## **Supporting Information**

# One-pot Synthesis and Property Study on Thieno[3,2b]furan Compounds

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### 1. GC Standard curve of BTBF

Table S1. GC standard curve of BTBF with 1,1,2,2-tetrachloroethane (TCE).

(total ri	un time: 17.5 min	. Retention time	: TCE 4.69 min; BTE	3F 12.86 mi	n	
Entry	Mass of BTBF	Mass of TCE	M = Mass of BTBF	GC Area	GC Area	$r - \frac{Area \ of \ BTBF}{area}$
	(mg)	(mg)	$y = \frac{1}{Mass of TCE}$	of BTBF	of TCE	$x = \frac{1}{Area of TCE}$
1	0	0	0	0	0	0
2	0.075	160	0.00046875	20717	12180674	0.001700809
3	0.15	160	0.0009375	36760	9931586	0.003701322
4	0.225	160	0.00140625	38648	7151579	0.005404121
5	0.3	160	0.001875	53975	7461543	0.007233758
6	0.375	160	0.00234375	74013	8133414	0.009099869

GC Method: 50 °C hold for 2 min, followed by a temperature increase of 20 °C / min to 300 °C, hold 3 min (total run time: 17.5 min). Retention time: TCE 4.69 min; BTBF 12.86 min.



Figure S1. The standard curve of BTBF with TCE as an internal reference.<sup>1</sup>

## 2. DFT calculations <sup>2</sup>

DFT calculation of BTBF (3a)

Atom	Х	Y		Ζ
С	4.36895612	0.14128040	0.00021046	
С	3.86527687	1.45544452	0.00003437	
С	2.49206350	1.69436855	-0.00009193	
С	1.60556944	0.60272821	-0.00002395	
С	2.13049073	-0.71911233	0.00013641	
С	3.50283266	-0.95765756	0.00025835	
С	0.17743775	0.55610888	-0.00014655	
С	-0.41776321	-0.68024402	-0.00006972	
S	0.81012717	-2.01162283	0.00014675	
Ο	-0.77354594	1.58211870	-0.00052399	
С	-2.01955807	0.92143699	-0.00012229	
С	-1.84328106	-0.48987468	-0.00013359	
С	-3.26119658	1.53883765	0.00001216	
С	-4.38096038	0.69862965	0.00010660	
С	-4.24094028	-0.70417851	0.00006707	
С	-2.98259724	-1.31015710	-0.00004763	
Н	5.44103080	-0.02509812	0.00030129	
Н	4.55511398	2.29273599	-0.00000896	
Н	2.10090338	2.70568888	-0.00023432	
Н	3.89275555	-1.96957149	0.00038224	
Н	-3.34973380	2.61825883	-0.00004977	
Н	-5.37327833	1.13650570	0.00016748	
Н	-5.13084464	-1.32475937	0.00015145	
Н	-2.88759559	-2.39040856	-0.00000407	

 Table S2. B3LYP/6-31G optimized standard orientation of BTBF (3a).

				_
Atom	Х	Y	Z	
С	1.99322160	0.56881678	-0.00006849	
С	2.42910857	-0.78470963	0.00004425	
С	3.78274872	-1.11316185	0.00010013	
С	4.71890429	-0.07334581	0.00002496	
С	4.30343902	1.27137913	-0.00007423	
С	2.94912648	1.60020930	-0.00010162	
С	0.56528890	0.61629756	-0.00004920	
С	-0.10934973	-0.57949759	-0.00001164	
Н	4.10574160	-2.14828199	0.00022768	
Н	5.77761166	-0.31011324	0.00006284	
Н	5.04702960	2.06118083	-0.00012845	
Н	2.62540621	2.63507940	-0.00014736	
С	-3.89612599	-0.33300540	-0.00016067	
С	-2.70424527	-1.04424080	-0.00026168	
С	-1.51741851	-0.29488476	-0.00015969	
С	-1.60092206	1.12597358	-0.00008532	
С	-2.80000857	1.82337208	0.00018058	
С	-3.97583993	1.06573331	0.00011014	
Н	-2.70999887	-2.12635423	-0.00038132	
Н	-2.81951464	2.90572368	0.00039655	
Н	-4.94889109	1.53967452	0.00043954	
0	-0.31472870	1.70230213	0.00005429	
S	1.02701852	-1.98851820	0.00009850	
F	-5.09104625	-1.05029448	0.00006612	

 Table S3. B3LYP/6-31G optimized standard orientation of F-BTBF (3c).

