

## Supporting Information

### Improved positive polaron stability of the p-type host for long lifetime in phosphorescent organic light-emitting diodes

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## Experimental

### General information

3,6-Dibromo-9H-carbazole, 4-dimethylaminopyridine, di-tert-butyl-dicarbonate, phenylboronic acid, 1,10-phenanthroline (Alfa), 3,6-diphenyl-9H-carbazole (GOM tech.), 2-bromodibenzo[b,d]thiophene (Sunfine Global Co. Ltd.), 4-iododibenzo[b,d]thiophene, tri-tert-butylphosphine (Inco Co.), potassium carbonate (Daejung), tetrakis(triphenylphosphine)-palladium(0), sodium tert-butoxide, copper iodide, palladium acetate (Samyoung Ino. Co), and tris(dibenzylideneacetone)dipalladium(0) (P&H tech.) were used with no further purification. Dehydrated tetrahydrofuran, o-xylene (TCI), toluene, and N,N-dimethylformamide (Duksan. Sci. Co) were used as solvents.

The UV-vis spectrum was measured by UV-vis spectrophotometer (JASCO, V-730) using a transmittance mode. The PL spectrum was obtained by using PerkinElmer, LS-55. Cyclic

voltammetry was measured by Ivium Tech., Iviumstat. The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were obtained by Bruker 300 MHz and 500 MHz NMR, respectively, using deuterated chloroform solvent.

## Synthesis

### Synthesis of tert-butyl 3,6-dibromo-9H-carbazole-9-carboxylate (P3)

Firstly, 3,6-dibromo-9H-carbazole (10 g, 30.8 mmol), 4-(dimethylamino)pyridine (0.75 g, 6.16 mmol), and di-tert-butyl dicarbonate (10.6 ml) in THF (50 ml) were refluxed under a nitrogen atmosphere for 6 h and cooled down to room temperature. By pouring methanol, tert-butyloxycarbonyl (BOC) protected - 3,6- dibromo-carbazole was precipitated. After filtering the precipitate, the filtered material was just dried without further purification.

Yield 92%, NMR (500 MHz, )  $\delta$  8.08 (d,  $J = 8.9$  Hz), 7.96 (d,  $J = 2.0$  Hz), 7.49 (dd,  $J = 8.9, 2.1$  Hz), 1.67 (s).

### Synthesis of tert-butyl 3-bromo-6-phenyl-9H-carbazole-9-carboxylate (P2)

BOC protected-3,6-dibromocarbazole (10.0 g, 23.5 mmol), phenylboronic acid (1.92g, 15.7 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.82 g, 0.71 mmol) were poured in THF (100 ml) and potassium carbonate (5.46 g, 39.5 mmol) dissolved in deionized (DI) water (40 ml) was dropped into the THF solution. The mixture was refluxed under nitrogen for overnight and cooled down to room temperature. After reaction, the solution was extracted with DI water and dichloromethane, and the organic layer was stirred with magnesium sulfate. After filtering, the filtrate was dried under vacuum by evaporator. The filtrate was purified by silica column chromatography (dichloromethane : hexane (1:9)).

Yield 38%, NMR (500 MHz, )  $\delta$  8.29 (d,  $J = 8.7$  Hz), 8.17 (d,  $J = 8.8$  Hz), 8.10 (dd,  $J = 6.1, 2.0$  Hz), 7.70 (dd,  $J = 8.7, 1.8$  Hz), 7.66 (d,  $J = 7.3$  Hz), 7.53 (ddd,  $J = 8.9, 3.3, 1.2$  Hz), 7.45 (t,  $J = 7.6$  Hz), 7.34 (dd,  $J = 10.9, 3.8$  Hz), 1.74 (s).

