

# Novel and Stable D-A- $\pi$ -A Dyes for Efficient Solid-state Dye-sensitized Solar Cells

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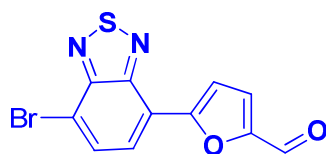
## Syntheses and Characterization

### General procedure for Suzuki coupling reaction:

#### 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole:

A solution was prepared by dissolving the 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.0g, 3.40 mmol), 2-thiophene boronic acid (0.5g, 3.91 mmol), tolylphosphine (0.21g, 0.68 mmol), palladium Acetate (38 mg, 0.17 mmol) and potassium carbonate (0.70g, 5.10 mmol) in 30 mL of DMF. The reaction mixture was stirred at 90 °C for 6 h under N<sub>2</sub> gas. After that the mixture was treated with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over Mg<sub>2</sub>SO<sub>4</sub> anhydrous and evaporated to remove the solvent under reduced pressure. The crude product was purified by column chromatography (Hexane: ethyl acetate; 8:2) to obtain a pure product (0.8, 79 %) as a yellow powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (dd,  $J$  = 3.7, 0.9 Hz, 1H), 7.84 (d,  $J$  = 7.7 Hz, 1H), 7.72 (s, 2H), 7.48 (dd,  $J$  = 5.1, 0.8 Hz,

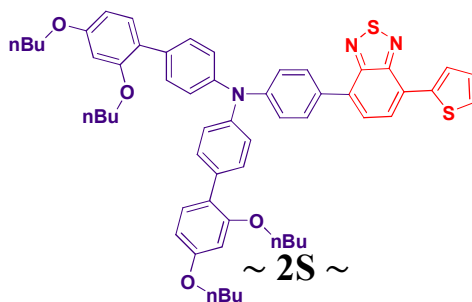
1H), 7.20 (dd,  $J = 5.0, 3.8$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.78, 152.97, 151.83, 138.51, 132.38, 132.27, 128.17, 128.07, 127.31, 127.12, 125.89, 113.92, 112.38 ppm.



#### General procedure for Vilsmeier-Haack Reaction

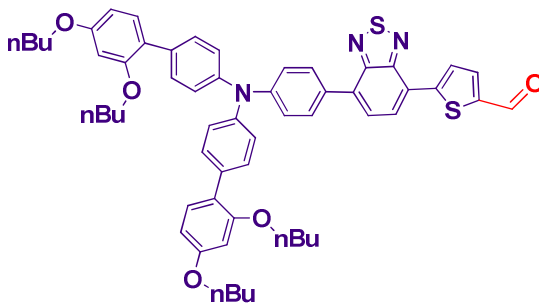
##### 5-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde:

A solution of dimethyl formamide (DMF) 5 mL was cooled to 0 °C and phosphorus oxychloride (68 mg, 0.44 mmol) was added at same temperature. The mixture was stirred for 20 min. After that the 4-bromo-7-(furan-2-yl)benzo[c][1,2,5]thiadiazole (0.5g, 1.78 mmol) was dissolved in 10 mL of DMF and added drop-wise for 20 min. The reaction mixture was stirred for 12 h at r.t. then heated at 80 °C for 1 h and allowed to cool to room temperature. The reaction mixture was quenched with sodium acetate solution and extracted with ethyl acetate. The organic layer was dried over  $\text{Mg}_2\text{SO}_4$  anhydrous and removed to solvent. The crude product was applied to column chromatography using hexane and ethyl acetate (7:3) to obtained a title product as deep yellow solid (0.35g, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.76 (s, 2H), 8.18 (d,  $J = 7.8$  Hz, 2H), 7.98 (d,  $J = 7.8$  Hz, 2H), 7.91 (d,  $J = 3.7$  Hz, 2H), 7.46 (d,  $J = 3.7$  Hz, 2H), 7.28 (s, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.54, 154.20, 153.80, 152.07, 150.71, 132.26, 126.31, 123.89, 121.28, 115.45, 114.68 ppm.



