Electronic supplementary information

Open-shell singlet diradicaloid difluoreno[4,3-*b*:3′,4′-*d*]furan and its radical cation and dianion

Sakura Mori,[a] Motoko Akita,[b] Shuichi Suzuki,[c] Motoko S. Asano,[d]
Michihisa Murata,[e] Taisuke Matsumoto,[f] Tsuyoshi Akiyama,[a]
Chitoshi Kitamura,[a] and Shin-ichiro Kato*[a]

[a] *Department of Materials Science, School of Engineering, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone, Shiga 522-8533, Japan*
[b] *Graduate School of Material Science, Josai University, 1-1 Sakado, Saitama 350-0295, Japan*
[c] *Department of Chemistry, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan*
[d] *Division of Molecular Science, Faculty of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan*
[e] *Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585, Japan*
[f] *Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-1 Kasuga-koh-en, Kasuga 816-8580, Japan*

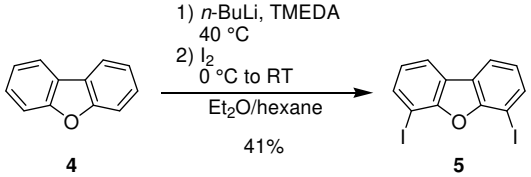
Table of Contents

1. General experimental methods

Commercially available reagents and solvents were used as received. Oil bath was used as the heat source. Column chromatography and plug filtrations were carried out with SiO_2. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254}. Melting points (M.p.) were measured with a hot-stage apparatus (Yanako MP-S3) and are uncorrected. Recycling gel-permeation chromatography (JAIGEL LC-918) was performed with UV detectors using 1H and 2H polystyrene columns eluting with $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on a spectrometer (JEOL JNM-LA400 or JNM-ECS400) at 400 MHz for ^1H and 100 MHz for ^{13}C, respectively. Residual solvent signals in the ^1H and ^{13}C NMR spectra were used as an internal reference. ESI- (Thermo Fisher Scientific LTQ Orbitrap XL) and EI-MS (JEOL JMS-T100 GCV 4G) spectrometries were conducted in a positive or negative mode. Electronic absorption spectra (JASCO V-670 or JV-550) were measured in a cuvette of 1 cm at room temperature. Cyclic voltammetry (EC Frontier ECstat-100) was performed by using a cell equipped with a platinum as working electrode, a platinum wire as counter electrodes, and $Ag/AgNO_3$ as a referential electrode. All electrochemical measurements were performed in CH_2Cl_2 solution (*ca.* 5×10^{-4} mol L^{-1}) containing 0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6] at room temperature. All potentials are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple, used as a standard. In situ UV–vis–NIR spectroclectrochemical studies (ALS Electrochemical Analyzer 420) were conducted by using a thin layer cell (1 mm) with a platinum mesh as working electrode, a platinum wire as counter electrode, and Ag/Ag^+ as a referential electrode; sample was electrolyzed for 90 sec for oxidation. X-Ray crystal structure analysis for a single crystal was performed with an X-ray diffractometer (Rigaku FR-E+) for which a Mo-Kα was used. ESR spectra (JEOL JES-TE200 or Bruker EMX Plus) were taken on instruments equipped for variable-temperature experiments. Quantum chemical calculations were performed by Gaussian 09 package of ab initio MO calculations.[1] The anisotropy of current-induced density (ACID) plots were analyzed by the ACID 2.0.1 program provided by Prof. Rainer Herges (Institut für Organische Chemie, Universität Kiel).[2,3] Elemental analysis was performed in A Rabbit Science Japan Co.,Ltd.

2. Synthesis

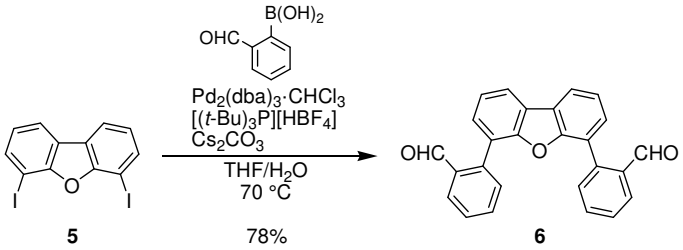
Preparation of iodide 5



A *n*-BuLi (1.55 mol L^{-1} solution in hexane, 24 mL, 37.6 mmol, 3.0 eq.) was added dropwise to a solution of dibenzofuran (**4**) (2.11 g, 12.5 mmol) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (5.6 mL,

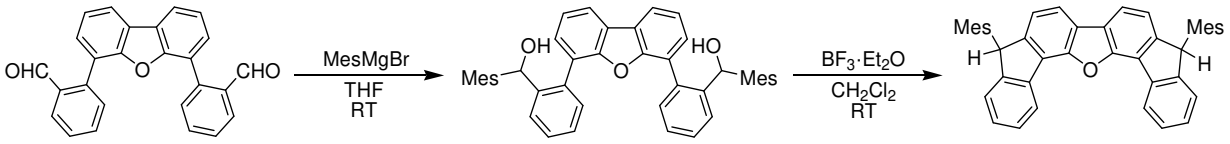
37.6 mmol, 3.0 eq.) in Et_2O/hexane (134 mL, 2:3) at room temperature under nitrogen atmosphere. The resulting mixture was stirred at 40 °C for 3 h. The mixture was cooled to 0 °C, and iodine (14.4 g, 57.7 mmol, 4.6 eq.) was added. The resulting mixture was warmed to room temperature and stirred for 3 h. After addition of aqueous $NaHSO_3$ (5%, 150 mL), the organic phase was separated and evaporated under reduced pressure, and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 4). The combined organic phase was washed with H_2O (100 mL × 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The combined residue was purified by recrystallization from hexane to give **5** (2.2 g, 5.2 mmol, 41%) as pale brown solids. M.p. 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (2H, dd, J = 1.2 & 7.6 Hz), 7.85 (2H, dd, J = 1.2 & 7.6 Hz), 7.13 (2H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.11, 136.70, 124.94, 121.13, 75.74 (5 signals out of 6 expected); UV–vis (CH_2Cl_2): λ_{max}^{abs} (relative intensity) 257 (sh, 0.51), 265 (0.61), 277 (sh, 0.65), 287 (1.0), 302 (0.38), 313 (0.32) nm; HR-EI-MS (TIC, positive): m/z calcd for $C_{12}H_6I_2O$ 419.8508, found 419.8495 [M^+].

Preparation of aldehyde 6



A solution of iodide **5** (1.0 g, 2.38 mmol), 2-formylphenylboronic acid (856 mg, 5.71 mmol, 2.4 eq.), Cs_2CO_3 (1.71 g, 5.24 mmol, 2.2 eq.), $Pd_2(dba)_3$·$CHCl_3$ (123 mg, 0.119 mmol, 0.05 eq.), and [(*t*-Bu)$_3$P][HBF_4] (69 mg, 0.24 mmol, 0.1 eq.) in degassed THF/H_2O (30:1, 60 mL) was stirred at 70 °C for 12 h under nitrogen atmosphere. After addition of H_2O (100 mL), the organic phase was separated and evaporated under reduced pressure, and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 4). The combined organic phase was washed with H_2O (10 mL × 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The combined residue was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 4:1) to give **6** (700 mg, 1.9 mmol, 78%) as white solids. M.p. 186–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (2H, s), 8.09 (2H, dd, J = 1.4 & 7.4 Hz), 8.02 (2H, dd, J = 0.8 & 7.6 Hz), 7.67 (2H, td, J = 1.4 & 7.4 Hz), 7.57–7.50 (4H, m), 7.51 (2H, t, J = 7.6 Hz), 7.44 (2H, dd, J = 1.4 & 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.88, 191.78, 153.81, 139.39, 133.94, 133.86, 131.61, 129.74, 128.58, 128.01, 124.58, 123.57, 122.64, 121.20 (13 signals out of 14 expected); UV–vis (CH_2Cl_2): λ_{max}^{abs} (relative intensity) 295 (1.0), 320 (sh, 0.54) nm; HR-ESI-MS (FT, positive): m/z calcd for $C_{26}H_{16}O_3Na$ 399.0991, found 399.0991 [(M+Na)$^+$].

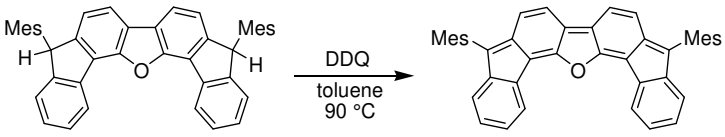
Preparation of dihydrodifluorenofuran 7



6 70% **7**

Mesitylmagnesium bromide (1 mol L^{-1} solution in THF, 10 mL, 10.0 mmol, 4.2 eq.) was added in a THF solution (20 mL) of aldehyde **6** (904 mg, 2.40 mmol) at room temperature, and the resulting solution was stirred for 20 h. After addition of H_2O (20 mL), the organic phase was separated and evaporated under reduced pressure. After the aqueous phase was extracted with CH_2Cl_2 (10 mL × 4), the combined organic phase was washed with H_2O (10 mL × 4), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The combined residue was subjected to column chromatography (SiO_2, CH_2Cl_2/hexane 5:1) and recrystallization (hexane/CH_2Cl_2) to give crude alcohol (1.06 g). To a solution of crude alcohol (1.06 g) in CH_2Cl_2 (110 mL) was added $BF_3{\cdot}OEt_2$ (2.2 mL, 17.2 mmol) at room temperature under nitrogen atmosphere. After the mixture was stirred for 20 min, aqueous $NaHSO_3$ (5%, 100 mL) was added. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 3). The combined organic phase was washed with H_2O (5 mL × 3), dried over anhydrous $NaSO_4$, and evaporated under reduced pressure to give **7** (970 mg, 1.67 mmol, 70%) as white solids. M.p. 279 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, diastereomer mixture): δ 8.51 (2H, d, J = 7.6 Hz), 7.86 (2H, d, J = 7.6 Hz), 7.63 (2H, t, J = 7.4 Hz), 7.37 (2H, t, J = 7.4 Hz), 7.32 (2H, d, J = 7.4 Hz), 7.25 (2H, d, J = 7.4 Hz), 7.07 (2H, s), 6.67 (2H, s), 5.71 (2H, s), 2.75 (6H, s), 2.30 (6H, s), 1.13, 1.11 (6H, 2s); ^{13}C NMR (100 MHz, $CDCl_3$, diastereomer mixture): δ 151.54, 147.51, 147.19, 147.18, 138.74, 138.73, 138.14, 137.86, 136.55, 133.94, 133.92, 130.71, 129.04, 127.45, 127.31, 125.47, 124.15, 123.82, 123.36, 119.14, 119.00, 50.80, 21.98, 21.97, 21.03, 18.85, 18.83 (27 signals out of 44 expected); UV–vis (CH_2Cl_2): λ_{max}^{abs} (relative intensity) 258 (1.0), 271 (0.86), 281 (sh, 0.79), 291 (sh, 0.66), 299 (0.66), 310 (sh, 0.25), 322 (0.15), 330, (0.02) nm; HR-ESI-MS (FT, positive): m/z calcd for $C_{44}H_{37}O$ 581.2838, found 581.2837 [$(M+H)^+$].

Preparation of difluorenofuran DFFu

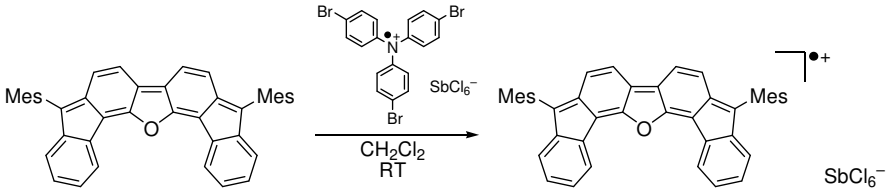


7 quant. **DFFu**

To a solution of dihydrodifluorenofuran **7** (201 mg, 345 μmol) in toluene (40 mL) was added dropwise a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (141 mg, 621 μmol, 1.8 eq.) in toluene (12 mL) at room temperature under nitrogen atmosphere. After the solution was stirred at 90 °C for 16 h, the resulting solution was diluted with toluene and filtered through a bed of silica gel. The filtrate was evaporated under reduced pressure to give **DFFu** (200 mg, quant.) as dark blue solids. M.p. 276–278 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (2H, d, J = 7.4 Hz), 7.30 (2H, t, J = 7.4 Hz), 7.14 (2H, td,

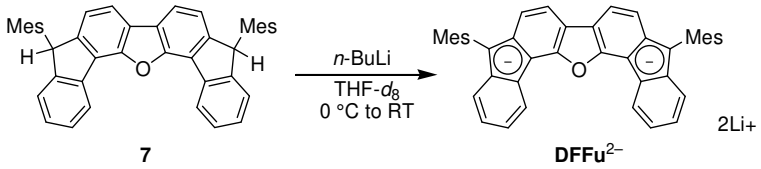
J = 7.5 & 1.1 Hz), 7.01 (4H, s), 6.96 (2H, d, J = 7.4 Hz), 6.95 (2H, d, J = 8.8 Hz), 6.75 (2H, d, J = 8.8 Hz), 2.38 (6H, s), 2.14 (12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.90, 143.95, 141.97, 137.68, 137.37, 136.57, 134.27, 130.67, 128.92, 128.38, 127.37, 127.16, 125.11, 124.17, 122.84, 118.76, 116.58, 21.33, 20.53 (19 signals out of 19 expected); UV–vis–NIR (CH_2Cl_2): λ_{max}^{abs} (ε) 268 (60000), 403 (6400), 601 (62500), 670 (20200), 830 (2600) nm; HR-ESI-MS (FT, positive): m/z calcd for $C_{44}H_{35}O$ 579.2682, found 579.2675 [$(M+H)^+$].

Preparation of radical cation salt DFFu$^{\bullet+}$[SbCl$_6$]$^-$



A suspension of difluorenofuran (**DFFu**) (51 mg, 88 μmol) and tris(4-bromophenyl)aminium hexachloroantimonate (36 mg, 4.3 μmol, 1.0 eq.) in CH_2Cl_2 was stirred at room temperature under nitrogen atmosphere for 30 min. After CH_2Cl_2 was removed by evaporation under reduced pressure, the residue was purified by washing with Et_2O to give **DFFu**$^{\bullet+}$[$SbCl_6$]$^-$ (14 mg, 15 μmol, 35%) as dark green solids. ^{1}H NMR (400 MHz, CD_2Cl_2): no peak was observed; UV–vis–NIR (CH_2Cl_2): λ_{max}^{abs} (ε) 267 (43900), 455 (11800), 625 (26200), 955 (16300), 1045 (18000), 1399 (7300) nm; HR-ESI-MS (FT, positive): m/z calcd for $C_{44}H_{34}O$ 578.2604, found 578.2599 [$(M–SbCl_6)^+$], (FT, Negative): m/z calcd for $SbCl_6^-$ 330.7174, found 330.7173 [$(M–C_{44}H_{34}O)^-$]; Elemental analysis: $C_{44}H_{36}O$ calcd for C 57.87; H 3.75; Cl 23.29; O 1.75; Sb 13.33, found C 57.94; H 3.98; N 0.00.

Generation of dianion DFFu^{2-}



A solution of dihydrodifluorenofuran **7** (10 mg, 17 μmol) in THF-d_8 (0.4 mL) in an NMR tube was purged with nitrogen for 40 min. To this THF solution was added dropwise a n-BuLi (1.55 mol L^{-1} solution in hexane, 0.04 mL, 28 μmol, 3.0 eq.) at 0 °C under nitrogen atmosphere, and the mixture was stirred at room temperature for 20 min. The reaction mixture turned to deep orange color and gave the solution of the dianion **DFFu^{2-}**. According to the NMR monitoring, the dianion **DFFu^{2-}** was generated almost quantitatively. ^{1}H NMR (400 MHz, THF-d_8): δ 8.66 (2H, d, J = 7.6 Hz), 7.28 (2H, d, J = 7.6 Hz), 6.95 (2H, d, J = 8.1 Hz), 6.88 (4H, s), 6.84 (2H, t, J = 7.6 Hz), 6.83 (2H, d, J = 8.1 Hz), 6.61 (2H, t, J = 7.6 Hz), 2.32 (6H, s), 2.11 (12H, s). Due to its instability under ambient condition, its ^{13}C NMR and mass spectra were not characterized.

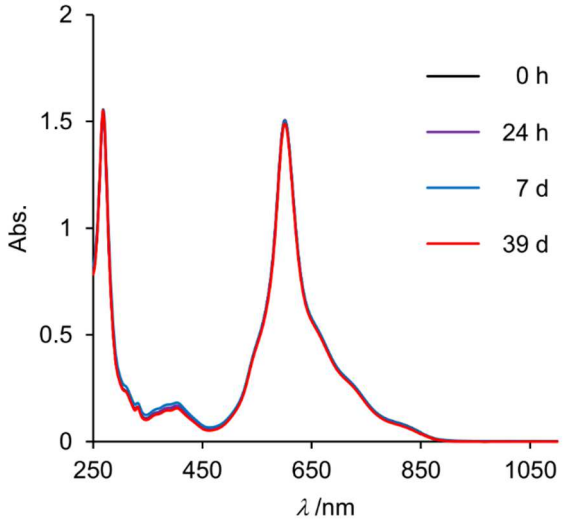
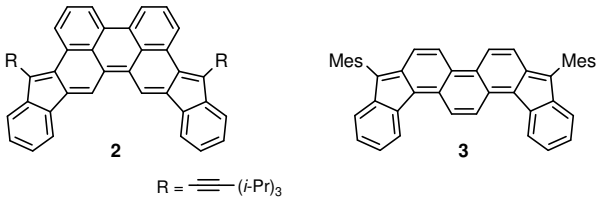


Figure S1. Time profiles of UV-vis-NIR spectra of **DFFu** in CH_2Cl_2 at RT under aerobic condition.

Compound **2**, synthesized by Frigoli and co-workers, is stable for more than 6 months in non-degassed toluene in the dark and for 1 week in the laboratory environment.[4] Compound **3**, synthesized by Stępień and co-workers, is stable for more than 25 days in CH_2Cl_2 under ambient conditions.[5] Overall, the stability of **DFFu** in solution is probably comparable to that of **2** and **3**.



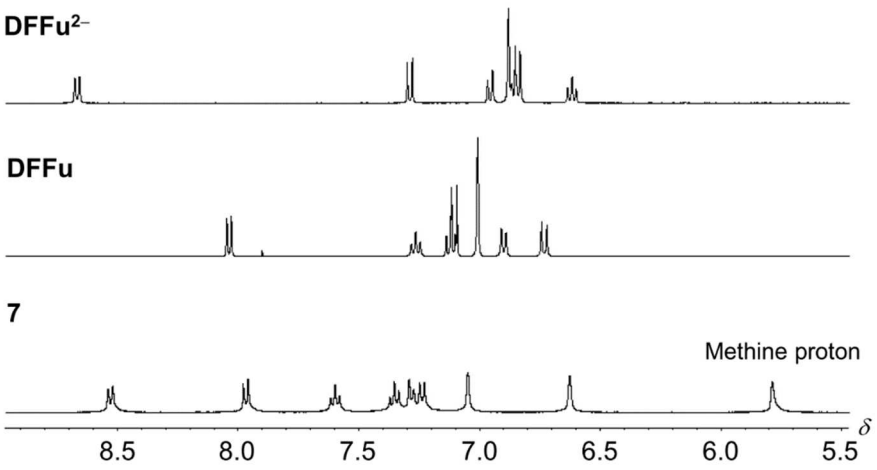


Figure S2. ^{1}H NMR spectra of **DFFu**$^{2-}$, **DFFu**, and **7** in THF-d_8.

