

## Supporting Information

### Highly Efficient All Solution Processed Non-Doped Deep Blue Electroluminescent Devices from Oligocarbazole-End Capped Spirobifluorenes

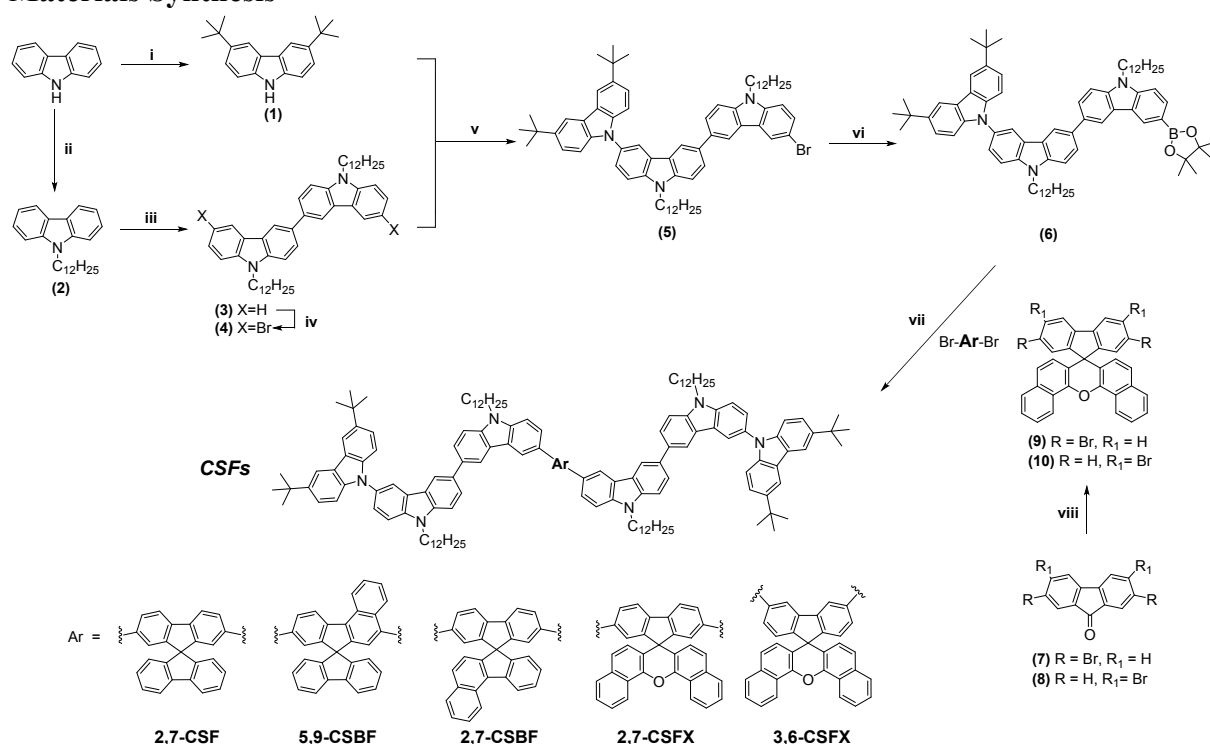
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#### Materials Synthesis



**Scheme S1** Synthesis of oligocarbazole-end capped spirobifluorenes (**CSFs**). *Reagents and conditions:* i) *tert*-BuCl, DCM, CH<sub>3</sub>NO<sub>2</sub>; ii) C<sub>12</sub>H<sub>25</sub>Br, KOH, DMF; iii) FeCl<sub>3</sub>, CHCl<sub>3</sub>; iv) NBS, THF, 0 °C; v) ( $\pm$ )-*trans*-1,2-diaminocyclohexane, CuI, K<sub>3</sub>PO<sub>4</sub>, toluene, reflux; vi) bis(pinacolato)diboron, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub>K, toluene, reflux; vii) dibromo spirobifluorenes, Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M Na<sub>2</sub>CO<sub>3</sub>, THF, reflux; viii) 1-naphthol, CH<sub>3</sub>SO<sub>3</sub>H.

**9-Dodecyl-9H-carbazole (2):** Carbazole (20.00 g, 0.1196 mol) was dissolved in DMF (200 ml). Then, KOH (26.84 g, 0.4784 mol) was added. The mixture was stirred at room temperature for 1 hour. After that, the 1-bromododecane (57.44 ml, 0.2392 mol) was added to the mixture. Reaction mixture was stirred at room temperature for 18 hours. The reaction was quenched with

water, and then extracted by dichloromethane. The combine organic layer was dried over sodium sulfate anhydrous and concentrated by vacuum. The crude product was purified by silica gel column chromatography using hexane as eluent and dried the product in vacuum. The product was obtained as yellow liquid (38.52 g, 96%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.16 (2H, d, *J* = 7.7 Hz), 7.52 (2H, t, *J* = 7.6Hz), 7.46 (2H, d, *J* = 8.2 Hz), 7.29 (2H, t, *J* = 7.4Hz), 4.34 (2H, t, *J* = 7.3 Hz), 1.92 (2H, m), 1.44 (2H, m), 1.36 (4H, m), 1.31 (12H, s), 0.95 (3H, t, *J* = 7.0 Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 140.49, 125.58, 122.88, 120.36, 118.72, 108.68, 43.11, 31.95, 29.64, 29.64, 29.61, 29.54, 29.45, 29.37, 29.00, 27.35, 22.72, 14.15; MADI-TOF (m/z) calcd for C<sub>24</sub>H<sub>33</sub>N: 335.5350, found 336.1631 (M+H<sup>+</sup>).

**9,9'-Didodecyl-9H,9'H-3,3'-bicarbazole (3):** FeCl<sub>3</sub> (38.71 g, 0.2386 mol) was added slowly to a stirred solution of **2** (20.00 g, 0.0597 mol) in 200 ml CHCl<sub>3</sub>. The mixture was stirred at room temperature for 18 hours. After that, the reaction mixture was poured into methanol, then filtrated. The crude product was purified by silica gel column chromatography using hexane as eluent and dried the product in vacuum. The product was obtained as yellow liquid (31.93 g, 80%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.40 (2H, s), 8.18 (2H, d, *J* = 7.7 Hz), 7.82 (2H, d, *J* = 8.4 Hz), 7.48 (4H, m), 7.42 (2H, d, *J* = 8.1 Hz), 7.25 (2H, m), 4.34 (4H, t, *J* = 7.2 Hz), 1.91 (4H, q, *J* = 7.4 Hz), 1.42 (4H, q, *J* = 7.5Hz), 1.35 (4H, q, *J* = 6.7Hz), 1.25 (28H, m), 0.87 (6H, t, *J* = 6.9Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 140.94, 139.56, 133.39, 125.64, 125.54, 123.43, 123.09, 120.45, 118.95, 118.78, 108.87, 108.78, 43.25, 31.92, 29.62, 29.60, 29.53, 29.45, 29.34, 29.05, 27.36, 22.69, 14.11; MADI-TOF (m/z) calcd for C<sub>48</sub>H<sub>64</sub>N<sub>2</sub>: 669.0540; found 669.1518 (M<sup>+</sup>).

**6,6'-Dibromo-9,9'-didodecyl-9H,9'H-3,3'-bicarbazole (4):** Solution of NBS (0.56 g, 3.1388 mol) in THF (20 ml) was very slowly added to the solution of **3** (1.00 g, 1.4947 mmol) in THF (80 ml) at 0 °C. The reaction was quenched with sodium thiosulphate solution, and then extracted by dichloromethane. The combine organic layer was dried over sodium sulfate anhydrous and concentrated by vacuum. The crude product was purified by silica gel column chromatography using hexane as eluent and dried the product in vacuum. The product was obtained as light-yellow liquid (0.93 g, 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.33 (2H, s), 8.29 (2H, s), 7.83 (2H, d, *J* = 8.5Hz), 7.55 (2H,d, *J* = 8.6Hz), 7.49 (2H, d, *J* = 8.4Hz), 7.30 (2H, d, *J* = 8.6Hz), 4.31 (4H, t, *J* = 7.1Hz), 1.89 (4H, m), 1.39 (4H, m), 1.34 (4H, m), 1.24 (28H, m), 0.87 (6H, t, *J* = 6.9Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 139.8899, 139.5724, 133.4916, 128.3657, 126.1788, 124.7765, 123.2127, 122.4721, 119.0395, 111.6130, 110.2660, 109.2327, 43.3966, 31.9195, 29.6066, 29.5689, 29.5011, 29.4061, 29.3342, 28.9906, 27.3085, 22.6894, 14.1144; MADI-TOF (m/z) calcd for C<sub>48</sub>H<sub>62</sub>Br<sub>2</sub>N<sub>2</sub>: 826.8460; found 827.2778 (M+H<sup>+</sup>).

**6-Bromo-3'',6''-di-tert-butyl-9,9'-didodecyl-9H,9'H-3,3':6',9''-tercarbazole (5):** A dried mixture of **4** (12.00 g, 0.0145 mol), 3,6-di-tert-butyl-9H-carbazole (1.31 g, 0.0047 mol) and K<sub>3</sub>PO<sub>4</sub> (2.49 g, 0.0118 mol) were added CuI (0.45 g, 0.0023 mol) and toluene (100 ml), and then stirred at room temperature until dissolved. The mixture was degassed in N<sub>2</sub> atmosphere for 5 times followed by addition of (±)-*trans*-diaminocyclohexane (0.27 ml, 0.0023 mol). The reaction mixture was stirred at reflux under N<sub>2</sub> for 24 hours. After being cooled to room temperature, water was added and extracted with dichloromethane. The combined organic phases were dried over sodium sulfate anhydrous and the solvent was removed under pressure. The crude product was purified by silica gel column chromatography using hexane as eluent and dried the product in vacuum. The product obtains as pale-yellow solid (2.55 g, 53%). m.p. 75 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.39 (2H, d, *J* = 8.8Hz), 8.35 (1H, s), 8.32 (1H, s), 8.24 (2H, s), 7.90 (1H, d, *J* = 8.3Hz), 7.86 (1H, d, *J* = 8.3Hz), 7.64 (2H, m), 7.58 (2H, m), 7.51 (3H, m), 7.41 (2H, d, *J* = 8.3Hz), 7.31 (1H, d, *J* = 8.5Hz), 4.45 (2H, t, *J* = 6.3Hz), 4.31 (2H, t, *J* =

6.3Hz), 2.04 (2H, m), 1.91 (2H, m), 1.53 (18H, s), 1.45 (2H, m), 1.41 (2H, m), 1.30 (20H, m), 1.26 (12H, m), 0.90 (6H, m);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  142.42, 140.39, 140.26, 139.87, 139.84, 139.55, 133.51, 133.41, 129.47, 128.32, 126.15, 126.02, 125.12, 124.79, 123.91, 123.48, 123.22, 123.19, 123.09, 122.48, 119.32, 119.08, 119.00, 116.19, 111.60, 110.22, 109.66, 109.32, 109.25, 109.22, 43.56, 43.36, 34.76, 32.10, 31.93, 31.91, 29.66, 29.64, 29.59, 29.56, 29.49, 29.39, 29.36, 29.32, 29.18, 28.97, 27.43, 27.29, 22.70, 22.68, 14.11; MADI-TOF (m/z) calcd for  $\text{C}_{68}\text{H}_{86}\text{BrN}_3$ : 1025.3610; found 1025.8345 ( $\text{M}^+$ ).

