Supporting Experimental Information

General Procedures for Molecular Weight Analysis. End group titration was used to characterize the molecular weight of polymers that were not soluble in organic solvents. Fluoroacrylate homopolymers prepared from **1** using 4,4'-azobis(4-cyanovaleric acid) as an initiator were prepared as analogs of **3** and were assumed to have –CO_2H groups on each end. These analogs were titrated to a phenophthalein end point using a biphasic mixture of 1,1,2-trichlorotrifluoroethane containing the homopolymer and ethanol containing 0.01 N NaOH. These molecular weight values were then compared to a similar copolymer of **1** and **2** prepared using 4,4'-azobis(4-cyanovaleric acid) as an initiator. This direct analog of **3** was presumed to contain –CO_2H groups at each terminus. The resulting homopolymer and carboxyl-terminated analog of **3** had M_n values of 120,000 and 108,000 g/mol, respectively, based on such titrations.

Fluoroacrylate Copolymer Synthesis (3). 1*H*, 1*H*, 2*H*, 2*H*-heptadecafluorodecyl acrylate (**1**) (6.64 g, 12.8 mmol) *N*-acryloxysuccinimide (NASI, **2**) (0.114 g, 0.77 mmol) were dissolved in 50 mL of benzotrifluoride. The flask was evacuated and flushed with N_2 three times and then fitted with a reflux condenser. After heating to 80 ^oC, AIBN (0.025 g, 0.15 mmol) in 5 mL of benzotrifluoride was added. The reaction was stirred for 2 d at 100 ^oC and was then cooled to room temperature. The copolymer **3** was precipitated into 75 mL of methanol. ^1H NMR analysis indicated the presence of monomer, so the dissolution and precipitation were repeated again. The copolymer was isolated by filtration and dried under vacuum overnight to give 6.29 g (96%) of a white solid: ^1H NMR (300 MHz) (the samples were dissolved in 1,1,2-trichlorotrifluoroethane with a small amount of acetone-d_6 for locking) □ 1.5-1.9 (br m, 1H), 2.6 (br m, 4H), 2.9 (br s, 0.35H), 4.5 (br s, 2H); IR (KBr, cm^{-1}) 3000 (aliphatic C-H stretch); 1820-1740 (C=O); 1220-1150 (C-F). Obsd: 30.23% C, 1.23% H, 0.27% N and 55.12% F. These values are in agreement with values of 30.34 % C, 1.37 % H, 0.09 % N and 60.63 % F calculated for polymer **3** containing a 10:1 ratio of the fluoroacrylate to NASI groups and a formula $C_{411}H_{231}N_3O_{72}F_{510}$.

Synthesis of Diphenylphosphinopropylamine-ligated Fluorous Copolymer-Ligated Rh(I) Catalyst (5). In a typical procedure, copolymer **3** (0.50 g, ~0.01 mequiv) was dissolved in 5 mL of FC-77[17] under nitrogen in an oven-dried flask. After the flask was flushed with nitrogen, 15 mL of THF was transferred via syringe to the flask followed by the addition of 5 drops (~0.5 g, ~2.0 mmol) of diphenylphosphinopropylamine via syringe. The reaction was stirred vigorously overnight at room temperature under N_2. The top layer was removed by syringe. Fresh THF was introduced into the reaction and the mixture stirred for 10 - 15 min and the top layer was again withdrawn by syringe to remove any excess diphenylphosphinopropylamine. This was repeated twice. The lower fluorocarbon layer was then transferred into a N_2-flushed vial and stored under nitrogen until use. ^1H NMR (300 MHz., FC-77 with an external acetone-d_6 lock) δ 1.5-1.9 (br s, 2H), 2.6 (br s, 3H), 4.5 (br s, 2H), 7.3-

This phosphine-containing copolymer **4** (50 mg) was then dissolved in 5 mL of FC-77 and transferred via syringe into a N_2-flushed, oven-dried flask. $[RhCl(CH_2CH_2)_2]_2$, (4 mg) was dissolved in 10 mL of THF and transferred via syringe into this copolymer solution. The resulting heterogeneous reaction mixture was stirred vigorously overnight at room temperature. The following day the stirring was stopped, the lower fluorocarbon layer was removed, transferred to a hydrogenation vessel and stored under nitrogen until use**.** ^{31}P NMR (121 MHz., $CDCl_3$) δ –16.5, 32.8 (very broad, no splitting was seen). The Rh-containing polymer **16** was also analyzed by combustion analysis: Calcd for structure **16** ($C_{444}H_{270}N_3O_{63}F_{510}P_3RhCl$), 30.66 % C, 1.45 %H, .09 % N, 60.63 %F, .22 %Cl, .19 % P; Obsd 31.32% C, 1.49% H, 0.28% N, 57.96% F, 0.40% Cl, 0.14% P and 0.14% Rh. This corresponds to a Rh loading of 0.013 mmol of Rh/g of polymer and a 3.3/1 ratio of phosphine ligand to Rh.

Typical Procedure for Hydrogenation Reactions. Hydrogenation reactions were generally carried out in a 50-mL, one-necked round-bottomed flask fitted with an adapter connected to a hydrogen gas burette with a leveling bulb. The gas buret had a three-way stopcock that connected one arm to the reaction flask and the other to a manifold attached to a hydrogen gas cylinder. THF and FC-77 were used as solvents for the substrate and catalyst and the reactions were run at atmospheric pressure. The system was flushed with hydrogen 10 times before starting the stirring and following the uptake of H_2

from the gas burette. Upon completion of the reaction the catalyst was recovered by allowing the layers to separate and removing the THF solution via syringe. The catalyst solution was washed with THF (2x10 mL) to ensure complete removal of the product.