

Supplementary information

Terminally fluorinated ether as a solvent for high-performance lithium metal batteries electrolyte

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Experimental section

General materials. 2,2-difluoroethanol, 2,2,2-trifluoroethanol (>99.0%) were purchased from P&M-Invest. Sodium hydride (60% in mineral oil), ethylene carbonate (>99%) were purchased from Sigma-Aldrich. THF (>99.8%), para-toluenesulfonic acid chloride (>99.0%) and dichloromethane (>99.9%) were purchased from Chemical Line. Hydrochloric acid (>98.0%) and sodium sulphate (>99.0%) were purchased from Rushim. Polyvinylidene fluoride (>99.5%), LiPF₆ (>99.95%), lithium metal chips (>99.9%) were purchased from Gelon Lib. LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ was purchased from Rustor. Fluoroethylene carbonate (>99.95%), dimethyl carbonate (>99.9%), polypropylene separators (25 μm thick), 2032-type coin-cell cases, springs and spacers were all purchased from Xiamen TOB New Energy Technology. Conductive additive Super P carbon was purchased from Timcal. N-methyl-2-pyrrolidone (>99%) was purchased from Acros Organics.

General materials characterization. 1D NMR spectra ¹H and ¹³C were recorded on the Bruker Fourier 300 spectrometer (300 MHz/54 m), the internal standard is tetramethylsilane (δ = 0 ppm). NMR spectra of ¹⁹F were recorded on the Bruker VRX-400 spectrometer, the internal standard is CFCl₃ (δ = 0 ppm). ESI MS was recorded on the DuoSpray AB Sciex TripleTOF 5600+ mass-spectrometer. Samples were injected through a direct injection circuit into a 100 μL/min methanol stream. Viscosity measurements were carried out using an electromagnetic Viscometer EMS-1000 by Kyoto Electronics Manufacturing Co. Ltd. with a rotating head at a temperature of 25°C, the volume of the liquid sample was 0.3 cm³. For the conductivity measurements the bulk electrolytes (2.65 ml) were contained in cell described in work [1]. The cell consists of two stainless steel cylinders. One of them have a cavity and the second one has a cylindrical ledge that fits in the cavity. The metal cylinders were insulated with a Teflon insert leaving two disk-shape electrode-electrolyte contact surfaces with an area of 1.77 cm² at a distance of 0.7 cm from each other. Between two

Teflon inserts free space for electrolyte expansion was provided. To obtain the cell constant the solution with known conductivity (1M K₂SO₄) was used. In the common conductivity measurement 2.65 ml of the electrolyte were poured in the cell and sealed with three screw bolts inserted in three holes and tighten up. The assembly provided in argon-filled glovebox (MBraun, p(O₂) = 0.1 ppm, p(H₂O) = 0.1 ppm). The assembled cell was thermostatically controlled at 25°C and the impedance spectroscopy data was obtained. The cell constant divided by the initial value of the resistance real part provides conductivity data. The spectroscopy data was obtained using Ellins- P-5X (frequency range of 100 kHz to 100 mHz, alternating voltage of 5 mV). The morphology and elemental composition of the samples were studied using scanning electron microscopy on a FEI Quattro S microscope in high vacuum mode with a current of up to 1.7 nA and a voltage of 10 kV. roughly estimated solubility. Roughly estimated solubility: Portions of 7.6 mg (0.05 mmol) of the salt were successively added to 1 mL of the test liquid at 25 °C until dissolution ceased. The solution was then allowed to stand for several hours to ensure that dissolution was complete before concluding that no further salt would dissolve.

