Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Efficient NDT small molecule solar cell with high fill factor by pendant group engineering

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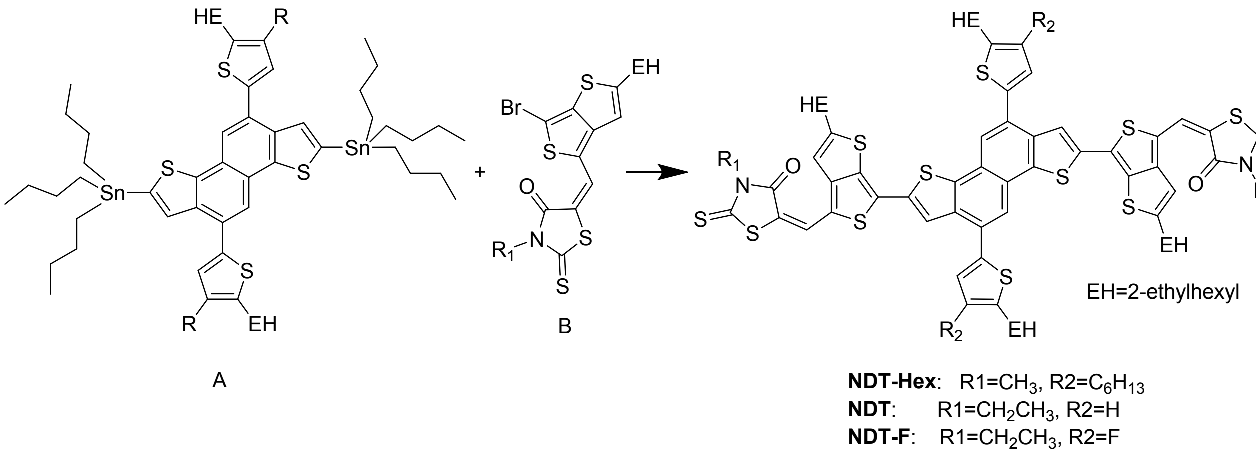
Contents

Part 1. Experimental Section

1.1 Materials synthesis and characterization

All reactions involving air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Unless stated otherwise, starting materials were obtained from Adamas, Aldrich or J&K, and were used without further purification. Anhydrous THF and toluene were distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH_2 prior to use.

The synthetic routes of NDT-Hex, NDT-F and NDT are shown in Scheme 1. Compound A and B were prepared according to the published procedures. All NDTs were synthesized through Stille-coupling reaction.



Scheme 1 Synthesis routes of NDT-Hex, NDT and NDT-F.

Synthesis of NDTs: Under nitrogen atmosphere, Compound A (1 equiv) and B (2.5 equiv.) was dissolved in toluene:DMF (1:1 in volumn), then the $Pd(PPh_3)_4$ was added (0.1 equiv). The solution was stirred at 120 °C overnight with the reaction protected under nitrogen atmosphere all the time. Then the reacted solution was extracted with DCM. **NDT-Hex:** ^{1}H NMR: 7.88(s, 2H), 7.83(s, 2H), 7.65(s, 2H), 7.29(s, 2H), 6.84(s, 2H), 3.54(s, 6H), 2.8(m, 12H), 1.8-0.8(m, 82H); ^{13}C NMR: 191.5, 167.3, 157.3, 152.6, 139.6, 139.4, 139.0, 137.3, 136.4, 136.2, 133.6, 132.1, 129.6, 128.6, 124.4, 123.3, 122.5, 122.4, 120.6, 117.8, 114.7, 41.8, 40.7, 3.8, 32.9, 32.6, 32.5, 31.9, 31.5, 31.2, 29.6, 29.0, 28.8, 25.8, 25.5, 23.3, 23.1, 22.9, 14.3, 14.2, 14.1, 11.1, 10.7. HRMS (MALDI-TOF): calcd for $C_{88}H_{110}N_2O_2S_{12}$, [M]+: 1610.52, found, 1612.58. **NDT**: ^{1}H NMR: 7.51(s, 2H), 7.45(s, 2H), 7.38(s, 2H), 7.18(d, 2H), 6.98(d, 2H), 6.72(s, 2H), 4.17(m, 4H), 2.98(m, 4H), 2.76(m, 4H), 1.82-0.99(m,60H); ^{13}C NMR: 190.12, 165.7, 153.4, 146.4, 144.5, 141.9, 138.2, 137.6, 134.7, 133.3, 130.3, 128.0, 125.4, 125.2, 123.0, 121.2, 121.0, 119.6, 117.8, 114.2, 40.4, 39.6, 39.0, 35.7, 33.5, 31.6, 30.9, 29.0, 28.7, 28.4, 28.0, 27.9, 24.7, 24.6, 22.2, 22.1, 21.7, 13.3, 13.2, 11.3, 9.9, 9.8. HRMS (MALDI-TOF) calcd for $C_{78}H_{90}N_2O_2S_{12}$, [M]+: 1470.36, found, 1472.31. **NDT-F**: ^{1}H NMR: 7.41(s, 2H), 7.15(s, 2H), 7.08(d, 2H), 6.94(s, 2H), 6.68(s, 2H), 4.12(m, 4H), 2.91(m, 4H), 2.77(m, 4H), 1.96-0.85(m, 60H); ^{13}C NMR: 190.8, 166.7, 157.7, 155.8, 153.3, 152.4, 138.6, 136.5, 135.1, 134.0, 128.3, 123.5, 122.6, 122.2, 122.0, 121.6, 120.7, 120.2, 118.0, 116.7, 116.4, 114.7, 40.8, 40.6, 40.0, 36.8, 32.8, 32.7, 29.6, 28.9, 25.7, 25.6, 23.3, 22.8, 14.4, 14.3, 12.4, 10.8, 10.7. HRMS (MALDI-TOF): calcd for $C_{78}H_{88}F_2N_2O_2S_{12}$, [M]+: 1506.35, found, 1508.29.

Characterization: ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker Avance III 400 or 300 HD spectrometer. Chemical shifts for hydrogens are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent ($CDCl_3$: 7.26). ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: 77.2). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in hertz (Hz), and integration.Matrix-assisted laser desorption/ionization time-of-fight mass spectrometry (MALDI-TOF) measurements were performed on an Applied Biosystems 4700 Proteomics Analyzer. UV-vis spectra were recorded by a JASCO V-570 spectrometer. Cyclic voltammetry (CV) measurements were carried out on a CHI640C analyzer in a scan rate of 100 mV/s under a conventional three-electrode test mode, with a glassy-carbon working electrode, platinum-wire counter electrode, and Ag/Ag+ reference electrode. The test was carried out at room temperature under nitrogen atmosphere with using ferrocene/ferrocenium (Fc/Fc+) as an external potential marker, which was made in an anhydrous CH_2Cl_2 solution with 0.1 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte. The HOMO/LUMO was calculated by equation: EHOMO/LUMO = − (4.8 + $E_{\mathrm{ox/red}} - E_{\mathrm{Fc/Fc+}}$) eV. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere by a Shimadzu DTG 60 instrument, which records the weight loss from 25 °C to 550 °C under a heating rate of 10 °C min^{-1}.