### DFT calculation of F,Cl-BTBF (**3d**)

Atom	Х		Y	Ζ
С	-1.38145731	0	.05133421	-0.00002335
С	-1.59779874	-1.35411568	0.00006672	
С	-2.88388238	-1.88914131	0.00044388	
С	-3.97663227	-1.01573103	0.00037199	
С	-3.75274842	0.36734640	0.00011163	
С	-2.48310981	0.92557362	-0.00023198	
С	0.01961649	0.32636114	-0.00003111	
С	0.87360141	-0.74877902	-0.00020283	
Н	-3.04505080	-2.96107076	0.00051414	
Н	-4.98805022	-1.40188925	0.00042294	
Н	-2.33910024	1.99837396	-0.00045829	
С	4.43089944	1.48562114	0.00001967	
С	4.57348345	0.09168148	-0.00003151	
С	3.50898481	-0.79879618	-0.00007036	
С	2.21922453	-0.24558086	-0.00019265	
С	2.07684262	1.17055185	-0.00012286	
С	3.15061264	2.04874477	-0.00001571	
Н	5.31668171	2.10749251	0.00008457	
Н	3.68633371	-1.86629914	-0.00013237	
Н	2.99916032	3.12058002	0.00000575	
0	0.71536398	1.53674469	0.00019009	
S	-0.02539247	-2.31949350	-0.00030785	
F	5.86572189	-0.42778418	0.00037486	
Cl	-5.20023075	1.48119914	-0.00005616	

 Table S4. B3LYP/6-31G optimized standard orientation of F,Cl-BTBF (3d).

Atom	Х	Y	ζ	Z
С	2.02184757	0.55916418	-0.00005499	
С	2.44163328	-0.79969524	0.00001991	
С	3.79101255	-1.14488516	0.00011544	
С	4.74082116	-0.11726992	0.00016289	
С	4.34175340	1.23227607	0.00009922	
С	2.99138945	1.57784902	-0.00001288	
С	0.59453779	0.62499042	-0.00016256	
С	-0.09601541	-0.56120458	-0.00018100	
Н	4.10064275	-2.18419398	0.00016454	
Н	5.79652747	-0.36741263	0.00025312	
Н	5.09498988	2.01305992	0.00013210	
Н	2.68073711	2.61676956	-0.00007044	
С	-3.93739670	1.10803129	0.00009828	
С	-3.92398532	-0.30903059	0.00007990	
С	-2.70081874	-0.99049442	-0.00001463	
С	-1.50212657	-0.25955919	-0.00008017	
С	-1.56637256	1.15851206	-0.00004460	
С	-2.76112536	1.86266797	0.00003487	
Н	-4.89315531	1.62334729	0.00021028	
Н	-2.68266636	-2.07547909	-0.00010293	
Н	-2.77380505	2.94575503	0.00005093	
0	-0.27273033	1.72200353	-0.00012050	
С	-5.23221611	-1.07153231	0.00012946	
Н	-5.06258749	-2.15257202	0.00065843	
Н	-5.83754442	-0.82877356	0.88262296	
Н	-5.83710335	-0.82964495	-0.88290478	
S	1.02363605	-1.98473758	-0.00007406	

 Table S5. B3LYP/6-31G optimized standard orientation of M-BTBF (3e).

