

Supporting Information

Oxygen heterocycle-fused indacenodithiophenebithiophene enables efficient non-fullerene molecular acceptor

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Part 1. Experimental Section

1.1 Materials and general methods

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 CaH₂ prior to use. Compounds **1-11** were prepared according to published procedures. ¹H and ¹³C NMR spectra were measured with Bruker Avance 400 spectrometers. 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 (CDCl₃: 7.26). ¹³C 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 (CDCl₃: 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. MALDI measurements were performed with a MALDI-FT 9.4 T, Bruker solariX, or MALDI-TOF MS Bruker Autoflex III. UV-vis was recorded with Jasco V-570 spectrometers. Cyclic voltammetry (CV) was performed with a CHI620D potentiostat equipped with a glassy-carbon electrode, a platinum counter-electrode, and an Ag/Ag⁺ reference electrode. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). The measurement was carried out in a scan rate of 100 mV s⁻¹ under nitrogen atmosphere. All potentials were corrected against Fc/Fc⁺.

1.2 Device fabrication and characterization

Single-junction solar cells were fabricated with an ITO/PEDOT:PSS/active layer/ZnO/Al structure. ITO-coated glass substrates (15 Ω sq⁻¹) were cleaned by sequential ultrasonication in soap deionized water, deionized water, acetone, and isopropanol. The washed substrates were further treated with oxygen plasma for 20 min to eliminate any remaining organic component. A thin layer (ca. 30 nm) of PEDOT:PSS was first spin-coated on the ITO substrates at 3,000 r.p.m. and baked at 150 °C for 30 min in air. The substrates were then transferred into a nitrogen-filled glovebox. Subsequently, the active layer was spin-coated on the PEDOT:PSS layer from a chloroform solution of 9 mg ml⁻¹ PBDB-T and 9 mg ml⁻¹ IDTODTs at various spin rates. The resulting film thickness was measured

via a surface profilometer (Dektak XT, Bruker). Thermal annealing (TA) was used to optimize the blend morphology and performance. Then, 10 mg ml⁻¹ ZnO in n-butanol was spin-coated on the active layer. At the final stage, aluminum (100 nm) was thermally evaporated as the top electrode. Shadow masks were used to define the active area to be 0.04 cm².

The current density–voltage (J–V) characteristics of photovoltaic devices were measured under N₂ using a Keithley 2400 source meter. A 300 W xenon arc solar simulator (Oriel) with an AM 1.5 global filter operated at 100 mW cm⁻² was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was performed using certified IPCE equipment from Enlitech, Taiwan. Space charge-limited currents (SCLCs) were tested in electron-only devices with a configuration of ITO/ZnO/active layer/Al and hole-only devices with a configuration of ITO/PEDOT:PSS/active layer/MoO₃/Ag. The mobilities were determined by fitting the dark current to the single carrier SCLC model, which is described as

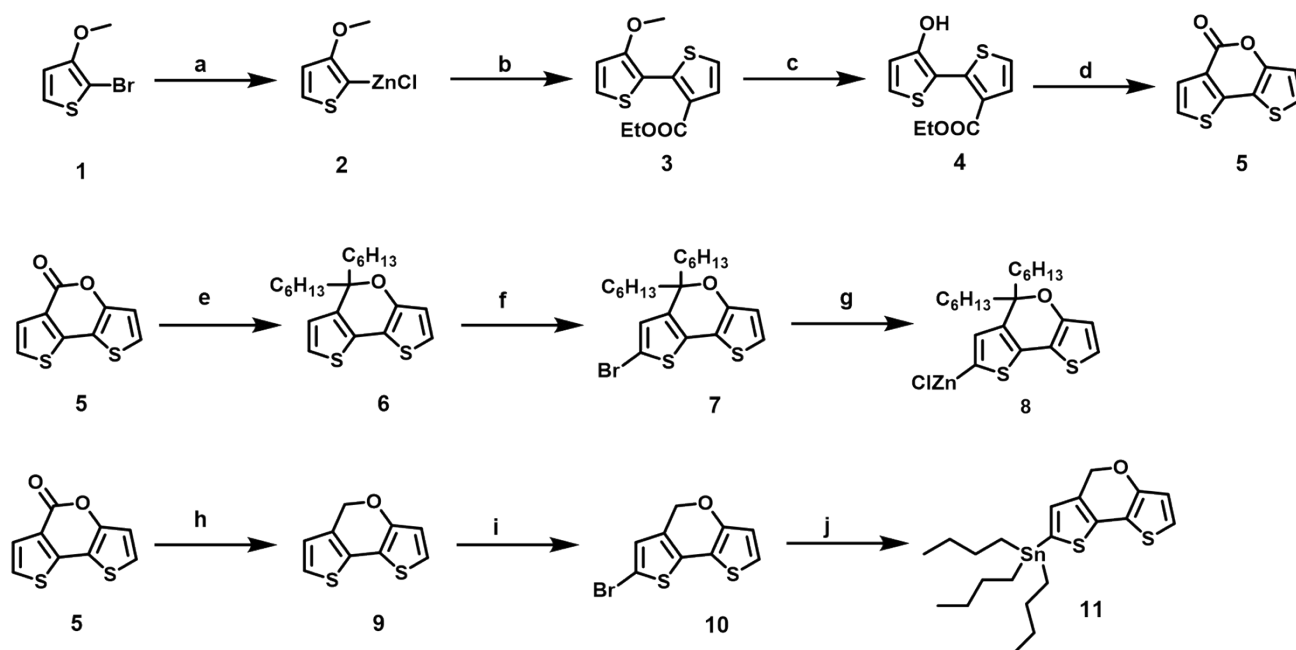
$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \quad (1)$$

Where J is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the active layer. From the plots of J^{0.5} vs V, hole and electron mobilities can be deduced.

GIXD characterization: PLS-II 9A USAXS beam line was employed to perform Grazing incidence X-ray diffraction (GIXD) characterization of the thin films. X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength $\lambda = 1.109\ 94\ \text{\AA}$) using a double crystal monochromator and focused both horizontally and vertically (450 (H) \times 60 (V) μm^2 in fwhm at sample position) using K-B type mirrors. GIXD patterns were recorded with a 2D CCD detector (Rayonix SX165), and X-ray irradiation time was 6-9 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, a = 10.8631 \AA , b = 8.7044 \AA , c = 7.7624 \AA , $\beta = 102.938\ \text{\AA}$) and the sample-to-detector distance was ~231 mm.

Photo-induced force microscopy (PiFM): The PiFM images were monitored by a microscope from VistaScope, Molecular Vista, Inc., operated in a dynamic mode using commercial gold-coated silicon cantilevers (NCHAu) bought from Nanosensors. The excitation laser is a LaserTune IR Source from Block Engineering.

1.3 Synthetic details



Scheme S1. Synthetic routes for precursors 1-12, a): *i*-Pr-MgCl·LiCl, ZnCl₂, THF; b): 2-bromo-3-methylthiophene, Pd(PPh₃)₄, THF; c): BBr₃, CH₂Cl₂; d): *p*-TSOH, Toluene reflux; e): Hexylmagnesium chloride, THF; *p*-TSOH, Toluene, reflux; f) NBS, DMF; g) *i*-Pr-MgCl·LiCl, ZnCl₂ h): BF₃Et₂O, NaBH₄, THF ; i): NBS, DMF; j): *i*-Pr-MgCl·LiCl, Tri-*n*-butyltin chloride, THF.

Synthesis of Compound-12: Under nitrogen atmosphere, compounds-12 (970mg, 2.206 mmol) and 2,5-Dibromatephthalic acid diethyl ester 380 mg, 0.94 mmol, 0.45 equiv.) were dissolved in THF, then the Pd(PPh₃)₄ was added (0.1 equiv). The reaction solution was stirred at 75 °C overnight under nitrogen atmosphere and then extracted with ethyl acetate. The crude product was purified on a silica-gel column chromatography to give 350 mg of compound-17 as an orange solid (38%). ¹H NMR (400 MHz, CDCl₃): 7.74 (s, 2H), 7.01 (d, 2H), 6.70 (s, 2H), 6.68 (d, 2H), 4.26 (q, 4H), 1.87(m, 8H), 1.41-1.25 (m, 38H), 0.85(m, 12H) ; ¹³C NMR(400 MHz, CDCl₃): δ 167.9, 151.7, 135.6, 133.7, 133.3, 132.5, 131.2, 130.5, 124.6, 121.3, 118.6, 109.7, 86.2, 61.8, 40.0, 31.8, 29.6, 23.8, 22.7, 14.1; HRMS (MALDI-TOF) calcd for C₅₄H₇₀O₆S₄ [M]⁺ : 942.41, found, 943.39.

Synthesis of Compound-13: Under -78°, *n*-BuLi (30 equiv) was slowly added into 1-bromo-4-hexyl-benzene's (30 equiv) solution of THF under N₂. The result solution was stirred for 0.5h. then compound-16(100mg) was added and stirring for 0.5h, quench with water and extract with dichloromethane, after remove the solvent, the intermediate product was reacted by a ratio of *n*-octane: acetic acid: sulfuric acid= 1000:100:6 without further purification, then extract with

dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 90 mg of **compound-17** (yield: 58%). ¹H NMR (400 MHz, CDCl₃): 7.29(d, 8H), 7.07(d, 8H), 7.01(s, 2H), 6.87(d, 2H), 6.54(d, 2H), 2.55(m, 8H), 1.63(m, 8H), 1.35-0.81(m, 88H); ¹³C NMR(400 MHz, CDCl₃): δ 156.9, 151.2, 151.0, 140.6, 138.4, 137.4, 132.5, 130.9, 128.0, 127.8, 127.0, 119.4, 116.9, 113.3, 109.6, 86.9, 63.0, 40.0, 34.6, 30.8, 30.3, 28.4, 28.3, 22.3, 21.7, 13.1; HRMS (MALDI-TOF) calcd for C₉₈H₁₂₆O₂S₄ [M]⁺: 1463.86, found, 1464.32.

Synthesis of Compound-14: Under -78°, n-BuLi (4 equiv) was slowly added into **Compound-17** (50mg) solution of THF under N₂. The resulting solution was stirred for 1h. then the dry-DMF (10 equiv) was dropped in and stirred for 0.5h, then warm to room temperature and continue stirred for 2 hours, extract with dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 27 mg of **compound-17** (52%). ¹H NMR (400 MHz, CDCl₃): 9.69(s, 2H), 7.24(d, 8H), 7.11(s, 2H), 7.07(d, 8H), 2.56(m, 8H), 1.60(m, 8H), 1.57-0.6(m, 88H); ¹³C NMR(400 MHz, CDCl₃): δ 181.7, 158.5, 152.4, 152.0, 143.2, 142.0, 137.6, 136.0, 133.8, 133.0, 130.6, 128.8, 128.2, 124.4, 122.4, 115.0, 88.4, 64.1, 41.0, 35.6, 31.7, 31.6, 31.3, 29.7, 29.2, 23.2, 22.6, 14.0; HRMS (MALDI-TOF) calcd for C₁₀₀H₁₂₆O₄S₄ [M]⁺: 1518.85, found, 1520.34.

Synthesis of IDTODT-1: Compound-18 (10mg) and 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (5 equiv) were added to a solvent mixture of chloroform (2 mL) and pyridine (1 drops). The reaction was placed in an oil bath at 75° C and was stirred overnight. The mixture was directly purified by silica-gel column chromatography using trichloromethane as eluent to give IDTODT-3 (95%) as blue-black solid. ¹H NMR (400 MHz, CDCl₃): 8.66(s, 2H), 8.64(m, 0.4H), 8.32(m, 1.6H), 7.86(m, 1.6H), 7.50(m, 0.4H), 7.38(m, 2H), 7.35(m, 2H), 7.27(s, 2H), 7.14(m, 16H), 2.58(m, 8H), 1.61(m, 8H), 1.40-0.68(m, 88H) ¹³C NMR(400 MHz, CDCl₃): δ 187.2, 167.9, 165.3, 159.3, 153.6, 153.2, 147.2, 142.4, 137.1, 136.5, 136.2, 134.3, 133.0, 132.2, 131.4, 130.0, 128.8, 128.4, 125.3, 121.3, 121.0, 120.9, 115.7, 114.7, 112.8, 112.5, 88.8, 68.4, 64.2, 41.3, 35.6, 31.7, 32.2, 29.7, 29.2, 23.2, 22.6, 14.0; HRMS (MALDI-TOF) calcd for C₁₂₄H₁₃₂F₂N₄O₄S₄ [M]⁺: 1906.91, found, 1908.68.

Synthesis of Compound-15: Under nitrogen atmosphere, compound-9 (400mg, 2.06 mmol) and 2,5-Dibromatephthalic acid diethyl ester (356 mg, 0.94 mmol, 0.45 equiv.) were dissolved in toluene, after that, Tri(o-toyl)phosphine (0.06 equiv) and Tris(dibenzylideneacetone)dipalladium were added to the solution, respectively. The reagent solution was stirred at 115 °C overnight under nitrogen atmosphere and then extracted with ethyl acetate. The crude product was purified by silica-gel column chromatography to give 450 mg of compound-9 as an orange solid (40%). ¹H

NMR (400 MHz, CDCl₃): 7.78 (s, 2H), 7.06 (d, 2H), 6.86 (s, 2H), 6.74 (d, 2H), 5.31 (s, 4H), 4.29 (q, 4H), 1.25 (t, 6H); ¹³C NMR(400 MHz, CDCl₃):δ 167.5, 152.2, 136.7, 133.6, 132.6, 131.7, 131.3, 126.9, 123.9, 122.0, 118.3, 118.2, 112.4, 67.6, 61.8, 53.4, 29.7, 13.9; HRMS (MALDI-TOF) calcd for C₃₀H₂₁O₆S₄ [M]⁺: 606.03, found, 606.74.

Synthesis of Compound-16 (IDTODT-2): Under -78°, n-BuLi (30 equiv) was slowly added into 1-bromo-4-hexyl-benzene's (30 equiv) solution of THF under N₂. The result solution was stirred for 0.5h. then compound-13(100mg) was added and stirring for 0.5h, quench with water and extract with dichloromethane, after remove the solvent, the intermediate product was reacted by a ratio of n-octane: acetic acid: sulfuric acid= 1000:100:6 without further purification, then extract with dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 97 mg of **compound-14 (IDTODT-2, yield: 52%)**. ¹H NMR (400 MHz, CDCl₃): 7.74 (s, 2H), 7.01 (d, 2H), 6.70 (s, 2H), 6.68 (d, 2H), 4.26 (q, 4H), 1.87(m, 8H), 1.41-1.25 (m, 38H), 0.85(m, 12H); ¹³C NMR(400 MHz, CDCl₃):δ 167.9, 151.7, 135.6, 133.7, 133.3, 132.5, 131.2, 130.5, 124.6, 121.3, 118.6, 109.7, 86.2, 61.8, 40.0, 31.8, 29.6, 23.8, 22.7, 14.1; HRMS (MALDI-TOF) calcd for C₇₄H₇₈O₂S₄ [M]⁺: 1126.48, found, 1127.68.