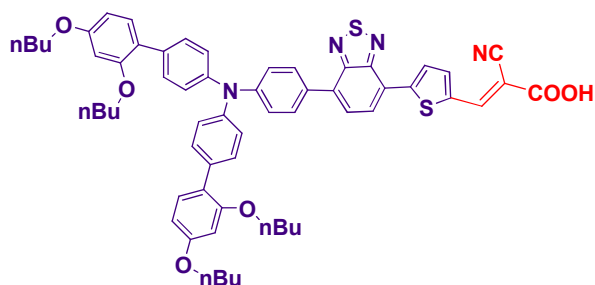
**2',4'-dibutoxy-N-(2',4'-dibutoxybiphenyl-4-yl)-N-(4-(7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)biphenyl-4-amine**

To a 100 mL two-necked round bottom flask was added 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.15, 0.51 mmol), 2',4'-dibutoxy-N-(2',4'-dibutoxybiphenyl-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)biphenyl-4-amine (0.49g, 0.61 mmol), tolylphosphine (31mg, 0.10 mmol), tris(dibenzylideneacetone)dipalladium(0) (14.5 mg, 0.025 mmol) and potassium phosphate (0.32g, 1.51 mmol). The mixture was dissolved in toluene and methanol (6:4). The flask was fitted with a reflux condenser, magnetic stir bar and filled with N<sub>2</sub>. The reaction mixture was refluxed for 6 h, then allowed to cool to room temperature and 50 mL of ethyl acetate was added. The organic layer was dried over Mg<sub>2</sub>SO<sub>4</sub> anhydrous and removed the solvent. The crude product was purified over SiO<sub>2</sub> using petroleum ether and ethyl (9:1) to obtain a pure compound as yellow solid (0.21g, 46%).  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.91 (dd, *J* = 10.3, 8.1 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 4H), 7.45 – 7.43 (m, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 2.2 Hz, 2H), 7.23 (s, 2H), 7.20 (dd, *J* = 5.3, 1.5 Hz, 1H), 6.56 (s, 4H), 6.54 (d, *J* = 2.3 Hz, 2H), 3.98 (q, *J* = 15.1 Hz, 8H), 1.82 – 1.71 (m, 8H), 1.56 – 1.42 (m, 8H), 0.99 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.60, 157.01, 153.98, 152.95, 148.24, 145.59, 145.56, 139.62, 133.44, 133.39, 132.57, 130.89, 130.44, 130.30, 129.93, 129.86, 129.80, 128.00, 127.30, 127.15, 126.55, 126.13, 125.65, 124.25, 123.00, 122.93, 105.30, 100.46, 68.17, 67.80, 31.43, 31.24, 19.41, 19.34, 13.95, 13.91 ppm.



**5-(7-(4-(bis(2',4'-dibutoxybiphenyl-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde:**

The compound was synthesized according to above mentioned method. The crude product was applied to column chromatography using hexane and ethyl acetate (7:3) as eluted to obtain reddish solid (0.13g, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.98 (s, 1H), 8.22 (dd, *J* = 3.8, 2.7 Hz, 1H), 8.06 (dd, *J* = 8.1, 4.6 Hz, 2H), 7.99 (d, *J* = 7.1 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.86 (dd, *J* = 4.0, 1.3 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 8.7, 7.2 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 3H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 9.1 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.59 – 6.51 (m, 3H), 3.99 (q, *J* = 9.3 Hz, 8H), 1.84 – 1.71 (m, 8H), 1.56 – 1.41 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 183.10, 159.63, 156.99, 145.36, 136.82, 133.69, 130.88, 130.34, 130.00, 129.68, 129.47, 128.45, 127.79, 127.11, 124.43, 122.91, 122.54, 122.26, 105.30, 100.44, 68.16, 67.81, 31.41, 31.22, 19.39, 19.32, 13.92, 13.89 ppm.