### Synthesis of 3',6,6'-triphenyl-9H-3,9'-bicarbazole (P1)

BOC protected 3-bromo-6-phenylcarbazole (3.7 g, 8.79 mmol), 3,6-diphenyl-9H-carbazole (3.1 g, 9.7 mmol), sodium-tert-butoxide (2.11 g, 21.9 mmol), tri-tert-butylphosphine (0.22 ml), and tris(dibenzylideneacetone)dipalladium(0) (0.24 g, 0.26 mmol) in toluene (55.5 ml) were refluxed under a nitrogen atmosphere for overnight and cooled down to room temperature. The purification method was the same as that of tert-butyl 3-bromo-6-phenyl-9H-carbazole-9-carboxylate.

Yield 42%, NMR (500 MHz, )  $\delta$  8.45 (d,  $J = 1.3$  Hz), 8.33 – 8.29 (m), 7.76 (dt,  $J = 8.5, 1.9$  Hz), 7.72 – 7.66 (m), 7.62 (dd,  $J = 8.5, 2.0$  Hz), 7.58 (d,  $J = 8.1$  Hz), 7.52 – 7.44 (m), 7.38 – 7.33 (m).

### Synthesis of 9-(dibenzo[b,d]thiophen-2-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (2-TPhDCz)

2-Bromodibenzo[b,d]thiophene (0.96 g, 3.65 mmol), BOC protected 3',6,6'-triphenyl-3,9'-bicarbazole (1.5 g, 2.68 mmol), palladium acetate (0.114 g, 0.51 mmol), sodium-tert-butoxide (0.71 g, 7.34 mmol), and tri-tert-butylphosphine (0.71 ml) in toluene (25 ml) were refluxed for 6 h and cooled down to room temperature. The purification procedure was the same as that of tert-butyl 3',6,6'-triphenyl-9H-[3,9'-bicarbazole]-9-carboxylate. After column purification using a dichloromethane : n-hexane (1 : 8) eluent, the crude product was purified by

recrystallization using toluene and hexane solvents. Finally, the final product was purified through vacuum sublimation.

Yield 68%, <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 8.45 (t, J = 1.7 Hz, 1H), 8.43 (d, J = 1.8 Hz, 1H), 8.39 (d, J = 1.4 Hz, 1H), 8.21 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.76 (dd, J = 9.7, 4.6 Hz, 2H), 7.73 (dd, J = 8.3, 1.2 Hz, 1H), 7.70 (dd, J = 8.5, 1.8 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.64 (dd, J = 8.5, 2.0 Hz, 1H), 7.56 (ddd, J = 8.1, 3.8, 1.3 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.37 – 7.34 (m, 1H). <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ 142.08, 137.32, 128.88, 128.80, 127.36, 127.32, 125.69, 112.96, 110.24. MS (HR-FAB) (m/z) : 742.2440 , [M<sup>+</sup>] calculated for C<sub>54</sub>H<sub>34</sub>N<sub>2</sub>S 742.2443

#### **Synthesis of 9-(dibenzo[b,d]thiophen-4-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (4-TPhDCz)**

4-Iododibenzo[b,d]thiophene (1.66g, 5.35 mmol), BOC protected 3',6,6'-triphenyl-3,9'-bicarbazole (1.5g, 2.68 mmol), copper iodide (0.25g, 1.34 mmol), 1,10-phenanthroline (0.24g, 1.34 mmol) and potassium carbonate (2.27g, 10.68 mmol) in DMF (15ml) were put inside a pressure tube and reacted in oil bath at 220 °C for overnight. The purification method was the same as that of 2-TPhDCz.

Yield 52%, <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 8.45 (d, J = 1.8 Hz, 1H), 8.41 (d, J = 1.2 Hz, 1H), 8.40 (dd, J = 7.1, 1.9 Hz, 1H), 8.31 (d, J = 7.3 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.76 (ddd, J = 6.4, 5.7, 4.1 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.60 (dd, J = 8.5, 2.0 Hz, 1H), 7.55 (ddd, J = 11.8, 8.9, 1.2 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 (d, J = 8.6 Hz, 1H), 7.37 – 7.31 (m, 1H). <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>) δ 143.37, 141.80, 128.85, 128.80, 127.36, 126.54, 125.68, 123.86, 123.42, 118.90. MS (HR-FAB) (m/z) : 742.2437 , [M<sup>+</sup>] calculated for C<sub>54</sub>H<sub>34</sub>N<sub>2</sub>S 742.2443

