Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplemental Experimental Procedures

Carborane RAFT Agents as Tunable and Functional Molecular Probes for Polymer Materials

Marco S. Messina,*[a] Christian T. Graefe,[c] Paul Chong,[a,e] Omar M. Ebrahim,[a] Ramya S. Pathuri,[a] Nicholas A. Bernier,[a] Harrison A. Mills,[a] Arnold L. Rheingold,[d] Renee R. Frontiera,*[c] Heather D. Maynard,*[a,b] and Alexander M. Spokoyny*[a,b]

[a] Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095-1569, United States.

[b] California NanoSystems Institute, University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, California 90095-1569, United States.

[c] Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455, United States.

[d] Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California, 92093, United States.

[e] Department of Chemistry, Stanford University, 333 Campus Dr., Stanford, California, 94305, United States.

*Correspondence: messina@chem.ucla.edu, rrf@umn.edu, maynard@chem.ucla.edu, and spokoyny@chem.ucla.edu

Table of Contents

I. General Information

Methods and Materials

Reagent Information:

All commercially available chemicals were used as received unless otherwise stated. All polymerizations were prepared in the glovebox under nitrogen atmosphere unless otherwise stated. Benzene, diethyl ether, and tetrahydrofuran were purified *via* a solvent purification system and kept in the glovebox over 4 Å molecular sieves. Toluene (Fisher) and ethyl acetate (Fisher) were degassed and stored over 4 Å molecular sieves. Dichloromethane (Fisher), hexanes (Fisher), pentane (Sigma-Aldrich), and 1,4-dioxane (Sigma-Aldrich) were used as received. All monomers were degassed and stored with 4Å molecular sieves. Styrene (≥99%), 4-chlorostyrene (97%), methyl acrylate (99%), *N*-isopropylacrylamide (97%), tributylphosphine (97%), 1-hexylamine (99%), 2-hydroxyethyl acrylate (96%), dithranol (>90%), silver trifluoroacetate (98%), *n*-butyllithium (2.5 M solution in hexanes), and carbon disulfide (99%) were purchased from Sigma-Aldrich. *O*-carborane was purchased from Boron Specialties (USA). Tetrabutylammonium fluoride hydrate (TBAF) (97%) was purchased from Oakwood Chemicals. 1-chloro-1-phenylethane (97%) was purchased from Acros Organics. 2,2′-Azobis(2-methylpropionitrile) was purchased from Sigma-Aldrich and recrystallized from methanol. 1,2,3,4-tetrahydronapthalene (tetralin) was purchased from TCI.

Abbreviations:

AIBN: 2,2′-Azobis(2-methylpropionitrile)
pNIPAAm: Poly(*N*-isopropylacrylamide)
PS: Polystyrene
PMA: poly(methyl acrylate)
(4-Cl)-PS: poly(4-chlorostyrene)

General Analytical Information:

NMR spectra were recorded on DRX 400, DRX 500, and AVIII 500 spectrometers at 500 MHz (^{1}H), 125 MHz (^{13}C), and 80 MHz (^{11}B) reported in δ (parts per million) relative to tetramethylsilane (^{1}H, ^{13}C) or $BF_3{\cdot}Et_2O$ (^{11}B), and referenced to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ) $CDCl_3$ 7.26; ^{13}C (δ) $CDCl_3$ 77.16; ^{1}H (δ) $(CD_3)_2CO$ 2.05; ^{1}H (δ) CD_3CN 1.94; ^{11}B (δ) $BF_3{\cdot}Et_2O$ 0.00 ppm). Deuterated solvents (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were stored over 4Å molecular sieves. Gel permeation chromatography (GPC) was conducted on a Shimadzu HPLC Prominence-I system equipped with a UV detector, Wyatt DAWN Heleos-II Light Scattering detector, Wyatt Optilab T-rEX RI detector, one MZ-Gel SDplus guard column, and two MZ-Gel SDplus 100 Å 5μm 300x8.0 mm columns. Eluent was THF at 40 °C (flow rate: 0.70 mL/min). Chromatograms from THF GPC were analyzed using Astra 6.0 software using dn/dc values of 0.1828 for polystyrenes and 0.048 for poly(methyl acrylate) at 664 nm. Polymer analysis of poly(NIPAAm) was performed on a Shimadzu high performance liquid chromatography (HPLC) system with a refractive index RID-10A, one Polymer Laboratories PLgel guard column, and two Polymer Laboratories PLgel 5 μm mixed D columns in DMF eluent with LiBr (0.1 M) at 40 °C (flow rate: 0.80 mL/min). Calibration was performed using near-monodisperse pMMA standards from Polymer Laboratories. Chromatograms from DMF GPC were analyzed using LabSolutions software. All GPC samples were dissolved in HPLC grade solvent at a concentration of 4-5 mg/mL and filtered through a 0.2 μm TFE filter. UV-Vis spectroscopy was performed on an Agilent / HP 8453 spectrophotometer with an Agilent 89090A Peltier temperature controller. Thin-layer chromatography (TLC) samples for carborane-containing compounds were stained with 1 wt. % $PdCl_2$ in 6M HCl and were developed with heat. Mass spectrometry was performed on a Q Exactive™ Plus Hybrid Quadrupole-Orbitrap™ Mass Spectrometer with Dionex UltiMate 3000 RSLCnano Systems.

Isothermal Titration Calorimetry:

Isothermal Titration Calorimetry (ITC) data were recorded on a MicroCal™ iTC_{200} System (GE Healthcare Life Sciences) housed in the University of California, Los Angeles (UCLA) Department of Energy (DOE) Biochemistry Instrumentation Core Technology Center. All titrations were recorded at 25 ºC in neat water. Syringe concentration was typically 10-20 times larger than the cell concentration. The syringe volume is approximately 39 µL and the cell volume is approximately 250 µL. The first data point (a 0.4µL injection) was removed before data processing using MicroCal Analysis Software and Origin Software. Heats of dilution were determined by titrating the titrant of interest into neat water at the same injection volume used for each experiment. Heats of dilution were subtracted from the data prior to curve fitting. Exact concentrations, number of injections, and volume of injection are reported for each experiment.

Raman Experimental Details

Samples for Raman imaging were prepared by dissolving 4.44 mg of **1-pNIPAAm** in 0.888 mL of water and drop casting the solution onto a quartz coverslip. A sharp edge was created by scraping some of the **1-pNIPAAm** off of the coverslip with a razor blade.

Imaging was completed using a 633 nm HeNe continuous wave laser (Thorlabs). A 20x objective with a numerical aperture of 0.40 was used to focus the laser onto the sample. The sample was mounted on a 3D nano-positioning stage (Mad City Labs Nano-3D200 Stage). The laser power at the sample was 1.09 mW. Raman scattering was collected in a backscatter orientation, focused into a spectrograph, and dispersed by a 600 gr/mm grating blazed at 750 nm. The signal was then detected with a PIXIS 400BR CCD array detector (Princeton Instruments) with 100 rows binned. Three exposures of 12 s were averaged together at each postion.

The relative Raman cross section for the B-H vibration can be approximated by comparing the number of B-H bonds to the number of C-H bonds in an average-sized **1-pNIPAAm** polymer and the relative intensities of their Raman peaks. The efficiency of the detector at the wavelength of the vibration must also be considered. For a given Raman peak,

$$I \propto QnR \qquad (1)$$

$$R \propto \frac{I}{Qn} \qquad (2)$$

where I is the area under the peak, Q is the quantum efficiency of the detector at the center wavelength of the peak, n is the number of bonds in the polymer undergoing the particular vibration, and R is the Raman cross section for that vibration. By dividing equation (2) for B-H by equation (2) for C-H, an equation for the ratio of the Raman cross sections is obtained.

$$\frac{R_{BH}}{R_{CH}} = \frac{Q_{CH} n_{CH} I_{BH}}{Q_{BH} n_{BH} I_{CH}} \qquad (3)$$

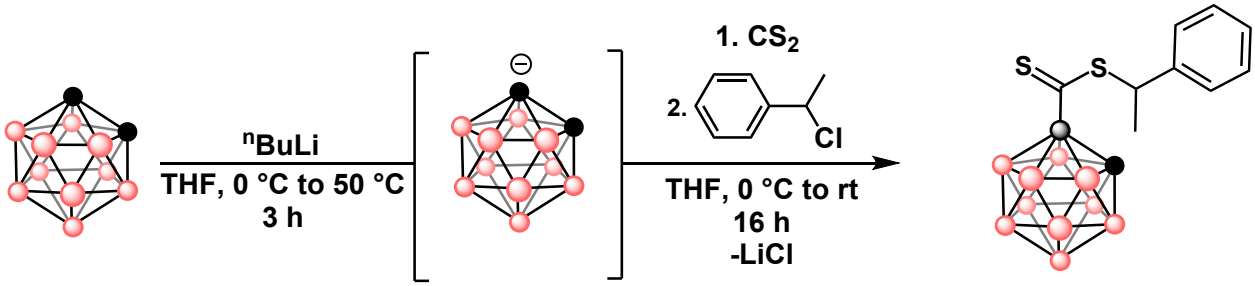
Q_{CH} and Q_{BH} are 0.95 and 0.94 respectively The average **1-pNIPAAm** polymer was composed of 20 NIPAm subunits and one **1**. This results in 210 C-H bonds and 10 B-H bonds per molecule. Signal intensities for I_{CH} and I_{BH} were calculated to be 73900 and 10500 respectively by fitting the spectrum using a multipeak Gaussian fit with a linear baseline. By entering these values into equation (3), we can determine $R_{BH} \approx 3R_{CH}$. As C-H stretches are frequently used for Raman imaging, this relationship demonstrates carborane's exciting potential as a Raman probe.

II. Small Molecule Synthesis and Characterization

Purification of *o*-carborane purchased from Boron Specialties

O-carborane (15g, 10.4 mmol) was charged to a round bottom flask with MeOH (150 mL). 12 M HCl (50 mL) was added slowly to the reaction vessel, and the resulting mixture was heated to 50 ˚C and stirred for 16 hours. The solution was then cooled, charged with H_2O (200 mL) and the resulting white solid was isolated by vacuum filtration, washed with water, and air dried. The solid was then dissolved in CH_2Cl_2, dried over $MgSO_4$, and filtered through Celite. The solution was dried *in vacuo* to afford a white powder. The powder was then sublimed at 60 ˚C under dynamic vacuum. After sublimation away from the yellow residue, the white crystals were taken up in $C_2H_4Cl_2$, charged with activated carbon/charcoal, and stirred for 2-3 hours at 75˚C. The suspension was then filtered and the filtrate was evaporated under vacuum. The resulting white solid was again sublimed at 60˚C to produce white crystals.

Synthesis of 1



O-carborane (324 mg, 2.24 mmol, 1.0 eq.) was dissolved in dry THF (3 mL) in a dry and degassed round-bottom flask equipped with magnetic stir bar. The reaction temperature was lowered to 0 °C at which point ^{n}BuLi (2.5 M in hexanes, 988.0 µL, 2.47 mmol, 1.1 equiv) was added dropwise slowly, the immediate formation of white precipitate was observed. The reaction temperature was raised to 50 °C and stirred for 3 h. After 3 h, the reaction was cooled to 0 °C at which point carbon disulfide (148.0 µL, 2.47 mmol, 1.1 equiv) was added slowly dropwise, an immediate red color change was observed. The reaction was stirred at room temperature for 1 h. After 1 h, the reaction temperature was lowered to 0 °C and 1-chloro-1-phenylethane (328.0 µL, 2.47 mmol, 1.1 equiv) was then added dropwise slowly. An immediate dark purple color change was observed. The reaction was stirred at room temperature for 16 h at which point the solvent was removed under reduced pressure to afford the crude material as a dark orange oil. The product was purified *via* column chromatography using (90:10 hexanes: CH_2Cl_2). Product was further purified via crystallization from dichloromethane layered with pentane at -30 °C to remove excess 1-chloro-1-phenylethane. Pure product is a bench-stable crystalline orange solid. Yield: 60%.

Single crystals suitable for x-ray crystallographic analysis were obtained from a concentrated solution of dichloromethane layered with pentane at -20 °C.

Rf = 0.67 (90:10 hexanes : CH_2Cl_2; $PdCl_2$ stain)

^{1}H NMR (500MHz, Chloroform-*d*, 298K): δ 7.37-7.25 (m, 5H, H_{Ar}), 4.91 (q, *J* = 7.1 Hz, 1H, -C*H*), 4.81 (s, 1H, cage-C*H*), 3.30-1.60 (bm, 10H, cage-B*H*), 1.72 (d, *J* = 7.1 Hz, 3H, -CH_3).

^{13}C{^{1}H} NMR (125MHz, Chloroform-*d*, 298K): δ 217.40, 139.56, 129.00, 128.41, 127.92, 82.31, 60.74, 53.28, 20.45.

^{11}B{^{1}H} NMR (128 MHz, Chloroform-*d*, 298K) δ -3.24, -8.76, -10.93, -11.37, -13.43.

IR: $\tilde{\nu}$ (cm^{-1}): 3053, 2972, 2926, 2572, 1493, 1445, 1371, 1195, 1126, 1087, 1038, 1013, 931, 766, 719, 694.

HRMS (Q-Exactive Plus) [M-H]$^-$: 323.19 (calc'd for $C_{11}H_{20}B_{10}S_2$ 323.19) m/z

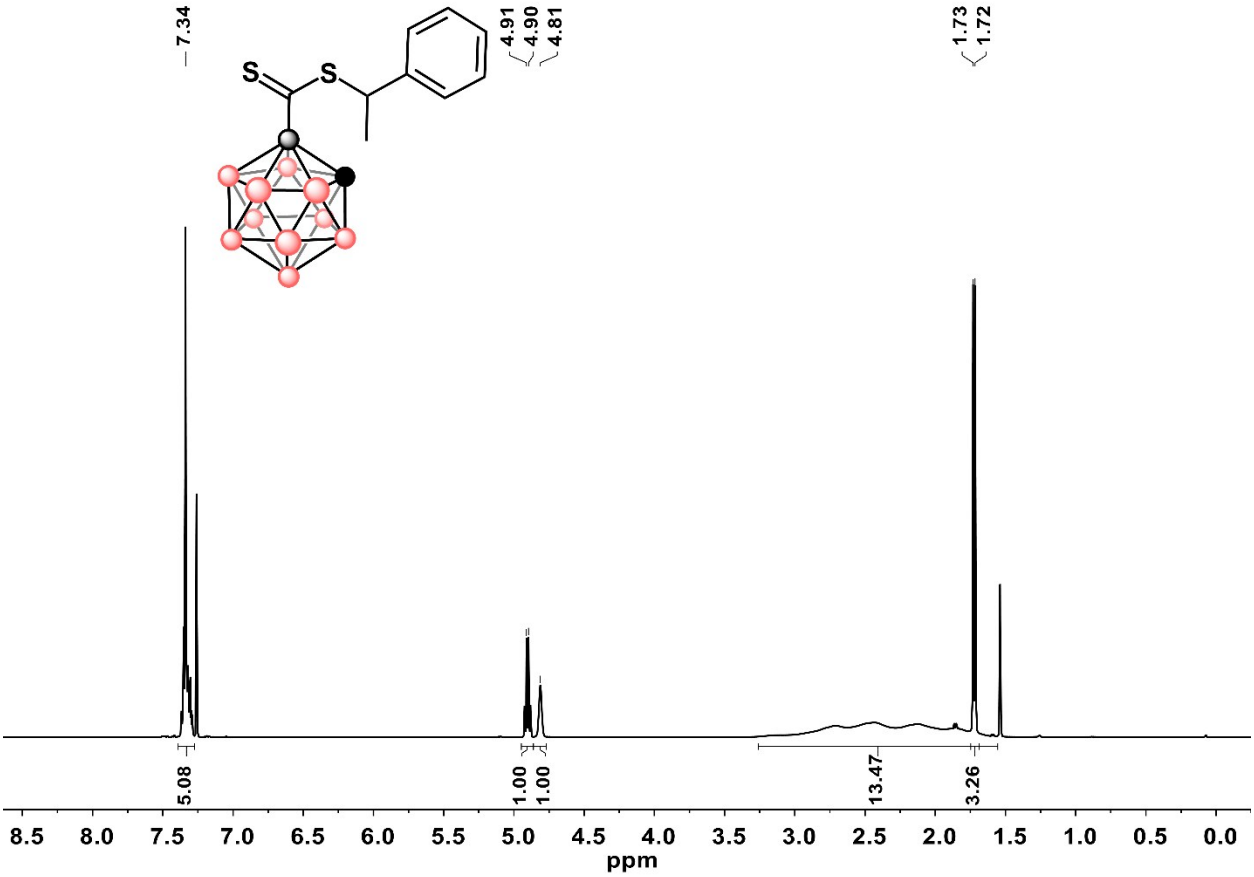


Figure S1. ^{1}H NMR spectrum of **1** in chloroform-*d* at 298 K.

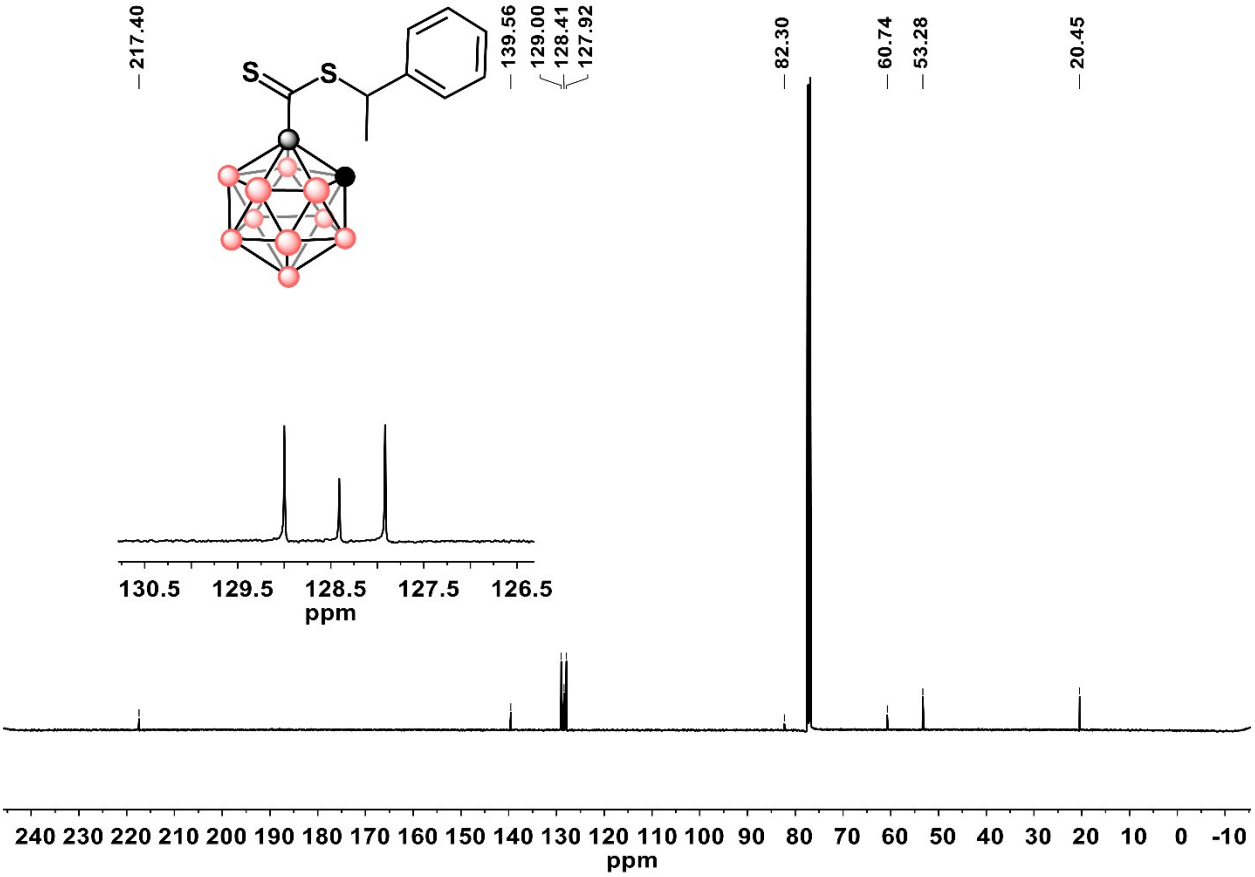


Figure S2. ^{13}C NMR spectrum of **1** in chloroform-*d* at 298 K.

