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Supporting Information

Triethylamine catalyzed S→O Acyl Migration Reaction for Generating Thiols and Its Combination with Thiol-click Chemistry

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Experimental

Chemicals:

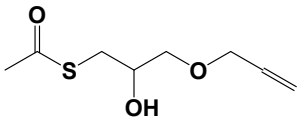
Allyl glycidyl ether, 1,6-diisocyanatohexane, *n*-butyl acrylate, propylene oxide, methyl acrylate, propargyl alcohol, thiolacetic acid, N-isopropylacrylamide, glycidyl methacrylate, 2,2'-azobisisobutyronitrile, 4-Dimethylaminopyridine (DMAP), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and 2,2-dimethoxy-2-phenylacetophenone were purchased from Aladdin Chemical Co., China. Propargyl glycidyl ether was obtained from DaTang Pharmacy Co., China. Allyl isocyanate and ally isothiocyanate were acquired from Sigma Aldrich. 1-Octyne and triglycidyl isocyanurate were purchased from TCI Shanghai. Octavinyl-T8-silsesquioxane was purchased from Hybrid Plastics, Co.. Epoxy terminated polydimethylsiloxane (PDMS) (M_n = 2300) was supplied by Evonik Co.. Triethylamine (TEA), CH_2Cl_2, $CHCl_3$, tetrahydrofuran, methanol, toluene, and diethyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran and toluene were dried over CaH_2 and distilled. All other reagents were used without further purification.

Measurements:

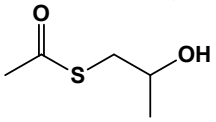
^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) spectroscopy was carried out on a Varian Mercury plus 400 NMR spectrometer at 20 °C. The samples were dissolved with $CDCl_3$ and the solutions were measured with tetramethylsilane as an internal reference. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). Gel permeation chromatography (GPC) was recorded on a Perkin Elmer HP 1100, using THF as the eluent at a flow rate of 1 mL min^{-1}, RI-WAT 150 CVt+ as the detector and linear polystyrene for calibration at 40 °C for characterization of apparent molecular weights. Mass spectrum was record by Bruker Esquire 3000plus ion trap mass spectrometer (Brucker-Franzen Analytik GmbH, Bremen, Germany). Nitrogen was used as nebulizing gas at a pressure of 10 psi and drying gas at a flow rate of 5 L min^{-1}. The drying gas temperature was set at 250 °C and the capillary voltage was set at 4000 V. Solutions were infused to the mass spectrometer with a syringe pump at a flow rate of 6 μL min^{-1}.

General procedure for thiol-epoxy reactions between epoxy compounds 1 and thioacetic acid to generate 2

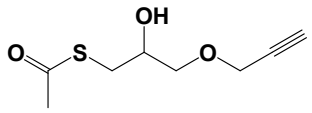
A CH_2Cl_2 (12 mL) solution of thioacetic acid (1.84 g, 24.0 mmol) was mixed with a CH_2Cl_2 solution of epoxy compounds (20.0 mmol). Then, TEA (100.0 mg, 1.0 mmol) was injected into the mixture through a microsyringe. After vigorous stirring for 10 h at room temperature, the mixture was diluted with another 40 mL of CH_2Cl_2, washed with 1 M HCl aqueous solution, saturated $NaHCO_3$ aqueous solution, and deionized water, successively, dried by anhydrous $MgSO_4$. All the volatiles were evaporated to afford **2** in nearly quantitative yield.



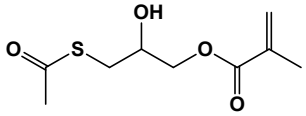
2a: ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.98-3.11 (m, 2H), 3.90 (m, H), 2.65 (m, H), 3.39-3.51(m, 2H), 4.00 (m, 2H), 5.89 (m, H), 5.20 (m, H). (Figure S1)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.60, 196.43, 32.79, 69.89, 72.81, 72.42, 134.60, 117.52. (Figure S2)
FTIR: 3456 cm^{-1} (-OH). (Figure S3)



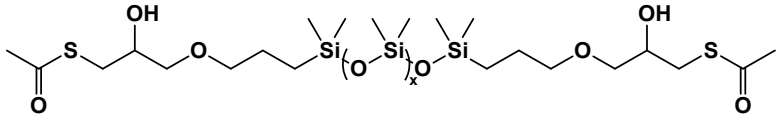
2b: ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.87-3.13 (m, 2H), 3.92 (m, 1H), 2.60 (s, 1H), 1.99-2.28 (m, H), 1.26 (d, 3H). (Figure S4)



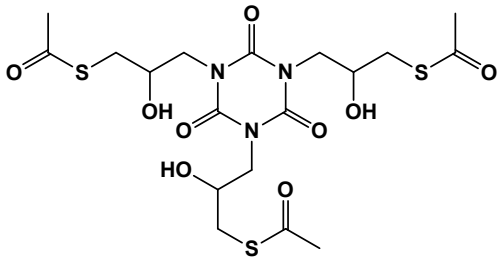
2c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (s, 3H), 2.97-3.16 (m, 2H), 3.94 (m, H), 2.59 (m, H), 3.48-3.63 (m, 2H), 4.19 (s, 2H), 2.46 (s, H). (Figure S5)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.60, 196.56, 32.49, 69.66, 72.28, 58.66, 75.32, 79.49. (Figure S6)
FTIR: 3456 cm^{-1} (-OH). (Figure S7)



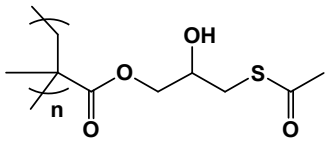
2d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.97-3.12 (m, 2H), 3.98 (m, H), 2.90 (m, H), 4.15 (m, 2H), 5.57, 6.12 (s, 2H), 1.91 (s, 3H). (Figure S8)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.51, 196.08, 32.46, 66.91, 69.05, 167.16, 135.72, 126.20, 18.20. (Figure S9)



2e: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.96-3.17 (m, 2H), 2.57 (m, H), 3.91 (m, H), 3.40 (m, 2H), 3.46 (m, 2H), 1.58 (m, 2H), 0.52 (m, 2H). (Figure S10)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.52, 196.36, 32.81, 69.68, 73.13, 74.28, 23.51, 14.23. (Figure S11)



2f: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00-4.12 (m, 2H), 3.85-3.95 (m, H), 2.95-3.19 (m, 2H), 2.36 (s, 3H). (Figure S12)
^{13}C NMR (400 MHz, *d6*-DMSO): δ 47.88, 66.68, 33.73, 195.60, 30.97, 149.72. (Figure S13)



2g: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.75-1.13 (br m, 3H), 1.89 (br m, 2H), 3.75-4.37 (br m, 2H), 3.75-4.37 (br m, H), 2.10 (m, H), 2.96-3.22(br m, 2H), 2.40 (s, 3H). (Figure S14)

General procedure for SOAM reaction to transform 2 into 3

1) Procedure employing TEA as a catalyst：

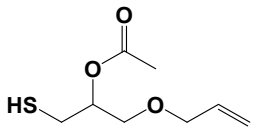
The prepared **2** (5.0 mmol) was dissolved in 16 mL of $CHCl_3$. Then, the solution was added dropwise into a mixture of $CHCl_3$ (30 mL) and TEA (6 mL) under N_2 atmosphere at a concentration of 0.1 mol/L. After vigorous stirring for 6 h at 25 °C, the reaction mixture was evaporated on a rotary evaporation. The residual was diluted with diethyl ether, washed with 1 M HCl aqueous solution to remove residual TEA and deionized water, successively, dried by anhydrous $MgSO_4$, and finally evaporated to afford **3** as a major product and **4** and **5** as minor products. The molar ratios of **3**, **4**, and **5** in the products could be obtained by comparing the integrations of proton signals of -$SCOCH_3$ and -$OCOCH_3$. Pure products, **3a** ~ **3d,** could be acquired be flash chromatography. The products derived from **1e** ~ **1g** were mixtures. The yields were presented in Table 2.

2) Procedure employing DMAP as a catalyst：

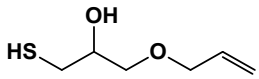
The prepared **2** (2.0 mmol) was dissolved in 5 mL of $CHCl_3$. Then, the solution was added dropwise into a mixture of $CHCl_3$ (15 mL) and DMAP (2 mmol) under N_2 atmosphere at a concentration of 0.1 mol/L. After vigorous stirring for 6 h at 25 °C, the reaction mixture was evaporated on a rotary evaporation. The residual was diluted with diethyl ether, washed with 1 M HCl aqueous solution to remove residual DMAP and deionized water, successively, dried by anhydrous $MgSO_4$, and finally evaporated to afford **3** as a major product and **4** and **5** as minor products. The molar ratios of **3**, **4**, and **5** in the products could be obtained by comparing the integrations of proton signals of -$SCOCH_3$ and -$OCOCH_3$.

3) Procedure employing DBU as a catalyst：

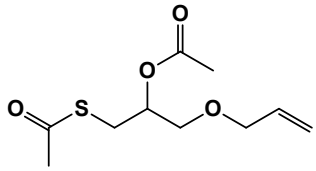
The prepared **2** (2.0 mmol) was dissolved in 5 mL of $CHCl_3$. Then, the solution was added dropwise into a mixture of $CHCl_3$ (15 mL) and DBU (2 mmol) under N_2 atmosphere at a concentration of 0.1 mol/L. After vigorous stirring for 6 h at 25 °C, the reaction mixture was evaporated on a rotary evaporation. The residual was diluted with diethyl ether, washed with 1 M HCl aqueous solution to remove residual DBU and deionized water, successively, dried by anhydrous $MgSO_4$, and finally evaporated to afford **3** as a major product and **4** and **5** as minor products. The molar ratios of **3**, **4**, and **5** in the products could be obtained by comparing the integrations of proton signals of -$SCOCH_3$ and -$OCOCH_3$.



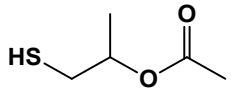
3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (t, H), 2.68-2.87 (m, 2H), 4.99 (m, H), 2.09 (s, 3H), 3.56-3.68 (m, 2H), 4.01 (m, 2H), 5.83-5.94 (m, H), 5.17-5.31 (m, 2H). (Figure S15)
^{13}C NMR (400 MHz, $CDCl_3$): δ 24.72, 73.64, 72.26, 68.45, 134.28, 117.73, 170.44, 21.24. (Figure S16)
FTIR: 2564 cm^{-1} (-SH). (Figure S3)



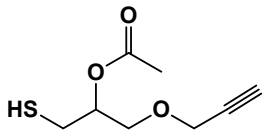
4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (t, H), 2.66 (m, 2H), 3.8 (m, H), 3.49 (m, 2H), 4.03 (d, 2H), 5.81-5.98 (m, H), 5.14-5.31 (m, 2H). (Figure S17)
^{13}C NMR (400 MHz, $CDCl_3$): δ 28.14, 71.56, 77.75, 72.80, 134.48, 117.74. (Figure S18)
FTIR: 2564 cm^{-1} (-SH), 3456 cm^{-1} (-OH). (Figure S3)



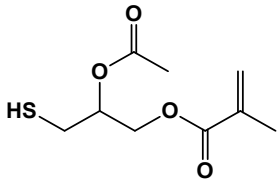
5a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.04-3.32 (m, 2H), 5.04-5.24 (m, H), 3.53 (d, 2H), 3.99 (d, 2H), 5.81-5.93 (m, H), 5.30 (d, 2H), 2.34 (s, 3H). (Figure S19)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.13, 195.26, 30.91, 70.07, 71.23, 72.74, 134.42, 117.72, 170.43, 21.19. (Figure S20)