Synthesis. 5FDEE was synthesized as described in [2]; the target product was distilled under reduced pressure, bp = 78°C at 100 mmHg. (24.0 g, 0.114 mol, yield 52%). ¹H NMR (CDCl₃): δ 3.68–3.95 (m, 8H), 5.88 (1H, tt, *J*₁ = 4.0 Hz, *J*₂ = 55.4 Hz, CHF₂). ¹³C NMR (CDCl₃): δ 68.8 (q, *J*_{C-F} = 34.0 Hz, C-CF₃), 70.6 (t, *J*_{C-F} = 27.2 Hz, C-CF₂), 71.5, 71.9, 114.3 (t, *J*_{C-F} = 241.0 Hz, C-CF₂), 123.9 (q, *J*_{C-F} = 279.6 Hz, C-CF₃).

Preparation of electrodes. To prepare cathodes suspensions of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ active material powder (90 wt.% or 89 wt.% respectively), Super P carbon (5 wt.%), and polyvinylidene fluoride (5 wt% or 6 wt%, respectively) were mixed with N-methyl-2-pyrrolidone (9.75 ml per 10 g of the mixture). The resulting suspensions were applied onto carbon-coated aluminum foil using the doctor blade technique and then dried in vacuum at 120°C for 12 hours. The loading of NMC811 was 13-18 mg/cm².

Electrolyte preparation. The following electrolyte compositions were used in this work: 1M LiPF₆ in EC/DMC (1:1 by vol.), 1M LiPF₆ 5FDEE/FEC (9:1 by vol.). LiPF₆ (152 mg) was dissolved in mixture of ethylenecarbonate and dimethylcarbonate (0.5 ml and 0.5 ml) or in mixture of 2,2-difluoro-1,3-dimethoxypropane and fluoroethylenecarbonate (0.9 ml and 0.1 ml correspondingly). All electrolytes were prepared in an argon glovebox with water and oxygen content of less than 0.1 ppm. The LiPF₆ salt was dried in a dynamic vacuum at room temperature for a day. The water content in electrolyte solvents was determined by coulometric Fisher titration, and a value of less than 20 ppm was considered acceptable.

Electrochemical measurements. Linear sweep voltammetry was carried out using a multichannel Biologic VMP-3 potentiostat equipped with the ECLab V9.97 interface, in stainless steel coin-type cells Li||CR2032 with a potential sweep rate of 0.2 mV/s within the range from 2.5 to 5 V. Galvanostatic charge/discharge tests were performed in the potential range of 2.7 – 4.5 V vs. Li⁺/Li using the Neware battery test system. The test regime included 3 cycles at a charge/discharge rate of 0.1C/0.1C, followed by cycles at charge/discharge rate of 0.2C/0.5C. Two-electrode coin cells were assembled in an argon-filled box (MBraun, p(O₂) = 0.1 ppm, p(H₂O) = 0.1 ppm), with lithium metal (99.9%, Gelon Lib) as the anode, polypropylene separator and 1.77 cm² round-shaped electrodes with an active cathode material of NMC811.

