Synthesis of Fluorene-Based Oligomeric Organoboron Reagents *via* Kumada, Heck and Stille Cross-Coupling Reactions

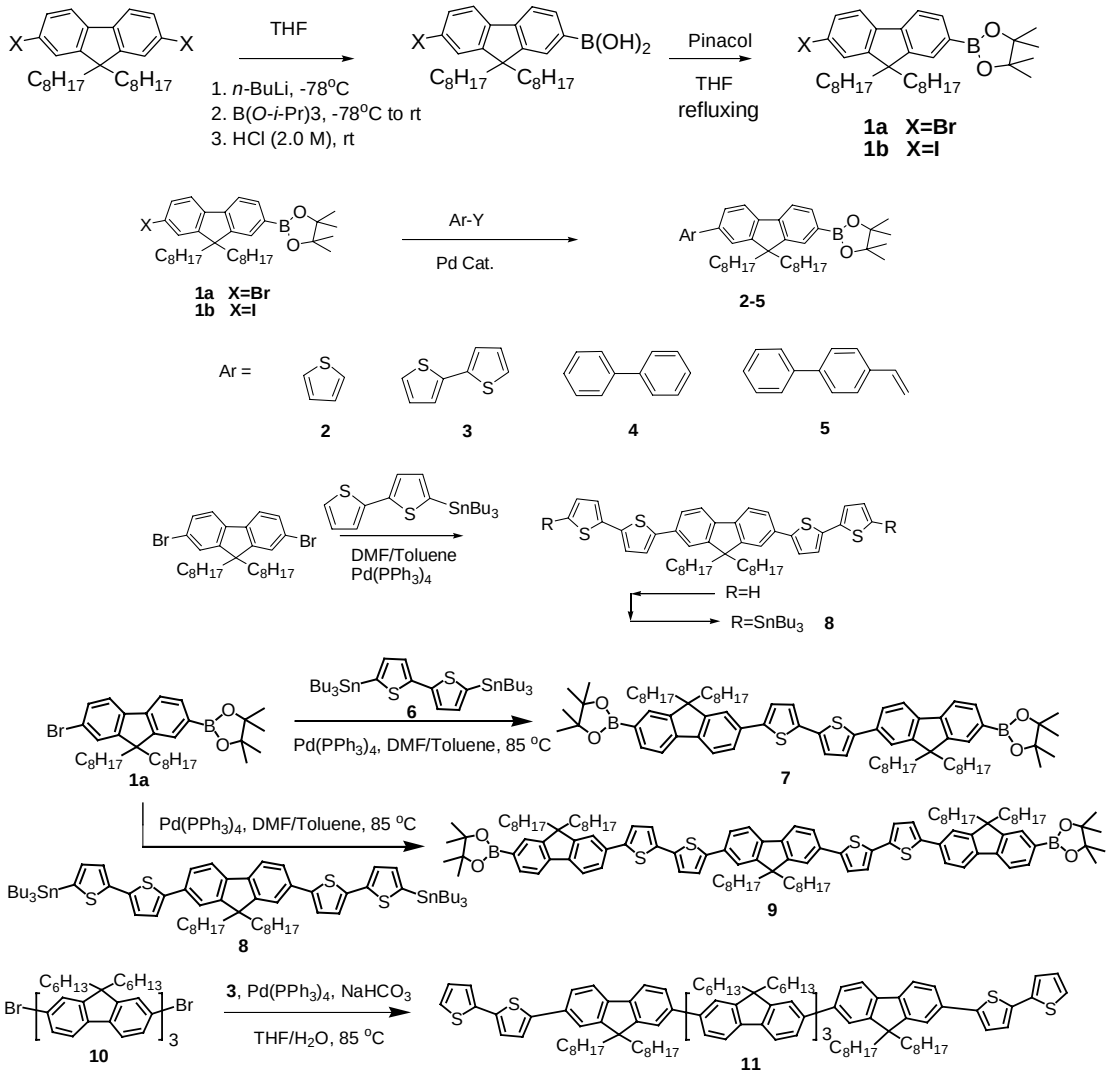
Xiaojie Zhang, Hongkun Tian, Qin Liu, Lixiang Wang, Yanhou Geng* and Fosong Wang

Supporting Information

Contents

* E-mail: yhgeng@ciac.jl.cn

Scheme S1. Synthesis route of intermediates and target compounds.



General. Nuclear magnetic resonance spectra were taken on a 300 MHz spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Molecular mass was measured with MALDI-TOF mass spectrometer or Gas Chromatography-Mass spectrometer. The purity of the compounds was characterized with High Performance Liquid Chromatography (HPLC).

Materials. All chemical reagents and solvents were used as received from

commercial sources without further purification except ethyl ether, tetrahydrofuran (THF) and toluene that had been distilled over sodium/benzophenone. 2,7-Dibromo-9,9-dioctylfluorene and 2,7-diodo-9,9-dioctylfluorene[1]; thienyl magnesium bromide[2]; 2-Tributylstannylthiophene, 5-tributylstannyl-2,2'-bithiophene, 5,5'-bis(tributylstannyl)-2,2'-bithiophene and 4-tributylstannylbiphenyl[3]; 4-phenylbenzaldehyde [4], 4-phenylstyrene [5] and 2,7''-dibromo-[9,9,9',9',9'',9''-hexahexyl] –7,2';7',2''-terfluorene (**10**) [6] were synthesized according to the reported methods. ^{1}H NMR spectra of these compounds are identical to those reported in the references.

7'-Bromo-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane

(1a)

Into a solution of 2,7-dibromo-9,9-dioctylfluorene (7.27 g, 13.3 mmol) in anhydrous THF (130 ml) was added *n*-BuLi (2.86 M in hexane, 4.80 ml, 13.3 mmol) at –78 ^{o}C. The reaction mixture was stirred for 1 h before triisopropyl borate (2.51 g, 3.10 mL, 13.3 mmol) was added in one portion. The mixture was warmed to room temperature, stirred over night and then quenched with aqueous HCl (2.0 M, 40 mL) before adding a large amount of water for extraction with ethyl ether. The organic extracts were washed with brine and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product of 7-bromo-9,9-dioctyl-fluoren-2-yl-boronic acid was obtained. The crude product was refluxed with Pinacol (1.80 g, 14.6 mmol) in anhydrous THF (100 mL) overnight. The mixture was cooled to room temperature, extracted with ethyl ether,

washed with water and dried over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether: ethyl acetate (8:1) as the eluent to afford **1a** (5.94 g, 75%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J*=7.14 Hz, 1H), 7.72 (s, 1H), 7.66 (d, *J*=7.68 Hz, 1H), 7.58 (dd, *J*=6.97 Hz, *J*=1.92 Hz, 1H), 7.44-7.46 (m, 2H), 1.94-1.97 (m, 4H), 1.39 (s, 12H), 1.03-1.27 (m, 20H), 0.80-0.88 (m, 6H), 0.48-0.63 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.0, 150.0, 143.4, 140.4, 134.3, 130.3, 129.3, 126.6, 121.9, 119.4, 84.2, 77.5, 55.9, 40.5, 32.2, 30.3, 29.6, 25.3, 24.0, 23.0, 14.4. Anal. Calcd. for $C_{35}H_{52}BBrO_2$: C, 70.59; H, 8.80. Found: C, 70.85; H, 8.48. Molecular Mass: Calcd for $C_{35}H_{52}BBrO_2$: 596. Found: 596. (GC-MS: 98.89%).

7'-Iodo-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (1b)

The procedure for the synthesis of 7'-bromo-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (**1a**) was followed to prepare **1b** as a light-yellow oil in a 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J*=7.62 Hz, 1H), 7.72 (s, 1H), 7.64-7.67 (m, 3H), 7.46 (d, *J*=8.46 Hz, 1H), 1.91-1.97 (m, 4H), 1.39 (s, 12H), 1.03-1.22 (m, 20H), 0.80-0.85 (m, 6H), 0.46-0.66 (m, 4H). Anal. Calcd. For $C_{35}H_{52}BIO_2$: C, 65.43; H, 8.16. Found: C, 65.65; H, 7.96. Molecular Mass: Calcd for $C_{35}H_{52}BIO_2$: 642. Found: 642. (GC-MS: 96.91%).

2,7-Bis (2,2'-bithien-5-yl)-9,9-dioctylfluorene

A solution of 2,7-dibromo-9,9-bis(*n*-octyl)-fluorene (2.70 g, 5.00 mmol),

5-tributylstannyl-2,2'-bithiophene (4.60 g, 10.0 mmol), and $Pd(PPh_3)_4$ (230 mg, 0.200 mmol) in 100 mL of anhydrous DMF and Toluene (1:1) was stirred for 24 h at 85 ^oC. The mixture was cooled to room temperature then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with KF aqueous solution and brine before dried over $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum/methylene chloride (10:1) as the eluent to afford 2,7-bis (2,2'-bithien-5-yl)-9,9-dioctylfluorene (2.60 g, 72%) as a yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J*=3.96 Hz, 2H), 7.55-7.62 (m, 4H), 7.30 (d, *J*=1.88 Hz, 2H), 7.23-7.25 (m, 4H), 7.19 (d, *J*=1.89 Hz, 2H), 7.04-7.07 (m, 2H), 2.00-2.05 (m, 4H), 1.08-1.17 (m, 20H), 0.77-0.81 (m, 6H), 0.70 (m, 4H). Anal. Calcd. For $C_{45}H_{50}S_4$: C, 75.16; H, 7.01. Found: C, 75.30; H, 7.04.