Synthesis of Compound-16 (IDTODT-3): Under -78°, n-BuLi (30 equiv) was slowly added into 1-bromo-4-(2-ethylhexyl) benzene's (30 equiv) solution of THF under N₂. The result solution was stirred for 0.5h. then compound-13(100mg) was added and stirring for 0.5h, quench with water and extract with dichloromethane, after remove the solvent, the intermediate product was reacted by a ratio of n-octane: acetic acid: sulfuric acid= 1000:100:6 without further purification, then extract with dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 108 mg of **compound-14 (IDTODT-3, yield: 53%)**. ¹H NMR (400 MHz, CDCl₃): 7.30(s, 2H), 7.15(d, 8H), 6.95(d, 8H), 6.64(s, 2H), 5.02(s, 4H), 2.49(d, 8H), 1.27(m, 34H), 0.86(m, 26H); ¹³C NMR(400 MHz, CDCl₃):δ 154.5, 152.2, 140.8, 139.8, 138.1, 135.2, 132.0, 129.3, 127.8, 122.4, 120.9, 118.2, 115.8, 133.4, 67.3, 62.9, 40.8, 39.7, 32.4, 29.7, 28.9, 25.5, 23.0, 14.1, 10.8; HRMS (MALDI-TOF) calcd for C₈₂H₉₄O₂S₄ [M]⁺: 1238.61 found, 1239.89.

Synthesis of Compound-17 (IDTODT-2): Under -78°, n-BuLi (4 equiv) was slowly added into **Compound-14 (IDTODT-2)** (40mg) solution of THF under N₂. The result solution was stirred for 1h. then the dry-DMF (10 equiv) was dropped in and stirred for 0.5h, then warm to room temperature and continue stirred for 2 hours, extract with dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 23 mg of **compound-15 (IDTODT-2, yield: 50%)**: ¹H NMR (400 MHz, CDCl₃): 9.74 (s, 2H), 7.36(s,2H), 7.22(s, 2H),

7.12(m,16H), 5.09(s, 4H), 2.58(m, 8H), 1.60-0.85 (m, 44H); ¹³C NMR(400 MHz, CDCl₃):δ 181.6, 155.2, 152.6, 151.0, 142.3, 141.8, 139.1, 136.3, 135.4, 130.6, 128.7, 127.8, 126.3, 124.9, 124.4, 116.5, 67.2, 63.0, 53.4, 35.5, 31.7, 31.2, 29.7, 29.1, 22.6, 14.1; HRMS (MALDI-TOF) calcd for C₇₆H₇₈O₄S₄ [M]⁺ : 1182.47, found, 1183.70.

Synthesis of Compound-17 (IDTODT-3): Under - 78°, n-BuLi (4 equiv) was slowly added into **Compound-14 (IDTODT-3)** (40mg) solution of THF under N₂, The result solution was stirred for 1h. then the dry-DMF (10 equiv)was dropped in and stirred for 0.5h, then warm to room temperature and continue stirred for 2 hours, extract with dichloromethane, remove the solvent. The crude product was purified by silica-gel column chromatography to give 20 mg of **compound-15 (IDTODT-3, yield: 48%)**: ¹H NMR (400 MHz, CDCl₃): 9.73(s, 2H), 7.37(s, 2H), 7.22(s, 2H), 7.12(d, 8H), 7.07(d, 8H), 5.08(s, 4H), 2.5(m, 8H), 1.27-0.85(m, 60H), ¹³C NMR(400 MHz, CDCl₃):δ 181.7, 155.2, 151.0, 141.8, 141.2, 139.0, 136.2, 135.5, 130.6, 129.5, 127.6, 126.3, 124.9, 124.5, 116.5, 67.2, 63.0, 40.8, 39.7, 32.4, 29.7, 28.8, 25.5, 23.0, 14.1, 10.8; HRMS (MALDI-TOF) calcd for C₈₄H₉₄O₄S₄ [M]⁺ : 1294.60, found, 1295.91.

Synthesis of IDTODT-2: Compound-15 (IDTODT-2) (10mg) and 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (5 equiv) were added to a solvent mixture of chloroform (2 mL) and pyridine (1 drops). The reaction was placed in an oil bath at 75° C and was stirred overnight. The mixture was directly purified by silica-gel column chromatography using trichloromethane as eluent to give IDTODT-2 (95%) as blue-black solid. ¹H NMR (400 MHz, CDCl₃):8.69(s, 2H), 8.66(m, 0.4H), 8.34(d, 1.6H), 7.88(m, 1.6H), 7.52(m, 0.4H), 7.44(s, 2H), 7.38(m, 2H), 7.29(m, 2H), 7.15(m, 16H), 5.15(s, 4H), 2.59(m, 8H), 1.61(m, 8H), 1.34-0.88(m, 36H) ;¹³C NMR(400 MHz, CDCl₃):δ 186.2, 166.9, 164.4, 157.6, 155.2, 152.4, 151.1, 144.4, 141.4, 140.6, 137.4, 135.6, 135.0, 133.0, 132.8, 132.0, 130.9, 130.2, 129.8, 128.6, 128.1, 126.6, 124.6, 124.5, 120.5, 116.1, 113.5, 111.8, 111.6, 68.1, 66.4, 62.0, 39.8, 38.7, 31.4, 28.7, 27.8, 24.5, 22.0, 21.7, 13.1, 9.75; HRMS (MALDI-TOF) calcd for C₁₀₀H₈₄F₂N₄O₄S₄ [M]⁺: 1570.54, found, 1572.03.

Synthesis of IDTODT-3: Compound-15 (IDTODT-3) (10mg) and 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (5 equiv) were added to a solvent mixture of chloroform (2 mL) and pyridine (1 drops). The reaction was placed in an oil bath at 75° C and was stirred overnight. The mixture was directly purified by silica-gel column chromatography using trichloromethane as eluent to give IDTODT-3 (95%) as blue-black solid. ¹H NMR (400 MHz, CDCl₃): 8.68(s, 2H), 8.65(m, 0.4H), 8.33(d, 1.6H), 7.87(m, 1.6H), 7.50(m, 0.4H), 7.46(s, 2H), 7.37(m, 2H), 7.27(m, 2H), 7.14(m, 16H), 5.14(s, 4H), 2.53(m, 8H), 1.57-0.86(m, 60H); ¹³C NMR(400 MHz, CDCl₃):δ 186.2, 166.9,

164.4, 157.6, 155.2, 152.4, 151.1, 144.4, 141.4, 140.5, 137.4, 135.6, 135.0, 133.0, 132.8, 132.0, 130.9, 130.2, 129.8, 128.6, 128.1, 126.6, 124.6, 120.5, 116.1, 113.5, 111.8, 111.6, 68.1, 66.4, 62.0, 39.8, 38.7, 31.4, 28.7, 27.8, 24.5, 22.0, 21.7, 13.1, 9.8; HRMS (MALDI-TOF) calcd for $C_{108}H_{100}F_2N_4O_4S_4[M]^+$: 1682.66, found, 1684.25.

Part 2. Figures and Tables

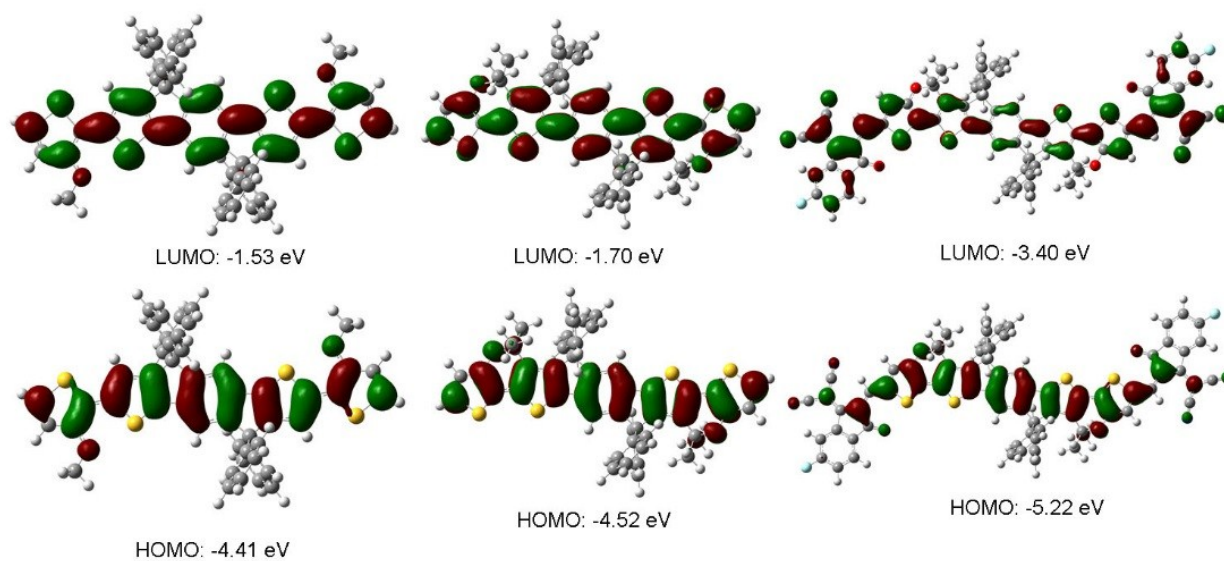


Fig. S1 Theoretical calculation for IDTDT (left), IDTODT core (middle) and IDTODT NFAs (right) at the DFT B3LYP/6-31G (d) level with the Gaussian 03 program package. All substituents have been replaced by methyl groups to simplify the calculation.

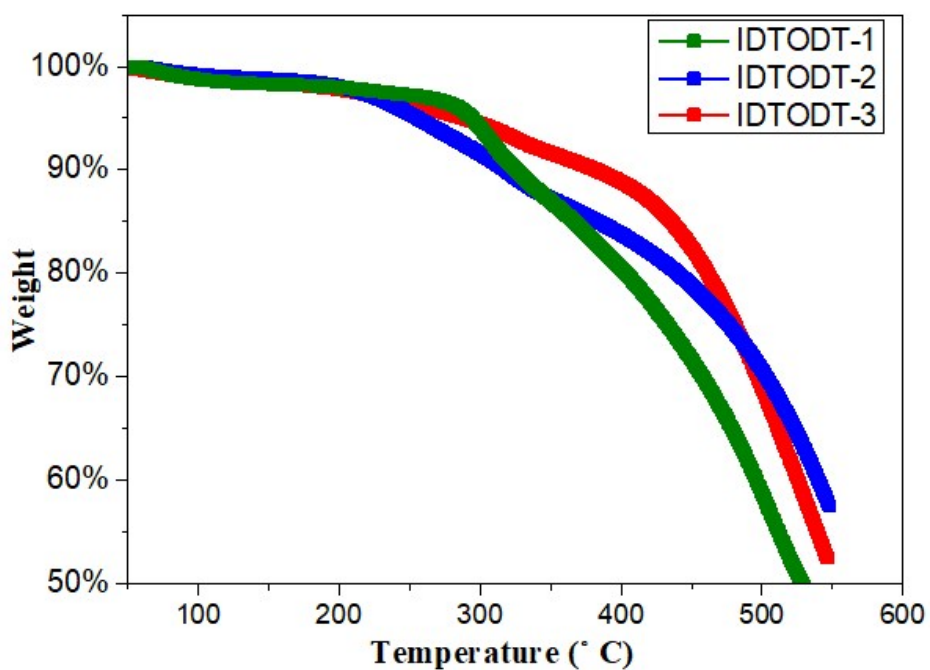


Fig. S2 TGA of IDTODT-1, IDTODT-2, IDTODT-3.

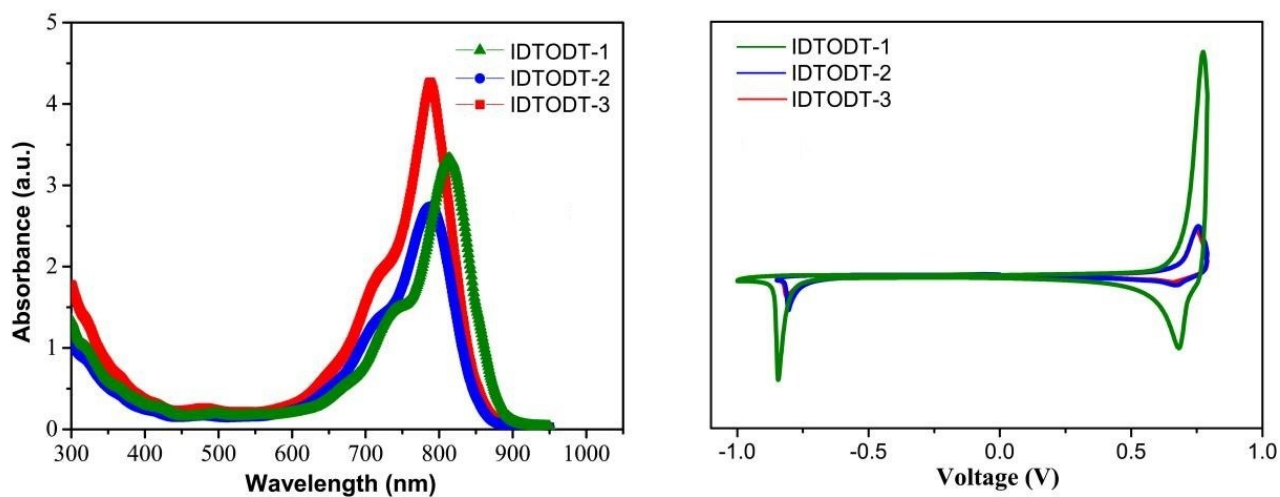


Fig. S3 (a) Absorption spectra of **IDTODT-1**, **IDTODT-2**, **IDTODT-3** in solution; (b) Cyclic voltammetry of **IDTODT-1**, **IDTODT-2** and **IDTODT-3** as thin films in CH₃CN/0.1 M [n-Bu₄N]⁺[PF₆]⁻ at a scan rate of 0.1 V/s.

