

Electronic Supplementary Information

Approach to tune short-circuit current and open-circuit voltage of dye-sensitized solar cells: π -linker modification and photoanode selection†

Shengbo Zhu,^a Zhongwei An,^{*a,b} Xinbing Chen,^a Pei Chen^a and Qianfeng Liu^c

^aKey Laboratory of Applied Surface and Colloid Chemistry, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China.

^bXi'an Modern Chemistry Research Institute, Xi'an 710065, China.

^cXi'an Ruilian Modern Electronic Chemicals Co. Ltd., Xi'an 710077, China.

* E-mail: gmecazw@163.com

Contents:

1. Synthesis of intermediates and characterizations.
2. **Fig. S1** The linear fit about theoretical values E_g and their experimental values E_{ec} g.
3. Morphology of photoanodes.
4. **Fig. S3** Schematic diagrams of NC, NC-SP200, and NC-MS400 photoanodes.
5. Experimental procedures of desorption.
6. **Fig. S5** The $J-V$ characteristics of AZ261 based on NC, NC-SP200, and NC-MS400 photoanodes.

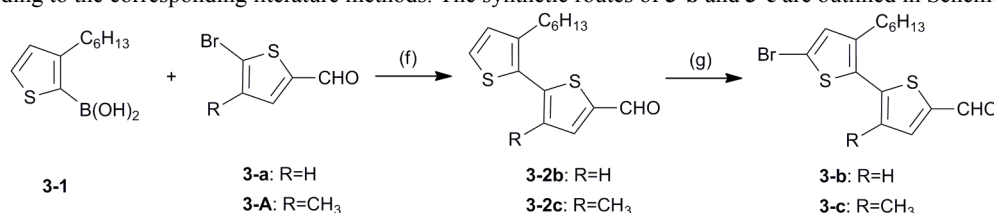
1. Synthesis of intermediates and characterizations

1.1. Instruments

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV-300 MHz (75 MHz for ^{13}C NMR) and Bruker AV-400 MHz (100 MHz for ^{13}C NMR) instruments with tetramethylsilane (TMS) as the internal standard. Gas chromatography mass spectra were acquired in the electron ionization mode (EI) on Thermo DSQII. Mass spectra measured on Bruke MALDI-TOF MS and a Bruker msXis impact instrument in the negative mode. Elemental analysis (C H N) was carried out on a VARIO-EL-III elemental analyzer.

1.2. Synthesis procedures

5-bromothiophene-2-carbaldehyde (**3-a**) was purchased from Aladdin-reagent Co. and used as received. 2-(3-hexylthienyl)boronic acid (**3-1**)^{S1} and 5-bromo-4-methylthiophene-2-carbaldehyde (**3-A**)^{S2} were synthesized according to the corresponding literature methods. The synthetic routes of **3-b** and **3-c** are outlined in Scheme S1.



Scheme S1 Synthetic routes of **3-b** and **3-c**. Reaction conditions: (f) Na_2CO_3 aqueous solution, $\text{Pd}(\text{PPh}_3)_4$, TBAB, THF, 70 °C, 3 h; (g) NBS, THF, 0 °C, 8 h.

General procedure for synthesis of **3-2b** and **3-2c**.

In a 100 mL 3-necked flask, compound **3-1** (15 mmol), **3-a** or **3-A** (15 mmol), tetra-*n*-butylammonium bromide (TBAB) (4.50 mmol), tetrahydrofuran (THF) (50 mL) and $\text{Pd}(\text{PPh}_3)_4$ (0.15 mmol) were added in turn under a nitrogen atmosphere. Following this, Na_2CO_3 aqueous solution (3 mol/L, 10 mL) was added dropwise and the reaction mixture was stirred for 3 h at 70 °C. The reaction mixture was then poured into dichloromethane (DCM). The organic layer was washed with water and dried over anhydrous MgSO_4 . After removing the solvent, the crude product obtained was purified by column chromatography (silica gel, 200-300 mesh; PE-EA mixture as the eluent; where PE is petroleum ether, and EA is ethyl acetate) to obtain compound **3-2b** or **3-2c** as a light yellow oily liquid.

3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3-2b). Yield: 49.7%. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 9.87 (s, 1H), 7.69(d, $J = 3.9$ Hz, 1H), 7.27 (d, $J = 5.1$ Hz, 1H), 7.21 (d, $J = 3.9$ Hz 1H), 6.97 (d, $J = 5.1$ Hz, 1H), 2.80 (t, $J = 7.8$ Hz, 2H), 1.69-1.59 (m, 2H), 1.39-1.29(m, 6H), 0.87 (t, $J = 6.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 182.61, 146.61, 142.38, 142.07, 136.75, 130.67, 129.61, 126.21, 125.77, 31.63, 30.39, 29.57, 29.18, 22.58, 14.05. GC-MS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{18}\text{OS}_2$: 278.08. Found: 278.17.

3'-hexyl-3-methyl-[2,2'-bithiophene]-5-carbaldehyde (3-2c). Yield: 52.8%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.75 (s, 1H), 7.50 (s, 1H), 7.26(d, $J = 5.2$ Hz, 1H), 6.90 (d, $J = 4.8$ Hz, 1H), 2.46 (t, $J = 7.8$ Hz, 2H), 2.13 (s, 3H), 1.49-1.44 (m, 2H), 1.18-1.11(m, 6H), 0.75 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 181.68, 142.07, 141.04, 139.53, 137.72, 136.99, 128.10, 126.32, 125.45, 30.52, 29.55, 27.96, 27.91, 21.51, 13.78, 13.00. GC-MS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{20}\text{OS}_2$: 292.10. Found: 292.24.

General procedure for synthesis of **3-b** and **3-c**.

In a 50 mL 3-necked flask, a solution of **3-2b** or **3-2c** (6.0 mmol) in dry THF (30 mL) was cooled to 0 °C under a nitrogen atmosphere. NBS (6.6 mmol) was added slowly in portions and allowed to stir in an ice-bath for 8 h at approximately 0 °C. The reaction mixture was then poured into DCM. The organic layer was washed with water and dried over anhydrous MgSO_4 . After removing the solvent, the crude product obtained was purified by column chromatography (PE-EA mixture as the eluent) to obtain compound **3-b** or **3-c** as a light yellow oily liquid.

5'-bromo-3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3-b). Yield: 73.1%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.88 (s, 1H), 7.69 (d, $J = 4.0$ Hz, 1H), 7.14 (d, $J = 3.6$ Hz, 1H), 6.93 (s, 1H), 2.74 (t, $J = 7.8$ Hz, 2H), 1.65-1.57 (m, 2H), 1.38-1.27(m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 182.58, 144.94, 142.76, 142.58, 136.61, 133.29, 131.02, 126.46, 112.99, 31.57, 30.26, 29.51, 29.09, 22.54, 14.03. GC-MS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{17}\text{BrOS}_2$: 357.99. Found: 358.10.

5'-bromo-3'-hexyl-3-methyl-[2,2'-bithiophene]-5-carbaldehyde (3-c). Yield: 86.6%. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.76 (s, 1H), 7.50 (s, 1H), 6.88 (s, 1H), 2.40 (t, $J = 7.6$ Hz, 2H), 2.14 (s, 3H), 1.47-1.40 (m, 2H), 1.19-1.13 (m, 6H), 0.76 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 181.69, 142.85, 141.44, 137.82, 137.57, 137.49, 130.87, 127.77, 112.37, 30.47, 29.40, 28.57, 27.90, 21.49, 13.78, 12.99. GC-MS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{BrOS}_2$: 372.00. Found: 372.18.

Synthesis of (4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1*H*-benzo[d]imidazol-5-yl)

amino)phenyl)boronic acid (2). In a 250 mL 3-necked flask, a solution of **1** (10.0 g, 12.42 mmol) in dry THF

(180 mL) was cooled to -78 °C under a nitrogen atmosphere. *n*-BuLi in hexane (9.0 mL, 22.36 mmol) was added dropwise and the mixture was stirred for 1.5 h at -78 °C. Following this, B(OBu)₃ (5.7 g, 24.77 mmol) was added dropwise and the reaction was stirred again at -78 °C for 2 h. The reaction mixture was then poured into 200 mL of 1 mol L⁻¹ HCl aqueous solution and extracted with EA. The combined organic extract was then washed to neutral with water. The organic layer was dried over anhydrous MgSO₄ and the solvent removed. Then 200 mL of PE-EA (20:1, v/v) mixture was added to the crude product, the white precipitate was filtered and to give the compound **2** (7.8 g, 81.6 %) as a off-white powder. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 2.0 Hz, 2H), 7.01 (dd, *J*₁ = 1.6 Hz, *J*₂ = 2.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.25 (t, *J* = 7.2 Hz, 4H), 4.16 (t, *J* = 7.2 Hz, 4H), 1.72-1.69 (m, 4H), 1.61-1.57 (m, 4H), 1.33-1.25 (m, 12H), 1.17-1.10 (m, 12H), 0.83 (t, *J* = 7.0 Hz, 6H), 0.74 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 168.59, 149.72, 142.65, 135.32, 132.42, 128.25, 120.80, 118.76, 110.24, 106.89, 43.93, 43.66, 30.83, 30.71, 27.29, 27.12, 25.69, 25.54, 21.91, 21.77, 13.75, 13.65.

General procedure for synthesis of **4-a**, **4-b**, and **4-c**.

In a 100 mL 3-necked flask, compound **2** (0.90 mmol), intermediate **3-a**, **3-b**, or **3-c** (1.0 mmol), TBAB (0.27 mmol), N, N-dimethylformamide (DMF) (50 mL) and Pd(PPh₃)₄ (0.01 mmol) were added in turn under a nitrogen atmosphere. Following this, K₂CO₃ aqueous solution (0.18 mol L⁻¹, 10 mL) was added dropwise and the reaction mixture was stirred for 2 h at 75 °C and then poured into EA. The organic layer was washed with water and dried over anhydrous MgSO₄. After removing the solvent, the crude product obtained was purified by column chromatography (PE-EA mixture as the eluent) to obtain **4-a**, **4-b**, or **4-c** as an orange semisolid.

5-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)thiophene-2-carbaldehyde (4-a). Yield: 79.6%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.75 (s, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.95-6.90 (m, 6H), 4.20 (t, *J* = 7.6 Hz, 4H), 4.10 (t, *J* = 7.2 Hz, 4H), 1.76-1.73 (m, 4H), 1.67-1.63 (m, 4H), 1.35-1.16 (m, 24H), 0.80 (t, *J* = 7.0 Hz, 6H), 0.76 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 181.47, 168.59, 153.15, 148.42, 141.65, 140.42, 136.69, 132.14, 128.09, 126.33, 125.07, 121.87, 120.22, 119.68, 108.68, 105.32, 43.90, 43.71, 30.45, 30.37, 26.90, 26.78, 25.55, 25.42, 21.52, 21.44, 13.00, 12.96. MS (MALDI-TOF) *m/z* calcd. for C₄₉H₆₅N₅OS₃: 835.44. Found: 835.48.

5'-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)-3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (4-b). Yield: 85.2%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.78 (s, 1H), 7.62 (d, *J* = 4.0 Hz 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 4.0 Hz, 1H), 7.02 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.95-6.88 (m, 6H), 4.20 (t, *J* = 7.6 Hz, 4H), 4.10 (t, *J* = 7.4 Hz, 4H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.79-1.71 (m, 4H), 1.67-1.59 (m, 6H), 1.38-1.32 (m, 6H), 1.28-1.15 (m, 24H), 0.83-0.79 (m, 9H), 0.74 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 182.63, 169.66, 148.36, 146.73, 144.04, 143.46, 143.27, 142.10, 137.03, 133.30, 128.98, 128.44, 127.29, 126.77, 125.89, 125.81, 122.19, 120.51, 109.76, 106.11, 45.08, 44.88, 31.80, 31.63, 31.57, 30.42, 30.11, 29.38, 28.09, 27.97, 26.73, 26.60, 22.74, 22.69, 22.62, 14.20, 14.15, 14.13. MS (MALDI-TOF) *m/z* calcd. for C₅₉H₇₉N₅OS₄: 1001.51. Found: 1001.56.

5'-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)amino)phenyl)-3'-hexyl-3-methyl-[2,2'-bithiophene]-5-carbaldehyde (4-c). Yield: 89.1%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.75 (s, 1H), 7.51 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.05 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.96-6.87 (m, 6H), 4.19 (t, *J* = 7.6 Hz, 4H), 4.10 (t, *J* = 7.6 Hz, 4H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.20 (s, 3H), 1.78-1.71 (m, 4H), 1.68-1.61 (m, 4H), 1.54-1.47 (m, 2H), 1.37-1.32 (m, 6H), 1.27-1.16 (m, 24H), 0.80 (t, *J* = 7.0 Hz, 6H), 0.78-0.72 (m, 9H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 181.64, 168.43, 146.97, 143.64, 143.18, 142.23, 140.92, 139.43, 137.89, 136.84, 132.11, 127.70, 126.58, 125.56, 125.03, 123.27, 121.29, 119.23, 108.57, 104.82, 43.90, 43.69, 30.55, 30.46, 30.40, 29.58, 28.67, 28.24, 27.99, 26.92, 26.80, 25.56, 25.43, 21.52, 21.45, 13.99, 13.02, 12.99, 12.96. MS (MALDI-TOF) *m/z* calcd. for C₆₀H₈₁N₅OS₄: 1015.53. Found: 1015.65.

