

Supporting Information:

General: ^1H and ^{13}C nuclear magnetic resonance spectra were recorded at 300MHz and 75 MHz respectively. The chemical shifts are reported in ppm relative to tetramethylsilane in deuterated chloroform which was used as an internal standard. All glassware was oven dried and reactions were run under an inert atmosphere of argon. The yields reported were from isolated products determined to be pure from by thin layer chromatography and NMR spectroscopy. The solvents used were dried by established distillation methods under an inert atmosphere of argon from the appropriate drying reagents. A 254nm UV light and *p*-anisaldehyde in ethanol and acetic acid were used as indicators to visualize the plates. For the ICP-MS experiments, the sample was administered in nitric acid.

Soluble Chloromethylated Polystyrene 7: This procedure was modified from that of Narita.² A solution of styrene (13.6 g, 131 mmol), 4-vinylbenzylchloride (9.9 g, 65.4 mmol), and AIBN (0.21 g, 1.3 mmol) was stirred in benzene (48 mL). The mixture was degassed with argon for 20 min and subsequently heated to reflux for a period of 40 h. The solution was slowly poured into methanol at -40°C and allowed to cool for a short time. The precipitate was collected by filtration, and dried under vacuum for 12h to yield 19.36g white solid identical in all respects to that of Narita.²

Soluble Allylether Polystyrene 8: Sodium hydride (60% in oil, 3.21g, 80.2 mmol) was stirred in pentanes (3 x 15mL) to remove the mineral oil. Dimethylacetamide (20 mL) was added to the base and a solution of allyl alcohol (4.23 g, 72.9 mmol) dissolved in dimethylacetamide (50 mL) added slowly, and the mixture was allowed to stir at room temperature for 1h under Ar. The deprotonated allyl alcohol solution was added via cannula to the benzyl chloride polymer (9 g, 24.3 mmol) which was dissolved in dimethylacetamide (65mL). The mixture was stirred at room temperature for 24 h and then slowly poured into cold methanol (-78°C). The yellow precipitate was isolated by partial vacuum filtration to give 6.66 g of polymer after full pump under vacuum for 12h. ^1H NMR δ 7.3-6.3 (m, 14H), 6.0 (s, 1H), 5.3-5.2 (m, 2H), 4.4 (s, 2H), 4.0 (s, 2H), 2.2-1.2 (m, 10H).

Soluble Allylstannane Polystyrene (2b): Dibutyltindichloride (3.15 g, 10.4 mmol) and the allylether polymer **8** (2.5 g, 6.5mmol) were dissolved in distilled benzene in a pyrex test tube filled under an inert atmosphere of argon. Fresh dibutyltindihydride (2.43 g, 10.4 mmol) was added dropwise. The solution was irradiated as close as possible to a the water jacket of a 450 watt photochemical apparatus for 20 h. Excess solvent from the solution was removed by a rotary evaporator. The mixture was extracted with ethyl acetate, and washed with water and brine solution. The ethyl acetate was removed under reduced pressure, and the remaining viscous mixture was dissolved in the minimal amount of THF (3mL), and poured into cold methanol. The gray precipitate was collected through vacuum filtration to yield 3.1 g. ^1H NMR δ 7.3-6.1 (m, 14H), 4.4 (s, 2H), 3.3 (s, 2H), 2.0-0.7 (m, 36H).

A solution of the tin chloride polymer (2.0 g, 3.6 mmol) dissolved in dry THF was placed under an atmosphere of argon and cooled to 0 °C. Allylmagnesiumbromide (3.12 g, 21.5 mmol) was added dropwise and the resulting solution was stirred at reflux for 8 h. The solvent was removed by reduced pressure and the remaining gray gel-like solution was extracted with ethyl acetate. The organic layer was then washed with water and an ammonium chloride solution. The ethyl acetate was removed through the use of the rotary evaporator, and the mixture was redissolved in the minimal amount THF (2 mL). The solution was poured into cold methanol (-40 °C), and the white solid was collected by filtration to give 1.64 g. ¹H NMR 7.2-6.2 (m, 15H), 5.9 (m, 1H), 4.8-4.6 (m, 2H), 4.3 (s, 2H), 3.3 (s, 2H), 2.0-0.8 (m, 42H)

General Procedure for the Free Radical Allylation: Allylstannane polymer **2b** (1.5 g, 1.44 mmol) dissolved in the minimal amount of distilled benzene. AIBN (63 mg) and an alkyl bromide (0.16 g 0.96mmol) were added and the solution was degassed with argon for 20 min. After the starting material was consumed by GC or TLC analysis, the mixture was slowly poured into cold methanol. The white precipitate was then separated by vacuum filtration and the filtrate was concentrated under reduced pressure. The crude oil was then subjected to flash chromatography to afford the allylated product.

3-Allyldihydrofuran-2-one (10): Spectral data was identical in all respects to that reported by Molander and Harris.⁷

3-Allyl-3-methyldihydrofuran-2-one (12): Spectral data is identical in all respects to that reported by Toru and co-workers.⁸

2-2-Dimethyl-1-phenyl-4-pentene (14): Spectral data is identical in all respects to that reported by Barentson and co-workers.⁹

1-Phenyl-4-pentenone (16): Spectral data is identical in all respects to that reported by Yasuda and co-workers.¹⁰

Bromide 18: ¹H NMR: δ 5.8 (m, 1H), 5.2 (m, 2H), 3.6 (d, 1H), 3.2 (d, 1H), 2.5 (m, 1H), 2.4 (m, 2H), 1.6 (m, 3H), 0.9 (s, 3H), 0.8 (s, 3H); ¹³C NMR (CDCl₃) δ 219.5, 135.9, 116.3, 59.4, 48.9, 43.9, 39.8, 31.4, 30.6, 19.4, 16.6, 9.8, 1.4, 1.0; IR (NaCl) cm⁻¹: 2952.9, 1740.6, 1638.9, 1447.4; HRMS (EI) calcd for C₁₃H₁₉BrO 270.061926, found 270.061938.

Ketone 20: Spectral data is identical in all respects to that reported by Ng and Alper.¹¹