### DFT calculation of BTNF (3j)

Atom	Х	Y		Ζ
С	-2.76976957	0.59410781	-0.00002392	
С	-3.27470436	-0.73556589	0.00012537	
С	-4.64341135	-0.99439766	0.00035385	
С	-5.52522851	0.09189557	0.00045317	
С	-5.04126658	1.41377824	0.00032510	
С	-3.67207958	1.67311378	0.00008318	
С	-1.34175178	0.57027159	-0.00030296	
С	-0.72908677	-0.65566479	-0.00037655	
Н	-5.01865602	-2.01180849	0.00046048	
Н	-6.59474399	-0.09018030	0.00063351	
Н	-5.74370605	2.24049811	0.00040556	
Н	-3.29540867	2.68989385	-0.00002320	
С	5.54882627	-0.82952447	0.00039471	
С	4.30499347	-1.42316174	0.00010562	
С	3.11181249	-0.63937574	-0.00010221	
С	3.23423757	0.80286575	0.00001190	
С	4.53781362	1.37910020	0.00031742	
С	5.66657487	0.58682093	0.00050258	
Н	1.75002898	-2.32925800	-0.00023993	
Н	6.44496354	-1.44158742	0.00053807	
Н	4.21269781	-2.50555952	0.00002105	
С	1.82775586	-1.24691826	-0.00034140	
С	2.06385009	1.61441400	-0.00017040	
Н	4.62631442	2.46172213	0.00039960	
Н	6.65147745	1.04252442	0.00073564	
С	0.85127409	0.98129327	-0.00051619	
С	0.69566639	-0.44920722	-0.00044881	
Н	2.13704082	2.69554716	-0.00012832	
0	-0.41136396	1.61820638	-0.00047977	
S	-1.93450837	-2.00628220	-0.00008169	

 Table S6. B3LYP/6-31G optimized standard orientation of BTNF (3j).



Figure S2. HOMOs and LUMOs of BTBF (3a), F-BTBF (3c), F,Cl-BTBF (3d), M-BTBF (3e) and BTNF (3j) by DFT calculations at the B3LYP/6-31G level.



Figure S3. Energy level (E<sub>HOMOs</sub> and E<sub>LUMOs</sub>) diagrams of BTBFs and BTNF.

#### 3. Experimental section

#### General information

All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed using TLC silica gel 60 F254 glass plates. Silica gel 60 (200-300 mesh) was used for column chromatography. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were measured on JEOL 400YH spectrometer. Chemical shifts for hydrogens are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane ( $\delta = 0$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplate), and coupling constant (Hz). Detection and analysis of compounds by gas chromatography (Shimadzu GC-2010 plus). High resolution mass spectra (HRMS) were determined on a Bruker Apex IV Fourier Transform Mass Spectrometer (EI). UV-Vis spectra were measured by Shimadzu UV-1800 ENG240V, SOFT. Fluorescence spectra were measured by Shimadzu-RF-5301pc.

Synthesis and characterization of related compounds:

2,3-Dibromobenzo[*b*]thiophene:

Benzo[*b*]thiophene (5.4 g, 40 mmol) was dissolved in 50 ml CHCl<sub>3</sub>, and then Br<sub>2</sub> (4.3 ml, 84 mmol) was added to the solution under ice-water bath. After it was stirred for 18 h at room temperature, NaHCO<sub>3</sub> aqueous solution was added to neutralize hydrobromic acid formed in the reaction mixture. The organic layer was extracted with dichloromethane (DCM) and washed with saturated brine, and then dried with MgSO<sub>4</sub>. The solvents were removed and the residue was recrystallized from methanol/ethanol co-solvents (v/v = 2/1), affording 2,3-dibromobenzo[*b*]thiophene (10 g, 34 mmol, 85%) as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76-7.71 (m, 2H), 7.45-7.36 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.96, 137.56, 125.79, 125.65, 123.44, 121.97, 114.34, 111.83. These data are consistent with those reported in the literature <sup>3</sup>.



