

Support Information

A–D–C–D–A Type Non-fullerene Acceptors Based on the Benzotriazole (BTA) Unfused Core for Organic Solar Cells

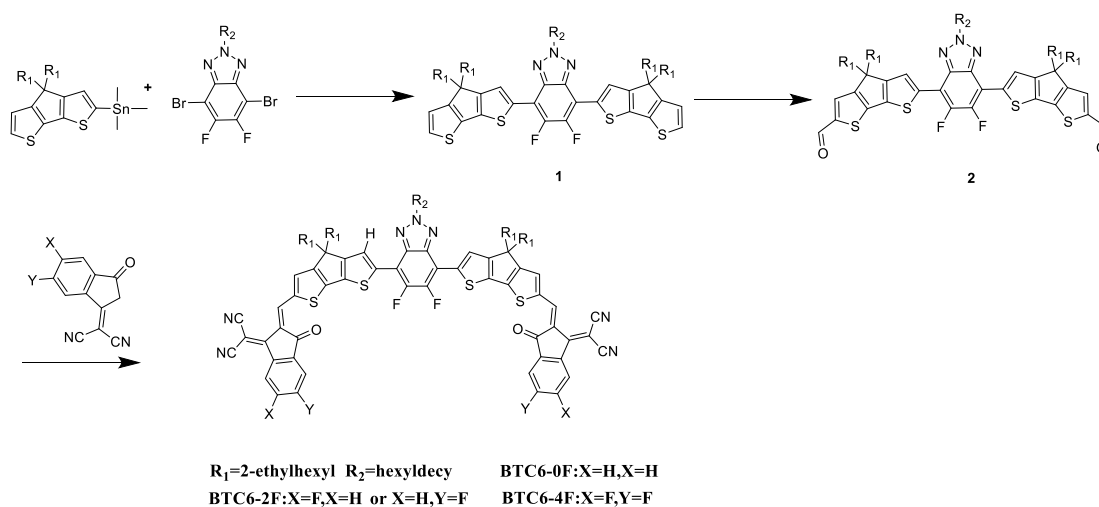
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Experimental Section

1. Materials and synthesis

All solvents and reagents were used as received from commercial sources and used without further purification unless otherwise specified.



Scheme S1. Synthetic route to the target molecules

4,7-Bis(4,4-dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole (Compound 1). Under nitrogen atmosphere the catalyst Pd(PPh₃)₂Cl₂ (7 mg, 0.01 mol) was added to a mixture solution of 4,7-dibromo-5,6-difluoro-2-(2-hexyldecyl)-2Hbenzo[d][1,2,3]triazole (50 mg, 0.093 mmol) and (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)trimethylstannane (126 mg, 0.22 mmol) in anhydrous tetrahydrofuran (10 mL). The reaction mixture was stirred and refluxed for 24 h under dark. The reaction mixture was filtered and washed with chloroform. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatograph to give 86 mg of **compound 1** in 78%

yield as a dark-red solid. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J*=2.16 Hz, 2H), 7.23 (d, *J*=6.48 Hz, 2H), 6.98 (d, *J*=6.44 Hz, 2H), 4.77 (d, *J*=7.76 Hz, 2H), 2.30 (s, 1H), 1.88–2.07 (m, 8H), 1.26–1.43 (m, 24H), 0.86–0.99 (m, 40H), 0.63–0.77 (m, 26H); ¹³C NMR (100 MHz, CDCl₃): δ 10.68, 10.82, 13.99, 14.11, 14.16, 14.17, 22.73, 22.80, 26.49, 26.55, 26.71, 27.36, 27.54, 28.54, 28.69, 29.39, 29.66, 29.74, 29.99, 31.63, 31.97, 34.23, 34.37, 35.16, 39.19, 43.29, 53.67, 59.93, 76.63, 77.05, 77.47, 110.09, 122.41, 124.9, 125.44, 132.00, 136.99, 137.54, 140.40, 145.10, 145.37, 148.43, 148.69, 157.88, 158.62. HRMS (MALDI-TOF): Calcd for C₇₂H₁₀₇F₂N₃S₄ [M]⁺, 1179.7316; found, 1179.7297.

6,6'-(5,6-Difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole-4,7-diyl)bis(4,4-dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (**Compound 2**). To a Schlenk flask under Ar atmosphere at 0 °C, 1.5 mL DMF and 1 mL POCl₃ were injected successively. After being stirred for 15 min at 0 °C, the **Compound 1** (86 mg, 0.073 mmol) was added into the reaction system through anhydrous 1,2-dichloroethane (10 mL) as the solvent. The mixture was refluxed at 85 °C for 8 h. After cooling to r.t., the mixture was extracted with a syringe and injected into an iced aqueous KOH solution dropwise, then stirred for another 3 h. The crude product was washed with water and dichloromethane to obtain the organic phase. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (1:2~1:3, v/v) as the eluent, yielding **Compound 2** as a pink red solid (80 mg, 89%). ¹H NMR (400 MHz, CDCl₃): δ 9.88 (s, 2H), 8.20 (s, 2H), 7.62 (s, 2H), 4.80 (d, *J*=7.72 Hz, 2H), 2.34 (m, 1H), 2.02–2.12 (m, 8H), 1.43–1.96 (m, 24H), 0.86–0.99 (m, 40H), 0.63–0.77 (m, 26H); ¹³C NMR (100 MHz, CDCl₃): δ 10.62, 10.74, 13.91, 14.05, 14.12, 22.69, 22.74, 26.39, 26.46, 27.29, 27.61, 28.44, 28.59, 29.33, 29.57, 29.66, 29.93, 31.55, 31.91, 34.10, 34.48, 35.30, 39.17, 43.13, 54.17, 60.18, 125.06, 130.61, 136.49, 137.35, 139.18, 143.89, 147.49, 158.51, 161.92, 182.54. HRMS (MALDI-TOF): Calcd for C₇₄H₁₀₇F₂N₃S₄O₂ [M]⁺, 1235.7214; found, 1235.7186.