## Supporting Figures

**Fig. S1** Dihedral angle of 2-TPhDCz and 4-TPhDCz

**Fig. S2** Energy levels and chemical structures of materials fabricated device

**Fig. S3** EL spectra of device (a) 2-TPhDCz, (b) 4-TPhDCz and (c) mCBP with increasing voltage

**Fig. S4**  $^1\text{H-NMR}$  of tert-butyl 3,6-dibromo-9H-carbazole-9-carboxylate (P3)

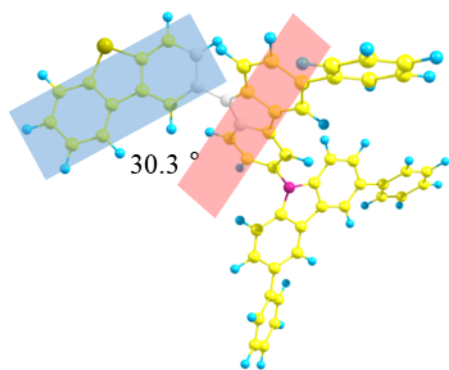
**Fig. S5**  $^1\text{H-NMR}$  of tert-butyl 3-bromo-6-phenyl-9H-carbazole-9-carboxylate (P2)

**Fig. S6**  $^1\text{H-NMR}$  of 3',6,6'-triphenyl-9H-3,9'-bicarbazole (P1)

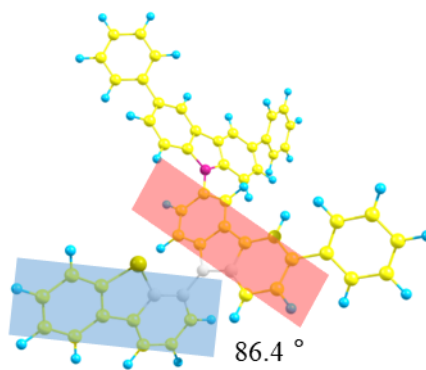
**Fig. S7**  $^1\text{H-NMR}$  (a) and  $^{13}\text{C-NMR}$  (b) of 9-(dibenzo[b,d]thiophen-2-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (2-TPhDCz)

**Fig. S8**  $^1\text{H-NMR}$  (a) and  $^{13}\text{C-NMR}$  (b) of 9-(dibenzo[b,d]thiophen-4-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (4-TPhDCz)

