

Electronic Supplementary Information

for

Thiophene-Fused Fulminenes (FuDTs): Promising Platforms for High-Mobility Organic Semiconductors with a Zigzag Shape

Shohei Kumagai,^{a†} Takumi Ishida,^{b†} Shin Kakiuchi,^{b†} Masakazu Yamagishi,^c Hiroyasu Sato,^d Hiroyuki Ishii,^e Yasushi Nishihara,^{b*} and Toshihiro Okamoto^{a*}

^a *Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259-G1-7 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.*

^b *Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan.*

^c *National Institute of Technology, Toyama College, 13 Hongo-machi, Toyama, Toyama 939-8630, Japan.*

^d *Rigaku Corporation, Akishima, Tokyo 196-8666, Japan.*

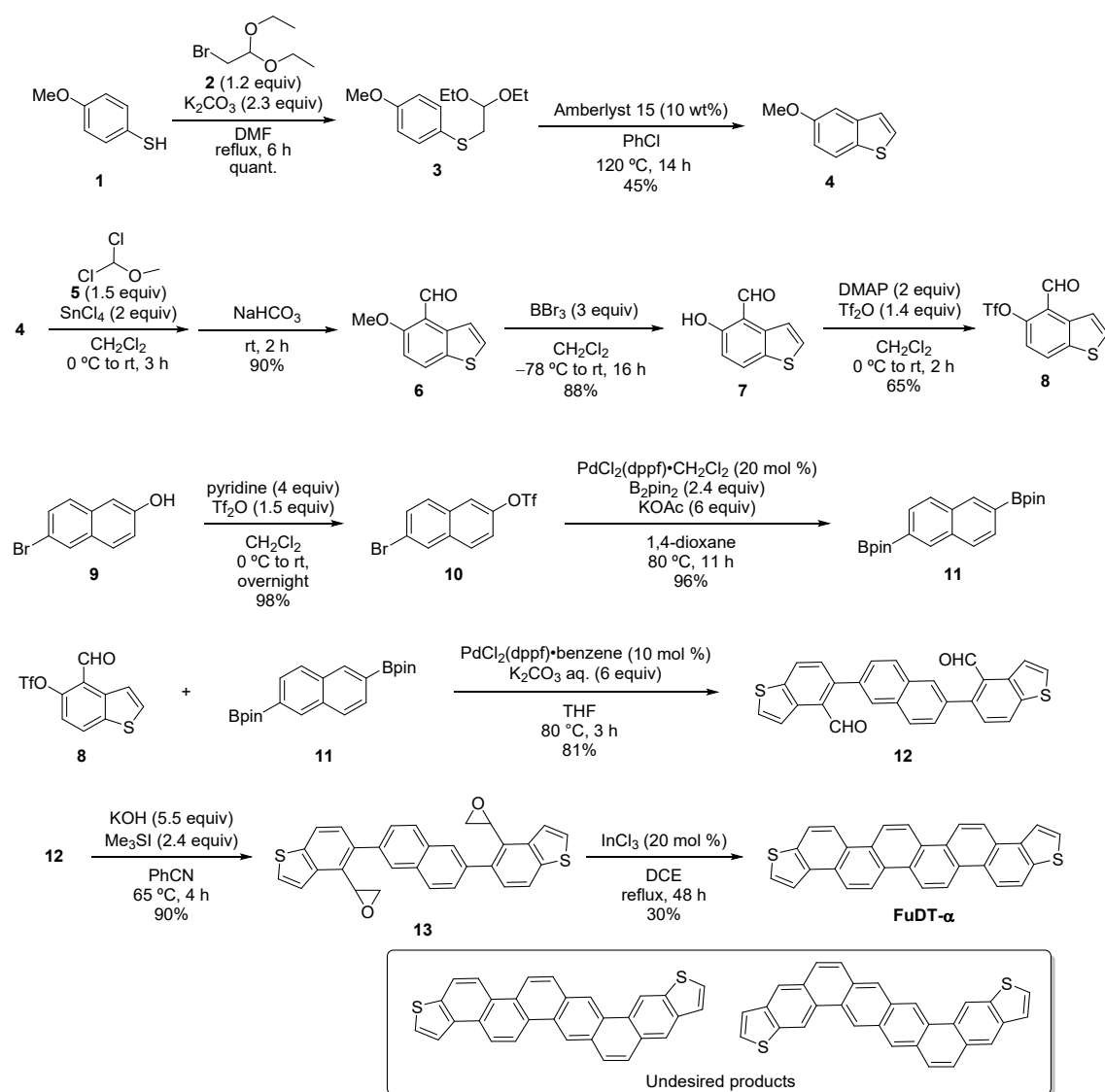
^e *Department of Applied Physics, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.*

General materials and methods.

All other chemicals were used without further purification unless otherwise indicated. Dehydrated tetrahydrofuran (THF), and dehydrated dichloromethane were purchased from Kanto Chemicals Co., Ltd. Dehydrated 1,4-dioxane, benzonitrile, and dehydrated 1,2-dichloroethane (DCE) were purchased from WAKO Chemicals Co., Ltd. Dehydrated 1,4-dioxane was degassed by freeze-pump-thaw method for the reaction. Dichloromethyl methyl ether (TCI), sodium hydrogen carbonate (Kanto), boron tribromide (TCI), 4-dimethylaminopyridine (TCI), trifluoromethanesulfonic anhydride (TCI), bis(pinacolato)diboron (Aldrich), potassium acetate (Nacalai Tesque), potassium carbonate (Nacalai Tesque), trimethylsulfonium iodide (Aldrich), potassium hydroxide (Nacalai Tesque), indium chloride (TCI), methanesulfonic acid (WAKO), sodium iodide (Nacalai Tesque), and acetonitrile (TCI) were used as received.

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure prior to use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF 254, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40–100 μm) from Kanto Chemicals Co., Ltd. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian INOVA-600 (600 MHz) spectrometer. Elemental analyses were carried out with a PerkinElmer 2400 CHN elemental analyzer at Okayama University. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer and reported in wave numbers (cm^{-1}). High-resolution mass spectrometry (HRMS) was carried out on a JEOL JMS-700 MStation.

Scheme S 1. Synthetic route of FuDT- α .



*Synthesis of 1-[(2,2-diethoxyethyl)thio]-4-methoxybenzene (3)*¹. To a solution of **1** (4.9 mL, 40 mmol) · K_2CO_3 (12.7 g, 92 mmol) in DMF (37 mL) in a 50 mL of Schlenk tube were added bromoacetaldehyde diethyl acetal (**2**) (7.3 mL, 48 mmol). The reaction mixture was refluxed for 6 h. The reaction mixture was quenched with water, then extracted with diethyl ether (25 × 4 mL). The combined organic layers were washed with sat. NH_4Cl aq., water and sat. $NaHCO_3$ aq. Then, the organic layers were dried over $MgSO_4$. After the volatiles were evaporated (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:Et₂O = 9:1) to give **3** (10.2 g, 39.8 mmol) in 99% yield as a colorless oil. ¹H NMR (600 MHz, $CDCl_3$, rt): δ 7.39 (d, J = 6.6 Hz, 2H), 6.83 (d, J = 6.6 Hz, 2H), 4.59 (t, J = 5.4 Hz, 1H), 3.79 (s, 3H), 3.66-3.61 (m, 2H), 3.55-3.50 (m, 2H), 3.02 (d, J = 5.4 Hz, 2H), 1.19 (t, J = 7.2 Hz, 6H).

*Synthesis of 5-methoxybenzo[b]thiophene (4)*². To a solution of **3** (24.5 g, 95.7 mmol) in chlorobenzene (975 mL) in a 1 L of three-necked flask were added Amberlyst 15 (2.45 g, 95.7 mmol). The resulting mixture was stirred at 120 °C for 14 h. After filtration, the volatiles were removed under reduced pressure (50 Torr, 80 °C). The residue was purified by silica gel column chromatography (hexane:EtOAc = 10:1) to give **4** (7.0 g, 42.6 mmol) in 45% yield as a white solid. $R_f = 0.44$ (hexane:EtOAc = 10:1). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.69 (d, $J = 9.0$ Hz, 1H), 7.35 (d, $J = 2.4$ Hz, 1H), 7.26-7.24 (m, 2H), 7.00 (dd, $J = 9.0, 2.4$ Hz, 1H), 3.88 (s, 3H).

Synthesis of 5-methoxybenzo[b]thiophene-4-carboxaldehyde (6). To a solution of **4** (3.38 g, 18.3 mmol) in CH₂Cl₂ (37 mL) in a 200 mL of three-necked flask were added dropwise SnCl₄ (1.0 M in CH₂Cl₂, 36.6 mL, 36.6 mmol) and dichloromethyl methyl ether (**5**) (2.4 mL, 27.5 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with sat. NaHCO₃ aq. at 0 °C and stirred at room temperature. After 2 h, the reaction mixture was extracted with CH₂Cl₂ (70 × 3 mL). The combined organic layers were washed with brine and dried over MgSO₄. After the volatiles were evaporated (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:CHCl₃ = 1:2) to give **6** (3.45 g, 17.9 mmol) in 90% yield as a yellow solid. $R_f = 0.25$ (hexane:CHCl₃ = 1:2). Mp = 90-91 °C. FT-IR (KBr, cm⁻¹): 3091 (w), 3084 (w), 2848 (w), 1660 (s), 1560 (s), 1392 (m), 1251 (s), 1180 (m), 1074 (m), 705 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 10.74 (s, 1H), 8.42 (d, $J = 5.4$ Hz, 1H), 8.03 (d, $J = 9.0$ Hz, 1H), 7.68 (d, $J = 5.4$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 3.98 (s, 3H); ¹³C {¹H} NMR (151 MHz, CDCl₃, rt): δ 190.4, 162.2, 138.7, 134.0, 132.1, 130.0, 124.3, 118.5, 109.7, 56.8. Anal. Calcd for C₁₀H₈O₂S: C, 62.48; H, 4.19. Found: C, 62.17; H, 3.83.

Synthesis of 5-hydroxy-benzo[b]thiophene-4-carboxaldehyde (7). To a solution of **6** (7.07 g, 36.4 mmol) in dehydrated CH₂Cl₂ (97 mL) in 500 mL of three-necked flask was added dropwise boron tribromide (1.0 M in CH₂Cl₂, 54.6 mL, 54.6 mmol) at -78 °C. The reaction mixture was stirred at room temperature for 16 h. The reaction was quenched with MeOH and water, and extracted with CH₂Cl₂ (80 × 3 mL). The combined organic layers were washed with sat. NaHCO₃ aq. and brine, and dried over MgSO₄. After the volatiles were evaporated under reduced pressure (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 10:1) to give **7** (5.64 g, 31.6 mmol) in 88% yield as a yellow solid. $R_f = 0.29$ (hexane:EtOAc = 10:1). Mp = 120-122 °C. FT-IR (KBr, cm⁻¹): 3099 (m), 3080 (w), 2855 (w), 1645 (s), 1630 (s), 1585 (m), 1427 (s), 1288 (s), 1273 (s), 1177 (s), 845 (m), 843 (m), 773 (m), 708 (m), 478 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 11.97 (s, 1H), 10.56 (s, 1H), 7.96 (d, $J = 9.0$ Hz, 1H), 7.77 (d, $J = 5.4$ Hz, 1H), 7.72 (d, $J = 5.4$ Hz, 1H), 7.02 (d, $J = 9.0$ Hz, 1H); ¹³C {¹H} NMR (151 MHz, CDCl₃,

rt): δ 193.9, 162.1, 140.6, 132.1, 131.7, 131.6, 118.4, 115.9, 113.8. Anal. Calcd for C₉H₆O₂S: C, 60.66; H, 3.39. Found: C, 60.58; H, 3.71.

Synthesis of 5-(trifluoromethanesulfonyloxy)benzo[b]thiophene-4-carboxaldehyde (8). To a solution of **7** (1.26 g, 7.1 mmol) and DMAP (1.73 g, 14.2 mmol) in dehydrated CH₂Cl₂ (43 mL) in 50 mL of Schlenk tube was added dropwise trifluoromethanesulfonic anhydride (1.8 mL, 9.9 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with sat. NaHCO₃ aq. and extracted with CH₂Cl₂ (80 × 3 mL). The combined organic layers were washed with brine and dried over MgSO₄. After the volatiles were removed under reduced pressure (400 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 20:1) to give **8** (1.42 g, 4.6 mmol) in 65% yield as a white solid. R_f = 0.22 (hexane:EtOAc = 20:1). Mp = 68-69 °C. FT-IR (KBr, cm⁻¹): 3123 (m), 2886 (w), 1686 (s), 1556 (s), 1416 (s), 1396 (m), 1173 (s), 1140 (s), 972 (s), 862 (s) 787 (m), 600 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 10.61 (s, 1H), 8.46 (d, J = 6.0 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 5.4 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 187.1, 150.0, 141.3, 138.7, 134.1, 129.8, 124.1, 122.4, 118.8 (CF₃, J = 318.5 Hz, 1C), 117.7; ¹⁹F{¹H} NMR (564 MHz, CDCl₃, rt): δ -73.1. Anal. Calcd for C₁₀H₅F₃O₄S₂: C, 38.71; H, 1.62. Found: C, 38.71; H, 1.53.

*Synthesis of 6-bromo-2-(naphthyl)trifluoromethanesulfonate (10)*³. To a solution of **9** (294 mg, 1.3 mmol) and pyridine (0.4 mL, 5.2 mmol) in CH₂Cl₂ (2.8 mL) in a 20 mL of Schlenk tube were added dropwise trifluoromethanesulfonic anhydride (0.3 mL, 2.0 mmol) at 0 °C. The resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with 1 M HCl at 0 °C, stirred at room temperature for 5 min, and extracted with CH₂Cl₂ (30 × 3 mL). The combined organic layers were washed with sat. NaHCO₃ aq. and brine, and dried over MgSO₄. After the volatiles were evaporated (350 Torr, 40 °C), the residue was purified by silica gel pad (hexane) to give **10** (465 mg, 1.3 mmol) in 98% yield as a colorless oil. ¹H NMR (600 MHz, CDCl₃, rt): δ 8.07 (s, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 8.4, 1.8 Hz, 1H), 7.40 (dd, J = 9.0, 2.4 Hz, 1H).

*Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (11)*⁴. To B₂pin₂ (792 mg, 3.1 mmol) in a 20 mL of Schlenk tube were added PdCl₂(dppf)·CH₂Cl₂ (106 mg, 0.13 mmol) and KOAc (765.6 mg, 7.8 mmol). The resulting mixture was dried under reduced pressure for 10 min. Compound **10** (465 mg, 1.3 mmol) and dehydrated and degassed 1,4-dioxane (13 mL) were added. The reaction mixture was stirred at 80 °C for 11 h. The reaction mixture was quenched with water and extracted with EtOAc (30 × 3 mL). The combined organic layers were washed

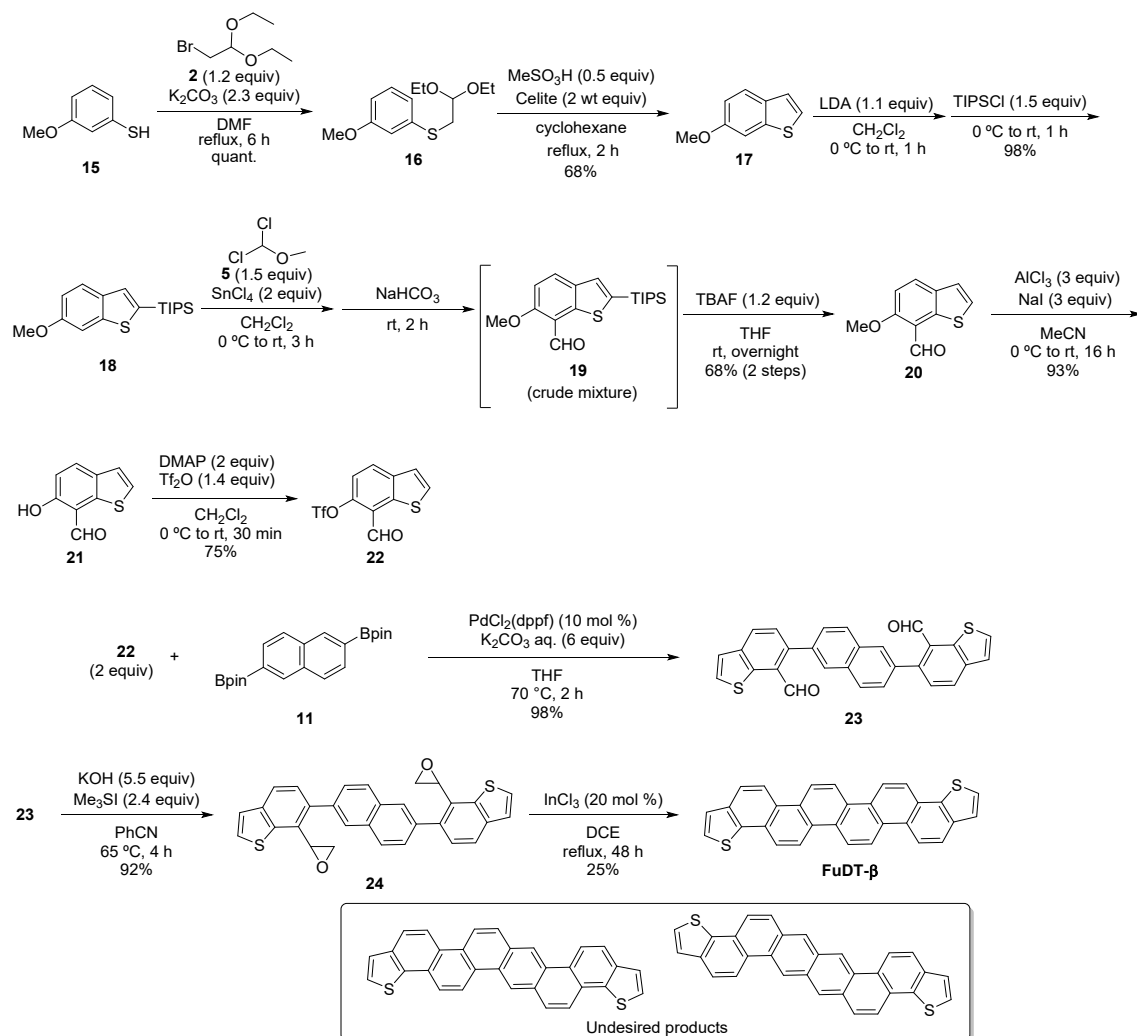
with brine, and dried over MgSO₄. After the volatiles were removed under reduced pressure (110 Torr, 40 °C), the residue was purified by a plug of silica (hexane:EtOAc = 4:1) to give **11** (495.8 mg, 1.3 mmol) in 96% yield as a white solid. $R_f = 0.59$ (hexane:EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 8.35 (s, 2H), 7.85 (d, $J = 14.4$ Hz, 2H), 7.83 (d, $J = 14.4$ Hz, 2H), 1.39 (s, 24H).

Synthesis of 5,5'-(naphthalene-2,6-diyl)bis(benzo[b]thiophene-4-carbaldehyde) (12). To a 50 mL of Schlenk tube containing **8** (914 mg, 2.95 mmol) were added **11** (560 mg, 1.47 mmol), PdCl₂(dppf)·benzene (119 mg, 0.15 mmol), THF (15 mL), and K₂CO₃ aq. (3 M, 2.9 mL). The resulting mixture was refluxed for 3 h. After the reaction mixture was cooled to room temperature, the reaction was quenched with water and poured into MeOH. The precipitates were filtered and washed with water, MeOH and hexane successively. The residue was purified by plug of silica (CHCl₃) to give **12** (581 mg, 1.2 mmol) in 81% yield as a yellow solid. $R_f = 0.14$. (hexane:EtOAc = 10:1) Mp = 267-269 °C. FT-IR (KBr, cm⁻¹): 3082 (w), 3061 (w), 2872 (w), 1684 (s), 1541 (m), 1389 (m), 1173 (m), 800 (m), 714 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 10.20 (s, 2H), 8.55 (d, $J = 5.4$ Hz, 2H), 8.20 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H), 7.97 (d, $J = 1.8$ Hz, 2H), 7.79 (d, $J = 5.4$ Hz, 2H), 7.69 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 193.0, 144.8, 141.1, 137.7, 136.7, 132.3, 131.2, 130.1, 129.4, 128.5, 128.2, 127.9, 127.1, 124.5. Anal. Calcd for C₂₈H₁₆O₂S₂: C, 74.98; H, 3.60. Found: C, 74.71; H, 3.44.

Synthesis of 2,6-bis(4-(oxiran-2-yl)benzo[b]thiophen-5-yl)naphthalene (13). To a 20 mL of Schlenk tube containing potassium hydroxide (46.3 mg, 0.83 mmol) was added benzonitrile (5 mL). The reaction mixture was stirred at room temperature. After 10 min, **12** (75 mg, 0.15 mmol) and trimethylsulfonium iodide (73.5 mg, 0.36 mmol) were added, and the resulting mixture was stirred at 65 °C for 4 h. After the reaction mixture was allowed to reach room temperature, the volatiles were removed under vacuum. The precipitates were washed with water, MeOH, hexane, and EtOAc successively to give **13** (64 mg, 0.13mmol) in 90% yield as a white solid. Mp = 247-249 °C. FT-IR (KBr, cm⁻¹): 3076 (w), 3046 (w), 2989 (w), 2972 (w), 1438 (m), 1249 (m), 1174 (m), 1155 (m), 894 (m), 843 (s), 810 (s), 804 (s) 711 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.96-7.93 (m, 6H), 7.87 (d, $J = 5.4$ Hz, 2H), 7.63 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.57 (d, $J = 6.0$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 4.40-4.39 (m, 2H), 2.97-2.95 (m, 2H), 2.70-2.68 (m, 2H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 140.1, 138.8, 138.5, 138.0, 132.3, 129.4, 128.6, 128.2, 128.0, 127.6, 126.7, 123.2, 122.4, 52.1, 49.4. HRMS (EI⁺) m/z : [M]⁺ Calcd for C₃₀H₂₀O₂S₂, 476.0905; Found,476.0910.

*Synthesis of benzo[b]thieno[4',5':9,10]piceno[3,4:b]thiophene (Fulmineno[2,1-b:10,9-b']dithiophene: **FuDT- α**).* To a 50 mL of Schlenk tube containing **13** (76.3 mg, 0.16 mmol) were added indium(III) chloride anhydrous (7.1 mg, 0.03 mmol) and dehydrated 1,2-dichloroethane (40 mL). The reaction mixture was refluxed for 48 h. After the mixture was allowed to reach room temperature, the volatiles were removed under reduced pressure (90 Torr, 60 °C). The residue was washed with water, MeOH, hexane, and CHCl₃ successively. The sum of the four times participates were purified by vacuum sublimation (source temperature, 400 °C under 10⁻³ Pa) to give **FuDT- α** (86.3 mg, 0.2 mmol) in 30% yield as a white solid. Mp > 300 °C. FT-IR (KBr, cm⁻¹): 3099 (w), 3078 (w), 1404 (w), 1276 (m), 833 (m), 800 (s), 771 (s), 721 (s), 682 (m). The ¹H and ¹³C{¹H} NMR spectra were not obtained owing to its poor solubility. Anal. Calcd for C₃₀H₁₆S₂: C, 81.79; H, 3.66. Found: C, 81.62; H, 3.57.

Scheme 2. Synthetic route of FuDT- β



Synthesis of 1-[1-(2,2-diethoxyethylthio)-3-methoxybenzene] (**16**)⁵. To a solution of **15** (12.2 mL, 100 mmol), K₂CO₃ (31.4 g, 227 mmol) in DMF (90 mL) in a 500 mL of three-necked flask was added bromoacetaldehyde diethyl acetal (**2**) (18.5 mL, 120 mmol). The reaction mixture was refluxed for 6 h. The reaction mixture was quenched with water and extracted with diethyl ether (50 × 4 mL). The combined organic layers were washed with sat. NH₄Cl aq., water and sat. NaHCO₃ aq. Then, the organic layers were dried over MgSO₄. After the volatiles were evaporated (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 4:1) to give **16** (25.6 g, 100.0 mmol) in 100% yield as a colorless oil. *R*_f = 0.54 (hexane:EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.96-6.94 (m, 1H), 6.92 (t, *J* = 2.4 Hz, 1H), 6.73-6.70 (m, 1H), 4.65 (t, *J* = 5.6 Hz, 1H), 3.79 (s, 3H), 3.72-3.64 (m, 2H), 3.59-3.51 (m, 2H), 3.14 (d, *J* = 5.6 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 6H).

*Synthesis of 6-methoxybenzo[b]thiophene (17)*⁵. To a solution of **16** (6.8 g, 26.5 mmol), methanesulfonic acid (0.85 mL, 13.1 mmol) in cyclohexane (730 mL) in a 1 L of three-necked flask were added celite (12 g). The resulting mixture was refluxed for 2 h. The reaction mixture was quenched with triethylamine. After filtration, the volatiles were removed under reduced pressure (100 Torr, 60 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 30:1) to give **17** (3.0 g, 18.0 mmol) in 68% yield as a clear oil. $R_f = 0.29$ (hexane:EtOAc = 30:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.70 (d, $J = 8.8$ Hz, 1H), 7.36 (d, $J = 2.4$ Hz, 1H), 7.27-7.24 (m, 2H), 7.00 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.89 (s, 3H).

Synthesis of 2-triisopropylsilane-6-methoxybenzo[b]thiophene (18). To a solution of diisopropylamine (9.7 mL, 69.2 mmol) in THF (125 mL) in a 200 mL of three-necked flask were added dropwise *n*-butyllithium (1.6 M in hexane, 44 mL, 70.4 mmol) and the solution was stirred at -78 °C. After 1 h, to the solution was added **4** (10.3 g, 62.8 mmol, 1 equiv), and mixture was stirred for 1 h. Then, to the solution was added chlorotriisopropylsilane (16 mL, 75.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water, the reaction mixture was extracted with CH₂Cl₂ (30 × 3 mL). The combined organic layers were washed with brine, and dried over MgSO₄. After the volatiles were evaporated (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 10:1) to give **18** (19.6 g, 61.0 mmol) in 97% yield as a white solid. $R_f = 0.70$ (hexane:EtOAc = 10:1). Mp = 50-51 °C. FT-IR (KBr, cm⁻¹): 2940 (s), 2863 (s), 1601 (s), 1474 (s), 1262 (s), 1224 (s), 1057 (s), 961 (s), 856 (m), 658 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.72 (d, $J = 9.0$ Hz, 1H) 7.42 (s, 1H), 7.37 (d, $J = 1.8$ Hz, 1H), 7.00 (dd, $J = 8.4, 2.4$ Hz, 1H), 3.89 (s, 3H) 1.41 (sep, $J = 7.8$ Hz, 3H), 1.16 (d, $J = 7.2$ Hz, 18H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 157.5, 145.3, 135.3, 133.7, 132.3, 123.9, 114.4, 104.2, 55.7, 18.7, 11.9; Anal. Calcd for C₁₈H₂₈OSSi: C, 67.44; H, 8.80. Found: C, 67.40; H, 8.74.

Synthesis of 6-methoxybenzo[b]thiophene-7-carboxaldehyde (20). To a solution of **18** (14.2 g, 44.4 mmol) in CH₂Cl₂ (89 mL) in a 300 mL of three-necked flask were added dropwise SnCl₄ (1.0 M in CH₂Cl₂, 89.0 mL, 89.0 mmol) and dichloromethyl methyl ether (5.9 mL, 66.7 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with sat. NaHCO₃ aq. at 0 °C and stirred at room temperature. After 2 h, the reaction mixture was extracted with CH₂Cl₂ (30 × 3 mL). The combined organic layers were washed with brine, and dried over MgSO₄. After the volatiles were evaporated (350 Torr, 40 °C), **19** (14.9 g) was obtained as a yellow oil.

Then, to a solution of **19** (14.9 g) in THF (61 mL) in a 200 mL of three-necked flask were added tetrabutylammonium fluoride (1.0 M in THF, 67 mL, 67.0 mmol). The resulting mixture

was stirred at room temperature overnight. The reaction mixture was quenched with water, then extracted with EtOAc (30 × 3 mL). The combined organic layers were washed with brine, and dried over MgSO₄. After the volatiles were evaporated (50 Torr, 60 °C), the residue was purified by silica gel column chromatography (hexane:CHCl₃ = 1:2) to give **20** (5.8 g, 30.2 mmol) in 68% yield as a yellow solid. *R*_f = 0.25 (hexane:CHCl₃ = 1:2). Mp = 86-88 °C. FT-IR (KBr, cm⁻¹): 2887 (w), 1660 (s), 1565 (s), 1456 (m), 1314 (m), 1263 (s), 1179 (m), 1057 (s), 808 (m), 705 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 10.71 (s, 1H) 7.99 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.28 (d, *J* = 6.0 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 1H), 4.01 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 188.5, 161.5, 139.1, 134.8, 131.0, 128.2, 122.3, 118.6, 109.4, 56.6; C₁₀H₈O₂S: C, 62.48; H, 4.19. Found: C, 62.48; H, 3.87.

