Supporting Information for

Impact of dihedral angle in aryl group on photocyclization reactivity of inverse-type diarylethenes

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Experimental

General

Commercially available reagents were used as they were for synthesis. Solvents used for spectroscopy were of spectroscopic grade or purified by distillation before use. High-performance liquid chromatography (HPLC) was carried out using a Hitachi L-7150/L-2400 HPLC system equipped with a Kanto Chemical Mightysil Si 60 Column. ^{1}H NMR (300 MHz) spectra and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were measured on a JEOL AccTOF LC mass spectrometer. UV-Vis absorption spectra were recorded using a JASCO V-560 absorption spectrometer. Photoirradiation to solution was conducted using a 200 W mercury-xenon lamp (Moritex MUV-202) as the light source. Monochromatic light at 365 nm was obtained by passing the light through a JOBIN YVON H10-UV monochromator and glass filters. The solution samples were not degassed. Density functional theory (DFT) calculations (geometry optimizations and frequency calculations) of open-ring and closed-ring isomers were performed using Gaussian16 Rev.C.01 program package. The frequency calculations were carried out to confirm that there is no imaginary frequencies. The B3LYP functional in combination with a 6-31G(d) basis set was used for the calculations. Single crystal X-ray crystallographic analysis was carried out using a Rigaku AFC/Mercury CCD diffractometer or Rigaku VariMax diffractometer with MoKα radiation (λ = 0.71073 Å), and a Rigaku XtaLAB Synergy-S diffractometer with CuKα radiation (λ =1.54184 Å). The crystal structures were solved by a direct method using SIR92 and refined by the full matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-2014. The face indices of the crystals were determined by powder X-ray diffraction (PXRD) measurement using a Rigaku MiniFlex 600

diffractometer employing CuKα radiation (λ = 1.54184 Å). The polarized absorption spectra were measured using a Nikon ECLIPSE E600POL polarizing optical microscope equipped with a Hamamatsu PMA-11 photonic multi-channel analyzer as the photodetector. Photoirradiation to crystal was carried out using a super high-pressure mercury lamp (100 W; UV-1A filter (365-nm light)) attached with the polarizing optical microscope.

Materials

1o was synthesized according to the procedures described in the previous work.[S1] **2o**–**7o** were also synthesized according to a similar procedure. The detailed procedures are described in the synthesis section below. All compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry.

Transient absorption spectroscopy

Two different setups were used. Transient absorption measurements of **6o** was performed using a home-built setup based on a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire, 802 nm, 100 fs, 1 kHz, 1 W). This instrument affords to measure transient spectra until 1000 nm but time delay is limited to 1 ns. The fundamental output was split into two portions and respectively introduced into a pair of optical parametric amplifiers (Light Conversion, TOPAS, OPAs) for wavelength conversion. One was converted to a visible pulse at 700 nm and further frequency-doubled with a beta-barium borate crystal. The thus-generated second harmonics at 350 nm was used for photoexcitation of the sample. The excitation power and spot size were respectively 120

nJ and 130 μm FWHM. The wavelength of the other OPA was tuned to 1180 nm and this near-infrared pulse was focused into a CaF_2 window for generation of white light continuum. The resultant probe pulse was divided into signal and reference pulses. The signal pulse was detected after passing through the sample while the reference pulse was directly detected with multichannel photodiodes (Hamamatsu, PMA-10). The relative polarization of the excitation and probe pulses was set to the magic angle with respect to each other with a Berek compensator. The time delay between the excitation and probe pulses was controlled with an optical delay stage. The chirping of the probe pulse was corrected on the basis of an optical Kerr effect of carbon tetrachloride. The temporal resolution was evaluated as < 200 fs, which is dependent on the observation wavelengths. The sample solution was filled into a rotation cell with an optical length of 2 mm. So as to keep high concentration of the open-ring isomer during the measurements, absorbance of the sample was set to as high as 3 at the excitation wavelength of 350 nm and continuous wave (CW) visible light from a xenon lamp was irradiated to the sample cell. Steady-state absorption spectra before and after the measurements detected no absorption band due to the closed-ring isomer, indicating that accumulation of the closed-ring isomer is negligible. The measurements were performed at 22.5 ℃.

Transient absorption spectra of **2o**, **3o**, **4o**, **5o**, and **6o** were measured in a similar manner using another setup (Ultrafast Systems, HELIOS) coupled with a Ti:sapphire amplifier (Coherent, Astrella, 800 nm, 40 fs, 1 kHz, 5 W). This instrument allows to measure time delay until 6 ns but with limited spectral range until 750 nm. The pump beam at 350 nm (200 nJ, 200 μm, 70 fs FWHM) is generated using an OPA (Coherent, OPerA Solo) and the probe beam used here is obtained by using CaF_2 windows. In this commercial setup, the samples were placed inside a flow Harrick cell (3 mL solution) combined with Micro annular gear pumps (HNP Mikrosysteme, 7255

model) with 1 mm CaF_2 windows and an internal thickness of 2 mm to refresh the probe volume between consecutive pump pulses. Due to cyclization conversion of the compounds by the pump pulse, samples were irradiated in an external reservoir with a CW LED (Thorlabs), at 480 nm. The measurements were performed at 22 ℃.

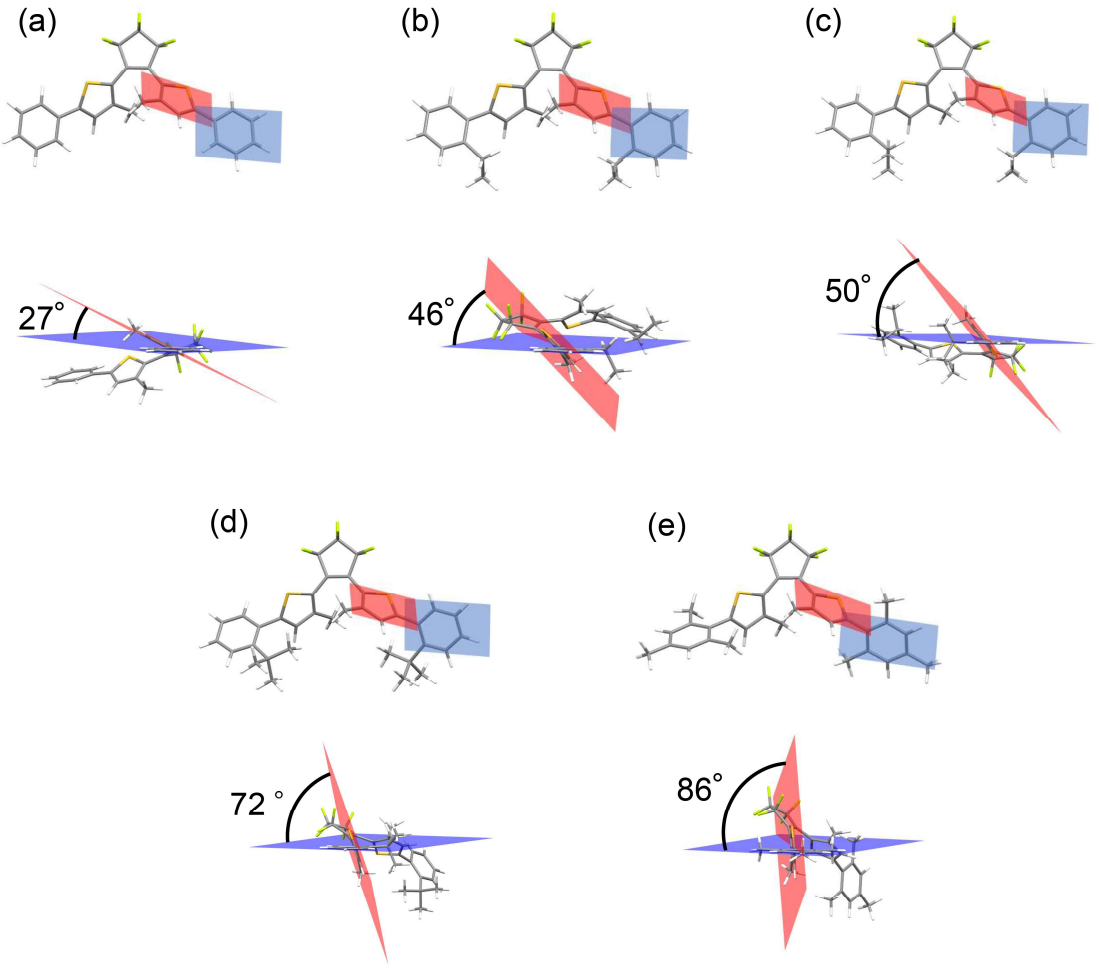


Figure S1. Optimized molecular structures and the dihedral angles in aryl groups of open-ring isomers in solution by DFT calculation for (a) **1o**, (b) **3o**, (c) **4o**, (d)**5o**, and (e) **6o**.

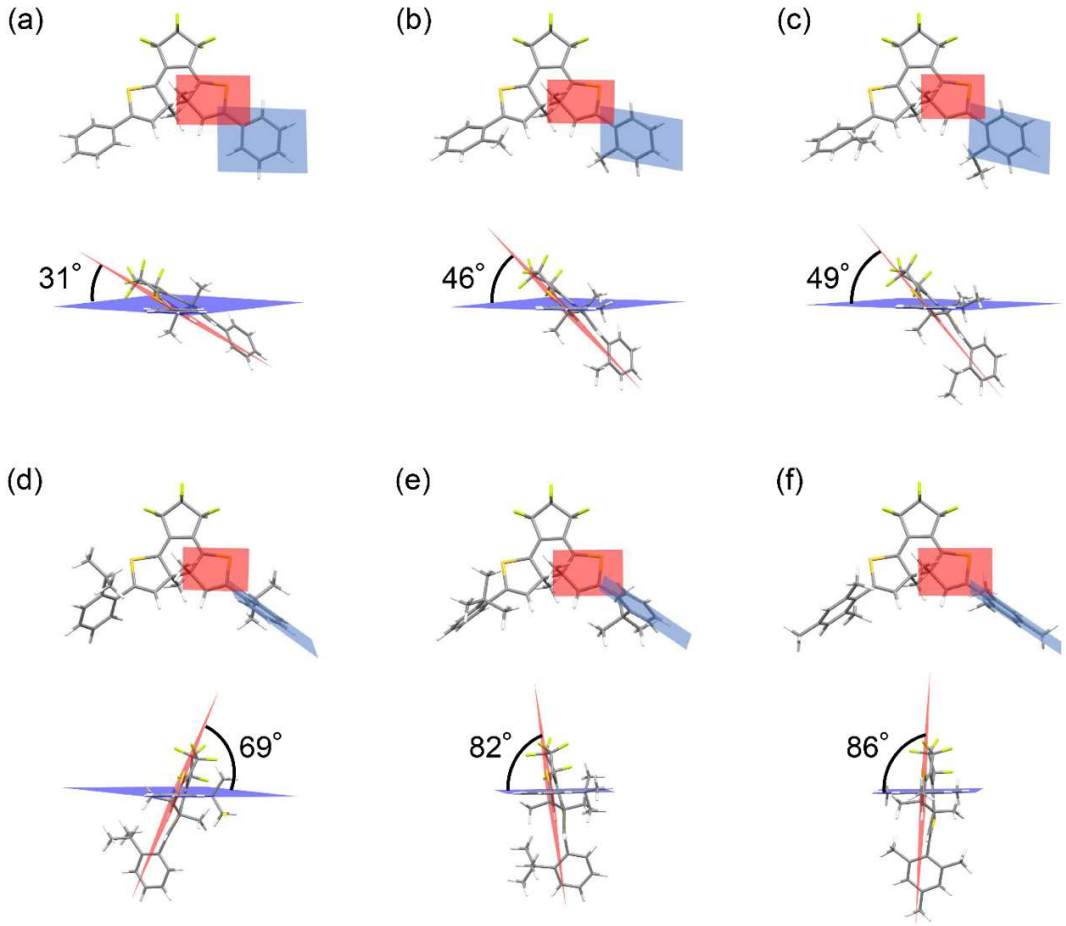


Figure S2. Optimized molecular structures and the dihedral angles in aryl groups of closed-ring isomers in solution by DFT calculation for (a) **1c**, (b) **2c**, (c) **3c**, (d) **4c**, (e) **5c**, and (f) **6c**.

