

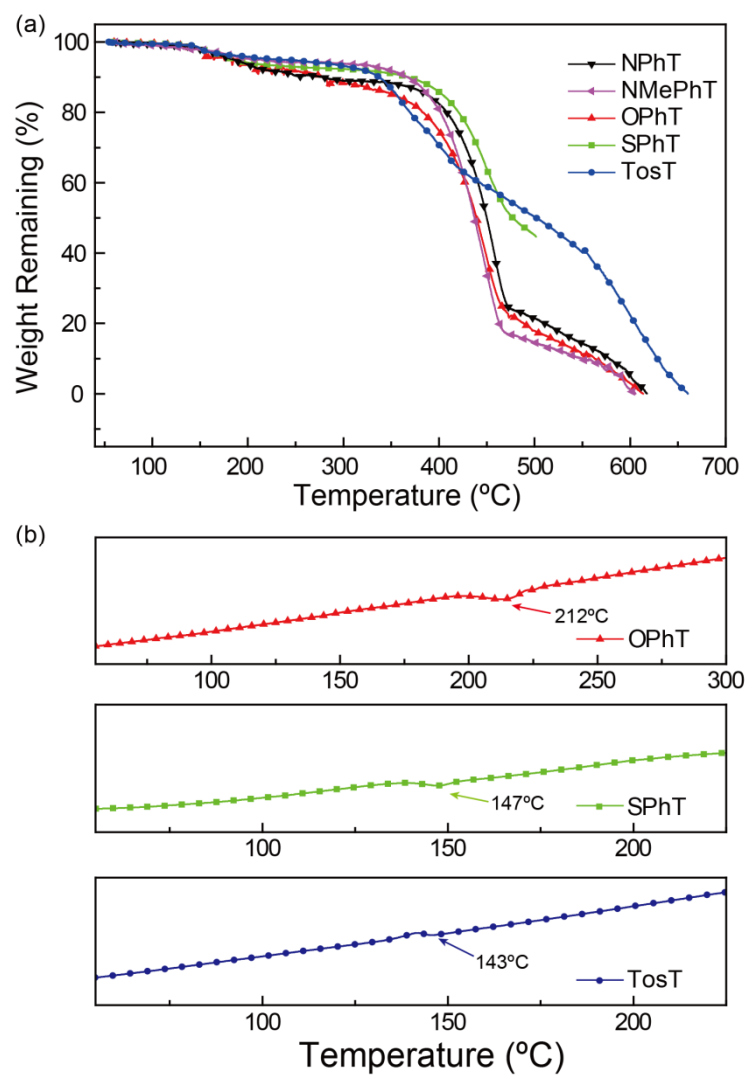
## Modulation of Singlet and Triplet Excited States Through $\sigma$ Spacers in Ternary 1,3,5-Triazines

