

# Novel Oligo-9,9'-spirobifluorenes through *ortho*-linkage as Full Hydrocarbon Host for Highly Efficient Phosphorescent OLEDs

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**General Information.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were measured on Varian Unity 300 MHz spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on Vario EL-III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from  $30\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$  under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of  $15\text{ }^\circ\text{C min}^{-1}$  from  $25\text{ }^\circ\text{C}$  to  $700\text{ }^\circ\text{C}$ . UV-Vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer.

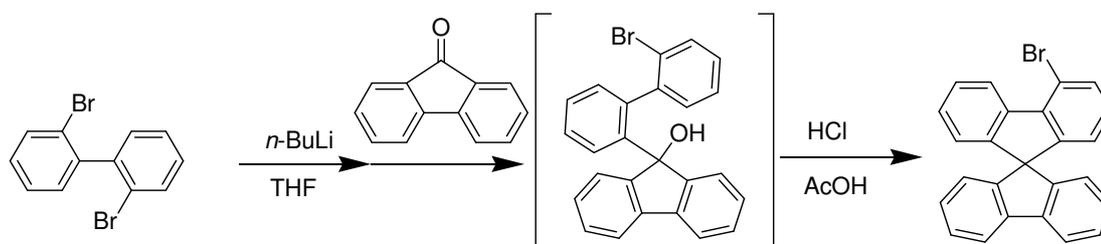
*n*-Butyllithium in hexane was purchased from Alfa Asia Chemical Co. All reagents commercial available were used as received unless otherwise stated. The solvents (THF, diethyl ether, dichloromethane) were purified by conventional procedure and distilled under dry argon before using. All reactions were carried out using Schlenk

technique in an argon atmosphere.

***OLED Fabrication and measurement.*** The hole-injection  $\text{MoO}_3$ , hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), hole-blocking material BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and electron-transporting materials  $\text{Alq}_3$  (tris(8-hydroxyquinoline)aluminum) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of  $10\Omega/\square$  was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/ $\text{O}_3$  for 2 min. Then the sample was transferred to the deposition system. 10 nm of  $\text{MoO}_3$  was firstly deposited to ITO substrate, followed by 40 nm NPB, 30 nm emissive layer, 10 nm BCP, and 30 nm  $\text{Alq}_3$ . Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminum were sequentially deposited onto the substrate in the vacuum of  $10^{-6}$  Torr to construct the device. The I-V-B of EL devices was measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

### ***Synthesis details***

#### **Synthesis of 4-bromo-9,9'-spirobifluorene (1)**

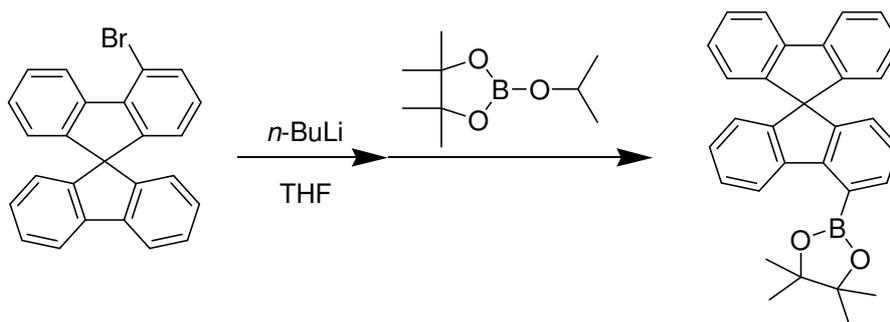


A solution of 2,2'-dibromo-biphenyl (3.12 g, 10 mmol) in THF (50 mL) was treated

with *n*-BuLi (4 mL, 2.5 M in hexane, 10 mmol) under argon at -90 °C. The mixture was stirred at -90 °C for 30 min, and a solution of fluorenone (1.80 g, 10 mmol) in THF (25 mL) was added dropwise. The resulting mixture was stirred at -90 °C for 30 min and at room temperature for 12 h. The organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using 1:1 CH<sub>2</sub>Cl<sub>2</sub>/petroleum as eluent to afford 9-(2'-bromo-biphenyl-2-yl)-9*H*-fluoren-9-ol. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.40 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.301-7.04 (m, 9H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 6.9 Hz, 1H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.47 (t, *J* = 7.8 Hz, 1H), 5.79 (d, *J* = 7.8 Hz, 1H), 2.18 (s, 1H); Anal. Calcd. for C<sub>25</sub>H<sub>17</sub>BrO (%): C, 72.65; H, 4.15. Found: C, 72.21; H, 3.70. MS (EI) *m/z* 413.8 [M<sup>+</sup>].

