

## Supporting Information for

### Thiazolo[5,4-*d*]thiazole-based organic sensitizers with strong visible light absorption for transparent, efficient and stable dye-sensitized solar cells

Alessio Dessì,<sup>[a,b]</sup> Massimo Calamante,<sup>[a,b]</sup> Alessandro Mordini,<sup>[a,b]</sup> Maurizio Peruzzini,<sup>[b]</sup> Adalgisa Sinicropi,<sup>[c]</sup> Riccardo Basosi,<sup>[c]</sup> Fabrizia Fabrizi de Biani,<sup>[c]</sup> Maurizio Taddei,<sup>[c]</sup> Daniele Colonna,<sup>[d]</sup> Aldo di Carlo,<sup>[d,e]</sup> Gianna Reginato<sup>[b]\*</sup> and Lorenzo Zani<sup>[b]\*</sup>

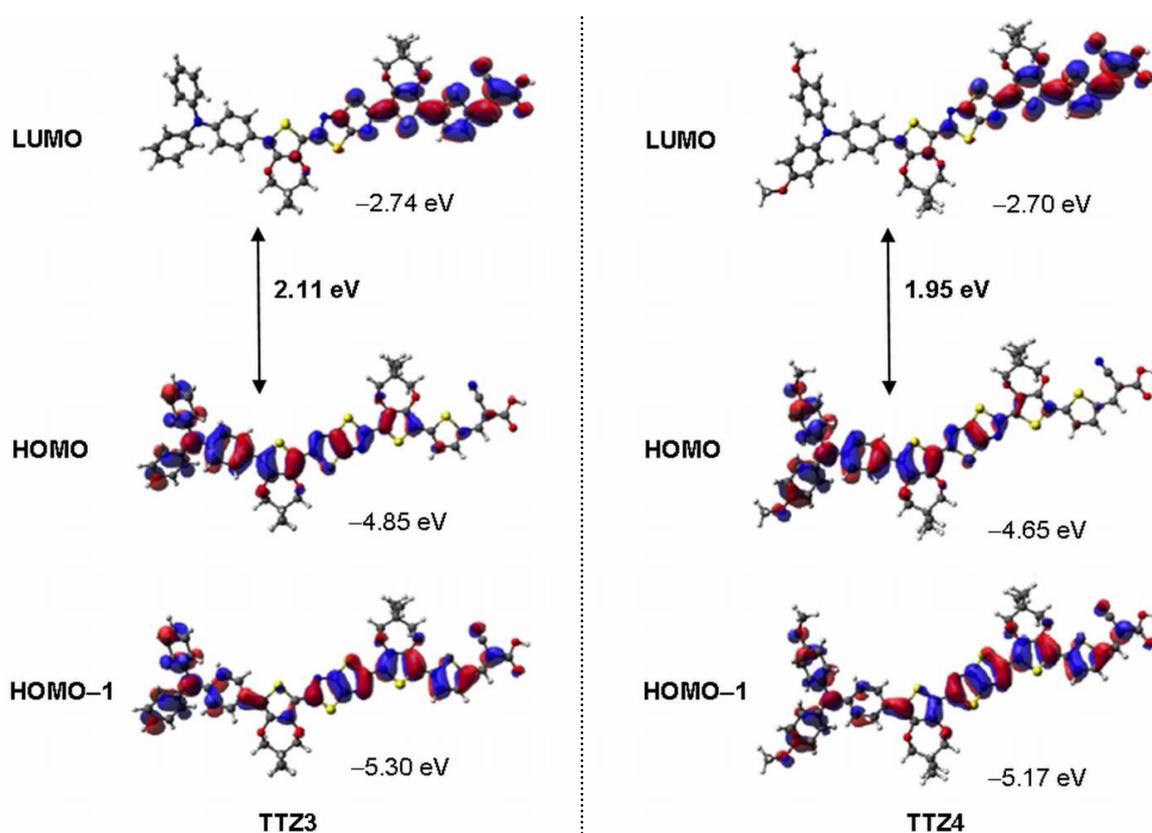
*[a] Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy; [b] Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; [c] Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena, Via A. Moro 2, 53100 Siena, Italy; [d] Dyepower Consortium, Viale Castro Pretorio 122, 00185 Rome, Italy; [e] Center for Hybrid and Organic Solar Energy (C.H.O.S.E.), Dipartimento di Ingegneria Elettronica, Università di Roma "Tor Vergata", Via del Politecnico 1, 00133 Rome, Italy.*

### Table of Contents

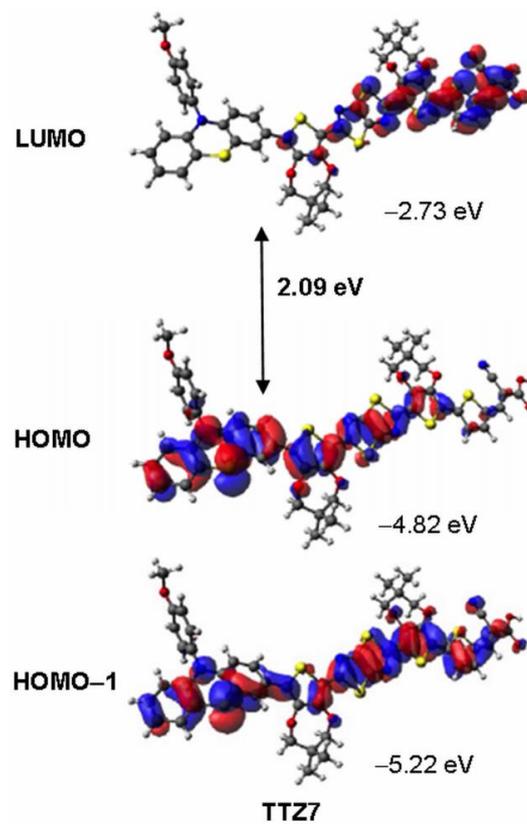
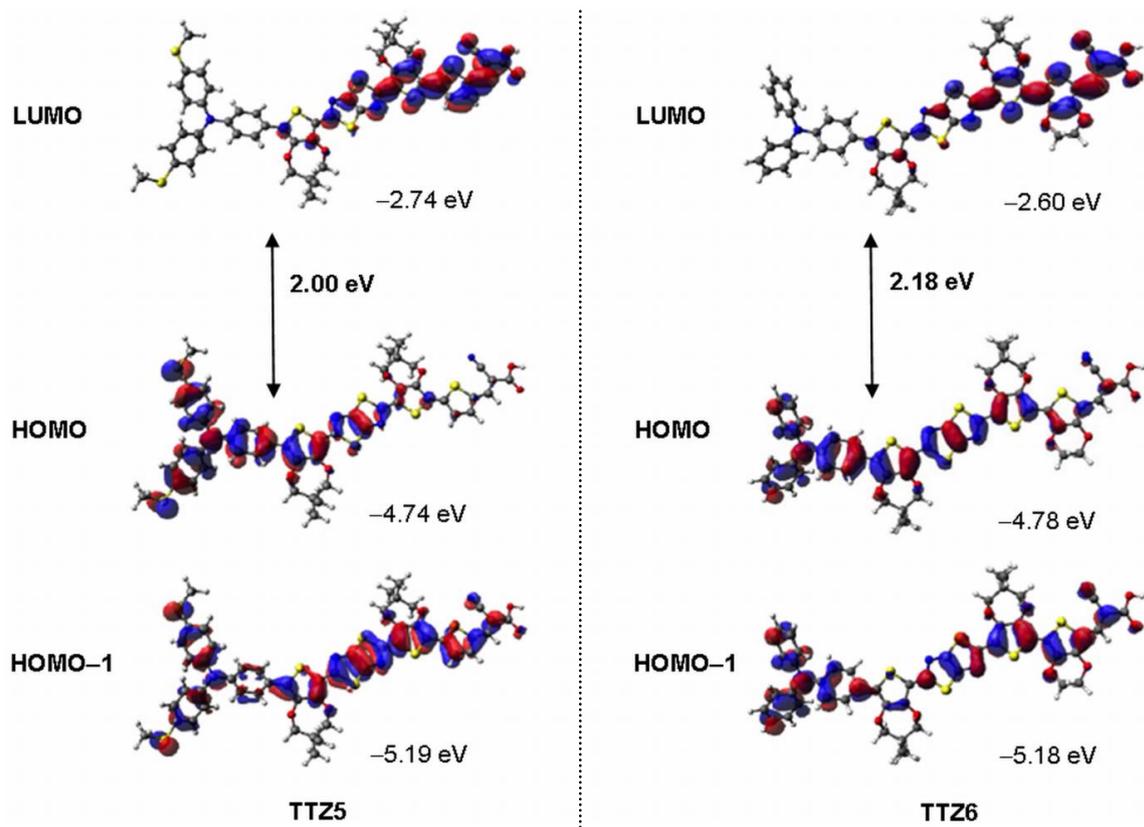
1. Computational analysis	S2
2. General synthetic remarks	S5
3. Synthetic procedures for compounds <b>7</b> , <b>10-12</b> , <b>15</b> , <b>19-20</b> , <b>23</b> and <b>TTZ6-7</b>	S6
4. Characterization of compounds <b>2-6</b> , <b>16-18</b> , <b>TTZ3-5</b>	S10
5. Additional spectroscopic characterization	S14
6. Measurement of the density of adsorbed dyes on TiO <sub>2</sub>	S15
7. Electrochemical characterization	S16
8. Structures of references dyes used in this study	S17
9. Photoelectrochemical measurements	S18
10. EIS Spectra	S22
11. Copies of the <sup>1</sup> H- and <sup>13</sup> C-NMR spectra of compounds <b>7</b> , <b>15</b> , <b>19-20</b> , <b>23</b> and <b>TTZ6-7</b>	S23
12. References	S36

## 1. Computational analysis

DFT calculations were performed with the Gaussian09 program package,<sup>[1]</sup> replacing the alkyl groups originally present on compounds **TTZ3-7** with methyl groups to reduce computational effort. Geometry optimization was carried out *in vacuo* using the B3LYP functional<sup>[2]</sup> and the standard 6-31G\* basis set for all atoms. The absorption maximum ( $\lambda^a_{max}$ ), 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\*<sup>[3]</sup> level. Solvent effects have been included by using the polarizable continuum model (PCM).<sup>[4]</sup>



**Figure S1.** Isodensity plots and computed energies for the frontier molecular orbitals of compounds **TTZ3** and **TTZ4** at the B3LYP/6-31G\* level.



**Figure S1 (continued).** Isodensity plots and computed energies for the frontier molecular orbitals of compounds TTZ5-7 at the B3LYP/6-31G\* level.

**Table S1.** CAMB3LYP/6-31G\* absorption maxima ( $\lambda_{max}^a$ ), oscillator strengths ( $f$ ), vertical excitation energies ( $E_{exc}$ ) and main electronic transitions for dyes **TTZ1** (taken as a reference) and **TTZ3-7** in THF.

Compound	$\lambda_{max}^a$ [nm]	$f$	$E_{exc}$ [eV]	Main transitions (%)
<b>TTZ1</b> <sup>[a]</sup>	482	2.45	2.57	H-1 → L 51.2 H → L 29.2
<b>TTZ3</b>	503	2.61	2.46	H → L 42.0 H-1 → L 38.2
<b>TTZ4</b>	507	2.67	2.45	H-1 → L 47.4 H → L 30.5
<b>TTZ5</b>	504	2.66	2.46	H-1 → L 48.7 H → L 29.3
<b>TTZ6</b>	509	2.54	2.43	H → L 47.0 H-1 → L 36.6
<b>TTZ7</b>	501	2.59	2.47	H → L 45.4 H-1 → L 34.6

[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.<sup>[6]</sup> Solvents used in cross-coupling reactions were previously degassed by means of the “freeze-pump-thaw” method. Microwave-assisted transformations were carried out using a *CEM Discover Bench-Mate* reactor at fixed temperature and variable power. Tetrahydrofuran (THF) was distilled over metallic sodium in the presence of benzophenone, methanol (MeOH) was distilled over metallic magnesium in the presence of a catalytic amount of iodine, CH<sub>2</sub>Cl<sub>2</sub> was distilled over CaH<sub>2</sub>, toluene, diethyl ether and acetonitrile were dried on a resin exchange Solvent Purification System (*MBraun*). Anhydrous *N,N*-dimethylformamide (DMF) and CHCl<sub>3</sub> were stored under nitrogen over 4 Å molecular sieves. 3,3-Dipentyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine-6-carbaldehyde (**1**),<sup>[7]</sup> 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**9**),<sup>[8]</sup> 10-(4-methoxyphenyl)-10*H*-phenothiazine (**13**)<sup>[9]</sup> and 2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (**22**)<sup>[10]</sup> were prepared according to published procedures or slight modifications thereof. The preparation of dyes **TTZ3-5** (and of all the relevant intermediates) was already reported in the preliminary communication preceding this work.<sup>[11]</sup> 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 was performed using Merck Kieselgel 60 (300-400 mesh) as the stationary phase. <sup>1</sup>H-NMR spectra were recorded at 300 or 400 MHz, and <sup>13</sup>C-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 (CDCl<sub>3</sub>, δ 7.26 ppm for <sup>1</sup>H-NMR and δ 77.16 ppm for <sup>13</sup>C-NMR; THF-*d*<sub>8</sub> δ 1.72 and 3.58 ppm for <sup>1</sup>H-NMR, δ 67.21 and 25.31 ppm for <sup>13</sup>C-NMR; C<sub>6</sub>D<sub>6</sub>, δ 7.16 ppm for <sup>1</sup>H-NMR, δ 128.06 ppm for <sup>13</sup>C-NMR). FT-IR spectra were recorded with a *Perkin-Elmer Spectrum BX* instrument in the range 4000–400 cm<sup>-1</sup> with a 2 cm<sup>-1</sup> resolution. GC-MS spectra were measured with a *Shimadzu* gas-chromatograph (*GC-17A* or *GC-2010*) connected to a *Shimadzu* mass spectrometer (*MS-QP2010S* or *MS-QP5050a*) and are reported in the form *m/z* (intensity relative to base = 100). ESI-MS spectra were obtained by direct injection of the sample solution using a *Thermo Scientific* LCQ-FLEET instrument. 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 *Thermo Finnigan* Elemental Analyser; the results were found to be in good agreement with the calculated values. Melting points are uncorrected.

