

Experimental procedures and Characterization data

7-bromoindoline-2,3-dione (1): Chloral hydrate (2.9 g, 18 mmol, 1.1eq) and Na₂SO₄ (7.4 g, 52 mmol, 3eq) were dissolved in water (40 ml) in a 250 ml three-neck flask and warmed to 35 °C. A warm solution of the appropriate commercial 2-bromoaniline (3.0 g, 17.4 mmol, 1eq) in 10 ml water, and an aqueous solution of concentrated HCl (2 ml, 37%) was added, a white precipitate of the amine sulfate was formed, followed by a warm solution of hydroxylamine hydrochloride (3.6 g, 52 mmol, 3 eq) in 60 ml water. The mixture was stirred and heated at 80-85 °C for 2 h and then allowed to cool to room temperature. Filtered the yellow cream product and washed it with water. Dry overnight afforded the intermediate isonitrosoacetanilide, Compound 1a. Sulfuric acid (50 ml) was heated in a 100 ml flask at 60 °C. The dry isonitrosoacetanilide was added in small portion with stirring over 30 mins so that temperature did not exceed 65 °C. The mixture was then heated to 80 °C for 15 mins, allowed to cool to room temperature. Cooled it on the ice and left to stand overnight. Filtering the orange-red precipitate, wash it with water. Dry overnight by the vacuum afforded **1** as orange-red powders (1.84 g, 46% yields over two steps). ¹H NMR (300 MHz, DMSO, ppm) δ 11.31 (br, 1H), 7.77 (dd, *J* = 8.5, 3.8 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.00 (td, *J* = 7.7, 3.7 Hz, 1H). ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.92-7.80 (br, 1H), 7.71 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.59 (d, 1H), 7.06 (td, *J* = 7.8, 2.8 Hz, 1H).

7-bromoindolin-2-one (2): 7-Bromoisatin (2.31 g, 10.2 mmol, 1eq) was suspended in 12 mL methanol, followed by 2.3 g of hydrazine hydrate (25.5 mmol, 35% hydrazine content, 2.5eq) added in one portion. The solution was reflux for one hour. The solution was then cooled in an ice bath and the yellow crystals were filtered. (2.0 g, 84% yields). 0.54g of sodium was completely dissolved in 13ml of fresh anhydrous ethanol, 2 g of the above hydrazone derivative was added in small portions, with shaking, at 60-70 °C. The solution was heated to reflux until the evolution of nitrogen gas has ceased. The brown solution was then carefully poured on ice and acidified to pH = 1 with 10% HCl solution. Filtered and dry overnight by the vacuum afforded **2** as yellow powders (1.4 g, 67% yields over two steps). ¹H NMR (300 MHz, DMSO,

ppm) δ 10.61 (s, 1H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.18 (d, $J = 7.3$ Hz, 1H), 6.86 (t, $J = 7.7$ Hz, 1H), 3.60 (s, 2H).

(E)-7,7'-dibromo-[3,3'-biindolinylidene]-2,2'-dione (**3**): 7-Bromooxindole (1.36 g, 6.4 mmol, 1eq) and 7-bromoisatin (1.45 g, 2.36 mmol, 1eq) were diluted in 42 ml Acetic acid. Then the conc HCl solution (0.25mL) was added to the mixture under argon. The reaction mixture was kept under stirring and reflux for 26 h. After cooling, the mixture was filtered. The solid was successively washed with water, ethanol and ethyl acetate. After drying under vacuum, Dry overnight by the vacuum afforded **3** as deep red powders (2.17 g, 85% yields). $^1\text{H NMR}$ (300 MHz, DMSO, ppm) δ 11.22 (s, 2H), 9.02 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 6.95 (t, $J = 8.1$ Hz, 2H). $^{13}\text{C NMR}$ not available because of solubility issues.