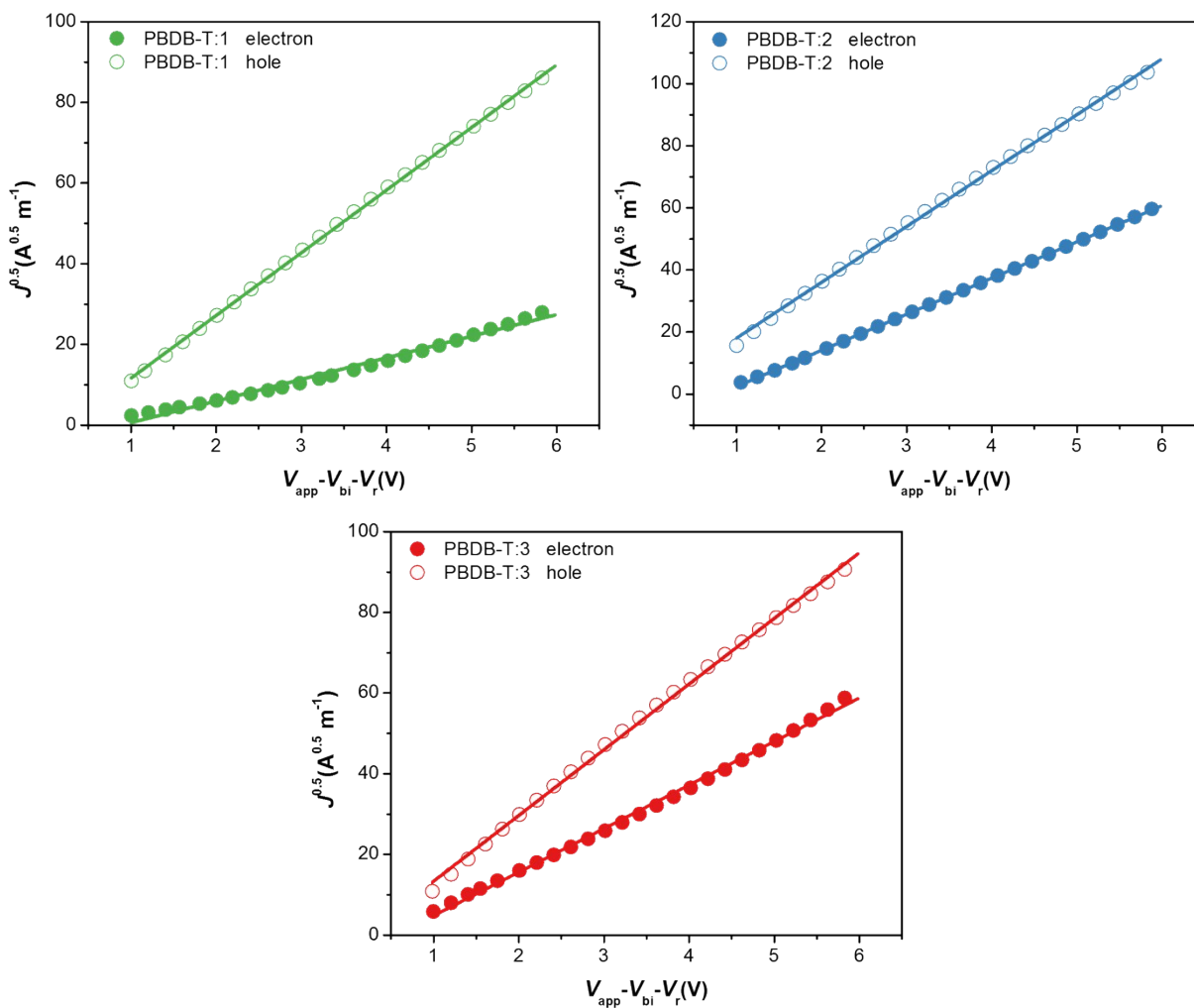


Fig. S4 Space-charge-limited-current test of **IDTODT-1**, **IDTODT-2**, **IDTODT-3**

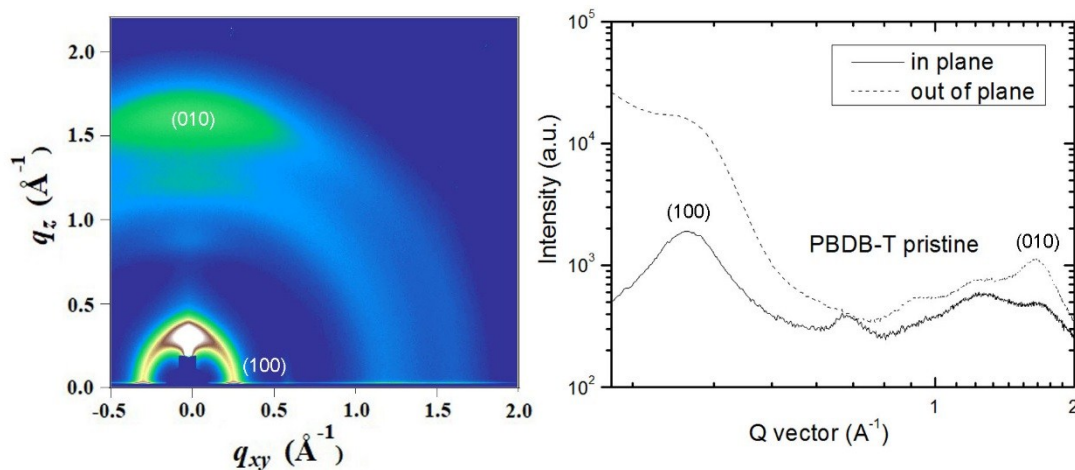


Fig. S5 2D GIXS images (left) and corresponding line-cuts (right) of PBDB-T pristine film.

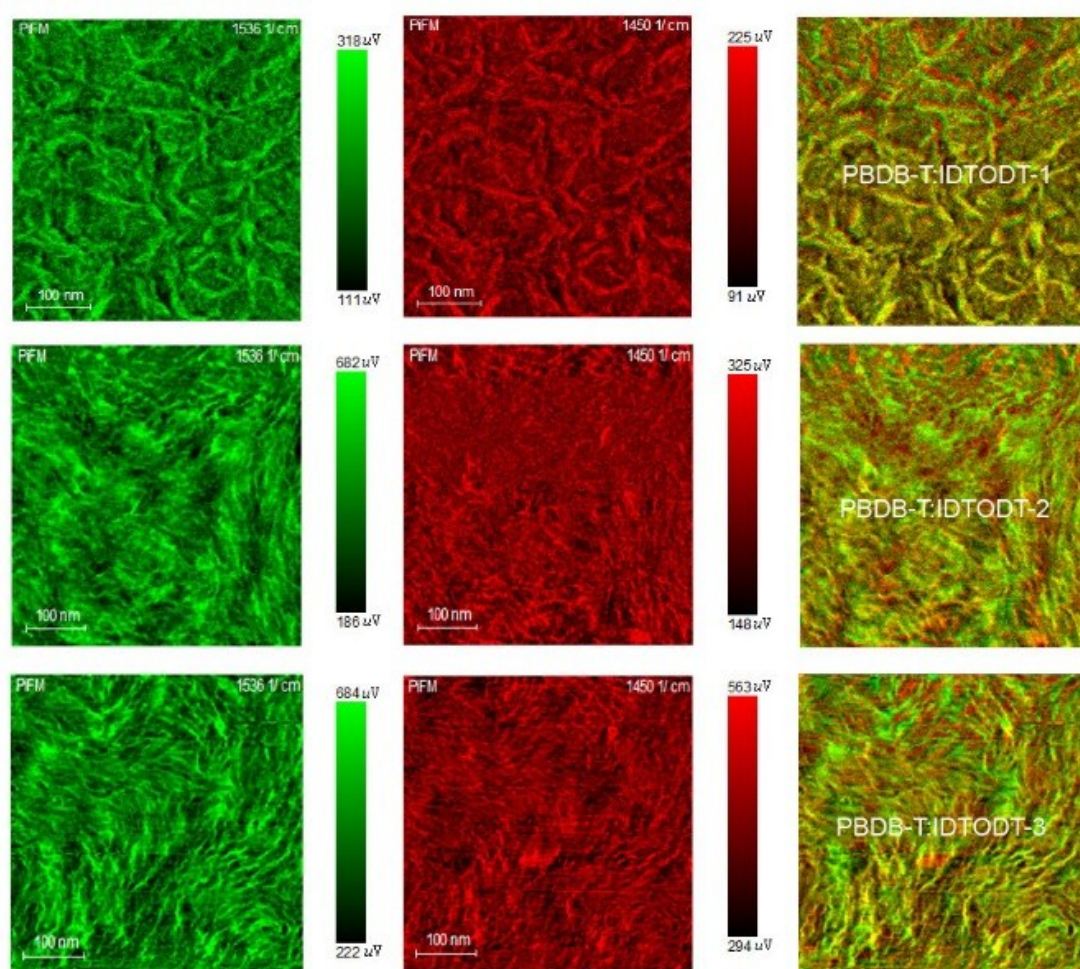


Fig. S6 PiFM images of PBDB-T:IDTODT blends. Left column: images probed at $\sim 1536 \text{ cm}^{-1}$ reflecting the characteristic response of IDTODT acceptors (painted in green). Middle column: images probed at $\sim 1450 \text{ cm}^{-1}$ reflecting the characteristic response of PBDB-T donor (painted in red). Right column: combined images mapping the donor- and acceptor-rich phases.

Table S1 Photovoltaic parameters of solar cells based on PBDB-T:IDTODT-1 at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
as-cast	0.829	13.63	51.91	5.87
100	0.810	13.98	55.32	6.26
120	0.802	14.49	59.10	6.87
140	0.780	11.91	57.78	5.37

Table S2. Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:IDTODT-1 at 1:1 weight ratio with thermal annealing at 130°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
90	0.802	14.03	59.87	6.74
110	0.802	14.49	59.10	6.87
125	0.799	14.87	56.21	6.68

Table S3. The device performance parameters for the OPVs based on PBDB-T:IDTODT-2 at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
as-cast	0.793	12.60	54.46	5.44
120	0.782	14.43	59.97	6.77
140	0.770	15.28	59.25	6.99
160	0.767	13.55	52.47	5.46

Table S4. Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:IDTODT-2 at 1:1 weight ratio with thermal annealing at 130°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
90	0.769	14.88	60.01	6.87
110	0.770	15.28	59.25	6.99
125	0.770	15.	57.49	6.80

Table S5. The device performance parameters for the OPVs based on PBDB-T:IDTODT-3 at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

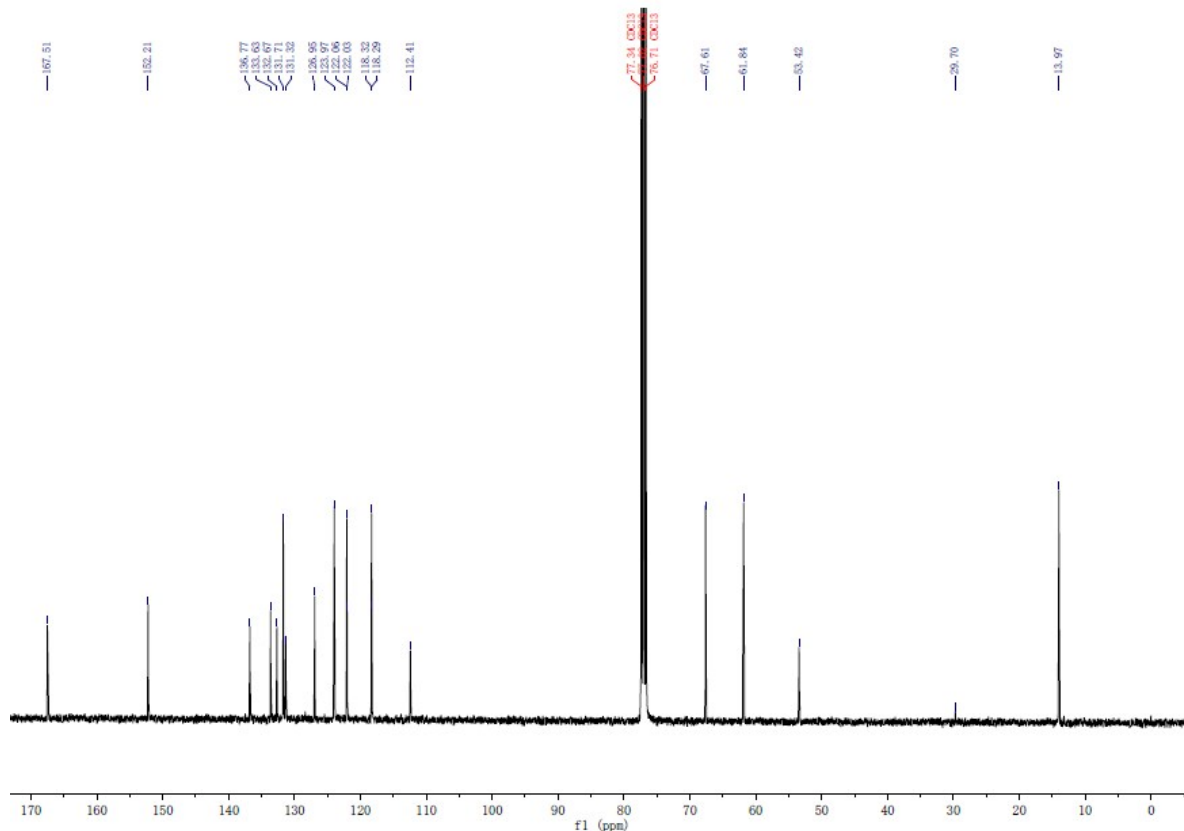
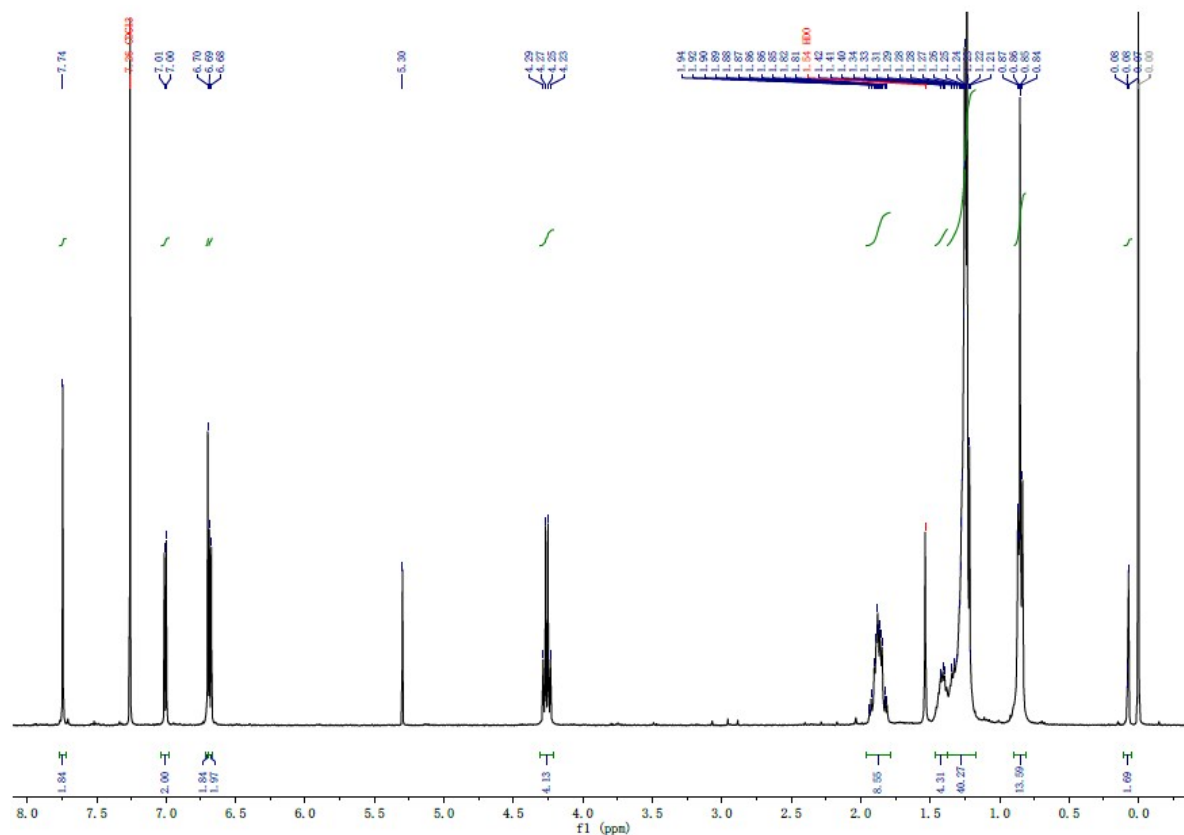
Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
as-cast	0.814	15.09	51.32	6.31
120	0.800	17.29	56.17	7.78
140	0.794	17.32	60.63	8.34
160	0.775	17.28	61.68	8.25

Table S6. Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:IDTODT-3 at 1:1 weight ratio with thermal annealing at 130°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

