Electronic Supplementary Information

Turn-on mode fluorescent diarylethene containing neopentyl substituents that undergoes all-visible-light switching

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Movie S1 Colour changes of 1,4-dioxane solutions of **1** (left) and **3** (right) upon irradiation with 405 nm (ca. 230 mW cm^{-2}) and 525 nm (ca. 150 mW cm^{-2}) LED light.

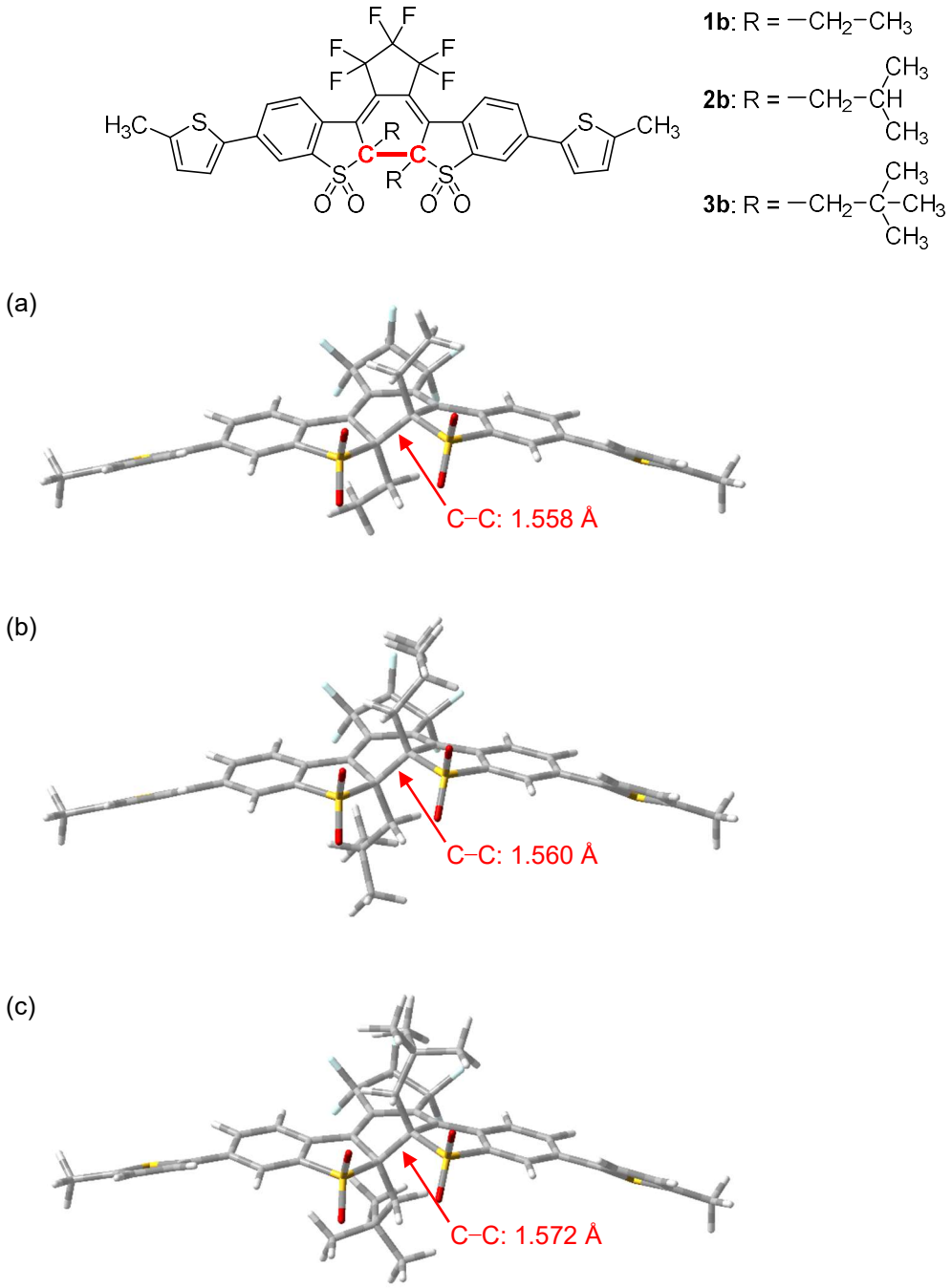


Fig. S1 Molecular geometries of **1b** (a), **2b** (b) and **3b** (c) in the ground states calculated at ωB97XD/6-31G(d) level of theory. The lengths of the covalent bond between the reactive carbon atoms, which is broken in the cycloreversion reaction, are 1.558 Å, 1.560 Å and 1.572 Å for **1b**, **2b** and **3b**, respectively.

