Supporting Information

Benzo[4,5]thieno-*S*,*S*-dioxide-[3,2-*b*]benzofurans: Synthesis, Properties and Application in Electroluminescent Devices

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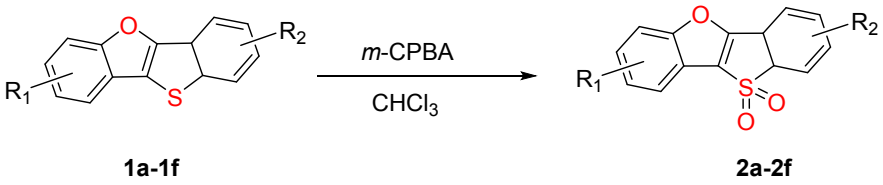
1. Materials and synthesis

Compound BTBFs and BTNF (**1a-1f**) were prepared according our published one-pot reaction.[1] The one-pot reaction, with $Pd(PPh_3)_4$ and CuOAc as the catalysts, K_3PO_4•$3H_2O$ as the base and *tert*-butanol as the solvent, afforded good yields up to 77% among varieties of substrates. Compound BTBFs are oxidized by *m*-CPBA in trichloromethane solution, affording BTOBFs and BTONF (**2a-2f**), as shown in Scheme S1.[2, 3]



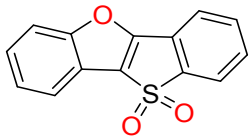
1a-1f **2a-2f**

Scheme S1. Synthesis of BTOBFs and BTONF

General procedure for the synthesis of 2a-2f:

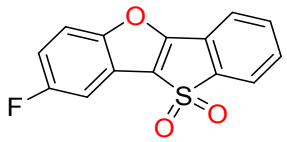
Compounds **2a-2f** (1 equivalent) and *m*-CPBA (4 equivalent) were dissolved in a suitable amount of trichloromethane solvent and heated to reflux for 5 h. The reaction system was washed three times with saturated Na_2CO_3 solution, and the organic phase was dried with anhydrous $MgSO_4$. Solvents were removed by rotatory evaporation and the target products **2a-2f** were separated by column chromatography.

Compound **2a**:



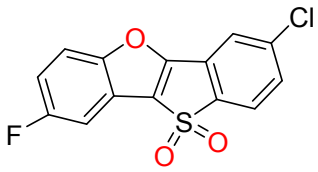
Using the general procedure, compound **2a** was prepared from BTBF **1a** (110 mg, 0.5 mmol) and *m*-CPBA (350 mg, 2.0 mmol) as white solid (79 mg, 0.31 mmol, yield 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.81 (m, 2H), 7.60-7.68 (m, 3H), 7.53-7.57 (m, 1H), 7.40-7.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 159.04, 145.36, 133.40, 130.98, 126.71, 125.66, 125.01, 122.38, 120.62, 120.55, 120.31, 120.22, 112.93. HRMS (ESI^+) m/z calcd for $C_{14}H_8O_3SNa^+$ $[M+Na]^+$ 279.0092, found 279.0089.

Compound **2b:**



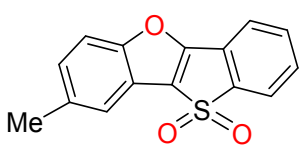
Using the general procedure, compound **2b** was prepared from F-BTBF **1b** (2.89 g, 11.9 mmol) and *m*-CPBA (8.3 g, 47.8 mmol) as white solid (2.9 g, 10.59 mmol, yield 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.3 Hz, 1H), 7.65 (m, 2H), 7.55-7.60 (m, 2H), 7.46 (dd, J = 8.0, 2.5 Hz, 1H), 7.13-7.18 (m, 1H); ^{13}C NMR(101MHz, $CDCl_3$) δ 161.22 (d, J = 89.9 Hz), 157.22 (d, J = 407.0 Hz), 145.35, 133.49, 131.36, 124.69, 122.50, 121.49, 121.38, 120.47, 120.22, 114.55 (d, J = 27.3 Hz), 113.86 (d, J = 10.1 Hz), 106.70 (d, J = 27.3 Hz). HRMS (MALDI-TOF) m/z calcd for $C_{14}H_8FO_3S$ $[M+H]^+$ 275.0178, found 275.0175.

Compound **2c**:



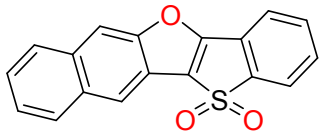
Using the general procedure, compound **2c** was prepared from F,Cl-BTBF **1c** (2.3 g, 8.3 mmol) and *m*-CPBA (7.6 g, 33.2 mmol) as white solid (2.4 g, 7.8 mmol, yield 94%). ^{1}H NMR (400 MHz,) δ 7.71 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.57 (dd, J = 9.2, 3.9 Hz, 1H), 7.53 (dd, J = 8.2, 1.8 Hz, 1H), 7.45 (dd, J = 7.8, 2.6 Hz, 1H), 7.17 (td, J = 9.0, 2.7 Hz, 1H); ^{13}C NMR (101MHz, $CDCl_3$) δ 160.52 (d, J = 245.4 Hz), 157.21(d, J = 377.7Hz), 143.32, 140.08, 130.96, 126.36, 123.62, 121.57, 121.28, 121.16, 120.86, 115.14 (d, J = 27.3 Hz), 114.04 (d, J = 407.0 Hz), 106.83(d, J = 407.0 Hz). HRMS (ESI+) m/z calcd for $C_{14}H_7ClFO_3S$ $[M+H]^+$ 308.9788, found 308.9781.

Compound **2d**:



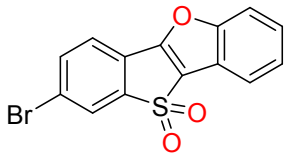
Using the general procedure, compound **2d** was prepared from M-BTBF **1d** (100 mg, 0.42 mmol) and *m*-CPBA (220 mg, 1.26 mmol) as white solid (79 mg, 0.28 mmol，yield 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H), 7.53-7.66 (m, 4H), 7.48-7.51 (m, 1H), 7.24 (dd, J = 8.7, 1.8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.21, 157.56, 145.35, 135.64, 133.35, 130.81, 127.93, 125.20, 122.33, 120.61, 120.33, 120.20, 119.92, 112.37, 21.49. HRMS (ESI+) m/z calcd for $C_{15}H_{10}O_3S$ $[M+H]^+$ 271.0429, found 271.0429.

Compound **2e**:



Using the general procedure, compound **2e** was prepared from BTNF **1e** (137 mg, 0.5 mmol) and *m*-CPBA (350 mg, 2 mmol) as white solid (83 mg, 0.31 mmol, yield 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.02 (s, 1H), 7.95-8.01 (m, 2H), 7.83 (d, J = 6.9 Hz, 1H), 7.72 (d, J = 7.3 Hz, 1H), 7.63 (m, 2H), 7.52-7.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.60, 157.44, 145.55, 133.44, 131.92, 131.54, 131.51, 128.53, 128.15, 126.58, 125.88, 124.93, 122.44, 120.73, 120.24, 119.53, 119.07, 109.17. HRMS (ESI^+) m/z calcd for $C_{18}H_{10}O_3SNa^+$ $[M+Na]^+$ 329.0243, found 329.0222

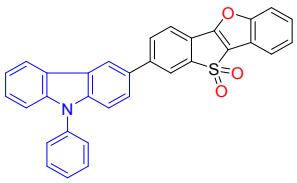
Compound **2f:**



Using the general procedure, compound **2f** was prepared from Br-BTBF **1f** (4.4 g, 14.5 mmol) and *m*-CPBA (10.0 g, 58 mmol) as white solid (3.8 g, 11.3 mmol, yield 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 1.6 Hz, 1H), 7.79–7.74 (m, 2H), 7.64–7.58 (m, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.49–7.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.10, 158.30, 146.54, 136.33, 127.03, 125.85 (two carbon signals are overlapped),

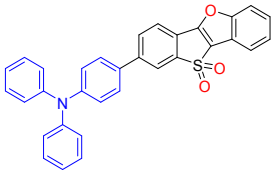
125.11, 123.75, 121.36, 120.56, 120.45, 120.36, 113.01. HRMS (ESI+) m/z calcd for $C_{14}H_7BrO_3SNa^+$ $[M+Na]^+$ 356.9197, found 356.9200.

Compound 2-NPhCz-BTOBF



Br-BTOBF **2f** (67 mg, 0.2 mmol) and 9-phenyl-3-carbazole boric acid (86 mg, 0.3 mmol) were dissolved into dioxane-H_2O cosolvent (v/v = 4:1, 5 mL) in a Schlenk tube. Then K_2CO_3 (70 mg, 0.5 mmol) was added to the solution. After the solution was bubbled with N_2 for 10 min, $Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 5 mol%) was added to the solution. The reaction was heated to 90 °C overnight under dark. After the reaction mixture was cooled to room temperature, the organic layer was separated and dried with anhydrous $MgSO_4$. It was filtered and the filtrate was evaporated under vacuum, the residue was purified by flash chromatography (eluting with ethyl acetate/hexane) to afford the 2-NPhCz-BTOBF (85.6 mg, 0.17 mmol, 85%) as bright yellow-green solid, Mp: 280.8-281.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 1.6 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 1.4 Hz, 1H), 7.93 (dd, J = 7.9, 1.6 Hz, 1H), 7.78-7.80 (dd, J = 9.6, 3.5 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.67-7.57 (m, 6H), 7.55–7.39 (m, 6H), 7.37-7.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 159.06, 146.35, 145.37, 141.59, 141.19, 137.35, 131.49, 130.54, 130.16, 127.94, 127.16, 126.69, 126.47, 125.63, 125.08, 124.26, 123.24, 122.55, 121.02, 120.82, 120.62, 120.44, 119.88, 119.04, 112.87, 110.59, 110.20. HRMS (ESI^+) m/z calcd for $C_{32}H_{19}NO_3SNa^+$ $[M+Na]^+$ 520.0983, found 520.0986.

Compound 2-TPA-BTOBF



Br-BTOBF (67 mg, 0.2 mmol) and 4-(diphenylamino)phenylboric acid (87 mg, 0.3 mmol) were dissolved into dioxane-H_2O cosolvent (v/v = 4:1, 5 mL) in a Schlenk tube. Then K_2CO_3 (70 mg, 0.5 mmol) was added to the solution. After the solution was bubbled with N_2 for 10 min, $Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 5 mol%) was added to the solution. The reaction was heated to 90 ^oC overnight under dark. After the reaction mixture was cooled to room temperature, the organic layer was separated and dried with $MgSO_4$. It was filtered and the filtrate was evaporated under vacuum, the residue was purified by flash chromatography (eluting with ethyl acetate/hexane) to afford the 2-TPA-BTOBF (89.0 mg, 0.178 mmol, 89%) as bright yellow solid, Mp: 257.1-259.2 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 1.3 Hz, 1H), 7.81–7.71 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.61–7.55 (m, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.43–7.35 (m, 2H), 7.35–7.26 (m, 4H), 7.21–7.05 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.38, 159.05, 148.81, 147.27, 146.34, 143.96, 131.50, 130.74, 129.58, 127.77, 126.50, 125.63, 125.14, 124.04, 122.99, 122.65, 120.83, 120.60, 120.42, 120.34, 119.92, 112.88. HRMS (ESI+) m/z calcd for $C_{32}H_{22}NO_3S^+$ $[M+H]^+$ 500.1315, found 500.1318.

2. The cyclic voltammetric investigations of related compounds

In order to further understand the electrochemical properties of the compounds before and after oxidation, we measured oxidation-reduction potentials of F,Cl-BTBF, F,Cl-BTOBF, 2-NPhCz-BTOBF and 2-TPA-BTOBF. The cyclic voltammetry curves of these compounds were measured by three-phase electrodes, that is, a glassy carbon electrode was used as a working electrode, a platinum wire electrode was used as a counter electrode, and an Ag/AgCl electrode was used as a reference electrode. The test

conditions were as follows: tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte, ferrocene (10^{-3} M) as external standard, CH_3CN as solvent, sample concentration of 10^{-3} M, sweeping speed 100 mv s^{-1}, room temperature and nitrogen atmosphere. Before the test, the prepared solution was bubbled with nitrogen for 20 min.