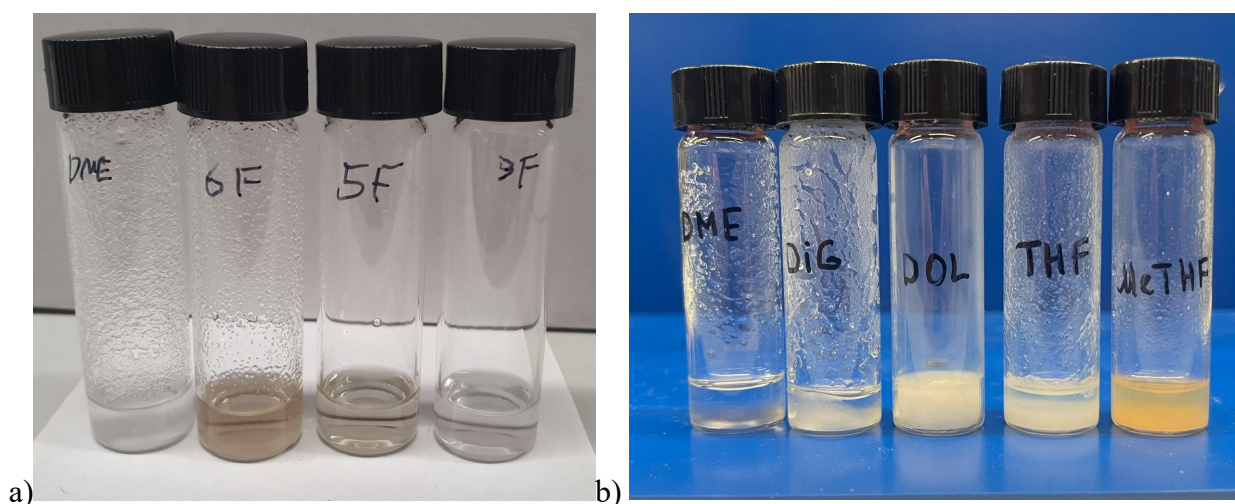


Figure S1. Digital photo of LiPF_6 in a) 1,2-dimethoxyethane (DME), 2-[2-(2,2,2-trifluoroethoxy)ethoxy]-1,1,1-trifluoroethane (6FDEE), 2-[2-(2,2-difluoroethoxy)ethoxy]-1,1,1-trifluoroethane (5FDEE) and 1-methoxy-2-(2,2,2-trifluoroethoxy)ethane (3FEME) 25 minutes after dissolution; b) in commonly used ether-electrolyte solvents (DME, diglyme, DOL, THF, MeTHF) 12 days after dissolution.

DOSY-NMR. Diffusion-ordered NMR spectroscopy were performed at the Shared Facility Center of Frumkin Institute of Physical Chemistry and Electrochemistry (Russian Science Academy). The ^1H and ^7Li NMR spectra for DOSY NMR were recorded on a Bruker Avance III 600 spectrometer at 600.13 MHz and 233.23 MHz, respectively. Chemical shifts of ^1H were measured relative to the signal of the residual protons of the deuterated solvent. Chemical shift of ^7Li was measured relative to the external reference (1M of the LiCl solution in D_2O). Diffusion measurements were made at 303 K by the 2D NMR spectroscopy with internal reference (DOSY NMR) on ^1H and ^7Li . Toluene was used as an internal standard. It was added to the test solution at a concentration of 10% by volume. Due to its low polarity and low donor number, toluene does not participate in the solvation of the cation and anion and can be used to account for changes in the viscosity of the system. DOSY spectra were recorded using the `dstepg3s` stimulated echo pulse sequence from the Topspin Bruker library. The strength of the gradient pulse was varied linearly in steps (32 increments) from 5 to 95% of the maximum current of 10 A. Phase correction and baseline correction were applied to the experimental data. The obtained diffusion attenuation curves were approximated by a monoexponential function. Li coord. numbers and α were calculated using described method [3].

Table S1. Calculation results from DOSY NMR.

	$D_{\text{Li}}^{[a]}$	$D_{\text{tol}}^{[a]}$	$D_{\text{FEC}}^{[a]}$	$D_{5\text{FDEE}}^{[a]}$	α_{FEC}	$\alpha_{5\text{FDEE}}$	5FDEE Li coord. number ^[b]	FEC Li coord. number ^[b]
5FDEE:FEC (9:1 by vol.)	n/a	11.8	9.7	7.6	n/a	n/a	n/a	n/a
5FDEE:FEC (9:1 by vol.) 1M LiPF_6	3.1	7.2	3.6	3.9	0.56	0.25	1.42	0.70

[a] Diffusion coefficients are in the unit of $10^{-10} \text{ m}^2/\text{s}$.

[b] Coordination number of Li was calculated by multiplying the coordination ratios of electrolyte solvents with their molar ratios.