Synthesis of 6-hydroxy-benzo[b]thiophene-7-carboxaldehyde (21). To a solution of **20** (1.53 g, 7.9 mmol) in dehydrated MeCN (27 mL) in 50 mL of Schlenk tube was added sodium iodide (3.57 g, 23.8 mmol) and aluminum chloride (3.72 g, 27.9 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with sat. Na₂S₂O₃ aq., and extracted with CH₂Cl₂ (20 × 3 mL). Then, after back extraction with 1 M KOH aq. (20 × 3 mL), conc. HCl aq. was added to the water phase until pH = 7, and the precipitated solid was filtered. In addition, the filtrate was extracted with CH₂Cl₂ (20 × 3 mL). The combined organic layers were washed with brine, and dried over MgSO₄. After the volatiles were evaporated under reduced pressure (350 Torr, 40 °C), the residue and precipitated solid were purified by silica gel column chromatography (hexane:EtOAc = 4:1) to give **21** (1.39 g, 7.8 mmol) in 93% yield as a yellow solid. *R*_f = 0.52 (hexane:EtOAc = 1:1). Mp = 130-131 °C. FT-IR (KBr, cm⁻¹): 3067 (m), 2847 (w), 1632 (s), 1571 (s), 1369 (m), 1281 (m), 1180 (w), 1086 (m), 823 (m), 694 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 11.54 (s, 1H), 10.34 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H); ¹³C{¹H} NMR (151 MHz, CDCl₃, rt): δ 192.8, 161.4, 142.9, 134.0, 132.1, 124.0, 123.2, 116.2, 114.1; Anal. Calcd for C₉H₆O₂S: C, 60.66; H, 3.39. Found: C, 60.71; H, 3.25.

Synthesis of 6-(trifluoromethanesulfonyloxy)benzo[b]thiophene-7-carboxaldehyde (22). To a solution of **21** (1.49 g, 8.3 mmol) and DMAP (2.10 g, 17.2 mmol) in dehydrated CH₂Cl₂ (52 mL) in 100 mL of two-necked flask was added dropwise trifluoromethanesulfonic anhydride (2.0 mL, 11.9 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with sat. NaHCO₃ aq., and extracted with CH₂Cl₂ (20 × 3 mL). The combined organic layers were washed with 1 M HCl and brine, then dried over MgSO₄. After the volatiles were removed under reduced pressure (350 Torr, 40 °C), the residue was purified by silica gel column chromatography (hexane:EtOAc = 5:1) to give **22** (1.94 g, 6.2 mmol) in 75%

yield as a white solid. $R_f = 0.49$ (hexane:EtOAc = 5:1). Mp = 77-78 °C. FT-IR (KBr, cm^{-1}): 1679 (s), 1558 (m), 1416 (s), 1218 (s), 1142 (s), 936 (m), 828 (m), 812 (w), 627 (m), 599 (m). ^1H NMR (600 MHz, CDCl_3 , rt): δ 10.60 (s, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 5.4$ Hz, 1H), 7.46 (d, $J = 9.0$ Hz, 1H), 7.45 (d, $J = 5.4$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , rt): δ 185.9, 149.0, 140.7, 139.1, 133.3, 130.6, 122.6₀, 122.5₆, 118.8 (CF₃, q, $J = 321.5$ Hz), 118.3; $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3 , rt): δ -72.9. Anal. Calcd for $\text{C}_{10}\text{H}_5\text{F}_3\text{O}_4\text{S}_2$: C, 38.71; H, 1.62. Found: C, 38.88; H, 1.51.

Synthesis of 6,6'-(naphthalene-2,6-diyl)bis(benzo[b]thiophene-7-carbaldehyde) (23). To a 20 mL of Schlenk tube containing **22** (206 mg, 0.66 mmol) were added **11** (126 mg, 0.33 mmol), $\text{PdCl}_2(\text{dppf})$ (24 mg, 0.03 mmol), THF (5 mL), and K_2CO_3 aq. (3 M, 0.7 mL). The resulting mixture was stirred at 70 °C for 2 h. After the reaction mixture was allowed to reach room temperature, the reaction was quenched with water and poured into MeOH. The precipitates were filtered and washed with water, MeOH and hexane successively. The residue was purified by plug of silica (CHCl_3) to give **23** (144 mg, 0.32 mmol) in 98% yield as a yellow solid. $R_f = 0.10$. (hexane:EtOAc = 10:1). Mp = 283-286 °C. FT-IR (KBr, cm^{-1}): 3101 (w), 3060 (w), 2871 (w), 1665 (s), 1552 (m), 1399 (m), 1333 (m), 1083 (m), 1019 (m), 842 (m). ^1H NMR (600 MHz, CDCl_3 , rt): δ 10.29 (s, 2H), 8.19 (d, $J = 7.8$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 1.8$ Hz, 2H), 7.73₃ (d, $J = 7.8$ Hz, 2H), 7.73₀ (d, $J = 7.2$ Hz, 2H), 7.63 (d, $J = 7.8$ Hz, 2H), 7.51 (d, $J = 5.4$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , rt): δ 191.6, 144.4, 140.5, 138.3, 136.3, 132.4, 131.3, 130.2, 129.4, 129.1, 128.6, 127.7, 127.5, 122.8. HRMS (EI^+) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{28}\text{H}_{16}\text{O}_2\text{S}_2$, 448.0592. Found, 448.0576.

Synthesis of 2,6-bis(7-(oxiran-2-yl)benzo[b]thiophen-6-yl)naphthalene (24). To a 20 mL of Schlenk tube containing potassium hydroxide (87.0 mg, 1.6 mmol) was added benzonitrile (10 mL). The reaction mixture was stirred at room temperature. After 10 min, **23** (127 mg, 0.28 mmol) and trimethylsulfonium iodide (157 mg, 0.77 mmol) were added, and the reaction mixture was stirred at 65 °C for 2 h. After the reaction mixture was allowed to reach room temperature, the volatiles were removed under vacuum. The precipitates were washed with water, MeOH, hexane, and EtOAc successively to give **24** (123 mg, 0.26 mmol) in 92% yield as a white solid. Mp = 235-240 °C. FT-IR (KBr, cm^{-1}): 3097 (w), 3055 (w), 3001 (w), 1459 (w), 1383 (w), 1252 (m), 1088 (w), 826 (s), 634 (m), 481 (w). ^1H NMR (600 MHz, CDCl_3 , rt): δ 7.98-7.96 (m, 4H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 6.0$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 5.4$ Hz, 2H), 4.26-4.24 (m, 2H) 3.17-3.15 (m, 2H), 3.11-3.09 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , rt): δ 140.5, 138.6, 137.3, 136.7, 132.4, 128.9, 128.7, 128.5, 128.4, 128.2, 127.1,

123.1₁, 123.0₅, 52.7, 48.9. HRMS (EI⁺) *m/z*: [M]⁺ Calcd for C₃₀H₂₀O₂S₂, 476.0905; Found, 476.0892.

Synthesis of benzo[b]thieno[6',7':9,10]piceno[3,4:b]thiophene (Fulmineno[1,2-b:9,10-b']dithiophene: FuDT-β). To a 50 mL of Schlenk tube containing **24** (50.1 mg, 0.11 mmol), were added indium(III) chloride anhydrous (4.8 mg, 0.02 mmol) and dehydrated 1,2-dichloroethane (25 mL). The reaction mixture was refluxed for 48 h. After the mixture was allowed to reach room temperature, the volatiles were removed under reduced pressure (90 Torr, 60 °C). The residue was washed with water, MeOH, hexane and CHCl₃ successively. The sum of the four times participates were purified by vacuum sublimation (source temperature, 400 °C under 10⁻³ Pa) to give **FuDT-β** (60.0 mg, 0.14 mmol) in 25% yield as a yellow solid. Mp > 300 °C. FT-IR (KBr, cm⁻¹): 2360 (w), 2322 (w), 1457 (m), 1332 (m), 1281 (m), 1085 (w), 804 (s), 768 (w), 715 (w), 682 (m). The ¹H and ¹³C{¹H} NMR spectra were not obtained owing to its poor solubility. Anal. Calcd for C₃₀H₁₆S₂: C, 81.79; H, 3.66. Found: C, 81.78; H, 3.55.

Computational methods

Quantum chemical calculations were performed with Gaussian 09 program.⁶ Reorganization energy was calculated according to the literature method⁷ at the B3LYP/6-31+G(d) level of density functional theory (DFT). Transfer integrals were calculated at the PBE/PBE/6-31G(d) level of DFT. Other energy calculations were performed at the B3LYP/6-311G(d) level of DFT with or without a geometry optimization at the B3LYP/6-31G(d) level of DFT. Electronic band structures were calculated based on the tight-binding approximation. Effective mass of holes was calculated as $m^* = \hbar^2(\partial^2 E(k)/\partial k^2)^{-1}$, where \hbar and k stands for the Dirac's constant the wavevector, respectively, and the m^* is shown in unit of the rest mass of an electron.

Thermal analyses

Thermogravimetry–differential thermal analysis (TG–DTA) was carried out on a Rigaku Thermo plus EVO2 TG8121 under a stream of nitrogen (100 cm³ min⁻¹). α -Alumina was used as a reference, and temperature was increased at 5 K min⁻¹.

UV–vis spectroscopy

The UV–vis absorption spectra were recorded with a JASCO V-670 spectrometer. Thin films were coated by vacuum deposition on synthetic quartz substrates with a nominal thickness of 100 nm at a deposition rate of 1.0 Å s⁻¹. The base pressure was 10⁻⁴ Pa.

Photoelectron yield spectroscopy

The photoelectron yield spectra were acquired with a Sumitomo Heavy Industries Advanced Machinery PYS-202 in air. A D₂ light source was used for excitation. Thin films were prepared by the same way as described above but ITO-coated glass substrates were used instead of synthetic quartz.

Electrochemical measurements

Electrochemical measurements were carried out by using a BAS electrochemical analyzer (ALS 622D) in conjunction with a three-electrode cell. For solution-state characterization, a differential pulse voltammetry (DPV) technique was performed using a glassy carbon as the working electrode, a Pt wire as the counter electrode, and a Pt wire in 0.01 M AgNO₃ in benzonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the quasi-reference electrode. The FuDT samples were dissolved into N₂-bubbled *o*-dichlorobenzene containing 0.1 M TBAPF₆ as the supporting electrolyte at a nominal

concentration of 0.2 mM (while incompletely dissolved) on a hotplate at 140 °C. As for thin-film characterization, a linear sweep voltammetry (LSV) technique was performed using a Pt wire as the counter electrode, a Pt wire in 0.01 M AgNO₃ in benzonitrile containing 0.1 M TBAPF₆ as the quasi-reference electrode. The 100 nm-thick film on an ITO-coated glass substrate prepared as mentioned above was used as the working electrode. Measurements were carried out at room temperature in N₂-bubbled acetonitrile containing 0.1 M TBAPF₆ as the supporting electrolyte at the scan rate of 0.05 V s⁻¹. In both techniques, the potential was calibrated using ferrocene (Fc)/ferrocenium (Fc⁺) redox couple ($E(\text{Fc}/\text{Fc}^+) = 0 \text{ V}$) as an internal standard.

Single crystal growth

Colorless, thin plate-shape single crystals of FuDT- α and FuDT- β were grown by the PVT technique with the two-zone furnace system under a stream of argon gas.

X-ray crystallography

X-ray diffraction data were collected on a Rigaku XtaLAB Synergy-Custom four-circle X-ray diffractometer with CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). The structure was solved by direct methods (SHELXT⁸ (2018/2)) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL⁹ (Ver. 2018/3)). While all hydrogen atoms were placed at calculated positions, all other atoms were refined anisotropically. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single-crystal OTFT fabrication and characterization

Single-crystal OTFTs were fabricated in the bottom-gate/top-contact architecture. An n⁺-Si wafer with thermally oxidized SiO₂ layer (500 nm) was sequentially washed by ultrasonication in acetone and 2-propanol, and dried on a hotplate at 100 °C in air. After UV-O₃ treatment, the SiO₂ surface was modified with vaporized triethoxy-1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl-silane (F-DTS) at 120 °C for 3 hours. The substrate was sequentially ultrasonicated in toluene and 2-propanol, followed by drying on a hotplate at 100 °C. After carefully laminating a single crystal to the F-DTS treated surface by hands, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) (2 nm) and Au (40 nm) were sequentially deposited by vacuum evaporation through a metal shadow mask. To define the channel dimensions for accurate estimation of a carrier mobility, single crystals were patterned by laser ablation so as to make the channels nearly parallel to the column

direction. Electrical evaluations were carried out by using a Keithley 4200-SCS semiconductor parameter analyzer under ambient atmosphere and in the dark. Transfer characteristics in the saturation regime were fitted by the following equations:

$$\sqrt{|I_D|} = -\sqrt{(W\mu_h C_i)/2L}(V_G - V_{th})$$

where I_D stands for the source–drain current, V_G the source–gate voltage, W the channel width, L the channel length, C_i the gate capacitance per unit area (6.9 nF cm^{-2}), μ_h the hole mobility and V_{th} the threshold voltage.

Table S1. Crystallographic data.

Compound	FuDT-α ^{a)}	FuDT-β ^{b)}
Radiation type, Wavelength (Å)	CuK α , 1.54184	CuK α , 1.54184
Formula	C ₃₀ H ₁₆ S ₂	C ₃₀ H ₁₆ S ₂
Formula mass	440.55	440.55
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
CCDC No.	2289377	2289378
Crystal size (mm ³)	0.436 × 0.205 × 0.007	0.205 × 0.111 × 0.003
<i>a</i> (Å)	19.1356(11)	18.7888(18)
<i>b</i> (Å)	6.0329(3)	7.9386(8)
<i>c</i> (Å)	8.5434(6)	6.7725(6)
β (°)	95.954(7)	92.602(10)
<i>V</i> (Å ³)	980.96(10)	1009.12(17)
<i>Z</i>	2	2
<i>T</i> (K)	293	298
μ (mm ⁻¹)	2.579	2.507
ρ_{calcd} (g cm ⁻³)	1.492	1.450
<i>F</i> (000)	456	456
GOF on <i>F</i> ²	1.029	1.131
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1277, 0.3270	0.0786, 0.1570
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.1472, 0.3999	0.1442, 0.1860
Reflns. measured	1796	2114
θ Range for data collection (°)	2.321–68.192	2.354–75.987
<i>R</i> _{int}	0.0514	0.0813

$$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$$

$$^a) w = 1 / [s^2(F_o^2) + (0.2000P)^2], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$^b) w = 1 / [s^2(F_o^2) + (0.0791P)^2], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

Additional comments on the crystallographic data.

