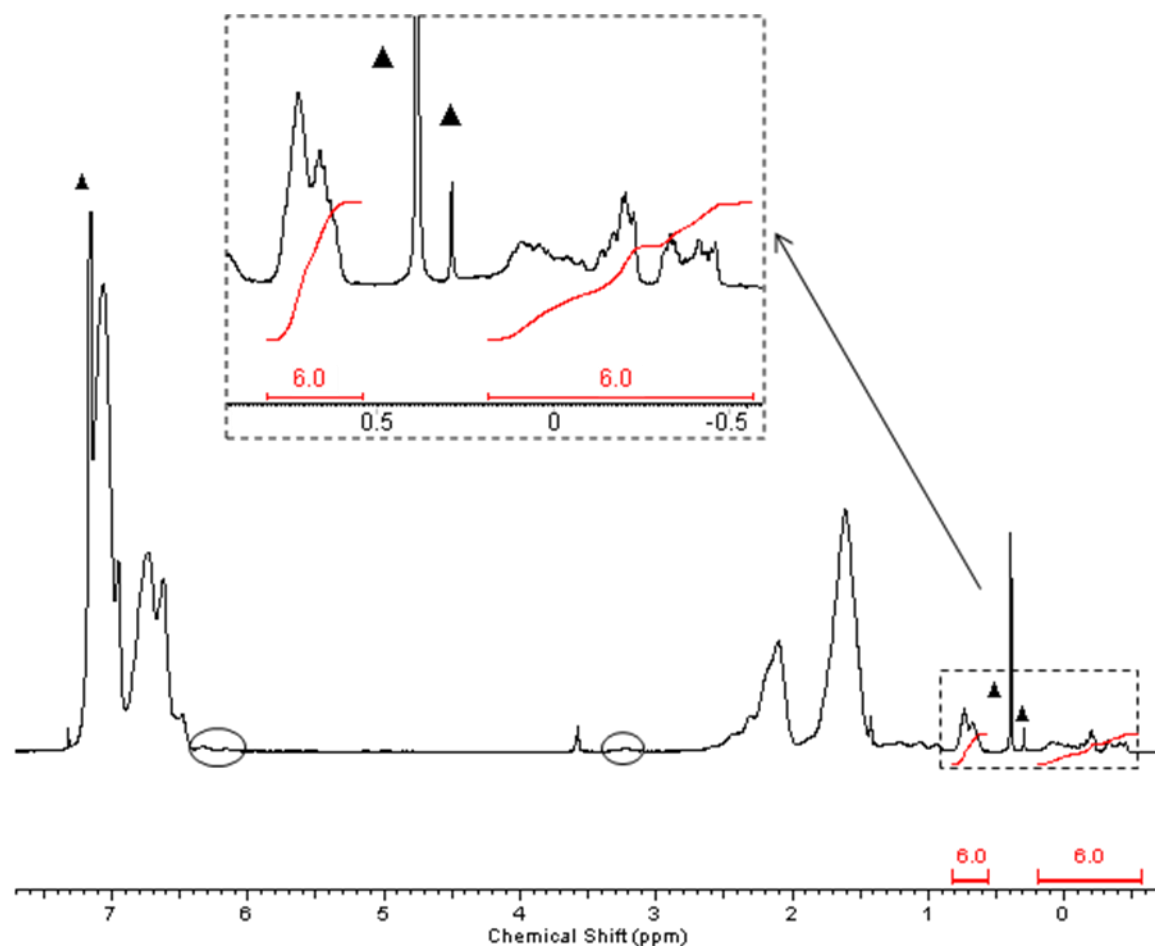**Supporting Information**

Organic-Metalloblock Copolymers via Photocontrolled Living Anionic Ring-Opening Polymerization

Laurent Chabanne, Inmaculada Matas, Sanjib K. Patra and Ian Manners*

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^{1}H NMR spectrum (C$_6$D$_6$) for Cp-capped polystyrene 1d.

Figure S1. ^{1}H NMR spectrum (C$_6$D$_6$, 499.9 MHz) for Cp-capped polystyrene **1d**. Circled: resonances attributed to Cp protons. ▲ notes residual benzene (7.16), water (0.4) and silicone grease (0.29). The inset shows the integrations for the CH_3CH$_2$CH(CH_3)– and –Si(CH_3)Cp end groups.

