

## Electronic Supplementary Information

### Frustrated Lewis pairs with thermally activated delayed fluorescence properties: activation of formaldehyde

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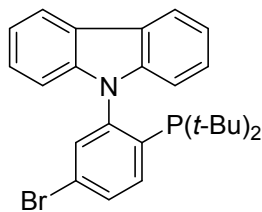
## 1. Experimental

### 1.1. General considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques. Anhydrous-grade solvents (Aldrich) were dried over activated molecular sieves (5Å). Spectrophotometric-grade toluene, and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were used as received from Merck. Commercial reagents were used without further purification after purchase. Deuterated solvents from Eurisotop were used. NMR spectra were recorded on a Bruker AM 300 (300.13 MHz for <sup>1</sup>H, 75.48 MHz for <sup>13</sup>C, 96.29 MHz for <sup>11</sup>B, 121.49 MHz for <sup>31</sup>P, and 282.38 MHz for <sup>19</sup>F) spectrometer at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C), BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B, <sup>19</sup>F), and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Elemental analyses were performed on a Flash 2000 elemental analyzer (Thermo Scientific). Melting (mp) points were measured by Melting Point Apparatus SMP30 (Stuart Equipment). 9-(2,5-Dibromophenyl)-9*H*-carbazole, 9-(5-(dimesitylboryl)-2-(diphenylphosphino)phenyl)-9*H*-carbazole (CzmBP, **1b**) and 9-(2-(diisopropylphosphino)-5-(dimesitylboryl)phenyl)-9*H*-carbazole (CzmBPi, **2b**) were synthesized according to the reported procedures.<sup>1</sup>

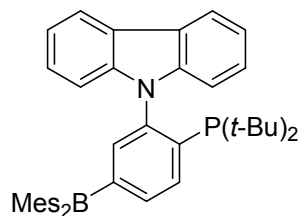
### 1.2. Synthesis

#### 9-(5-Bromo-2-(di-*tert*-butylphosphino)phenyl)-9*H*-carbazole



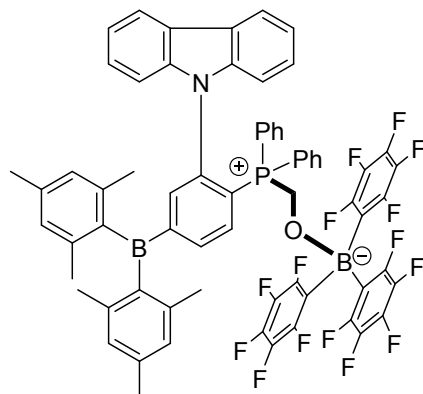
To a solution of 9-(2,5-dibromophenyl)-9*H*-carbazole (0.50 g, 1.25 mmol) in dry THF (20 mL) was added dropwise *n*-BuLi (0.5 mL, 1.25 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then di-*tert*-butylchlorophosphine (0.25 mL, 1.32 mmol) in dry THF (5 mL) was slowly added. After stirring at room temperature overnight, the resulting turbid yellow solution was dried under reduced pressure and then methanol (20 mL) was added. After stirring for 1 h at room temperature, the pale yellow precipitate was corrected by filtration and purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:9, v/v) as an eluent to give 9-(5-bromo-2-(di-*tert*-butylphosphino)phenyl)-9*H*-carbazole as a white powder (Yield: 0.065 g, 11%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.17 (dq, *J* = 7.7, 0.9 Hz, 2H), 8.00 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.54 (sq, *J* = 2.1 Hz, 1H), 7.40 (td, *J* = 7.8, 1.2 Hz, 2H), 7.30 (td, *J* = 7.5, 0.9 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 1.16 (s, 9H, -CH<sub>3</sub>), 1.12 (s, 9H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 145.6, 145.3, 142.1, 142.0, 138.1, 138.0, 137.6, 133.3, 133.3, 130.9, 130.8, 125.3, 124.1, 124.0, 123.1, 120.0, 119.7, 111.1 (Ar-C), 32.3, 32.0, 30.8, 30.6 (*t*-Bu-C). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 17.8 (s).

### 9-(5-(Dimesitylboryl)-2-(di-*tert*-butylphosphino)phenyl)-9*H*-carbazole (**CzmBPt**, **3b**)



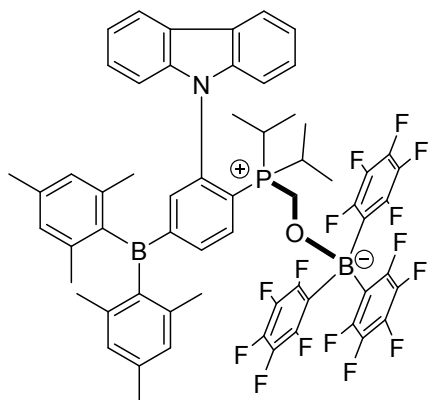
To a solution of 9-(5-bromo-2-(di-*tert*-butylphosphino)phenyl)-9*H*-carbazole (0.15 g, 0.322 mmol) in dry ether (15 mL) was added dropwise *n*-BuLi (0.13 mL, 0.325 mmol) at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h and then Mes<sub>2</sub>BF (0.09 g, 0.336 mmol) in dry ether (5 mL) was slowly added. After stirring at room temperature overnight, the resulting yellow solution was concentrated under reduced pressure and purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:5, v/v) as an eluent to give **CzmBPt** as a yellow powder (Yield: 0.14 g, 68%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.13 (d,  $J = 7.8$  Hz, 3H), 7.64 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.41 (dd,  $J = 4.2, 1.2$  Hz, 1H), 7.36 (td,  $J = 7.5, 1.2$  Hz, 2H), 7.25 (td,  $J = 7.4, 0.9$  Hz, 2H), 7.02 (d,  $J = 8.1$  Hz, 2H), 6.82 (s, 4H, Mes-*H*), 2.77 (s, 6H, Mes-CH<sub>3</sub>), 2.07 (s, 12H, Mes-CH<sub>3</sub>), 1.16 (s, 9H, *t*-Bu-CH<sub>3</sub>), 1.12 (s, 9H, *t*-Bu-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  143.8, 143.5, 143.0, 142.6, 142.3, 140.7, 139.2, 136.8, 136.7, 134.4, 128.2, 125.1, 122.8, 119.9, 119.2, 111.0 (Ar-C), 32.4, 32.1, 30.9, 30.7, 23.2, 20.9 (Mes-CH<sub>3</sub> and *t*-Bu-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  75.3 (s, br). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  18.9 (s). Anal. Calcd for C<sub>44</sub>H<sub>51</sub>BNP: C, 83.14; H, 8.09; N, 2.20. Found: C, 82.76; H, 7.94; N, 2.47. mp = 246 °C.

