Electronic Supplementary Information (ESI)

Substitution effect on photochromic properties of benzo[*b*]thiophene-1,1-dioxide based diarylethenes

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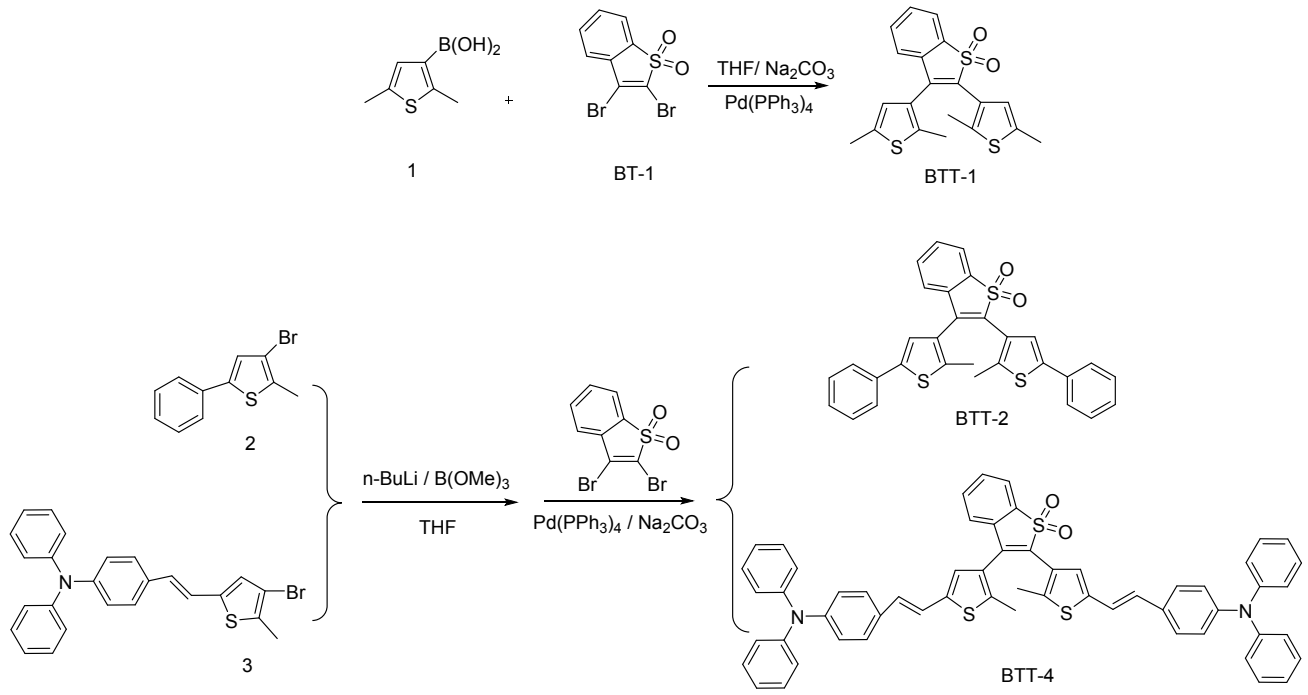


Scheme S1 Synthetic routes for the photochromic compounds BTT-1, BTT-2, and BTT-4

