

## Supporting Information For:

### ROMP-Spheres: A Novel High-Loading Polymer Support Using Cross Metathesis Between Vinyl Polystyrene and Norbornene Derivatives

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**General Considerations.** All solvents used were freshly distilled according to standard procedures. TLC was performed on Merck silica gel 60 F<sub>254</sub> plates on aluminium. Melting points were recorded on a Gallenkamp variable heat melting point apparatus. Multiple evaporations were performed on a Genevac HT-12 centrifugal evaporator or a Jouan RC10.22 centrifugal evaporator. IR spectra (KBr and film) were recorded using a Mattson 5000 FTIR. Single bead IR spectra were recorded on a Mattson ATI Quantum Infrared Microscope fitted with a Mattson Infinity Series FTIR Spectrometer. All spectra are measured in cm<sup>-1</sup>, relative to polystyrene (1630 cm<sup>-1</sup>). NMR spectra were recorded in CDCl<sub>3</sub>, unless otherwise specified. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a JEOL GSX 270 (270 MHz) spectrometer or a Bruker DRX 300 (300 MHz) spectrometer. Chemical shifts are measured in ppm relative to CHCl<sub>3</sub> (<sup>1</sup>H; δ 7.26 ppm, <sup>13</sup>C; δ 77.0 ppm). GC/MS data was obtained from a Hewlett-Packard HP5 capillary column GC/MS machine: column 25m long, 0.25 mm internal diameter; carrier gas: helium; MS detector EI+, The following abbreviations apply: EI = electron impact, CI = chemical ionisation, FAB = fast atom bombardment, ES = electrospray. Suffix positive or negative signs refer to the charge of the ions detected

#### Preparation of Bis(tricyclohexylphosphine)alkylidene Ruthenium(IV) Dichloride Resin **3**.

To a suspension of vinyl polystyrene **2** (100-200 mesh, 100 mg, 0.8 mmol g<sup>-1</sup>, 0.08 mmol) in dichloromethane (2 mL) was added a solution of bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs catalyst, 5.5 mg, 6.6 μmol) in dichloromethane (0.1 mL) and the mixture was shaken for 1h. The resin was filtered under an atmosphere of nitrogen and washed thoroughly with dichloromethane and ether. The resin was dried under vacuum at 40 °C to give the supported catalyst **3** (0.101g) as a brown resin.

#### Preparation of Bromobenzoate Resin **8**.

To a suspension of the supported catalyst **3** (100 mg) in dichloromethane (2 mL) was added a solution of norborn-5-en-2-ylmethyl 4-bromobenzoate **7** (0.41 g, 1.34 mmol) in dichloromethane (1 mL), and the mixture was shaken overnight. A few drops of ethyl vinyl ether were added and the mixture was shaken for 30 min. The mixture was filtered and the resin was washed with dichloromethane (5 × 3 mL), methanol (3 mL), dichloromethane (3 mL), methanol (3 mL) and dried under vacuum at 40 °C overnight to give **8** (0.44 g, 83% monomer incorporation) as a pale brown resin. IR (single bead) 1716-1725 (vs). Loading 2.5 mmol g<sup>-1</sup>.

**Hydrolysis of Bromobenzoate Resin **8**.** To a suspension of bromobenzoate resin **8** (100 mg, 2.8 mmol g<sup>-1</sup>, 0.28 mmol) in THF (2 mL) was added lithium hydroxide (58.8 mg, 1.4 mmol)

in water (0.4 mL) and methanol (0.4 mL) and the mixture was shaken for 3 d. The mixture was filtered and the resin was washed with THF (2 × 3 mL), water (2 × 3 mL) and methanol (2 × 3 mL). The combined filtrates were diluted further with water (10 mL) and acidified to pH 1 with concentrated hydrochloric acid, forming a white precipitate. The mixture was extracted with ethyl acetate (3 × 15 mL), the organics washed with water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to give 4-bromobenzoic acid **10a** (55 mg, 95%) as a white solid, identical (<sup>1</sup>H NMR) to an authentic sample. The resin was washed further with dichloromethane (3 × 3 mL) and methanol (3 × 3 mL) and dried under vacuum at 40 °C overnight to give hydroxy resin **9** (55 mg, 100%). IR (single bead) 3340 (br). Loading 5.1 mmol g<sup>-1</sup>.

**Transesterification of Bromobenzoate Resin 8.** To a suspension of bromobenzoate resin **8** (100 mg, 2.8 mmol g<sup>-1</sup>, 0.28 mmol) in THF (4 mL) was added sodium methoxide (4.5 mg, 0.08 mmol) in methanol (1 mL) and the mixture was shaken for 48 h. The resin was filtered and washed with THF (2 × 3 mL), methanol (2 × 3 mL), dichloromethane (2 × 3 mL) and methanol (2 × 3 mL). The filtrate was evaporated to dryness to give methyl 4-bromobenzoate **10b** (62 mg, 95%), identical (<sup>1</sup>H NMR) to an authentic sample. Hydroxy resin **9** was recovered as detailed above.