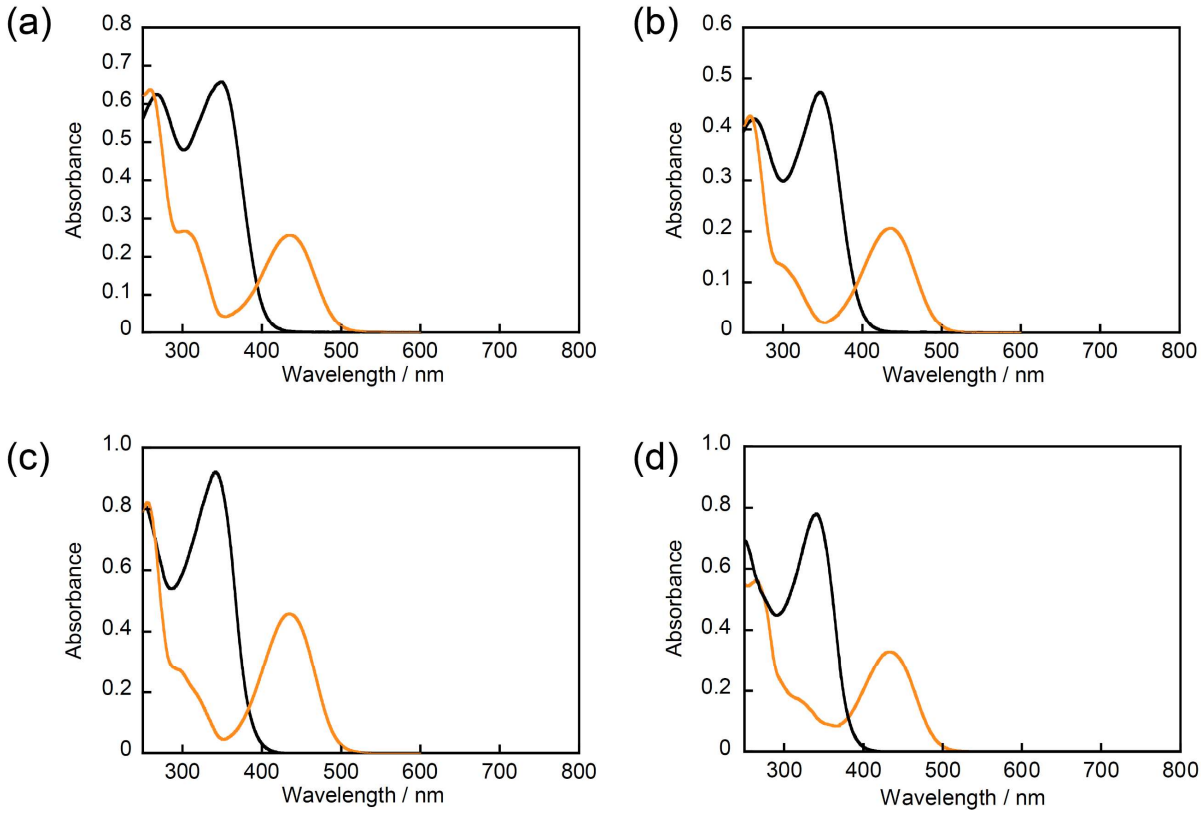


Figure S3. Absorption spectra of (a) **3** (3.8×10^{-5} mol L^{-1}), (b) **4** (3.2×10^{-5} mol L^{-1}), (c) **5** (6.2×10^{-5} mol L^{-1}), and (d) **6** (4.9×10^{-5} mol L^{-1}) in *n*-hexane: the open-ring isomer (black solid line) and the closed-ring isomer (orange solid line).

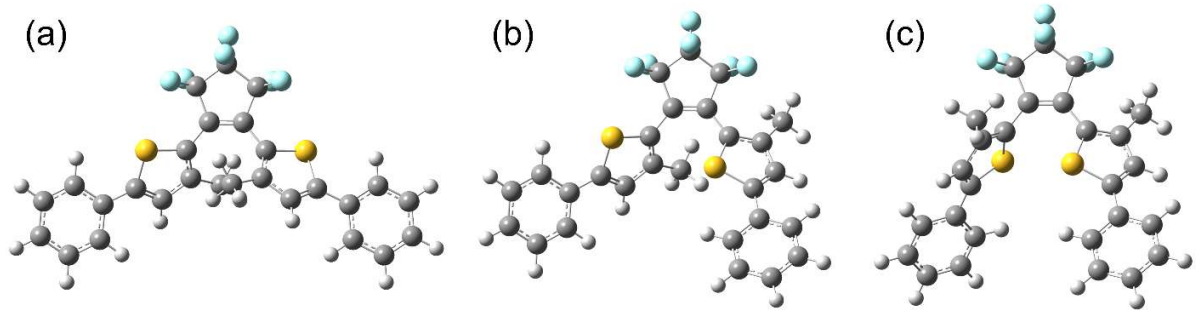


Figure S4. Molecular geometries of three different conformers of **1o**. (a) AP1, (b) P1, (c) AP2. The geometries were optimized in the ground state at the B3LYP level using the 6-31G(d) basis set.

Table S1. Relative population of different conformers (AP1, P1 AP2) of **1o**–**6o** in the ground state. Each population was calculated from the zero-point corrected total energies in thermal equilibrium under the Boltzmann distribution. Note that the relative population of the conformers (AP1 : P1 : AP2 = 63% : 31% : 6%) in **1o** is slightly deviated from that reported in our previous work (AP1 : P1 : AP2 = 46% : 46% : 8%)[S2], which is due to a more stable AP1 found in the geometrical optimization. A major structural difference is the dihedral angle between the thiophene and phenyl rings although both the structures show no imaginary frequency.

	1o	**2o**	**3o**	**4o**	**5o**	**6o**
AP1 / %	63	63	63	63	52	61
P1 / %	31	33	30	32	39	32
AP2 / %	6	4	7	5	9	7

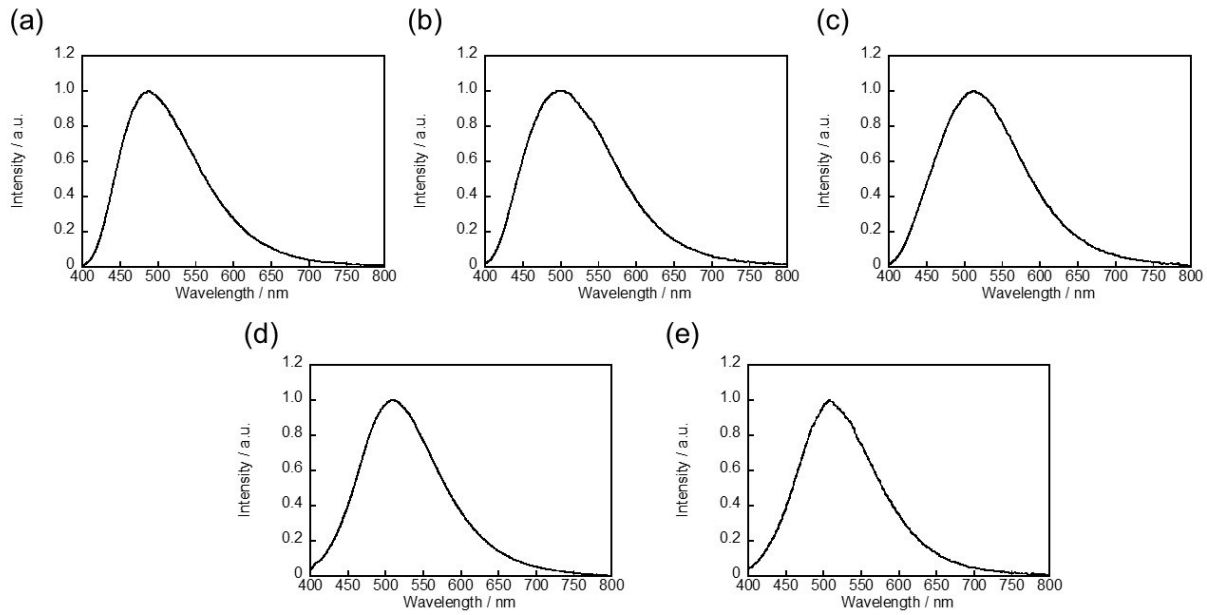


Figure S5. Fluorescence spectra of (a) **2**, (b) **3**, (c) **4**, (d) **5**, and (d) **6** in *n*-hexane upon excitation with 365 nm light.

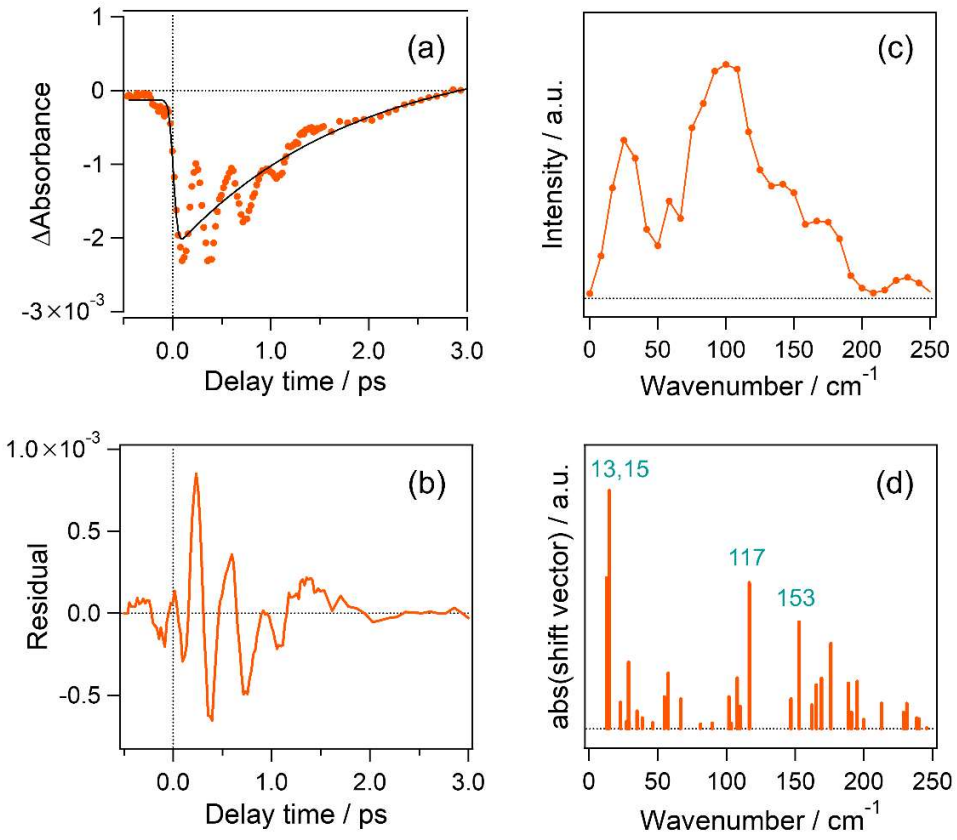


Figure S6. (a) Time profile of transient absorbance of **6o** in *n*-hexane monitored at 450 nm. (b) Oscillatory component extracted from curve fitting analysis. (c) Fourier transform (FT) power spectrum of the signal in the panel b. (d) absolute value of shift vector between the geometries optimized in the S_0 and S_1 states plotted as a function of vibrational frequencies. The vibrational modes at 13, 15, 117 and 153 cm^{-1} have larger intensity, which roughly reproduced with the FT power spectrum in the panel c. This result indicates that the nuclear displacement in these vibrational modes is parallel to structural difference between the S_0 and S_1 minima, leading to large Franck-Condon activity.

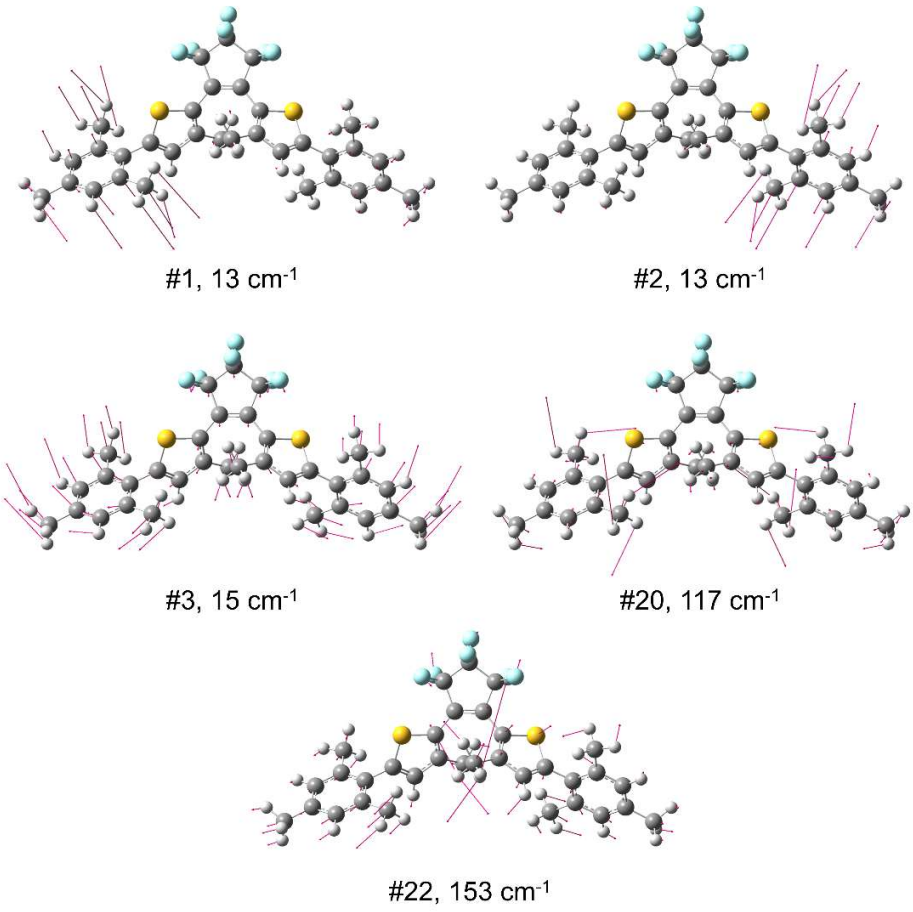


Figure S7. Nuclear displacement of **6o** in low-frequency modes contributing to the oscillatory signal in the transient absorption.

