Supporting Information:

to

Rapid, Selective and Reversible Nitroxide Radical Coupling (NRC) Reactions at Ambient Temperature.

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Synthesis of tris(2-(dimethylamino)ethyl)amine (Me_6TREN)

Me_6TREN was synthesized using the previously described method of Ciampolini *et al*. The ^{1}H and ^{13}C NMR spectra of the product were consistent with those reported in the literature. ^{1}H NMR ($CDCl_3$): δ 2.19 (s, 18H, $N(CH_2CH_2N(C\boldsymbol{H}_3)_2)_3$), 2.35 (m, 6H, $N(CH_2C\boldsymbol{H}_2N(CH_3)_2)_3$), 2.57 (m, 6H, $N(C\boldsymbol{H}_2CH_2N(CH_3)_2))_3$); ^{13}C NMR ($CDCl_3$): δ 45.84 ($N(CH_2CH_2N(\boldsymbol{C}H_3)_2))_3$), 53.01 ($N(CH_2\boldsymbol{C}H_2N(CH_3)_2))_3$), 57.42 ($N(\boldsymbol{C}H_2CH_2N(CH_3)_2))_3$). Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966,** 5, 41-44.

Synthesis of functional nitroxides

(i) TEMPO-OH (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxyl)

To a solution of 2,2,6,6-tetramethyl-4-piperidinol (5.00 g, 3.18 x 10^{-2} mol) in MeOH (59.2 mL) and MeCN (4.23 mL) was added $NaHCO_3$ (2.13 g, 2.54 x 10^{-2} mol) and $Na_2WO_4.2H_2O$ (0.305 g, 9.23 x 10^{-4} mol). H_2O_2 30% w/w (11.8 mL, 0.110 mol) was then added dropwise. After stirring in air at room temperature for 38 h the orange/red solution was diluted with brine (100 mL) and extracted with dichloromethane (3 x 60 mL). The combined organic phases were washed with brine (60 mL) and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a bright orange oil which was triturated with hexane to yield 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxyl, TEMPO-OH, as an orange solid (4.84 g, 88%). R_f (50% EtOAc/hexane) 0.22; IR (ATR) $\upsilon_{(max)}$ 3402 (br), 2974, 2948, 2928, 2858 (br) cm^{-1}; GC-MS (EI^+) *m/z* 172 (M^+, 11 %), 158 (6 %), 142 (8 %), 85 (33 %), 71 (100 %), 57 (51 %), 41 (97 %). Only one peak was observed in the GC-MS chromatogram.

(ii) TEMPO-≡ (2,2,6,6-tetramethyl-4-(prop-2-ynyloxy)piperidine-1-yloxyl)

TEMPO-≡ was synthesized according to the procedure of Reiser *et al*. To a stirred suspension of NaH (60% in mineral oil, 850 mg, 2.13 x 10^{-2} mol) in dry DMF (100 mL) at 0 °C, TEMPO-OH (3.0 g, 1.74 x 10^{-2} mol) was added portion wise. The reaction mixture was then stirred at room temperature for 30 min, with the visible evolution of hydrogen gas. Propargyl bromide (80 wt% in toluene, 2.0 mL, 1.80 x 10^{-2} mol) was added dropwise at 0 °C. The resulting mixture was stirred for 3 h at room temperature after which water (100 mL) was added and the solution extracted with EtOAc (2 x 50 mL). The organic phase was washed with water (2 x 50 mL), dried over anhydrous $MgSO_4$, filtered, evaporated under reduced pressure and purified by column chromatography (silica gel, 10% EtOAc in hexane) to give the title compound as a dark orange solid (2.34 g, 64%). R_f (50% EtOAc/hexane) 0.61; IR (ATR) $\upsilon_{(max)}$ 3229 (sharp, strong), 2996, 2974, 2936 (br), 2111 (sharp, weak) cm^{-1}; GC-MS (EI^+) *m/z* 210 (M^+, 13 %), 196 (15 %), 180 (19 %), 154 (20 %), 124 (27 %), 109 (35 %), 82 (76 %), 55 (59 %), 41 (100 %); microanalysis theory (C-68.54%, H-9.59%, N-6.66%), found (C-68.54%, H-9.72%, N-6.62%). Only one peak was observed in the GC-MS chromatogram. Unreacted TEMPO-OH was also recovered during column chromatography. Reiser, O.; Gheorghe, A.; Matsuno, A. *Adv. Synth. Catal.* **2006,** 348(9), 1016-1020.

(iii) TEMPO=O (4-oxo-TEMPO; 2,2,6,6-tetramethylpiperidon-1-yloxyl)

To a solution of 2,2,6,6-tetramethyl-4-piperidinone (2.43 g, 1.57 x 10^{-2} mol) in MeOH (29.0 mL) and MeCN (2.1 mL) was added $NaHCO_3$ (1.05 g, 1.25 x 10^{-2} mol) and $Na_2WO_4.2H_2O$ (0.150 g, 4.54 x 10^{-4} mol). H_2O_2 30% w/w (5.80 mL, 0.055 mol) was then added dropwise. After stirring in air at room temperature for 48 h the

orange/red solution was diluted with water (50 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic phases were washed with brine (30 mL) and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave an orange oil which crystallized in the freezer to yield 4-oxo-TEMPO, TEMPO=O, as an orange solid (2.20 g, 83%). R_f (50% EtOAc/hexane) 0.43; IR (ATR) $\upsilon_{(max)}$ 2999, 2981, 2937, 2898 (br), 1706 (sharp, strong) cm^{-1}; GC-MS (EI^+) *m/z* 170 (M^+, 7 %), 114 (28 %), 83 (15 %), 56 (100 %), 41 (51 %). Only one peak was observed in the GC-MS chromatogram.

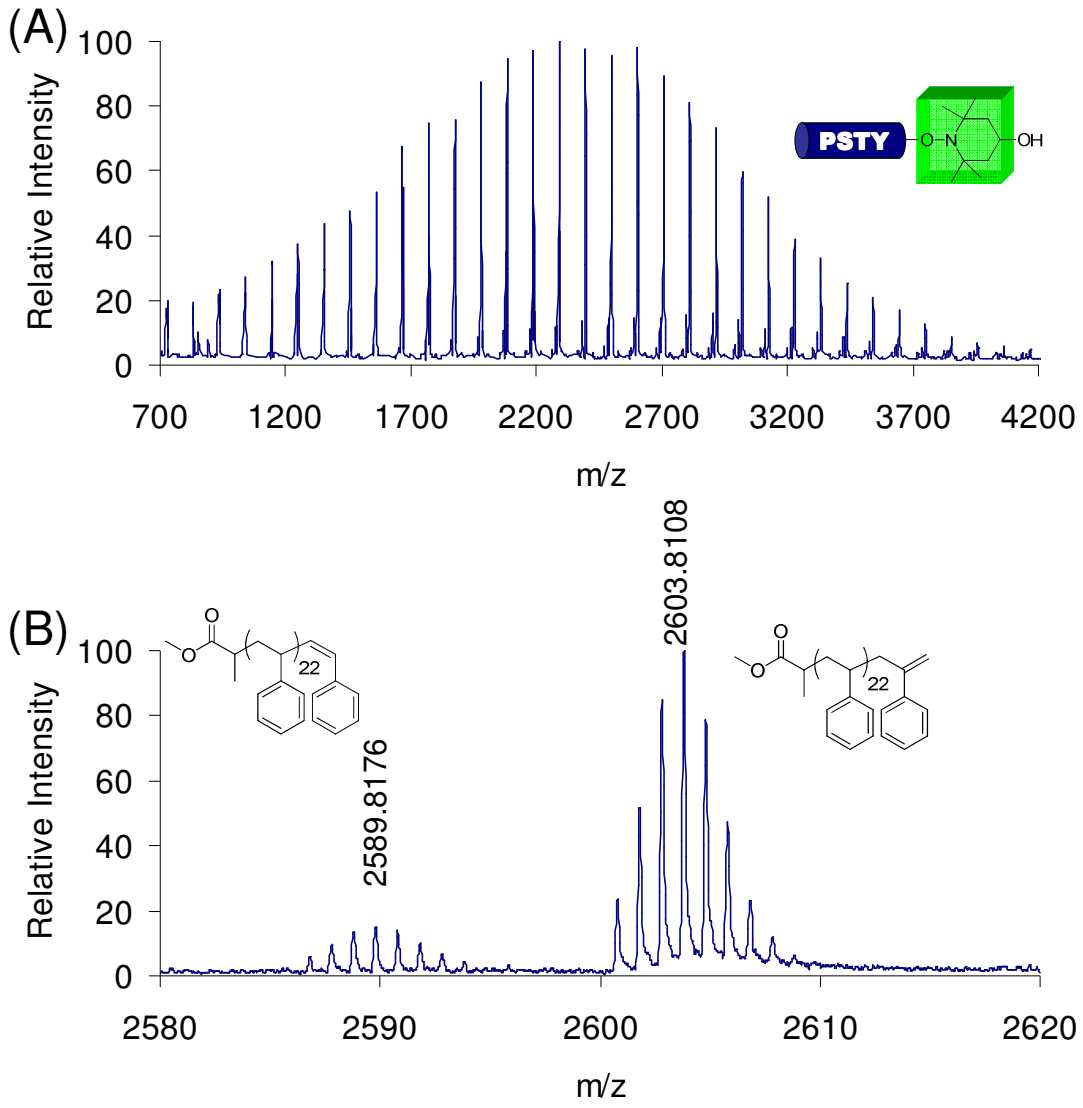

Figure S1. MALDI-ToF MS spectra of PSTY-TEMPO-OH formed from NRC of PSTY-Br and TEMPO-OH. (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