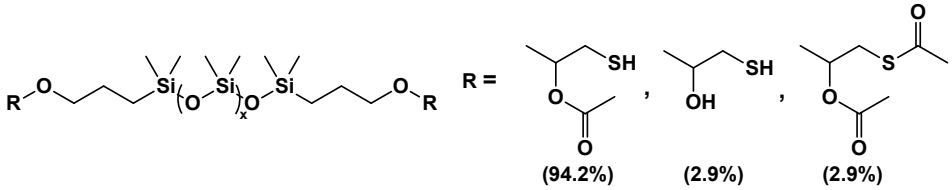
3b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (m, H), 2.57-2.73 (m, 2H), 4.91 (m, H), 1.28 (d, 2H), 2.03 (s, 3H). (Figure S21)
^{13}C NMR (400 MHz, $CDCl_3$): δ 30.25, 72.29, 19.18, 170.81, 21.98. (Figure S22)



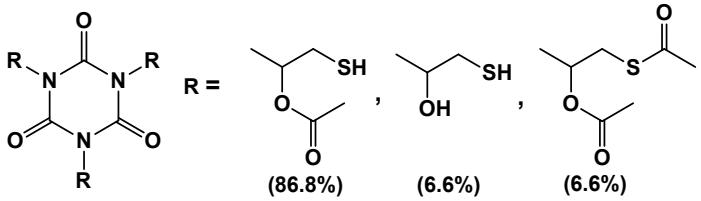
3c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, H), 2.65-2.86 (m, 2H), 4.93-5.03 (m, H), 3.63-3.81 (m, 2H), 4.17 (s, 2H), 2.45 (m, H), 2.06 (s, 3H). (Figure S23)
^{13}C NMR (400 MHz, $CDCl_3$): δ 24.76, 69.09, 73.21, 58.51, 75.22, 79.33, 170.41, 21.33. (Figure S24)
FTIR: 2564 cm^{-1} (-SH). (Figure S7)



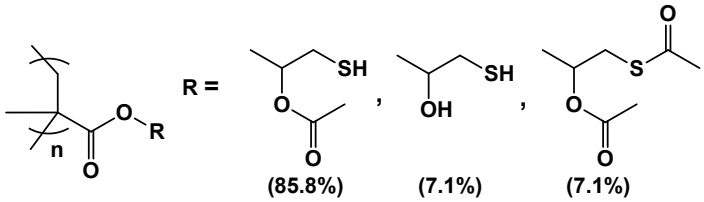
3d: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (t, H), 2.78 (m, 2H), 5.13 (m, H), 4.26-4.43 (m, 2H), 5.61, 6.12 (s, 2H), 1.95 (s, 3H), 2.09 (s, 3H). (Figure S25)
^{13}C NMR (400 MHz, $CDCl_3$): δ 23.67, 71.22, 62.26, 165.29, 134.96, 125.66, 17.13, 169.07, 20.21. (Figure S26)



(3,4,5)e: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (t, H), 2.70-2.88 (m, 2H), 5.00 (m, H), 3.55-3.70 (m, 2H), 3.36-3.52 (m, 2H), 1.62 (m, 2H), 0.45-0.58 (m, 2H), 2.10 (s, 3H). (Figure S27)
^{13}C NMR (400 MHz, $CDCl_3$): δ 25.04, 69.67, 73.72, 74.65, 23.48, 14.18, 170.76, 21.30. (Figure S28)



(3,4,5)f: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (m, 2H), 5.16 (m, H), 2.75 (m, 2H), 1.64 (m, H), 2.05 (s, 3H), 4.19 (m, 3H), 3.96 (m, H), 2.72 (m, 2H), 1.63 (m, H), 4.29 (m, 3H), 5.34 (m, H), 2.98 (m, 2H), 2.36 (s, 3H), 2.02 (s, 3H). (Figure S29)



(3,4,5)g: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86,1.02 (m, 3H), 1.82 (m, 2H), 3.86-4.43 (m, 3H), 5.08 (m, H), 2.77 (m, 2H), 1.61 (m, H), 2.12 (s, 3H), 5.33 (m, H), 3.10, 3.25 (m, 2H), 2.38 (s, 3H). (Figure S30)
FTIR: 2564 cm^{-1} (-SH), 3456 cm^{-1} (-OH). (Figure S31)
GPC: PGMA (Mn=17122, Mw=50478), 2g (Mn=15284, Mw=30280), 3g (Mn=9642, Mw=14514). (Figure S32)

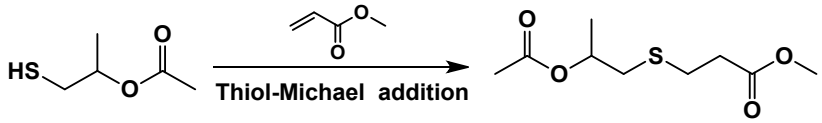
Table S1. The yield of migration reactions catalyzed by different amines.

Catalyst	Yield (%)							
	3		4		Total thiol groups (3+4)		5	
	1a	**1f**	**1a**	**1f**	**1a**	**1f**	**1a**	**1f**
TEA	90.8	86.8	4.6	6.6	95.4	93.4	4.6	6.6
DMAP	80.6	83.4	9.7	8.3	90.3	91.7	9.7	8.3
DBU	76.8	82.0	11.6	9.0	88.4	91.0	11.6	9.0

Diluted solution and slow addition operation for improving the yield of 3a from 2a

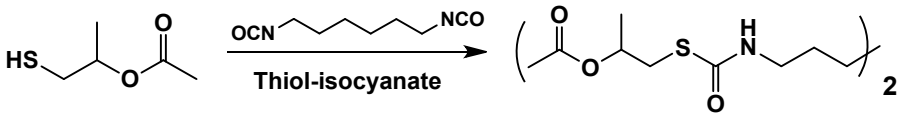
2a (1.0 g, 5.2 mmol) was dissolved in 4 mL of $CHCl_3$ and the solution was added very slowly into a mixture of $CHCl_3$ (150 mL) and TEA (30 mL) in a speed of 1 mL/h by using a Laboratorial Syringe Pump (Baoding Longer Precision Pump Co., Ltd.). After the addition, the reaction system was stirred for another 2 h. All the volatiles were removed under reduced pressure. The residual was diluted with diethyl ether, washed with 1 M HCl aqueous solution to remove residual TEA and deionized water, successively, dried by anhydrous $MgSO_4$, and finally evaporated. Before applying flash chromatography, the residual was characterized by ^{1}H NMR. By comparing the integrations of proton signals of -$SCOCH_3$ and -$OCOCH_3$, the yield of **3a** was above 97%.

Thiol-click reactions of 3b with five selected compounds to test the reactivity of the thiol group

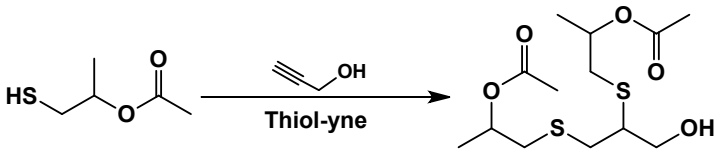


3b (0.2 g, 1.5 mmol) and methyl acrylate (0.17 g, 2.0 mmol) were dissolved in 2 mL of CH_2Cl_2. A CH_2Cl_2 (1 mL) solution of TEA (10 mg) was added dropwise into this solution. After vigorous stirring for 3 h at room temperature, 20 mL of diethyl ether was added and the mixture was washed with 1 M HCl and deionised water. The organic phase was dried over anhydrous $MgSO_4$, and then all the volatiles

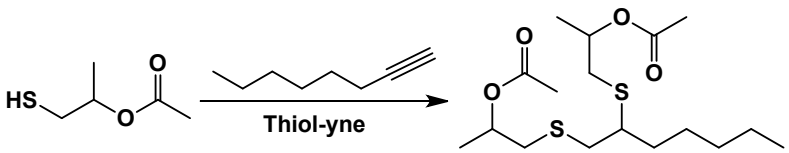
were removed on a rotary evaporator at 0 °C to afford 0.32 g of the product (97%).
3b-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (d, 3H), 4.96 (m, H), 2.67 (m, 2H), 2.78 (m, 2H), 2.57 (m, 2H), 3.65 (s, 3H), 2.00 (s, 3H). (Figure S33)
^{13}C NMR (400 MHz, $CDCl_3$): δ 19.59, 70.58, 28.20, 38.19, 35.43, 171.17, 52.32, 173.24, 21.66. (Figure S34)
Electrospray ionization mass spectroscopy (ESI-MS) (product + Na^+): 242.8 Da (calculated: 243.1 Da). (Figure S35)



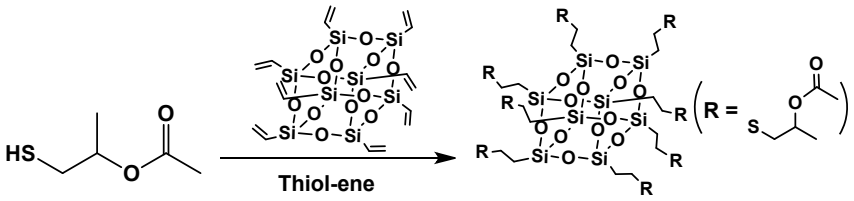
3b (0.60 g, 4.5 mmol) and 1,6-diisocyanatohexane (0.34 g, 2.0 mmol) were dissolved in 5 mL of diethyl ether. TEA (16 μL) was injected into this solution. After vigorous stirring for 3 h at room temperature, 40 mL of diethyl ether was added and the mixture was washed with 1 M HCl and deionised water. The organic phase was dried over anhydrous $MgSO_4$, and then all the volatiles were removed on a rotary evaporator at 0 °C. The residual was purified using flash chromatography and 0.82 g of the product was obtained (99%).
3b-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02-1.39 (m, 3H), 4.87-5.06 (m, H), 2.92-3.21 (m, 2H), 2.03 (s, 3H), 3.10-3.34 (m, 2H), 1.39-1.60 (m, 2H), 1.30 (m, 2H). (Figure S36)
^{13}C NMR (400 MHz, $CDCl_3$): δ 19.66, 70.64, 35.16, 166.72, 41.71, 30.00, 26.55, 171.21, 22.08. (Figure S37)
Electrospray ionization mass spectroscopy (ESI-MS) (product + Na^+): 459.1 Da (calculated: 459.2 Da). (Figure S38)



3b (0.295 g, 2.2 mmol), propargyl alcohol (56 mg, 1.0 mmol) and 2,2'-azobisisobutyronitrile (8.2 mg, 0.05 mmol) were dissolved in 5 mL of toluene in a 25 mL flask. After being purged with N_2, the flask was placed in an oil bath at 70 °C for 3 h. All the volatiles were removed on a rotary evaporator. The residual was purified using flash chromatography and 0.31 g of the product was obtained (95%).
3b-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (m, 3H), 4.93 (m, H), 2.50-2.72 (m, 2H), 1.98 (s, 3H), 2.72-2.84 (m, 2H), 2.84-3.07 (m, H), 3.62-3.75 (m, 2H). (Figure S39)
^{13}C NMR (400 MHz, $CDCl_3$): δ 63.71, 49.92, 38.64, 35.50, 70.61, 19.81, 171.26, 22.00. (Figure S40)
Electrospray ionization mass spectroscopy (ES-MS) (product + Na^+): 346.9 Da (calculated: 347.1 Da). (Figure S41)