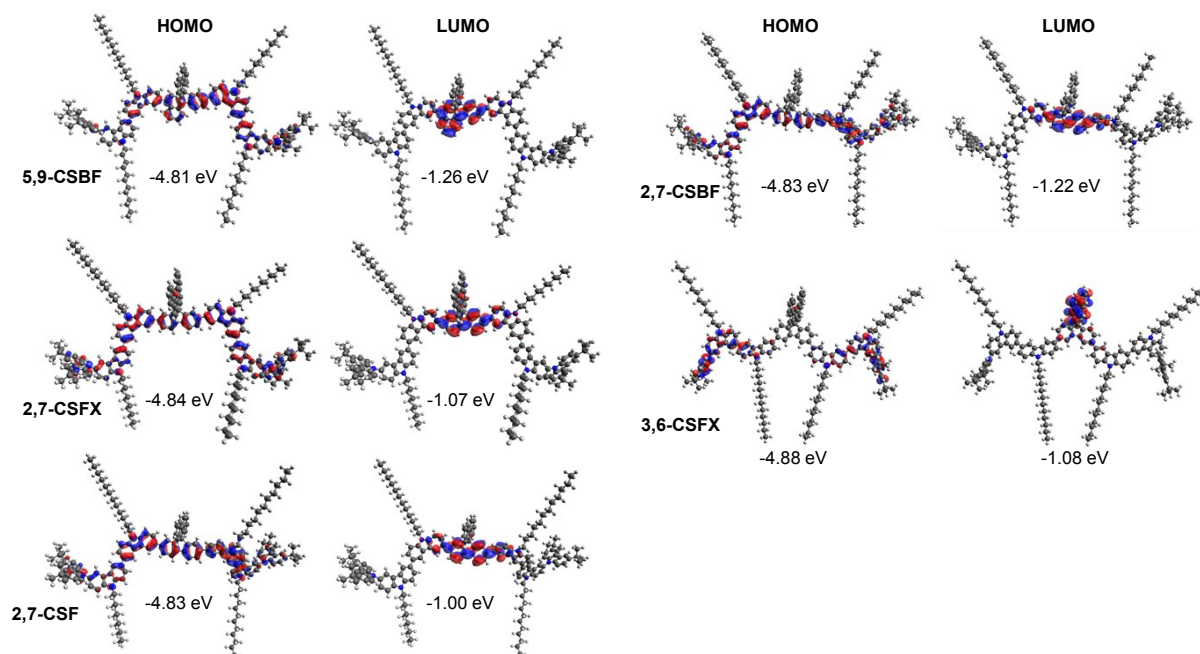
**3',6''-Di-tert-butyl-9,9'-didodecyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H,9'H-3,3':6',9''-tercarbazole (6):** 5 (1.00 g, 0.9753 mmol), bis(pinacolato)diboron (0.50 g, 1.9501 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.04 g, 0.0488 mmol), and  $\text{CH}_3\text{CO}_2\text{K}$  (1.15 g, 0.0117 mol) were dissolved in dry toluene (30 ml). The mixture was degassed in  $\text{N}_2$  atmosphere for 5 times. Then, the mixture was stirred at reflux temperature for 24 hours under  $\text{N}_2$  atmosphere. After being cooled to room temperature, water was added and extracted with dichloromethane. The combined organic phases were dried over sodium sulfate anhydrous and the solvent was removed under pressure. The pure compound was obtained by silica gel column chromatography using a mixture of dichloromethane and hexane as eluent and dried the product in vacuum. The product was obtained as pale-yellow solid (0.84 g, 80%). m.p. 98 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (1H, s), 8.47 (1H, s), 8.37 (1H, s), 8.32 (1H, s), 8.18 (2H, s), 7.91 (1H, d,  $J = 8.2\text{Hz}$ ), 7.89 (1H, d,  $J = 8.5\text{Hz}$ ), 7.81 (1H, d,  $J = 8.5\text{Hz}$ ), 7.60 (3H, m), 7.47 (3H, m), 7.39 (3H, m), 4.43 (2H, t,  $J = 7.1\text{Hz}$ ), 4.32 (2H, t,  $J = 7.1\text{Hz}$ ), 2.01 (2H, m), 1.89 (2H, m), 1.48 (18H, s), 1.39 (16H, m), 1.27 (20H, m), 1.23 (12H, s), 0.86 (6H, m);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  143.08, 142.33, 140.37, 140.21, 139.82, 139.69, 133.60, 133.35, 132.14, 129.42, 127.93, 126.00, 125.27, 125.02, 123.96, 123.78, 123.52, 123.18, 123.05, 122.82, 119.30, 119.08, 119.00, 116.13, 109.61, 109.28, 109.01, 108.19, 83.56, 43.57, 43.27, 34.75, 32.10, 31.93, 31.90, 29.66, 29.64, 29.59, 29.50, 29.42, 29.36, 29.32, 29.20, 29.01, 27.45, 27.31, 24.95, 22.70, 22.68, 14.12, 14.10; MADI-TOF (m/z) calcd for  $\text{C}_{74}\text{H}_{98}\text{BN}_3\text{O}_2$ : 1072.4270; found 1072.4045 ( $\text{M}^+$ ).

**2',7'-Dibromospiro[dibenzo[c,h]xanthene-7,9'-fluorene] (9):** A mixture of 2,7-Dibromo-9-fluorenone (1.00 g, 2.9586 mmol) 1-naphthol (1.71 g, 11.8344 mmol) and methane sulfonic acid (0.8 ml, 11.8344 mmol) was heated at 150 °C under nitrogen atmosphere for 24 h. The reaction mixture was then slowly added into water (20 ml) and extracted with DCM, washed with water and brine. The combined extracts were dried over sodium sulfate anhydrous, evaporated, and purified by column chromatography using hexane as eluent to obtain white solid product (1.28 g, 73%). m.p. 336 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (2H, d,  $J = 8.4\text{ Hz}$ ), 7.78 (2H, d,  $J = 8.1\text{ Hz}$ ), 7.71 (4H, dd,  $J = 16.8, 7.9\text{ Hz}$ ), 7.59 (2H, t,  $J = 7.5\text{ Hz}$ ), 7.53 (2H, dd,  $J = 8.2, 1.5\text{ Hz}$ ), 7.32 (2H, d,  $J = 8.6\text{ Hz}$ ), 7.26 (2H, m), 6.37 (2H, d,  $J = 8.6\text{ Hz}$ );  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  157.39, 145.81, 137.75, 133.72, 131.58, 129.70, 127.71, 127.00, 126.53, 125.05, 124.59, 123.50, 122.59, 121.77, 121.43, 116.36, 54.41; MALDI-TOF (m/z) calcd for  $\text{C}_{33}\text{H}_{18}\text{Br}_2\text{O}$  589.9704; found 590.1997 ( $\text{M}^+$ ).

**3',6'-Dibromospiro[dibenzo[c,h]xanthene-7,9'-fluorene] (10):** A mixture of 3,6-Dibromo-9H-fluorene-9-one (0.50 g, 1.4793 mmol) 1-naphthol (0.85 g, 5.9172 mmol) and methane sulfonic acid (3.0 ml, 14.7930 mmol) was heated at 150 °C under nitrogen atmosphere for 24

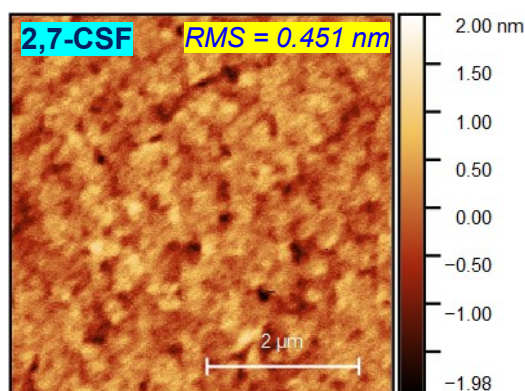
h. The reaction mixture was then slowly added into water (20 ml) and extracted with DCM, washed with water and brine. The combined extracts were dried over sodium sulfate anhydrous, evaporated, and purified by column chromatography using hexane as eluent to obtain white solid product (0.41 g, 47%). m.p. 318 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (2H, d,  $J = 8.4$  Hz), 7.98 (2H, d,  $J = 1.1$  Hz), 7.77 (2H, d,  $J = 8.1$  Hz), 7.71 (2H, t,  $J = 7.6$  Hz), 7.58 (2H, t,  $J = 7.5$  Hz), 7.35 (2H, m), 7.29 (2H, d,  $J = 8.6$  Hz), 7.03 (2H, d,  $J = 8.1$  Hz), 6.37 (2H, d,  $J = 8.6$  Hz);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  154.84, 145.83, 140.56, 133.66, 132.03, 127.96, 127.72, 126.89, 126.46, 125.01, 124.58, 123.50, 123.38, 122.40, 121.69, 116.53, 53.92; MALDI-TOF ( $m/z$ ) calcd for  $\text{C}_{33}\text{H}_{18}\text{Br}_2\text{O}$  589.9704; found 590.1997 ( $\text{M}^+$ ).

### DFT calculation data

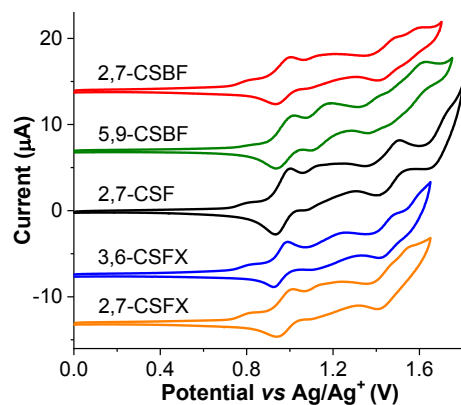


**Fig. S1** The optimized structures, HOMOs and LUMOs of CSFs calculated by TD-DFT B3LYP/6-31G(d) in  $\text{CH}_2\text{Cl}_2$ .