1.2 Device fabrication and characterization

Small molecule organic solar cells were fabricated in a traditional ITO/PEDOT:PSS/active layer/Ca/Al structure with general processing procedures shown below. Prior to device fabrication, patterned indium tin oxide (ITO) glass (1.5 cm × 1.5 cm, sheet resistance, 15 Ω □$^{-1}$) was cleaned in an ultrasonic bath of detergent, deionized water, acetone and isopropanol, subsequently. After being treated for 20 min in an ultraviolet-ozone chamber, the clean ITO glass was spin-coated with a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P VP AI 4083) layer(~40nm) , which was dried at 150 °C for 20 min. After that, the photoactive blend was spin coated onto the surface of PEDOT:PSS from a chloroform solution to form the active layer. Then the FPI was spin-coated from a methanol solution (concentration: 0.5 mg/ml) at 3000 rpm for 30 s onto the active layer. Finally, ~60 nm thick aluminum (Al) were thermally evaporated in a vacuum chamber (10^{-4} Pa) to form the electode. The active area of each device was 3.08 mm^2, defined by a shadow mask. For photovoltaic measurement, the J-V curve was recorded by a Precision Source/Measure Unit (B2912A, Agilent Technologies) and an AAA grade solar simulator (XES-70S1, SAN-EI Electric Co. Ltd, 7 ×7 cm^2 beam size) coupled with AM 1.5G solar spectrum filters was taken as the light source. The incident light power onto the surface of samples was calibrated to be 100 mW cm^{-2} by a standard monocrystalline silicon reference cell (SRC-1000-TC-QZ, VLSI Standards Inc., 2 × 2 cm^2). The external quantum efficiency (EQE) was measured by a Solar Cell Spectral Response Measurement System (QE-R3011, Enlitech Co. Ltd) with the light intensity calibrated by a standard single crystal Si photovoltaic cell.

For morphology characterization, atomic force microscopy (AFM) measurements were carried out by a Nanoscope IIIa AFM (Digital Instruments) system in a tapping mode. Transmission electron microscopy (TEM) observation was also performed by using a JEOL 2200FS at 160 kV accelerating voltage. To examine the charge transporting property, space charge-limited current (SCLC) method was used with the mobilities determined by fabricating hole- or electron-only devices. The hole-only device is configured to be ITO/PEDOT:PSS/active layer/MnO3/Al while the electron-only one is of an Al/active layer/Al structure. The active layers for the two single-carrier-transporting devices are spin-coated following the same condition as that of the real devices. The mobilities were determined by fitting the dark current to a SCLC model, which is described as:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3} exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

where J is the current density, L is the film thickness of the active layer, μ is the mobility, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the transport medium, V (= V_{appl} - V_{bi}) is the internal voltage in the device, where V_{appl} is the applied voltage and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Part 2. Figures and Tables

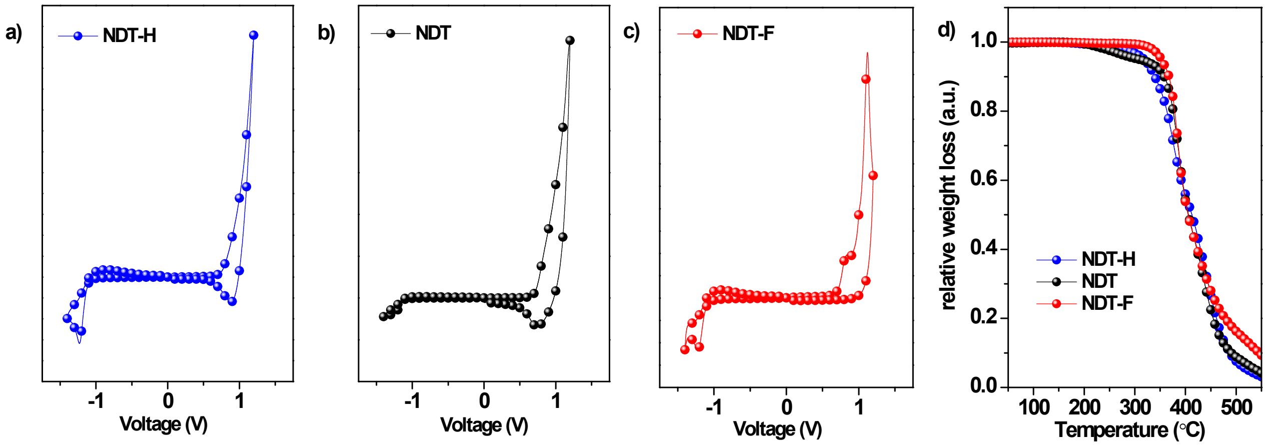


Figure S1 Cyclic voltammetry curves (a, b, c) of NDT-Hex, NDT and NDT-F films in CH3CN/0.1 M [n-Bu4N]$^{+}$[PF6]$^{-}$ solution at a scan rate of 0.1 V/s and TGA of three materials (d).

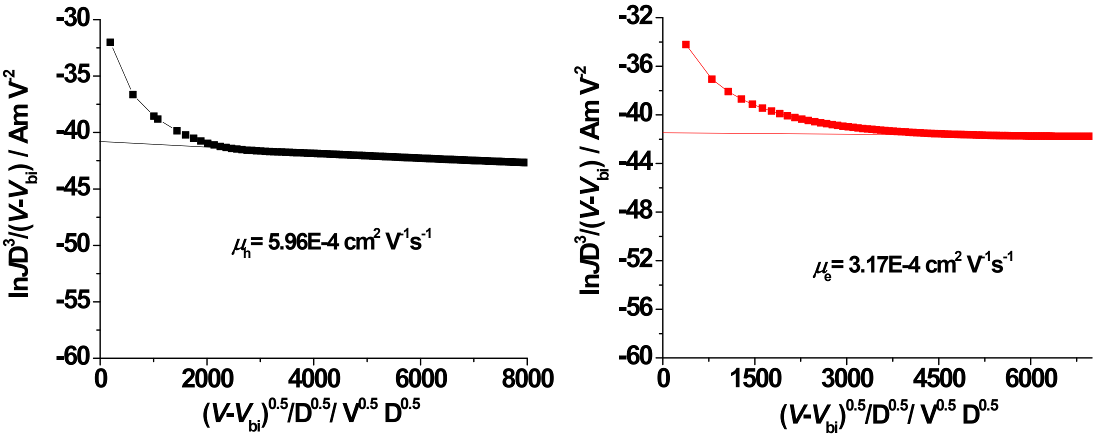


Figure S2 SCLC hole and electron mobility of as-cast NDT-Hex:PC$_{71}$BM blend film.