(E)-7,7'-dibromo-1,1'-dihexyl-[3,3'-biindolinylidene]-2,2'-dione (**4**): Under an argon atmosphere, the fresh dry potassium carbonate (0.08 g, 0.63 mmol, 2.4eq) were dissolved in 5 ml of anhydrous DMF, followed by adding 7,7-bromoisindigo (0.11 g, 0.26 mmol, 1eq). The reaction mixture was stirred for about 20 min at 90 °C. Then 1-bromohexane (0.1 g, 0.63 mmol, 2.4eq) was injected, and then the mixture was stirred for 2 h at 100 °C. Remove the solvent. After the reaction, the cooled solution was extracted with ethyl acetate. The organic phase was combined and washed with brine and water, and then dried with anhydrous Na_2SO_4 . After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:3). Dry overnight by the vacuum afforded **4** as deep red powder (0.15 g, 86%-90% yields). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm) δ 9.02 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 7.5$ Hz, 2H), 6.88 (t, $J = 9.0$ Hz, 2H), 4.18 (t, $J = 7.6$ Hz, 4H), 1.77-1.64 (m, 4H), 1.42-1.26 (m, 12H), 0.88 (t, 6H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm) δ 167.92, 141.82, 138.50, 133.24, 128.61, 124.87, 123.16, 101.80, 41.73, 31.51, 29.47, 26.34, 22.59, 14.04. **HRMS (ESI)** calculated for $\text{C}_{28}\text{H}_{32}\text{Br}_2\text{N}_2\text{O}_2$: 586.0831; Found: 586.0829.

7-bromo-1-hexylindoline-2,3-dione (**5**): The oven dry flask, compound **1** (0.92 g, 4.10 mmol, 1eq) and fresh dried K_2CO_3 (0.68 g, 4.90 mmol, 1.2eq) were dissolved in 15 ml of anhydrous dimethylformamide. The mixture was heated for 30 mins to slight reflux and 0.70 ml (4.90

mmol, 1.2eq) of 1-bromohexane was added via syringe. Then increase the temperature to 90 °C. Stirring and heating was continued overnight. Remove the solvent. Ethyl acetate was added and the organic layer was wash with water 3 times. The organic phase was dried over anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:2) afforded **5** as orange-red oil. (77% yields). ¹H NMR (CDCl₃, 300 MHz, ppm) δ 7.70 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.58 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.98 (t, 1H), 4.16 – 4.09 (t, 2H), 1.73-1.62 (m, 2H), 1.46-1.27 (m, 6H), 0.90 (t, 3H).

1-hexyl-7-phenylindoline-2,3-dione (6): Adding compound **5** (330 mg, 1.06 mmol, 1eq) and phenylboronic acid (160 mg, 1.28 mmol, 1.2eq) into flask. Adding dried KF (290 mg, 5.0 mmol, 4.8eq) into the flask and remove the O₂ by argon for 20 mins. Adding 6 ml MeOH via syringe. Using 4% of the catalysist Pd(OAc)₂. Increase the temperature to 100 °C and react overnight. The reaction was finished checked by TLC. Remove the solvent. Extracted with EA and wash with water for 3 times. The organic layers were dried over Na₂SO₄. Using hexane to remove the small impurity. Dry overnight by the vacuum afforded **6** as orange-red oil. (67% yields). ¹H NMR (CDCl₃, 300 MHz, ppm) δ 7.63 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.45 (m, 3H), 7.41 – 7.33 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 3.34 – 3.25 (t, 2H).

(E)-1,1'-dihexyl-7,7'-diphenyl-[3,3'-biindolinylidene]-2,2'-dione (7): The compound **4** (270 mg, 0.46 mmol), phenylboronic acid (223 mg, 1.82 mmol, 4eq), P(o-tyl)₃ (21 mg, 0.07 mmol) and K₃PO₄ (488 mg, 2.30 mmol, 5eq) were loaded under argon. Toluene (5 mL) and water (0.2 ml) was then added to flask. After stirred in rt for 0.5 h, Pd₂(dba)₃ (40 mg, 0.04 mmol) was added and then increase the temperature to 100 °C. Stirring and heating was continued overnight. Remove the solvent. After the reaction, the cooled solution was extracted with ethyl acetate. The organic phase was combined and washed with brine and water, and then dried with anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:1) afforded **7** as yellow-red solid. (220 mg, 82% yields). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 9.09 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.47-7.34 (m, 10H), 7.14 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 2H), 3.33 (t, 2H). ¹³C NMR

(CDCl₃, 100 MHz, ppm) δ 168.85, 141.22, 139.08, 135.83, 133.55, 129.61, 128.55, 128.04, 127.77, 124.98, 123.13, 121.44, 41.92, 31.31, 27.67, 26.09, 22.44, 13.99. **HRMS (ESI)** calculated for C₄₀H₄₂N₂O₂: 582.3246; Found: 582.3244.

