

Supporting Information

Hydrophobic Evaporable Fullerene Indanone Ketone with Low Sublimation Temperature and Amorphous Morphology for Inverted Perovskite Solar Cells

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Table of Contents

1. General	S3
2. Synthesis of CF ₃ -FIDO	S5
3. FT-IR of CF ₃ -FIDO	S8
3. Single crystal structure	S9
4. ¹ H NMR spectrum of evaporated	S10
5. TEM image of evaporated CF ₃ -FIDO film	S10
6. Cyclic voltammograms of fullerenes	S11
7. UV-visible spectroscopy	S12
8. SEM picture of perovskite layer	S12
9. PSCs performance	S13
10. Long-term stability of CF ₃ -FIDO based device	S14
11. Water contact angle	S14
12. NMR and MAIDI-TOF spectrum	S15

1. General

Methods

To ensure optimal reaction conditions, all reactions that were sensitive to air or moisture were conducted in a dehydrated reaction vessel, under a carefully controlled nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed using a glass plate coated with 0.25mm 230-400 mesh silica gel containing a fluorescent indicator, allowing for precise detection and analysis of the reaction components. To remove the organic solutions, a diaphragm pump through a rotary evaporator was employed for evacuation. Nuclear Magnetic Resonance (NMR) was taken by ECS 400 and ECA 600 (JEOL Co., Ltd.) at room temperature reported in parts per million (ppm). ^1H NMR spectra were internally referenced to tetramethylsilane (0.00 ppm) or CDCl_3 (7.260 ppm). ^{13}C NMR spectra were internally referenced to tetramethylsilane (0.0 ppm) or CDCl_3 (77.16 ppm). The data were presented as following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet and/or multiplet resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was taken by AXIMA Performance (SHIMADZU Co., Ltd.). Super Photon ring-8 GeV (Spring-8) was employed to analyse the structure of single crystal CF3-FIDO.

Materials

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers (Sigma-Aldrich, TCI, Wako) and used without further purification.

Photovoltaic Device fabrication and evaluation

Perovskite solar cells fabrication

The perovskite solar cells structure was fabricated using ITO/PEDOT: PSS/Perovskite/Fullerene/BCP/Ag. ITO-coated glass (sheet resistance $\leq 10 \Omega \text{ cm}^2$)

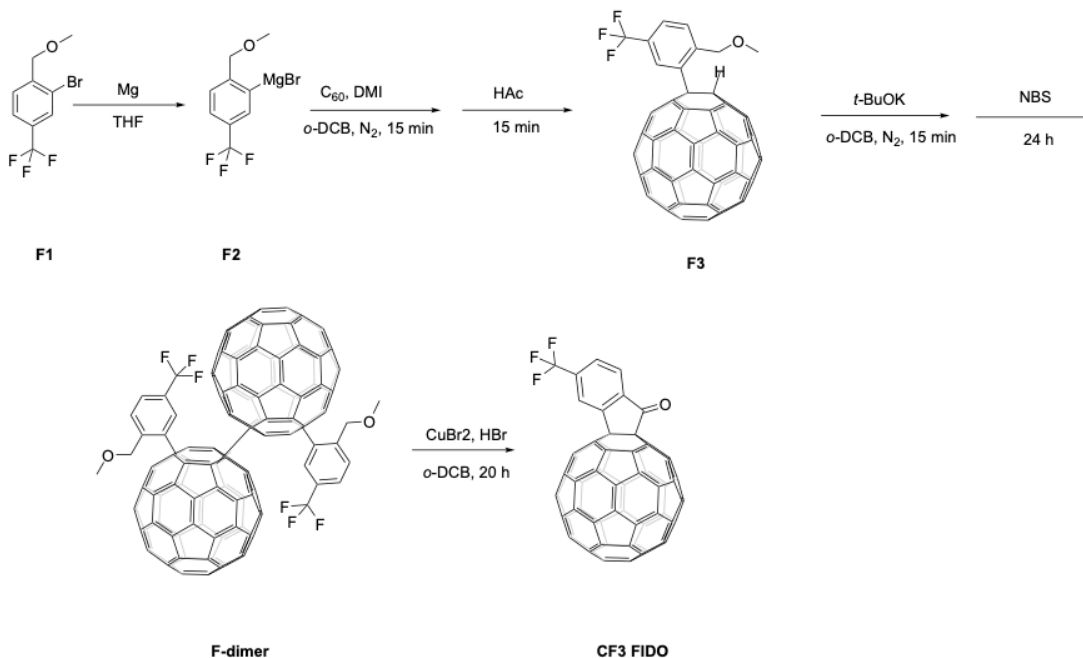
was cleaned consecutively in deionized water, acetone, isopropanol, and ethanol ultrasonic baths for 15 min, respectively. The ITO glass was treated with UV-Ozone for 15 min before use. The PEDOT: PSS was spin-coated on the ITO glass at 3000 r for 30 s and annealed at 110 °C for 10 min. After annealing the PEDOT: PSS substrates was transferred to glovebox. The perovskite precursor solution with a formula MAPbI_3 was prepared by mixing the 122 mg MAI and 355 mg PbI_2 in 0.55 ml solvent with a DMF: DMSO volume ratio of 5: 1. To prepare the perovskite film 45 μL of the perovskite precursor solution was spin-coated on the substrate at 4000 rpm for 20 s. 150 μL of CB was dropped onto the film after at 5 s. Then the substrate was annealed at 110 °C for 10 min. 15 nm CF3-FIDO or C60, 3 nm BCP and 100 nm Ag were deposited by thermal evaporation under high vacuum (10^{-4} mbar).

Evaluation of photovoltaic performance

The $J-V$ measurement was performed via the solar simulator (HAL-C100, Asahi spectral) along with AM 1.5G spectra at 100 mW cm^2 . The source unit (B2902A, Keysight) was used to measure the $J-V$ curve.

2. Synthesis of CF₃-FIDO

2.1 Fullerene cation intermediate route



Synthesis of Grignard reagent (F2). An anhydrous tetrahydrofuran (THF) (10.0 mL) solution of **F1** (6 mmol) was slowly dropped into polished Mg powder (220.0 mg, 9 mmol) in a trace amount of I₂ as initiator under N₂ atmosphere at 0 °C. After being vigorously stirred for 1 h, the prepared Grignard solution (**F2**) was transferred by Schlenk operation and stocked in a Schlenk bottle. The concentration was confirmed before using through anhydrous titration by using menthol as titrant with a trace amount of 1,10-phenanthroline as indicator under N₂ atmosphere.

Synthesis of (2-CH₂OCH₃-5-CF₃)C₆₀H (F3). C₆₀ (1080 mg, 1.5 mmol) was dissolved in ortho-dichlorobenzene (o-DCB) (50.0 mL) containing 1,3-dimethyl-2-imidazolidinone (DMI) (5.0 mL, 45 mmol) with three times degass-N₂ refill at r.t., then the stocked Grignard reagent **F2** (7.5 mL, 4.5 mmol) was added under a N₂ atmosphere. After stirring for 15 min at r.t., the dark green reaction mixture was quenched by CH₃COOH (300 μL). The dark green reaction mixture immediately

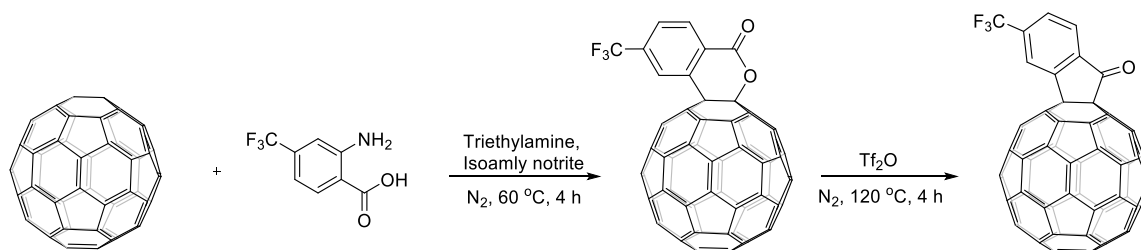
turned into brown, and the reaction mixture was condensed through evaporating the solvent under vacuum. Next, a silica gel chromatography with CS₂ as eluent was utilized to afford brownish powder **F3** Yield: **F3**, 955 mg, 70%. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.68 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 1H), 5.73 (s, 2H), 3.74 (s, 3H). ¹³C NMR (99 MHz, CHLOROFORM-D) δ 152.87, 147.72, 147.40, 146.72, 146.55, 146.52, 146.36, 146.21, 145.80, 145.59, 145.57, 144.89, 144.59, 143.51, 142.83, 142.78, 142.22, 141.85, 141.59, 141.38, 140.59, 132.23, 131.23, 130.90, 126.78, 126.74, 126.70, 126.66, 125.60, 125.56, 125.52, 125.48, 122.62, 72.42, 68.05, 62.70. MALDI-TOF MS *m/z* calcd for C₆₉H₉F₃O 910.06, found 909.99.

Synthesis of fullerene F-dimer. To a solution of **F3** (560.0 mg, 0.62 mmol) in 50.0 mL anhydrous *o*-DCB solution was added a solution of *t*-BuOK (0.74 mL, 0.74 mmol, 1M) in THF at r.t. under a N₂ atmosphere. After stirring for 15 mins, *N*-bromosuccinimide (NBS) (441.0 mg, 2.48 mmol) was added. The reaction mixture was vigorously stirred for 24 hours at r.t. under a N₂ atmosphere. Then the resulting brownish suspension was quenched by 1 mL H₂O and an excess amount of MeOH was added to precipitate the crude product. Finally, titled **F-dimer** was collected as residue by filtration without necessities of further purifications.