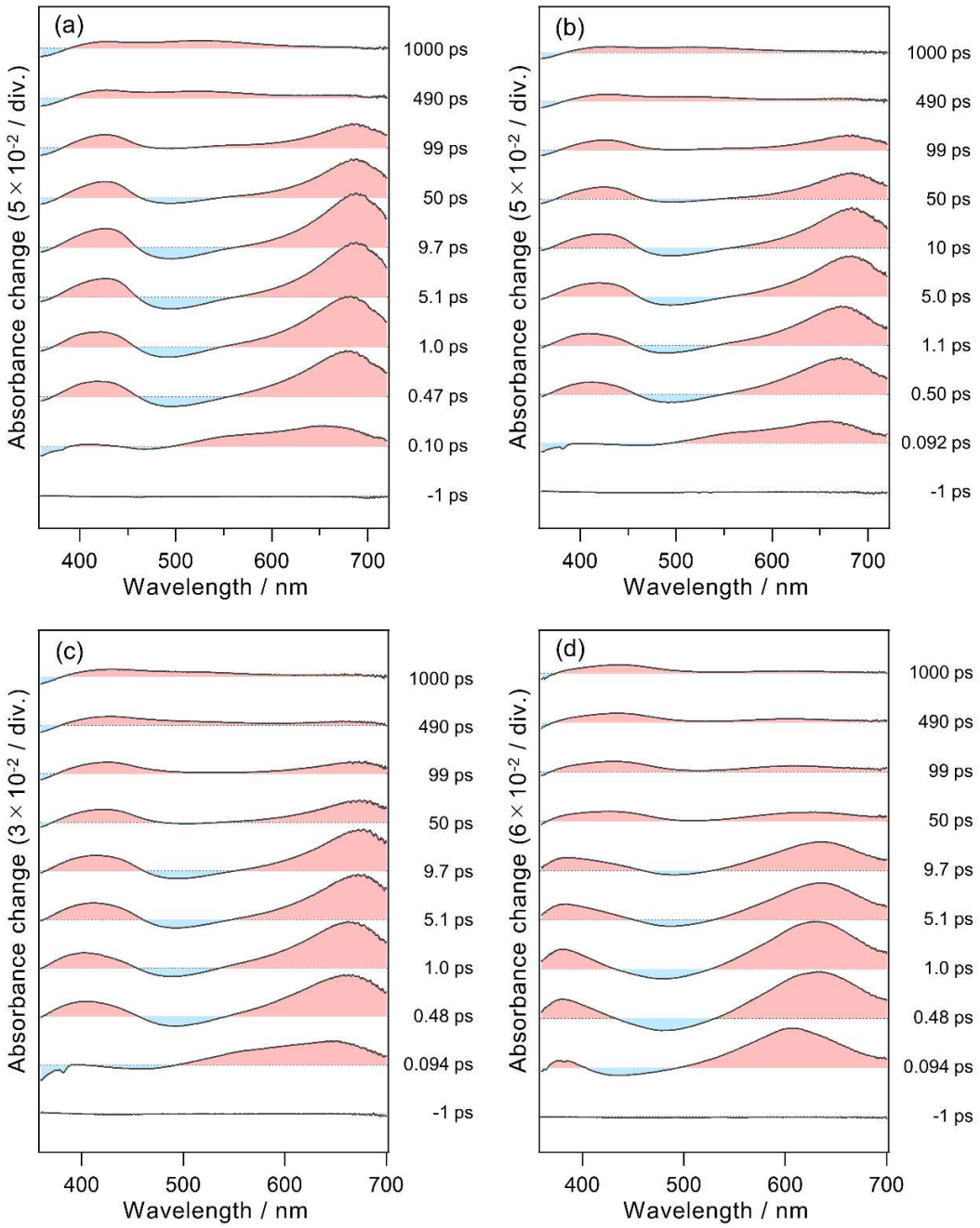


Figure S8. Transient absorption spectra of (a) **2o**, (b) **3o**, (c) **4o** and (d) **5o** in *n*-hexane excited with a femtosecond laser pulse at 350 nm.

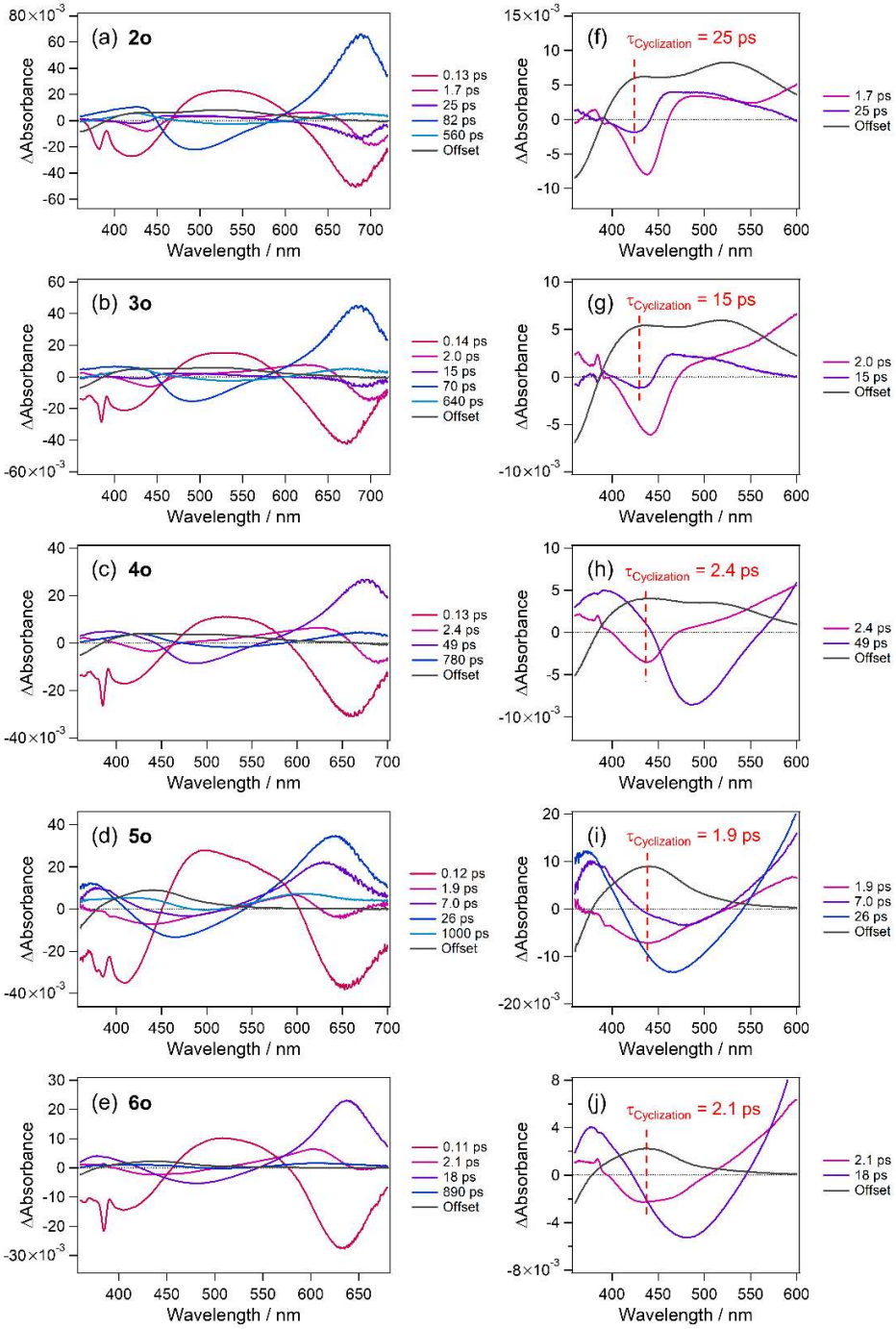


Figure S9. Decay-associated spectra (DAS) of (a) **2o**, (b) **3o**, (c) **4o**, (d) **5o** and (e) **6o** in *n*-hexane. (f-j) Enlarged views of the panels a, b, c, d and e. Global analysis of **2o**, **3o**, **4o**, **5o** and **6o** was

performed in the 6 ns time window. Accordingly, we obtained additional components with longer time constants, which are probably due to the excited state of unreactive conformers and resultant triplet state. The cyclization timescale of each derivative was obtained by precise comparison of DAS. In case of **2o** in the panel e, for example, a positive band around 425 nm in the offset component corresponds to the formation of the closed-ring isomer and this band is well correlated with a negative part of the 25 ps DAS, as denoted by a red dashed line. This spectral agreement supports that the time constant of 25 ps is ascribable to the cyclization reaction of **2o**. Similarly, the cyclization timescale was determined to be 15, 2.4, 1.9 ps and 2.1 ps for **3o**, **4o**, **5o** and **6o**, respectively. It should be noted that the second DAS of each compound with the time constant of ca. 2 ps has a common spectral pattern in 600-700 nm and is probably ascribable to the vibrational relaxation. Thus, the second DAS of **4o**, **5o** and **6o** includes contribution of not only the cyclization process but also the vibrational relaxation.

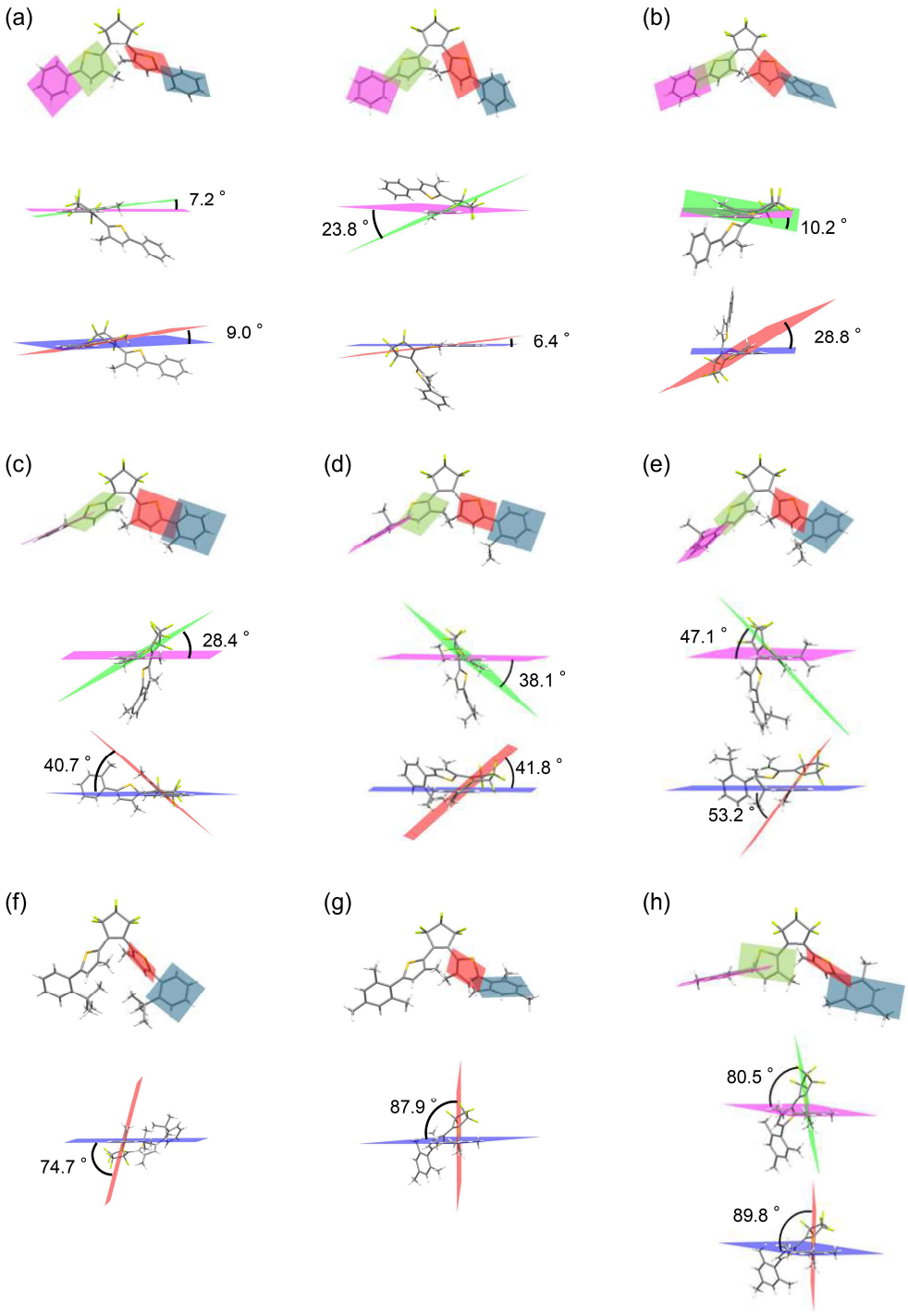


Figure S10. Molecular structure and the dihedral angles in aryl groups of crystal (a) **1o-α**, (b) **1o-β**, (c) **2o**, (d) **3o**, (e) **4o**, (f) **5o**, (g) **6o-α**, and (h) **6o-β** determined by X-ray crystallographic analysis.