2,7-Bis (5-tributylstannyl -2,2'-bithien-5'-yl)-9,9-dioctylfluorene (8)

Into a solution of 2,7-bis (2,2'-bithien-5-yl)-9,9-dioctylfluorene (1.00 g, 1.40 mmol) in anhydrous THF (28 mL) was added *n*-BuLi (2.50 M in hexane, 1.20 mL, 3.00 mmol) at -78 ^oC. The reaction mixture was stirred for 1 h before tributyltin chloride (1.10 g, 0.90 mL, 3.30 mmol) was added in one portion. The mixture was warmed to room temperature, stirred over night and then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with Na_2CO_3 aqueous solution and brine before dried over $MgSO_4$. Upon evaporating off the solvent, the crude product of **8** was obtained for next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J*=3.96 Hz, 2H), 7.60 (dd, *J*=3.96 Hz, *J*=0.72 Hz, 2H), 7.55 (d, *J*=0.71 Hz, 2H), 7.35 (d, J=1.67 Hz, 2H), 7.30 (d, *J*=1.91 Hz, 2H), 7.18 (d, *J*=1.86 Hz, 2H), 7.10 (d, *J*=1.67 Hz, 2H), 2.00-2.02 (m, 4H), 1.57-1.61 (m, 6H), 1.33-1.41 (m, 6H), 1.07-1.17 (m, 26H), 0.80-0.95(m, 15H), 0.70 (m, 4H).

7'-(Thien-2-yl)-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (2)

A. From 1a by Stille reaction

In absence of light, a solution of 2-tributylstannyl thiophene (1.45 g, 3.90 mmol), **1a** (2.32 g, 3.90 mmol), and $Pd(PPh_3)_4$ (135 mg, 0.120 mmol) in 80 mL of anhydrous DMF and Toluene (1:1) was stirred for 24 h at 85 ^{o}C. The mixture was cooled to room temperature then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine before dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (16:1) as the eluent to afford **2** (1.80 g, 77%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J*=7.56 Hz, 1H), 7.11-7.78 (m, 3H), 7.59-7.65 (m, 2H), 7.42 (dd, *J*=7.20 Hz, *J*=1.05 Hz, 1H), 7.33 (dd, *J*=10.2 Hz, *J*=1.02Hz, 1H), 7.15 (m, 1H), 2.02-2.05 (m, 4H), 1.43 (s, 12H), 1.06-1.20 (m, 20H), 0.81-0.98 (m, 6H), 0.55-0.71 (m, 4H). Molecular Mass: Calcd for $C_{39}H_{55}BO_2S$: 598.4016. Found: 598.4020 (MALDI-TOF MS). (HPLC: 95.67%)

B. From 1b by Stille reaction

The procedure for the synthesis of **2** from **1a** was followed to prepare **2** (0.22 g, 58.4%) from **1b** and 2-tributylstannyl thiophene. (HPLC: 92.27%)

C. From 1a by Kumada reaction

A solution of thienyl magnesium bromide (1.1 mL, 0.8 M/L, 0.88 mmol), **1a** (0.50 g, 0.84 mmol), and Pd(dppf)Cl_2 (7.0 mg, 0.0086 mmol) in 10 mL of anhydrous THF was stirred for 48 h at room temperature. The mixture was poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (16:1) as the eluent to afford **2** (0.42 g, 86%) as a light yellow oil. (HPLC: 96.30%)

D. From 1b by Kumada reaction

The procedure for the synthesis of **2** from **1a** by Kumada reaction was followed to prepare **2** (0.12 g, 22%) as a yellow oil from **1b** and thienyl magnesium bromide. (HPLC: 52.35%)

7'-(2,2'-bithien-5-yl)-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (3)

A. From 1a by Stille reaction

The procedure for the synthesis of **2** from **1a** by Stille reaction was followed to prepare **3** from **1a** and 5-tributylstannyl-2,2'-bithiophene in a yield of 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J*=7.59 Hz, 1H), 7.71-7.78 (m, 3H), 7.58-7.64 (m, 2H), 7.33 (d, *J*=3.72 Hz, 1H), 7.26-7.27 (m, 2H), 7.21 (d, *J*=3.81 Hz,

1H), 7.06-7.09 (m, 1H), 2.01-2.08 (m, 4H), 1.43 (s, 12H), 1.07-1.23 (m, 20H), 0.80-0.90 (m, 6H), 0.61-0.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.6, 150.5, 144.3, 143.9, 141.1, 137.9, 136.9, 134.2, 133.7, 129.3, 128.3, 127.9, 125.0, 124.9, 124.7, 124.0, 120.9, 120.3, 119.4, 84.1, 77.8, 77.6, 77.4, 74.0, 55.6, 40.6, 32.2, 30.3, 29.6, 28.3, 27.3, 25.3, 24.1, 23.0, 17.9, 14.4, 14. Anal. Calcd. for $C_{43}H_{57}BO_2S_2$: C, 75.85; H, 8.44. Found: C, 75.63; H, 8.11. Molecular Mass: Calcd for $C_{43}H_{57}BO_2S_2$: 680.3893. Found: 680.3808 (MALDI-TOF MS).

B. From 2b by Stille reaction

The procedure for the synthesis of **3** from **1a** by Stille reaction was followed to prepare **3** from **1b** and 5-tributylstannyl-2,2'-bithiophene in a yield of 60%.

7'-(4,4'-Diphenyl)-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (4)

The procedure for the synthesis of **3** by Stille reaction was followed to prepare **4** from **1a** and 4-tributylstannyl-biphenyl in a yield of 45%.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.60-7.84 (m, 15H), 7.31-7.50 (m, 4H), 2.02-2.05 (m, 4H), 1.43 (s, 12H), 1.07-1.23 (m, 20H), 0.80-0.90 (m, 6H), 0.61-0.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.1, 150.2, 143.8, 140.8, 140.6, 140.0, 133.9, 128.9, 127.6, 127.4, 127.1, 121.5, 120.5, 120.5, 119.1, 83.8, 77.5, 77.0, 76.6, 55.4, 31.8, 30.1, 29.2, 25.0, 23.8, 22.6, 16.2, 14.1. Molecular Mass: Calcd for $C_{47}H_{61}BO_2$: 668.4765. Found: 668.4766 (MALDI-TOF MS).

7'-(4-Phenyl-styrenyl)-9',9'-dioctyl-fluoren-2'-yl-4,4,5,5,-tetramethyl-[1,3,2]dioxaborolane (5)

A. From 1a

In absence of light, a solution of 4-phenylstyrene (0.21 g, 1.16 mmol), **1a** (0.69 g, 1.16 mmol), tris(*o*-tolyl)phosphine (77 mg, 0.25 mmol), and $Pd(OAc)_2$ (13 mg, 0.057 mmol) in 10 mL of anhydrous DMF and 10 mL of Et_3N was stirred for 24 h at 110 ^oC. The mixture was cooled to room temperature and then poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine and dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:ethyl acetate (16:1) as the eluent to afford **5** (0.44g, 55%) as a light yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J*= 7.92 Hz, 1H), 7.64-7.76 (m, 9H), 7.34-7.55 (m, 4H), 7.24 (d, J=4.44 Hz, 2H), 1.99-2.05 (m, 4H), 1.40 (s, 12H), 1.05-1.25 (m, 20H), 0.79-0.83 (m, 6H), 0.63 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.3, 150.6, 144.2, 141.3, 141.1, 140.6, 137.2, 137.0, 134.2, 129.8, 129.2, 128.0, 127.8, 127.3, 126.0, 121.3, 119.4, 84.1, 77.9, 77.4, 77.0, 66.3, 55.5, 40.7, 32.2, 30.4, 29.6, 25.4, 24.1, 23.0, 15.7, 14.5. Anal. Calcd. for $C_{49}H_{63}BO_2$: C, 84.70; H, 9.14. Found: C, 84.92; H, 9.15. Molecular Mass: Calcd for $C_{49}H_{63}BO_2$: 694.4921. Found: 694.5467 (MALDI-TOF MS).

B. From 1b

The procedure for the synthesis of **5** from **1a** by Heck reaction was followed to prepare **5** from **1b** in a yield of 50%.

References

[1] (a) Geng, Y.; Culligan, S.; Trajkovska, A.; Wallace, J.; Chen, S. *Chem. Mater.* **2003**, *15*, 542. (b) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. *Chem. Eur. J.* **2004,** *10*, 2681. (c) Geng, Y.; Trajkovska, A.; Katsis, D.; Ou, J.; Culligan, S.; Chen, S. *J. Am. Chem. Soc.* **2002**, *124*, 8337. (d) Ding, J.; Day, M.; Robertson, G; Roovers, J. *Macromolecules* **2002**, *35*, 3474. (e) Grisorio, R.; Mastrorilli, P.; Nobile, C.; Romanazzi, G..; Suranna, G.; Meijer, E. *Tetrahedron Letters* **2004**, *45*, 5367. (f) Lee, S.; Toshikazu, N.; Tetsuo, T. *Org. Lett.* **2001**, *3*, 2005.