Synthesis of 5,5'-((4-vinylphenyl)azanediy)bis(1,3-dihexyl-1H-benzo[d]imidazole

-2(3H)-thione (6). In a 100 mL 3-necked flask, a solution of methyltriphenylphosphonium bromide (3.12 g, 8.74 mmol) in dry THF (20 mL) was cooled to -10 °C under a nitrogen atmosphere. Following this, *t*-BuOK (0.98 g, 8.74 mmol) was added slowly and the reaction mixture was stirred for 2 h at -10 °C. A solution of compound **5** (4.40 g, 5.83 mmol) in dry THF (30 mL) was added dropwise and the reaction mixture was stirred at 10 °C for 5 h. The reaction mixture was then poured into DCM. The organic layer was washed with water and dried over anhydrous MgSO₄. After removing the solvent, the crude product obtained was purified by column chromatography (PE-EA mixture as the eluent, 25:1, v/v) to obtain compound **6** as a yellow oily liquid (2.40 g, 54.8%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.22 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.91-6.84 (m, 6H), 6.61 (dd, *J*₁ = 10.8 Hz, *J*₂ = 11.2 Hz, 1H), 5.57 (d, *J* = 17.6 Hz, 1H), 5.09 (d, *J* = 11.2 Hz, 1H), 4.18 (t, *J* = 7.6 Hz, 4H), 4.08 (t, *J* = 7.6 Hz, 4H), 1.77-1.70 (m, 4H), 1.67-1.60 (m, 4H), 1.36-1.13 (m, 24H), 0.80 (t, *J* = 7.0 Hz, 6H), 0.73 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 169.43, 147.91, 143.64, 136.15, 133.18, 131.86, 128.63, 127.27, 122.43, 120.20, 112.37, 109.63, 105.76, 45.00, 44.77, 31.57, 31.49, 28.03, 27.89, 26.66, 26.51, 22.62, 22.53, 14.09, 14.06. MS (MALDI-TOF) *m/z* calcd. for C₄₆H₆₅N₅S₂: 751.46. Found: 751.54.

Synthesis of (E)-5'-(4-(bis(1,3-dihexyl-2-thioxo-2,3-dihydro-1H-benzo[d]imidazol-5-yl)

amino)styryl]-3'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (7). In a 100 mL 3-necked flask, compound **6** (1.50 g, 2.00 mmol), **3-b** (1.10 g, 3.08 mmol), TBAB (0.65 g, 2.02 mmol), DMF (70 mL), Pd(OAc)₂ (0.03 g, 0.13 mmol) and K₂CO₃ (0.69 g, 5.0 mmol) were added in turn under a nitrogen atmosphere. Then, the reaction mixture was stirred for 24 h at 120 °C. After cooling to room temperature, the solution was poured into EA. The organic layer was washed with water and dried over anhydrous MgSO₄. After removing the solvent, the crude product obtained was purified by column chromatography (PE-EA mixture as the eluent, 10:1, v/v) to obtain compound **7** as an orange semisolid (0.84 g, 40.5%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.78 (s, 1H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.98 (s, 1H), 6.93-6.87 (m, 8H), 6.82 (d, *J* = 16.4 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 4H), 4.08 (t, *J* = 7.4 Hz, 4H), 2.70 (t, *J* = 7.8 Hz, 2H), 1.78-1.71 (m, 4H), 1.68-1.55 (m, 6H), 1.37-1.32 (m, 6H), 1.27-1.15 (m, 24H), 0.81 (t, *J* = 7.0 Hz, 9H), 0.75 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 182.49, 169.41, 148.04, 146.55, 143.21, 143.06, 142.86, 141.94, 136.89, 133.10, 130.37, 129.40, 129.10, 128.74, 128.06, 127.47, 125.71, 121.98, 120.34, 119.40, 109.58, 105.91, 44.92, 44.70, 31.65, 31.48, 31.41, 30.10, 29.84, 29.22, 27.94, 27.81, 26.58, 26.44, 22.58, 22.54, 22.46, 14.07, 14.02, 14.00. MS (MALDI-TOF) *m/z* calcd. for C₆₁H₈₁N₅OS₄: 1027.53. Found: 1027.89.

2.

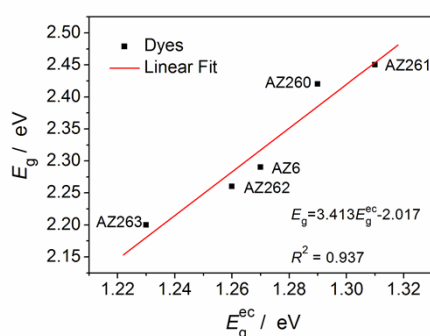


Fig. S1 The linear fit about theoretical values E_g and their experimental values E_{ec} . R^2 is the square correlation coefficient.

3. Morphology of photoanodes

First, a preliminary study on surface morphology of TiO₂ monolayer films were conducted by SEM. Fig. S2a and b show the top view SEM images of 20 nm nanocrystalline TiO₂ film (labeled **NC**) and 400 nm mesoporous spherical TiO₂ film (labeled **MS400**), respectively. It is observed that the surface roughness of **MS400** was significantly higher than that of **NC**. In DSSCs, large-size particles have been utilized to enhance light-harvesting by the light-scattering effect, thus improving the conversion efficiency.⁵³ Therefore, **MS400** as a scattering layer was covered on **NC** to form the bilayered photoanode (**NC-MS400**). Fig. S2c and d show the cross-sectional SEM images of **NC** and **NC-MS400**, respectively. The bilayered architecture of **NC-MS400** can be obviously observed. The thickness of the underlayer is ~6.5 μm, and that of the overlayer is ~3.5 μm. The scattering layer composed of 200 nm spheric particles TiO₂ (**SP200**) was also employed to form another bilayered photoanode (**NC-SP200**) for comparison.

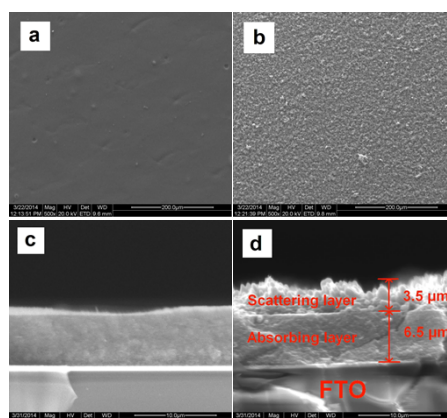


Fig. S2 Top view SEM images of **NC** (a) and **MS400** (b); cross-sectional SEM images of **NC** (c) and **NC-MS400** (d).

4.

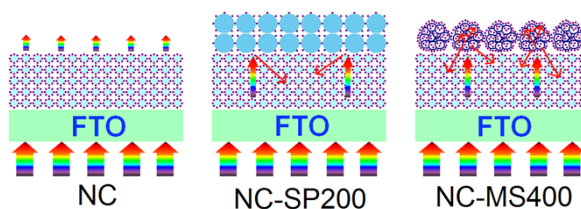


Fig. S3 Schematic diagrams of **NC**, **NC-SP200**, and **NC-MS400** photoanodes.

5. Experimental procedures of desorption

To quantify the dye-loading capacity of the three photoanodes (**NC**, **NC-SP200**, and **NC-MS400**), the desorption experiments were carried out. Absorption spectra of **AZ261** in 0.1 g/mL NaOH solution [H_2O -Ethanol-THF (1:1:1, v/v/v) mixture as the solvent] for various concentration are shown in Fig. S4a. The various concentration and the corresponding absorption intensity ($\lambda = 348 \text{ nm}$) are recorded in Table S1. Fig. S4b shows the linear fit about concentration (C) and absorption intensity (A).

As the next step, the three photoanodes (**NC**, **NC-SP200**, and **NC-MS400**) with **AZ261** were immersed into 7.5 mL 0.1g mL⁻¹ NaOH solution, respectively; the corresponding absorption spectra are shown in Fig. S4c. The concentration of eluted **AZ261** in solution was calculated by linear regression; then the amount of absorbed dye was figured out, which are $1.60 \times 10^{-7} \text{ mol cm}^{-2}$, $1.74 \times 10^{-7} \text{ mol cm}^{-2}$ and $2.18 \times 10^{-7} \text{ mol cm}^{-2}$ for **NC**, **NC-SP200**, and **NC-MS400**, respectively.

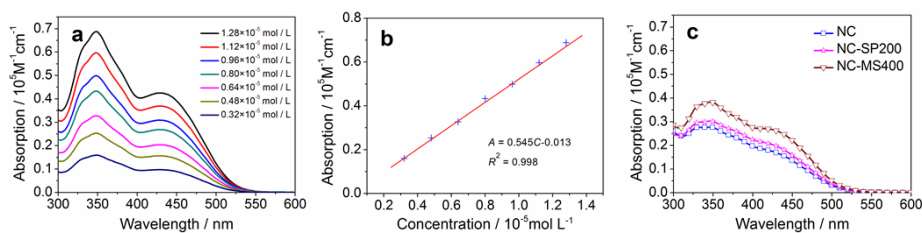


Fig. S4 Absorption spectra of **AZ261** in 0.1 g/mL NaOH solution (H_2O -Ethanol-THF (1:1:1, v/v/v) mixture as the solvent) for various concentration (a); linear fit about concentration and absorption intensity (b); absorption spectra of the eluted **AZ261** in 7.5 mL 0.1 g/mL NaOH solution (c).

Table S1 Different concentration (C) and corresponding absorption intensity (A) of **AZ261** in 0.1 g mL⁻¹ NaOH solution at 348 nm.

Sample	1	2	3	4	5	6	7
C ($10^{-5} \text{ mol L}^{-1}$)	0.32	0.48	0.64	0.80	0.96	1.12	1.28
A ($10^{-5} \text{ M}^{-1} \text{ cm}^{-1}$)	0.688	0.597	0.499	0.433	0.327	0.254	0.160

6.

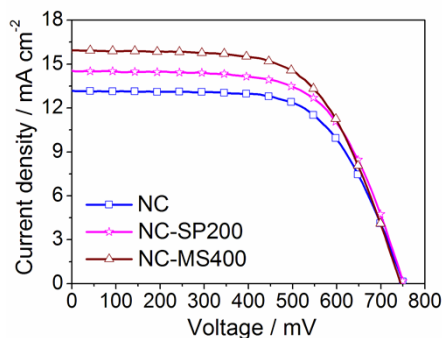
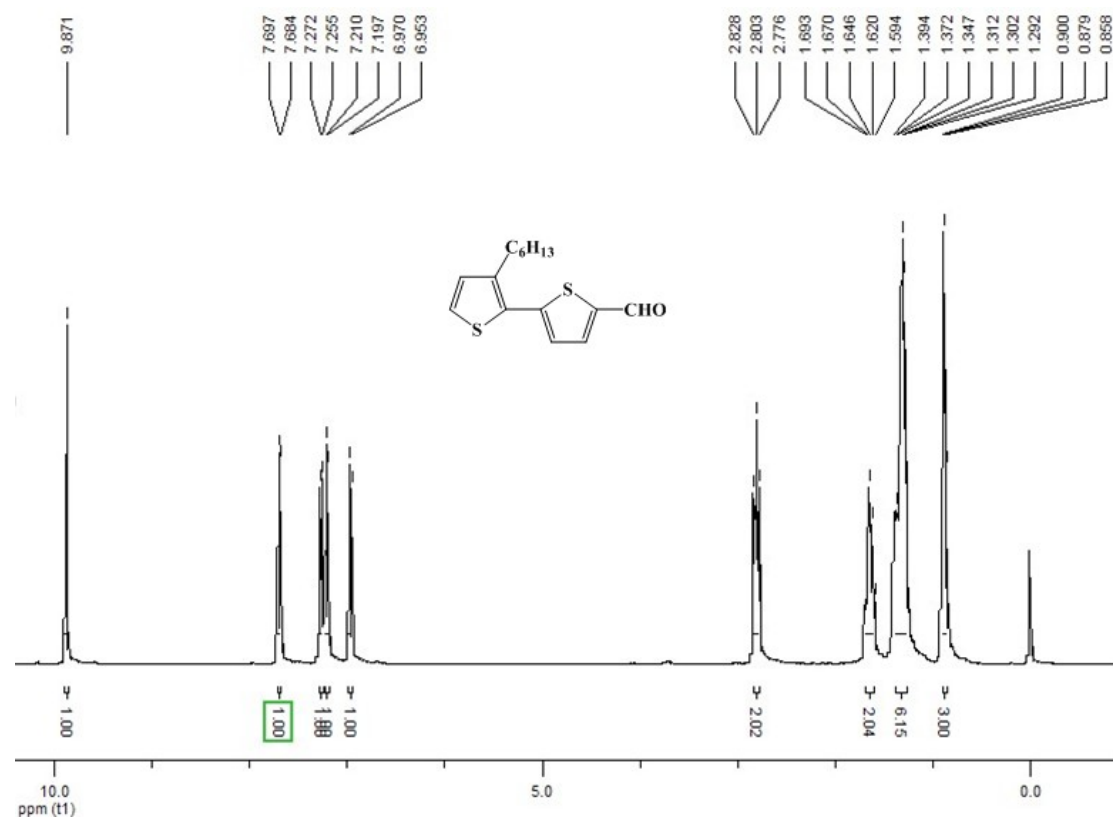


Fig. S5 The J - V characteristics of **AZ261** based on **NC**, **NC-SP200**, and **NC-MS400** photoanodes.

