

## Supporting Information

### Rational Design of Blocking Groups for High Triplet Energy N-type Host Materials

Junsu Ha<sup>+</sup>, Seung Chan Kim<sup>+</sup>, Mina Jung, Jun Yeob Lee\*

School of Chemical Engineering, Sungkyunkwan University  
2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Korea

\* Corresponding author

E-mail : [leej17@skku.edu](mailto:leej17@skku.edu)

<sup>+</sup>Junsu Ha and Seung Chan Kim contributed equally.

## Experimental

### General information

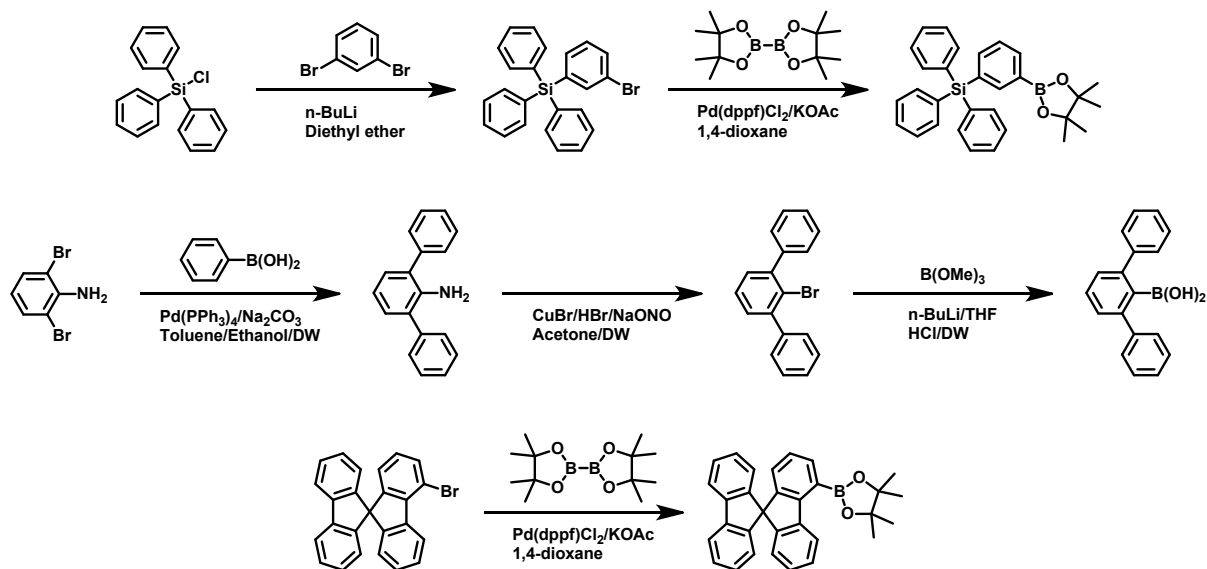
1,3-Dibromobenzene, chlorotriphenylsilane and cyanuric chloride were purchased from Alfa Aesar. n-Butyllithium solution (2.5M in hexane) and copper(I) bromide (CuBr) were purchased from Acros. 9H-Carbazole and trimethyl borate were purchased from Sigma aldrich. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl<sub>2</sub>) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) were purchased from P&H tech Co.. 2,6-dibromoaniline, dicyclohexyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine (X-phos) and phenylboronic acid were products of SY innovation. 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (B<sub>2</sub>pin<sub>2</sub>) and 4-bromo-9,9'-spirobi[fluorene] were purchased from GOM tech.. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), potassium

acetate (KOAc), hydrobromic acid (HBr) and hydrochloric acid (HCl) were obtained from Daejung Chemical & Metal Co.. Sodium nitrite was from Samchun Chemicals. Toluene, Tetrahydrofuran (THF), n-hexane (HEX), methylene chloride (MC), and 1,4-dioxane were purchased from Duksan Chemical Industry Co.

Before using THF and toluene, it were distilled for purification with sodium and calcium hydride in a nitrogen condition. All purifications were carried out through column chromatography, recrystalization and vacuum sublimation. The column chromatography was performed using a mixture of MC and HEX on a silica gel column. Silica gel was supplied by Merck (Silica Gel 60, 0.040-0.063mm, 230-400 Mesh) The vacuum sublimation was conducted before PhOLEDs performance test. The mass spectra of all materials were detected with an (Advion, Expression CMS spectrometer) in Atmospheric-pressure chemical ionization (APCI) mode. The mass of final product mSi-2CzTrz, tPh-2CzTrz and SBF-2CzTrz confirmed by using high resolution mass spectrometer (JEOL, JMS-700) in fast atom bombardment (FAB) mode. After purification, the  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) analysis was executed by a Unity Inova (Varian, 500 MHz, 300 MHz) spectrometer to identify the materials. The CV measurements of the compound for calculating the HOMO and LUMO were carried out by (Ivium Tech, Iviumstat). The standard material was ferrocene, working electrode was carbon electrode, reference electrode was Ag/AgCl electrode and counter electrode was Pt electrode. An UV-vis spectrophotometer (JASCO, V-730) for detecting the UV-vis absorption spectra and a fluorescence spectrophotometer (PerkinElmer, LS-55) for observing the PL spectra were used. Both measurements were carried out with the sample dissolved in toluene ( $1.0 \times 10^{-5}$  M for UV-vis absorption,  $1.0 \times 10^{-3}$  M for fluorescence and phosphorescence). When measuring singlet and triplet energy of the materials, the analysis was performed at 77 K under a liquid nitrogen state. The EL

performances of all devices were measured by a source meter (Keithley, SourceMeter® 2400) and a spectroradiometer (Konica Minolta, CS-2000).

## Synthesis



**Scheme S1.** Synthesis Scheme of intermediates for mSi-2CzTrz, tPh-2CzTrz and SBF-2CzTrz.

### (3-Bromophenyl)triphenylsilane and triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane

These two intermediates were synthesized according to the synthesis method in our previous work.<sup>31</sup>

### [1,1':3',1''-Terphenyl]-2'-amine

A solution of 2,6-dibromoaniline (5.0 g, 20.0 mmol), phenylboronic acid (5.59 g, 45.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.23 g, 0.20 mmol) and sodium carbonate (7.42g, 70.0 mmol) in mixture of toluene (70 ml), ethanol (35 ml), and distilled water (35 ml) was stirred in a two-necked flask at 70 °C for 10 hours under a nitrogen atmosphere condition. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then

purified through a silica gel column chromatography using MC/HEX. As a result, a white powdery product was obtained (2.9 g, 60% yield).