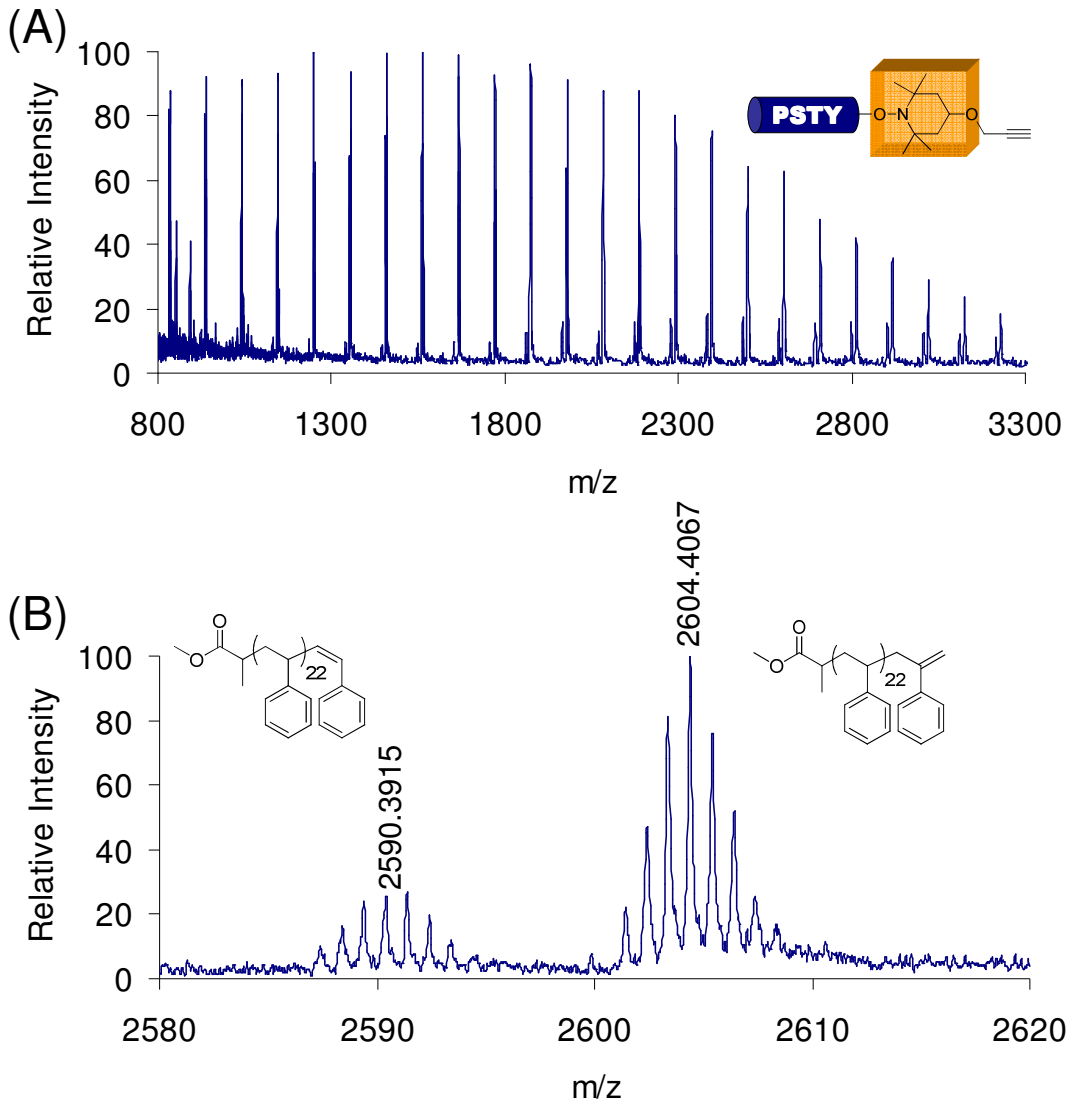

Figure S2. MALDI-ToF MS spectra of PSTY-TEMPO-≡ formed from PSTY-TEMPO-OH exchange with TEMPO-≡. (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

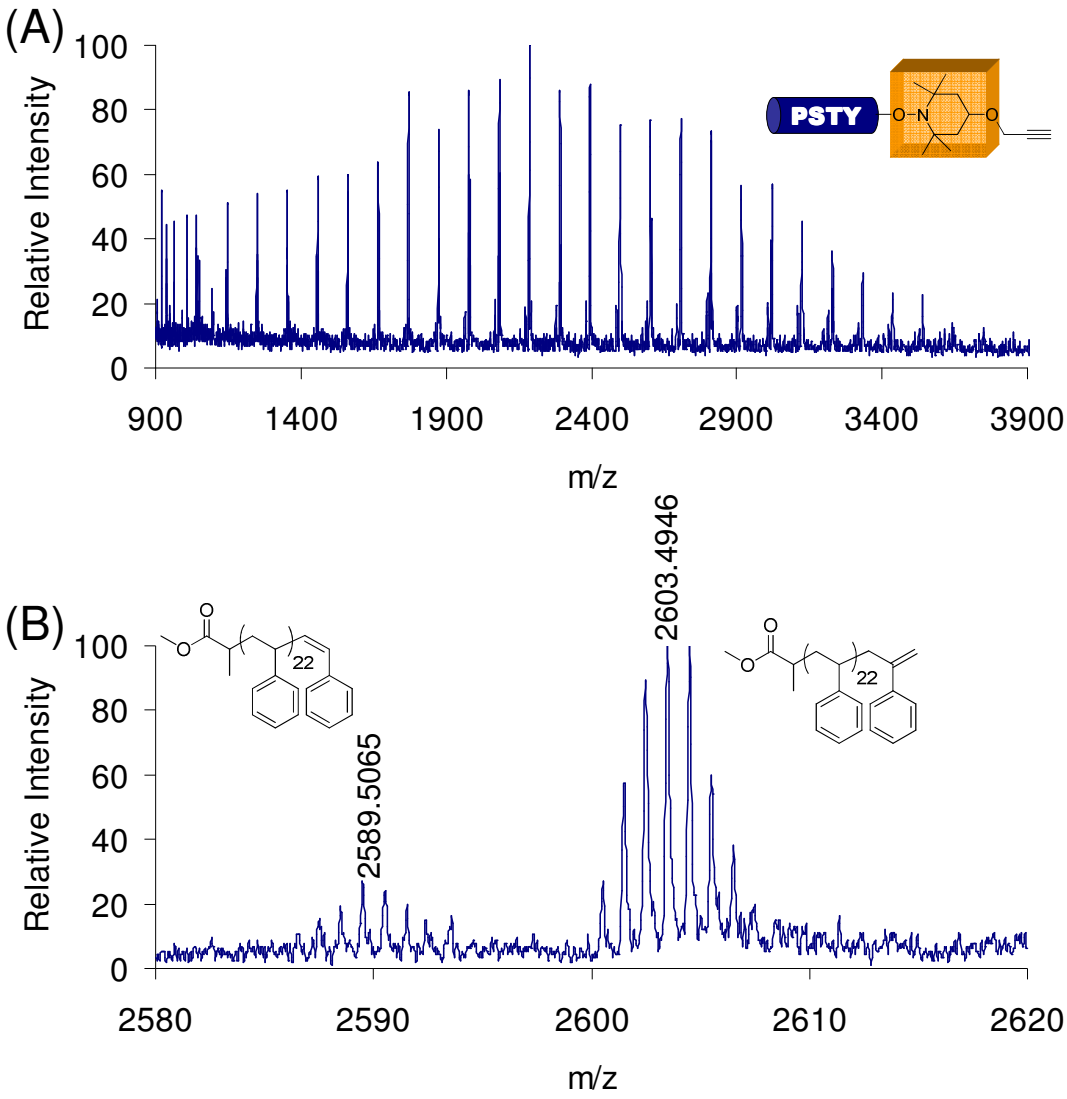

Figure S3. MALDI-ToF MS spectra of PSTY-TEMPO-≡ formed from NRC of PSTY-Br and TEMPO-≡. (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

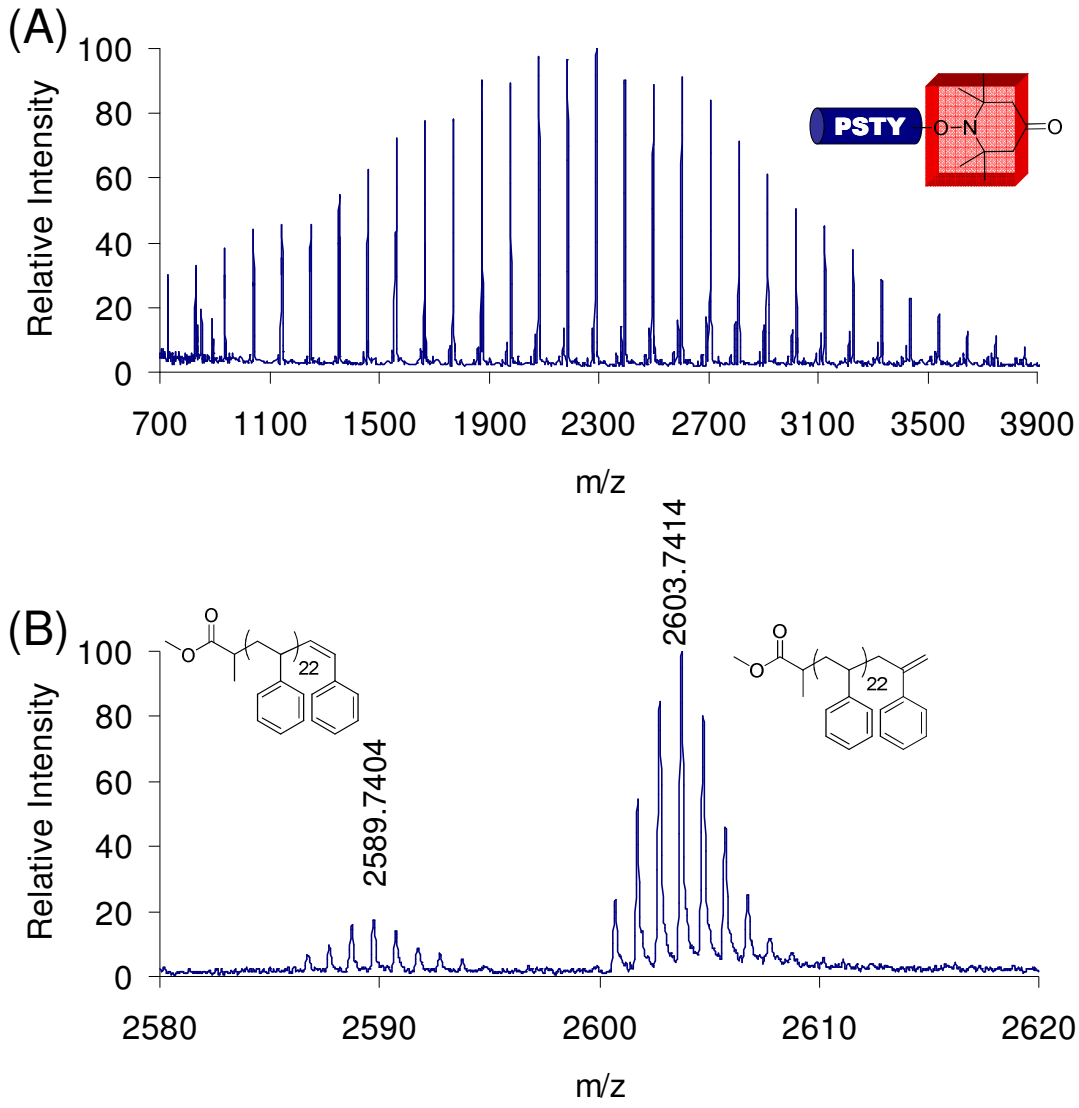

Figure S4. MALDI-ToF MS spectra of PSTY-TEMPO=O formed from NRC of PSTY-Br and TEMPO=O. (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

