

Electronic Supplementary Information

Organic dyes with intense light absorption especially suitable for application in thin-layer dye-sensitized solar cells

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1. Computational Details

Density Functional Theory (DFT) calculations were performed with the Gaussian09 program package,^[1] replacing the alkyl groups originally present on compounds **TTZ3-5** with methyls to reduce computational effort. Geometry optimization was carried out *in vacuo* using the B3LYP functional^[2] and the standard 6-31G* basis set for all atoms. The absorption maximum ($\lambda_{\text{max}}^{\text{a}}$), vertical excitation energy (E_{exc}) and oscillator strength (f) in THF solution were calculated on the optimized structures via time-dependent DFT (TD-DFT) at the CAM-B3LYP/6-31G*^[3] level. Solvent effects have been included by using the polarizable continuum model (PCM).^[4]

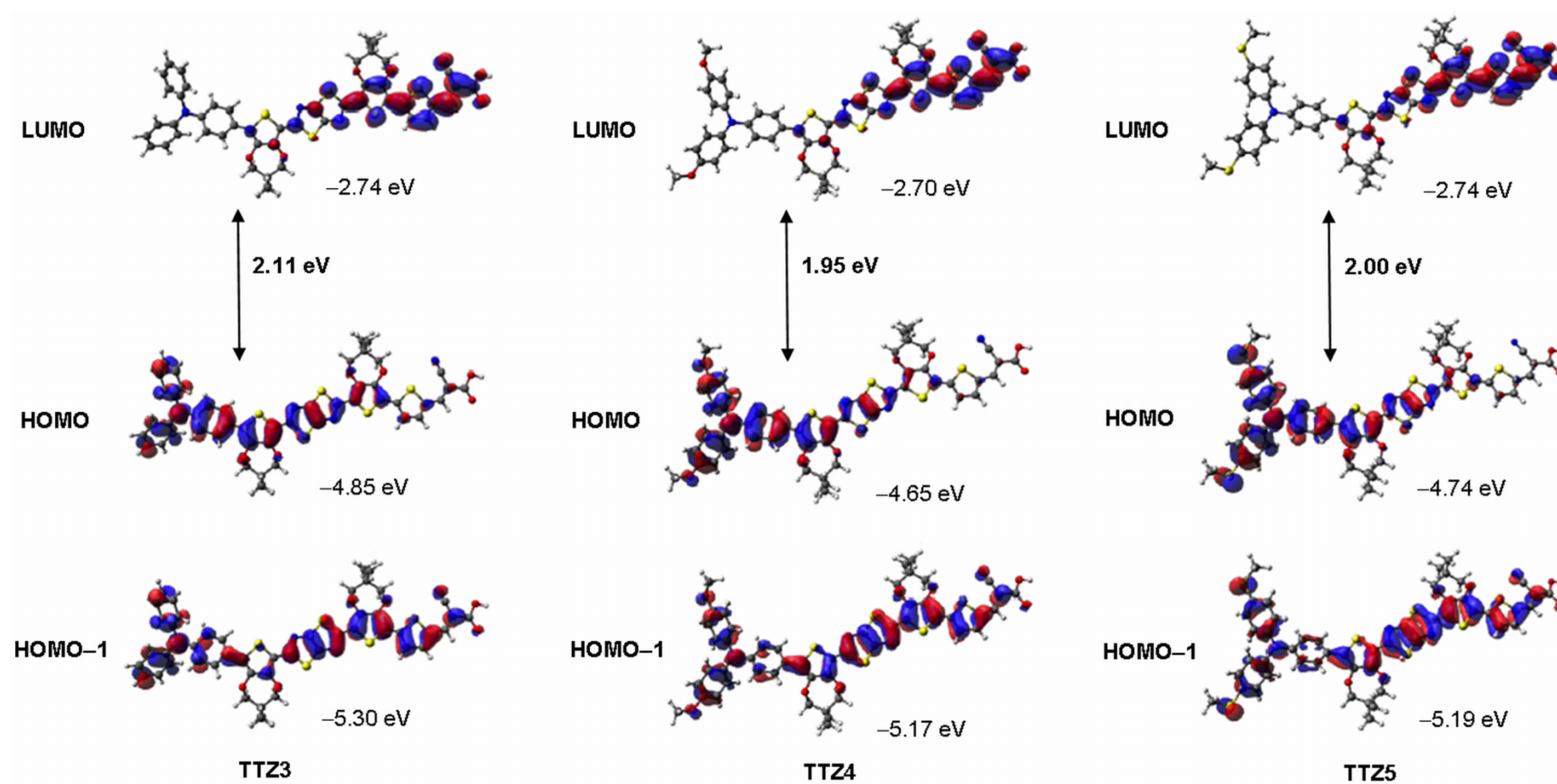


Figure S1. Isodensity surface plots and computed energies (*in vacuo*) for the frontier molecular orbitals of compounds **TTZ3-5** at the B3LYP/6-31G* level.

Table S1. CAMB3LYP/6-31G* absorption maxima (λ_{max}^a), oscillator strengths (f), vertical excitation energies (E_{exc}) and main electronic transitions for dyes **TTZ1** (taken as a reference) and **TTZ3-5** in THF.

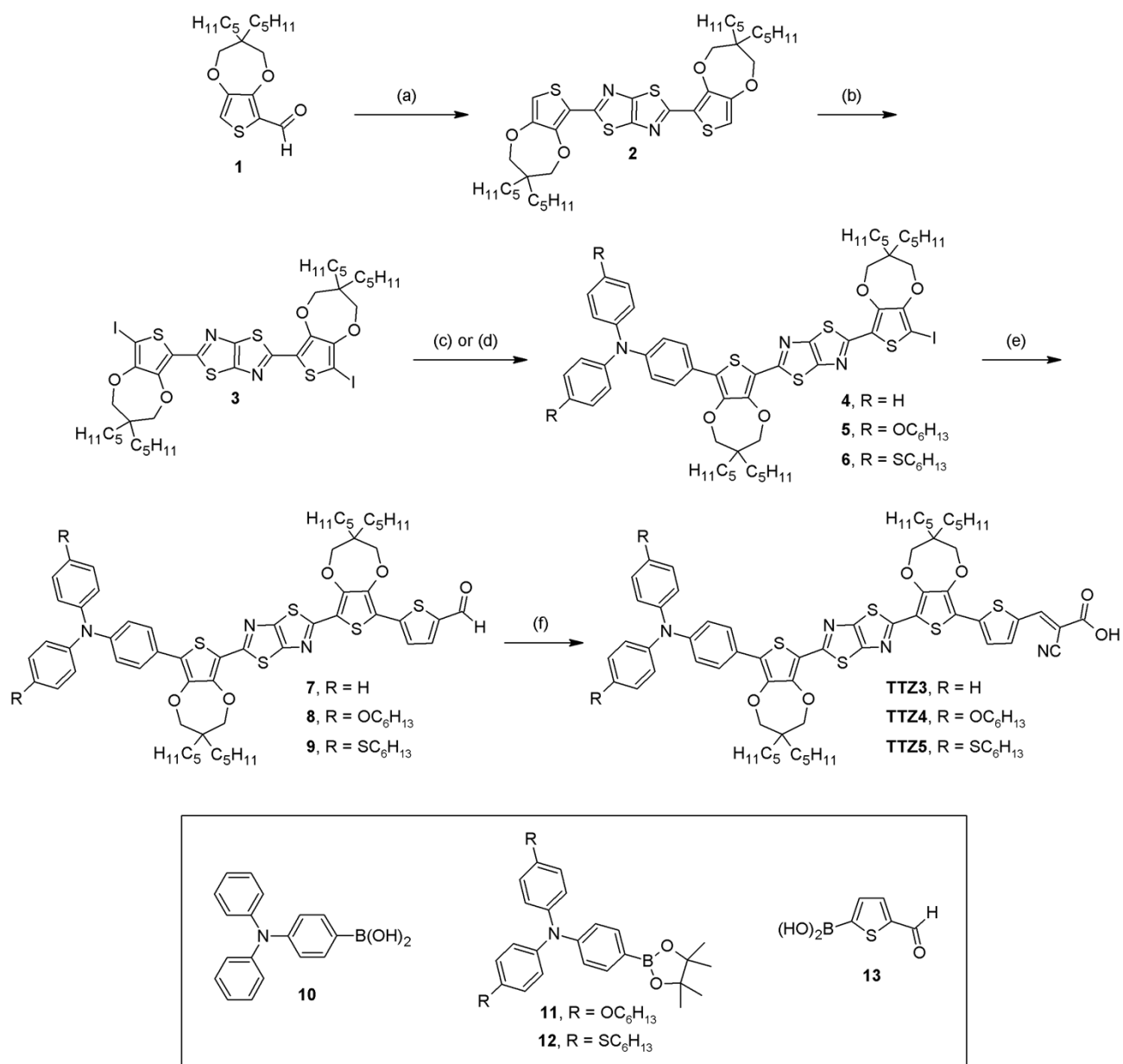
Compound	λ_{max}^a [nm]	f	E_{exc} [eV]	Main transitions (%)	
TTZ1 ^[a]	482	2.45	2.57	H-1 $\rightarrow$ L	51.2
				H $\rightarrow$ L	29.2
TTZ3	503	2.61	2.46	H $\rightarrow$ L	42.0
				H-1 $\rightarrow$ L	38.2
TTZ4	507	2.67	2.45	H-1 $\rightarrow$ L	47.4
				H $\rightarrow$ L	30.5
TTZ5	504	2.66	2.46	H-1 $\rightarrow$ L	48.7
				H $\rightarrow$ L	29.3

[a] Values taken from ref. [5]

2. General Synthetic Remarks

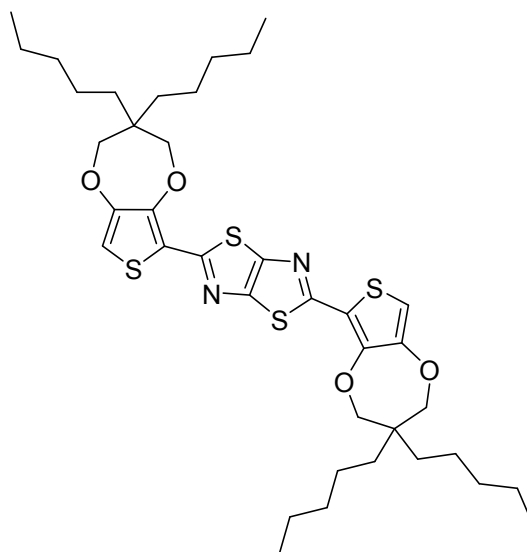
All air-sensitive reactions were performed under inert atmosphere in a flame- or oven-dried apparatus using Schlenk techniques.^[6] Microwave-assisted transformations were carried out using a *CEM Discover Bench-Mate* reactor at fixed temperature and variable power. Methanol (MeOH) was distilled over metallic magnesium in the presence of a catalytic amount of iodine, while toluene was dried on a resin exchange Solvent Purification System (*MBraun*). 3,3-Dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-carbaldehyde (**1**) was prepared following a reported procedure.^[7] 4-(Hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**10**)^[8] and 4-(hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**11**)^[9,10] were prepared according to published procedures or modifications thereof. All other chemicals employed were commercially available and, unless specified, used as received. Petroleum ether was the 40-60 °C boiling fraction. Thin layer chromatography was carried out on aluminum-supported *Merck* 60 F254 plates; detection was carried out using UV light and permanganate or molybdophosphoric acid solutions followed by heating. Flash column chromatography^[11] was performed using *Merck* Kieselgel 60 (300-400 mesh) as the stationary phase. ¹H-NMR spectra were recorded at 300 or 400 MHz, and ¹³C-NMR spectra were recorded at 75.5 or 100.6 MHz, respectively, on *Bruker* Avance or *Varian* Mercury series instruments. Chemical shifts were referenced to the residual solvent peak (CHCl₃, δ 7.26 ppm for ¹H-NMR and δ 77.16 ppm for ¹³C-NMR; C₆D₆ δ 7.16 ppm for ¹H-NMR and δ 128.06 ppm for ¹³C-NMR; THF-*d*₈ δ 1.72 and 3.58 ppm for ¹H-NMR, δ 67.21 and 25.31 ppm for ¹³C-NMR). FT-IR spectra were recorded with a *Perkin-Elmer Spectrum BX* instrument in the range 4000–400 cm⁻¹ with a 2 cm⁻¹ resolution. ESI-MS spectra were obtained by direct injection of the sample solution using a *Thermo Scientific* LCQ-FLEET instrument and are reported in the form *m/z* (intensity relative to base = 100). UV-Vis spectra were recorded with a *Varian Cary* 400 spectrometer, and fluorescence spectra were recorded with a *Varian Eclipse* instrument, irradiating the sample at the wavelength corresponding to maximum absorption in the UV spectrum. Elemental analyses were determined using a CHN-S Flash E1112 *ThermoFinnigan* Elemental Analyzer; the results were found to be in good agreement with the calculated values. Melting points are uncorrected.

3. Synthetic Scheme and Procedures



Scheme S1. Reagents and conditions: (a) dithiooxamide (0.5 eq.), *n*-butanol, MW, 120°C, 2.5 h then chloranil (0.25 eq.), THF, reflux, 10 mins, 42%; (b) *N*-iodosuccinimide (2.5 eq.), CHCl₃ / AcOH 1:1, rt, 16 h, 93%; (c) **10** or **11** (1.0 eq.), Pd(PPh₃)₄ (10 mol%), Na₂CO₃ (5.0 eq.), toluene, 100°C, 16 h, 18-29%; (d) **12** (1.0 eq.), [Pd(dppf)Cl₂] (15 mol%), KF (5.0 eq.), toluene / EtOH, 78°C, 7 h, 18%; (e) **13** (1.5 eq.), [Pd(dppf)Cl₂]·CH₂Cl₂ (5 mol%), KF (6.0 eq.), toluene / MeOH, MW, 70°C, 30 mins, 57-74%; (f) cyanoacetic acid (10.0 eq.), NH₄OAc (4.0 eq.), toluene / AcOH, 110°C, 6 h, 84-97%;

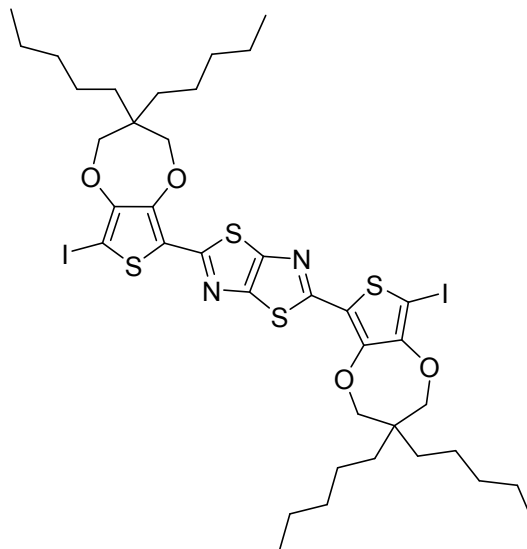
Synthesis of 2,5-bis(3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazole (2)



Dithiooxamide (106 mg, 0.88 mmol), aldehyde **1** (570 mg, 1.76 mmol.) and *n*-butanol (1.5 mL) were introduced in a microwave vial equipped with a magnetic stirrer. The resulting mixture was heated under microwave irradiation at 120°C for 2.5 h. After cooling to room temperature, THF (*ca.* 5 mL) and chloranil (108 mg, 0.44 mmol) were added to the reaction mixture, which was transferred to a flask, heated to reflux and stirred for 10 min. Removal of the solvent *in vacuo* afforded a dark thick oil, which was purified by flash column chromatography (SiO₂; petroleum ether / toluene 3:2) to give compound **2** as a light brown solid (269 mg, 0.37 mmol, 42% yield).

(**2**): mp = 207–208 °C. ¹H NMR (400 MHz, CDCl₃): δ = 6.56 (s, 2H), 4.10 (s, 4H), 3.92 (s, 4H), 1.42–1.46 (m, 8H), 1.28–1.36 (m, 24H), 0.91 (t, *J* = 6.8 Hz, 12H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 159.7, 150.2, 149.7, 148.6, 117.5, 107.0, 78.1, 77.9, 44.1, 32.8, 32.2, 22.7, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3100, 2930, 2860, 1500, 1039 cm⁻¹. ESI-MS: *m/z* = 731.32 [M]⁺.

Synthesis of 2,5-bis(8-iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazole (3)



Thiazolo[5,4-*d*]thiazole **2** (847 mg, 1.16 mmol) and *N*-iodosuccinimide (652 mg, 2.89 mmol) were dissolved into a mixture of CHCl₃ (20 mL) and glacial acetic acid (20 mL). The reaction mixture was stirred overnight in the dark, at room temperature. The solid obtained was filtered and washed with several portions (50 mL) of methanol and ethyl acetate to afford diiodide **3** as a yellow solid (1.06 g, 1.08 mmol, 93% yield). Compound **3** was used in the following steps without any further purification.

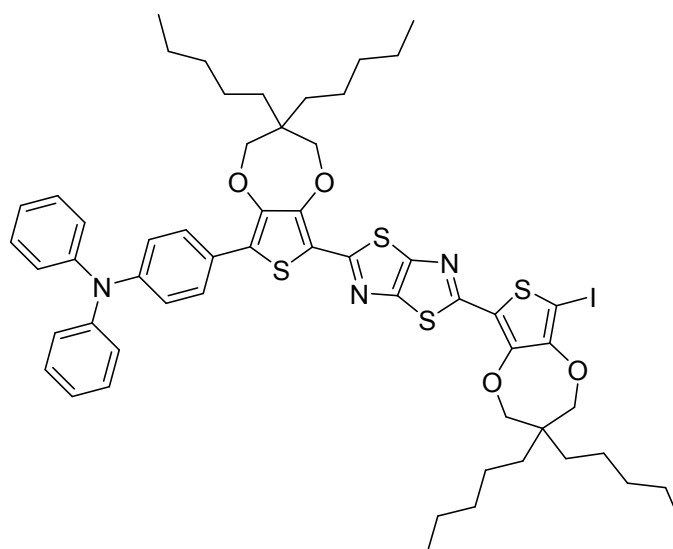
(**3**): mp = 228–230 °C. ¹H NMR (400 MHz, CDCl₃): δ = 4.09 (s, 4H), 3.98 (s, 4H), 1.42–1.46 (m, 8H), 1.28–1.36 (m, 24H), 0.91 (t, *J* = 6.7 Hz, 12H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 159.0, 152.0, 150.4, 146.8, 122.0, 78.3, 78.2, 61.0, 44.1, 32.7, 32.1, 22.7, 22.6, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2858, 1492, 1370, 1057 cm⁻¹. ESI-MS: *m/z* = 983.09 [M]⁺

General procedure for the synthesis of compounds 4 and 5

2,5-Bis(8-iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazole (**3**), (1.0 eq.) was dissolved in toluene together with [Pd(PPh₃)₄] (0.1 eq.). The appropriate boronic acid or ester (**10** or **11**) (1.0 eq.) was then added, followed by Na₂CO₃ (2.0 M aqueous solution, 5.0 eq.). The resulting mixture was heated at 100°C and stirred for 6h, then allowed to cool to room temperature and diluted with H₂O (150 mL) and CH₂Cl₂ (2 × 150 mL). The phases were separated and the aqueous layer washed with CH₂Cl₂ (2 × 50 mL). The combined organic layers were washed

with brine and dried with Na₂SO₄. After filtration and evaporation of the solvent, the crude product was purified by flash column chromatography.