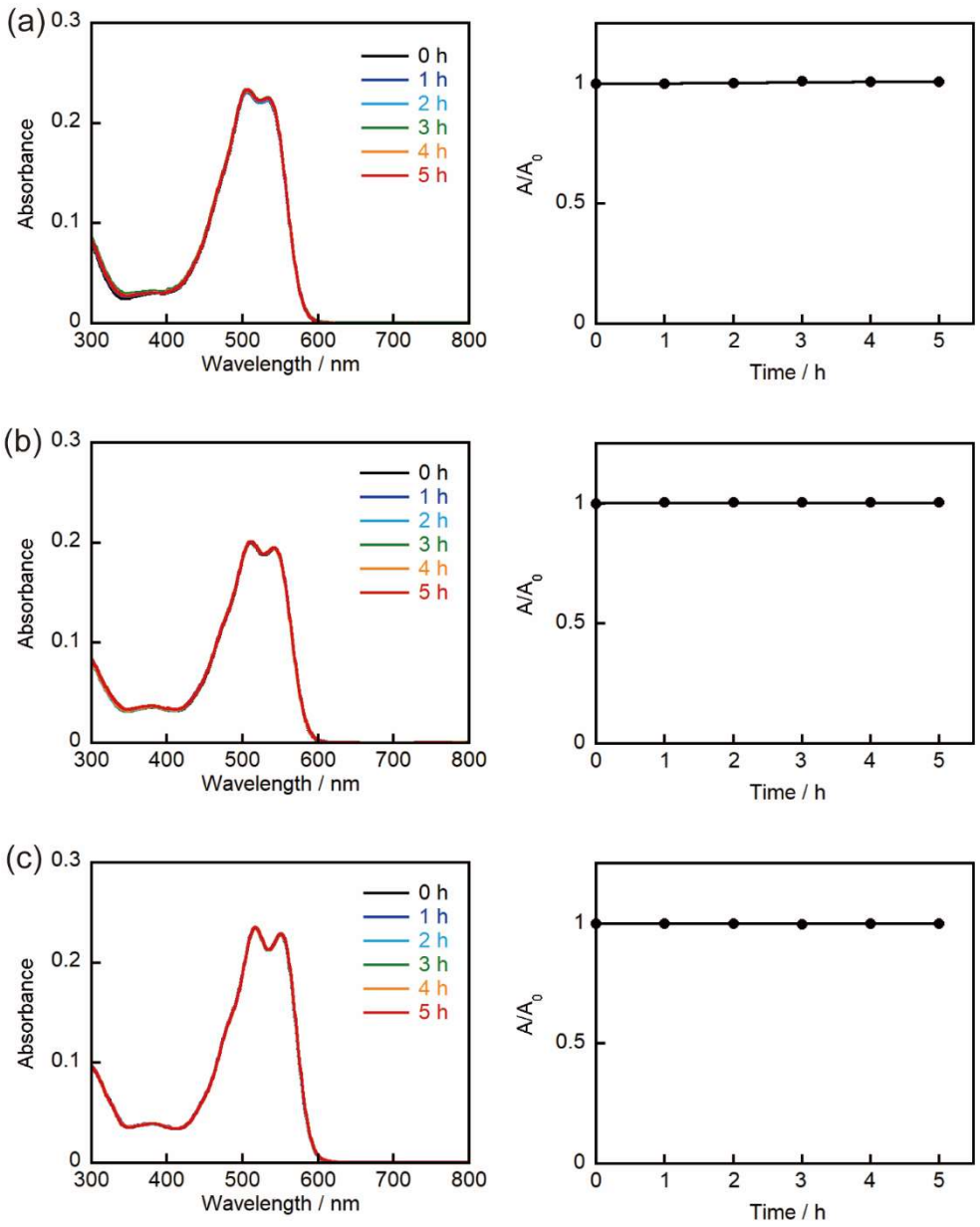


Fig. S2 Absorption spectra (left) and absorbance changes (right) of **1b** (a), **2b** (b) and **3b** (c) in 1,4-dioxane at 80 °C under a dark condition. Absorbances at 506 nm, 510 nm and 516 nm were monitored for **1b**, **2b** and **3b**, respectively.

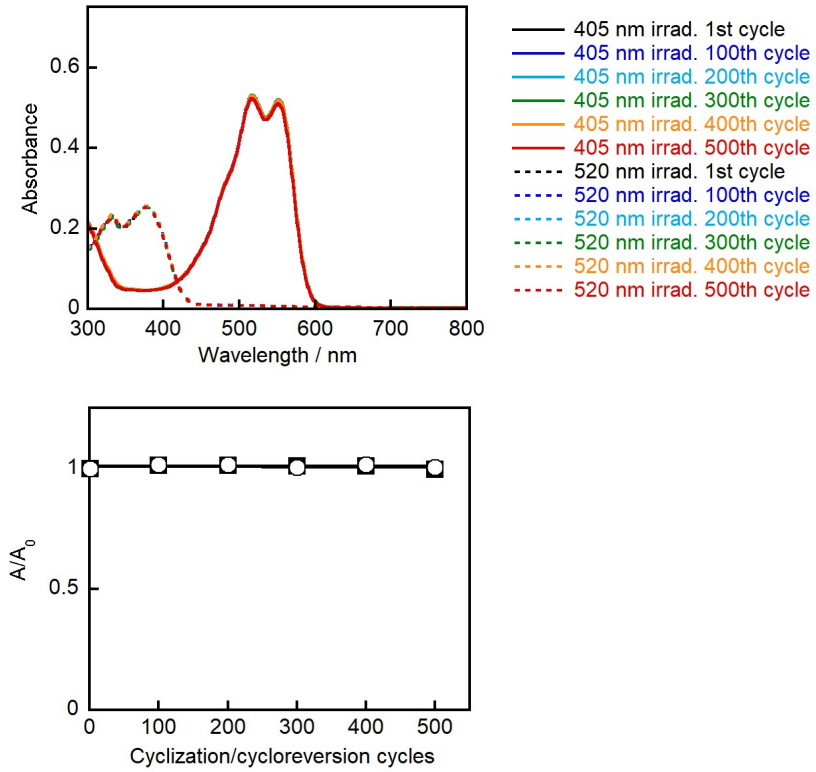


Fig. S3 Fatigue resistance of **3** against repeating cyclization and cycloreversion reactions in 1,4-dioxane by alternate irradiation with 405 nm light (15.6 mW cm^{-2}, 60 sec) and 520 nm light (11.3 mW cm^{-2}, 600 sec). Top: absorption spectra of **3b** after 405 nm light irradiation (solid lines) and **3a** after 520 nm light irradiation (dotted lines) in every 100 cycles. Bottom: absorbance changes of **3b** at 516 nm after 405 nm light irradiation (black squares) and **3a** at 377 nm after 520 nm light irradiation (open circles) in every 100 cycles.