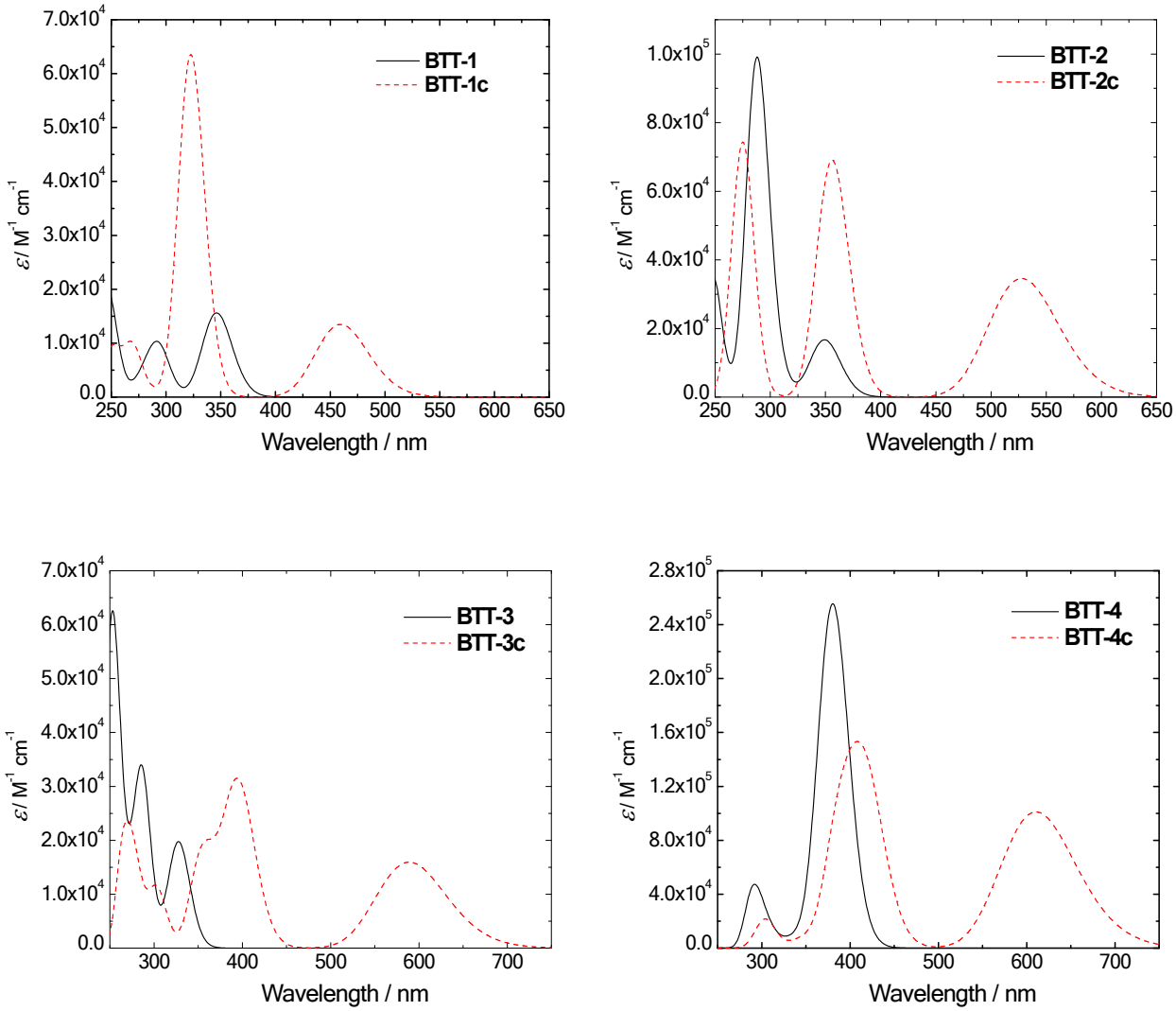


Fig. S1 Simulated absorption spectra of the photochromic molecules BTT-1 to BTT-4: λ_{max} =250, 458 nm for BTT-1 and BTT-1c; λ_{max} =288, 529 nm for BTT-2 and BTT-2c; λ_{max} =253, 592 nm for BTT-3 and BTT-3c; λ_{max} =378, 611 nm for BTT-4 and BTT-4c.

Table S1 The frontier orbitals of compounds BTT-1 to BTT-4 (isovalue = 0.04 a.u.)

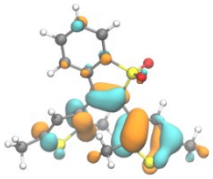
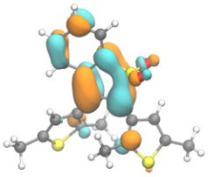
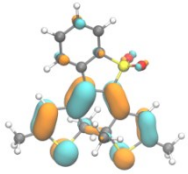
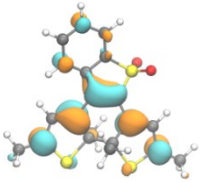
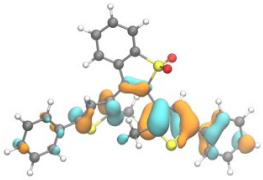
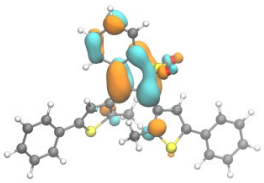
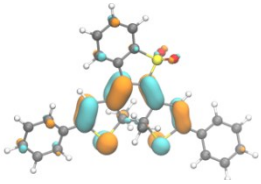
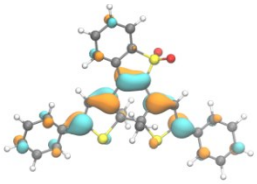
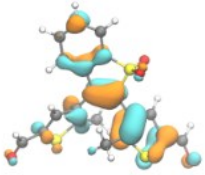
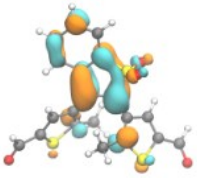
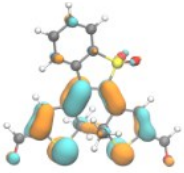
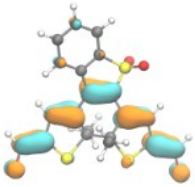
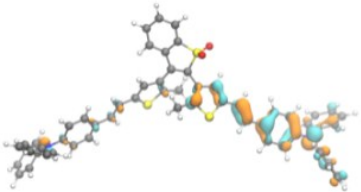
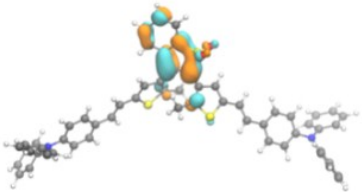
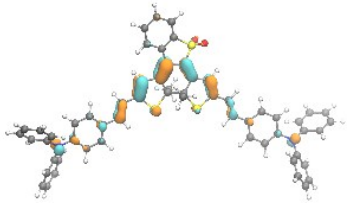
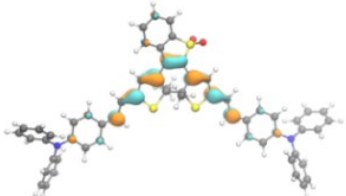
	HOMO	LUMO
BTT-1		
BTT-1c		
BTT-2		
BTT-2c		
BTT-3		
BTT-3c		
BTT-4		
BTT-4c		

Table S2 Computed self-consistent field energies for the photochromic molecules.

Compound	open-ring isomer	closed-ring isomer	energy difference
BTT-1	-2118.05608805 a.u.	-2118.04609003 a.u.	–26.2 kJ/mol
BTT-2	-2501.58660643 a.u.	-2501.57554288 a.u.	–29.0 kJ/mol
BTT-3	-2266.06466067 a.u.	-2266.04126384 a.u.	**–61.4 kJ/mol**
BTT-4	-3691.46746019 a.u.	-3691.46254823 a.u.	–22.9 kJ/mol

Table S3 Crystal data of BTT-1, BTT-2, and BTT-3

	Compound		
	BTT-1	BTT-2	BTT-3
Formula	$C_{20}H_{18}O_2S_3$	$C_{30}H_{22}O_2S_3$	$C_{20}H_{14}O_4S_3$
Formula weight	386.55	510.66	414.49
Temperature	293 K	573 k	166 K
Crystal system	prismatic	orthorhombic	orthorhombic
Space group	P2(1)/n	P212121	C2/c
Unit cell dimension a (Å)	9.2440(11)	9.973(4)	19.5864(18)
b (Å)	21.127(3)	12.164(4)	12.1795(11)
c (Å)	10.5457(12)	21.090(7)	15.8503(15)
α (°)	90.00	90.00	90.00
β (°)	114.609(2)	90.00	93.133(2)
γ (°)	90.00	90.00	90.00
Volume	1871.3(4)	2558.3(16)	3775.5(6)
z	4	4	8
Density calc. (g/cm^3)	1.372	1.326	1.458
Goodness of fit on p^2	0.973	1.016	1.024
Final R1	0.0596	0.0419(2991)	0.0378(3365)
wR2(I>*2S(I)*)	0.1395(3462)	0.0906(4187)	0.1039(4295)
R1 (all data)	0.0915	0.0716	0.0527
wR2 (all data)	0.1267	0.0795	0.0953