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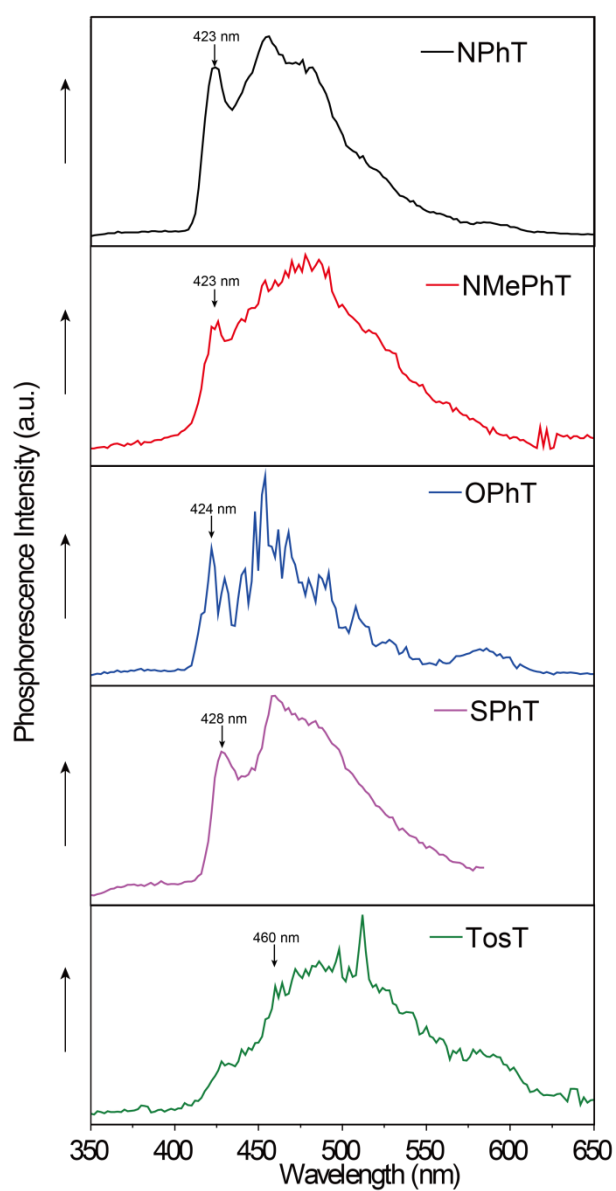
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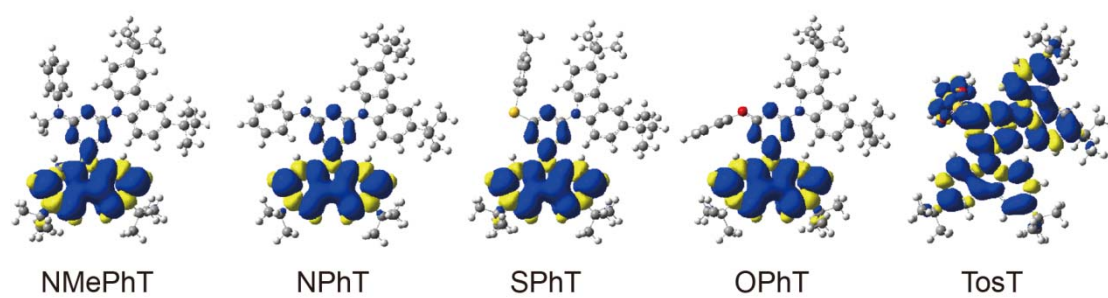
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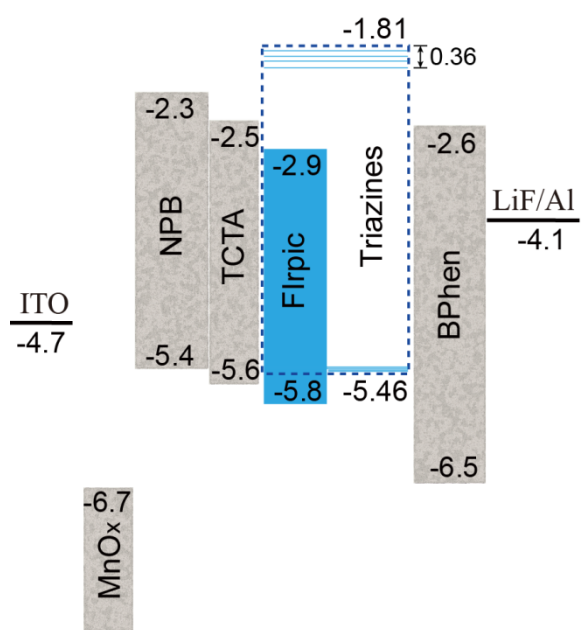
**Figure S1.** Thermal properties of  $\sigma$ -spaced triazines. (a) TGA and (b) DSC curves



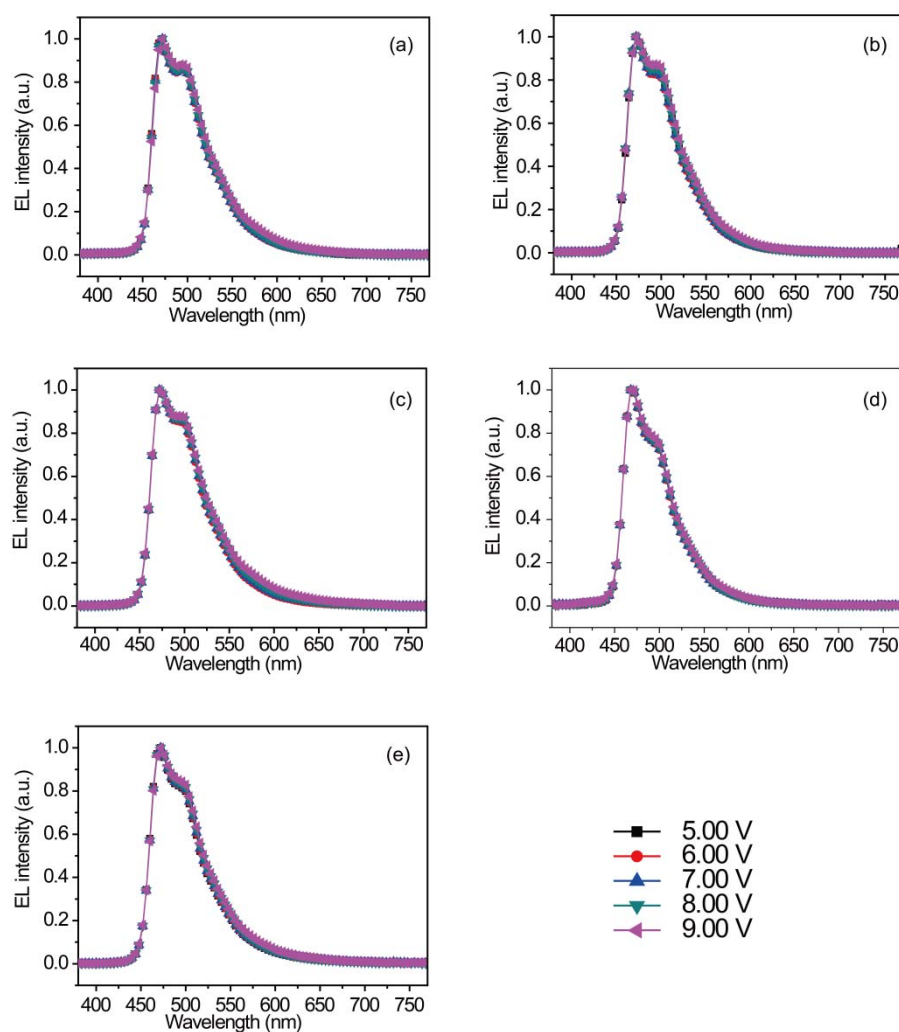
**Figure S2.** The normalized phosphorescent spectra of  $\sigma$ -spaced triazines in chloroform glass at 77 K after a delay of 5 ms.



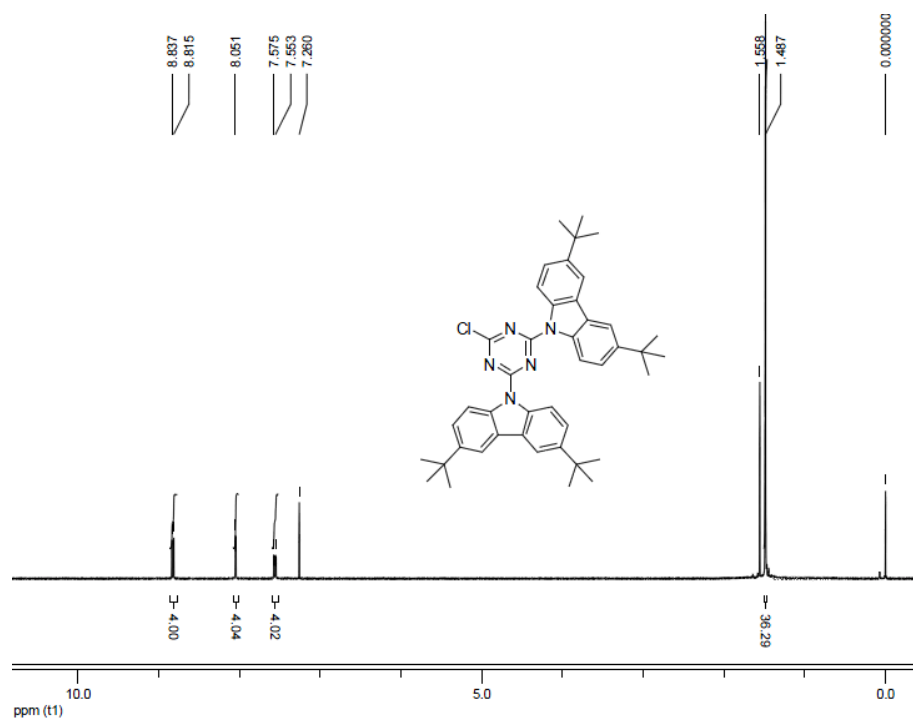
**Figure S3.** Spin density distribution of  $\sigma$ -spaced triazines



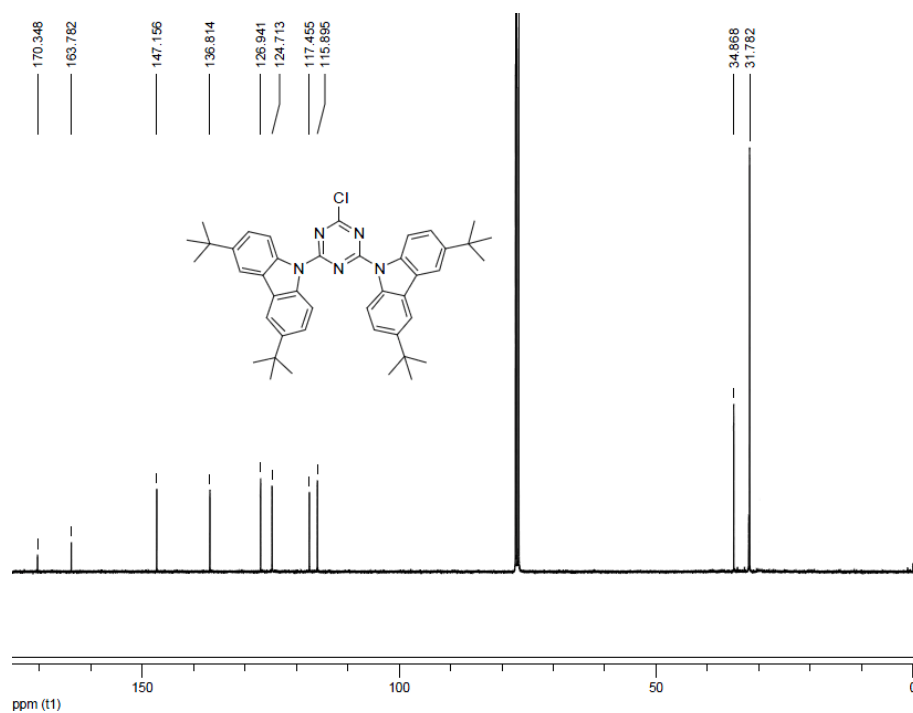
**Figure S4.** Energy level diagram of the device configurations



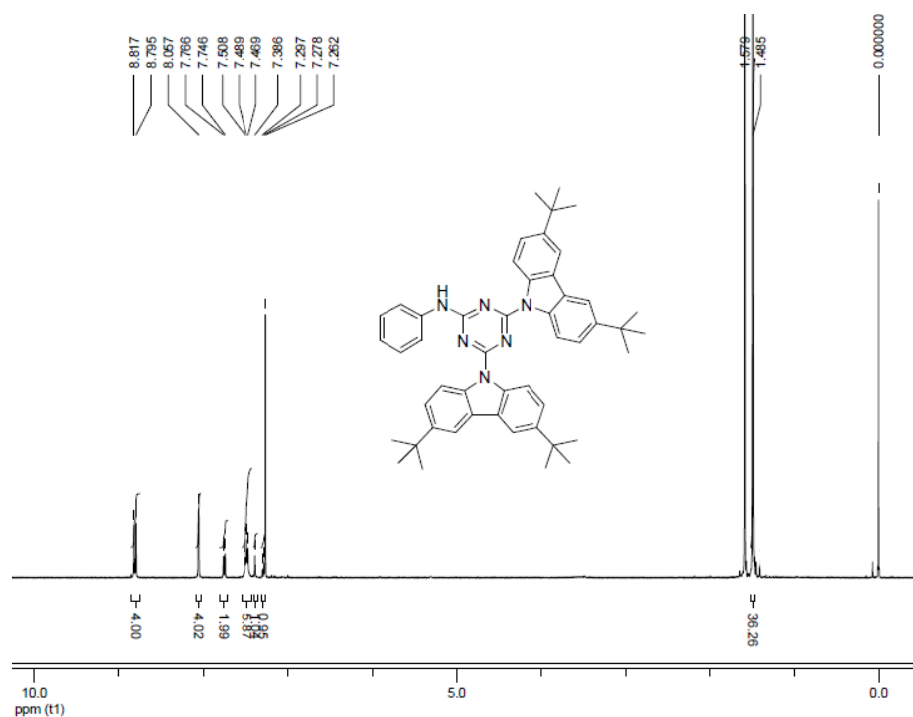
**Figure S5.** EL spectra of (a) NPhT, (b) NMePhT, (c) OPhT, (d) SPhT and (e) TosT at different voltages



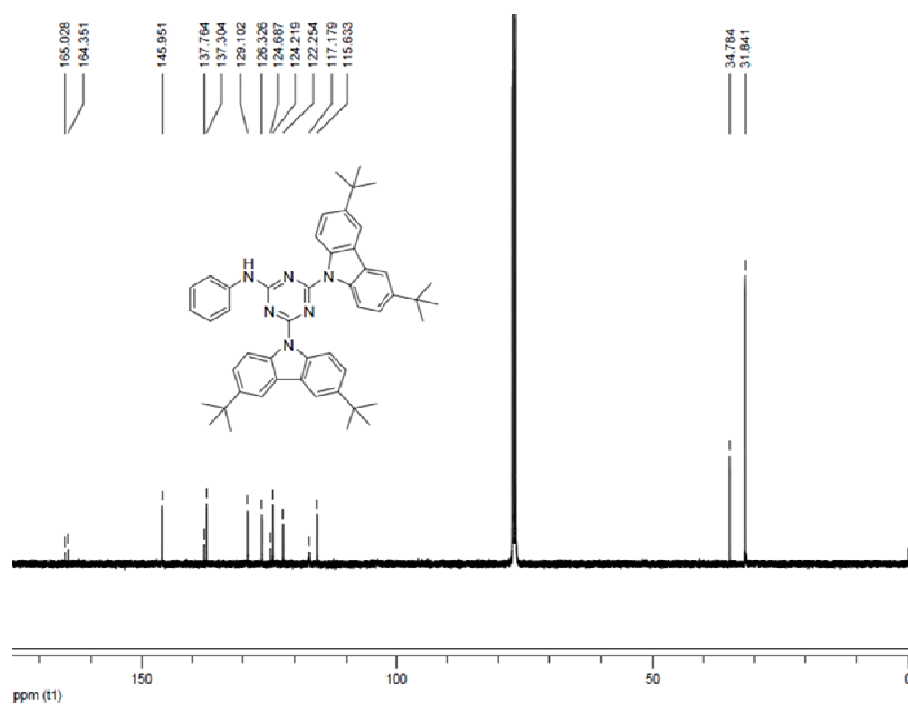
**Figure S6-1.** <sup>1</sup>H NMR spectrum of CIT in CDCl<sub>3</sub>