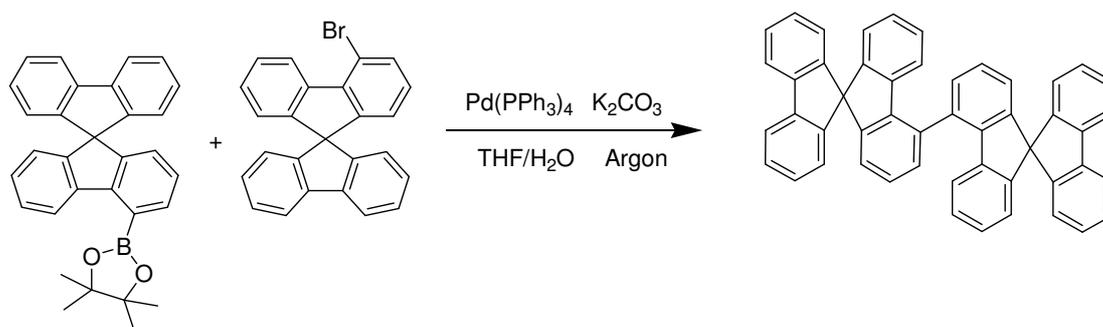
A mixture of 9-(2'-bromo-biphenyl-2-yl)-9*H*-fluoren-9-ol, concentrated aqueous HCl (6 mL) and acetic acid (70 mL) was heated at reflux for 2 h. The mixture was then cooled, diluted with water, and extracted with CHCl<sub>3</sub>. The combined organic extracts were washed with saturated aqueous NaHCO<sub>3</sub>, water, and brine. After the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using 1:2 CH<sub>2</sub>Cl<sub>2</sub>/petroleum as the eluent to give a white solid (3.32 g, yield: 83 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.69 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45-7.35 (m, 3H), 7.20-7.10 (m, 3H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.92-6.73 (m, 3H), 6.67 (d, *J* = 6.9 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 151.76, 149.10, 148.51, 141.88, 141.11, 140.07, 132.83, 128.79, 128.66, 128.14, 127.67, 124.19, 124.07, 123.71, 123.17, 120.28, 120.24, 116.89, 66.03 (spiro carbon). Anal. Calcd. for C<sub>25</sub>H<sub>15</sub>Br (%): C, 75.96; H, 3.82. Found: C, 75.51; H, 3.96. MS (GC-MS) *m/z* 394 [M<sup>+</sup>].

### Synthesis of 4-(9,9-spirobifluorenyl) pinacol boronate (2)



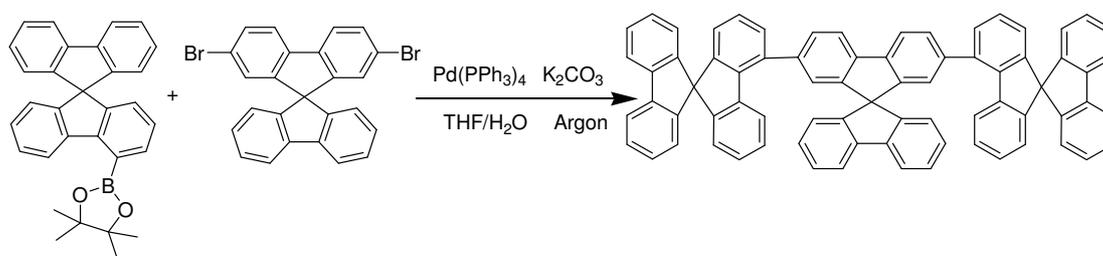
To a solution of 4-bromo-9,9'-spirobifluorene (1.6 g, 4.1 mmol) in THF (40 ml) was added *n*-BuLi (2 ml, 2.5 M in hexane, 5 mmol) dropwise at -78 °C. After stirring for 1 hour at -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.1 ml, 5.5 mmol) was added in one portion. The resulting mixture was stirred for another 12 hours at -78 °C and gradually warmed to room temperature. The reaction was quenched with water and extracted with dichloromethane. The crude product was purified by column chromatography on silica gel using 1:3 CH<sub>2</sub>Cl<sub>2</sub>/petroleum as eluent to afford product as a white solid. (1.3 g, yield: 72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.79 (d, *J* = 8.1 Hz, 1H), 7.83-7.78 (m, 3H), 7.36-7.31 (m, 3H), 7.25-7.08 (m, 4H), 6.77-6.67 (m, 4H), 1.50 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 149.35, 149.20, 149.02, 146.63, 143.19, 141.99, 136.00, 128.00, 127.91, 127.81, 126.91, 124.29, 124.09, 123.90, 120.15, 84.39, 65.82 (spiro carbon), 25.26. Anal. Calcd. for C<sub>31</sub>H<sub>27</sub>BO<sub>2</sub> (%): C, 84.17; H, 6.15. Found: C, 84.41; H, 6.20. MS (GC-MS) *m/z* 442 [M<sup>+</sup>].

