Supporting Information

Cyclic Macromonomer from a Multifunctional Atom Transfer Radical Polymerization Initiator via Sulfoxide-Based Vinyl Protection

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Materials

Styrene (St, DEAJUNG, 99.0%) and methyl methacrylate (MMA, DEAJUNG, 99.0%) were passed through a basic alumina column to remove radical inhibitors. Copper(I) bromide (CuBr, Aldrich, 98.0%) was stirred with a mixture of ascorbic acid and distilled water for 30 min and filtered. 3,4-Dihydro-2H-pyran (DHP, Aldrich, 97%), *p*-toluenesulfonyl acid monohydrate (*p*-TsOH, Aldrich, 98.5%), propargyl alcohol (Aldrich, 99%), sodium bicarbonate ($NaHCO_3$, Aldrich, ≥ 99.7%), *n*-butyllithium solution (*n*-BuLi, Aldrich, 2.5 M in hexane), *tert*-butyldimethylchlorosilane (TBDMSCl, Aldrich, 97.0%), ammonium chloride (NH_4Cl, Aldrich) phosphorus tribromide (PBr_3, Aldrich, 99%), thiophenol (Aldrich, 97.0%), methacrylic acid (Aldrich, 99.0%), potassium carbonate (K_2CO_3, Aldrich, 99.99%), tetrabutylammonium fluoride trihydrate ($TBAF{\cdot}3H_2O$, Aldrich, ≥ 97.0%), sodium hydrate (NaH, Aldrich, 90%), DOWEX®50W X4-100 ion exchange resin (Aldrich), 4-dimethylaminopyridine (DMAP, Aldrich, 99.0%), N,N′-dicyclohexylcarbodiimide (DCC, Aldrich, 99.0%), 2-bromo-2-methylpropanoyl bromide (BiBB, Aldrich, 98.0%), acetic acid (AcOH, Aldrich, 99.9%), hydrogen peroxide solution 30% (w/w) in water (H_2O_2, Aldrich), copper(II) bromide ($CuBr_2$, Aldrich, 99.0%), tris(2-(dimethylamino)ethyl)amine (Me_6TREN, Aldrich, 97.0%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99.0%), tin(II) 2-ehtylhexanoate ($Sn(Oct)_2$, Aldrich, 98.5-100.0%), and 2-bromoisobutyryl bromide (EBiB, Aldrich, 98.0%). Cu^0 wire (1.0 mm diameter, Fisher, 99.9%), sodium azide (NaN_3, TCI, 99.0%), hexane (DUKSAN, 95.0%), ethyl acetate (EtOAc, DUKSAN, 99.5%), methylene chloride (CH_2Cl_2, SAMCHUN, 99.5%), acetone (Ace, 99.5%), methanol (MeOH, DUKSAN, 99.8%), triethylamine (TEA; NEt_3, DUKSAN, 98.0%), molecular sieves 4Å (DEAJUNG), diethyl ether (Et_2O, DEAJUNG), tetrahydrofuran (THF, DEAJUNG, 99.0%), N,N-dimethylformamide (DMF, DEAJUNG, 99.5%), anisole (DEAJUNG, 99.0%), magnesium sulfate heptahydrate ($MgSO_4$, DEAJUNG, 99%), HPLC-grade THF (Fisher, 99.9%), HPLC-

grade Acetonitrile (CH_3CN, Aldrich, 99.9%), silver trifluoroacetate (Aldrich, ≥ 99.99%), *trans*-2-(3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB, Aldrich, 99.0%), tetrabutylammonium fluoride (TBAF, TCI, ca. 1.0 mol L^{-1} in THF), dichloromethane deuterated solvent (BKI, CD_2Cl_2-d_2, 99.8%), chloroform deuterated solvent (BKI, $CDCl_3$-d_2, 99.8%), and all other chemicals were used as received.

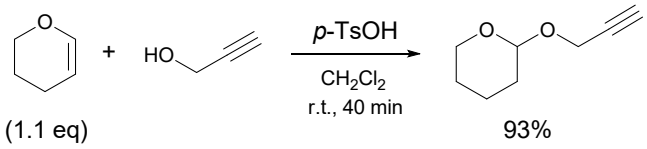
Instruments

HP 5890 gas chromatography equipped with HP101 column (methyl silicone fluid, 25.0 m × 0.32 mm × 0.30 μm) for monomer conversion. Size exclusion chromatography (SEC) was equipped with a Waters 515 HPLC pump, Agilent 1260 refractive index detector, Agilent 1100 UV detector, PSS SDV precolumn (5.0 μm; 50.0 × 8.0 mm), and PSS SDV columns (5.0 μm; 10^5, 10^3, and 10^2 Å; 300.0 × 8.0 mm). The temperature of the columns was maintained at 40 °C using a column oven. The THF elution was delivered at a flow rate of 1.0 mL min^{-1}. SEC was calibrated with polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards, respectively. For recycling preparative SEC, YMC-GPC T30000 and T2000 columns were used. HPLC-grade THF was used as the mobile phase and delivered using a YMC K-50 HPLC pump at a flow rate of 10.0 mL min^{-1}. ^1H NMR spectra were obtained on 400 MHz JEOL superconducting FT-NMR spectrometer using dichloromethane-d_2 (CD_2Cl_2) and chloromethane-*d* ($CDCl_3$), respectively, as the NMR solvent in the presence of drying agent (molecular sieves). Infrared spectra data were acquired using a Nicole 6700 FT-IR spectrometer. The electrospray ionization quadrupole time-of-flight (ESI-Q-ToF) mass spectrum was obtained by a Bruker Ultra High Resolution ESI mass spectrometer. The ESI mass spectrometer was performed at 4 kV in a desolvation temperature of 200 ºC. The mass spectrometer was operating in the positive ion mode. Nitrogen was used as the nebulizer and drying gas. The concentration of the samples was 10.0 μg mL^{-1}, and all samples were injected

using a constant flow rate (3.0 μL min^{-1}) of sample solution. A mixture of chloroform and acetonitrile was used as a solvent. The ESI-Q-ToF MS instrument was calibrated in the *m*/*z* range 100-3000 using a calibration standard (tune mix solution) which is supplied from Agilent. All data were processed via Bruker Data Analysis software version 4.1. MALDI-ToF MS was performed using a Bruker Autoflex LRF speed mass spectrometer with a 2 kHz smart beam-II laser. The instrument was operated at an accelerating potential of 20 kV in the positive mode. The DCTB and silver trifluoroacetate was used as a MALDI matrix and cationization agent, respectively. The MALDI samples were prepared by making stock solutions in THF of the matrix (15.0 g L^{-1}), polymer analyte (5.0 g L^{-1}), and cationization agent (2.0 g L^{-1}). The stock solutions were mixed in a 5/1/1 volume ratio of matrix/analyte/cation and deposited onto a MALDI target plate. The mass spectrometer data was processed by calibrating using five peaks of 5 kg mol^{-1} polystyrene standard. For absolute molecular weight, triple detection SEC was performed using two mixed-bed columns (Agilent PL gel Mixed-E, 3.0 μm; 300.0 × 7.5 mm) and a Viscotek TDA 302 detector. The temperature of the columns was maintained at 40 °C using a column oven. The THF elution was delivered by a Bischoff HPLC compact pump (Shimadzu LC-20 AD) at a flow rate of 0.6 mL min^{-1}. DSC analyses were performed using a TA Instruments Q100 device. The DSC instrument was operated at 10 °C min^{-1} heating rate under a nitrogen atmosphere. Heating and cooling temperature range was from 40 to 150 °C (1st and 2nd cycles: heat up to 150 °C, cool to 40 °C at a rate of 10 °C min^{-1}) under a nitrogen atmosphere. The T_g values were determined from 2nd heating run.

Synthesis

2-(Prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (THP ether).[1] A solution of 3,4-dihydro-2*H*-pyran (19.5 mL, 215.1 mmol) and *p*-TsOH (0.02 g, 0.1 mmol) in CH_2Cl_2 (10.0 mL) was stirred at room temperature for 10 min. Propargyl alcohol (11.5 mL, 195.4 mmol) was drop-wised in this solution and stirred for 40 min. The reaction was terminated using sodium bicarbonate (1.2 g, 14.6 mmol). This solution was filtered and evaporated under reduced pressure to obtain the desired product (24.5 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (t, J = 3.2 Hz, 1H), 4.28 (q, J = 13.5 Hz, 2H), 3.84 (t, J = 15.8 Hz, 1H), 3.58-3.52 (m, 1H), 2.42 (t, J = 2.3 Hz, 1H), 1.89-1.71 (m, 2m, 2H), 1.65-1.54 (m, 4H).



Scheme S1. Synthesis of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (THP ether).