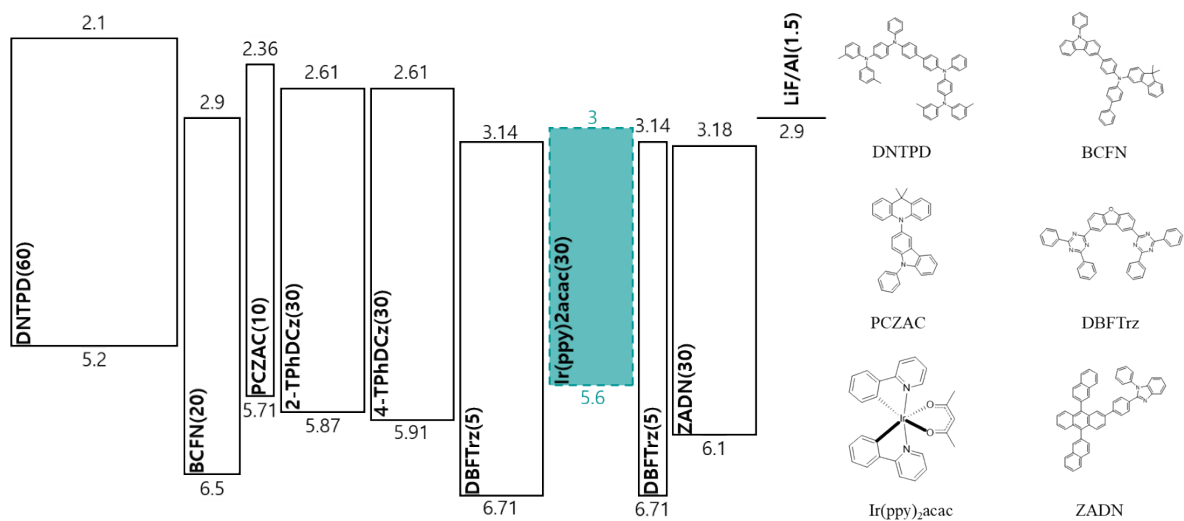
**2-TPhDCz**



**4-TPhDCz**

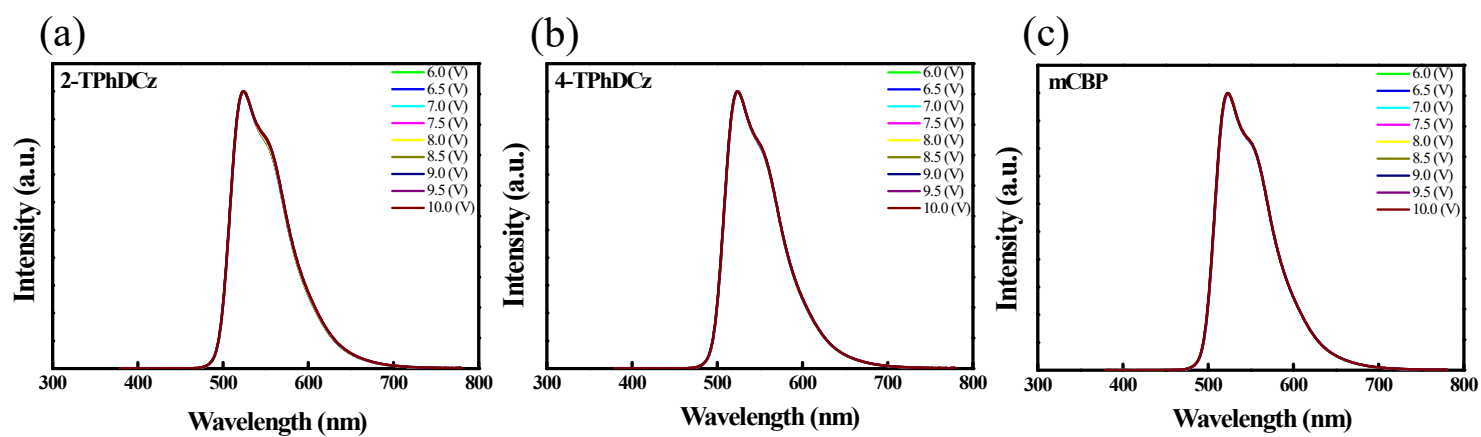


**Fig. S1** Dihedral angle of 2-TPhDCz and 4-TPhDCz



Device structure : DNTPD(60)/BCFN(20)/PCZAC(10)/P-type Host : DBFTrz :  
 Ir(ppy)<sub>2</sub>acac(30:75%:5%)/DBFTrz (5)/ZADN(30)/LiF(1.5)/Al(200)