Experimental section

1a was synthesized according to the previous literature.[S1] Solvents used for spectral measurement were of spectroscopic grade.

^{1}H and ^{13}C NMR spectra were recorded with JEOL ECX-400P NMR spectrometer. For $CDCl_3$ solution, tetramethylsilane (TMS) was used as an internal standard. For CD_2Cl_2 solution, the solvent signal (CH_2Cl_2: 5.32 ppm, $^{13}CH_2Cl_2$: 53.8 ppm) was used as a standard. Mass spectra (MS) were recorded with Shimadzu GCMS-QP2010Plus mass spectrometer based on electron-impact (EI) ionization. High-resolution mass spectra (HRMS) were recorded with JEOL JMS-T100LP mass spectrometer based on electrospray ionization (ESI).

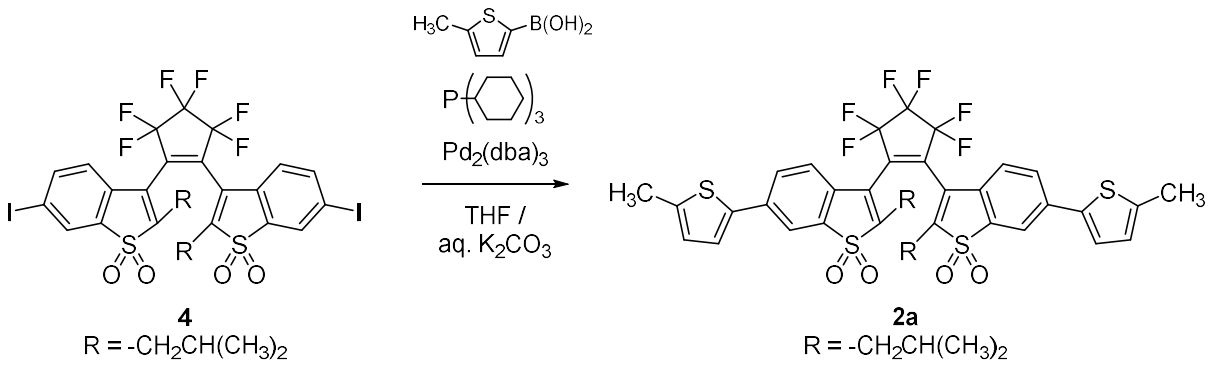
UV-visible absorption spectra were recorded with Hitachi U-4100 absorption spectrophotometer. In the experiment on thermal stability and fatigue resistance of closed-ring isomer, absorption spectra were recorded with JASCO V-630 absorption spectrophotometer. In the experiment on thermal stability, the temperature of sample solutions was controlled by using a temperature controller (ESPEC SH-221).

Fluorescence spectra and fluorescence quantum yields were measured with an absolute PL quantum yield measurement system (Hamamatsu Photonics C9920-02G). Before the fluorescence measurement, sample solutions were deaerated by bubbling with nitrogen gas.

Photoirradiation for photoreactions was carried out using a 300 W xenon lamp (Asahi spectra MAX-303) with band-pass optical filters or a monochromator (Ritsu MC-10N), or an LED irradiation system (Asahi spectra CL-1501, LED head: CL-H1-405-9-1 for 405 nm, CL-H1-525-7-1 for 525 nm).

The cyclization quantum yields of **2a** and **3a** in 1,4-dioxane under irradiation with 330 nm light were determined using **1a** in 1,4-dioxane (Φ_{oc} = 0.23)[S2] as a reference. The cycloreversion quantum yields of **2b** and **3b** in 1,4-dioxane under irradiation with 520 nm light were determined using 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane (Φ_{co} = 0.0223)[S3] as a reference. The cycloreversion quantum yield of **3b** in ethanol under irradiation with 520 nm light was determined using **3b** in 1,4-dioxane as a reference.

The molecular geometries of **1**–**3** were calculated at ωB97XD/6-31G(d) level of theory (Gaussian 09 program).[S4]



4
R = -$CH_2CH(CH_3)_2$

2a
R = -$CH_2CH(CH_3)_2$

Scheme S1 Synthesis of **2a**.

1,2-Bis(2-isobutyl-6-(5-methylthiophen-2-yl)-1-benzothiophen-1,1-dioxide-3-yl)perfluoro-cyclopentene (2a)