(E)-1,1'-dihexyl-7,7'-di(thiophen-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (**8**): The compound **4** (180 mg, 0.30 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3-dioxolane (257 mg, 1.22 mmol, 4eq), P(o-tyl)₃ (14 mg, 0.05 mmol) and K₃PO₄ (324 mg, 1.53 mmol, 5eq) were loaded under argon. Toluene (6 mL) and water (0.2 ml) was then added to flask. After stirred in rt for 0.5 h, Pd₂(dba)₃ (30 mg, 0.03 mmol) was added and then increase the temperature to 100 °C. Stirring and heating was continued overnight. Remove the solvent. After the reaction, the cooled solution was extracted with ethyl acetate. The organic phase was combined and washed with brine and water, and then dried with anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:3) afforded **8** as yellow-red solid. (140 mg, 79% yields). **¹H NMR** (CDCl₃, 400 MHz, ppm) δ 9.04 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.33 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.17 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.03-7.00 (m, 2H), 6.98-6.97 (m, 2H), 6.94 (t, 2H), 3.37 (t, 4H). **¹³C NMR** (CDCl₃, 100 MHz, ppm) δ 168.69, 139.12, 137.16, 129.58, 128.19, 126.75, 126.22, 123.14, 121.22, 116.74, 42.11, 31.37, 28.26, 26.34, 22.48, 14.00. **HRMS (ESI)** calculated for C₃₆H₃₈N₂O₂S₂: 594.2375; Found: 584.2379.

(E)-1,1'-dihexyl-7,7'-bis (5-hexylthiophen-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (**9**): The compound **4** (110 mg, 0.18 mmol), 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3-dioxolane (0.22 mg, 0.75 mmol, 4eq), P(o-tyl)₃ (8 mg, 0.03 mmol) and K₃PO₄ (200 mg, 0.93 mmol, 5eq) were loaded under argon. Toluene (6 mL) and water (0.2 ml) was then added to flask. After stirred in rt for 0.5 h, Pd₂(dba)₃ (16 mg, 0.02 mmol) was added and then increase the temperature to 100 °C. Stirring and heating was continued overnight. Remove the solvent. After the reaction, the cooled solution was extracted with ethyl acetate. The organic phase was combined and washed with brine and water, and then dried with anhydrous Na₂SO₄. After removing the solvent by rotational evaporation, the residue was chromatographed on silica gel (chloroform/hexane = 1:4) afforded **9** as yellow-red solid. (93 mg, 68% yields). **¹H NMR**

(CDCl₃, 400 MHz, ppm) δ 9.01 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.17 (dd, $J = 7.7, 1.3$ Hz, 2H), 6.92 (t, $J = 7.9$ Hz, 2H), 6.75 (d, $J = 3.4$ Hz, 2H), 6.66 (dt, $J = 3.4, 0.9$ Hz, 2H), 3.43 (t, 4H), 2.77 (t, $J = 7.6$ Hz, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 168.71, 146.98, 137.19, 136.25, 133.40, 129.36, 127.82, 123.60, 123.12, 121.15, 117.36, 42.12, 31.82, 31.57, 31.43, 30.11, 28.82, 28.31, 26.44, 22.60, 22.55, 14.10, 14.02. **HRMS (ESI)** calculated for C₄₈H₆₂N₂O₂S₂: 762.4253; Found: 762.4261.

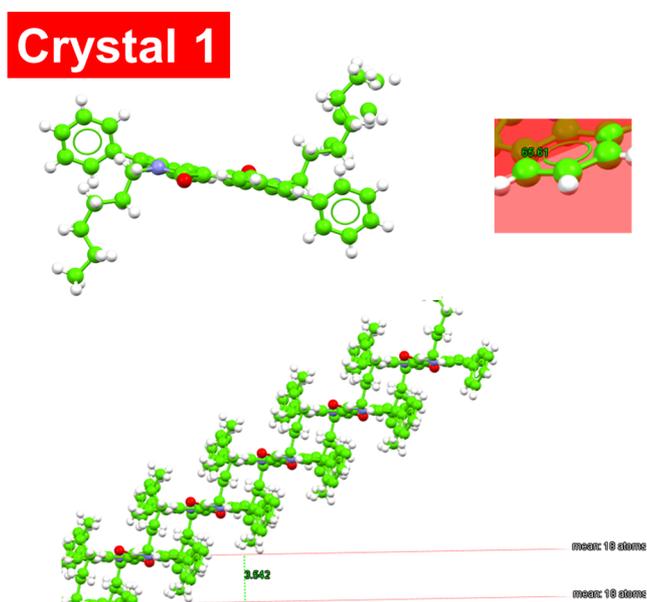


Figure S1. The crystal structure of 7Ph7Ph.

