

## Supporting Information

# Tuning the Optical and Electrochemical Properties of Conjugated *all*-Thiophene Dendrimers via Core Functionalization with Benzothiadiazole Unit

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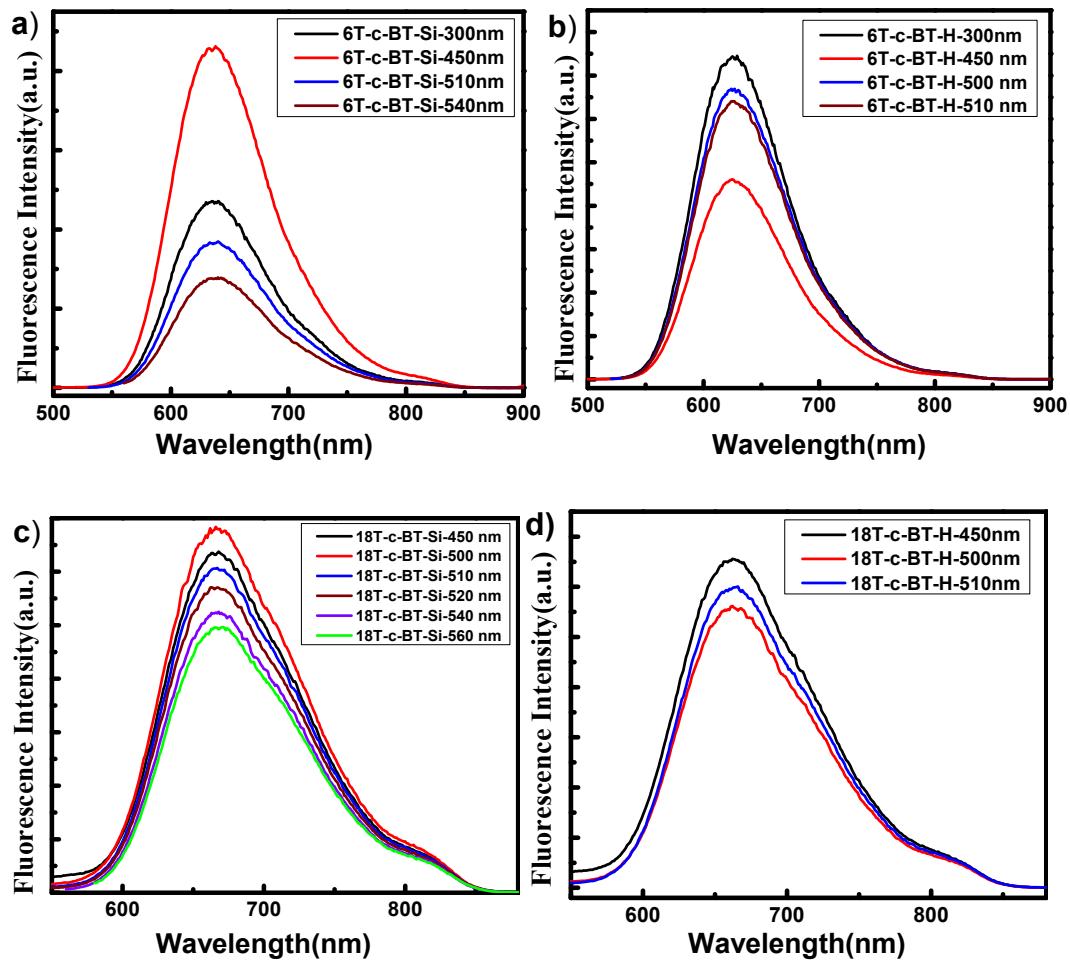


Figure S1. Emission spectra of DOT-c-BTs measured at different excitation wavelengths.

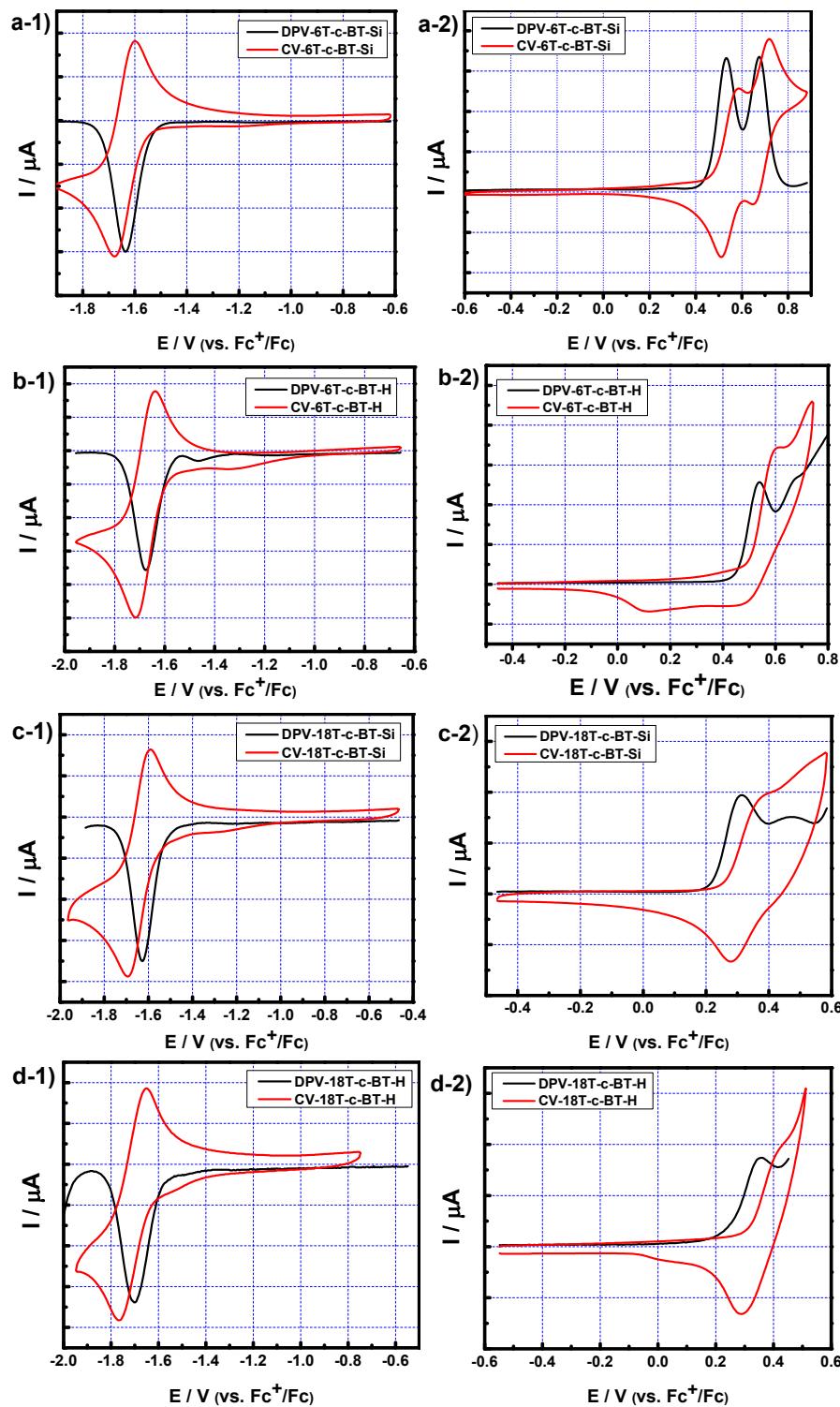


Figure S2. a, b, c) CV and DPV of 6T-c-BT-Si, 6T-c-BT-H, 18T-c-BT-Si at  $1 \times 10^{-3}$  mol·L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> TBAPF<sub>6</sub>(0.1 M), room temperature, V = 100 mV·S<sup>-1</sup>; d) CV and DPV of 18T-c-BT-H at  $1 \times 10^{-3}$  mol·L<sup>-1</sup> in o-dichlorobenzene, room temperature, TBAPF<sub>6</sub>(0.1 M), V = 100 mV·S<sup>-1</sup>.