MS (APCI)  $m/z$  246.15 [(M + H)<sup>+</sup>]. <sup>1</sup>H NMR: (300 MHz, DMSO)  $\delta$  7.52 – 7.30 (m, 10H), 7.01 (d, J = 7.5 Hz, 2H), 6.82 – 6.73 (m, 1H).

### **2'-Bromo-1,1':3',1''-terphenyl**

The reaction procedure was conducted in open air condition. A solution of [1,1':3',1''-terphenyl]-2'-amine (1.87 g, 7.62 mmol) in acetone (25ml) was stirred in a two-necked flask at room temperature followed by slow addition of HBr (48% in water) (5.4 ml, 21.5 mmol), lowering the temperature to 0 °C and stirring for 10 min. After this, a solution of sodium nitrite (0.74 g, 5.19 mmol) in distilled water (9 ml) was added and stirred for 30 min followed by addition of a dispersion of CuBr (1.87 g, 13.0 mmol) and HBr (48% in water) (1.5 ml, 5.97 mmol) with stirring for 6 hours at room temperature. To quench the reaction, neutralization of the reaction mixture with NaOH aqueous solution was carried out. The crude reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through a silica gel column chromatography with eluent of MC/HEX. A white powdery product was obtained (1.98 g, 84% yield).

MS (APCI)  $m/z$  309.07 [(M + H)<sup>+</sup>]. <sup>1</sup>H NMR: (300 MHz, DMSO)  $\delta$  7.55 – 7.46 (m, 2H), 7.46 – 7.37 (m, 9H), 7.36 – 7.32 (m, 2H).

### **[1,1':3',1''-Terphenyl]-2'-ylboronic acid**

2'-Bromo-1,1':3',1''-terphenyl (2.68 g, 8.67 mmol) in an anhydrous THF under a nitrogen atmosphere was stirred in a two-necked flask at -77 °C, and then n-butyllithium solution

(2.5M in hexane) (4.2 ml, 10.4 mmol) was added dropwisely. The reaction mixture was stirred for 1 h at -77 °C. Trimethy borate (1.5 ml, 13.0 mmol) was added slowly into the solution. The reaction mixture was allowed to warm up to room temperature gradually and stirred for 12 h. Distilled water was added slowly into the reaction mixture. The reaction mixture was extracted using MC and distilled water. The organic layer was evaporated to remove solvent. After dissolving in minimal MC, HEX was added to precipitate. The precipitated material was obtained by filtration. A white solid was obtained (1.4 g, 59% yield)

MS (APCI)  $m/z$  275.21 [(M + H)<sup>+</sup>].

### **2-(9,9'-Spirobi[fluoren]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**

A solution of 4-bromo-9,9'-spirobi[fluorene] (2.47 g, 6.25 mmol), B<sub>2</sub>pin<sub>2</sub> (2.38 g, 9.38 mmol), potassium acetate (1.23 g, 12.5 mmol) and Pd(dppf)Cl<sub>2</sub> (0.137 g, 0.19 mmol) in 1,4-dioxane (50 mL) was refluxed in a two-necked flask with stirring for 10 hours under a nitrogen atmosphere condition. The reaction mixture was extracted using MC and distilled water. The extracted product was evaporated and then purified through a silica gel column chromatography using MC/HEX. A white powdery product was obtained (1.88 g, 68% yield).

MS (APCI)  $m/z$  443.29 [(M + H)<sup>+</sup>]. <sup>1</sup>H NMR: (300 MHz, DMSO)  $\delta$  8.71 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.5 Hz, 2H), 7.69 (dd, J = 7.4, 1.2 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.15 – 7.06 (m, 4H), 6.65 (dd, J = 7.6, 1.2 Hz, 1H), 6.57 (dd, J = 7.4, 3.7 Hz, 3H), 1.45 (s, 12H).

### **9,9'-(6-Chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole)**

9H-carbazole (1.60 g, 9.55 mmol) in an anhydrous THF (25ml) under a nitrogen atmosphere was stirred in a two-necked flask (A) at 0 °C, and another two-necked flask (B) containing a solution of cyanuric chloride (0.825 g, 4.54 mmol) in an anhydrous THF (20ml) was stirred at 0 °C under a nitrogen atmosphere. n-Butyllithium solution (2.5M in hexane) (4 ml, 10.0 mmol) was added to A flask dropwisely. After 1 hour, the reaction mixture inside the flask was carefully pull out with a syringe, and it was injected into the B flask. The reaction mixture was stirred for 1 h at same temperature. Distilled water was added slowly into the reaction mixture. The reaction mixture was extracted using MC and distilled water. The organic layer was evaporated to remove solvent. After washing the dry material with acetone, undissolved material was obtained by filtration. A yellowish powder was obtained (1.38 g, 68% yield)

MS (APCI) m/z 446.09 [(M + H)<sup>+</sup>]. <sup>1</sup>H NMR: (300 MHz, DMSO) δ 8.84 (d, J = 8.2 Hz, 4H), 8.29 (dd, J = 7.5, 1.0 Hz, 4H), 7.61 – 7.54 (m, 4H), 7.50 (td, J = 7.4, 1.1 Hz, 4H).

### **9,9'-(6-(3-(Triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (mSi-2CzTrz)**

A solution of 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (0.52 g, 1.17 mmol), triphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (0.59 g, 1.28 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.040 g, 0.03 mmol) and potasisum carbonate (1.38 g, 10 mmol) in mixture of THF (5 ml) and distilled water (5 ml) was stirred in a two-necked flask at 60 °C for 10 hours under a nitrogen atmosphere condition. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through a silica gel column chromatography using THF/HEX. As a result, a white powdery product was obtained (0.8 g, 92% yield).

MS (HR-FAB)  $m/z$  : Found 746.2735  $[(M + H)^+]$ . Calculated for  $C_{51}H_{36}N_5Si$  746.2740.

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  9.09 (s, 1H), 8.94 (dd,  $J = 7.4, 1.1$  Hz, 4H), 8.81 – 8.78 (m, 1H), 8.09 – 8.05 (m, 4H), 7.87 (dt,  $J = 7.3, 1.1$  Hz, 1H), 7.70 – 7.66 (m, 7H), 7.48 – 7.43 (m, 3H), 7.43 – 7.34 (m, 14H).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  173.4, 164.9, 141.1, 139.1, 137.0, 136.6, 135.9, 135.8, 134.0, 130.7, 130.1, 128.8, 128.3, 127.2, 126.7, 123.5, 119.8, 117.8.