Synthesis of CF3-FIDO. F-Dimer (700.0 mg, 0.38 mmol) was dissolved in *o*-DCB (50.0 mL), and CuBr₂ (678.9 mg, 3.04 mmol) was added as oxidant. After vigorously stirring at 135 °C for 1 hours, 1 mL Hydrogen bromide solution (47% HBr in water) was added. Then keeping vigorously stirring at 135 °C for 10 hours. Finally, the reaction mixture was condensed through evaporating the solvent under vacuum and followed by a silica gel column chromatography (CS₂) to afford brownish powder **CF3-FIDO**. 330.0 mg, 48.6%. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.92 (s, 1H), 8.81 (d, *J* = 8.9 Hz, 1H), 8.01 (d, *J* = 10.4 Hz, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 197.88, 156.96, 153.32, 152.56,

147.65, 147.52, 147.41, 146.62, 146.37, 146.33, 145.94, 145.75, 145.68, 145.66, 145.61, 144.80, 144.45, 143.35, 143.01, 142.95, 142.62, 142.32, 142.30, 142.19, 142.17, 141.81, 140.91, 140.88, 138.83, 138.50, 137.40, 135.88, 135.62, 128.12, 127.37, 127.33, 124.23, 124.19, 83.67, 70.77. MALDI-TOF MS m/z calcd for $C_{68}H_3F_3O$ 892.01, found 891.88.

2.2 Retro Baeyer–Villiger reaction



Synthesis the CF₃-C₆₀-fused lactone. C₆₀ (360.3 mg, 0.5 mmol) was dissolved into ortho-dichlorobenzene (*o*-DCB) (30.0 mL) in a 100 ml 2-neck flask with three times degass-N₂ refill at room temperature. Then the 2-Amino-4-(trifluoromethyl) benzoic Acid (513.0 mg, 2.5 mmol), triethylamine (416 μ L, 3.0 mmol), isoamyl nitrite (399 μ L, 3.0 mmol) was added into solution and keep stirring at 60 °C for 4 h. After the cooling down to the r.t. The reaction mixture was condensed through evaporating the solvent under vacuum. A short silica gel chromatography with *o*-DCB as eluent was utilized to afford crude brownish powder CF₃-C₆₀-fused lactone. Yield 140 mg, 30.8%. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.76 (dt, J = 1.5, 0.7 Hz, 1H), 8.59 (dp, J = 8.1, 0.8 Hz, 1H), 8.16 – 8.09 (m, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 160.19, 153.03, 148.99, 148.45, 147.97, 147.05, 147.01, 146.71, 146.68, 146.67, 145.93, 145.70, 145.13, 144.97, 144.77, 144.47, 143.35, 143.15, 143.12, 142.88, 142.55, 142.30, 141.56, 141.46, 140.40, 140.37, 138.64, 137.03, 136.70, 135.74, 135.09, 133.11, 126.70, 125.62. MALDI-TOF MS m/z calcd for $C_{68}H_3F_3O_2$ 908.01, found 908.10.

Synthesis the CF3-FIDO. CF3-C₆₀-fused lactone (45.4 mg, 0.05 mmol) and Tf₂O (25 μ L, 0.15 mmol) was dissolved into anhydrous *o*-DCB (5.0 ml) in a 15 ml glass tube with three times degass-N₂ refill at room temperature. After stirring for 4 h at 120 $^{\circ}$ C, the reaction mixture was flited through a short silica-gel column to remove some insoluble materials. Then methanol was utilized to settle the crude production. The CF3-FIDO then was purified by preparative HPLC to afford using toluene as eluant. Yield 15 mg, 34.0%.

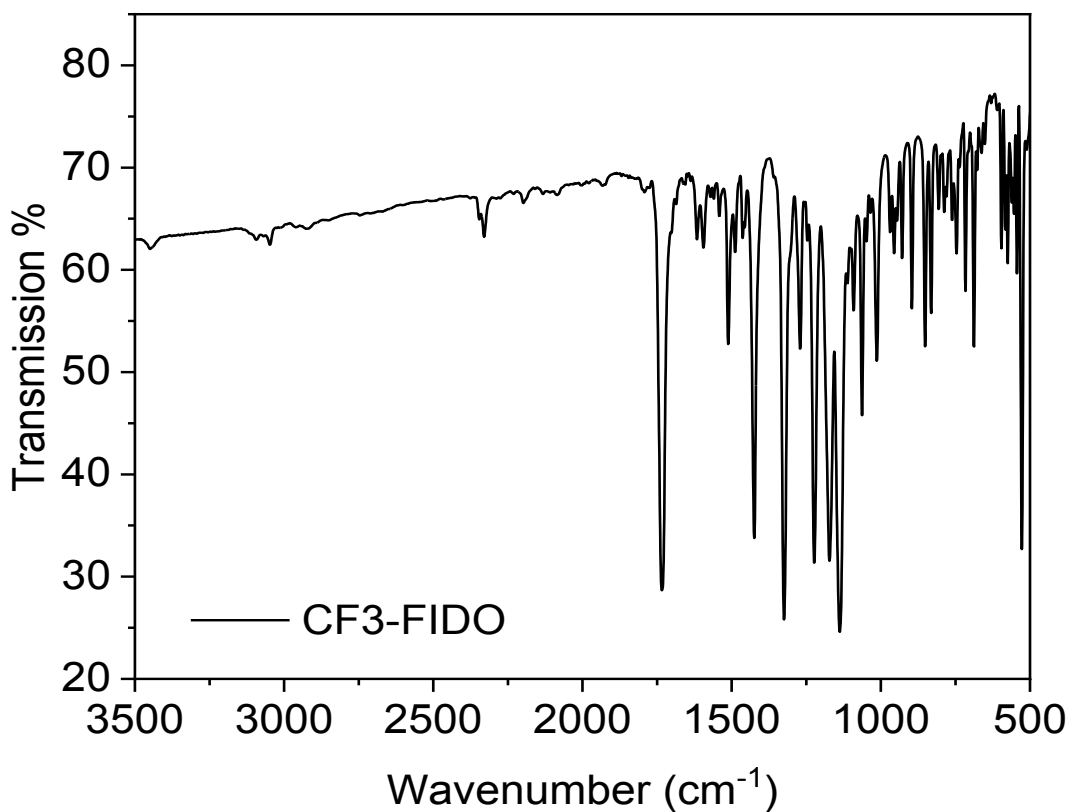


Figure S1. FT-IR of CF3-FIDO.

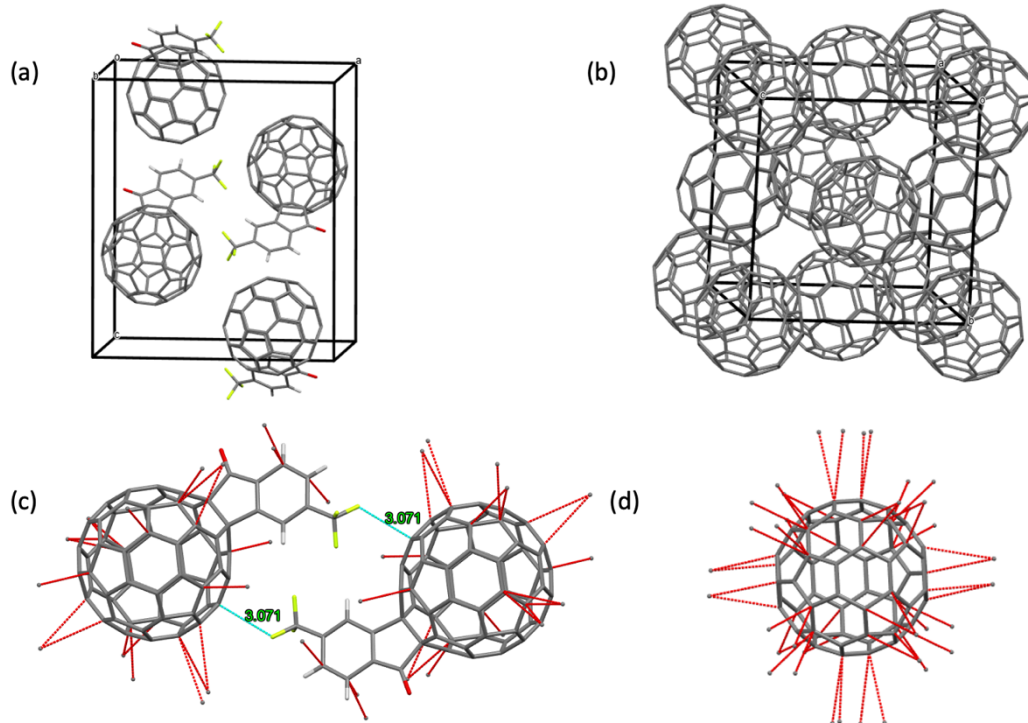


Figure S2. Single crystal structure of CF3-FIDO and C₆₀. (a-b) The unit cell of CF3-FIDO and C₆₀. (c-d) The short-contact of CF3-FIDO and C₆₀. Mercury software was used to compare the CF3-FIDO and C₆₀ previously reported. [1]