It was noted that the wR_2 value of FuDT- α is very high (39.9%), and the crystal was additionally reported as a two component twin. Attempts were made to address these points:

- 1) The single crystals of a size appropriate for X-ray diffraction study commonly showed the twin.
- 2) A HKLF5 refinement could not improve the data quality efficiently because of difficult separation of twinned reflections that become broad and wide at 293 K.
- 3) Both empirical and numerical absorption corrections could not improve the wR_2 value.
- 4) Submicron crystalline flakes did not exhibit the twin by means of a microED crystal structure determination. (Though, the obtained crystallographic data is not reported herein because of its insufficient quality for publication and charge-transport calculations due to low resolution.)

The connectivity of the structure FuDT- α is not in question, however there are some other unexplained issues (see images in Figs S1-S4).

As for FuDT- β , a level B alert of the poor data/parameter ratio is attributed to the small crystal size with a thin platelet shape. The quality of crystal may also be worse as discussed in the device section.

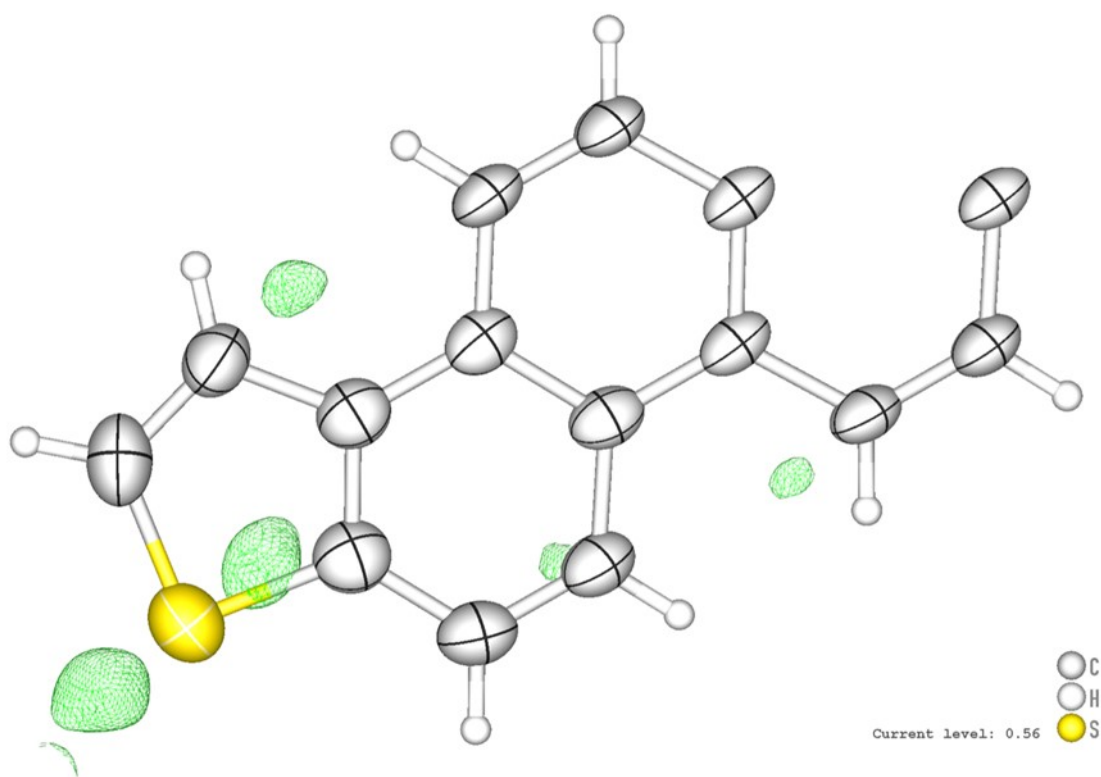


Figure S1. Residual electron density map for the cif of FuDT- α .

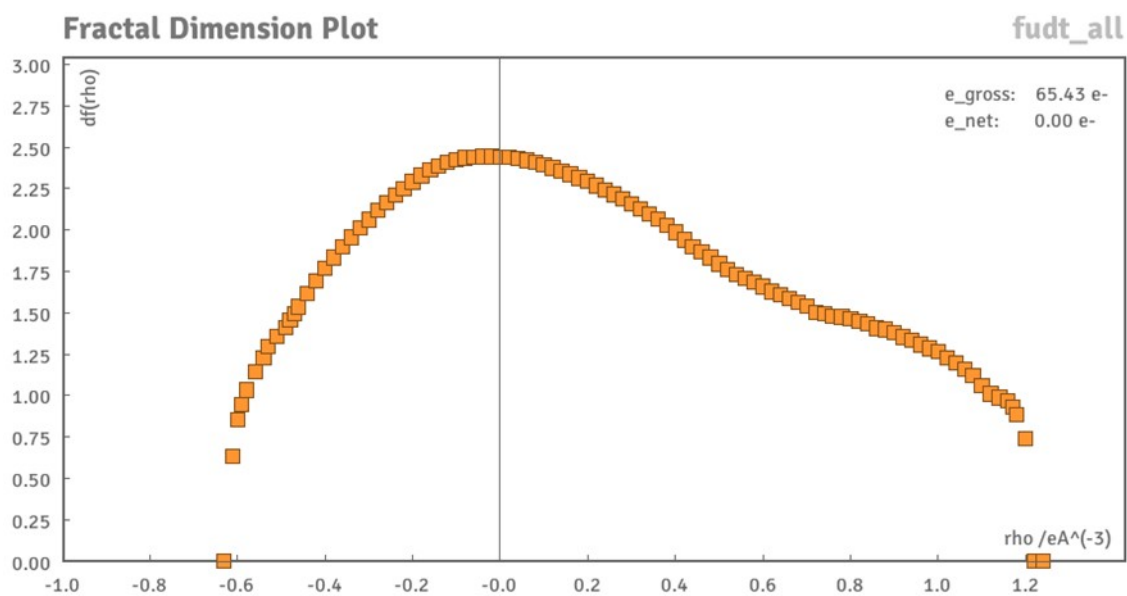


Figure S2. Fractal dimension plot for the cif of **FuDT- α** .

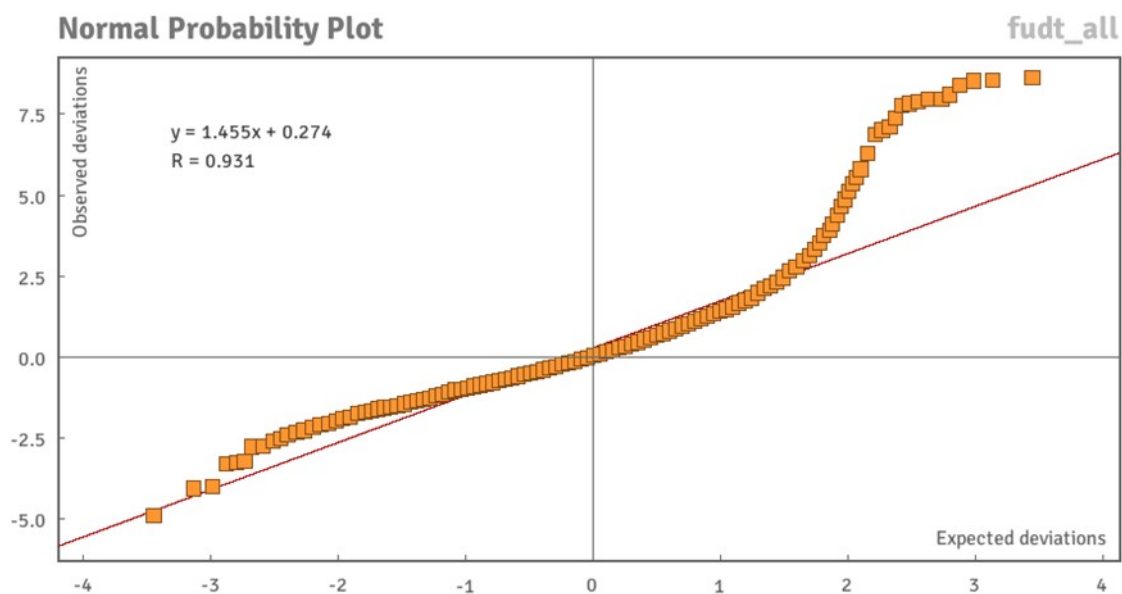


Figure S3. Normal probability plot for the cif of **FuDT- α** .

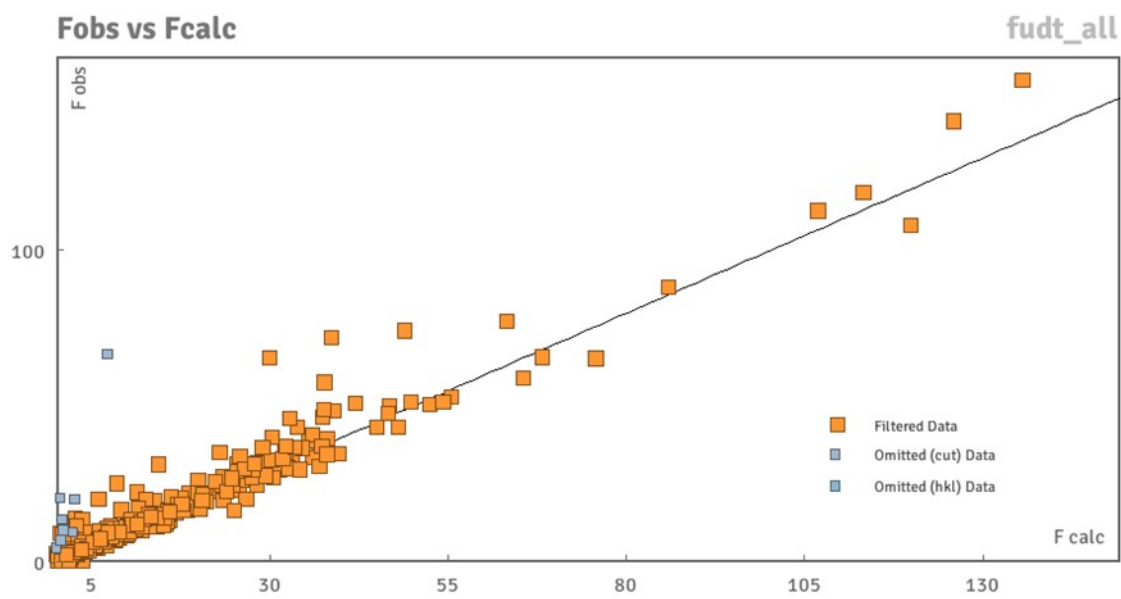


Figure S4. F_o-F_c plot for the cif of **FuDT- α** .

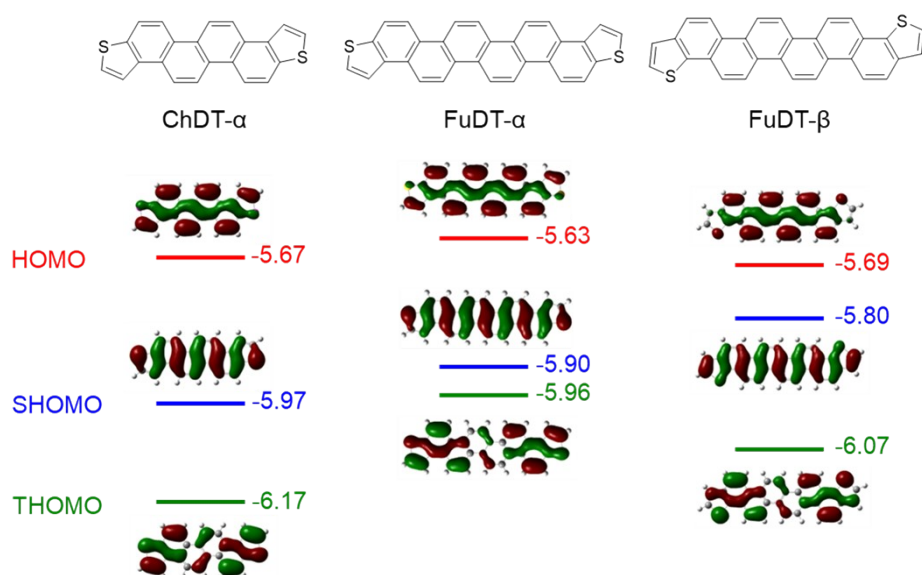


Figure S5. Occupied molecular orbital energy diagram of ChDT and FuDT at the B3LYP/6-311G(d)//B3LYP/6-31G(d) level of DFT. SHOMO and THOMO mean the second and third HOMO, respectively.

Table S2. Reorganization energy for a hole carrier (λ_h).

	ChDT-α	ChDT-β	FuDT-α	FuDT-β	Fulminene	[8]phenacene
λ_h (eV) ^{a)}	0.176	0.174	0.135	0.143	0.146 ^{b)}	0.120

^{a)} The calculations were performed at the B3LYP/6-31+G(d) level of theory. ^{b)} The result is in good agreement with the reported value of 0.144 eV in Ref. 10.

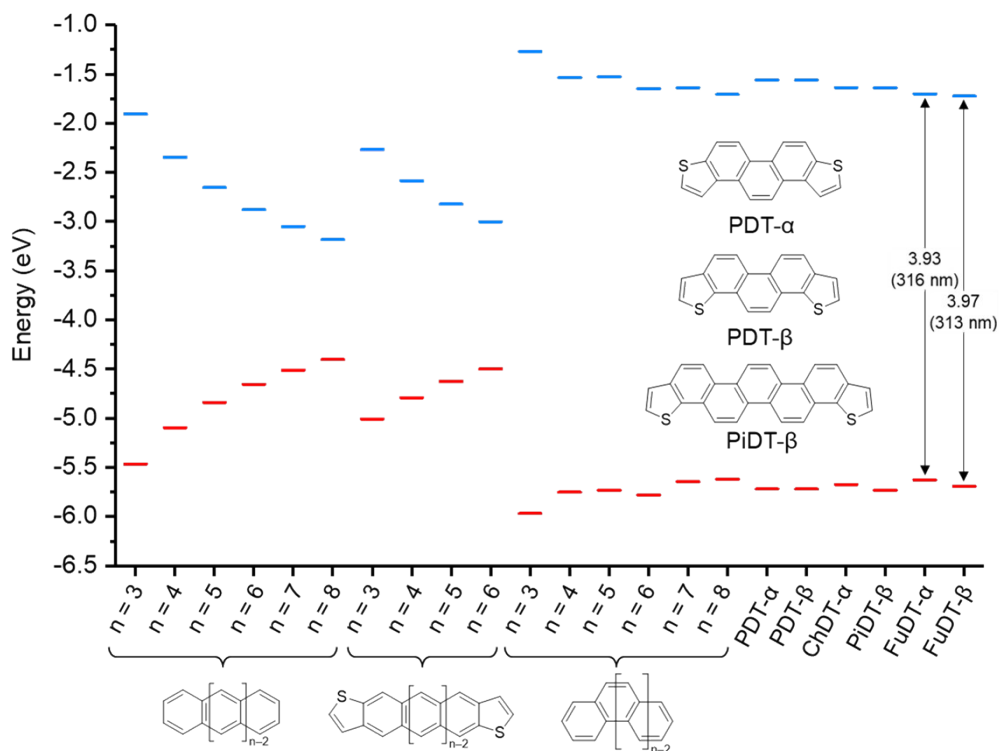


Figure S6. HOMO (red) and LUMO (blue) energy diagram of acene, phenacene and their thiophene-fused analogues. Energy levels were derived from DFT calculations at the B3LYP/6-311G(d)//B3LYP/6-31G(d) level of theory using Spartan '20 (Wavefunction Inc.). PDT- α : phenanthro[2,1-*b*:7,8-*b'*]dithiophene¹¹. PDT- β : phenanthro[1,2-*b*:8,7-*b'*]dithiophene¹². PiDT- β : piceno[4,3-*b*:9,10-*b'*]dithiophene¹³.