Crystal 2

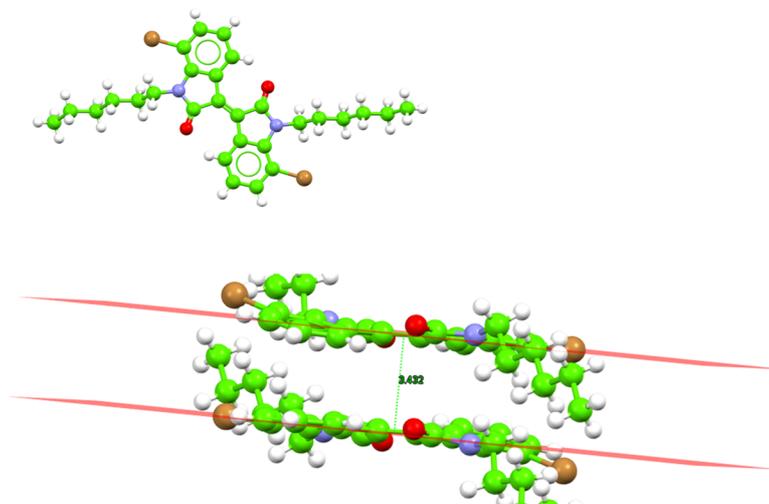


Figure S2. The crystal structure of 7Br7'Br.

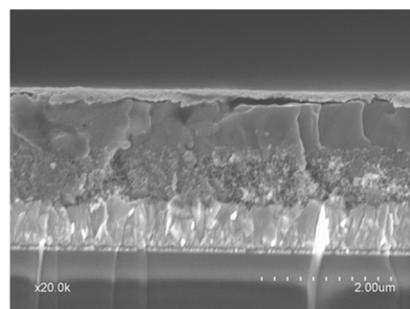
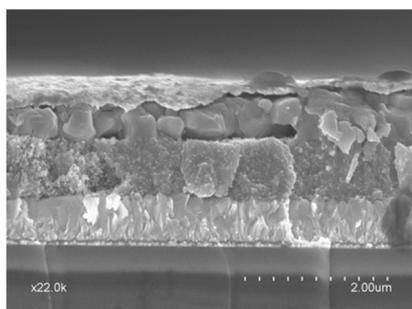
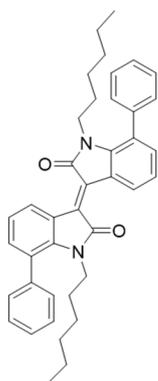


Figure S3. SEM image of perovskite solar cell based on 7Ph7'Ph.

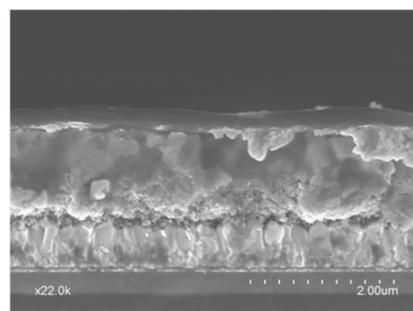
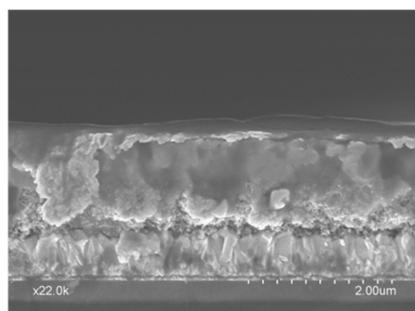
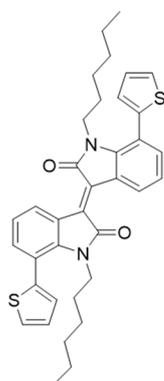


Figure S4. SEM image of perovskite solar cell based on 7Th7'Th.