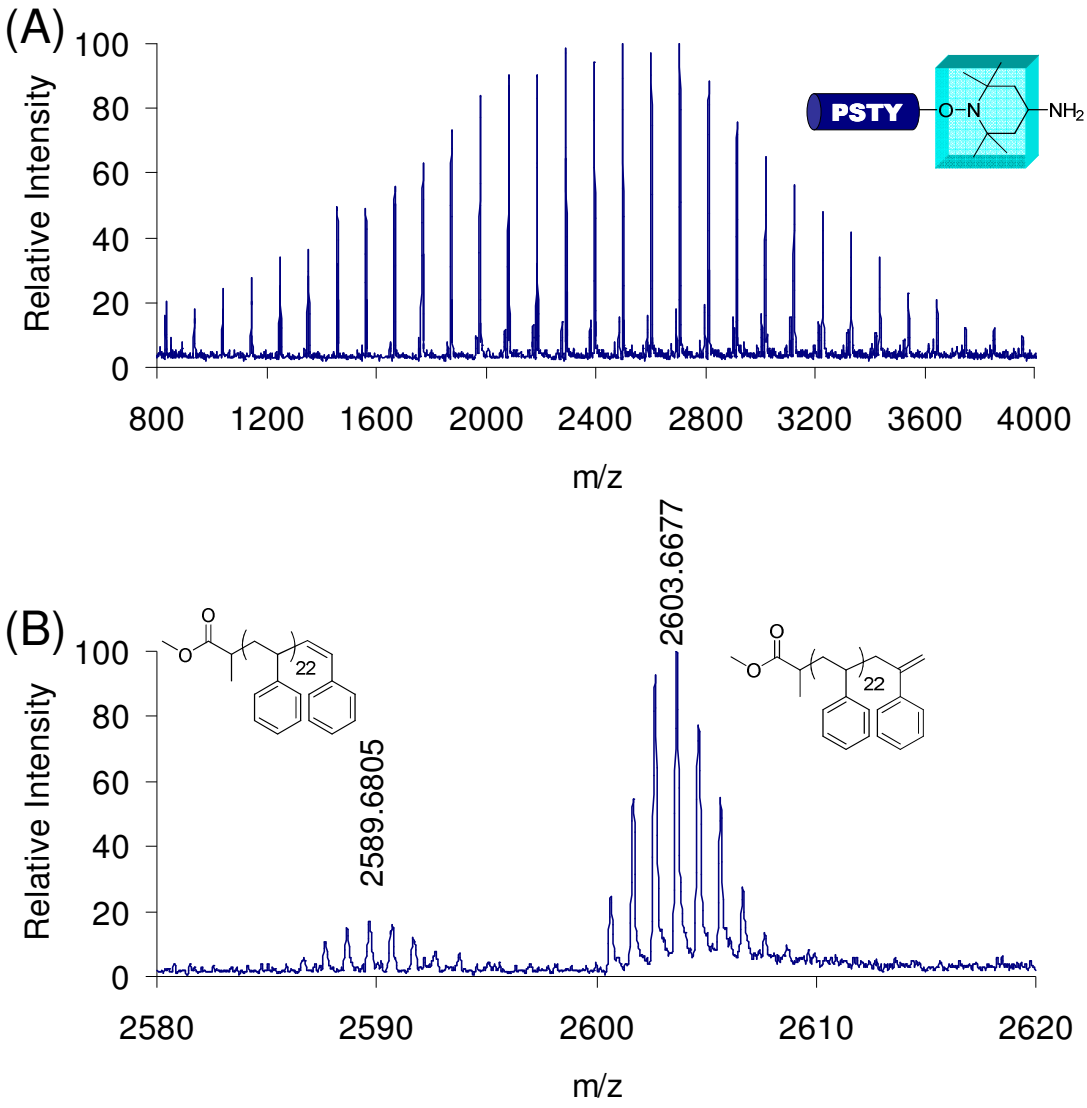

Figure S5. MALDI-ToF MS spectra of PSTY-TEMPO-NH_2 formed from NRC of PSTY-Br and Tempo-NH_2 (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

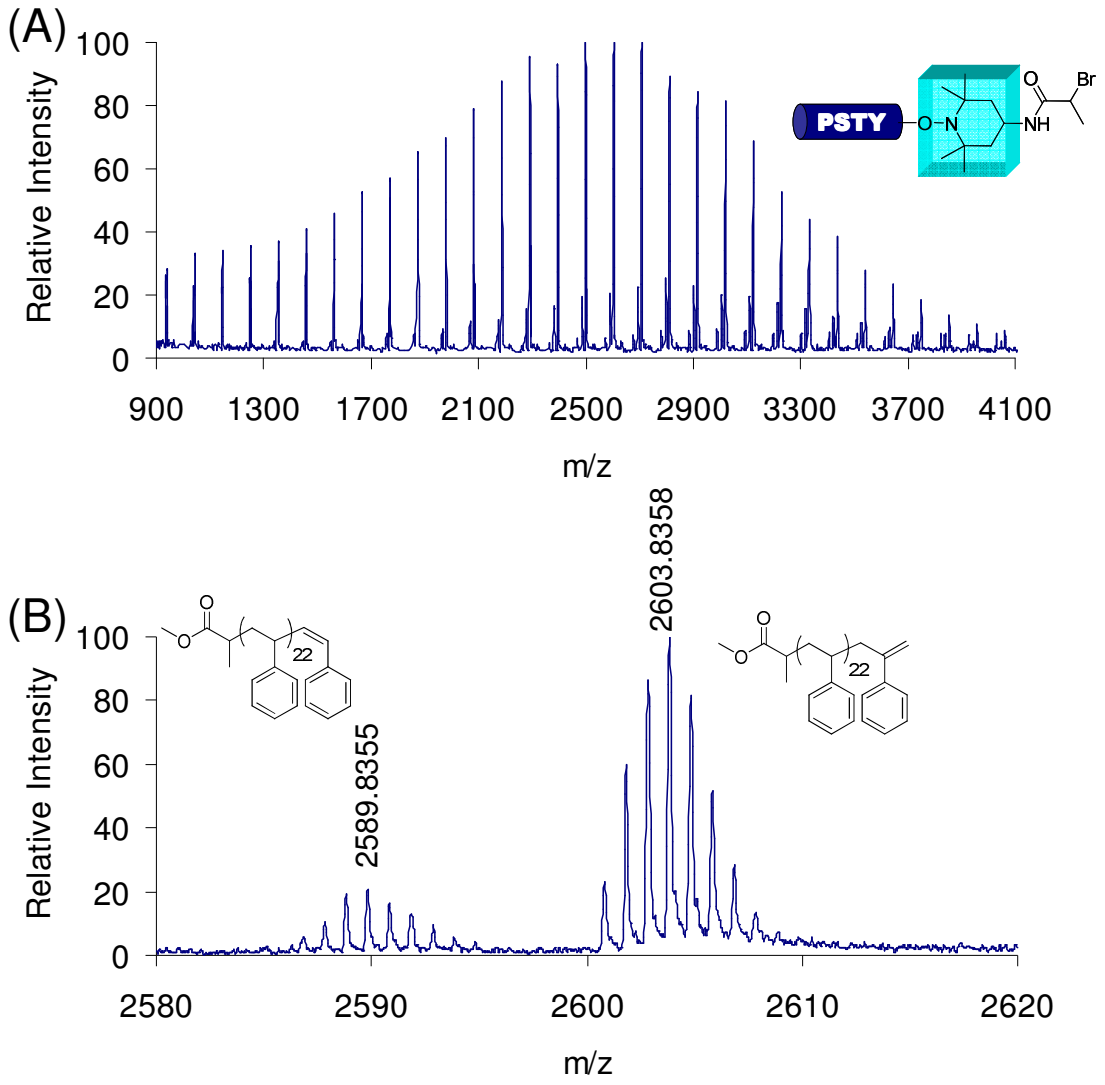

Figure S6. MALDI-ToF MS spectra of PSTY-TEMPO-2-bromopropanamide formed from acylation of PSTY-TEMPO-NH_2 with 2-bromopropionyl bromide (A) Full distribution and (B) expanded section of the spectrum showing peaks with isotopic resolution. The sample was acquired in reflectron mode using Ag(CF_3COO) as the cationization source and DCTB as the matrix.

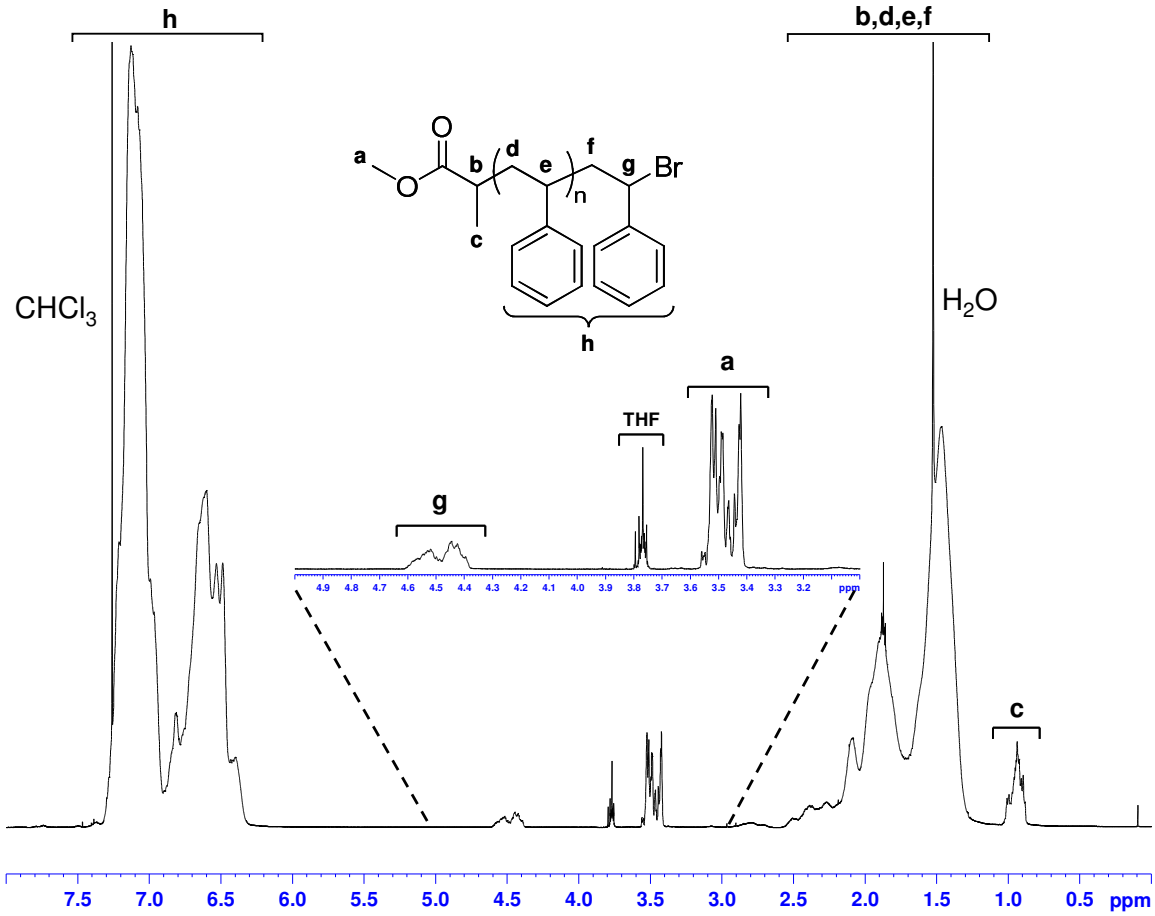

Figure S7. ^{1}H NMR spectra of PSTY-Br with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