Matrix-Assisted Laser Desorption-Ionization-Time-of-Flight (MALDI-TOF) analysis of Cp-capped polystyrene 1d. MALDI-TOF analysis using standard conditions for polystyrene (dithranol/silver trifluoroacetate) mainly showed silanol-terminated polystyrene (Fig. S2.a). The peaks were separated by an average of 104 mass units, which corresponds to a polystyrene unit. For example, the peak at m/z 2635.1 corresponds to $C_4H_9(C_8H_8)_{23}Si(CH_3)_2OH \cdot Ag^+$. The presence of the silver ion seems to catalyse the hydrolysis of the silicon-Cp bond and only a small amount of 1d could be observed (i.e. $C_4H_9(C_8H_8)_{23}Si(CH_3)_2C_5H_5 \cdot Ag^+$, m/z 2682.4). The same behaviour was reported with silicon hydride-terminated polystyrene and the authors attributed it to oxidation of the silicon hydride group, a problem that was overcome by using sodium trifluoroacetate (NaTFA) instead of the silver salt.[1] Using the same salt, a spectrum corresponding to the expected polymer 1d was obtained (Fig. S2.b), with for example, a peak corresponding to $C_4H_9(C_8H_8)_{23}Si(CH_3)_2C_5H_5 \cdot Na^+$ at m/z 2598.9. A small series with a signal of ca. m/z 2638 ± 104 could be seen. No obvious structure corresponding to this distribution could be attributed (PS terminated with –H, -OH, -Si(CH_3)_2OH, Cl, other counterion, etc.).
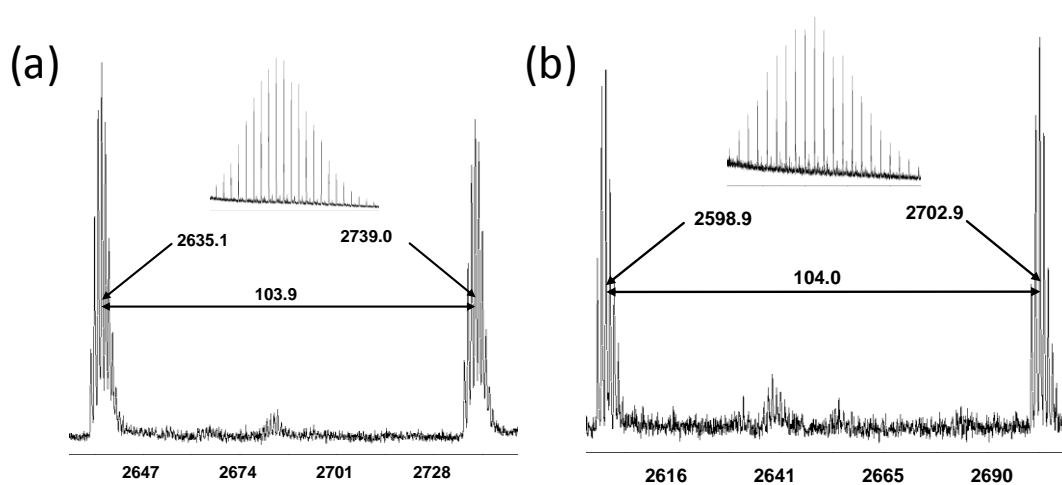

Figure S2. MALDI-TOF mass spectra of **1d** using dithranol/THF and a) AgTFA, b) NaTFA.

Synthesis and characterization of methyl(trimethylsilyl)ethynylsila[1]ferrocenophane 3b. The monomer was prepared using a similar approach to previously reported syntheses of other alkyne-containing sila[1]ferrocenophanes.[2] *n*-BuLi (1.6 M, 20.0 mL, 32.0 mmol) was added dropwise to a solution of ethynyltrimethylsilane (4.75 mL, 33.6 mmol) in Et_2O (50 mL) at 0 °C. The solution was kept at 0 °C for 1 h, and it was added dropwise to a solution of $[Fe(\eta-C_5H_4)_2Si(CH_3)Cl]$ (8 g, 30.4 mmol) in Et_2O (200 mL) at -78 °C. The reaction mixture was allowed to warm to 20 °C and was stirred for a further 3 h. $ClSiMe_3$ (10 drops) was added and the orange suspension was stirred for 30 min. All volatile materials were removed under vacuum, and the orange residue was dried under vacuum overnight. The solid was dissolved in hexanes, and the red solution was filtered through celite on a glass frit to remove LiCl. The solvent was evaporated and the solid was sublimed to yield 9.3 g of crude monomer. Three recrystallizations in hexanes followed by three sublimations gave highly purified red crystals, with a yield of 6.12 g (18.9 mmol, 62%). This stringent purification protocol is necessary to obtain highly pure monomer for photocontrolled living anionic ROP reactions.

^{1}H NMR (300.5 MHz, C_6D_6, 25°C): δ 4.44 (m, 2H, Cp), 4.42 (m, 2H, Cp), 4.36 (m, 2H, Cp), 3.85 (m, 2H, Cp), 0.51 (s, 3H, Si(C*H*$_3$)), 0.16 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75.6 MHz, C_6D_6, 25°C): δ 117.0 (C≡*C*Si(CH$_3$)$_3$), 108.9 (*C*≡CSi(CH$_3$)$_3$), 78.3, 78.2, 76.7, 74.6 (Cp), 30.0 (*ipso*-Cp), -0.06 (Si(CH$_3$)$_3$) - 3.2 (CH$_3$); ^{29}Si DEPT NMR (59.6 MHz, C_6D_6, 25°C): δ -17.8 (*Si*(CH$_3$)$_3$), -29.0 (*Si*(CH$_3$)); EI MS accurate mass (+ mode): calculated 324.0453, observed 324.0461. Elemental analysis calculated for $C_{16}H_{20}FeSi_2$ (%): C 59.25, H 6.22; found C 59.42, H 6.22.