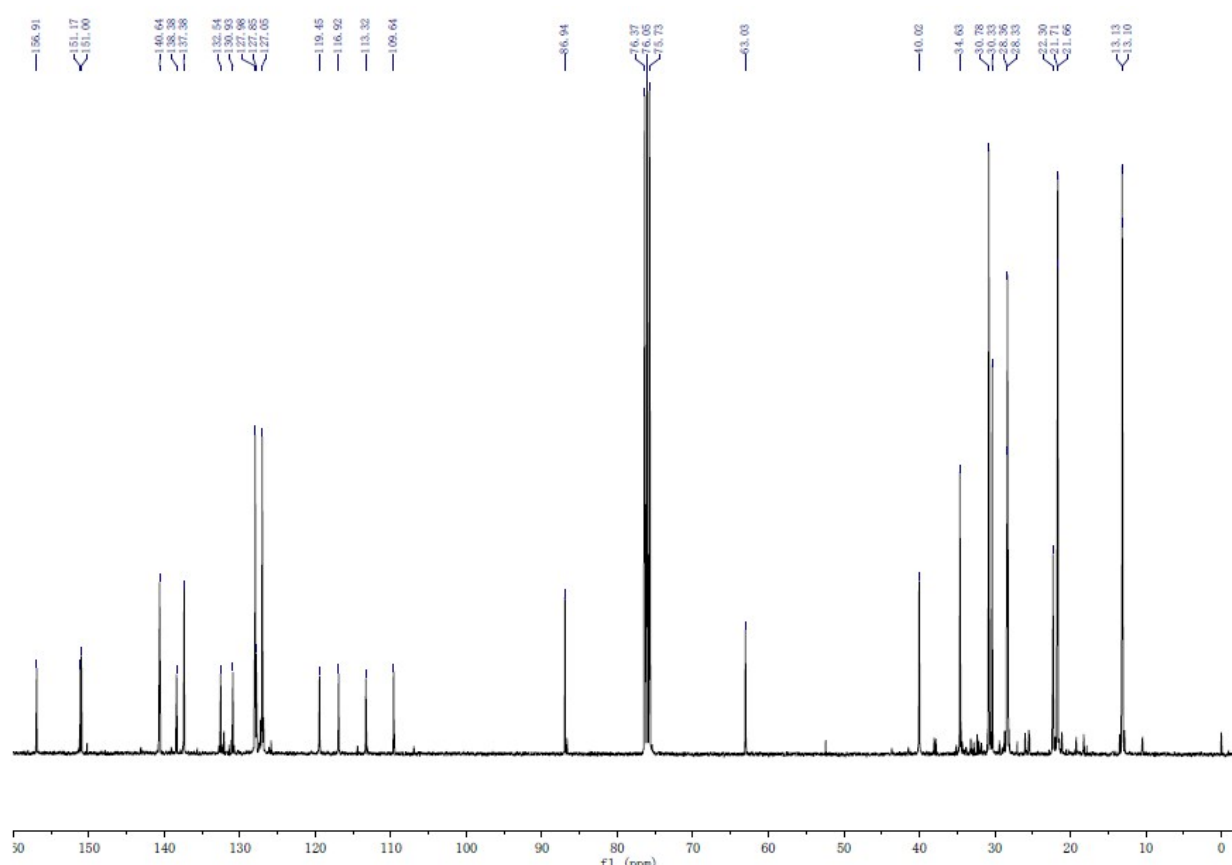
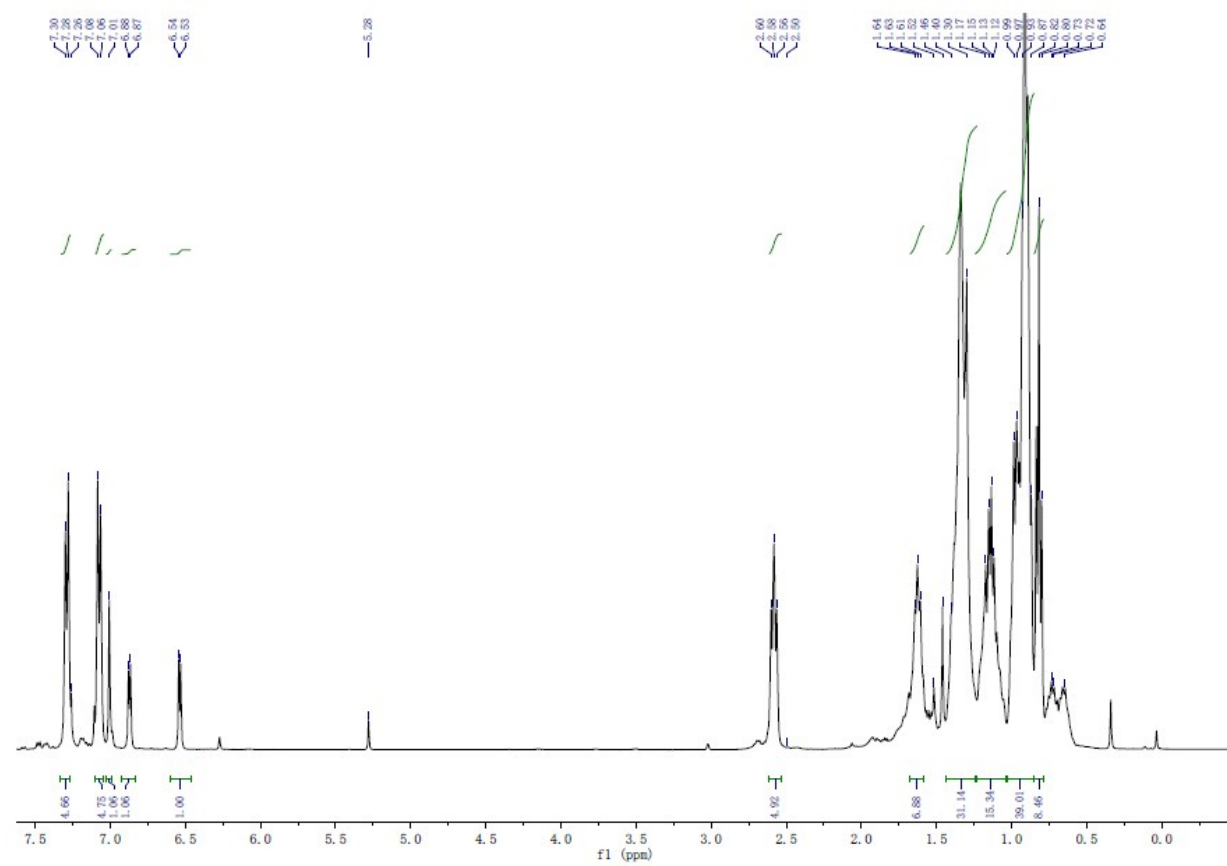
Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
90	0.796	16.84	61.22	8.21
110	0.794	17.32	60.63	8.34
125	0.794	17.45	59.42	8.18

Part 3. NMR Charts

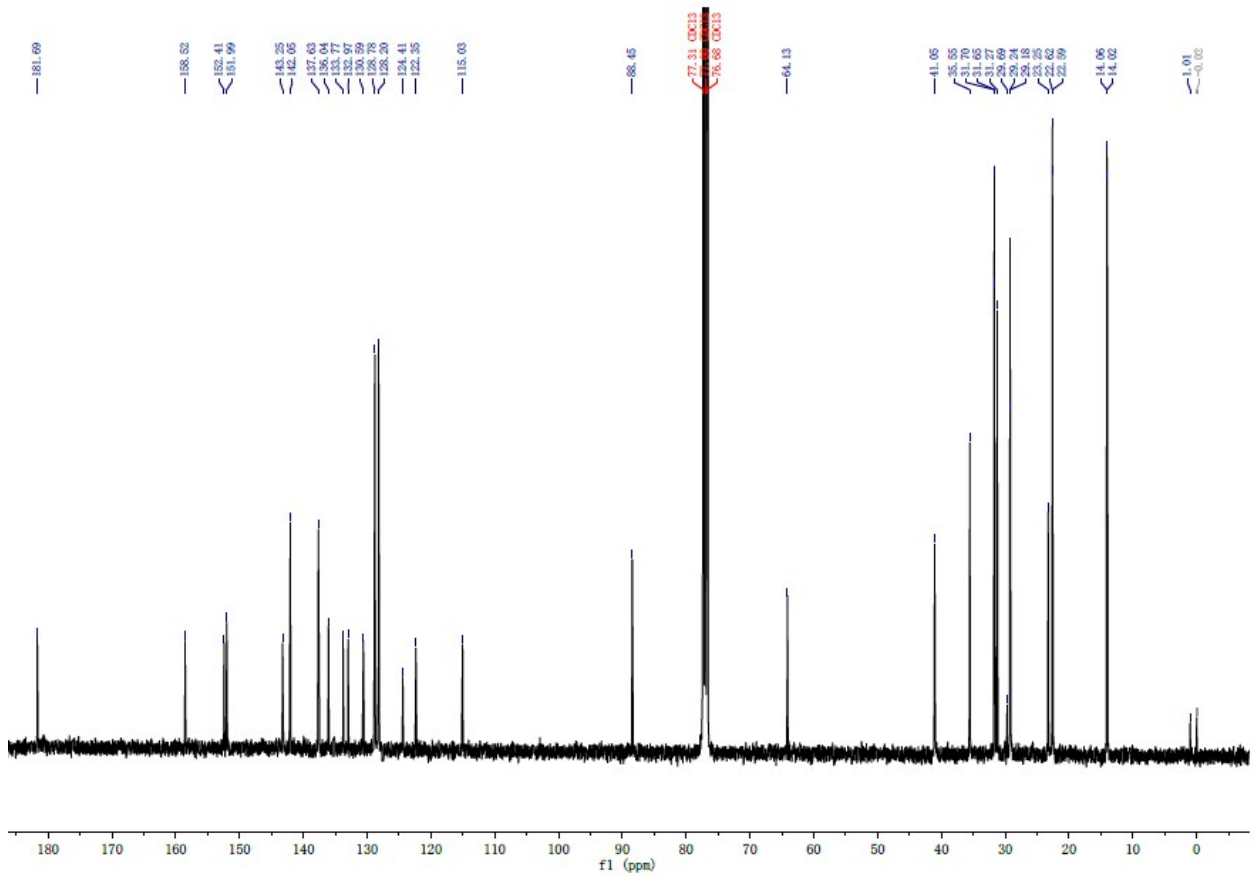
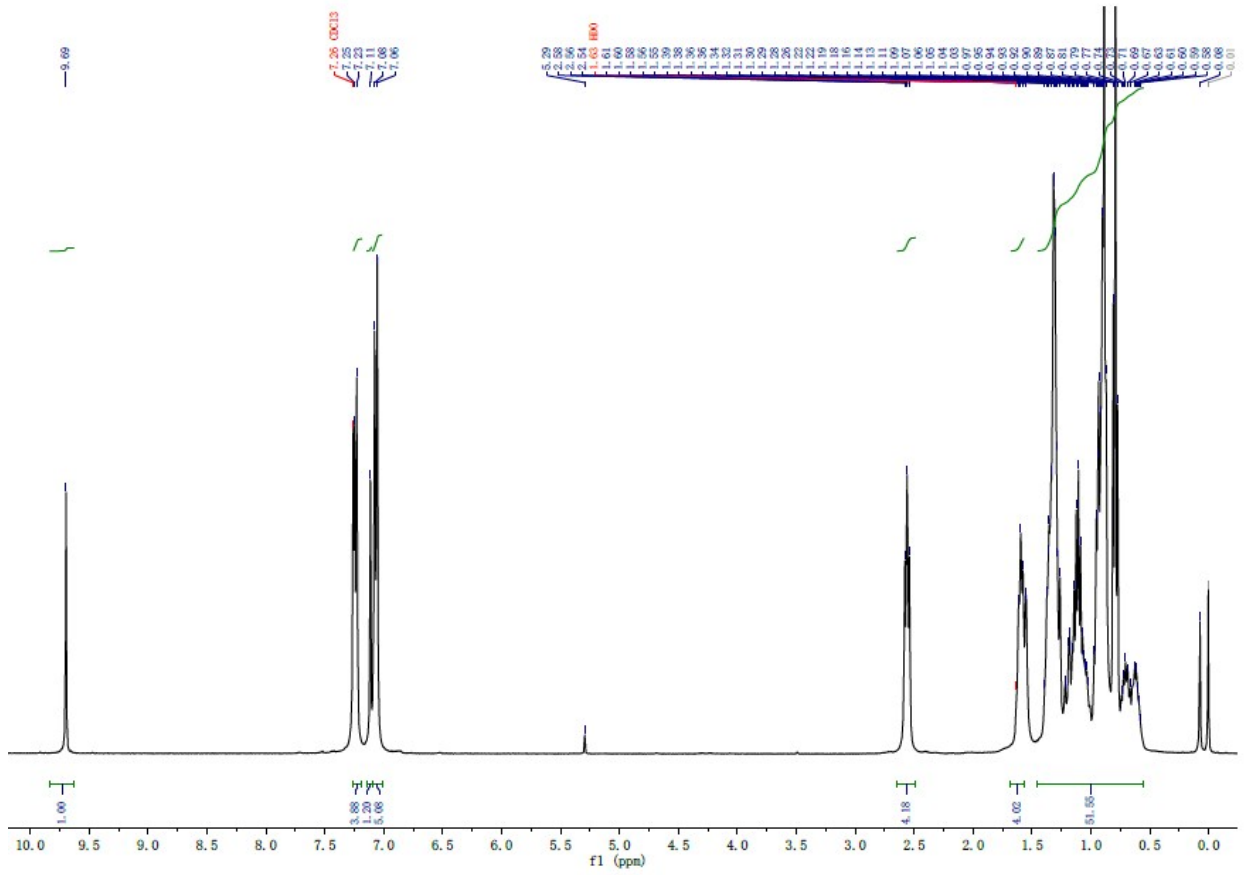
Compound-12