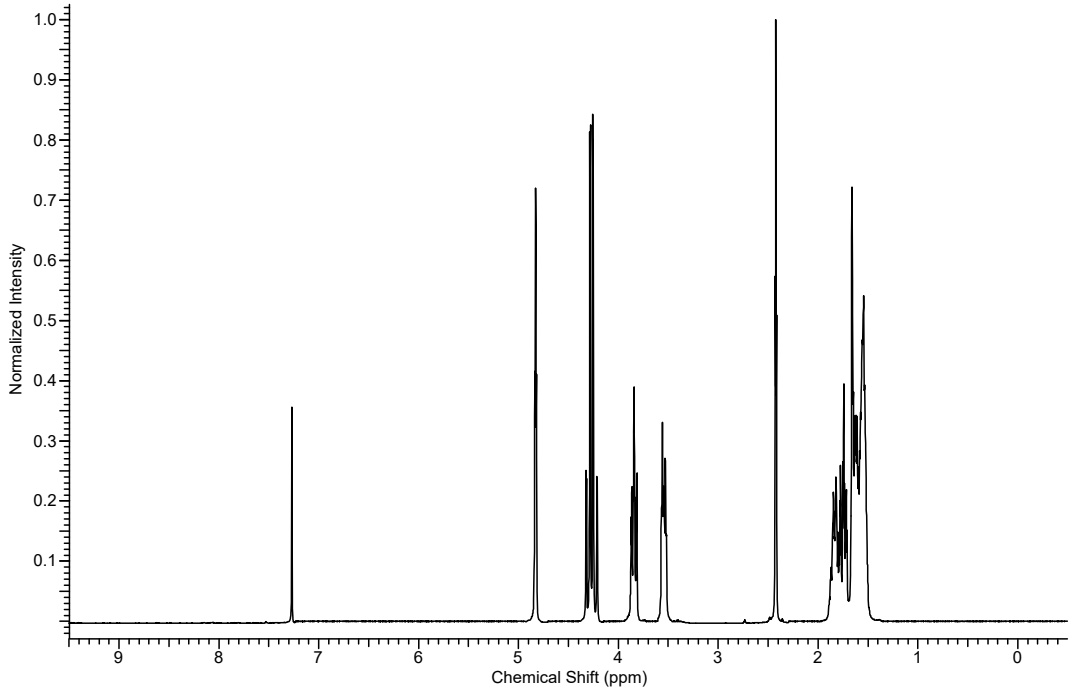
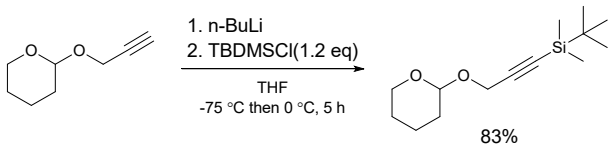


Fig. S1. ^{1}H NMR of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (THP ether).

***tert*-Butyldimethyl(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)silane.**[2] A solution of THP ether (10.0 g, 71.0 mmol) in THF (200.0 mL) was stirred for 10 min at -78 °C. To the solution was added dropwise *n*-BuLi (33.0 mL, 0.082 mmol). After stirred for 15 min, a solution of TBDMSCl (13.0 g, 86.3 mmol) in THF (100.0 mL) was drop-wised to the solution for 20 min at -78 °C. The resulting solution was warmed to 0 °C and stirred for 5 h. The reaction was terminated using saturated aqueous NH_4Cl solution. The reaction mixture was extracted three times using brine and diethyl ether. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to obtain the desired product as a colorless liquid (15.5 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (t, J = 3.4 Hz, 1H), 4.28 (s, 2H), 3.88 (t, J = 10.1 Hz, 1H), 3.55-3.52 (m, 1H), 1.86-1.53 (m, 6H), 0.94 (s, 9H), 0.12 (s, 6H).



Scheme S2. Synthesis of *tert*-butyldimethyl(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)silane.

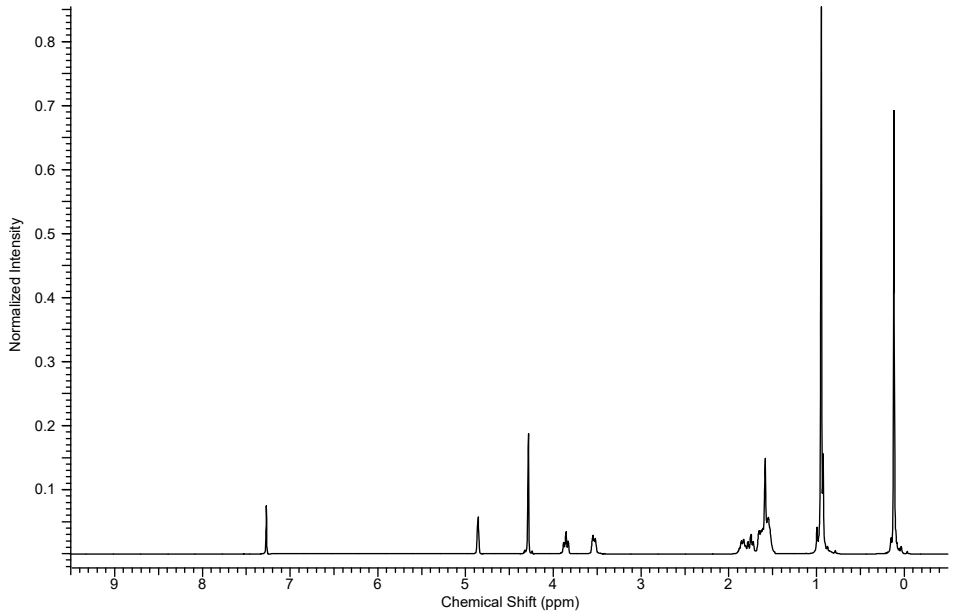
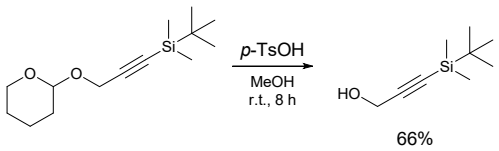


Fig. S2. ^{1}H NMR of *tert*-butyldimethyl(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)silane.

3-(*tert*-Butyldimethylsilyl)prop-2-yn-1-ol. A solution of *tert*-butyldimethyl (3-(tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)silane (36.0 g, 141.5 mmol) and *p*-TsOH (4.0 g, 21.1 mmol) in methanol (250.0 mL) was stirred at room temperature for 8 h. The reaction was terminated using saturated aqueous $NaHCO_3$ solution. The reaction mixture was evaporated under reduced pressure to remove methanol. The resulting solution was extracted three times using H_2O and CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to obtain the desired product (16.0 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (d, J = 5.9 Hz, 2H), 1.62 (t, J = 6.4 Hz, 1H), 0.94 (s, 9H), 0.12 (s, 6H).



Scheme S3. Synthesis of 3-(*tert*-butyldimethylsilyl)prop-2-yn-1-ol.

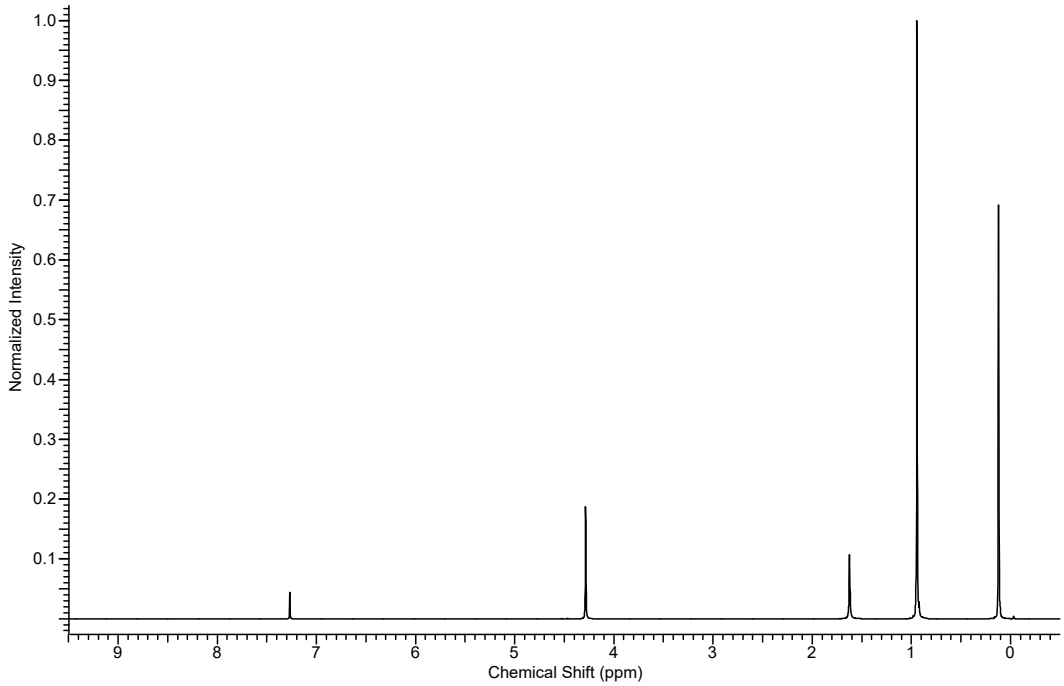
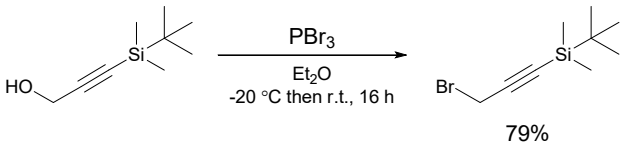


Fig. S3. ^{1}H NMR of 3-(*tert*-butyldimethylsilyl)prop-2-yn-1-ol.

(3-Bromoprop-1-yn-1-yl)(*tert*-butyl)dimethylsilane. A solution of 3-(*tert*-butyldimethylsily l)prop-2-yn-1-ol (0.2 g, 1.2 mmol) in Et_2O (20.0 mL) was stirred at -20 °C for 10 min. Phosphorus tribromide (13.3 g, 48.9 mmol) was added to this solution and stirred at room temperature for 16 h. The reaction was quenched with distilled water. The reaction mixture was extracted three times using brine and Et_2O. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to obtain the desired product as a colorless liquid (15.0 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 2H), 0.95 (s, 9H), 0.12 (s,6H).



