Simple Amination of Polystyrene via Radical sp^3 C–H Imination

Mengnan Hu, Lizhe He, Robert J. Comito*

The University of Houston, Houston, Texas 77004

Supporting Information

Contents

S1. General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. All the commercially available liquid substrates or reagents were degassed by freeze-pump-thaw method and stored over molecular sieves (3Å). Chromatographic purification of small-molecule products was accomplished using force-flow chromatography on Silicycle or Davisil silica gel according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Compounds were visualized by irradiation with UV light or by treatment with a solution of potassium permanganate followed by heating, or exposure to iodine. Yields refer to pure compounds, unless otherwise indicated.

^{1}H-, ^{19}F- and ^{13}C-NMR spectra were recorded on a JEOL spectrometer (400 MHz, 500 MHz, or 600 MHz). ^{1}H-NMR are internally referenced relative to residual protio solvent signals ($CDCl_3$) at δ = 7.26 ppm (^{1}H) for $CDCl_3$ and D_2O at δ = 4.79 ppm (^{1}H) for D_2O. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). ^{13}C-NMR spectra are referenced relative to $CDCl_3$ at δ = 77.00 ppm (^{13}C) and dioxane added as a ^{13}C standard in D_2O at δ = 67.2 ppm. Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm). ^{19}F-NMR spectra are referenced relative to 1,3-*bis*(trifluoromethyl)benzene = -63.00 ppm. Data for ^{19}F-NMR are reported in terms of chemical shift (δ ppm). Diffusion Ordered NMR Spectroscopy (DOSY) of polymers was performed in $CDCl_3$ at 40°C using an ECA-600 (600 MHz) NMR spectrometer. The parameters of the experiment for the diffusion time were set to 0.55 s, delta = 8.5 ms, relaxation delay = 6 s. An exponential array function between 10 mT/m and 275 mT/m for points = 32 with 64 scans was applied.

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals.* 3rd ed., Pergamon Press, Oxford, 1988.
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics.* **1996**, *15*, 1518.
(3) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

Gel Permeation Chromatography (GPC) - Analyses were performed using a Tosoh high performance GPC system HLC-8320 equipped with an auto injector, a dual differential refractive index (RI) detector, and three TSKgel HHR series columns connected in series (7.8×300 mm TSKgel G5000HHR, TSKgel G4000HHR, TSKgel G3000HHR). A Wyatt DAWN 8+ multiangle laser light scattering (MALS) detector and Wyatt ViscoStar III differential viscometer detector were added as external detectors for triple-detection SEC analysis. UV-vis traces were collected predominantly at 300 nm.

Mass spectra were performed by a Thermo Scientific high-resolution Orbitrap MS instrument equipped with a TriVersa NanoMate nano-electrospray (nESI) source at the mass spectrometry facility at the University of Illinois at Urbana-Champaign.

UV-vis absorption measurements were recorded using a Cary 50 UV-Vis spectrophotometer. wavelength measurement range: 200-500 nm). Samples were housed in 1 cm quartz cuvettes with a septum-sealed screw cap.

Solution phase emission spectra were recorded using a Horiba FluoroMax‑4 spectrofluorometer with appropriate long‑pass filters to exclude stray excitation light from detection. Samples were prepared as solutions in CH_2Cl_2 and transferred to a 1 cm wide quartz cuvette with Teflon screw cap for measurement.

Differential Scanning Calorimetry (DSC) was conducted on a Discovery TA DSC 2500. The samples were heated from 40 °C to 200 °C, cooled to 0 °C at a rate of 10 °C/minute, and then heated to 200 °C at a rate of 10 °C/minute. DSC data discussed in the manuscript were obtained from the second heating cycles. DSC thermographs are displayed with the cooling and the re-heating curves.

Water contact angles were obtained using a Ramé-Hart model 100 contact angle goniometer at room temperature. To prepare the polymer samples, we dissolved 5 mg of polymer in 0.5 mL of chloroform and cast the solution on a clean glass plate. After the solvent evaporated at room temperature, one drop of pure water (approximately 0.3 μL) was placed on the membrane, and the static contact angle measurement was performed.

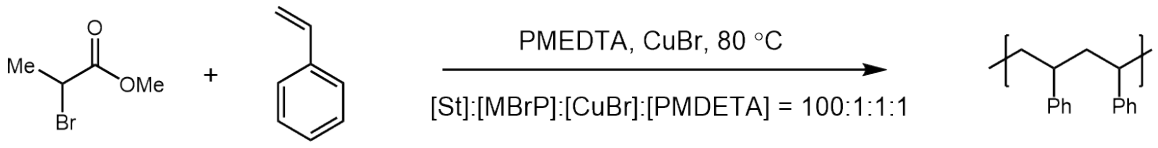
Thermogravimetric analysis (TGA) data were obtained using a Discovery TGA 5500. Scan temperature start from 30 °C to 600 °C at a rate of 10 °C/ minute.

Density functional theory (DFT) calculations were performed using the Gaussian 16 Software package on the Sabine Cluster at the University of Houston.

Infrared (IR) spectroscopy was performed on a Thermo Fisher Nicolet iS10 spectrometer with Smart iTR diamond plate and the data are reported in terms of wavenumber of absorption (cm^{-1}).

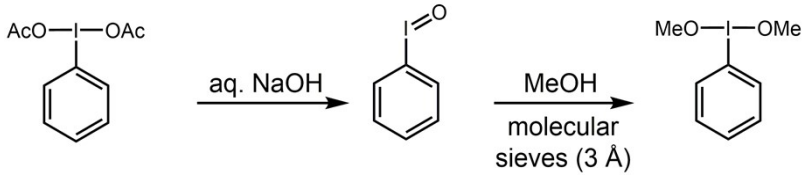
S2. Synthesis of polymers.

S2.1. Synthesis of polystyrene (**2**-13,200).



Following a reported procedure for ATRP polymerization,[4] CuBr (1.435 g, 10 mmol, 1 equiv.) was degassed in a Schlenk flask by three vacuum/nitrogen-inletting cycles. Then, degassed styrene (114.4 mL, 1000 mmol, 100 equiv.) and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 1.733 g, 10 mmol, 1 equiv.) were injected into the flask. After stirring for 30 minutes at room temperature to form the catalyst complex, the flask was placed in an oil bath set at a temperature of 90°C. Then the degassed methyl 2-bromopropionate (1.65 g, 10 mmol, 1 equiv.) was injected into the flask to start the reaction. After 8 hours, the reaction was stopped by cooling to room temperature and opening the flask to air. The mixture was passed through a neutral aluminum oxide column to remove the oxidized catalyst. The polymer was purified by precipitation of a CH_2Cl_2 solution from cold methanol. After drying under vacuum, the product was obtained as a white polymer powder. GPC: M_n= 1.32*10^4, $Đ$ = 1.06, UV-300 nm negative.

S2.2. Synthesis of $PhI(OCH_3)_2$ (**5**).



We prepared $PhI(OCH_3)_2$, following our previously developed procedure.[5] A round bottom flask was charged with *bis*(acetoxy)iodobenzene (10 g, 31.04 mmol) and aqueous NaOH

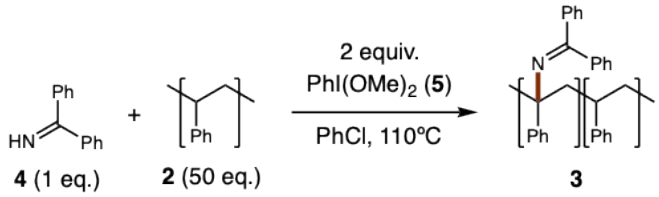
[4] Kwak, Y.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 6627

[5] Ghosh, S. K.; Hu, M.; Comito, R. J. *Chem. Eur. J.* **2021**, *27*, 17601

(3 M, 220 mL) solution. The reaction mixture was stirred vigorously for 18 hours at room temperature. Then, the precipitate formed was filtered off and washed with water until pH of water was almost neutral. Then the solid was washed (2 × 25 mL) with chloroform to remove unreacted *bis*(acetoxy)iodobenzene. The obtained solid was dried under vacuum without heating to yield iodosylbenzene [$(PhIO)_n$] (6.8 g, 30.9 mmol, 99% yield) as yellow-tinted white solid which was directly used in the next step. *Note: We found that heating the material resulted in a white solid which did not form a homogeneous solution with methanol. We attribute this difference to a disproportionation of iodosylbenzene resulting in $PhIO_2$ and PhI. Heating of this compound is also not recommended due to a potential explosion hazard.*

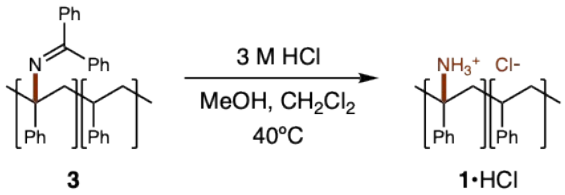
A round bottom flask was charged with iodosylbenzene (6.8 g, 30.90 mmol) and methanol (70 mL) with stirring. There was initial rapid formation of a milky white suspension followed by its nearly complete dissolution within 1 hour. Then activated molecular sieves (6.08 g, 3Å) were added to the mixture and stirred for additional 4 hours. The reaction mixture was filtered and the solvent or other volatiles were removed from the filtrate by oil pump vacuum to get a light yellow solid. The resultant solid was recrystallized from hexanes at -35°C to get white needle shaped crystals. The crystals were dried under vacuum to give *bis*(methoxy)iodobenzene (**5**, 5.79 g, 21.76 mmol, 70% overall in two steps) as white solid, which was stored in a glovebox freezer at –30ºC until use. NMR ($CDCl_3$, δ in ppm): ^{1}H (400 MHz) 8.02-7.90 (m, 2H), 7.55-7.42 (m, 3H), 3.72 (s, 6H); ^{13}C (100 MHz) 130.9 (s), 130.8 (s), 130.4 (s), 119.6 (s), 57.1 (s). Our ^{1}H- and ^{13}C-NMR are consistent with what we reported previously for this compound.

S2.3. Imination of polystyrene.



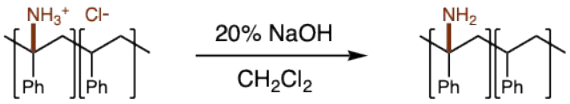
3-13,000. A solution of polystyrene (**2**-13,200, 1.04 g, 10 mmol, 50 equiv., prepared in Section S2.1), $PhI(OMe)_2$ (0.106 g, 0.4 mmol, 2 equiv.), benzophenone imine (0.036 g, 0.2 mmol, 1 equiv.), and chlorobenzene (2 mL) in a sealed tube under nitrogen was heated to 110ºC for 24 hours with magnetic stirring. After cooling, the solution was precipitated from cold methanol. The polymer was purified by redissolving in CH_2Cl_2 and then reprecipitating from cold methanol 3 times, to obtain the purified iminyl-polystyrene **3** as a slightly yellow powder (0.95g, 91% recovery). GPC: M_n = 1.30*10^4, $Đ$ = 1.07, UV active at λ = 300 nm (see spectrum in Figure S3.5).

S2.4. Hydrolysis of 3.



1•HCl-13,000. A solution of iminyl-polystyrene (**3**-M_n = 1.30*10^4, 0.52 g, 5 mmol, prepared freshly in Section S2.3) and CH_2Cl_2 (2.0 mL), was treated with a freshly prepared solution of methanol (0.5 mL) and hydrochloric acid (3 M, 2.0 mL), and then stirred overnight at 40ºC. After the hydrolysis was complete, the organic and aqueous phases were separated in a separatory funnel, washing the organic solution with water (3 x 10 mL). The polymer was precipitated out from CH_2Cl_2 solution with cold methanol three times to obtain the polymer **1**•HCl as a fine white powder. 0.47 g, 90% recovery. GPC: M_n = 1.35*10^4, $Đ$ = 1.08, UV inactive at λ = 300 nm.

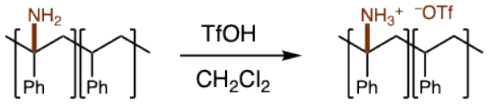
Section S2.5. Freebasing of 1•HCl.



1•HCl **1**

1-13,500. A solution of polymer **1**•HCl (M_n = 1.35*10^4, 0.45 g, 4.3 mmol, prepared in section S2.4) in CH_2Cl_2 (2 mL) was stirred with 20% NaOH solution (2 mL) overnight. The organic and aqueous phases were then separated, and the organic phase was washed with brine. The organic solution was then dried with $MgSO_4$, filtered, and then concentrated under vacuum to get amino-polystyrene **1**. 0.41 g, 90 % recovery. GPC: M_n = 1.36*10^4, $Đ$ = 1.08, UV inactive at λ = 300 nm (see spectrum in Figure S3.6).

S2.6. ^{19}F-NMR analysis of amino content of 1.



1 **1**•HOTf

S2.6.1. Analysis of isolated **1**; **1**•HOTf. A solution of amino-polystyrene **1** (250 mg, 2.4 mmol, M_n = 1.36*10^4, $Đ$ = 1.08 prepared in Section S2.5), trifluoromethanesulfonic acid (75 mg, 0.5 mmol), and CH_2Cl_2 (1 mL) was stirred for 18 hours. Then, the solution was extracted with water (3 x 30 mL). The polymer (221 mg, 88% recovery) was then precipitated out of the CH_2Cl_2 solution with cold methanol. A portion of this sample (80 mg, 0.768 mmol of polystyrene) was combined with 1,3-*bis*(trifluoromethyl)benzene (12.4 μL, 17 mg, 0.0798 mmol) and then dissolved in $CDCl_3$ (0.5 mL) for ^{19}F-NMR analysis. An ^{19}F-NMR ratio of 0.0129 : 1 was obtained for the ratio of triflate ion (–78.13 ppm) to 1,3-*bis*(trifluoromethyl)benzene (internally referenced to –63.00 ppm). From that we obtained an amination ratio of 0.27% per styrene unit.

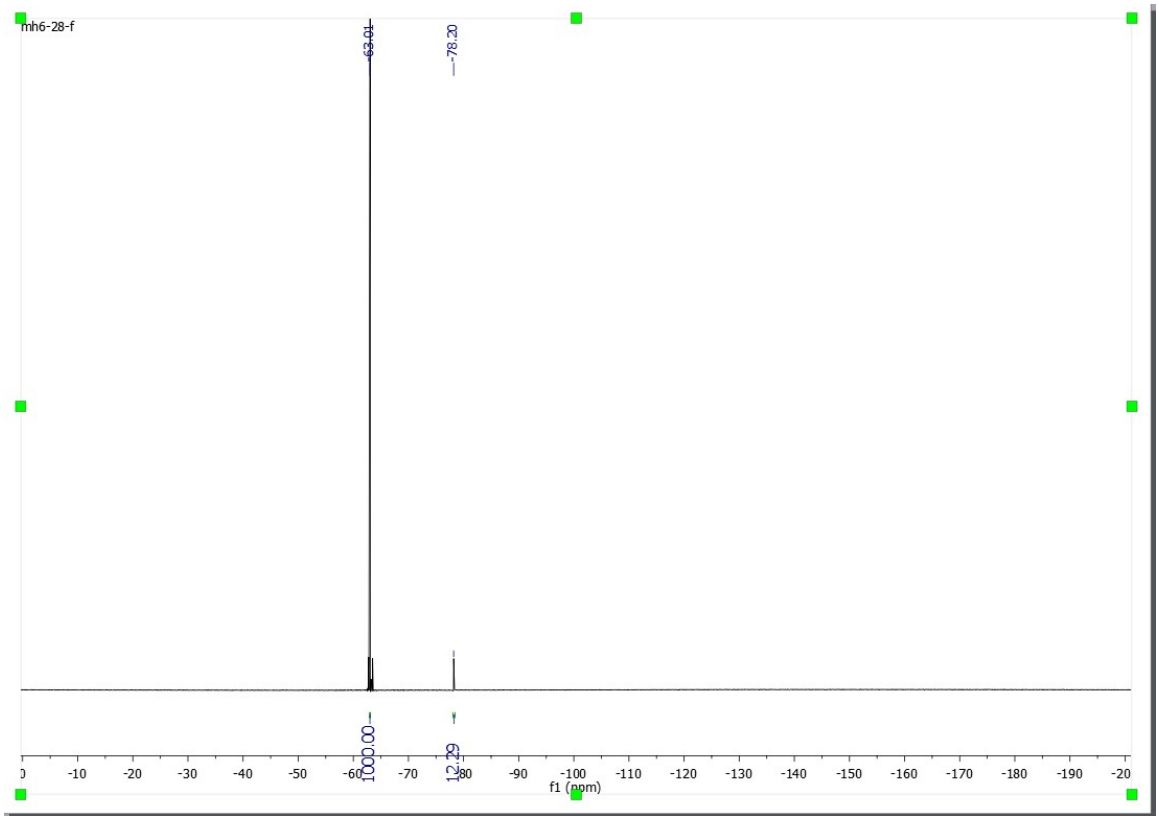
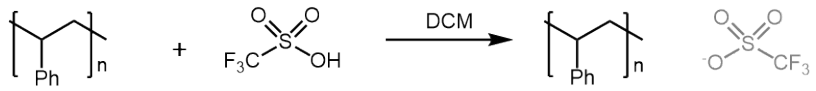


Figure S2.1. ^{19}F-NMR analysis of **1**•HOTf and 1,3-*bis*(trifluoromethyl)benzene.

To confirm that our workup removed all residual triflic acid, we also repeated this procedure on unmodified styrene (Section S2.6.2). The ^{19}F-NMR chemical shift for the triflate ion was confirmed by preparing the triflic acid salt of cumylamine (Section S2.6.3).



*Section S2.6.2. Assay control with unmodified polystyrene **2***: A solution of unmodified polystyrene **2** (250 mg), trifluoromethanesulfonic acid (75 mg, 0.5 mmol), and CH_2Cl_2 (1 mL) was stirred for 18 hours. Then, the solution was extracted with water (3 x 30 mL). The polymer (220 mg) was then precipitated out of CH_2Cl_2 solution with cold methanol. A portion of this sample (80 mg, 0.8 mmol of polystyrene) was combined with 1,3-*bis*(trifluoromethyl)benzene (17 mg, 0.08 mmol) and then dissolved in $CDCl_3$ for NMR analysis. ^{19}F-NMR analysis performed under the same conditions as in Section S2.6.1 did

not show the same peak assigned to **1**•HOTf, confirming that our workup removes HOTf and that the peak observed with **1** arises from the formation of an ammonium salt.

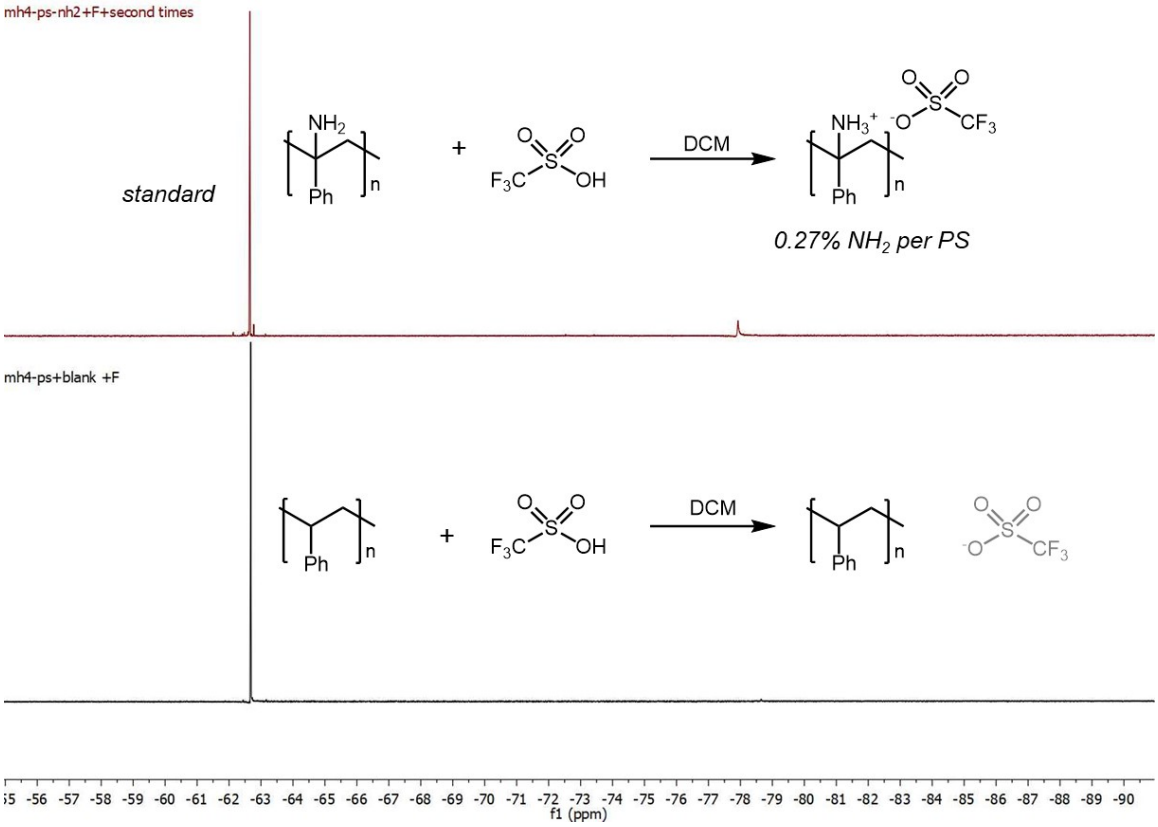
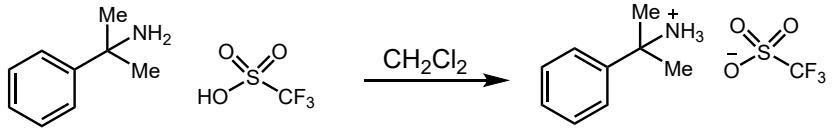


Figure S2.2. ^{19}F-NMR comparison of CF_3SO_3H-treated polystyrene (**2**) and amino-polystyrene (**1**).



S2.6.3. ^{19}F-NMR standard produced from cumylamine and triflic acid. A solution of cumylamine (13.5 mg, 0.1 mmol), trifluoromethanesulfonic acid (15 mg, 0.1 mmol), and CH_2Cl_2 (1 mL) was stirred for 1 hour. The solvent was removed under vacuum. Then the sample was combined with 1,3-*bis*(trifluoromethyl)benzene (21.4 mg, 0.1 mmol) and dissolved in $CDCl_3$ for ^{19}F-NMR analysis.

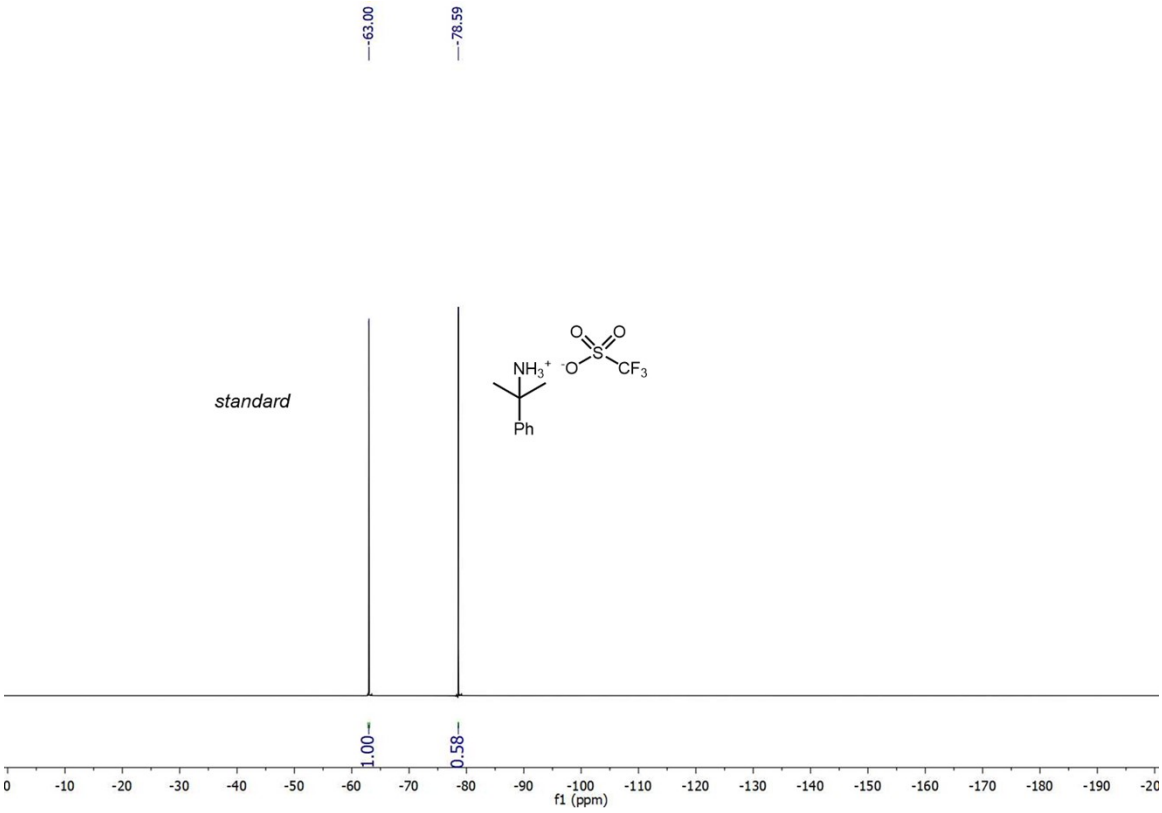
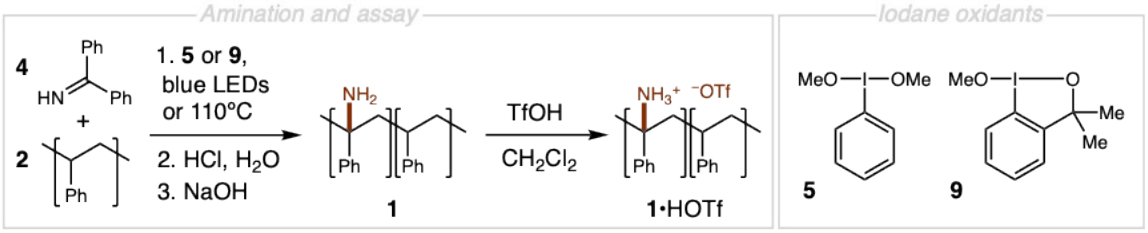


Figure S2.3. ^{19}F-NMR of CF_3SO_3H-treated cumylamine.