### 3. Synthetic Procedures for Compounds 7, 10-12, 15, 19-20, 23 and TTZ6-7

**4-(Hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-phenylaniline (10):** 1-Bromo-4-hexylthiobenzene (4.74 g, 17.3 mmol)<sup>[12a]</sup> was dissolved in toluene (55 mL). The solution was degassed, then Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (300 mg, 0.29 mmol) and 1,1'-bis-(diphenylphosphino)ferrocene (321 mg, 0.57 mmol) were added. The mixture was stirred for 15 min at room temperature while the color turned from black to red, then aniline (539 mg, 5.79 mmol) and sodium *tert*-butoxide (2.22 g, 23.1 mmol) were added. The reaction mixture was heated to reflux and stirred for 20 h. After cooling and filtration over Celite<sup>®</sup>, the resulting solution was diluted with Et<sub>2</sub>O (200 mL), washed with water (150 mL) and brine (200 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. Filtration, removal of the solvent and purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/toluene, gradient from 10:1 to 5:1) gave compound **10** (2.22 g, 4.65 mmol, 80% yield) as a pale yellow oil. (**10**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.21 (d, *J* = 8.5 Hz, 4H), 7.04 (m, 4H), 6.95 (d, *J* = 8.5 Hz, 4H), 6.84 (m, 1H), 2.67 (t, *J* = 7.2 Hz, 4H), 1.53 (q, *J* = 7.5 Hz, 4H), 1.05–1.32 (m, 12H), 0.83 (t, *J* = 7.1 Hz, 6H) ppm. The analytical data were in agreement with those reported in the literature.<sup>[12b]</sup>

**4-Bromo-*N,N*-bis(4-(hexylthio)phenyl)aniline (11):** compound **10** (1.53 g, 3.20 mmol), was dissolved in dry CHCl<sub>3</sub> (30 mL) together with *N*-bromosuccinimide (569 mg, 3.20 mmol). The brown solution was stirred at room temperature in the dark for 4 hours, while the color turned to pale yellow, then diluted with CHCl<sub>3</sub> (100 mL), washed with water (150 mL) and brine (200 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent gave compound **11** (1.75 g, 3.15 mmol, 98% yield) as a pale orange oil, which was used for the following reaction without further purification. (**11**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.20 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 4H), 1.54 (q, *J* = 7.4 Hz, 4H), 1.06–1.32 (m, 12H), 0.83 (t, *J* = 7.1 Hz, 6H) ppm. The analytical data were in agreement with those reported in the literature.<sup>[12b]</sup>

**4-(Hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (12):** compound **11** (1.23 g, 2.20 mmol) was dissolved in anhydrous *N,N*-DMF (20 mL). The solution was degassed, then Pd(dppf)Cl<sub>2</sub> (161 mg, 0.22 mmol), *bis*(pinacolato)diboron (838 mg, 3.30 mmol) and potassium acetate (648 mg, 6.60 mmol) were added. The reaction mixture was warmed at 80°C and stirred for 16 h, then filtered over Celite<sup>®</sup>. The filtrate was diluted with ethyl acetate (200 mL), washed with water (6 × 150 mL) and brine (200 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. Filtration, evaporation of the solvent and purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/toluene, gradient from 1:1 to 1:2) gave compound **12** (788 mg, 1.31 mmol, 60% yield) as a light green oil. (**12**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.66 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 4H), 6.98–7.03 (m, 6H), 2.88 (t, *J* = 7.4 Hz, 4H), 1.64 (q, *J* = 7.5 Hz, 4H), 1.37–1.46 (m, 4H), 1.33 (s, 12H), 1.24–1.32 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 6H) ppm. Analytical data were in agreement with those found in the literature.<sup>[12b]</sup>

**Synthesis of 10-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (15).** 10-(4-Methoxyphenyl)-3-bromo-10H-phenothiazine (**14**): 10-(4-methoxyphenyl)-10H-phenothiazine<sup>[9]</sup> (**13**, 3.05 g, 10.0 mmol) was dissolved in a mixture of dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and dry CH<sub>3</sub>CN (60 mL), and treated with pyridinium bromide perbromide<sup>[13]</sup> (2.72 g, 8.50 mmol, 0.85 eq.), which was added in four portions during 20 minutes. The reaction mixture was stirred at room temperature for 10 minutes, the solvents were removed and ethyl acetate (150 mL) was added. The organic phase was washed with a saturated aqueous solution of NaHCO<sub>3</sub> (100 mL), water (100 mL) and brine (100 mL). After anhydridification with Na<sub>2</sub>SO<sub>4</sub>, filtration and removal of the solvent, the crude product was purified by flash column chromatography (SiO<sub>2</sub>, petroleum ether/toluene 3:1). Purification yielded a 3:1 mixture of the title compound and starting material, which was used as such in the next step. (**14**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.06 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 7.4 Hz, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.77 (dd, *J* = 8.8 Hz, *J* = 2.3 Hz, 1H), 6.54–6.70 (m, 4H), 6.17 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 8.8 Hz, 1H), 3.24 (s, 3H) ppm.

10-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**15**): in a Schlenk tube equipped with a magnetic stirrer were placed anhydrous degassed *N,N*-DMF (20 mL) and the 3:1 mixture of compounds resulting from the previous step (corresponding to 2.00 g, 3.86 mmol of 10-(4-Methoxyphenyl)-3-bromo-10H-phenothiazine **14**). [Pd(dppf)Cl<sub>2</sub>] (283 mg, 0.39 mmol, 0.1 eq.), *bis*(pinacolato)diboron (1.47 g, 5.79 mmol, 1.5 eq.) and potassium acetate (1.14 g, 11.6 mmol, 3.0 eq.) were added and the resulting brown mixture was stirred for 16 hours at 80°C. After cooling to room temperature and filtration over Celite<sup>®</sup>, the reaction mixture was diluted with ethyl acetate (150 mL). The organic phase was washed with H<sub>2</sub>O (5 × 100 mL) and brine (2 × 100 mL), then dried with Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave a brown oil which was purified by flash column chromatography (SiO<sub>2</sub>, toluene) to give compound **15** (1.38 g, 3.20 mmol, 83% yield) as a colorless solid. (**15**): mp = 197–199 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 8.03 (d, *J* = 1.4 Hz, 1H), 7.73 (dd, *J* = 8.2 Hz, *J* = 1.3 Hz, 1H), 6.87 (dd, *J* = 7.3 Hz, *J* = 1.9 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.54–6.59 (m, 2H), 6.35 (d, *J* = 8.2 Hz, 1H), 6.16 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 3.20 (s, 3H), 1.09 (s, 12H) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 159.5, 147.7, 144.8, 134.4, 134.1, 133.3, 132.3, 127.1, 126.9, 123.0, 120.6, 119.6, 116.3, 116.1, 115.5, 83.6, 54.9, 24.9 ppm. IR (KBr): ν = 3058, 2976, 2924, 1598, 1510, 1351, 1295, 1143, 1032 cm<sup>-1</sup>. ESI-MS: *m/z* = 431.33 [M]<sup>+</sup>.

**3-(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)-10-(4-methoxyphenyl)-10H-phenothiazine (7).** 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) and mixed with Pd(dppf)Cl<sub>2</sub> (56 mg, 0.08 mmol, 0.1 eq.), 10-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (**15**) (329 mg, 0.76 mmol, 1.0 eq.), KF (222 mg, 3.82 mmol, 5.0 eq.) and ethanol (15 mL). After stirring at 78°C for 5h, a second portion of Pd(dppf)Cl<sub>2</sub> (28 mg, 0.04 mmol, 0.05 eq.) was added and the reaction was continued for further 16 h. Work-up and evaporation of the solvent gave a dark-red oil, which was purified by flash column

chromatography (SiO<sub>2</sub>, petroleum ether/toluene 2:1 to 1:1) to give compound **7** (102 mg, 0.09 mmol, 12% yield) as a sticky orange solid, as well as starting material **3** (117 mg, 16% recovery). (**7**): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.85 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.7 Hz, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.91 (dd, *J* = 7.5 Hz, *J* = 1.6 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.63–6.69 (m, 1H), 6.57–6.61 (m, 1H), 6.23 (dd, *J* = 8.2 Hz, *J* = 1.2 Hz, 1H), 6.19 (d, *J* = 8.7 Hz, 1H), 3.72 (s, 2H), 3.58 (s, 4H), 3.51 (s, 2H), 3.29 (s, 3H), 0.98–1.36 (m, 32H), 0.93 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 6H) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 160.0, 159.7, 158.7, 152.4, 151.3, 151.0, 149.7, 147.0, 145.6, 144.8, 144.5, 133.4, 132.5, 127.1, 125.9, 125.4, 123.8, 122.9, 120.7, 120.1, 116.2, 114.8, 78.0, 77.8, 77.7, 77.6, 61.3, 55.1, 43.74, 43.71, 33.0, 32.9, 32.4, 32.1, 23.0, 22.9, 22.8, 22.7, 14.4, 14.3 ppm. IR (KBr): ν = 3064, 2928, 2857, 1510, 1461, 1057 cm<sup>-1</sup>. ESI-MS: *m/z* = 1160.06 [M]<sup>+</sup>.

**5-(8-(5-(8-(10-(4-Methoxyphenyl)-10H-phenothiazin-2-yl)-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 (20).** Compound **7** (97 mg, 0.08 mmol) was dissolved in anhydrous toluene together with PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (3.0 mg, 0.004 mmol, 0.05 eq.) and introduced in a microwave vial equipped with a magnetic stirrer. 5-Formyl-2-thiopheneboronic acid **21** (19 mg, 0.12 mmol, 1.5 eq.) and KF (29 mg, 0.50 mmol, 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<sub>2</sub>Cl<sub>2</sub> (30 mL), the layers were separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The combined organic layers were washed with brine (50 mL) and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent *in vacuo* yielded a black solid, which was purified by flash column chromatography (SiO<sub>2</sub>; Toluene) to give compound **20** (70 mg, 0.06 mmol, 73% yield) as a dark-red solid. (**20**): mp = 232–235 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 9.57 (s, 1H), 7.87 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.7 Hz, *J* = 2.1 Hz, 1H), 6.90–6.97 (m, 4H), 6.88 (d, *J* = 4.0 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.64–6.69 (m, 1H), 6.56–6.62 (m, 1H), 6.25 (dd, *J* = 8.2 Hz, *J* = 1.2 Hz, 1H), 6.20 (d, *J* = 8.6 Hz, 1H), 3.72 (s, 2H), 3.61 (s, 2H), 3.57 (s, 2H), 3.54 (s, 2H), 3.29 (s, 3H), 1.15–1.36 (m, 24H), 1.00–1.13 (m, 8H), 0.94 (t, *J* = 7.2 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 6H) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 182.2, 160.3, 159.7, 158.3, 152.0, 151.3, 150.0, 148.6, 147.5, 145.7, 144.8, 144.6, 143.4, 143.0, 136.1, 133.3, 132.4, 127.2, 125.9, 125.4, 124.2, 123.8, 123.0, 120.8, 120.0, 117.7, 116.22, 116.19, 114.7, 78.2, 78.0, 77.8 (×2), 55.0, 43.72, 43.70, 33.01, 32.96, 32.4, 32.2, 23.0, 22.9, 22.83, 22.77, 14.4 ppm. IR (KBr): ν = 3064, 2929, 2857, 1661, 1439, 1055 cm<sup>-1</sup>. ESI-MS: *m/z* = 1158.20 [M+CH<sub>3</sub>]<sup>+</sup>.

**7-(Tributylstannyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (23).** 2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (**22**, 900 mg, 5.29 mmol)<sup>[10]</sup> was dissolved in a mixture of anhydrous chloroform (10 mL) and anhydrous methanol (25 mL). Trimethyl orthoformate (842 mg, 7.93 mmol, 1.5 eq.) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 60 mg, 0.26 mmol, 0.05 eq.) were added and the reaction mixture was stirred at 50°C for 2 h. The solvent was removed and anhydrous THF (30 mL) was added. The resulting solution was cooled to –78°C and reacted with *n*-BuLi (1.6 M solution in hexanes, 4.96 mL, 7.93 mmol, 1.5 eq.). After

stirring at  $-78^{\circ}\text{C}$  for 2 h, tributylstannyl chloride (3.44 g, 10.6 mmol, 2.0 eq.) was added. The reaction mixture was warmed to room temperature and stirred for 16 h, then  $\text{KHSO}_4$  was added (40 mL, 2.5 M solution in water) and stirring was continued for further 2 h. After dilution with  $\text{CH}_2\text{Cl}_2$  (150 mL) and  $\text{Na}_2\text{CO}_3$  (150 mL, 0.1 M solution in water), the layers were separated and the organic phase washed with brine (100 mL) and dried with  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent yielded a dark oil, which was purified by column chromatography ( $\text{SiO}_2$ ; petroleum ether/AcOEt 8:1) to afford compound **23** (1.62 g, 3.53 mmol, 67% yield) as a light yellow oil. (**23**):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.80 (s, 1H), 4.29–4.34 (m, 2H), 4.20–4.24 (m, 2H), 1.52–1.59 (m, 6H), 1.28–1.36 (m, 6H), 1.12–1.19 (m, 6H), 0.85–0.93 (m, 9H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 179.4, 148.5, 147.6, 125.5, 124.0, 65.3, 64.4, 29.0, 27.3, 13.8, 10.9 ppm. IR (KBr):  $\nu$  = 2957, 2924, 2846, 1649, 1469, 1083  $\text{cm}^{-1}$ . ESI-MS:  $m/z$  = 461.08  $[\text{M}+1]^+$ .

**7-(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)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (19)**. Compound **4** (200 mg, 0.18 mmol) was dissolved in toluene (8.0 mL) together with 7-tributylstannyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (**23**) (125 mg, 0.27 mmol, 1.5 eq.), and  $[\text{Pd}(\text{PPh}_3)_4]$  (11 mg, 0.009 mmol, 0.05 eq.). The resulting mixture was stirred at  $110^{\circ}\text{C}$  for 24h, then it was allowed to cool to room temperature and diluted with  $\text{H}_2\text{O}$  (150 mL) and  $\text{CH}_2\text{Cl}_2$  (150 mL). The phases were separated and the organic layer was washed with brine (200 mL) and dried with  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation of the solvent, a dark-red oil was obtained, which was purified by flash column chromatography ( $\text{SiO}_2$ ; Toluene) to give compound **19** (154 mg, 0.13 mmol, 74% yield) as a dark red solid. (**19**): mp =  $305\text{--}306^{\circ}\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.87 (s, 1H), 7.62 (d,  $J$  = 9.0 Hz, 2H), 7.25–7.32 (m, 4H), 7.10–7.17 (m, 4H), 7.10–7.17 (m, 4H), 4.43 (s, 4H), 4.16 (s, 2H), 4.14 (s, 2H), 4.09 (s, 2H), 4.02 (s, 2H), 1.43–1.59 (m, 8H), 1.26–1.40 (m, 24H), 0.86–0.994 (m, 12H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 180.0, 159.7, 158.5, 150.9, 150.5, 149.5, 147.9, 147.8, 147.5, 147.1, 145.1, 137.7, 129.5, 127.7, 126.3, 125.0, 124.5, 123.5, 123.0, 121.0, 117.9, 116.3, 115.4, 113.7, 78.4, 78.3, 78.0, 77.9, 65.4, 65.0, 44.1, 44.0, 32.8, 32.7, 32.3, 32.1, 29.8, 22.7, 14.2 ppm. IR (KBr):  $\nu$  = 3034, 2928, 2857, 1638, 1459, 1061  $\text{cm}^{-1}$ . ESI-MS:  $m/z$  = 1142.37  $[\text{M}]^+$ .