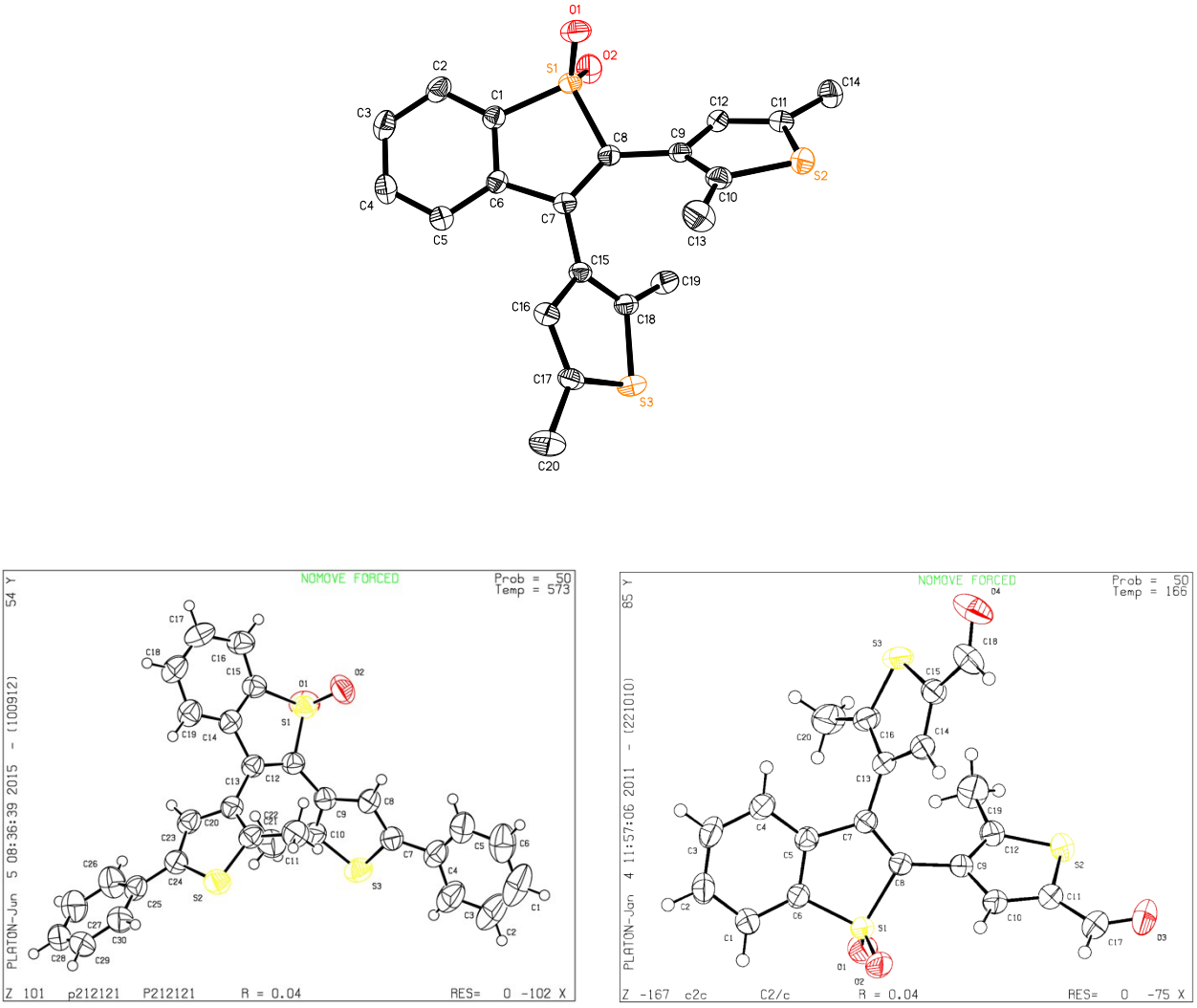


Fig. S2 ORTEP drawings showing 50% probability displacement ellipsoids: (A) BTT-1, (B) BTT-2, and (c) BTT-3.