To a THF solution (17 mL) containing **4**[S5] (0.17 g, 0.20 mmol) and 5-methylthiophen-2-yl boronic acid (0.075 g, 0.53 mmol) were added saturated K_2CO_3 aqueous solution (17 mL), tris(dibenzylideneacetone)dipalladium(0) (0.095 g, 0.10 mmol) and 18% tricyclohexylphosphine toluene solution (8 drops) and the mixture was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$ and the organic layer was washed with dilute hydrochloric acid, $Na_2S_2O_3$ aqueous solution and brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **2a** as orange solids (0.083 g, 0.10 mmol; 52%). The obtained product was further purified by preparative HPLC (pump: Hitachi L-6250, detector: Hitachi L-7400 (313 nm), column: Wakosil® 5SIL (ϕ20 mm × 250 mm), hexane : ethyl acetate = 90 : 10, 7 mL min^{-1}). The purity was confirmed by analytical HPLC (pump: Hitachi L-2130, detector: Hitachi L-2420 (313 nm), column: Wakosil® 5SIL (ϕ4.6 mm × 250 mm), hexane : ethyl acetate = 90 : 10, 1 mL min^{-1}), as shown in Fig. S4.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.72 (d, 6H, *J* = 6.4 Hz), 0.86 (d, 6H, *J* = 6.4 Hz), 0.98 (d, 2.1H, *J* = 6.4 Hz), 1.07 (d, 2.1H, *J* = 6.4 Hz), 1.99-2.17 (m, 6H), 2.19-2.25 (m, 2.3H), 2.49 (s, 2.1H), 2.54 (s, 6H), 6.75 (dd, 0.8H, *J* = 4, 0.8 Hz), 6.82 (dd, 2H, *J* = 4, 0.8 Hz), 7.06 (d, 0.9H, *J* = 8.4 Hz), 7.18 (d, 0.7H, *J* = 3.6 Hz), 7.27-7.29 (m, 4H), 7.53 (dd, 0.9H, *J* = 8.4, 2.0 Hz), 7.76 (dd, 2H, *J* = 8.4, 1.6 Hz), 7.80 (d, 0.7H, *J* = 2.0 Hz), 7.94 (d, 2H, *J* = 2.0 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 15.67, 15.72, 21.92, 22.56, 22.60, 23.70, 26.47, 26.63, 35.07, 35.10, 118.91, 119.11, 124.46, 124.52, 125.33, 125.83, 125.96, 127,25, 127.33, 127.45, 127.47, 129.74, 129.97, 137.05, 137.09, 138.23, 138.27, 138.81, 138.85, 143.08, 143.27, 146.65, 146.78; MS (EI) *m*/*z* 808 $[M]^+$; HRMS (ESI, positive) *m*/*z* calcd for $C_{39}H_{34}F_6O_4S_4Na$ $[M+Na]^+$ 831.1142, found 831.1125; Mp 191–192 °C.

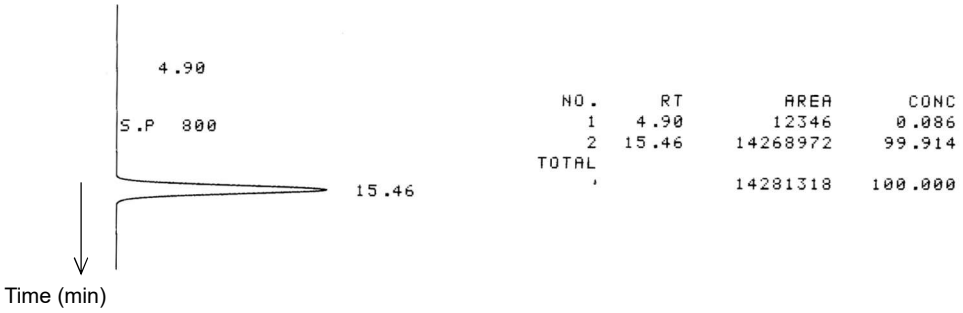


Fig. S4 HPLC chromatogram of **2a**.