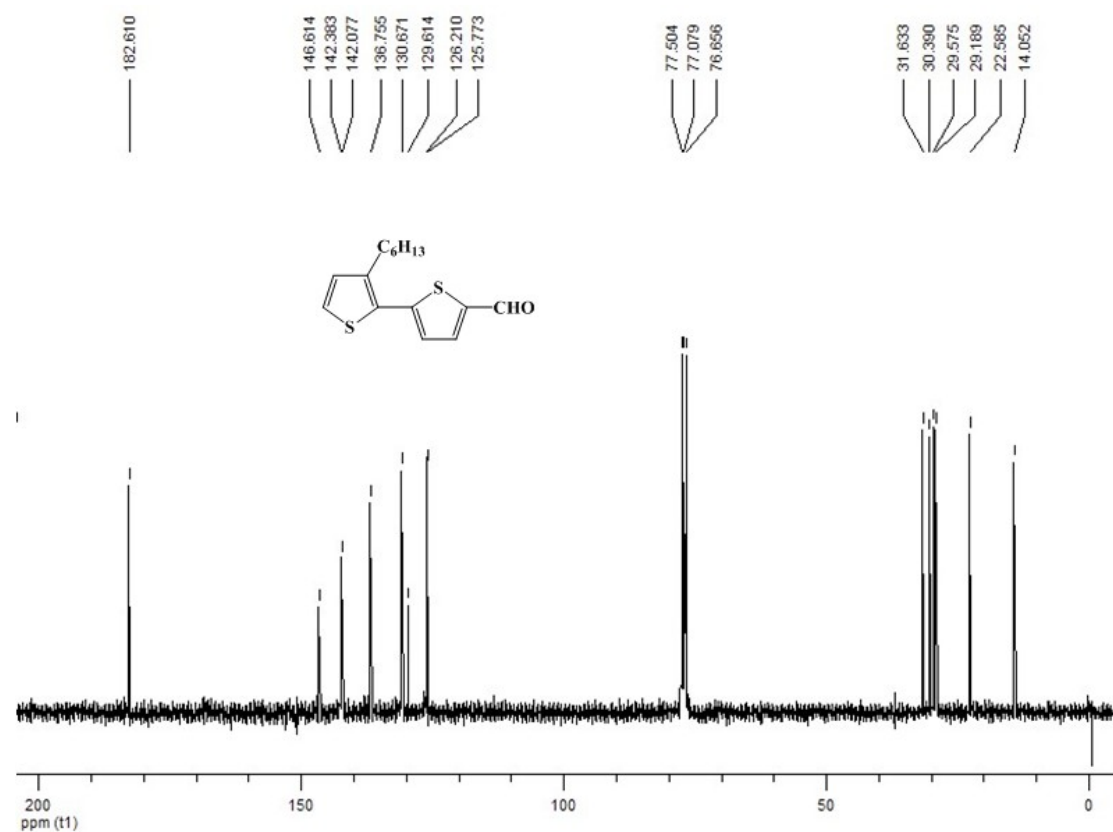
References:

- S1. (a) Y. Li, G. Vamvounis and S. Holdcroft, *Macromolecules*, 2002, **35**, 6900-6906; (b) H. Kanato,; K. Takimiya,; T. Otsubo,; Y. Aso,; T. Nakamura,; Y. Araki and O. Ito, *J. Org. Chem.*, 2004, **69**, 7183-7189.
- S2. P. Innocenti, K.-M. J. Cheung, S. Solanki, C. Mas-Droux, F. Rowan, S. Yeoh, K. Boxall, M. Westlake, L. Pickard, T. Hardy, J. E. Baxter, G. W. Aherne, R. Bayliss, A. M. Fry and S. Hoelder, *J. Med. Chem.*, 2012, **55**, 3228-3241.
- S3. W. Peng and L. Han, *J. Mater. Chem.*, 2012, **22**, 20773-20777.

