Supporting Information for:

Scalable Synthesis of Multivalent Macromonomers for ROMP

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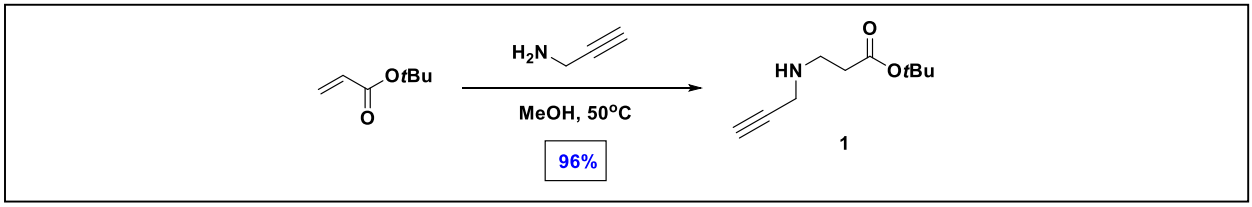
Section A. Materials / General Methods / Instrumentation

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Grubbs 3rd generation bispyridyl catalyst **Ru**,[1] 1st generation macromonomer precursors **G1-PEG**,[2] and **TEG-N$_3$**[3] were prepared according to literature procedures. Liquid chromatography mass spectrometry (LC/MS) was performed on an Agilent 1260 LC system equipped with a Zorbax SB-C18 rapid resolution HT column using a binary solvent system (MeCN and H_2O with 0.1% CH_3COOH). Recycling preparative HPLC was performed on a LaboACE system (Japan Analytical Industry) using a JAIGEL-2.5HR column. Size exclusion chromatography (SEC) analyses were performed on an Agilent 1260 Infinity setup with two Shodex KD-806M columns in tandem and a 0.025 M LiBr DMF mobile phase run at 60 °C. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector. For polystyrene-containing samples, SEC analyses were performed in THF on the same Agilent system calibrated with monodisperse linear polystyrene standards and equipped with a UV diode array detector and a differential refractive index (dRI) detector at a flow rate of 1 mL/min at 35 °C with three columns assembled in tandem: Agilent Technologies PLgel 5μm 10E5A, 10E4A, and 10E3A (all of which are 300 x 7.5 mm in dimension). Column chromatography was carried out on silica gel 60F (EMD Millipore, 0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE III-400 spectrometer, with working frequencies of 400 (^{1}H), and 100 (^{13}C) MHz, or AVANCE-600 spectrometer with working frequencies of 600 (^{1}H), and 151 (^{13}C) MHz. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents: $CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) using an electrospray ionization (ESI) source. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analyses were collected on a Bruker OmniFlex instrument using sinapinic acid as the matrix. For SAXS measurements, dried samples from ROMP reactions were wet with 15-50 μL of THF to form thick, barely dissolved solutions. A small amount of the material was removed with a spatula or pipet tip and used to fill the hole of a circular washer that acted as a sample holder (outer diameter: 24 mm, inner diameter: 2 mm, thickness: 1 mm). Samples were then placed in a vacuum oven, evacuated, and heated to 145 °C for 6 h. The vacuum oven was allowed to cool overnight and then vented to the atmosphere. Transmission SAXS was conducted at the Advanced Photon Source at Argonne National Lab. The sample to detector distance used was 1.9081 m and the wavelength of the beam was 0.886 Å.

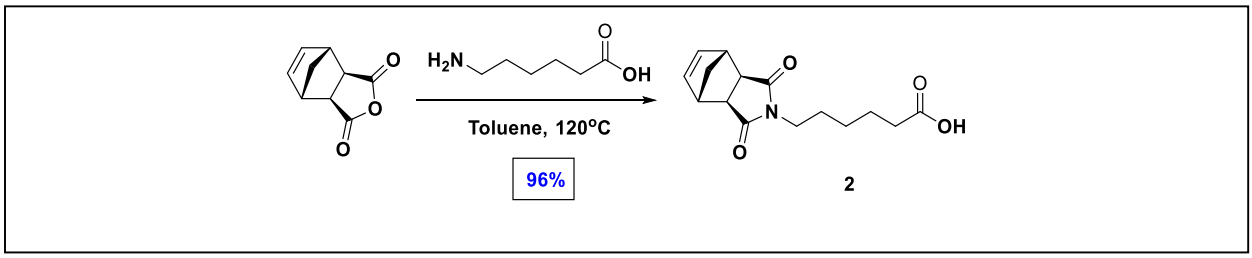
B. Synthetic Protocols

1) Branched macromonomer precursors:



Synthesis of 1. **1** was prepared following a literature procedure with slight modifications.[4] Propargylamine (7.2 mL, 6.2 g, 0.11 mol, 2.2 eq) and *tert*-butyl acrylate (7.6 mL, 6.7 g, 0.052 mol, 1.0 eq) were added to a round-bottom flask (RBF). Methanol (120 mL) was added, and the reaction mixture was stirred for 24 hours at 50 °C. The solution was then concentrated under vaccum, affording **1** as an orange liquid (9.1 g, 96 % yield).

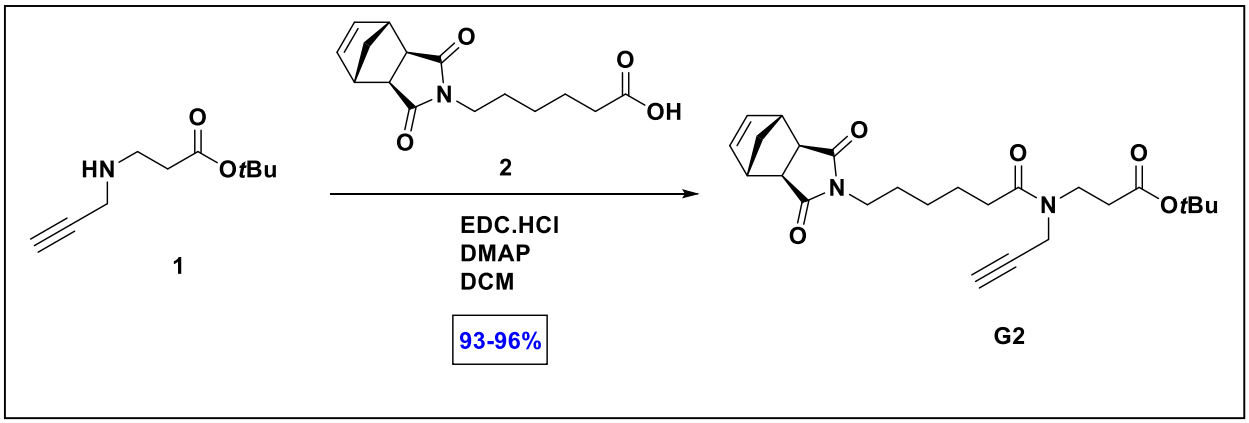
<u>*Large scale synthesis of* ***1***</u>. Propargylamine (43.2 mL, 37.1 g, 0.674 mol, 2.16 eq) and *tert*-butyl acrylate (45.7 mL, 40.0 g, 0.312 mol, 1.00 eq) were added to a RBF. Methanol (720 mL) was added, and the reaction mixture was stirred for 24 hours at 50 °C. The solution was then concentrated under vaccum, affording **1** as an orange liquid (56.1 g, 98 % yield). HRMS-ESI: Calcd for $C_{10}H_{17}NO_2$: *m/z* = 184.1338 $[M + H]^+$; Found: 184.1346 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 3.43 (d, *J* = 2.4 Hz, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.22 (t, *J* = 2.4 Hz, 1H), 2.04 (b, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 172.1, 82.1, 80.8, 71.5, 44.3, 38.3, 35.8, 28.3.



Synthesis of 2. **2** was prepared following a literature procedure with slight modifications.[5] *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (0.50 g, 3.0 mmol, 1.0 eq) and 6-aminohexanoic acid (0.48 g, 3.7 mmol, 1.2 eq) were added to a RBF fitted with a condenser. Toluene (15 mL) was then added, and the solution was stirred overnight at 120 °C. The mixture was then allowed to cool to room temperature, and concentrated under vacuum. DCM was then added, and the solution was

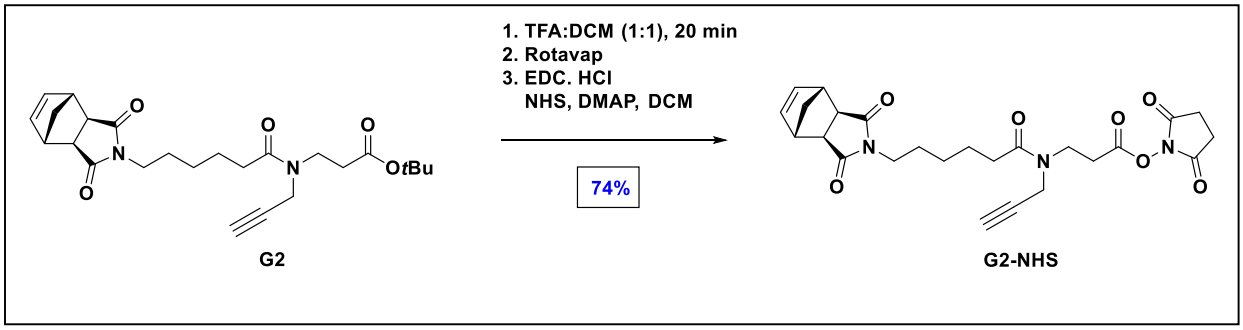
washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording the product as a white solid (0.83 g, 96% yield).

*Large scale synthesis of **2***. *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (75.0 g, 0.456 mol, 1.00 eq) and 6-aminohexanoic acid (71.9 g, 0.548 mol, 1.20 eq) were added to a RBF fitted with a condenser. Toluene (2.25 L) was then added, and the solution was stirred overnight at 120 °C. The mixture was then allowed to cool to room temperature, and concentrated under vacuum. DCM was then added, and the solution was washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording the product as a white solid (121.5 g, 96% yield). HRMS-ESI: Calcd for $C_{15}H_{19}NO^-_4$: *m/z* = 276.1241 [*M* - H]$^-$; Found: 276.1234 [*M* - H]$^-$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 6.28 (t, *J* = 1.8 Hz, 2H), 3.46 (t, *J* = 7.4 Hz, 2H), 3.27 (t, *J* = 1.6 Hz, 2H), 2.67 (d, *J* = 1.2 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.69-1.61 (m, 2H), 1.59-1.53 (m, 2H), 1.52-1.49 (dt, *J* = 9.6, 1.6, 1H), 1.38-1.31 (m, 2H), 1.25-1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 179.2, 178.2, 137.9, 47.9, 45.3, 42.8, 38.5, 33.8, 27.5, 26.5, 24.3.



Synthesis of G2. Into a RBF, **1** (400 mg, 2.18 mmol, 1.0 eq), **2** (908 mg, 3.27 mmol, 1.5 eq), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl) (628 mg, 3.27 mmol, 1.5 eq), 4-dimethylaminopyridine (DMAP) (133 mg, 1.09 mmol, 0.5 eq), and DCM (90 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (MeOH/DCM) of the crude mixture yielded **G2** as a white solid (899 mg, 93% yield).

*Large scale synthesis of **G2***. Into a RBF, **1** (45.0 g, 0.246 mol, 1.0 eq), **2** (102 g, 0.368 mol, 1.5 eq), EDC·HCl (70.6 g, 0.368 mol, 1.5 eq), DMAP (15.0 mg, 0.123 mol, 0.5 eq), and DCM (4.50 L) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. DCM was then added, and the crude mixture was washed with water and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded **G2** as an off-white solid (94.2 g, 87% yield). Alternatively, pure **G2** (43.0 g, 96% yield, obtained as white crystals) could be readily isolated from the crude reaction following washing, Na_2SO_4 drying, filtration, and concentration under vacuum (as outlined above) via recrystallization from 3:1 MeOH:DCM (300 mL for 45 g of crude **G2**). HRMS-ESI: Calcd for $C_{25}H_{34}N_2O_5$: *m/z* = 443.2540 $[M + H]^+$; Found: 443.2556 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 6.27 (t, *J* = 2.0 Hz, 2H), 4.21 (d, *J* = 2.8 Hz, 1H), 4.09 (d, *J* = 2.4 Hz, 1H), 3.69 (t, *J* = 7.2 Hz, 1H), 3.63 (t, *J* = 6.8 Hz, 1H), 3.45 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 1.8 Hz, 2H), 2.66 (d, *J* = 1.2 Hz, 2H), 2.54 (td, *J* = 7.1, 1.3 Hz, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.28 (t, *J* = 2.4 Hz, 0.5H), 2.19 (t, *J* = 2.6 Hz, 0.5H), 1.69-1.62 (m, 2H), 1.59-1.53 (m, 2H), 1.51-1.49 (dt, *J* = 10.0, 1.6 Hz, 1H), 1.43 (d, *J* = 6.0 Hz, 9H), 1.38-1.30 (m, 2H), 1.22-1.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.1, 172.6, 172.3, 171.4, 170.3, 137.8, 81.4, 80.7, 79.1, 78.9, 72.6, 71.8, 47.8, 45.2, 43.0, 42.8, 42.7, 38.5, 34.7, 34.1, 34.0, 33.0, 32.8, 28.1, 28.0, 27.6, 26.7, 24.6, 24.4.

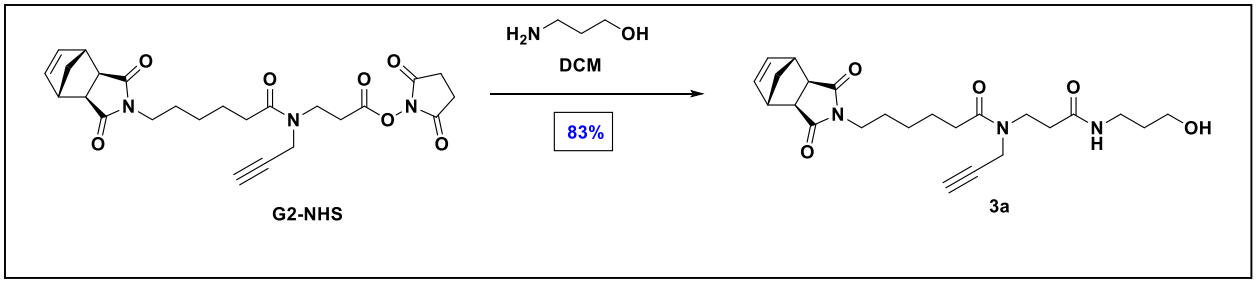


Synthesis of G2-NHS.

Synthesis of G2-COOH. (200 mg) was added to a RBF. A solution of TFA and DCM (1:1) was then added (13 mL). The solution was stirred for 20 minutes, resulting in the complete conversion of **G2** to the corresponding carboxylic acid (**G2-COOH**) as determined by TLC for the disappearance of **G2**. The solution was then concentrated under vacuum and used directly in

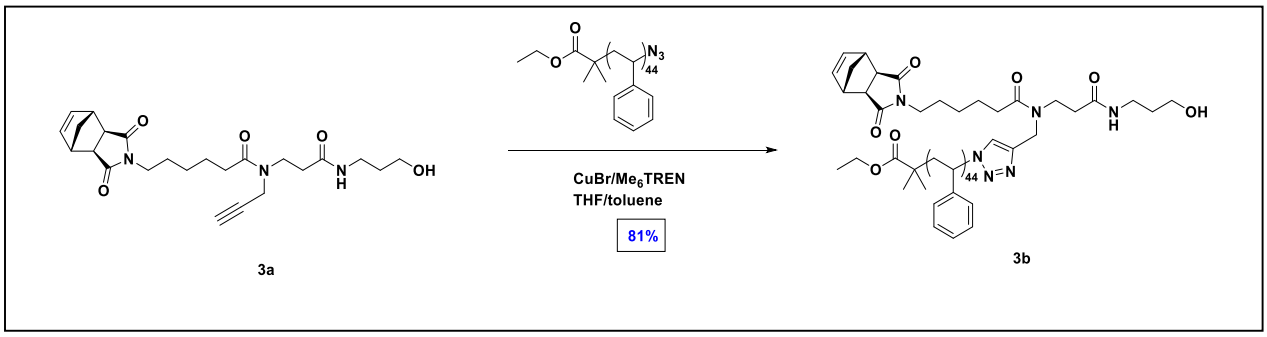
subsequent steps. For characterization purposes, the concentrated **G2-COOH** was re-dissolved in DCM, washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording **G2-COOH** as a white solid (166 mg, 94% yield). HRMS-ESI: Calcd for $C_{21}H_{26}N_2O_5$: *m/z* = 387.1914 $[M + H]^+$; Found: 387.1926 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 6.28 (t, *J* = 2.0 Hz, 2H), 4.25 (d, *J* = 2.4 Hz, 0.8H), 4.12 (d, *J* = 2.4 Hz, 1.2H), 3.79 (t, *J* = 7.0 Hz, 0.8H), 3.69 (t, *J* = 6.6 Hz, 1.2H), 3.46 (t, *J* = 7.4 Hz, 2H), 3.26 (t, *J* = 1.8 Hz, 2H), 2.72-2.67 (overlap, 4H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.32 (t, *J* = 2.4 Hz, 0.6H), 2.22 (t, *J* = 2.6 Hz, 0.4H), 1.70-1.63 (m, 2H), 1.60-1.54 (m, 2H), 1.52-1.49 (d, *J* = 10.0 Hz, 1H), 1.38-1.28 (m, 2H), 1.22-1.20 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.6, 178.3, 176.0, 174.6, 173.5, 172.7, 138.0, 79.0, 78.7, 73.1, 72.3, 48.0, 47.9, 45.3, 43.2, 42.9, 42.7, 38.9, 38.7, 34.1, 33.2, 33.0, 32.9, 32.4, 27.7, 27.5, 26.7, 26.6, 24.5, 24.4.