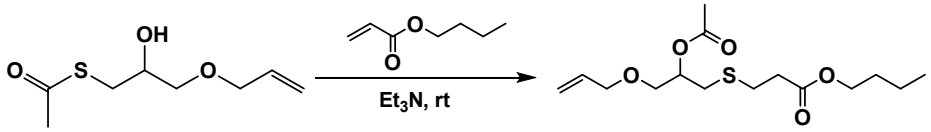


3b (0.295 g, 2.2 mmol), 1-octyne (56 mg, 1.0 mmol), 2,2-dimethoxy-2-phenylacetophenone (8.2 mg, 0.05 mmol) and tetrahydrofuran (4 mL) were charged into a 25 mL flask. After being purged with N_2, the flask was placed under a UV lamp (8 W) at 25 °C for 1 h. Then, tetrahydrofuran was removed by rotary evaporation. The residual was purified using flash chromatography and 0.35 g of the product was obtained (96%).
3b-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H), 4.87-5.05 (m, H), 1.30 (d, 3H), 2.02 (d, 2H), 2.81-2.94 (m, 2H), 2.62-2.81 (m, H), 1.67-1.86 (m, 2H), 1.26-1.56 (m, 2H, 2H, 2H, 2H), 0.86 (m, 3H). (Figure S42)
^{13}C NMR (400 MHz, $CDCl_3$): δ 170.33, 18.87, 69.98, 35.82, 38.64, 46.16, 33.31, 26.39, 28.89, 32.03, 22.63, 13.54. (Figure S43)



3b (0.295 g, 2.2 mmol), octavinyl-T8-silsesquioxane (56 mg, 1.0 mmol), 2,2-dimethoxy-2-phenylacetophenone (8.2 mg, 0.05 mmol) and tetrahydrofuran (4 mL) were charged into a 25 mL flask. After being purged with N_2, the flask was placed under a UV lamp (8 W) at 25 °C for 1 h. Then, tetrahydrofuran was removed by rotary evaporation. The residual was purified using flash chromatography and 0.35 g of the product was obtained (96%).
3b-5: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89-1.06 (m, 2H), 2.70 (m, 2H), 2.50-2.64 (m, 2H), 4.92-5.04 (m, H), 1.20-1.34 (d, 3H), 2.01 (s, 3H). (Figure S44)
^{13}C NMR (400 MHz, $CDCl_3$): δ 13.54, 27.02, 37.69, 70.29, 19.80, 170.95, 22.00. (Figure S45)

One-pot two-step processes

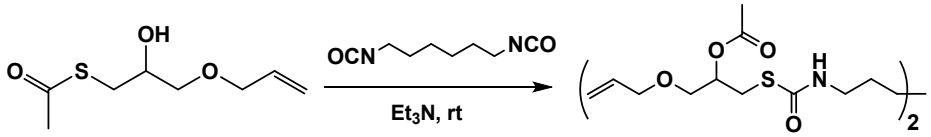


6 mL of TEA, 30 mL of tetrahydrofuran, and 256 mg of *n*-butyl acrylate (2.0 mmol) were mixed. At room temperature, **2a** (0.46 g, 2.4 mmol) was added dropwise to this mixture. After being stirred for 5 h, all the volatiles were removed by rotary evaporation. The residual was purified using flash chromatography and 0.56 g of the product was obtained (88%).

2a-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29-5.17 (m, 2H), 5.92-5.83 (m, H), 4.04-3.96 (m, 2H), 3.65-3.55 (m, 2H), 5.09-5.03 (m, H), 2.75-2.68 (m, 2H), 2.63-2.59 (m, 2H), 2.84-2.79 (m, 2H), 4.11-4.07 (t, 2H), 1.64-1.57 (m, 2H), 1.42-1.33 (m, 2H), 0.94-0.91 (t, 3H), 2.08 (s, 3H). (Figure S46)

^{13}C NMR (400 MHz, $CDCl_3$): δ 116.96, 134.28, 72.01, 71.80, 69.27, 32.06, 27.39, 34.61, 117.51, 64.09, 30.51, 18.98, 13.53, 170.05. (Figure S47)

Electrospray ionization mass spectroscopy (ESI-MS) (product + NH_4^+): 336.3 Da (calculated: 336.1 Da). (Figure S48)

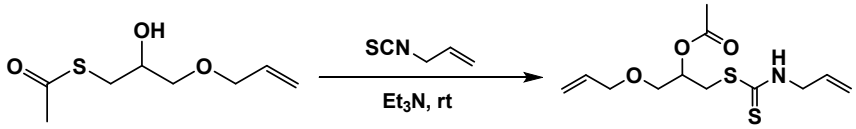


6 mL of TEA, 30 mL of dried tetrahydrofuran, and 1,6-diisocyanatohexane (0.34 g, 2.0 mmol) were mixed in a 100 mL flask. **2a** (0.95 g, 5.0 mmol) was added dropwise to the mixture. After reacting for 5 h, all the volatiles were removed under reduced pressure. The residual was purified using flash chromatography and 0.89 g of the product was obtained (81%).

2a-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30-5.18 (m, 2H), 5.92-5.83 (m, H), 4.06-3.96 (m, 2H), 3.63-3.57 (m, 2H), 5.14-5.09 (m, H), 3.20-3.06 (m, 2H), 5.63 (s, H), 3.32-3.28 (m, 2H), 1.52-1.51 (m, 2H), 1.34 (m, 2H), 2.10 (s, H). (Figure S48)

^{13}C NMR (400 MHz, $CDCl_3$): δ 117.03, 134.21, 77.83, 71.90, 69.56, 29.96, 165.81, 41.10, 29.28, 26.01, 20.90, 170.23. (Figure S49)

Electrospray ionization mass spectroscopy (ESI-MS) (product + Na^+): 571.5 Da (calculated: 571.2 Da). (Figure S51)



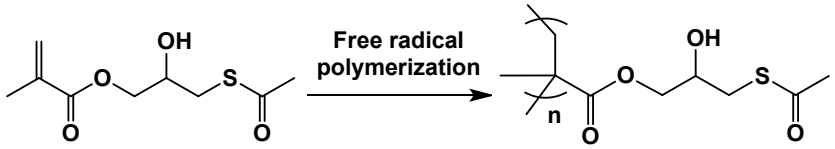
6 mL of TEA, 30 mL of dried tetrahydrofuran, and allyl isothiocyanate (0.17 g, 2.0 mmol) were mixed in a 100 mL flask. **2a** (0.48 g, 2.5 mmol) was added dropwise to the mixture. After reacting for 5 h, all the volatiles were removed under reduced pressure. The residual was purified using flash chromatography and 0.50 g of the product was obtained (86%).

2a-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.28-5.17 (m, 2H), 5.93-5.81 (m, 2H), 4.01-3.97 (t, 2H), 3.63-3.62 (m, 2H), 5.09-5.06 (m, H), 3.55-3.36 (m, 2H), 7.83 (s, H), 4.36-4.34 (t, 2H), 5.93-5.81 (m, H), 5.28-5.17 (m, 2H), 2.07 (s, 3H). (Figure S50)

^{13}C NMR (400 MHz, $CDCl_3$): δ 117.19, 134.16, 71.98, 71.58, 69.54, 35.08, 196.17, 49.43, 132.00, 117.73, 20.93, 170.51. (Figure S51)

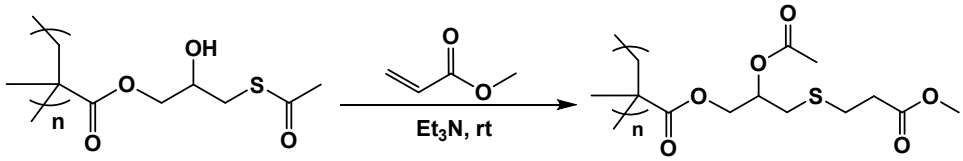
Electrospray ionization mass spectroscopy (ESI-MS) (product + Na^+): 312.3 Da (calculated: 312.1 Da). (Figure S54)

Preparation of the latent polythiols



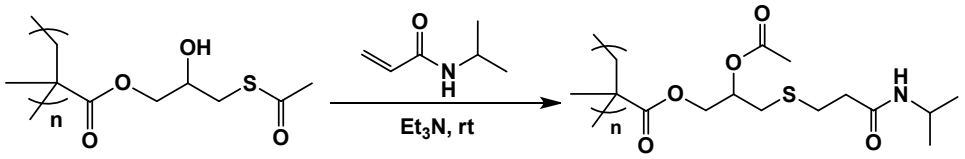
To a 25 mL flask, **2d** (3.27 g, 15.0 mmol), 2,2'-azobisisobutyronitrile (24.6 mg, 0.15 mmol) and freshly distilled toluene (3 mL) were charged. The flask was sealed with rubber septum, purged with N_2, and placed in an oil bath at 68 °C for 10 h. The reaction solution was poured into cold diethyl ether (0 °C). The obtained solids were further purified by dissolvation and precipitation twice, and finally dried in vacuo at room temperature. 2.53 g of latent polythiols was obtained (77%).

Postfunctionalization of the latent polythiols employing one-pot two-step processes



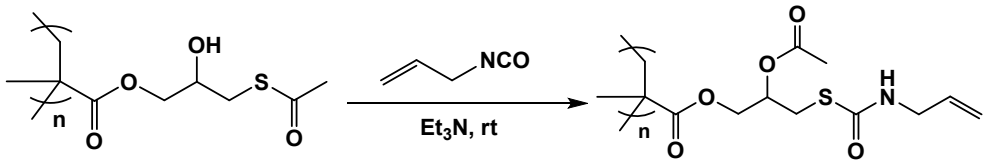
The latent polythiols (0.44 g) was dissolved in 10 mL of CH_2Cl_2. Methyl acrylate (0.26 g, 3.0 mmol), TEA (6 mL), and CH_2Cl_2 (30 mL) were mixed. To this mixture, the latent polythiols was added dropwise. After reacting for 5 h, the reaction mixture was concentrated and poured into cold methanol (0 °C). The obtained solids were further purified by dissolvation and precipitation twice, and finally dried in vacuo at room temperature to give 0.55 g of the addition product.

2d-1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (br s, 3H), 1.02 (br s, 3H), 1.90 (br m, 2H), 4.07 (br m, 2H), 5.15 (br s, H), 2.75 (br s, 2H), 2.10 (br m, 3H), 2.84 (br s, 2H), 2.64 (br s, 2H), 3.69 (br s, 3H). (Figure S52)



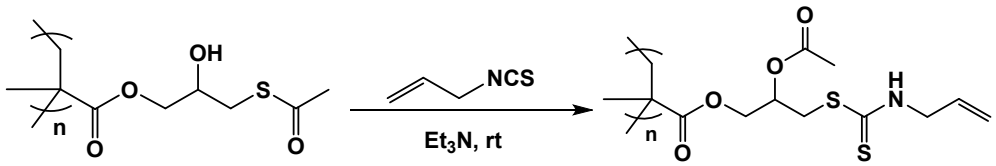
The latent polythiols (0.44 g) was dissolved in 10 mL of CH_2Cl_2. N-isopropylacrylamide (0.34 g, 3.0 mmol), TEA (6 mL), and CH_2Cl_2 (30 mL) were mixed. To this mixture, the latent polythiols was added dropwise. After reacting for 5 h, the reaction mixture was concentrated and poured into cold diethyl ether (0 °C). The obtained solids were further purified by dissolvation and precipitation twice, and finally dried in vacuo at room temperature to give 0.62 g of the addition product.