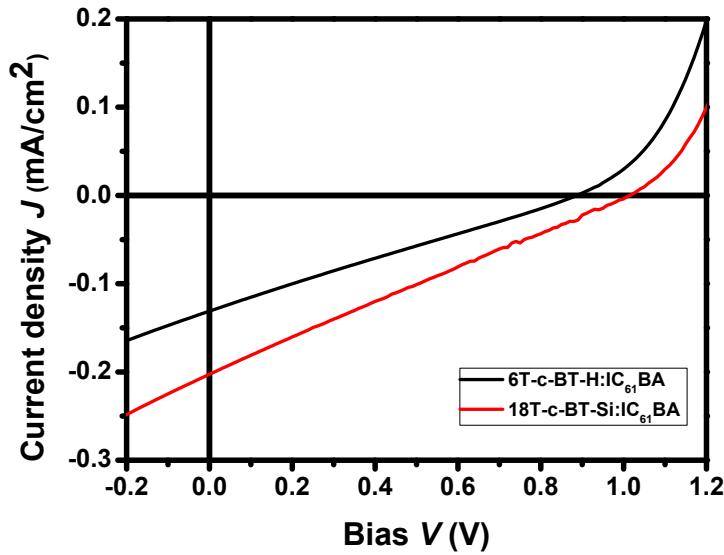


Figure S3.  $J$ - $V$  curves of the optimized **DOT-c-BT**: IC<sub>61</sub>BA based BHJ solar cells illuminated under standard AM1.5G conditions (100 mW cm<sup>-2</sup>)

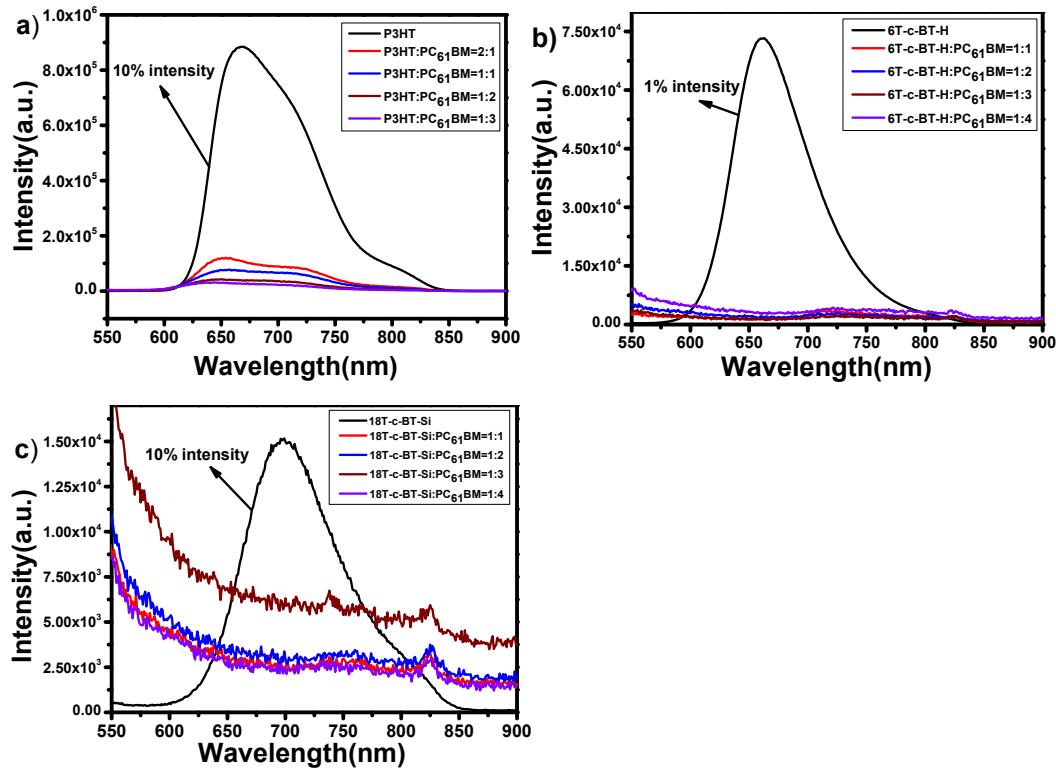
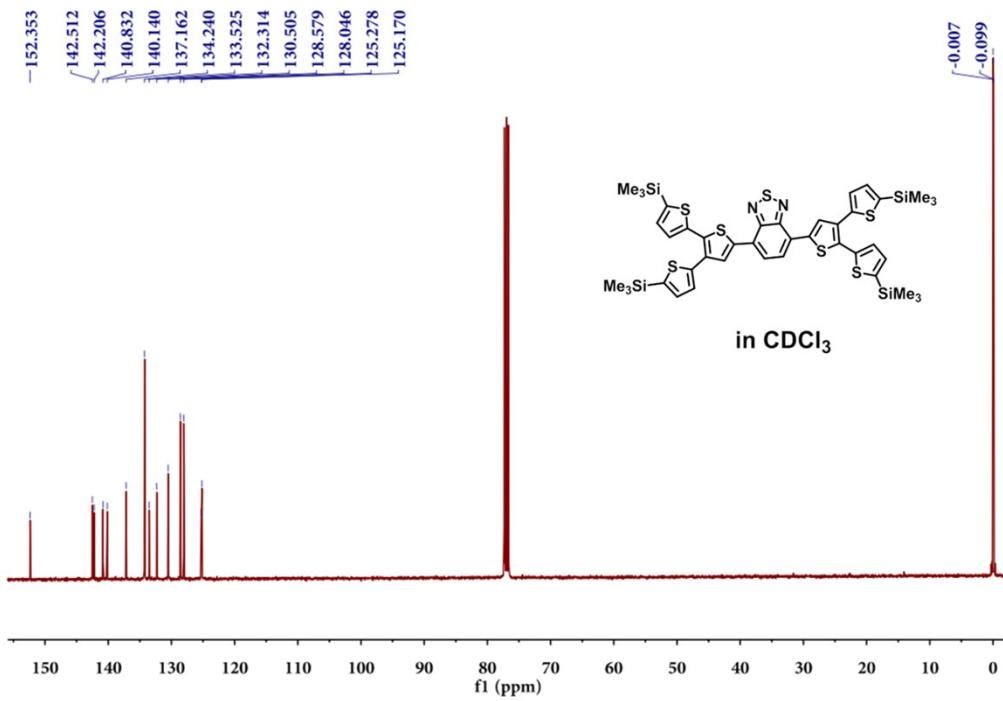
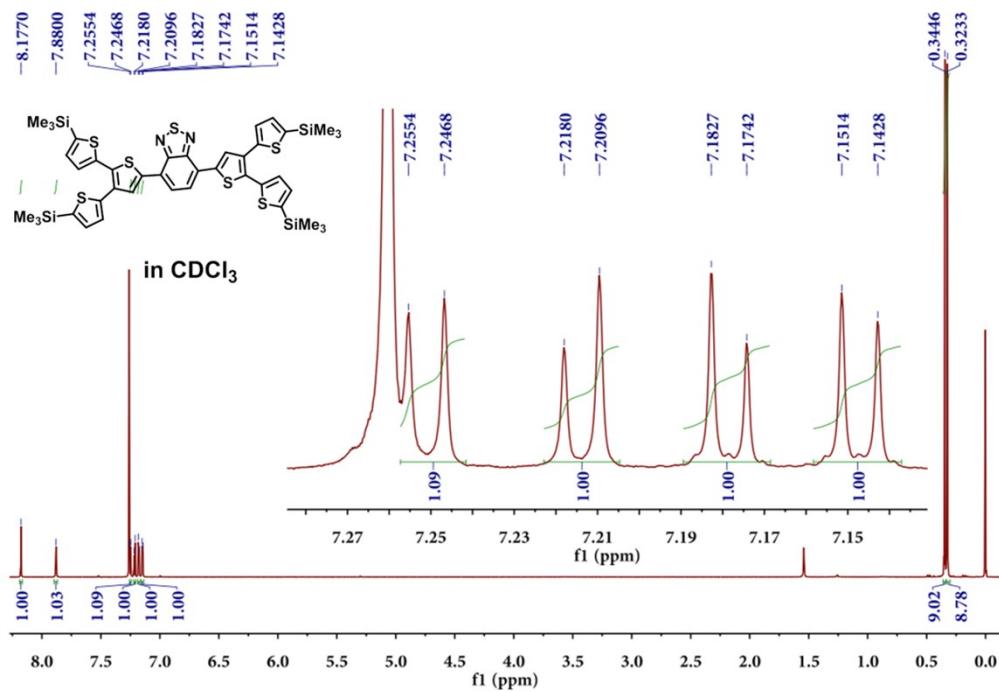
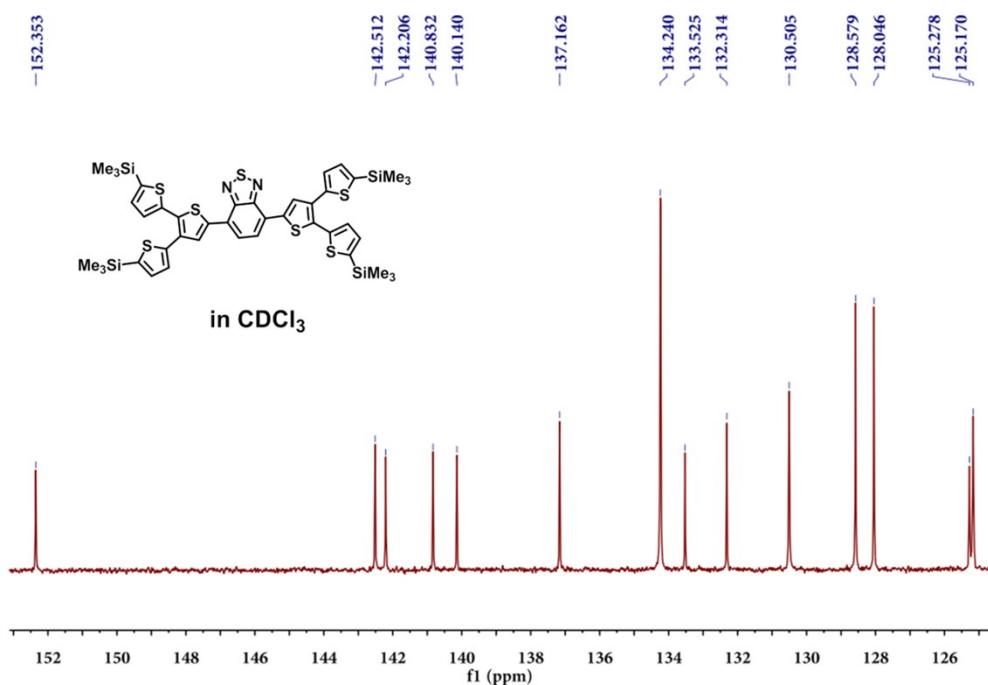


