Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Oxadiazabicyclooctenone as A Versatile Monomer for Construction of pH Sensitive Functional Polymer *via* ROMP

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General information

All reactions were carried out in oven-dried glassware under nitrogen or argon atmosphere unless otherwise noted. All reagents and starting materials were purchased from commercial sources and used as received and solvents were purified following standard literature procedures. Thin layer chromatography was performed using Merck TLC silica gel 60 F254 plate. Visualization of TLC was achieved through irradiation with UV light at 254 nm and by staining with basic solution of potassium permanganate or ceric ammonium molybdate. Purification of product was performed by flash column chromatography using silica gel 60 (0.010–0.063 mm). HRMS spectra were recorded on a Waters Q-Tof premier^{TM} massSpectrometer. IR spectra were recorded using FTIR Restige-21 (Shimadzu) either on solid KBr Platte or neat. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker DPX 400, and Bruker AMX 500 spectrometer using deuterated solvents (obtained from Cambridge Isotope Laboratories) using TMS as internal standard (TMS at 0.00 ppm). The coupling constant (*J*) are reported in Hz. Multiplicities are reported as follows: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublet); ddd (doublet of doublet of doublet); dt (doublet of triplet); m (multiplet) and etc. Mass spectra were obtained using an Agilent 6230 TOF LC/MS with an atmospheric pressure photo-ionization (APPI) or electrospray (ESI) source with purine and HP-0921 as an internal calibrates. Slow addition of reagents was performed with syringe pump (model: NE-300) from New Era Pump Systems Inc. Gel permeation chromatography (GPC) was carried out on a Shimadzu liquid chromatography system equipped with a Shimadzu refractive index detector (RID-10A) and two Polargel columns operating at 40 ℃ using DMF or THF as the eluent at a flow rate of 1 mL/min to determine M_n, M_w, and polydispersity index (PDI=M_n/M_w) using polystyrene kit as standard. KUBOTA centrifuge machine (model: 2420) was used to separate the solid polymers from the solution. Glass translation Temperature (T_g) of polymers were determined by differential scanning calorimetry (DSC) using a TA Instruments DSC-Q10 instrument operating at a heating rate of 10 ^{o}C/min from 0 to 130 ^{o}C under nitrogen atmosphere. The thermal stability of polymers was determined by thermal mechanical analysis (TGA) using a Perkin Elmer *Diamond* TG/DTA instrument running at a heating rate of 10 ^{o}C/min from the room temperature to 700 ^{o}C under nitrogen or air atmosphere. Fisherbrand^{TM} Cellulose dialysis tube (molecular cut off with 3.5 K or 12-14 K d) were used for purification in some cases. For the copolymer **5**(*x*)-*co*-**12**(*y*) indicates that x% of polymer

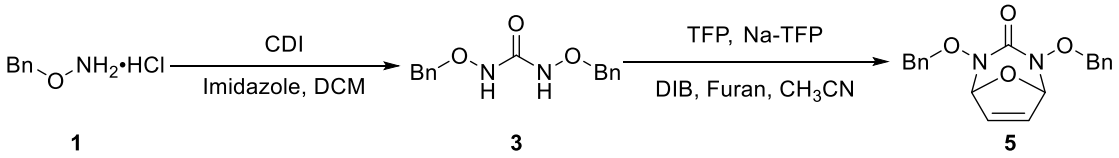
5 and y% of polymer **12** present in the backbone and also similar applicable for other copolymers.

Materials

Tetrahydrofuran (THF) was distilled over sodium/benzophenone and dichloromethane and triethylamine were distilled over calcium hydride. Dimethylsulfoxide (DMSO), *N*,*N*-dimethyl formamide (DMF), diethyl ether, hexanes, and ethyl acetate (EtOAc) were used as received. 2,2,3,3-tetrafluoro-1-propanol (TFP) and ^{t}Butyldimethylsilyl chloride (TBDMSCl) were purchased from Sigma-Aldrich Chemical Company and used without further purification. TFP-Na salt was prepared following the reported procedure.[1] All other reagents were purchased from Sigma-Aldrich Chemical Company and used without any further purification.

Synthesis of monomers 5-15

Synthesis of monomer 5



1 **3** **5**

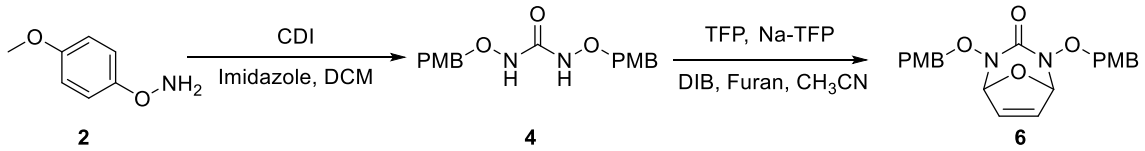
Preparation of compound **3**: The compound **1** (5.0 g, 31.45 mmol) was dissolved in 75 mL dry DCM and then cooled to 0 ℃ followed by addition of imidazole (3.20 g, 47.17 mmol) to make the corresponding free amine. The coupling reagent 1,1′-Carbonyldiimidazole (CDI) (2.54 g, 15.72 mmol) was dissolved in 20 mL DCM and added to the mixture at 0 ℃ over 10 min, and the mixture was stirred overnight. The reaction was quenched by adding 50 mL water and the organic layer was separated and washed with water (50 mL × 3) and brine, dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was recrystallized from DCM/hexane giving white solid **3** (6.9 g, 80% Yield). The white solid was characterized, and all the data was in match with the reported literature.[1]

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.66 (s, 1H), 7.38-7.32 (m, 5H), 4.78 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): 159.6, 135.0, 129.2, 128.8, 128.7, 78.7; IR ($\tilde{\upsilon}_{max}$): 3236, 2924, 2866, 2360, 2345, 1662, 1489, 1307 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{16}H_{17}N_2O_3$ 273.1241, found 273.1241.

Preparation of monomer **5**: To a 250 mL round-bottom flask (Flask-A), 40 mL of dried CH_3CN was added and cooled to 0 ℃, Na-salt of 2,2,3,3-tetrafluoro-1-propanol (1.132 g, 7.350 mmol) and 1 mL of 2,2,3,3-tetrafluoro-1-propanol were added. Then (diacetoxyiodo)benzene (DIB) (2.360 g, 7.350 mmol) was added to the solution and the mixture was stirred vigorously at 0 ℃. A solution of Furan (1.34 mL, 18.350 mol) and compound **3** (1.0 g, 3.670 mol) in 20 mL of dried CH_3CN were prepared in another flask (Flask-B) and was added to Flask-A through syringe pump over 60 min. After finishing the addition, the mixture was stirred for another 15 min. After consumption of the starting material (compound **3**), the reaction was quenched by adding 20 mL of cold water and 100 mL ethyl acetate was added. The organic layer was separated and washed twice with water, brine and dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **5** (1.03 g, Yield: 83%)[1].

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.46-7.45 (m, 2H), 7.38-7.37 (m, 8H), 6.34 (s, 2H), 5.25 (s, 2H), 5.03 (d, J = 11.0 Hz, 2H), 4.94 (d, J = 11.0 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): 160.2, 135.7, 133.6, 129.6, 128.7, 128.5, 92.5, 78.8; IR ($\tilde{\upsilon}_{max}$): 2939, 2866, 2364, 1728, 1454, 1342, 1195, 1080 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{19}H_{19}N_2O_4$ 339.1345, found 339.1352.

Synthesis of monomer 6



Preparation of compound **4**: Compound **2** was prepared by following reported procedure.[2] The compound **2** (3.0 g, 19.60 mmol) was dissolved in 50 mL dry DCM and cooled to 0 ℃. Imidazole (1.620 g, 23.53 mol) was added to the mixture followed by addition of coupling reagent 1,1′-Carbonyldiimidazole (CDI) (1.587 g, 9.80 mmol in 20 mL DCM) at 0 ℃ over 10 min, and the mixture was stirred overnight. The reaction was quenched by adding 50 mL water and the organic layer was separated and washed with water (50 mL ×3) and brine, dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was recrystallized from DCM/hexane giving **4** (2.45 g, 74% Yield).

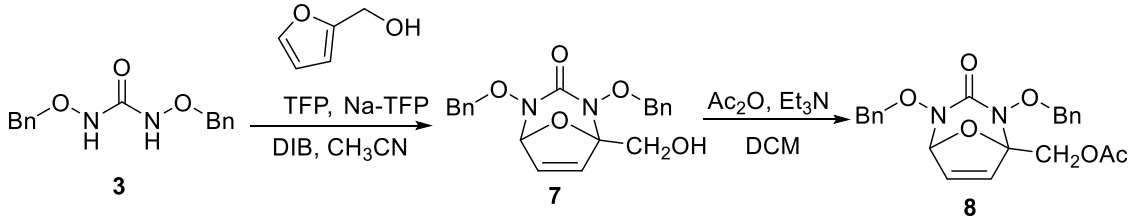
^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.50 (s, 1H), 7.24 (d, J = 8.6, 2H), 6.87 (d, J = 8.6, 2H), 4.71 (s, 2H), 3.81 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): 160.1, 159.5, 130.9, 127.1, 114.0,

78.3, 55.3; IR ($\tilde{\upsilon}_{max}$): 3228, 2924, 2835, 2360, 1670, 1512, 1473, 1033 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{17}H_{21}N_2O_5$ 333.1450, found 333.1454.

Preparation of monomer **6**: To a 250 mL round-bottom flask (Flask-A), 40 mL of dried CH_3CN was added and cooled to 0 ℃, Na-salt of 2,2,3,3-tetrafluoro-1-propanol (0.700 g, 4.64 mmol) and 0.85 mL of 2,2,3,3-tetrafluoro-1-propanol were added. Then (diacetoxyiodo)benzene (DIB) (1.840 g, 5.80 mmol) was added to the solution and the mixture was stirred vigorously at 0 ℃. A solution of Furan (1.00 mL, 14.450 mol) and the compound **4** (0.960 g, 2.90 mol) in 20 mL of dried CH_3CN were taken in another flask (Flask-B). Then the solution from Flask-B, was added to Flask-A through syringe pump over 60 min. After finishing the addition, the mixture was stirred for another 15 min. After consumption of the starting material (compound **4**), the reaction was quenched by adding 20 mL of cold water and 100 mL ethyl acetate was added. The organic layer was separated and washed twice with water, brine and dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **6** (1.15 g, Yield: 79%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, J = 8.5 Hz, 4H), 6.89 (d, J = 8.5 Hz, 4H), 6.34 (s, 2H), 5.20 (s, 2H), 4.95 (d, J = 11.0 Hz, 2H), 4.86 (d, J = 11.0 Hz, 2H), 3.81 (s, 6H); ^{13}C-NMR ($CDCl_3$, 75 MHz): 160.0, 133.6, 131.2, 127.9, 113.9, 92.5, 78.4, 55.2; IR ($\tilde{\upsilon}_{max}$): 2935, 2860, 2360, 1724, 1612, 1512, 1249 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{21}H_{23}N_2O_6$ 399.1556, found 399.1553.

Synthesis of monomer 7 and 8



Preparation of monomer **7**: To a 250 mL round-bottom flask (Flask-A), 40 mL of dried CH_3CN was added and cooled to 0 ℃, Na-salt of 2,2,3,3-tetrafluoro-1-propanol (0.670 g, 4.41 mmol) and 0.81 mL of 2,2,3,3-tetrafluoro-1-propanol were added. Then (diacetoxyiodo)benzene (DIB) (1.420 g, 4.41 mmol) was added to the solution and the mixture was stirred vigorously at 0 ℃. A solution of Furan (0.80 mL, 11.0 mol) and the compound **3** (0.600 g, 2.20 mol) in 15 mL ofdried CH_3CN were prepared in another flask (Flask-B) and was added to Flask-A through syringe pump over 60 min. After finishing the addition, the mixture was stirred for another 15 min. After consumption of the starting

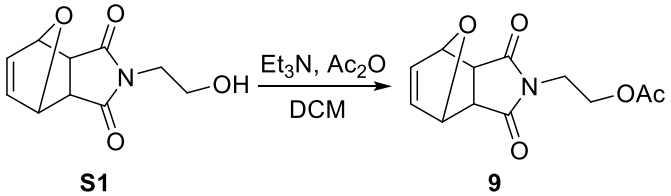
material (compound **3**), the reaction was quenched by adding 20 mL of cold water and 100 mL ethyl acetate was added. The organic layer was separated and washed twice with water, brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure at 38 ℃ to give crude product (heating during evaporation may lead to decomposition of product). The crude product was purified by column chromatography giving the product **7** (0.598 g, Yield: 73%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50-7.48 (m, 4H), 7.42-7.40 (m, 6H), 6.48 (d, J = 6.0 Hz, 1H), 6.43 (d, J = 5.8 Hz, 1H), 5.32 (d, J = 5.2,Hz, 1H), 5.17 (d, J = 10.0 Hz, 1H), 5.09 (d, J = 11.2 Hz, 1H), 4.97 (d, J = 10.4, 11.6 Hz, 1H), 3.96 (dd, J = 12.8, 7.6 Hz, 1H), 3.89 (dd, J = 12.8, 7.6 Hz, 1H), 1.69-1.66 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 161.9, 135.6, 135.0, 134.8, 134.3, 129.9, 129.6, 128.8, 128.6, 101.9, 92.4, 79.6, 78.7, 60.8; IR ($\tilde{\upsilon}_{max}$): 3437, 2934, 2360, 1708, 1454, 1276, 1068 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{20}H_{21}N_2O_5$ 369.1450, found 369.1454.

Preparation of monomer **8**: Compound **7** (200 mg, 0.545 mmol) was dissolved in 10 mL DCM and acetylated with Et_3N (148 µL, 1.1mmol) and Ac_2O (62 µL, 0.6 mmol) to get the crude product. The final product **8** was obtained via column chromatography (208 mg, Yield: 94 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.41-7.33 (m, 4H), 7.32-7.30 (m, 6H), 6.41(dd, J = 5.7, 0.9 Hz, 1H), 6.35 (d, J = 5.7, Hz, 1H), 5.27 (d, J = 1.2 Hz, 1H), 5.11 (d, J = 9.9 Hz, 1H), 5.00 (d, J = 9.9 Hz, 1H), 4.46 (d, 11.1 Hz, 1H), 4.80 (d, J = 10.0 Hz, 1H) 4.51 (d, J = 12.6, 1H), 4.30 (d, J = 12.6, 1H), 2.03 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 170.2, 161.6, 135.6, 134.8, 134.5, 134.4, 129.8, 129.5, 128.9, 128.8, 128.6, 128.5, 100.2, 92.3, 79.7, 78.7, 60.9, 20.6; IR ($\tilde{\upsilon}_{max}$): 2860, 2360, 1739, 1369, 1226, 1022 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{22}H_{23}N_2O_6$ 411.1556, found 411.1551.

Synthesis of monomer 9

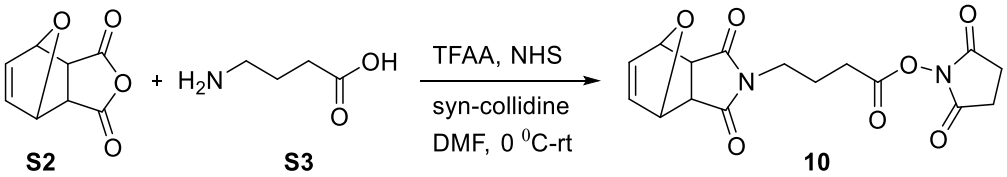


The compound **S1** was prepared by following reported procedure. [3] To a solution of **S1** (350 mg, 1.675 mmol) in 5 mL DCM was added Et_3N (0.45 mL, 3.350 mmol) and Ac_2O (0.20 mL 0.6 mmol). The reaction mixture was stirred at room temperature for 6 h and quenched by adding 20 mL water. The organic layer was separated and washed with

water (50 mL × 3) and brine, dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **9** (381 mg, Yield: 90%).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.48 (s, 2H), 5.23 (s, 2H), 4.21-4.17 (m, 2H), 3.74-3.71 (m, 2H), 2.83 (s, 2H), 1.97 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 176.0, 170.8, 136.5, 80.9, 60.5, 47.4, 37.8, 20.7; IR ($\tilde{\upsilon}_{max}$): 3008, 2958, 1739, 1693, 1431, 1234, 1029 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{12}H_{14}NO_5$ 252.0872, found 252.0876.

Synthesis of monomer 10

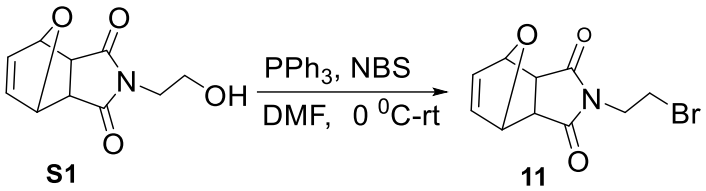


S2 **S3** **10**

The starting material **S2**[3] (3.0 g, 18.0 mmol) was dissolved in 90 mL of dry DMF followed by addition of 4-aminobutanoic acid (**S3**, 1.86 g, 18.0 mmol) at 0 ℃ and stirred at room temperature for 6 h. The resulting solution was cooled to 0 ℃ and *sym*-collidine (4.98 mL, 37.8 mmol) was added dropwise to the reaction flask (Flask A). In a separate flask (Flask B), a solution of *N*-hydroxysuccinimide (NHS, 8.280 g, 72.0 mmol) in 90 mL DMF, was stirred at 0 ℃ followed by addition of trifluoroacetic anhydride (TFAA, 10.1 mL, 72.0 mmol) dropwise. The reaction mixture was stirred for 10 min followed by addition of *sym*-collidine (9.5 mL, 72 mmol) dropwise. After stirred for 10 min, the solution in Flask B was added by positive-pressure cannula to Flask A over a period of 1 h. Both flasks were kept at 0 ℃ during the addition. After addition was complete, the reaction mixture was warmed to room temperature and stirred overnight. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with DCM (300 mL) and 1 M HCl (250 mL). The organic layer was separated and washed with 1 M HCl (2 × 250 mL) and dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **10** (4.65 g, Yield: 74%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.53 (s, 2H), 5.28 (s, 2H), 3.63 (t, J=6.9 Hz, 2H), 2.89-2.84 (m, 6H), 2.65 (t, J=7.6 Hz, 2H) 2.08-2.03 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 176.2, 168.9, 167.8, 136.5, 80.9, 47.4, 37.6, 28.2, 25.5, 22.5; IR ($\tilde{\upsilon}_{max}$): 3014, 2964, 1736, 1698, 1643, 1400, 1231, 1024 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{16}H_{17}N_2O_7$ 349.1036, found 349.1038.

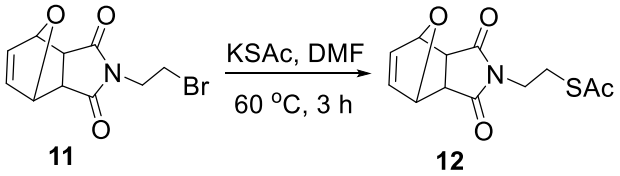
Synthesis of monomer 11



The compound **S1** (2.80 g, 13.4 mmol) was dissolved in 15 ml of dry DMF followed by addition of triphenylphosphine (7.00 g, 26.7 mmol) and the mixture was cooled to 0 ^{o}C. NBS (3.92 g, 22.0 mmol) was added to the mixture and allowed to warm up to room temperature and stirred for 12 h. Then 50 mL ice cold water was added and extracted with 50 mL of ethyl acetate. The organic layer was combined and washed with water (25 mL × 2), dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **11** (2.07 g, Yield: 57 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.54 (s, 2H); 5.31-5.30 (m, 2H); 3.92 (t, 2H, J = 6.9 Hz); 3.50 (t, 2H, J = 6.9 Hz); 2.91 (s, 2H). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 175.7, 136.3, 80.9, 47.4, 40.1, 26.9. IR: 2931, 2854, 2341, 1701, 1396, 1334, 1253, 1192, 1110, 1026 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{10}H_{10}BrNNaO_3$ 293.9742, found 293.9746.

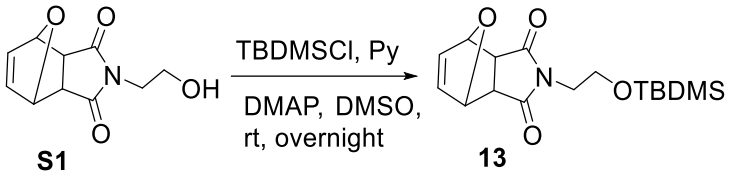
Synthesis of monomer 12



To a solution of bromo compound **11** (485 mg, 1.78 mmol) in 3 mL of dry DMF, Potassium thioacetate (1.01 g, 8.87 mmol) was added and the mixture was heated at 60 ^{o}C for 3h and thereafter stirred at room temperature overnight. The mixture was diluted with 20 mL of water. The organic layer was separated and washed with water (25 mL×2) and brine, dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **12** (421 mg, Yield: 88 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.50 (s, 2H); 5.25 (s, 2H); 3.69 (t, 2H, J = 6.6 Hz); 3.10 (t, 2H, J = 6.6 Hz); 2.83 (s, 2H), 2.30 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 194.9, 175.9, 136.5, 80.8, 47.4, 38.0, 30.5, 26.6; IR: 2931, 1743, 1701, 1431, 1392, 1165, 1134, 1010 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{12}H_{14}NO_7S$ 268.0644, found 268.0647.

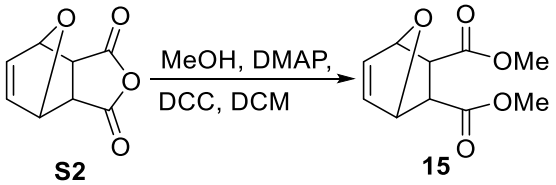
Synthesis of monomer 13



The compound **S1** (365 mg, 1.75 mmol) was dissolved in 2 mL of dry DMSO and Pyridine (0.20 mL, 2.63 mmol) was added to the solution at 0 ºC. TBDMSCl (315 mg, 2.10 mmol) and DMAP (21 mg, 0.17 mmol) were added to the reaction mixture. The mixture was stirred at room temperature overnight. The mixture was diluted with 20 mL of water and 20 mL ethyl acetate was added. The organic layer was combined and washed with water (25 mL × 2), dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **13** (334 mg, Yield: 88 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.50 (s, 2H); 5.20 (s, 2H); 3.74-3.3.70 (m, 2H); 3.64-3.60 (t, 2H); 2.86 (s, 2H), 0.85 (s, 9H); 0.01 (s, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 176.1, 136.5, 80.8, 59.1, 47.4, 41.0, 25.7, 18.1, -5.54; IR: 3055, 2931, 2322, 1705, 1435, 1396, 1184, 1118, 1024 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{16}H_{26}NO_4Si$ 324.1631, found 324.1641.

Synthesis of monomer 15



The starting material **S2**[3] (3.0 g, 18.0 mmol) was dissolved in 150 mL of dry DCM followed by addition dry MeOH (2 mL, 50 mmol) at 0 ℃, and catalytic amount of DMAP (220 mg, 1.80 mmol) was added. The mixture was stirred at room temperature for 6 h, thereafter, the mixture was cooled to 0 ℃ and DCC (3.8 g, 18.5 mmol) was added portionwise and the mixture was warmed up to room temperature and stirred overnight and quenched by adding 100 mL water. The organic layer was separated and washed with water (50 mL×3) and brine, dried over Na_2SO_4, filtered and concentrated to give crude product. The crude product was purified by column chromatography giving the product **15** (2.65 g, Yield: 69%).[5]

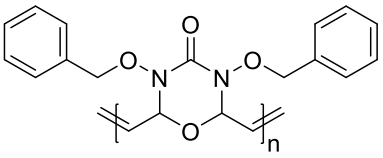
^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.45 (s, 2H), 5.26 (s, 2H), 3.70 (s, 6H), 2.891 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 171.9, 136.6, 80.4, 52.2, 46.9; IR ($\tilde{\upsilon}_{max}$): 2944, 1746, 1430,

1367, 1360, 1249, 1151, 1004 cm^{-1}; HRMS (ESI): m/z [M+H] calcd for $C_{10}H_{13}O_5$ 213.073, found 213.079.

General procedure for homopolymerization

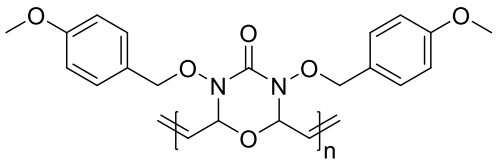
The exact amount of monomer (0.15 mmol) was dissolved in degassed THF and stirred at room temperature for 5 min. Also, suitable Grubbs catalyst was dissolved in minimum amount of solvent and added to the reaction mixture under inert condition. The mixture was stirred for 2 h at room temperature. The reaction was quenched with ethyl vinyl ether (100 µL) and the solution was allowed to stir overnight at room temperature. The resulted polymer was precipitated out by adding Et_2O/hexane or MeOH (30 mL) and isolated via centrifugation and dried under vacuum for 6 h to remove all the solvent.

Synthesis of homopolymer Poly-5



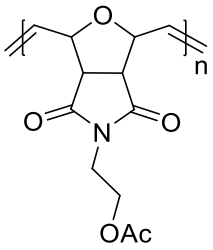
Poly-**5** was synthesized following the general procedure using monomer **5**. Conversion: 84-98 %**;** ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.28 (brs), 5.79 (m), 5.47-4.70 (m); IR ($\tilde{\upsilon}_{max}$): 3032, 2939, 2881, 2322, 1716, 1330, 1226 cm^{-1}.

Synthesis of homopolymer Poly-6



Poly-**6** was synthesized following the general procedure using monomer **6**. Conversion: 93%**;** ^{1}H-NMR ($CDCl_3$, 300MHz): δ 7.26 (brs), 6.75 (brs,), 5.82-5.47 (m), 5.10-4.67 (m), 3.69 (brs). IR ($\tilde{\upsilon}_{max}$): 3027, 2941, 2878, 1715, 1427, 1231, 1032 cm^{-1}.

Synthesis of homopolymer Poly-9



Poly-**9** was synthesized following the general procedure using monomer **9**. Conversion: 88%**;** ^{1}H-NMR ($CDCl_3$, 300MHz): δ 6.10 (brs), 5.84 (brs), 5.03 (brs), 4.52 (brs), 4.27 (brs), 3.77 (brs), 3.36 (brs), 2.04-1.72 (m); IR ($\tilde{\upsilon}_{max}$): 2927, 2854, 2341, 1778, 1739, 1701, 1426, 1230, 1033 cm^{-1}.

Procedure for determining reaction kinetics

The progress of the reaction was monitored by ^{1}H-NMR spectroscopy by performing the polymerization in NMR tube under inert condition. The monomer **5** (20 mg) was dissolved in 0.5 mL $CDCl_3$ and degassed by freeze thaw technique. At this point, ^{1}H-NMR was recorded and the monomer peak at 6.36 ppm for olefinic proton will serve as standard at time = t_0. Thereafter, 1 mg of Grubbs 1st generation catalyst was dissolved in another vial in 100 µL DCM-d_2 (degassed) and added to the NMR tube. The ^{1}H-NMR was recorded by different time intervals. The increase of peak area at 5.80 ppm is corresponding to newly formed polymer. Finally, the plot of $\ln[A_0/A_t]$ against time gave a straight line which suggested that the polymerization reaction follows the pseudo first-order reaction kinetics.

General procedure for copolymerization

Both the monomers with appropriate molar ratio were taken in a vial and dissolved completely in the respective solvent. Thereafter, Grubbs catalyst was dissolved in minimum amount of solvent and added to the reaction mixture. The mixture was allowed to stir at room temperature for 6 hours. The reaction was quenched with ethyl vinyl ether (100 µL) and the solution was stirred overnight at room temperature. The reaction mixture was triturated using Et_2O or MeOH (30 mL) and the resulting solid was isolated via centrifugation and dried under vacuum for 6 hours to remove trace solvent. The observed ratio of the respective monomer in the polymer was calculated from the ^{1}H-NMR spectra.

Synthesis of copolymer 5(49)-co-9(51)

Both the monomers **5** (50 mg, 0.148 mmol) and **9** (37.1 mg, 0.148 mmol) were taken in 1:1 molar ratio and dissolved in THF (250 µL) and dissolved Grubbs 1st generation catalyst (4.8 mg, 0.006 mmol, in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 50:50 for **5** and **9** and from the ^{1}H-NMR, the observed ratio was 49:51 for **5** and **9** respectively.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.33 (brs), 6.09-5.08 (m), 5.32-4.23 (m), 3.77 (brs), 3.34 (brs), 2.01 (brs); IR ($\tilde{\upsilon}_{max}$): 3032, 2954, 2881, 1712, 1392, 1369, 1041, cm^{-1}.

Synthesis of block copolymer 9-block-5

The monomer **9** (37.2 mg, 0.148 mmol) was dissolved in 250 µL degassed THF and Grubbs 1st generation catalyst (4.8 mg, 0.006 mmol, in 50 µL of THF) was added to the mixture. The mixture was allowed to stir at room temperature for 6 h, after consumption of the monomer **9**, monomer **5** (50 mg, 0.148 mmol) was added to the mixture. The reaction mixture was allowed to stir for 6 h. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 50:50 (**9**:**5**) but from the ^{1}H-NMR, the observed ratio was 60:40 for monomer **9** and **5** respectively. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.26 (brs), 6.09-5.82 (m), 5.13-4.51 (m), 4.25 (m), 3.76 (brs), 3.37 (brs), 2.03 (m,); IR ($\tilde{\upsilon}_{max}$): 2958, 2881, 2333, 17781708, 1392, 1230, 1033, cm^{-1}.

Synthesis of copolymer 5(37)-co-10(63)

Both the monomers **5** (50 mg, 0.148 mmol) and **10** (51.7 mg, 0.148 mmol) were taken in 50:50 molar ratio and dissolved in THF (250 µL) then dissolved Grubbs 1st generation catalyst (4.8 mg, 0.006 mmol, in 50 µL THF) was added. The final polymer was obtained followed the general procedure (Conversion: 62%). Feeding ratio for two monomers was 1:1 for **5** and **10** and from the ^{1}H-NMR, the observed ratio was 37:63 for **5** and **10** respectively.

^{1}H-NMR (300, DMSO-D_6): 7.28 (brs), 5.94-5.71 (m), 4.88-4.42 (m), 3.37 (brs), 2.77 (brs), 1.82 (brs); IR ($\tilde{\upsilon}_{max}$): 3043, 2943, 2881, 2368, 1728, 1360, 1219, 1030 cm^{-1}.

Synthesis of copolymer 5(10)-co-10(90)

Both the monomers **5** (10 mg, 0.029 mmol) and **10** (92.9 mg, 0.267 mmol) were taken in 10:90 molar ratio and dissolved in 210 µL THF and then Grubbs 1st generation catalyst (4.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure (Conversion: 78%). Feeding ratio for two monomers was 1:10 for **5** and **10** and from the ^{1}H-NMR, the observed ratio was 10:90 for **5** and **10** respectively.

^{1}H-NMR (DMSO-D_6, 300 MHz): δ 7.51-7.35 (m), 5.98 (brs), 5.75 (brs), 4.89 (brs), 4.46 (brs), 3.46 (brs), 2.80-2.722 (m), 1.86-1.84 (m); IR ($\tilde{\upsilon}_{max}$): 2947, 2870, 1782, 1732, 1708, 1685, 1400, 1365, 1072 cm^{-1}.

Synthesis of copolymer 5(81)-co-11(19)

Both the monomers **5** (78 mg, 0.230 mmol) and **11** (27 mg, 0.100 mmol) were taken in 70:30 molar ratio and dissolved in 270 μL THF and then Grubbs 1st generation catalyst (5.3 mg in 50 μL THF) was added. The final polymer was obtained followed the general procedure. From the ^{1}H-NMR, the observed ratio was 81:19 for **5** and **11** respectively.

^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.22 (brs), 5.80 (m), 5.12-4.63 (m), 3.77 (brs), 3.50 (brs), 3.21 (brs); IR: 3032, 2881, 1712, 1330, 1226, 1038 cm^{-1}

Synthesis of copolymer 5(66)-co-11(34)

Both the monomers **5** (51 mg, 0.151 mmol) and **11** (41 mg, 0.151 mmol) were taken in 50:50 molar ratio and dissolved in 250 μL THF and then Grubbs 1st generation catalyst (5.0 mg in 50 μL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 50:50 for **5** and **11** and from the ^{1}H-NMR, the observed ratio was 66:34 for **5** and **11** respectively.

