

SUPPORTING INFORMATION

## Prins-type Polymerization Using Ionic Liquid Hydrogen Fluoride Salts

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### Experimental Section

#### *Measurements*

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL EX-270 ( $^1\text{H}$ : 270 MHz,  $^{13}\text{C}$ : 67.8 MHz,  $^{19}\text{F}$ : 254 MHz) spectrometer. The chemical shifts for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were given in  $\delta$  (ppm) from internal TMS,  $\text{CDCl}_3$ , and monofluorobenzene (-36.5 ppm), respectively. GPC measurement was performed on a SHIMADZU Prominence GPC system (Shim-pack GPC-803C column) with chloroform as an eluent after calibration with polystyrene standards.

### Materials

All Chemicals were obtained commercially and were used without further purification. HF-based ionic liquid is toxic and may cause serious burns if they come in contact with unprotected skin. (4-Diethoxymethyl-2,3,5,6-tetrafluoro)benzaldehyde was prepared by the similar procedure to the literature.<sup>1</sup>

### Synthesis

#### 1-(4-Diethoxymethyl)phenyl-3-buten-1-ol (**1a**)

4-(Diethoxymethyl)benzaldehyde (2.904 g, 10.05 mmol) was dissolved in THF (50 ml). After cooled at -20 °C, allylmagnesium bromide (1.0 M solution in Et<sub>2</sub>O, 12.0 ml) was added dropwise to the solution and the reaction mixture was stirred for 1 h at -20 °C. Then the temperature of the mixture was allowed to rise to room temperature. After 1 h stirring, the reaction was quenched by the addition of water. The water phase was extracted repeatedly with ether, and the extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the organic solvents gave a colorless oil (yield: 97%). <sup>1</sup>H NMR (270.05 MHz, CDCl<sub>3</sub>, ppm): δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.72 (m, 1H), 5.43 (s, 1H), 5.03 (d, *J* = 18 Hz, 1H), 5.02 (d, *J* = 10 Hz, 1H), 4.60 (t, *J* = 6.5 Hz, 1H), 3.52 (m, 4H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (67.8 MHz, CDCl<sub>3</sub>, ppm): δ 143.82, 138.13, 134.26, 126.53, 125.49, 118.21, 101.24, 73.00, 60.95, 43.81, 15.21. Anal. Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>: C 71.97; H 8.86; O 19.17; found: C 71.72; H 8.57; O 18.92.

1-(4-Diethoxymethyl-2,3,5,6-tetrafluoro)phenyl-3-buten-1-ol (**1b**)

To a stirred solution of (4-diethoxymethyl-2,3,5,6-tetrafluoro)benzaldehyde (4.01 g, 14.3 mmol) in THF (60 ml) was added allylmagnesium bromide (1.0 M solution in Et<sub>2</sub>O, 15.0 ml) at -20 °C. After stirring for 1 h at -20 °C, the reaction mixture was further stirred for 1 h at room temperature. Then, the reaction was quenched by the addition of saturated NaHCO<sub>3</sub> (aq). The separated water phase was extracted repeatedly with ether, and the extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the organic solvents gave a colorless oil (yield: quant.). <sup>1</sup>H NMR (270.05 MHz, CDCl<sub>3</sub>, ppm): δ 5.75 (m, 1H), 5.72 (s, 1H), 5.2-5.1 (m, 3H), 3.68 (m, 4H), 2.68 (m, 2H), 2.31 (d, *J* = 7.7 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (67.8 MHz, CDCl<sub>3</sub>, ppm): δ 144.9 (dm, *J* = 256 Hz), 144.2 (dm, *J* = 249 Hz), 132.4 (s), 122.34 (t, *J* = 15 Hz), 119.4 (s), 116.1 (t, *J* = 12 Hz), 96.6 (m), 66.1 (s), 66.0 (m), 41.2 (t, *J* = 1.5 Hz); <sup>19</sup>F NMR (254.05 MHz, CDCl<sub>3</sub>, ppm): δ -67.8 (m, 2F), -67.9 (m, 2F); HRMS Calcd for C<sub>15</sub>H<sub>18</sub>F<sub>4</sub>O<sub>3</sub>: 322.1192. Found: 322.1194.

*Polymerization*

A typical procedure for the polymerization is as follows. In a plastic vessel, monomer (0.1 M) was dissolved in 1.5 ml of CH<sub>2</sub>Cl<sub>2</sub>. To the stirred solution, Et<sub>4</sub>NF·5HF (1.5 ml) (and Lewis acid for **1b**) was added and stirred at room temperature for 24 h. The reaction was quenched by addition of water (3.0 ml). The separated organic layer was repeatedly washed with NaHCO<sub>3</sub> (aq) and water. The solution of crude polymer was poured into a large amount of CH<sub>3</sub>OH. After centrifugation,

light-yellow powder was obtained.

**2a.** Yield: 42%;  $^1\text{H}$  NMR (270.05 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.4 (Ar-*H*, 4H), 4.8-5.1 ( $>\text{CHF}$ , 1H), 4.5-4.7 ( $>\text{CHPh}$ , 2H), 2.4 and 1.8 ( $>\text{CH}_2$ , 4H);  $^{13}\text{C}$  NMR (67.8 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  140.8, 126.2, 90-88, 70.5, 40.3;  $^{19}\text{F}$  NMR (254.05 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -94. Anal. Calcd. for  $(\text{C}_{11}\text{H}_{11}\text{FO})_n$ : C 74.2; H 6.2; F 10.6; O 9.0. Found: C, 76.2; H, 6.4; F, 8.7.