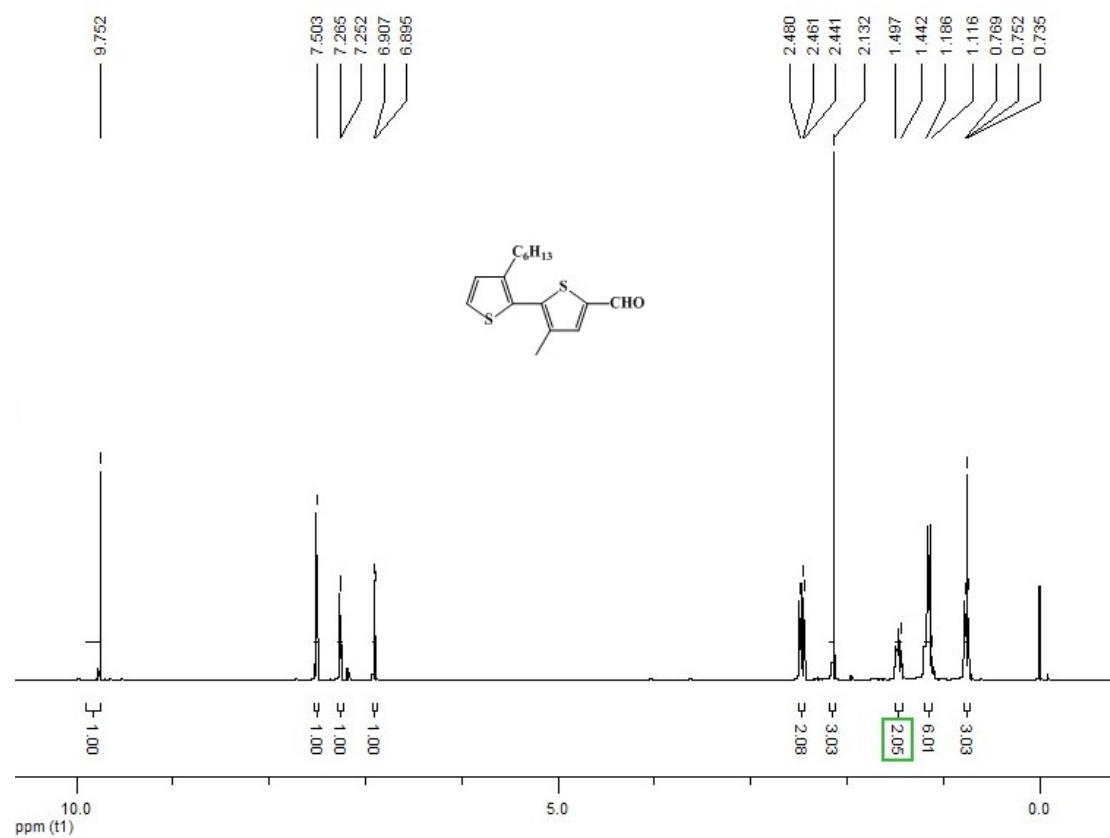
¹H NMR of 3-2b



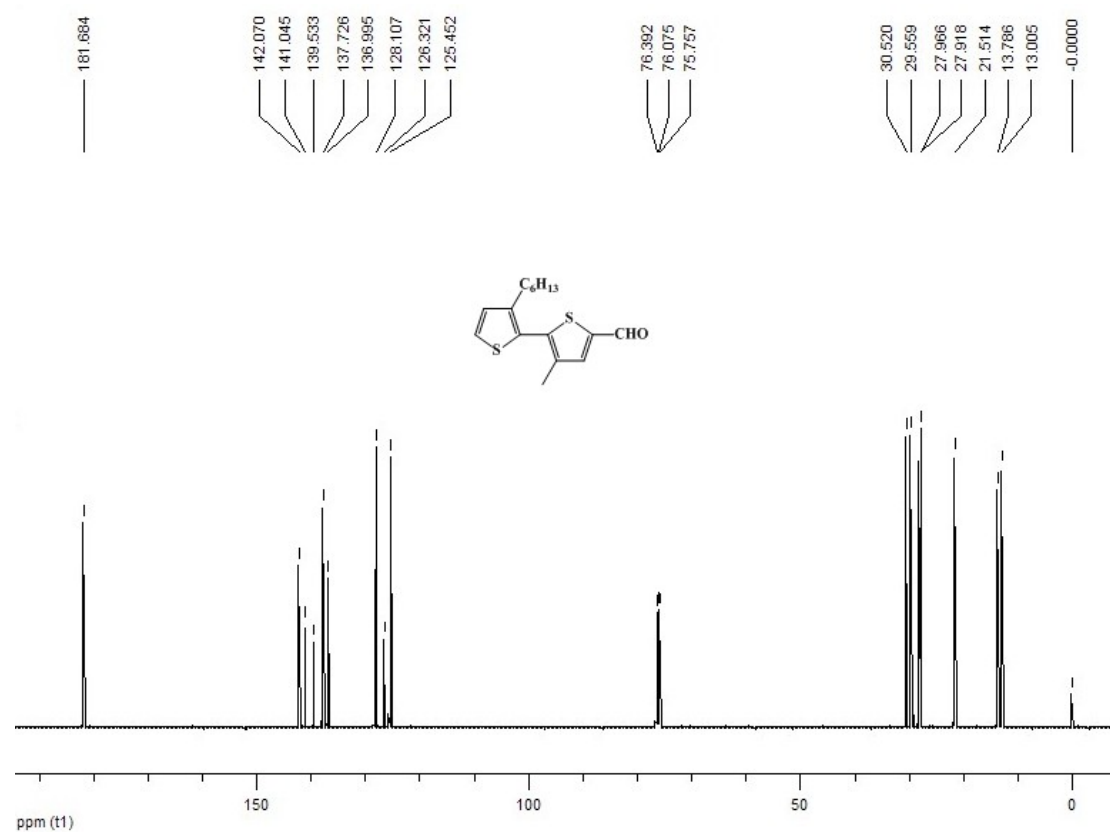
¹³C NMR of 3-2b



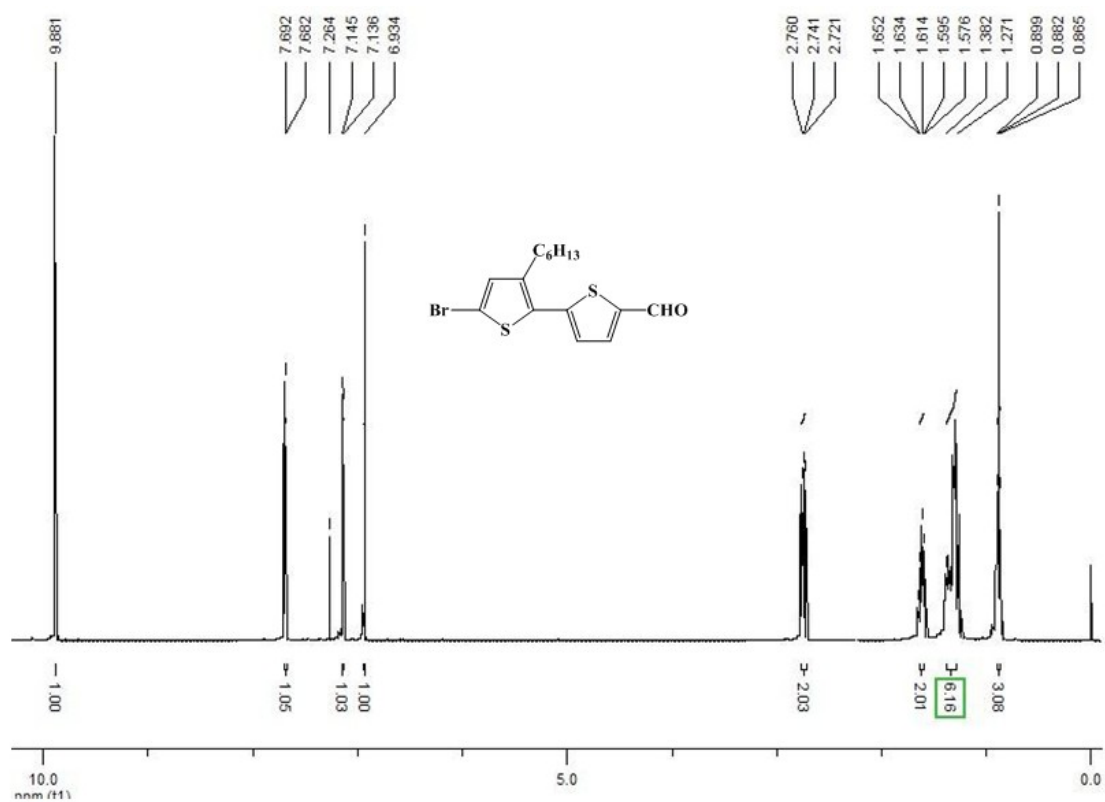
¹H NMR of 3-2c



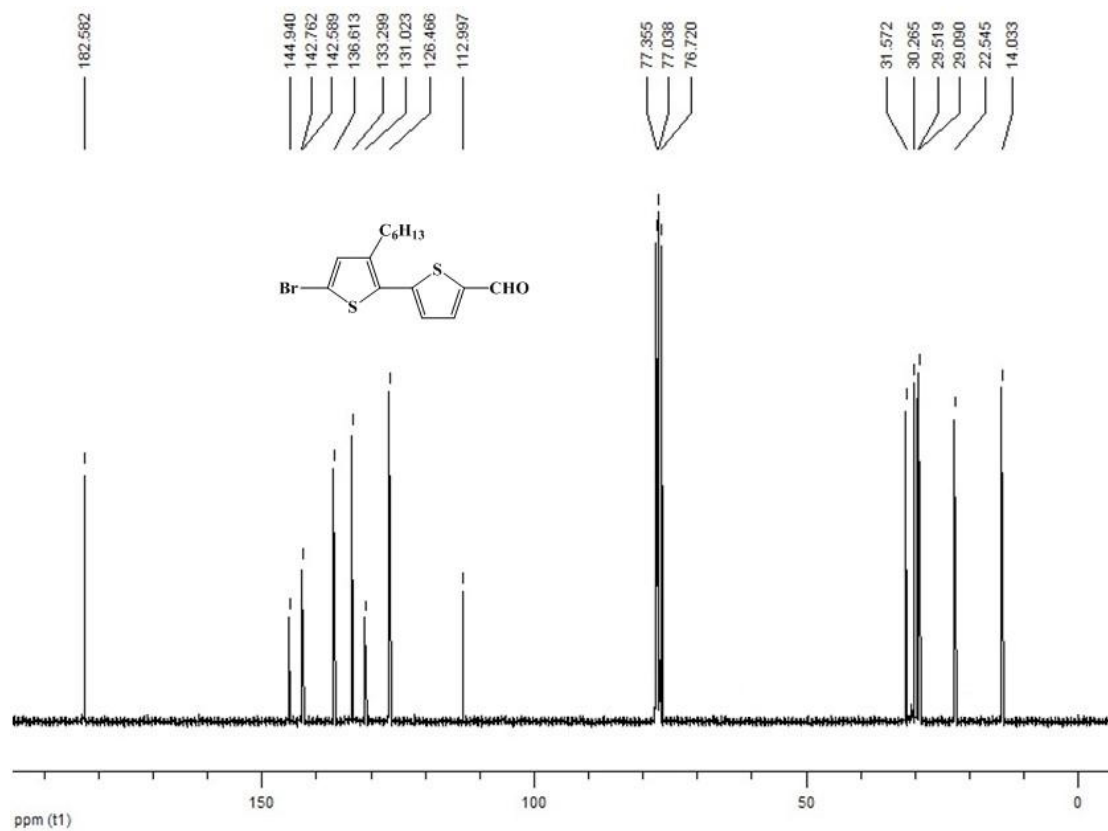
¹³C NMR of 3-2c



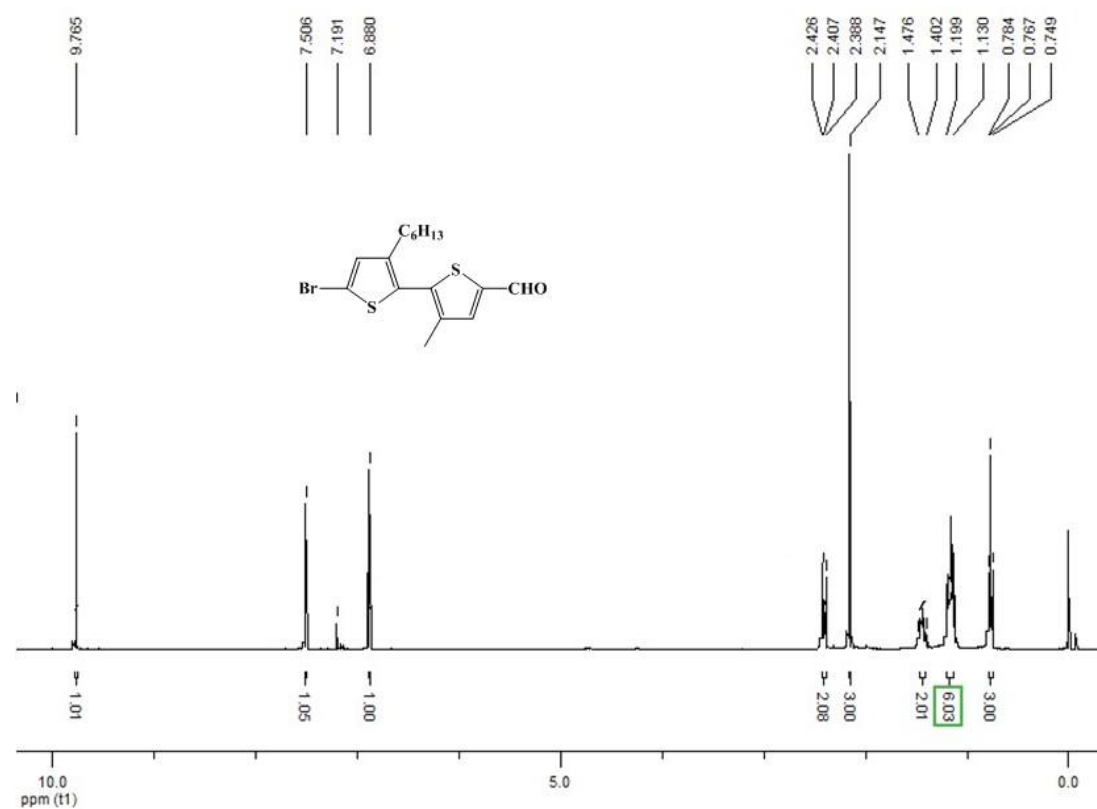
¹H NMR of 3-b



