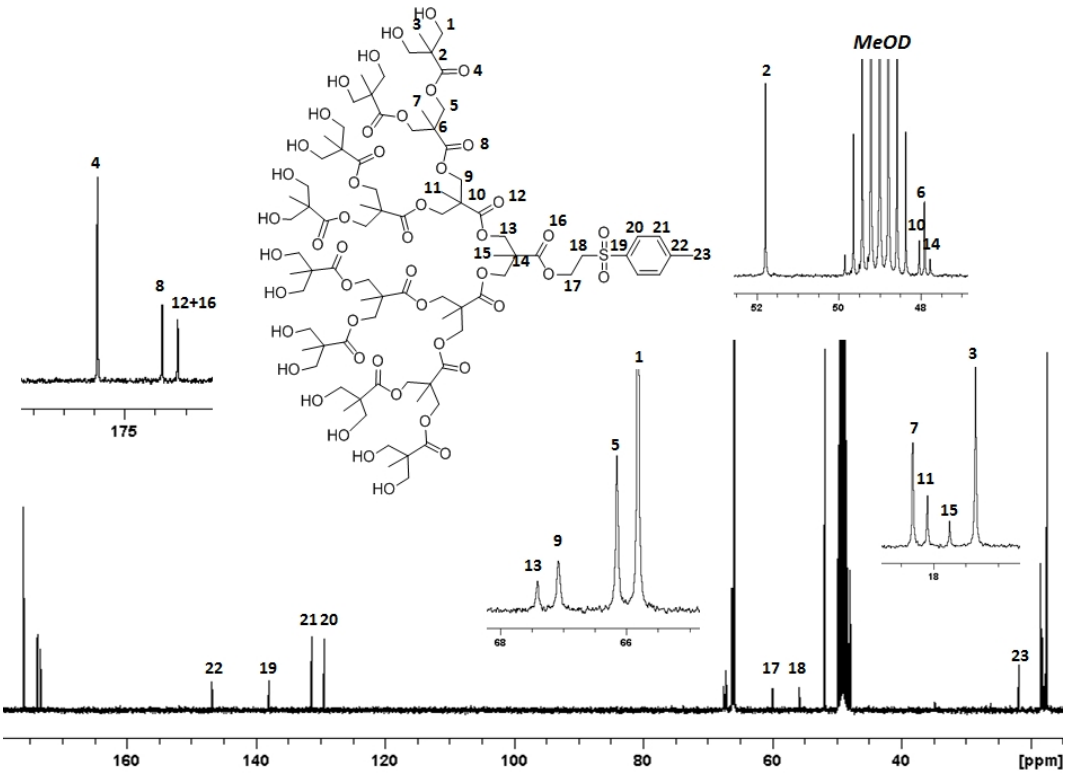

Figure S25. ^{13}C NMR (400 MHz, MeOD) of **OH_{16}-G_4-TSe, 12**

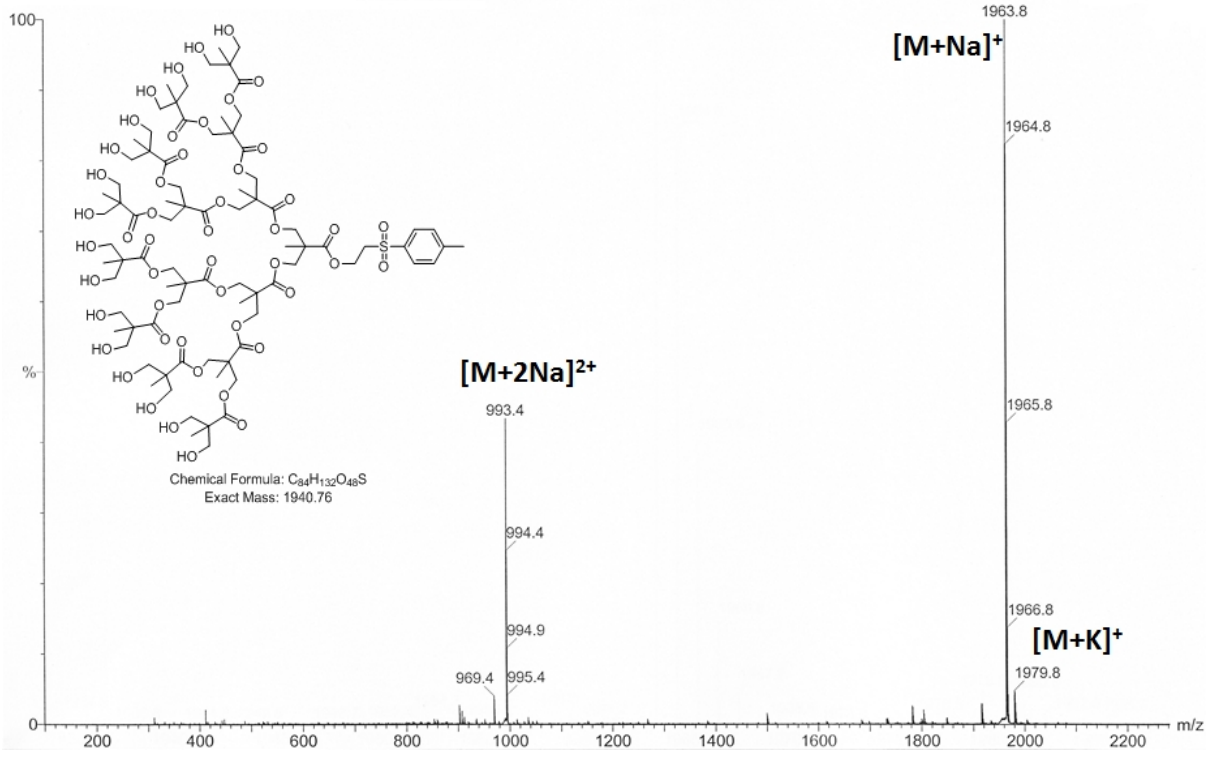

Figure S26. ESI-MS (MeOH) of **OH_{16}-G_4-TSe, 12**

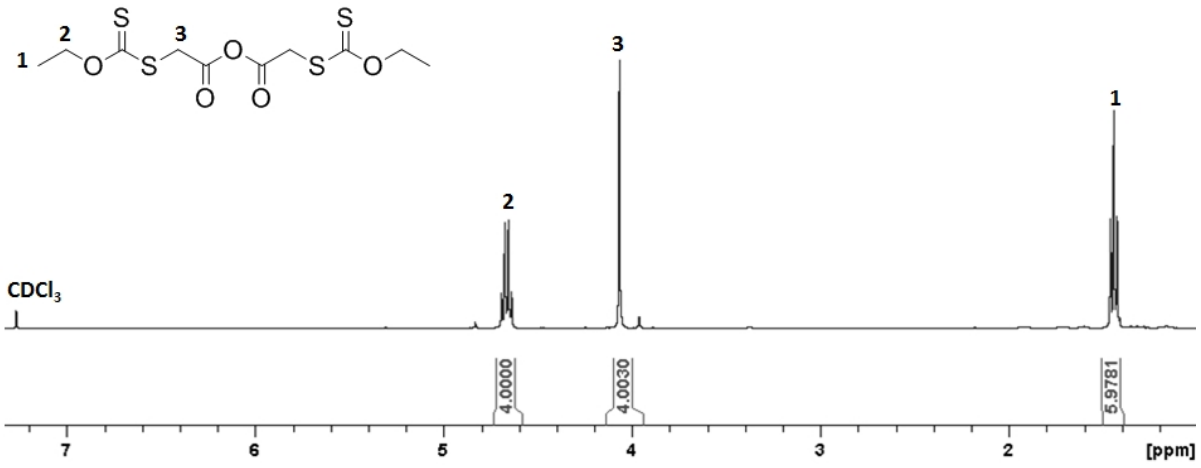

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride, 14**

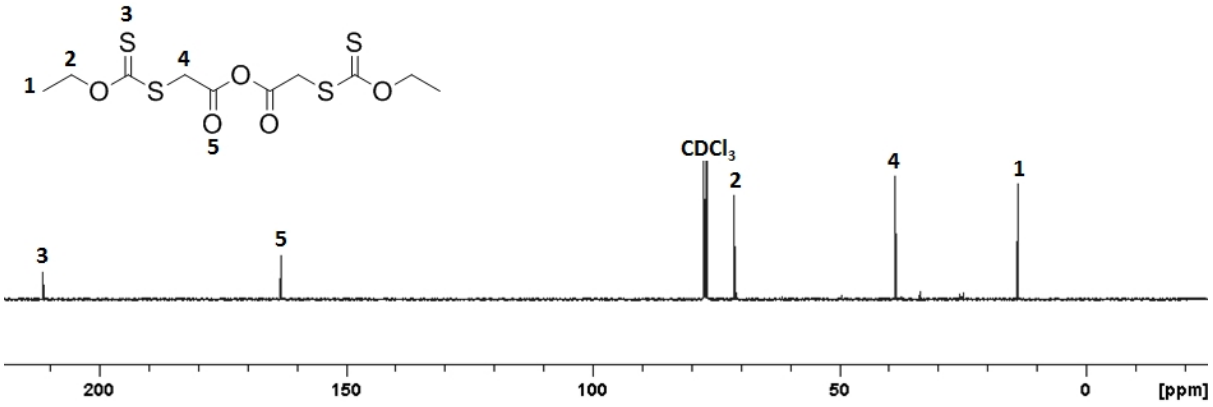

Figure S28. ^{13}C NMR (400 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride, 14**

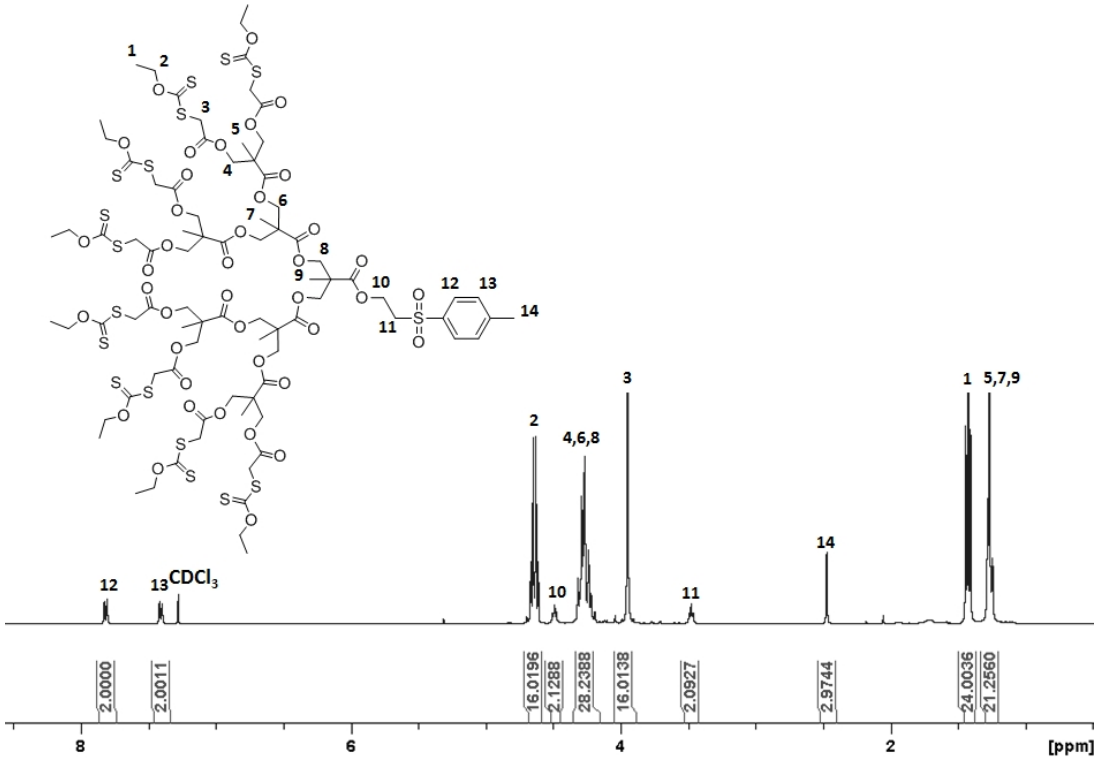

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-TSe, 17**

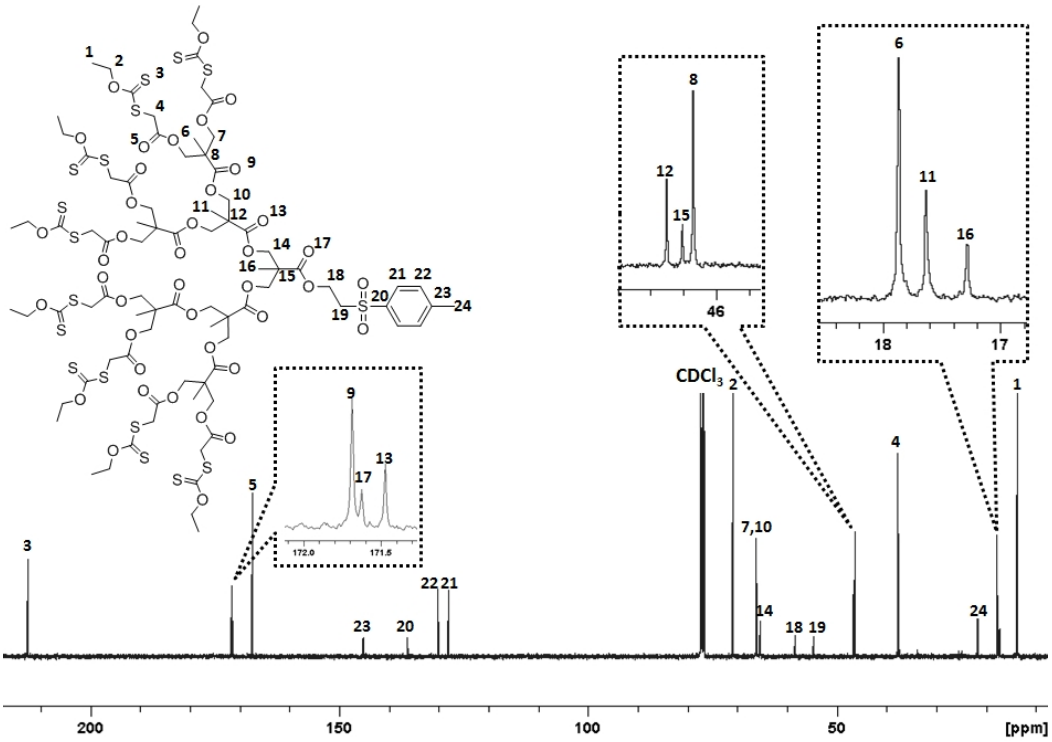

Figure S30. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-TSe, 17**

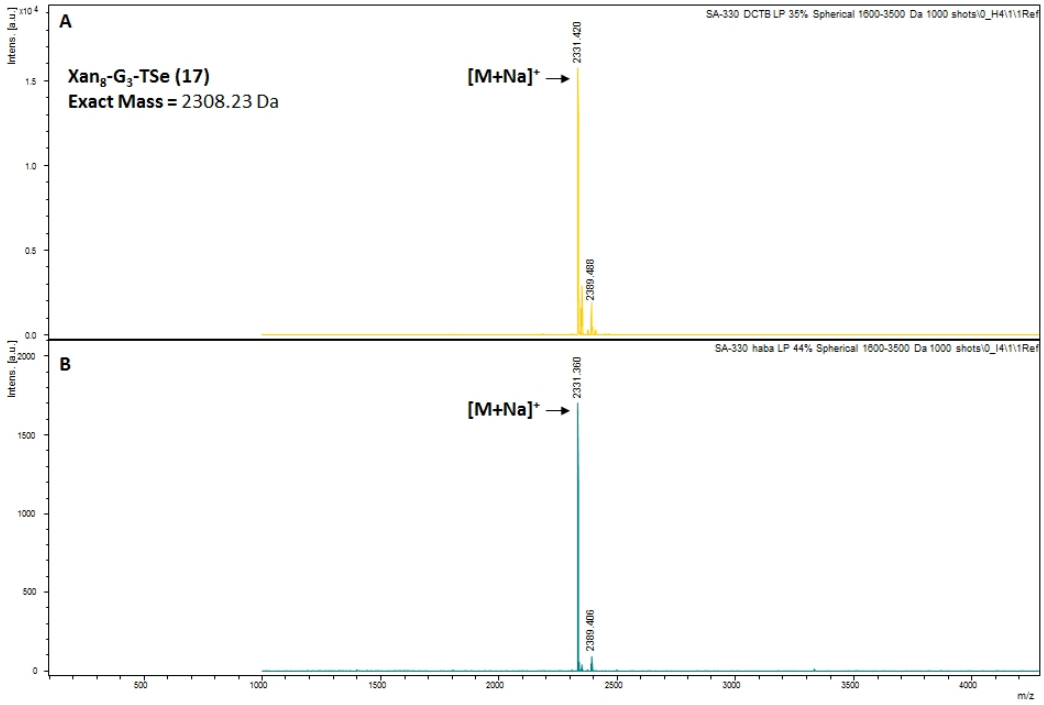

Figure S31. MALDI-TOF of **Xan_8-G_3-TSe (17).** (A) – Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB); (B) – Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA)