Synthesis of BTC6-0F/2F/4F. The **Compound 2** (80 mg, 0.065 mmol) and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (24 mg, 0.12 mmol) / 2-(5 or 6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (28 mg, 0.13 mmol) / 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (30 mg, 0.13 mmol) were dissolved in chloroform (10 mL). 1 drop of pyridine (*ca.* 0.1 mL) was then added and the mixture stirred and refluxed for two days. The resulting mixture was extracted with chloroform, washed with water, and dried over anhydrous MgSO₄. After removal the solvent, the crude product was purified on a silica-gel column chromatography to afford 94/95/97 mg of **BTC6-0F/2F/4F** in 92%/90%/90% yield respectively as dark-green solid.

2,2'-((2*Z*,2'*Z*)-((5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole-4,7-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (**BTC6-0F**). ¹H NMR (400 MHz, CDCl₃): δ 8.91 (s, 2H), 8.67 (d, *J*=8.24 Hz, 2H), 8.25 (s, 2H), 7.93 (t, *J*=5.58 Hz, 2H), 7.70–7.76 (m, 6H), 4.81 (d, *J*=8.20 Hz, 2H), 2.36 (s, 1H), 2.02–2.14 (m, 8H), 1.25–1.57 (m, 24H), 0.83–0.99 (m, 40H), 0.66–0.77 (m, 26H); ¹³C NMR (100 MHz, CDCl₃): δ 10.57, 13.87, 14.00, 14.04, 22.63, 22.72, 22.78, 26.44, 26.50, 27.31,

27.58, 28.47, 28.53, 29.30, 29.56, 29.91, 31.63, 31.84, 31.88, 34.09, 34.5, 35.53, 39.23, 43.13, 43.25, 43.45, 54.09, 60.55, 67.88, 76.78, 76.99, 77.20, 101.99, 106.63, 109.20, 110.97, 112.45, 114.56, 115.01, 120.79, 123.50, 125.13, 125.38, 134.15, 134.82, 136.97, 137.36, 137.84, 138.05, 139.61, 139.73, 140.00, 140.15, 157.02, 159.98, 160.56, 164.67, 188.3. HRMS (MALDI-TOF): Calcd for C₉₈H₁₁₅F₂N₇S₄O₂ [M]⁺, 1587.7963; found, 1587.7934.

2,2'-((2Z,2'Z)-(((5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole-4,7-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(6-fluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (**BTC6-2F**). ¹H NMR (400 MHz, CDCl₃): δ 8.92 (s, 2H), 8.36–8.72 (m, 2H), 8.26 (s, 2H), 7.56–7.91 (m, 2H), 7.71 (m, 2H), 7.42 (m, 2H), 4.80 (m, 2H), 2.36(s, 1H), 2.04–2.09(m, 8H), 1.26–1.53 (m, 24H), 0.87–1.08 (m, 40H), 0.65–0.74 (m, 26H); ¹³C NMR (100 MHz, CDCl₃): δ 10.62, 10.97, 13.68, 13.93, 14.06, 22.68, 22.74, 22.80, 26.44, 27.27, 27.59, 28.43, 28.50, 29.34, 29.59, 29.65, 29.94, 31.58, 31.92, 34.00, 34.43, 35.47, 35.52, 39.17, 39.27, 39.37, 43.18, 43.37, 54.09, 60.49, 67.59, 68.46, 110.44, 110.59, 110.97, 112.62, 112.79, 114.60, 114.74, 114.77, 114.88, 114.91, 115.04, 120.48, 120.55, 121.00, 125.34, 125.59, 127.61, 133.09, 135.80, 137.30, 138.00, 139.60, 139.64, 140.00, 140.06, 142.25, 142.32, 146.67, 146.79, 148.36, 148.49, 157.58, 157.74, 159.15, 159.54, 160.09, 164.97, 165.01, 165.36, 165.76, 167.09, 167.46, 187.00. HRMS (MALDI-TOF): Calcd for C₉₈H₁₁₃F₄N₇S₄O₂ [M]⁺, 1623.7775; found, 1623.7747.

2,2'-((2Z,2'Z)-(((5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole-4,7-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (**BTC6-4F**). ¹H NMR (400 MHz, CDCl₃): δ 8.92 (s, 2H), 8.55 (t, *J* = 10.90 Hz, 2H), 8.27 (s, 2H), 7.70 (t, *J* = 10.10 Hz, 4H), 4.82 (d, *J* = 8.04 Hz, 2H), 2.36 (s, 1H), 2.05–2.10(m, 8H), 1.25–1.57 (m, 24H), 0.83–1.01 (m, 40H), 0.65–0.76 (m, 26H); ¹³C NMR (100 MHz, CDCl₃): δ 14.11, 22.6, 22.70, 22.79, 26.50, 27.26, 27.57, 28.42, 28.40, 29.34, 29.59, 29.66, 29.95, 31.58, 31.92, 34.03, 34.43, 35.48, 35.54, 39.18, 39.28, 39.37, 43.19, 43.27, 43.36, 54.12, 60.50, 68.27, 76.81, 77.02, 77.24, 111.03, 111.07, 112.45, 112.58, 114.59, 114.64, 114.80, 114.95, 119.81, 125.38, 134.48, 134.51, 136.49, 136.53, 137.30, 138.20, 139.53, 140.04, 140.27, 146.71, 146.84, 148.41, 148.53, 153.36, 153.45, 155.11, 155.17, 155.20, 160.24, 165.26, 186.04. HRMS (MALDI-TOF): Calcd for C₉₈H₁₁₁F₆N₇S₄O₂ [M]⁺, 1659.7586; found, 1659.7561.

2. Instruments and Measurements

¹H NMR and ¹³C NMR spectra of the compounds were taken on a Bruker AVANCE 400 spectrometer at room temperature. High-resolution mass spectrometry (HRMS) spectra were recorded with a solarix spectrometer. DFT calculations were performed by using Gaussian09 at the B3LYP/6-31G* level, and the long alkyl chain was simplified as methyl. UV-Vis absorption spectra were recorded on a PerkinElmer Lambda 950 UV-Vis spectrophotometer. A CHI660E electrochemical workstation was utilized to determine the energy levels of small molecule acceptors, and ferrocene/ferrocenium (Fc/Fc⁺) was used as the external standard. Differential scanning calorimetry (DSC) measurements were tested on Perkin-Elmer Diamond DSC

instrument, under a nitrogen atmosphere at a heating/cooling rate of 10 °C/min from 100 °C to 350 °C. The height and phase images of blend films were obtained using an atomic force microscopy (AFM, Bruker-Multimode 8) in the tapping-mode. TEM images were obtained by the JEOL JEM-1011 transmission electron microscope.