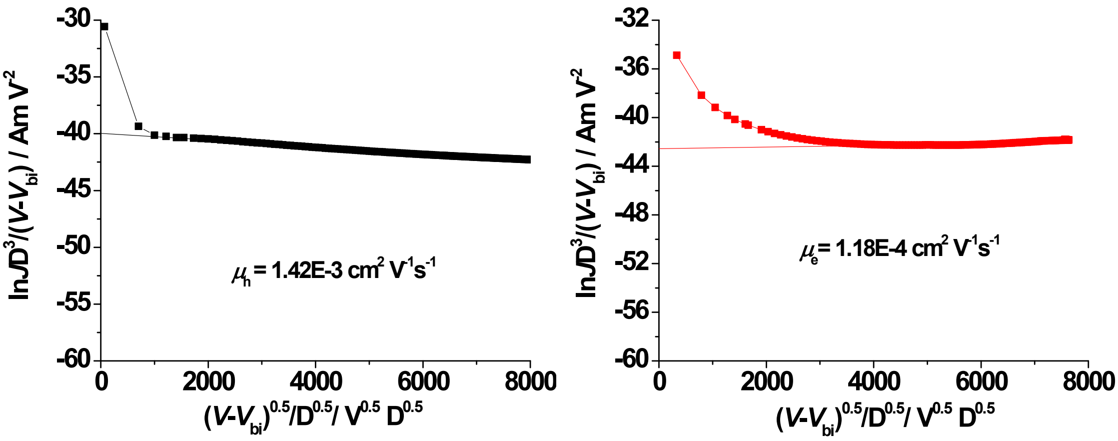


Figure S3 SCLC hole and electron mobility of as-cast NDT:PC$_{71}$BM blend film.

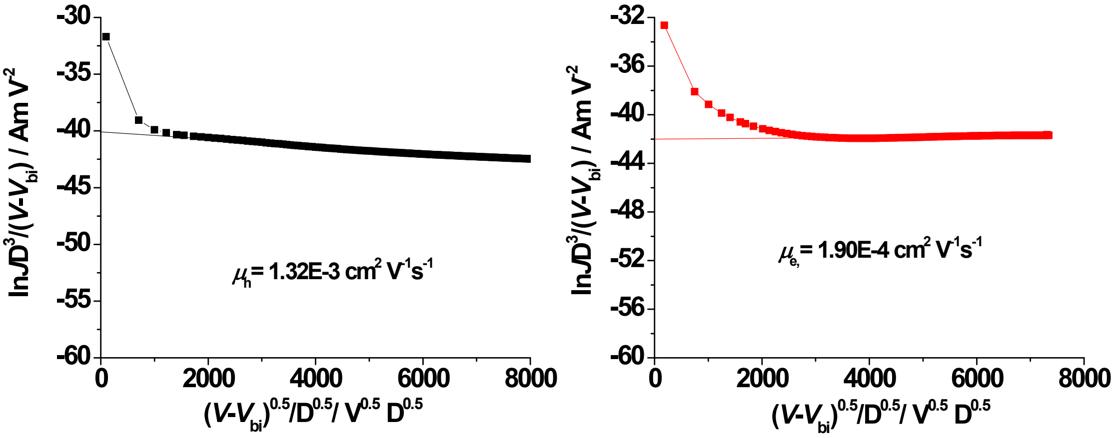


Figure S4 SCLC hole and electron mobility of as-cast NDT-F:$PC_{71}BM$ blend film.

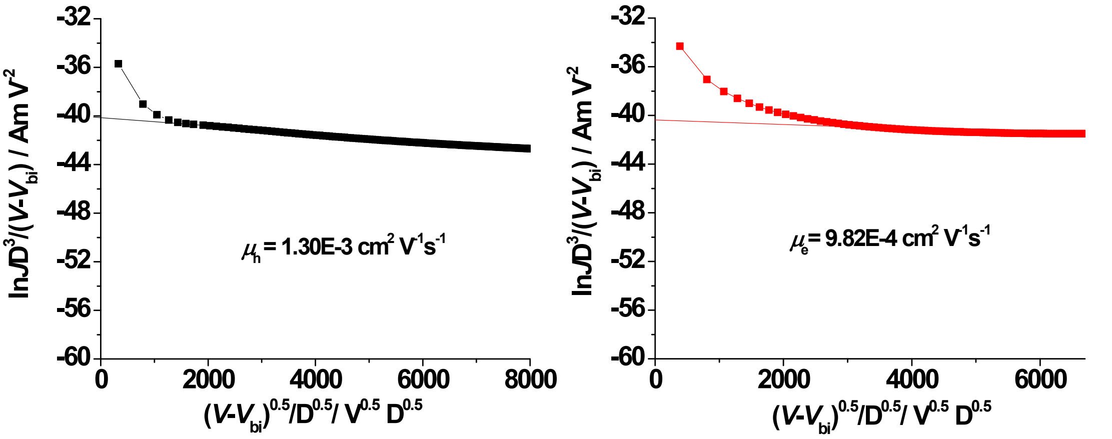


Figure S5 SCLC hole and electron mobility of SVA-treated NDT-Hex:$PC_{71}BM$ blend film.

Table S1 Photovoltaic performance of NDT-Hex:$PC_{71}BM$ solar cells under different SVA conditions.

SVA conditions	*Voc (V)*	*Jsc (mA cm^{-2})*	*FF (%)*	*PCE* [a] *(%)*
25ul, 150s	0.956	10.19	59.44	5.79
35ul, 60s	0.957	8.98	64.71	5.56
45ul, 60s	0.947	7.40	69.31	4.86
55u, 30s	0.940	7.57	62.77	4.47

[a] All devices adopt an ITO/PEDOT:PSS/NDT-Hex:$PC_{71}BM$/Ca/Al device configuration.

Table S2 Combined effect of ETL and SVA condition on photovoltaic performance of NDT-Hex:$PC_{71}BM$ solar cells.

SVA condition [a]	*ETL*	*Voc (V)*	*Jsc (mA cm^{-2})*	*FF (%)*	*PCE (%)*
25ul,150s	Ca/Al	0.956	10.19	59.44	5.79
	PFN/Al	0.987	9.59	58.39	5.52
	ZrAcAc/Al	0.972	9.91	60.38	5.82
	FPI/Al	0.970	10.08	58.93	5.76
	PDINO/Al	0.984	9.90	57.60	5.62
35ul,60s	Ca/Al	0.957	8.98	64.71	5.56
	PFN/Al	0.956	9.43	68.16	6.15
	ZrAcAc/Al	0.963	9.53	66.95	6.15
	FPI/Al	0.966	9.76	65.38	6.16
	PDINO/Al	0.958	9.66	66.04	6.11
45ul,60s	Ca/Al	0.947	7.40	69.31	4.86
	PFN/Al	0.955	8.39	70.24	5.63
	ZrAcac/Al	0.957	8.12	71.38	5.55
	FPI/Al	0.956	8.70	71.70	5.96
	PDINO/Al	0.963	8.09	68.80	5.36

Table S3 Photovoltaic parameters of NDT-Hex:$PC_{71}BM$ solar cells fabricated from solutions with varied concentration.

