Labeling Polymers and Micellar Nanoparticles via Initiation, Propagation and Termination of ROMP

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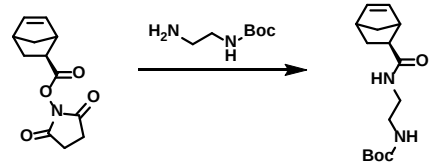
General Methods

All reagents were purchased from commercial sources and used without further purification. Anhydrous toluene and dichloromethane were purified using a Dow-Grubbs two-column purification system (Glasscontour System, Irvine, CA)[1]. Monomers **1**, **3**, **4** and **10** as well as initiator II, $(IMesH_2)(C_5H_5N)_2(Cl)_2Ru{=}CHPh$ were prepared as previously described[2-5]. Polymerizations were performed under dry dinitrogen atmospheres with anhydrous solvents. Polymer polydispersity and molecular weight were determined by size-exclusion chromatography (Phenomenex Phenogel 5u 10, 1K-75K, 300 x 7.80 mm in series with a Phenomex Phenogel 5u 10, 10K-1000K, 300 x 7.80 mm (0.05 M LiBr in DMF)) or (Jordi Gel DVB 1000A, 500 × 10 mm, ($CHCl_3$)) using a Shimadzu LC-AT-VP pump equipped with a multi-angle light scattering detector (DAWN-HELIOS: Wyatt Technology), a refractive index detector (Hitachi L-2490) and a UV-Vis detector (Shimadzu SPD-10AVP) normalized to a polystyrene standard. The dn/dc values used were 0.179 (DMF) and 0.166 ($CHCl_3$) calculated by averaging several runs for homopolymers of **3** assuming 100% mass elution from the columns. HPLC analysis was performed on a Jupiter Proteo90Å phenomenex column (150 × 4.60 mm) using a Hitachi-Elite LaChrom L-2130 pump equipped with a UV-Vis detector (Hitachi-Elite LaChrome L-2420). Purification was done using a Jupiter Proteo90 Å Phenomenex column (2050 x 25.0 mm) on a Waters DeltaPrep 300 system. Buffer A was 0.1% TFA in water and Buffer B was 99.9% ACN and 0.1% TFA. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus spectrometer (400 MHz) or Varian VX 500 spectrometer (500MHz). Chemical shifts (^1H) and (^{13}C) are reported in (ppm) relative to the residual solvent peak. UV-Vis experiments were conducted using a Hitachi U-2810 or a Thermo NanoDrop spectrophotometer. Fluorescent measurements were obtained using a Photon Technology International fluorescence detector or a Horiba fluorolog-3 fluorimeter system. DLS data was obtained on a Wyatt DynaPro Nanostar. TEM images were acquired on carbon grids (Ted Pella, INC.) with 1% uranyl acetate stain on a FEI Tecnai G2 Sphera at 200 KV. Fluorescent lifetime measurements were obtained on a Horiba fluorolog-3 fluorimeter system. MALDI-TOF mass spectrometry was performed on an ABI MALDI Voyager (equipped with ThermoLaser Science, VSL-337ND) using a matrix solution of dithranol in THF (20mg/ml), polymer in THF (10mg/ml), and CF_3COOAg in THF (10mg/ml). The matrix solution was mixed in a 10:10:1 ratio (polymer : dithranol : AgTFA). Mass spectra were obtained at the UCSD Chemistry and Biochemistry Molecular Mass Spectrometry Facility.

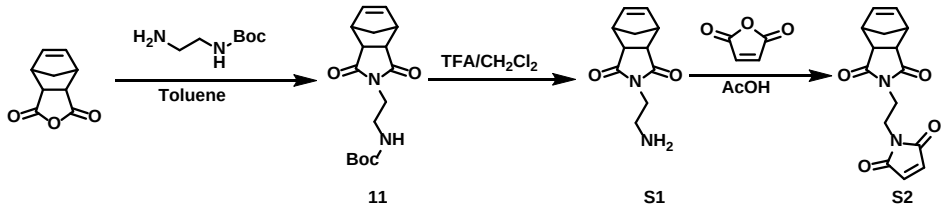
Monomer Synthesis



1 2

tert-butyl-(2-((2*S*)-bicyclo[2.2.1]hept-5-ene-2-carboxamido)ethyl)carbamate [**2**]

To a stirred solution of norbornene NHS ester **1** (538 mg, 2.28 mmol) and mono-Boc protected ethylenediamine[6] (500 mg, 3.42 mmol) in dry CH_2Cl_2 was added DIPEA (794 μL, 4.56 mmol). The reaction was left to stir under nitrogen atmosphere for 48 hrs. The reaction mixture was washed twice with 10% HCl and the organic layer dried with $MgSO_4$, filtered and concentrated to dryness to give 562 mg (88%) of **2** as a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.28-1.34 (m, 2H, 1 × CH_2, CH), 1.43 (s, 9H, CH_3), 1.67 (d, 1H, J = 8 Hz, CH_2), 1.86-1.91 (m, 1H, CH), 1.99-2.02 (m, 1H, CH), 2.89-2.91 (m, 2H, 2 × CH), 3.25-3.40 (m, 4H, 2 × CH_2), 5.09 (bs, 1H, NH), 6.07-6.14 (m, 2H, 2 × HC =CH), 6.40 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.31, 30.40, 40.22, 40.75, 41.50, 44.57, 46.30, 47.05, 79.56, 135.94, 138.10, 156.96, 176.38. LRMS (ESI), 280.84 $[M+H]^+$, HRMS, expected $[M+Na]^+$: 303.1679 , found: 303.1681.



11 S1 S2

tert-butyl-(2-(1,3-dioxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindol-2(3*H*)-yl)ethyl)carbamate [**11]**

To a stirred solution of *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (500 mg, 3.04 mmol) in 20 mL dry toluene was added mono-Boc protected ethylenediamine[6] (585 mg, 3.65 mmol) in 2 mL dry toluene. The reaction was heated to reflux with a Dean Stark trap in place for 18 hrs. Upon cooling to room temperature the reaction mixture was washed with 1 M HCl (×3) followed by $NaHCO_3$ (sat.). The organic layer was dried Na_2SO_4, filtered and concentrated to dryness to give a tan solid, 600 mg (65%). ^{1}H NMR

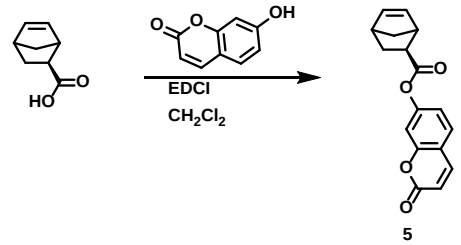
($CDCl_3$): δ (ppm) 1.24 (d, 1H, 1 × CH_2, J = 8 Hz), 1.39-1.50 (m, 10H, 3 × CH_3, CH), 2.68 (2, 2H, 2 × CH), 3.25-3.36 (m, 4H, 2 × CH, CH_2), 3.61 (t, 2H, CH_2, J = 4Hz), 4.82 (bs, 1H, NH), 6.27 (s, 2H, HC=CH). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.52, 38.64, 39.32, 43.05, 45.34, 48.09, 79.64, 138.01, 156.07, 178.41.LRMS (ESI) 307.11 $[M + H]^+$, HRMS, expected $[M+Na]^+$: 329.1472, found: 329.1475.

2-(2-aminoethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione[**S1**]

The protected amine **11** (0.60g, 1.98 mmol) was dissolved in a 1:1 TFA : CH_2Cl_2 solution (20 mL) and stirred at room temperature for 6 hrs. The reaction was concentrated to dryness to give a brown residue that was precipitated by the addition of ether. Removal of the solvent gave the free amine as a tan solid. ^{1}H NMR (CD_3OD): δ (ppm) 1.25 (d, 1H, CH_2, J = 12 Hz), 1.50 (d, 1H, CH_2, J= 12 Hz), 2.78 (s, 2H, 2 × CH), 3.14 (t, 2H, CH_2, J = 8 Hz), 3.21 (m, 2H, 2 × CH), 3.79 (t, 2H, CH_2, J = 8 Hz), 6.34 (s, 2H, HC=CH). ^{13}C NMR (CD_3OD): δ (ppm) 37.11, 39.21, 43.86, 46.50, 48.94, 139.08, 179.99. LRMS (ESI) 207.18 $[M+H]^+$, HRMS, expected $[M+H]^+$: 207.1128, found: 207.1127.

2-(2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione [**S2**]

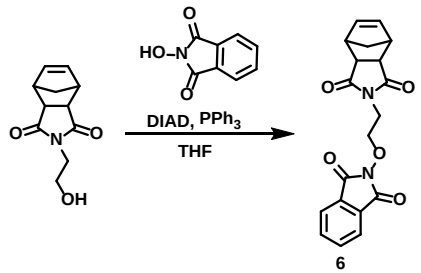
A solution of the amine **S1** (250 mg, 1.20 mmol) and maleic anhydride (238 mg, 2.40 mmol) in acetic acid (10 mL) was heated to reflux for 18 hrs. After cooling to room temperature, the solution was diluted with HCl (1 M) and extracted with CH_2Cl_2 (×3). The combined organic layers were washed with saturated $NaHCO_3$ (×2), dried Na_2SO_4, filtered and concentrated to dryness to give a brown oily solid that was purified by flash chromatography (2:1, EtOAc:Hexanes) to give 120 mg (35%) of **S2** as a white solid. . ^{1}H NMR ($CDCl_3$): δ (ppm) 1.21 (d, 1H, 1 x CH_2, J = 8 Hz), 1.46 (d, 1H, 1 x CH_2, J= 8 Hz), 2.62 (s, 2H, 2 x CH), 3.18 (s, 2H, 2 x CH), 3.65-3.70 (m, 4H, 2 x CH_2), 6.22 (s, 2H, HC=CH), 6.66 (s, 2H, HC=CH). ^{13}C NMR ($CDCl_3$): δ (ppm) 36.30, 37.44, 43.05, 45.06, 48.02, 134.32, 137.88, 170.71, 178.08. LRMS (ESI), 286.99 $[M+H]^+$, HRMS, expected $[M+H]^+$: 287.1026, found: 287.1027.



5

(2*S*)-2-*oxo*-2*H*-chromen-7-yl bicyclo[2.2.1]hept-5-ene-2-carboxylate [**5**]

A solution of *exo*-5-norbornene-2-carboxylic acid (1.00 g, 7.24 mmol), 7-hydroxycoumarin (1.41 g, 8.68 mmol) and EDCI (1.67 g, 8.68 mmol) in dry CH_2Cl_2 was stirred under nitrogen atmosphere for 48 hrs. The solvent was removed under reduced pressure to give a brown solid that was purified by flash chromatography (2:1, hexanes:EtOAc) to give **5** as a white solid, 1.02 g (50%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.47-1.61 (m, 3H, 3 × CH_2), 2.05-2.10 (m, 1H, CH), 2.50-2.54 (m, 1H, 1 × CH_2), 3.03 (s, 1H, CH), 3.25 (s, 1H, CH), 6.18-6.24 (m, 2H, HC=CH), 6.40 (d, 1H, HC=CH, J = 9.6 Hz), 7.06 (dd, 1H, Ar, J = 8.4 Hz, 2.0 Hz), 7.13 (d, 1H, Ar, J = 2.0 Hz), 7.49 (d, 1H, Ar, J = 8.4 Hz), 7.70 (d, 1H, HC=CH, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 30.61, 41.76, 43.38, 46.38, 46.83, 110.38, 115.98, 116.53, 118.40, 128.47, 135.49, 138.43, 142.83, 153.52, 154.72, 160.35, 174.20. LRMS (ESI), 282.91 $[M+H]^+$, HRMS, expected $[M+H]^+$: 283.0965, found: 283.0967.

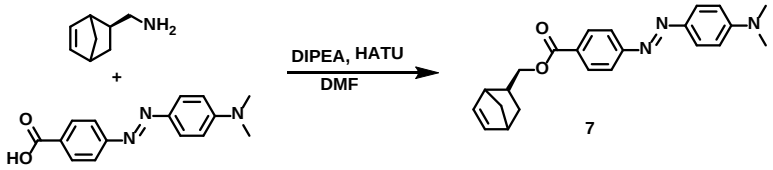


6

2-(2-((1,3-dioxoisoindolin-2-yl)oxy)ethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione [**6**]

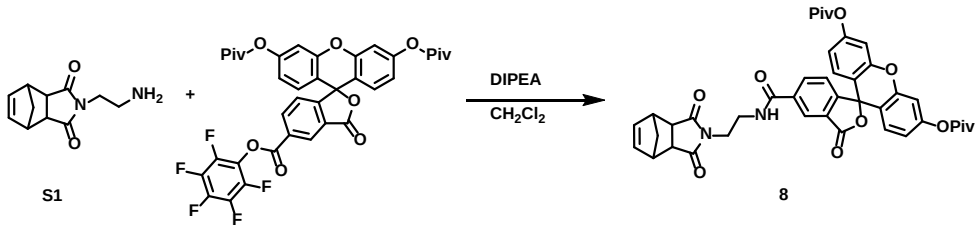
To a stirred solution of the *exo*-norbornene alcohol[7] (1 g, 4.82 mmol) in anhydrous THF (100 ml) under nitrogen atmosphere was added N-hydroxyphthalimide (4 g, 24.4 mmol) and triphenylphosphine (1.62 g, 6.18 mmol). Diisopropyl azodicarboxylate was added dropwise, allowing the solution to clear after each addition. The reaction was stirred under inert conditions for 8 hrs, after which time it was washed with H_2O (×3) followed by NaCl (sat.). The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness to give a white solid. Purification by flash chromatography (1:1 hexanes:EtOAc) gave **6** as a white powder, 1.44 g (85%). ^{1}H NMR ($CDCl_3$): δ, 1.57-

1.44 (m, 2H, 1 × CH_2), 2.76 (s, 2H, 2 × CH), 3.27 (s, 2H, 2 × CH), 3.85 (t, *J* = 10.7 Hz, 2H, 1 × CH2), 4.37 (t, *J* = 10.7 Hz, 2H, 1 × CH_2), 6.27 (s, 2H, CH=CH), 7.79-7.64 (m, 4H, 4 × CH). ^{13}C NMR ($CDCl_3$): δ (ppm) 37.85, 43.99, 45.79, 49.25, 75.56, 124.96, 129.94, 135.96, 139.20, 164.28, 179.23. LRMS (ESI), 375.36 $[M+H]^+$, HRMS, expected $[M+Na]^+$: 375.0951, found: 375.0953.



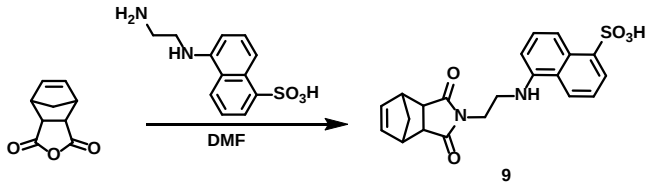
4-((*E*)-(4-(((2*S*)-bicyclo[2.2.1]hept-5-en-2-ylmethyl)amino)phenyl)diazenyl)-*N*,*N*-dimethylaniline [**7**]

To a stirred solution of the amine[3] (45.75 mg, 0.37 mmol) in DMF (1 mL) was added a solution of DABCYL (100 mg, 0.37 mmol), DIPEA (128 uL), and HBTU (140.83 mg, 0.37 mmol) in DMF. The reaction mixture was stirred under nitrogen atmosphere in the dark for 48 hrs then concentrated to dryness to give a red/orange solid. Purification by flash chromatography (3:1, hexanes:EtOAc) gave **7** as an orange solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.40-1.50 (m, 4H, 2 × CH_2), 1.7 (m, 1H, CH), 2.70 (s, 1H, CH), 2.86 (bs, 1H, CH), 3.10 (s, 6H, 2 × CH_3), 3.40-3.55 (m, 2H, CH_2), 6.11 (m, 2H, HC=CH), 6.29 (bs, 1H, NH), 6.78 (d, 2H, 2 × CH, J = 8 Hz), 7.87-7.92 (m, 6H, 6 × CH). ^{13}C NMR ($CDCl_3$): δ (ppm) 30.96, 39.23, 40.28, 41.77, 44.39, 45.12, 45.33, 111.43, 122.22, 125.36, 127.72, 134.77, 36.24, 136.91, 143.60, 152.76, 154.98, 167.02. LRMS (ESI), 375.36 $[M+H]^+$, HRMS, expected $[M+H]^+$: 375.2179, found: 375.2181.



5-((2-(1,3-dioxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindol-2(3*H*)-yl)ethyl)carbamoyl)-3-*oxo*-3H-spiro[isobenzofuran-1,9'-xanthene]-3',6'-diyl bis(2,2-dimethylpropanoate) [**8**]

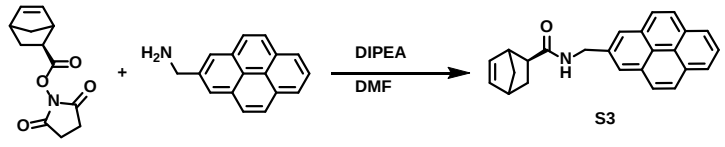
To a stirred solution of 5(6)-Carboxy-3',6'-O-dipivlicfluorescein pentafluorophenyl ester[8] (200 mg, 0.284 mmol) and norbornene amine **S1** (35.23 mg, 0.281 mmol) in dry CH_2Cl_2 was added DIPEA (98 µl, 0.563 mmol). After stirring under N_2 for 4 days the solution was concentrated to dryness and the isomers were separated by flash chromatography (7:3, Toluene : EtOAc) to give both isomers of **8** as white solids. (5)- . ^{1}H NMR ($CDCl_3$): δ (ppm) 1.24 (dd, 1H, 1 × CH_2, J = 9.9, J = 3.03 Hz), 1.37 (s, 18H, 6 × CH_3), 1.53 (dd, 1H, 1 × CH_2, J = 9.9, J = 1.50 Hz), 2.77 (s, 2H, 2 × CH), 3.31 (bs, 2H, 2 × CH), 3.72 (m, 2H, CH_2), 3.86 (m, 2H, CH_2), 6.31 (m, 2H, HC=CH), 6.81 (m, 4H, Ar), 7.07 (m, 2H, Ar), 7.26 (d, 1H, Ar, J = 7.98 Hz), 8.11 (dd, 1H, Ar, J = 7.98, J = 1.65 Hz), 8.38(s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ (ppm) 27.05, 37.94, 39.21, 40.30, 42.78, 45.24, 47.96, 81.88, 110.44, 115.52, 117.82, 123.71, 124.55, 126.56, 128.76, 134.17, 136.49, 137.78, 151.49, 152.72, 155.45, 165.78, 168.22, 176.49, 178.82. LRMS (ESI), 733.11 $[M+H]^+$, HRMS, expected 755.2575 $[M+Na]^+$:, found: 755.2581.



9

5-((2-(1,3-dioxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindol-2(3*H*)-yl)ethyl)amino)naphthalene-1-sulfonic acid [**9**]

To a dry round bottom flask containing EDANS (200 mg, 0.751 mmol) and norbornene anhydride (118 mg, 0.716 mmol) was added 8 mL of DMF and triethylamine (110 µL, 0.789 mmol). This mixture was then stirred at 130 ºC overnight under N_2. The solvent was removed under reduced pressure to give a brown oil that was purified by flash chromatography (10% MeOH, 1% TEA, and CH_2Cl_2) resulting in 286 mg of a green solid (97% yield) ^{1}H NMR (MeOD): δ (ppm) 1.15-1.22 (dd, 2H, CH_2) 2.58 (s, 2H, 2 × CH), 3.02 (s, 2H, 2 × CH), 3.34 - 3.37 (t, 2H, CH_2), 3.74 – 3.77 (t, 2H, CH_2), 6.14 (s, 2H, HC=CH), 6.60-6.62 (d, 1H, Ar), 7.31 – 7.35 (m, 2H, Ar), 7.98 – 8.11 (m, 3H, Ar). ^{13}C NMR (MeOD): δ (ppm) 38.57, 42.90, 43.69, 49.15, 105.19, 116.69, 124.04, 125.46, 125.71, 126.79, 128.72, 131.50, 138.92, 142.43, 145.29. LRMS (ESI), 413.05 $[M+H]^+$, HRMS, expected $[M+H]^+$: 413.116, found: 413.1171.



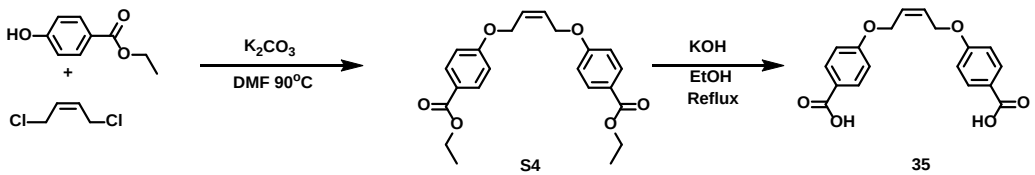
1

(2S)-*N*-(pyren-2-ylmethyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide (**S3**)

Under anhydrous conditions, **1** (102 mg, 0.432 mmol) and pyren-2-ylmethanamine (100 mg, 0.432 mmol) were added to a round bottom Schlenk flask in dry DMF (10.8 mL). DIPEA (150 μL) was added to the mixture and the solution was stirred under a nitrogen atmosphere at room temperature for one hour and then concentrated to dryness. Purification by flash chromatography in 2:2:1 toluene/hexanes/ethyl acetate followed by recrystallization from ethanol gave **S3** as a white solid, 170 mg (77%). ^{1}H NMR ($CDCl_3$) δ (ppm), 8.29-7.98 (m, 9H), 6.14-6.03 (d, 2H), 5.81 (s, 1H), 5.26-5.12 (m, 2H), 2.98 (s, 1H), 2.95 (s, 1H), 2.01 (m, 2H), 1.41-1.30 (m, 3H). ^{13}C NMR, ($CDCl_3$), δ (ppm), 174.77, 137.94, 135.58, 131.08, 130.92, 130.42, 128.76, 127.90, 127.24, 127.00, 125.08, 125.03, 124.43, 124.37. LRMS (ESI), 374.17 $[M+Na]^+$, 352.06 $[M+H]^+$, HRMS, expected 352.4403 $[M+H]^+$:, found: 352.06.