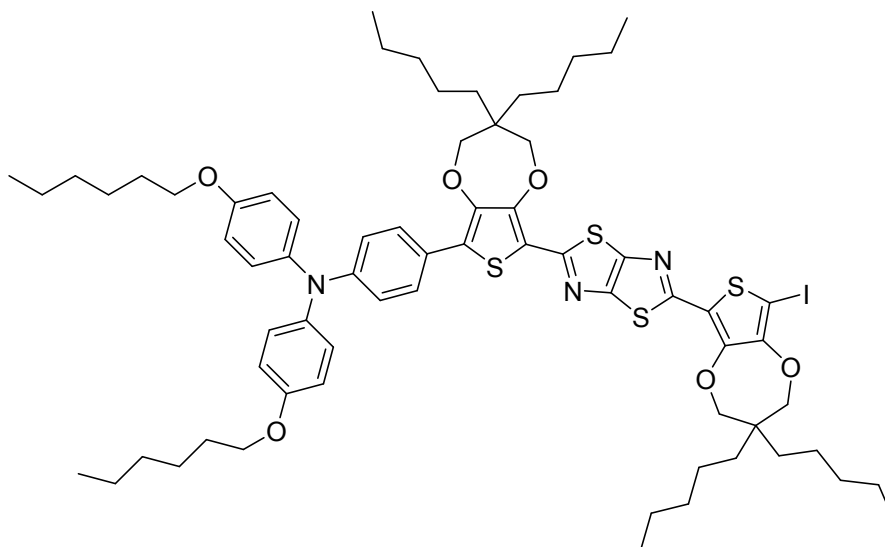
4-(8-(5-(8-Iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)-*N,N*-diphenylaniline
(4)



Diiodide **3** (800 mg, 0.81 mmol) was dissolved in toluene (30 mL) with [Pd(PPh₃)₄] (94 mg, 0.08 mmol) and reacted with 4-(diphenylamino)benzeneboronic acid (**10**, 235 mg, 0.81 mmol) and Na₂CO₃ (2.0 M aqueous solution, 2.0 mL, 4.07 mmol) at 100°C for 6h. After work-up, evaporation of the solvent gave a dark-red oil which was purified by flash column chromatography (SiO₂; petroleum ether /toluene 3:1 to 1:1) to give pure **4** (285 mg, 0.26 mmol, 29% yield) as an orange solid as well as starting material **3** (239 mg, 30% recovery).

(**4**): mp = 91–93 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 8.7 Hz, 2H), 7.27 (t, *J* = 8.2 Hz, 4H), 7.13 (d, *J* = 7.8 Hz, 4H) 7.03–7.07 (m, 4H), 4.15 (s, 2H), 4.09 (s, 2H), 4.01 (s, 2H), 3.98 (s, 2H), 1.44–1.48 (m, 8H), 1.28–1.36 (m, 24H), 0.91 (t, *J* = 6.7 Hz, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 159.8, 158.4, 152.0, 150.5, 150.2, 149.4, 147.5, 146.6, 145.1, 129.5, 127.7, 126.4, 125.0, 124.4, 123.5, 123.0, 122.1, 118.0, 113.7, 78.3, 78.2, 77.93, 77.89, 60.7, 44.11, 44.08, 32.8, 32.7, 32.3, 32.1, 29.8, 22.71, 22.69, 22.67, 22.6, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2927, 2857, 1590, 1491, 1057 cm⁻¹. ESI-MS: *m/z* = 1100.26 [M+1]⁺

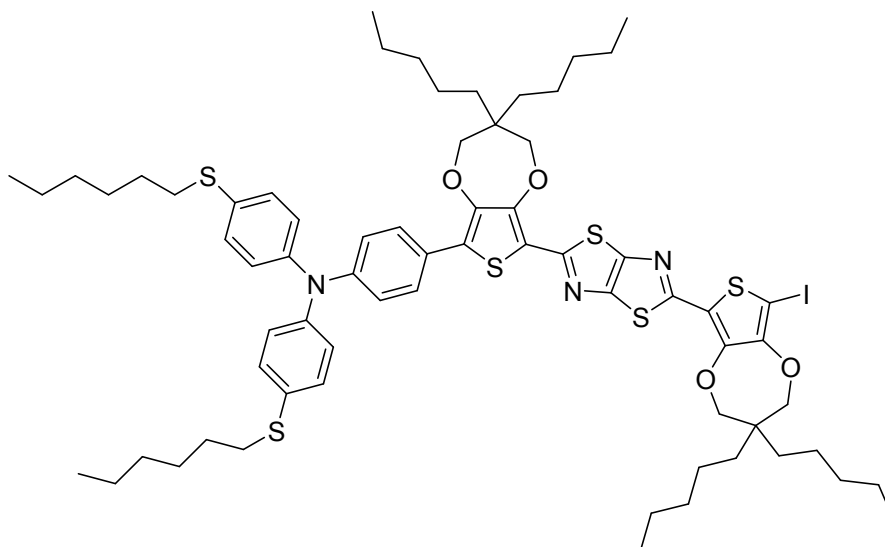
4-(Hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(8-(5-(8-iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)phenyl)aniline (5)



Diiodide **3** (750 mg, 0.76 mmol) was dissolved in toluene (30 mL) with $[\text{Pd}(\text{PPh}_3)_4]$ (176 mg, 0.15 mmol) and reacted with 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**11**, 436 mg, 0.76 mmol) and Na_2CO_3 (2.0 M aqueous solution, 1.9 mL, 3.82 mmol) at 100°C for 6h. After work-up, evaporation of the solvent gave a dark-red oil which was purified by flash column chromatography (SiO_2 , petroleum ether/toluene 2:1 to 1:1) to give pure **5** (174 mg, 0.13 mmol, 18% yield) as a sticky orange solid, as well as starting material **3** (223 mg, 30% recovery).

(**5**): ^1H NMR (400 MHz, C_6D_6): δ = 7.84 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.9 Hz, 6H), 6.80 (d, J = 8.9 Hz, 4H), 3.69 (s, 2H), 3.65 (t, J = 6.4 Hz, 4H), 3.61 (s, 2H), 3.54 (s, 2H), 3.49 (s, 2H), 1.62 (q, J = 6.5 Hz, 4H), 1.05–1.47 (m, 44H), 0.84–0.97 (m, 18H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 160.3, 158.6, 156.4, 152.4, 151.3, 151.0, 150.0, 149.0, 146.9, 145.3, 141.0, 128.8, 127.3, 125.5, 125.3, 123.0, 120.7, 115.8, 114.5, 78.0, 77.7, 77.6, 68.2, 61.2, 43.8, 43.7, 33.0, 32.9, 32.4, 32.1, 31.9, 30.2, 29.7, 26.1, 23.0, 22.94, 22.90, 22.8, 22.7, 14.34, 14.32, 14.27 ppm. IR (KBr): $\tilde{\nu}$ = 2952, 2925, 2852, 1602, 1508, 1060 cm^{-1} . ESI-MS: m/z = 1300.52 $[\text{M}+1]^+$.

Synthesis of 4-(Hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(8-(5-(8-iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)phenyl)aniline (6)



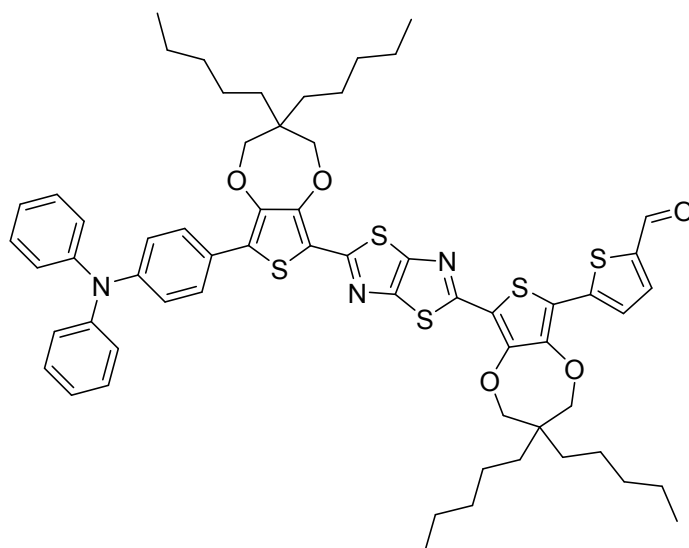
2,5-Bis(8-iodo-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazole (**3**) (750 mg, 0.76 mmol) was dissolved in toluene (15 mL) together with [Pd(dppf)Cl₂] (56 mg, 0.08 mmol, 0.1 eq.), 4-(hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**12**) (461 mg, 0.76 mmol, 1.0 eq.), KF (5.0 eq.) and ethanol (15 mL). The resulting mixture was heated at 78°C and stirred for 5 hours, then a second portion of [Pd(dppf)Cl₂] (0.05 eq.) was added and stirring was continued for 2 hours. The reaction mixture was then allowed to cool to room temperature and, after filtration over a short pad of Celite®, solvent was removed under vacuum. The residue obtained was purified by flash column chromatography (SiO₂, petroleum ether /toluene 2:1 to 1:1) to give compound **6** (178 mg, 0.13 mmol, 18% yield) as a sticky orange solid, as well as starting material **3** (495 mg, 66% recovery).

(**6**): ¹H NMR (400 MHz, C₆D₆): δ = 7.81 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 4H), 3.68 (s, 2H), 3.62 (s, 2H), 3.53 (s, 2H), 3.48 (s, 2H), 2.70 (t, *J* = 7.2 Hz, 4H), 1.55 (q, *J* = 7.6 Hz, 4H), 1.04–1.38 (m, 44H), 0.91 (m, 12H), 0.84 (t, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = 160.0, 159.3, 158.8, 152.4, 151.3, 151.1, 149.8, 147.3, 147.2, 147.0, 145.8, 145.7, 131.9, 131.2, 125.4, 124.6, 123.7, 122.9, 115.1, 77.9, 77.7, 77.6, 61.4, 43.7, 43.6, 34.6, 33.0, 32.9, 32.3, 32.1, 31.7, 29.6, 28.8, 22.93, 22.91, 22.89, 22.8, 22.7, 14.3, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2928, 2857, 1587, 1490, 1060 cm⁻¹. ESI-MS: *m/z* = 1332.11 [M+1]⁺

General procedure for cross-coupling with 5-formylthiophen-2-ylboronic acid (**13**)

Compound **4-6** (1.0 eq.) was dissolved in anhydrous toluene together with $[\text{Pd}(\text{dppf})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$ (0.05 eq.) and introduced in a microwave vial equipped with a magnetic stirrer. Boronic acid **13** (1.5 eq.) and KF (6.0 eq.) were dissolved in MeOH and the resulting pink solution was transferred into the microwave vial. The reaction mixture was heated under microwave irradiation at 70°C for 30 min. After cooling to room temperature, the reaction mixture was diluted with water (30 mL) and CH_2Cl_2 (30 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4 . Removal of the solvent *in vacuo* yielded a black solid, which was purified by flash column chromatography.

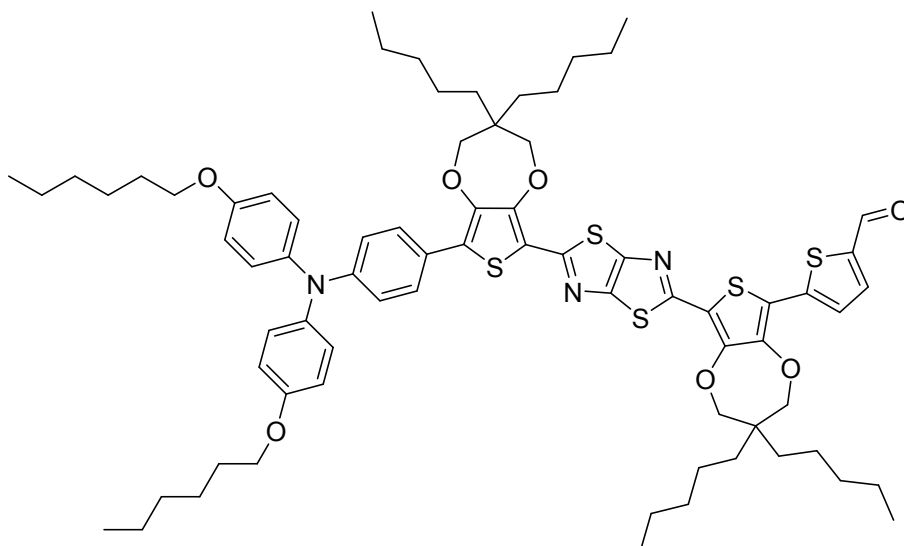
5-(8-(5-(8-(4-(Diphenylamino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophene-2-carbaldehyde (**7**)



Compound **4** (123 mg, 0.11 mmol) and $[\text{Pd}(\text{dppf})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$ (5 mg, 0.006 mmol) were dissolved in toluene (6.0 mL) and reacted with 5-formyl-2-thiopheneboronic acid (**13**) (26 mg, 0.17 mmol) and KF (39 mg, 0.67 mmol) in MeOH (3.0 mL) under microwave irradiation at 70°C for 30 min. Work-up and evaporation of the solvent yielded a black solid, which was purified by flash column chromatography (SiO_2 , toluene/petroleum ether 3:1) to give compound **7** (89 mg, 0.08 mmol, 74% yield) as a dark-red solid.

(**7**): mp = 229–231 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.89 (s, 1H), 7.67 (d, *J* = 4.1 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.26–7.32 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 4H), 7.03–7.07 (m, 4H), 4.16 (s, 4H), 4.13 (s, 2H), 4.02 (s, 2H), 1.46–1.52 (m, 8H), 1.29–1.36 (m, 24H), 0.89–0.94 (m, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 183.0, 160.1, 157.9, 151.1, 150.5, 149.6, 148.1, 147.5, 147.4, 147.3, 145.1, 144.1, 142.0, 136.7, 129.5, 127.7, 126.2, 125.0, 124.6, 123.8, 123.5, 122.9, 117.0, 116.9, 113.5, 78.4, 78.1, 77.9, 44.2, 44.0, 32.8, 32.7, 32.2, 32.1, 29.8, 22.7, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2928, 2857, 1654, 1054 cm⁻¹. ESI-MS: *m/z* = 1083.62 [M]⁺.

5-(8-(5-(8-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophene-2-carbaldehyde (8**)**

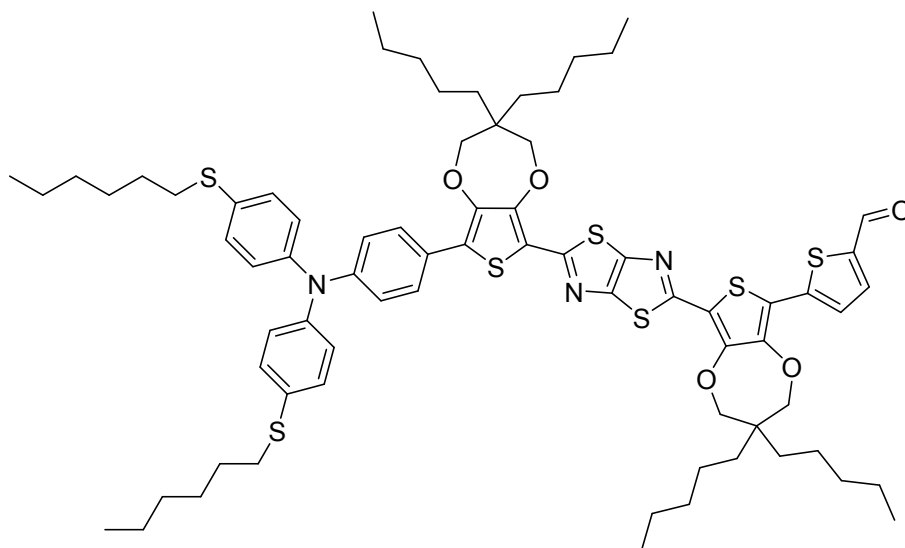


Compound **5** (187 mg, 0.14 mmol) and [Pd(dppf)Cl₂]·CH₂Cl₂ (6 mg, 0.007 mmol) were dissolved in toluene (4.0 mL) and reacted with 5-formyl-2-thiopheneboronic acid (**13**) (42 mg, 0.22 mmol) and KF (50 mg, 0.86 mmol) in MeOH (2.0 mL) under microwave irradiation at 70°C for 30 min. Work-up and evaporation of the solvent yielded a black solid, which was purified by flash column chromatography (SiO₂, toluene/petroleum ether 3:1) to give compound **8** (116 mg, 0.09 mmol, 63% yield) as a dark-red sticky solid.

(**8**): ¹H NMR (400 MHz, C₆D₆): δ = 9.57 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.10–7.17 (m, 6H), 6.97 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 4.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 4H), 3.78 (s, 2H), 3.64–3.68 (m, 8H), 3.60 (s, 2H), 1.63 (q, *J* = 8.8 Hz, 4H), 1.02–1.41 (m, 44H), 0.93 (t, *J* = 7.1 Hz, 12H), 0.88 (t, *J* = 6.8 Hz, 6H)

ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 182.2, 160.6, 158.2, 156.4, 152.0, 151.2, 150.2, 149.1, 148.6, 147.5, 145.3, 143.4, 143.0, 140.9, 136.1, 127.3, 126.6, 125.8, 125.2, 123.8, 120.6, 117.7, 117.6, 115.8, 114.3, 78.1, 78.0, 77.7, 77.6, 68.2, 43.7, 33.0, 32.9, 32.3, 32.2, 32.0, 30.2, 29.7, 26.1, 23.0, 22.9, 22.8, 22.7, 14.3, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3036, 2929, 2857, 1655, 1438, 1054 cm^{-1} . ESI-MS: m/z = 1285.40 $[\text{M}+1]^+$.

5-(8-(5-(8-(4-(Bis(4-(hexylthio)phenyl)amino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophene-2-carbaldehyde (9)



Compound **6** (160 mg, 0.12 mmol) and $[\text{Pd}(\text{dppf})\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$ (5 mg, 0.006 mmol) were dissolved in toluene (6.0 mL) and reacted with 5-formyl-2-thiopheneboronic acid (**13**) (35 mg, 0.18 mmol) and KF (42 mg, 0.72 mmol) in MeOH (3.0 mL) under microwave irradiation at 70°C for 30 min. Work-up and evaporation of the solvent yielded a black solid, which was purified by flash column chromatography (SiO_2 ; Toluene) to give compound **9** (90 mg, 0.07 mmol, 57% yield) as a dark-red sticky solid.