**Fig. S2** Energy levels and chemical structures of materials fabricated device

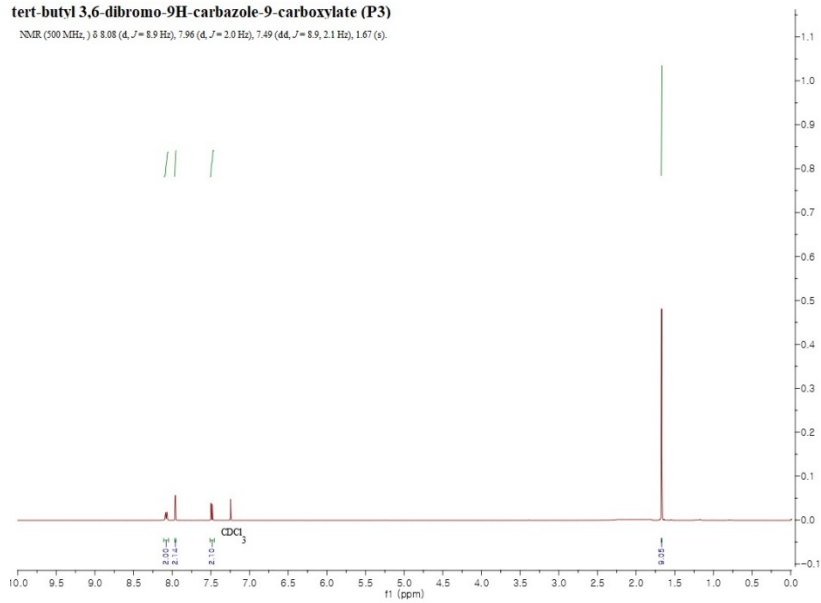


**Fig. S3** EL spectra of device (a) 2-TPhDCz, (b) 4-TPhDCz and (c) mCBP with increasing voltage



**tert-butyl 3,6-dibromo-9H-carbazole-9-carboxylate (P3)**

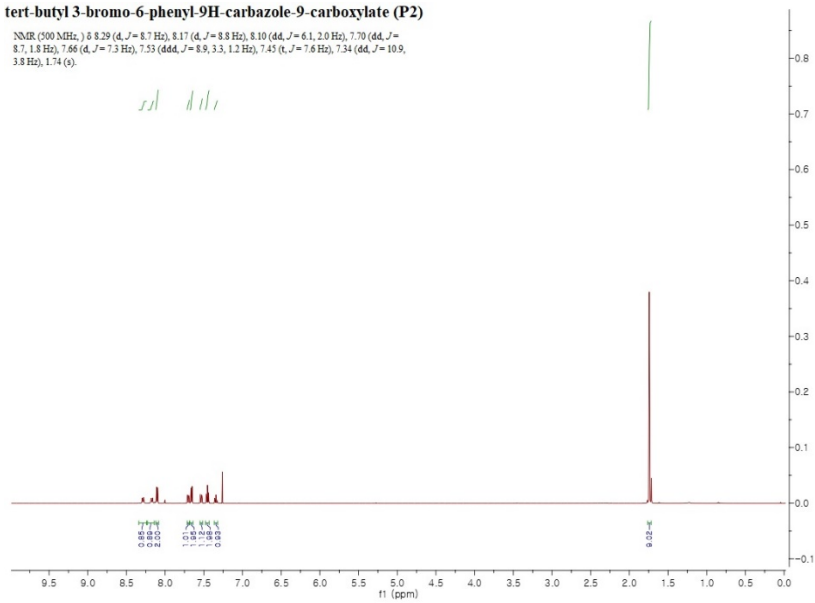
NMR (500 MHz, )  $\delta$  8.08 (d,  $J = 8.9$  Hz), 7.96 (d,  $J = 2.0$  Hz), 7.49 (dd,  $J = 8.9, 2.1$  Hz), 1.67 (s).



**Fig. S4**  $^1\text{H-NMR}$  of tert-butyl 3,6-dibromo-9H-carbazole-9-carboxylate (P3)

**tert-butyl 3-bromo-6-phenyl-9H-carbazole-9-carboxylate (P2)**

NMR (500 MHz)  $\delta$  8.29 (d,  $J=8.7$  Hz), 8.17 (d,  $J=8.8$  Hz), 8.10 (dd,  $J=6.1, 2.0$  Hz), 7.70 (dd,  $J=8.7, 1.8$  Hz), 7.56 (d,  $J=7.3$  Hz), 7.53 (ddd,  $J=8.9, 3.3, 1.2$  Hz), 7.43 (t,  $J=7.6$  Hz), 7.34 (dd,  $J=10.9, 3.8$  Hz), 1.74 (s).