2,3-Dibromo-5-chlorobenzo[b]thiophene:

2,3-Dibromo-5-chlorobenzo[*b*]thiophene was synthesized from 5-chlorobenzo[*b*]thiophene (3 g, 17.8 mmol) following the similar procedure with the synthesis of 2,3-dibromo-benzo[*b*]thiophene. After purification by recrystallization from methanol/ethanol co-solvents (v/v = 2/1), 2,3-dibromo-5-chlorobenzo[*b*]thiophene (2.7 g, 8.3 mmol, 47%) was obtained as white solid. <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>)  $\delta$  7.72 (d, J = 2.1, 1H), 7.61 (d, J = 8.4, 1H), 7.34 (dd, J = 8.6, 1.9, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.70, 137.04, 132.22, 126.27, 123.10, 123.03, 116.25, 111.02. MS (EI): [M]<sup>+</sup> 326. These data are consistent with those reported in the literature <sup>3</sup>.

2,3-Dibromo-6-octylbenzo[b]thiophene:



First step: preparation of 6-octylbenzo[b]thiophene:

6-Bromobenzo[*b*]thiophene (200 mg, 0.94 mmol) and NiCl<sub>2</sub>(dppp) (49 mg, 0.1 mmol) was added into a 50 ml round-bottomed 2-necked flask containing 15 ml of distilled THF under N<sub>2</sub> atmosphere. C<sub>8</sub>H<sub>17</sub>MgBr (0.7 ml, 1.9 mmol) was added to the tube slowly. It was stirred for 24 h at room temperature. The reaction mixture was quenched by NH<sub>4</sub>Cl solution (1 mol/L) and then extracted for three times with ethyl acetate. The organic layer was washed with saturated brine, and then dried with MgSO<sub>4</sub>. After the solvents were removed, the residue was purified by flash column chromatography on silica gel, affording 6-octylbenzo[*b*]thiophene (185 mg, 0.75 mmol, 80%) as colorless oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.35 (d, *J* = 5.5 Hz, 1H), 7.28 (d, *J* = 4.9 Hz, 1H), 7.19 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.76 – 2.68 (m, 2H), 1.72 – 1.61 (m, 2H), 1.35 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.02, 139.29, 137.61, 125.43, 125.24, 123.58, 123.22, 121.70, 36.09, 31.91, 31.84, 29.49, 29.41, 29.27, 22.73, 14.09. MS (EI): [M]<sup>+</sup> 246. All the data are consistent with the literature reported <sup>3</sup>.

Second step: preparation of 2,3-dibromo-6-octylbenzo[b]thiophene:

2,3-Dibromo-6-octylbenzo[*b*]thiophene (2.0 g, 8.1 mmol) was synthesized following the similar condition as the synthesis of 2,3-dibromobenzo[*b*]thiophene except that the temperature was not above 10 °C. 2,3-Dibromo-6-octylbenzo[*b*]thiophene (2.9 g, 7.2 mmol, 89%) was obtained as light yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d, *J* = 8.2 Hz, 1H), 7.48 (s, 1H), 7.22 (dd, *J* = 8.3, 1.3 Hz, 1H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.63-1.70 (m, 2H), 1.26-1.30 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  141.15, 139.06, 135.57, 126.69, 123.06, 121.20, 112.88, 111.54, 36.07, 32.01, 31.69, 29.60, 29.46, 29.39, 22.82, 14.28. MS (EI): [M]<sup>+</sup> 404.