**9,9'-(6-([1,1':3',1''-Terphenyl]-2'-yl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (tPh-2CzTrz)**

A solution of 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (0.89 g, 2.00 mmol), [1,1':3',1''-terphenyl]-2'-ylboronic acid (0.576g, 2.10 mmol),  $Pd(PPh_3)_4$  (0.116 g, 0.10 mmol), X-phos (0.095 g, 0.20 mmol) and sodium carbonate (1.06 g, 10 mmol) in mixture of toluene (10 ml), ethanol (5 ml), and distilled water (5 ml) was stirred in a two-necked flask at 70 °C for 10 hours under a nitrogen atmosphere condition. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through a silica gel column chromatography using MC/HEX. A white powder was obtained with poor yield (0.36 g, 28% yield).

MS (HR-FAB)  $m/z$  : Found 640.2495  $[(M + H)^+]$ . Calculated for  $C_{45}H_{30}N_5$  640.2501.

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  8.29 (d,  $J = 7.8$  Hz, 4H), 8.09 – 8.05 (m, 4H), 7.78 (dd,  $J = 8.6, 6.7$  Hz, 1H), 7.73 – 7.70 (m, 2H), 7.52 (dd,  $J = 8.2, 1.1$  Hz, 4H), 7.41 (pd,  $J = 7.2, 1.4$  Hz, 8H), 7.38 – 7.34 (m,  $J = 7.8$  Hz, 4H), 7.22 – 7.17 (m, 2H).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  177.7, 163.9, 142.0, 141.4, 138.8, 136.1, 130.2, 130.0, 129.4, 128.7, 127.5, 127.0, 126.4, 123.5, 119.6, 117.5.



**9,9'-(6-(9,9'-Spirobi[fluoren]-5-yl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (SBF-2CzTrz)**

A solution of 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (0.424 g, 0.952 mmol), 2-(9,9'-spirobi[fluoren]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.40 g, 0.904 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.011 g, 0.01 mmol), X-phos (0.009 g, 0.019 mmol) and sodium carbonate (0.252 g, 2.380 mmol) in mixture of toluene (5 ml), ethanol (2.5 ml), and distilled water (2.5 ml) was stirred in a two-necked flask at 60 °C for 10 hours under a nitrogen atmosphere condition. The reaction mixture was extracted with MC and distilled water. The extracted product was evaporated and then purified through a silica gel column chromatography using MC/HEX. A white powder was obtained (0.39 g, 57% yield).

MS (HR-FAB) m/z : Found 726.2653 [(M + H)<sup>+</sup>]. Calculated for C<sub>52</sub>H<sub>32</sub>N<sub>5</sub> 726.2658.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.14 – 9.11 (m, 4H), 8.12 – 8.08 (m, 5H), 8.05 (dd, J = 7.6, 1.1 Hz, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.47 – 7.41 (m, 10H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 (td, J = 7.5, 1.0 Hz, 2H), 7.03 (td, J = 7.4, 1.1 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.92 (d, J = 7.5 Hz, 2H), 6.76 (d, J = 7.0 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 175.8, 164.9, 151.0, 149.6, 148.8, 142.1, 140.5, 140.4, 139.1, 133.7, 130.9, 128.7, 128.3, 128.1, 127.7, 127.2, 127.0, 126.7, 125.5, 124.3, 123.9, 123.8, 120.4, 119.9, 118.5.

## Device fabrication

The blue PhOLEDs consisted of the following structures for the device performance measurement: indium tin oxide (ITO) (50 nm)/N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine: 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (BCFN:HATCN) (40 nm:30%)/BCFN (10 nm)/mCBP (10 nm)/EML (30 nm)/2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan (DBFTrz) (5 nm)/2-[4-(9,10-di-naphthalen-2-yl-anthracene-2-yl)-phenyl]-1-phenyl-1H-benzimidazole (ZADN) (20 nm)/LiF (1.5 nm)/Al (200 nm). The EMLs were mCBP:mSi-2CzTrz:CNImIr, mCBP:tPh-2CzTrz:CNImIr and mCBP:SBF-2CzTrz:CNImIr. p-type host and n-type host were mixed at a 1 : 1 ratio. The phosphorescent emitter, fac-tris(3-(1-(2,6-diisopropylphenyl)-1H-imidazol-2-yl)benzotrile)iridium (CNImIr) was doped in each EMLs at a concentration of 15 wt%.

**Table S1.** Summarized the triplet energy from phosphorescence spectra in toluene solution and film state of mSi-2CzTrz, tPh-2CzTrz and SBF-2CzTrz.

Compound	solution <sup>(a)</sup>		film <sup>(b)</sup>		shift	
	(nm)	(eV)	(nm)	(eV)	(nm)	(eV)
<b>mSi-2CzTrz</b>	408	3.04	416	2.98	8	0.06
<b>tPh-2CzTrz</b>	409	3.03	434	2.86	25	0.17
<b>SBF-2CzTrz</b>	435	2.85	472	2.63	37	0.22

(a). Calculated from the onset point of the phosphorescence spectra in frozen toluene ( $10^{-3}$  M) at 77K with 1 ms delay time.

(b). Calculated from the onset point of the phosphorescence spectra in neat film at 77K with 0.2 ms delay time.

**Table S2.** Summarized the Device Performances Data of the 5CzCN-doped mCBP:mSi-2CzTrz, mCBP:tPh-2CzTrz and mCBP:SBF-2CzTrz devices.

Devices	V <sub>d</sub> <sup>(a)</sup> (V)	I <sup>(b)</sup> (mA/cm <sup>2</sup> )	CIE <sup>(c)</sup> (x, y)	EQE <sup>(d)</sup> / EQE <sub>max</sub> (%)	PE <sup>(e)</sup> / PE <sub>max</sub> (lm/W)	CE <sup>(f)</sup> / CE <sub>max</sub> (cd/A)
<b>mCBP:mSi-2CzTrz</b>	6.9	3.5	0.17, 0.32	14.2 / 15.4	13.4 / 19.5	29.3 / 32.4
<b>mCBP:tPh-2CzTrz</b>	7.2	4.3	0.16, 0.30	12.2 / 13.3	9.8 / 14.2	23.8 / 26.3
<b>mCBP:SBF-2CzTrz</b>	7.6	5.7	0.17, 0.33	8.6 / 12.4	7.8 / 15.0	17.9 / 26.2

(a) ~ (f). Driving voltage, current density, color coordinate, external quantum efficiency, power efficiency, current efficiency at luminance of 1000 cd m<sup>-2</sup>. The emitter was 5CzCN: 2,3,4,5,6-penta(9H-carbazol-9-yl)benzotrile

## List of figures

**Figure S1.** CV curves of (a). mSi-2CzTrz, (b). tPh-2CzTrz, (c). SBF-2CzTrz and (d). ferrocene standard.

**Figure S2.** (a) DSC and (b) TGA scanning of mSi-2CzTrz, tPh-2CzTrz and SBF-2CzTrz at a heating rate of 10 °C/min.

**Figure S3.** The PL spectra of the single host and mCBP mixed hosts in neat film at room temperature. (a). mSi-2CzTrz, (b). tPh-2CzTrz and (c). SBF-2CzTrz.