^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.22 (m), 6.09-5.80 (m), 5.13-4.41 (m), 3.78 (brs), 3.26 (brs), 3.20 (brs); IR: 3032, 2943, 2858, 1712, 1362, 1330, 1291, 1159, cm^{-1}.

Synthesis of copolymer 5(47)-co-11(53)

Both the monomers **5** (21 mg, 0.06 mmol) and **11** (40 mg, 0.147 mmol) were taken in 30:70 molar ratio and dissolved in 150 μL THF and then Grubbs 1st generation catalyst (3.5 mg in 50 μL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 30:70 for **5** and **11** and from the ^{1}H-NMR, the observed ratio was 47:53 for **5** and **11** respectively.

^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.24 (brs), 5.99-5.73 (m), 5.13-4.24 (m), 3.79 (brs), 3.51 (brs), 3.28 (brs); IR: 3032, 2951, 2881, 2337, 1712, 1392, 1330, 1226, 1149, cm^{-1}.

Synthesis of copolymer 5(83)-co-12(17)

Both the monomers **5** (40 mg, 0.118 mmol) and **12** (13.5 0.050 mmol) were taken in 70:30 molar ratio and dissolved in 150 μL THF and then Grubbs 1st generation catalyst (2.7 mg in 50 μL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 70:30 for **5** and **12** and from the ^{1}H-NMR, the observed ratio was 66:34 for **5** and **12** respectively.

^{1}H-NMR (DMSO-d_6, 500 MHz): 7.28 (m), 6.02-5.64 (m), 4.86-4.73 (m), 3.56 (brs), 3.32 (brs), 3.05 (brs), 2.26 (brs); IR: 2939, 2881, 1712, 1446, 1388, 1330, 1226, 1157, 975 cm^{-1}.

Synthesis of copolymer 5(60)-co-12(40)

Both the monomers **5** (20 mg, 0.059 mmol) and **12** (15.8 mg, 0.059 mmol) were taken in 50:50 molar ratio and dissolved in 100 µL THF and then Grubbs 1st generation catalyst (1.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 50:50 for **5** and **12** and from the ^{1}H-NMR, the observed ratio was 66:34 for **5** and **12** respectively.

^{1}H-NMR (DMSO-d_6, 500 MHz): 7.22 (brs), 6.21-5.66 (m), 4.91-4.23 (m), 3.56 (brs), 3.39 (brs), 3.06 (brs), 2.30 (brs); IR: 2947, 2881, 2098, 1708, 1643, 1388, 1230, 1161 cm^{-1}.

Synthesis of copolymer 5(32)-co-12(68)

Both the monomers **5** (20 mg, 0.059 mmol) and **12** (36.7 mg, 0.137 mmol) were taken in 30:70 molar ratio and dissolved in 150 µL THF and then Grubbs 1st generation catalyst (3.2 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 30:70 for **5** and **12** and from the ^{1}H-NMR, the observed ratio was 32:68 for **5** and **12** respectively.

^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.44-7.35 (m), 6.09-5.82 (m), 5.07-4.35 (m), 3.69 (brs), 3.35 (brs), 3.11 (brs), 2.32 (brs); IR: 2939, 2881, 1778, 1712, 1392, 1334, 1226, 1157, 1134, 1029 cm^{-1}.

Synthesis of copolymer 5(69)-co-13(31)

Both the monomers **5** (70 mg, 0.207 mmol) and **13** (30 mg, 0.0.091 mmol) were taken in 70:30 molar ratio and dissolved in 250 µL THF and then Grubbs 1st generation catalyst (4.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 70:30 for **5** and **13** and from the ^{1}H-NMR, the observed ratio was 69:31 for **5** and **13** respectively.

^{1}H-NMR (CD_2Cl_2, 500 MHz): 7.31 (brs), 6.19-5.68 (m), 5.12-4.63 (m), 5.26-4.26 (m), 3.72-3.28 (m), 0.83 (brs), 0.01 (brs); IR: 2951, 2858, 2360, 1708, 1361, 1308, 1226, 1192, 1036 cm^{-1}.

Synthesis of copolymer 5(49)-co-13(51)

Both the monomers **5** (50 mg, 0.149 mmol) and **13** (48 mg, 0.149 mmol) were taken in 50:50 molar ratio and dissolved in 250 µL THF and then Grubbs 1st generation catalyst (4.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general

procedure. Feeding ratio for two monomers was 50:50 for **5** and **13** and from the ^{1}H-NMR, the observed ratio was 49:51 for **5** and **13** respectively.

^{1}H-NMR (CD_2Cl_2, 400 MHz): 7.30 (brs), 6.16-5.76 (m), 5.15-4.41 (m), 3.71 (brs), 3.58 (brs), 3.33-3.28 (m), 0.82 (brs), 0.00 (brs); IR: 2951, 2858, 1712, 1392, 1330, 1226, 1188, 1122, 1037 cm^{-1}.

Synthesis of copolymer 5(31)-co-13(69)

Both the monomers **5** (30 mg, 0.089 mmol) and **13** (70 mg, 0.212 mmol) were taken in 30:70 molar ratio and dissolved in 250 µL THF and then Grubbs 1st generation catalyst (4.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 30:70 for **5** and **13** and from the ^{1}H-NMR, the observed ratio was 31:69 for **5** and **13** respectively.

^{1}H-NMR (CD_2Cl_2, 500 MHz): 7.43-7.30 (m), 6.18-5.74 (m), 5.16-4.41 (m), 3.72 (brs), 3.58 (brs), 3.34-3.29 (m), 0.84 (brs), 0.01 (brs); IR: 2931, 2858, 1708, 1391, 1330, 1253, 1188, 1122, 1037 cm^{-1}.

Synthesis of copolymer 5(36)-co-14(64)

Both the monomers **5** (50 mg, 0.148 mmol) and **14** (14.6 mg, 0.148 mmol) were dissolved in 250 µL THF and then Grubbs 1st generation catalyst (4.8 mg, 0.006 mmol, in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 50:50 for **5** and **14** but from the ^{1}H-NMR, the observed ratio was 36:64 for **5** and **14** respectively.

^{1}H-NMR (DCM-D_2, 300 MHz): δ 7.29 (brs, 10H), 5.84-5.35 (m, 4H), 5.13-4.78 (m, 6H), 2.78-2.43 (m, 4H), 1.88-1.74 (m, 6H), 1.35-1.26 (m, 4H), 1.26-1.00 (m, 2H); IR ($\tilde{\upsilon}_{max}$): 2943, 2866, 2357, 1724, 1454, 1337, 1226 cm^{-1}.

Synthesis of copolymer 5(73)-co-15(27)

Both the monomers **5** (50 mg, 0.148 mmol) and **15** (13.5 mg, 0.063 mmol) were taken in 70:30 molar ratio and dissolved in 250 µL THF and then Grubbs 1st generation catalyst (3.4 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure. Feeding ratio for two monomers was 70:30 for **5** and **15** and from the ^{1}H-NMR, the observed ratio was 73:27 for **5** and **15** respectively.

^{1}H-NMR (DCM-D_2, 300 MHz): δ 7.21 (m), 5.79-5.49 (m), 5.09-4.63 (m), 3.57-2.97 (m); IR ($\tilde{\upsilon}_{max}$): 3032, 2951, 2881, 2360, 1732, 1334, 1226, 1001 cm^{-1}.

Synthesis of copolymer 5(39)-co-15(61)

Both the monomers **5** (47 mg, 0.141 mmol) and **15** (30 mg, 0.141 mmol) were dissolved in 230 µL THF and then Grubbs 1st generation catalyst (4.6 mg, in 50 µL THF) was added. The final polymer was obtained followed the general procedure (Conversion:68%). Feeding ratio for two monomers was 50:50 for **5** and **15** but from the ^{1}H-NMR, the observed ratio was 39:61 for **5** and **15** respectively.

^{1}H-NMR (DCM-D_2, 300 MHz): δ 7.25 (brs), 5.97-5.50 (m), 5.06-4.57 (m), 3.57-2.99 (m); IR ($\tilde{\upsilon}_{max}$): 2961, 2865, 1732, 1436, 1340, 1211, 1002 cm^{-1}.

Synthesis of copolymer 5(27)-co-15(73)

Both the monomers **5** (20 mg, 0.059 mmol) and **15** (29 mg, 0.137 mmol) were taken in 30:70 molar ratio and dissolved in 250 µL THF and then Grubbs 1st generation catalyst (3.2 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure (Conversion: 82%). Feeding ratio for two monomers was 30:70 for **5** and **15** and from the ^{1}H-NMR, the observed ratio was 27:73 for **5** and **15** respectively.

^{1}H-NMR (DCM-D_2, 300 MHz): δ 7.22 (m), 5.78-5.49 (m), 5.12-4.58 (m), 3.57-3.00 (m); IR ($\tilde{\upsilon}_{max}$): 2951, 2361, 1732, 1435, 1361, 1211, 1001 cm^{-1}.

Synthesis of copolymer 5(9)-co-15(91)

Both the monomers **5** (10.1 mg, 0.03 mmol) and **15** (64.0 mg, 0.30 mmol) were taken in 10:90 molar ratio and dissolved in 280 µL THF and then Grubbs 1st generation catalyst (2.8 mg in 50 µL THF) was added. The final polymer was obtained followed the general procedure (Conversion: 70%). Feeding ratio for two monomers was 1:10 for **5** and **15** and from the ^{1}H-NMR, the observed ratio was 9:91 for **5** and **15** respectively.

^{1}H-NMR (DCM-D_2, 300 MHz): δ 7.27 (m), 5.78 (brs), 5.50 (m), 4.93 (brs), 4.57 (brs), 3.58-3.00 (m); IR ($\tilde{\upsilon}_{max}$): 2961, 2864, 1739, 1430, 1361, 1041 cm^{-1}.

Degradation studies in acidic medium

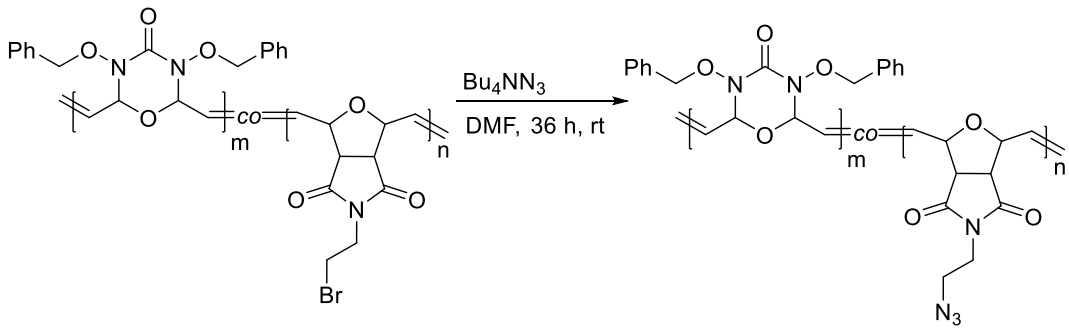
A stock solution of HCl in methanol-d_4 (3.20 M) was prepared and diluted with suitable deuterated (acetone-d_6, THF-d_8 or DMSO-d_6, depending on the solubility of the polymers) solvents to obtained different pH solutions (pH 1.0, pH 2.0, pH 3.0 pH 4.0). 5 mg of the respective polymer was dissolved in 1 mL of the different pH solution and monitored by ^{1}H-NMR spectroscopy and GPC.

Degradation studies in basic medium

Preparation of NaOMe-d_3: 200 mg of Na was added to 5 ml of MeOH-d_4 at 0 ℃ under nitrogen atmosphere and then allowed to stir at room temperature for 2 h. After consumption of all the Na, the excess solvent was evaporated at 50 ℃ under reduced pressure. The round bottom flask containing NaOMe-d_3 product was flushed with nitrogen before removing the flask from rotary evaporator. The NaOMe-d_3 product was stored under nitrogen in the refrigerator.

The different basic solutions were prepared by dissolving NaOMe-d_3 in suitable deuterated solvents depending on the solubility of the polymers. 25 mg of the NaOMe-d_3 was dissolved in MeOH-d_4 to get a stock solution of 0.4 M of NaOMe-d_3, and the stock solution was diluted with DMSO-d_6 to get different pH solutions (pH 10.5, pH 11.5, pH 12.5, pH 13.5). 5 mg of the respective polymer was dissolved in 1 mL of respective pH solution and monitored by ^{1}H-NMR spectroscopy and GPC.

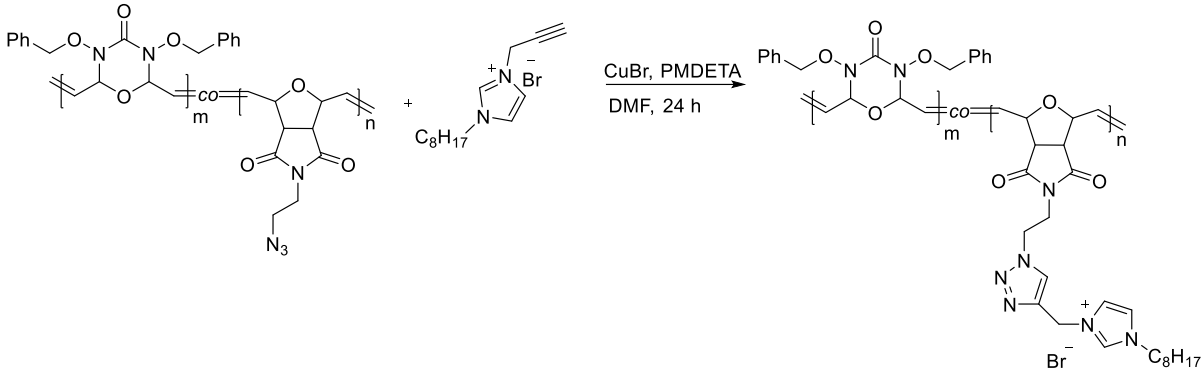
Polymer modification (substitution of bromo with azide)



The bromo polymer **5**(47*)-co-***12***(53 (65 mg) was dissolved in 2 mL DMF followed by addition tetrabutylammonium azide (250 mg) at room temperature. The mixture was allowed to stir at room temperature for 36 h. After that, the polymer was precipitated out by adding excess MeOH and dried under reduced pressure. The strong absorption at 2110 cm^{-1} in IR spectra confirmed formation of the product.

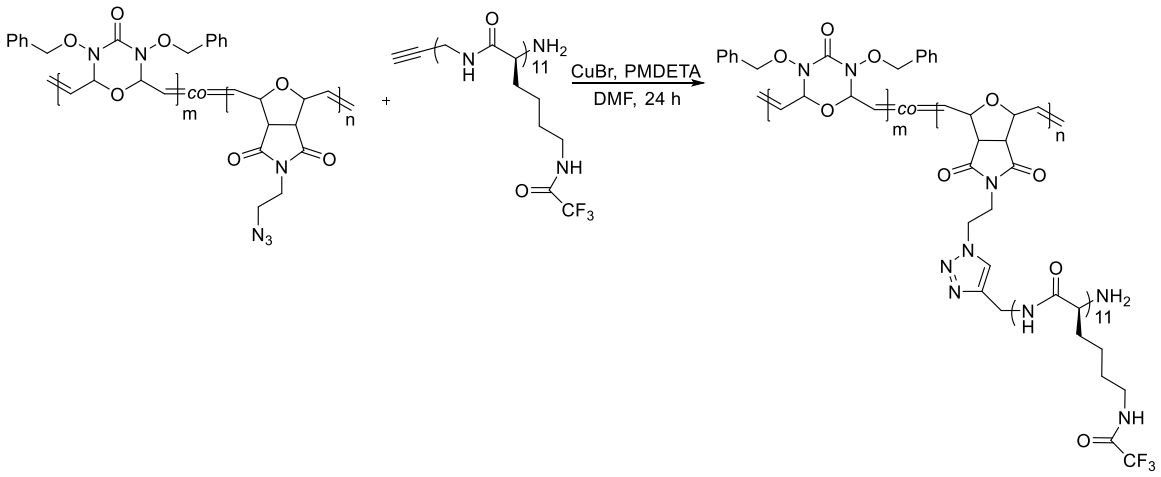
^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.25-7.24 (m), 6.00-5.74 (m), 5.13-4.26 (m), 3.60 (brs), 3.43 (brs), 3.31 (brs); IR: 2947, 2881, 2110, 1708, 1396, 1330, 1226, 1176, 1037 cm^{-1}.

Conjugation of imidazolium and polylysine by click reaction



Linking of imidazolium derivative **16**: The azido polymer (14 mg) and corresponding imidazolium salt[6] **16** were dissolved in 1 mL DMF in vial followed by addition of CuBr (9 mg) and PMDETA (10 µL) at room temperature. The mixture was degassed by freeze thaw technique and stirred at room temperature overnight under N_2 atmosphere. After that, the polymer was precipitated out by adding excess MeOH and the unreacted reagents and CuBr were removed by washing with MeOH and dried under reduced pressure.

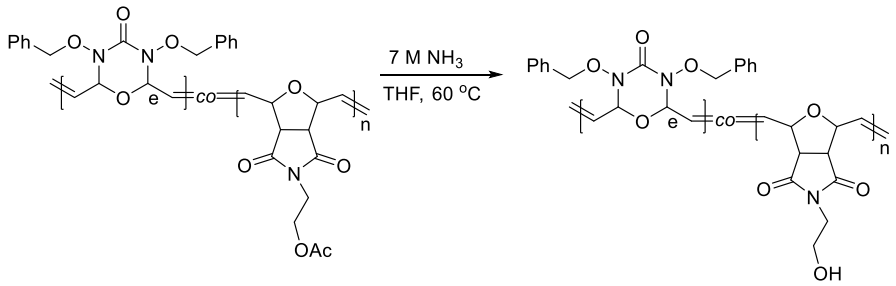
^{1}H-NMR (DMSO-d_6, 500 MHz): 9.13 (brs), 8.33-7.91 (m), 7.26 (brs), 6.05-5.68 (m), 4.74-4.10 (m), 2.87-2.67 (m), 1.69-0.84 (m); IR: 2934, 2855, 2098, 1708, 1654, 1438, 1373, 1210, 1182, 1037 cm^{-1}.



Linking of imidazolium derivative **17**: The azido polymer (10 mg) and poly-lysine **17**,[7] were dissolved in 1 mL DMF in vial followed by addition of CuBr (9 mg) and PMDETA (10 µL) at room temperature. The mixture was degassed by freeze thaw technique and stirred at room temperature overnight under N_2 atmosphere. After that, the polymer was precipitated out by adding excess MeOH and the unreacted reagents and CuBr were removed by washing with MeOH and dried under reduced pressure. Further, purification was done by dialysis with MWCO 3.5k.

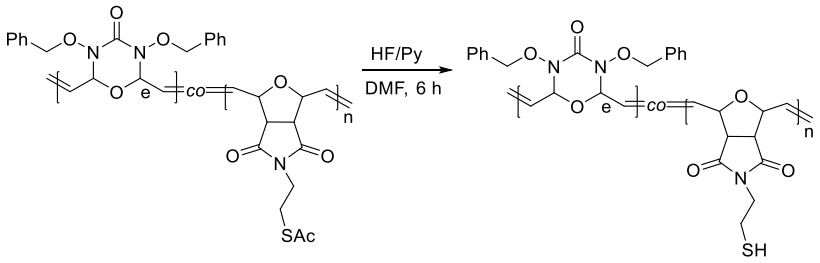
^{1}H-NMR (DMSO-d_6, 500 MHz): 9.26 (brs), 8.14-7.84 (m), 7.27 (brs), 6.05-5.68 (m), 4.81-4.69 (m), 3.78 (m), 1.82-1.29 (m); IR: 2924, 2861, 2098, 1778, 1705, 1654, 1438, 1373, 1203, 1176, 1029 cm^{-1}.

Removal of protecting group on the copolymers



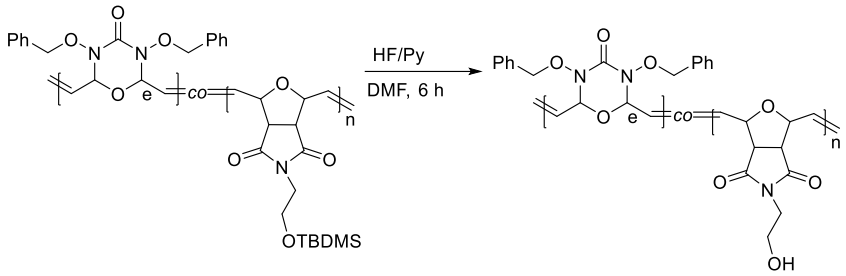
Removal of the acetate (-OAc) group from the polymer **5**(*49*)-*co*-**9**(*51*): The polymer **5**(*49*)-*co*-**9**(*51*) (12 mg) was dissolved in 1 mL of THF and 0.5 mL of 7 M NH_3 was added. The mixture was heated at 60 °C in a seal tube and stirred overnight. Thereafter, the mixture was transferred in to a round bottom flask and all the solvent was evaporated under reduced pressure. The residue was washed several times with MeOH and the solid was collected with centrifugation. The disappearance of the peak at 1.97 ppm in the ^{1}H-NMR spectra compare to the starting material confirmed complete deprotection of acetate group in the final product.

^{1}H-NMR (DMSO-d_6, 300 MHz): 7.35(brs), 6.31-5.72 (m), 5.07-4.36 (m), 3.35-2.92 (m); IR: 2951, 2863, 1708, 1362, 1337, 1226, 1176, 1037 cm^{-1}.



Removal of the thioacetate (-SAc) group from the polymer **5**(*32*)-*co*-**12**(*68*): The polymer **5**(*32*)-*co*-**12**(*68*) (6.0 mg) was dissolved in 0.5 mL of DMA (dimethylacetamide) followed by addition of triethyl amine (15 µl) and 1,4-dithiothreitol (12.0 mg) at room temperature. The mixture was allowed to stir overnight, and the product was precipitated out by addition of excess Et_2O (3.2 mg). The disappearance of the peak at 2.32 ppm and appearance of broad singlet at 1.41 ppm in the ^{1}H-NMR spectra compare to the starting material confirmed the deprotection of TBDMS group in the product.

^{1}H-NMR (CD_2Cl_2, 300 MHz): 7.41-7.31 (m), 6.16-5.76 (m), 5.01-4.29 (m), 3.62 (brs), 3.33 (brs), 3.74 (brs), 1.41 (brs); IR: 2947, 2861, 1710, 1356, 1335, 1226, 1176, 1037 cm^{-1}.



Removal of the silyl ether (-OTBDMS) group from the polymer **5**(*31*)-*co*-**13**(*69*): To the solution of the polymer **5**(*31*)-*co*-**13**(*69*) (5.0 mg) in 1 mL of DMF was added 0.2 mL of HF/Pyridine at 0 ^{o}C. The mixture was stirred at room temperature for 6 h. After the reaction, the product was isolated by adding excess Et_2O. The trace amount of remaining pyridine was removed by dialysis to get pure product (3.0 mg). The disappearance of the peaks at 0.84 and 0.01 ppm in the ^{1}H-NMR spectra compare to the starting material confirmed complete deprotection of TBDMS group in the product.

^{1}H-NMR (DMSO-d_6, 300 MHz): 7.33-7.28 (m), 5.94-5.72 (m), 4.87-4.39(m), 3.44-3.36 (m); IR: 2947, 2861, 1710, 1366, 1335, 1226, 1176, 1037 cm^{-1}.

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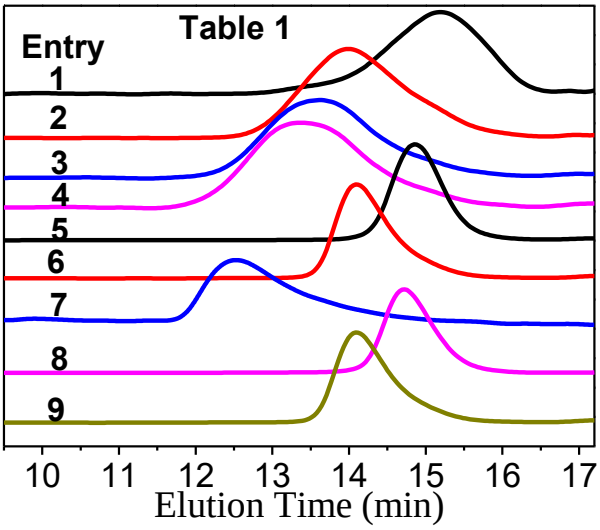


Figure S1. The GPC traces of the homopolymers in Table 1 of the main text.

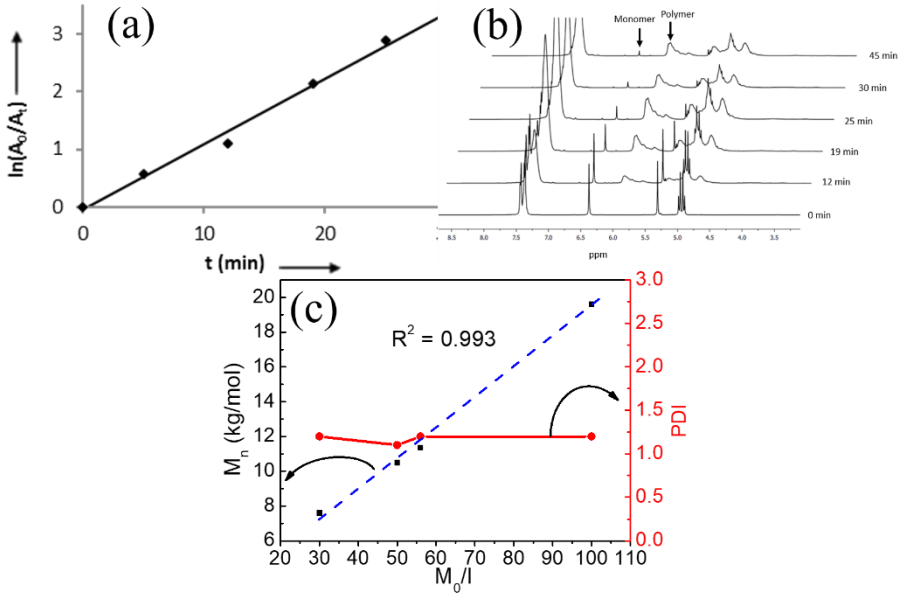


Figure S2. (a) Polymerization reaction follows the 1st order reaction kinetics; (b) ^{1}H-NMR observation for polymerization of monomer **5**; (c) Linear dependence of M_n (filled squares) on monomer-to-initiator ratio (M_0/I) and polydispersities (PDIs, filled circles).

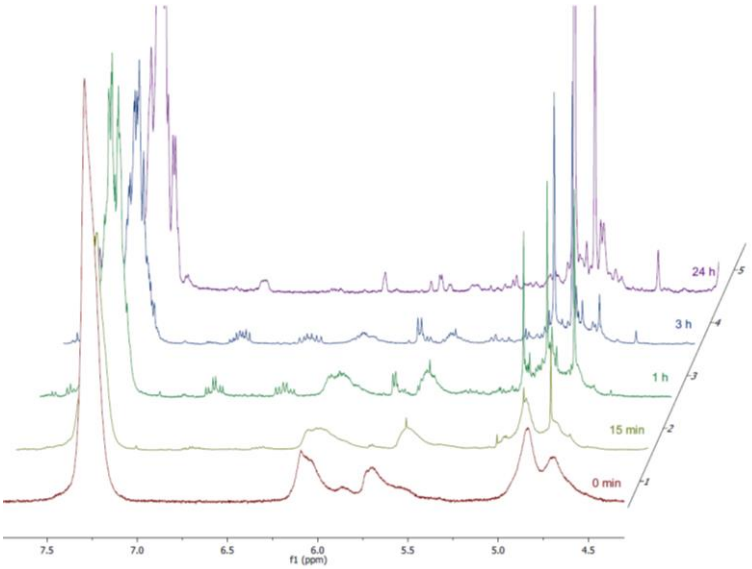


Figure S3. Degradation of *poly*-**5** at pH 1 over 24 h.

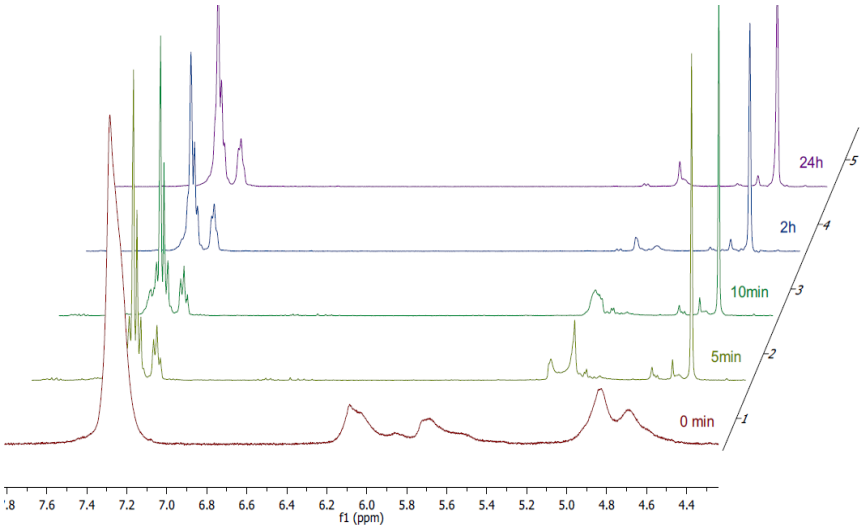


Figure S4. Degradation of *poly*-**5** at pH 13.5 over 24 h.

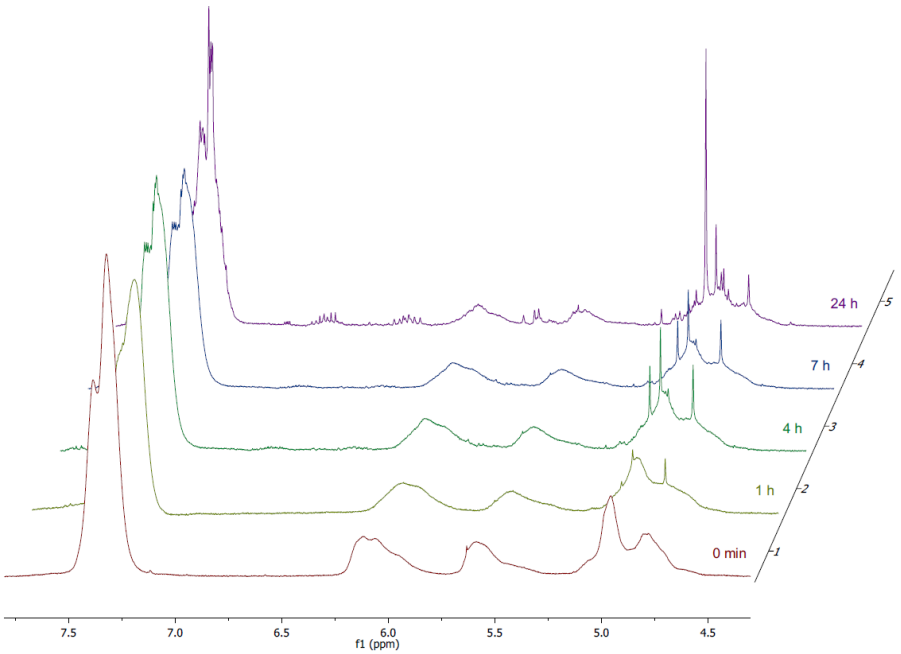


Figure S5. Degradation of *poly*-**5** at pH 2 over 24 h

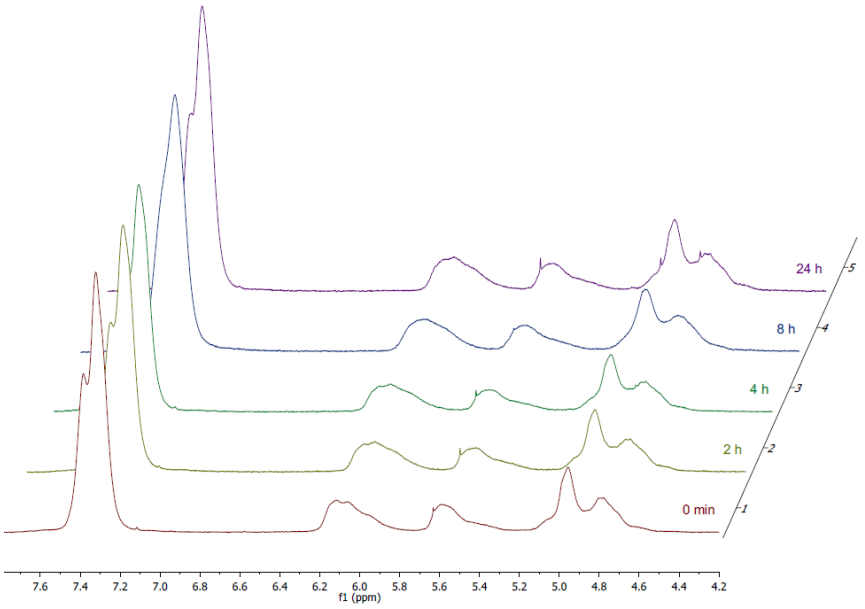


Figure S6. Degradation of *poly*-**5** at pH 3 over 24 h.