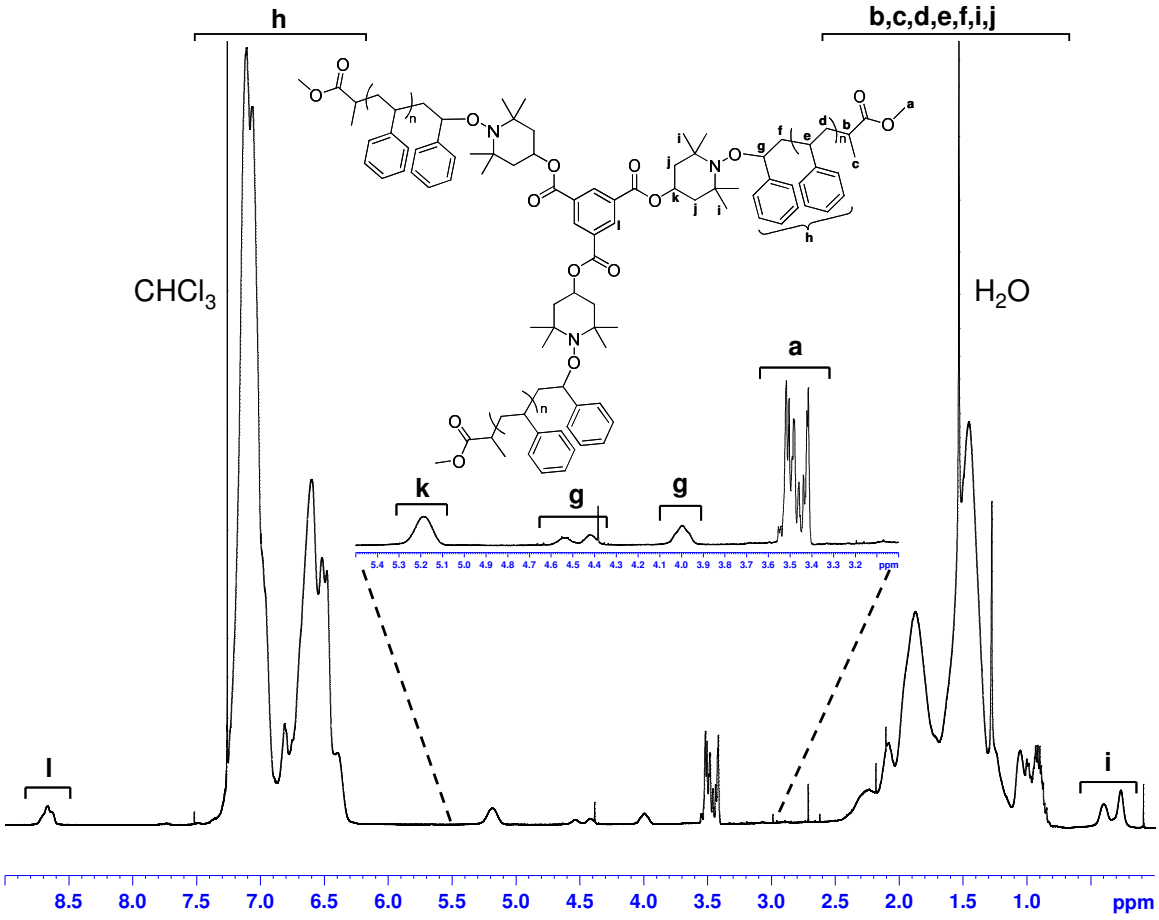

Figure S8. ^{1}H NMR spectra of 3-arm star with expanded view of region between 3-5.5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

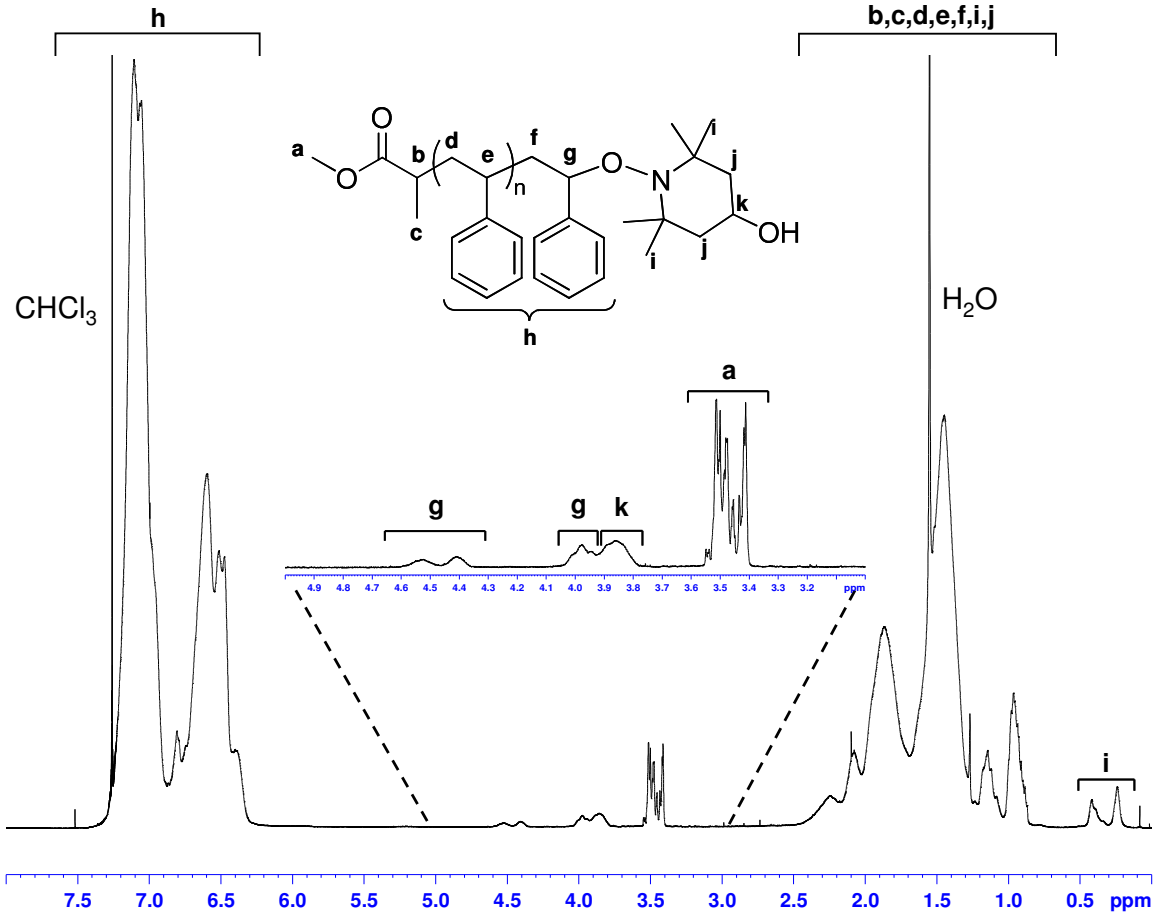

Figure S9. ^{1}H NMR spectra of PSTY-TEMPO-OH formed from NRC of PSTY-Br and Tempo-OH, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

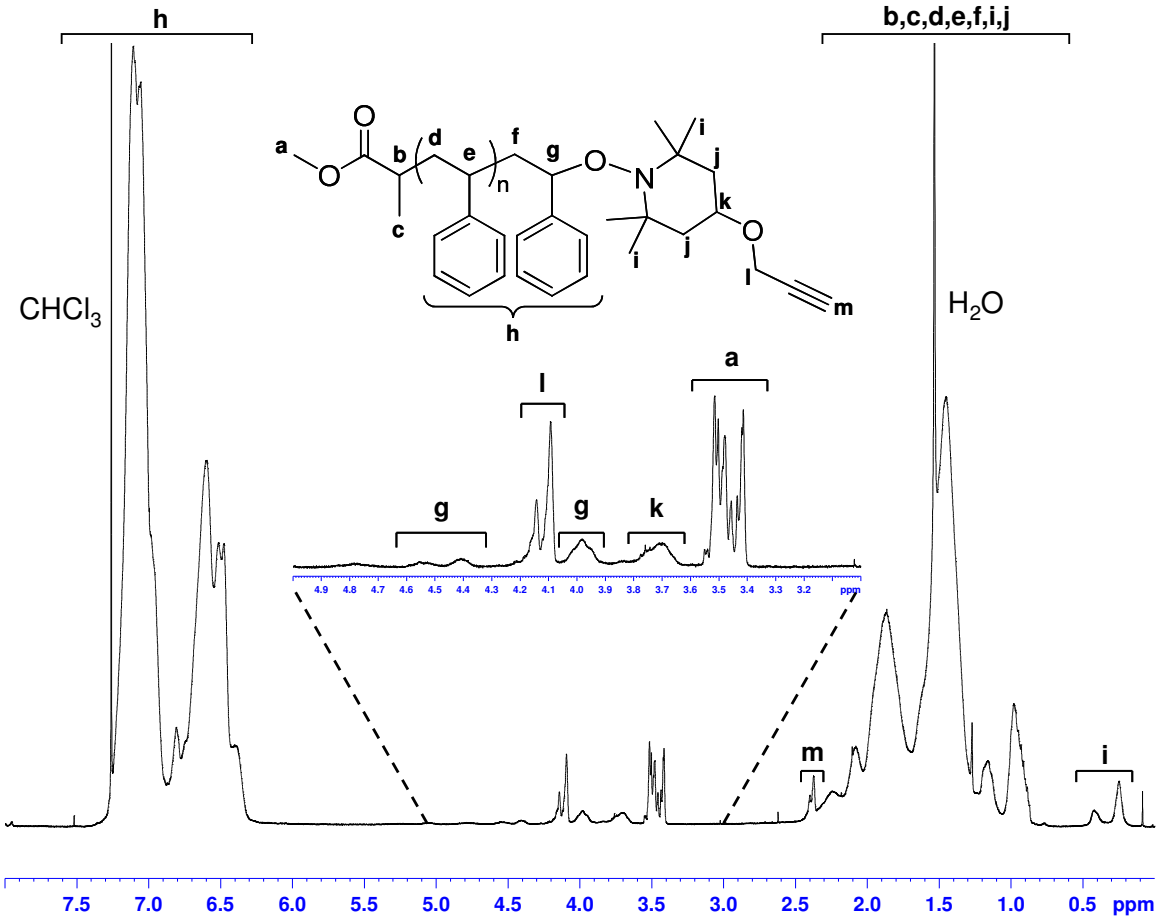

Figure S10. ^{1}H NMR spectra of PSTY-TEMPO-≡ formed from PSTY-TEMPO-OH exchange with TEMPO-≡, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