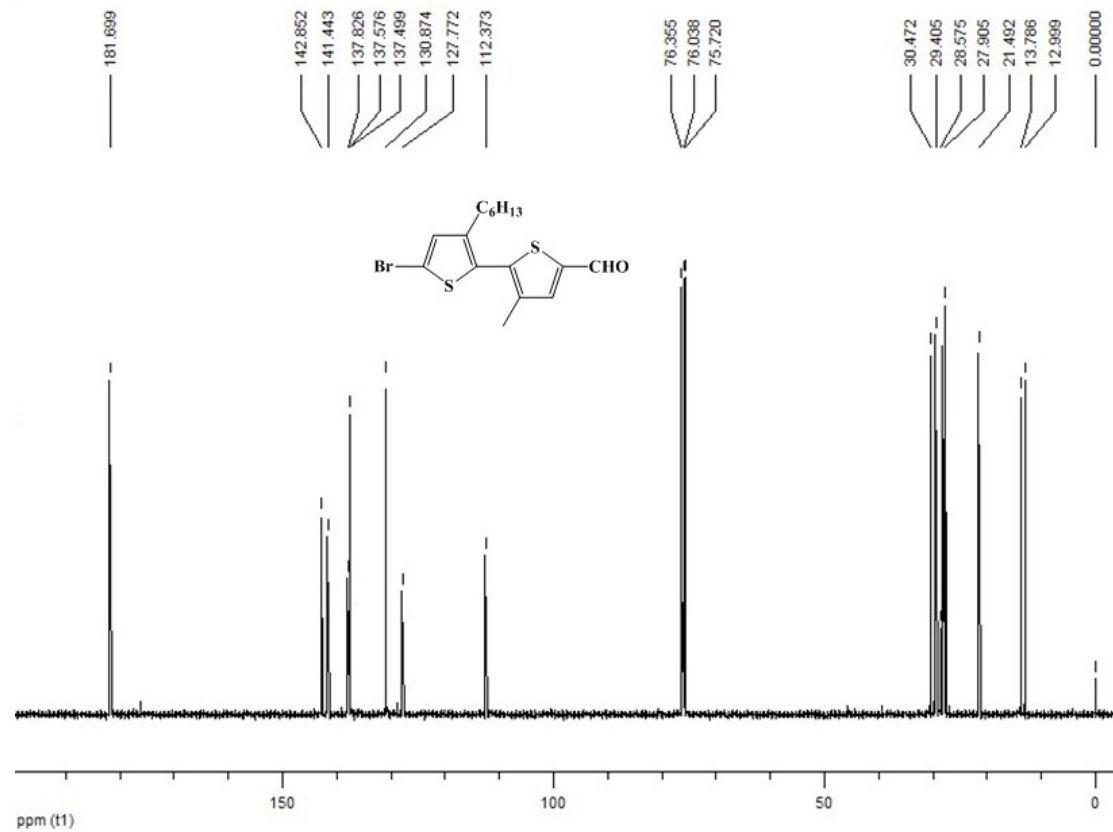
¹³C NMR of 3-b



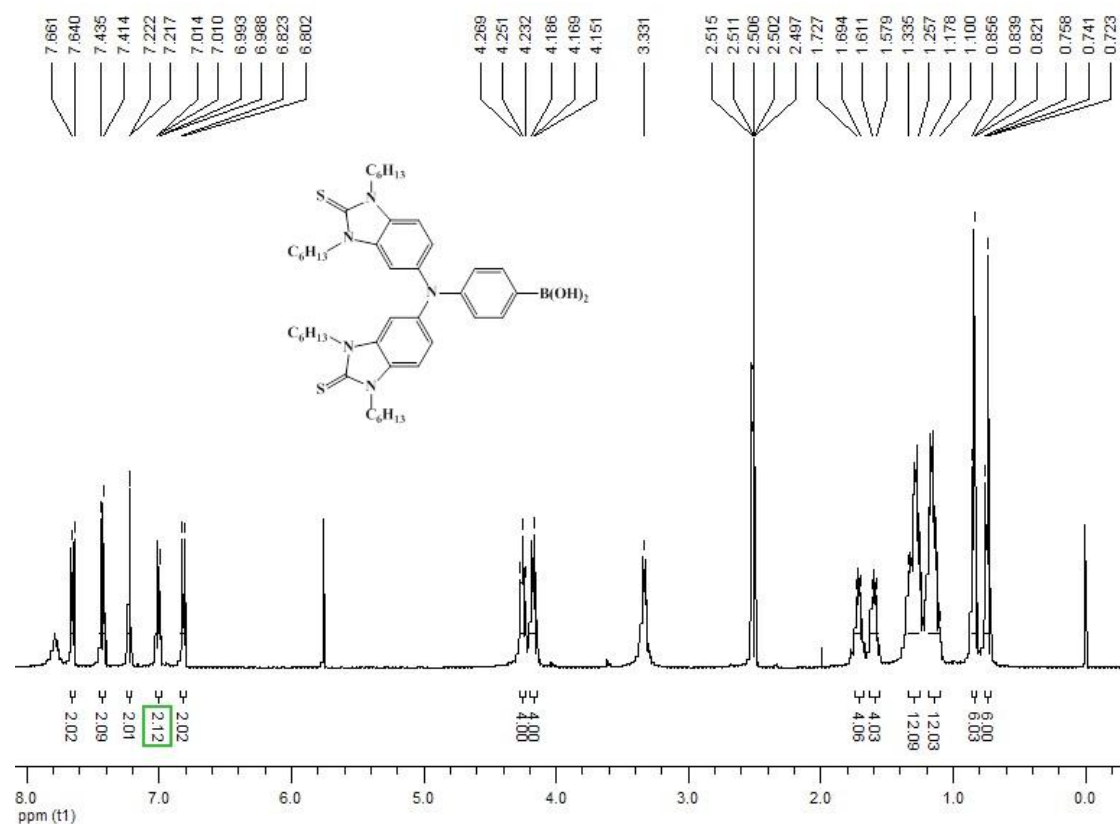
¹H NMR of 3-c



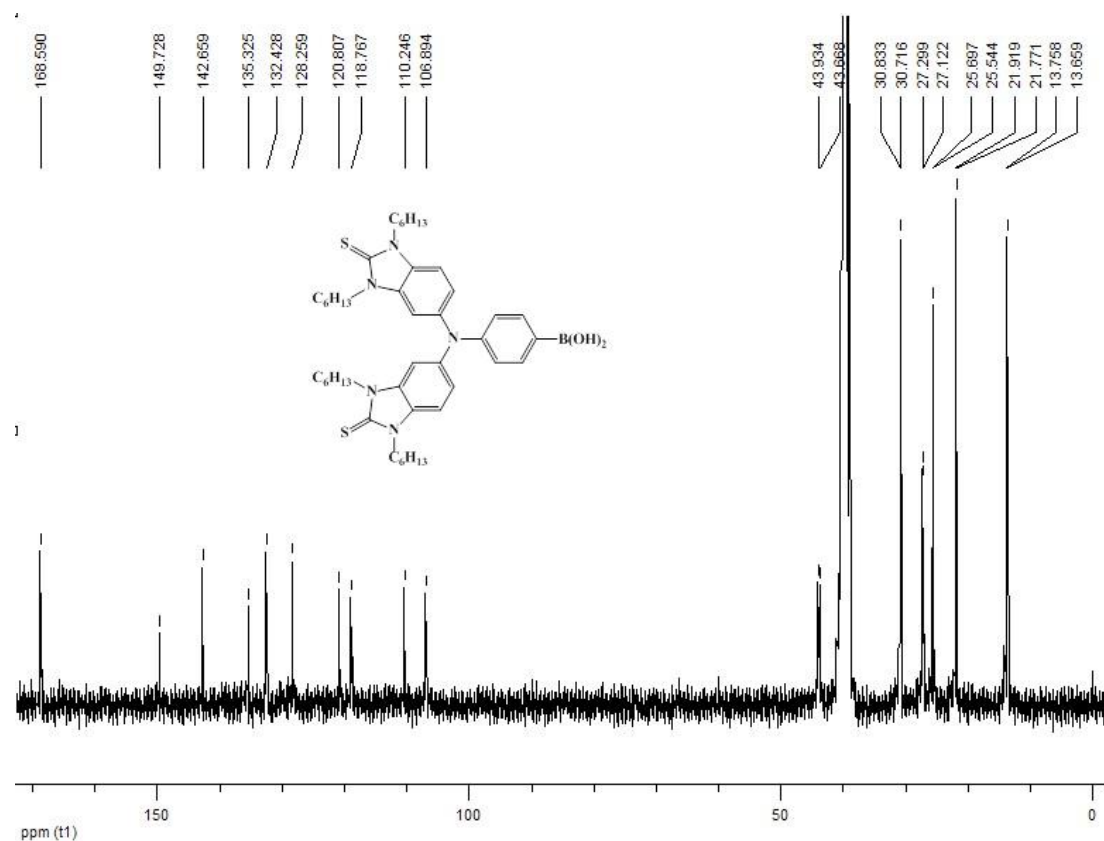
¹³C NMR of 3-c



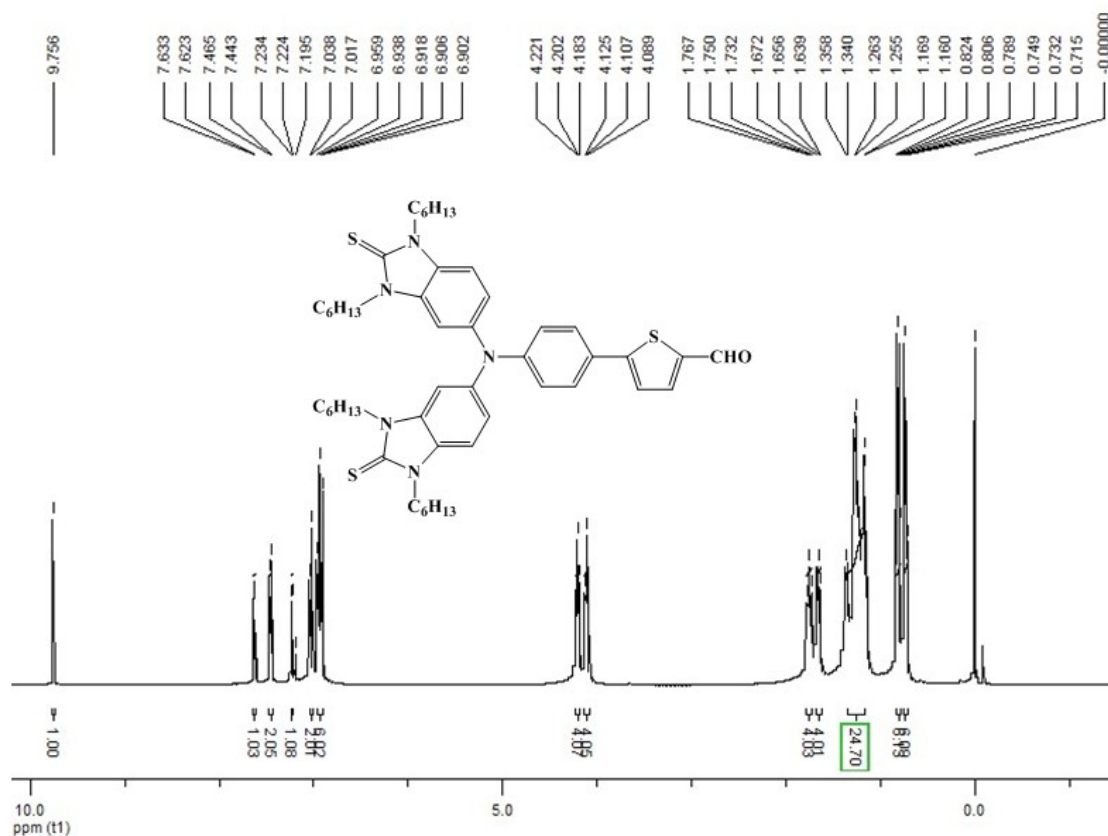
¹H NMR of 2



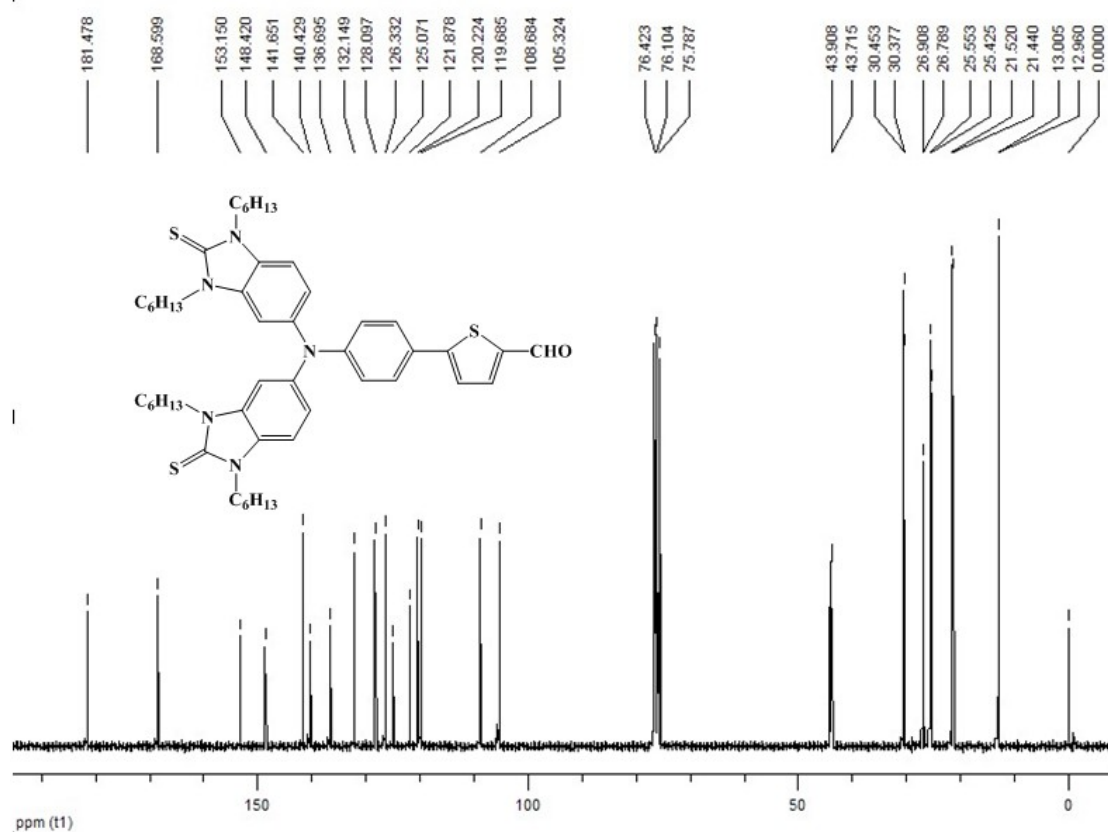
¹³C NMR of 2



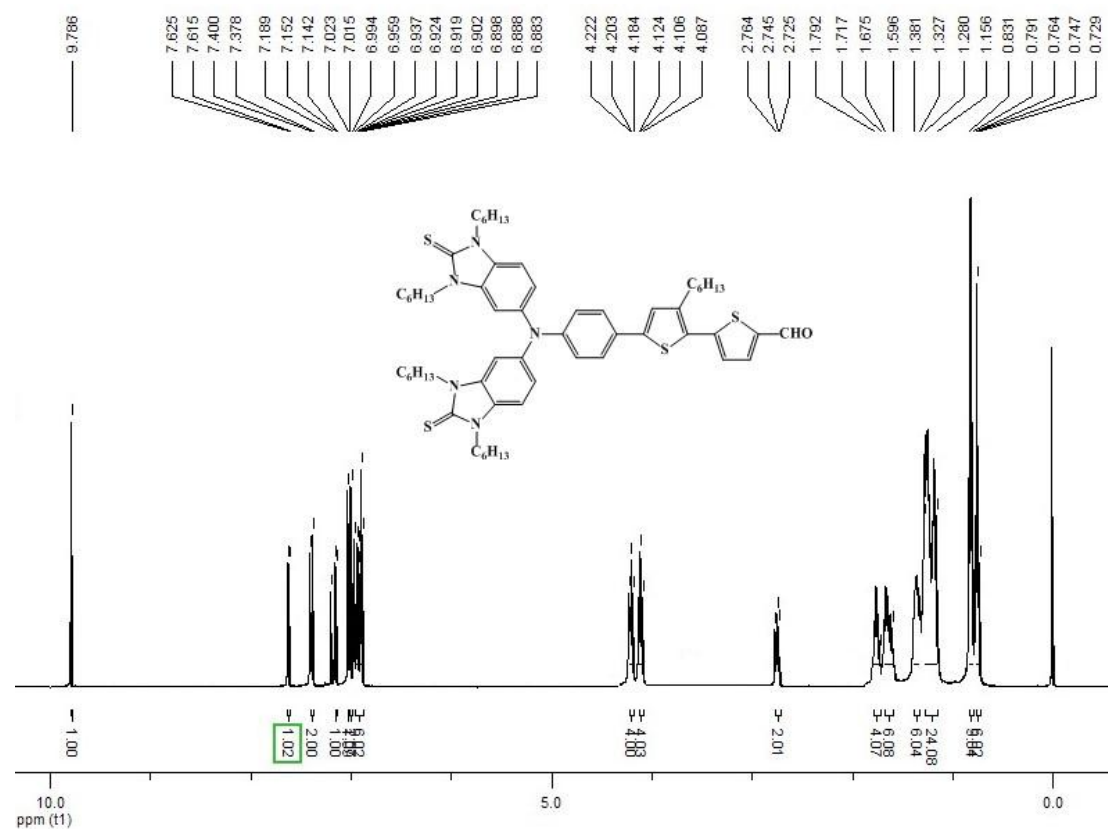