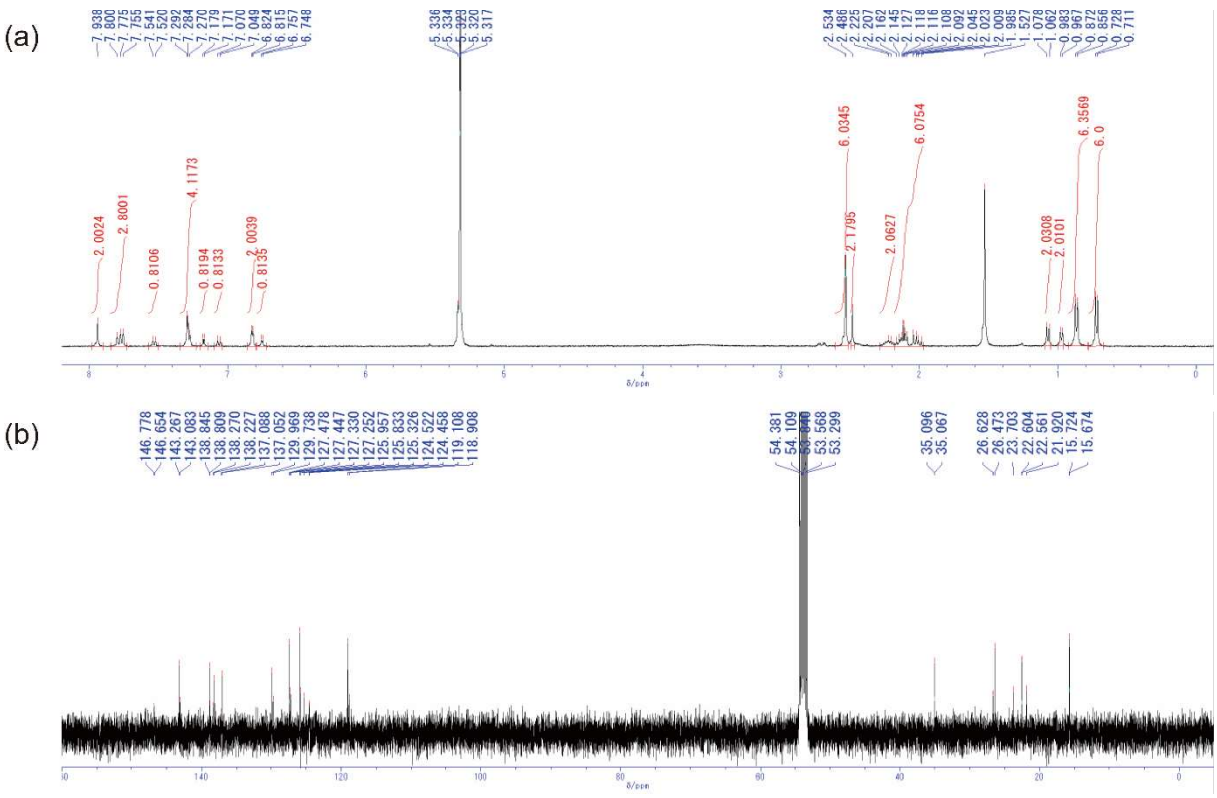
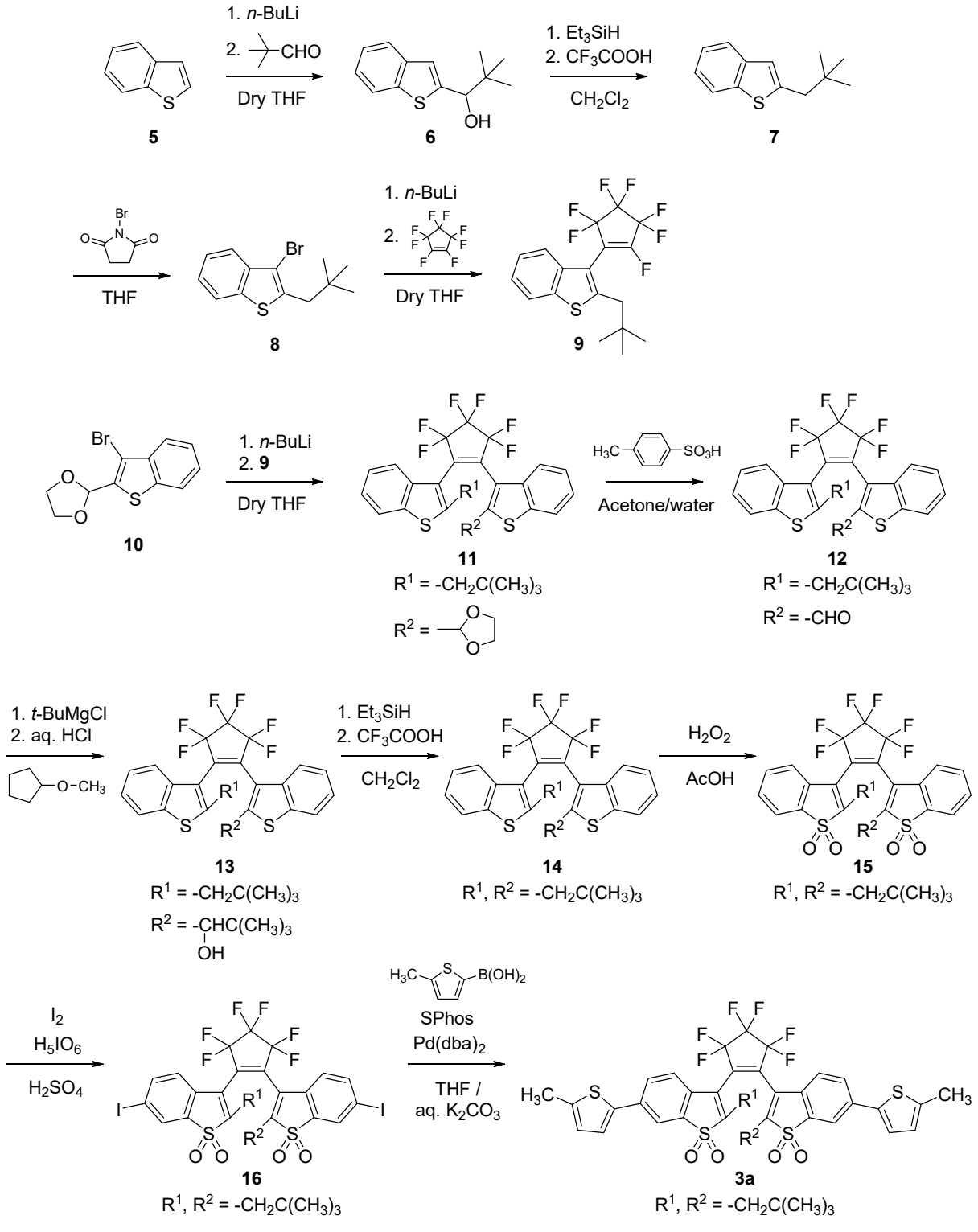


Fig. S5 400 MHz ^{1}H NMR (a) and 100 MHz ^{13}C NMR spectra (b) of **2a** in CD_2Cl_2.



Scheme S2 Synthesis of **3a**.

1-(Benzo[*b*]thiophen-2-yl)-2,2-dimethylpropan-1-ol (6)

To a dry THF solution (60 mL) containing benzo[*b*]thiophene (**5**) (10 g, 75 mmol) was slowly added 1.6 M *n*-BuLi hexane solution (58 mL, 93 mmol) at –78 °C under a nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. Pivalaldehyde (10 mL, 91 mmol) was slowly added at –78 °C and the mixture was stirred for 1 h at –78 °C followed by stirring for 17 h at room temperature. The reaction was quenched by adding water. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9 : 1) to give **6** as white solids (11 g, 50 mmol; 67%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (s, 9H), 2.13 (d, 1H, J = 3.2 Hz), 4.73 (d, 1H, J = 3.2 Hz), 7.18 (s, 1H), 7.28-7.36 (m, 2H), 7.73 (d, 1H, J = 7.6 Hz), 7.81 (d, 1H, J = 8.0 Hz); MS (EI) m/z 220 $[M]^+$.

2-Neopentylbenzo[*b*]thiophene (7)

To a CH_2Cl_2 solution (40 mL) containing **6** (4.0 g, 18 mmol) was slowly added triethylsilane (4.0 mL, 25 mmol) at 0 °C and the mixture was stirred for 25 min at 10 °C. After cooled down to 0 °C again, trifluoroacetic acid (4.0 mL, 52 mmol) was slowly added. The mixture was stirred for 17 h at room temperature. The resulting mixture was extracted with hexane and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. Recrystallization from methanol afforded **7** as white solids (3.2 g, 16 mmol; 86%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.02 (s, 9H), 2.77 (s, 2H), 6.98 (s, 1H), 7.24-7.33 (m, 2H), 7.69 (d, 1H, J = 7.6 Hz), 7.76 (d, 1H, J = 8.0 Hz); MS (EI) m/z 204 $[M]^+$.