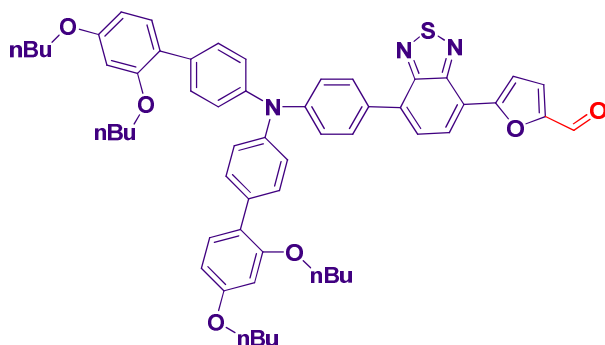


**(E)-3-(5-(7-(4-(bis(2',4'-dibutoxybiphenyl-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (**W8**)**

A solution of aldehyde (35 mg, 0.037 mmol), cyanoacetic acid (19.2 mg, 0.23 mmol) and piperidine (0.025 g, 0.30 mmol) was refluxed in CHCl<sub>3</sub> (10 mL) for 6 h. After that the solvent was removed in vacuum. Flash chromatography over SiO<sub>2</sub> was applied for the residue using gradient elution DCM (+2% formic acid) followed by washing of the combined dye fractions with HCl (1 M, 3 × 15 mL) gave **WS8**

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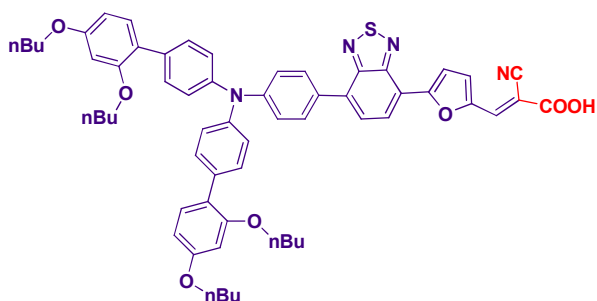
(24 mg, 64%) as a purple solid.  $^1\text{H}$  NMR (400 MHz, Acetone)  $\delta$  8.50 (s, 1H), 8.41 (s, 1H), 8.31 (d,  $J$  = 4.1 Hz, 1H), 8.22 (d,  $J$  = 7.1 Hz, 1H), 8.18 (d,  $J$  = 4.1 Hz, 1H), 8.08 (dd,  $J$  = 9.7, 5.5 Hz, 1H), 7.97 (d,  $J$  = 4.1 Hz, 1H), 7.91 (d,  $J$  = 8.7 Hz, 2H), 7.81 (dt,  $J$  = 13.7, 6.8 Hz, 1H), 7.74 (d,  $J$  = 7.6 Hz, 1H), 7.48 (d,  $J$  = 8.5 Hz, 4H), 7.20 (d,  $J$  = 8.4 Hz, 2H), 7.14 (d,  $J$  = 4.3 Hz, 2H), 7.12 (d,  $J$  = 4.2 Hz, 2H), 6.60 (d,  $J$  = 2.2 Hz, 1H), 6.53 (d,  $J$  = 2.2 Hz, 1H), 6.51 (d,  $J$  = 2.2 Hz, 1H), 3.98 (q,  $J$  = 14.9 Hz, 8H), 1.80 (m, 8H), 1.47 (m, 8H), 0.99 (t,  $J$  = 7.4 Hz, 6H), 0.90 (t,  $J$  = 7.4 Hz, 6H) ppm.  $^{13}\text{C}$  NMR (100 MHz, Acetone- $d_6$ )  $\delta$  163.05, 159.84, 157.02, 153.43, 148.49, 148.36, 146.49, 145.19, 139.17, 136.45, 134.08, 130.70, 130.33, 130.17, 129.93, 128.47, 127.74, 127.35, 126.65, 124.28, 123.35, 122.42, 122.10, 121.84, 116.02, 105.67, 100.15, 67.83, 67.40, 31.31, 31.15, 19.17, 19.09, 13.34, 13.32 ppm. HR-MS (ESI)  $m/z$  :  $[\text{M}]^+$  calcd for  $\text{C}_{60}\text{H}_{60}\text{N}_4\text{O}_6\text{S}_2$ , 996.3948; found, 996.3395.