S2.6.4. Assaying the amination of polystyrene under various conditions.



General Procedure. A solution of polystyrene (**2**), iodane ($PhI(OMe)_2$ **4** or cyclic iodane **9**), benzophenone imine (**5**), and chlorobenzene (2 mL) in a sealed tube under nitrogen was heated to 110 ºC for 24 hours with magnetic stirring. After cooling, the solution was precipitated from cold methanol. The polymer was purified by redissolving in CH_2Cl_2 and then reprecipitating from cold methanol 3 times, to obtain the purified iminyl-polystyrene **3** as a slightly yellow powder. Then the product went through

hydrolysis and alkaline treatment to get the amino polystyrene. The amino content was then assayed as in Section S2.6.1. A solution of amino polystyrene (250 mg), trifluoromethanesulfonic acid (75 mg, 0.5 mmol), and 1 mL of CH_2Cl_2 (1 mL), was stirred for 18 hours. Then, the solution was extracted with water (3 x 30 mL). The polymer was then precipitated out of the CH_2Cl_2 solution with cold methanol. A portion of this sample (80 mg, 0.77 mmol of polystyrene) was combined with 1,3-*bis*(trifluoromethyl)benzene (17 mg, 0.080 mmol) and then dissolved in $CDCl_3$ (0.5 mL) for NMR analysis. From ^{19}F-NMR a ratio of $CF_3SO_3^-$ incorporation per mass unit was obtained by relative integration of the peaks corresponding to standard and $CF_3SO_3^-$.

Table S2.1. Percent yield and amination loading calculated by our ^{19}F-NMR assay from different conditions for C–H imination.

Entry	Oxidant	Ratio of **2**:iodane:**4**	Energy source	Yield wrt **4**	Amine loading
1	$PhI(OMe)_2$ (**5**)	100:2:1	110°C	17%	0.17%
2	$PhI(OMe)_2$ (**5**)	50:1:1	110°C	8.0%	0.16%
3	$PhI(OMe)_2$ (**5**)	50:2:1	110°C	13%	0.26%
4	$PhI(OMe)_2$ (**5**)	25:2:1	110°C	8.5%	0.34%
5	$PhI(OMe)_2$ (**5**)	12.5:2:1	110°C	5.4%	0.43%
6	$PhI(OMe)_2$ (**5**)	50:2:1	blue LED	7.0%	0.14%
7	**9**	50:2:1	110°C	19%	0.38%
8	**9**	12.5:2:1	110°C	5.5%	0.44%
9a	$PhI(OMe)_2$ (**5**)	12.5:2:1	110°C	6.6%	0.52%

[a]Performed at a higher concentration, 5 mmol polymer in 0.5 mL PhCl.

Table S2.1, entry 1. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 100 equiv.), $PhI(OMe)_2$ (**5**, 53 mg, 0.20 mmol, 2.0 equiv.), benzophenone imine (**4**, 18 mg, 0.10 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL).

Table S2.1, entry 2. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 50 equiv.), $PhI(OMe)_2$ (**5**, 53 mg, 0.20 mmol, 2.0 equiv.), benzophenone imine (**4**, 36 mg, 0.20 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL).

Table S2.1, entry 3. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 50 equiv.), $PhI(OMe)_2$ (**5**, 106 mg, 0.398 mmol, 2.0 equiv.), benzophenone imine (**4**, 36 mg, 0.20 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL).

Table S2.1, entry 4. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 25 equiv.), $PhI(OMe)_2$ (**5**, 212 mg, 0.797 mmol, 2.0 equiv.), benzophenone imine (**4**, 72 mg, 0.40 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL).

Table S2.1, entry 5. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 12.7 equiv.), $PhI(OMe)_2$ (**5**, 424 mg, 1.59 mmol, 2.03 equiv.), benzophenone imine (**4**, 142 mg, 0.784 mmol, 1.00 equiv.), and chlorobenzene (2.0 mL).

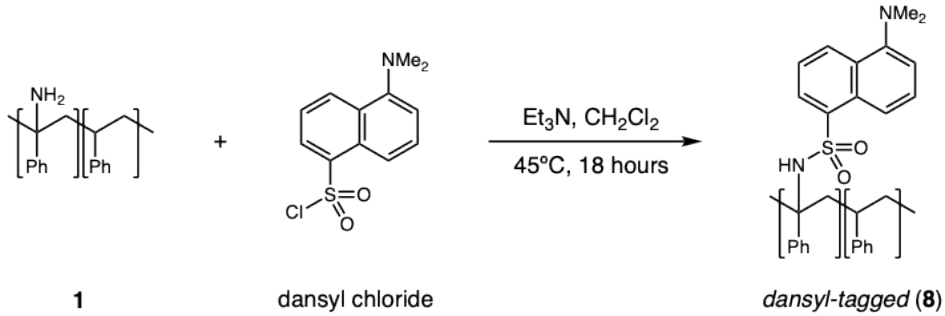
Table S2.1, entry 6. A sealed tube containing a solution of polystyrene (**2**, 1.04 g, 10.0 mmol, 50 equiv.), $PhI(OMe)_2$ (**5**, 106 mg, 0.398 mmol, 2.0 equiv.), benzophenone imine (**4**, 36 mg, 0.20 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL) was irradiated with blue LEDs for 24 hours with magnetic stirring. Then, the reaction was worked up, hydrolyzed, free based, and analyzed as described in the general procedure.

Table S2.1, entry 7. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 50 equiv.), cyclic iodane **9** (117 mg, 0.401 mmol, 2.0 equiv.), benzophenone imine (**4**, 36 mg, 0.20 mmol, 1.0 equiv.), and chlorobenzene (2.0 mL), except that iodane **9** was used in place of $PhI(OMe)_2$ (**5**).

Table S2.1, entry 8. By the general method with polystyrene (**2**, 1.04 g, 10.0 mmol, 12.6 equiv.), cyclic iodane **9** (467 mg, 1.60 mmol, 2.01 equiv.), benzophenone imine (**4**, 144 mg, 0.795 mmol, 1.00 equiv.), and chlorobenzene (2.0 mL), except that iodane **9** was used in place of $PhI(OMe)_2$ (**5**).

Table S2.1, entry 9. By the general method with polystyrene (**2**, 520 mg, 4.99 mmol, 12.7 equiv.), $PhI(OMe)_2$ (**5**, 212 mg, 0.797 mmol, 2.03 equiv.), benzophenone imine (**4**, 66 μL, 0.393 mmol, 1.0 equiv.), and chlorobenzene (0.5 mL).

S2.7. Dansyl tagging.



1 dansyl chloride *dansyl-tagged* (**8**)

S2.7.1. Dansyl tagging of amino polystyrene **1**: A sealed tube charged with dichloromethane (2 mL), Et_3N (20.2 mg, 0.2 mmol, 0.1 equiv.), Dansyl chloride (5 mg, 0.02 mmol, 0.01 equiv.), and **1** (M_n = 1.36*10^4, 200 mg, 2 mmol, 1.0 equiv.) was heated at 45°C overnight. The product was purified by adding a dichloromethane solution directly to cold methanol to precipitate the polymer three times. The purified product was then dissolved in CH_2Cl_2 (2 mL) and stirred with 50% NaOH solution overnight at room temperature. The two phases were then separated, and then the organic phase was rinsed with 1 M HCl (3 x 5 mL) solution and water (3 x 5 mL). The resulting dichloromethane solution was then dried over Na_2SO_4 and then precipitated from cold methanol three times as described above to give the product as a white solid (180 mg, 90% recovery). Fluorescence analysis (Section S2.6.1) indicated the presence of the Dansylamide (Figure S3.19). We repeated the same procedure on polystyrene (**2**, Section S2.7.2), and did not observe the incorporation of the Dansylamide. We also prepared the Dansylamide (**S1**) from cumylamine as a spectroscopic standard (Section S4.2).

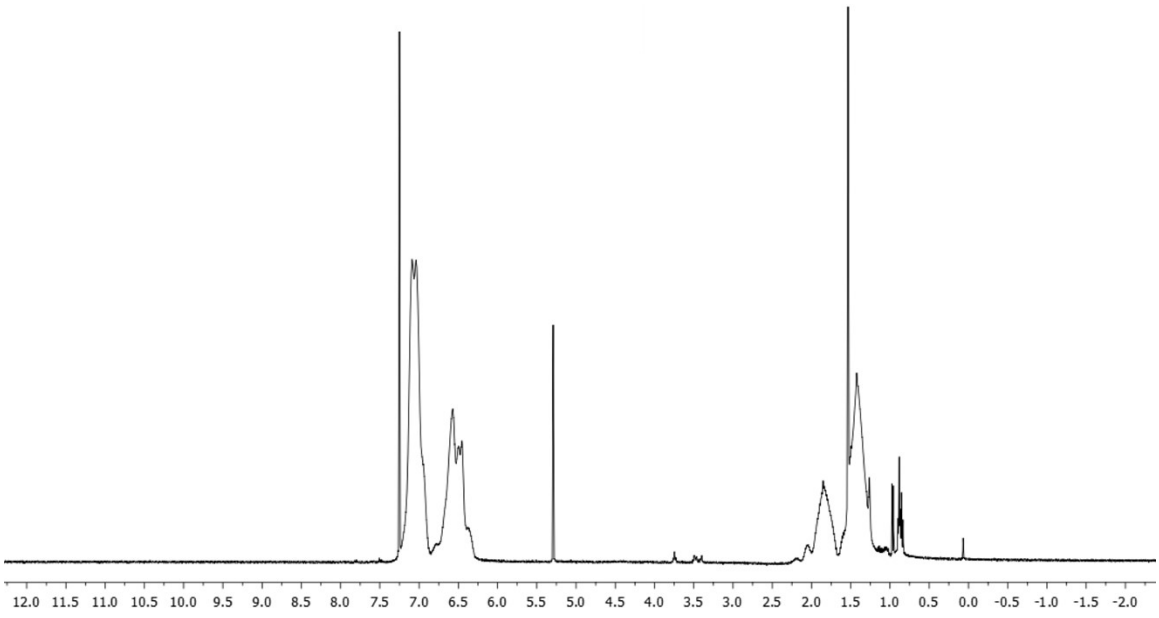
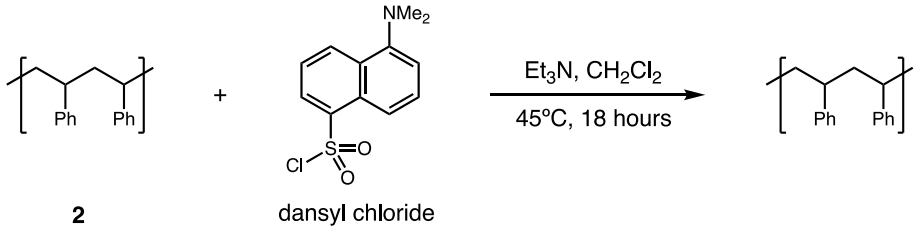


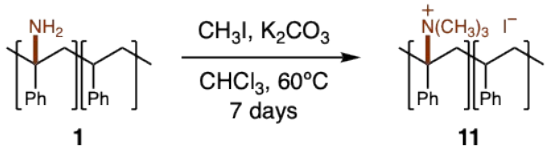
Figure S2.4. ^{1}H-NMR of **8**; Dansyl chloride treated amino-polystyrene **1**.



2 dansyl chloride

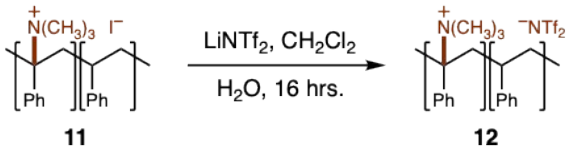
S2.7.2. Control experiment with polystyrene **2**. A sealed tube charged with dichloromethane (2 mL), Et_3N (20.2 mg, 0.2 mmol, 0.1 equiv.), Dansyl chloride (5 mg, 0.02 mmol, 0.01 equiv.), and unmodified polystyrene **2** (200 mg, 2 mmol, 1.0 equiv.) was heated at 45°C overnight. The product was purified by adding a dichloromethane solution directly to cold methanol to precipitate the polymer three times. The purified product was then dissolved in CH_2Cl_2 (1 mL) and stirred with 50% NaOH solution overnight at room temperature. The two phases were then separated, and then the organic phase was rinsed with 1 M HCl (10 mL) solution and water (3 x 10 mL). The resulting dichloromethane solution was then dried over Na_2SO_4 and then precipitated from cold methanol as described above to give the product as a white solid. Fluorimetry did not indicate the presence of a Dansylamide (Section S2.6.1).

S2.8. *N*-Methylation of amino polystyrene 1



1 **11**

S2.8.1. **11***; methylation of* ***1***: In a nitrogen glovebox, methyl iodide (99 mg, 0.70 mmol, 3.1 equiv.), amino polystyrene (**1**, 400 mg, 3.84 mmol, NH_2 loading = 0.38%, 0.0146 mmol, M_n = 12,500, $Đ$ = 1.12), potassium carbonate (30 mg, 0.22 mmol, 15 equiv.) and chloroform (2 mL) were combined in a 6-dram vial equipped with magnetic stirbar. The vial was then sealed tightly and covered with aluminum foil, and the mixture was heated to 60 °C with magnetic stirring on an aluminum heating block for one week. The resulting yellow suspension was filtered, and then the solid was rinsed with CH_2Cl_2 (10 mL). The solution was concentrated under reduced pressure. The product was obtained as a white powder (300 mg, 2.88 mmol, 75% recovery) by precipitation from cold methanol (50 mL) and filtration.



11 **12**

The methylated amino polystyrene (**11**, 200 mg) and $LiNTf_2$ (100 mg) were added to a 6-dram vial equipped with stir bar in a nitrogen glovebox. The vial was capped with a septum cap and then transferred outside the glove box. Water (0.5 mL) and CH_2Cl_2 (0.5 mL) were added to the vial via syringe. The reaction mixture was stirred at room temperature for 16 hours. The resultant mixture was extracted with deionized water three times. The organic fractions were combined and dried with Na_2SO_4. The solution was concentrated under reduced pressure. The product **12** was obtained by precipitation from cold methanol (160 mg, 1.54 mmol, 80% recovery).

To assay the product, a portion of the polymer was combined with 1,3-*bis*(trifluoromethyl)benzene and $CDCl_3$ for analysis by ^{19}F-NMR; from a stock solution of 1,3-*bis*(trifluoromethyl)benzene (12.4 µL, 0.0798 mmol) and $CDCl_3$ (10 mL; 0.00798 M),

1 mL (0.008 mmol) was added to polymer (40 mg, 0.384 mmol) to prepare the NMR sample. In ^{19}F-NMR, relative integration of the 1,3-*bis*(trifluoromethyl)benzene (CF_3, –63.0 ppm) was compared to the bistriflimide ion (NTf_2^-, –78.78 ppm) paired to the tetraalkylammonium unit on polystyrene backbone. This chemical shift was consistent with what we observed for $[PhCMe_2NMe_3]^+[NTf_2]^-$ (**S2**, Section S4.3), which we prepared as a model compound. The degree of methylation on the polystyrene was 0.17%. The starting amino polymer has 0.38% NH_2 incorporation. On this basis, we assign a 47% yield for trimethylation of the $–NH_2$ units on the polymer backbone.

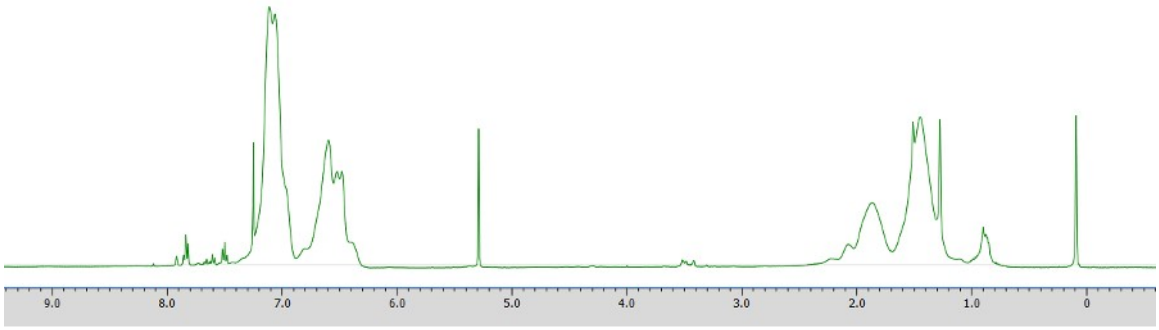


Figure S2.5. ^{1}H-NMR of **12** ($LiNTf_2$-treated *N*-methylated polystyrene) prepared in Section S2.8.1, $CDCl_3$, 400 MHz.

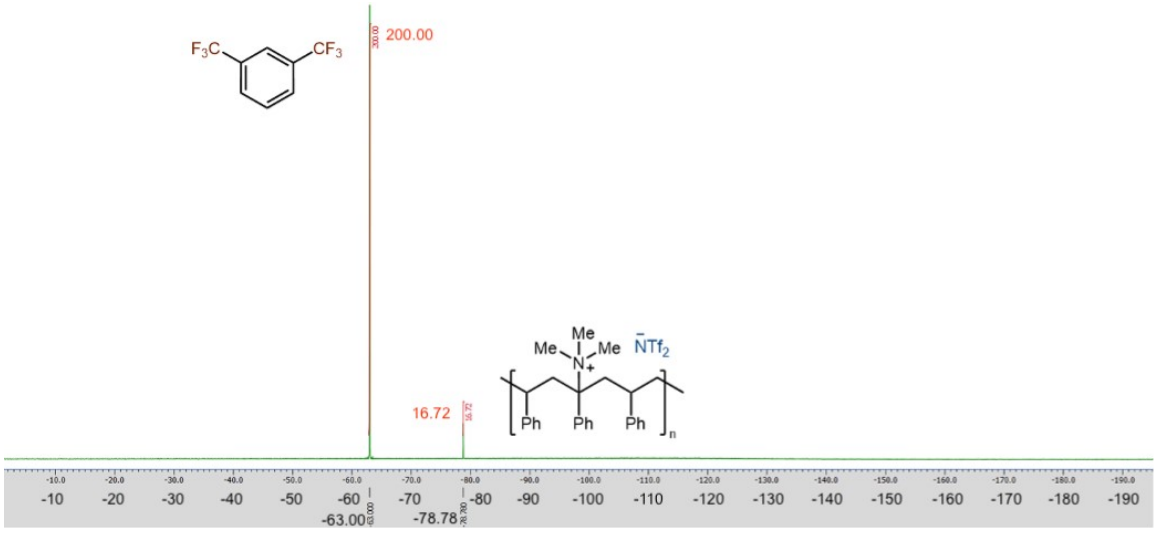


Figure S2.6. ^{19}F-NMR of **12** ($LiNTf_2$-treated *N*-methylated amino-polystyrene) prepared in Section S2.8.1, with peak assignments, $CDCl_3$, 376 MHz.

As a control, we also analyzed a solution of virgin polystyrene (40 mg, 0.38 mmol) and 1,3-*bis*(trifluoromethyl)benzene (12.4 μL, 0.0798 mmol) by ^{19}F-NMR. As can be seen below, there is no visible signal at –78.780 ppm corresponding to the $^{-}N(SO_2CF_3)_2$ ion.

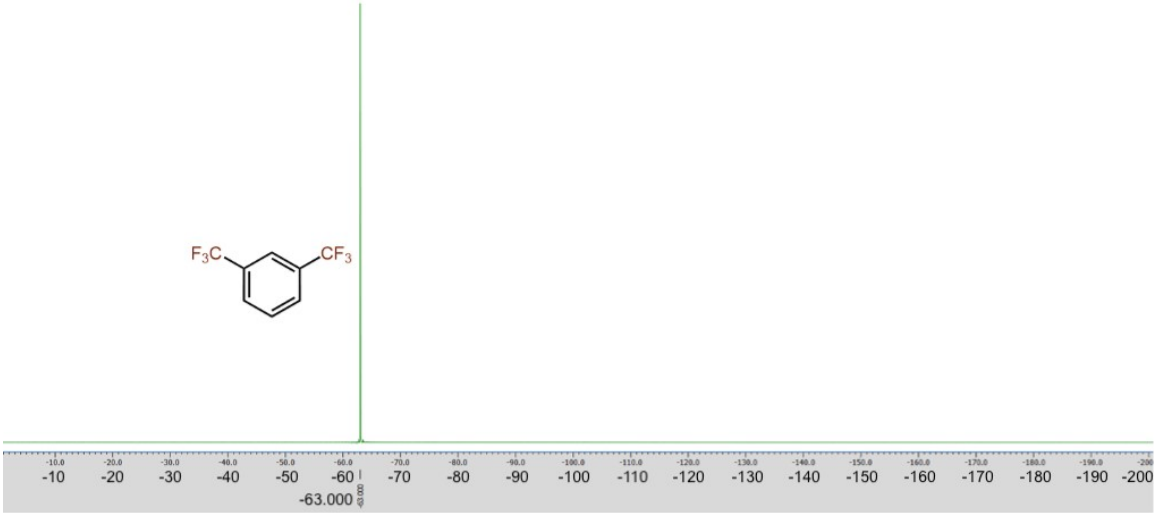
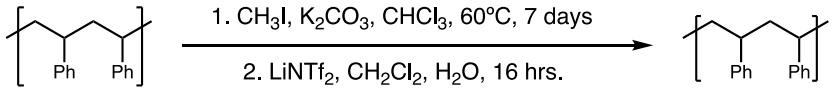


Figure S2.7. ^{19}F-NMR of $LiNTf_2$ and virgin polystyrene, $CDCl_3$, 376 MHz.

To confirm that this signal arises from anion exchange with a tetraalkylammonium polymer, we have additionally performed a control experiment with unmodified polystyrene **2** (Section S2.8.2) and prepared an analogous tetraalkylammonium bistriflamide salt (**S2**, Section S2.8.3) as a spectroscopic standard. We also repeated this procedure with ^{13}C-labeled CH_3I for ^{13}C-NMR analysis of the product (Section S2.8.4).



Section S2.8.2. Control experiment with polystyrene **2.** In a nitrogen glovebox, methyl iodide (99 mg, 0.70 mmol, 3.1 equiv.) was added to a suspension of polystyrene **2** (M_n = 1.36*10^4, 0.52 g, 5.0 mmol, 23 equiv.), K_2CO_3 (31 mg, 0.22 mmol, 1.0 equiv.), and $CHCl_3$ (2.0 mL) in a pressure tube equipped with a magnetic stirbar. The tube was then sealed tightly and covered with aluminum foil, and the mixture was heated to 60 °C with magnetic stirring on an oil bath for one week. The resulting yellow suspension was filtered, rinsing

with $CHCl_3$. The product was obtained by precipitation from methanol (0.47 g, 4.5 mmol, 90% recovery).

A portion of that polymer (0.26 g, 2.5 mmol, 6.23 equiv.) was dissolved in CH_2Cl_2 (2.0 mL), and treated with $LiNTf_2$ (115 mg, 0.401 mmol, 1.0 equiv.). The filtrate was concentrated, and then precipitated from cold MeOH to obtain a white solid (240 mg, 2.30 mmol, 92% recovery). A portion of this sample (80 mg, 0.77 mmol of polystyrene) was combined with 1,3-*bis*(trifluoromethyl)benzene (17 mg, 0.079 mmol) and then dissolved in $CDCl_3$ (0.5 mL) for NMR analysis. We did not observe a peak at –78.80 ppm in this spectrum, the peak that we assigned to the $^{-}NTf_2$ ion.