### **CzmBP-CH<sub>2</sub>O-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** (**1**)



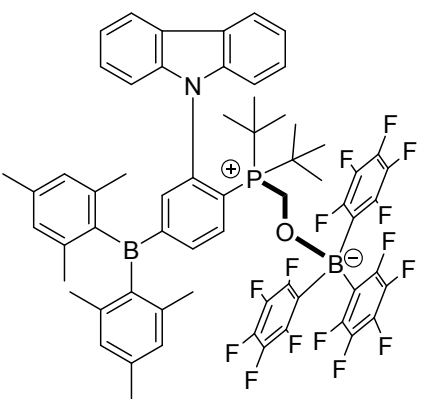
In a Schlenk flask, **CzmBP** (**1b**) (0.1 g, 0.148 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.09 g, 0.176 mmol) were dissolved in toluene (5 mL) and stirred for 0.5 h, then paraformaldehyde (0.01 g, 0.333 mmol) was added to the reaction mixture. After stirring overnight at room temperature, the resulting solution was filtered and dried under reduced pressure. The crude powder was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3) as an eluent to give **1** as a pale yellow powder (Yield : 0.063 g, 35%). Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of **1** in diethyl ether, affording pale yellow crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.07–8.00 (m, 1H), 7.91 (dd,  $J = 6.9, 1.2$  Hz, 2H), 7.87 (dq,  $J = 7.8, 1.2$  Hz, 1H), 7.61–7.56 (m, 3H), 7.32–7.28 (m, 8H), 7.22–7.13 (m, 4H), 6.83 (s, 4H, Mes-*H*), 4.18 (d,  $J = 2.1$  Hz, 2H, -CH<sub>2</sub>O-), 2.27 (s, 6H, Mes-CH<sub>3</sub>), 2.04 (s, 12H, Mes-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  141.7, 141.3, 140.8, 140.3, 139.1, 136.8, 136.2, 136.1, 134.2, 133.3, 133.1, 129.2, 129.0, 128.6, 126.2, 124.1, 123.2, 123.0, 120.6, 120.3, 117.6, 116.5, 108.8, 100.0 (Ar-C), 23.3, 20.9 (Mes-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -2.3 (s, -OB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 81.8 (s, br, -BMes<sub>2</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  18.0 (s). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -134.2, -162.5, -166.9. Anal. Calcd for **1**·2C<sub>4</sub>H<sub>10</sub>O (C<sub>75</sub>H<sub>65</sub>B<sub>2</sub>F<sub>15</sub>NO<sub>3</sub>P): C, 65.95; H, 4.80; N, 1.03. Found: C, 66.18; H, 4.93; N, 1.10. mp = 145 °C.

### CzmBPi-CH<sub>2</sub>O-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**2**)



This compound was prepared in a manner analogous to the synthesis of **1** using CzmBPi (**2b**) (0.1 g, 0.165 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.1 g, 0.195 mmol), and paraformaldehyde (0.01 g, 0.333 mmol) to give **2** as a white powder (Yield: 0.098 g, 52%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.91–7.86 (m, 2H), 7.51 (d, *J* = 4.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.2 Hz, 2H), 7.31 (td, *J* = 7.5, 0.9 Hz, 2H), 6.83 (s, 4H, Mes-*H*), 6.70 (d, *J* = 8.1 Hz, 2H), 3.29 (d, *J* = 3.3 Hz, -CH<sub>2</sub>O-), 3.10 (septet, *J* = 7.2 Hz, 2H, *i*-Pr-CH-), 2.27 (s, 6H, Mes-CH<sub>3</sub>), 2.00 (s, 12H, Mes-CH<sub>3</sub>), 1.43 (d, *J* = 7.2 Hz, 3H, *i*-Pr-CH<sub>3</sub>), 1.37 (d, *J* = 7.2 Hz, 3H, *i*-Pr-CH<sub>3</sub>), 1.29 (d, *J* = 7.5 Hz, 3H, *i*-Pr-CH<sub>3</sub>), 1.23 (d, *J* = 6.9 Hz, 3H, *i*-Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 142.2, 141.8, 140.8, 140.4, 139.4, 136.2, 132.6, 128.9, 128.6, 128.1, 126.4, 125.2, 123.3, 122.7, 121.9, 121.0, 120.8, 108.7 (Ar-C), 23.3, 21.9, 21.4, 16.4, 15.8 (Mes-CH<sub>3</sub> and *i*-Pr-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -2.4 (s, -B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 75.2 (s, br, -BMes<sub>2</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 36.7 (s). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -135.1, -162.2, -166.8. Anal. Calcd for **2**·C<sub>6</sub>H<sub>14</sub> (C<sub>67</sub>H<sub>63</sub>B<sub>2</sub>F<sub>15</sub>NOP): C, 65.12; H, 5.14; N, 1.13. Found: C, 65.20; H, 4.93; N, 1.40. mp = 148 °C.

### CzmBPt-CH<sub>2</sub>O-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**3**)



This compound was prepared in a manner analogous to the synthesis of **1** using CzmBPt (**3b**) (0.06 g, 0.094 mmol), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.05 g, 0.098 mmol), and paraformaldehyde (0.01 g, 0.333 mmol) to give **3** as a pale green powder (Yield: 0.065 g, 59%). **3** is light-sensitive so it should be kept in the dark for long-term use. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.19 (t, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 4.4 Hz, 1H), 6.79 (s, 4H, Mes-*H*), 6.71 (d, *J* = 8.0 Hz, 2H), 4.20 (d, *J* = 2.0 Hz, 2H, -CH<sub>2</sub>O-), 2.25 (s, 6H, Mes-CH<sub>3</sub>), 1.95 (s, 12H, Mes-CH<sub>3</sub>), 1.65 (s, 9H, *t*-Bu-CH<sub>3</sub>), 1.62 (s, 9H, *t*-Bu-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 143.1, 142.9, 140.8, 140.4, 140.1, 140.0, 135.1, 135.0, 134.6, 134.5, 128.5, 126.8, 126.3, 124.1, 123.5, 122.8, 121.1, 120.9, 109.2, 100.0 (Ar-C), 36.6, 36.2, 28.8, 23.2, 20.9 (Mes-CH<sub>3</sub> and *t*-Bu-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -3.0 (s, -OB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), 83.9 (s, br, -BMes<sub>2</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 40.9 (s). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -133.2, -162.2, -166.6. Anal. Calcd for **3** (C<sub>63</sub>H<sub>53</sub>B<sub>2</sub>F<sub>15</sub>NOP): C, 64.25; H, 4.54; N, 1.19. Found: C, 64.60; H, 4.88; N, 1.10. mp = 228 °C.

### 1.3. X-ray crystallography

Single crystals of suitable size and quality (**1**) were coated with Paratone oil and mounted onto a glass capillary. Diffraction data were obtained at 296 K. The crystallographic measurements were performed on a Bruker SMART Apex II CCD area detector diffractometer with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and refined by full-matrix least-squares fitting on  $F^2$  using SHELXL-2014.<sup>2</sup> Because of the disordered solvents, pentafluorophenyl, and carbazole groups, the crystal diffracted weakly so geometrical restraints, i.e., DFIX, and ISOR were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions and all hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Full details of the structure determinations have been deposited as a cif with the Cambridge Crystallographic Data Collection under CCDC deposition number 2016208. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

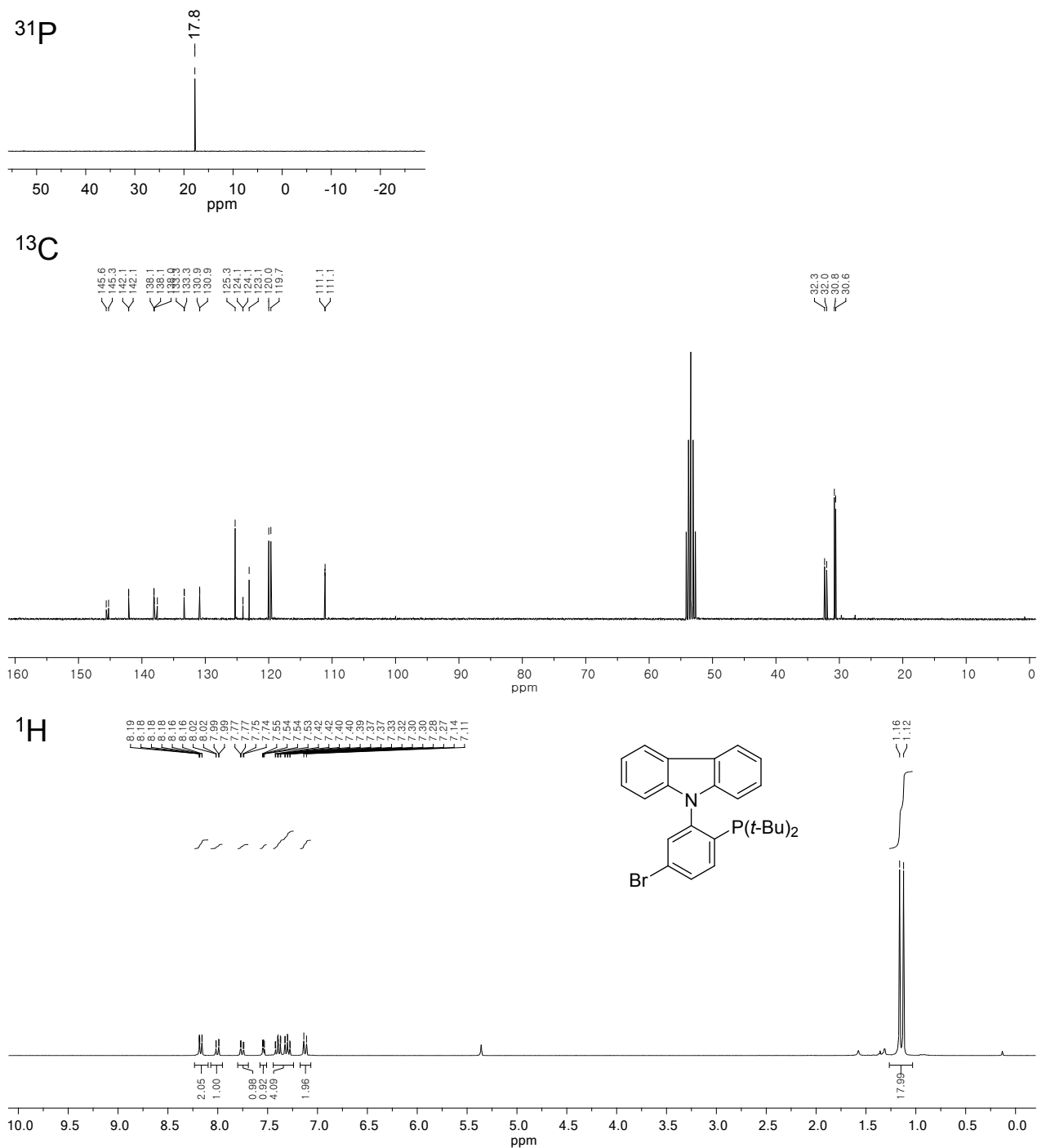
### 1.4. Photophysical measurements

UV/vis absorption and photoluminescence (PL) spectra were recorded on a Varian Cary 100 and FS5 spectrophotometer, respectively. Solution PL spectra were obtained from oxygen-free and air-saturated solutions. Dilute sample solutions (typically  $5.0 \times 10^{-5} \text{ M}$ ) were prepared in a glovebox at ambient conditions. Absolute photoluminescence quantum yields (PLQYs,  $\Phi_{\text{PL}}$ ) of solutions were measured on an absolute PL quantum yield spectrophotometer (Quantaaurus-QY C11347-11, Hamamatsu Photonics) equipped with a 3.3 inch integrating sphere. Transient PL decays were measured on an FS5 spectrophotometer (Edinburgh Instruments) in either time-correlated single-photon counting (TCSPC) mode (an EPL-375 picosecond pulsed diode laser) or multi-channel scaling (MCS) mode (a microsecond Xenon flashlamp as a light source). The lifetimes of prompt fluorescence ( $\tau_{\text{p}}$ ) were estimated by fitting decay curves measured via the TCSPC mode, while those of delayed fluorescence ( $\tau_{\text{d}}$ ) were estimated with curves measured via the MCS mode. PLQYs of prompt ( $\Phi_{\text{PF}}$ ) and delayed ( $\Phi_{\text{DF}}$ ) fluorescence were estimated from the prompt and delayed components of the transient decay curves, respectively. The temperature-dependence of PL decay was obtained with an OptistatDN<sup>TM</sup> cryostat (Oxford Instruments).

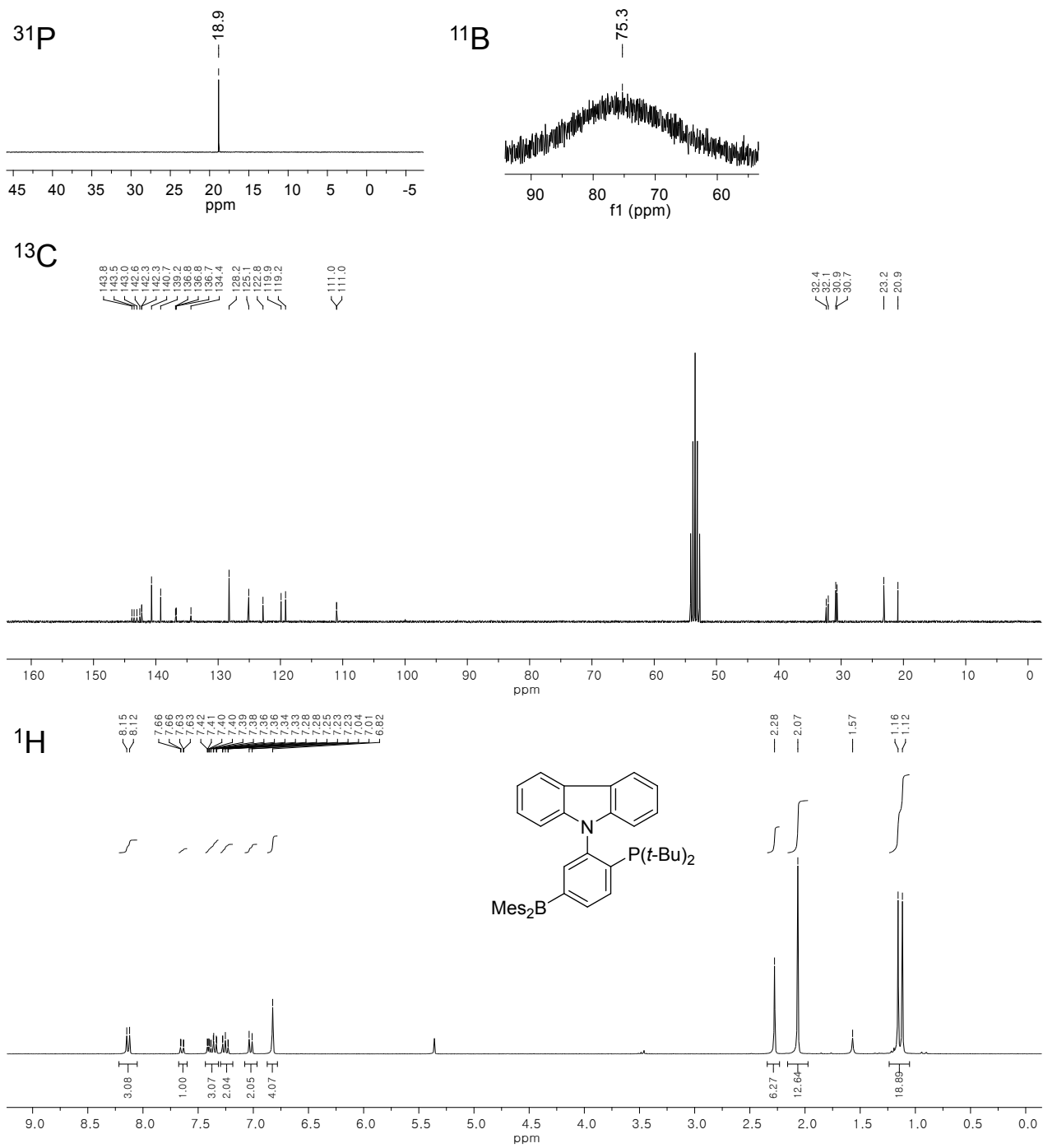
### 1.5. Theoretical calculations

All calculations were performed using the Gaussian 09 program package.<sup>3</sup> The geometry optimization of ground states was computed with density functional theory (DFT) at the M062X/6-31g(d) levels,<sup>4</sup> and the energy minima were confirmed by the calculation with zero imaginary mode of vibrations. The

calculated absorptions and emissions were obtained using the time-dependent density functional theory (TD-DFT) method within the Tamm–Dancoff approximation,<sup>5</sup> taking the optimized geometries at  $S_0$  and  $S_1$  states, respectively. The ground state optimized geometry was used for the investigation of the vertical excitation and the optimized geometries at lowest singlet and triplet excited states were used for the calculation of  $\Delta E_{ST}$ . All the calculations are performed in dichloromethane using polarizable continuum model (PCM).<sup>6</sup> The overlap integral extents were computed using Multiwfn program.<sup>7</sup>

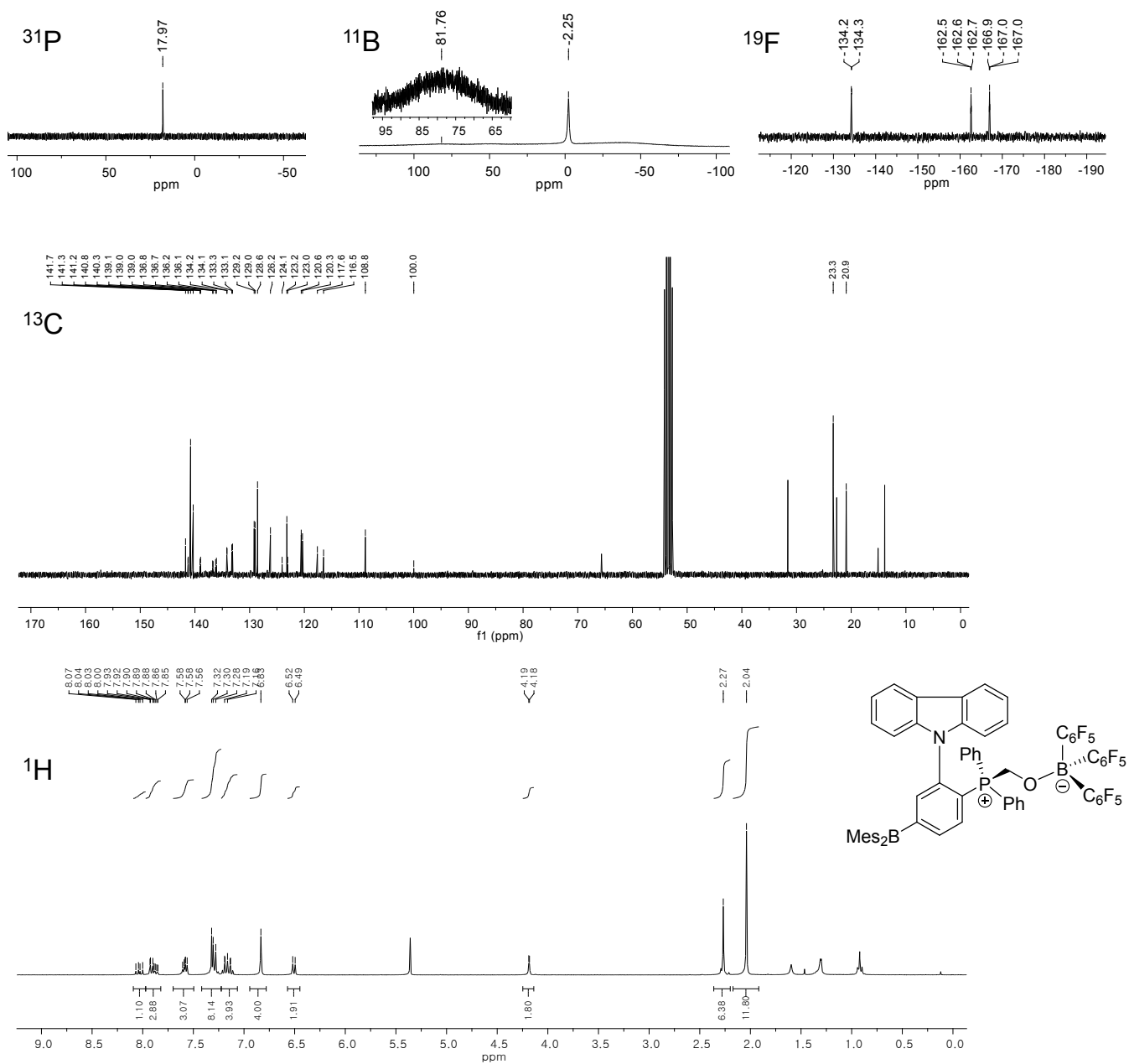


**Fig. S1.** NMR spectra of 9-(5-bromo-2-(*di-tert*-butylphosphino)phenyl)-9*H*-carbazole in CD<sub>2</sub>Cl<sub>2</sub>.

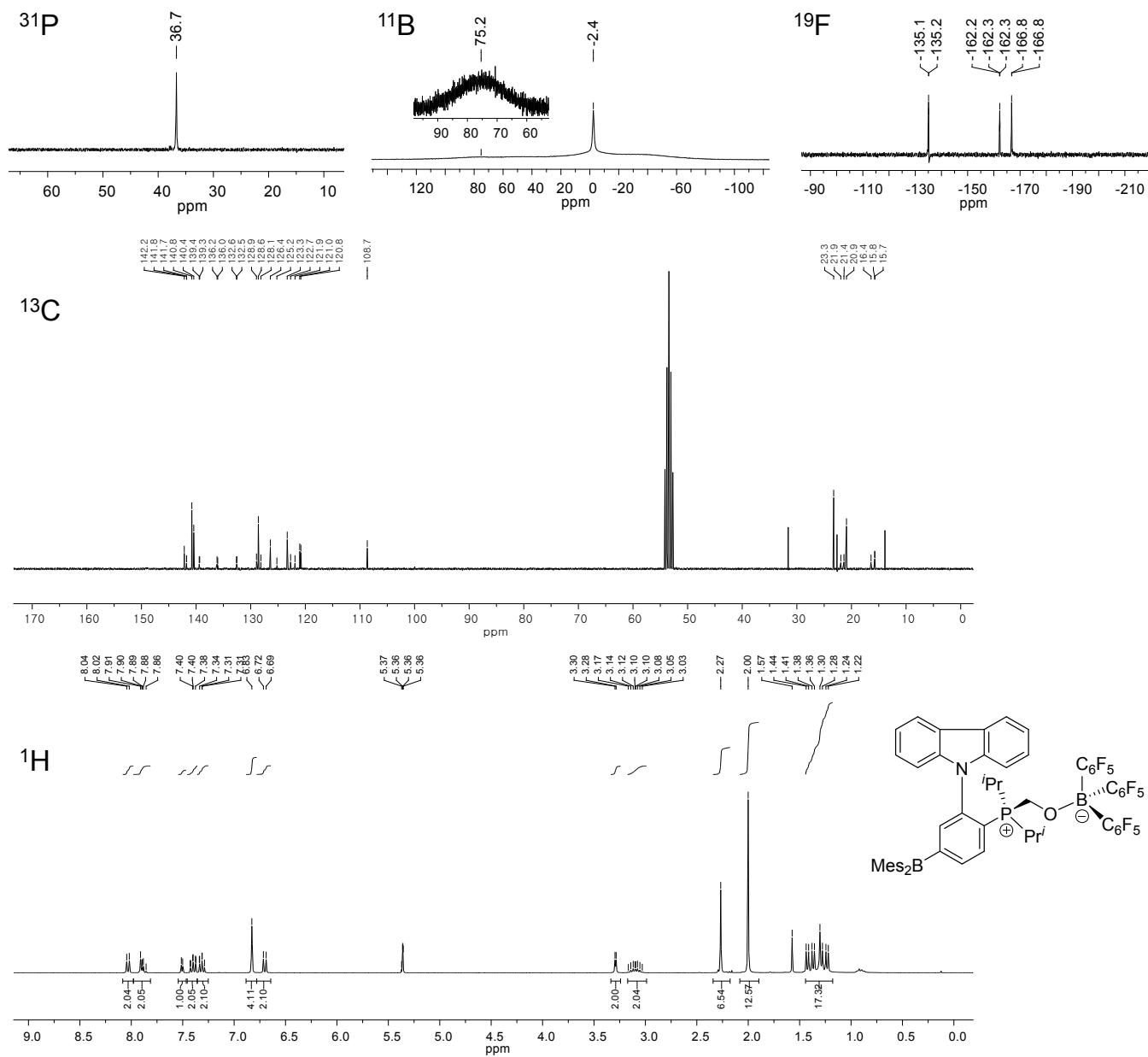


**Fig. S2.** NMR spectra of CzmBPt (**3b**) in CD<sub>2</sub>Cl<sub>2</sub>.

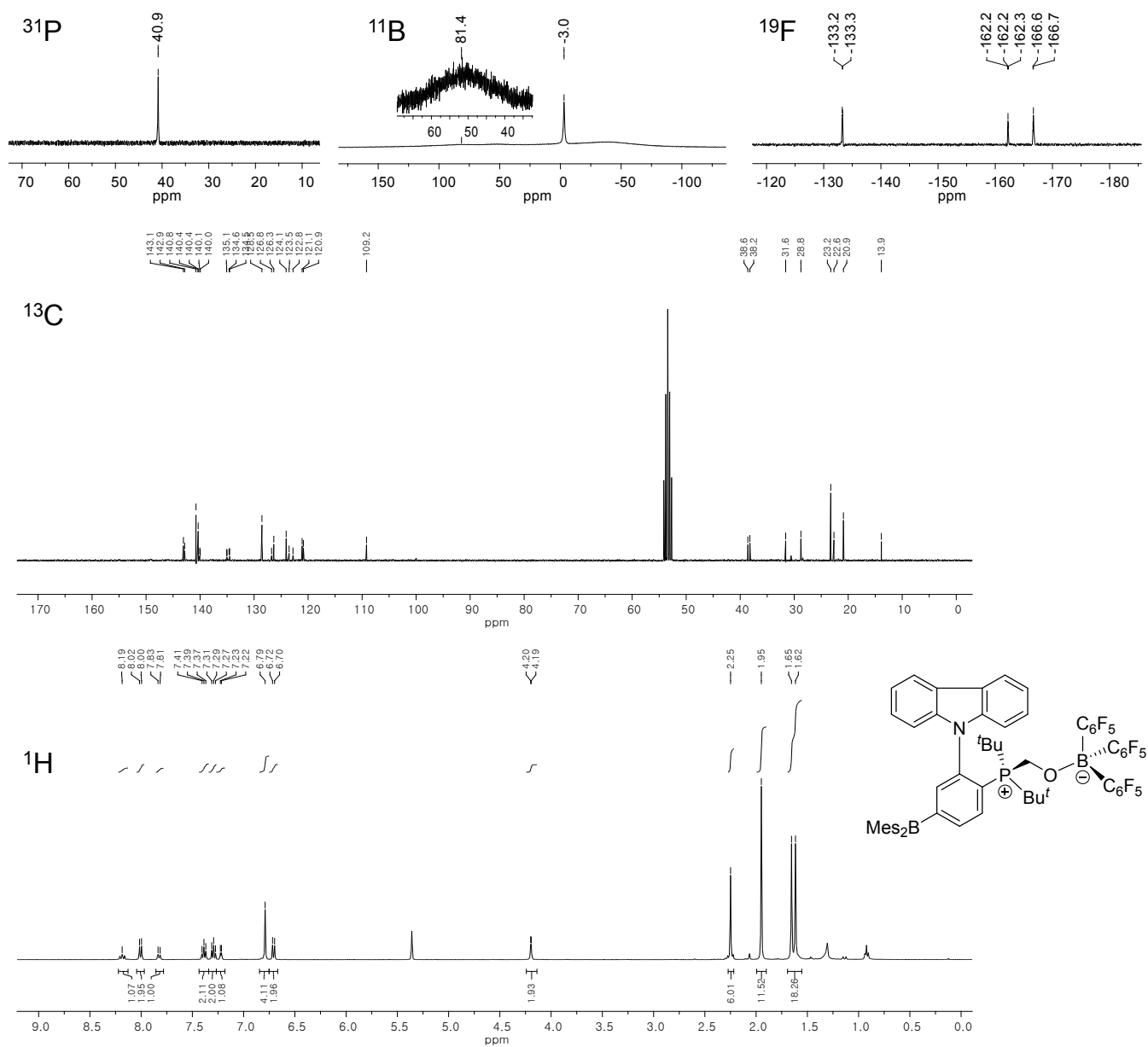




**Fig. S3.** NMR spectra of **1** in  $\text{CD}_2\text{Cl}_2$ .



**Fig. S4.** NMR spectra of **2** in  $\text{CD}_2\text{Cl}_2$ .

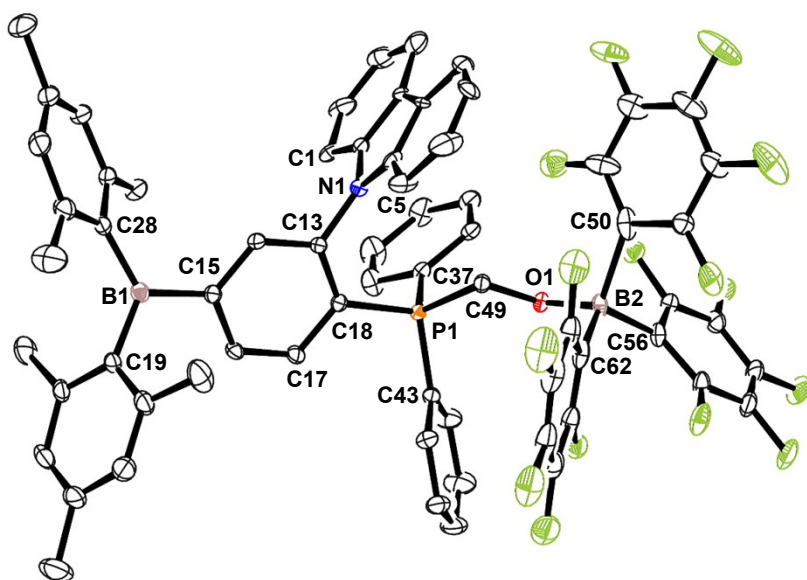


**Fig. S5.** NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$ .

**Table S1.** Crystallographic data and parameters for **1**.

	<b>1</b>
formula	C <sub>67</sub> H <sub>45</sub> B <sub>2</sub> F <sub>15</sub> NOP, 2(C <sub>2</sub> H <sub>5</sub> O <sub>0.5</sub> )
formula weight	1291.82
crystal system	Monoclinic
space group	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	14.2411(3)
<i>b</i> (Å)	23.1001(5)
<i>c</i> (Å)	20.8633(4)
$\alpha$ (°)	90
$\beta$ (°)	100.6709(11)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	6744.7(2)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.272
$\mu$ (mm <sup>-1</sup> )	0.126
<i>F</i> (000)	2656
<i>T</i> (K)	100
<i>hkl</i> range	-17→17, -28→28, -25→25
measd reflns	105922
unique reflns [ <i>R</i> <sub>int</sub> ]	12902 (0.0434)
reflns used for refinement	12902
refined parameters	1099
R1 <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0688
wR2 <sup>b</sup> all data	0.2237
GOF on <i>F</i> <sup>2</sup>	1.024
$\rho_{\text{fin}}$ (max/min) (e Å <sup>-3</sup> )	1.073/-0.414

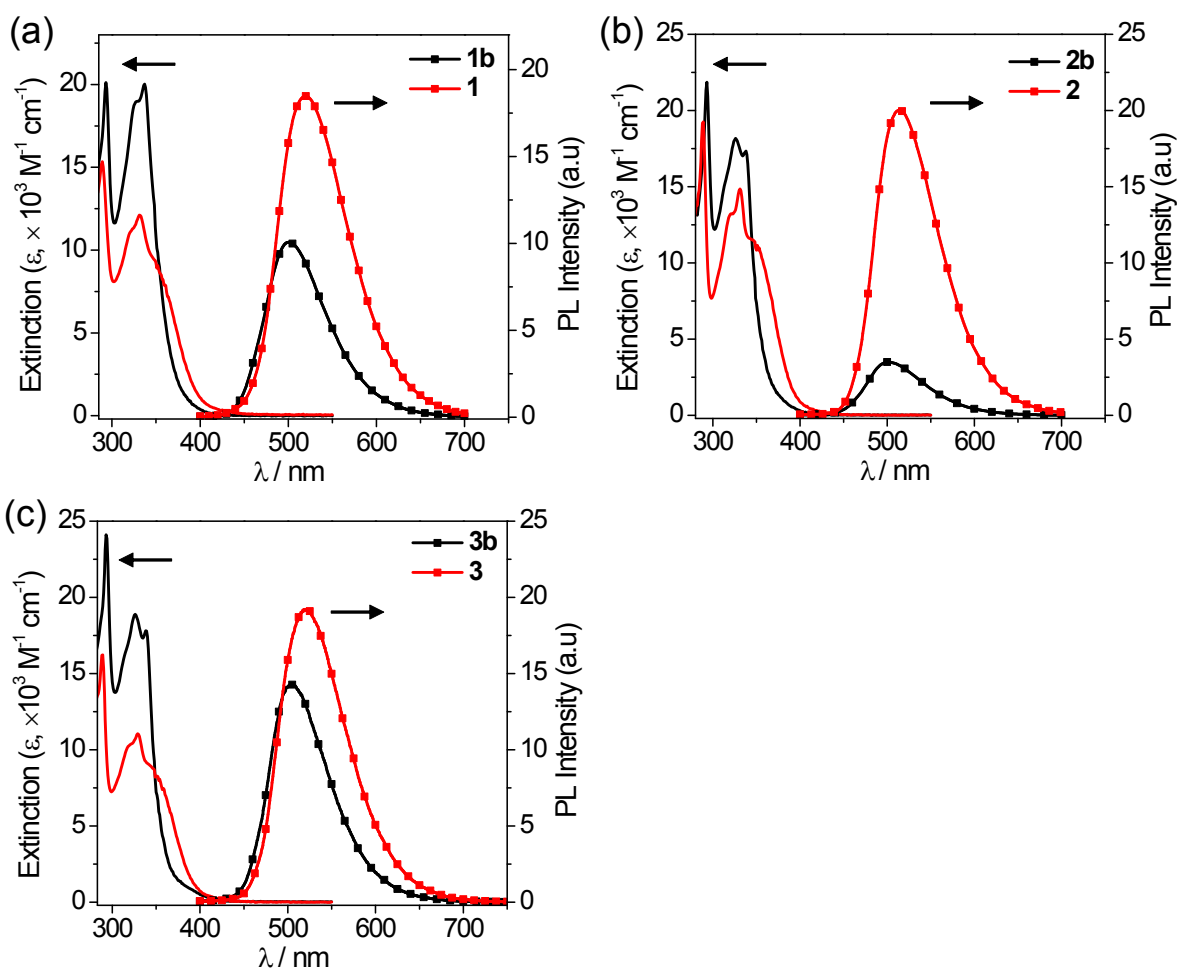
<sup>a</sup> R1 =  $\sum||F_o| - |F_c||/\sum|F_o|$ . <sup>b</sup> wR2 =  $\{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ .



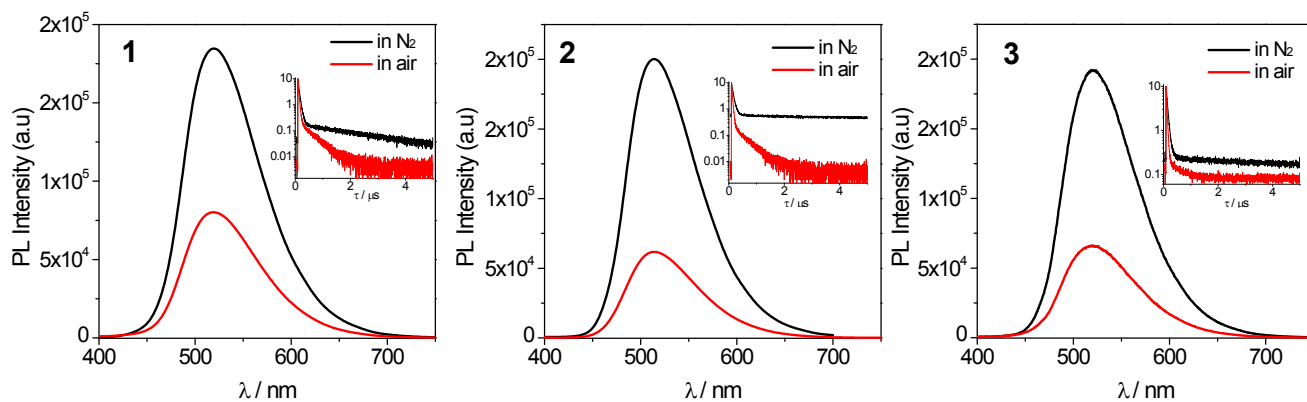
**Fig. S6.** Crystal structure of **1** (30% thermal ellipsoids) with atom labels. H atoms and a solvent molecule are omitted for clarity.

**Table S2.** Selected bond lengths (Å) and angles (deg) for **1**.

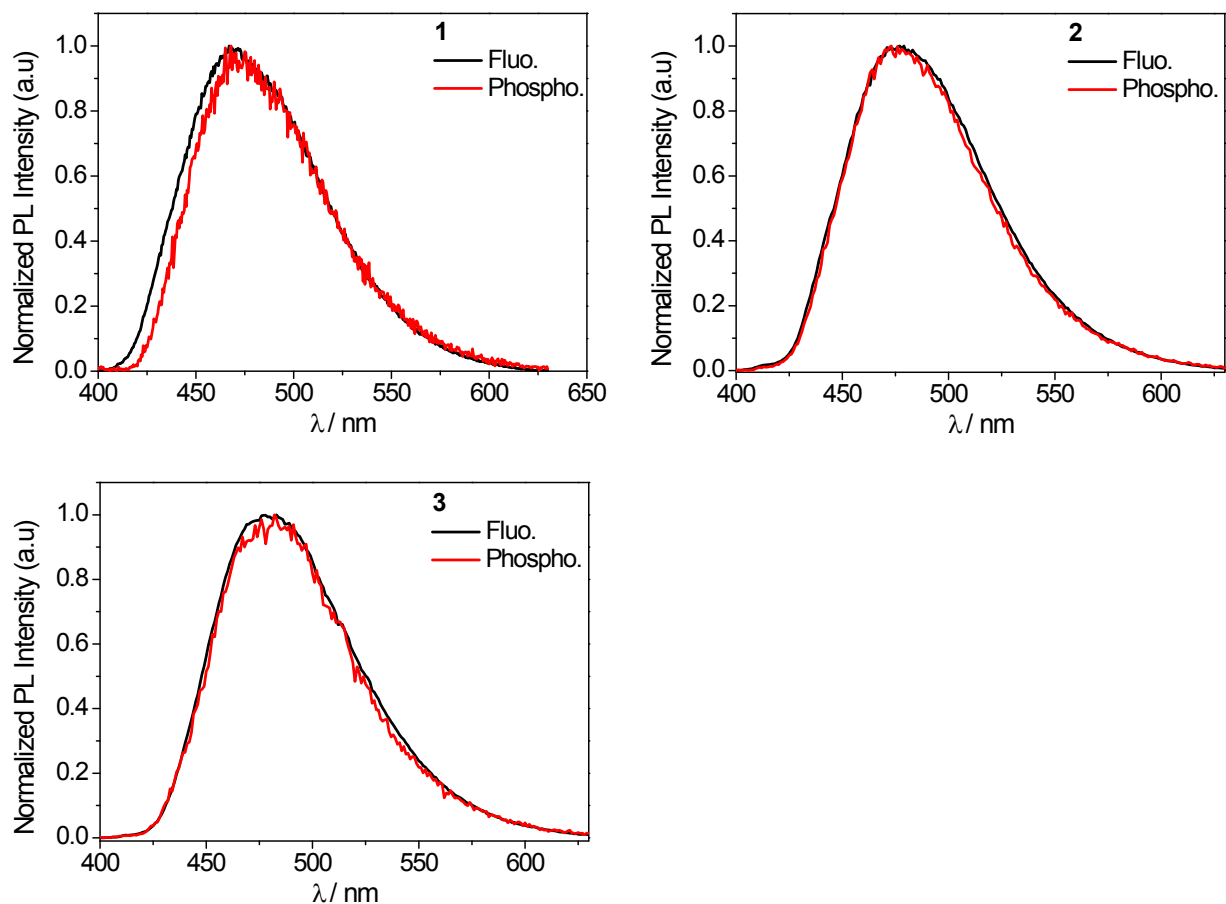
Lengths (Å)		Angles (°)	
B(1)–C(28)	1.563(4)	C(18)–P(1)–C(49)	110.86(12)
B(1)–C(19)	1.573(4)	C(37)–P(1)–C(18)	110.11(12)
B(1)–C(15)	1.589(4)	C(37)–P(1)–C(43)	109.33(13)
N(1)–C(13)	1.452(10)	C(37)–P(1)–C(49)	111.55(12)
B(2)–C(50)	1.816(6)	C(43)–P(1)–C(18)	107.37(11)
B(2)–C(56)	1.656(4)	C(43)–P(1)–C(49)	107.47(12)
B(2)–C(62)	1.648(4)	C(28)–B(1)–C(15)	119.7(2)
B(2)–O(1)	1.492(3)	C(28)–B(1)–C(19)	126.7(2)
P(1)–C(18)	1.810(2)	C(15)–B(1)–C(19)	113.6(2)
P(1)–C(37)	1.783(3)	C(18)–C(13)–N(1)	117.3(4)
P(1)–C(49)	1.826(3)	O(1)–C(49)–P(1)	106.88(17)
P(1)–C(43)	1.791(3)	C(13)–C(18)–P(1)	122.76(18)
C(49)–O(1)	1.399(3)	O(1)–B(2)–C(56)	105.4(2)
		O(1)–B(2)–C(62)	107.4(2)
		O(1)–B(2)–C(50)	108.7(3)
		C(56)–B(2)–C(50)	103.3(3)
		C(62)–B(2)–C(56)	114.2(2)
		C(62)–B(2)–C(50)	117.1(3)



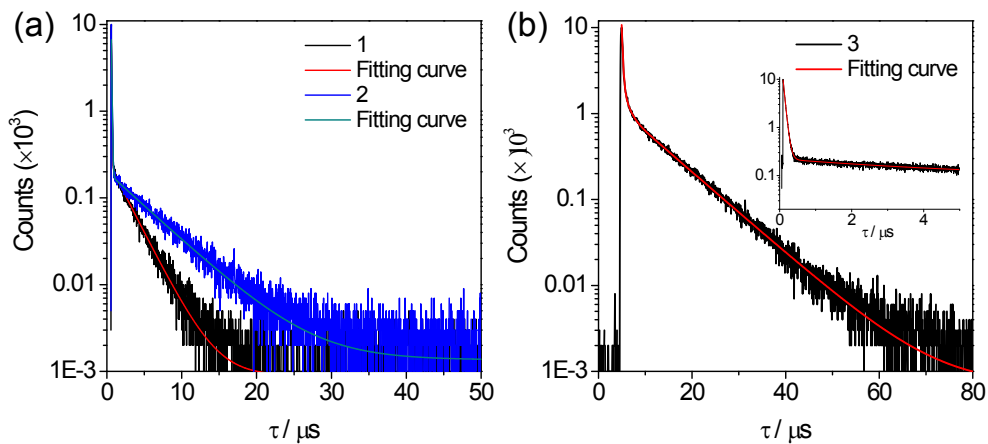
**Fig. S7.** UV/vis absorption and PL spectra of (a) CzmBP (**1b**) and **1**, (b) CzmBPi (**2b**) and **2**, and (c) CzmBPt (**3b**) and **3** in oxygen-free toluene ( $5.0 \times 10^{-5}$  M) at 298 K.



**Fig. S8.** PL spectra of **1–3** in oxygen-free (black line) and air-saturated (red line) toluene at 298 K. Insets: transient PL decay curves.

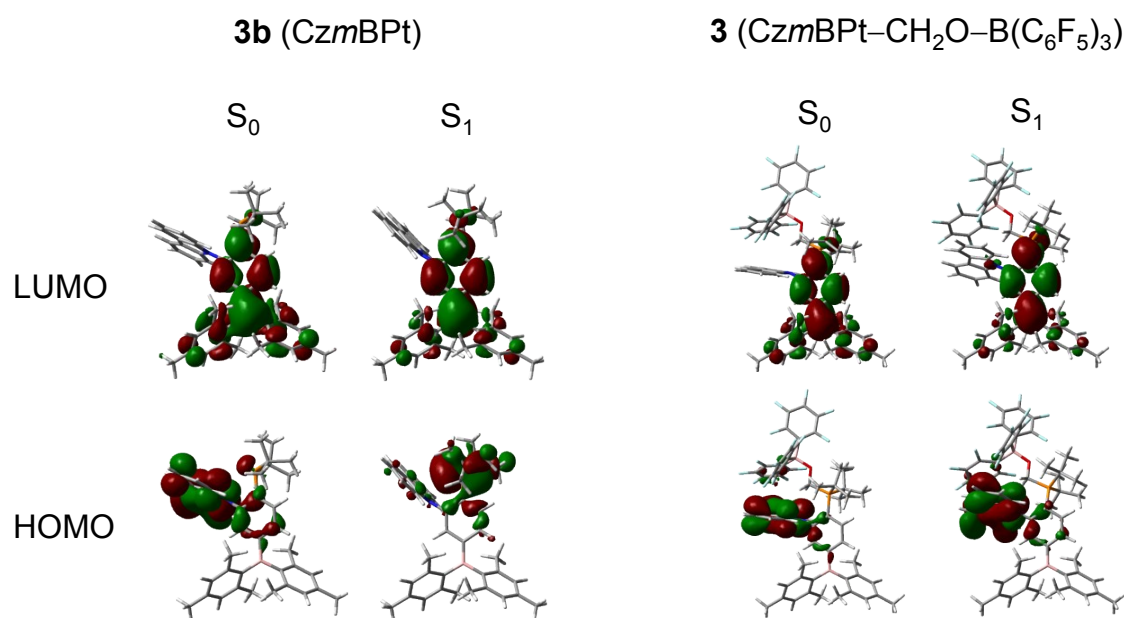


**Fig. S9.** Fluorescence and phosphorescence (delay time = 1 ms) spectra of compounds (1–3) in toluene at 77 K.



**Fig. S10.** Transient PL decay curves of 1–3 in oxygen-free  $\text{CH}_2\text{Cl}_2$  at 298 K.

## 2. Computational results



**Fig. S11.** The frontier molecular orbitals, HOMO and LUMO, of **3b** and **3** (isovalue = 0.02) at their S<sub>0</sub> and T<sub>1</sub> optimized geometries.

**Table S3.** Molecular orbital energies (in eV) and the contribution (in %) of donor and acceptor moieties to the frontier molecular orbitals at the ground state (S<sub>0</sub>) optimized geometries and the overlap integral ( $I_{H/L}$ , in %) between HOMO and LUMO for **3b** and **3**.

	MO	energy (eV)	donor (Cz)	acceptor (Mes <sub>2</sub> BPh)	acceptor (R <sub>2</sub> P or R <sub>2</sub> P-FA-BAr <sup>F</sup> <sub>3</sub> )	$I_{H/L}$
<b>3b</b>	LUMO	-1.22	0.50	96.13	3.37	22.65
	HOMO	-6.75	89.48	7.67	2.85	
<b>3</b>	LUMO	-1.68	0.66	92.59	6.75	17.99
	HOMO	-7.10	92.67	3.82	3.51	



**Table S4.** The computed absorption wavelength ( $\lambda_{\text{abs}}$ , in nm), corresponding oscillator strength ( $f$ ), and major contribution for the transition in **3b** and **3**.

	$\lambda_{\text{abs}}$	$f$	major contribution
<b>3b</b>	322	0.090	HOMO→LUMO (69%) HOMO-3→LUMO (13%)
<b>3</b>	336	0.059	HOMO→LUMO (58%) HOMO-2→LUMO (31%)

**Table S5.** The computed vertical emission wavelength ( $\lambda_{\text{em}}$  in nm), corresponding oscillator strength ( $f$ ), and reorganization energy ( $\lambda_{\text{ROE}}$ ) at the excited singlet states ( $S_1$ ) of **3b** and **3**.

	$\lambda_{\text{em}}$	$f$	$\lambda_{\text{ROE}}$ (eV)
<b>3b</b>	713	0.003	0.59
<b>3</b>	426	0.039	0.06

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