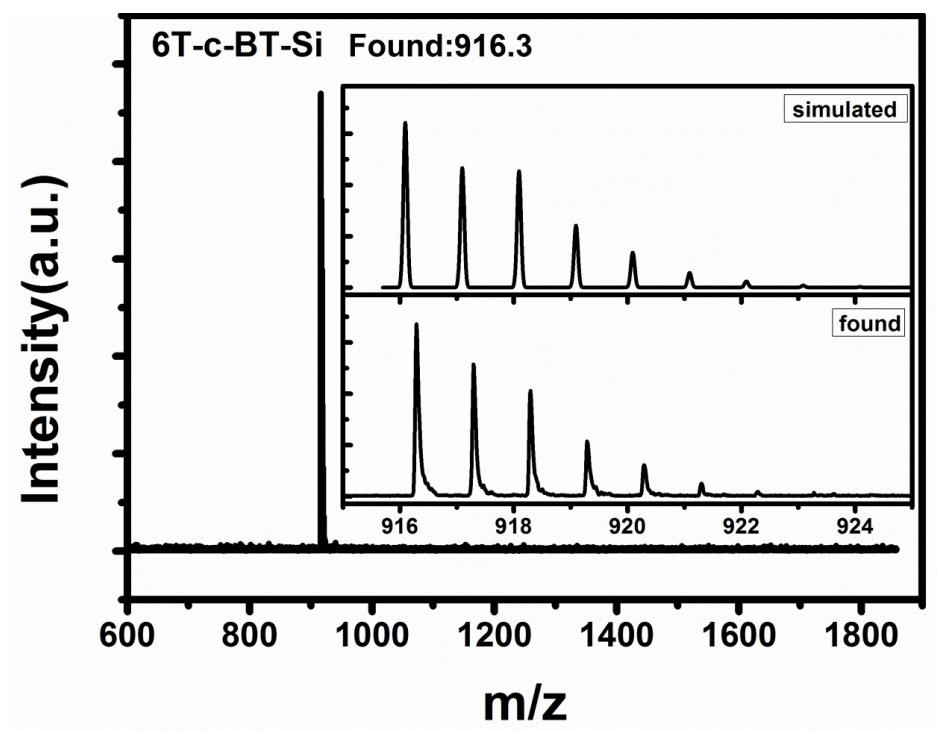
Figure S4. a) Emission spectrum of pure P3HT, and in the presence of PC<sub>61</sub>BM at different P3HT:PC<sub>61</sub>BM weight ratio; b) Emission spectrum of pure 6T-c-BT-H, and in the presence of PC<sub>61</sub>BM at different 6T-c-BT-H:PC<sub>61</sub>BM weight ratio; b) Emission spectrum of pure 18T-c-BT-Si, and in the presence of PC<sub>61</sub>BM at different 18T-c-BT-Si:PC<sub>61</sub>BM weight ratio.