**Figure S4.** The phosphorescence spectra of the hosts in toluene solution and neat film at 77 K with 1ms delay. (a). mSi-2CzTrz, (b). tPh-2CzTrz and (c). SBF-2CzTrz.

**Figure S5.** Current density-Voltage curve of electron only (a) and hole only (b) devices data of the CzBFPmSi host.

**Figure S6.** Voltage rise of electron only (a) and hole only (b) devices of the hosts during electrical stress.

**Figure S7.** <sup>1</sup>H NMR spectrum of mSi-2CzTrz.

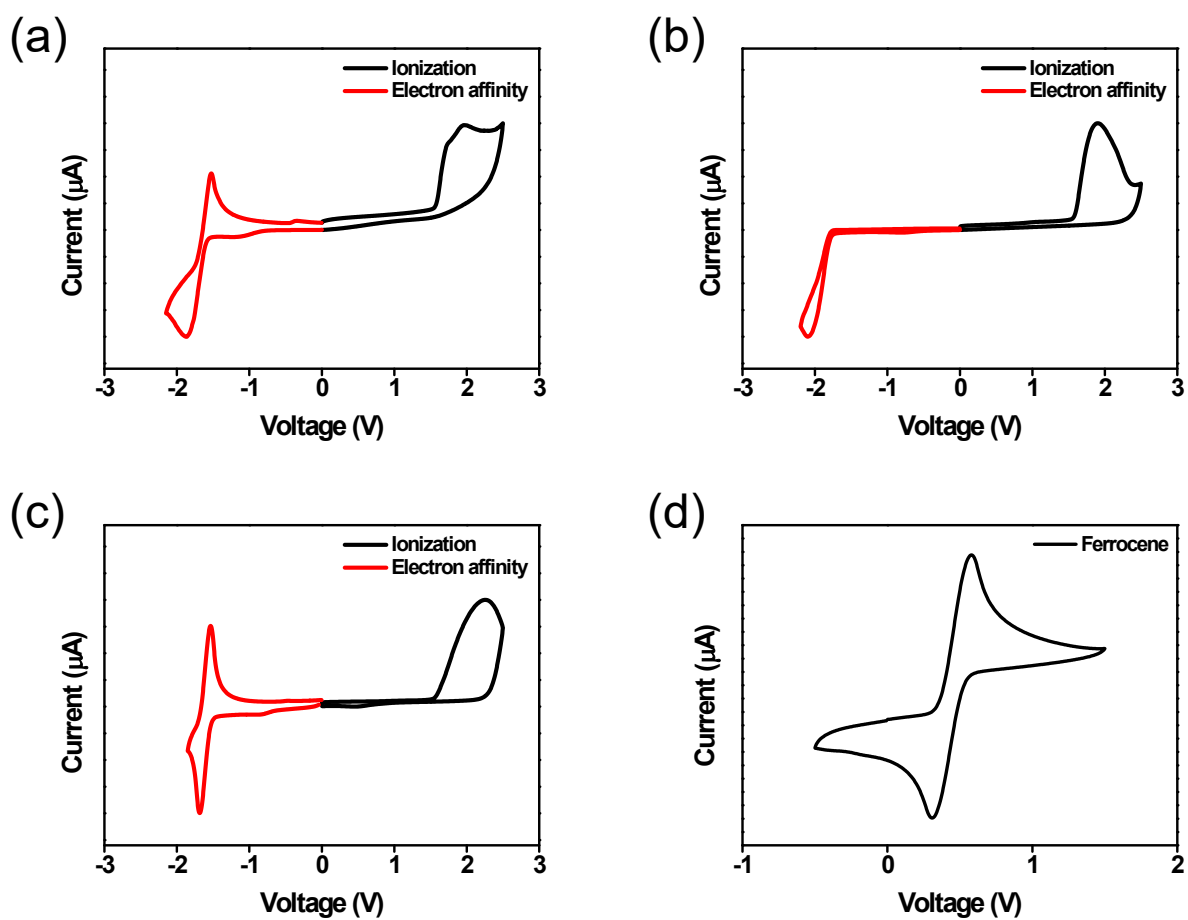
**Figure S8.** <sup>13</sup>C NMR spectrum of mSi-2CzTrz.

**Figure S9.** <sup>1</sup>H NMR spectrum of tPh-2CzTrz.

**Figure S10.** <sup>13</sup>C NMR spectrum of tPh-2CzTrz.

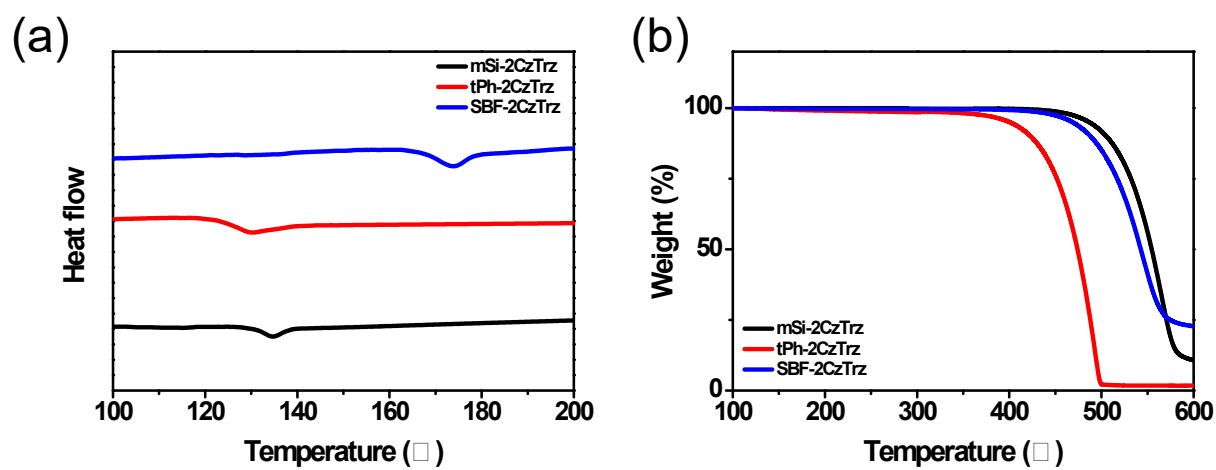
**Figure S11.** <sup>1</sup>H NMR spectrum of SBF-2CzTrz.

