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Electronic supplementary information

Chemical transformations of push–pull fluorenones: push–pull dibenzodicyanofulvenes as well as fluorenone– and dibenzodicyanofulvene–tetracyanobutadiene conjugates

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1. General experimental methods

Commercially available reagents were used as received. THF was distilled from Na and benzophenone. 4-Ethynyl-*N*,*N*-diphenylaniline (**3e**) was prepared according to the literature procedures.[1] Column chromatography were carried out with SiO_2 or Al_2O_3. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254}. Melting points (Mp) were measured with a hot-stage apparatus and are uncorrected. Analytical sample was obtained by recycling gel-permeation chromatography with UV detectors using 1H and 2H polystyrene columns. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 400 or 600 MHz for ^{1}H and 75 or 150 MHz for ^{13}C. Residual and deuterated solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference, respectively ($CDCl_3$, ^{1}H: δ 7.26; ^{13}C: δ 77.16). Variable-temperature NMR spectra were obtained by No-D (no-deuterium proton) NMR method with 1,1,2,2-tetrachloroethane.[2] Mass spectral analyses were performed with a MALDI-TOF or FT mode. Electronic absorption and fluorescence spectra were recorded at 10^{-5}–10^{-6} mol L^{-1}. Cyclic voltammetry and differential pulse voltammetry were performed by using a cell equipped with a platinum as working electrode, a platinum wire as counter electrodes, and Ag/Ag^+ as a referential electrode. All electrochemical measurements were performed in *o*-DCB solution (*ca.* 5×10^{-4} mol L^{-1}) containing 0.1 mol L^{-1} $[(n\text{-Bu})_4N][PF_6]$ at RT. Transient absorption spectra were measured by using ns laser flash photolysis system.[3] The third harmonic (355 nm) of a nanosecond Nd^{3+}: YAG laser (pulse width 6 ns) was utilized for the excitation source. The transient signal was recorded on a digital storage oscilloscope (500 MHz 2G Samples/s), and transferred to a personal computer for analyses.

2. Chemical structures of push–pull chromophores in the present work

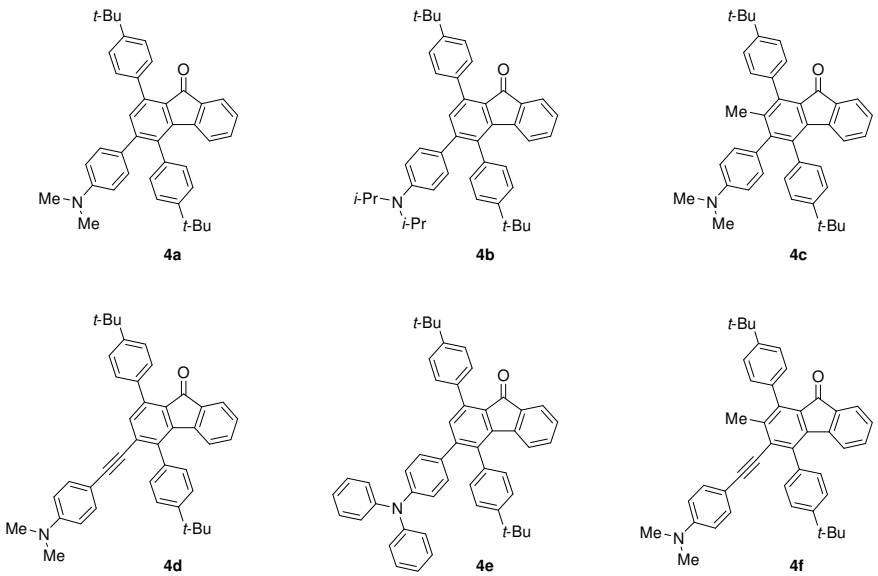


Figure S1. Chemical structures of push–pull fluorenones (FOs) **4a–f**.

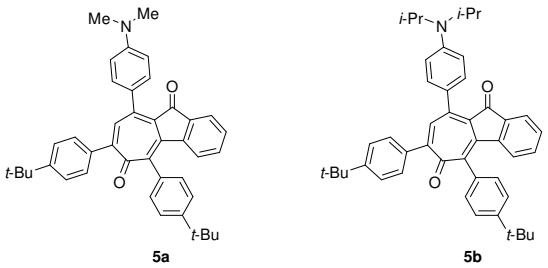


Figure S2. Chemical structures of push–pull benzazulenequinones (BAQs) **5a**,**b**.

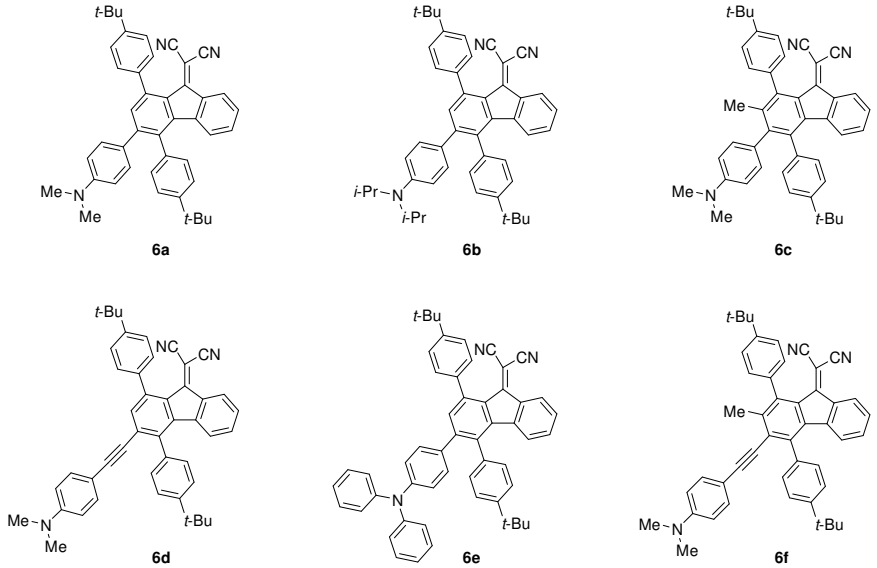


Figure S3. Chemical structures of push–pull dibenzodicyanofulvenes (DBDCFs) **6a**–**f**.

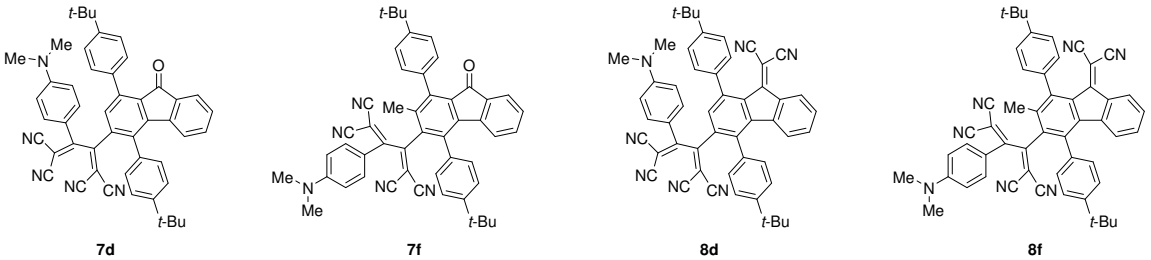


Figure S4. Chemical structures of push–pull tetracyanobutadiene (TCBD) conjugates **7d**,**f** and **8d**,**f**.

3. Synthesis

General Procedure for the Cycloaddition of Benzopentalenequinone 2 with Alkynes. A mixture of benzopentalenequinone **2** and alkyne was dissolved with *p*-xylene (general procedure A) or 1-butanol (general procedure B) and bubbled with argon for 30 min. The mixture was refluxed under argon atmosphere. The solvent was removed under reduced pressure, and the residue was purified by column chromatography with SiO_2.

Preparation of 4e. According to the general procedure A, **2** (30 mg, 0.07 mmol) was allowed to react with **3e** (15 mg, 0.08 mmol) in *p*-xylene (10 mL) for 5 h to afford **4e** (26 mg, 0.04 mmol, 62%) as orange solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). According to the general procedure B, the reaction of **2** (70 mg, 0.16 mmol) with **3e** (47 mg, 0.17 mmol) in 1-butanol (15 mL) for 1 h gave **4e** (42 mg, 0.05 mmol, 39%). **4e**: Mp 265–267 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (3H, m), 7.49 (2H, d, J = 8.4 Hz), 7.39 (2H, d, J = 8.4 Hz), 7.28 (1H, s), 7.23–7.15 (7H, m), 7.15 (1H, dt, J = 1.2, 7.6 Hz), 7.02–6.94 (8H, m), 6.84 (2H, d, J = 8.8 Hz), 6.34 (1H, d, J = 7.6 Hz), 1.40 (9H, s), 1.39 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.05, 151.17, 150.93, 148.15, 147.61, 146.68, 144.02, 143.51, 141.16, 135.72, 135.31, 135.07, 134.18, 134.12, 134.70, 133.10, 130.43, 129.97, 129.30, 129.08, 128.82, 128.59, 125.41, 124.94, 124.44, 123.73, 123.47, 123.03, 122.52, 34.84, 31.62, 31.55 (32 signals out of 33 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 255 (49700), 293 (33000), 411 (8400) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 688.1 $[M+H]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{51}H_{46}NO$ 688.3573, found 688.3576 $[M+H]^+$.