After failed attempts at determining the CMC of our ROMP-based micelles using conventional methods including the use of the solvochromatic dye pyrene we synthesized monomer **S3** for use in tagging polymers. Our hypothesis was that by polymerizing small blocks of pyrene we could increase fluorescence signal of the particle solution to allow us to observe lower concenrations of the particles and hence possibly observe the break-up of the particles. Monomer **S3** undergoes polymerization well however small blocks of **S3** resulted in excimer formation which made it unsuitable for our purposes.

Termination Agent Synthesis

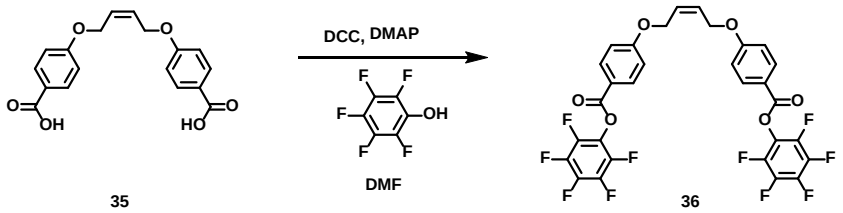


(*Z*)-diethyl 4,4'-(but-2-ene-1,4-diylbis(oxy))dibenzoate [**S4**]

To a dry round bottom flask containing ethyl 4-hydroxybenzoate (3.49 g, 21 mmol) and K_2CO_3 (4.56 g, 33 mmol) was added dry DMF (100 mL) followed by (Z)-1,4-dichlorobut-2-ene (1.25 g, 10 mmol). The mixture was stirred at 90^{o}C overnight under a nitrogen atmosphere. The reaction was cooled to room temperature, filtered and concentrated to dryness. The residue was taken up in EtOAc, washed with H_2O (×3), dried with $MgSO_4$, filtered and concentrated to dryness to give a white solid that was crystallized from ether to yield **S3**, 2.7 g (71%). ^{1}H NMR, ($CDCl_3$) δ (ppm), 8.01 (m, 4H), 6.93 (m, 4H), 5.97 (m, 2H), 4.75 (d, 4H, J=4.22 Hz), 4.35 (q, 4H, J=7.15 Hz), 1.39 (t, 6H, J=7.15 Hz). ^{13}C NMR, ($CDCl_3$) δ (ppm), 166.22, 161.89, 131.55, 128.25, 123.31, 114.10, 64.22, 60.66, 14.35. LRMS (ESI), 384.87, $[M+H]^+$, HRMS, expected 407.1465 $[M+Na]^+$:, found: 407.1467.

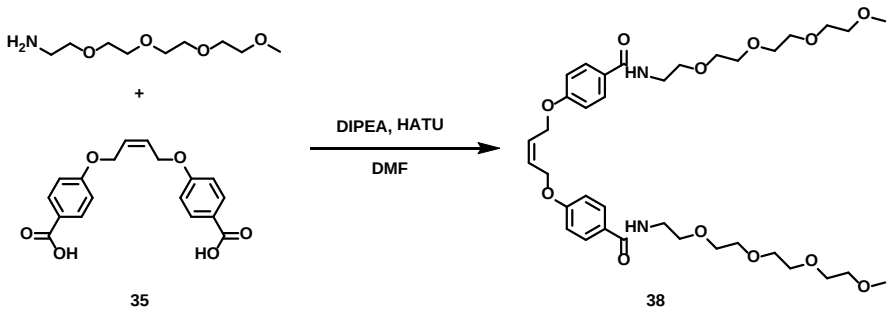
(*Z*)-4,4'-(but-2-ene-1,4-diylbis(oxy))dibenzoic acid [**35**]

To a round bottom flask containing **S4** (2.7 g, 7.0 mmol) was added EtOH (95%) containing KOH (3.93 g, 70.0 mmol). The mixture was heated to reflux for 5 hrs during which a white precipitate formed. The reaction was cooled to room temperature, diluted with water and acidified with HCl (conc.). The resulting precipitate was collected by vacuum filtration, washed with water then dried under vacuum to give **35** as a white solid in quantitative yield. ^{1}H NMR, (DMSO-d_6), δ (ppm), 7.89 (d, 4H, J=8 Hz), 7.05 (d, 4H, J=8Hz), 5.91 (m, 2H,), 4.83 (m, 4H). ^{13}C NMR, (DMSO-d_6), δ (ppm), 166.98, 161.72, 131.34, 128.33, 123.18, 114.50, 64.11. LRMS, 327.03 $[M-H]^-$, HRMS, expected: 327.0874 $[M-H]^-$, found: 327.0877.



(*Z*)-bis(perfluorophenyl) 4,4'-(but-2-ene-1,4-diylbis(oxy))-dibenzoate [**36**]

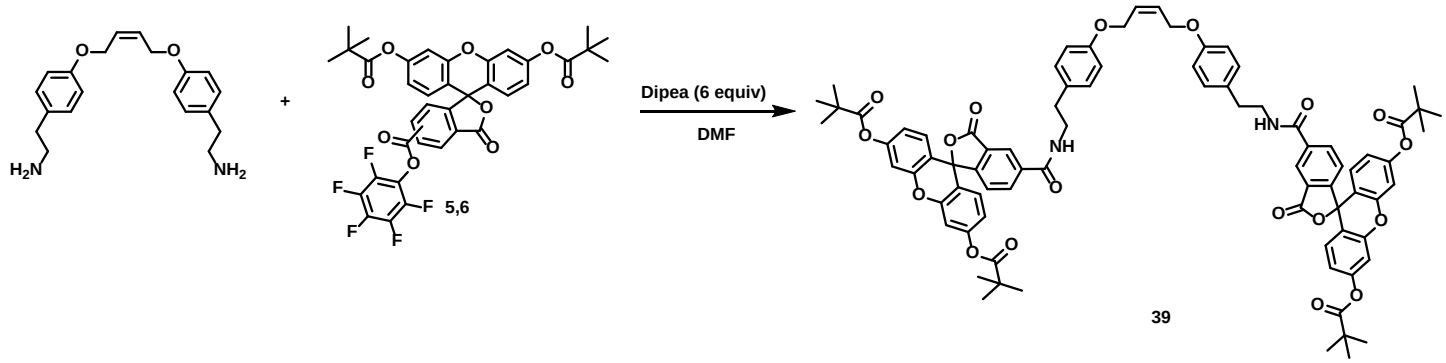
To a solution of **35** (800 mg, 2.4 mmol) DMAP (119 mg, 0.97 mmol) and pentafluorophenol (987 mg, 5.4 mmol) in dry DMF (10 mL) was slowly added a solution of DCC (1110 mg, 5.4 mmol) in dry DMF (5 mL). The solution was stirred under a nitrogen atmosphere overnight. The reaction mixture was filtered then concentrated to dryness. The residue was purified by flash chromatography (5:1, hexanes:EtOAc) to give a white/clear solid, 1.1 g (69%). ^{1}H NMR, ($CDCl_3$), δ (ppm), 8.17 (m, 4H), 7.04 (m, 4H), 6.03 (m, 2H), 4.82 (m, 4H). ^{19}F NMR, ($CDCl_3$), δ (ppm), -152 (d, 2F, J=19.74), -158.6 (t, 2F, J=19.74), 162.88 (t, 2F, J=19.74). ^{13}C NMR, ($CDCl_3$), δ (ppm), 163.40, 162.10, 142.74-136.62(C-F), 133.02, 128.20, 119.49, 114.74, 64.42. HRMS, expected 683.0523 [M+Na]+, found: 683.0522.



(*Z*)-4,4'-(but-2-ene-1,4-diylbis(oxy))bis(N-(2,5,8,11-tetraoxatridecan-13-yl)benzamide) [**38**]

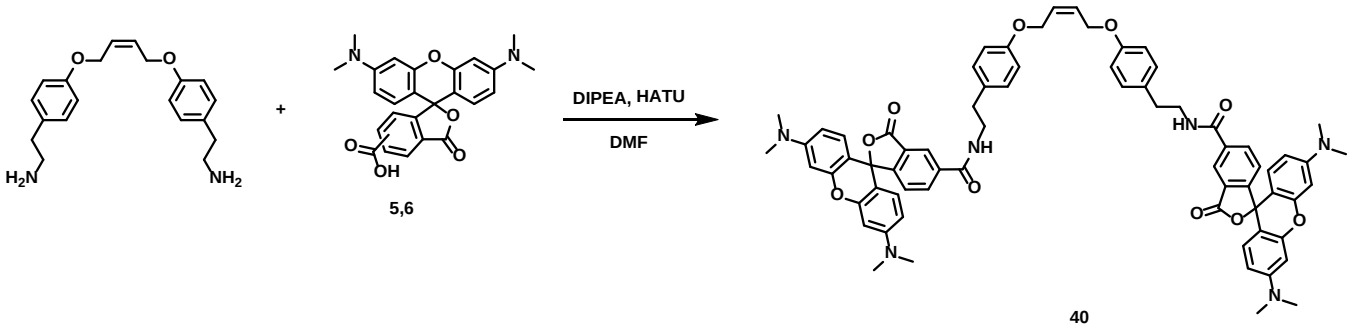
To a solution of **35** (100 mg, 0.30 mmol) in DMF (3 mL) was added DIPEA (212 μL, 1.22 mmol) and HATU (255 mg, 0.67 mmol). To this was added a solution of PEG amine (132 mg, 0.64 mmol) in DMF (300 μL). The resulting bright yellow solution was stirred under nitrogen for 48 hrs then concentrated to dryness. The residue was taken up in CH_2Cl_2 and washed with water (×2), 1M HCl (×1), dried with Na_2SO_4, filtered and concentrated to dryness. The resulting orange residue was purified by flash chromatography (10% MeOH in CH_2Cl_2) to give a pale yellow oil. ^{1}H NMR, ($CDCl_3$), δ (ppm), 7.80 (d, 4H, J=8 Hz), 7.16 (bs, 2H), 6.91 (d, 4H, J=8 Hz), 5.93 (m, 2H), 4.70

(m, 4H), 3.65 (m, 28H), 3.50 (m, 4H), 3.33 (s, 6H). ^{13}C NMR, ($CDCl_3$), δ (ppm), 167.00, 160.72, 128.98, 128.30, 127.28, 114.22, 71.78, 70.43, 70.33, 69.99, 70.10, 64.21, 58.87, 39.74. LRMS (ESI), 729.35 $[M+Na]^+$, 707.26 $[M+H]^+$, HRMS, expected 729.3569 $[M+Na]^+$:, found: 729.3566.



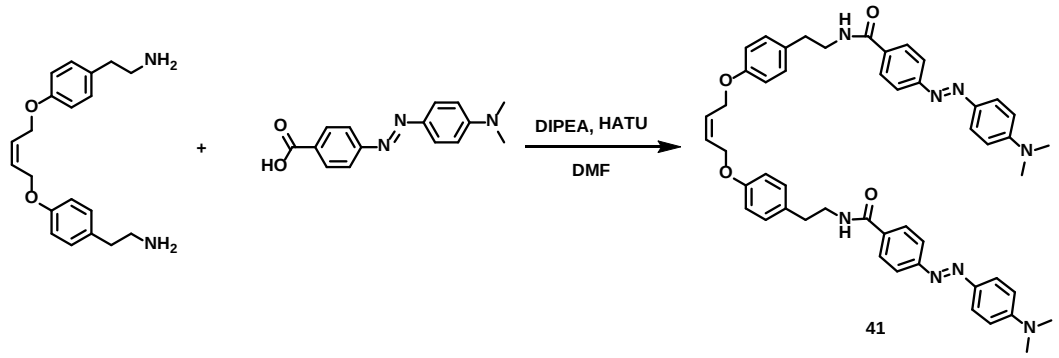
Fluorescein termination agent [**39**]

To a stirred solution of 5-carboxyfluorescein-pentafluoro phenol ester dipivlate (532 mg, 0.75 mmol) in dry CH_2Cl_2 (7 mL) was added a solution of the diamine[9] (207 mg, 0.37 mmol), and DIPEA (260 μL, 1.5 mmo) in dry CH_2Cl_2 (3 mL). The reaction was stirred under a nitrogen atmosphere for 48 hrs then washed with 1M HCl (×2) dried with $MgSO_4$, and concentrated to dryness. Purification by flash chromatography (1:1 hexanes:EtOAc) gave the desired product as a white solid (66%). ^{1}H NMR, ($CDCl_3$), δ (ppm), 8.35 (s, 2H), 8.16 (d, 2H, J=8 Hz), 7.23 (d, 2H, J=8 Hz), 7.14 (d, 4H, J=8 Hz), 7.05 (m, 4H), 6.86 (d, 4H, J=8 Hz), 6.76, (m, 8H), 5.91 (m, 2H), 4.65 (m, 4H), 3.70, (m, 4H), 2.89 (m, 4H), 1.36 (bs, 36H). ^{13}C NMR, ($CDCl_3$), δ (ppm), 176.49, 168.38, 165.56, 157.16, 155.17, 152.72, 151.50, 136.99, 134.74, 130.90, 129.73, 128.69, 128.53, 126.39, 124.50, 123.19, 117.83, 114.96, 110.43, 82.09, 64.24, 41.52, 39.17, 34.55, 27.01. LRMS (ESI), 1379.42 $[M+H]^+$, HRMS, expected 1379.5322 $[M+H]^+$, found: 1379.5316.



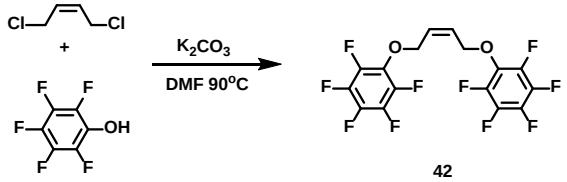
Rhodamine termination agent [**40**]

To a stirred solution of 5-carboxyrhodamine (150 mg, 0.35 mmol) in dry DMF (0.6mL) was added DIPEA (242 μL, 1.40 mmol) and HATU (132 mg, 3.50 mmol) followed by a solution of the diamine[9] (80 mg, 0.145 mmol), and DIPEA (242 μL, 1.40 mmol) in dry DMF (1 mL). The reaction was stirred under a nitrogen atmosphere for 48 hrs then precipitated by addition to cold ether and collected by centrifugation. Purification by Prep HPLC (40-50% B) followed by lylophylization gave **42** as a red powder. ^{1}H NMR, (CD_3OD), δ (ppm), 8.72 (s, 2H), 8.20 (d, 2H, 12 Hz), 7.50 (d, 2H, J=12 Hz), 7.22-6.90 (m, 20H), 5.86 (m, 2H), 4.70 (m, 4H), 3.66 (m, 4H), 3.31 (bs, 24H), 2.92 (m, 4H). ^{13}C NMR, (DMSO-d_6), 125 MHz, δ (ppm), 164.69, 156.60, 136.16, 131.60, 129.68, 114.66, 97.01, 63.83, 48.64, 41.29, 40.25, 34.15, 29.67, due to very poor solubility in all solvents not all carbons could be observed. LRMS (ESI), 1151.43 $[M+H]^+$, HRMS, expected 576.2493 $[M+2H]^{2+}$, found: 576.2500.



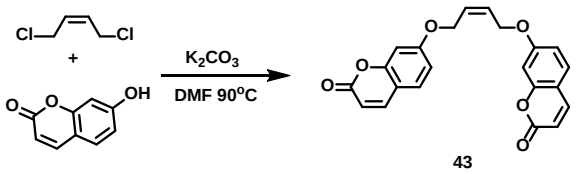
Dabcyl termination agent [**41**]

To a stirred solution of the diamine[9] (205 mg, 0.371 mmol) in DMF (6.18 mL) was added DIPEA (258.5 µL, 1.48 mmol) and let stir under N_2 at room temperature. In a separate flask, a solution of DABCYL acid (200 mg, 0.743 mmol) in DMF (6.18 mL) with DIPEA (285.5 µL, 1.64 mmol) was stirred for 5 minutes. To the basic DABCYL solution was added HATU (282 mg, 0.743 mmol) and the solution was allowed to stir for 3 minutes. The activated DABCYL solution was added to the diamine termination agent and stirred under N_2 at room temperature overnight. The orange solution was then concentrated to dryness and triturated with cold THF resulting in an orange solid (50% yield). ^{1}H NMR, (DMSO-d_6), δ (ppm),: 8.65 (t, 1H), 7.97-7.79 (m, Ar, 12H), 7.18 (d, 4H), 6.91-6.83 (m, 8H), 5.84 (t, 2H), 4.69 (d, 4H), 3.47 (q, 4H), 3.07 (s, 12H), 2.80 (t, 3H). ^{13}C NMR, (DMSO-d_6), δ (ppm),: 165.71, 156.72, 154.07, 153.02, 129.78, 128.68, 128.43, 125.28, 121.66, 114.78, 111.80, 63.98, 34.41 (note: some peaks are not visible due to poor solubility and are believed to be under the solvent peak of DMSO-d_6). LRMS (ESI), 829.34 [M+H]+, 851.37 [M+Na]+, HRMS, expected [M+H]+: 829.4176, found 829.4184.



(*Z*)-1,4-bis(perfluorophenoxy)but-2-ene [**42]**

To a flame dried flask containing K_2CO_3 (3.65g, 26.4 mmol) and dry DMF 50 mL was added a solution of pentafluorophenol (3.09 g, 16.8 mmol), in dry DMF (10 mL) followed by (Z)-1,4-dichlorobut-2-ene (1.0g, 8.0 mmol). The reaction was heated at 90^{o}C overnight under a nitrogen atmosphere. The solution was cooled, filtered, and concentrated to dryness. The oil was dissolved in ethyl acetate, washed with water (×3), dried with $MgSO_4$, filtered and concentrated to give an amber oil. Purification by flash chromatography (hexanes) gave a clear oil that crystallized over time. ^{1}H NMR, ($CDCl_3$), δ (ppm), 8.17 (m, 4H), 7.04 (m, 4H), 6.03 (m, 2H), 4.82 (m, 4H). ^{19}F NMR, ($CDCl_3$), δ (ppm), -152 (d, 2F, J=19.74), -158.6 (t, 2F, J=19.74), 162.88 (t, 2F, J=19.74). ^{13}C NMR, ($CDCl_3$), δ (ppm), 163.40, 162.10, 142.74-136.62(C-F), 133.02, 128.20, 119.49, 114.74, 64.42. HRMS, expected 683.0523 $[M+Na]^+$, found: 683.0522.



43

(*Z*)-7,7'-(but-2-ene-1,4-diylbis(oxy))bis(2H-chromen 2-one) [**43**]

To a mixture of 7-hydroxycoumarin (200 mg, 1.23 mmoles) and K_2CO_3 (268 mg, 1.94 mmol) in dry DMF (10 mL) was added (*Z*)-1,4-dichlorobut-2-ene (73 mg, 0.59 mmol). The reaction was heated to 90^{o}C overnight under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into water. The resulting precipitate was collected by vacuum filtration and dried under vacuum. Recrystallization from EtOAc/Acetone gave **43** as a white solid, 170 mg (77%). %). ^{1}H NMR, $CDCl_3$, 400MHz, 7.66 (d, 2H, J=12 Hz), 7.40 (d, 2H, J=8Hz), 6.88 (m, 2H), 6.83 (m, 2H), 6.27 (d, 2H, J=12 Hz), 5.99 (m, 2H), 4.77 (m, 4H).^{13}C NMR, $CDCl_3$, 100MHz, 161.34, 161.07, 155.76, 143.33, 128.92, 128.19, 113.36, 112.99, 112.85, 101.54, 64.63. LRMS (ESI), 399.11 [M+Na]+, 377.25 [M+H]+, HRMS, expected: 377.1020 [M+H]+, found: 377.1019.

Polymerization Reactions

General procedure for NMR-scale reactions.

A ^{1}H NMR spectrum of the monomer in CD_2Cl_2 was obtained and to this was added a solution of the catalyst in CD_2Cl_2, The solutions were mixed, and spectra obtained at 5-minute intervals after addition. Complete consumption of monomer was observed in all cases within 20 minutes of catalyst addition.

General procedure for ring-opening cross metathesis (ROCM) reactions.

To a stirred solution of catalyst (**II**) (10.0 mg, 0.0143 mmol) in dry CH_2Cl_2 (1.5 mL) was added a solution of **2** (80 mg, 0.285 mmol) and styrene (297 mg, 2.85 mmol) in dry CH_2Cl_2 (1.5 mL). After 1.5 hrs the reaction was concentrated to dryness and purified by column chromatography (7:3, toluene:EtOAc) to give the desired product as a white solid.

General procedure for ROM-ROMP reactions.