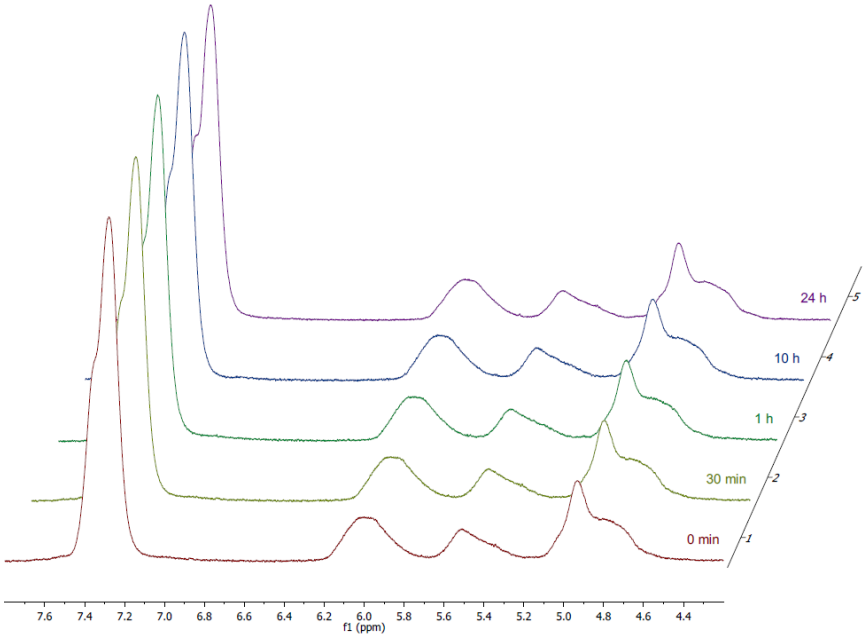


Figure S7. Degradation of *poly*-**5** at pH 4 over 24 h (no degradation observed).

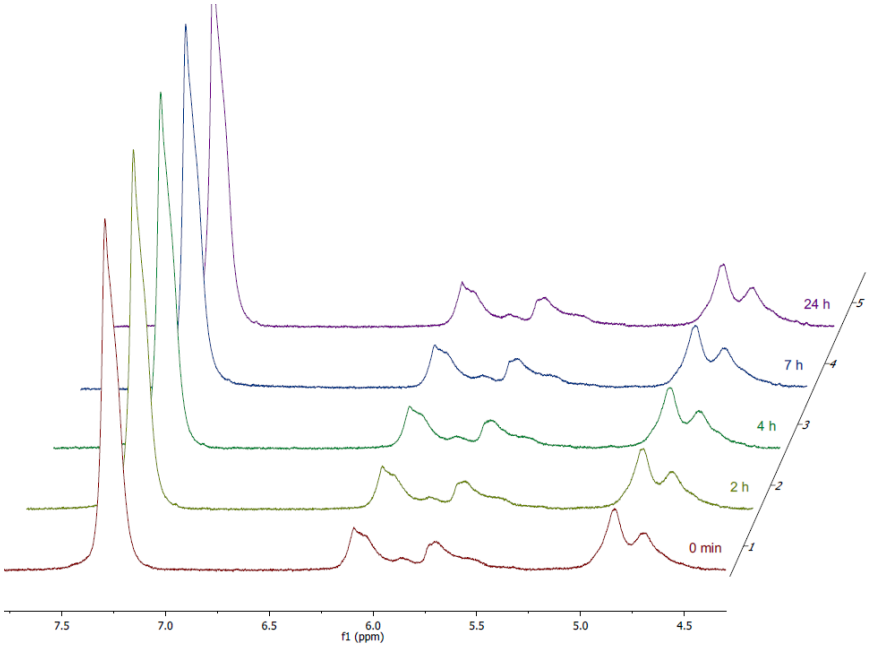


Figure S8. Degradation of *poly*-**5** at pH 10.5 over 24 h (no degradation observed).

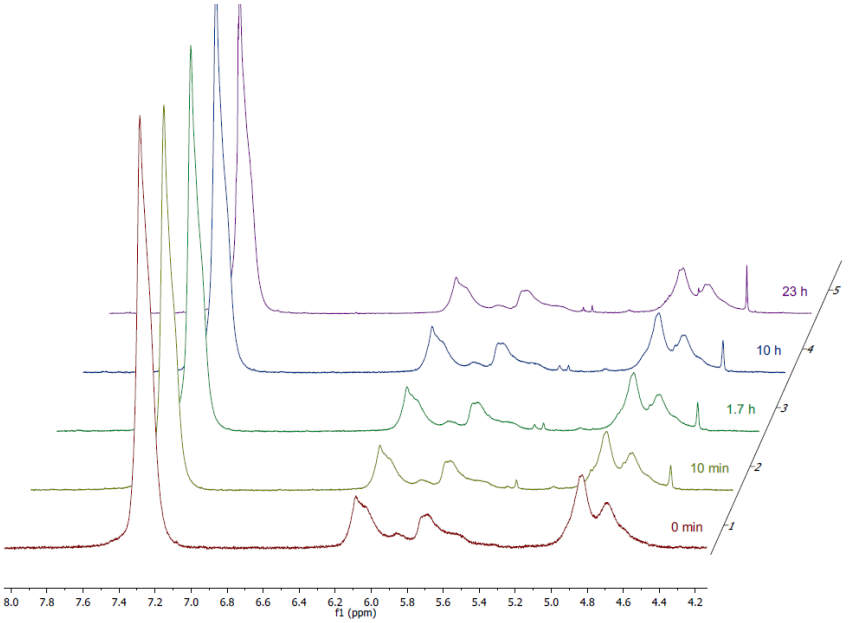


Figure S9. Degradation of *poly*-**5** at pH 11.5 over 24 h.

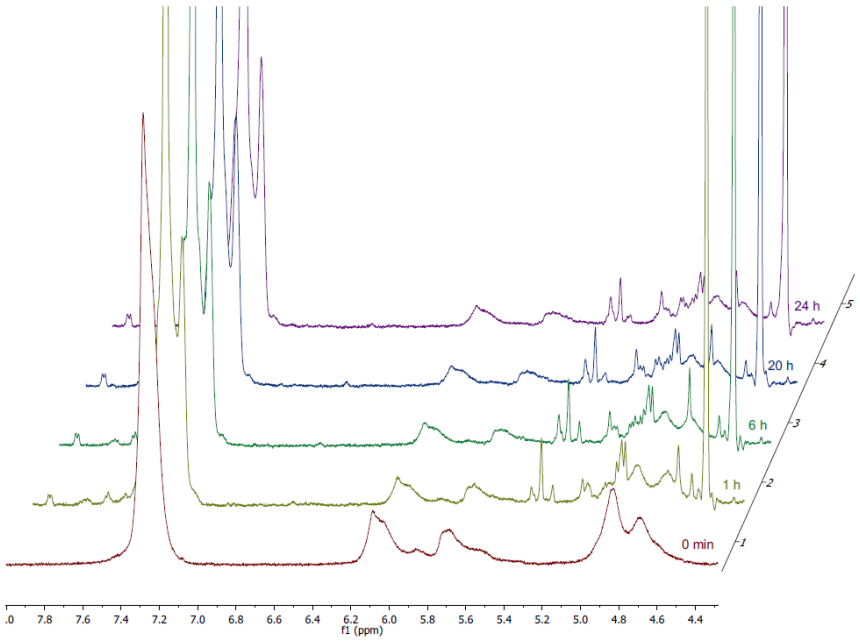


Figure S10. Degradation of *poly*-**5** at pH 12.5 over 24 h.

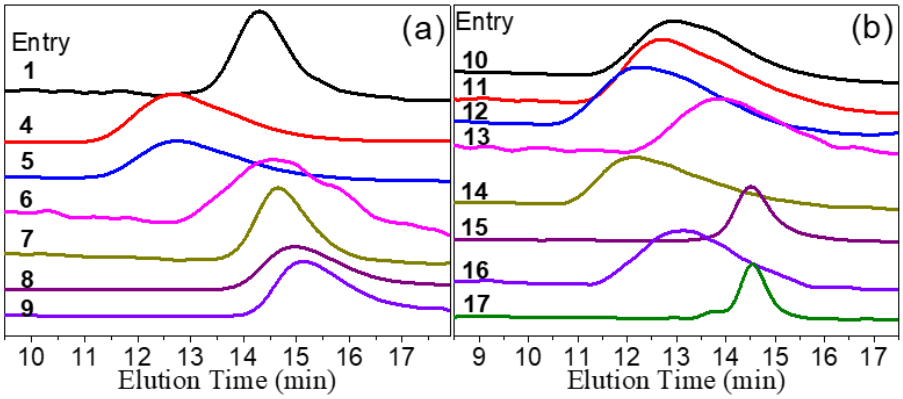


Figure S11. The GPC traces of the homopolymers in Table 2 of the main text. (Note: The GPC traces of entries 2 and 3 are missing)

Equation S1: Fineman Ross equation

$$\frac{(\mathbf{X}-1)}{\mathbf{Y}} = -(\frac{\mathbf{X}}{\mathbf{Y}^2})\boldsymbol{r}_2 + \boldsymbol{r}_1$$

Y: mol fraction of the monomer

X: mol fraction of the Polymer at certain mole fraction of the monomer

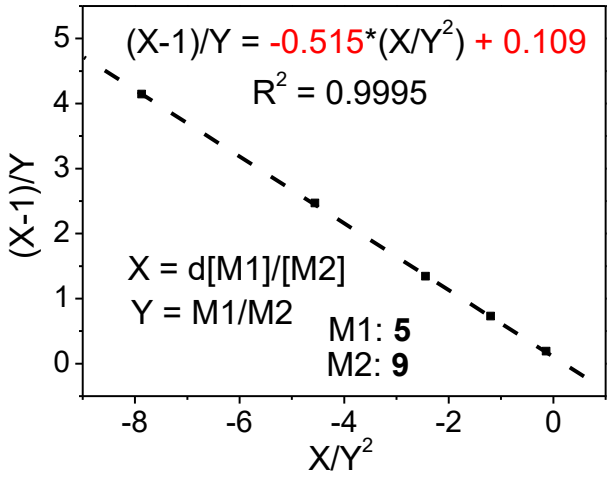


Figure S12. Determination of the reactivity ratios by the Fineman−Ross formalism for the system monomer **5** (M1) and **9** (M2) in THF at the room temperature.

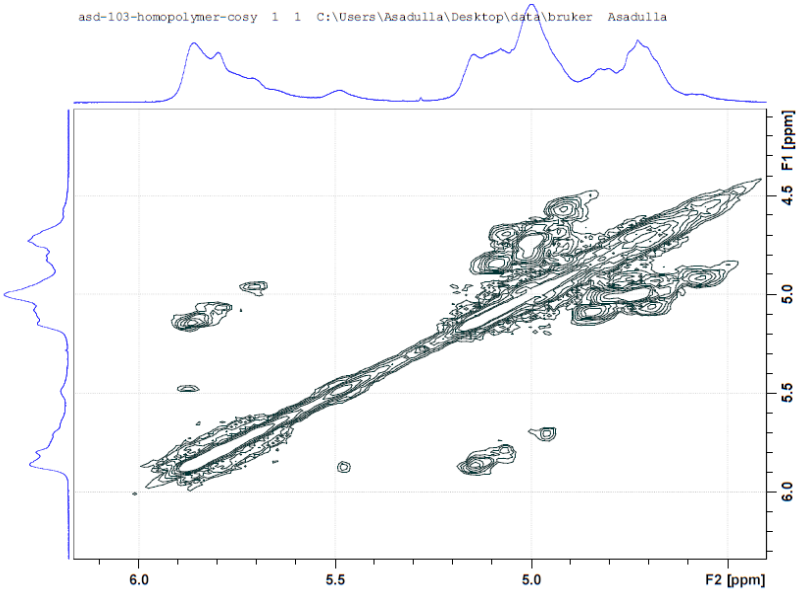


Figure S13. ^{1}H-^{1}H COSY experiment for the *poly*-**5**.

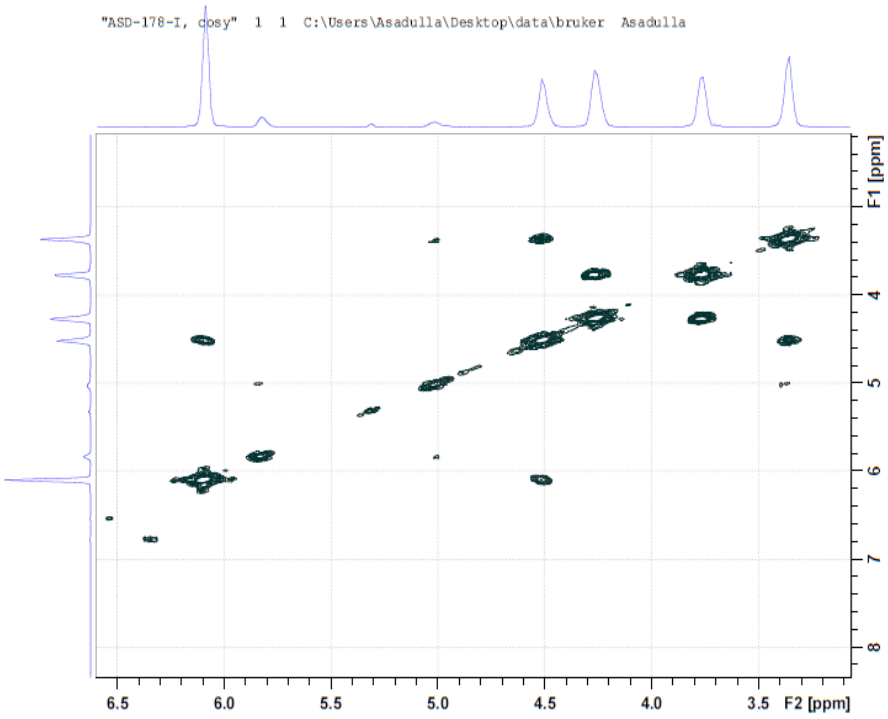


Figure S14. ^{1}H-^{1}H COSY experiment for *poly*-**9**.

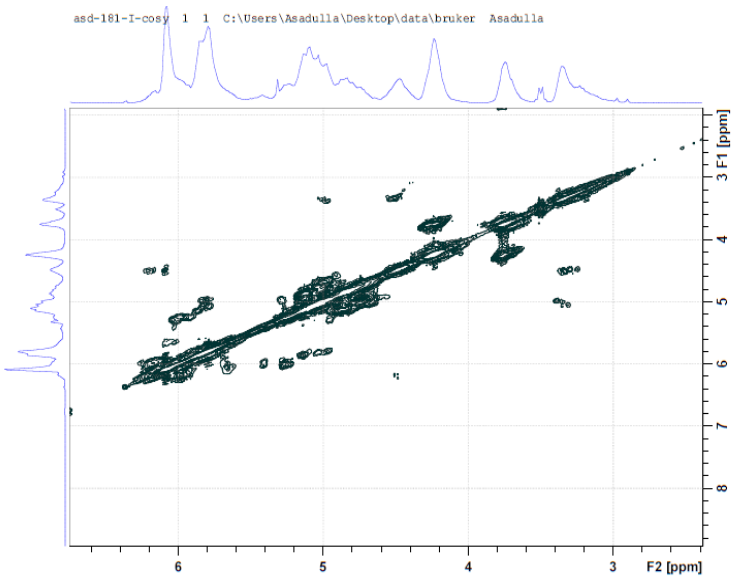


Figure S15. ^{1}H-^{1}H COSY experiment for the copolymer **5(*49*)**-*co*-**9(*51*)**.

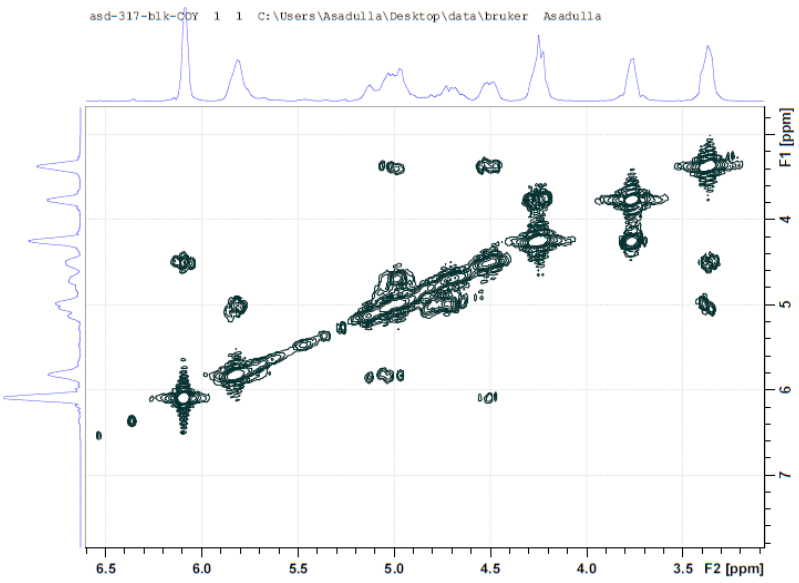


Figure S16. ^{1}H-^{1}H COSY experiment for the copolymer **9**-*block*-**5**.

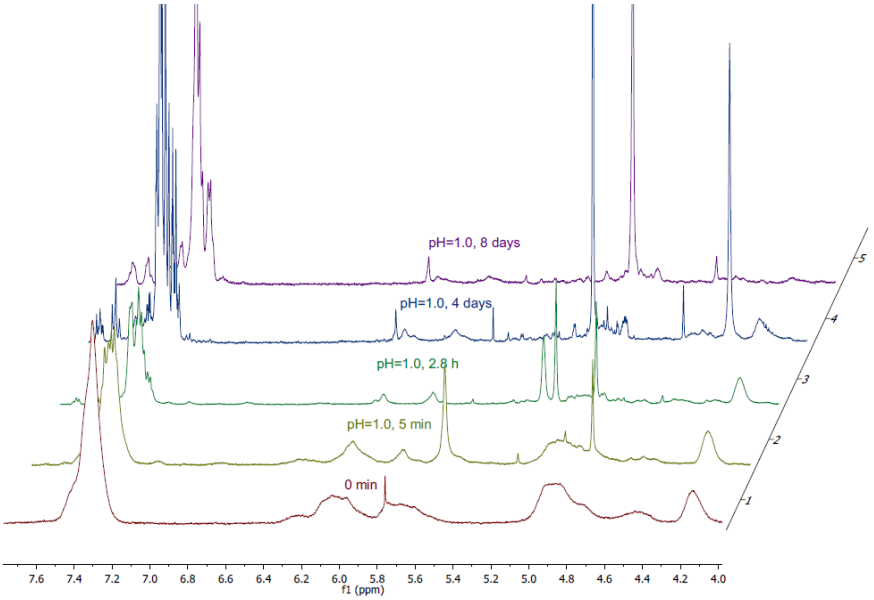


Figure S17. Degradation of polymer **5(*49*)-*co*-9(*51*)** at pH 1, over 8 days

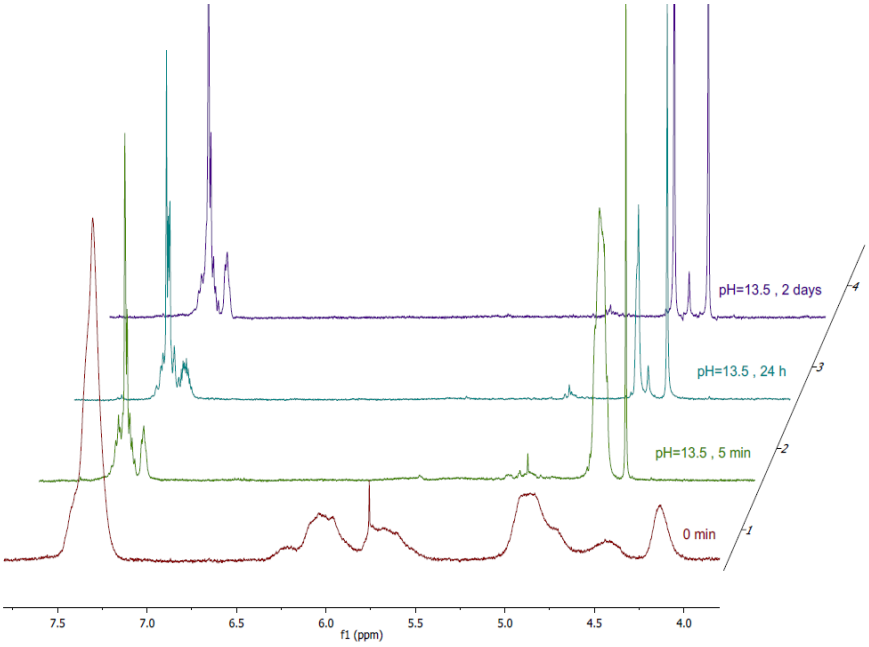


Figure S18. Degradation of polymer **5**(*49*)-*co*-**9**(*51*) at pH 13.5, over 2 days.

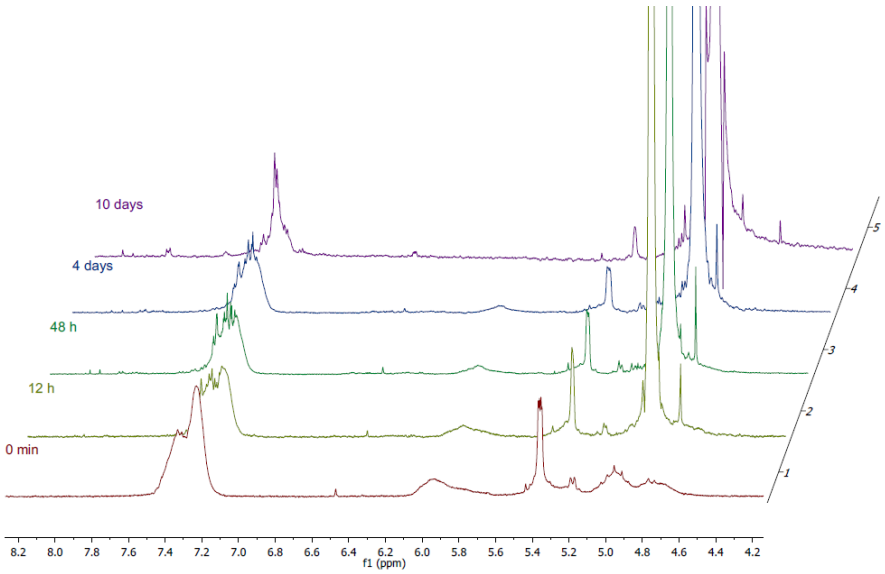


Figure S19. Degradation of polymer **5(***36***)**-*co*-**14(***64***)** at pH 1, over 10 days.

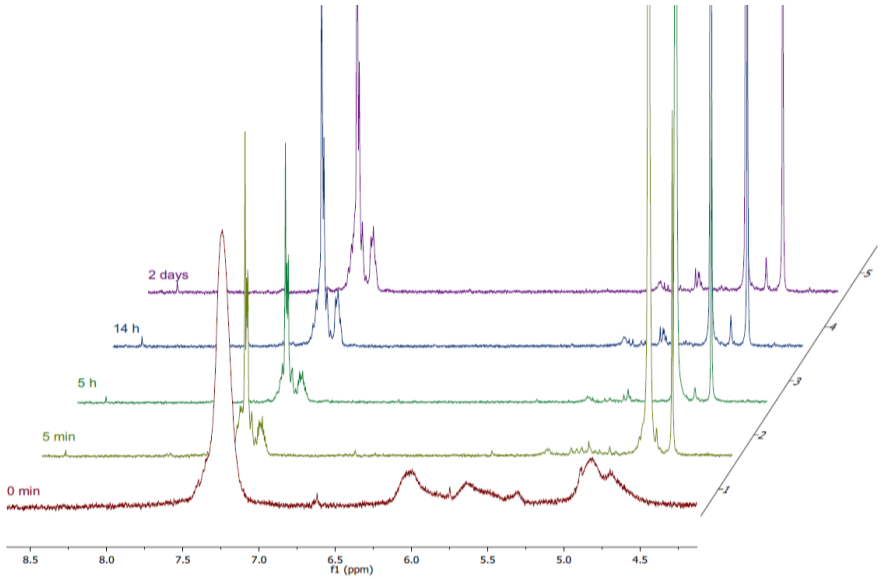


Figure S20. Degradation of polymer **5(***36***)**-*co*-**14(***64***)** at pH 13.5, over 2 days.

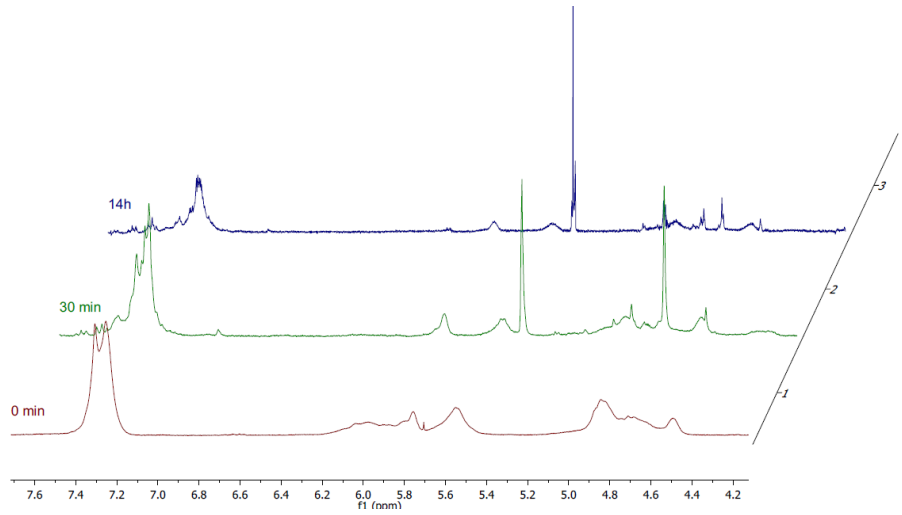


Figure S21. Degradation studies for **5(***39***)-*co*-15(***61***)** at pH 1.

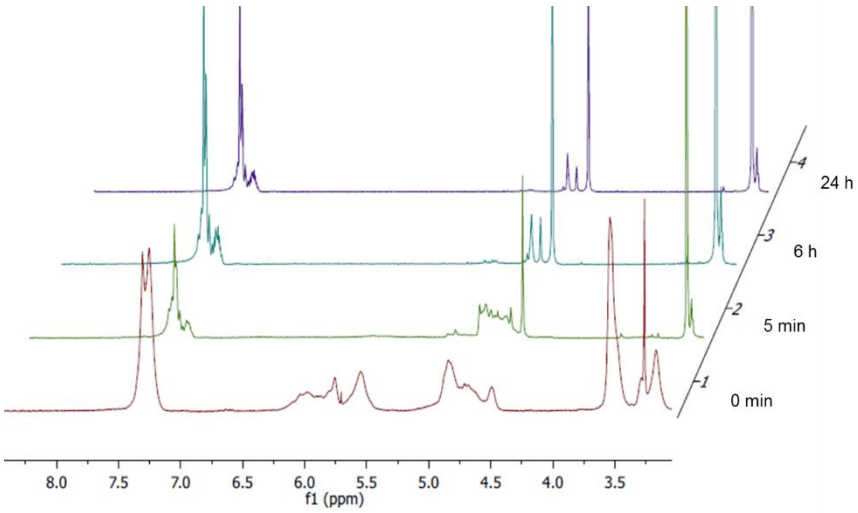


Figure S22. Degradation studies for **5**(*39*)-ran-**15**(*61)* at pH 13.5.

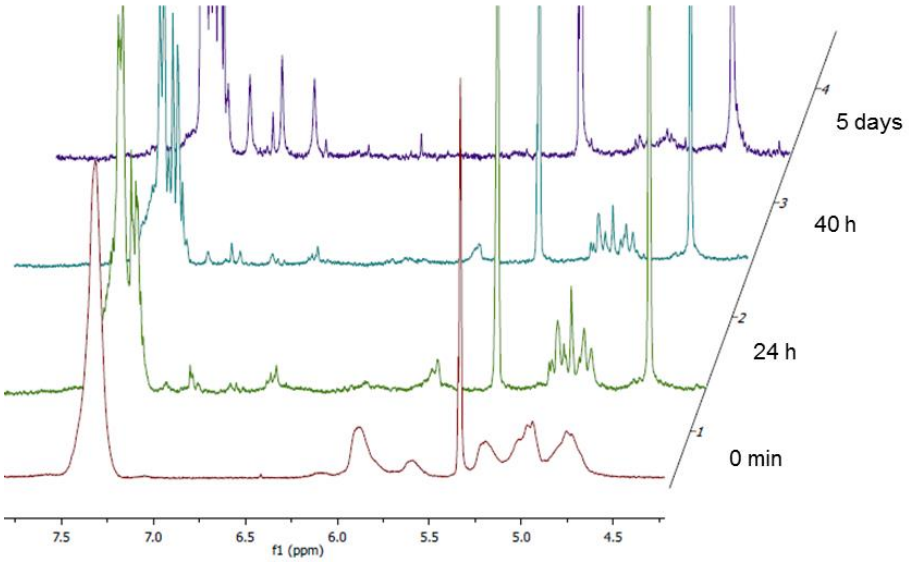


Figure S23. Degradation studies for **5***(73)*-*co*-**15(***27***)** at pH 1.

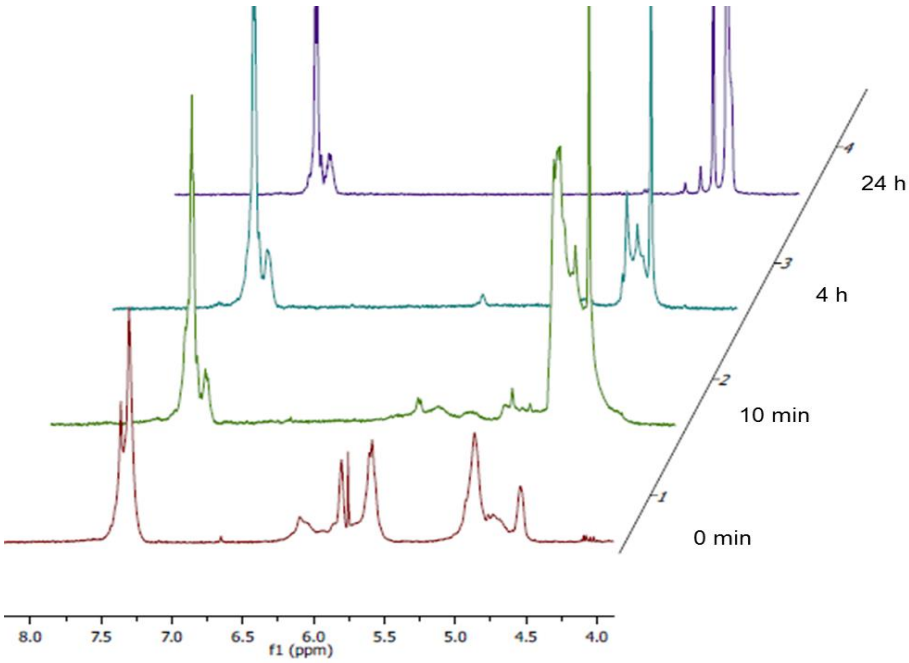


Figure S24. Degradation studies for **5**(*73*)-*co*-**15**(*27*) at pH 13.5.