**Figure S6-2.** <sup>13</sup>C NMR spectrum of CIT in CDCl<sub>3</sub>

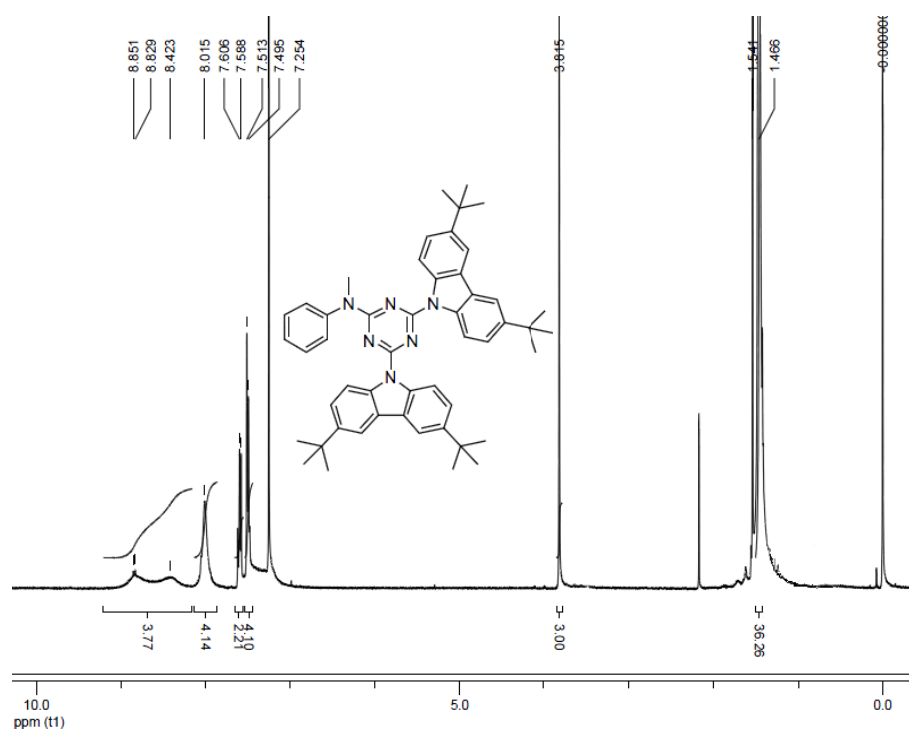


**Figure S7-1.**  $^1\text{H}$  NMR spectrum of NPhT in  $\text{CDCl}_3$

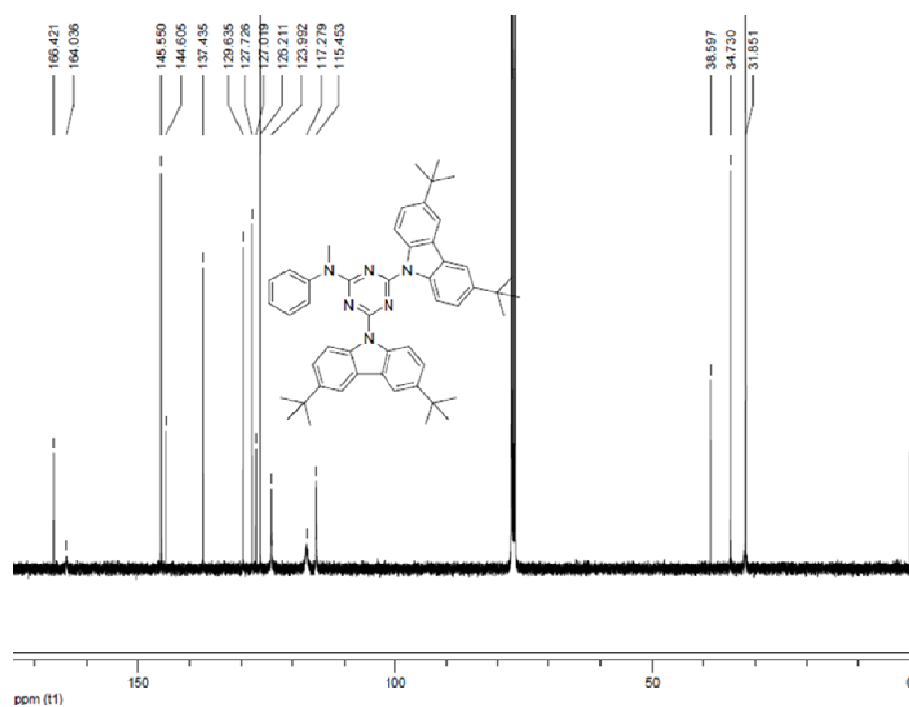