To a stirred solution of **1** (5.0 mg, 0.0212 mmol) in dry CH_2Cl_2 (1 mL) cooled to –78^oC was added a solution of catalyst (**II**) (15.42 mg, 0.0212 mmol) in dry CH_2Cl_2 (1.0 mL) also cooled to –78^oC. After 5 min, the cold bath was removed and the reaction was left to stir under nitrogen while warming to room temperature. After 40 min, a solution of **3** (108 mg, 0.424 mmol) was added and left to stir for an additional 60 min after which the reaction was quenched with ethyl vinyl ether (EVE). After 30 min the solution was concentrated to 1/3 of its volume then precipitated by addition to cold CH_3OH to give the copolymer as an off white solid characterized by ^1H NMR, SEC-MALS and MALDI.

Note: Products obtained from reactions with monomer **2** could be separated into different isomers via column chromatography.

Synthesis of Polymers 33 and 34.

To a stirred solution of **3** (324 mg, 1.37 mmol) in dry CH_2Cl_2 (10.7 mL) at -78^oC was added catalyst (**II**) (29.0 mg, 0.04 mmol). The reaction was left to stir under nitrogen while warming to room temperature. An aliquot of the reaction was removed (0.1 mL) and quenched with EVE (0.09 mL). To the remaining solution was added **10** (185 mg, 0.566 mmol) and the reaction was stirred under nitrogen at room temperature for 90 min. An aliquot of the reaction was removed (0.1 mL) and quenched with EVE (0.200 mL). The remaining solution was split into 2 aliquots (5.25 mL each) and treated with either **7** (22.8 mg, 0.061 mmol) or **9** (25.0 mg, 0.061 mmol), after 1 hr the reactions were quenched with EVE (0.20 mL), concentrated and precipitated by addition of cold ether to give block copolymers **34** and **33** respectively as powders that were characterized by SEC-MALS (Table 3 Main Text).

Synthesis of Polymers 44-47.

To a stirred solution of **3** (153 mg, 0.604 mmol) in dry DMF (6.7 mL) was added catalyst (**II**) (8.78 mg, 0.012 mmol). The reaction was left to stir under nitrogen at room temperature for 20 min. An aliquot of the reaction was removed (0.1 mL) and quenched with EVE (0.09 mL). To the remaining solution was added **10** (213 mg, 0.604 mmol) and the reaction was stirred under nitrogen at room temperature for 20 min, after which the solution was split into 4 aliquots (1.65 mL each) and quenched by adding EVE (0.09 mL), **39** (8.28 mg, 0.006 mmol, 2 equiv.), **40** (6.91 mg, 0.006 mmol, 2 equiv.), or **41** (4.97 mg, 0.006 mmol, 2 equiv.). After 1 hour, each of the respective solutions were concentrated to dryness and precipitated by addition of cold ether to give block copolymers **44, 45, 46,** and **47** respectively as glassy solids that were characterized by SEC-MALS (Table 4 Main Text).

Initiator study.

To a flame dried Schlenk flask containing a stirred solution of **39** (30 mg, 0.022 mmol, 2 equiv.) in dry CH_2Cl_2 (1.0 mL) was added a solution of the catalyst (**II**) (7.86 mg, 0.011 mmol) in dry CH_2Cl_2 (1.0 mL). The solution was stirred under nitrogen for 30 min. A solution of **3** (21.0 mg, 0.082 mmol, 25 equiv) in dry CH_2Cl_2 (1.0 mL) was added to the reaction mixture and stirred for 3 minutes. The solution was split in two with one half quenched with an excess of ethyl vinyl ether and the other half quenched with **37** (10.8 mg, 0.021 mmol, 10 equiv). After 30 minutes the solution containing **37** was treated with an excess of ethyl vinyl ether. Pure polymer samples were obtained by repeated precipitations from CH_2Cl_2 by addition to cold methanol to yield white solids that were analyzed by NMR and SEC-MALS. Ratio of units was determined by ^{1}H NMR by comparing Pivalic protons of **39** to Phenyl protons of **3** to Boc protons of **37.** EVE terminated polymer: 1 : 30 : 0, polymer terminated with **37**: 0.8 : 37 : 1. SEC-MALS: EVE terminated polymer: M_w = 7527, M_n/M_w = 1.01, polymer terminated with **37**: M_w = 7506, M_n/M_w = 1.00.

Termination efficiency studies.

General Procedure: A ^{1}H NMR spectrum of catalyst (**II**) (1.98 mg, 2.72 μmoles) in CD_2Cl_2 was recorded. A solution of monomer **11** (10.0 mg, 32.6 μmoles) in CD_2Cl_2 (0.1 mL) was added to the NMR tube and vortexed for several seconds to ensure complete mixing. After 20 min a ^{1}H NMR was recorded of the corresponding polymer. A solution

of TA **36** (3.6 mg, 5.44 μmole) in CD_2Cl_2 (100 μL) was added to the NMR tube and vortexed to ensure complete mixing. ^1H NMR spectra were recorded at various time points to monitor the reaction. After 60 min, complete reaction was observed by a shift in the alkylidene peak and the reaction was treated with ethyl vinyl ether.

Conjugation efficiency study.

To a solution of polymer **12** (20.0 mg, 3.15 μmol) in dry CH_2Cl_2 (2.0 mL) was added 4-hydroxycoumarin (2.55 mg, 15.7 μmol) followed by diisopropyl ethylamine (5.5 μL, 31.5 μmol). The reaction was stirred at room temperature under nitrogen overnight then concentrated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and precipitated by addition to cold methanol. This was repeated 3 times to give the polymer as a white solid.

UV Analysis

Determination of the number of coumarin units in a polymer was determined from the ratio of extinction coefficients at 325 nm for polymer vs. monomer.

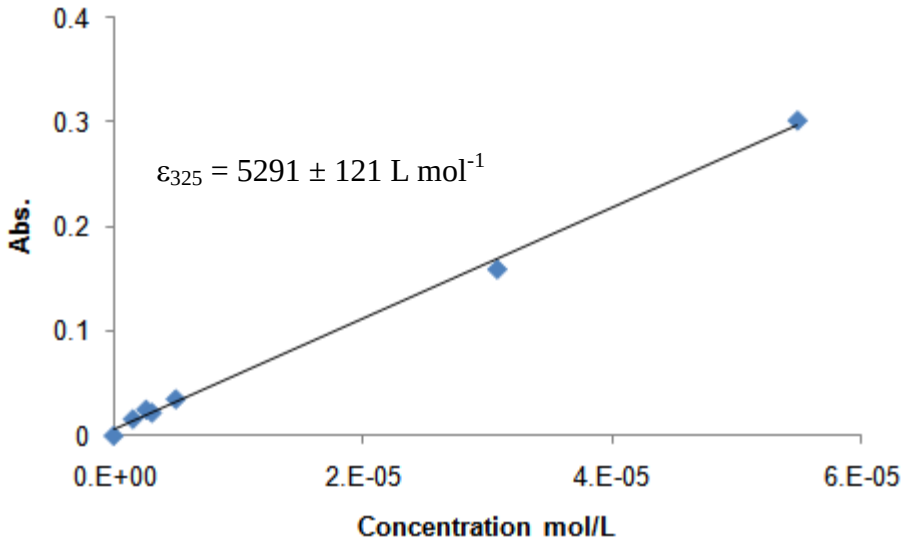


Figure S1: Plot of UV absorption vs. concentration for monomer **5** in chloroform.

Table S1: UV data obtained for polymers **18**, **23**, **27**, and **28** of Table 2 (Main Text)

Polymer	Conc. (mol/L)	Abs. (325 nm)	$\varepsilon_{det.}$	Number[a]
18	9.68E-07	0.01825	18860	3.6
23	2.60E-06	0.014	5385	1.02
27	4.84E-05	0.2596	5409	1.02
28	1.35E-04	0.7194	5329	1.00

[a] determined by the ratio of $\varepsilon_{det}/\varepsilon_5$

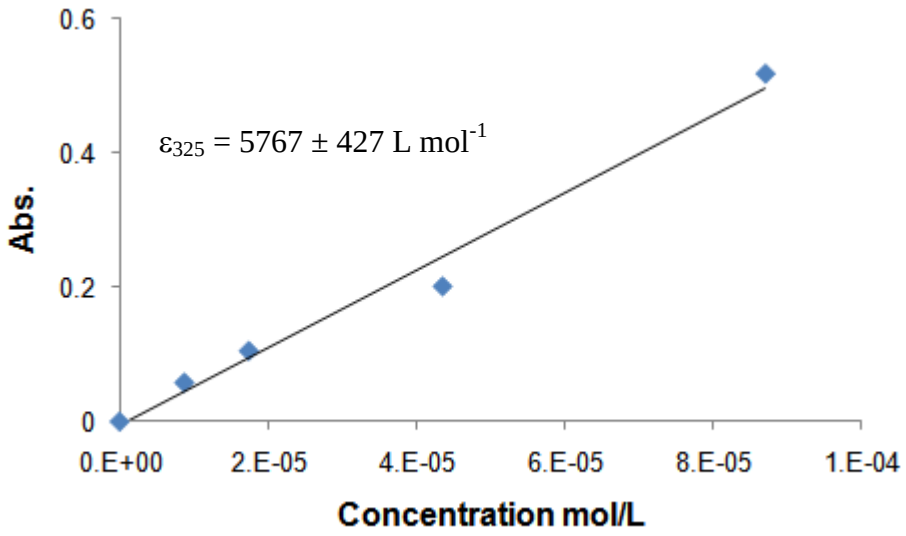


Figure S2: Plot of UV absorption vs. concentration for polymer **24** in chloroform.

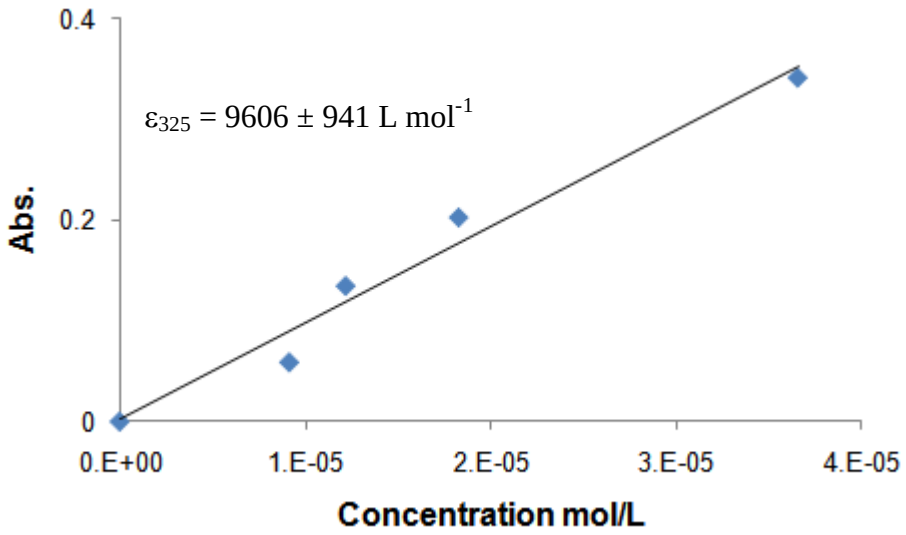


Figure S3: Plot of UV absorption vs. concentration for polymer **25** in chloroform.

Determination of the number of fluorescein units in a polymer was determined from the ratio of extinction coefficients at 510 nm for polymer vs. 5/6-carboxyfluorescein.

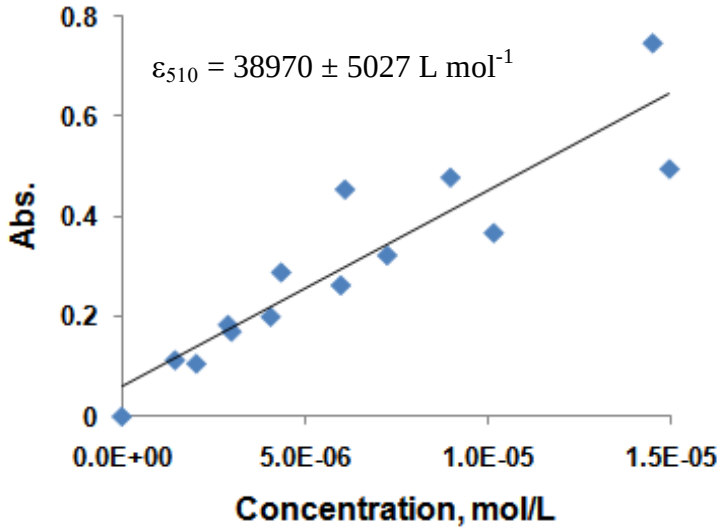


Figure S4: Plot of UV absorption vs. concentration for 5/6-carboxyfluorescein in DMF.

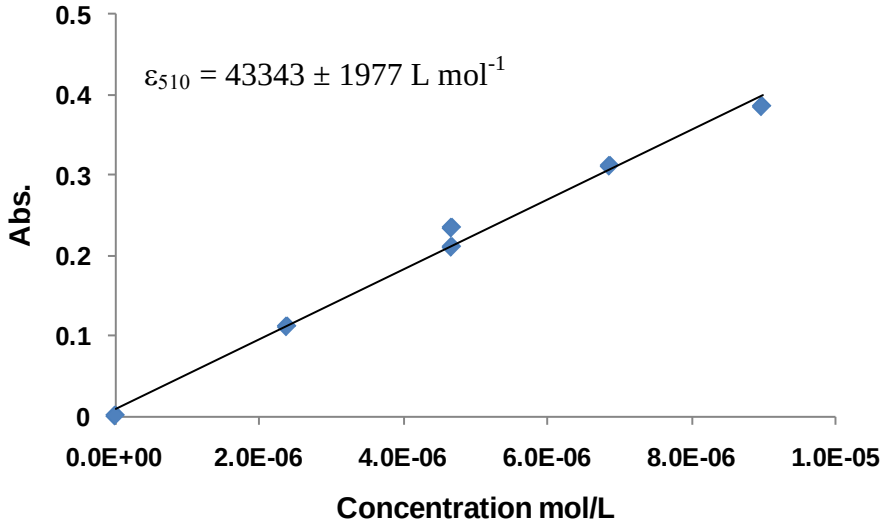


Figure S5: Determination of the molar absorptivity for polymer **32** (Table 2 main text). Plot of UV absorption vs. concentration for polymer **32** in DMF.

Particle Preparation

Preparation of P1 and P2. 5 mg of polymer was dissolved in 1 mL of DMF and transferred to a 3500 MWCO snakeskin dialysis tubing. This solution was dialyzed against 1 L of 50 mM Tris, 0.1% NaN_3 at pH 7.4 over 2 days with 2 buffer changes. The resulting opalescent solution was then concentrated by ½ the volume and centrifuged at 13,500 rpm for 5 min. The remaining supernatant was analyzed by DLS and TEM.

Preparation of P3. 3.6 mg of **33** and 4.1 mg of **34** were dissolved in 1 mL of DMF and transferred to a 3500 MWCO snakeskin dialysis tubing. This solution was dialyzed against 2 L of 50 mM Tris, 0.1% NaN_3 at pH 7.4 over 2 days with 2 buffer changes (note: a small amount of orange precipitate formed during dialysis). The orange, opalescent solution was then concentrated by ½ the volume and centrifuged at 13,500 rpm for 5 min. The remaining supernatant was analyzed by DLS and TEM.

Preparation of P4 – P7. 1 mg of polymer was dissolved in 1 mL of DMSO followed by addition of 1 mL of H_2O drop-wise giving a final concentration of 0.5 mg/mL of polymer in 1:1 DMSO:H_2O. This solution was transferred to a 3500 MWCO snakeskin dialysis tubing and dialyzed against 2 L of nanopure water. After 24 hrs, the solution was transferred to a 10,000 MWCO snakeskin dialysis tubing with continued dialysis against 2 L of water for 48 hrs with two water changes (note: for **P7** a small amount of orange precipitate formed during dialysis, this sample was centrifuged at 13,500 rpm for 5 min prior to analysis and use) .

Preparation of P8. A solution of polymer **45** in DMSO (1.7 µL, 11mg/mL) and a solution of **44** in DMSO (220 µL, 8.5 mg/mL) was added to 1.7 mL of DMSO, giving a final polymer concentration of 1 mg/mL (DMSO). To this solution, 1.9 mL of water was added drop-wise, resulting in an opalescent solution at a concentration of 0.5 mg/mL (1:1 DMSO:H_2O). This solution was transferred to a 3500 MWCO snakeskin dialysis tubing and dialyzed against 2 L of nanopure water. After 24 hrs the solution was transferred to a 10,000 MWCO snakeskin dialysis tubing with continued dialysis for 48 hrs against 2 L of nanopure water with two subsequent water changes.

Preparation of P9. A solution of polymer **45** DMSO (2.3 µL, 8.3 mg/mL) and a solution of polymer **46** in DMSO (675 µL/5.6 mg/mL) was added to 3.1 mL of DMSO, resulting in a final polymer concentration of 1 mg/mL (DMSO). To this solution was added 3.8 mL of H_2O, drop-wise followed by 30 µL of 4 M NaOH to keep the solution opalescent. This 0.5 mg/mL solution was then transferred to a 3500 MWCO snakeskin dialysis tubing and dialyzed against 1 L of nanopure water. After 24 hrs the solution was transferred to a 10,000 MWCO snakeskin dialysis tubing with continued dialysis for 48 hrs against 1 L of nanopure water with two water changes.

Preparation of P10. A solution of polymer **45** in DMSO (1.7 µL, 11 mg/mL) and a solution of **47** in DMSO (553.1 µL, 6.8 mg/mL) were added to 3.2 mL of DMSO, resulting in a final polymer concentration of 1 mg/mL (DMSO). To this solution was added 3.8 mL of H_2O, drop-wise. The solution was transferred to a 3500 MWCO snakeskin dialysis tubing and dialyzed against 2 L of nanopure water. After 24 hrs the solution was transferred to a 10,000 MWCO snakeskin dialysis tubing with continued dialysis for 48 hrs against 2 L of nanopure water with two water changes (note: a small amount of orange precipitate formed during dialysis, this sample was centrifuged at 13,500 rpm for 5 min prior to analysis and use).

Preparation of P11. A solution of polymer **45** in DMSO (1.7 µL, 11 mg/mL) and a solution of **46** in DMSO (200.1 µL, 9.4 mg/mL) were added to 1.7 mL of DMSO, resulting in a final polymer concentration of 1 mg/mL (DMSO). To this solution was added 1.9 mL of H_2O dropwise. The solution was transferred to a 3500 MWCO snakeskin dialysis tubing and dialyzed against 2 L of nanopure water. After 24 hrs the solution was transferred to a 10,000 MWCO snakeskin dialysis tubing with continued dialysis for 48 hrs against 2 L of nanopure water with two water changes.

Polymer Concentration Determination

P1 – P3. The concentration of each of the labeled polymers within the particle solutions was determined by UV-Vis using the following extinction coefficients: EDANS, ε_{335} = 5,900 $M^{-1}cm^{-1}$, DABCYL, ε_{453} = 32,000. **P1** = 86.4 µM, **P2 =** 23.9 µM and **P3** = 54.9 µM with respect to EDANS and 12.5 µM with respect to DABCYL.

General Procedure for P5 – P11. The concentration of each labeled polymers within the particle solutions was determined by UV-Vis as follows: A known volume of stock particle solution was concentrated to dryness and re-dissolved in a known volume of DMSO and/or DMSO containing 5% NH_4OH and the absorbance was measured by a UV-Vis. The extinction coefficients were calculated in each of the respective solvents and determined to be the following ($M^{-1}cm^{-1}$): Rhodamine (DMSO), ε_{552} = 164.6 ± 13.4. DABCYL (5% NH_4OH/DMSO), ε_{428} = 14,035 ± 2487 and ε_{514} = 2,379 ± 283. Fluorescein (5% NH_4OH/DMSO), ε_{428} = 52.1 ± 14.93 and ε_{514} = 4322 ± 330.5 (note: no significant absorbance was measured for rhodamine in 5% NH_4OH/DMSO, or for fluorescein in DMSO).

P5 and **P7.** 400 µL of **P5** and **P7** was concentrated to dryness and re-dissolved in 150 µL of 5% NH_4OH/DMSO. [Fluorescein] in **P5 =** 27.0 µM. [DABCYL] in **P7** = 41.2 µM

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P6. 1,200 µL of **P6** was concentrated to dryness and re-dissolved in 125 µL of DMSO. [Rhodamine] = 38.6 µM

P8: 550 µL of **P8** was concentrated to dryness and re-dissolved in 125 µL of 5% NH_4OH/DMSO. [Fluoroscein] = 6.4 µM. Since the EVE does not have a specific absorption, the concentration could not be determined by UV-Vis.

P9 and **P10**: 1,550 µL of **P9** and **P10** were concentrated to dryness and re-dissolved in 125 µL of DMSO. [Rhodamine] in **P9** = 39.7 µM, **P10** = 47.5 µM. Add 6.25 µL of 5% NH_4OH to the solutions to deprotect the fluorescein. [Fluorescein] in **P9** = 4.31 µM, **P10** = 6.64 µM.

P11: 225 µL of **P11** was concentrated to dryness and re-dissolved in 150 µL of 5% NH_4OH/DMSO. The absorbance at 428 nm and 514 nm was measured by UV-VIS and using equations 1 and 2 below the concentration was determined for to be 29.7 µM for DABCYL and 19.9 µM for fluorescein.

$$A_{428} = \varepsilon_{D428}C_D + \varepsilon_{F428}C_F \quad (1)$$

$$A_{514} = \varepsilon_{D514}C_D + \varepsilon_{F514}C_F \quad (2)$$

Fluorescence Measurements

Fluorescence of P1 – P3. Particles **P1** and **P2** were diluted to 54.9 µM and 12.5 µM respectively with 50 mM Tris buffer (pH 7.4). Emission scans of particles **P1 – P3** were performed with λ_{ex} = 335 nm (excitation of EDANS).