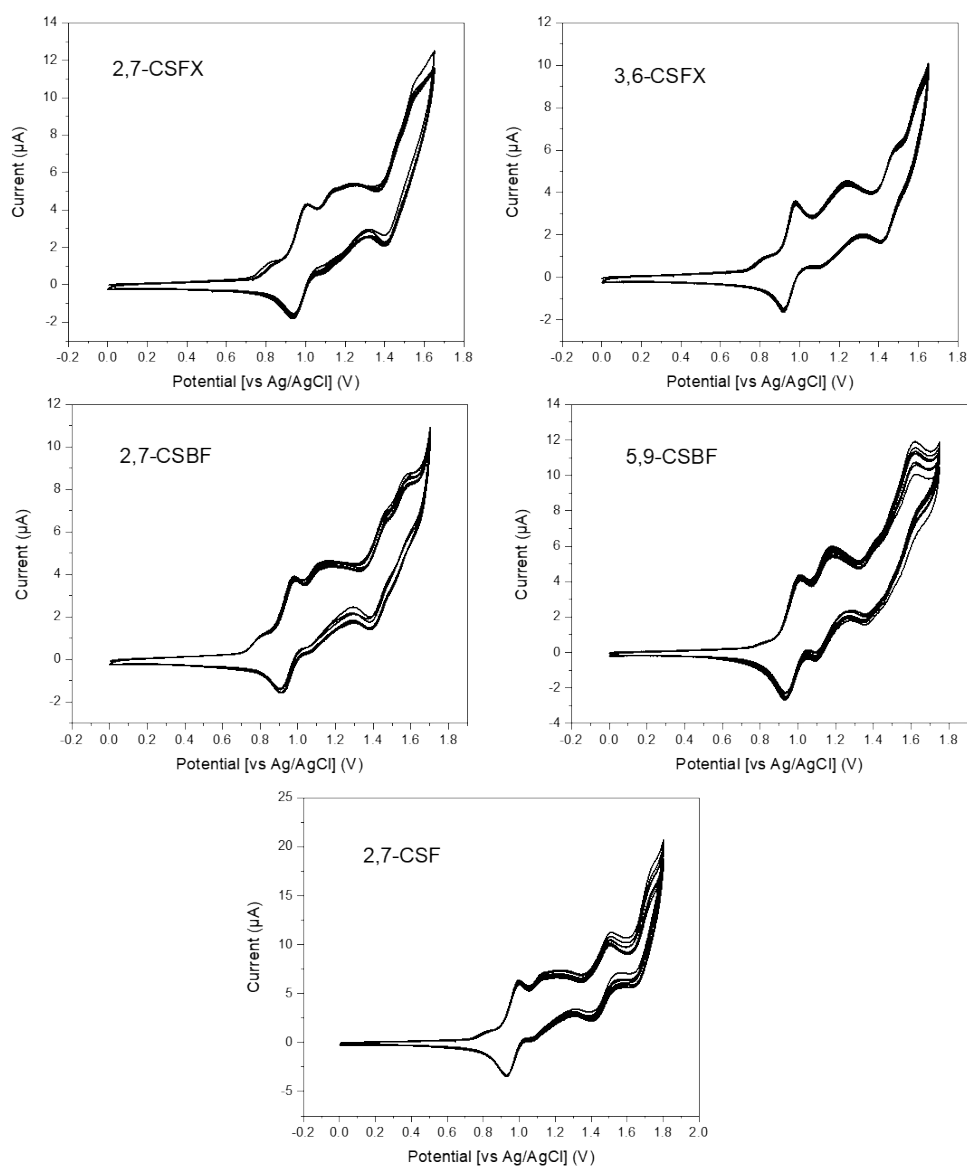
### Characterization data



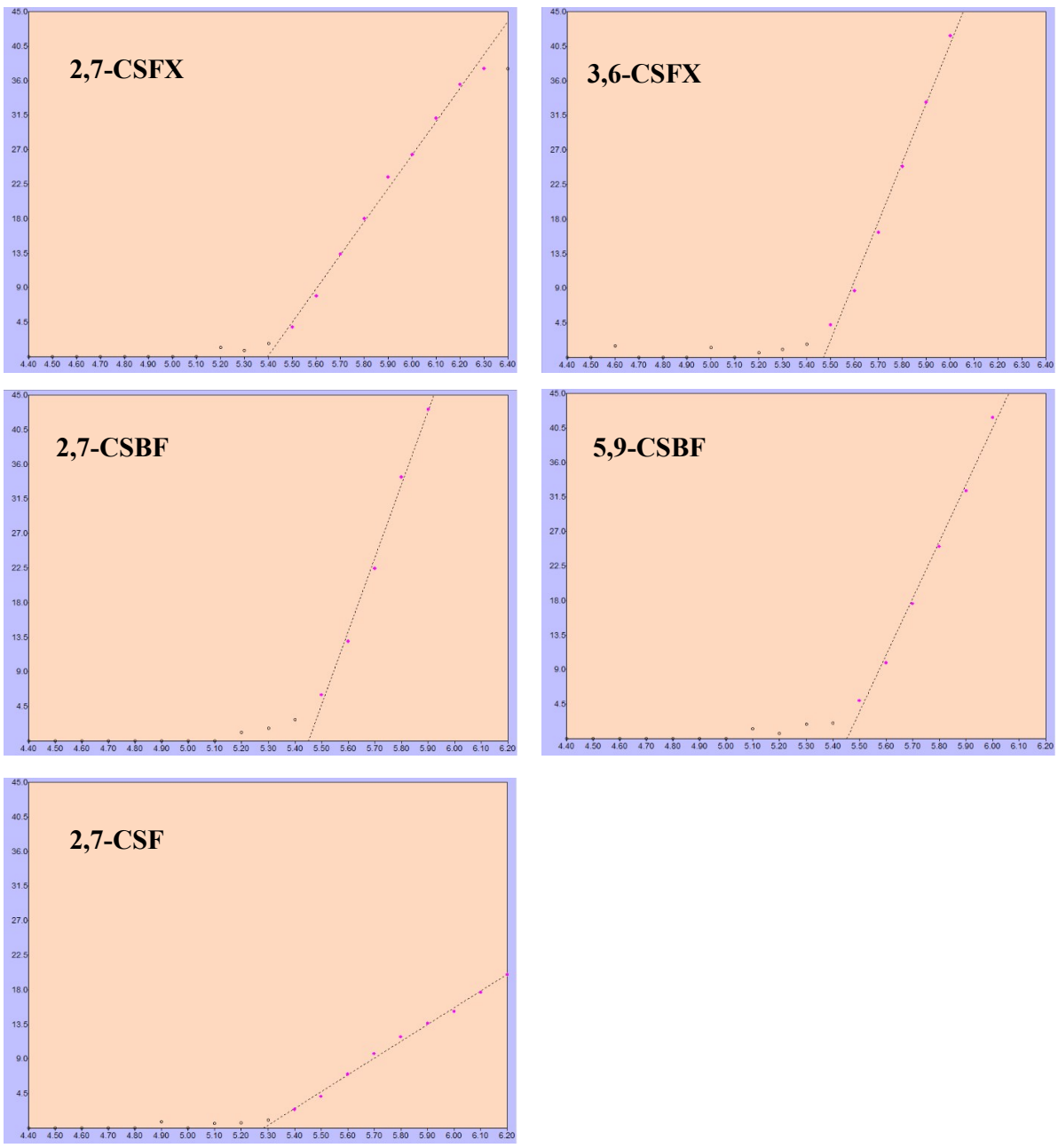
**Fig. S2** Non-contact mode AFM image of 2,7-CSF thin films spin-coated on ITO glasses.



**Fig. S3** CV curves of CSFs analysed in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{TBAPF}_6$  as a supporting electrolyte (scan rate of  $50 \text{ mV s}^{-1}$ ; concentration of 1 mM) under argon atmosphere.

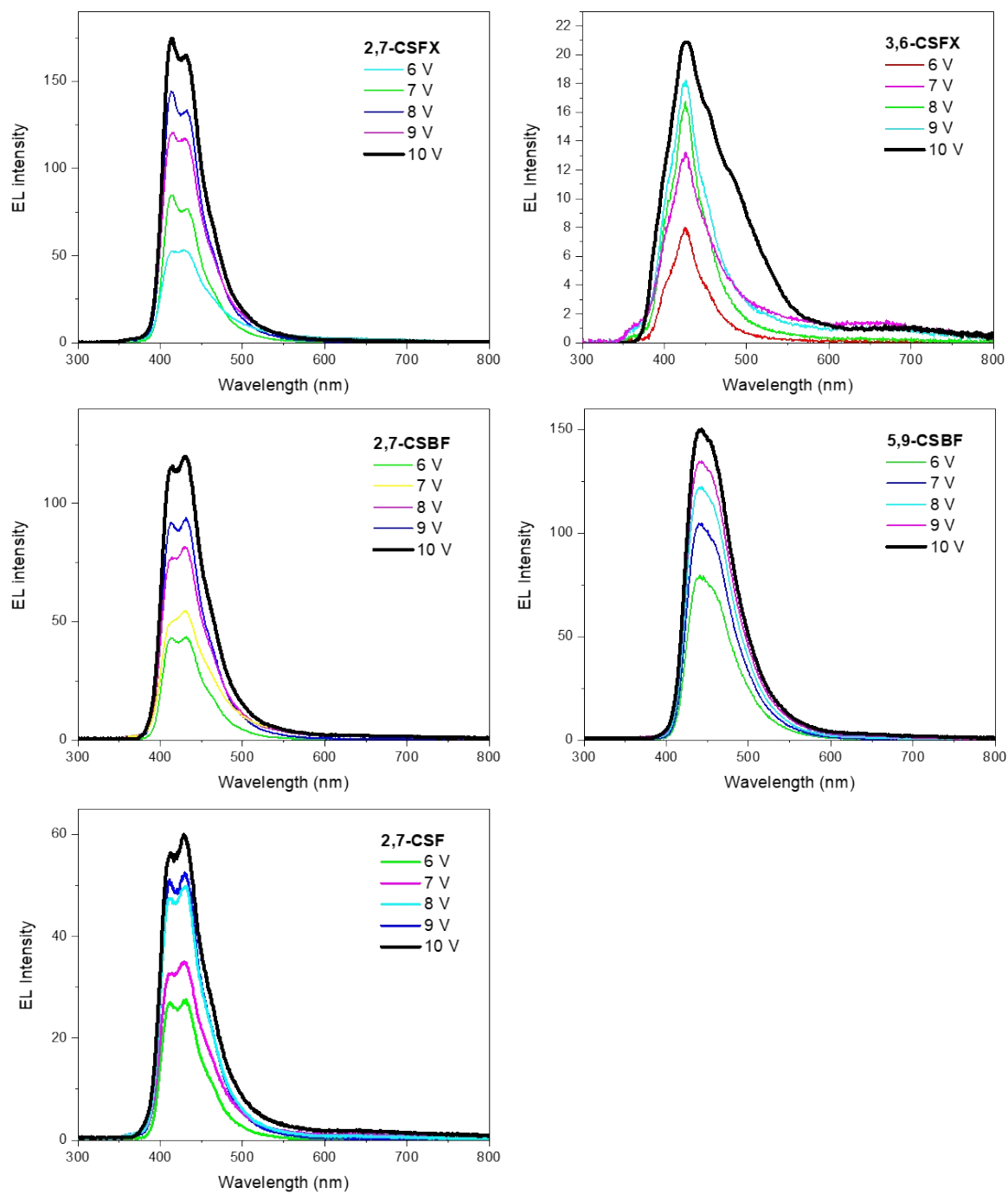


**Fig. S4** Multiple CV scan traces of CSFs analysed in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{TBAPF}_6$  as a supporting electrolyte (scan rate of  $50 \text{ mV s}^{-1}$ ; concentration of 1 mM) under argon atmosphere.



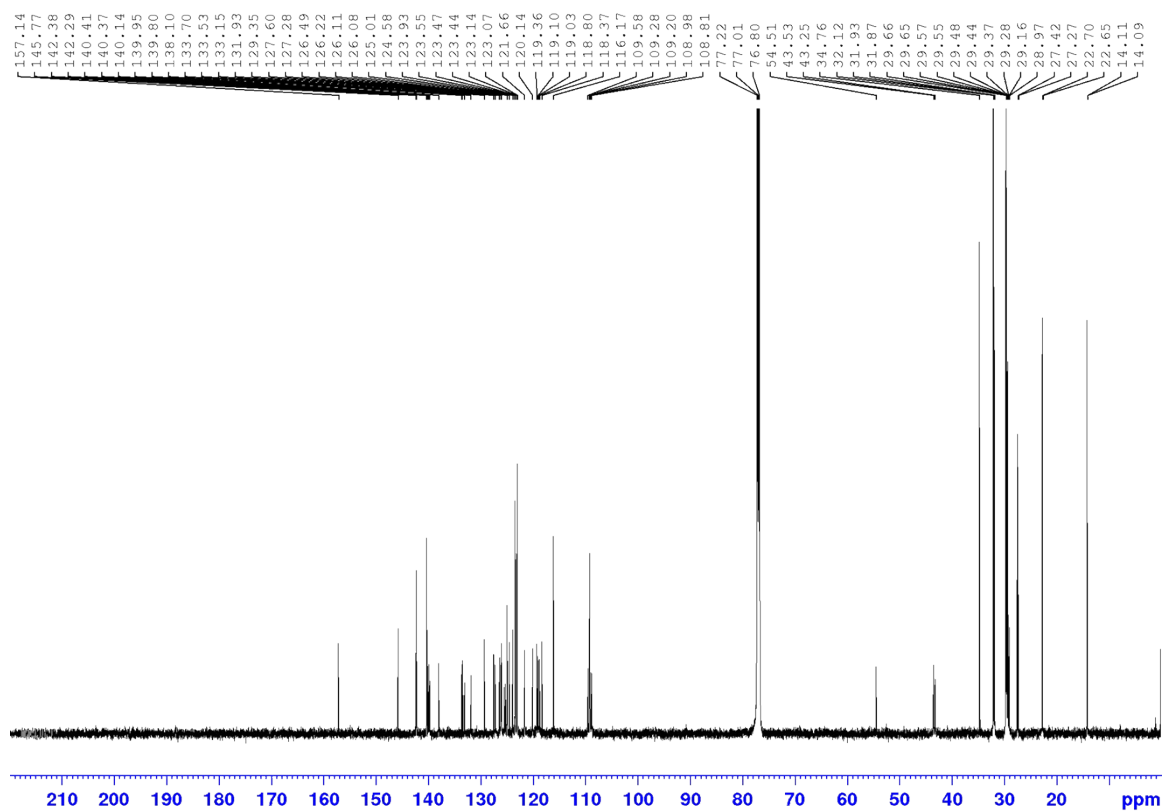
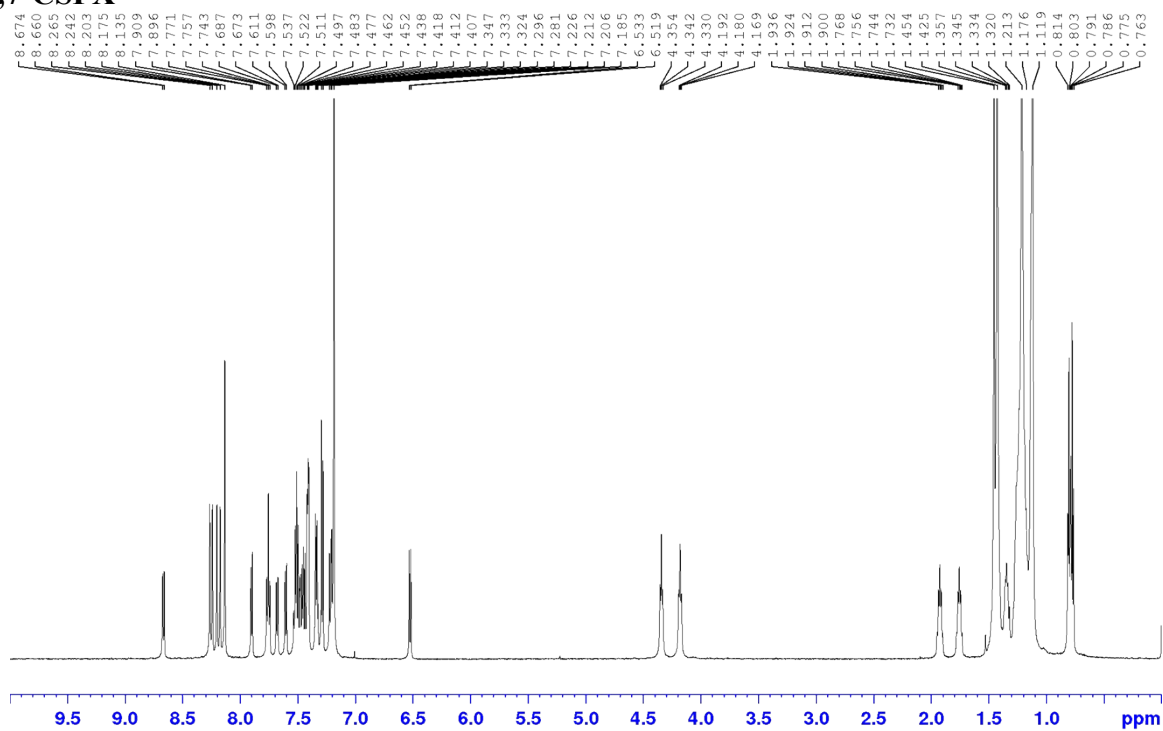
**Fig. S5** Photoemission yield spectroscopy in air (PYSA) spectra of CSFs.