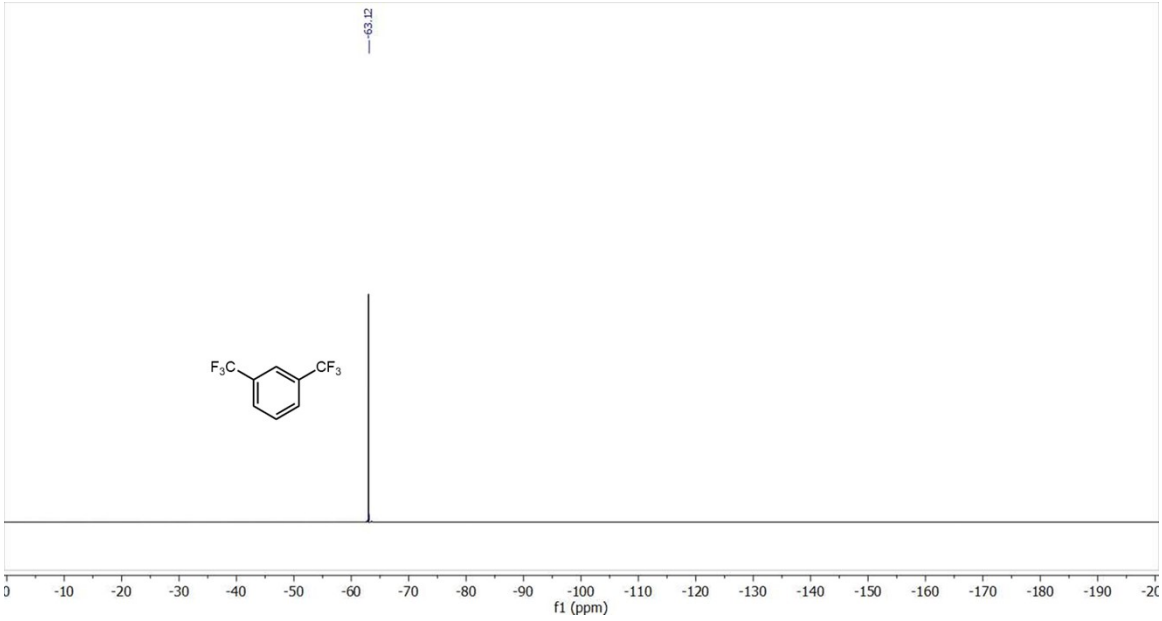
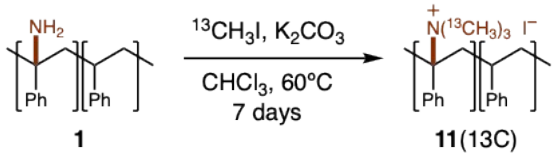
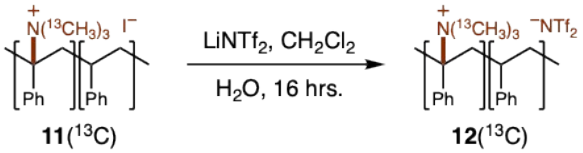


Figure S2.8. ^{19}F-NMR of polystyrene treated with CH_3I, and then $LiNTf_2$.



Section S2.8.3. **11**(^{13}C). *N-methylatation of **1** with $^{13}CH_3I$.* In a nitrogen glovebox, ^{13}C-labeled methyl iodide (99 mg, 99% ^{13}C, formula weight = 142.9313, 0.69 mmol, 38 equiv.), amino polystyrene (**1**, 500 mg, 4.80 mmol or polymer; NH_2 loading = 0.38%, 0.0182 mmol, 1 equiv.; M_n = 12,500, $Đ$ = 1.12), potassium carbonate (30 mg, 0.22 mmol, 12 equiv.) and

chloroform (2 mL) were combined in a 6-dram vial equipped with a magnetic stirbar. The vial was then sealed tightly and covered with aluminum foil, and the mixture was heated to 60 °C with magnetic stirring on an aluminum heating block for one week. The resulting yellow suspension was filtered, and then the solid was rinsed with $CHCl_3$ (10 mL). The solution was concentrated under reduced pressure. The product was obtained as a white powder (420 mg, 4.038 mmol, 84% recovery) by precipitation from cold methanol (50 mL).



11(^{13}C) **12**(^{13}C)

A portion of the methylated amino polystyrene (**11**(^{13}C), 200 mg, 1.92 mmol polystyrene; 0.00730 mmol nitrogen) and $LiNTf_2$ (100 mg, 0.348 mmol) were added to a 6-dram vial equipped with stir bar in a nitrogen glove box. The vial was capped with septum cap. The vial was then transferred outside the glove box. Water (0.5 mL) and CH_2Cl_2 (0.5 mL) were added to the vial via syringe. The reaction mixture was stirred at room temperature for 16 hours. The resultant mixture was treated with CH_2Cl_2 (5 mL), and then extracted with deionized water (3 x 10 mL). The dichloromethane solution was dried with Na_2SO_4. The solution was decanted and concentrated under reduced pressure. The product was obtained as a white powder (**12**(^{13}C), 160 mg, 1.54 mmol, 80% recovery) by precipitation from cold methanol (20 mL).

To assay the product, a portion of the polymer was combined with 1,3-*bis*(trifluoromethyl)benzene and $CDCl_3$ for analysis by ^{19}F-NMR; from a stock solution of 1,3-*bis*(trifluoromethyl)benzene (12.4 μL, 0.0798 mmol) and $CDCl_3$ (10 mL; 0.00798 M), 1 mL (0.00798 mmol) was added to polymer (**12**(^{13}C)50 mg, 0.480 mmol) to prepare the NMR sample. The degree of methylation on the polystyrene was 0.14%. The starting amino polymer has 0.38% NH_2 incorporation. 37% of the NH_2 units on the polymer backbone was functionalized. ^{13}C-NMR analysis resulted in a peak 52.3-51.4 ppm that we assigned

to the $N(^{13}CH_3)_3^+$ functional group. This ^{13}C-NMR chemical shift was consistent with what we obtained for $[PhCMe_2NMe_3]^+[NTf_2]^-$ (chemical shift at 50.1 ppm), (**S2**, Section S4.3).

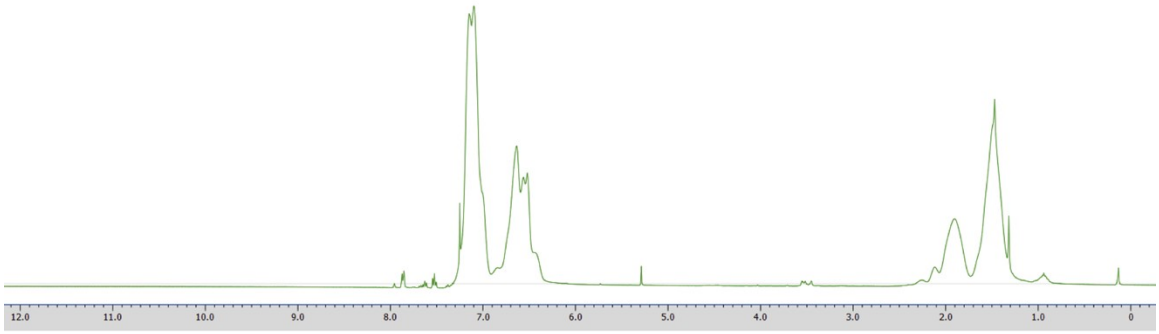


Figure S2.9. ^{1}H-NMR of **12**(^{13}C) ($LiNTf_2$-treated N-Methylated (MeI-^{13}C) polystyrene), prepared in Section S2.8.3, $CDCl_3$, 400 MHz.

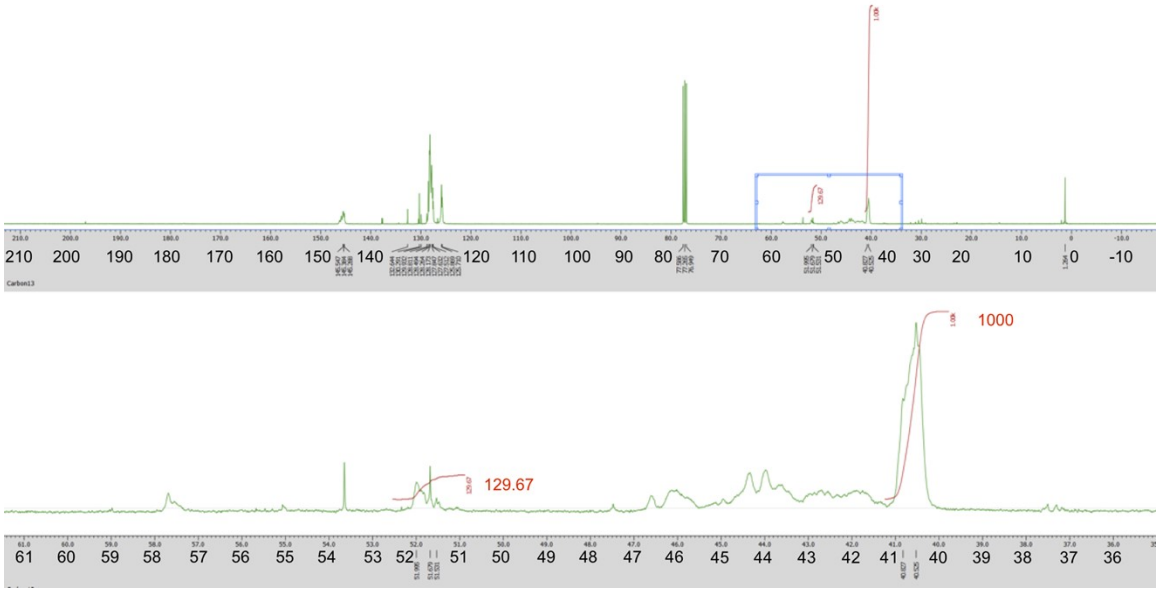


Figure S2.10. ^{13}C-NMR of **12**(^{13}C) ($LiNTf_2$-treated *N*-Methylated (MeI-^{13}C) polystyrene), prepared in Section S2.8.3, $CDCl_3$, 100 MHz.

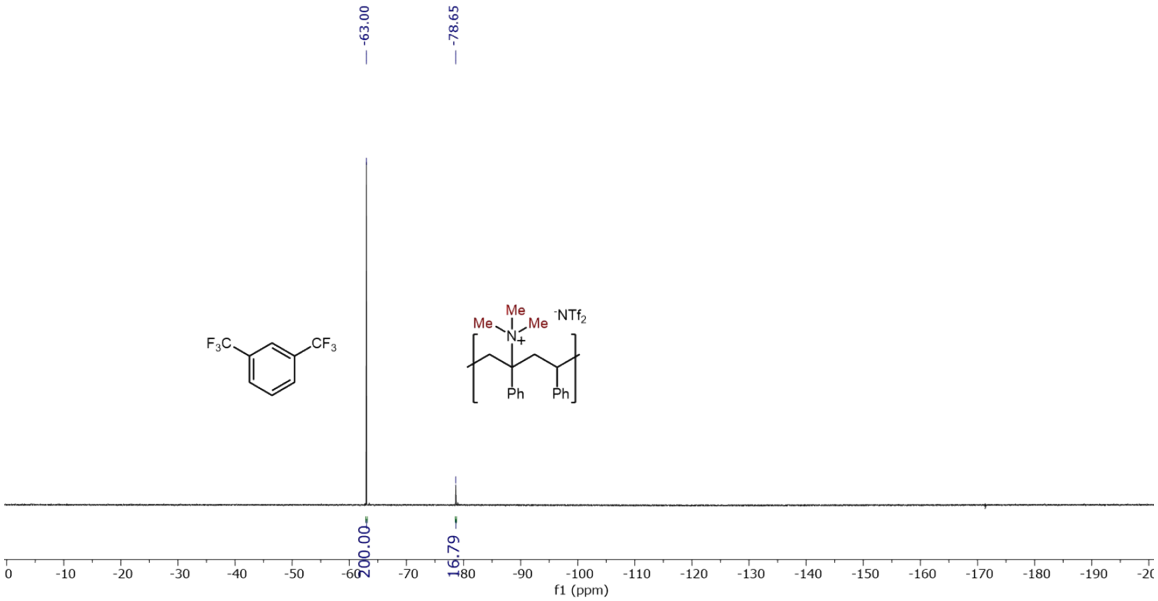
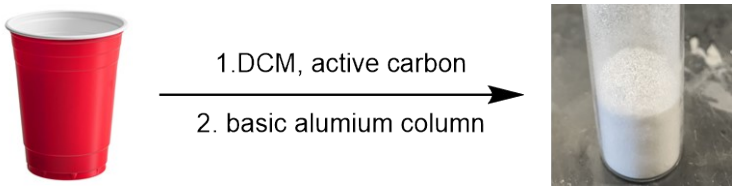


Figure S2.11. ^{19}F-NMR of **12**(^{13}C) ($LiNTf_2$-treated *N*-Methylated (MeI-^{13}C) polystyrene), prepared in section S2.8.3, $CDCl_3$, 376 MHz.

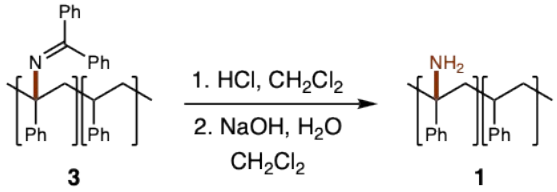
S2.9 Amination of commercial polystyrene.

S2.9.1. Isolation of polystyrene.



As a commercial source of polystyrene, we used Comfy Package Disposable Party Plastic Cups [18 oz. - 50 Count] Red Drinking Cups, purchased from Amazon.com (part number B09J6PRLY6). The red plastic cup was cut into pieces (5 g) and stirred magnetically with CH_2Cl_2 (50 mL) at room temperature until a homogeneous solution was obtained. Activated carbon (10 g) was then added to decolorize the solution. Bubbles formed upon the addition of activated carbon. The solution was then filtered after bubbling ceased. The grey filtrate was then passed through a basic alumina column to remove impurities. The colorless polymer solution was concentrated under reduced pressure to about 10 mL. Transferring this solution to cold methanol (100 mL) yielded the product as a white powder (4.2 g, 84% recovered, M_n = 16,500, $Đ$ = 1.067).

S2.9.2. Imination. A solution of the polystyrene sample isolated in Section S2.9.1 (**2**, 1.000 g, 9.601 mmol, 48.5 equiv.), $PhI(OMe)_2$ (**5**, 106 mg, 0.398 mmol, 2.01 equiv.), benzophenone imine (**4**, 33.3 µL, 0.198 mmol, 1.0 equiv.), and chlorobenzene (4 mL) in a sealed tube under nitrogen was heated to 110 ºC for 24 hours with magnetic stirring. After cooling, the solution was precipitated from cold methanol (50 mL). The polymer was purified by redissolving in CH_2Cl_2 (5 mL) and then reprecipitating from cold methanol (50 mL) three times.



S2.9.3. Hydrolysis. A solution of CH_2Cl_2 (3 mL) and the iminyl-polystyrene intermediate (**3**, 1.8 g, 17.3 mmol) prepared in Section S2.9.2, was treated with 5 mL of concentrated HCl (12.0 M), and then stirred overnight at room temperature in a 100 mL round bottom flask. The solution was concentrated to a suspension using a stream of compressed air. The polymer was redissolved in CH_2Cl_2 (10 mL) and stirred with sodium hydroxide solution (3 M, 30 mL) for 5 hours at room temperature. The solution pH was evaluated by pH paper, and found to be greater than 12. The two solutions were partitioned and the CH_2Cl_2 solution was rinsed with deionized water (3 x 30 mL). The CH_2Cl_2 solution was then dried over Na_2SO_4, decanted, and concentrated under reduced pressure. The polymer was precipitated by dropping a concentrated CH_2Cl_2 solution (5 mL) into cold methanol (50 mL), and obtained as a powder by filtration (1.6 g, 15.4 mmol, 89% recovery).

S2.9.4. Analysis of isolated **1**; **1**•HOTf. A solution of amino-polystyrene **1** prepared from the Comfy Package Disposable Party Plastic Cups in Section S2.9.3 (104 mg, 1.00 mmol) was combined with trifluoromethanesulfonic acid (170 mg, 1.33 mmol) and CH_2Cl_2 (2 mL) and stirred for 18 hours. Then, the solution was extracted with water (3 x 10 mL). The polymer was then precipitated by pouring this solution into cold methanol (20 mL). Filtration afforded the product as a pale powder (80 mg, 0.77 mmol, 77% recovery). A portion of this sample (40 mg, 0.38 mmol) was combined with 1,3-*bis*(trifluoromethyl)benzene (12.4 µL, 0.0798 mmol) and then dissolved in $CDCl_3$ (0.5 mL) for ^{19}F-NMR analysis. An ^{19}F-NMR ratio of 9.95:1000 was obtained for the ratio of triflate

ion (–78.13 ppm) to 1,3-*bis*(trifluoromethyl)benzene (internally referenced to –63.00 ppm). From that, we obtained an amination ratio of 0.42% per styrene unit.

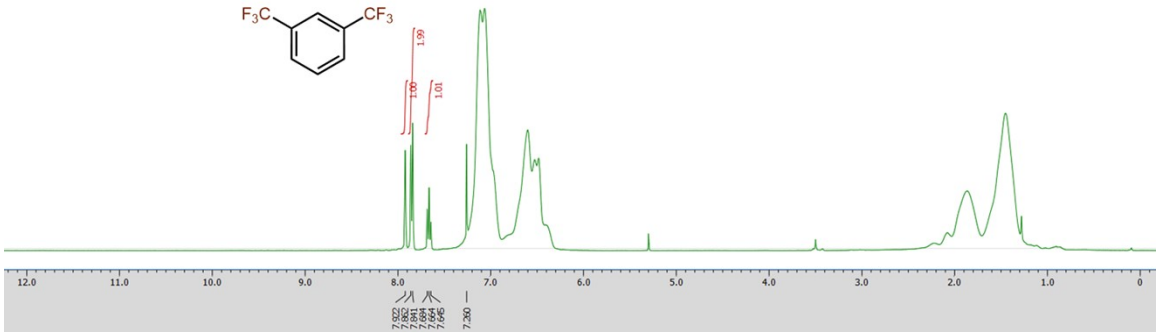


Figure S2.12. ^{1}H-NMR analysis of **1**•HOTf (Section S2.9.4) and 1,3-*bis*(trifluoromethyl) benzene, 400 MHz, $CDCl_3$.

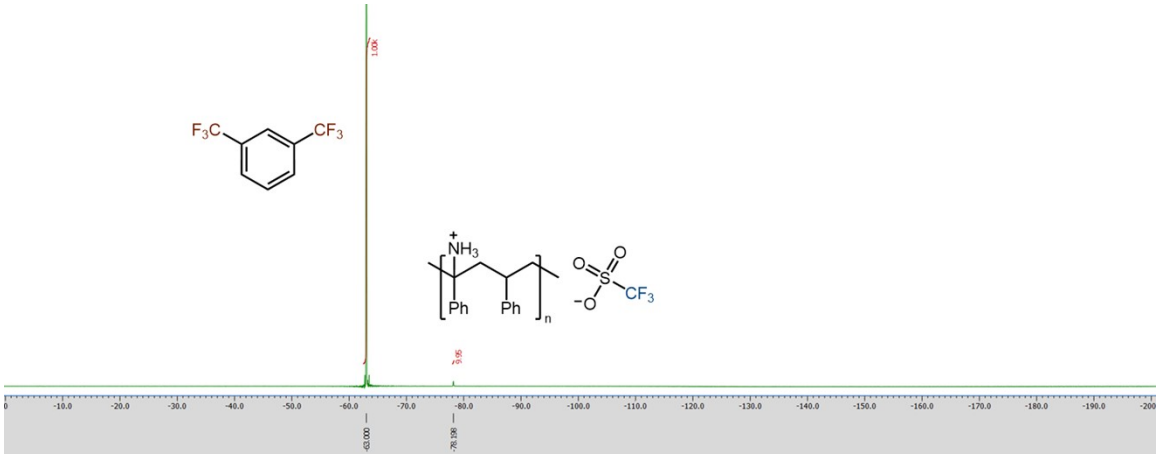
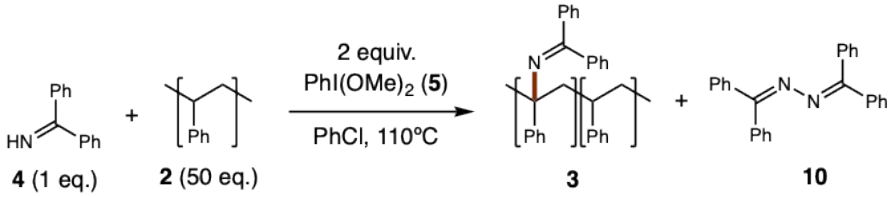


Figure S2.13. ^{19}F-NMR analysis of **1**•HOTf (Section S2.9.4) and 1,3-*bis*(trifluoromethyl) benzene, 376 MHz, $CDCl_3$.

S2.10. Byproduct analysis, formation of benzophenone azine (10)



A solution of polystyrene (**2**-13,200, 520 mg, 5 mmol, 50 equiv.), $PhI(OMe)_2$ (**5**, 0.053 g, 0.2 mmol, 2 equiv.), benzophenone imine (**4**, 0.017 g, 0.1 mmol, 1 equiv.), and chlorobenzene (1 mL) in a sealed tube under nitrogen was heated to 110 ºC for 24 hours with magnetic stirring. After cooling to room temperature, 200 µL of benzene-d_6 was added to the mixture. NMR experiments were performed to detect the formation of benzophenone azine. We assign the ^{13}C-NMR peak at 160 ppm to the azine by comparison to the literature.[6]

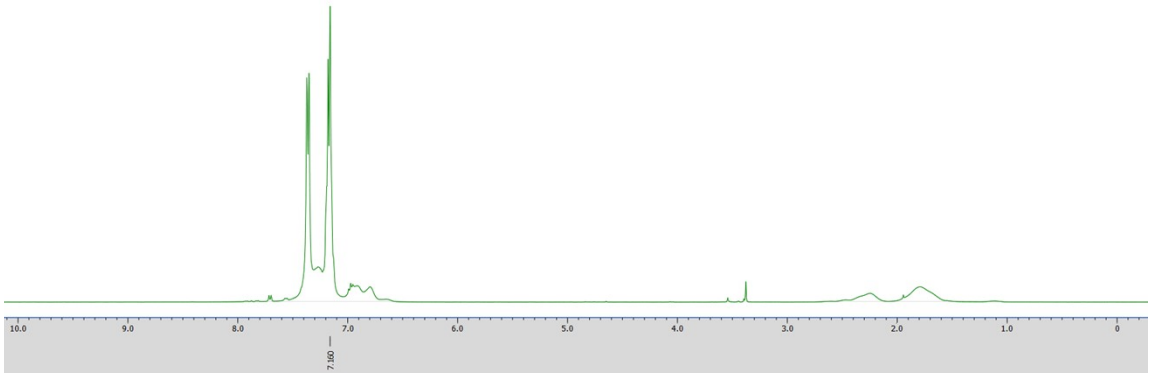


Figure S2.14. ^{1}H-NMR (C_6H_5Cl/C_6D_6, 400 MHz) of crude iminyl polystyrene.

[6] δ 159 ppm was reported for this signal in $CDCl_3$. Han, W.; Zhang, G.; Li, G.; Huang, H. *Org. Lett*. **2014**, *16*, 3532-3535.

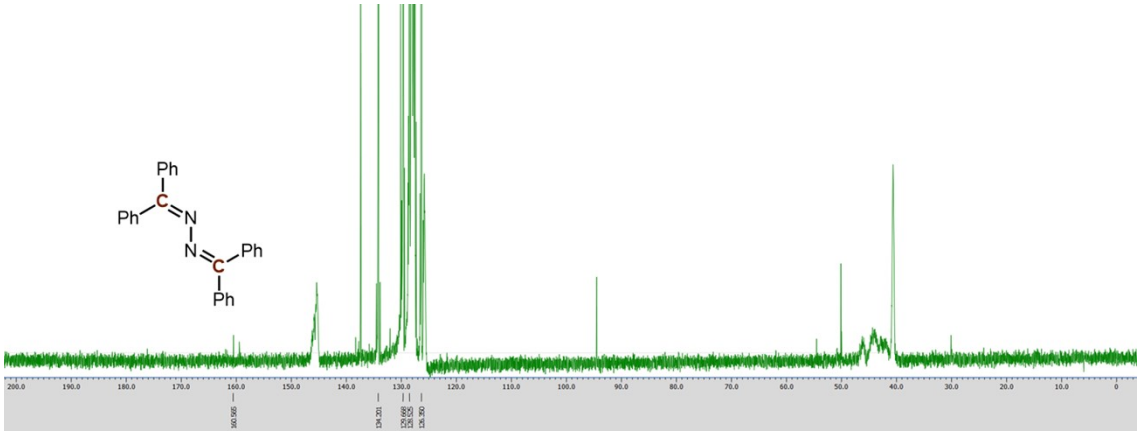


Figure S2.15. ^{13}C-NMR (C_6H_5Cl/C_6D_6, 100 MHz) of crude iminyl polystyrene. Chemical shift at 160 ppm indicates the presence of benzophenone azine (**10**).[6]

S3. Analysis of polymers.