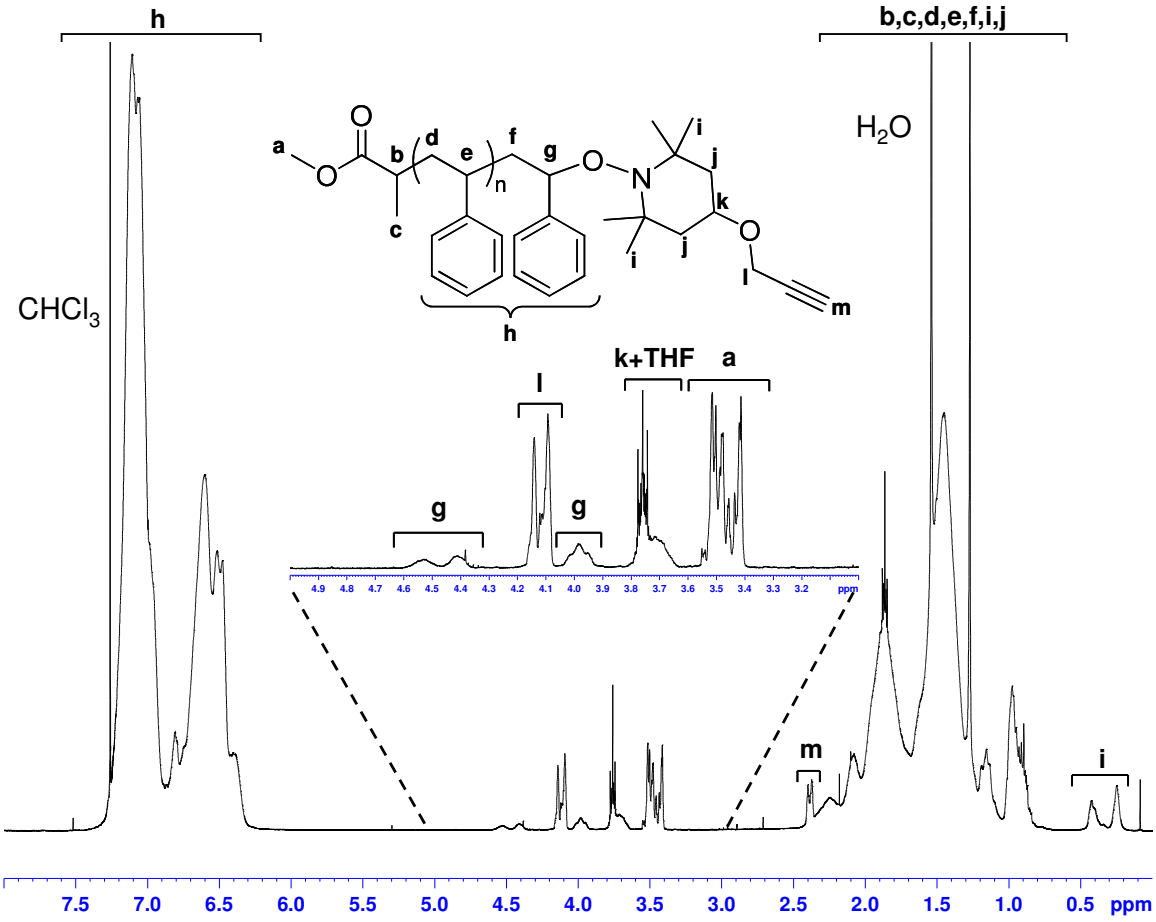

Figure S11. ^{1}H NMR spectra of PSTY-TEMPO-≡ formed from NRC of PSTY-Br and TEMPO-≡, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

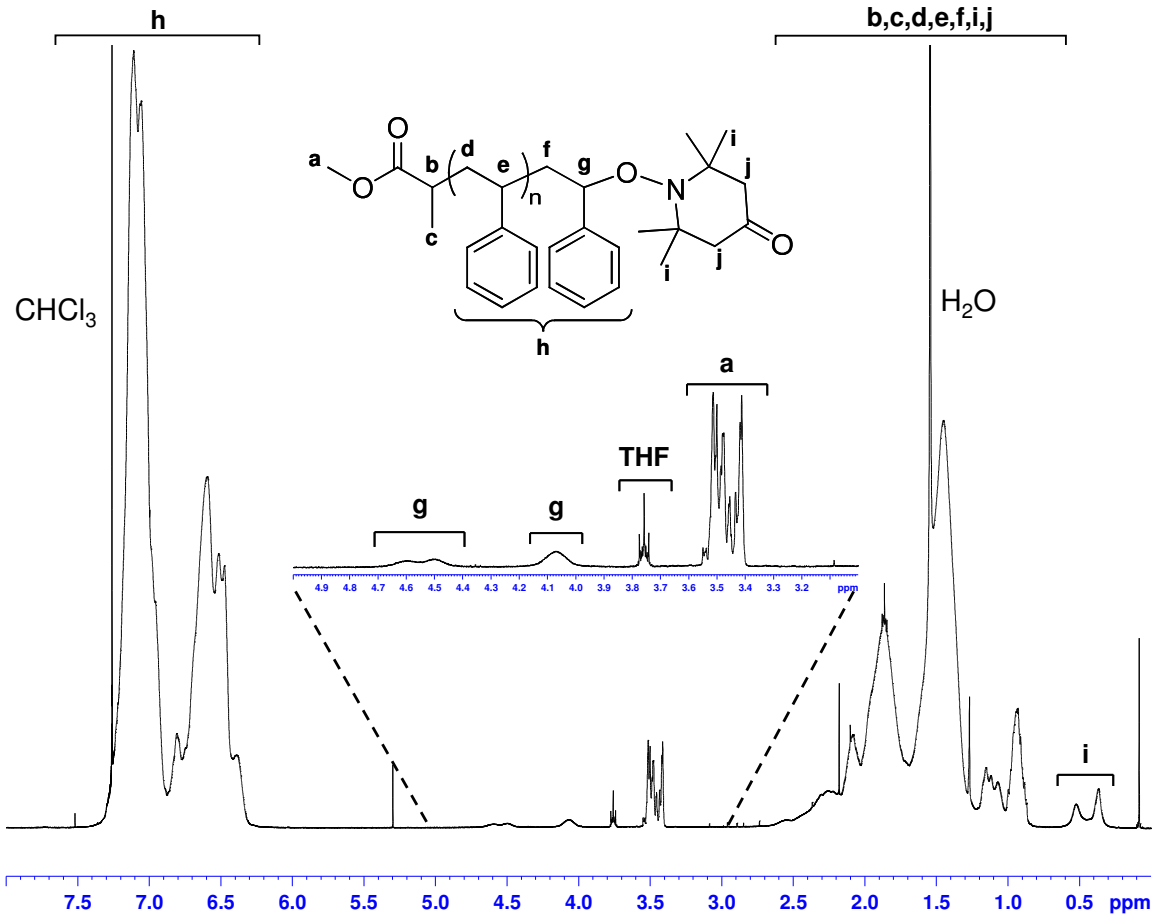

Figure S12. ^{1}H NMR spectra of PSTY-TEMPO=O formed from NRC of PSTY-Br and TEMPO=O, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

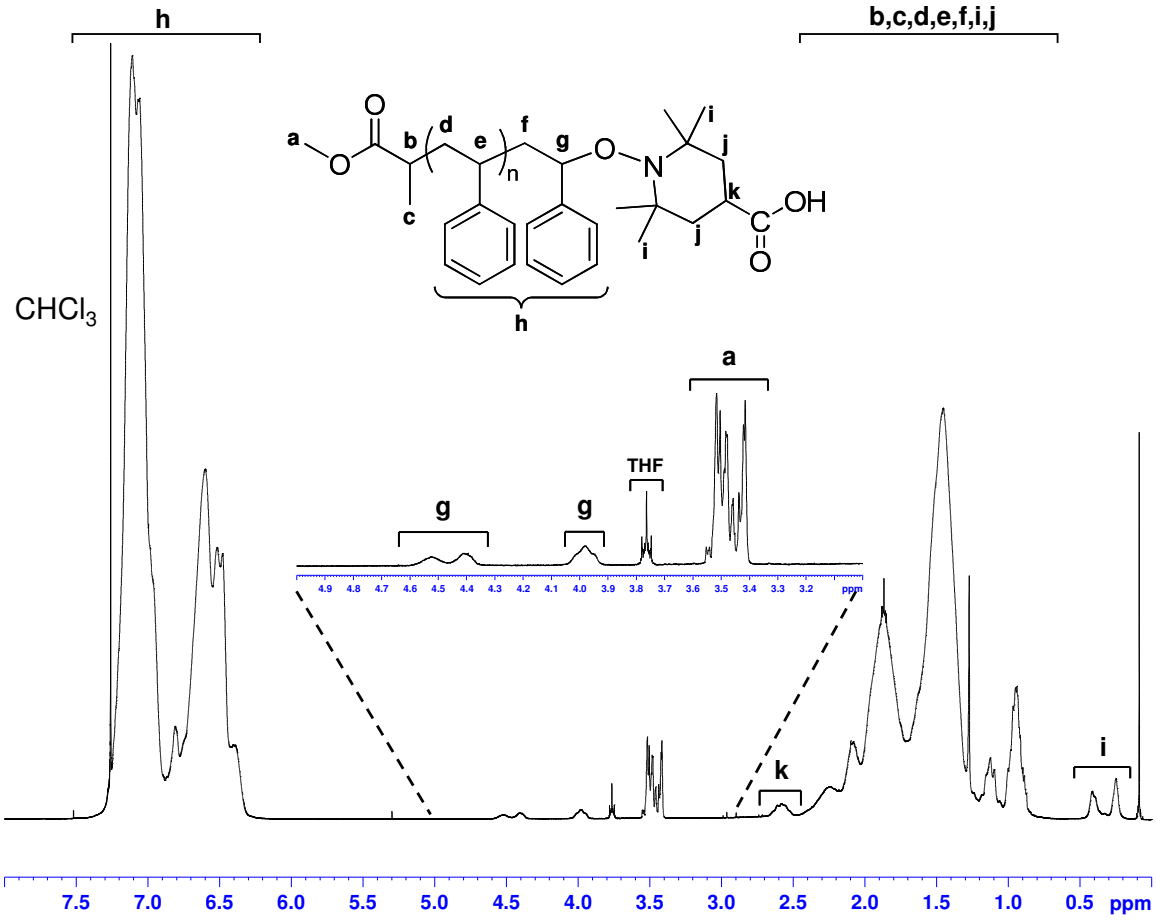

Figure S13. ^{1}H NMR spectra of PSTY-TEMPO-COOH formed from NRC of PSTY-Br and TEMPO-COOH, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