## OLED device data



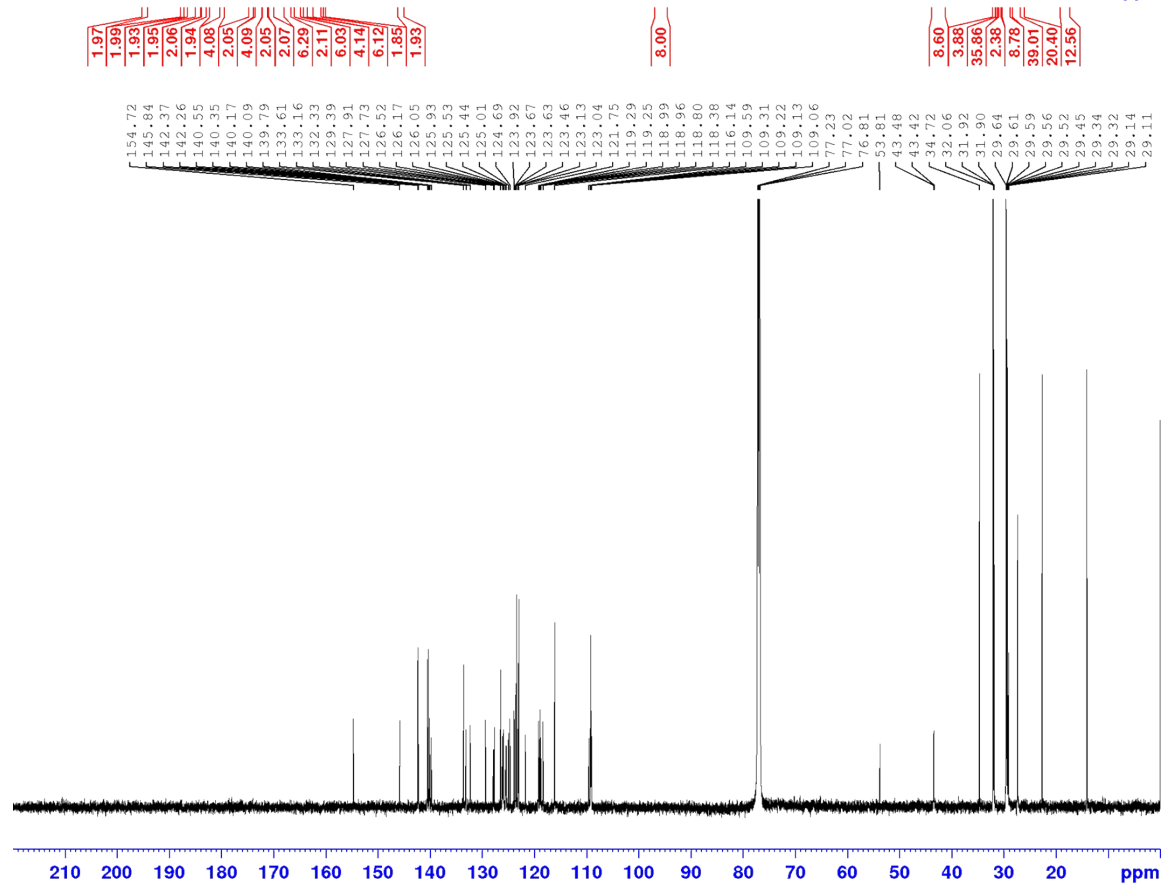
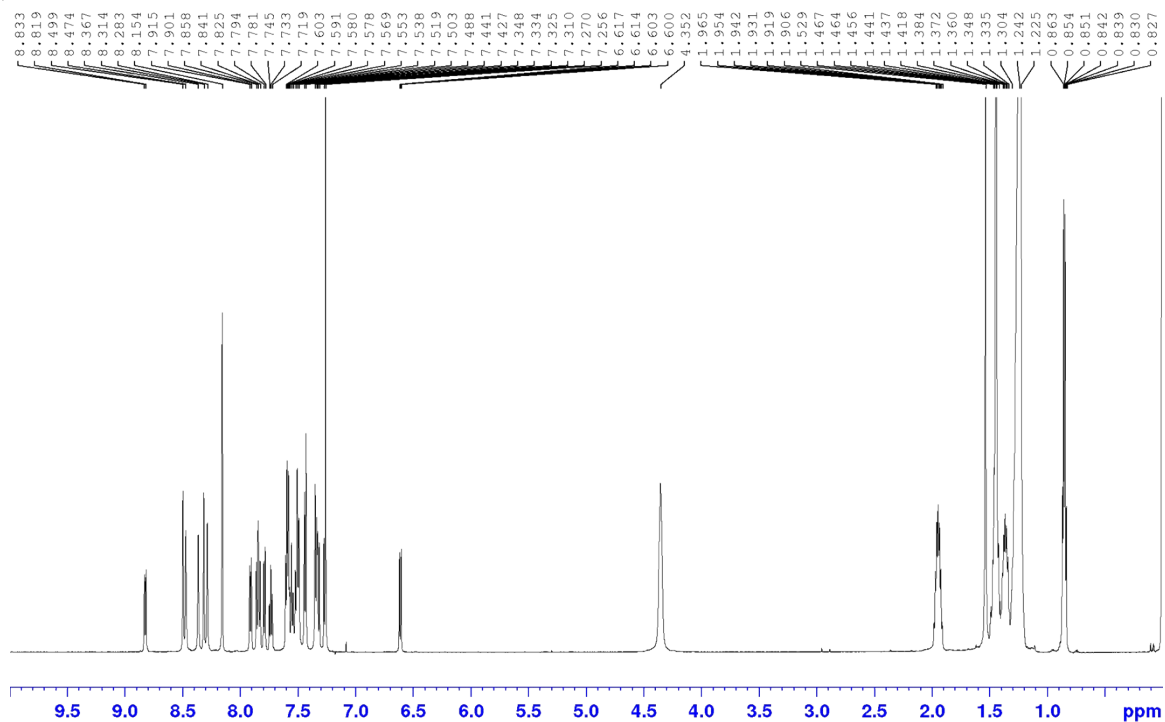
**Fig. S6** EL spectra of the fabricated OLEDs at different applied voltages.

# Copies of NMR spectra and HRMS mass spectra 2,7-CSEFX

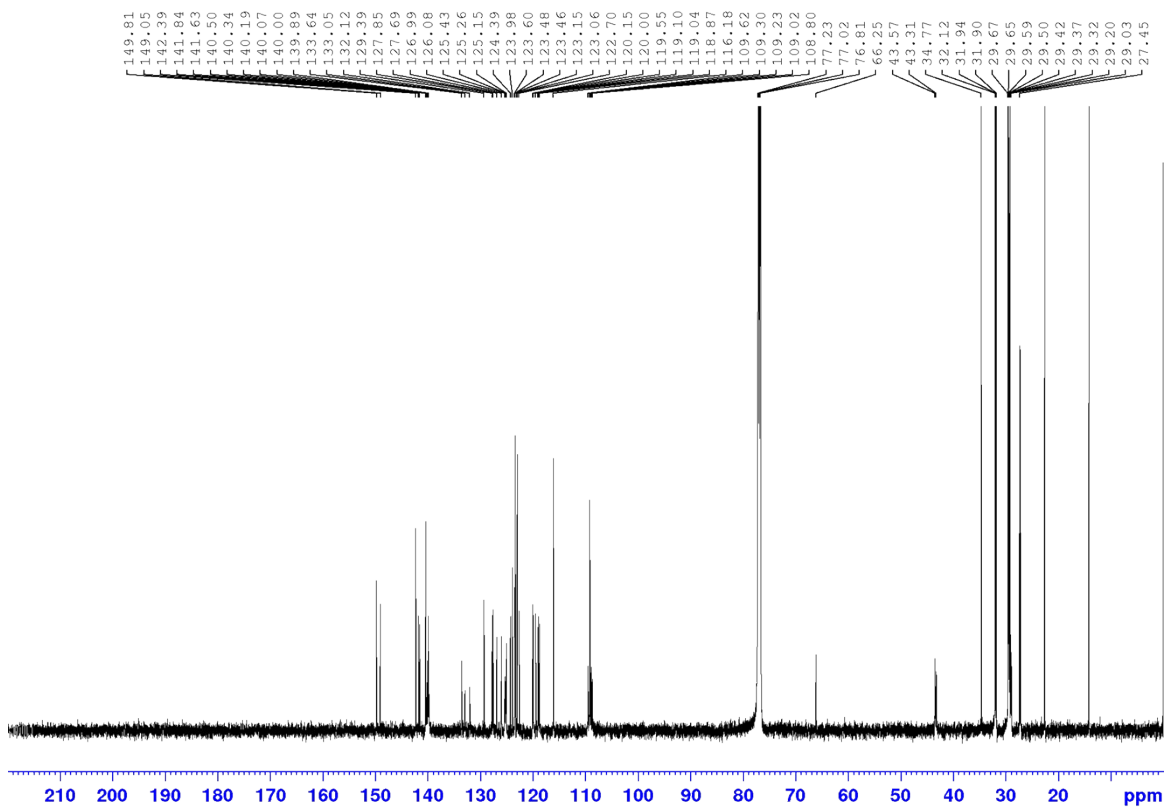
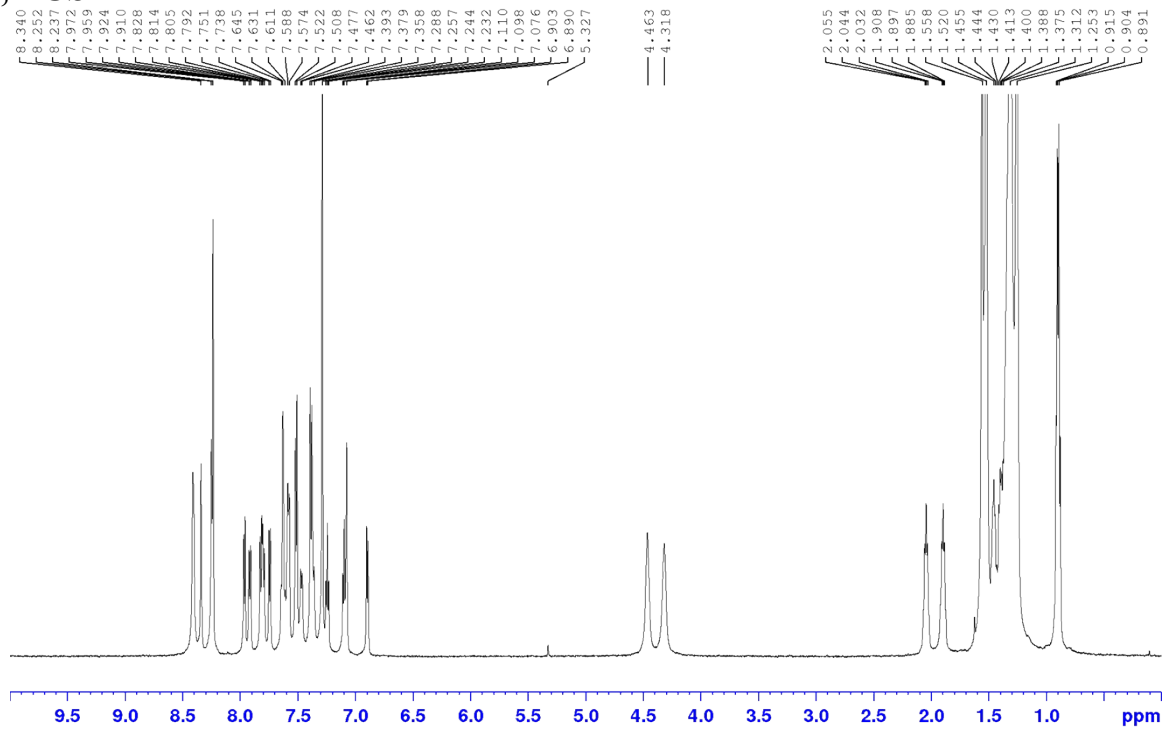