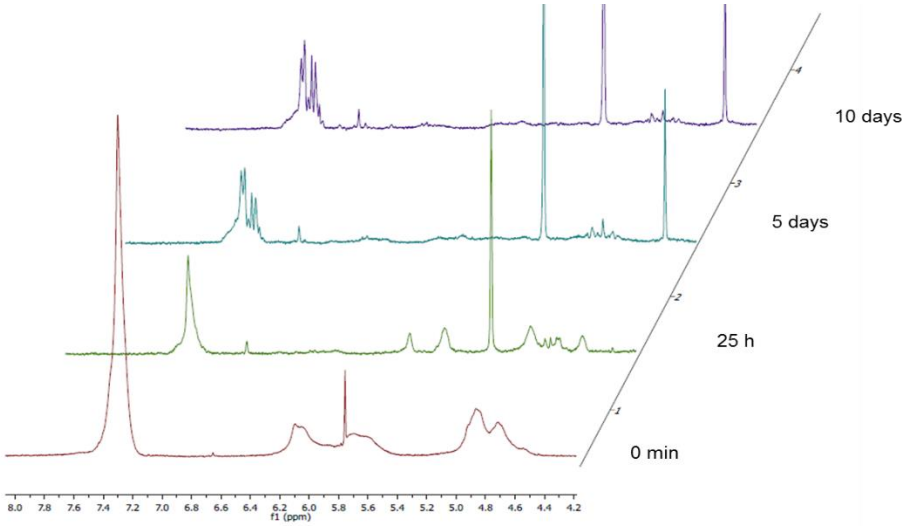


Figure S25. Degradation of the polymer **5**(27)-*co*-**15**(73) at pH 1.0.

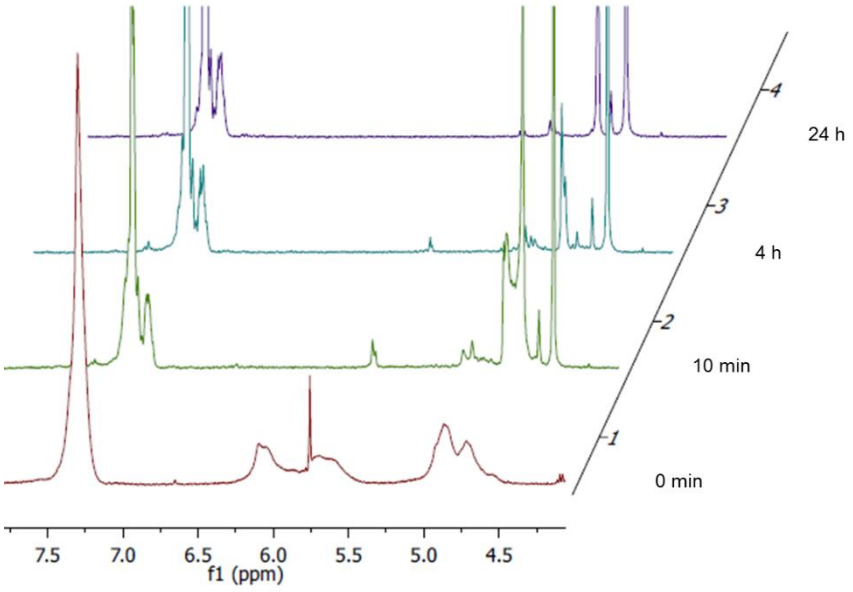


Figure S26. Degradation of the polymer **5**(*27*)-*co*-**15**(*73*) at pH 13.5.

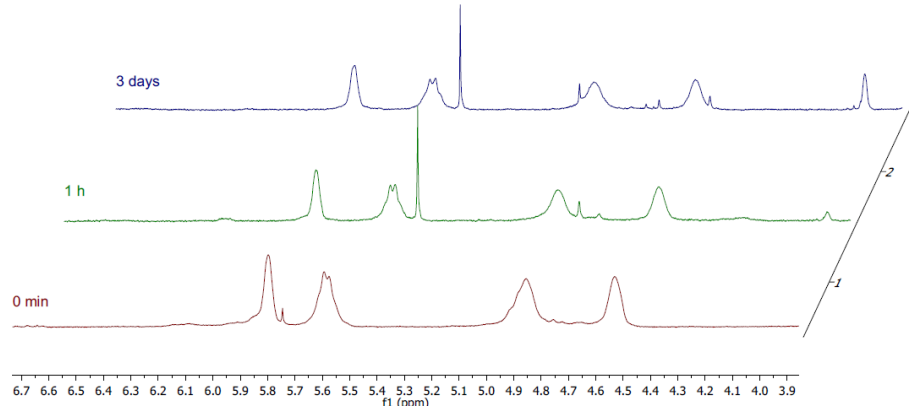


Figure S27. Degradation of **5(*9*)-*co*-15(*91*)** at pH 1 (no significant degradation was observed after 3 days)

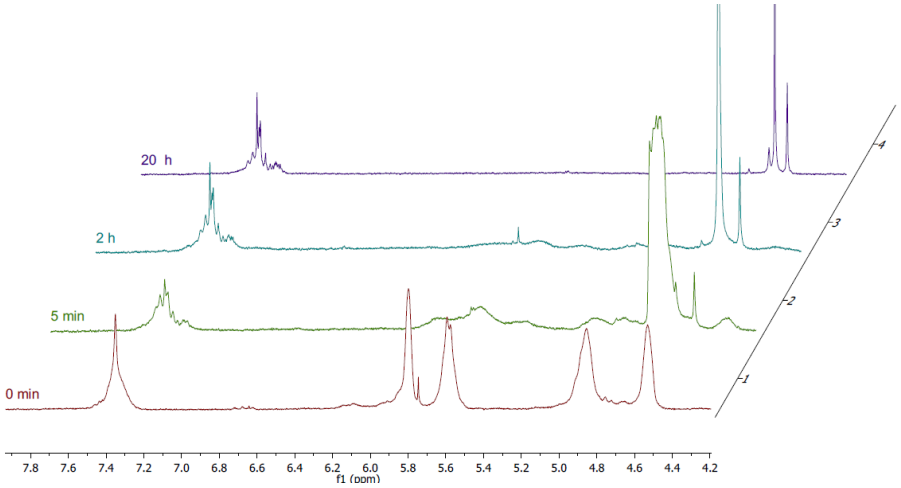


Figure S28. Degradation studies for **5(*9*)-*co*-15(*91*)** at pH 13.5.

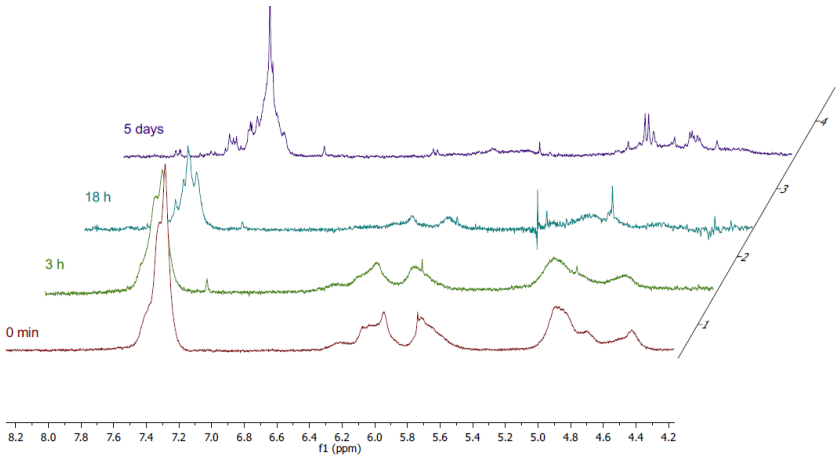


Figure S29. Degradation of polymer for **5(***37***)-***co*-**10(***63***)** at pH=1.

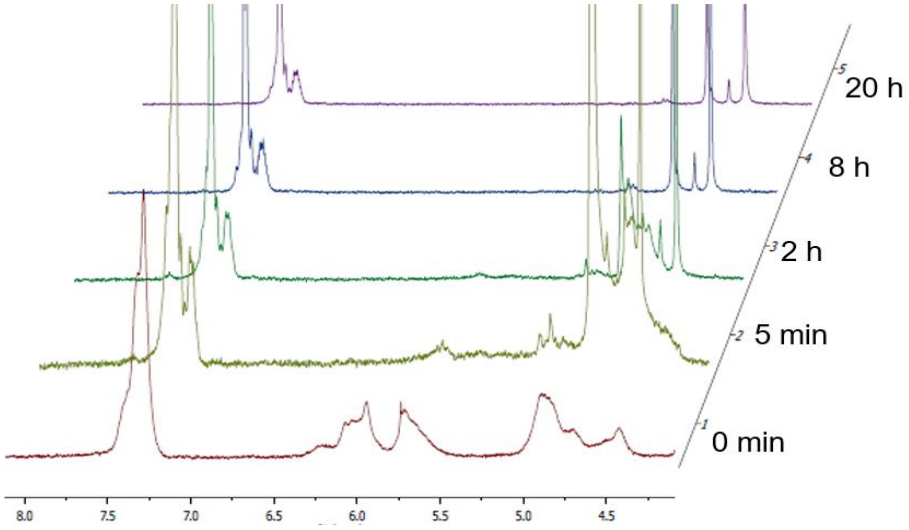


Figure S30. Degradation of for **5(***37***)-***co*-**10(***63*) at pH=13.5

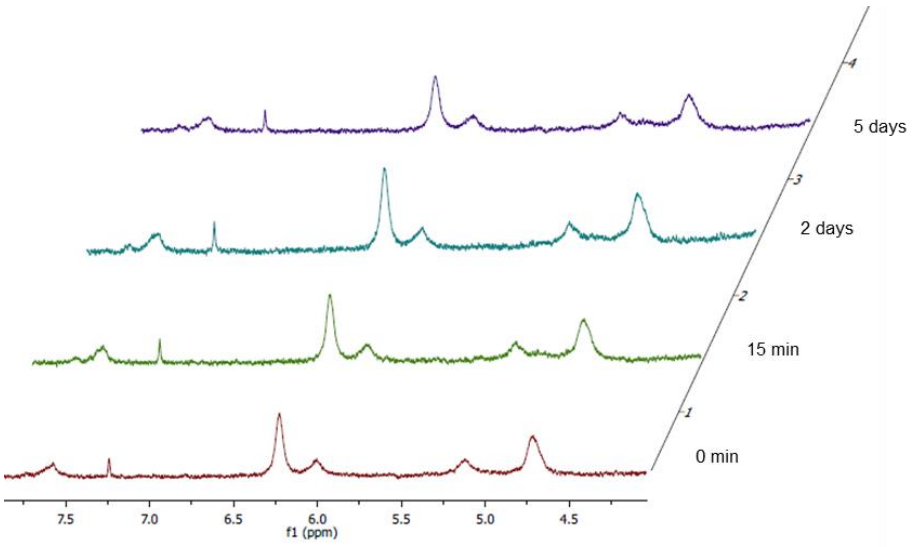


Figure S31. Degradation of polymer **5**(*10*)-*co*-**10**(*90*) at pH 1 (no degradation was observed).

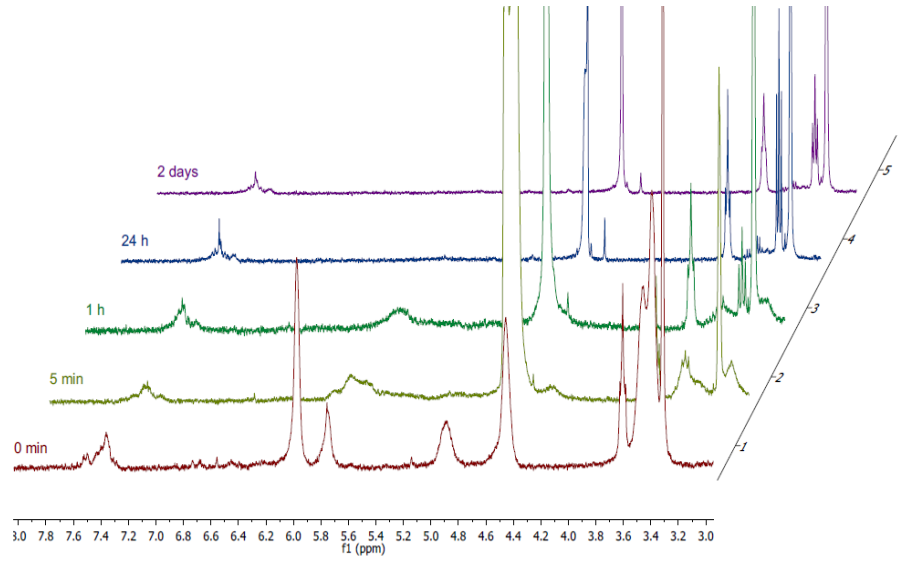


Figure S32. Degradation of polymer **5**(*10*)-*co*-**10**(*90*) at pH=13.5.

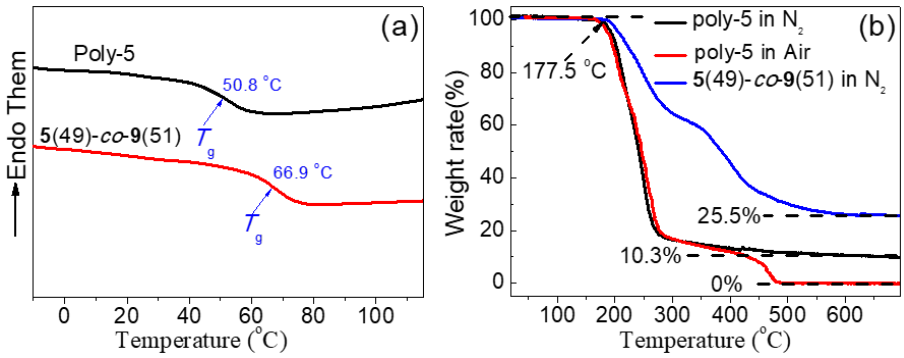


Figure S33. (a)The second heating curve based on DSC of the poly-**5** and **5**(49)-*co*-**9**(51), and (b) TGA results of the poly-**5** and **5**(49)-*co*-**9**(51). Heating rate: 10 ºC/min for DSC and TGA.

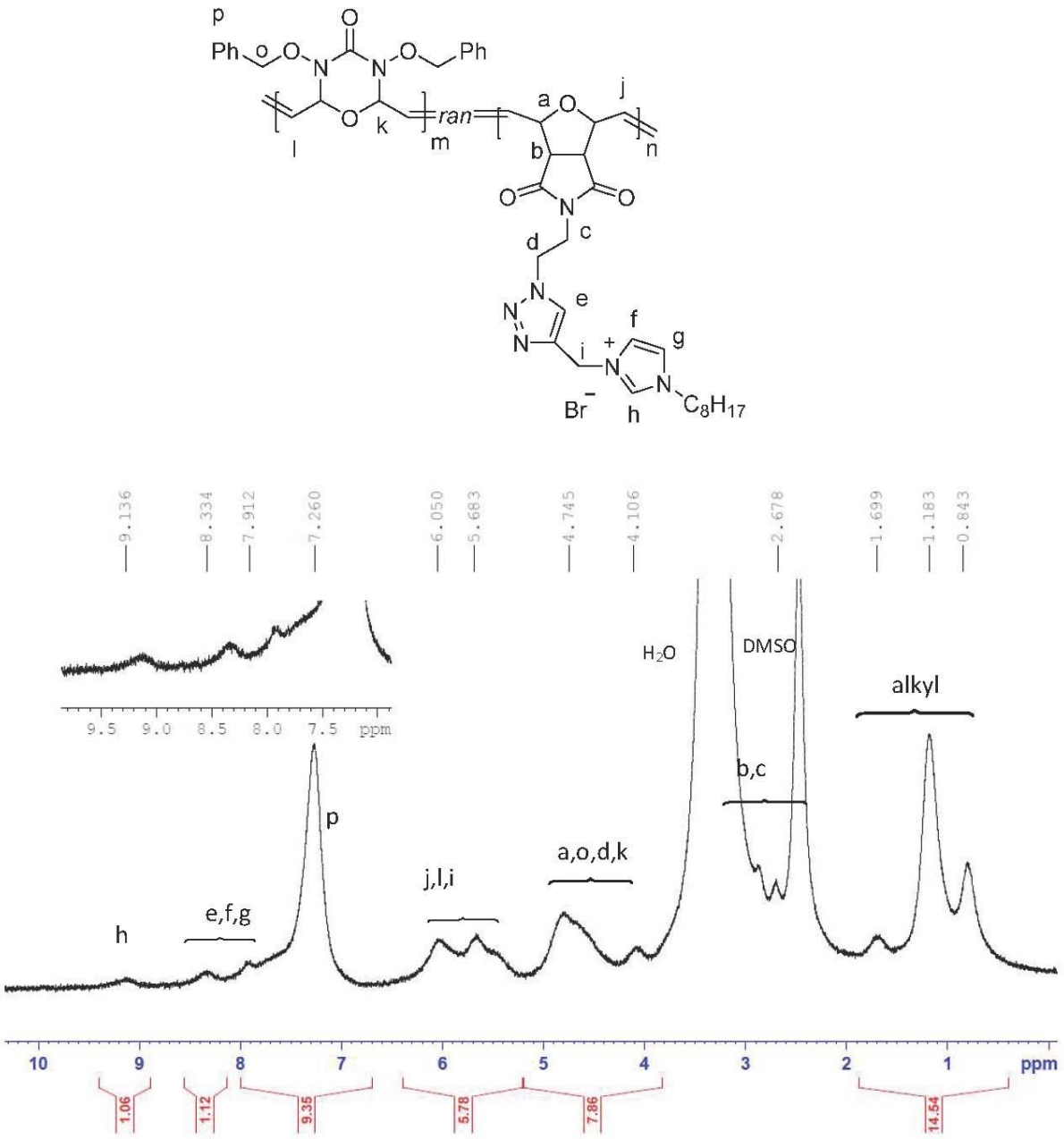


Figure S34. ^{1}H-NMR spectrum of the polymer conjugated with imidazolium salt.

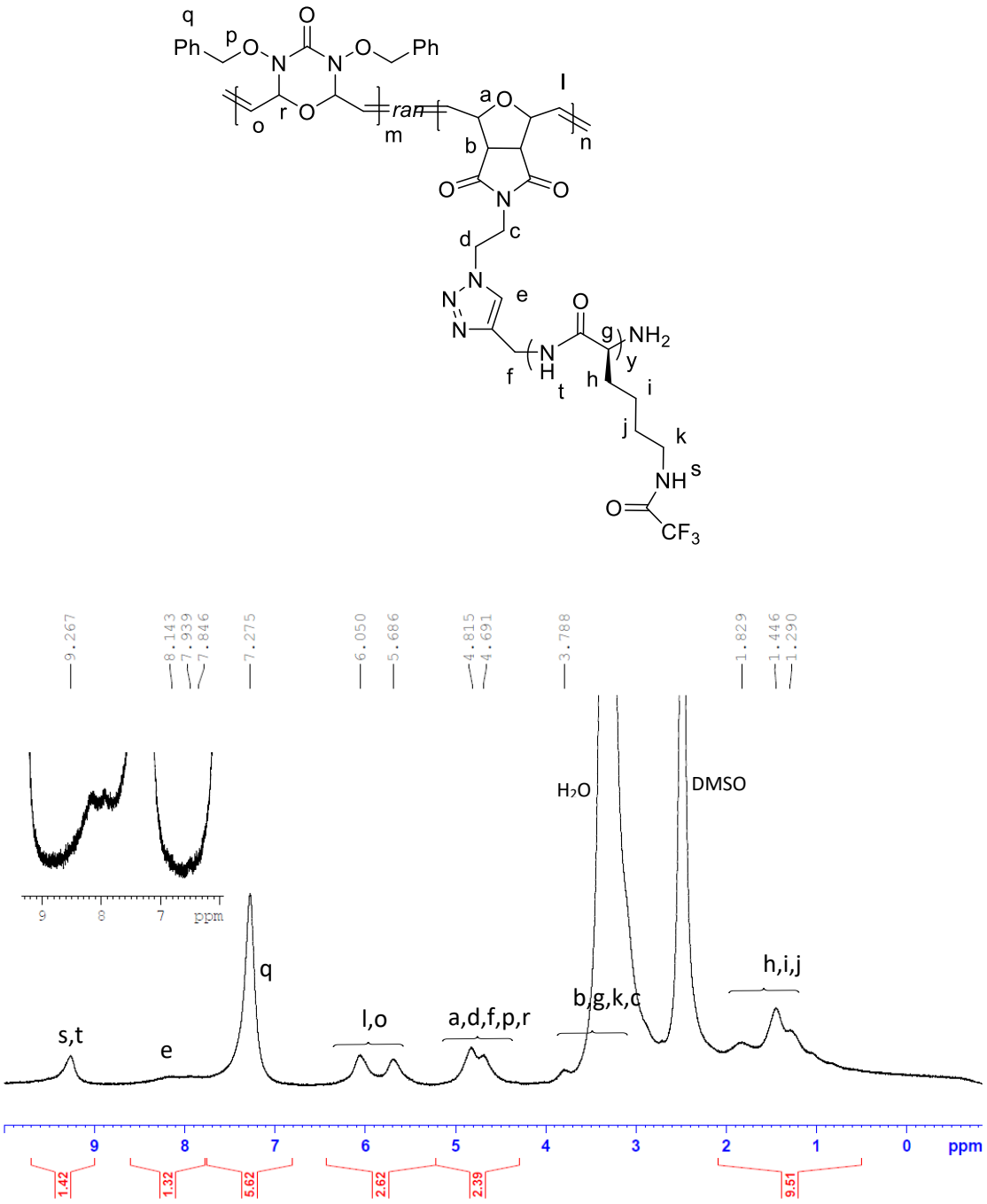
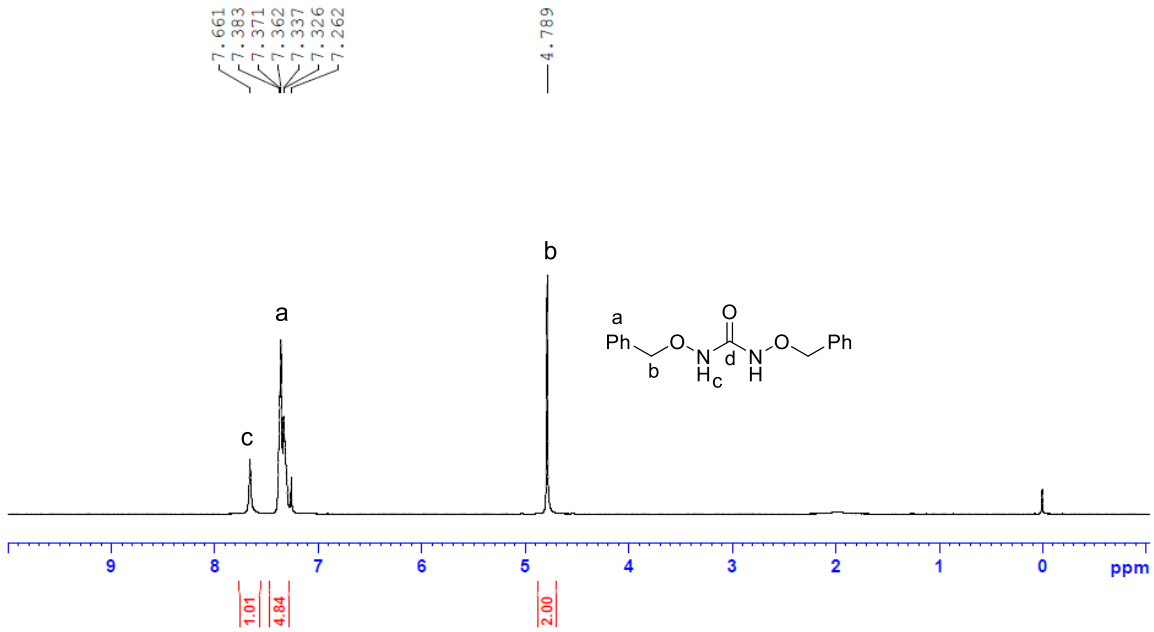
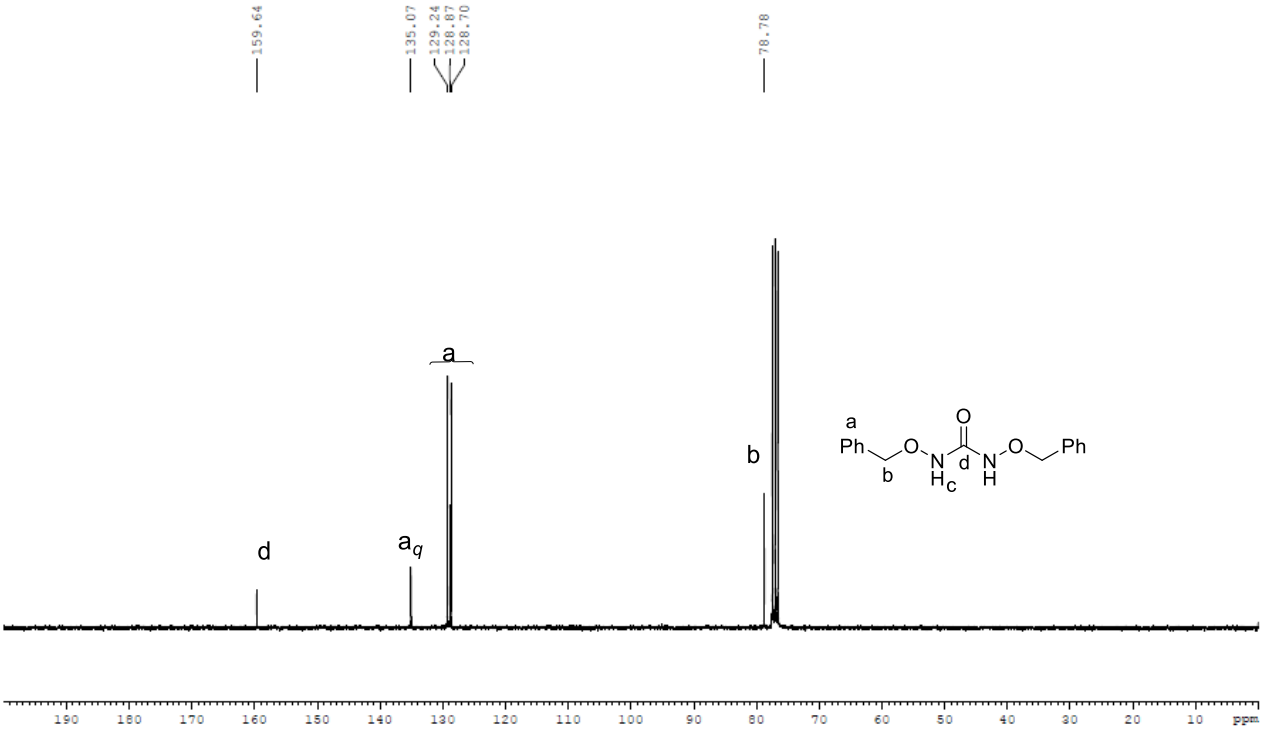


Figure S35. ^{1}H-NMR spectrum of the polymer conjugated with PolyLys(TFA).

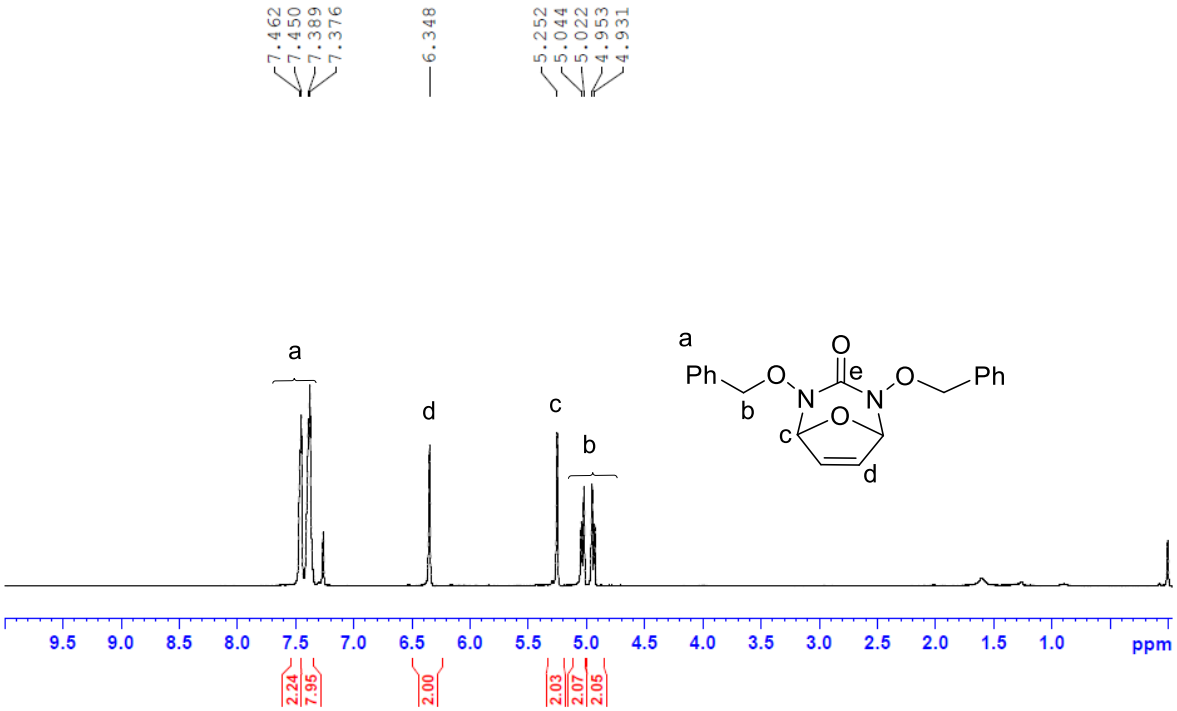
NMR Spectra of precursors, monomers, and synthesized polymers



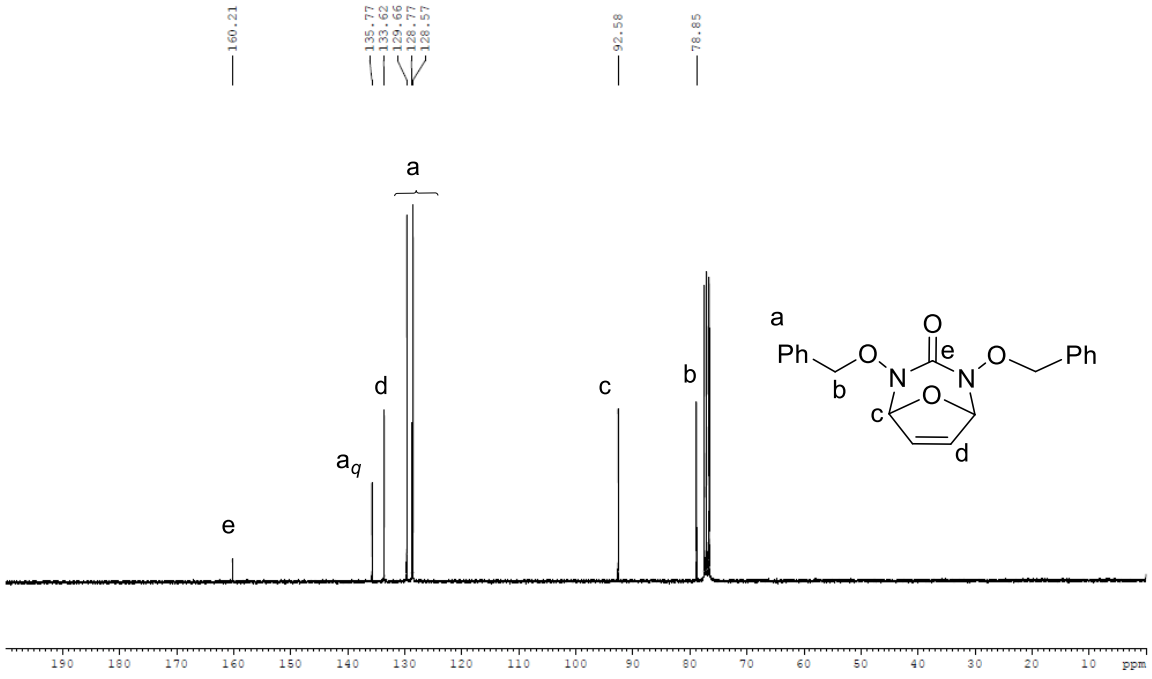
^{1}H-NMR Spectrum of compound **3**.