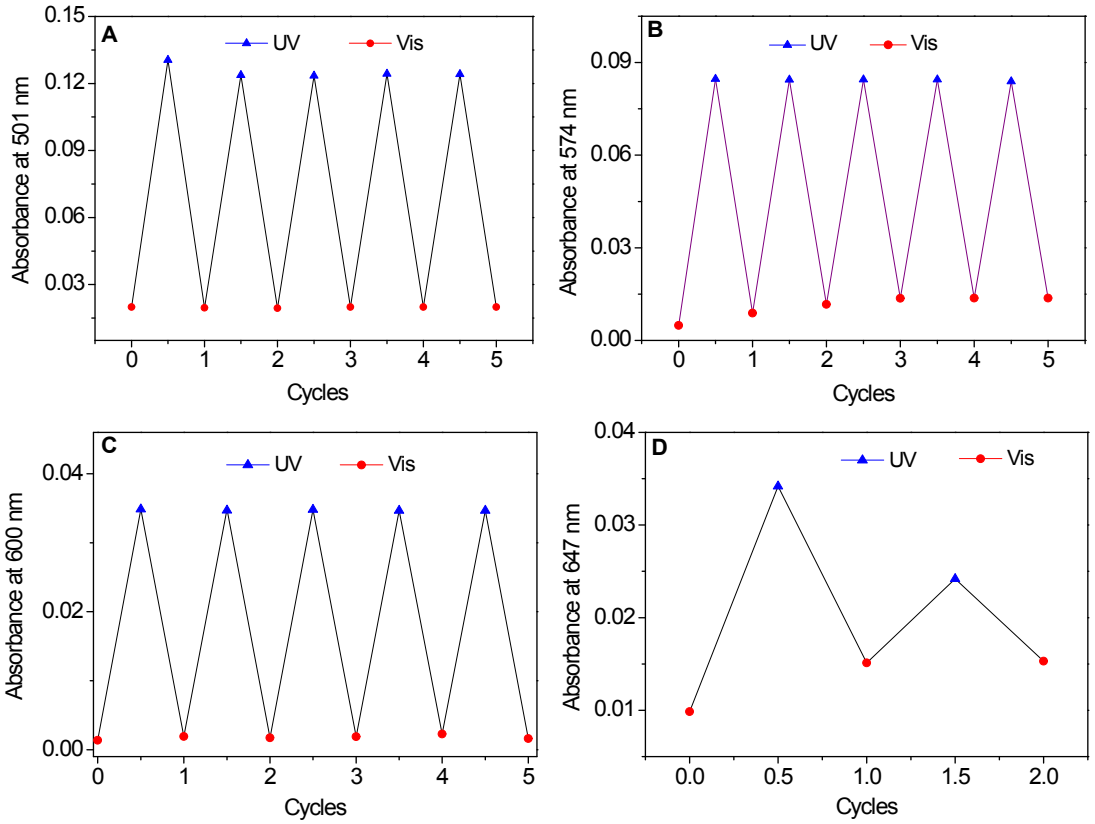


Fig. S3 (A) Changes in the absorbance of PMMA films upon alternative irradiation with UV (365 nm) and visible light (>450 nm) light; (A) PMMA-BTT-1, (B) PMMA-BTT-2, (C) PMMA-BTT-3, and (D) PMMA-BTT-4.

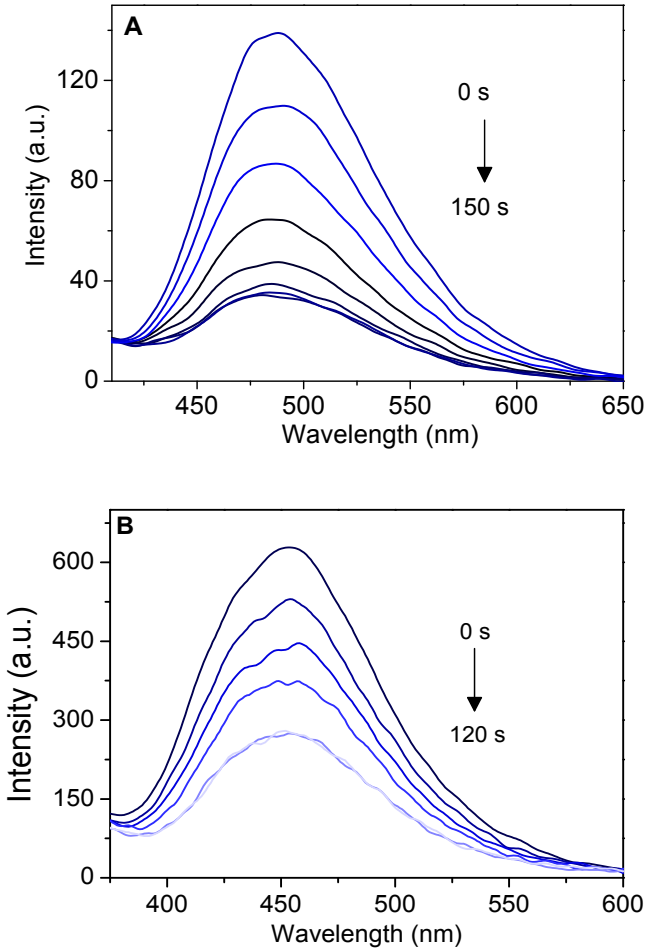


Fig. S4 Fluorescence spectra changes upon UV irradiation at 365 nm with the excitation at the isobestic point in ethyl acetate: (A) BTT-2, 2.15×10^{-5} mol L^{-1} and (B) BTT-3, 2.10×10^{-5} mol L^{-1}

Fig. S5-S16 NMR(^{1}H, ^{13}C) spectra and High resolution mass spectrum of BTT-1 to BTT-4

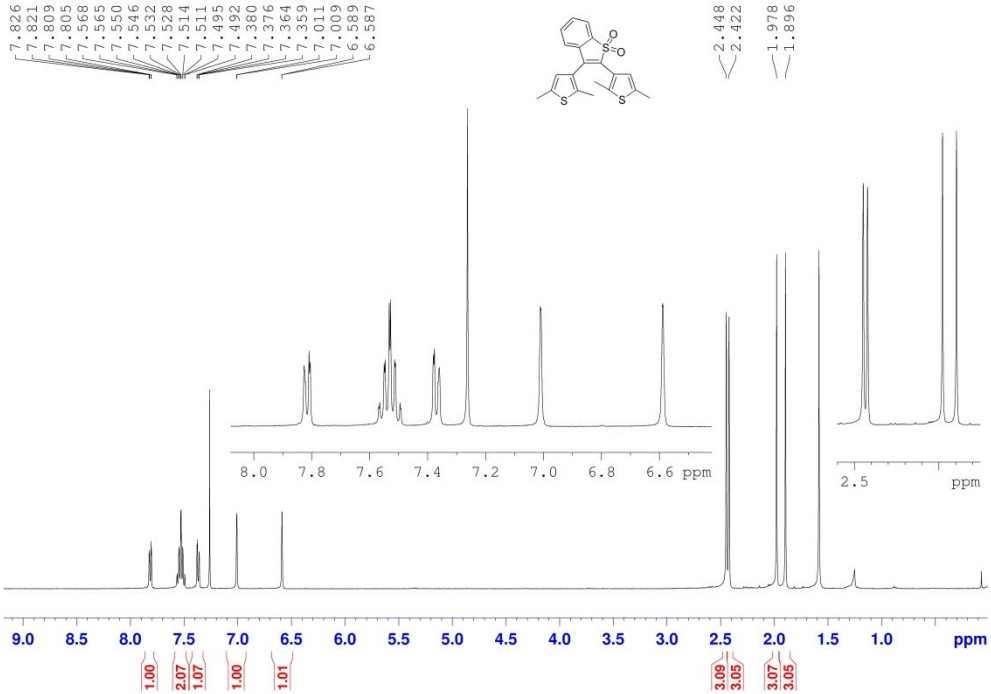


Fig. S5 ^{1}H NMR spectra of BTT-1 in $CDCl_3$ (400 MHz)