Fabrication and characterization of photovoltaic cells

The organic solar cells were fabricated on glass substrates with the conventional structure of ITO/PEDOT:PSS/Active layer/PDINO/Al.^[1] All glass substrates were pre-cleaned by an ultrasonic bath of deionized water, acetone and isopropanol consecutively, and then treated in an ultraviolet ozone generator for 15 min. After that, PEDOT:PSS (4083, Heraeus-Clevios) were spin coated onto the substrates at 4500 rpm for 30 s, and annealed at 150 °C for 10 min. The PEDOT:PSS-coated substrates were then transferred to the glovebox, and the blend CF solution based on PBDB-T:BTC6-XF was spin coated on them at 3000 rpm for 30 s. 1-chloronaphthalene (CN) was added into the solution 30 min before spin-coating process. An extra post-annealing for 5 min was also carried out. After that, a 5 nm PDINO^[2] film was deposited as the cathode buffer layer. Finally, the Al (800 nm) electrode was deposited by thermal evaporation, the device was completed with an active area of 4 mm².

***J-V* measurements**

The current density-voltage (*J-V*) curves of OSCs was measured under a calibrated solar simulator (Enli Technology) at 100 mW cm⁻², whose light intensity was calibrated by a standard Si solar cell at 100 mV cm⁻². The EQE data were measured by a Solar Cell Spectral Response Measurement System.

SCLC measurements

The charge carrier mobility of the Donor:Acceptor films was measured using the space charge limited current (SCLC) method. Electron-only devices were fabricated in a structure of ITO/ZnO/Active-layer/PDINO/Al, whereas Hole-only devices utilizing the structure of ITO/PEDOT:PSS/Active-layer/MoO₃/Ag. The device characteristics were extracted by modeling the dark current under forward bias the SCLC expression described by the Mott-Gurney Law: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where ϵ_r is the average dielectric constant of the blend film, ϵ_0 is the permittivity of the free space, μ is the carrier mobility, L is the thickness of the active layer, and V is the applied voltage.

GIWAXS measurements

GIWAXS data were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and Pilatus3R 300K detector. The incidence angle of 0.18° was chosen which gave the optimized signal-to background ratio.

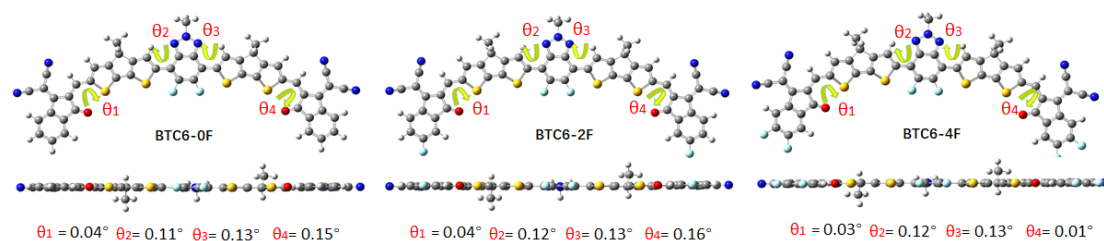


Figure S1. The geometries of BTC6-XF optimized at the B3LYP/6-31G* level

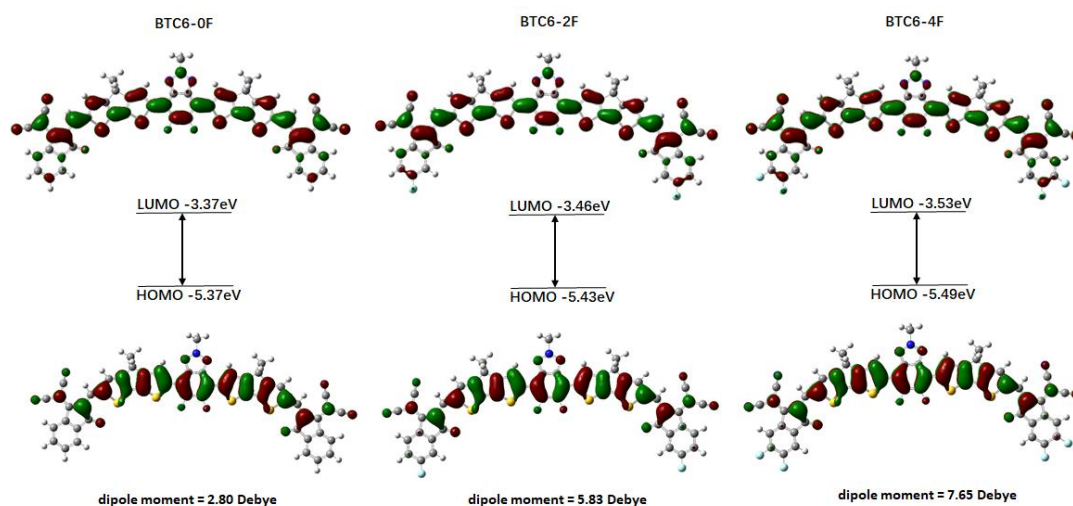


Figure S2. The HOMO and LUMO energy levels of optimized geometries of BTC6-XF and corresponding dipole moments.

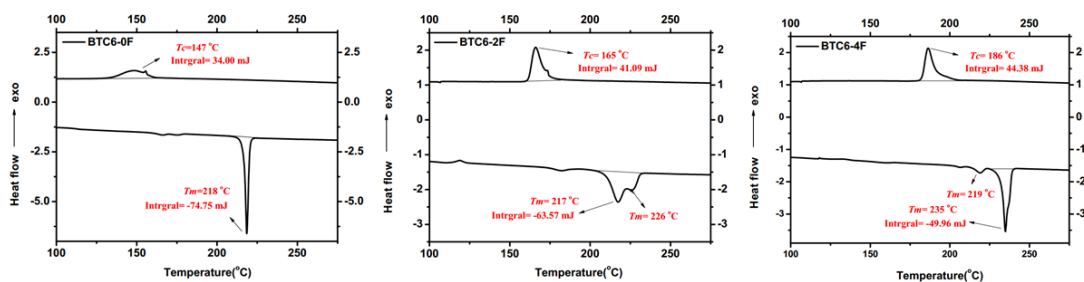


Figure S3. DSC curves of BTC6-0F (a), BTC6-2F (b), and BTC6-4F (c) on the first cooling and the second heating process.