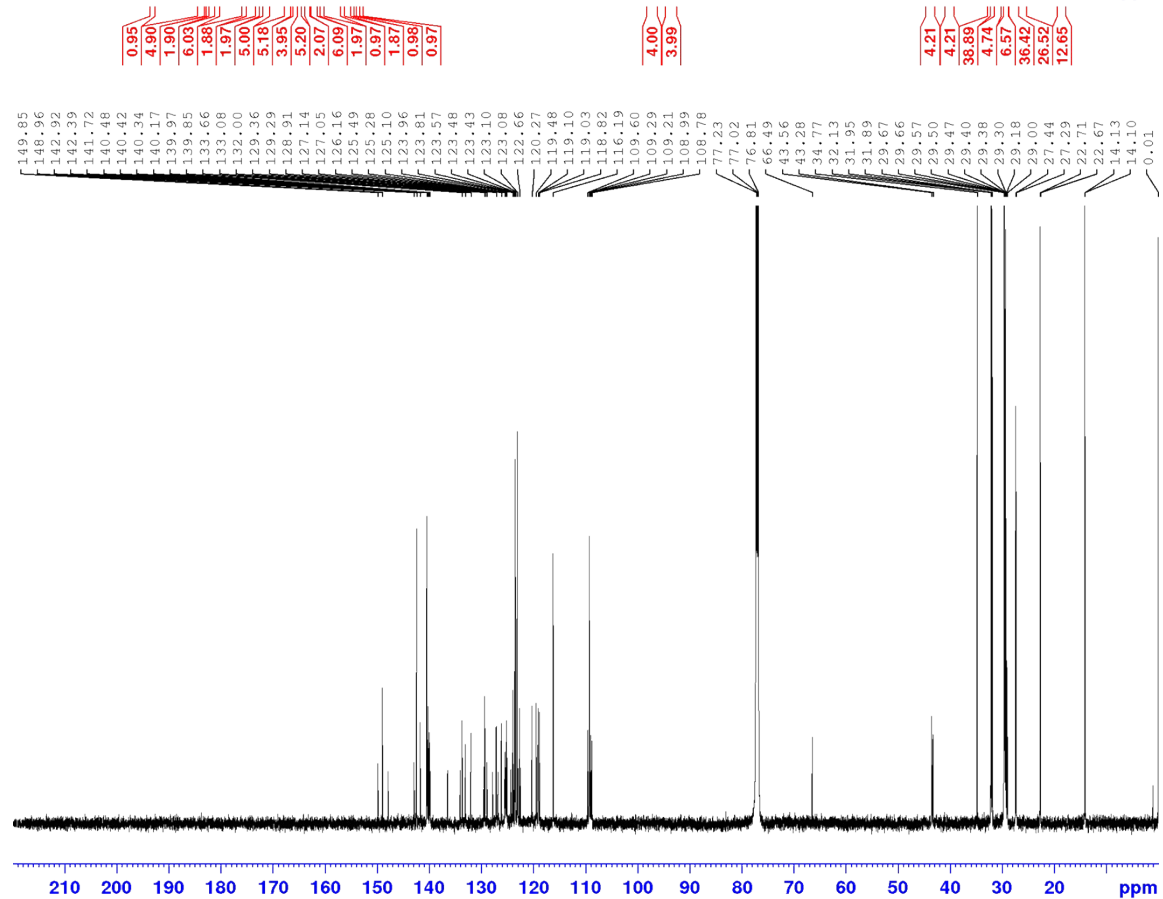
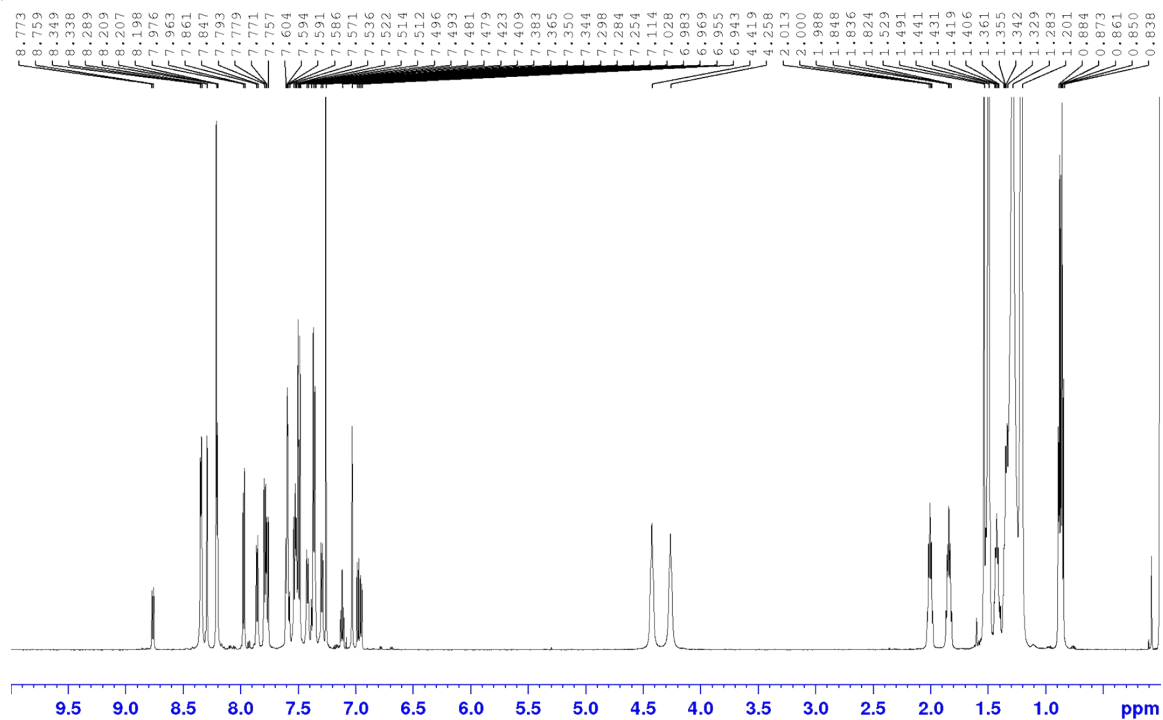
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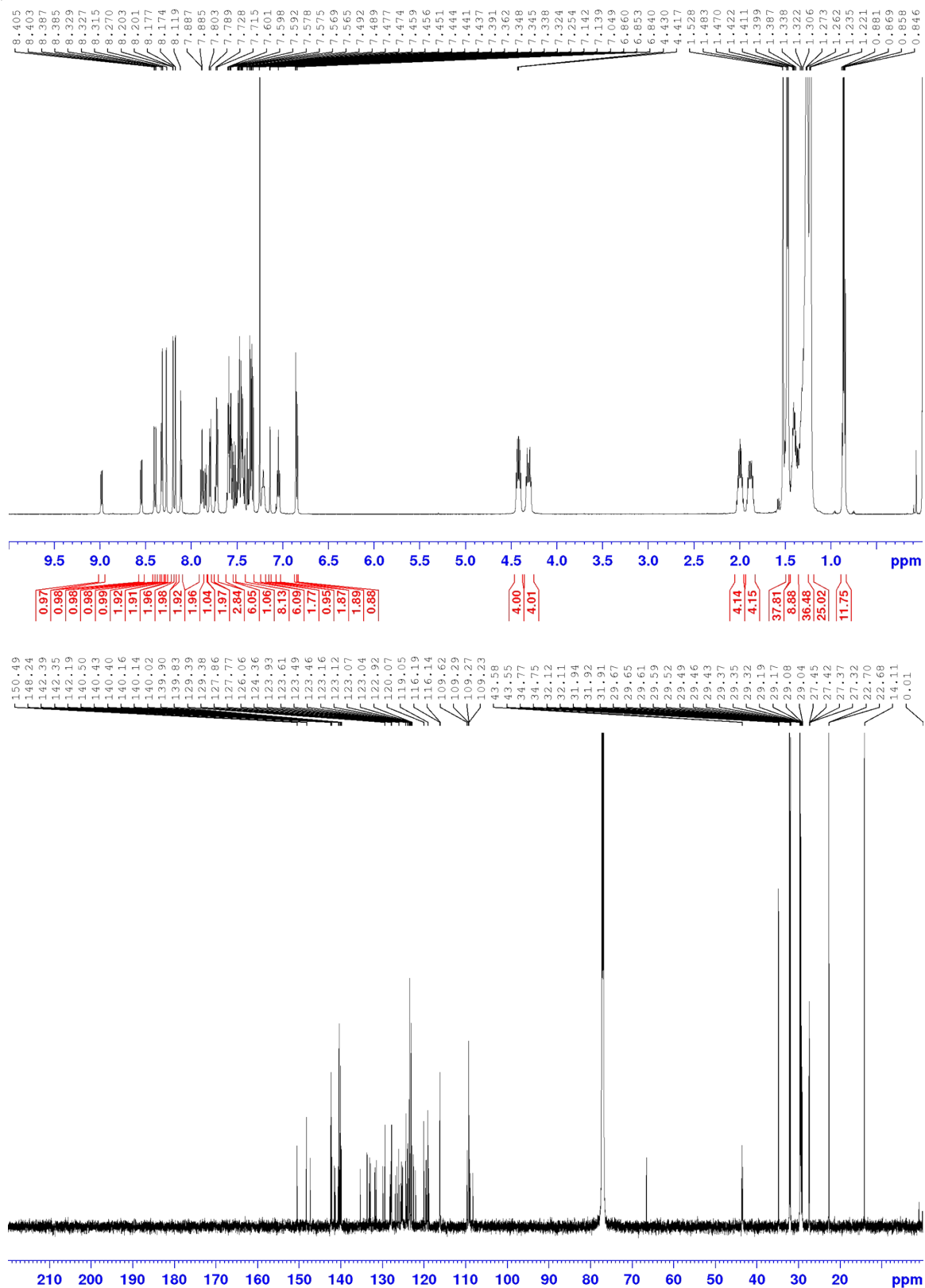
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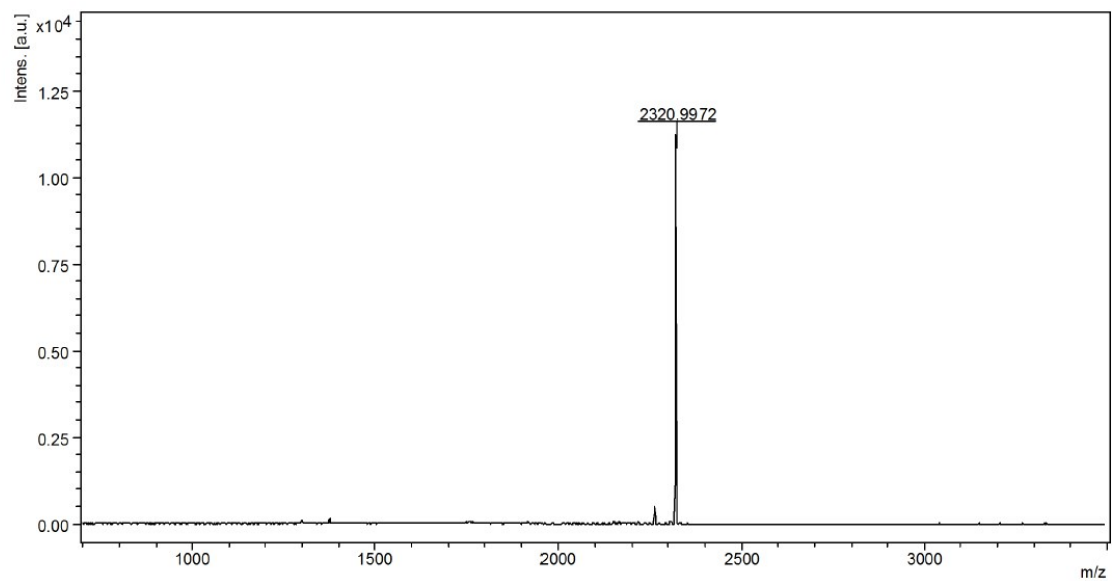
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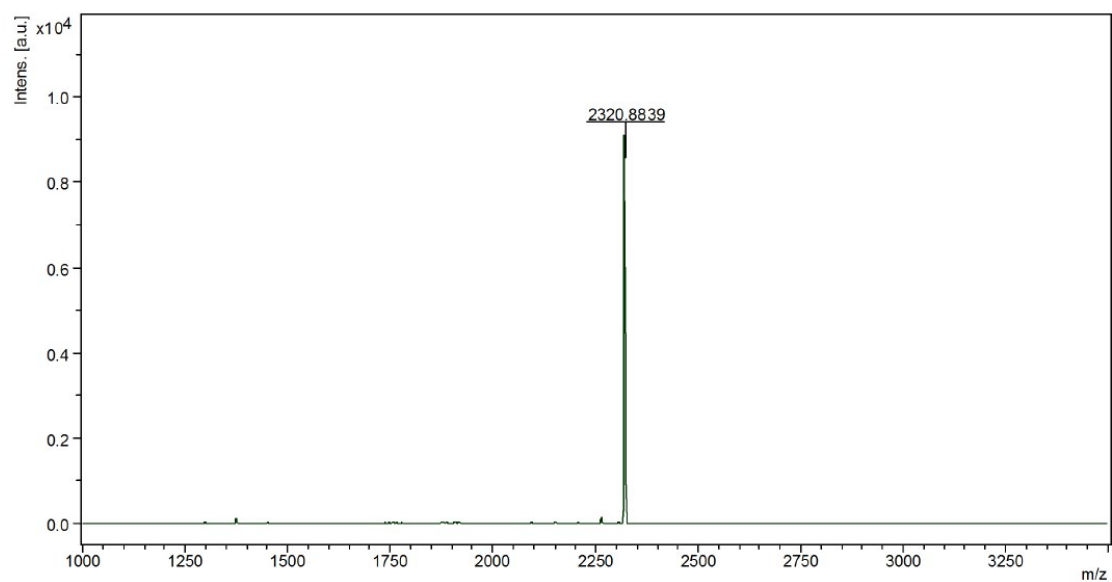
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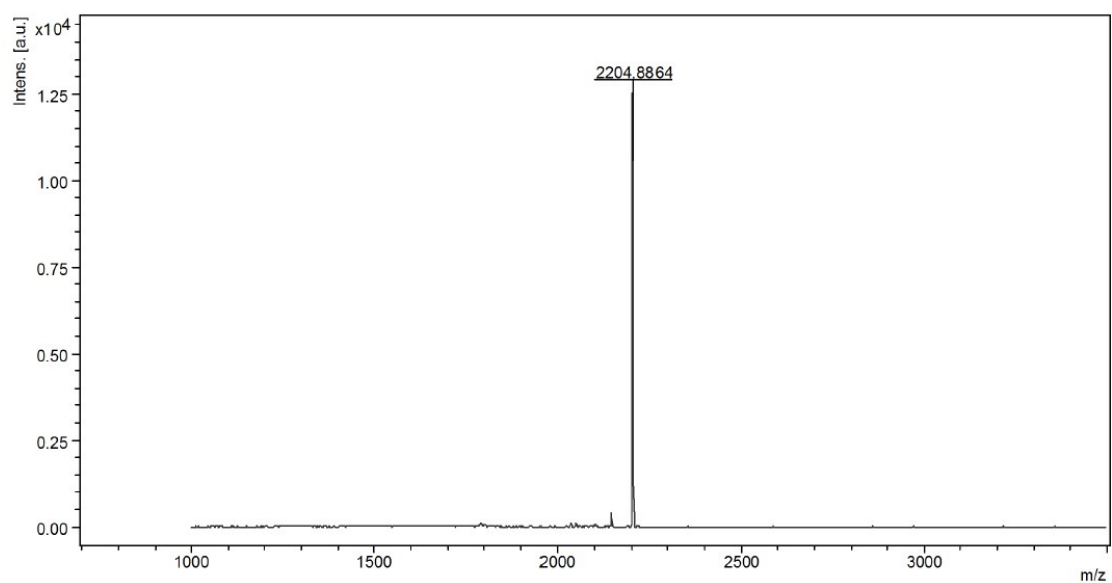