## Experimental Section

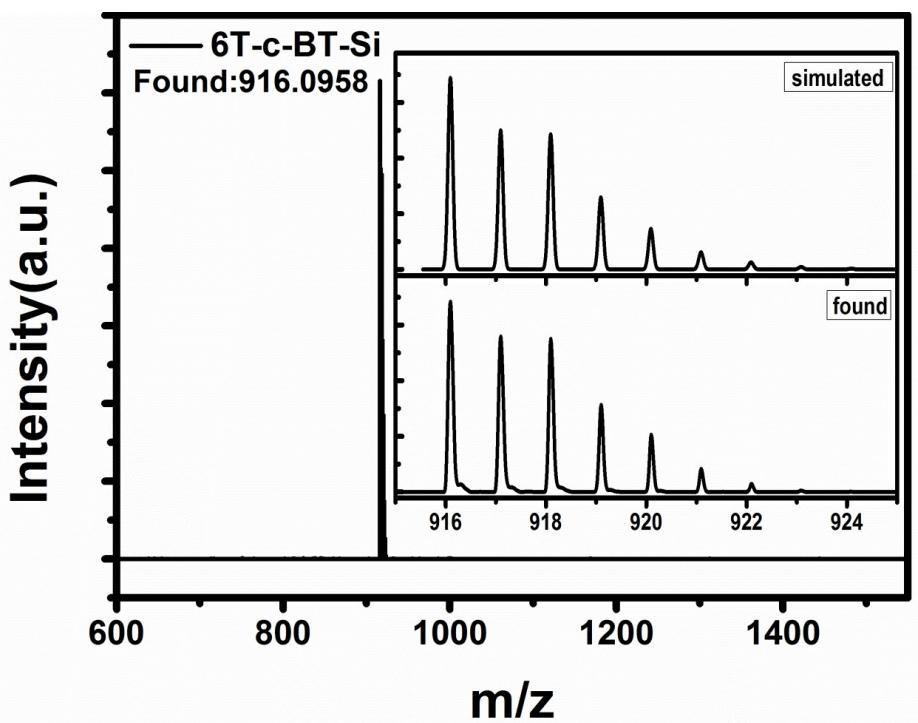




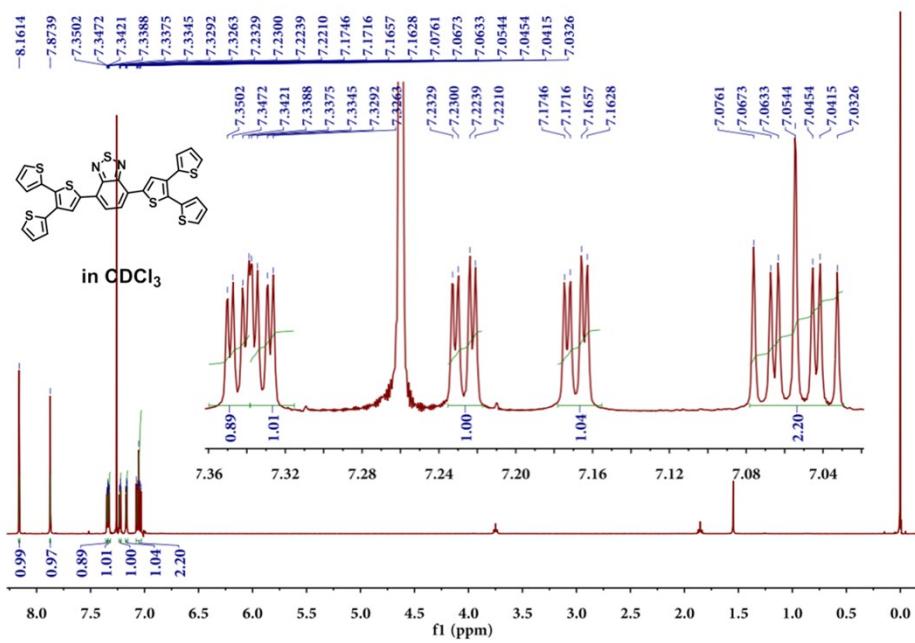
$^{13}\text{C}$  NMR of **6T-c-BT-Si**



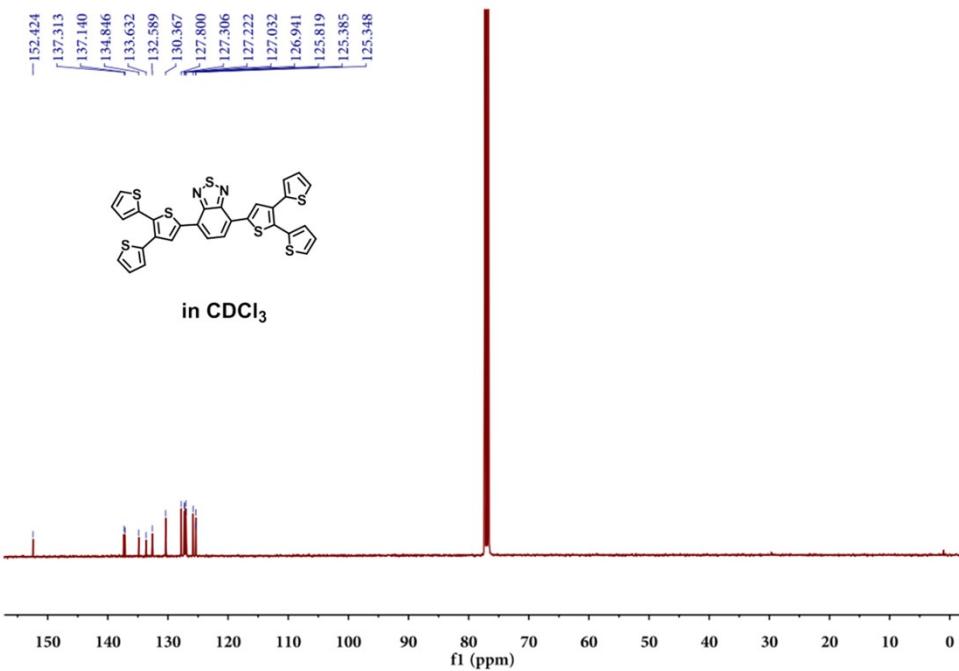
MALDI-TOF MS of **6T-c-BT-Si**