### Synthesis of 4-(9,9'-spirofluorenyl-4-yl)-9,9'-spirofluorene (44BSF, 3)



A mixture of 4-bromo-9,9'-spirobifluorene (434 mg, 1.1 mmol), 4-(9,9'-spirobifluorenyl) pinacol boronate (486 mg, 1.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (65 mg, 5 % mmol) and potassium carbonate (1.9 g, 14 mmol) in 21 ml of THF and 7 ml of distilled water in a 100 ml round bottom was refluxed for 2 days under argon. The mixture was extracted with chloroform. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using 1: 4 ethyl acetate/petroleum as eluent to afford the product 44BSF (0.50 g, yield: 72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.90-7.88 (m, 4H), 7.48-7.38 (m, 6H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.21-7.14 (m, 4H), 7.01-6.99 (m, 4H), 6.91 (d, *J* = 7.2 Hz, 4H), 6.83 (d, *J* = 6.6 Hz, 2H), 6.71-6.63 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 149.86, 149.49, 149.20, 148.84, 142.30, 141.99, 141.92, 139.90, 135.77, 128.92, 128.31, 128.17, 127.97, 127.70, 124.56, 124.22, 124.11, 123.86, 122.75, 120.41, 120.31, 66.09 (spiro carbon). Anal. Calcd. for C<sub>50</sub>H<sub>30</sub> (%): C, 95.21; H, 4.79. Found: C, 95.10; H, 5.11. MS (EI) *m/z* 630.1 [M<sup>+</sup>].

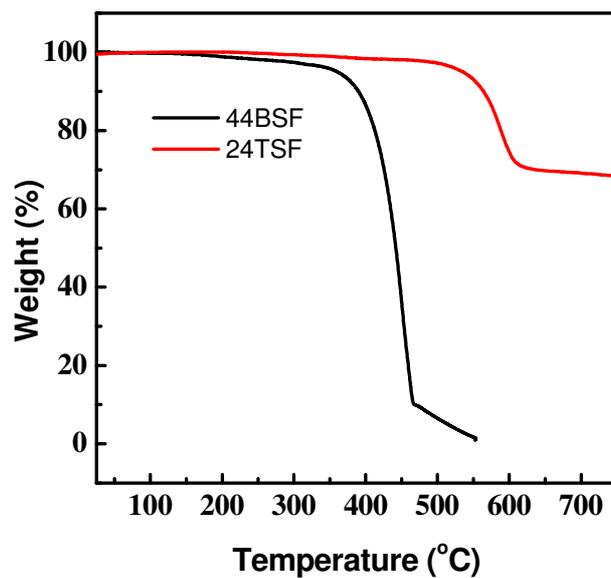
#### Synthesis of 2,7-di(9,9'-spirofluorenyl-4-yl)- 9,9'-spirofluorene (24TSF, 4)



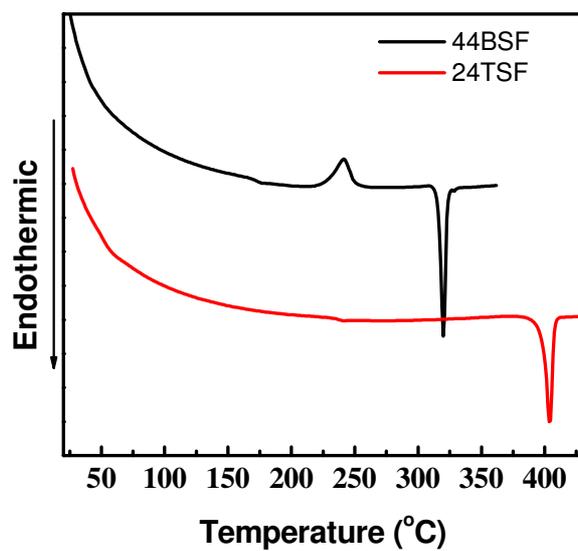
24TSF was synthesized according to the similar procedure for 44BSF by using 2,7-dibromo-9,9'-spirobifluorene (261 mg, 0.55 mmol), 4-(9,9'-spirobifluorenyl) pinacol boronate (486 mg, 1.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (65 mg, 5 % mmol) and potassium carbonate (1.9 g, 14 mmol) in 21 ml of THF and 7 ml of distilled water. A white powder was obtained (0.42 g, yield: 81 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.16 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 8H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.38-7.67 (m, 8H), 7.17-7.01 (m, 12H), 7.96-6.84 (m, 4H), 6.74 (m, 4H), 6.62 (t, *J* = 6.6 Hz, 4H); <sup>13</sup>C

NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 149.20, 148.89, 148.79, 148.59, 141.45, 141.07, 140.72, 140.26, 138.16, 137.31, 129.64, 129.02, 127.63, 127.56, 127.40, 127.13, 126.99, 126.78, 125.07, 124.01, 123.80, 123.47, 122.78, 122.62, 120.20, 119.69, 65.93, 65.25 (spiro carbon). Anal. Calcd. for C<sub>75</sub>H<sub>44</sub> (%): C, 95.31; H, 4.69. Found: C, 95.56; H, 4.90. MS (EI)  $m/z$  944.7 [M<sup>+</sup>].

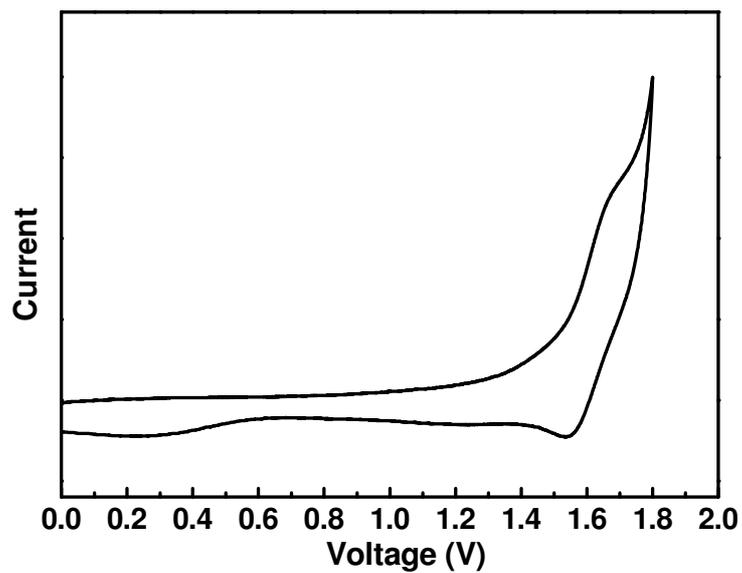
***X-Ray structural analysis.*** Single-crystal X-ray diffraction data were obtained from a Bruker AXS Smart CCD diffractometer using a graphite-monochromated MoK $\alpha$  ( $\lambda=0.71073\text{\AA}$ ) radiation. The data were collected using the  $\omega/2\theta$  scan mode and corrected for Lorentz and polarization effects as well as the absorption during data reduction using Shelxtl 97 software. Crystal data for 44BSF: C<sub>50</sub>H<sub>30</sub>, orthorhombic, Ccc2, cell parameters:  $a = 14.1090(12)\text{\AA}$ ,  $b = 33.689(3)\text{\AA}$ ,  $c = 7.2290(6)\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3436.1(5)\text{\AA}^3$ ,  $Z = 4$ ,  $M_r = 630.74$ ,  $D_c = 1.219\text{ g/cm}^3$ ,  $F(000) = 1320$ ,  $\mu = 0.069\text{ mm}^{-1}$ .



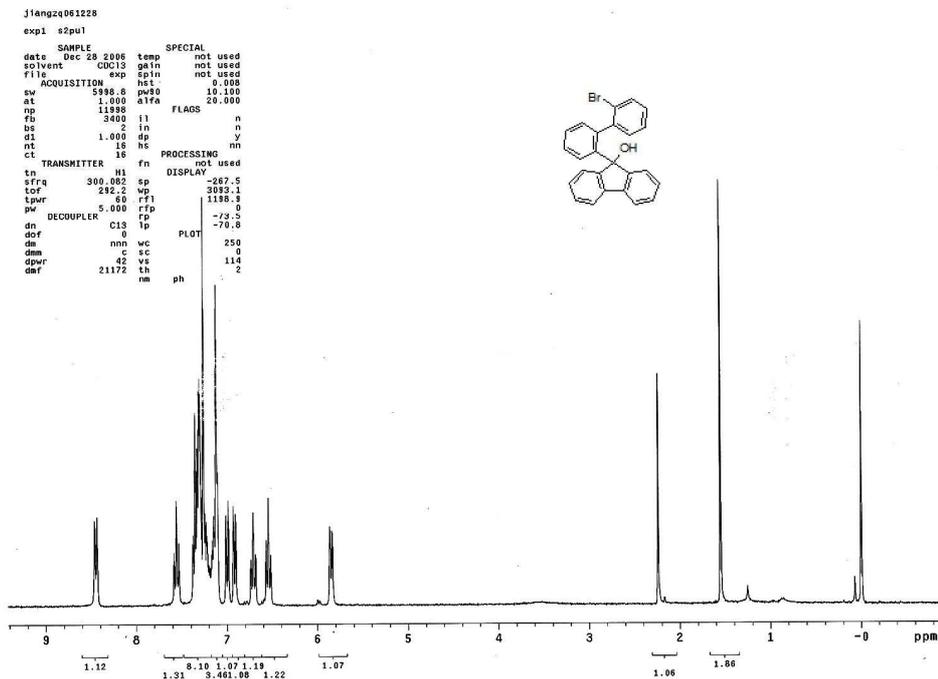
**Figure S1.** TGA thermograms of 44BSF and 24TSF.