#### General procedure for Knoevenagel condensation with cyanoacetic acid

In a Schlenk flask equipped with a magnetic stirrer aldehyde **19-20** (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  $110^{\circ}\text{C}$  for 6 h, then cooled to room temperature and diluted with  $\text{CHCl}_3$  (150 mL). The organic phase was washed with a saturated solution of  $\text{NaHCO}_3$  (100 mL) and brine (100 mL), and then it was dried with  $\text{Na}_2\text{SO}_4$ . 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-(7-(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)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)acrylic acid (TTZ6).** Aldehyde **19** (102 mg, 0.09 mmol), cyanoacetic acid (76 mg, 0.89 mmol, 10.0 eq.) and ammonium acetate (28 mg, 0.36 mmol, 4.0 eq.) were dissolved in toluene (3.0 mL) and glacial acetic acid (4.0 mL). The reaction mixture was stirred at 110°C for 3 h. Work-up and purification afforded compound **TTZ6** (102 mg, 0.08 mmol, 94% yield) as a dark amorphous solid. (**TTZ6**): mp = 292–294 °C. <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>): δ = 8.30 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.27 (m, 4H), 7.10 (d, *J* = 7.7 Hz, 4H), 7.04 (m, 4H), 4.49 (s, 4H), 4.25 (s, 4H), 4.18 (s, 2H), 4.07 (s, 2H), 1.48–1.64 (m, 8H), 1.32–1.46 (m, 24H), 0.87–0.99 (m, 12H). IR (KBr): ν = 3025, 2928, 2578, 2217, 1689, 1058 cm<sup>-1</sup>. ESI-MS: *m/z* = 1209.42 [M]<sup>+</sup>. Anal. calcd. for C<sub>66</sub>H<sub>72</sub>N<sub>4</sub>O<sub>8</sub>S<sub>5</sub>: C, 65.53; H, 6.00; N, 4.63. Found: C, 66.17; H, 6.35; N, 4.32.

*Note: due to its limited solubility in a vast range of organic solvents, a <sup>13</sup>C-NMR spectrum of compound TTZ6 could not be recorded.*

**2-Cyano-3-(5-(8-(5-(8-(10-(4-methoxyphenyl)-10H-phenothiazin-3-yl)-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 (TTZ7).** Aldehyde **20** (70 mg, 0.06 mmol), cyanoacetic acid (52 mg, 0.61 mmol, 10.0 eq.) and ammonium acetate (19 mg, 0.24 mmol, 4.0 eq.) were dissolved in toluene (3.0 mL) and glacial acetic acid (3.0 mL). The reaction mixture was stirred at 110°C for 5 h. Work-up and purification afforded compound **TTZ7** (67 mg, 0.05 mmol, 91% yield) as a dark solid. (**TTZ7**): mp = 277–279 °C. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ = 8.30 (s, 1H), 7.83 (d, *J* = 4.1 Hz, 1H), 7.43 (d, *J* = 4.1 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.17–7.24 (m, 3H), 6.95 (dd, *J* = 7.3 Hz, *J* = 1.6 Hz, 1H), 6.75–6.82 (m, 2H), 6.18 (d, *J* = 8.9 Hz, 1H), 6.15 (d, *J* = 8.7 Hz, 1H), 4.27 (s, 2H), 4.23 (s, 2H), 4.21 (s, 2H), 4.05 (s, 2H), 3.82 (s, 3H), 1.50–1.63 (m, 8H), 1.25–1.46 (m, 24H), 0.89–0.96 (m, 12H) ppm. <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>): δ = 164.0, 160.6, 160.1, 158.1, 151.7, 151.1, 150.3, 149.1, 148.0, 146.0, 145.9, 144.9, 144.8, 144.0, 138.2, 136.2, 133.7, 132.8, 127.6, 127.5, 127.1, 125.9, 124.9, 124.8, 124.2, 123.1, 120.6, 119.9, 117.9, 117.8, 116.7, 116.4, 116.2, 114.4, 99.2, 78.9, 78.8, 78.5, 78.4, 55.6, 44.7, 44.5, 33.8, 33.52, 33.49, 32.8, 31.6, 30.5, 23.3, 14.3 ppm. IR (KBr): ν = 2957, 2862, 2213, 1560, 1415, 1096 cm<sup>-1</sup>. ESI-MS: *m/z* = 1211.34 [M]<sup>+</sup>. Anal. calcd. for C<sub>65</sub>H<sub>70</sub>N<sub>4</sub>O<sub>7</sub>S<sub>6</sub>: C, 64.43; H, 5.82; N, 4.62. Found: C, 63.97; H, 5.90; N, 4.58.

#### 4. Characterization of compounds 2-6, 16-18, TTZ3-5 (Reproduced from ref.[11])

**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).** Light brown solid; mp = 207–208 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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): ν = 3100, 2930, 2860, 1500, 1039 cm<sup>-1</sup>. ESI-MS: *m/z* = 731.32 [M]<sup>+</sup>.

**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).** Yellow solid; mp = 228–230 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>):  $\delta$  = 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):  $\nu$  = 2929, 2858, 1492, 1370, 1057 cm<sup>-1</sup>. ESI-MS:  $m/z$  = 983.09 [M]<sup>+</sup>

**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).** Orange solid; mp = 91–93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 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. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 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):  $\nu$  = 3058, 2927, 2857, 1590, 1491, 1057 cm<sup>-1</sup>. ESI-MS:  $m/z$  = 1100.26 [M+1]<sup>+</sup>

**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).** Amorphous orange solid; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 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. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 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):  $\nu$  = 2952, 2925, 2852, 1602, 1508, 1060 cm<sup>-1</sup>. ESI-MS:  $m/z$  = 1300.52 [M+1]<sup>+</sup>

**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).** Amorphous orange solid; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 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. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 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):  $\nu$  = 3025, 2928, 2857, 1587, 1490, 1060 cm<sup>-1</sup>. ESI-MS:  $m/z$  = 1332.11 [M+1]<sup>+</sup>

**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 (16).** Dark red solid; mp = 229–231 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 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. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 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):  $\nu = 3025, 2928, 2857, 1654, 1054 \text{ cm}^{-1}$ . 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 (17).** Amorphous dark red solid;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 9.57$  (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.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 182.2, 160.6, 158.2, 156.4, 152.0, 151.2, 150.2, 149.1, 148.6, 147.5, 145.3, 143.4, 143.0, 140.9, 136.1, 127.3, 126.6, 125.8, 125.2, 123.8, 120.6, 117.7, 117.6, 115.8, 114.3, 78.1, 78.0, 77.7, 77.6, 68.2, 43.7, 33.0, 32.9, 32.3, 32.2, 32.0, 30.2, 29.7, 26.1, 23.0, 22.9, 22.8, 22.7, 14.3, 14.2$  ppm. IR (KBr):  $\nu = 3036, 2929, 2857, 1655, 1438, 1054 \text{ cm}^{-1}$ . ESI-MS:  $m/z = 1285.40 [M+1]^+$ .

**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 (18).** Amorphous dark red solid;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 9.57$  (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.  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 182.2, 160.3, 158.4, 151.9, 151.4, 150.0, 148.7, 147.5, 147.4, 145.7, 143.4, 143.0, 136.1, 132.0, 131.2, 131.0, 127.4, 125.7, 125.5, 124.9, 123.8, 123.6, 117.7, 117.6, 115.0, 78.2, 78.0, 77.7, 43.8, 34.6, 33.0, 32.96, 32.4, 32.3, 31.7, 29.6, 28.8, 22.95, 22.93, 22.85, 22.78, 14.4, 14.3$  ppm. IR (KBr):  $\nu = 3025, 2924, 2852, 1653, 1438, 1057 \text{ cm}^{-1}$ . ESI-MS:  $m/z = 1315.27 [M]^+$ .

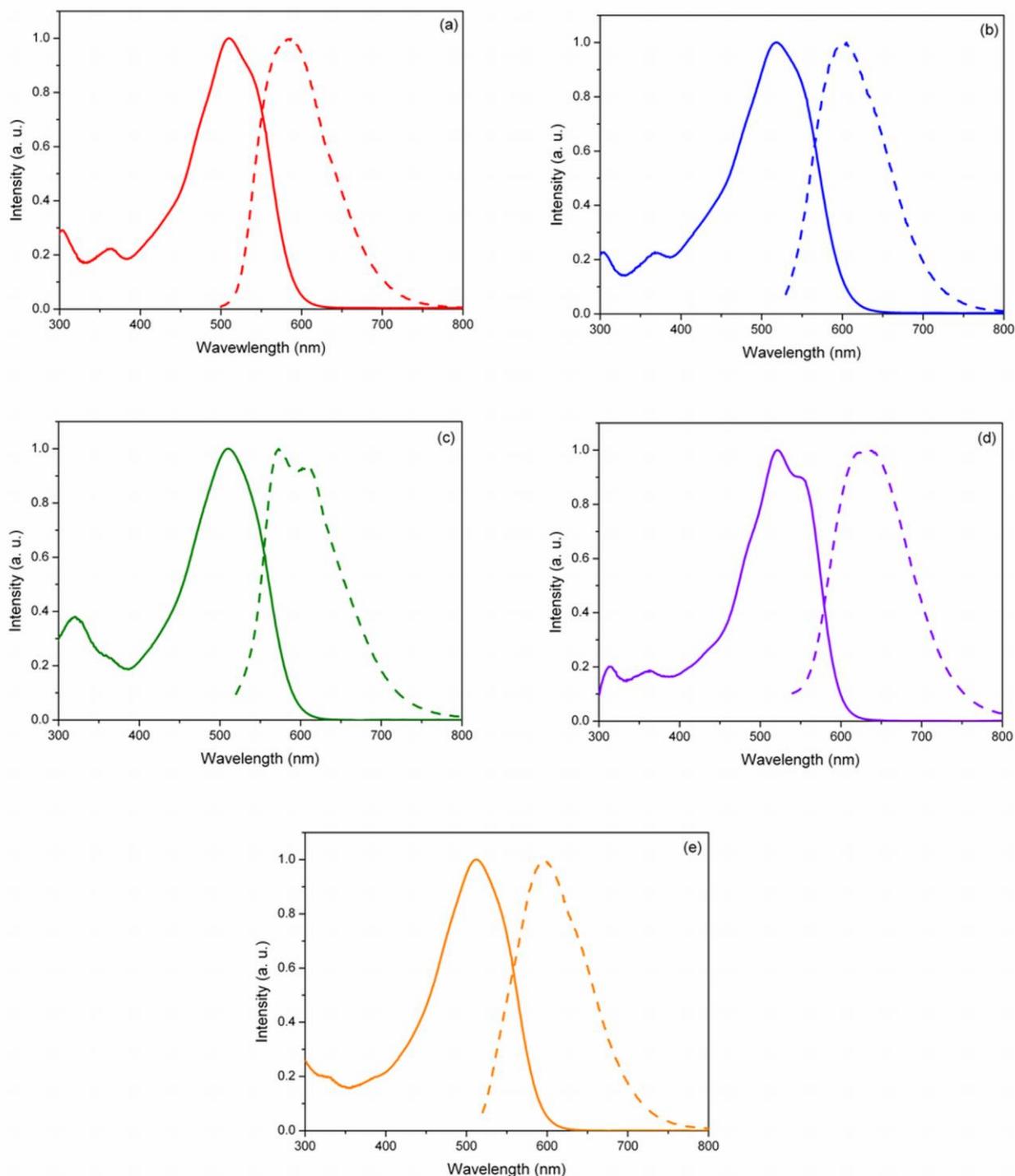
**2-Cyano-3-(5-(8-(5-(8-(4-(diphenylamino)phenyl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiazolo[5,4-*d*]thiazol-2-yl)-3,3-dipentyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepin-6-yl)thiophen-2-yl)acrylic acid (TTZ3).** Dark solid; mp = 288–291 °C.  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta = 8.31$  (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.  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta = 160.2, 158.2, 151.7, 151.1, 150.4, 149.1, 148.3, 148.0, 145.9, 143.9, 138.0, 136.3, 130.0, 128.2, 127.2, 125.5, 125.2, 125.0, 124.0, 123.4, 117.9, 117.8, 116.7, 116.6, 114.5, 78.9, 78.8, 78.5, 78.4, 44.7, 44.5, 33.50, 33.48, 32.8, 23.2, 14.2$  ppm. IR (KBr):  $\nu = 3025, 2928, 2578, 2217, 1689, 1058 \text{ cm}^{-1}$ . ESI-MS:  $m/z = 1151.47 [M]^+$ . 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).** Amorphous dark solid;  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta = 8.33$  (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),

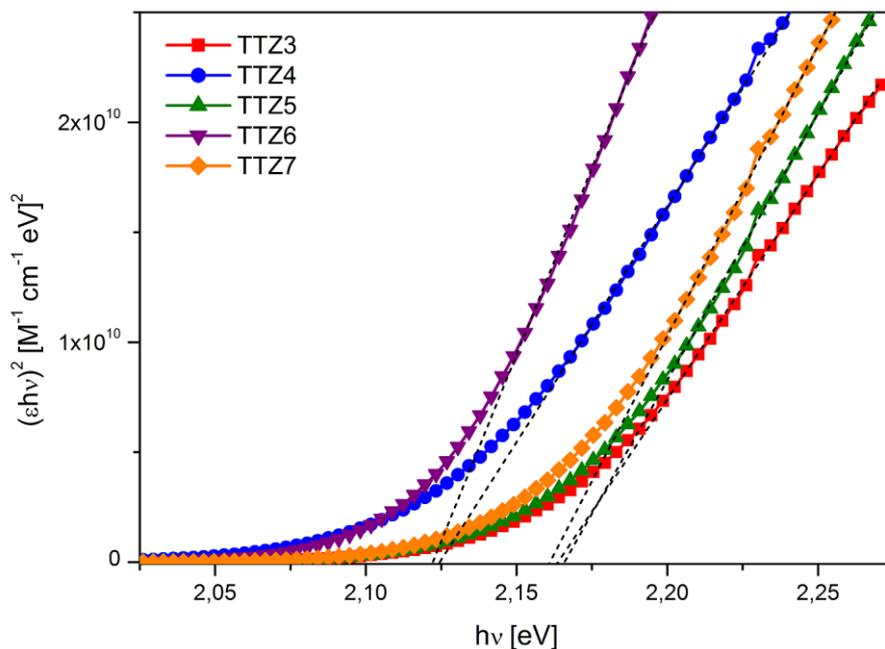
4.04 (s, 2H), 3.94 (t,  $J = 6.4$  Hz, 4H), 1.73–1.79 (m, 4H), 1.32–1.60 (m, 44H), 0.90–0.95 (m, 18H) ppm.  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta = 164.0, 160.3, 158.0, 156.9, 151.7, 151.0, 150.5, 149.4, 149.0, 148.0, 146.0, 145.4, 144.1, 140.9, 138.2, 136.1, 128.0, 127.6, 125.9, 124.91, 124.89, 120.0, 117.84, 117.77, 116.6, 115.9, 113.8, 99.1, 78.9, 78.8, 78.4, 78.3, 68.6, 44.7, 44.5, 33.51, 33.49, 32.80, 32.75, 32.4, 30.1, 26.6, 23.4, 23.3, 14.3, 14.2$  ppm. IR (KBr):  $\nu = 3030, 2928, 2852, 2213, 1684, 1505, 1057$   $\text{cm}^{-1}$ . 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).** Amorphous dark solid;  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta = 8.30$  (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.  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta = 164.0, 160.1, 158.2, 151.7, 151.1, 150.3, 149.1, 148.0, 147.7, 146.0, 145.9, 144.0, 138.2, 136.2, 132.3, 131.3, 128.2, 127.4, 125.7, 125.0, 124.9, 123.5, 117.9, 117.7, 116.7, 114.5, 99.2, 78.9, 78.8, 78.5, 78.3, 67.8, 44.7, 44.5, 34.6, 33.50, 33.49, 32.8, 32.7, 32.2, 30.0, 29.2, 23.27, 23.26, 14.3, 14.2$  ppm. IR (KBr):  $\nu = 3020, 2924, 2857, 2213, 1678, 1563, 1407, 1057$   $\text{cm}^{-1}$ . 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.