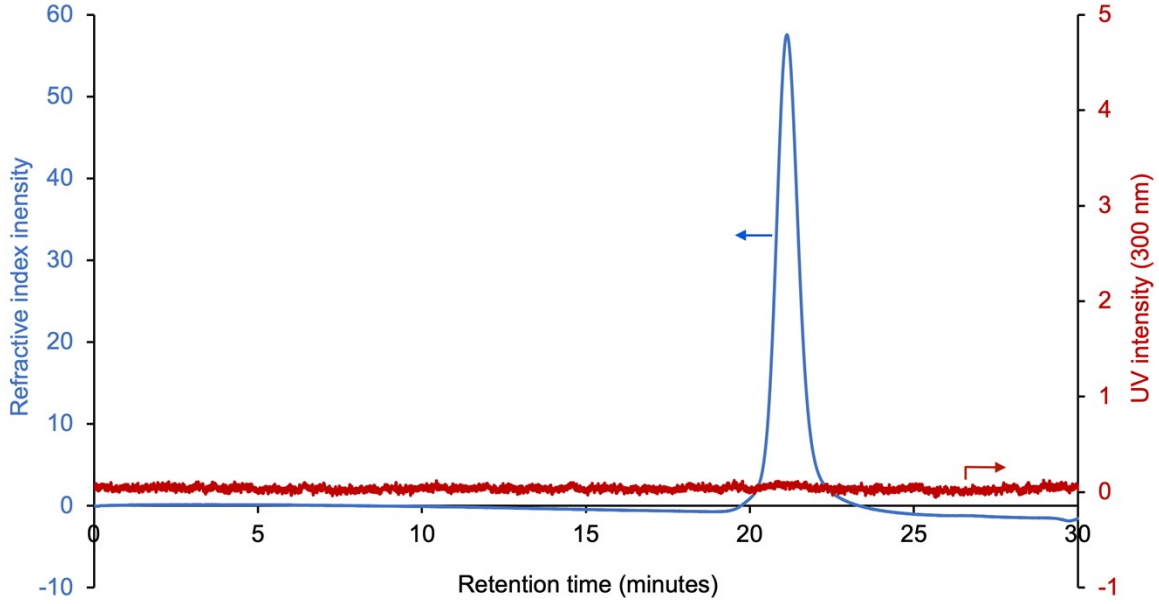


Figure S3.1. GPC analysis of polymer **2** (polystyrene) with RI and UV (300 nm) detection, $CHCl_3$.

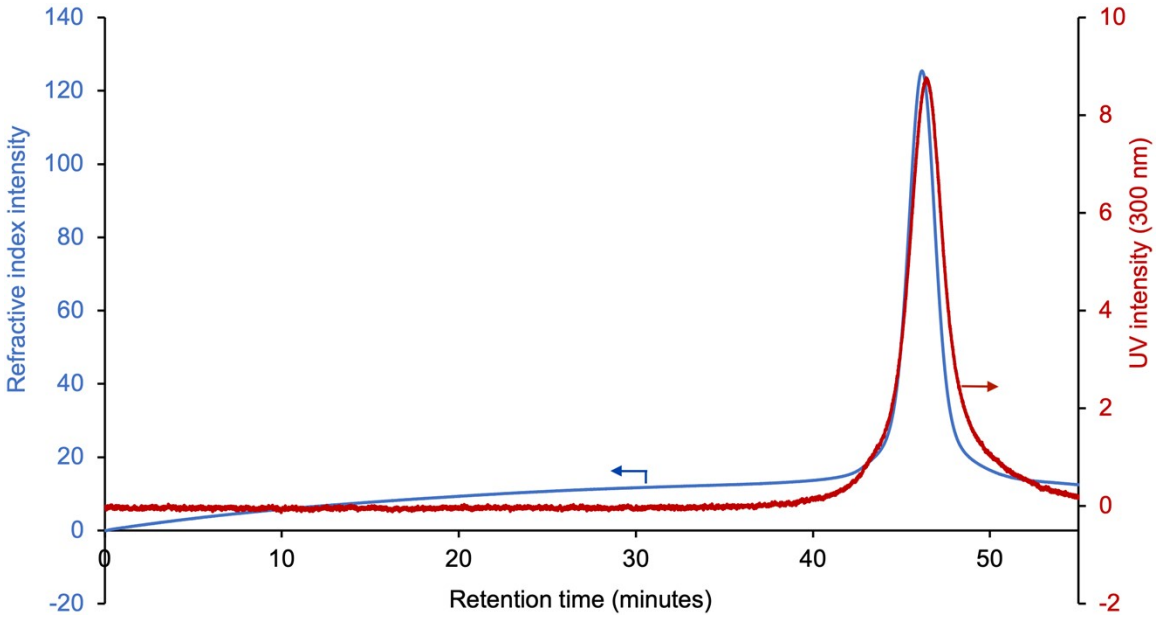


Figure S3.2. GPC analysis of polymer **3** (iminated polystyrene) with RI and UV (300 nm) detection, THF.

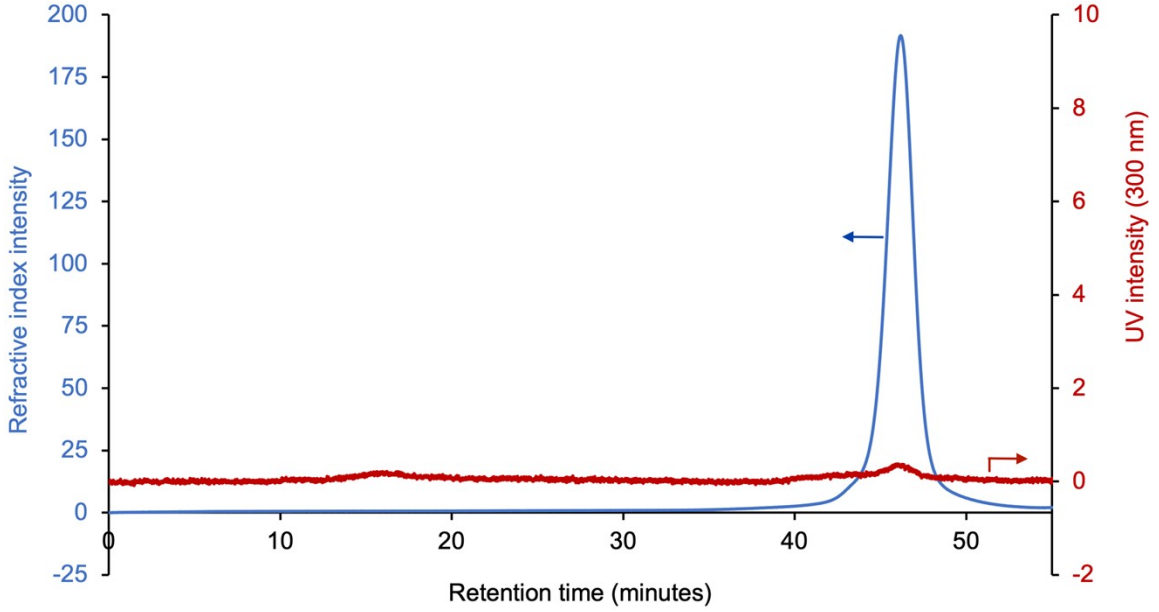


Figure S3.3. GPC analysis of polymer **1** (amino polystyrene) with RI and UV (300 nm) detection, THF.

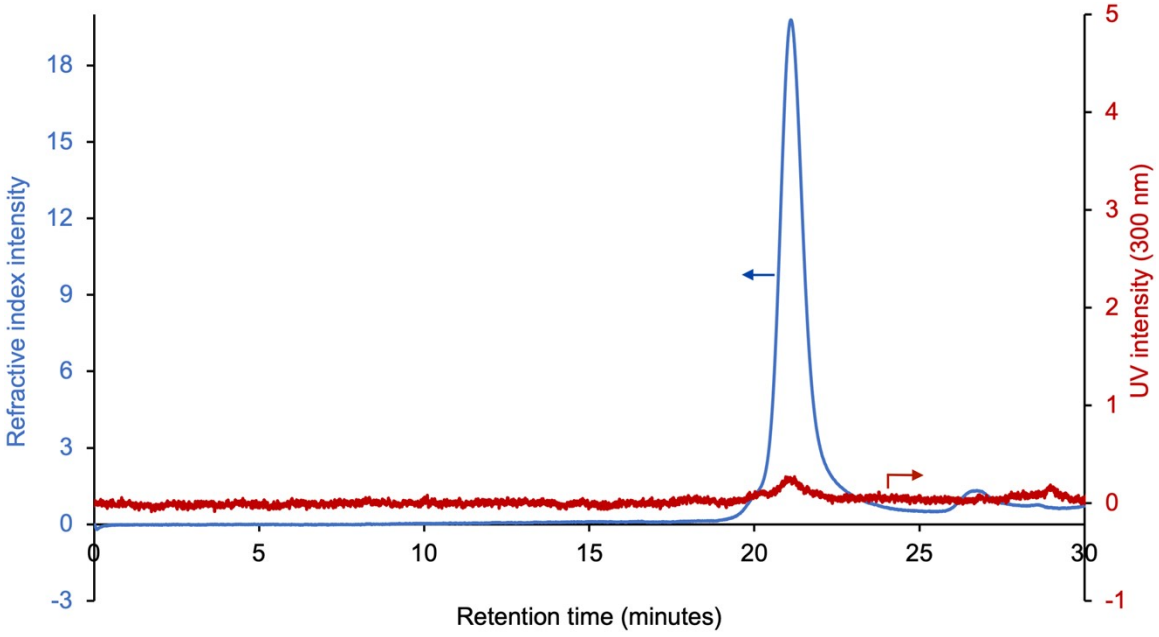


Figure S3.4. GPC analysis of polymer **1**•HCl (amino-polystyrene, HCl salt) with RI and UV (300 nm) detection, $CHCl_3$.

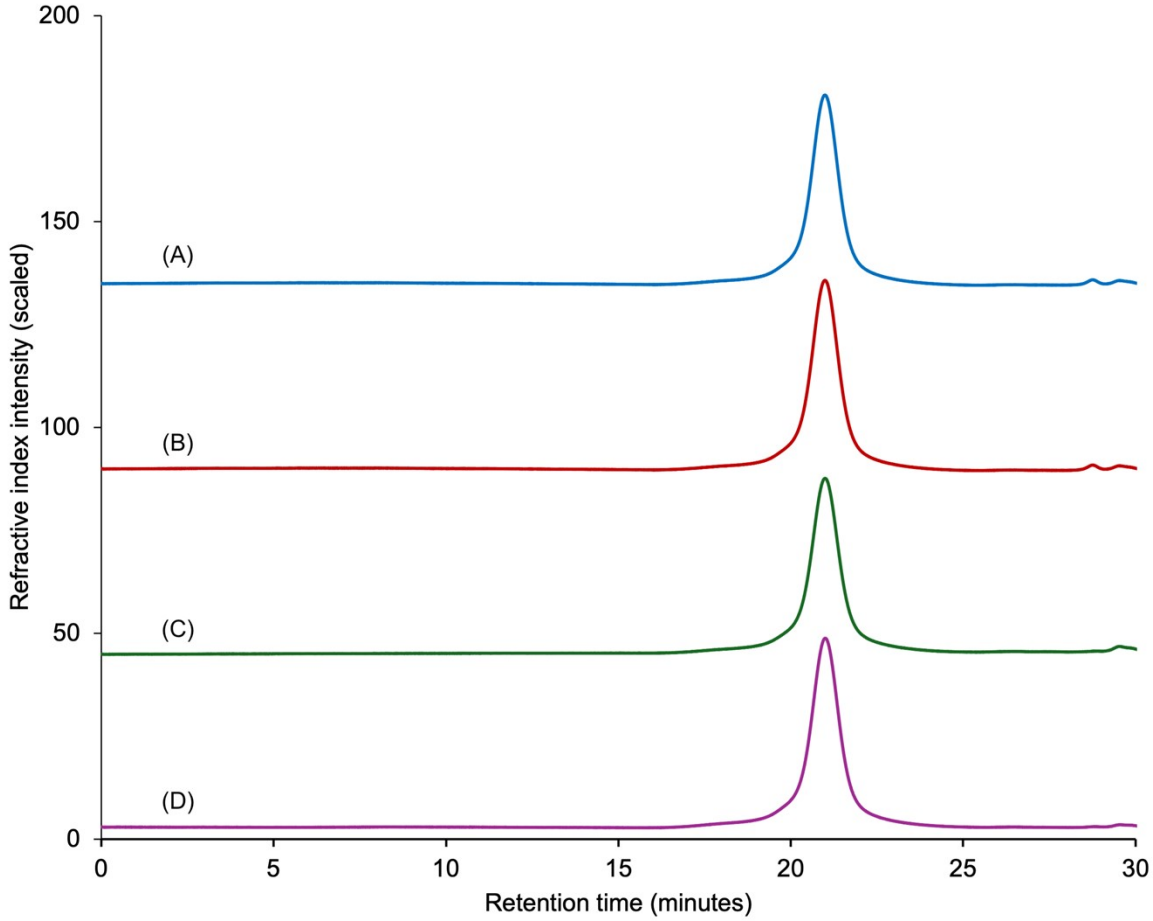


Figure S3.5. GPC Comparison of A) unmodified polystyrene (**2**), M_n = 1.31*10^4; B) iminated polystyrene (**3**), M_n = 1.24*10^4; C) amino polystyrene hydrochloride salt (**1**•HCl), M_n = 1.25*10^4; D) amino polystyrene (**1**), M_n = 1.26*10^4, 0.38% NH_2 incorporation.

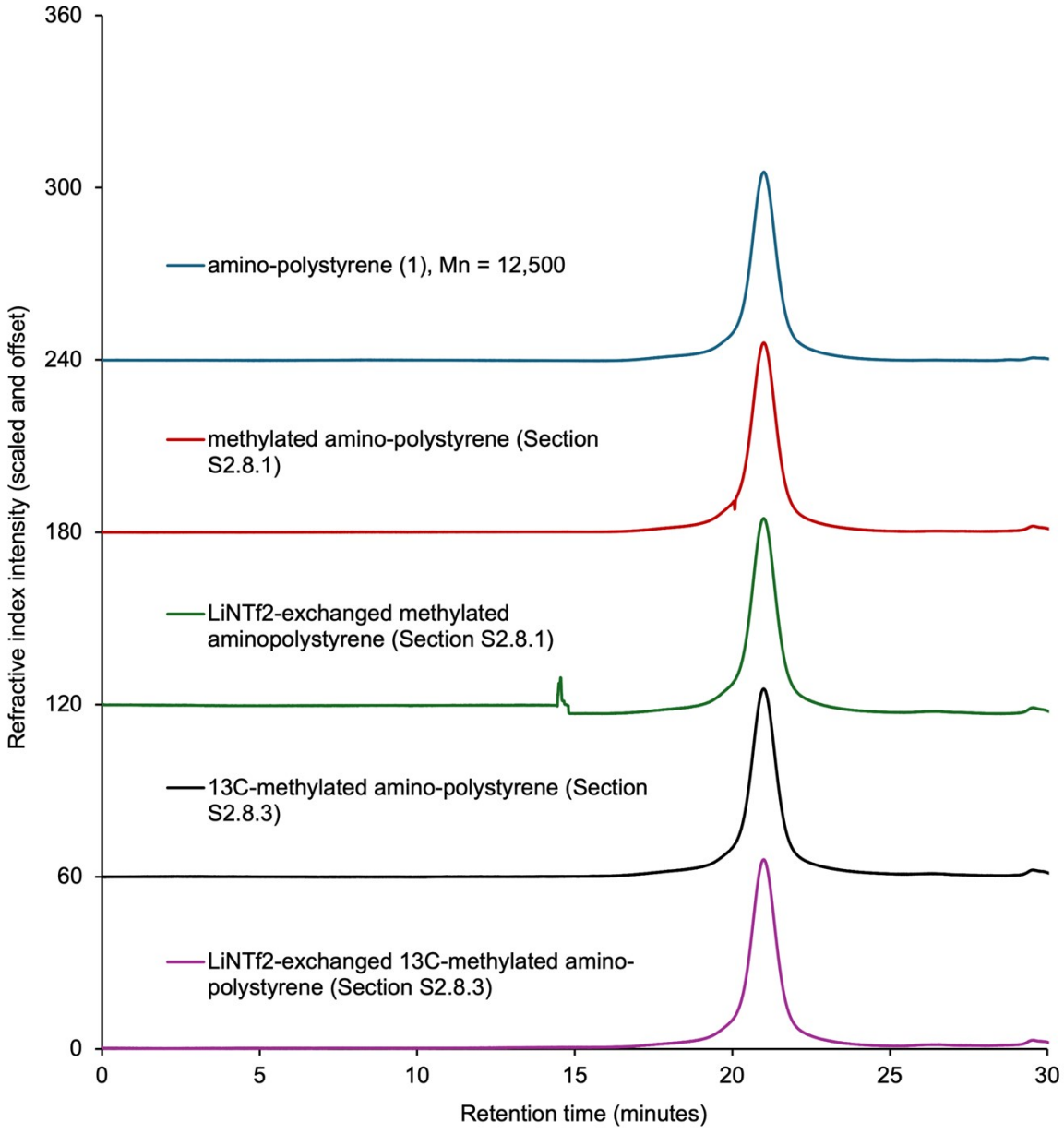


Figure S3.6. GPC comparison of polymers prepared by methylation of **1** (Section S2.8, THF).

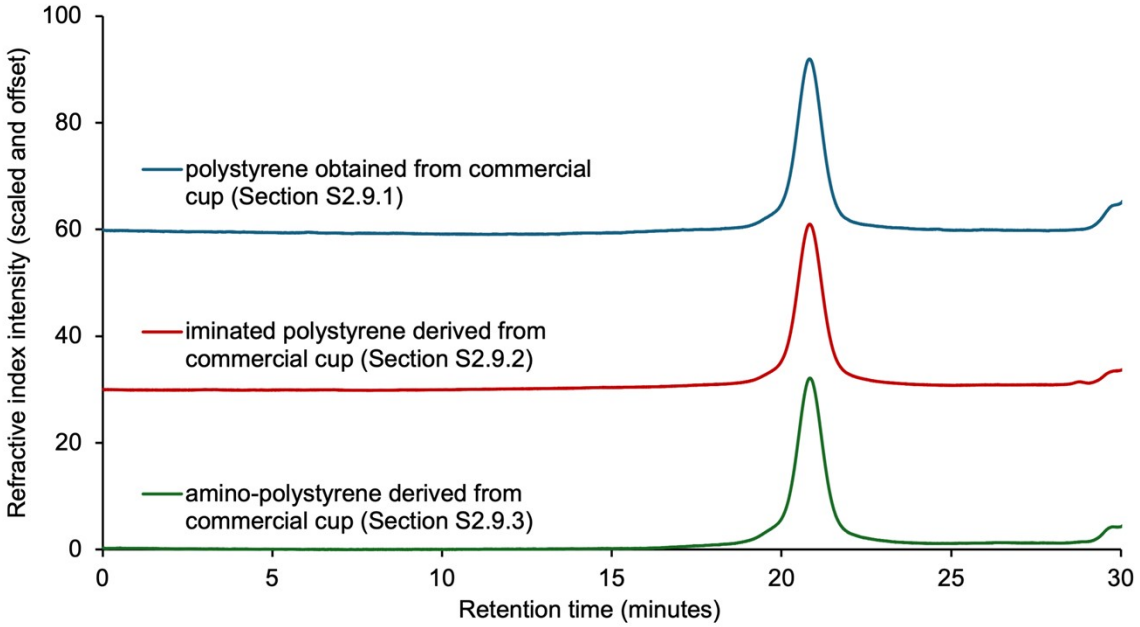
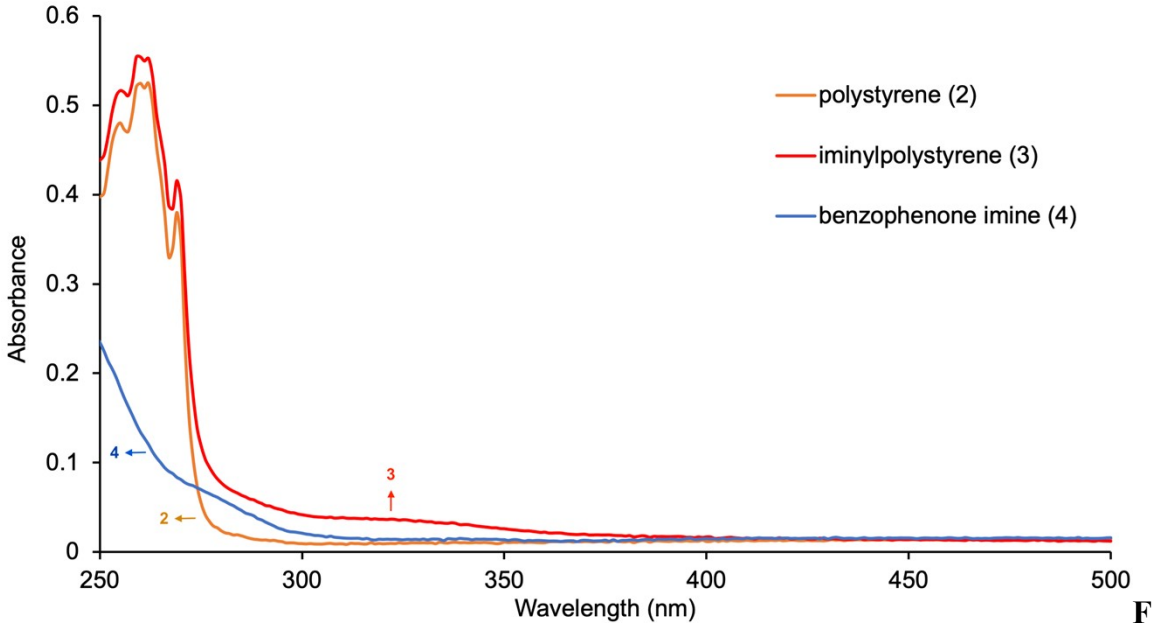


Figure S3.7. GPC comparison of aminated polymers prepared from the commercial Comfy cup polystyrene (Section S2.9).

Section S3.1. UV Absorption spectroscopy analysis of polymer samples. We analyzed several samples by UV absorption in the wavelength range 200–500 nm on an Agilent Cary 60 UV-Vis spectrophotometer, using a quartz cuvette with a 1 cm path length. All samples were analyzed as 0.002 M solutions in CH_2Cl_2. The following samples were used for analysis: amino-polystyrene **1** (M_n = 1.36*10^4, 0.27% –NH_2 loading; Section S2.5), ammonium polystyrene **1**•HCl (M_n = 1.28*10^4; Section S2.4), unmodified polystyrene **2** (M_n = 1.31*10^4; Section S2.1), iminyl polystyrene **3** (M_n = 1.29*10^4; Section S2.3). The UV absorbance of benzophenone imine (**4**) was too high at 0.002 M, resulting in saturation. So we performed UV/Vis spectroscopy of benzophenone imine (**4**) as a 2*10^{-5} M solution in CH_2Cl_2. The data for these spectra are reported and compared in Figures S3.8–9.



F

igure S3.8. UV/Vis comparison of imino-polystyrene **3**, unmodified polystyrene **2**, and benzophenone imine.

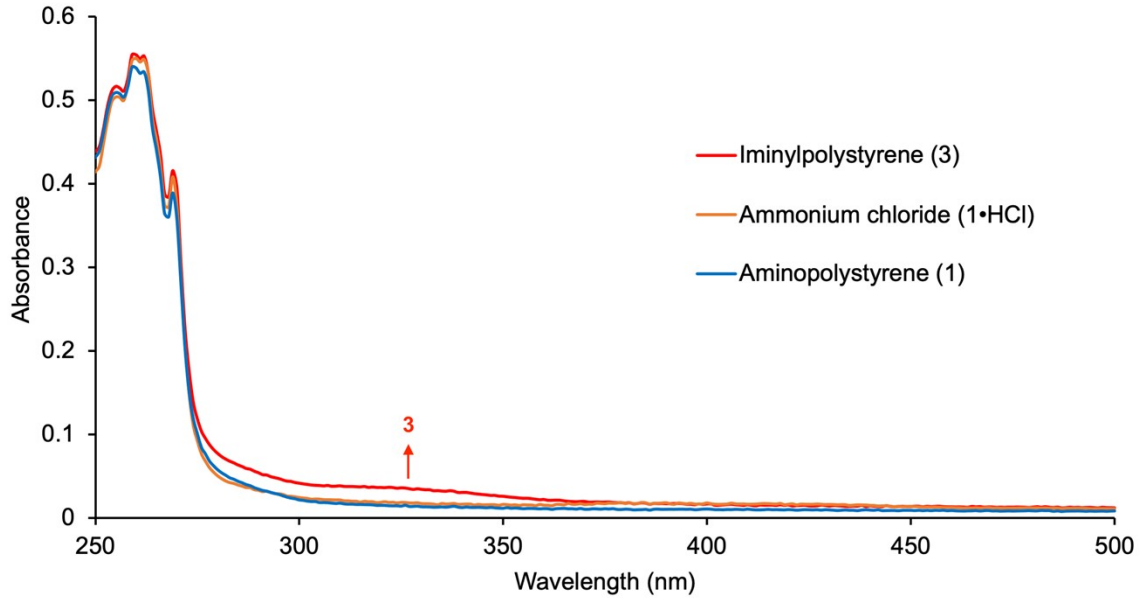


Figure S3.9. UV/Vis comparison of amino-polystyrene **1**, unmodified polystyrene **2**, and benzophenone imine.