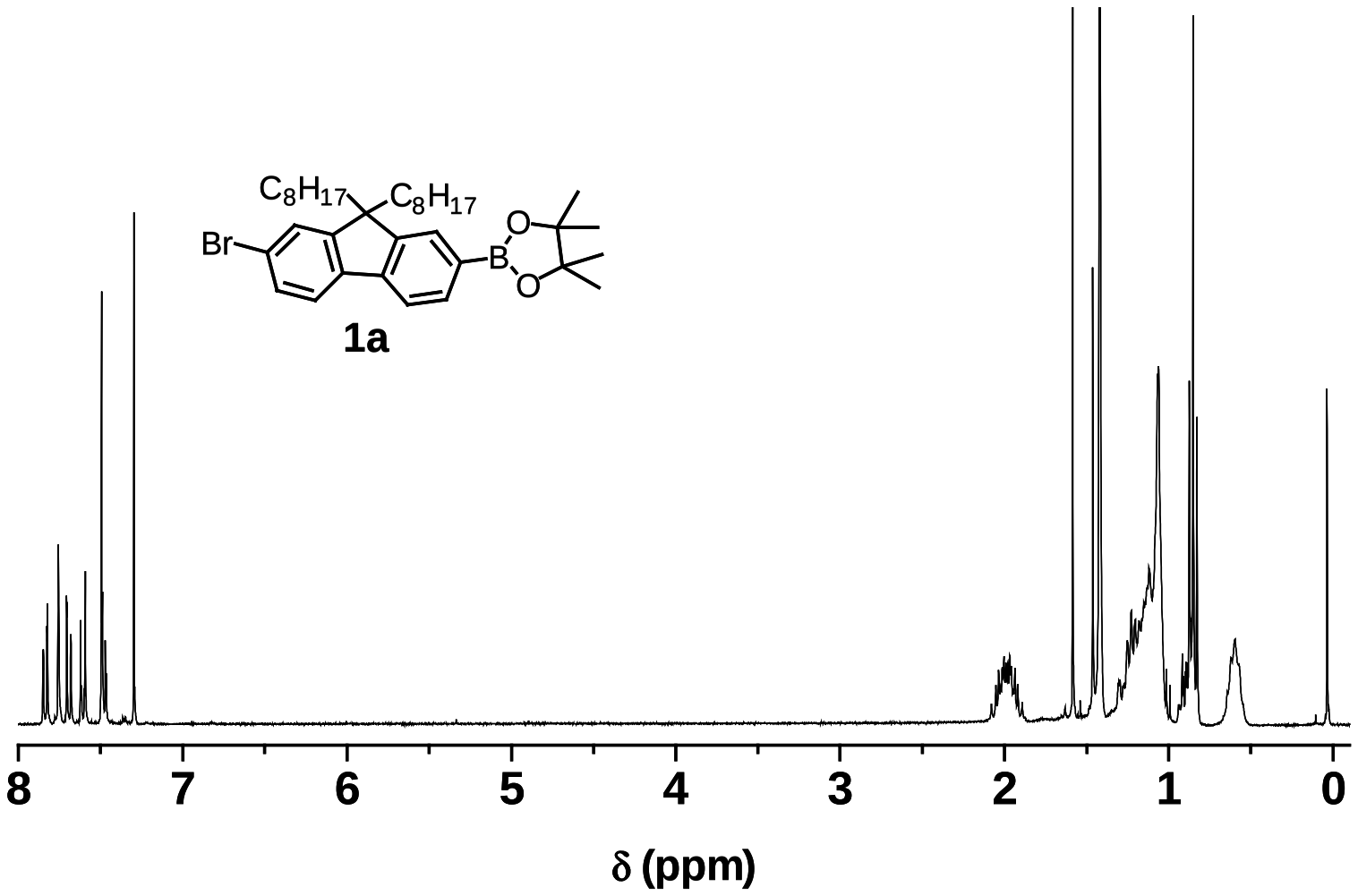
[2] Bäuerle, P.; Würthner, F.; Götz, G.; Effenberger, F. *Synthesis* **1993**, 1099.

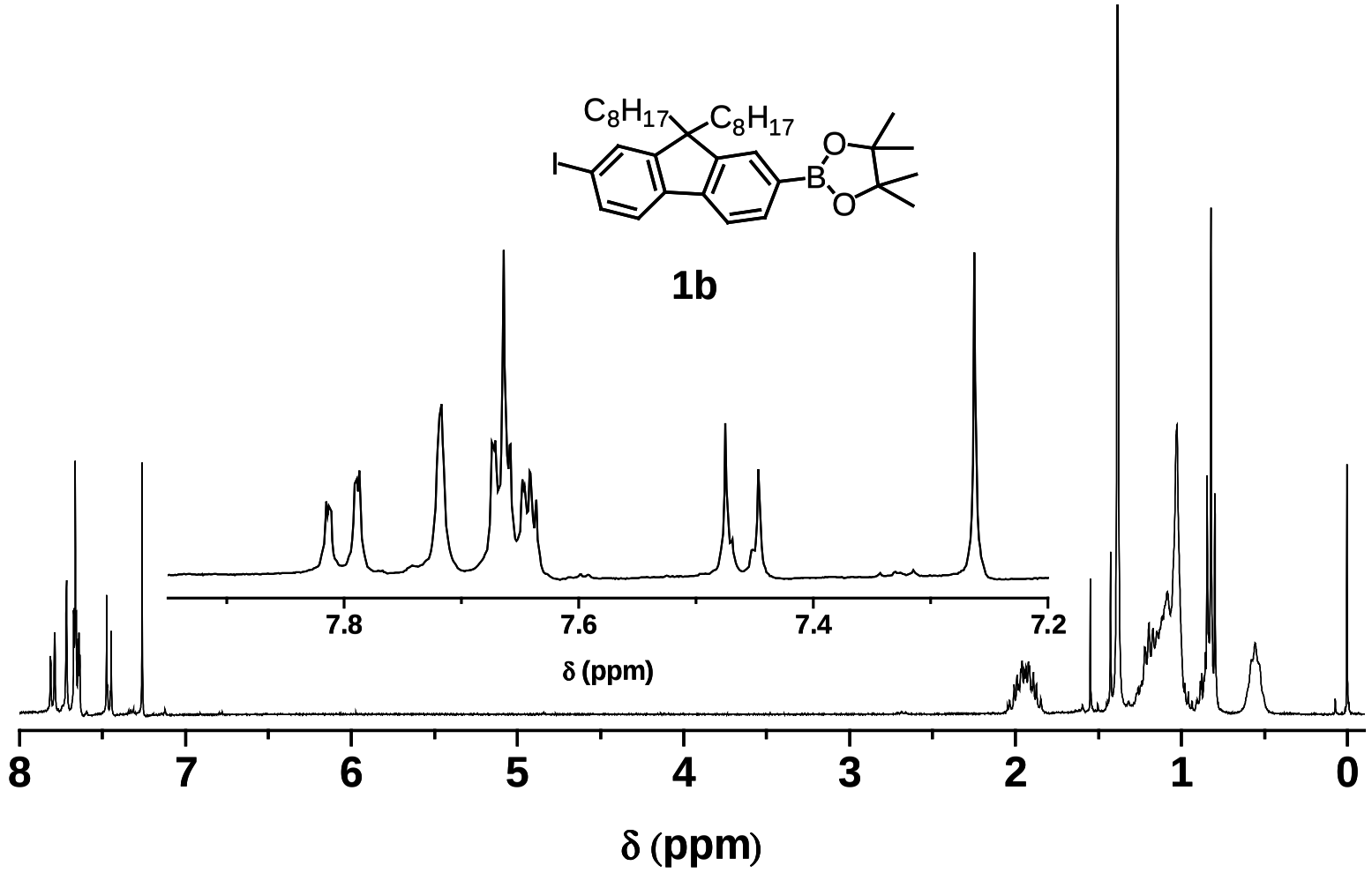
[3] (a) Keigo, F.; Masanori, K. *Topic in Current Chemistry* **2002**, *129*, 88. (b) Barbarella, G..; Favaretto, L.; Sotgiu, G..; Zambianchi, M.; Fattori, V.; Cocchi, M.; Cacialli, F.; Gigli, G.; Cingolani, R. *Adv. Mater* **1999** *11* 1378. (c) Geng, Y.; Chen, A.; Ou, J.; Chen, S. *Chem. Mater.* **2003**, *15*, 4352. (d) Nehls, B.; Asawapirom, U.; Füldner, S.; Preis, E.; Farrell, T. *Adv. Funct. Mater.* **2004**, *14*, 352. (e) May, P.; Larsen, S. *Syn. Lett.* **1997**, *8*, 895.

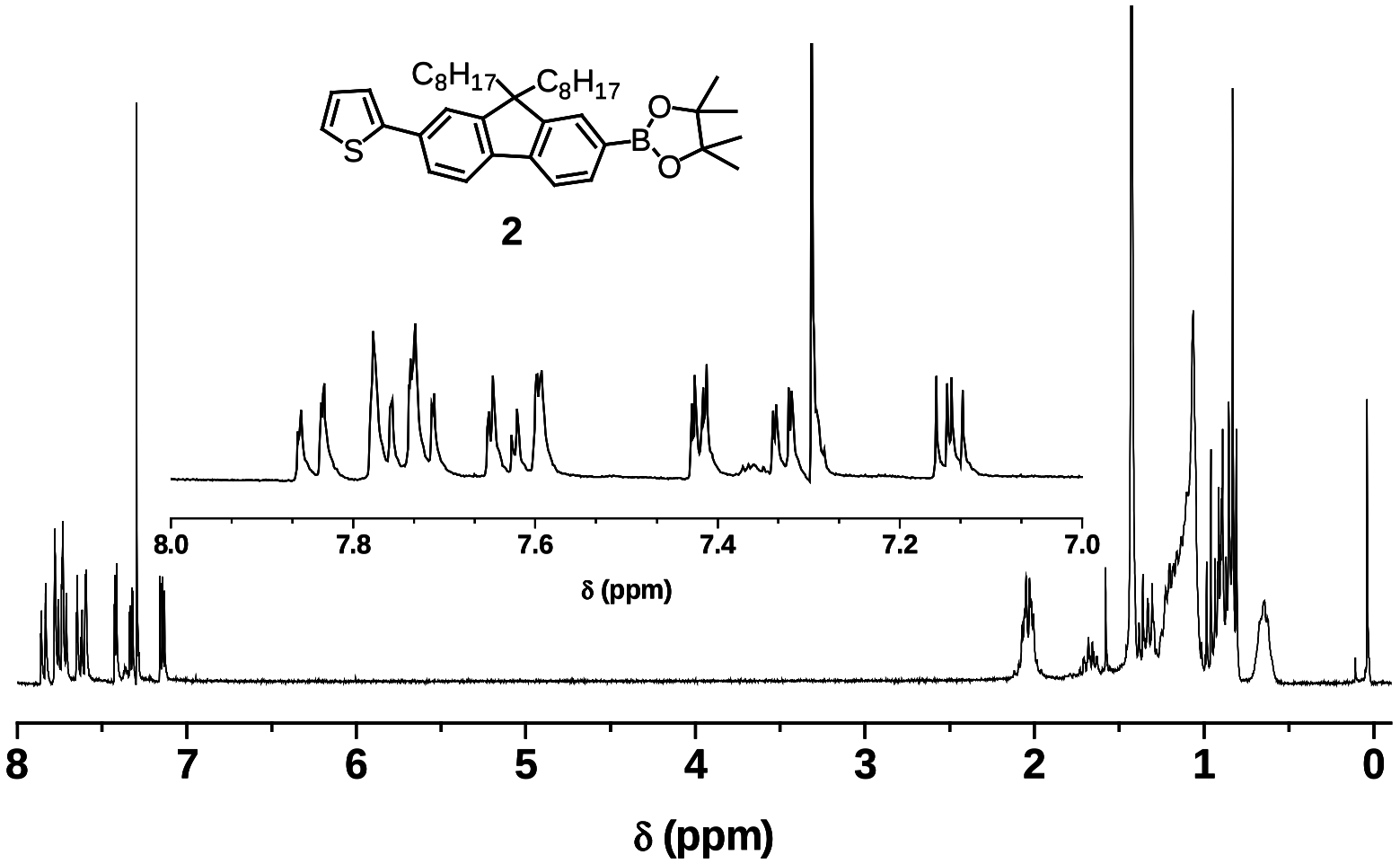
[4] (a) Li, B.; Li, Jing.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430. (b) Thiemann, D.; Pearson, D.; Thoennes, D. *Can. J. Chem.* **1973,** *51*, 3808