Scheme S4. Synthesis of (3-bromoprop-1-yn-1-yl)(*tert*-butyl)dimethylsilane.

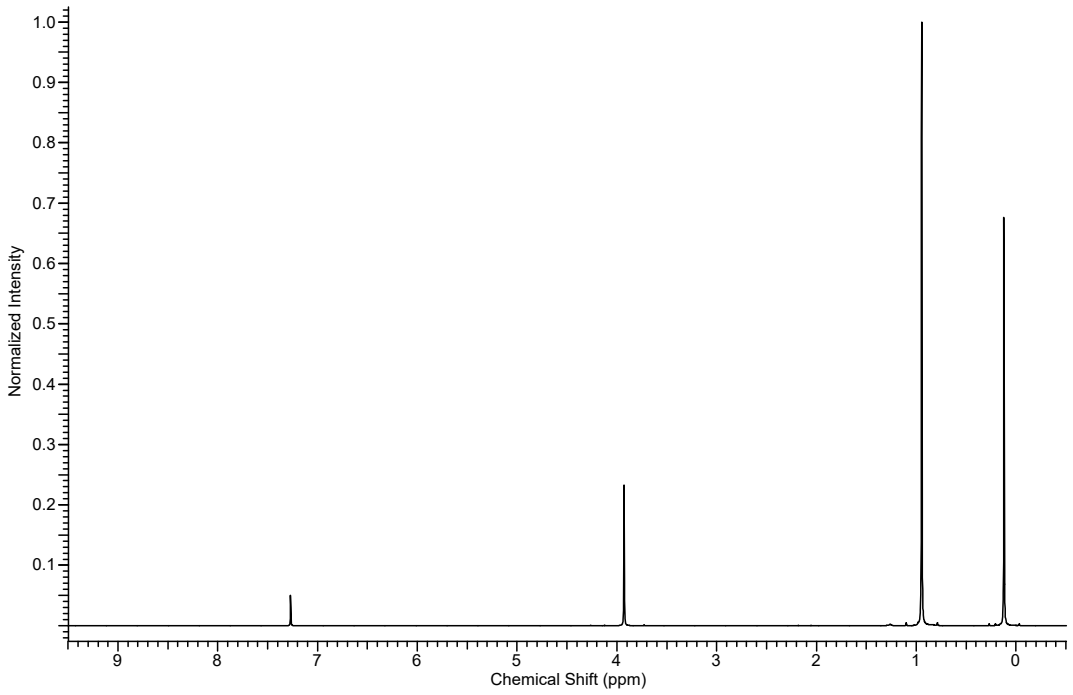
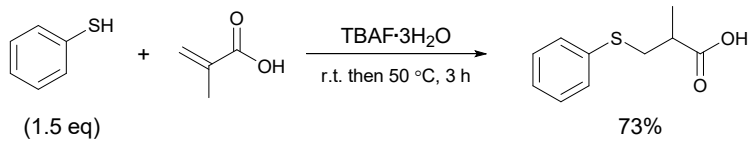


Fig. S4. ^{1}H NMR of (3-bromoprop-1-yn-1-yl)(*tert*-butyl)dimethylsilane.

2-Methyl-3-(phenylthio)propanoic acid.[3] To the solution of thiophenol (10.8 mL, 100.6 mmol) and methacrylic acid (6.0 mL, 68.2 mmol) was added TBAF·$3H_2O$ (2.8 g, 9.0 mmol) at room temperature and the solution was warmed to 50 °C and stirred for 3 h. The reaction mixture was directly separated by silica gel column chromatography (hexane/EtOAc = 3/1) to obtain the desired product (10.0 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 3.30 (dd, J = 13.1, 7.1 Hz, 1H), 2.94 (dd, J = 13.3, 6.9 Hz, 1H), 2.73 (q, J = 7.0 Hz, 1H), 1.32 (d, J = 7.3 Hz, 3H).



Scheme S5. Synthesis of 2-methyl-3-(phenylthio)propanoic acid.

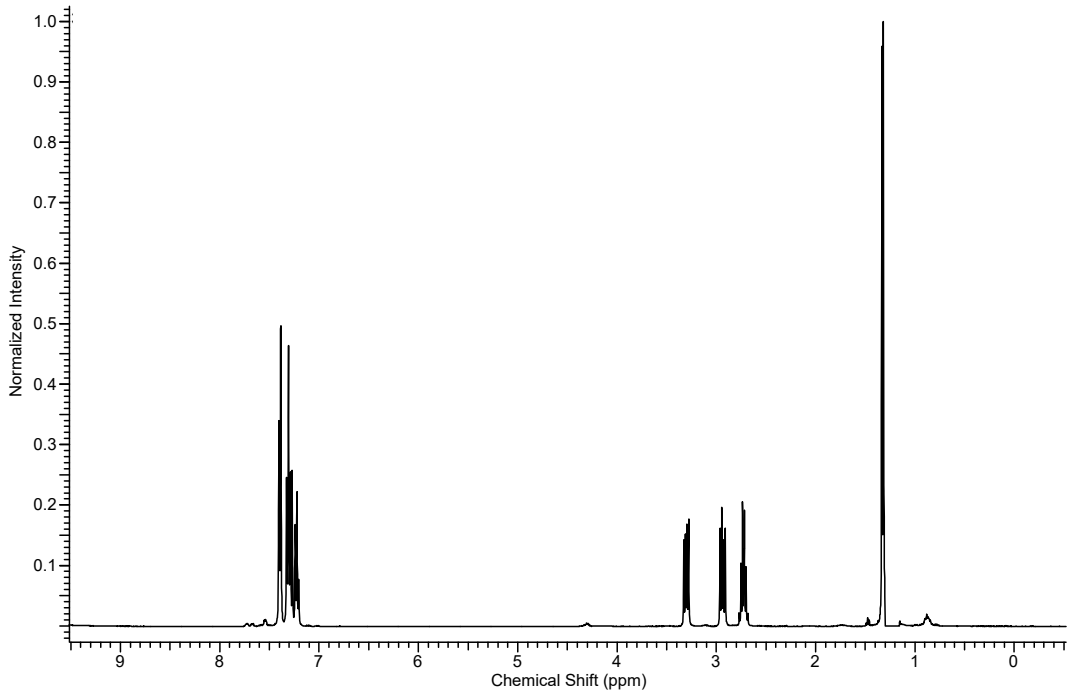
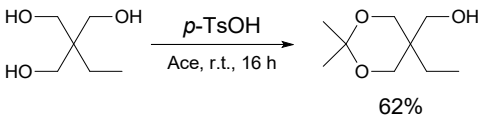


Fig. S5. ^{1}H NMR of 2-methyl-3-(phenylthio)propanoic acid.

(5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol. [4] To a solution of 1,1,1-tris(hydroxymethyl)

propane (20.0 g, 149.1 mmol) in acetone (140.0 mL) was stirred *p*-TsOH (0.3 g, 1.5 mmol) at room temperature. After the solution was stirred for 16 h, K_2CO_3 (0.2 g, 1.5 mmol) was added and stirred for 1 hr to terminate the reaction. Acetone was evaporated under reduced pressure and extracted three times with EtOAc. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to obtain the desired product as a colorless liquid (16.0 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2H), 3.67 (q, J = 11.7 Hz, 4H), 1.43 (d, J = 14.6 Hz, 6H), 1.30 (q, J = 7.8 Hz, 2H), 0.85 (t, J = 6.0 Hz, 3H).



Scheme S6. Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol.

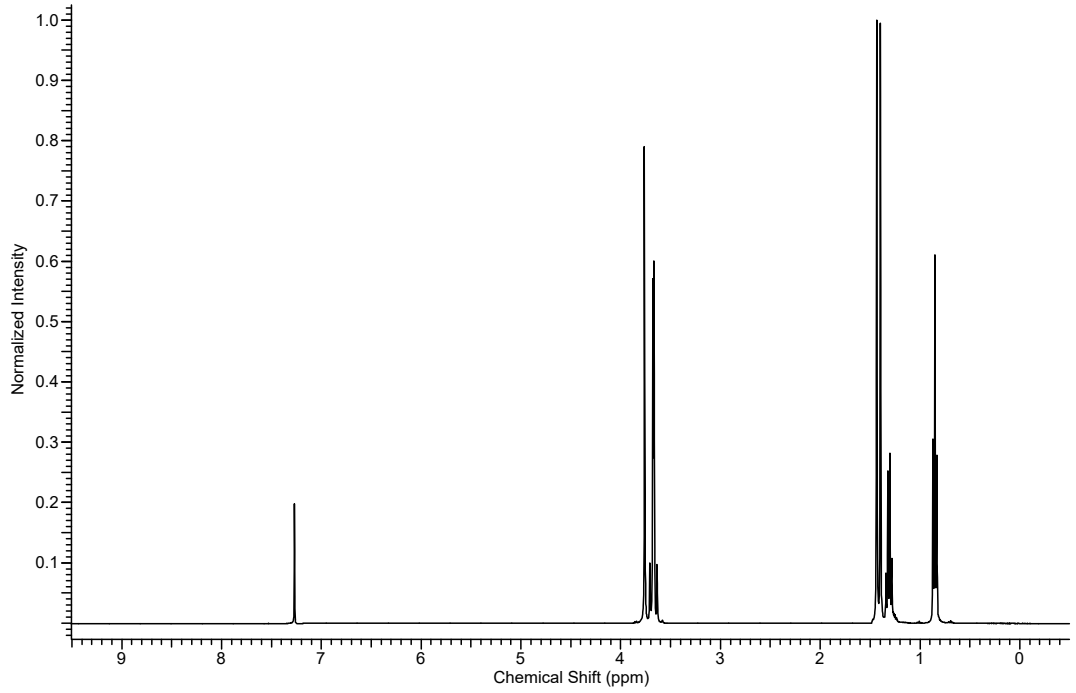
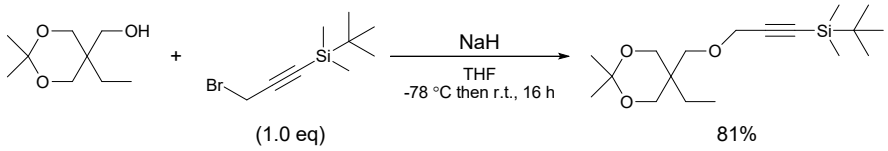


Fig. S6. ^{1}H NMR of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol.