3-Bromo-2-neopentylbenzo[*b*]thiophene (8)

To a THF solution (80 mL) containing **7** (4.5 g, 22 mmol) was added *N*-bromosuccinimide (4.3 g, 24 mmol) in several portions at 0 °C and the mixture was stirred for 18 h at room temperature. The resulting mixture was treated with $NaHCO_3$ aqueous solution followed by $Na_2S_2O_3$ aqueous solution and extracted with hexane. The organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane) to give **8** as a colourless oil (6.1 g, 22 mmol; 98%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.90 (s, 2H), 7.34 (t, 1H, J = 7.6 Hz), 7.42 (t, 1H, J = 7.6 Hz), 7.73-7.78 (m, 2H); MS (EI) m/z 284 $[M+2]^+$, 282 $[M]^+$.

2-Neopentyl-3-(perfluorocyclopent-1-en-1-yl)benzo[*b*]thiophene (9)

To a dry THF solution (25 mL) containing **8** (1.7 g, 6.0 mmol) was slowly added 1.6 M *n*-BuLi hexane solution (3.8 mL, 6.1 mmol) at –78 °C under a nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. Octafluorocyclopentene (2.4 mL, 18 mmol) was added in one portion at –78 °C. The mixture was stirred for 1 h at –78 °C and then stirred for 18 h at room temperature. The reaction was quenched by adding water. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane). Recrystallization from methanol afforded **9** as white solids (1.5 g, 3.8 mmol; 63%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.02 (s, 9H), 2.77 (s (br), 2H), 7.35-7.43 (m, 3H), 7.81 (d, 1H, J = 8.4 Hz); MS (EI) m/z 396 $[M]^+$.

2-(3-(3,3,4,4,5,5-Hexafluoro-2-(2-neopentylbenzo[*b*]thiophen-3-yl)cyclopent-1-en-1-yl)-benzo[*b*]thiophen-2-yl)-1,3-dioxolane (11)

To a dry THF solution (60 mL) containing 2-(3-bromobenzo[*b*]thiophen-2-yl)-1,3-dioxolane[S6] (**10**) (2.8 g, 9.8 mmol) was slowly added 1.6 M *n*-BuLi hexane solution (6.2 mL, 9.9 mmol) at –78 °C under a nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. A dry THF solution (20 mL) containing **9** (4.2 g, 11 mmol) was slowly added at –78 °C and the mixture was stirred for 20 h at –50 °C. The reaction was quenched by adding water. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane) to give **11** as white solids (4.0 g, 6.9 mmol; 70%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.86 (s, 9H), 1.04 (s, 3.79H), 1.89 (d, 1H, J = 14.8 Hz), 2.54 (d, 0.42H, J = 14.8 Hz), 2.68 (d, 1H, J = 14.8 Hz), 2.81 (d, 0.42H, J = 14.8 Hz), 3.41 (q, 1H, J = 7.2 Hz), 3.73-3.78 (m, 1H), 3.86-3.94 (m, 2H), 3.99-4.04 (m, 0.42H), 4.07-4.13 (m, 0.42H), 4.16-4.25 (m, 0.84H), 5.45 (s, 1H), 6.03 (s, 0.42H),7.05 (t, 0.42H, J = 7.2 Hz), 7.22 (t, 0.42H, J = 7.2 Hz), 7.26 (t, 0.42H, J = 7.2 Hz), 7.33-7.48 (m, 5H), 7.65 (d, 0.42H, J = 8.4 Hz), 7.70 (d, 0.42H, J = 8.4 Hz), 7.76-7.84 (m, 4.4H); MS (EI) m/z 582 $[M]^+$.

3-(3,3,4,4,5,5-Hexafluoro-2-(2-neopentylbenzo[*b*]thiophen-3-yl)cyclopent-1-en-1-yl)-benzo[*b*]thiophene-2-carbaldehyde (12)

To an acetone/water (v/v 9 : 1) solution (100 mL) containing **11** (3.9 g, 6.7 mmol) was added *p*-toluene sulfonic acid monohydrate (15.5 g, 81.5 mmol) and the mixture was stirred for 24 h at 60 °C. After the solvent was removed by evaporation, the resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 5 : 1) to give **12** as orange powders (3.5 g, 6.5 mmol; 97%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.91 (s, 9H), 1.01 (s, 6.27H), 1.99 (d, 1H, J = 14.8 Hz), 2.37 (d, 0.68H, J = 14.8 Hz), 2.71 (d, 1H, J = 14.8 Hz), 2.73 (d, 0.68H, J = 14.8 Hz), 7.18 (t, 0.76H, J = 7.2 Hz), 7.29 (t, 0.68H, J = 7.2 Hz), 7.34-7.46 (m, 3.31H), 7.54-7.68 (m, 4.21H), 7.74 (d, 1H, J = 8.4 Hz), 7.79 (d, 1.38H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.0 Hz), 7.95 (d, 1H, J = 8.4 Hz), 9.85 (s, 1H), 10.13 (s, 0.64H); MS (EI) m/z 538 $[M]^+$.