2d-2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70-1.09 (br s, 3H), 1.75-2.02 (br m, 2H), 4.11-4.44 (br m, 2H), 5.15 (br s, H), 2.77 (br s, 2H), 2.12 (br s, 3H), 2.88 (br s, 2H), 2.47 (br s, 2H), 5.52 (br s, H), 1.15 (br d, 3H), 3.89-4.12 (br m, H). (Figure S53)



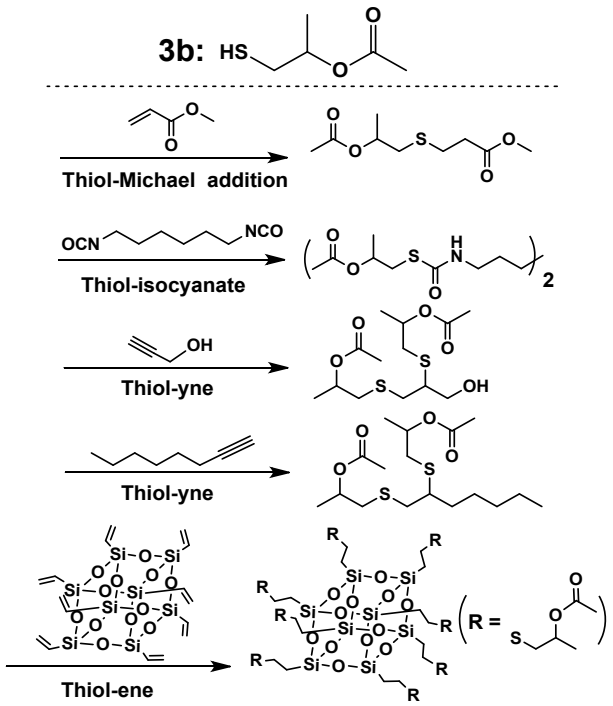
The latent polythiols (0.44 g) was dissolved in 10 mL of CH_2Cl_2. Allyl isocyanate (0.21 g, 2.5 mmol), TEA (6 mL), and CH_2Cl_2 (30 mL) were mixed. To this mixture, the latent polythiols was added dropwise. After reacting for 5 h, the reaction mixture was concentrated and poured into cold diethyl ether (0 °C). The obtained solids were further purified by dissolvation and precipitation twice, and finally dried in vacuo at room temperature to give 0.59 g of the addition product.

2d-3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (br s, 3H), 1.25 (br s, 3H), 1.8 (br m, 2H), 4.17 (br m, 2H), 5.18 (br m, H), 3.22 (br m, 2H), 6.52 (br s, H), 3.93 (br s, 2H), 5.84 (br m, H), 5.21 (br m, 2H). (Figure S54)



The latent polythiols (0.44 g) was dissolved in 10 mL of CH_2Cl_2. Allyl isothiocyanate (0.25 g, 2.5 mmol), TEA (6 mL), and CH_2Cl_2 (30 mL) were mixed. To this mixture, the latent polythiols was added dropwise. After reacting for 5 h, the reaction mixture was concentrated and poured into cold diethyl ether (0 °C). The obtained solids were further purified by dissolvation and precipitation twice, and finally dried in vacuo at room temperature to give 0.54 g of the addition product.

2d-4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (br s, 3H), 1.06 (br s, 3H), 1.97 (br m, 2H), 4.12 (br m, 2H), 5.28 (br m, H), 3.61 (br m, 2H), 8.12 (br s, H), 4.39 (br s, 2H), 5.33 (br m, H), 5.93 (br s, 2H), 2.12 (br s, 3H). (Figure S55)



Scheme S1. Thiol-click reactions of 3b with five selected compounds.

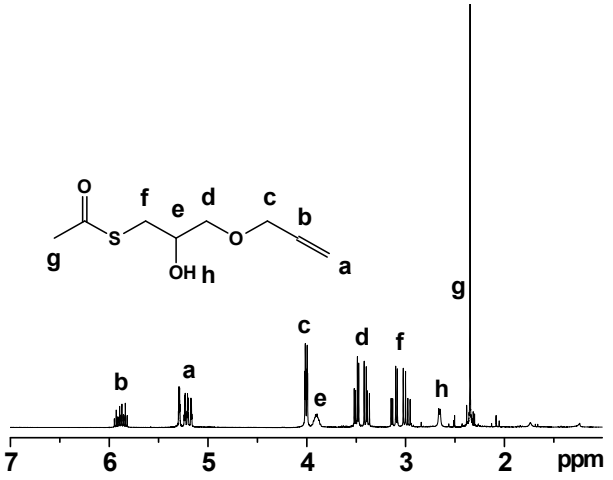


Figure S1. ^{1}H NMR spectrum of **2a**.

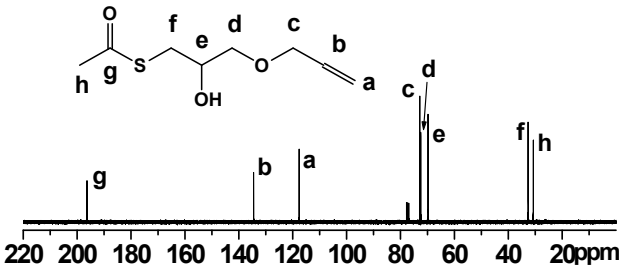


Figure S2. ^{13}C NMR spectrum of **2a**.

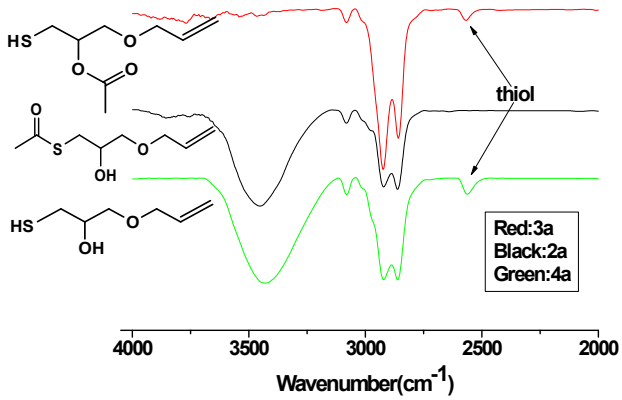


Figure S3. FTIR spectra of **2a**, **3a** and **4a**.

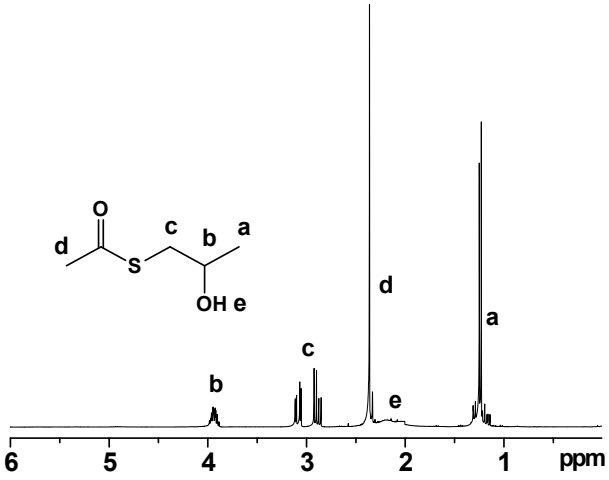


Figure S4. ^{1}H NMR spectrum of **2b**.

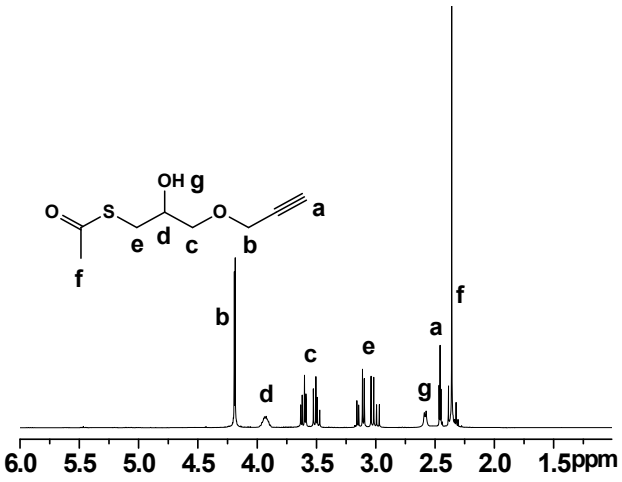


Figure S5. ^{1}H NMR spectrum of **2c**.

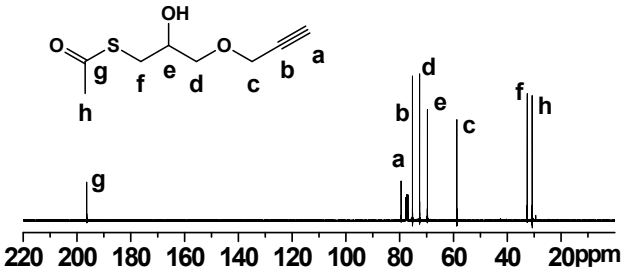


Figure S6. ^{13}C NMR spectrum of **2c**.

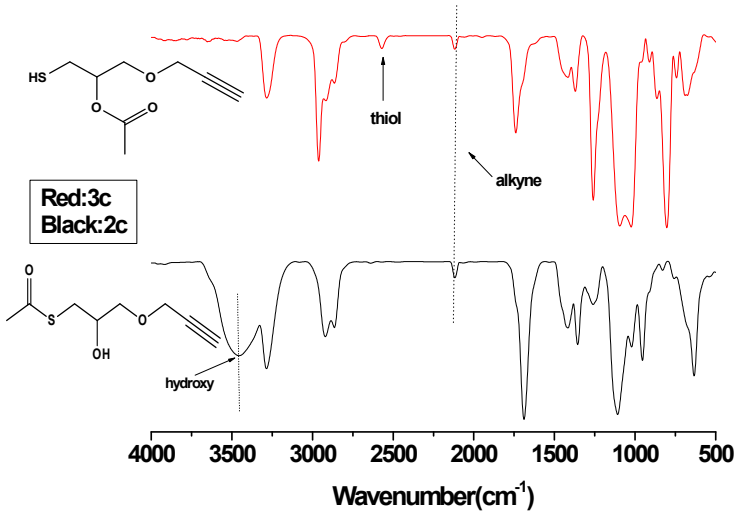


Figure S7. FTIR spectra of **2c** and **3c**.

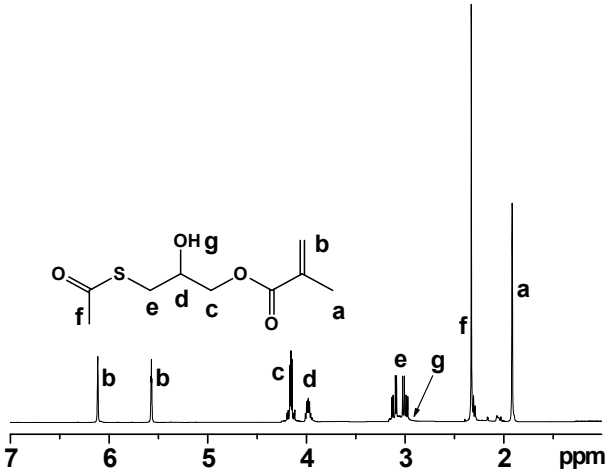


Figure S8. ^{1}H NMR spectrum of **2d**.

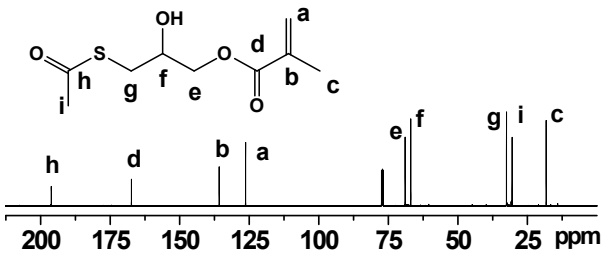


Figure S9. ^{13}C NMR spectrum of **2d**.