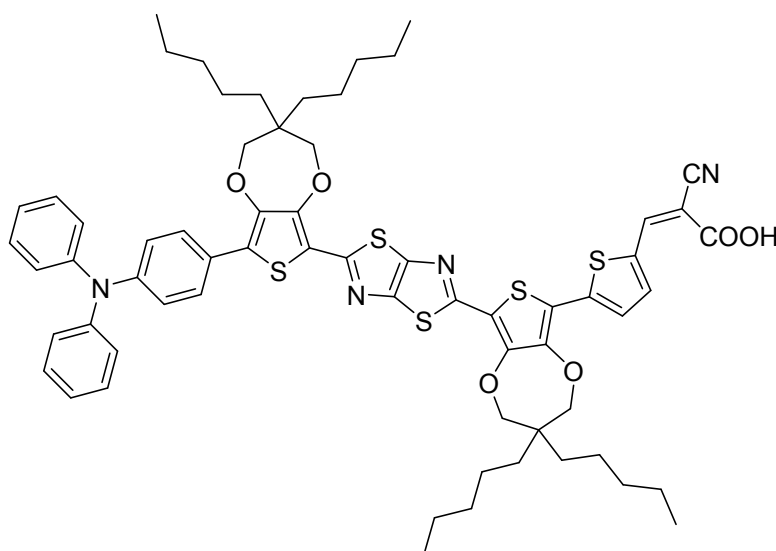
(**9**): ^1H NMR (400 MHz, C_6D_6): δ = 9.57 (s, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.6 Hz, 4H), 7.05 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 4.0 Hz, 1H), 6.87 (d, J = 4.0 Hz, 1H), 3.73 (s, 2H), 3.64 (s, 2H), 3.61 (s, 2H), 3.55 (s, 2H), 2.70 (t, J = 7.3 Hz, 4H), 1.56 (q, J = 7.5 Hz, 4H), 0.96–1.41 (m, 44H), 0.93 (t, J = 7.0 Hz, 12H), 0.85 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 182.2, 160.3, 158.4, 151.9, 151.4, 150.0, 148.7, 147.5, 147.4, 145.7, 143.4, 143.0, 136.1, 132.0, 131.2,

131.0, 127.4, 125.7, 125.5, 124.9, 123.8, 123.6, 117.7, 117.6, 115.0, 78.2, 78.0, 77.7, 43.8, 34.6, 33.0, 32.96, 32.4, 32.3, 31.7, 29.6, 28.8, 22.95, 22.93, 22.85, 22.78, 14.4, 14.3 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2924, 2852, 1653, 1438, 1057 cm^{-1} . ESI-MS: m/z = 1315.27 $[\text{M}]^+$.

General procedure for Knoevenagel condensation with cyanoacetic acid

In a Schlenk flask equipped with a magnetic stirrer aldehyde **7-9** (1.0 eq.) was dissolved in toluene together with cyanoacetic acid (10.0 eq.), ammonium acetate (4.0 eq.), and glacial acetic acid. The reaction mixture was stirred at 110°C for 6 h, then cooled to room temperature and diluted with CHCl_3 (150 mL). The organic phase was washed with a saturated solution of NaHCO_3 (100 mL) and brine (100 mL), and then it was dried with Na_2SO_4 . Evaporation of the solvent gave a black solid, which was purified by consecutive washing with ethyl acetate, methanol and pentane and dried under vacuum.

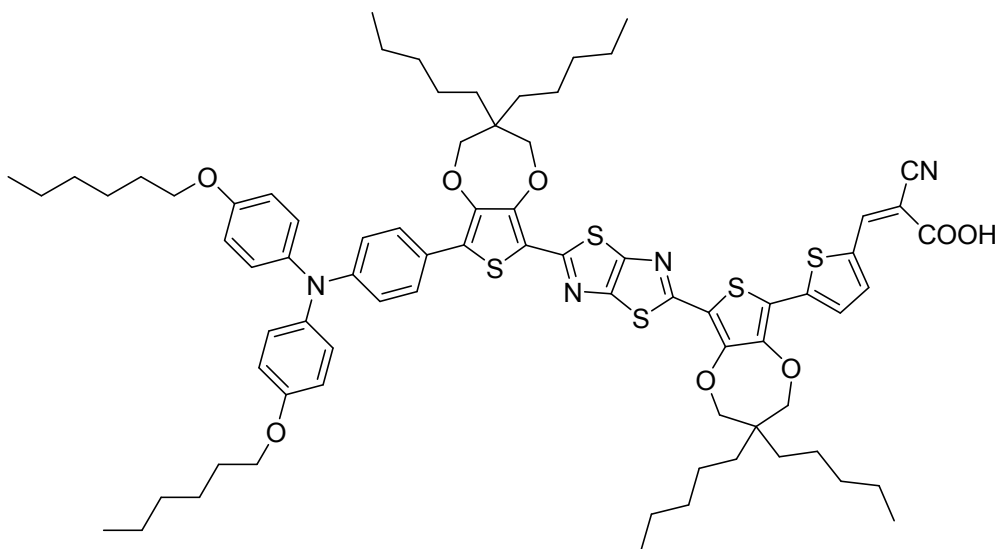
2-Cyano-3-(5-(8-(5-(8-(4-(diphenylamino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophen-2-yl)acrylic acid (TTZ3)



Aldehyde **7** (89 mg, 0.08 mmol), cyanoacetic acid (70 mg, 0.82 mmol) and ammonium acetate (25 mg, 0.33 mmol) were dissolved in toluene (4.0 mL) and glacial acetic acid (6.0 mL). The reaction mixture was stirred at 110°C for 6 h. Work-up and purification afforded compound **TTZ3** (80 mg, 0.07 mmol, 84% yield) as a dark solid.

(TTZ3): mp = 288–291 °C. ^1H NMR (400 MHz, THF- d_8): δ = 8.31 (s, 1H), 7.83 (d, J = 4.2 Hz, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 4.1 Hz, 1H), 7.23–7.30 (m, 4H), 7.09–7.12 (m, 4H), 7.00–7.08 (m, 4H), 4.28 (s, 2H), 4.24 (s, 2H), 4.22 (s, 2H), 4.06 (s, 2H), 1.52–1.59 (m, 8H), 1.28–1.42 (m, 24H), 0.89–0.96 (m, 12H) ppm. ^{13}C NMR (100 MHz, THF- d_8): δ = 160.2, 158.2, 151.7, 151.1, 150.4, 149.1, 148.3, 148.0, 145.9, 143.9, 138.0, 136.3, 130.0, 128.2, 127.2, 125.5, 125.2, 125.0, 124.0, 123.4, 117.9, 117.8, 116.7, 116.6, 114.5, 78.9, 78.8, 78.5, 78.4, 44.7, 44.5, 33.50, 33.48, 32.8, 23.2, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2928, 2578, 2217, 1689, 1058 cm^{-1} . ESI-MS: m/z = 1151.47 $[\text{M}]^+$. Anal. calcd. for $\text{C}_{64}\text{H}_{70}\text{N}_4\text{O}_6\text{S}_5$: C, 66.75; H, 6.13; N, 4.87. Found: C, 66.46; H, 6.35; N, 4.52.

3-(5-(8-(5-(8-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (TTZ4)

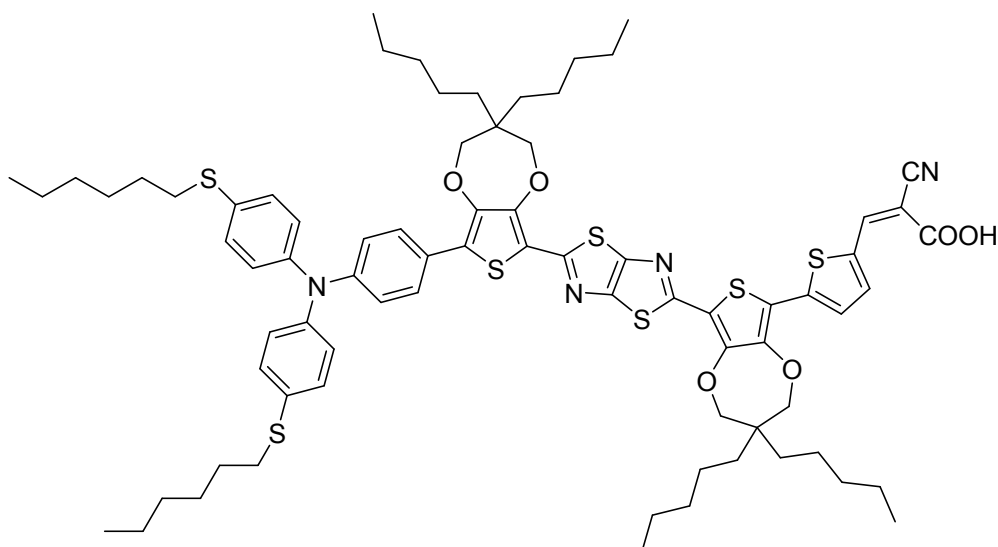


Aldehyde **8** (108 mg, 0.08 mmol), cyanoacetic acid (72 mg, 0.84 mmol) and ammonium acetate (26 mg, 0.34 mmol) were dissolved in toluene (5.0 mL) and glacial acetic acid (7.0 mL). The reaction mixture was stirred at 110°C for 4 h. Work-up and purification afforded compound **TTZ4** (103 mg, 0.08 mmol, 90% yield) as a dark sticky solid.

(TTZ4): ^1H NMR (400 MHz, THF- d_8): δ = 8.33 (s, 1H), 7.85 (d, J = 4.2 Hz, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 4.1 Hz, 1H), 7.04 (d, J = 8.9 Hz, 4H), 6.85 (d, J = 8.9 Hz, 6H), 4.27 (s, 2H), 4.23 (s, 2H), 4.22 (s, 2H), 4.04 (s, 2H), 3.94 (t, J = 6.4 Hz, 4H), 1.73–1.79 (m, 4H), 1.32–1.60 (m, 44H), 0.90–0.95 (m, 18H) ppm. ^{13}C NMR (100 MHz, THF- d_8): δ = 164.0, 160.3, 158.0, 156.9, 151.7, 151.0, 150.5,

149.4, 149.0, 148.0, 146.0, 145.4, 144.1, 140.9, 138.2, 136.1, 128.0, 127.6, 125.9, 124.91, 124.89, 120.0, 117.84, 117.77, 116.6, 115.9, 113.8, 99.1, 78.9, 78.8, 78.4, 78.3, 68.6, 44.7, 44.5, 33.51, 33.49, 32.80, 32.75, 32.4, 30.1, 26.6, 23.4, 23.3, 14.3, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2928, 2852, 2213, 1684, 1505, 1057 cm^{-1} . ESI-MS: m/z = 1351.38 $[\text{M}+1]^+$. Anal. calcd. for $\text{C}_{76}\text{H}_{94}\text{N}_4\text{O}_8\text{S}_5$: C, 67.52; H, 7.01; N, 4.14. Found C, 66.98; H, 7.11; N, 4.08.

3-(5-(8-(5-(8-(4-(Bis(4-(hexylthio)phenyl)amino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophen-2-yl)-2-cyanoacrylic acid (TTZ5)



Aldehyde **9** (84 mg, 0.06 mmol), cyanoacetic acid (54 mg, 0.64 mmol) and ammonium acetate (20 mg, 0.25 mmol) were dissolved in toluene (3.0 mL) and glacial acetic acid (3.0 mL). The reaction mixture was stirred at 110°C for 3 h. Work-up and purification afforded compound **TTZ5** (85 mg, 0.06 mmol, 97% yield) as a dark sticky solid.

(**TTZ5**): ^1H NMR (400 MHz, THF-d_8): δ = 8.30 (s, 1H), 7.83 (d, J = 4.0 Hz, 1H), 7.64 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 4.0 Hz, 1H), 7.26 (d, J = 8.5 Hz, 4H), 7.00–7.05 (m, 6H), 4.28 (s, 2H), 4.24 (s, 2H), 4.22 (s, 2H), 4.06 (s, 2H), 2.90 (t, J = 7.3 Hz, 4H), 1.62–1.68 (m, 4H), 1.53–1.59 (m, 8H), 1.27–1.51 (m, 36H), 0.88–0.95 (m, 18H) ppm. ^{13}C NMR (100 MHz, THF-d_8): δ = 164.0, 160.1, 158.2, 151.7, 151.1, 150.3, 149.1, 148.0, 147.7, 146.0, 145.9, 144.0, 138.2, 136.2, 132.3, 131.3, 128.2, 127.4, 125.7, 125.0, 124.9, 123.5, 117.9, 117.7, 116.7, 114.5, 99.2, 78.9, 78.8, 78.5, 78.3, 67.8, 44.7, 44.5, 34.6, 33.50, 33.49, 32.8, 32.7, 32.2, 30.0, 29.2, 23.27, 23.26, 14.3, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 3020, 2924, 2857,

2213, 1678, 1563, 1407, 1057 cm^{-1} . ESI-MS: $m/z = 1383.89$ $[\text{M}+1]^+$. Anal. calcd. for $\text{C}_{76}\text{H}_{94}\text{N}_4\text{O}_6\text{S}_7$: C, 65.95; H, 6.85; N, 4.05. Found: C, 65.69; H, 6.94; N, 4.00.

4. Spectroscopic Characterization

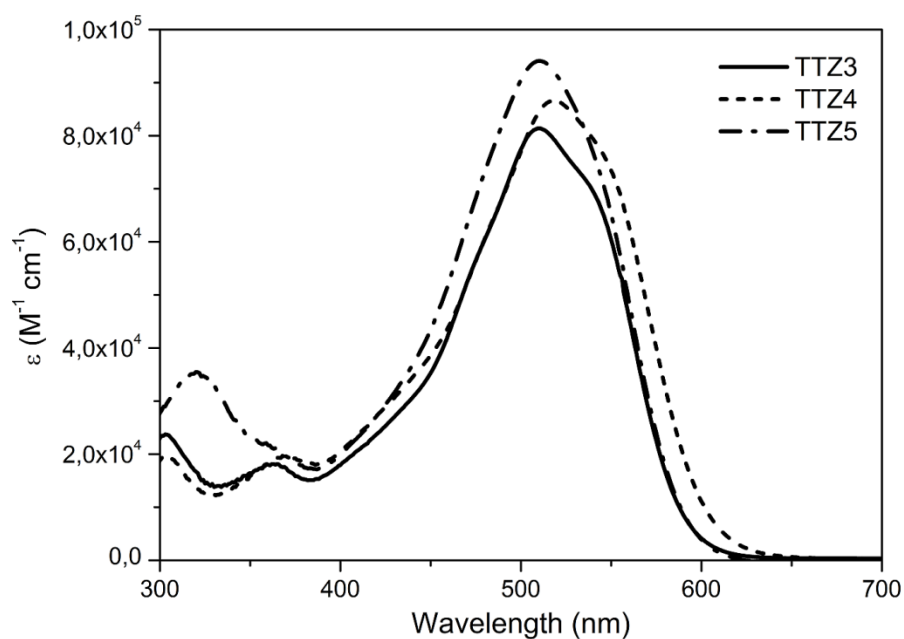


Figure S2. UV-Vis spectra of compounds **TTZ3-5** recorded in THF solution. Concentrations: **TTZ3**, 8.47×10^{-6} M; **TTZ4**, 8.89×10^{-6} M; **TTZ5**, 8.96×10^{-6} M.

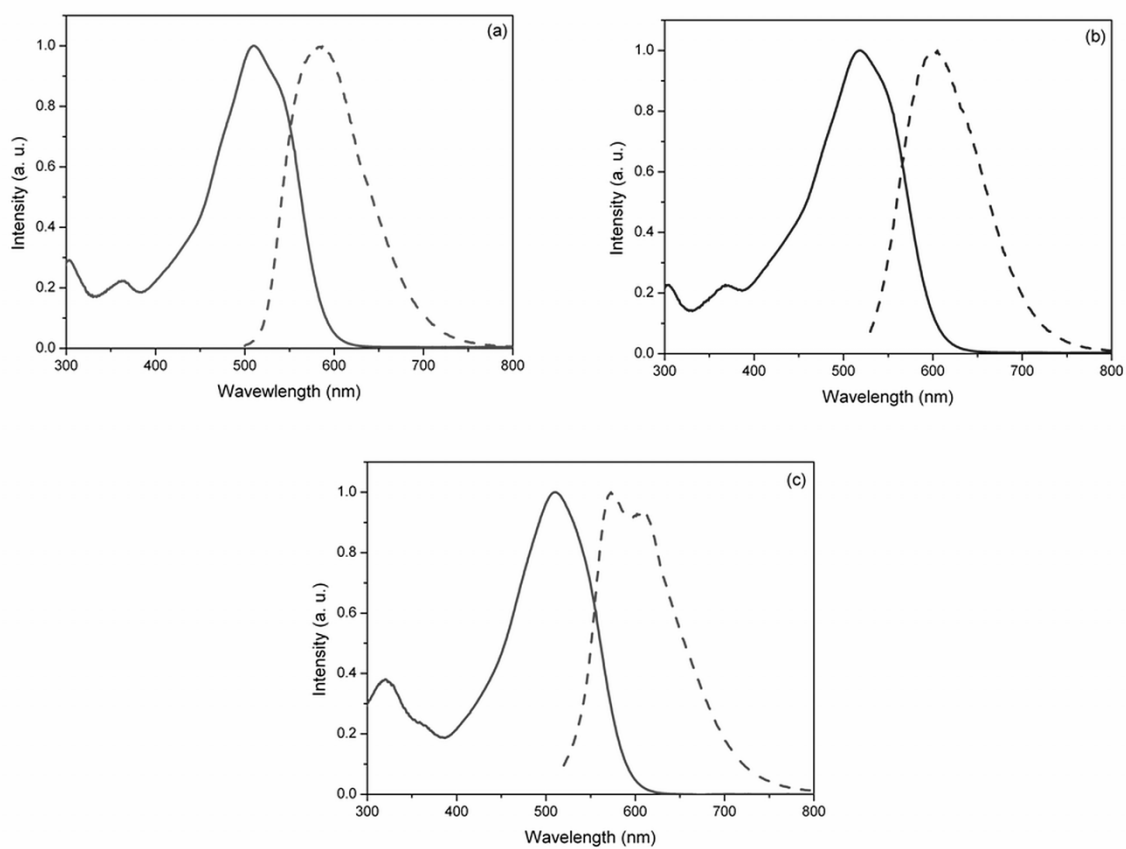


Figure S3. Intersection between the normalized UV-Vis absorption (solid line) and fluorescence emission (dashed line) spectra for compounds **TTZ3-5** in THF solution: (a) **TTZ3**; (b) **TTZ4**; (c) **TTZ5**.