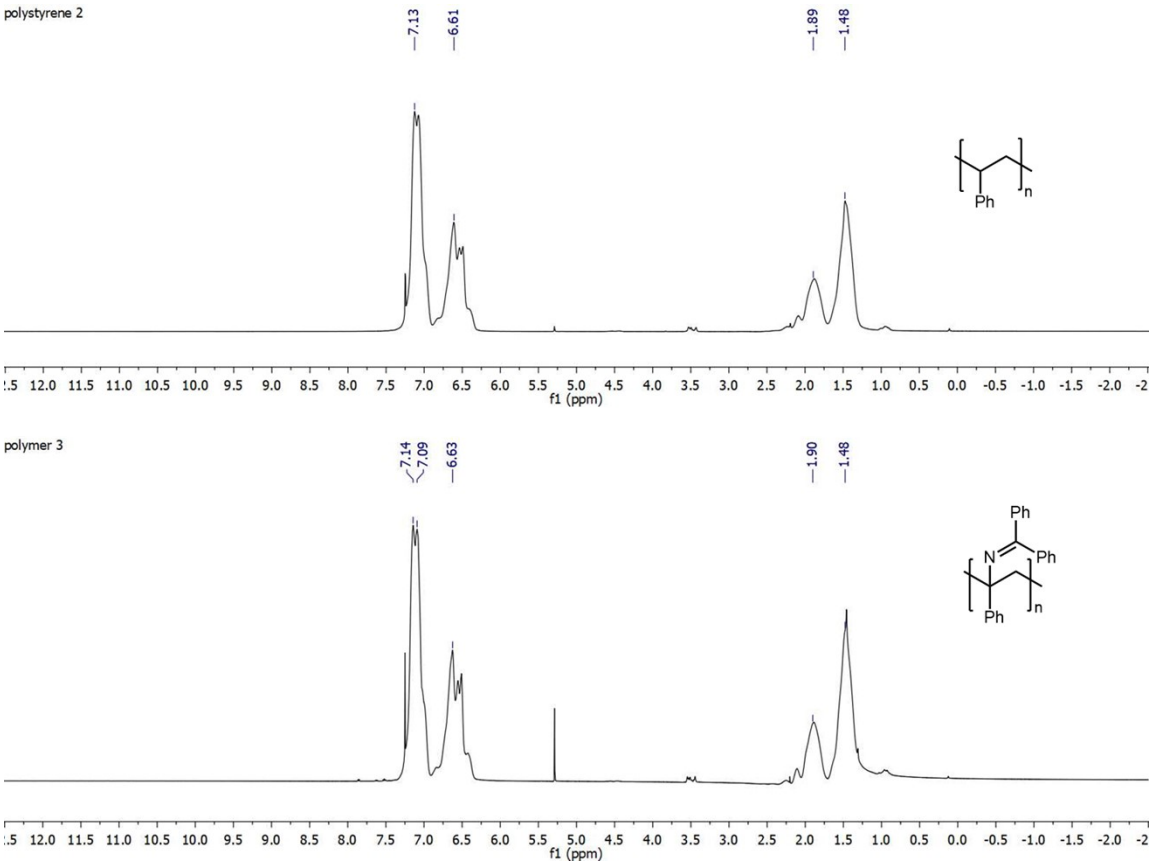


Figure S3.10. ^{1}H-NMR comparison between unmodified polystyrene **2** and imino-polystyrene **3**.

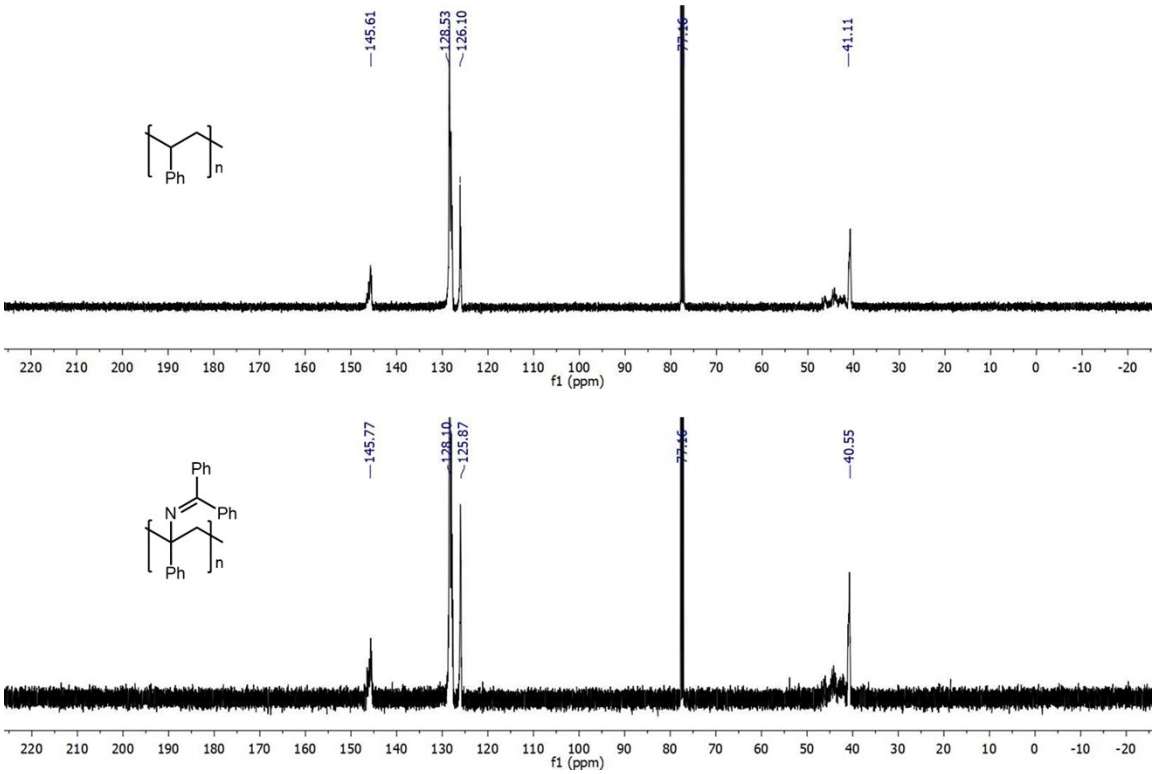


Figure S3.11. ^{13}C-NMR comparison between unmodified polystyrene **2** and imino-polystyrene **3**.

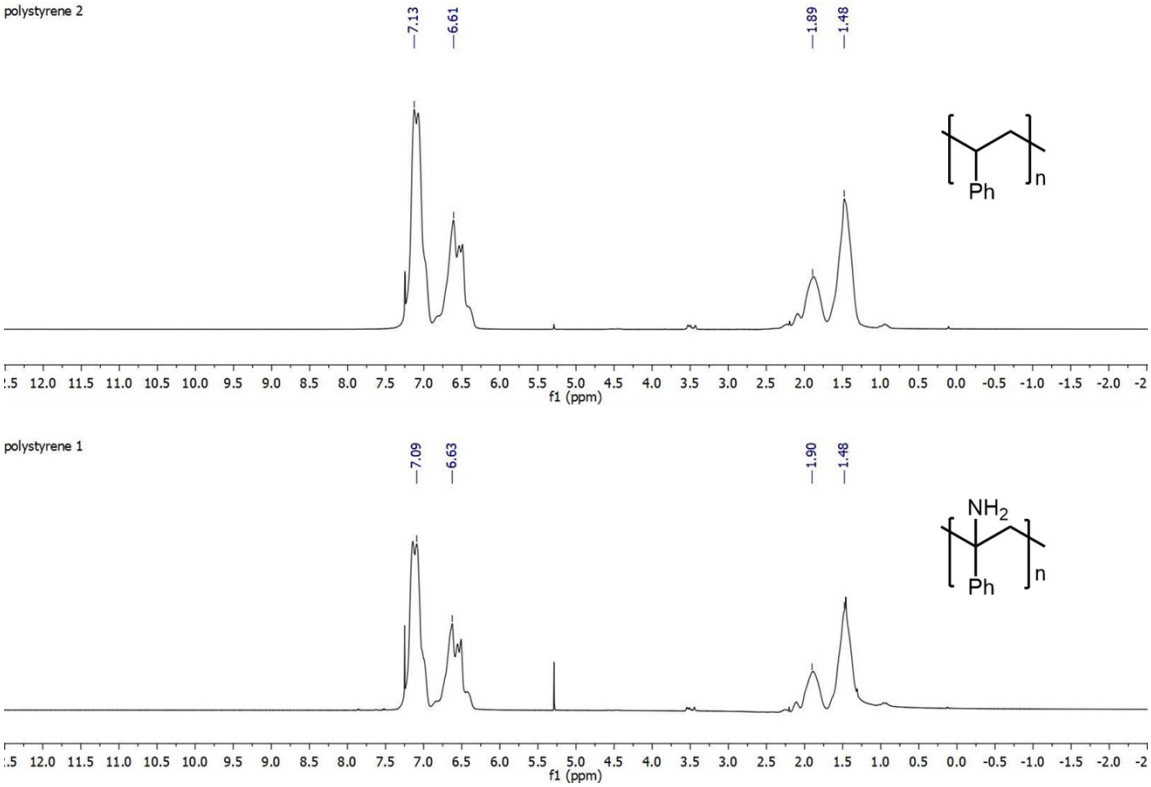


Figure S3.12. ^{1}H-NMR comparison between unmodified polystyrene **2** and amino-polystyrene **1**.

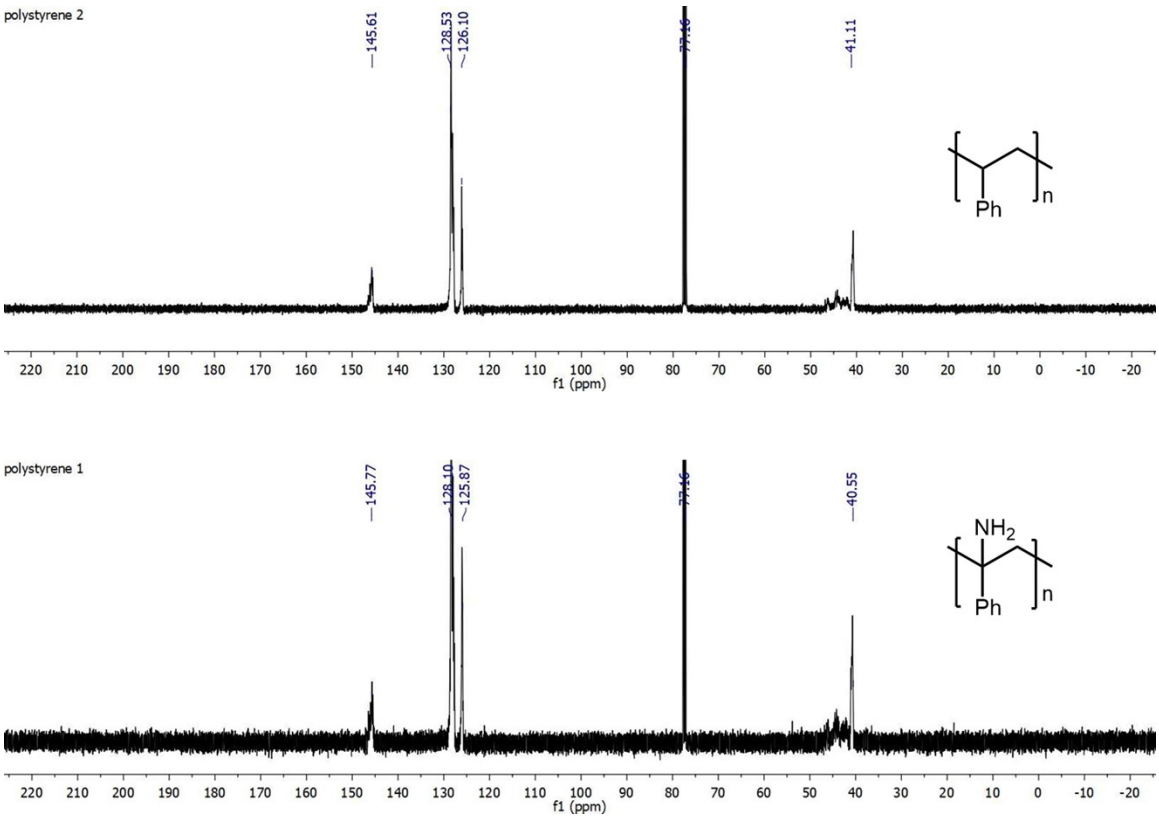


Figure S3.13. ^{13}C-NMR comparison between unmodified polystyrene **2** and amino-polystyrene **1.**

Section S3.2. IR analysis of polymer samples. The following samples were analyzed by infrared spectroscopy in transmission mode as KBr pellets. The following samples were used for analysis: amino-polystyrene **1** (M_n = 1.36*10^4, 0.29% –NH_2 loading), ammonium polystyrene **1**•HCl (M_n = 1.35*10^4, 0.29% –NH_2 loading), unmodified polystyrene **2** (M_n = 1.32*10^4), and iminyl polystyrene **3** (M_n = 1.30*10^4, 0.29% –NH_2 loading). The data for these spectra are reported and compared in Figure S3.11. A peak at 1650 cm^{-1} was observed only for iminyl polystyrene **3**, and we attribute this peak to the imine ν(C=N) stretching mode. For comparison, the ν(C=N) stretching mode has been reported at slightly lower wavenumbers for Ph_2C=NH (**4**) (1597 cm^{-1}, neat;[7] 1598 cm^{-1},[8] neat; 1601 cm^{-1}, KBr[9]) and

[7] Kondo, Y.; Kadota, T.; Hirazawa, Y.; Morisaki, K.; Morimoto, H.; Ohshima, T. Scandium(III) triflate catalyzed direct synthesis of N-unprotected ketimines. *Org. Lett*.

for N-alkyl benzophenone imines (Ph_2C=NtBu, 1605 cm^{-1},[10] KBr; Ph_2C=NCH_2Ph, 1620 cm^{-1}, ATR[11]).

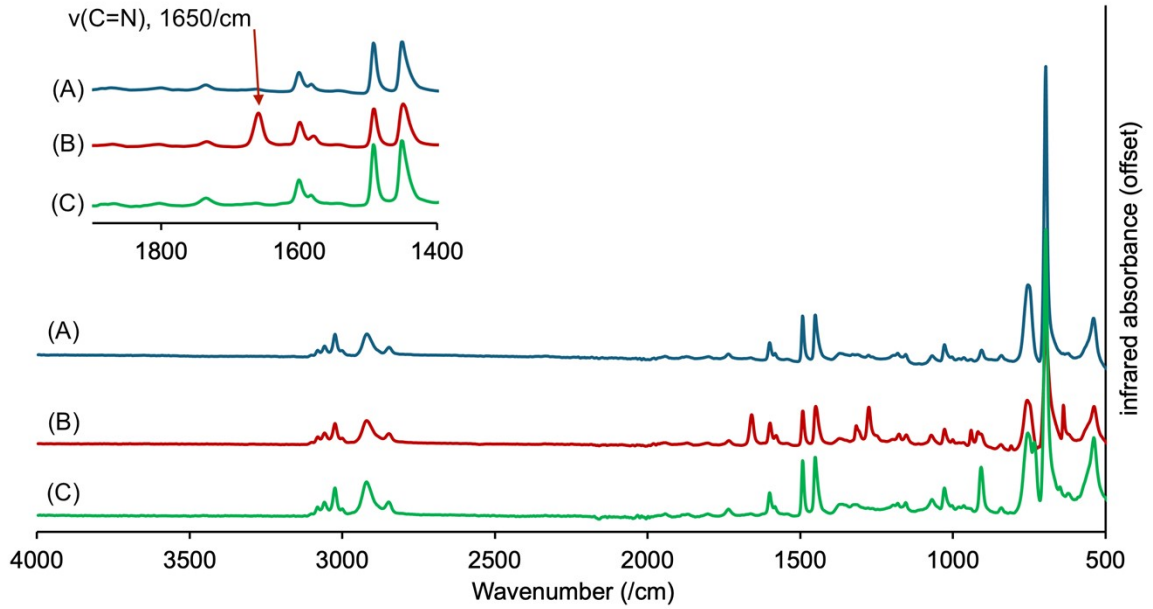


Figure S3.14. IR comparison of (A) unmodified polystyrene **2** (Section S2.1), (B) iminyl polystyrene **3** (Section S2.3), and (C) amino-polystyrene **1** (Section S2.4).

2019, *22*, 120-125.

[8] Shibata, S.; Masui, Y.; Narukawa, N.; Shiroshita, T.; Miya, H.; Sato, R.; Tokutake, S.; Tanaka, Y.; Onaka, M. Synthesis of N-unprotected diaryl ketimines and alkyl ketimines from ketones and ammonia using porous solid acids with analysis of their adsorption behavior. *Bull. Chem. Soc. Japan* **2023**, *96*, 555-567.

[9] Pintér, A.; Haberhauer, G.; Hyla-Kryspin, I.; Grimme, S. Configurationally stable propellar-like triarylphosphine and triarylphosphine oxide. *Chem. Commun*. **2007**, 3711-3713.

[10] Tran, C. C.; Kawagushi, S.-i.; Kabitei, Y.; Matsubara, H.; Tran, D. P.; Kodama, S.; Nomoto, A.; Ogawa, A. Palladium-catalyzed diarylation of isocyanides with tetraarylleads for the selective synthesis of imines and α-diimines. *J. Org. Chem*. **2019**, *84*, 11741-11751.

[11] Crochet, E.; Anthore-Dalion, L.; Cantat, T. Alkyl formats as transfer hydroalkylation reagents and their use in the catalytic conversion of imines to alkylamines. *Angew. Chem. Int. Ed*. **2023**, *62*, e202214069.

Section S3.3. Differential scanning calorimetry (DSC) analysis of polymers. All polymer samples were prepared for DSC analysis by sealing about 4 mg in an aluminum crimped pan. The reference sample was an empty crimped pan of similar size. The thermal program for analysis was as follows:

Heating: The process initiated at room temperature and steadily progressed to 200 ℃ at a rate of 10 ℃ per minute.

Cooling: Subsequently, the sample was cooled from 200 ℃ to 0 ℃ at a rate of 10 ℃ per minute.

Reheating: Finally, the sample was reheated from 0 ℃ to 200 ℃ at a rate of 10 ℃ per minute.

The glass transition temperatures (T_g) featured in the manuscript were determined from the heating scan and were reported as the inflection point of the glass transition. The comprehensive results of this analysis are presented and compared in Figures S3.15–18 and Table S3.1. It is essential to note that the analysis encompasses the data obtained from both the heating and cooling scans.

Glass transition temperatures (T_g) reported in the manuscript were derived from the reheating scan and cooling scan and reported as the inflection point of the glass transition feature. The data from this analysis are reported and compared in Figures S3.12–15 and in Table S3.1. They include the reheating and cooling scans only. The following samples were used for analysis: amino-polystyrene **1** (Mn = 1.36*10^4, 0.29% –NH_2 loading), ammonium polystyrene **1**•HCl (M_n = 1.35*10^4, 0.29% –NH_2 loading), unmodified polystyrene **2** (M_n = 1.32*10^4), and iminyl polystyrene **3** (M_n = 1.30*10^4, 0.29% –NH_2 loading).

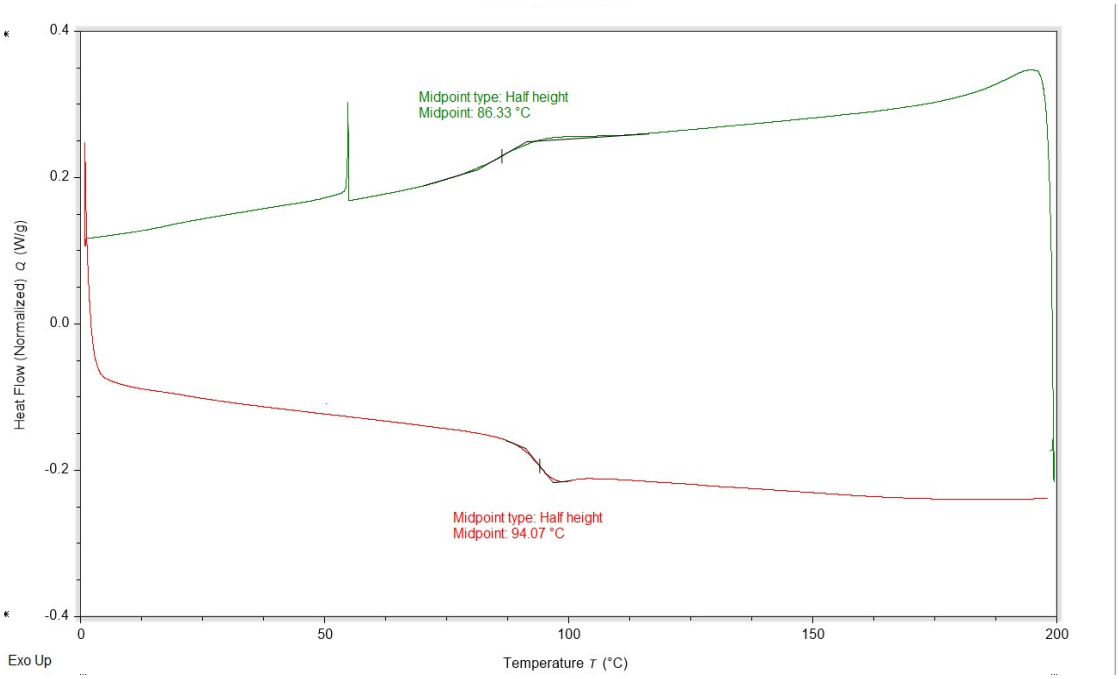


Figure S3.15. DSC analysis of polystyrene (**2**).

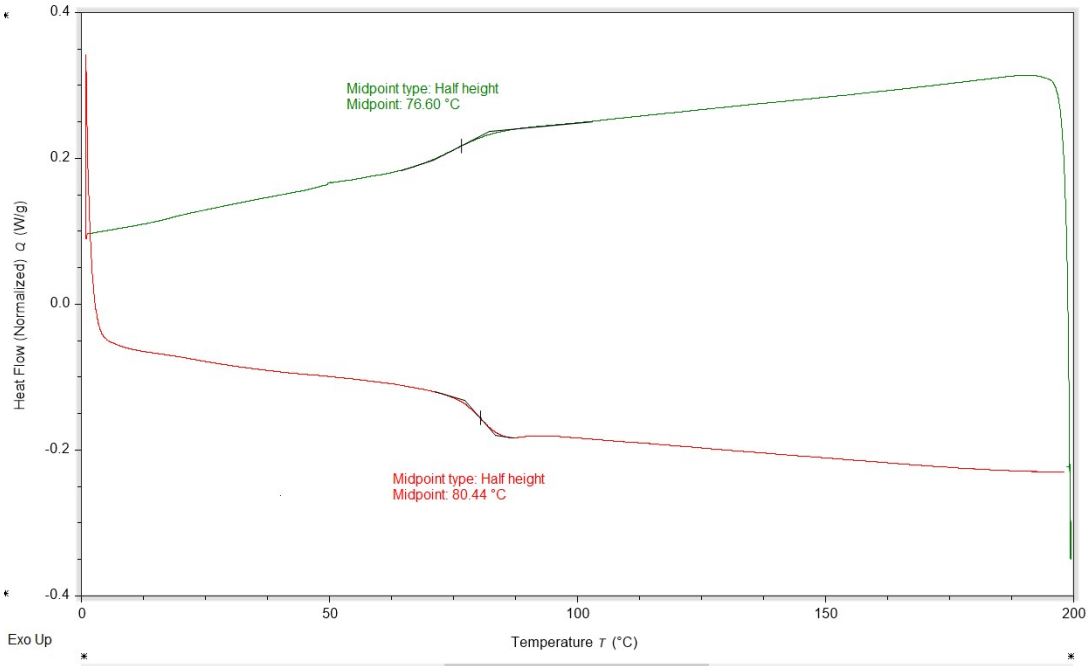


Figure S3.16. DSC analysis of iminated polystyrene (**3**).

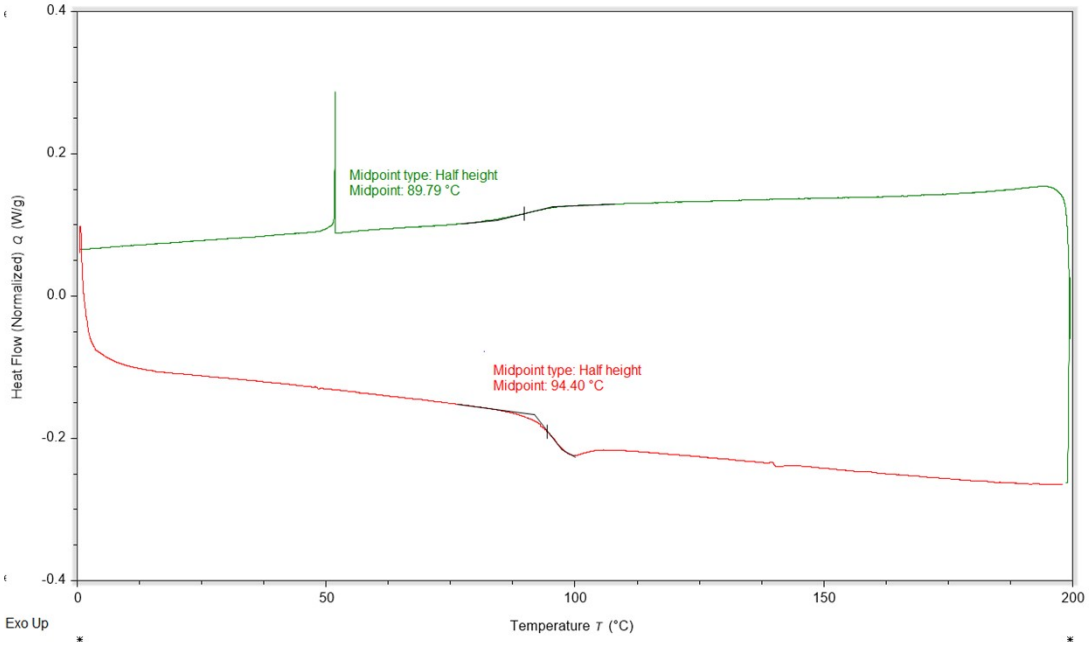


Figure S3.17. DSC analysis of amino-polystyrene, hydrochloride salt (**1**•HCl).