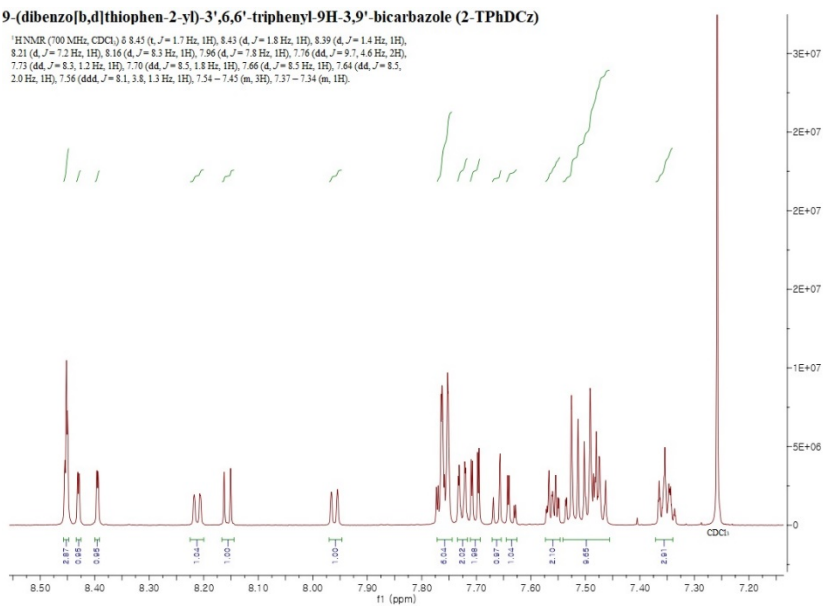
**Fig. S5** <sup>1</sup>H-NMR of tert-butyl 3-bromo-6-phenyl-9H-carbazole-9-carboxylate (P2)



(a)

**9-(dibenzo[b,d]thiophen-2-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (2-TPhDCz)**

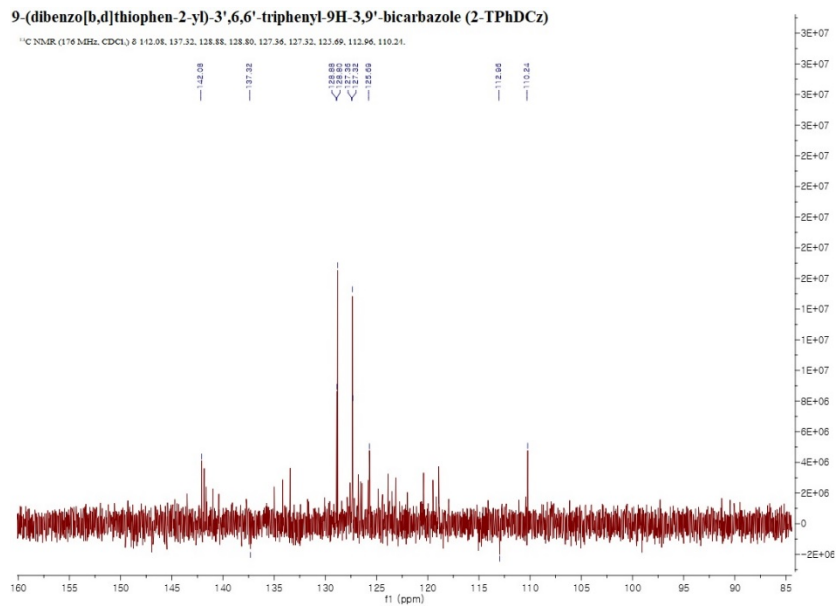
<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 8.45 (t, *J* = 1.7 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.39 (d, *J* = 1.4 Hz, 1H), 8.21 (d, *J* = 7.2 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, *J* = 9.1, 4.6 Hz, 2H), 7.73 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.64 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.56 (ddd, *J* = 8.1, 3.8, 1.3 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.37 – 7.34 (m, 1H).