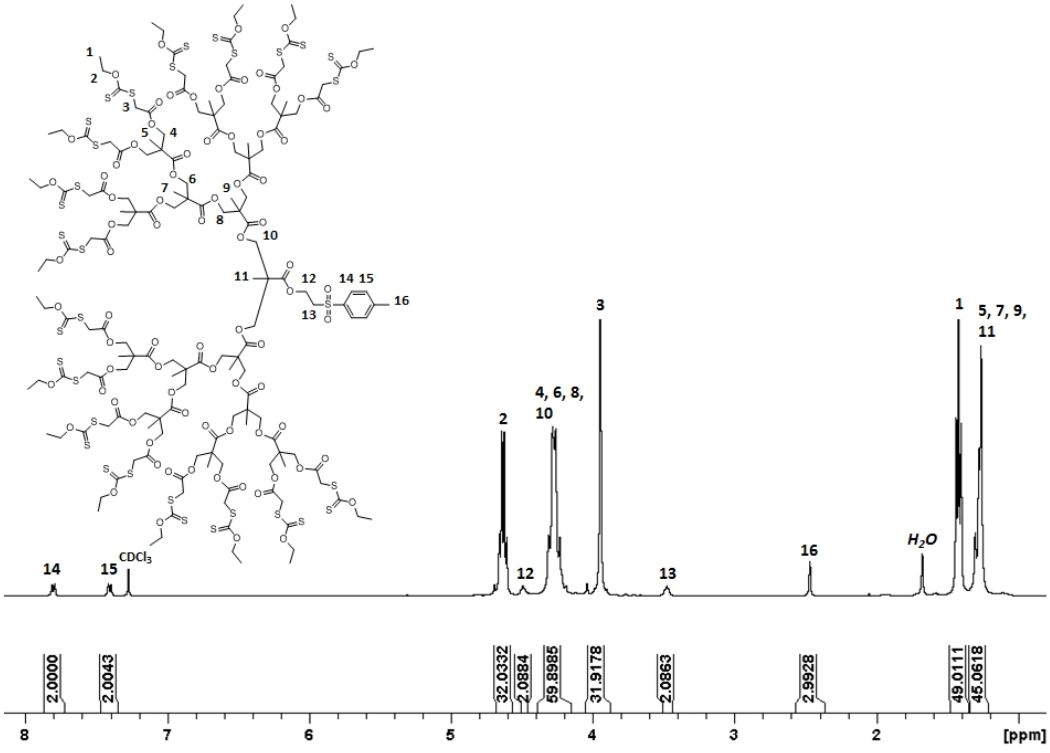

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-TSe, 18**

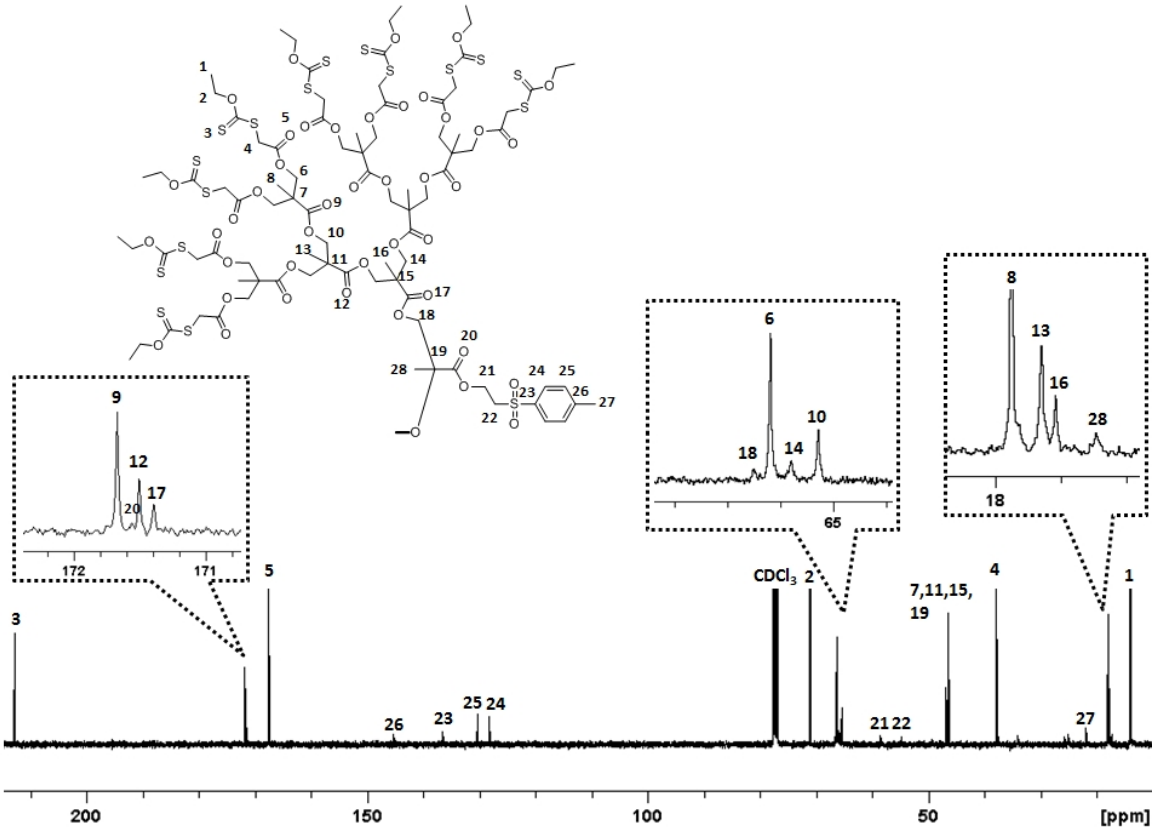

Figure S33. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-TSe, 18**

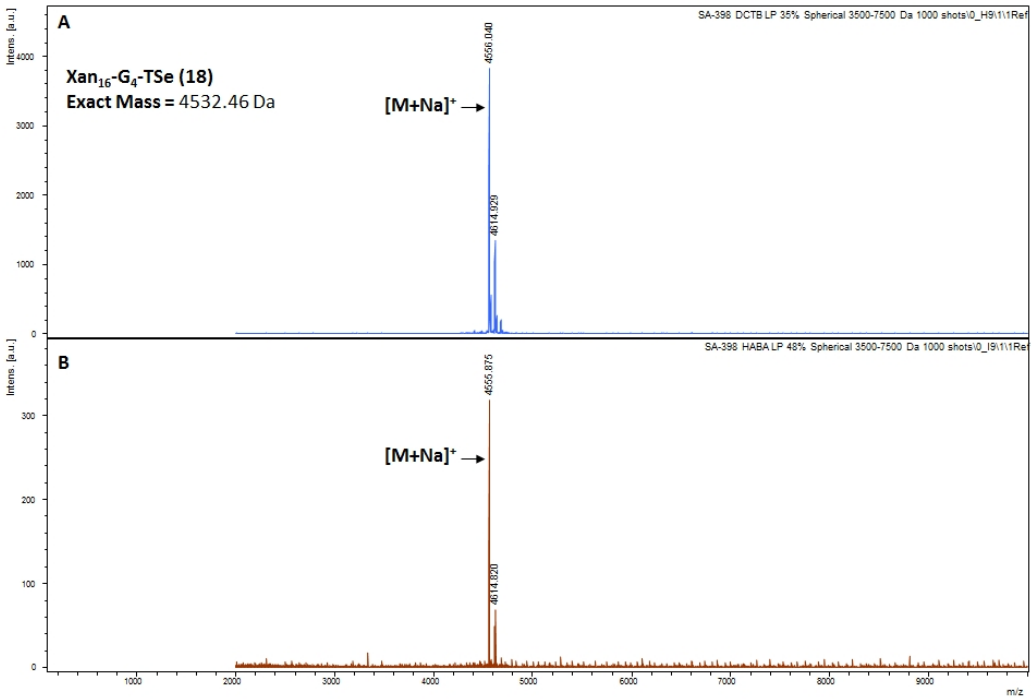

Figure S34. MALDI-TOF of **Xan_{16}-G_4-TSe (18).** (A) – Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB); (B) – Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA)

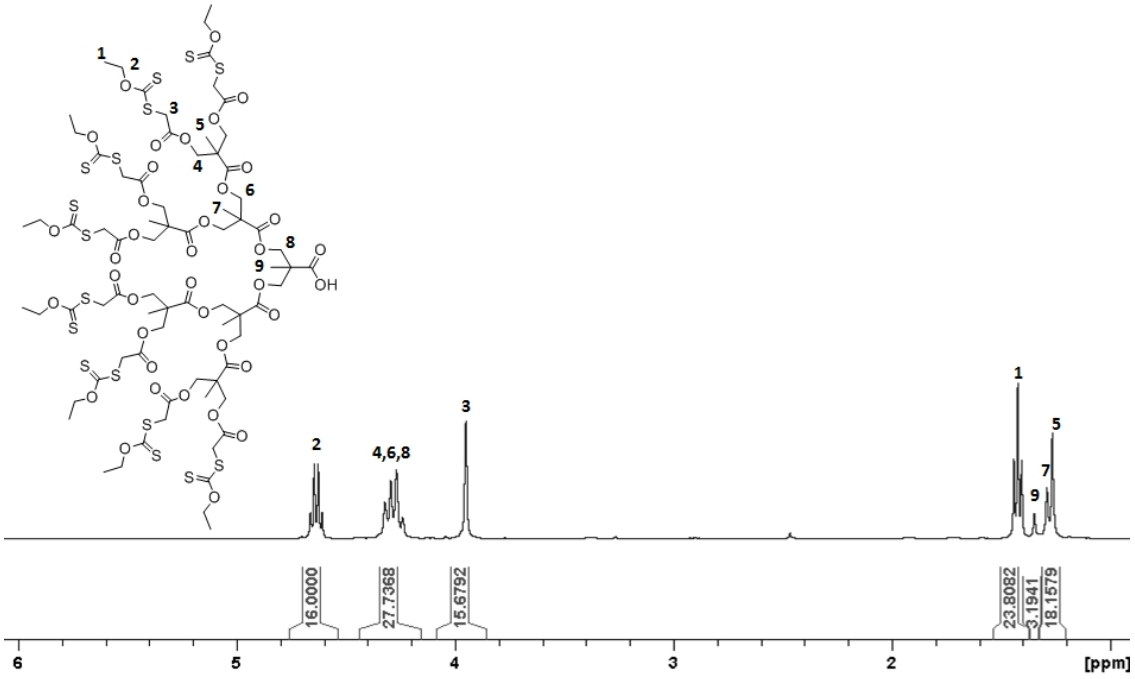

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-COOH, 21**

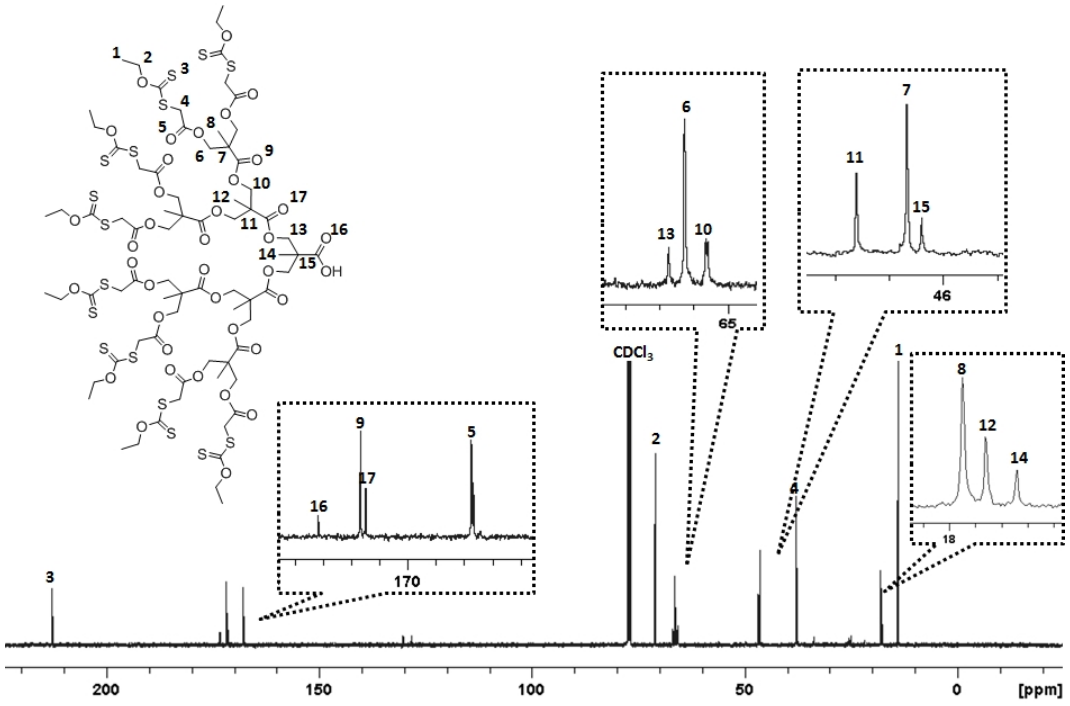

Figure S36. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-COOH, 21**

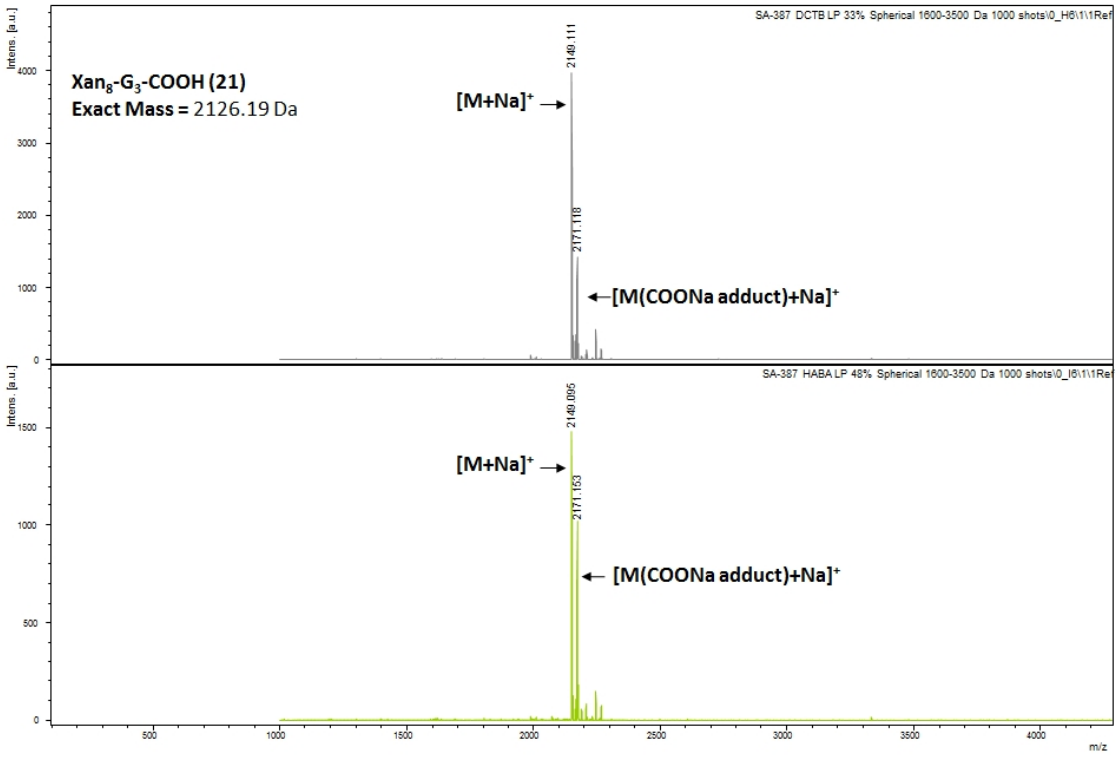

Figure S37. MALDI-TOF of **Xan_8-G_3-COOH (21)** (A) – Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB); (B) – Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA)

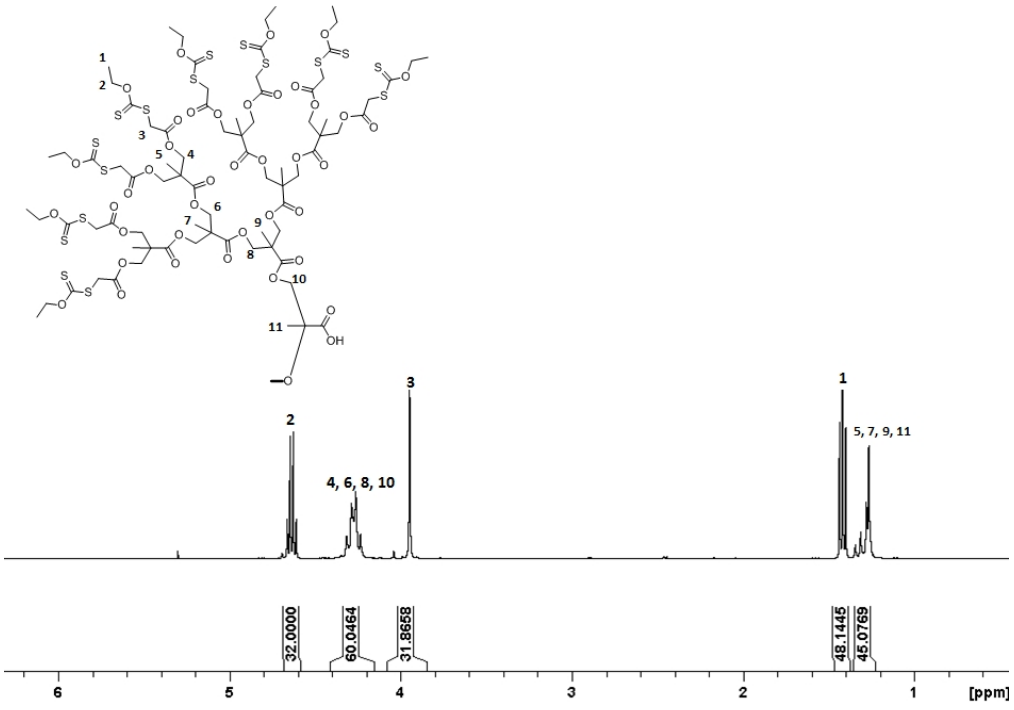

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-COOH, 22**

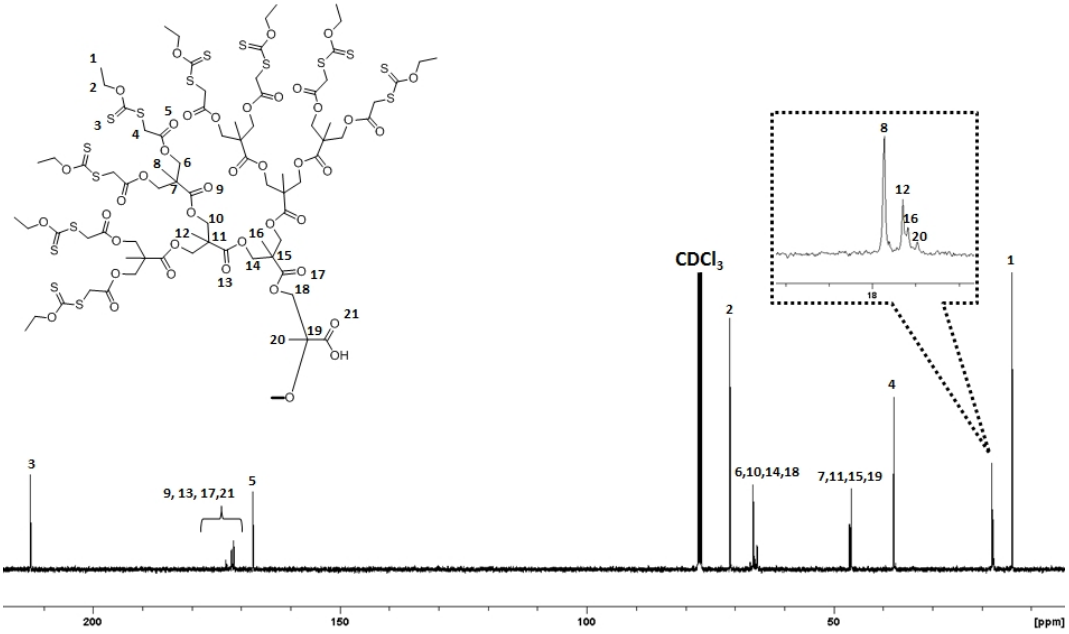

Figure S39. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-COOH, 22**

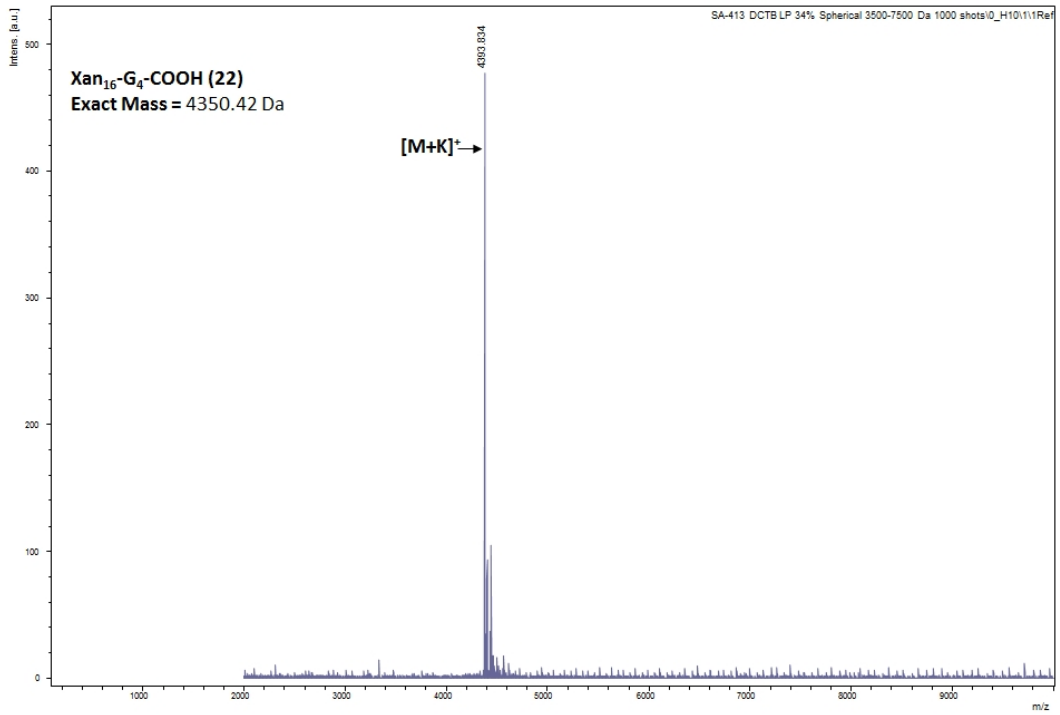

Figure S40. MALDI-TOF of **Xan_{16}-G_4-COOH (22).** Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)

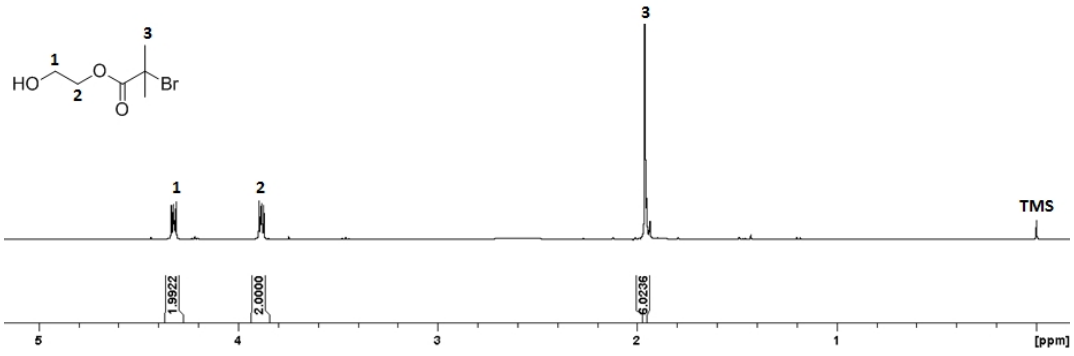

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-Hydroxyethyl 2-bromoisobutyrate, 23**

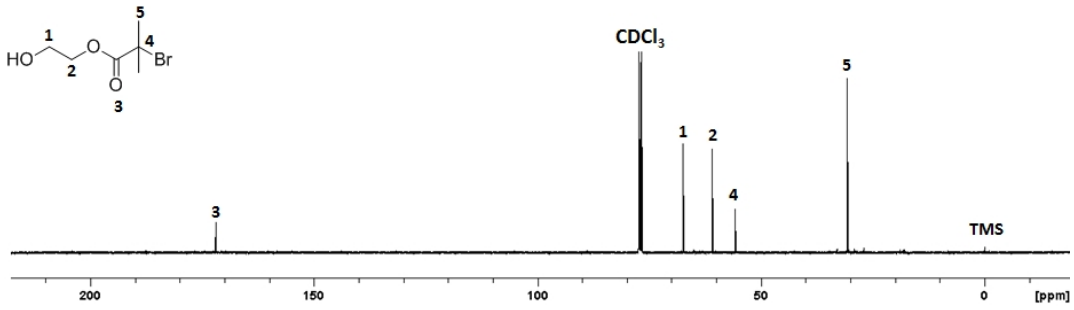

Figure S42. ^{13}C NMR (400 MHz, $CDCl_3$) of **2-Hydroxyethyl 2-bromoisobutyrate, 23**