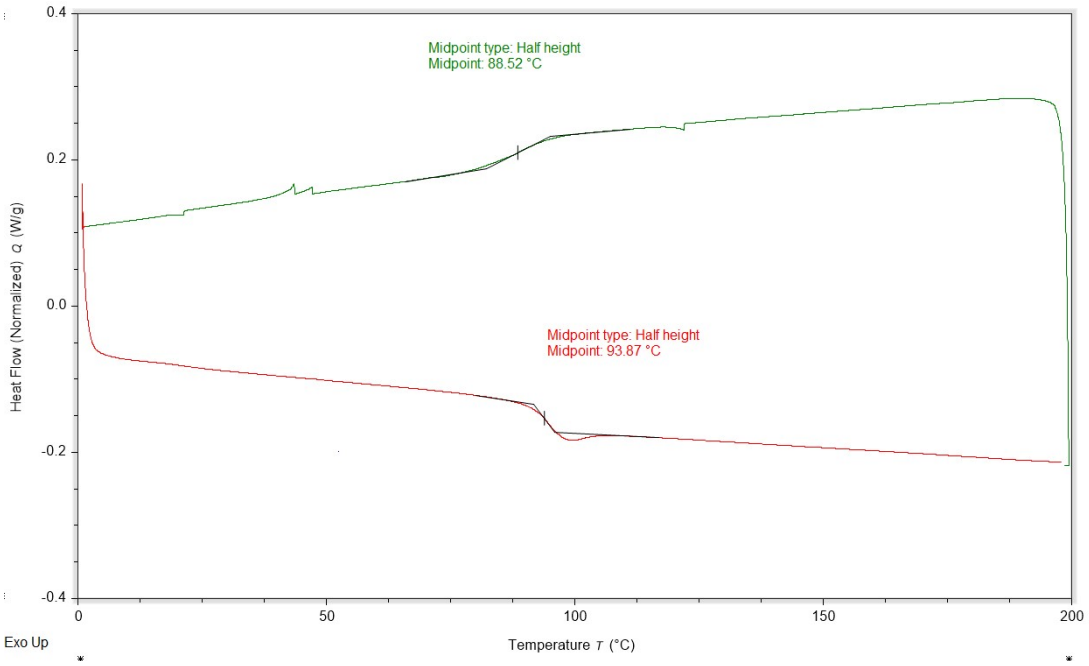


Figure S3.18. DSC analysis of amino-polystyrene (**1**).

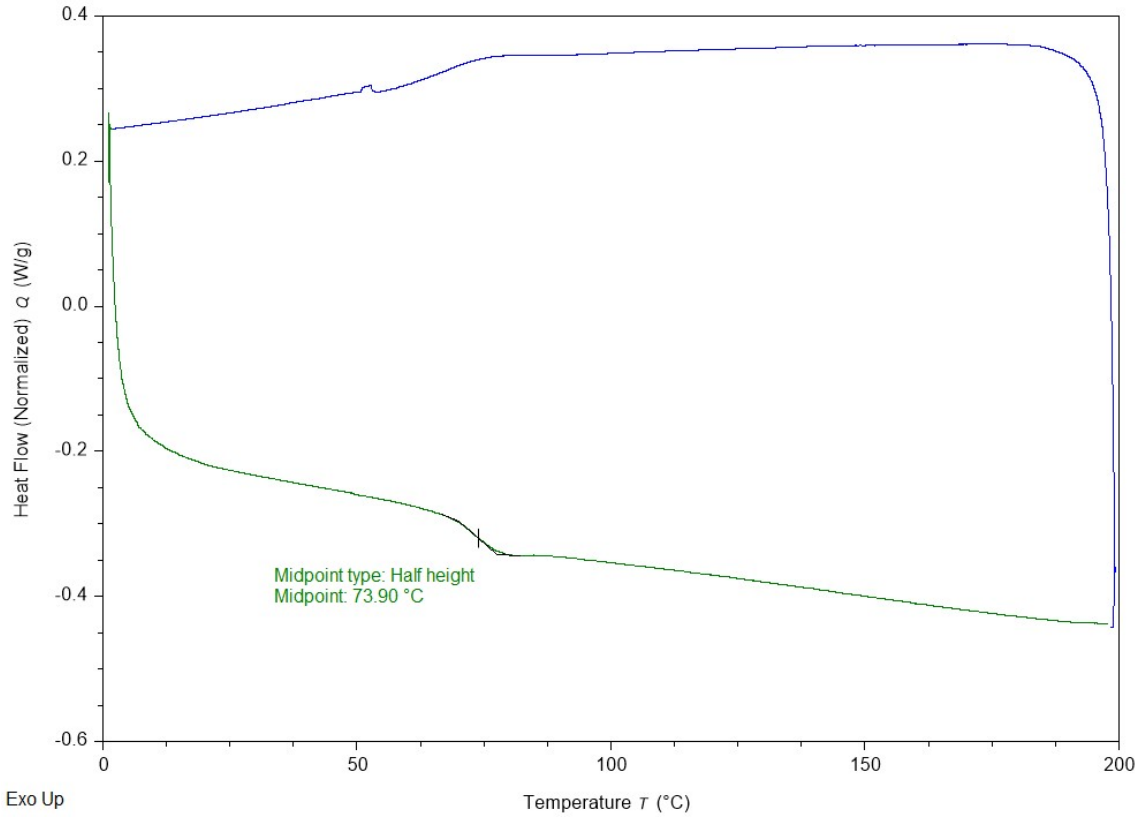


Figure S3.19. DSC analysis of amino-polystyrene (**1**), 0.52% –NH_2 loading, from Table 2 entry 9.

Table S3.1. Glass transition temperatures of modified polymers.

Sample	T_g, cooling (ºC)	T_g, heating, second-scan (ºC)
Polystyrene (**2**)	94.1	86.33
Iminated polystyrene (**3**)	80.4	76.6
Amino-polystyrene, hydrochloride (**1**•HCl)	94.40	89.79
Amino-polystyrene (**1**)	93.9	88.5

Section S3.4. Thermogravimetric analysis (TGA) of polymer samples. TGA analysis was performed by scanning from 30–600°C at a continuous scan rate of 10°C/minute. The data from this analysis are reported and compared in Figures S3.16–17. The following samples were used for analysis: amino-polystyrene **1** (M_n = 1.36*10^4, 0.29% –

NH_2 loading), ammonium polystyrene **1**•HCl (M_n = 1.35*10^4, 0.29% –NH_2 loading), unmodified polystyrene **2** (M_n = 1.32*10^4), and iminyl polystyrene **3** (M_n = 1.30*10^4, 0.29% –NH_2 loading).

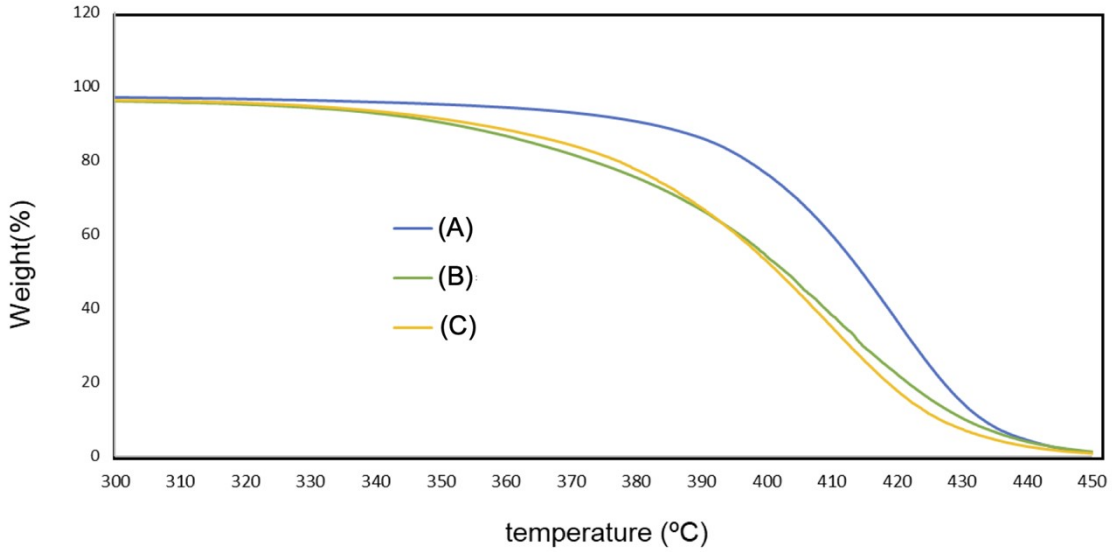


Figure S3.20. TGA comparison of A) unmodified polystyrene (**2**), B) amino-polystyrene **1**, and C) amino-polystyrene hydrochloride **1**•HCl.

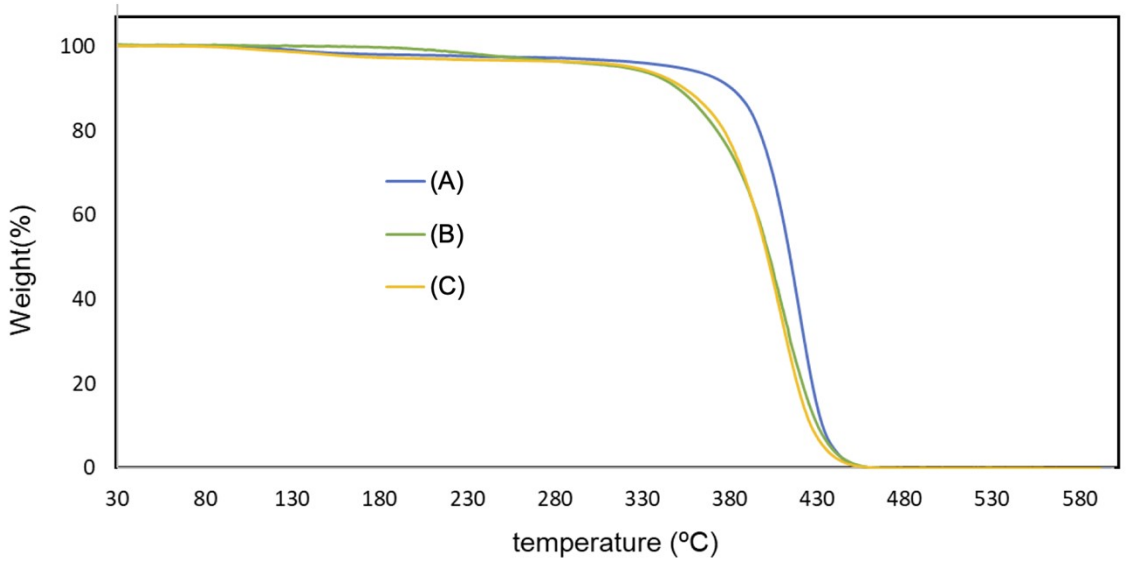
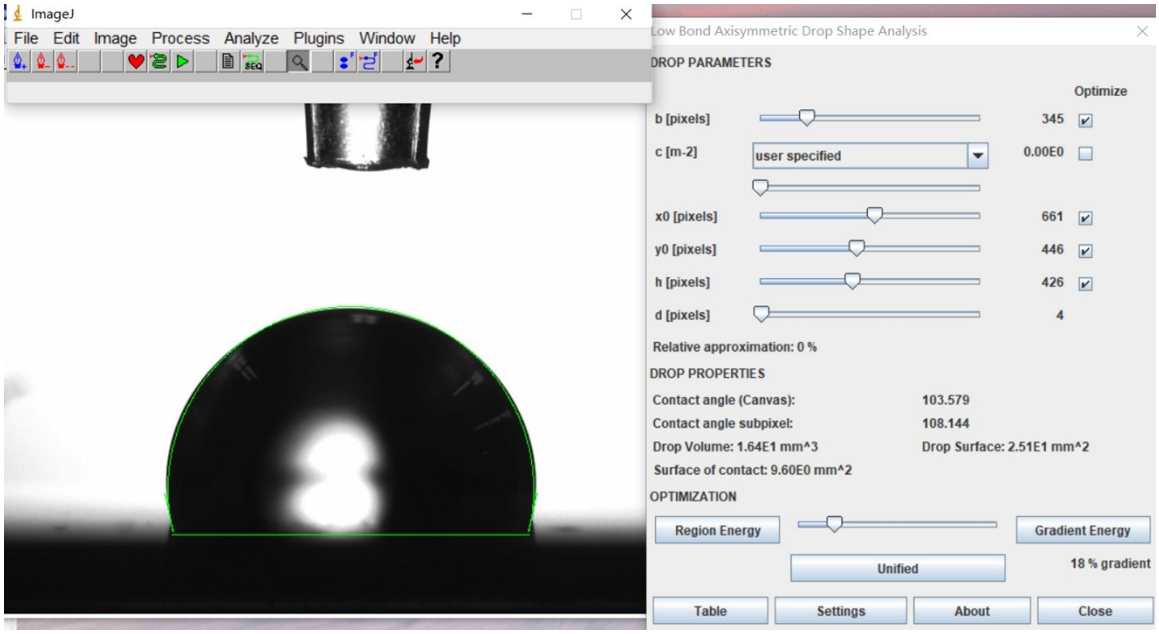
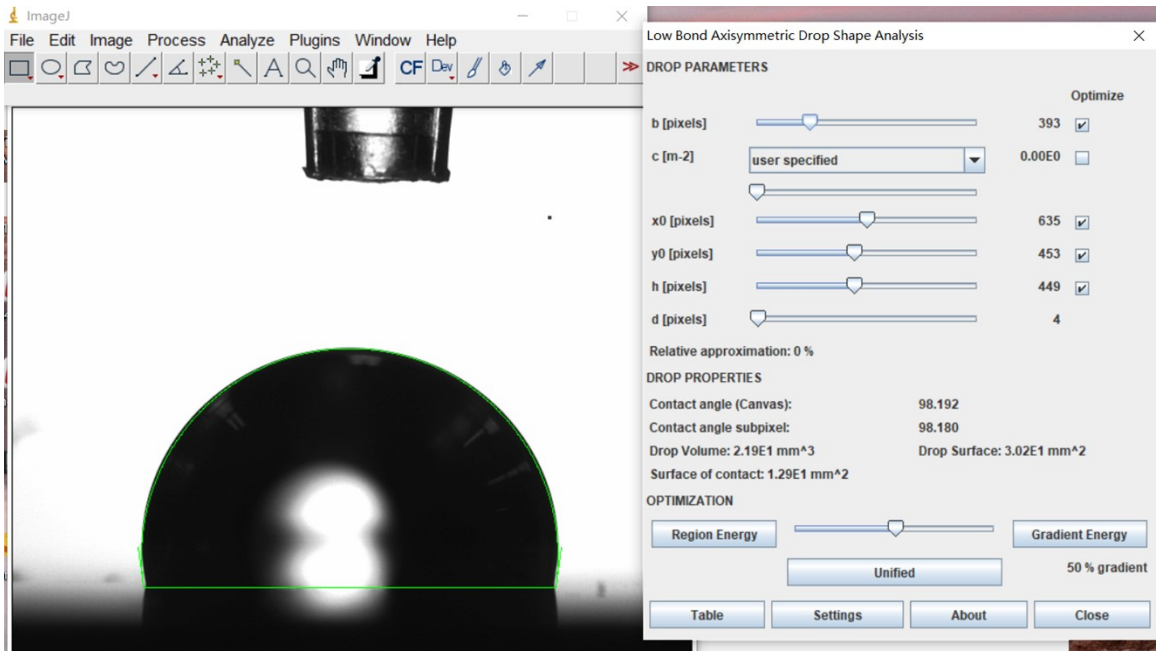


Figure S3.21. TGA comparison of A) unmodified polystyrene (**2**), B) imino-polystyrene (**3**), and C) amino-polystyrene hydrochloride **1**•HCl.

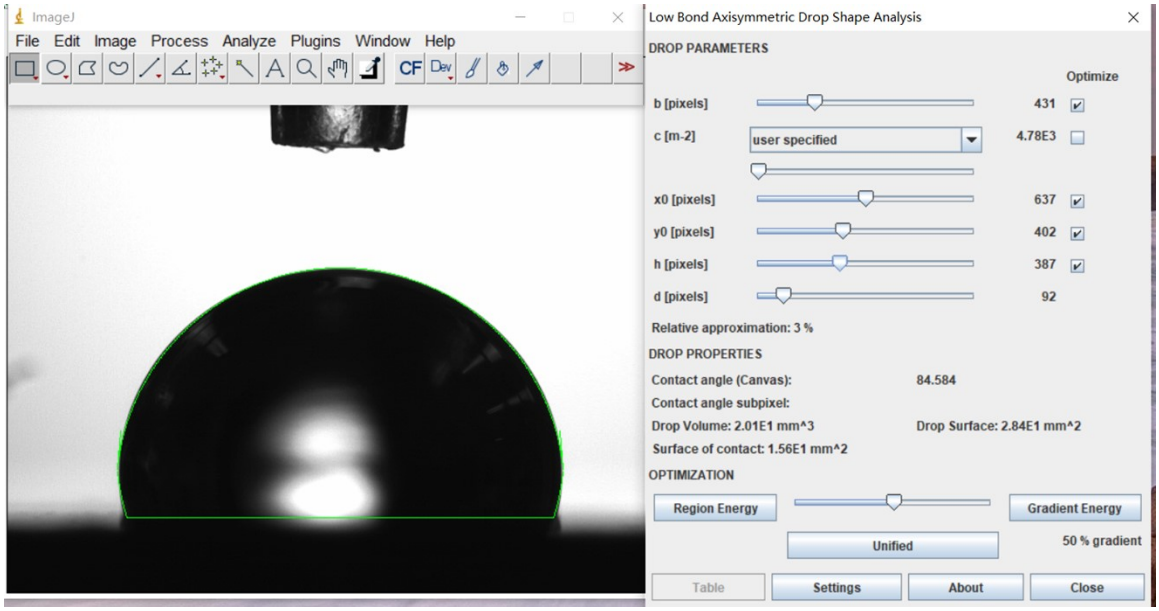
Section S3.5. Sessile drop test. To control for variation in drop size and surface morphology, the analysis was performed three times for each sample. The test sample was prepared as follows: 0.2 g of the polymer was dissolved in 1 mL of dichloromethane. The resulting solution was carefully applied to a smooth plate. Once the solvent had evaporated, a solid polymer film was formed and subsequently subjected to a Sessile Drop Test. To obtain the contact angle picture, 20 µL of water was immediately dropped onto the polymer surface. Pictures of the droplets used and their analysis are reported in Figures S3.18. Water contact angles, their average, and their standard deviation are reported in Table S3.2. The following samples were used for analysis: amino-polystyrene **1** (M_n = 1.36*10^4, 0.29% –NH_2 loading), ammonium polystyrene **1**•HCl (M_n = 1.35*10^4, 0.29% –NH_2 loading), unmodified polystyrene **2** (M_n = 1.32*10^4), iminyl polystyrene **3** (M_n = 1.30*10^4, 0.29% –NH_2 loading), and amino-polystyrene **1** (M_n = 1.36*10^4, 0.52% –NH_2 loading).



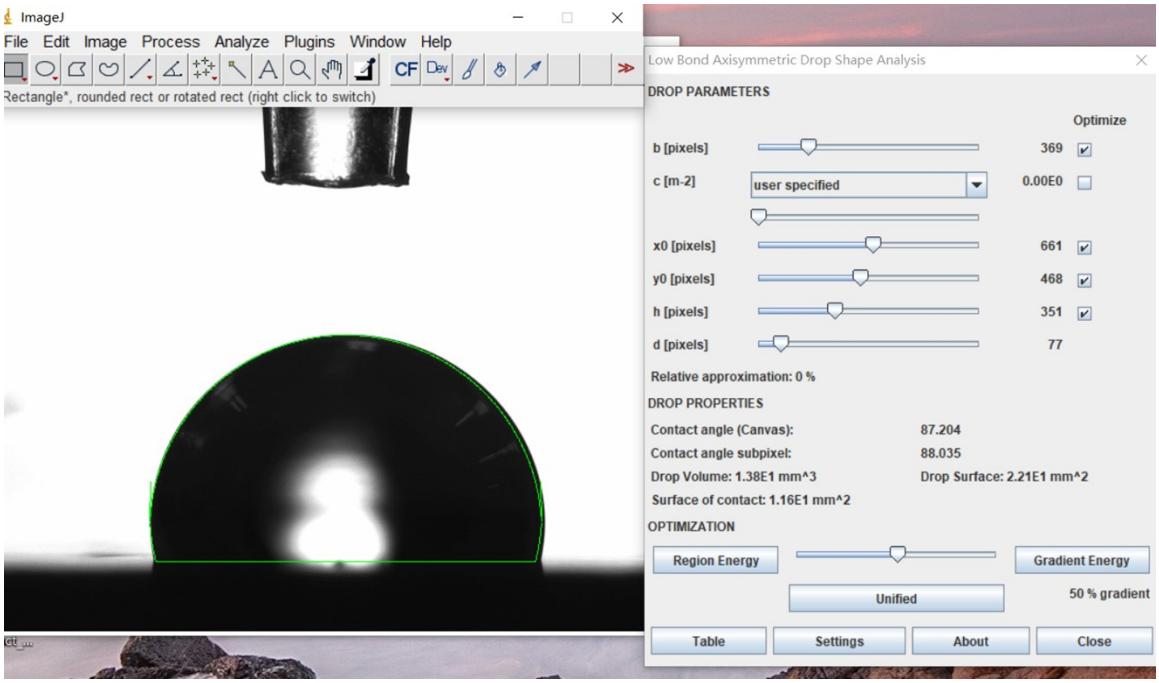
A. polystyrene (**2**), (0.29% –NH_2 loading)



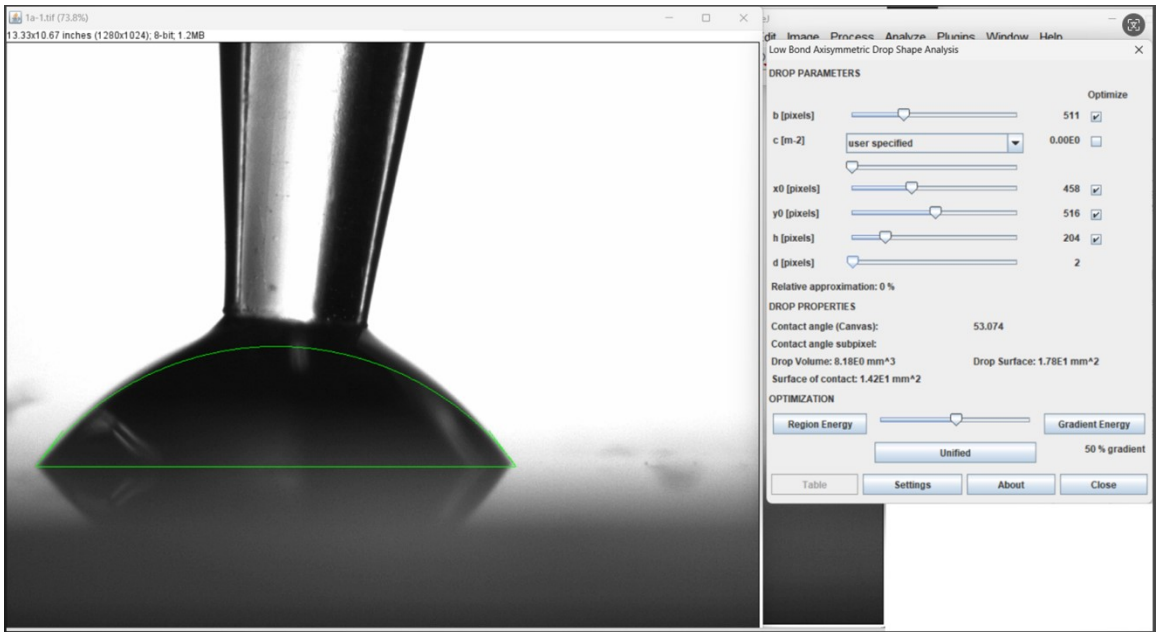
B. iminated polystyrene (**3**), (0.29% –NH_2 loading)



C. amino-polystyrene hydrochloride salt (**1**•HCl), (0.29% –NH_2 loading)



D. amino-polystyrene (**1**), (0.29% $-NH_2$ loading)



(E) amino-polystyrene **1**, 0.52% $-NH_2$ loading, from Table 2 entry 9.

Figure S3.22. Drop used for water contact angle analysis, for A) polystyrene (**2**), B) iminated polystyrene (**3**), C) amino-polystyrene hydrochloride salt (**1**•HCl), D) amino-polystyrene (**1**). (E) amino-polystyrene **1** from Table 2, entry 9.

Table S3.2. Water contact angles measured for modified polystyrenes by the Sessile drop test.

Sample	Contact angle (º) individual measurements	Contact angle (º) average	Standard deviation
Polystyrene (**2**)	108.144, 109.098, 105.618	107.620	1.798
Iminated polystyrene (**3**)	98.180, 97.216, 97.115	97.503	0.588
Amino-polystyrene, hydrochloride (**1**•HCl)	83.984, 84.794, 84.584	84.454	0.343
Amino-polystyrene (**1**)	88.035, 86.349, 87.495	87.293	0.861
Amino polystyrene (0.52% $-NH_2$) (Table 2, entry 9)	53.074, 51.586, 47.171	50.61	2.51

Section S3.6. Fluorimetry analysis.