3. TGA curves of 2-NPhCz-BTOBF and 2-TPA-BTOBF

Thermogravimetric analyses (TGA) were carried out on a TA Instrument Q50 thermogravimetric analyzer between 20−600 °C at a heating rate of 10 °C min^{-1} under nitrogen. TGA curves of 2-NPhCz-BTOBF and 2-TPA-BTOBF were shown in Fig. S1.

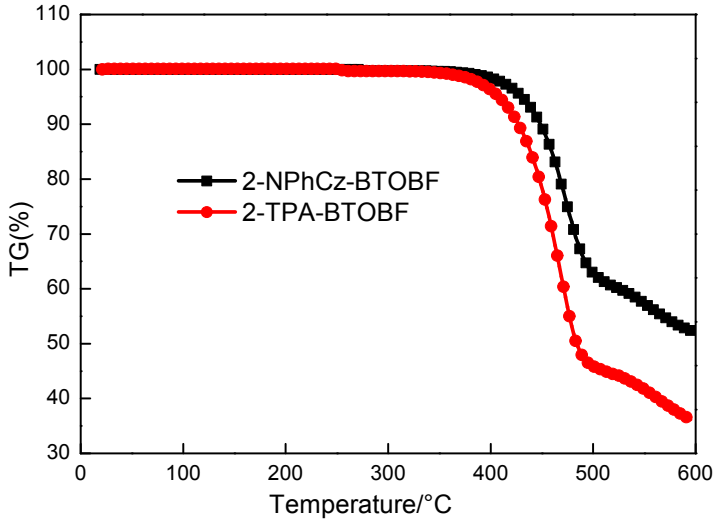


Fig. S1 The TGA curves of 2-NPhCz-BTOBF and 2-TPA-BTOBF.

4. Device fabrication

OLEDs were fabricated on patterned ITO-coated glass substrates with a sheet resistance of 15 Ω/sq. Before device fabrication, the ITO glass substrates were sequentially cleaned with detergents, deionized water, acetone, ethanol, dried in an oven at 75 ℃, and treated with oxygen plasma for 10 min. After that, the clean substrates were transferred into a vacuum deposition system for organic and metal deposition. The devices were fabricated at a pressure below 1×10^{-4} Pa by evaporating organic materials onto the substrate at a rate of 1–2 Å s^{-1}, while LiF at a rate of 0.05 Å s^{-1} and Al metal through a rate of 2 Å s^{-1}. EL luminescence spectra and CIE color coordinates were measured with a Spectrascan PR655 photometer and the current-voltage-brightness characteristics were measured with a computer-controlled Keithley 2400 SourceMeter with CS-200 under ambient atmosphere.

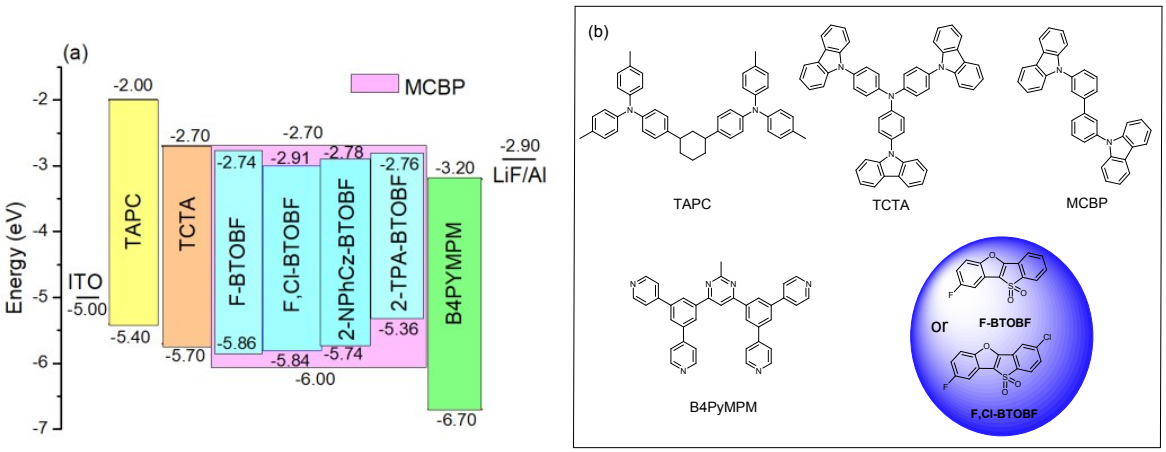
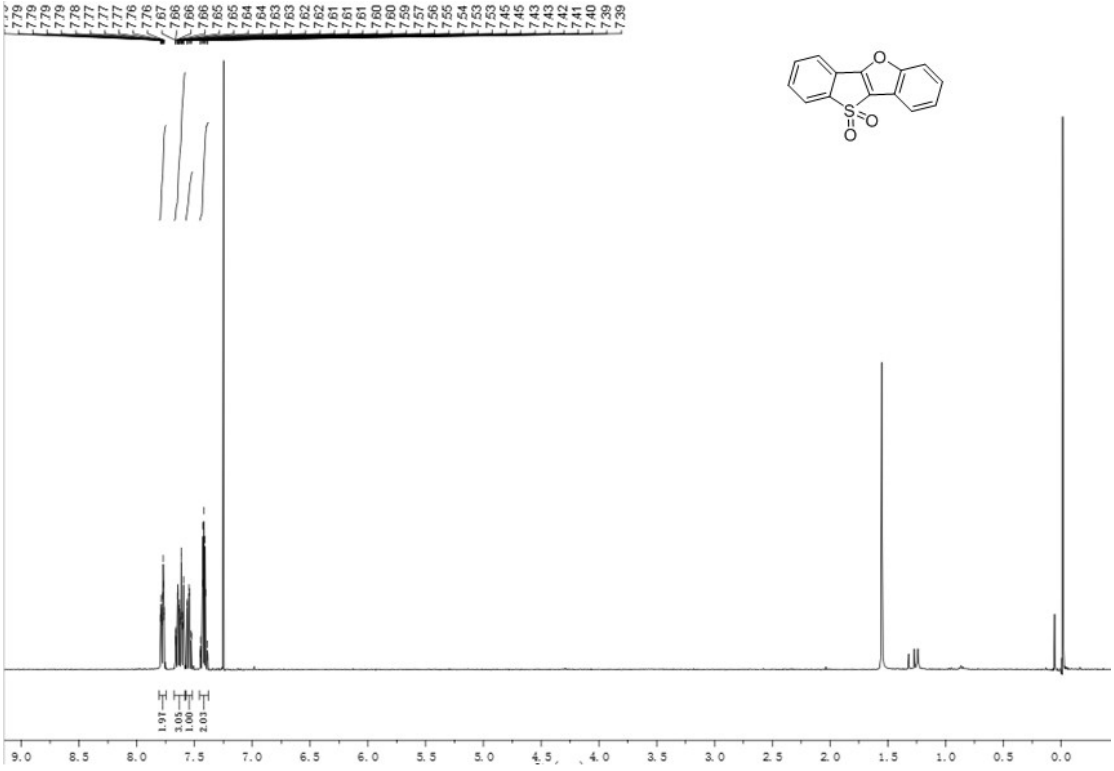


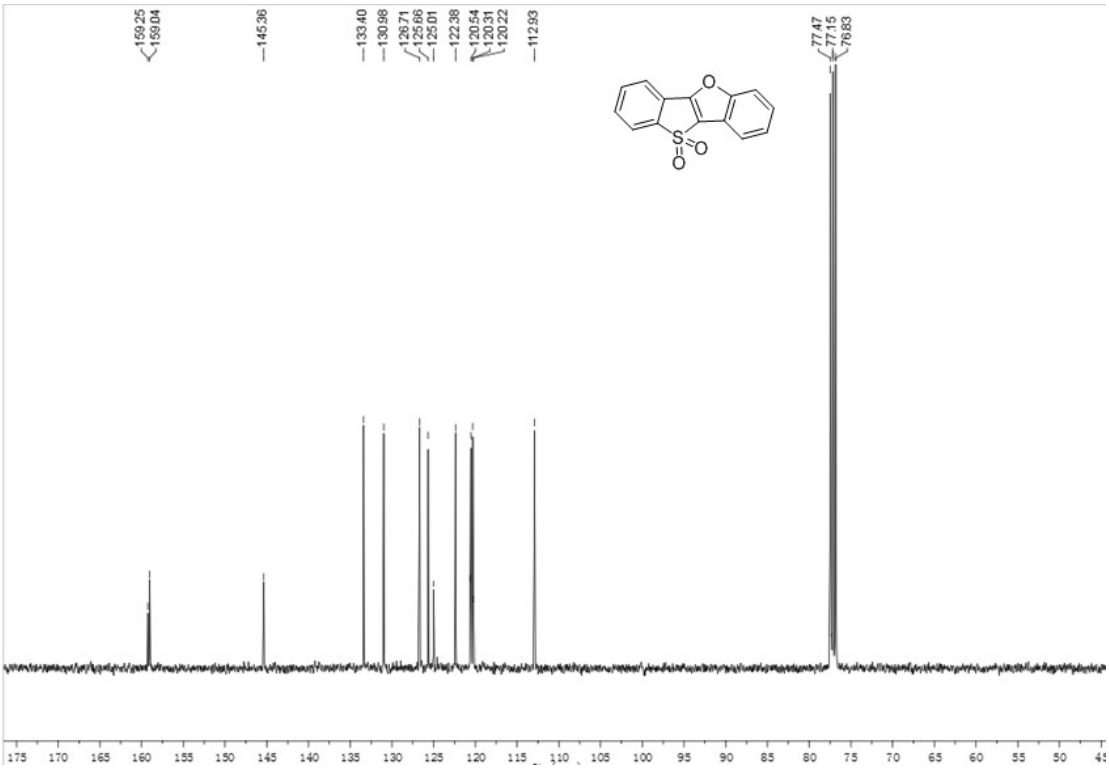
Fig. S2 (a) The energy level diagrams of the OLEDs; (b) Related molecular structures in OLED devices.