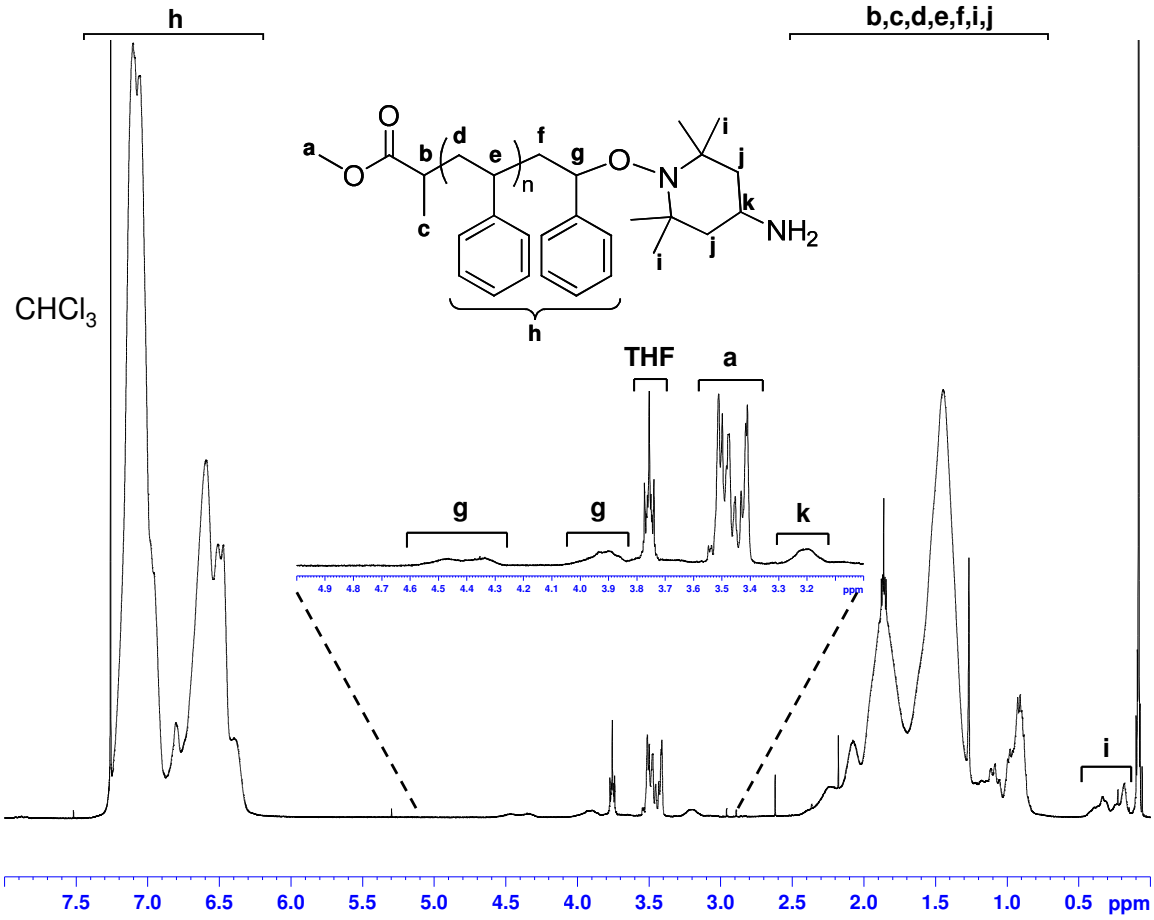

Figure S14. ^{1}H NMR spectra of PSTY-TEMPO-NH_2 formed from NRC of PSTY-Br and TEMPO-NH_2, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

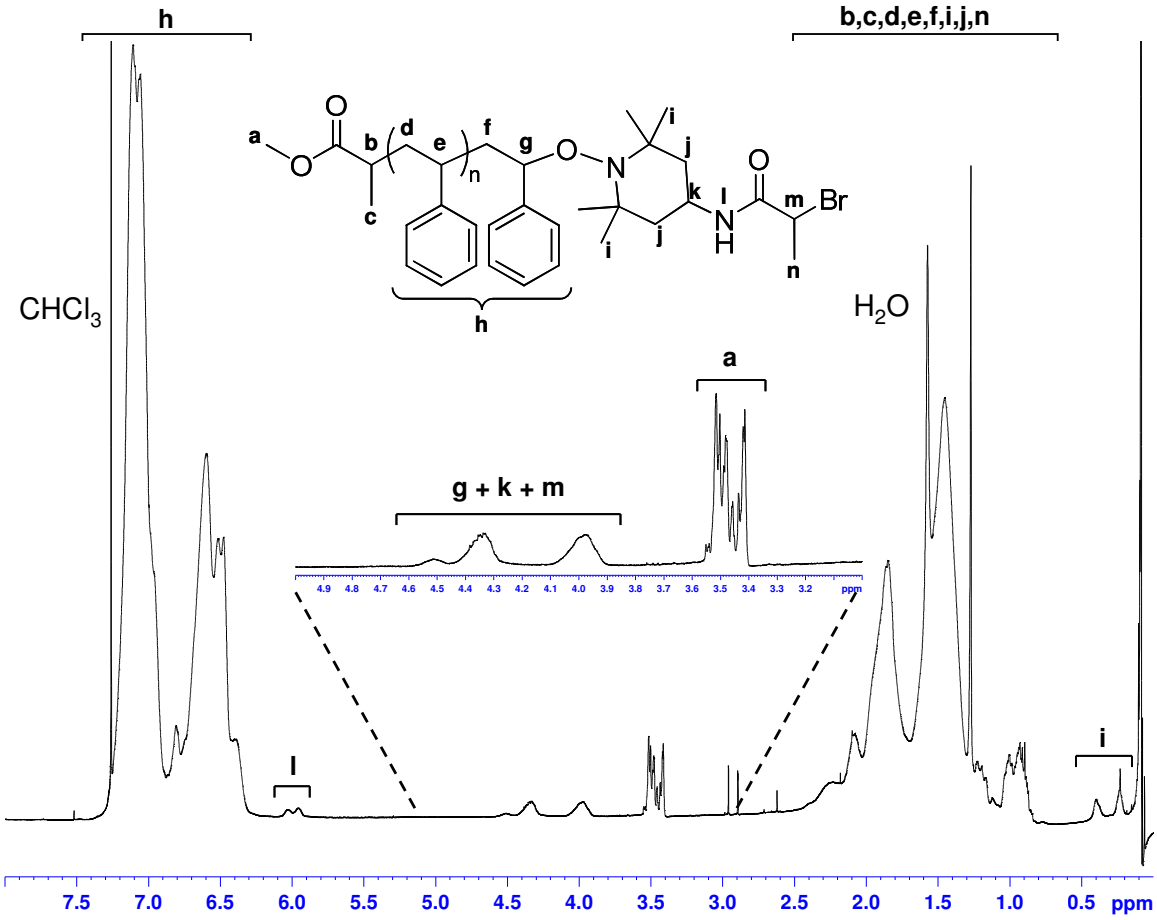

Figure S15. ^{1}H NMR spectra of PSTY-TEMPO-2-bromopropanamide formed from esterification of PSTY-TEMPO-NH_2 with 2-bromopropionyl bromide, with expanded view of region between 3 and 5 ppm. The sample was obtained on a Bruker DRX 400 MHz spectrometer and the solvent used was $CDCl_3$.

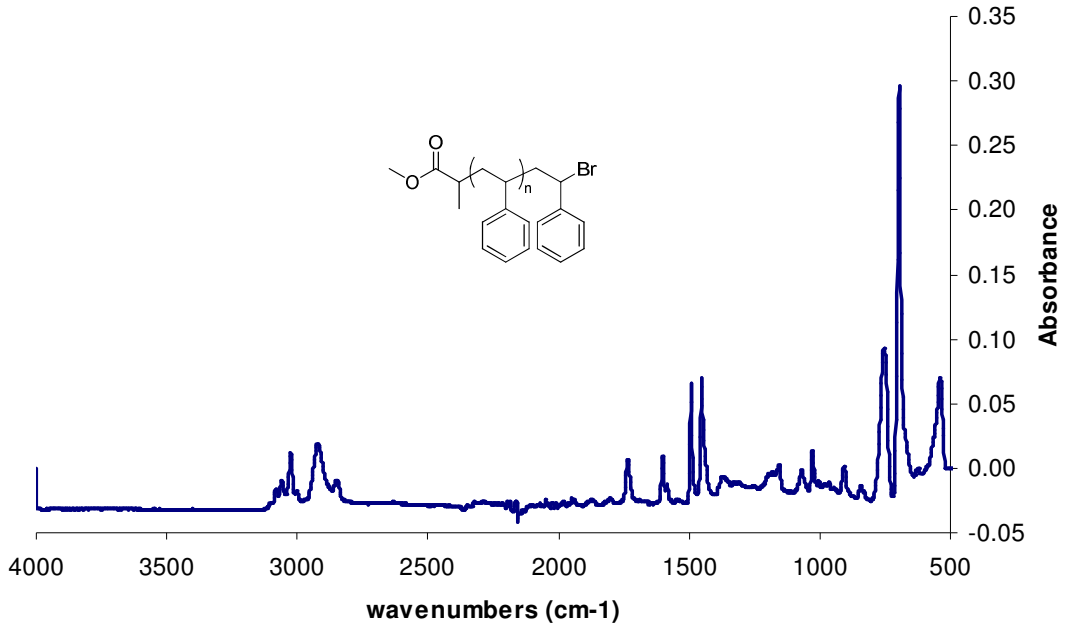

Figure S16. ATR-FTIR spectrum of PSTY-Br.