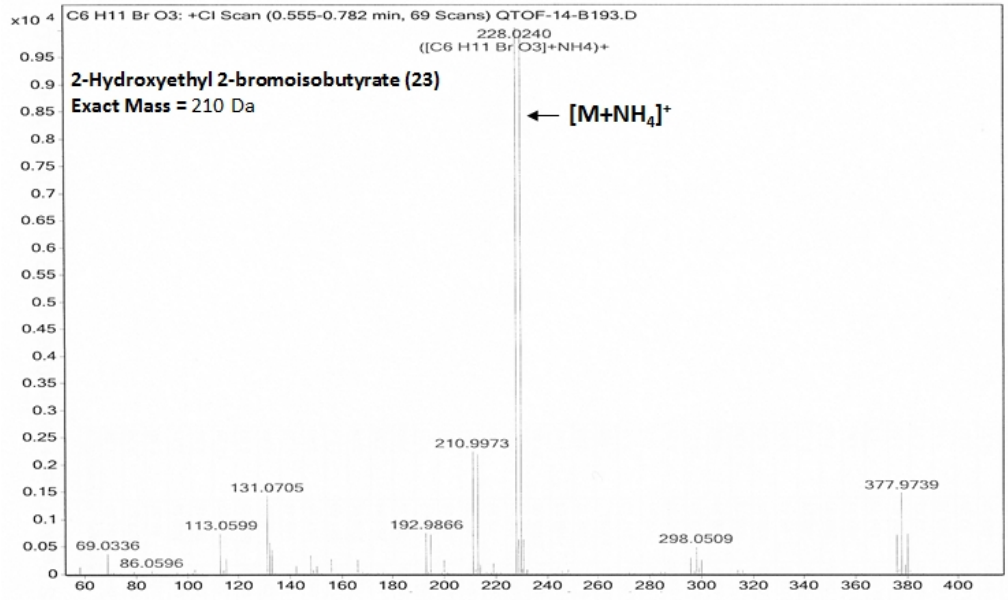

Figure S43. CI-MS (MeOH) of **2-Hydroxyethyl 2-bromoisobutyrate, 23**

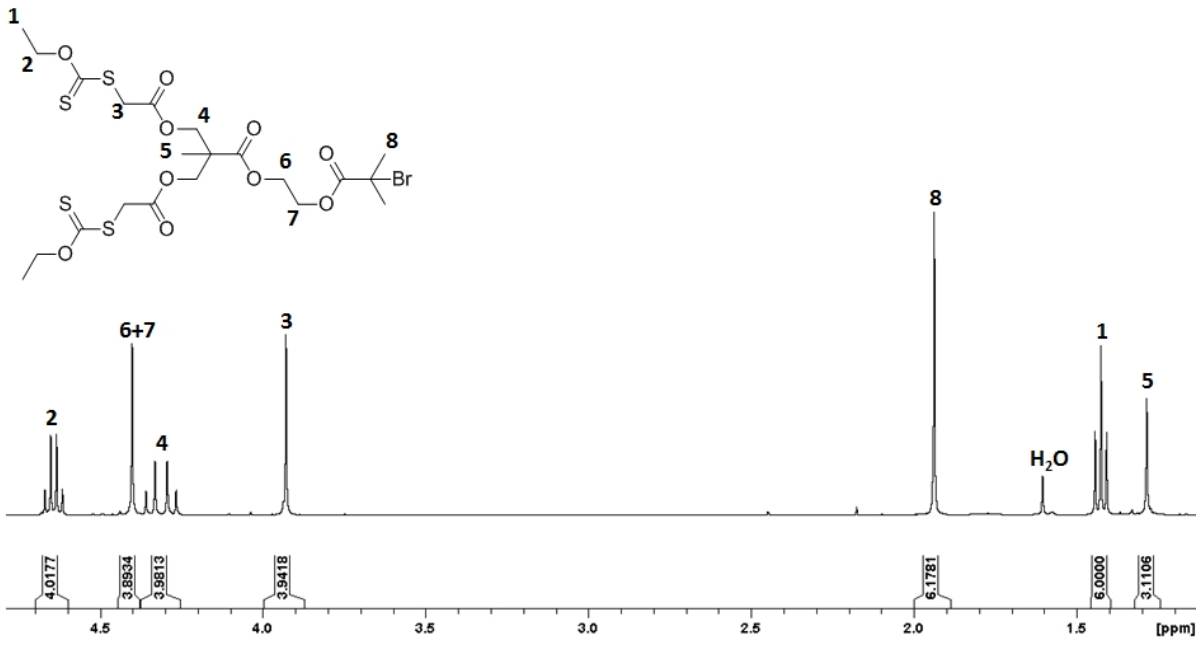

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1-BiB, 24**

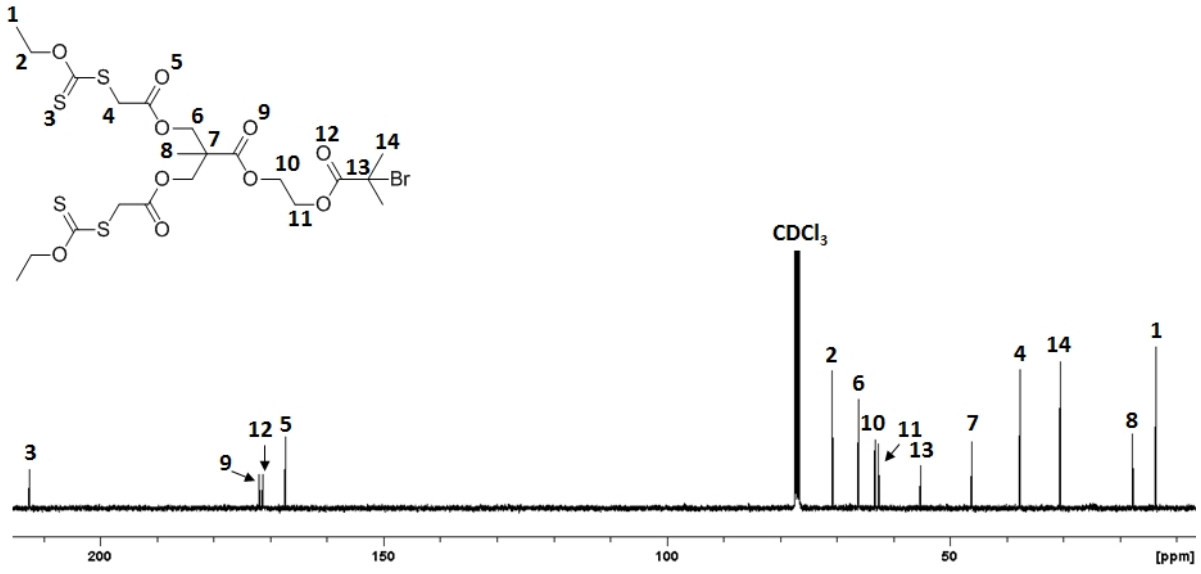

Figure S45. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1-BiB, 24**

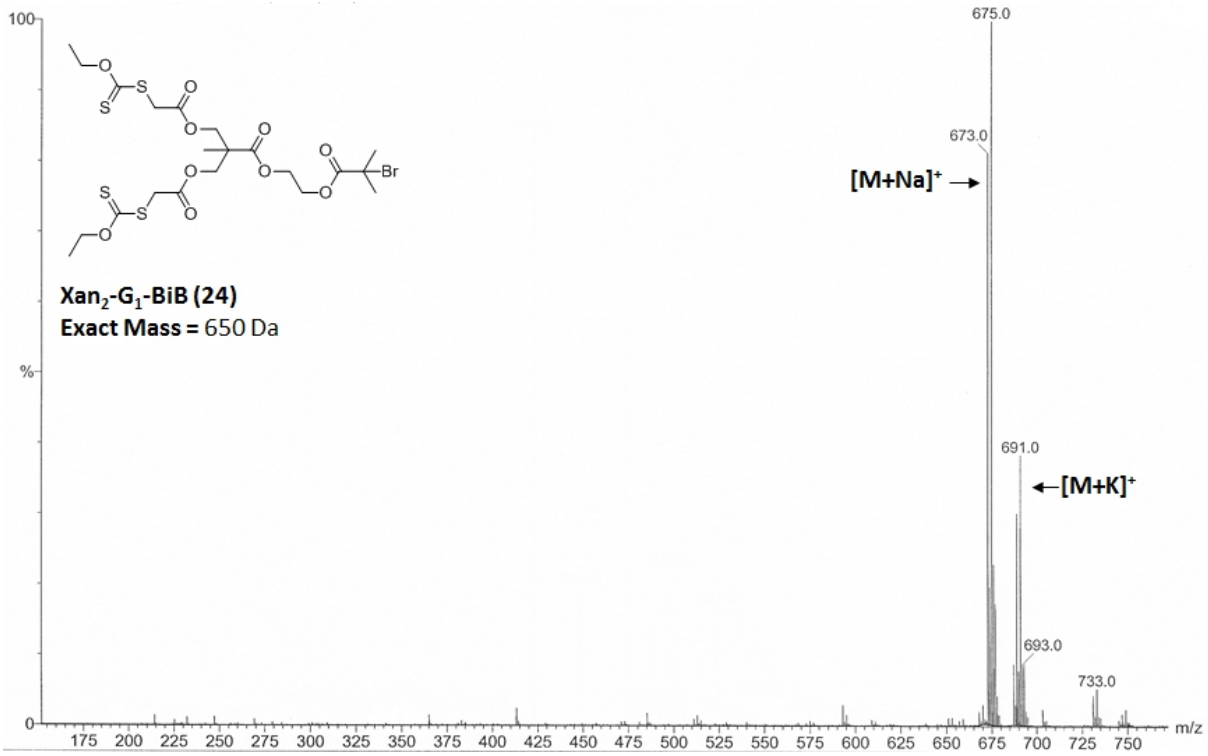

Figure S46. ESI-MS (MeOH) of **Xan_2-G_1-BiB, 24**

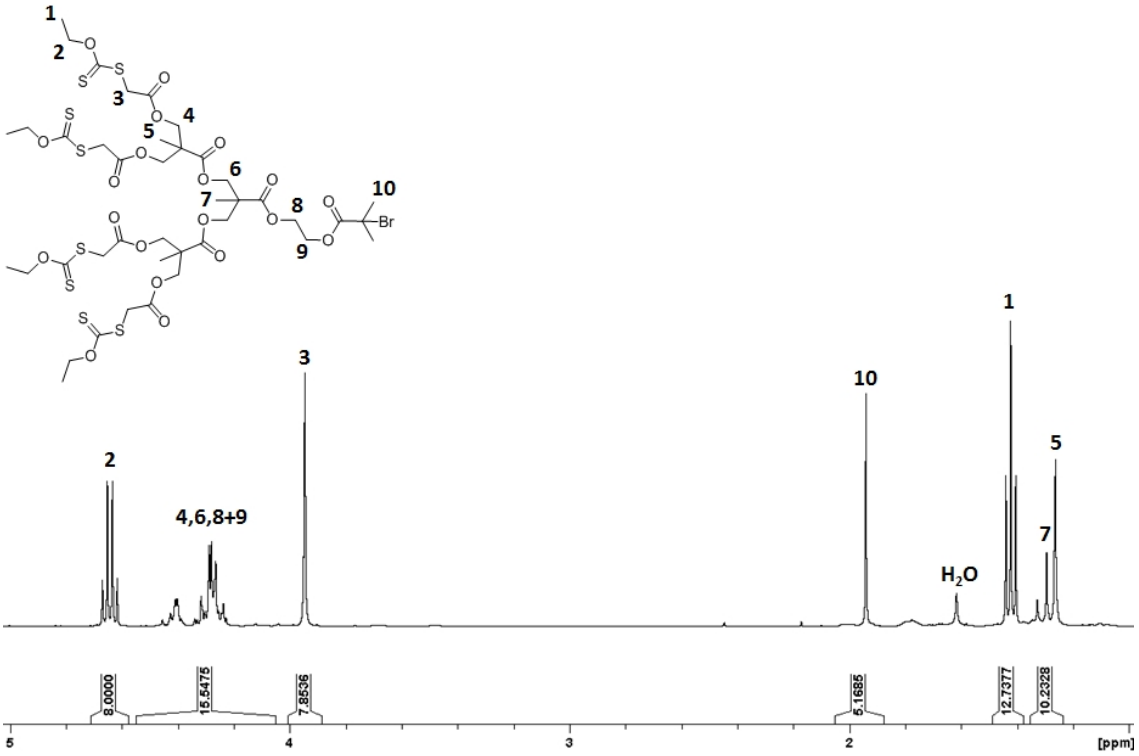

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_4-G_2-BiB, 25**

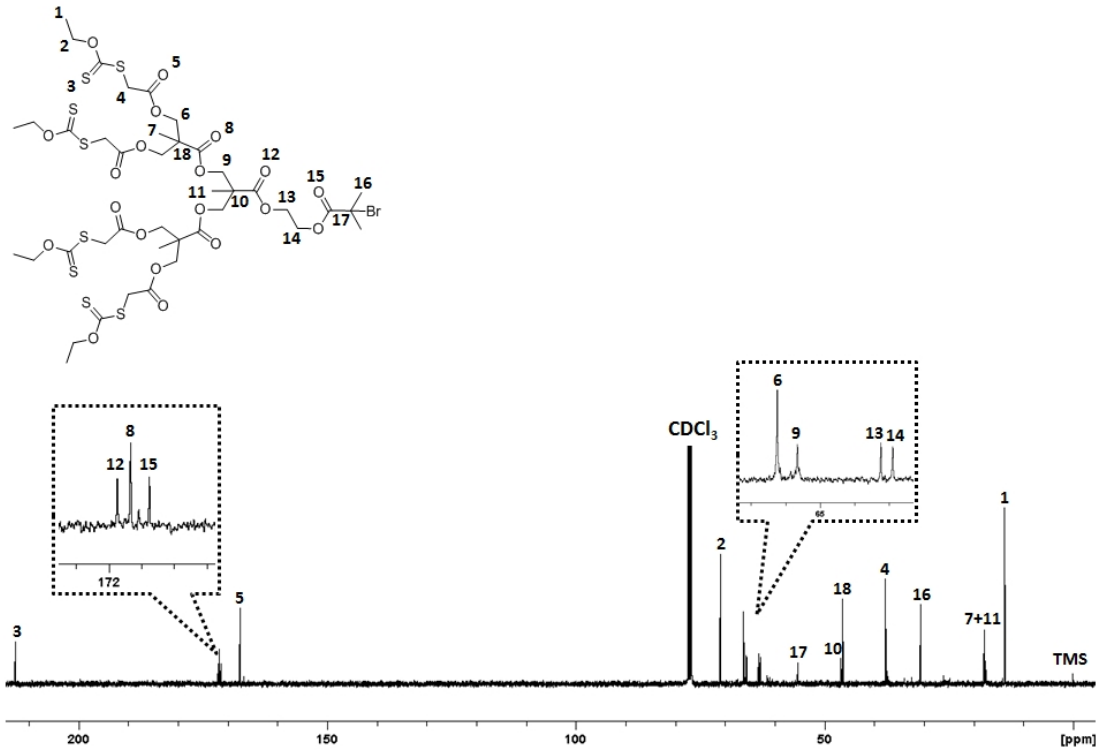

Figure S48. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_4-G_2-BiB, 25**

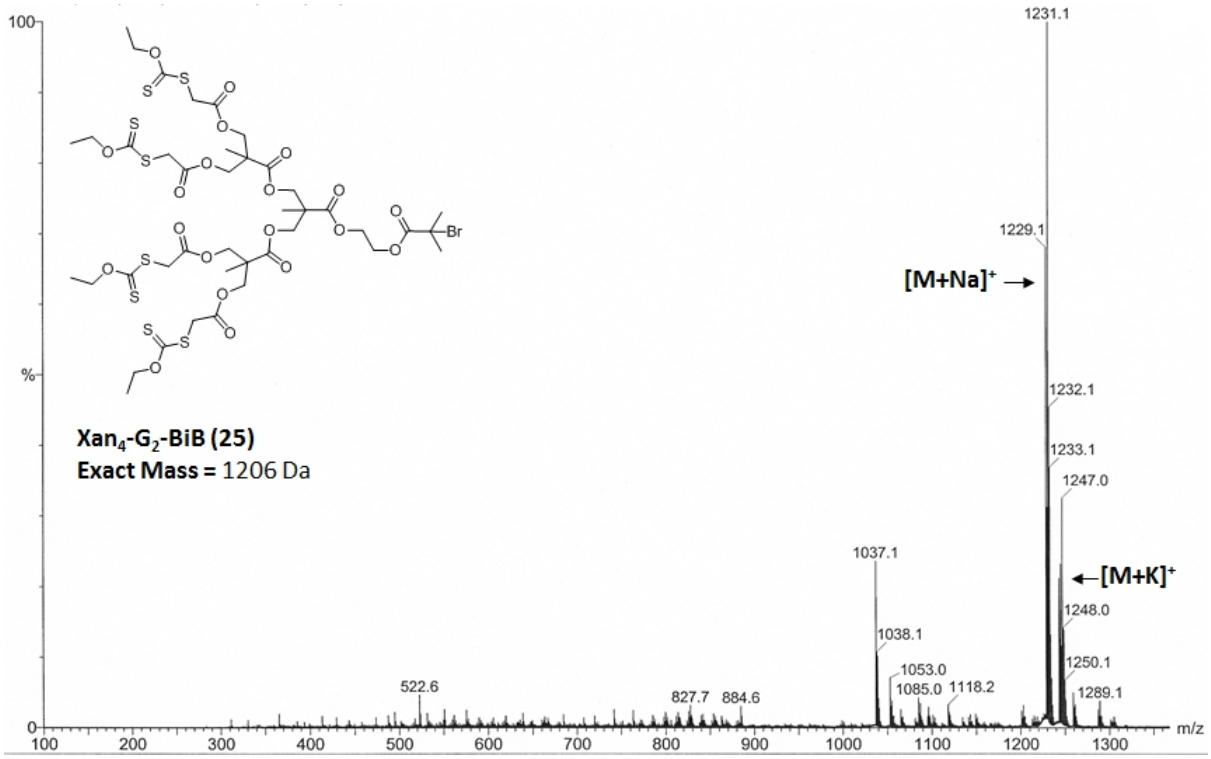

Figure S49. ESI-MS (MeOH) of **Xan_4-G_2-BiB, 25**

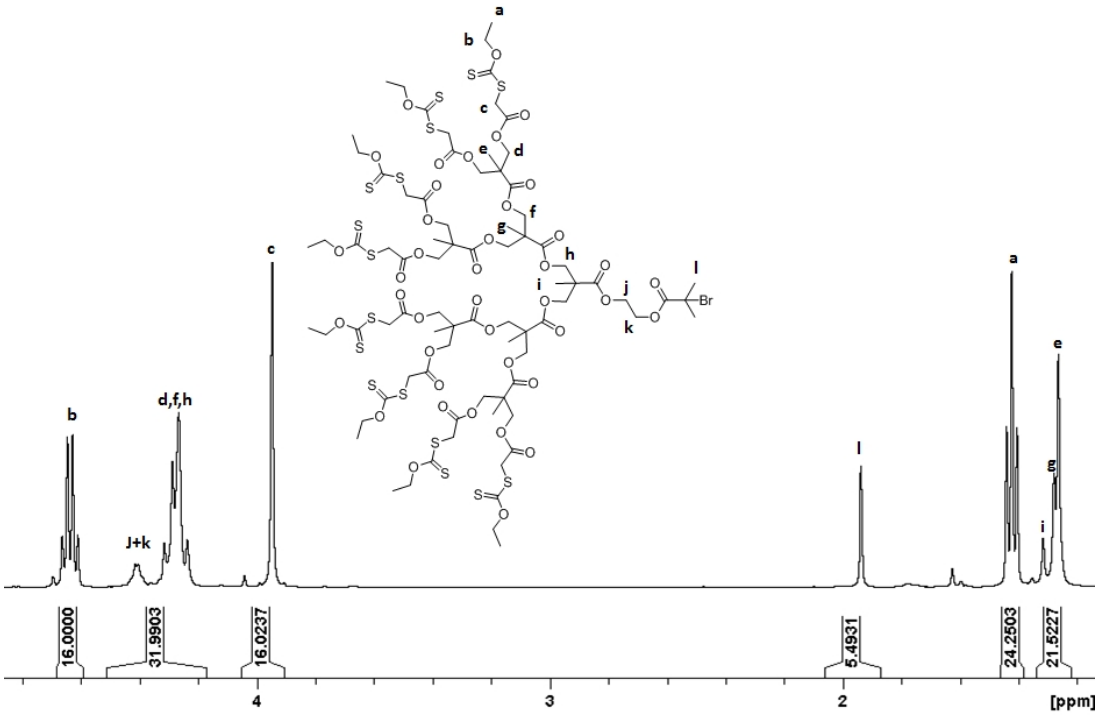

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-BiB, 26**

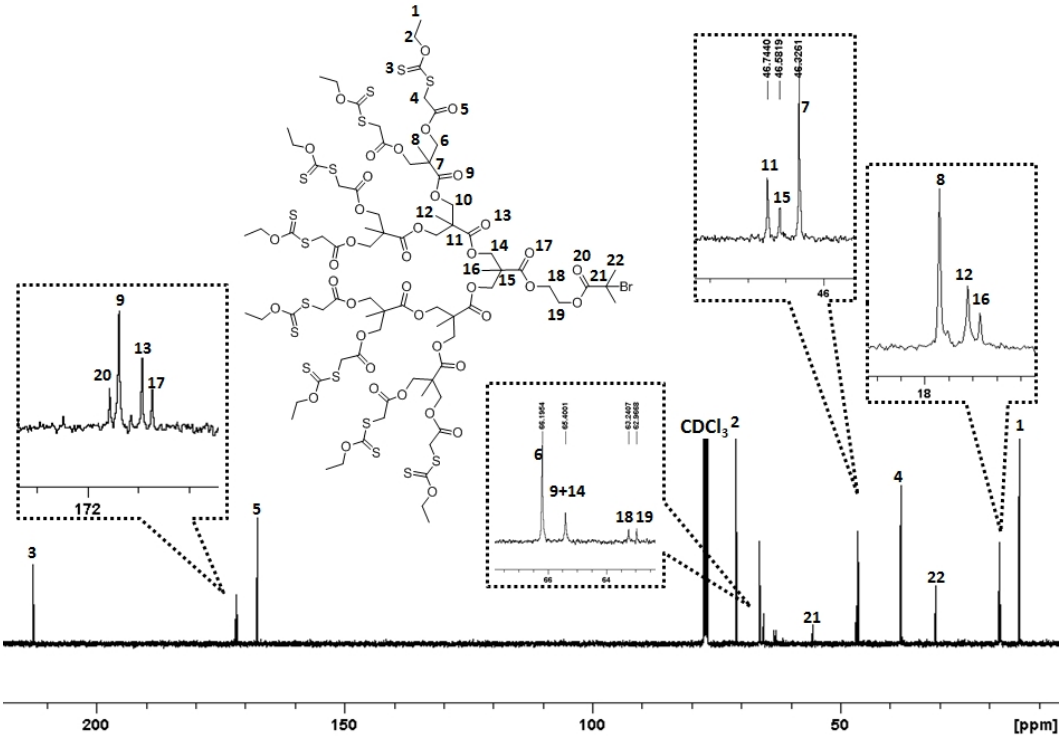

Figure S51. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-BiB, 26**

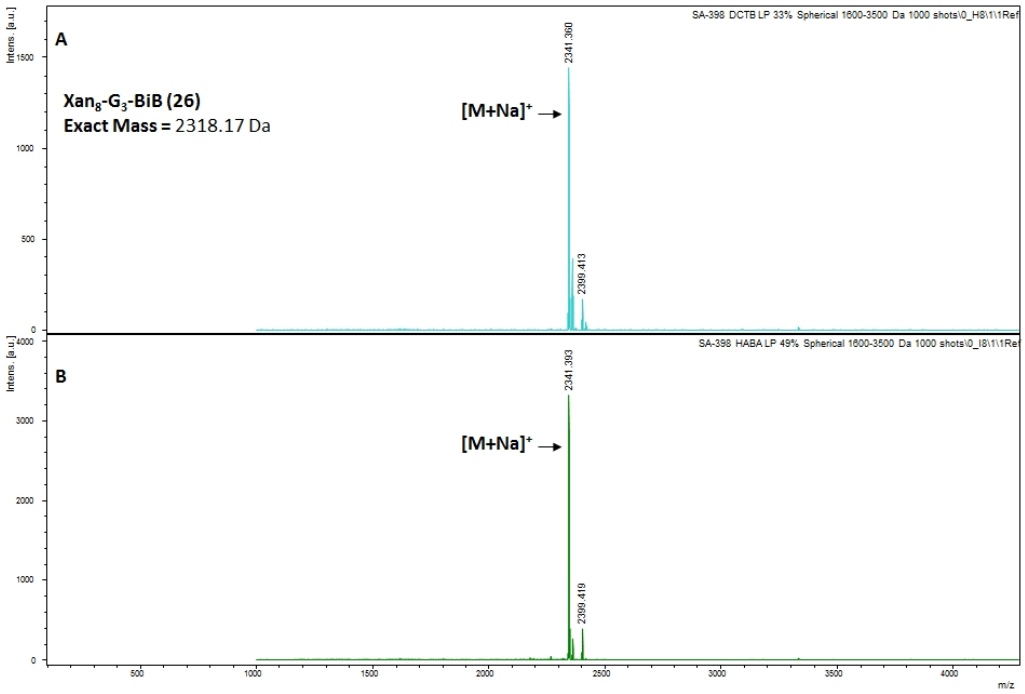

Figure S52. MALDI-TOF of **Xan_8-G_3-BiB (26).** (A) – Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB); (B) – Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA)

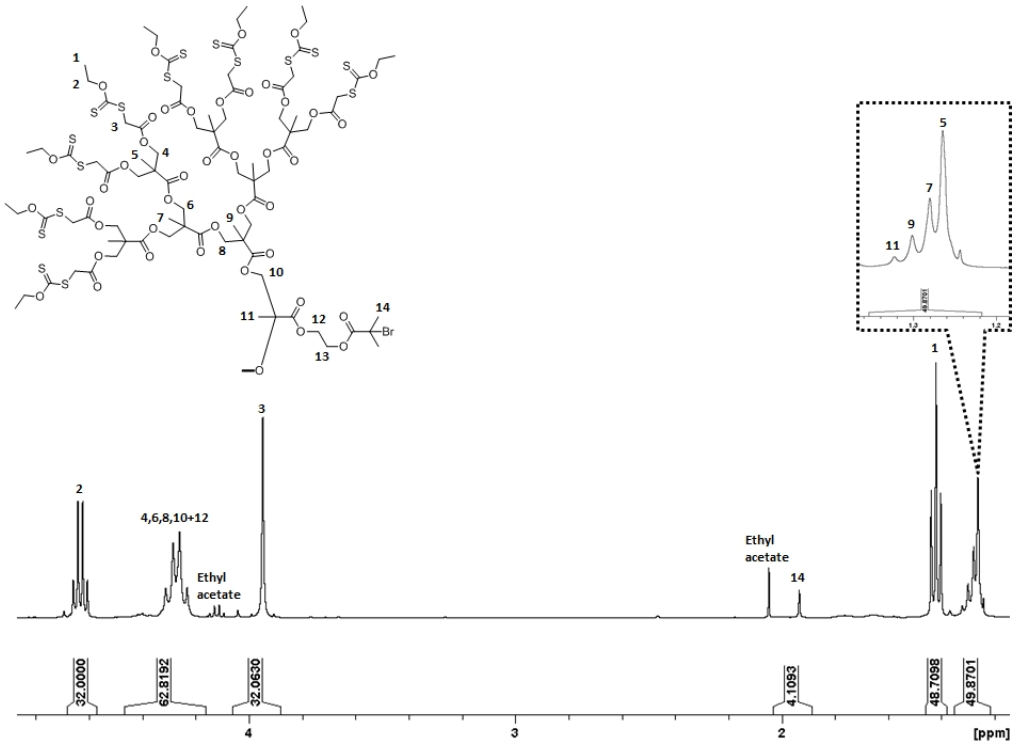

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-BiB, 27**

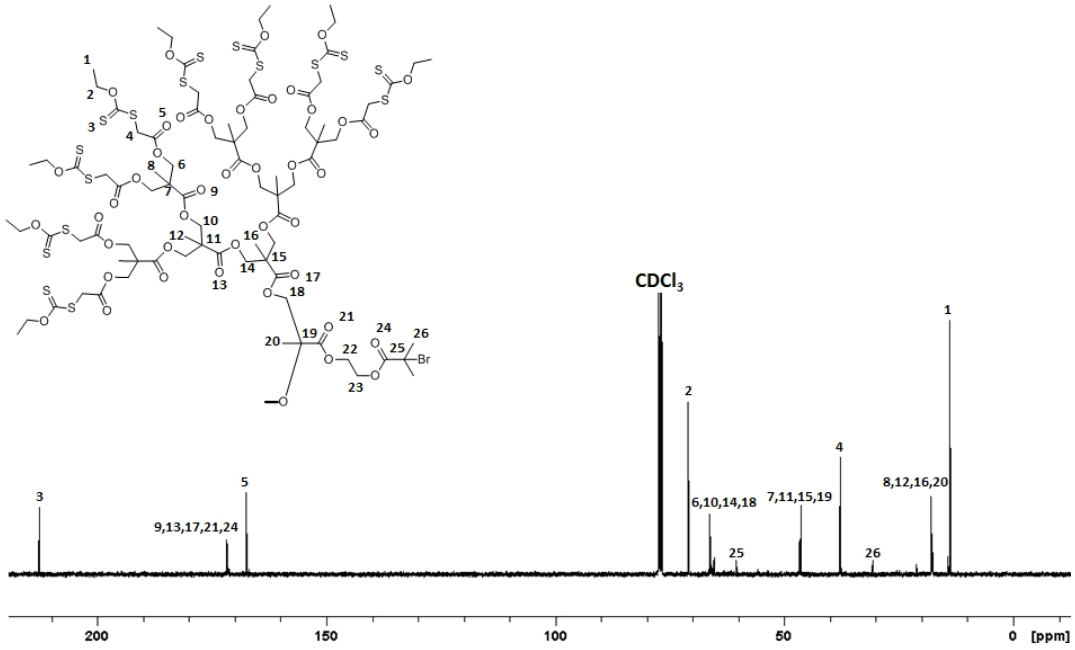

Figure S54. ^{13}C NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4-BiB, 27**

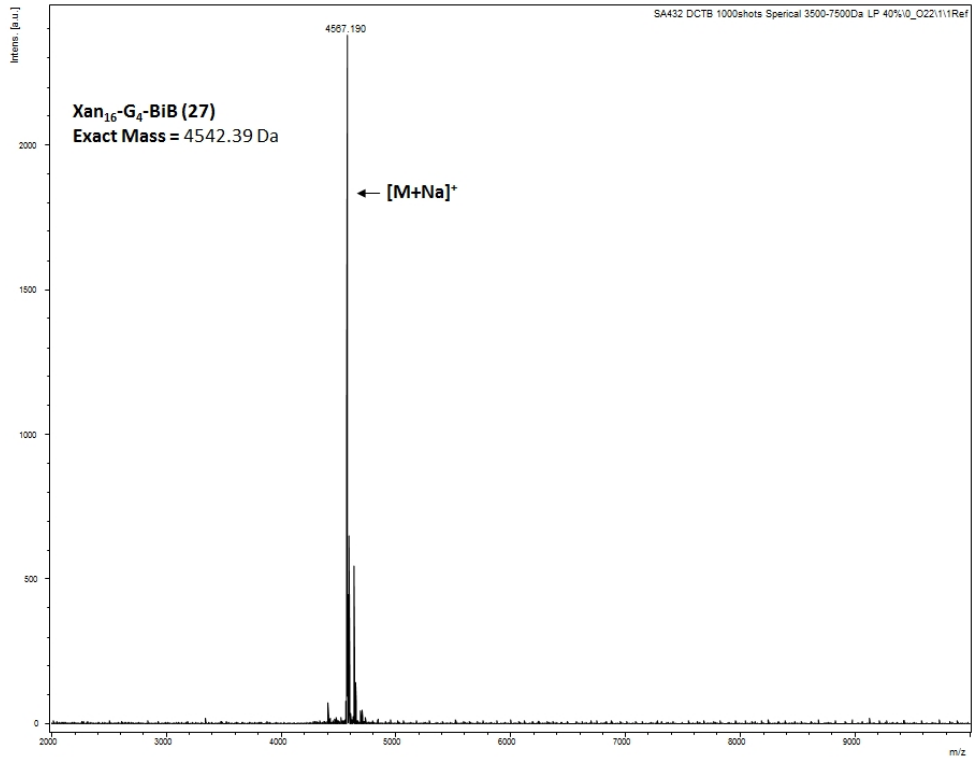

Figure S55. MALDI-TOF of **Xan_{16}-G_4-BiB (27).** Matrix = Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)

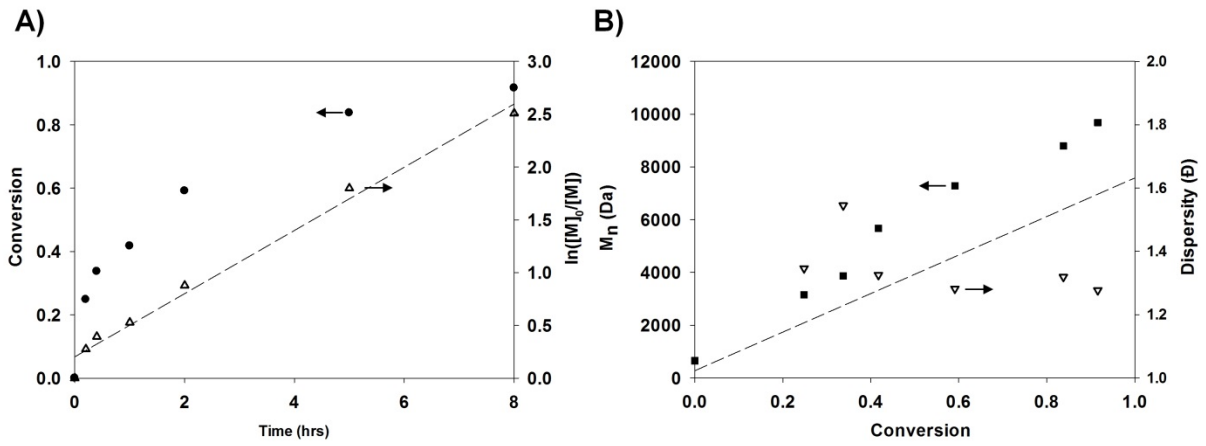

Figure S56. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for 2-isopropanol/water (92.7/7.5 v/v) ATRP of tertiary butyl methacrylate using **Xan_2-G_1-BiB, 24,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