Preparation of 4f. According to the general procedure A, **2** (50 mg, 0.11 mmol) was allowed to react with **3f** (22 mg, 0.12 mmol) in *p*-xylene (10 mL) for 26 h to afford **4f** (59 mg, 0.098 mmol, 88%) as orange solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). According to the general procedure B, the reaction of **2** (50 mg, 0.11 mmol) with **3f** (22 mg, 0.12 mmol) in 1-butanol (10 mL) for 4 h gave **4f** (30 mg, 0.050 mmol, 45%). Mp 225–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (2H, d, J = 8.0 Hz), 7.50 (2H, d, J = 8.4 Hz), 7.47 (1H, dd, J = 3.2, 6.8 Hz), 7.41 (2H, d, J = 8.0 Hz), 7.20 (2H, d, J = 8.0 Hz), 7.12–7.10 (2H, m), 6.89 (2H, d, J = 8.8 Hz), 6.50 (2H, d, J = 8.8 Hz), 6.42 (1H, dd, J = 3.2, 6.8 Hz), 2.96 (6H, s), 2.32 (3H, s), 1.49 (9H, s), 1.42 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.91, 149.95, 136.13, 135.76, 135.59, 130.53, 128.00, 127.00, 126.85, 126.27, 124.48, 123.55, 122.90, 122.64, 121.80, 120.61, 118.85, 118.20, 118.13, 115.91, 115.52, 114.37, 113.82, 104.73, 103.32, 98.37, 85.32, 47.67, 43.39, 43.27, 40.81, 40.73, 30.54 (33 signals out of 33 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 258 (39400), 299 (28100), 437 (16600) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 602.9 $[M+H]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{44}H_{44}NO$ 602.3417, found 602.3427 $[M+H]^+$.

General Procedure for the Knovenagel Condensation of Fluorenones 4a–f with Manolonitrile. A mixture of fluorenone derivative and malononitrile was dissolved with 1,2-dichloroethane and bubbled with argon for 30 min. Pyridine (19 equiv) and $TiCl_4$ (11 equiv) were added to the mixture at

0 °C, and the resulting mixture was stirred at room temperature for 1 h under argon atmosphere. After the mixture was poured into CH_2Cl_2/H_2O, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography.

Preparation of 6a. According to the general procedure, **4a** (60 mg, 0.11 mmol) was allowed to react with malononitrile (35 mg, 0.53 mmol) in 1,2-dichloroethane (10 mL) to give **6a** (46 mg, 0.075 mmol, 71%) as purple solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). Mp 230–233 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (1H, d, J = 7.6 Hz), 7.56 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.4 Hz), 7.39 (2H, d, J = 8.4 Hz), 7.35 (1H, s), 7.18 (1H, dt, J = 0.8, 7.6 Hz), 7.13 (2H, d, J = 8.4 Hz), 7.06 (1H, dt, J = 0.8, 7.6 Hz), 6.99 (2H, d, J = 8.8 Hz), 6.51 (2H, d, J = 8.8 Hz), 6.13 (1H, d, J = 7.6 Hz), 2.92 (6H, s), 1.40 (9H, s), 1.38 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.00, 151.81, 151.04, 149.68, 148.34, 142.41, 141.85, 141.52, 137.40, 137.15, 135.47, 134.89, 133.29, 132.78, 132.77, 130.53, 129.80, 128.11, 128.02, 127.27, 127.04, 125.82, 125.46, 124.14, 115.01, 111.98, 111.55, 40.43, 34.88, 34.83, 31.56, 31.40 (32 signals out of 33 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 270 (52000), 551 (7100) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 611.8 (M^+); HR-FT-MS (APCI, positive) *m/z* calcd for $C_{44}H_{42}N_3$ 612.3373, found 612.3372 $[M+H]^+$.

Preparation of 6b. According to the general procedure, **4b** (40 mg, 0.065 mmol) was allowed to react with malononitrile (21 mg, 0.32 mmol) in 1,2-dichloroethane (10 mL) to give **6b** (29 mg, 0.043 mmol, 67%) as purple solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). Mp 211–213 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (1H, d, J = 7.6 Hz), 7.55 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.4 Hz), 7.36 (2H, d, J = 8.0 Hz), 7.36 (1H, s), 7.18 (1H, dt, J = 7.6, 1.0 Hz), 7.10 (2H, d, J = 8.4 Hz), 7.07 (1H, dt, J = 7.6, 1.0 Hz), 6.89 (2H, d, J = 8.8 Hz), 6.62 (2H, d, J = 8.0 Hz), 6.25 (1H, d, J = 7.6 Hz), 3.74 (2H, sept, J = 6.8 Hz), 1.39 (9H, s), 1.35 (9H, s), 1.17 (12H, d, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.02, 151.81, 150.97, 150.68, 148.61, 147.41, 142.43, 141.87, 141.29, 137.44, 137.17, 135.53, 134.88, 133.30, 132.61, 132.28, 129.88, 128.31, 128.13, 128.04, 127.04, 125.69, 125.49, 124.14, 117.01, 115.03, 112.00, 47.54, 34.88, 34.82, 31.56, 31.40, 21.29 (33 signals out of 34 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 271 (42400), 560 (6700) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 668.1 $[M+H]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{48}H_{50}N_3$ 668.3999, found 668.3996 $[M+H]^+$.

Preparation of 6c. According to the general procedure, **4c** (50 mg, 0.11 mmol) was allowed to react with malononitrile (10 mg, 0.15 mmol) in 1,2-dichloroethane (10 mL) to give **6c** (38 mg, 0.061 mmol, 70%) as purple solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). Mp 236–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (1H, d, J = 7.6 Hz), 7.53 (2H, d, J = 8.8 Hz), 7.31 (2H, d, J = 8.4 Hz), 7.27 (2H, d, J = 8.0 Hz), 7.11 (1H, dt, J = 1.2, 7.6 Hz), 7.02–6.97 (3H, m), 6.81 (2H, d, J = 8.8 Hz), 6.54 (2H, d, J = 8.8 Hz), 6.48 (1H, d, J = 7.6 Hz), 2.87 (6H, s), 2.01 (3H, s), 1.39 (9H, s), 1.31 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.39, 151.33, 150.27, 145.69, 145.17, 142.36, 141.98, 138.22, 137.61, 136.80, 135.49, 135.20, 133.96, 133.21, 131.18, 130.31, 129.38, 127.91, 127.54, 126.29, 125.38, 123.63, 115.26, 112.18, 111.18, 40.66, 34.86, 34.70, 31.50, 31.39, 20.00 (31

signals out of 34 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 275 (51800), 283 (54300), 493 (3900) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 625.1 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{45}H_{44}N_3$ 626.3529, found 626.3530 $[M+H]^+$.

Preparation of 6d. According to the general procedure, **4d** (50 mg, 0.09 mmol) was allowed to react with malononitrile (17 mg, 0.26 mmol) in 1,2-dichloroethane (10 mL) to give **6d** (43 mg, 0.068 mmol, 80%) as purple solids after purification by column chromatography (Al_2O_3, CH_2Cl_2/hexane = 2:3). Mp 270–272 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (1H, d, J = 7.7 Hz), 7.58 (2H, d, J = 8.4 Hz), 7.55 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.8 Hz), 7.43 (1H, s), 7.36 (2H, d, J = 8.4 Hz), 7.22 (1H, dt, J = 1.0, 7.7 Hz), 7.13 (1H, dt, J = 1.0, 7.7 Hz), 6.92 (2H, d, J = 8.8 Hz), 6.51–6.49 (3H, m), 2.96 (6H, s), 1.48 (9H, s), 1.39 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.97, 152.01, 151.37, 150.57, 142.56, 141.25, 140.36, 137.85, 137.01, 136.94, 134.83, 133.30, 133.21, 132.12, 131.77, 129.24, 128.42, 128.07, 127.08, 125.75, 125.61, 124.05, 114.99, 111.60, 109.17, 100.91, 97.08, 87.98, 42.27, 35.01, 34.90, 31.70, 31.39 (33 signals out of 35 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 270 (40200), 328 (32500), 527 (15300) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 636.1 $[M+H]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{46}H_{42}N_3$ 636.3373, found 636.3373 $[M+H]^+$.

Preparation of 6e. According to the general procedure, **4e** (50 mg, 0.11 mmol) was allowed to react with malononitrile (24 mg, 0.37 mmol) in 1,2-dichloroethane (10 mL) to give **6e** (53 mg, 0.072 mmol, quant.) as purple solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 2:1). Mp 187–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, d, J = 7.6 Hz), 7.55 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.4 Hz), 7.38 (2H, d, J = 8.4 Hz), 7.35 (1H, s), 7.24–7.18 (5H, m), 7.11–7.07 (3H, m), 7.03–6.99 (6H, m), 6.91 (2H, d, J = 8.8 Hz), 6.83 (2H, d, J = 8.8 Hz), 6.32 (1H, d, J = 7.6 Hz), 1.39 (9H, s), 1.38 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.98, 151.97, 151.24, 148.23, 147.51, 146.98, 142.44, 141.69, 141.15, 137.21, 137.07, 135.68, 134.48, 133.45, 133.40, 132.64, 130.33, 129.87, 129.35, 128.21, 128.14, 127.09, 125.60, 124.57, 124.15, 123.19, 122.39, 114.85, 111.88, 34.89, 34.86, 31.59, 31.39 (33 signals out of 36 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 272 (50200), 288 (39000), 488 (8300) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 735.4 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{54}H_{46}N_3$ 736.3686, found 736.3684 $[M+H]^+$.