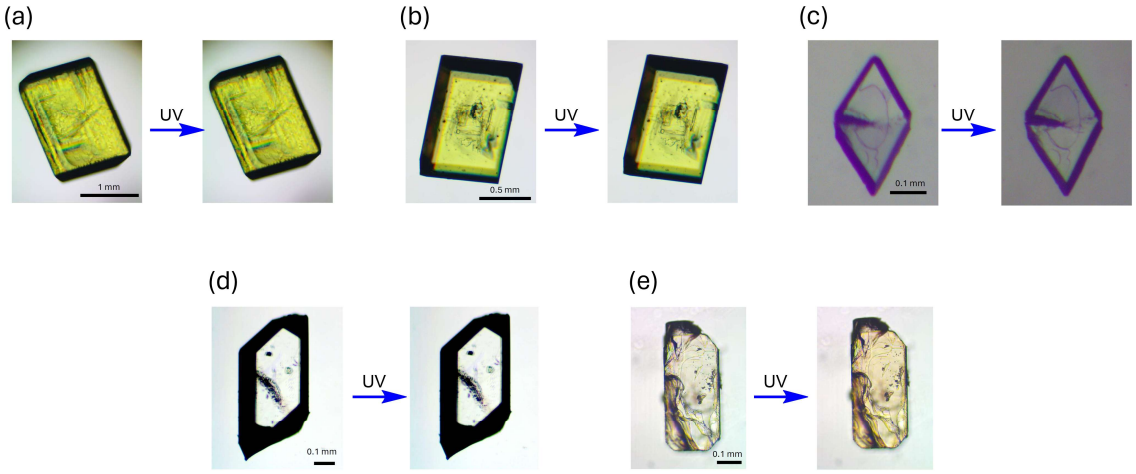


Figure S11. Optical microphotographs of crystal (a) **2o**, (b) **3o**, (c) **4o**, (d) **5o**, and (e) **6o-β** before and after upon irradiation with 365 nm light.

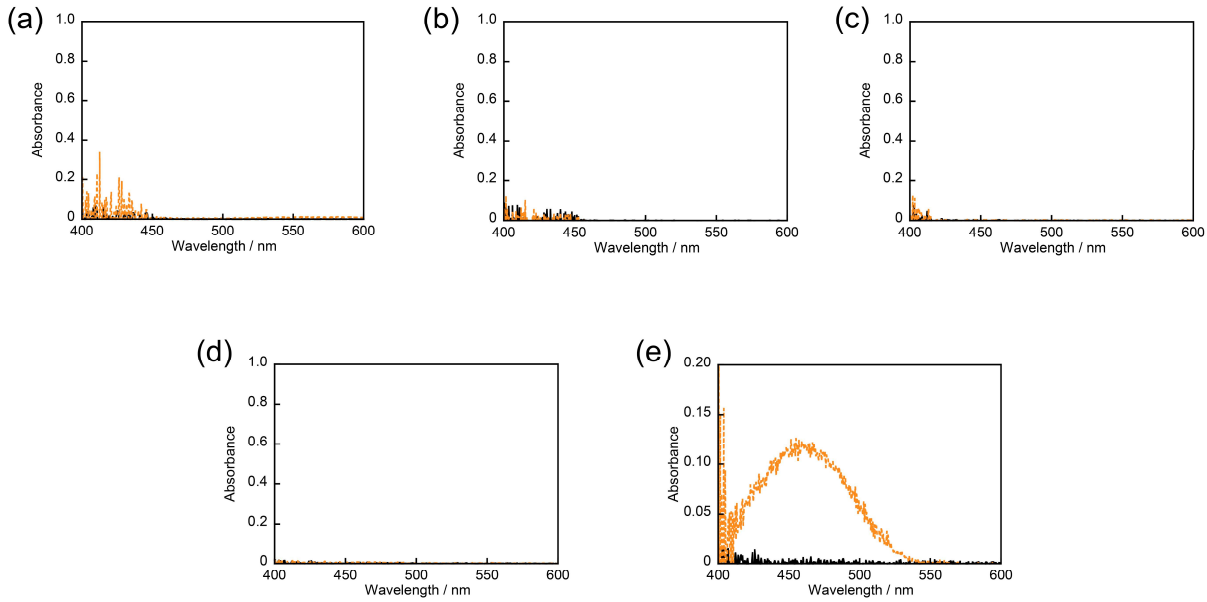


Figure S12. Absorption spectra of crystal (a) **2o**, (b) **3o**, (c) **4o**, (d) **5o**, and (e) **6o-β** before (black line) and after (orange line) upon irradiation with 365 nm light.

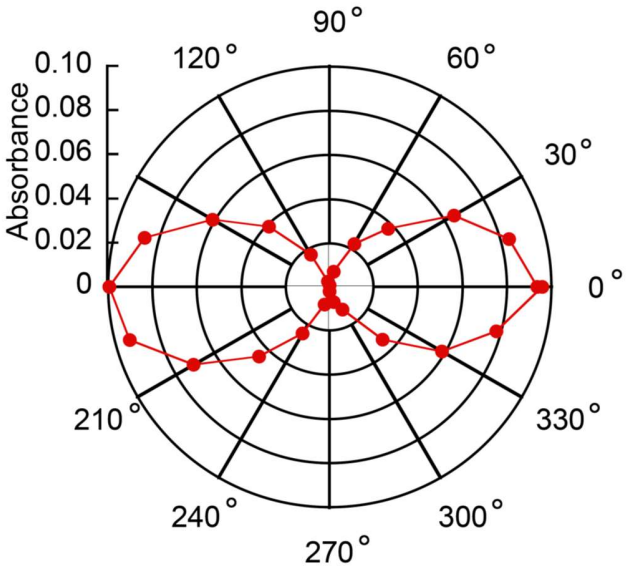


Figure S13. Polar plots of the polarized absorption spectra of crystal **6o-β** at 455 nm on the (001) face.

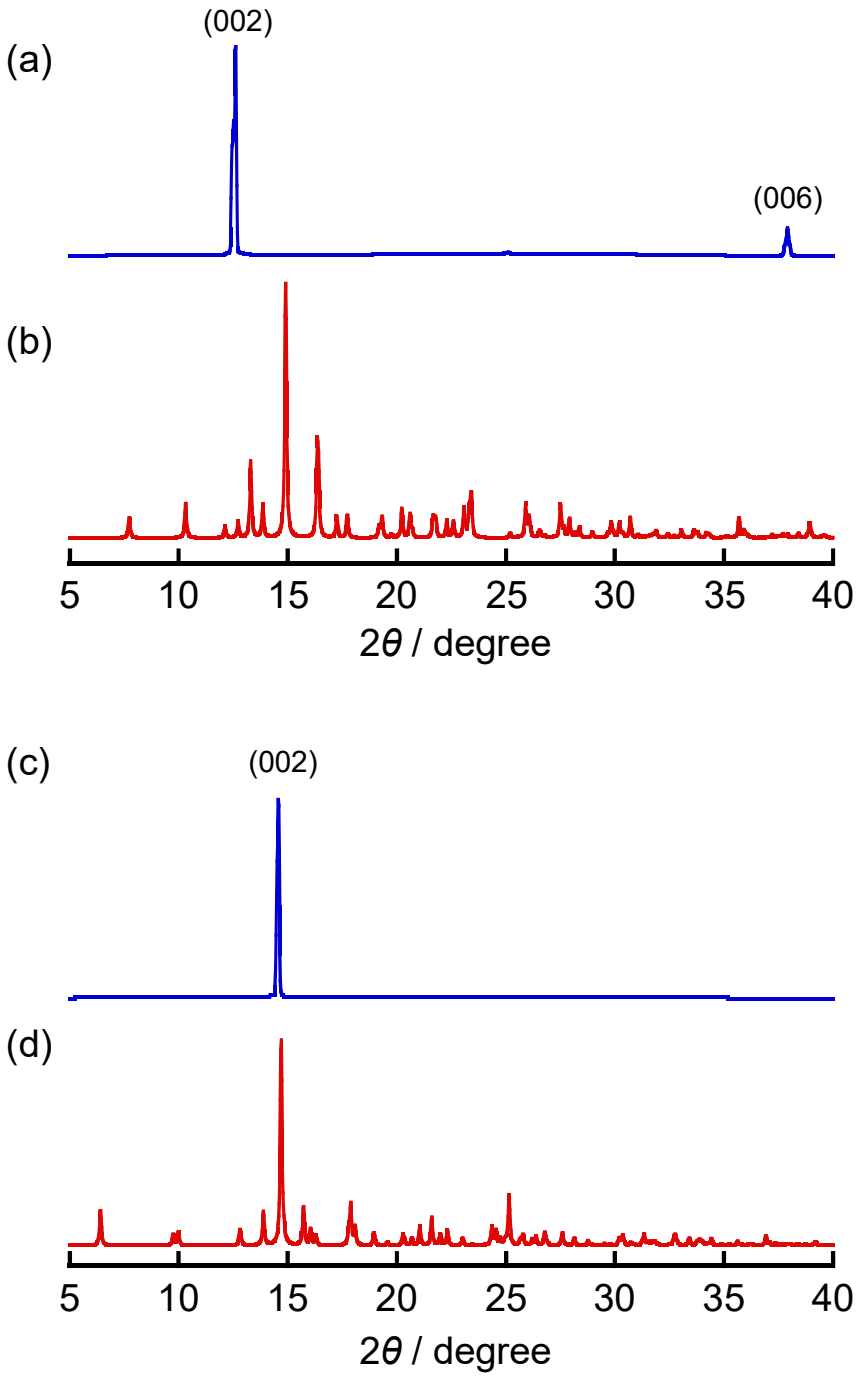


Figure S14. PXRD patterns of crystal (a) **6o-α** and (c) **6o-β**. The patterns calculated from single crystal X-ray crystallographic data of (b) **6o-α** and (d) **6o-β**.

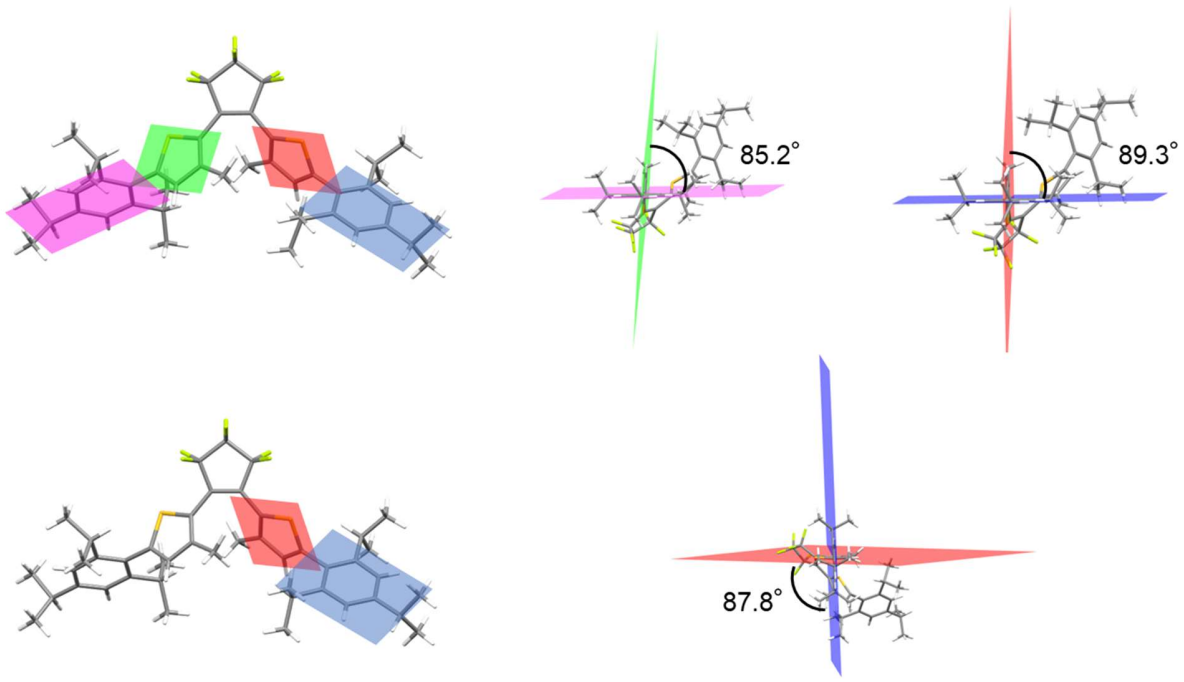


Figure S15. Molecular structure and the dihedral angles in aryl groups of crystal **7o** determined by X-ray crystallographic analysis.

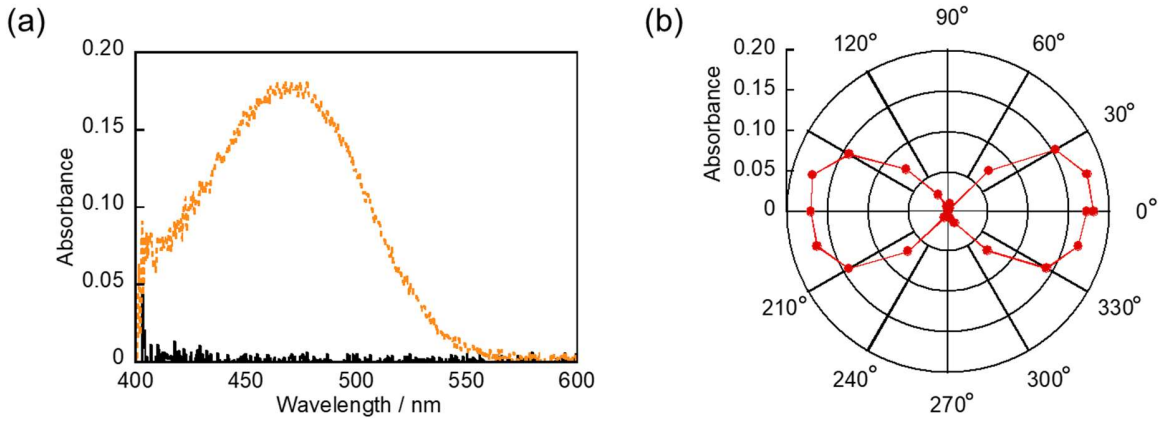


Figure S16. (a) Absorption spectra of crystal **7o** before and after UV irradiation, and (b) polar plots of the polarized absorption spectra of crystal **7o** at 470 nm on the (001) face.

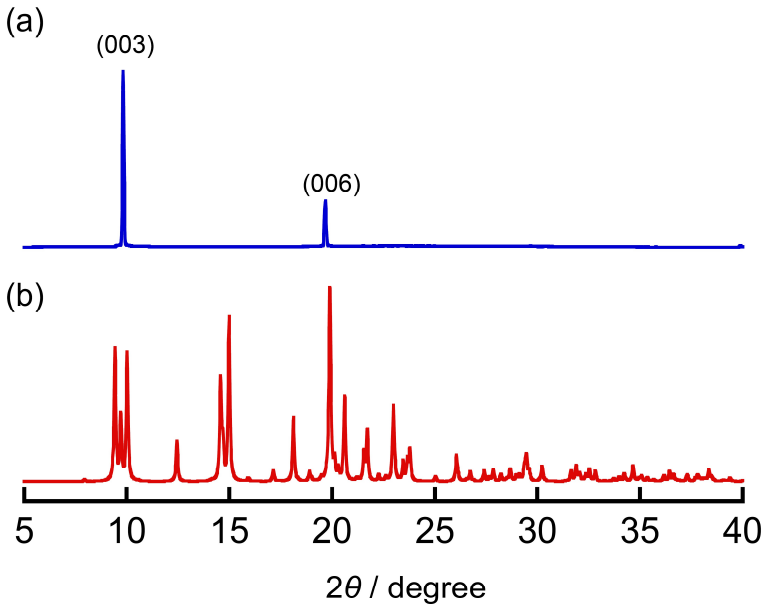


Figure S17. (a) PXRD pattern of crystal **7o** and the pattern calculated from single crystal X-ray crystallographic data of **7o**.

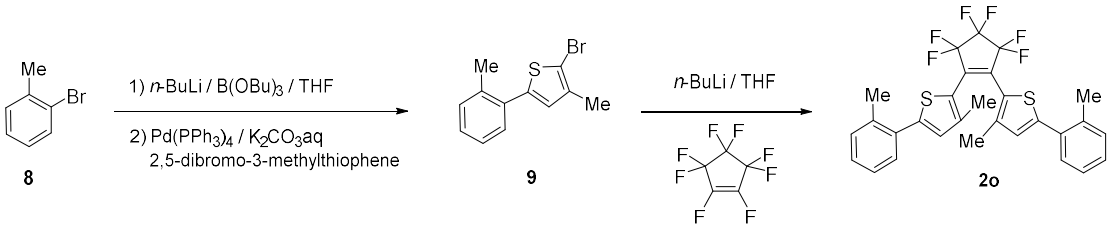
Table S2. X ray crystallographic data for **1o–7o**.

	1o-α[a]	**1o-β**[a]	**2o**	**3o**	**4o**	**5o**	**6o-α**	**6o-β**	**7o**
Formula	$C_{27}H_{18}F_6S_2$	$C_{30}H_{25}F_6S_2$	$C_{29}H_{22}F_6S_2$	$C_{31}H_{26}F_6S_2$	$C_{33}H_{30}F_6S_2$	$C_{35}H_{34}F_6S_2$	$C_{33}H_{30}F_6S_2$	$C_{33}H_{30}F_6S_2$	$C_{45}H_{54}F_6S_2$, C_3H_6O
Formula weight	520.53	563.62	548.59	576.64	604.69	632.74	604.69	604.69	831.08
Temperature/K	200(2)	200(2)	110(2)	110(2)	250(2)	100(2)	150(2)	150(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$Pbcn$	$Pca2_1$	$C2$
a/Å	17.8941(6)	8.7527(17)	8.794(4)	8.615(5)	11.4689(2)	20.544(7)	22.8674(15)	27.5476(7)	23.9547(5)
b/Å	16.9519(5)	12.902(3)	11.522(6)	12.566(7)	13.9131(3)	12.248(4)	9.2455(5)	8.8577(2)	10.3420(2)
c/Å	15.9772(5)	13.709(3)	13.183(6)	13.128(7)	18.9810(3)	15.448(5)	13.9064(9)	12.0476(3)	29.3845(7)
α/deg	90	110.982(2)	74.384(14)	72.681(14)	90	90	90	90	90
β/deg	102.933(2)	101.756(2)	83.177(15)	83.144(17)	91.3956(17)	126.469(3)	90	90	111.651(2)
γ/deg	90	101.9380(10)	78.470(14)	82.304(16)	90	90	90	90	90
Volume/Å^3	4723.6(3)	1347.2(5)	1257.4(11)	1339.9(13)	3027.86(10)	3126.0(17)	2940.1(3)	2939.72(12)	6766.1(3)
Z	8	2	2	2	4	4	4	4	6
Density/g cm^{-3}	1.464	1.389	1.449	1.429	1.326	1.344	1.366	1.366	1.224
Goodness-of-fit on F^2	1.166	1.055	0.978	0.919	1.047	1.054	1.109	1.033	1.057
R (I > 2σ(I))	R_1 = 0.0582	R_1 = 0.0528	R_1 = 0.0378	R_1 = 0.039	R_1 = 0.0521	R_1 = 0.0383	R_1 = 0.0465	R_1 = 0.0369	R_1 = 0.0548
R (all data)	$wR2$ =0.1490	$wR2$ =0.1425	$wR2$ =0.1016	$wR2$ =0.0916	$wR2$ =0.152	$wR2$ =0.0928	$wR2$ =0.1224	$wR2$ =0.0929	$wR2$ =0.1641
CCDC No.	1509478	1509479	2401652	2401653	2401654	2401655	2401656	2401657	2416015

[a]Ref. [S3]

Synthesis

*1,2-Bis(3-methyl-5-(2-methylphenyl)-2-thienyl)perfluorocyclopentene (**2o**)*



1-Bromo-2-methylbenzene (**8**) (2.5 g, 14 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (9.6 mL, 15 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1.5 h. Tri-*n*-butyl borate (4.1 mL, 15 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 2 h. An adequate amount of distilled water was added to the mixture to quench the reaction. 2,5-Dibromo-3-methylthiophene (3.7 g, 14 mmol), tetrakis(triphenylphosphine)palladium(0) (350 mg 0.30 mmol), and 20 wt% Na_2CO_3 aqueous solution (25 mL) were added to the solution, and the mixture was refluxed for 8 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear oil of mixture of 2-bromo-3-methyl-5-(2-methylphenyl)thiophene (**9**) and 2-bromo-4-methyl-5-(2-methylphenyl)thiophene (**9'**) (**9** : **9'** = 1 : 0.15) was obtained by column chromatography on silica gel using *n*-hexane as the eluent in 2.5 g. The mixture was used for the next reaction without further purification. The mixture (1.6 g, 6.0 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (4.0 mL, 6.3 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Octafluorocyclopentene (0.41 mL, 3.0 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 2 h. An

adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane as the eluent and recrystallization from *n*-hexane/ethanol to give 650 mg of **2o** in 39% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.87 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 6.83 (s, 2H, Thienyl H), 7.23-7.28 (m, 6H, Aromatic H), 7.37-7.40 (m, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.5, 21,3, 123.3, 126.2, 128.7, 130.2, 130.3, 131.1, 133.1,136.1, 141.3, 147.4. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{29}H_{23}F_6S_2^+$ = 549.1145; found, 549.1153.

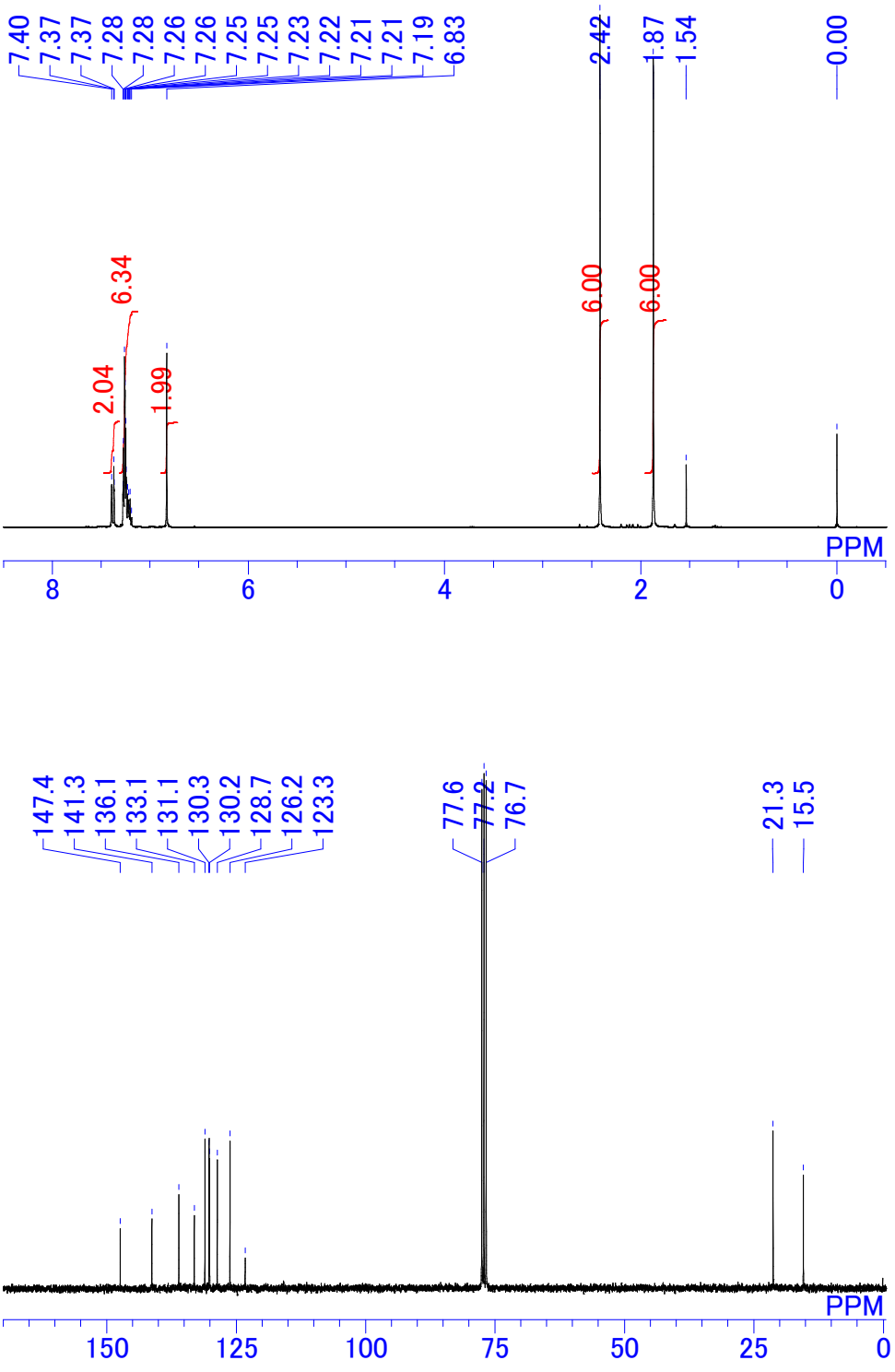
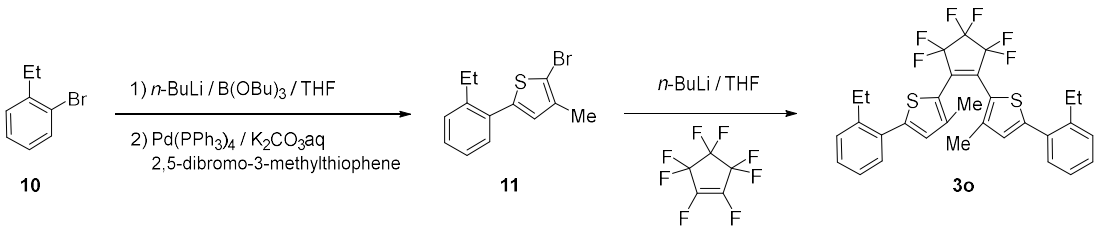


Figure S18. ^{1}H NMR and ^{13}C NMR spectra for **2o** in $CDCl_3$.