***tert*-Butyl(3-((5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methoxy)prop-1-yn-1-yl)dimethylsilane.** A solution of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol (11.2 g, 64.3 mmol) in THF (180.0 mL) was stirred at 0 °C for 10 min. NaH (1.7 g, 64.3 mmol) was slowly added to the solution at 0 °C and stirred for 2 h. After the resulting solution was cooled to -78 °C, (3-bromoprop-1-yn-1-yl)(*tert*-butyl)dimethylsilane (15.0 g, 64.3 mmol) was drop-wised. The resulting solution was warmed to room temperature and stirred for 18 h. And then, THF was evaporated under reduced pressure. The residue was separated by silica gel column chromatography (hexane/EtOAc = 8/1) to obtain the desired product as a brown oily liquid (16.3 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 2H), 3.62 (q, J = 17.8 Hz, 4H), 3.48 (s, 2H), 3.17 (s, 2H), 1.30 (q, J = 7.5 Hz, 2H), 0.90 (s, 9H), 0.82 (t, J = 7.5 Hz, 3H), 0.08 (s, 6H).



Scheme S7. Synthesis of *tert*-butyl(3-((5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methoxy)prop-1-yn-1-yl)dimethylsilane.

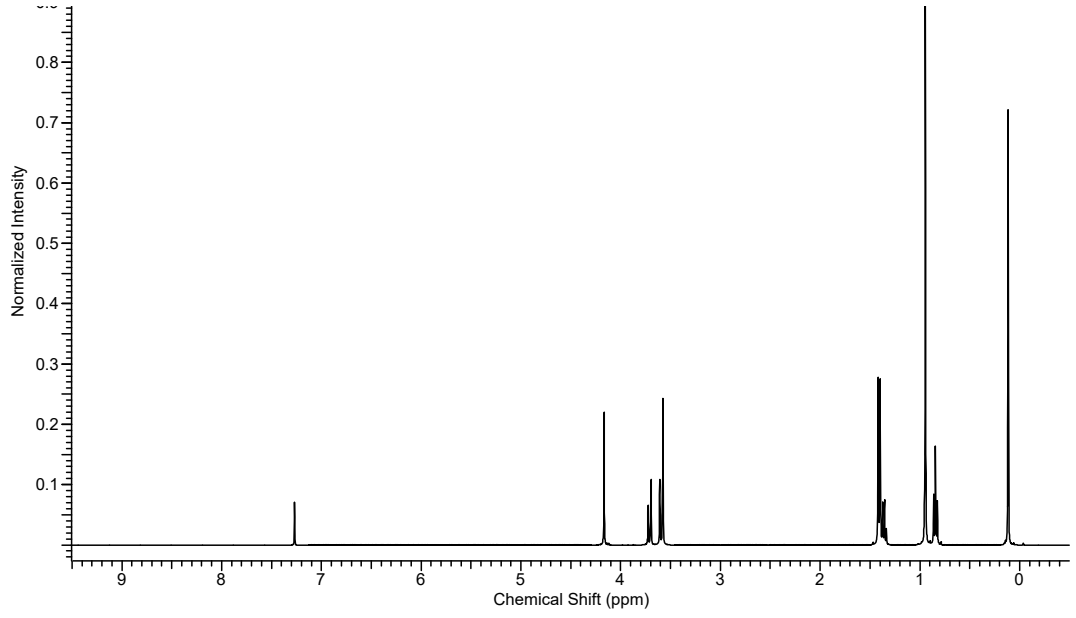
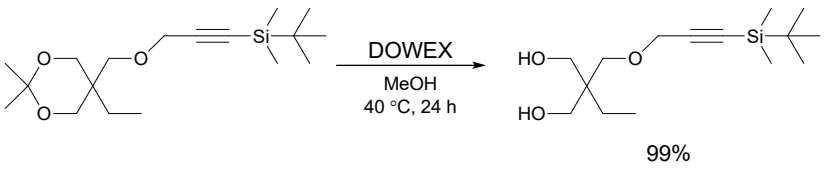


Fig. S7. ^{1}H NMR of *tert*-butyl(3-((5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methoxy)prop-1-yn-1-yl)dimethylsilane.

2-(((3-(*tert*-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-ethylpropane-1,3-diol. To a solution of *tert*-butyl (3-(5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyloxy)prop-1-yn-1-yl) dimethylsilane (6.0 g, 18.4 mmol) in methanol (35.0 mL) was added DOWEX (3.5 g).[5] After the solution was stirred at 40 °C for 24 h, DOWEX was removed by filtration under reduced pressure to obtain the desired product as a colorless liquid (5.9 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 2H), 3.62 (q, J = 17.8 Hz, 4H), 3.48 (s, 2H), 3.17 (s, 2H), 1.30 (q, J = 7.5 Hz, 2H), 0.90 (s, 9H), 0.82 (t, J = 7.5 Hz, 3H), 0.08 (s, 6H).



Scheme S8. Synthesis of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-ethylpropane-1,3-diol.

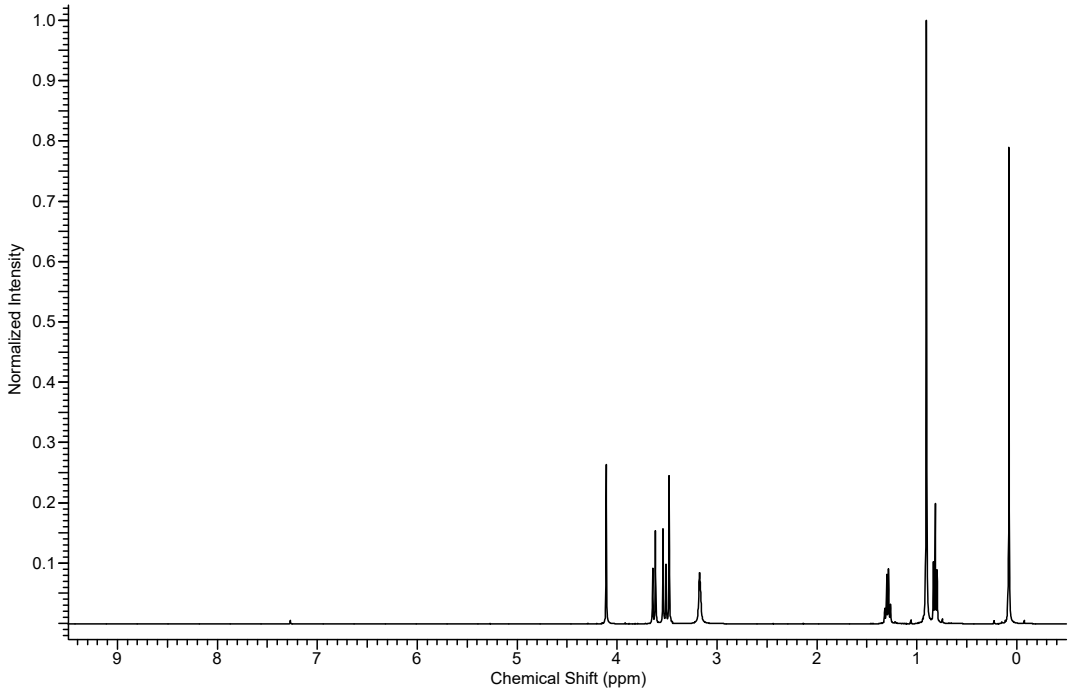
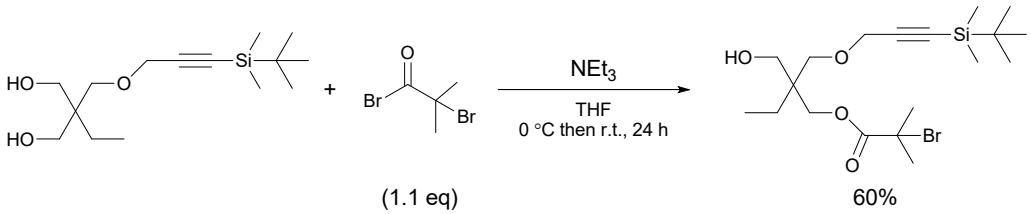


Fig. S8. ^{1}H NMR of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-ethylpropane-1,3-diol.