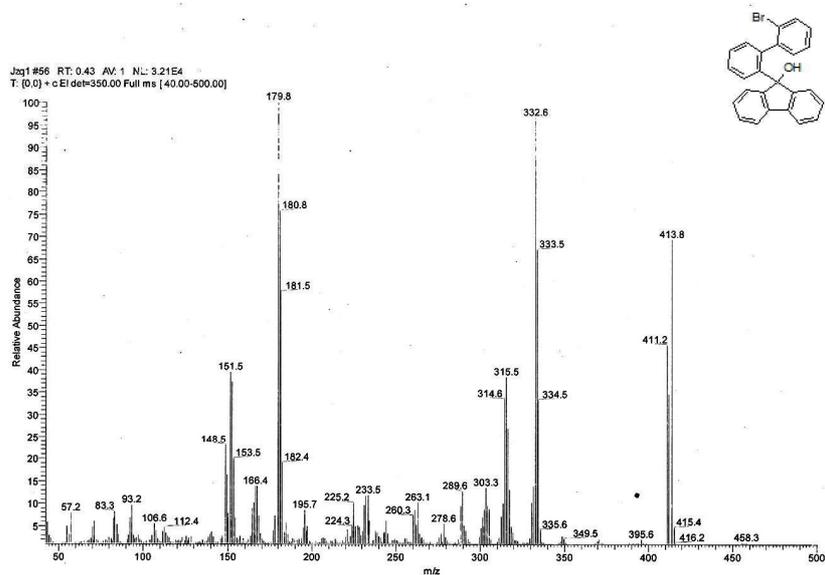
**Figure S2.** DSC thermograms of 44BSF and 24TSF.



**Figure S3.** Cyclic voltammogram of 24TSF in 0.1 M/TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> (internal standard, ferrocene/ferrocenium ion (Fc/Fc<sup>+</sup>) redox couple,  $E_{1/2}$  = 0.50 V).