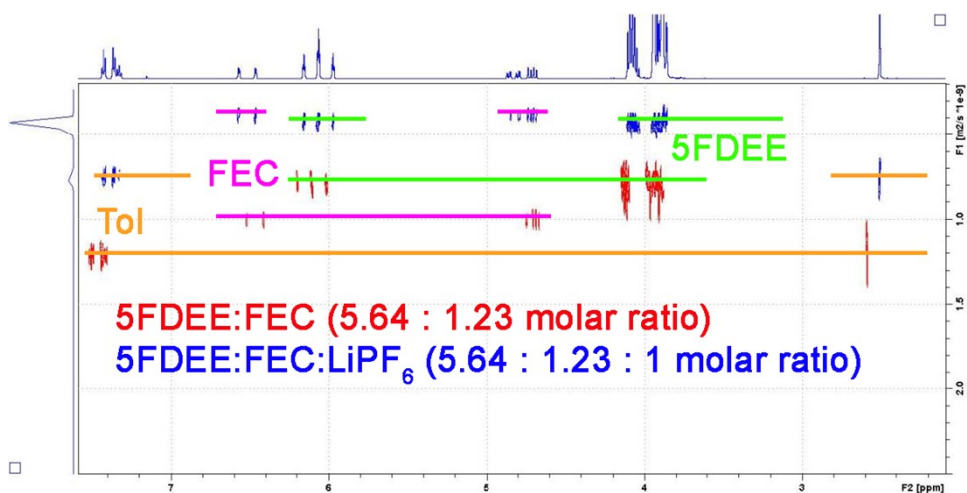


Figure S2. ^1H DOSY-NMR spectra of (9:1 by vol.) 5FDEE:FEC (red) and (9:1 by vol.) 5FDEE:FEC 1M LiPF_6 electrolyte (blue) with toluene added as an internal reference.

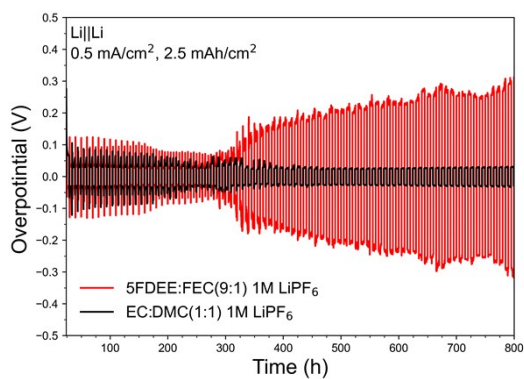


Figure S3. Cycling performance of $\text{Li}||\text{Li}$ symmetric cells at 0.5 mA/cm^2 with 1M LiPF_6 in EC:DMC (1:1 by vol.) and 1M LiPF_6 in 5FDEE:FEC (9:1 by vol.) electrolytes.

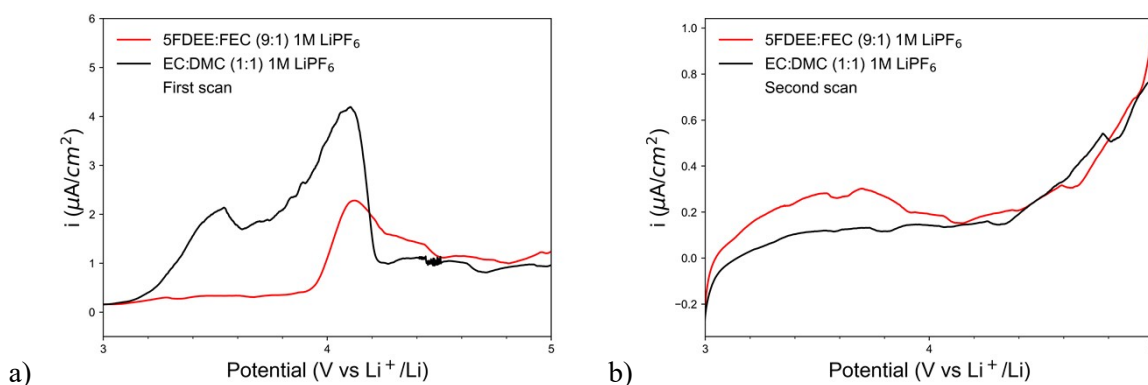


Figure S4. LSVs of $\text{Li}||\text{SS}$ half cells of 1M LiPF_6 in EC:DMC (1:1 by vol.) and 1M LiPF_6 in 5FDEE:FEC (9:1 by vol.) electrolytes: a) First scan, b) Second scan.