Synthesis of G2-NHS. Into a RBF, **G2-COOH** (175 mg, 0.452 mmol, 1.0 eq), *N*-hydroxysuccinimide (NHS) (78.0 mg, 0.678 mmol, 1.5 eq), EDC·HCl (130 mg, 0.678 mmol, 1.5 eq), DMAP (27.6 mg, 0.226 mmol, 0.5 eq), and DCM (5 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded product as a white solid (171 mg, 78% yield). HRMS-ESI: Calcd for $C_{25}H_{29}N_3O_7$: *m/z* = 483.2078 $[M + H]^+$; Found: 484.2056 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 6.26 (t, *J* = 2.0 Hz, 2H), 4.24 (d, *J* = 2.8 Hz, 0.6H), 4.10 (d, *J* = 2.4 Hz, 1.4H), 3.85 (t, *J* = 7.2 Hz, 0.6H), 3.74 (t, *J* = 6.4 Hz, 1.4H), 3.44 (t, *J* = 7.4 Hz, 2H), 3.25 (t, *J* = 1.8 Hz, 2H), 2.99-2.95 (m, 2H), 2.82 (s, 4H), 2.65 (s, 2H), 2.40-2.34 (m, 2H), 2.31 (t, *J* = 2.4 Hz, 0.7H), 2.25 (t, *J* = 2.4 Hz, 0.3H), 1.70-1.62 (q, *J* = 7.5 Hz, 2H), 1.60-1.52 (m, 2H), 1.50-1.48 (dt, *J* = 10.0, 1.6 Hz, 1H), 1.38-1.28 (m, 2H), 1.21-1.18 (d, *J* = 10.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.2, 173.2, 172.3, 169.1, 168.9, 167.6, 166.4, 137.9, 78.8, 78.6, 73.1, 72.7, 47.9, 45.3, 43.0, 42.9, 42.4, 39.1, 38.7, 38.6, 34.3, 33.1, 32.9, 30.6, 30.2, 27.7, 26.7, 25.7, 24.5, 24.4.

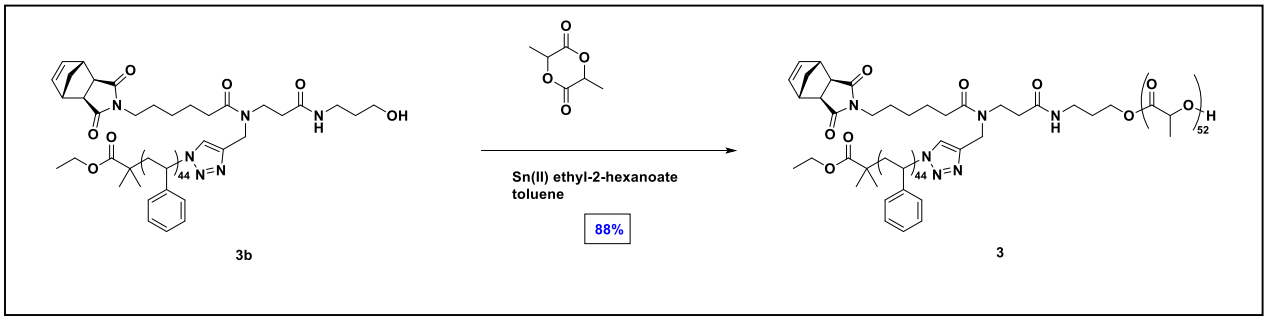


Synthesis of 3a. **G2-NHS** (640mg, 1.32 mmol, 1.0 eq) was dried in a 20 mL glass vial and the vial was evacuated and backfilled with N_2 three times. The starting material was dissolved in 13 mL of anhydrous DCM. Neat 3-aminopropan-1-ol (150mg, 2.0 mmol, 1.5 eq) was added via syringe; a white precipitate formed. After 20 minutes, the reaction was determined to be complete by LC-MS and the reaction mixture was loaded directly onto a silica column. The material was chromatographed using a 0 → 8% MeOH/DCM gradient and the product eluted at approximately 6% MeOH. The product was isolated as a colorless, viscous oil (483 mg, 83% yield). HRMS-ESI: Calcd for $C_{24}H_{34}N_3O_5$: *m/z* = 444.2493 $[M + H]^+$; Found: 444.2498 $[M +H]^+$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (m, 0.6H), 6.84 (t, *J* = 6.0 Hz, 0.4H), 6.23 (t, *J* = 1.8 Hz, 2H), 4.14 (d, *J* = 2.5 Hz, 0.7H), 4.05 (d, *J* = 2.5 Hz, 1.3H), 3.72 (t, *J* = 7.0 Hz, 1H), 3.62 (t, *J* = 6.6 Hz, 1H), 3.57 (t, *J* = 5.8 Hz, 1H), 3.54 (t, *J* = 5.7 Hz, 1.H), 3.40 (t, *J* = 6.9 Hz, 3H), 3.32 (m, 2H), 3.20 (s, 2H), 2.62 (s, 2H), 2.48 (t, *J* = 6.5 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.30 (d, *J* = 2.4 Hz, 0.7H), 2.21 (d, *J* = 2.5 Hz, 0.3H), 1.56-1.66 (m, 4H), 1.51 (p, *J* = 7.4, 6.8 Hz, 2H), 1.46 (d, *J* = 9.8 Hz, 1H), 1.32 – 1.23 (m, 2H), 1.15 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.20, 178.13, 173.47, 172.72, 171.86, 170.85, 137.77, 79.47, 78.53, 77.34, 77.12, 76.91, 72.90, 71.88, 59.72, 59.26, 50.48, 47.78, 45.11, 43.91, 43.50, 42.73, 42.70, 38.51, 38.42, 38.41, 36.83, 36.30, 35.53, 35.02, 34.55, 32.90, 32.41, 32.08, 31.89, 27.48, 27.39, 26.51, 26.45, 24.44, 24.33.

2) Branched Diblock Macromonomers:

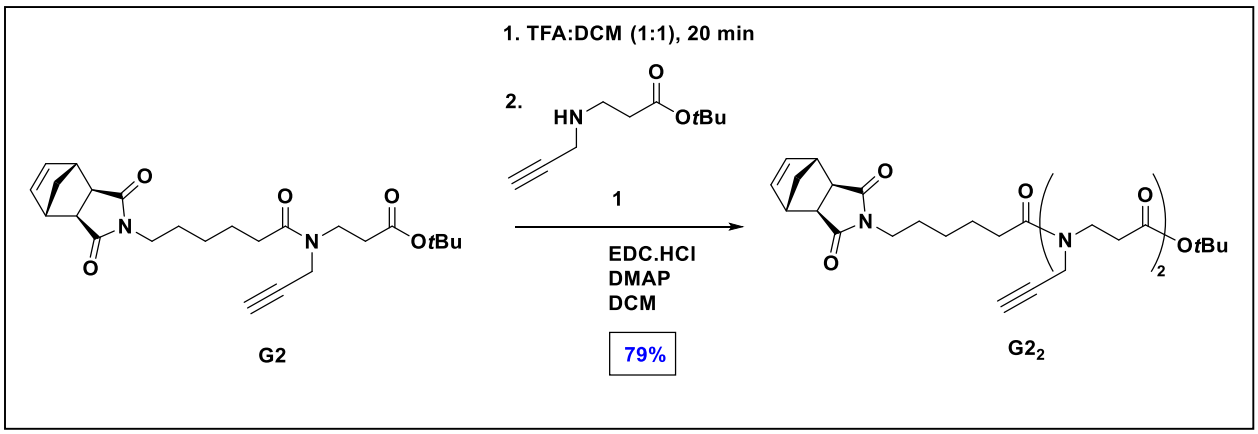


Synthesis of 3b. **3a** (287 mg, 0.71 mmol, 1.0 eq) was coupled to PS-N_3[6] (M_n = 4700 Da, $Đ$ = 1.19) (3.99g, 0.848 mmol, 1.2 eq) according to a previously published procedure.[6] The product was isolated as a white solid (2.92g, 81% yield). The ^{1}H NMR spectrum and GPC trace for **3b** are shown in **Section C. Spectral Data** and **Section D. Size Exclusion Chromatography**, respectively.



Synthesis of 3. **3b** (1.36 g, 0.267 mmol, 1.0 eq) was used as a macroinitiator for the tin(II) ethyl-2-hexaonate catalyzed ring opening polymerization of *DL*-lactide (1.54 g, 10.6 mmol, 39.7 eq). The polymerization was carried out according to previously published procedures.[7] The M_n of PLA was determined to be 3.8 kDa by ^{1}H NMR. The ^{1}H NMR spectrum and GPC trace for 3 are shown in **Section C. Spectral Data** and **Section D. Size Exclusion Chromatography**, respectively.

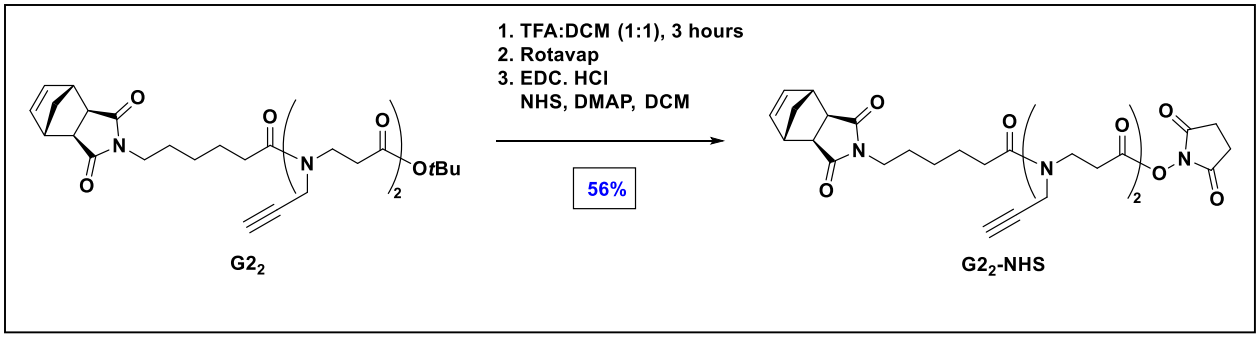
3) Multi-alkyne branched macromonomer precursors.



Synthesis of G2$_2$.

G2 was converted to **G2-COOH** following the same procedure reported above using a solution of TFA and DCM (1:1). The solution was stirred for 20 minutes, washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording **G2-COOH** as a white solid.

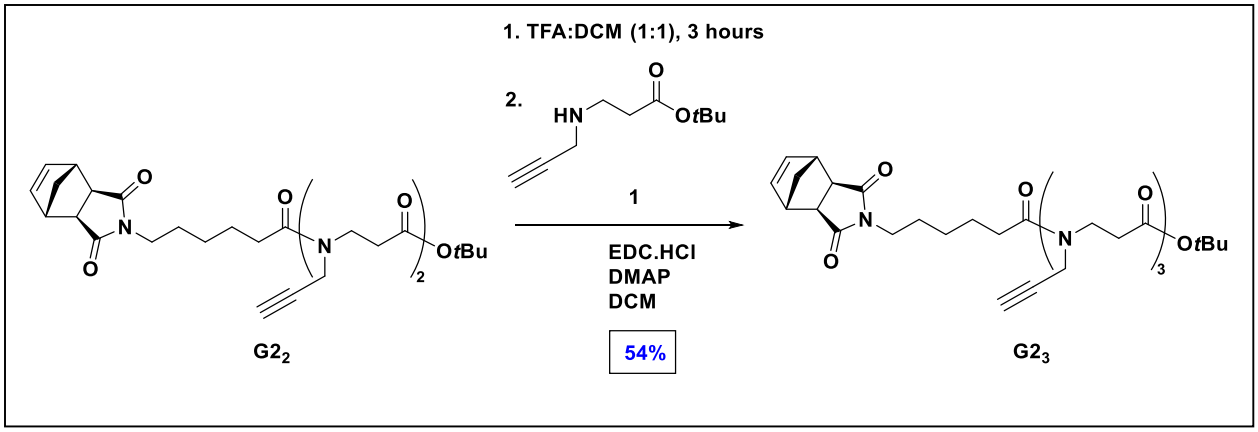
Into a RBF, **G2-COOH** (1.49 g, 3.86 mmol, 1.0 eq), EDC·HCl (0.740 g, 3.86 mmol, 1.0 eq), DMAP (0.267 g, 2.19 mmol, 0.6 eq), **1** (0.530 g, 2.89 mmol, 0.75 eq), and DCM (100 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded the product as a light yellow viscous oil (1.34 g, 84% yield, 79% yield from **G2**). HRMS-DART: Calcd for $C_{31}H_{42}N_3O_6$: *m/z* = 552.3068 $[M + H]^+$; Found: 552.3044 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 6.26 (t, *J* = 1.8 Hz, 2H), 4.21-4.09 (m, 4H), 3.79-3.60 (m, 4H), 3.46-3.41 (m, 2H), 3.24 (t, *J* = 1.8 Hz, 2H), 2.79-2.70 (m, 2H), 2.64 (s, 2H), 2.57-2.50 (m, 2H), 2.38-2.32 (m, 2H), 2.28-2.25 (m, 1H), 2.21-2.17 (m, 1H), 1.68-1.61 (m, 2H), 1.59-1.52 (m, 2H), 1.50-1.47 (dt, *J* = 10.0, 1.6 Hz, 1H), 1.42 (s, 9H), 1.36-1.28 (m, 2H), 1.19 (1H, d, *J* = 9.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.1, 173.0, 172.5, 172.4, 171.4, 171.2, 171.1, 170.3, 170.2, 170.1, 137.9, 81.6, 81.4, 81.0, 80.9, 79.5, 79.2, 79.1, 78.7, 77.4, 73.1, 72.8, 72.5, 72.2, 71.9, 71.8, 47.9, 45.2, 43.8, 43.7, 43.6, 43.5, 43.3, 43.30, 42.9, 42.8, 39.1, 38.6, 38.5, 34.7, 34.6, 34.4, 34.2, 34.1, 33.1, 32.9, 32.3, 32.0, 31.9, 28.2, 28.1, 27.7, 26.8, 24.7, 24.5.



Synthesis of G2$_2$-NHS.

G2$_2$ (7.02 g, 12.7 mmol) was exposed to a solution of TFA and DCM (1:1, 30 mL TFA in 30 mL DCM). The solution was stirred for 3 hours, resulting in the complete conversion to **G2$_2$-COOH** as determined by TLC. DCM (70 mL) was then added to the reaction mixture, and the solution was washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording **G2$_2$-COOH** as an off-white solid (6.24 g, 99% yield).

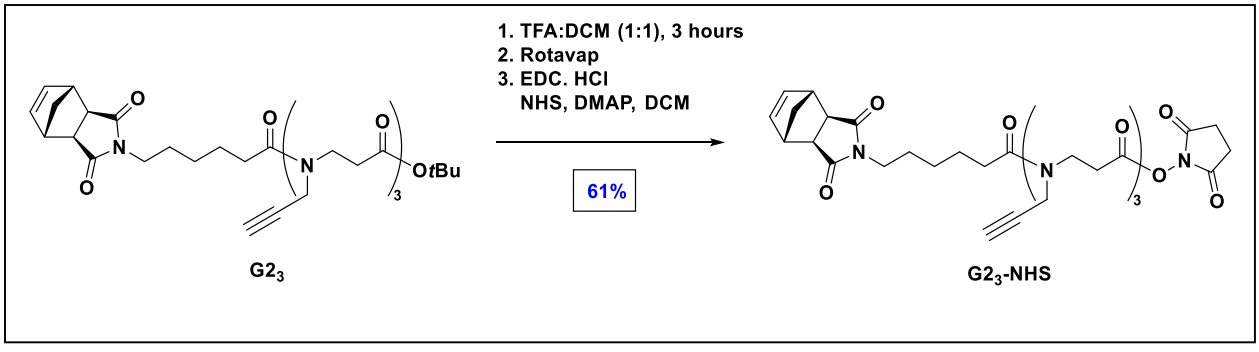
Into a RBF, **G2$_2$-COOH** (1.87 g, 3.77 mmol, 1.0 eq), EDC·HCl (1.09 g, 5.67 mmol, 1.5 eq), DMAP (0.114 g, 0.94 mmol, 0.25 eq), NHS (0.653 g, 5.68 mmol, 1.5 eq), and DCM (100 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded the product as a white solid (1.27 g, 57% yield, 56% yield from **G2$_2$**). HRMS-DART: Calcd for $C_{31}H_{37}N_4O_8$: *m/z* = 593.2606 $[M + H]^+$; Found: 593.2617 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 6.26 (t, *J* = 1.6 Hz, 2H), 4.27-4.12 (m, 4H), 3.90-3.68 (m, 4H), 3.44 (td, *J* = 7.4, 2.4 Hz, 2H), 3.24 (s, 2H), 3.02-2.96 (m, 2H), 2.85-2.73 (m, 6H), 2.65 (s, 2H), 2.39-2.21 (m, 4H), 1.69-1.62 (m, 2H), 1.59-1.52 (m, 2H), 1.51-1.48 (dt, *J* = 9.6, 1.7 Hz, 1H), 1.37-1.29 (m, 2H), 1.20 (1H, d, *J* = 9.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.2, 173.1, 172.6, 171.9, 171.1, 170.9, 169.1, 168.9, 167.5, 166.4, 137.9, 79.8, 79.6, 79.3, 78.7, 78.3, 78.2, 77.4, 73.6, 73.3, 73.1, 72.7, 72.6, 71.9, 47.9, 45.3, 44.0, 43.8, 43.6, 43.4, 43.1, 42.9, 42.8, 42.4, 42.3, 39.2, 39.1, 39.0 38.6, 35.0, 34.8, 34.5, 34.1, 33.1, 32.9, 32.8, 32.4, 32.3, 31.9, 30.6, 30.4, 30.2, 30.1, 27.7, 26.9, 26.8, 25.7, 24.7, 24.5.



Synthesis of G2$_3$.

4.0 g **G2$_2$-COOH** was prepared as described above.

Into a RBF, **G2$_2$-COOH** (0.458 g, 0.92 mmol, 1.0 eq), EDC·HCl (0.196 g, 1.02 mmol, 1.1 eq), DMAP (0.070 g, 0.57 mmol, 0.6 eq), **1** (0.130 g, 0.71 mmol, 0.75 eq) and DCM (20 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded the product as a yellow viscous oil (0.340 g, 55% yield, 54% yield from **G2$_2$**). HRMS-DART: Calcd for $C_{37}H_{49}N_4O_7$: *m/z* = 661.3596 $[M + H]^+$; Found: 661.3589 $[M + H]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 6.27 (t, *J* = 1.8 Hz, 2H), 4.22-4.10 (m, 6H), 3.82-3.63 (m, 6H), 3.47-3.41 (m, 2H), 3.26 (s, 2H), 2.85-2.72 (m, 4H), 2.66 (s, 2H), 2.59-2.53 (m, 2H), 2.42-2.18 (m, 5H), 1.71-1.63 (m, 2H), 1.61-1.54 (m, 2H), 1.52-1.49 (d, *J* = 10.0, 1H), 1.43 (s, 9H), 1.39-1.27 (m, 2H), 1.21 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.2, 173.0, 172.6, 172.5, 171.8, 171.7, 171.3, 171.2, 171.0, 170.7, 170.3, 170.2, 137.9, 81.6, 81.4, 81.0, 80.9, 79.6, 79.3, 79.1, 78.9, 78.7, 77.3, 73.2, 72.9, 72.7, 72.6, 72.2, 71.9, 71.8, 49.3, 47.9, 45.3, 43.8, 43.6, 43.4, 43.1, 42.9, 39.2, 39.0, 38.7, 38.6, 34.6, 34.4, 34.2, 34.1, 33.1, 32.9, 32.4, 32.2, 32.0, 31.8, 28.2, 28.1, 27.7, 26.8, 24.7, 24.5.