NDT-Hex concentration[a)]	*ETL*	*Voc (V)*	*Jsc (mA cm^{-2})*	*FF (%)*	*PCE (%)*[b)]
6mg/ml	Ca/Al	0.957	8.98	64.71	5.56
	FPI/Al	0.966	9.76	65.38	6.16
7mg/ml	Ca/Al	0.963	8.74	69.97	5.89
	FPI/Al	0.962	9.21	71.01	6.29
8mg/ml	Ca/Al	0.957	9.52	69.97	5.96
	FPI/Al	0.954	9.78	71.72	6.70
9mg/ml	Ca/Al	0.934	9.38	67.30	5.90
	FPI/Al	0.952	9.62	71.02	6.50

[a)] NDT-Hex:$PC_{71}BM$ (*w/w*) = 1:1.7. [b)]All devices were SVA-treated for 60s by 35ul CF.

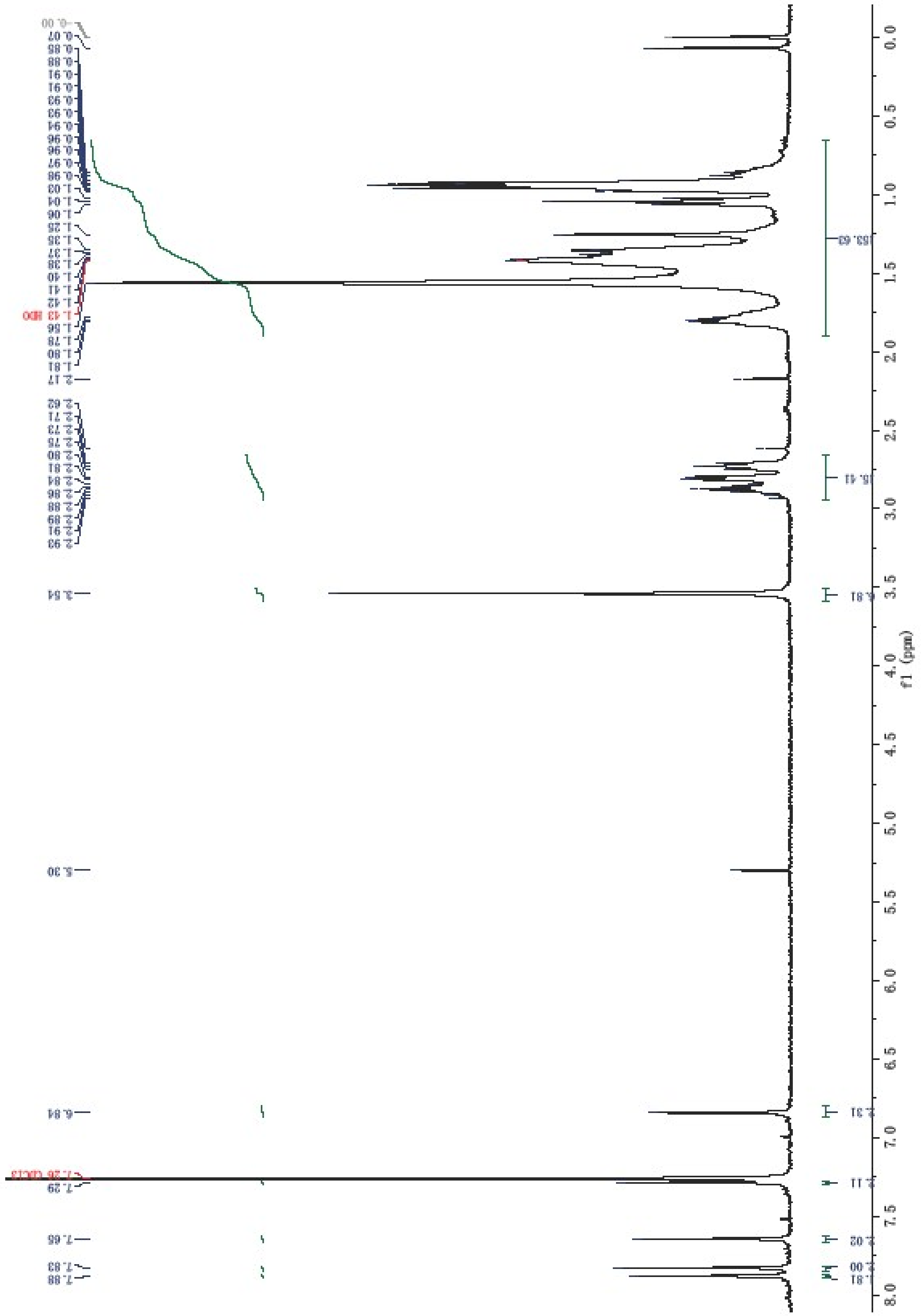
Table S4 Photovoltaic parameters of NDT-Hex:NBDTP-F_{out} solar cells.

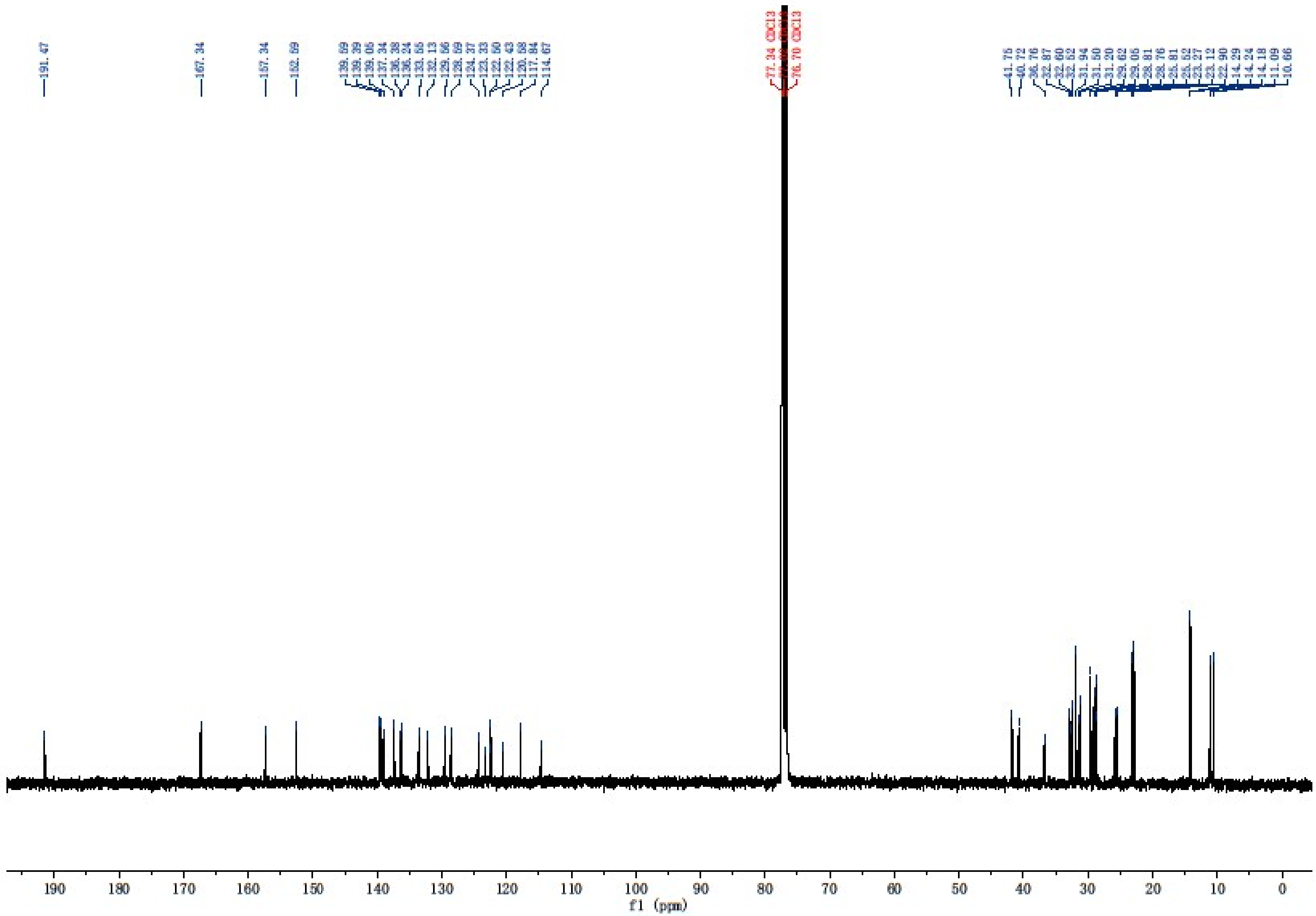
NDT-Hex:NBDTP-F_{out}	*ETL*	*Voc (V)*	*Jsc (mA cm^{-2})*	*FF (%)*	*PCE (%)*[a)]
1:1.1	FPI/Al	0.795	12.84	62.03	6.34
1:1.4	FPI/Al	0.804	15.68	62.65	7.90
1:1.7	FPI/Al	0.794	16.98	63.80	8.61
1:2	FPI/Al	0.791	12.56	49.18	6.35