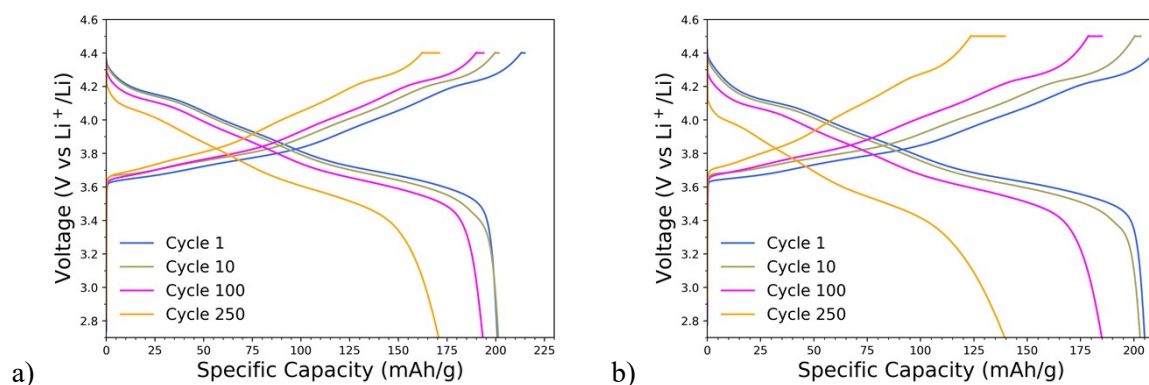


Figure S5. Charge/discharge curves of Li||NMC811 (2.3 mAh/cm^2) coin cell with 1M LiPF_6 5FDEE:FEC(9:1 by vol.) at 0.2C charge 0.5C discharge at cutoff voltage of: a) 4.4 V b) 4.5 V .

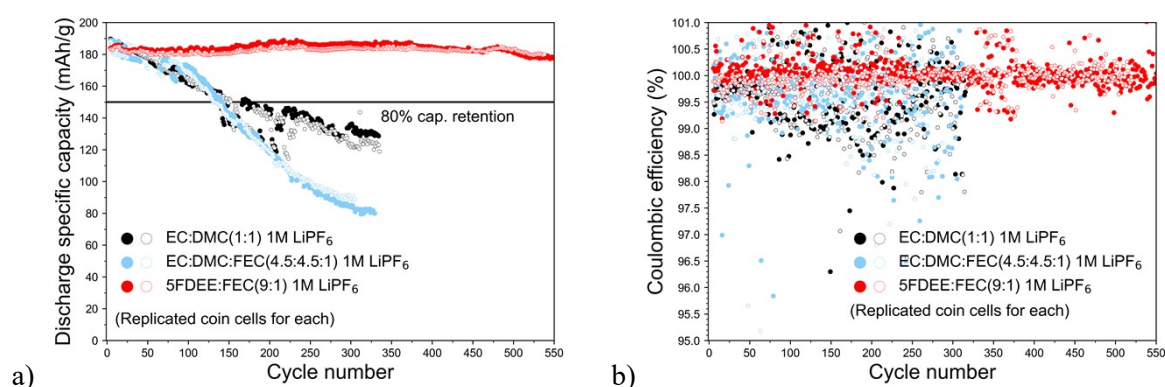


Figure S6. Electrochemical performance of Li||NMC811 (2.3 mAh/cm^2) coin cells with 1M LiPF_6 in EC:DMC (1:1 by vol.), 1M LiPF_6 in EC:DMC:FEC (4.5:4.5:1 by vol.) and 1M LiPF_6 in 5FDEE:FEC (9:1 by vol.) electrolytes in the voltage range of $2.7 - 4.3 \text{ V}$: a) Specific discharge capacity retention at the $0.2\text{C}/0.5\text{C}$ charge/discharge mode with three pre-cycles at 0.1C ; b) Comparison of Coulombic efficiencies.

