

Supporting Information

Dicyanoquinodimethane substituted benzothiadiazole for efficient small-molecule solar cells

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Experimental details:

Chemicals were used as received unless otherwise indicated. All the oxygen or moisture sensitive reactions were carried out under argon/nitrogen atmosphere. ¹H NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard {CDCl₃, 7.26 ppm}. ¹³C NMR spectra were recorded using a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as internal standard {CDCl₃, 77.0 ppm}. The ¹H NMR splitting patterns have been described as “s (singlet), d (doublet) and m (multiplet)”. UV-visible absorption spectra of all compounds were recorded in DCM. The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G** level for C, N, S, H in the Gaussian 09 program. HRMS was recorded on TOF-Q mass spectrometer.

Preparation of BTD 2

To a stirred solution of 3-ethynylpyridine (1.2 mmol), BTD 1 (1 mmol) in THF, and TEA (1:1, v/v) were added [PdCl₂(PPh₃)₂] (10 mg, 0.014 mmol) and CuI (2 mg, 0.01 mmol) under an argon flow at room temperature. The reaction mixture was stirred for 15 h at 70 °C, and then cooled to room temperature. The solvent was evaporated under reduced pressure, and the mixture was purified by SiO₂ chromatography with DCM, to obtain BTD 2 as red solid (362 mg, yield: 72%). ¹H NMR (400 MHz, CDCl₃, δ in ppm): 8.88 (s, 1H), 8.59 (s, 1H), 7.93 (d, *J* = 8 Hz, 1H),

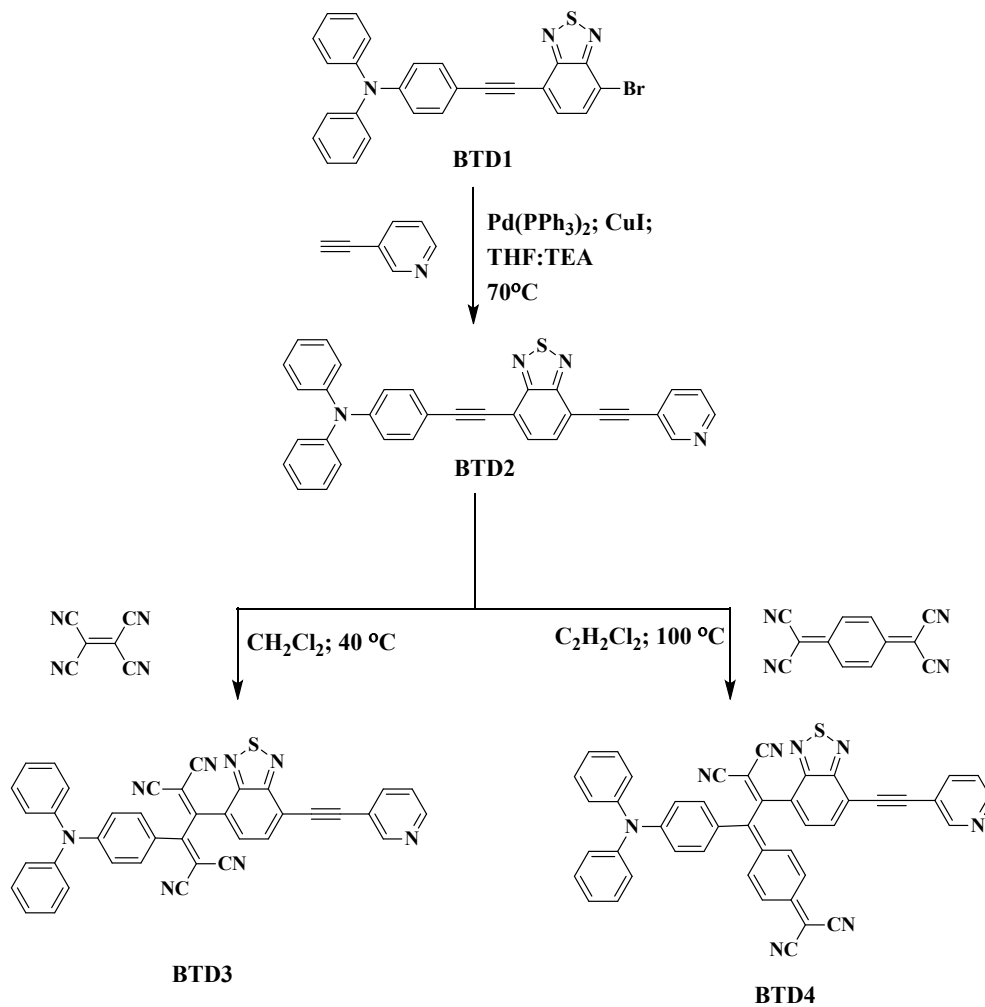
7.79 (d, J = Hz, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.30–7.24 (m, 6H), 7.13–7.00 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 155.2, 153.1, 152.40, 152.38, 148.9, 148.7, 148.5, 147.2, 138.7, 134.8, 133.5, 130.0, 129.9, 129.4, 126.4, 125.1, 123.5, 123.1, 122.4, 114.1, 100.5, 92.0, 88.7; HRMS (ESI - TOF) m/z calcd for $\text{C}_{33}\text{H}_{20}\text{N}_4\text{S}+\text{H}$: 505.1481 $[\text{M}+\text{H}]^+$, found 505.1481 $[\text{M} + \text{H}]^+$.