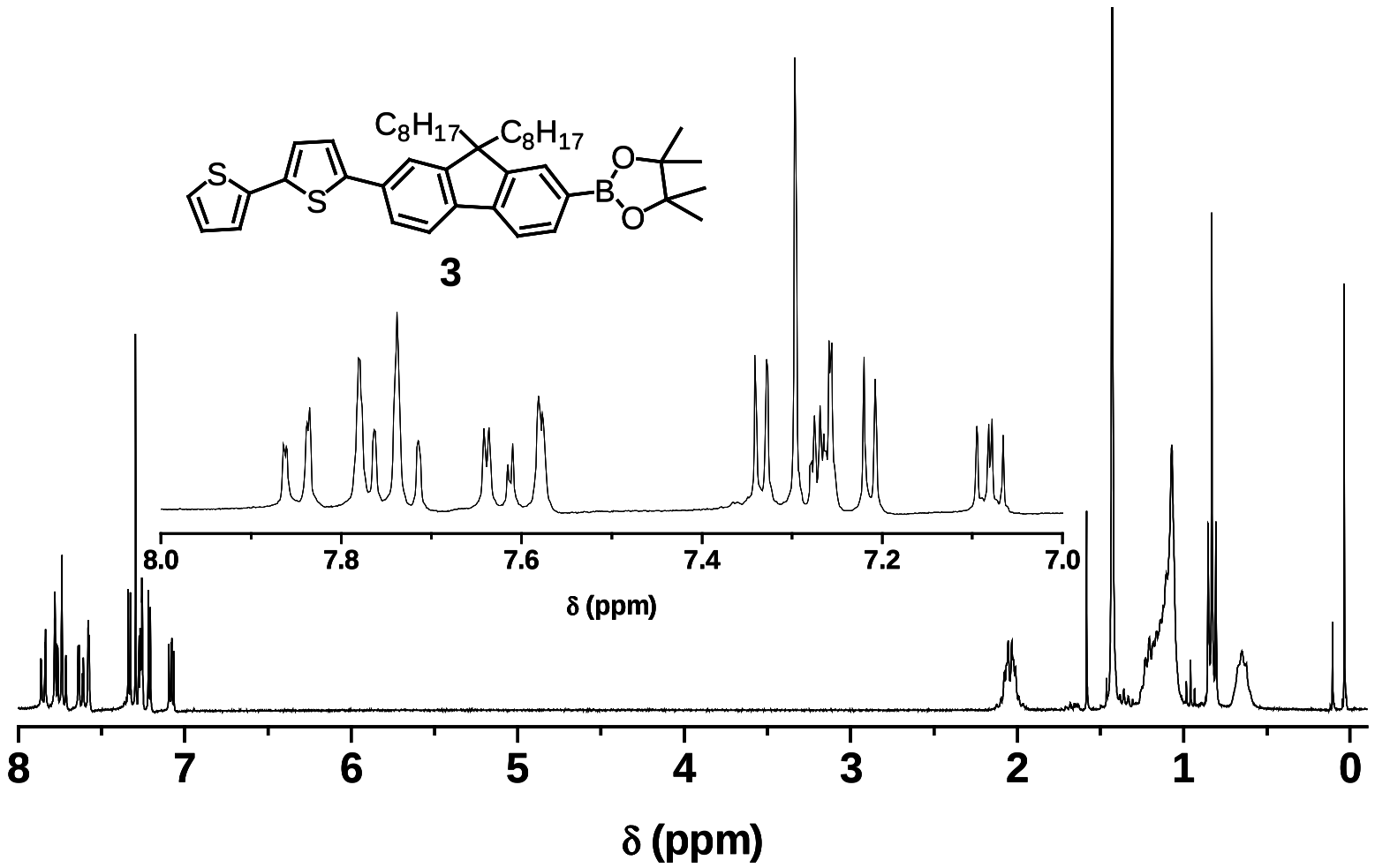
[5] Thomas, K.; Manfred, E.; Petra, F.; Ursula, H.; Wilfried, K. *Chem. Ber*. **1994**, *127*, 127.

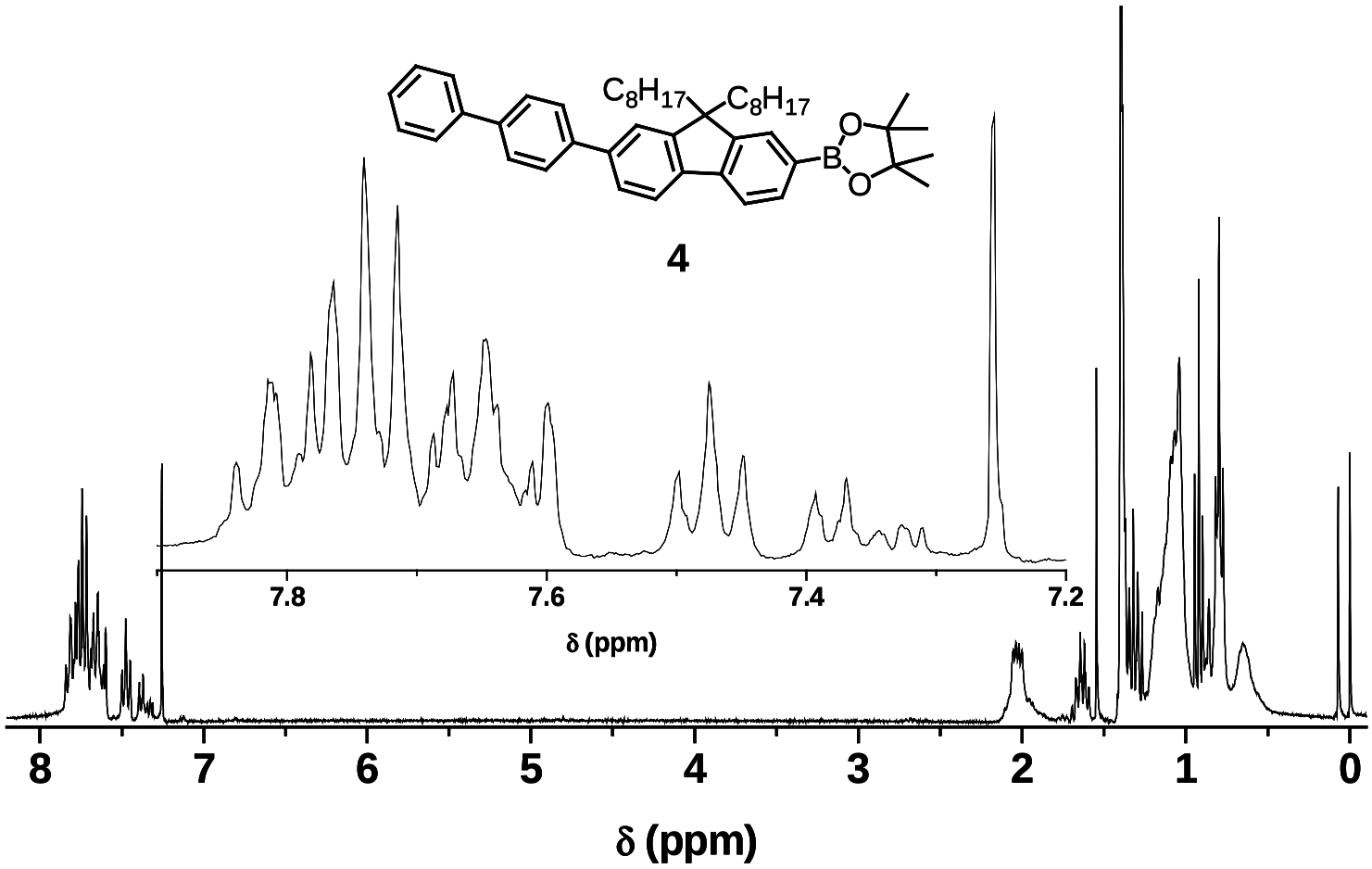
[6] Tsolakis, P. K.; Kallitsis, J. K. *Chem. Eur. J.* **2003,** *9*, 936.