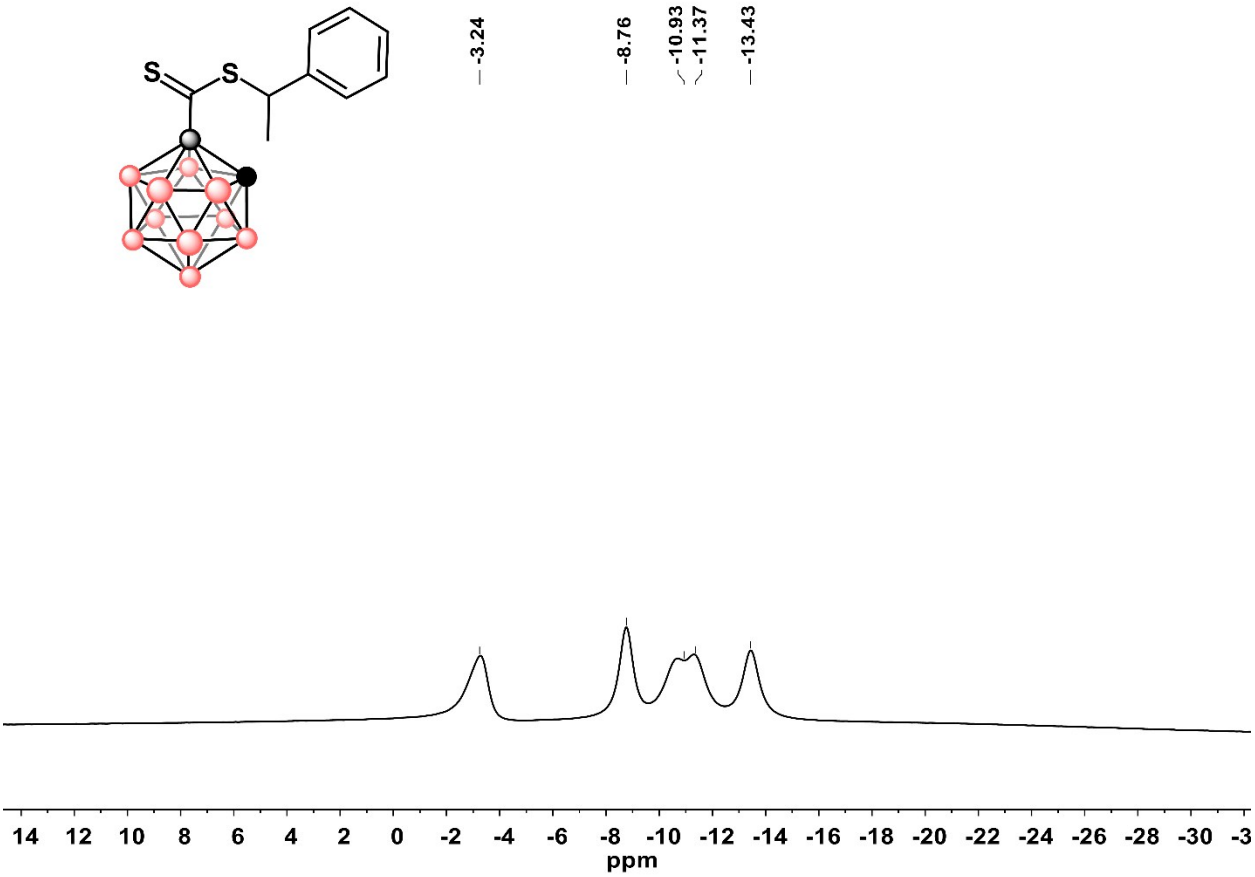


Figure S3. ^{11}B NMR spectrum of **1** in chloroform-*d* at 298 K.

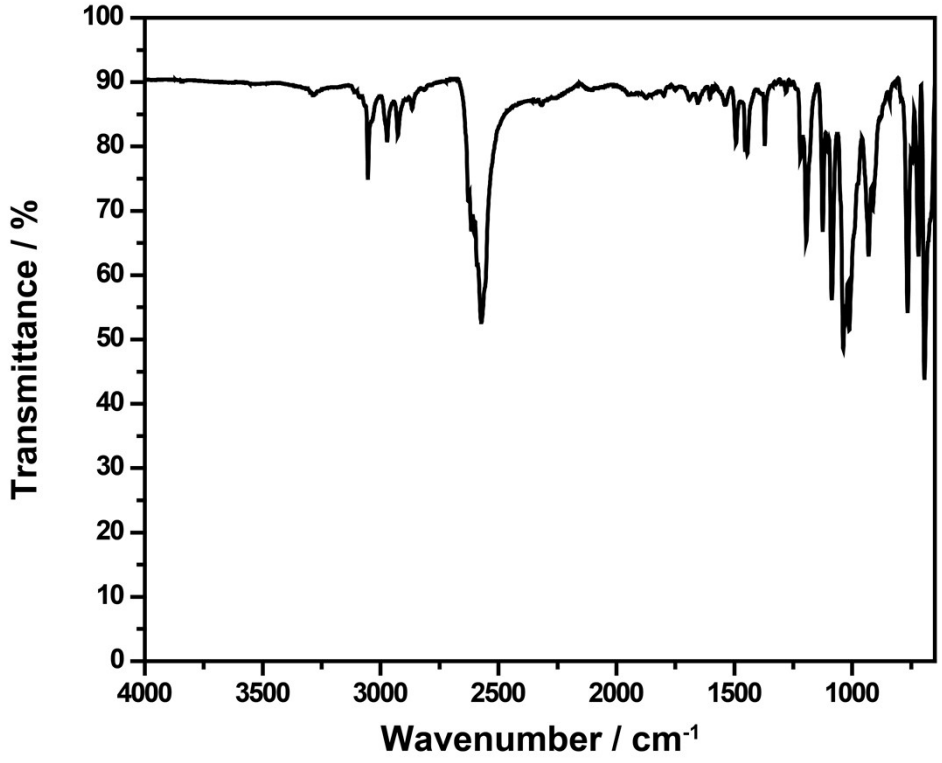


Figure S4. Infrared spectrum of **1**.

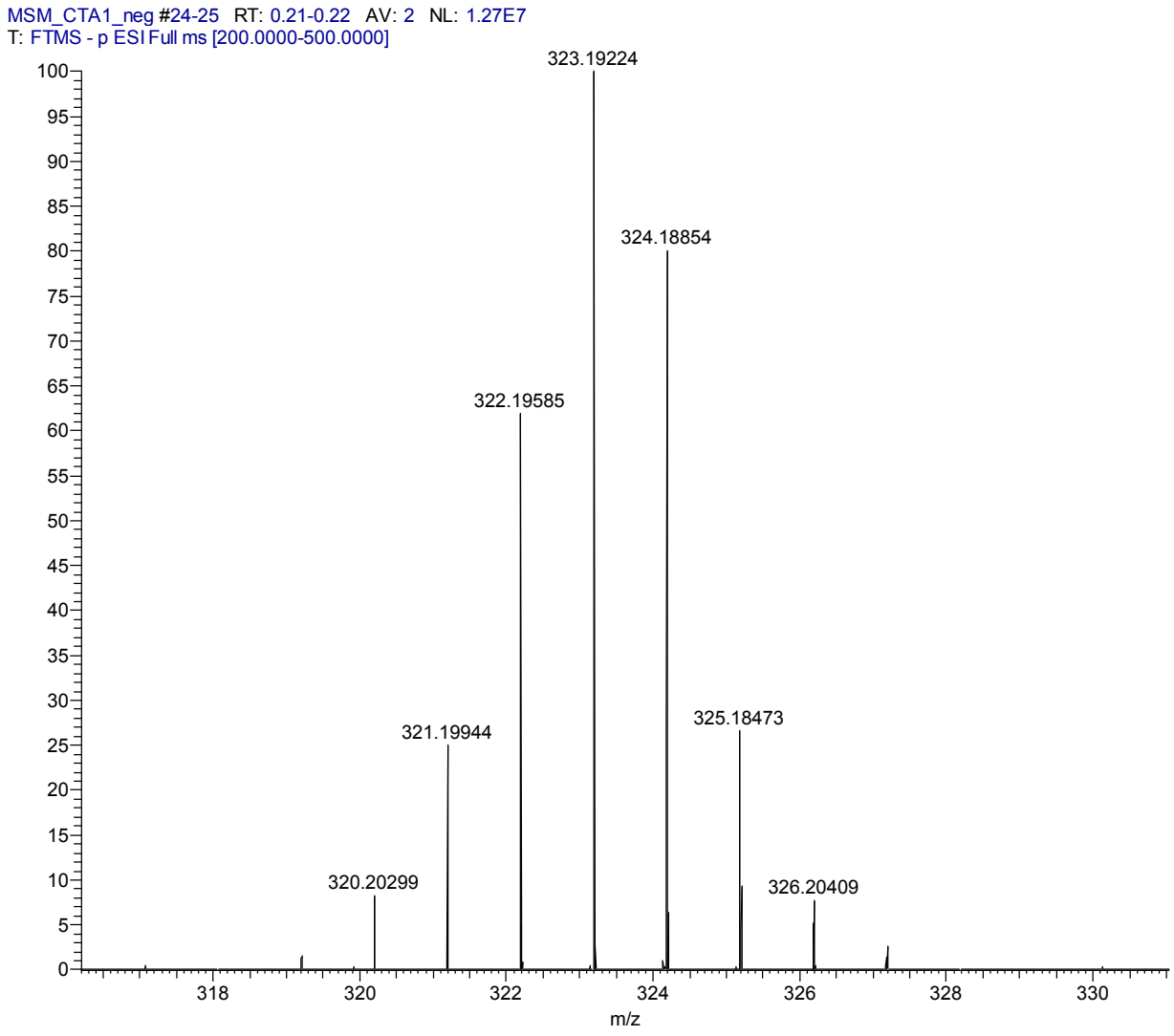
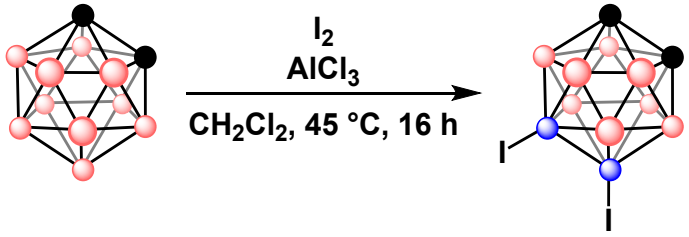


Figure S5. HRMS of **1**.

Synthesis of 9,12-diiodo-*o*-carborane

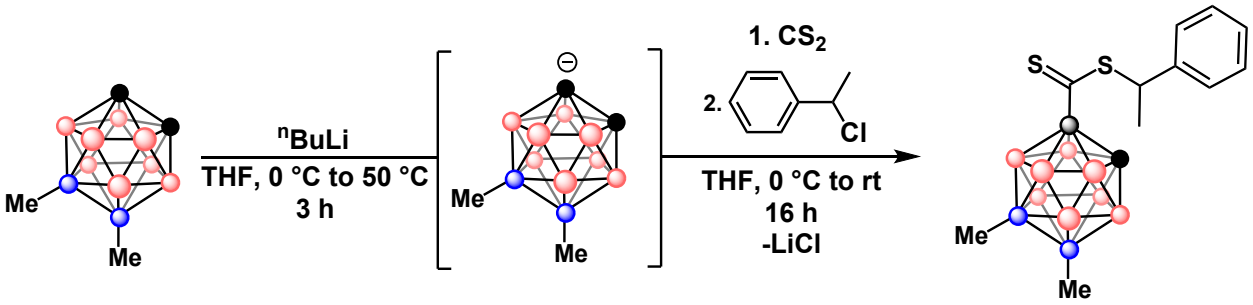


Ortho-$C_2B_{10}H_{12}$ (1.44 g, 10.0 mmol), was added to an oven-dried Schlenk flask capped with a rubber septum and evacuated/backfilled with N_2 three times. I_2 (2.54 g, 10.0 mmol) was added under a positive N_2 flow before the addition of dry CH_2Cl_2 (50 mL) via cannula. $AlCl_3$ (0.266 g, 20 mol%) was added to the stirring solution under a positive N_2 flow before the rubber septum was replaced with a greased glass stopper. The reaction mixture was subsequently refluxed (~37 °C) until the color faded to pale yellow (~4 h). A second equivalent of I_2 (2.54 g, 10.0 mmol) and $AlCl_3$ (0.133 g, 10 mol%) were added and the reaction was stirred at 37 °C overnight. The dark brown reaction mixture was diluted with deionized H_2O (25 mL), and unreacted I_2 was quenched by the dropwise addition of a saturated aqueous $Na_2S_2O_3$ solution until the solution was no longer colored. The opaque organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The organic portions were combined and dried with $MgSO_4$ resulting in a clear, colorless solution. The solution was then filtered through a pad of Celite on a fritted funnel and the CH_2Cl_2 was removed under reduced pressure to yield an off-white solid that was further purified by sublimation at 130 °C to produce the title compound as a white solid. Spectral data matches that previously reported in the literature (see: Kirlikovali, K. O.; Axtell, J. C.; Gonzalez, A.; Phung, A. C.; Khan, S. I.; Spokoyny, A. M. *Chem. Sci.* **2016**, *7*, 5132-5138).

Synthesis of 9,12-dimethyl-*o*-carborane

9,12-dimethyl-*o*-carborane was prepared from 9,12-diiodo-*o*-carborane according to the procedure reported in the following manuscript: Li, J.; Logan, C. F.; Jones, M. *Inorg. Chem.* **1991**, *30* (25), 4866-4868.

Synthesis of 2



9,12-dimethyl-*o*-carborane (770.6 mg, 4.48 mmol, 1.0 equiv) was dissolved in dry THF (6 mL) in a dry and degassed round-bottom flask equipped with magnetic stir bar. The reaction temperature was lowered to 0 °C at which point ^{n}BuLi (2.5 M in hexanes, 1.98 mL, 4.94 mmol, 1.1 equiv) was added dropwise slowly, the immediate formation of white precipitate was observed. The reaction temperature was raised to 50 °C and left stirring for 3 hours. After 3 hours, the reaction was cooled to 0 °C at which point carbon disulfide (296.0 µL, 4.94 mmol, 1.1 equiv) was added dropwise slowly, an immediate red color change was observed. The reaction was stirred at room temperature for 1 hour. After 1 hour, the reaction temperature was lowered to 0 °C and 1-chloro-1-phenylethane (656.0 µL, 4.94 mmol, 1.1 equiv) was then added dropwise slowly. The reaction was stirred at room temperature for 16 hours at which point the solvent was removed under reduced pressure. The product was purified *via* column chromatography (95:5 hexanes:acetone) to remove residual carborane. Excess 1-chloro-1-phenylethane was removed under dynamic vacuum and heating (100 mTorr at 95 °C). Pure product is a bench-stable dark orange oil. Yield: 69%.

Rf = 0.8 (95:5 hexanes:acetone; $PdCl_2$ stain)

^{1}H NMR (500MHz, Chloroform-*d*, 298K): δ 7.36 – 7.30 (m, 5H, H_{Ar}), 4.90 (q, *J* = 7.0 Hz, 1H, -C*H*), 4.61 (s, 1H, cage-C*H*), 3.12 – 1.59 (bm, 10H, cage-B*H*), 1.72 (d, *J* = 7.2 Hz, 3H, -CH_3), 0.23 (s, 3H, -BCH_3), 0.20 (s, 3H, -BCH_3).

^{13}C{^{1}H} NMR (125MHz, Chloroform-*d*, 298K): δ 218.32, 139.70, 128.96, 128.33, 127.92, 76.36, 54.44, 53.13, 20.42.

^{11}B{^{1}H} NMR (161 MHz, Chloroform-*d*, 298K) δ 6.95, 6.37, -7.00, -11.56, -12.18, -13.78.

IR: $\tilde{\nu}$ (cm^{-1}): 3059, 2906, 2591, 1493, 1452, 1314, 1199, 1094, 1071, 1022, 990, 912, 761, 738, 695.