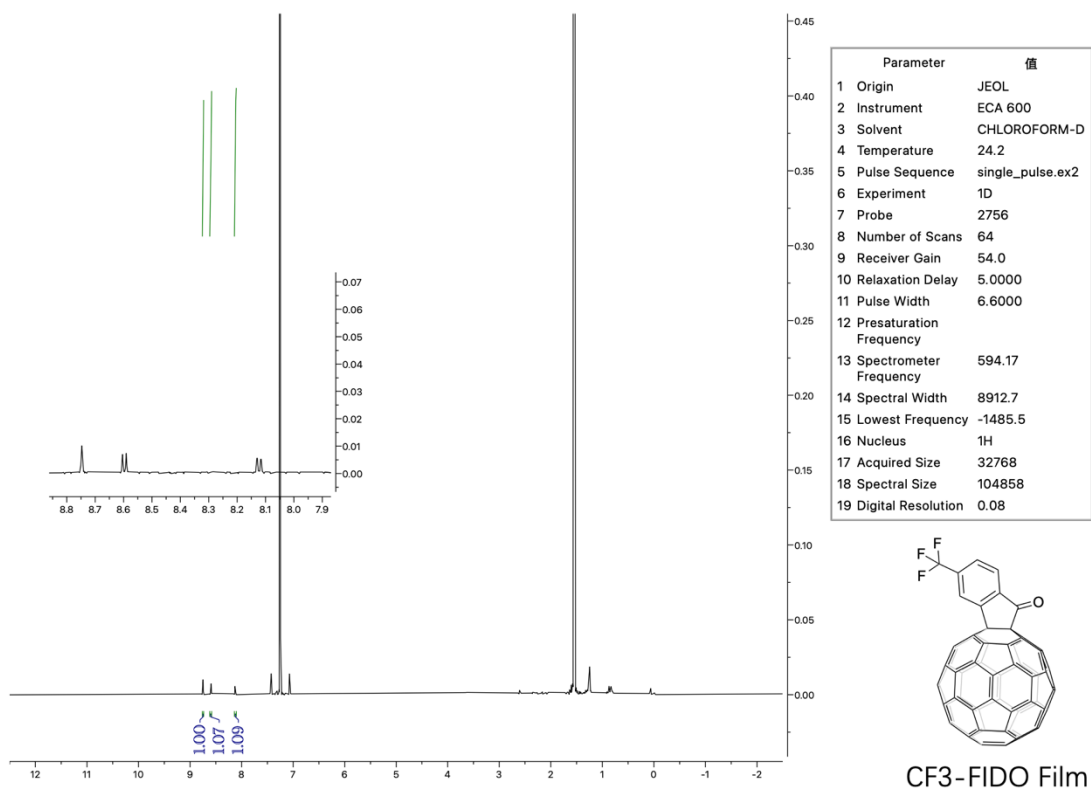


Figure S3. The ^1H NMR of evaporated CF3-FIDO film. (The symmetrical peaks at 7.43 ppm and 7.08 ppm are satellite peaks of chloroform.)

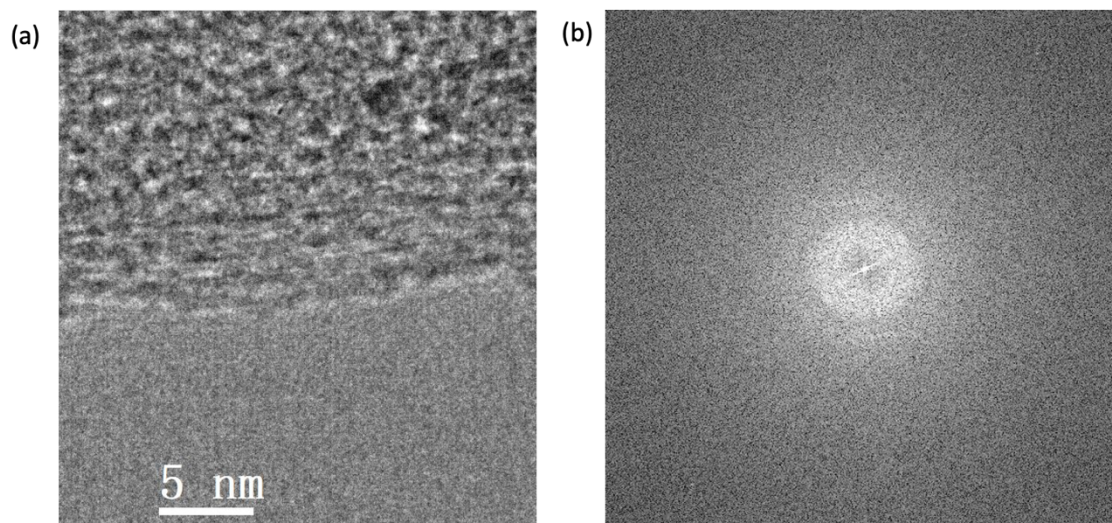


Figure S4. TEM image of evaporated CF3-FIDO film.

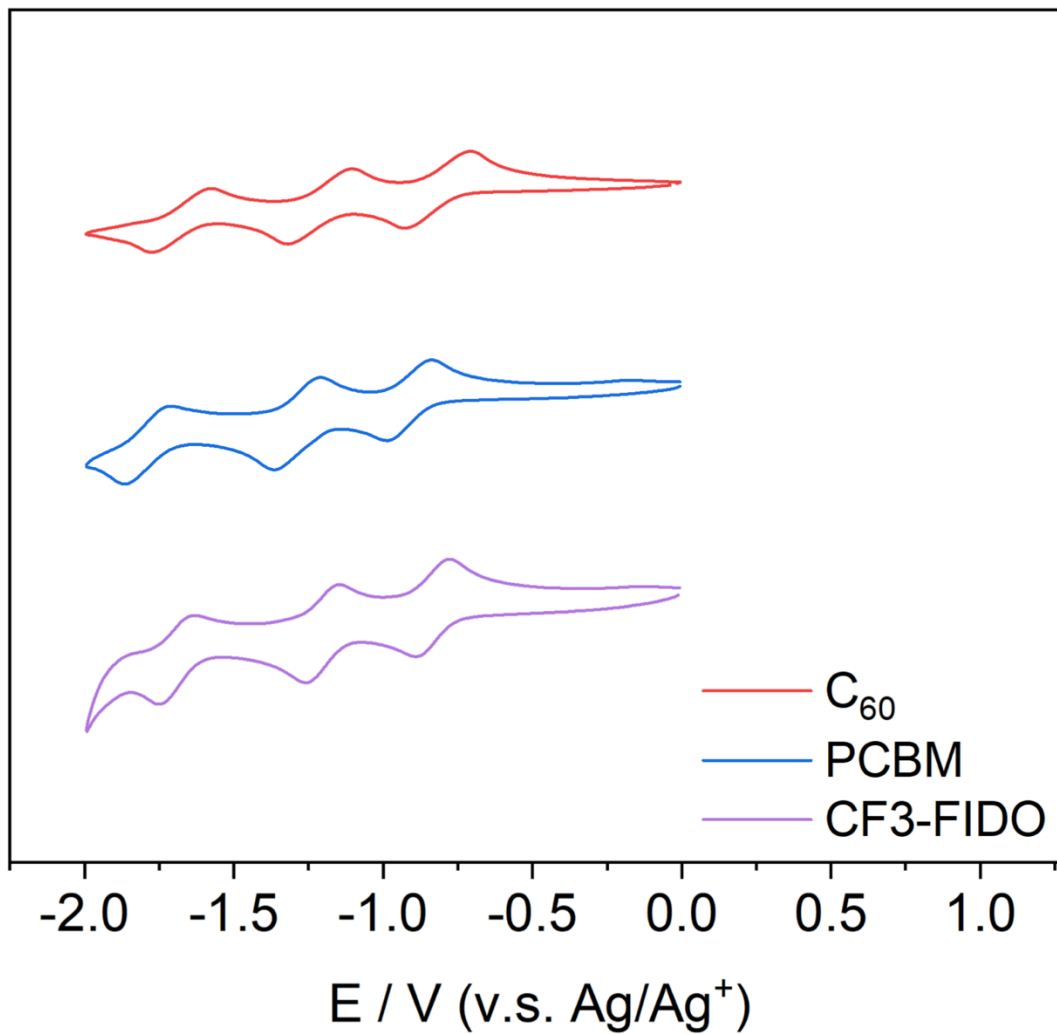


Figure S5. Cyclic voltammograms of fullerene derivatives in *o*-DCB solution containing $\text{Bu}_4\text{N}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (0.1 M) as supporting electrolyte at 25 °C with a scan rate of 0.05 V/s. Glassy carbon, platinum wire, and Ag/Ag^+ electrodes were used as the working, counter, and reference electrodes, respectively.