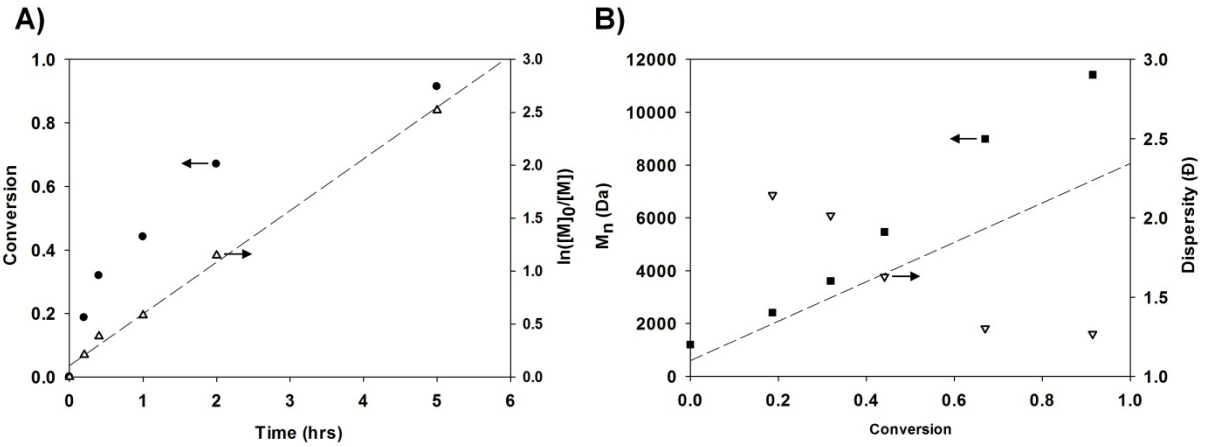

Figure S57. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for 2-isopropanol/water (92.7/7.5 v/v) ATRP of tertiary butyl methacrylate using **Xan_4-G_2-BiB, 25,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

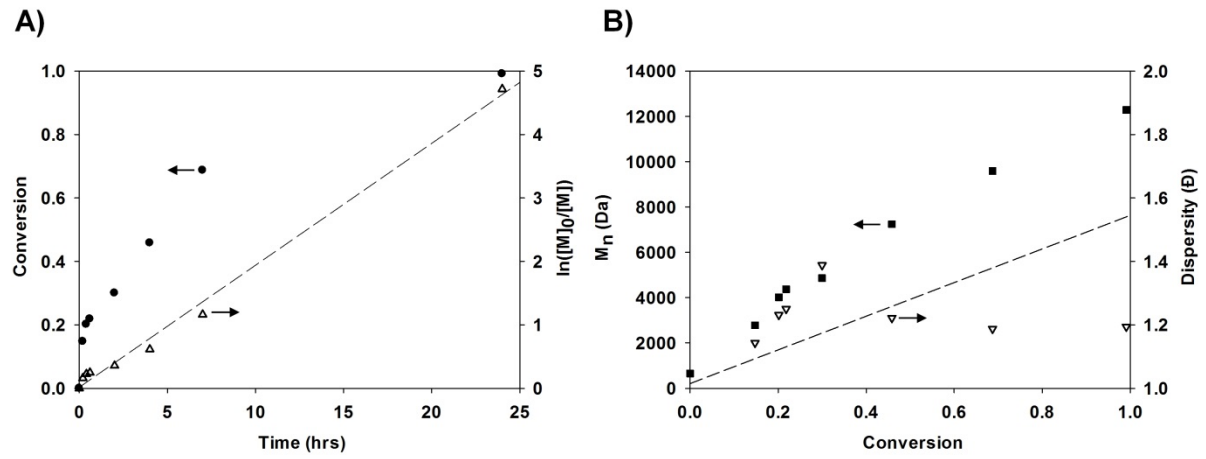

Figure S58. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for acetone ATRP of tertiary butyl methacrylate using **Xan$_2$-G$_1$-BiB, 24,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

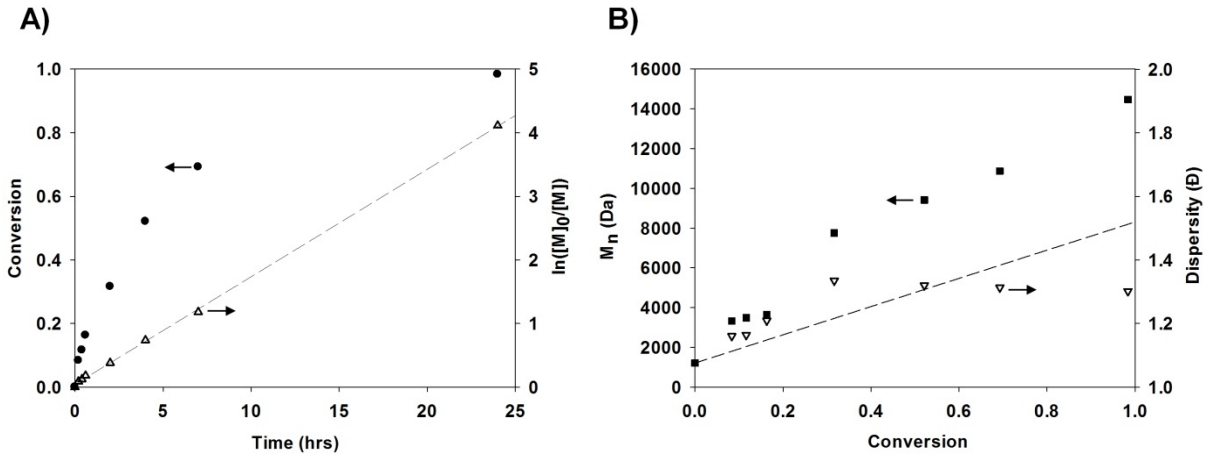

Figure S59. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for acetone ATRP of tertiary butyl methacrylate using **Xan$_4$-G$_2$-BiB , 25,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

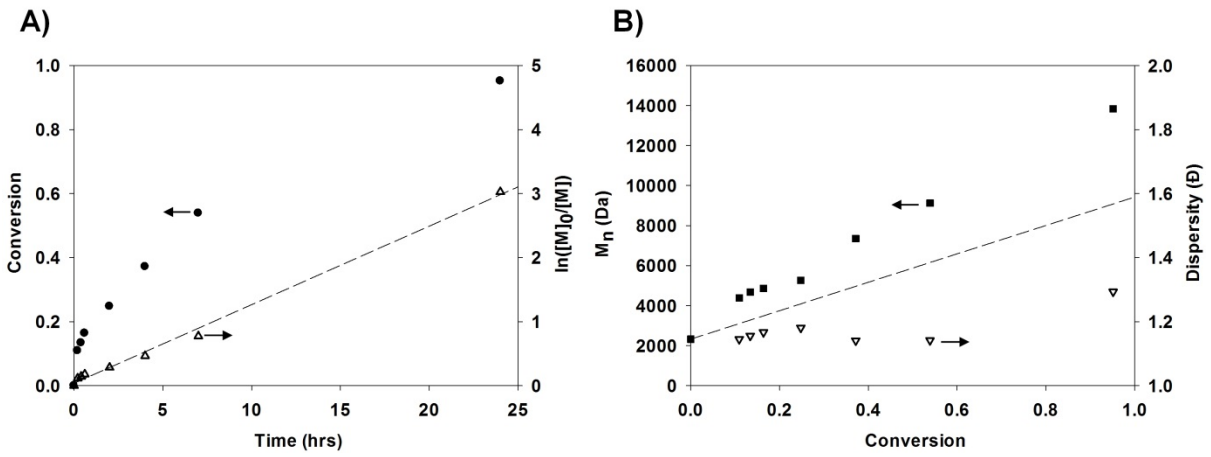

Figure S60. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for acetone ATRP of tertiary butyl methacrylate using **Xan$_8$-G$_3$-BiB, 26,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

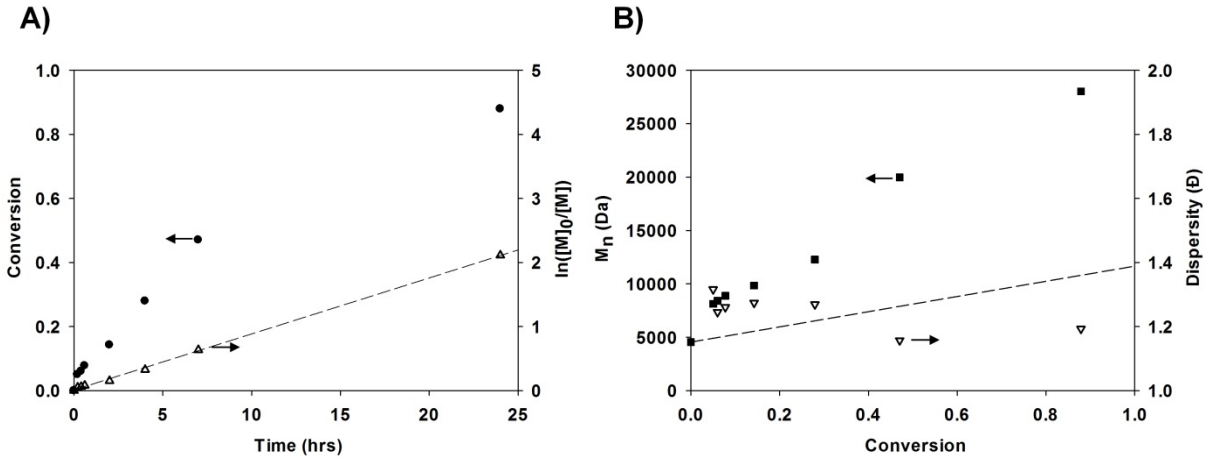

Figure S61. Kinetic studies of conversion *vs.* polymerisation time and evolution of molecular weight for acetone ATRP of tertiary butyl methacrylate using **Xan$_{16}$-G$_4$-BiB, 27,** to a targeted DP_n = 50 monomer units. (**A**) – Conversion *vs.* time plot (closed black circles) and corresponding semi-logarithmic plot (open black upward triangles). The dotted line represents a linear regression of the semi-logarithmic plot. (**B**) – M_n *vs.* conversion (closed black squares) and corresponding dispersity (Đ) *vs.* conversion (open black downward triangles). The dotted line represents the theoretical M_n.