#### 5-(7-(4-(bis(2',4'-dibutoxybiphenyl-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde:

To a 100 mL two-necked round bottom flask was added 5-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde (017, 0.55 mmol), 2',4'-dibutoxy-N-(2',4'-dibutoxybiphenyl-4-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)biphenyl-4-amine (0.56g, 0.68 mmol), Sphos (45.15 mg, 0.11 mmol), tris(dibenzylideneacetone)dipalladium(0) (15.8 mg, 0.027 mmol) and potassium phosphate (0.35g, 1.65 mmol). The mixture was dissolved in toluene and methanol (6:4). The flask was fitted with a reflux condenser, magnetic stir bar and filled with  $\text{N}_2$ . The reaction mixture was refluxed for 6 h, then allowed to cool to room temperature and 50 mL of ethyl acetate was added. The organic layer was dried over  $\text{MgSO}_4$  anhydrous and removed the solvent. The crude product was purified over  $\text{SiO}_2$  using petroleum ether and ethyl (9:1) to obtain a pure compound as deep yellow solid (0.30g, 60%).  $^1\text{H}$  NMR (500 MHz,

CDCl<sub>3</sub>)  $\delta$  9.75 (s, 1H), 8.38 (d,  $J$  = 7.6 Hz, 2H), 7.95 (d,  $J$  = 8.6 Hz, 1H), 7.93 (d,  $J$  = 3.7 Hz, 1H), 7.82 (d,  $J$  = 7.6 Hz, 1H), 7.78 (d,  $J$  = 16.0 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.52 (d,  $J$  = 8.5 Hz, 4H), 7.48 (d,  $J$  = 3.7 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.35 (d,  $J$  = 8.6 Hz, 2H), 7.31 (d,  $J$  = 8.9 Hz, 2H), 7.28 (d,  $J$  = 8.7 Hz, 4H), 7.12 (d,  $J$  = 15.9 Hz, 1H), 6.59 (m, 3H), 4.02 (q,  $J$  = 11.1 Hz, 8H), 1.93 – 1.72 (m, 8H), 1.52 (m, 8H), 1.03 (t,  $J$  = 7.4 Hz, 6H), 0.98 (t,  $J$  = 7.4 Hz, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.94, 177.36, 159.65, 157.02, 155.40, 153.85, 152.00, 151.80, 148.74, 145.38, 143.36, 134.96, 134.82, 133.71, 130.88, 130.53, 130.34, 130.07, 129.75, 128.99, 128.42, 126.73, 126.65, 125.44, 124.41, 122.96, 122.57, 119.67, 113.90, 105.37, 100.50, 68.19, 67.81, 31.42, 31.24, 19.39, 19.32, 13.92, 13.88 ppm. HR-MS (ESI)  $m/z$  : [M]<sup>+</sup> calcd for C<sub>57</sub>H<sub>59</sub>N<sub>3</sub>O<sub>6</sub>S, 913.4119; found, 913.4161.



**(E)-3-(5-(7-(4-(bis(2',4'-dibutoxybiphenyl-4-yl)amino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)furan-2-yl)-2-cyanoacrylic acid (**W7**)**

A solution of aldehyde (110 mg, 0.12 mmol), cyanoacetic acid (61 mg, 0.72 mmol) and piperidine (0.12 g, 1.44 mmol) was refluxed in CHCl<sub>3</sub> (20 mL) for 6 h. After that the solvent was removed in vacuum. Flash chromatography over SiO<sub>2</sub> was applied for the residue using gradient elution DCM (+2% formic acid) followed by washing of the combined dye fractions with HCl (1 M, 3 × 15 mL) gave **WS7** (84 mg, 71%) as a dark red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d,  $J$  = 7.6 Hz, 1H), 7.99 (s, 1H), 7.94 (d,  $J$  = 3.8 Hz, 1H), 7.87 (d,  $J$  = 8.6 Hz, 2H), 7.81 (d,  $J$  = 7.6 Hz, 1H), 7.42 (d,  $J$  = 8.5 Hz, 4H), 7.27 – 7.20 (m, 4H), 7.19 (s, 6H), 7.17 (s, 2H), 6.50 (d,  $J$  = 2.4 Hz, 1H), 6.49 (d,  $J$  = 2.2 Hz, 1H), 6.48 (d,  $J$  = 2.3 Hz, 1H), 3.92 (q,  $J$  = 9.6 Hz, 8H), 1.87 – 1.59 (m, 8H), 1.48 – 1.35 (m, 8H), 0.93 (t,  $J$  = 7.4 Hz, 6H), 0.88 (t,  $J$  = 7.4 Hz, 6H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.54, 163.81, 161.07, 159.64, 157.04, 157.01, 153.80, 151.87, 149.01, 147.74, 141.42, 139.73, 139.70, 130.90, 130.39, 130.34, 130.11, 127.20, 127.15, 124.52, 124.50, 111.63, 110.62, 105.28, 100.43, 96.02, 68.16, 67.80, 31.41, 31.21, 19.39, 19.32, 13.92, 13.89 ppm. HR-MS (ESI)  $m/z$  : [M]<sup>+</sup> calcd for C<sub>60</sub>H<sub>60</sub>N<sub>4</sub>O<sub>7</sub>S, 980.4177; found, 980.4247.