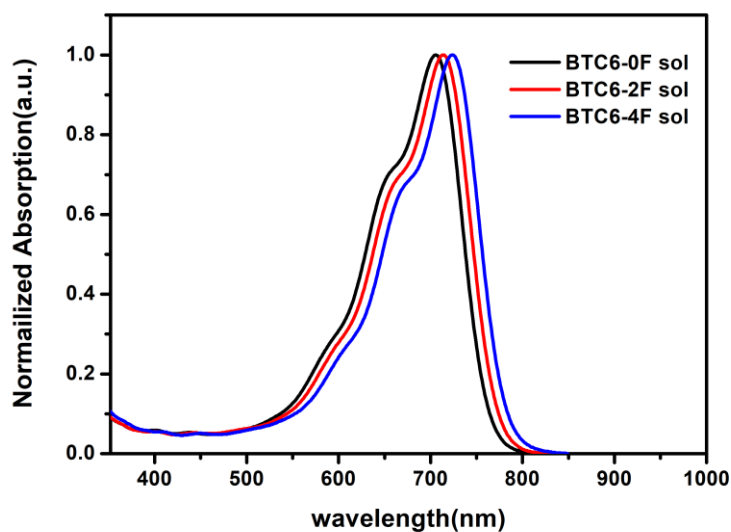
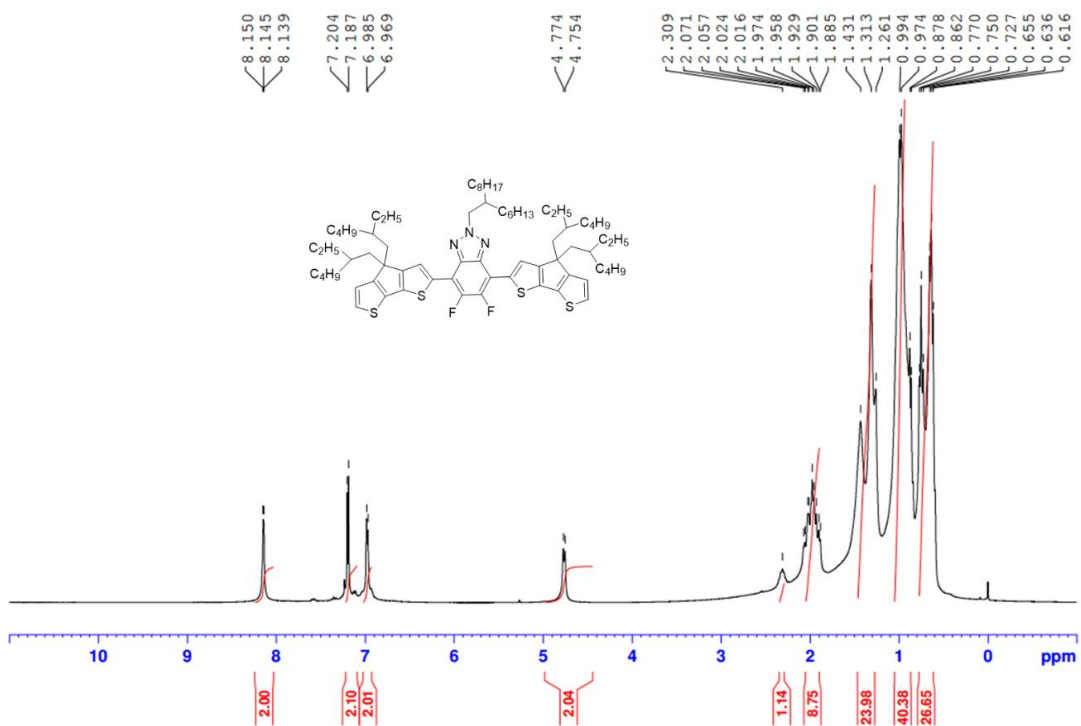


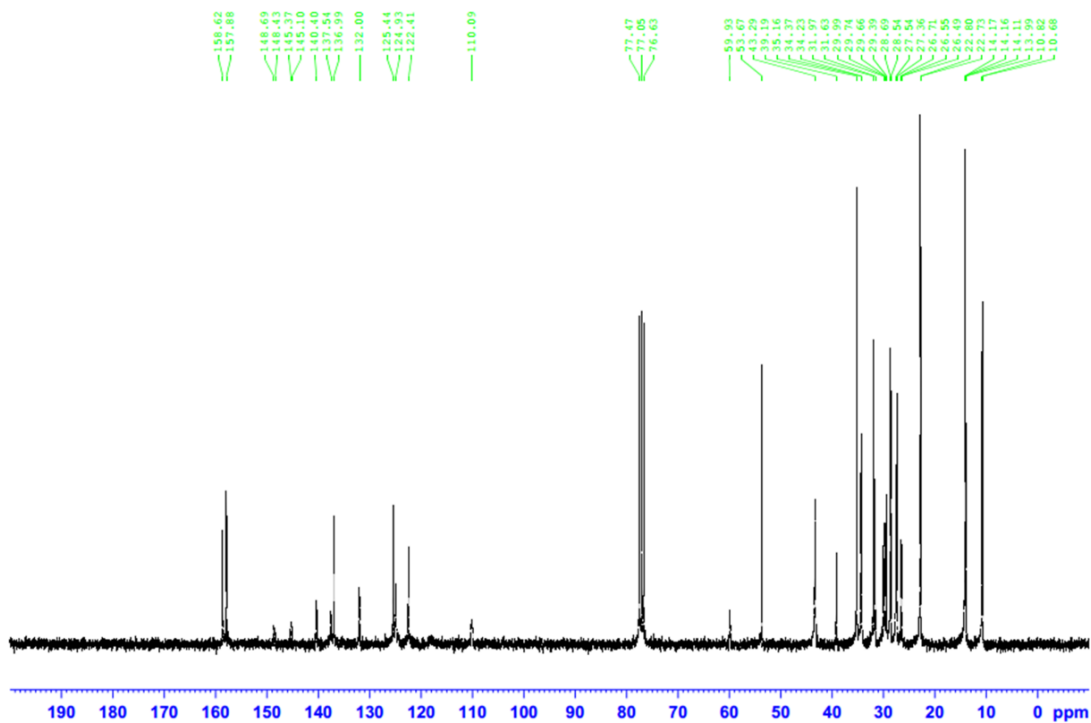
Figure S4. UV-vis absorption spectra of **BTC6-XF** in CHCl_3 solution.