Preparation of 6f. According to the general procedure, **4f** (50 mg, 0.08 mmol) was allowed to react with malononitrile (27 mg, 0.40 mmol) in 1,2-dichloroethane (10 mL) to give **6f** (42 mg, 0.065 mmol, 78%) as purple solids after purification by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1). Mp 256–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (1H, d, J = 7.6 Hz), 7.58 (2H, d, J = 8.4 Hz), 7.54 (2H, d, J = 8.0 Hz), 7.36 (2H, d, J = 8.4 Hz), 7.30 (2H, d, J = 8.4 Hz), 7.15 (1H, dt, J = 1.2, 7.6 Hz), 7.09 (1H, dt, J = 1.2, 7.6 Hz), 6.89 (2H, d, J = 8.6 Hz), 6.51 (2H, d, J = 8.6 Hz), 6.37 (1H, d, J = 7.6 Hz), 2.97 (6H, s), 2.48 (3H, s), 1.48 (9H, s), 1.41 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.49, 151.55, 151.18, 150.54, 141.92, 141.37, 138.58, 138.21, 138.06, 137.86, 137.52, 135.73, 134.64, 134.57, 133.50, 133.16, 133.07, 132.38, 130.93, 129.21, 127.89, 126.39, 125.76, 125.47, 123.61, 115.30, 112.10, 111.59, 109.54, 105.66, 40.29, 35.01, 34.90, 31.72, 31.40 (35 signals out of 36 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 267 (39000), 329 (32600), 534 (14500) nm; MALDI-TOF-MS

(dithranol, positive): *m/z* 649.2 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{47}H_{44}N_3$ 650.3529, found 650.3528 $[M+H]^+$.

General Procedure for the Cycloaddition of Alkynes with TCNE. Alkyne **4d**,**f** or **6d**,**f** was dissolved with CH_2Cl_2 or 1,2-dichloroethane under argon atmosphere. After addition of TCNE, the CH_2Cl_2 solution was stirred at room temperature for 30 min, and the 1,2-dichloroethane solution was stirred at 60 °C for 30 min. The solvent was removed under reduced pressure, and the residue was purified by column chromatography.

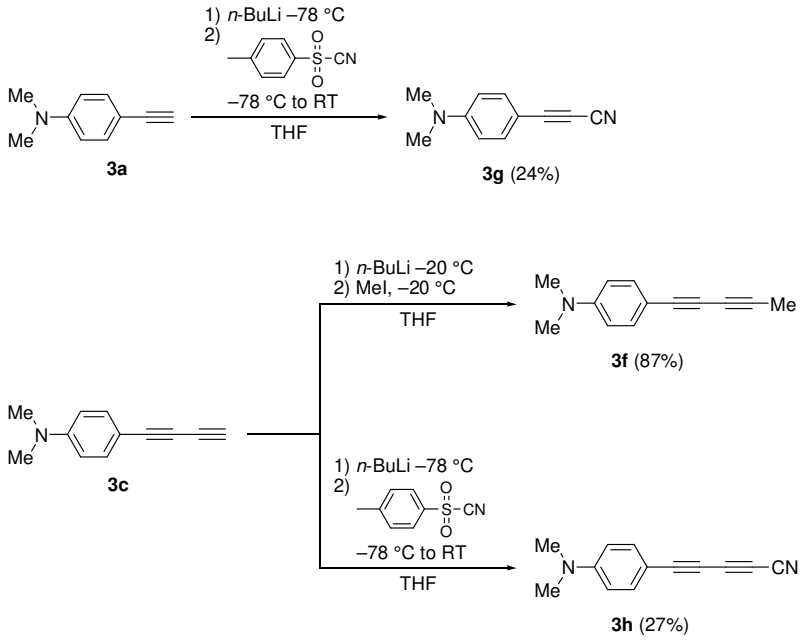
Preparation of 7d. According to the general procedure, **4d** (45 mg, 0.08 mmol) was allowed to react with TCNE (24 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) to give **7d** (42 mg, 0.059 mmol, 76%) as green solids after purification by column chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65–7.62 (3H, m), 7.57–7.55 (5H, m), 7.20–7.15 (5H, m), 7.10 (1H, dt, J = 0.8, 7.8 Hz), 6.55 (2H, d, J = 9.0 Hz), 6.02 (1H, d, J = 7.8 Hz), 3.07 (6H, s), 1.48 (9H, s), 1.42 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.73, 169.15, 161.91, 153.72, 153.41, 152.11, 144.80, 142.68, 141.32, 139.33, 136.40, 135.80, 134.87, 134.58, 133.08, 132.96, 132.91, 132.64, 129.63, 129.24, 127.16, 125.27, 124.32, 123.58, 117.63, 114.26, 113.57, 112.34, 111.47, 111.08, 94.26, 80.27, 40.16, 35.28, 34.96, 31.51, 31.47 (37 signals out of 38 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 339 (17000), 425 (13800), 575 (6500) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 715.4 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{49}H_{42}N_5O$ 716.3383, found 716.3388 $[M+H]^+$.

Preparation of 7f. According to the general procedure, **4f** (40 mg, 0.06 mmol) was allowed to react with TCNE (21 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) to give **7f** (48 mg, 0.066 mmol, quant.) as black solids after purification by column chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, dd, J = 2.0, 8.0 Hz), 7.54–7.46 (3H, m), 7.45 (1H, dd, J = 2.0, 8.0 Hz), 7.37 (1H, dd, J = 2.0, 8.0 Hz), 7.28–7.15 (7H, m), 6.48 (2H, d, J = 5.4 Hz), 5.84 (1H, d, J = 7.6 Hz), 3.07 (6H, s), 2.21 (3H, s), 1.43 (9H, s), 1.42 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.28, 169.08, 163.95, 154.06, 153.08, 150.75, 142.91, 142.14, 141.46, 141.05, 138.51, 135.28, 134.67, 134.61, 133.76, 133.38, 133.20, 133.03, 129.94, 129.50, 129.22, 128.32, 127.86, 127.18, 125.60, 125.29, 124.28, 122.90, 122.22, 115.24, 112.82, 111.86, 111.82, 109.55, 98.12, 81.81, 40.18, 35.18, 34.85, 31.64, 31.61, 19.68; UV–vis (CH_2Cl_2): λ_{max} (ε) 335 (16800), 377 (12200), 673 (6300) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 729.9 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{50}H_{44}N_5O$ 730.3540, found 730.3543 $[M+H]^+$.

Preparation of 8d. According to the general procedure, **6d** (40 mg, 0.06 mmol) was allowed to react with TCNE (20 mg, 0.16 mmol) in 1,2-dichloroethane (10 mL) to give **8d** (32 mg, 0.06 mmol, 67%) as green solids after purification by column chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (1H, d, J = 7.8 Hz), 7.65 (1H, s), 7.62 (2H, d, J = 8.4 Hz), 7.60 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.8 Hz), 7.24 (1H, dt, J = 1.0, 7.6 Hz), 7.16 (2H, d, J = 9.2 Hz), 7.14 (2H, d, J = 8.4 Hz), 7.09 (1H, dt, J = 1.0, 7.8 Hz), 6.57 (2H, d, J = 9.2 Hz), 6.02 (1H, d, J = 7.8 Hz), 3.08 (6H, s), 1.47 (9H, s), 1.41 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.48, 162.75, 161.65, 153.78, 153.62,

152.87, 142.43, 142.20, 140.09, 139.17, 137.34, 136.63, 135.53, 135.41, 135.24, 134.02, 132.82, 132.02, 129.43, 129.22, 128.27, 127.57, 127.33, 125.93, 124.29, 117.52, 114.23, 114.15, 113.57, 112.09, 111.55, 110.97, 94.45, 80.09, 80.03, 40.21, 35.29, 34.98, 31.43, 31.30 (40 signals out of 41 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 357 (28800), 461 (11600), 596 (5700) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 764.4 $[M+H]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{52}H_{42}N_7$ 764.3496, found 764.3494 $[M+H]^+$.