5. ^{1}H and ^{13}C NMR spectra and HRMS spectra

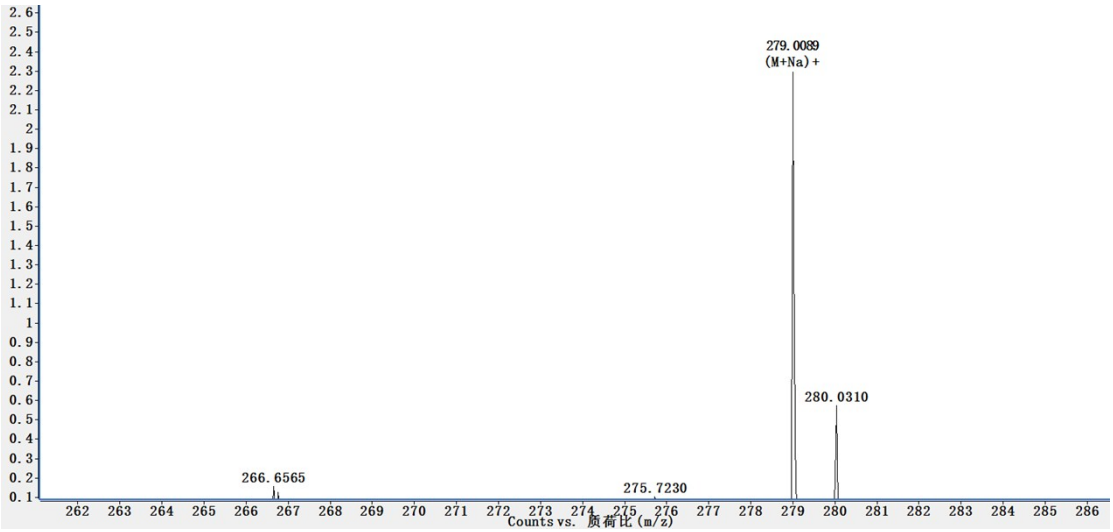
^{1}H NMR of **2a**



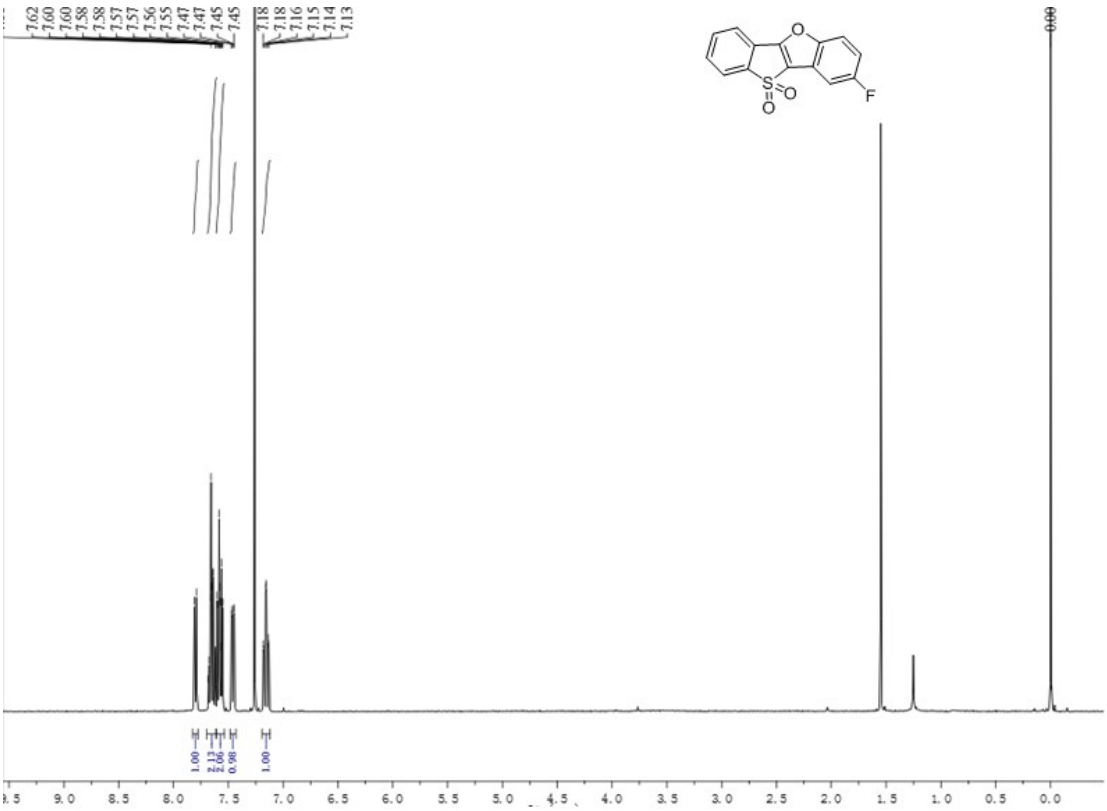
^{13}C NMR of **2a**



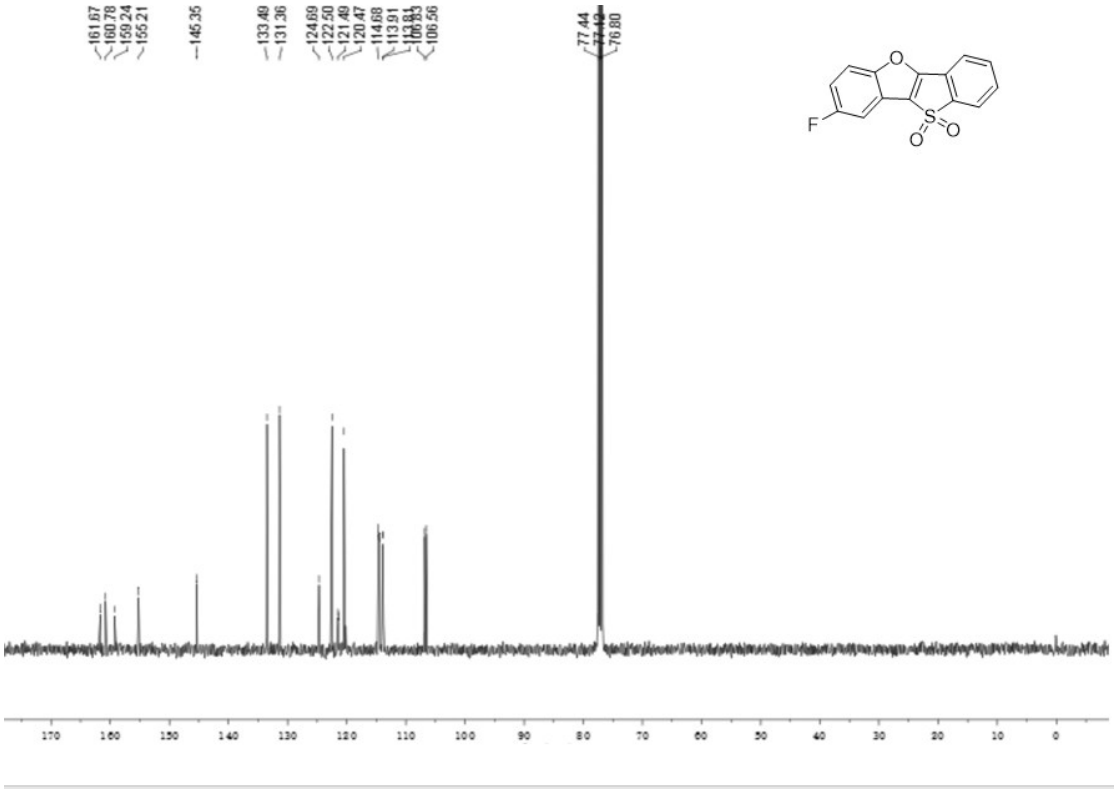
HRMS of **2a**



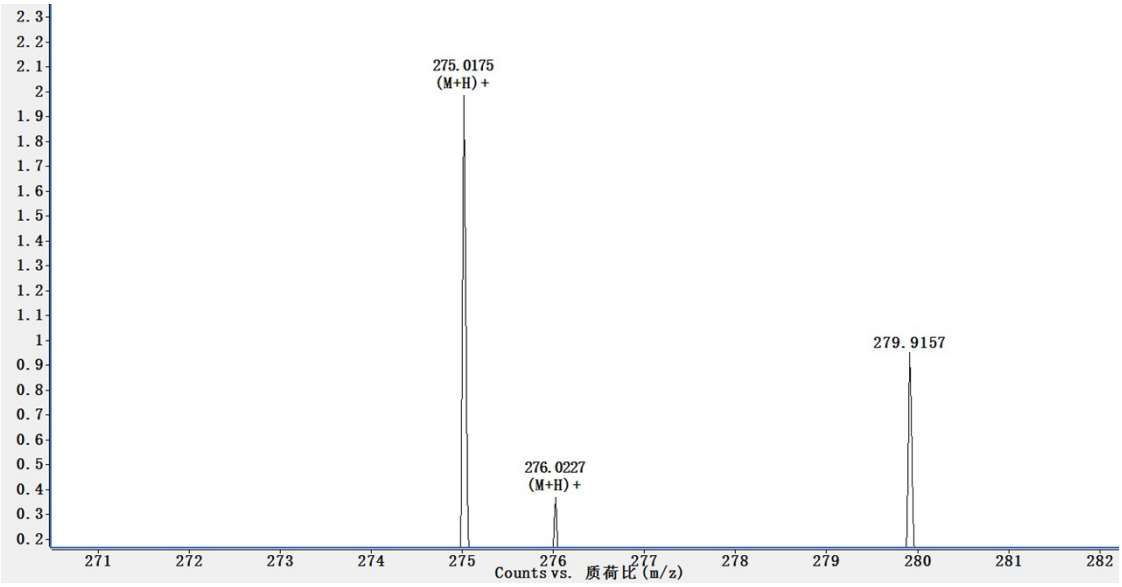
^{1}H NMR of **2b**



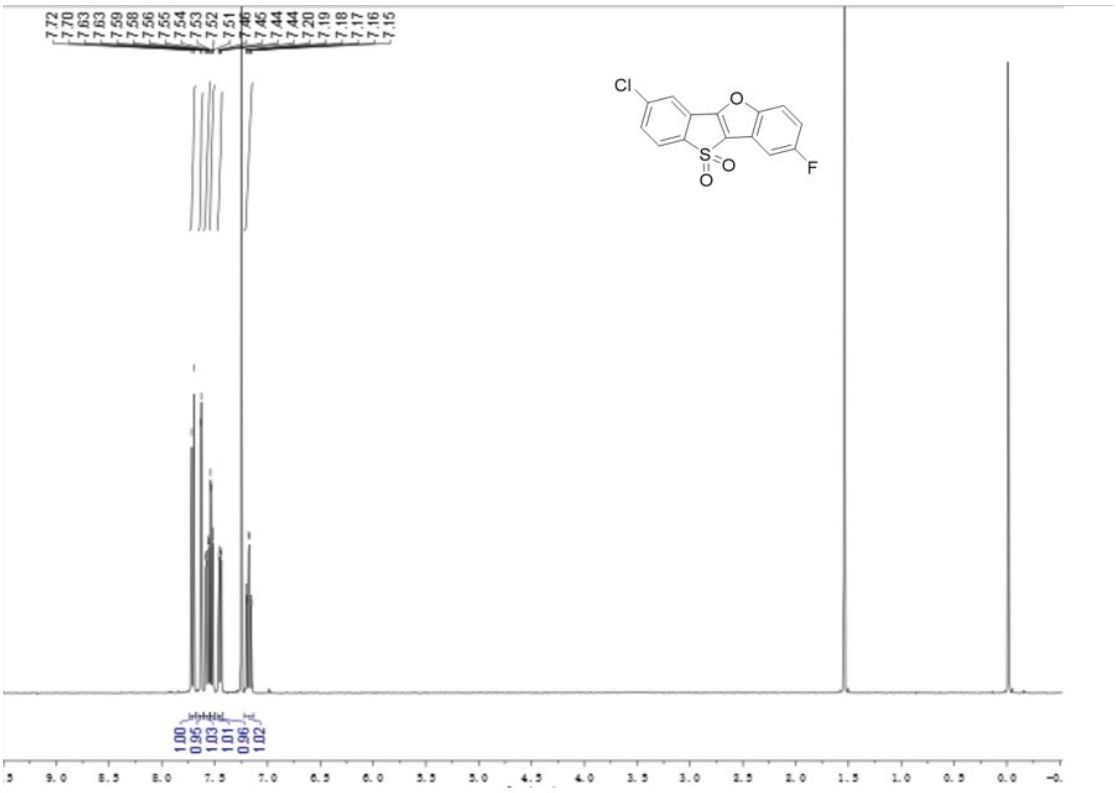
^{13}C NMR of **2b**



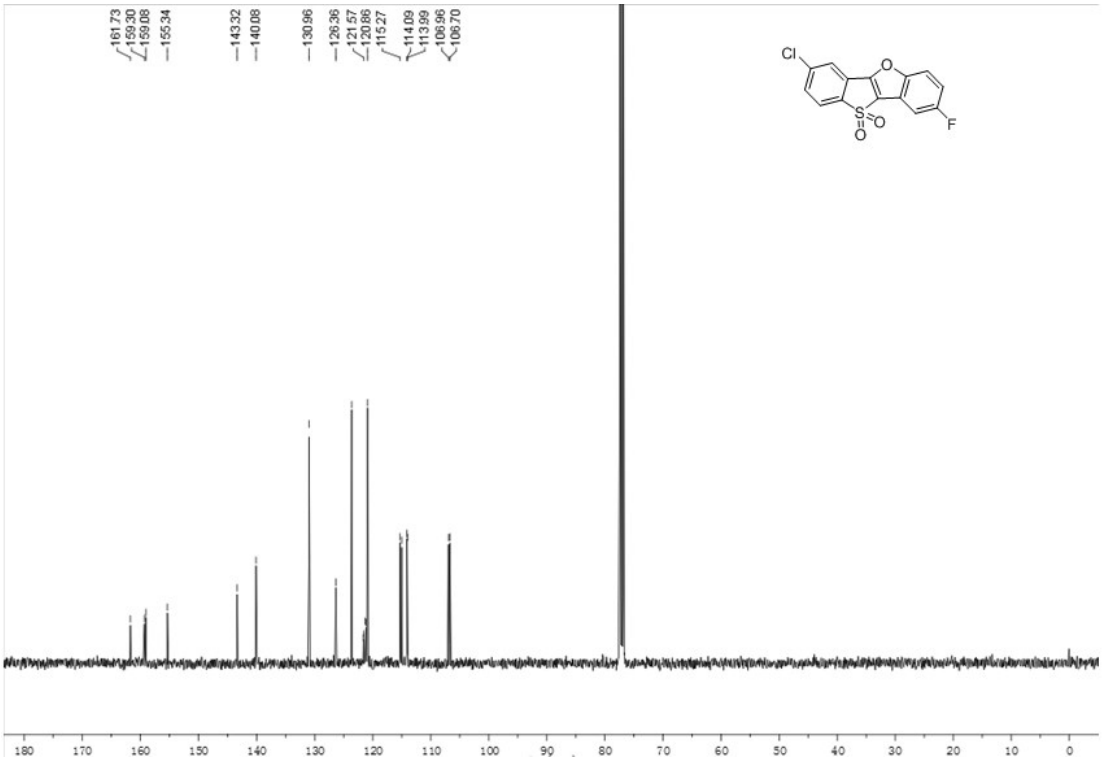
HRMS of **2b**



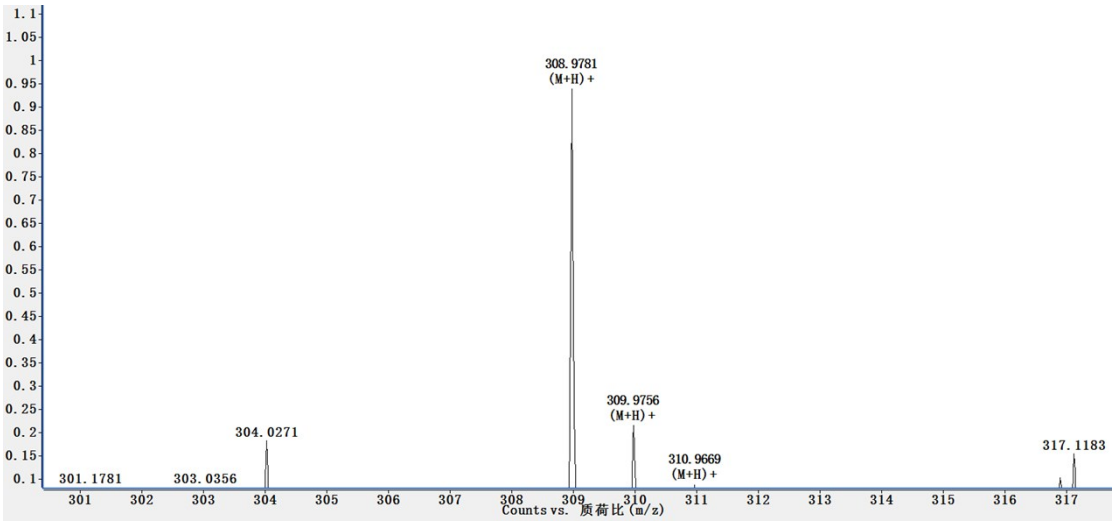
^{1}H NMR of **2c**



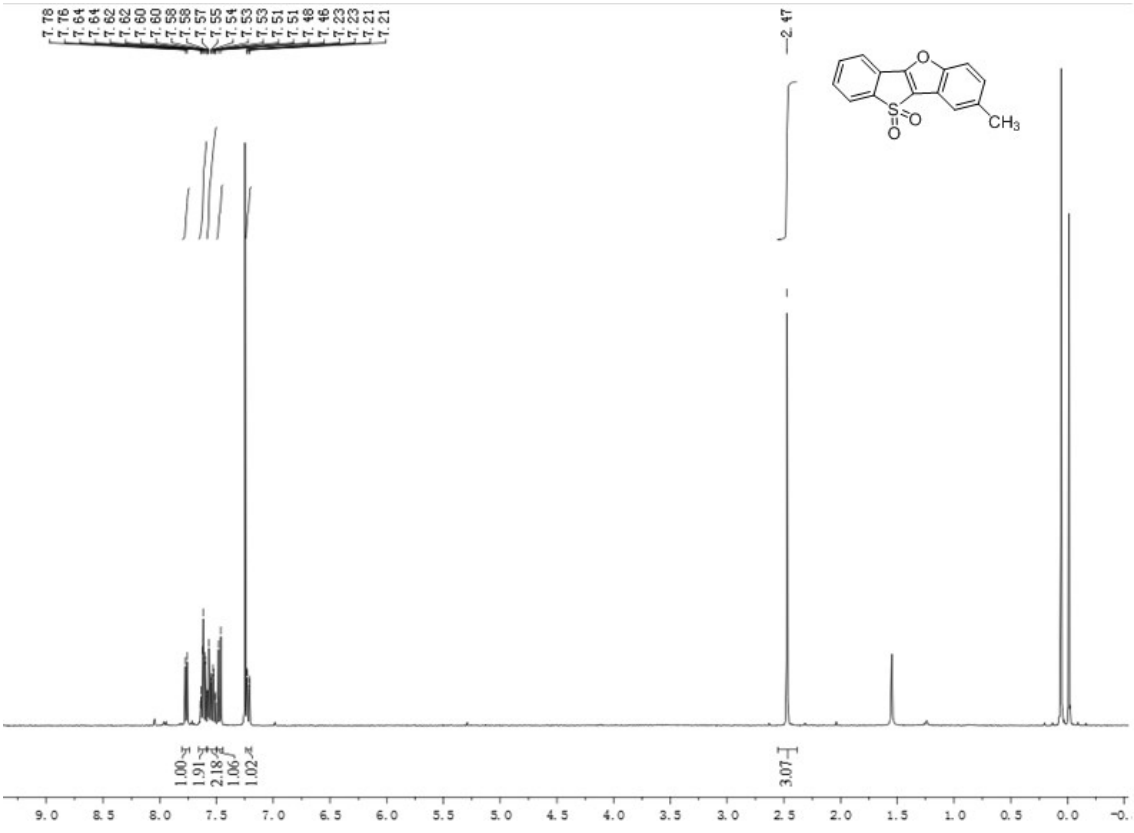
^{13}C NMR of **2c**



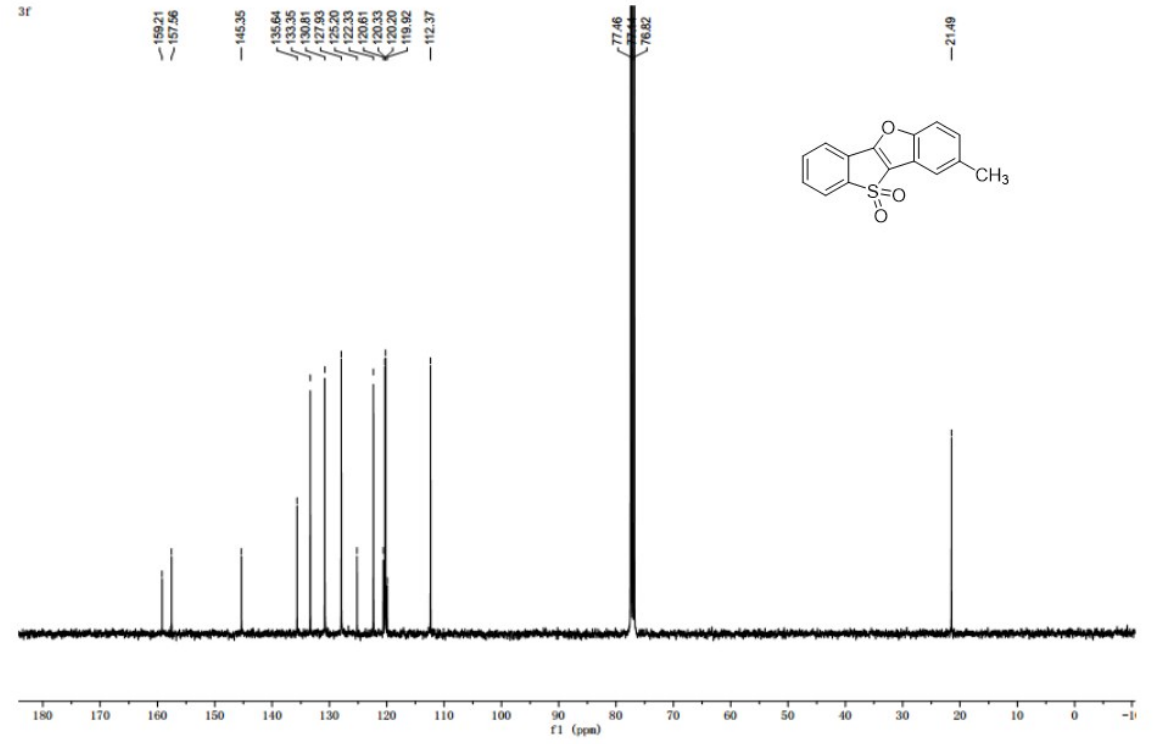
HRMS of **2c**



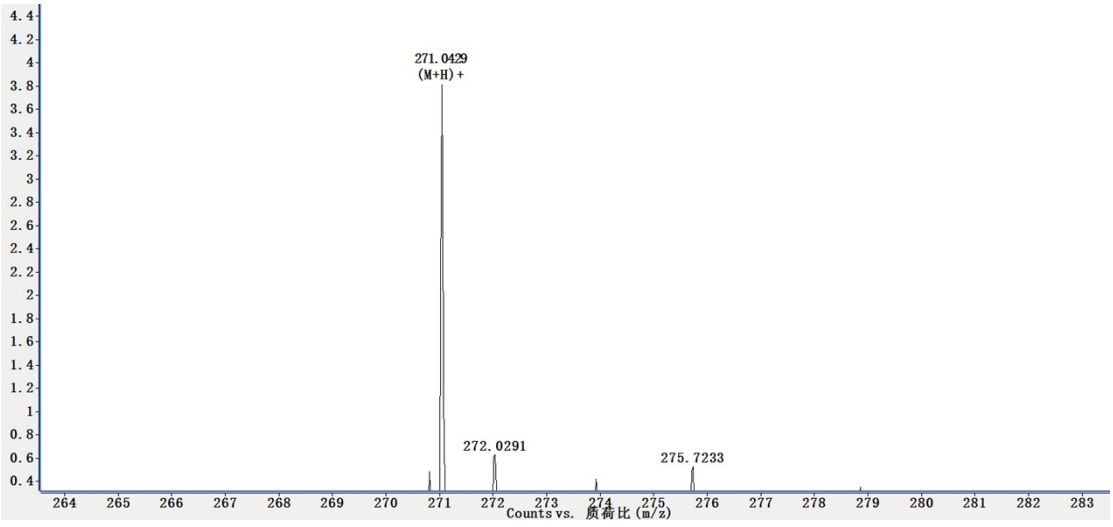
^{1}H NMR of **2d**



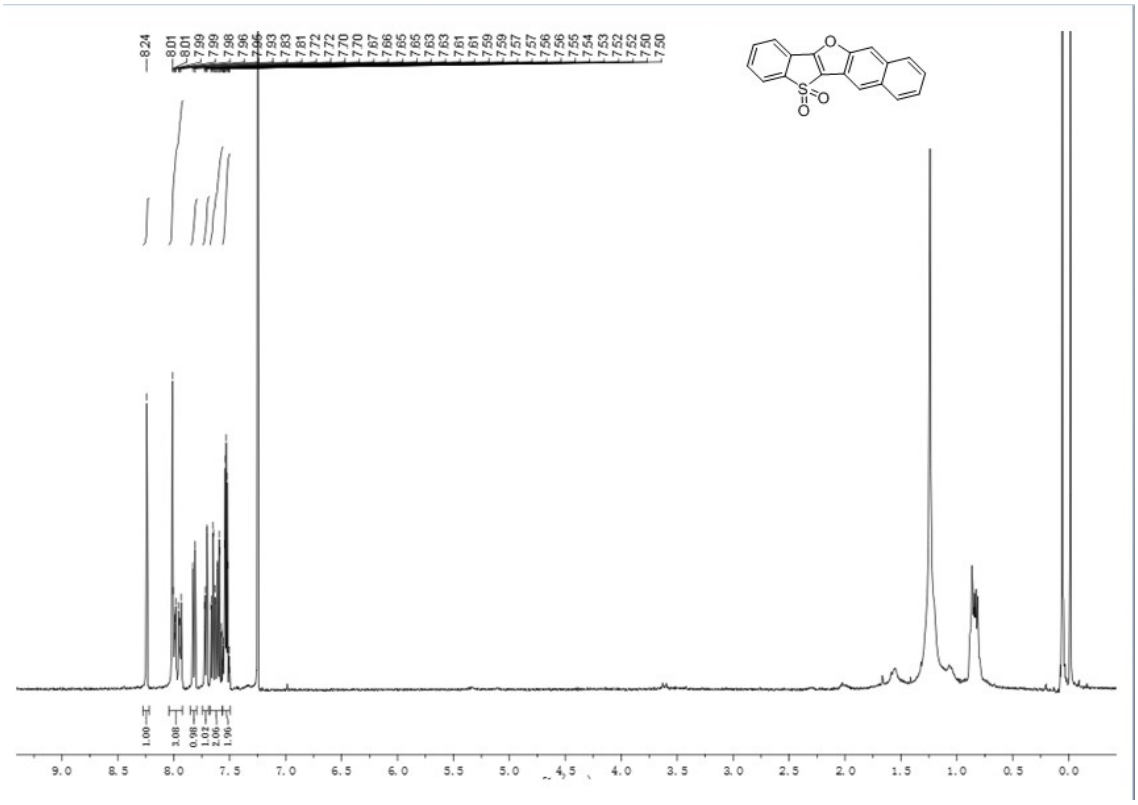
^{13}C NMR of **2d**



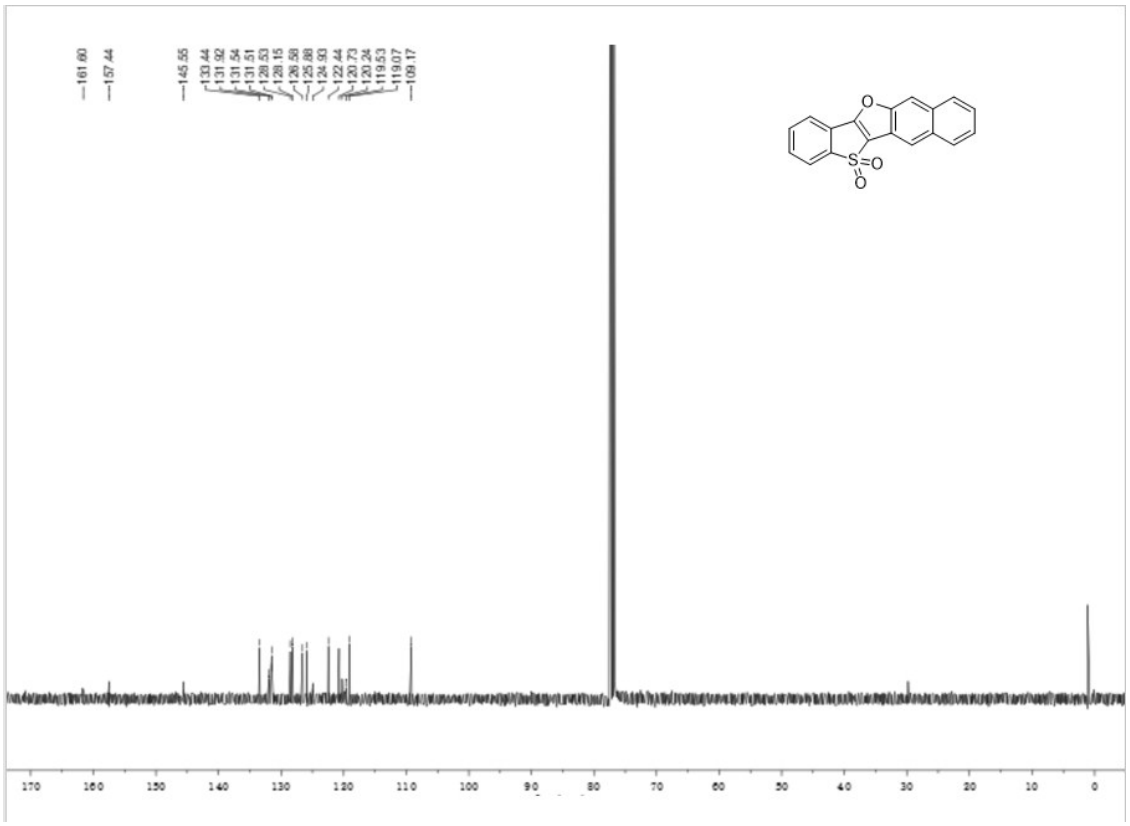