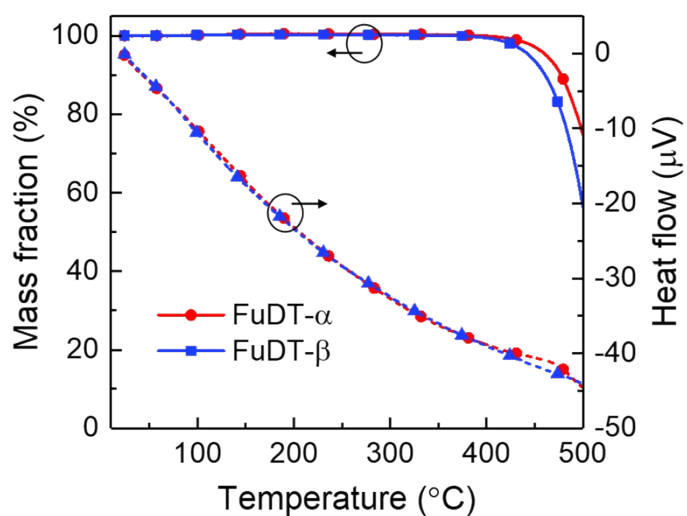


Figure S7. TG-DTA traces under a stream of nitrogen.

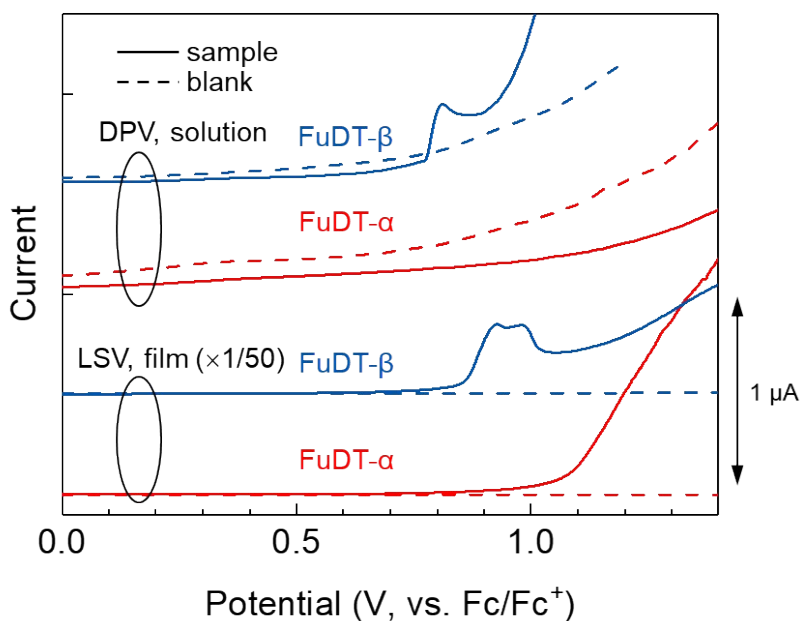


Figure S8. Electrochemical characterization of FuDT isomers. The differential pulse voltammetry (DPV) data were collected with *o*-dichlorobenzene solutions at 140 °C. The linear sweep voltammetry (LSV) data were acquired with thin films on ITO-coated glass substrates in acetonitrile at room temperature. The oxidation potential was extracted from the peak top and the onset for DPV and LSV, respectively.

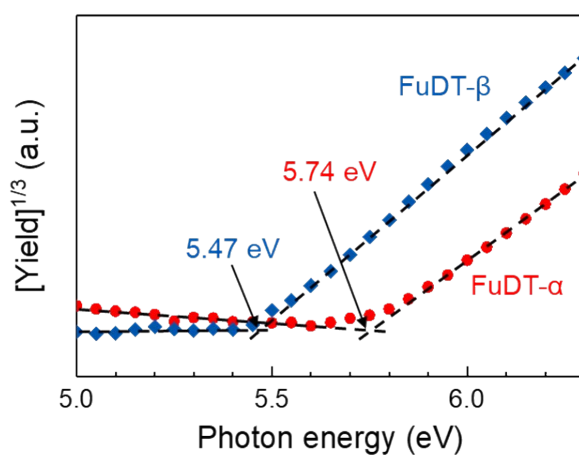
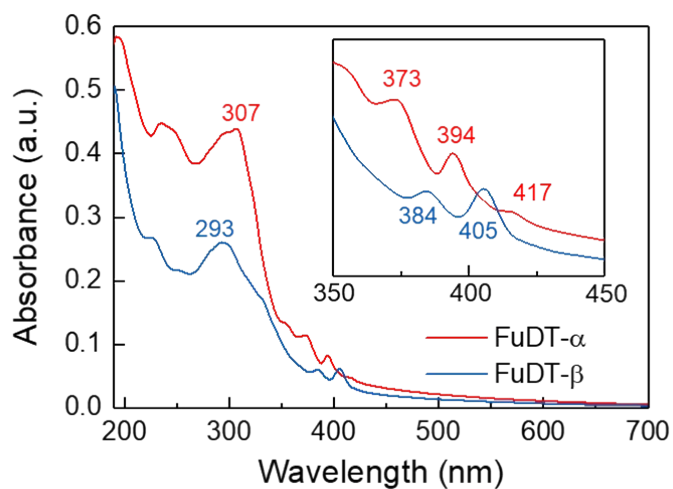


Figure S9. Photoelectron yield spectra in air. The ionization potentials under vacuum were comparable for both FuDT- α (5.72 eV) and FuDT- β (5.47 eV).

Table S3. HOMO properties of FuDT isomers.

	E_{ox}^{DPV} ^{a)} (V vs. Fc/Fc ⁺)	E_{HOMO}^{DPV} ^{b)} (eV vs. vac.)	E_{ox}^{LSV} ^{c)} (V vs. Fc/Fc ⁺)	E_{HOMO}^{LSV} ^{d)} (eV vs. vac.)	IP ^{e)} (eV vs. vac.)	E_{HOMO}^{DFT} ^{f)} (eV vs. vac.)
FuDT- α	N.D. ^{g)}	N.D. ^{g)}	+1.08	-5.88	5.74	-5.632
FuDT- β	+0.81	-5.61	+0.85	-5.65	5.47	-5.692

^{a)} Oxidation potential extracted from the peak top of DPV. ^{b)} HOMO level calculated by $E_{HOMO}^{DPV} = E_{Fc} - E_{ox}^{DPV}$, where E_{Fc} (= -4.8) is the half wave potential for Fc/Fc⁺ redox couple measured as an internal standard. ^{c)} Oxidation potential extracted from the onset of LSV. ^{d)} HOMO level calculated by $E_{HOMO}^{LSV} = E_{Fc} - E_{onset}^{LSV}$. ^{e)} Ionization potential measured by photoelectron yield spectra in air. ^{f)} HOMO level calculated based on the B3LYP/6-311G(d)//B3LYP/6-31G(d) level of density functional theory. ^{g)} Not determined.

**Figure S10.** UV-vis absorption spectra of thin films. Inset shows the magnified spectra around the absorption onset region.

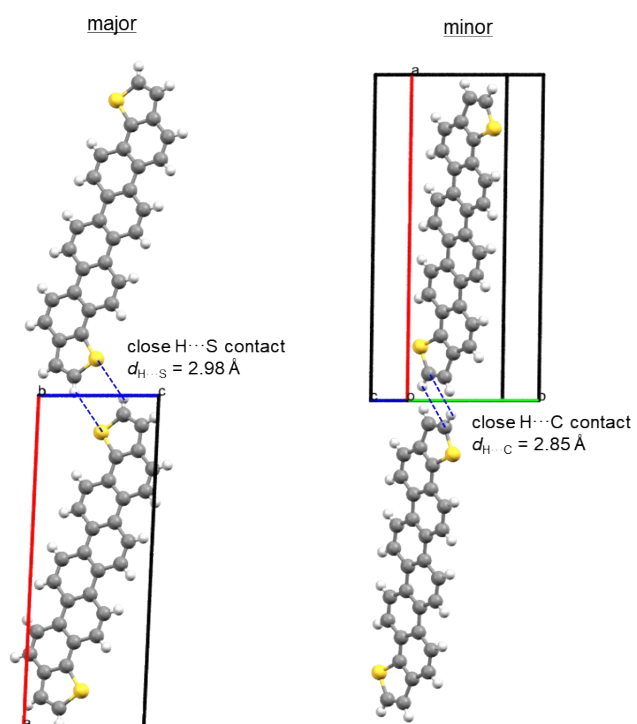


Figure S11. Close contacts between the adjacent herringbone layers in FuDT- β with the major/minor occupancy.

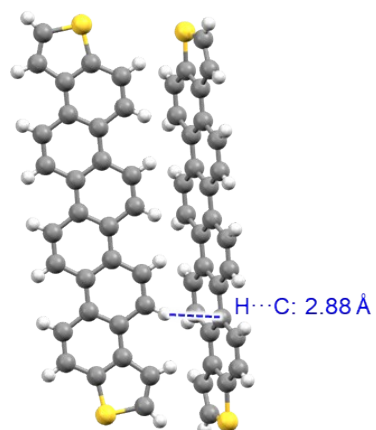


Figure S12. C-H... π interaction in FuDT- α .

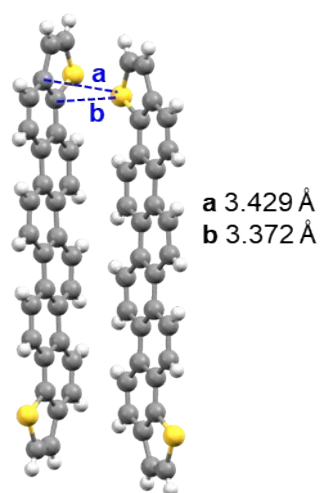


Figure S13. S... π interaction in the minor part (site occupancy = 0.36) of FuDT- β .

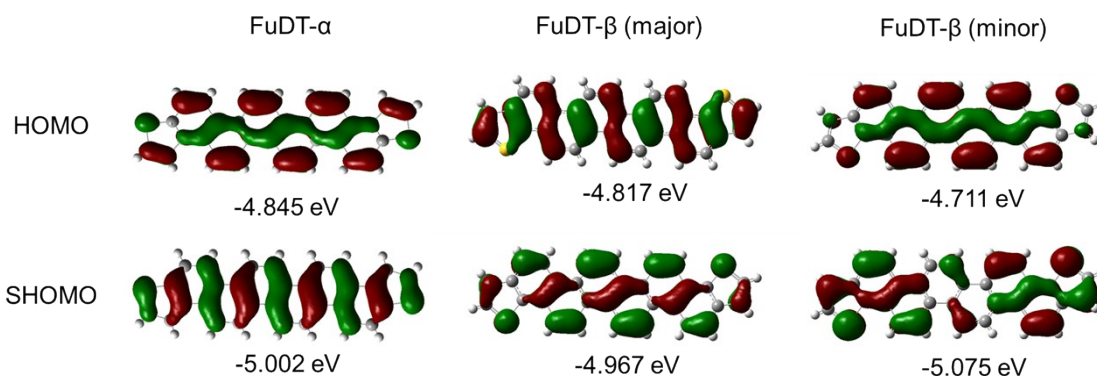
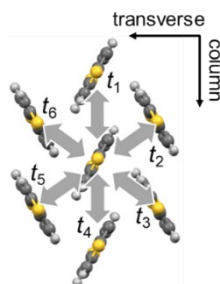


Figure S14. HOMO and SHOMO of FuDT- α and FuDT- β at the PBEPBE/6-31G(d) level of DFT using the geometry in a crystal structure.

Table S4. Summary of transfer integrals in FuDT- α and FuDT- β (PBEPBT/6-31G(d), unit: meV).



		t_1	t_2	t_3	t_4	t_5	t_6
FuDT- α	t^{HH} a)	+80.7	-56.2	-56.2	+80.7	-56.2	-56.2
	t^{HS} b)	-7.5	+2.7	+2.7	-7.5	+45.7	+2.7
	t^{SS} c)	+23.5	+1.5	+1.5	+23.5	+1.5	+1.5
FuDT- β (major)	t^{HH} a)	+5.8	+11.8	+11.8	+5.8	+11.8	+11.8
	t^{HS} b)	-36.0	-14.4	-14.4	-36.0	+11.2	-14.4
	t^{SS} c)	+74.8	-65.2	-65.2	+74.8	-65.2	-65.2

a) Transfer integral for HOMO \rightarrow HOMO. a) Transfer integral for HOMO \rightarrow SHOMO. a) Transfer integral for SHOMO \rightarrow SHOMO.