Preparation of 8f. According to the general procedure, **6f** (40 mg, 0.06 mmol) was allowed to react with TCNE (20 mg, 0.15 mmol) in 1,2-dichloroethane (10 mL) to give **8g** (42 mg, 0.054 mmol, 88%) as black solids after purification by column chromatography (SiO_2, CH_2Cl_2). Mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (1H, d, J = 7.6 Hz), 7.73 (1H, dd, J = 1.2, 8.0 Hz), 7.66 (2H, d, J = 7.6 Hz), 7.45 (1H, d, J = 7.2 Hz), 7.34 (2H, dd, J = 1.2, 8.0), 7.26–7.20 (4H, m), 7.07 (1H, t, J = 7.6 Hz), 6.49–6.47 (3H, m), 5.84 (1H, d, J = 7.6 Hz), 3.08 (6H, s), 2.33 (3H, s), 1.42 (9H, s), 1.40 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.53, 162.56, 154.10, 153.35, 152.30, 143.41, 140.33, 139.58, 137.76, 137.22, 133.71, 133.15, 130.89, 129.86, 129.45, 128.74, 127.38, 127.20, 126.78, 125.97, 123.61, 122.10, 115.14, 114.76, 111.97, 111.83, 111.36, 109.47, 81.71, 81.19, 40.18, 35.20, 34.95, 31.73, 31.59, 31.33 (36 signals out of 42 expected); UV–vis (CH_2Cl_2): λ_{max} (ε) 345 (27800), 430 (6800), 677 (6200) nm; MALDI-TOF-MS (dithranol, positive): *m/z* 777.9 $[M]^+$; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{53}H_{44}N_7$ 778.3652, found 778.3655 $[M+H]^+$.



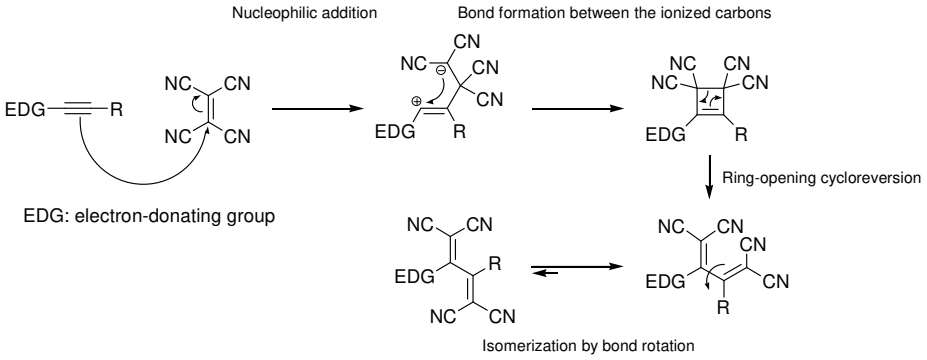
Scheme S1. Synthesis of alkynes **3f**,**g**,**h**.

Preparation of 3g. To a solution of **3a** (53 mg, 0.34 mmol) in THF (15 mL) was added dropwise a *n*-BuLi hexane solution (1.6 mol L^{-1}, 0.3 mL, 0.40 mmol) at −78 °C under argon atmosphere. After stirring at −78 °C for 1 h, tosyl cyanide (0.10 g, 0.55 mmol) in THF (10 mL) was added dropwise to

the mixture, and the mixture was stirred for 1 h at room temperature. After the mixture was poured into water, the resulting solution was extracted with CH_2Cl_2 (40 mL × 3). The combined organic phase was washed with water (50 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/hexane = 2:3) to give **3g** (18 mg, 0.11 mmol, 24%) as white solids. The ^{1}H NMR data are in agreement with those reported in the precedent literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (2H, d, J = 9.2 Hz), 6.61 (2H, d, J = 9.2 Hz), 3.04 (6H, s).

Preparation of 3f. To a solution of **3c** (200 mg, 1.18 mmol) in THF (20 mL) was added dropwise a *n*-BuLi hexane solution (1.6 mol L^{-1}, 0.89 mL, 1.42 mmol) at −20 °C under an argon atmosphere. After stirring at −20 °C for 1 h, iodomethane (0.22 mL, 3.55 mmol) was added dropwise to the mixture, and the mixture was stirred for 1 h at room temperature. After the mixture was poured into water, the resulting solution was extracted with EtOAc (40 mL × 3). The combined organic phase was washed with water (50 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1) to give **3f** (188 mg, 1.03 mmol, 87%) as brown solids. No clear Mp was observed (decomp.). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (2H, d, J = 9.0 Hz), 6.59 (2H, d, J = 9.0 Hz), 2.98 (6H, s), 2.01 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.46, 133.88, 111.79, 108.43, 79.26, 75.83, 72.50, 64.96, 40.28, 4.84; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{13}H_{14}N$ 184.1120, found 184.1120 $[M+H]^+$.

Preparation of 3h. To a solution of **3c** (93 mg, 0.55 mmol) in THF (15 mL) was added dropwise a *n*-BuLi hexane solution (1.6 mol L^{-1}, 0.4 mL, 0.61 mmol) at −78 °C under an argon atmosphere. After stirring at −78 °C for 1 h, tosyl cyanide (0.15 g, 0.83 mmol) in THF (10 mL) was added dropwise to the mixture, and the mixture was stirred for 30 min at room temperature. After the mixture was poured into water, the resulting solution was extracted with CH_2Cl_2 (40 mL × 3). The combined organic phase was washed with water (50 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1) to give **3h** (27 mg, 0.14 mmol, 27%) as white solids. No clear Mp was observed (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (2H, d, J = 9.0 Hz), 6.60 (2H, d, J = 9.0 Hz), 3.04 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.86, 135.54, 111.72, 106.26, 103.43, 84.23, 71.71, 69.42, 55.33, 40.12; HR-FT-MS (APCI, positive) *m/z* calcd for $C_{13}H_{11}N_2$ 195.0916, found 195.0918 $[M+H]^+$.



Scheme S2. Proposed mechanism for the reaction of donor-substituted alkyne with TCNE.

4. X-ray crystallographic data

The X-ray crystal structures were solved by direct methods (Sir2011,[5] Sir2014,[6] or SHELXS-2014[6]) and refined by full-matrix least-squares analysis (SHELXL-2014[7]), using an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically, whereby hydrogen positions are based on stereochemical considerations. CCDC-1920262 (**4e**), CCDC-1920264 (**4f**), CCDC-1920268 (**6a**), CCDC-1920269 (**6b**), CCDC-1920271 (**6c**), CCDC-1920274 (**6d**), CCDC-1920276 (**6e**), CCDC-1920277 (**6f**), CCDC-1920294 (**7d**), CCDC-1920296 (**7f**), CCDC-1920298 (**8d**), and CCDC-1920299 (**8f**) contain the supplementary crystallographic data for this paper. The crystal structures of **4a**, **4b**, **4c**, **4d**, and **5b** were reported in our previous communication.[8]

Crystal Structural Data of **4e**: Crystal data at 113 K for $C_{51.5}H_{45.5}Cl_{1.5}NO$, M_r = 747.56, Triclinic, space group *P*-1, D_{calcd} = 1.214 g cm^{-3}, Z = 4, a = 15.5095(19) Å, b = 16.419(2) Å, c = 17.6112(15) Å, α = 79.615(13)°, β = 68.069(7)°, γ = 84.517(12)°, V = 4090.1(8) Å^3; Mo-*K*α radiation, λ = 0.71075 Å, μ = 1.65 cm^{-1}. Numbers of measured and unique reflections were 133202 and 18648, respectively (R_{int} = 0.0339). Final $R(F)$ = 0.0414, $wR(F^2)$ = 0.1130 for 1003 parameters and 18648 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0525 for all data).

Crystal Structural Data of **4f** Crystal data at 113 K for $C_{45}H_{44}Cl_3NO$, M_r = 721.21, Monoclinic, space group $P2_1/c$, D_{calcd} = 1.226 g cm^{-3}, Z = 4, a = 17.038(9) Å, b = 21.523(8) Å, c = 11.237(5) Å, β = 108.547(13)°, V = 3907(3) Å^3; Cu-*K*α radiation, λ = 1.54187 Å, μ = 23.83 cm^{-1}. Numbers of measured and unique reflections were 39859 and 7054, respectively (R_{int} = 0.1701). Final $R(F)$ = 0.0824, $wR(F^2)$ = 0.2265 for 488parameters and 7054 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.1041 for all data).

Crystal Structural Data of **6a**: Crystal data at 113 K for $C_{44}H_{41}N_3$, M_r = 661.80, Triclinic, space group *P*-1, D_{calcd} = 1.118 g cm^{-3}, Z = 6, a = 14.607(4) Å, b = 16.157(4) Å, c = 27.290(4) Å, α = 106.338(3)°, β = 90.856(3)°, γ = 116.601(7)°, V = 5451(2) Å^3; Cu-*K*α radiation, λ = 1.54187 Å, μ =

49.5 cm^{-1}. Numbers of measured and unique reflections were 63900 and 19529, respectively (R_{int} = 0.0550). Final $R(F)$ = 0.0603, $wR(F^2)$ = 0.1670 for 1350 parameters and 19529 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0746 for all data).

Crystal Structural Data of **6b**: Crystal data at 113 K for $C_{48}H_{49}N_3$, M_r = 667.94, Triclinic, space group P-1, D_{calcd} = 1.170 g cm^{-3}, Z = 2, a = 11.1504(15) Å, b = 11.5820(11) Å, c = 14.992(2) Å, α = 85.880(6)°, β = 86.682(6)°, γ = 79.303(7)°, V = 1895.6(4) $Å^3$; Mo-$K\alpha$ radiation, λ = 0.71075 Å, μ = 0.676 cm^{-1}. Numbers of measured and unique reflections were 31529 and 8639, respectively (R_{int} = 0.0335). Final $R(F)$ = 0.0433, $wR(F^2)$ = 0.1229 for 470 parameters and 8639 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0531 for all data).