Synthesis of 5-(tert-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol:



First step: preparation of 2-bromo-5-(tert-butyl)phenol:

3-(Tert-butyl)phenol (3 g, 20 mmol) was dissolved in 50 ml DCM and then Br<sub>2</sub> (1.04 ml, 20.3 mmol) was added into the solution under ice-water bath. After it was stirred for 7 h at room temperature, NaHCO<sub>3</sub> aqueous solution was added to neutralize the hydrobromic acid. The organic

layer was extracted with DCM and washed with saturated brine, and then dried with MgSO<sub>4</sub>. After the solvent was removed, 2-bromo-5-(*tert*-butyl)phenol (4.1 g, 18 mmol, 90%) was obtained as yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 8.5 Hz, 1H), 7.08 (dd, J = 2.3, 1.1 Hz, 1H), 6.85 (dd, J = 8.5, 2.3 Hz, 1H), 5.56 (s, 1H), 1.30 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.18, 151.83, 131.42, 119.28, 113.54, 106.93, 34.73, 31.26. These data are consistent with those reported in the literature <sup>4</sup>.

Second step: preparation of 5-(*tert*-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol:

2-Bromo-5-(*tert*-butyl)phenol (1.2 g, 5 mmol) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi-1,3,2-dioxaborolane (B<sub>2</sub>Pin<sub>2</sub>) (1.5 g, 6 mmol) was dissolved in 50 ml dioxane-H<sub>2</sub>O co-solvents (v/v = 4:1) in a 100 ml two-necked round bottom flask, then KOAc (0.8 g, 7.5 mmol) was added to the solution. After the solution was bubbled with N<sub>2</sub> for 20 min, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (123 mg, 0.15 mmol) was added. Then the reaction was heated to 90 °C for 12 h. After the reaction mixture was cooled to room temperature, the organic layer was separated and dried with MgSO<sub>4</sub>. It was filtered and the filtrate was evaporated under vacuum, the residue was purified by flash chromatography to afford the 5-(*tert*-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (0.54 g, 2.2 mmol, 44%) as white solid (mp 157.6 -158.8 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 6.94–6.92 (m, 2H), 1.34 (s, 12H), 1.29 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.63, 158.03, 135.41, 117.09, 112.57, 84.39, 35.08, 31.14, 24.88. HRMS (ESI) calcd for C<sub>16</sub>H<sub>26</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 277.1975, found 277.1971.



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthalenol (2j):

3-Iodo-2-naphthalenol (4 g, 14.8 mmol) and B<sub>2</sub>Pin<sub>2</sub> (7.4 g, 29.6 mmol) was dissolved in 50 ml dioxane-H<sub>2</sub>O co-solvents (v/v = 4:1) in a 100 ml two-necked round bottom flask, then KOAc (3.3 g, 29.6 mmol) was added to the solution. After the solution was bubbled with N<sub>2</sub> for 20 min, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (855 mg, 0.74 mmol, 5 mol %) was added. Then the reaction mixture was heated to 90 °C for 12 h. After the reaction mixture was cooled to room temperature, the organic layer was separated and dried with MgSO<sub>4</sub>. It was filtered and the filtrate was evaporated under vacuum, the residue was purified by flash chromatography to afford 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthalenol (2.1 g, 7.8 mmol, 53%) as light-yellow solid (mp 56.3 - 57.1 °C). <sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>)  $\delta$  8.33 (s, 1H), 7.25 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.57-6.53 (m, 1H), 6.40-6.36 (m, 1H), 6.25 (s, 1H), 0.42 (s, 12H); <sup>13</sup>C NMR (101 MHz, DMSO-D<sub>6</sub>)  $\delta$  158.87, 138.01, 136.29, 128.30, 127.47, 127.30, 125.75, 122.86, 118.18, 108.48, 83.58, 24.70. HRMS (ESI) calcd for C<sub>16</sub>H<sub>19</sub>BO<sub>3</sub> [M-H]<sup>-</sup> 269.1354, found 269.1352.