Fluorescence of P5 – P11. Dilutions of particles **P5 - P11** were made according to table 5. An emission scan was measured for each of the particles except **P10** (only used for fluorescence lifetime measurements), exciting at a wavelength of 470 nm.

Table S2. Particle concentrations used for fluorescent measurements

Particle	Final Concentration in 5% NH_4OH/H_2O (μM)
P5	4.15 μM fluorescein
P6	36.7 μM rhodamine
P7	6.19 μM DABCYL
P8	4.15 μM fluorescein
P9	4.15 μM/37.7 μM fluorescein/rhodamine
P10	4.15 μM/6.19 μM fluorescein/DABCYL
P11	4.15 μM/29.7 μM fluorescein/rhodamine

Distance distribution of **P5, P10,** and **P11** via fluorescent lifetime: A range of D–A distances are considered where the distance is expressed as a probability function *P(r)* distributed along the *r* axis. A Gaussian distribution was used to describe the distance distribution, as in the equation below:

$$P(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\bar{r} - r}{\sigma}\right)^2\right] \quad (3)$$

In this equation $\bar{r}$ is the mean of the Gaussian with a standard deviation of σ. The distance distribution is described by two standard deviations from the mean, with the probability of finding donor and acceptor within this range as 95.4%. The donor intensity decay is a summation of the intensity decays for all accessible distances, and is written as:

$$I_{DA}(t) = \int_{r=0}^{\infty} P(r) I_{DA}(r,t)\, dr$$

$$= I_D^0 \int_{r=0}^{\infty} P(r) \exp\left[-\frac{t}{\tau_D} - \frac{t}{\tau_D}\left(\frac{R_0}{r}\right)^6 \right] dr \qquad (4)$$

This expression indicates that the intensity decay for an ensemble of flexible D–A pairs is given by the weighted average of the decays for each D–A distance. From this analysis, the distance distribution is calculated as 6.57 ± 0.14 nm nm for **P10** and 6.55 ± 0.08 nm for **P11** shown in Figure 11d and 11e and written as *r*.

The lifetime in **P10** and **P11** (τ_{DA}) was then calculated from the standard treatment of FRET efficiency (*E*):

$$E = \frac{R_0^6}{R_0^6 + r^6} \qquad (5)$$

where R_0 is the Förster distance between donor and acceptor, applied as 47 Å for **P10** (fluorescein and dabcyl) and 55 Å for **P11** (fluorescein and rhodamine) in this work assuming that rotation of the dyes is free and that therefore the orientation factor, $\kappa^2 = 2/3$. The transfer efficiency can then be used to calculate the lifetime of the donor-acceptor (τ_{DA}):

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \qquad (6)$$

In this work, lifetimes of Fluorescein-labeled micelle (**P5**), Fluorescein-DABCYL labeled micelle (**P10**) and Fluorescein-Rhodamine labeled micelles (**P11**) were obtained as 3.01 ± 0.22 ns, 2.66 ± 0.23 ns and 2.23 ± 0.13 ns respectively from fluorescence lifetime measurements (see Figure 11 in the Main text).

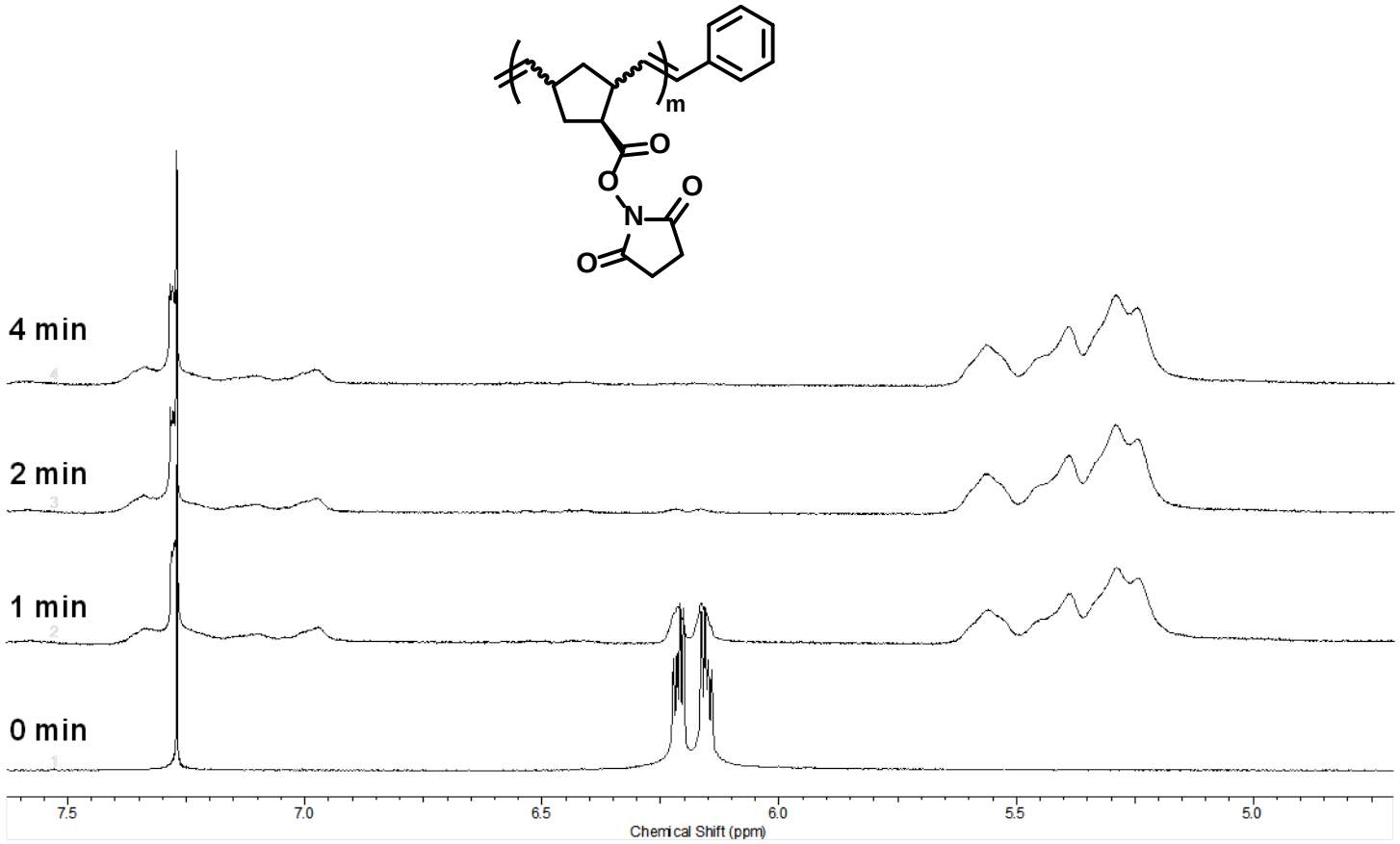


Figure S6: NMR time course of the polymerization of monomer **1.**

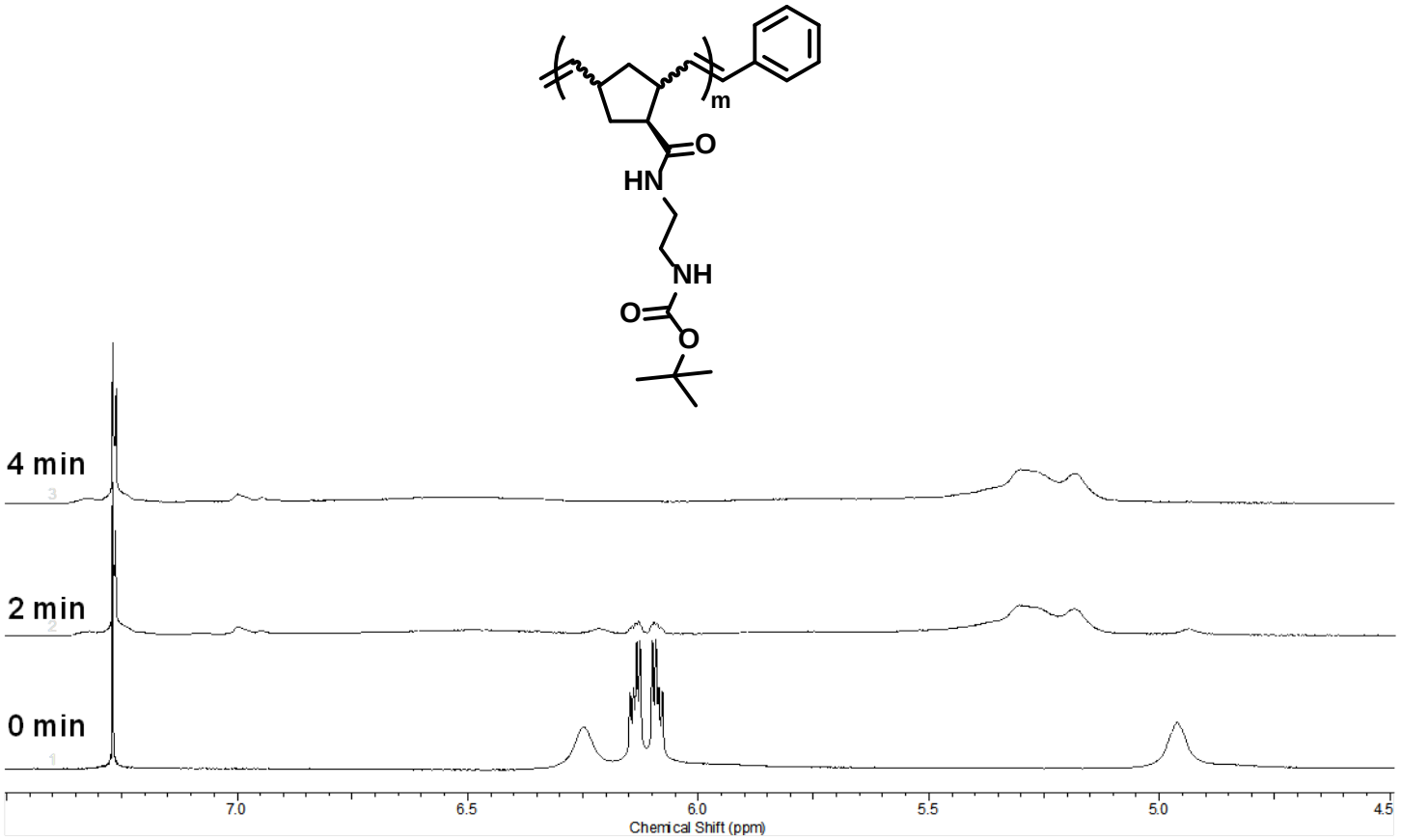


Figure S7: NMR time course of the polymerization of monomer **2.**

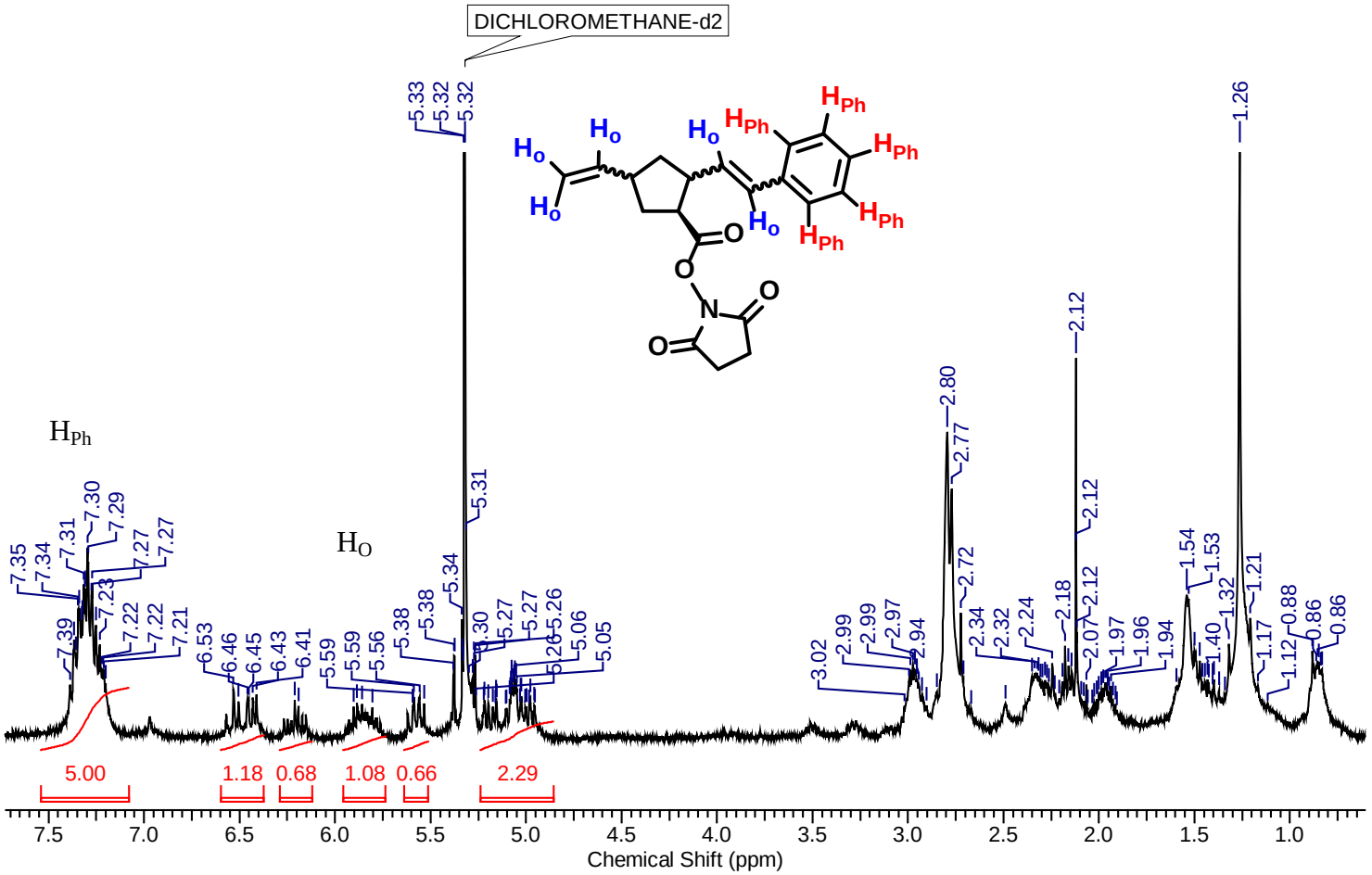


Figure S8: ^{1}H NMR of monomer **1** subjected to ROM conditions (M:I = 1:1). HRMS, expected 362.1363 $[M+Na]^{+}$, found: 362.1365.

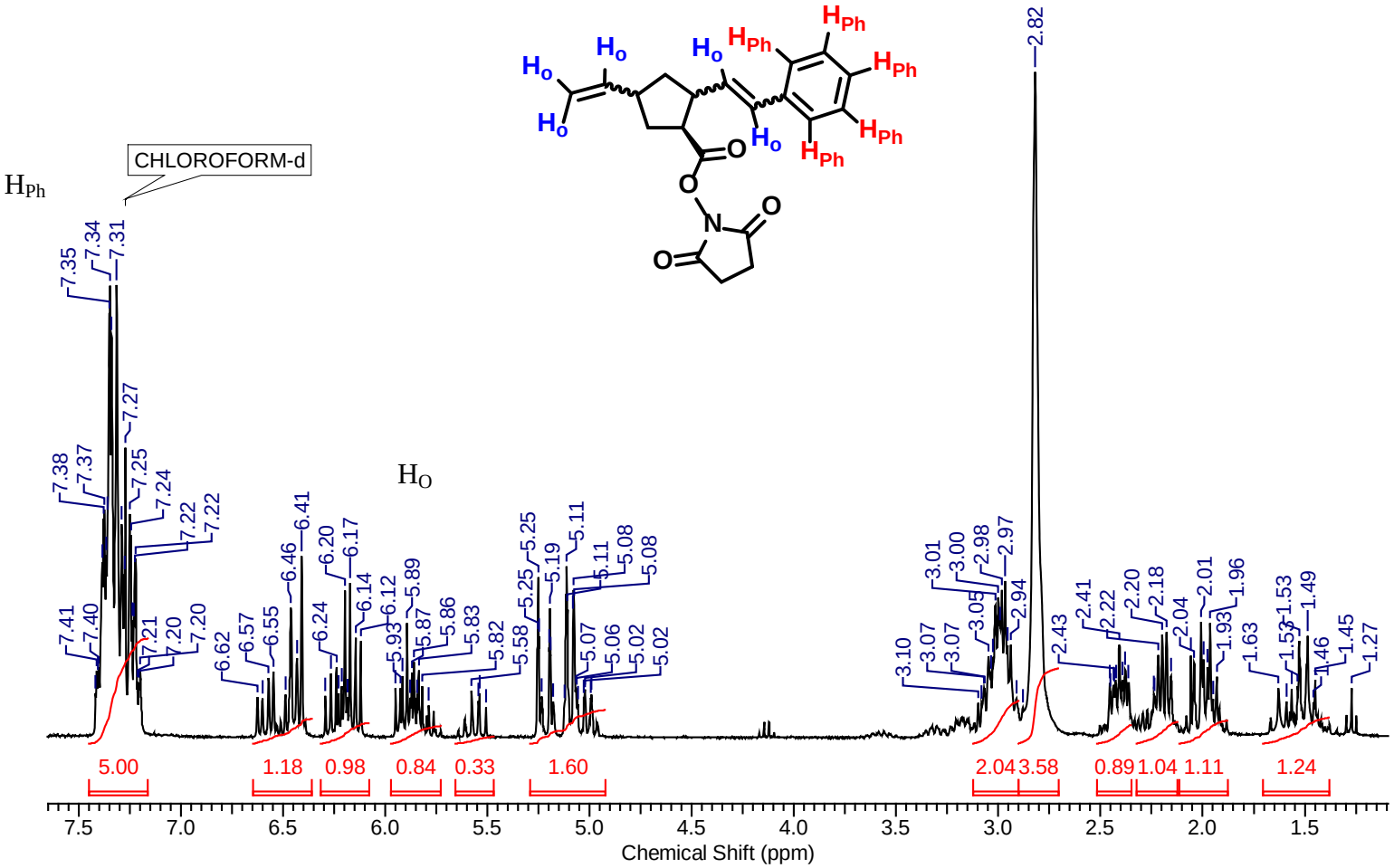


Figure S9: ^{1}H NMR of monomer **1** subjected to ROCM conditions (5% **I**, 10 equiv. styrene). HRMS, expected 362.1363 $[M+Na]^{+}$, found: 362.1367.

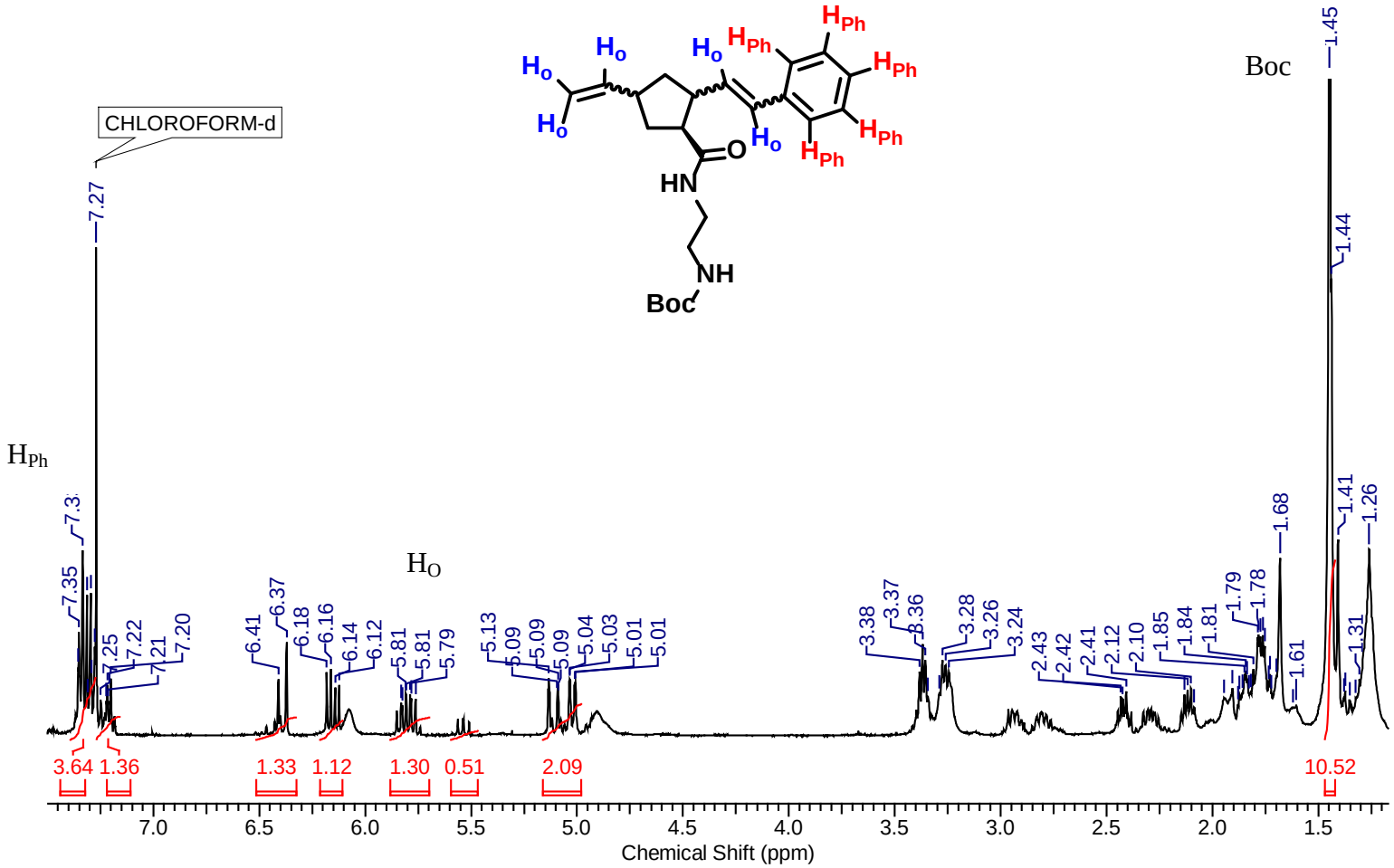


Figure S10: ^{1}H NMR of monomer **2** subjected to ROM conditions (M:I = 1:1). LRMS, ESI, 384.87 $[M+H]^{+}$, HRMS, expected 407.2305 $[M+Na]^{+}$, found: 407.2307.