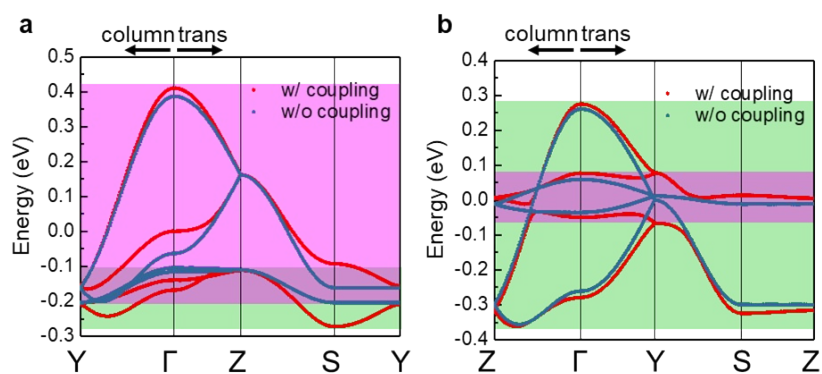
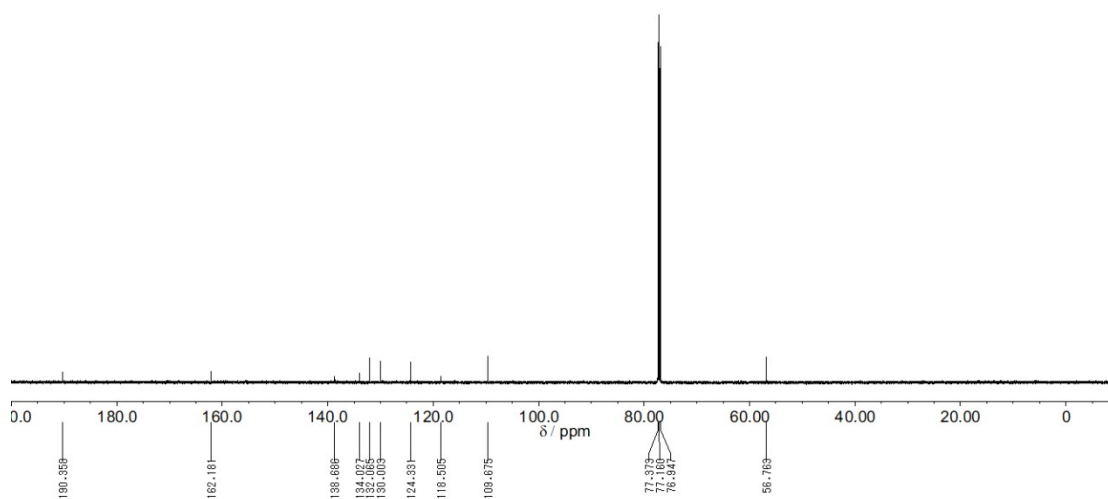
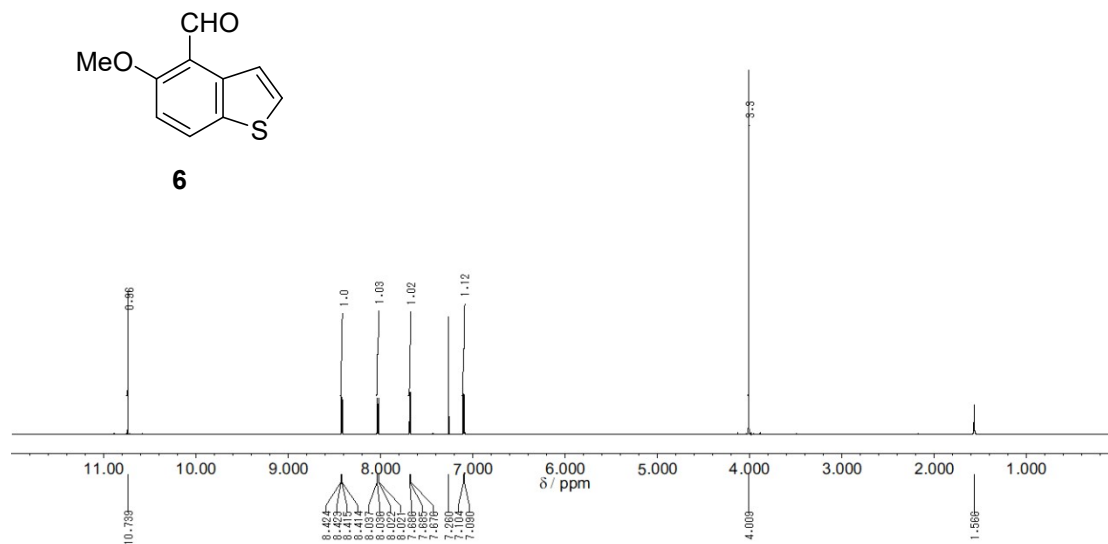
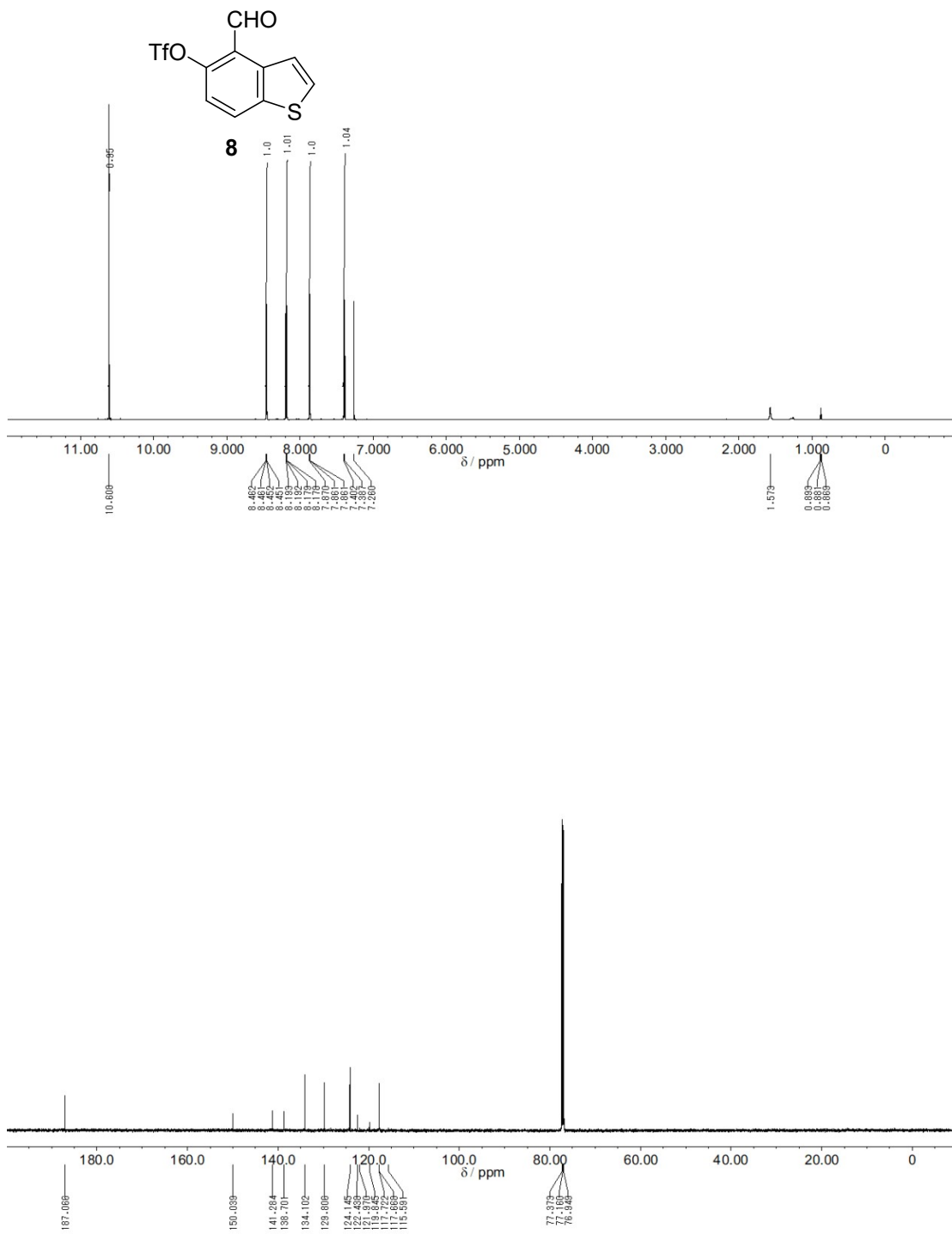


Figure S15. Valence bands of (a) FuDT- α and (b) FuDT- β (major), calculated based on the tight-binding approximation. t^{HH} and t^{SS} were used as calculated (Table S2) in all calculations. Whereas t^{HS} was used as calculated for taking HOMO–SHOMO hybridization into account (w/ coupling), that was considered to be 0 meV for ignoring the hybridization (w/o coupling). The regions shaded by pink and green colors almost consist of HOMO and SHOMO, respectively.

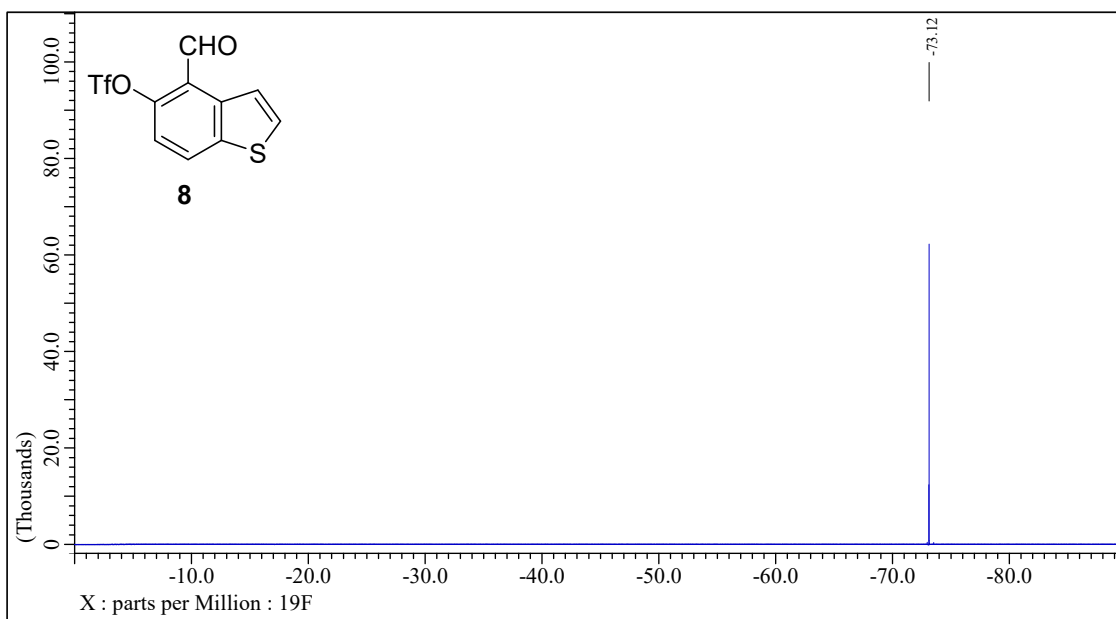
¹H NMR chart of new compounds



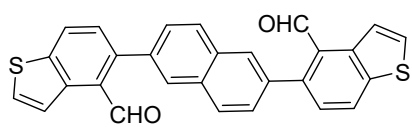
¹H NMR (600 MHz) and ¹³C{¹H} NMR (150 MHz) spectra of **6** (CDCl₃, rt).



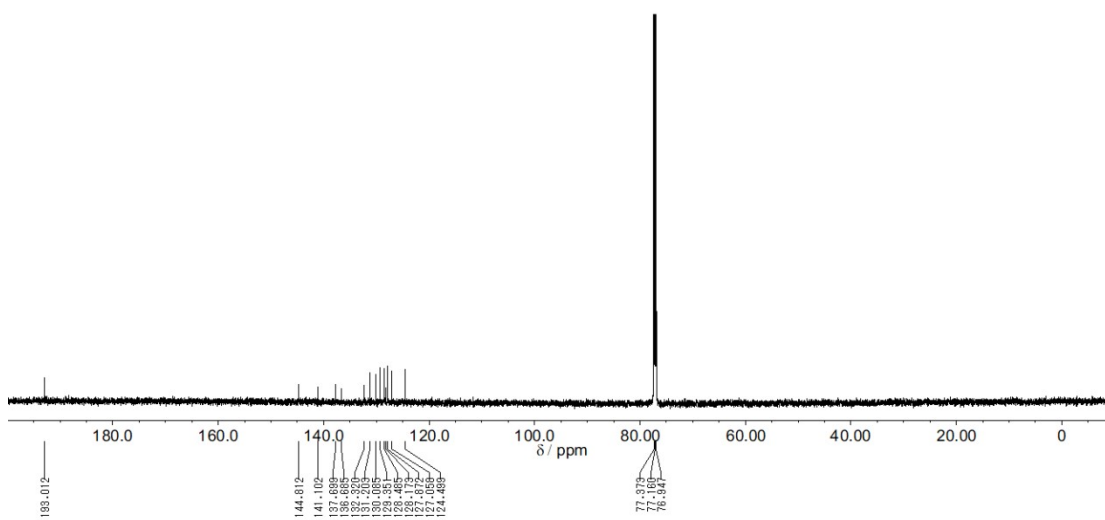
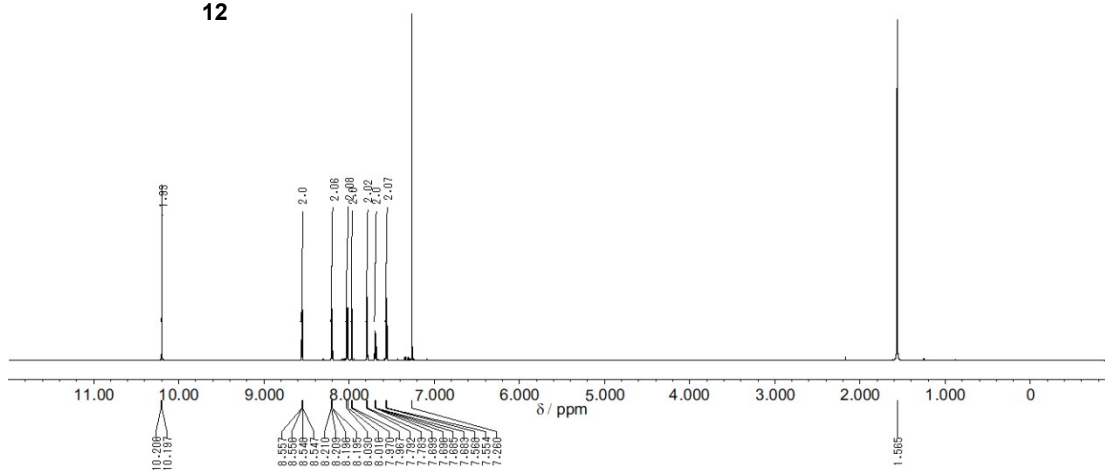
¹H NMR (600 MHz) and ¹³C{¹H} NMR (150 MHz) spectra of **8** (CDCl₃, rt).