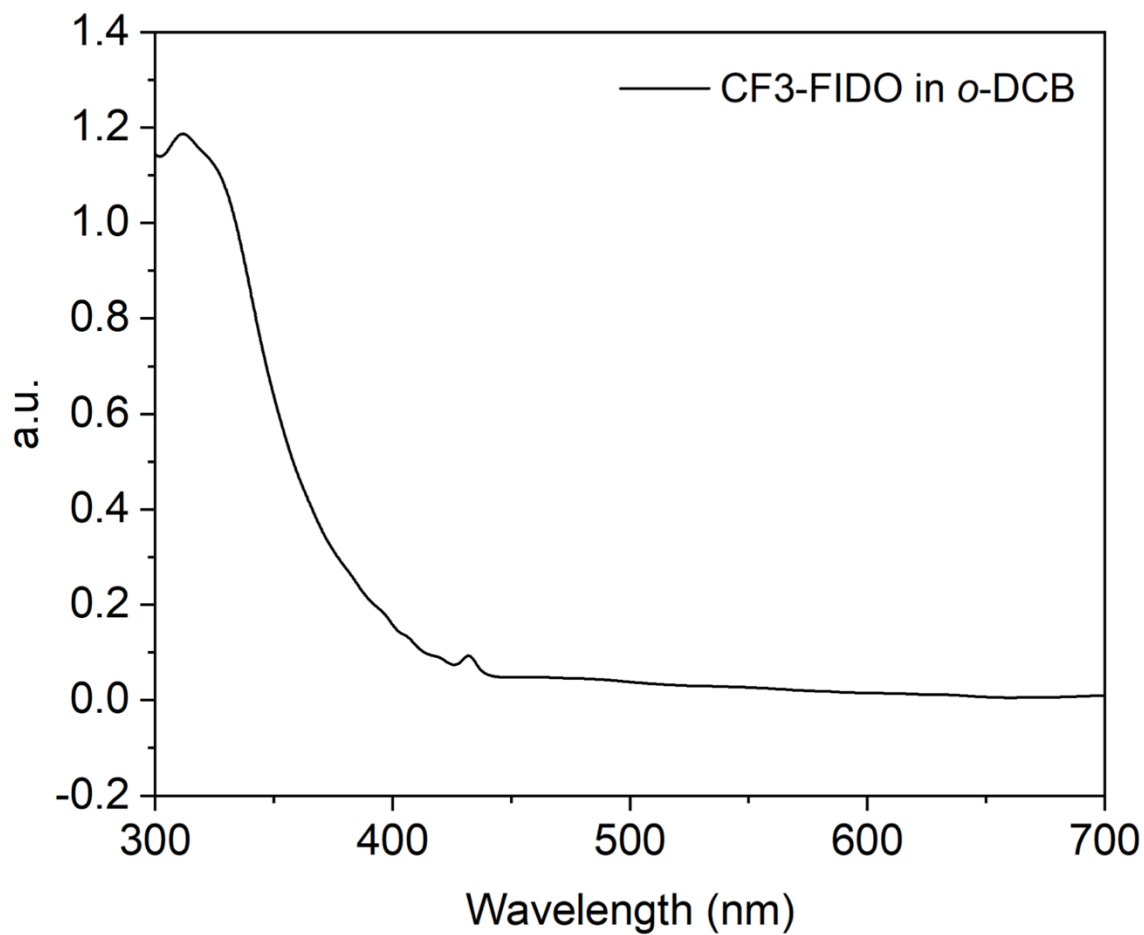


Figure S6. UV-visible spectroscopy of CF3-FIDO.

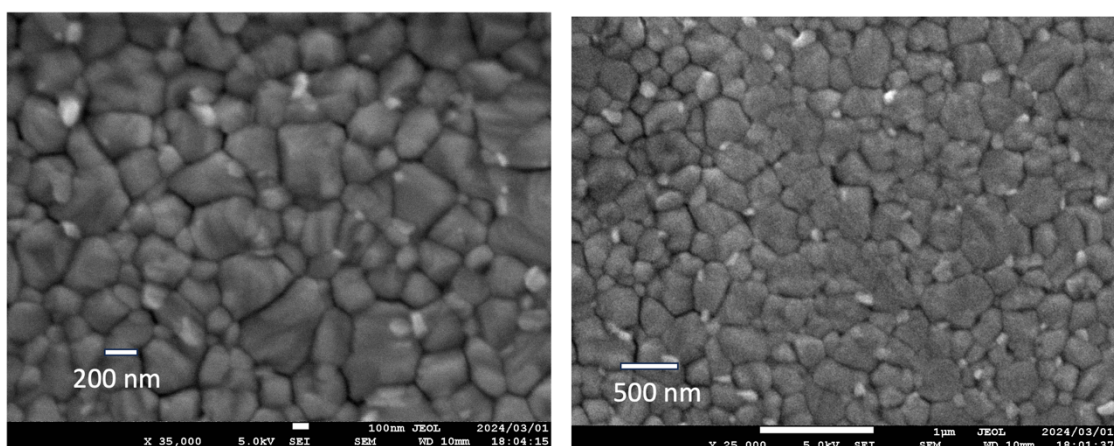


Figure S7. SEM picture of perovskite layer.

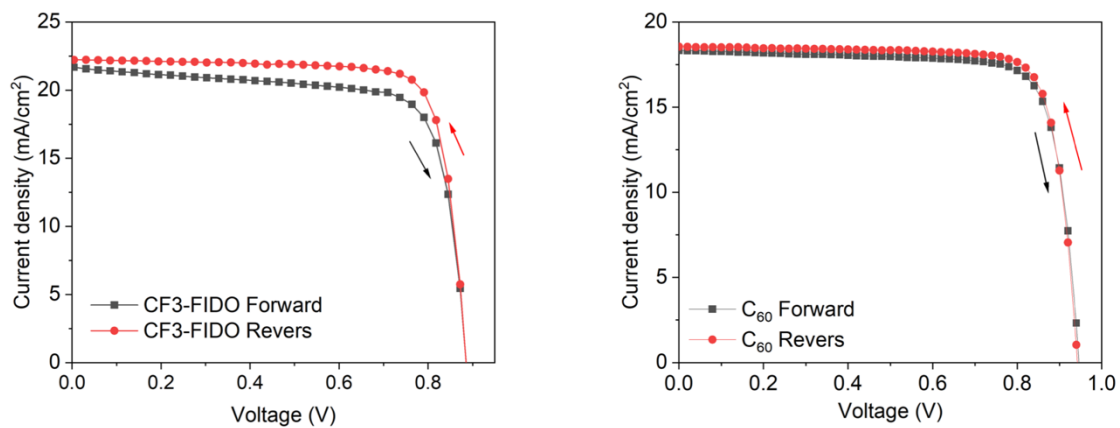


Figure S8. The J - V curve of PSCs with forward and revers scan.

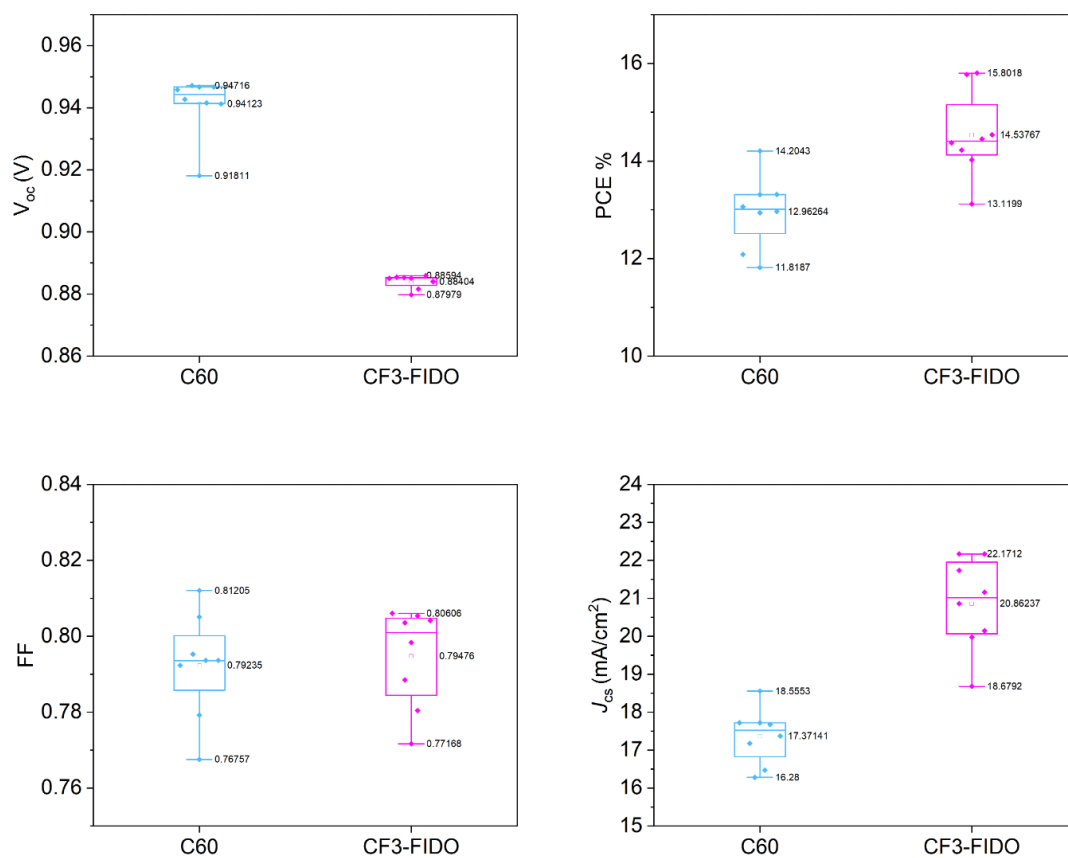


Figure S9. The performance distributions of PSCs.