Preparation of BTD 3

To a stirred solution of BTD 2 (0.5 mmol) was added TCNE (64 mg, 0.5 mmol) under an argon flow at room temperature. The mixture was refluxed at 40 °C for 24 h. The solvent was removed in vacuo, and the product was purified by SiO_2 column chromatography with $\text{DCM}:\text{EtOAc}$ (100:1) as the eluent to yield BTD 3 as a dark colored solid (240mg, yield: 76%). ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 8.91–8.90 (m, 1H), 8.66–8.64 (m, 1H), 8.05 (d, J = 7.56 Hz, 1H), 7.97–7.91 (m, 2H), 7.64 (m, J = 7.52, 2H), 7.38–7.34 (m, 4H), 7.25–7.21 (m, 4H), 7.17 (d, J = 7Hz, 3H), 6.87 (d, J = 7.56 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 163.9, 163.4, 154.5, 153.6, 152.6, 150.8, 149.9, 144.5, 139.0, 132.4, 132.1, 131.8, 130.0, 126.9, 126.6, 125.0, 122.4, 121.8, 118.0, 113.5, 113.0, 111.5, 110.8, 97.6, 92.4, 87.6, 79.7; HRMS (ESI - TOF) m/z calcd for $\text{C}_{39}\text{H}_{20}\text{N}_8\text{S}+\text{H}$: 633.1604 $[\text{M}+\text{H}]^+$, found 633.1603 $[\text{M} + \text{H}]^+$.

Preparation of BTD 4

To a stirred solution of BTD 2 (0.5 mmol) was added TCNQ (102 mg, 0.5 mmol) under an argon flow at room temperature. The mixture was refluxed at 100 °C for 24 h. The solvent was removed in vacuo, and the product was purified by SiO_2 column chromatography with $\text{DCM}:\text{EtOAc}$ (100:5) as the eluent to yield BTD 3 as a dark colored solid (230 mg, yield: 62%). ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 8.90–8.89 (m, 1H), 8.66–8.64 (m, 1H), 7.97–7.94 (m, 1H), 7.89–7.82 (m, 2H), 7.45–7.27 (m, 9H), 7.22–7.12 (m, 8H), 6.86 (d, J = 7.3, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 167.4, 154.5, 153.8, 152.6, 151.6, 151.1, 150.3, 149.9, 145.2, 139.0, 135.7, 134.9, 134.4, 133.7; 131.8, 131.6, 129.9, 128.3, 126.7, 126.6, 126.2, 125.9, 123.2, 121.3, 118.9, 114.0, 112.4, 111.9, 96.7, 92.0, 87.6, 75.2; HRMS (ESI-TOF) m/z calcd for $\text{C}_{45}\text{H}_{24}\text{N}_8\text{S}+\text{H}$: 709.1917 $[\text{M}+\text{H}]^+$, found 709.1931 $[\text{M} + \text{H}]^+$.



Scheme1. Synthesis of BTD2-4

Table S1 Hole and electron mobilities in the active layers processed under different conditions

Active layer	μ_h (cm ² /Vs)	μ_e (cm ² /Vs)	μ_h/μ_e
BTD3:PC₇₁BM^a	5.04x10 ⁻⁶	2.56x10 ⁻⁴	50.2
BTD3:PC₇₁BM^b	5.45x10 ⁻⁵	2.46x10 ⁻⁴	4.52
BTD4:PC₇₁BM^a	6.48x10 ⁻⁶	2.52x10 ⁻⁴	39
BTD4:PC₇₁BM^b	8.4x10 ⁻⁵	2.41x10 ⁻⁴	2.86

