Experimental Section

Measurements

\(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F NMR spectra were recorded on a JEOL EX-270 (\(^1\)H: 270 MHz, \(^{13}\)C: 67.8 MHz, \(^{19}\)F: 254 MHz) spectrometer. The chemical shifts for \(^1\)H, \(^{13}\)C, and \(^{19}\)F NMR spectra were given in \(\delta\) (ppm) from internal TMS, 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.¹

**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 Et₂O, 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 Na₂SO₄. Evaporation of the organic solvents gave a colorless oil (yield: 97%). ¹H NMR (270.05 MHz, CDCl₃, 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); ¹³C NMR (67.8 MHz, CDCl₃, 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 C₁₅H₂₂O₃: 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 Et₂O, 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 NaHCO₃ (aq). The separated water phase was extracted repeatedly with ether, and the extracts were dried over Na₂SO₄. Evaporation of the organic solvents gave a colorless oil (yield: quant.).

$^1$H NMR (270.05 MHz, CDCl₃, ppm): $\delta$ 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); $^{13}$C NMR (67.8 MHz, CDCl₃, ppm): $\delta$ 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); $^{19}$F NMR (254.05 MHz, CDCl₃, ppm): $\delta$ -67.8 (m, 2F), -67.9 (m, 2F); HRMS Calcd for C₁₅H₁₈F₄O₃: 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 CH₂Cl₂. To the stirred solution, Et₄NF·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 NaHCO₃ (aq) and water. The solution of crude polymer was poured into a large amount of CH₃OH. After centrifugation,
light-yellow powder was obtained.

2a. Yield: 42%; $^1$H NMR (270.05 MHz, CDCl$_3$, ppm): $\delta$ 7.4 (Ar-$H$, 4H), 4.8-5.1 (>CHF, 1H), 4.5-4.7 (>CHPh, 2H), 2.4 and 1.8 (>CH$_2$, 4H); $^{13}$C NMR (67.8 MHz, CD$_2$Cl$_2$, ppm): $\delta$ 140.8, 126.2, 90-88, 70.5, 40.3; $^{19}$F NMR (254.05 MHz, CDCl$_3$, ppm): $\delta$ -94. Anal. Calcd. for (C$_{11}$H$_{11}$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%. $^{19}$F NMR (254.05 MHz, CDCl$_3$, ppm): $\delta$ -65.2 (Ar-F, 4F), -95.3 (>CHF, cis), -110.5 (>CHF, trans). Anal. Calcd. for (C$_{11}$H$_7$F$_5$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. $^{13}$C NMR spectrum of 2a in CD$_2$Cl$_2$.

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

Reference