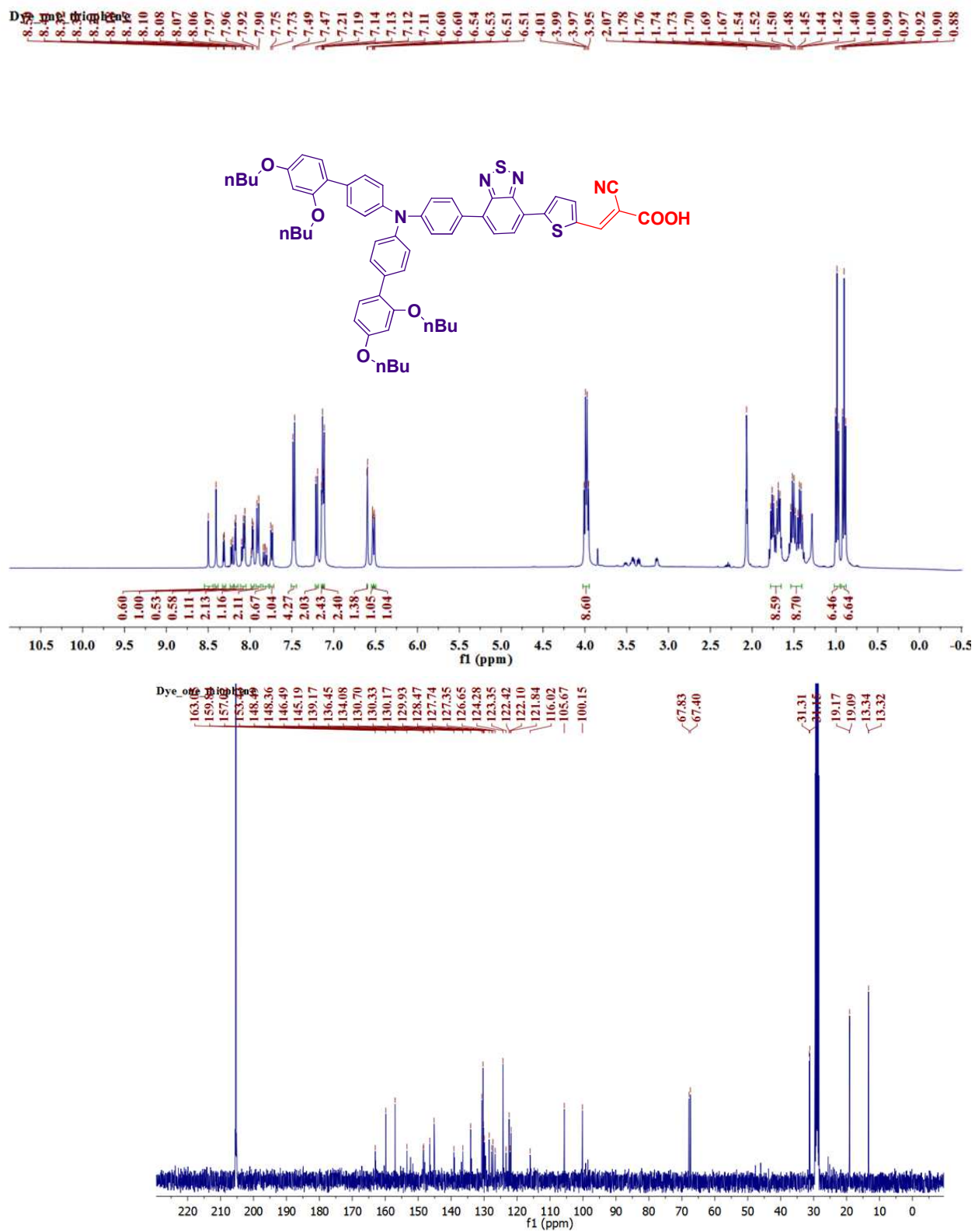


Figure S1. NRM of W7 sensitizer

