Supplementary Material:

General Procedures. Materials were obtained from Aldrich, Acros and Strem and used without further purification. Solvents, triethylamine and triphenylphosphine were purified according to standard procedures. The ^{1}H and ^{13}C spectra were obtained on a Varian Inova 500 MHz spectrometer. Chemical shifts are reported in δ using solvent as the internal reference. A Varian 3800 gas chromatograph fitted with a CP Sil regular phase column (15.0 m x 0.25 mm i.d.) was used for to collect GC data. Peak areas were measured using the Varian Star 6.2 software package, and response factors of authentic materials versus methyl benzoate (internal standard) were calculated for determining reaction conversion. The ICP analysis was performed by the Nutrient and Elemental Analysis Lab in the Department of Horticulture at Cornell University.

Preparation of PdxRMs (2). Cross-linked reverse micelles were synthesized according to the literature procedure with an approximate ω value of 1 (ω = [water]/[amphiphile]). $Pd(OAc)_2$ (0.1 mol %) was added to the toluene xRM solution and briefly sonicated to give a pale yellow solution. After rocking for 8-10 hours, the solution turned to a deep brown color and the toluene was removed, leaving a brown glassy solid. The solid was sonicated into ethanol and allowed to incubate over night. The brown solid was then recovered with 20 minutes of centrifugation. The supernatant was removed and saved for further precipitation. The isolated solid was then washed (x3) and centrifuged from ethanol. The brown solid was then dried under vacuum. The brown powder was dissolved in concentrated nitric acid and sent for ICP and found to be 2.51% Pd by weight.

Preparation of Nonpolymerizable Amphiphile (3). The acid terminated amphiphile, **1**, (1.0 g, 1.9 mmol) was added to a hydrogenation vessel and dissolved in ethyl acetate. The solution was then flushed with N_2. A spatula tip full of 10% Pd/C was added to the vessel. The reaction was shaken under hydrogen (35 psi) using a Parr hydrogenator for 24 hours. The crude reaction mixture was then filtered through celite and concentrated, yielding 0.82 g (82%) of **3** as colorless oil. This crude product showed no evidence of polymerizable groups and was used for RM experiments. For analytical data, the compound was further purified by chromatography (Hexanes: 1:1 Hexanes: Ethyl Acetate). ^{1}HNMR (500 MHz, $CDCl_3$): δ 4.30-4.20 (m, 4H), 3.56-3.54 (m, 2H), 3.42-3.48 (m, 2H), 3.29-3.25 (m, 4H), 2.76-2.70 (m, 2H), 1.46-1.13 (m, 27H), 0.88-0.81 (m, 12H). ^{13}CNMR (500 MHz, $CDCl_3$): δ 178.02, 174.47, 74.35, 72.80, 65.31, 46.59, 40.46, 39.74, 30.72, 29.30, 24.02, 23.34, 17.82, 14.37, 14.14, 11.28.

Preparation of PdRMs (4). The hydrogenated amphiphile (**3**) (0.131 g, 0.25 mmol) was dissolved in 5 mL of benzene. Sodium hydroxide (0.0125 g, 0.3 mmol) was added to the mixture along with 6 μL H_2O (0.3 mmol). This mixture was sonicated for 5 minutes to produce a clear solution. $Pd(OAc)_2$ (0.005 g, 0.023 mmol) was added. The mixture was briefly sonicated to break up large $Pd(OAc)_2$ crystals and then rocked. The solution maintained a yellow color and was reduced by stirring under a H_2 atmosphere for about 12-18 hours. The resulting heterogeneous black solution was added directly to a Heck reaction mixture appropriate for its size.

General Heck Reaction Procedure. A 2 mL stock solution containing triethylamine (55 μL, 0.39 mmol, 1.5 eq), methyl benzoate (GC internal standard, 23 μL, 0.02 mmol, 0.08 eq), palladium catalyst (0.45 mol% Pd), aryl iodide (0.78 mmol, 3 eq), and benzene, was made in order to more consistently run small scale reactions. The stock solution (0.3 mL) was added to a 2.0 mL GC autosampler vial with a stir bar. Methyl acrylate (23 μL, 0.26 mmol) was added to the reaction and the vial was sealed with an aluminum crimp lid. The reaction was then placed in a pre-heated oil bath at 60˚ C. All reaction times were started when the vial was immersed in the oil bath as the reactions are extremely slow at room temperature.

General Kinetic Procedure. When measuring rates at low conversions, 5μL aliquots were drawn through the septa cap of the reaction and quenched via dilution in 1.5 mL CH_2Cl_2. The product peak was compared to methyl benzoate, the internal standard. The change in product to standard ratio over time was used to determine k_{rel} value for the reaction, lag times were left out when approximating initial rates. The GC was calibrated using methyl benzoate and trans-methyl cinnamate at known concentrations. This allowed for low conversion yields to be calculated directly from the GC data. When NMR data was necessary, 10 μL samples were drawn from the reaction mixture and quenched in 0.5 mL of d6-benzene. All rate data, whether analyzed by GC or NMR, was collected in triplicate and averaged.

Examples of Raw Rate Plots Reflecting the Induction Period: