

## Electronic supplementary Information

### 3,4-[(3-Decyloxy)-1,2-propylenedioxy]thiophene (**6**)

(2,3-Dihydro-thieno[3,4-*b*][1,4]dioxin-2-yl)methanol **1** (7.60 g, 44.1 mmol) and catalytic amount of 18-crown-6 (230 mg, 0.86 mmol, 2 mol. %) were dissolved in dry THF (100 mL) under nitrogen and cooled to  $-5\text{ }^{\circ}\text{C}$ . Sodium hydride (60 % suspension in oil, 2.30 g, 57.5 mmol) was added to this solution in several portions at  $-5\text{ }^{\circ}\text{C}$  for 15–20 min, the mixture was allowed to warm to room temperature and stirred at room temperature for 2 h. Decyl bromide (12.5 g, 56.5 mmol) was added in one portion and the mixture was stirred with reflux for 3 days. THF was evaporated on rotavapor, the residue was diluted with DCM/H<sub>2</sub>O (250/150 mL) and acidified. DCM layer was washed with H<sub>2</sub>O (2 × 150 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and solvent removed. Chromatography of the residual brown oil on silica gel with petroleum ether (PE) : Et<sub>2</sub>O (4:1) afforded desired product **2** (12.35 g, 89.5 %) as yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ

6.333 (1H, d, <sup>4</sup>*J*<sub>2,5</sub> = 3.7 Hz, thiophene-2),

6.323 (1H, d, <sup>4</sup>*J*<sub>2,5</sub> = 3.7 Hz, thiophene-5),

4.30 [1H, m, -OCH<sub>2</sub><sup>ab</sup>CH<sup>c</sup>(CH<sub>2</sub>OR)O-],

4.25 [1H, dd, <sup>2</sup>*J*<sub>ab</sub> = 11.6 Hz, <sup>3</sup>*J*<sub>b,c</sub> = 2.1 Hz, -OCH<sup>a</sup>H<sup>b</sup>CH<sup>c</sup>(CH<sub>2</sub>OR)O-],

4.06 [1H, dd, <sup>2</sup>*J*<sub>ab</sub> = 11.6 Hz, <sup>3</sup>*J*<sub>a,c</sub> = 7.6 Hz, -OCH<sup>a</sup>H<sup>b</sup>CH<sup>c</sup>(CH<sub>2</sub>OR)O-],

3.68 [1H, dd, <sup>2</sup>*J*<sub>de</sub> = 10.4 Hz, <sup>3</sup>*J*<sub>d,e</sub> = 5.0 Hz, -OCH<sub>2</sub>CH<sup>c</sup>(CH<sup>d</sup>H<sup>e</sup>OR)O-],

3.59 [1H, dd, <sup>2</sup>*J*<sub>de</sub> = 10.4 Hz, <sup>3</sup>*J*<sub>e,c</sub> = 6.0 Hz, -OCH<sub>2</sub>CH<sup>c</sup>(CH<sup>d</sup>H<sup>e</sup>OR)O-],

3.49 (2H, t, <sup>2</sup>*J* = 6.7 Hz, OCH<sub>2</sub>C<sub>9</sub>H<sub>19</sub>),

1.57 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>C<sub>8</sub>H<sub>17</sub>),

1.26 [14H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>],

0.88 (3H, t, <sup>2</sup>*J* = 6.7 Hz, CH<sub>3</sub>),

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 141.74, 141.69 (thiophene-3,4), 99.59, 99.50 (thiophene-2,5), 72.74, 71.13, 69.17, 66.32, 31.88, 29.57 (2C), 29.54, 29.42, 29.28, 26.05, 22.64, 14.02 (CH<sub>3</sub>).