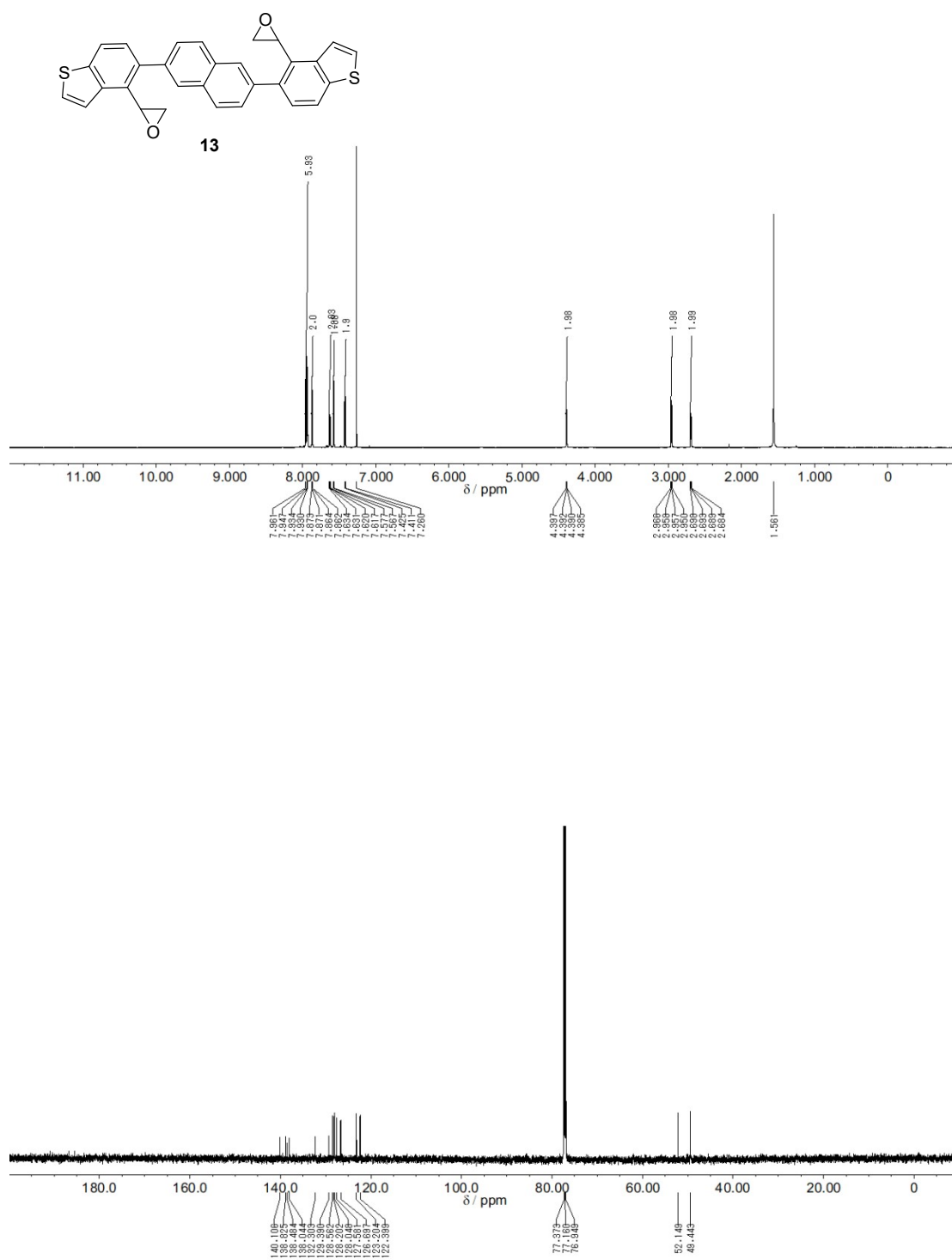
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz) spectra of **8** (CDCl_3 , rt).

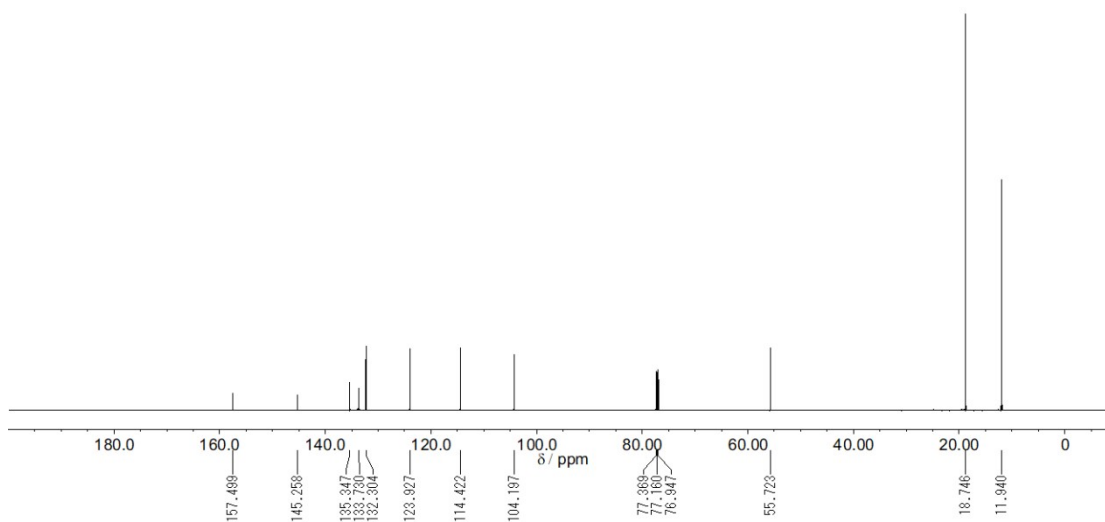
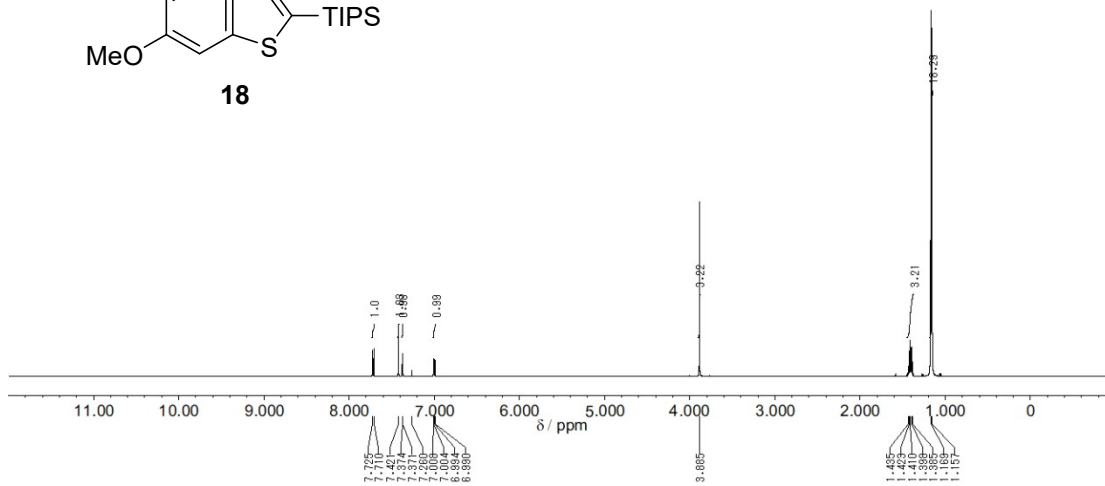
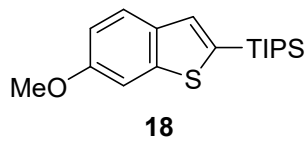


12

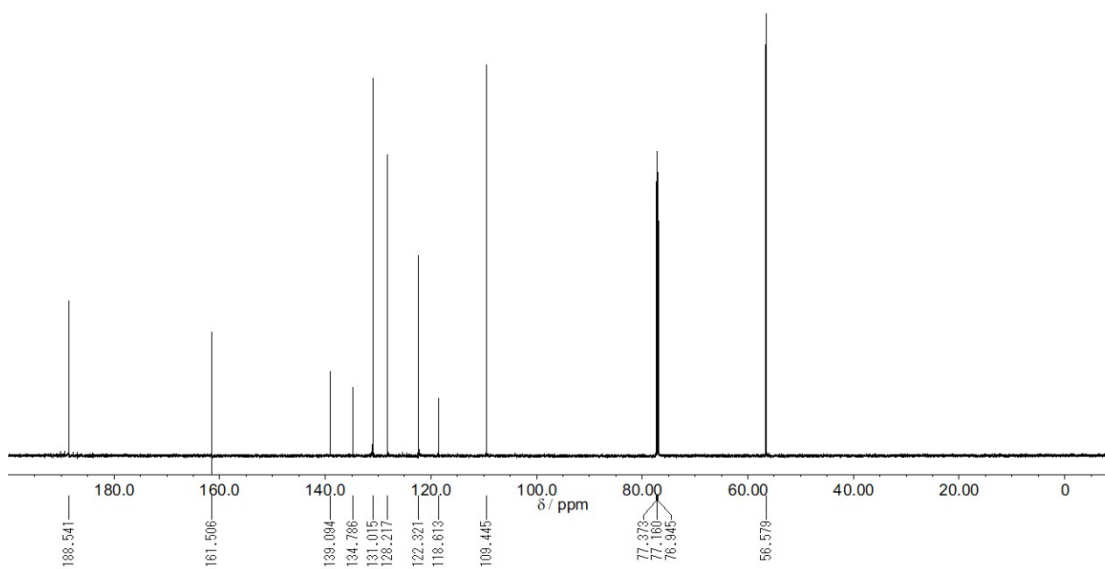
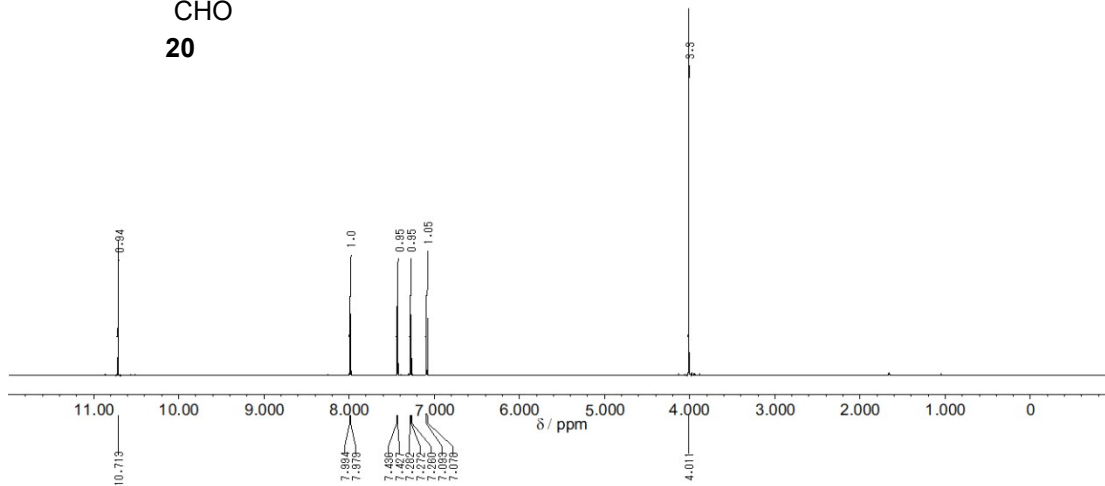
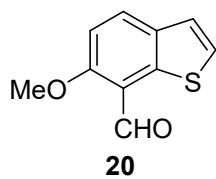


^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) spectra of **12** (CDCl_3 , rt).

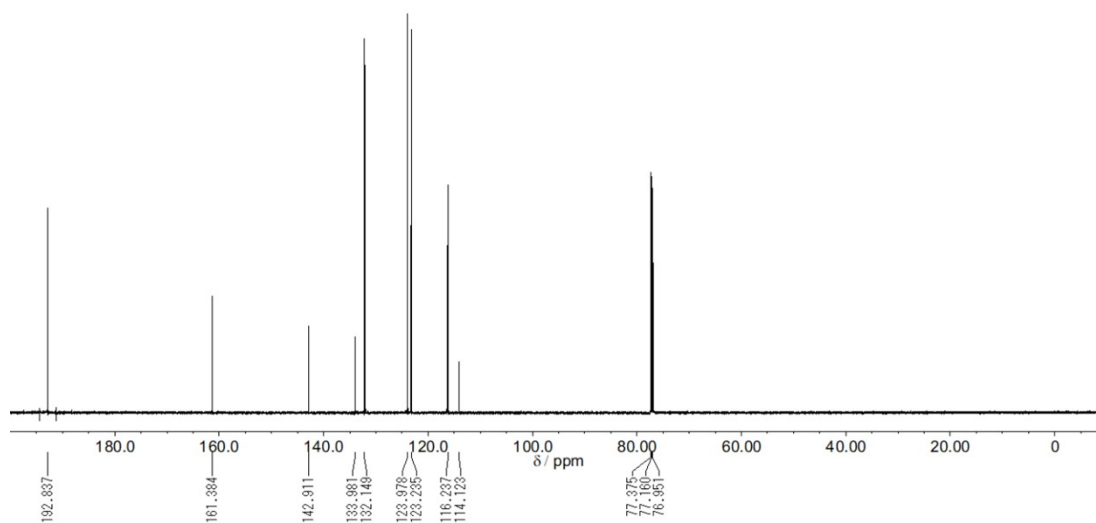
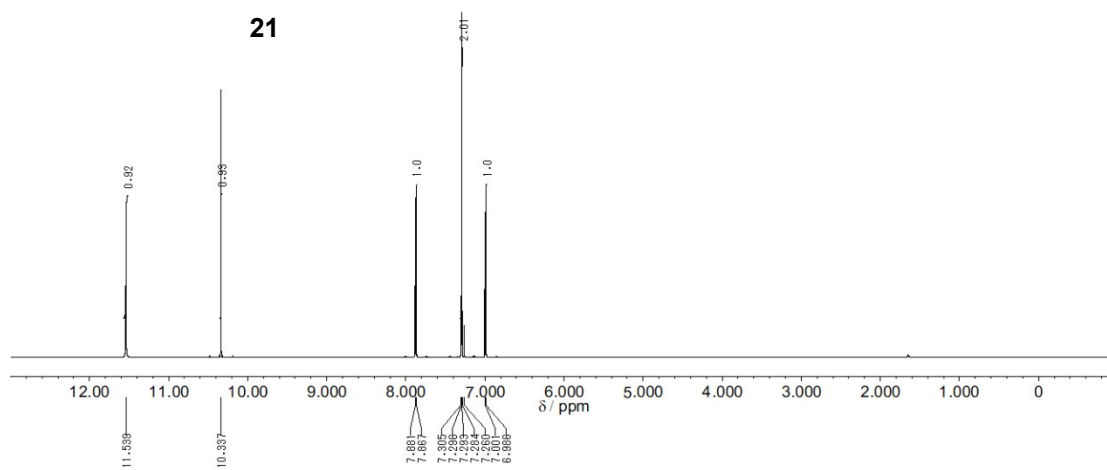
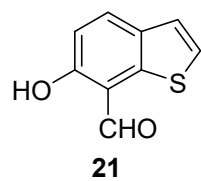