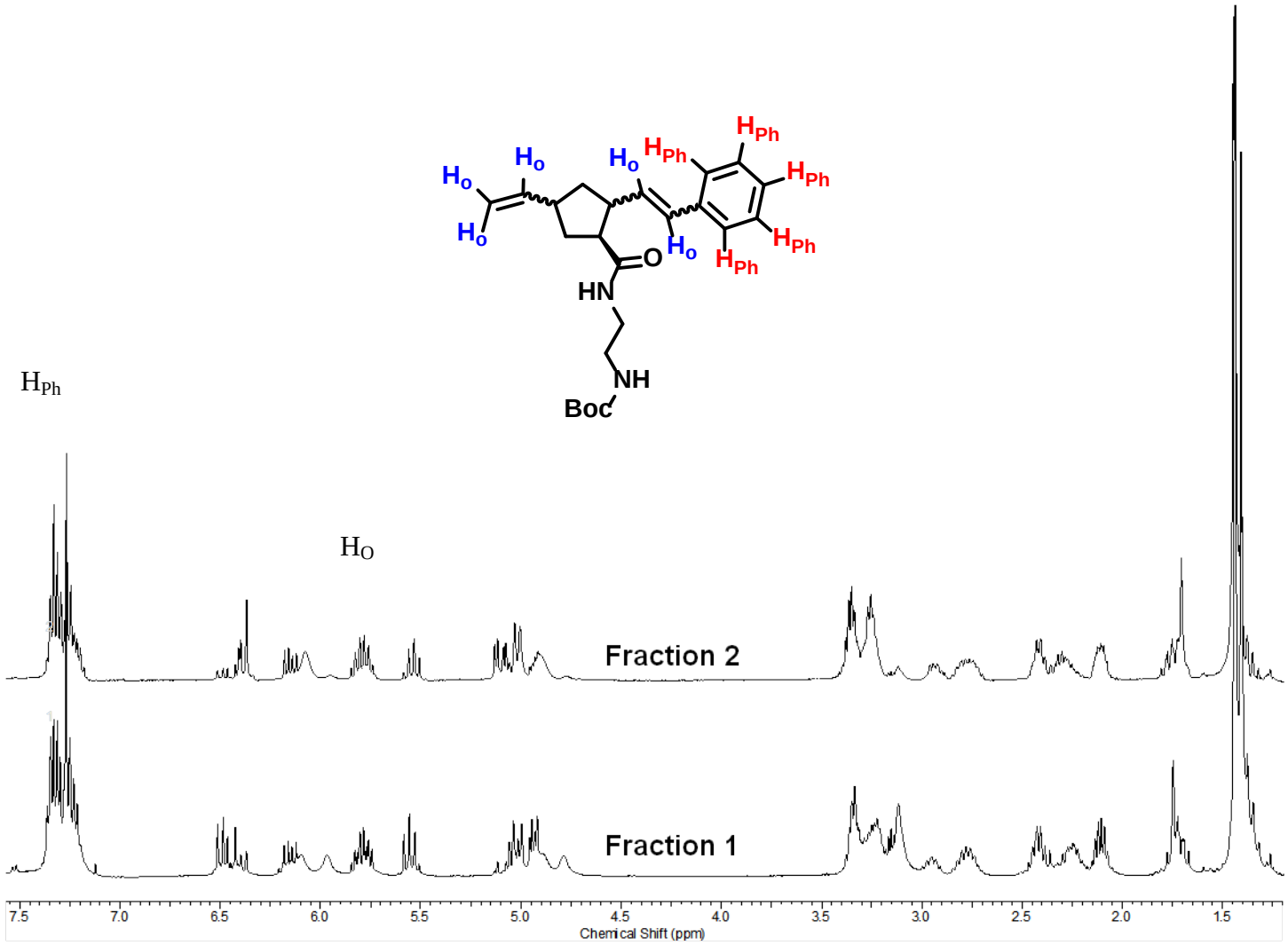


Figure S11: ^{1}H NMR of monomer **2** after reaction under ROCM conditions (5% **I**, 10 equiv. styrene). LRMS, ESI, 384.87 $[M+H]^{+}$ (fraction 1), LRMS, ESI, 384.84 $[M+H]^{+}$ (fraction 2).