¹H NMR of 4-a



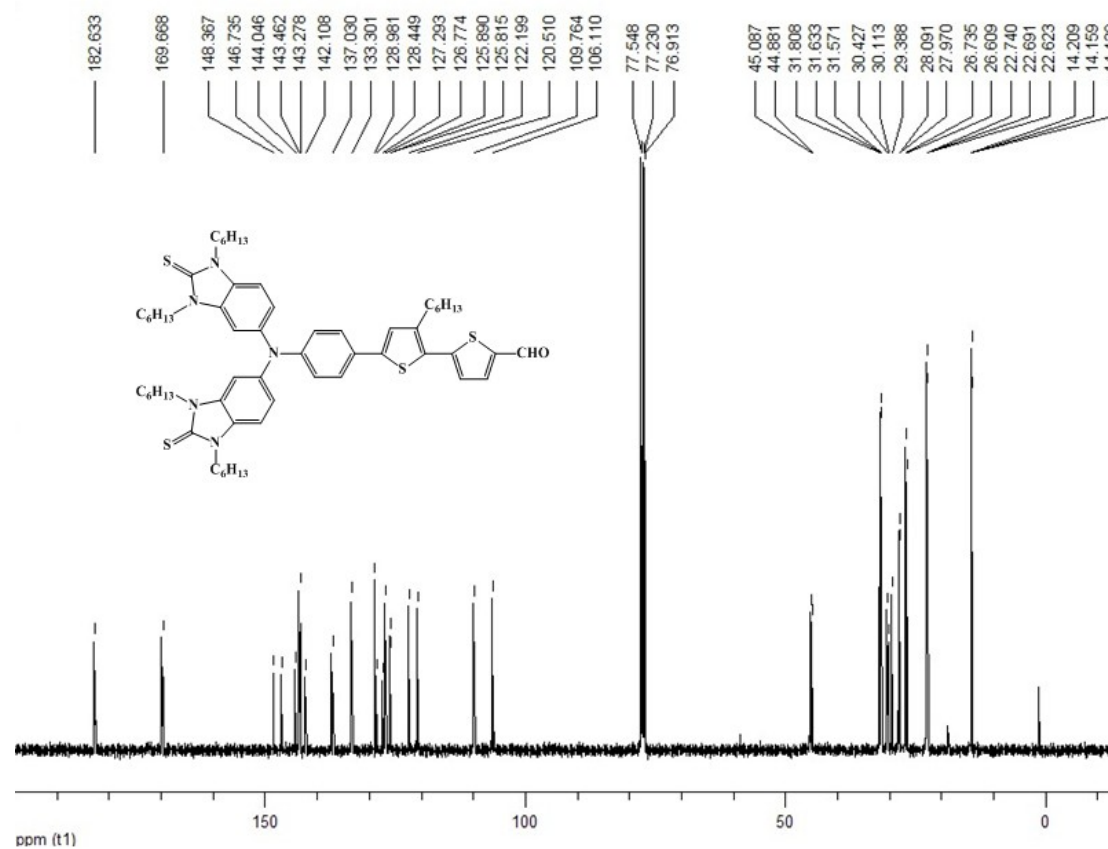
¹³C NMR of 4-a



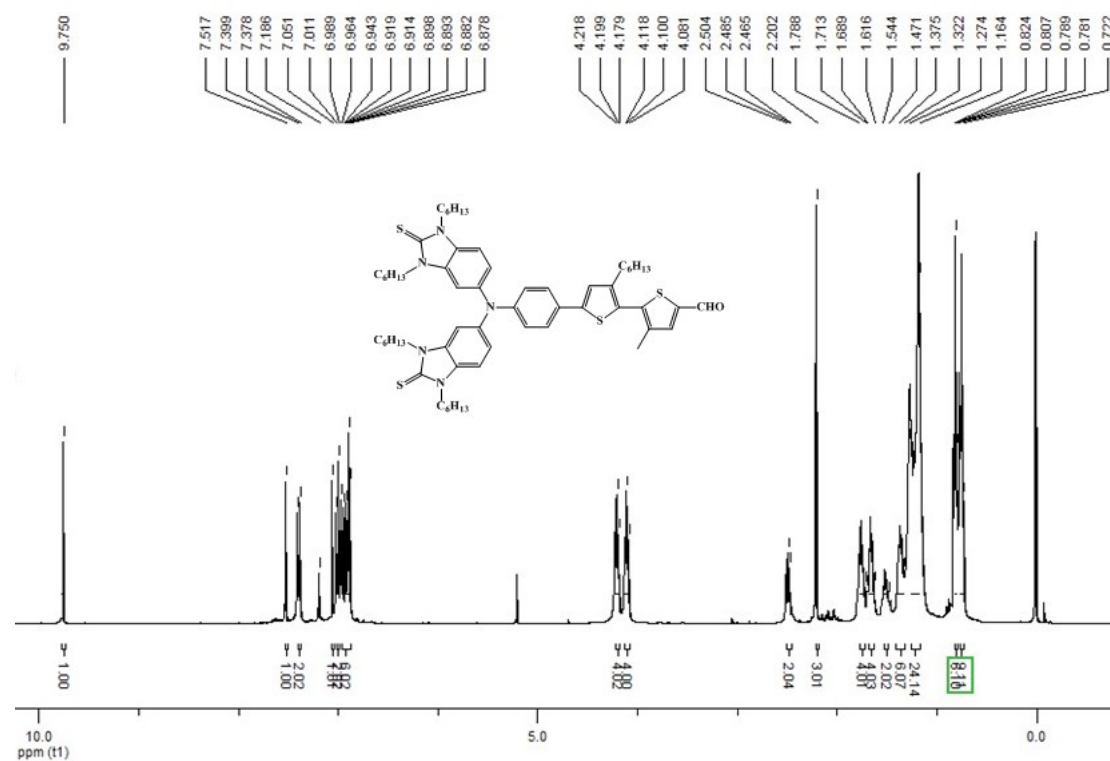
¹H NMR of 4-b



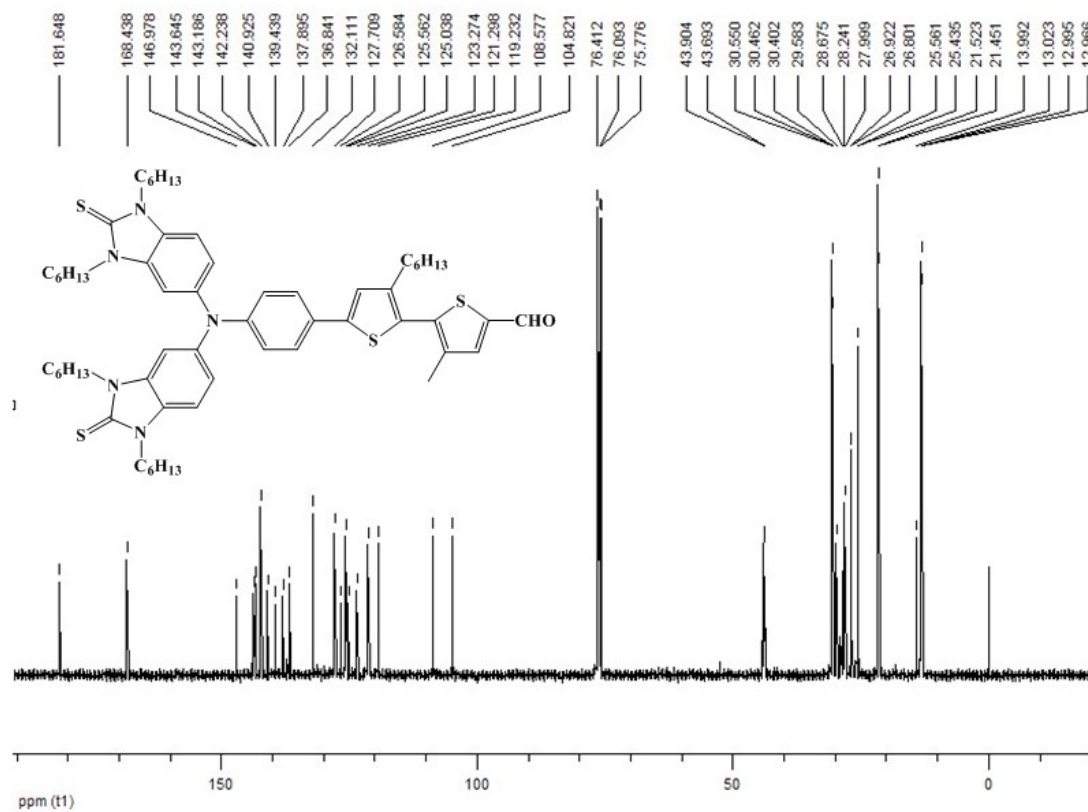
¹³C NMR of 4-b



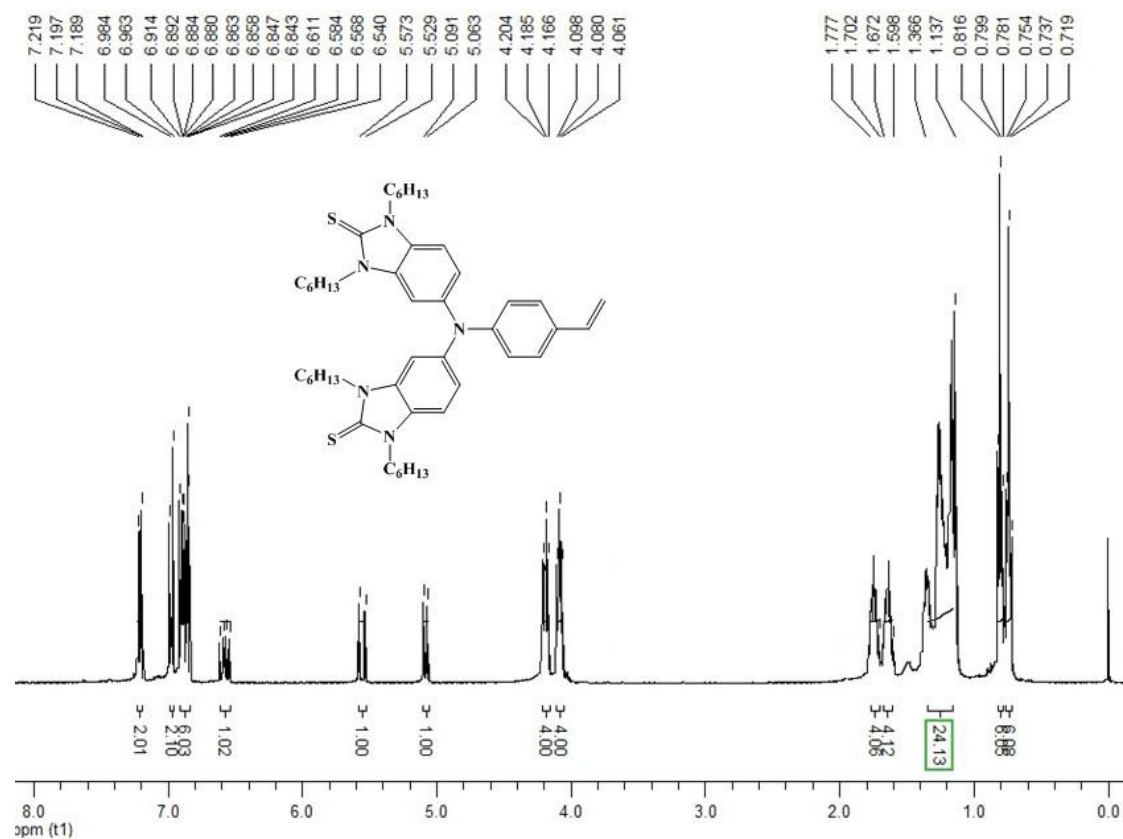
¹H NMR of 4-c



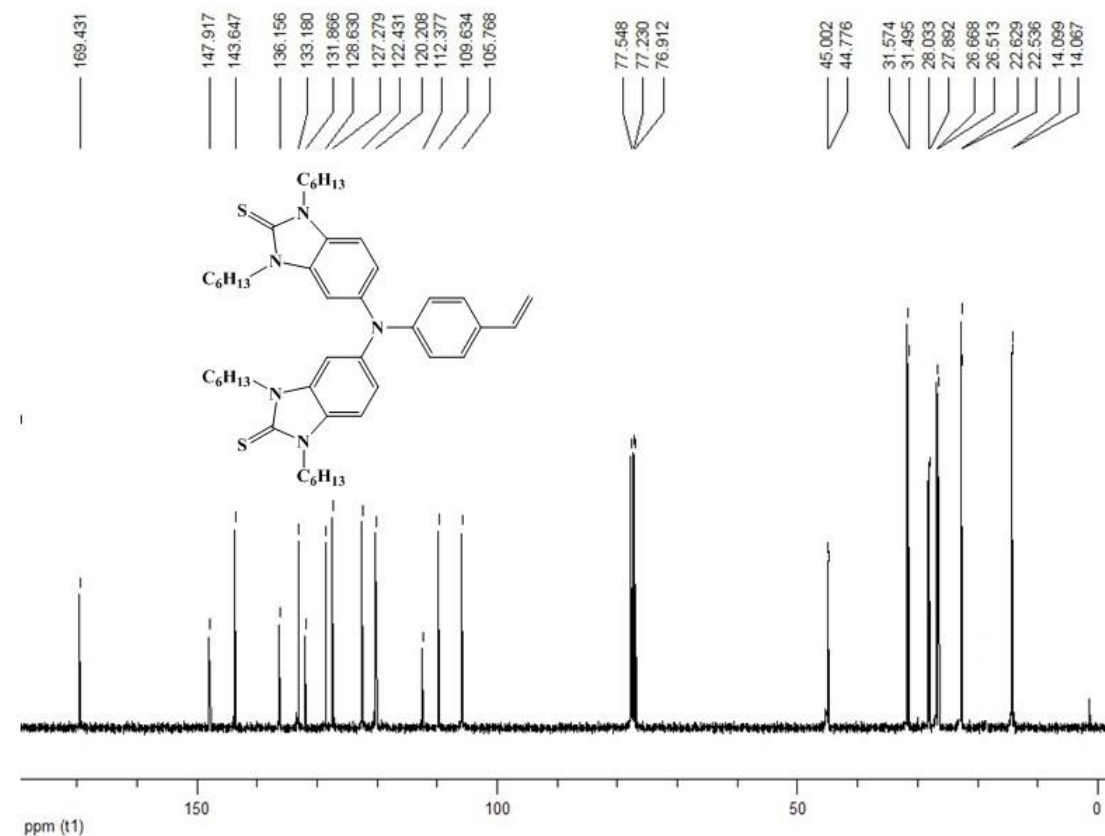