**2b.** Yield: 29%.  $^{19}\text{F}$  NMR (254.05 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -65.2 (Ar-*F*, 4F), -95.3 ( $>\text{CHF}$ , *cis*), -110.5 ( $>\text{CHF}$ , *trans*). Anal. Calcd. for  $(\text{C}_{11}\text{H}_7\text{F}_5\text{O})_n$ : C 52.8; H 2.8, F 38.0; O 6.4. Found: C, 52.6; H, 3.5; F, 35.0.

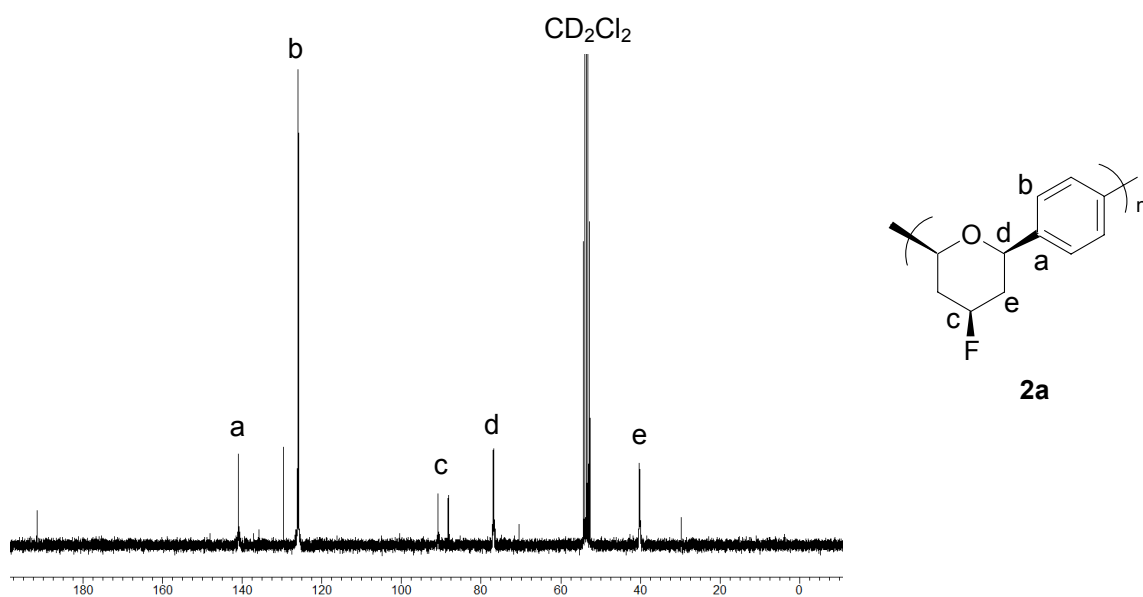


Fig. S1.  $^{13}\text{C}$  NMR spectrum of **2a** in  $\text{CD}_2\text{Cl}_2$ .

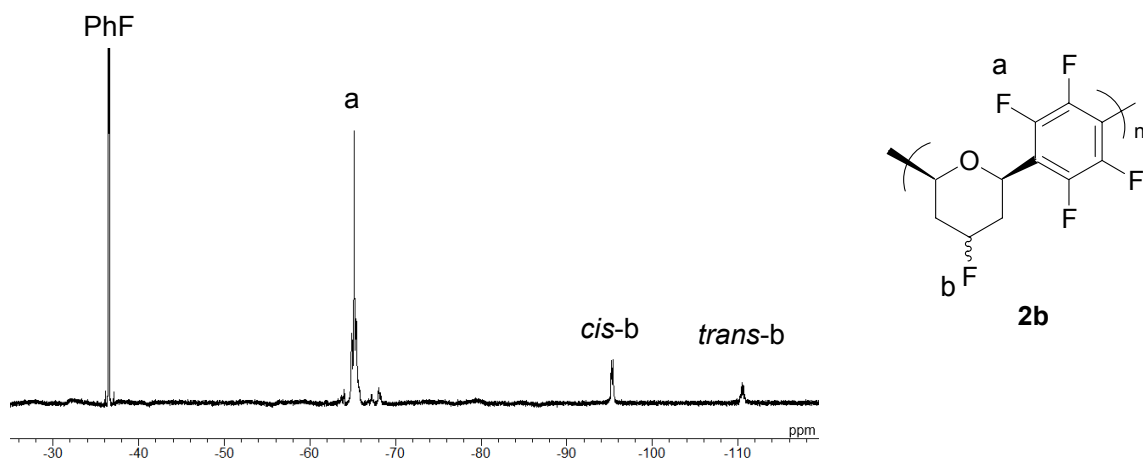


Fig. S2.  $^{19}\text{F}$  NMR spectrum of **2b** in  $\text{CDCl}_3$  with monofluorobenzene as a standard (-36.5 ppm).

## Reference

1. F. C. Krebs and T. Jensen, *J. Fluorine Chem.*, 2003, **120**, 77-84.