Crystal Structural Data of **6c**: Crystal data at 123 K for $C_{45}H_{43}N_3$, M_r = 625.82, Triclinic, space group P-1, D_{calcd} = 1.183 g cm^{-3}, Z = 2, a = 11.6137(17) Å, b = 12.3195(16) Å, c = 14.2724(13) Å, α = 64.628(11)°, β = 72.187(13)°, γ = 82.043(15)°, V = 1756.5(4) $Å^3$; Mo-$K\alpha$ radiation, λ = 0.71075 Å, μ = 0.69 cm^{-1}. Numbers of measured and unique reflections were 57446 and 8043, respectively (R_{int} = 0.1343). Final $R(F)$ = 0.0568, $wR(F^2)$ = 0.1366 for 473 parameters and 8043 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.1071 for all data).

Crystal Structural Data of **6d**: Crystal data at 113 K for $C_{46.5}H_{43}N_3O_{0.5}$, M_r = 651.87, Triclinic, space group P-1, D_{calcd} = 1.159 g cm^{-3}, Z = 4, a = 13.3124(11) Å, b = 17.3674(16) Å, c = 17.7864(16) Å, α = 78.525(8)°, β = 77.087(8)°, γ = 70.127(7)°, V = 3735.5(6) $Å^3$; Mo-$K\alpha$ radiation, λ = 0.71075 Å, μ = 0.681 cm^{-1}. Numbers of measured and unique reflections were 122723 and 17126, respectively (R_{int} = 0.0511). Final $R(F)$ = 0.0716, $wR(F^2)$ = 0.2415 for 903 parameters and 17126 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.1070 for all data).

Crystal Structural Data of **6e**: Crystal data at 123 K for $C_{55}H_{46}Cl_3N_3$, M_r = 855.35, Triclinic, space group P-1, D_{calcd} = 1.261 g cm^{-3}, Z = 2, a = 9.2808(17) Å, b = 15.164(2) Å, c = 16.814(4) Å, α = 74.57(2)°, β = 84.71(2)°, γ = 81.550(16)°, V = 2252.7(8) $Å^3$; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 21.499 cm^{-1}. Numbers of measured and unique reflections were 23010 and 7909, respectively (R_{int} = 0.0747). Final $R(F)$ = 0.0786, $wR(F^2)$ = 0.2312 for 593 parameters and 7909 reflections with $I > 2\sigma(I)$ (the corresponding R values is 0.1015 for all data).

Crystal Structural Data of **6f**: Crystal data at 123 K for $C_{47}H_{43}N_3$, M_r = 649.88, Monoclinic, space group $P2_1/c$, D_{calcd} = 1.168 g cm^{-3}, Z = 8, a = 15.001(2) Å, b = 16.5592(18) Å, c = 30.270(4) Å, β = 100.711(4)°, V = 7388.2(16) $Å^3$; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 5.17 cm^{-1}. Numbers of measured and unique reflections were 85332 and 13480, respectively (R_{int} = 0.0612). Final $R(F)$ = 0.0586, $wR(F^2)$ = 0.1748 for 919 parameters and 13480 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0664 for all data).

Crystal Structural Data of **7d**: Crystal data at 123 K for $C_{49}H_{41}N_5O$, M_r = 715.90, Monoclinic, space group C_2/c, D_{calcd} = 1.047 g cm^{-3}, Z = 24, a = 54.620(9) Å, b = 13.2972(19) Å, c = 44.552(9) Å, β = 122.652(3)°, V = 27244(8) $Å^3$; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 4.937 cm^{-1}. Numbers of measured and unique reflections were 94732 and 24626, respectively (R_{int} = 0.0846). Final $R(F)$ = 0.1246, $wR(F^2)$ = 0.3619 for 1510 parameters and 24626 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.1452

for all data).

Crystal Structural Data of **7f**: Crystal data at 123 K for $C_{51}H_{44}Cl_3N_5O$, M_r = 849.30, Triclinic, space group P-1, D_{calcd} = 1.130 g cm^{-3}, Z = 2, a = 11.977(2) Å, b = 12.739(2) Å, c = 17.798(3) Å, α = 98.842(4)°, β = 98.679(4)°, γ = 107.964(4)°, V = 2495.07(7) Å^3; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 19.644 cm^{-1}. Numbers of measured and unique reflections were 28848 and 8893, respectively (R_{int} = 0.0498). Final $R(F)$ = 0.1182, $wR(F^2)$ = 0.3340 for 550 parameters and 8893 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.1260 for all data).

Crystal Structural Data of **8d**: Crystal data at 123 K for $C_{52}H_{41}N_7$, M_r = 763.94, Monoclinic, space group $P2_1/n$, D_{calcd} = 1.090 g cm^{-3}, Z = 4, a = 17.349(3) Å, b = 13.933(3) Å, c = 19.572(3) Å, β = 100.366(4)°, V = 4653.8(15) Å^3; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 5.084 cm^{-1}. Numbers of measured and unique reflections were 31900 and 8459, respectively (R_{int} = 0.0487). Final $R(F)$ = 0.0616, $wR(F^2)$ = 0.1617 for 540 parameters and 8459 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0665 for all data).

Crystal Structural Data of **8f**: Crystal data at 123 K for $C_{53}H_{43}N_7$, M_r = 777.97, Triclinic, space group P-1, D_{calcd} = 1.111 g cm^{-3}, Z = 2, a = 12.037(5) Å, b = 13.922(5) Å, c = 16.102(5) Å, α = 91.4728(7)°, β = 111.807(8)°, γ = 109.604(14)°, V = 2324.9(15) Å^3; Cu-$K\alpha$ radiation, λ = 1.54187 Å, μ = 5.167 cm^{-1}. Numbers of measured and unique reflections were 30788 and 8320, respectively (R_{int} = 0.0388). Final $R(F)$ = 0.0413, $wR(F^2)$ = 0.1193 for 550 parameters and 8320 reflections with $I > 2\sigma(I)$ (the corresponding R value is 0.0507 for all data).

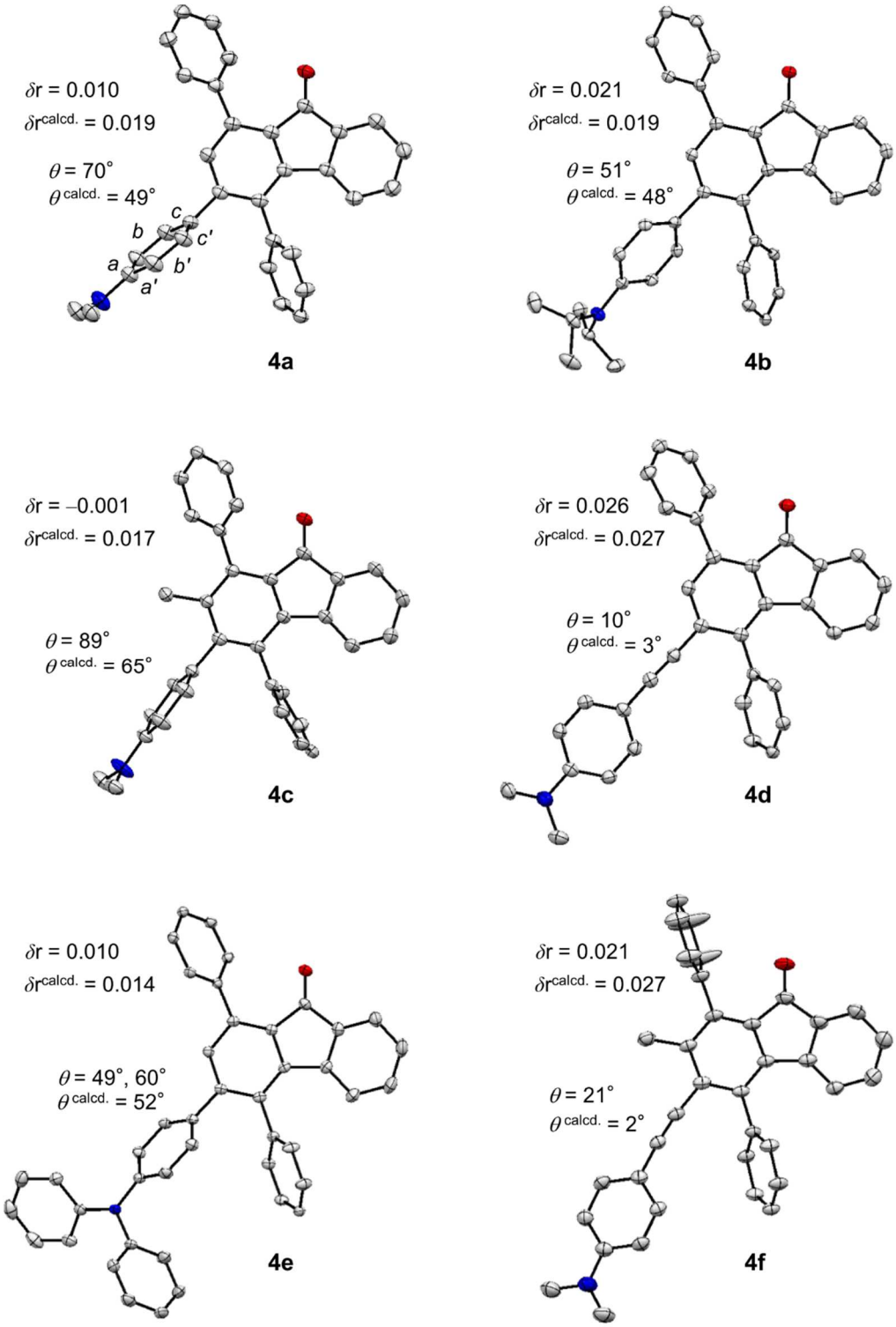


Figure S5. ORTEPs of FOs **4a**–**f**. The *t*-Bu groups and hydrogen atoms are omitted for clarity. One of the two independent molecules in the unit cell is shown for **4e**. Quinoid character: $\delta r = \{[(a + a')/2 - (b + b')/2] + [(c + c')/2 - (b + b')/2]\}/2$. The $\delta r^{calcd.}$ and $\theta^{calcd.}$ values are those estimated by DFT calculations (PBE0/6-31G(d)).