Table S1. Photovoltaic parameters of the **BTC6-4F**-based devices based on different polymer donor materials, solution concentrations, and thermal annealing temperatures.

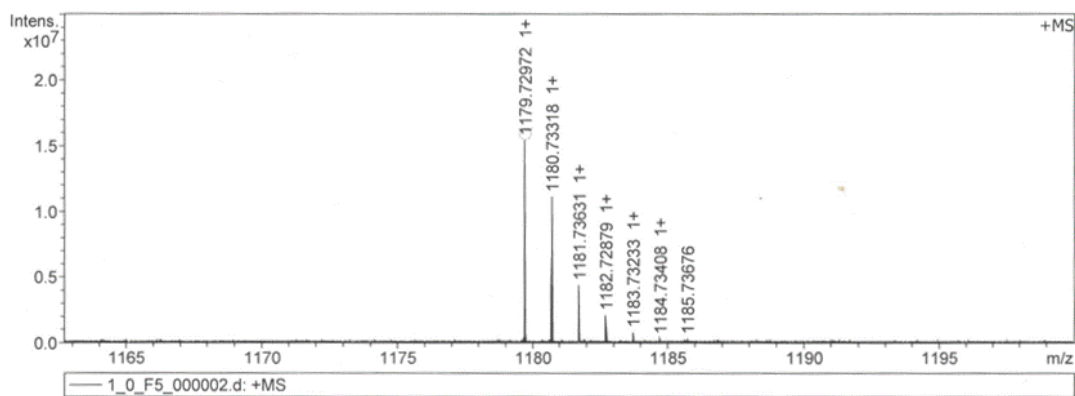
polymer	Concentration (mg/ml in CF)	additive	Thermal annealing	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE(%)
PM6	16	/	/	0.88	14.58	53. 63	6.86
PM6	16	CN	130°C	0.87	14.51	54. 48	6.91
PBDB-T	16	/	/	0.79	18.99	56. 19	8.47
PBDB-T	16	CN	130°C	0.79	19.81	71. 65	11.23
PBDB-T	16	CN	150°C	0.79	19.47	67. 30	10.45
PBDB-T	16	CN	120°C	0.79	19.87	69. 50	10.96
PBDB-T	18	CN	130°C	0.78	19.96	60. 26	9.59
PBDB-T	14	CN	130°C	0.79	18.41	67. 10	9.80
PBDB-T	12	CN	130°C	0.80	12.44	72. 22	7.24