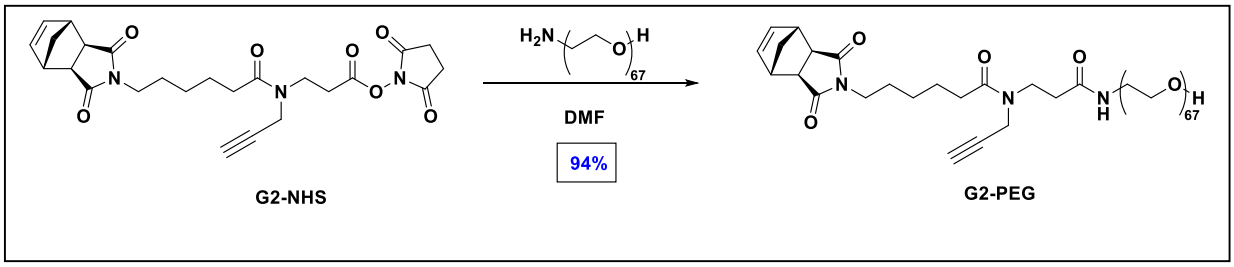


Synthesis of G2$_3$-NHS.

G2$_3$ (1.68 g, 2.54 mmol) was exposed to a solution of TFA and DCM (1:1, 20 mL TFA in 20 mL DCM). The mixture was stirred for 3 hours, resulting in the complete conversion to **G2$_3$-COOH** as determined by TLC. DCM (40 mL) was then added to the reaction mixture, and the solution was washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording **G2$_3$-COOH** as an off-white solid (1.50 g, 97% yield).

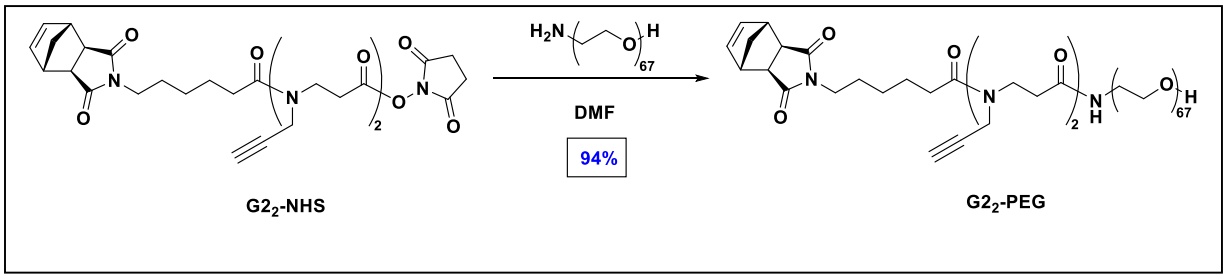
Into a RBF, **G2$_3$-COOH** (1.50 g, 2.48 mmol, 1.0 eq), EDC·HCl (0.713 g, 3.72 mmol, 1.5 eq), DMAP (0.151 g, 1.24 mmol, 0.5 eq), NHS (0.428 g, 3.72 mmol, 1.5 eq), and DCM (100 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EtOAc/hexane) of the crude mixture yielded product as a white solid (1.10 g, 63% yield, 61% yield from **G2$_3$**). HRMS-DART: Calcd for $C_{37}H_{44}N_5O_9$: *m/z* = 702.3134 [*M* + H]$^+$; Found: 702.3132 [*M* + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ_H 6.27 (s, 2H), 4.26-4.12 (m, 6H), 3.88-3.66 (m, 6H), 3.44 (td, *J* = 7.6, 2.4 Hz, 2H), 3.25 (s, 2H), 3.03-2.95 (m, 2H), 2.86-2.69 (m, 8H), 2.65 (s, 2H), 2.39-2.18 (m, 5H), 1.69-1.48 (m, 5H), 1.37-1.27 (m, 2H), 1.20 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ_C 178.2, 173.0, 172.9, 172.6, 171.8, 171.7, 171.3, 169.1, 168.9, 167.6, 137.9, 79.8, 79.6, 79.3, 79.0, 78.3, 78.2, 77.4, 73.6, 73.3, 73.1, 72.8, 72.7, 72.6, 72.5, 71.9, 47.9, 45.3, 43.9, 43.8, 43.5, 43.4, 43.1, 42.9, 42.8, 42.4, 39.2, 39.1, 38.6, 35.0, 34.9, 34.4, 34.1, 33.1, 32.9, 32.4, 32.3, 32.2, 30.2, 30.1, 29.8, 27.7, 26.8, 25.7, 24.7, 24.5.

4) Multivalent Macromonomers:

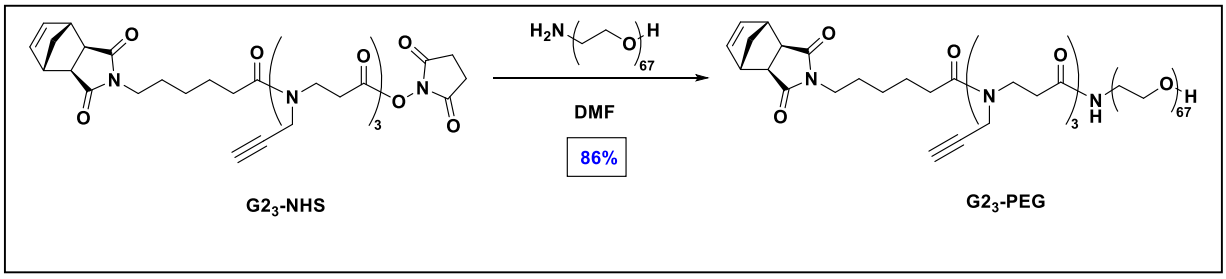


Synthesis of G2-PEG. **G2-PEG** was prepared following a literature procedure for a related macromonomer (from **G1**) with slight modifications.[2] Into a RBF, **G2-NHS** (0.260 g, 0.538 mmol, 1.24 eq) and *O*-(2-aminoethyl)poly(ethylene glycol) (1.30 g, 0.434 mmol, 1.0 eq) were added. DMF (26.0 mL) was then added, and the resulting solution was stirred overnight. The solution was then added dropwise into stirring diethyl ether (300 mL), affording **G2-PEG** as a white precipitate.

The mixture was then subjected to centrifugation (4000 rpm, 15 min), and the ether was decanted. The white solid was washed with ether followed by centrifugation and decantation two additional times, affording pure **G2-PEG** as a white solid (1.37 g, 94% yield). ^{1}H NMR and MALDI-TOF spectra spectra are provided in **Section C. Spectral Data**.

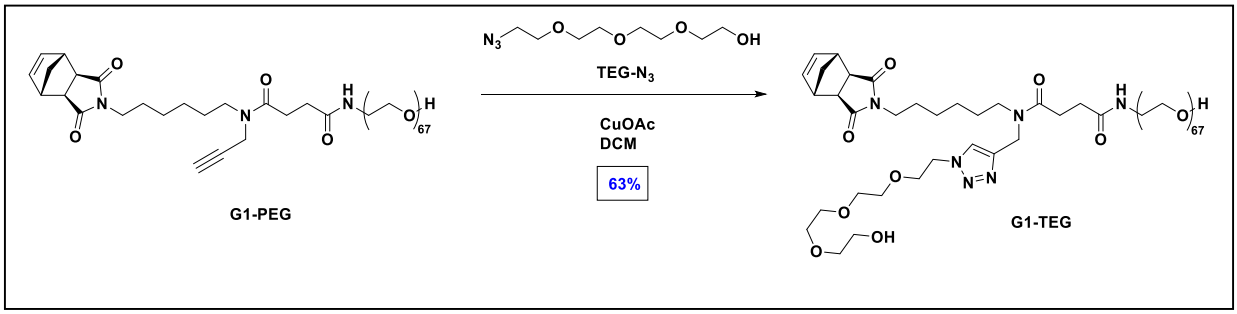


Synthesis of G2$_2$-PEG. **G2$_2$-PEG** was prepared similarly to **G2-PEG**. Into a RBF, **G2$_2$-NHS** (70 mg, 0.118 mmol, 1.2 eq) and *O*-(2-aminoethyl)poly(ethylene glycol) (295.3 mg, 0.098 mmol, 1.0 eq) were added. DMF (4.0 mL) was then added, and the resulting solution was stirred overnight. The solution was then added dropwise into stirring diethyl ether (150 mL), affording **G2$_2$-PEG** as a white precipitate. The mixture was then subjected to centrifugation (4000 rpm, 15 min), and the ether can then be decanted. The white solid was washed with ether followed by centrifugation and decantation two additional time, affording pure **G2$_2$-PEG** as a white solid (313.3 mg, 94% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.

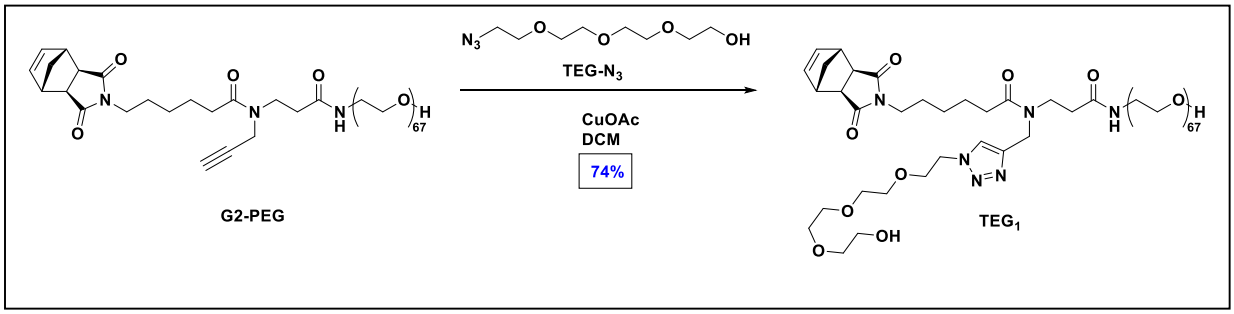


Synthesis of G2$_3$-PEG. **G2$_3$-PEG** was prepared similarly to **G2-PEG** and **G2$_2$-PEG**. Into a round-bottom flask (RBF), **G2$_3$-NHS** (0.767 g, 1.09 mmol, 1.2 eq) and *O*-(2-aminoethyl)poly(ethylene glycol) (2.74 g, 0.913 mmol, 1.0 eq) were added. DMF (44.0 mL) was then added, and the resulting solution was stirred overnight. The solution was then added dropwise into stirring diethyl ether (150 mL), affording **G2$_3$-PEG** as a white precipitate. The mixture was then subjected to centrifugation (4000 rpm, 15 min), and the ether can then be decanted. The white solid was washed with ether followed by centrifugation and decantation another 2 times, affording pure **G2$_3$-PEG**

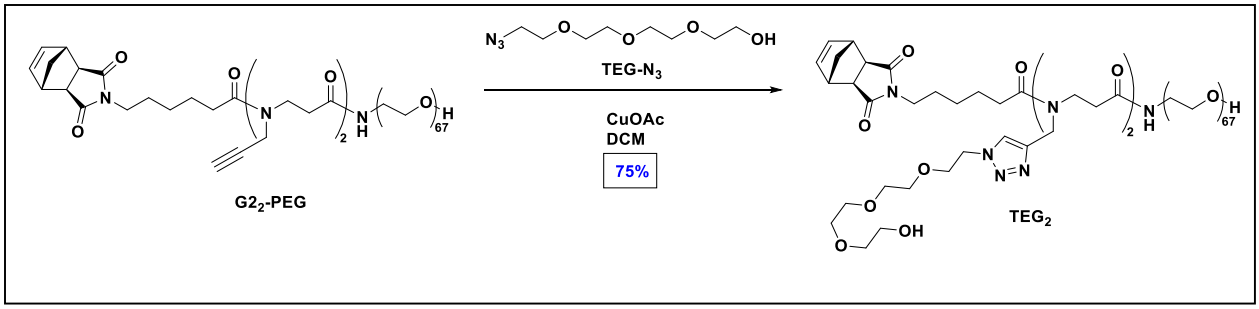
as a white solid (2.81 g, 86% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.



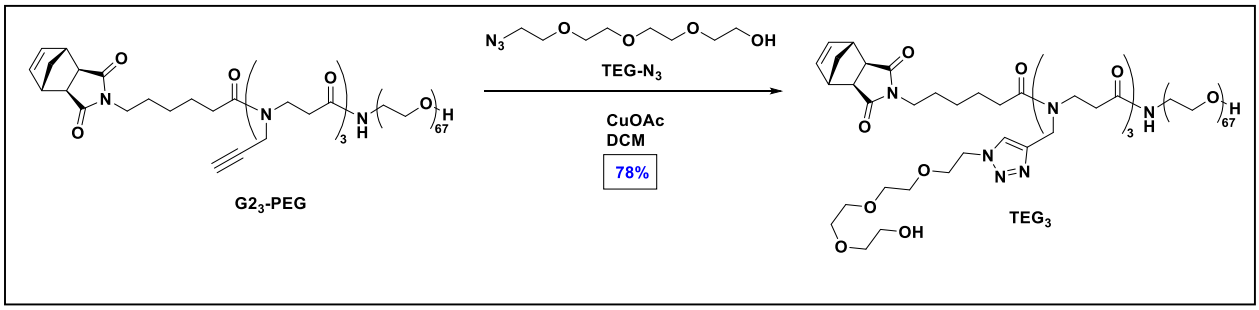
Synthesis of G1-TEG. To a vial, **G1-PEG** (340.0 mg, 0.1 mmol, 1.0 eq), **TEG-N$_3$** (33.0 mg, 0.15 mmol, 1.5 eq), and DCM (2 mL) were added. A pinch of CuOAc was then added, and the reaction mixture was stirred under nitrogen. The reaction was complete in ~1 hour as determined by LC-MS. The reaction mixture was filtered through a 0.45 µm filter (Nalgene) upon complete conversion. The crude mixture was concentrated under vacuum, redissolved in chloroform, and subjected to recycling preparative HPLC, affording the pure product as a white solid (227 mg, 63% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.



Synthesis of TEG$_1$. To a vial, **G2-PEG** (150.0 mg, 0.044 mmol, 1.0 eq), **TEG-N$_3$** (14.5 mg, 0.066 mmol, 1.5 eq), and DCM (2.0 mL) were added. Copper(I) acetate (CuOAc) (a pinch) was then added, and the reaction mixture was stirred under nitrogen. The reaction was complete in ~1 hour as determined by LC-MS. The reaction mixture was filtered through a 0.45 µm filter (Nalgene). The crude mixture was concentrated under vacuum, redissolved in chloroform, and subjected to recycling preparative HPLC, affording the pure product as a white solid (119 mg, 74% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.



Synthesis of TEG$_2$. To a vial, **G2$_2$-PEG** (130.0 mg, 0.037 mmol, 1.0 eq), **TEG-N$_3$** (19.7 mg, 0.090 mmol, 2.4 eq) and DCM (3.0 mL) were added. Copper(I) acetate (CuOAc) (a pinch) was then added, and the reaction mixture was stirred under nitrogen. The reaction was complete in ~2.5 hours as determined by LC-MS. The reaction mixture was filtered through a 0.45 µm filter (Nalgene). The crude mixture was concentrated under vacuum, redissolved in chloroform, and subjected to recycling preparative HPLC, affording the pure product as a white solid (110 mg, 75% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.



Synthesis of TEG$_3$. To a vial, **G2$_3$-PEG** (130.0 mg, 0.036 mmol, 1.0 eq), **TEG-N$_3$** (28.6 mg, 0.130 mmol, 3.6 eq) and DCM (3.0 mL) were added. Copper(I) acetate (CuOAc) (a pinch) was then added, and the reaction mixture was stirred under nitrogen. The reaction was complete in ~3 hours as determined by LC-MS. The reaction mixture was filtered through a 0.45 µm filter (Nalgene). The crude mixture was concentrated under vacuum, redissolved in chloroform, and subjected to recycling preparative HPLC, affording the pure product as a white solid (120.4 mg, 78% yield). ^{1}H NMR and MALDI-TOF spectra are provided in **Section C. Spectral Data**.

5) General Procedure for Bottlebrush Polymer Syntheses:

Note: *All ROMP syntheses were performed in a glovebox under N_2 atmosphere; however, similar results are expected under ambient conditions. All ROMP reactions followed the same general procedure, which was modified from previously published literature.*[2,3,6,7]

Synthesis of PS-branch-PLA Janus Bottlebrush Copolymers

To a vial containing a stir bar, **3** (50.0 mg) was dissolved in 50 µL of THF. To another vial, a solution of Grubbs 3rd generation bispyridyl catalyst (**Ru**, 5 mg/mL in THF) was freshly prepared. Appropriate volumes of the **Ru** solution to achieve the desired degrees of polymerization (DP) were then added to the vial containing **3**. The reaction mixture was allowed to stir for 2.5 h at room temperature. To quench the polymerization, a few drops of ethyl vinyl ether were then added.

Synthesis of $TEG_1$40 (representative bottlebrush polymer synthesis)

To a vial containing a stir bar, **TEG_1** (15.9 mg, 4.43 µmol, 40.0 eq) was added. To another vial, a solution of **Ru** (0.005 M in THF) was freshly prepared. THF (66.5 µL) was then added to the vial containing **TEG_1**, followed by the addition of **Ru** solution (22.2 µL, 0.11 µmol, 1.0 eq) to give the desired DP of 40, while achieving a total **TEG_1** concentration of 0.05 M. The yellow reaction mixture was allowed to stir for 3 hours at room temperature. To quench the polymerization, a drop of ethyl vinyl ether was then added.