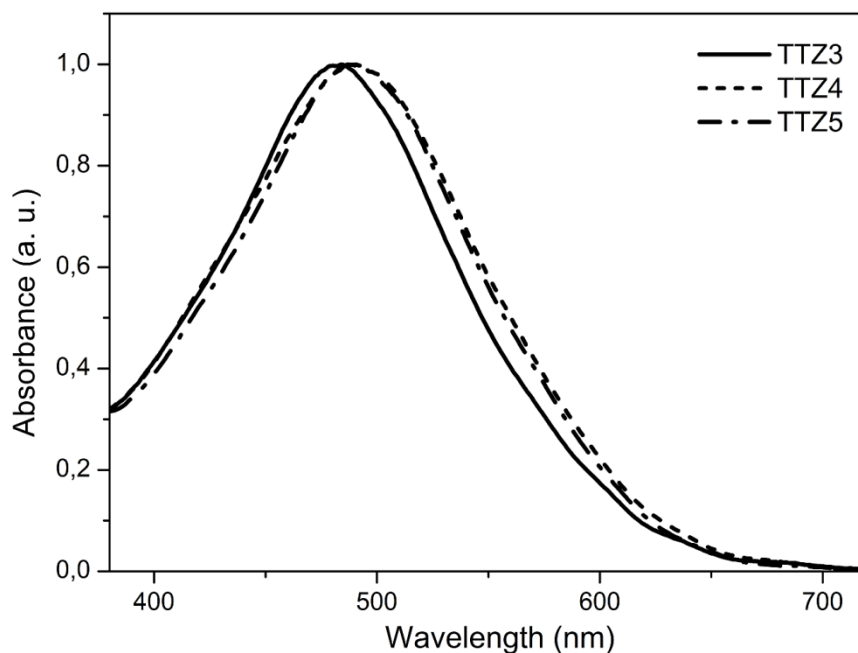


Figure S4. Normalized UV-Vis spectra of compounds **TTZ3-5** adsorbed on nanocrystalline TiO_2 .

5. Measurement of the Density of Adsorbed Dyes on TiO_2

A transparent nanocrystalline TiO_2 electrode (surface area 0.88 cm^2) similar to those used for the photovoltaic measurements (see section n.7) was immersed in $1.0 \times 10^{-4} \text{ M}$ solutions of dyes **TTZ3-5** in THF at rt for 16 h. For each dye, the stained electrode was removed from the solution, dried under a stream of nitrogen and immersed in 10 mL of a 0.1 M KOH solution in THF/MeOH 4:1 at rt until full discoloration was observed (approx. 1 h). The absorbance of the resulting pink-red solution was measured by UV-Vis spectroscopy and compared to that of a standard $8.0 \cdot 10^{-6} \text{ M}$ solution of the sensitizer in the same solvent/base mixture. The amount of dye present in the unknown solution was calculated and divided by the electrode surface area, yielding density values of approx. $0.99 \cdot 10^{-7} \text{ mol cm}^{-2}$, $1.08 \cdot 10^{-7} \text{ mol cm}^{-2}$ and $1.19 \cdot 10^{-7} \text{ mol cm}^{-2}$ for compounds **TTZ3-5**, respectively.

6. Cyclic voltammetry measurements

The measurements were carried out in commercially available anhydrous 99.9%, HPLC grade dichloromethane for electrochemistry. The supporting electrolyte used was electrochemical grade $[N(Bu)_4]PF_6$. Cyclic voltammetry was performed in a three-electrode C-3 BAS Cell having a glassy carbon working electrode, a platinum counter electrode and the aqueous Ag/AgCl NaCl (3M) reference electrode. A BAS 100A electrochemical analyzer was used as a polarizing unit. Under these experimental conditions, the one-electron oxidation of ferrocene occurs at $E^{\circ'} = + 0.42$ V.

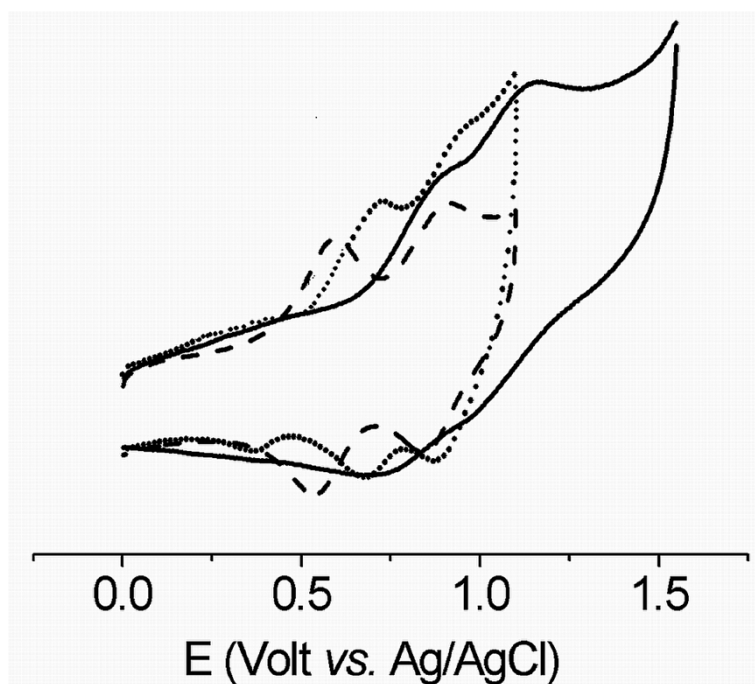


Figure S5. Cyclic Voltammetry plots relative to compounds **TTZ3** (full line), **TTZ4** (dashed line) and **TTZ5** (dotted line.)

7. DSSC Fabrication and Photoelectrochemical Measurements

Transparent photoanodes for DSSCs were prepared by screen-printing a commercial TiO₂ paste (*Dyesol* 18NR-T) on a 8Ω/sq conductive glass substrate (*Pilkington*), and by sintering the resulting electrodes at 520 °C for 30 minutes. After sintering, the thickness of the semiconductor layer was measured by means of a profiler (*Dektak* 150, *Veeco*) and determined to be 5.5 μm. Opaque photoanodes were obtained following an analogous procedure, but employing a different commercial titania paste (*Dyesol* 18NR-AO); their final thickness was 6.5 μm. In both cases, the electrode active area was 0.25 cm². Counter electrodes (CE) were obtained by screen printing a commercial platinum-containing paste (*Chimet*) on pre-drilled conductive glass plates and by heating at 420 °C for 15 minutes. Titania photo-electrodes were sensitized by overnight immersion at rt into the appropriate dye solution (0.1mM in THF for dyes **TTZ3-5**, 0.2 mM in EtOH for dye **D5**, 0.3 mM in EtOH for dye **Z907**), either in the absence or in the presence of 1 mM chenodeoxycholic acid (CDCA). After sensitization, the photoanodes were rinsed with THF or EtOH depending on the dye solvent, and then dried. A TiO₂-sensitized photoanode and a Pt counter electrode were assembled into a sealed sandwich-type cell using either a 25 μm or a 60 μm hot-melt Surlyn[®] gasket (*Solaronix*). A drop of the I⁻/I₃⁻-containing commercial HPE electrolyte solution (*Dyesol*) was placed on the drilled hole on the back of the counter electrode and was driven into the cell by vacuum backfilling. The hole was finally sealed by using additional sealing film and a small glass cover.

The devices underwent photovoltaic characterization by using a AM 1.5G solar simulator equipped with a Xenon lamp (*KHS* Solar Constant 1200). The measurements were performed with a power of incoming radiation of 100 mW/cm². *J/V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a *Keithley* model 2400 digital source-meter. A black shading mask was used to avoid overestimation of the measured parameters. IPCE spectra were measured with a special apparatus built using the following components: *Newport* model 70 612 Xenon lamp (150 W), *Cornerstone* 130 1/8 m monochromator and *Keithley* model 2400 digital source-meter.

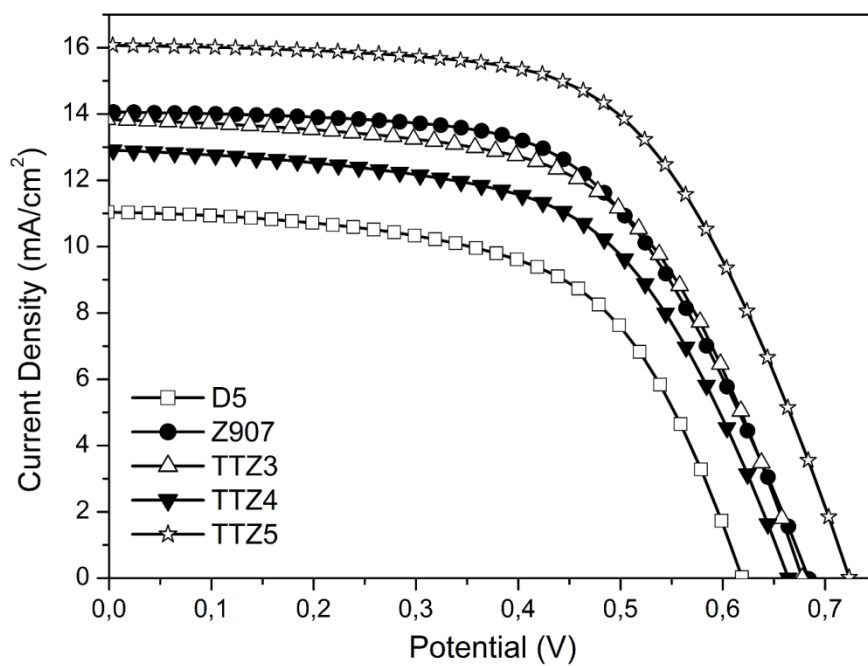


Figure S6. J/V curves measured for opaque DSSCs built with dyes **D5**, **Z907** and **TTZ3-5**.

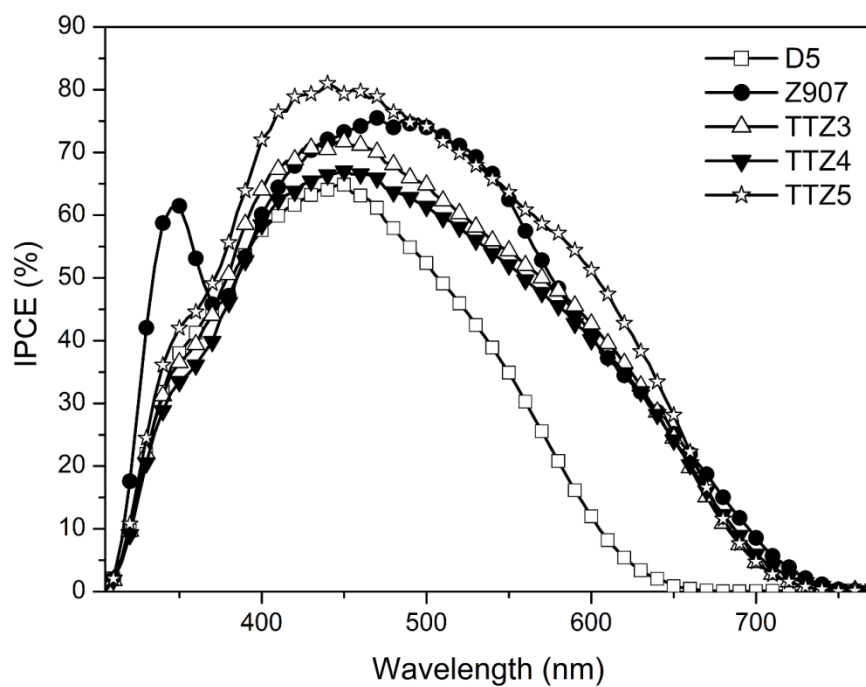


Figure S7. IPCE spectra measured for opaque DSSCs built with dyes **D5**, **Z907** and **TTZ3-5**.

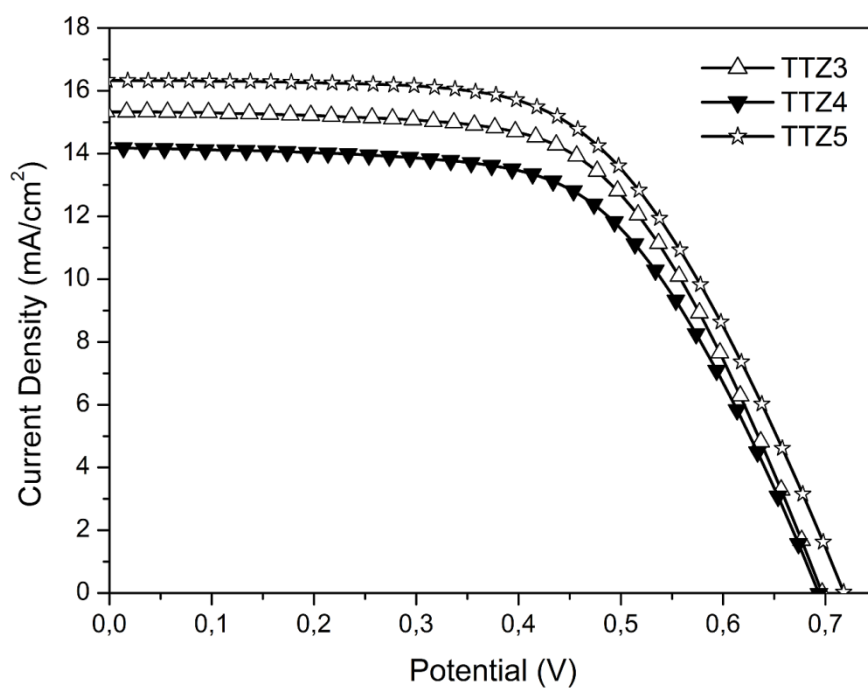


Figure S8. J/V curves measured for transparent DSSCs built with dyes **TTZ3-5** in the presence of CDCA.

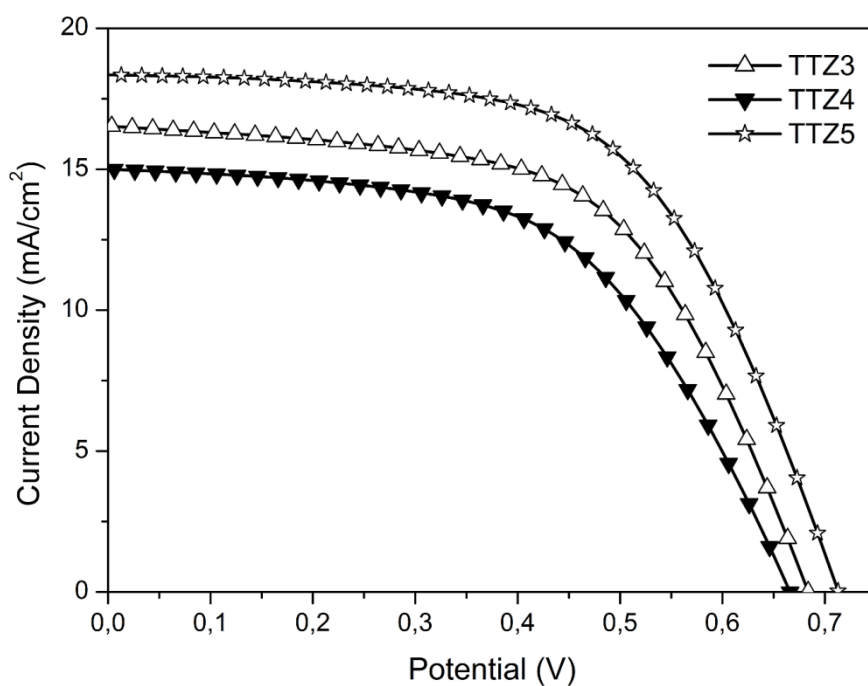
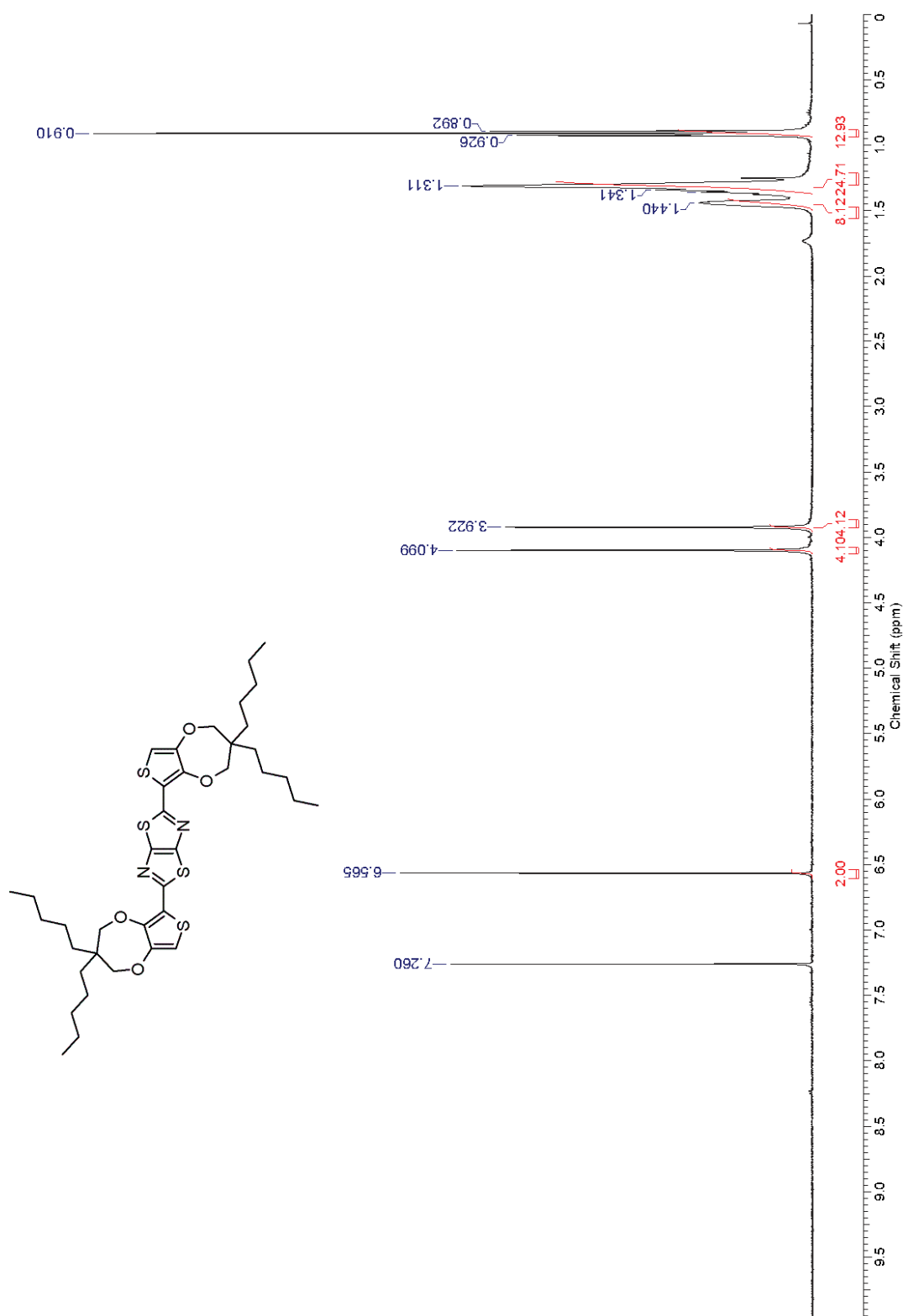
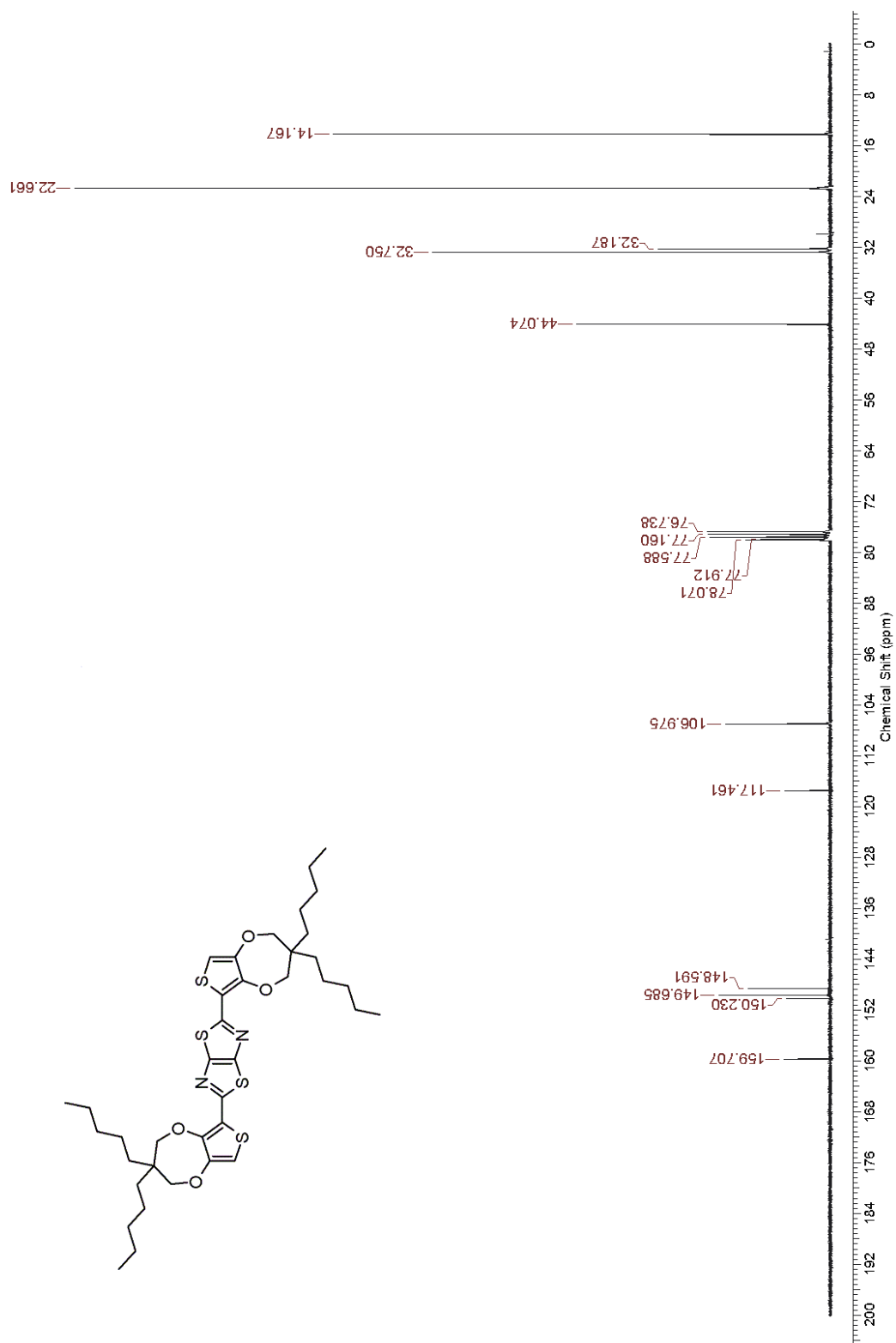