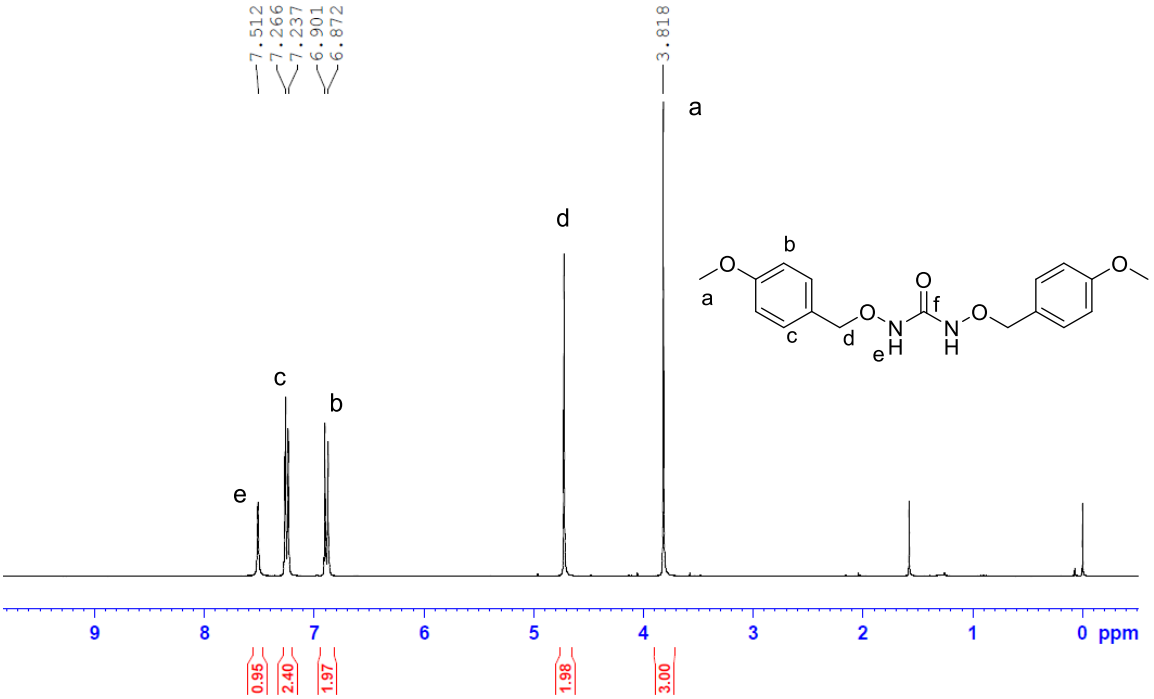
^{13}C-NMR Spectrum of compound **3**.



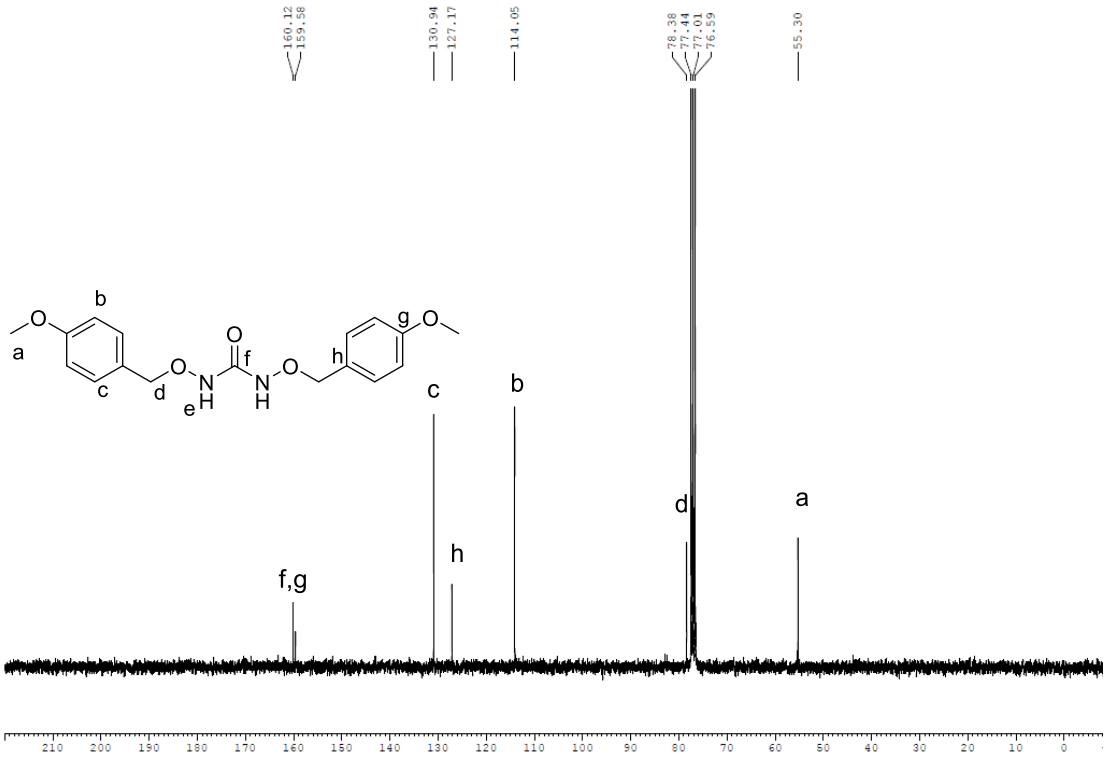
^{1}H-NMR Spectrum of compound **5**.



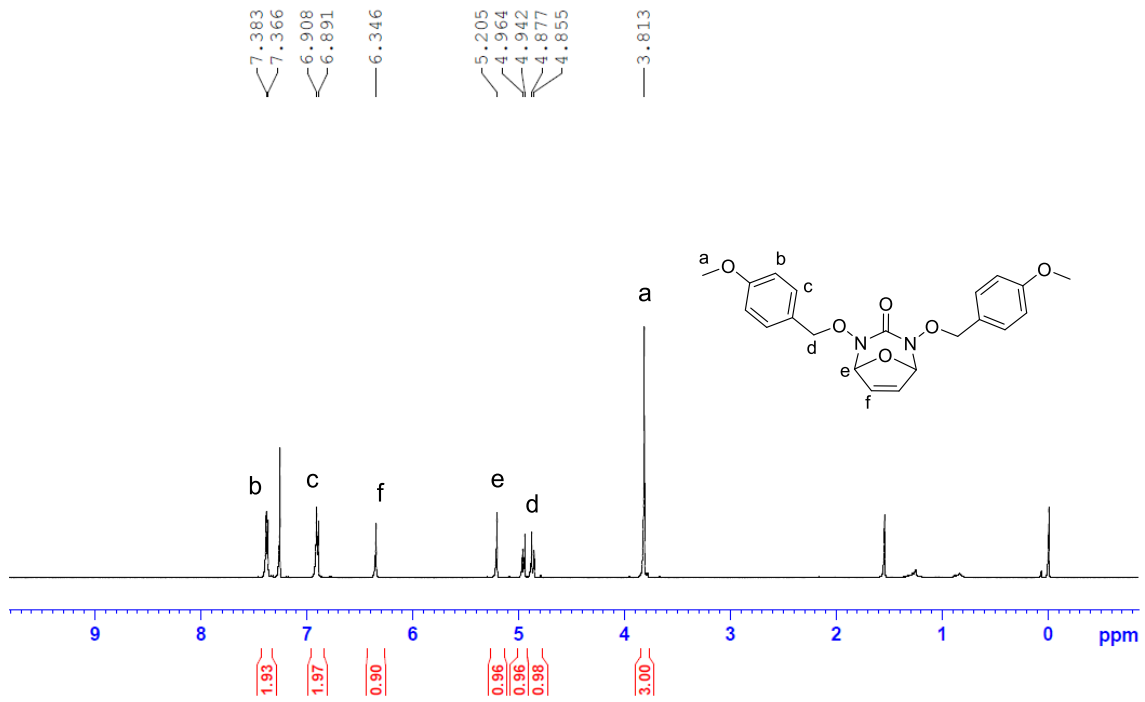
^{13}C-NMR Spectrum of compound **5**.



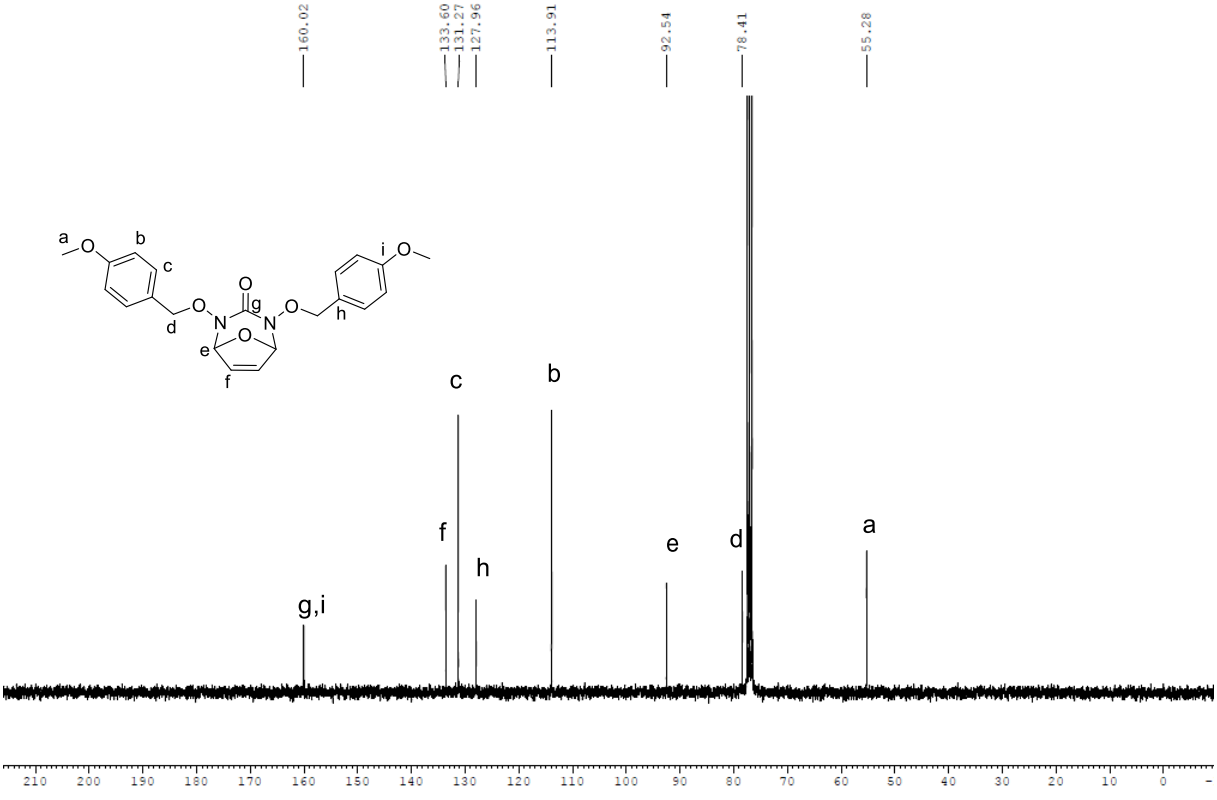
^{1}H-NMR Spectrum of compound **4**.



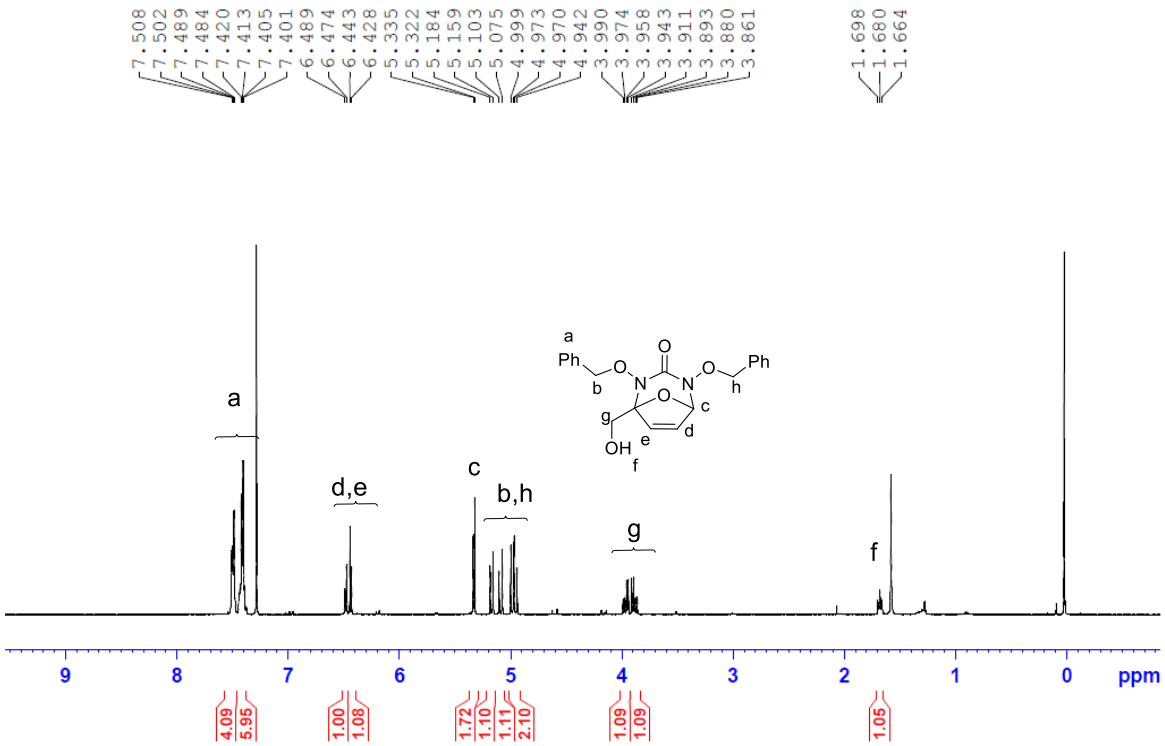
^{13}C-NMR Spectrum of compound **4.**



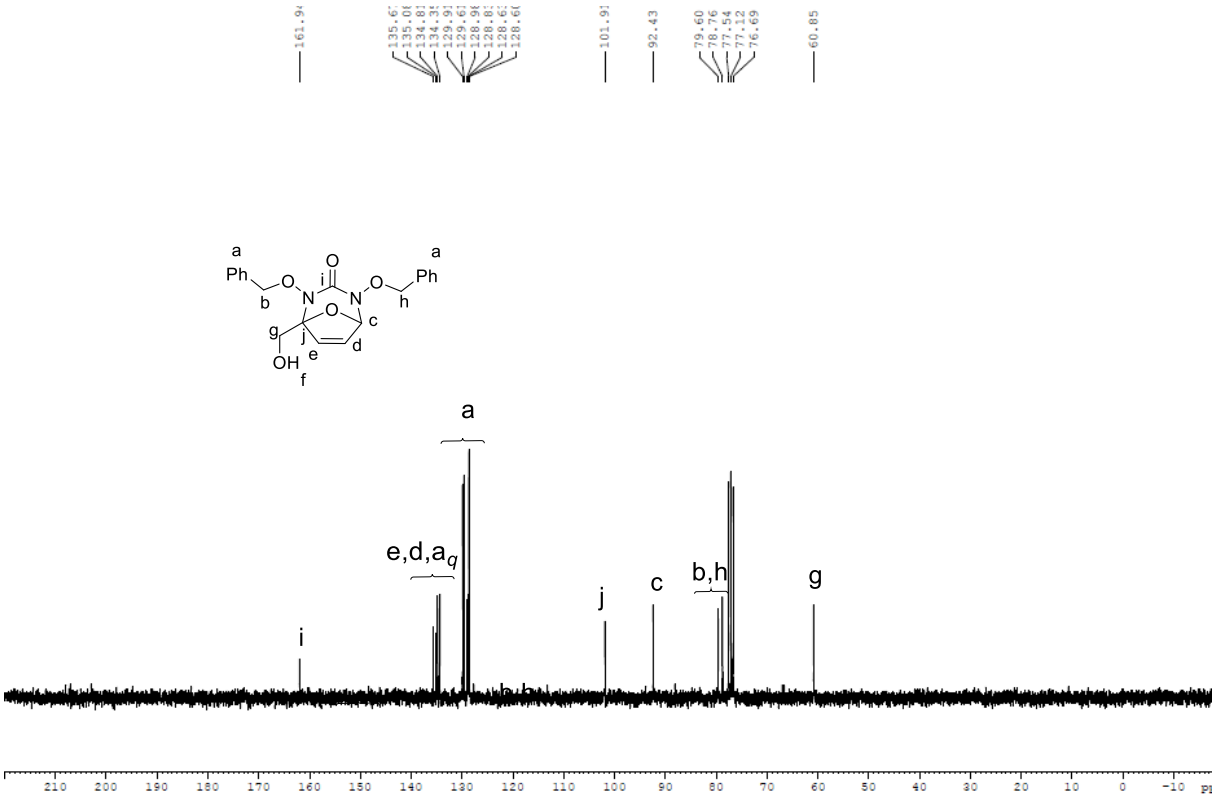
^{1}H-NMR Spectrum of compound **6.**



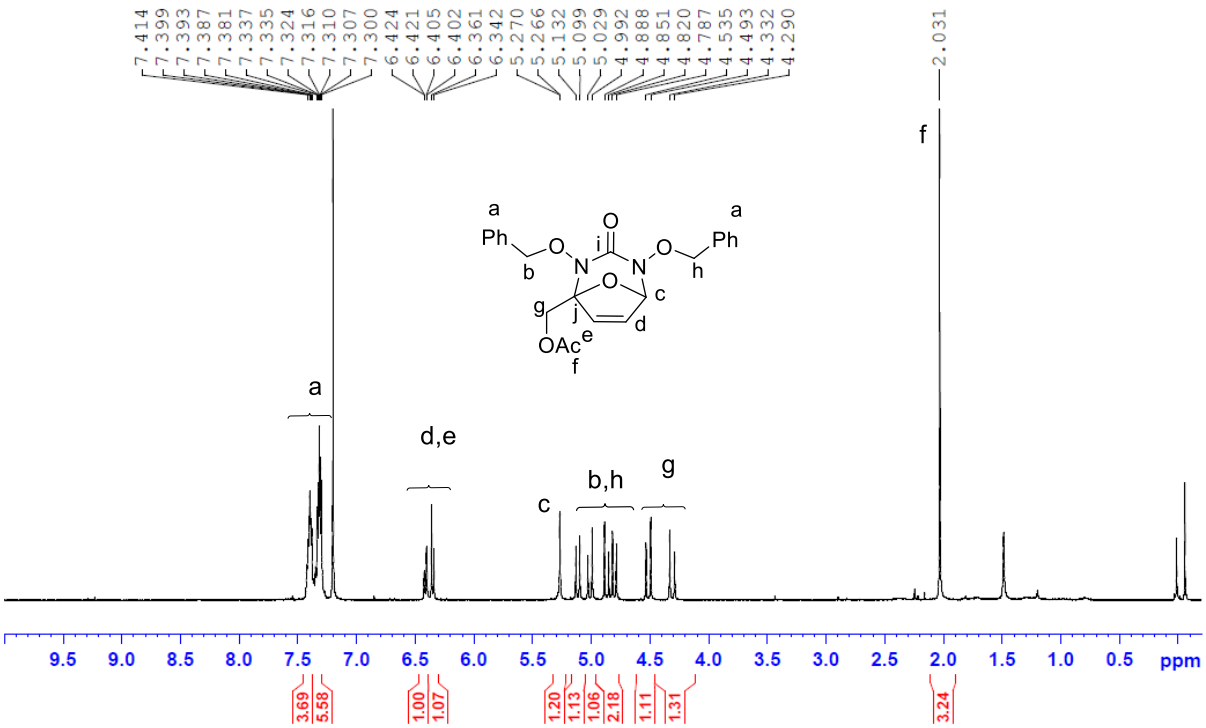
^{13}C-NMR Spectrum of compound **6.**



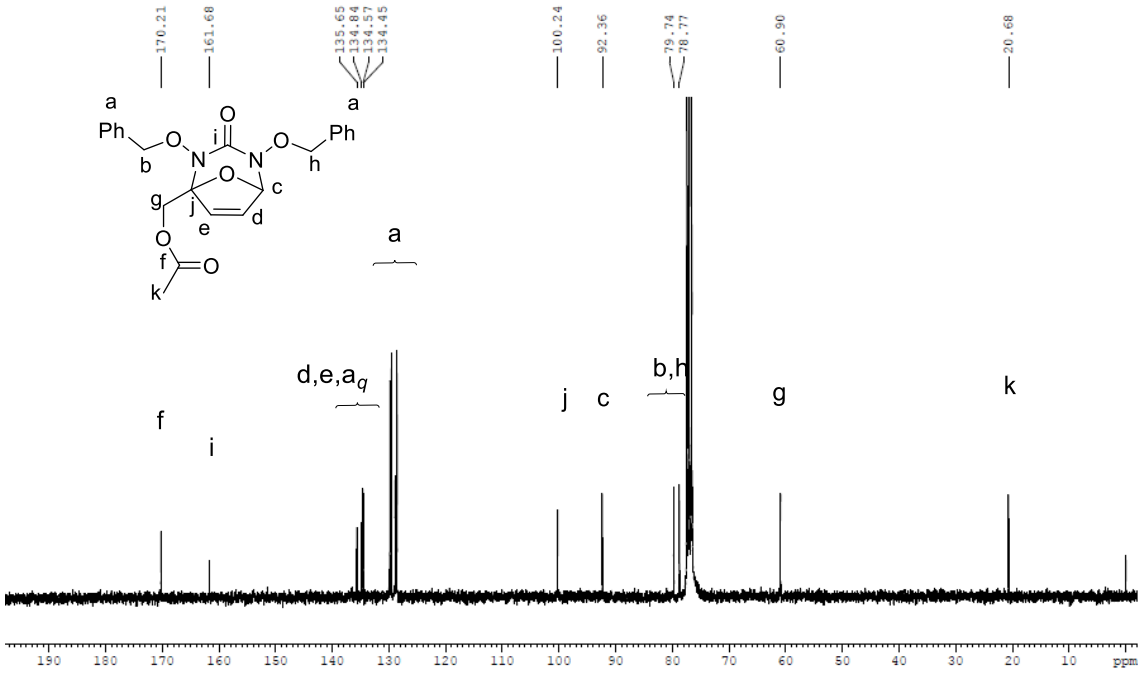
^{1}H-NMR Spectrum of compound **7.**



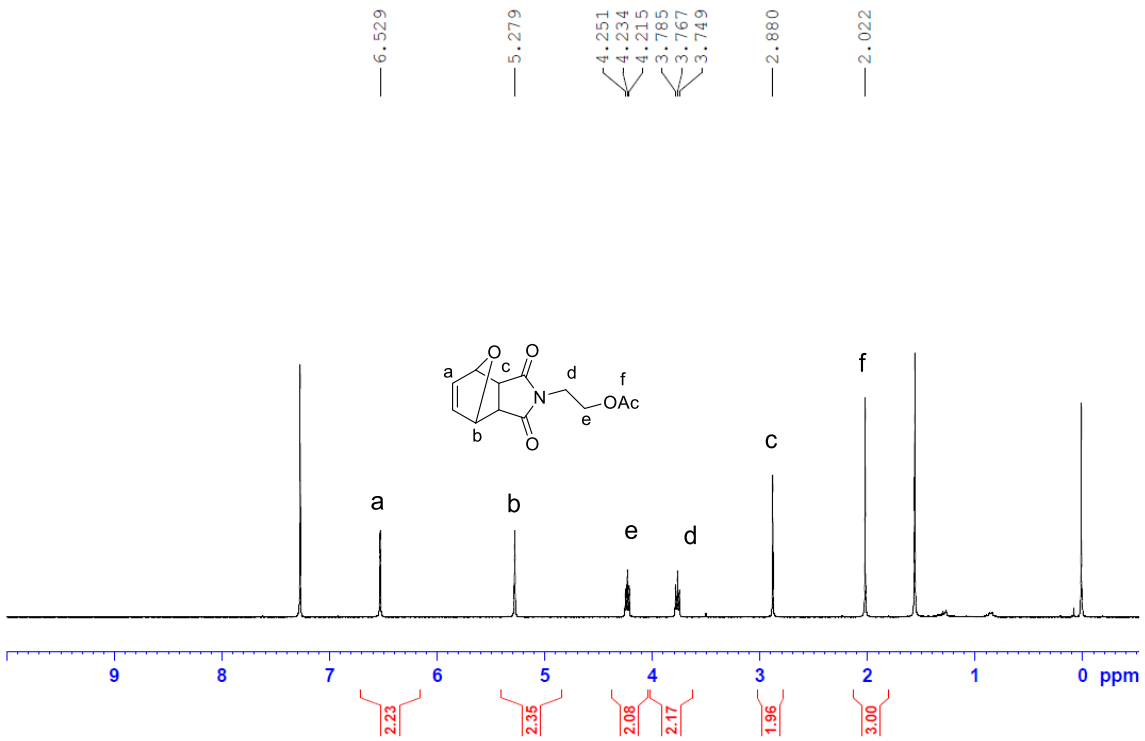
^{13}C-NMR Spectrum of compound **7**.



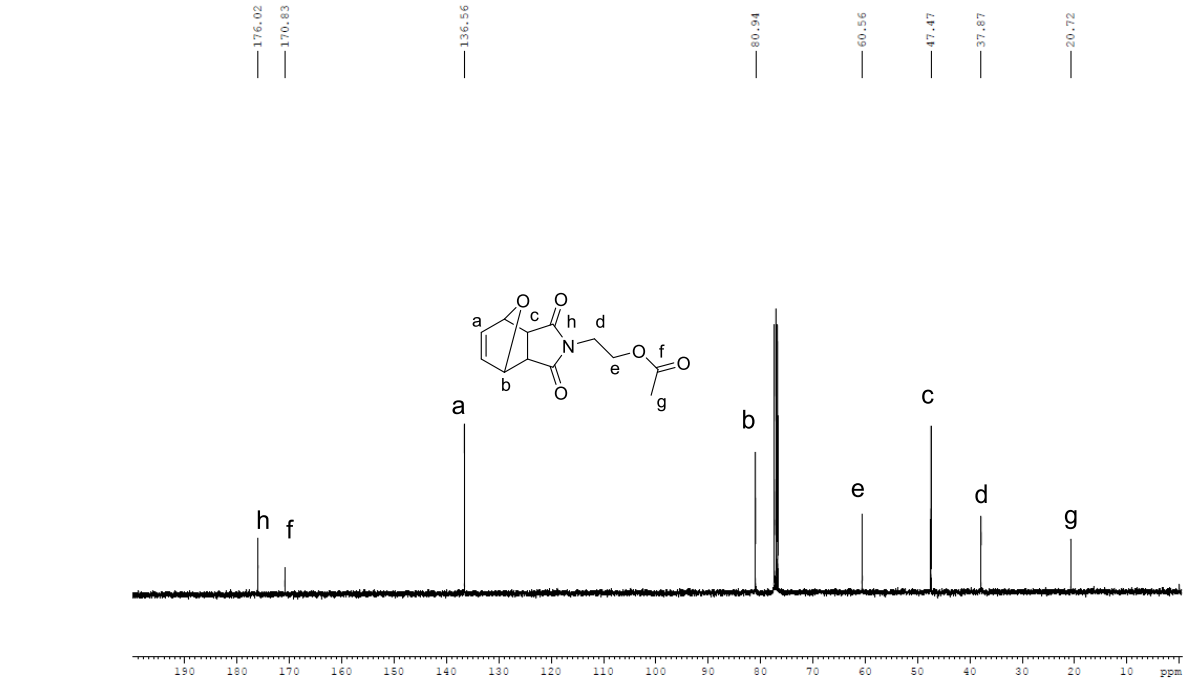
^{1}H-NMR Spectrum of compound **8.**



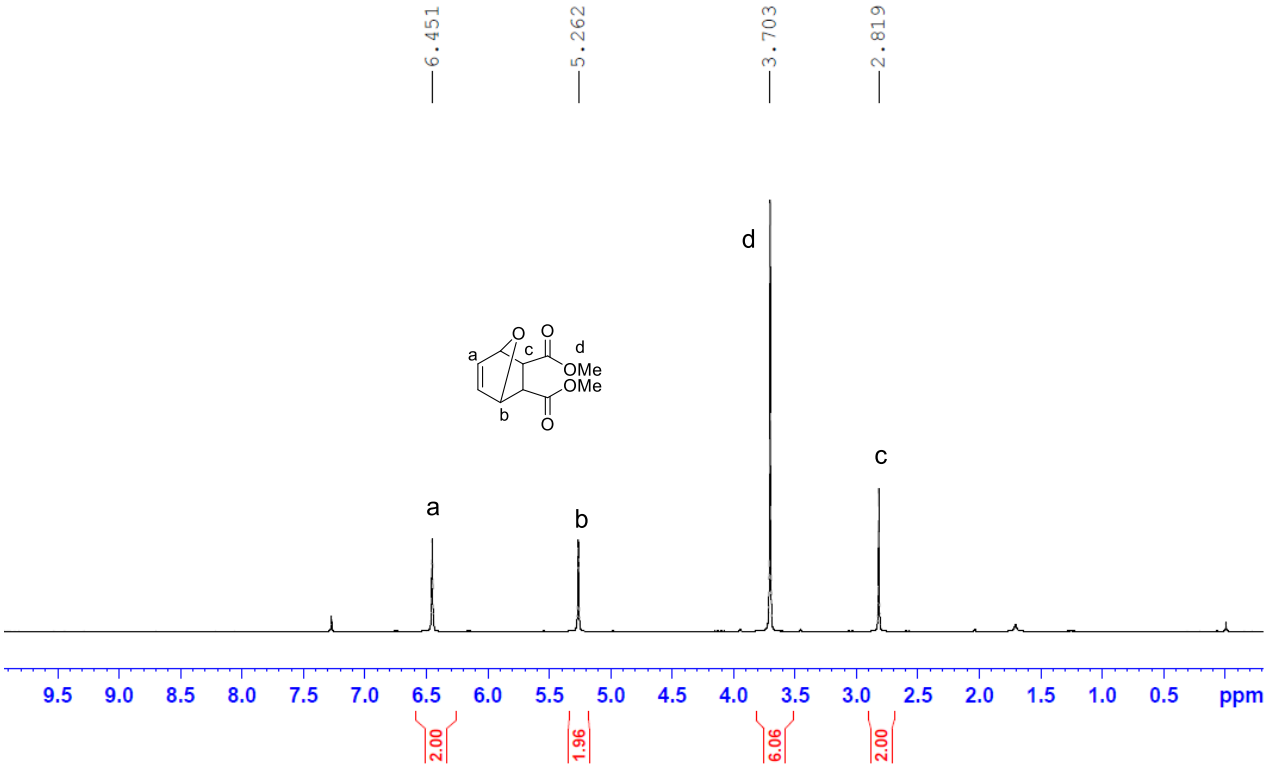
^{13}C-NMR Spectrum of compound **8**.