The structure of monomer **3b** was further confirmed by single-crystal X-ray crystallography. The ORTEP diagram of **3b** is shown in Fig. S3 and Table S1 lists selected bond lengths and angles. Two independent molecules of **3b** were located in the asymmetric unit with similar structural metrics. The Fe-Si distances was found to be 2.6711 (3) and the tilt angle (α) between the planes of the two Cp rings was 19.18(13)°. Both values are similar to other ferrocenophanes.[3] The C12-C13 carbon-carbon length (1.2108(2) Å) is typical for a carbon-carbon triple bond[4] and the Si1-C12-C13 and C12-C13-Si2 bond angles (177.3(2) ° and 176.6(4) °) indicated a nearly linear C12-C13 bond.
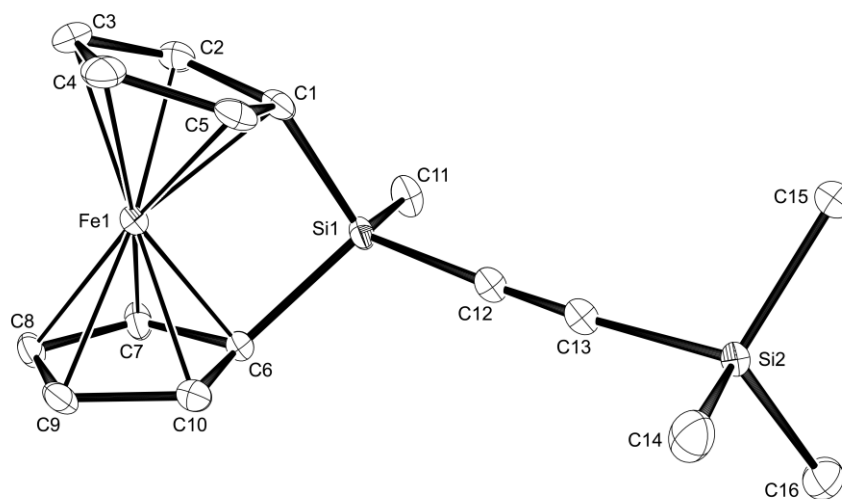
Figure S3. Molecular structure of monomer **3b**. Thermal ellipsoids are displayed at 50 % probability. For clarity, hydrogen atoms have been omitted.

Red-orange colored single crystals of monomer **3b** suitable for X-ray crystallography were obtained by recrystallisation from a dilute hexanes solution at -40 °C. Single-crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data was collected at 100(2) K using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[5] and the data were corrected for absorption using the SADABS program.[6] The structure was solved and refined using the SHELX suite of programs.[7] All molecular structures were generated by using ORTEP-3 for Windows Version 2.02.[8] The hydrogen atoms were included in geometrically calculated positions in the final stages of the refinement and were refined according to the typical riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-832439 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single X-Ray diffraction: $C_{16}H_{20}FeSi_2$; FW = 324.35 g/mol; Triclinic, P-1; a = 11.043(3) Å, b = 13.2414(15) Å, c = 13.5068(15) Å; α = 119.056(2) °, β = 94.309(2) °, γ = 102.937(2) °; V = 1643.0(5) Å^3; Z = 4; 100(2) K; R_1 = 0.0298, ωR_2 = 0.0758 [I>2σ(I)]; GOF = 1.088; of 3490 reflections collected, 3490 were independent.

Table S1 Selected bond lengths (Å) and angles (°) for monomer **3b**.

Si1-C1	1.8796 (2)	C1-Si1-C6	96.62 (6)
Si1-C6	1.8787 (4)	C11-Si1-C12	113.32 (7)
Si1-C11	1.8553 (2)	Si1-C12-C13	177.3 (2)
Si1-C12	1.8391 (3)	C12-C13-Si2	176.6 (4)
C12-C13	1.2108 (2)	α	19.88(13)
Fe1-Si1	2.6711 (3)	β	38.49