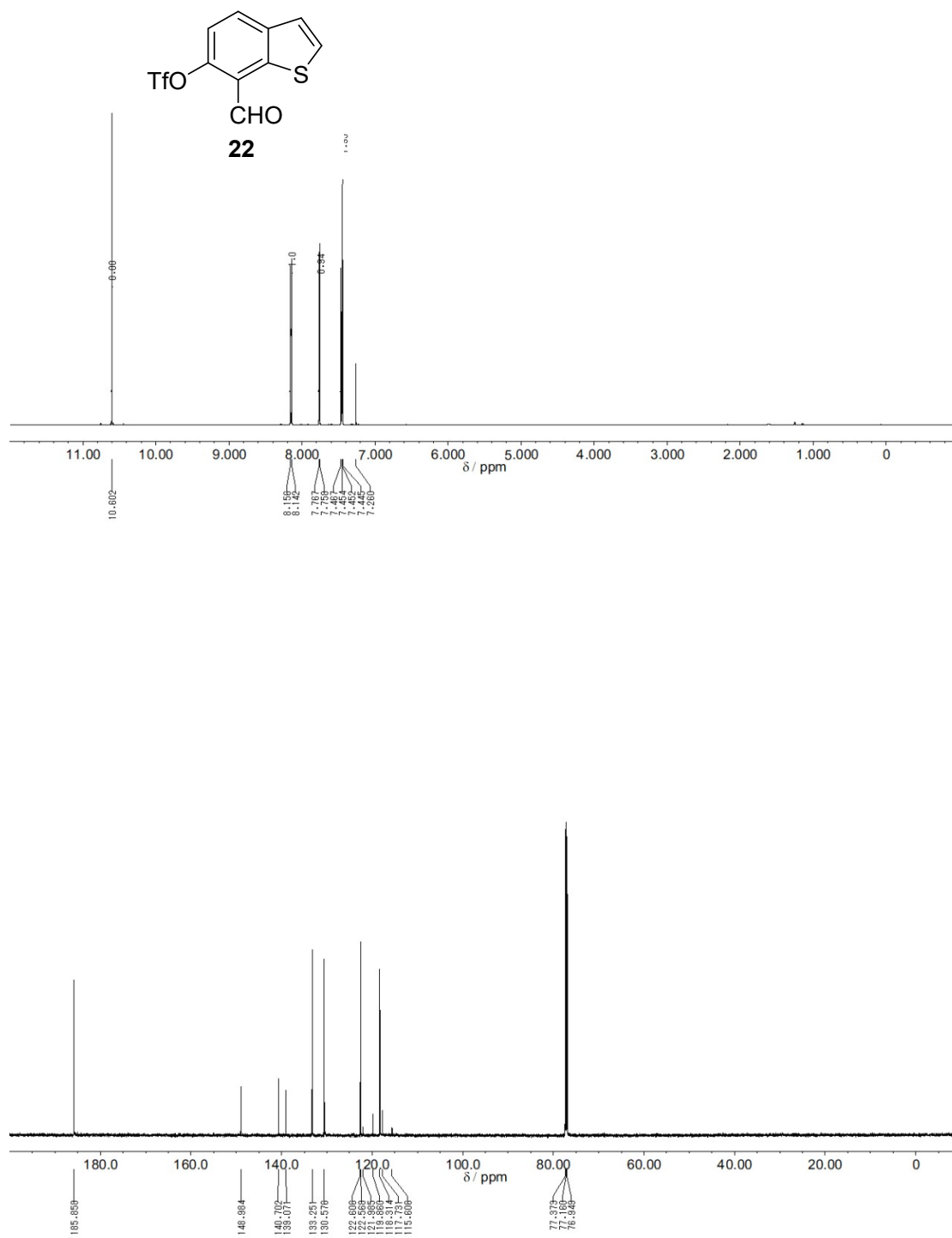
^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) and spectra of **18** (CDCl_3 , rt).



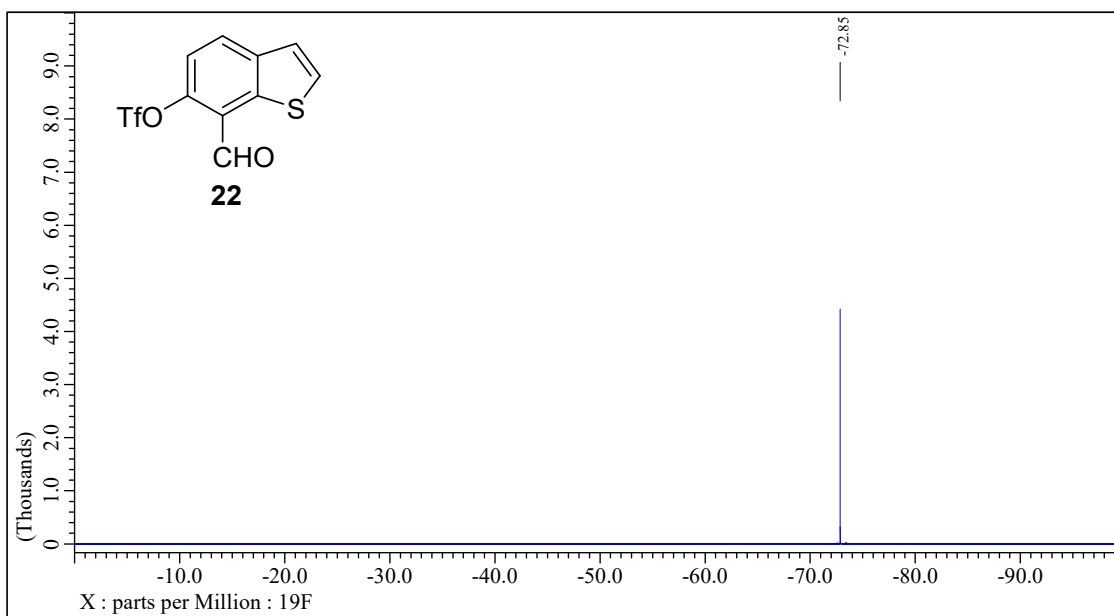
^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) and spectra of **20** (CDCl_3 , rt).



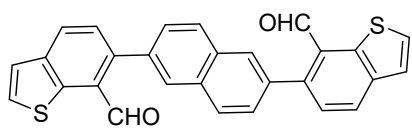
^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) and spectra of **21** (CDCl_3 , rt).



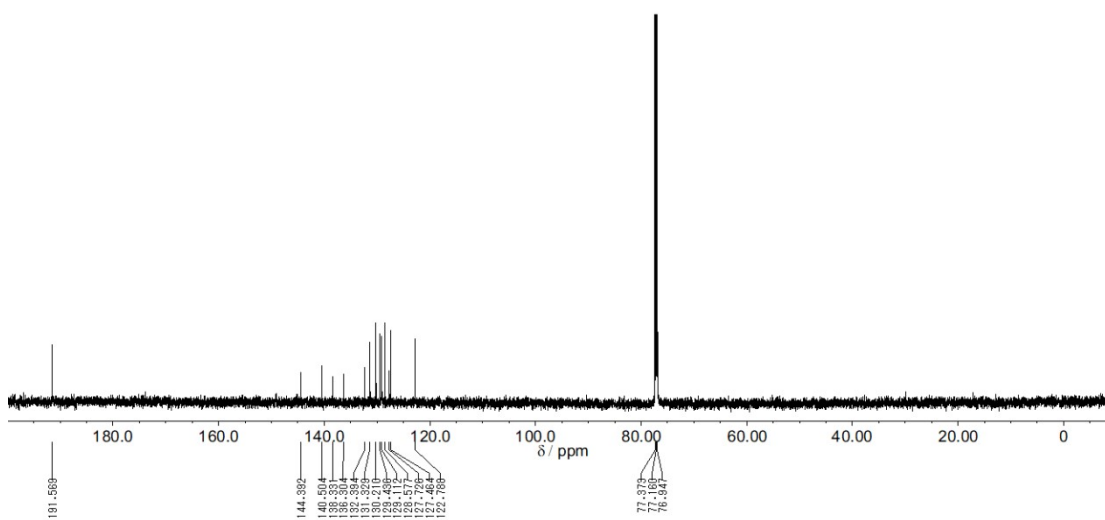
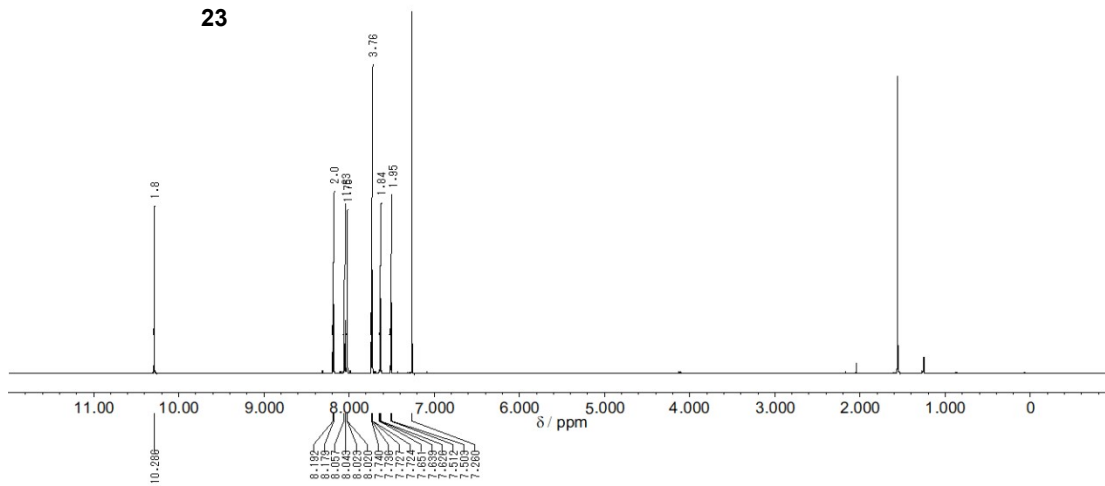
¹H NMR (600 MHz), and ¹³C{¹H} NMR (150 MHz) and spectra of **22** (CDCl₃, rt).



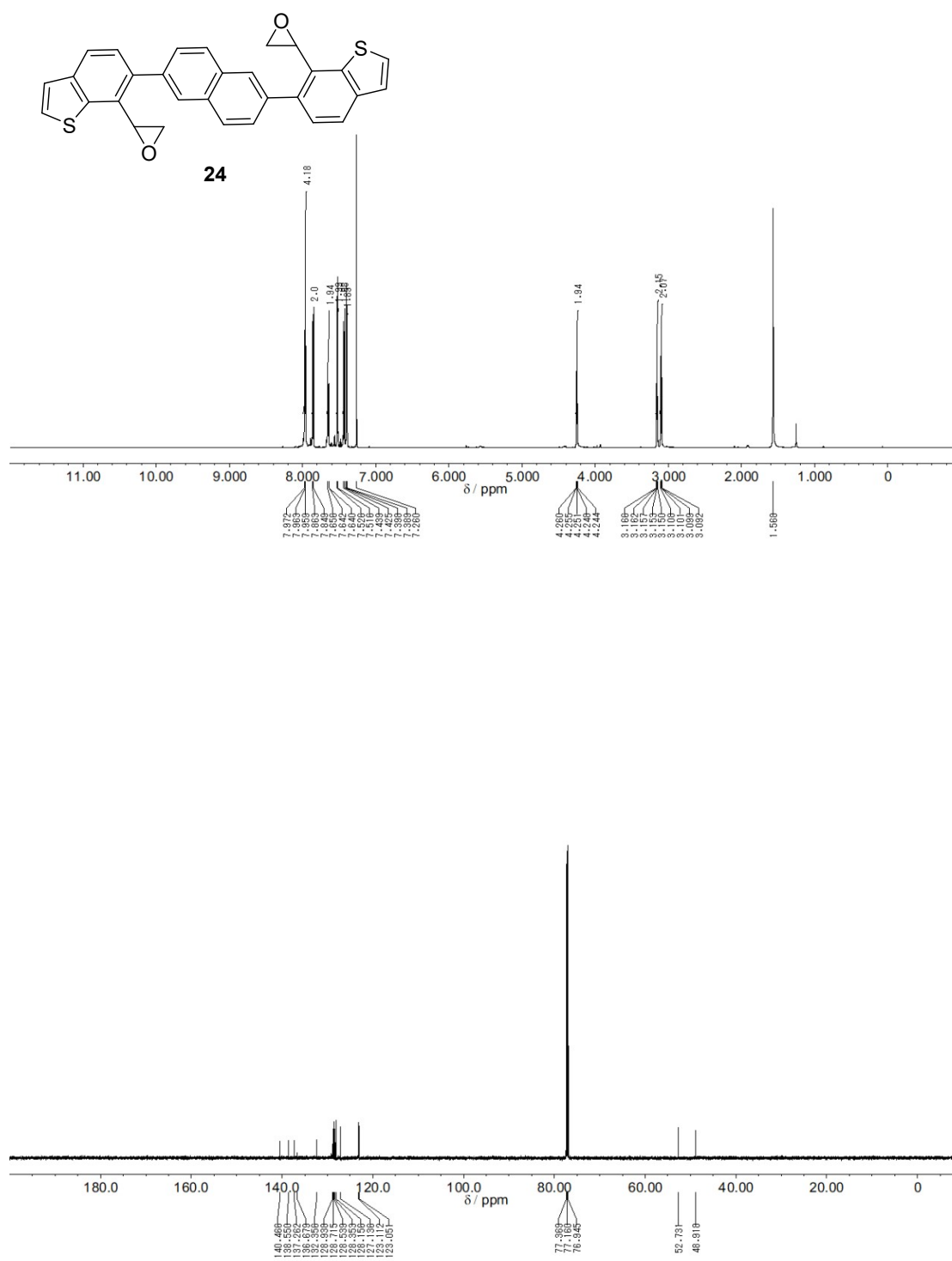
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz) spectra of **22** (CDCl_3 , rt).



23



^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) and spectra of **23** (CDCl_3 , rt).



^1H NMR (600 MHz), and $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz) and spectra of **24** (CDCl_3 , rt).

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