[a)]All devices were SVA-treated for 60s by 35ul CF.

Part 3. NMR Charts

NDT-Hex

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MALDI,3

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Comment			

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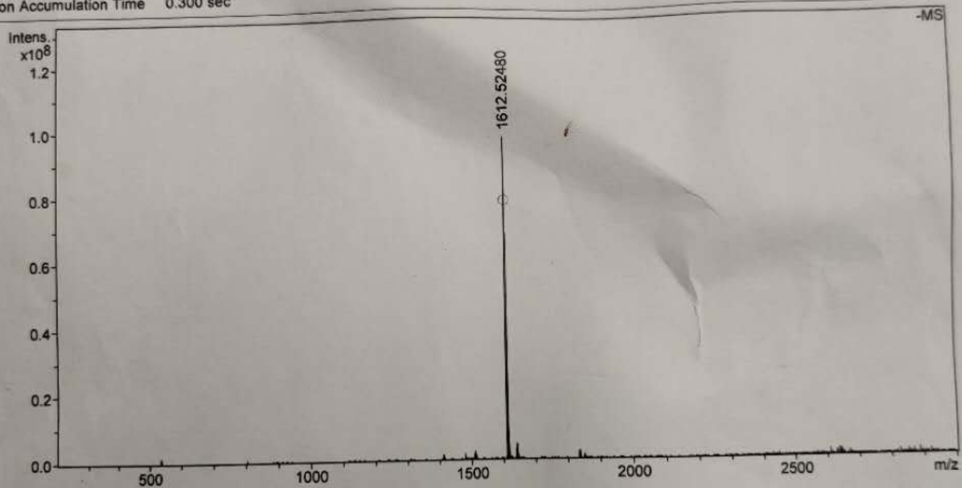