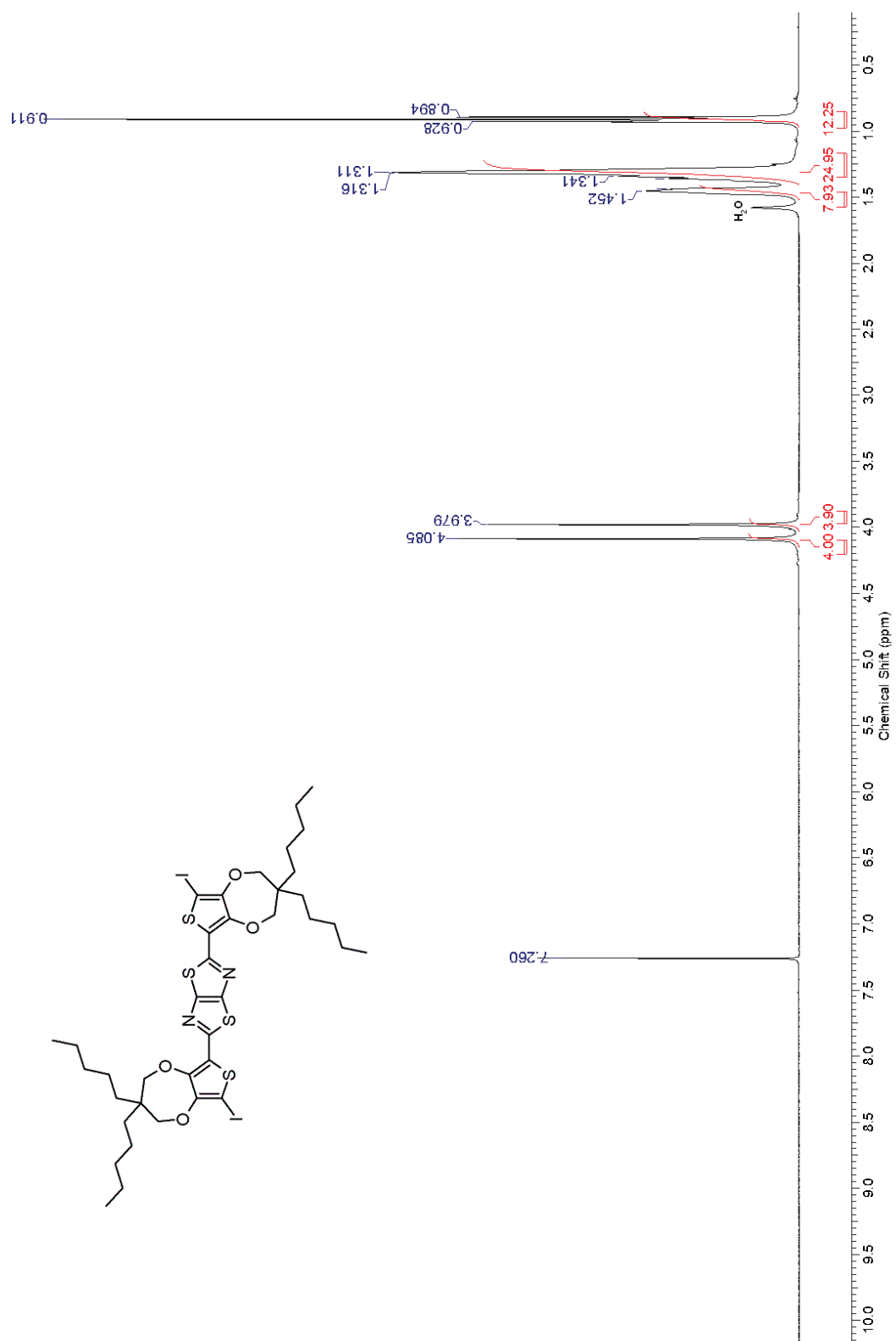
Figure S9. J/V curves measured for opaque DSSCs built with dyes **TTZ3-5** in the presence of CDCA.

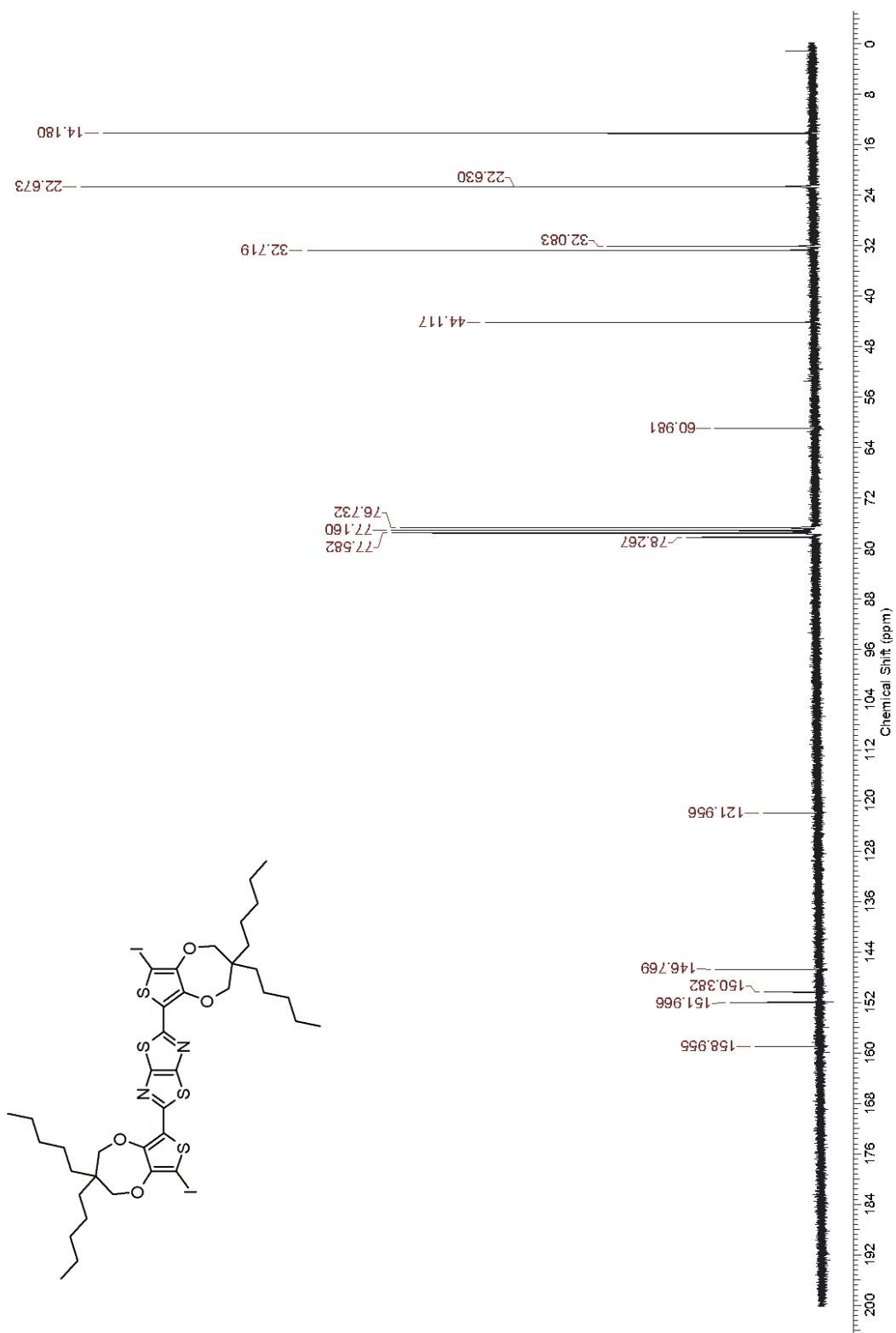
8. Copies of the ^1H - and ^{13}C -NMR spectra of compounds 2-9 and TTZ3-5

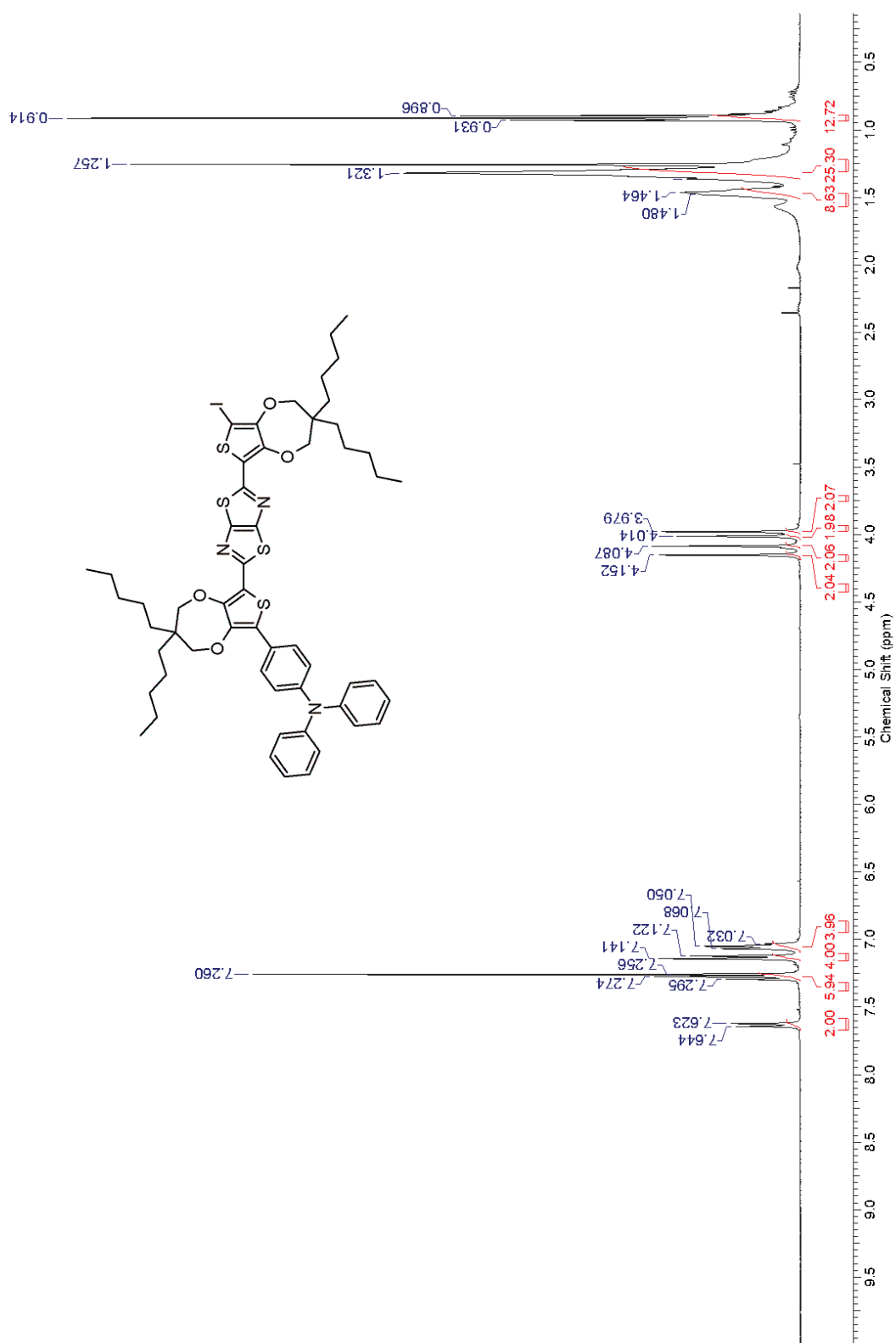
2

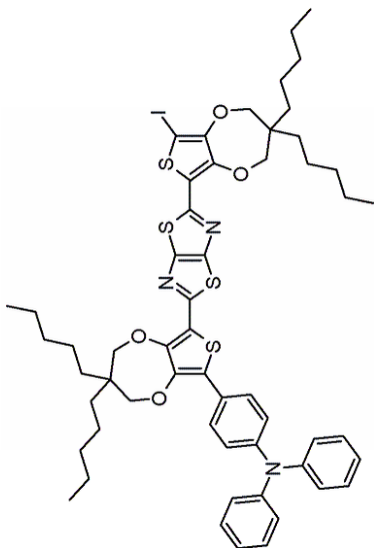


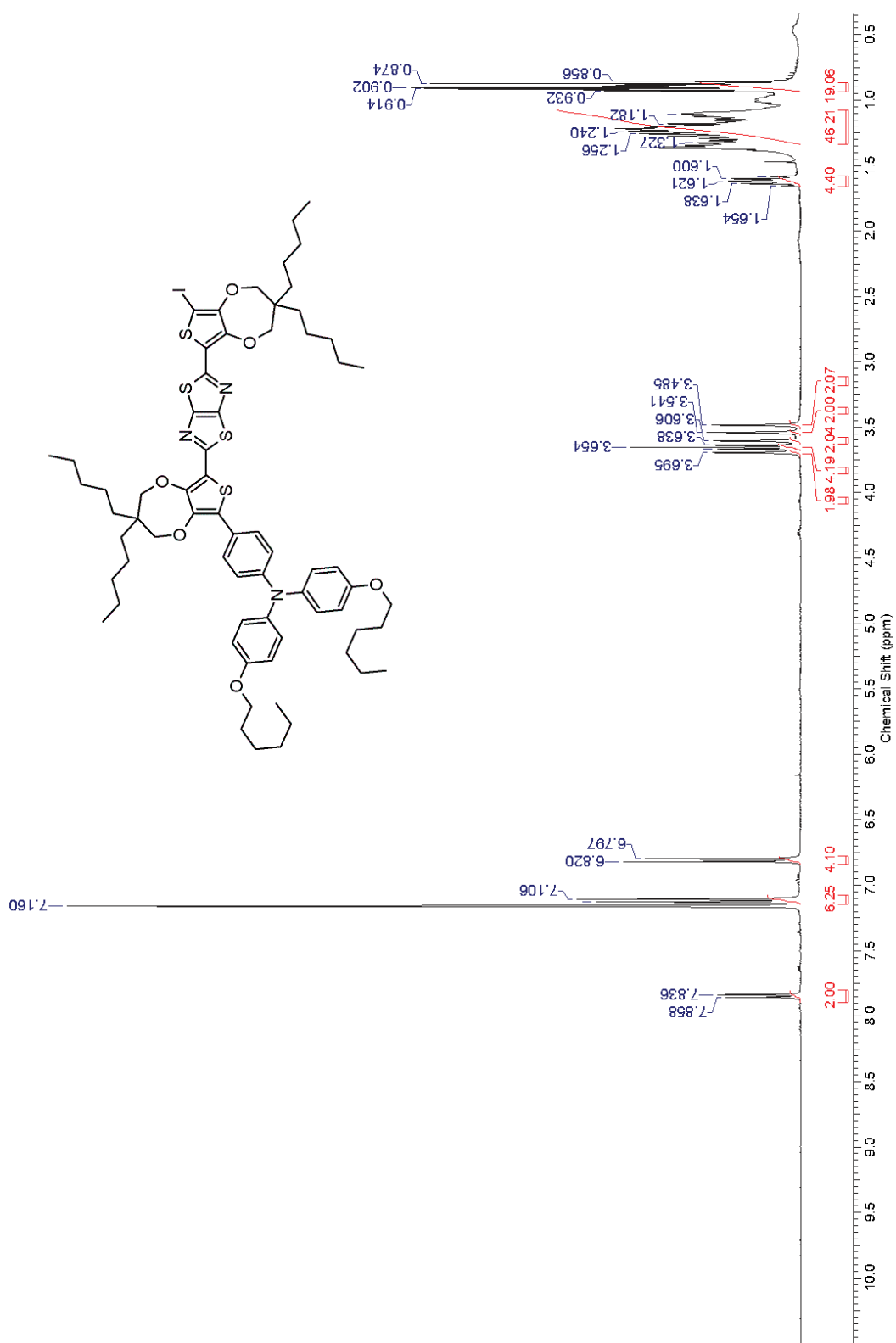


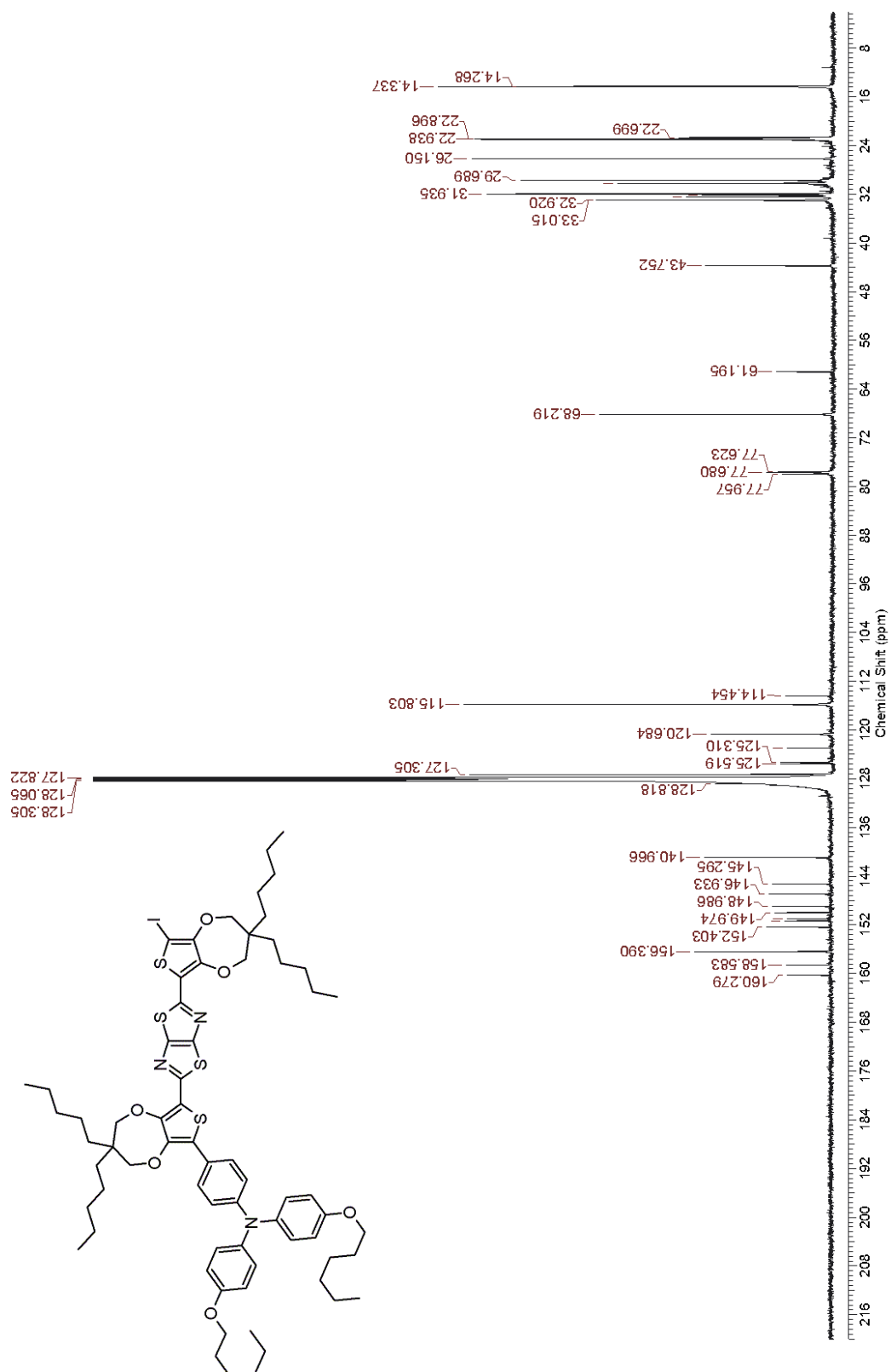


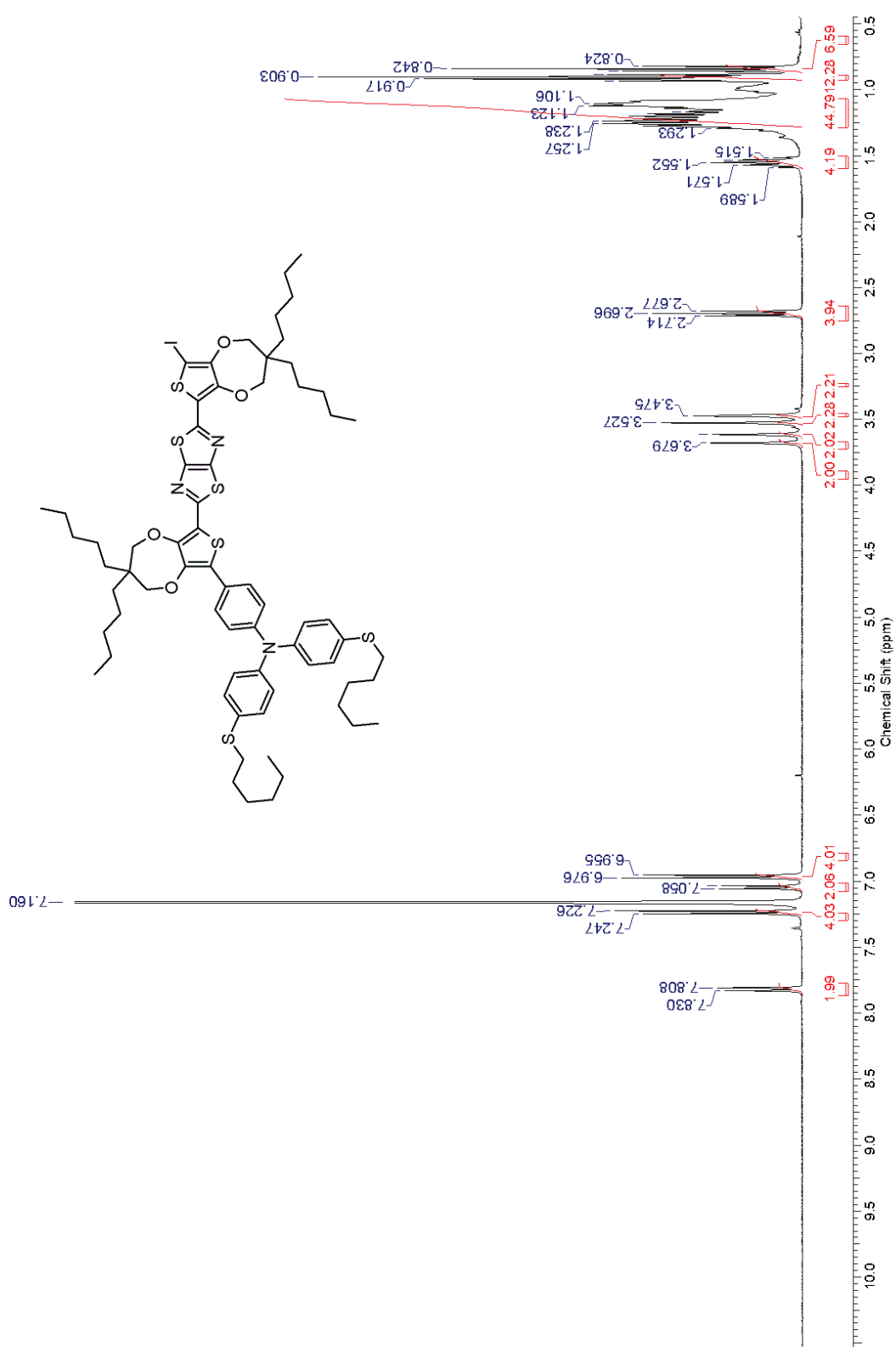


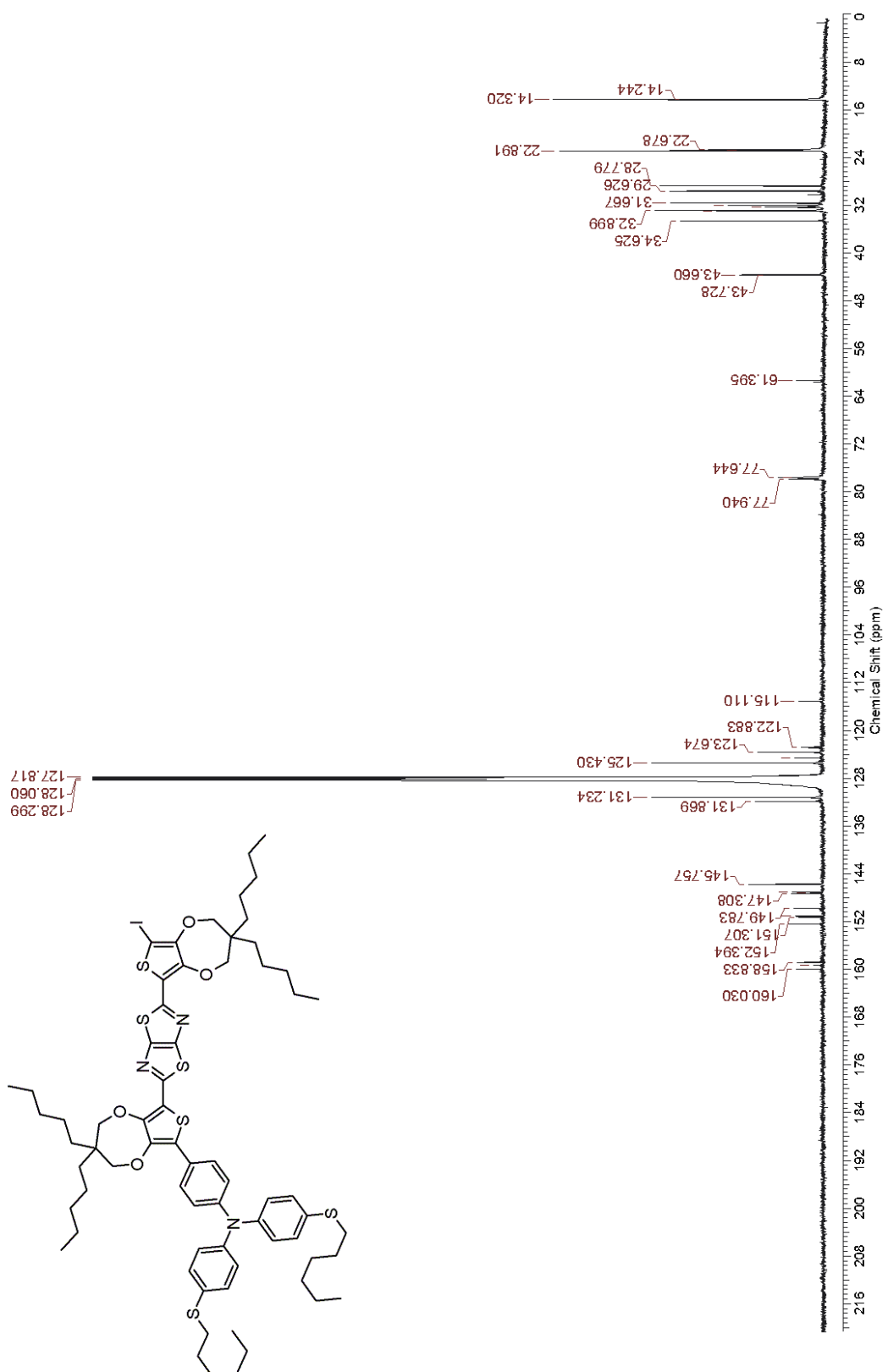