**Re-esterification of Hydroxy Resin 9.** To a suspension of hydroxy resin **9** (100 mg, 4.5 mmol g<sup>-1</sup>, 0.45 mmol) in dichloromethane (3 mL) was added 4-nitrobenzoyl chloride (0.37 g, 2 mmol) in dichloromethane (3 mL) followed by 4-dimethylaminopyridine (0.12 g, 1.0 mmol). The mixture was shaken for 3 d, filtered and washed with dichloromethane (2 × 3 mL), methanol (2 × 3 mL), water (2 × 3 mL), aqueous NaHCO<sub>3</sub> (3 mL), water (2 × 3 mL), DMF (2 × 3 mL), methanol (2 × 3 mL), dichloromethane (2 × 3 mL) and methanol (3 × 3 mL). The resin was dried under vacuum at 40 °C, overnight to give nitrobenzoate resin **11** (170 mg). IR (single bead) 1725 (vs), 1526 (m), 1345 (m). Loading 2.64 mmol g<sup>-1</sup>.

**General Procedure for Palladium Catalysed Coupling Between Bromobenzoate Resin 8 and an Aryl Zincate.** To a stirred solution of fused zinc chloride (0.48 g, 3.5 mmol) in THF (8 mL) at -20 °C was added dropwise 4-fluorophenylmagnesium bromide (1.25 mL, 2M solution in ether, 2.5 mmol). The resultant mixture was allowed to warm to room temperature and was added to a heated mixture of bromobenzoate resin **8** (180 mg, 2.85 mmol g<sup>-1</sup>, 0.5 mmol), [1,1'-Bis(diphenylphosphino)-ferrocene]dichloropalladium(II) (37 mg, 0.05 mmol) and DME (0.38 mL, 0.4 mmol) in THF (3 mL) at reflux. The mixture was heated at reflux for 24 h. The mixture was allowed to cool and was filtered using acetone to assist in the transfer, and the resin was washed with acetone, water, hydrochloric acid (1M) water, DMF, dichloromethane, methanol and dried under vacuum at 40 °C overnight to give the 4-(4-fluorophenyl)benzoate resin **15** (0.183 g). Loading 2.73 mmol g<sup>-1</sup>.

**Transesterification of 4-(4-Fluorophenyl)benzoate Resin 15.** To a suspension of 4-(4-fluorophenyl)benzoate resin **16** (0.183g, 2.73 mmol g<sup>-1</sup>, 0.5 mmol) in THF (8 mL) was added sodium methoxide (27 mg, 0.5 mmol) in methanol (2 mL). The mixture was heated at reflux overnight. After cooling, the resin was filtered and washed with dichloromethane (3 × 10 mL) and methanol (2 × 10 mL). The filtrate was further diluted with dichloromethane (20 mL), washed with water and dried over sodium sulfate. The solvents were removed on a rotary evaporator to give methyl 4-(4-fluorophenyl)benzoate **16** as an off-white solid (83mg, 72%). mp 95-97 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.10 (2H, d, *J* = 8.5 Hz, Ar-H), 7.60 (4H, m, Ar-H), 7.15 (2H, t, *J* = 8.7 Hz, Ar-H), 3.94 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 166.9, 164.1, 144.6, 136.1,

130.1, 128.9, 128.8, 126.8, 115.9, 115.7, 52.1; IR (neat) 1725 (s), 1294, 1113, 833; MS (CI, NH<sub>3</sub>): m/e 248 [M + NH<sub>4</sub>]<sup>+</sup>, 230 [M + H]<sup>+</sup>, 199 [M - CH<sub>3</sub>O]<sup>+</sup>, HRMS: Calcd. for C<sub>14</sub>H<sub>15</sub>FNO<sub>2</sub>, 248.108682 [M + NH<sub>4</sub>]<sup>+</sup>, Found: 248.108175.

**Preparation of a Block Co-Polymer (Bromobenzoate 7)-(Nitrobenzoate 14) Resin 18.** To a suspension of the supported catalyst **3** (100 mg) in dichloromethane (1 mL) was added norborn-5-en-2-ylmethyl 4-bromobenzoate **7** (0.2 g, 0.65 mmol) in dichloromethane (0.5 mL) and the mixture was shaken for 75 min. The resin was filtered under an atmosphere of nitrogen and washed with dichloromethane (6 × 3 mL). The resin was resuspended in dichloromethane (1.5 mL) and treated with norborn-5-en-2-ylmethyl 4-nitrobenzoate **14** (0.18 g, 0.66 mmol) in dichloromethane (0.5 mL). The mixture was then shaken overnight before addition of a few drops of ethyl vinyl ether. The mixture was filtered and washed with dichloromethane (3 × 3 mL), methanol (2 × 3 mL), dichloromethane (2 × 3 mL), methanol (2 × 3 mL) and dried under vacuum at 40°C overnight to give the block co-polymer **18** (0.3 g).