^aas cast from CF

^bTSA

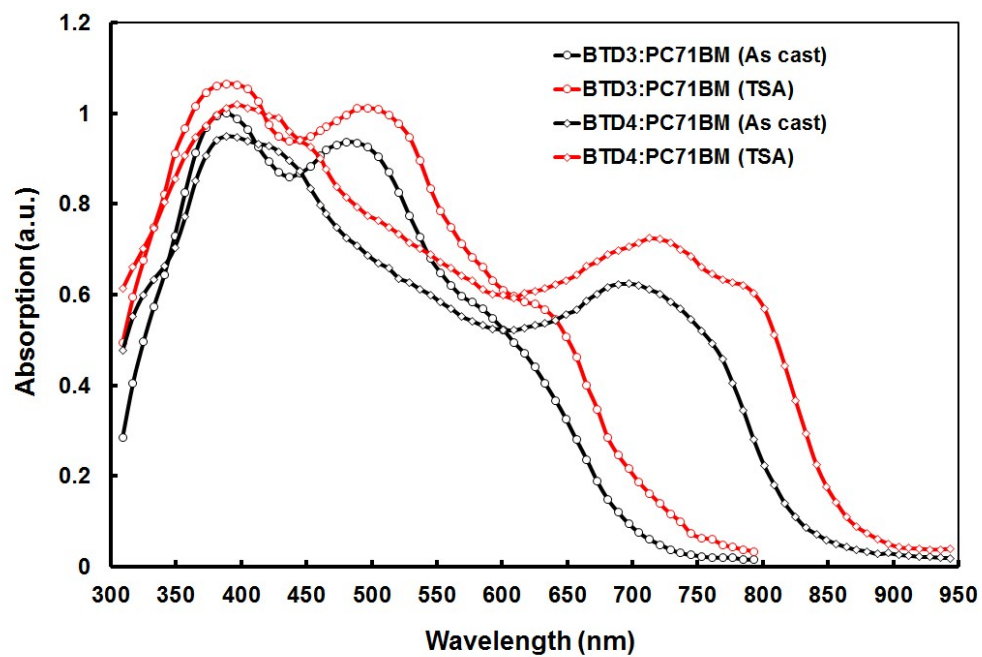


Figure S1 Normalized absorption spectra of **BTD3:PC₇₁BM (1:2)** and (b) **BTD4:PC₇₁BM (1:2)** thin films processed under different conditions

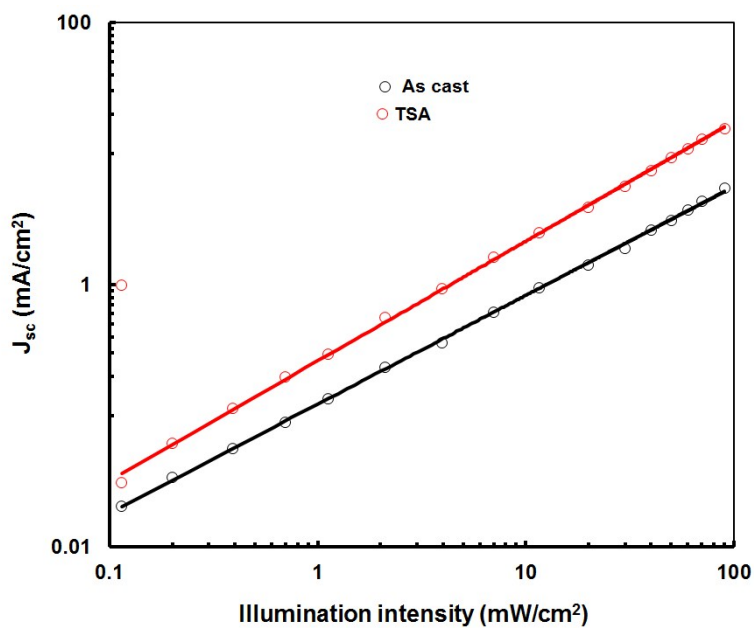


Figure S2 Variation of J_{sc} with illumination intensity for the devices based on **BTD4:PC₇₁BM**