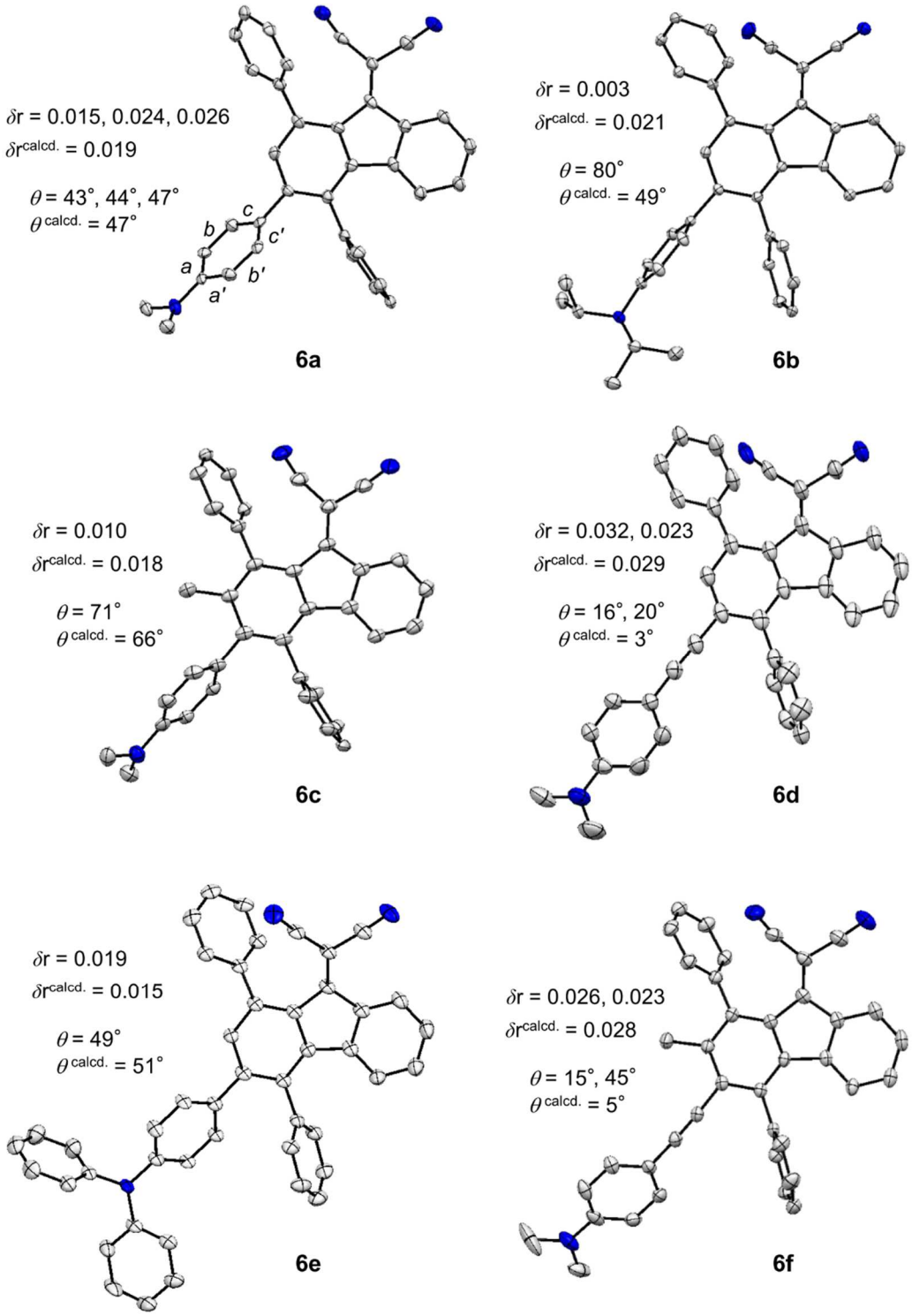


Figure S6. ORTEPs of DBDCFs **6a**–**f**. The *t*-Bu groups and hydrogen atoms are omitted for clarity. One of the two or three independent molecules in the unit cell is shown for **6a**,**d**,**f**. Quinoid character: $\delta r = \{[(a + a')/2 - (b + b')/2] + [(c + c')/2 - (b + b')/2]\}/2$. The $\delta r^{calcd.}$ and $\theta^{calcd.}$ values are those estimated by DFT calculations (PBE0/6-31G(d)).

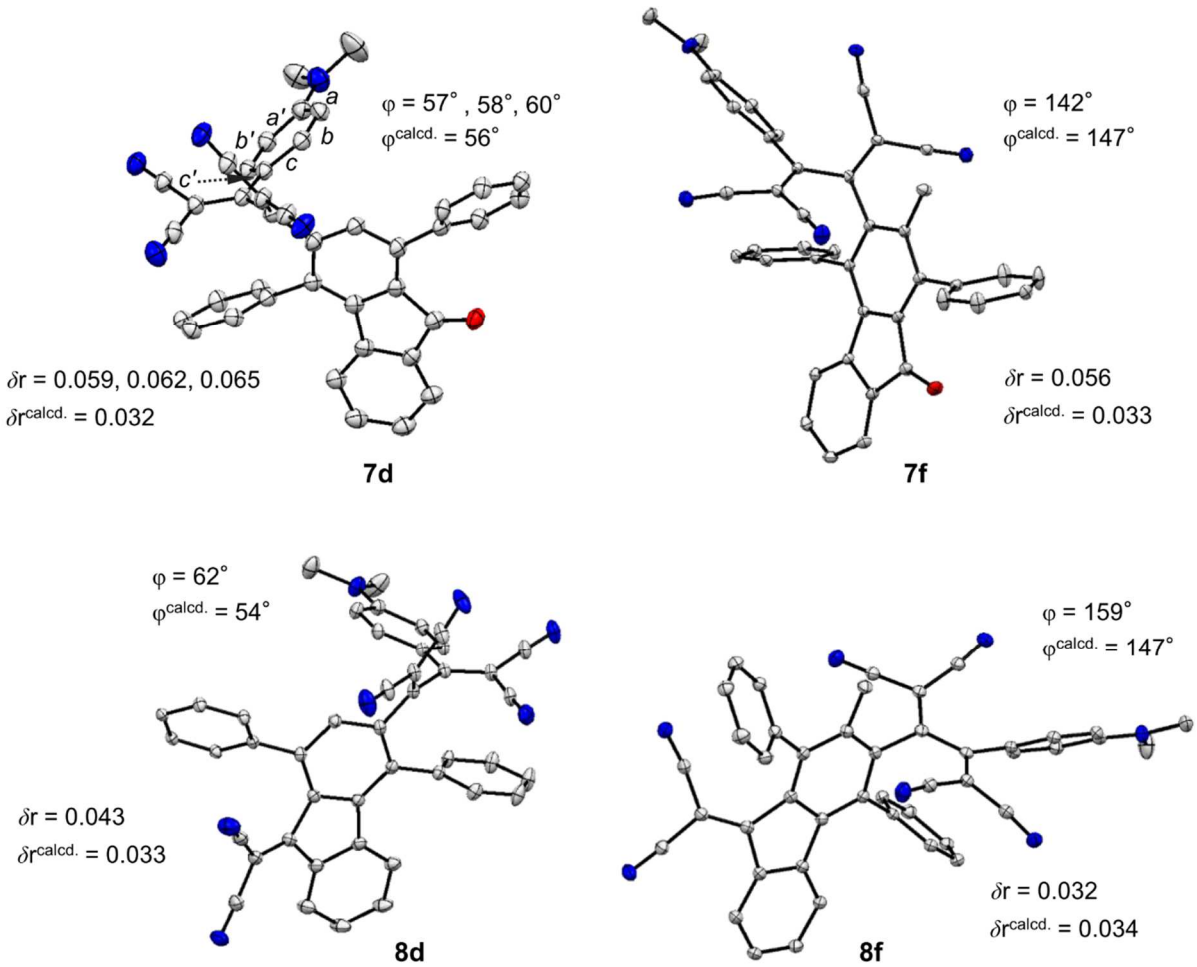
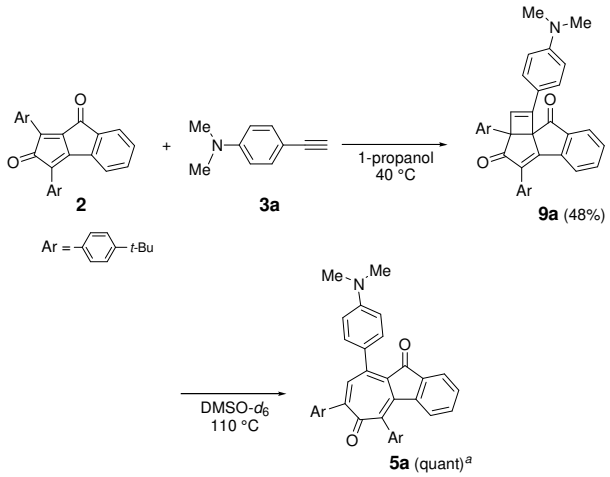