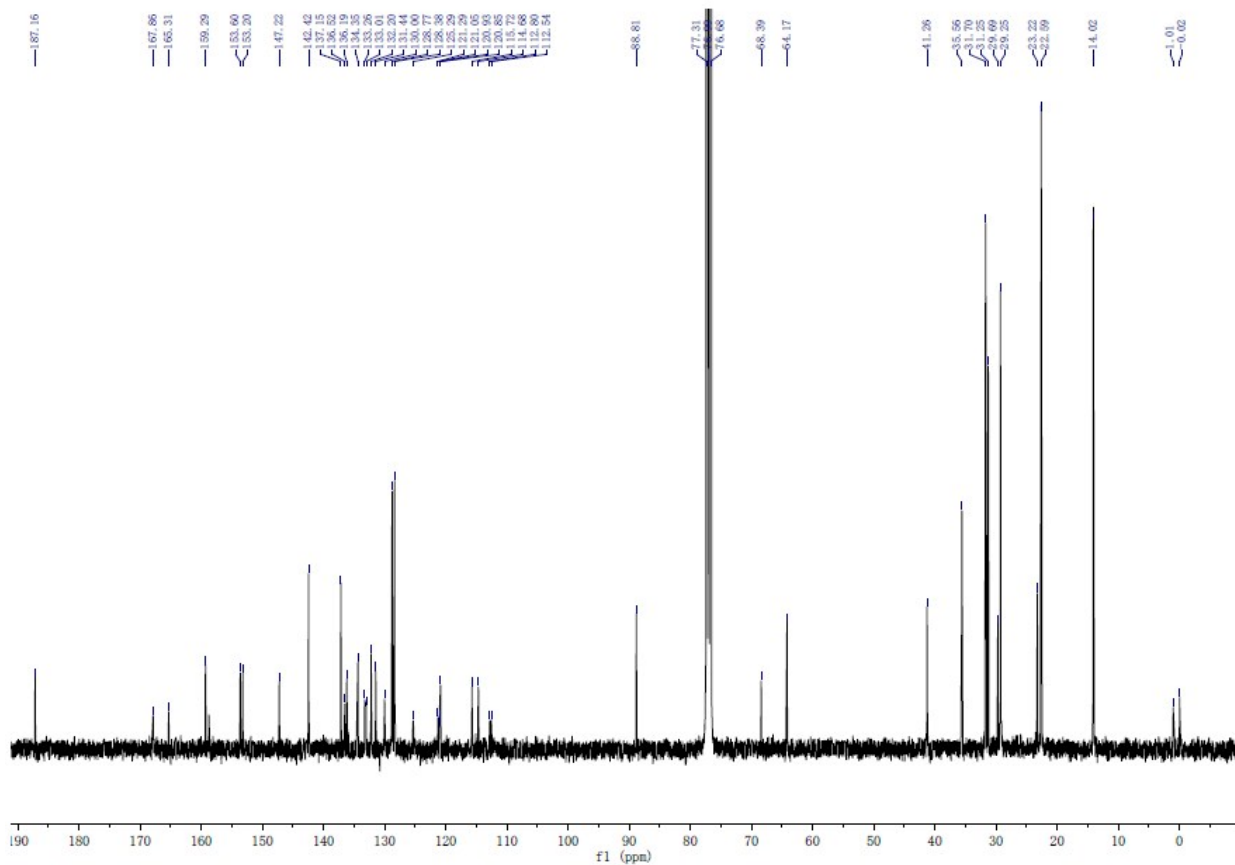
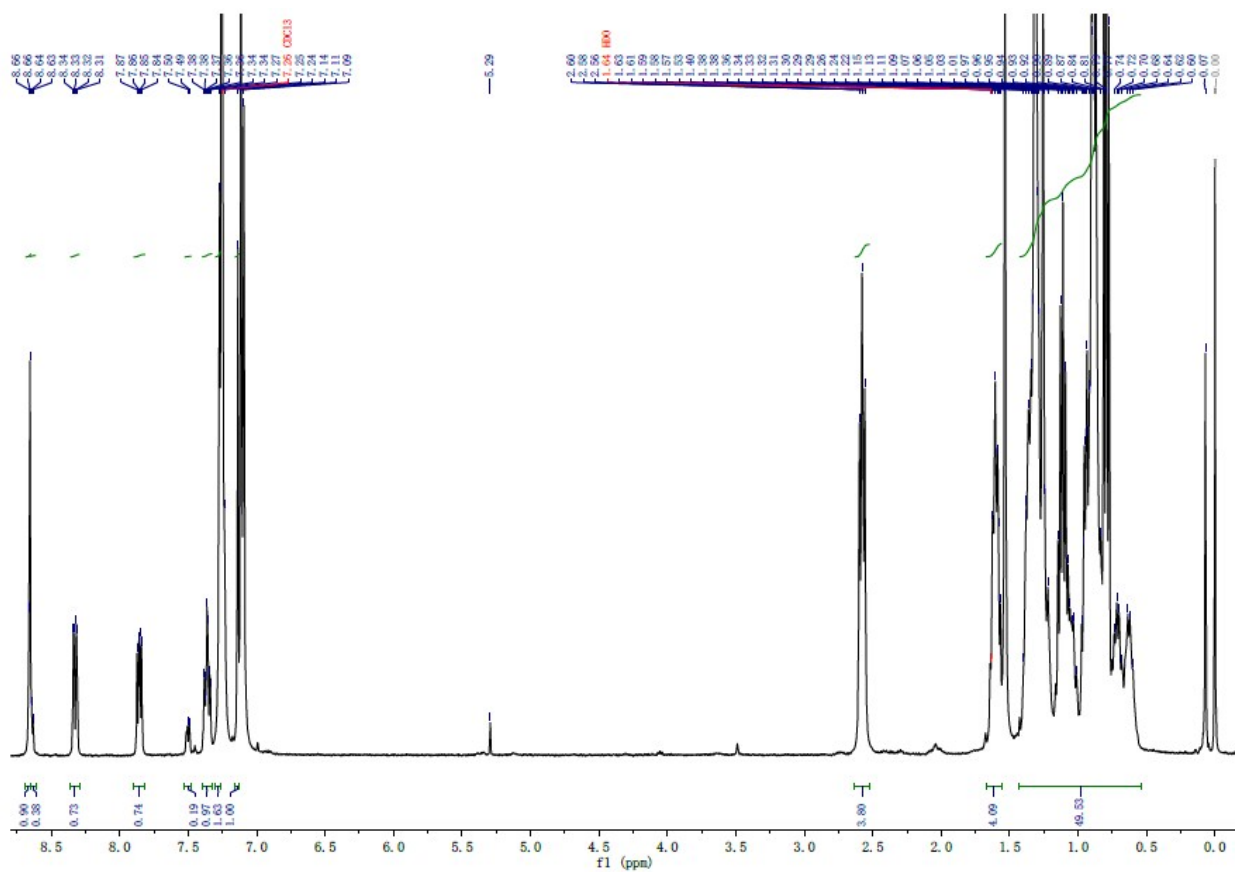
Compound-13



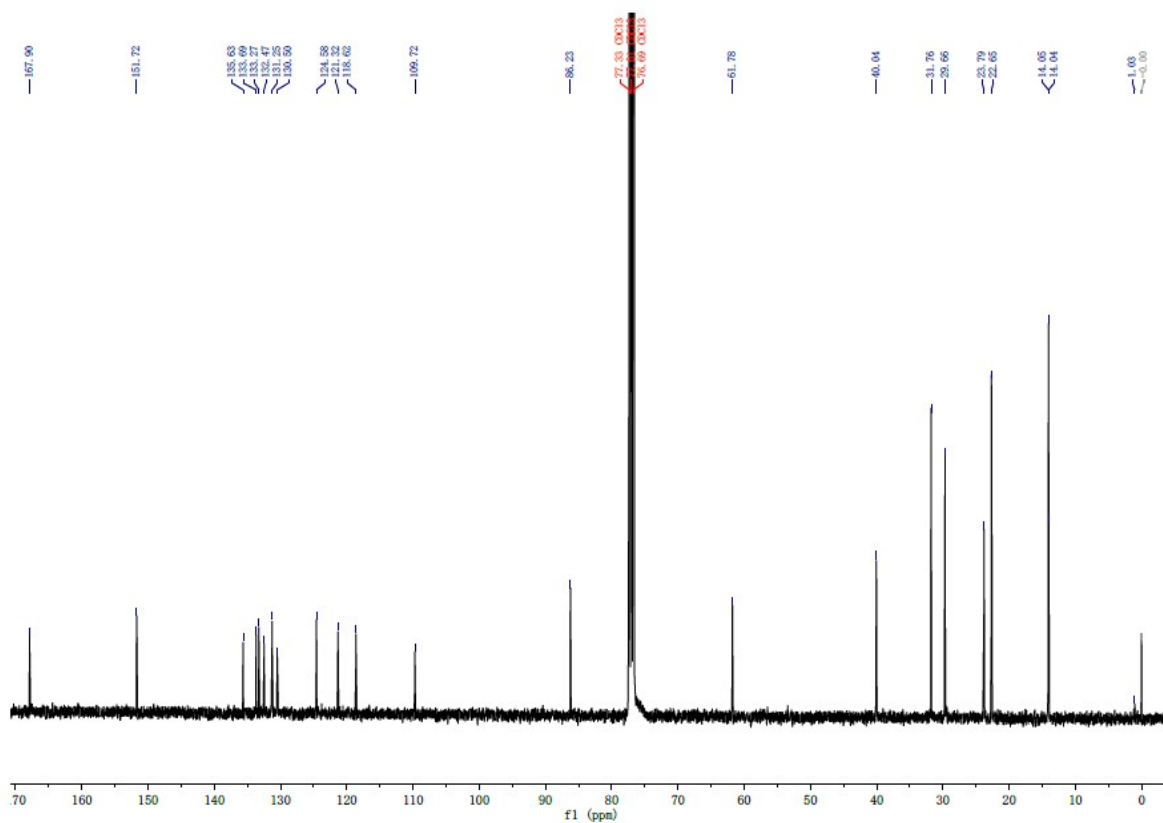
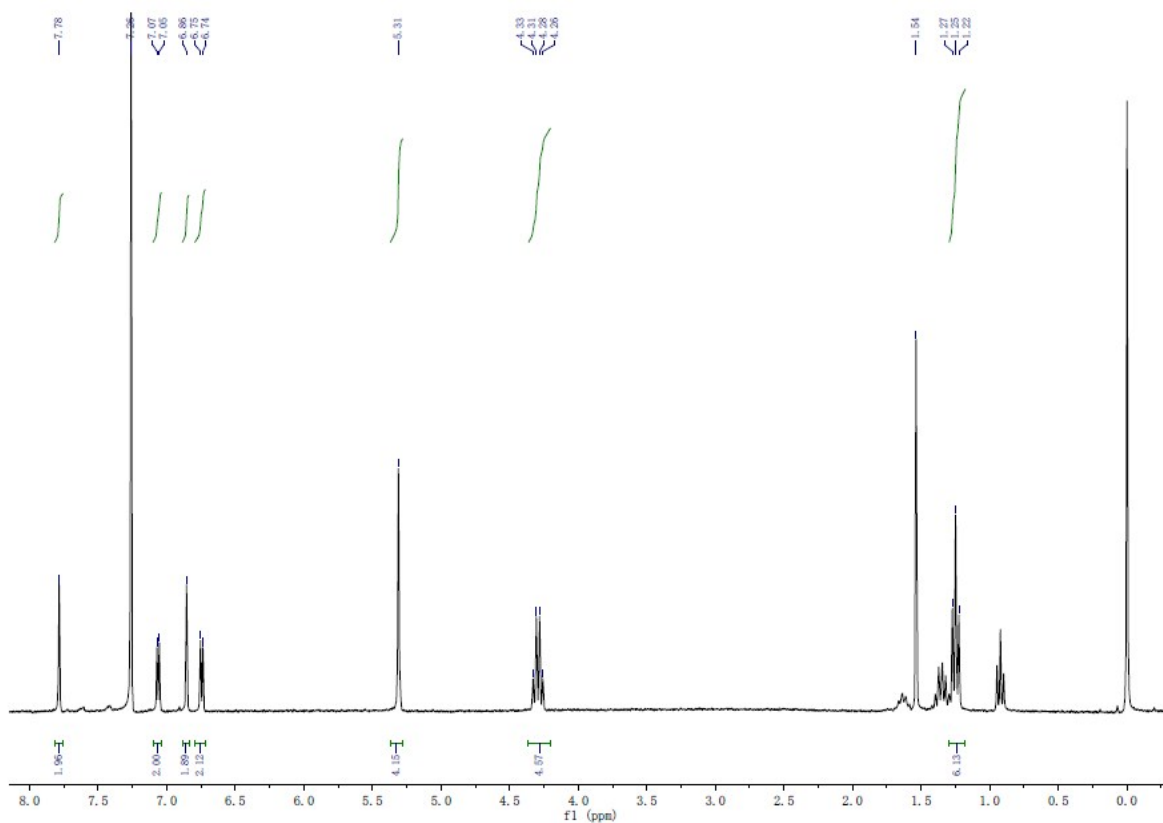
Compound-14



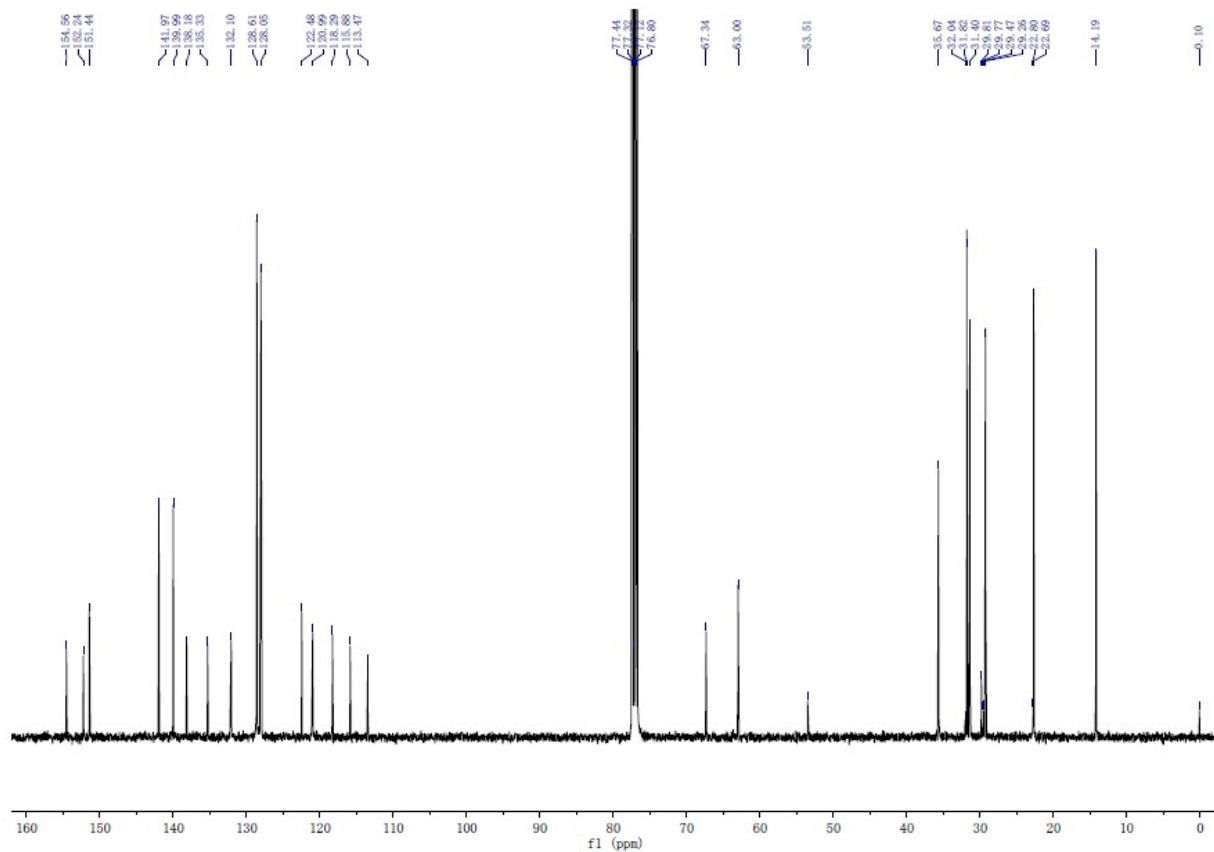
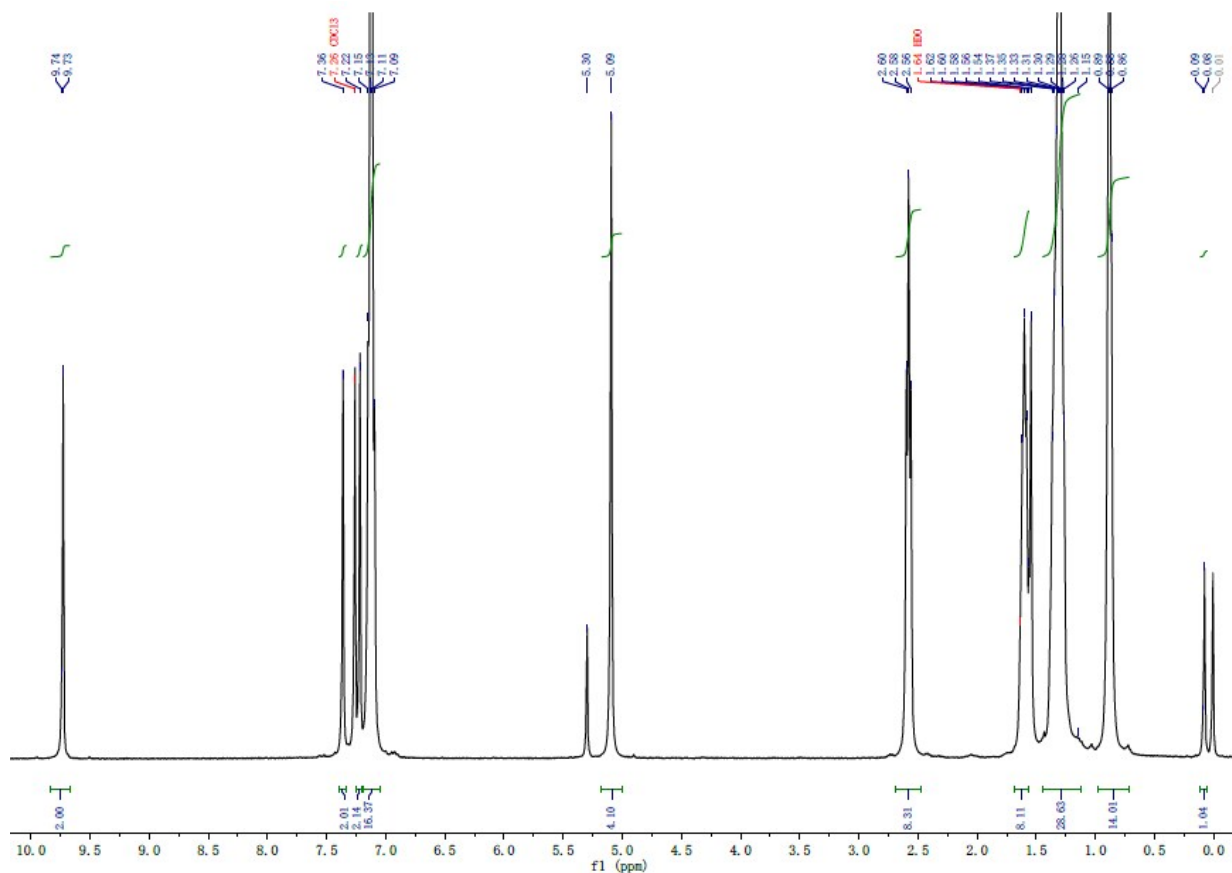
IDTODT-1