## 5. Additional spectroscopic characterization



**Figure S2.** Intersection between the normalized UV-Vis absorption (solid line) and fluorescence emission (dashed line) spectra for compounds **TTZ3-7** in THF solution. (a) **TTZ3**; (b) **TTZ4**; (c) **TTZ5**; (d) **TTZ6**; (e) **TTZ7**.



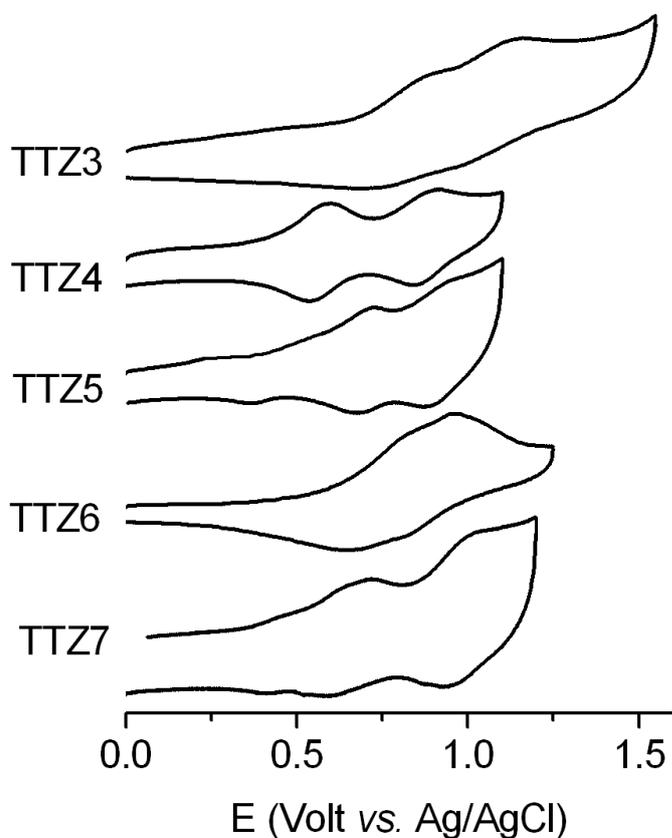
**Figure S3.** Tauc plot<sup>[14,15]</sup> for the determination of the optical band-gap of sensitizers **TTZ3-7** in THF solution.

## 6. Measurement of the density of adsorbed dyes on TiO<sub>2</sub>

A nanocrystalline TiO<sub>2</sub> electrode (surface area 0.88 cm<sup>2</sup>) similar to those used for the photovoltaic measurements was immersed in 1.0 × 10<sup>-4</sup> M solutions of dyes **TTZ3-7** in THF at rt for 16 h. The stained electrode was removed from the solution, washed with EtOH, dried under a stream of nitrogen and immersed in 5 mL of a 0.1 M KOH solution in THF/MeOH 9:1 at rt until full discoloration was observed. The absorbance of the resulting orange-yellow solution was measured by UV-Vis spectroscopy and compared to that of a standard solution of 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 the density values.

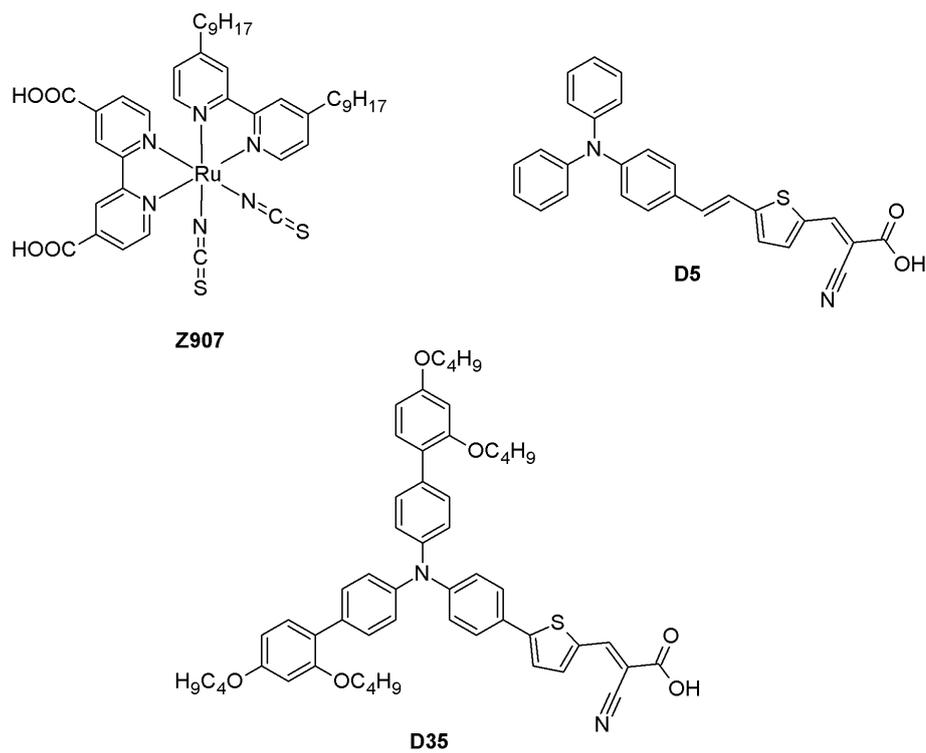
## 7. Electrochemical characterization

Cyclic voltammetry 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.



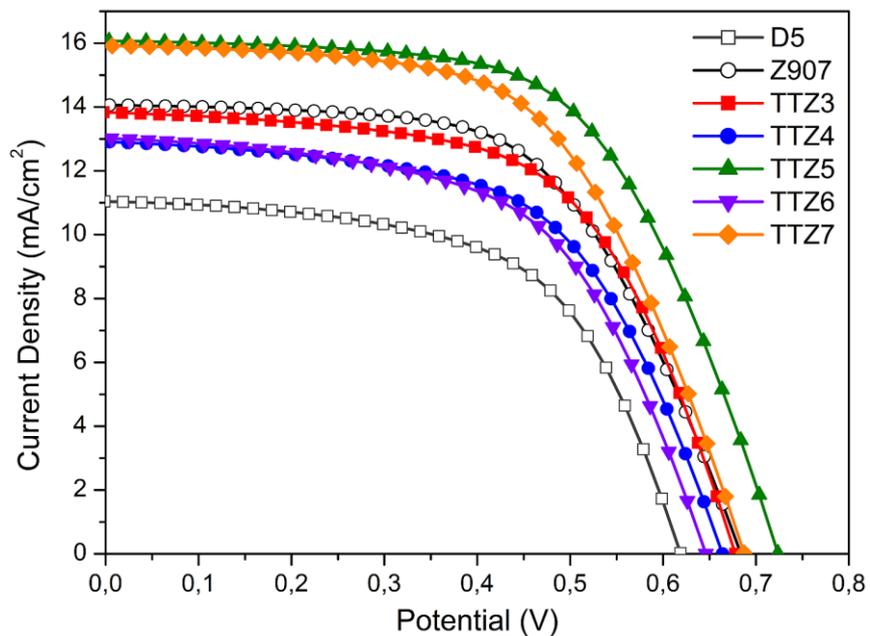
**Figure S4.** Cyclic Voltammetry plots relative to compounds TTZ3-TTZ7.

## 8. Structures of reference dyes used in this study

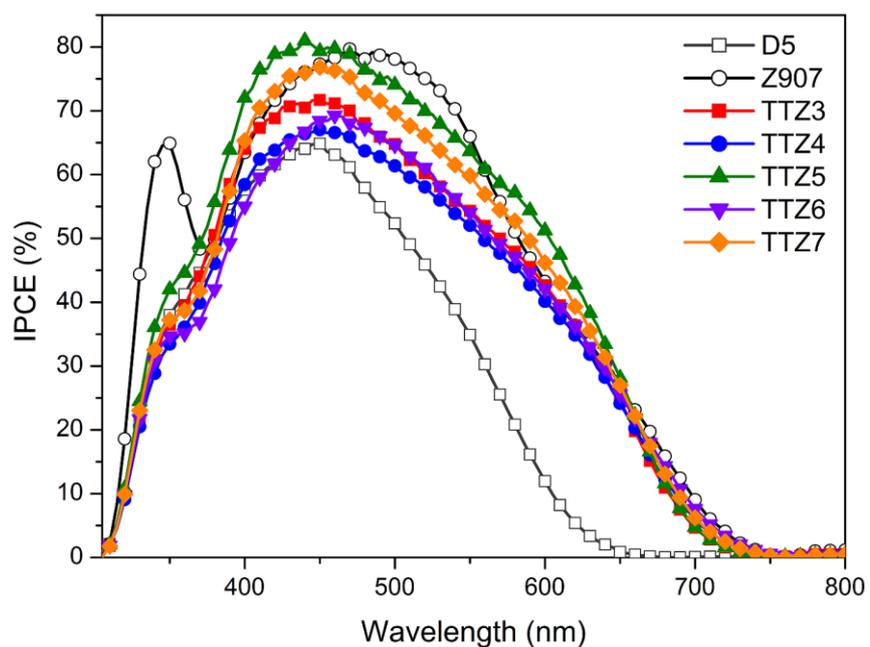


**Figure S5.** Structures of the reference dyes used in this study.

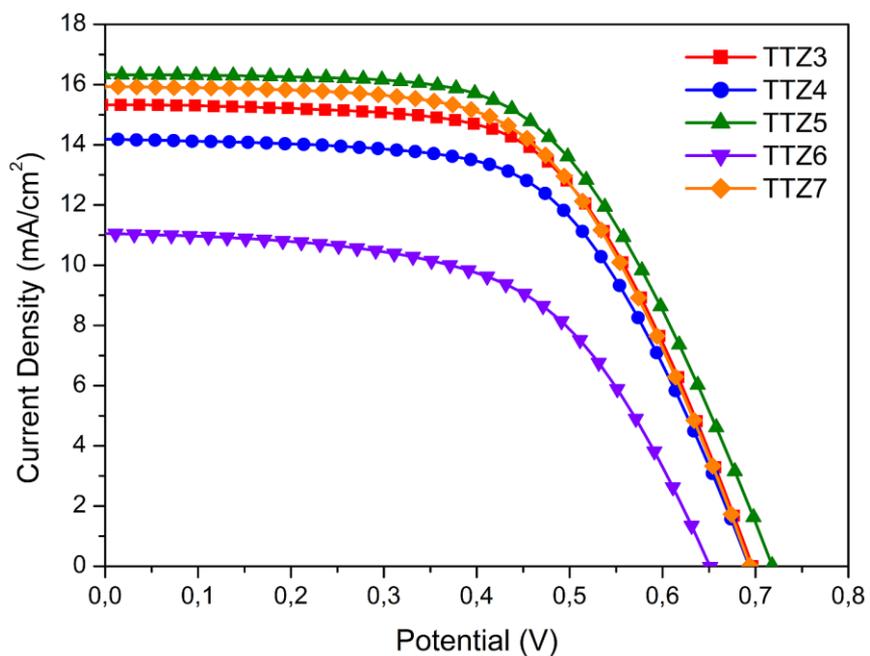
## 9. Photoelectrochemical measurements



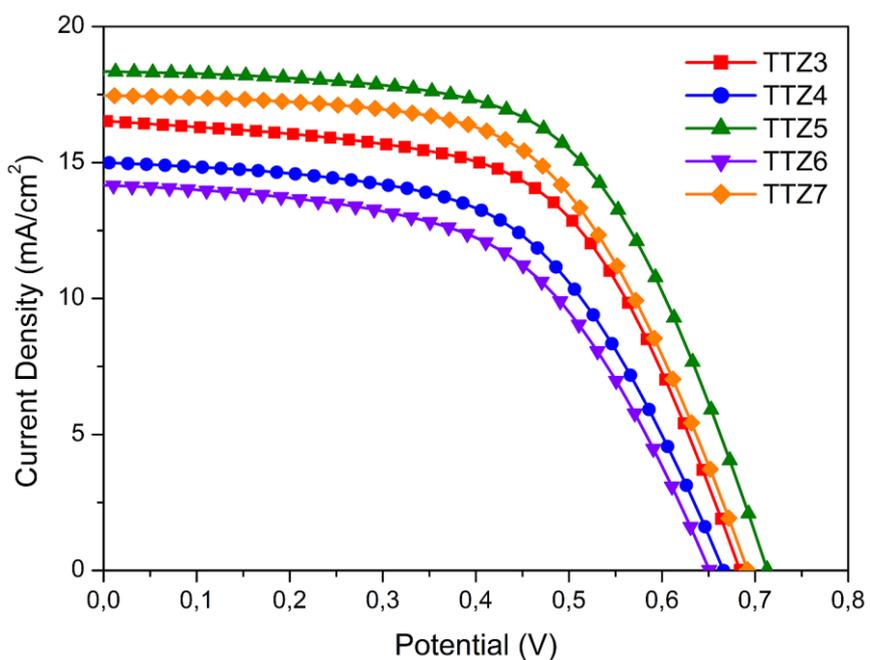
**Figure S6.**  $J/V$  curves measured for opaque small-scale DSSCs built with dyes **D5**, **Z907** and **TTZ3-7**.