Figure S7. ORTEPs of TCBD conjugates **7d**,**f** and **8d**,**f**. The *t*-Bu groups and hydrogen atoms are omitted for clarity. One of the three independent molecules in the unit cell is shown for **7d**. Quinoid character: $\delta r = \{[(a + a')/2 - (b + b')/2] + [(c + c')/2 - (b + b')/2]\}/2$. The $\delta r^{calcd.}$ and $\varphi^{calcd.}$ values are those estimated by DFT calculations (PBE0/6-31G(d)).

5. Kinetic studies

In our previous communication, we reported the regioselective [2+2] CA of **2** with **3a** at 40 °C in 1-propanol to furnish cyclobutene **9a** (Scheme S3), followed by the ring-opening reaction of **9a** at 110 °C in DMSO-d_6 to form BAQ **5a** in almost quantitative yield. In the present study, we carried out a kinetic study of the ring-opening reaction of intermediate **9a** to gain insight into the reaction mechanism. The reactions were monitored using ^{1}H NMR spectroscopy, and the kinetics corresponded well to a first-order reaction (Figure S8). Arrhenius and Eyring analyses of the kinetic data yielded an activation energy (E_a), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) of 27.3 kcal mol^{-1}, 26.5 kcal mol^{-1}, and –6.4 cal mol^{-1} K^{-1}, respectively (Table S1 and Figure S8). Given that these E_a and $\Delta H^{\ddagger}$ values are much smaller than the typical dissociation energies of C–C bonds and that the $\Delta S^{\ddagger}$ value is negative, the ring-

opening of **9a** likely involves a concerted mechanism, namely, a 4π electrocyclic reaction.



Scheme S3. [2+2] Cycloaddition of **2** with **3a** and ring-opening reaction of **9a**.
[a] Yield determined using ^{1}H NMR spectroscopy.

Experimental Procedure:

A solution of **9a** in DMSO-d_6 was placed in a NMR tube and equilibrated at the corresponding temperature within an oil bath, and a timer was started. For each data point, the tube was taken out of the oil bath, the timer was stopped, and a ^{1}H NMR spectrum was recorded at 25 °C using a JEOL ECA600 spectrometer, after which the heating and the timer were resumed. Rate constants k at the corresponding temperature T were determined by monitoring the concentrations of disappearing **9a** and forming **5a** using ^{1}H NMR spectroscopy.

As shown in Figure 1 in the manuscript, the thermal ring-opening reaction of **9a** to **5a** shows a first-order dependence on the concentration of **9a** in accord with Eq. (1).

$\ln(1 + [\mathbf{5a}]/(\mathbf{9a})) = kt$ (1)

The rate constants are listed in Table S1. Plotting $\ln k$ or $\ln(k/T)$ vs. T^{-1} and fitting the data to a linear function afford the slope and y-intercept (Figure S8). The thermodynamic parameters were determined by using the following equations, where R, k_B, and h are the gas constant, the Boltzmann constant, and the Planck constant, respectively.

$\ln k = -E_a/RT + \ln A$ (2)

$\ln(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln k/h$ (3)

$\Delta G^{\ddagger} = RT(\ln(k_B T/h) - \ln k)$ (4)

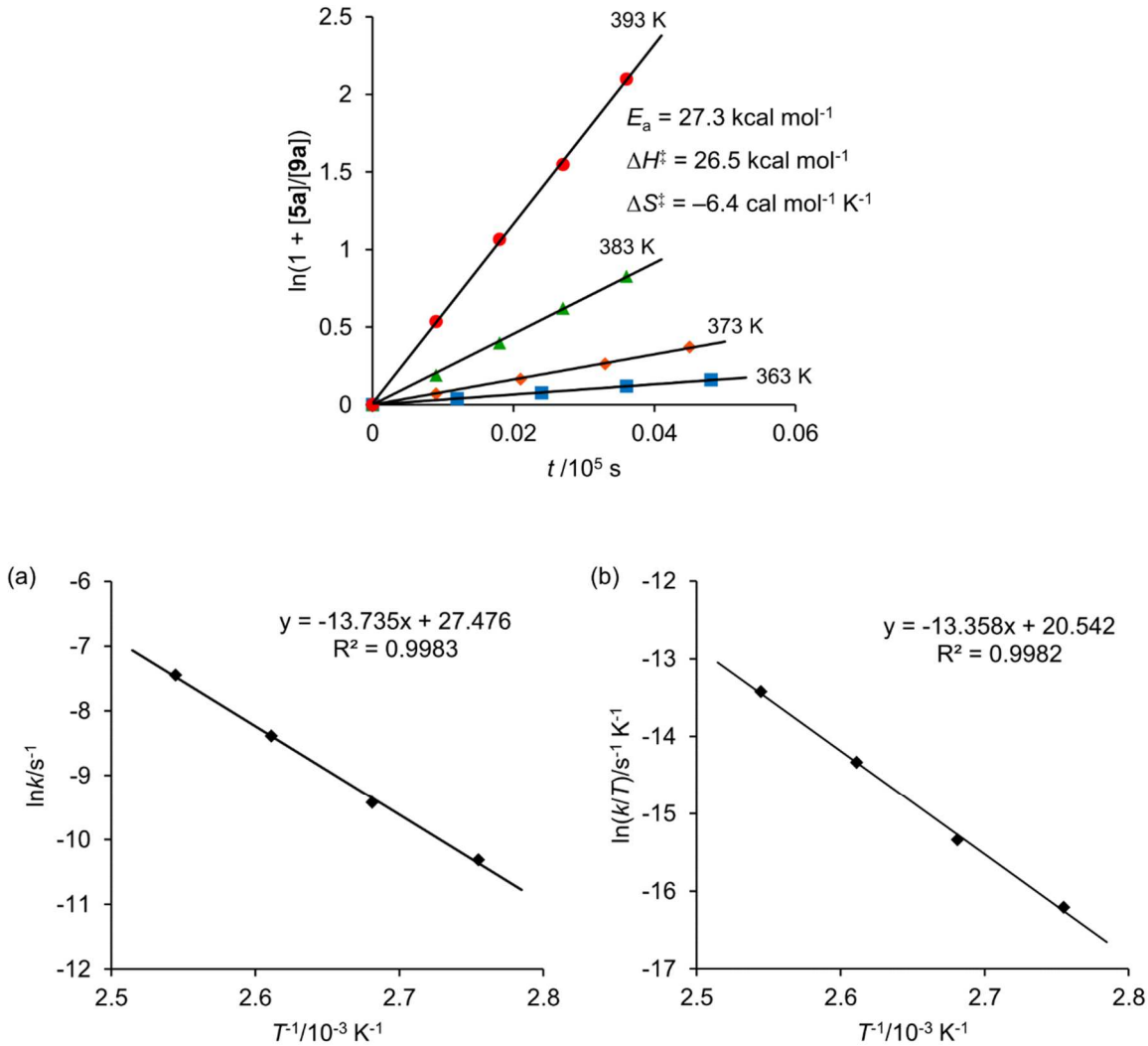


Figure S8. (Top) Plots of ln(1 + [**5a**]/[**9a**]) as a function of t for the ring-opening reaction of **9a** in DMSO-d_6 to form **5a**. (Bottom: a) Arrhenius plot used to determine E_a and (Bottom: b) Eyring plot used to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the transformation of **9a** to **5a** in DMSO-d_6.

Table S1. Thermodynamic Parameters for the Transformation of **9a** to **5a** in DMSO-d_6

T (K)	k (10^5 s^{-1})	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
		27.3	26.5	–6.4
363	3.31			
373	8.11			
383	22.8			
393	58.2			

6. Photophysical data

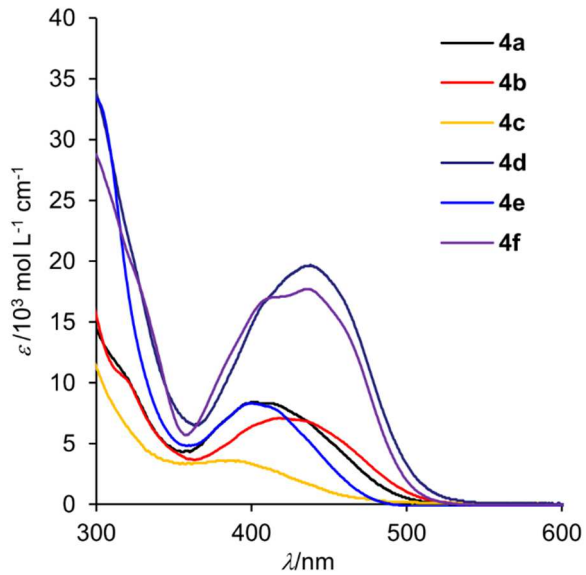


Figure S9. Electronic absorption spectra of FOs **4a**–**f** in THF at RT.