5

Gel Permeation Chromatography for PS-PFS block copolymer 4, block copolymers 5, 6 and their precursor 1b and PS$_{365}$-*b*-(AuPFS)$_{122}$ 8
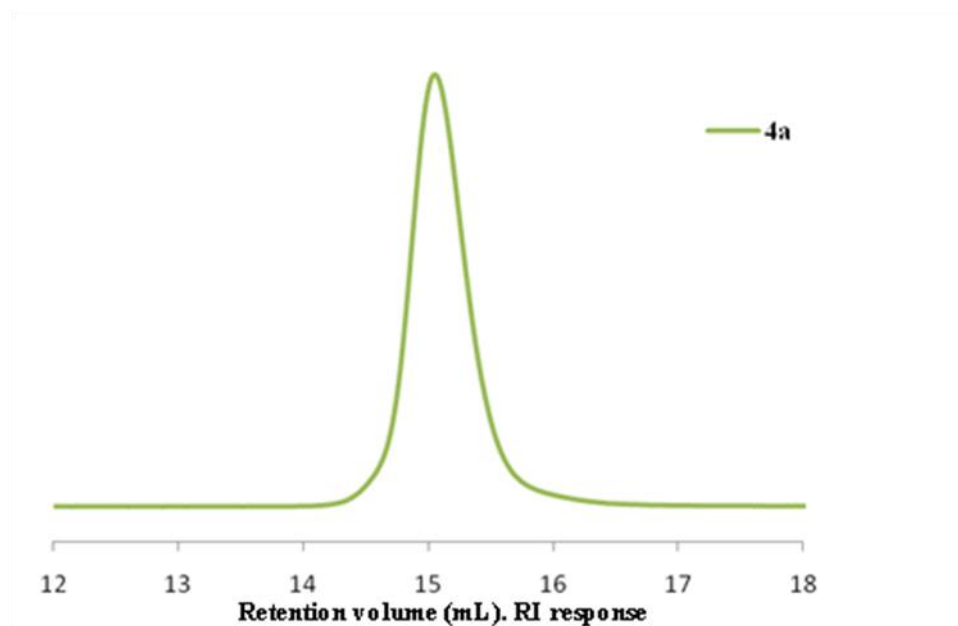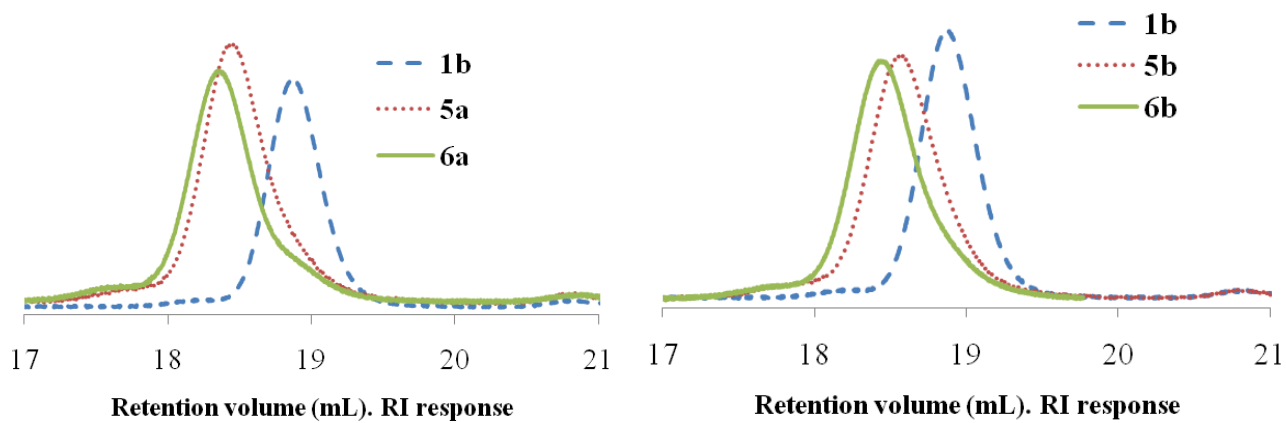

Figure S4. Gel Permeation Chromatography of diblock copolymer **4a** in THF.