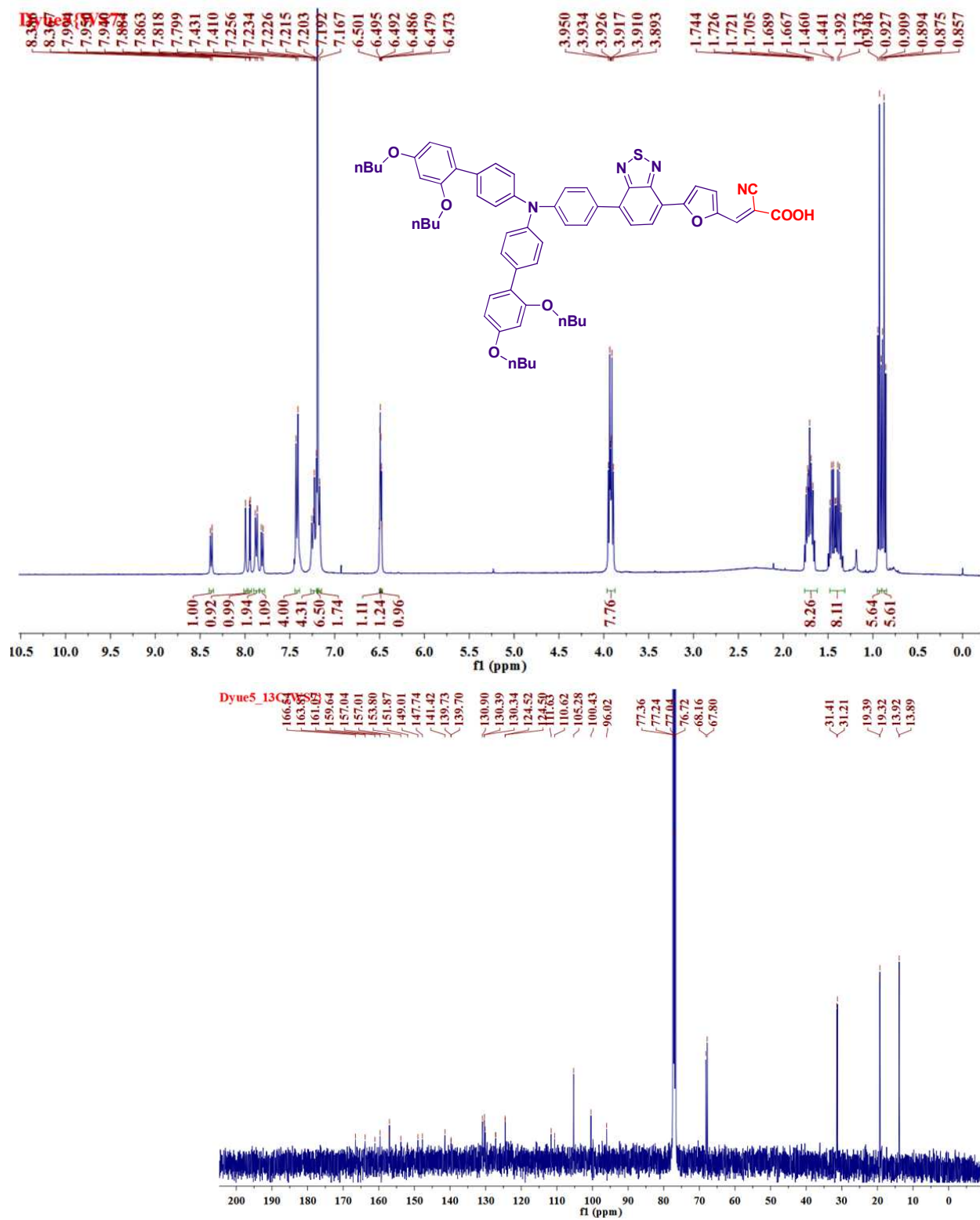


Figure S2. NMR spectra of W8.