HRMS of **2d**



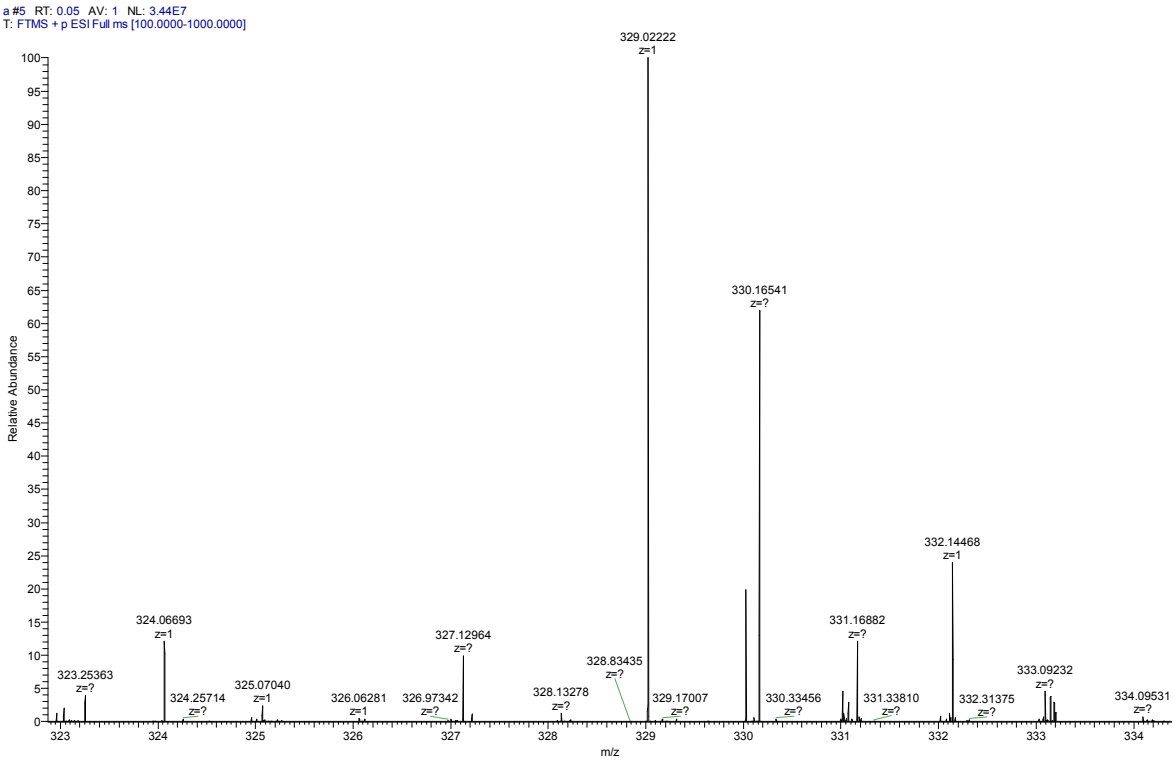
^{1}H NMR of **2e**



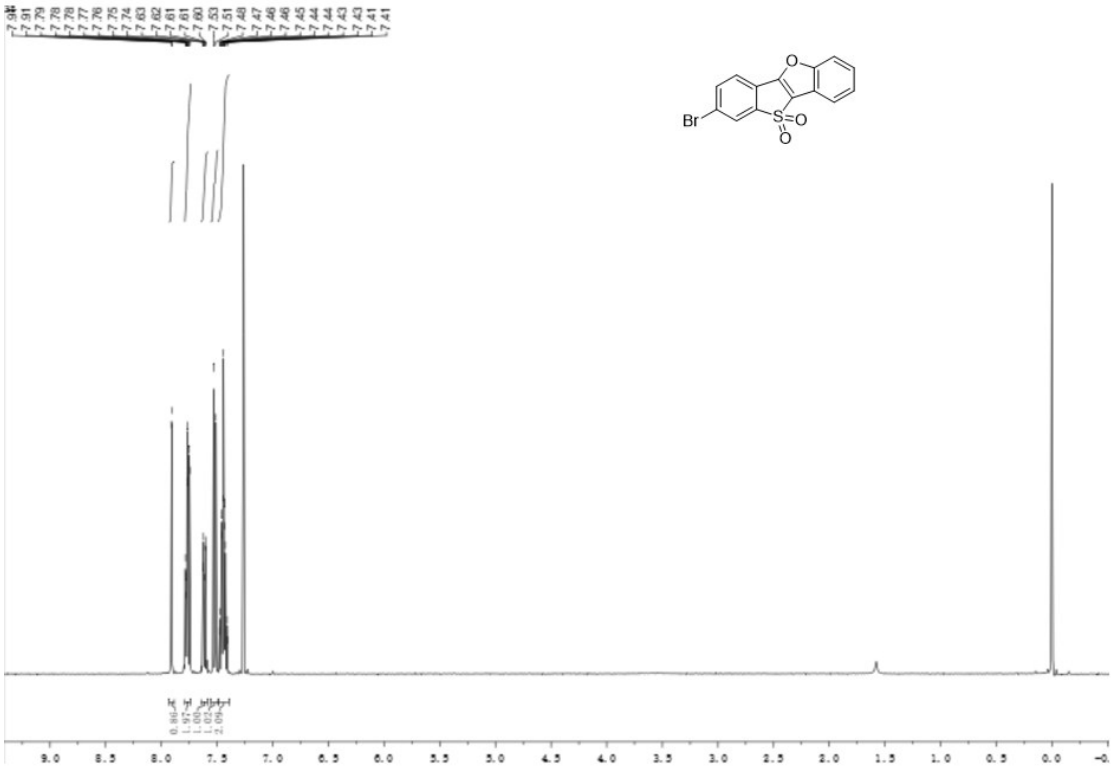
^{13}C NMR of **2e**



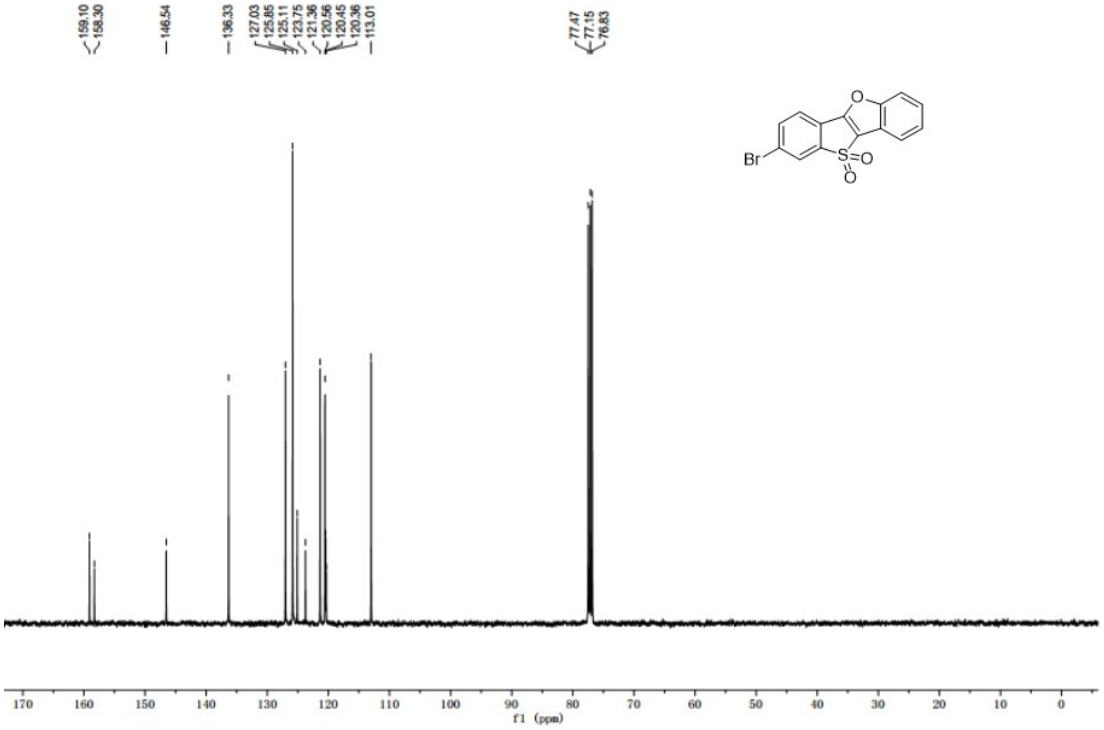
HRMS of **2e**



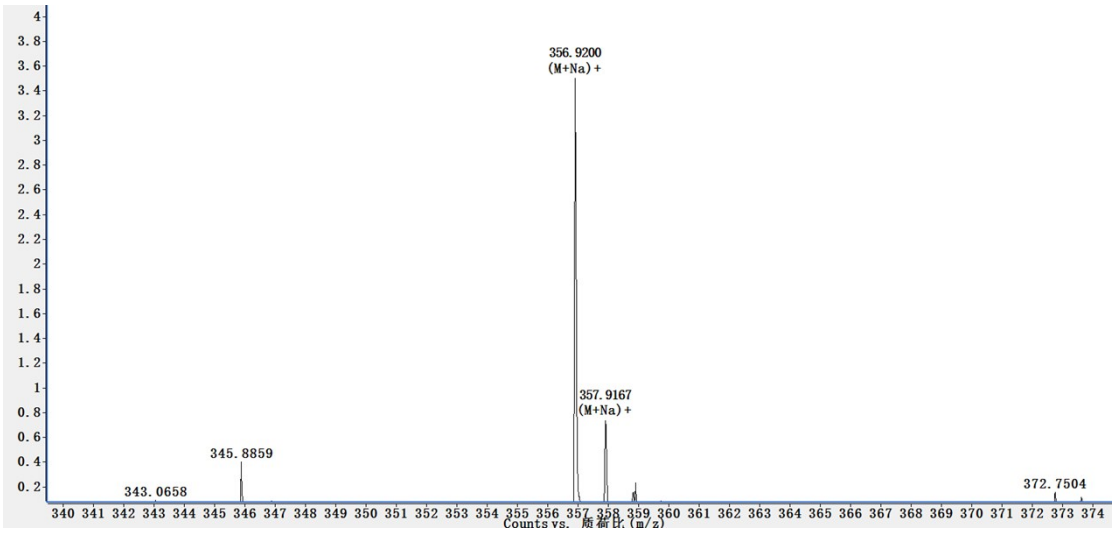
^{1}H NMR of **2f**



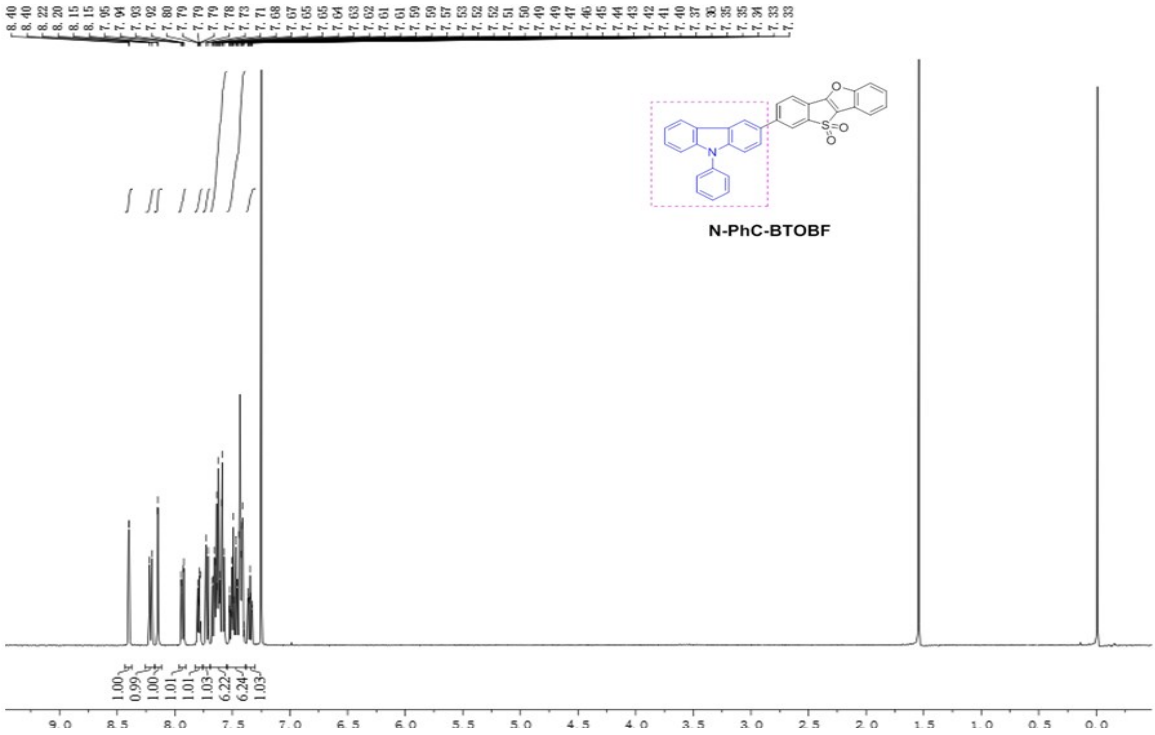
^{13}C NMR of **2f**



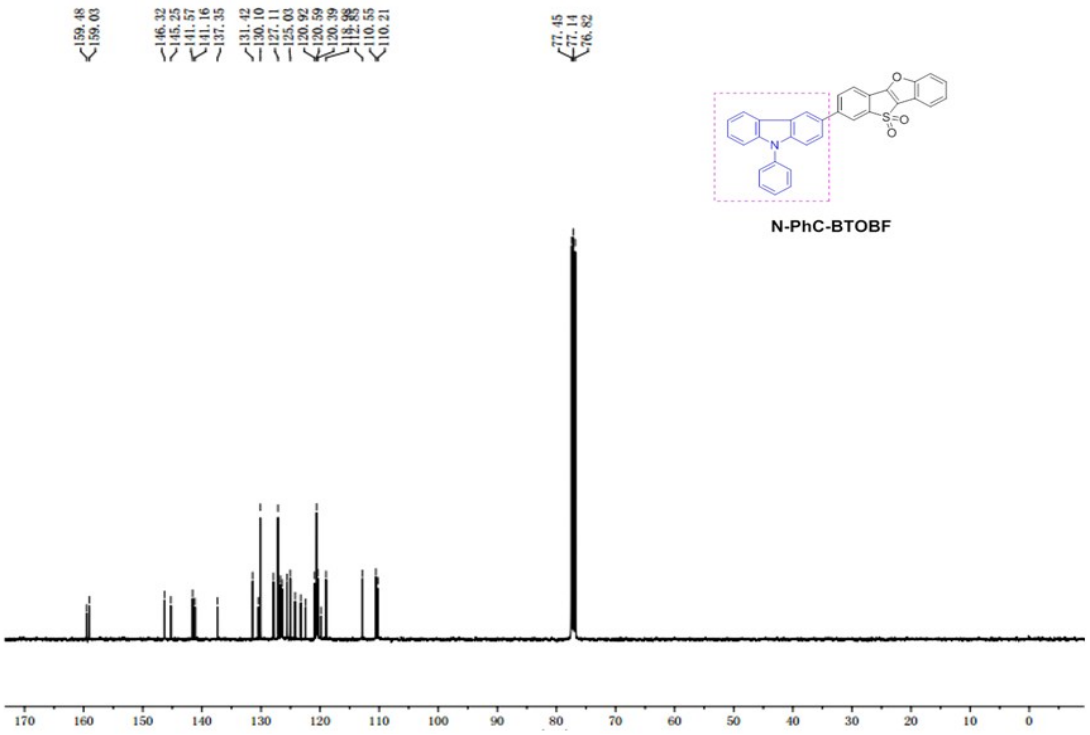
HRMS of **2f**



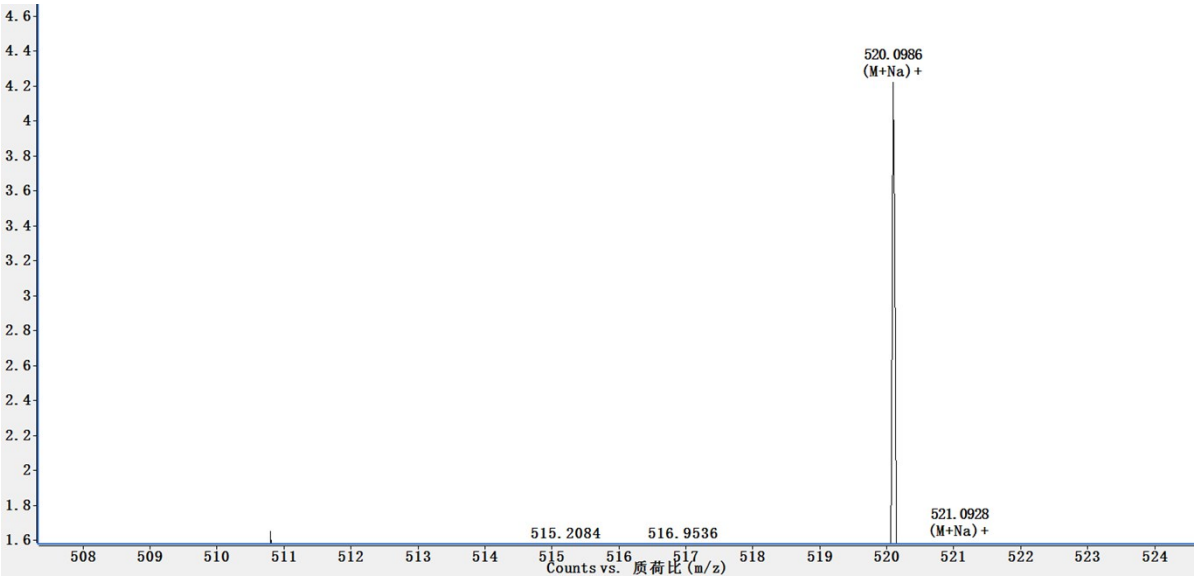
^{1}H NMR of 2-NPhCz-BTOBF



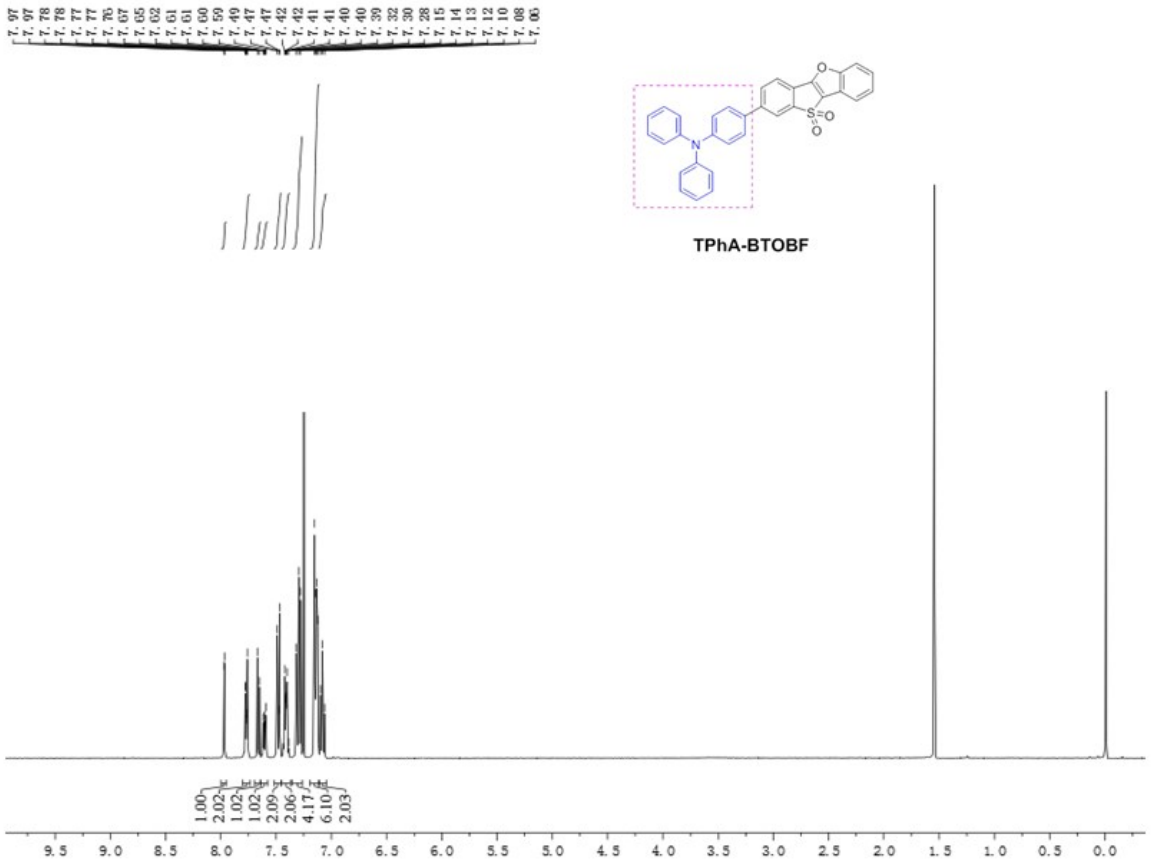
^{13}C NMR of 2-NPhCz-BTOBF



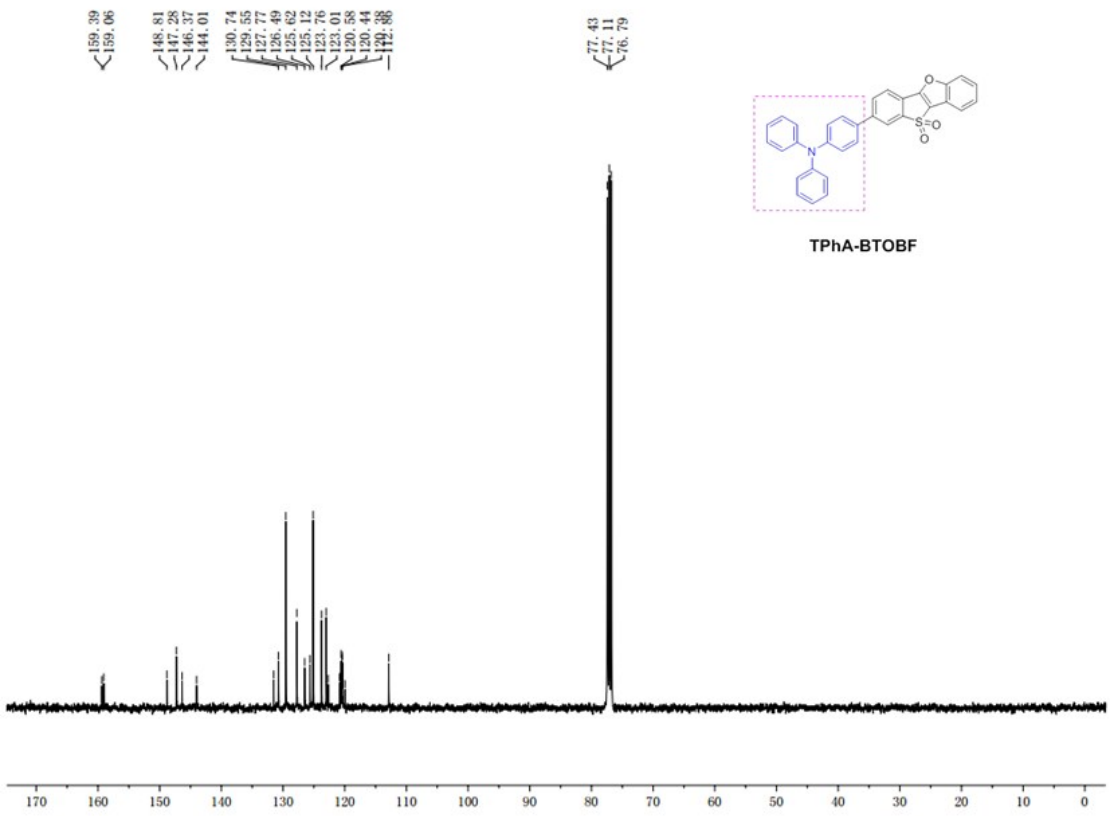
HRMS of 2-NPhCz-BTOBF



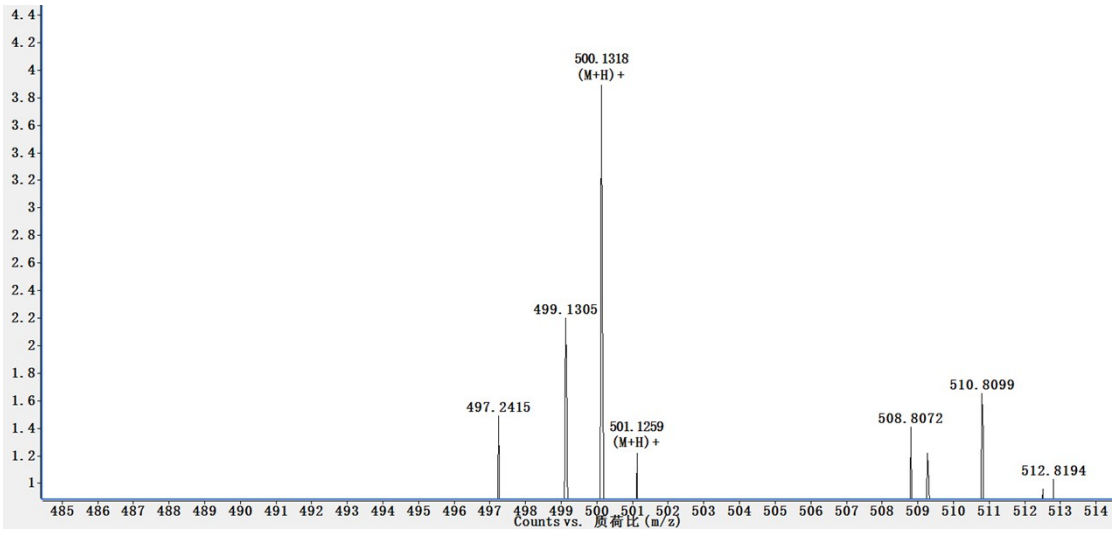
^{1}H NMR of 2-TPA-BTOBF



^{13}C NMR of 2-TPA-BTOBF



HRMS of 2-TPA-BTOBF



6. DFT calculations