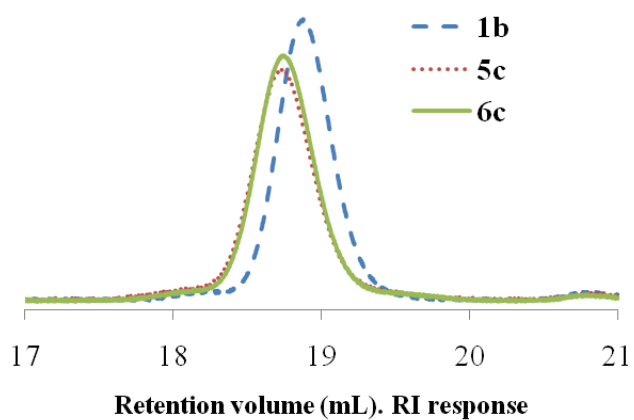
Figure S5. Gel Permeation Chromatography of diblock copolymers **5a-c** and **6a-c**, and their precursor **1c** in THF.
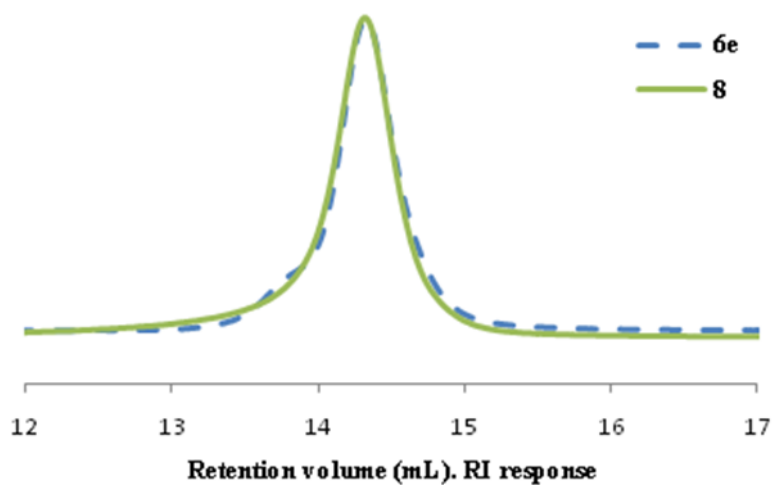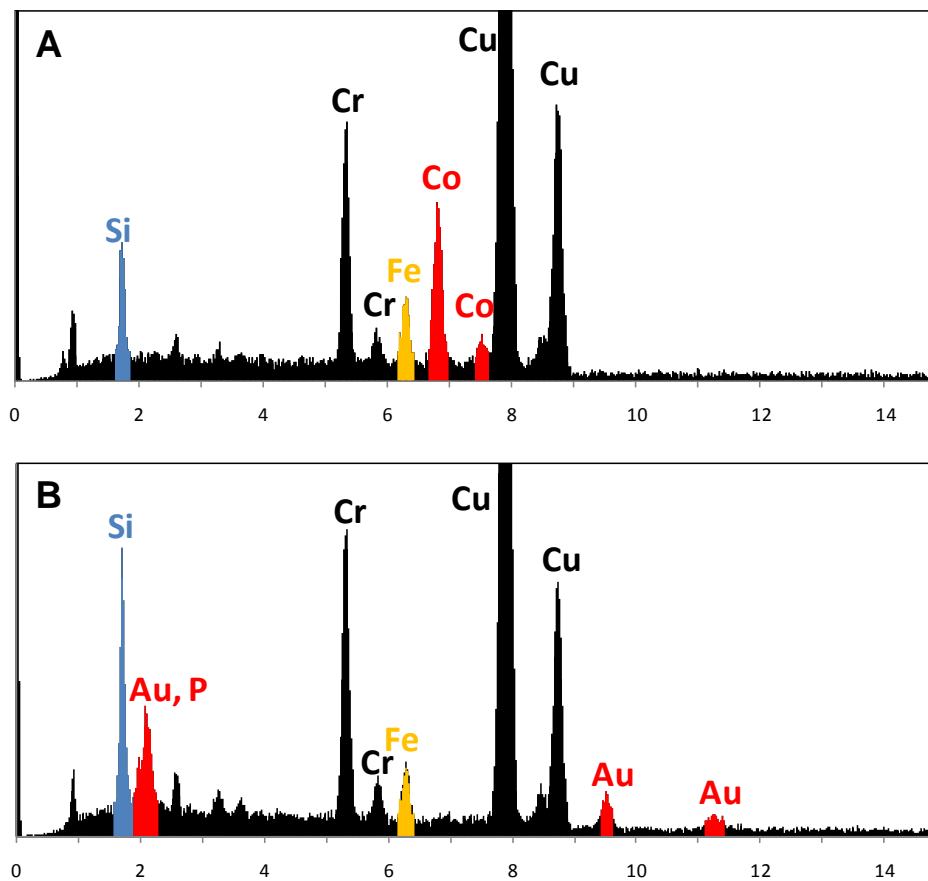