Compound-15

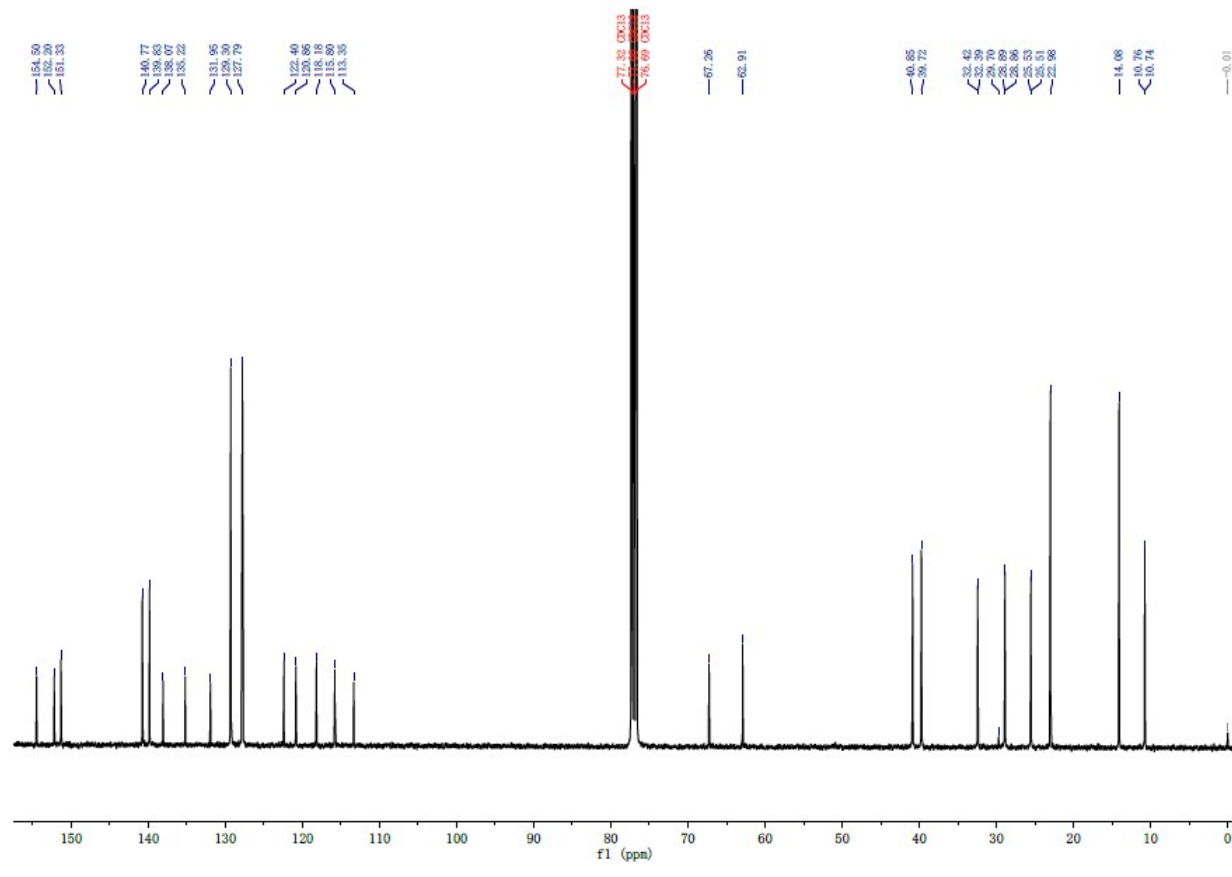
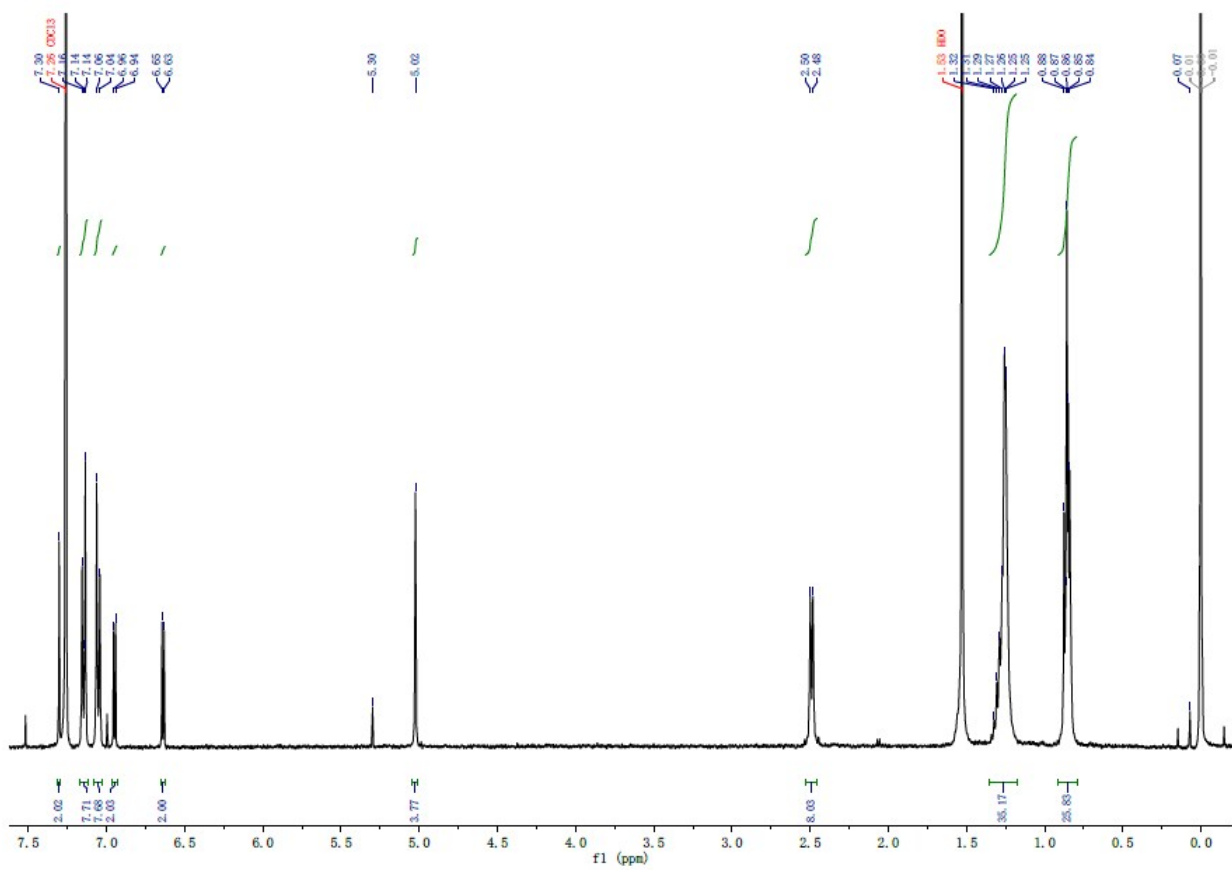


Compound-16 (IDTODT-2)

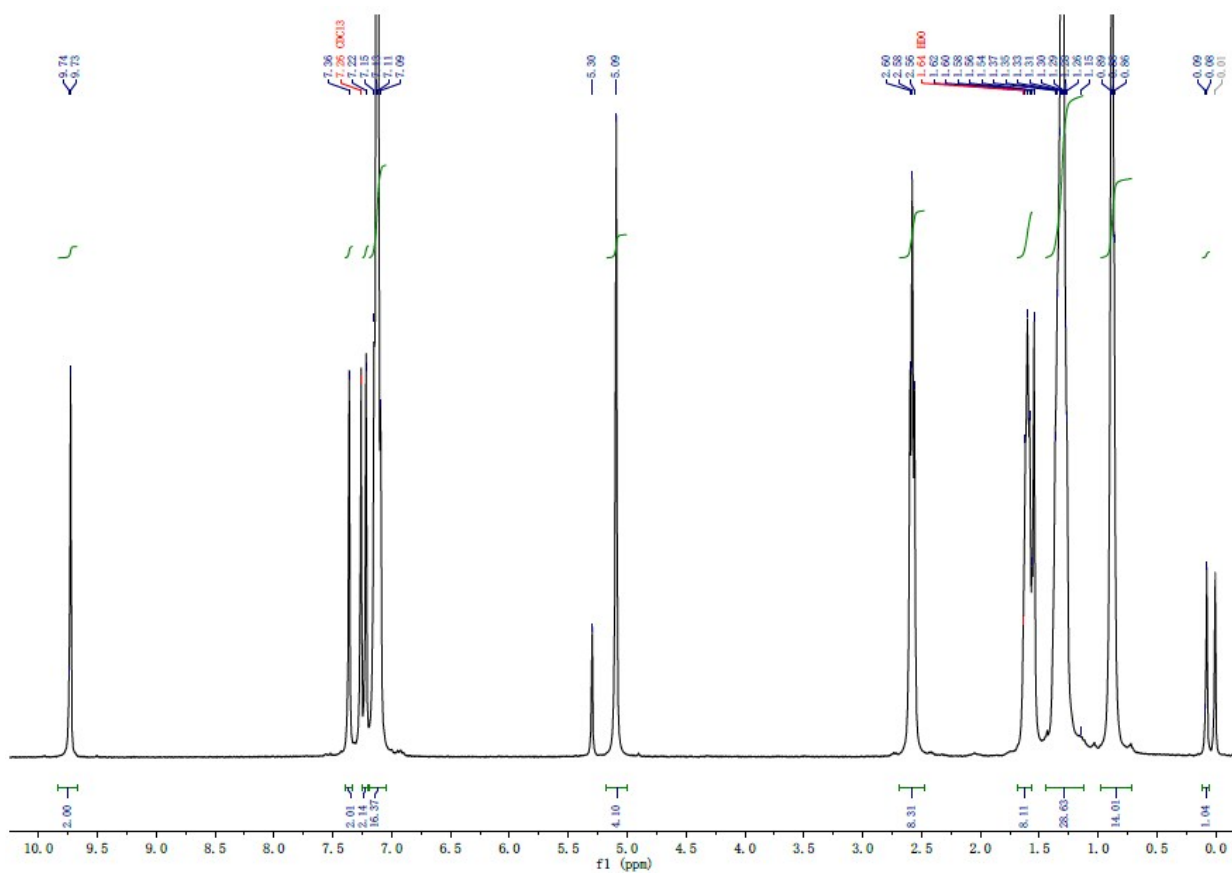


Co

mpound-16 (IDTODT-3)