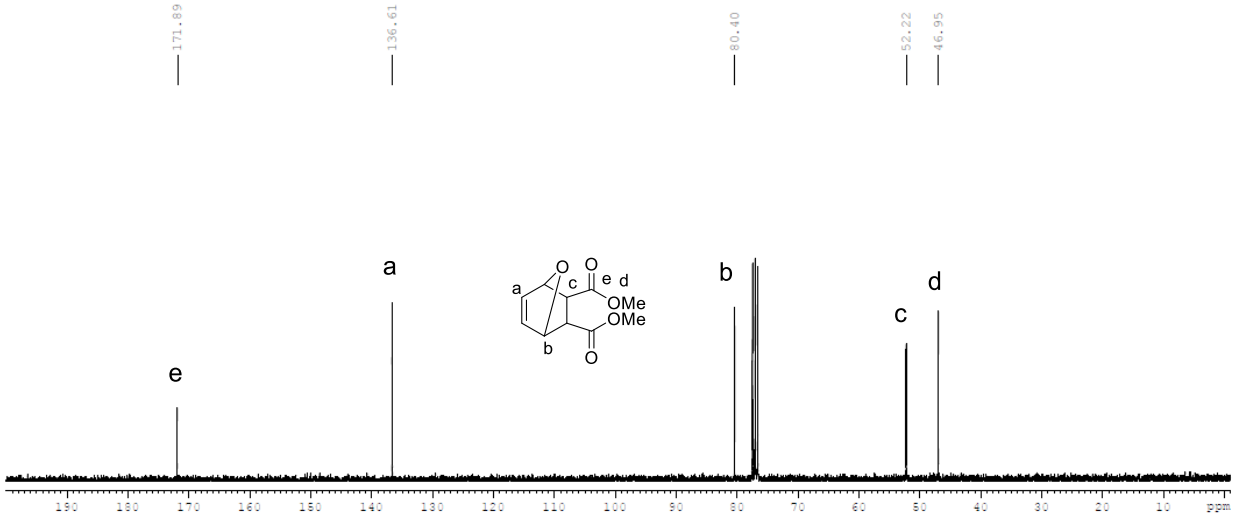
^{1}H-NMR Spectrum of compound **9.**



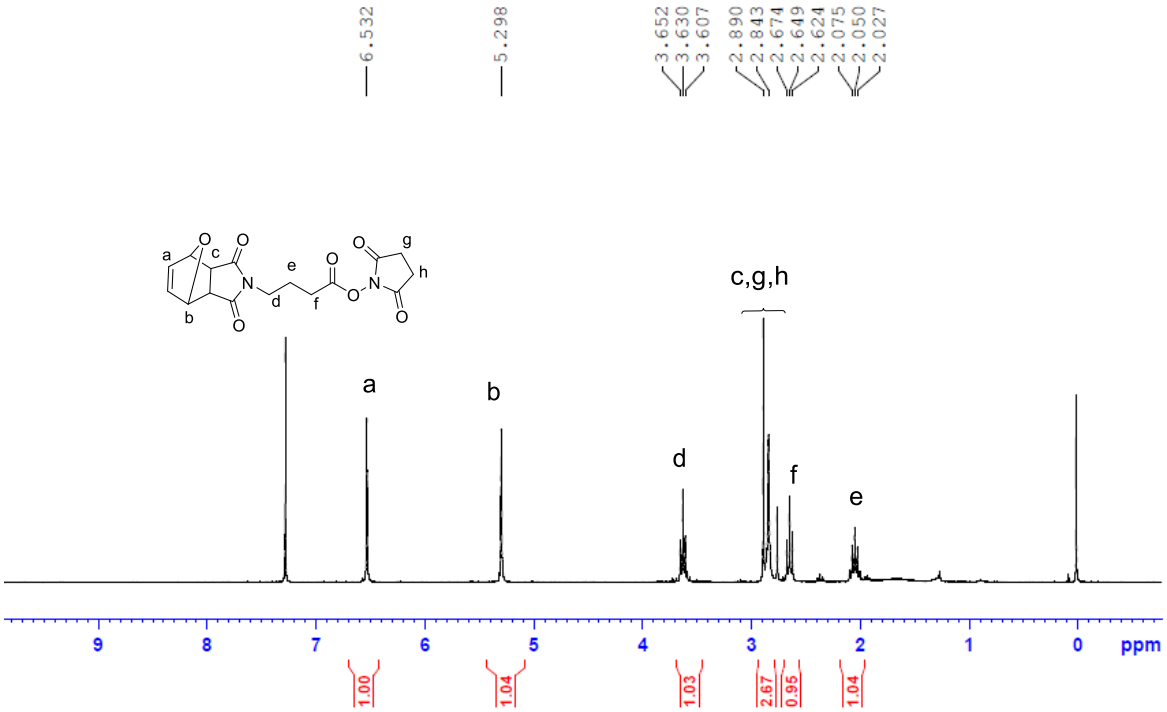
^{13}C-NMR Spectrum of compound **9**.



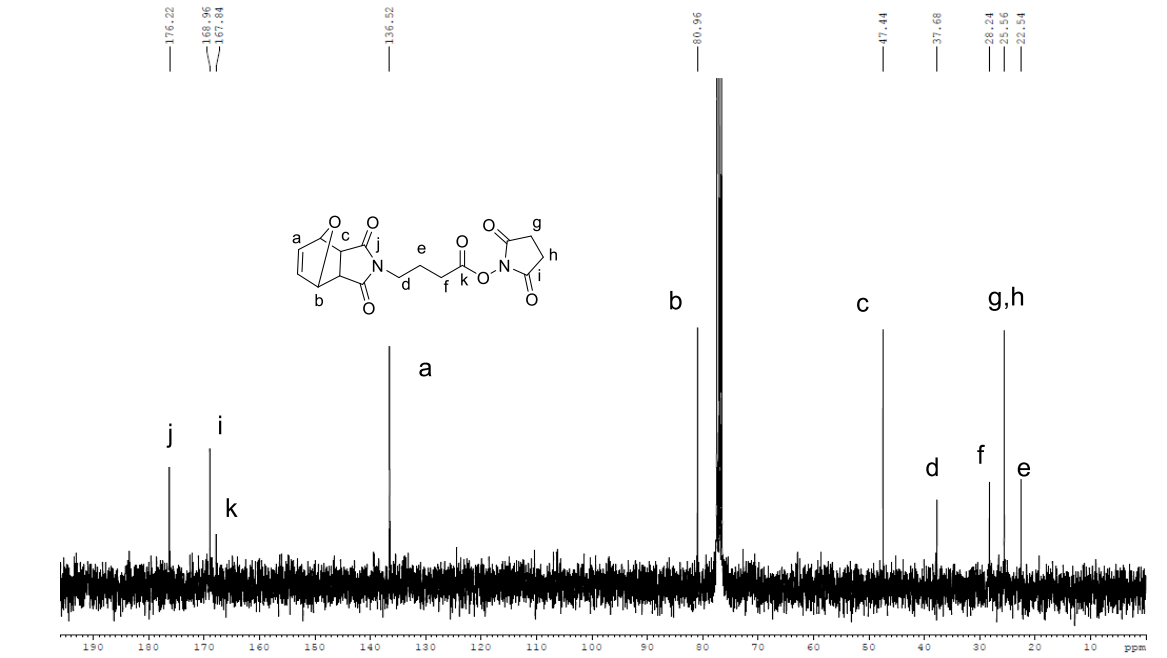
^{1}H-NMR Spectrum of compound **15.**



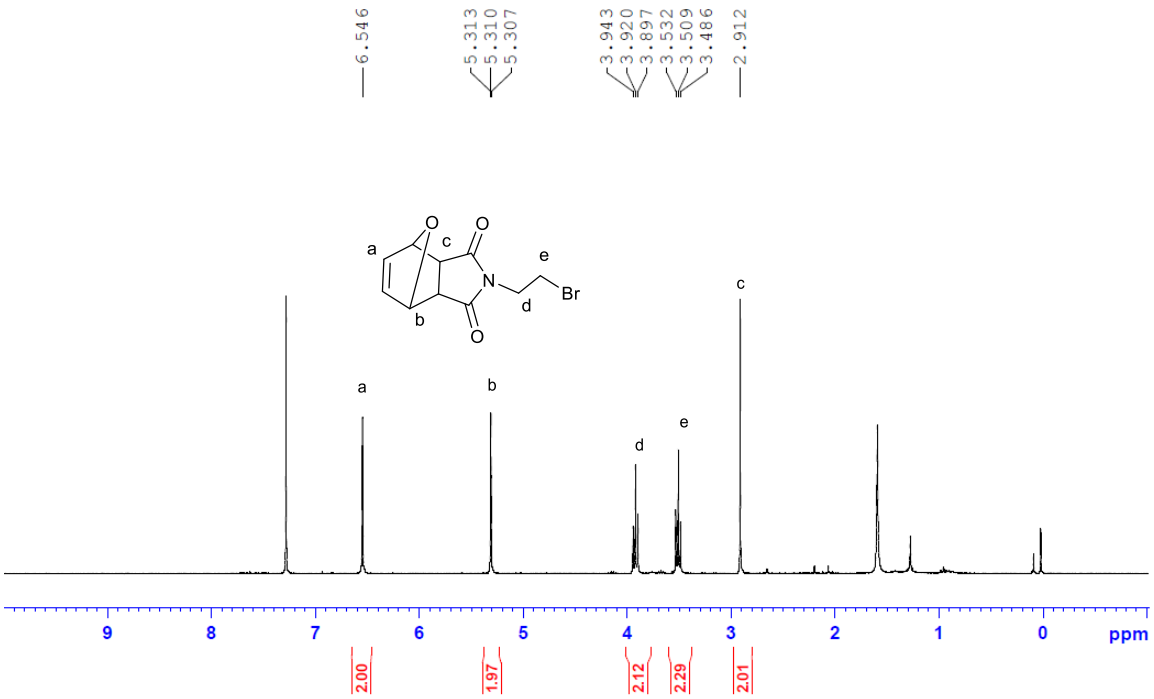
^{13}C-NMR Spectrum of compound **15.**



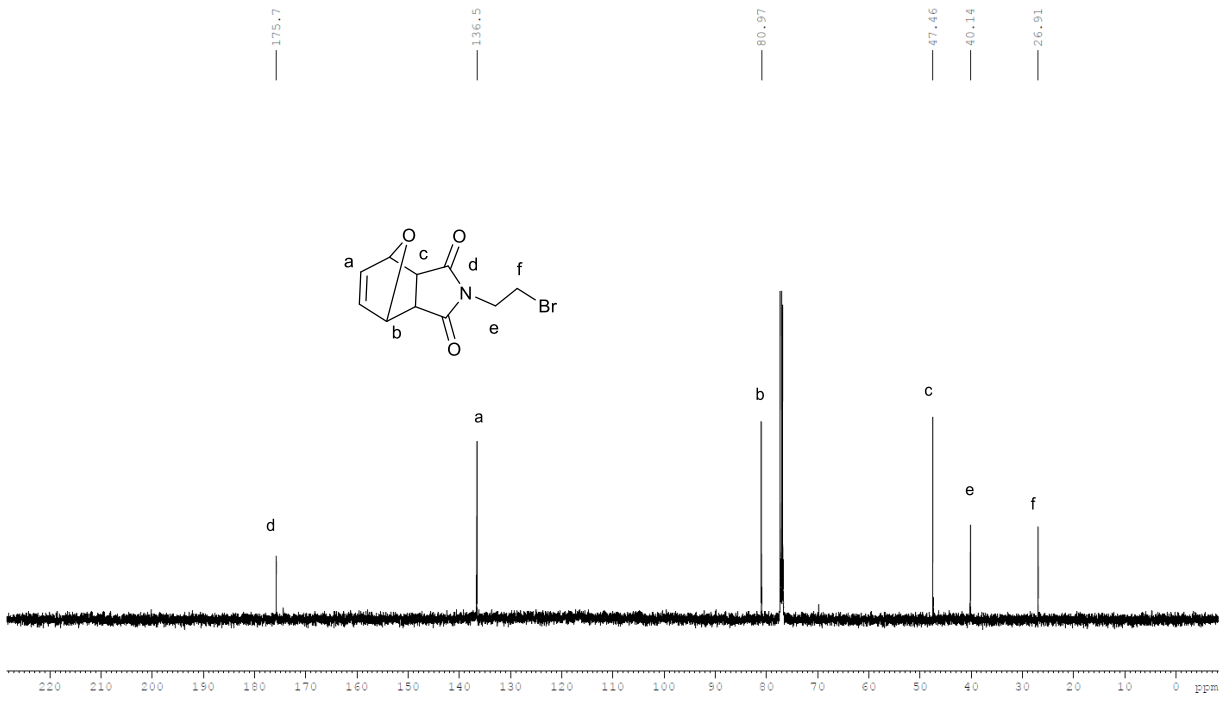
^{1}H-NMR Spectrum of compound **10**.



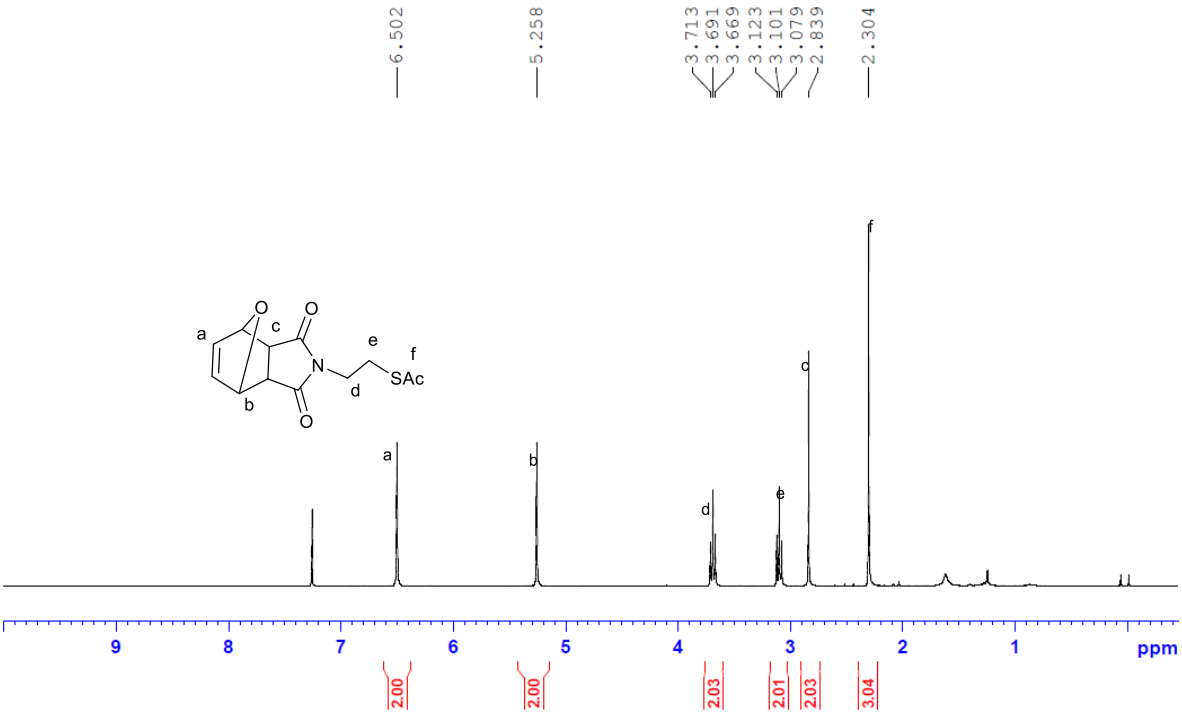
^{13}C-NMR Spectrum of compound **10.**



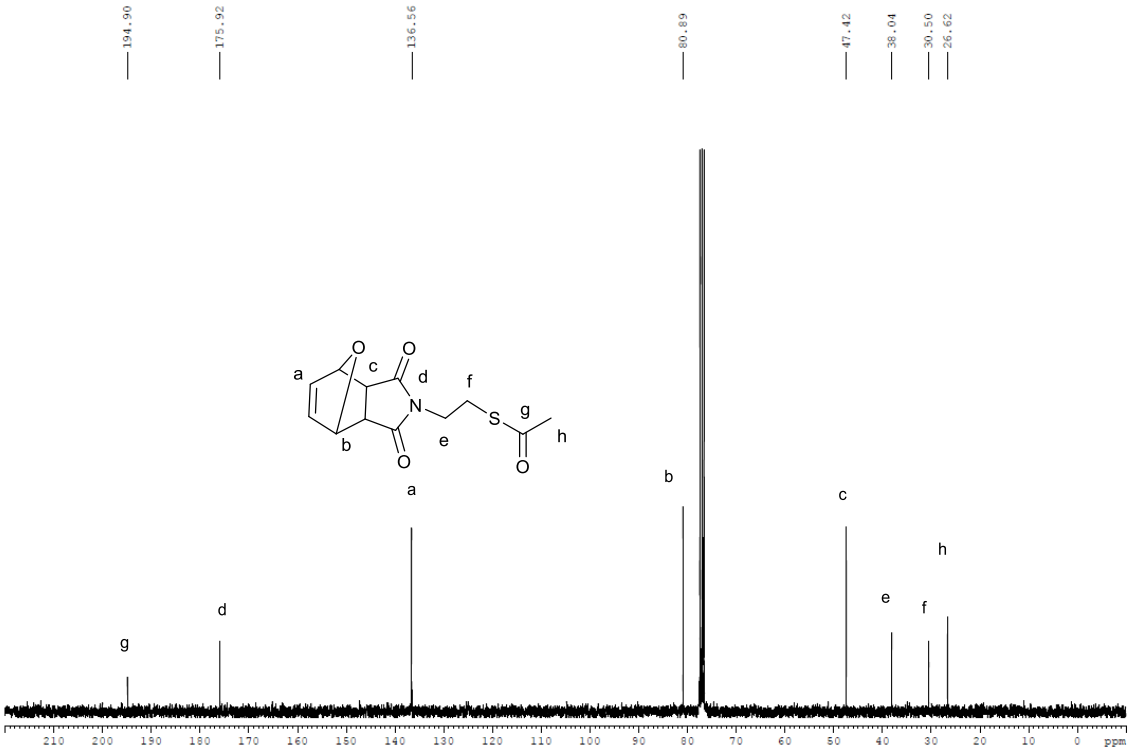
^{1}H-NMR Spectrum of compound **12**.



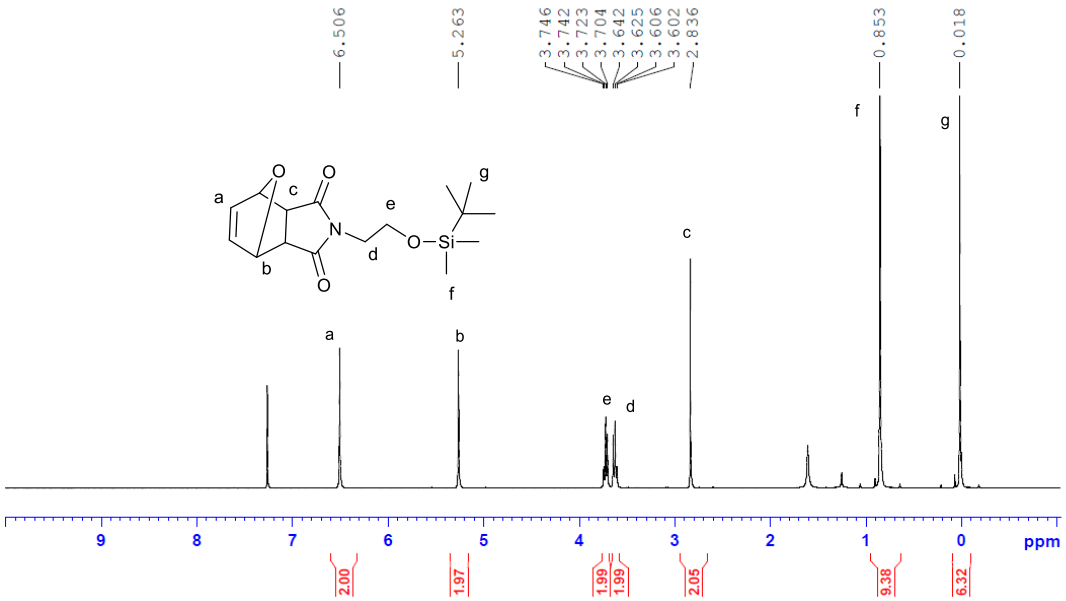
^{13}C-NMR Spectrum of compound **12**.



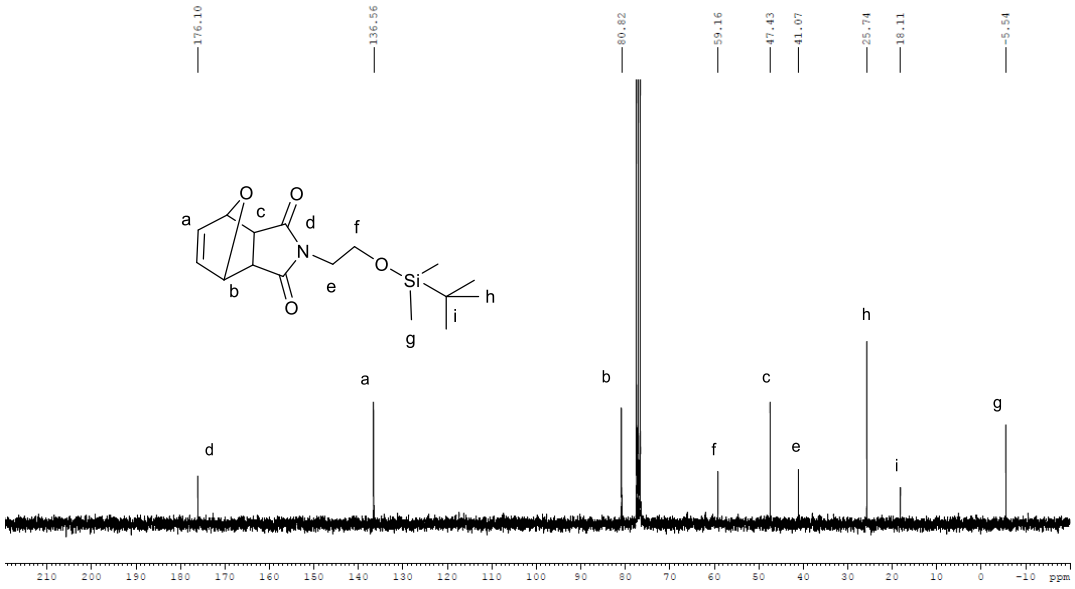
^{1}H-NMR Spectrum of compound **12.**



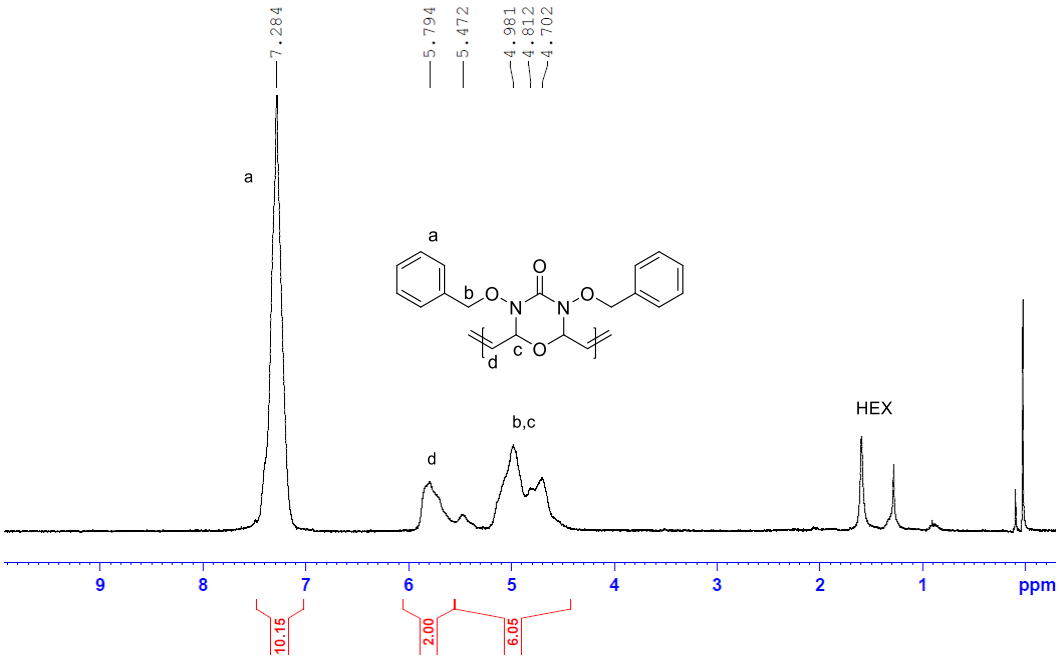
^{13}C-NMR Spectrum of compound **12.**



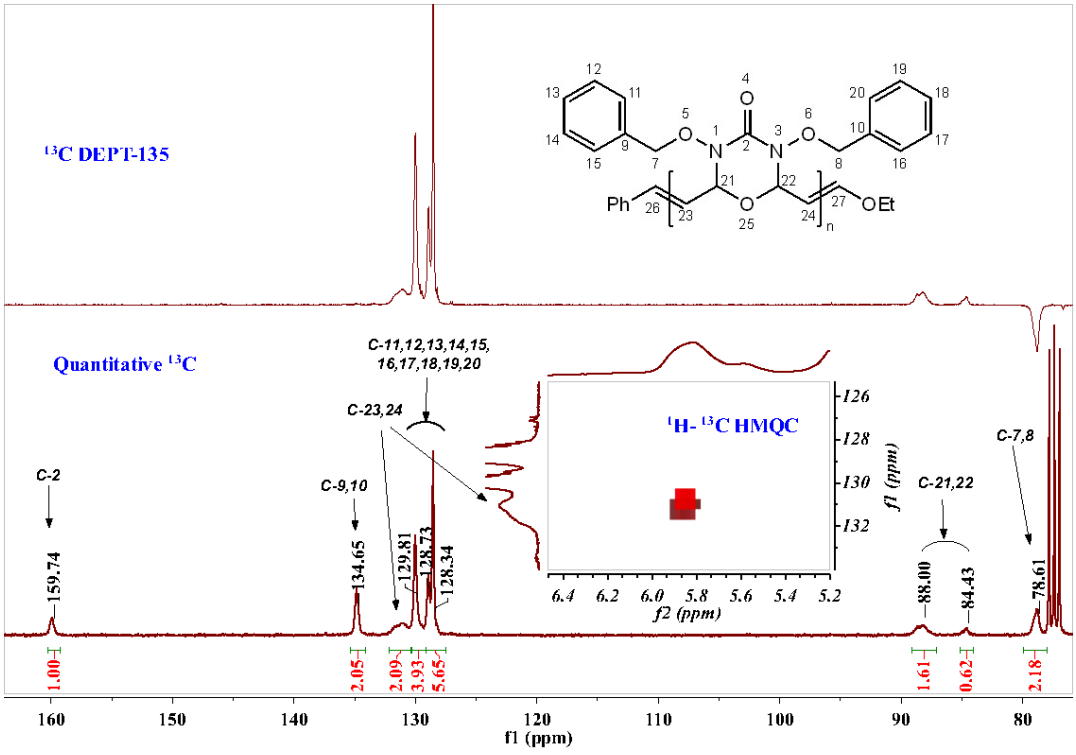
^{1}H-NMR Spectrum of compound **13**.



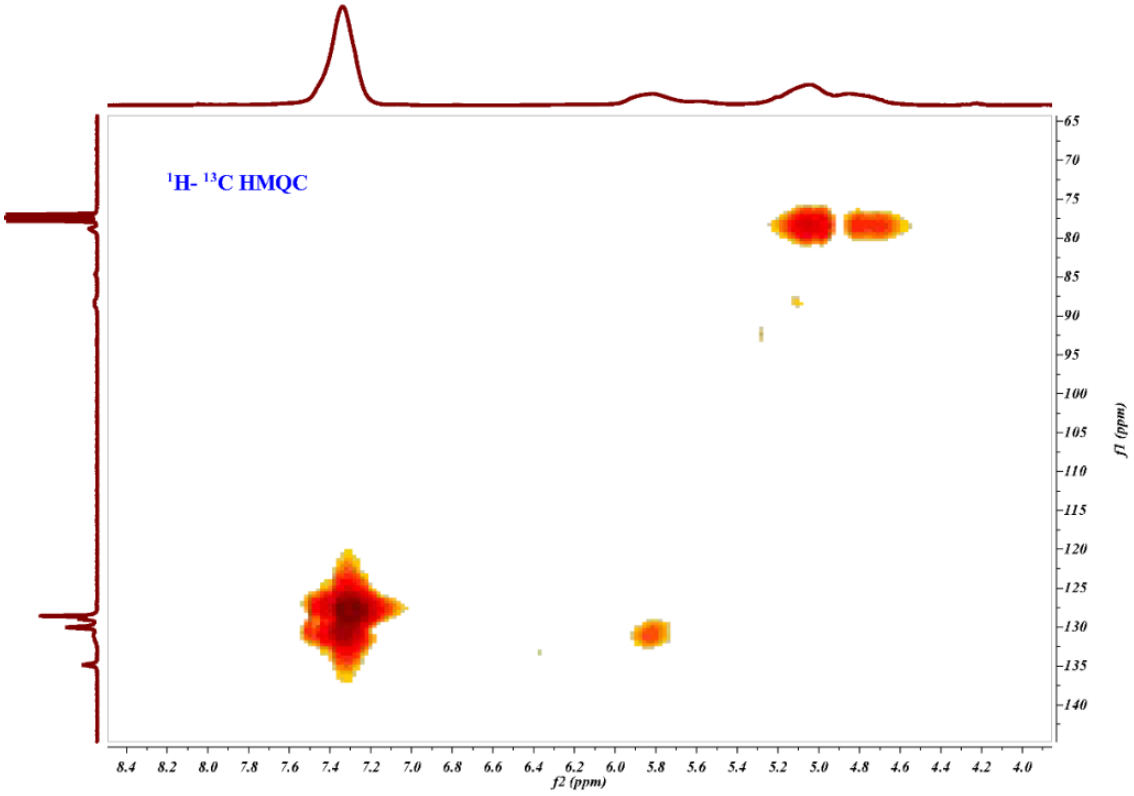
^{13}C-NMR Spectrum of compound **13.**



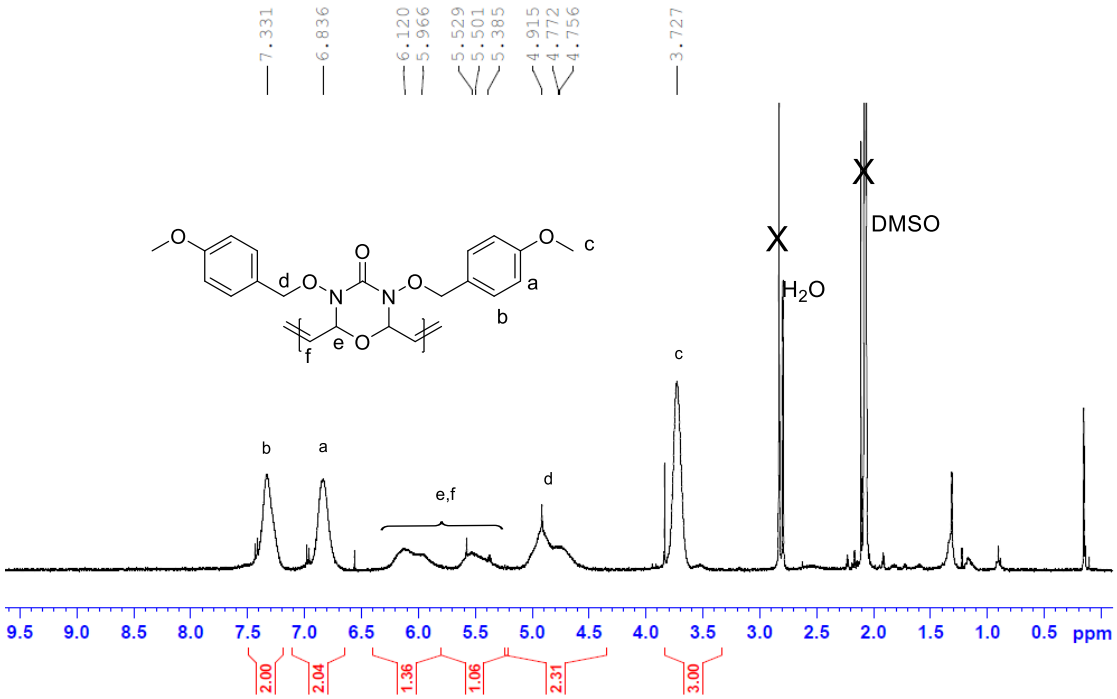
^{1}H-NMR Spectrum of *poly*-**5**



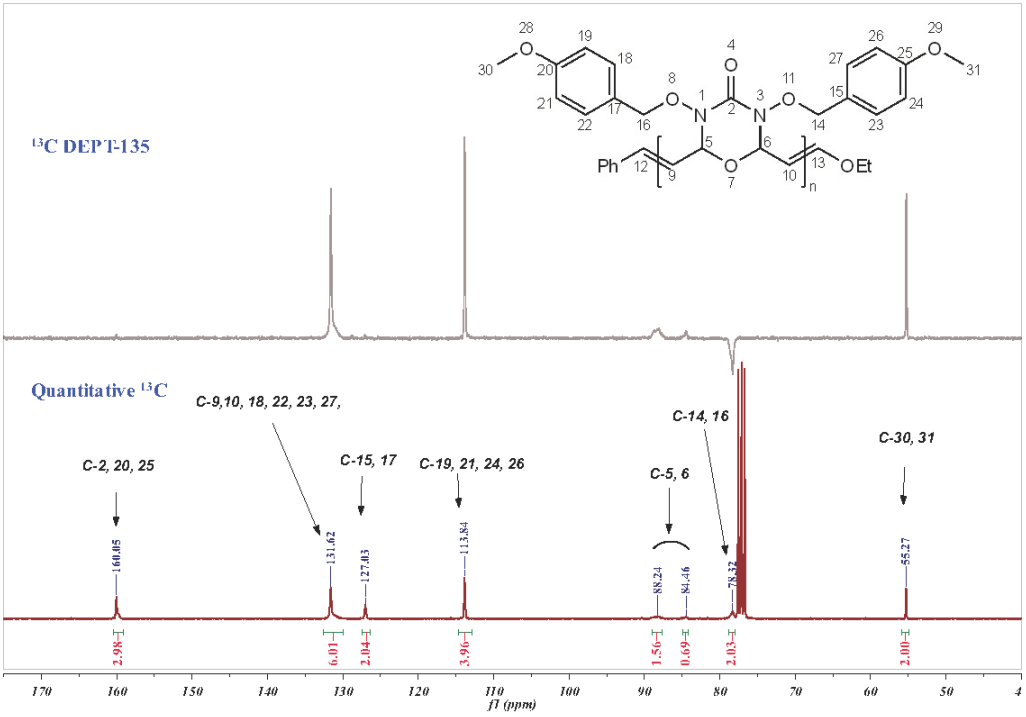
^{13}C-NMR Spectrum of *poly*-**5**



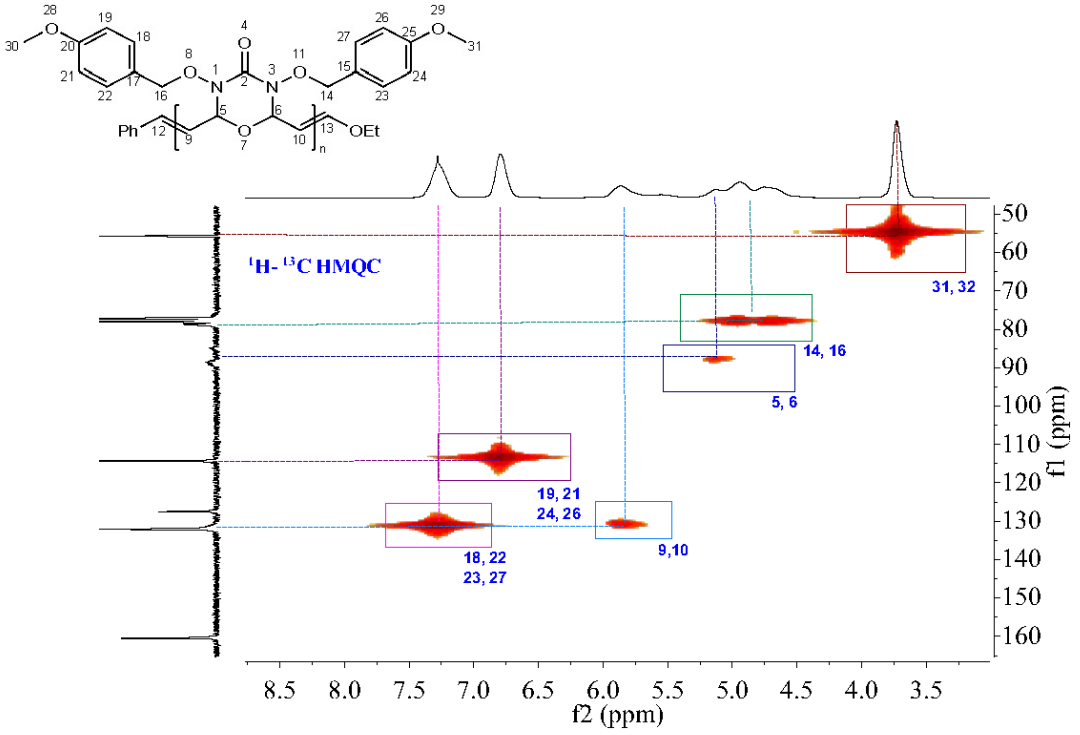
^{1}H-^{13}C HMQC NMR Spectrum of *poly*-**5**