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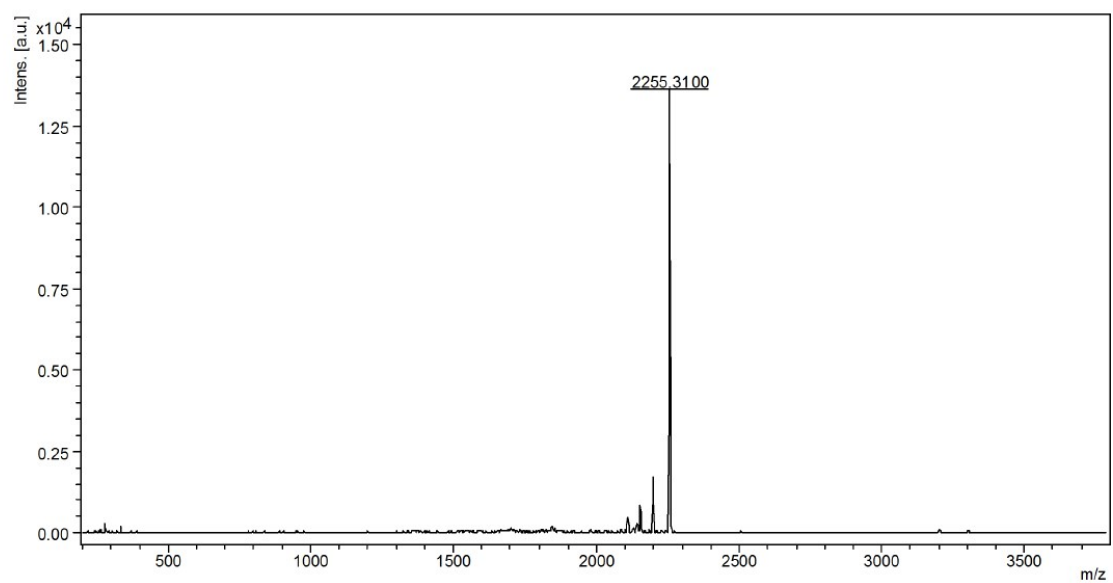
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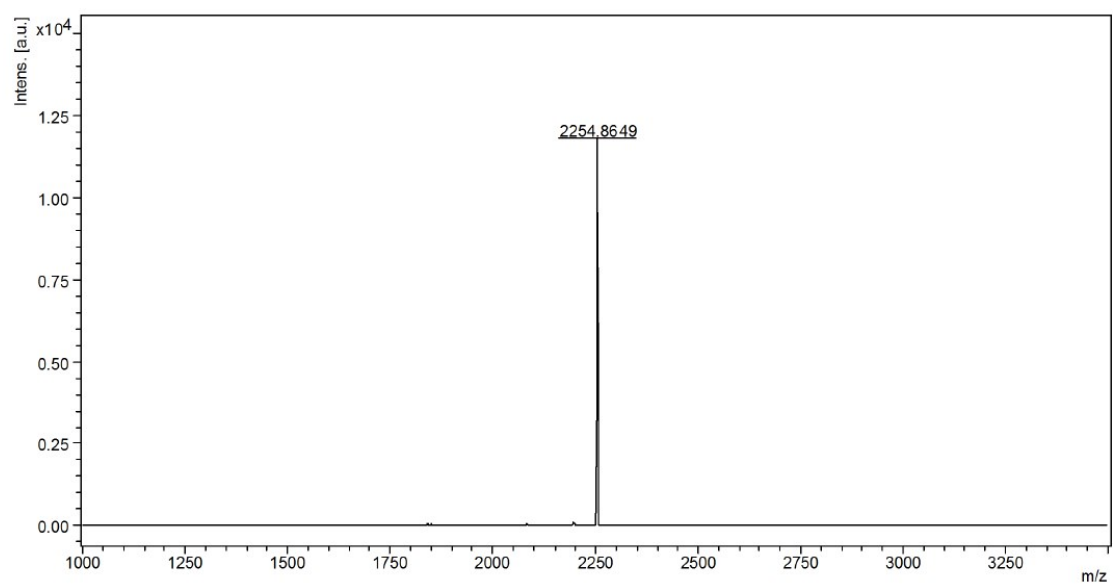
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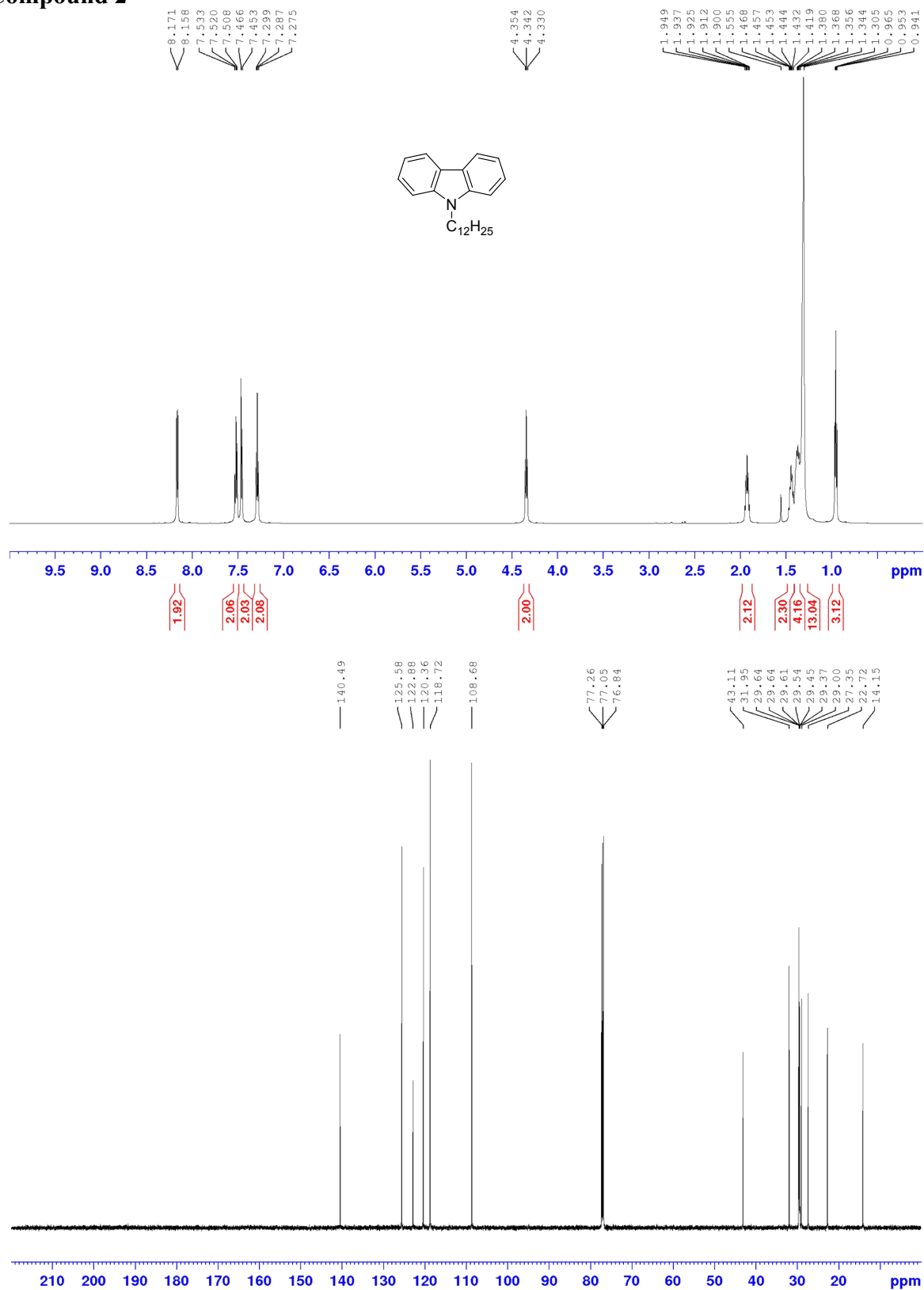
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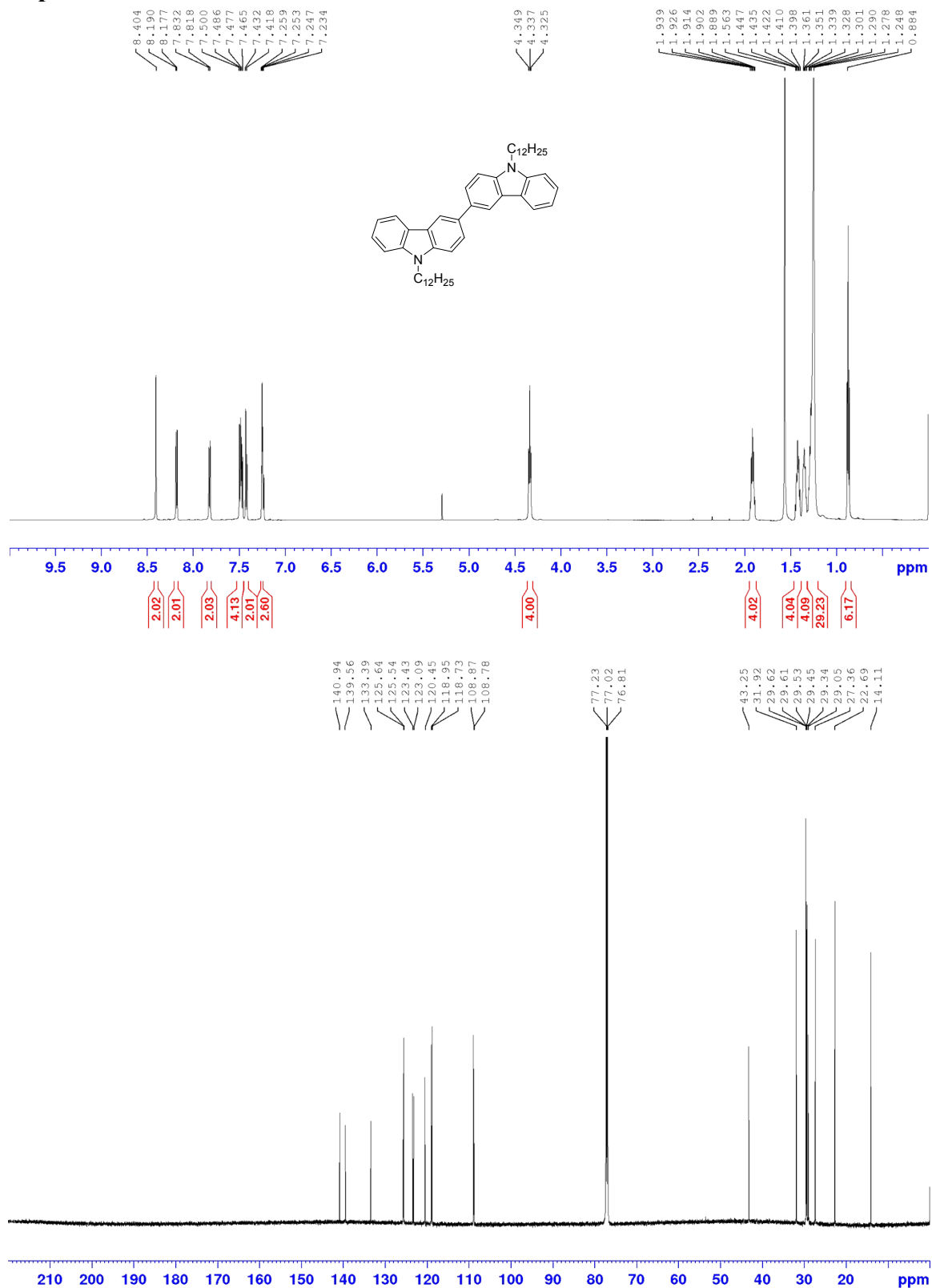
## 2,7-CSBF