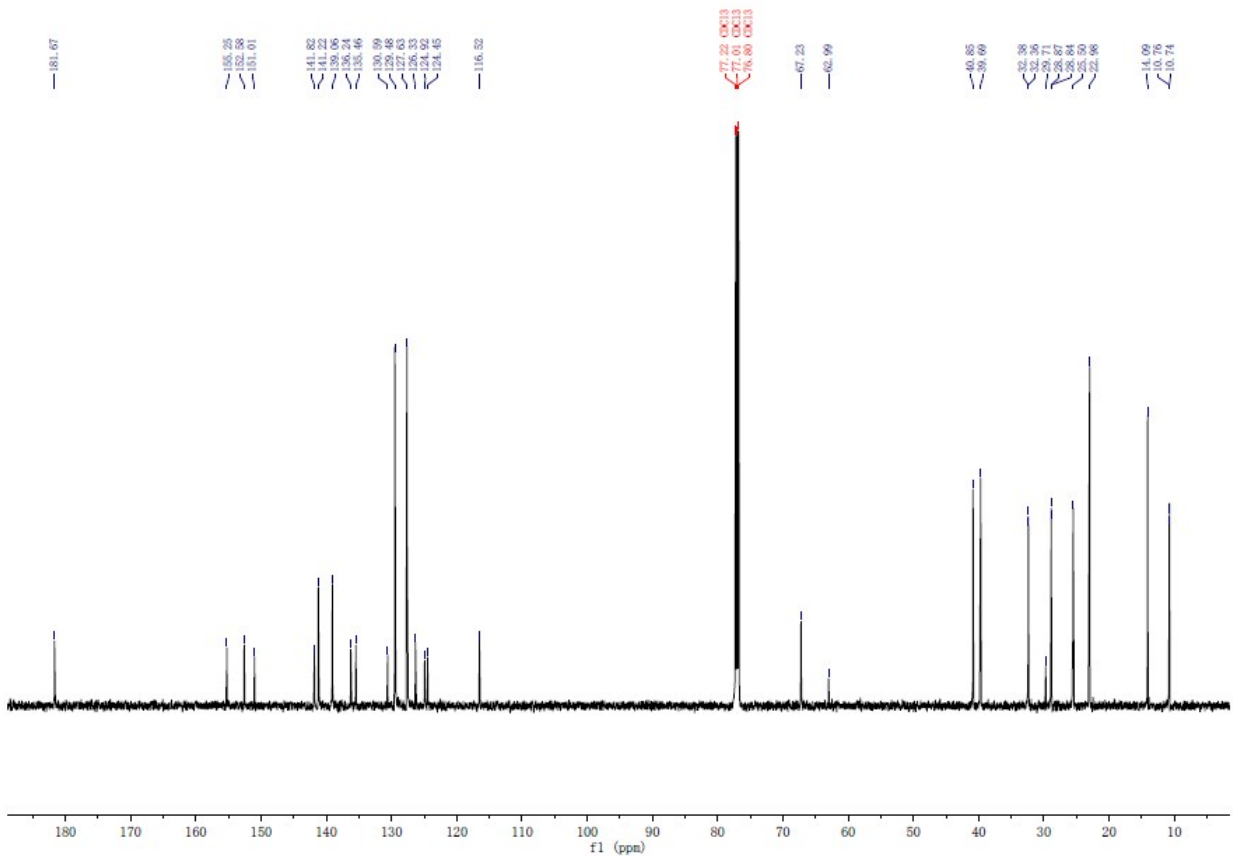
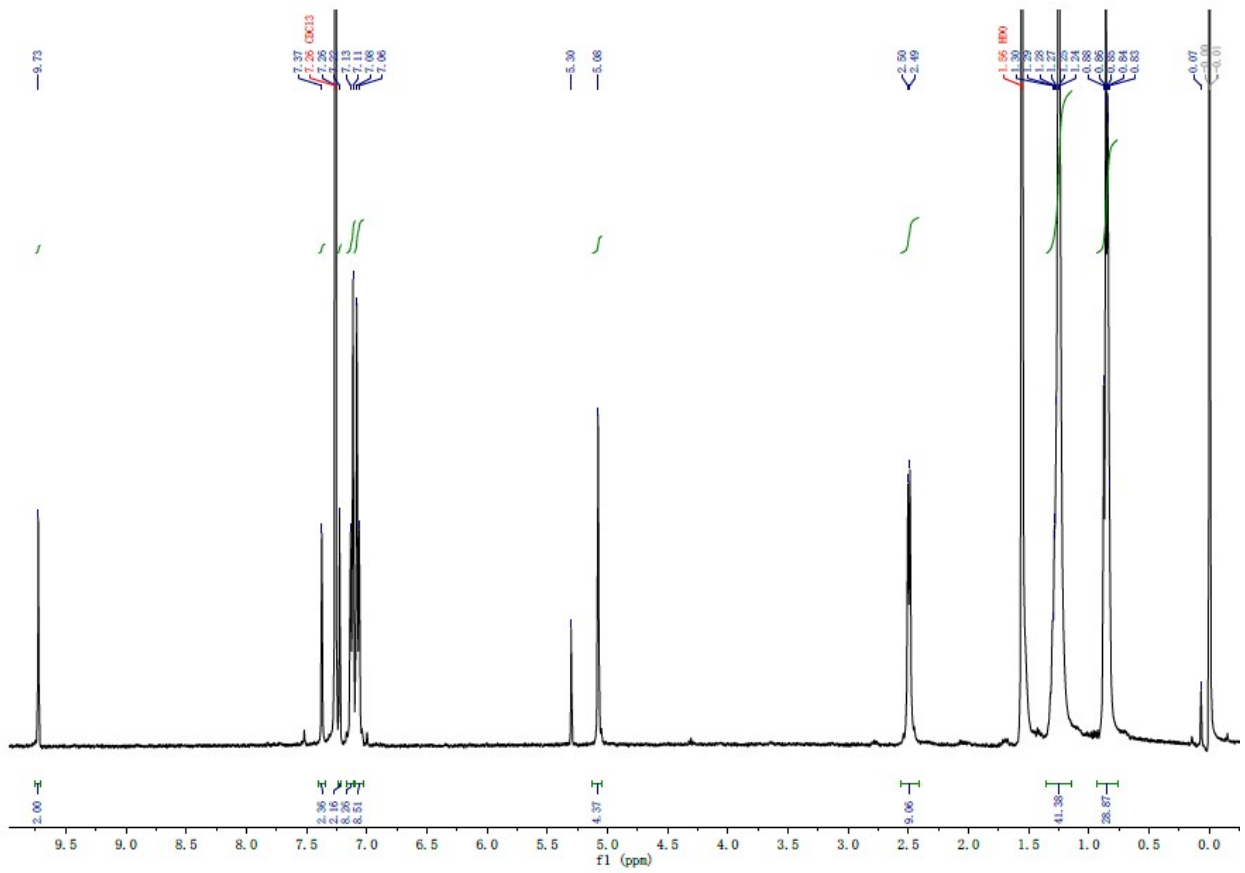


Compound-17 (IDTODT-2)

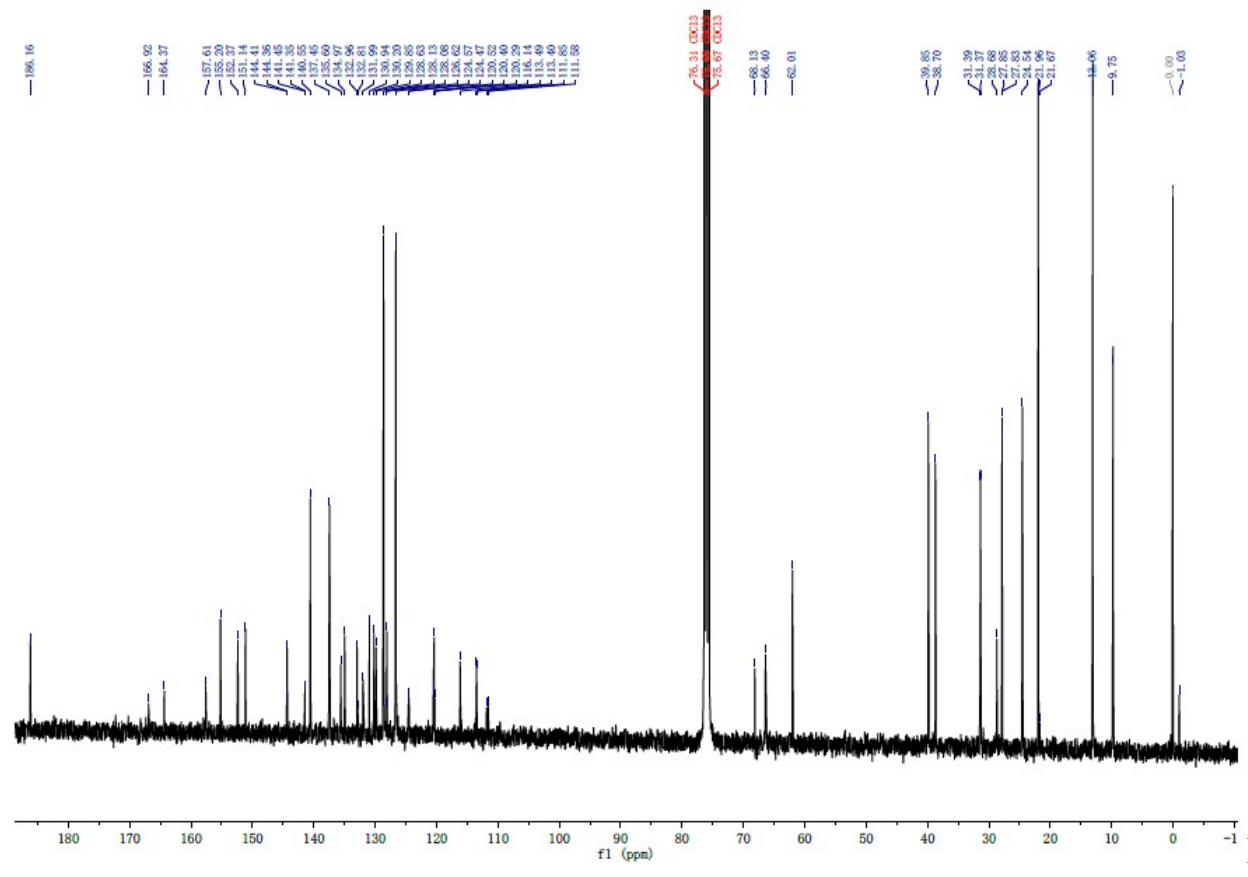
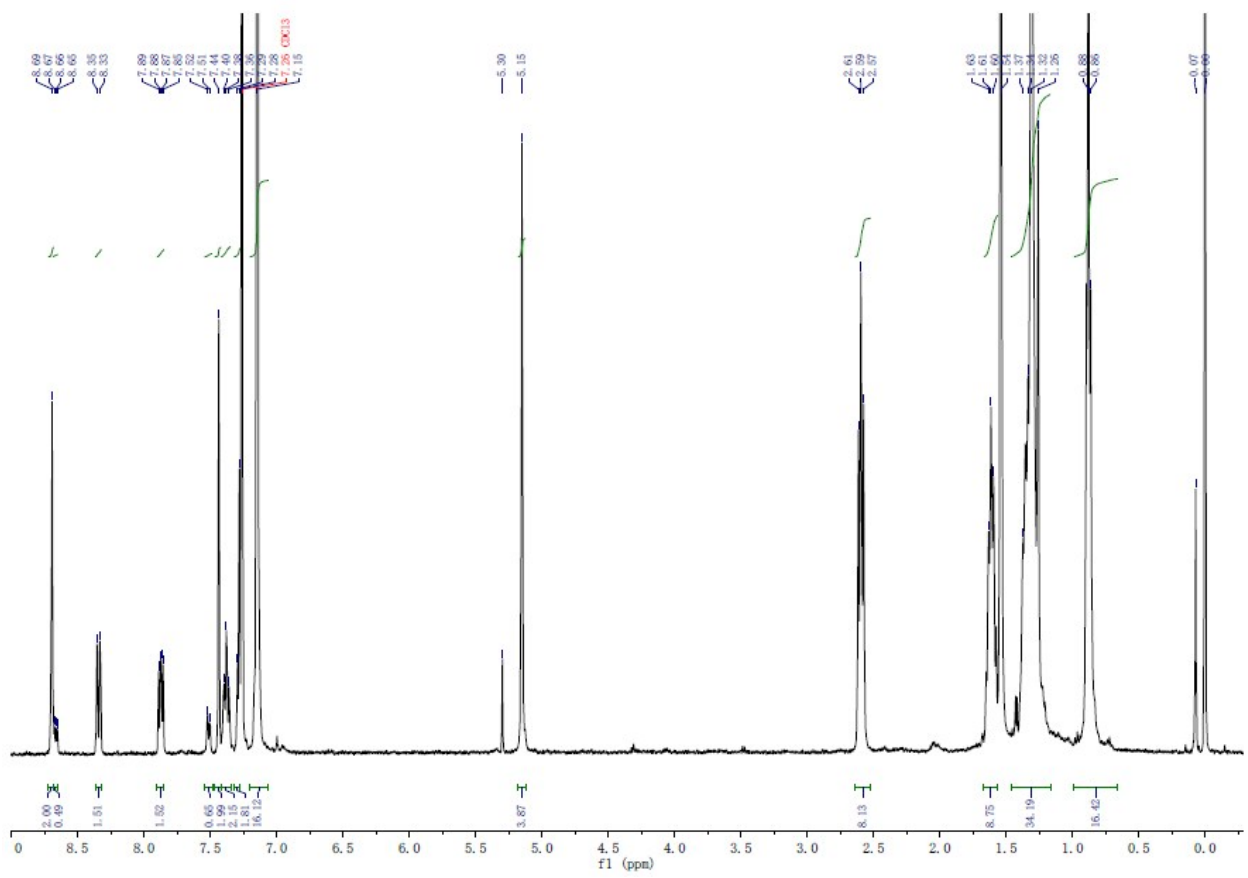


Co

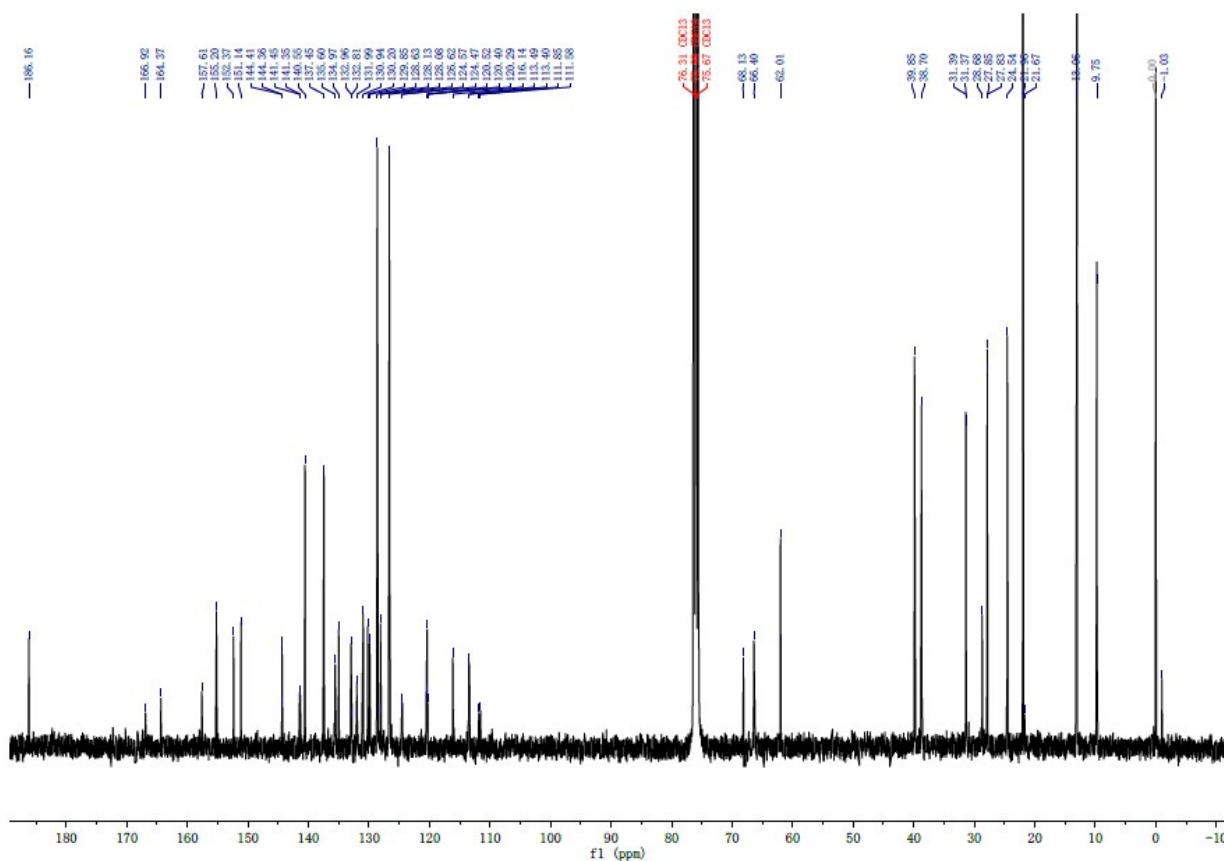
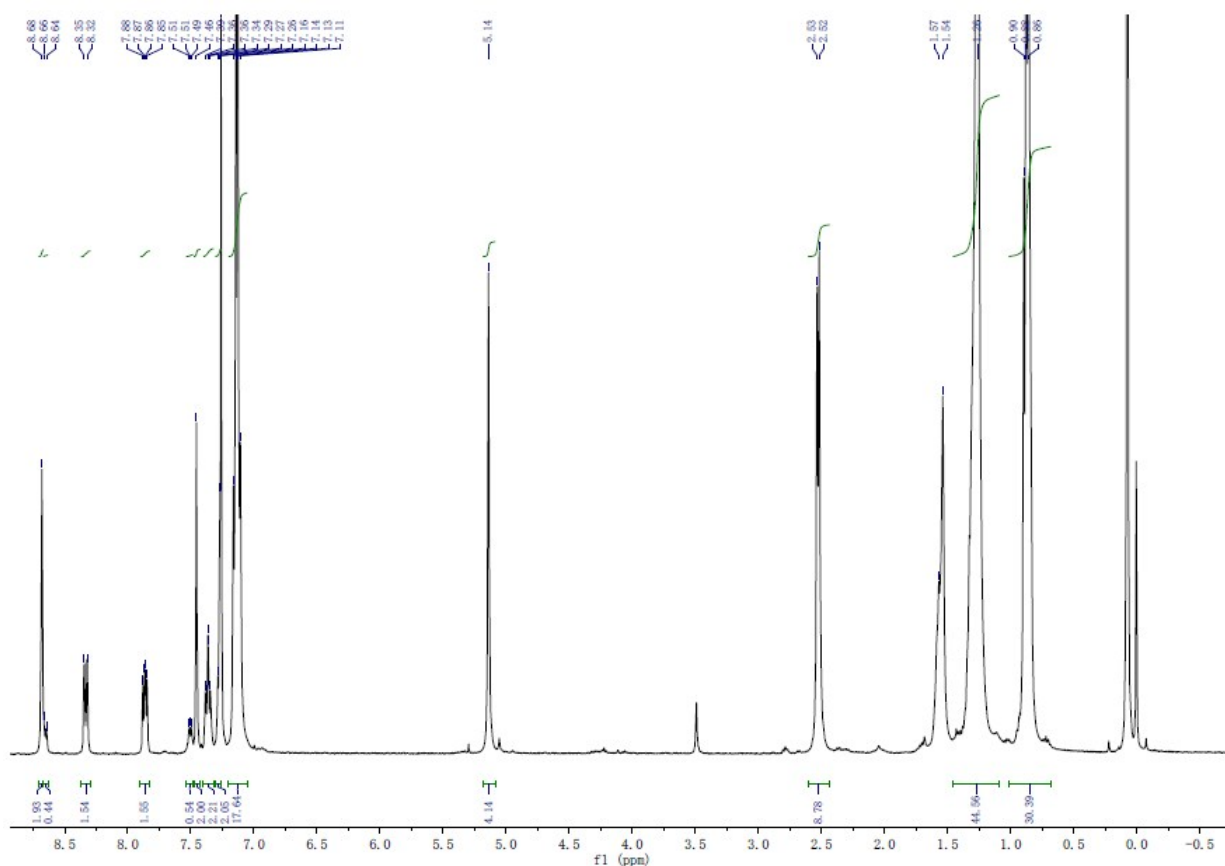
mpound-17 (IDTODT-3)