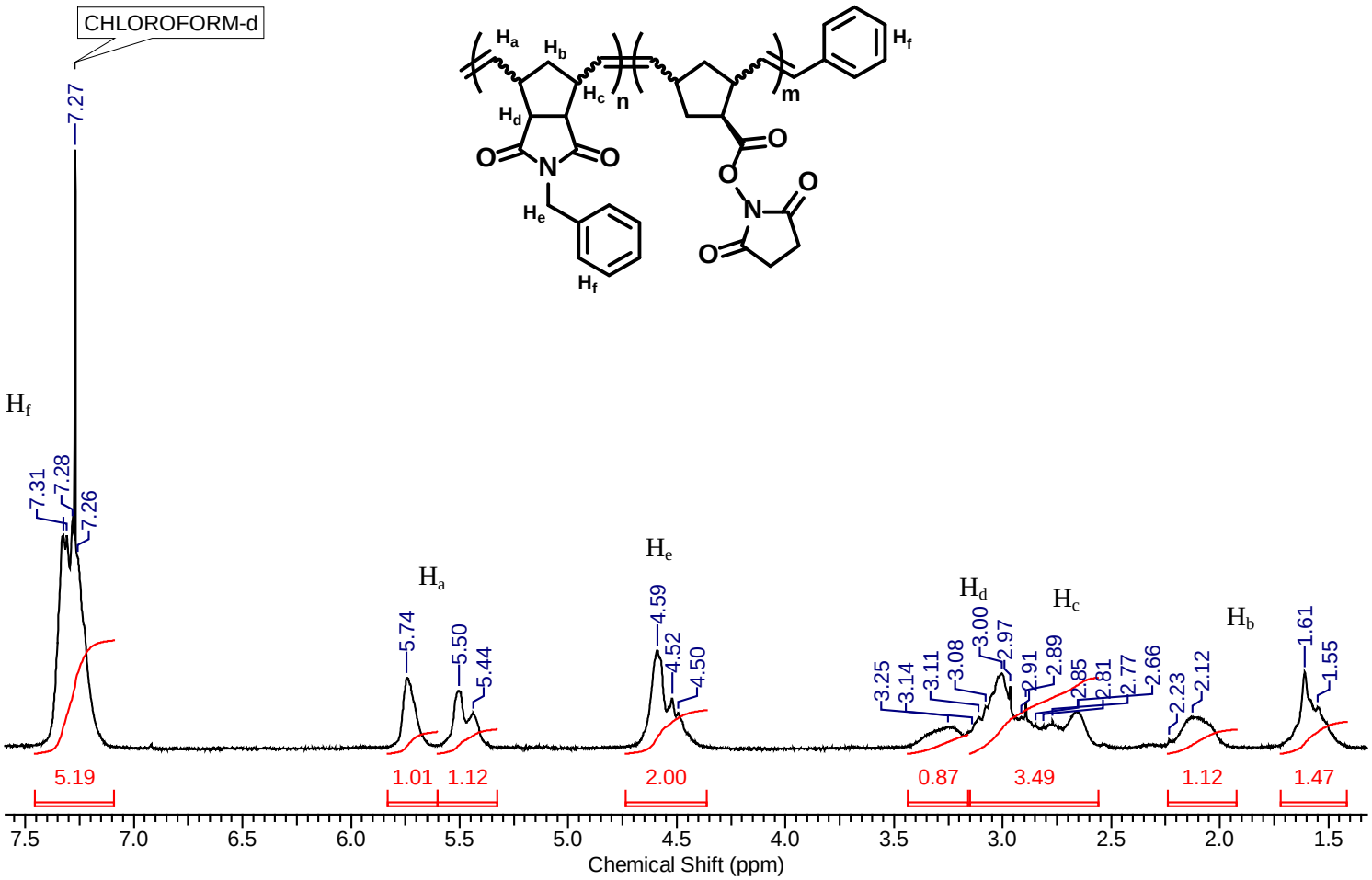


Figure S12: ^{1}H NMR of polymer **13.**

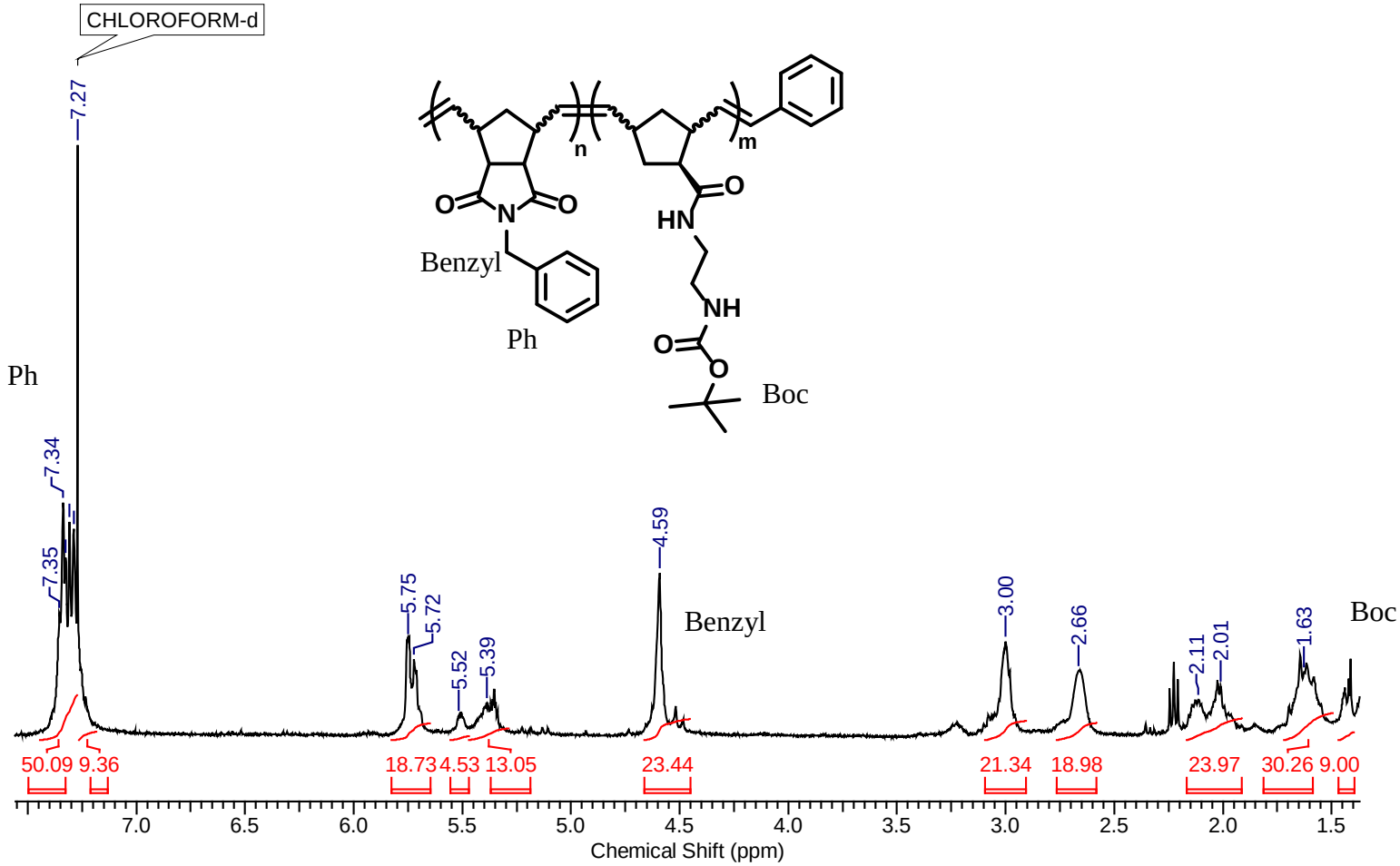


Figure S13: ^{1}H NMR of polymer **17.**

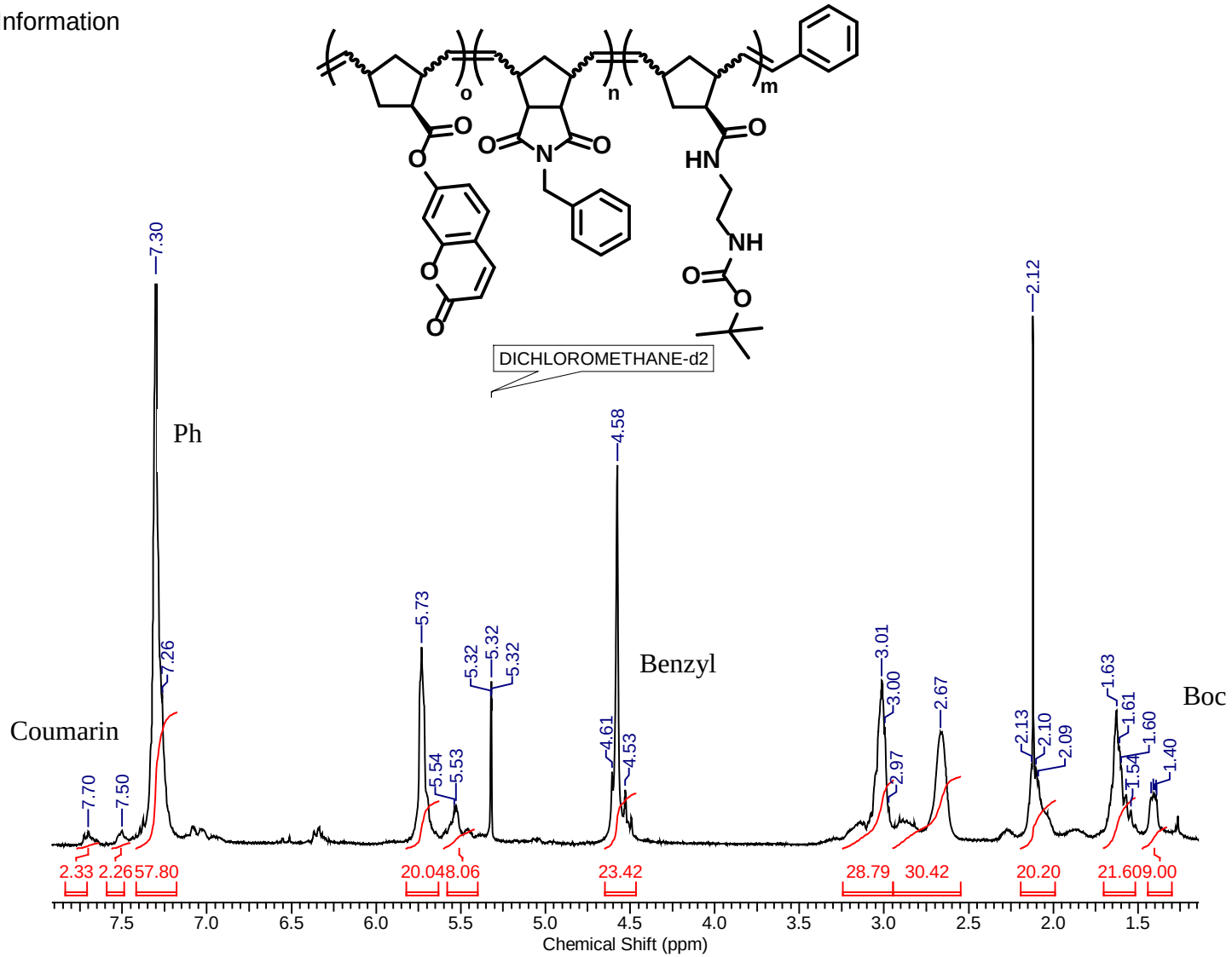


Figure S14: ^{1}H NMR of polymer **18.**

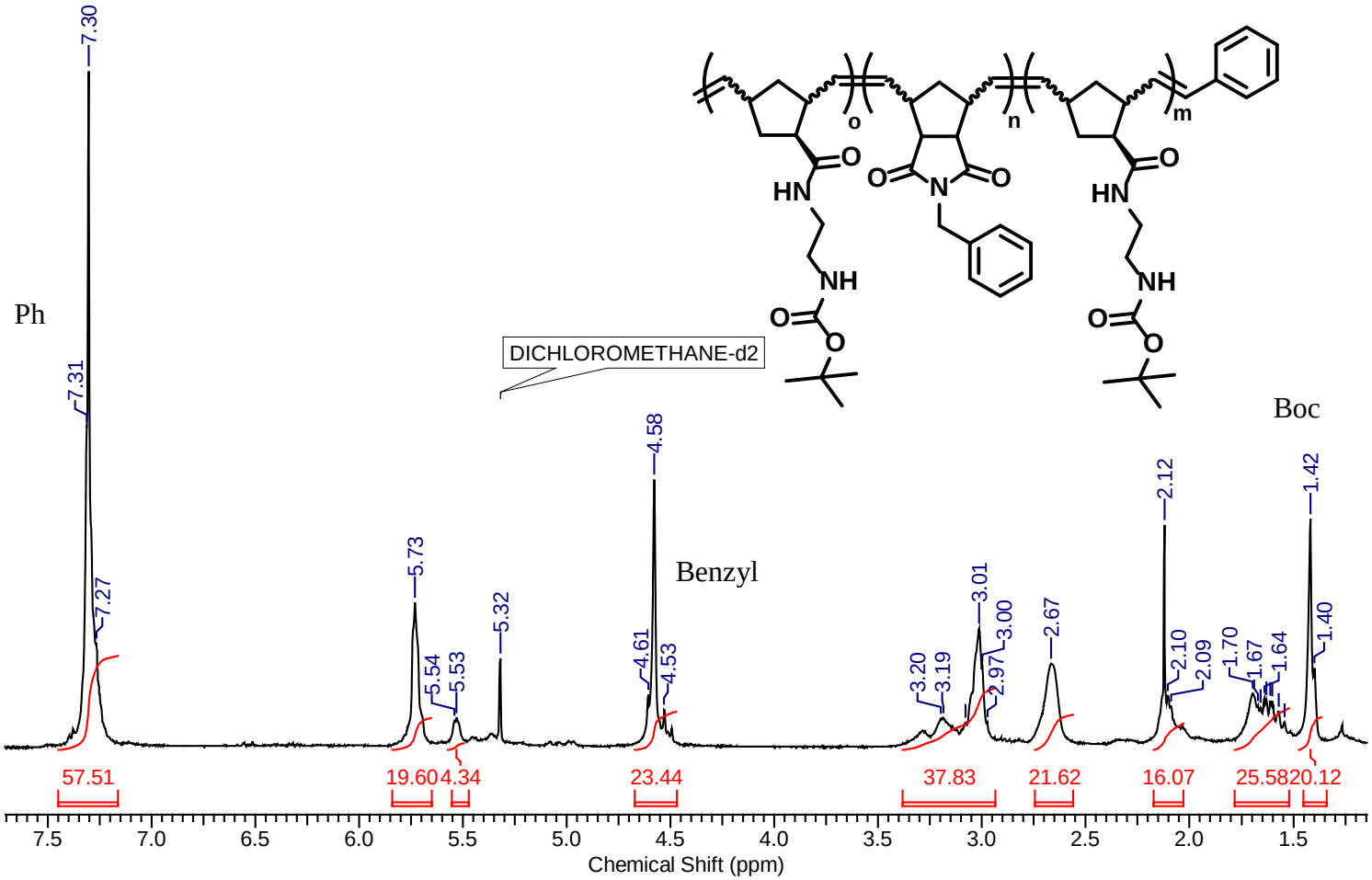


Figure S15: ^{1}H NMR of polymer **19.**

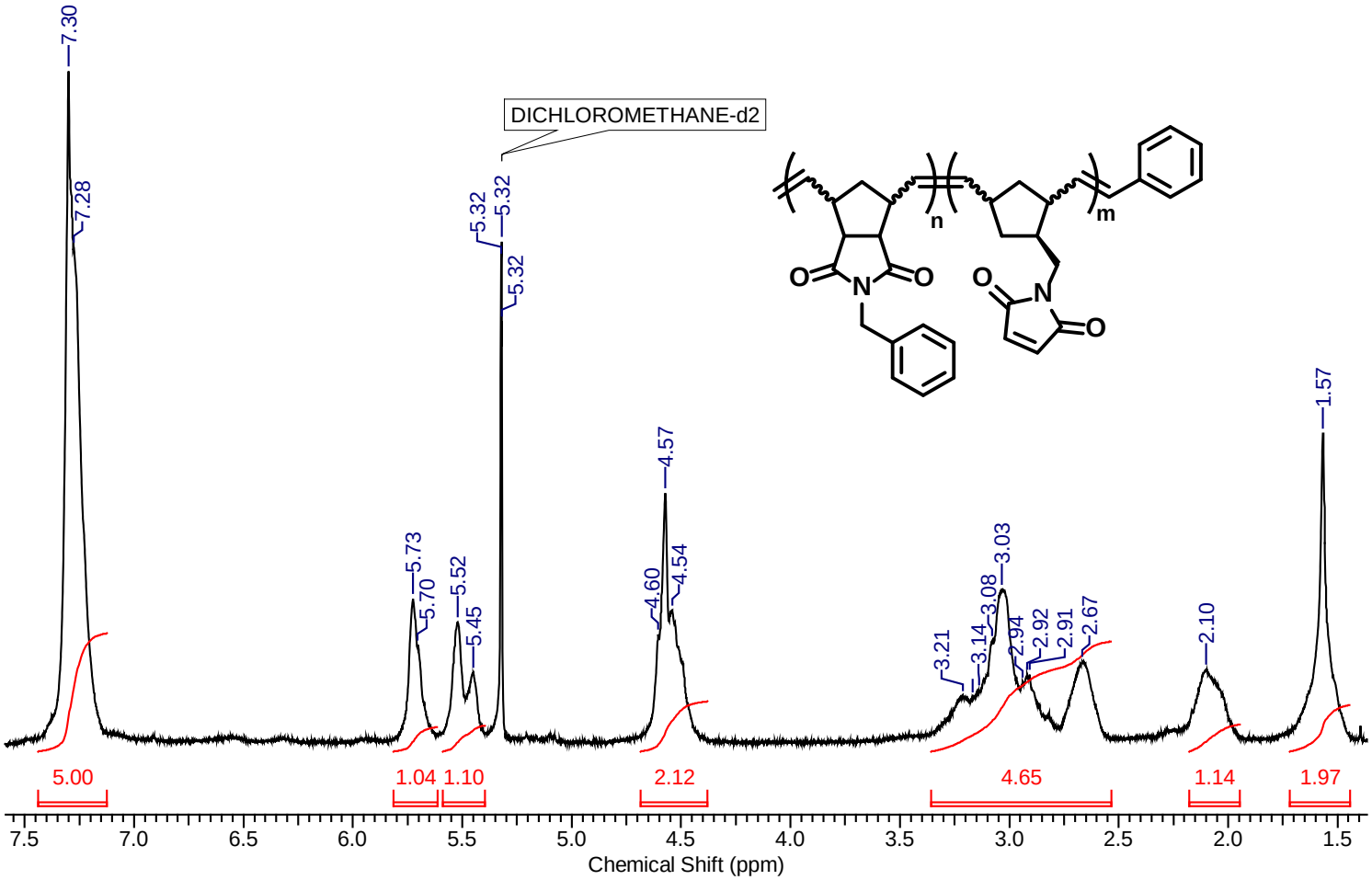


Figure S16: ^{1}H NMR of polymer **21.**

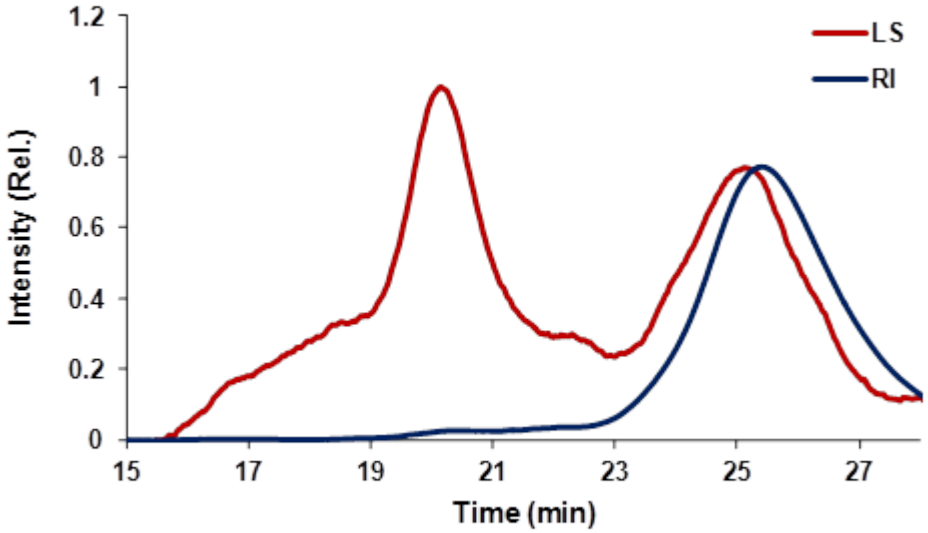


Figure S17: SEC-MALS trace of polymer **21** with light scattering (red) and refractive index (blue).

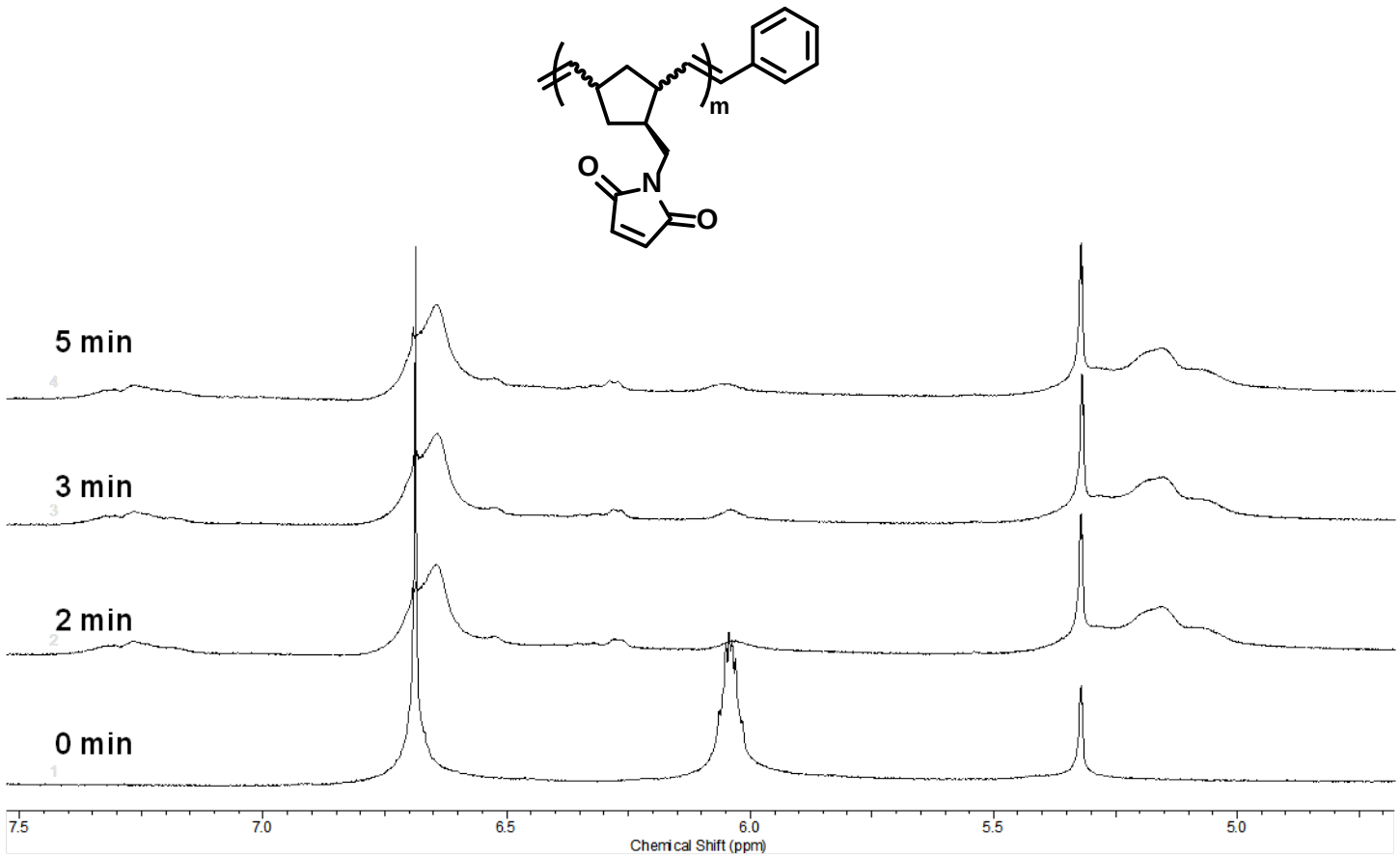


Figure S18: ^{1}H NMR time course of monomer **4** forming polymer **21.**

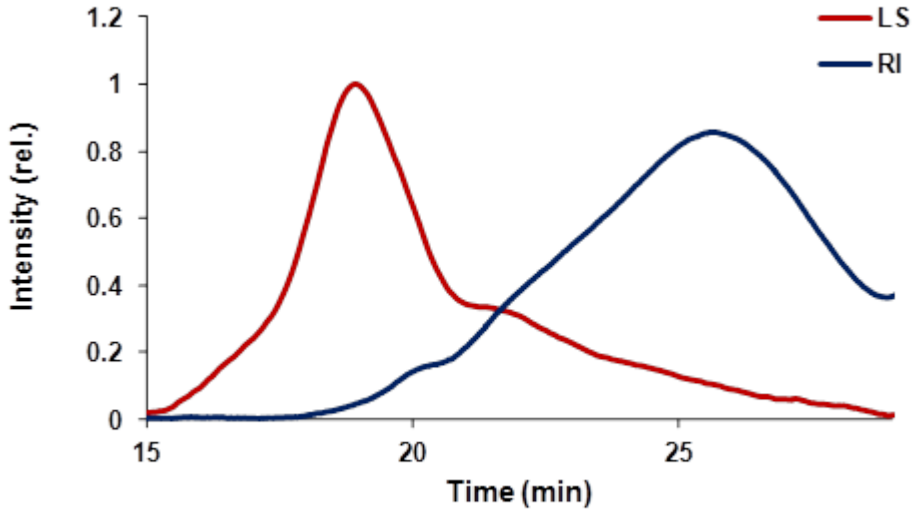


Figure S19: SEC-MALS trace of a homopolymer of monomer **4**, light scattering (red) and refractive index (blue).

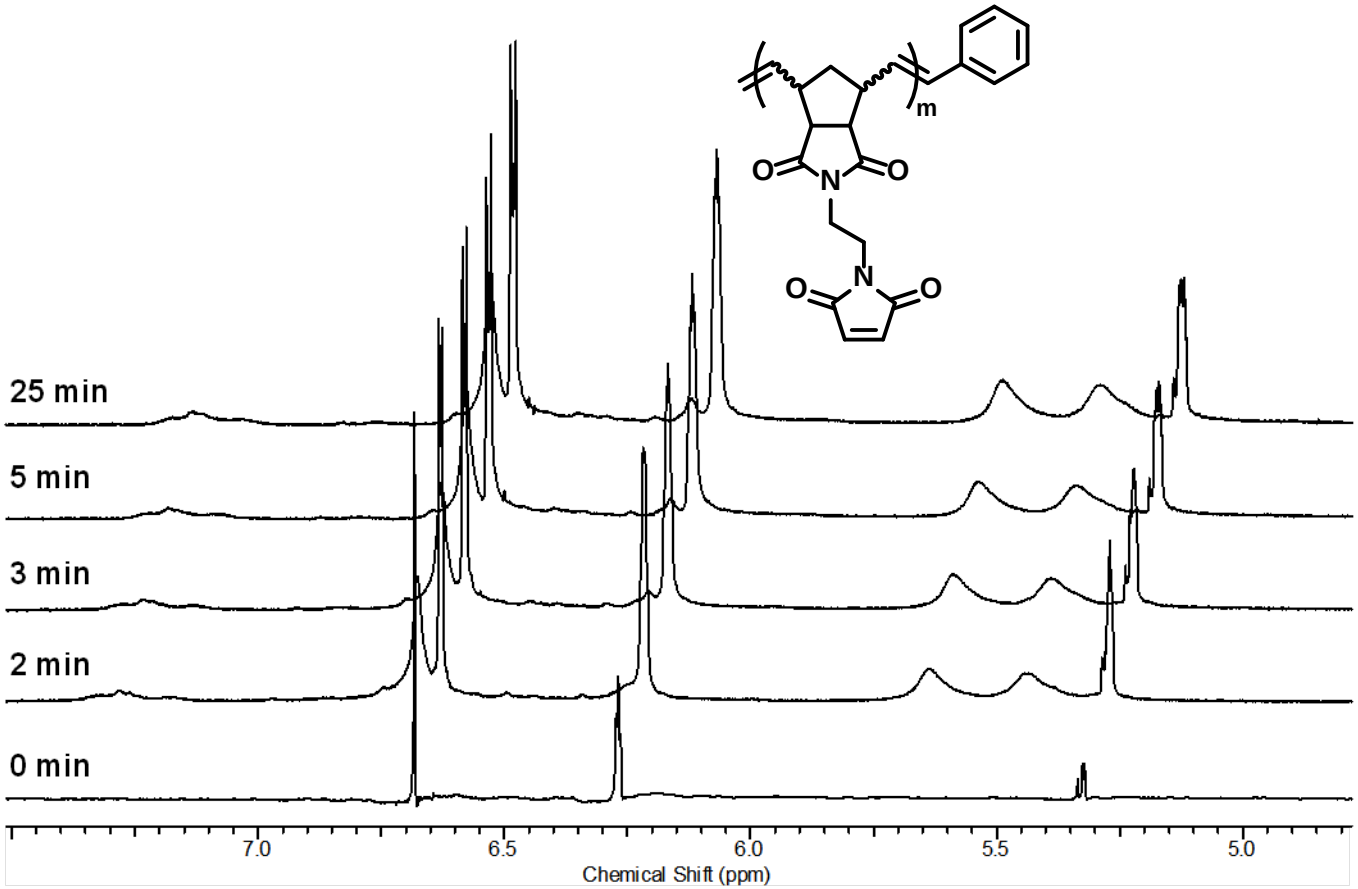


Figure S20: ^{1}H NMR time course of monomer **S2** showing incomplete monomer conversion. Conversion of monomer stops after 2 minutes. Monomer **S2** was synthesized in an attempt to improve the polymers generated with a maleimide end group. However as shown above the polymerization reaction is incomplete with no monomer conversion after 2 minutes. Interestingly if a monomer to initiator ratio of 1:1 is used complete conversion of the monomer is observed and a second monomer can be add and does polymerize fully although the resulting polymers do show similar SEC-MALS traces to those obtained of polymers incorporating monomer **4** (Figure S19).

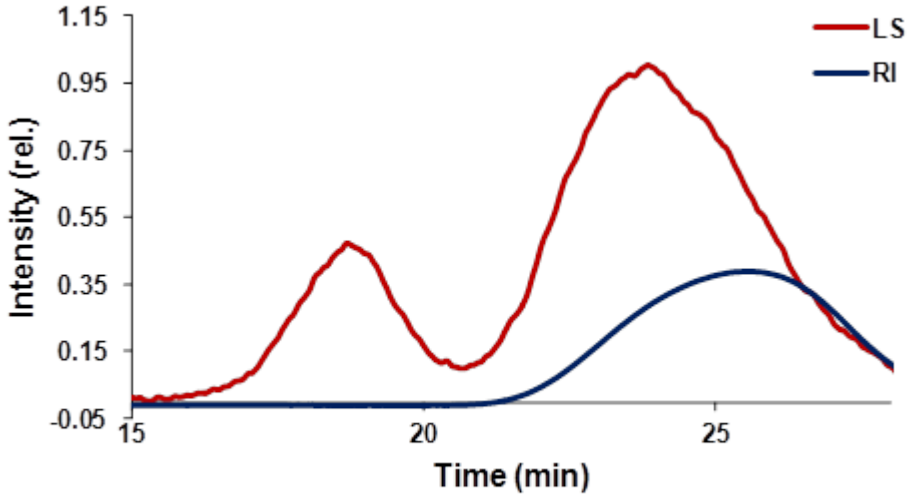


Figure S21: SEC-MALS of the polymerization reaction from **S2** shown in Figure S20, light scattering (red) and refractive index (blue).