¹H NMR of compound 1

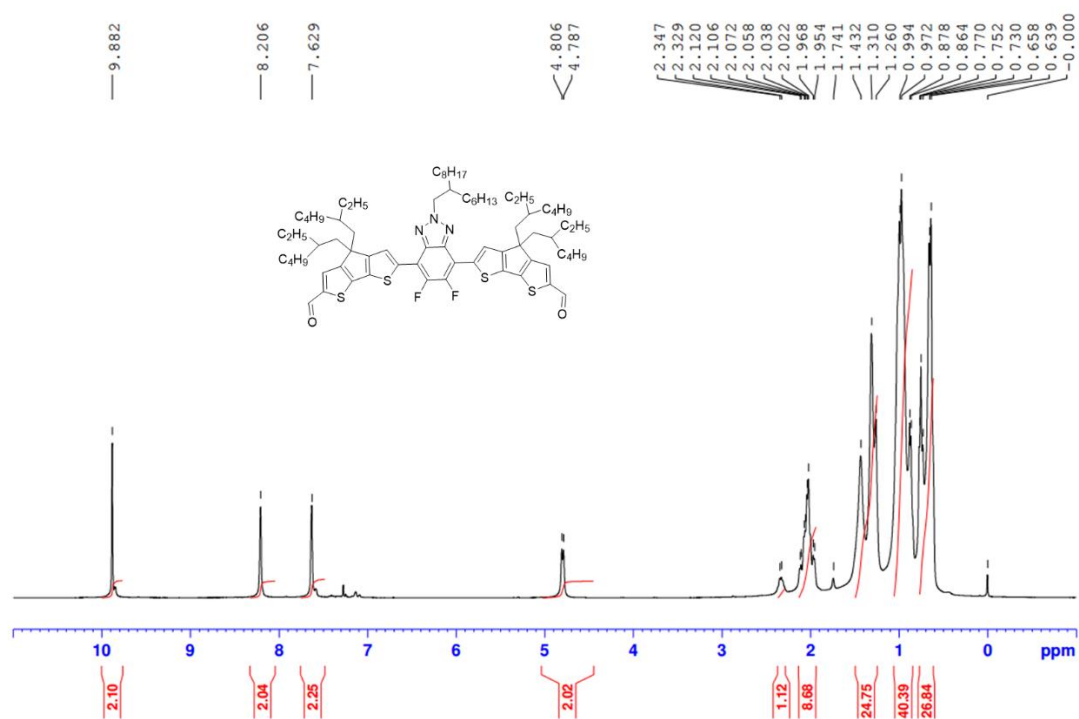


¹³C NMR of compound 1

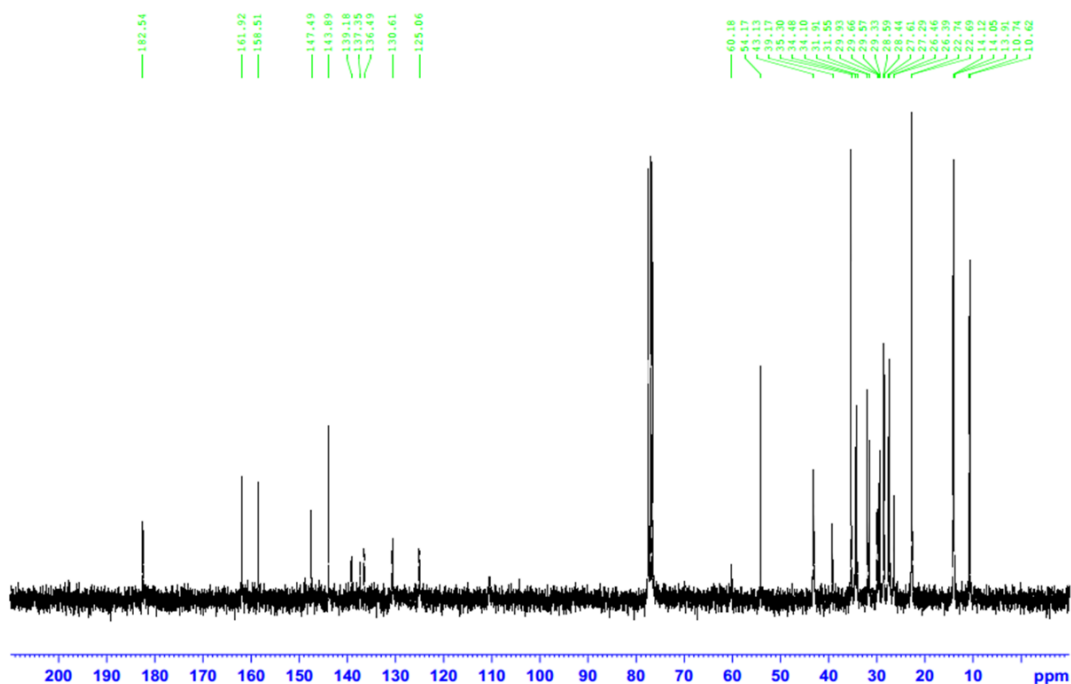


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1179.729722	1	C72H107F2N3S4	100.00	1179.731042	-1.1	0.8	107.9	20.0	odd	ok