**Figure S12.** <sup>13</sup>C NMR spectrum of SBF-2CzTrz.

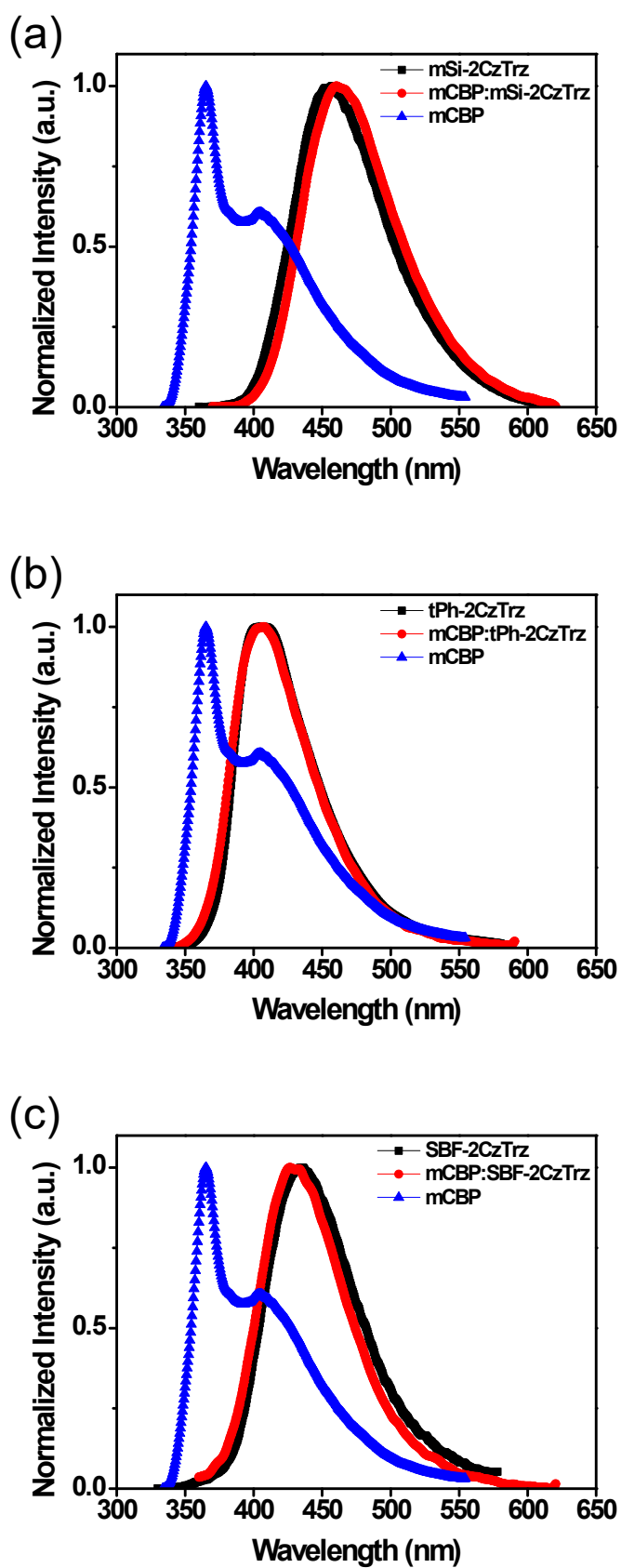


**Figure S1.** CV curves of (a). mSi-2CzTrz, (b). tPh-2CzTrz, (c). SBF-2CzTrz and (d).

ferrocene standard.



**Figure S2.** (a) DSC and (b) TGA scanning of mSi-2CzTrz, tPh-2CzTrz and SBF-2CzTrz at a heating rate of 10 °C/min.



**Figure S3.** The PL spectra of the single and mCBP mixed hosts in neat film at room temperature. (a). mSi-2CzTrz, (b). tPh-2CzTrz and (c). SBF-2CzTrz.