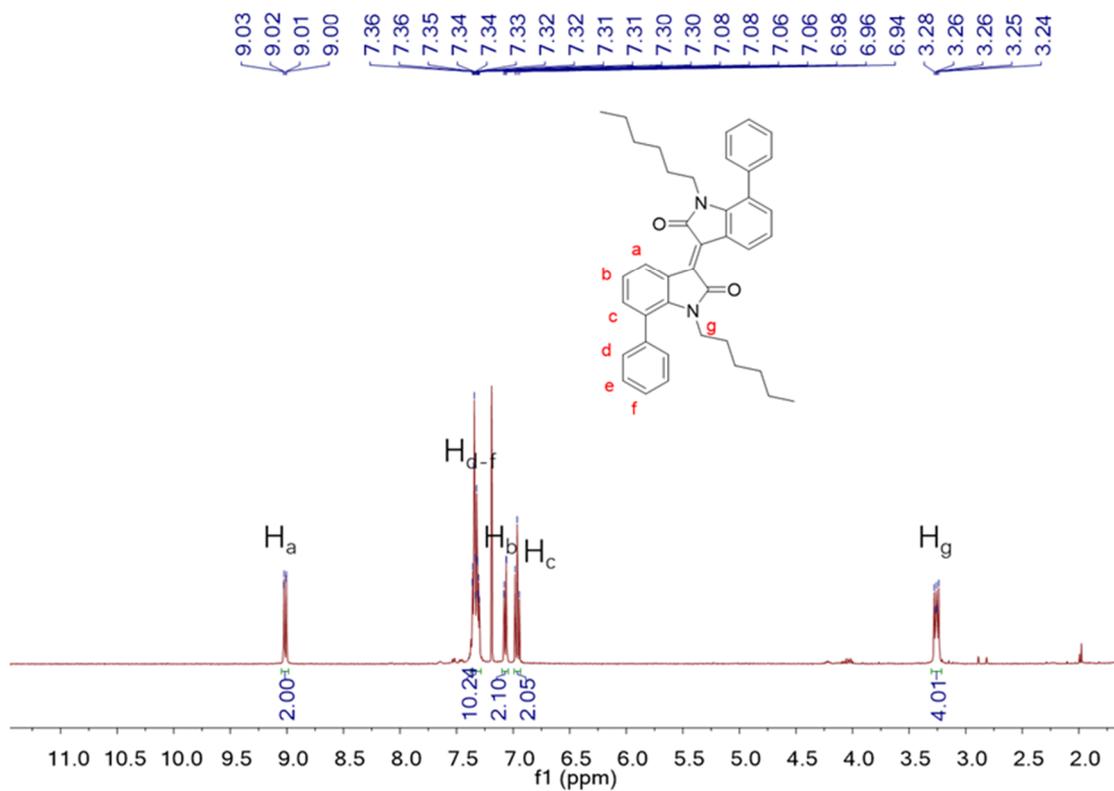


Figure S5. ^1H NMR spectra of compound 7.