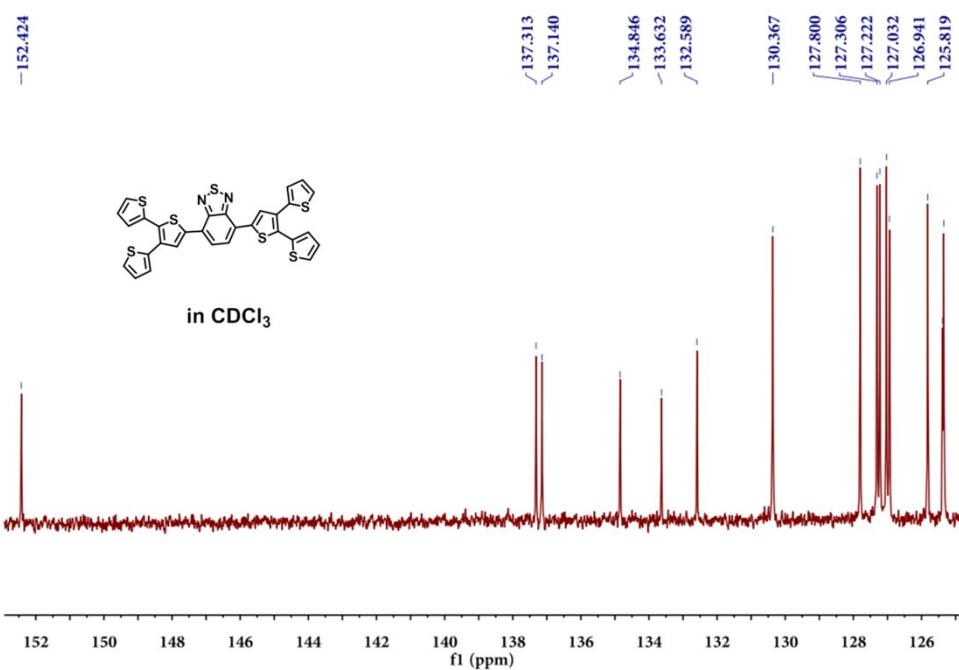
HR MS of 6T-c-BT-Si



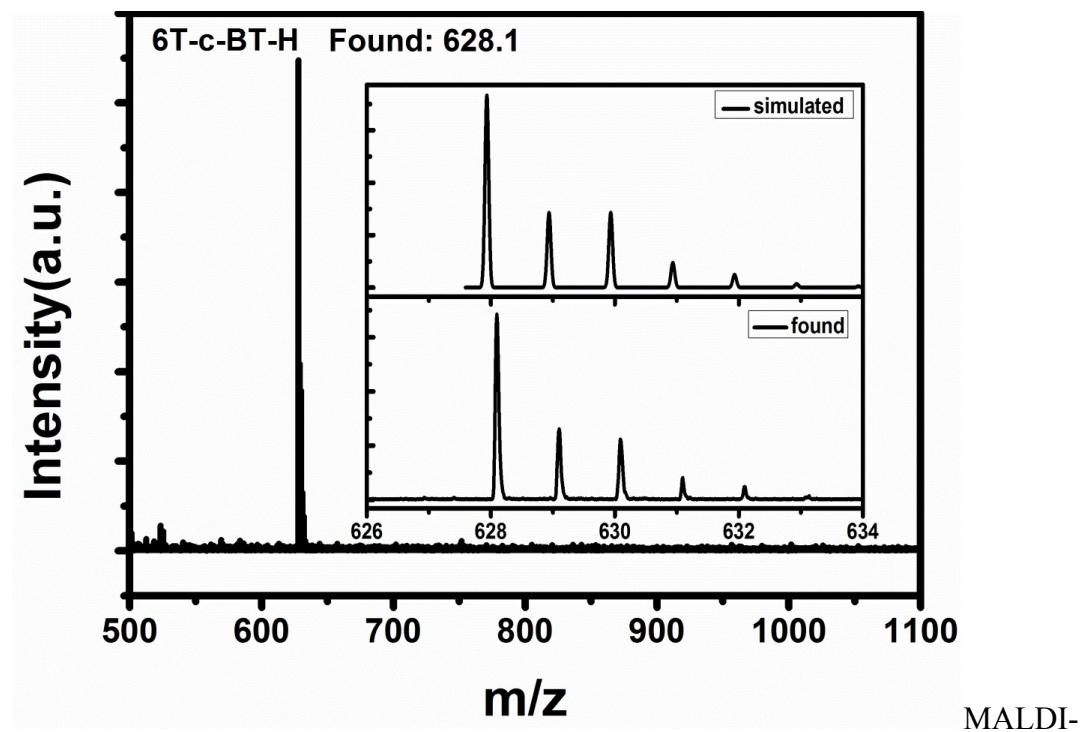
$^1\text{H}$  NMR of 6T-c-BT-H



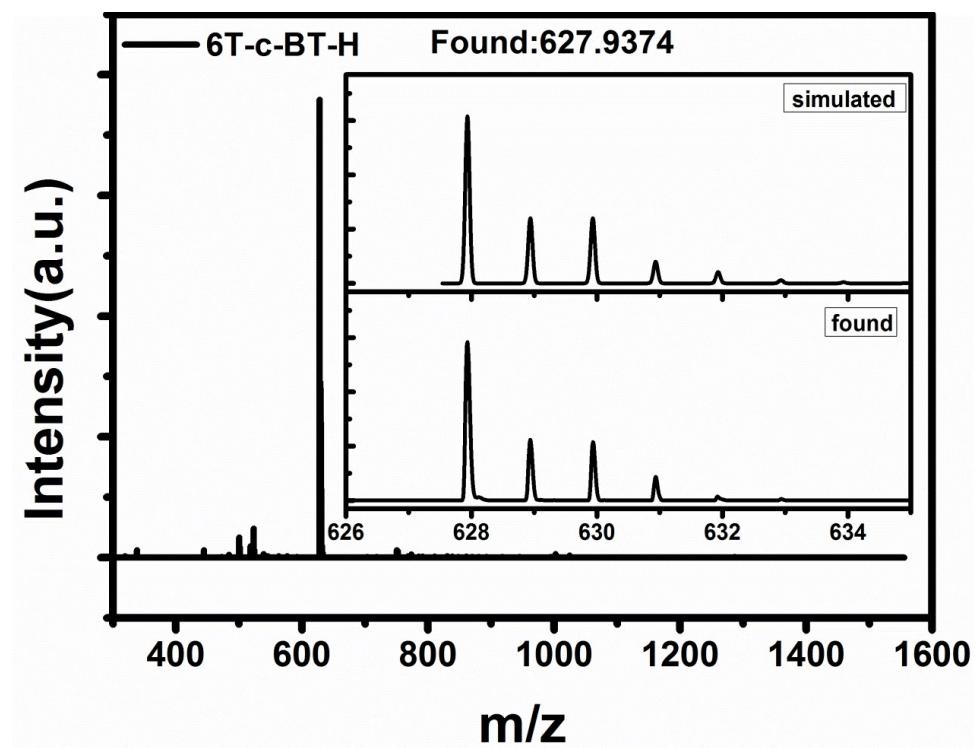
<sup>13</sup>C NMR of **6T-c-BT-H**