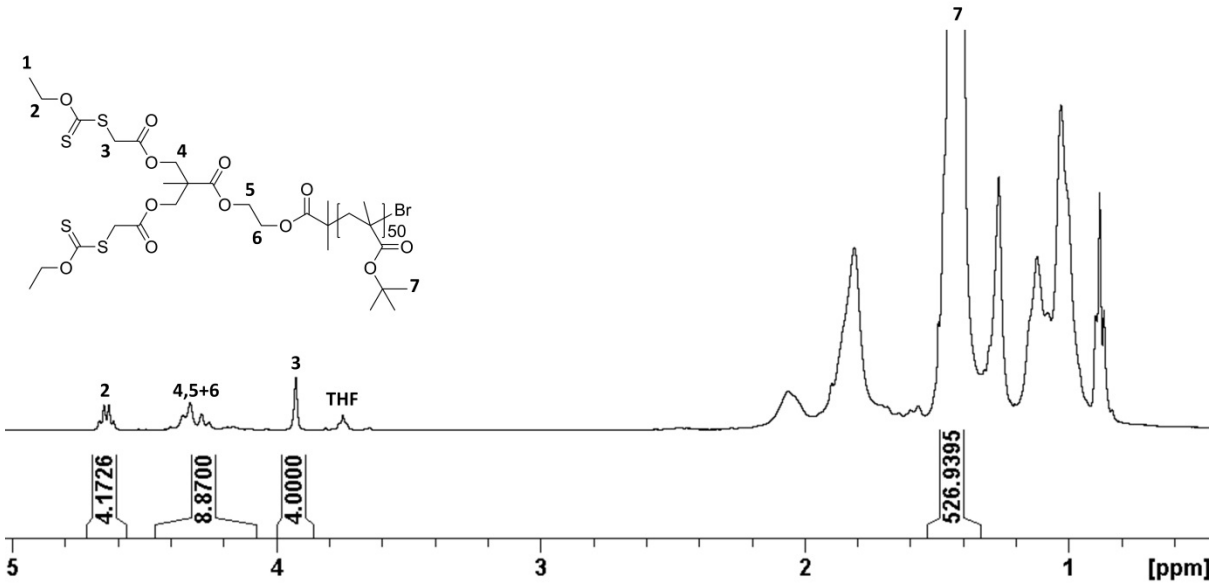

Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1p(tBuMA$_{50}$), 29**

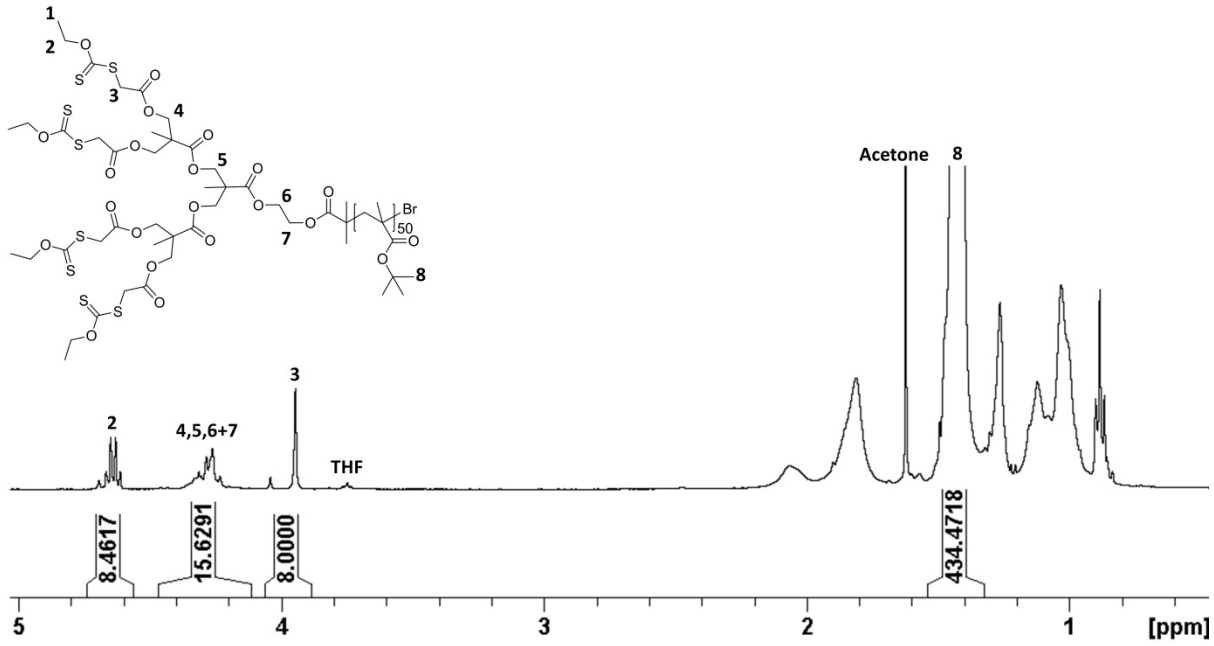

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_4-G_2p(tBuMA$_{50}$), 30**

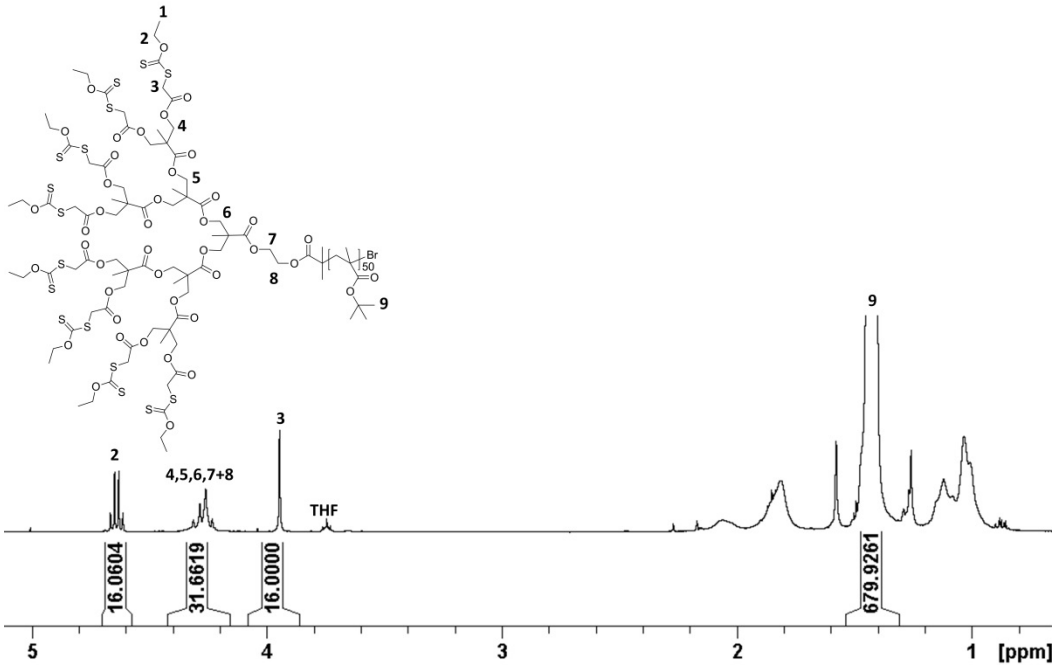

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3p(tBuMA$_{50}$), 33**

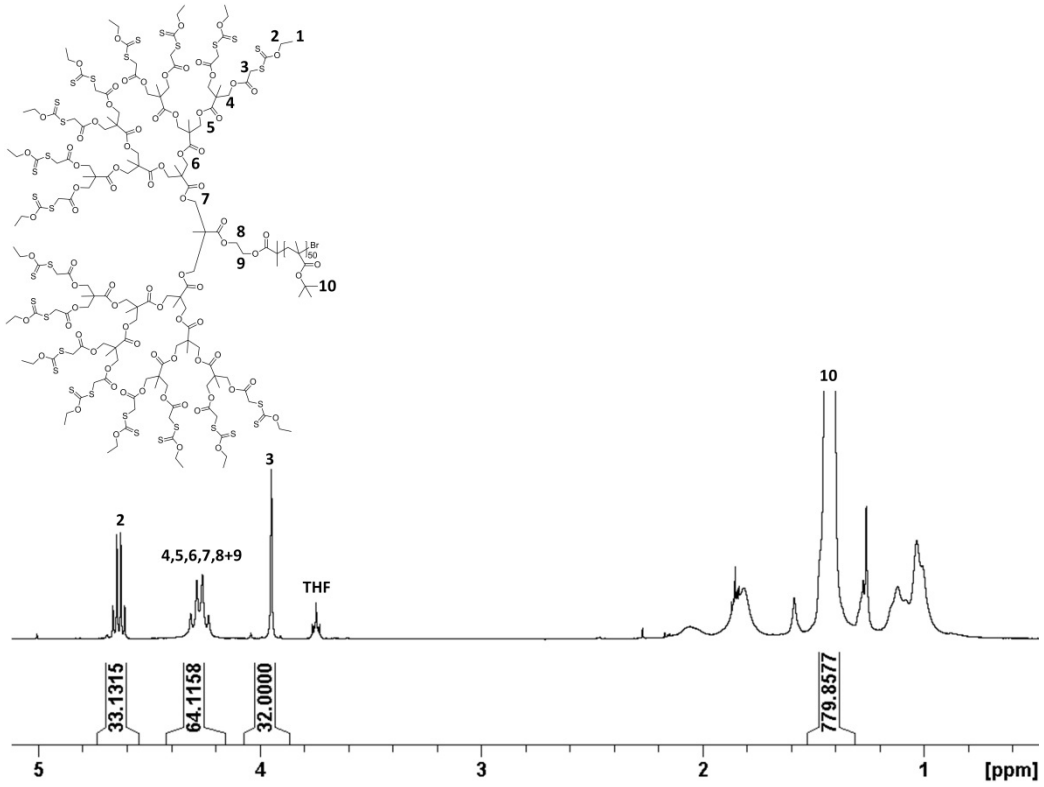

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_{16}-G_4p(tBuMA$_{50}$), 34**

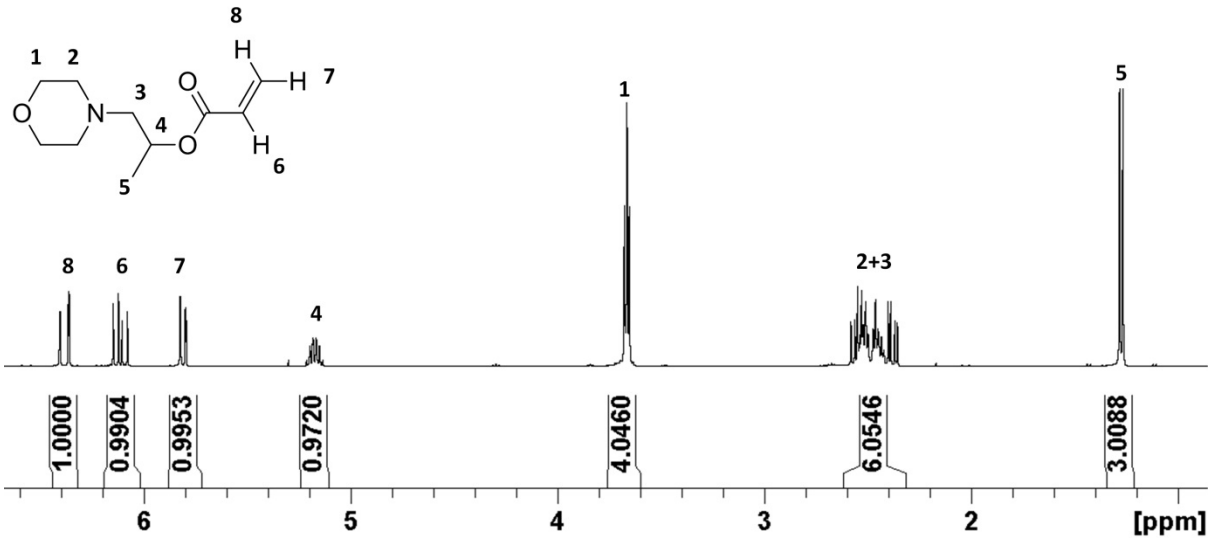

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of **Morpholino propanyl acrylate, 41**

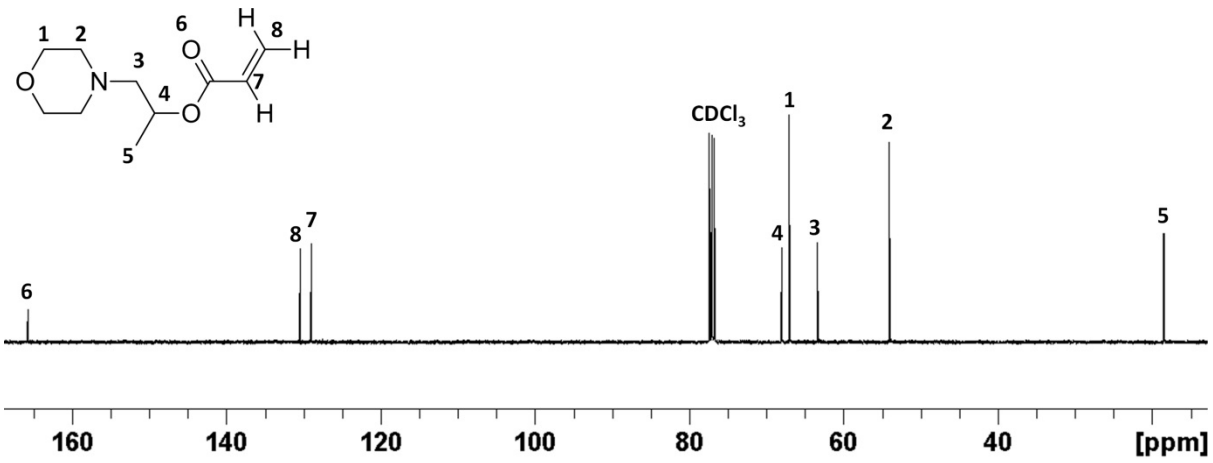

Figure S67. ^{13}C NMR (400 MHz, $CDCl_3$) of **Morpholino propanyl acrylate, 41**

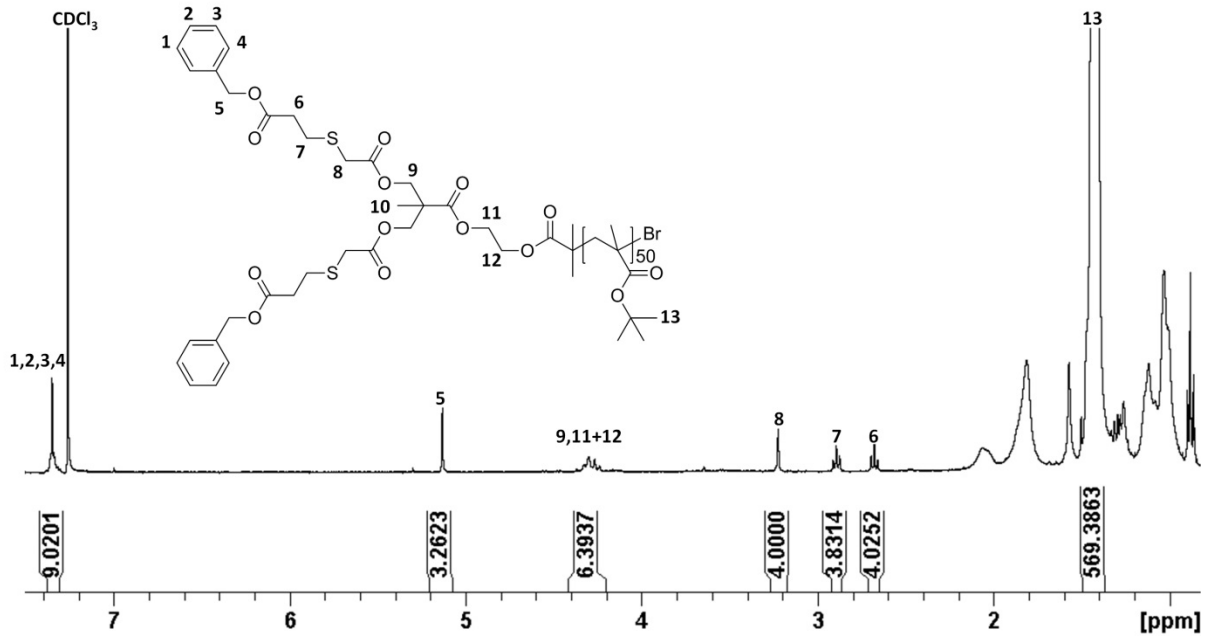

Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of **Bzy_2-G_1p($tBuMA_{50}$), 42**

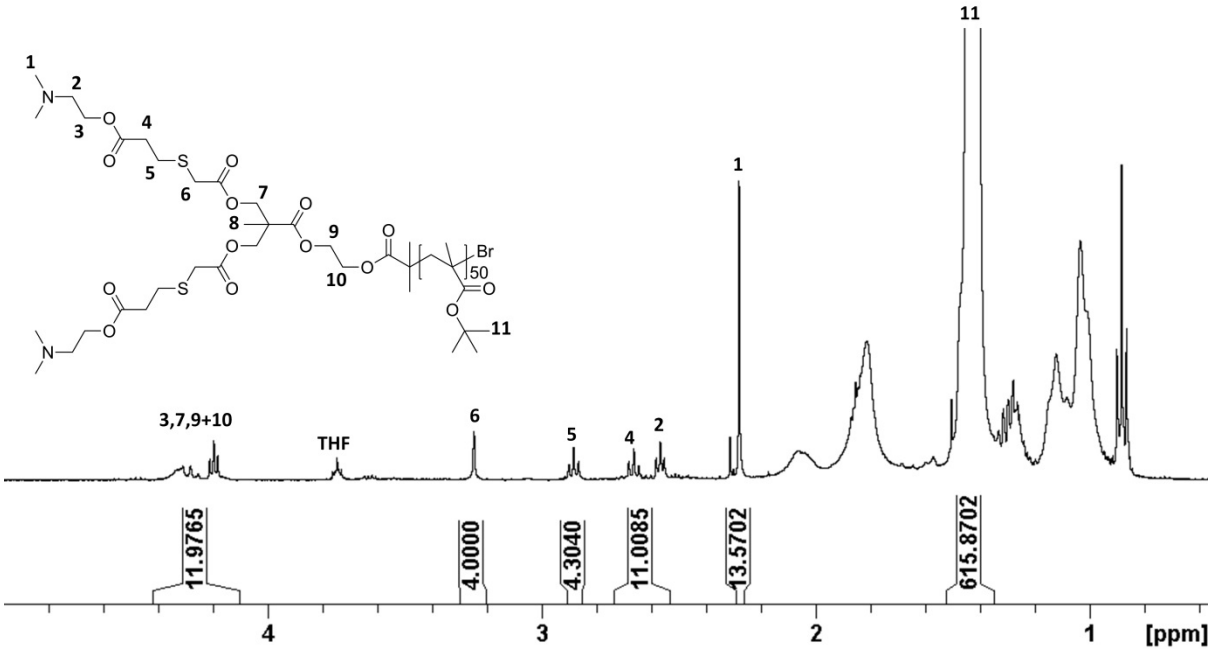

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) of **Am_2-G_1p($tBuMA_{50}$), 43**