HRMS (Q-Exactive Plus) [M-H]$^{1-}$: 351.22 (calc'd for $C_{13}H_{24}B_{10}S_2$ 351.22) m/z

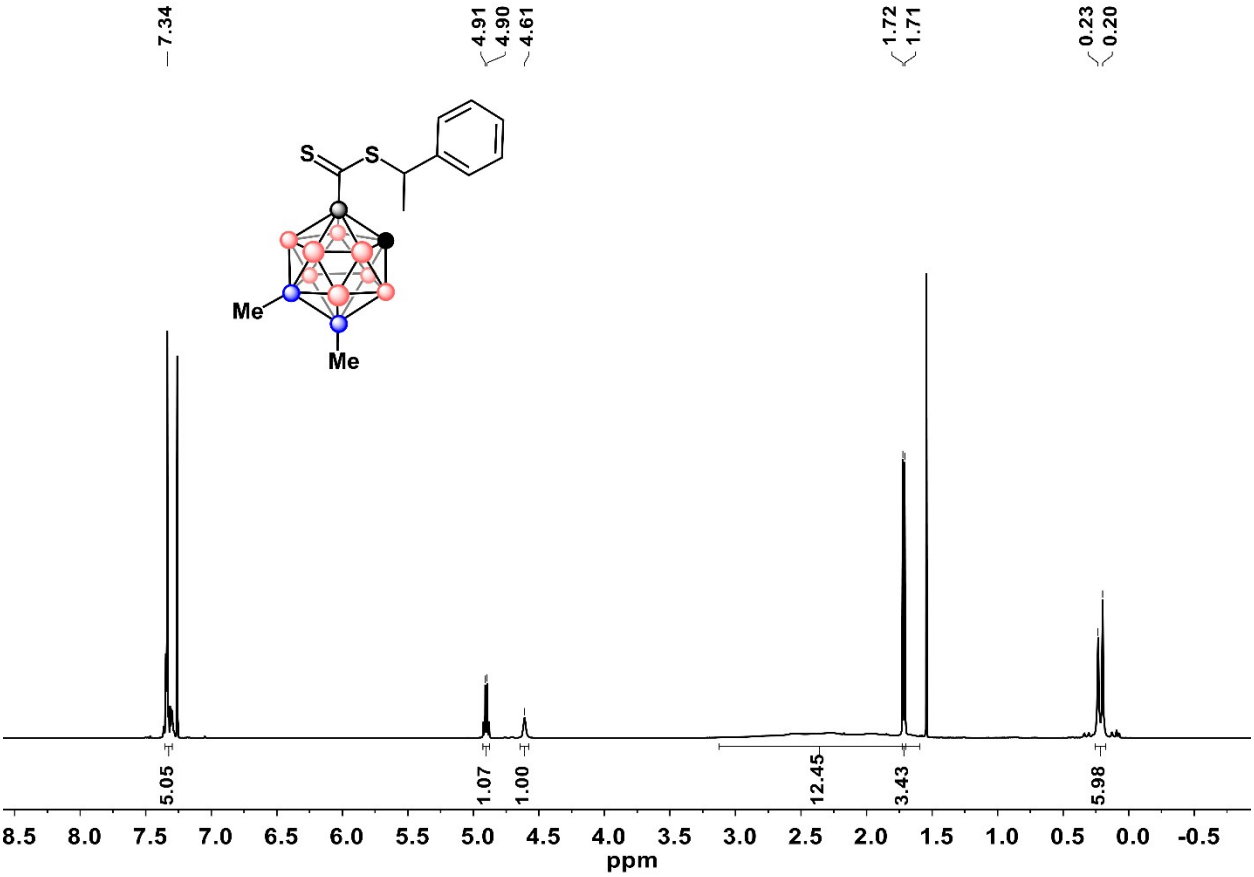


Figure S6. ^{1}H NMR spectrum of **1** in chloroform-*d* at 298 K.

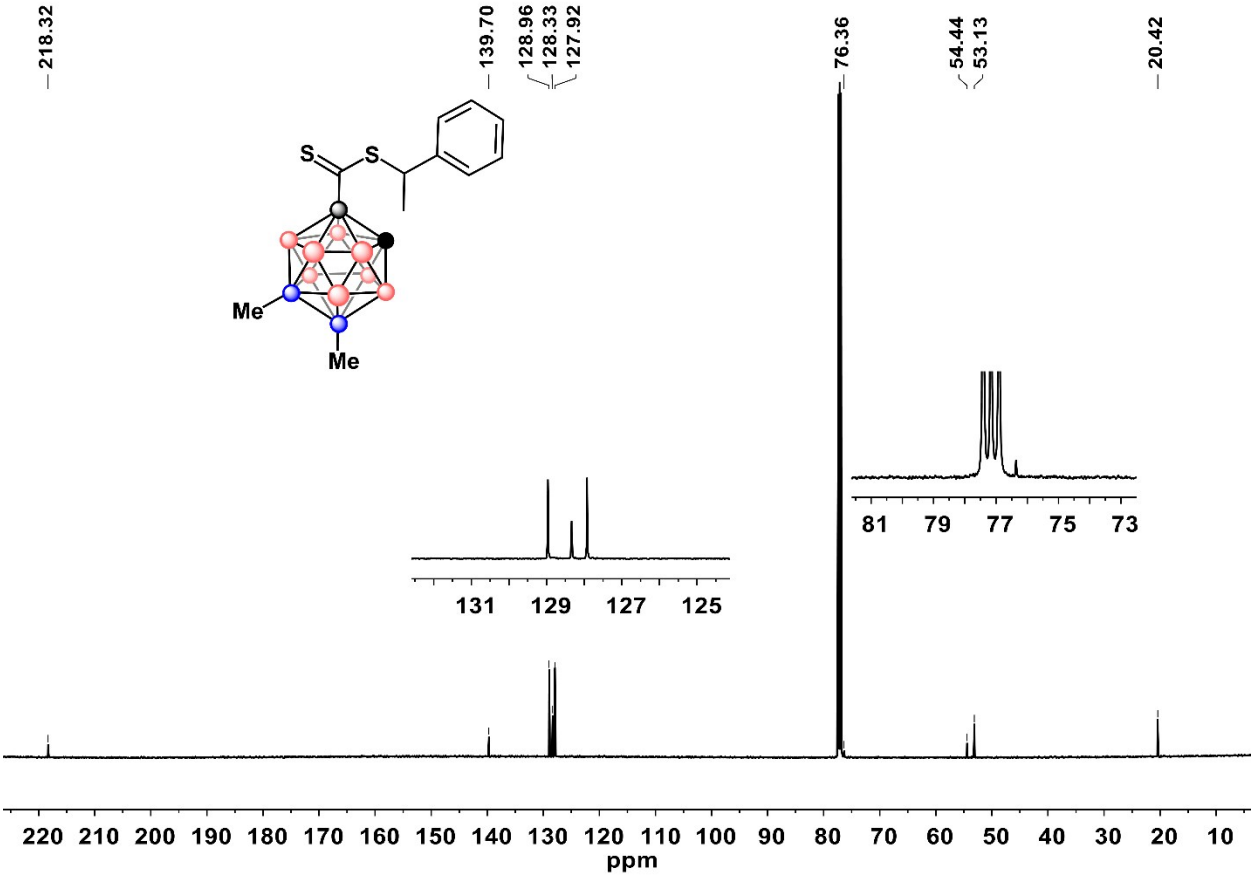


Figure S7. ^{13}C NMR spectrum of **1** in chloroform-*d* at 298 K.

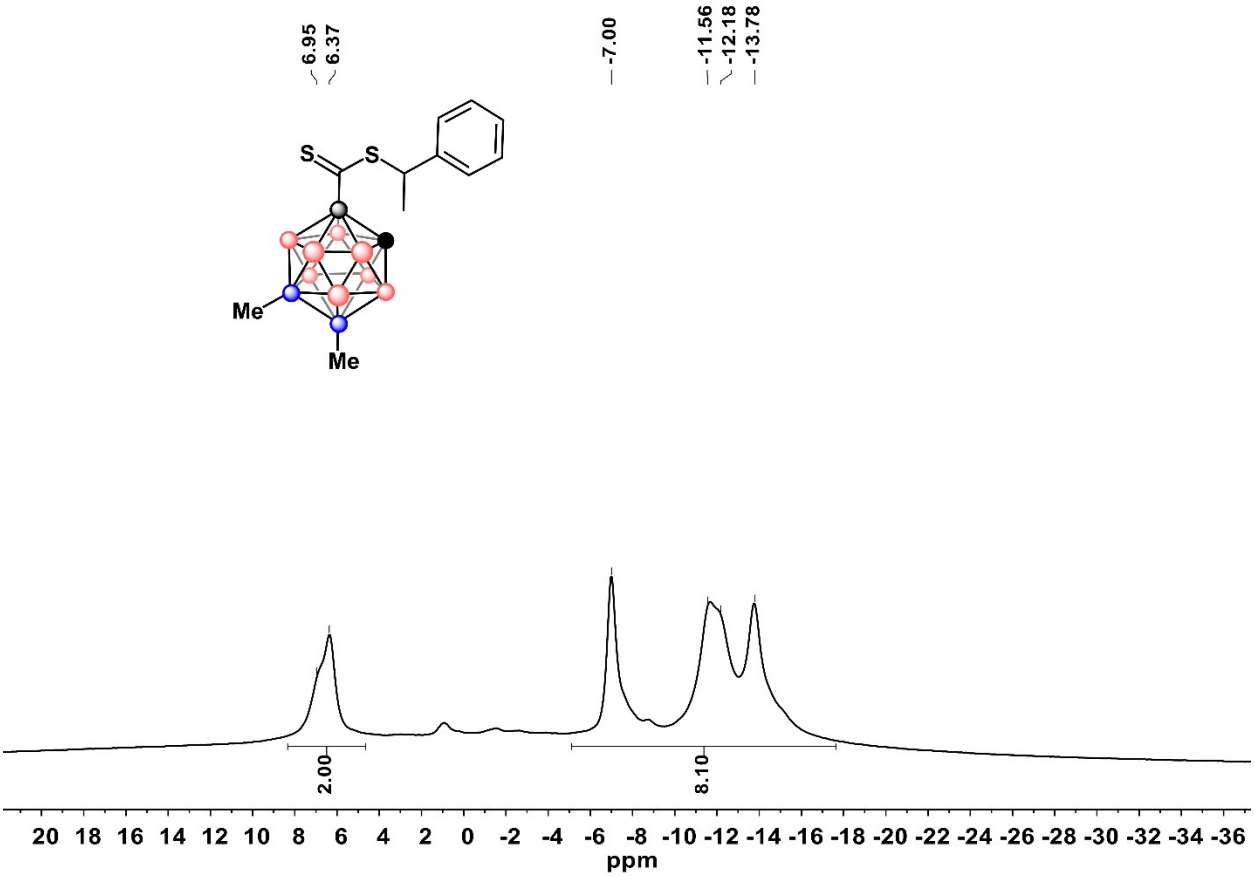


Figure S8. ^{11}B NMR spectrum of **1** in chloroform-*d* at 298 K.

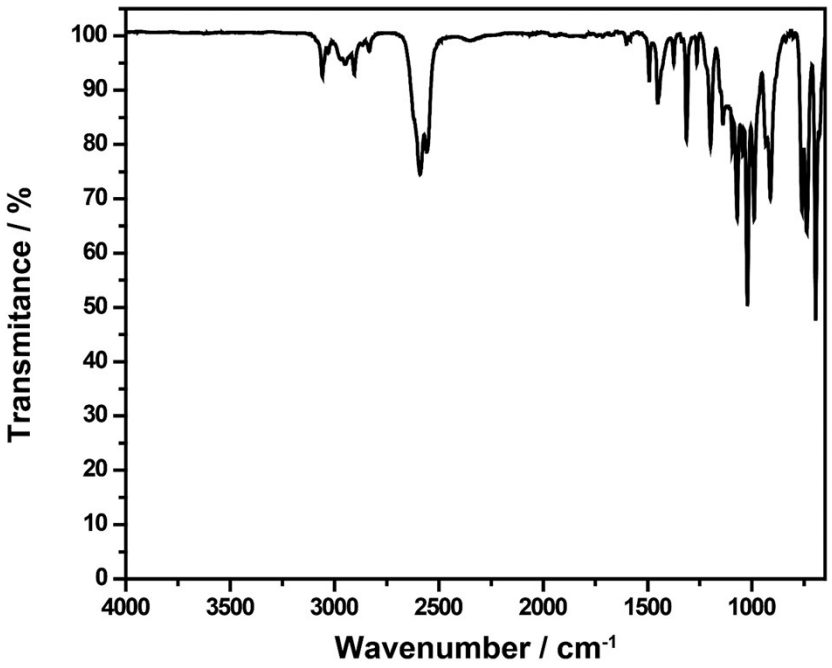


Figure S9. Infrared spectrum of **1**.

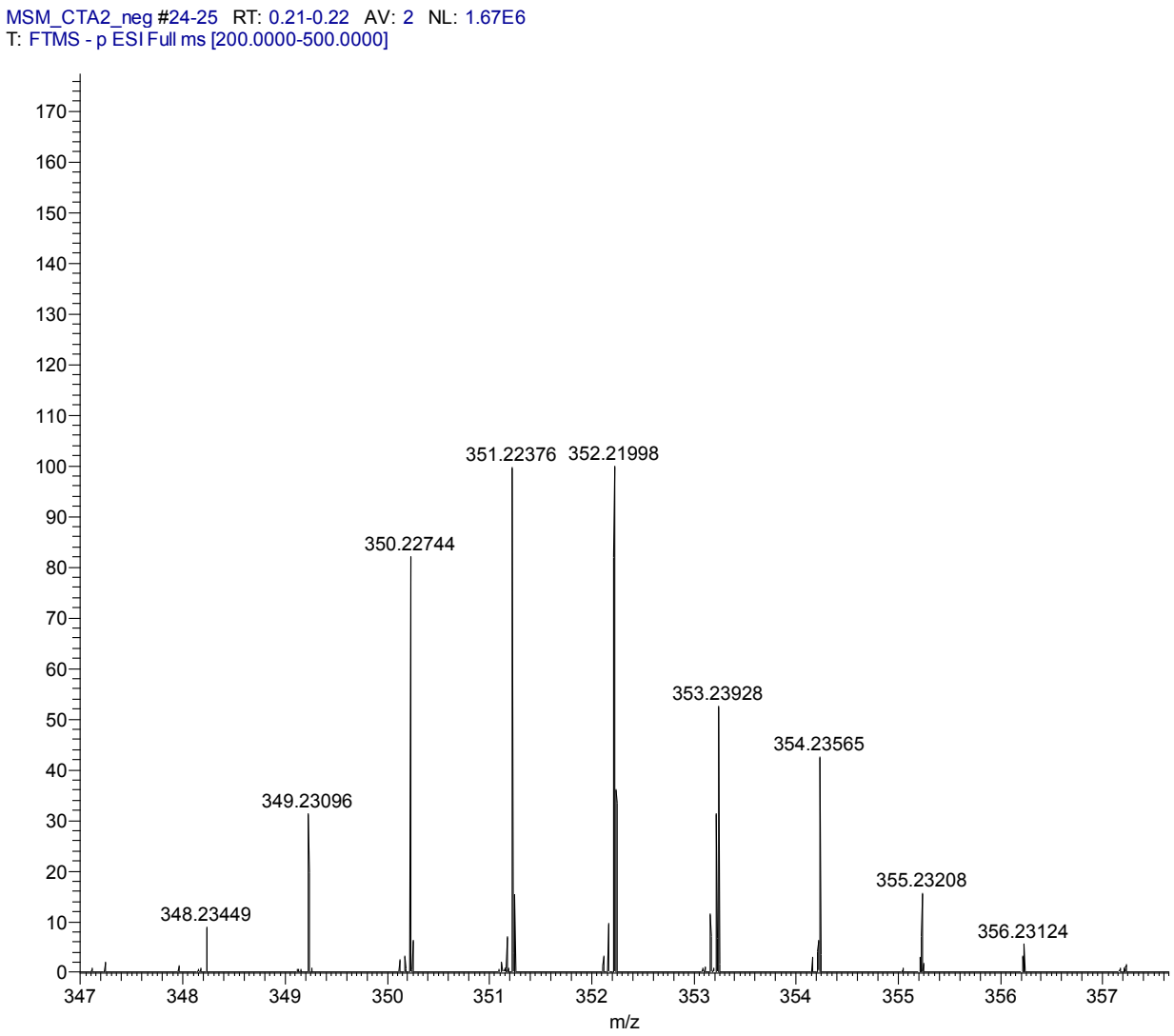


Figure S10. HRMS of **2**.

III. Polymer Synthesis, Characterization, and End-group Modification

General Polymerization Procedure for Liquid Monomers (Methyl Acrylate, Styrene, 4-chlorostyrene)

Polymerizations were prepared in the glovebox under nitrogen atmosphere. Methyl acrylate (0.20 mL, 2.20 mmol, 60 equiv.) was passed through dry activated basic alumina and added to a dram vial equipped with a magnetic stir bar. CTA **2** (12.7 mg, 0.036 mmol, 1 equiv.) and AIBN (1.8 mg, 0.011 mol, 0.3 equiv.) were dissolved in a minimal amount of EtOAc (~70 µL) and transferred to the dram vial containing the monomer. Tetralin (20 µL) was then added to the solution. The solution was stirred for 1 minute before collecting a 50 µL aliquot (t=0 min). The dram vial was then sealed with a polypropylene cap containing a Teflon coated septum and brought out of the glove box. The polymerization was initiated by immersing the dram vial in an 80 ˚C oil bath. Aliquots (50 µL) of the reaction mixture were collected at pre-determined time intervals and added into 700 µL of $CDCl_3$ to determine monomer conversion via ^1H NMR spectroscopy. The reaction was quenched by opening the dram vial to the atmosphere and the polymer was purified *via* precipitation from cold methanol.

General Polymerization Procedure for NIPAAm

All reactions were prepared in a glovebox under nitrogen atmosphere. *N*-isopropylacrylamide (500.0 mg, 4.42 mmol, 60 equiv), **2** (25.9 mg, 7.31×10^{-5} mol, 1 equiv), and AIBN (6.05 mg, 3.68×10^{-5} mol, 0.3 equiv) were added to a dram vial equipped with a magnetic stir bar. The reagents were dissolved in 2.2 mL toluene making a 2 M solution. The dram vial was sealed with a polypropylene cap containing a Teflon coated septum and brought out of the glove box. The polymerization was started by immersing the dram vial in an 80 ˚C oil bath. The reaction was quenched by the opening dram vial to atmosphere and the polymer was purified *via* precipitation from cold methanol or diethyl ether.

Polymer conversion experiments: The reactions were prepared using optimized conditions (*vide supra*) along with the addition of an internal standard (≈20 µL tetralin). Aliquots (50 µL) of the reaction mixture were collected at predetermined time intervals and added into $CDCl_3$ (700 µL) for analysis *via* ^1H NMR spectroscopy. Monomer conversion was calculated by ^1H NMR spectroscopy by integration of unreacted vinyl monomer signal to the tetralin proton resonance at ~2.75-2.8 ppm.

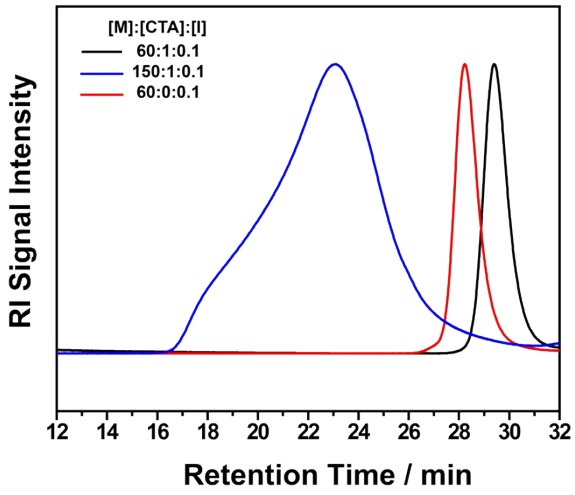


Figure S11. GPC overlay of **1-PS**.