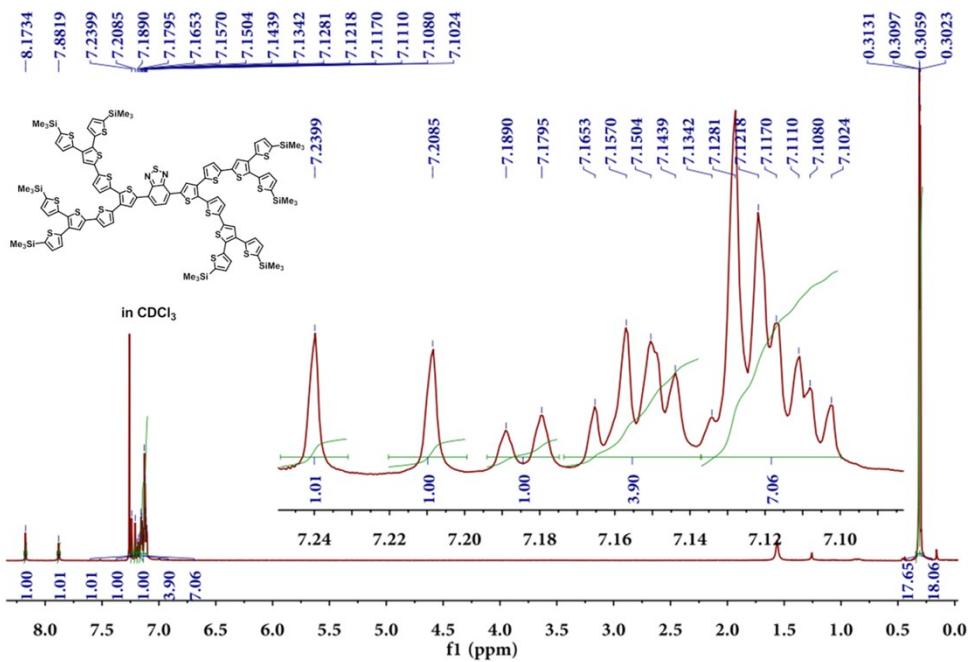
<sup>13</sup>C NMR of **6T-c-BT-H**



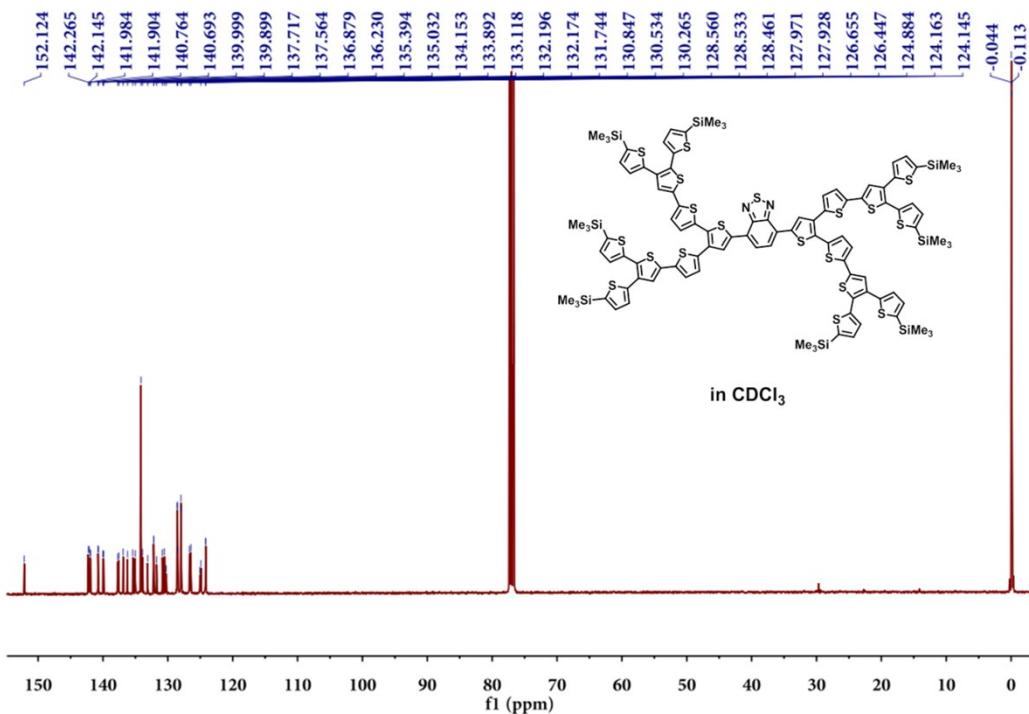
TOF MS of 6T-c-BT-H



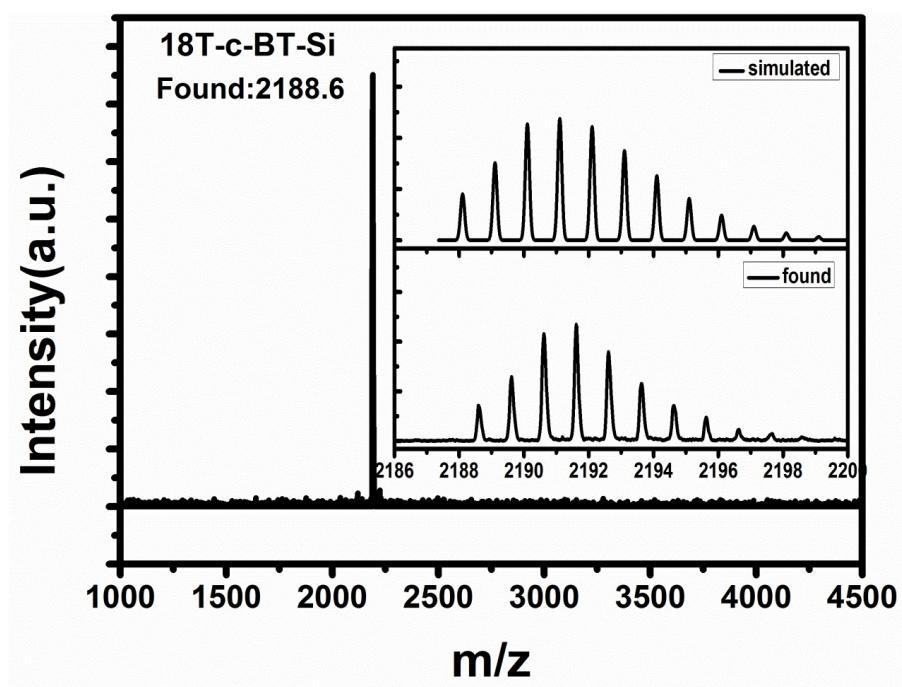
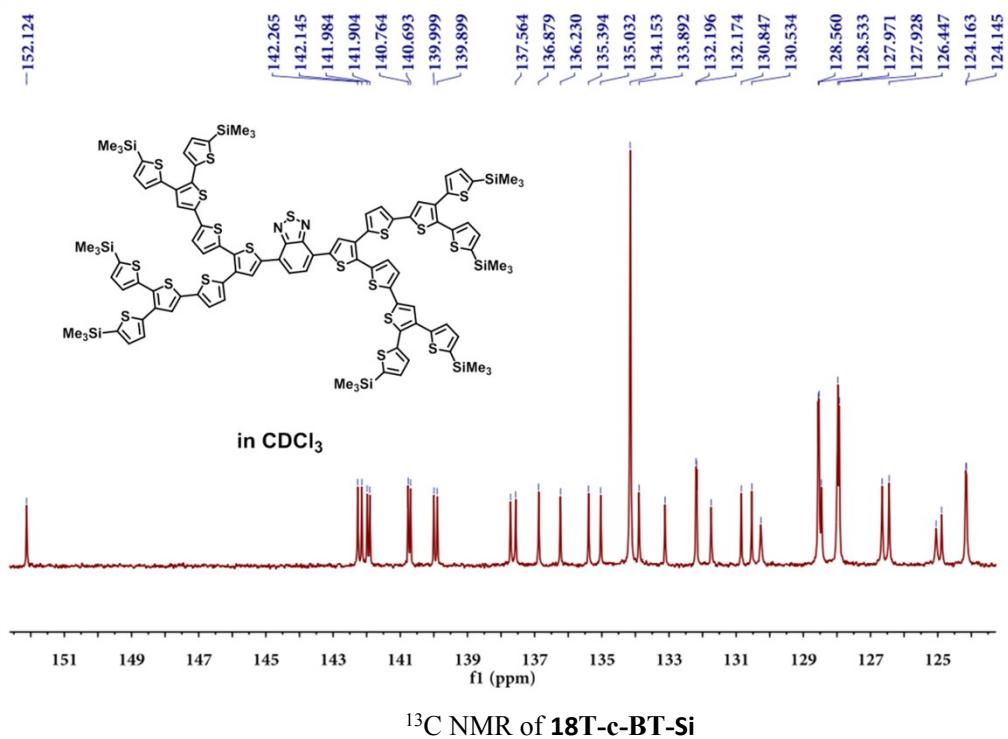
HR MS of 6T-c-BT-Si