*1,2-Bis(3-methyl-5-(2-ethylphenyl)-2-thienyl)perfluorocyclopentene (**3o**)*



1-Bromo-2-ethylbenzene (**10**) (3.5 g, 19 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (13 mL, 20 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1.5 h. Tri-*n*-butyl borate (5.4 mL, 20 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 2 h. An adequate amount of distilled water was added to the mixture to quench the reaction. 2,5-Dibromo-3-methylthiophene (4.9 g, 19 mmol), tetrakis(triphenylphosphine)palladium(0) (350 mg 0.30 mmol), and 20 wt% Na_2CO_3 aqueous solution (25 mL) were added to the solution, and the mixture was refluxed for 6 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear oil of mixture of 2-bromo-3-methyl-5-(2-ethylphenyl)thiophene (**11**) and 2-bromo-4-methyl-5-(2-ethylphenyl)thiophene (**11'**) (**11** : **11'** = 1 : 0.13) was obtained by column chromatography on silica gel using *n*-hexane as the eluent in 3.5 g. The mixture was used for the next reaction without further purification. The mixture (1.8 g, 6.5 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (4.3 mL, 6.8 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Octafluorocyclopentene (0.44 mL, 3.2 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 2 h. An adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column

chromatography on silica gel using *n*-hexane as the eluent and recrystallization from *n*-hexane/ethanol to give 680 mg of **3o** in 37% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.16 (t, 6H, *J* = 7.6 Hz, CH_3), 1.89 (s, 6H, CH_3), 2.74(q, 4H, *J* = 7.6 Hz, CH_2), 6.80 (s, 2H, Thienyl H), 7.19-7.25 (m, 2H, Aromatic H), 7.28-7.35 (m, 6H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.5, 15.9, 26.8, 123.3, 126.0, 129.0, 129.3, 130.2, 130.8, 132.6, 141.2, 142.6, 147.3. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{31}H_{27}F_6S_2^+$ = 577.1458; found, 577.1462.

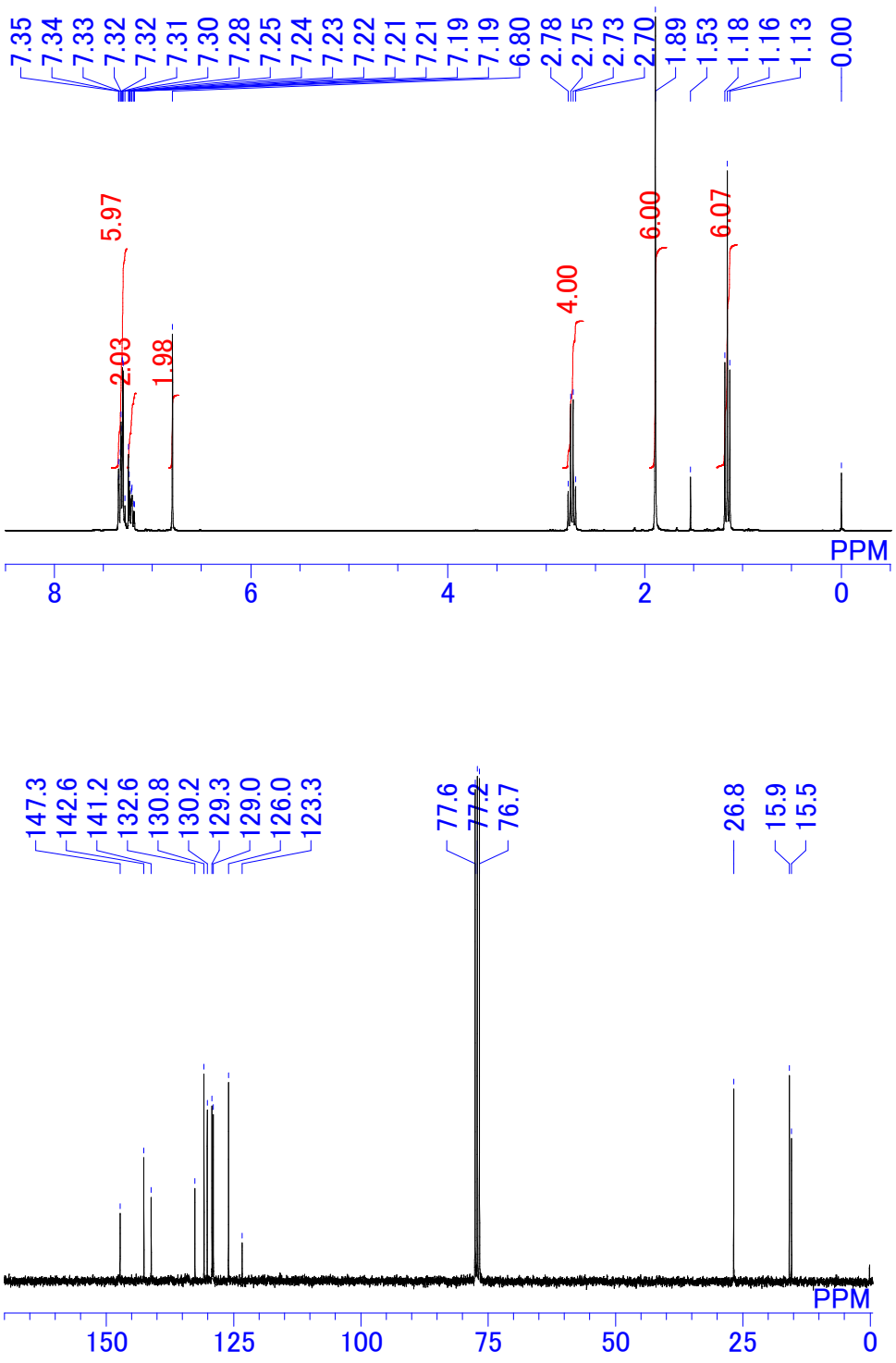
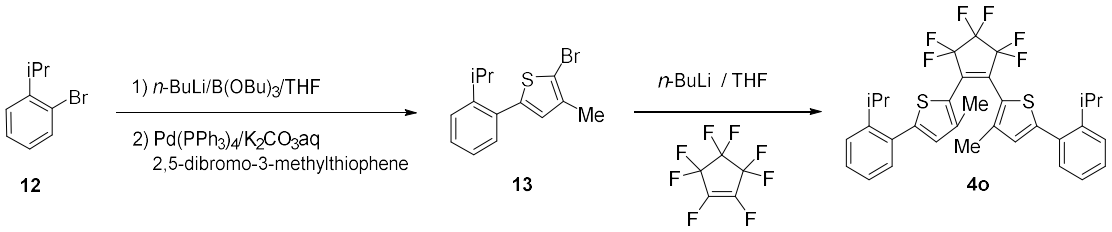


Figure S19. ^{1}H NMR and ^{13}C NMR spectra for **3o** in $CDCl_3$.

*1,2-Bis(3-methyl-5-(2-isopropylphenyl)-2-thienyl)perfluorocyclopentene (**4o**)*



1-Bromo-2-isopropylbenzene (**12**) (2.5 g, 13 mmol) was dissolved in anhydrous THF (20 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (8.2 mL, 13 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Tri-*n*-butyl borate (3.6 mL, 13 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 1 h. An adequate amount of distilled water was added to the mixture to quench the reaction. 2,5-Dibromo-3-methylthiophene (3.2 g, 13 mmol), tetrakis(triphenylphosphine)palladium(0) (220 mg 0.19 mmol), and 20 wt% Na_2CO_3 aqueous solution (15 mL) were added to the solution, and the mixture was refluxed for 6 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear oil of mixture of 2-bromo-3-methyl-5-(2-isopropylphenyl)thiophene (**13**) and 2-bromo-4-methyl-5-(2-isopropylphenyl)thiophene (**13'**) (**13** : **13'** = 1 : 0.19) was obtained by column chromatography on silica gel using *n*-hexane as the eluent in 1.5 g. The mixture was used for the next reaction without further purification. The mixture (1.4 g, 4.7 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (3.1 mL, 5.0 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 15 min. Octafluorocyclopentene (0.30 mL, 2.2 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 2 h. An adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in

vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane as the eluent and recrystallization from ethanol to give 550 mg of **4o** in 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.19 (d, 12H, J = 6.8 Hz, CH_3), 1.91 (s, 6H, CH_3), 3.23-3.27 (sep, 2H, CH), 6.76 (s, 2H, Thienyl H), 7.17-7.22 (m, 2H, Aromatic H), 7.27-7.30 (m, 2H, Aromatic H), 7.36-7.38 (m, 4H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.5, 24.4, 29.8, 123.4, 125.7, 126.0, 129.3, 130.4, 131.0, 132.1, 141.2, 147.4, 147.6. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{33}H_{31}F_6S_2^+$ = 605.1771; found, 605.1774.

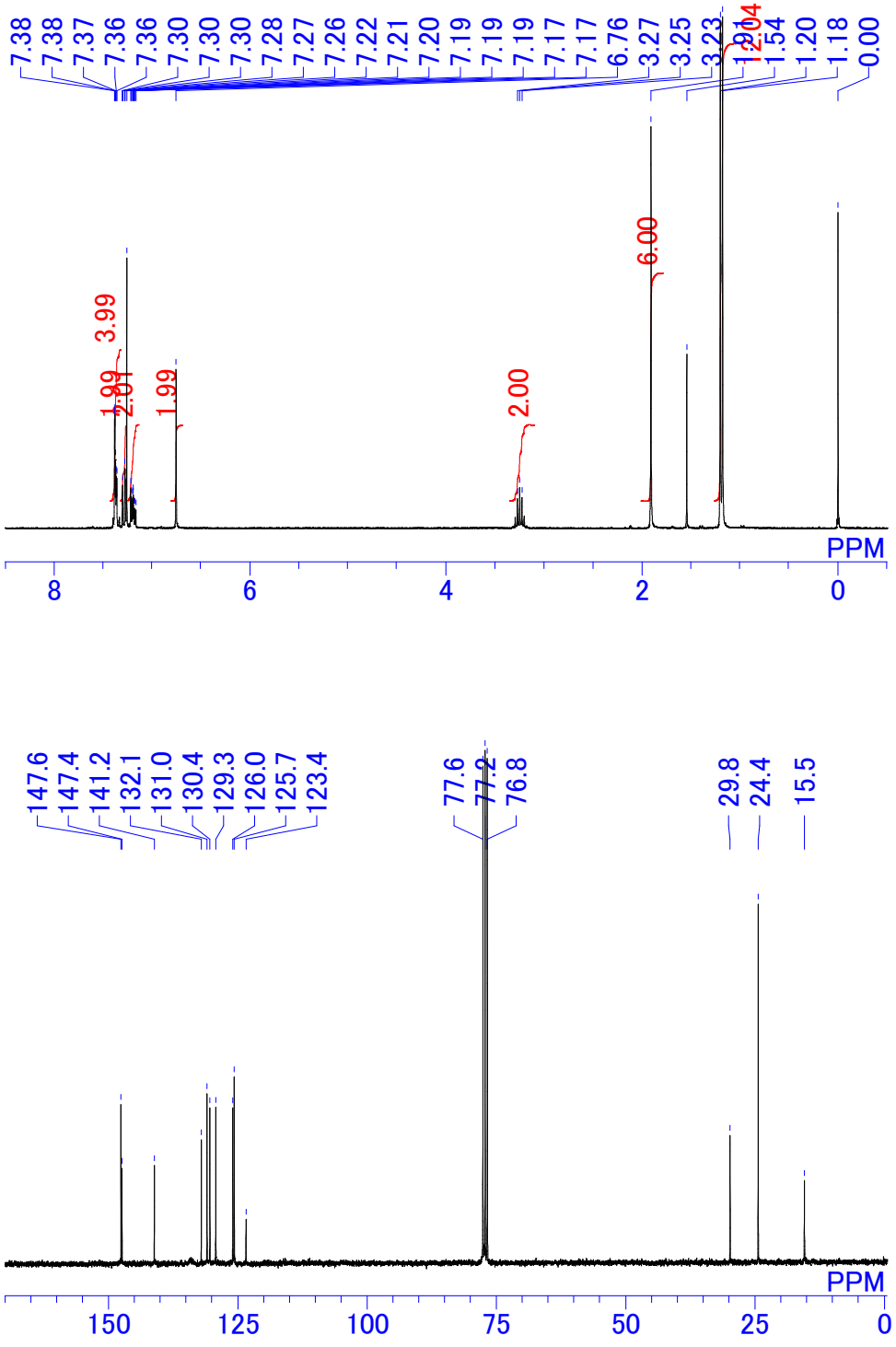
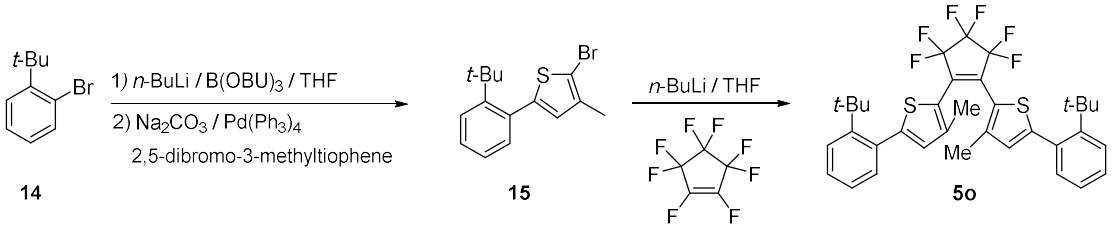


Figure S20. ^{1}H NMR and ^{13}C NMR spectra for **4o** in $CDCl_3$.