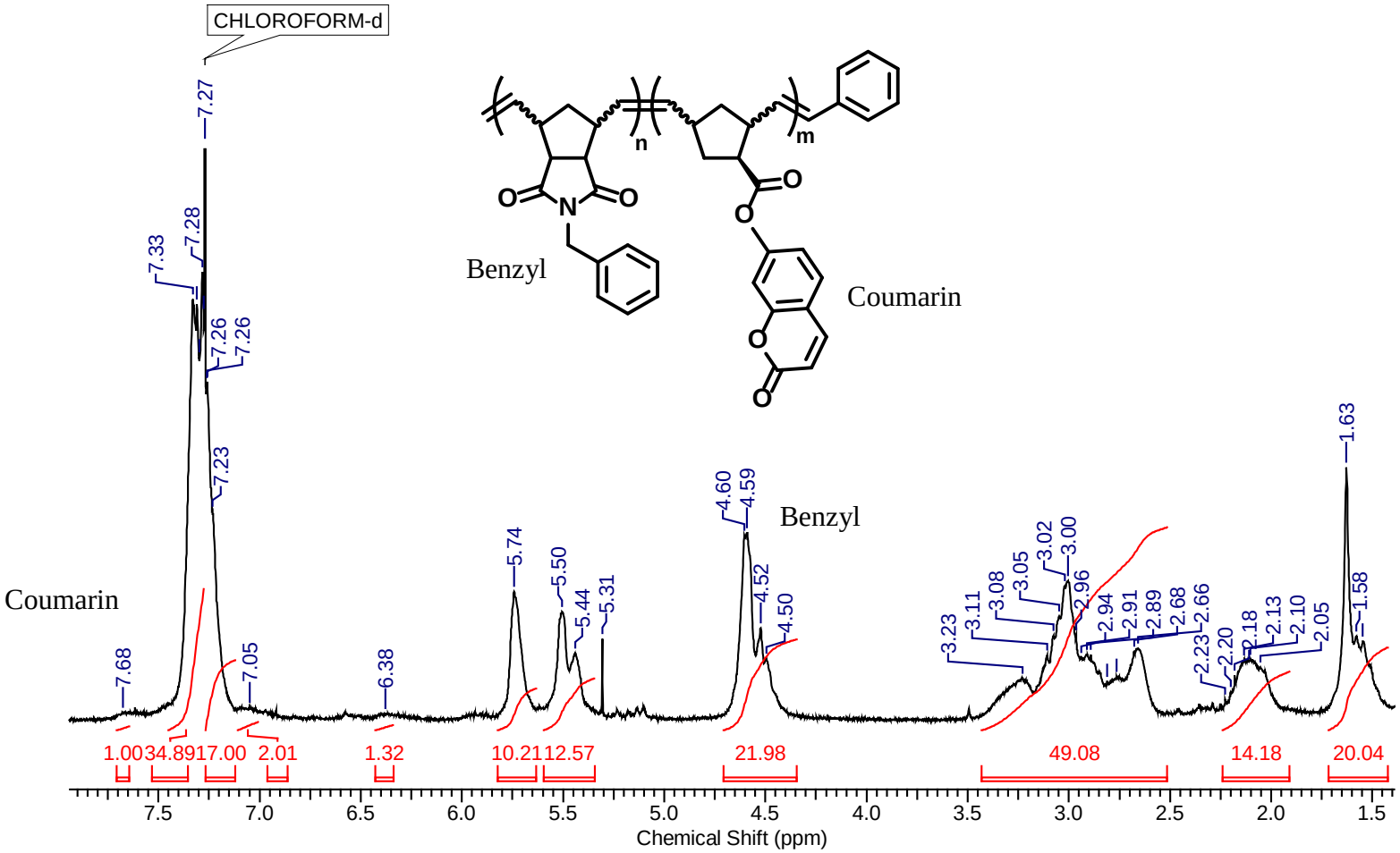


Figure S22: ^{1}H NMR of polymer **24.**

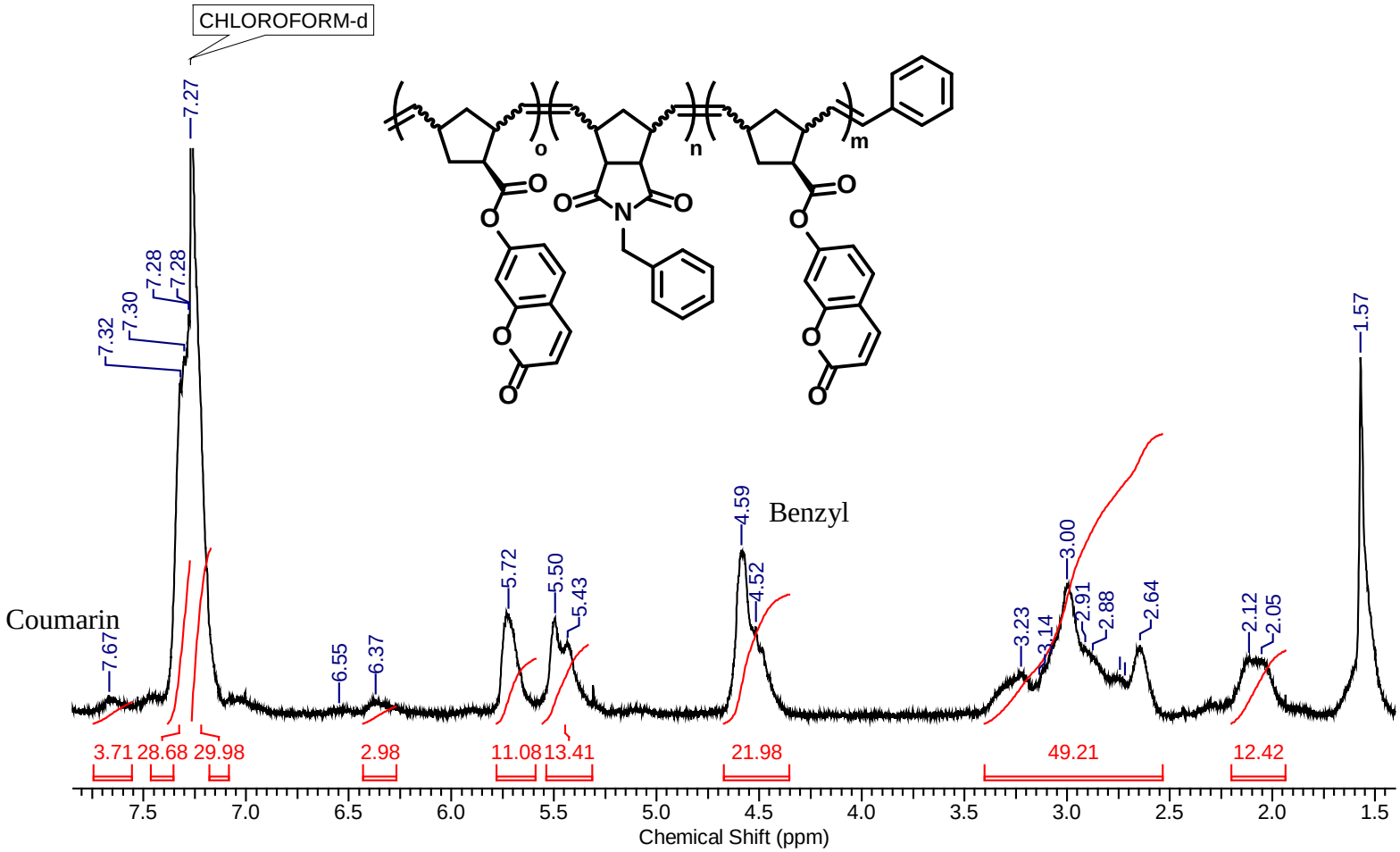


Figure S23: ^{1}H NMR of polymer **25.**

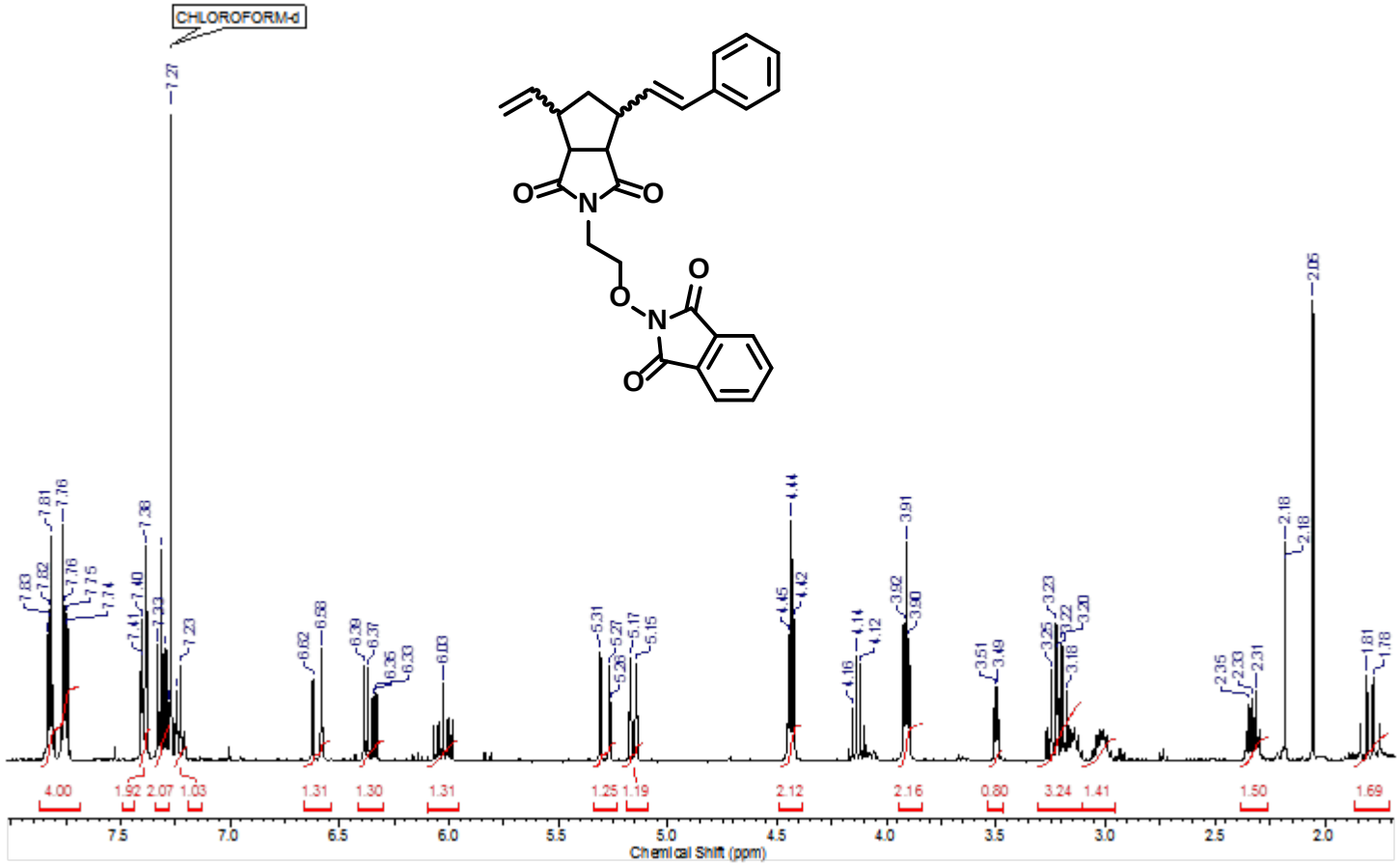


Figure S24: ^{1}H NMR of monomer **5** subjected to ROM conditions (M:I = 1:1).

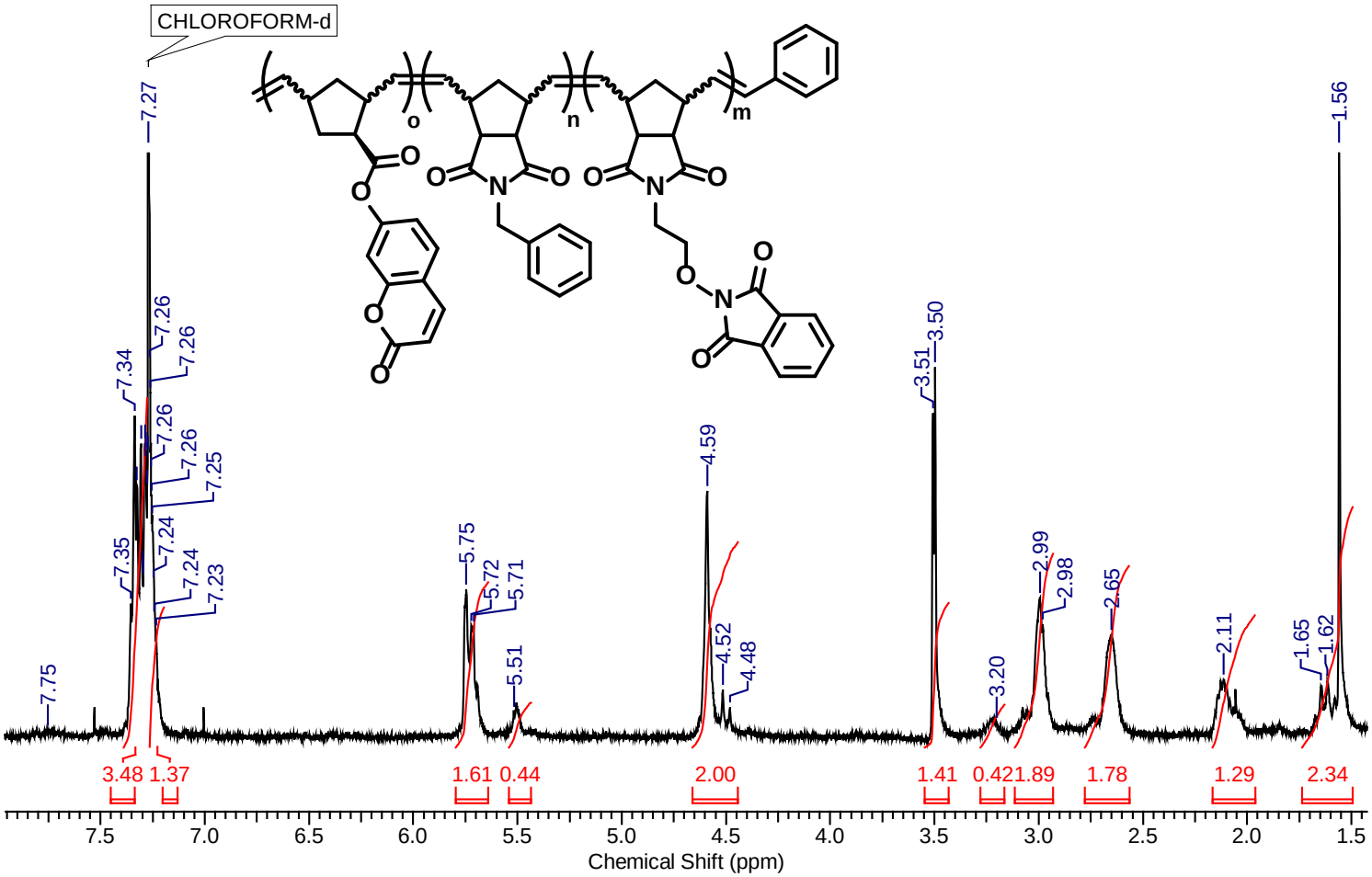


Figure S25: ^{1}H NMR of polymer **27.**

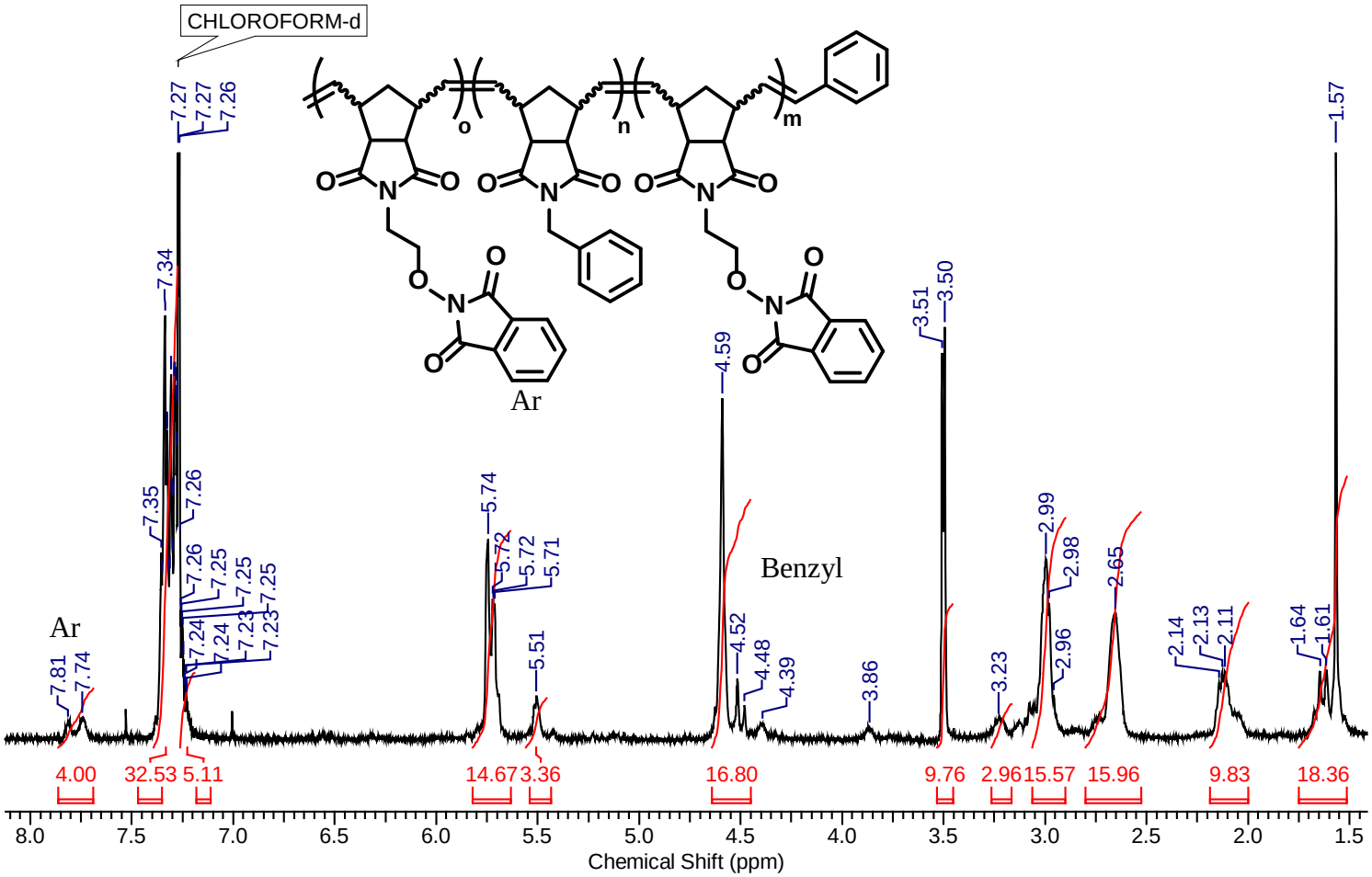


Figure S26: ^{1}H NMR of polymer **29.**

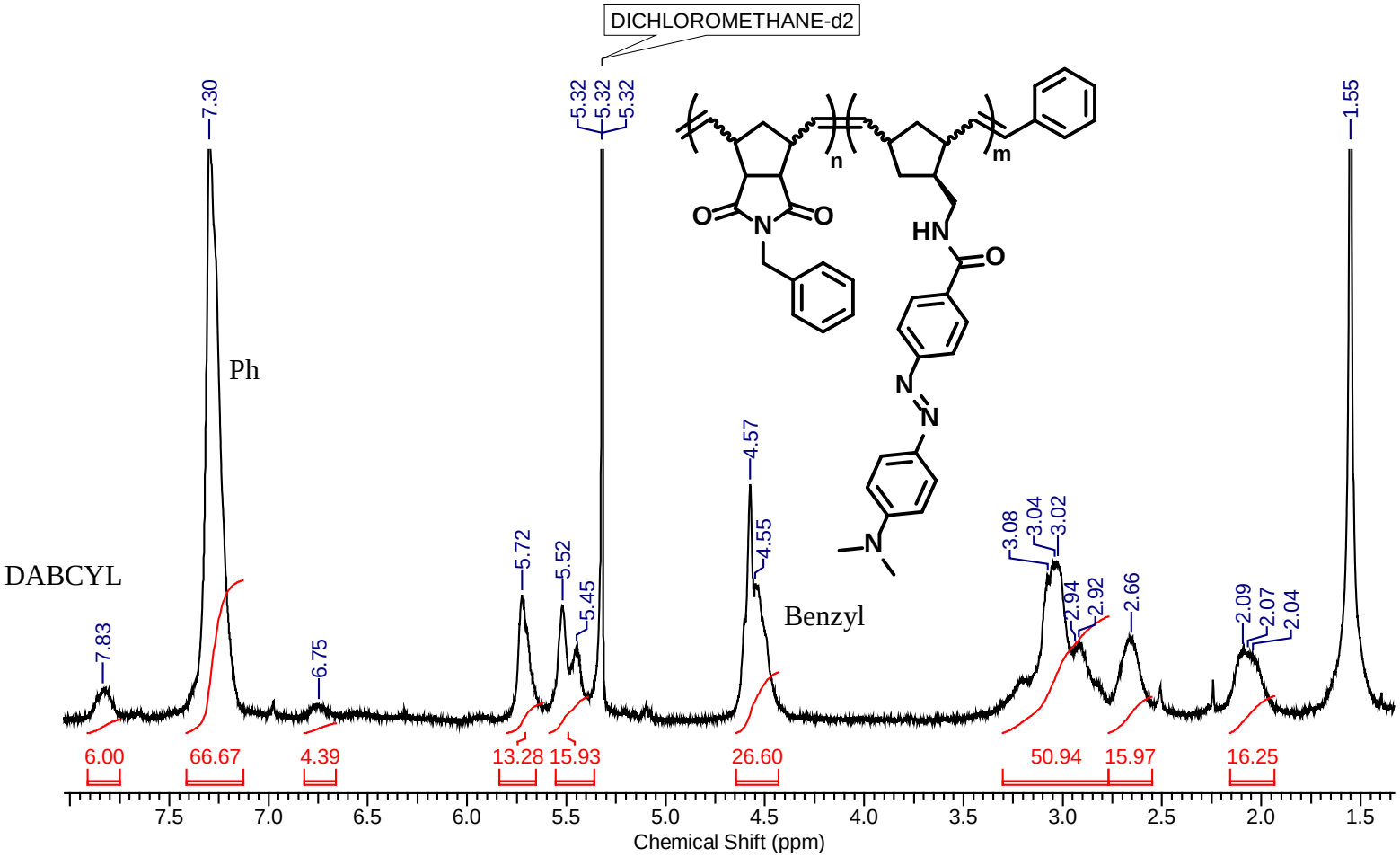


Figure S27: ^{1}H NMR of polymer **31.**

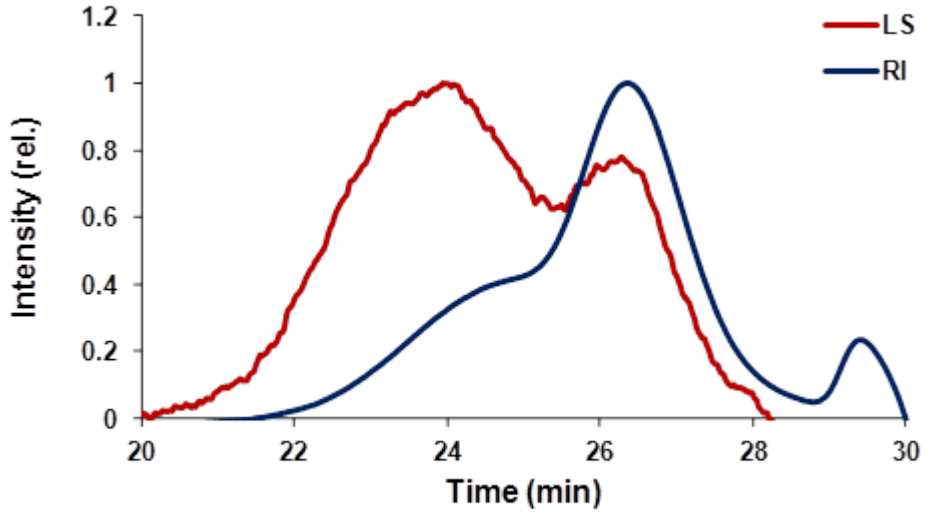


Figure S28: SEC-MALS trace of polymer **31**, light scattering (red) and refractive index (blue).