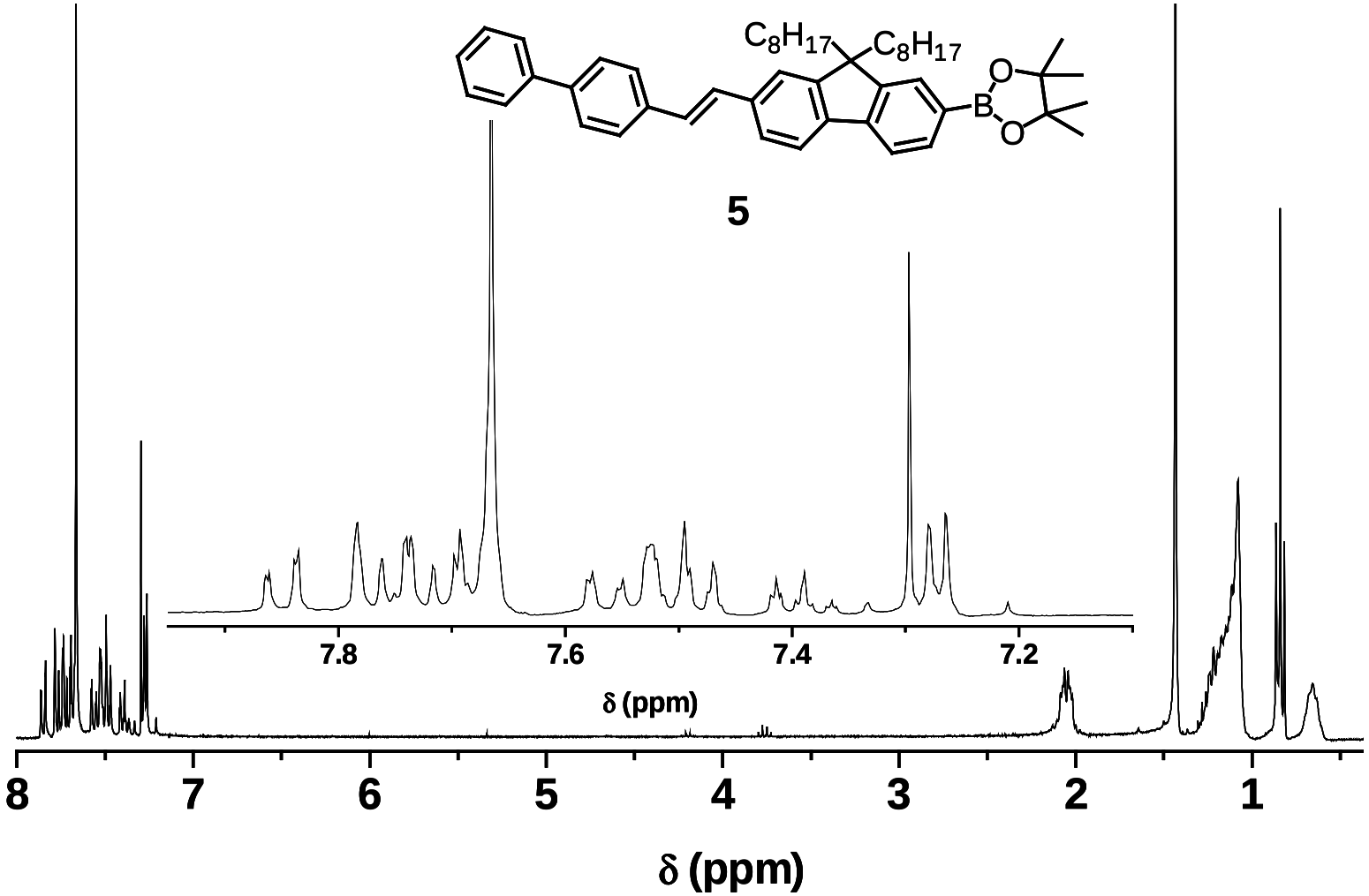

C8H17
C8H17
Br
B
O
O
1a
8
7
6
5
4
3
2
1
0
δ (ppm)

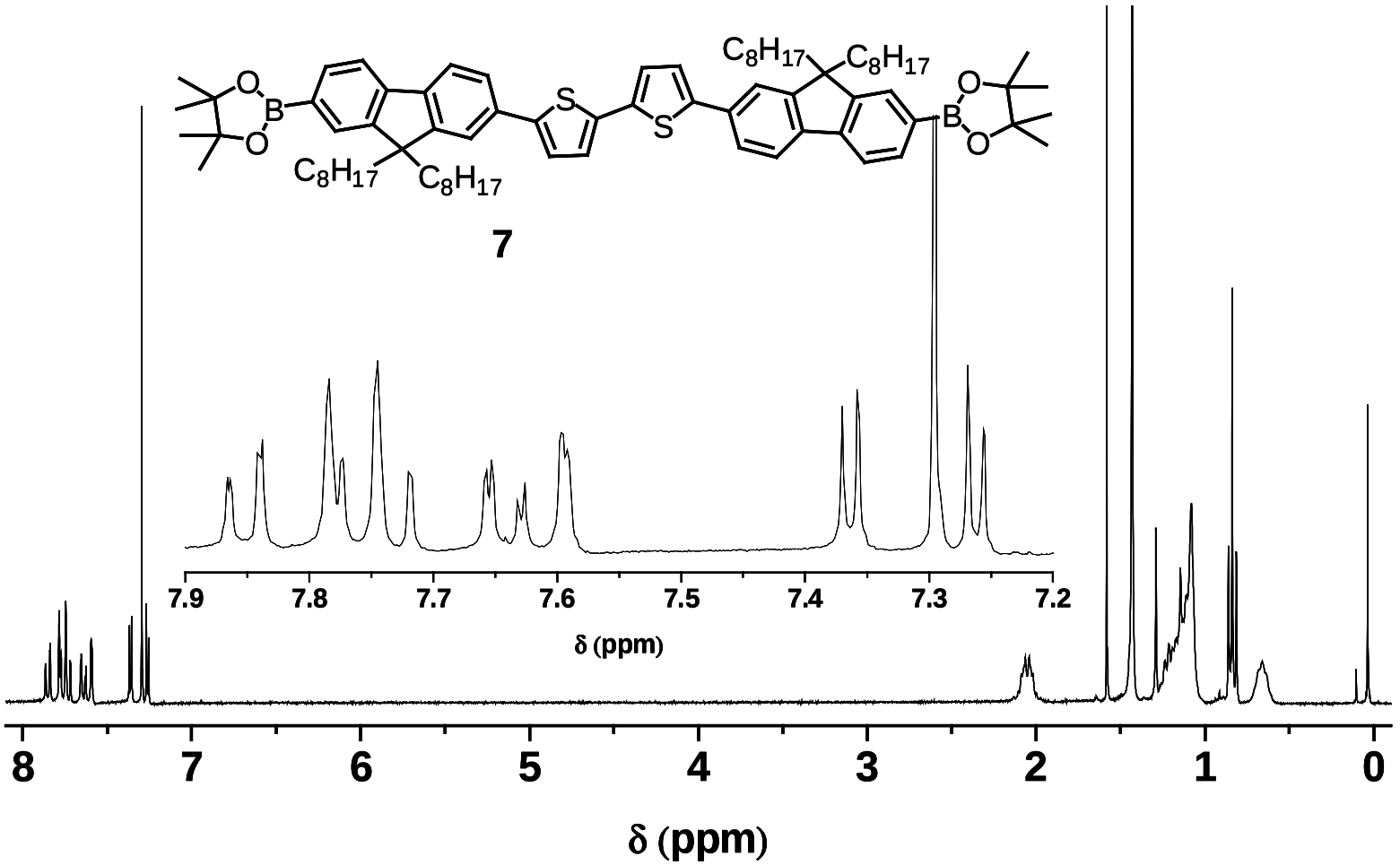

C8H17
C8H17
I
B
O
O
1b
7.8
7.6
7.4
7.2
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)


C8H17
C8H17
S
B
O
O
2
8.0
7.8
7.6
7.4
7.2
7.0
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

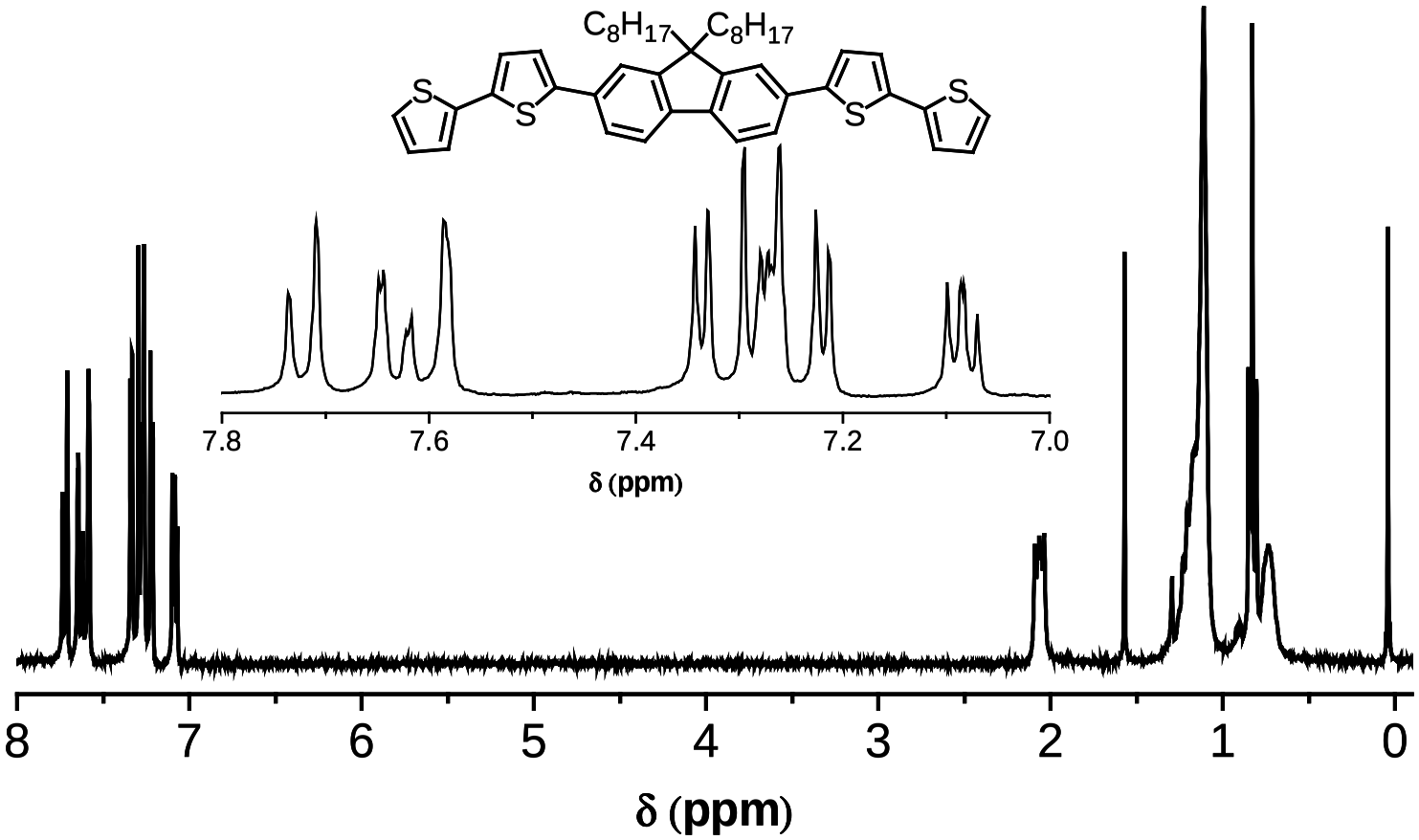

C8H17
C8H17
S
S
O
B
O
3
8.0
7.8
7.6
7.4
7.2
7.0
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