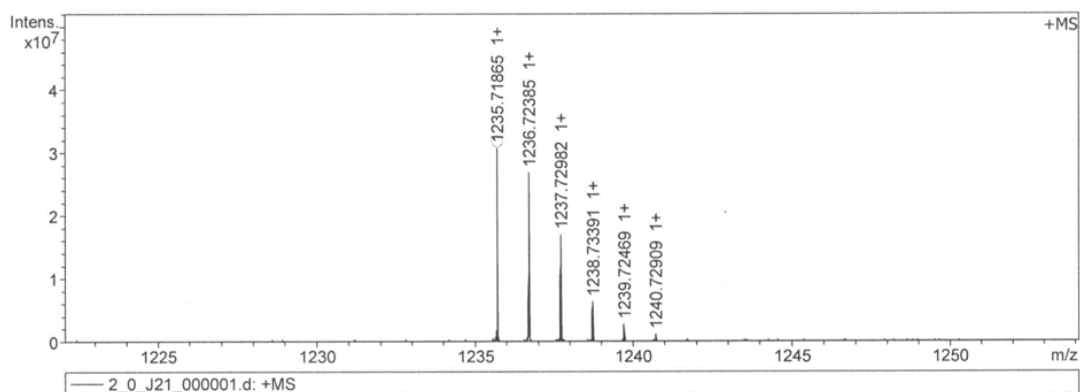
HRMS of compound 1



¹H NMR of compound 2

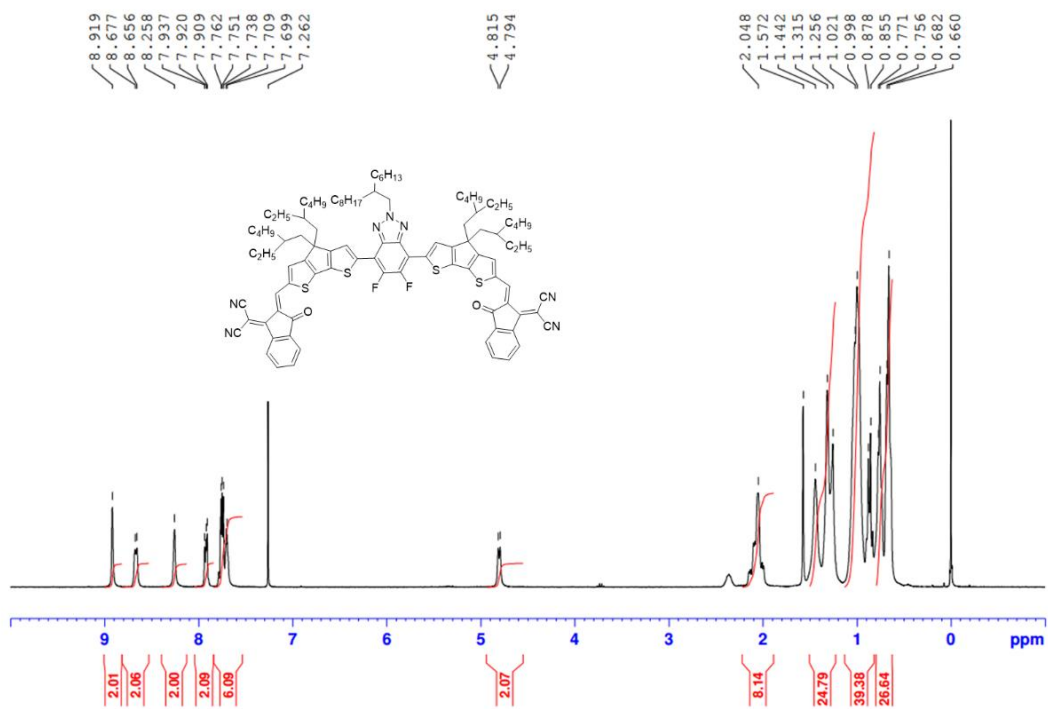


^{13}C NMR of compound **2**

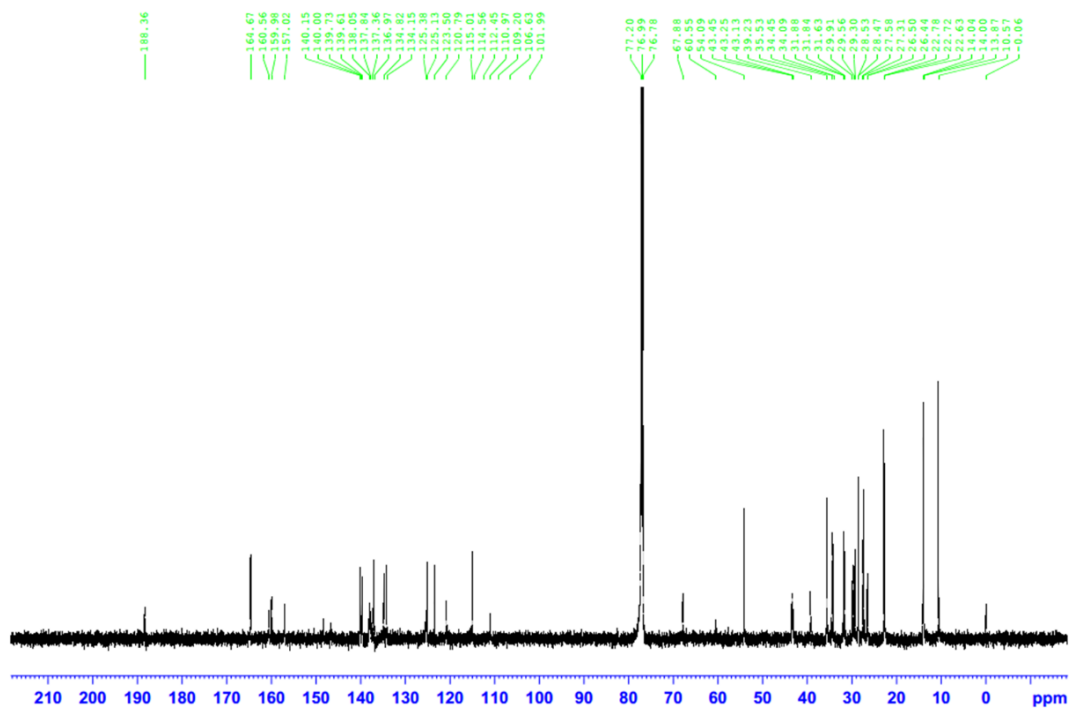


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1235.718647	1	C74H107F2N3O2S4	100.00	1235.720872	1.8	1.2	212.1	22.0	odd	ok