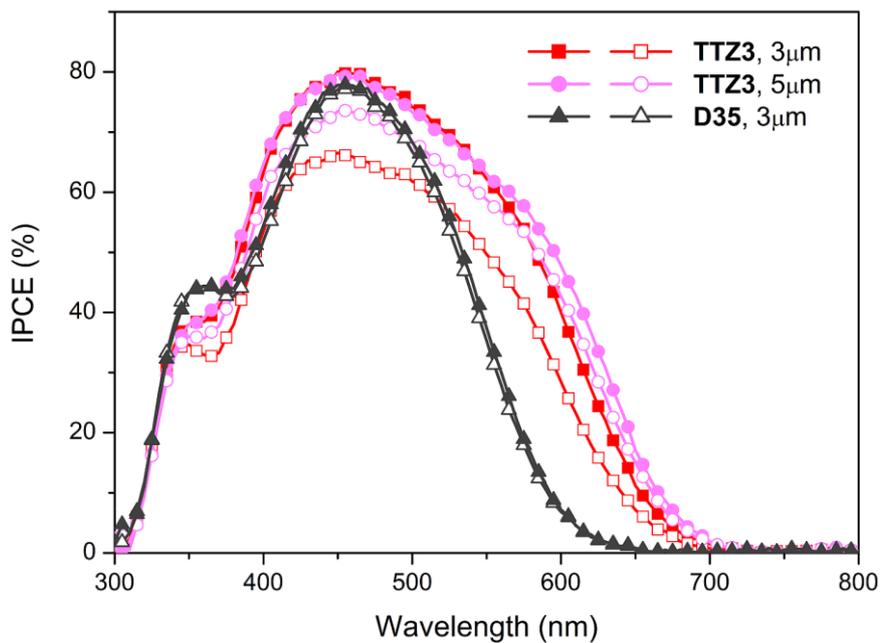
**Figure S7.** IPCE spectra measured for opaque small-scale DSSCs built with dyes **D5**, **Z907** and **TTZ3-7**.



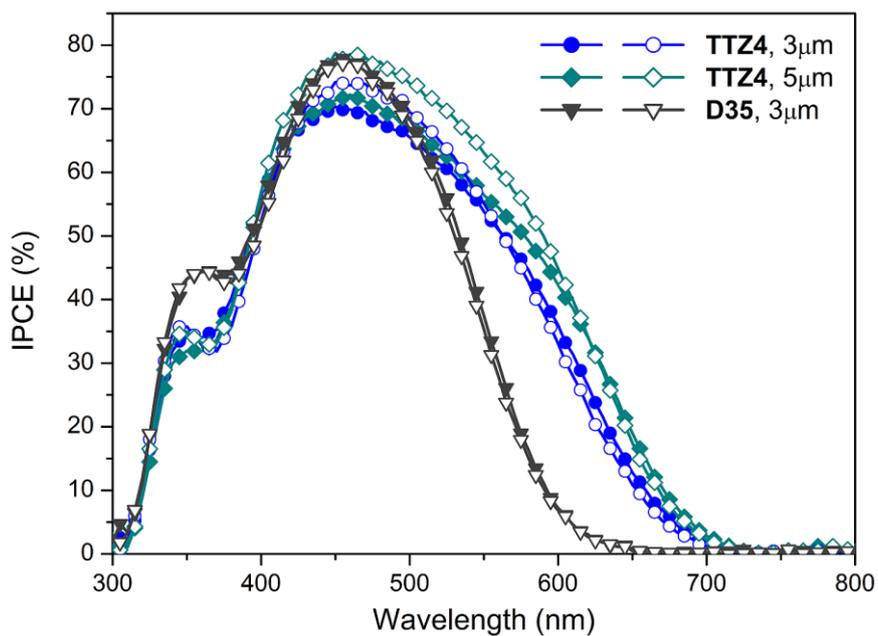
**Figure S8.**  $J/V$  curves measured for transparent small-scale DSSCs built with dyes **TTZ3-7** in the presence of CDCA.



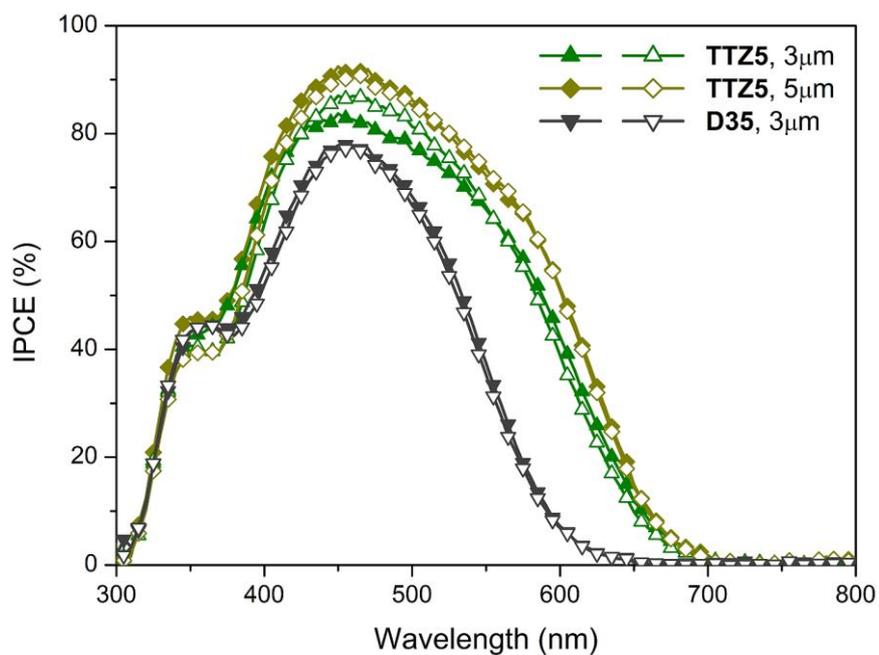
**Figure S9.**  $J/V$  curves measured for opaque small-scale DSSCs built with dyes **TTZ3-7** in the presence of CDCA.



**Figure S10.** IPCE curves measured for strip DSSCs built with dye **TTZ3**; solid symbols: no CDCA; hollow symbols: CDCA added to the sensitizing bath. The corresponding curves obtained with reference dye **D35** have been added for comparison.

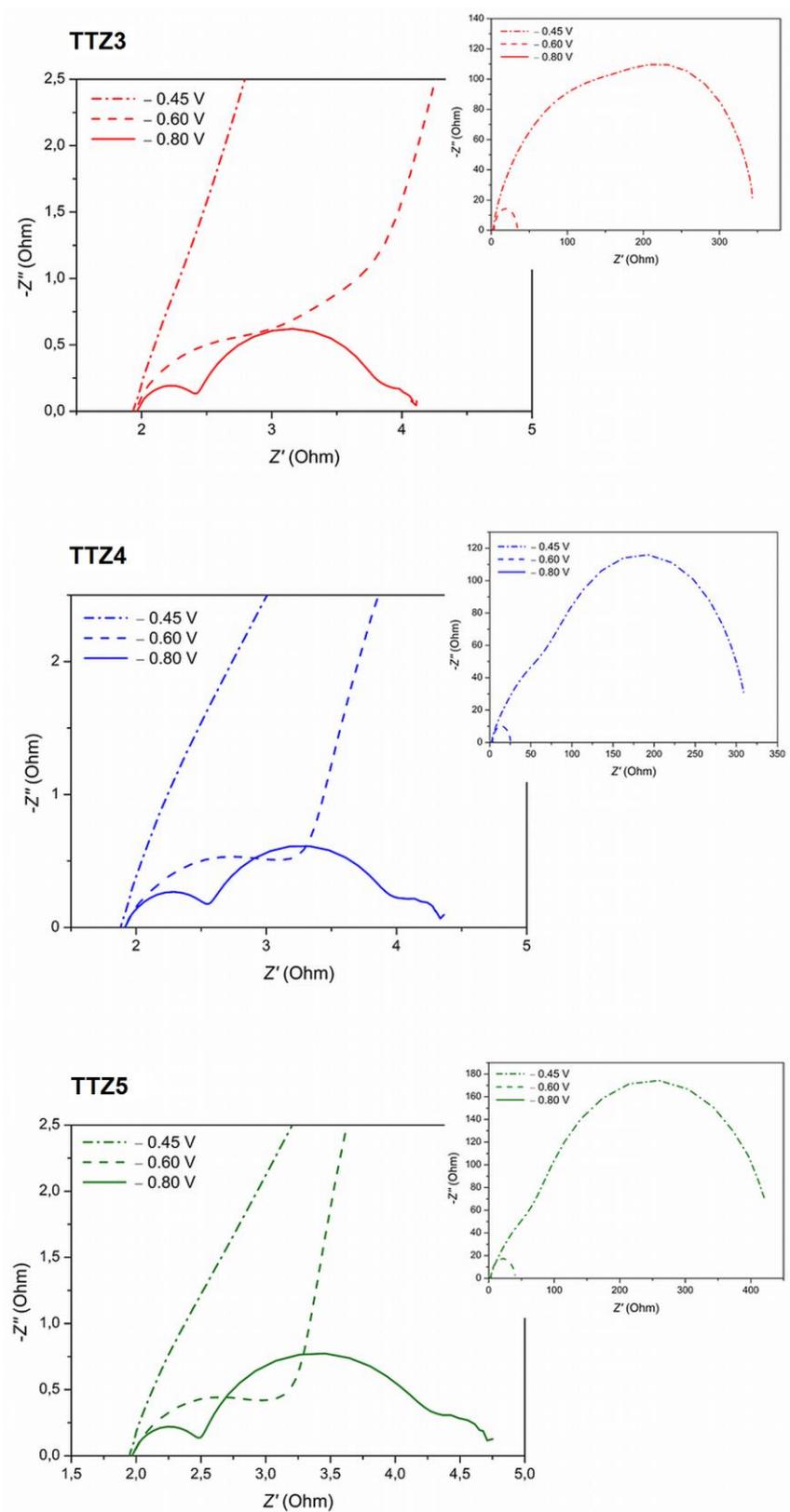


**Figure S11.** IPCE curves measured for strip DSSCs built with dye **TTZ4**; solid symbols: no CDCA; hollow symbols: CDCA added to the sensitizing bath. The corresponding curves obtained with reference dye **D35** have been added for comparison.



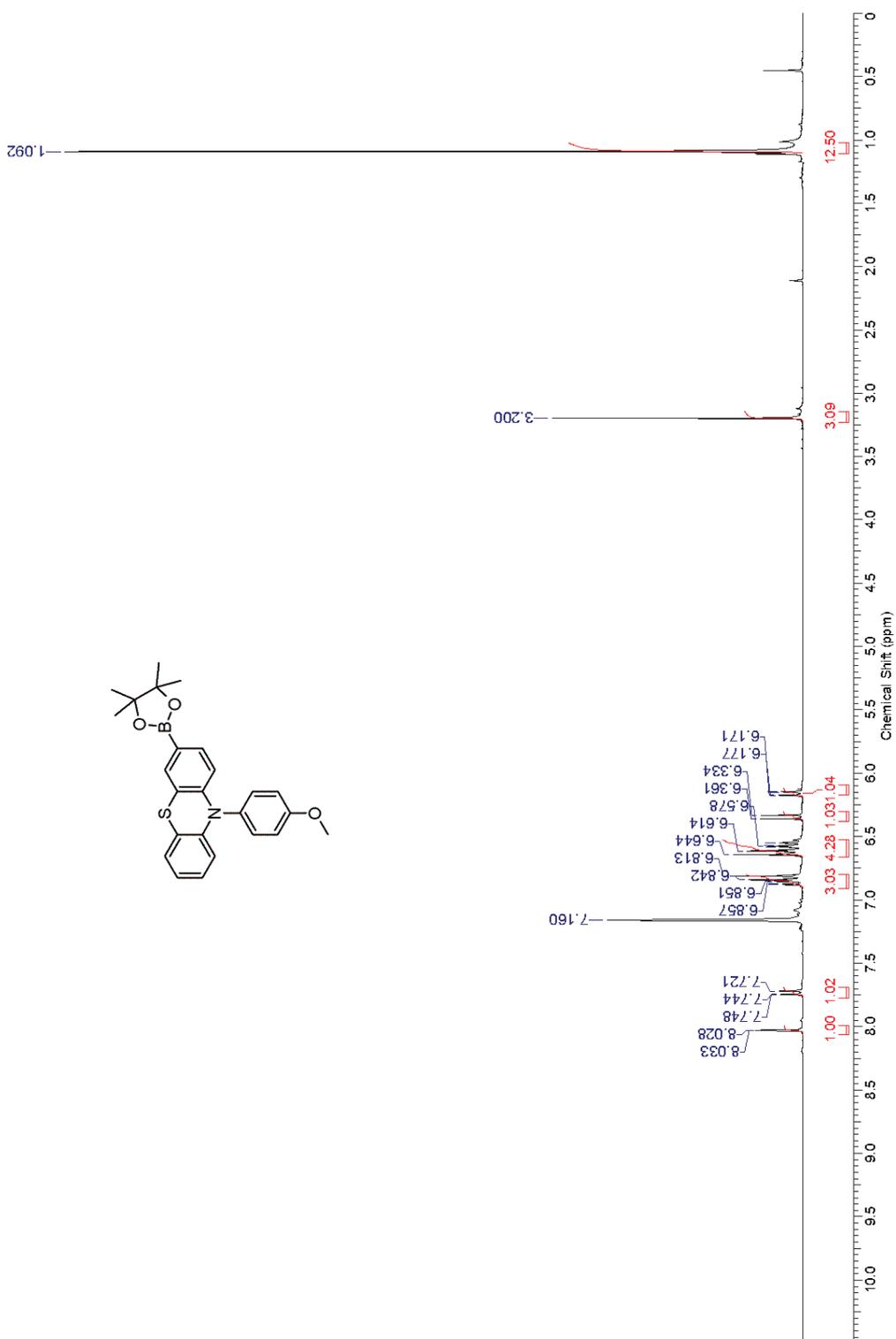
**Figure S12.** IPCE curves measured for strip DSSCs built with dye **TTZ5**; solid symbols: no CDCA; hollow symbols: CDCA added to the sensitizing bath. The corresponding curves obtained with reference dye **D35** have been added for comparison.