3. X-ray crystallographic data

Using Olex2,[6] the structure was solved with the ShelXT[7] structure solution program using Intrinsic Phasing and refined with the ShelXL[8] refinement package using Least Squares minimization.

DFFu (CCDC 1974502): crystal data at 123 K, $C_{44}H_{34}O$, M_r = 578.71, Monoclinic, space group $P2_1/n$, D_{calcd} = 1.249 g/cm^3, Z = 4, a = 8.0514(2) Å, b = 29.7733(7) Å, c = 12.8449(3) Å, β = 92.127(2)°, V = 3077.02(13) Å^3; Mo-$K\alpha$ radiation, λ = 0.71073 Å, μ = 0.073 mm^{-1}. A pale yellow crystal was obtained from THF/MeOH solution at 5 °C. Numbers of measured and unique reflections were 7055 and 6041, respectively. Final $R(F)$ = 0.0404 for 412 parameters and 6041 reflections with $I > 2\sigma(I)$ (for all data, $R(F)$ and $wR(F^2)$ values are 0.0478 and 0.1078, respectively).

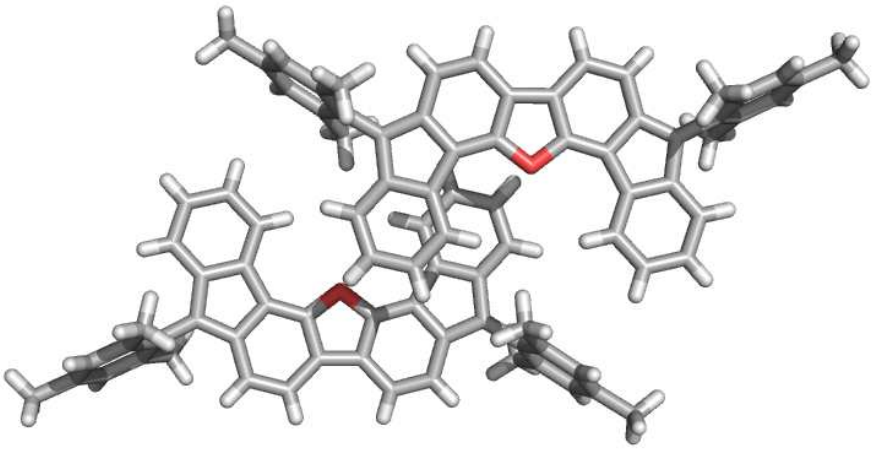


Figure S3. Dimeric structure of **DFFu** determined by the X-ray crystallographic analysis.

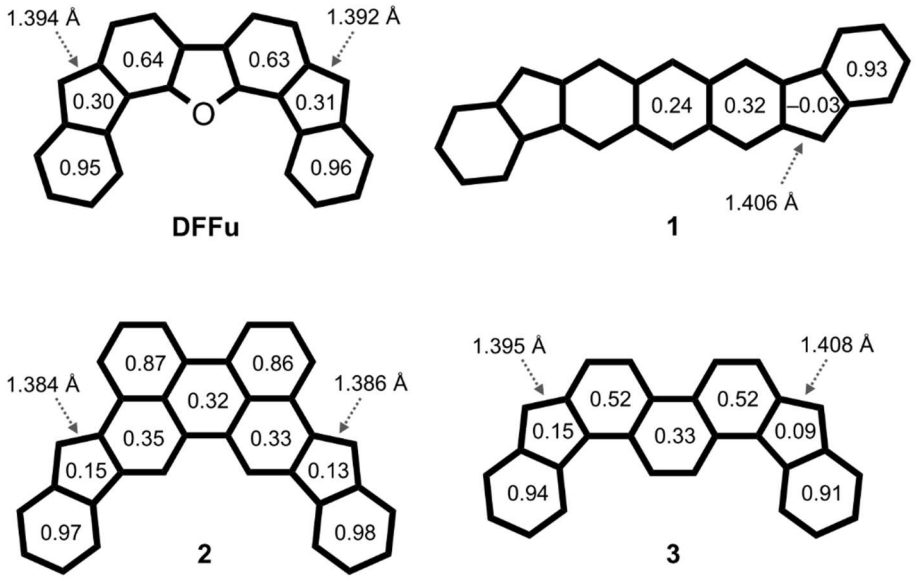


Figure S4. HOMA values of the π-conjugated frameworks of **DFFu**, **1**, **2**, and **3** determined by the X-ray crystallographic analyses.

4. Electrochemical data

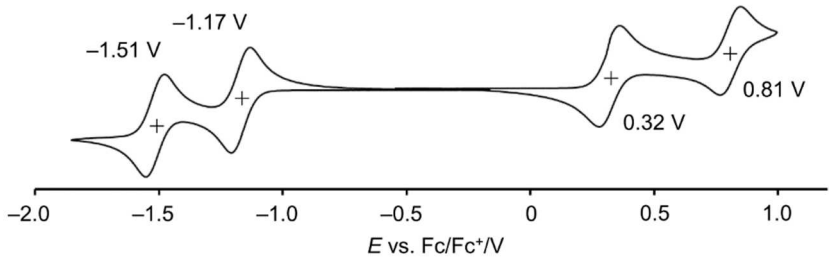


Figure S5. Cyclic voltammograms of **DFFu** at scan rate 100 mV s^{-1} in CH_2Cl_2 (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]).

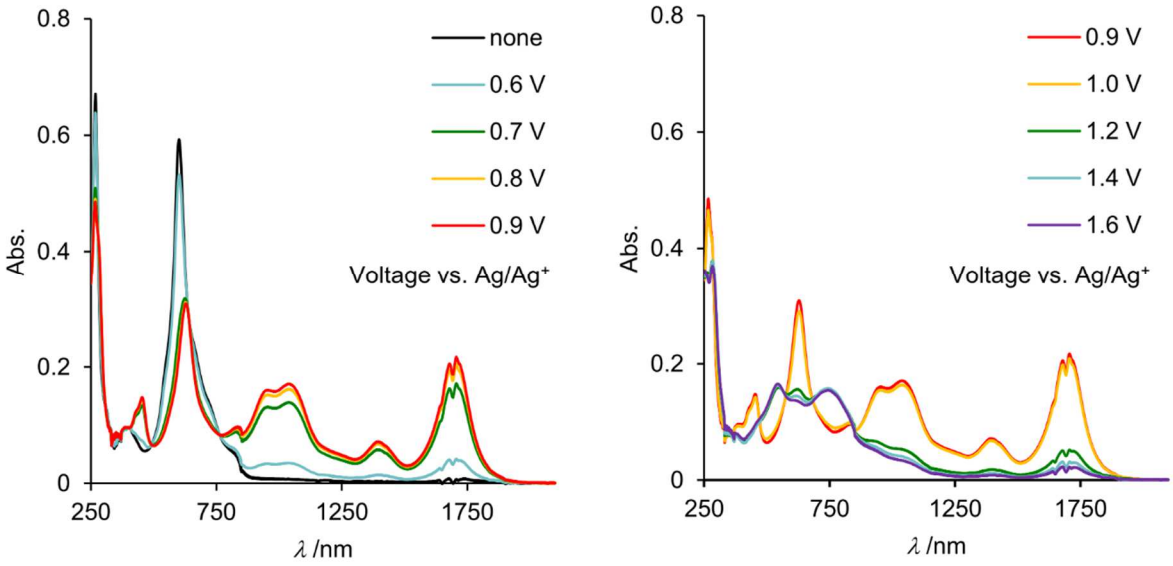


Figure S6. UV-vis-NIR spectra obtained during the potentiostatic oxidation of **DFFu** at scan rate 100 mV s^{-1} in CH_2Cl_2 (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]).

5. ESR data

The variable-temperature ESR data of **DFFu** (Figure S7) in the solid state were fitted with the following equation:

$$I_{(\mathrm{ESR})} = c\frac{3\exp(-\frac{\Delta E}{k_\mathrm{B}T})}{1+3\exp(-\frac{\Delta E}{k_\mathrm{B}T})}\ \frac{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)+\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}{1+\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)+\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)} \qquad \text{(Eq. S1)}$$

where, $I_{(\mathrm{ESR})}$ is the ESR intensity, T is the temperature, c is a constant, h is Planck constant (6.626×10^{-34} $\mathrm{Js^{-1}}$), k_B is Boltzmann constant (0.695 $\mathrm{cm^{-1}\ K^{-1}}$), ν is a microwave frequency (9.415 GHz), and ΔE is an excitation energy from the singlet ground state to the triplet excited state, i.e., $\Delta E = -2J$: $2J$ was estimated to be –4.3 kcal/mol (1490 $\mathrm{cm^{-1}}$). In our experiments, $h\nu$ is calculated as 0.314 $\mathrm{cm^{-1}}$. In Eq. S1, under the condition that $h\nu << k_\mathrm{B}T$ (0.314 $\mathrm{cm^{-1}}$ vs. 207 $\mathrm{cm^{-1}}$ at 298 K), $(1 + h\nu/k_\mathrm{B}T)$ is a good approximation for $\exp(h\nu/k_\mathrm{B}T)$. Accordingly, the following Eq. S2 is derived.

$$I_{(\mathrm{ESR})} = c\frac{3\exp(-\frac{\Delta E}{k_\mathrm{B}T})}{1+3\exp(-\frac{\Delta E}{k_\mathrm{B}T})}\ \frac{2h\nu}{3k_\mathrm{B}T} \qquad \text{(Eq. S2)}$$

Eq. S2 is equivalent to the following Bleaney–Bowers equation,

$$I_{(\mathrm{ESR})}T = c'\frac{1}{3+\exp(\frac{\Delta E}{k_\mathrm{B}T})} \qquad \text{(Eq. S3)}$$

and relation between constants c and c' is given by

$$c' = c\ \frac{2h\nu}{k_\mathrm{B}}$$

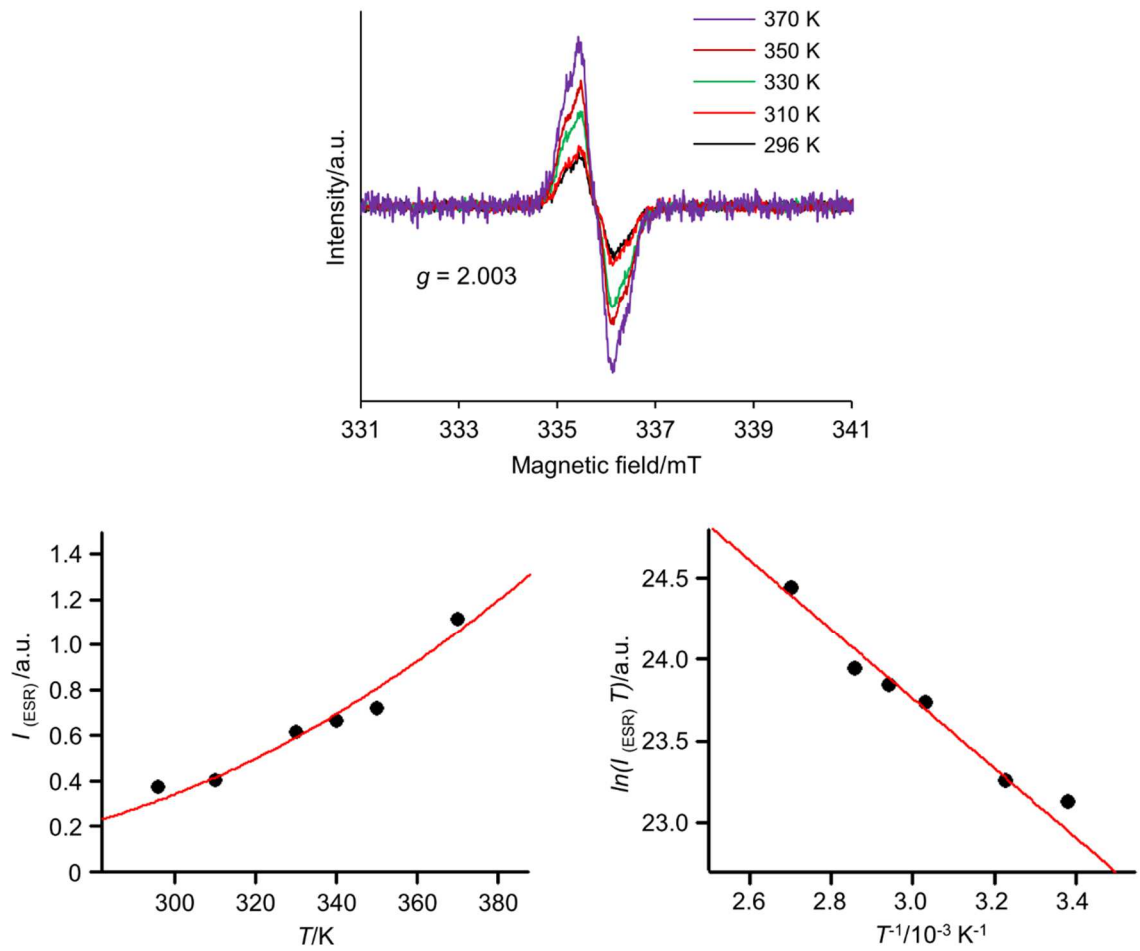


Figure S7. VT-ESR spectra of **DFFu** in the solid state (top) as well as fitted $I_{(ESR)} - T$ (bottom-left) and ln $I_{(ESR)}T - T^{-1}$ (bottom-right) plots, where $I_{(ESR)}$ is the ESR intensity and T is the temperature.

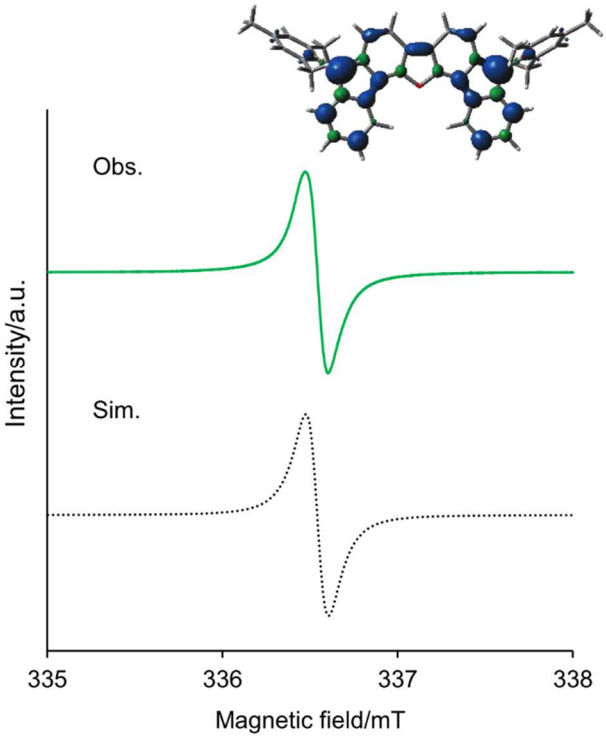


Figure S8. Observed ESR spectrum of **DFFu**$^{\bullet+}$ in benzene (g = 2.003) at room temperature and its simulation. Spin density distribution of **DFFu**$^{\bullet+}$ calculated at the UB3LYP/6-311G(d) level.

6. Theoretical data

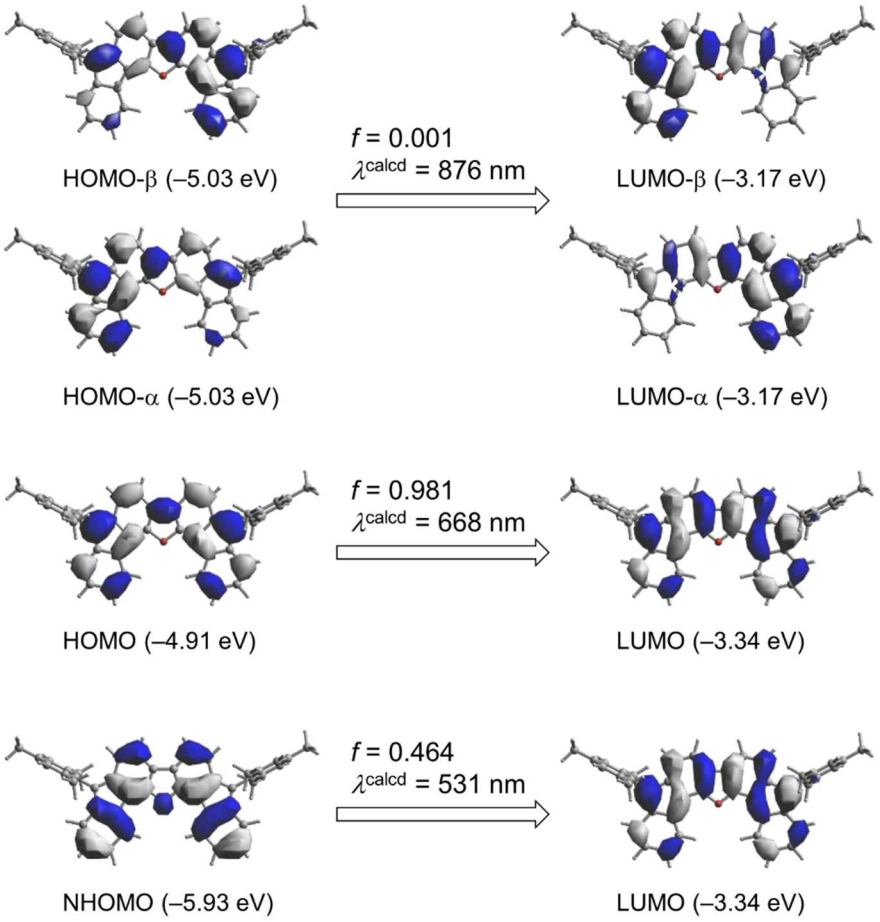


Figure S9. FMOs and the calculated absorption wavelengths (λ^{calcd}) and oscillator strengths (*f*) of **DFFu** at the (TD)(U)M06-2X/6-311+G(d,p)//(U)B3LYP/6-311G(d) level of theory.