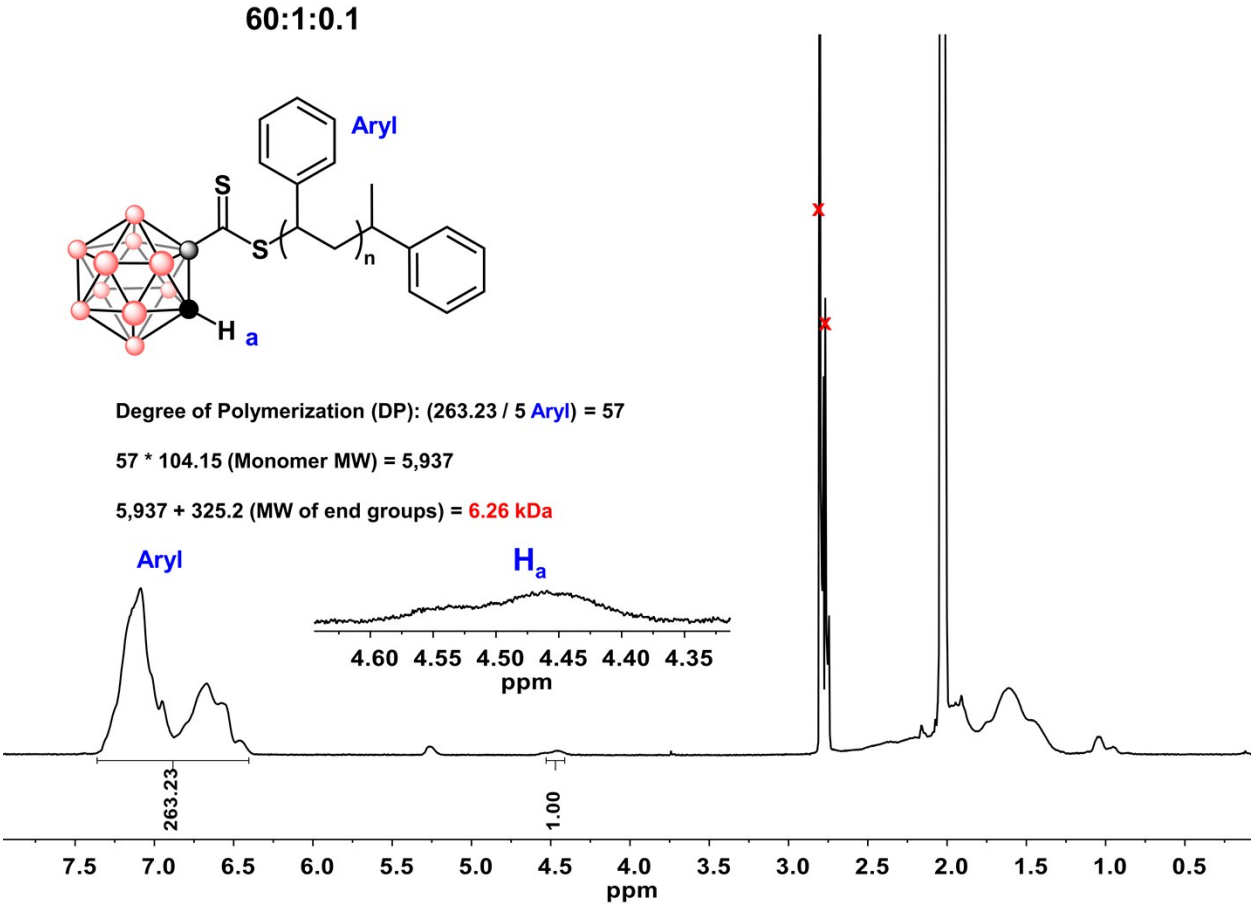


Figure S12. ^{1}H NMR spectrum of **1-PS** in acetonitrile-d_3 at 298 K and sample calculation of polymer molecular weight.

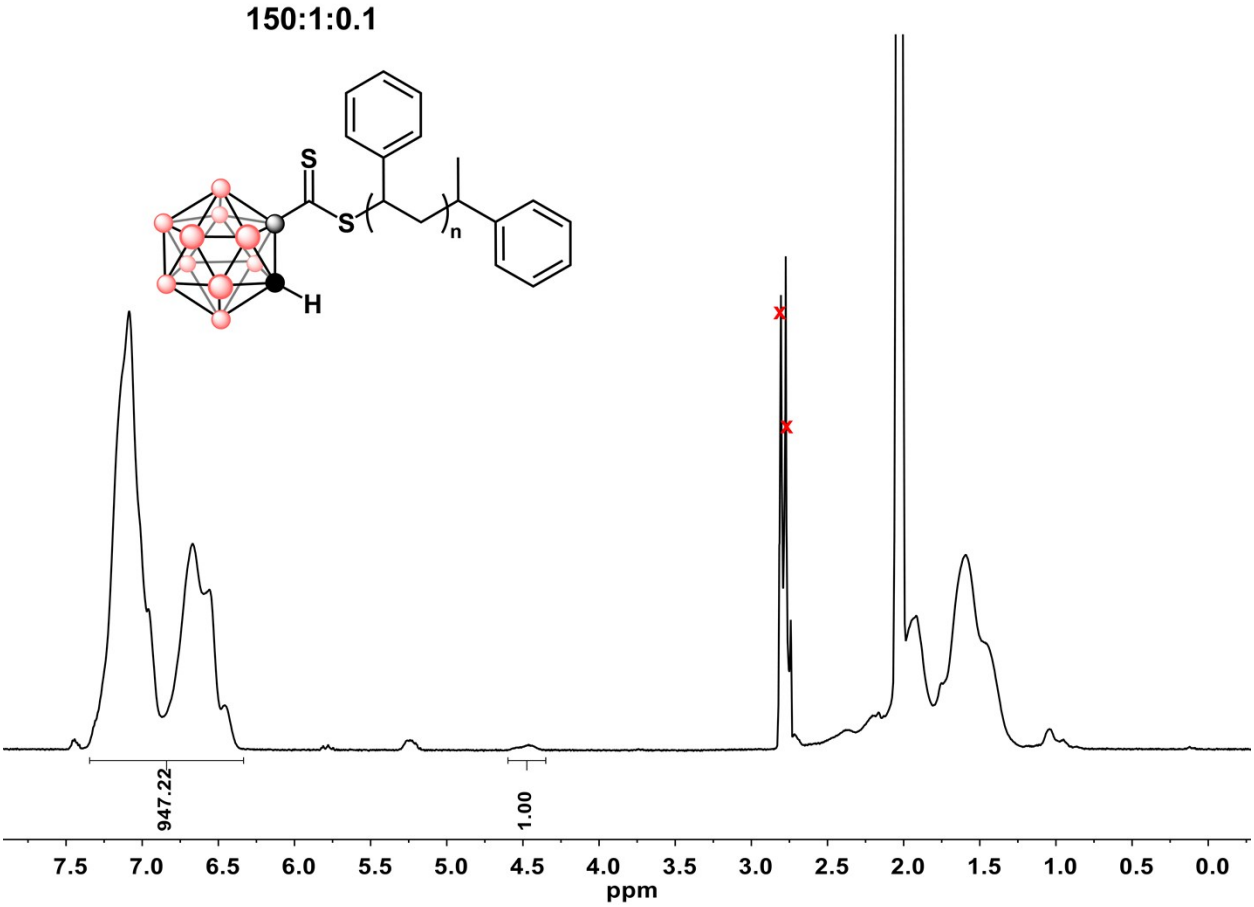


Figure S13. ^{1}H NMR spectrum of **1-PS** in acetonitrile-d_3 at 298 K and sample calculation of polymer molecular weight.

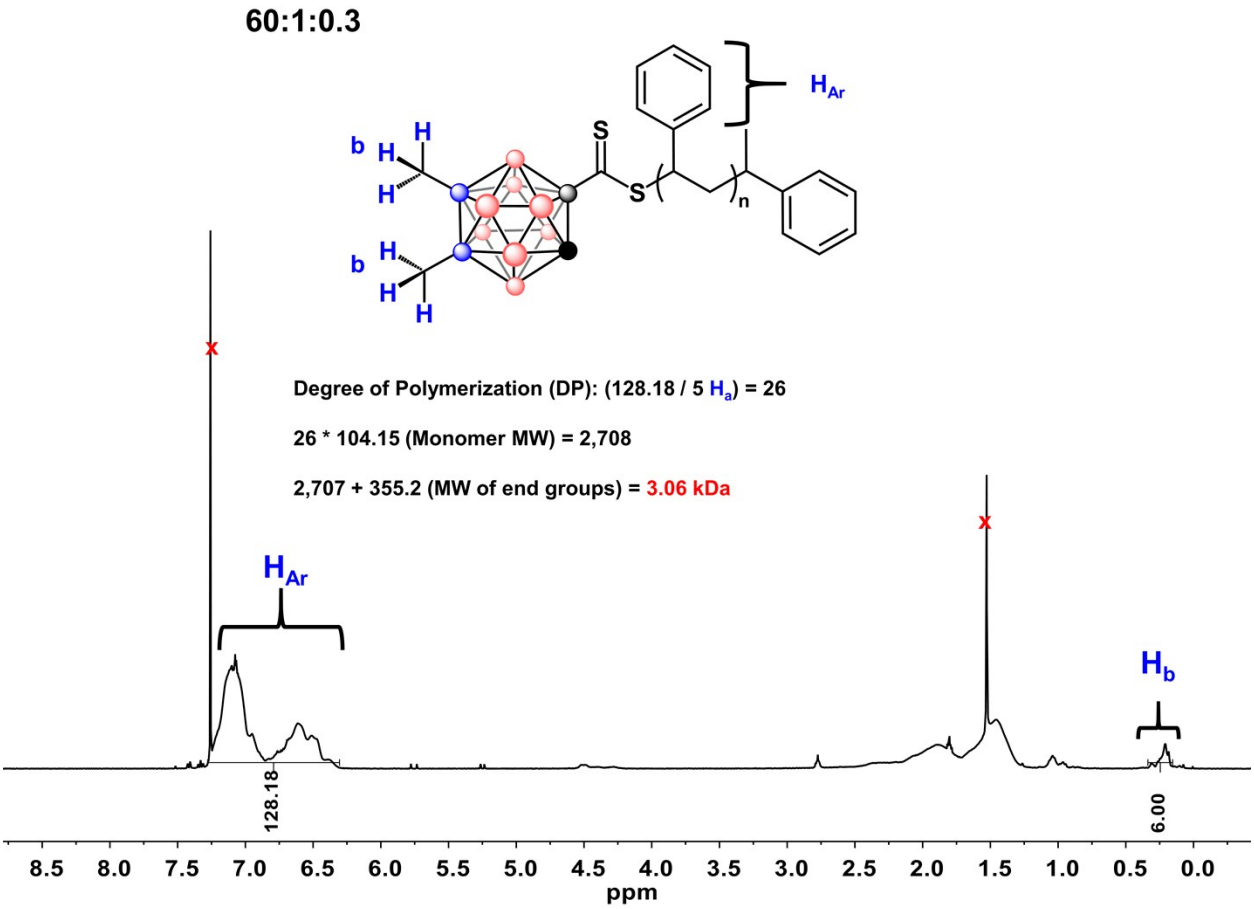


Figure S14. ^{1}H NMR spectrum of **2-PS** in chloroform-*d* at 298 K and sample calculation of polymer molecular weight.

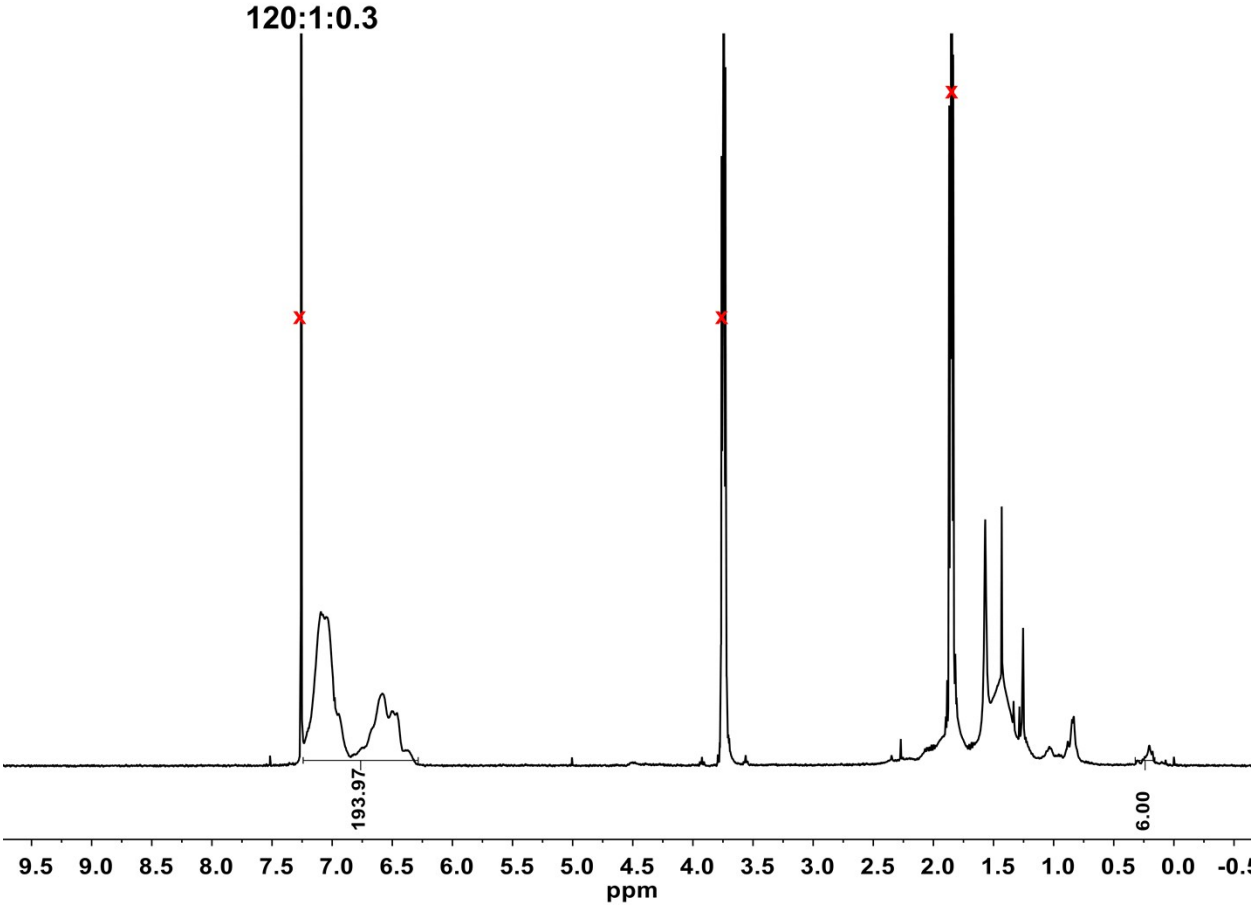


Figure S15. ^{1}H NMR spectrum of **2-PS** in chloroform-*d* at 298 K.

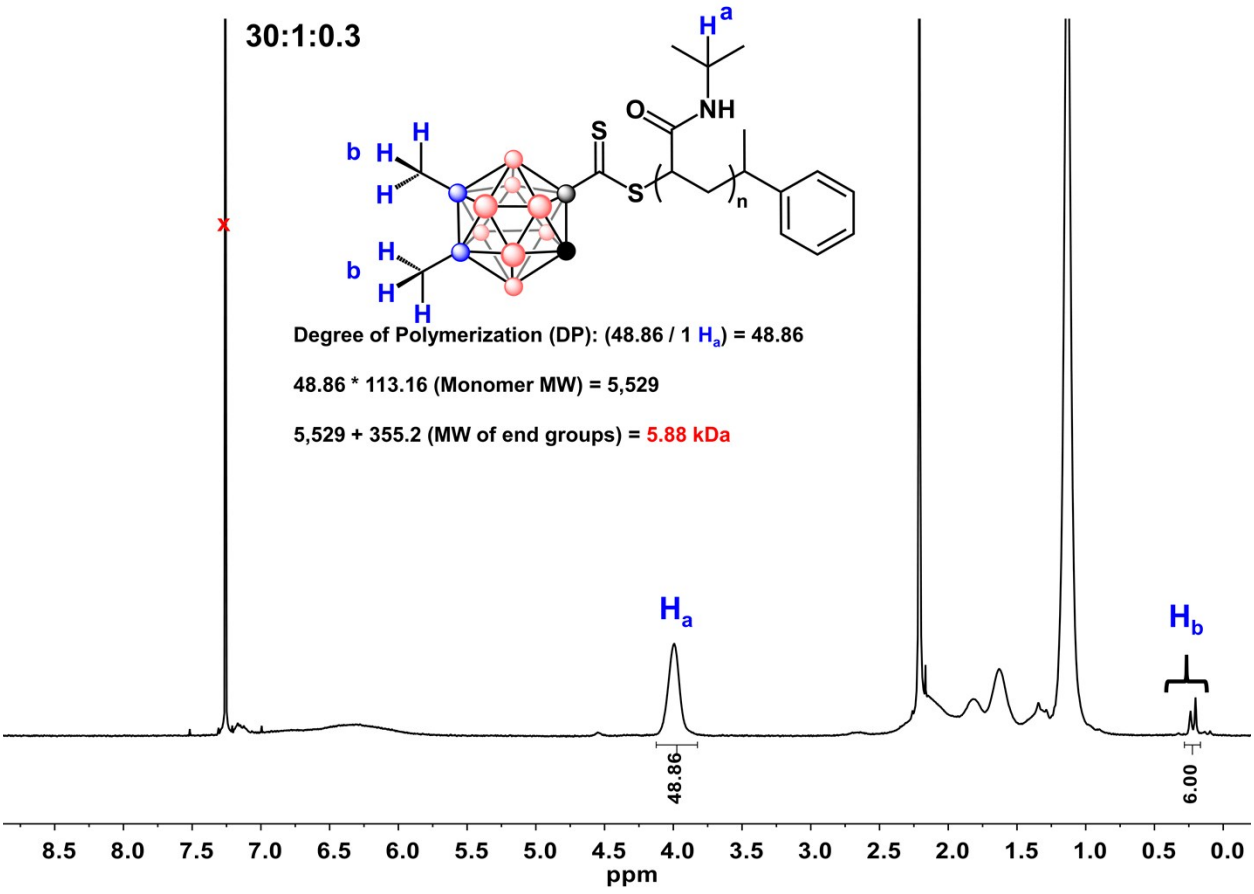


Figure S16. ^{1}H NMR spectrum of **2-pNIPAAm** in chloroform-*d* at 298 K and sample calculation of polymer molecular weight.