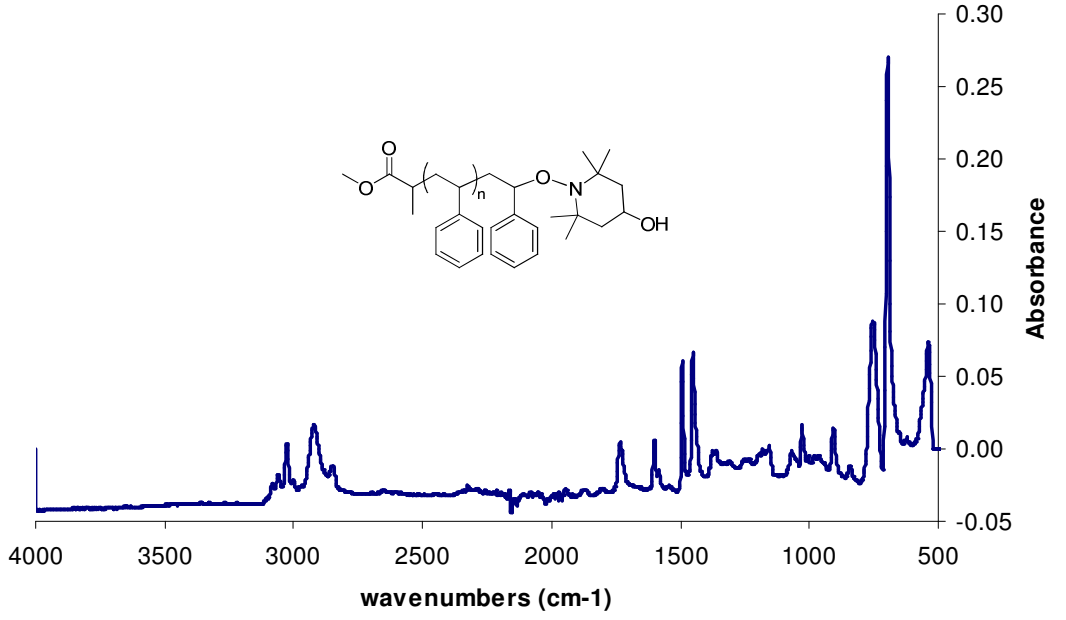

Figure S17. ATR-FTIR spectrum of PSTY-TEMPO-OH formed from 3-arm decoupling and exchange with TEMPO-OH.

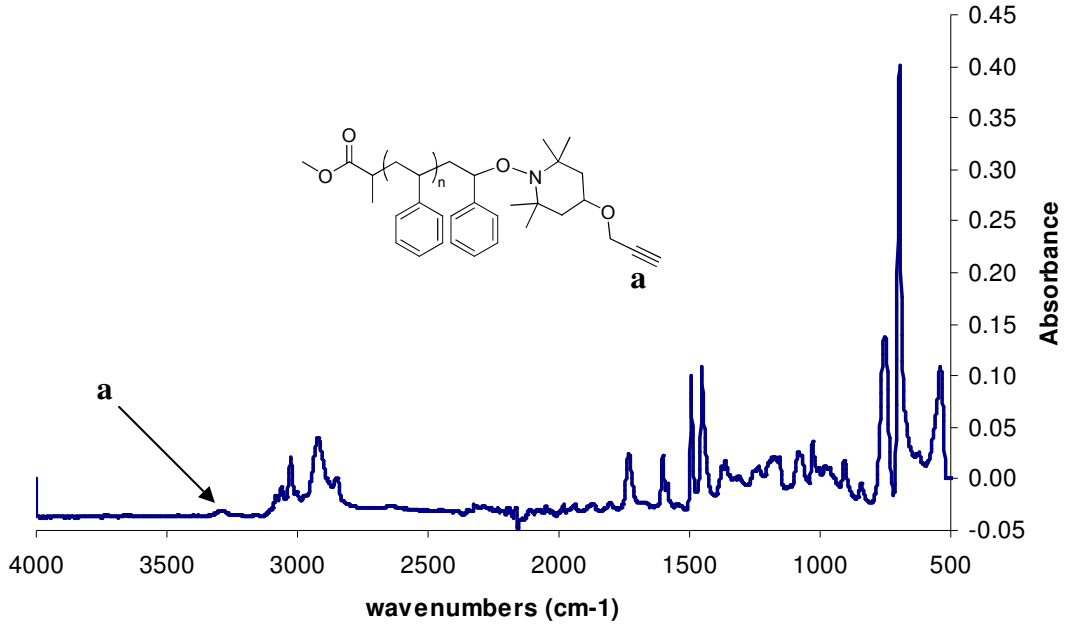

Figure S18. ATR-FTIR spectrum of PSTY-TEMPO-≡ formed from 3-arm decoupling and exchange with TEMPO-≡.

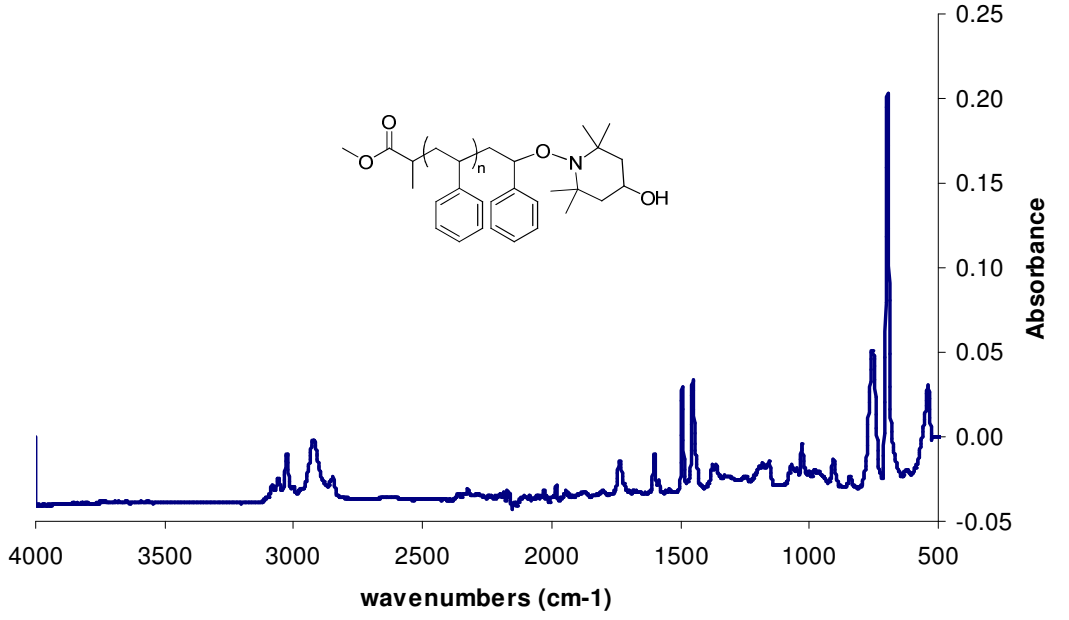

Figure S19. ATR-FTIR spectrum of PSTY-TEMPO-OH formed from NRC of PSTY-Br and TEMPO-OH.

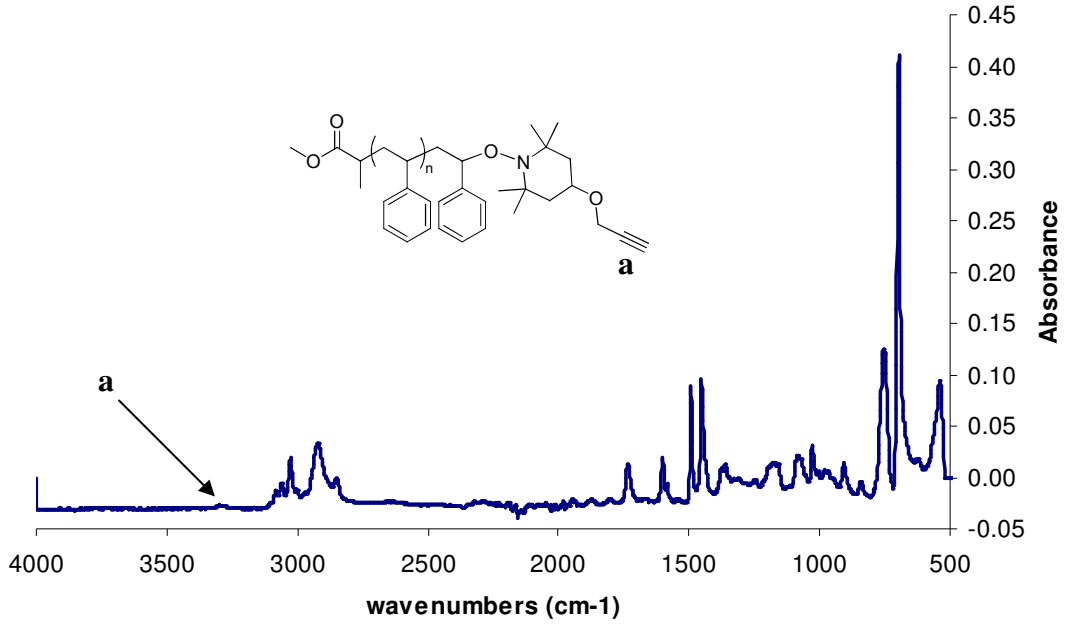

Figure S20. ATR-FTIR spectrum of PSTY-TEMPO-≡ formed from PSTY-TEMPO-OH exchange with TEMPO-≡.