*1,2-Bis(3-methyl-5-(2-tert-butylphenyl)-2-thienyl)perfluorocyclopentene (**5o**)*



1-Bromo-2-*tert*-butylbenzene (**14**) (3.2 g, 15 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (10 mL, 17 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Tri-*n*-butyl borate (4.5 mL, 17 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 1 h. An adequate amount of distilled water was added to the mixture to quench the reaction. 2,5-dibromo-3-methylthiophene (3.8 g, 15 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg 0.26 mmol), and 20 wt% Na_2CO_3 aqueous solution (25 mL) were added to the solution, and the mixture was refluxed for 15 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear oil of mixture of 2-bromo-3-methyl-5-(2-*tert*-butylphenyl)thiophene (**14**) and 2-bromo-4-methyl-5-(2-*tert*-butylphenyl)thiophene (**15'**) (**15** : **15'** = 1 : 0.10) was obtained by column chromatography on silica gel using *n*-hexane as the eluent in 2.1 g. The mixture was used for the next reaction without further purification. The mixture (2.0 g, 6.5 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (4.5 mL, 7.2 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Octafluorocyclopentene (0.44 mL, 3.2 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 15 h. Adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude

product was purified by column chromatography on silica gel using *n*-hexane as the eluent and recrystallization from *n*-hexane to give 520 mg of **5o** in 25% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.29 (s, 18H, CH3), 1.94 (s, 6H, CH3), 6.75 (s, 2H, Thienyl H), 7.15-7.17 (m, 4H, Aromatic H), 7.31-7.36 (m, 2H, Aromatic H), 7.51 (d, 2H, J = 7.9 Hz, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.6, 32.6, 36.8, 123.1, 125.1, 127.0, 128.9, 131.7, 132.4, 133.3, 134.2, 140.1, 149.8, 150.5. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{35}H_{35}F_6S_2^+$ = 633.2084; found, 633.2088.

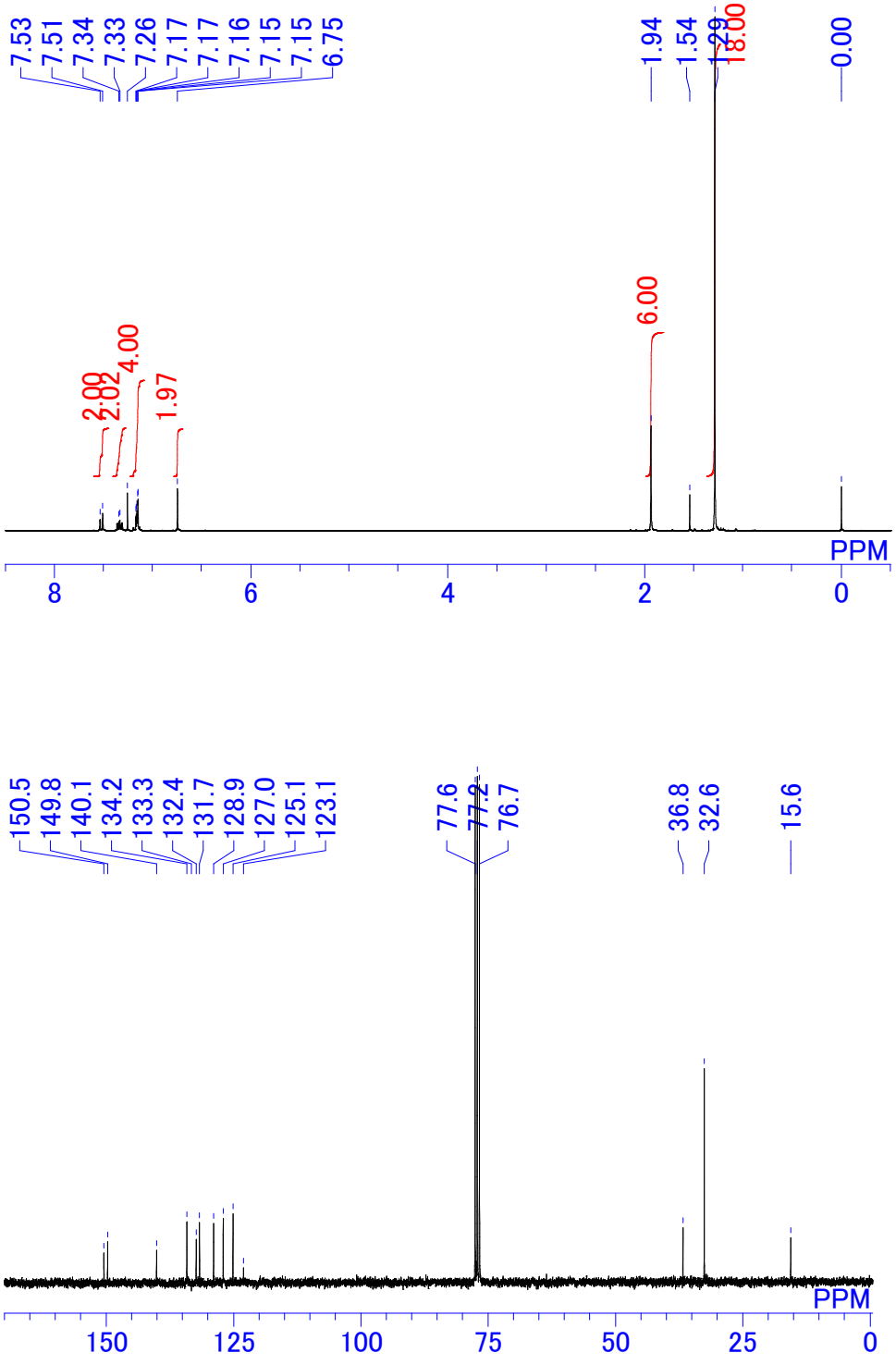
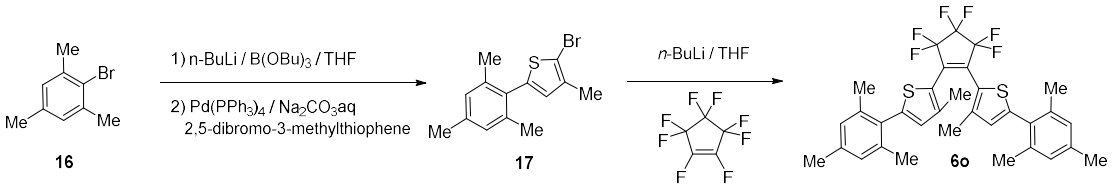


Figure S21. ^{1}H NMR and ^{13}C NMR spectra for **5o** in $CDCl_3$.

*1,2-Bis(3-methyl-5-(2,4,6-trimethylphenyl)-2-thienyl)perfluorocyclopentene (**6o**)*



1-Bromo-2,4,6-trimethylbenzene (**16**) (4.0 g, 20 mmol) was dissolved in anhydrous THF (40 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (13 mL, 21 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1.5 h. Tri-*n*-butyl borate (5.7 mL, 21 mmol) was slowly added to the solution at −78 °C, and the mixture was stirred for 2 h. Adequate amount of distilled water was added to the mixture to quench the reaction. 2,5-Dibromo-3-methylthiophene (5.1 g, 20 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg 0.26 mmol), and 20 wt% Na_2CO_3 aqueous solution (25 mL) were added to the solution, and the mixture was refluxed for 8 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The clear oil of mixture of 2-bromo-3-methyl-5-(2,4,6-trimetylphenyl)thiophene (**17**) and 2-bromo-4-methyl-5-(2,4,6-trimetylphenyl)thiophene (**17'**) (**17** : **17'** = 1 : 0.17) was obtained by column chromatography on silica gel using *n*-hexane as the eluent in 3.1 g. The mixture was used for the next reaction without further purification. The mixture (1.5 g, 5.1 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (3.4 mL, 5.3 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Octafluorocyclopentene (0.44 mL, 3.2 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 2 h. Adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate

(9:1) as the eluent and recrystallization from *n*-hexane/acetone to give 730 mg of **6o** in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.86 (s, 6H, CH_3), 2.12 (s, 12H, CH_3), 2.32 (s, 6H, CH_3), 6.57 (s, 2H, Thienyl H), 6.93 (s, 4H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.4, 20.8, 21.2, 123.7, 128.3, 130.0, 130.3, 137.9, 138.5, 141.2, 146.3. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{33}H_{31}F_6S_2^+$ = 605.1771; found, 605.1782.

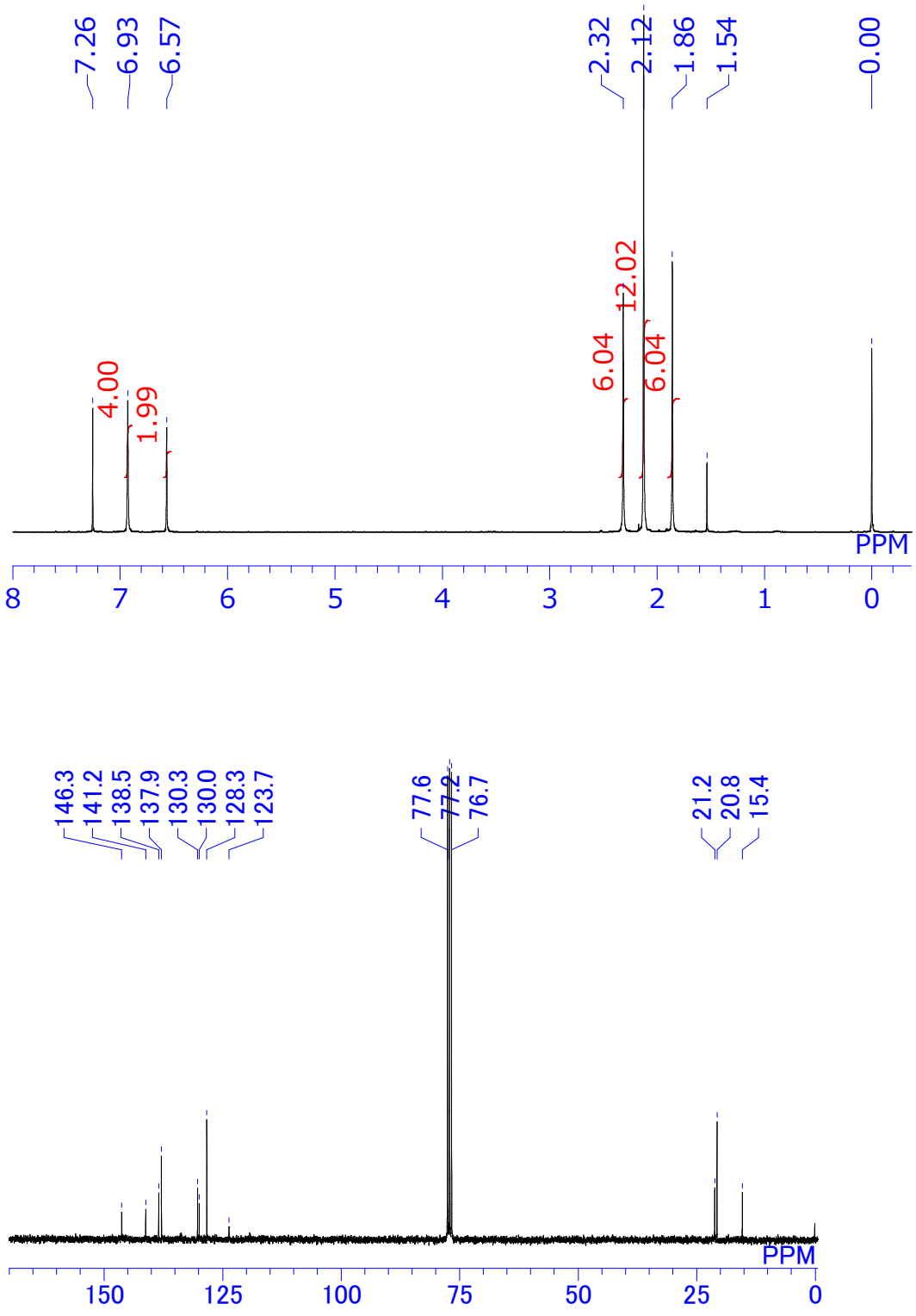
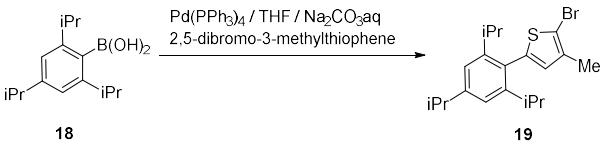


Figure S22. ^{1}H NMR and ^{13}C NMR spectra for **6o** in $CDCl_3$.