¹³C NMR of 4-c



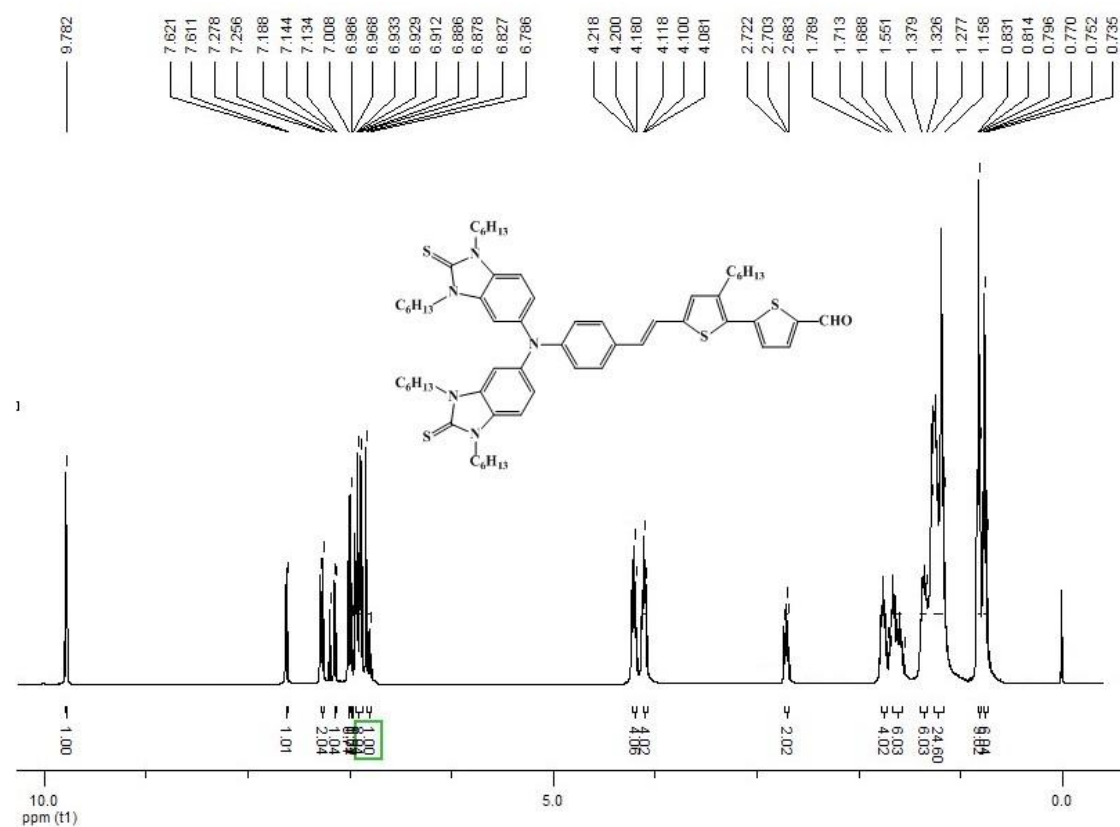
¹H NMR of 6



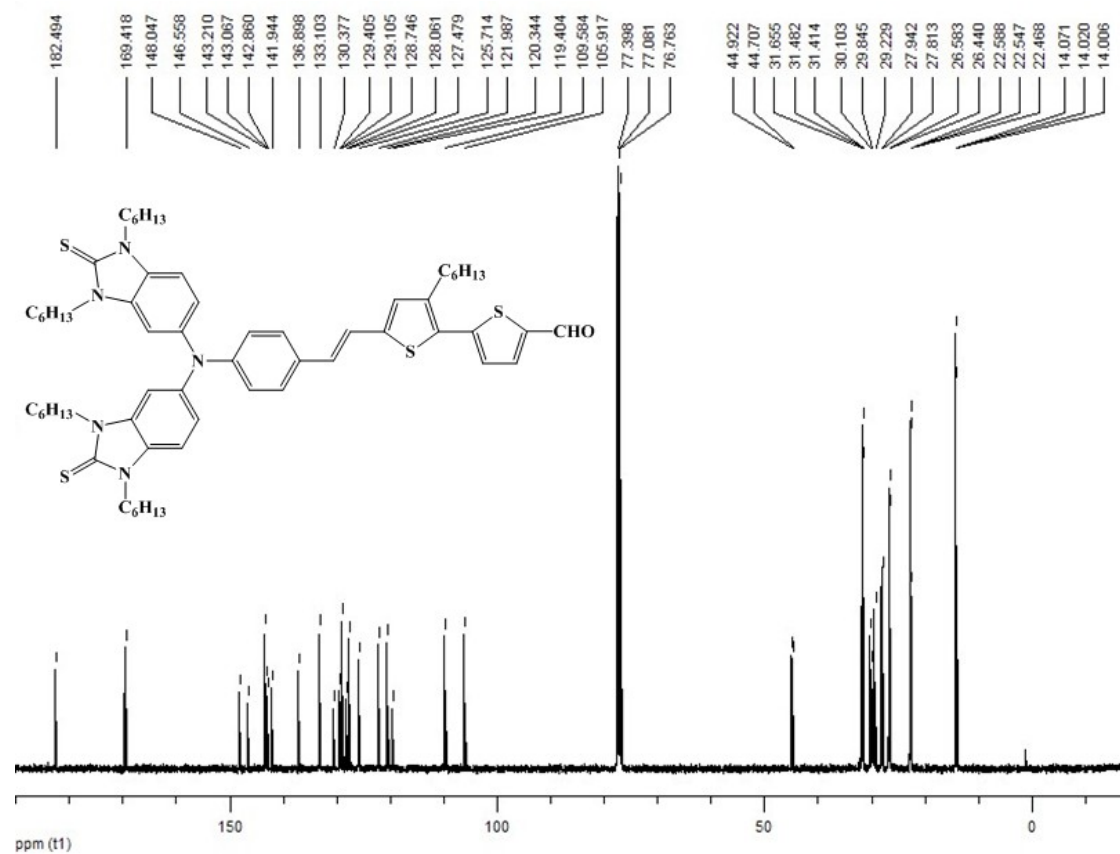
¹³C NMR of 6



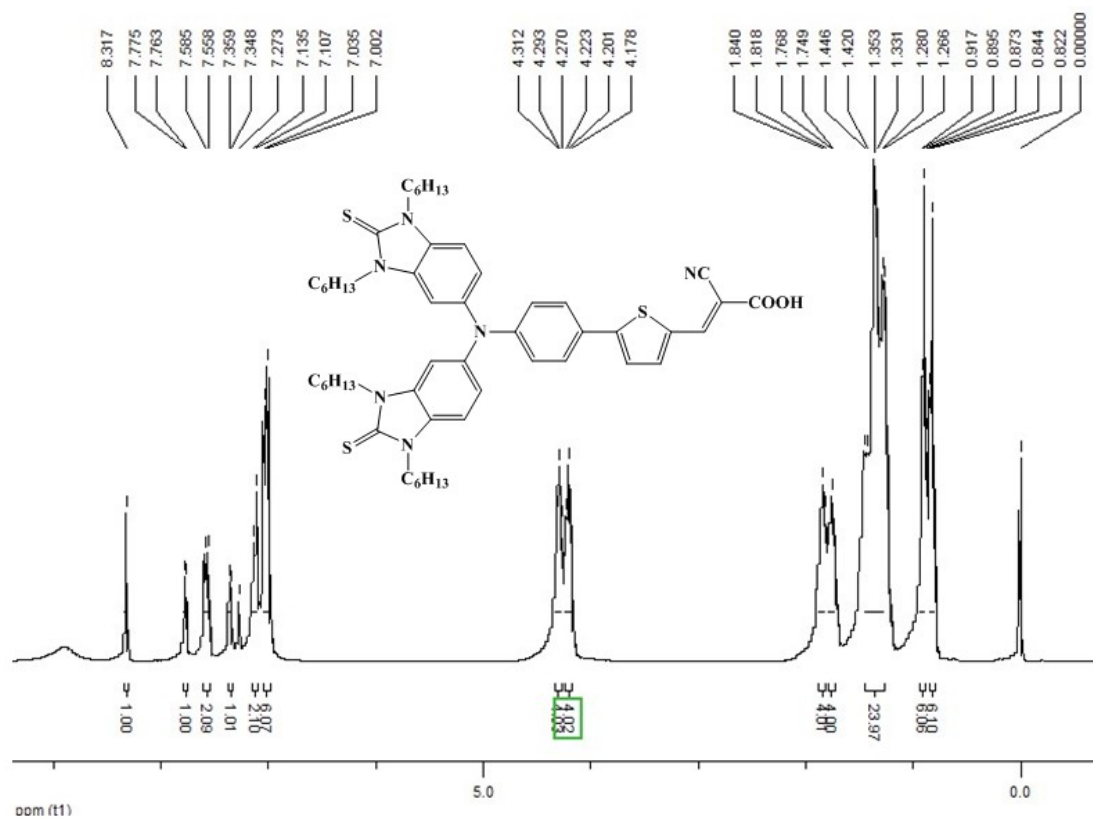
¹H NMR of 7



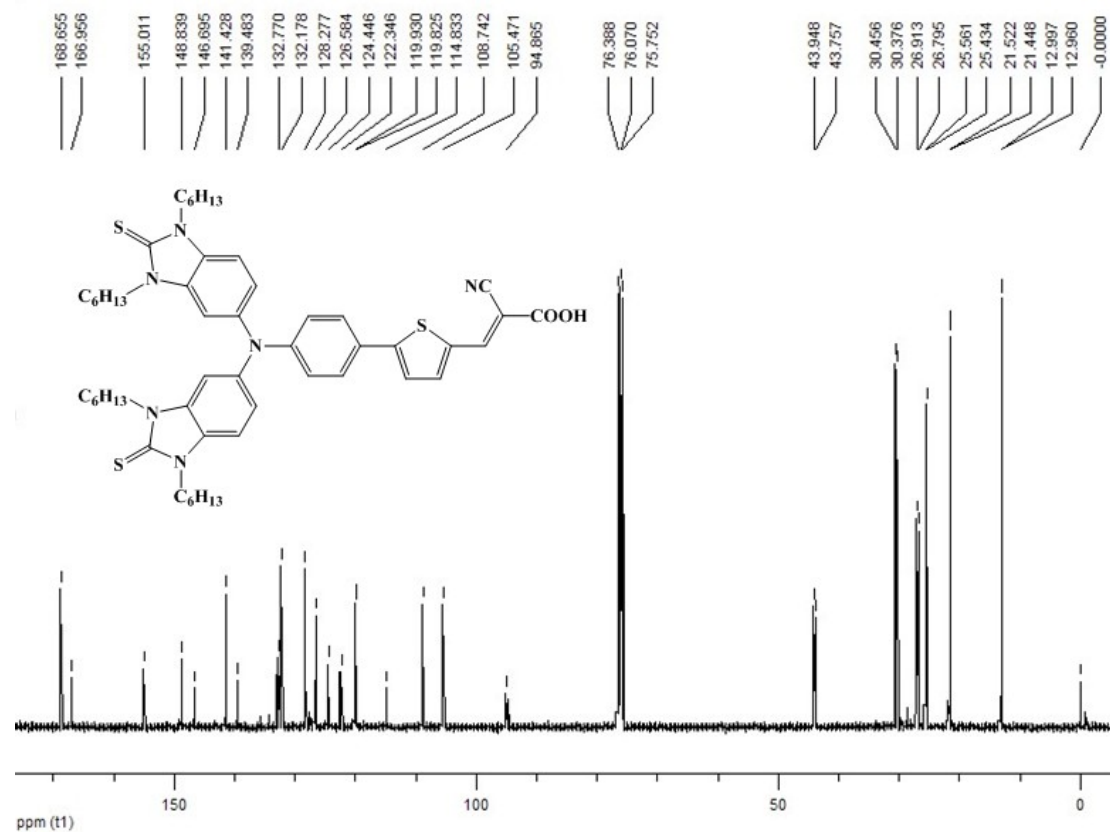
¹³C NMR of 7



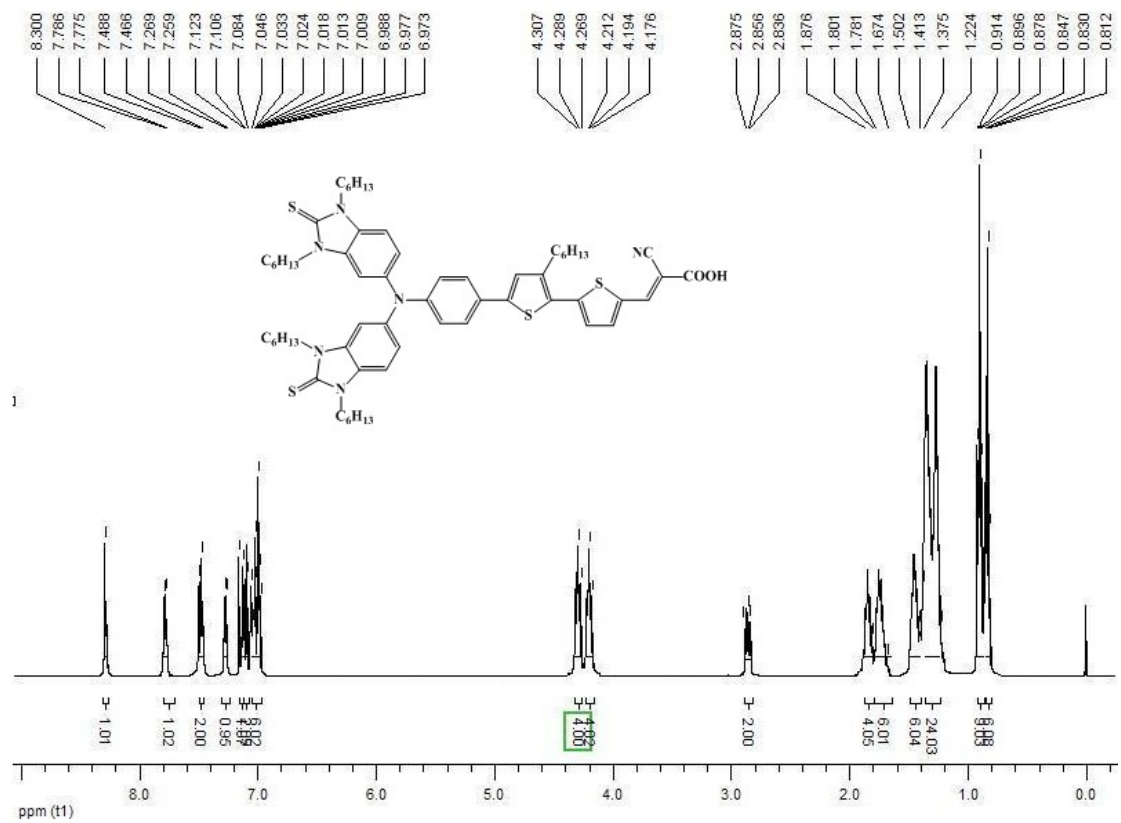
¹H NMR of AZ260