**Figure S6.** Gel Permeation Chromatography of diblock copolymer **8** and its precursor **6e** in THF.

Energy-dispersive X-ray spectroscopy of thin films of block copolymers 7 and 8

Figure S7. Energy-dispersive X-ray spectroscopy of (A) **PS-*b*-(Co-PFS) 7** and (B) **PS-*b*-(Au-PFS) 8** thin films. Samples were deposited on Cu grids, resulting in the presence of signals associated with copper. Cr comes from the sample holder.
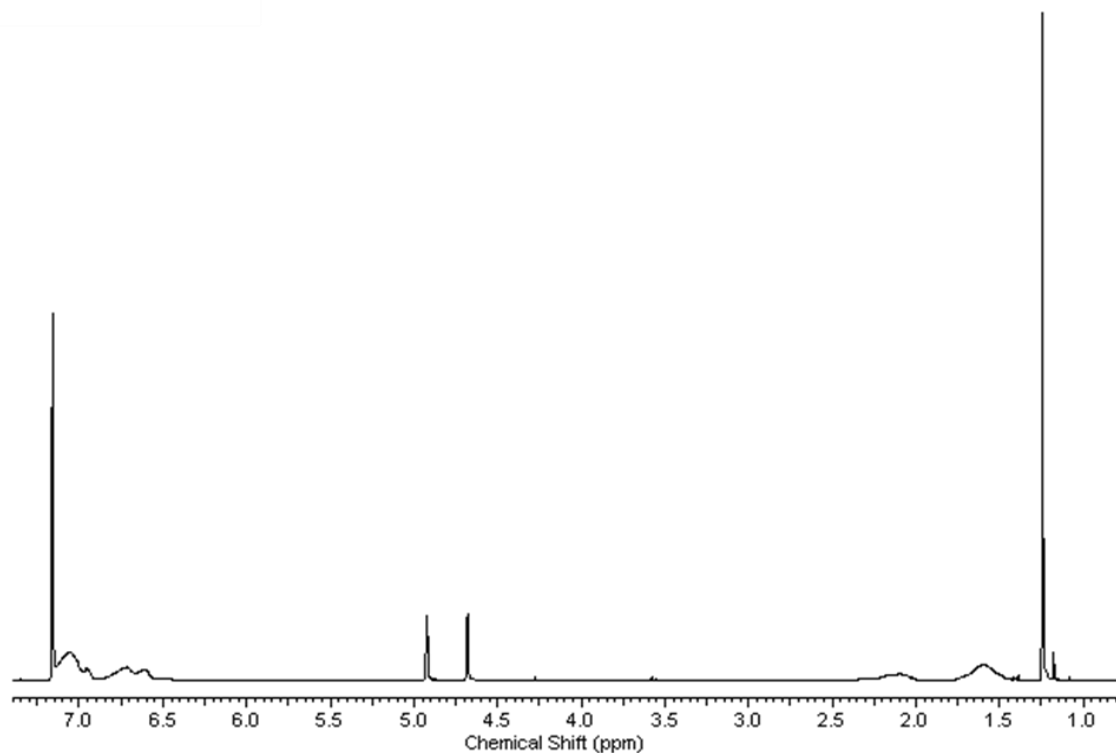
^{1}H NMR spectra for monomer 3b and block copolymers.
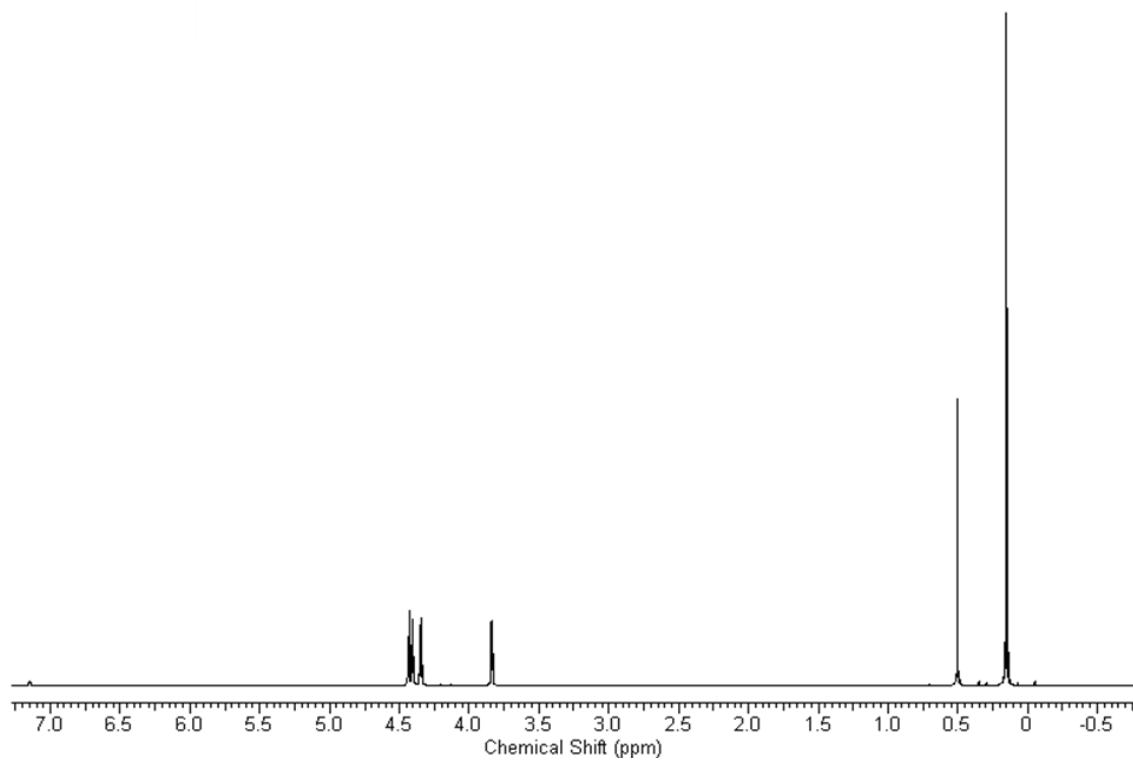
Figure S8. ^{1}H NMR spectrum (C_6D_6) for monomer **3b**.

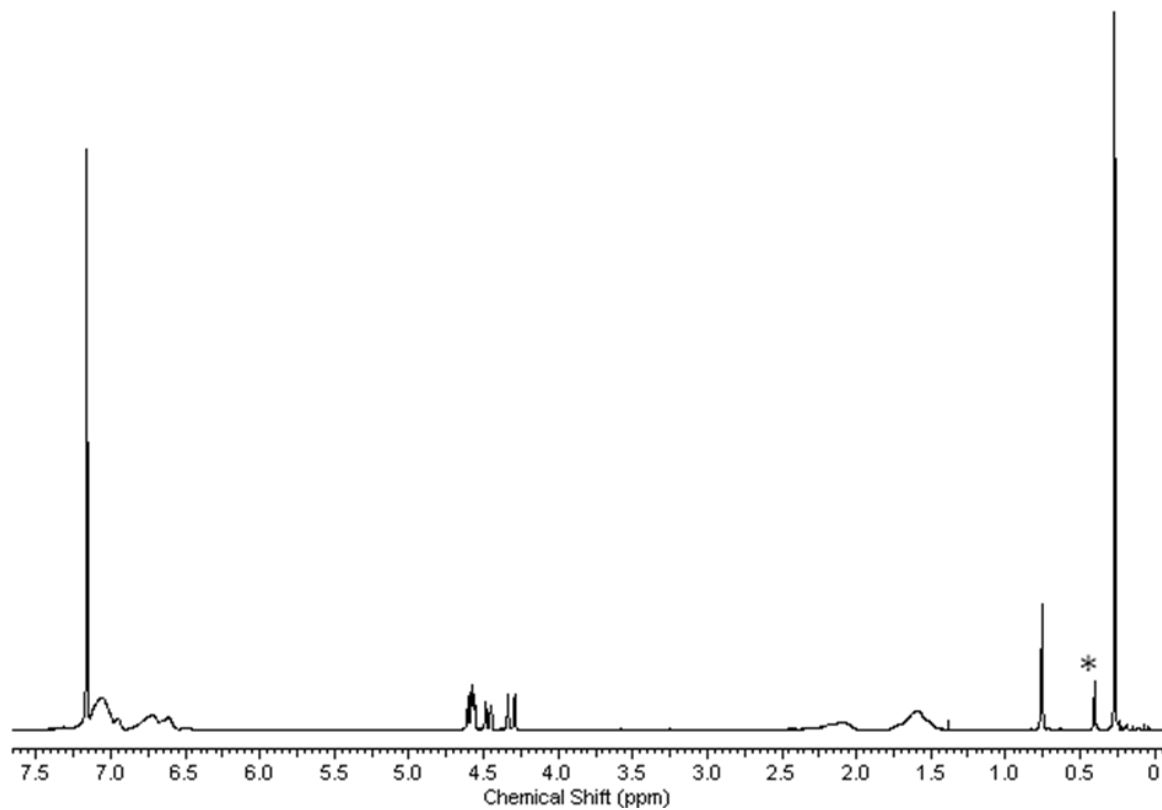**Figure S9**. ^{1}H NMR spectrum (C_6D_6) for block copolymer **4a**.