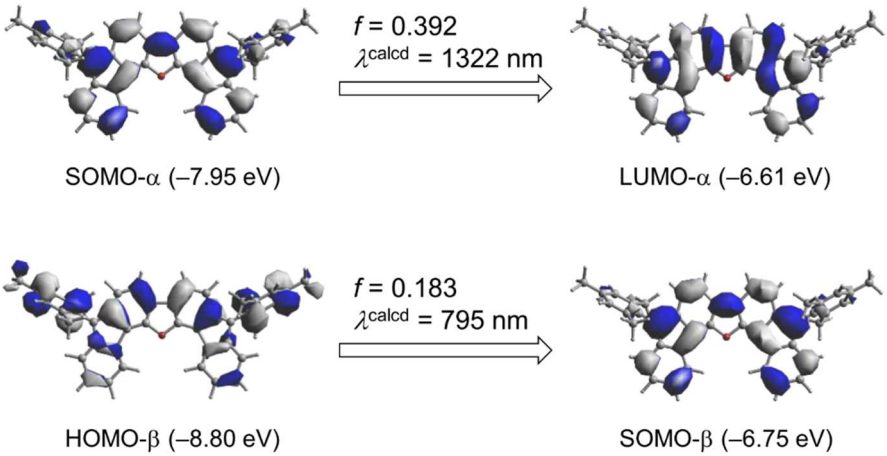


Figure S10. FMOs and the calculated absorption wavelengths (λ^{calcd}) and oscillator strengths (*f*) of radical cation **DFFu**$^{\bullet+}$ at the (TD)UM06-2X/6-311+G(d,p)//UB3LYP/6-311G(d) level of theory.

The open-shell singlet diradical character index y was calculated based on the natural orbital occupation number (NOON) of the LUMO in spin-unrestricted LC-BLYP calculation using 6-311G(d) basis set.[9] According to the Yamaguchi scheme,[10] y value is expressed as

$$y = 1 - (2T / (1 + T^2))$$

where T is the orbital overlap between the corresponding orbital pairs and it can be presented using the NOON of HOMO and LUMO.

$$T = (n_{HOMO} - n_{LUMO}) / 2$$

The y values obtained by this method are listed in Table S1.

Table S1. Relative Energies and Open-Shell Singlet Diradical Character Indexes

Compd	ΔE (OS – CS)[a]	ΔE ($S_0 - T_1$)[b]	y [c]
DFFu′ [d]	–0.8	–5.8	0.40
DFFu [d]	–1.1	–5.3	0.44
DFFucryst. [e]	N/A	N/A	0.35
1′ [d]	–1.6	–5.6	0.47
1cryst. [e]	N/A	N/A	0.43
2′ [d]	0	–16.3	0.05
2cryst. [e]	N/A	N/A	0.09
3′ [d]	–2.7	–3.5	0.55
3cryst. [e]	N/A	N/A	0.48

[a] Open-shell singlet energy minus closed-shell singlet energy ((U)B3LYP/6-311G(d)).
[b] Open-shell singlet energy minus unrestricted triplet energy ((U)B3LYP/6-311G(d)).
[c] Open-shell singlet diradical character index.
[d] Optimized at the UB3LYP/6-311G(d) level.
[e] X-Ray crystallographic structure.

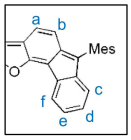


Table S2. Observed and Calculated ^{1}H Chemical Shifts of **DFFu**

Positions	Observed [a,b]	Calculated [c]	
		B3LYP/6-311G(d,p)	B3LYP/6-311++G(2d,2pd)
a	7.10	6.61	7.52
b	6.73	6.39	7.41
c	6.89	6.68	7.49
d	7.11	6.91	7.79
e	7.26	7.05	7.90
f	8.03	7.85	8.36

[a] In THF-d_8. [b] We assigned all aromatic protons by the NOESY experiment. [c] PCM model (THF).

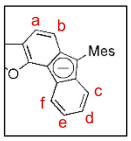


Table S3. Observed and Calculated ^{1}H Chemical Shifts of **DFFu**$^{2-}$

Positions	Observed [a,b]	Calculated [c]	
		B3LYP/6-311G(d,p)	B3LYP/6-311++G(2df,2pd)
a	7.28	7.85	7.99
b	6.83	7.02	7.29
c	6.95	7.07	7.44
d	6.84	7.25	7.41
e	6.61	7.00	7.13
f	8.66	9.06	9.42

[a] In THF-d_8. [b] We assigned all aromatic protons by the 1D NOE and ^{1}H-^{1}H COSY experiments. [c] PCM model (THF).

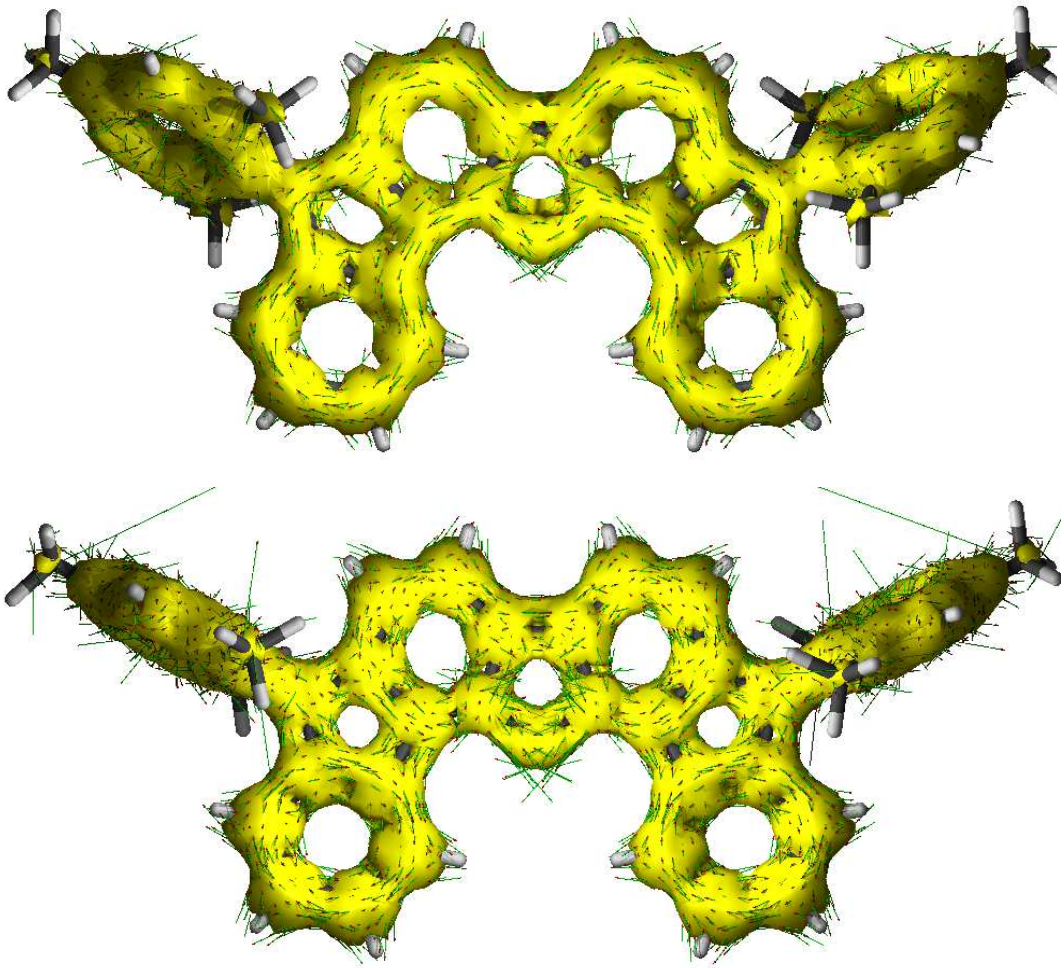


Figure S11. ACID plots of **DFFu**$^{2-}$ (top) and **DFFu** (open-shell singlet) (bottom) at the CSGT-(U)B3LYP/6-311+G(d,p)//(U)B3LYP/6-311G(d).

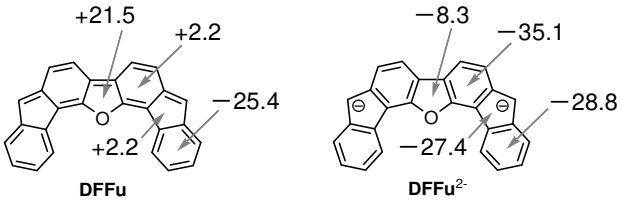


Figure S12. NICS(1) values of **DFFu′** and **DFFu′**$^{2-}$ calculated at the GIAO-HF/6-311G(d)//B3LYP/6-311G(d).

Table S4. Cartesian Coordinates of **DFFu′** (Closed-Shell Singlet) at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.697325	-2.172349	0.000010
2	6	0	-1.100265	-0.790270	0.000002
3	8	0	-0.000000	0.035797	-0.000016
4	6	0	1.100265	-0.790270	-0.000001
5	6	0	0.697324	-2.172349	0.000005
6	6	0	-1.694094	-3.196786	0.000016
7	6	0	-3.014594	-2.845429	0.000015
8	6	0	-3.405031	-1.467339	0.000016
9	6	0	-2.402781	-0.405515	0.000006
10	6	0	2.402781	-0.405515	-0.000000
11	6	0	3.405031	-1.467339	0.000013
12	6	0	3.014594	-2.845430	0.000008
13	6	0	1.694094	-3.196787	0.000009
14	6	0	3.112081	0.867483	0.000008
15	6	0	4.505665	0.558443	0.000023
16	6	0	4.656877	-0.879980	0.000084
17	6	0	-4.656877	-0.879980	0.000061
18	6	0	-4.505665	0.558443	-0.000003
19	6	0	-3.112081	0.867483	-0.000005
20	6	0	2.680926	2.186758	-0.000024
21	6	0	3.638551	3.207592	-0.000033
22	6	0	5.004195	2.910364	-0.000015
23	6	0	5.448576	1.587147	0.000009
24	6	0	-5.448576	1.587147	-0.000032
25	6	0	-5.004194	2.910364	-0.000058
26	6	0	-3.638551	3.207592	-0.000060
27	6	0	-2.680926	2.186758	-0.000035
28	1	0	-1.395925	-4.239248	0.000029
29	1	0	-3.783295	-3.611920	0.000033
30	1	0	3.783295	-3.611920	0.000025
31	1	0	1.395925	-4.239248	0.000018
32	1	0	5.603864	-1.406063	0.000121
33	1	0	-5.603864	-1.406062	0.000088
34	1	0	1.622814	2.424854	-0.000048
35	1	0	3.315860	4.243634	-0.000056
36	1	0	5.727656	3.719322	-0.000017
37	1	0	6.511562	1.365527	0.000035
38	1	0	-6.511561	1.365527	-0.000020
39	1	0	-5.727655	3.719322	-0.000073
40	1	0	-3.315859	4.243634	-0.000084
41	1	0	-1.622814	2.424853	-0.000044

No imaginary frequency.
Total energy = –1074.62774404 hartree.

Table S5. Cartesian Coordinates of **DFFu′** (Open-Shell Triplet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.724317	-2.197808	0.000021
2	6	0	-1.101238	-0.835466	0.000009
3	8	0	0.000000	-0.007670	0.000002
4	6	0	1.101238	-0.835466	0.000016
5	6	0	0.724317	-2.197808	0.000024
6	6	0	-1.707167	-3.197970	0.000026
7	6	0	-3.049142	-2.833205	0.000019
8	6	0	-3.409271	-1.472879	0.000009
9	6	0	-2.420613	-0.436499	0.000003
10	6	0	2.420613	-0.436499	0.000017
11	6	0	3.409271	-1.472879	0.000028
12	6	0	3.049142	-2.833205	0.000035

13	6	0	1.707167	-3.197970	0.000034
14	6	0	3.112395	0.848802	0.000005
15	6	0	4.518300	0.567014	0.000011
16	6	0	4.698319	-0.847895	0.000041
17	6	0	-4.698319	-0.847895	0.000013
18	6	0	-4.518300	0.567014	-0.000015
19	6	0	-3.112395	0.848802	-0.000013
20	6	0	2.658403	2.158053	-0.000014
21	6	0	3.597425	3.198737	-0.000027
22	6	0	4.971666	2.932176	-0.000022
23	6	0	5.442288	1.621718	-0.000004
24	6	0	-5.442288	1.621718	-0.000035
25	6	0	-4.971665	2.932176	-0.000050
26	6	0	-3.597425	3.198738	-0.000047
27	6	0	-2.658402	2.158053	-0.000030
28	1	0	-1.424611	-4.245241	0.000036
29	1	0	-3.819284	-3.597754	0.000026
30	1	0	3.819284	-3.597755	0.000046
31	1	0	1.424611	-4.245241	0.000043
32	1	0	5.649046	-1.366099	0.000055
33	1	0	-5.649046	-1.366098	0.000021
34	1	0	1.596195	2.376630	-0.000021
35	1	0	3.252793	4.227752	-0.000042
36	1	0	5.676452	3.757284	-0.000030
37	1	0	6.509312	1.420607	0.000004
38	1	0	-6.509312	1.420607	-0.000033
39	1	0	-5.676452	3.757284	-0.000062
40	1	0	-3.252793	4.227752	-0.000060
41	1	0	-1.596195	2.376630	-0.000030

No imaginary frequency.
Total energy = –1074.61974663 hartree.

Table S6. Cartesian Coordinates of **DFFu′** (Open-Shell Singlet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.706744	-2.182152	0.000022
2	6	0	-1.099992	-0.807449	0.000011
3	8	0	0.000000	0.019643	0.000005
4	6	0	1.099992	-0.807449	0.000018
5	6	0	0.706744	-2.182152	0.000026
6	6	0	-1.698343	-3.197525	0.000026
7	6	0	-3.026434	-2.841352	0.000020
8	6	0	-3.406059	-1.469558	0.000010
9	6	0	-2.408617	-0.417648	0.000005
10	6	0	2.408617	-0.417648	0.000019
11	6	0	3.406059	-1.469558	0.000029
12	6	0	3.026434	-2.841352	0.000036
13	6	0	1.698343	-3.197525	0.000035
14	6	0	3.110845	0.861241	0.000006
15	6	0	4.508150	0.562783	0.000009
16	6	0	4.669632	-0.869256	0.000038
17	6	0	-4.669632	-0.869256	0.000010
18	6	0	-4.508150	0.562783	-0.000017
19	6	0	-3.110845	0.861242	-0.000012
20	6	0	2.670391	2.176339	-0.000012
21	6	0	3.620833	3.205120	-0.000026
22	6	0	4.989012	2.919411	-0.000023
23	6	0	5.443496	1.600210	-0.000007
24	6	0	-5.443496	1.600210	-0.000037
25	6	0	-4.989011	2.919411	-0.000051
26	6	0	-3.620833	3.205120	-0.000046
27	6	0	-2.670391	2.176339	-0.000027
28	1	0	-1.405987	-4.241789	0.000036
29	1	0	-3.795660	-3.607160	0.000026

30	1	0	3.795660	-3.607160	0.000047
31	1	0	1.405987	-4.241789	0.000043
32	1	0	5.617877	-1.392752	0.000050
33	1	0	-5.617877	-1.392751	0.000016
34	1	0	1.610579	2.406663	-0.000016
35	1	0	3.289609	4.238495	-0.000039
36	1	0	5.705700	3.734331	-0.000032
37	1	0	6.508066	1.386346	-0.000002
38	1	0	-6.508066	1.386346	-0.000038
39	1	0	-5.705700	3.734332	-0.000065
40	1	0	-3.289609	4.238495	-0.000058
41	1	0	-1.610579	2.406664	-0.000026

No imaginary frequency.
Total energy = –1074.62902008 hartree.

Table S7. Cartesian Coordinates of **DFFu** (Closed-Shell Singlet) at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.698175	-1.216704	0.001772
2	6	0	1.100155	0.164446	0.001984
3	8	0	-0.000096	0.990960	0.002766
4	6	0	-1.100193	0.164247	0.003583
5	6	0	-0.697970	-1.216830	0.004023
6	6	0	1.696425	-2.238660	0.001198
7	6	0	3.017696	-1.885501	0.000506
8	6	0	3.405873	-0.507444	-0.001343
9	6	0	2.403103	0.549919	0.002589
10	6	0	-2.403216	0.549472	0.002314
11	6	0	-3.405799	-0.508048	0.005521
12	6	0	-3.017383	-1.886030	0.004049
13	6	0	-1.696044	-2.238954	0.004207
14	6	0	-3.108573	1.823051	-0.002223
15	6	0	-4.500796	1.517265	-0.003644
16	6	0	-4.670441	0.070283	0.001965
17	6	0	4.670408	0.071097	0.000203
18	6	0	4.500521	1.518059	0.005278
19	6	0	3.108261	1.823615	0.005596
20	6	0	-2.674816	3.141815	-0.001105
21	6	0	-3.630284	4.164378	-0.001154
22	6	0	-4.996474	3.869286	0.000433
23	6	0	-5.443148	2.546530	0.000835
24	6	0	5.442725	2.547437	-0.000987
25	6	0	4.995845	3.870130	-0.000696
26	6	0	3.629614	4.165014	0.002599
27	6	0	2.674294	3.142309	0.004408
28	6	0	5.974658	-0.636224	-0.011570
29	6	0	6.685988	-0.825999	1.191295
30	6	0	7.918161	-1.480397	1.154500
31	6	0	8.469288	-1.952445	-0.037410
32	6	0	7.752380	-1.749128	-1.216048
33	6	0	6.515151	-1.101042	-1.227183
34	6	0	5.785187	-0.896402	-2.534446
35	6	0	6.126663	-0.343988	2.509395
36	6	0	9.789779	-2.683774	-0.044492
37	6	0	-5.974669	-0.637085	0.011171
38	6	0	-6.682985	-0.827438	-1.193909
39	6	0	-7.911438	-1.488028	-1.161217
40	6	0	-8.464266	-1.962966	0.029280
41	6	0	-7.748207	-1.764103	1.208637
42	6	0	-6.513885	-1.109602	1.223879
43	6	0	-5.783118	-0.913795	2.532064
44	6	0	-6.119538	-0.346280	-2.510568
45	6	0	-9.809459	-2.647956	0.037119
46	1	0	1.400616	-3.281907	0.003275

47	1	0	3.789696	-2.648186	0.003468
48	1	0	-3.789223	-2.648877	0.000467
49	1	0	-1.400070	-3.282154	0.002208
50	1	0	-1.616067	3.377228	0.000828
51	1	0	-3.305576	5.199868	-0.000832
52	1	0	-5.718832	4.679330	0.002776
53	1	0	-6.505119	2.321757	0.006133
54	1	0	6.504724	2.322823	-0.007593
55	1	0	5.718085	4.680270	-0.004431
56	1	0	3.304748	5.200454	0.002160
57	1	0	1.615507	3.377563	0.003785
58	1	0	8.462013	-1.625780	2.084709
59	1	0	8.168036	-2.099474	-2.157538
60	1	0	4.845340	-1.455153	-2.566352
61	1	0	6.395300	-1.224839	-3.378251
62	1	0	5.529488	0.154801	-2.693650
63	1	0	6.799381	-0.589134	3.333672
64	1	0	5.155051	-0.798735	2.723107
65	1	0	5.972338	0.738688	2.514228
66	1	0	9.652905	-3.750875	0.163561
67	1	0	10.470449	-2.292570	0.715908
68	1	0	10.288725	-2.604579	-1.013207
69	1	0	-8.450082	-1.638819	-2.093675
70	1	0	-8.160579	-2.125301	2.147385
71	1	0	-4.847490	-1.479728	2.563466
72	1	0	-6.396274	-1.239544	3.374713
73	1	0	-5.519664	0.135035	2.693806
74	1	0	-5.963161	0.736075	-2.514477
75	1	0	-6.790909	-0.589691	-3.336452
76	1	0	-5.148265	-0.802732	-2.722334
77	1	0	-9.926206	-3.314515	-0.821610
78	1	0	-9.953984	-3.241230	0.942823
79	1	0	-10.626013	-1.918897	-0.008654

No imaginary frequency.
Total energy = –1772.77937663 hartree.