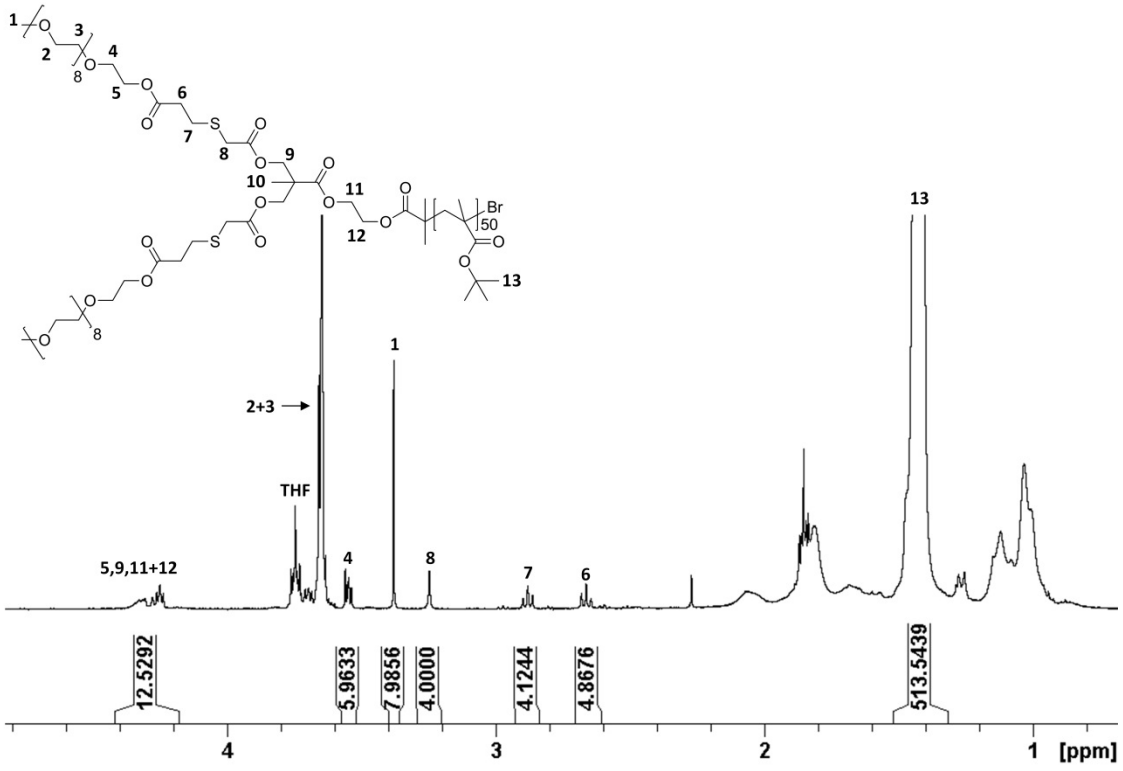

Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of **OEG_2-G_1p($tBuMA_{50}$), 44**

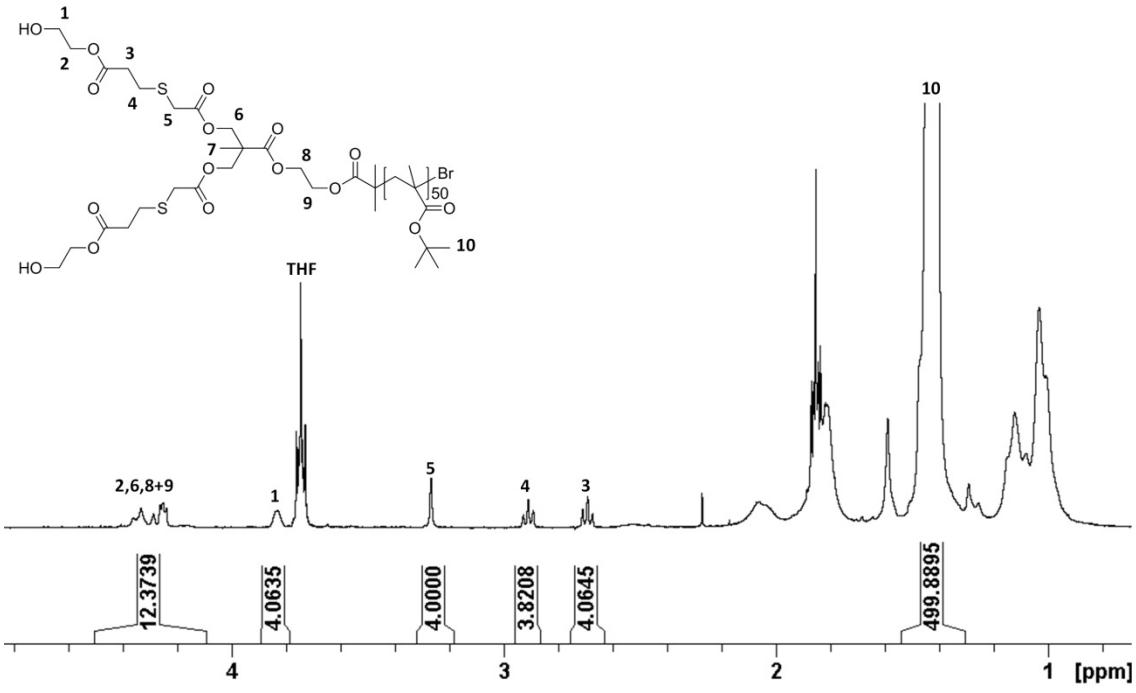

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Hydx_2$-G_1p($tBuMA_{50}$), 45**

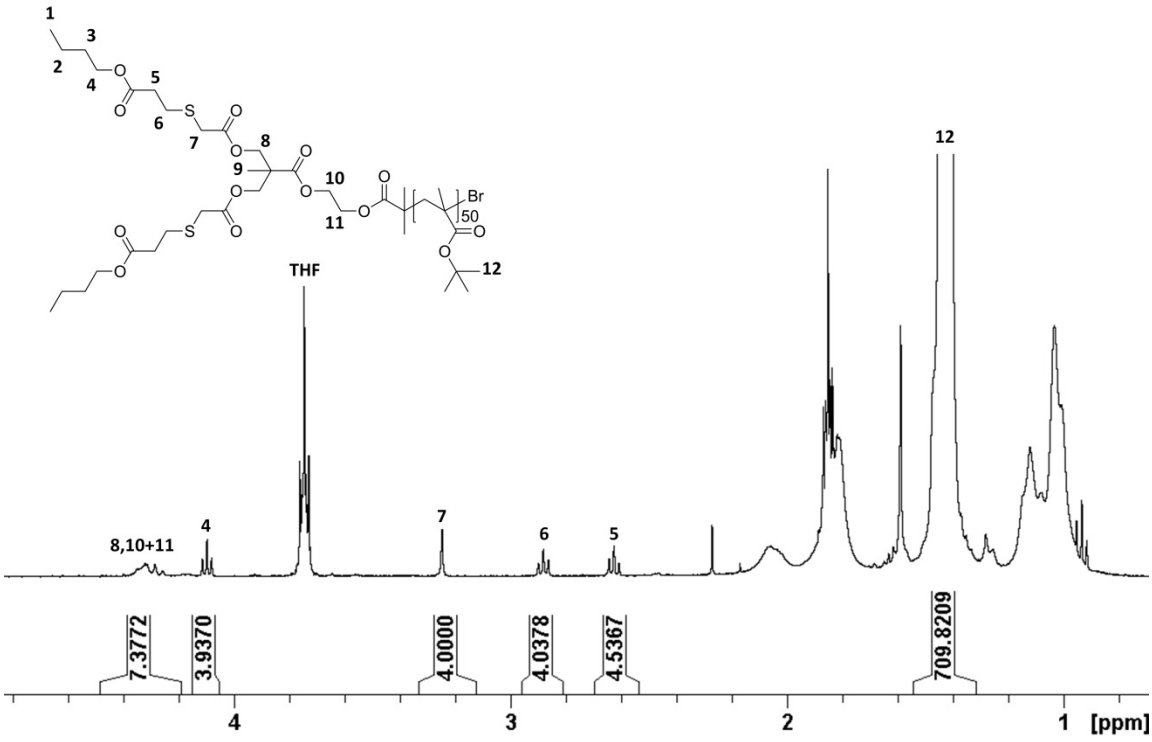

Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of **Butyl$_2$-G$_1$p(tBuMA$_{50}$), 46**

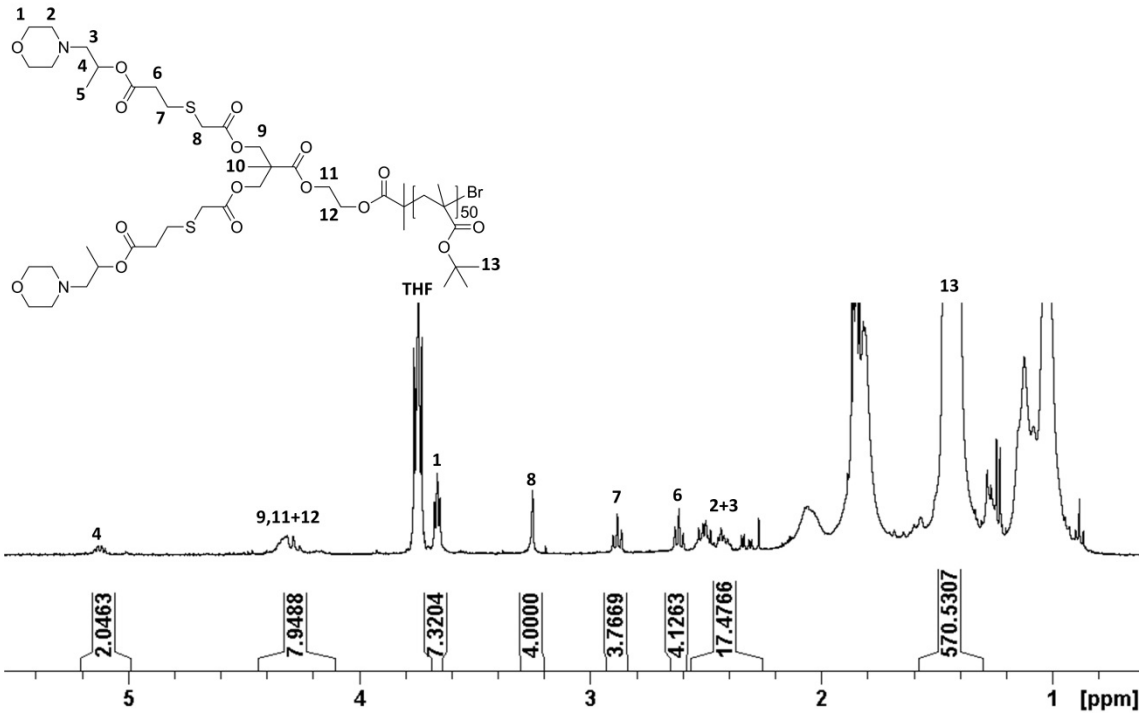

Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) of Morph$_2$-G$_1$p(tBuMA$_{50}$), **47**

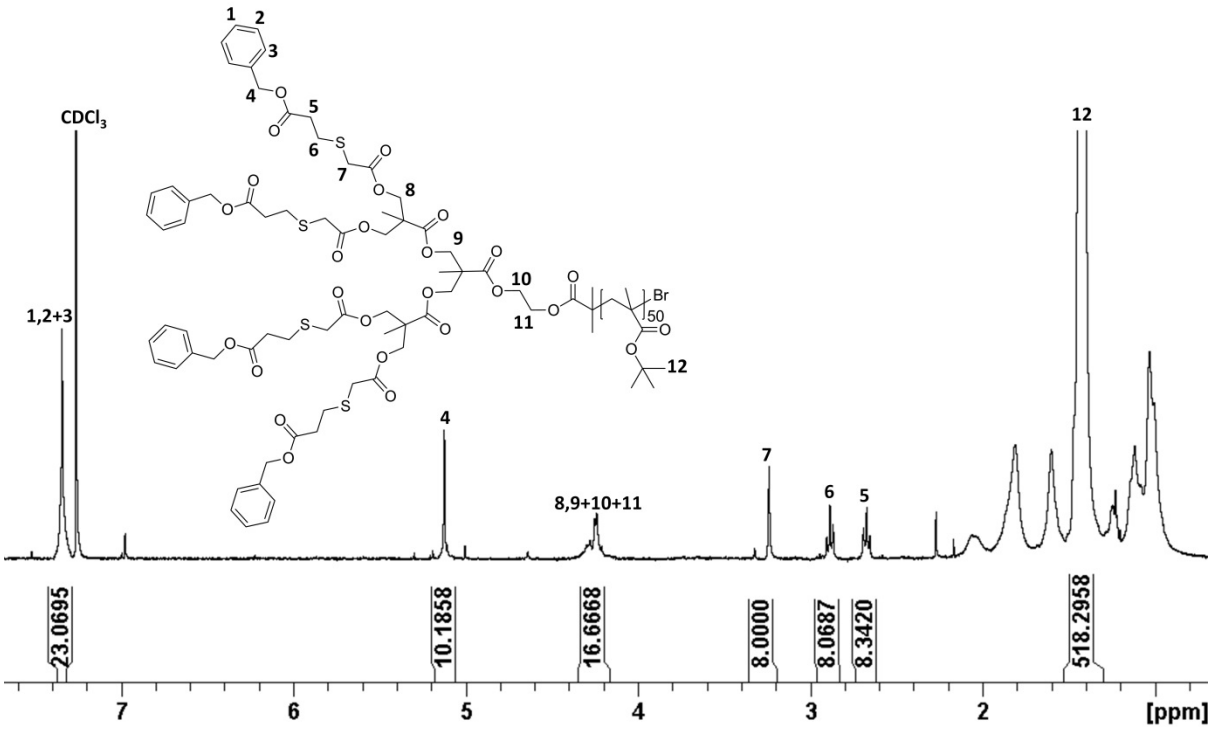

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of **Bzy_4-G_2p(tBuMA$_{50}$)**, **48**

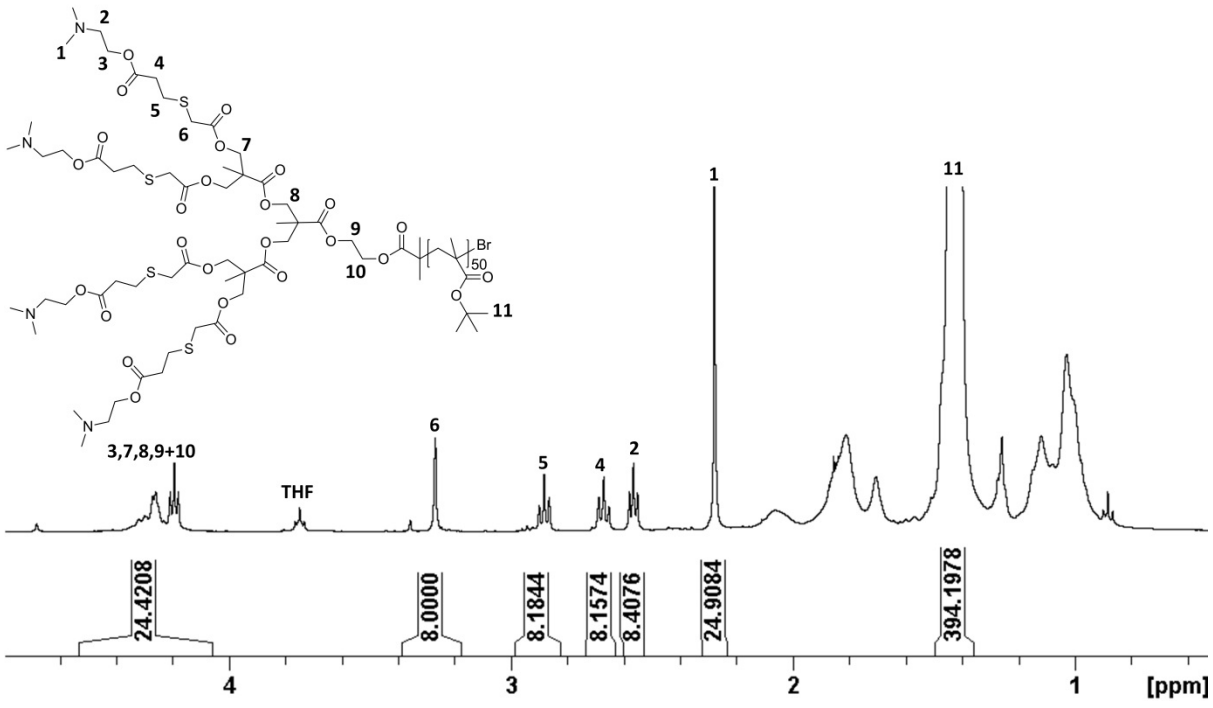

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of **Am_4-G_2p(tBuMA$_{50}$)**, **49**

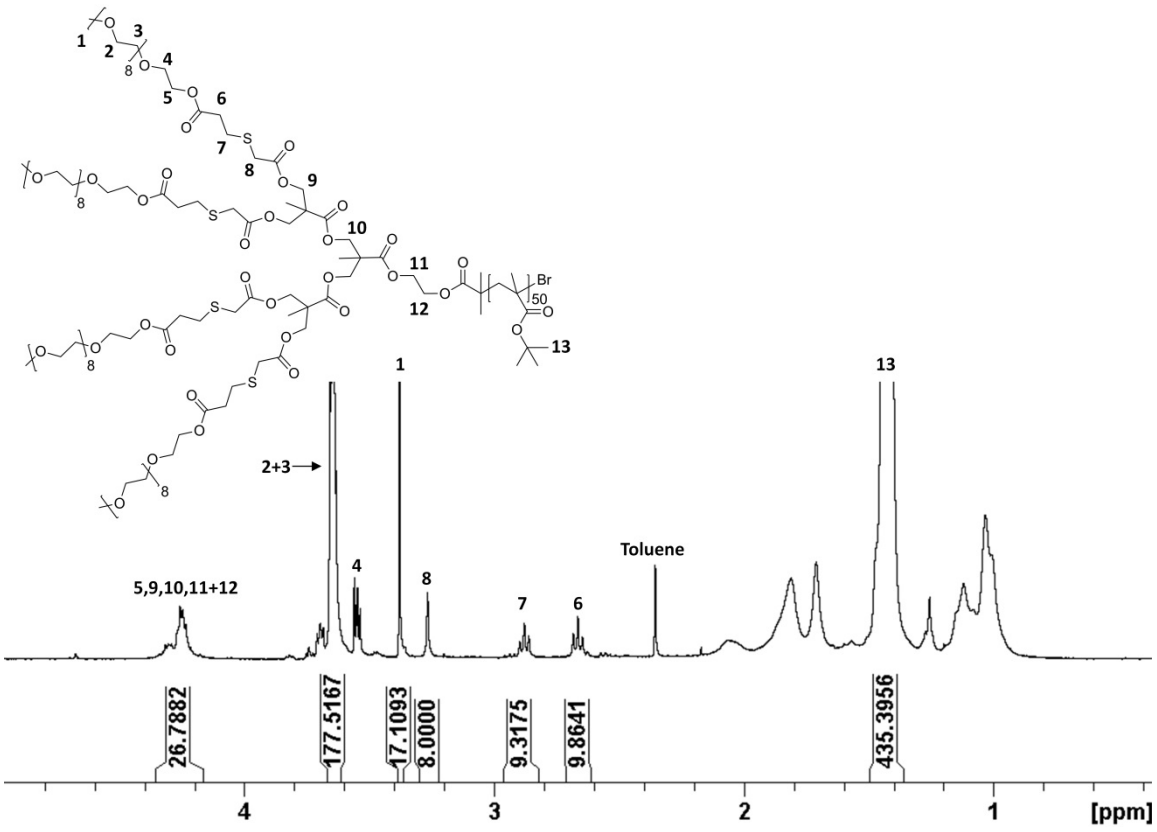

Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) of **OEG_4-G_2p($tBuMA_{50}$)**, **50**

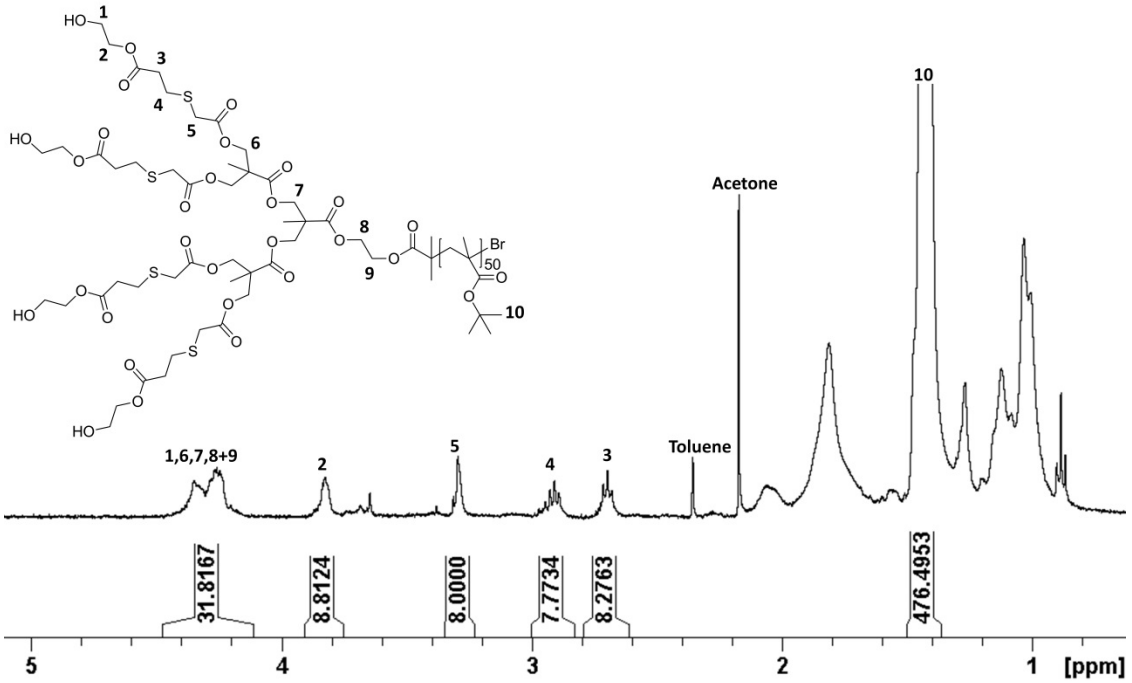

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Hydx_4$-G_2p($tBuMA_{50}$)**, **51**