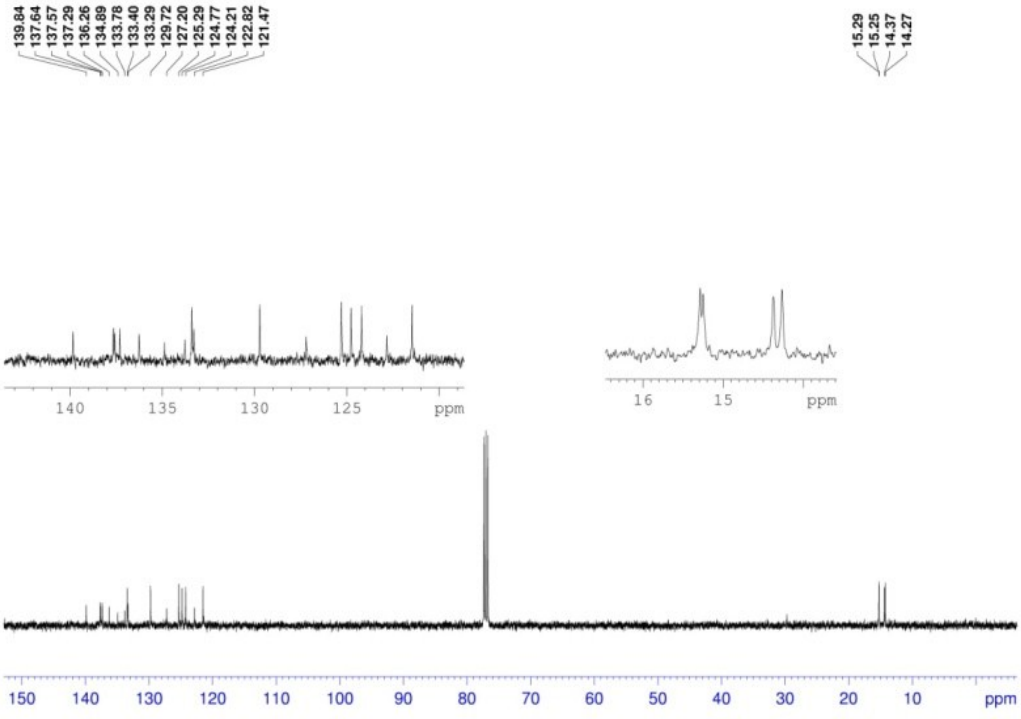


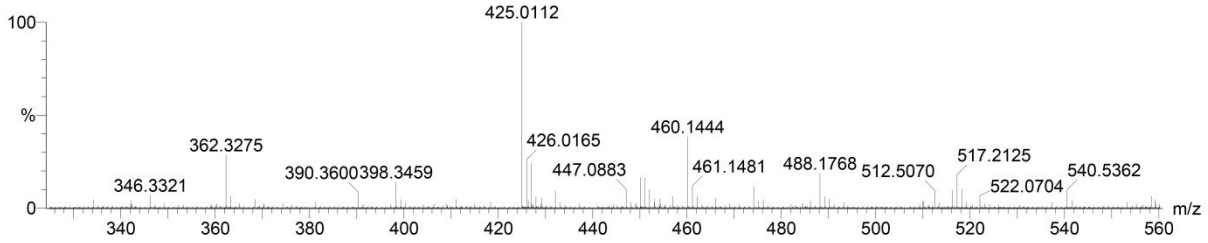
Fig. S6 ^{13}C NMR spectrum of BTT-1 in $CDCl_3$ (100 MHz)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
367 formula(e) evaluated with 4 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 20-32 H: 0-1000 O: 0-40 S: 0-3 K: 0-1

ZHU-WH LCT Premier
Key Lab for Advanced Materials --- ECUST
ZWH-CSJ-03 27 (0.841) Cm (18:31) 1: TOF MS ES+
7.93e+003



Minimum:				-1.5			
Maximum:		2.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
425.0112	425.0106	0.6	1.4	11.5	409.0	0.0	C20 H18 O2 S3 K

Fig. S7 High resolution mass spectrum of BTT-1

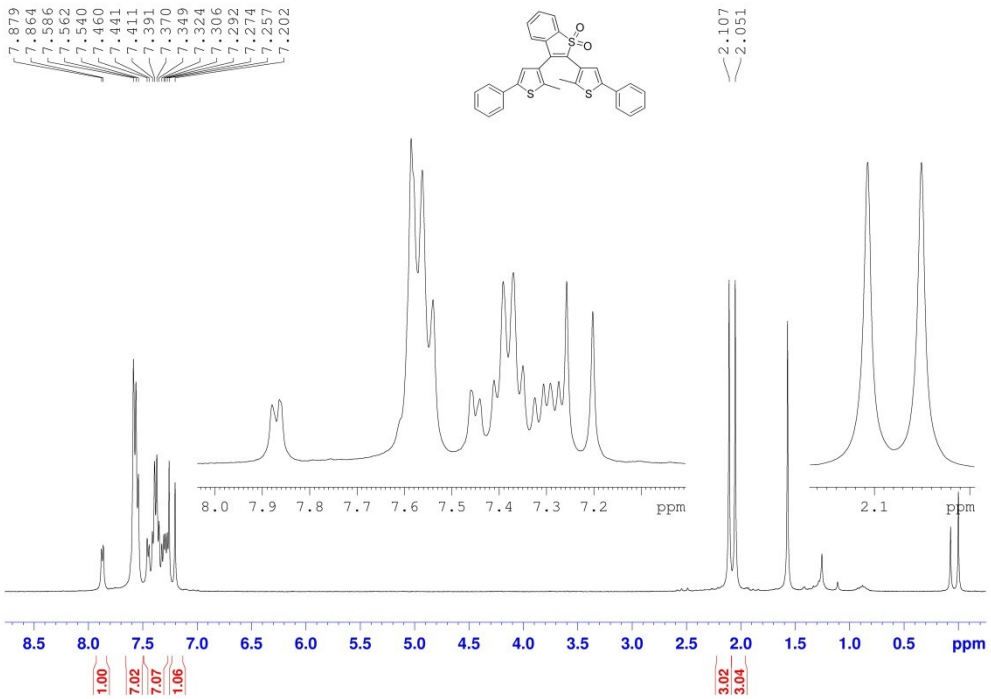


Fig. S8 ^{1}H NMR spectra of BTT-2 in $CDCl_3$ (400 MHz)