Table S8. Cartesian Coordinates of **DFFu** (Open-Shell Triplet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.724524	-1.253589	0.001439
2	6	0	1.101184	0.108217	0.000769
3	8	0	-0.000023	0.936294	0.003022
4	6	0	-1.100957	0.107857	0.005280
5	6	0	-0.723856	-1.253827	0.004929
6	6	0	1.709048	-2.252442	0.000962
7	6	0	3.050971	-1.886592	-0.001320
8	6	0	3.409032	-0.525908	-0.005241
9	6	0	2.420919	0.507934	-0.000560
10	6	0	-2.420825	0.507139	0.005819
11	6	0	-3.408597	-0.527027	0.009905
12	6	0	-3.050100	-1.887602	0.006496
13	6	0	-1.708053	-2.253006	0.005075
14	6	0	-3.110422	1.791954	-0.001916
15	6	0	-4.513958	1.512724	-0.005468
16	6	0	-4.712509	0.089770	0.003322
17	6	0	4.712755	0.091341	-0.000321
18	6	0	4.513719	1.514228	0.008014
19	6	0	3.110095	1.792981	0.005918
20	6	0	-2.653690	3.101190	-0.002121
21	6	0	-3.590141	4.143171	-0.005458
22	6	0	-4.964667	3.877728	-0.005214
23	6	0	-5.437165	2.567418	-0.003221
24	6	0	5.436563	2.569242	0.003715
25	6	0	4.963610	3.879388	0.005293

26	6	0	3.588992	4.144363	0.007105
27	6	0	2.652901	3.102058	0.005703
28	6	0	6.015012	-0.614004	-0.009100
29	6	0	6.739173	-0.777494	1.189728
30	6	0	7.967631	-1.439515	1.154796
31	6	0	8.501831	-1.944802	-0.030769
32	6	0	7.771203	-1.768754	-1.206005
33	6	0	6.537459	-1.115592	-1.218851
34	6	0	5.792315	-0.936535	-2.521134
35	6	0	6.198164	-0.259370	2.502025
36	6	0	9.817861	-2.684042	-0.036612
37	6	0	-6.014749	-0.615669	0.009096
38	6	0	-6.733194	-0.783806	-1.193275
39	6	0	-7.958022	-1.451397	-1.163135
40	6	0	-8.496928	-1.955209	0.021690
41	6	0	-7.769751	-1.779972	1.198399
42	6	0	-6.538615	-1.120642	1.216057
43	6	0	-5.795342	-0.946443	2.520077
44	6	0	-6.184773	-0.270970	-2.504553
45	6	0	-9.838983	-2.646221	0.028311
46	1	0	1.427735	-3.300145	0.003941
47	1	0	3.825082	-2.646731	0.002572
48	1	0	-3.823960	-2.647997	0.002132
49	1	0	-1.426401	-3.300618	0.002351
50	1	0	-1.590846	3.316902	0.001474
51	1	0	-3.244080	5.171757	-0.006212
52	1	0	-5.668811	4.703515	-0.004766
53	1	0	-6.503255	2.363252	0.002359
54	1	0	6.502720	2.365464	-0.003234
55	1	0	5.667475	4.705410	0.003246
56	1	0	3.242582	5.172832	0.007474
57	1	0	1.589977	3.317393	0.003136
58	1	0	8.521115	-1.565229	2.082137
59	1	0	8.173589	-2.145606	-2.143071
60	1	0	4.831715	-1.459630	-2.514358
61	1	0	6.374163	-1.320596	-3.361330
62	1	0	5.573852	0.116847	-2.718207
63	1	0	6.849114	-0.540607	3.332217
64	1	0	5.200107	-0.655668	2.709412
65	1	0	6.108673	0.830747	2.503126
66	1	0	9.671033	-3.755251	0.141280
67	1	0	10.489320	-2.316790	0.743418
68	1	0	10.331673	-2.583630	-0.995712
69	1	0	-8.504149	-1.585766	-2.093728
70	1	0	-8.170707	-2.164664	2.132779
71	1	0	-4.836771	-1.473329	2.514793
72	1	0	-6.380496	-1.329069	3.358629
73	1	0	-5.573168	0.105816	2.718812
74	1	0	-6.089119	0.818584	-2.506752
75	1	0	-6.834639	-0.549651	-3.336452
76	1	0	-5.188252	-0.673175	-2.708194
77	1	0	-9.975222	-3.268461	-0.860127
78	1	0	-9.958507	-3.285422	0.906010
79	1	0	-10.658747	-1.919387	0.040770

No imaginary frequency.
Total energy = –1772.77268195 hartree.

Table S9. Cartesian Coordinates of **DFFu** (Open-Shell Singlet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.708971	-1.231793	-0.004113
2	6	0	-1.100202	0.140942	-0.002325
3	8	0	0.000021	0.968476	-0.002350
4	6	0	1.099996	0.140618	-0.004245

5	6	0	0.708364	-1.232003	-0.006010
6	6	0	-1.701371	-2.243872	-0.005000
7	6	0	-3.031081	-1.885498	-0.003473
8	6	0	-3.406951	-0.514569	0.000746
9	6	0	-2.410184	0.532456	-0.001450
10	6	0	2.410096	0.531739	-0.003247
11	6	0	3.406556	-0.515577	-0.006998
12	6	0	3.030286	-1.886412	-0.006725
13	6	0	1.700464	-2.244379	-0.007125
14	6	0	3.108244	1.811249	0.002061
15	6	0	4.504314	1.517033	0.003119
16	6	0	4.685452	0.077605	-0.003145
17	6	0	-4.685691	0.079001	0.000398
18	6	0	-4.504104	1.518395	-0.002189
19	6	0	-3.107956	1.812180	-0.002331
20	6	0	2.664373	3.125743	0.002390
21	6	0	3.612004	4.156675	0.003488
22	6	0	4.981045	3.873946	0.001769
23	6	0	5.438608	2.555565	0.000076
24	6	0	-5.438065	2.557208	0.005519
25	6	0	-4.980085	3.875445	0.007060
26	6	0	-3.610957	4.157757	0.004032
27	6	0	-2.663660	3.126532	0.000604
28	6	0	-5.990275	-0.626180	0.010114
29	6	0	-6.697128	-0.820274	-1.194137
30	6	0	-7.929293	-1.475419	-1.159045
31	6	0	-8.483336	-1.944496	0.032351
32	6	0	-7.769837	-1.737482	1.212869
33	6	0	-6.533573	-1.088492	1.225734
34	6	0	-5.806245	-0.878421	2.533545
35	6	0	-6.134045	-0.340804	-2.511685
36	6	0	-9.802915	-2.677450	0.039251
37	6	0	5.990082	-0.627557	-0.010970
38	6	0	6.689521	-0.831378	1.196638
39	6	0	7.918193	-1.492021	1.165010
40	6	0	8.478653	-1.954374	-0.026678
41	6	0	7.770249	-1.743091	-1.208821
42	6	0	6.536578	-1.088031	-1.225164
43	6	0	5.812799	-0.877248	-2.534831
44	6	0	6.117579	-0.362305	2.514095
45	6	0	9.824214	-2.638648	-0.034107
46	1	0	-1.411612	-3.288986	-0.008444
47	1	0	-3.804023	-2.647063	-0.007211
48	1	0	3.802980	-2.648239	-0.004351
49	1	0	1.410398	-3.289414	-0.006545
50	1	0	1.603834	3.352751	0.000820
51	1	0	3.278243	5.189302	0.004202
52	1	0	5.696107	4.690387	0.000440
53	1	0	6.502315	2.339227	-0.005072
54	1	0	-6.501837	2.341212	0.011832
55	1	0	-5.694892	4.692092	0.012005
56	1	0	-3.276877	5.190278	0.005922
57	1	0	-1.603044	3.353191	0.001333
58	1	0	-8.470202	-1.623732	-2.090472
59	1	0	-8.187828	-2.086016	2.154044
60	1	0	-4.854610	-1.417021	2.559243
61	1	0	-6.407763	-1.225781	3.375893
62	1	0	-5.573194	0.177015	2.700220
63	1	0	-6.799561	-0.596510	-3.338571
64	1	0	-5.157230	-0.788151	-2.717215
65	1	0	-5.989702	0.743250	-2.521591
66	1	0	-9.659399	-3.752834	-0.114545
67	1	0	-10.464005	-2.323672	-0.755754
68	1	0	-10.326799	-2.554443	0.990226
69	1	0	8.450507	-1.652957	2.099385
70	1	0	8.188208	-2.095391	-2.148509
71	1	0	4.862474	-1.417987	-2.564798
72	1	0	6.417842	-1.221264	-3.376025
73	1	0	5.577889	0.178000	-2.699939

74	1	0	5.968317	0.721003	2.529165
75	1	0	6.780257	-0.619536	3.342784
76	1	0	5.141749	-0.815087	2.712455
77	1	0	9.951946	-3.283999	0.838947
78	1	0	9.958424	-3.253368	-0.927079
79	1	0	10.640454	-1.907952	-0.016313

No imaginary frequency.
Total energy = –1772.78109203 hartree.

Table S10. Cartesian Coordinates of **DFFu**$^{\bullet+}$ at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.709591	-1.210176	0.006644
2	6	0	-1.097810	0.166408	0.011081
3	8	0	0.000082	0.993053	-0.002232
4	6	0	1.097933	0.166346	-0.015722
5	6	0	0.709626	-1.210217	-0.011811
6	6	0	-1.690783	-2.225642	0.007426
7	6	0	-3.023324	-1.866497	0.016870
8	6	0	-3.389896	-0.499254	0.034849
9	6	0	-2.408306	0.550321	0.019470
10	6	0	2.408459	0.550182	-0.023362
11	6	0	3.389984	-0.499460	-0.038444
12	6	0	3.023316	-1.866694	-0.021086
13	6	0	1.690748	-2.225746	-0.012440
14	6	0	3.120198	1.832185	-0.001129
15	6	0	4.511257	1.527529	0.014879
16	6	0	4.684714	0.089106	-0.013901
17	6	0	-4.684601	0.089433	0.011982
18	6	0	-4.511050	1.527881	-0.015806
19	6	0	-3.119952	1.832398	-0.001151
20	6	0	2.687842	3.143385	-0.014090
21	6	0	3.653269	4.167226	-0.012205
22	6	0	5.016648	3.876298	-0.010491
23	6	0	5.460072	2.550974	-0.003569
24	6	0	-5.459741	2.551399	0.005278
25	6	0	-5.016177	3.876670	0.013188
26	6	0	-3.652771	4.167473	0.013323
27	6	0	-2.687442	3.143538	0.012772
28	6	0	-5.969814	-0.626252	0.027825
29	6	0	-6.791734	-0.624636	-1.124554
30	6	0	-8.002931	-1.311266	-1.080393
31	6	0	-8.439287	-1.979556	0.065983
32	6	0	-7.616434	-1.954161	1.192980
33	6	0	-6.383763	-1.302698	1.198952
34	6	0	-5.561832	-1.281950	2.468650
35	6	0	-6.363823	0.049144	-2.408908
36	6	0	-9.749038	-2.724710	0.074786
37	6	0	5.969946	-0.626631	-0.027755
38	6	0	6.787219	-0.629216	1.127919
39	6	0	7.994727	-1.322692	1.088791
40	6	0	8.433539	-1.990607	-0.056866
41	6	0	7.613335	-1.964728	-1.185726
42	6	0	6.384445	-1.306320	-1.196807
43	6	0	5.564128	-1.287841	-2.467568
44	6	0	6.354634	0.041459	2.412331
45	6	0	9.765648	-2.694818	-0.078654
46	1	0	-1.399730	-3.269314	-0.007534
47	1	0	-3.796723	-2.626021	0.002326
48	1	0	3.796641	-2.626282	-0.006095
49	1	0	1.399629	-3.269405	0.002199
50	1	0	1.631834	3.386920	-0.032017
51	1	0	3.328684	5.202009	-0.020601
52	1	0	5.738157	4.685280	-0.019557

53	1	0	6.520062	2.321721	-0.017814
54	1	0	-6.519731	2.322259	0.020990
55	1	0	-5.737606	4.685697	0.024321
56	1	0	-3.328080	5.202215	0.022526
57	1	0	-1.631388	3.386940	0.029758
58	1	0	-8.624323	-1.329042	-1.971379
59	1	0	-7.947776	-2.449147	2.101312
60	1	0	-4.665854	-1.904524	2.392758
61	1	0	-6.144879	-1.657741	3.310279
62	1	0	-5.228203	-0.272772	2.724209
63	1	0	-7.022261	-0.234715	-3.230742
64	1	0	-5.344407	-0.224690	-2.694121
65	1	0	-6.390610	1.139646	-2.333627
66	1	0	-9.627941	-3.730434	-0.341948
67	1	0	-10.505339	-2.216144	-0.527257
68	1	0	-10.142145	-2.837672	1.086852
69	1	0	8.609789	-1.348510	1.983911
70	1	0	7.942873	-2.467421	-2.090501
71	1	0	4.669885	-1.913126	-2.393226
72	1	0	6.149510	-1.661461	-3.308552
73	1	0	5.227924	-0.279561	-2.723151
74	1	0	6.376608	1.132093	2.337809
75	1	0	7.013408	-0.239987	3.234711
76	1	0	5.336069	-0.237093	2.696179
77	1	0	9.995794	-3.150067	0.887150
78	1	0	9.795819	-3.478412	-0.838133
79	1	0	10.574139	-1.991186	-0.304414

No imaginary frequency.
Total energy = –1772.56449603 hartree.

Table S11. Cartesian Coordinates of **DFFu**$^{2-}$ at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.726160	-1.264510	0.009452
2	6	0	-1.109035	0.085114	0.014247
3	8	0	-0.000201	0.914614	-0.000122
4	6	0	1.107946	0.084179	-0.013149
5	6	0	0.723930	-1.265117	-0.006091
6	6	0	-1.728788	-2.258200	0.002154
7	6	0	-3.067425	-1.896818	0.011940
8	6	0	-3.453429	-0.531129	0.040107
9	6	0	-2.439541	0.499700	0.025632
10	6	0	2.438791	0.497655	-0.025419
11	6	0	3.451891	-0.534015	-0.039144
12	6	0	3.064674	-1.899334	-0.007947
13	6	0	1.725740	-2.259585	0.002989
14	6	0	3.108987	1.767174	-0.006220
15	6	0	4.532137	1.495667	0.005701
16	6	0	4.745810	0.084575	-0.019190
17	6	0	-4.746878	0.088422	0.018568
18	6	0	-4.532144	1.499311	-0.006741
19	6	0	-3.108748	1.769714	0.004955
20	6	0	2.637045	3.083493	-0.014809
21	6	0	3.538625	4.144663	-0.018040
22	6	0	4.925602	3.891319	-0.028058
23	6	0	5.421739	2.594889	-0.023947
24	6	0	-5.420785	2.599346	0.023045
25	6	0	-4.923547	3.895364	0.026422
26	6	0	-3.536383	4.147568	0.015522
27	6	0	-2.635702	3.085627	0.012563
28	6	0	-6.048460	-0.596073	0.034703
29	6	0	-6.974223	-0.445080	-1.033690
30	6	0	-8.212757	-1.089605	-0.989818
31	6	0	-8.586591	-1.911985	0.073161

32	6	0	-7.674880	-2.063932	1.119097
33	6	0	-6.433368	-1.425276	1.124456
34	6	0	-5.539501	-1.567911	2.332350
35	6	0	-6.609969	0.362486	-2.255868
36	6	0	-9.911958	-2.637803	0.077308
37	6	0	6.047682	-0.599391	-0.035281
38	6	0	6.970520	-0.452119	1.036431
39	6	0	8.207426	-1.099826	0.995843
40	6	0	8.583564	-1.919959	-0.068130
41	6	0	7.671896	-2.073823	-1.113790
42	6	0	6.432088	-1.431753	-1.122555
43	6	0	5.536844	-1.581095	-2.328665
44	6	0	6.600531	0.347723	2.261911
45	6	0	9.938414	-2.588107	-0.103908
46	1	0	-1.450190	-3.309849	-0.021083
47	1	0	-3.832031	-2.669107	-0.028827
48	1	0	3.828515	-2.672245	0.034845
49	1	0	1.446315	-3.310956	0.028705
50	1	0	1.566720	3.269777	-0.024768
51	1	0	3.173740	5.169392	-0.022118
52	1	0	5.621691	4.729368	-0.047890
53	1	0	6.496084	2.426734	-0.066026
54	1	0	-6.495230	2.432201	0.066250
55	1	0	-5.618947	4.733978	0.046477
56	1	0	-3.170647	5.171995	0.018969
57	1	0	-1.565214	3.270994	0.022196
58	1	0	-8.897937	-0.962540	-1.828062
59	1	0	-7.949624	-2.680671	1.974976
60	1	0	-4.660788	-2.187693	2.130952
61	1	0	-6.083716	-2.012287	3.172599
62	1	0	-5.149631	-0.593029	2.636727
63	1	0	-7.301334	0.158491	-3.080683
64	1	0	-5.592073	0.129146	-2.578608
65	1	0	-6.619712	1.439587	-2.063517
66	1	0	-9.837829	-3.637309	-0.372516
67	1	0	-10.673678	-2.090153	-0.487420
68	1	0	-10.292308	-2.775990	1.095159
69	1	0	8.888608	-0.979883	1.838424
70	1	0	7.943524	-2.696962	-1.965908
71	1	0	4.659430	-2.201750	-2.124490
72	1	0	6.081109	-2.027047	-3.168046
73	1	0	5.144873	-0.607978	-2.635938
74	1	0	6.609658	1.425825	2.075139
75	1	0	7.289470	0.140419	3.087934
76	1	0	5.581818	0.111453	2.579921
77	1	0	10.330638	-2.754364	0.904876
78	1	0	9.897053	-3.560887	-0.605409
79	1	0	10.683590	-1.984843	-0.640450

No imaginary frequency.
Total energy = –1772.84312680 hartree.