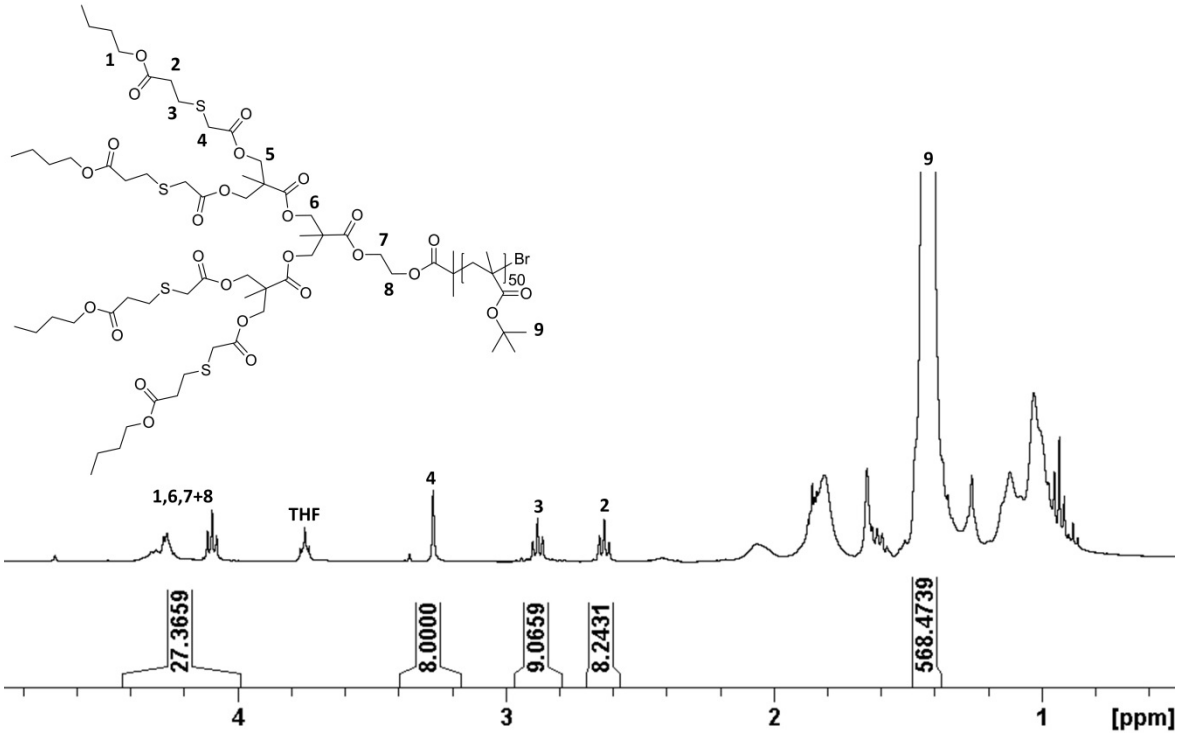

Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of **Butyl$_4$-G$_2$p(tBuMA$_{50}$)**, **52**

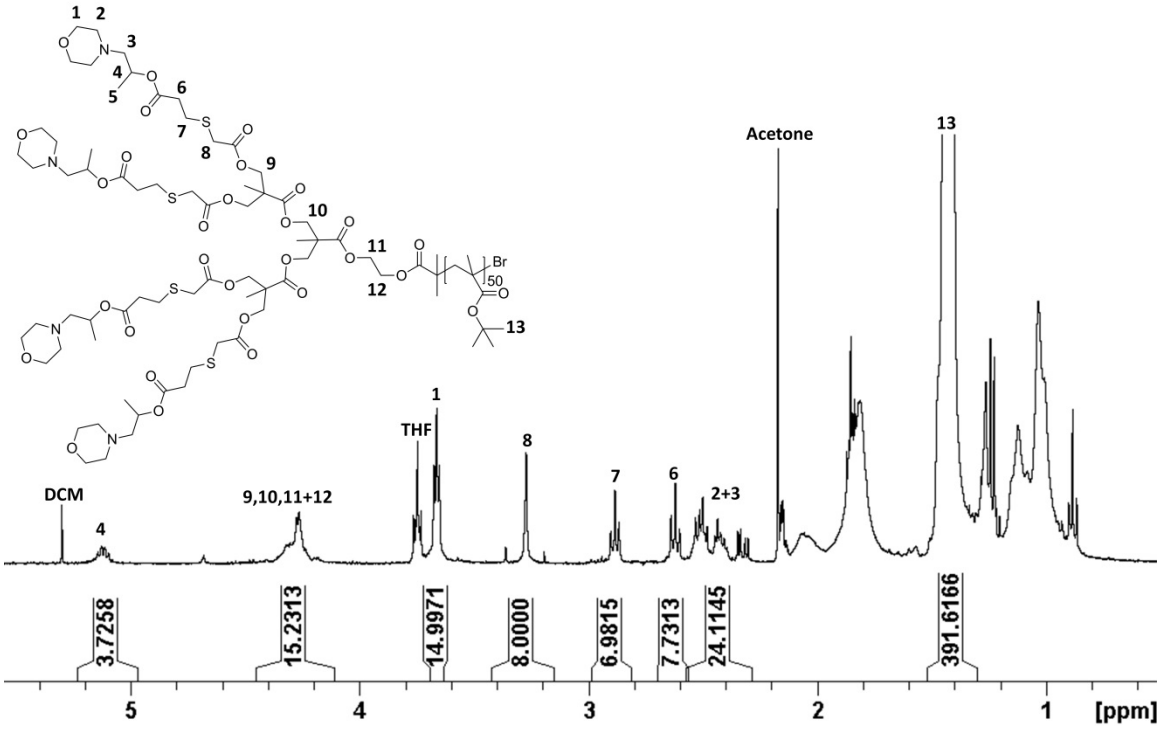

Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of **Morph$_4$-G$_2$p(tBuMA$_{50}$), 53**

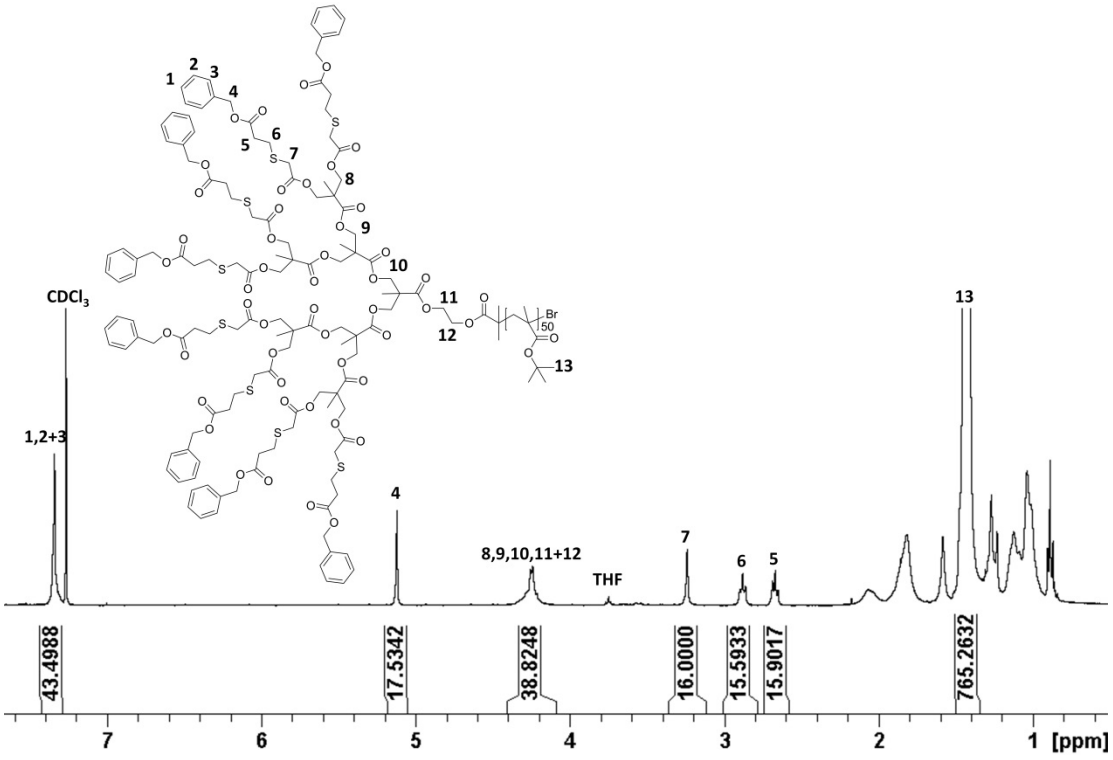

Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) of **Bzy_8-G_3p($tBuMA_{50}$)**, **54**

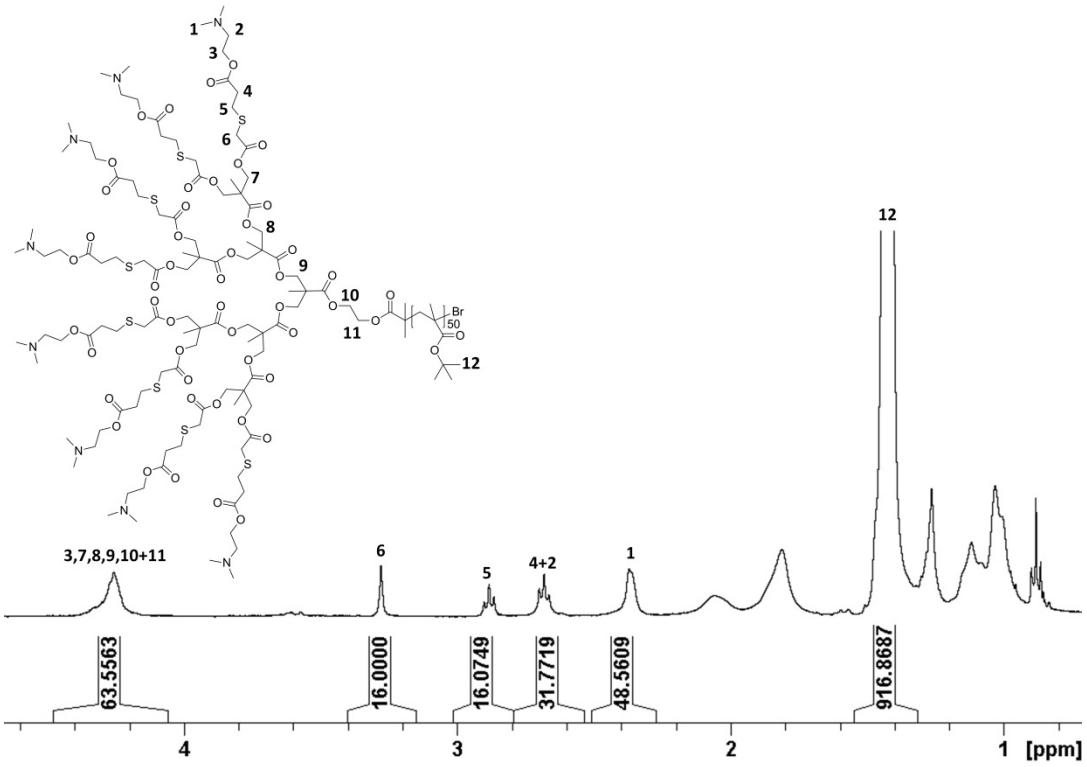

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) of **Am_8-G_3p($tBuMA_{50}$)**, **55**

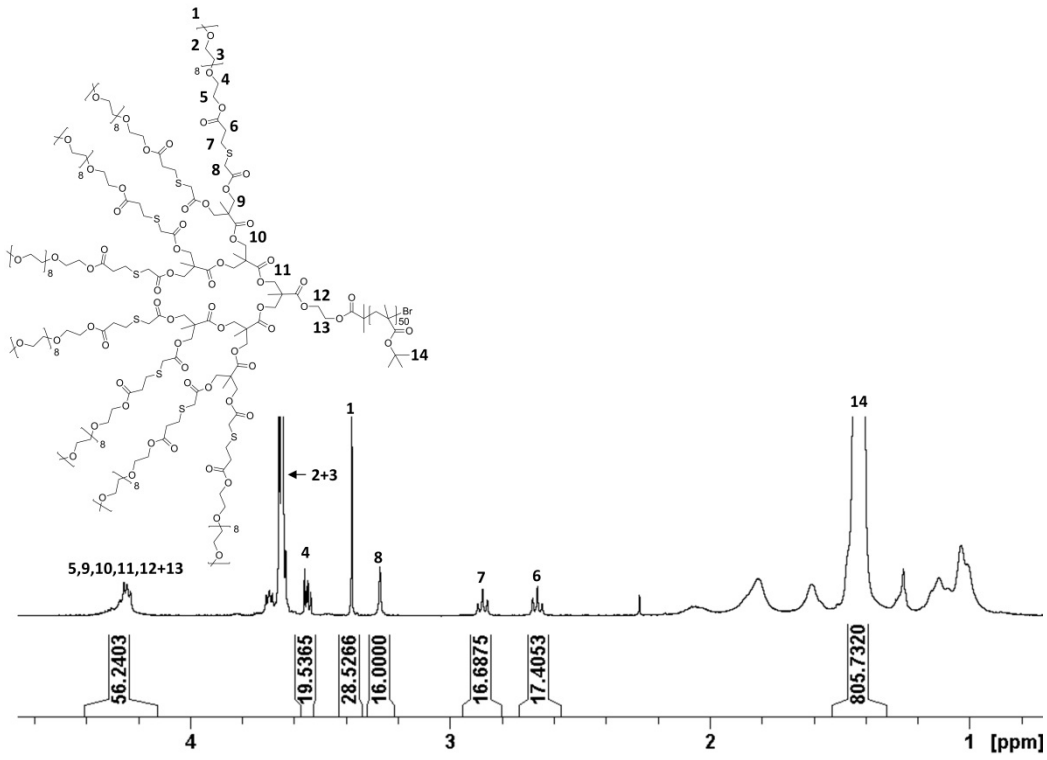

Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of **OEG_8-G_3p($tBuMA_{50}$), 56**

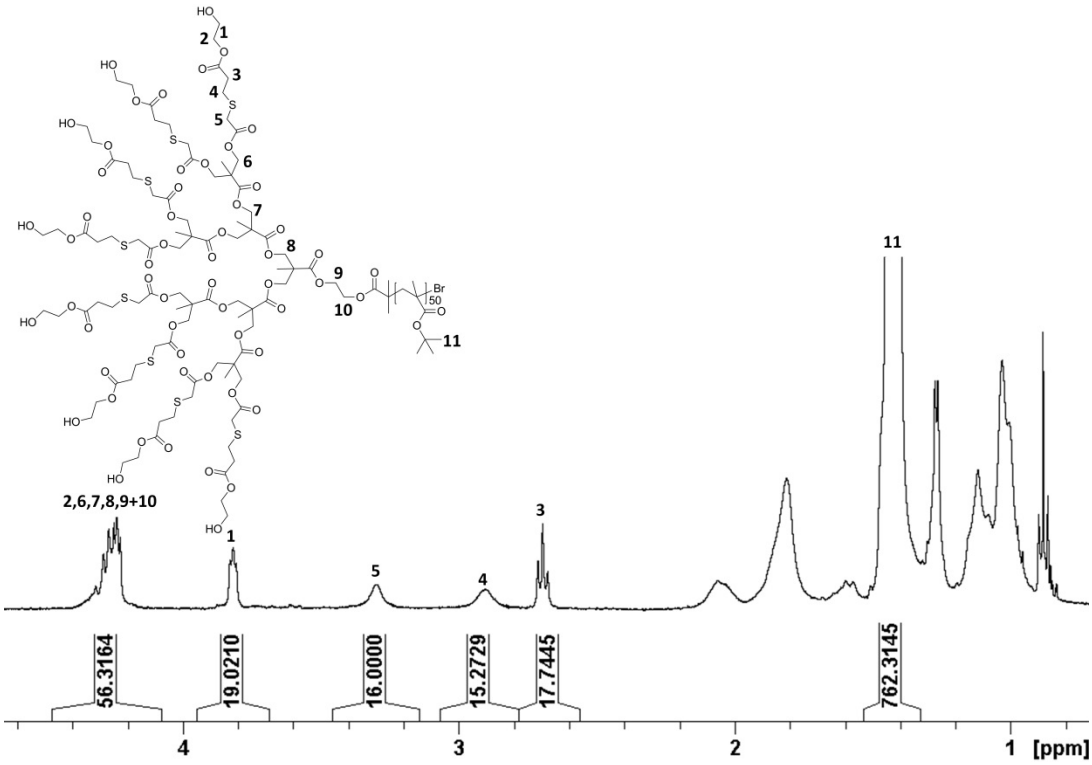

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Hydx_8$-G_3p($tBuMA_{50}$)**, **57**

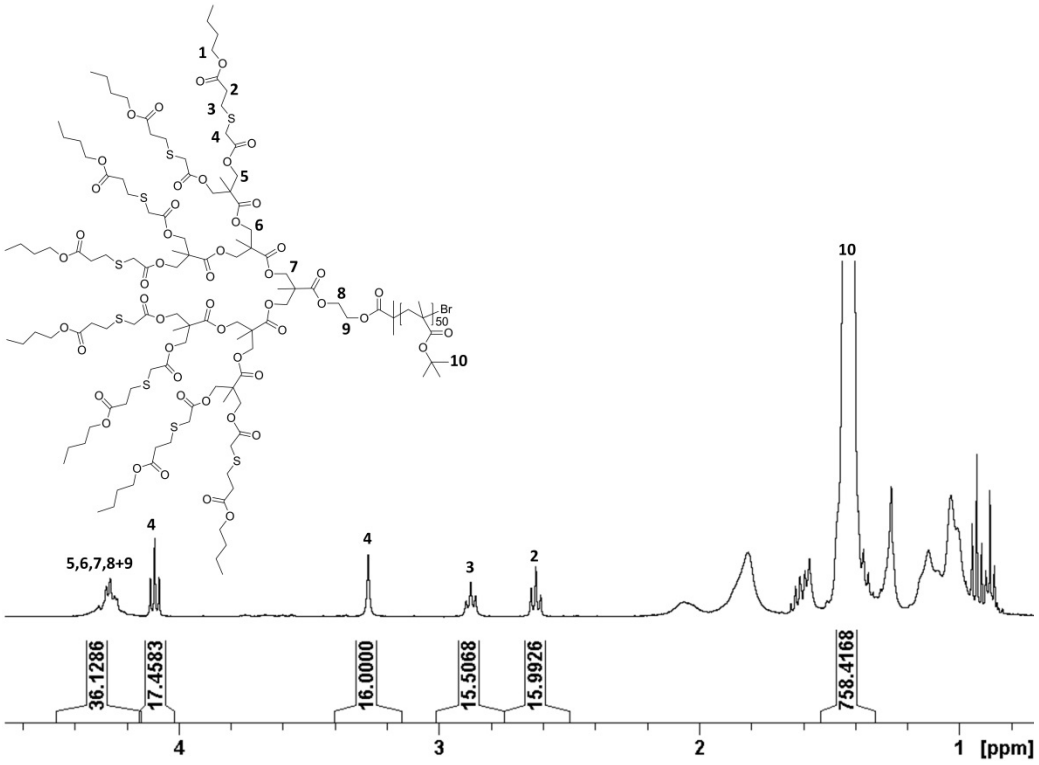

Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) of **Butyl$_8$-G$_3$p(tBuMA$_{50}$)**. **58**

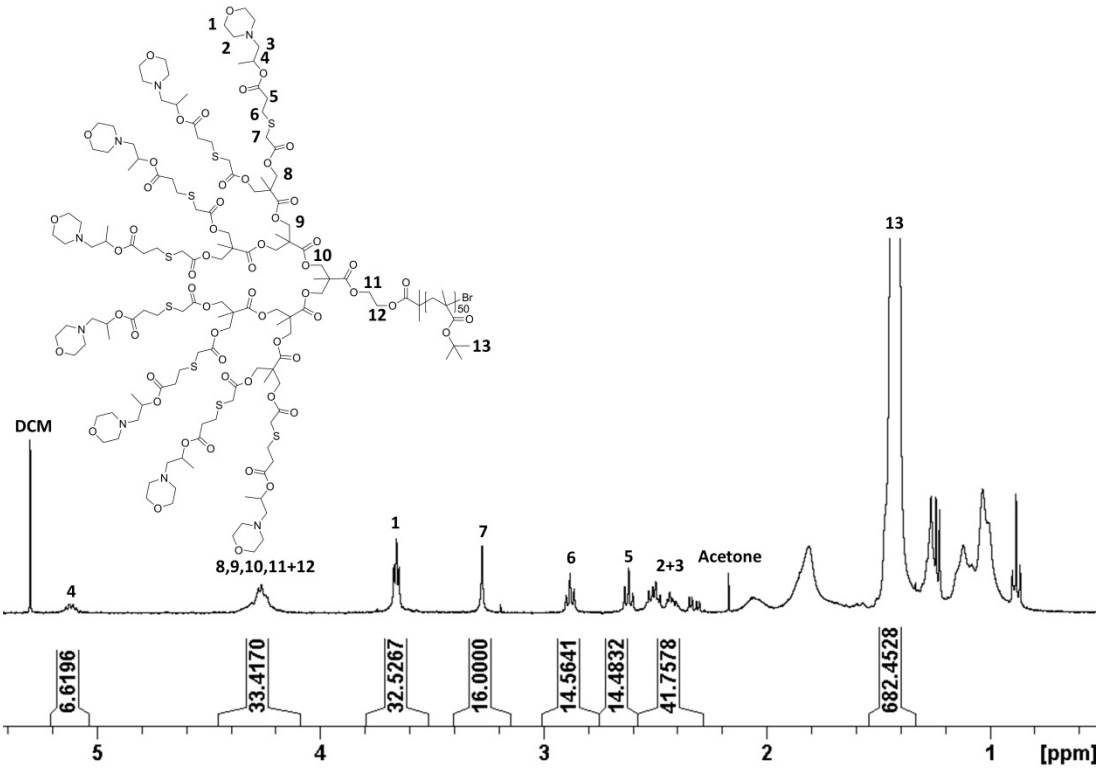

Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) of **Morph$_8$-G$_3$p(tBuMA$_{50}$)**, **59**