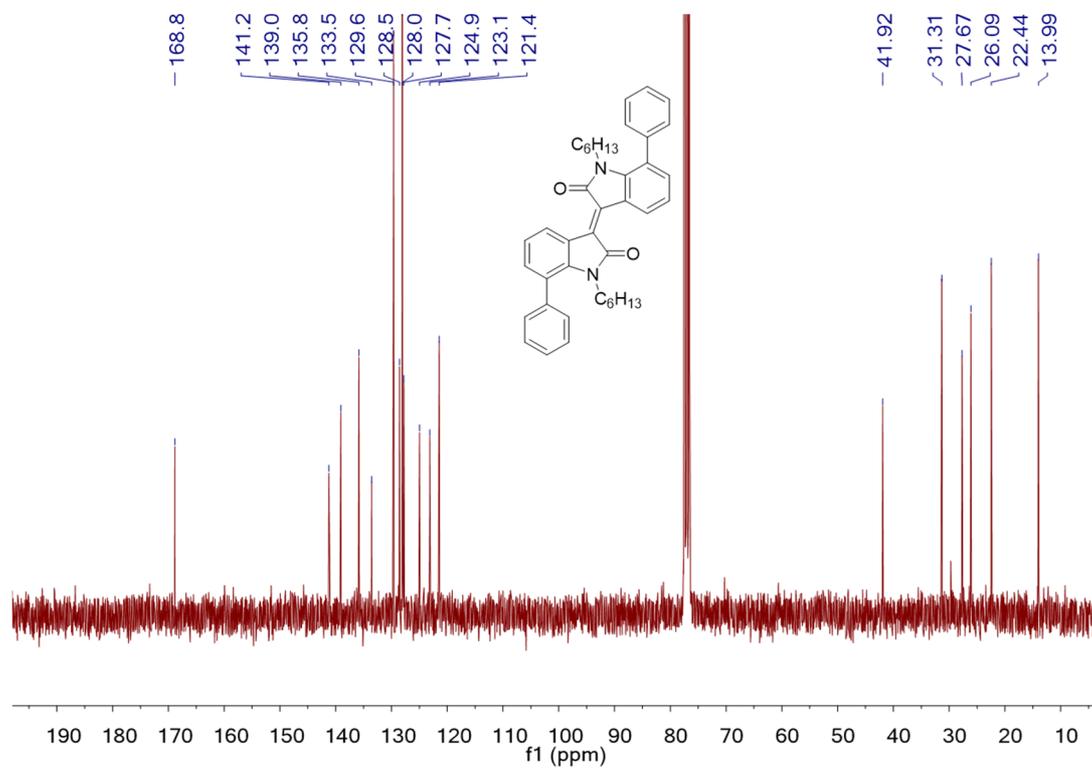


Figure S6. ^{13}C NMR spectra of compound 7.

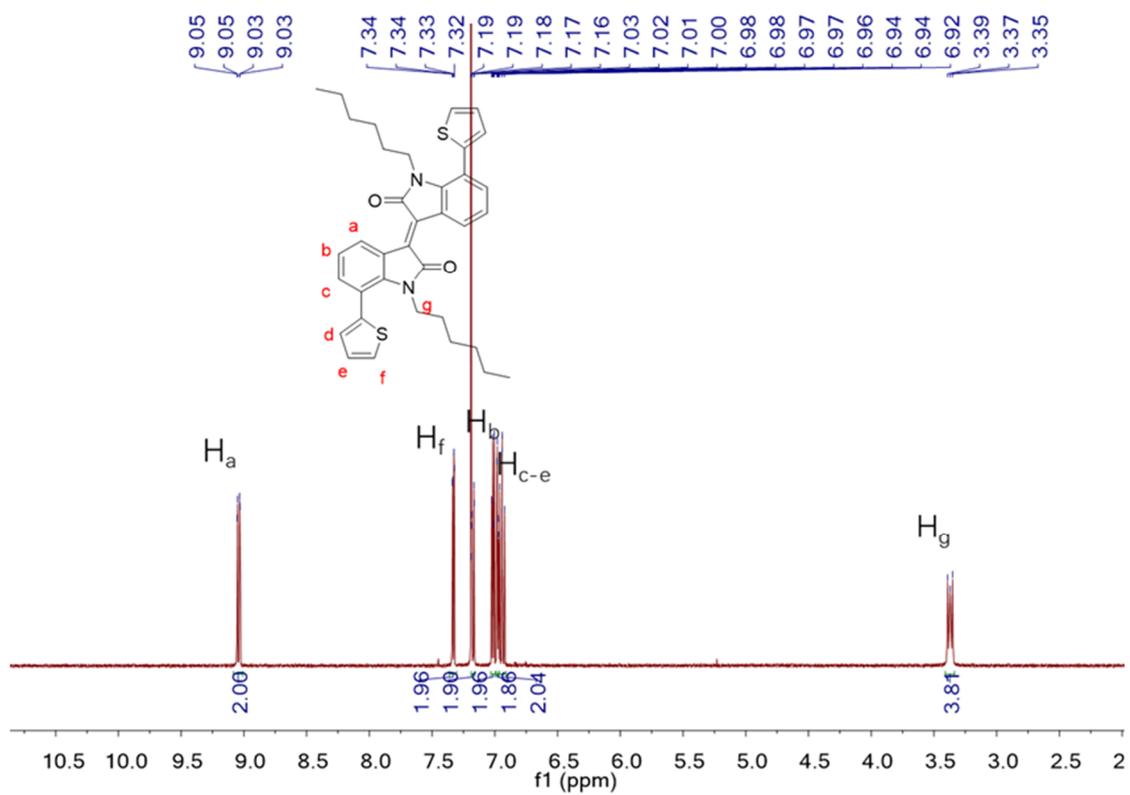


Figure S7. ^1H NMR spectra of compound 8.