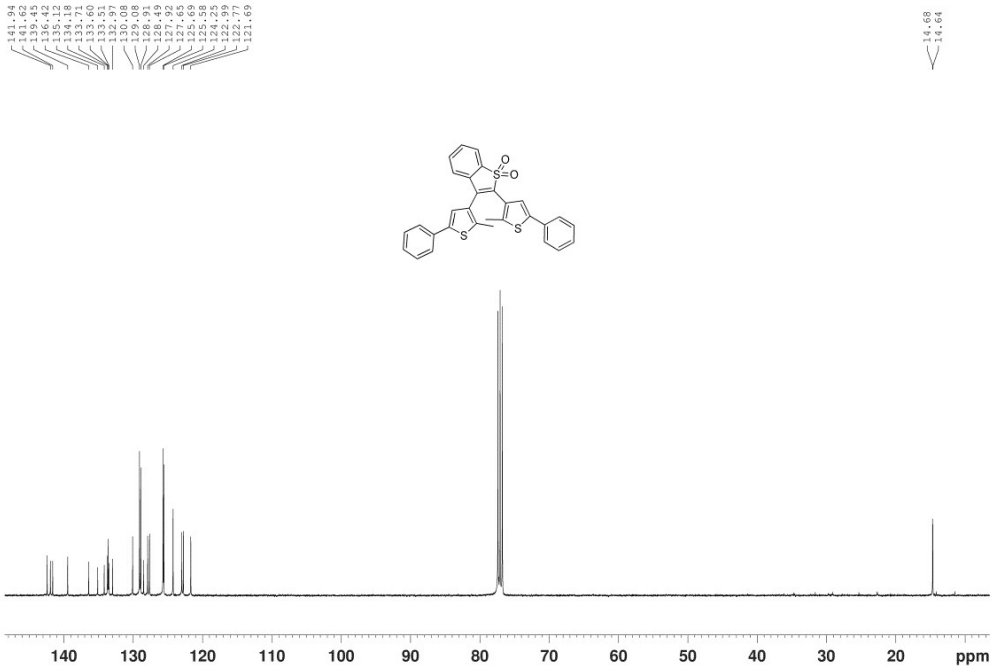


Fig. S9 ^{13}C NMR spectrum of BTT-2 in $CDCl_3$ (100 MHz)

Elemental Composition Report **Page 1**

Single Mass Analysis
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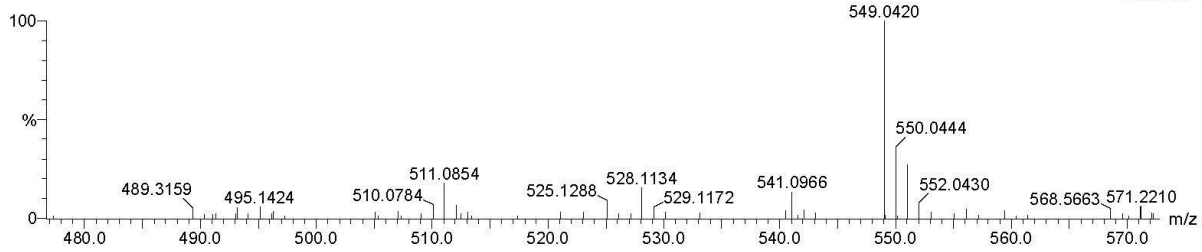
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-30 H: 0-23 O: 0-2 S: 0-3 K: 0-1

ZHU-WH
ZWH-CSJ-13 11 (0.421) Cm (10:28)

1: TOF MS ES+
1.45e+004



Minimum:				-1.5			
Maximum:		3.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
549.0420	549.0419	0.1	0.2	19.5	28.5	0.0	C30 H22 O2 S3 K

Fig. S10 High resolution mass spectrum of BTT-2

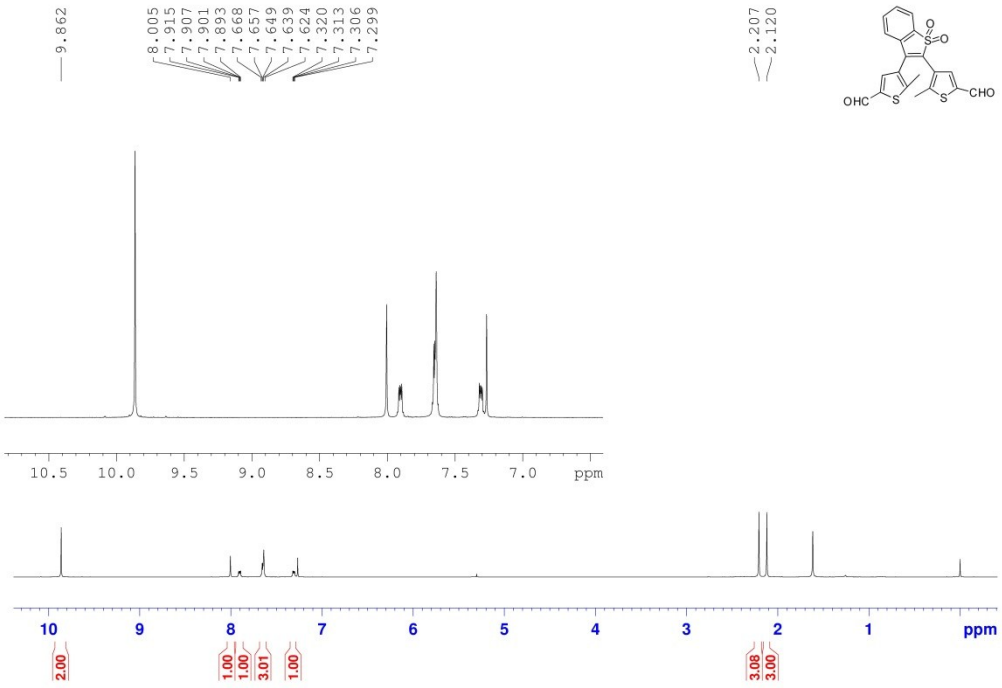


Fig. S11 ^{1}H NMR spectra of BTT-3 in $CDCl_3$ (400 MHz)