Synthesis of G1-TEG40, $TEG_2$40

Multivalent bottlebrush polymers were prepared in the same manner as reported for **$TEG_1$40**. Samples of DP 40 were prepared using 0.005 M **Ru** solution and the appropriate MM solution to ensure final MM concentration of 0.05 M and **MM-to-Ru** ratio of 40:1 (DP = 40).

Synthesis of TEG_3 with varying DP

Multivalent bottlebrush polymers were prepared in the same manner as reported for **G2-$TEG_1$40**. Samples with the desired DPs (10, 25, 35, 40, 50) were prepared using 0.005 M **Ru** solution and the appropriate MM solution to ensure final MM concentration of 0.05 M and desired **MM-to-Ru** ratio (DP). Samples with DP 10 to 35 were prepared using 0.02 M **Ru** and allowed to stir for 60 minutes. Samples with DP 40 and 50 were allowed to stir for 6 hours.

Section C. Spectral Data

1) Branched Macromonomer Precursors:

Spectra Data for 1.

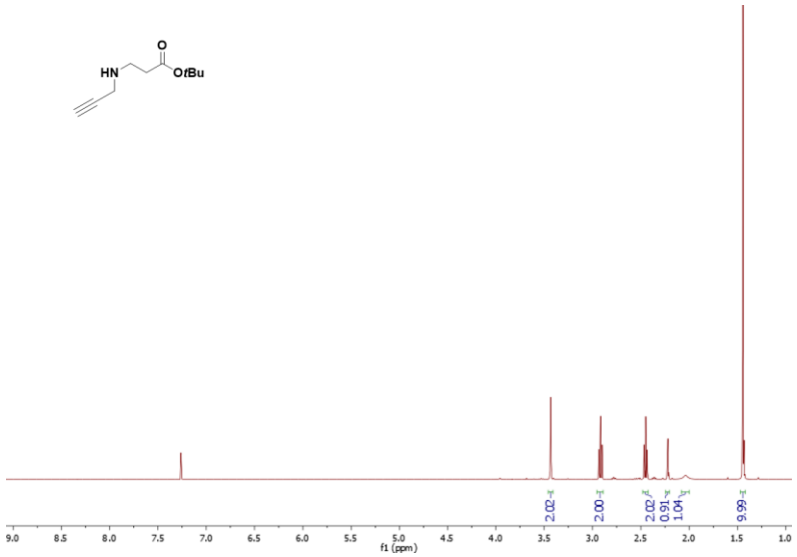


Figure S1. ^{1}H NMR Spectrum of **1** in $CDCl_3$

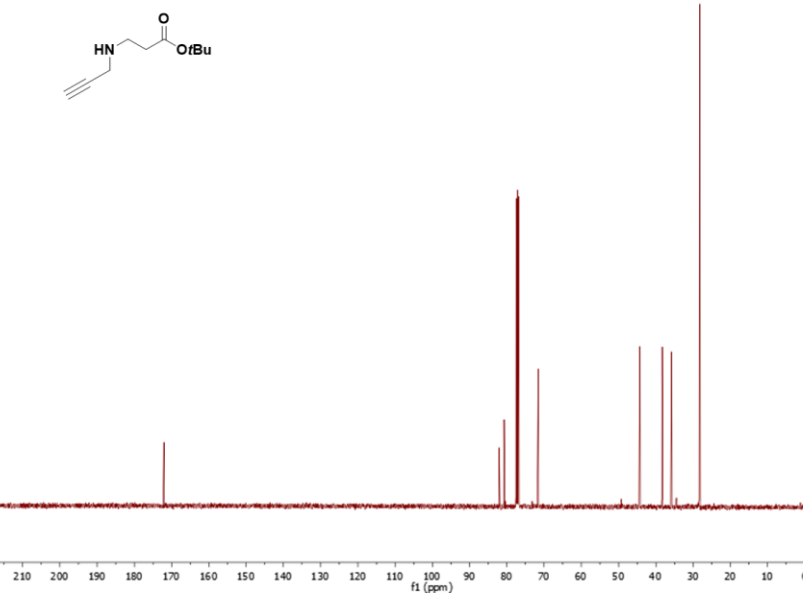


Figure S2. ^{13}C NMR Spectrum of **1** in $CDCl_3$

Spectra Data for 2

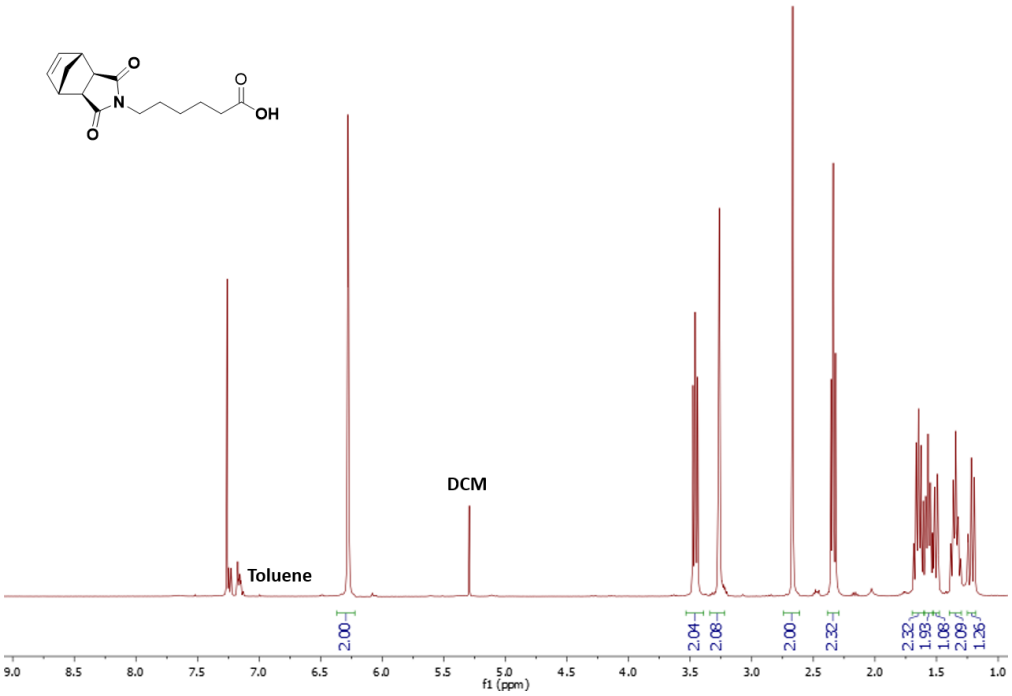


Figure S3. ^{1}H NMR Spectrum of **2** in $CDCl_3$

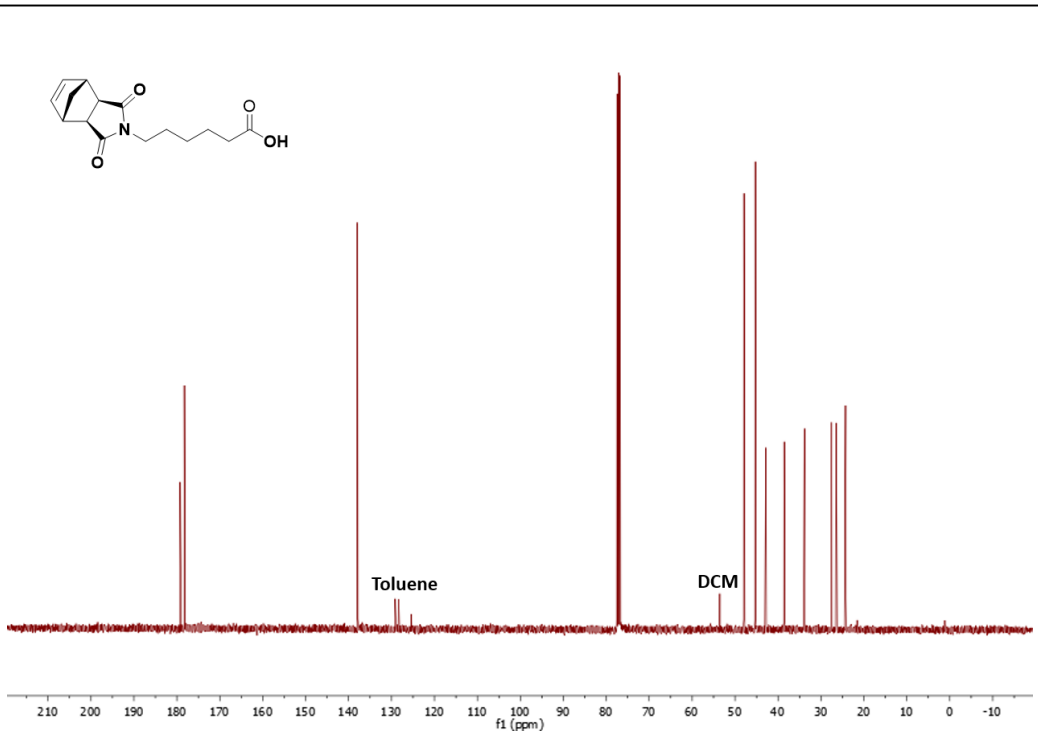


Figure S4. ^{13}C NMR Spectrum of **2** in $CDCl_3$

Spectra Data for G2.

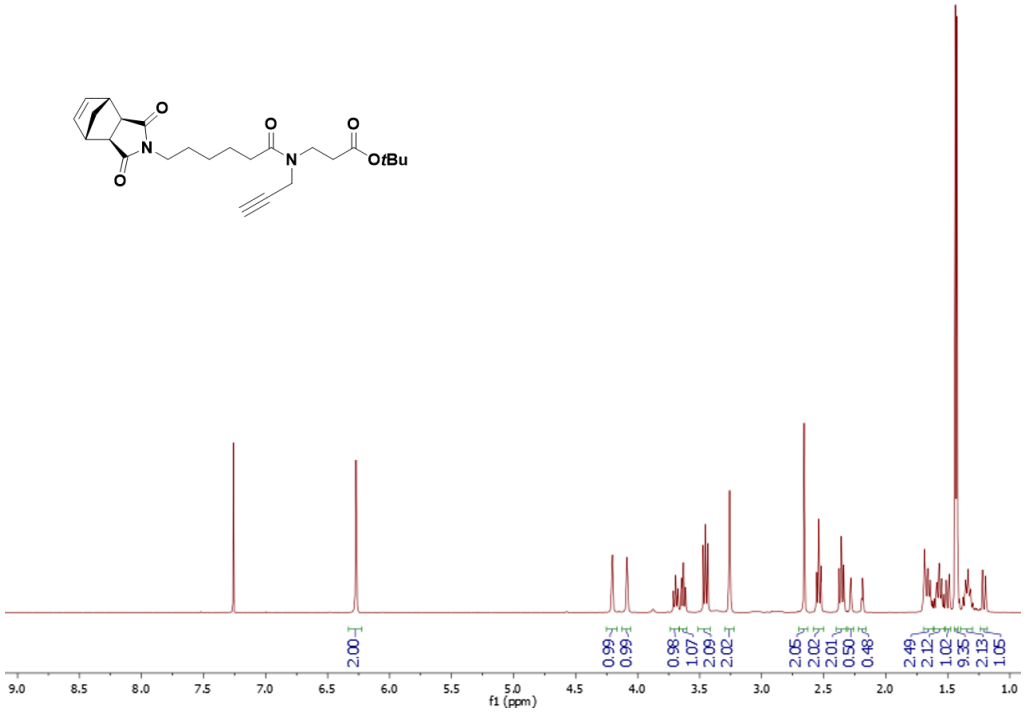


Figure S5. ^{1}H NMR Spectrum of **G2** in $CDCl_3$

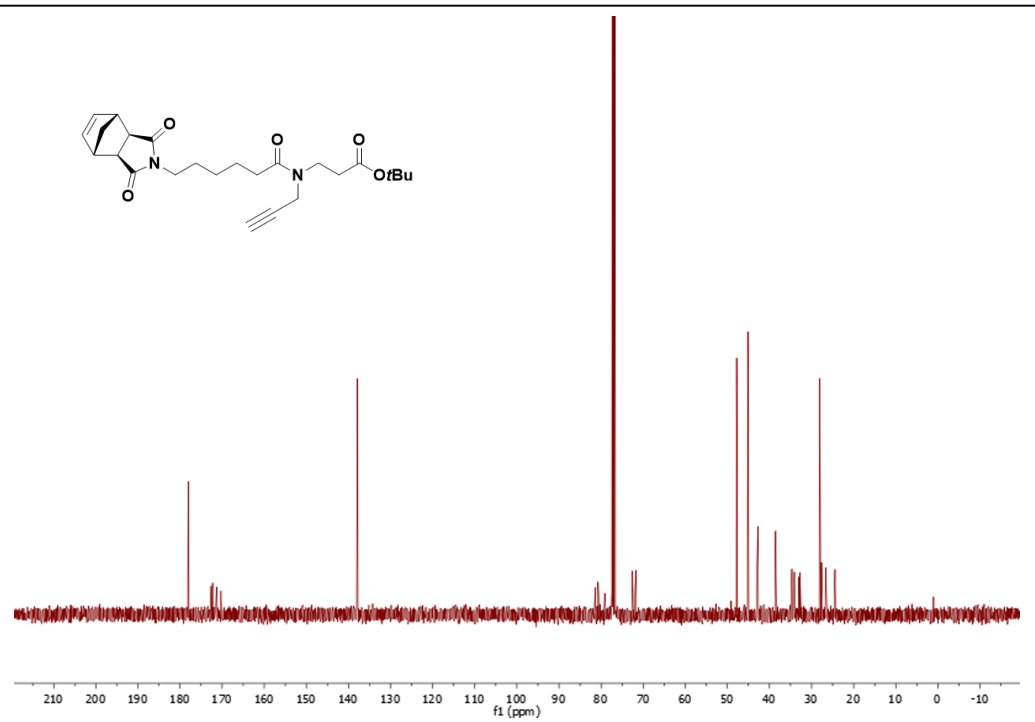


Figure S6. ^{13}C NMR Spectrum of **G2** in $CDCl_3$

Spectra Data for G2-COOH.

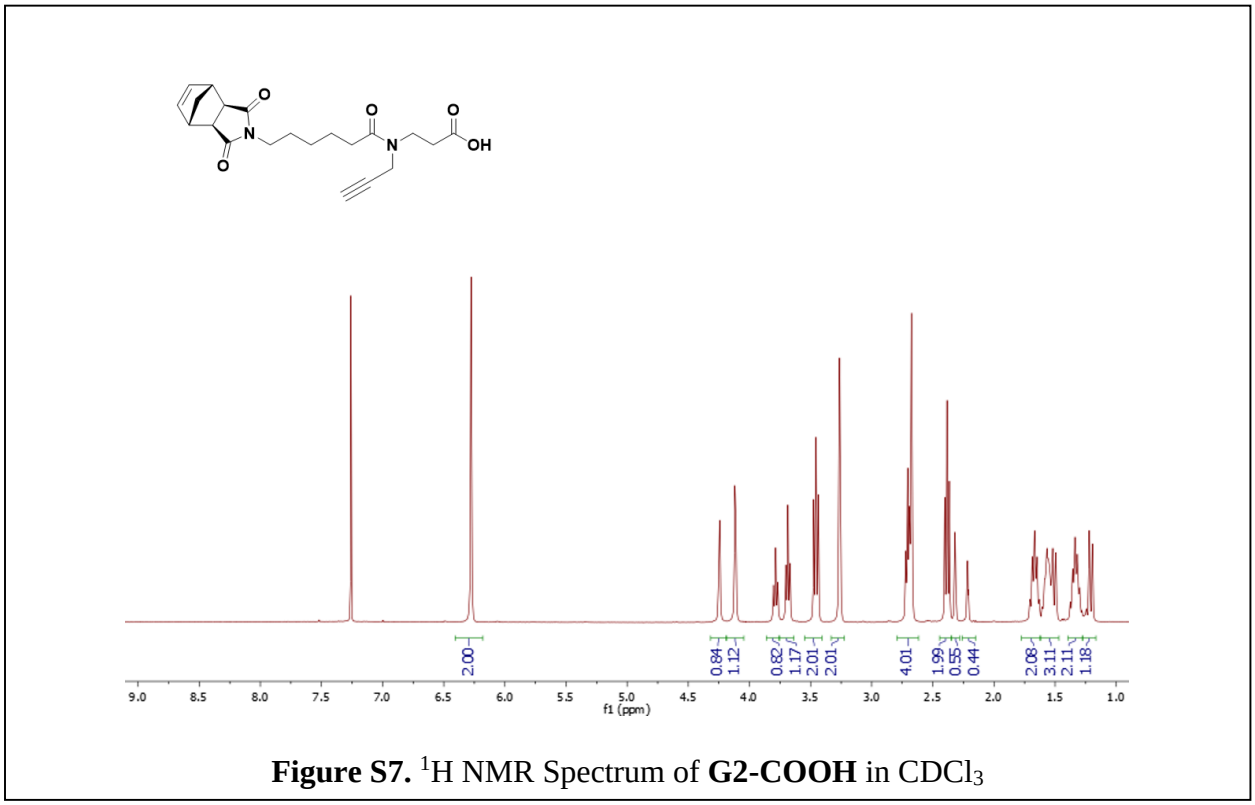


Figure S7. ^{1}H NMR Spectrum of **G2-COOH** in $CDCl_3$

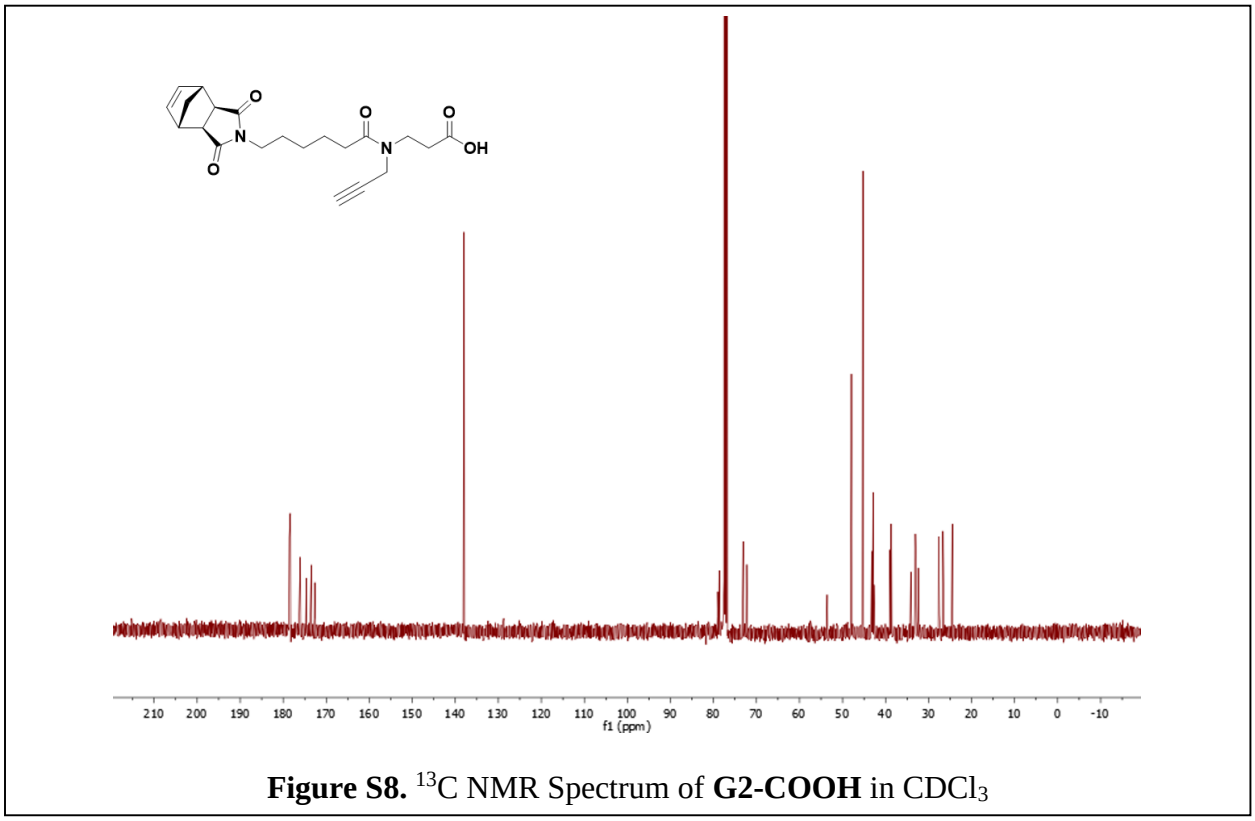


Figure S8. ^{13}C NMR Spectrum of **G2-COOH** in $CDCl_3$

Spectra Data for G2-NHS.