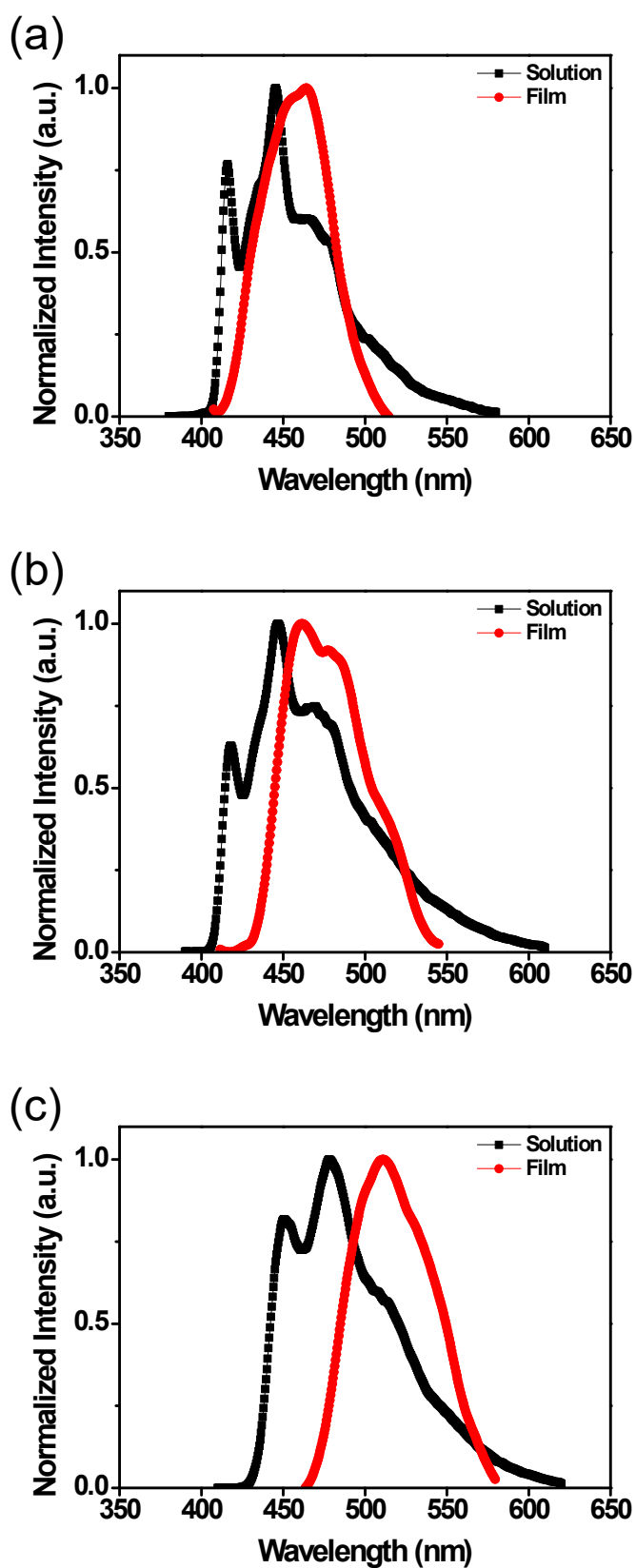
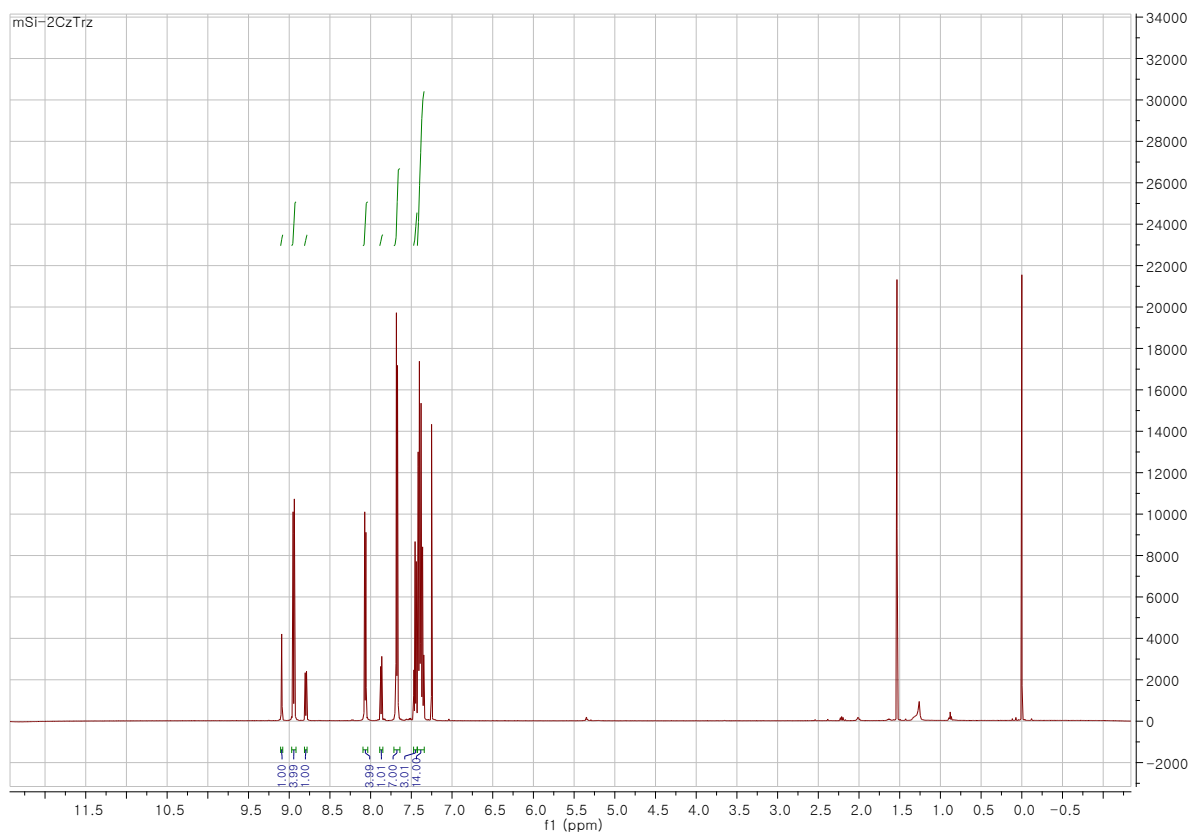
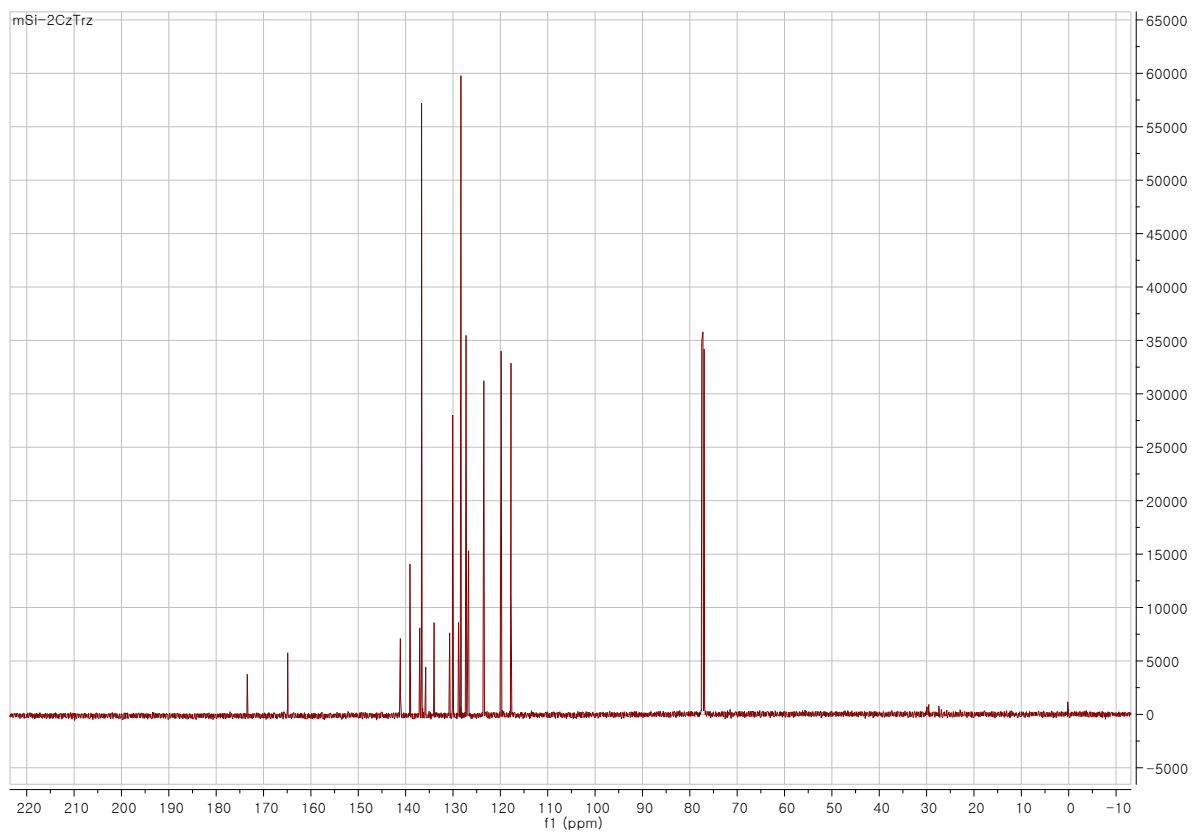