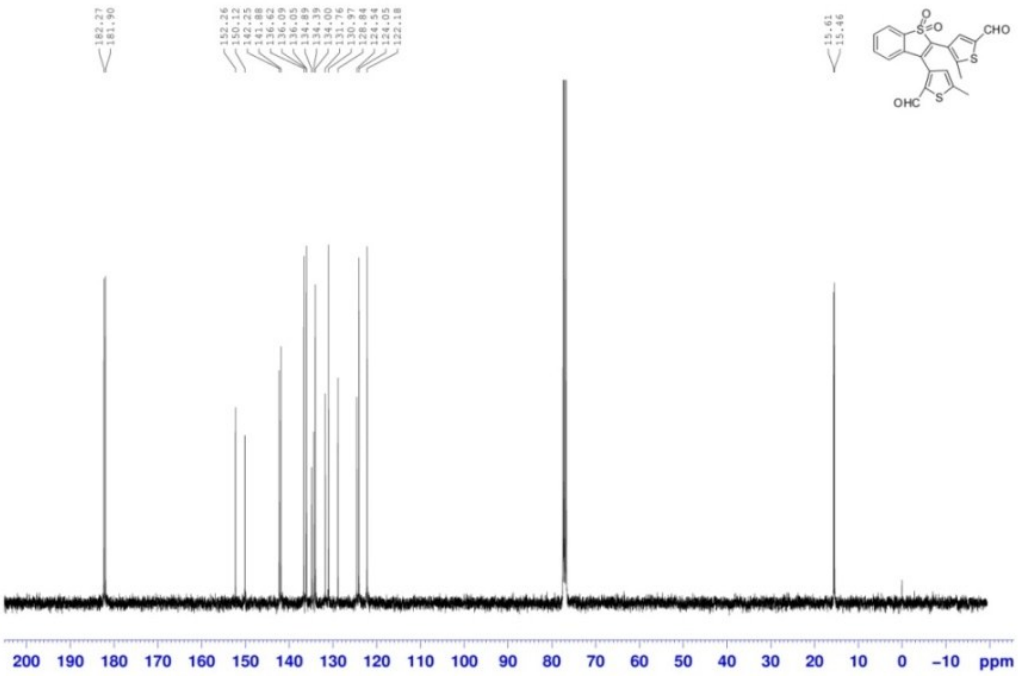


Fig. S12 ^{13}C NMR spectrum of BTT-3 in $CDCl_3$ (100 MHz)