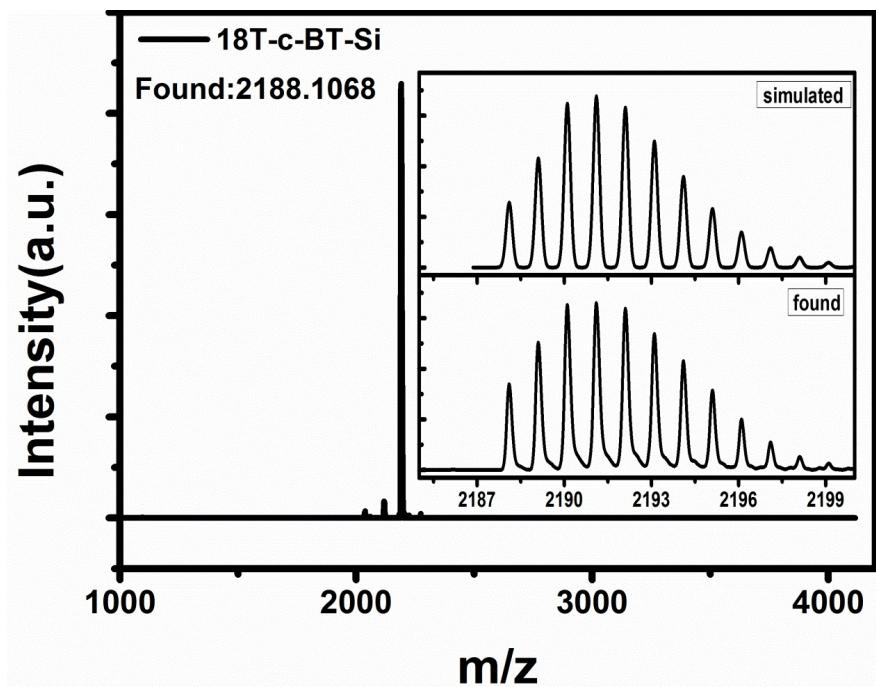


<sup>1</sup>H NMR of **18T-c-BT-Si**

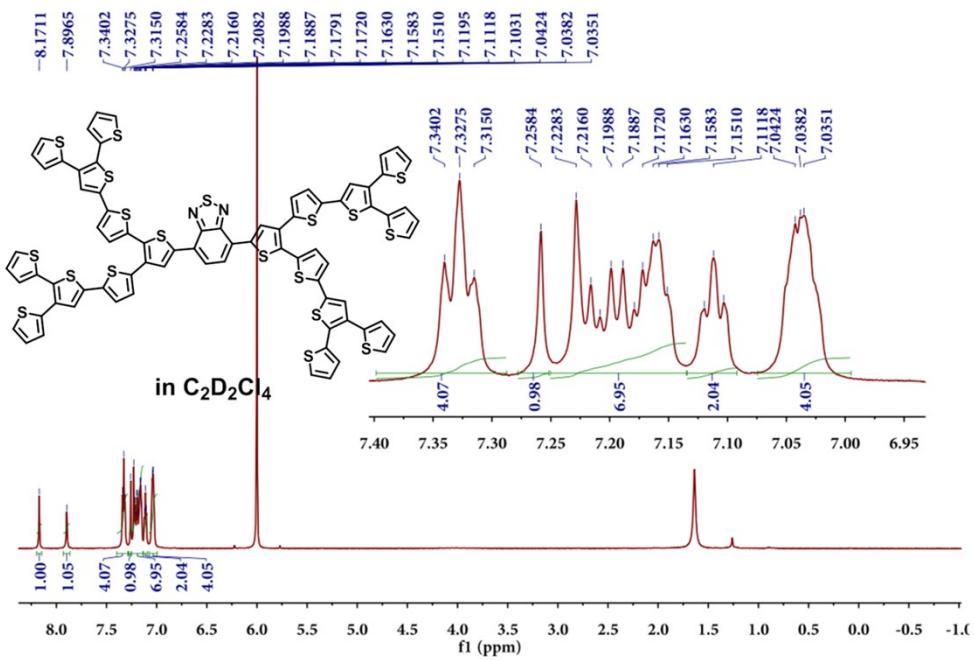


<sup>13</sup>C NMR of **18T-c-BT-Si**

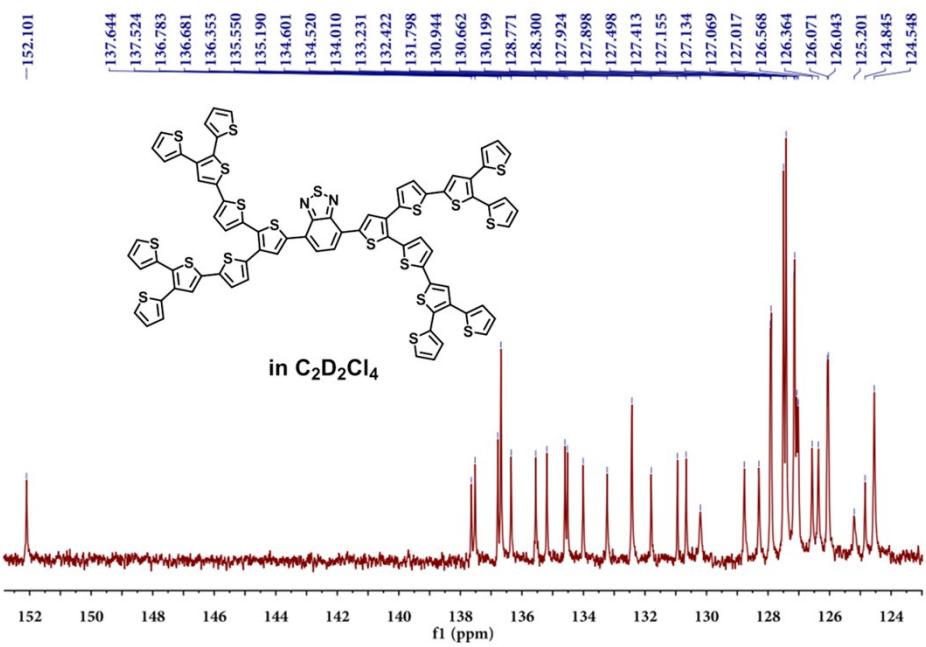
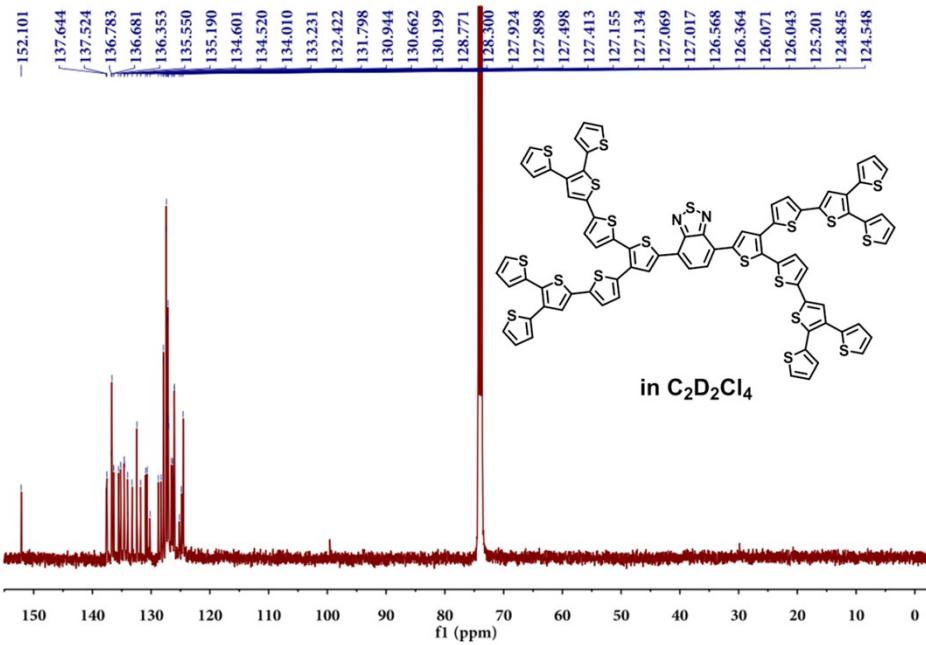