W7

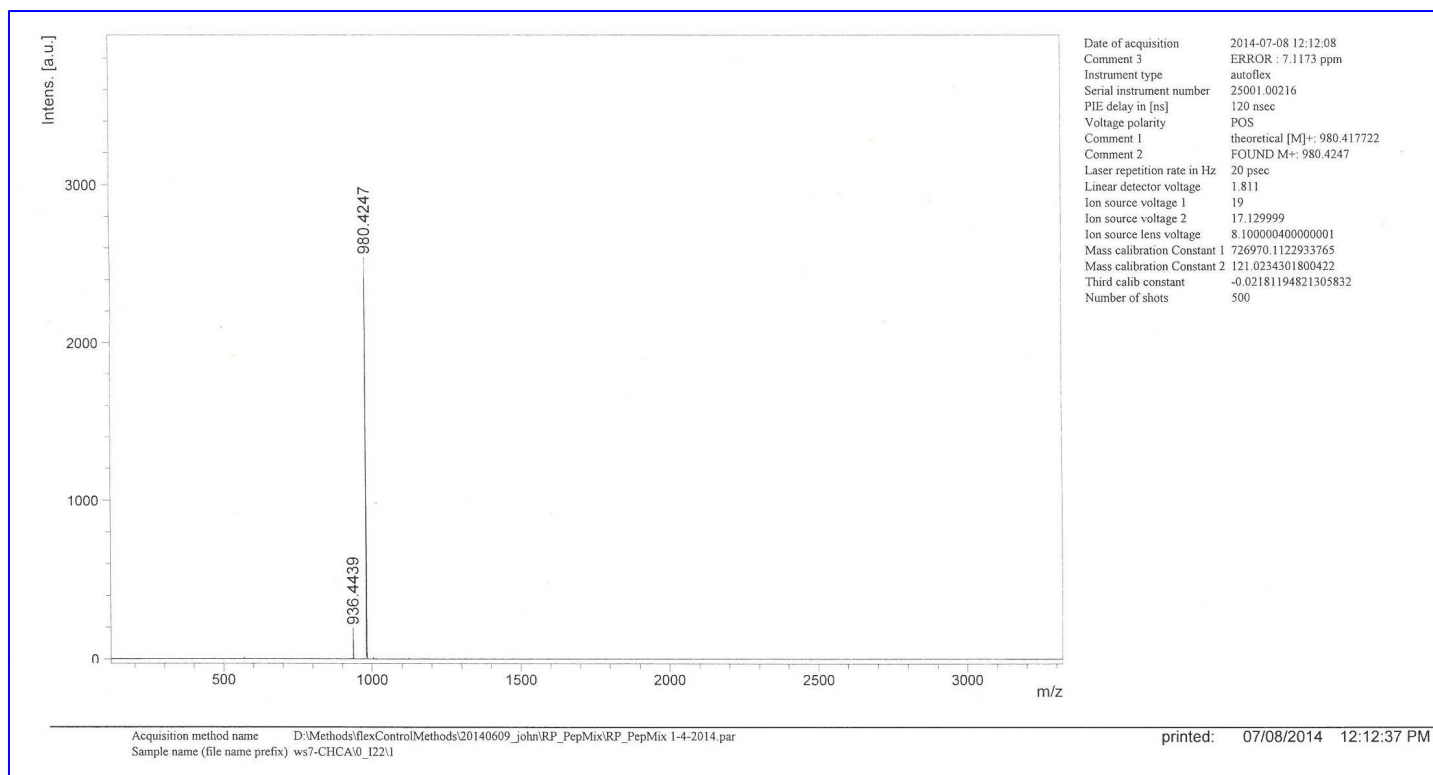


Figure S3. HR-MAA spectra of W7