Table S12. Cartesian Coordinates of **1′** (Closed-Shell Singlet) at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.725823	-0.217100	0.000046
2	6	0	-3.520461	1.236315	0.000039
3	6	0	-2.206119	1.752090	0.000088
4	6	0	-1.114743	0.896717	0.000090
5	6	0	-1.320508	-0.549830	0.000074
6	6	0	-2.666216	-1.065093	0.000064
7	6	0	0.225517	1.382573	0.000080
8	6	0	1.320508	0.549835	0.000072
9	6	0	1.114742	-0.896711	0.000085
10	6	0	-0.225517	-1.382568	0.000078

11	6	0	2.666217	1.065096	0.000067
12	6	0	3.725823	0.217102	0.000038
13	6	0	3.520460	-1.236313	0.000027
14	6	0	2.206117	-1.752086	0.000077
15	6	0	5.169739	0.435734	0.000016
16	6	0	5.788835	-0.851506	-0.000044
17	6	0	4.758125	-1.859429	-0.000098
18	6	0	-5.169738	-0.435735	0.000026
19	6	0	-5.788837	0.851504	-0.000038
20	6	0	-4.758128	1.859429	-0.000116
21	6	0	5.944442	1.589119	0.000009
22	6	0	7.335972	1.470256	-0.000065
23	6	0	7.946755	0.209621	-0.000132
24	6	0	7.184403	-0.955320	-0.000119
25	6	0	-5.944438	-1.589121	0.000013
26	6	0	-7.335969	-1.470261	-0.000069
27	6	0	-7.946755	-0.209627	-0.000138
28	6	0	-7.184404	0.955315	-0.000121
29	1	0	-2.044976	2.826880	0.000119
30	1	0	-2.803910	-2.143307	0.000143
31	1	0	0.378319	2.459088	0.000114
32	1	0	-0.378320	-2.459083	0.000109
33	1	0	2.803913	2.143309	0.000136
34	1	0	2.044972	-2.826876	0.000109
35	1	0	4.931868	-2.928658	-0.000138
36	1	0	-4.931873	2.928657	-0.000159
37	1	0	5.483493	2.572508	0.000081
38	1	0	7.951684	2.363798	-0.000079
39	1	0	9.030101	0.142238	-0.000199
40	1	0	7.667241	-1.927865	-0.000169
41	1	0	-5.483488	-2.572510	0.000098
42	1	0	-7.951678	-2.363804	-0.000090
43	1	0	-9.030100	-0.142247	-0.000213
44	1	0	-7.667244	1.927860	-0.000167

No imaginary frequency.
Total energy = –1076.82786896 hartree.

Table S13. Cartesian Coordinates of **1′** (Open-Shell Triplet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.719497	-0.193425	-0.000015
2	6	0	-3.513306	1.249180	-0.000011
3	6	0	-2.235597	1.769026	-0.000008
4	6	0	-1.106888	0.894588	-0.000011
5	6	0	-1.318520	-0.534609	-0.000013
6	6	0	-2.656934	-1.047102	-0.000015
7	6	0	0.206486	1.381636	-0.000012
8	6	0	1.318520	0.534609	-0.000012
9	6	0	1.106888	-0.894588	-0.000011
10	6	0	-0.206486	-1.381637	-0.000013
11	6	0	2.656934	1.047102	-0.000012
12	6	0	3.719497	0.193424	-0.000012
13	6	0	3.513306	-1.249180	-0.000009
14	6	0	2.235597	-1.769026	-0.000008
15	6	0	5.164867	0.416809	-0.000005
16	6	0	5.799255	-0.868894	-0.000006
17	6	0	4.794705	-1.880251	-0.000022
18	6	0	-5.164867	-0.416809	-0.000007
19	6	0	-5.799254	0.868894	-0.000008
20	6	0	-4.794705	1.880250	-0.000029
21	6	0	5.928957	1.575238	0.000004
22	6	0	7.323319	1.470111	0.000010
23	6	0	7.949849	0.215123	0.000010
24	6	0	7.201623	-0.955887	0.000002

25	6	0	-5.928957	-1.575238	0.000003
26	6	0	-7.323319	-1.470111	0.000011
27	6	0	-7.949849	-0.215123	0.000010
28	6	0	-7.201623	0.955886	0.000002
29	1	0	-2.069976	2.842711	-0.000012
30	1	0	-2.798885	-2.124516	-0.000011
31	1	0	0.365816	2.456913	-0.000012
32	1	0	-0.365816	-2.456913	-0.000013
33	1	0	2.798885	2.124516	-0.000009
34	1	0	2.069976	-2.842711	-0.000012
35	1	0	4.972300	-2.948290	-0.000028
36	1	0	-4.972300	2.948290	-0.000036
37	1	0	5.459334	2.554345	0.000006
38	1	0	7.929134	2.370357	0.000016
39	1	0	9.033817	0.160840	0.000013
40	1	0	7.693739	-1.923657	-0.000001
41	1	0	-5.459334	-2.554345	0.000005
42	1	0	-7.929134	-2.370357	0.000017
43	1	0	-9.033817	-0.160840	0.000014
44	1	0	-7.693739	1.923657	-0.000003

No imaginary frequency.
Total energy = –1076.82153125 hartree.

Table S14. Cartesian Coordinates of **1′** (Open-Shell Singlet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.722731	-0.205707	0.000007
2	6	0	-3.517018	1.242401	0.000004
3	6	0	-2.218527	1.759839	-0.000000
4	6	0	-1.110999	0.896090	0.000002
5	6	0	-1.319670	-0.542210	0.000006
6	6	0	-2.661331	-1.056234	0.000007
7	6	0	0.216835	1.381950	0.000003
8	6	0	1.319670	0.542210	0.000004
9	6	0	1.110999	-0.896090	0.000003
10	6	0	-0.216836	-1.381950	0.000005
11	6	0	2.661331	1.056234	0.000003
12	6	0	3.722731	0.205707	0.000004
13	6	0	3.517018	-1.242401	0.000004
14	6	0	2.218527	-1.759839	0.000002
15	6	0	5.167391	0.427023	-0.000006
16	6	0	5.793243	-0.858689	-0.000005
17	6	0	4.772524	-1.868832	0.000018
18	6	0	-5.167391	-0.427023	-0.000005
19	6	0	-5.793243	0.858689	-0.000006
20	6	0	-4.772524	1.868832	0.000021
21	6	0	5.937186	1.583104	-0.000019
22	6	0	7.329729	1.470644	-0.000028
23	6	0	7.947442	0.212718	-0.000026
24	6	0	7.191156	-0.955100	-0.000015
25	6	0	-5.937186	-1.583104	-0.000019
26	6	0	-7.329729	-1.470644	-0.000031
27	6	0	-7.947442	-0.212718	-0.000030
28	6	0	-7.191155	0.955100	-0.000019
29	1	0	-2.055136	2.834136	0.000005
30	1	0	-2.800969	-2.134105	0.000002
31	1	0	0.373177	2.457846	0.000001
32	1	0	-0.373177	-2.457846	0.000006
33	1	0	2.800969	2.134105	-0.000002
34	1	0	2.055136	-2.834136	0.000008
35	1	0	4.946999	-2.937755	0.000027
36	1	0	-4.946999	2.937754	0.000031
37	1	0	5.471930	2.564403	-0.000022
38	1	0	7.941110	2.367149	-0.000037

39	1	0	9.031089	0.151307	-0.000031
40	1	0	7.677948	-1.925640	-0.000010
41	1	0	-5.471929	-2.564403	-0.000021
42	1	0	-7.941110	-2.367149	-0.000040
43	1	0	-9.031089	-0.151307	-0.000037
44	1	0	-7.677947	1.925640	-0.000015

No imaginary frequency.
Total energy = –1076.83045019 hartree.

Table S15. Cartesian Coordinates of **2** (Closed-Shell Singlet) at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.434803	1.681085	-0.000007
2	6	0	-2.867409	1.689401	0.000002
3	6	0	-3.575640	0.425343	0.000031
4	6	0	-2.809647	-0.813847	-0.000076
5	6	0	-1.455806	-0.803937	-0.000086
6	6	0	-0.703465	0.429401	-0.000023
7	6	0	-0.730821	2.916622	-0.000017
8	6	0	-1.467921	4.114594	-0.000066
9	6	0	-2.852065	4.110063	-0.000078
10	6	0	-3.547757	2.906648	-0.000038
11	6	0	0.703464	0.429402	-0.000002
12	6	0	1.434802	1.681085	-0.000000
13	6	0	0.730820	2.916622	0.000015
14	6	0	2.867409	1.689402	-0.000002
15	6	0	3.547757	2.906649	0.000027
16	6	0	2.852064	4.110064	0.000068
17	6	0	1.467920	4.114594	0.000064
18	6	0	1.455806	-0.803937	0.000028
19	6	0	2.809647	-0.813846	0.000019
20	6	0	3.575640	0.425344	-0.000025
21	6	0	3.771575	-1.918858	0.000030
22	6	0	5.066254	-1.331484	-0.000032
23	6	0	4.911653	0.115433	-0.000080
24	6	0	-4.911653	0.115432	0.000146
25	6	0	-5.066253	-1.331485	0.000096
26	6	0	-3.771574	-1.918859	-0.000048
27	6	0	3.621522	-3.297875	0.000088
28	6	0	4.766578	-4.102438	0.000079
29	6	0	6.039273	-3.527792	0.000015
30	6	0	6.200846	-2.139716	-0.000041
31	6	0	-6.200845	-2.139717	0.000146
32	6	0	-6.039272	-3.527792	0.000039
33	6	0	-4.766578	-4.102439	-0.000117
34	6	0	-3.621521	-3.297875	-0.000162
35	1	0	-0.931097	-1.749627	-0.000146
36	1	0	-0.959665	5.069221	-0.000113
37	1	0	-3.394180	5.050145	-0.000126
38	1	0	-4.632272	2.912383	-0.000058
39	1	0	4.632271	2.912384	0.000029
40	1	0	3.394179	5.050146	0.000108
41	1	0	0.959663	5.069222	0.000115
42	1	0	0.931097	-1.749627	0.000089
43	1	0	5.739454	0.813673	-0.000136
44	1	0	-5.739454	0.813671	0.000272
45	1	0	2.636706	-3.756053	0.000140
46	1	0	4.664450	-5.182683	0.000122
47	1	0	6.915106	-4.168971	0.000007
48	1	0	7.195446	-1.703952	-0.000094
49	1	0	-7.195444	-1.703951	0.000265
50	1	0	-6.915105	-4.168971	0.000073
51	1	0	-4.664449	-5.182683	-0.000207
52	1	0	-2.636706	-3.756054	-0.000291

No imaginary frequency.
Total energy = –1306.76002693 hartree.

Table S16. Cartesian Coordinates of **2′** (Open-Shell Triplet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.444382	1.648872	0.043529
2	6	0	-2.881027	1.663099	0.089041
3	6	0	-3.578250	0.417781	0.054594
4	6	0	-2.851227	-0.797161	-0.026296
5	6	0	-1.463710	-0.795956	-0.052864
6	6	0	-0.735271	0.399629	-0.003857
7	6	0	-0.735984	2.890133	0.045543
8	6	0	-1.463303	4.074093	0.129923
9	6	0	-2.861564	4.078898	0.190700
10	6	0	-3.562477	2.894756	0.163420
11	6	0	0.735271	0.399629	0.003859
12	6	0	1.444382	1.648872	-0.043524
13	6	0	0.735984	2.890133	-0.045537
14	6	0	2.881026	1.663099	-0.089037
15	6	0	3.562477	2.894757	-0.163414
16	6	0	2.861564	4.078899	-0.190692
17	6	0	1.463302	4.074094	-0.129915
18	6	0	1.463710	-0.795956	0.052864
19	6	0	2.851227	-0.797161	0.026297
20	6	0	3.578250	0.417782	-0.054591
21	6	0	3.819177	-1.896738	0.061736
22	6	0	5.120488	-1.308044	-0.003549
23	6	0	4.965485	0.115065	-0.075069
24	6	0	-4.965485	0.115064	0.075071
25	6	0	-5.120487	-1.308045	0.003548
26	6	0	-3.819177	-1.896738	-0.061737
27	6	0	3.677328	-3.272069	0.140981
28	6	0	4.827787	-4.074297	0.155838
29	6	0	6.102127	-3.503464	0.091553
30	6	0	6.259600	-2.119722	0.011393
31	6	0	-6.259599	-2.119723	-0.011395
32	6	0	-6.102126	-3.503465	-0.091557
33	6	0	-4.827786	-4.074297	-0.155843
34	6	0	-3.677328	-3.272069	-0.140985
35	1	0	-0.947981	-1.745386	-0.118571
36	1	0	-0.953832	5.028345	0.155282
37	1	0	-3.389405	5.024895	0.256070
38	1	0	-4.646133	2.902798	0.201882
39	1	0	4.646133	2.902799	-0.201876
40	1	0	3.389405	5.024896	-0.256061
41	1	0	0.953831	5.028345	-0.155273
42	1	0	0.947981	-1.745386	0.118570
43	1	0	5.780000	0.825513	-0.131415
44	1	0	-5.780000	0.825512	0.131418
45	1	0	2.695894	-3.734291	0.192215
46	1	0	4.726408	-5.152918	0.218066
47	1	0	6.977313	-4.144893	0.104471
48	1	0	7.252225	-1.682157	-0.037795
49	1	0	-7.252224	-1.682158	0.037794
50	1	0	-6.977313	-4.144894	-0.104476
51	1	0	-4.726407	-5.152918	-0.218073
52	1	0	-2.695894	-3.734291	-0.192220

No imaginary frequency.
Total energy = –1306.73410138 hartree.

Table S17. Cartesian Coordinates of **2′** (Open-Shell Singlet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.434783	1.681149	0.002351
2	6	0	-2.867402	1.689449	0.004794
3	6	0	-3.575628	0.425353	0.005773
4	6	0	-2.809598	-0.813828	0.004085
5	6	0	-1.455766	-0.803868	0.001810
6	6	0	-0.703455	0.429461	0.001025
7	6	0	-0.730815	2.916674	0.001247
8	6	0	-1.467950	4.114660	0.002524
9	6	0	-2.852065	4.110116	0.004899
10	6	0	-3.547755	2.906662	0.006030
11	6	0	0.703455	0.429461	-0.001023
12	6	0	1.434783	1.681149	-0.002346
13	6	0	0.730815	2.916675	-0.001241
14	6	0	2.867402	1.689449	-0.004790
15	6	0	3.547754	2.906662	-0.006024
16	6	0	2.852064	4.110116	-0.004891
17	6	0	1.467950	4.114660	-0.002517
18	6	0	1.455767	-0.803868	-0.001809
19	6	0	2.809599	-0.813828	-0.004084
20	6	0	3.575628	0.425354	-0.005771
21	6	0	3.771492	-1.918860	-0.005342
22	6	0	5.066153	-1.331545	-0.007736
23	6	0	4.911599	0.115417	-0.007777
24	6	0	-4.911599	0.115417	0.007779
25	6	0	-5.066153	-1.331546	0.007735
26	6	0	-3.771491	-1.918860	0.005340
27	6	0	3.621388	-3.297900	-0.004726
28	6	0	4.766405	-4.102477	-0.006439
29	6	0	6.039133	-3.527854	-0.008779
30	6	0	6.200747	-2.139802	-0.009467
31	6	0	-6.200746	-2.139803	0.009465
32	6	0	-6.039132	-3.527855	0.008775
33	6	0	-4.766404	-4.102477	0.006434
34	6	0	-3.621387	-3.297900	0.004722
35	1	0	-0.931102	-1.749582	0.000410
36	1	0	-0.959709	5.069292	0.001628
37	1	0	-3.394212	5.050177	0.005841
38	1	0	-4.632265	2.912409	0.007862
39	1	0	4.632265	2.912410	-0.007856
40	1	0	3.394212	5.050177	-0.005831
41	1	0	0.959709	5.069293	-0.001619
42	1	0	0.931103	-1.749582	-0.000411
43	1	0	5.739479	0.813552	-0.009248
44	1	0	-5.739479	0.813552	0.009251
45	1	0	2.636545	-3.756010	-0.002931
46	1	0	4.664297	-5.182723	-0.005954
47	1	0	6.914924	-4.169091	-0.010079
48	1	0	7.195348	-1.704049	-0.011272
49	1	0	-7.195347	-1.704049	0.011271
50	1	0	-6.914923	-4.169092	0.010074
51	1	0	-4.664297	-5.182724	0.005947
52	1	0	-2.636544	-3.756010	0.002927

No imaginary frequency.
Total energy = –1306.76002690 hartree.

Table S18. Cartesian Coordinates of **3′** (Closed-Shell Singlet) at the B3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.704956	1.526497	-0.001518

2	6	0	-1.439856	0.263838	-0.005724
3	6	0	1.439852	0.263836	-0.005726
4	6	0	0.704952	1.526496	-0.001522
5	6	0	-1.466325	2.753227	0.002808
6	6	0	-2.823728	2.767392	0.003363
7	6	0	-3.547413	1.540145	0.001596
8	6	0	-2.827021	0.277669	-0.000902
9	6	0	2.827018	0.277666	-0.000910
10	6	0	3.547408	1.540143	0.001597
11	6	0	2.823724	2.767391	0.003358
12	6	0	1.466320	2.753226	0.002797
13	6	0	3.855696	-0.785086	0.000375
14	6	0	5.125452	-0.126183	0.000118
15	6	0	4.904373	1.300252	0.000950
16	6	0	-4.904377	1.300251	0.000936
17	6	0	-5.125453	-0.126185	0.000096
18	6	0	-3.855696	-0.785085	0.000386
19	6	0	3.825538	-2.175739	0.004998
20	6	0	5.026361	-2.899396	0.006070
21	6	0	6.257371	-2.247695	0.003558
22	6	0	6.313512	-0.852295	0.001123
23	6	0	-6.313509	-0.852304	0.001093
24	6	0	-6.257361	-2.247704	0.003554
25	6	0	-5.026347	-2.899400	0.006101
26	6	0	-3.825529	-2.175737	0.005040
27	6	0	-0.674804	-0.955898	-0.017783
28	6	0	0.674797	-0.955899	-0.017784
29	1	0	-0.946059	3.700404	0.005230
30	1	0	-3.363010	3.709784	0.005748
31	1	0	3.363006	3.709782	0.005737
32	1	0	0.946055	3.700402	0.005203
33	1	0	5.683938	2.052465	0.001467
34	1	0	-5.683944	2.052462	0.001438
35	1	0	2.897004	-2.731453	0.009885
36	1	0	4.990318	-3.983867	0.009357
37	1	0	7.175419	-2.826345	0.004379
38	1	0	7.271157	-0.340387	0.000635
39	1	0	-7.271157	-0.340402	0.000583
40	1	0	-7.175407	-2.826358	0.004371
41	1	0	-4.990301	-3.983871	0.009408
42	1	0	-2.896988	-2.731442	0.009951
43	1	0	-1.196392	-1.900855	-0.030848
44	1	0	1.196381	-1.900857	-0.030850

No imaginary frequency.
Total energy = –1076.81399616 hartree.