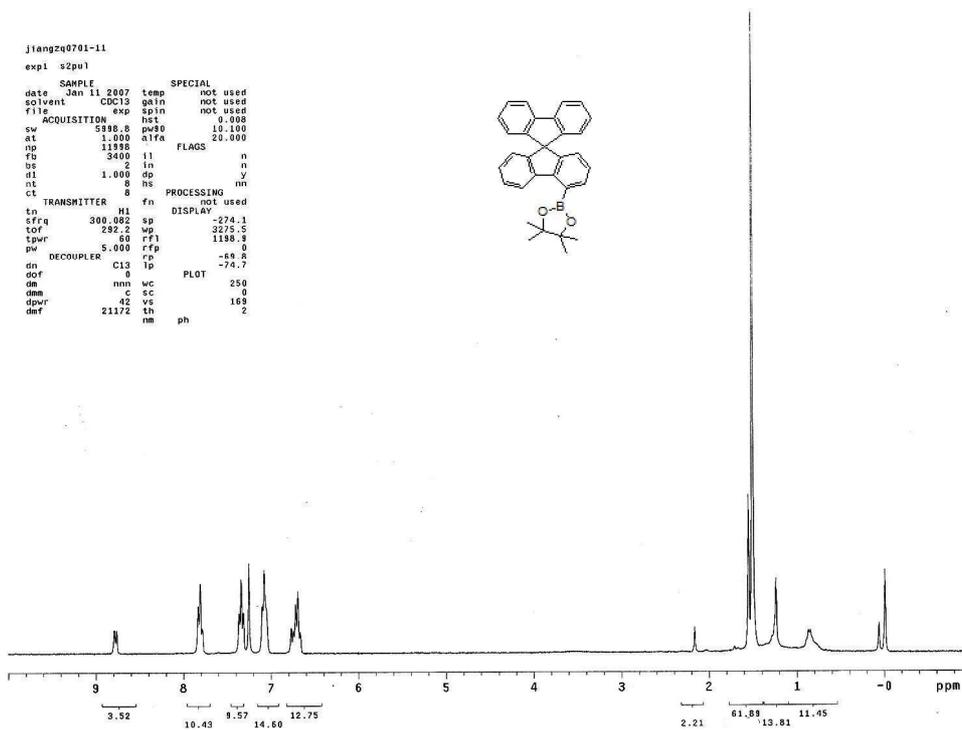


$^1\text{H}$ NMR spectrum of 9-(2'-bromo-biphenyl-2-yl)-9H-fluoren-9-ol



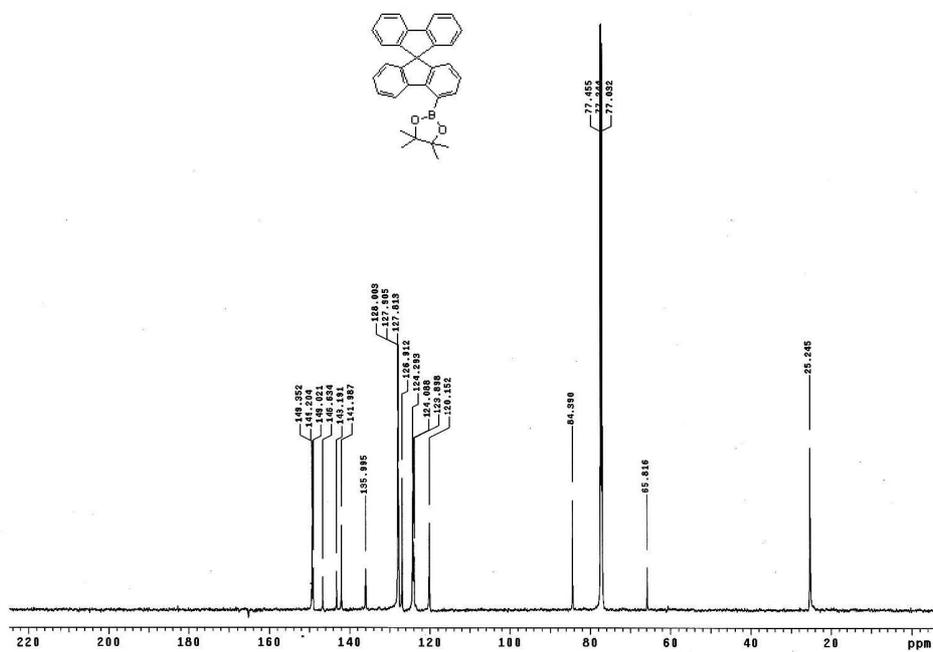
MS spectrum of 9-(2'-bromo-biphenyl-2-yl)-9H-fluoren-9-ol