Table S2. Comparison of the state-of-the-art Li||NMC811 performances.

Electrolyte	Cathode loading, mAh cm^{-2}	Cycling Condition, Capacity Retention and average Coulombic efficiency
LiFSI/TMS/TTE (1:3:3 by mol.) [4]	1.5	$2.7\text{-}4.3 \text{ V}$, $\text{C}/3$ charge/discharge rate, 80% capacity retention after 300 cycles, CE 98.8%
1 M LiPF_6 in FEC/FEMC/HFE (2:6:2) [5]	~ 2.0	$2.8\text{-}4.4 \text{ V}$, $\text{C}/4$ charge/discharge rate, 50% capacity retention after 30 cycles, CE 99.2%
LiFSI/DME/TTE (1:1.2:2 by mol) [6]	1.5	$2.8\text{-}4.5 \text{ V}$, $\text{C}/3$ charge/discharge rate, 87% capacity retention after 300 cycles, CE $> 99.0\%$
1M LiFSI in DME/TFEO (1:9 by weight) [7]	~ 1.5	$2.8\text{-}4.4 \text{ V}$, $\text{C}/3$ charge/discharge rate, 80% capacity retention after 300 cycles, CE 99.7%
LiFSI/DME/TFEO (1:1.3:2 by mol) [8]	~ 4.2	$2.8\text{-}4.4 \text{ V}$, 0.1C charge 0.3C discharge, 80% capacity retention after 215 cycles, CE $> 99.0\%$
1 M LiFSI in DMTMSA [9]	~ 1.7	$3.0\text{-}4.6 \text{ V}$, 0.5C charge/discharge rate, 88% capacity retention after 100 cycles, $>99.65\%$
1 M LiPF_6 in EC/DEC with	~ 4.3	$3.0\text{-}4.3 \text{ V}$, 0.3C charge 0.5C discharge rate,

10 mM In(OTf) ₃ and 0.5 M LiNO ₃ [10]		80% capacity retention after 160 cycles, CE >98.0%
1 M LiPF ₆ in FEC-EMC with 3 wt% LiNO ₃ and 1 wt% TFPFB [11]	4.0	3.0-4.5 V, 0.1C charge 0.3C discharge rate, 80% capacity retention after 140 cycles, CE ~98.5%
1.2 M LiFSI in F4DEE 1.2 M LiFSI in F5DEE [2]	4.9	2.8-4.4 V, 0.2C charge 0.3C discharge rate F4DEE, 80% capacity retention after 180 cycles, CE > 99.0% F5DEE, 80% capacity retention after >200 cycles, CE > 99.0%
1 M LiFSI in 1,3-DMP [12]	4.0	2.8-4.4 V, C/3 charge/discharge rate 85% capacity retention after 100 cycles, CE 99.4%
LiFSI:G:TTE (1:1:3 by mol.), where G1, G2, G3, G4 are glymes [13]	2.0	2.8-4.6 V, 0.3C charge/discharge rate G1 80% capacity retention after r 200 cycles, CE 99.7% G2 80% capacity retention after 270 cycles, CE 98.6% G3 80% capacity retention after 350 cycles, CE 99.8% G4 80% capacity retention after 230 cycles, CE 99.7%
1 M LiFSI in FDMB [14]	2.0	2.8-4.4 V, C/3 charge/discharge rate, 75% capacity retention after 70 cycles, CE > 99.0%
1.2 M LiPF ₆ in FDG/FEC (7:3) [15]	1.4	3.0-4.3 V C/3 charge/discharge rate, 92.4% capacity retention after 100 cycles, CE 99.90%
2 LiFSI in BFE [16]	3.5	2.8–4.4 V, 2C rate, 93% after 200 cycles, CE 99.75%
2M LiFSI in TFDMP [17]	1.6	2.8-4.4 V, C/3 charge/discharge rate, 100% capacity retention after 450 cycles, CE 99.6%
This work 1M LiPF ₆ in 5FDEE/FEC (9:1 by vol.)	2.3	2.7-4.3 V, 0.2C charge 0.5C discharge rate, 100% capacity retention after 550 cycles, CE 99.9%