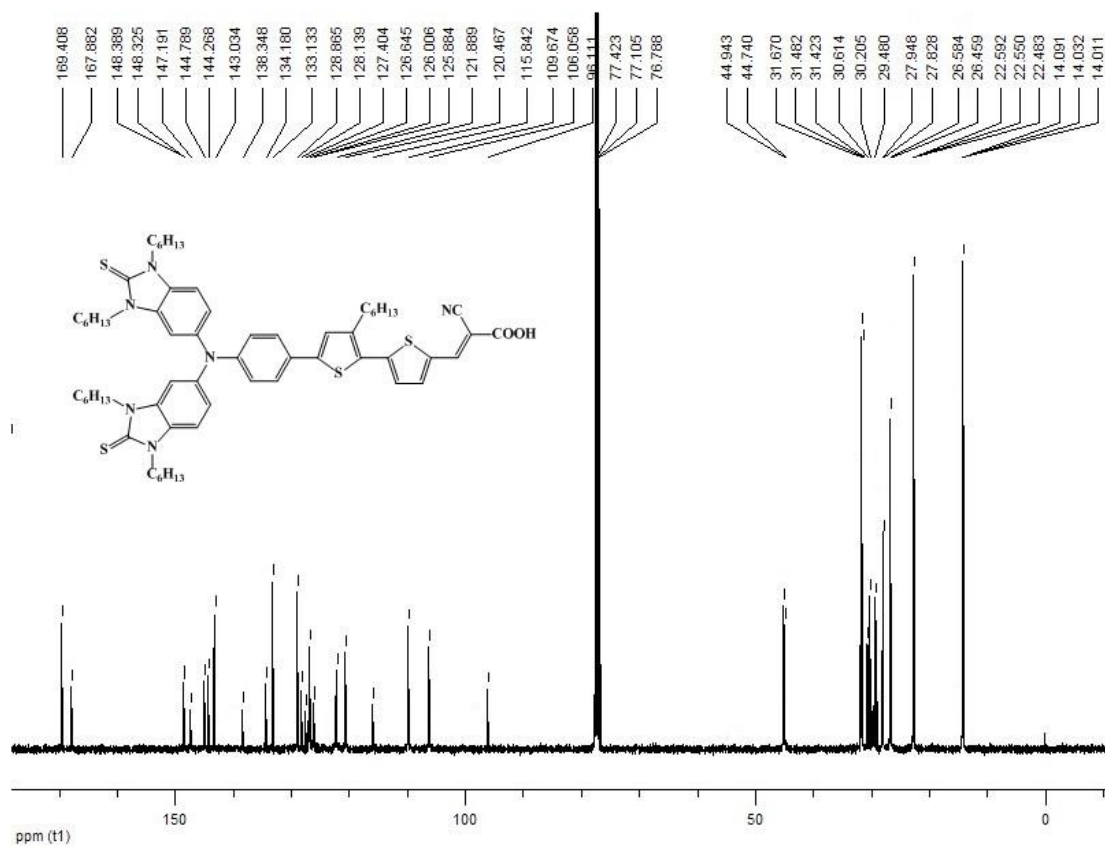
¹³C NMR of AZ260



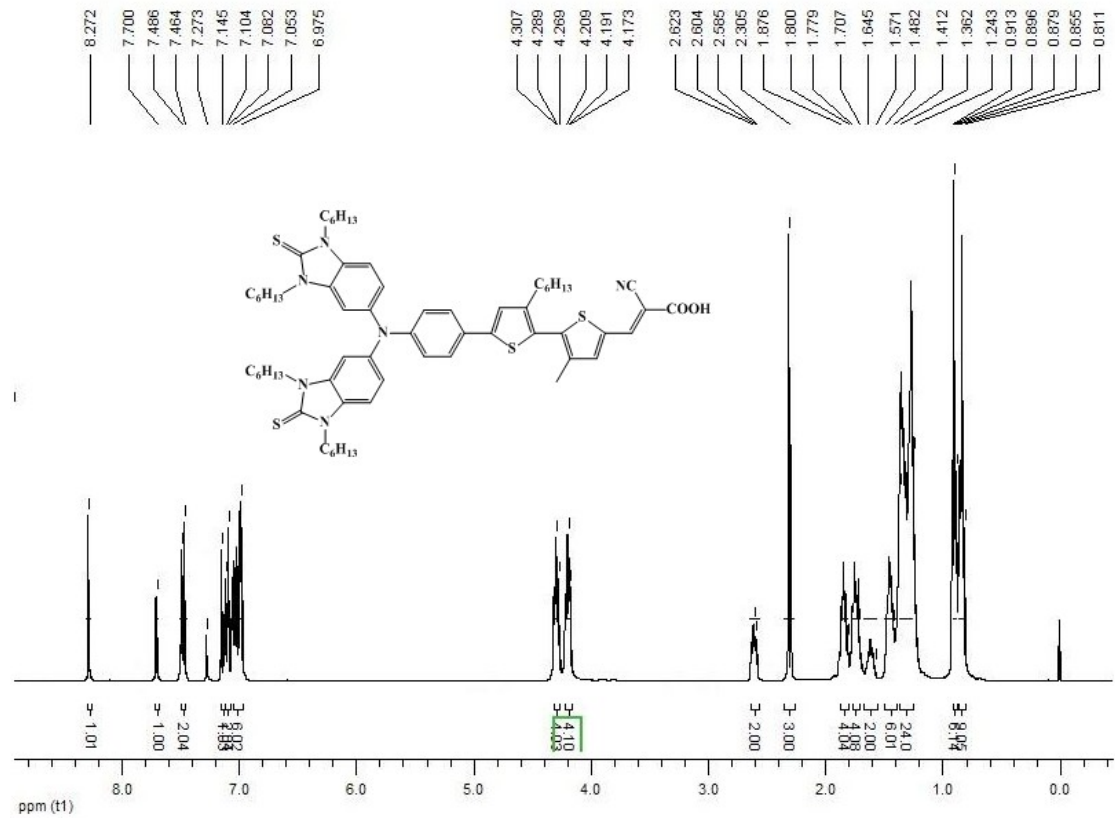
¹H NMR of AZ261



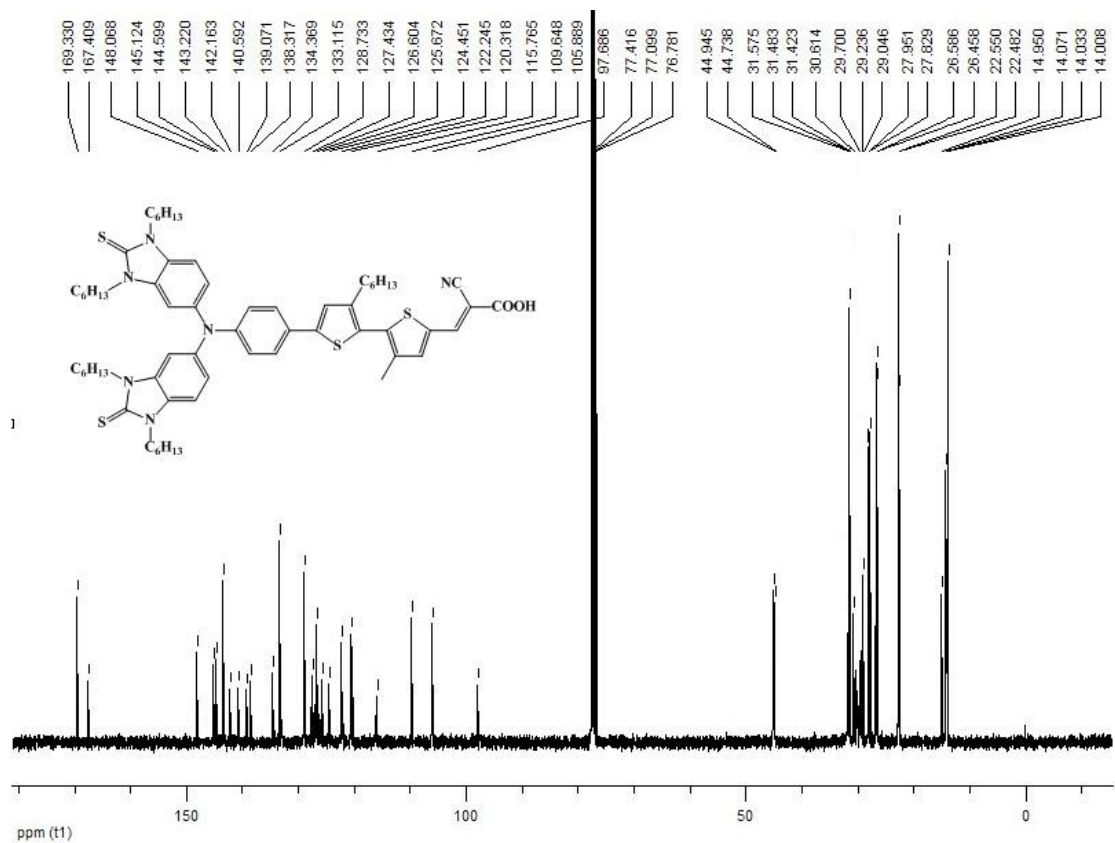
¹³C NMR of AZ261



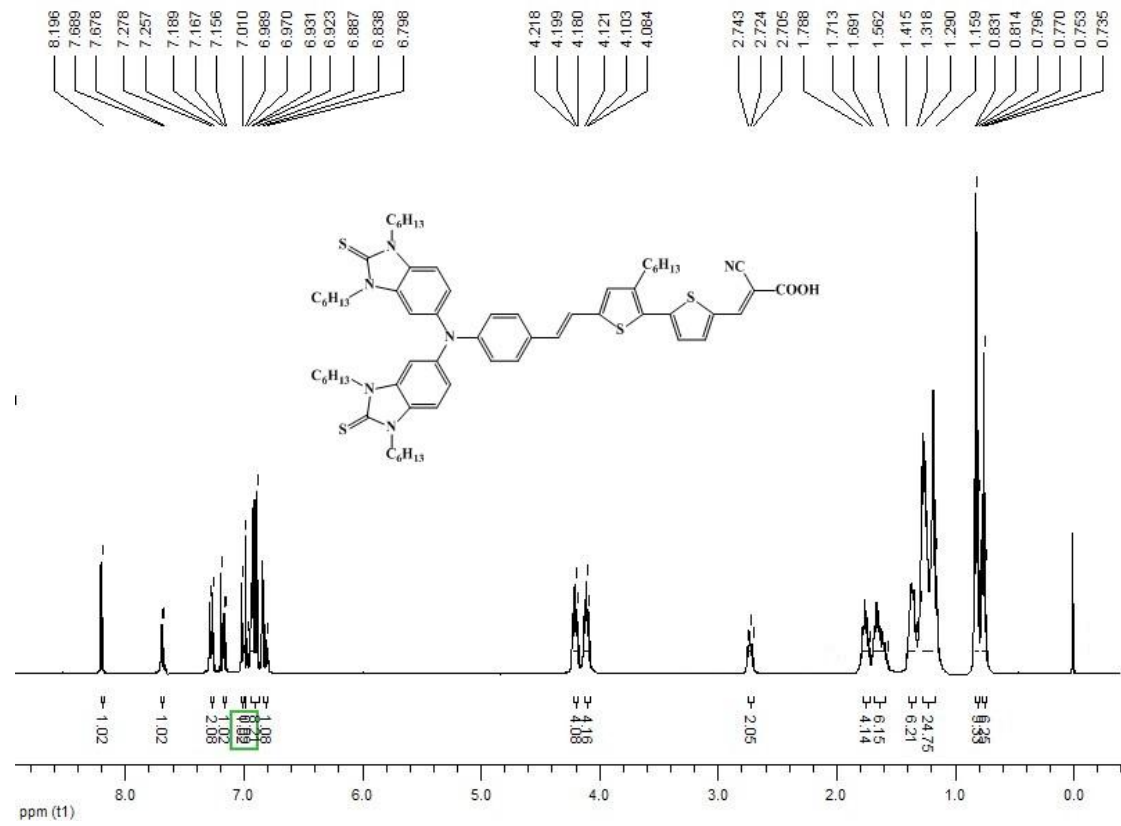
¹H NMR of AZ262



¹³C NMR of AZ262



¹H NMR of AZ263



¹³C NMR of AZ263