(b)

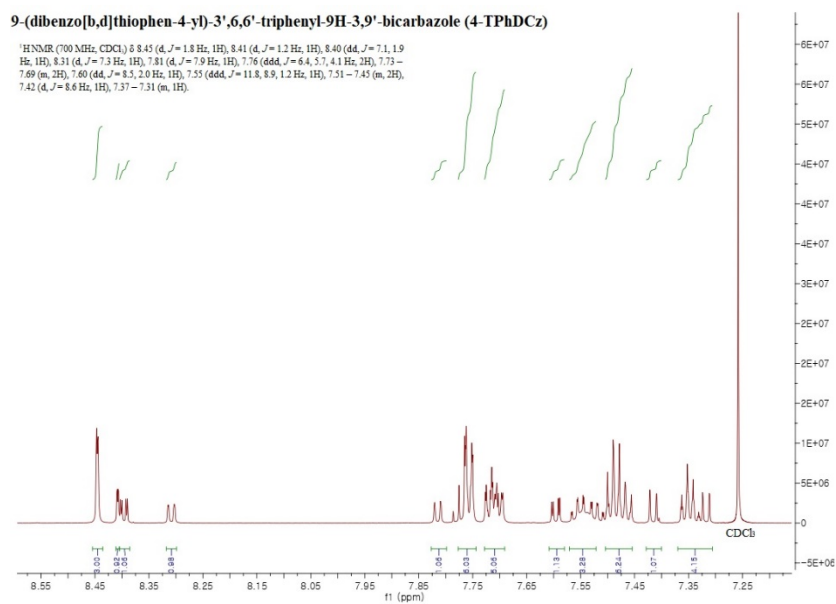
**9-(dibenzo[b,d]thiophen-2-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (2-TPhDCz)**

<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 142.08, 137.32, 128.88, 128.80, 127.36, 127.32, 123.69, 112.86, 110.24.

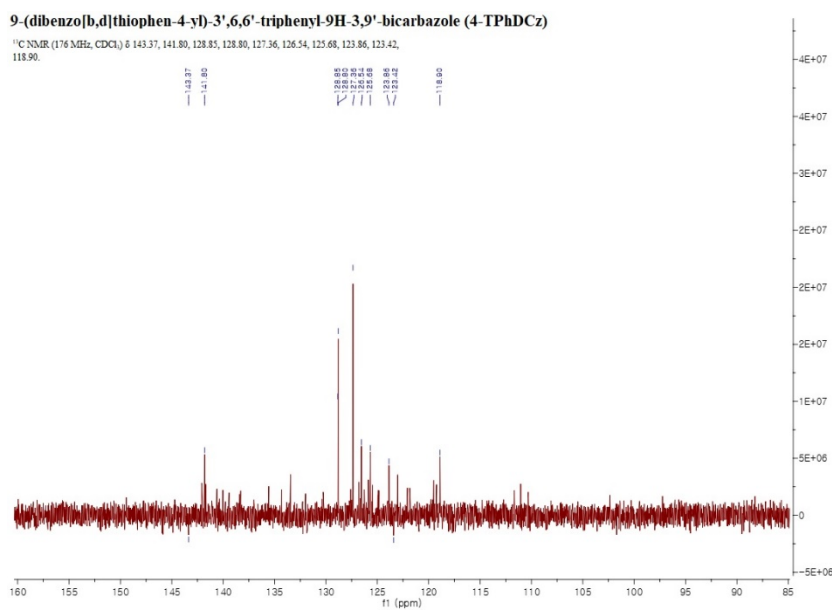


**Fig. S7** <sup>1</sup>H-NMR (a) and <sup>13</sup>C-NMR (b) of 9-(dibenzo[b,d]thiophen-2-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (2-TPhDCz)

(a)



(b)



**Fig. S8** <sup>1</sup>H-NMR (a) and <sup>13</sup>C-NMR (b) of 9-(dibenzo[b,d]thiophen-4-yl)-3',6,6'-triphenyl-9H-3,9'-bicarbazole (4-TPhDCz)