Table S19. Cartesian Coordinates of **3′** (Open-Shell Triplet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.729082	1.521499	0.000518
2	6	0	-1.442047	0.274274	0.000329
3	6	0	1.442048	0.274276	0.000329
4	6	0	0.729082	1.521500	0.000518
5	6	0	-1.469825	2.731162	0.000713
6	6	0	-2.846258	2.746067	0.000727
7	6	0	-3.550806	1.531033	0.000523
8	6	0	-2.856254	0.291554	0.000307
9	6	0	2.856255	0.291558	0.000308
10	6	0	3.550805	1.531037	0.000522
11	6	0	2.846255	2.746070	0.000725
12	6	0	1.469822	2.731164	0.000712
13	6	0	3.883827	-0.770303	0.000117
14	6	0	5.165243	-0.117671	0.000216
15	6	0	4.957299	1.289085	0.000482

16	6	0	-4.957300	1.289079	0.000484
17	6	0	-5.165242	-0.117677	0.000217
18	6	0	-3.883825	-0.770308	0.000115
19	6	0	3.848160	-2.160020	-0.000177
20	6	0	5.046132	-2.888919	-0.000340
21	6	0	6.287497	-2.248176	-0.000220
22	6	0	6.353723	-0.858483	0.000054
23	6	0	-6.353722	-0.858491	0.000055
24	6	0	-6.287493	-2.248184	-0.000222
25	6	0	-5.046128	-2.888925	-0.000346
26	6	0	-3.848157	-2.160025	-0.000182
27	6	0	-0.678428	-0.936861	0.000213
28	6	0	0.678430	-0.936861	0.000213
29	1	0	-0.953268	3.681194	0.000863
30	1	0	-3.381762	3.690572	0.000888
31	1	0	3.381758	3.690577	0.000884
32	1	0	0.953264	3.681195	0.000861
33	1	0	5.730246	2.047511	0.000614
34	1	0	-5.730247	2.047504	0.000616
35	1	0	2.916497	-2.710354	-0.000318
36	1	0	5.002763	-3.973323	-0.000572
37	1	0	7.199094	-2.836557	-0.000347
38	1	0	7.313971	-0.351395	0.000144
39	1	0	-7.313969	-0.351404	0.000147
40	1	0	-7.199090	-2.836565	-0.000349
41	1	0	-5.002758	-3.973329	-0.000580
42	1	0	-2.916494	-2.710357	-0.000326
43	1	0	-1.194872	-1.885420	0.000154
44	1	0	1.194875	-1.885418	0.000154

No imaginary frequency.
Total energy = –1076.81285948 hartree.

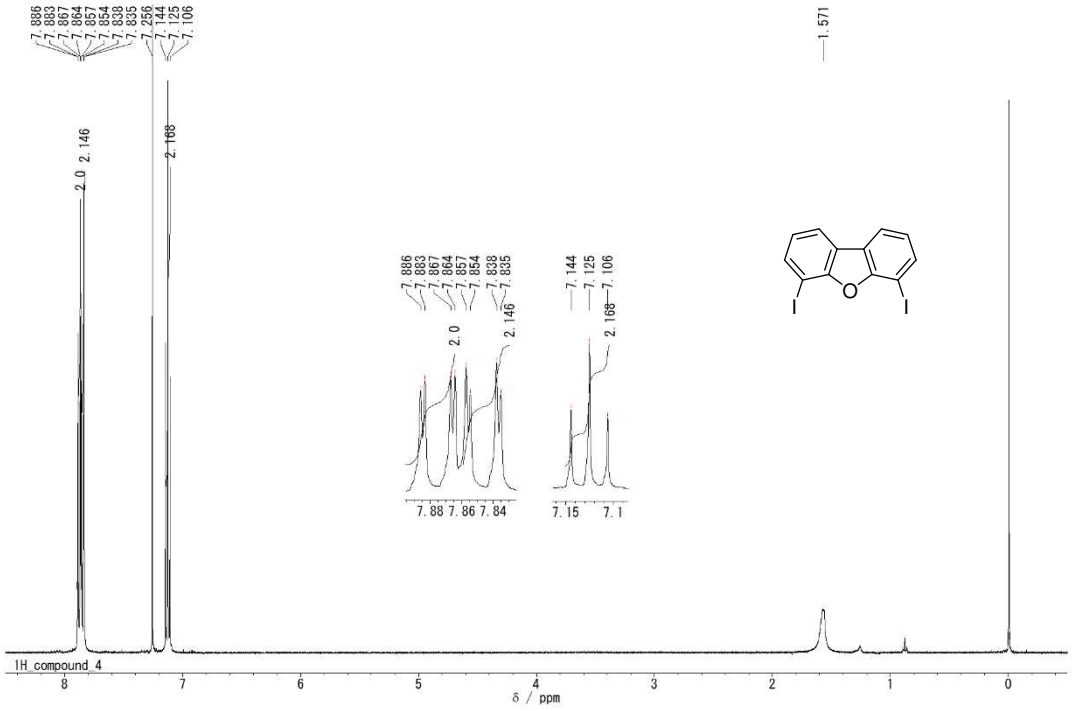
Table S20. Cartesian Coordinates of **3′** (Open-Shell Singlet) at the UB3LYP/6-311G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.718672	1.525912	0.000528
2	6	0	-1.439701	0.272820	0.000339
3	6	0	1.439701	0.272822	0.000339
4	6	0	0.718670	1.525913	0.000527
5	6	0	-1.468629	2.742659	0.000714
6	6	0	-2.836451	2.756806	0.000721
7	6	0	-3.549205	1.535887	0.000518
8	6	0	-2.843339	0.287865	0.000307
9	6	0	2.843339	0.287868	0.000307
10	6	0	3.549203	1.535892	0.000517
11	6	0	2.836448	2.756810	0.000719
12	6	0	1.468626	2.742661	0.000713
13	6	0	3.870936	-0.777748	0.000101
14	6	0	5.146515	-0.124209	0.000224
15	6	0	4.932423	1.293968	0.000481
16	6	0	-4.932424	1.293962	0.000482
17	6	0	-5.146514	-0.124215	0.000224
18	6	0	-3.870935	-0.777752	0.000100
19	6	0	3.835650	-2.167178	-0.000202
20	6	0	5.034607	-2.895614	-0.000351
21	6	0	6.270660	-2.251408	-0.000208
22	6	0	6.333305	-0.857961	0.000076
23	6	0	-6.333303	-0.857969	0.000076
24	6	0	-6.270656	-2.251415	-0.000211
25	6	0	-5.034602	-2.895619	-0.000354
26	6	0	-3.835646	-2.167182	-0.000205
27	6	0	-0.677070	-0.942472	0.000218
28	6	0	0.677072	-0.942471	0.000218
29	1	0	-0.950404	3.691489	0.000862

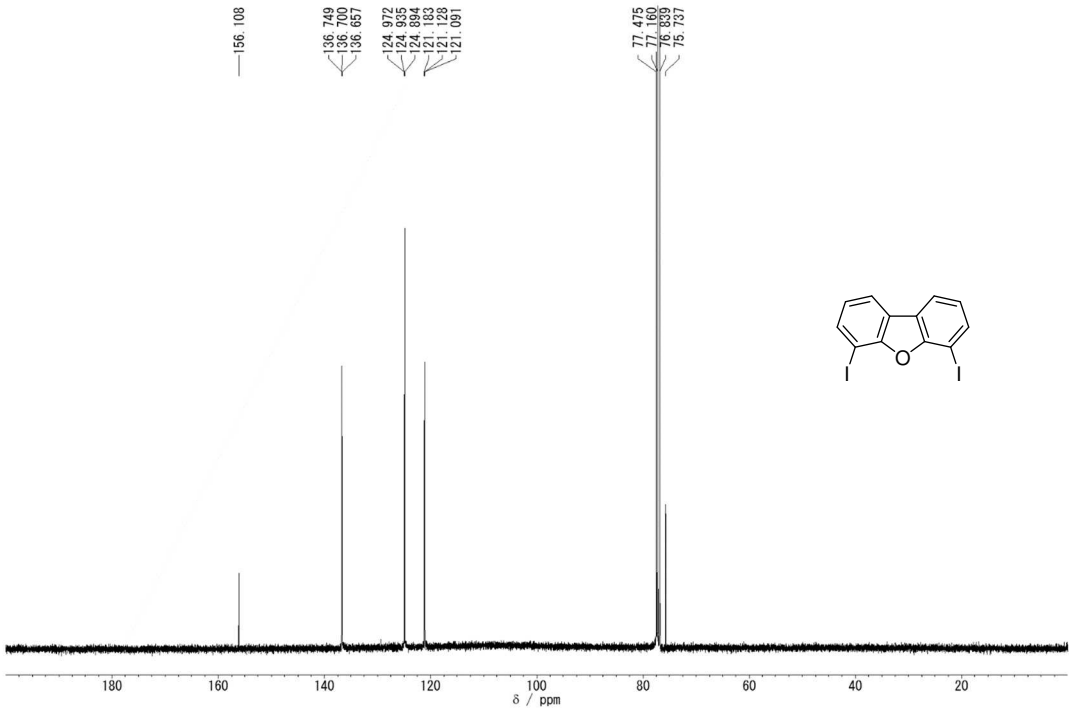
30	1	0	-3.374108	3.700103	0.000876
31	1	0	3.374104	3.700107	0.000874
32	1	0	0.950400	3.691490	0.000860
33	1	0	5.708930	2.049039	0.000614
34	1	0	-5.708932	2.049031	0.000616
35	1	0	2.904864	-2.719007	-0.000350
36	1	0	4.993122	-3.979994	-0.000585
37	1	0	7.185000	-2.835708	-0.000327
38	1	0	7.292854	-0.349605	0.000176
39	1	0	-7.292853	-0.349613	0.000176
40	1	0	-7.184996	-2.835716	-0.000330
41	1	0	-4.993116	-3.980000	-0.000590
42	1	0	-2.904860	-2.719010	-0.000354
43	1	0	-1.196178	-1.889177	0.000154
44	1	0	1.196181	-1.889176	0.000154

No imaginary frequency.
Total energy = –1076.81837063 hartree.

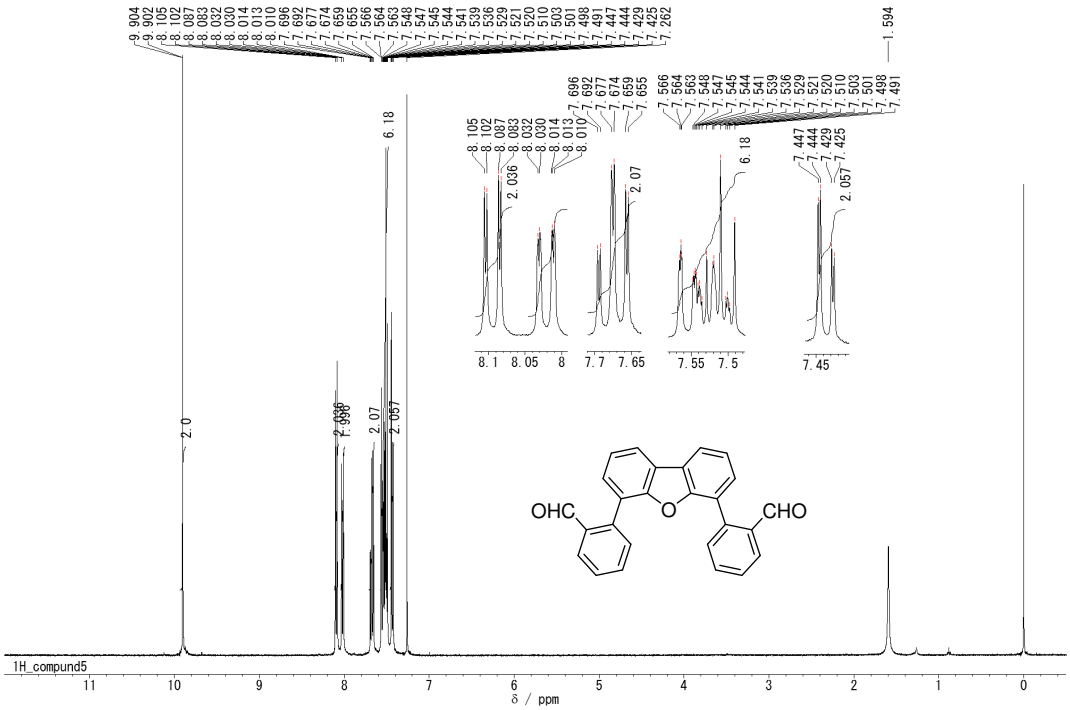
7. ^{1}H and ^{13}C NMR spectral data



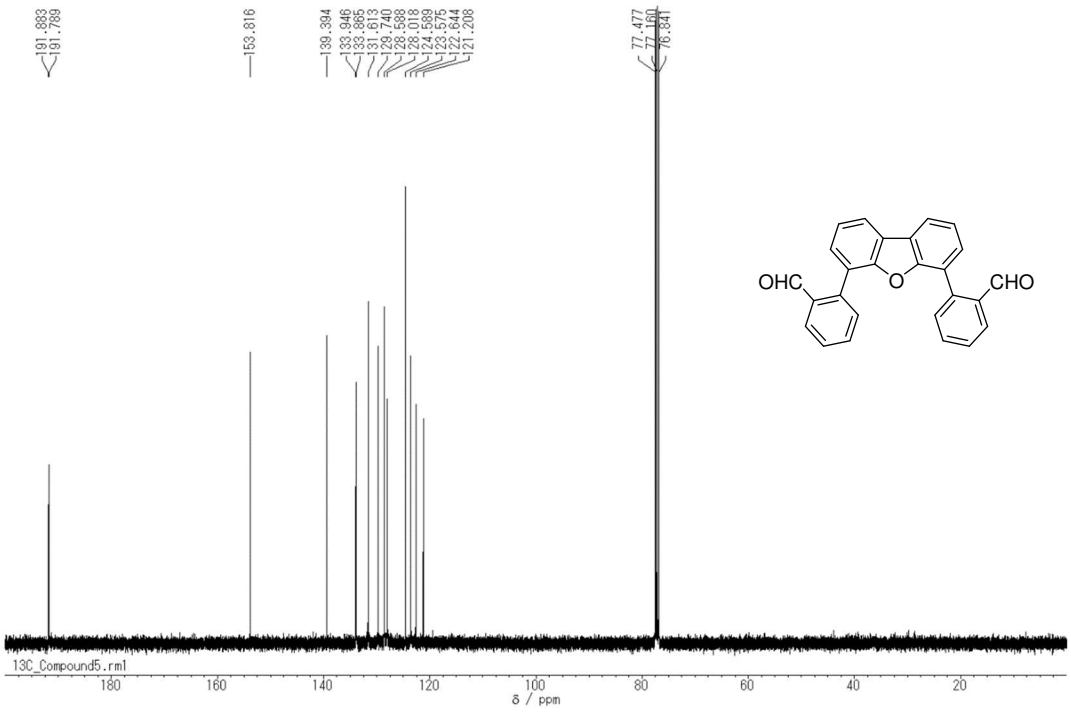
^{1}H NMR spectrum of **5** in $CDCl_3$ solution (400 MHz).



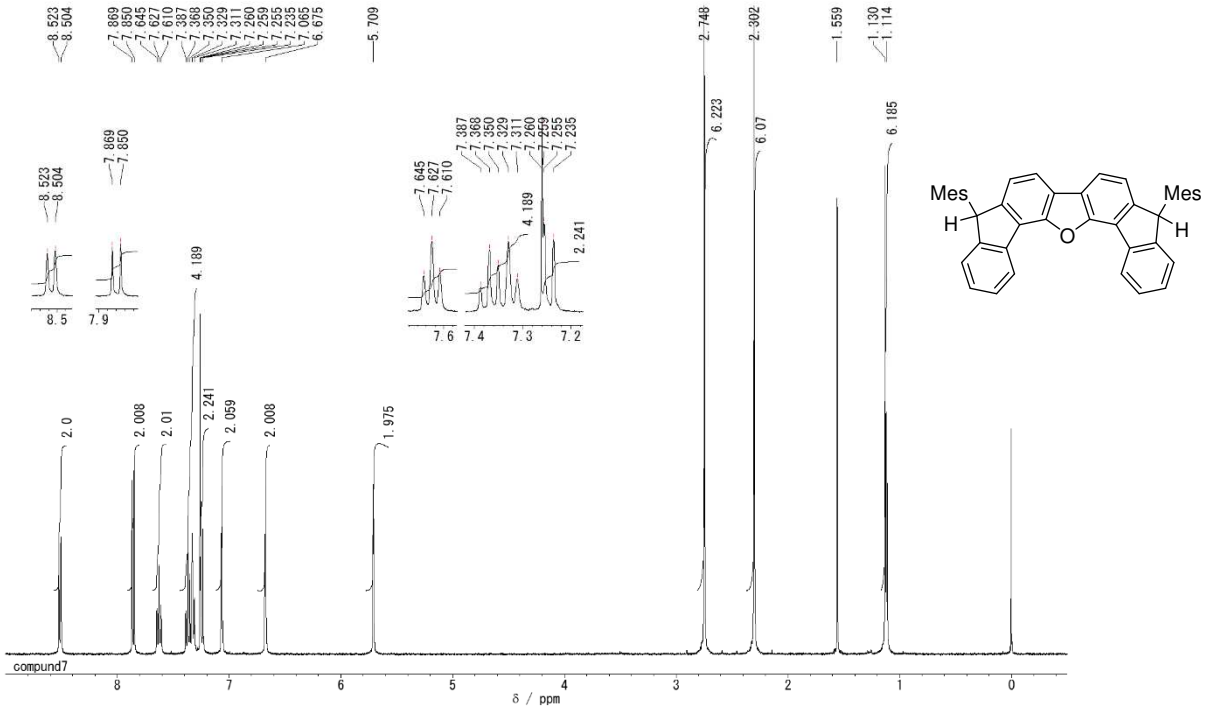
^{13}C NMR spectrum of **5** in $CDCl_3$ solution (100 MHz).



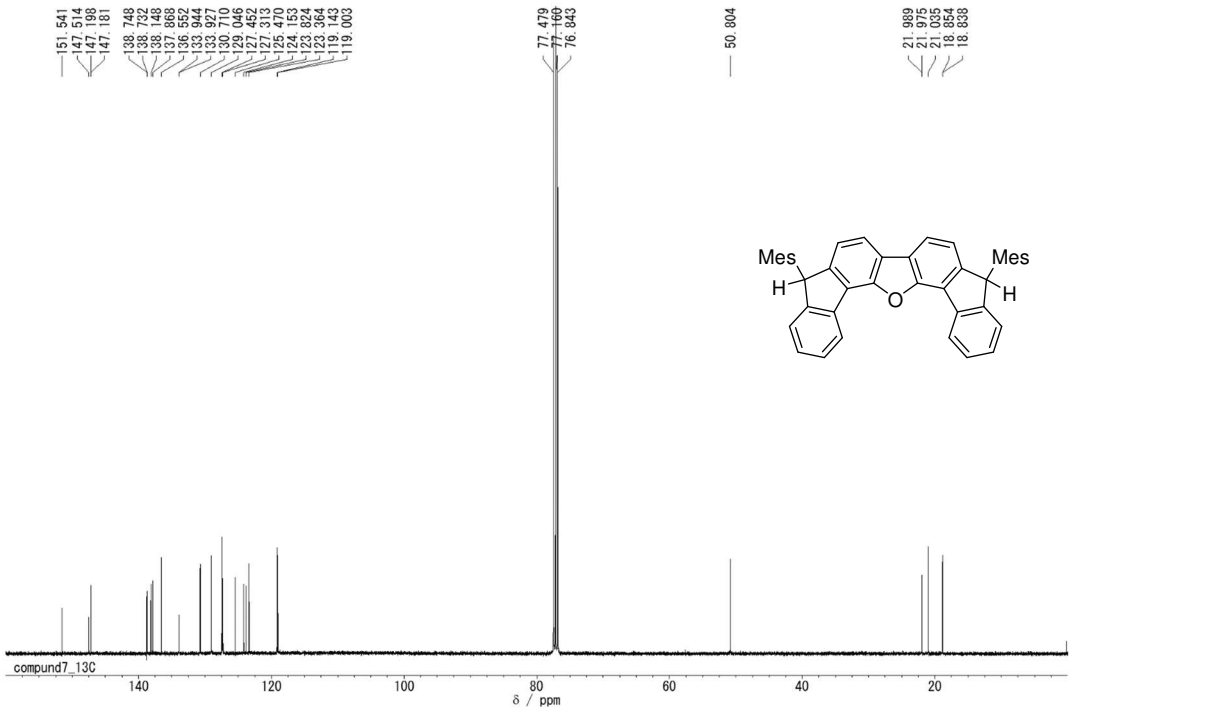
^{1}H NMR spectrum of **6** in $CDCl_3$ solution (400 MHz).