1-(3-(3,3,4,4,5,5-Hexafluoro-2-(2-neopentylbenzo[*b*]thiophen-3-yl)cyclopent-1-en-1-yl)-benzo[*b*]thiophen-2-yl)-2,2-dimethylpropan-1-ol (13)

To a cyclopentyl methyl ether solution (60 mL) containing **12** (1.3 g, 2.4 mmol) was slowly added 1.0 M *t*-BuMgCl THF solution (9.3 mL, 9.3 mmol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 21 h at room temperature. The reaction was quenched by adding dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 95 : 5) to give **13** as pale brown solids (1.1 g, 1.8 mmol; 76%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.80 (s, 9H), 0.85 (s, 9H), 1.61 (d, 2H J = 14.8 Hz), 2.49 (d, 2H, J = 14.8 Hz), 4.21 (d, 1H, J = 4.8 Hz), 7.35-7.48 (m, 4H), 7.76-7.84 (m, 4H); MS (EI) m/z 596 $[M]^+$, 595 $[M-H]^+$.

1,2-Bis(2-neopentylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene (14)

To a CH_2Cl_2 solution (25 mL) containing **13** (0.41 g, 0.69 mmol) was slowly added triethylsilane (0.44 mL, 2.8 mmol) at 0 °C and the mixture was stirred for 1 h at 10 °C. After cooled down to 0 °C again, trifluoroacetic acid (0.44 mL, 5.7 mmol) was slowly added and the mixture was stirred for 5 min at 0 °C. After that, the mixture was stirred for 12 h at room temperature. The resulting mixture was extracted with hexane and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 97 : 3) to give **14** as white solids (0.31 g, 0.53 mmol; 78%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.81 (s, 18H), 1.07 (s, 2.88H), 1.72 (d, 2H, *J* = 15.2 Hz), 2.52 (d, 0.32H, *J* = 14.4 Hz), 2.57 (d, 2H, *J* = 15.2 Hz), 2.94 (d, 0.32H, *J* = 14.4 Hz), 7.09-7.16 (m, 0.64H), 7.33 (t, 2H, *J* = 7.2 Hz), 7.38 (t, 2H, *J* = 7.2 Hz), 7.51 (d, 0.32H, *J* = 7.2 Hz), 7.56 (d, 0.32H, *J* = 7.2 Hz), 7.73 (d, 2H, *J* = 7.2 Hz), 7.78 (d, 2H, *J* = 7.2 Hz); MS (EI) *m*/*z* 580 $[M]^+$.

1,2-Bis(2-neopentylbenzo[*b*]thiophen-1,1-dioxide-3-yl)perfluorocycropentene (15)

To an acetic acid solution (20 mL) containing **14** (0.40 g, 0.69 mmol) was slowly added 2.8 mL of 30–35.5% hydrogen peroxide solution 120 °C. The mixture was heated at the same temperature for 30 min. The resulting mixture was poured into cold ice water, and precipitates were filtered and washed with water to give **15** as white solids (0.34 g, 0.53 mmol; 77%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.94 (s, 18H), 1.15 (s, 9H), 1.92 (d, 2H, *J* = 14.8 Hz), 2.08 (d, 2H, *J* = 14.8 Hz), 2.34 (d, 1H, *J* = 14.8 Hz), 2.61 (d, 1H, *J* = 14.8 Hz), 7.04 (d, 1H, *J* = 7.2 Hz), 7.30-7.35 (m, 3H), 7.42 (t, 1H, *J* = 7.6 Hz), 7.60-7.67 (m, 5H), 7.79 (m, 2H); MS (EI) *m*/*z* 644 $[M]^+$.

1,2-Bis(6-iodo-2-neopentylbenzo[*b*]thiophen-1,1-dioxide-3-yl)perfluorocycropentene (16)

A concentrated sulfuric acid solution (8 mL) containing **15** (0.15 g, 0.23 mmol) was cooled to 0 °C, and the mixture was stirred. Orthoperiodic acid (0.090 g, 0.40 mmol) and iodine (0.20 g, 0.79 mmol) were added to the solution, and the mixture was stirred at 0 °C for 4 h. The resulting mixture was poured into cold ice water. The mixture was extracted with $CHCl_3$ and the organic layer was washed with $NaHCO_3$ aqueous solution, $Na_2S_2O_3$ aqueous solution and brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **16** as yellow solids (0.12 g, 0.13 mmol; 57%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.96 (s, 18H), 1.15 (s, 9H), 1.97 (d, 2H, *J* = 15.2 Hz), 2.04 (d, 2H, *J* = 15.2 Hz), 2.31 (d, 1H, *J* = 14.8 Hz), 2.58 (d, 1H, *J* = 14.8 Hz), 6.69 (d, 1H, *J* = 8.0 Hz), 7,01 (dd, 2H, *J* = 8.0, 2.0 Hz), 7.66 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.95 (d, 2H, *J* = 1.2 Hz), 7.93 (d, 1H, *J* = 1.2 Hz), 8.08 (d, 2H, *J* = 1.6 Hz); MS (EI) *m*/*z* 896 $[M]^+$.

1,2-Bis(6-(5-methylthiophen-2-yl)-2-neopentylbenzo[*b*]thiophen-1,1-dioxide-3-yl)perfluoro-fluorocycropentene (3a)