General procedure for screening of reaction conditions (entries 1-20 in Table 1):

Compound **1a** (0.48 mmol), **2a** (0.4 mmol) and base (1.2 mmol) were added into 25 ml Schlenk tube. Then *tert*-butanol (5 ml, containing 5 mol % 18-crown-6 for some entries) was added under nitrogen atmosphere. After the solution was bubbled for 10 min with nitrogen, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.5-5 mol %) was added to the reaction system. After the reaction was stirred at 90 °C for 24 h, copper catalyst (2-5 mol %) were added to the mixture (200 mg activated 3 Å molecular sieves was added as water adsorbent for some entries), and then it was stirred for another 4 h. TCE (100 µl) was added as an internal standard for GC analysis. About 2 ml ethyl acetate and 2 ml petroleum ether were added for extraction. The GC sample was prepared by dilution of 0.1 ml the above organic layer with 2 mL ethyl acetate. GC yield was determined using standard curve with TCE as an internal standard (see Figure S1). The product has the same retention time with authentic sample which is synthesized by conventional method. <sup>4</sup>

#### General procedure for synthesis of **3a-3f**:

Compound 1 (0.48 mmol), 2 (0.4 mmol) and  $K_3PO_4 \cdot 3H_2O$  (319 mg, 1.2 mmol) were added to 25 ml Schlenk tube. *Tert*-butanol (5 ml) containing 5 mol % 18-crown-6 was added under nitrogen atmosphere. After the solution was bubbled for 10 min with nitrogen, Pd (PPh<sub>3</sub>)<sub>4</sub> (2 mol %) was added to the reaction system. After the reaction was stirred at 90 °C for 24 h, 200 mg activated 3Å molecular sieves and CuTc (2 mol %) were added to the mixture, and then it was stirred for another 4 h. After the removal of the solvents under reduced pressure, the residue was purified by flash chromatography with petroleum ether as an eluent to afford target molecules.



Benzo[4,5]thieno[3,2-*b*] benzofuran (**3a**): white solid (71 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.50-7.32 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.89, 153.10, 142.10, 125.24, 125.06, 125.03, 124.48, 124.16, 123.42, 119.82, 119.71, 118.69, 112.68. These data are consistent with those reported in the literature <sup>3</sup>.



3-Chlorobenzo[4,5]thieno[3,2-*b*]benzofuran (**3b**): white solid (52 mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 2.1 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.71 (dd, J = 7.7, 1.2 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.43 – 7.29 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.98, 151.91,

140.02, 131.41, 126.19, 125.58, 125.39, 125.28, 123.84, 123.61, 120.55, 119.89, 119.55, 112.83. All the data are consistent with the literature reported <sup>3</sup>.



8-Fluorobenzo[4,5]thieno[3,2-*b*]benzofuran (**3c**): white solid (45 mg, 44% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 9.0, 4.1 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.45 – 7.37 (m, 2H), 7.10 (td, *J* = 9.0, 2.7 Hz, 1H); <sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>)  $\delta$  159.33 (d, *J* = 238 Hz), 154.80 (d, *J* = 31 Hz), 142.25, 125.43, 125.14, 124.98, 124.83, 124.72, 124.47, 119.95, 118.39, 113.21 (d, *J* = 10 Hz), 112.38 (d, *J* = 26 Hz), 105.64 (d, *J* = 26 Hz). All the data are consistent with the literature reported <sup>3</sup>.



3-Chloro-8-fluorobenzo[4,5]thieno[3,2-*b*]benzofuran (**3d**): white solid (34 mg, 38% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 2.3 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.59 (dd, J = 9.1, 4.1 Hz, 1H), 7.42-7.36 (m, 2H), 7.13 (td, J = 9.1, 2.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.38 (d, J = 243 Hz), 155.03, 153.40, 140.13, 131.52, 125.92, 125.71, 125.37, 124.50, 124.39, 119.67, 113.43 (d, J = 10 Hz), 113.01 (d, J = 26 Hz), 105.82 (d, J = 26 Hz). All the data are consistent with the literature reported <sup>3</sup>.