All calculations were carried out using the Gaussian 09 program.[4] The geometries of substances were optimized using B3LYP/6-31G(d,p) method. The vibrational frequency was calculated at the same level to confirm whether the optimized geometry is a minimum on the potential energy surface. The optimized geometries of **2a**-**2e**, 2-NPhCz-BTOBF and 2-TPA-BTOBF were shown in follow Tables.

DFT calculation of **2a**

Atom	X	Y	Z
C	-4.01060000	1.09800000	-0.35330000
C	-4.19400000	-0.21410000	-0.82810000
C	-3.12390000	-1.11070000	-0.89370000
C	-1.88090000	-0.66700000	-0.47740000
C	-1.69860000	0.65150000	-0.00070000
C	-2.75250000	1.54130000	0.06600000
S	-0.57000000	-1.42490000	-0.44490000
C	0.31010000	-0.36080000	0.09850000
C	-0.31010000	0.80090000	0.34940000
C	1.69870000	-0.21150000	0.44870000
C	1.88090000	1.10700000	0.92550000
O	0.57000000	1.86490000	0.89290000
C	2.75260000	-1.10120000	0.38180000
C	4.01060000	-0.65800000	0.80120000
C	4.19400000	0.65410000	1.27620000
C	3.12390000	1.55070000	1.34180000
O	-0.63240000	-2.57660000	0.43380000
O	-0.14920000	-1.98910000	-1.71260000
H	-4.86900000	1.78450000	-0.31160000
H	-5.19380000	-0.53860000	-1.15220000
H	-3.26520000	-2.13660000	-1.26450000
H	-2.60690000	2.56640000	0.43740000
H	2.60700000	-2.12630000	0.01030000
H	4.86900000	-1.34450000	0.75940000
H	5.19380000	0.97860000	1.60030000
H	3.26520000	2.57660000	1.71260000

DFT calculation of **2b**

Atom	X	Y	Z
C	-4.01060000	1.09800000	-0.35330000
C	-4.19400000	-0.21410000	-0.82810000
C	-3.12390000	-1.11070000	-0.89370000
C	-1.88090000	-0.66700000	-0.47740000
C	-1.69860000	0.65150000	-0.00070000
C	-2.75250000	1.54130000	0.06600000
S	-0.57000000	-1.42490000	-0.44490000
C	0.31010000	-0.36080000	0.09850000
C	-0.31010000	0.80090000	0.34940000
C	1.69870000	-0.21150000	0.44870000
C	1.88090000	1.10700000	0.92550000
O	0.57000000	1.86490000	0.89290000
C	2.75260000	-1.10120000	0.38180000
C	4.01060000	-0.65800000	0.80120000
C	4.19400000	0.65410000	1.27620000
C	3.12390000	1.55070000	1.34180000
O	-0.63240000	-2.57660000	0.43380000
O	-0.14920000	-1.98910000	-1.71260000
F	5.04070000	-1.48180000	0.75110000
H	-4.86900000	1.78450000	-0.31160000
H	-5.19380000	-0.53860000	-1.15220000
H	-3.26520000	-2.13660000	-1.26450000
H	-2.60690000	2.56640000	0.43740000
H	2.60700000	-2.12630000	0.01030000
H	5.19380000	0.97860000	1.60030000
H	3.26520000	2.57660000	1.71260000