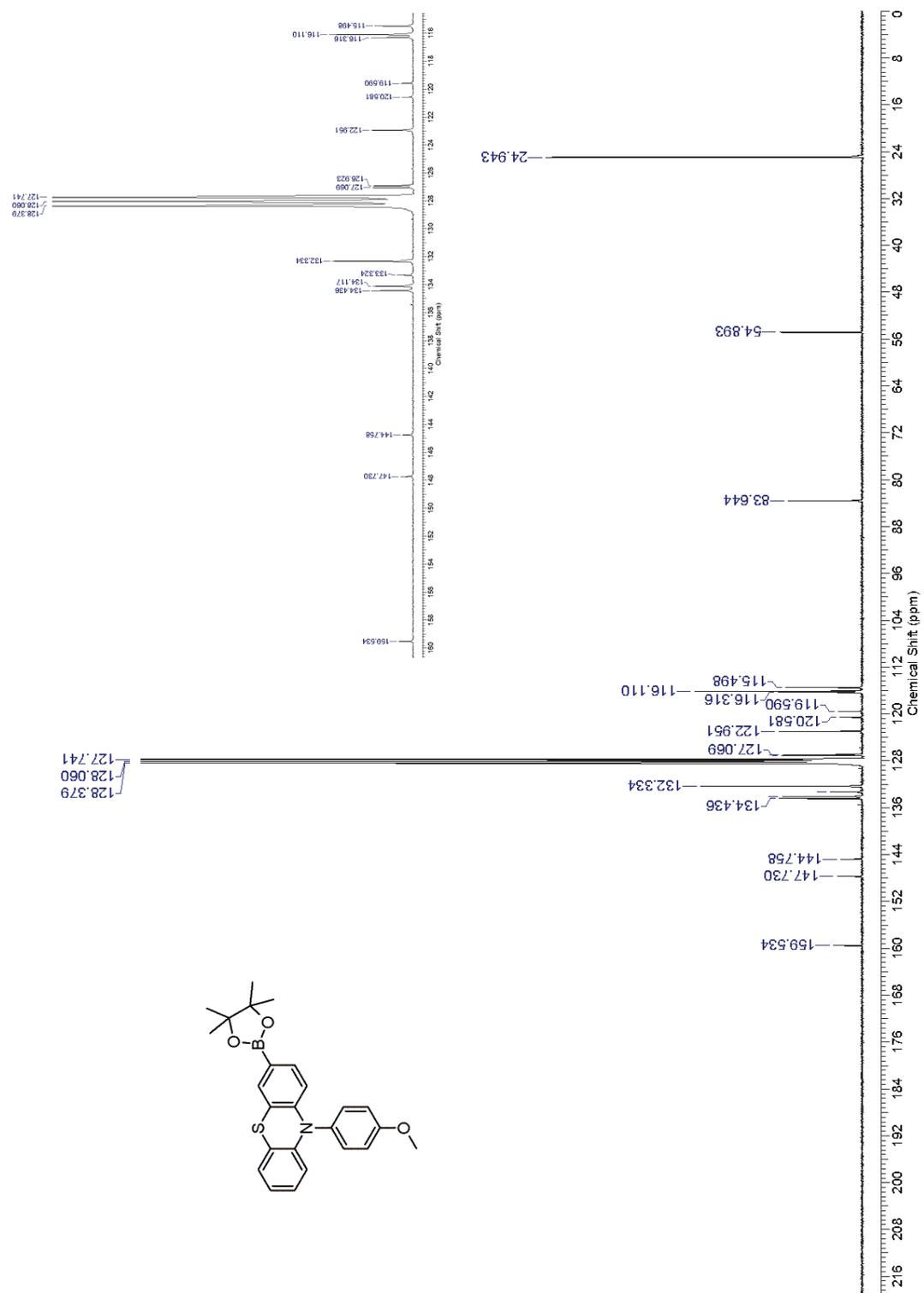
## 10. EIS Spectra

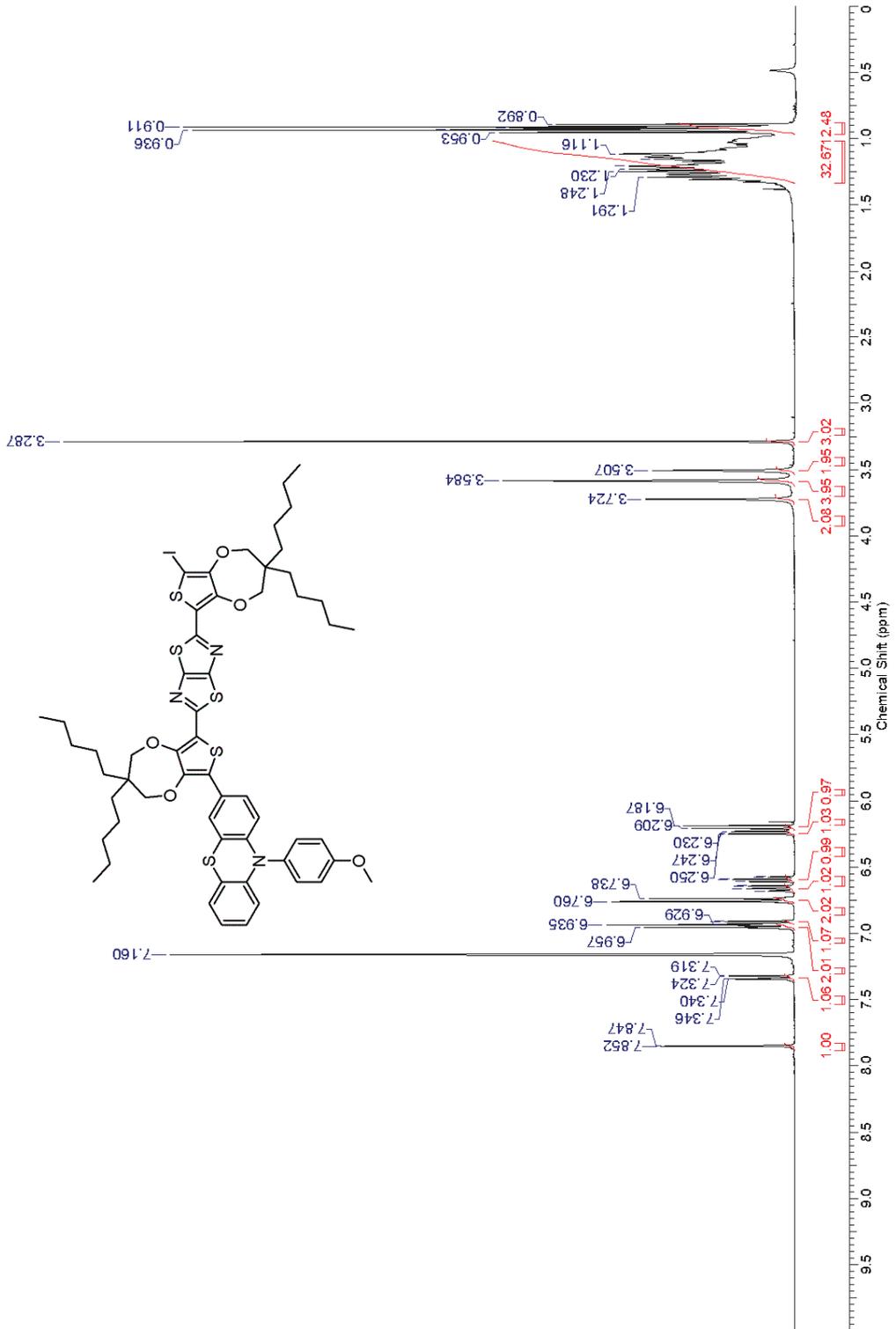


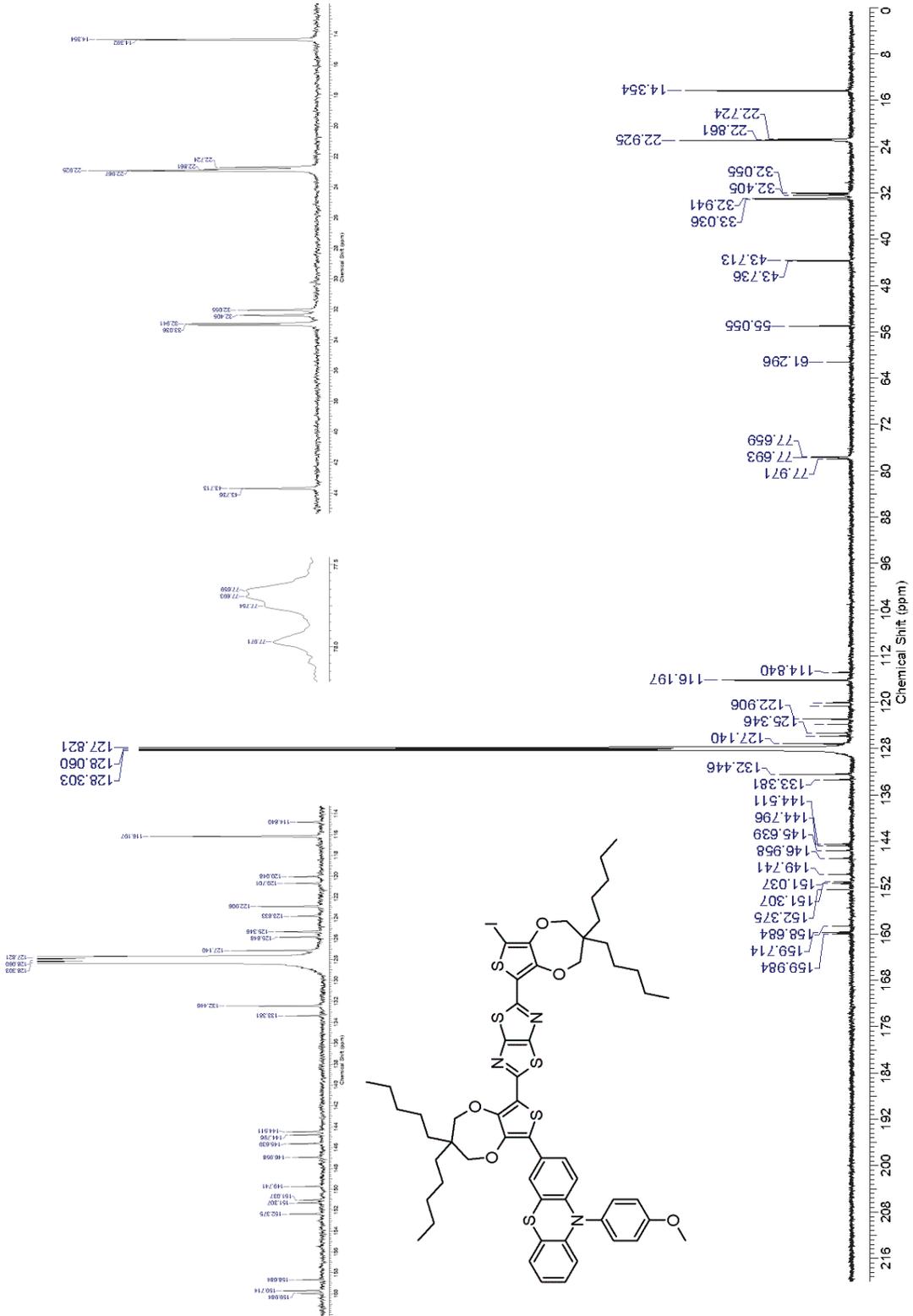
**Figure S13.** EIS spectra for compounds **TTZ3-5** registered at different potentials. The full range is shown in the inset.

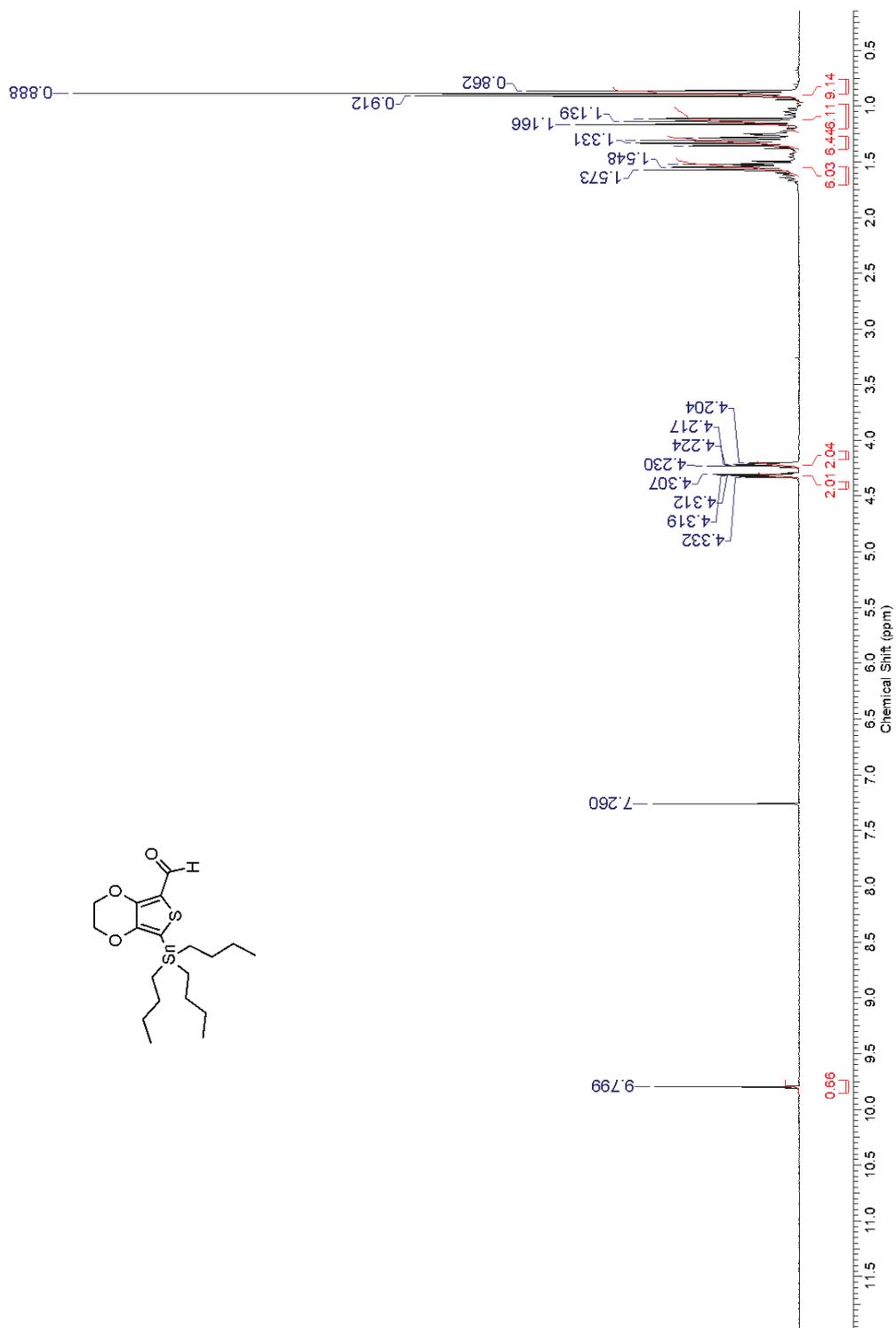
11. Copies of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of compounds 7,15, 19-20, 23 and TTZ6-7  
15