To a THF solution (10 mL) containing **16** (0.19 g, 0.21 mmol) and 5-methylthiophen-2-yl boronic acid (0.080 g, 0.56 mmol) were added saturated K_2CO_3 aqueous solution (10 mL). The oxygen dissolved in the mixture was removed by nitrogen-gas bubbling for 20 min. After that, bis(dibenzylideneacetone)palladium(0) (0.024 g, 0.042 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) (0.017 g, 0.041 mmol) were added, and the mixture was refluxed for 30 min. The resulting mixture was neutralized with dilute hydrochloric acid and extracted with $CHCl_3$, and the organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9 : 1) to give **3a** as orange solids (0.048 g, 0.057 mmol; 27%). The obtained product was further purified by preparative HPLC (pump: Hitachi L-2130, detector: Hitachi L-2420 (313 nm), column: Wakosil® 5SIL (ϕ20 mm × 250 mm), hexane : ethyl acetate = 85 : 15, 5 mL min^{-1}). The purity was confirmed by analytical HPLC (pump: Hitachi L-2130, detector: Hitachi L-2420 (313 nm), column: Wakosil® 5SIL (ϕ4.6 mm × 250 mm), hexane : ethyl acetate = 85 : 15, 1 mL min^{-1}), as shown in Fig. S6.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.96 (s, 18H), 1.16 (s, 8.3H), 1.98 (d, 2H, *J* = 14.8 Hz), 2.10 (d, 2H, *J* = 14.8 Hz), 2.34 (d, 0.91H, *J* = 14.8 Hz), 2.49 (s, 2.71H), 2.54 (s, 6H), 2.62 (d, 0.91H, *J* = 14.8 Hz), 6.75 (m, 0.93H), 6.83 (m, 2H), 7.00 (d, 0.93H, *J* = 8.4 Hz), 7.16 (d, 0.91H, *J* = 3.6 Hz), 7.28-7.30 (m, 4H), 7.45 (dd, 0.93 H, *J* = 8.4, 1.2 Hz), 7.75 (dd, 2.82 H, *J* = 8.4, 1.2 Hz), 7.95 (d, 2H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 15.66, 15.72, 30.21, 30.40, 32.81, 32.85, 40.54, 41.32, 118.83, 119.10, 124.78, 124.87, 124.94, 125.05, 125.87, 126.02, 127.27, 127.32, 127.46, 127.49, 129.41, 129.99, 136.95, 137.05, 138.13, 138.29, 138.81, 138.84, 143.12, 143.32, 146.95, 147.22; MS (EI) *m*/*z* 836 $[M]^+$; HRMS (ESI, positive) *m*/*z* calcd for $C_{41}H_{38}F_6O_4S_4Na$ $[M+Na]^+$ 859.1455, found 859.1442; Mp 222–223 °C.

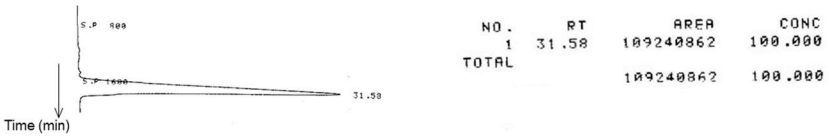


Fig. S6 HPLC chromatogram of **3a**.

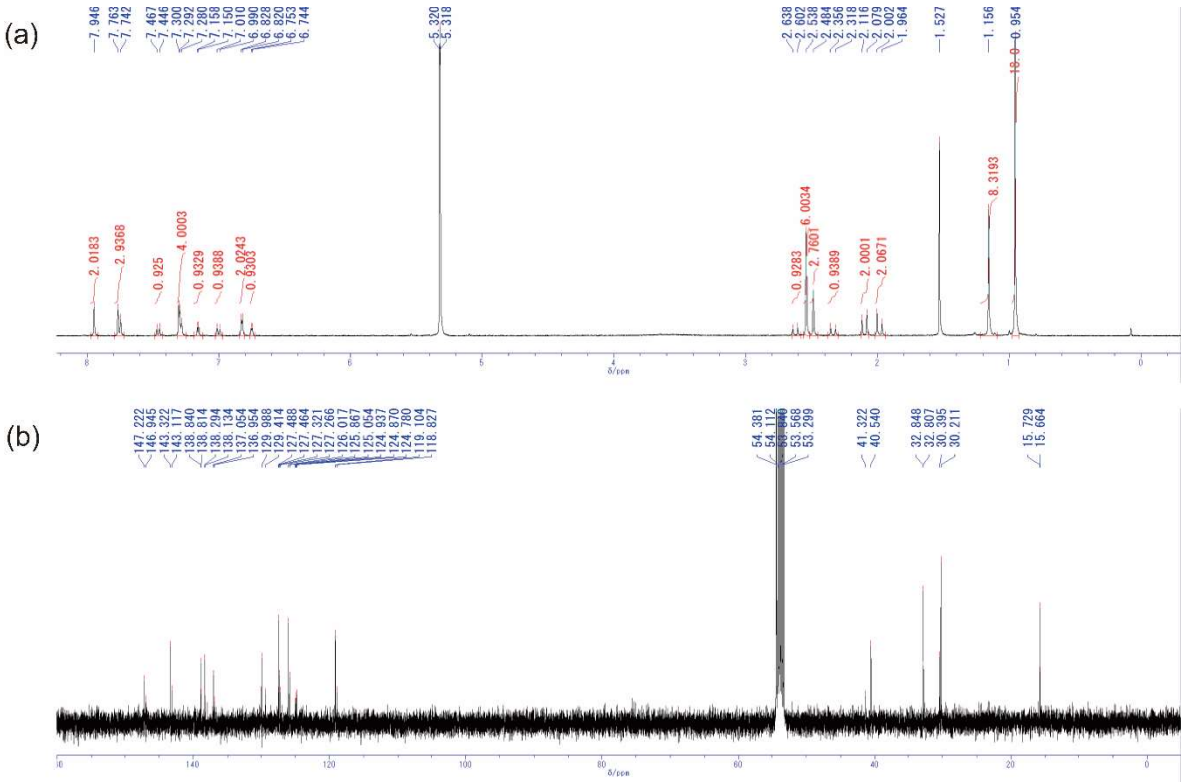


Fig. S7 400 MHz ^{1}H NMR (a) and 100 MHz ^{13}C NMR (b) spectra of **3a** in CD_2Cl_2.

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