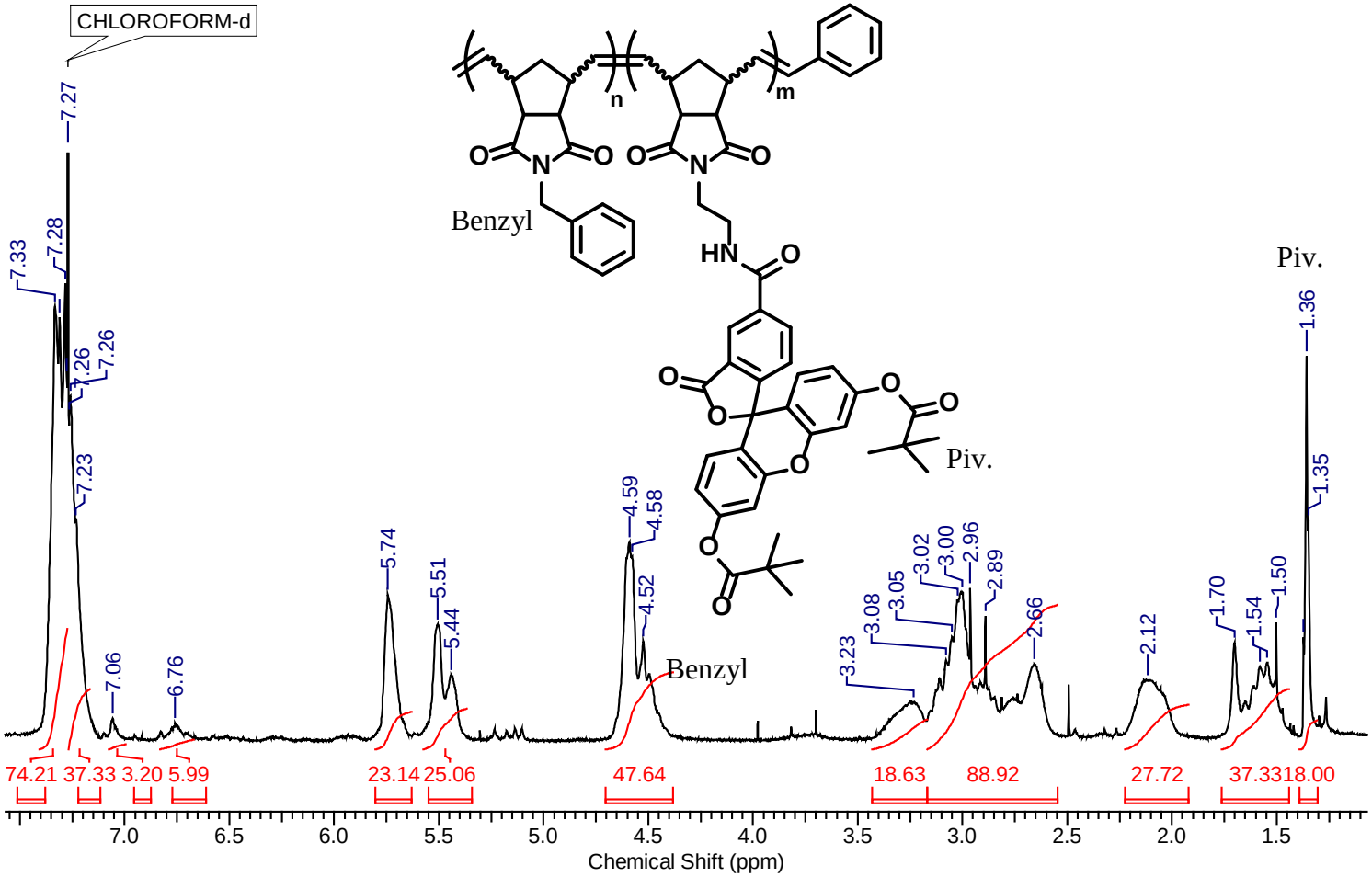


Figure S29: ^{1}H NMR of polymer **32.**

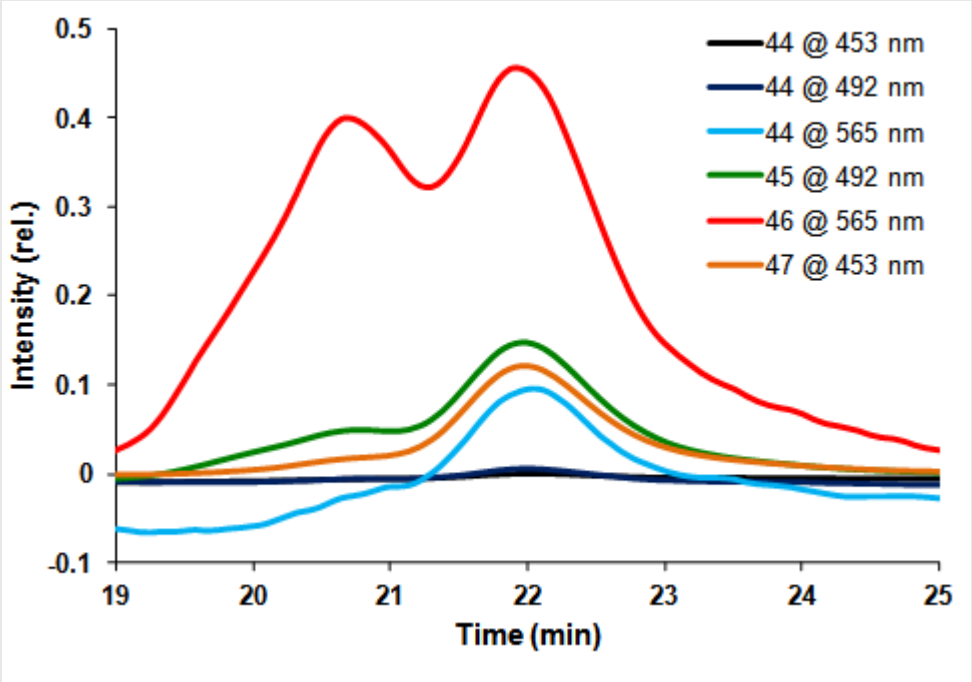


Figure S30: SEC trace of polymers **44-47** at different wavelengths corresponding to the absorption of the corresponding dyes used to terminate the polymerization reactions.

Critical Micelle Concentration

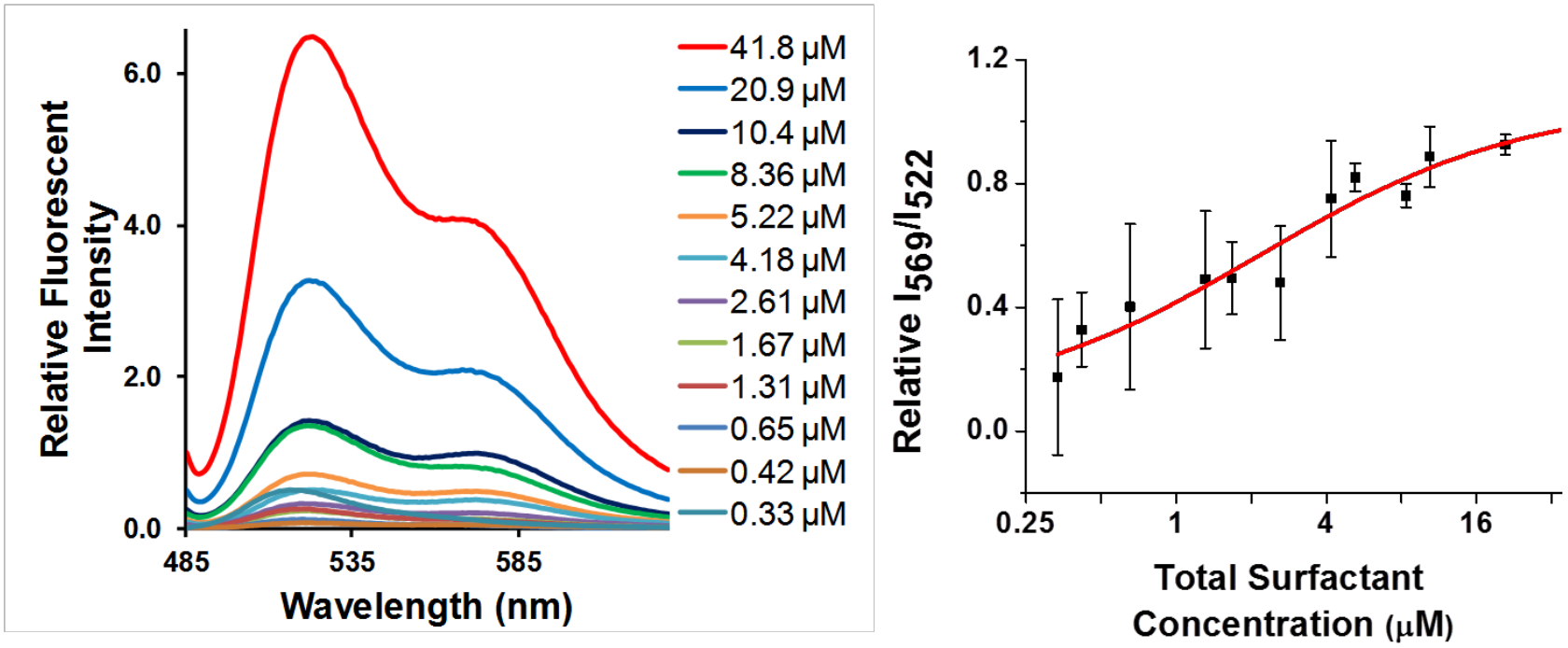
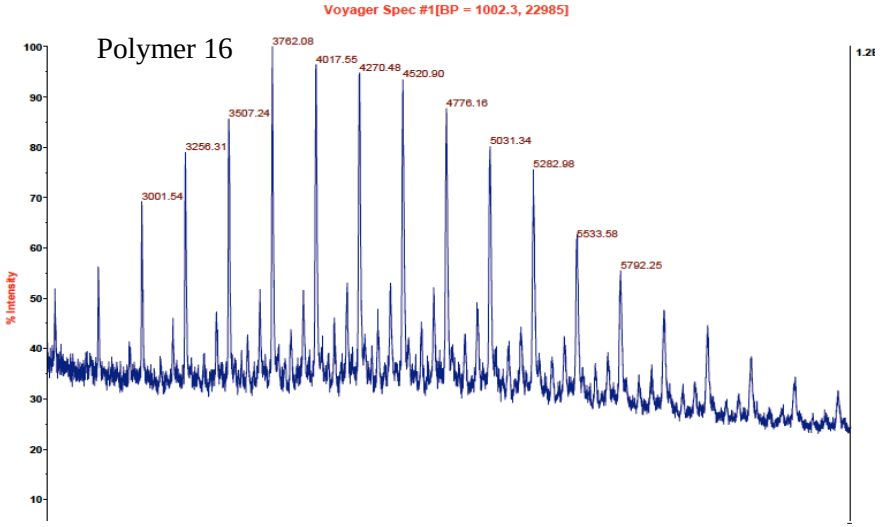


Figure S31: Critical Aggregation Concentration (CAC) for **P9**. A) Fluorescence emission spectra of **P9** at concentrations ranging from 0.3 µM to 42 µM (λ_{ex} = 470 nm). B) Maximum fluorescence intensity of rhodamine (I_{569}, λ_{em} = 569 nm) resulting from excitation of fluorescein (FRET intensity), divided by the maximum fluorescence intensity of fluorescein (I_{522}, λ_{em} = 522 nm) plotted vs total surfactant concentration. At a concentration of approximately 0.4 µM, a sharp drop is observed due to a loss in detectable signal. It is concluded that for this particular nanoparticle the CAC is less than or equal to 0.4 µM.

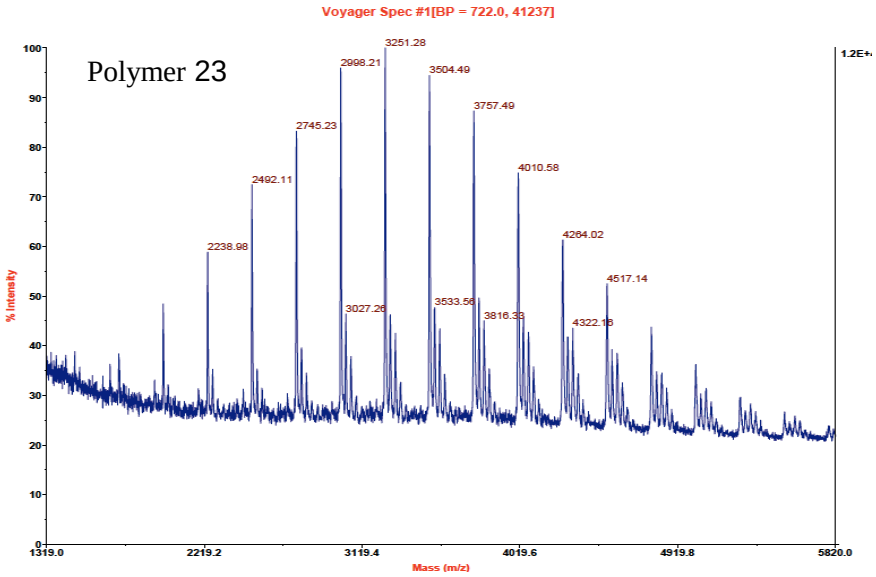
MALDI

The MALDI spectra shown below are representative of those obtained for the polymers listed in Table 2 (Main Text). Polymer **16** was obtained from a reaction mixture also used to isolate the single ring-opened product. Polymer **23** is representative of systems containing the dye coumarin. Polymer **25** is representative of a techelic system.

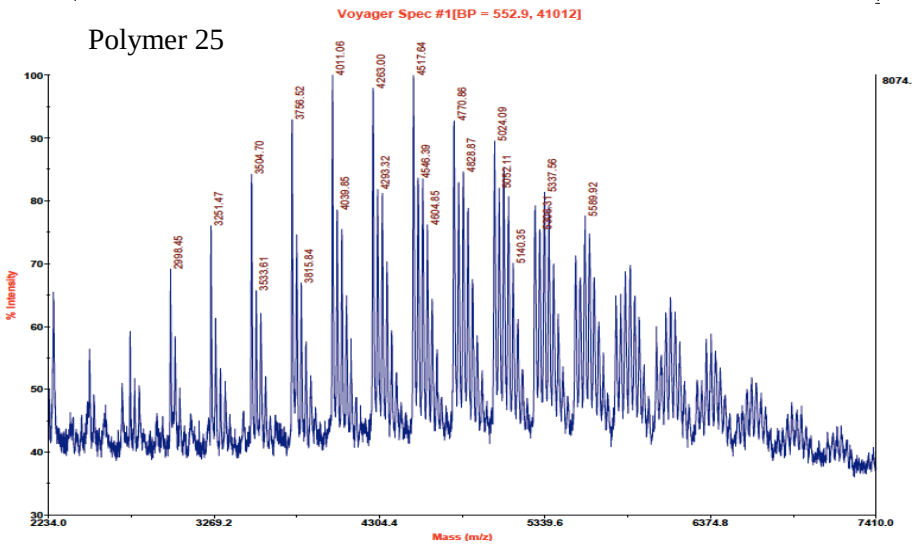
Polymer 16



Polymer 23



Polymer 25



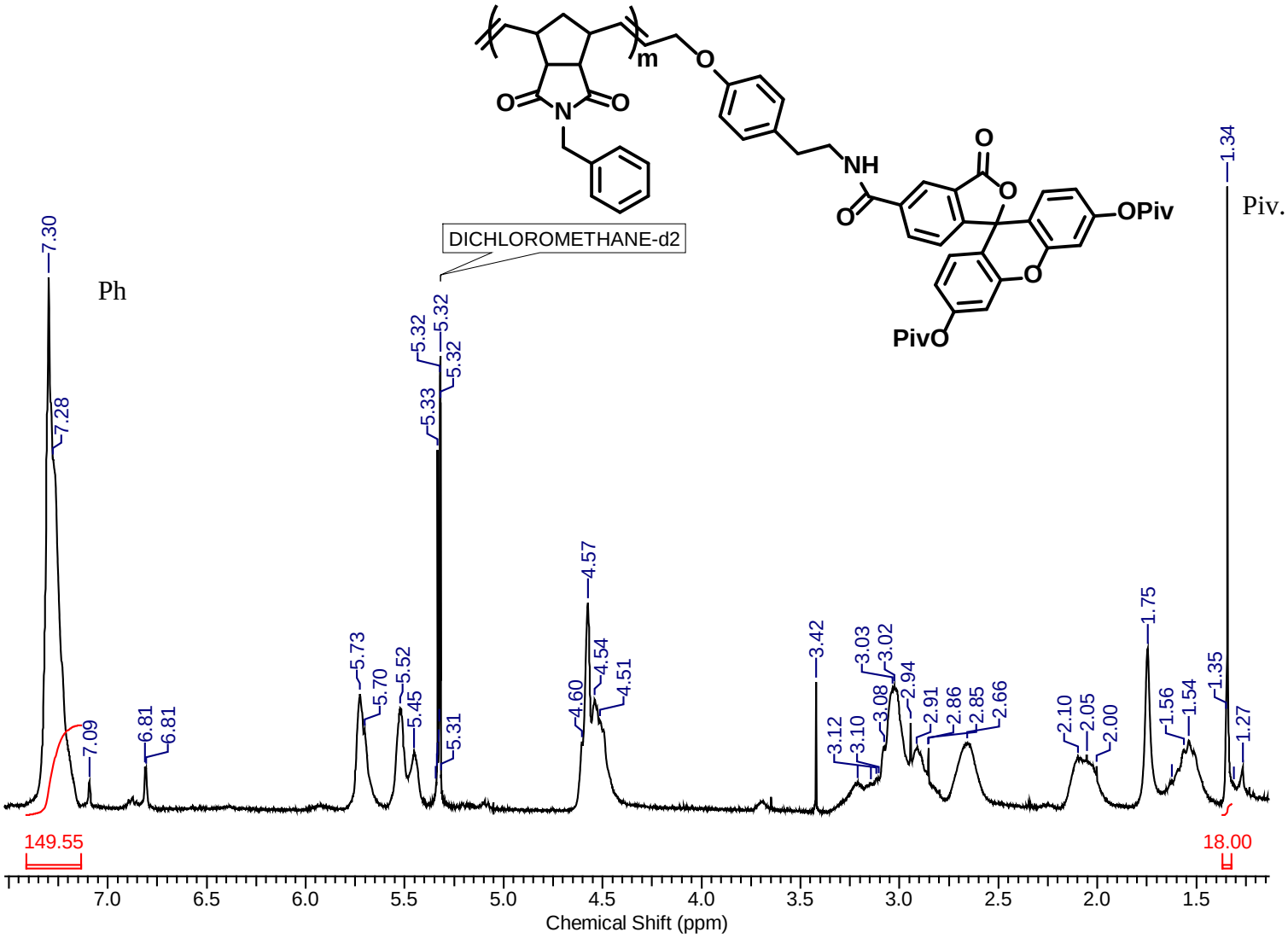


Figure S32: ^{1}H NMR of polymer **48** R = H, synthesized using the functional initiator method.

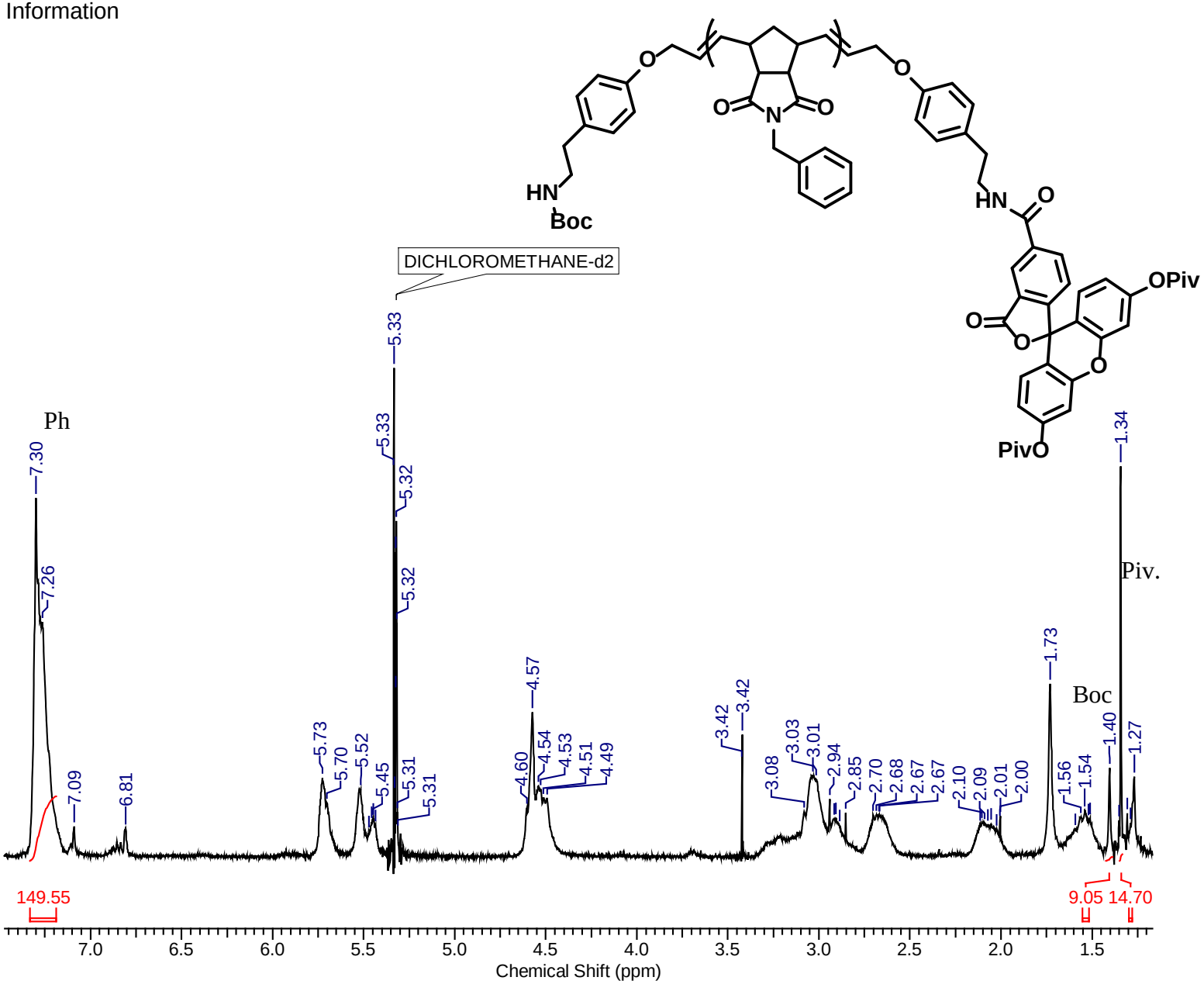


Figure S33: ^{1}H NMR of polymer **48** R = CH_2-OC_6H_4-CH_2CH_2-NH-BOC, synthesized using the functional initiator method.

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