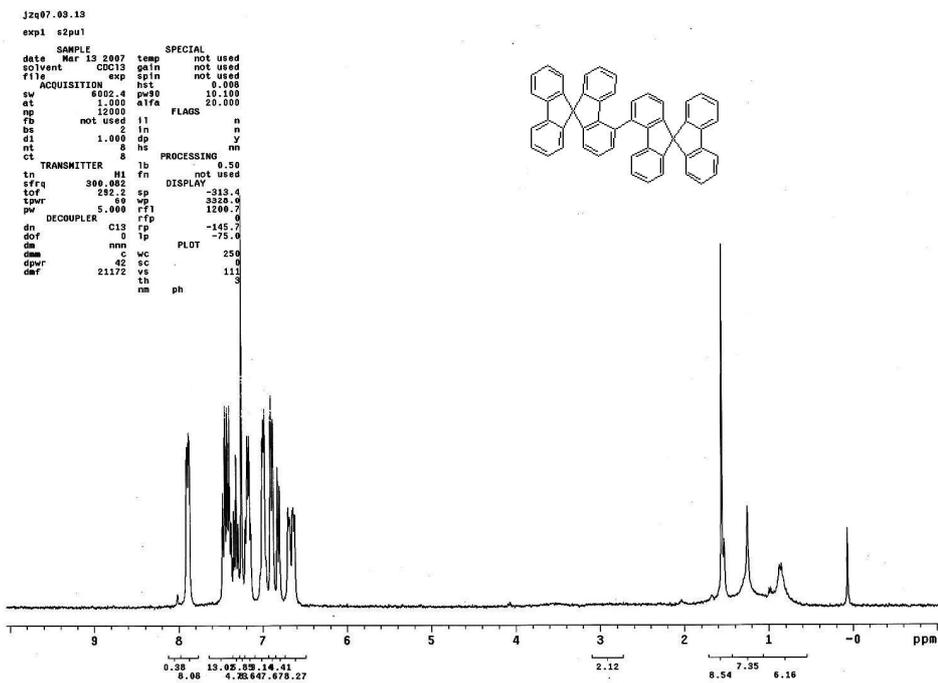


<sup>1</sup>H NMR spectrum of 2

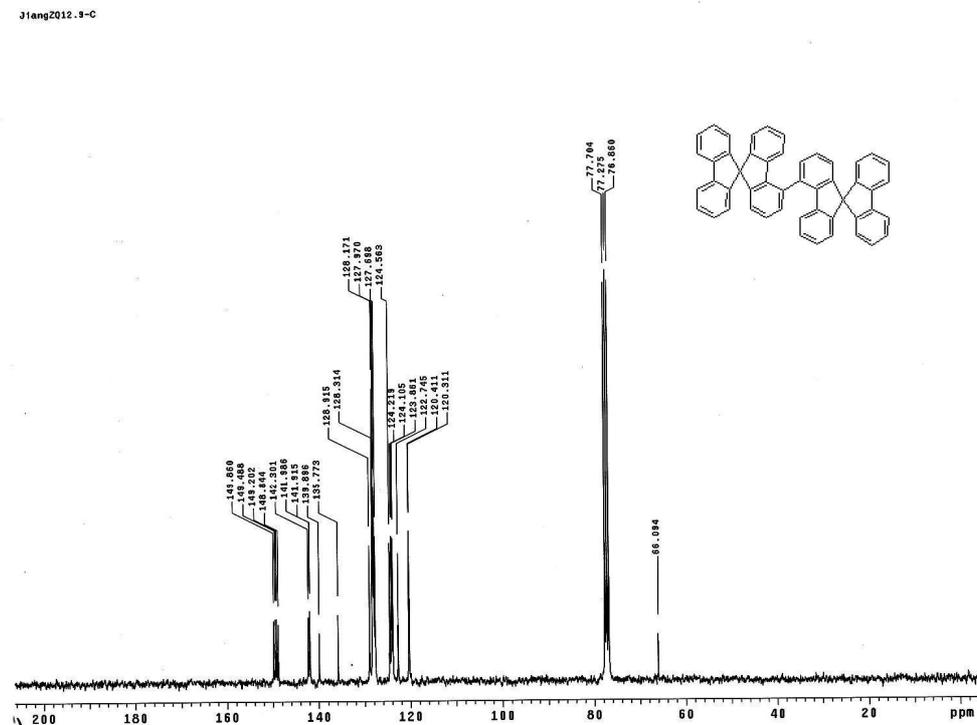
FanC4\_10-C



<sup>13</sup>C NMR spectrum of 2

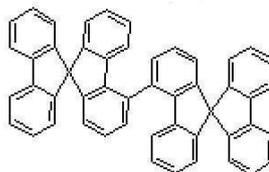
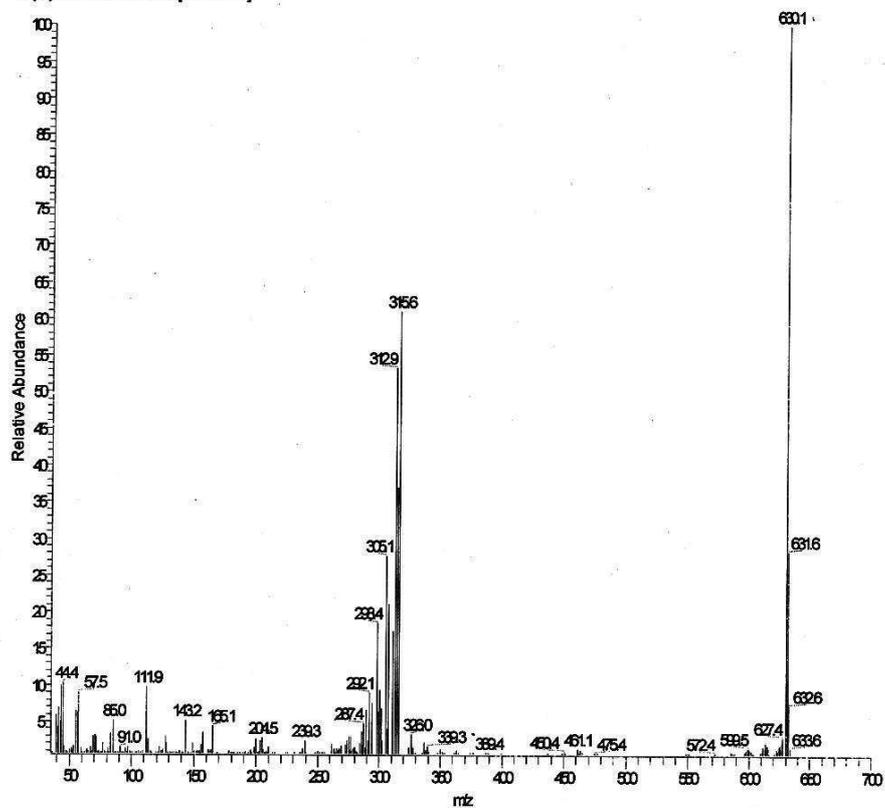