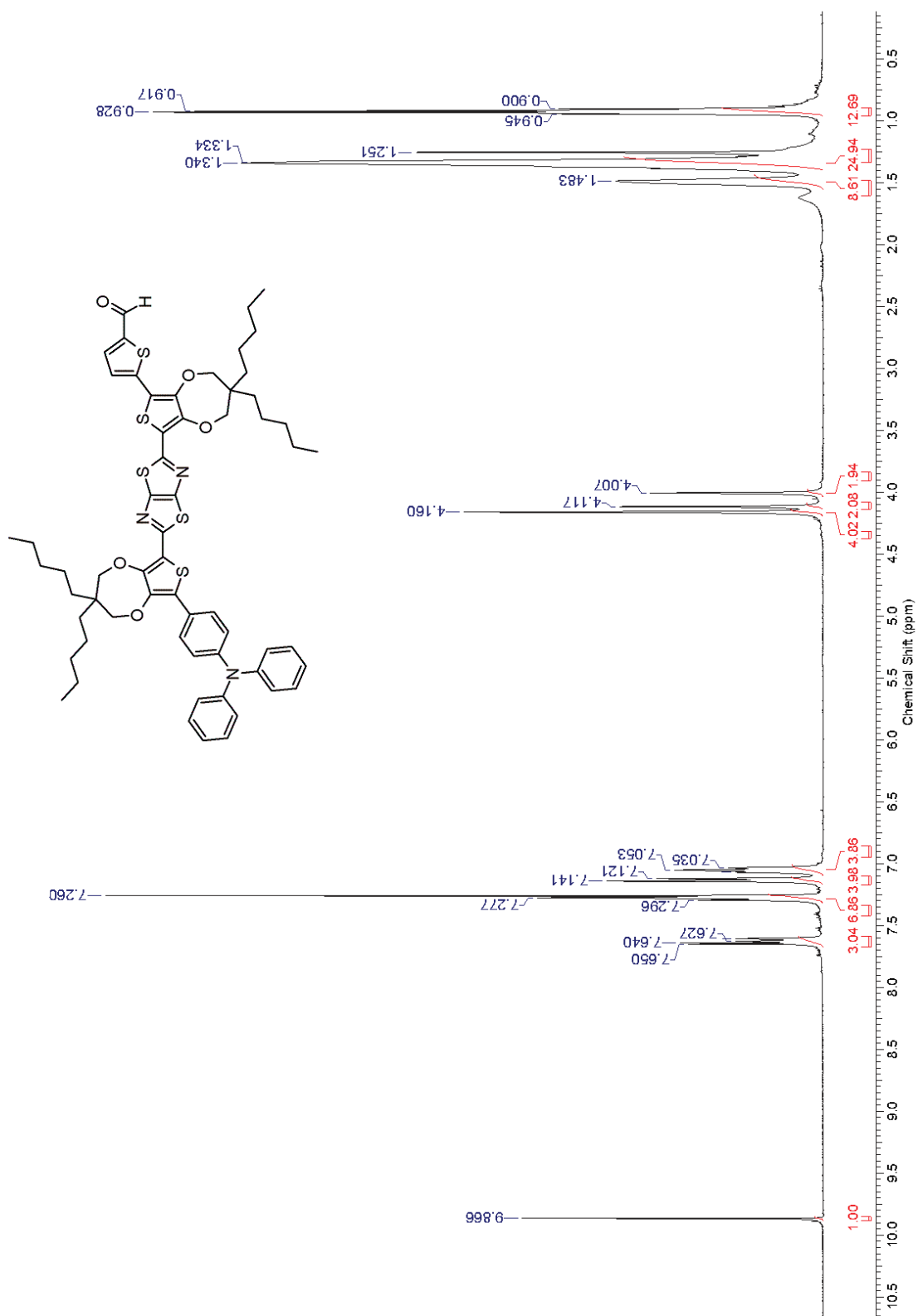


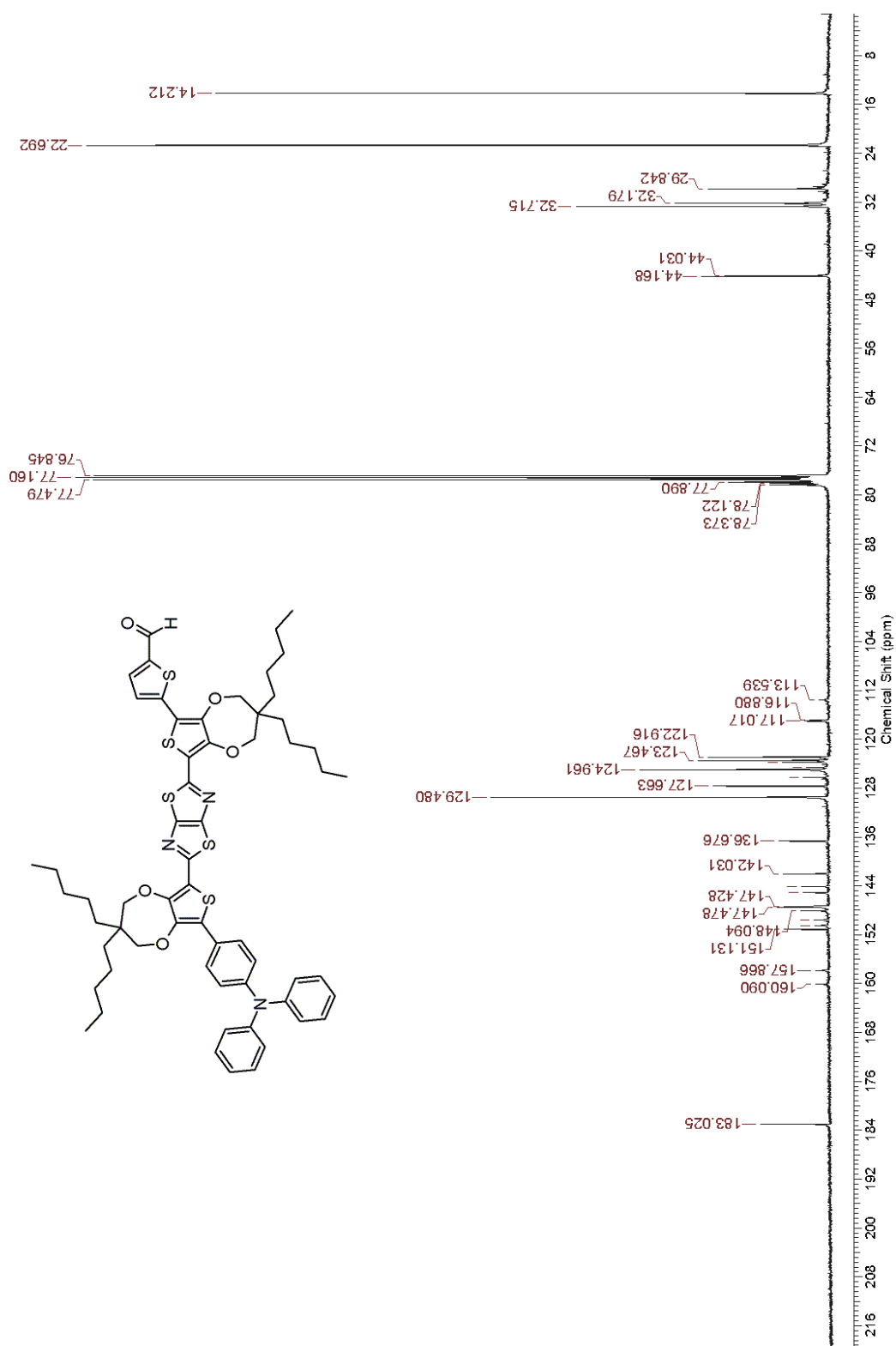


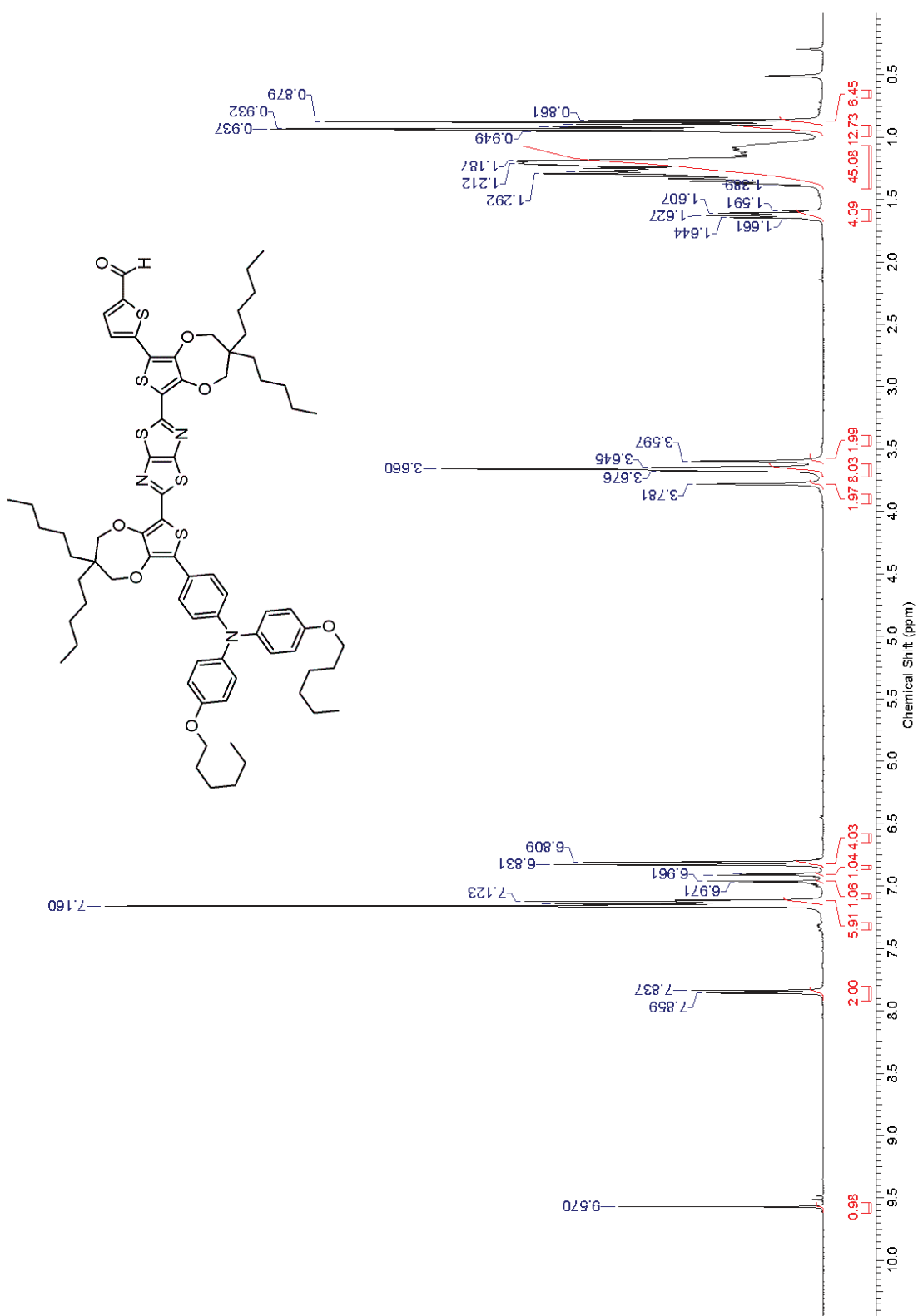


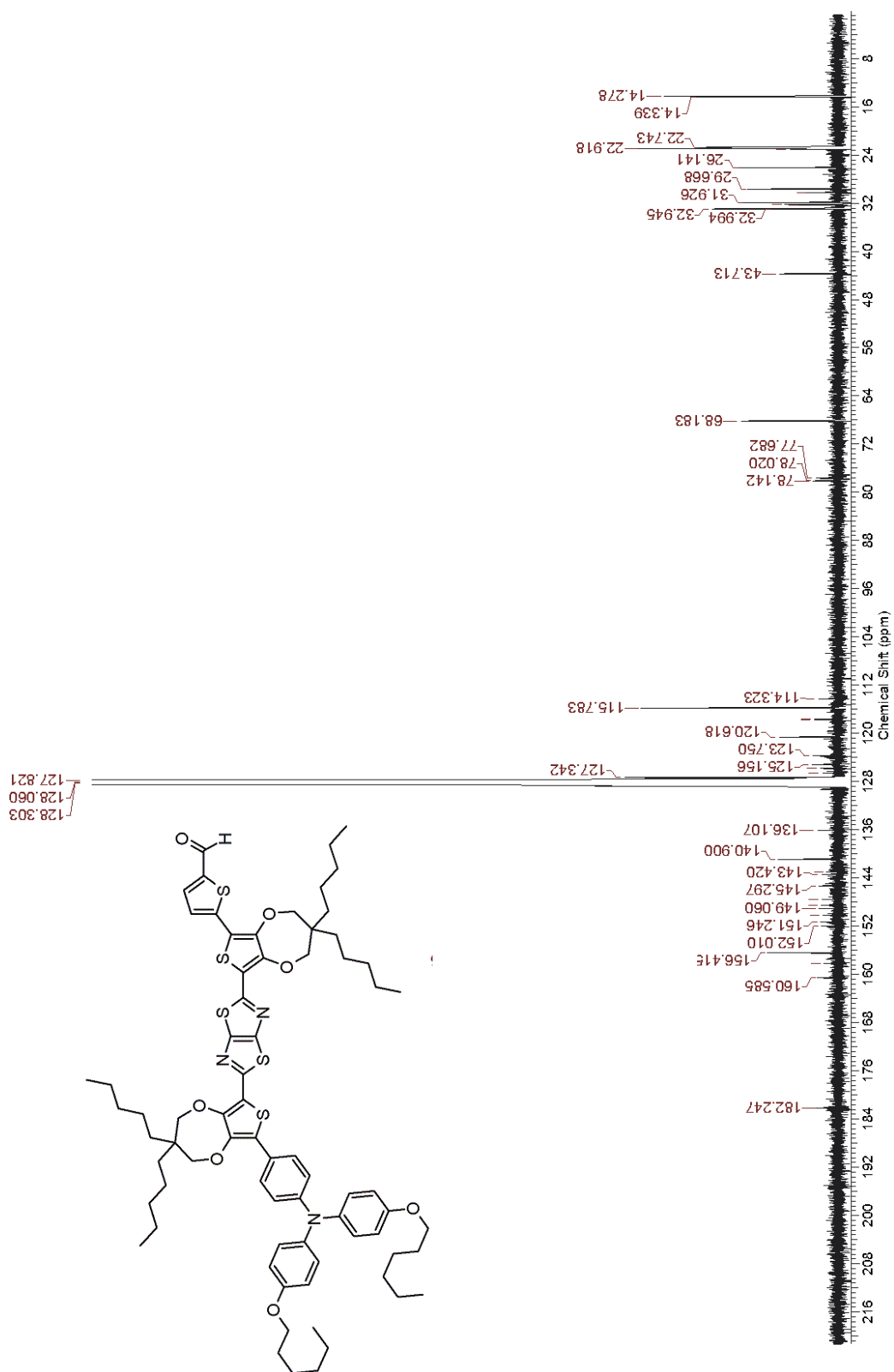


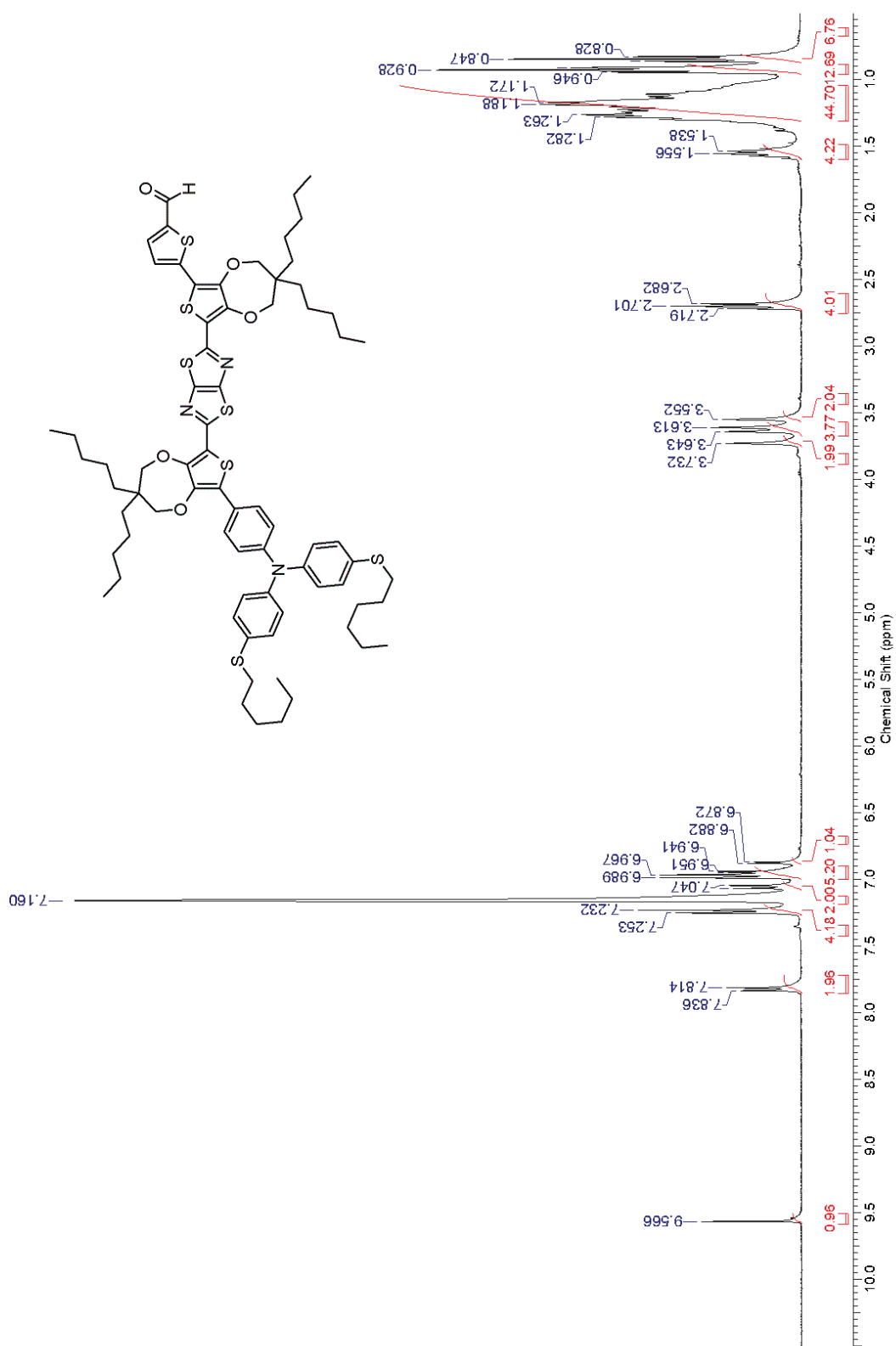


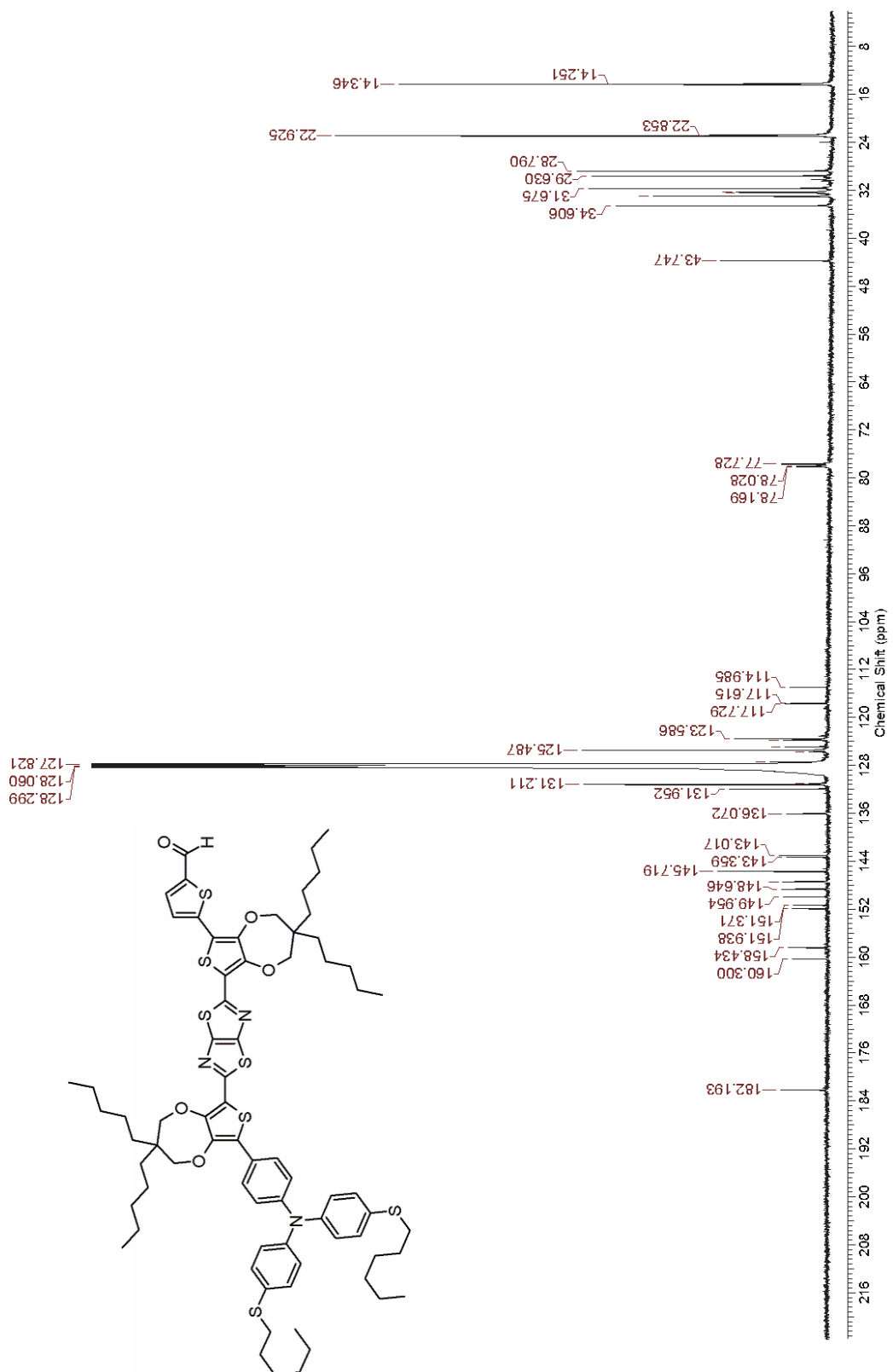


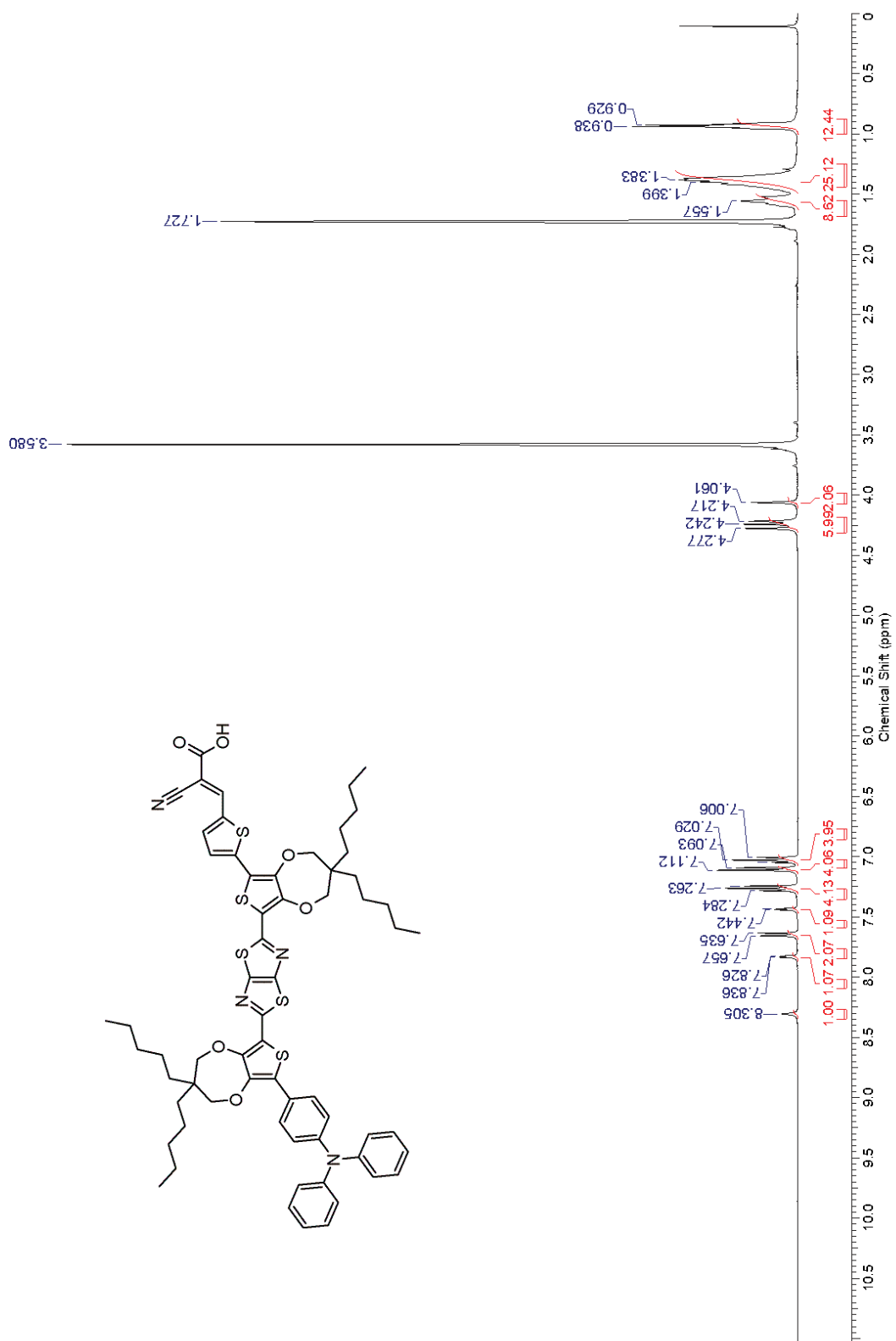