2-(((3-(*tert*-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-(hydroxymethyl)butyl 2-bromo-2-methylpropanoate. A solution of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-ethylpropane-1,3-diol (5.2 g, 18.2 mmol) and TEA (3.16 mL, 22.7 mmol) in THF (50.0 mL) was stirred at 0 °C for 10 min. To the solution, bromoisobutyryl bromide (2.5 mL, 19.9 mmol) was drop-wised and stirred at room temperature for 24 h. The reaction mixture was filtered to remove the generated salt and evaporated under reduced pressure to remove THF. The residue was separated by silica gel column chromatography (hexane/EtOAc = 5/1) to obtain the desired product as a colorless oily liquid (4.5 g, 60%), colorless oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, J = 7.8 Hz, 4H), 3.53 (d, J = 10.9 Hz, 4H), 2.39 (s, 1H), 1.92 (s, 6H), 1.43 (q, J = 7.3 Hz, 2H), 0.93 (s, 9H), 0.88 (t, J = 7.5 Hz, 3H), 0.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 101.8, 90.1, 71.4, 65.9, 64.8, 60.3, 59.4, 55.7, 42.8, 30.7, 25.9, 22.7, 16.4, 7.4, -4.8.



Scheme S9. Synthesis of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-(hydroxymethyl)butyl 2-bromo-2-methylpropanoate.

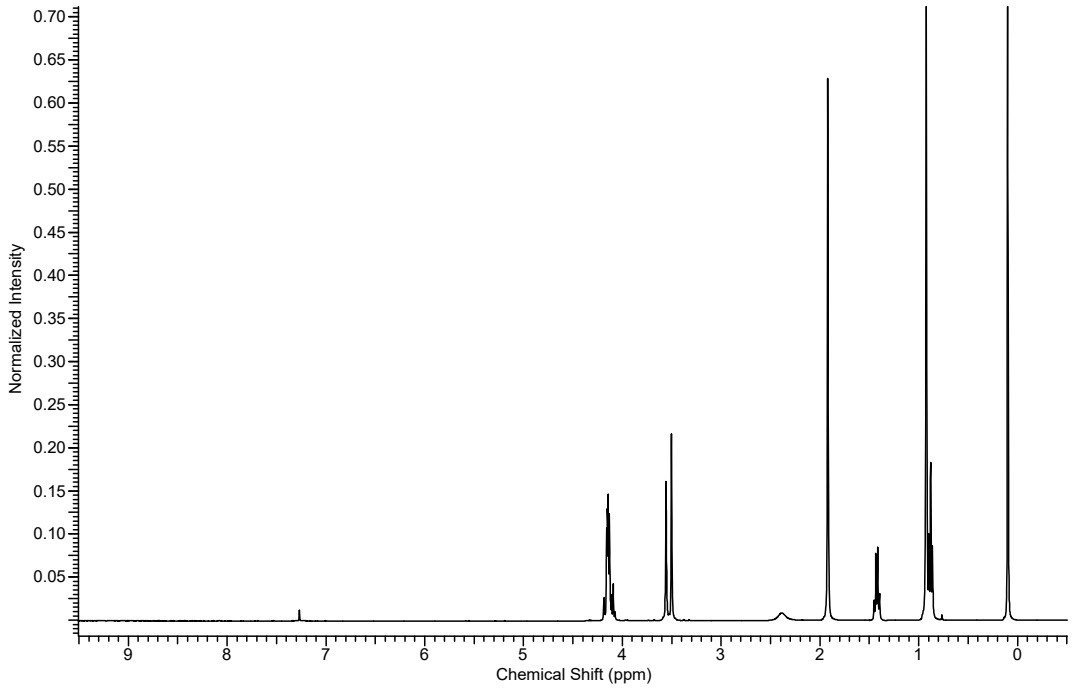


Fig. S9. ^{1}H NMR of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-(hydroxymethyl)butyl 2-bromo-2-methylpropanoate.

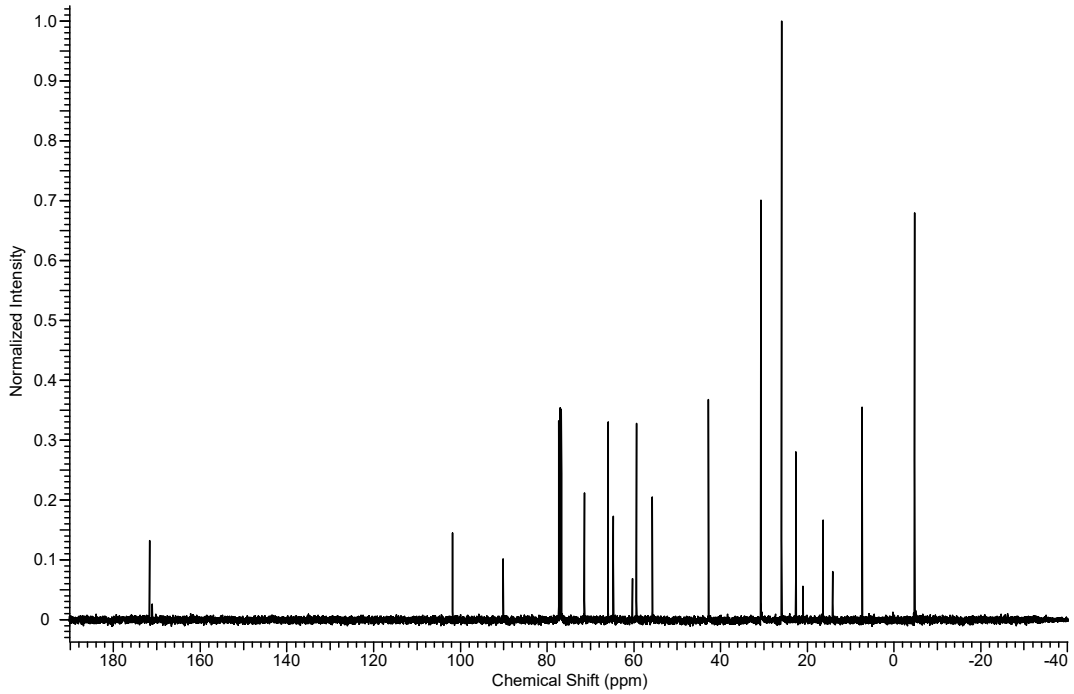
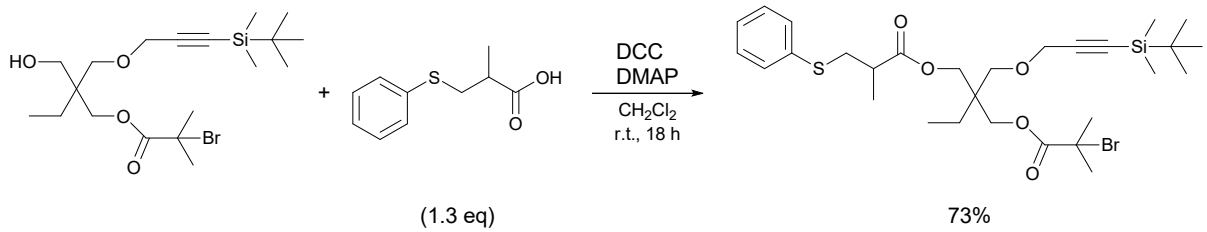


Fig. S10. ^{13}C NMR of 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-(hydroxymethyl)butyl 2-bromo-2-methylpropanoate.

2-(((2-Bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylthio)propanoate. A solution of 2-methyl-3-(phenylthio)propanoic acid (2.7 g, 13.6 mmol), 2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)-2-(hydroxymethyl)butyl 2-bromo-2-methylpropanoate (4.5 g, 10.7 mmol), and DMAP (1.1 g, 8.6 mmol) in CH_2Cl_2 (70.0 mL) was stirred at room temperature for 20 min. To the solution was added a solution of DCC (4.0 g, 19.3 mmol) in CH_2Cl_2 (30.0 mL), and stirred at room temperature for 18 h. The reaction mixture was extracted three times using CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was separated by silica gel column chromatography (hexane/EtOAc = 5/1) to obtain the desired product as a colorless oil (4.8 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 4.13 (s, 2H), 4.12 (d, *J* = 16.0 Hz, 4H), 3.45 (s, 2H), 3.25 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.95 (dd, *J* = 17.3, 6.9 Hz, 1H), 2.71 (q, *J* = 6.9 Hz, 1H), 1.93 (s, 6H), 1.52 (q, *J* = 7.3 Hz, 2H), 1.28 (d, *J* = 7.3 Hz, 4H), 0.94 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 171.6, 136.0, 130.2, 129.3, 126.8, 102.2, 90.2, 69.5, 66.1, 64.7, 59.7, 56.0, 42.0, 40.1, 37.6, 31.0, 26.3, 23.2, 17.1, 16.7, 7.7, -4.4.



Scheme S10. Synthesis of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylthio)propanoate.