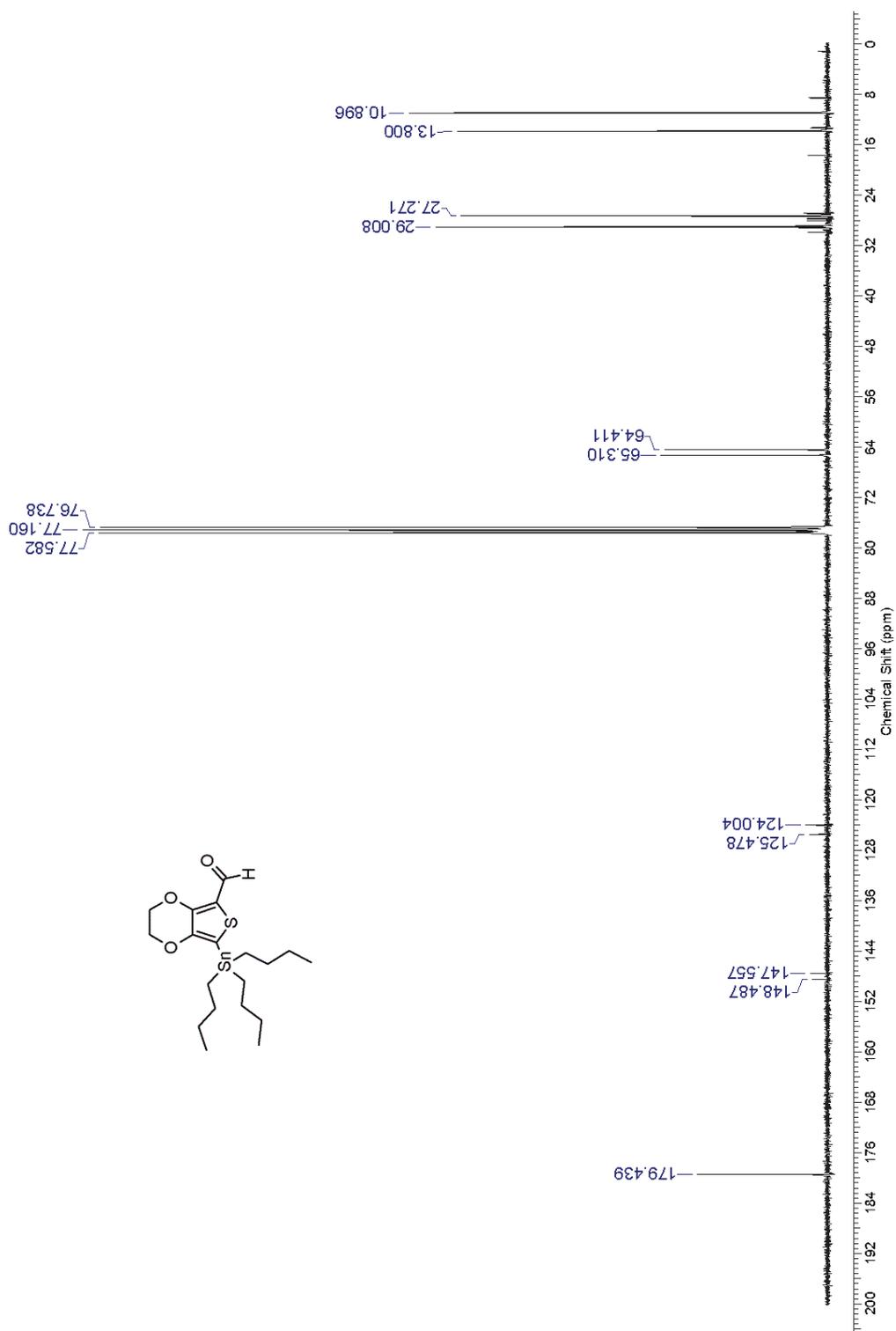


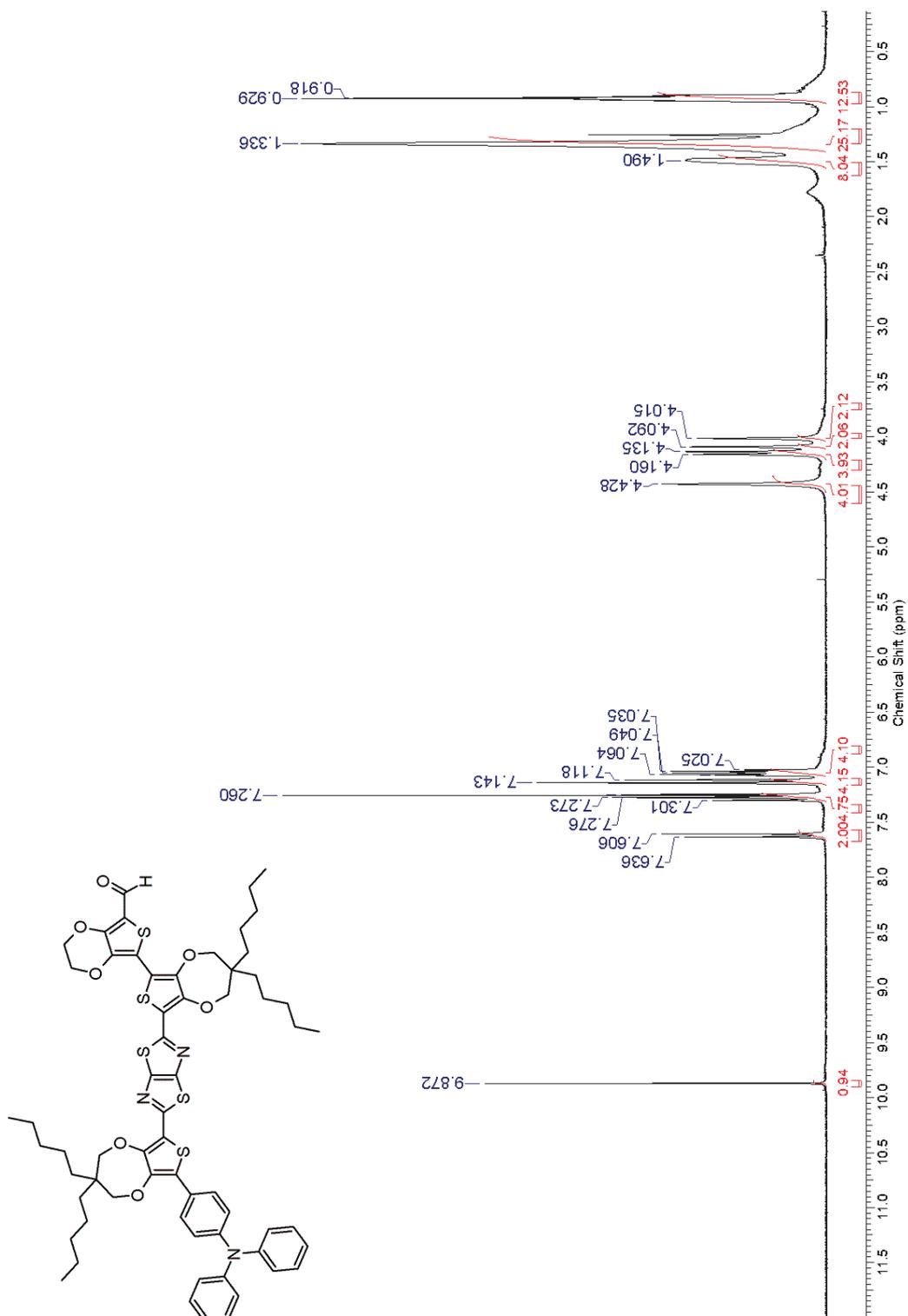


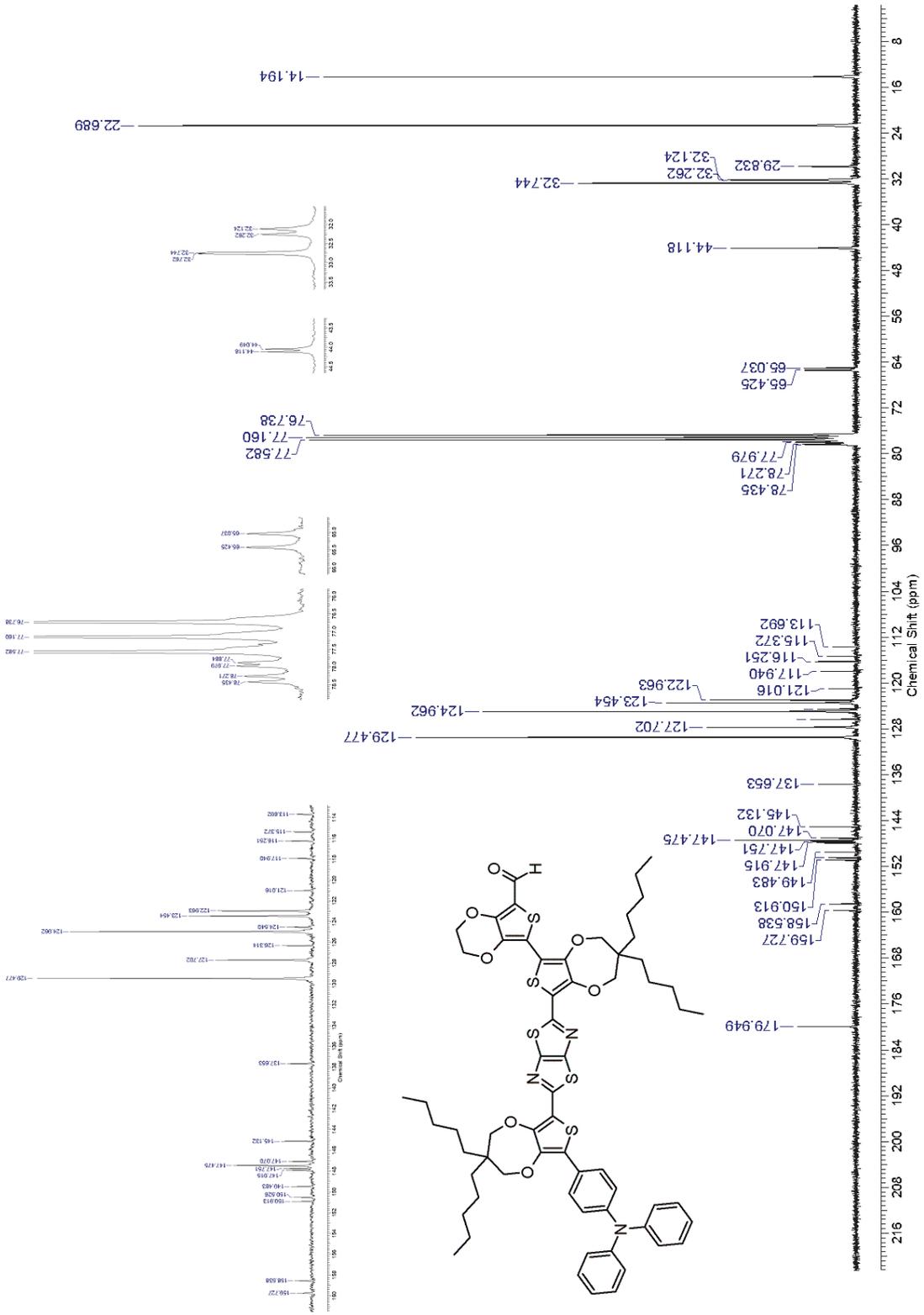


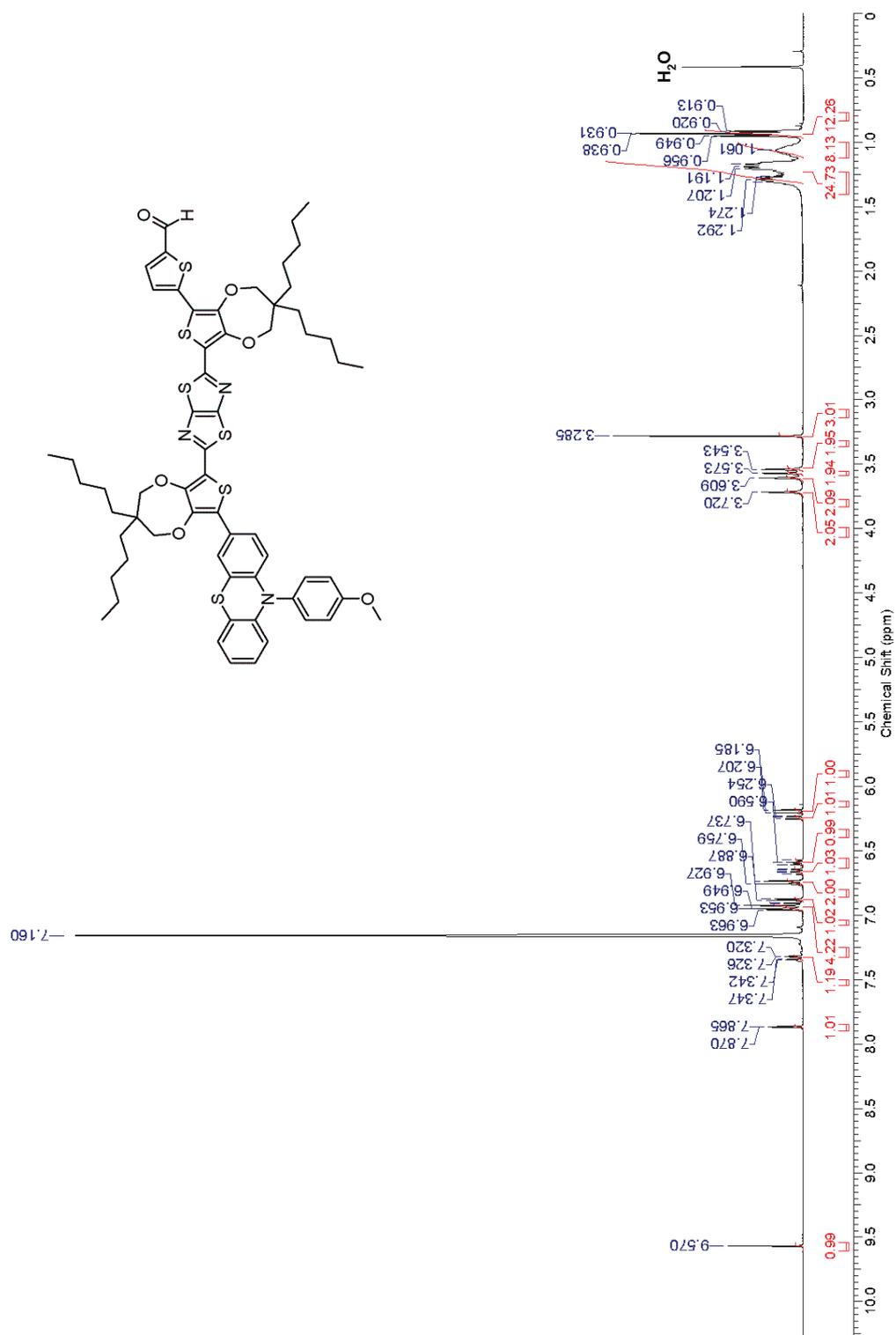


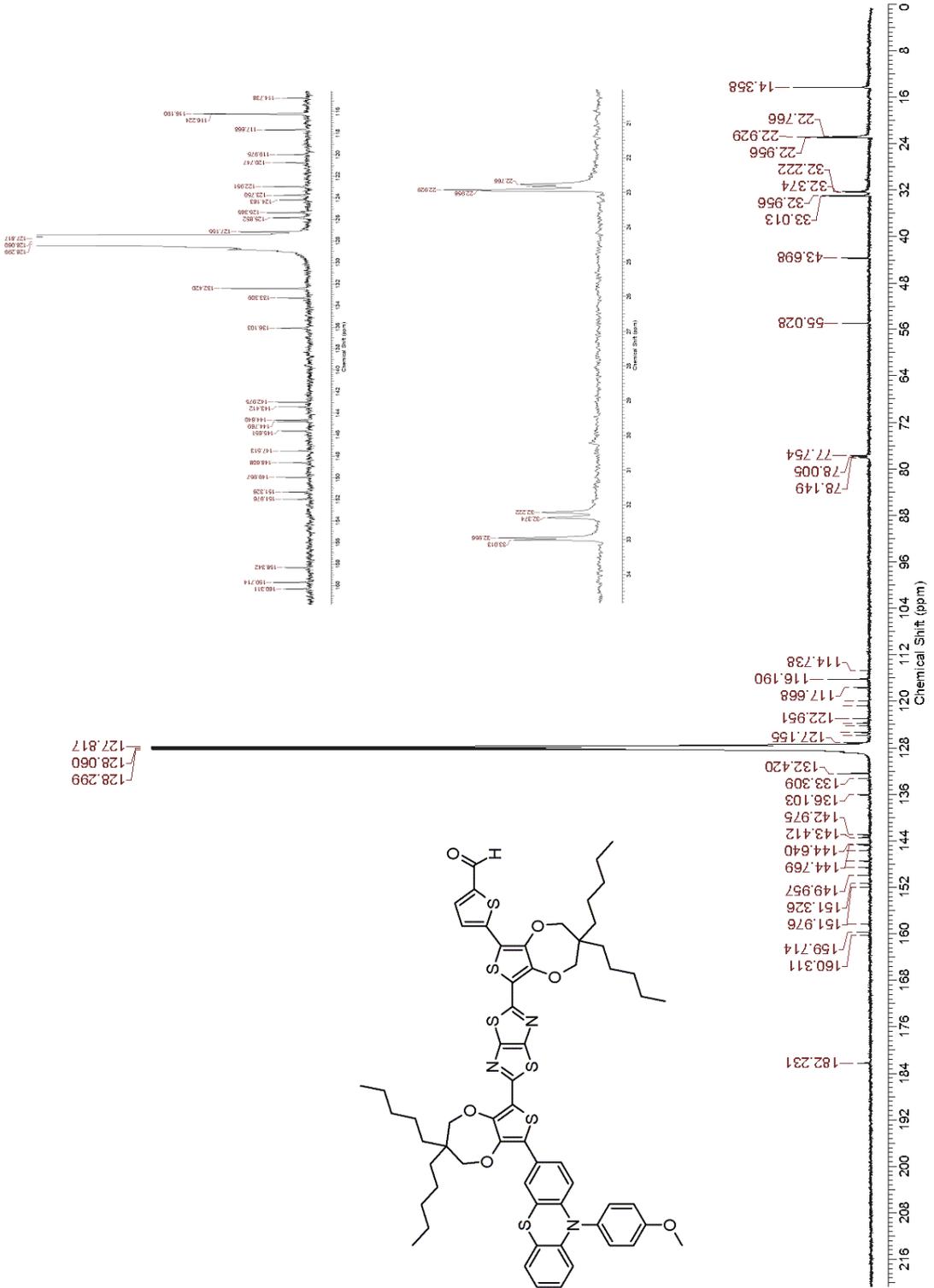




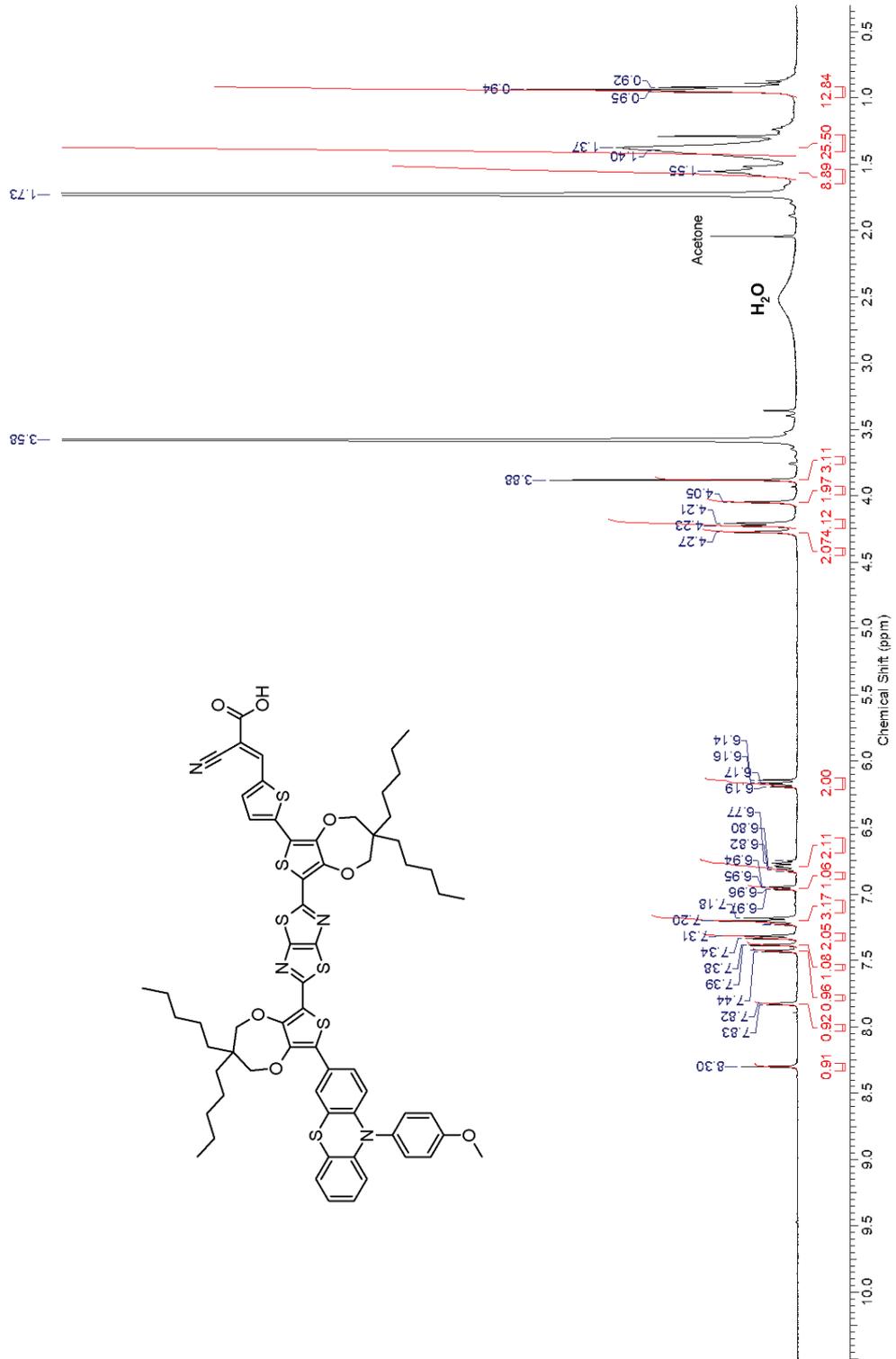


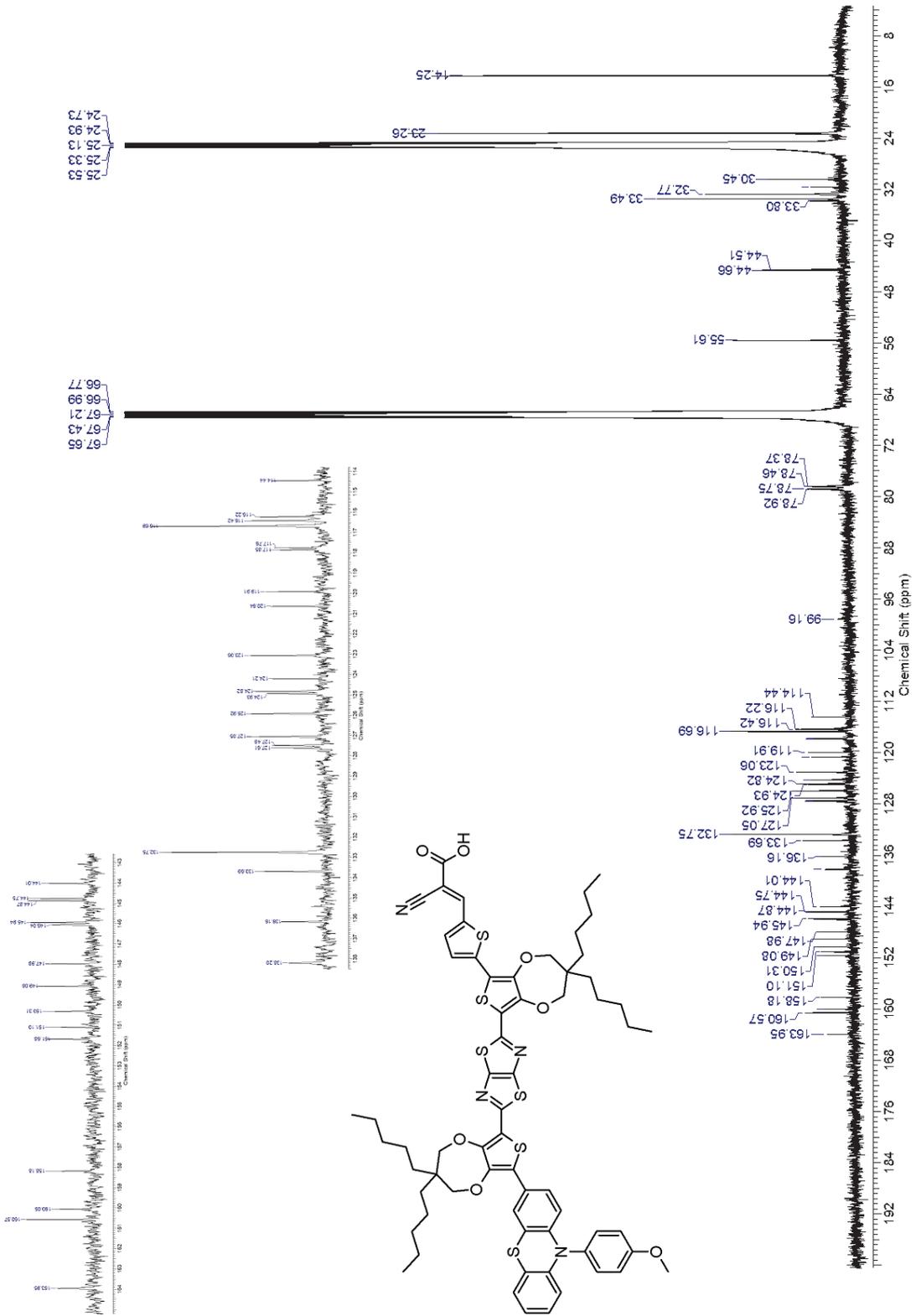












## 12. References

- [1] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [2] (a) A. D. J. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
- [3] T. Yanai, D. Tew, N. Handy, *Chem. Phys. Lett.* 2004, **393**, 51-57.
- [4] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.
- [5] A. Dessì, G. Barozzino Consiglio, M. Calamante, G. Reginato, A. Mordini, M. Peruzzini, M. Taddei, A. Sinicropi, M. L. Parisi, F. Fabrizi de Biani, R. Basosi, R. Mori, M. Spatola, M. Bruzzi and L. Zani, *Eur. J. Org. Chem.*, 2013, 1916-1926.
- [6] D. F. Shriver, M. A. Drezdson, "*The Manipulation of Air-Sensitive Compounds*", John Wiley & Sons, Hoboken, 1986.
- [7] B. C. Thompson, Y.-G. Kim, T. D. McCarley and J. R. Reynolds, *J. Am. Chem. Soc.*, 2006, **128**, 12714-12725.