IDTODT-2



TODT-3



Part 4. Mass Spectra

IDTODT-1

MALDI,1

Analysis Info

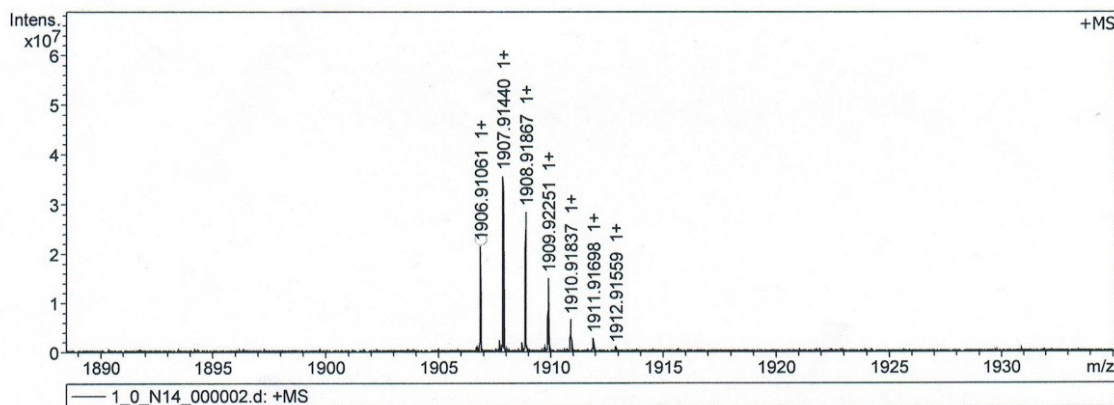
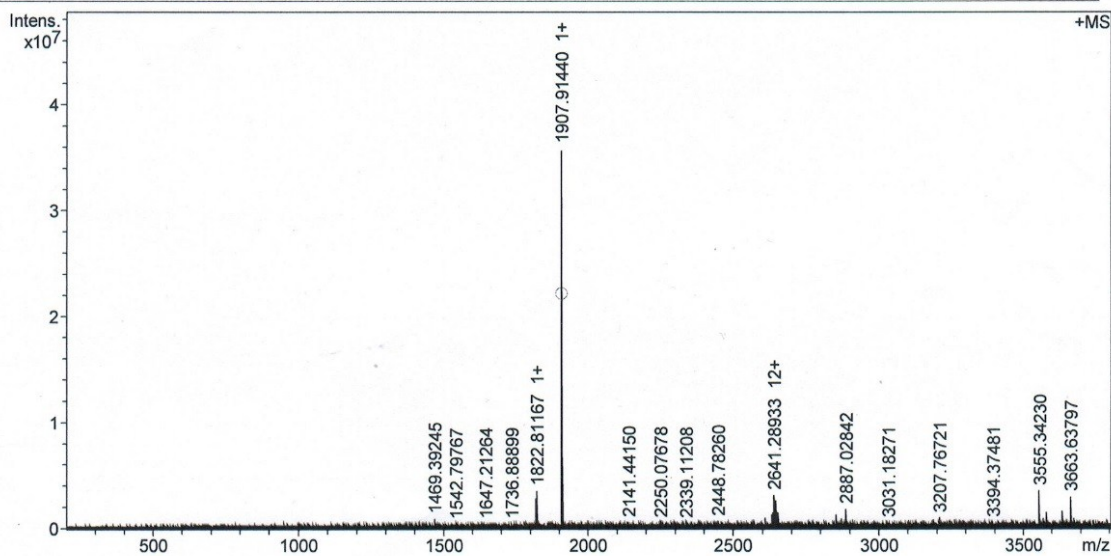
Analysis Name D:\Data\MALDI\2019\1014\1_0_N14_000002.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 10/14/2019 6:09:12 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	15	Calibration Date	Mon Oct 14 05:58:34
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2099152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	3800.0 m/z	Laser Power	11.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1906.91068	1	C ₁₂ H ₁₃ F ₂ N ₄ O ₄ S ₄	100.00	1906.909401	0.6	-1.6	55.8	60.0	odd	ok

IDTODT-2

MALDI,2

Analysis Info

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 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

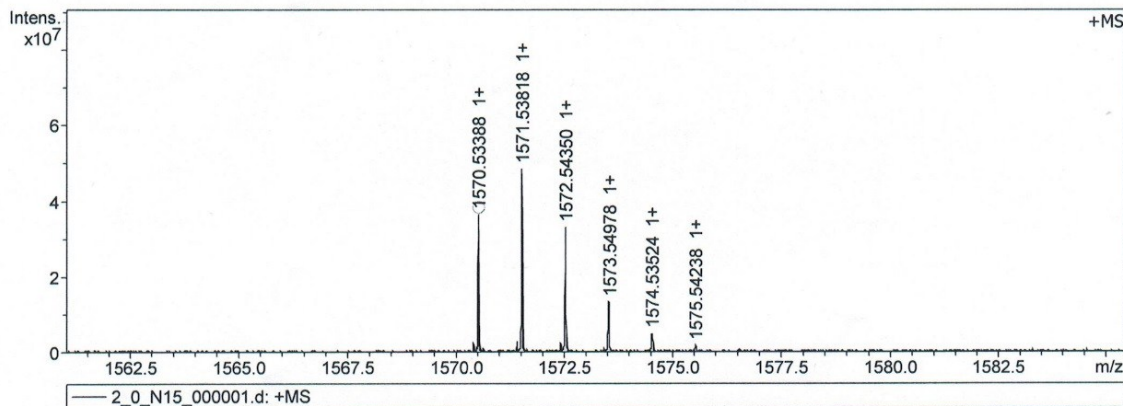
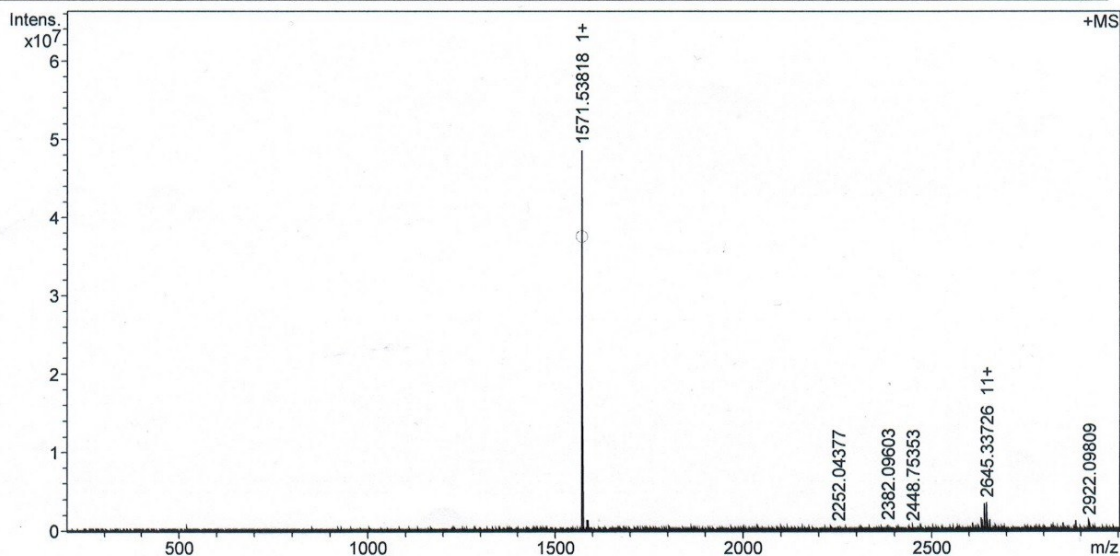
Acquisition Date 10/14/2019 6:11:16 PM

Operator

Instrument solarix

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	14	Calibration Date	Mon Oct 14 05:58:34
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2099152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	3000.0 m/z	Laser Power	16.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1570.533885	1	C100H84F2N4O4S4	100.00	1570.533799	0.1	-1.2	149.9	60.0	odd	ok

IDTODT-3

MALDI,3

Analysis Info

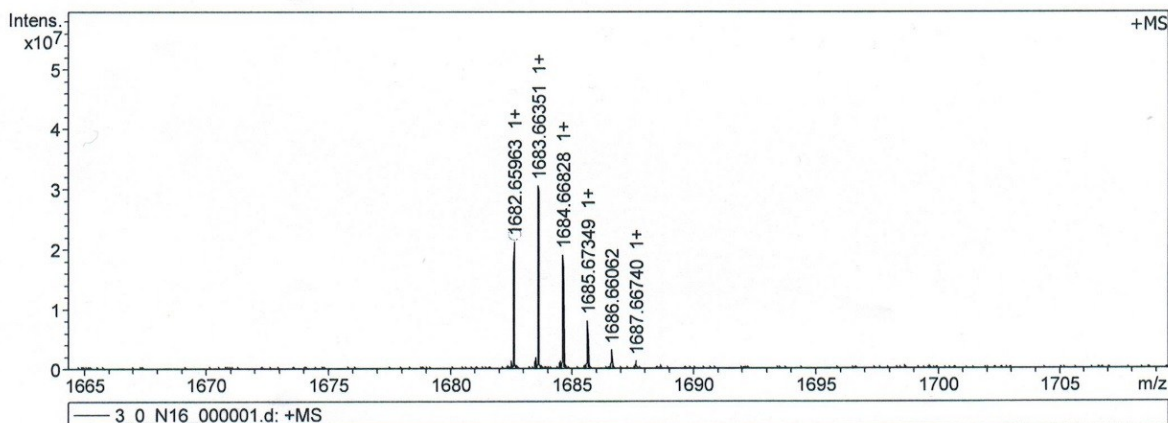
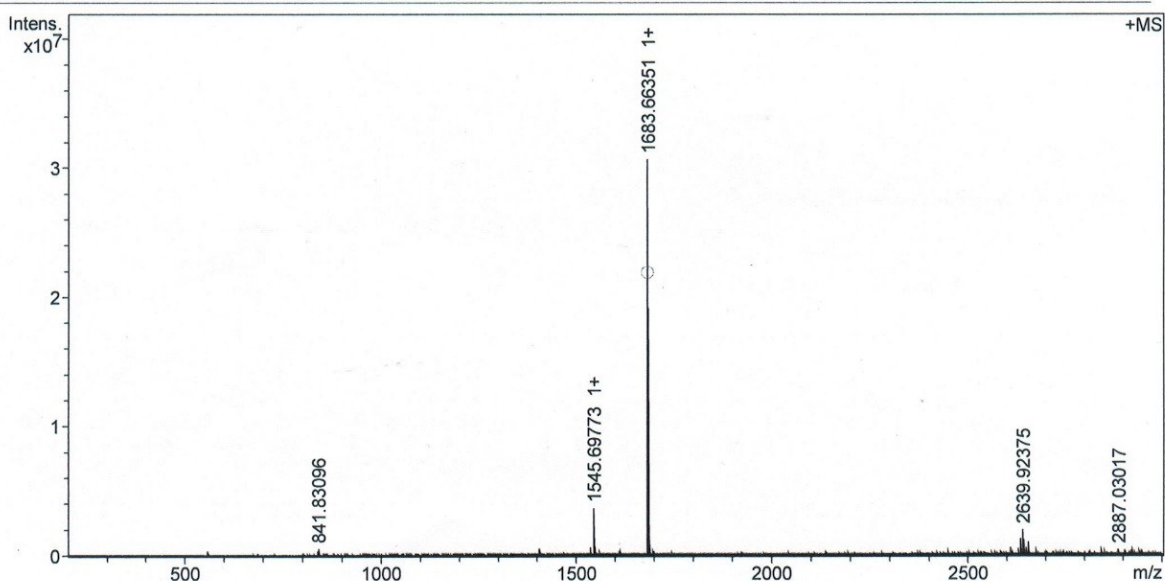
Analysis Name D:\Data\MALDI\2019\1014\3_0_N16_000001.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 10/14/2019 6:13:07 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	3	Calibration Date	Mon Oct 14 05:58:34
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2099152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	3000.0 m/z	Laser Power	16.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1682.659630	1	C108H100F2N4O4S4	100.00	1682.659000	0.4	-1.5	91.3	60.0	odd	ok