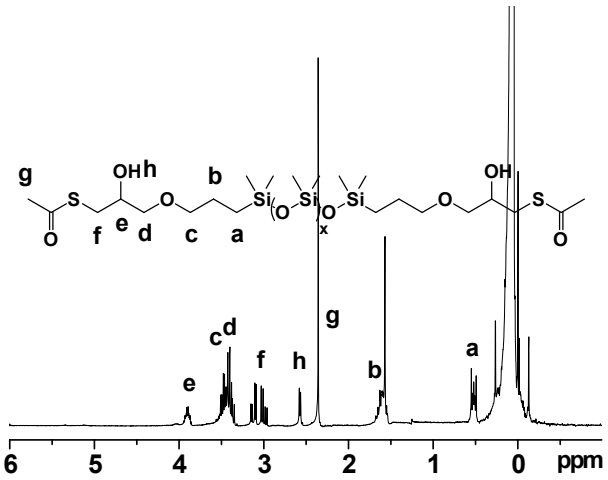


Figure S10. ^{1}H NMR spectrum of **2e**.

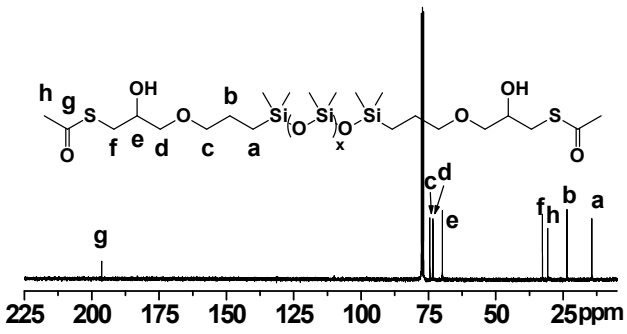


Figure S11. ^{13}C NMR spectrum of **2e**.

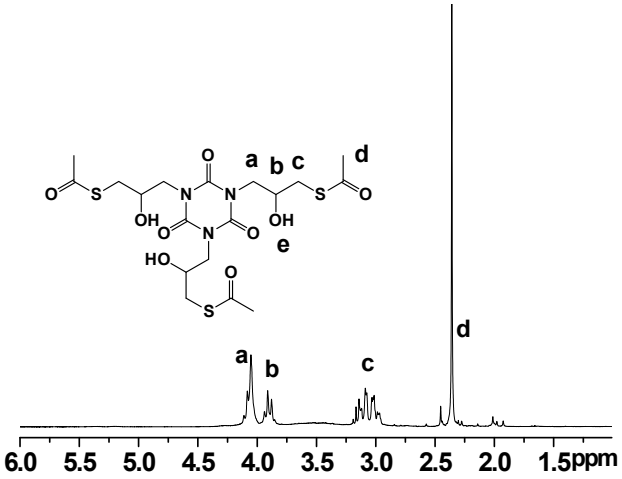


Figure S12. ^{1}H NMR spectrum of **2f**.

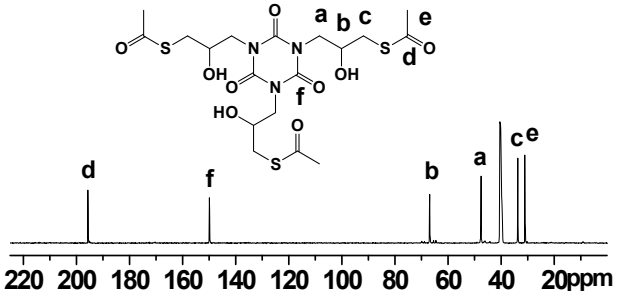


Figure S13. ^{13}C NMR spectrum of **2f**.

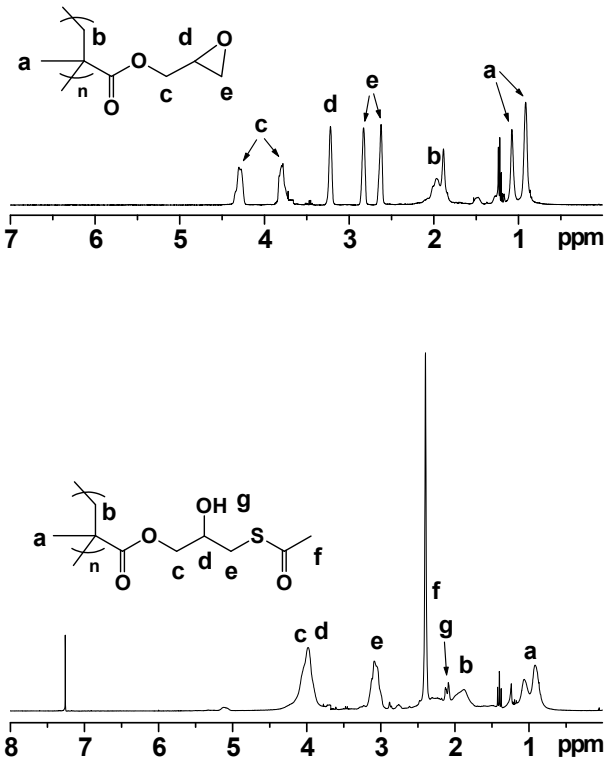


Figure S14. ^{1}H NMR spectrum of **2g**.

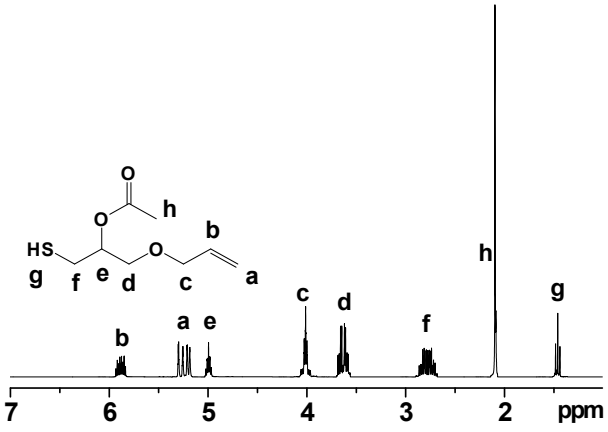


Figure S15. ^{1}H NMR spectrum of **3a**.

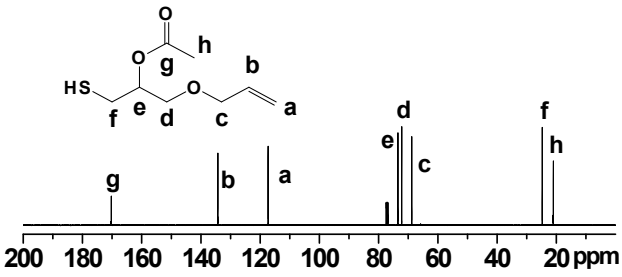


Figure S16. ^{13}C NMR spectrum of **3a**.

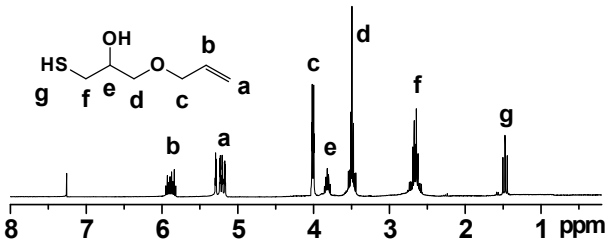


Figure S17. ^{1}H NMR spectrum of **4a**.

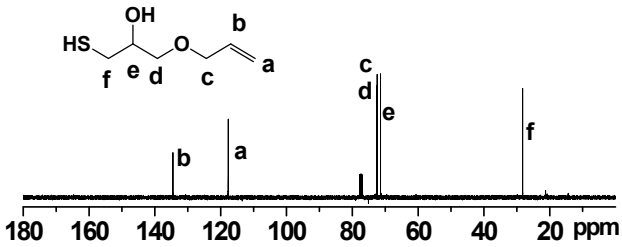


Figure S18. ^{13}C NMR spectrum of **4a**.

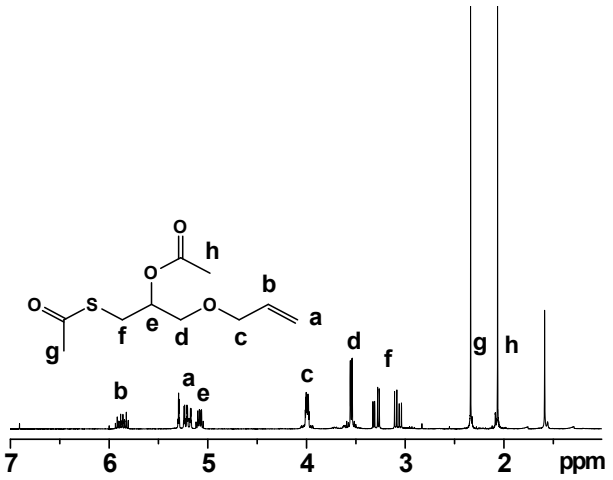


Figure S19. ^{1}H NMR spectrum of **5a**.

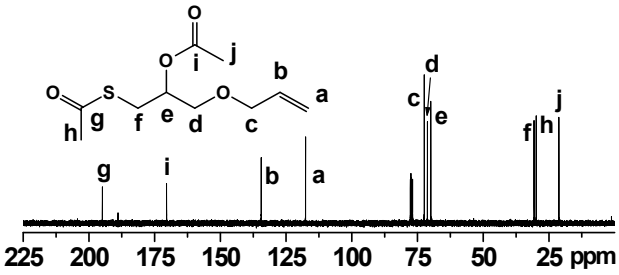


Figure S20. ^{13}C NMR spectrum of **5a**.

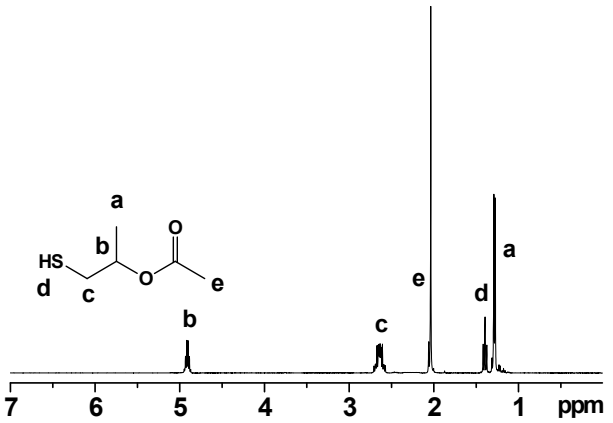


Figure S21. ^{1}H NMR spectrum of **3b**.

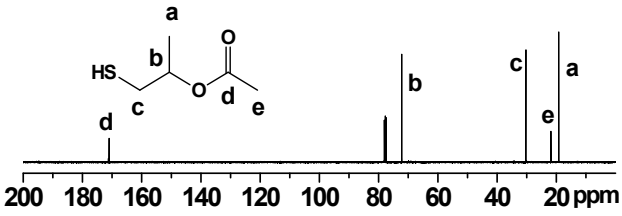


Figure S22. ^{13}C NMR spectrum of **3b**.

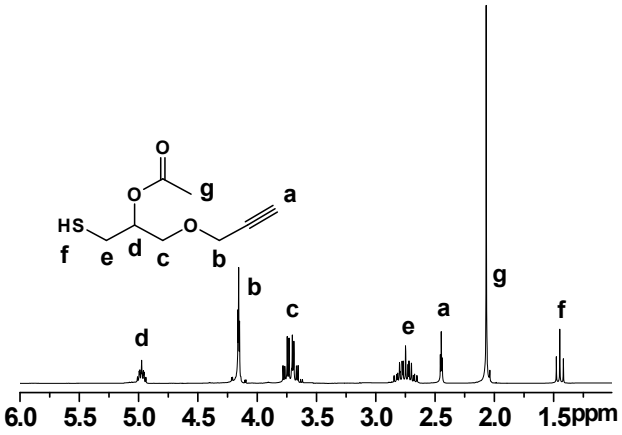


Figure S23. ^{1}H NMR spectrum of **3c**.