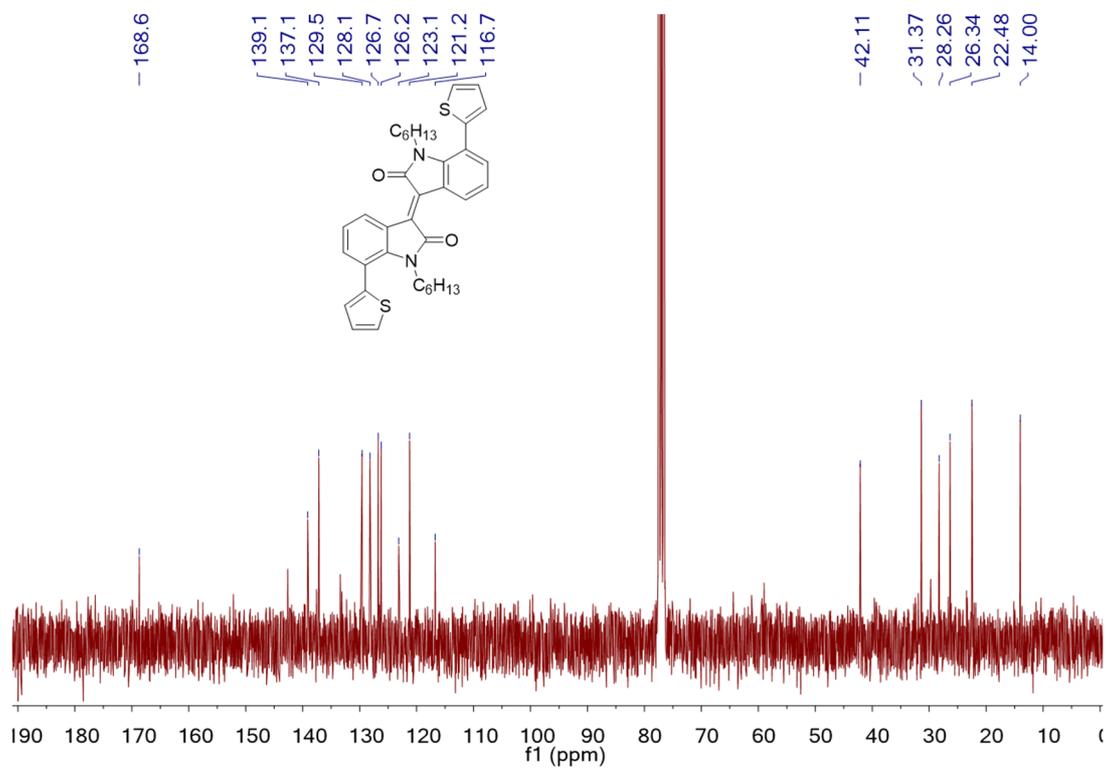


Figure S8. ^{13}C NMR spectra of compound 8.