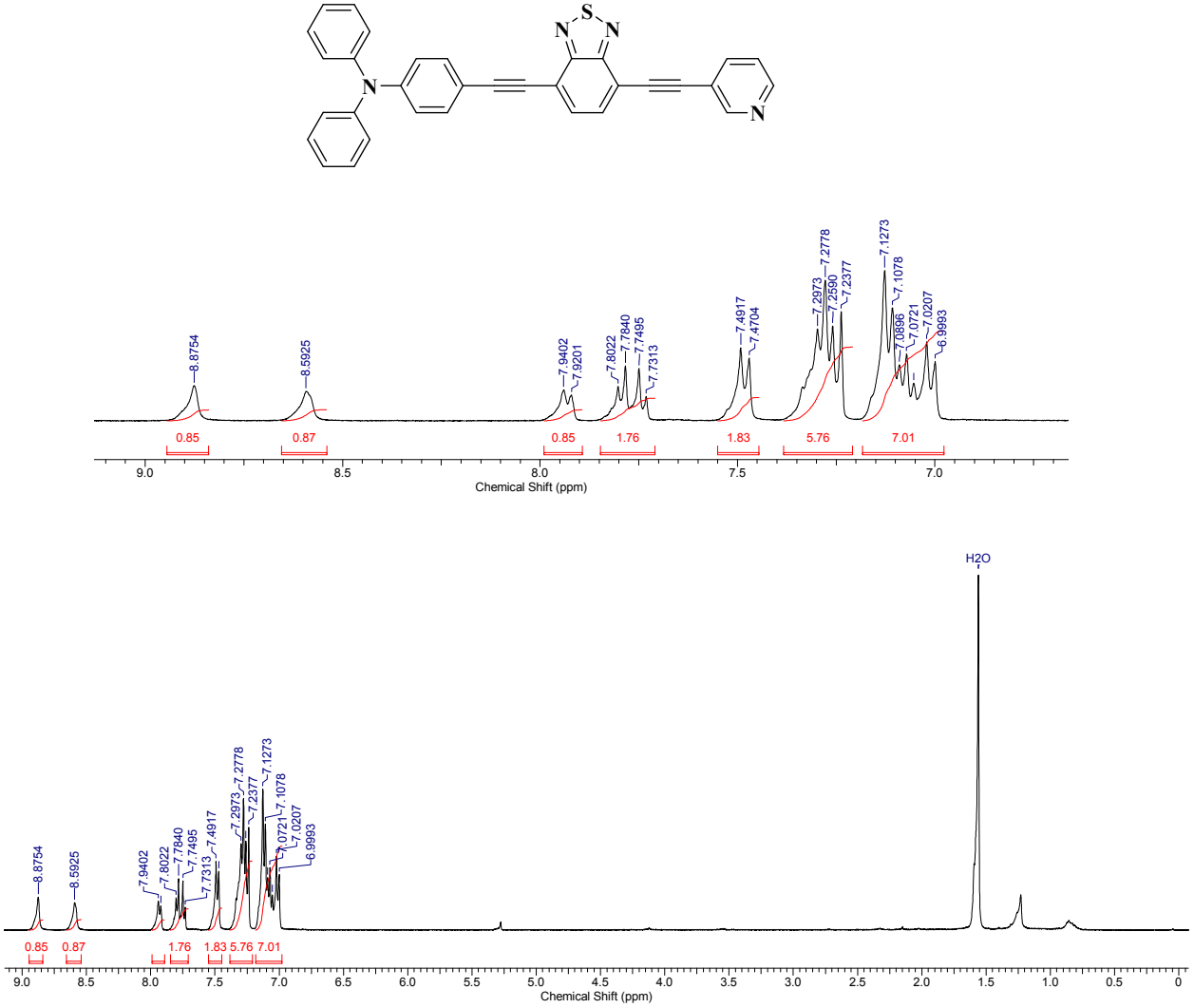
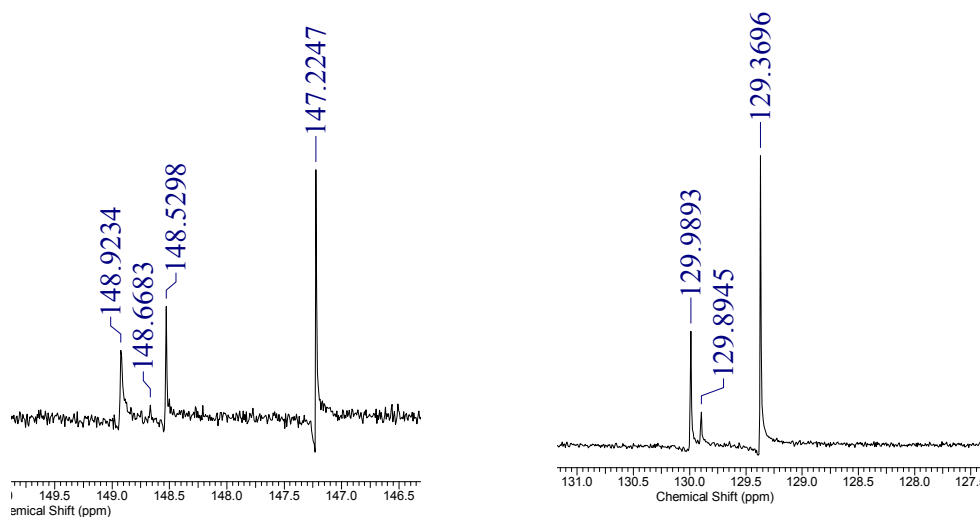
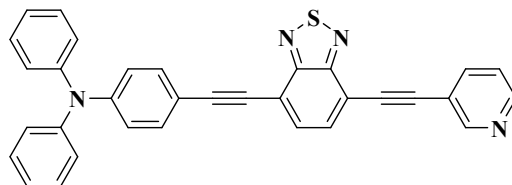