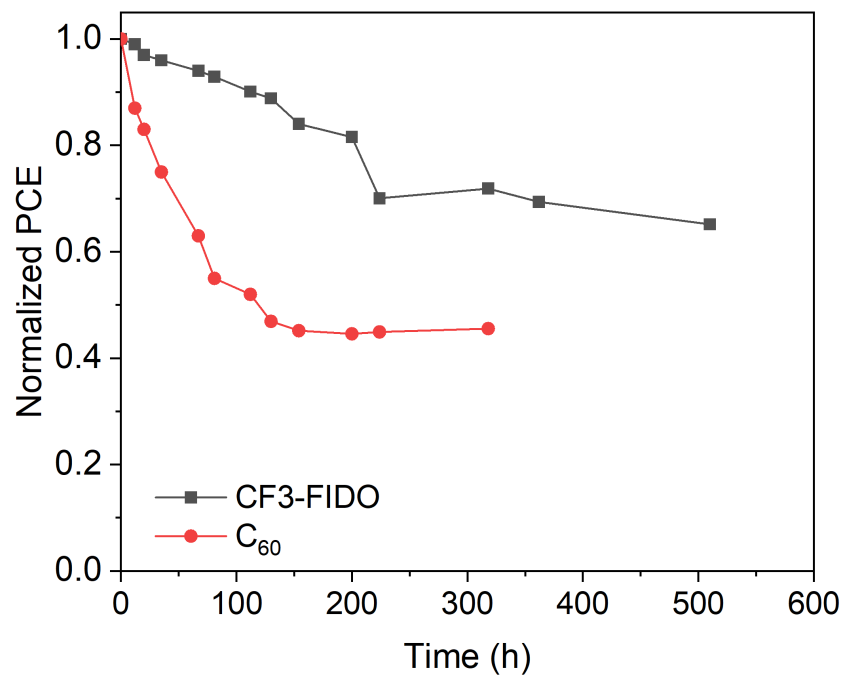


Figure S10. Long-term stability of perovskite solar cells. (Air, 20% humidity)

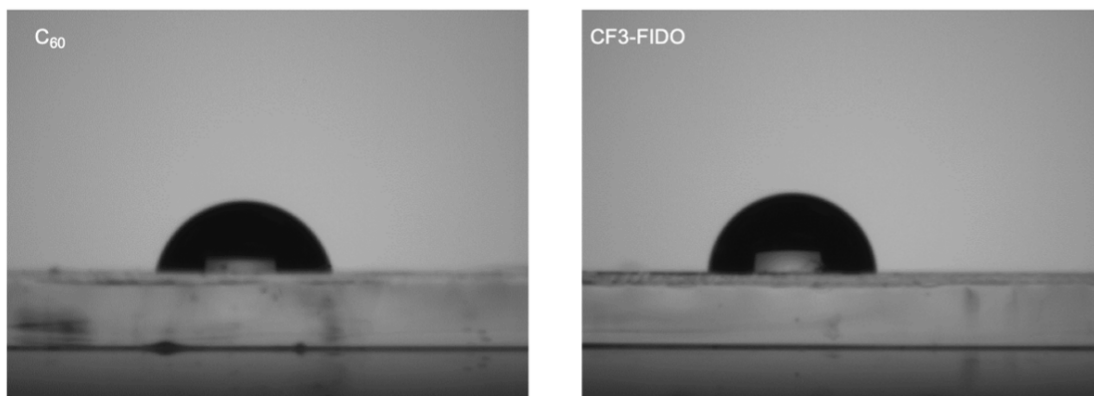
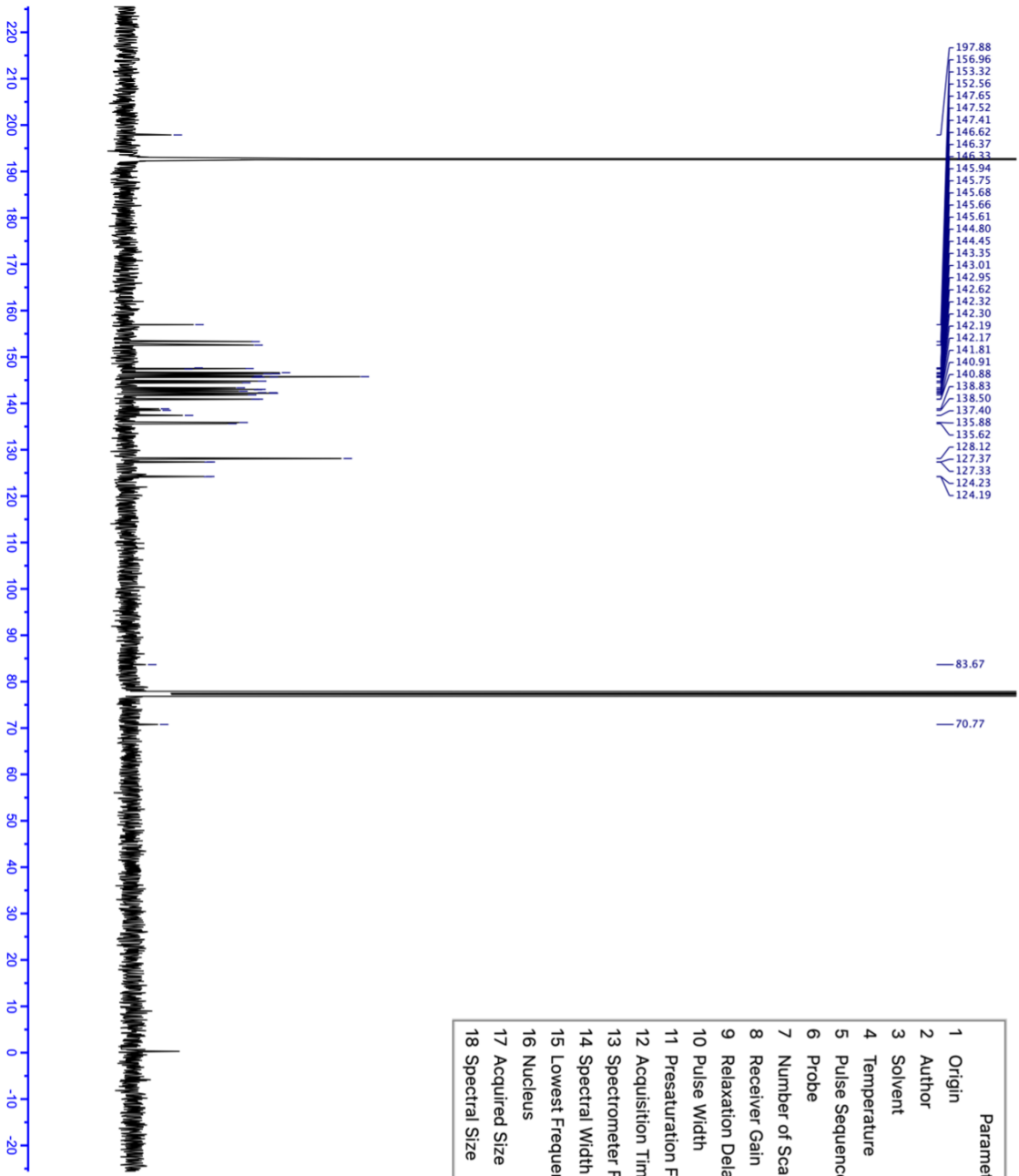
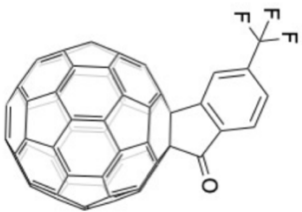


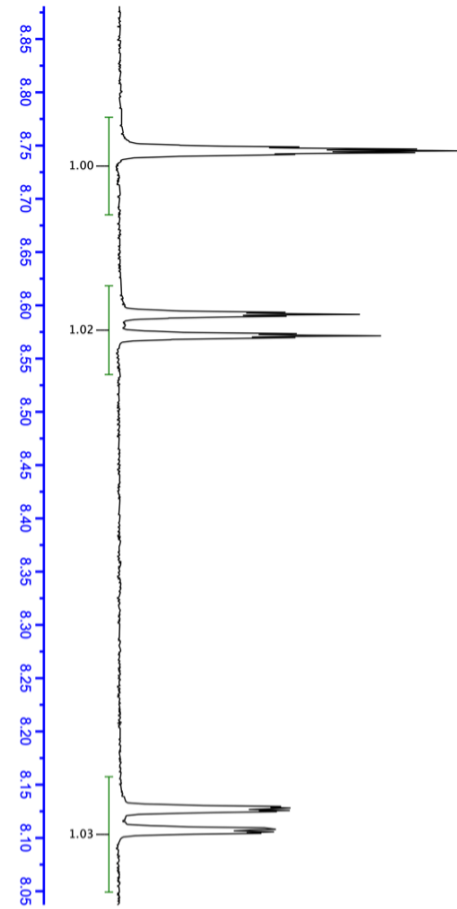
Figure S11. Water contact angle of fullerene derivatives. (20 nm evaporated C₆₀ or CF3-FIDO film on glass)



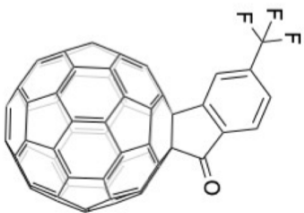
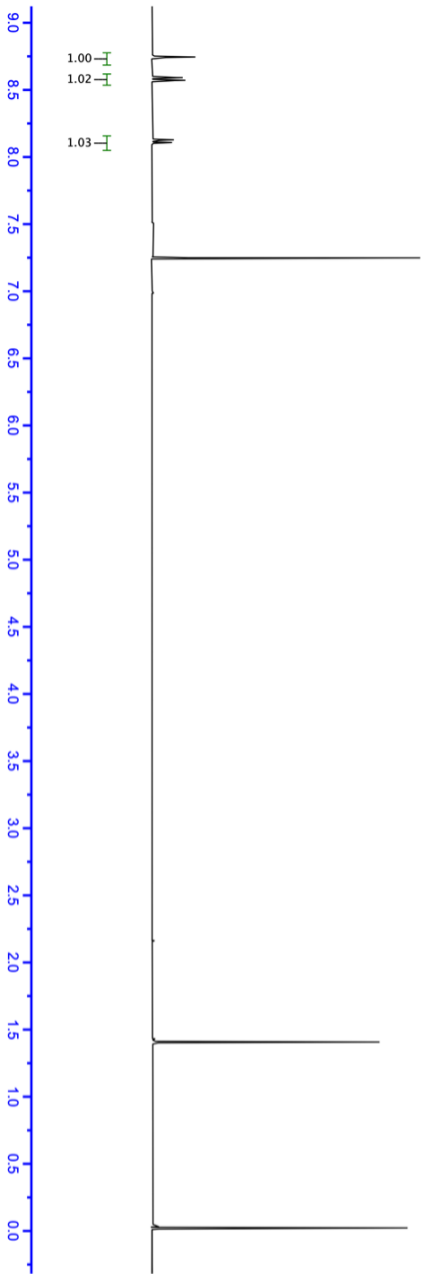
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7 Number of Scans	10240
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11 Presaturation Frequency	
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16 Nucleus	¹³ C
17 Acquired Size	22439
18 Spectral Size	52429