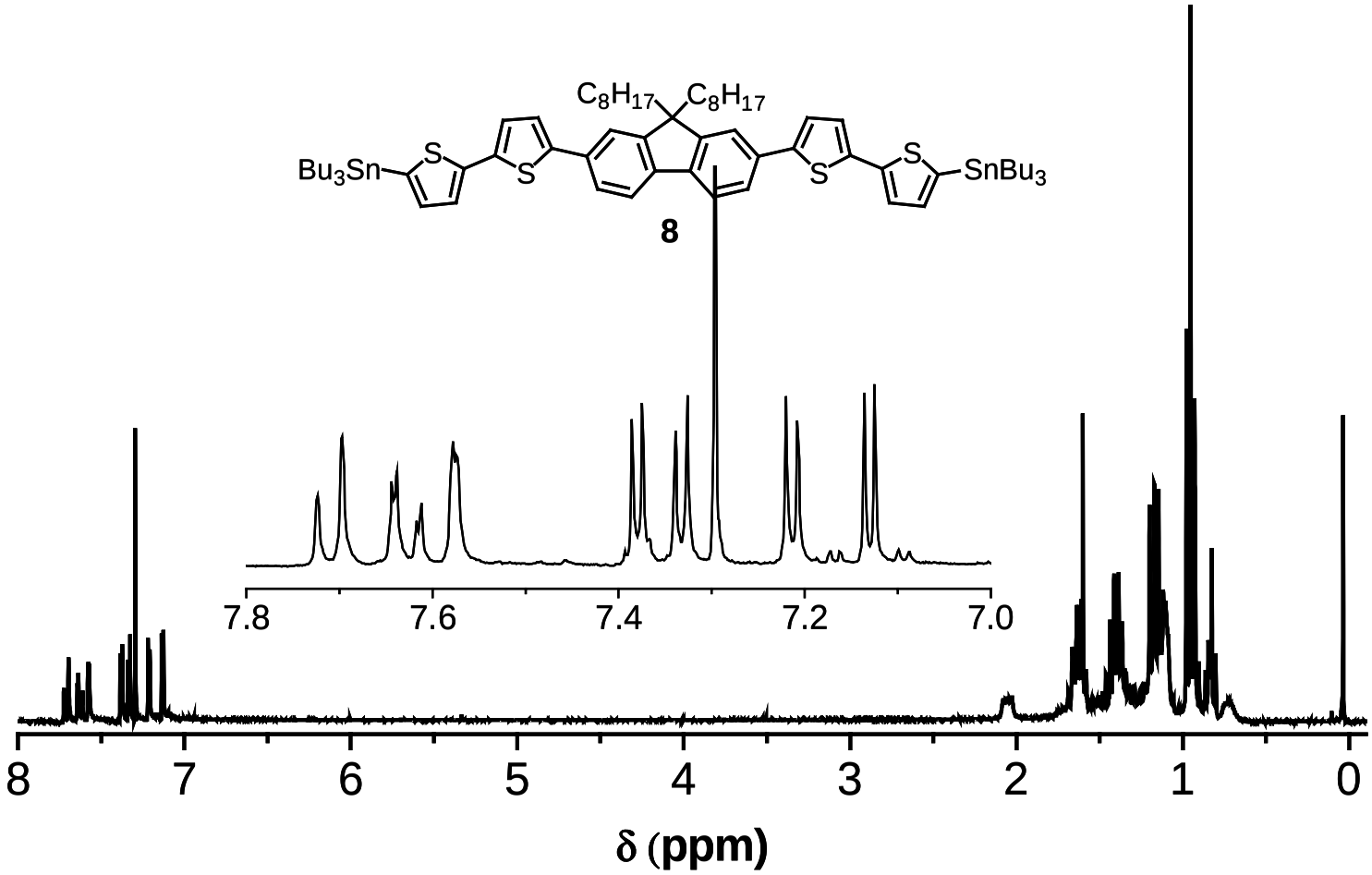

C8H17
C8H17
O
B
O
4
7.8
7.6
7.4
7.2
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

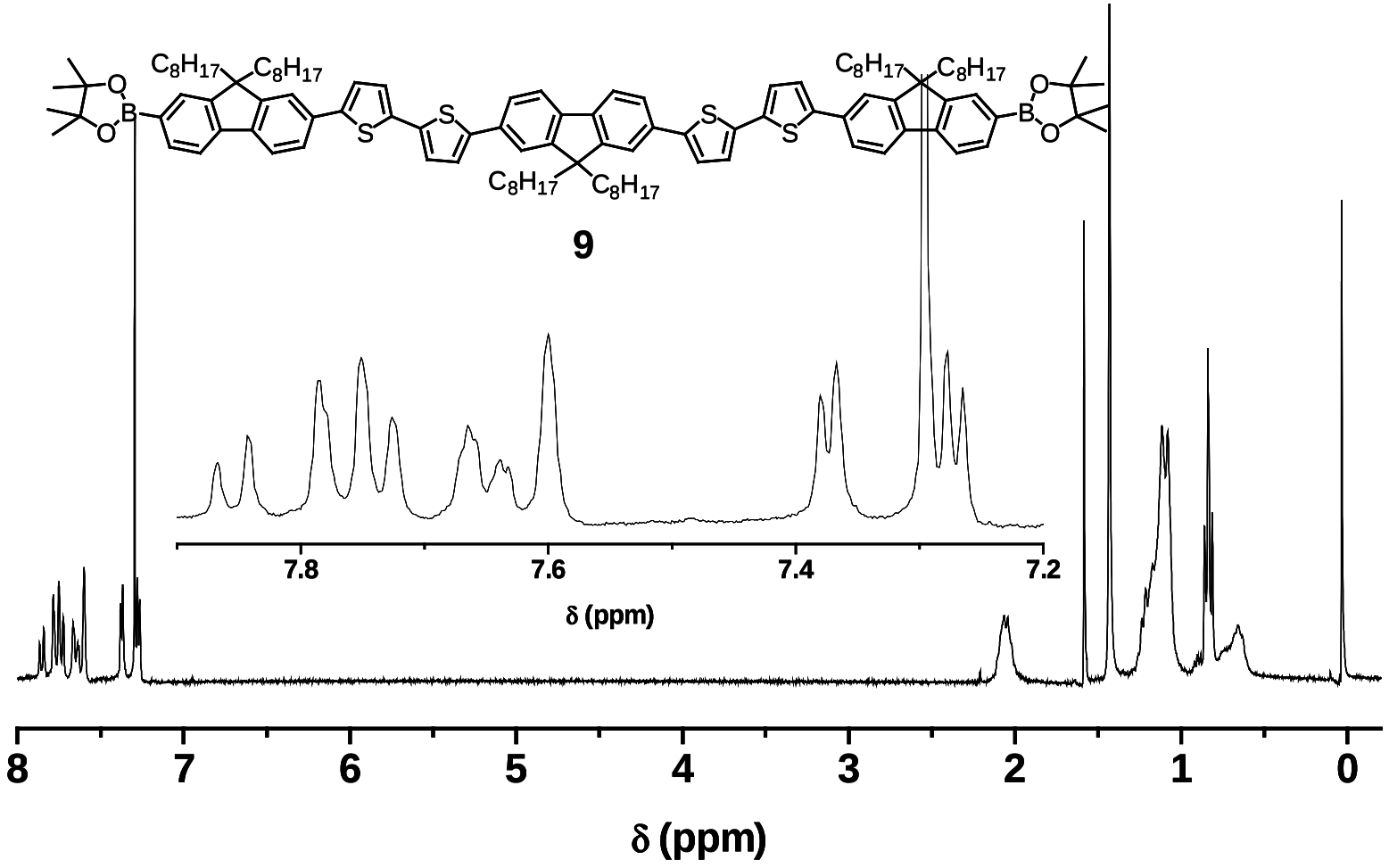

C8H17
C8H17
O
B
O
5
7.8
7.6
7.4
7.2
δ (ppm)
8
7
6
5
4
3
2
1
δ (ppm)

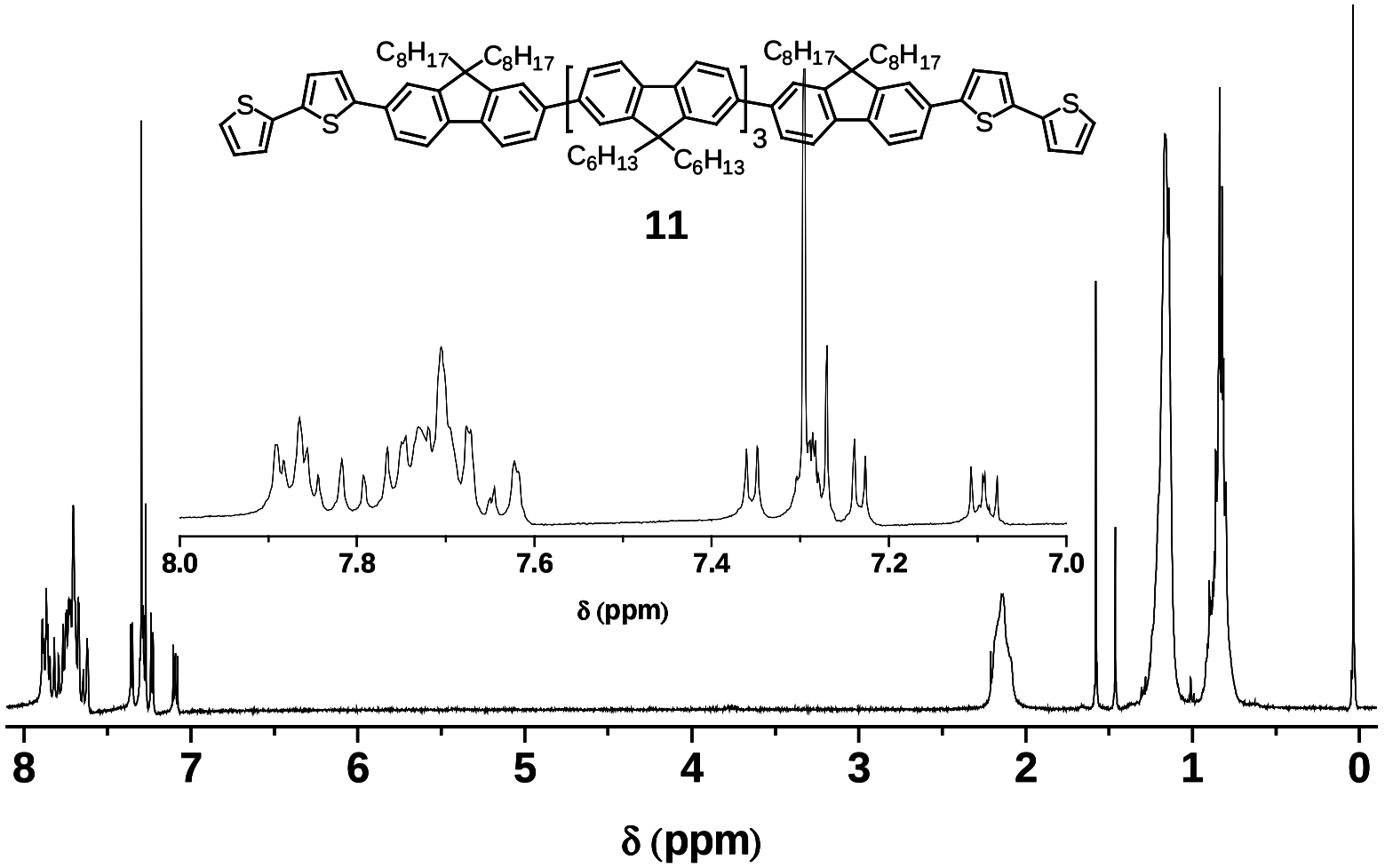

O
B
O
S
S
C_8H_{17}
C_8H_{17}
C_8H_{17}
C_8H_{17}
O
B
O
7
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

2,7-Bis (2,2’-bithien-5-yl)-9,9-dioctylfluorene

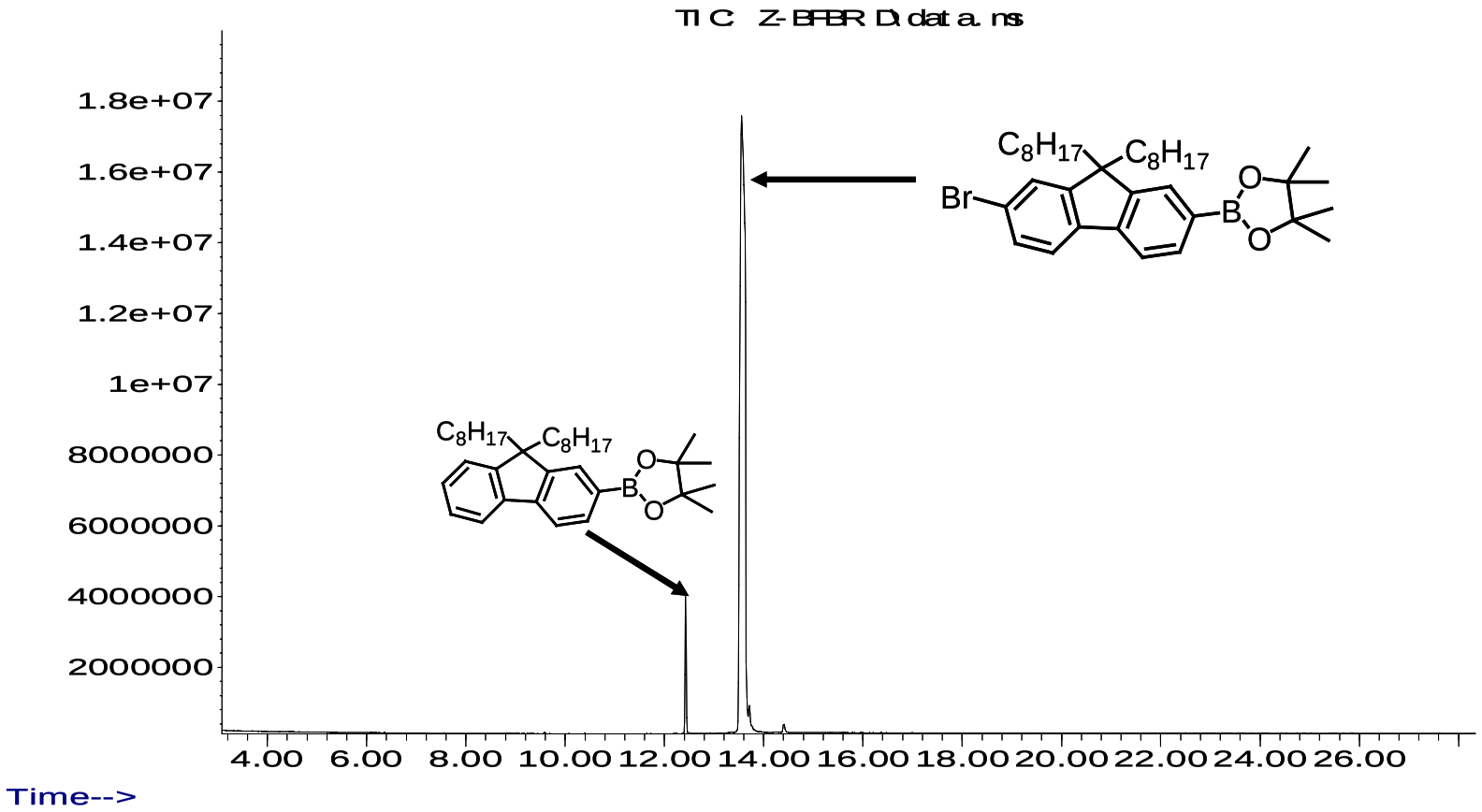



C8H17
C8H17
Bu3Sn
S
S
S
S
SnBu3
8
7.8
7.6
7.4
7.2
7.0
8
7
6
5
4
3
2
1
0
δ (ppm)

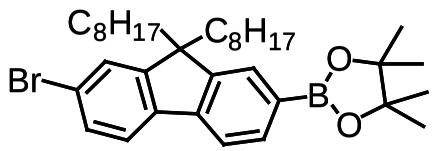

C8H17
C8H17
O
B
O
S
S
S
S
C8H17
C8H17
C8H17
C8H17
O
B
O
9
7.8
7.6
7.4
7.2
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

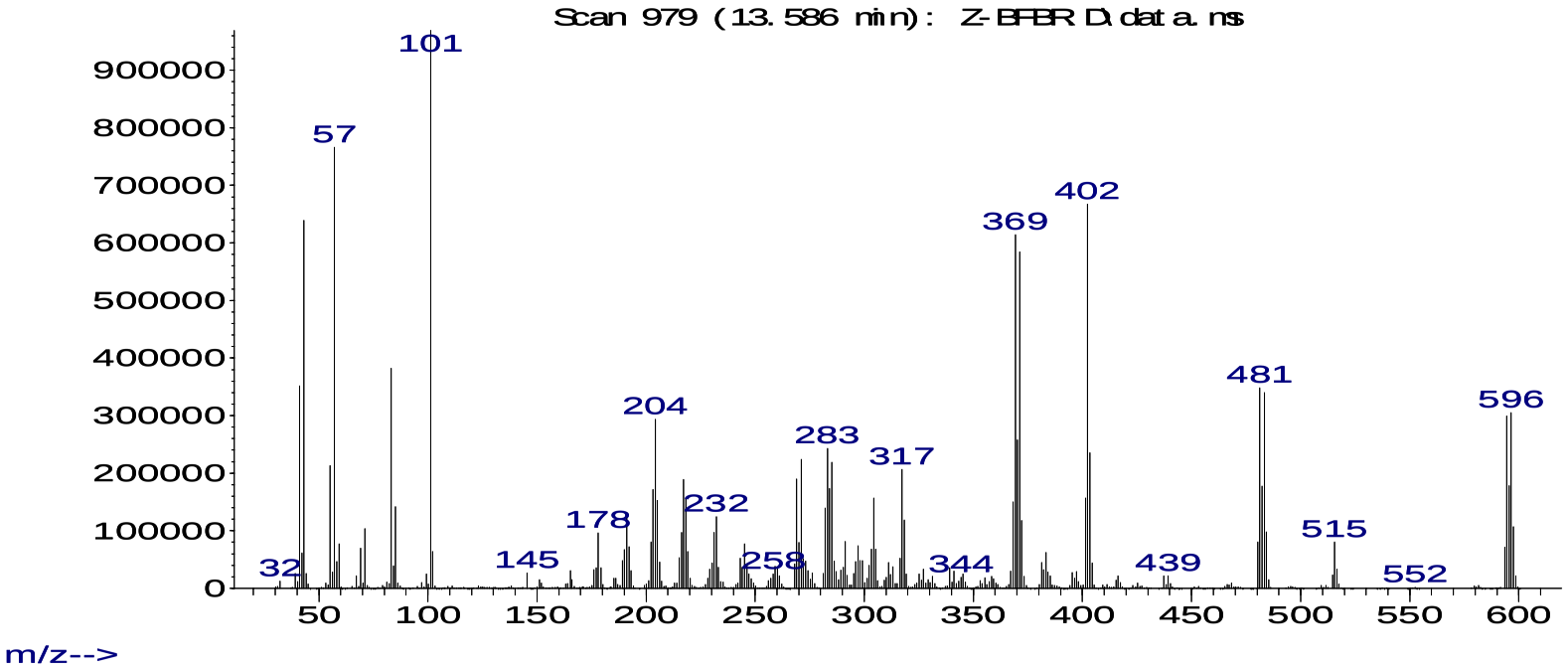

C8H17
C8H17
C8H17
C8H17
S
S
S
S
C6H13
C6H13
3
11
8.0
7.8
7.6
7.4
7.2
7.0
δ (ppm)
8
7
6
5
4
3
2
1
0
δ (ppm)