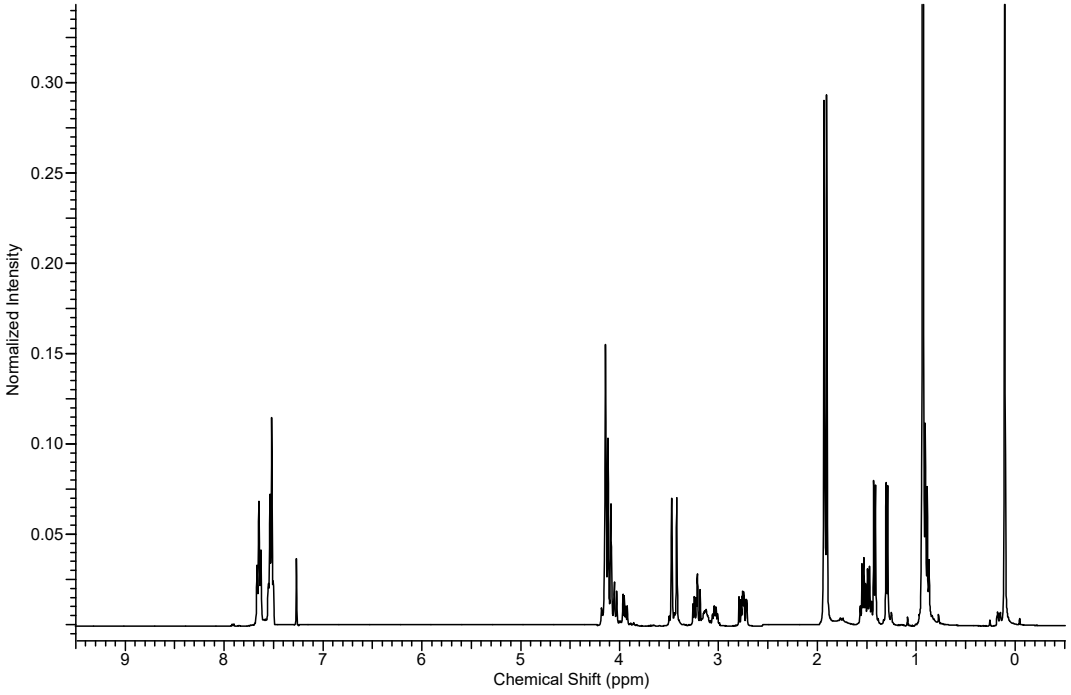


Fig. S11. ^{1}H NMR of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylthio)propanoate.

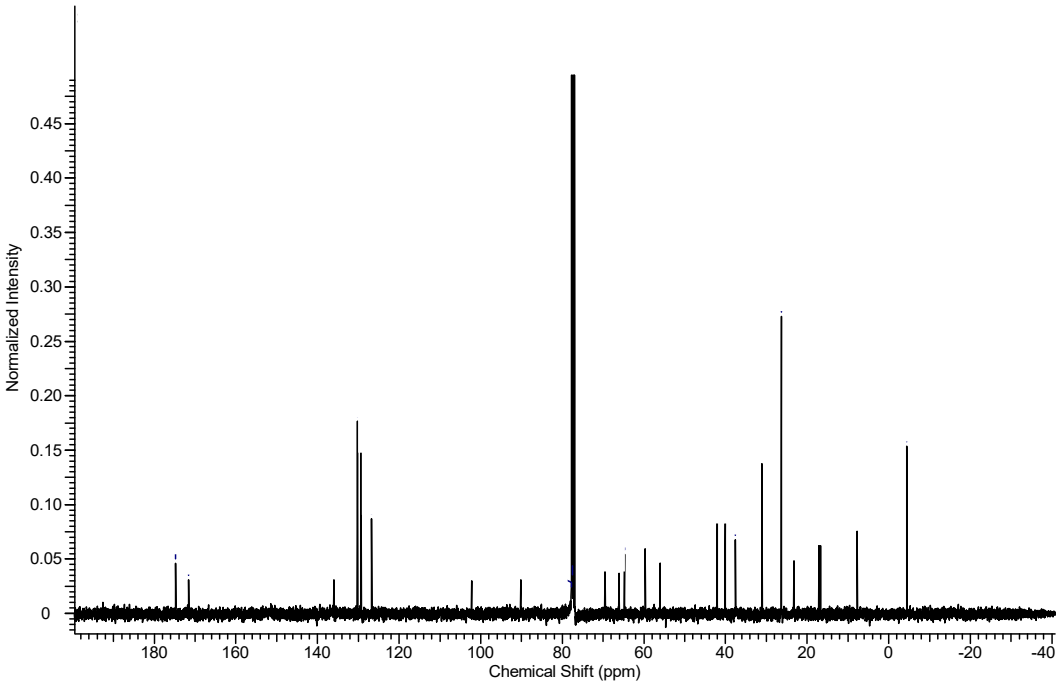
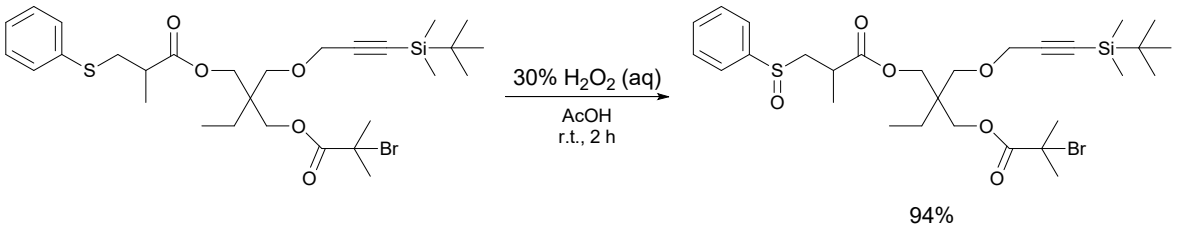


Fig. S12. ^{13}C NMR of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(tert-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylthio)propanoate.

2-(((2-Bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylsulfinyl)propanoate (trifunctional ATRP initiator). A solution of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylthio)propanoate (2.5 g, 40.7 mmol) and acetic acid (25.0 mL) was stirred at room temperature for 10 min. To this solution, hydrogen peroxide (1.7 mL, 16.3 mmol) was drop-wised and stirred at room temperature for 2 h.[6] The reaction mixture was extracted three times using CH_2Cl_2 and water. The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was separated by silica gel column chromatography (hexane/EtOAc = 5/1) to obtain the desired product as a colorless liquid (2.4 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 8.0 Hz, 4H), 7.52 (q, *J* = 6.9 Hz, 6H), 4.18-4.05 (m, 6H), 3.96 (q, *J* = 5.6 Hz, 1H), 3.45 (d, *J* = 10.0 Hz, 2H), 3.26-3.18 (m, 1H), 3.16-3.00 (m, 1H), 2.79-2.71 (m, 1H), 1.93 (d, *J* = 10.1 Hz, 6H), 1.58-1.46 (m, 2H), 1.43 (d, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 1H), 0.94 (s, 9H), 0.90 (t, *J* = 7.6 Hz, 3H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 171.2, 131.2, 129.3, 124.0, 123.8, 69.2, 65.7, 64.9, 61.2, 59.3, 55.7, 41.7, 34.6, 34.1, 30.7, 25.9, 22.9, 18.0, 16.9, 16.4, 7.3, -4.7.



Scheme S11. Synthesis of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(*tert*-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylsulfinyl)propanoate (trifunctional ATRP initiator).

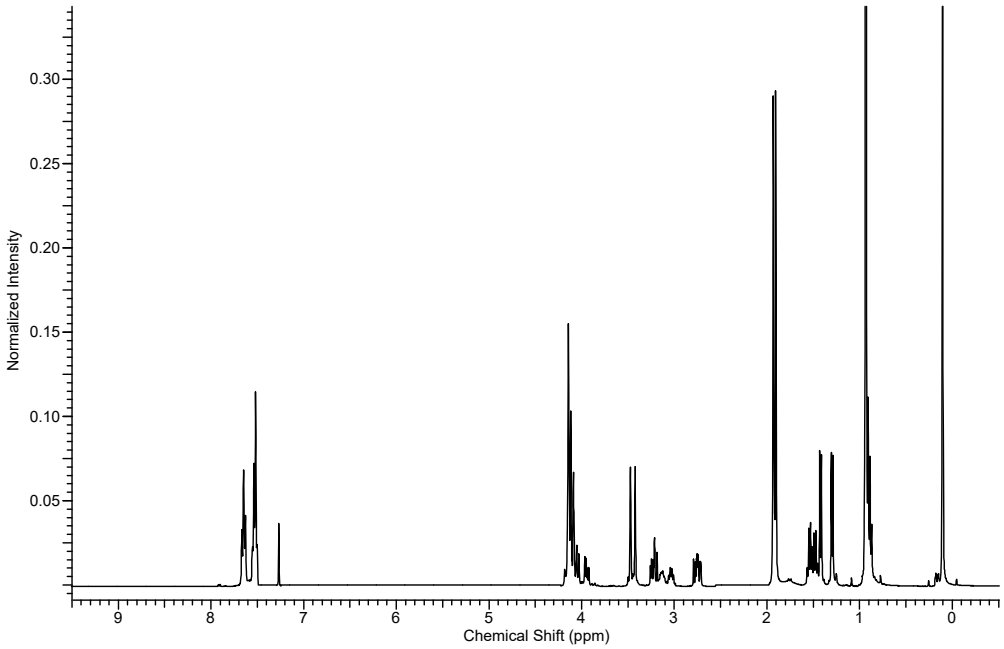


Fig. S13. ^{1}H NMR of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(tert-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylsulfinyl)propanoate (trifunctional ATRP initiator).