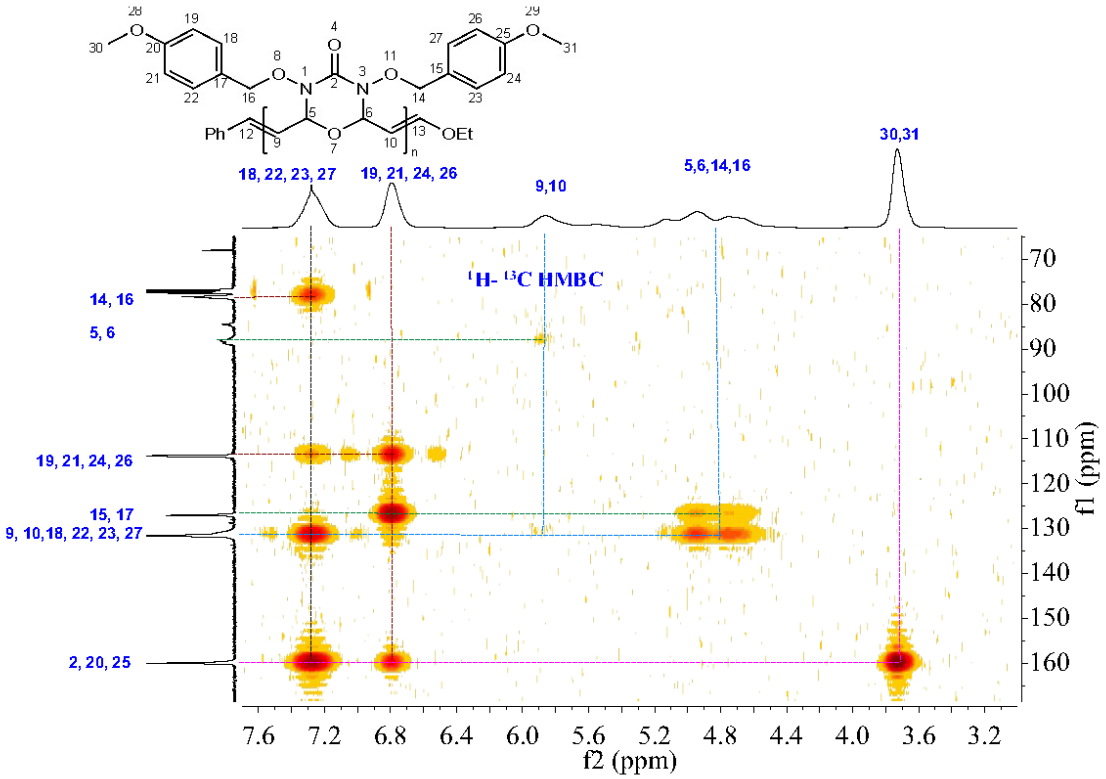
^{1}H-NMR Spectrum of *poly*-**6**.



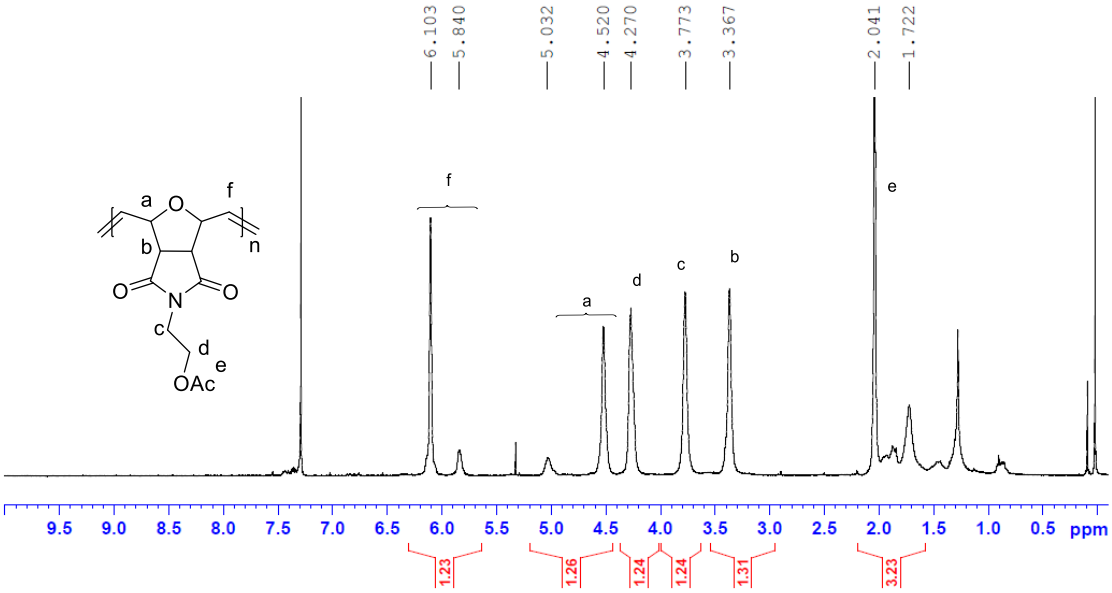
^{13}C-NMR Spectrum of *poly*-**6**.



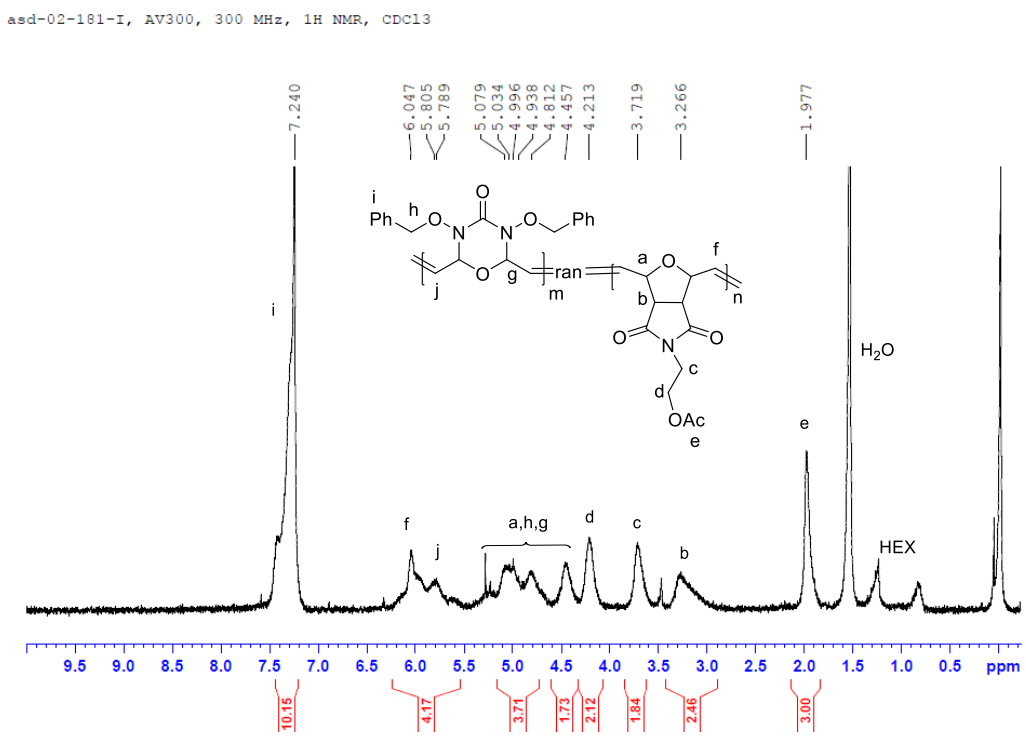
^{1}H-^{13}C HMQC NMR Spectrum of *poly*-**6**.



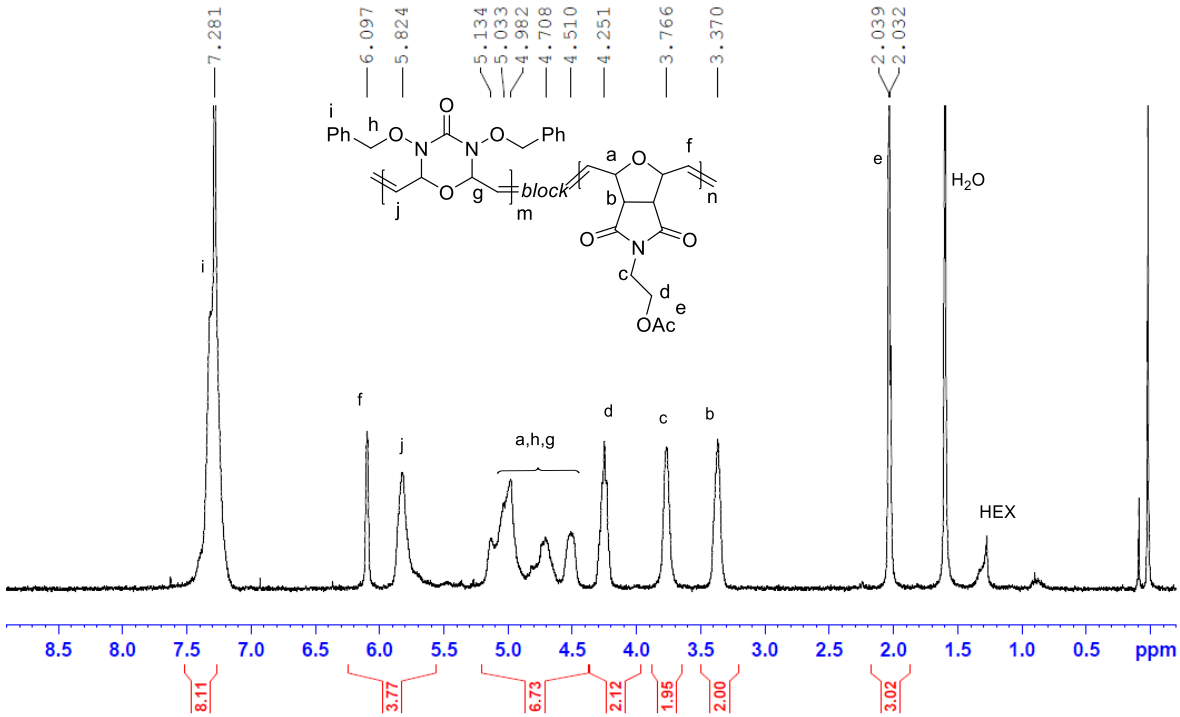
^{1}H-^{13}C HMBC NMR Spectrum of *poly*-**6**.



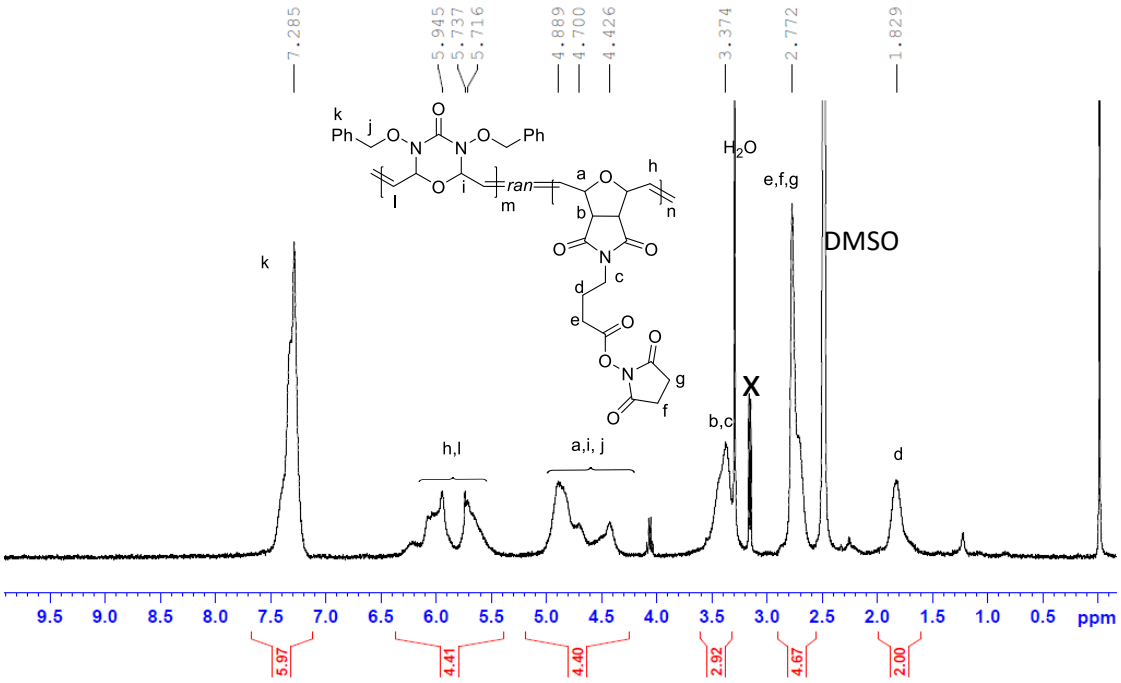
^{1}H-NMR Spectrum of *poly*-**9**.



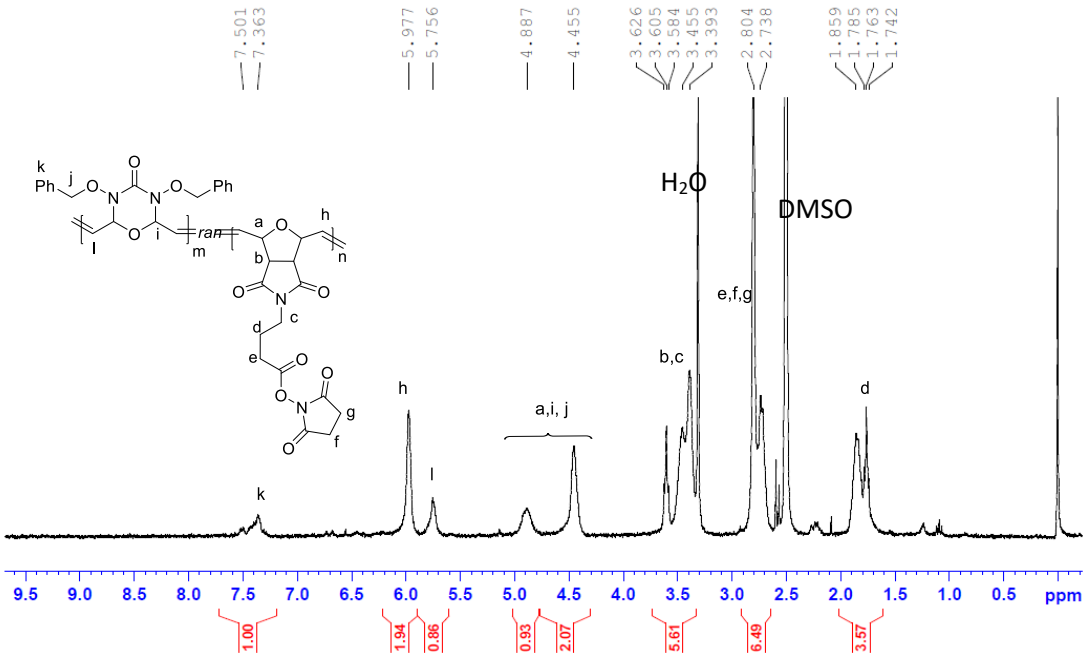
^{1}H-NMR Spectrum of polymer **5**(*49*)-*co*-**9**(51).



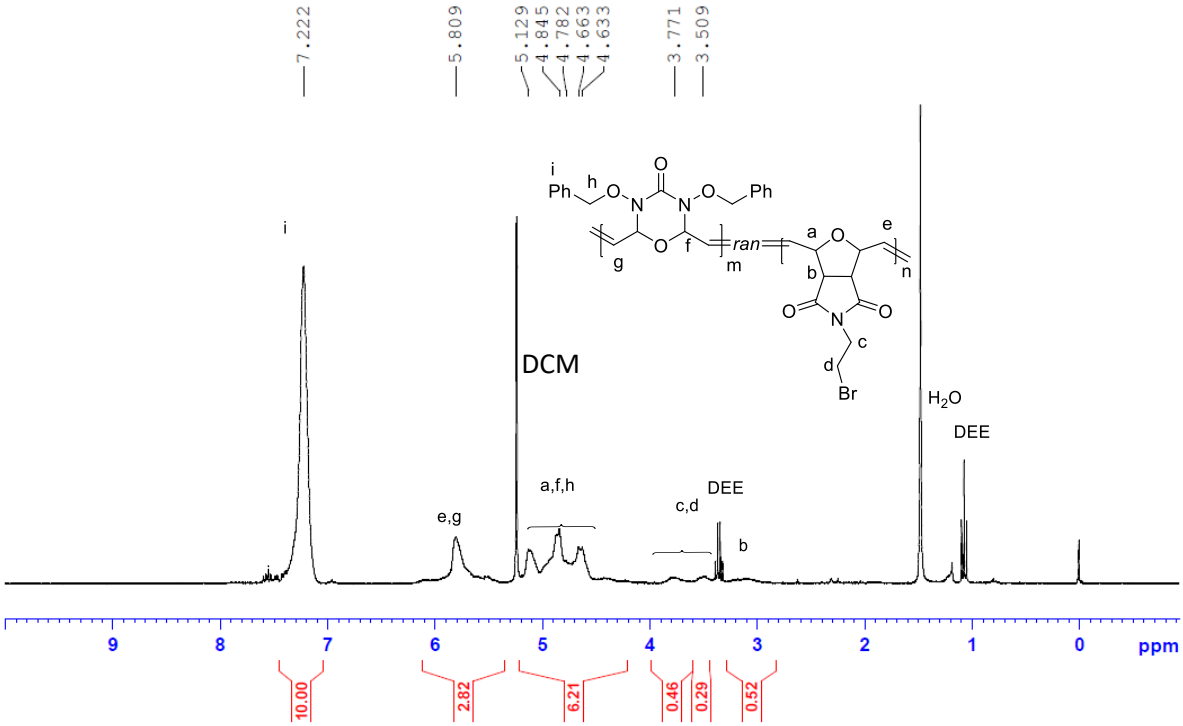
^{1}H-NMR Spectrum of **9**-*block*-**5.**



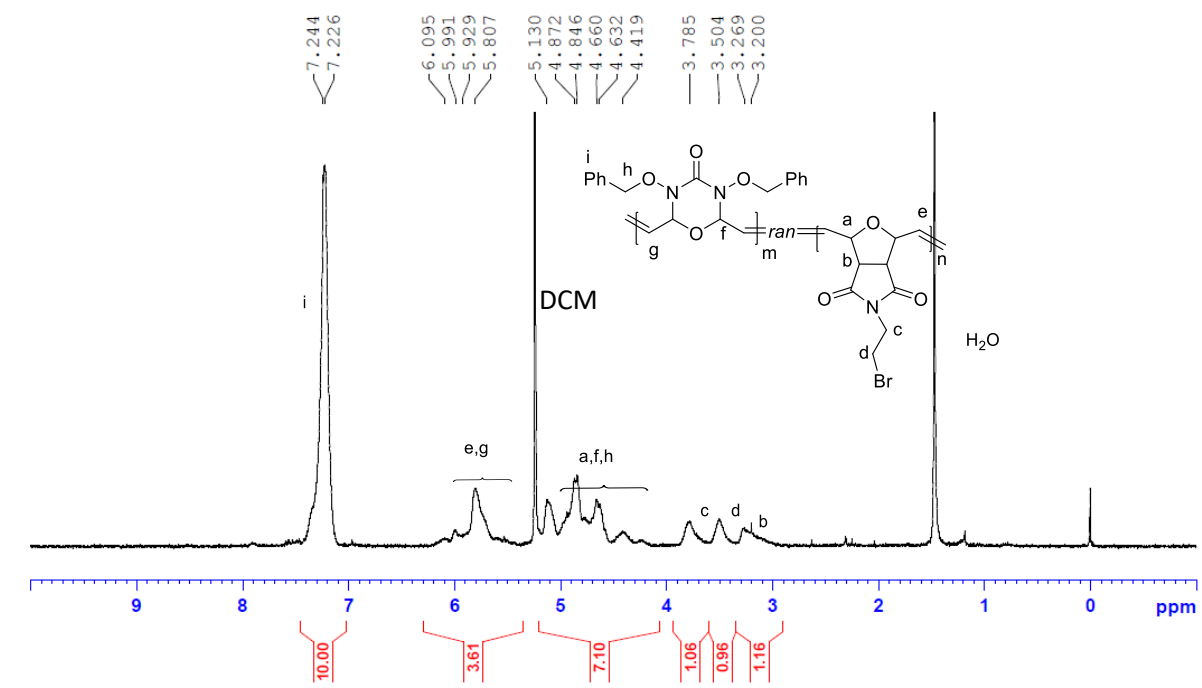
^{1}H-NMR Spectrum of polymer **5**(*37*)-*co*-**10**(*63*)**.**



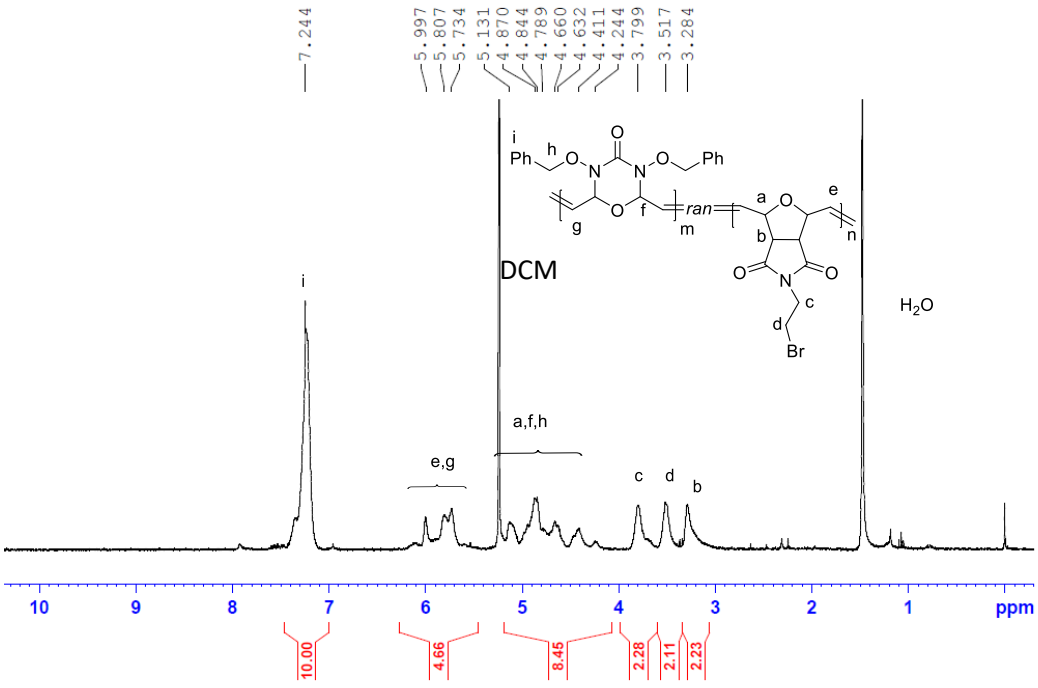
^{1}H-NMR Spectrum of polymer **5**(10)-*co*-**10**(90)**.**



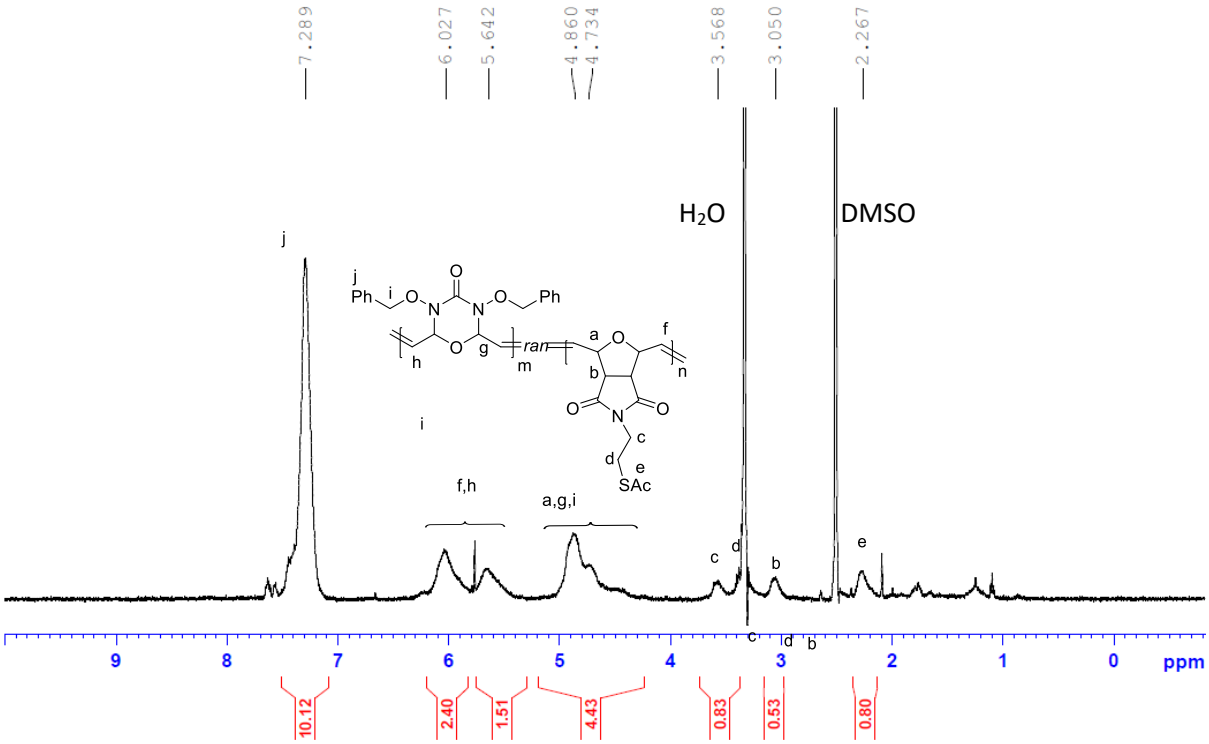
^{1}H-NMR Spectrum of polymer **5**(*81*)-*co*-**11**(*19*).



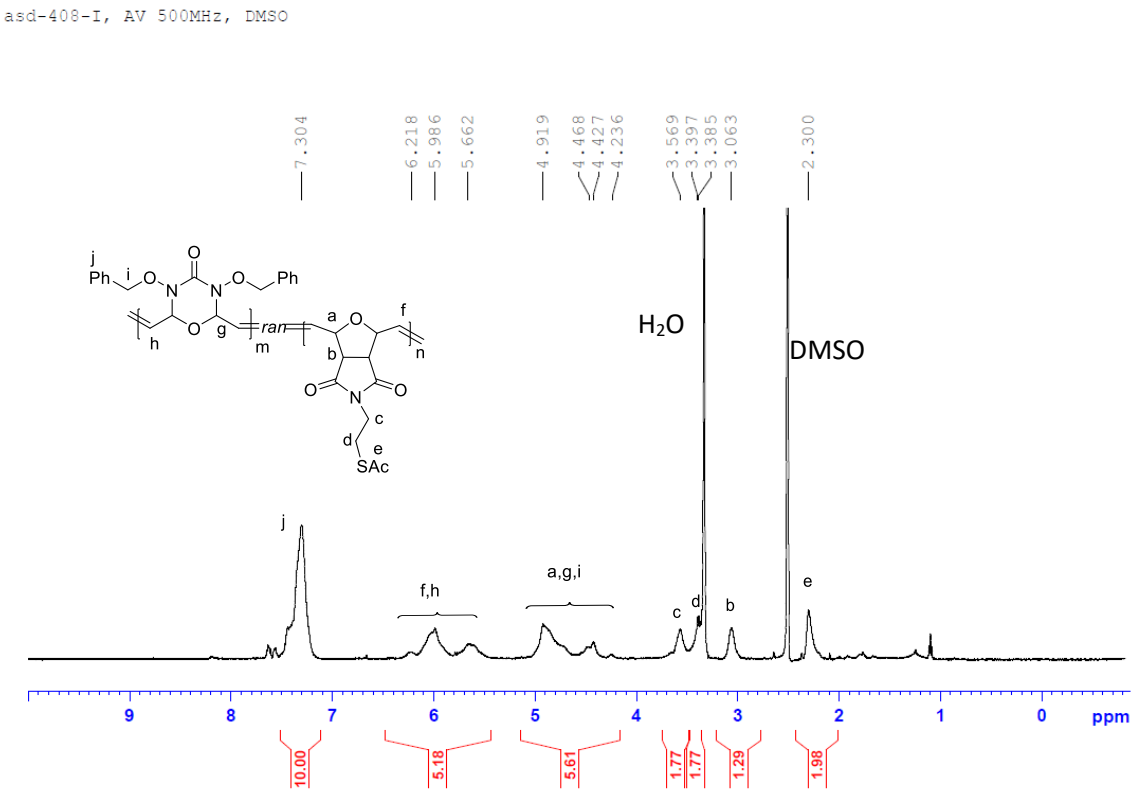
^{1}H-NMR Spectrum of polymer **5**(*66*)-*co*-**11**(*34*).