Gas chromatography of the compound **1a**

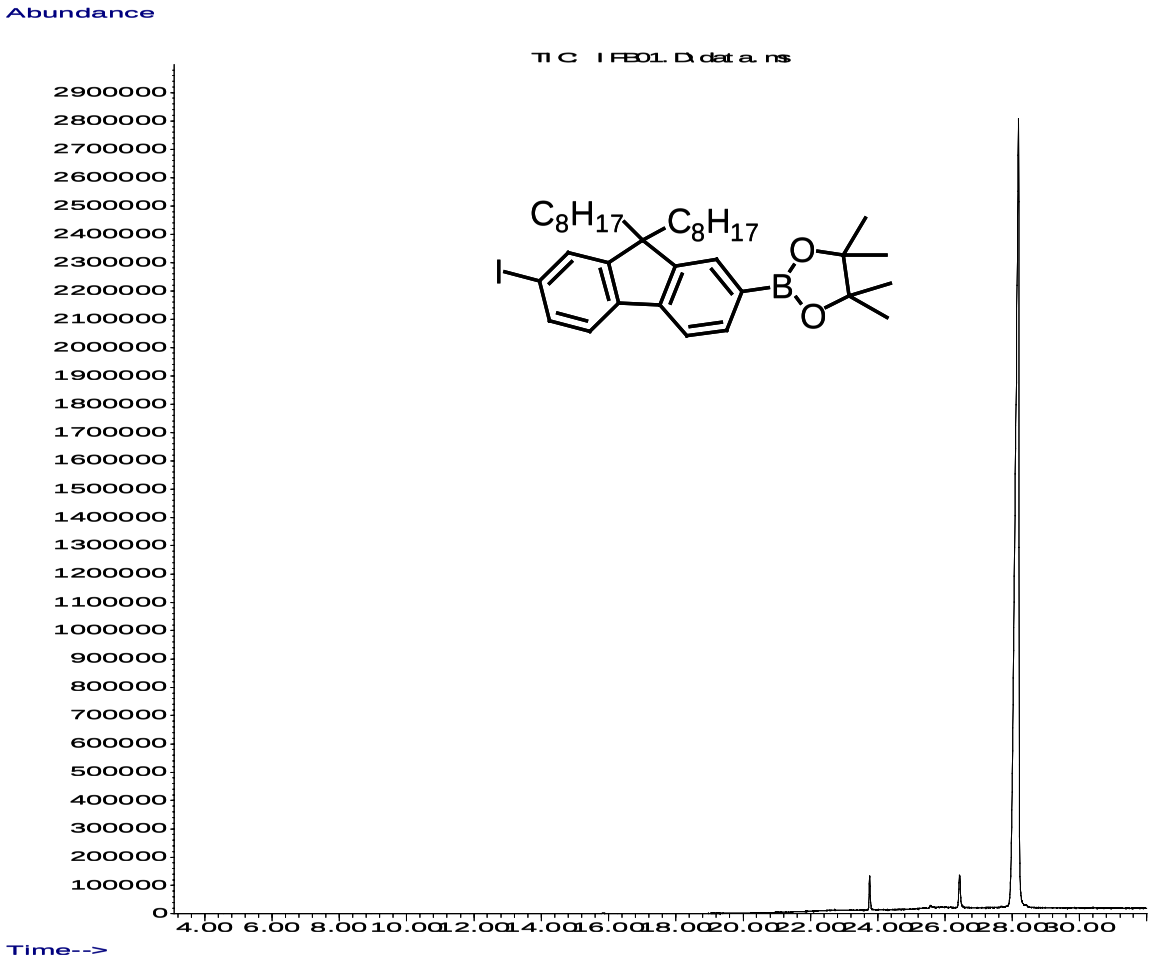


Mass spectrum of the compound **1a**.

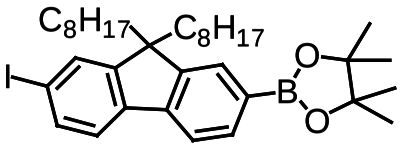


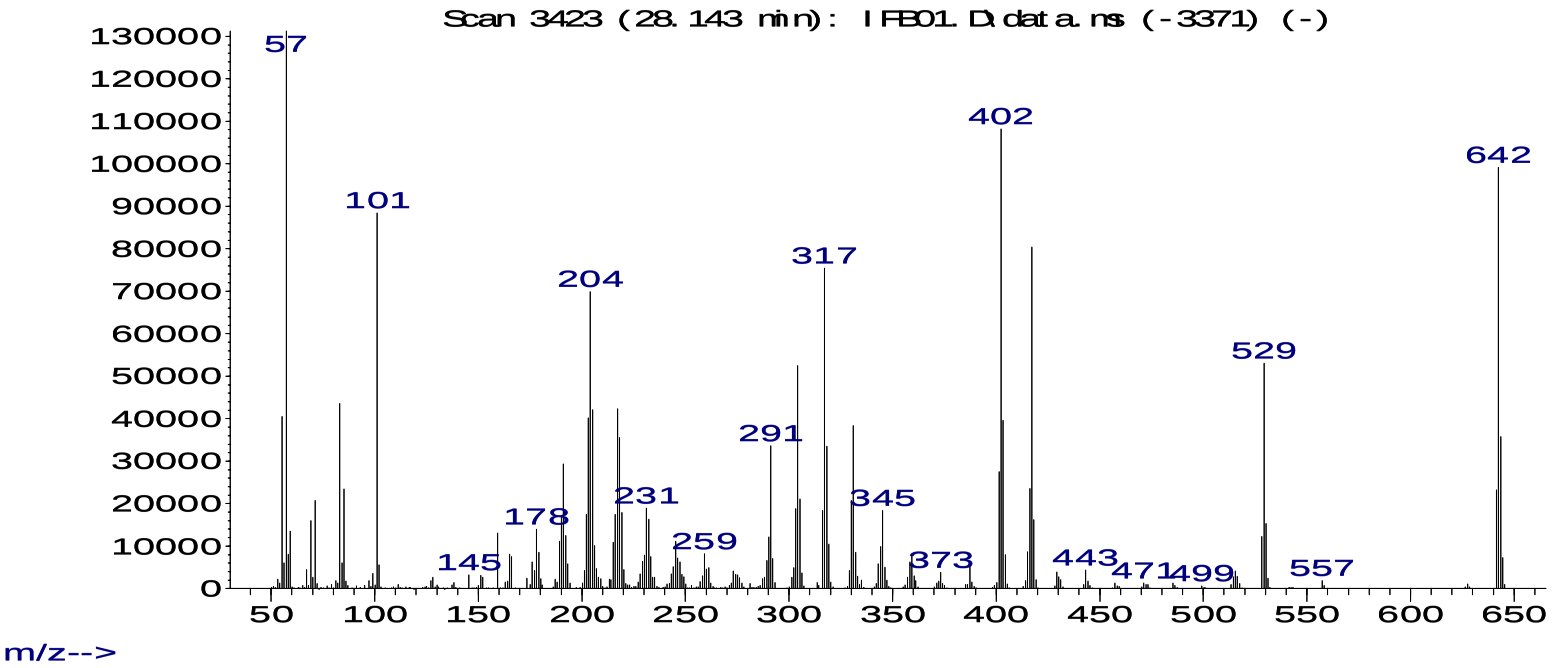


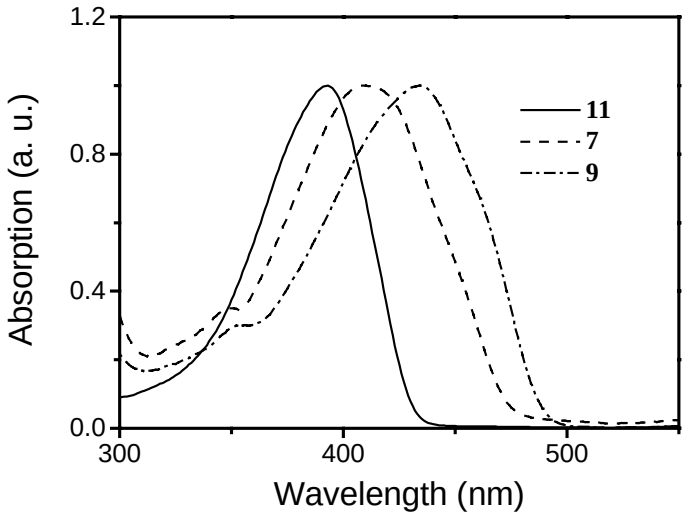
Gas chromatography of the compound **1b**.



Mass spectrum of the compound **1b**.







UV-vis absorption spectra of compound **7**, **9**, and **11** in $CHCl_3$ solution with the concentration of $3.5\pm0.5 \times 10^{-6}$ M.