**Figure S7-2.**  $^{13}\text{C}$  NMR spectrum of NPhT in  $\text{CDCl}_3$

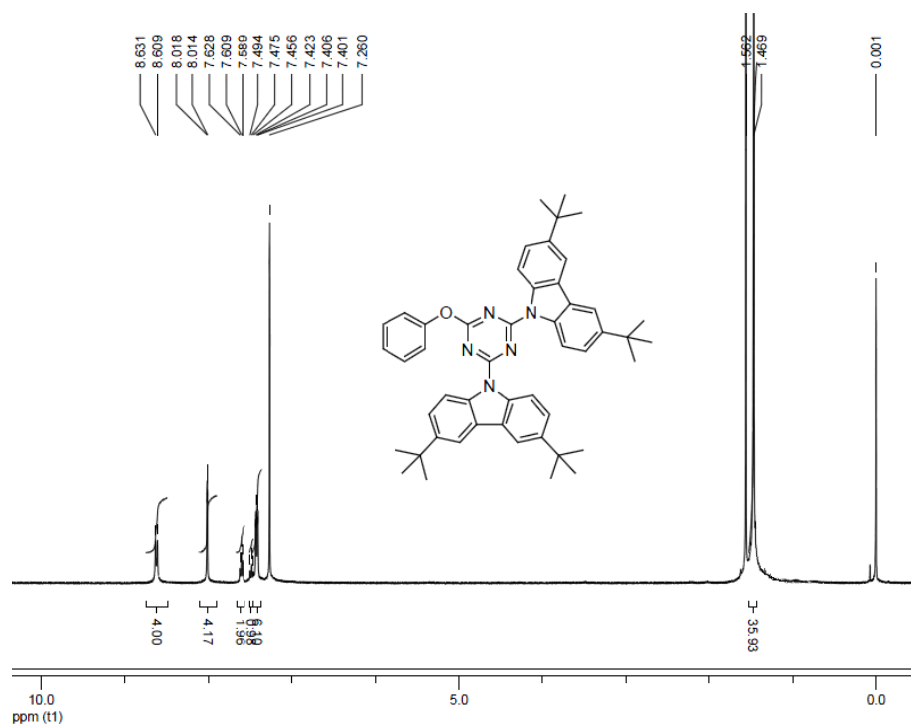




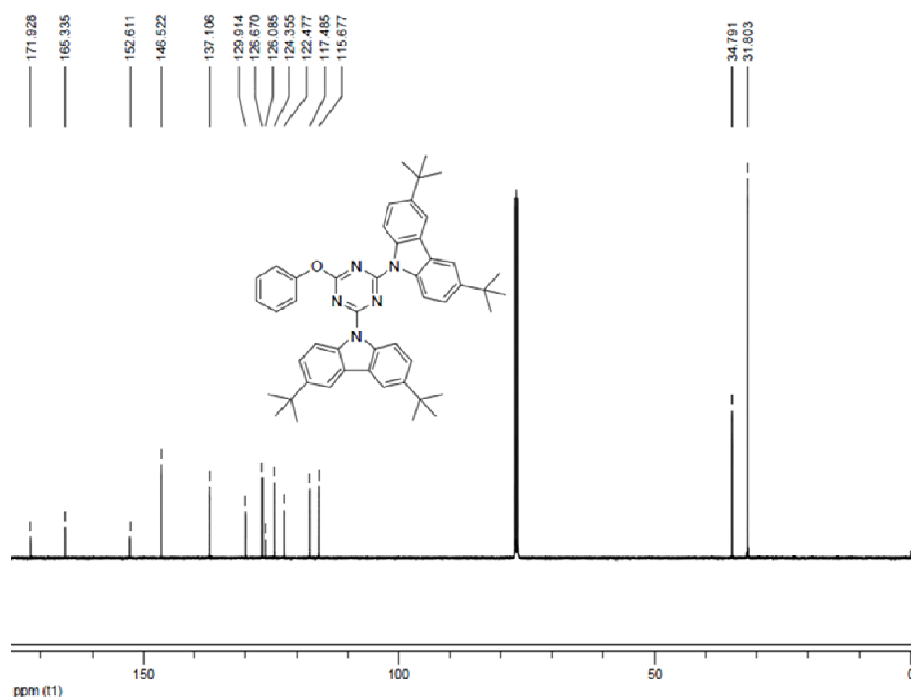
**Figure S8-1.** <sup>1</sup>H NMR spectrum of NMePhT in CDCl<sub>3</sub>