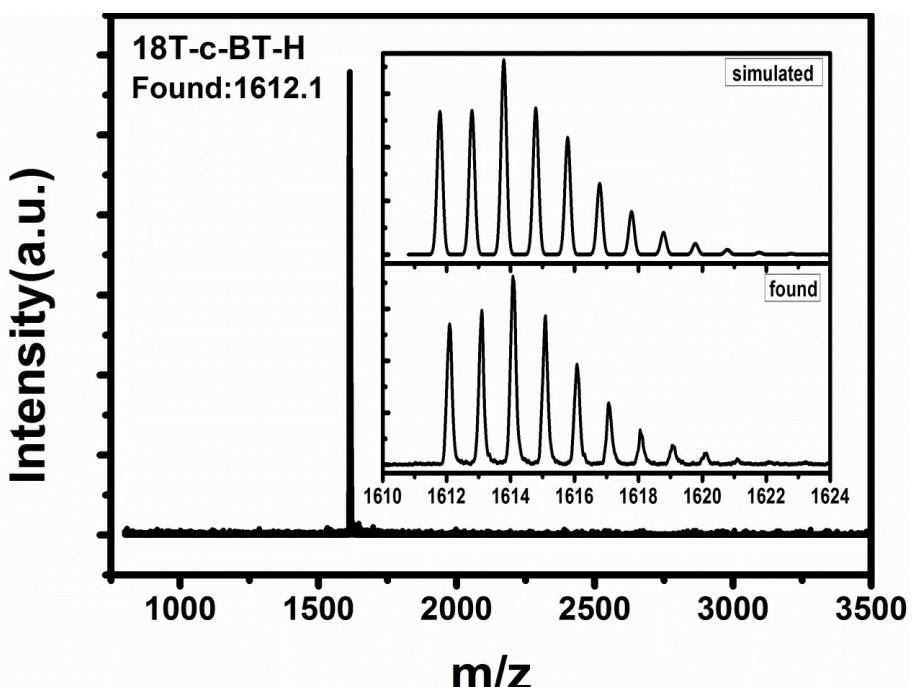
HR MS of 18T-c-BT-Si



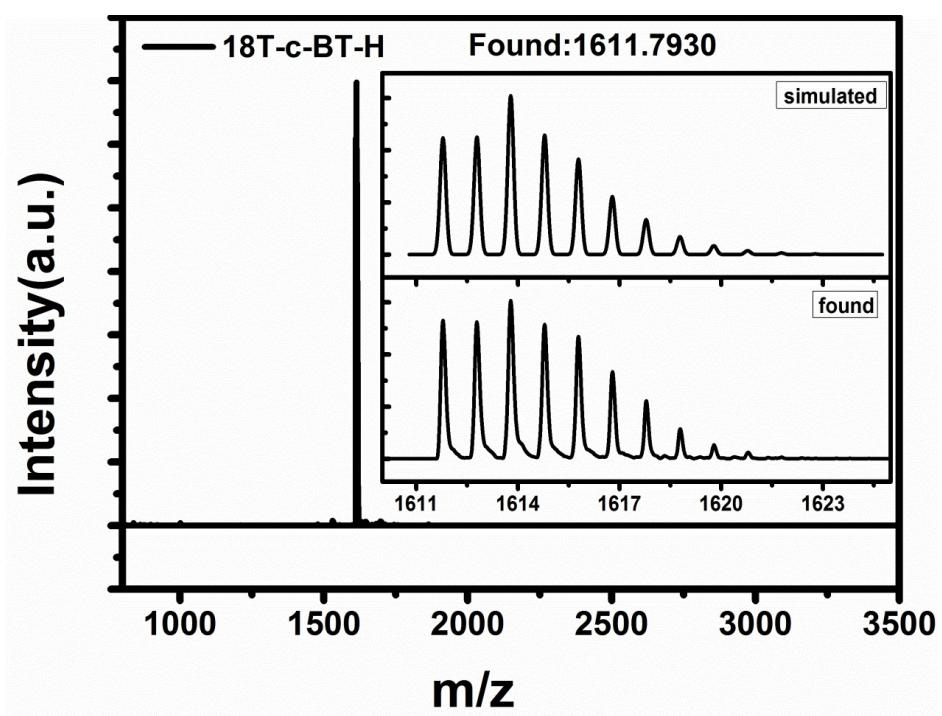
$^1H$  NMR of 18T-c-BT-H



<sup>13</sup>C NMR of **18T-c-BT-H**



MALDI-TOF MS of 18T-c-BT-H



HR MS of 18T-c-BT-H