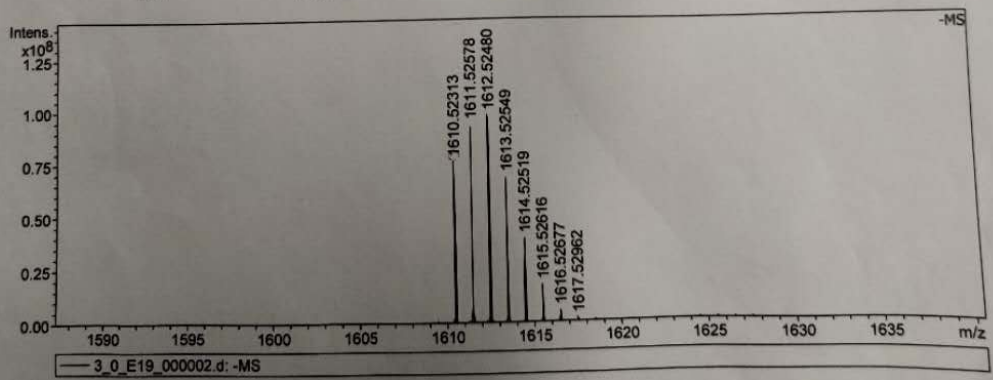

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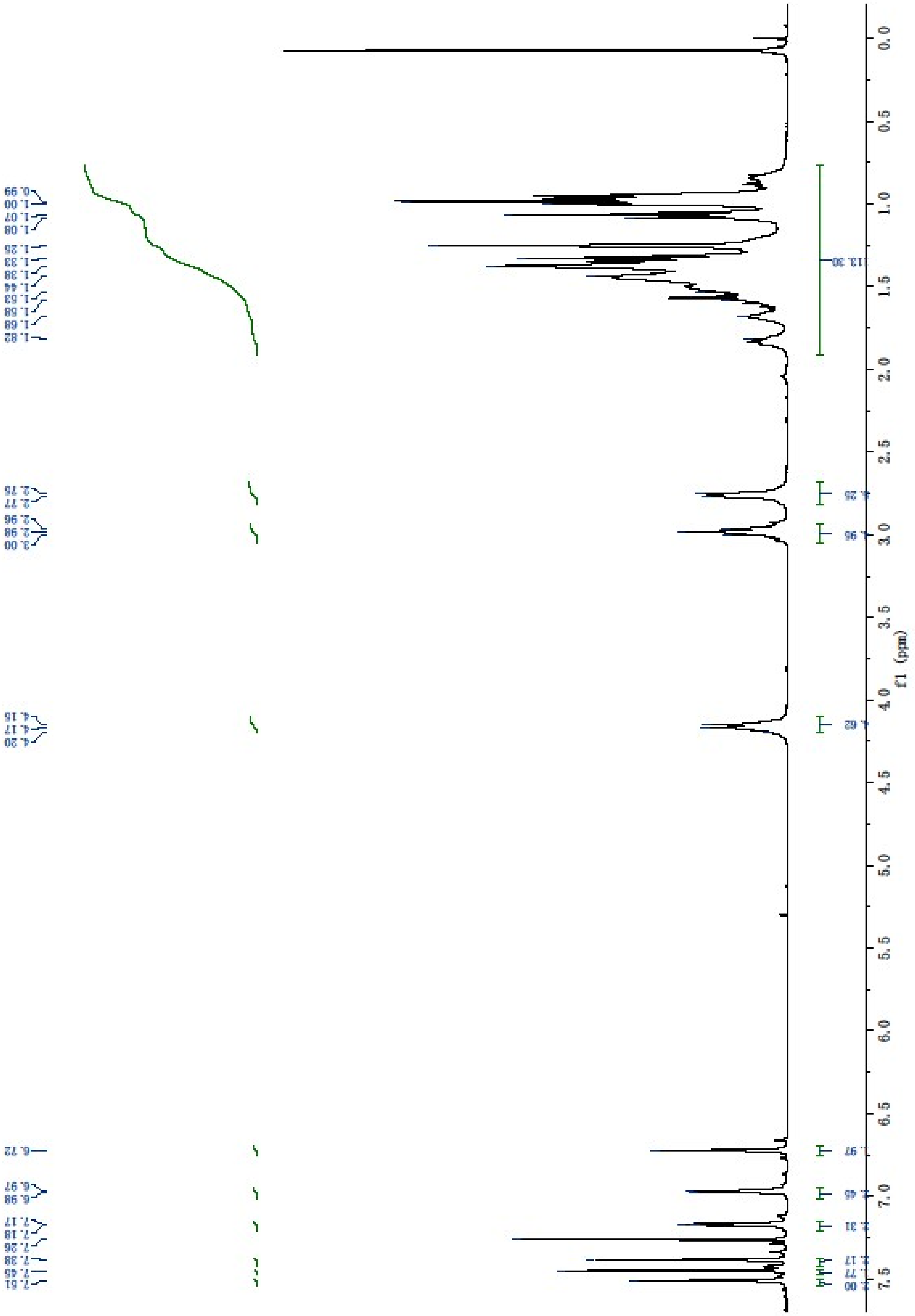

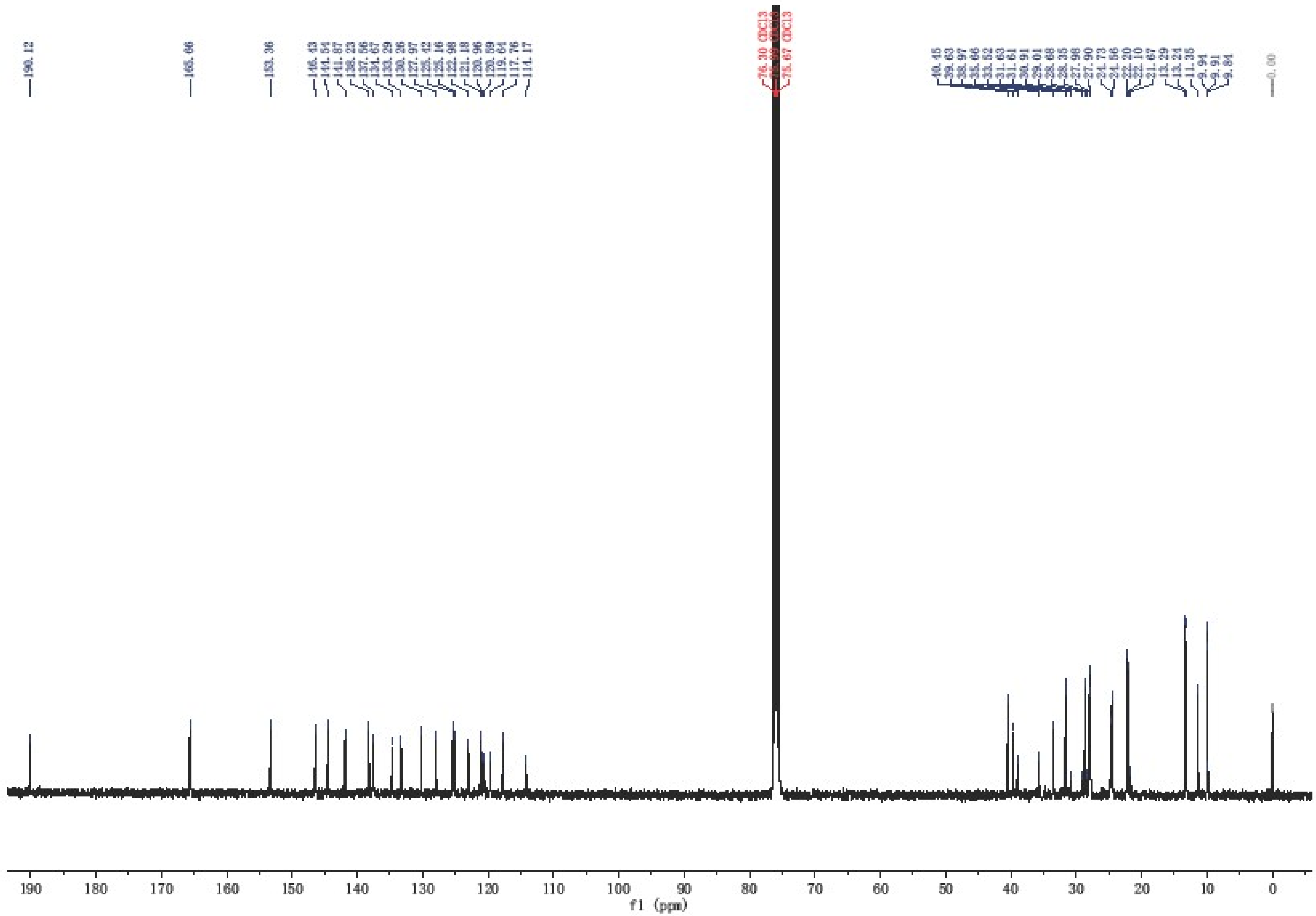
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38.97
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MALDI,2

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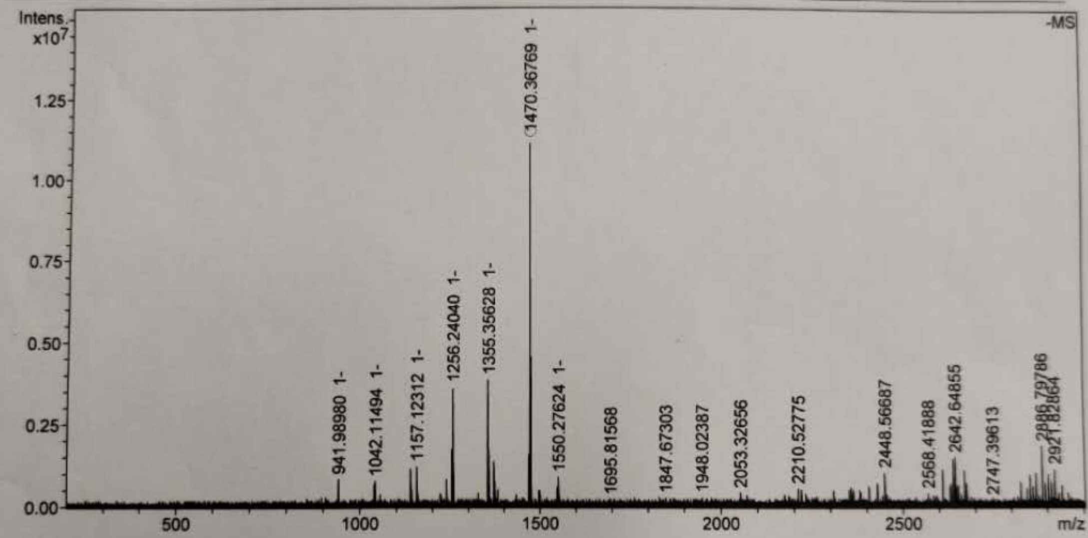