### 2{5}-Tributylstannyl-3,4-[(3-Decyloxy)-1,2-propylenedioxy]thiophene (**5**)

Oven-dried nitrogen flushed flask was charged with compound **6** (3.94 g, 12.6 mmol) and dry THF (50 mL), cooled to  $-70\text{ }^{\circ}\text{C}$ , and to this solution butyl lithium (2.5 M solution in hexane, 5.2 mL, 13.0 mmol) was added with stirring for 15 min. The mixture was allowed to warm to  $-20\text{ }^{\circ}\text{C}$  for 2.5 h, cooled again to  $-70\text{ }^{\circ}\text{C}$  and solution of tributyltin chloride (7.10 g, 12.6 mmol) in dry THF (15 mL) was added. The reaction mixture was allowed to warm to  $-10\text{ }^{\circ}\text{C}$  for 1 h and it was kept at this temperature overnight. The mixture was diluted with 5% aqueous NH<sub>4</sub>Cl (150 mL) and extracted with DCM (2 × 100 mL). DCM layer was washed with H<sub>2</sub>O and dried with Na<sub>2</sub>SO<sub>4</sub> affording compound **5** in 95 % yield as yellow oil. This product was used in further syntheses without further purification. (<sup>1</sup>H NMR showed the presence of ca. 10% of starting compound **5**).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ

6.582 + 6.575 (Σ 1H; s, thiophene-2 + s, thiophene-5),

4.24–4.20 [2H, m, OCH<sup>a</sup>H<sup>b</sup>CH<sup>c</sup>(CH<sub>2</sub>OR)O-],

4.03–3.98 [1H, m, OCH<sup>a</sup>H<sup>b</sup>CH<sup>c</sup>(CH<sub>2</sub>OR)O-],

3.69–3.64 (1H, m, CHHOC<sub>10</sub>H<sub>21</sub>),

3.59–3.52 (1H, m, CHHOC<sub>10</sub>H<sub>21</sub>),

3.48 (2H, t, <sup>2</sup>*J* = 6.6 Hz, OCH<sub>2</sub>C<sub>9</sub>H<sub>19</sub>),

1.57–1.55 [8H, m, OCH<sub>2</sub>CH<sub>2</sub>C<sub>8</sub>H<sub>17</sub> + Sn(CH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>],

1.35–1.26 [20H, m, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> + Sn[(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>]<sub>3</sub>],

1.09 [6H, t, *J* = 8.1 Hz, Sn[CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>3</sub>],

0.89 [12H, m, (CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub> + Sn[(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>3</sub>],

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ [147.59 + 147.51 (1C), 142.30 + 142.25 (1C), thiophene-3 and thiophene-4], [108.81 + 108.71 (1C), 105.84 + 105.75 (1C), thiophene-2 and thiophene-5], [72.68 + 72.56 (1C), 72.08 + 72.05 (1C), 69.35 + 69.26 (1C), 66.30 + 66.23 (1C), OCH<sub>2</sub>CH(O)CH<sub>2</sub>OCH<sub>2</sub>], 31.86, 29.55, 29.52, (29.44 + 29.40), 29.26, 28.95, 28.93, (27.13 + 27.09), (26.06 + 26.02), 22.62, 14.00, 13.59, (10.59 + 10.56).

### 2-Bromo-2,3-dihexylthieno[3,4-*b*]pyrazine (**3**)

2,3-Dihexylthieno[3,4-*b*]pyrazine (**4**) (1.20 g, 3.94 mmol) was dissolved in dry DMF (200 mL) under nitrogen and cooled to  $-55\text{ }^{\circ}\text{C}$  (some precipitation was observed below  $-35\text{ }^{\circ}\text{C}$ ). A solution of *N*-bromosuccinimide (NBS) (0.70 g, 3.93 mmol) in dry DMF (80 mL) was added for 30 min and the mixture was stirred for 3.5 h whereas the temperature was allowed to increase gradually from  $-50$  to  $0\text{ }^{\circ}\text{C}$ . The mixture was diluted with H<sub>2</sub>O (1.5 L) and extracted with DCM (10 × 100 mL). Combined DCM extracts were dried Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated on rotavapor affording dark-green solid which was chromatographed on silica gel. First elution by PE:DCM (3:1) afforded by-product dibromoderivative **6** (0.09 g, 5 %); further elution by PE:DCM (2:1) and then PE:DCM (1:1) afforded target monobromo-derivative **5** (0.91 g, 60 %) as yellow solid which becomes greenish when stored at room temperature.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (1H, s, thiophene-2), 2.90 (2H, t,  $J = 8.6$  Hz,  $\text{CH}_2\text{C}_5\text{H}_{11}$ ), 2.89 (2H, t,  $J = 8.6$  Hz,  $\text{CH}_2\text{C}_5\text{H}_{11}$ ), 1.84–1.77 (4H, m, 2  $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$ ), 1.47 (4H, m, 2  $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_3\text{H}_7$ ), 1.35 (8H, m, 2  $(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$ ), 0.91 (6H, m, 2  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.72, 156.48, 149.08, 129.98, 128.22, 115.35, 35.35, 35.27, 31.62, 31.52, 29.21, 29.15, 28.44, 27.86, 22.47, 22.37, 13.97, 13.93.