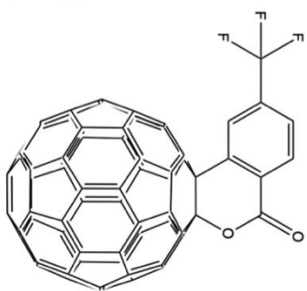
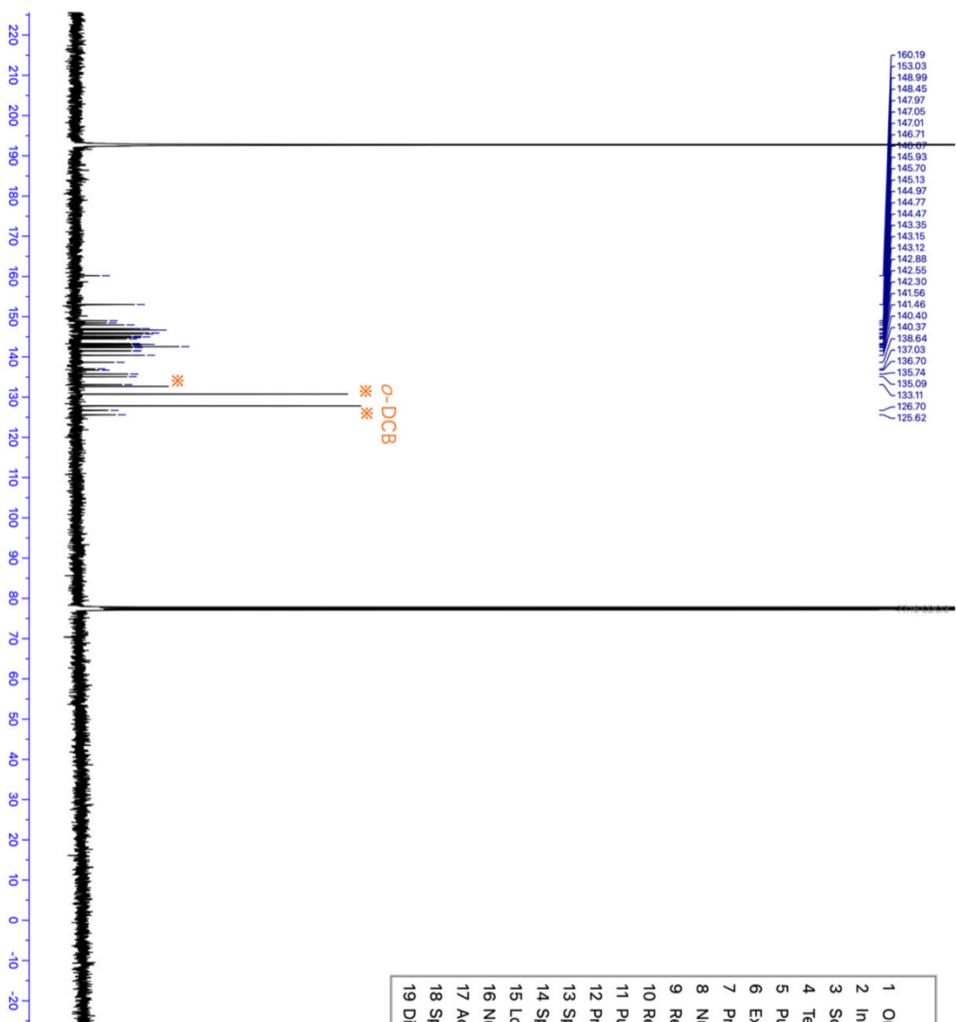
CF3-FIDO



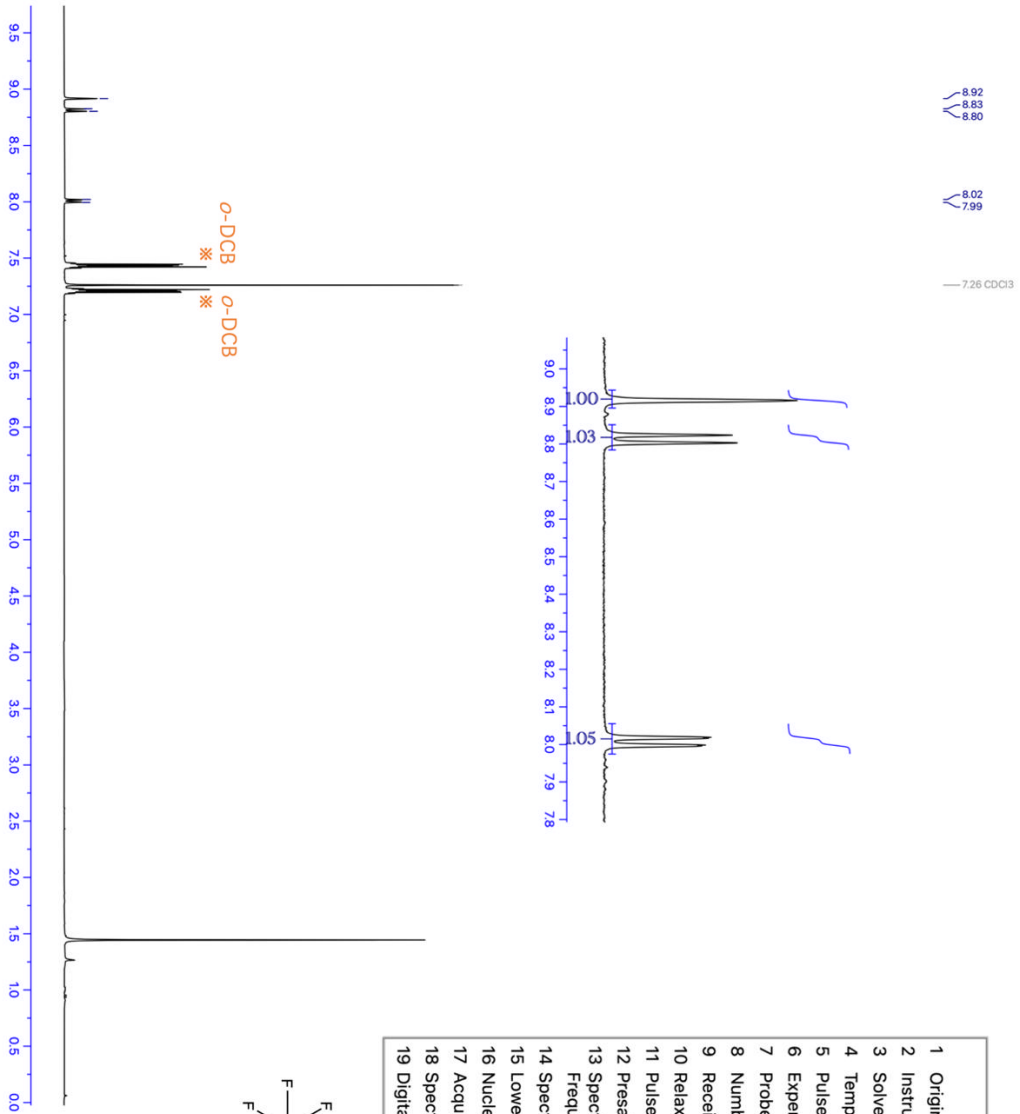
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17 Acquired Size	23897
18 Spectral Size	52430