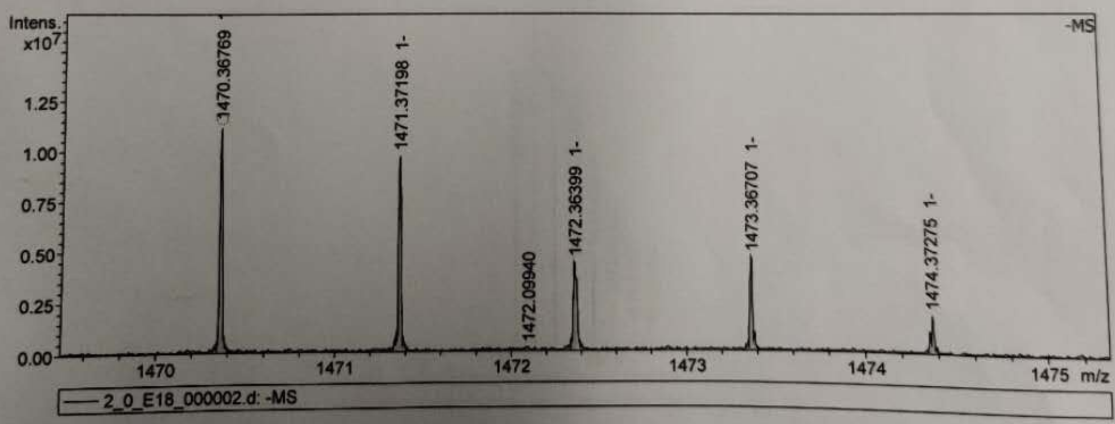

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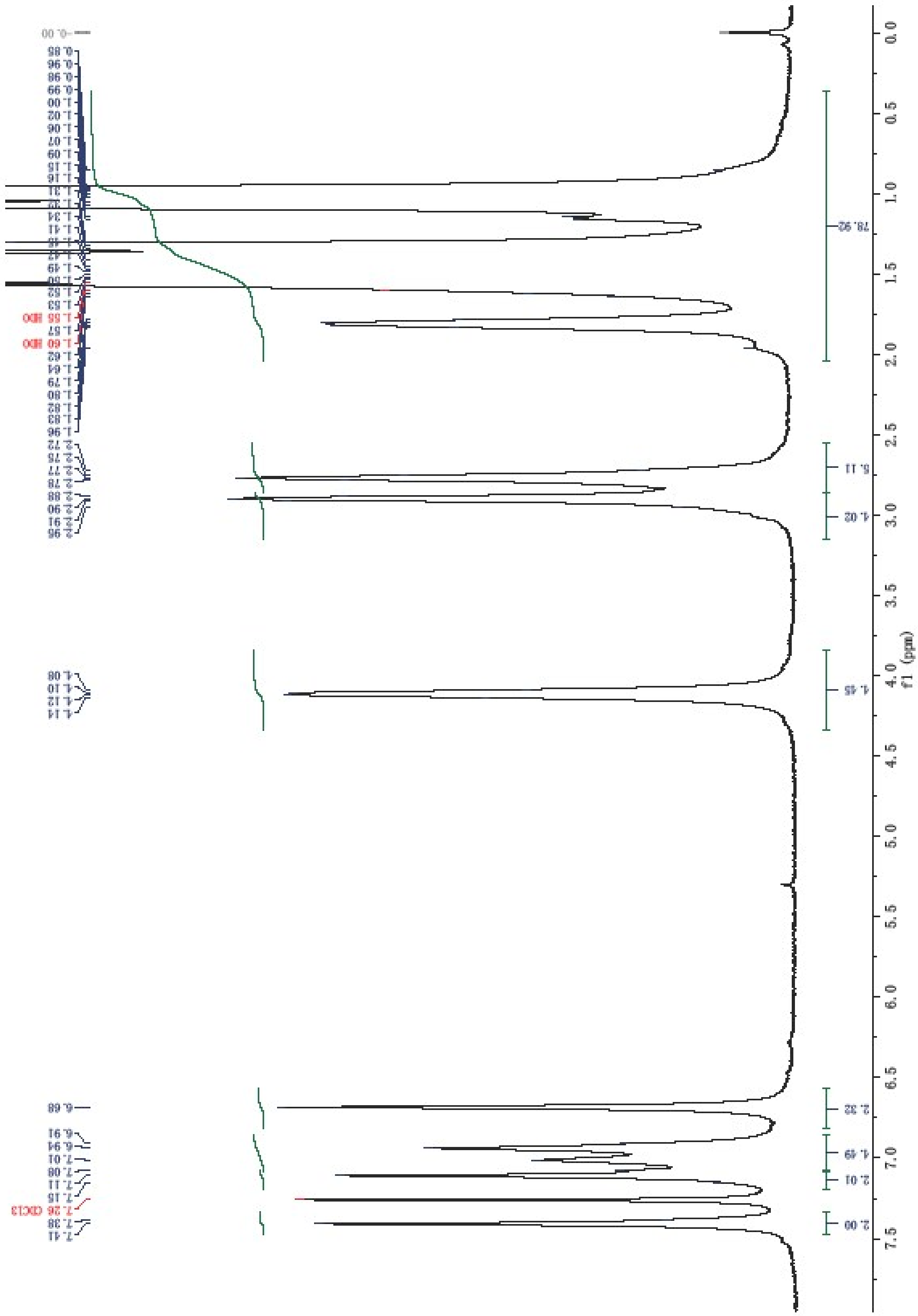
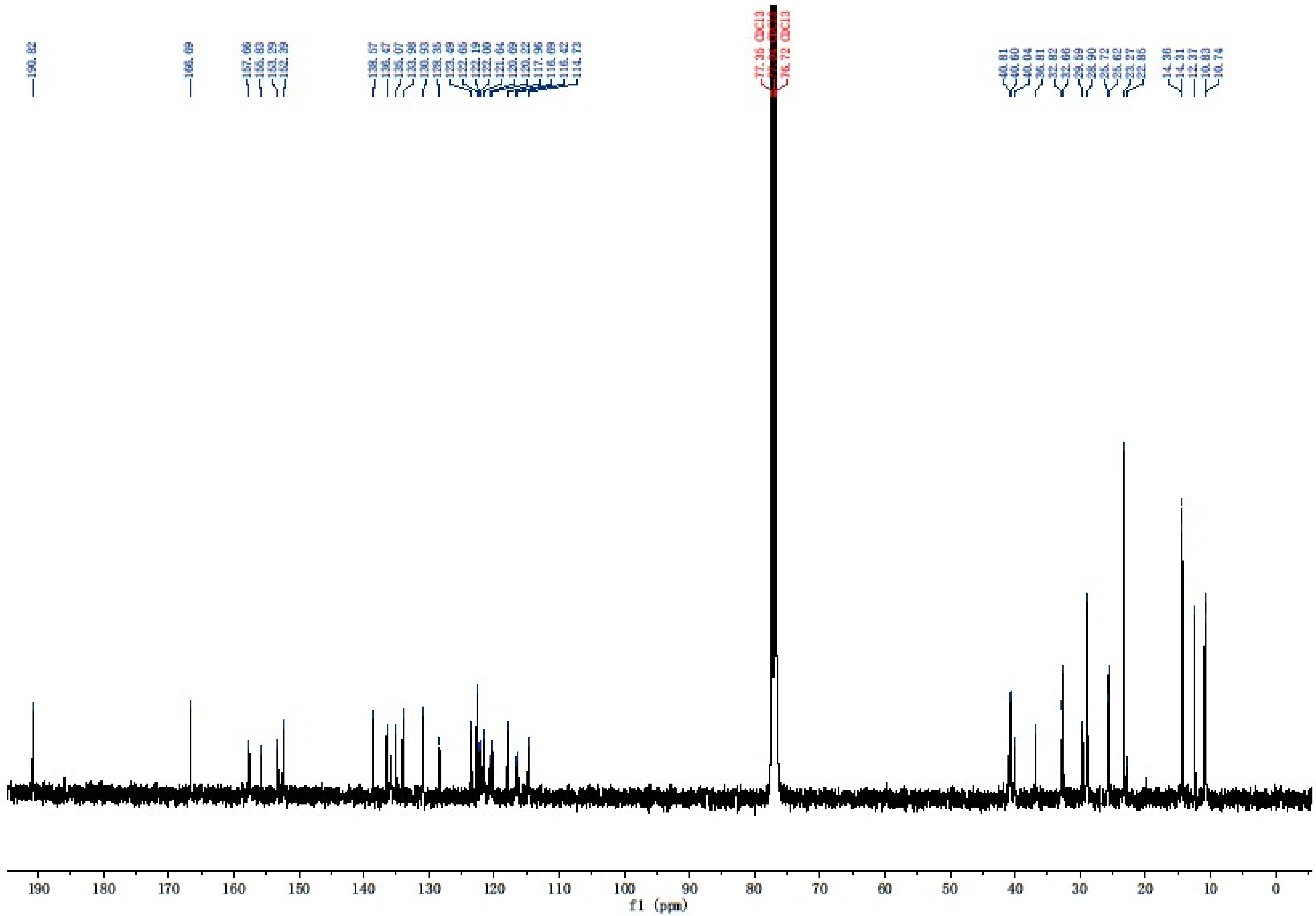
NDT-F