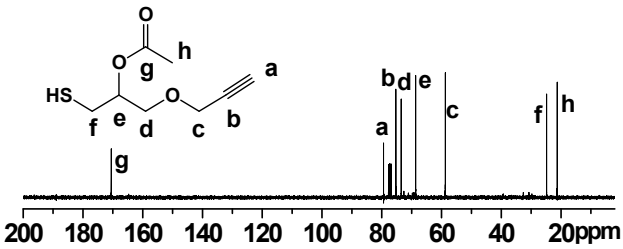


Figure S24. ^{13}C NMR spectrum of **3c**.

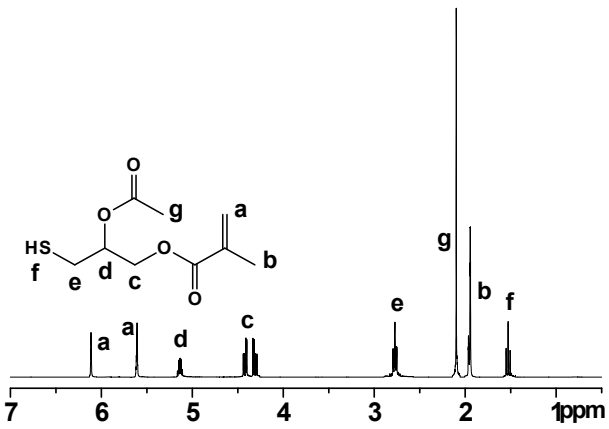


Figure S25. ^{1}H NMR spectrum of **3d**.

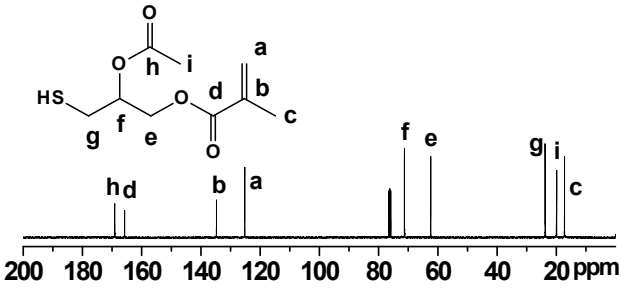


Figure S26. ^{13}C NMR spectrum of **3d**.

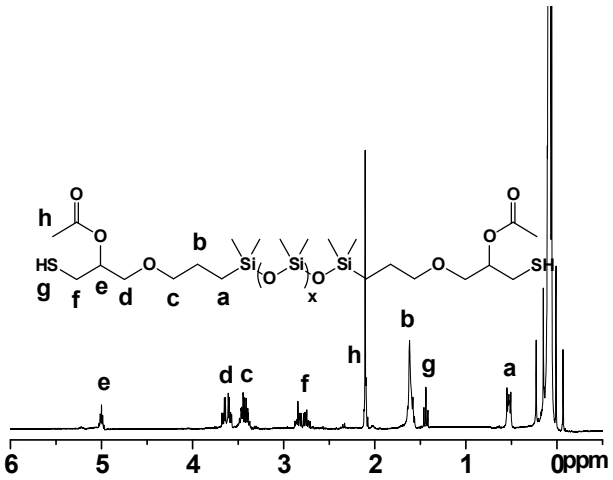


Figure S27. ^{1}H NMR spectrum of (**3**, **4**, **5**)**e**.

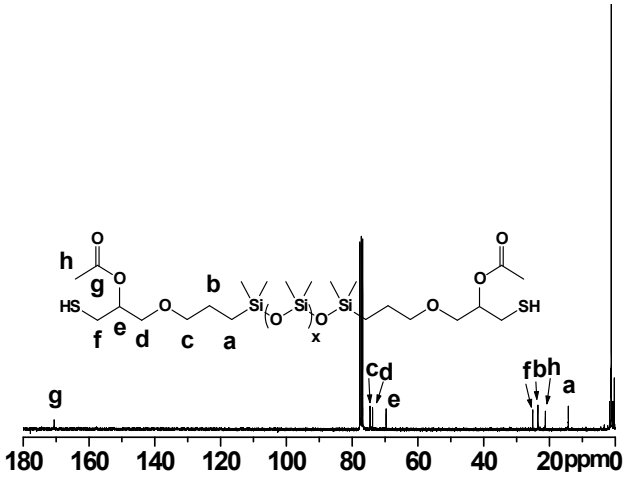


Figure S28. ^{13}C NMR spectrum of (**3**, **4**, **5**)**e**.

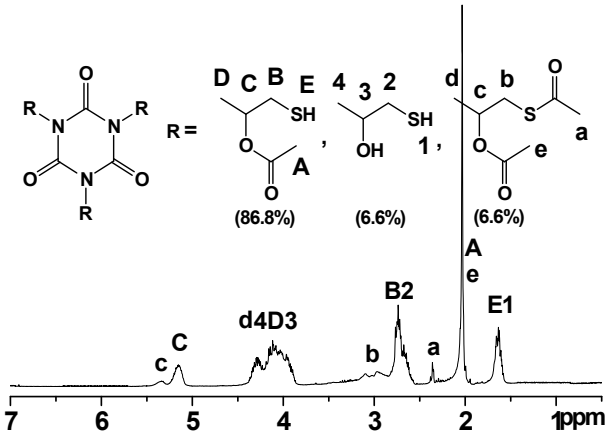


Figure S29. ^{1}H NMR spectrum of (**3**, **4**, **5**)**f**.

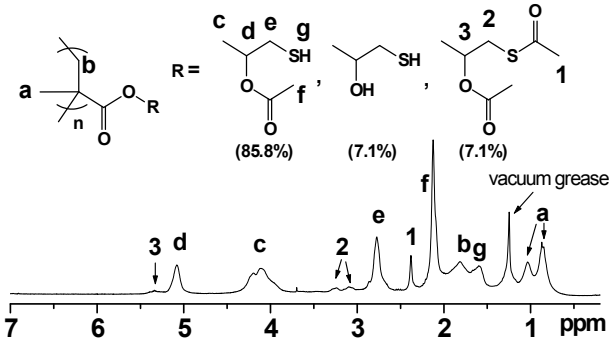


Figure S30. ^{1}H NMR spectrum of (**3**, **4**, **5**)**g**.

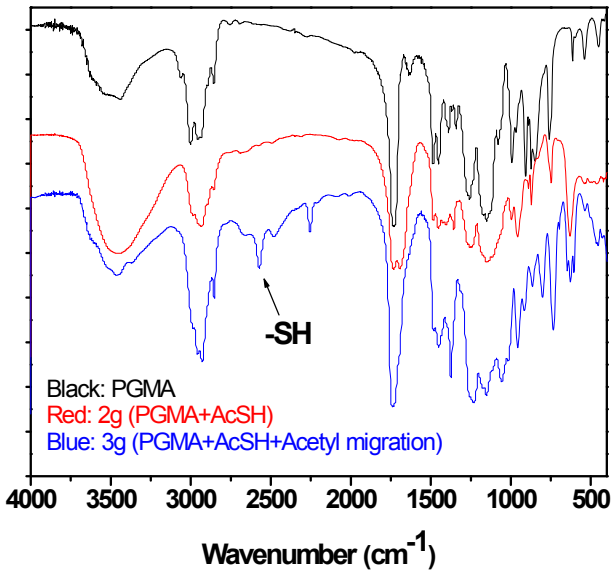


Figure S31. FTIR spectra of PGMA, **2g** and **3g**.

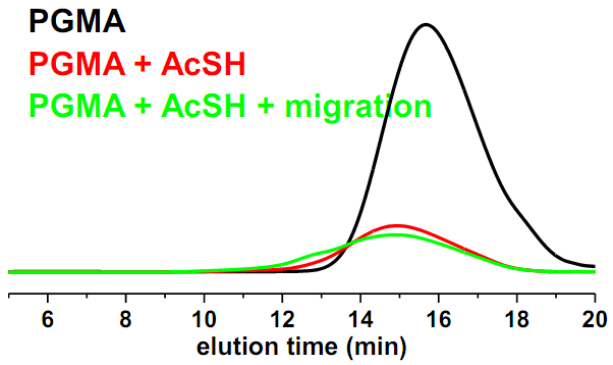


Figure S32. GPC curves of PGMA, **2g** and **3g**.

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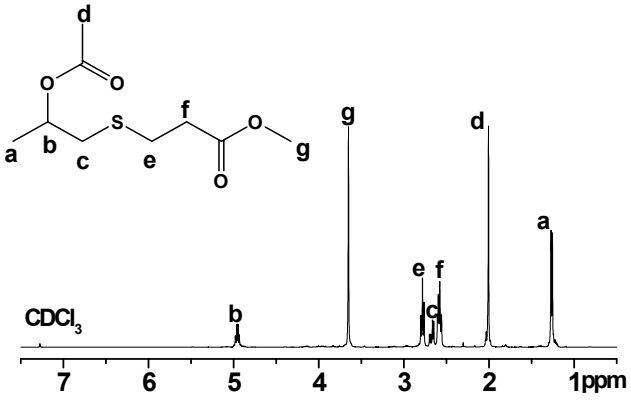

Figure S33. ^{1}H NMR spectrum of **3b-1**.

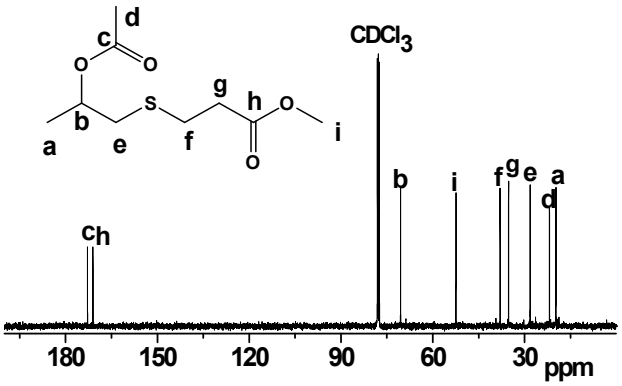

Figure S34. ^{13}C NMR spectrum of **3b-1**.

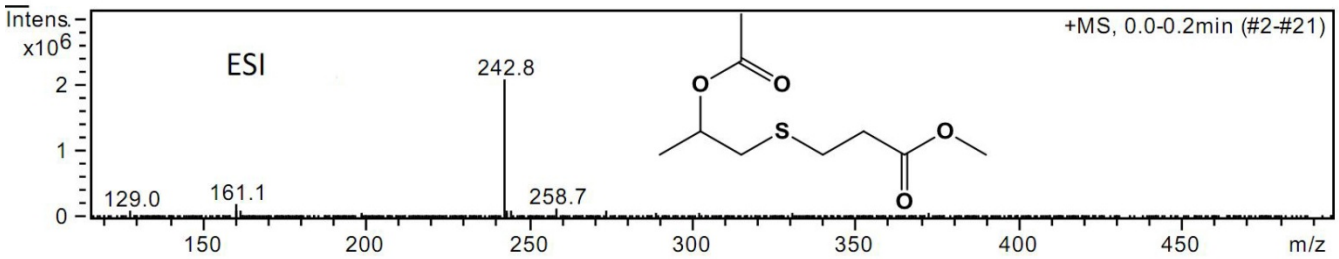

Figure S35. ESI-MS spectrum of **3b-1**.

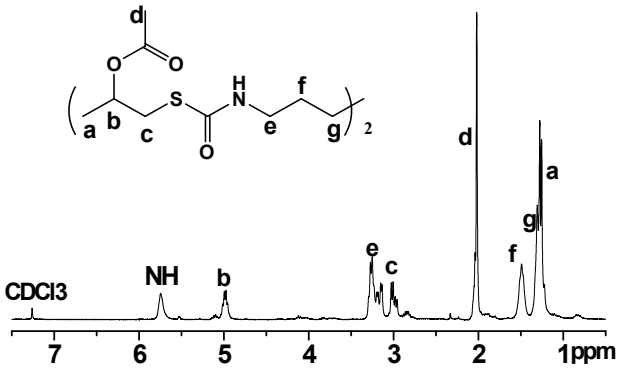

Figure S36. ^{1}H NMR spectrum of **3b-2**.