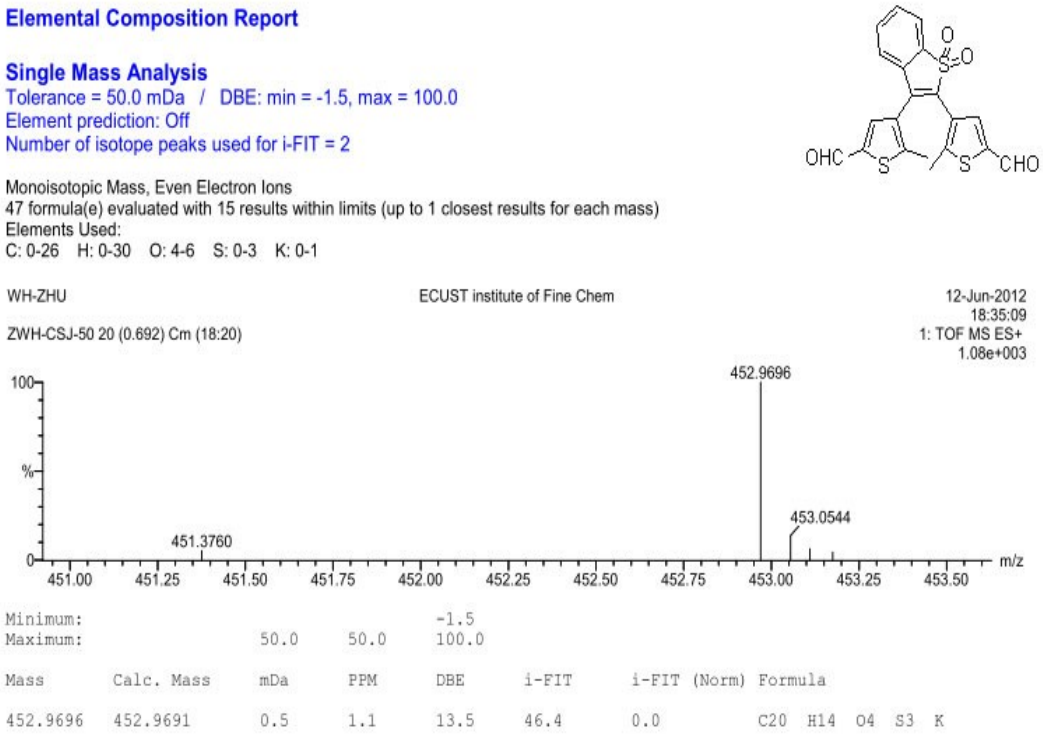


Fig. S13 High resolution mass spectrum of BTT-3

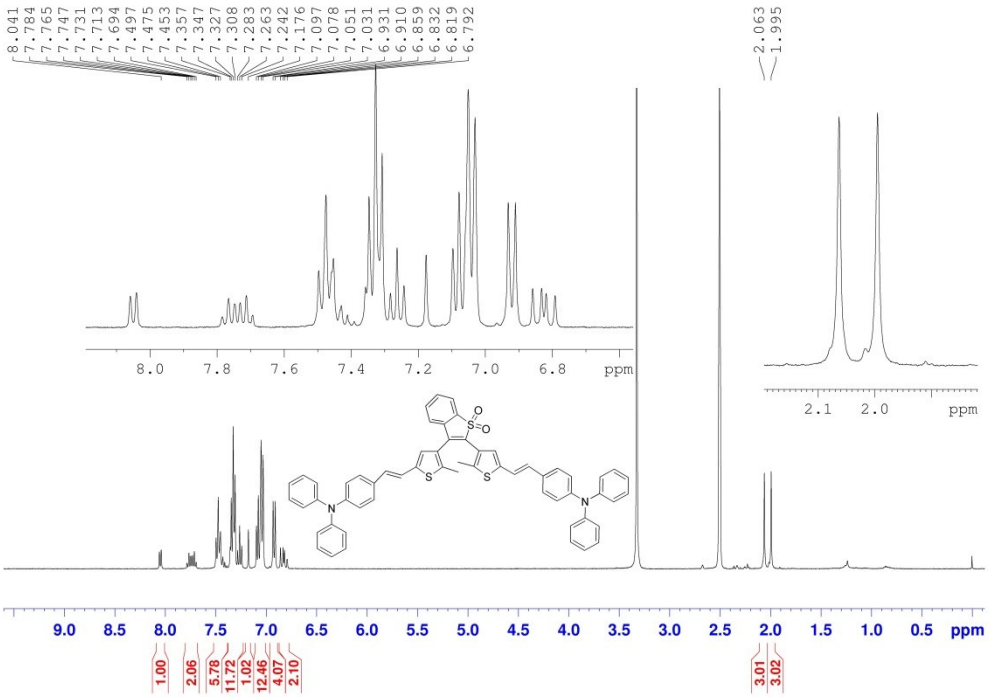


Fig. S14 ^{1}H NMR spectra of BTT-4 in DMSO-d_6 (400 MHz)

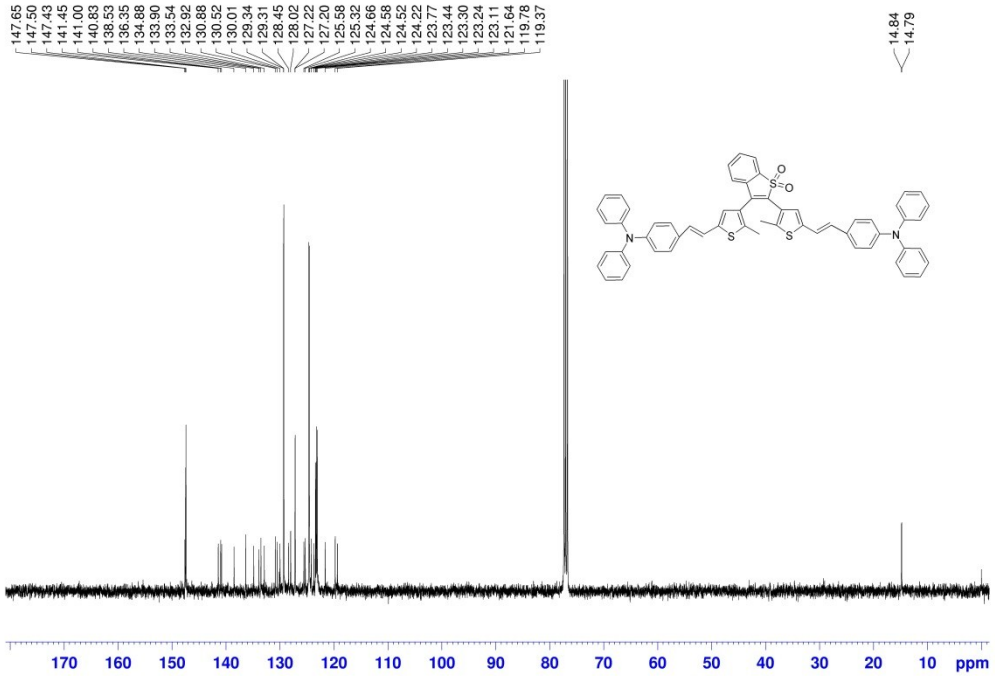


Fig. S15 ^{13}C NMR spectrum of BTT-4 in $CDCl_3$ (100 MHz)

Elemental Composition Report **Page 1**

Single Mass Analysis
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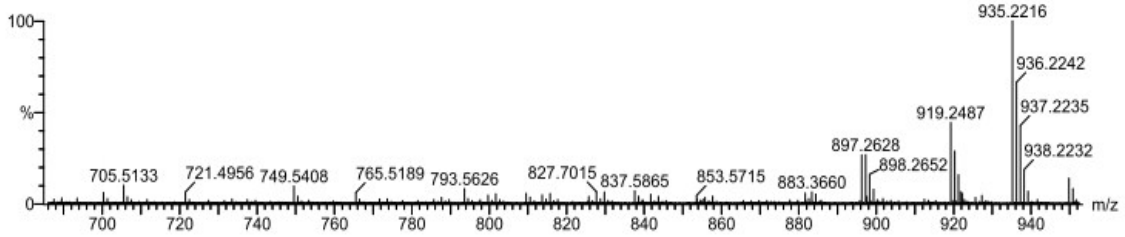
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
68428 formula(e) evaluated with 219 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 27-58 H: 0-1000 N: 0-200 O: 0-200 S: 0-6 K: 0-1
WU-XY LCT Premier

ZWH-CSJ-01 18 (0.724) Cm (7:25)

Key Lab for Advanced Materials --- ECUST
1: TOF MS ES+
1.29e+004



Minimum:				-1.5			
Maximum:		3.0	50.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
935.2216	935.2202	1.4	1.5	37.5	207.9	0.0	C58 H44 N2 O2 S3 K

Fig. S16 High resolution mass spectrum of BTT-4