8-Methylbenzo[4,5]thieno[3,2-*b*]benzofuran (**3e**): white solid (35 mg, 36% yield), mp 111.1-112.4 °C. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.51-7.53 (m, 2H), 7.46 (td, *J* = 7.5, 0.9 Hz, 1H), 7.35-7.39 (m, 1H), 7.17-7.19 (m, 1H), 2.50 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.29, 153.22, 142.00, 133.02, 126.19, 125.32, 125.01, 124.89, 124.46, 124.10, 119.73, 119.66, 118.46, 112.13, 21.54. HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>OS [M]<sup>+</sup> 238.0452, found 238.0443.



8-Octylbenzo[4,5]thieno[3,2-b]benzofuran (3f): white solid (74 mg, 61% yield), mp 57.4 - 58.7 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, J = 8.2 Hz, 1H), 7.63-7.72 (m, 3H), 7.29-7.39 (m, 3H), 2.76 (t, J = 7.5 Hz, 2H), 1.66-1.73 (m, 2H), 1.25-1.42 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.74, 153.18, 142.49, 140.44, 126.10, 124.67, 124.35, 123.81, 123.34, 123.22, 119.49, 119.47, 117.68, 112.58, 36.29, 32.02, 31.83, 29.62, 29.45, 29.39, 22.81, 14.26. HRMS (EI) calcd for C<sub>22</sub>H<sub>24</sub>OS [M]<sup>+</sup> 336.1548, found 336.1544.



2-Octyl-7-*tert*-butylbenzo[4,5]thieno[3,2-*b*]benzofuran (**3g**):

The title compound was prepared from was prepared from 2,3-dibromo-6-octylbenzo[b]thiophene (194 mg, 0.48 mmol) and 5-(tert-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (110 mg, 0.4 mmol) as colorless liquid (63 mg, 40% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 8.2 Hz, 1H), 7.70-7.65 (m, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.40 (dd, J = 8.2, 1.8 Hz, 1H), 7.29 (dd, J = 8.2, 1.4 Hz, 1H), 2.75 (t, J = 7.8 Hz, 2H), 1.65-1.73 (m, 2H), 1.42 (s, 9H), 1.27-1.39 (m, 10H), 0.88 (t, J = 6.9Hz, 3H);  ${}^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.19, 153.02, 148.81, 142.25, 140.10, 126.02, 123.80, 123.38, 121.71, 121.05, 119.26, 118.75, 117.58, 109.40, 36.29, 35.23, 32.02, 31.87, 31.78, 29.63, 29.47, 29.40, 22.81, 14.27. HRMS (EI) calcd for C<sub>26</sub>H<sub>32</sub>OS [M]<sup>+</sup> 392.2174, found 392.2165.



7-(*Tert*-butyl)benzo[4,5]thieno[3,2-*b*]benzofuran (**3h**):

The title compound was prepared from 2,3-dibromobenzo[b]thiophene (140 mg, 0.48 mmol) and 5-(tert-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (110 mg, 0.4 mmol) as white solid (56 mg, 47% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 1.2 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.34–7.48 (m, 3H), 1.42 (s, 9H); <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{CDCl}_3) \delta$  159.33, 152.91, 149.16, 141.85, 125.36, 124.90, 124.63, 124.38, 121.49, 121.07, 119.53, 118.89, 118.58, 109.41, 35.19, 31.70. All the data are consistent with the literature reported <sup>3</sup>.



3-Chloro-7-*tert*-butylbenzo[4,5]thieno[3,2-*b*]benzofuran (3i):

The title compound was prepared from 2,3-dibromo-5-chlorobenzo[b]thiophene (156 mg, 0.48 mmol) and 5-(tert-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (110 mg, 0.4 mmol): white solid (41 mg, 32% yield), mp 64.6 - 65.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, J = 2.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.68-7.65 (m, 2H), 7.43 (dd, J = 8.3, 1.6 Hz, 1H), 7.33 (dd, J = 8.6, 1.9 Hz, 1H), 1.42 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.42, 158.03, 154.90, 153.27, 140.00, 131.39, 125.78, 125.58, 125.25, 119.54, 113.35, 113.26, 105.63, 105.57, 29.70, 14.07. HRMS (EI) calcd for C<sub>18</sub>H<sub>15</sub>ClOS [M]<sup>+</sup> 314.0532, found 314.0529.