Figure S3 ¹H NMR of BTD2



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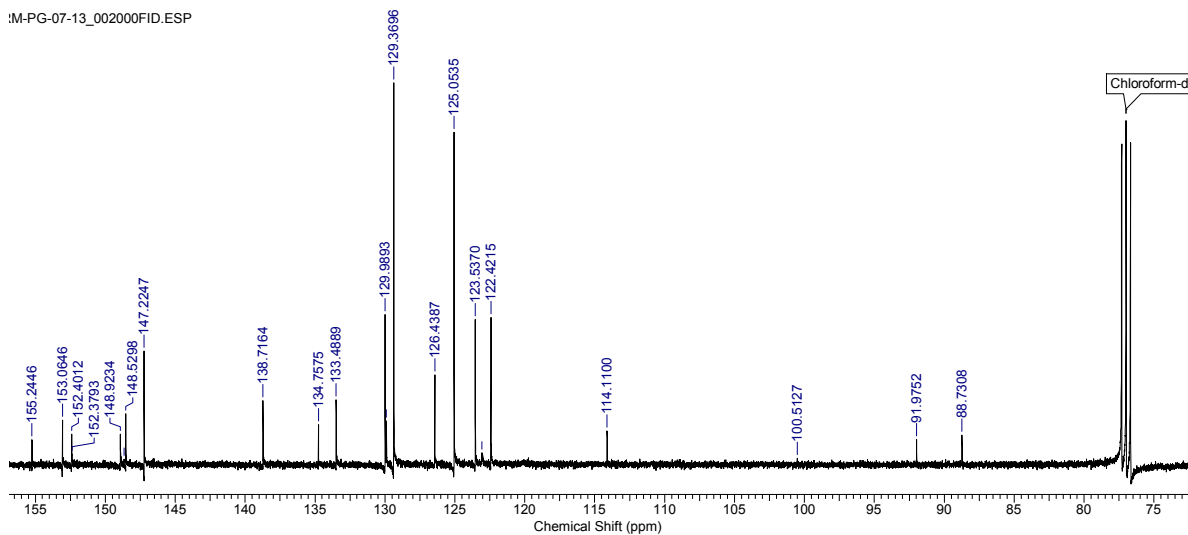


Figure S4 ^{13}C NMR of BTD2

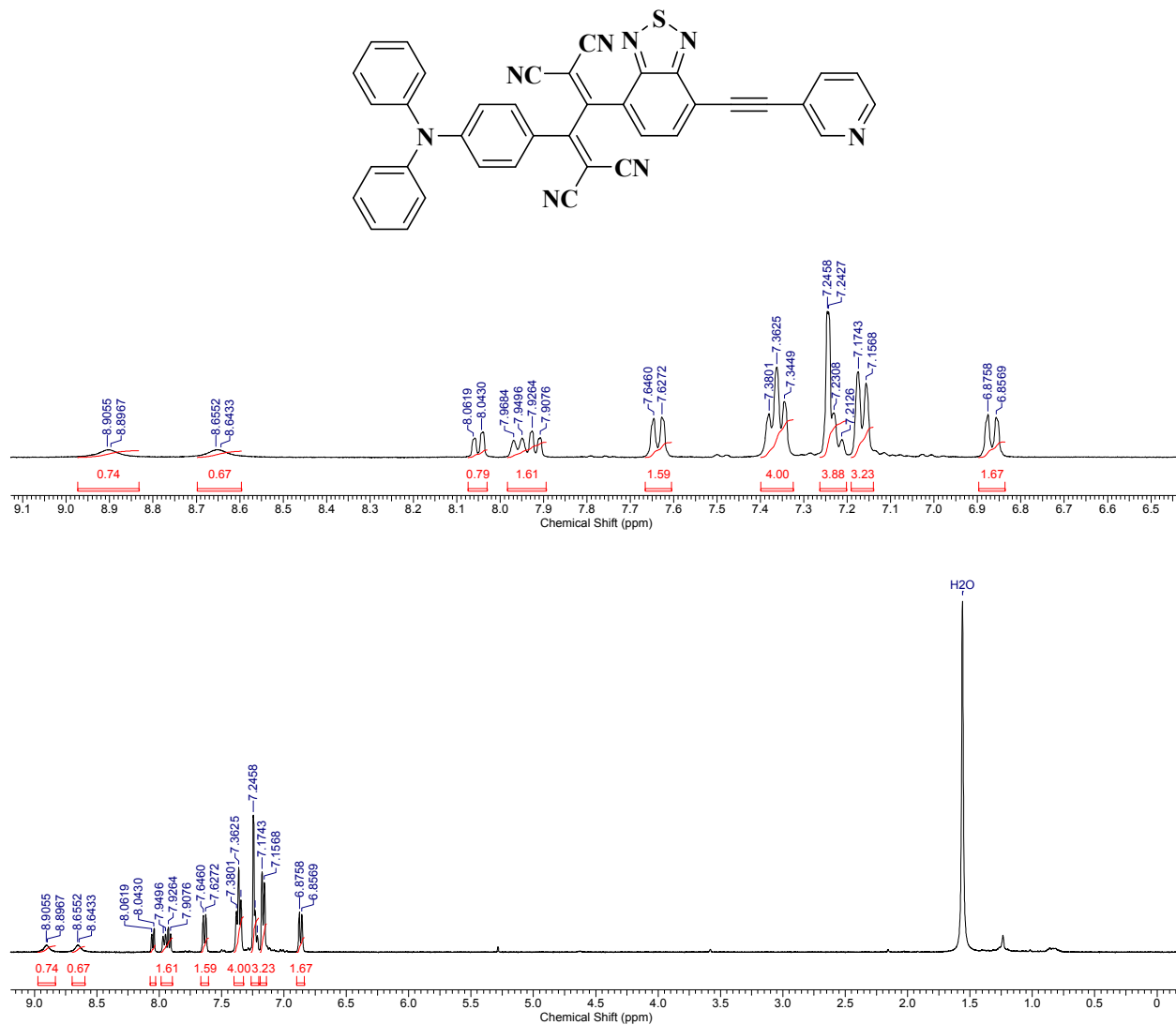
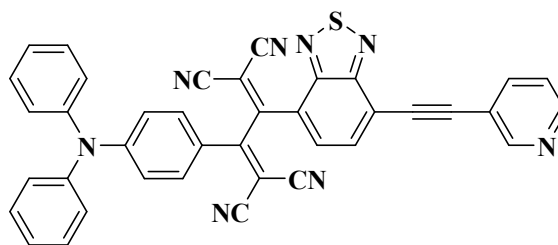
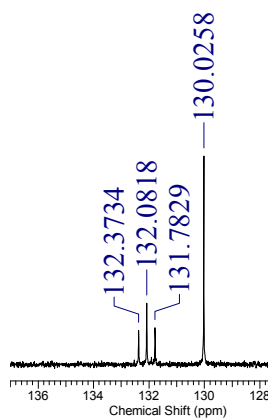