DFT calculation of **2c**

Atom	X	Y	Z
C	-3.55100000	1.54800000	0.08130000
C	-3.98050000	0.35970000	-0.37850000
C	-3.12610000	-0.66780000	-0.52020000
C	-1.83240000	-0.50820000	-0.20050000
C	-1.41840000	0.68820000	0.25830000
C	-2.25860000	1.72170000	0.40500000
S	-0.62300000	-1.83820000	-0.35790000
C	0.43330000	-0.52860000	0.26880000
C	-0.11090000	0.65990000	0.52160000
C	1.71760000	-0.37480000	0.59040000
C	1.78200000	0.90390000	0.99970000
O	0.69290000	1.48620000	0.94930000
C	2.78220000	-1.18220000	0.56780000
C	3.95680000	-0.67160000	0.97870000
C	4.03300000	0.60730000	1.39430000
C	2.95280000	1.40870000	1.41190000
O	-0.82500000	-2.85730000	0.66230000
O	-0.31910000	-2.11350000	-1.75510000
F	5.04070000	-1.43180000	0.97550000
Cl	-4.66400000	2.85730000	0.25730000
H	-5.04070000	0.21250000	-0.64570000
H	-3.49160000	-1.63680000	-0.89830000
H	-1.88690000	2.68770000	0.78350000
H	2.69650000	-2.22520000	0.22580000
H	5.00450000	1.00800000	1.72950000
H	3.02490000	2.45320000	1.75510000

DFT calculation of **2d**

Atom	X	Y	Z
C	-4.12790000	1.48810000	-0.19980000
C	-4.48300000	0.27470000	-0.65500000
C	-3.57300000	-0.70680000	-0.77050000
C	-2.29640000	-0.47270000	-0.42790000
C	-1.95580000	0.74850000	0.02640000
C	-2.85420000	1.73510000	0.14620000
S	-1.01410000	-1.73660000	-0.54830000
C	-0.04300000	-0.36570000	0.08470000
C	-0.65440000	0.79430000	0.31500000
C	1.22460000	-0.14150000	0.42950000
C	1.21370000	1.14170000	0.82690000
O	0.09680000	1.66500000	0.75000000
C	2.32890000	-0.89340000	0.43460000
C	3.47460000	-0.32790000	0.86160000
C	3.46660000	0.95970000	1.26490000
C	2.34910000	1.70780000	1.25600000
O	-1.18130000	-2.75730000	0.47670000
O	-0.66920000	-2.01000000	-1.93630000
C	4.76300000	-1.11620000	0.89490000
H	-4.88500000	2.28510000	-0.10990000
H	-5.53210000	0.08260000	-0.93660000
H	-3.87880000	-1.69740000	-1.14550000
H	-2.55710000	2.72830000	0.52010000
H	2.28900000	-1.94080000	0.09830000
H	4.40680000	1.41790000	1.61540000
H	2.36270000	2.75730000	1.59090000
H	4.63680000	-2.15920000	0.52780000
H	5.53210000	-0.62740000	0.25440000
H	5.15420000	-1.17280000	1.93630000

DFT calculation of **2e**

Atom	X	Y	Z
C	-3.38750000	2.64070000	-2.56260000
C	-4.21840000	1.61300000	-2.80490000
C	-3.93450000	0.38090000	-2.35070000
C	-2.80970000	0.17500000	-1.64760000
C	-1.98690000	1.21510000	-1.41290000
C	-2.25910000	2.44800000	-1.86060000
S	-2.35760000	-1.44630000	-0.99730000
C	-0.96440000	-0.47600000	-0.41390000
C	-0.92780000	0.82290000	-0.70320000
C	0.14590000	-0.68400000	0.29310000
C	0.71690000	0.53000000	0.33800000
O	0.06340000	1.39570000	-0.25480000
C	0.68800000	-1.75760000	0.87300000
C	1.85510000	-1.59470000	1.52730000
C	2.44350000	-0.37730000	1.58580000
C	1.87480000	0.69160000	0.99140000
O	-3.21220000	-1.82640000	0.11880000
O	-1.94160000	-2.34780000	-2.06240000
H	-3.63260000	3.64730000	-2.94120000
H	-5.14280000	1.78230000	-3.38250000
H	-4.62550000	-0.45300000	-2.55720000
H	-1.57420000	3.28730000	-1.65850000
H	0.17700000	-2.73130000	0.80420000
C	2.44370000	-2.64480000	2.12950000
C	3.60470000	-2.49800000	2.78530000
H	2.33470000	1.69280000	1.02720000
C	4.18830000	-1.29270000	2.84410000
C	3.60830000	-0.24060000	2.24680000
H	1.98330000	-3.64730000	2.09600000
H	4.07860000	-3.36510000	3.27520000
H	5.14280000	-1.16800000	3.38250000
H	4.11090000	0.73980000	2.31130000

DFT calculation of 2-NPhCz-BTOBF

Atom	X	Y	Z
C	0.66420000	1.27880000	2.53410000
C	0.35340000	0.71400000	1.34230000
C	1.42280000	0.32100000	0.60920000
C	2.69390000	0.47750000	1.01430000
C	2.93470000	1.04870000	2.20460000
C	1.92160000	1.45280000	2.97420000
S	4.10840000	-0.05260000	0.02600000
C	4.96730000	0.61510000	1.45400000
C	4.24330000	1.12520000	2.44750000
C	6.22790000	0.76320000	1.86000000
C	6.09890000	1.35280000	3.06150000
O	4.92120000	1.55180000	3.38000000
C	7.41390000	0.45670000	1.32620000
C	8.50580000	0.76210000	2.04840000
C	8.39500000	1.34930000	3.25480000
C	7.19240000	1.65070000	3.77670000
O	4.21730000	-1.50450000	0.00010000
O	4.29510000	0.80940000	-1.13270000
C	-0.93140000	0.54780000	0.91780000
C	-1.25760000	-0.01460000	-0.26670000
C	-2.53160000	-0.17330000	-0.65220000
C	-3.60200000	0.16730000	0.07830000
C	-3.28640000	0.79700000	1.22320000
C	-2.01090000	0.95830000	1.62080000
N	-4.70410000	-0.10260000	-0.53560000
C	-4.36150000	-0.61470000	-1.67000000
C	-5.90200000	0.10070000	-0.10160000
C	-6.97450000	0.25660000	-0.91090000
C	-8.22670000	0.47110000	-0.47530000
C	-8.48240000	0.53870000	0.83600000
C	-5.04860000	-1.18300000	-2.68190000
C	-4.42900000	-1.66860000	-3.77170000
C	-3.09270000	-1.63980000	-3.87490000
C	-2.37220000	-1.14670000	-2.85840000
C	-3.02280000	-0.66770000	-1.78890000
C	-7.45690000	0.38920000	1.68180000
C	-6.21630000	0.18080000	1.21150000
H	-0.09250000	1.63950000	3.24530000
H	1.33030000	-0.15710000	-0.37530000
H	2.12100000	1.91840000	3.95390000

H	7.48850000	-0.02530000	0.33890000
H	9.50540000	0.52610000	1.64570000
H	9.30720000	1.58760000	3.82780000
H	7.10500000	2.12980000	4.76490000
H	-0.50580000	-0.36720000	-0.98220000
H	-4.03870000	1.26480000	1.87290000
H	-1.91780000	1.49440000	2.57700000
H	-6.87970000	0.31960000	-2.00290000
H	-9.05010000	0.62190000	-1.19470000
H	-9.50540000	0.71220000	1.20770000
H	-6.13490000	-1.34030000	-2.66990000
H	-5.01990000	-2.12980000	-4.58200000
H	-2.59140000	-2.05510000	-4.76490000
H	-1.27300000	-1.15990000	-2.91890000
H	-7.64560000	0.41060000	2.76900000
H	-5.48220000	-0.02170000	2.00250000

DFT calculation of 2-TPA-BTOBF

Atom	X	Y	Z
C	0.00850000	3.22520000	1.17460000
C	-0.17490000	1.91310000	0.69990000
C	0.89510000	1.01650000	0.63420000
C	2.13810000	1.46020000	1.05050000
C	2.32040000	2.77870000	1.52720000
C	1.26660000	3.66850000	1.59400000
S	3.44910000	0.70240000	1.08310000
C	4.32910000	1.76640000	1.62650000
C	3.70900000	2.92810000	1.87740000
C	5.71770000	1.91570000	1.97670000
C	5.90000000	3.23420000	2.45340000
O	4.58900000	3.99210000	2.42090000
C	6.77160000	1.02600000	1.90980000
C	8.02960000	1.46920000	2.32920000
C	8.21310000	2.78130000	2.80410000
C	7.14300000	3.67790000	2.86970000
O	3.38660000	-0.44940000	1.96170000
O	3.86980000	0.13810000	-0.18460000
C	-1.39020000	1.51870000	0.30600000
C	-2.36840000	2.46710000	0.00720000
C	-3.63630000	2.05560000	-0.40360000
C	-3.92590000	0.69580000	-0.51570000

C	-2.94770000	-0.25260000	-0.21700000
C	-1.67980000	0.15890000	0.19390000
N	-5.07660000	0.32230000	-0.88860000
C	-5.96450000	1.18310000	-1.15970000
C	-5.33950000	-0.91190000	-0.99040000
C	-5.84710000	-1.42060000	-2.18580000
C	-6.13690000	-2.78040000	-2.29780000
C	-5.91880000	-3.63150000	-1.21450000
C	-7.23370000	1.07890000	-0.59060000
C	-8.21190000	2.02720000	-0.88950000
C	-7.92090000	3.07970000	-1.75730000
C	-6.65180000	3.18400000	-2.32630000
C	-5.67350000	2.23560000	-2.02750000
C	-5.41110000	-3.12290000	-0.01910000
C	-5.12150000	-1.76300000	0.09300000
H	-0.85000000	3.91170000	1.21640000
H	0.75380000	-0.00940000	0.26340000
H	1.41220000	4.69360000	1.96530000
H	6.62610000	0.00090000	1.53820000
H	8.88810000	0.78270000	2.28740000
H	9.21290000	3.10580000	3.12820000
H	7.28430000	4.70390000	3.24050000
H	-2.13990000	3.53950000	0.09550000
H	-4.40780000	2.80350000	-0.63920000
H	-3.17610000	-1.32500000	-0.30550000
H	-0.90830000	-0.58900000	0.42950000
H	-6.01900000	-0.74940000	-3.04020000
H	-6.53730000	-3.18160000	-3.24050000
H	-6.14730000	-4.70390000	-1.30290000
H	-7.46310000	0.24890000	0.09380000
H	-9.21290000	1.94500000	-0.44080000
H	-8.69240000	3.82760000	-1.99290000
H	-6.42230000	4.01410000	-3.01060000
H	-4.67260000	2.31770000	-2.47630000
H	-5.23910000	-3.79410000	0.83520000
H	-4.72110000	-1.36180000	1.03570000

7. References

1. W. Ma, J. Huang, C. Li, Y. Jiang, B. Li, T. Qi and X. Zhu, *RSC Adv.*, 2019, **9**, 7123.
2. J. Guo, S. Hu, W. Luo, R. Hu, A. Qin, Z. Zhao and B. Z. Tang, *Chem. Commun. (Camb)*, 2017, **53**, 1463.
3. A. Fukazawa, H. Oshima, S. Shimizu, N. Kobayashi and S. Yamaguchi, *J. Am. Chem. Soc.*, 2014, **136**, 8738.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, revision D; Gaussian, Inc.: Wallingfor, CT, 2009.*