5-[2(3)-decyloxy-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl]-2,3-dihexylthieno[3,4-b]pyrazine (**2**)

Tin derivative **5** (2.20g, 3.66 mmol), bromo derivative **3** (0.88 g, 2.30 mmol) and catalyst  $\text{PdCl}_2(\text{PPh}_3)_2$  (60 mg, 0.085 mmol, 3.7 mol %) in dry toluene were stirred at 90 °C under nitrogen for 16 h. The mixture was filtered through 4cm layer of silica gel, washed with toluene, the solvent was removed on rotavapor, and the residue was chromatographed on silica gel with toluene as an eluent. Yield 0.81 g (57 %), after repeating chromatography – 0.69 g (49 %),  $R_f = 0.24$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$

7.567 (s) + 7.561 (s) ( $\Sigma 1\text{H}$ , N–C=CH–S),

6.428 (s) + 6.417 (s) ( $\Sigma 1\text{H}$ , O–C=CH–S),

4.52 (m) + 4.41 (m) [ $\Sigma 1\text{H}$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OR})\text{O}-$ ],

4.51 (dd,  $^2J_{a,b} = 11.5$  Hz,  $^3J_{b,c} = 2.1$  Hz) + 4.35 (dd,  $^2J_{a,b} = 11.7$  Hz,  $^3J_{b,c} = 2.2$  Hz) [ $\Sigma 1\text{H}$ ,  $-\text{OCH}^a\text{H}^b\text{CH}^c(\text{CH}_2\text{OR})\text{O}-$ ],

4.27 (dd,  $^2J_{a,b} = 11.5$  Hz,  $^3J_{a,c} = 7.7$  Hz) + 4.17 (dd,  $^2J_{a,b} = 11.7$  Hz,  $^3J_{a,c} = 7.5$  Hz) [ $\Sigma 1\text{H}$ ,  $-\text{OCH}^a\text{H}^b\text{CH}^c(\text{CH}_2\text{OR})\text{O}-$ ],

3.84 (dd,  $^2J_{d,e} = 10.5$  Hz,  $^3J_{e,c} = 4.8$  Hz) + 3.74 (dd) [ $\Sigma 1\text{H}$ ,  $-\text{OCH}_2\text{CH}^c(\text{CH}^d\text{H}^e\text{OR})\text{O}-$ ],

3.74 (dd) + 3.66 (dd,  $^2J_{d,e} = 10.5$  Hz,  $^3J_{e,c} = 5.9$  Hz) [ $\Sigma 1\text{H}$ ,  $-\text{OCH}_2\text{CH}^c(\text{CH}^d\text{H}^e\text{OR})\text{O}-$ ],

2.92 (2H, t,  $^2J = 7.4$  Hz,  $\text{CH}_2\text{C}_5\text{H}_{11}$ ),

2.86 (2H, t,  $^2J = 7.4$  Hz,  $\text{CH}_2\text{C}_5\text{H}_{11}$ ),

1.99 (2H, tt,  $J = 7.4$  Hz,  $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$ ),

1.77 (2H, tt,  $J = 7.5$  Hz,  $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$ ),

1.61 (2H, m,  $\text{CH}_2$ )

1.50–1.24 (26H, m, 13 $\text{CH}_2$ )

0.91 (9H, m, 3 $\text{CH}_3$ ).