Figure S5 ¹H NMR of BTDD3



Chloroform-d

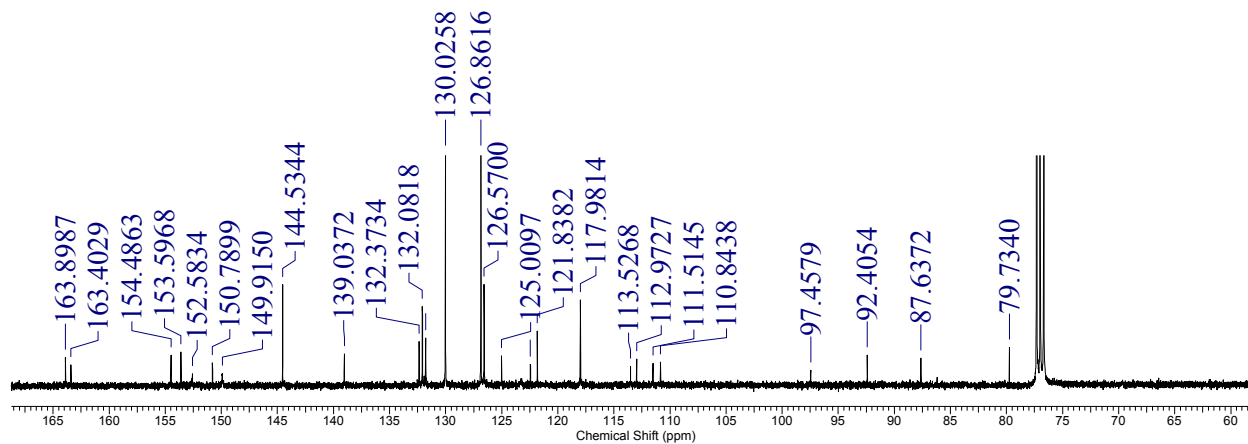
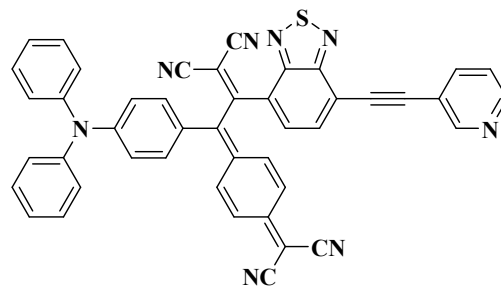
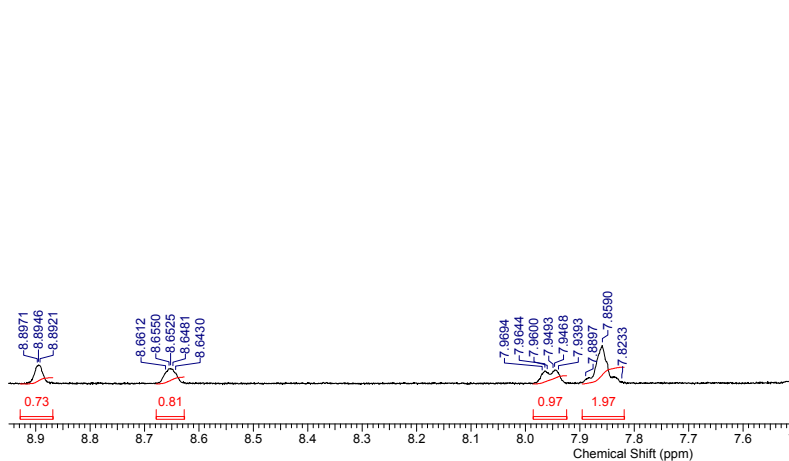