- [8] L. Chen, B. Zhang, Y. Cheng, Z. Xie, L. Wang, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2010, **20**, 3143-3153.
- [9] Y.-H. Seo, W.-H. Lee, J.-H. Park, C. Bae, Y. Hong, J.-W. Park and I.-N. Kang, *J. Polym. Sci. A: Polym. Chem.*, 2012, **50**, 649-658.
- [10] A. K. Mohanakrishnan, A. Hucke, M. A. Lyon, M. V. Lakshmikantham and M. P. Cava, *Tetrahedron*, 1999, **55**, 11745-11754.
- [11] A. Dessì, M. Calamante, A. Mordini, M. Peruzzini, A. Sinicropi, R. Basosi, F. Fabrizi de Biani, M. Taddei, D. Colonna, A. Di Carlo, G. Reginato and L. Zani, *Chem. Commun.*, 2014, **50**, 13952-13955.
- [12] (a) C. G. Bates, R. K. Gujadhur and D. Venkataraman, *Org. Lett.*, 2002, **4**, 2803-2806; (b) K. C. D. Robson, B. D. Koivisto and C. P. Berlinguette, *Inorg. Chem.*, 2012, **51**, 1501-1507.

- [13] C. Djerassi and C. R. Scholz, *J. Am. Chem. Soc.*, 1948, **70**, 417-418.
- [14] J. Tauc, *Mater. Res. Bull.* **1968**, *3*, 37-46.
- [15] C. Coluccini, N. Manfredi, M. M. Salamone, R. Ruffo, M. G. Lobello, F. De Angelis, A. Abbotto, *J. Org. Chem.* **2012**, *77*, 7945-7956.