*2-Bromo-3-methyl-5-(2,4,6-triisopropylphenyl)thiophene (**19**)*



18 **19**

2,4,6-Triisopropylphenylboronic acid (**18**) (4.0 g, 16 mmol) was dissolved in THF (150 mL). 2,5-Dibromo-3-methylthiophene (4.1 g, 16 mmol), tetrakis(triphenylphosphine)palladium(0) (300 mg 0.26 mmol), and 20 wt% Na_2CO_3 aqueous solution (25 mL) were added to the solution, and the mixture was refluxed for 10 h. The reaction mixture was neutralized by HCl aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane as the eluent to give 510 mg of **19** in 8.4% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.13 (d, 6H, *J* = 6.9 Hz CH_3), 1.15 (d, 6H, *J* = 6.9 Hz, CH_3), 1.28 (d, 6H, *J* = 6.9 Hz, CH_3), 2.22 (s, 3H, CH_3), 2.86 (sep, 2H, *J* = 6.9 Hz CH), 2.92 (sep, 1H, *J* = 6.9 Hz CH), 6.50 (s, 1H, Thienyl H), 7.03 (s, 2H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.5, 24.1, 24.8, 30.6, 34.5, 108.2, 120.9, 128.0, 129.4, 136. 9, 141.1, 149.1, 149.7. HRMS (DART+, *m*/*z*): $[M+H]^+$ calcd. for $C_{20}H_{28}FBrS^+$ = 379.1095; found, 379.1091.

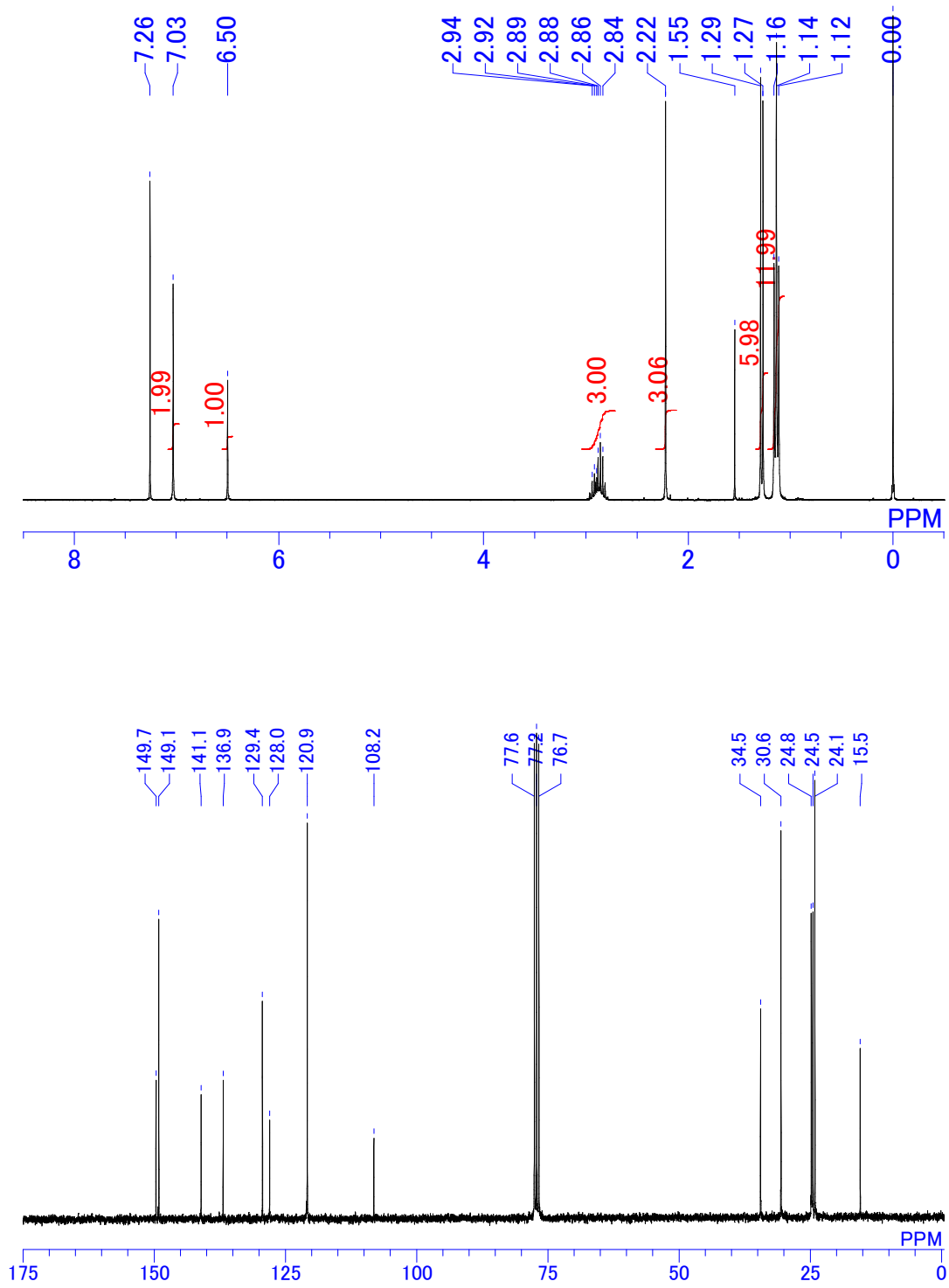
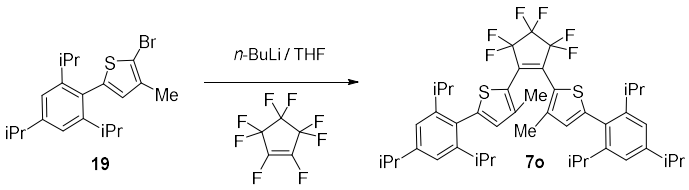


Figure S23. ^{1}H NMR and ^{13}C NMR spectra for **19** in $CDCl_3$.

*1,2-Bis(3-methyl-5-(2,4,6-triisopropylphenyl)-2-thienyl)perfluorocyclopentene (**7o**)*



Compound **19** (0.45 g, 1.2 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. 1.6 M *n*-BuLi hexane solution (0.82 mL, 1.3 mmol) was slowly added dropwise to the solution at −78 °C, and the mixture was stirred for 1 h. Octafluorocyclopentene (0.088 mL, 0.65 mmol) was slowly added to the solution at the temperature, and the mixture was stirred for 1 h. An adequate amount of distilled water was added to the mixture to quench the reaction. The reaction mixture was neutralized by HCl aqueous solution, extracted with dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (95:5) as the eluent and recrystallization from acetone/dichloromethane to give 130 mg of **7o** in 28% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.07 (d, 12H, *J* = 6.8 Hz, CH_3), 1.09 (d, 12H, *J* = 6.8 Hz, CH_3), 1.27 (d, 12H, *J* = 6.9 Hz, CH_3), 1.99 (s, 6H, CH_3), 2.77 (sep, *J* = 6.8 Hz, 4H, CH), 2.91 (sep, 2H, *J* = 6.9 Hz, CH), 6.59 (s, 2H, Thienyl H), 7.02 (s, 4H, Aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.4, 24.1, 24.6, 30.7, 34.5, 120.9, 123.6, 127.4, 131.1, 140.9, 146.5, 148.6,149.9. HRMS (ESI+, *m*/*z*): $[M+Na]^+$ calcd. for $C_{45}H_{54}F_6NaS_2^+$ = 795.3469; found, 795.3469.

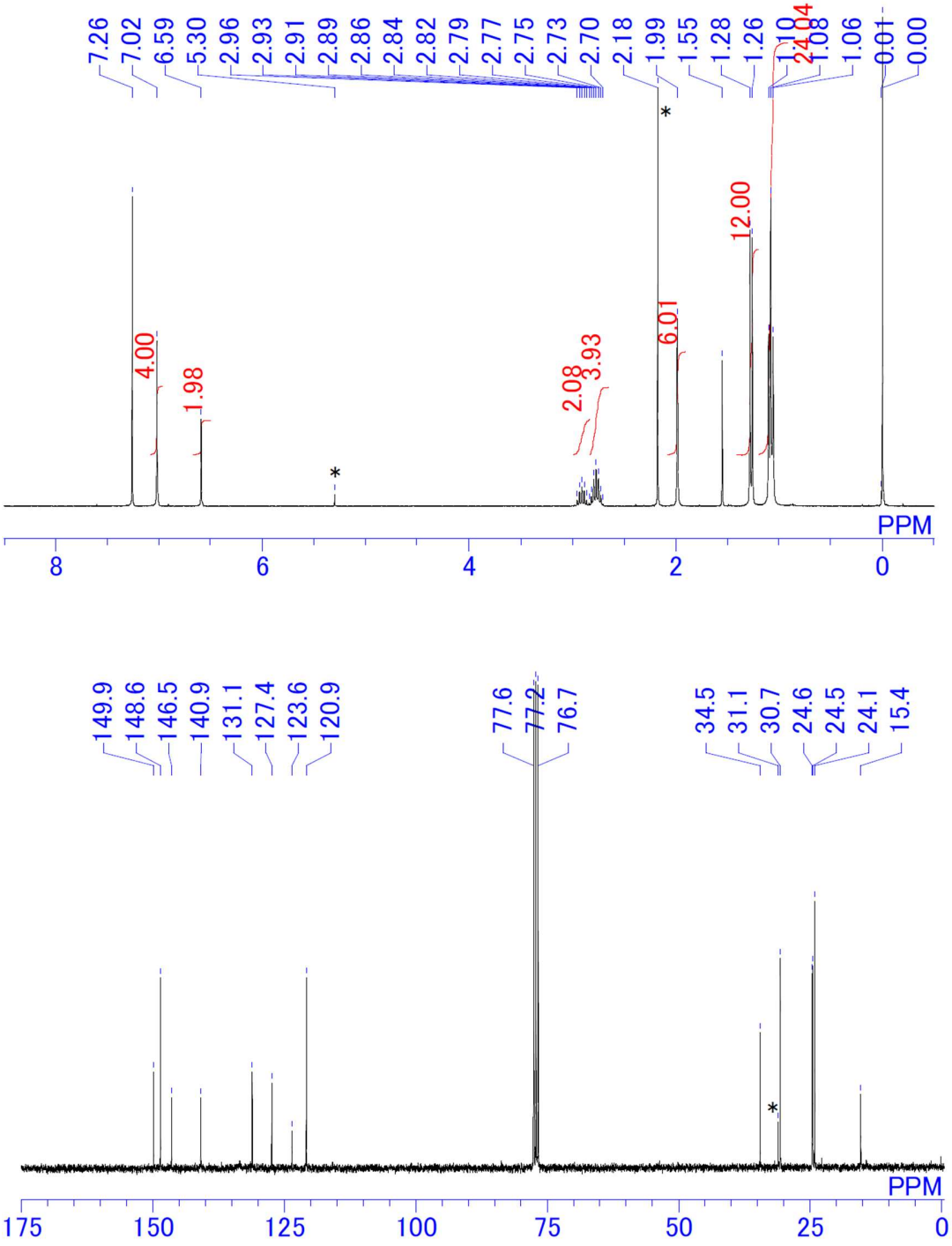


Figure S24. ^{1}H NMR and ^{13}C NMR spectra for **7o** in $CDCl_3$. Asterisk indicates solvent peaks of acetone and dichloromethane.

References

S1. K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi and M. Irie, *Tetrahedron*, 2001, **57**, 4559–4565.

S2. H. Sotome, D. Kitagawa, T. Nakahama, S. Ito, S. Kobatake, M. Irie and H. Miyasaka, *Phys. Chem. Chem. Phys.*, 2019, **21**, 8623–8632.

S3. D. Kitagawa, T. Nakahama, K. Mutoh, Y. Kobayashi, J. Abe, H. Sotome, S. Ito, H. Miyasaka and S. Kobatake, *Dyes Pigm.*, 2017, **139**, 233–238.