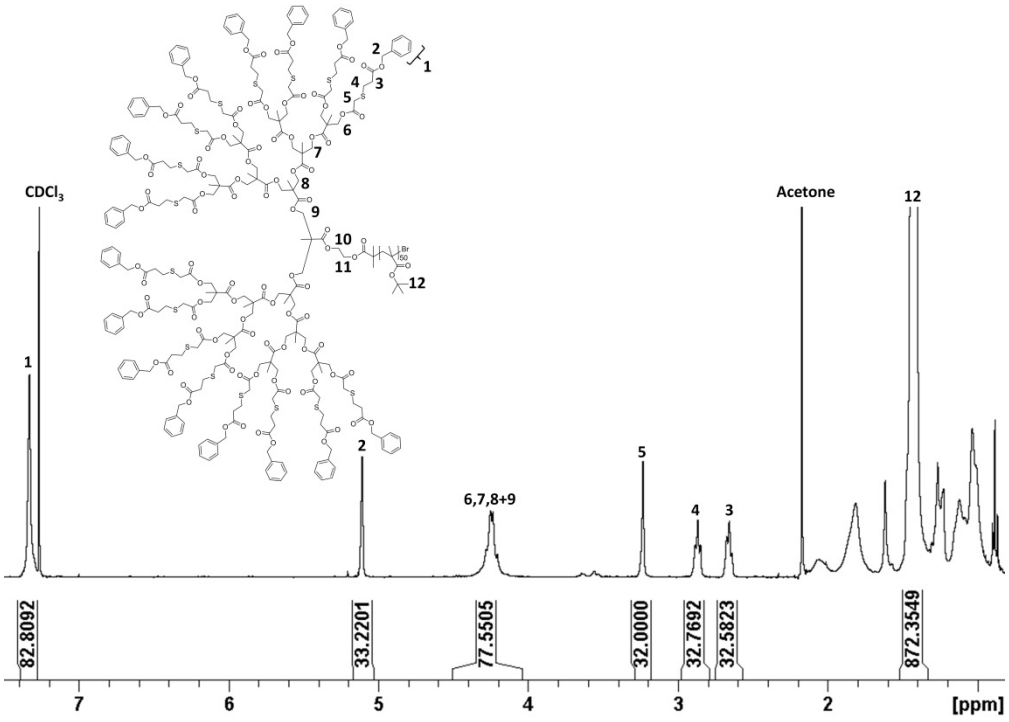

Figure S86. ^{1}H NMR (400 MHz, $CDCl_3$) of **Bzy_{16}-G_4p(tBuMA$_{50}$)**, **60**

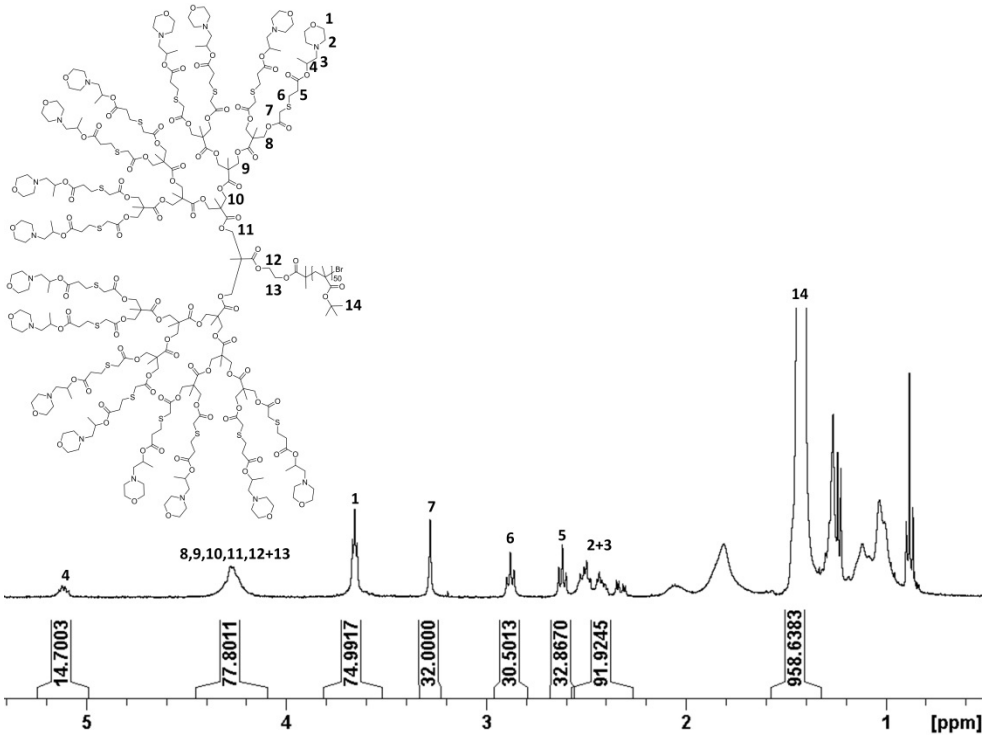

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Morph_{16}$-G_4p(tBuMA$_{50}$)**, **61**

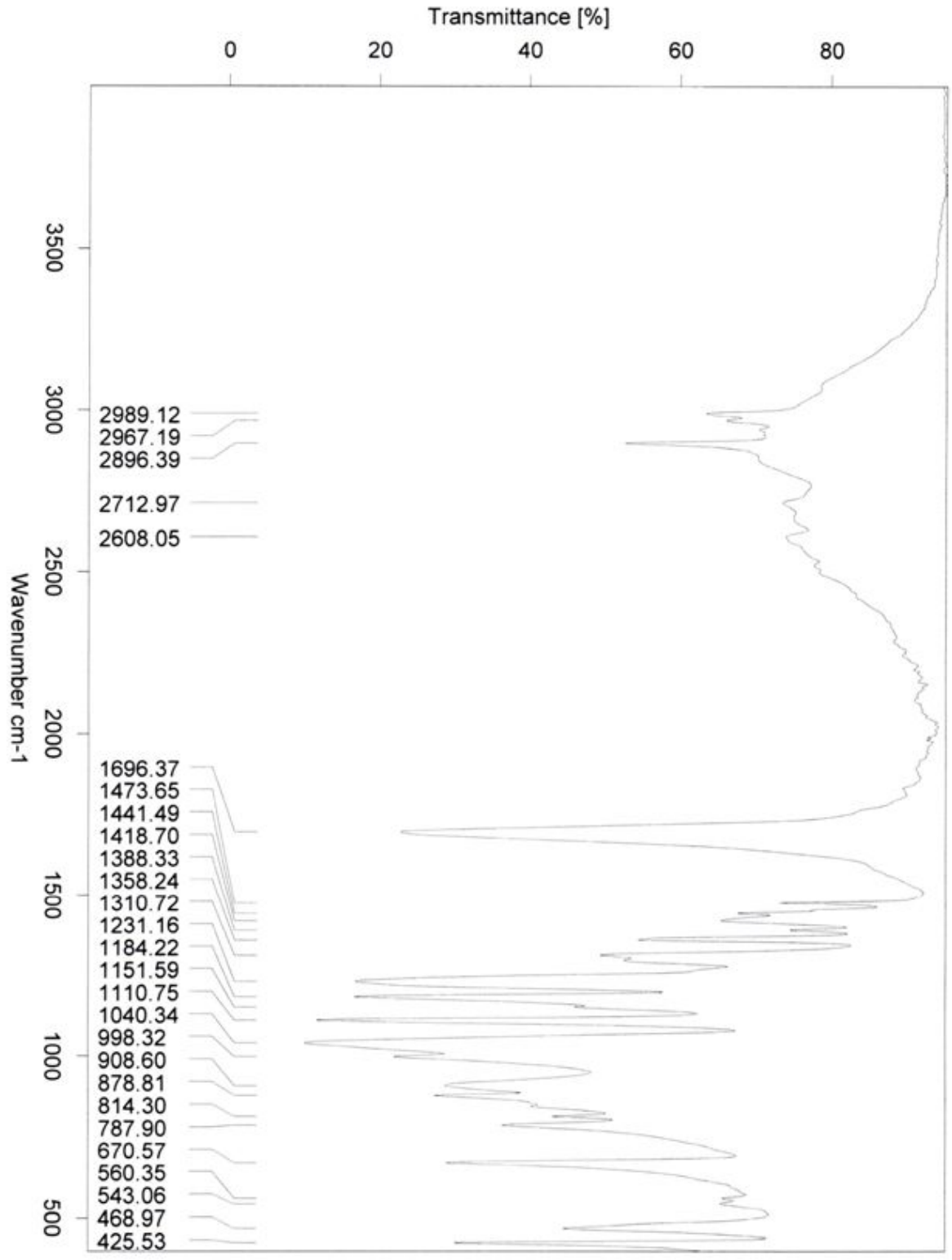

Figure S88. FTIR spectrum of **2-((Ethoxycarbonothioyl)thio)acetic acid (13)**.

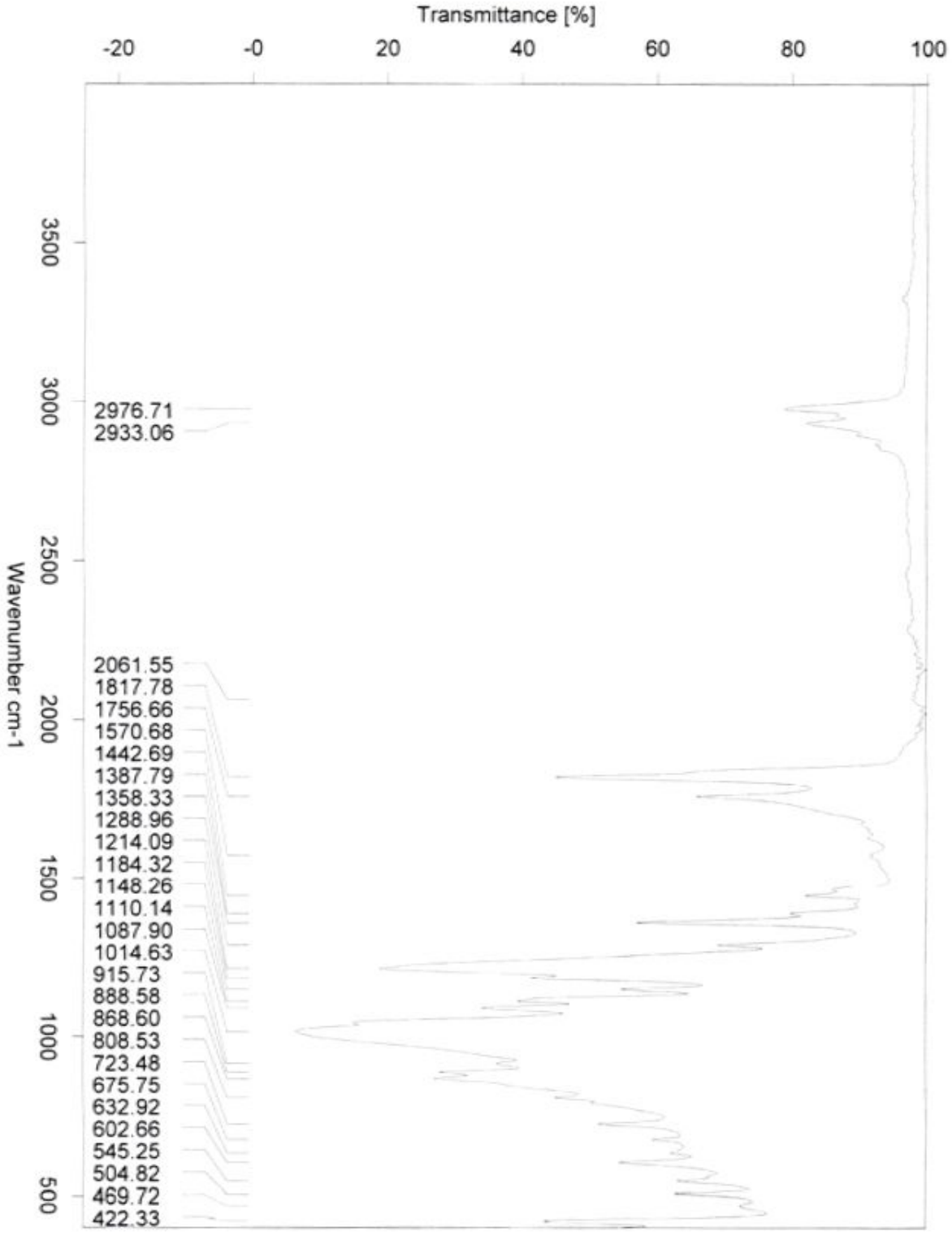

Figure S89. FTIR spectrum of **2-((Ethoxycarbonothioyl)thio)acetic anhydride (14)**.

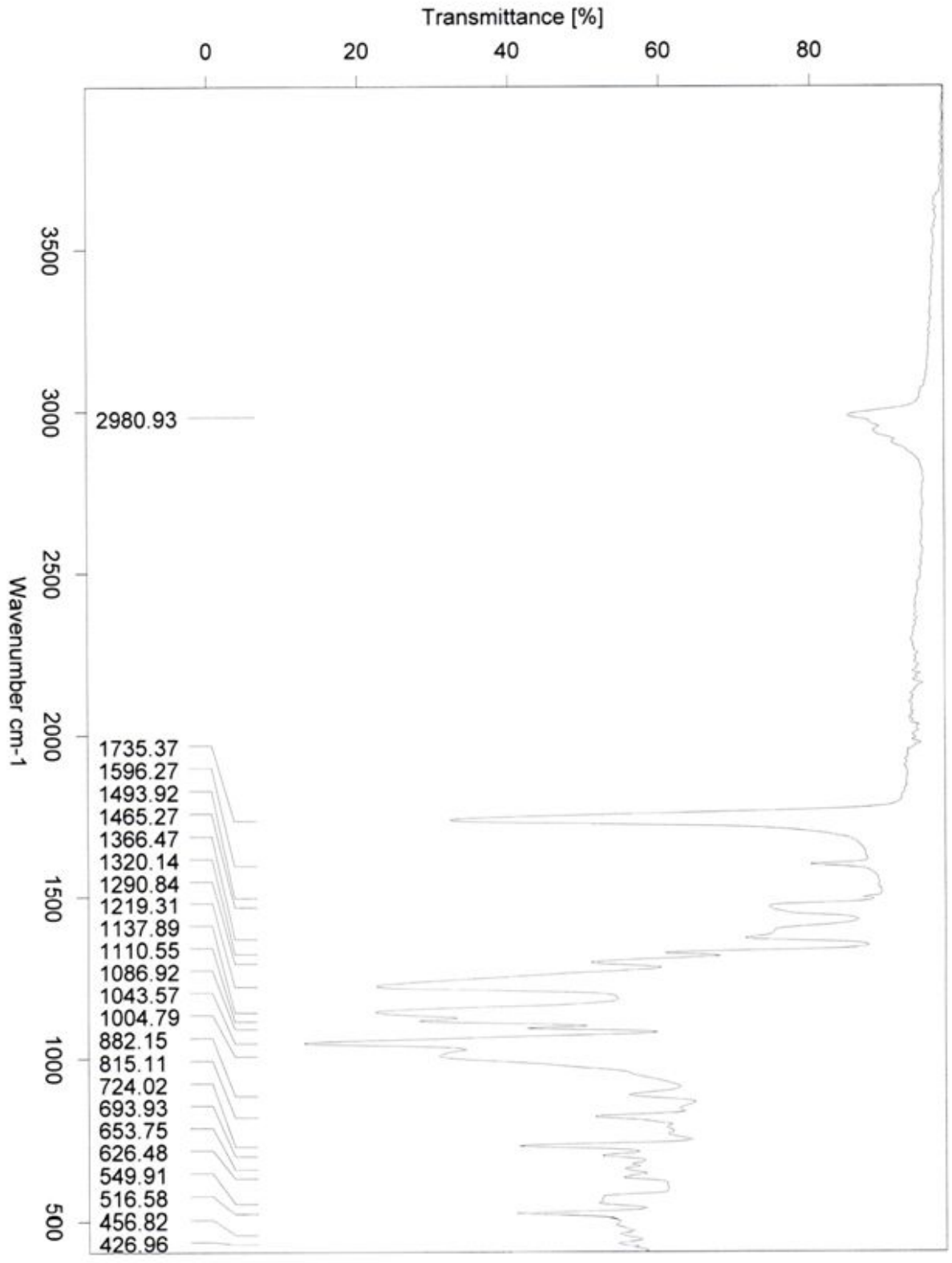

Figure S90. FTIR spectrum of **Xan_2-G_1-TSe (15)**.

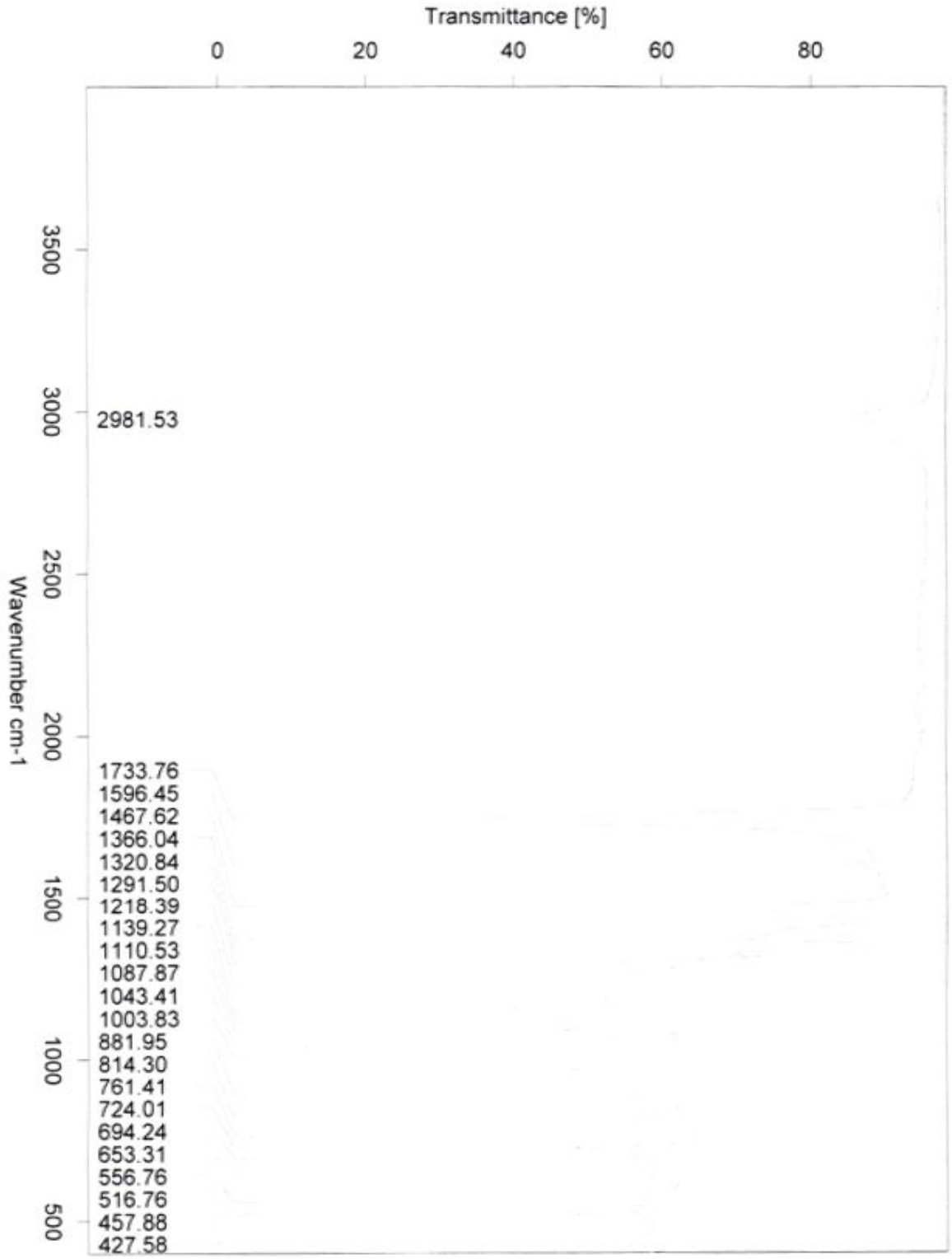

Figure S91. FTIR spectrum of **Xan_4-G_2-TSe (16)**.

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2. H. Ihre, A. Hult, J. M. J. Fréchet and I. Gitsov, *Macromolecules*, 1998, **31**, 4061-4068
3. M. Malkoch, E. Malmström and A. Hult, *Macromolecules*, 2002, **35**, 8307-8314.
4. S. E. R. Auty, O. Andrén, M. Malkoch and S. P. Rannard, *Chem. Commun.*, 2014, 50, 6574 – 6577.