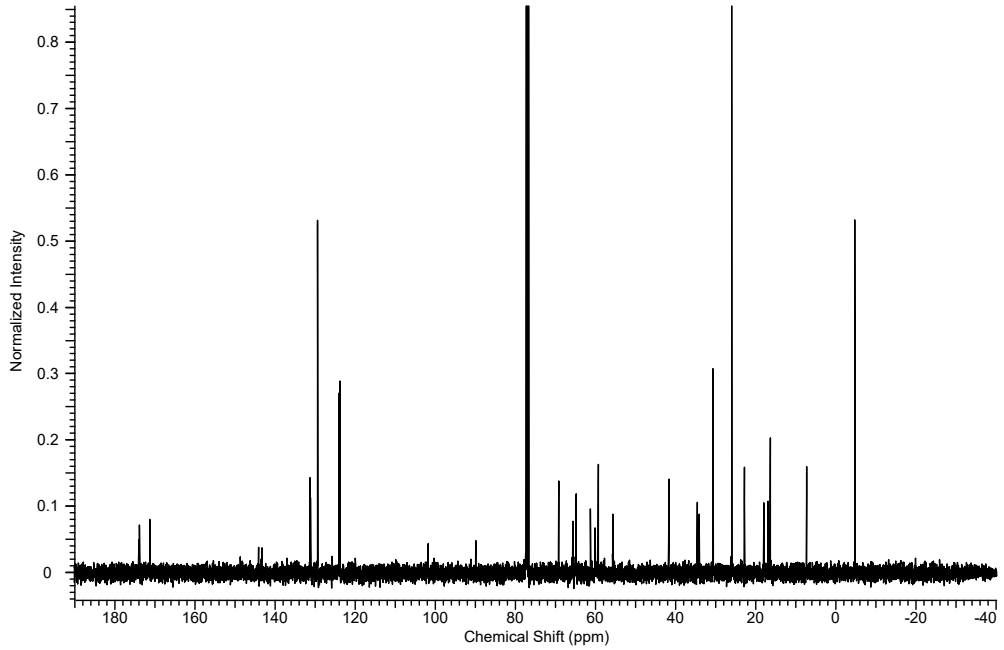


Fig. S14. ^{13}C NMR of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-(((3-(tert-butyldimethylsilyl)prop-2-yn-1-yl)oxy)methyl)butyl 2-methyl-3-(phenylsulfinyl)propanoate

(trifunctional ATRP initiator).

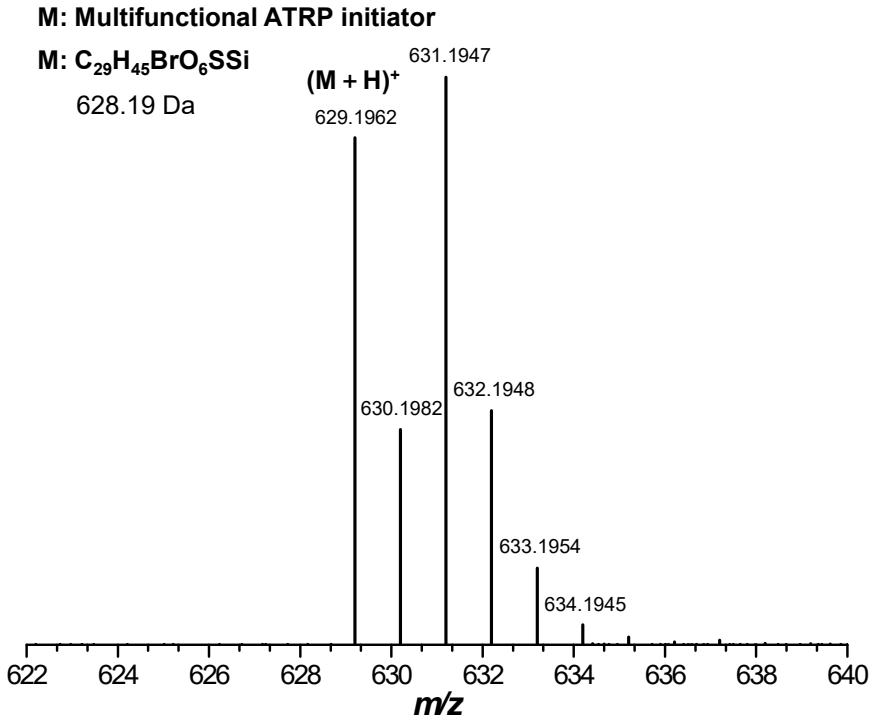


Fig. S15. Characterization of multifunctional ATRP initiator using electrospray ionization quadrupole time-of-flight mass spectroscopy.

Synthesis of trifunctional linear polystyrene (PS-Br). $CuBr_2$ (8.9 mg 0.039 mmol) and a stir bar were placed in a dried 100 mL Schlenk flask. The flask was sealed with a glass stopper, then evacuated and backfilled with N_2 three times. A mixture of trifunctional ATRP initiator (500.0 mg, 0.79 mmol), styrene (27.3 mL, 238.0 mmol), tin(II) 2-ehtylhexanoate (0.3 mL, 0.95 mmol), and Me_6TREN (37.0 μL, 0.14 mmol) in DMF (1.4 mL, internal standard) was N_2-bubbled for 30 min. The deoxygenated solution was added to the flask via a N_2-purged syringe. Then, the flask was placed in 35 °C set oil bath. After 40 h, the polymerization was quenched by adding THF, followed by passed through a neutral alumina column. After condensing the solution, the product was isolated via a precipitation into methanol, followed by filtration and

dried in vacuo.

Azidation of trifunctional linear polystyrene (PS-N_3). NaN_3 (141.0 mg, 2.2 mmol) was added into the 30 mL flask filled with polymer solution of PS-Br (2.0 g, 0.44 mmol) in DMF (8.1 mL), followed by N_2-bubbling for 30 min. Then, the flask was placed in 40 °C set oil bath for 18 h. The product was isolated via a precipitation into methanol, followed by filtration and dried in vacuo. White powder was obtained (1.9 g, yield: 95%).

Deprotection of silyl and sulfoxide group (cyclic precursor). PS-N_3 (1.8 g, 0.39 mmol) and TBAF solution (50.0 mL) were placed in a 200 mL flask with a stir bar. Then, the flask was placed in a 40 °C set oil bath. After 12 h, the mixture was condensed via a rotary evaporator and precipitated into methanol. After filtration and dried in vacuo, white powder was obtained (1.7 g, yield: 93%) and stored at 4 °C.

Cyclization of the precursor (cMM). CuBr (4.1 g, 2.8 mmol) and Cu^0 wire ($l \times d$ = 30.0 cm × 1.0 mm) were added to a 3 L flask with a stir bar and sealed with a glass stopper. The flask was charged with N_2. The solution of THF (1.5 L) and PMDETA (4.9 mL, 28.3 mmol) was N_2-bubbled for 1 hr for deoxygenation, followed by transferring to the flask via a N_2-purged cannula tube. The cyclic precursor (1.3 g, 0.28 mmol) in THF (20.0 mL) solution was prepared and N_2-bubbled for 20 min. Using an auto syringe pump, the precursor solution was injected into a flask at the rate of 2.0 mL h^{-1} at 40 °C. After a complete injection, the reaction was stirred for 5 h. The condensed solution via a rotary evaporator was precipitated into methanol and isolated (white powder, 0.85 g, yield: 63%).

Grafting through copolymerization (PMMA-*g*-P(cMM)) via ARGET. Stock solutions of $CuBr_2$ (0.26 M) were prepared by adding 57.3 mg of $CuBr_2$ and Me_6TREN (88.0 mg) in DMF. Inhibitor-removed MMA (0.54 mL, 5.1 mmol) and anisole (0.56 mL) were placed in a 10 mL Schlenk flask. EBiB (0.75 µL, 5.1 µmol) and $CuBr_2$ stock solution (11.5 µL) were added via a micro syringe. The Schlenk flask was deoxygenated via N_2-bubbling for 30 min before introducing $Sn(EH)_2$ (10.3 mg, 8.3 µL) to the flask which was placed in 60 °C set oil bath. The polymerization was stopped after 18 h by exposing the reaction mixture to air.

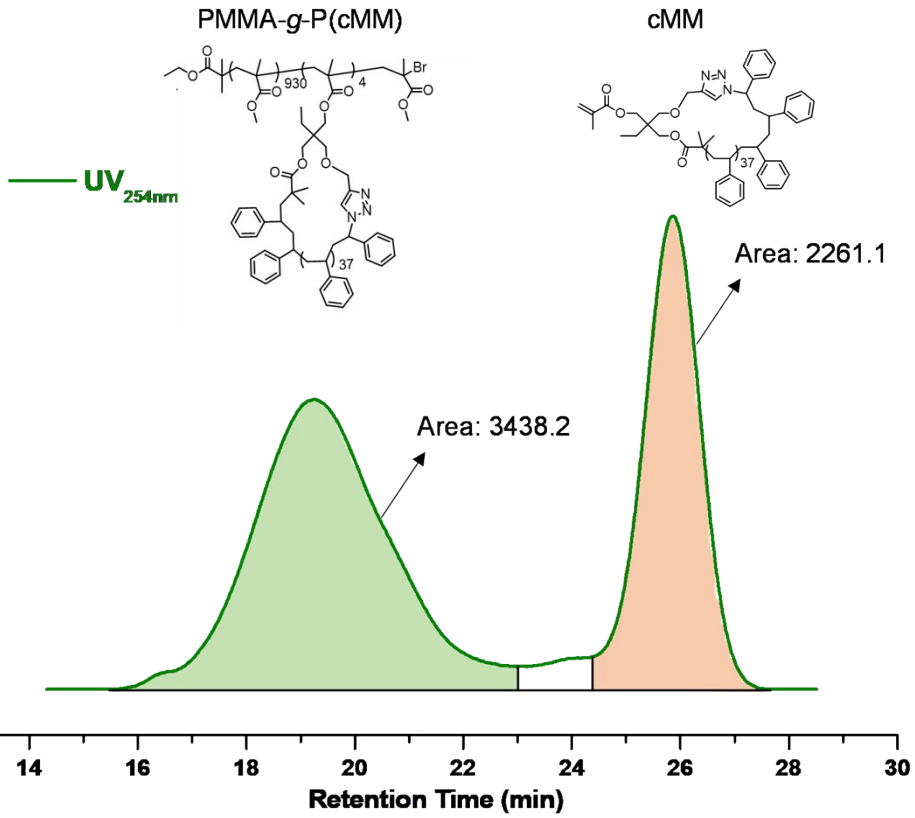


Fig. S16. Conversion calculation via area fraction (area of cMM / (area of PMMA-*g*-P(cMM) and cMM).