Figure S10. ^{1}H NMR spectrum (C_6D_6) for **5a.** * residual water.
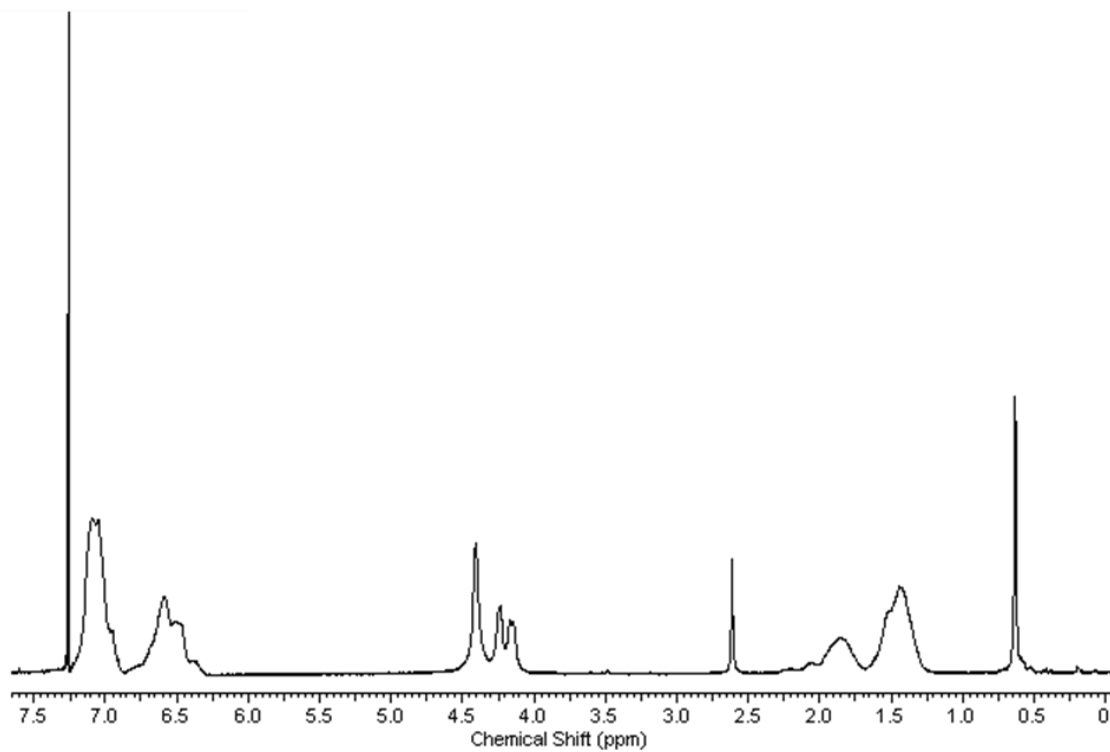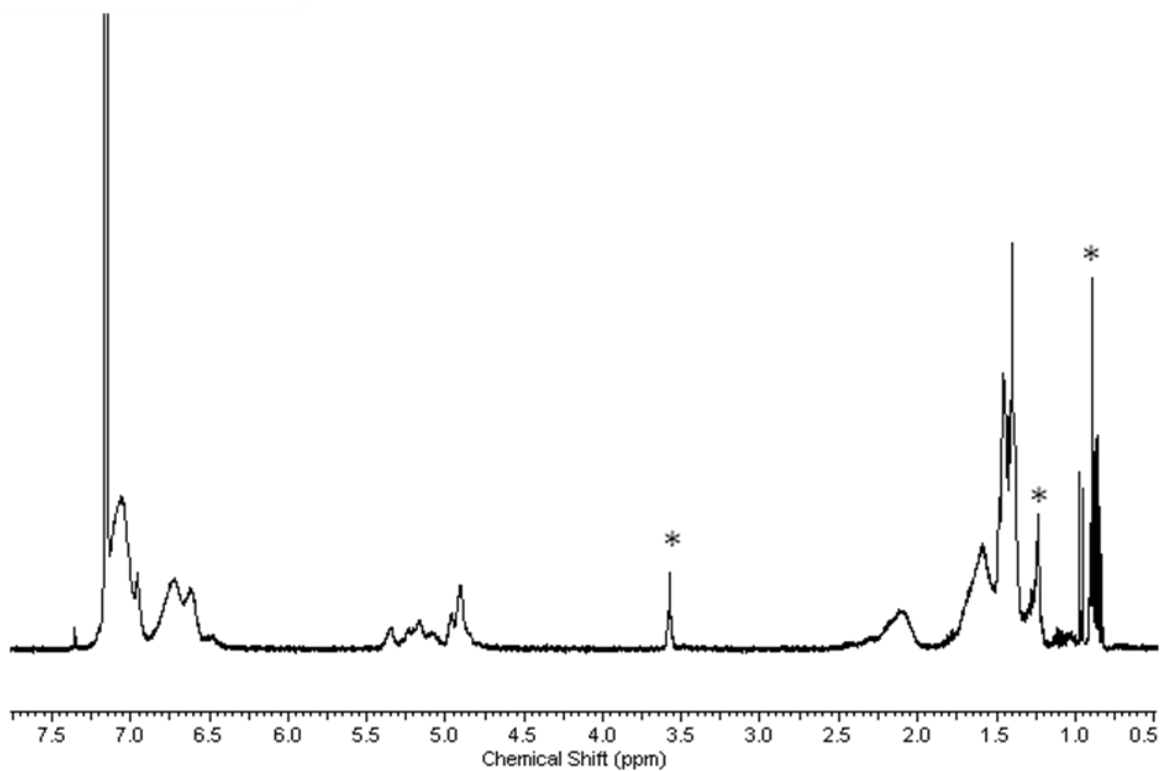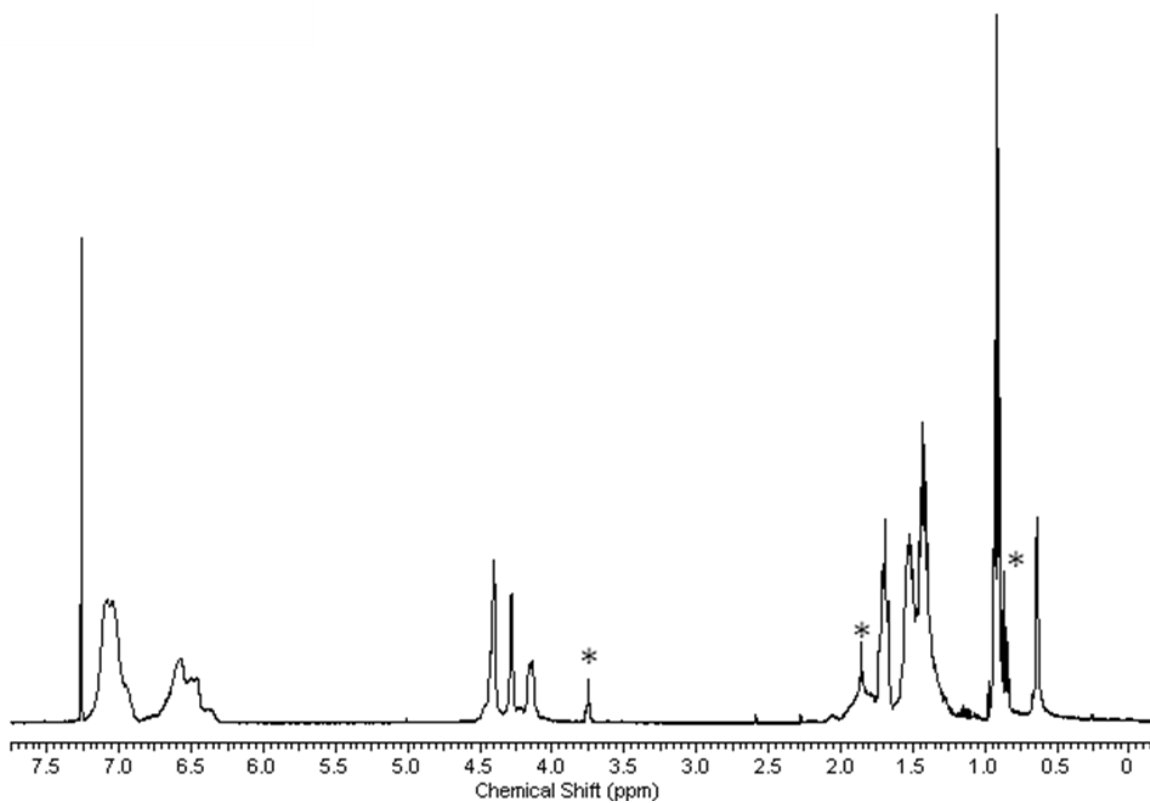

Figure S11. ^{1}H NMR spectrum ($CDCl_3$) for block copolymer **6a**.

Figure S12. ^{1}H NMR spectrum (C$_6$D$_6$) for **7.** * residual hexanes and THF.

Figure S13. ^{1}H NMR spectrum (CDCl$_3$) for **8.** * residual hexanes and THF.

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