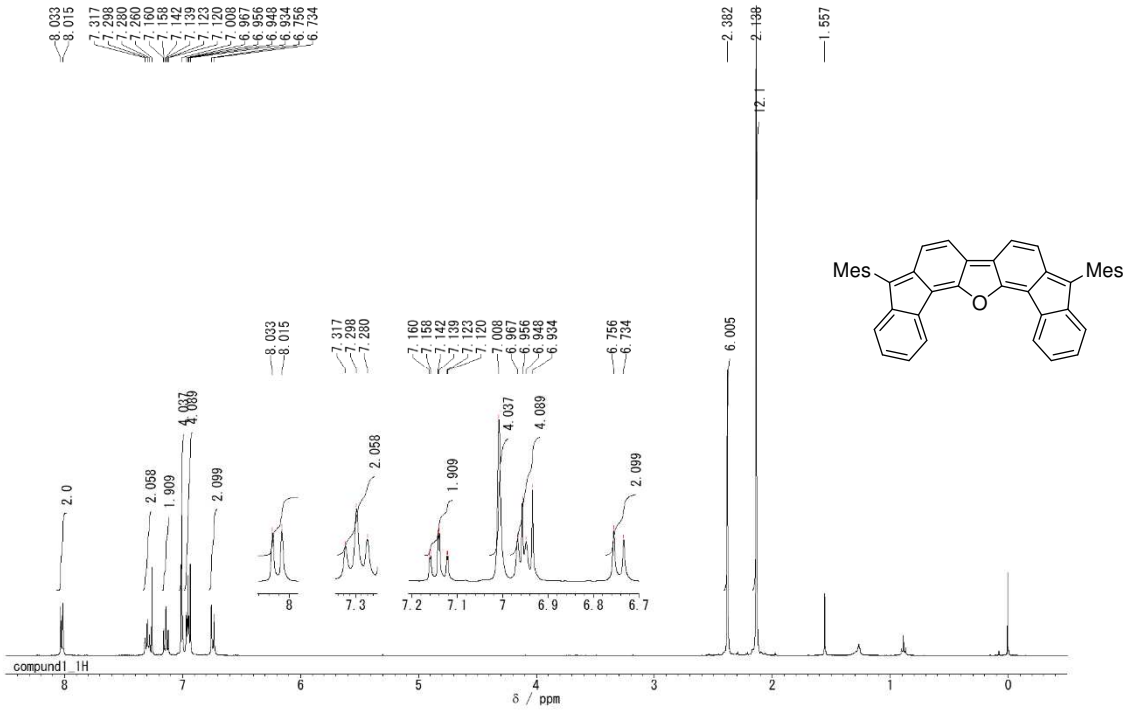
^{13}C NMR spectrum of **6** in $CDCl_3$ solution (100 MHz).



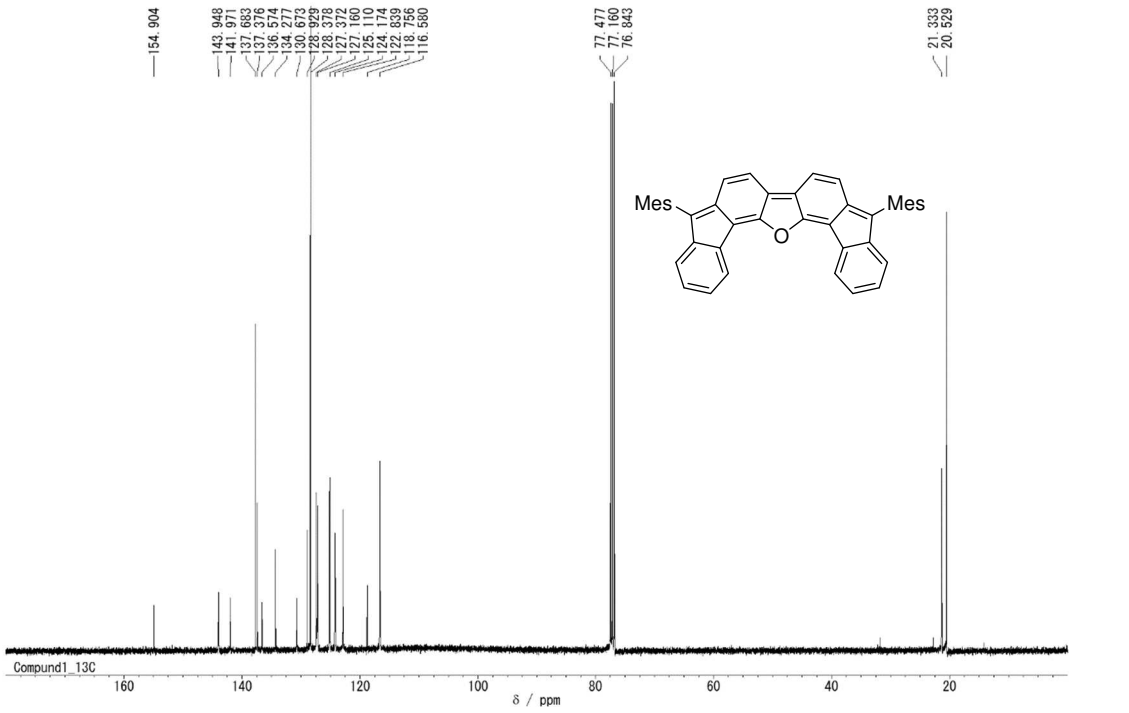
^{1}H NMR spectrum of **7** in $CDCl_3$ solution (400 MHz).



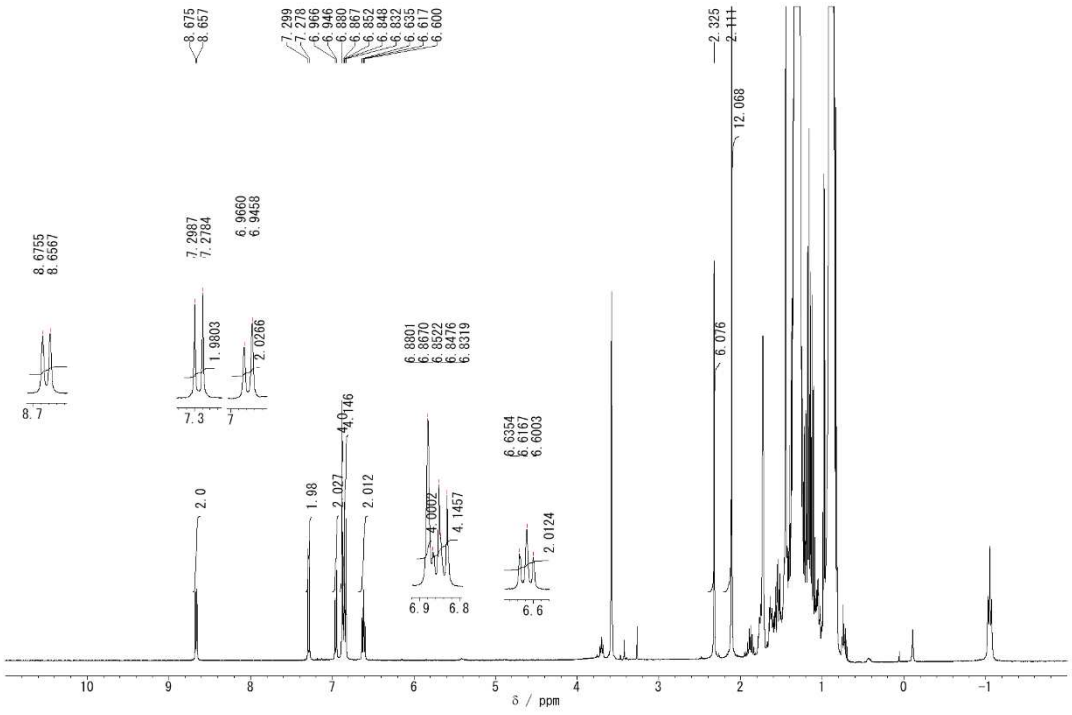
^{13}C NMR spectrum of **7** in $CDCl_3$ solution (100 MHz).



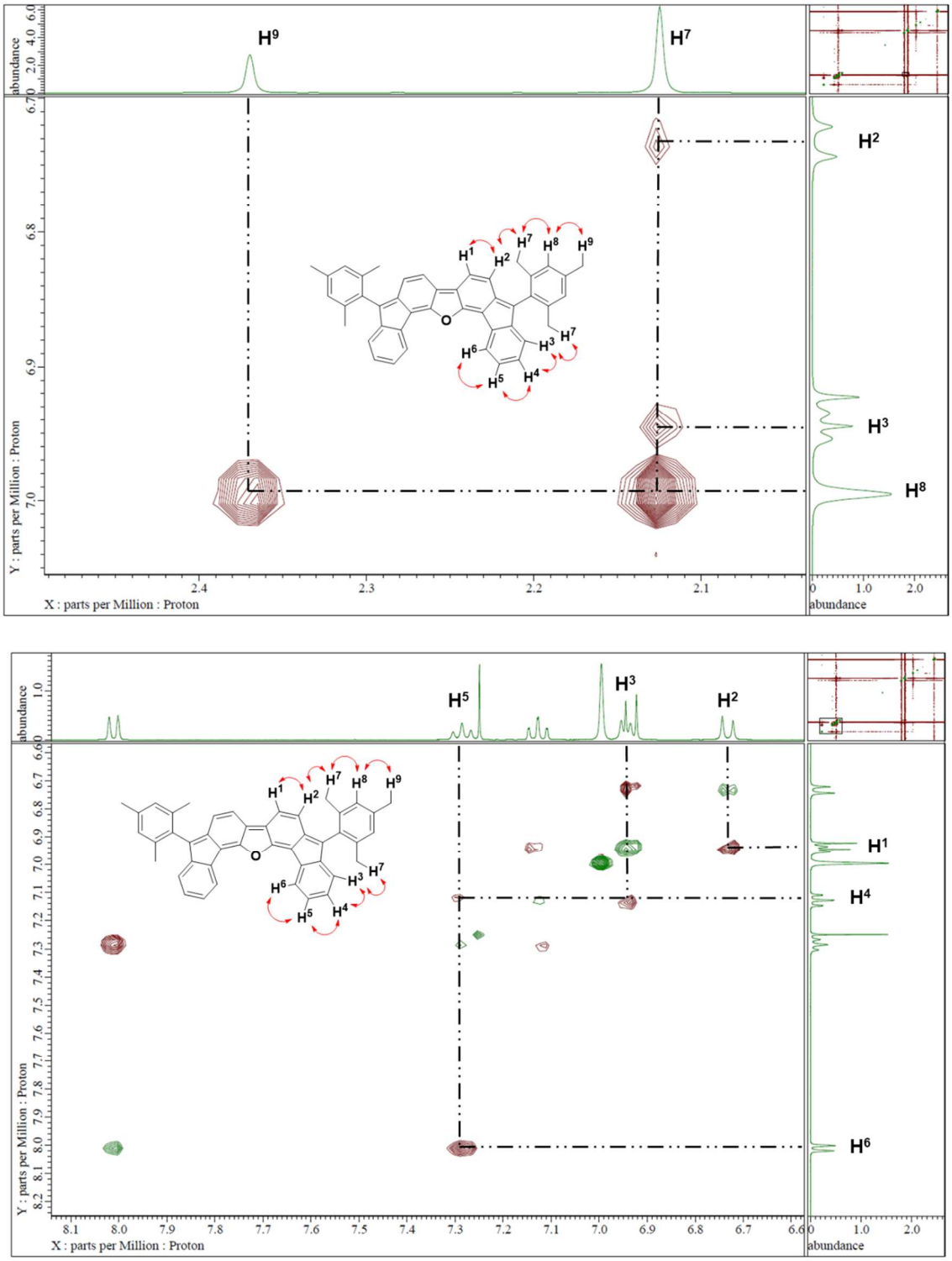
^{1}H NMR spectrum of **DFFu** in $CDCl_3$ solution (400 MHz).



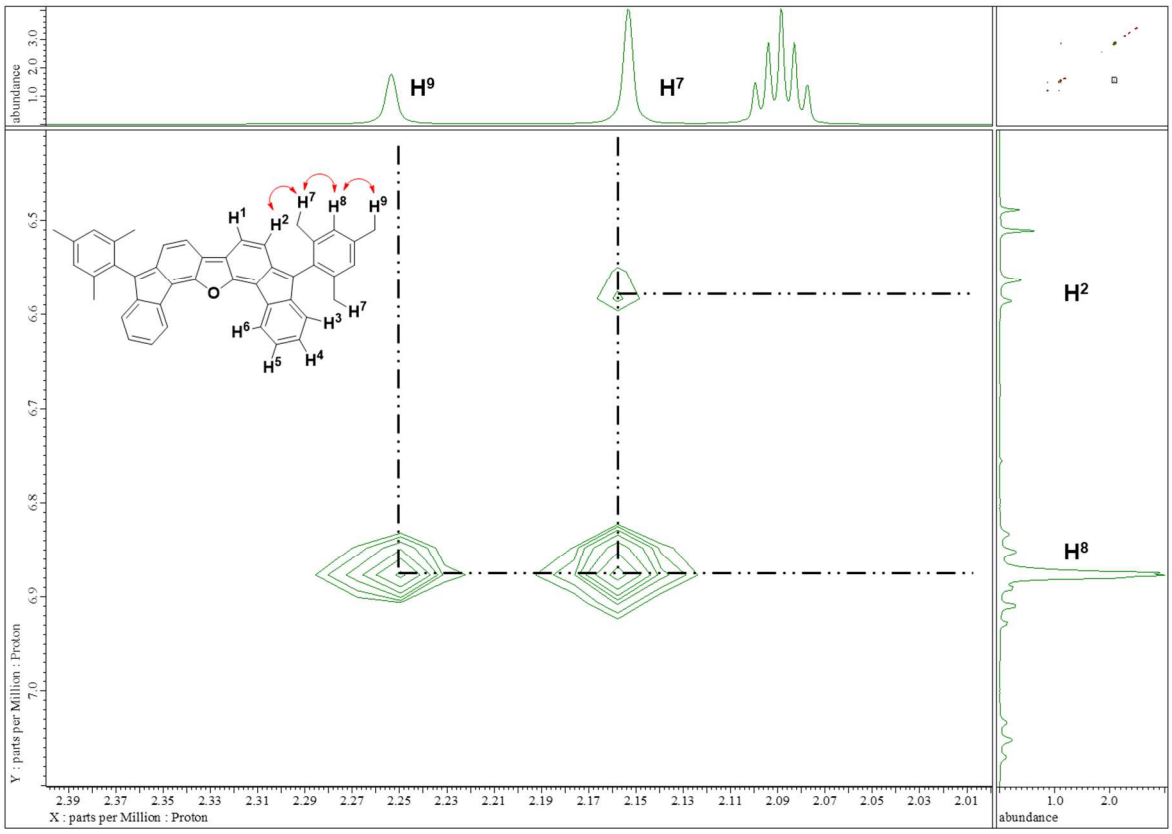
^{13}C NMR spectrum of **DFFu** in $CDCl_3$ solution (100 MHz).



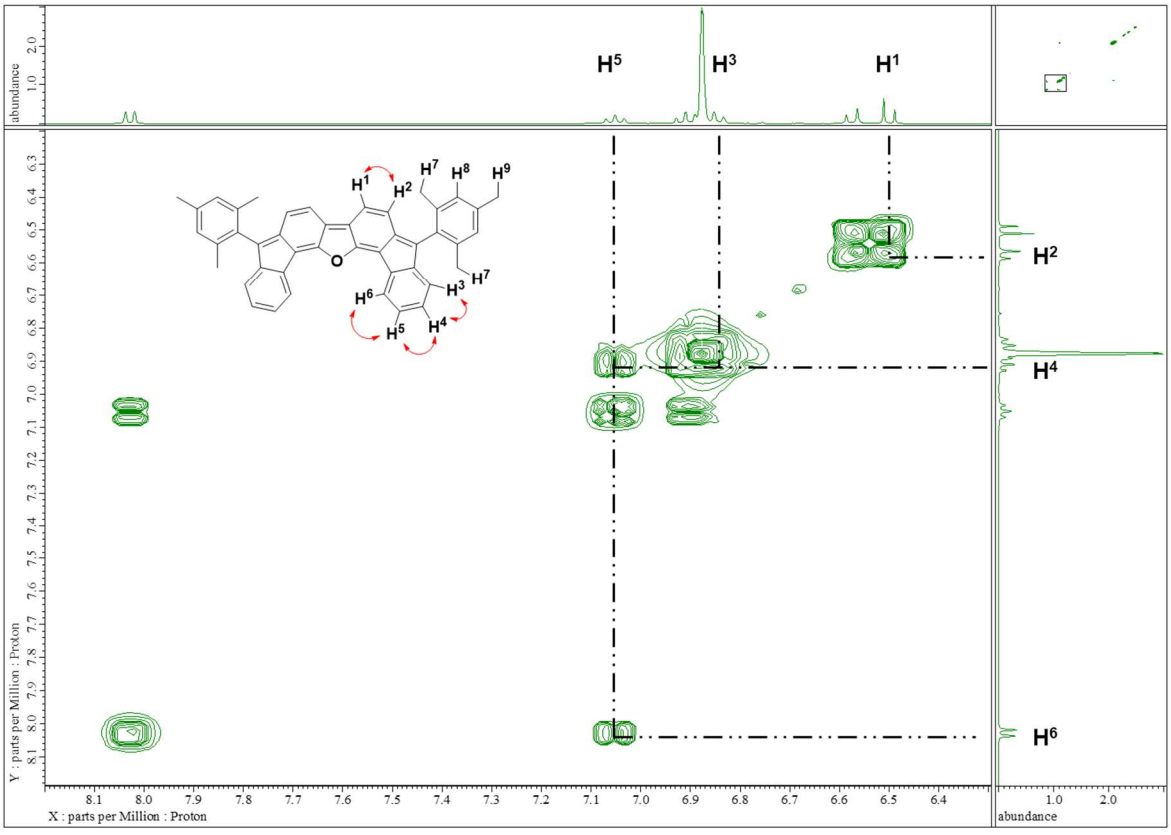
^{1}H NMR spectrum of **DFFu^{2-}** in THF-d_8 solution (400 MHz). Most aliphatic signals are due to an excess amount of *n*-BuLi in hexane.