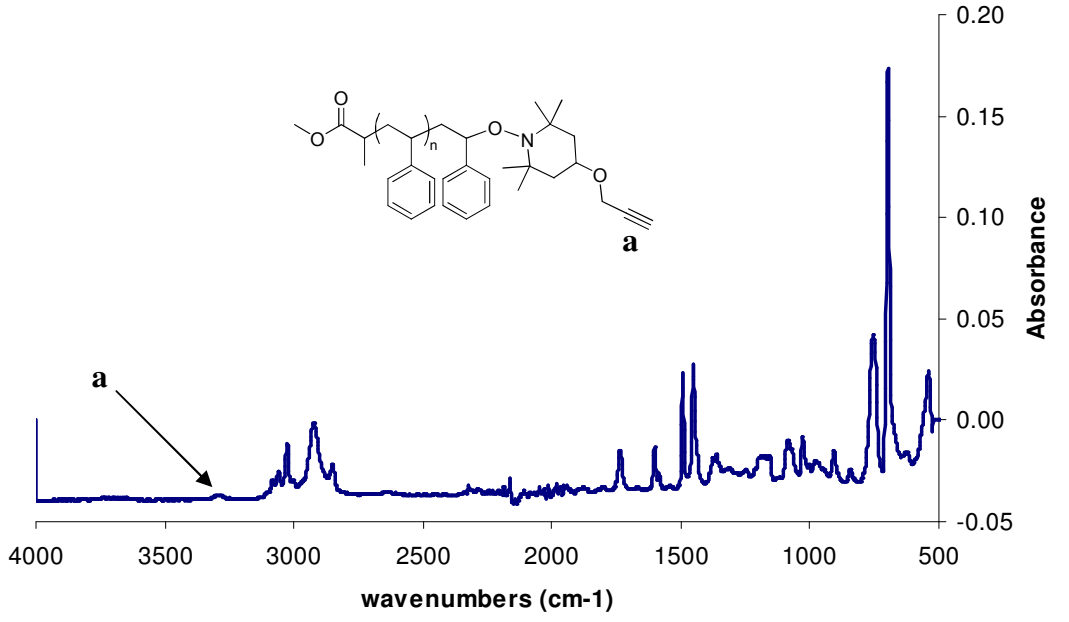

Figure S21. ATR-FTIR spectrum of PSTY-TEMPO-≡ formed from NRC of PSTY-Br and TEMPO-≡.

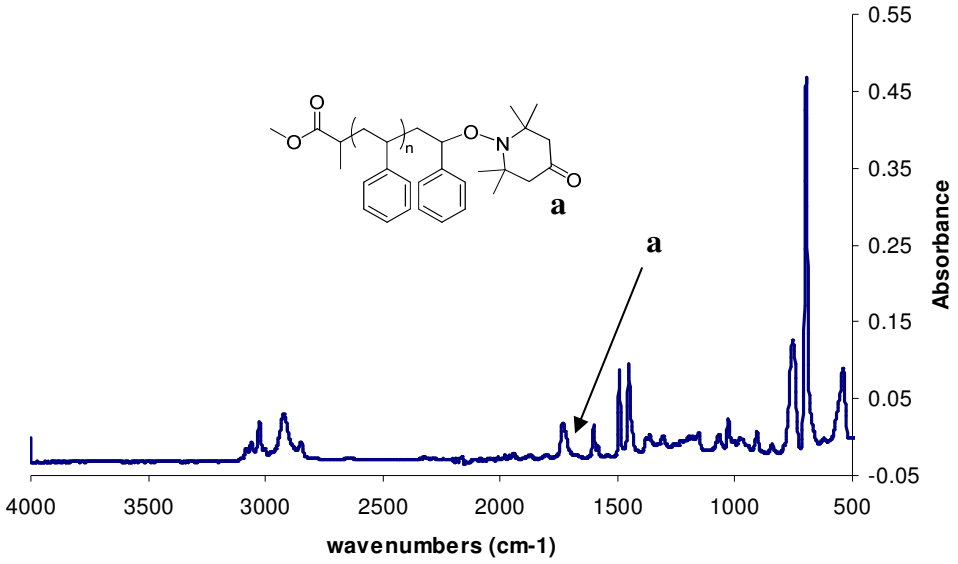

Figure S22. ATR-FTIR spectrum of PSTY-TEMPO=O formed from NRC of PSTY-Br and TEMPO=O. (a) corresponds to the C=O stretch from the initiator used (methyl-2-bromopropionate), which is definitively broadened by the presence of the TEMPO=O carbonyl stretch.

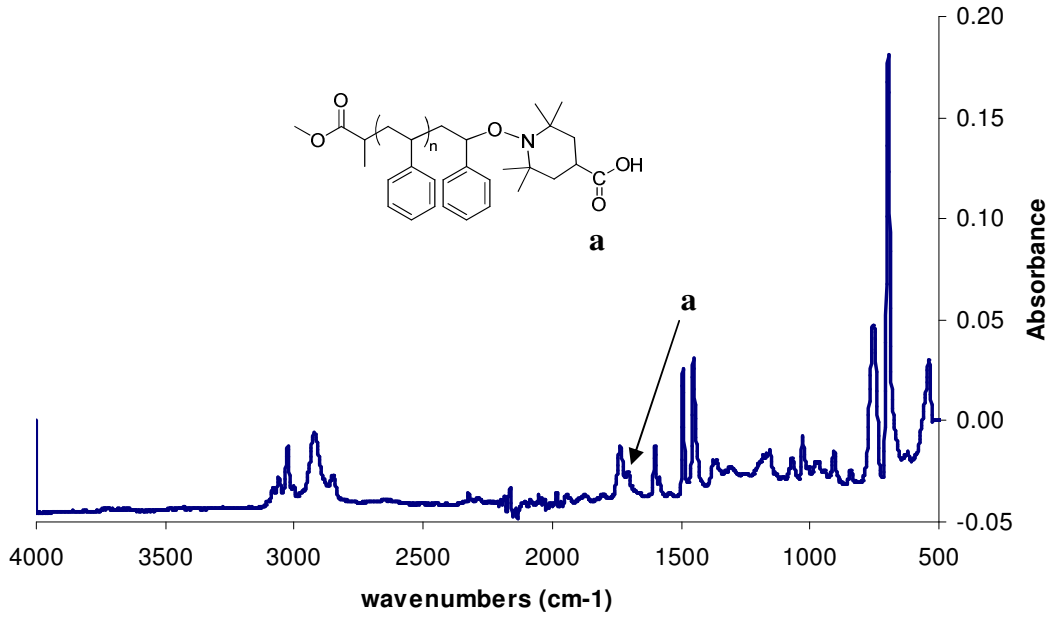

Figure S23. ATR-FTIR spectrum of PSTY-TEMPO-COOH formed from NRC of PSTY-Br and TEMPO-COOH.

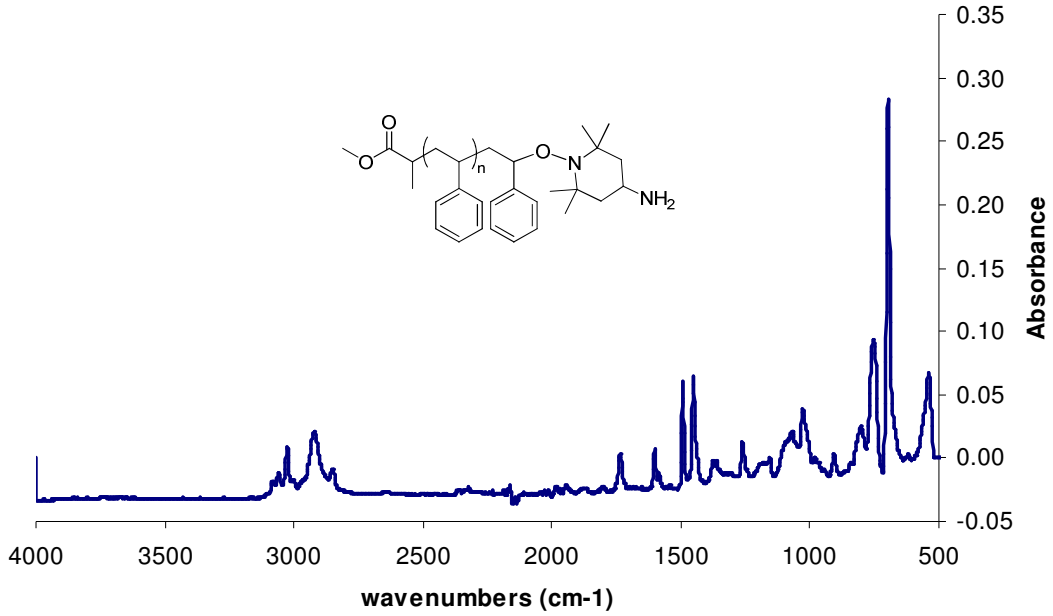

Figure S24. ATR-FTIR spectrum of PSTY-TEMPO-NH_2 formed from NRC of PSTY-Br and TEMPO-NH_2.

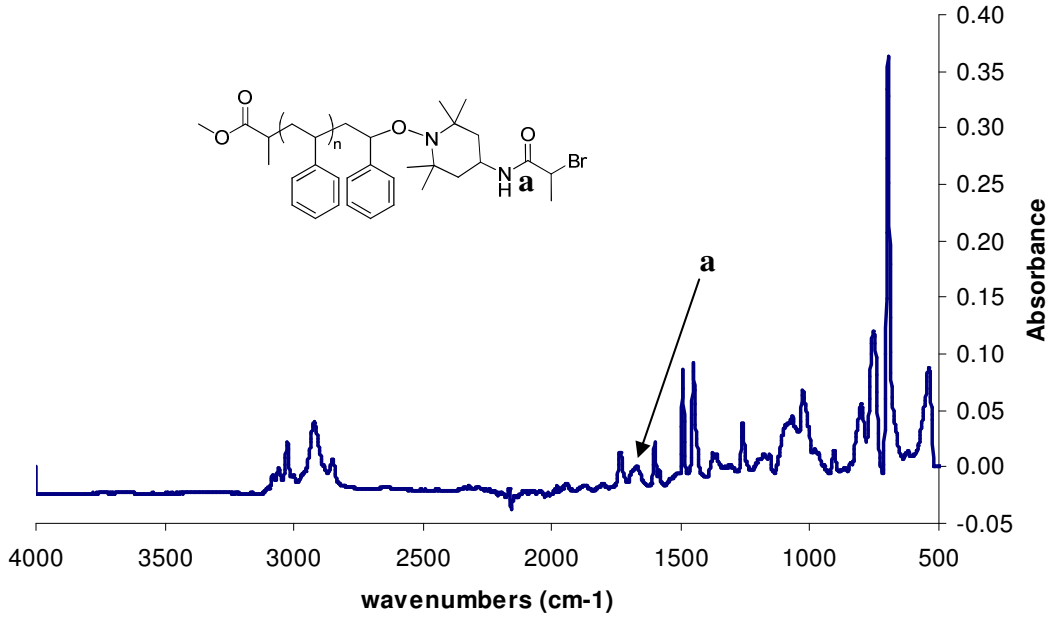

Figure S25. ATR-FTIR spectrum of PSTY-TEMPO-2-bromopropanamide formed from acylation of PSTY-TEMPO-NH_2 with 2-bromopropionyl bromide.