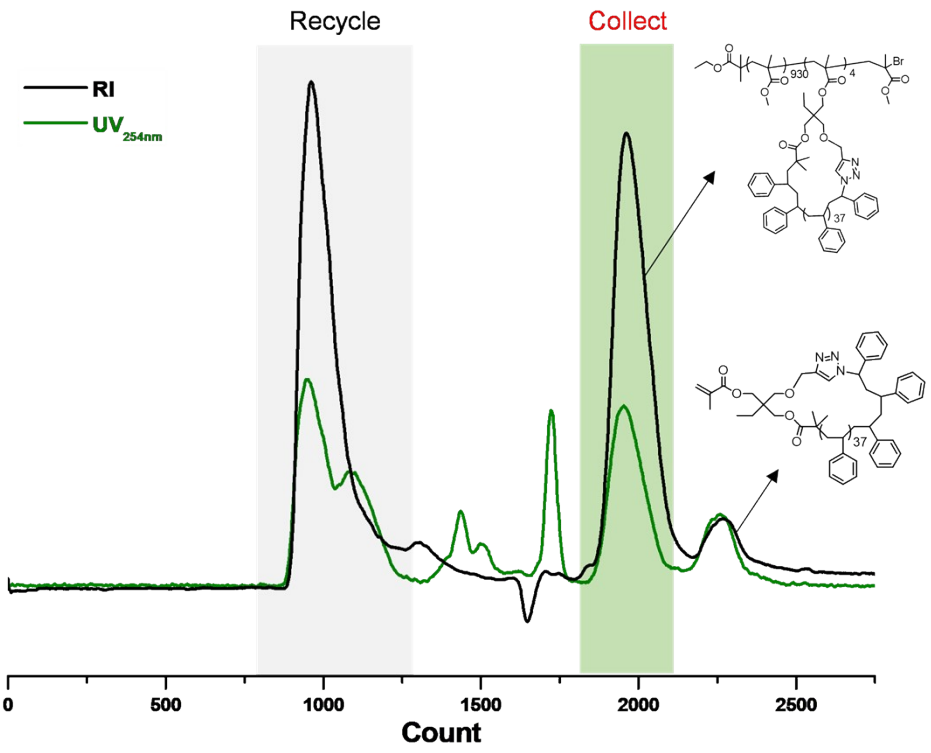


Fig. S17. Purification using preparative SEC to remove the unreacted precursors.

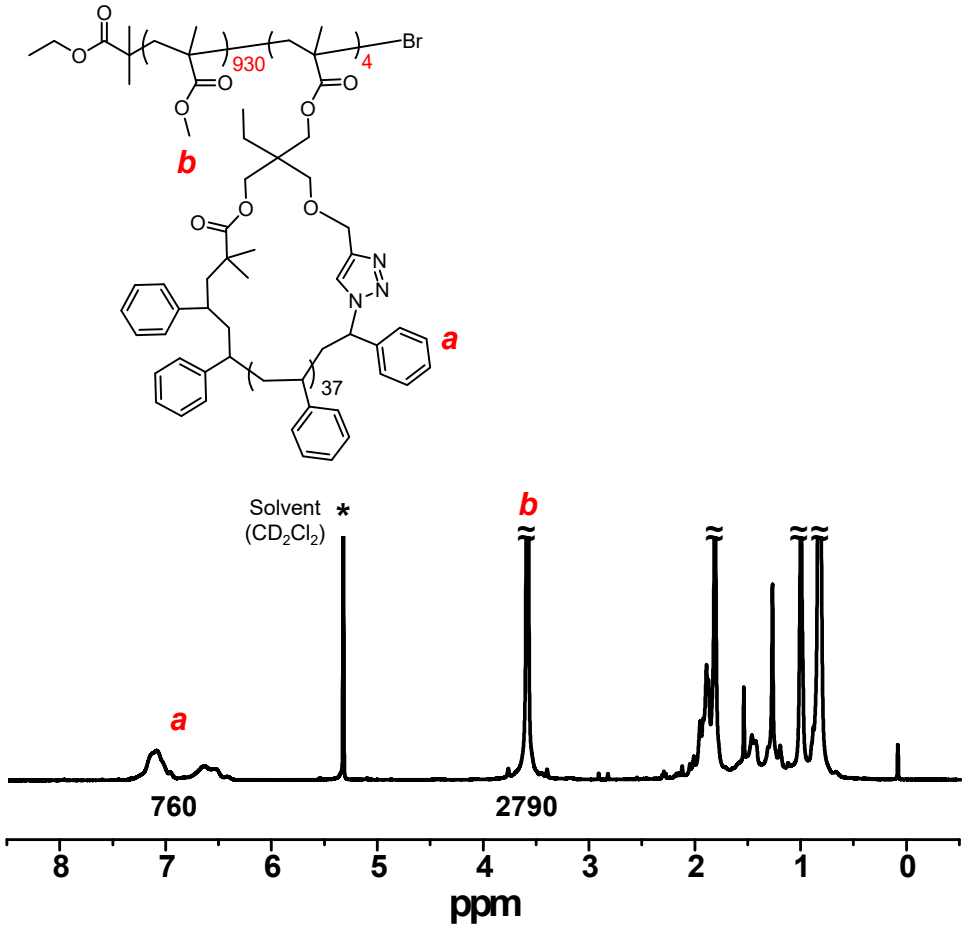


Fig. S18. Structure analysis of PMMA-*g*-P(cMM) using ^{1}H NMR spectroscopy (CD_2Cl_2, 25 °C).

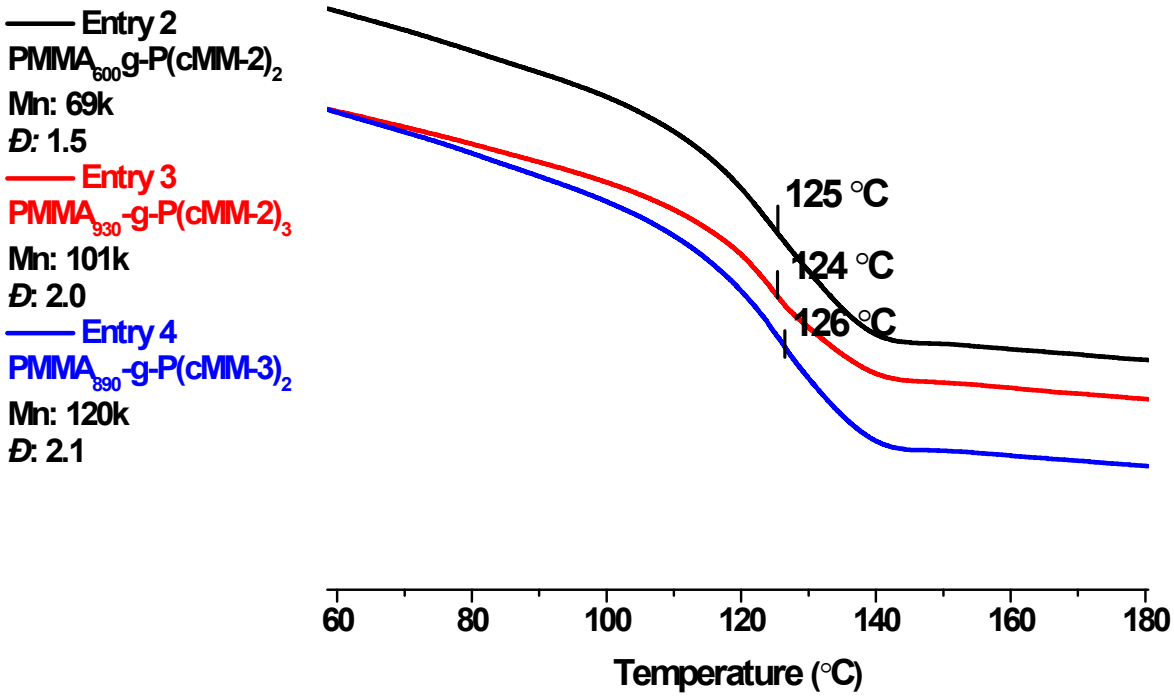


Fig. S19. T_g values of PMMA-*g*-P(cMM) using DSC instrument.

References

1 K. Mikami and A. Yoshida, *Tetradedron*, 2001, **51**, 889–898.

2 M. Schelper, A. de Meijere, *J. Org. Chem.*, 2005, 582–592.

3 S. Gao, C. Tseng, C. H. Tsai and C.-F. Yao, *Tetrahedron*, 2008, **64**, 1955–1961.

4 A. Cornille, M. Blain, R. Auvergne, B. Andrioletti, B. Boutevin and S. Caillol, *Polym. Chem.*, 2017, **8**, 592–604.

5 A. Aravind, M. G. Sankar, B. Varghese and S. Baskaran, *J. Org. Chem.*, 2009, **74**, 2858–2861.

6 H. Golchoubian and F. Hosseinpoor, *Molecules*, 2007, **12**, 304–311.