Benzo[4,5]thieno[3,2-*b*]naphthalenefuran (**3j**):

The title compound was prepared from 2,3-dibromobenzo[*b*]thiophene (140 mg, 0.48 mmol) and 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthalenol (108 mg, 0.4 mmol) as white solid (39 mg, 35% yield), mp 244.7 - 245.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (s, 1H), 8.02-8.05 (m, 2H), 7.96-8.00 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.46-7.52 (m, 3H), 7.40-7.44 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.93, 154.02, 141.64, 130.47, 129.57, 127.13, 127.00, 124.48, 124.41, 124.15, 123.75, 123.49, 119.18, 116.99, 116.50, 107.37. HRMS (EI) calcd for C<sub>18</sub>H<sub>10</sub>OS [M] + 274.0452, found 274.0448.

### 4. Measurement of photophysical data

UV-Visible spectra of **3a**, **3c**, **3d**, **3e** and **3j** were obtained on Shimadzu UV-1800ENG240V, SOFT spectrometer. Ca.  $6 \times 10^{-5}$  M of sample solutions in ethanol were used for ambient temperature measurement. As shown in Figure 1, the absorption spectra of these compounds exhibit fine structures, and the maximum absorption peaks at 318, 320, 319, 319 and 355 nm.

Fluorescence spectra of **3a**, **3c**, **3d**, **3e** and **3j** were obtained on Shimadzu-RF-5301pc spectrometer with Ca.  $2 \times 10^{-7}$  M of sample solutions in ethanol were used for ambient temperature measurement. Using the maximum absorption wavelength as the excitation wavelength for fluorescence measurement, we found that the maximum emission peaks of these compounds are located at 339, 342, 347, 340, 378 nm, respectively.

9,10-Diphenylanthracene ( $\Phi_f = 0.95$  in ethanol) is used as the reference compound for the measurement of fluorescence quantum yield. Ca.  $5 \times 10^{-6}$  M of sample and reference solutions in ethanol were used to make sure that the absorption intensity ( $A_u$  and  $A_s$ ) is below 0.1. Through software processing, we integrate the fluorescence spectra and get the integral area labeled  $F_u$  (Fluorescence intensity of the compounds to be measured). Similarly, the fluorescence spectra of

9,10-diphenylanthracene and the integral area labeled  $F_s$  (Fluorescence intensity of reference material) were measured.  $\mathcal{P}_u$  (Fluorescence quantum yield of the compounds to be measured) can be obtained from formula  $A_u \cdot \mathcal{P}_u \cdot F_s = A_s \cdot \mathcal{P}_s \cdot F_u$ .

### 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra and HRMS spectra

<sup>1</sup>H NMR spectrum of 2,3-dibromobenzo[*b*]thiophene





### <sup>13</sup>C NMR spectrum of 2,3-dibromobenzo[*b*]thiophene

<sup>13</sup>C NMR spectrum of 2,3-dibromo-5-chlorobenzo[*b*]thiophene





<sup>1</sup>H NMR spectrum of 2,3-dibromo-6-octylbenzo[*b*]thiophene





S20 / S39



<sup>13</sup>C NMR spectrum of 5-(*tert*-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol





HR-MS spectrum of 5-(*tert*-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol:



S23 / S39

### HRMS spectrum of 2j



### <sup>1</sup>H NMR spectrum of **3a**



### <sup>1</sup>H NMR spectrum of **3b**







S28 / S39



### HRMS spectrum of 3e





### HRMS spectrum of 3f





### HRMS spectrum of 3g



 $^1\mathrm{H}$  NMR spectrum of 3h



<sup>13</sup>C NMR spectrum of **3h** 





### HRMS spectrum of 3i







### 6. References

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