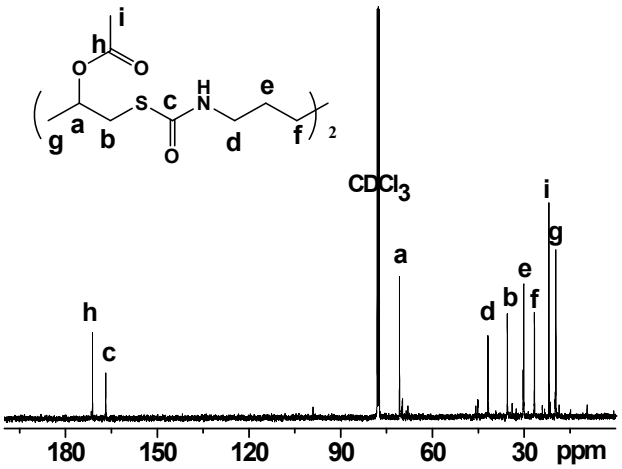

Figure S37. ^{13}C NMR spectrum of **3b-2**.

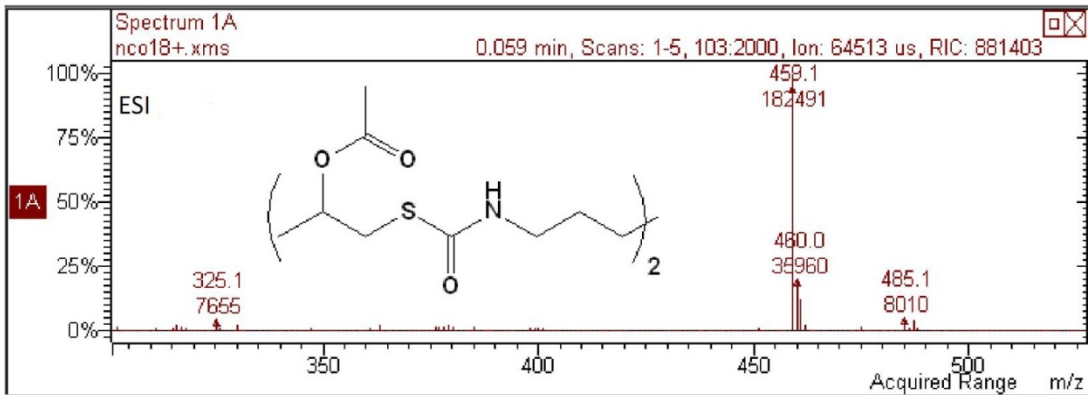

Figure S38. ESI-MS spectrum of **3b-2**.

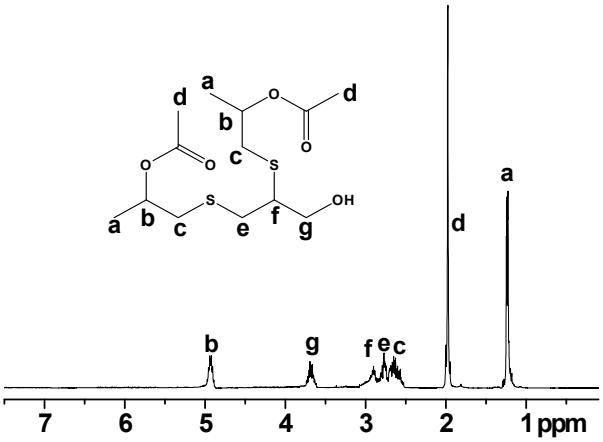

Figure S39. ^{1}H NMR spectrum of **3b-3**.

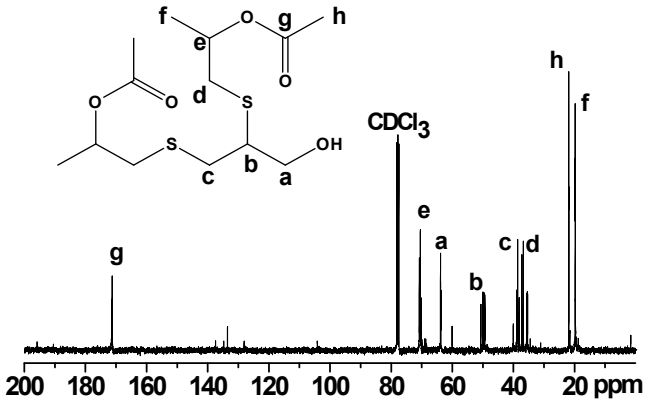

Figure S40. ^{13}C NMR spectrum of **3b-3**.

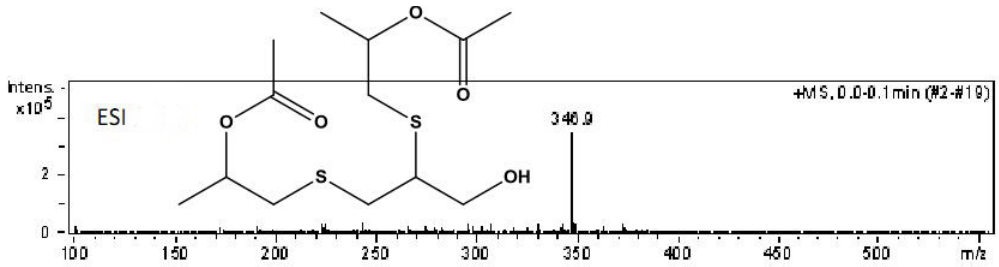

Figure S41. ESI-MS spectrum of **3b-3**.

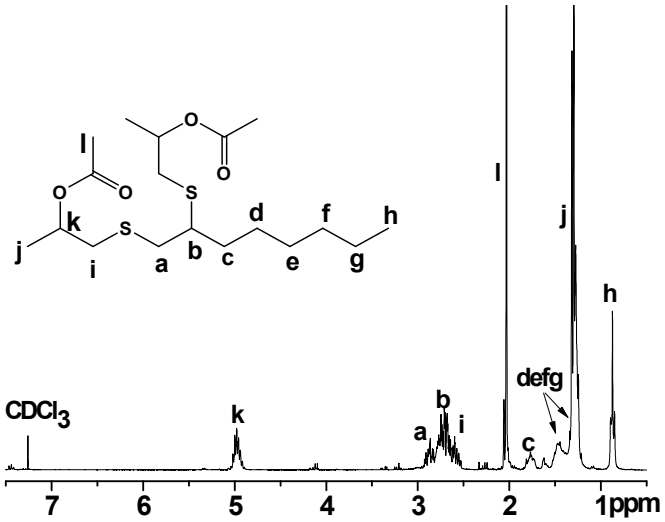

Figure S42. ^{1}H NMR spectrum of **3b-4**.

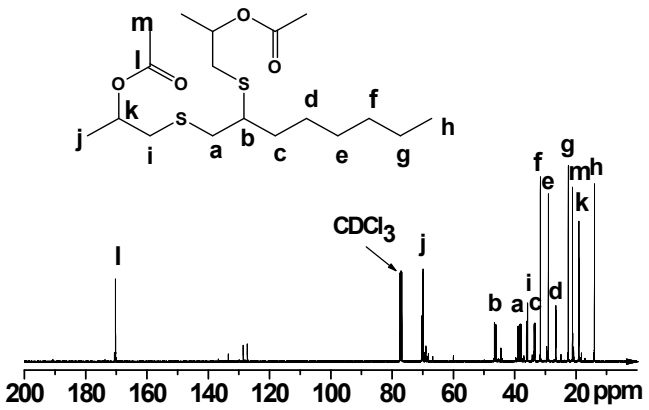

Figure S43. ^{13}C NMR spectrum of **3b-4**.

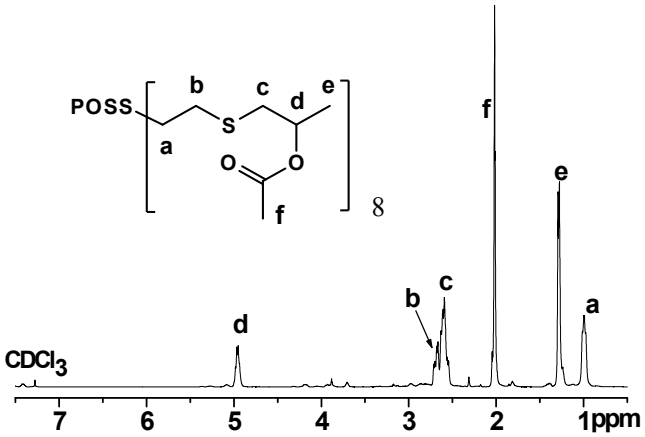

Figure S44. ^{1}H NMR spectrum of **3b-5**.

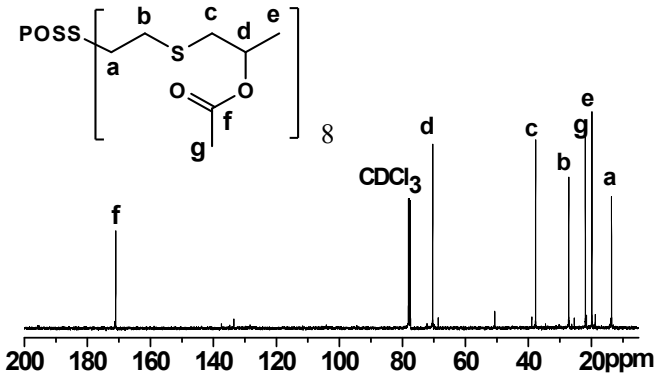

Figure S45. ^{13}C NMR spectrum of **3b-5**.

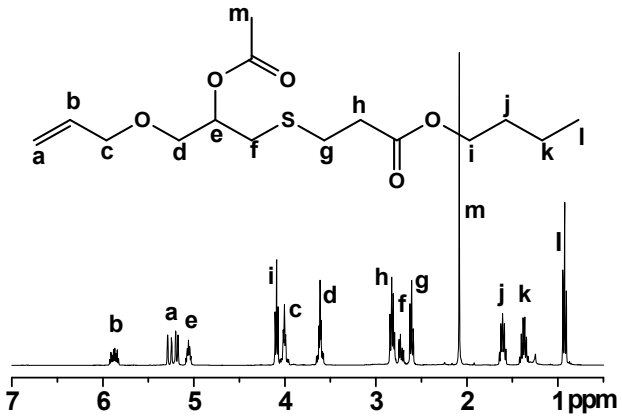

Figure S46. ^{1}H NMR spectrum of **2a-1**.

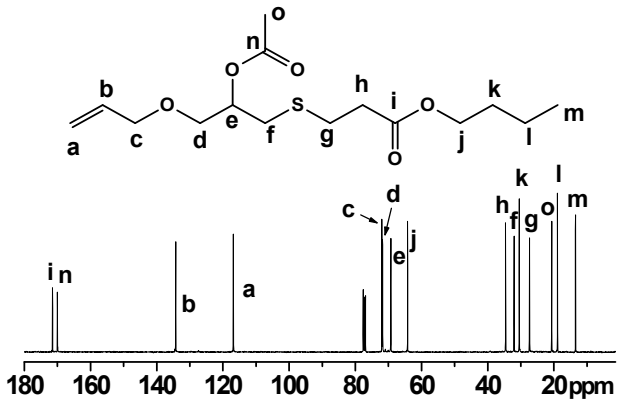

Figure S47. ^{13}C NMR spectrum of **2a-1**.