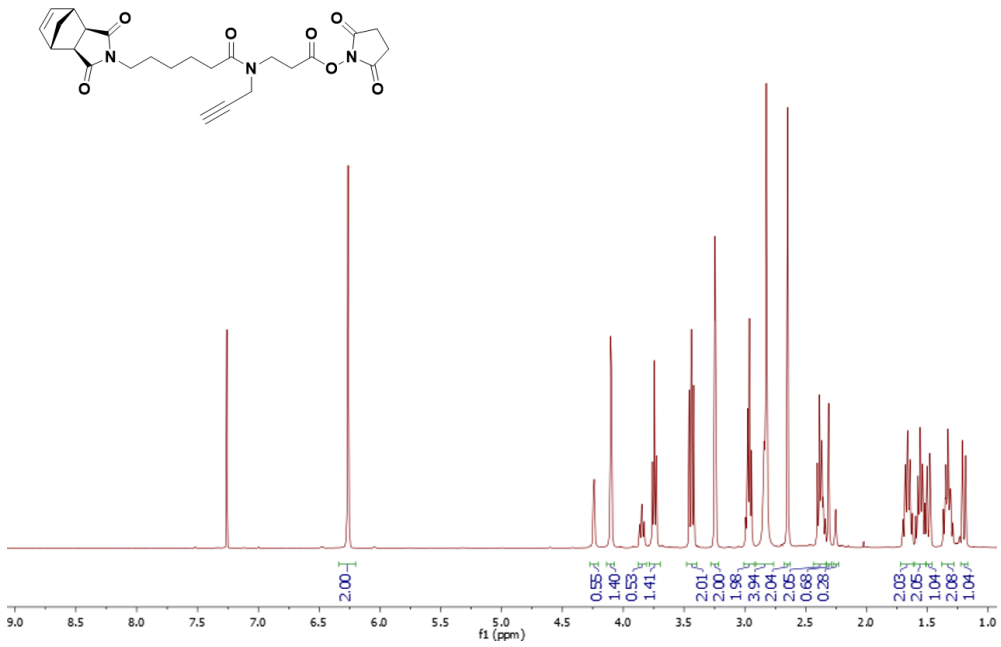


Figure S9. ^{1}H NMR Spectrum of **G2-NHS** in $CDCl_3$

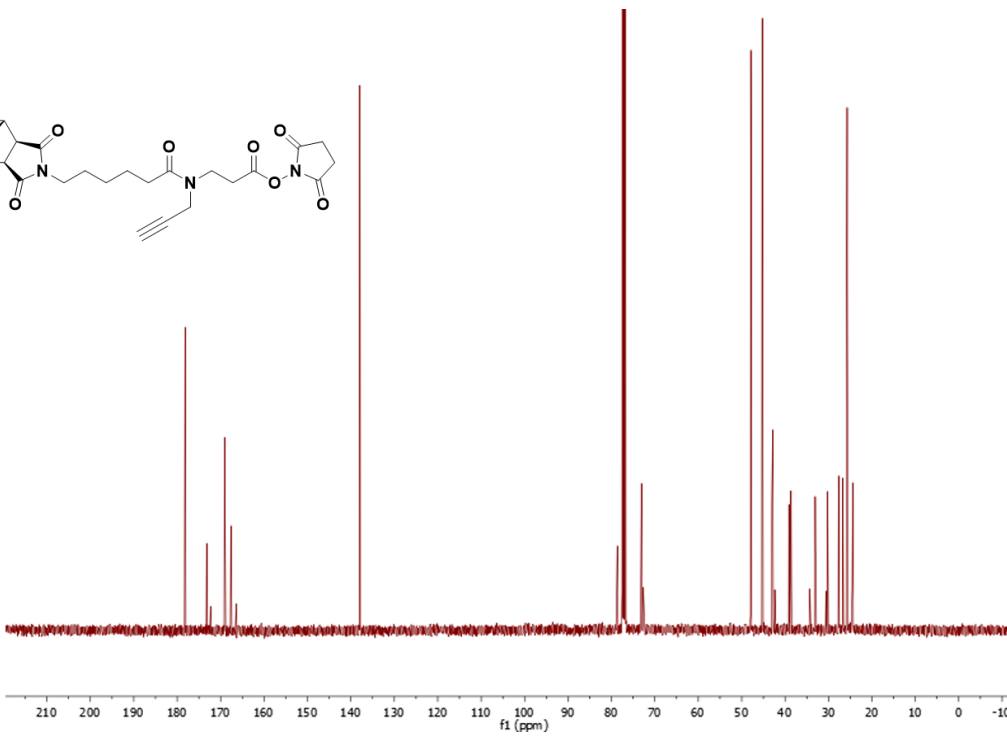


Figure S10. ^{13}C NMR Spectrum of **G2-NHS** in $CDCl_3$

Spectra Data for 3a.

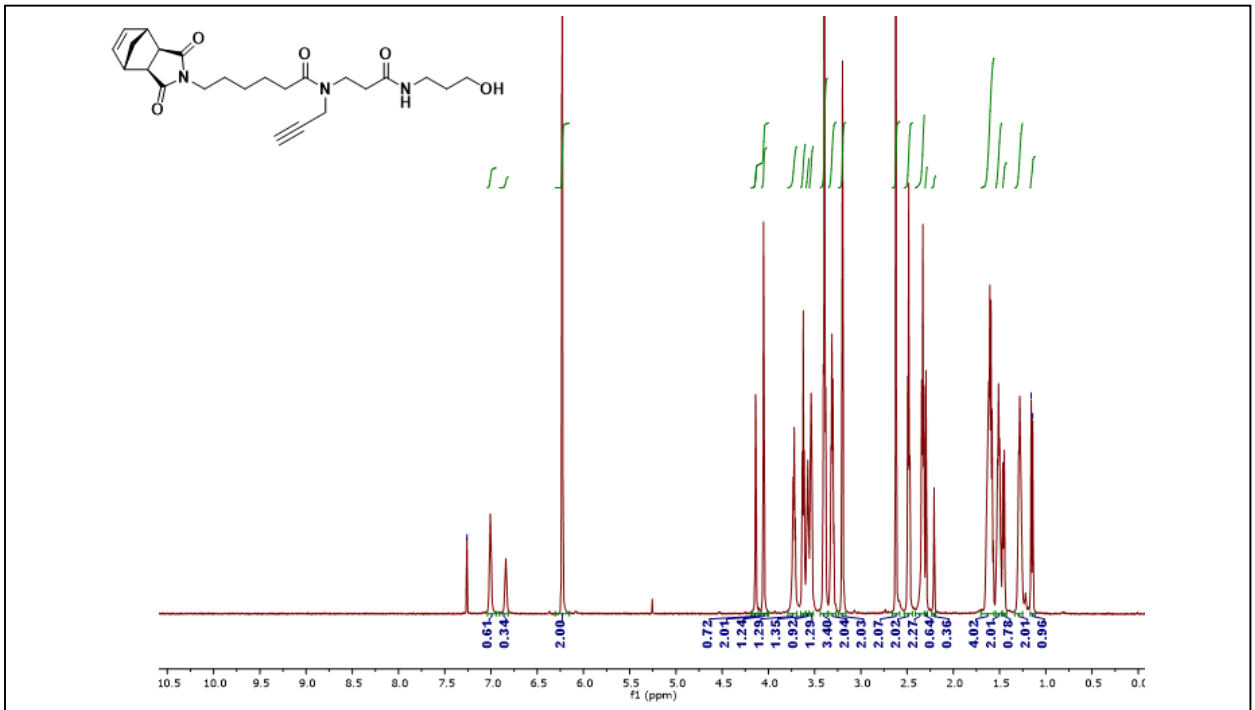


Figure S11. ^{1}H NMR Spectrum of **3a** in $CDCl_3$

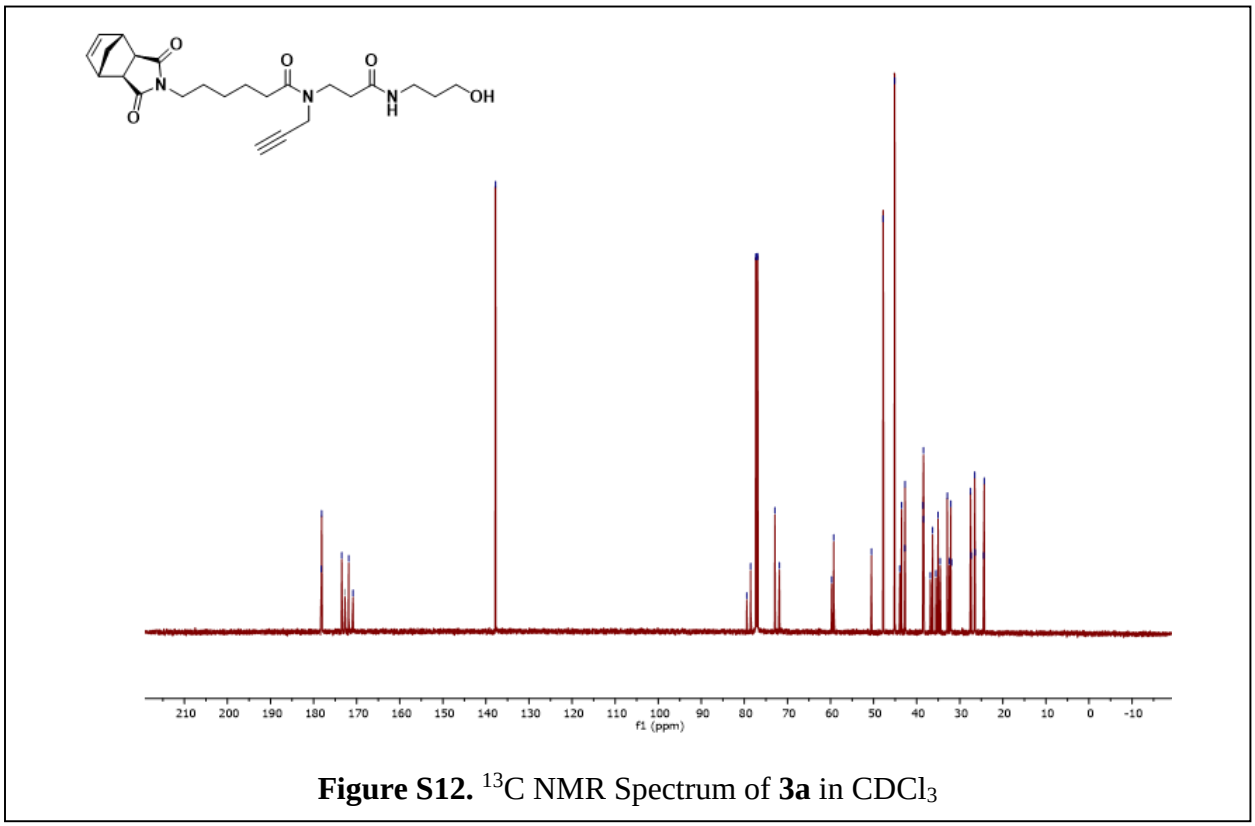


Figure S12. ^{13}C NMR Spectrum of **3a** in $CDCl_3$

2) Branched Diblock Macromonomers:

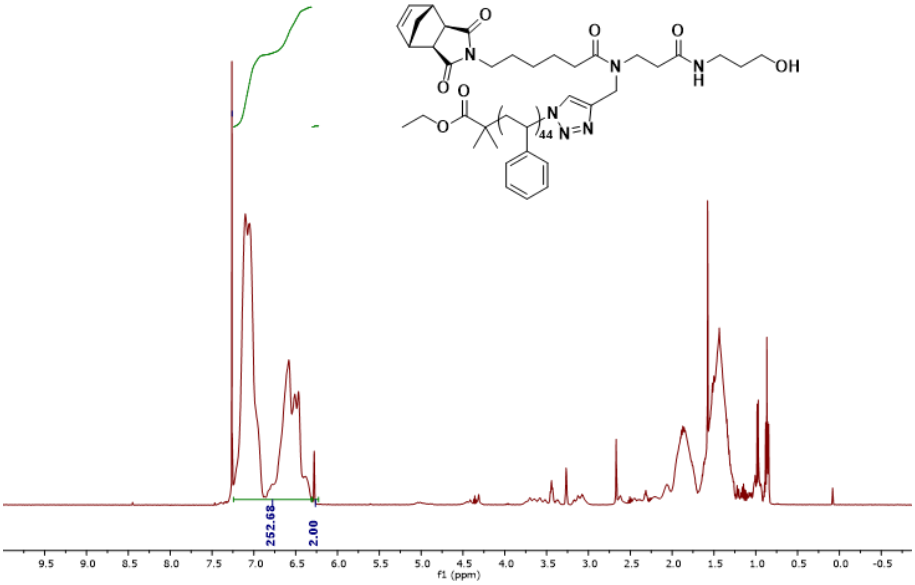


Figure S13. ^{1}H NMR Spectrum of **3b** in $CDCl_3$

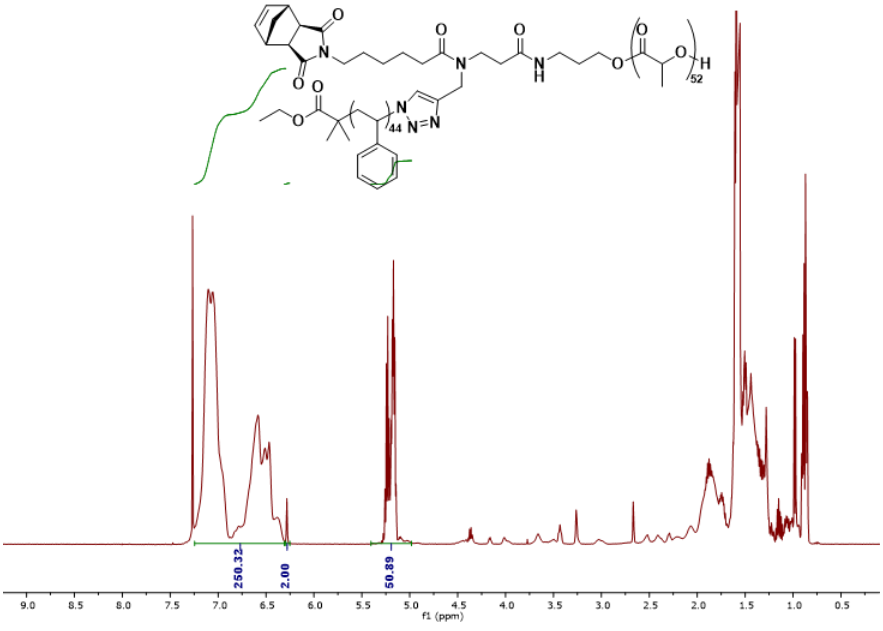


Figure S14. ^{1}H NMR Spectrum of **3** in $CDCl_3$

3) Multi-Alkyne Branched Macromonomer Precursors:

Spectra Data for G2$_2$.