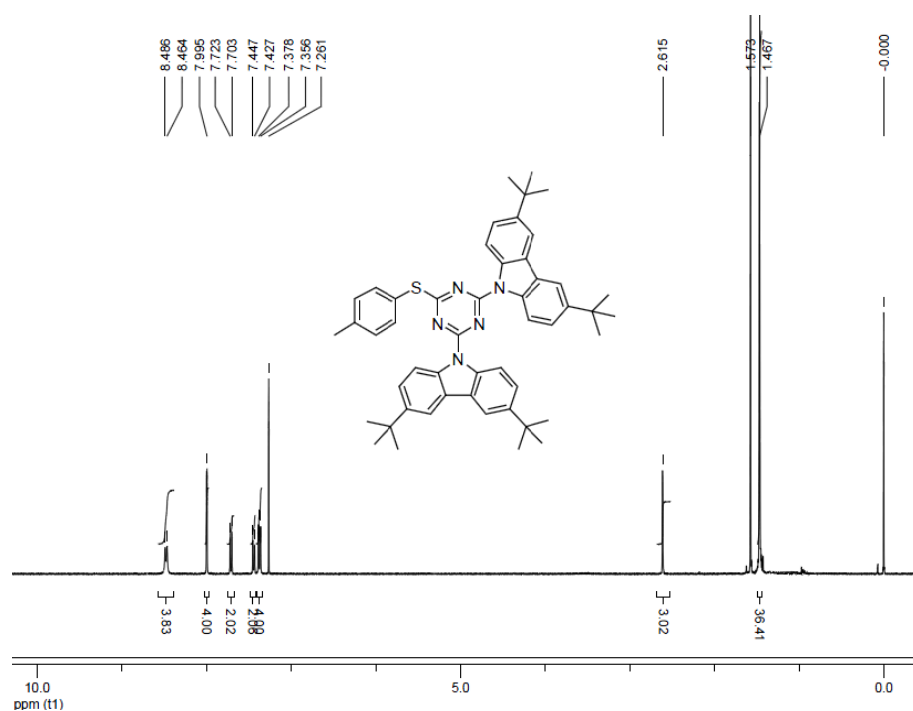
**Figure S8-2.** <sup>13</sup>C NMR spectrum of NMePhT in CDCl<sub>3</sub>



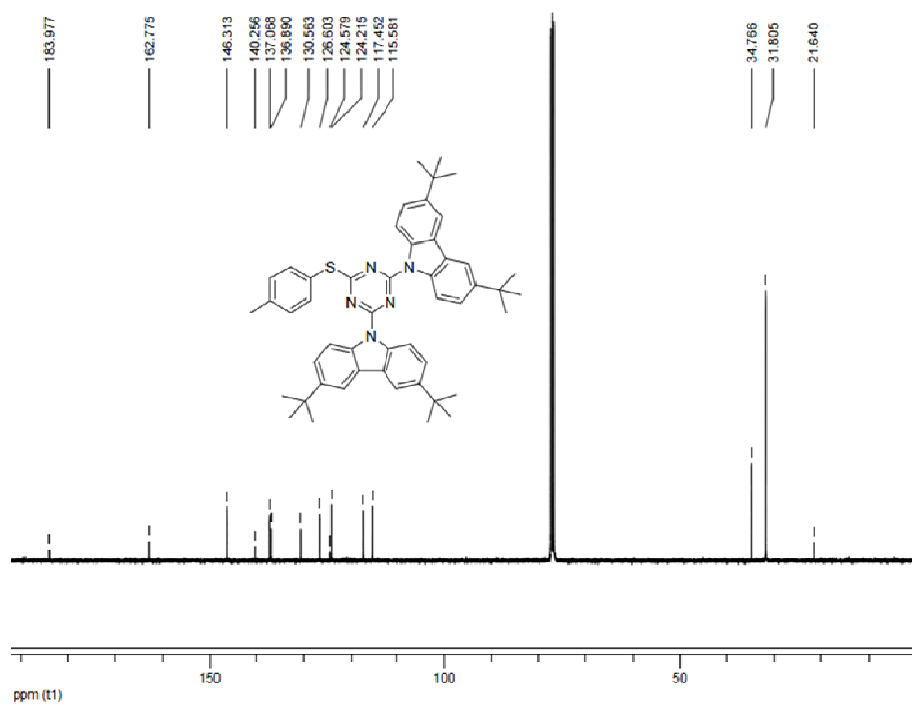
**Figure S9-1.** <sup>1</sup>H NMR spectrum of OPhT in CDCl<sub>3</sub>