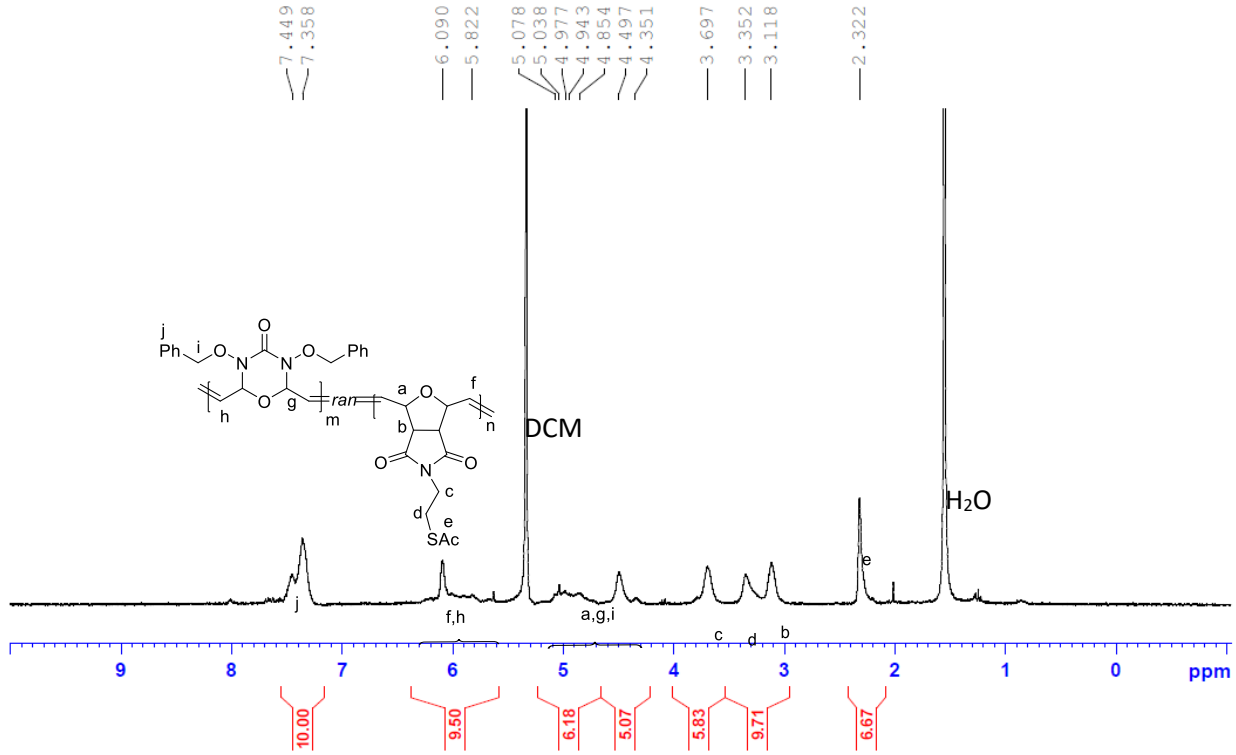
^{1}H-NMR Spectrum of polymer **5**(*47*)-*co*-**11**(53).



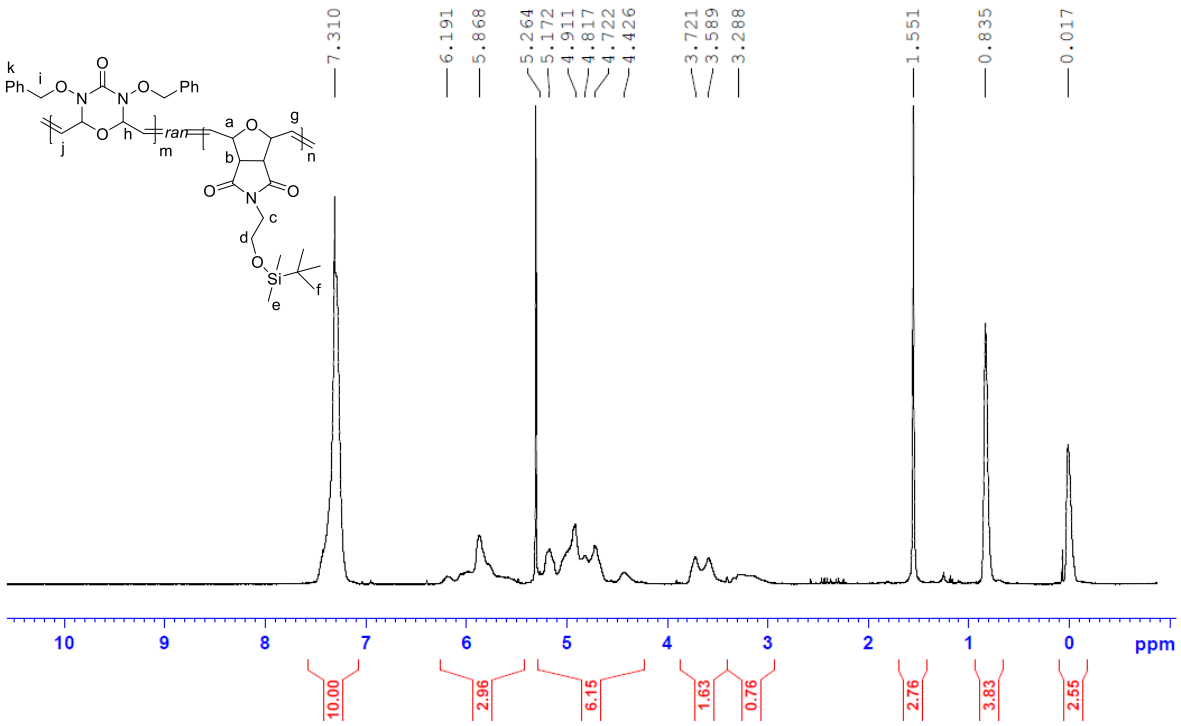
^{1}H-NMR Spectrum of polymer **5**(*83*)-*co*-**12**(*17*).



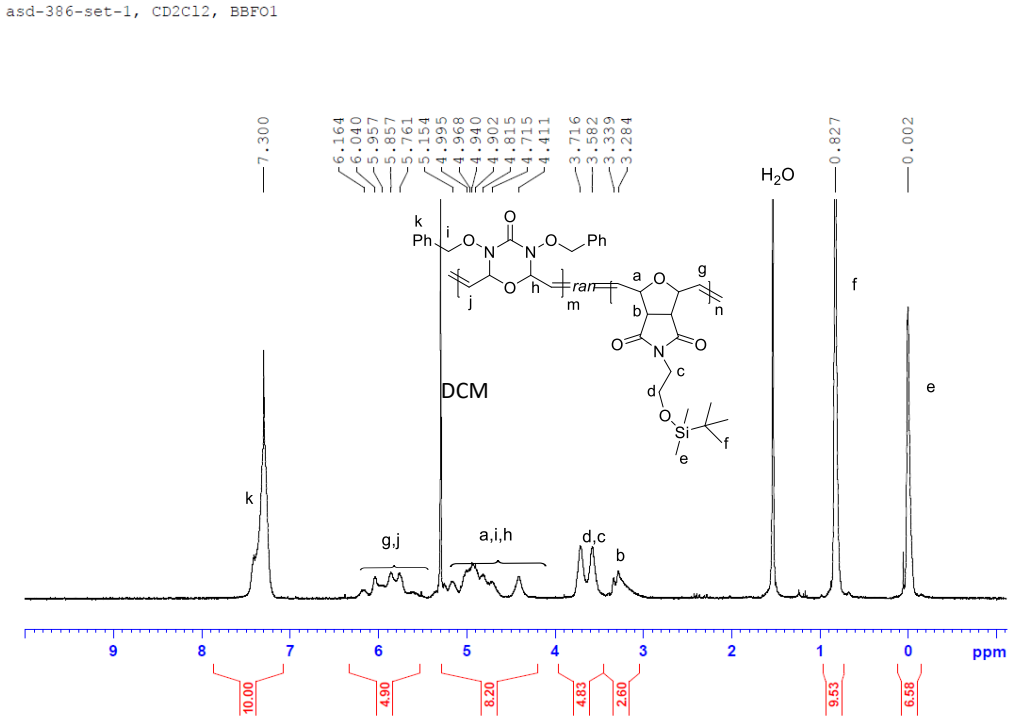
^{1}H-NMR Spectrum of polymer **5**(*60*)-*co*-**12**(*40*).



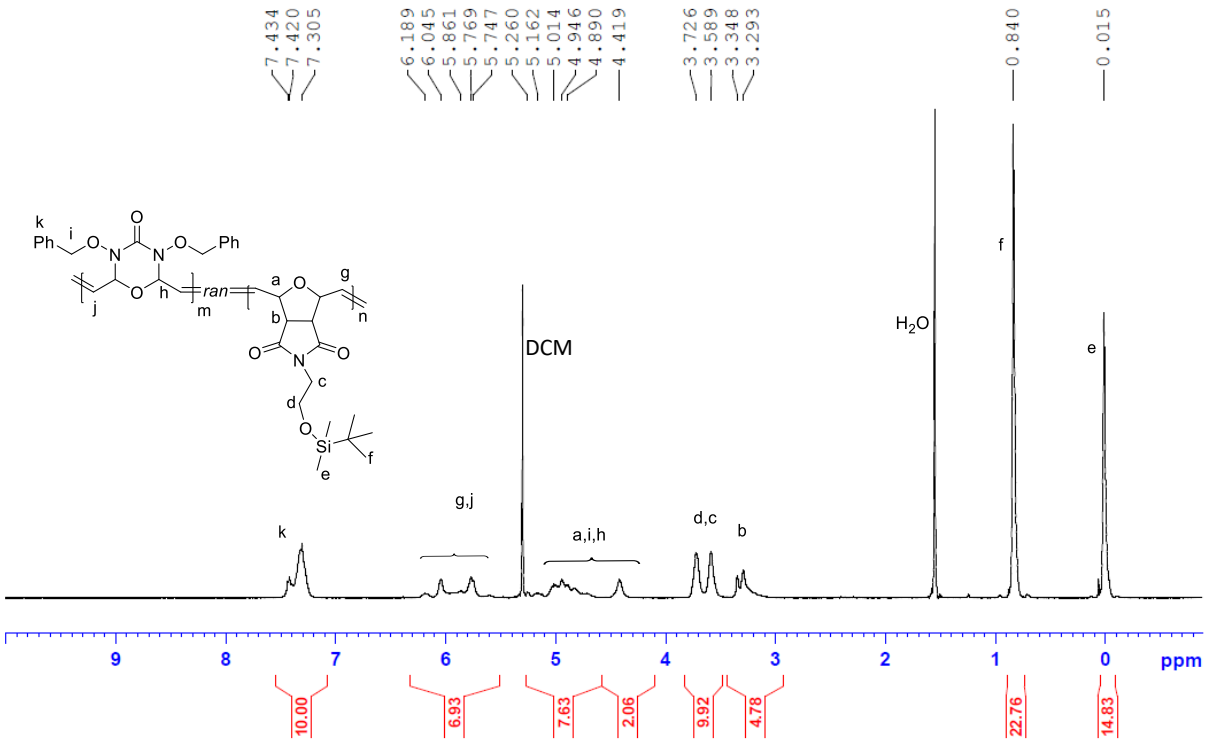
^{1}H-NMR Spectrum of polymer **5**(32)-*co*-**12***(68)*.



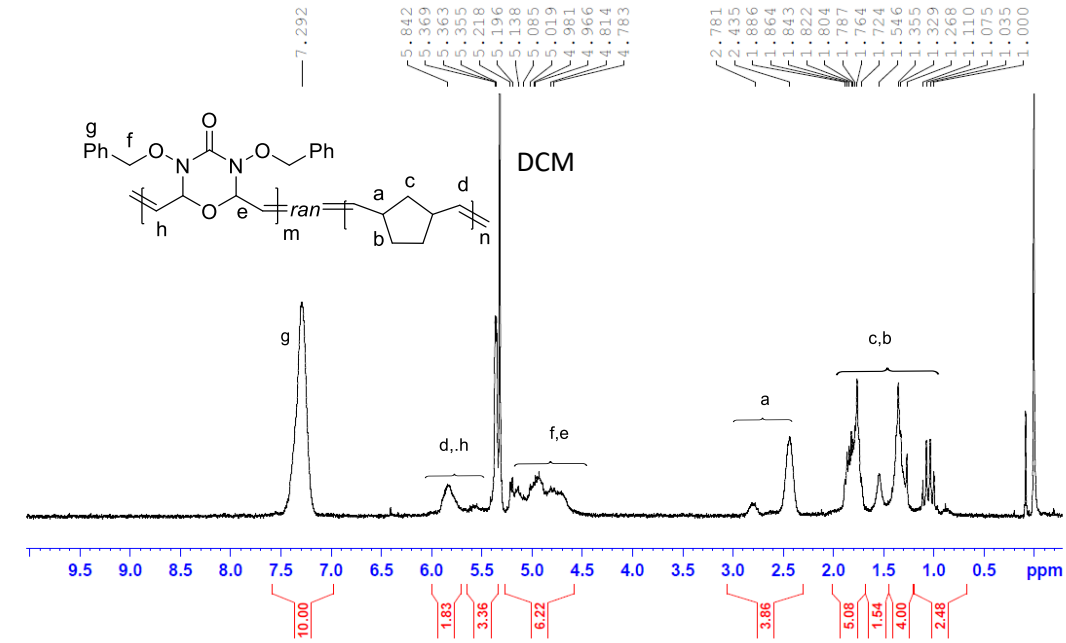
^{1}H-NMR Spectrum of polymer **5**(69)-*co*-**13***(31)*.



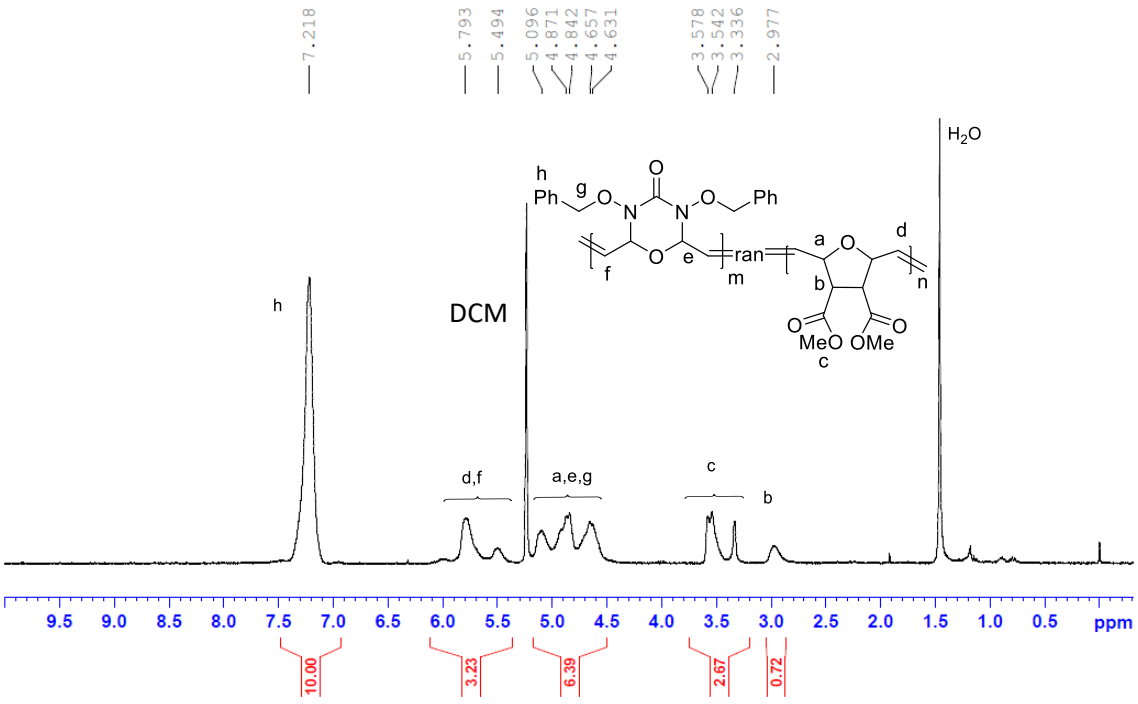
^{1}H-NMR spectrum for polymer **5**(*49*)-*co*-**13**(*51*).



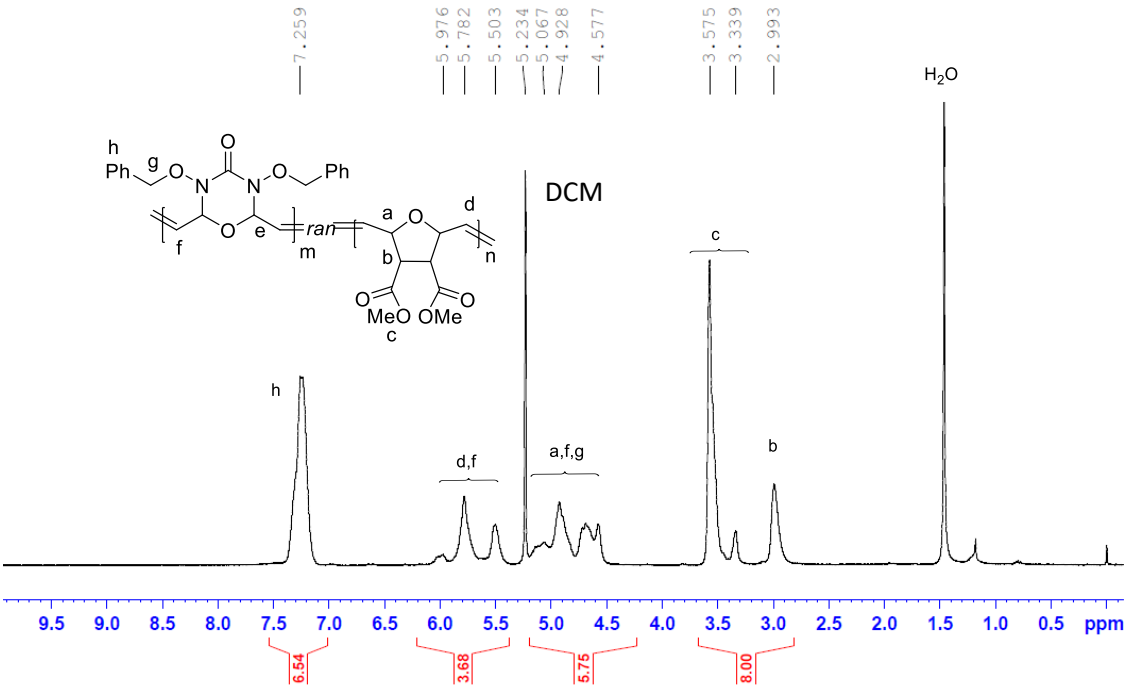
^{1}H-NMR spectrum for polymer **5**(*31*)-*co*-**13**(*69*).



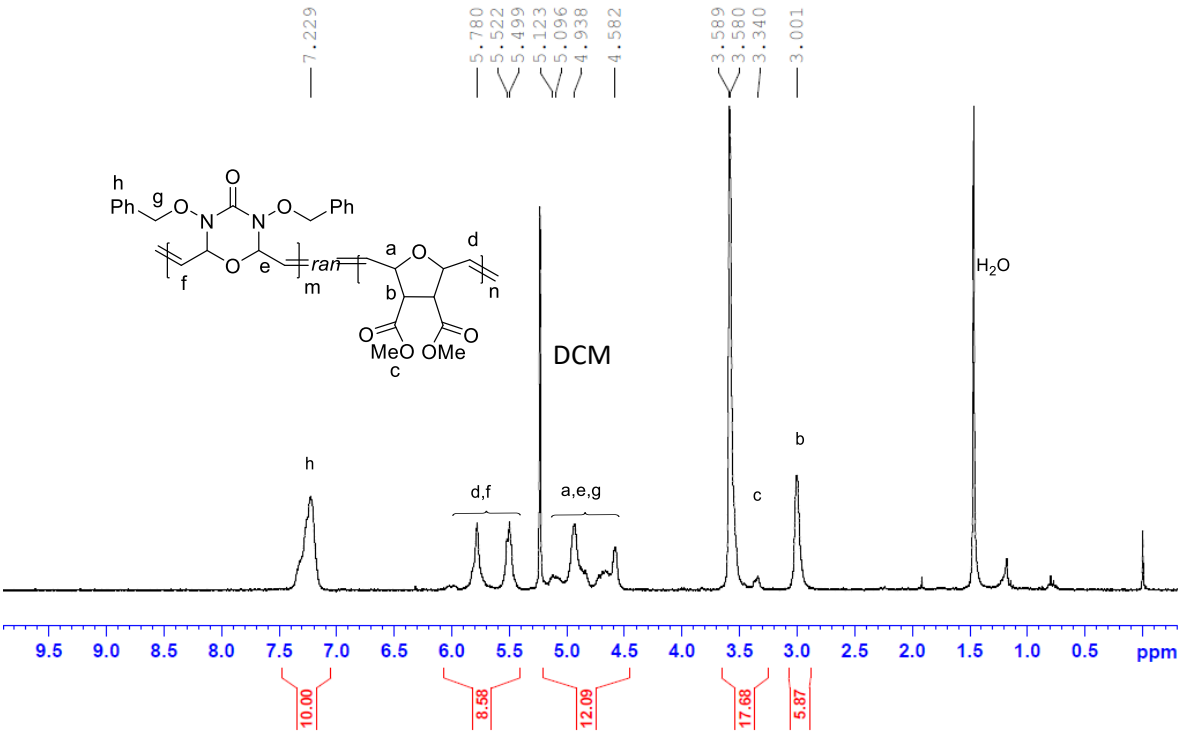
^{1}H-NMR Spectrum of polymer **5**(*36*)-*co*-**14**(*64*).



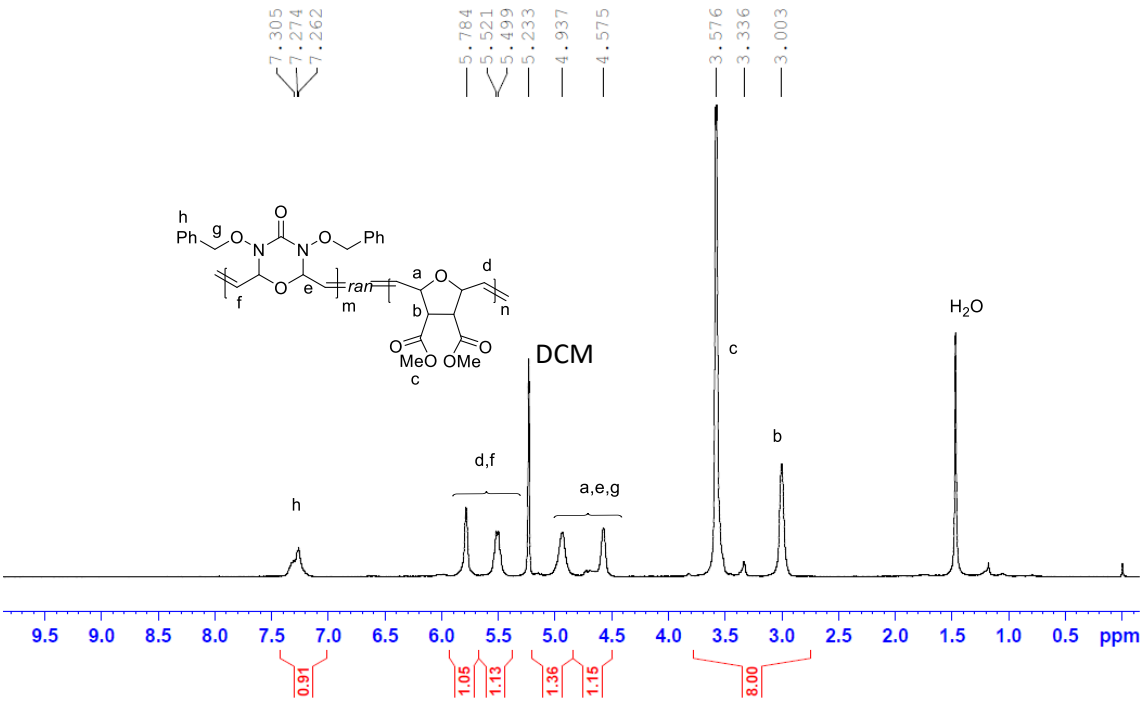
^{1}H-NMR spectra for the polymer **5**(*73*)-*co*-**15**(*27*)



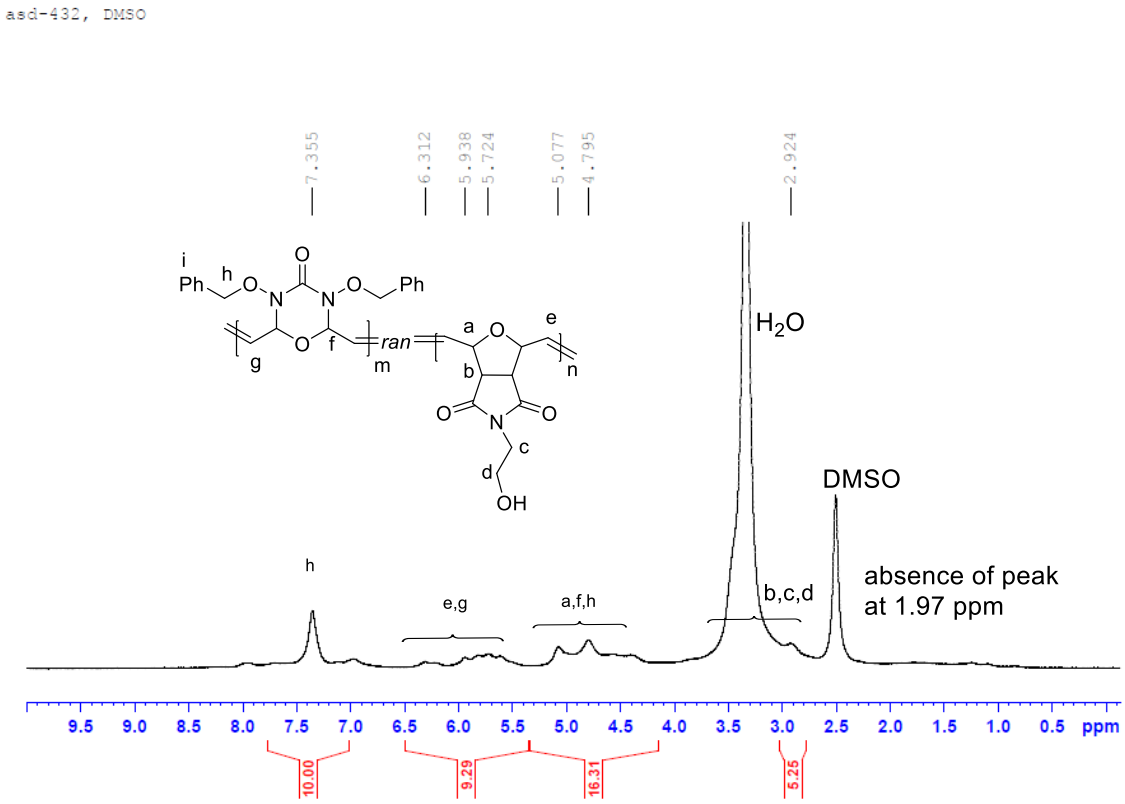
^{1}H-NMR Spectrum of polymer **5**(*39*)-*co*-**15**(*61*)



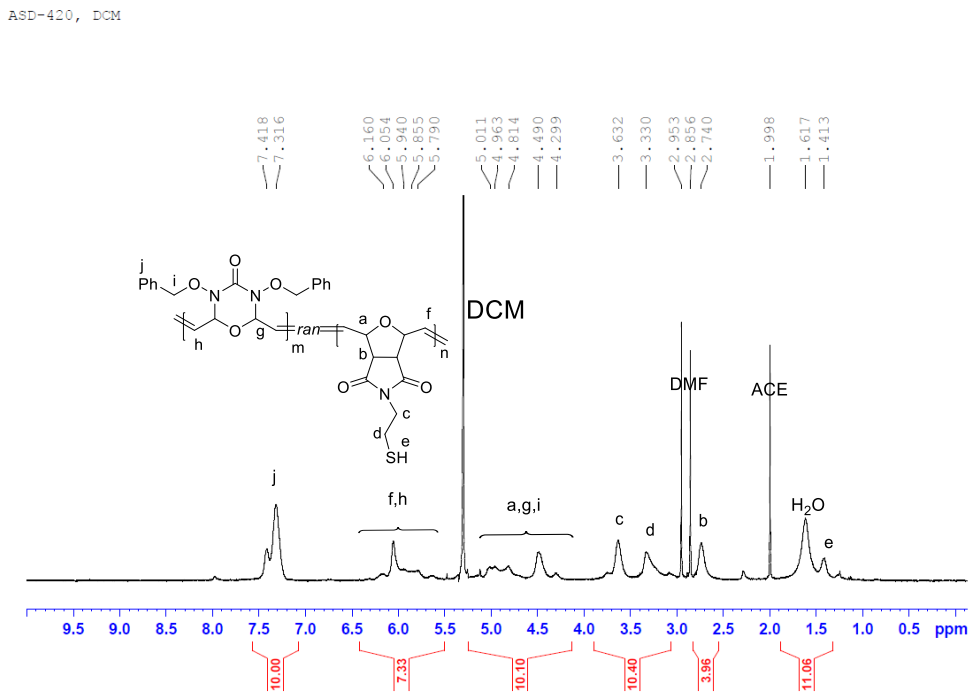
^{1}H-NMR spectra for the polymer **5**(*27*)-*co*-**15**(*73*)



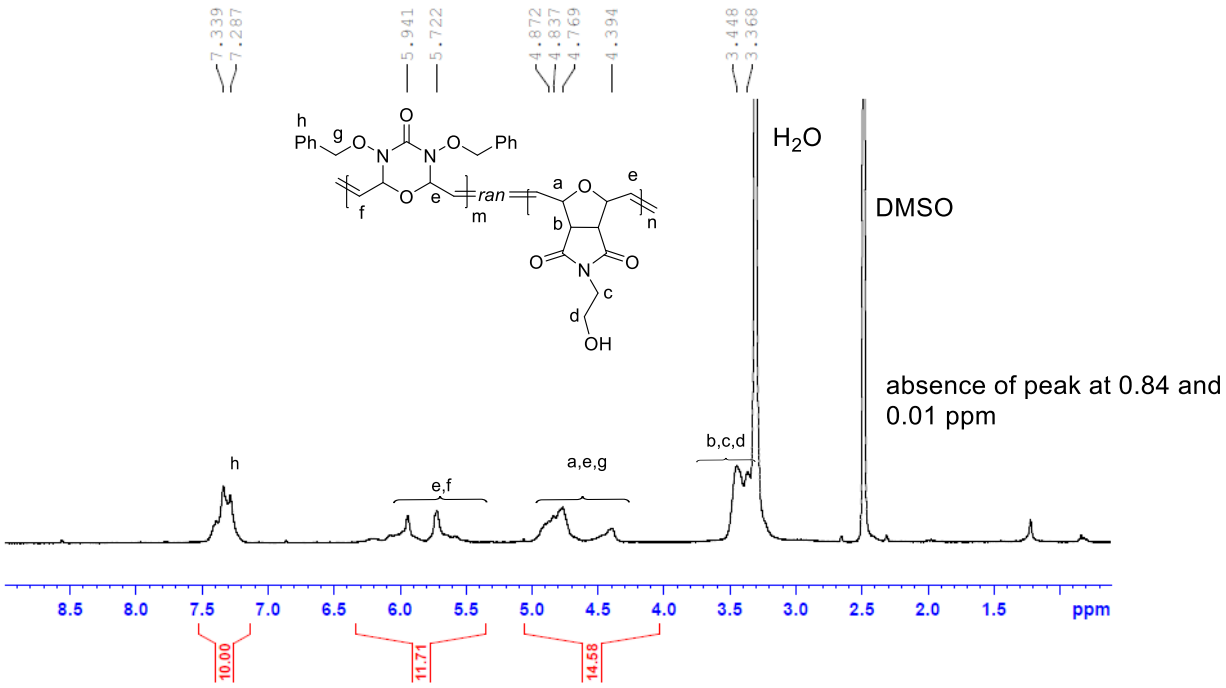
^{1}H-NMR Spectrum of polymer **5**(9)-*co*-**15**(*91*)**.**



^{1}H-NMR spectrum of the polymer after acetate group deprotection.



^{1}H-NMR spectrum of the polymer after thioacetate group deprotection.



^{1}H-NMR spectrum of the polymer after -OTBDMS group deprotection.