Figure S6 ¹³C NMR of BTDD3



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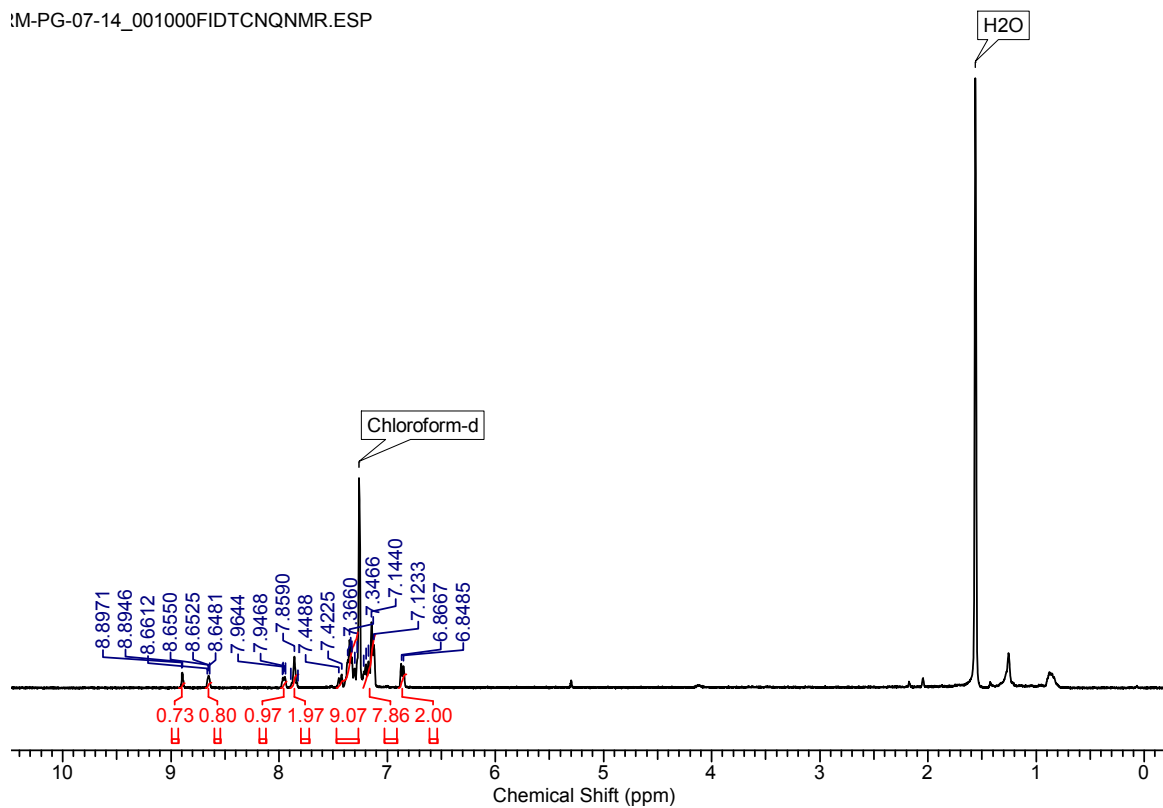