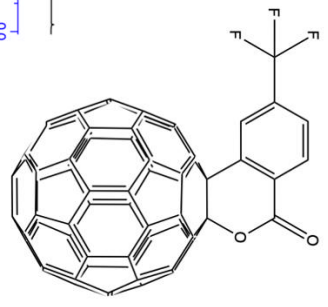
CF3-FIDO

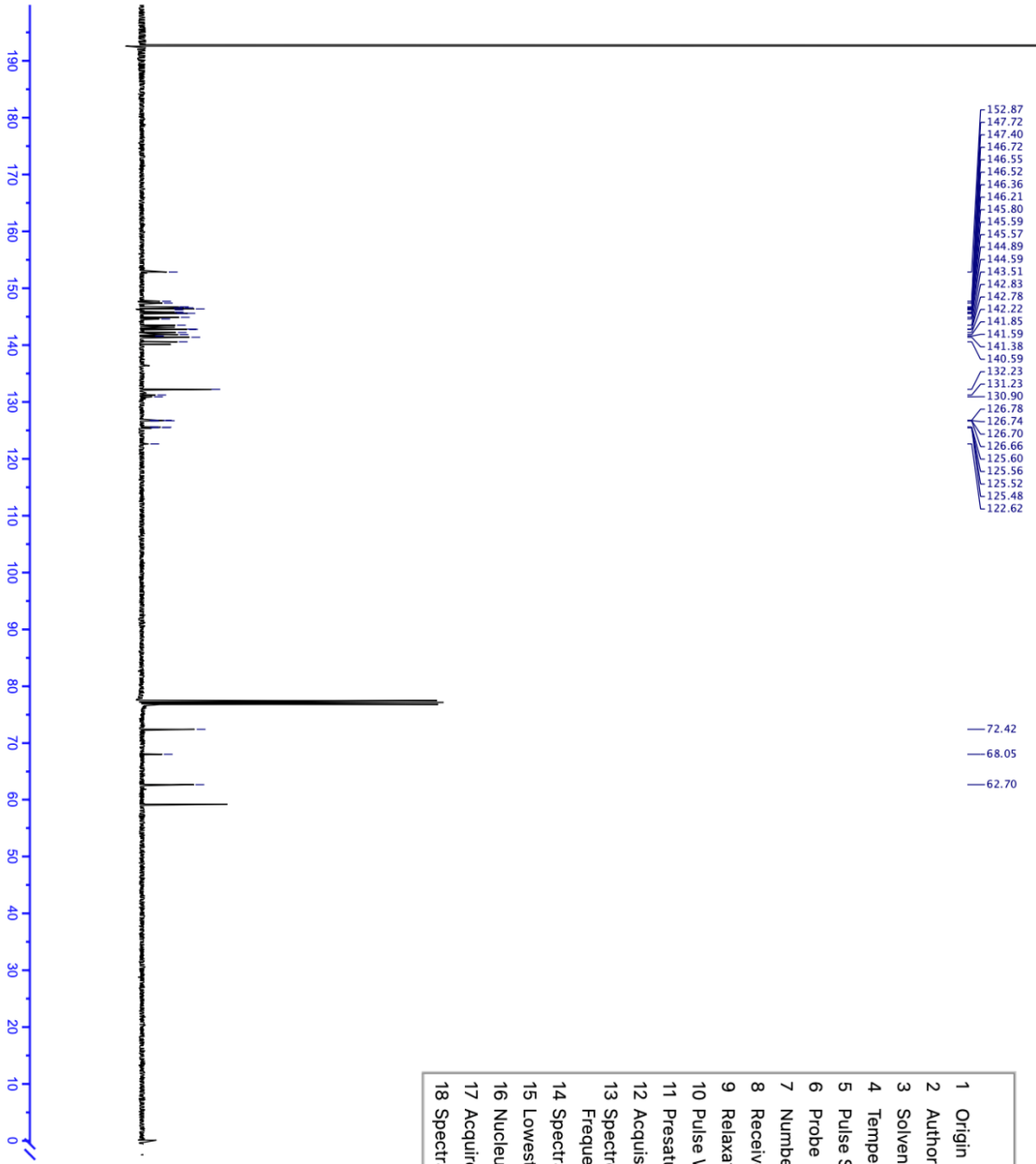


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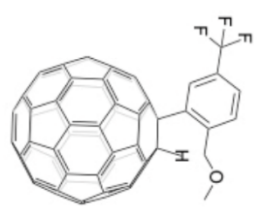


Parameter	值
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18 Spectral Size	52429
19 Digital Resolution	0.11

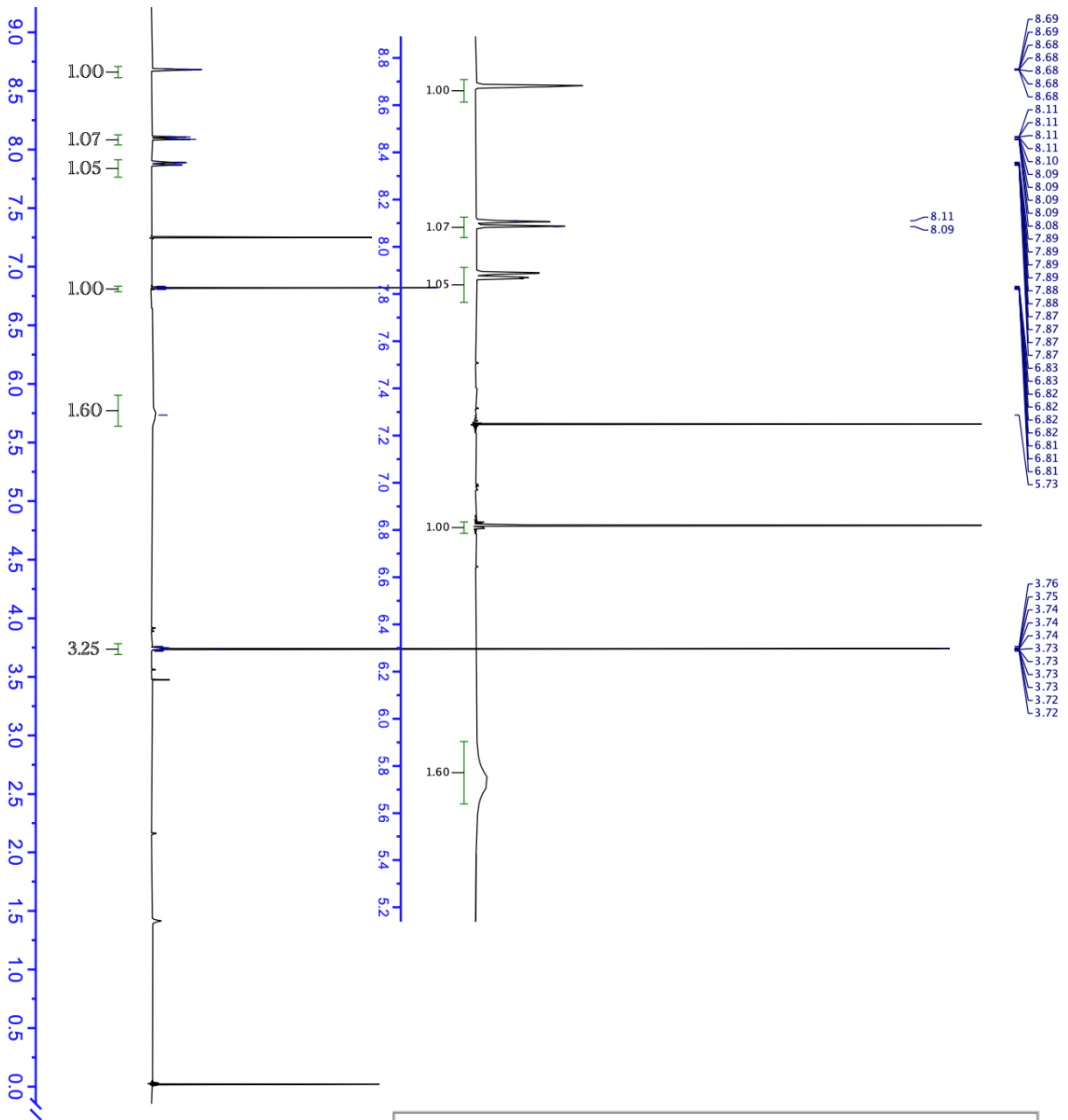




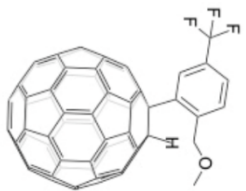
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18 Spectral Size	52430



F3



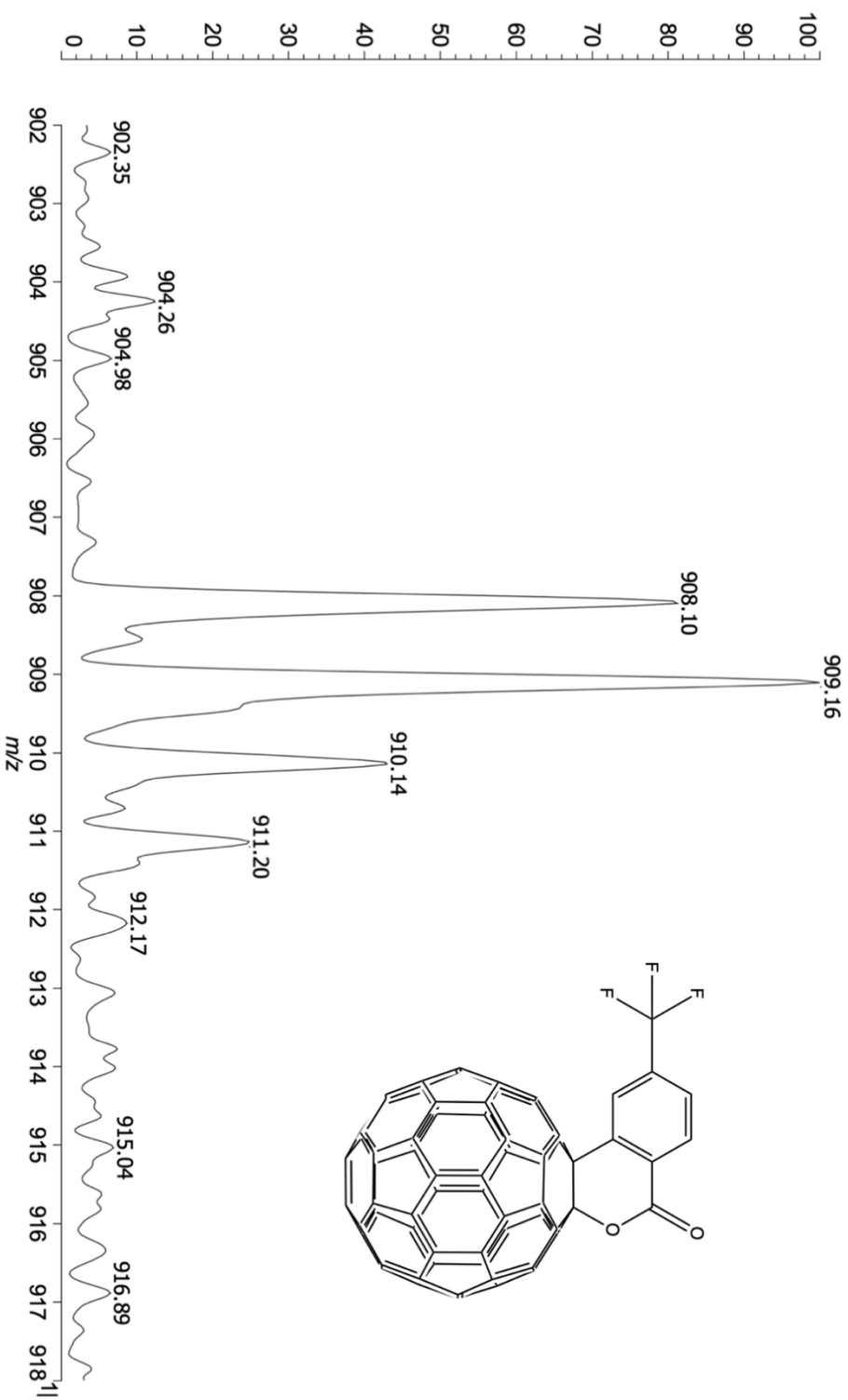
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18 Spectral Size	52430
19 Digital Resolution	0.11