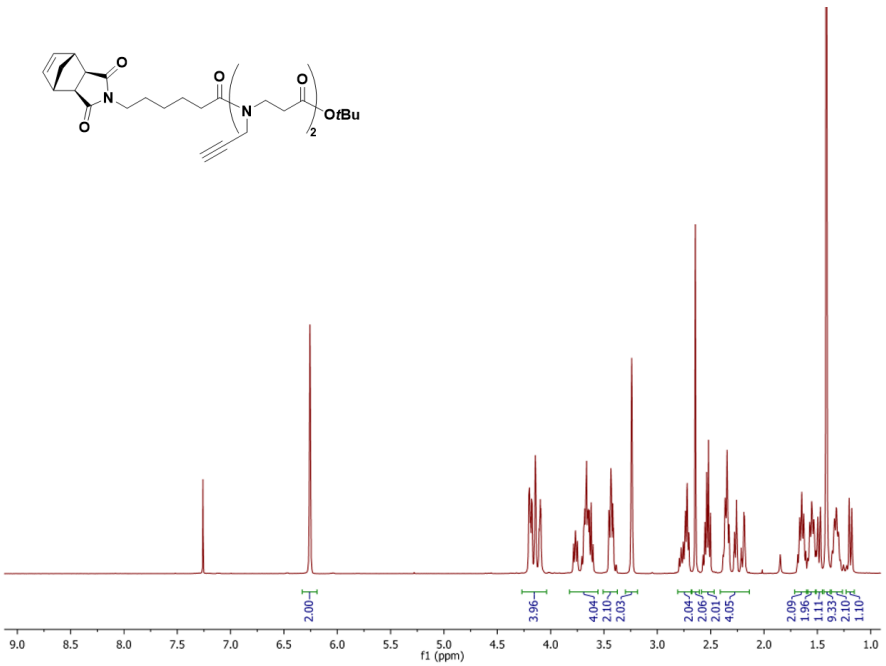


Figure S15. ^{1}H NMR Spectrum of **G2$_2$** in $CDCl_3$

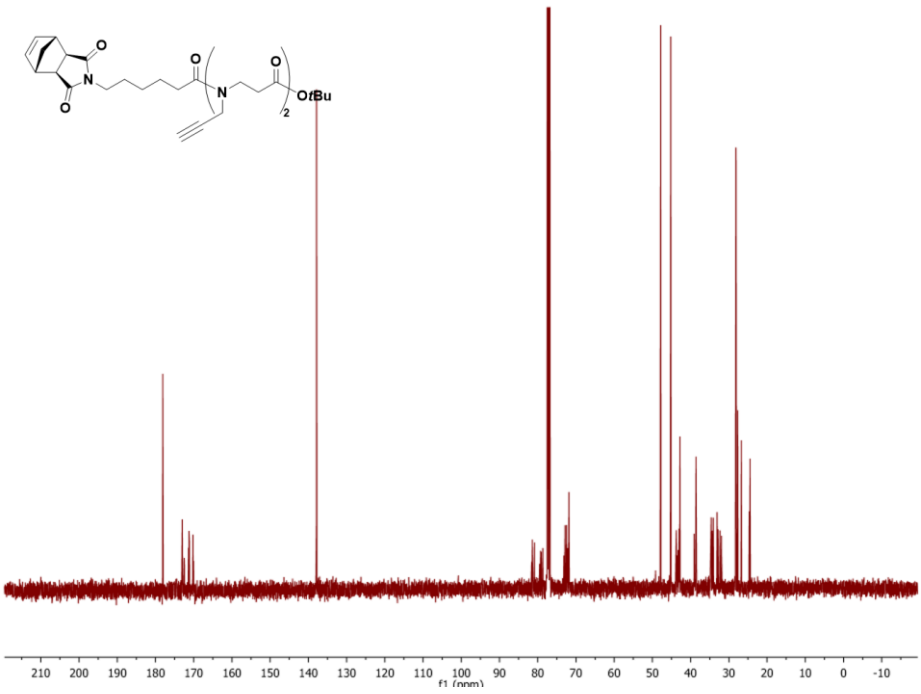


Figure S16. ^{13}C NMR Spectrum of **G2$_2$** in $CDCl_3$

Spectra Data for G2$_2$-NHS.

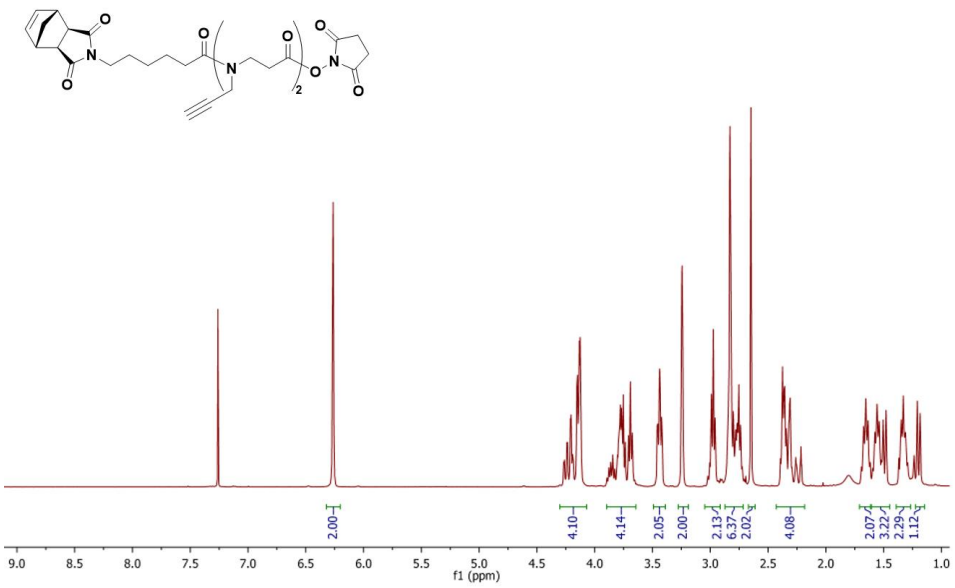


Figure S17. ^{1}H NMR Spectrum of **G2$_2$-NHS** in $CDCl_3$

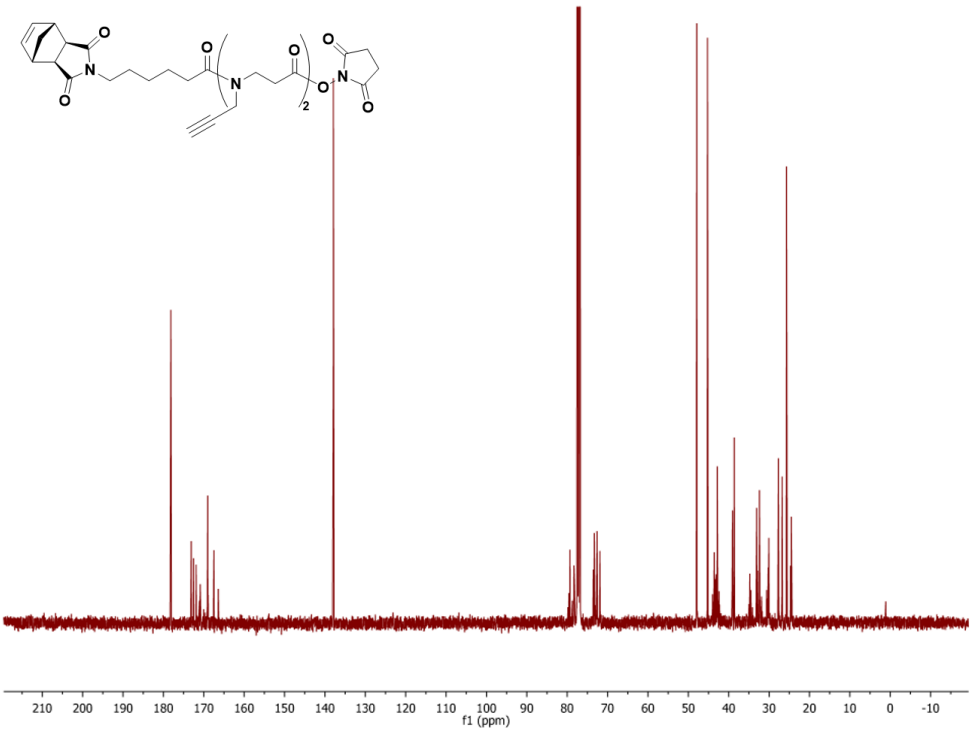


Figure S18. ^{13}C NMR Spectrum of **G2$_2$-NHS** in $CDCl_3$

Spectra Data for G2$_3$.

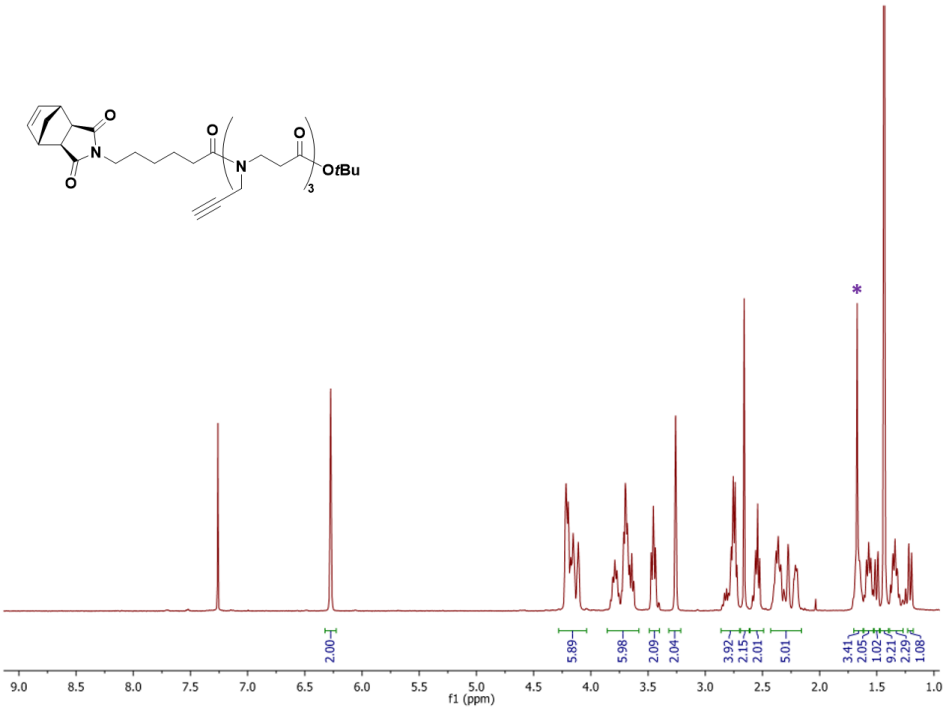


Figure S19. ^{1}H NMR Spectrum of **G2$_3$** in $CDCl_3$, * denotes minor solvent impurity.

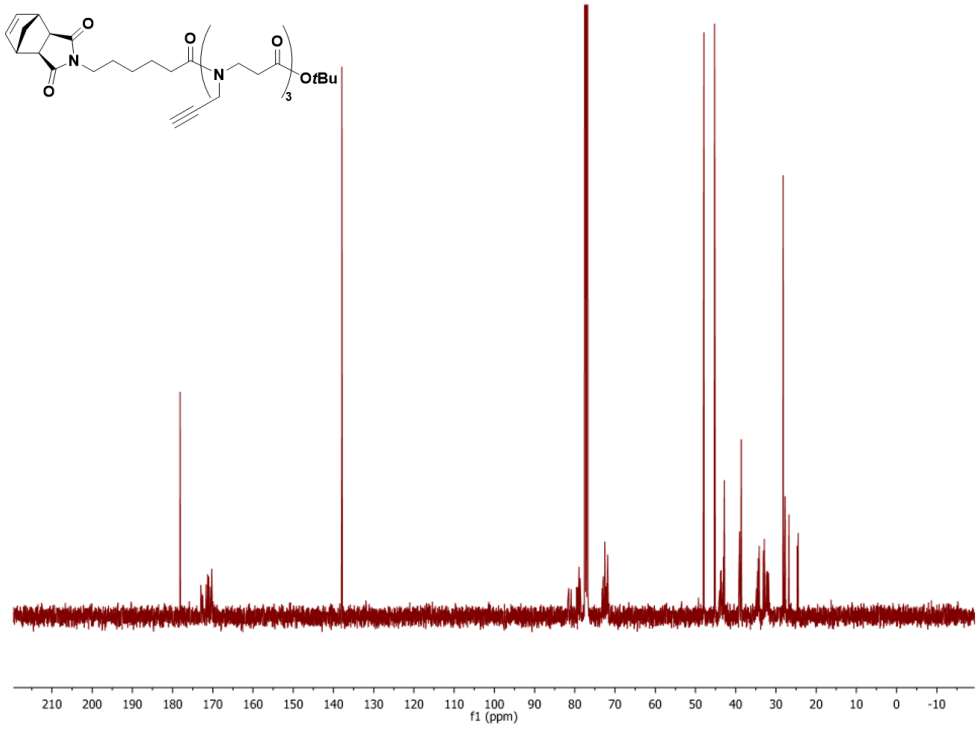


Figure S20. ^{13}C NMR Spectrum of **G2$_3$** in $CDCl_3$

Spectra Data for G2$_3$-NHS.

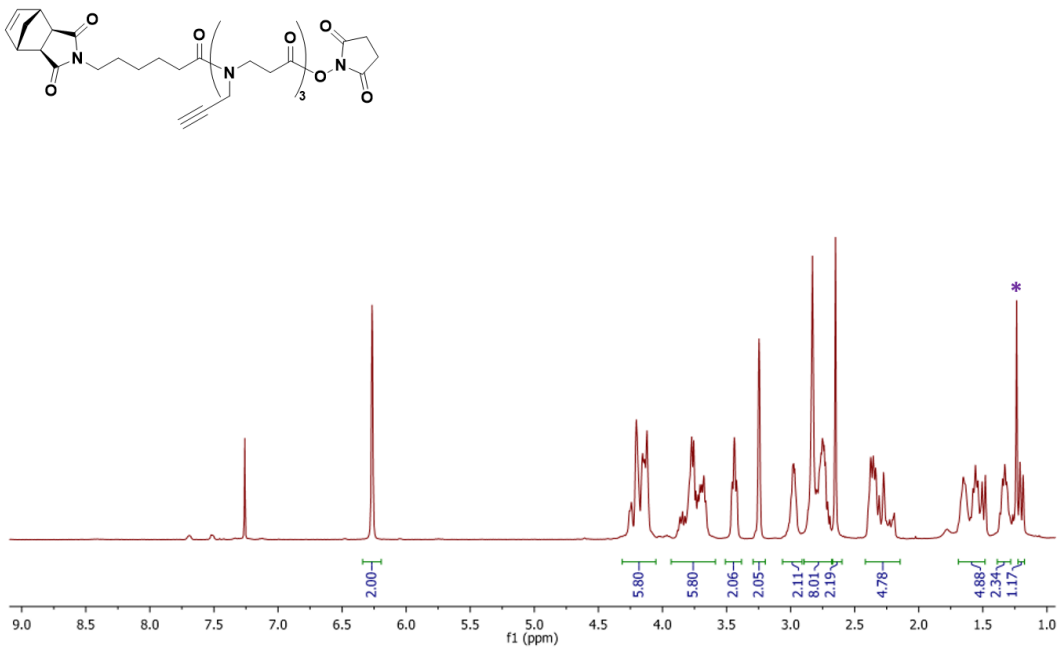


Figure S21. ^{1}H NMR Spectrum of **G2$_3$-NHS** in $CDCl_3$, * denotes minor solvent impurity.

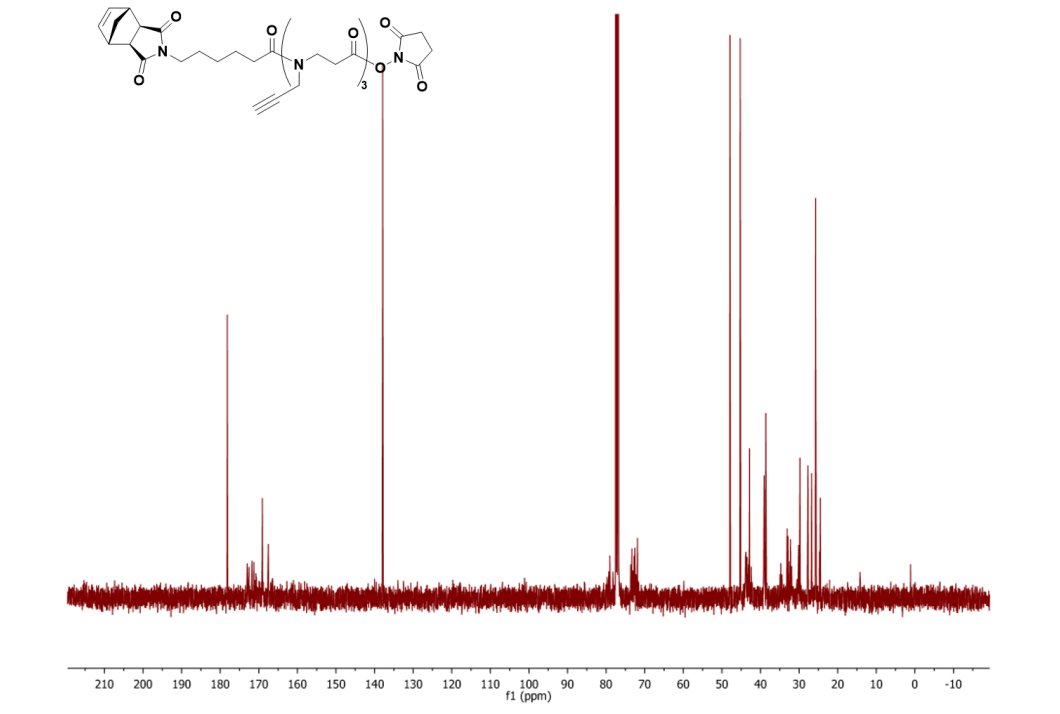


Figure S22. ^{13}C NMR Spectrum of **G2$_3$-NHS** in $CDCl_3$

4) Multivalent Macromonomers:

Spectra Data for G2-PEG.