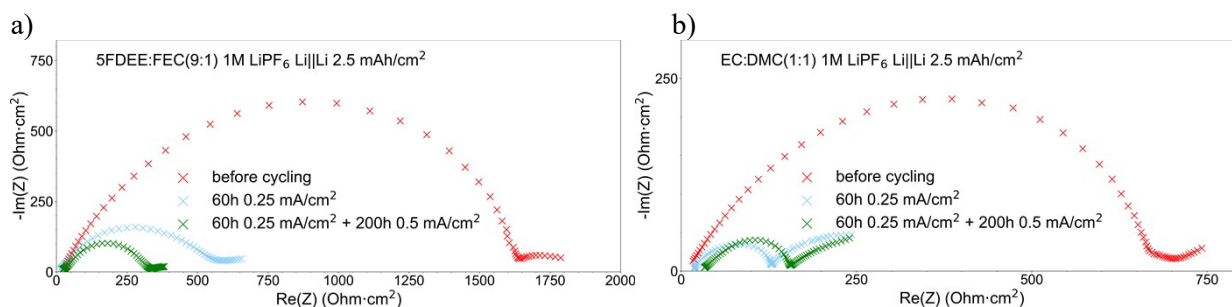


Figure S7. Symmetric Li|Li cell resistances in fluorinated ether and carbonate electrolytes. EIS spectra showing the evolution of the cell impedance: before cycling, after 60 hours of cycling at 0.25 mA/cm² and after 260 hours of combined cycling at 0.25 and 0.5 mA/cm² in (a) 5FDEE:FEC (9:1 by vol.) 1M LiPF₆ and (b) EC:DMC (1:1 by vol.) 1M LiPF₆.