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W8

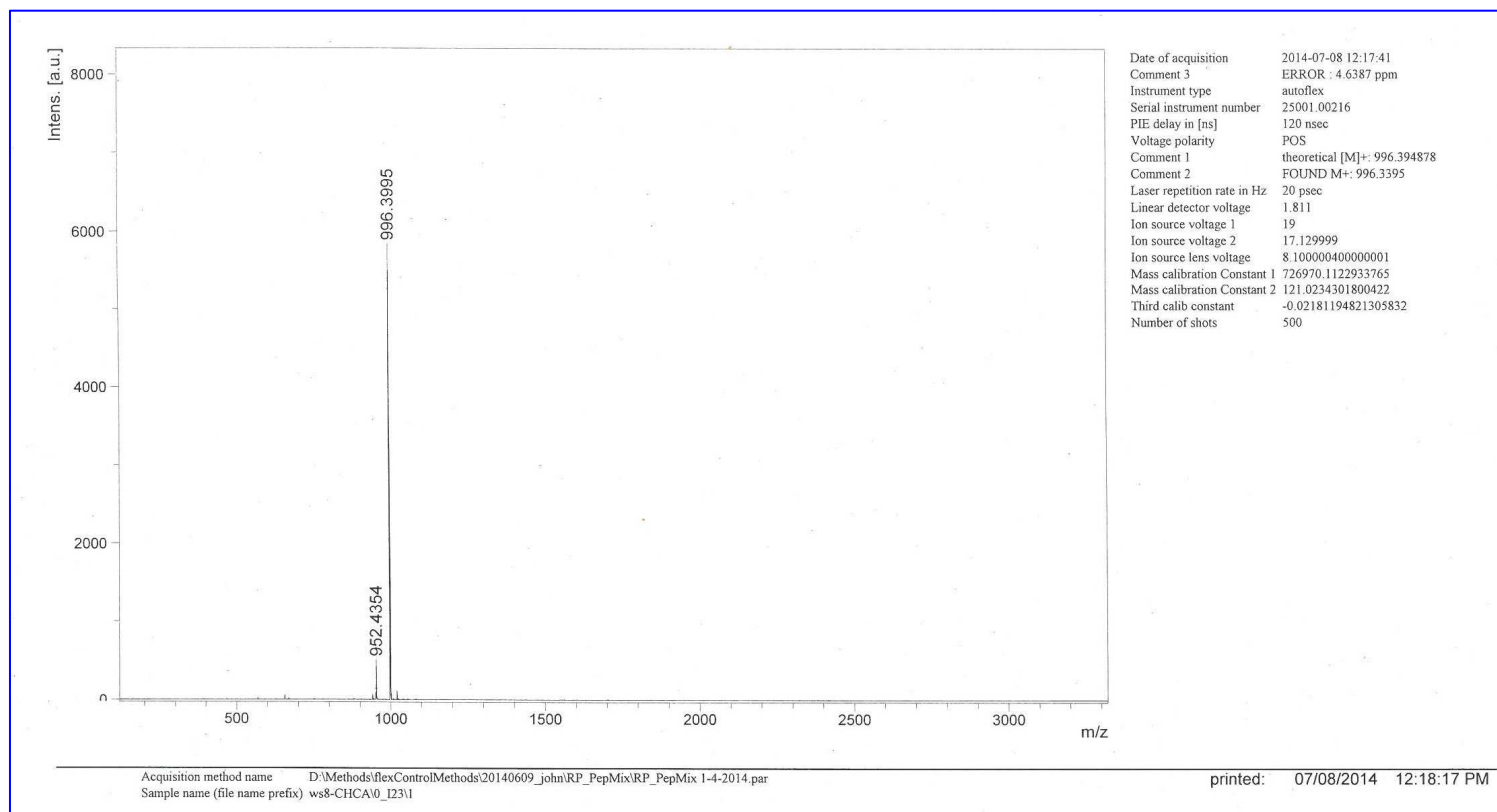


Figure S4. HR-MAA spectra of W8.