<sup>1</sup>H NMR spectrum of 3



<sup>13</sup>C NMR spectrum of 3

Y064281 RT: 3.07 A/1 N: 15385  
T: (0) +c8d4-6600FUms[30007000]

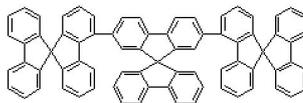


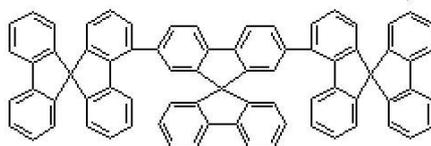
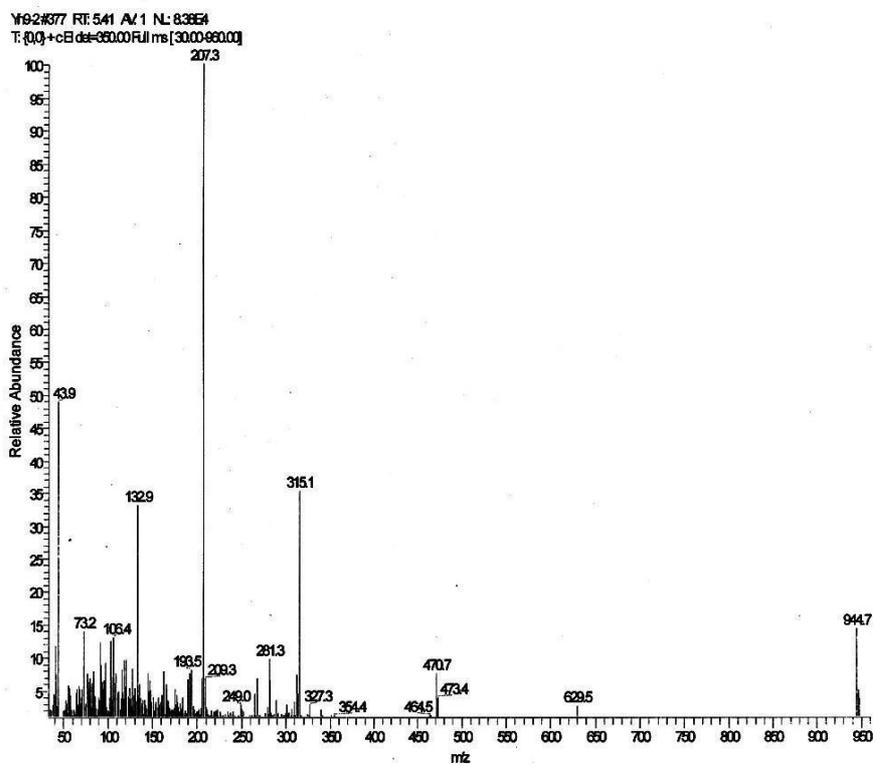
MS spectrum of 3

Jiangzq07-05-24

exp1 s2pu1

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| solvent     | CDCl3       | gain       | not used |
| file        |             | spin       | not used |
| ACQUISITION |             | ST         |          |
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| at          | 1.000       | pw90       | 10.000   |
| mp          | 10000       | alpha      | 20.000   |
| fb          | 3400        | l1         | n        |
| bs          | 2           | l2         | n        |
| dl          | 1.000       | sp         | y        |
| nt          | 8           | hs         | n        |
| ct          | 8           | PROCESSING |          |
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| effq        | 300.082     | not        | used     |
| topf        | 532.2       | sd         | -262.1   |
| tpwr        | 60          | wp         | 2837.8   |
| pw          | 5.000       | rfl        | 1200.7   |
| DECOUPLER   |             | rfp        |          |
| dn          | C13         | rp         | -109.5   |
| dof         | 0           | lp         | -68.8    |
| dm          | nm          | PLOT       |          |
| smm         | c           | wc         | 250      |
| dpwr        | 42          | sc         | 0        |
| dmr         | 21172       | vs         | 68       |
|             |             | th         | 4        |
|             |             | nm         | ph       |





MS spectrum of **4**