

Supplementary Material For:

## Convenient Catalytic Free Radical Reductions of Alkyl Halides Using an Organotin Reagent on Non-Cross-Linked Polystyrene Support

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***p*-Chloromethyl polystyrene 7.** To a solution of styrene (**5**) (15.9 g, 17.5 mL, 153 mmol), 4-vinylbenzyl chloride (**6**) (13.0g, 77.0mmol), and benzene (50mL) was added AIBN (0.122 g, 0.74 mmol). The solution was then degassed with a stream of argon and heated to 80°C in an oil bath. After a reaction time of 40 h, the solution was cooled to rt and then poured into methanol (250 mL). Subsequent vacuum filtration onto a Büchner funnel and washing with methanol yielded the *p*-chloromethyl polystyrene polymer **7** (25.9g, 94%) as a white solid (ACV=2.77mmol/g): <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ: 0.90-2.30 (m, 9H), 4.51 (m, 2H), 6.00-7.50 (m, 14H). Integration by proton NMR was utilized to determine a Cl-CH<sub>2</sub>- content of 33%.

**Allylether polymer 8.** Mineral oil was removed from NaH (60% in oil, 0.73g, 30mmol) with pentanes. Dimethylacetamide (DMA) (5mL) was added to the NaH under a stream of argon. At 0°C, allyl alcohol (1.76g, 2.08mL, 30.3mmol) was added dropwise to the NaH mixture. Upon completion of the addition, the solution was stirred for 1h. Meanwhile, **7** (2.0g) was dissolved in DMA (6mL). The polymer solution was then added to the allyl alcohol via cannula at 0°C. After stirring at room temperature for 24h, the solution was poured into vigorously stirring cold methanol (-40°C). Subsequent vacuum filtration onto a Büchner funnel and washing with methanol yielded a white crystalline solid (ACV=2.62mmol/g). The desired allylether polymer **8** was pumped dry to give 1.6g (74% yield): <sup>1</sup>H NMR integration indicated a 99% displacement of reactive sites: <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ: 1.0-2.3 (m, 10H), 3.98 (m, 2H), 4.42 (m, 2 H), 5.27 (m, 2 H), 5.94 (m, 1H), 6.14-7.40 (m, 14H).

**Dibutyltinchloride polymer 2b.** A solution of **8** (8.08g, 21.0mmol) and dibutyltin dichloride (10.2g, 33.6 mmol) in 20 mL benzene under argon was sealed in a pyrex tube. Slowly, dibutyltin dihydride (7.9g, 34mmol) was added and the solution was irradiated with a Hanovia 450 watt mercury lamp for 8h. The solution was then poured into 400 mL of vigorously stirring methanol. The liquid was decanted and MeOH (50mL) was added. The suspension was cooled to -78°C to solidify the product, and the solid was rinsed well before collecting by vacuum filtration. The product (ACV=1.53mmol/g) was pumped to dryness to yield the desired dibutyltin chloride polymer **2b** as a white-gray solid (12.74g, 93% yield). <sup>1</sup>H NMR integration indicated a 92% incorporation of tin at the active sites: <sup>1</sup>H NMR (CDCl<sub>3</sub>)δ: 0.8-2.1 (m, 36 H), 3.3 (m, 2H), 4.4 (m, 2H), 6.1-7.2 (m, 14 H).

**General procedure for radical dehalogenations.** To a solution of 1-bromoadamantane (**9**) (50mg, 0.23mmol) in DMA (0.19M, 1.3mL) was added AIBN (4mg, 0.1equiv), followed by decane (35mg, 0.24mmol, 1.1equiv) as an internal standard. Lastly, NaBH<sub>4</sub> (14mg, 0.35mmol) and **2b** (15mg, 0.1equiv) were added. The solution was heated to 80°C and after 2h, a GC sample was taken to evaluate the efficiency of the reaction. Comparison of product peak with that of the decane standard indicated 99% conversion. The solution was filtered, diluted with ether, extracted twice with water, then once with brine and dried with Na<sub>2</sub>SO<sub>4</sub>. Next, the solvent was evaporated and the product was purified by column

chromatography. Adamantane (**10**) was isolated as a white solid (38mg, 60% yield). Adamantane was identical in all respects to an original sample purchased from the Aldrich Chemical Co.

**Iodoxylose sugar 11.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.32 (s, 3H), 1.52 (s, 3H), 2.23 (d, 1H,  $J=5.1$  Hz), 3.29 (m, 2H), 4.43 (m, 2H), 4.57 (d, 1H,  $J=3.6$ Hz), 5.99 (d, 1H,  $J=3.6$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : -1.2, 26.2, 26.8, 74.8, 80.8, 85.0, 105.5, 112.1; HRMS (EI) calcd for  $\text{C}_8\text{H}_{13}\text{IO}_4$  (M+) 299.9859, found 299.9834.

**Deoxyxylose sugar 12.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.31 (s, 6 H), 1.50 (s, 3H), 2.33 (s, br, 1H), 3.99 (d, 1H,  $J=2.4$  Hz), 4.31 (m, 1H,  $J=2.7, 6.6$  Hz), 4.52 (d, 1H,  $J=3.6$  Hz), 5.89 (d, 1H,  $J=3.6$  Hz);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 12.71, 26.05, 26.49, 76.02, 76.18, 85.46, 104.30, 111.34; IR (neat)  $\text{cm}^{-1}$ : 1013.3, 1073.6, 1165.8, 1215.7, 1374.9, 1627.3, 3445.1; HRMS (EI) calcd for  $\text{C}_8\text{H}_{15}\text{O}_4$  (M+1) 175.0970, found 175.0952.

**ACV** = active content value = the amount of active sites in the polymer (in mmol/g) from NMR integration