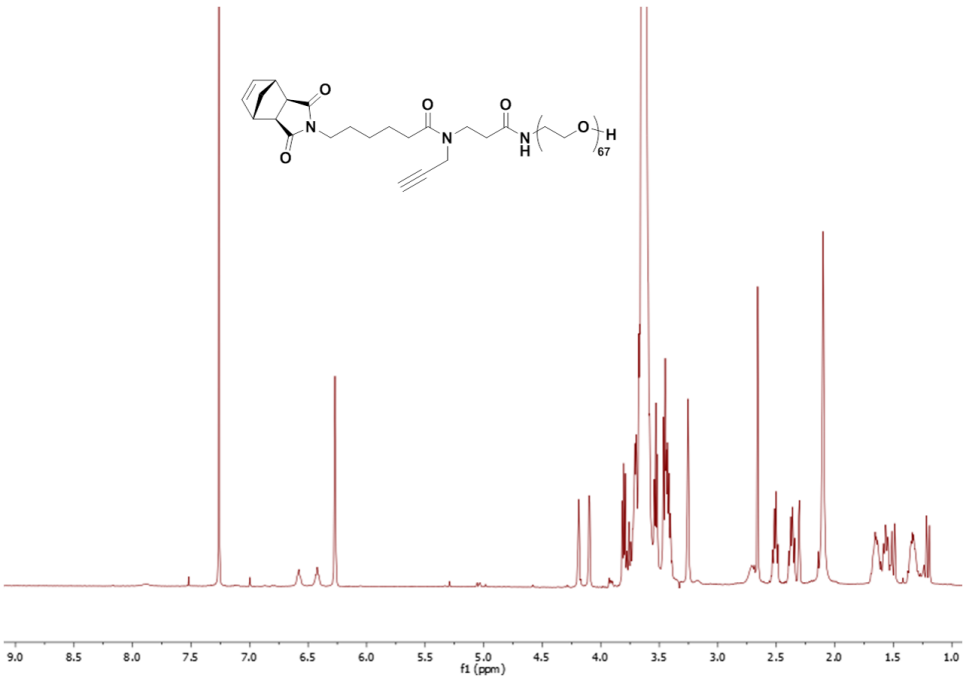


Figure S23. ^{1}H NMR Spectrum of **G2-PEG** in $CDCl_3$

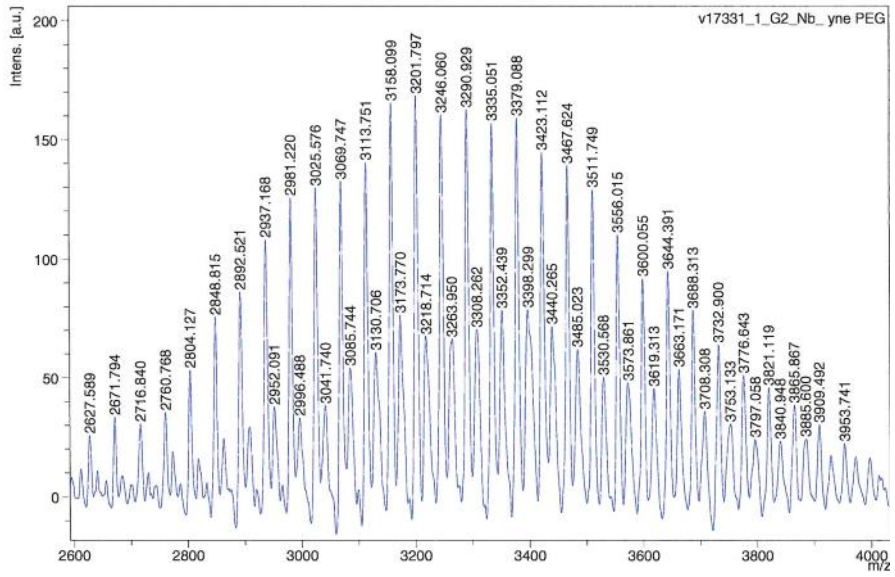


Figure S24. MALDI-TOF Spectrum of **G2-PEG**. $C_{157}H_{300}N_3O_{72}$: calcd m/z = 3380.24; Found: 3379.088 $[M + H]^+$. $C_{157}H_{302}N_3O_{73}$: calcd m/z = 3398.25; Found: 3398.299 $[M + H_3O]^+$

Spectra Data for G2$_2$-PEG.

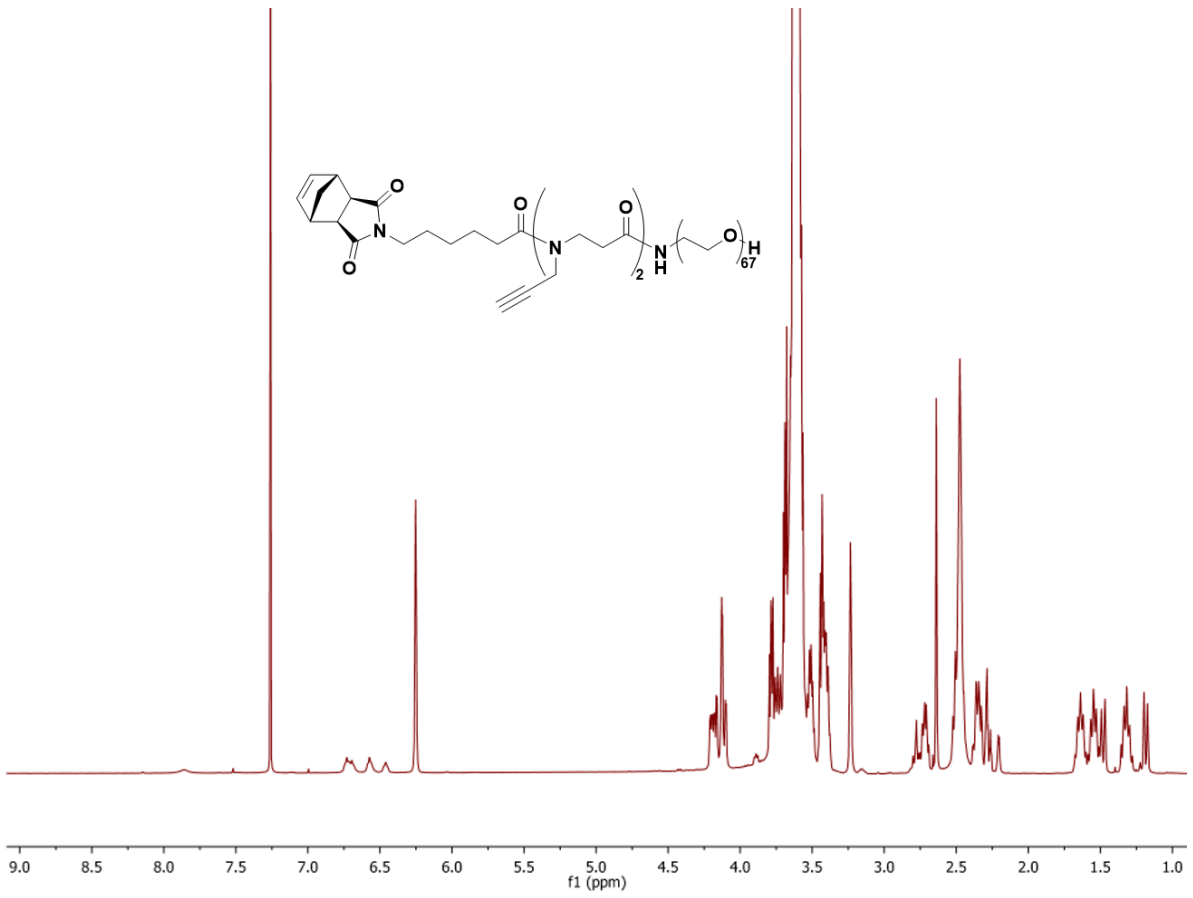


Figure S25. ^{1}H NMR Spectrum of **G2$_2$-PEG** in $CDCl_3$

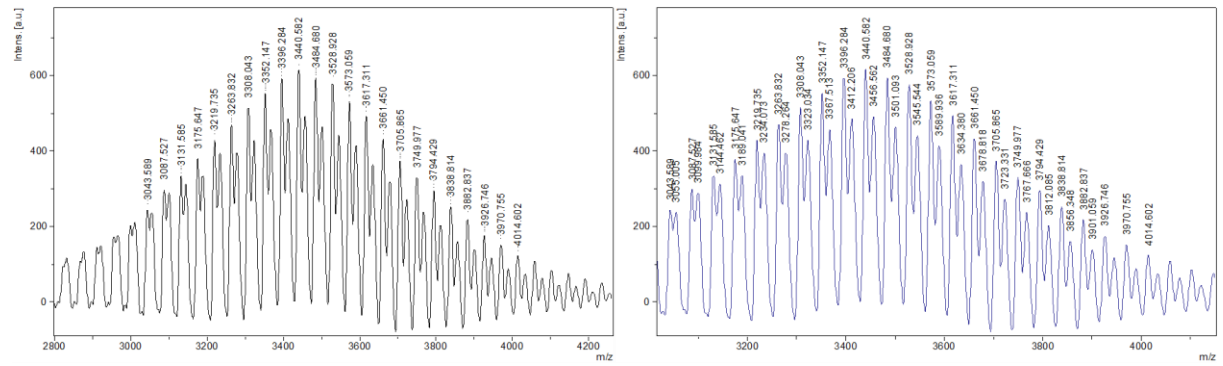


Figure S26. MALDI-TOF Spectrum of **G2$_2$-PEG**. $C_{163}H_{306}N_4O_{73}K$ calcd m/z = 3527.24; Found: 3528.928 $[M + K]^+$. $C_{163}H_{306}N_4O_{73}$: calcd m/z = 3545.25; Found: 3545.544 $[M + H_2O + K]^+$

Spectra Data for G2$_3$-PEG.

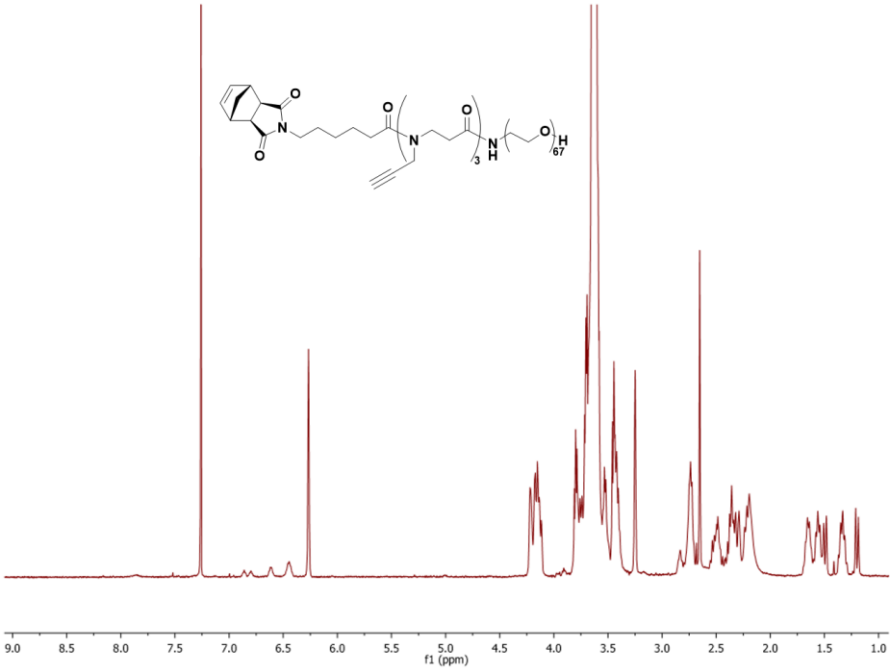


Figure S27. ^{1}H NMR Spectrum of **G2$_3$-PEG** in $CDCl_3$

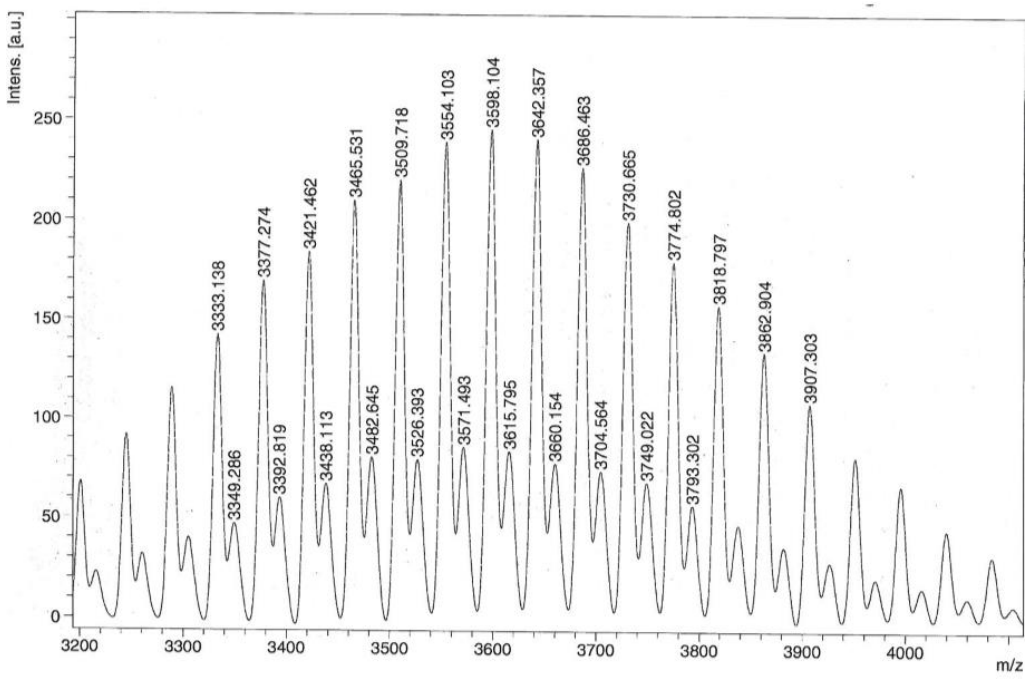


Figure S28. MALDI-TOF Spectrum of **G2$_3$-PEG**. $C_{169}H_{314}N_5O_{74}$: calcd m/z = 3598.34; Found: 3598.104 $[M + H]^+$. $C_{169}H_{316}N_5O_{75}$: calcd m/z = 3616.35; Found: 3615.795 $[M + H_3O]^+$

Spectra Data for G1-TEG.

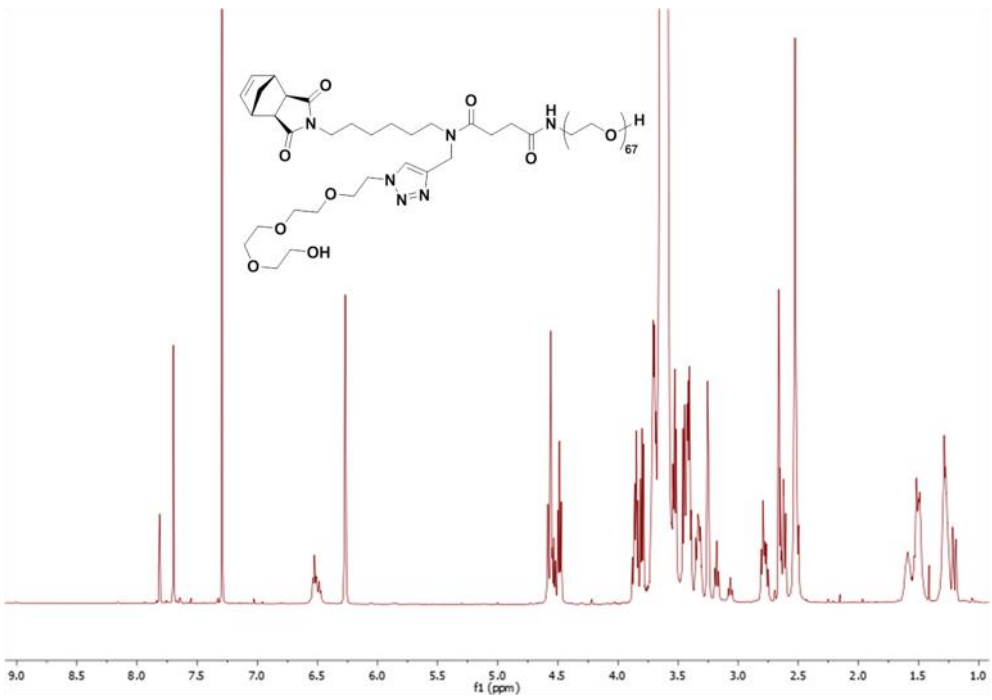


Figure S29. ^{1}H NMR Spectrum of **G1-TEG** in $CDCl_3$

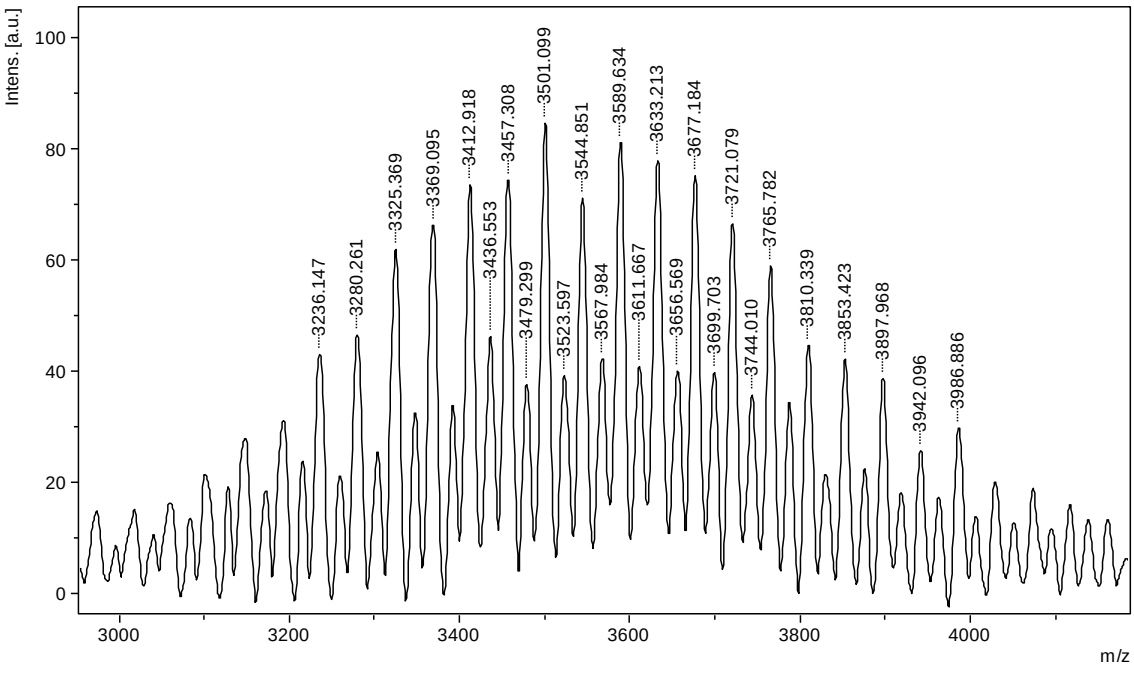


Figure S30. MALDI-TOF Spectrum of **G1-TEG**. $C_{164}H_{314}N_6O_{75}$: calcd m/z = 3591.082 $[M + Na]^+$; Found: 3589.634 $[M+Na]^+$. calcd m/z = 3569.100 $[M+H]^+$; Found: 3567.984 $[M+H]^+$

Spectra Data for TEG$_1$.