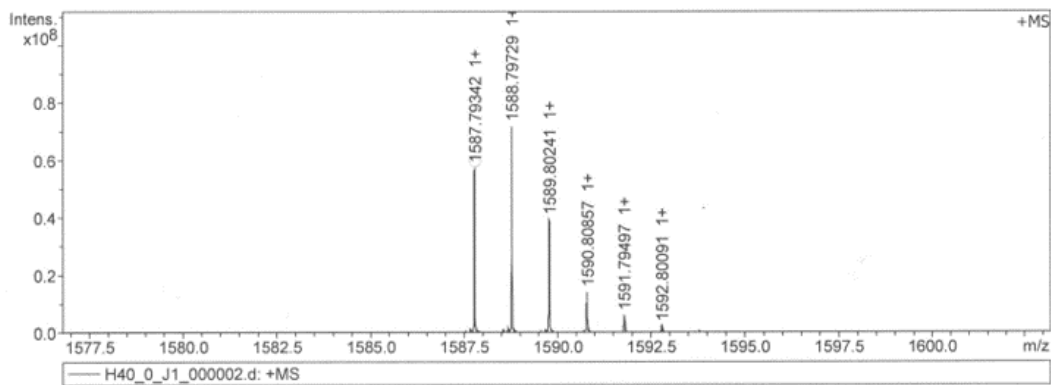
HRMS of compound **2**



¹H NMR of compound **BTC6-0F**

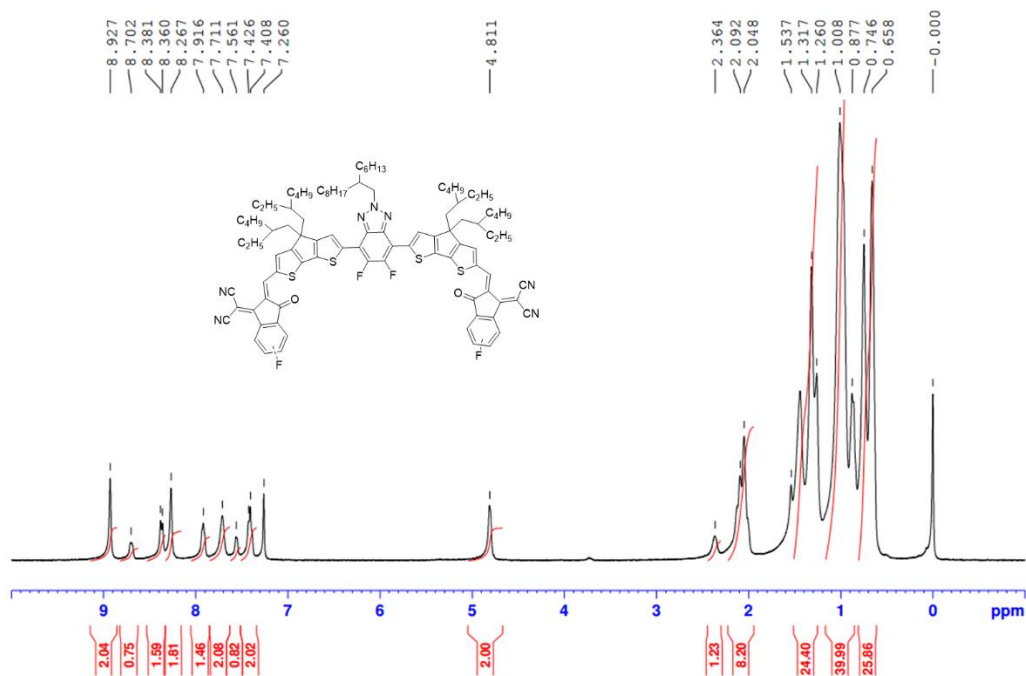


¹³C NMR of compound **BTC6-0F**

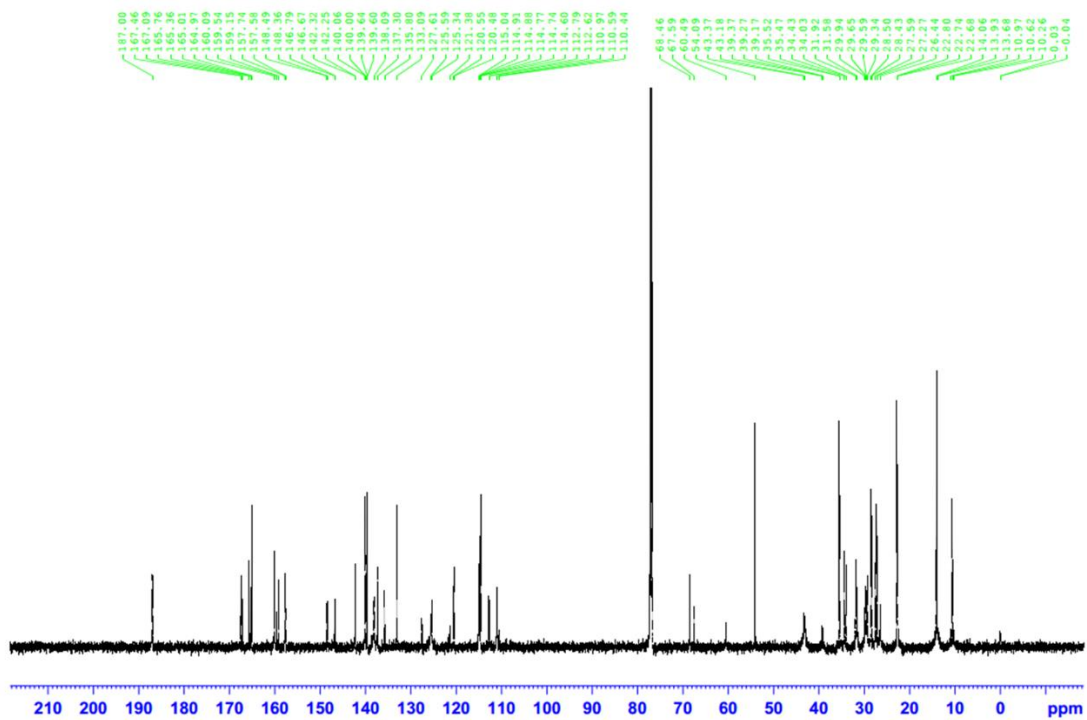


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdB	e ⁻ Conf	N-Rule
1587.793416	1	C98H115F2N7O2S4	100.00	1587.795768	-1.5	0.6	157.2	44.0	odd	ok

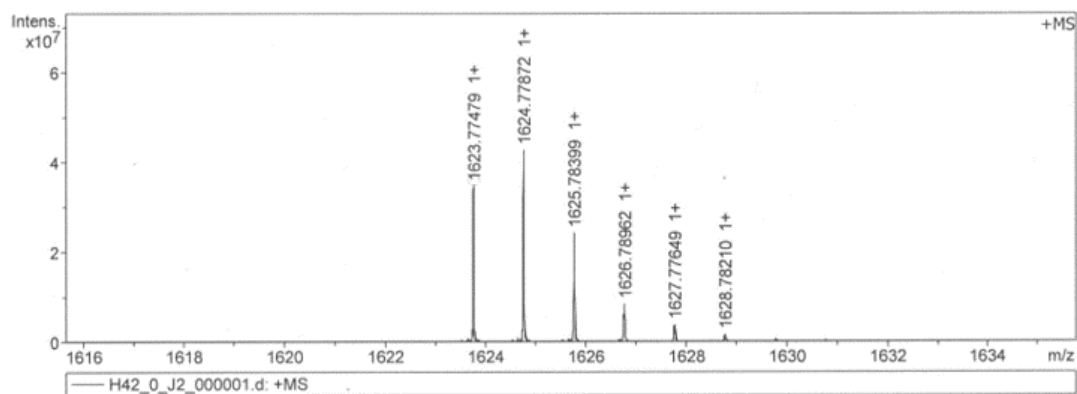
HRMS of compound **BTC6-0F**



¹H NMR of compound **BTC6-2F**

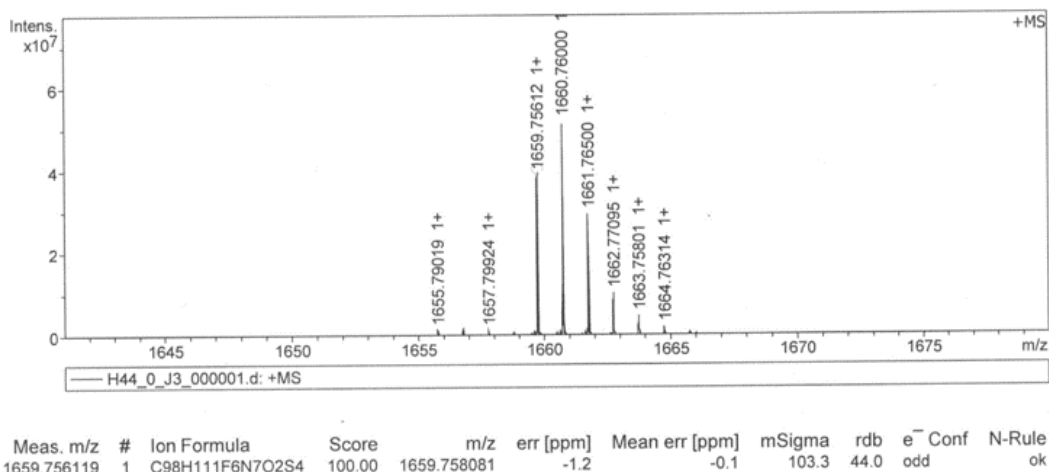


^{13}C NMR of compound **BTC6-2F**



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1623.774788	1	C ₉₈ H ₁₁₃ F ₄ N ₇ O ₂ S ₄	100.00	1623.776924	1.3	0.0	95.2	44.0	odd	ok

HRMS of compound **BTC6-2F**



HRMS of compound **BTC6-4F**

Figure S5. ¹H NMR, ¹³C NMR and HR MALDI-TOF MS spectra respectively of the intermediates and compound **1**, compound **2**, **BTC6-0F**, **BTC6-2F**, **BTC6-4F**.

Reference

- [1] C. He, Y. Li, S. Li, Yu, P. Z. Y. Li, X. Lu, M. Shi, Z. Li and H. Chen, *ACS Appl Mater Interfaces*, 2020, **12**, 16700–16706.
- [2] X. Liu, Y. Wei, X. Zhang, L. Qin, Z. Wei and H. Huang, *Science China Chemistry*, 2020, **64**, 228–231.