# Compound 2

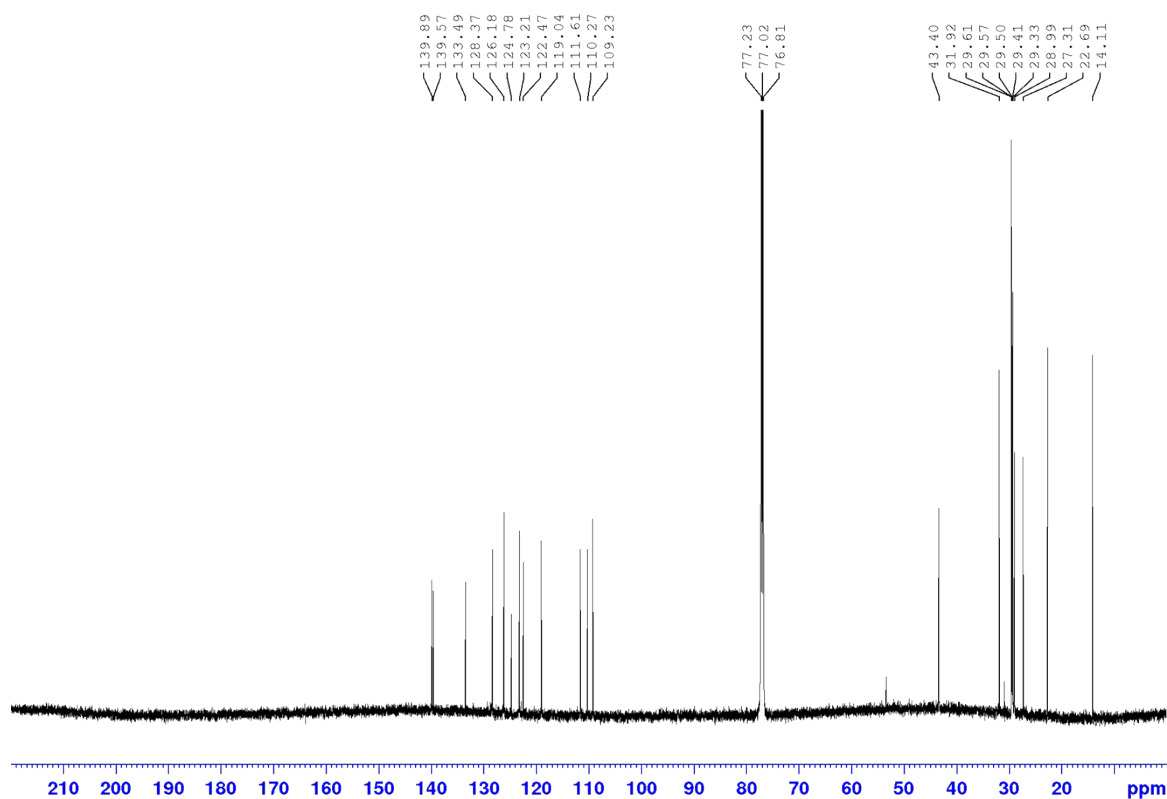
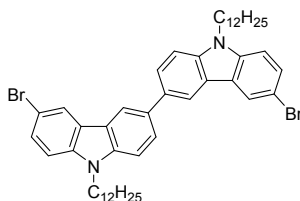
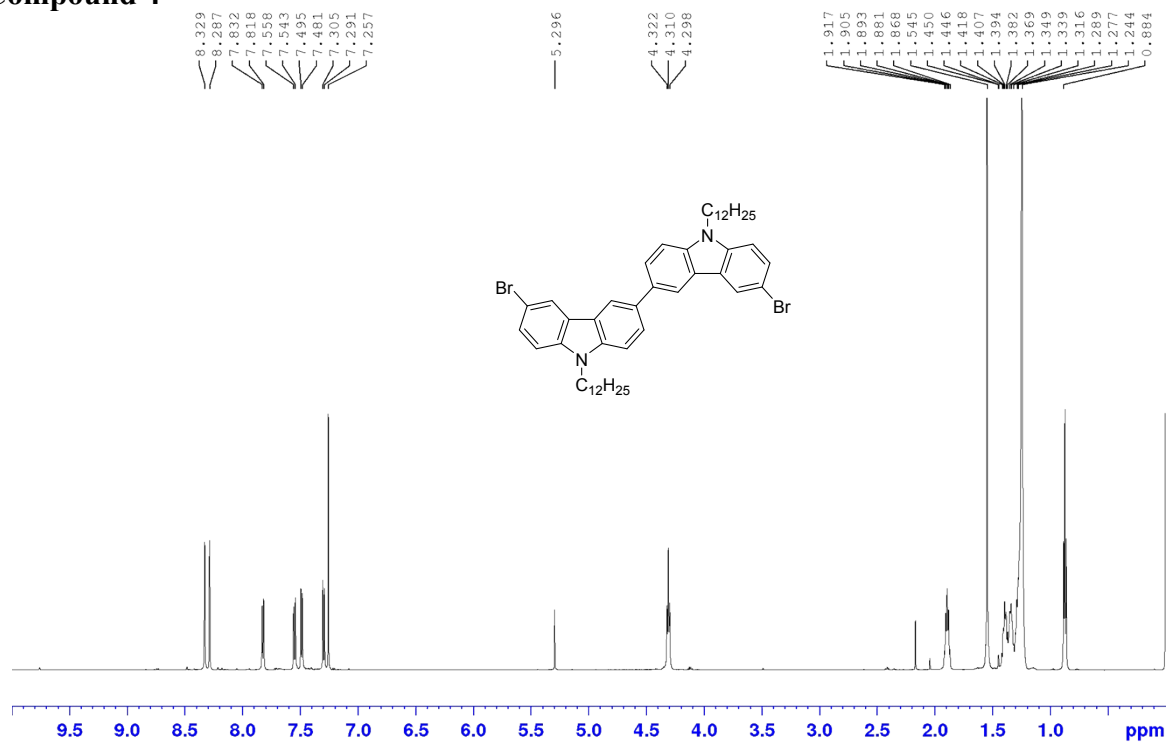