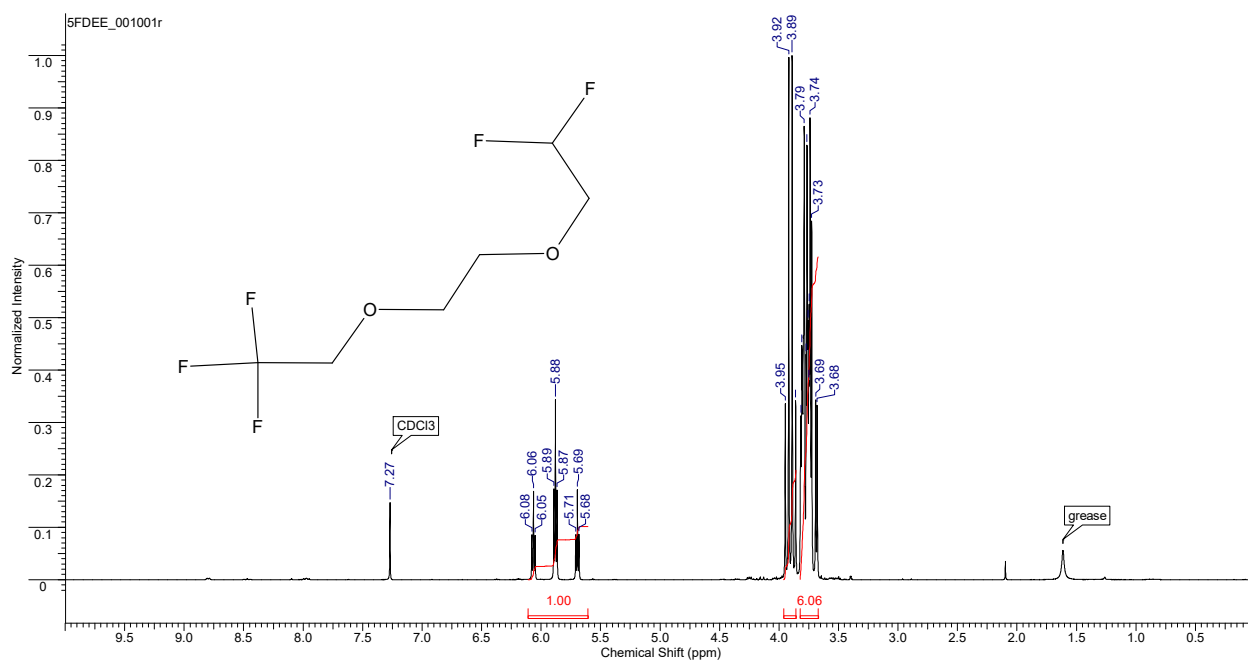


Figure S8. ¹H NMR spectra of 5FDEE.

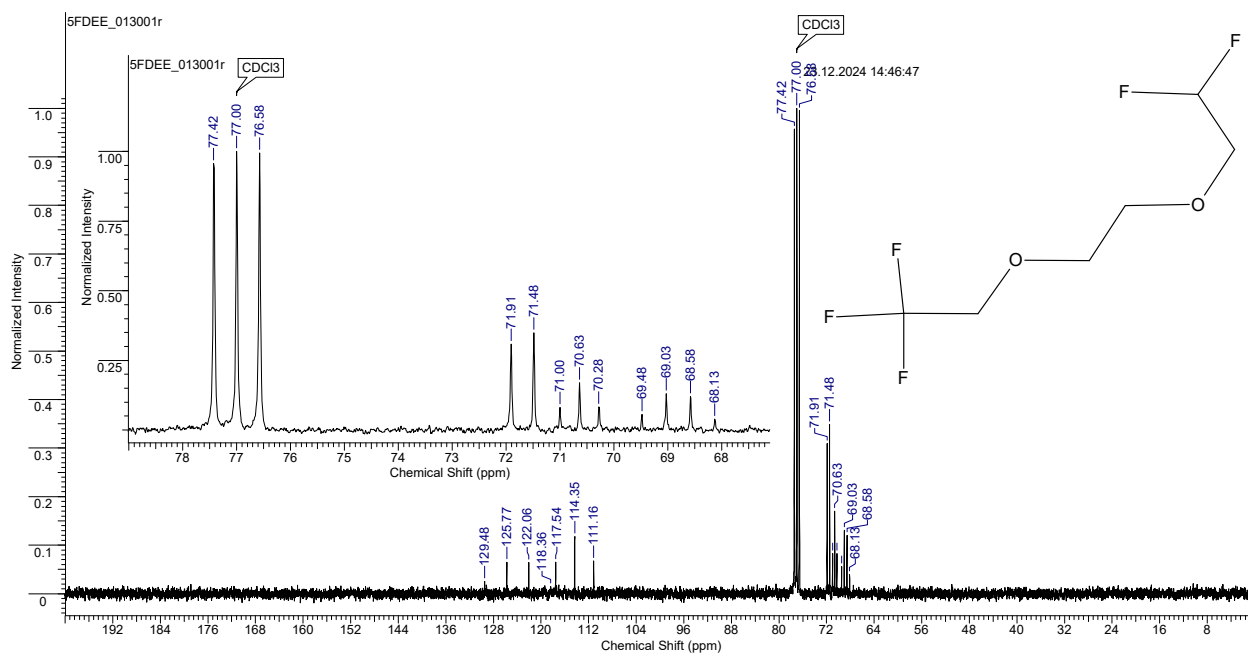


Figure S9. ¹³C NMR spectra of 5FDEE.

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