Section S2.6.1. Experimental details. We analyzed several samples by fluorimetry in the wavelength range 250-600 nm, using a 1 cm cuvette, and an applied wavelength of 320 nm. All samples were analyzed as 1 mg/mL solutions in CH_2Cl_2. The following samples were used for analysis: amino-polystyrene **1** (M_n = 1.36*10^4, 0.29% –NH_2 loading), unmodified polystyrene **2** (M_n = 1.32*10^4), Dansylamide polystyrene **8** (from Section S2.7.1), Dansyl chloride treated polystyrene **2** (from Section S2.7.2), model Dansylamide **S1** (from Section S4.2), and benzophenone imine **4**. The data for these spectra are reported and compared in Figures S3.19–21.

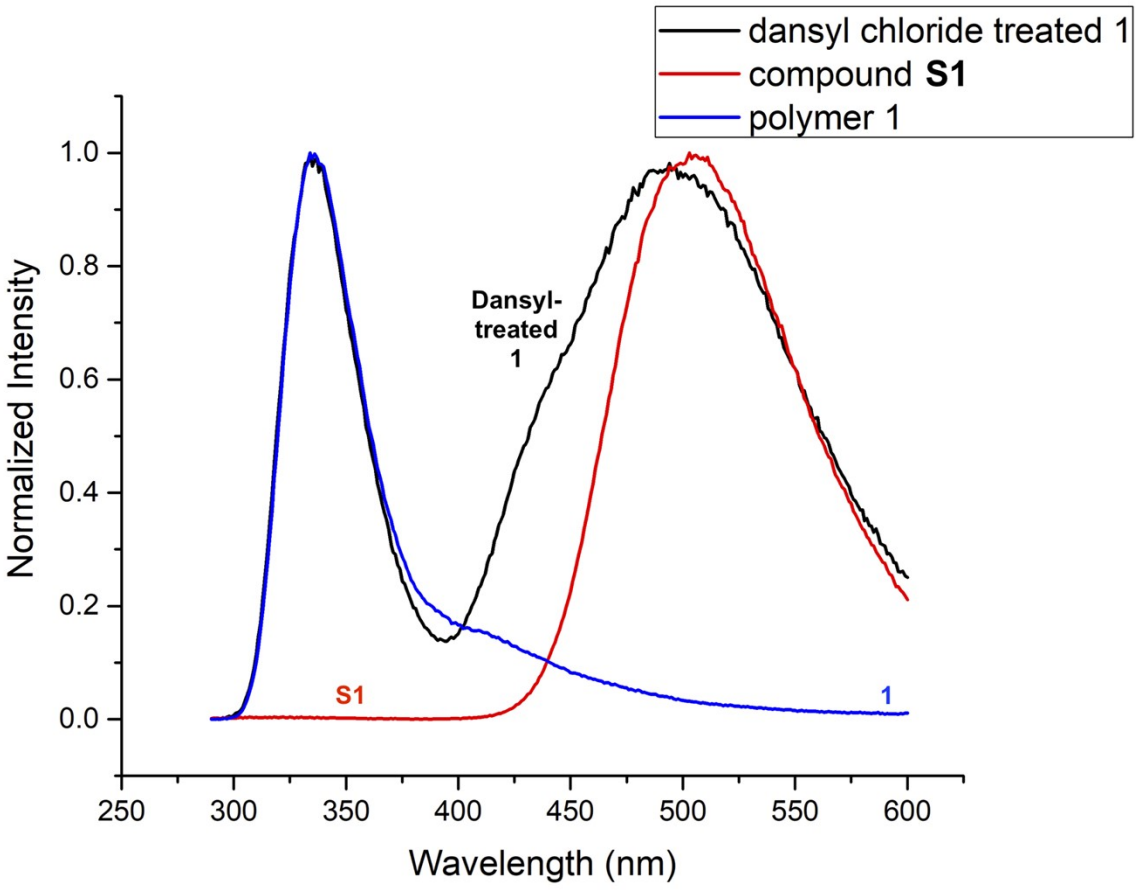


Figure S3.23. Fluorescence spectrum of amino-polystyrene **1**, its Dansylamide **8**, and the model compound Dansylamide **S1**.

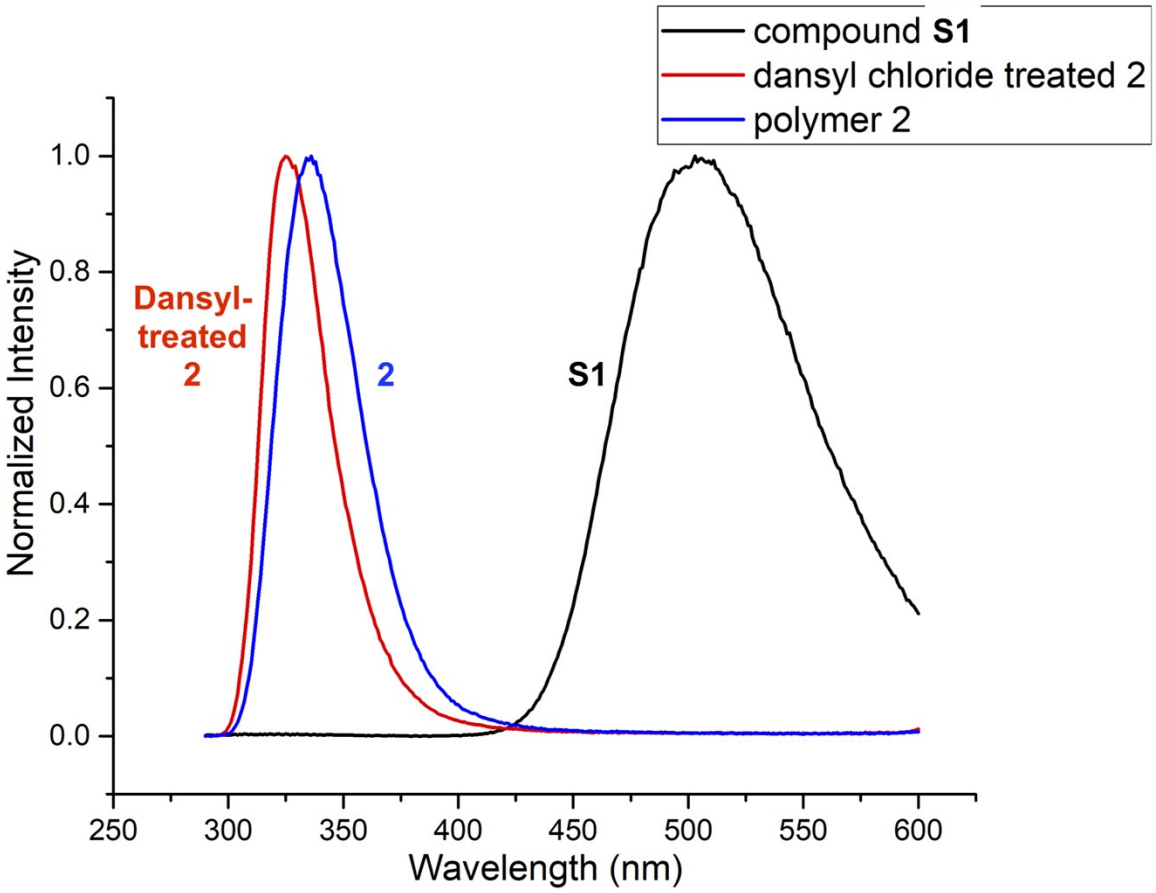


Figure S3.24. Fluorescence spectrum for unmodified polystyrene (**2**), its Dansyl chloride-treated control, and model Dansylamide **S1**.

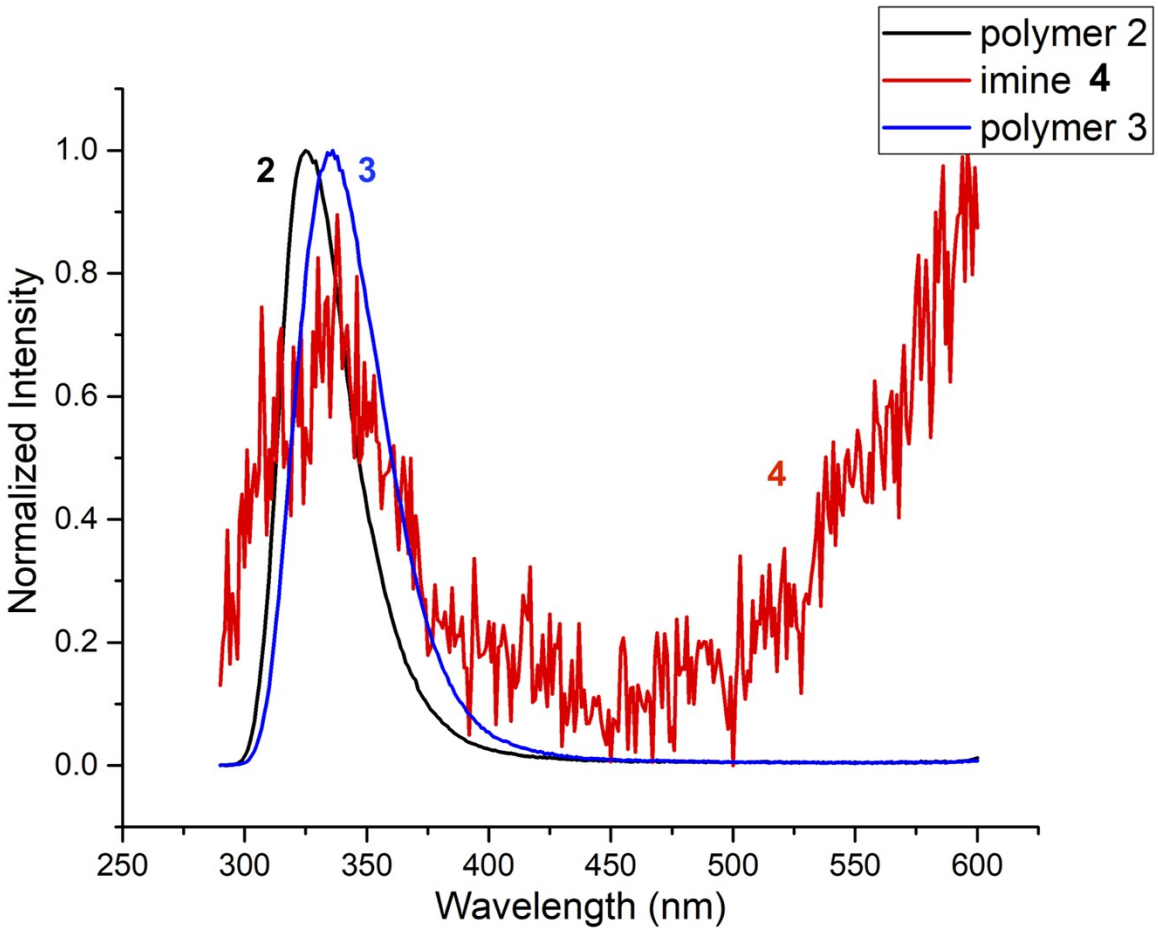


Figure S3.25. Fluorescence spectra of iminated polystyrene (**3**), unmodified polystyrene (**2**), and benzophenone imine (**4**).

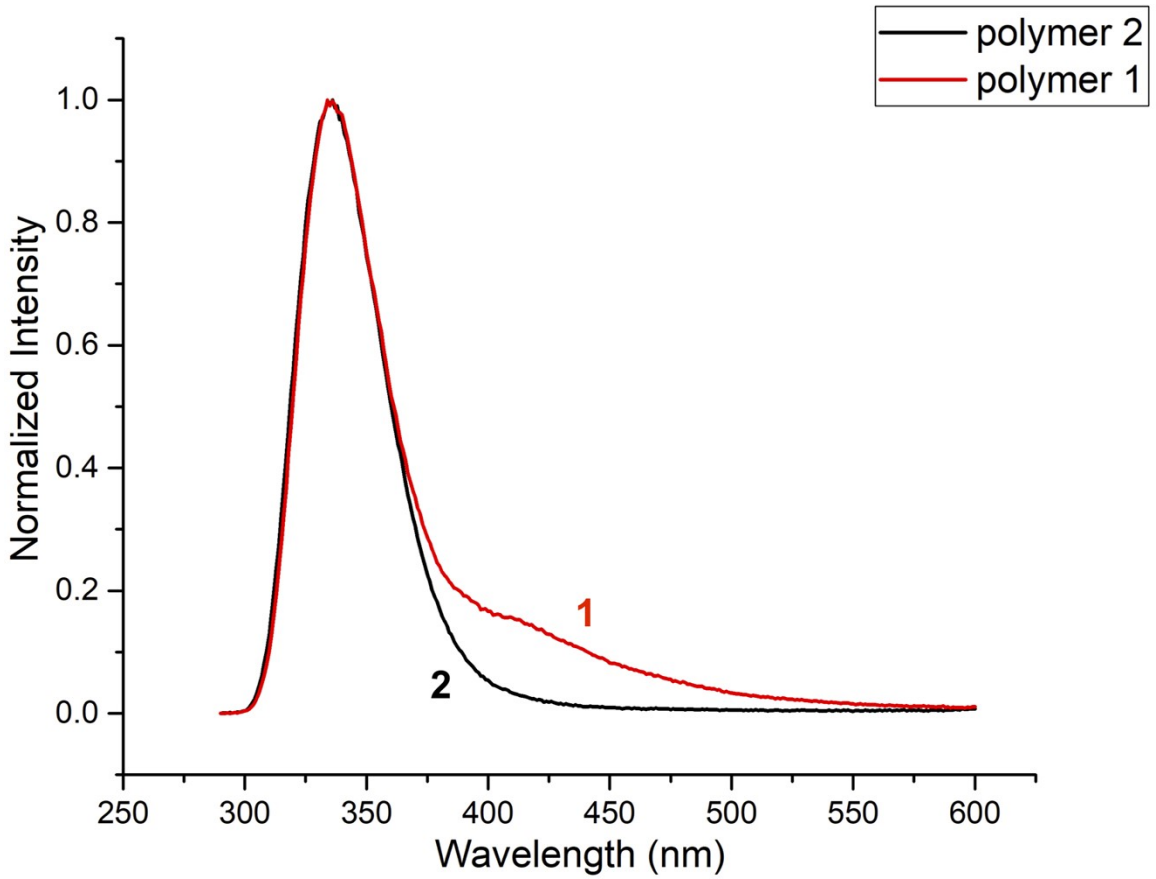


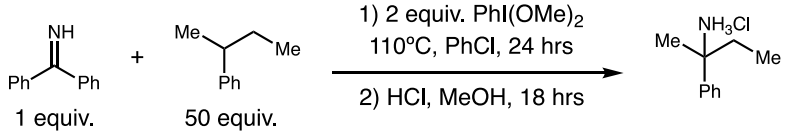
Figure S3.26. Fluorescence comparison of amino-polystyrene (**1**) to unmodified polystyrene (**2**).

S3.6.2. Analysis of fluorescence spectra. Dansyl amide **S1** (prepared with cumylamine, Section S4) shows strong fluorescence with a single peak at λ = 510 nm, while aminated polystyrene **1** has one fluorescence peak at λ = 335 nm (Figure S3.19). The polymer produced by Dansyl chloride treatment of **1** had two fluorescence peaks (λ = 335 nm, 505 nm) close to those for **1** and for **S1** (Figure S3.23), indicating incorporation of the Dansyl sulfonamide functional group into the polymer. By contrast, treatment of unmodified polystyrene **2** with Dansyl chloride results in a polymer that only has a fluorescence peak at λ = 335 nm only (Figure S3.24), indicating that the new fluorescence peak for Dansyl-treated **1** results from reaction with the amino group. Nevertheless, imine **4** does not show significant fluorescence at any wavelength (Figure S3.25). Aminated polystyrene **1** has a

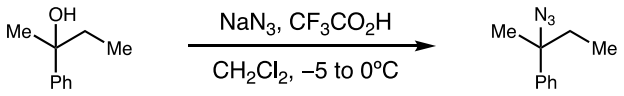
similar fluorescence maximum to unmodified polystyrene (**2**), although **1** appears to have an additional small fluorescence that **2** lacks (Figure S3.26).

S4. Small Molecule Study.

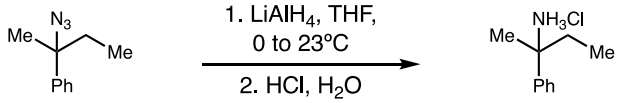
Section S4.1. 2-phenylbutan-2-amine hydrochloride as a model for amino polystyrene 1.



Section S4.2.1. 2-phenylbutan-2-amine hydrochloride (**7**) *via C–H imination of s-butylbenzene as a model for the imination of* **2**. Under nearly the same conditions as the imination of **2**, a solution of (2-butyl)benzene (1.34 g, 10 mmol, 50.0 equiv.), $PhI(OMe)_2$ (0.106 g, 0.398 mmol, 2.0 equiv.), benzophenone imine (**4**, 0.036 g, 0.199 mmol, 1.0 equiv.), and chlorobenzene (2 mL) were heated at 110 ºC in a sealed tube under nitrogen for 24 hours. Next, the cooled reaction was transferred to a 25 mL flask, treated with a solution prepared from aqueous hydrochloric acid (3 M, 4 mL) and methanol (2 mL), and then stirred vigorously overnight. The crude mixture was partitioned between hexanes (4 mL) and aqueous HCl (1.5 M, 6 mL) in a separatory funnel. The aqueous layer was washed twice with hexanes (3 x 10 mL), and the combined organic phases were extracted with aqueous HCl (1.5 M, 3 mL) and followed by C18 reverse phase chromatography. The combined aqueous fractions were then concentrated under vacuum to get the product as a white solid (33 mg, 0.00178 mol, 89% yield). The product obtained this way was sufficiently pure to analyze by NMR and MS, but contained significant impurities. We were unable to purify the product further. NMR (D_2O, 1,4-dioxane as standard, δ in ppm): ^1H (400 MHz) 7.46 (m, 5H), 2.03 (m, 2H), 1.70 (s, 3H), 0.75 (t, 3H); $^{13}C\{^1H\}$ (100 MHz) δ 140.31 (s), 129.68 (s), 129.02 (s), 125.69 (s), 60.29 (s), 34.00 (s), 24.42 (s), 8.04(s). HRMS (ESI/TOF) m/z calculated for $C_{10}H_{16}N$ ($[M]^+$) 150.1283, found 150.1287, difference 2.66 ppm. To positively confirm the structure of this product and to provide a publishable NMR, we prepared this compound in greater purity by a different method (Section S4.1.2).



Section S4.1.2. Synthesis of 2-phenylbutan-2-amine hydrochloride (**7**) *by a different route via 2-phenylbutan-2-ol*. In anhydrous CH_2Cl_2 (15 mL), 2-phenylbutan-2-ol (1.5 g, 10 mmol, 1 equiv.) was dissolved. NaN_3 (1.43 g, 22 mmol, 2.2 equiv.) was added under nitrogen at room temperature, and the mixture was cooled to -5 °C. A 1:2 (v/v) mixture of trifluoroacetic acid (TFA): CH_2Cl_2 (6.4 mL, 84 mmol, 8.4 equiv. of TFA) was dropwise added over 15 min at -5 °C. After stirring at 0 °C for 1-2 h, the reaction mixture was quenched with distilled H_2O (5 mL) and a 1:1 mixture of 14% aqueous NH_4OH solution (5.0 mL) and water. After 30 min, the mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude azide was directly used for the next step.



A solution of the crude azide (1.75 g, 10 mmol, 1.0 equiv.) and anhydrous THF (10 mL) was treated with $LiAlH_4$ (2 M solution in THF, 5.25 mL, 10.5 mmol, 1.05 equiv.) at 0 °C under nitrogen, and then stirred at room temperature for 4 hours. The reaction was then quenched by the addition of 1.0 M aqueous NaOH, followed by partitioning between Et_2O and 1.0 M aqueous HCl. After treatment with 28% aqueous NH_4OH, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic solution was concentrated under vacuum and purified by flash chromatography to give the free amine. The amine was then dissolved in 1M HCl (5 mL). This aqueous solution was rinsed with hexanes (3 x 20 mL) and then concentrated under vacuum to obtain the ammonium chloride salt as a white solid (1.62 g, 8.75 mmol, 88% yield over two steps). NMR (D_2O, δ in ppm): ^1H (400 MHz) 7.46 (m, 5H), 2.03 (m, 2H), 1.70 (s, 3H), 0.75 (t, 3H); $^{13}C\{^1H\}$ (100 MHz) δ 140.31 (s), 129.68 (s), 129.02 (s), 125.69 (s), 60.29 (s), 34.00 (s), 24.42 (s), 8.04(s). These NMR data are consistent with what we obtained in Section S4.1.1, confirming the identity of our product. These NMR

data are also consistent with those reported for this compound. NMR spectra obtained from this sample are reported below.

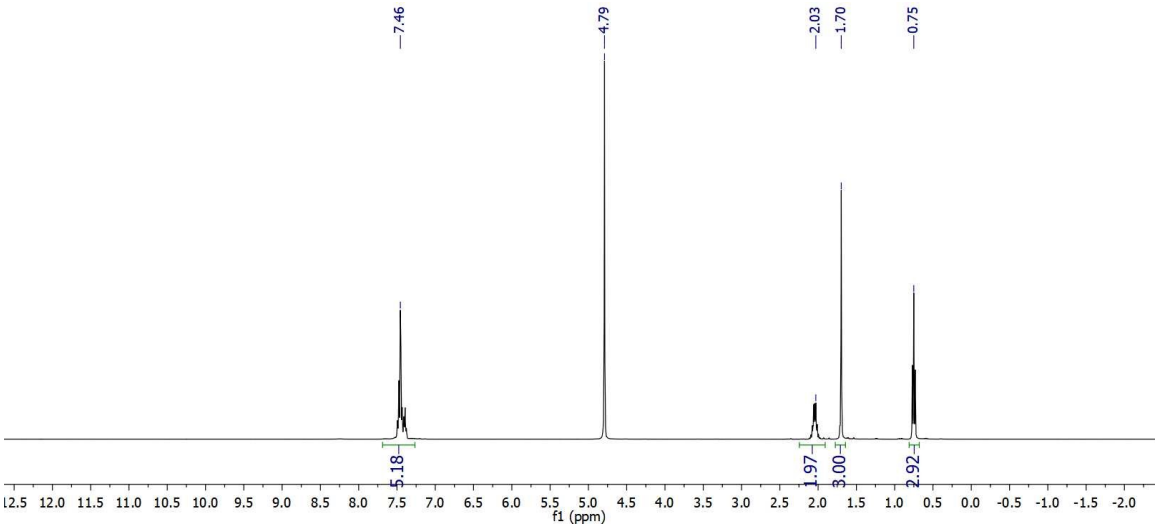


Figure S4.1. ^{1}H-NMR (400 MHz, D_2O) of **7**

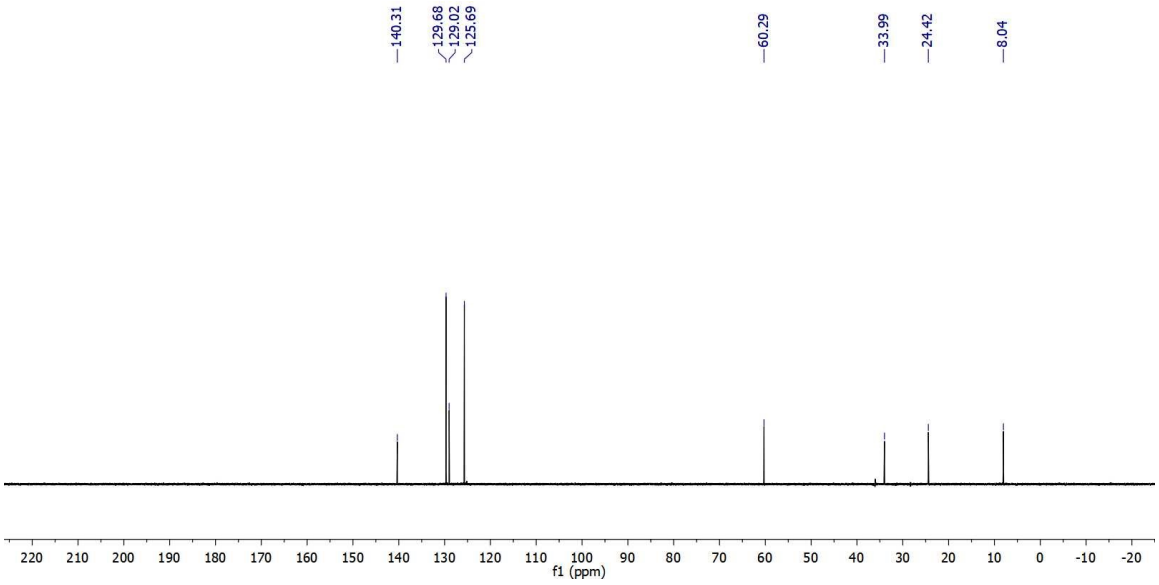
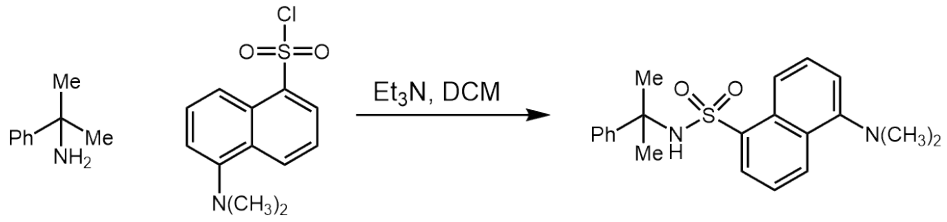


Figure S4.2. ^{13}C-NMR (100 MHz, D_2O) of **7**.