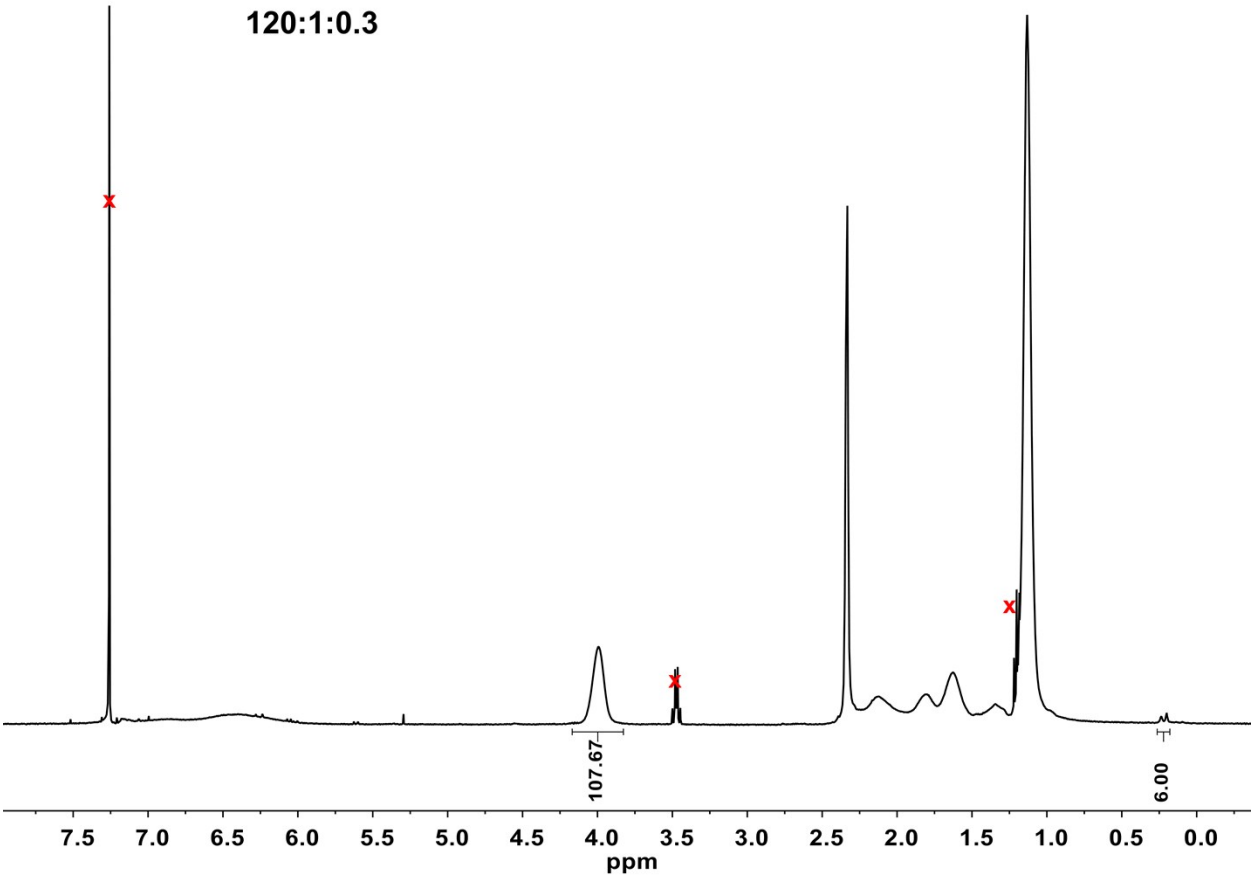


Figure S17. ^{1}H NMR spectrum of **2-pNIPAAm** in chloroform-*d* at 298 K.

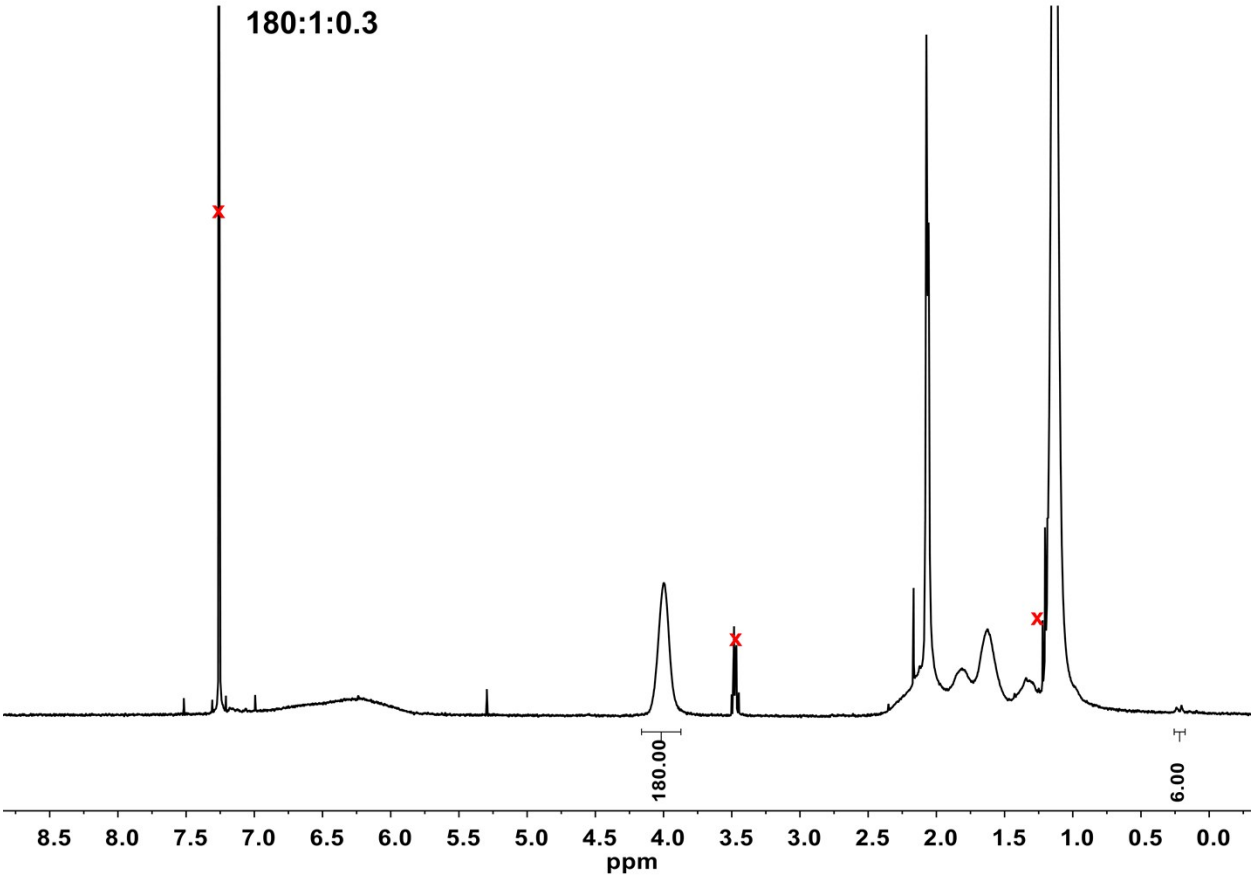


Figure S18. ^{1}H NMR spectrum of **2-pNIPAAm** in chloroform-*d* at 298 K.

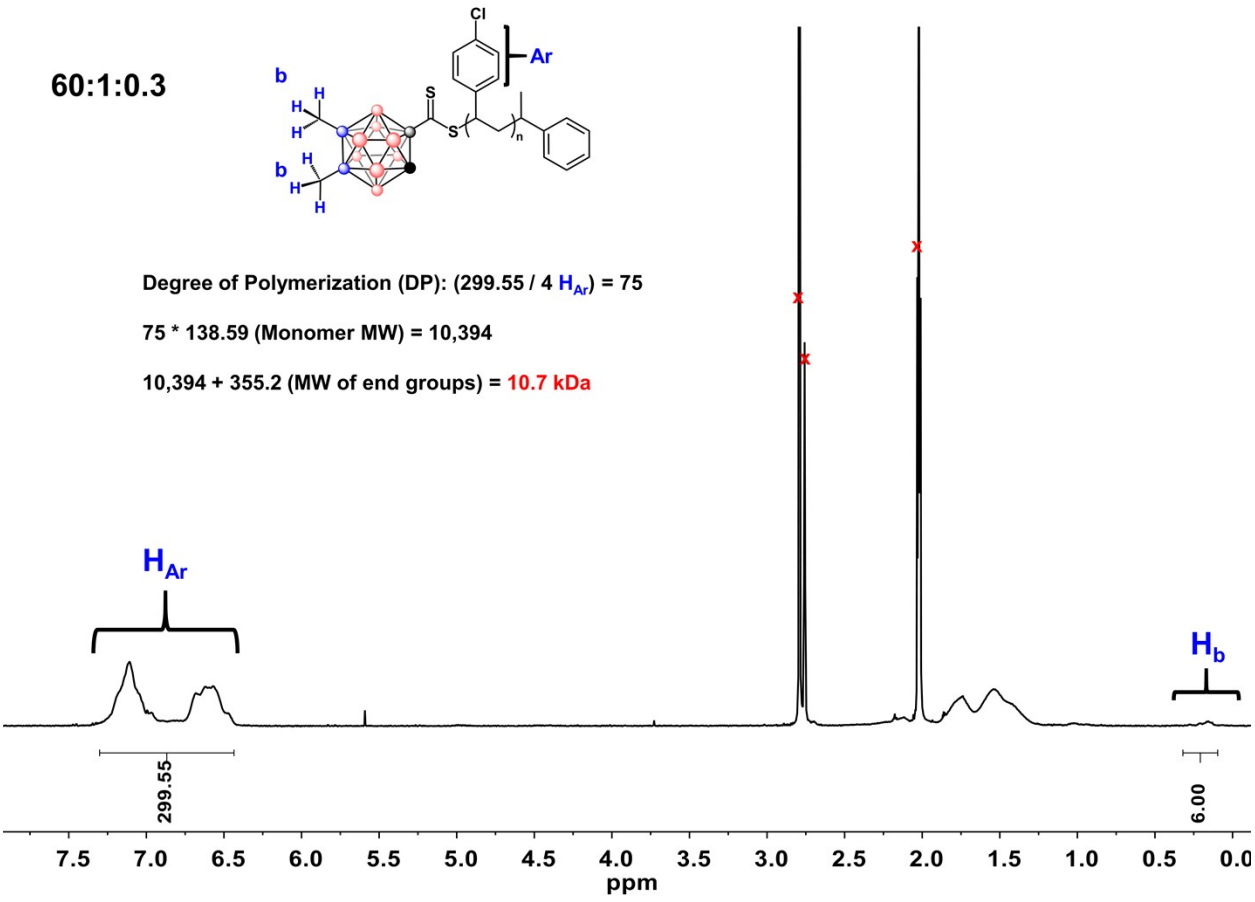


Figure S19. ^{1}H NMR spectrum of **2-(4-Cl)-PS** in acetone-d_6 at 298 K and sample calculation of polymer molecular weight.

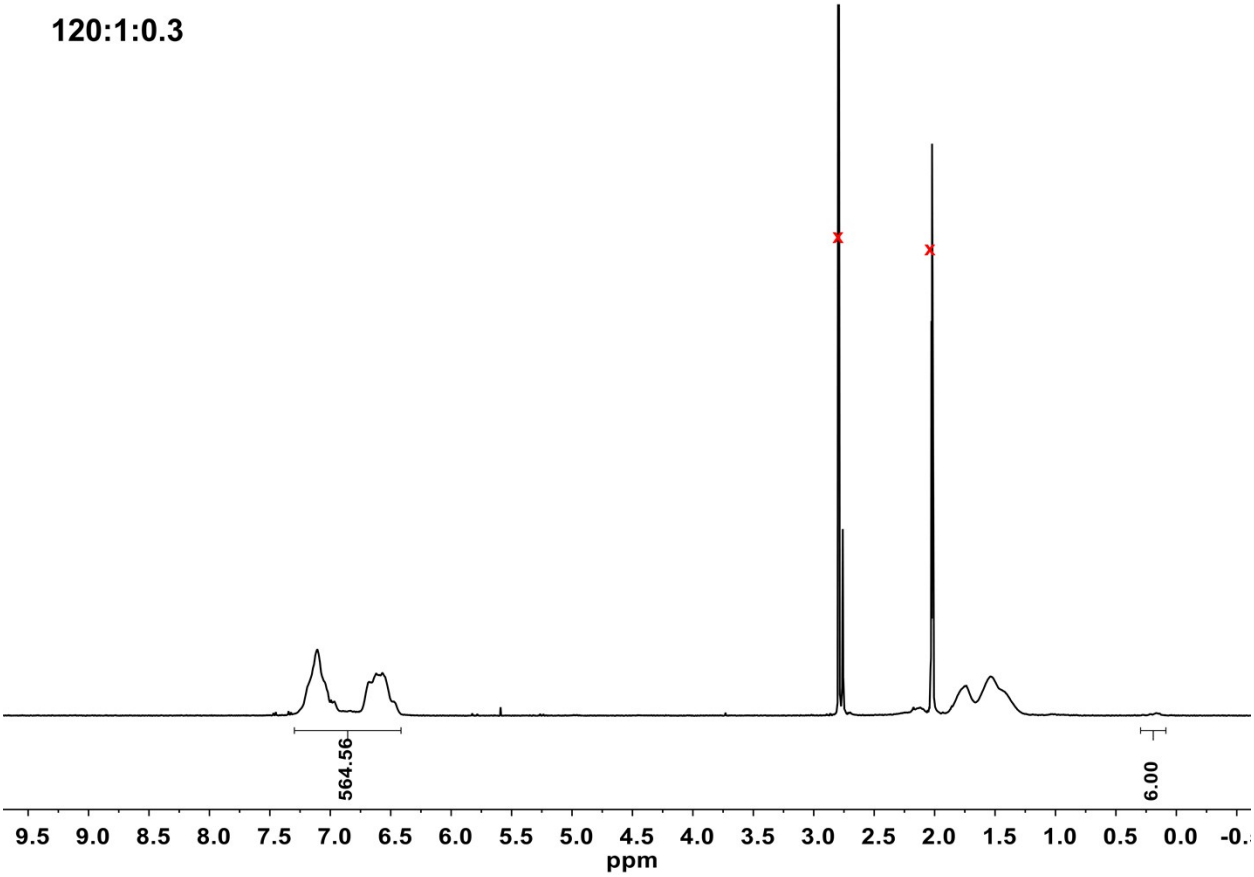


Figure S20. ^{1}H NMR spectrum of **2-(4-Cl)-PS** in in acetone-d_6 at 298 K.

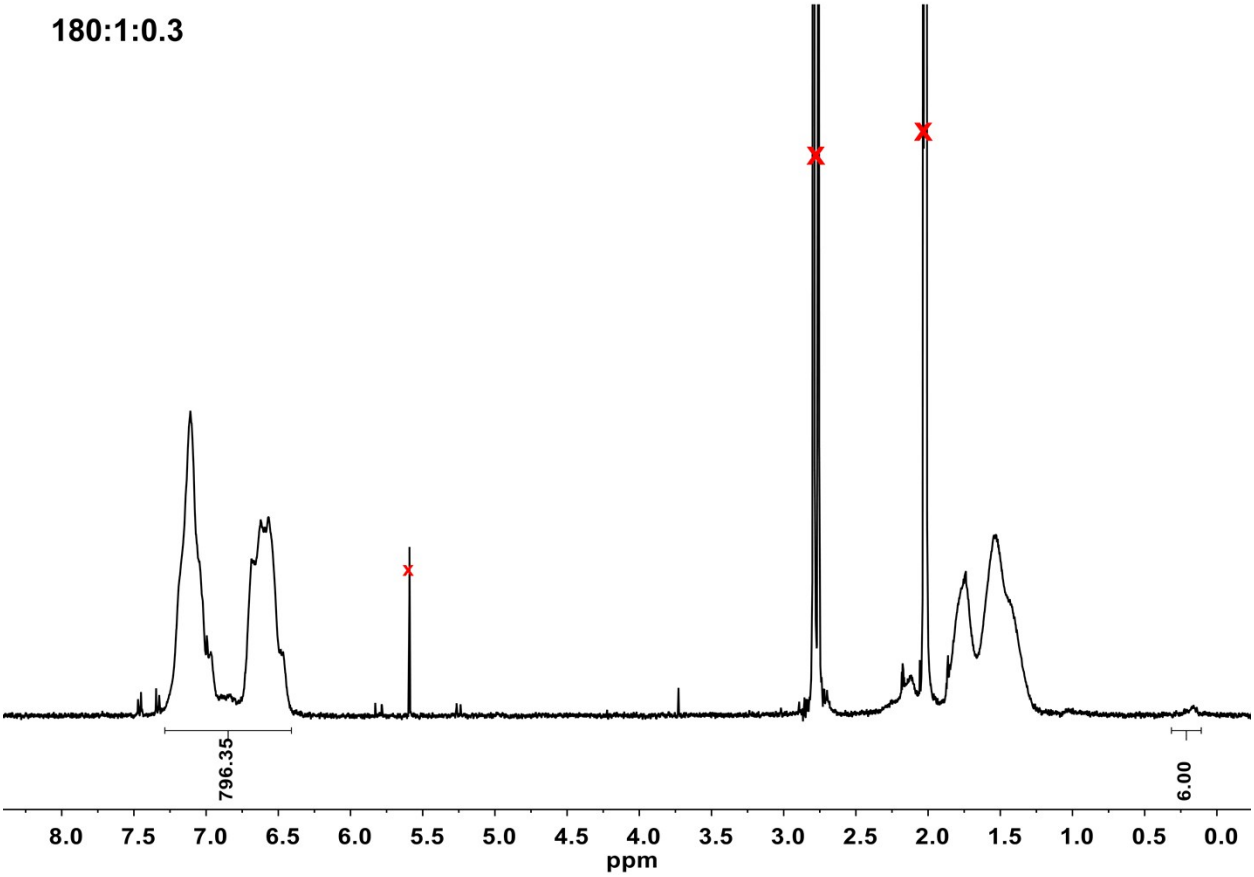


Figure S21. ^{1}H NMR spectrum of **2-(4-Cl)-PS** in in acetone-d_6 at 298 K.