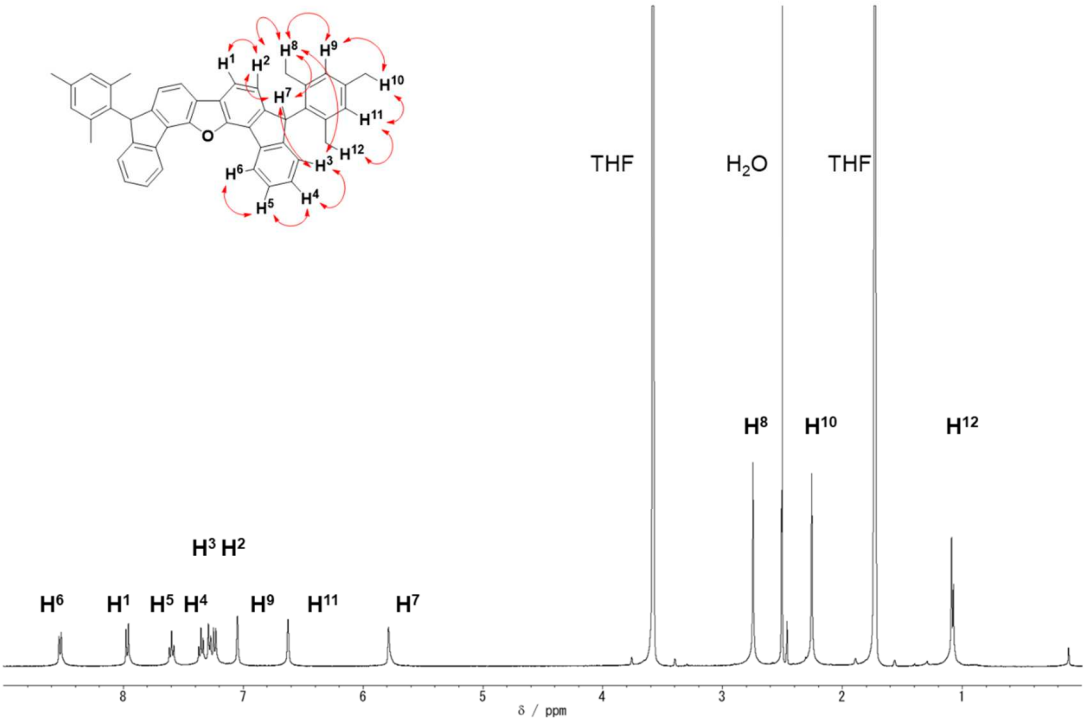
NOESY spectrum of **DFFu** in $CDCl_3$ solution.



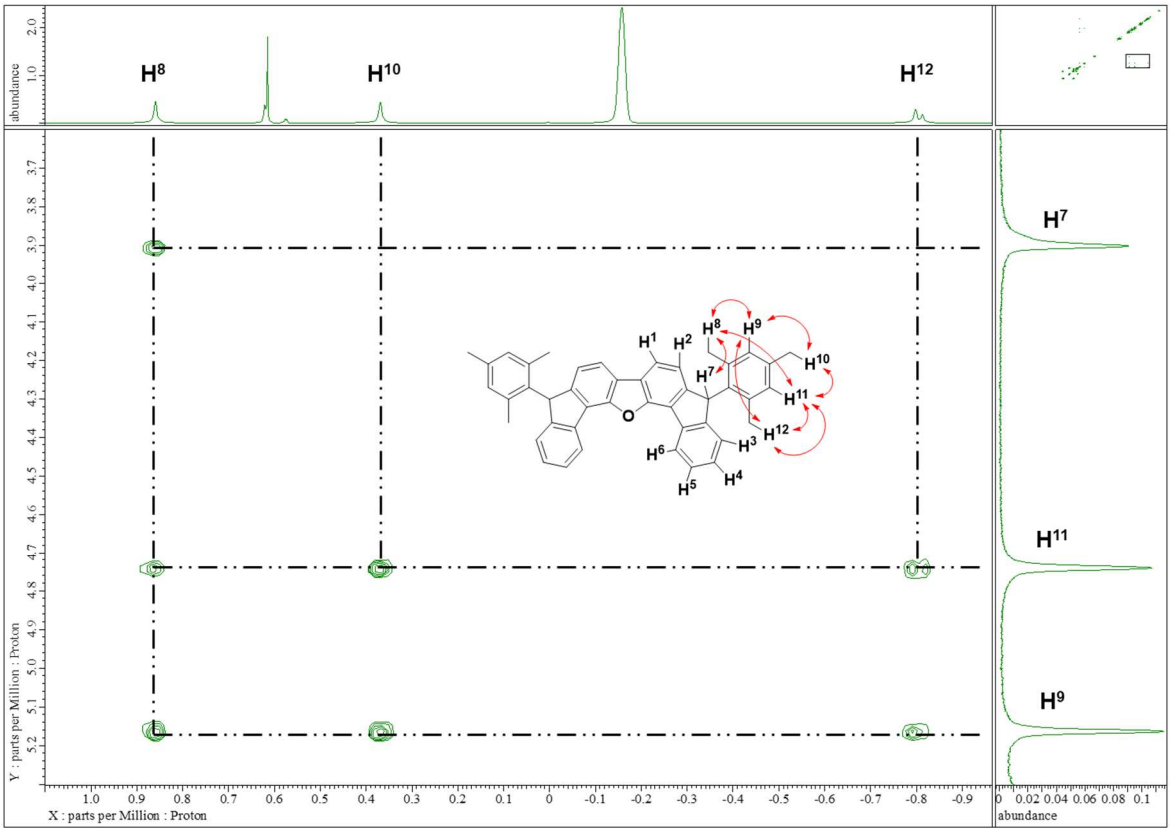
NOESY spectrum of **DFFu** in *p*-xylene-d_{10} solution.



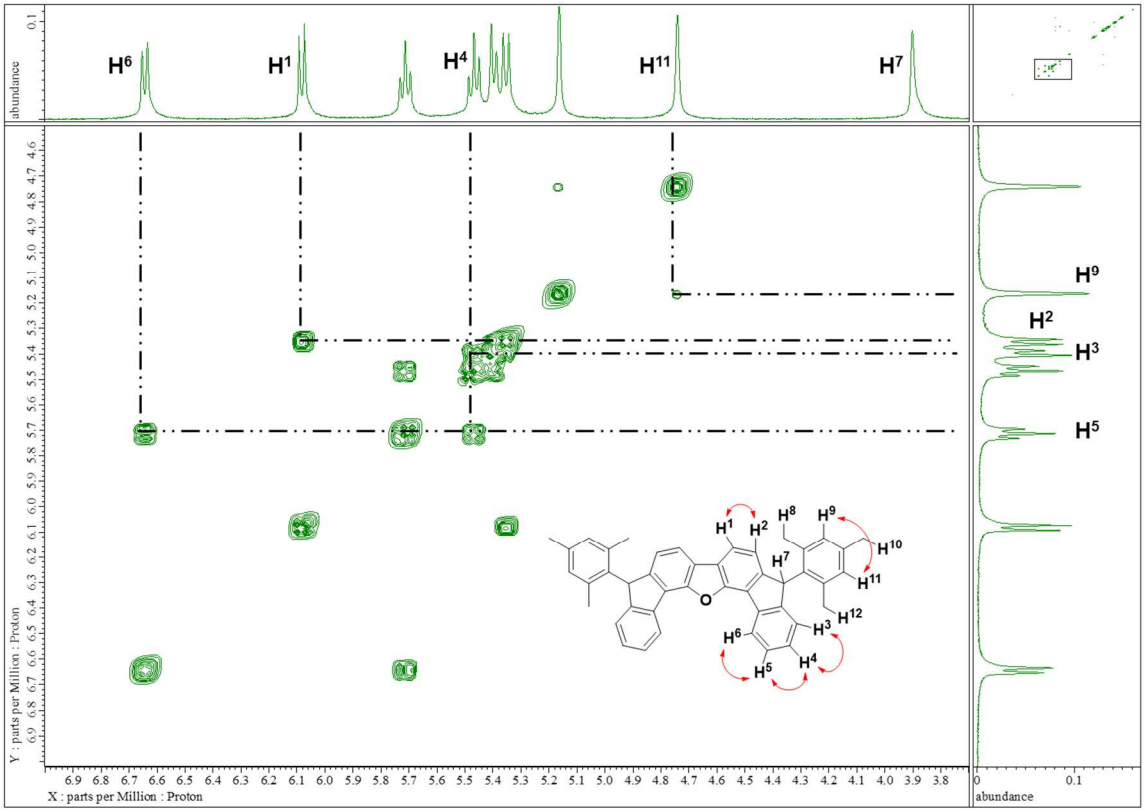
COSY spectrum of **DFFu** in *p*-xylene-d_{10} solution.



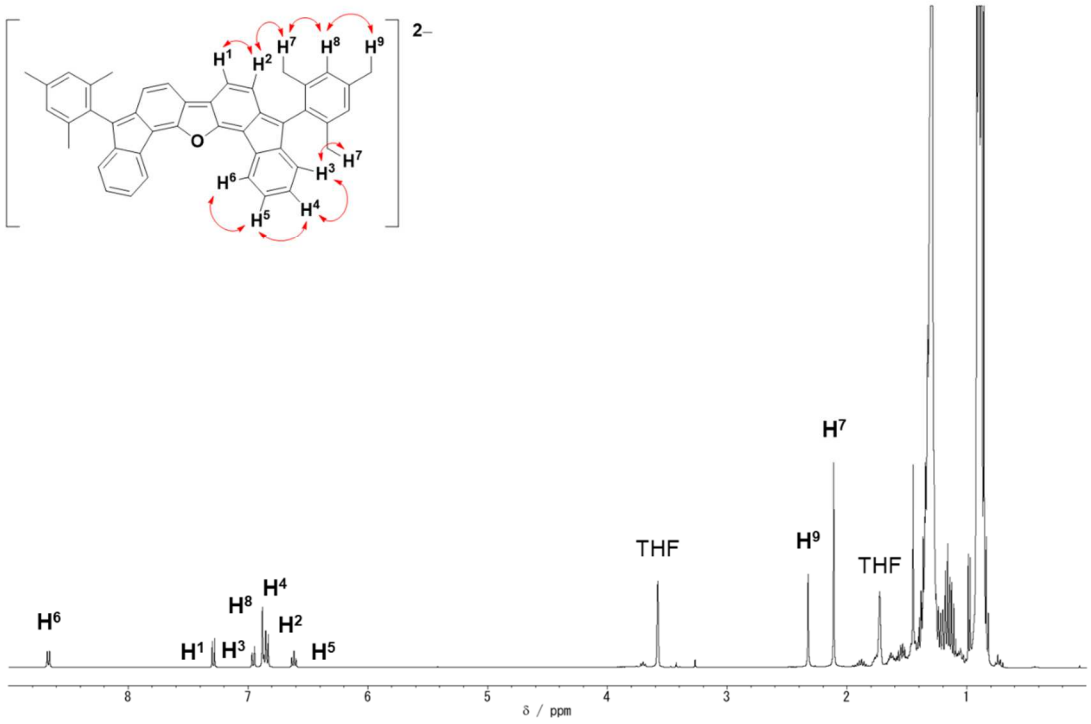
^{1}H NMR spectrum of **7** in THF-d_8 solution.
All the signals were fully assigned by 1D NOE and ^{1}H-^{1}H COSY experiments.



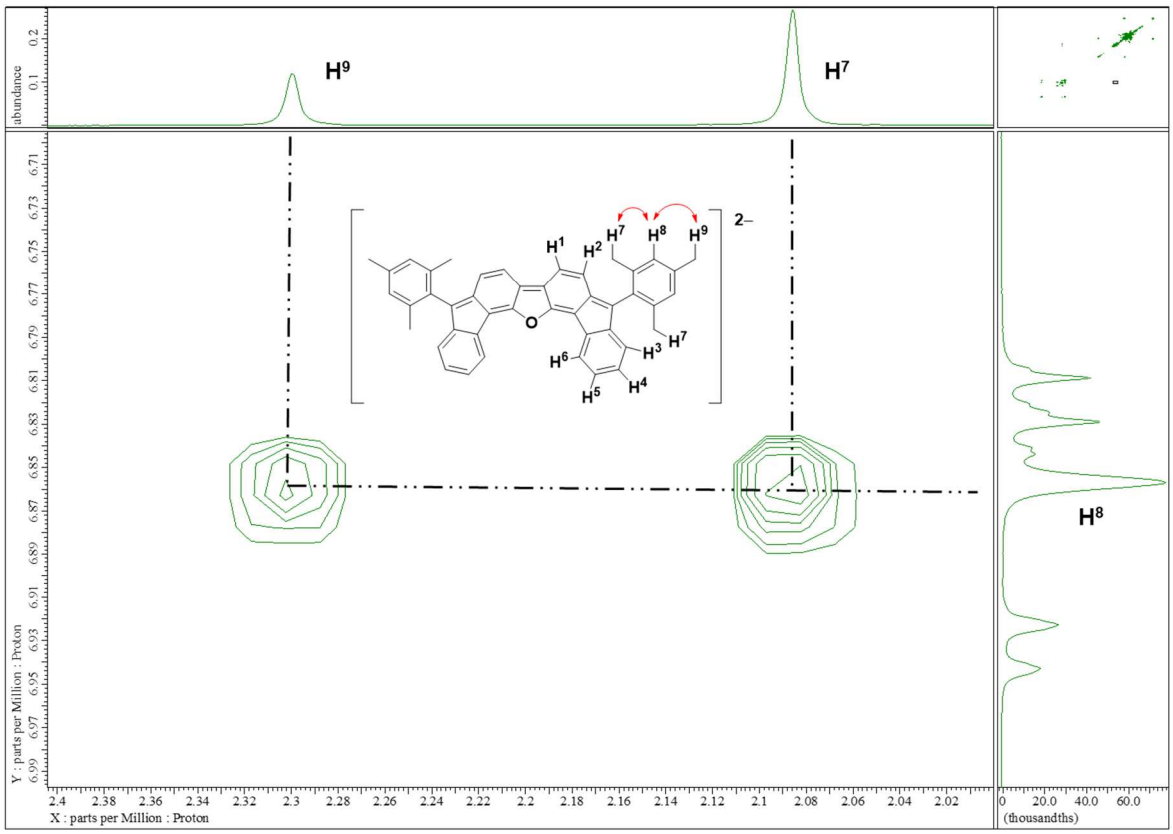
^{1}H-^{1}H COSY spectrum of **7** in THF-d_8 solution.



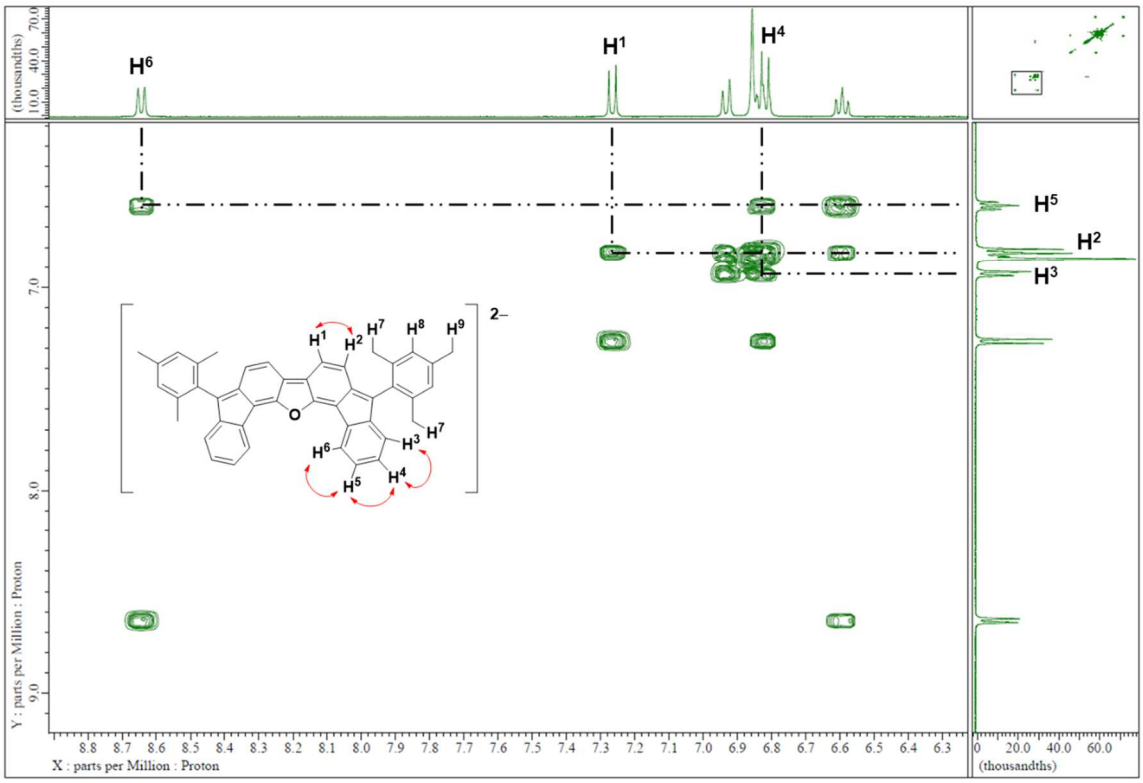
^{1}H-^{1}H COSY spectrum of **7** in THF-d_8 solution.



Fully assigned ^{1}H NMR spectrum of **DFFu**$^{2-}$ in $CDCl_3$ solution.
All the signals were fully assigned by 1D NOE and ^{1}H-^{1}H COSY experiments.



^{1}H-^{1}H COSY spectrum of **DFFu**$^{2-}$ in THF-d_8 solution.



^{1}H-^{1}H COSY spectrum of **DFFu**$^{2-}$ in THF-d_8 solution.

8. References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Revision D.01; Gaussian Inc.: Wallingford CT, 2009.
2. Herges, R.; Geuenich, D. *J. Phys. Chem. A* **2001**, *105*, 3214.
3. Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.
4. K. Sbargoud, M. Mamada, J. Marrot, S. Tokito, A. Yassar, M. Frigoli, *Chem. Sci.* **2015**, *6*, 3402.
5. M. A. Majewski, P. J. Chmielewski, A. Chien, Y. Hong, T. Lis, M. Witwicki, D. Kim, P. M. Zimmerman, M. Stępień, *Chem. Sci.* **2019**, *10*, 3413.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.
7. Sheldrick, G. *Acta Crystallogr., Sect. A* **2015**, *71*, 3.
8. Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015**, *71*, 3.
9. Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ortiz, R. P.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. *Nat. Chem*. **2016**, *8*, 753.
10. Yamaguchi, K. *Chem. Phys. Lett.* **1975**, *33*, 330.