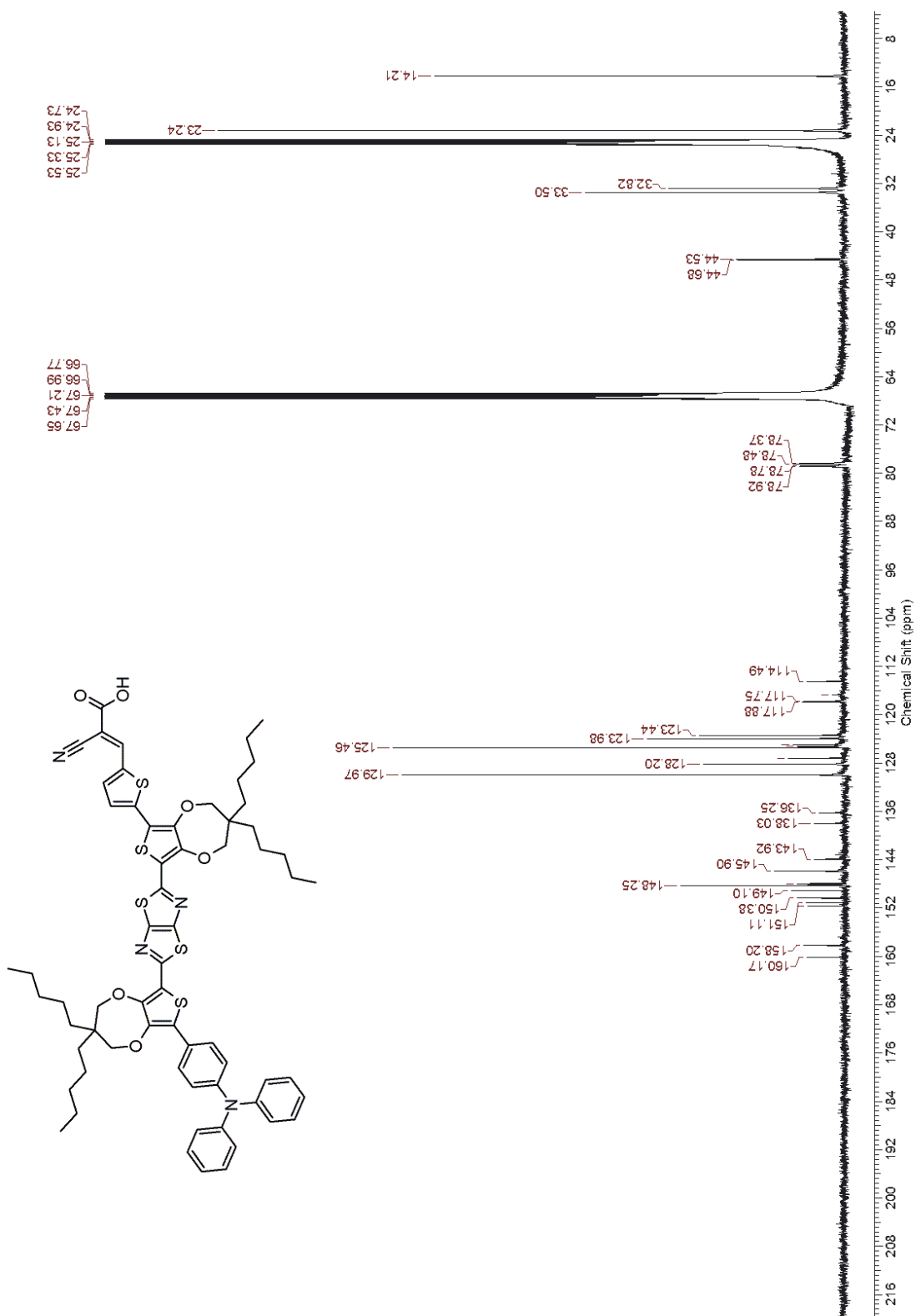


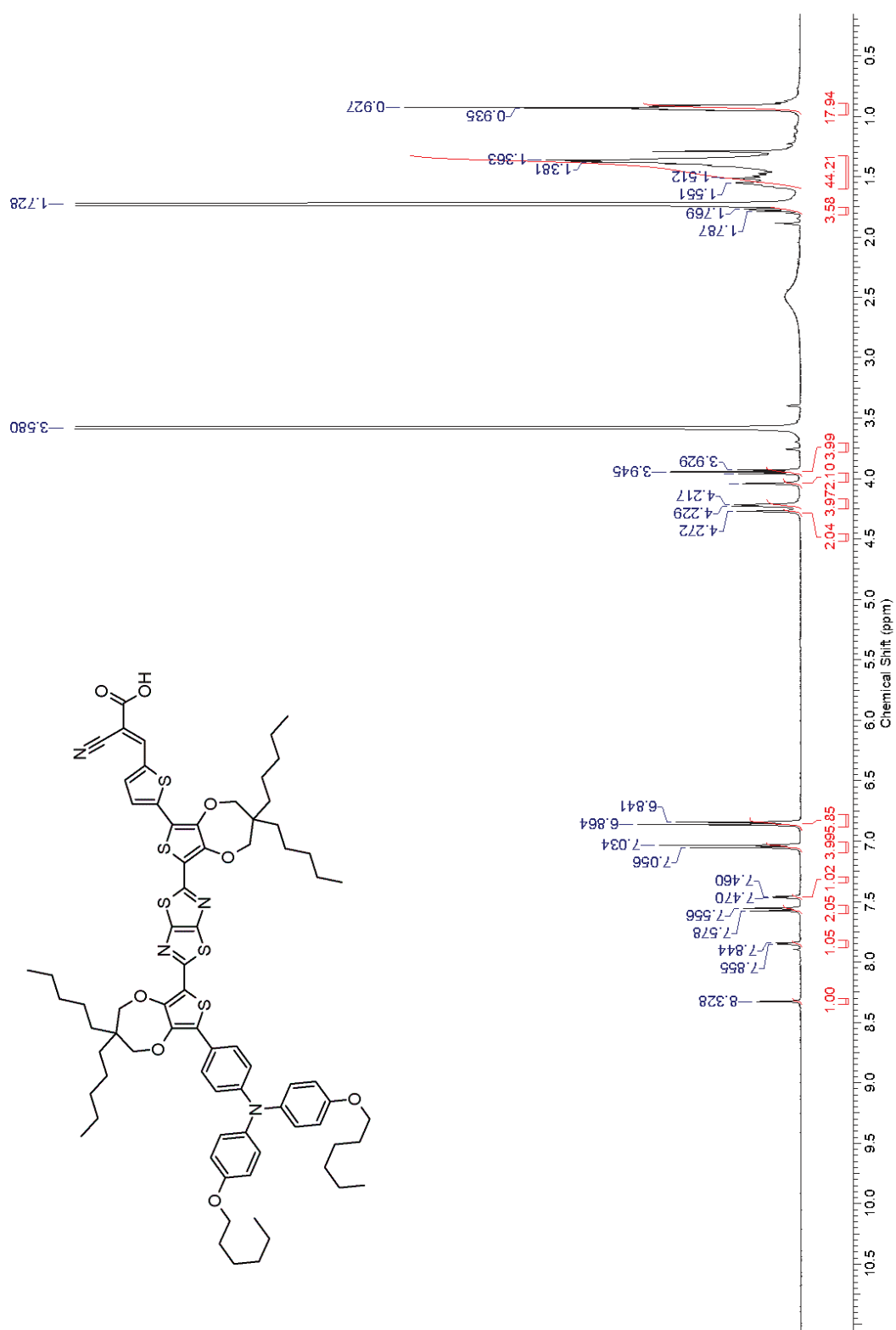


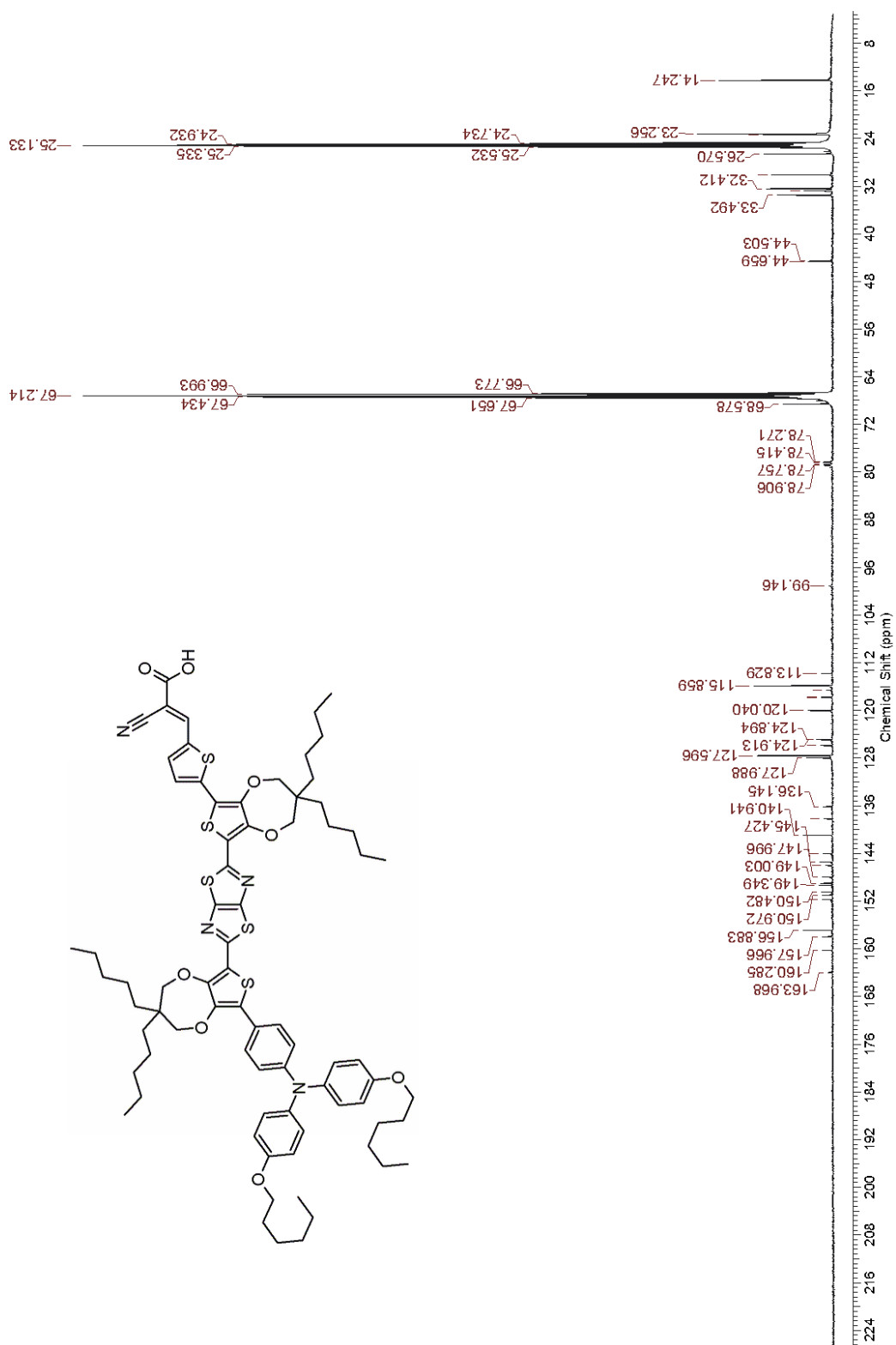


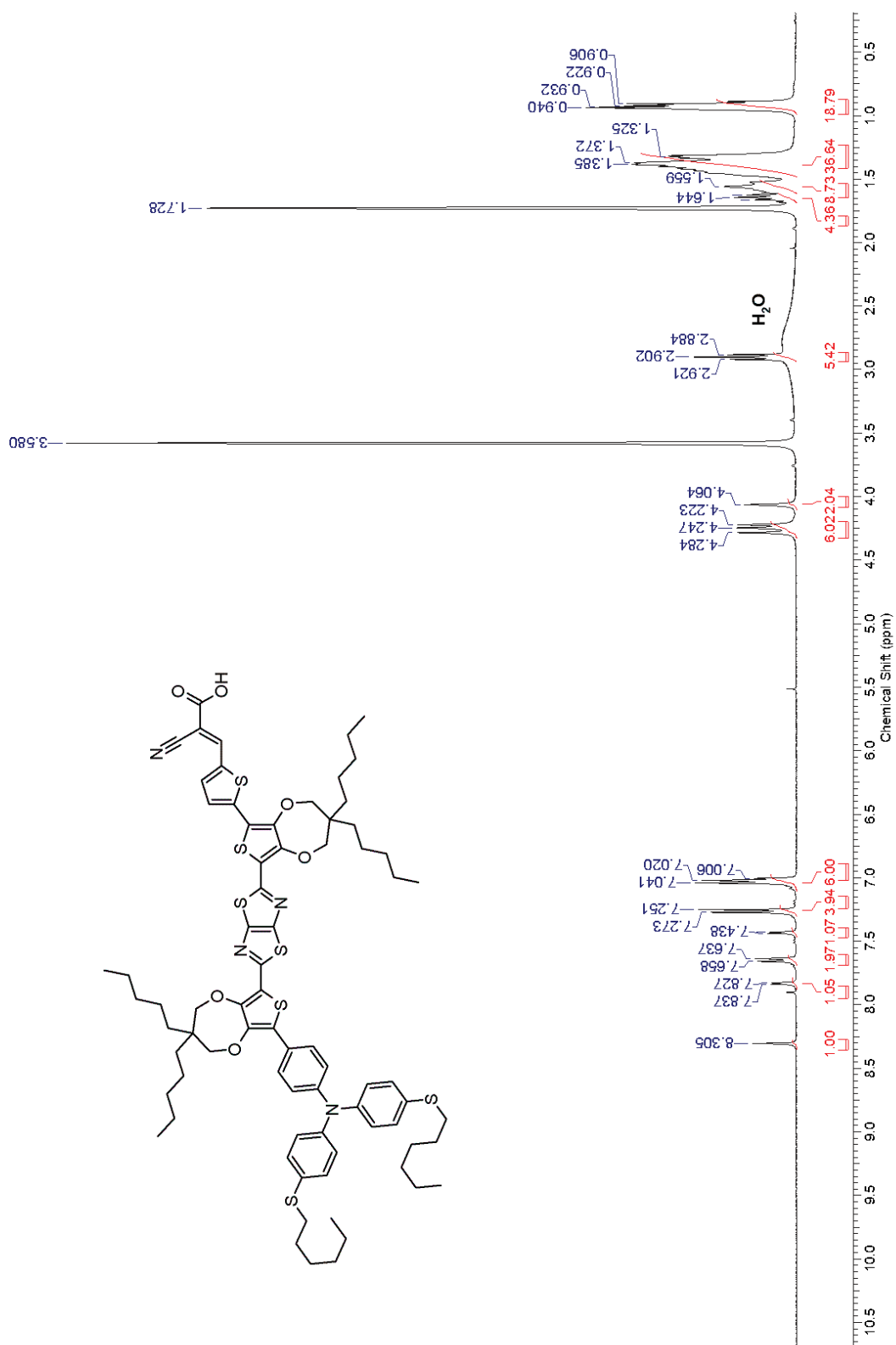


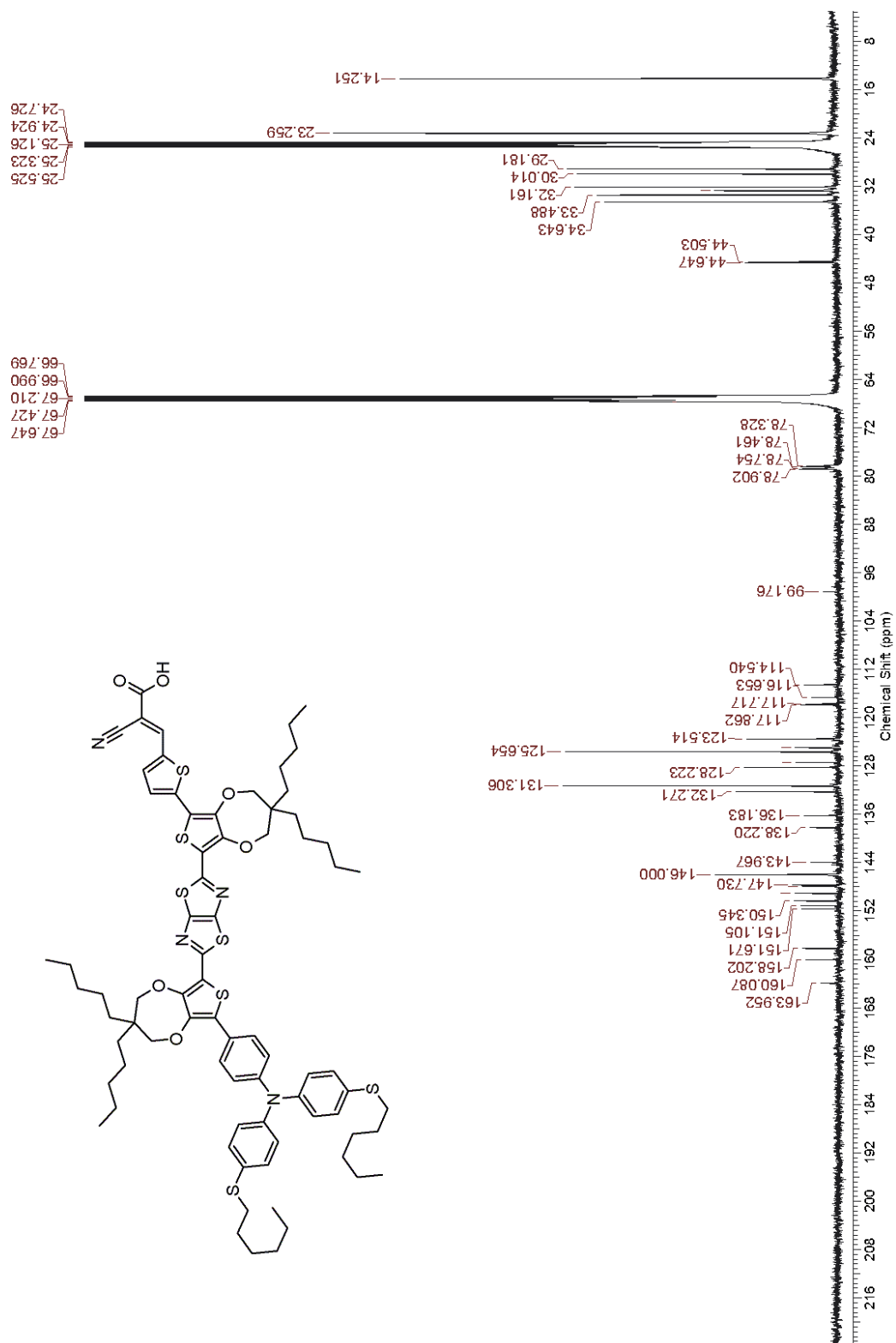












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