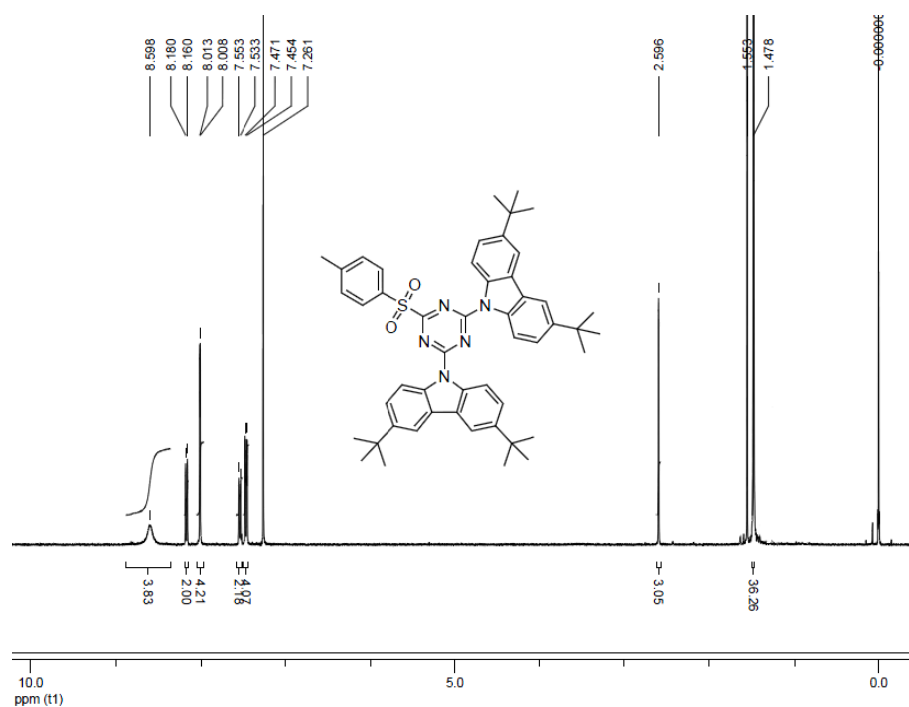
**Figure S9-2.** <sup>13</sup>C NMR spectrum of OPhT in CDCl<sub>3</sub>



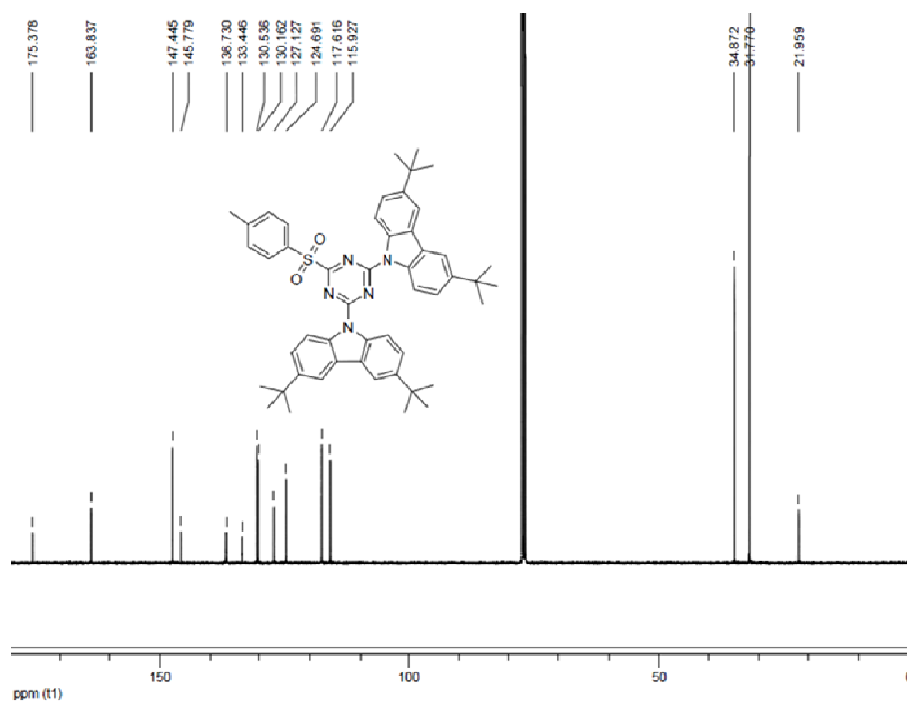
**Figure S10-1.**  $^1\text{H}$  NMR spectrum of SPhT in  $\text{CDCl}_3$



**Figure S10-2.**  $^{13}\text{C}$  NMR spectrum of SPhT in  $\text{CDCl}_3$



**Figure S11-1.** <sup>1</sup>H NMR spectrum of TosT in CDCl<sub>3</sub>



**Figure S11-2.** <sup>13</sup>C NMR spectrum of TosT in CDCl<sub>3</sub>

**Table S1.** Electroluminescent performance of the  $\sigma$ -spaced triazine hosts for FIrpic-based PhOLEDs.

Host	$\eta_{\max}$ [cd/A] <sup>[a]</sup>	$V_{\text{turn-on}}$ [V]	$B$ [cd/m <sup>2</sup> ] <sup>[b]</sup>	EQE <sub>max</sub> [%] <sup>[c]</sup>
NPhT	1.7	<5.0	825	0.6
NMePhT	4.9	<5.0	2628	2.0
OPhT	6.2	<4.0	815	1.9
SPhT	1.6	<5.0	647	1.0
TosT	1.9	<4.5	610	0.87

<sup>[a]</sup> Maximum current efficiency. <sup>[b]</sup> Luminance at 8.5 V. <sup>[c]</sup> External quantum efficiency