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116.42
114.73
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76.72 CDCl3
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MALDI,1

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Operator
Instrument solariX

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Broadband High Mass	3000.0 m/z	Laser Power	15.0 lp	Apodization	Sine-Bell Multiplication
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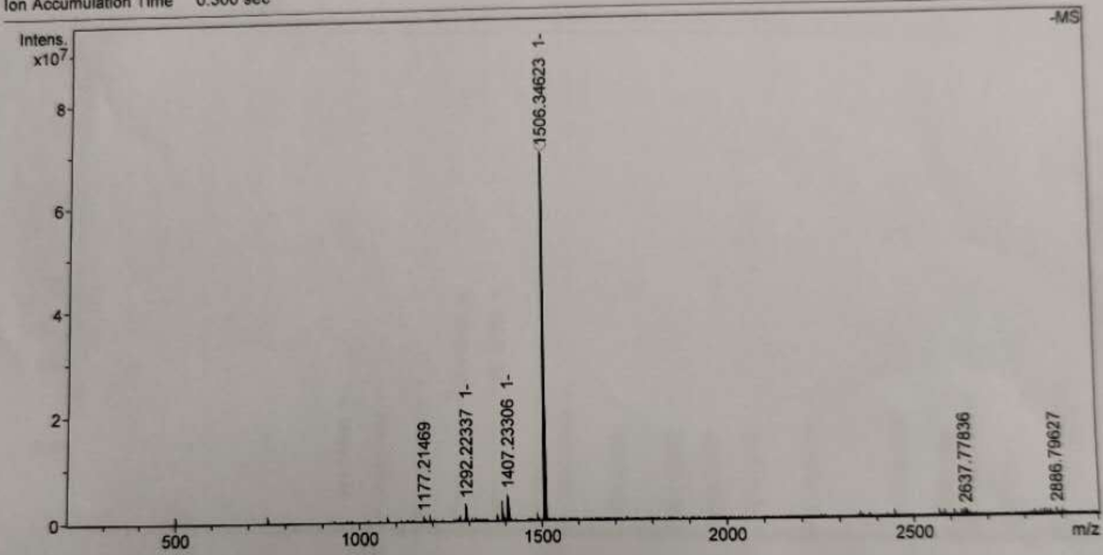

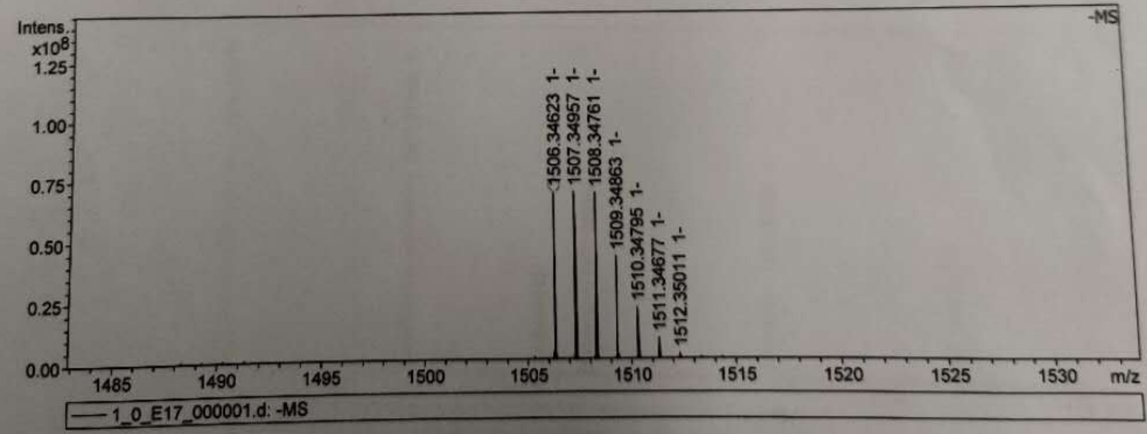

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