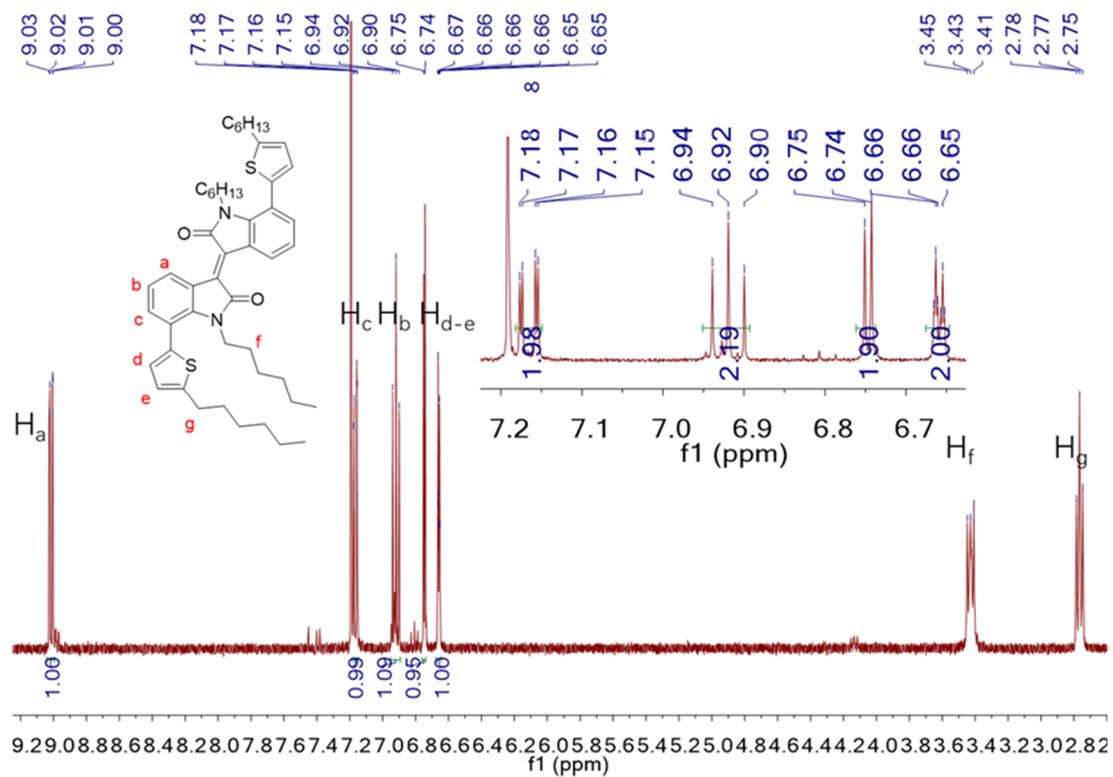


Figure S9. ^1H NMR spectra of compound 9.

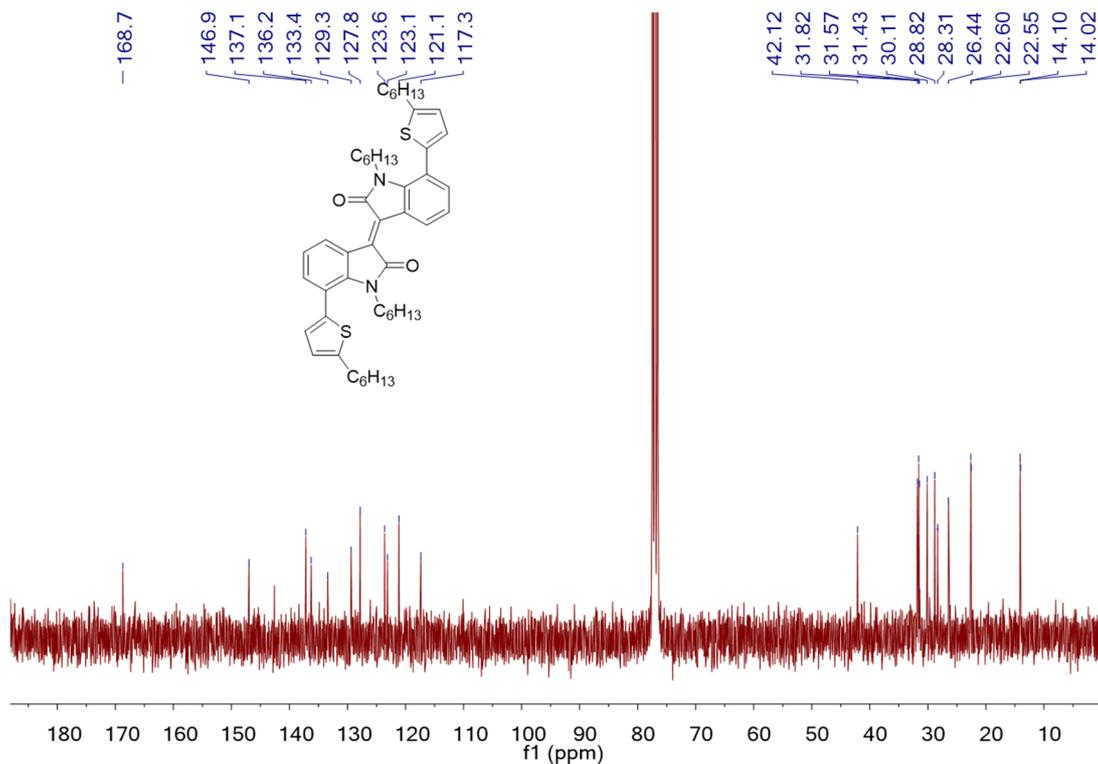


Figure S10. ^{13}C NMR spectra of compound 9.