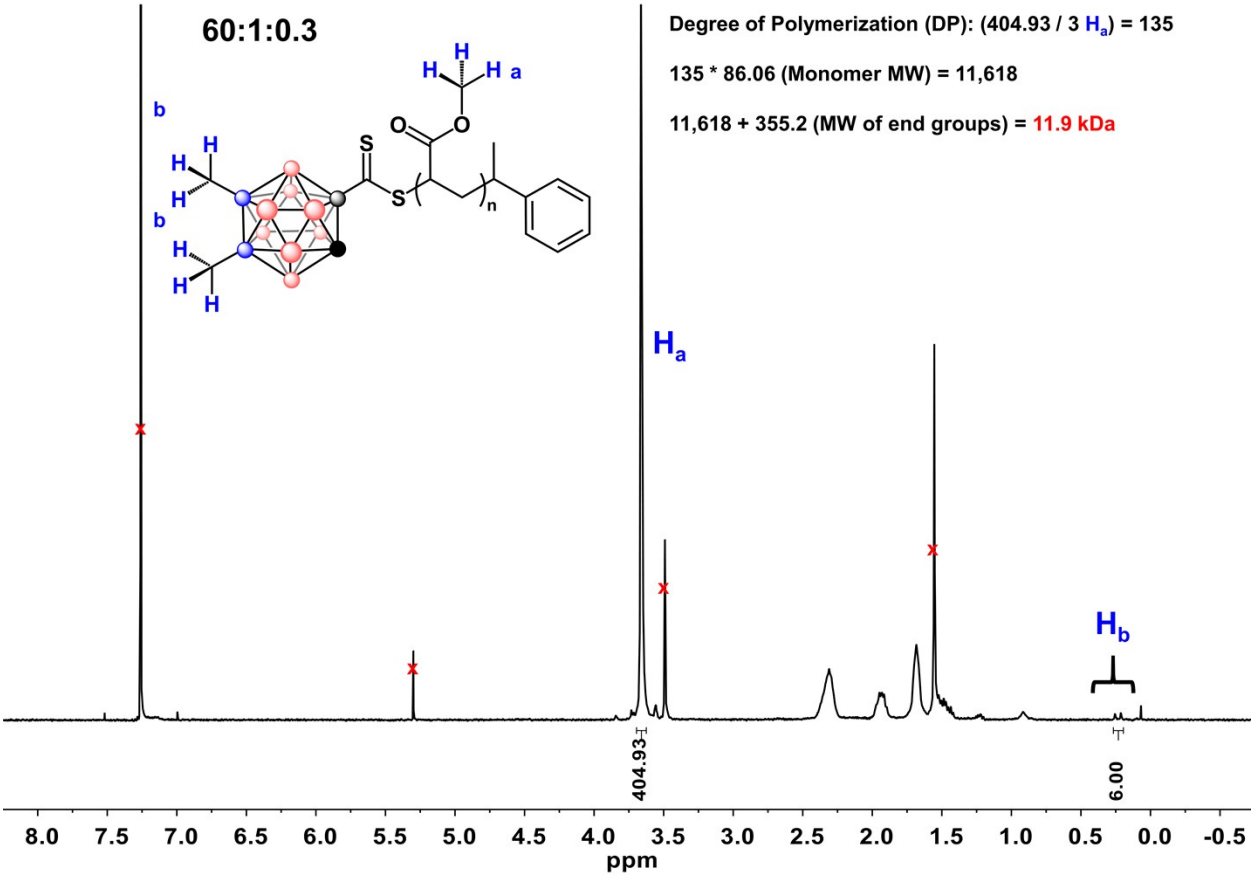


Figure S22. ^{1}H NMR spectrum of **2-PMA** in chloroform-*d* at 298 K and sample calculation of polymer molecular weight.

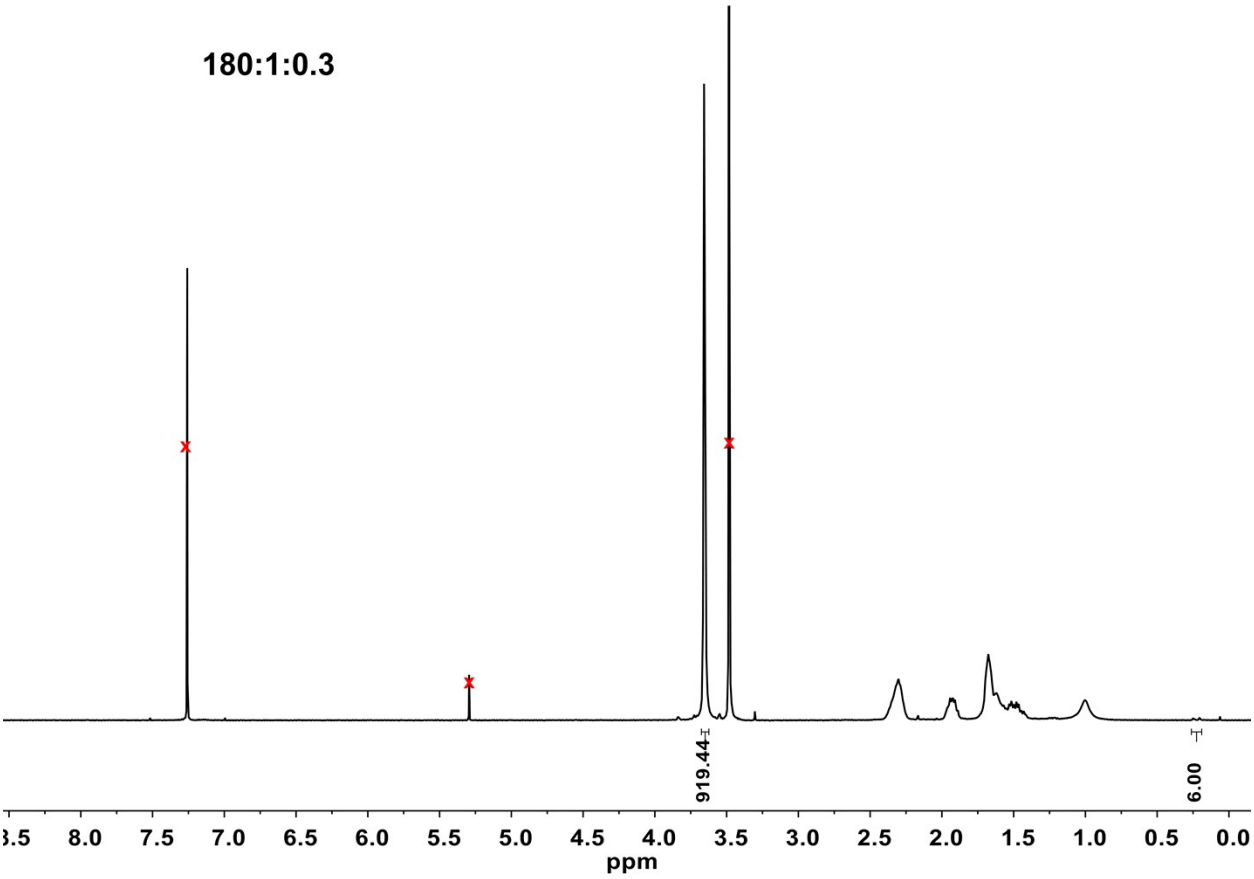


Figure S23. ^{1}H NMR spectrum of **2-PMA** in chloroform-*d* at 298 K.

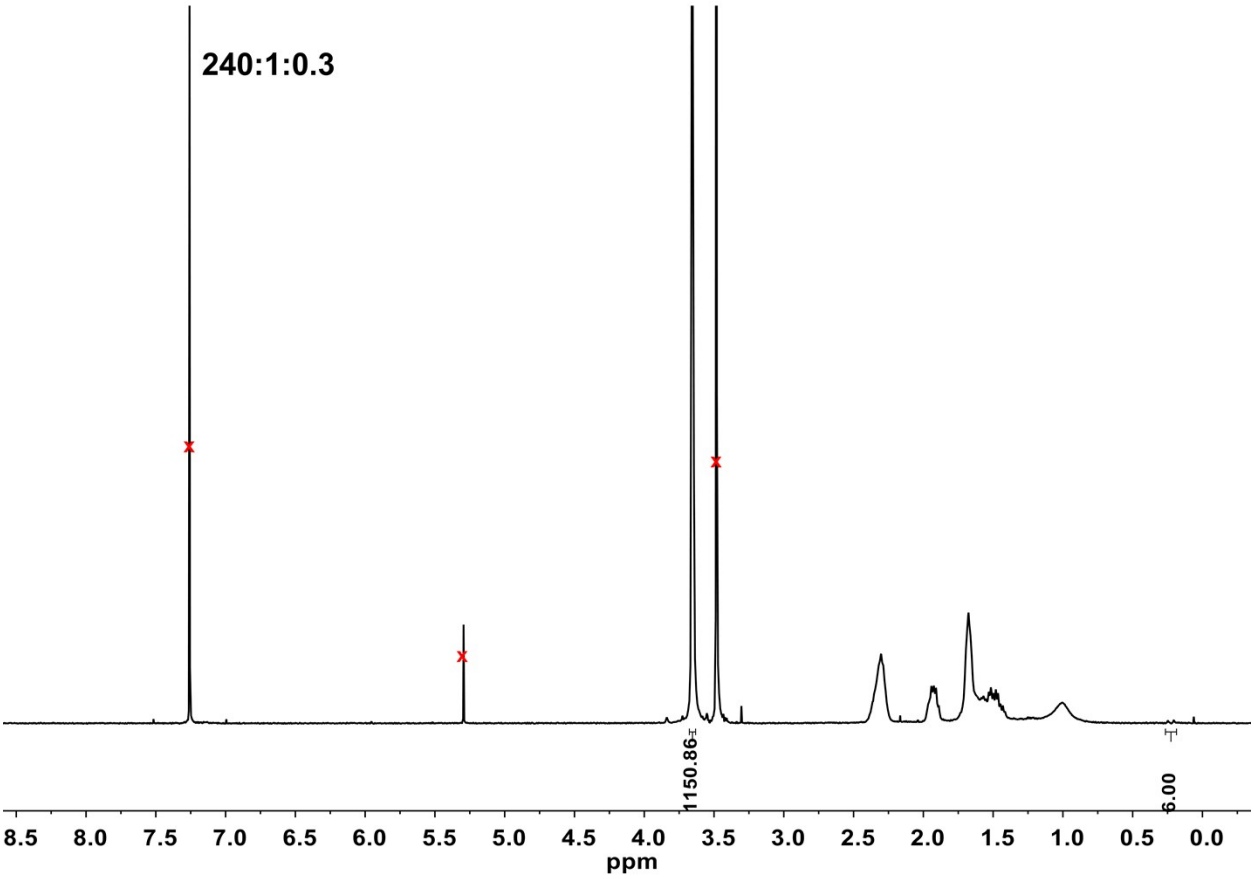


Figure S24. ^{1}H NMR spectrum of **2-PMA** in chloroform-*d* at 298 K.

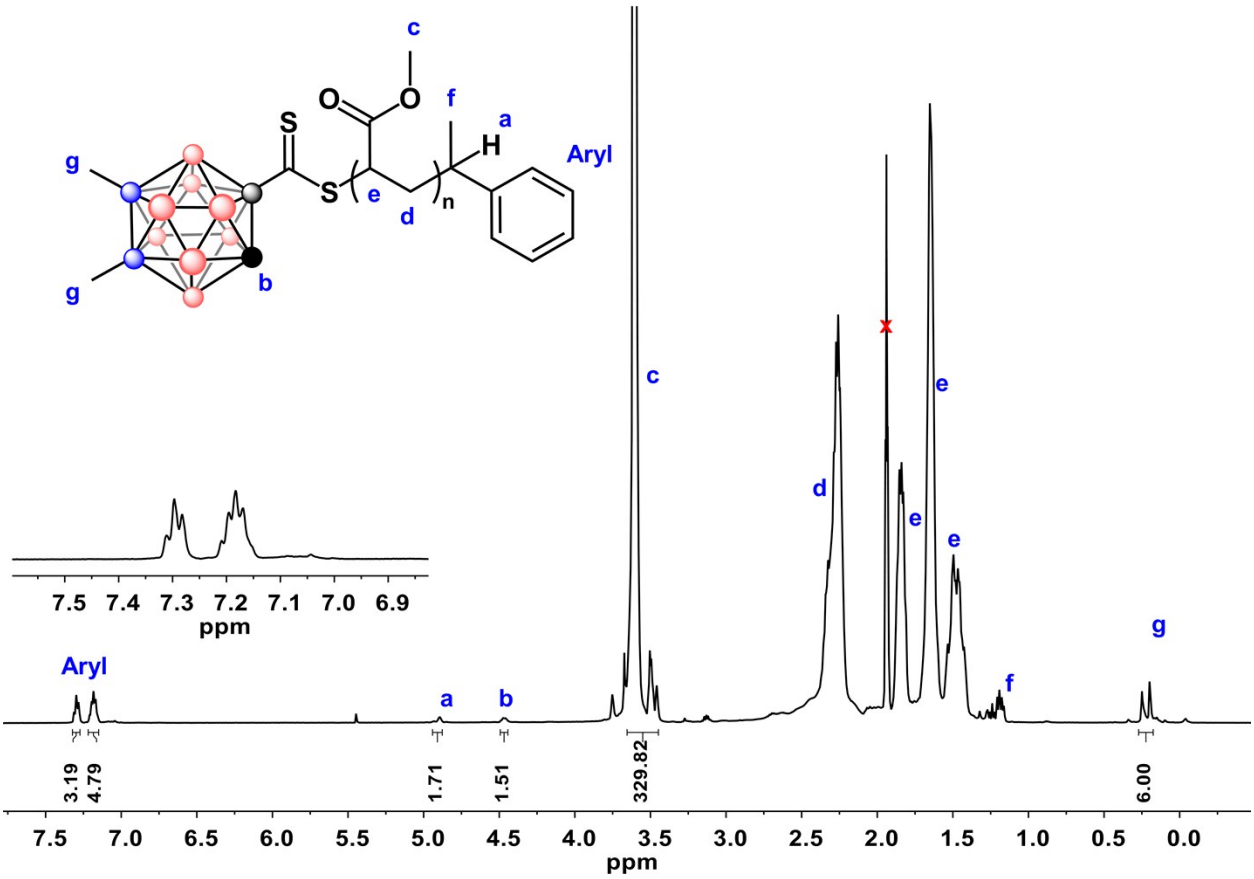


Figure S25. ^{1}H NMR spectrum of **2-PMA** in acetonitrile-d_3 at 298 K.

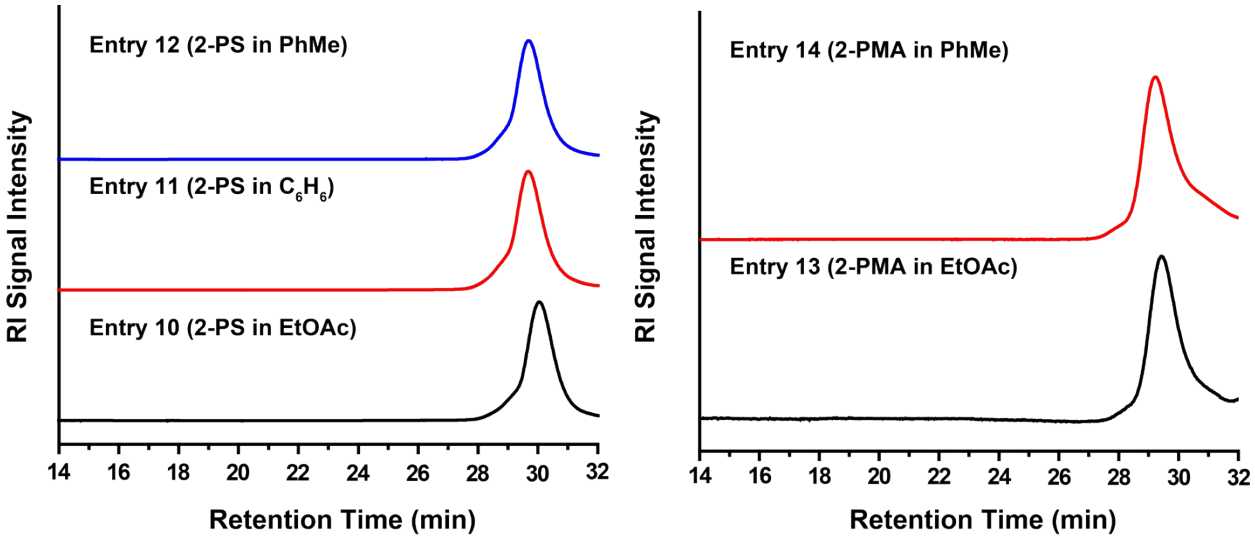


Figure S26. GPC traces of styrene and methyl acrylate in various solvents. GPC acquired using THF as the eluent.

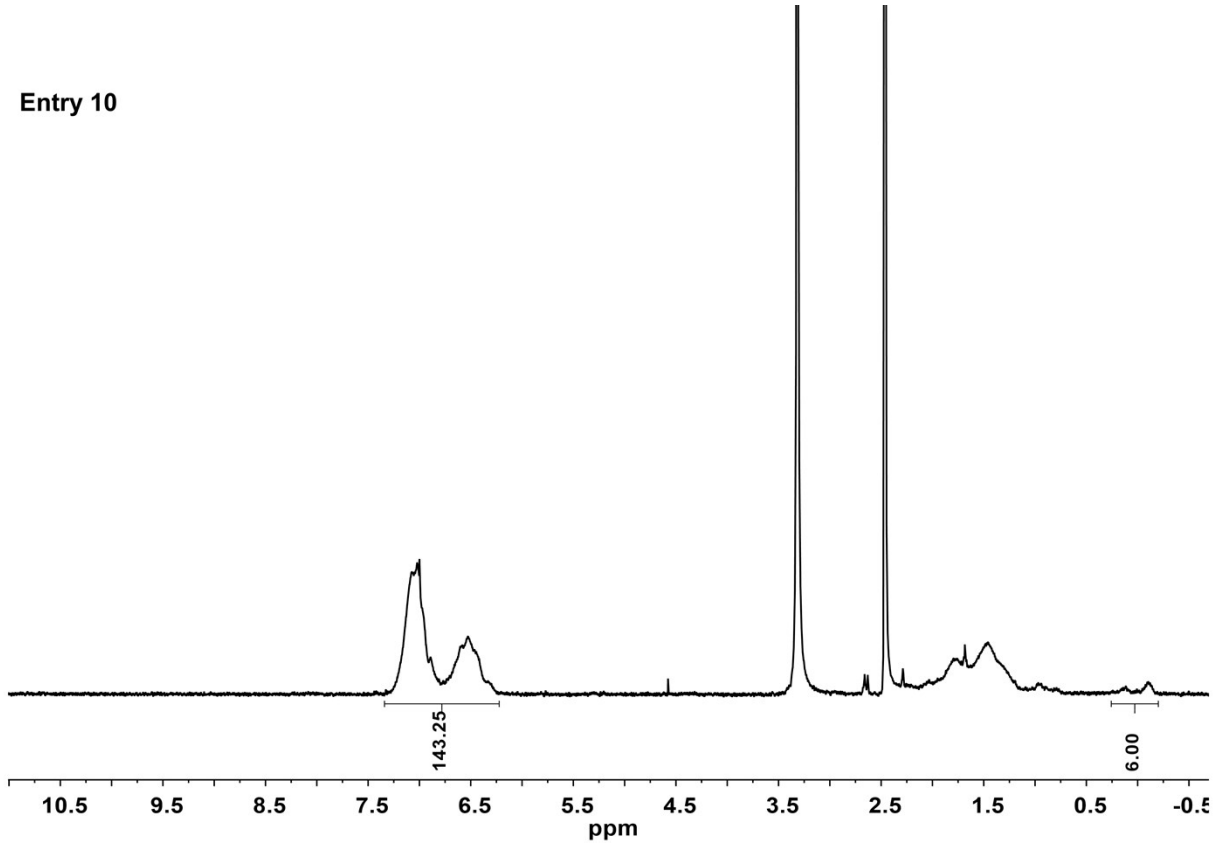


Figure S27. ^{1}H NMR spectrum of **2-PS** in acetone-d_6 at 298 K, related to entry 10, **Figure S19**.