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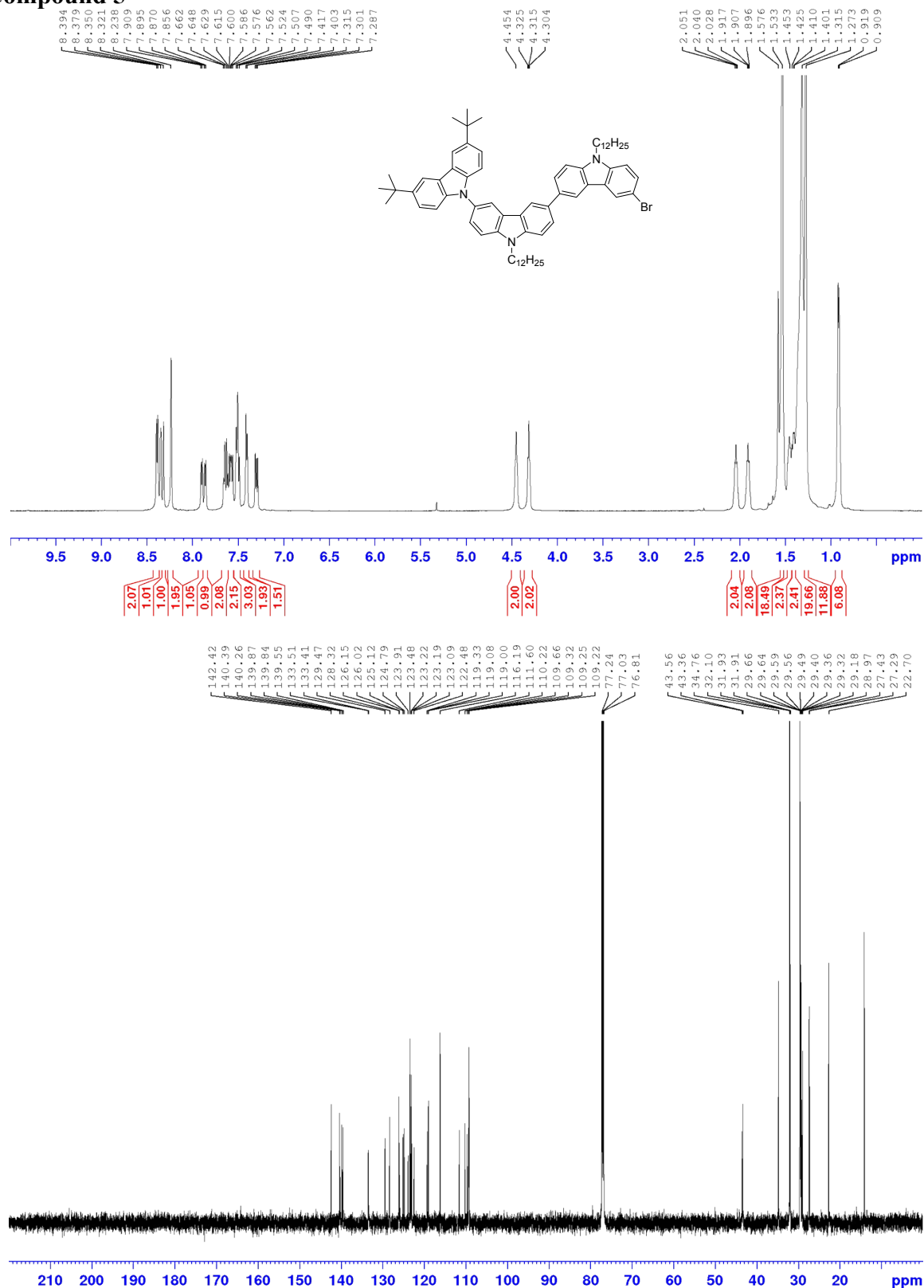




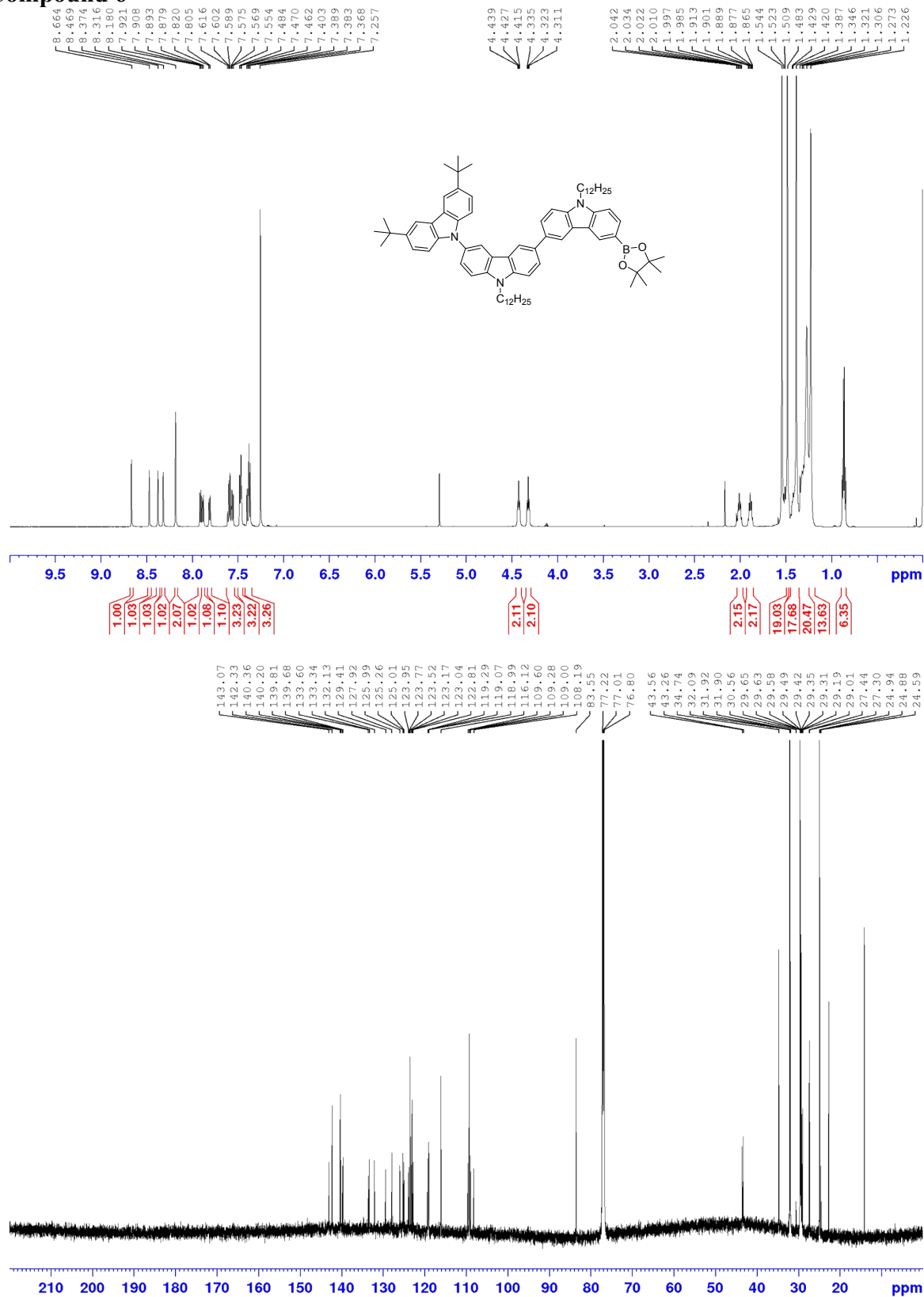
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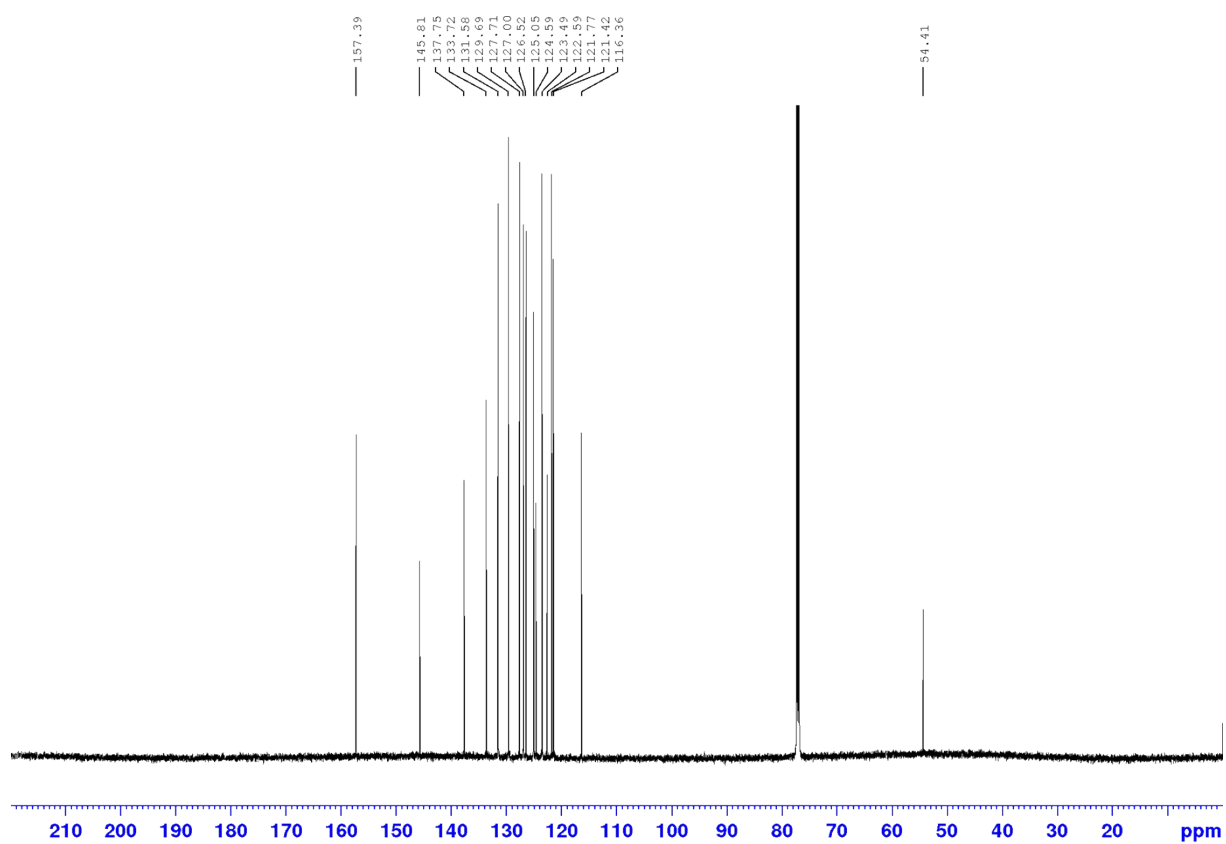
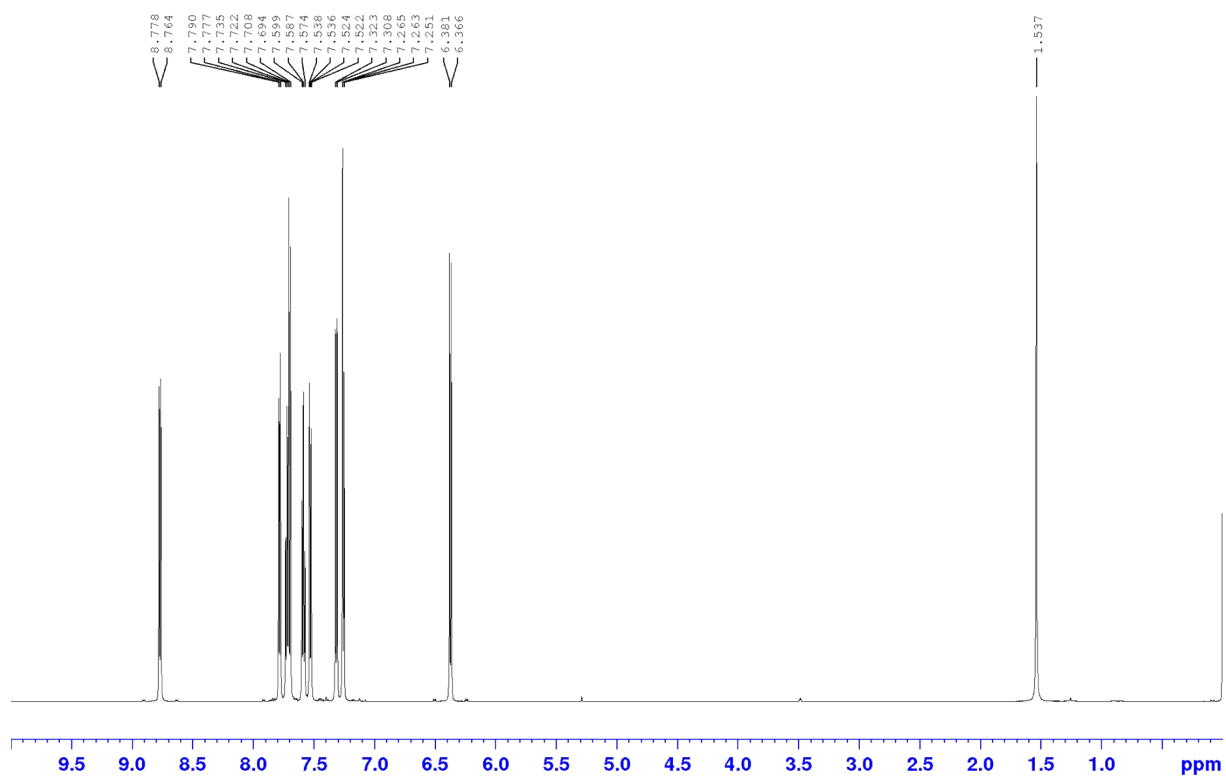
# Compound 5



# Compound 6



# Compound 9



# Compound 10