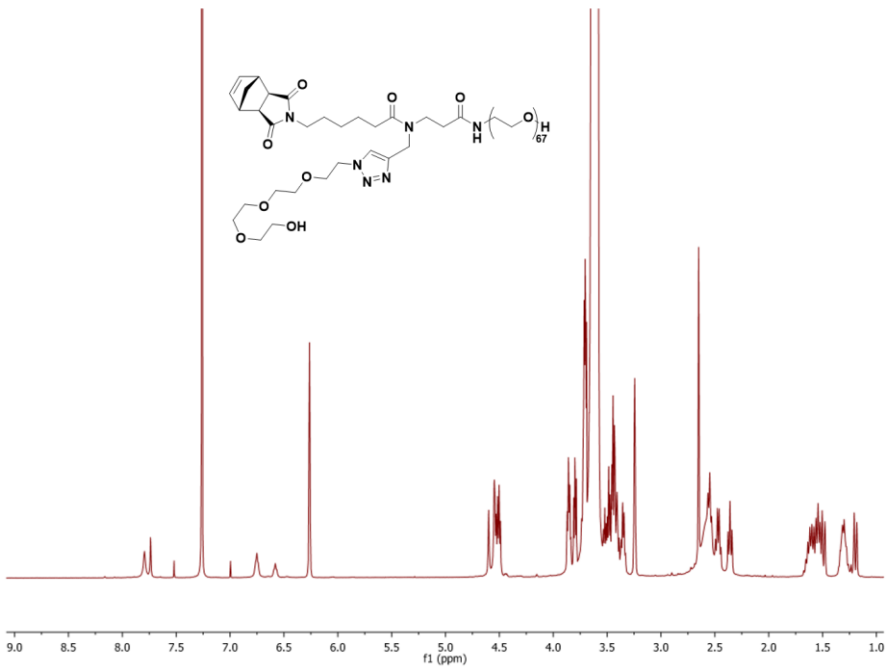


Figure S31. ^{1}H NMR Spectrum of **TEG** in $CDCl_3$

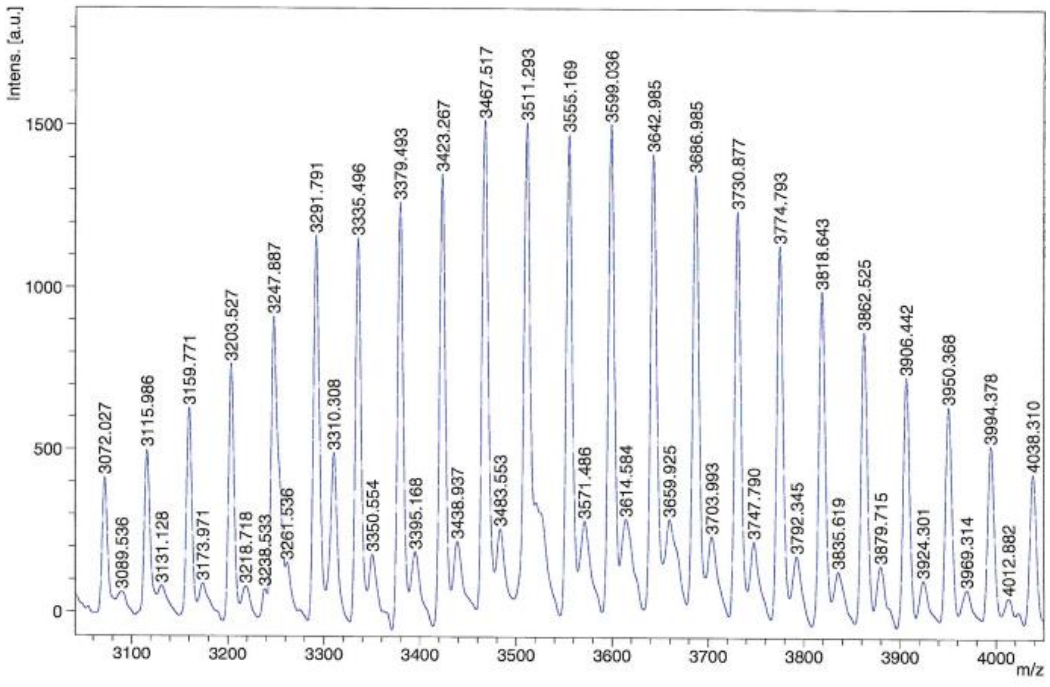


Figure S32. MALDI-TOF Spectrum of **TEG**. $C_{165}H_{317}N_6O_{76}$: calcd m/z = 3599.36; Found: 3599.036 $[M + H]^+$. $C_{165}H_{319}N_6O_{77}$ calcd m/z = 3616.35; Found: 3614.584 $[M + H_3O]^+$

Spectra Data for TEG$_2$.

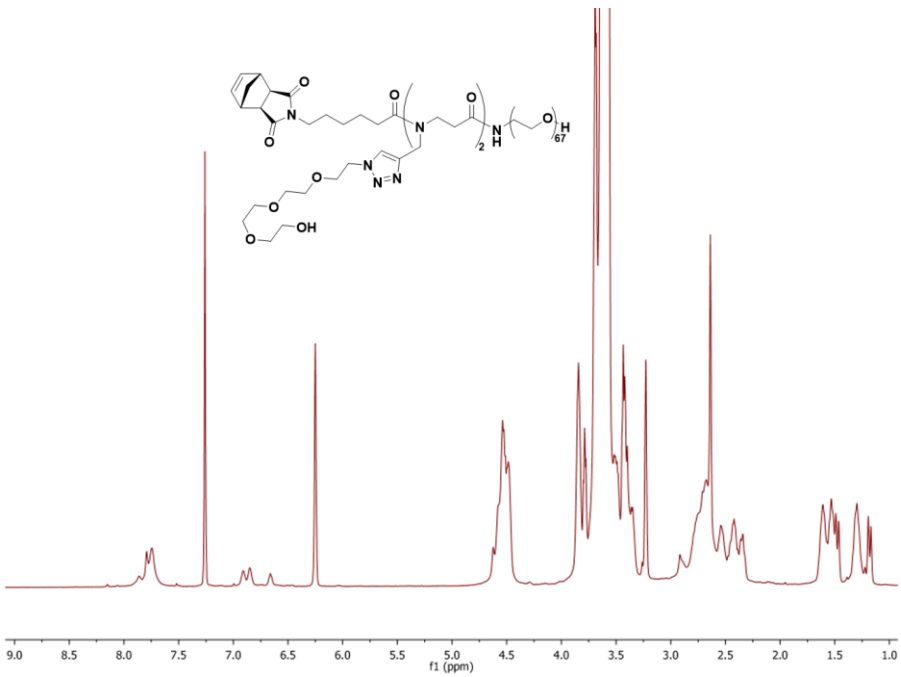


Figure S33. ^{1}H NMR Spectrum of **TEG$_2$** in $CDCl_3$

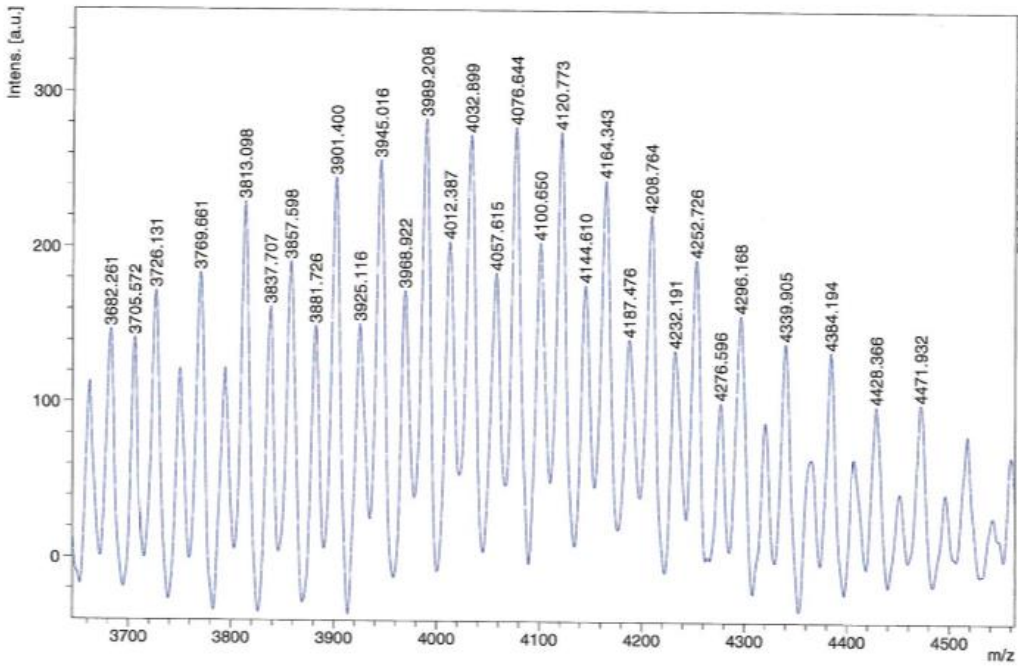


Figure S34. MALDI-TOF Spectrum of **TEG$_2$**. $C_{179}H_{341}N_{10}O_{81}$: calcd m/z = 3927.53; Found: 3925.116 $[M + H]^+$. $C_{179}H_{343}N_{10}O_{82}$: calcd m/z = 3945.54; Found: 3945.016 $[M + H_3O]^+$

Spectra Data for TEG$_3$.

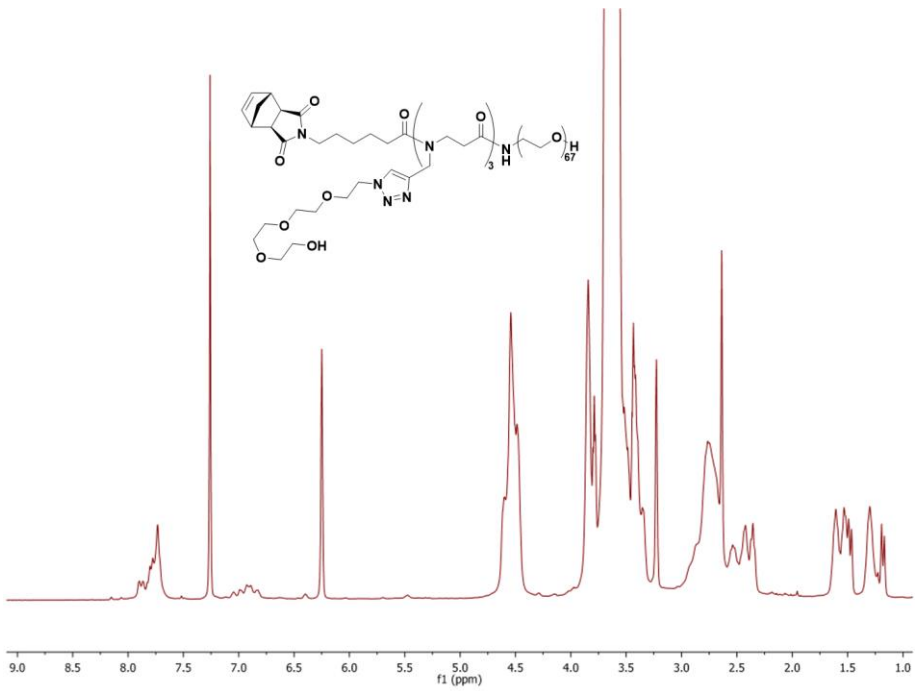


Figure S35. ^{1}H NMR Spectrum of **TEG$_3$** in $CDCl_3$

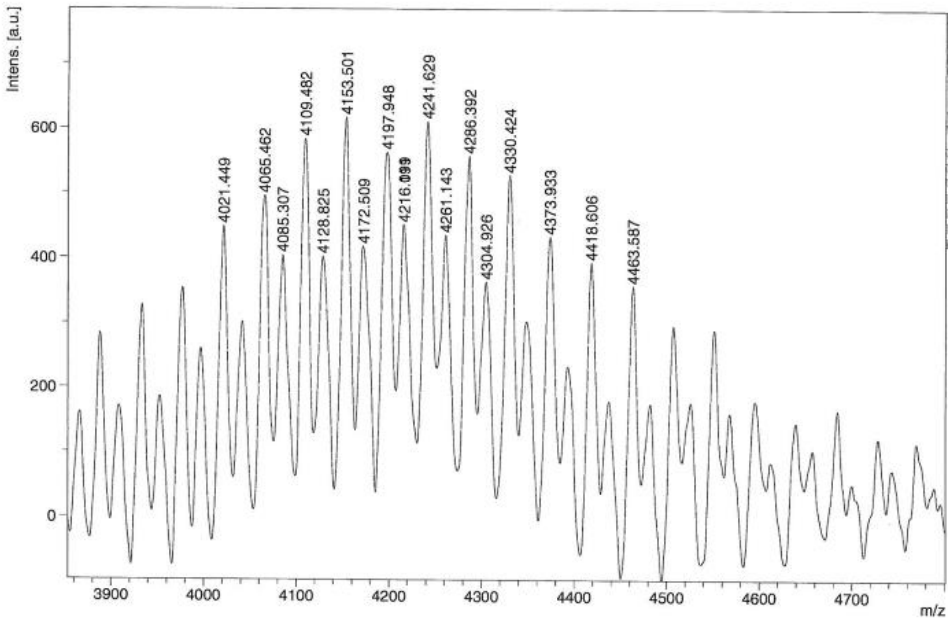


Figure S36. MALDI-TOF Spectrum of **TEG$_3$.** $C_{193}H_{364}N_{14}O_{86}Li$ calcd m/z = 4261.71; Found: 4261.143 $[M + Li]^+$. $C_{194}H_{369}N_{14}O_{87}$: calcd m/z = 4287.73; Found: 4286.392 $[M + MeOH + H]^+$

Section D. Size Exclusion Chromatography

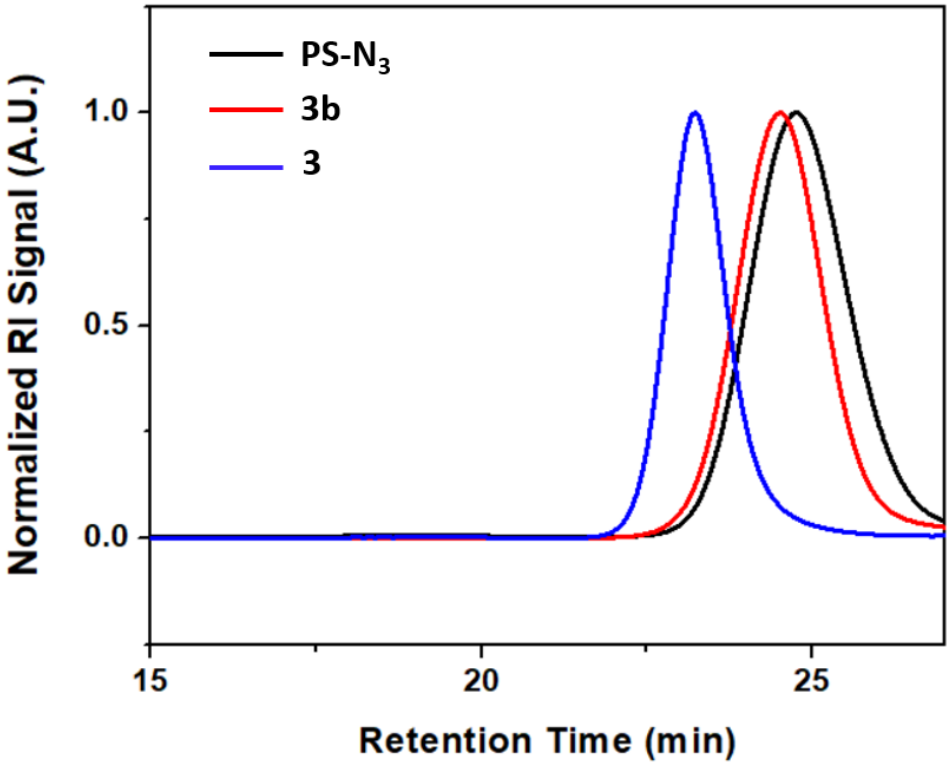


Figure S41. GPC traces of **3b** and **3**.

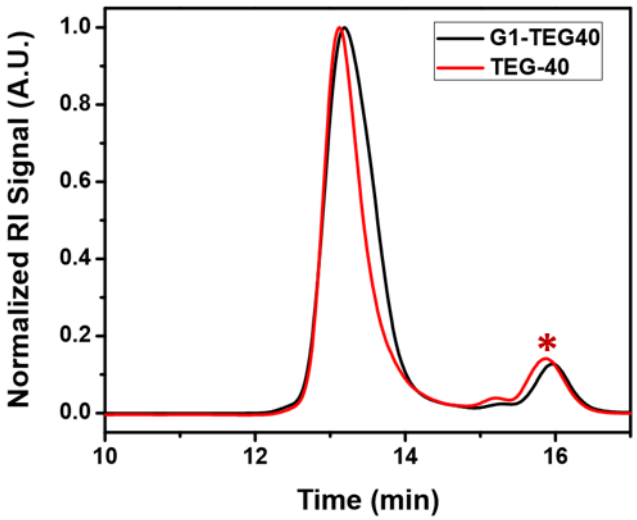


Figure S42. GPC Traces of **G1-TEG40** and **TEG40**. * indicates residual MM. The MM-to-BP conversions were determined be ≥ 90% for all polymerizations.

Section E. Supplementary Tables

Table S1. GPC Data for PS-*branch*-PLA BPPs. Molar masses were determined by comparison to PS standards.

DP	Theoretical M_n (kDa)	M_n (kDa)	M_w (kDa)	*Đ*
10	89.4	55.8	57.7	1.034
20	178.8	88.9	91.1	1.025
30	268.2	136.1	139.5	1.025

Table S2. GPC Data for TEG BPPs. Molar masses were determined by static light scattering.

Sample	*n*	DP	Theoretical M_n (kDa)	M_n (kDa)	M_w (kDa)	*Đ*
G1-TEG	1	40	144.1	180.7	210.8	1.167
TEG	1	40	143.5	159.2	191.9	1.205
TEG_2	2	40	156.6	167.6	230.8	1.377
TEG_3	3	40	169.8	175.1	240.5	1.373
TEG_3	3	10	42.4	56.9	62.9	1.104
TEG_3	3	25	106.1	115.3	137.0	1.188
TEG_3	3	35	148.6	140.2	167.4	1.194
TEG_3	3	50	212.2	206.6	247.9	1.200

Section F. References

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