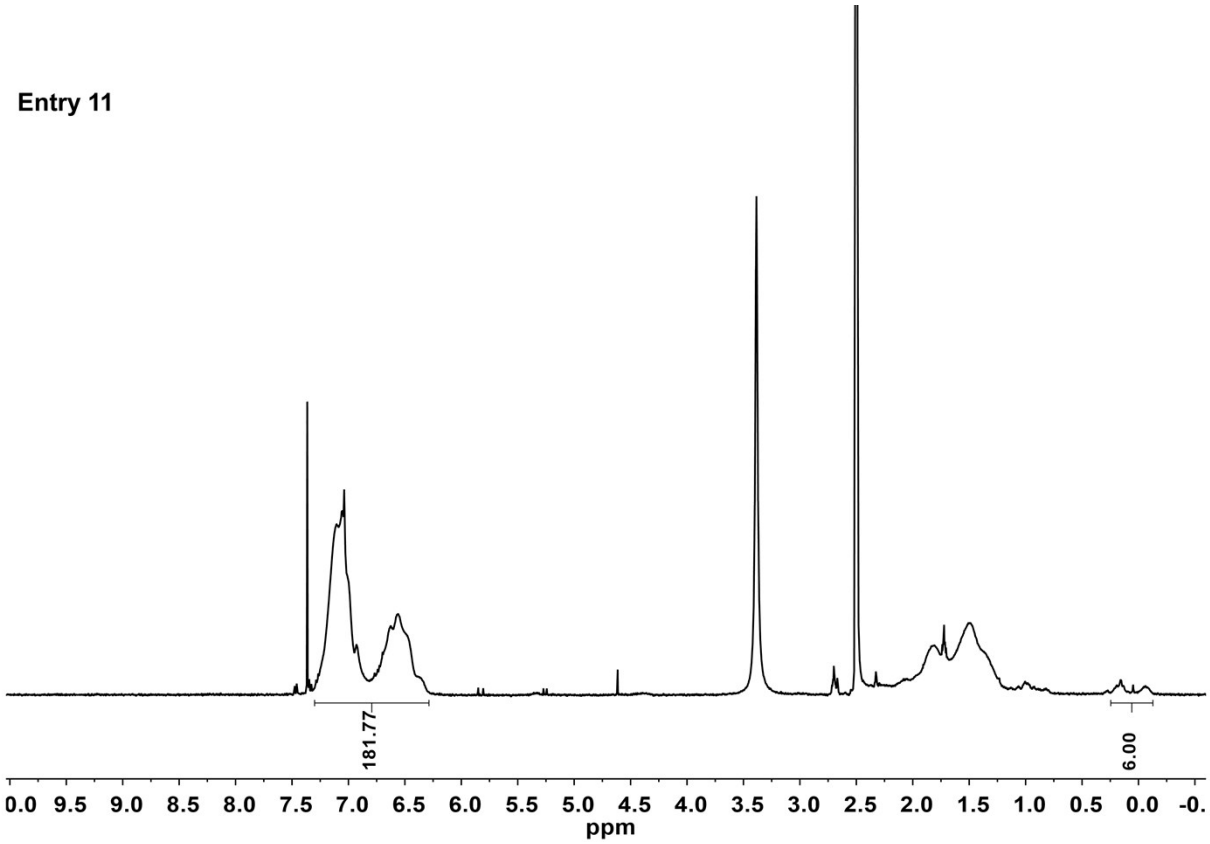


Figure S28. ^{1}H NMR spectrum of **2-PS** in chloroform-*d* at 298 K, related to entry 11, **Figure S19**.

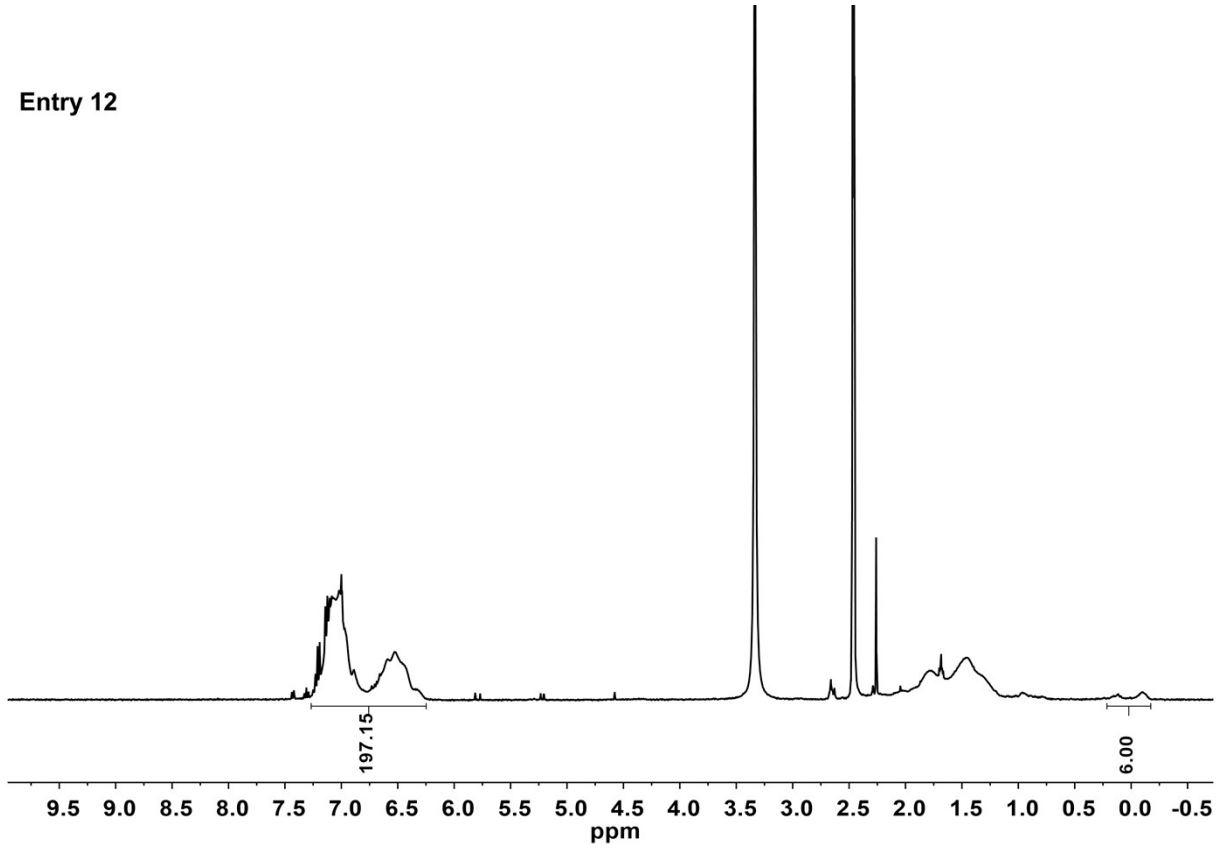


Figure S29. ^{1}H NMR spectrum of **2-PS** in acetone-d_6 at 298 K, related to entry 12, **Figure S19**.

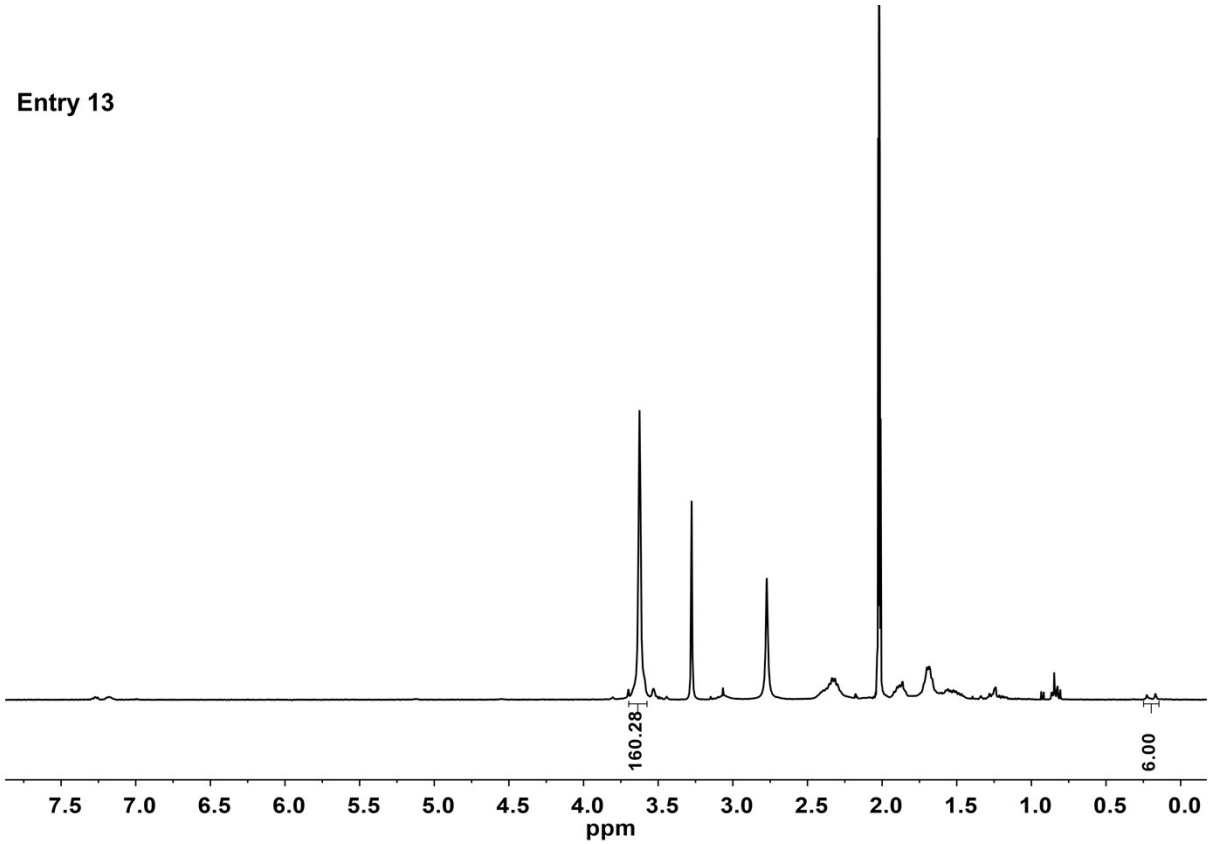


Figure S30. ^{1}H NMR spectrum of **2-PMA** in acetonitrile-d_3 at 298 K, related to Entry 13, **Figure S19**.

Entry 14

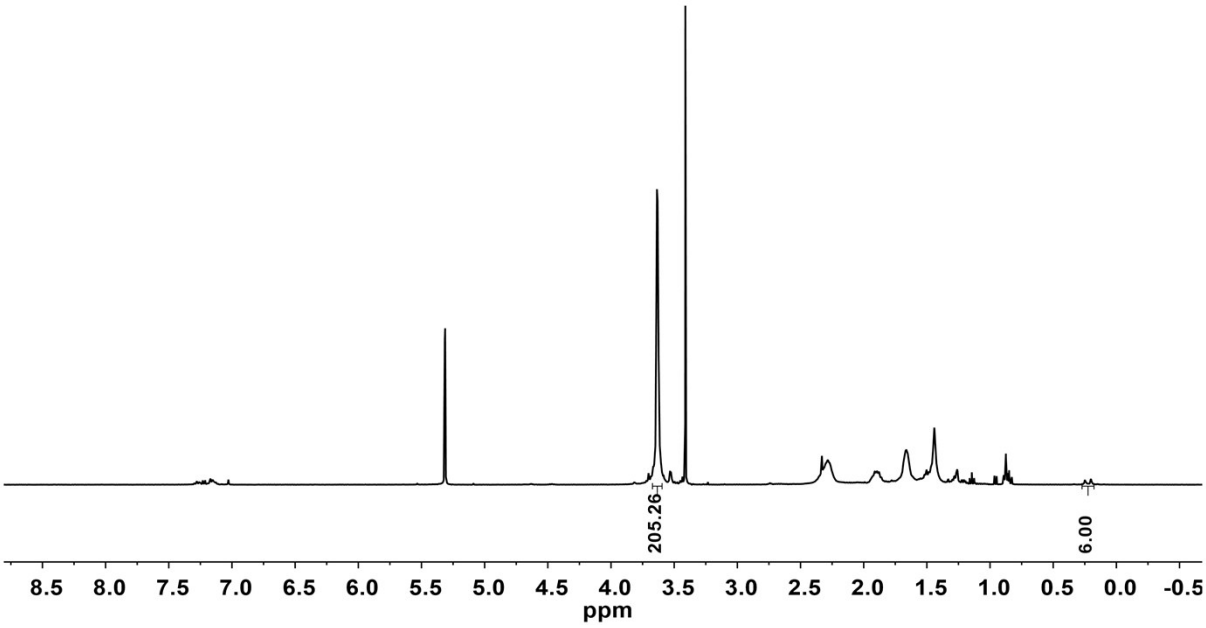


Figure S31. ^{1}H NMR spectrum of **2-PMA** in acetonitrile-d_3 at 298 K, related to Entry 14, **Figure S19**.

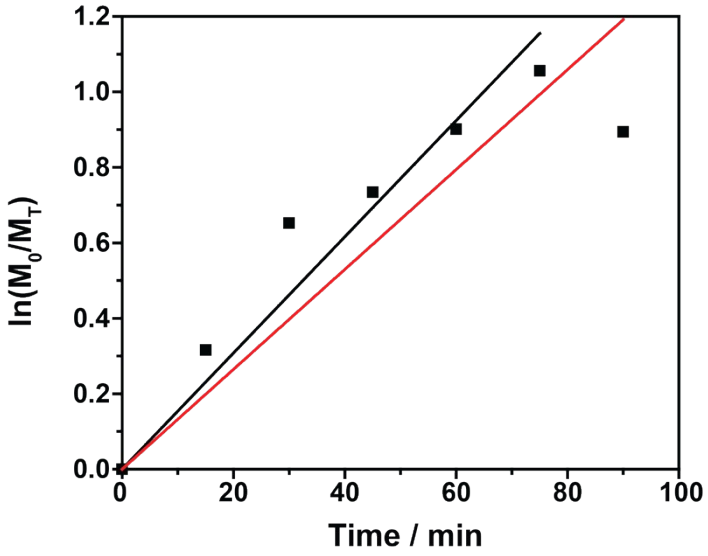


Figure S32. Polymer kinetic plot of polymerization of a bulk methyl acrylate solution. Black line indicates fitting without 90 minute time aliquot included (R^2 = 0.97). Red line indicates fitting with 90 minute time aliquot included (R^2 = 0.93). Experiment performed by making separate reaction aliquots in dram vials with Teflon coated caps from a stock solution of the monomer, initiator, and CTA. Aliquots were quenched at pre-determined time intervals by exposing the reaction mixture to air. It is possible that the final 90 minute aliquot losing linearity is due to minor pipetting error or due to the viscosity of the bulk solution.

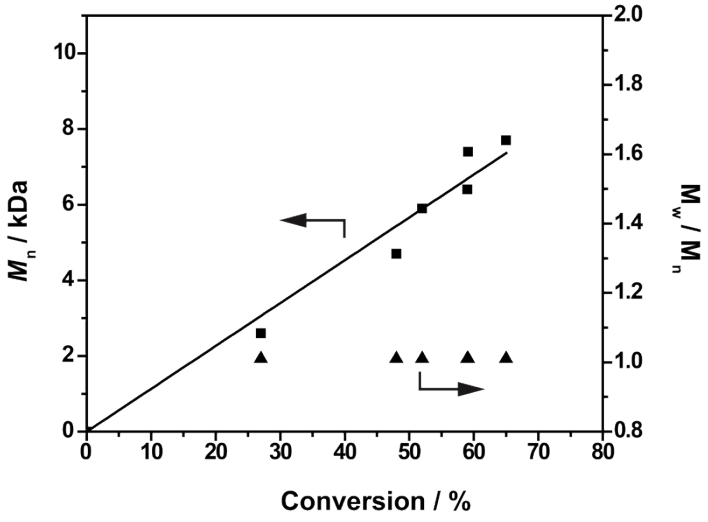


Figure S33. Evolution of M_n as a function of monomer conversion from the experiment in **Figure S32**.

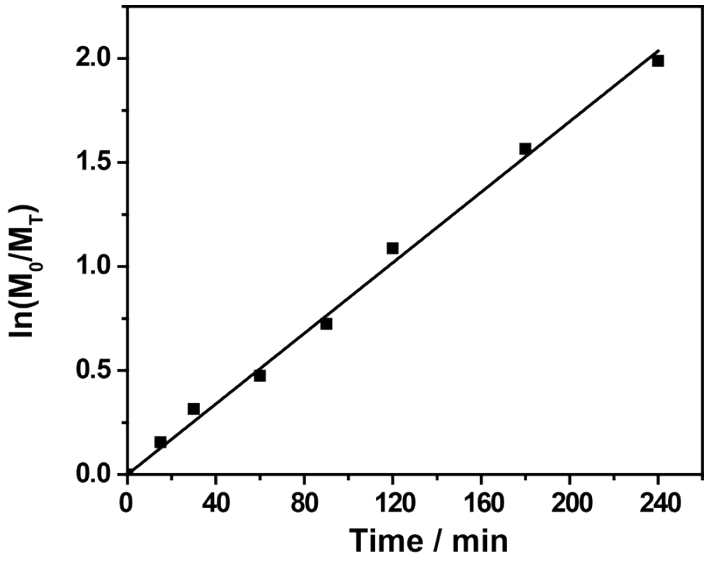


Figure S34. Polymer kinetic plot of polymerization of a 2M solution of methyl acrylate in PhMe (R^2 = 0.99).