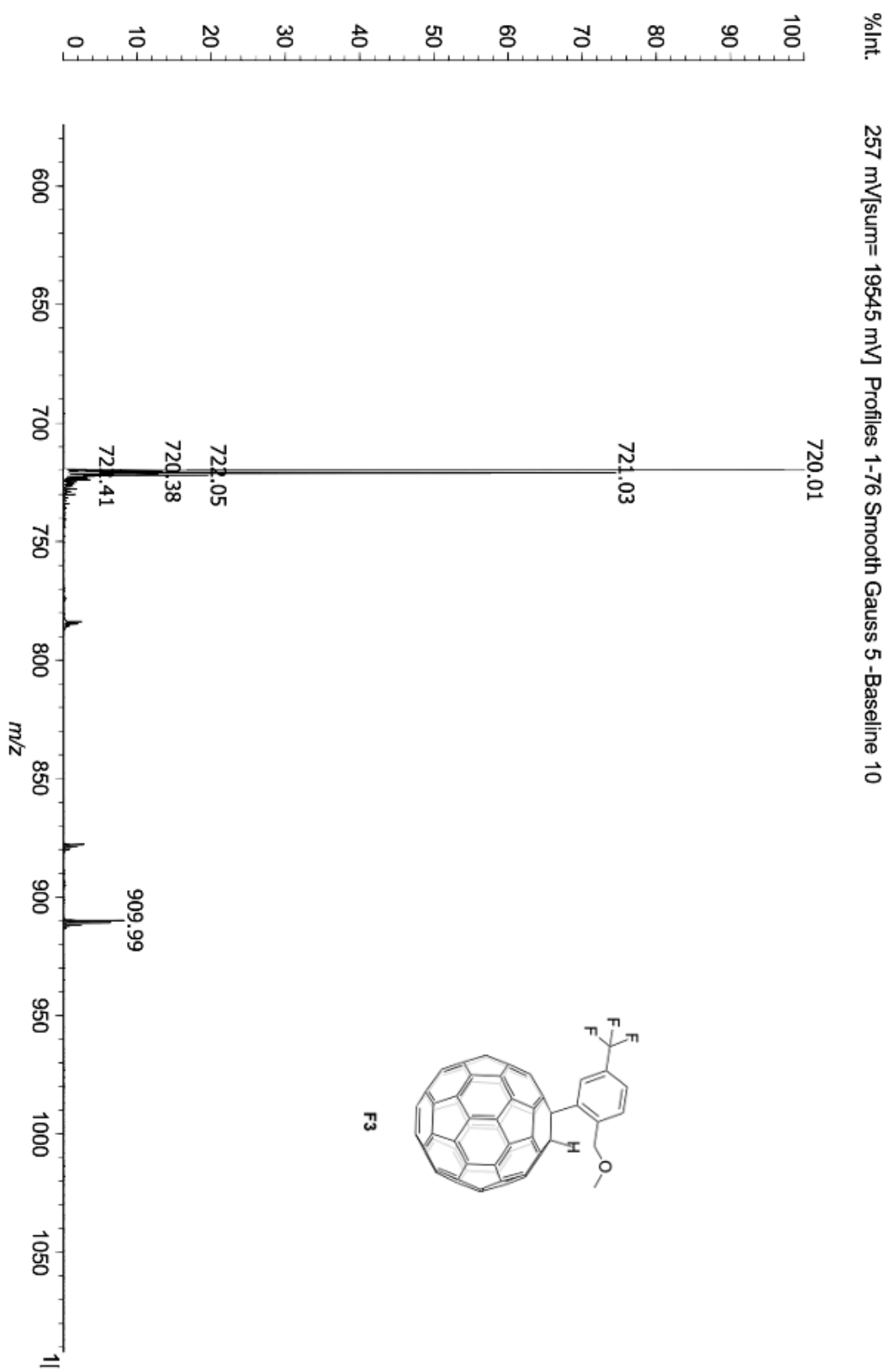


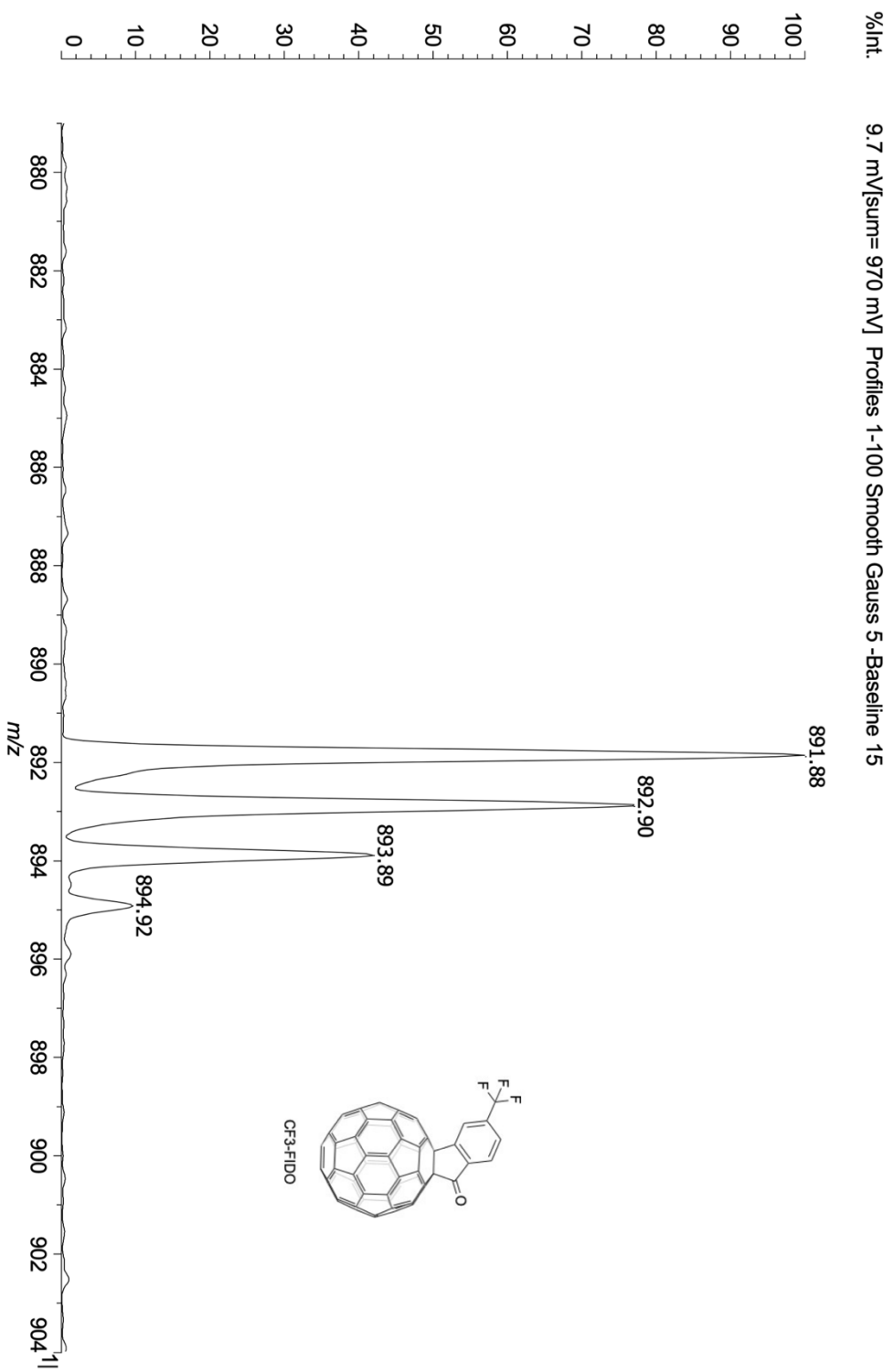
F3

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%Int. 3.4 mV[sum= 195 mV] Profiles 1-58 Smooth Gauss 5 -Baseline 10







Reference

- 1 David W I F, Ibberson R M, Matthewman J C, Prassides K, Dennis T J S, Hare J P Kroto H W, Taylor R, Walton D R M. *Nature* 1991, **353**, 147-149.