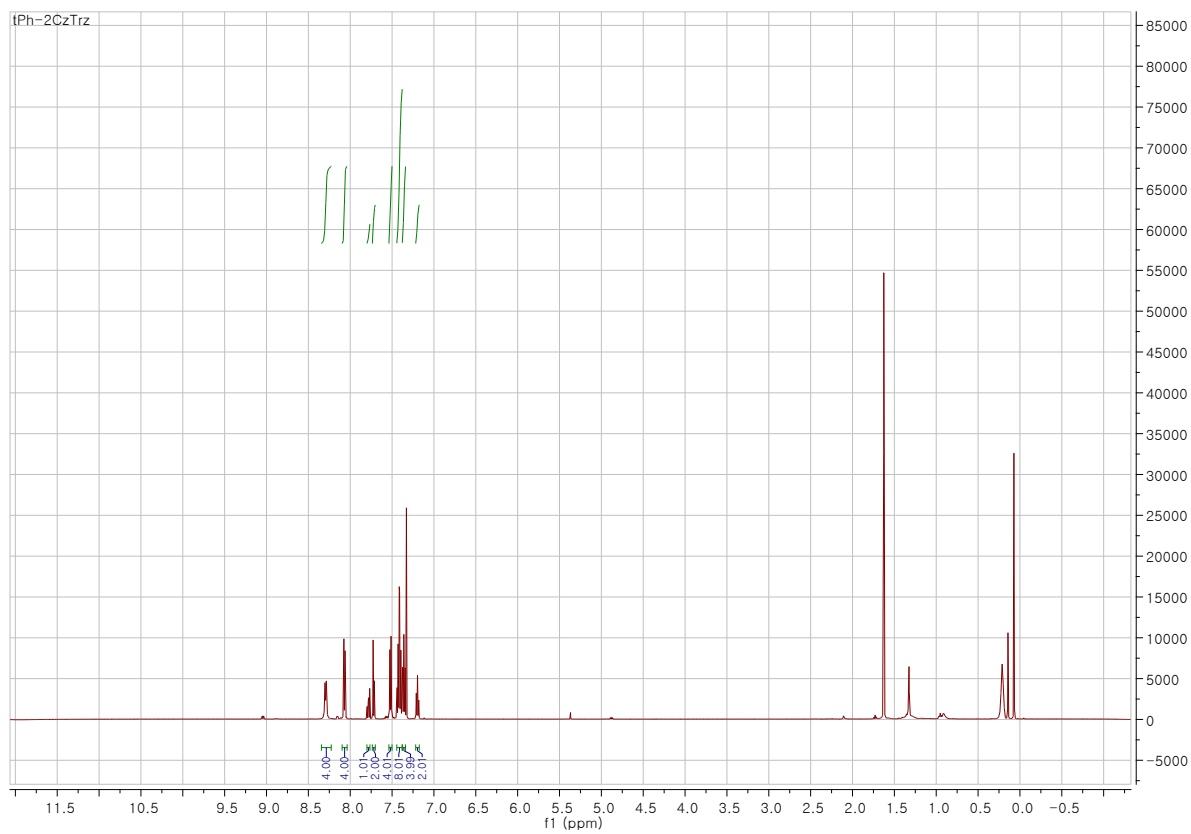
Figure S4. The phosphorescence spectra of the hosts in toluene solution and neat film at 77 K with 1ms delay. (a). mSi-2CzTrz, (b). tPh-2CzTrz and (c). SBF-2CzTrz.



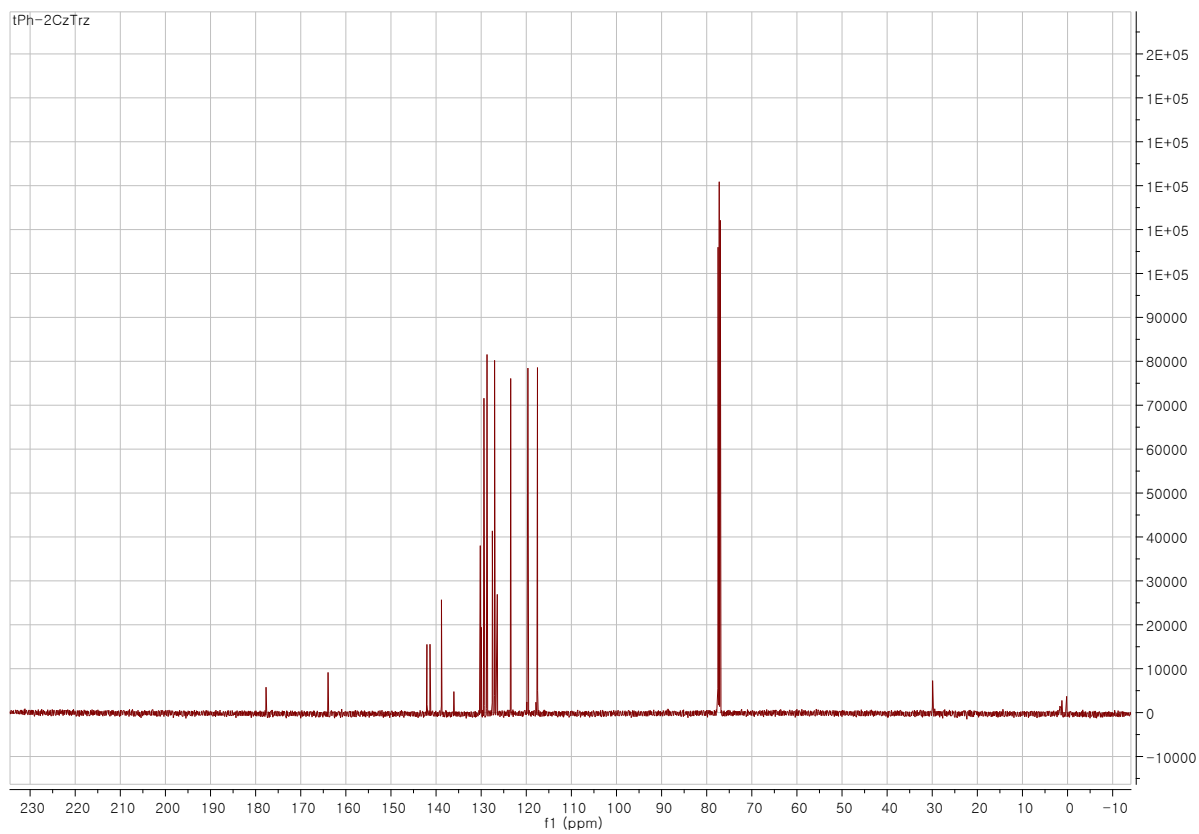
**Figure S5.**  $^1\text{H}$  NMR spectrum of mSi-2CzTrz.