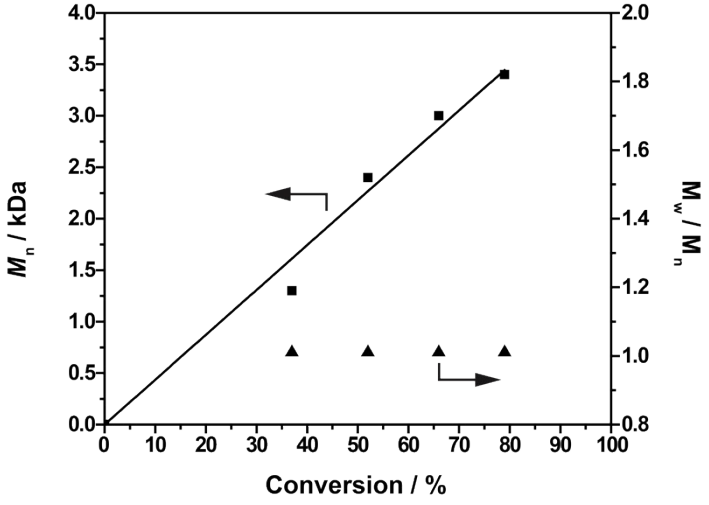
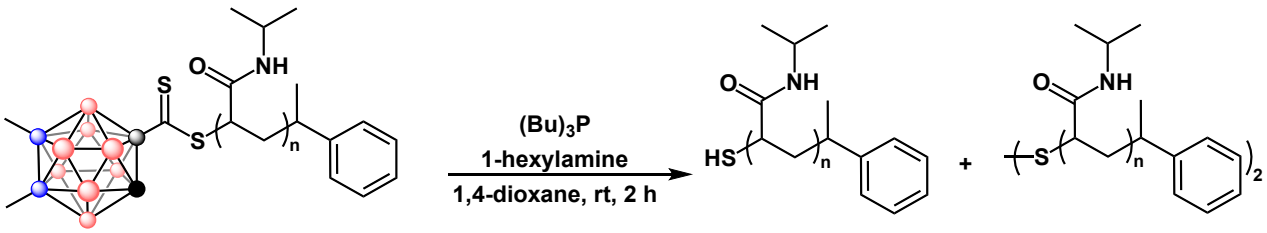


Figure S35. Evolution of M_n as a function of monomer conversion from the experiment in **Figure S34**.



2-pNIPAAm (370.0 mg mg, 2.66×10^{-5} mol, 1 equiv) was added to a dry and degassed 4-mL dram vial sealed with a Teflon coated septum cap and equipped with a magnetic stir bar. Tributylphosphine (66.4 uL, 0.27 mmol, 10 equiv) dissolved in 1,4-dioxane (5 mL) and added to the vial containing 2-pNIPAAm. The solution was sparged with argon for 10 minutes. After sparging, 1-hexylamine (176.0 uL, 1.33 mmol, 50 equiv) was added and the solution was stirred at room temperature for 16 hours. Precipitation of the polymer from cold methanol afforded both deprotected and coupled polymer products.

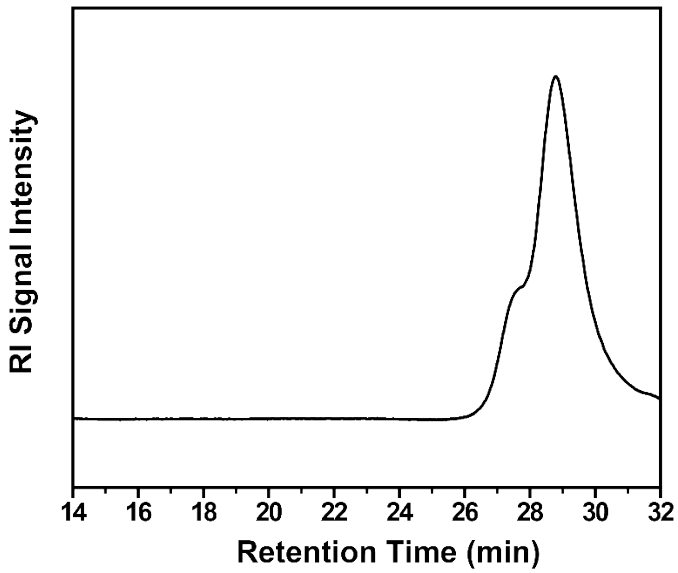
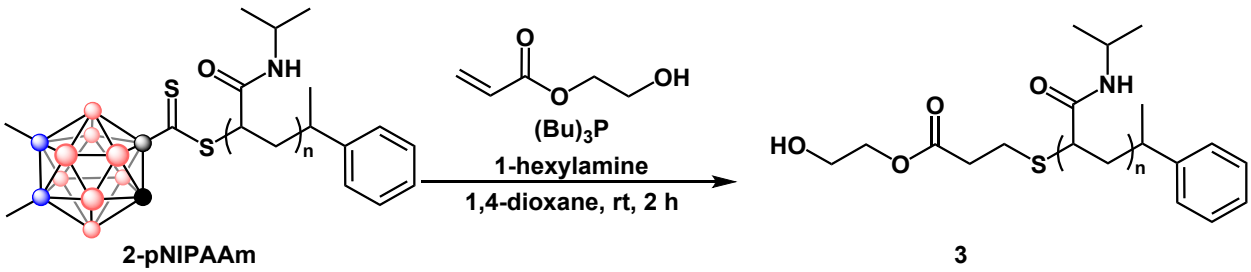


Figure S36. GPC spectrum of carborane deprotection reaction, which shows a high degree of polymer coupling over the course of the reaction. GPC acquired using DMF with 0.1 M LiBr as the eluent.



2-pNIPAAm 3

2-pNIPAAm (20.0 mg, 8.37x10^{-6} mol, 1 equiv) was added to a dry and degassed 4-mL dram vial sealed with a Teflon coated septum cap and equipped with a magnetic stir bar. Tributylphosphine (41.3 uL, 0.17 mmol, 20 equiv) and 2-hydroxyethyl acrylate (96.0 uL, 0.84 mmol, 100 equiv) were dissolved in 1,4-dioxane (1 mL) and added to the vial containing 2-pNIPAm. The solution was sparged with argon for 10 minutes. After sparging, 1-hexylamine (22.1 uL, 0.17 mmol, 20 equiv) was added and the solution was stirred at room temperature for 16 hours. Precipitation of the polymer from cold methanol afforded pure product as a light yellow solid.

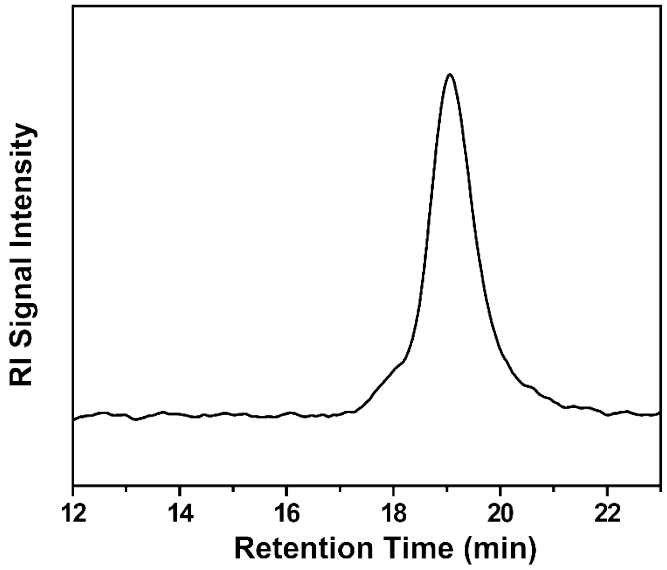
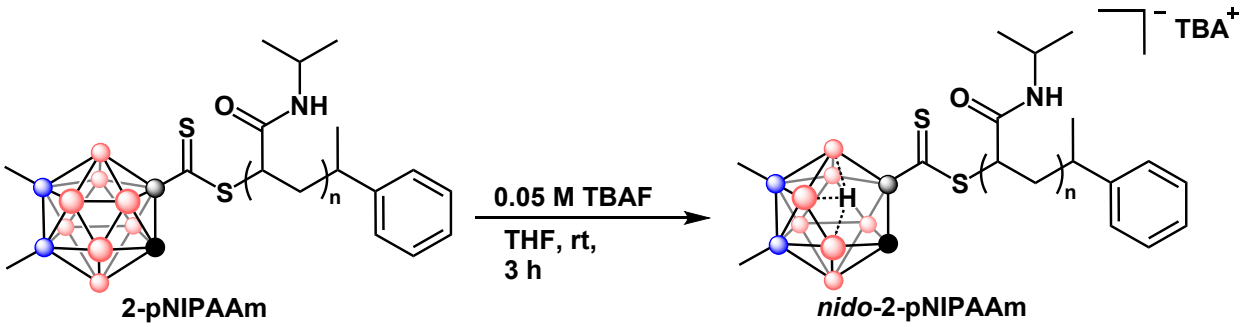


Figure S37. GPC spectrum of **3**. GPC acquired using DMF with 0.1 M LiBr as the eluent.



2-pNIPAAm (26.1 mg, 2.0x10^{-6} mol, 1 equiv) and TBAF (2.6 mg, 1.0x10^{-5} mol, 5 equiv) were added to a 4 mL scintillation vial equipped with a magnetic stir bar and dissolved in THF (200 µL). The reaction was left stirring at room temperature for 3 hours at which point the solution was diluted in water (2 mL) and purified *via* dialysis (MWCO = 3500 Da) against water for 2 days. The water was removed *via* lyophilization to produce the pure product as a yellow solid.

^{1}H NMR (500MHz, acetonitrile-d_3, 298K): δ 6.57 (bs, -N*H*), 3.94 (s, -C*H*$(CH_3)_2$), 2.43 (bs, -C*H*), 2.05 (bs, -CH_2), 1.67 (bs, -CH_2), 1.51 – 1.10 (bs, -CH(CH_3)$_2$), 0.23 (bs, -BCH_3), 0.16 (bs, -BCH_3), -2.1 (bs, $H_{Hydride}$).

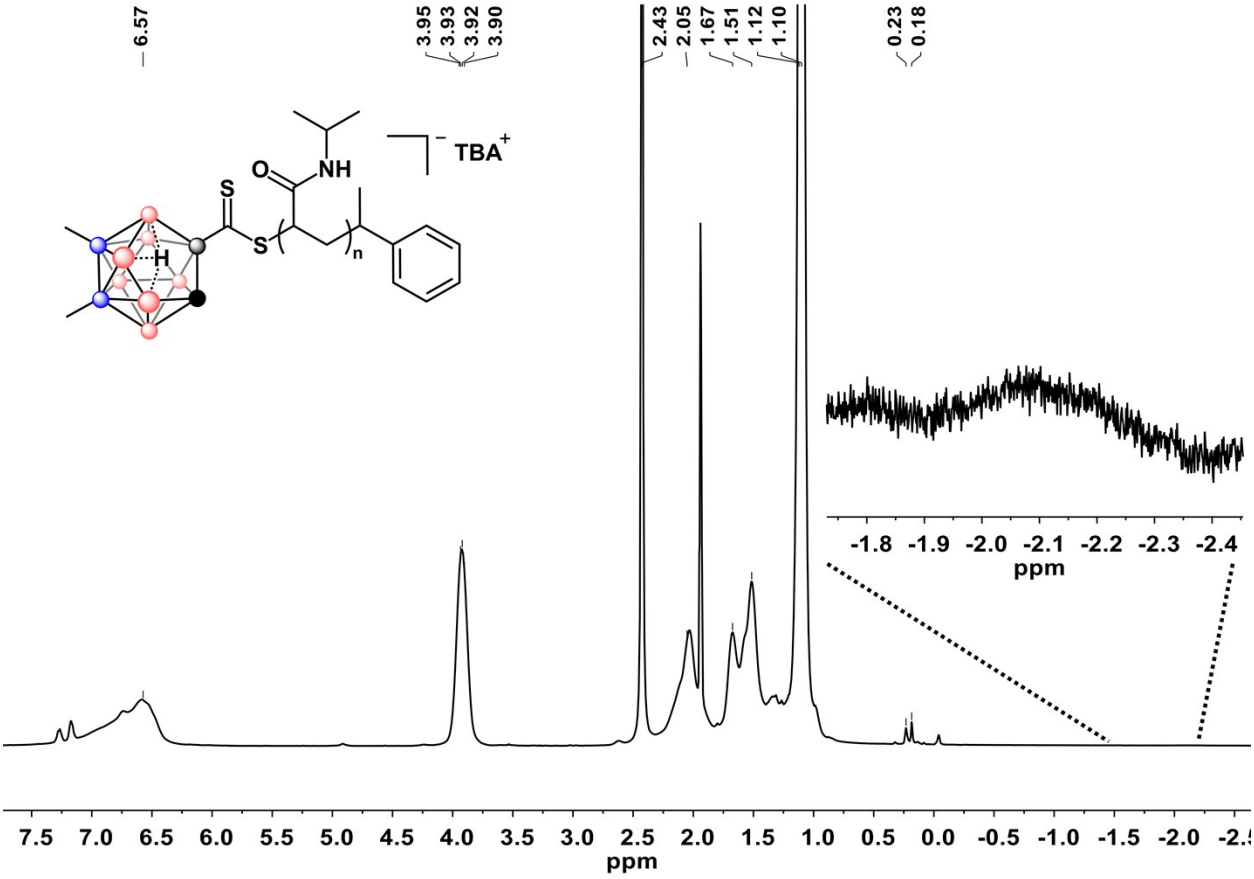


Figure S38. ^{1}H NMR spectrum of ***nido*-2-pNIPAAm** in acetonitrile-d_3 at 298 K.

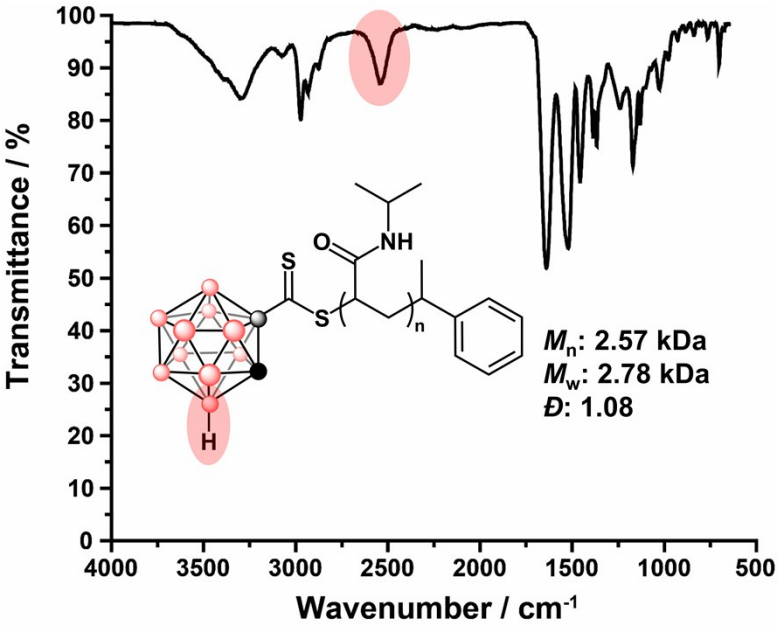


Figure S39. IR spectrum of **1-pNIPAAm**.

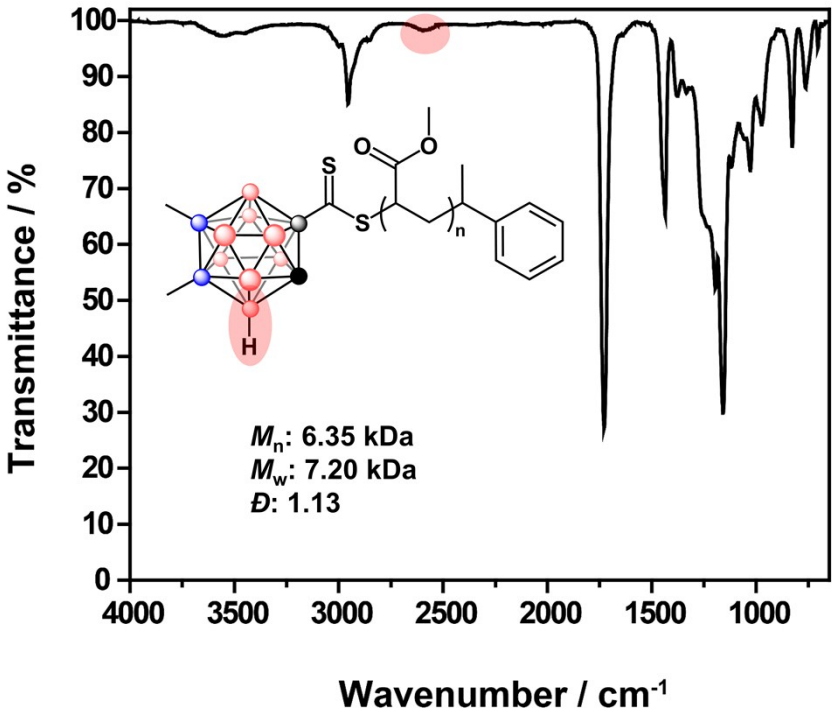


Figure S40. IR spectrum of **2-PMA**.

IV. Crystallographic Characterization

Identification code	PC18	
Empirical formula	C11 H20 B10 S2	
Formula weight	324.49	
Temperature	150.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.427(2) Å	□= 90°.
	b = 12.068(3) Å	□= 92.622(9)°.
	c = 11.6342(17) Å	□ = 90°.
Volume	1742.9(6) $Å^3$	
Z	4	
Density (calculated)	1.237 Mg/m^3	
Absorption coefficient	0.291 mm^{-1}	
F(000)	672	
Crystal size	0.98 x 0.28 x 0.26 mm^3	
Theta range for data collection	2.354 to 26.391°.	
Index ranges	-11<=h<=15, -15<=k<=9, -14<=l<=13	
Reflections collected	8343	
Independent reflections	3449 [R(int) = 0.0581]	
Completeness to theta = 25.242°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.5007	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3449 / 2 / 209	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0868, wR2 = 0.2110	
R indices (all data)	R1 = 0.1578, wR2 = 0.2405	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.454 and -0.546 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6670(1)	3636(2)	6609(1)	46(1)
S(2)	6367(1)	3491(2)	9154(1)	54(1)
C(2)	4718(3)	3759(5)	7501(3)	26(1)
C(6)	8734(3)	3121(5)	6248(3)	29(2)
C(1)	3881(3)	3648(5)	8541(3)	26(1)
C(4)	8068(4)	3620(6)	7190(4)	34(2)
C(5)	8417(4)	4763(7)	7591(4)	48(2)
C(3)	5911(4)	3636(6)	7825(4)	34(2)
B(10)	4154(4)	3263(6)	6241(4)	30(2)
B(7)	3951(4)	2579(7)	7579(4)	33(2)
B(3)	2709(5)	3030(7)	8097(5)	33(2)
B(9)	3027(4)	4126(7)	5935(4)	31(2)
B(2)	2794(5)	4480(7)	8342(4)	34(2)
B(8)	2834(5)	2792(7)	6596(5)	35(2)
B(1)	4107(5)	4943(7)	7986(4)	37(2)
B(6)	4245(5)	4688(7)	6490(4)	38(2)
B(4)	2130(5)	3985(7)	7070(5)	40(2)
B(5)	3000(6)	5160(8)	7013(5)	48(2)
C(9)	9953(4)	2202(8)	4554(5)	54(2)
C(11)	9022(6)	2040(7)	6296(5)	59(2)
C(10)	9618(7)	1568(7)	5441(5)	68(2)
C(8)	9686(5)	3280(7)	4504(5)	59(2)
C(7)	9075(4)	3779(5)	5343(4)	49(2)