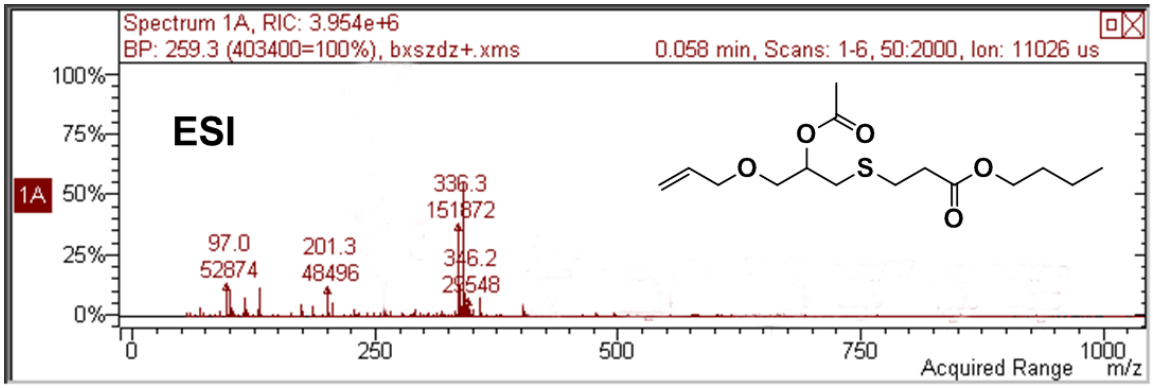

Figure S48. ESI-MS spectrum of **2a-1**.

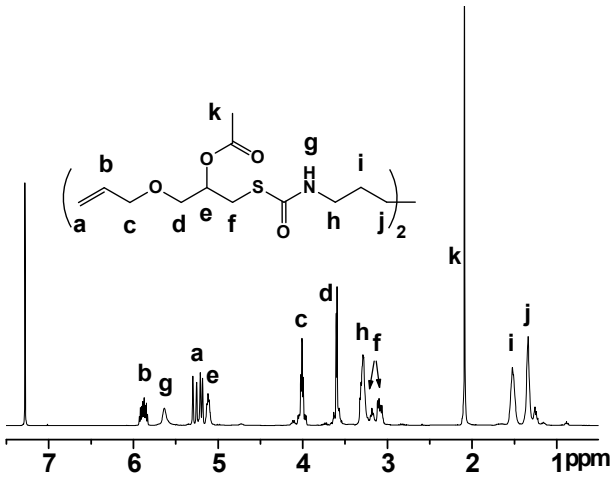

Figure S49. ^{1}H NMR spectrum of **2a-2**.

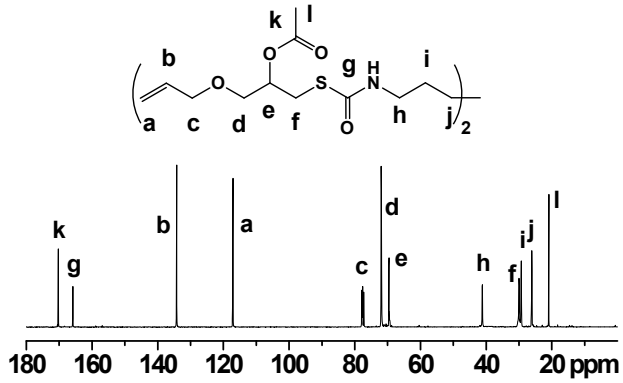

Figure S50. ^{13}C NMR spectrum of **2a-2**.

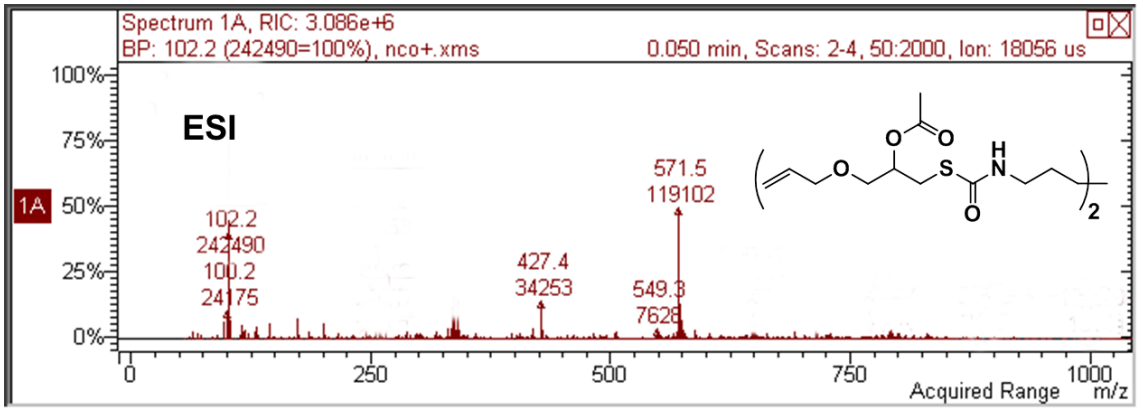

Figure S51. ESI-MS spectrum of **2a-2**.

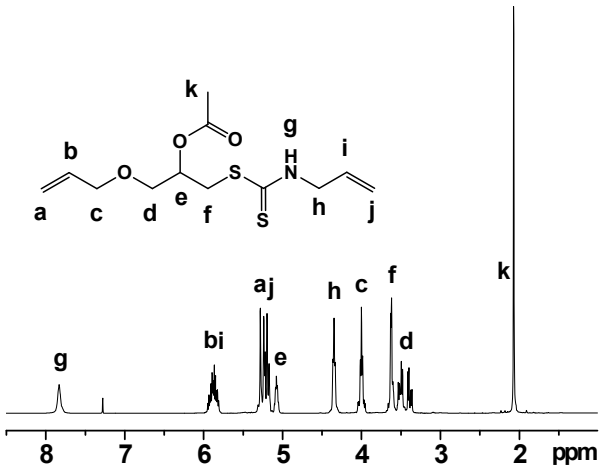

Figure S52. ^{1}H NMR spectrum of **2a-3**.

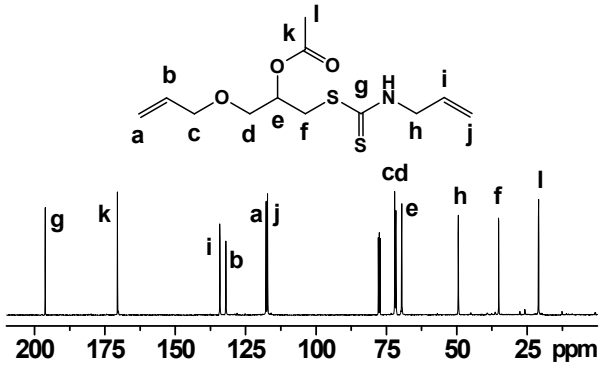

Figure S53. ^{13}C NMR spectrum of **2a-3**.

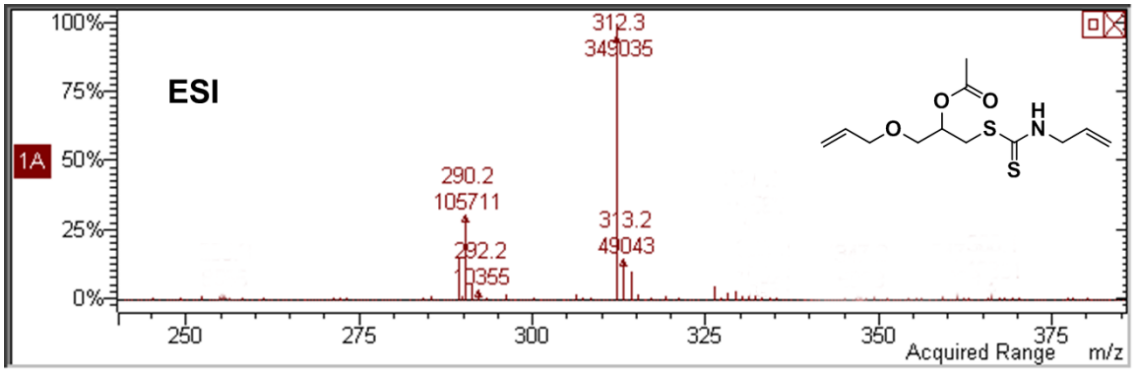

Figure S54. ESI-MS spectrum of **2a-3**.

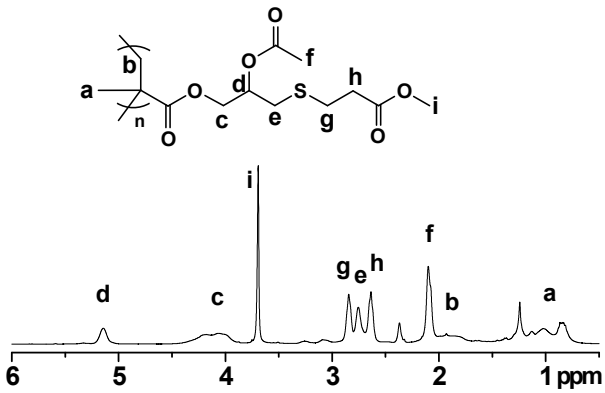

Figure S55. ^{1}H NMR spectrum of **2d-1**.

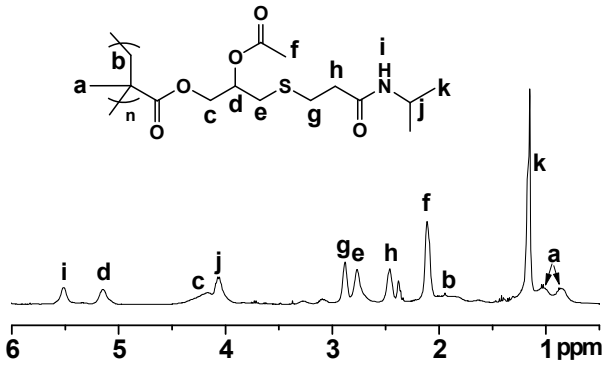

Figure S56. ^{1}H NMR spectrum of **2d-2**.

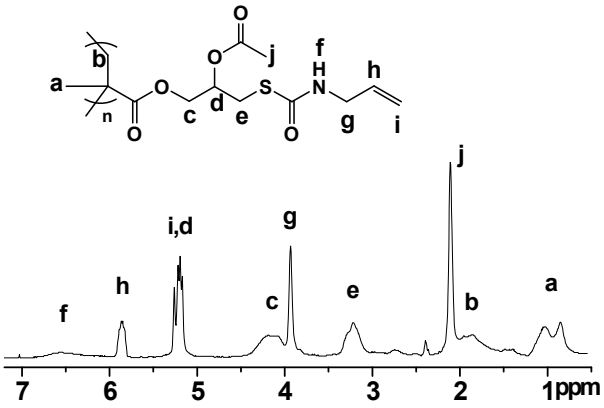

Figure S57. ^{1}H NMR spectrum of **2d-3**.

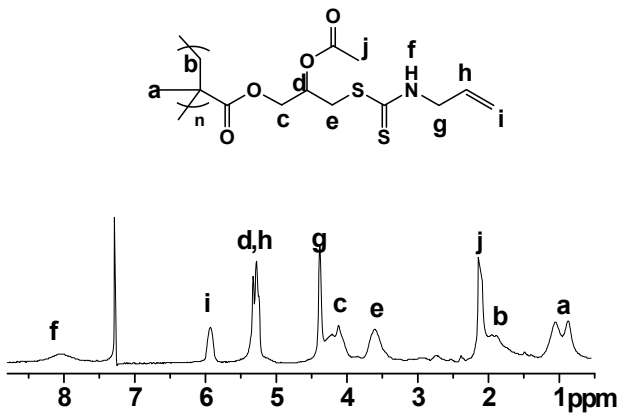

Figure S58. ^{1}H NMR spectrum of **2d-4**.