Figure S7 ¹H NMR of BTM4

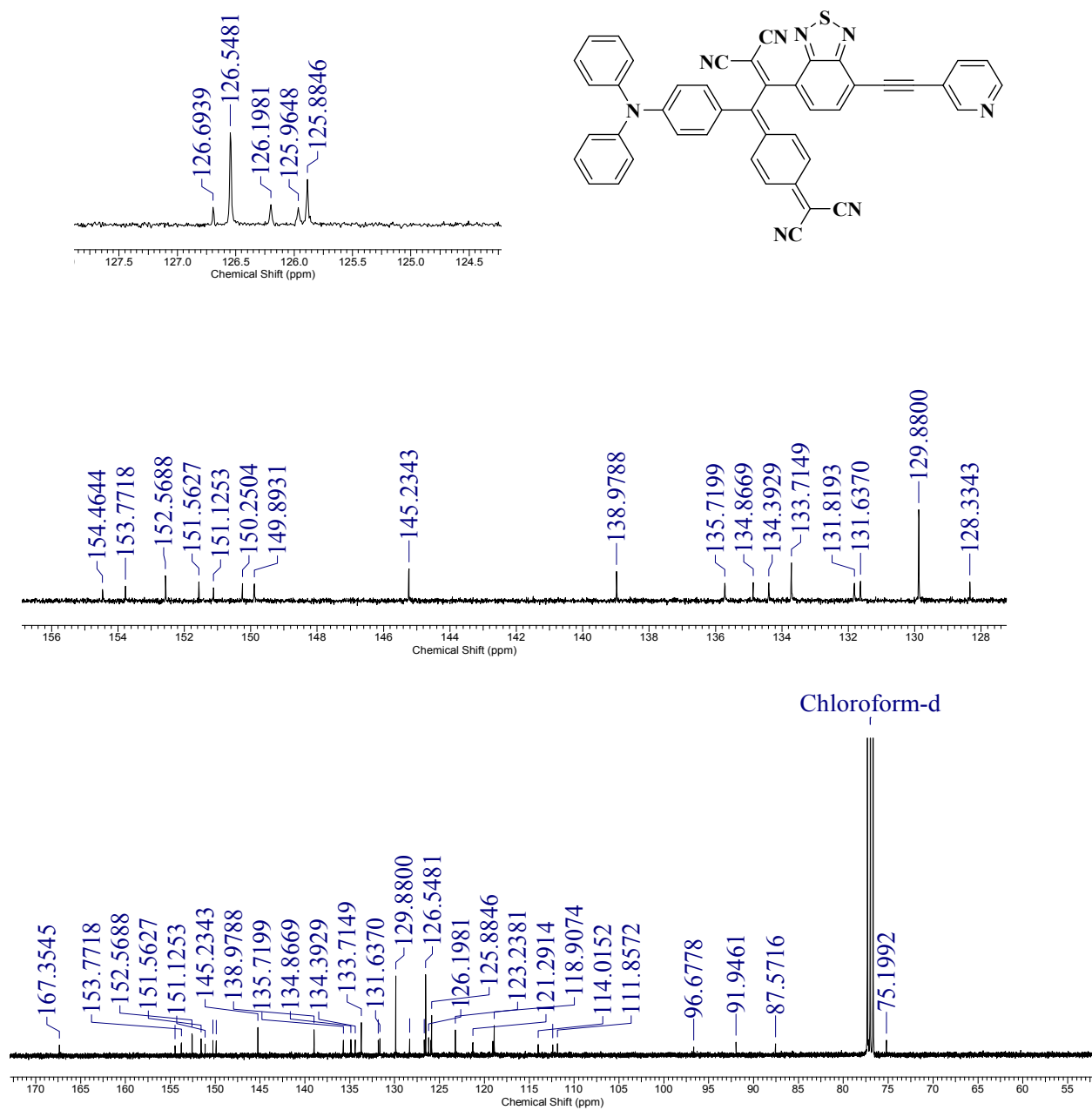


Figure S8 ^{13}C NMR of BT4

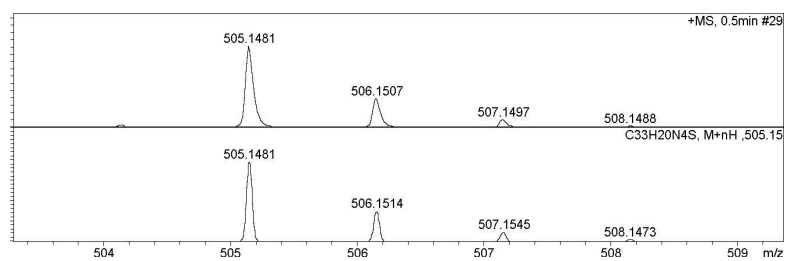


Figure S9 HRMSof BTD2

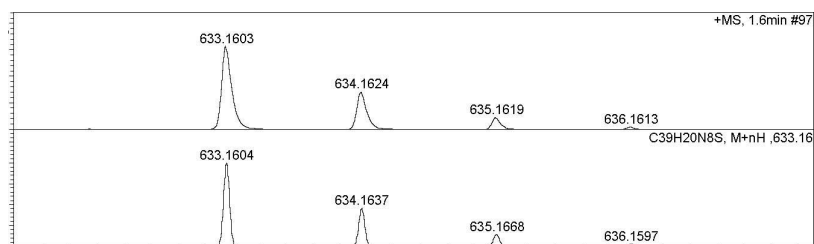


Figure S10 HRMSof BTD3

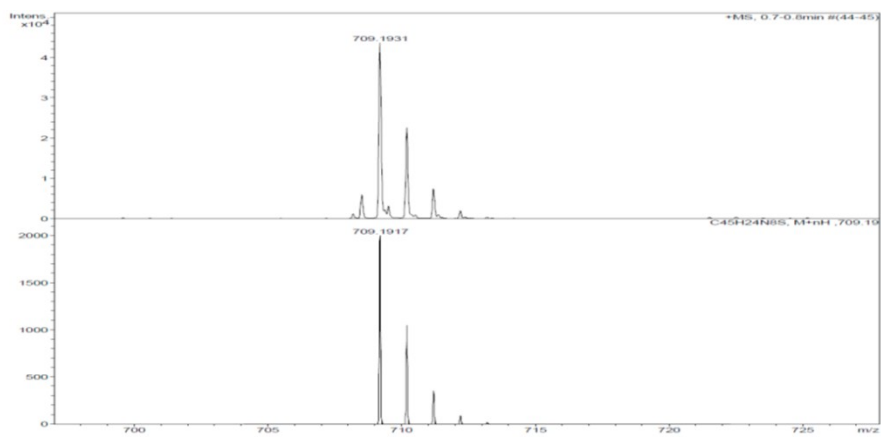


Figure S11 HRMSof BTD4