Supporting Information

Title: "Analysis of the products of the anionic oligomerisation of a phosphaalkene using MALDI-TOF mass spectrometry"

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General Procedure for MALDI-TOF MS

The MALDI spectra were acquired using a Bruker Biflex IV spectrometer. The samples were dissolved in dichloromethane (CH_2Cl_2) and deposited on the sample target with a layer of matrix previously deposited. The matrix, 2,5-dihydroxybenzoic acid, was dissolved in THF. The measurements were performed using the following conditions: positive polarity, reflection flight path, 18kV acceleration voltage, 20 shots per sample. Insulin Chain B, bovine insulin (oxidized) and Angiotensin II, human synthetic were obtained from Sigma-Aldrich and used as standards.

Anionic oligomerisation of 1. To a stirred solution at -78 °C of mesityl(diphenylmethylene)phosphine **1** (0.050 g, 0.16 mmol) dissolved in diethyl ether (20 mL) was added slowly 1.5M methyllithium in diethylether (0.13 mL, 0.19 mmol). After warming to room temperature, an aliquot was removed and analysed by ^{31}P NMR (Mes(Me)P-CPh_2Li, □= -45 ppm). After warming to room temperature, a solution of **1** (0.150 g, 0.47 mmol) dissolved in diethyl ether (20 mL) was added slowly to the reaction mixture. After stirring for 24 hours, the reaction was quenched with degassed water. The

solvent was removed in vacuo leaving a dark yellow oil. To the oil was added dichloromethane (10 mL) and the suspension was filtered then oxidized with hydrogen peroxide for 30 min. The organic layer was washed twice with water and dried over magnesium carbonate. The solvent was removed in vacuo leaving a pale yellow oil. The oil was dissolved in a small amount of dichloromethane precipitated from hexanes leaving a colourless, sticky solid. Yield=0.11 g (54%).

Anionic oligomerisation of 1. Prepared as above, but with an overall **1**:BuLi ratio of 2:1 rather than 1:4 above; thus, the lower molecular weight.

Figure A1. MALDI-TOF mass spectrum of BuLi initiated oligomers.