Section S4.2. 5-(dimethylamino)-N-(2-phenylpropan-2-yl) naphthalene-1-sulfonamide (**S1**). A solution of Dansyl chloride (27 mg, 0.1 mmol, 1.0 equiv.), cumylamine (14 mg, 0.1 mmol, 1.0 equiv.), triethylamine (12 mg, 0.12 mmol, 1.2 equiv.), and CH_2Cl_2 (1 mL) was stirred at room temperature for 18 hours. The reaction was then transferred to a separatory funnel, where it was rinsed with water (3 x 5 mL). The organic solution was then dried with $MgSO_4$, filtered, and concentrated under vacuum to a crude oil. The title compound was obtained by flash chromatography (Rf = 0.58, 1:4 ethyl acetate: hexanes; column conditions: gradient of 5% ethyl acetate to 25% ethyl acetate in hexanes) as a yellow solid (32 mg, 0.0869 mmol, 86.9% yield). NMR ($CDCl_3$, δ in ppm): ^1H (400 MHz) δ 8.40 (d, 1H), 8.23 (d, 1H), 7.89 (d, 1H), 7.55 (m, 1H), 7.29 (m, 1H), 7.17 (d, 1H), 7.09 (m, 2H), 7.00 (m, 1H), 6.96 (m, 2H), 2.88 (s, 6H), 1.59 (s, 6H); $^{13}C\{^1H\}$ (100 MHz) δ 151.94 (s), 144.34, 137.21, 129.92, 129.72, 129.45, 128.14, 127.84, 127.08, 125.55, 123.34, 119.90, 119.05, 114.96, 58.91, 45.55, 29.93. HRMS (ESI/TOF) m/z calculated for $C_{21}H_{25}N_2O_2S([M]^+)$ 369.1637, found 369.1637, difference 0.0 ppm.

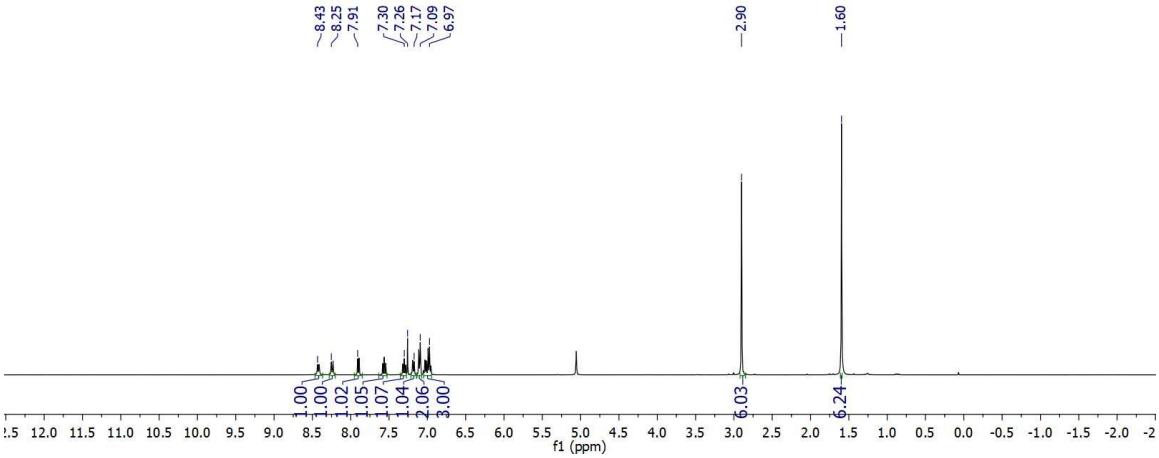


Figure S4.3. ^1H-NMR (400 MHz, $CDCl_3$) of **S1**

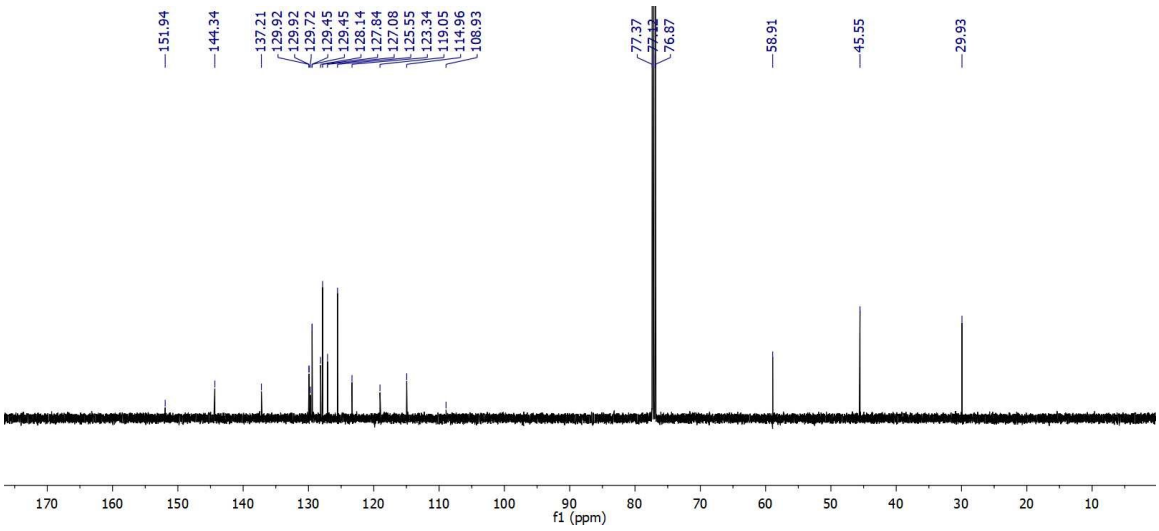
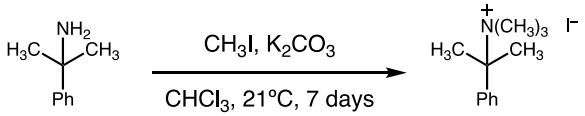


Figure S4.4. ^{13}C-NMR (100 MHz, $CDCl_3$) of **S2**.



***N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium iodide**. Cumylamine (340 mg, 2.51 mmol, 1.0 equiv.) was dissolved in $CHCl_3$ (10 mL) under a nitrogen atmosphere. K_2CO_3 (380 mg, 2.75 mmol, 1.10 equiv.) was added portion-wise at 0 °C. The reaction mixture was stirred, and methyl iodide (1.24 g, 8.74 mmol, 3.48 equiv.) was added dropwise. The reaction mixture was then warmed to room temperature and stirred in the dark (covered with aluminum foil) for one week. Afterward, the suspension was diluted with $CHCl_3$ (10 mL) and filtered. The filtrate was concentrated under vacuum, resulting in the crude product. The light-yellow product was recrystallized by dissolving in boiling CH_2Cl_2 and hexanes, then storing in a freezer at –20°C. The resulting product was a white solid (610 mg, 2.0 mmol, 82 % yield). NMR ($CDCl_3$, δ in ppm): ^{1}H (400 MHz): δ 7.70-7.61 (m, 2H), 7.52-7.44 (m, 3H), 3.32 (s, 9H), 2.10 (s, 6H). ^{13}C (100 MHz): δ 134.2 (s), 130.4 (s), 129.3 (s), 129.0 (s), 75.7 (s), 50.4 (s), 23.9 (s). HRMS (ESI/TOF) m/z calculated for $C_{12}H_{20}N([M]^+)$ 178.15903, found 178.1592, difference 1.1 ppm.

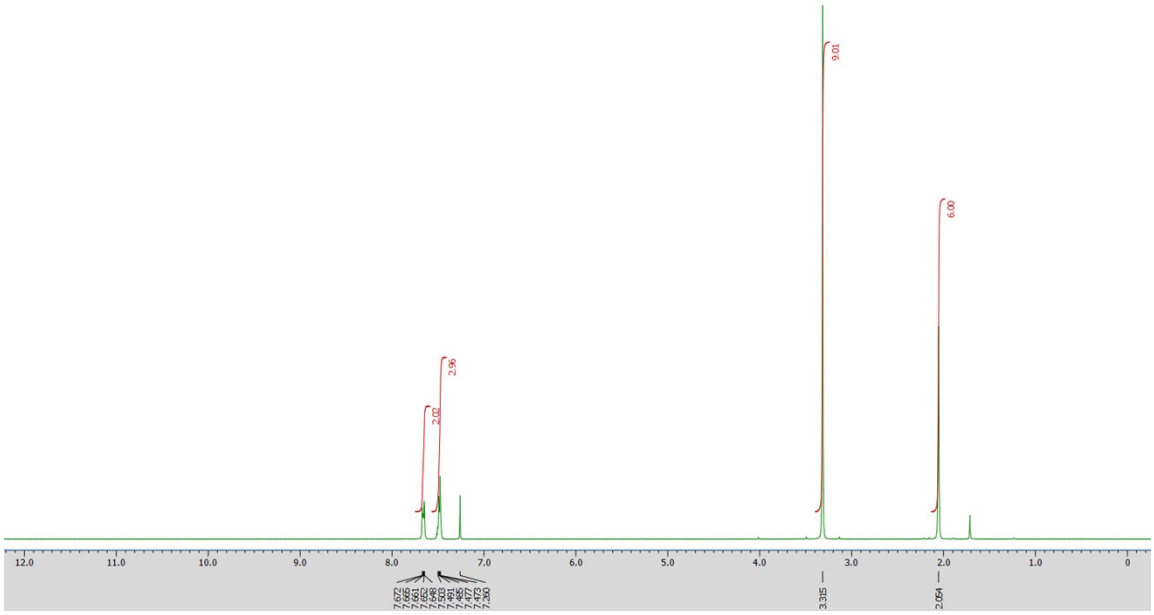


Figure S4.5. ^{1}H-NMR ($CDCl_3$, 400 MHz) analysis of *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium iodide.

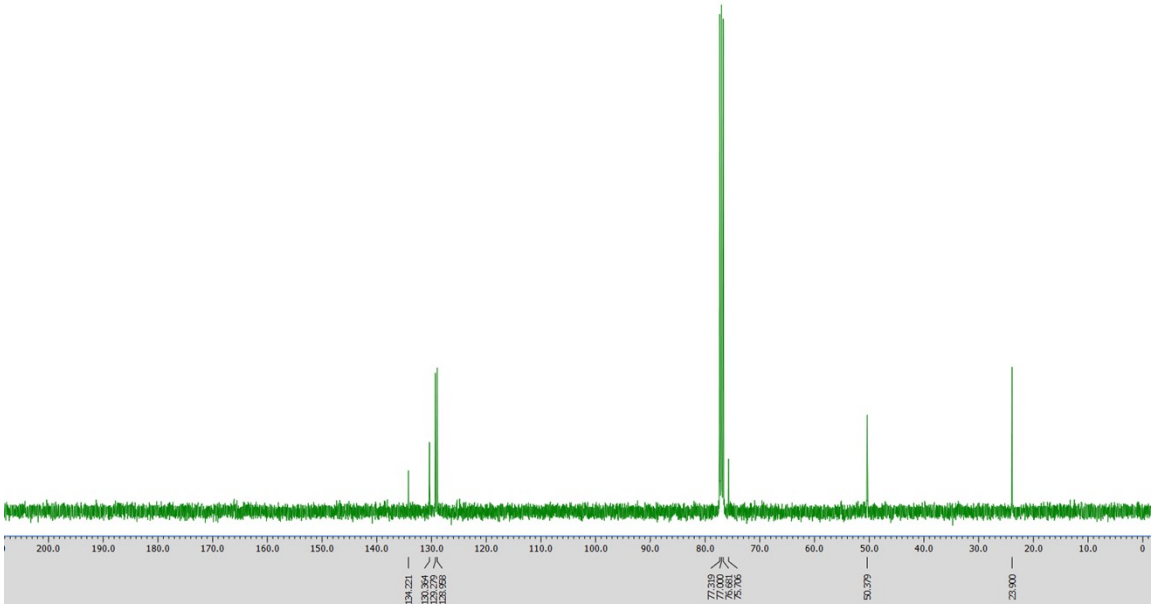
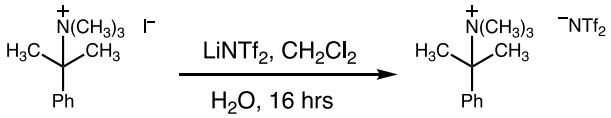


Figure S4.6. ^{13}C-NMR ($CDCl_3$, 100 MHz) analysis of *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium iodide.



***N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium *bis*(trifluoromethane)sulfonyl)amide salt** (**S2**). *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium iodide (50 mg, 0.16 mmol, 1 equiv.) and $LiNTf_2$ (66 mg, 0.23 mmol, 1.4 equiv.) were added to a 6-dram vial equipped with stir bar in a nitrogen glovebox. The vial was capped with a septum cap and then transferred outside the glove box. Water (1 mL) and CH_2Cl_2 (1 mL) were added to the vial via syringe. The reaction mixture was stirred at room temperature for 16 hours. The resultant mixture was extracted with deionized water three times. The organic fractions were combined and dried with Na_2SO_4. The solution was concentrated under reduced pressure, giving the product as a pale yellow solid (46 mg, 0.15 mmol, 93% yield). NMR ($CDCl_3$, δ in 7.26 ppm): ^{1}H (400 MHz): δ 7.66-7.59 (m, 2 H), 7.51-7.44 (m 3 H), 2.98 (s, 9 H), 1.95 (s, 6 H). ^{13}C (100 MHz): δ 133.9 (s), 130.7 (s), 129.2 (s), 129.0 (s), 75.4 (s), 49.9 (s), 23.3 (s). ^{19}F-NMR was performed on a mixture of **S2** (46 mg) and 1,3-*bis*(trifluoromethyl)benzene (17.12 mg, 0.08 mmol): ^{19}F (396 MHz): δ -63.0 (s) internal standard, -78.9 (s).

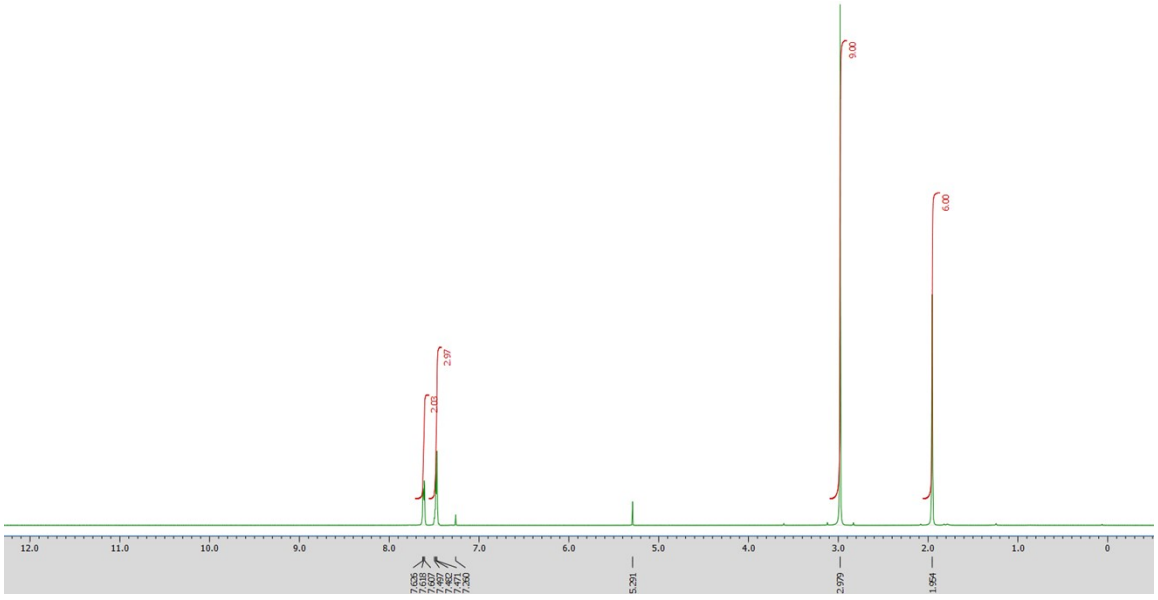


Figure S4.7. ^{1}H-NMR ($CDCl_3$, 400 MHz) analysis of *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium *bis*(trifluoromethanesulfonyl)amide.

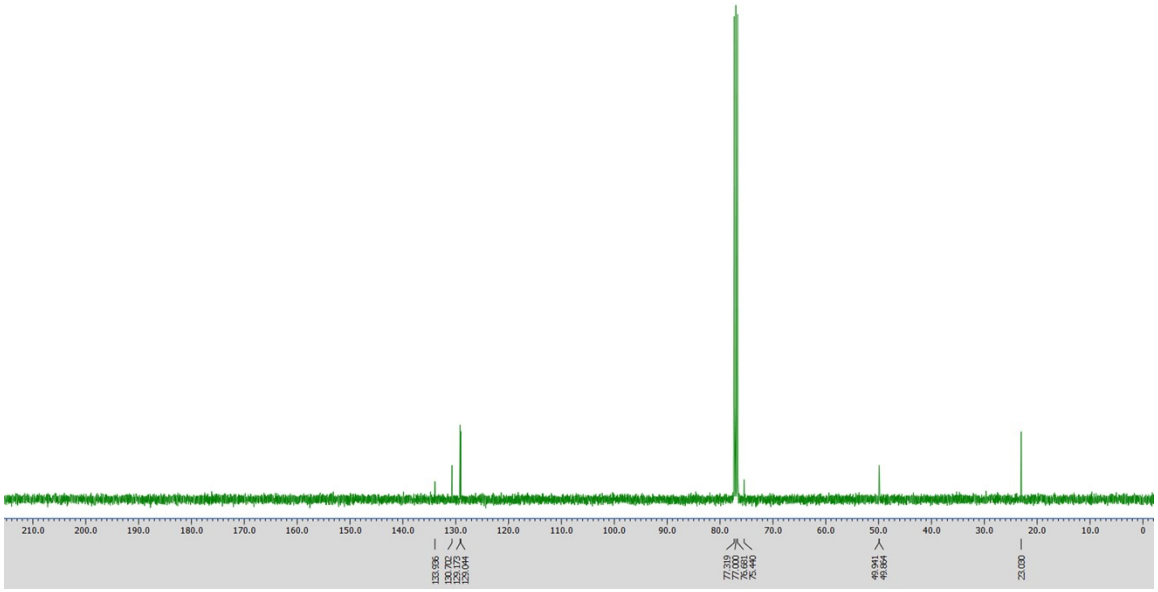


Figure S4.8. ^{13}C-NMR ($CDCl_3$, 100 MHz) analysis of *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium *bis*(trifluoromethanesulfonyl)amide.

Figure 4.9. ^{19}F-NMR (376 MHz, $CDCl_3$) of *N*,*N*,*N*-trimethyl-2-phenylpropan-2-aminium bis(trifluoromethyl)sulfonyl) amide salt (**S2**), with and without 1,3-*bis*(trifluoromethyl)benzene as reference.

S5. Computational Details.

Section S5.1 DFT analysis of the relative bond dissociation energies (Figure 1). All calculations were performed in the gas phase, using temperature = 298.15 K, pressure = 1 atm. A multiplicity of 2 and charge of 0 was assigned for all structures in this section. Geometries for the two radicals PhC•$(CH_3)CH_2CH_3$ (**S5-1**) and PhCH(CH_3)CH•CH_3 (**S5-2**) were all optimized at the level of UB3LYP/6-311G(2d,p). Free energies of formation were then obtained by a single frequency calculation at this same level. These energies are reported below in e.u., and were converted to kcal/mol using 1 e.u. = 627.50 kcal/mol. The geometry optimization and frequency steps were performed together in a single calculation using the Gaussian keyword combination "Opt Freq". For **S5-1** and **S5-2**, no negative harmonic frequencies were obtained, indicating that they were stable local minima on the energy surface.

To ensure that the resulting wavefunctions lacked any RHF to UHF instability, stability tests were then performed on **S5-1** and **S5-2**, using the Gaussian keyword "stable=opt". In all cases, the computation resulted in the output "The wavefunction is stable under the perturbations considered."

Below we list figures, xyz coordinates, and energies for all five of the computed structures.

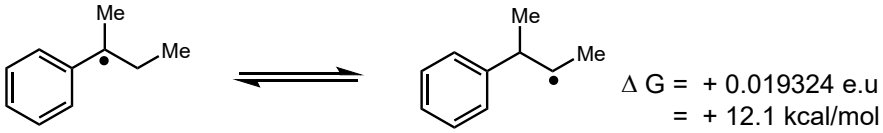
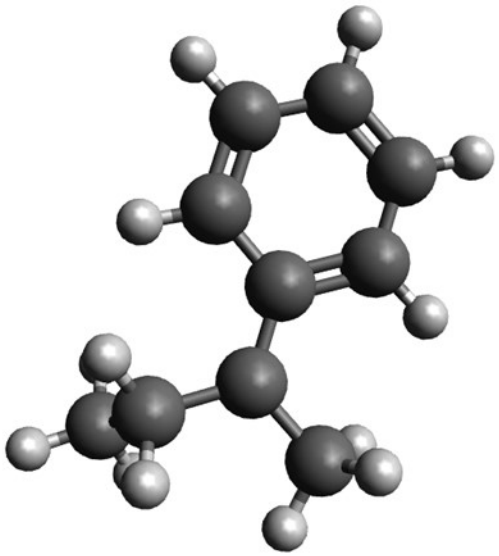


Figure S5.1. Computed energy differences for the butylbenzene radicals. (**S5-1**, **S5-2**)



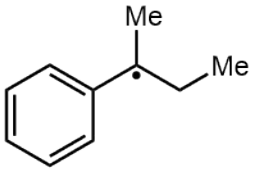
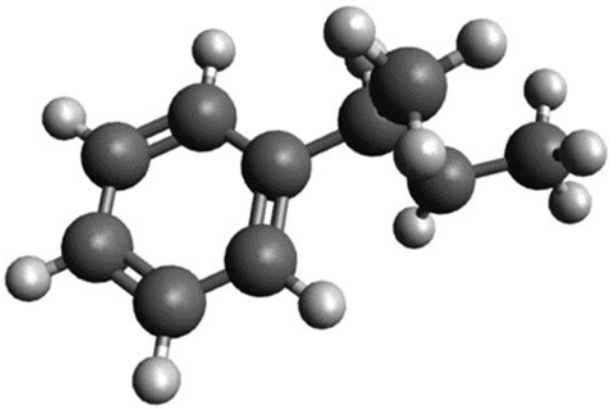


Figure S5.2. Optimized structure for **S5-1**.

XYZ coordinates for S5-1.

C	-2.49748	0.91683	-0.22173
C	-2.96030	-0.39478	-0.11915
C	-2.04163	-1.42069	0.10447
C	-0.69269	-1.14768	0.22618
C	-0.18800	0.17889	0.12654
C	-1.15005	1.20136	-0.10558
C	1.19803	0.47955	0.24812
C	1.70180	1.88039	0.04573
C	2.22755	-0.57125	0.55710
C	2.89203	-1.16510	-0.70174
H	-3.19977	1.72482	-0.39357
H	-4.01691	-0.61391	-0.21253
H	-2.38640	-2.44566	0.18256
H	-0.00969	-1.97023	0.39069
H	-0.82559	2.23037	-0.18439
H	2.79203	1.90240	0.00930
H	1.39316	2.54776	0.86133
H	1.33089	2.32979	-0.88073
H	1.79693	-1.38181	1.14862
H	3.00794	-0.12372	1.18230
H	2.15450	-1.66417	-1.33336
H	3.65867	-1.89480	-0.42896
H	3.36875	-0.38589	-1.30087

Sum of electronic and thermal Energies= -388.761846
Sum of electronic and thermal Enthalpies= -388.760901
Sum of electronic and thermal Free Energies= -388.808687



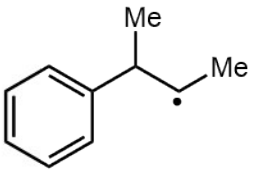


Figure S5.3. Optimized structure for **S5-2**.

XYZ coordinates for S5-2.

C	-2.55996	0.89082	-0.51227
C	-3.03199	-0.34341	-0.08286
C	-2.12983	-1.30154	0.36845
C	-0.76846	-1.02476	0.38999
C	-0.27982	0.21260	-0.03773
C	-1.19577	1.16283	-0.48860
C	1.20681	0.52546	0.01331
C	1.65989	0.79209	1.46827
C	2.03390	-0.52085	-0.67472
C	3.52330	-0.49667	-0.65468
H	-3.25310	1.64348	-0.87011
H	-4.09379	-0.55911	-0.10161
H	-2.48786	-2.26838	0.70338
H	-0.07223	-1.78011	0.73764
H	-0.83579	2.12846	-0.82855
H	1.35054	1.47710	0.52790
H	1.55159	-0.10624	2.08005
H	1.05307	1.58141	1.91558
H	2.70459	1.10675	1.50653
H	1.53652	-1.15456	-1.39919

H 3.92472 0.44493 -1.06210
H 3.94213 -1.31082 -1.24788
H 3.93124 -0.58230 0.35918

Sum of electronic and thermal Energies= -388.741219
Sum of electronic and thermal Enthalpies= -388.740274
Sum of electronic and thermal Free Energies= -388.789363

Table S5.1. Difference in energy between radicals **S5-1** and **S5-2**.

Energy	**E**	**H**	**G**
Δ(**S5-2** – **S5-1**)	12.9 kcal/mol	12.9 kcal/mol	12.1 kcal/mol