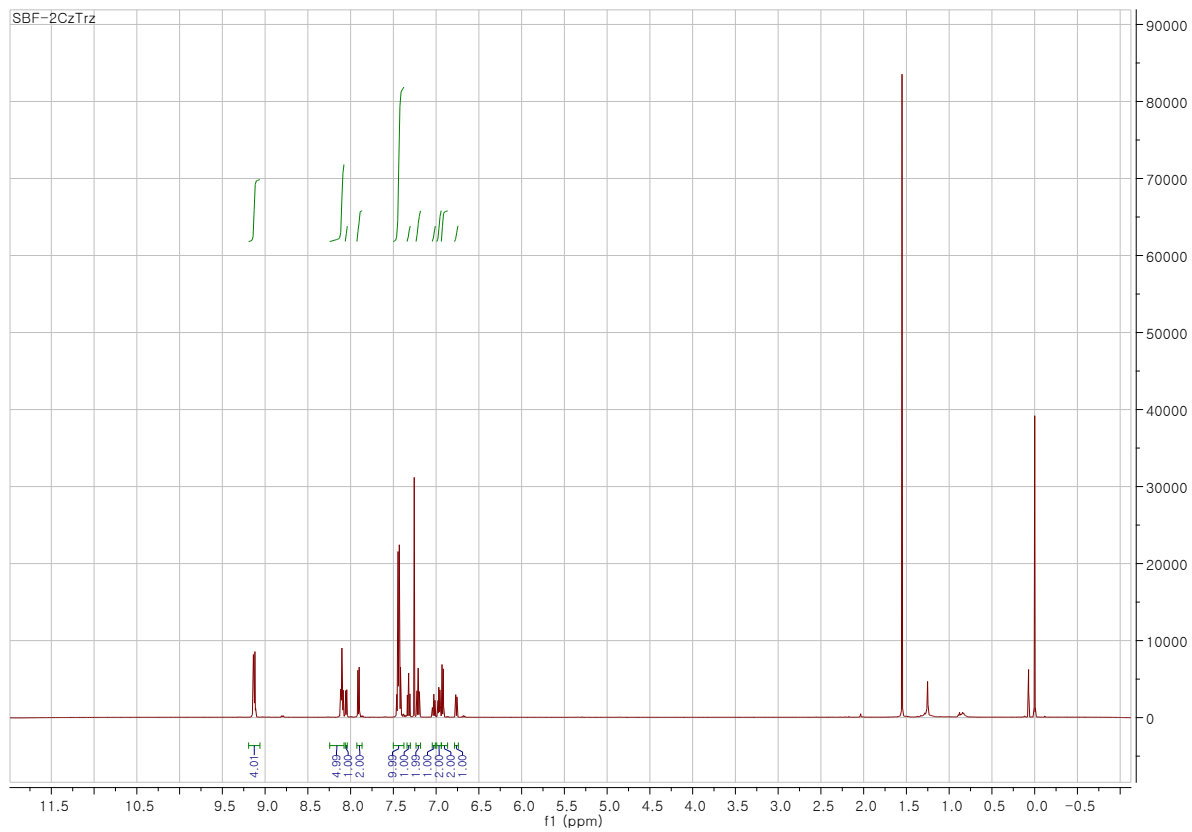
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of mSi-2CzTrz.



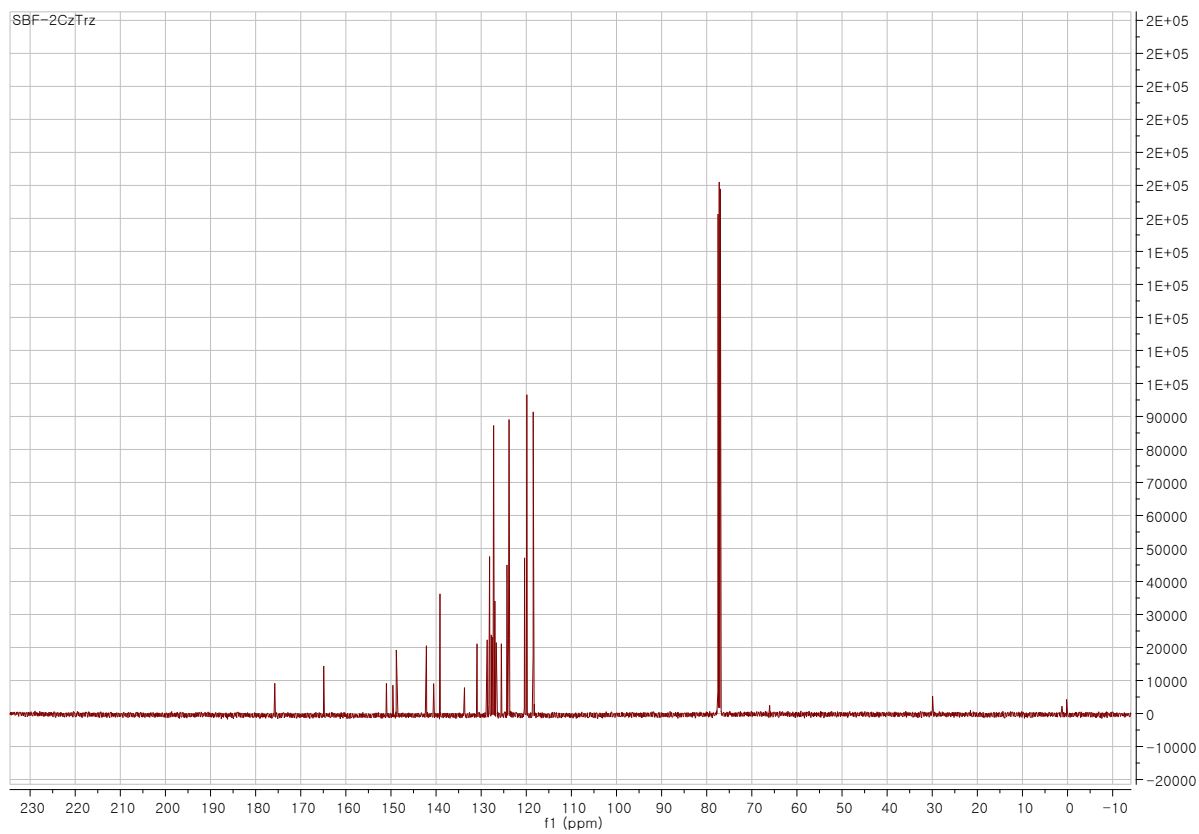
**Figure S7.**  $^1\text{H}$  NMR spectrum of tPh-2CzTrz.



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of tPh-2CzTrz.



**Figure S9.**  $^1\text{H}$  NMR spectrum of SBF-2CzTrz.



**Figure S10.**  $^{13}\text{C}$  NMR spectrum of SBF-2CzTrz.