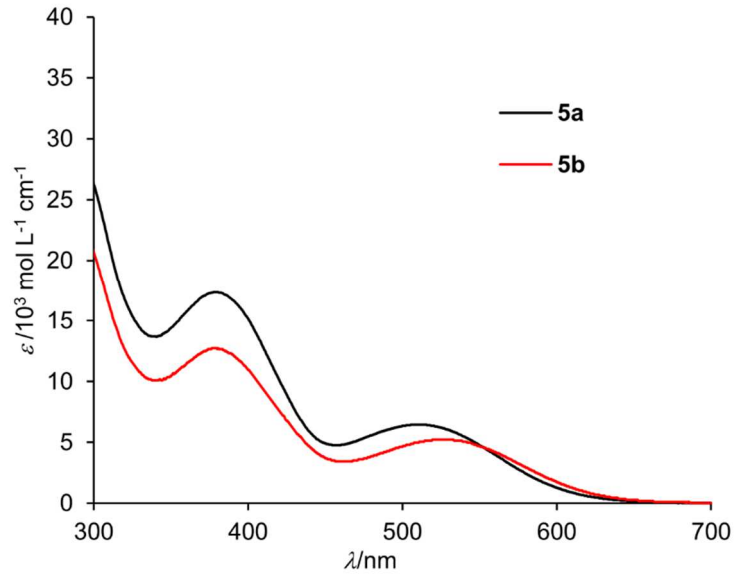


Figure S10. Electronic absorption spectra of BAQs **5a**,**b** in THF at RT.

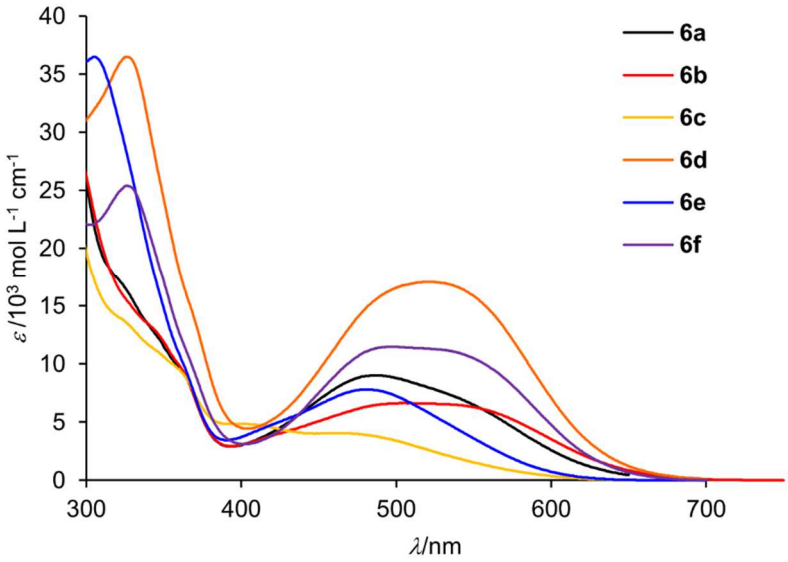


Figure S11. Electronic absorption spectra of DBDCFs **6a**–**f** in THF at RT.

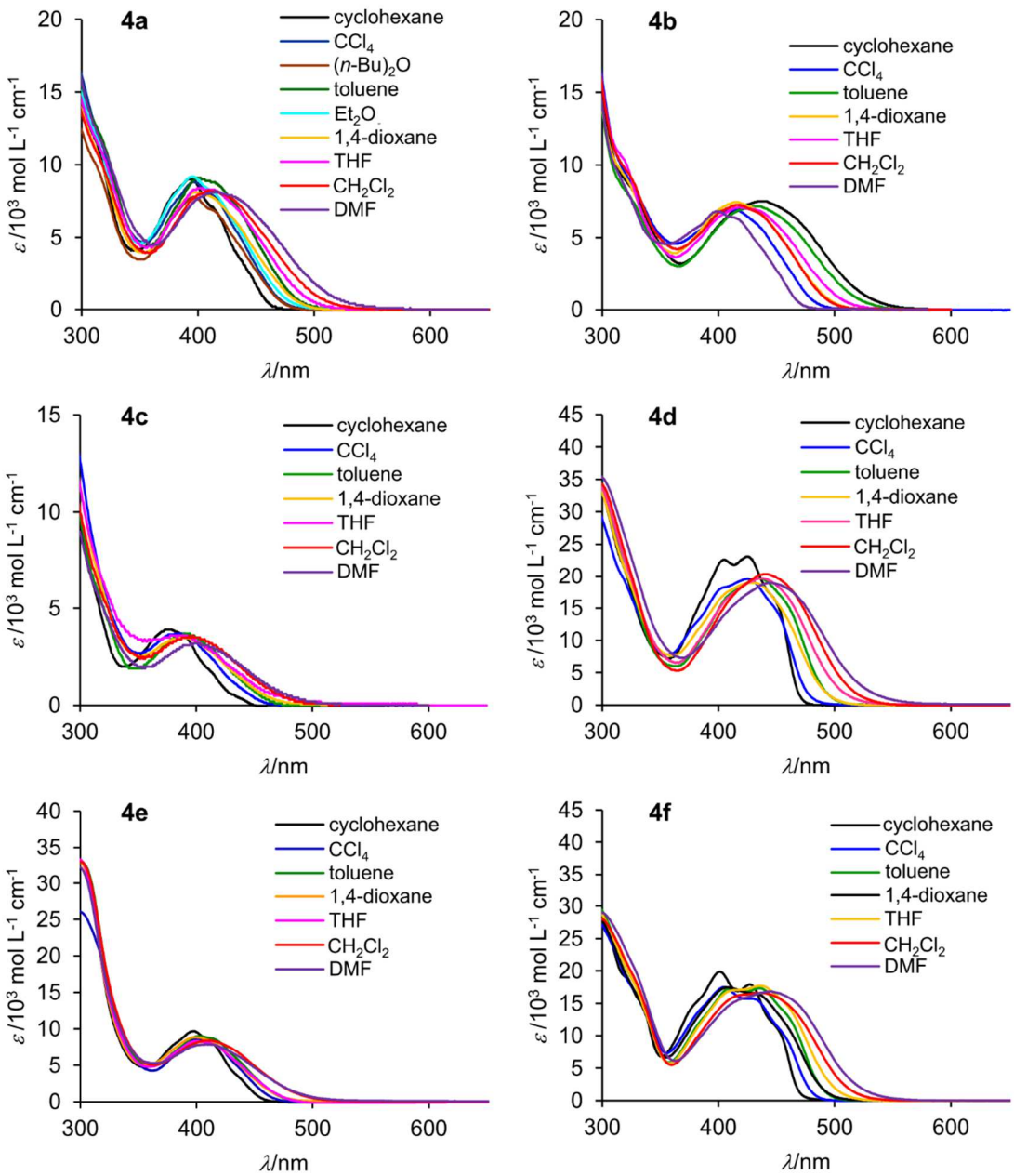


Figure S12. Electronic absorption spectra of FOs **4a**–**f** in various solvents at RT.

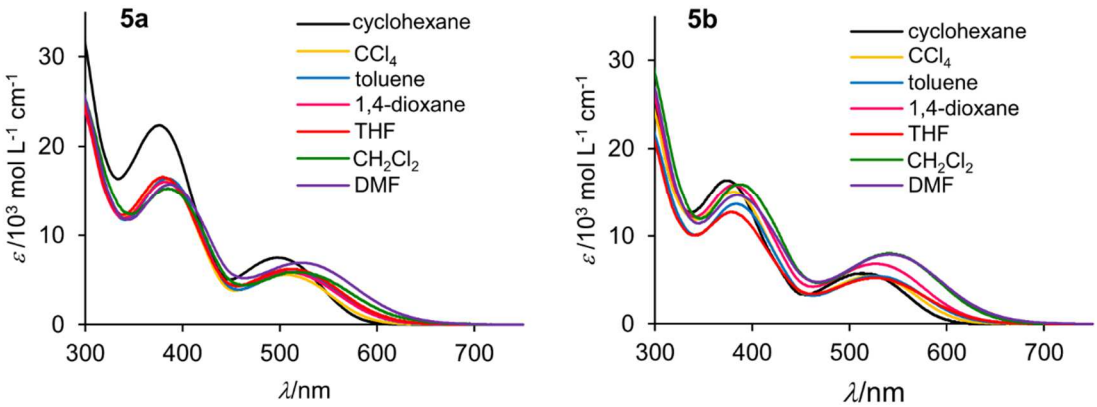


Figure S13. Electronic absorption spectra of BAQs **5a**,**b** in various solvents at RT.

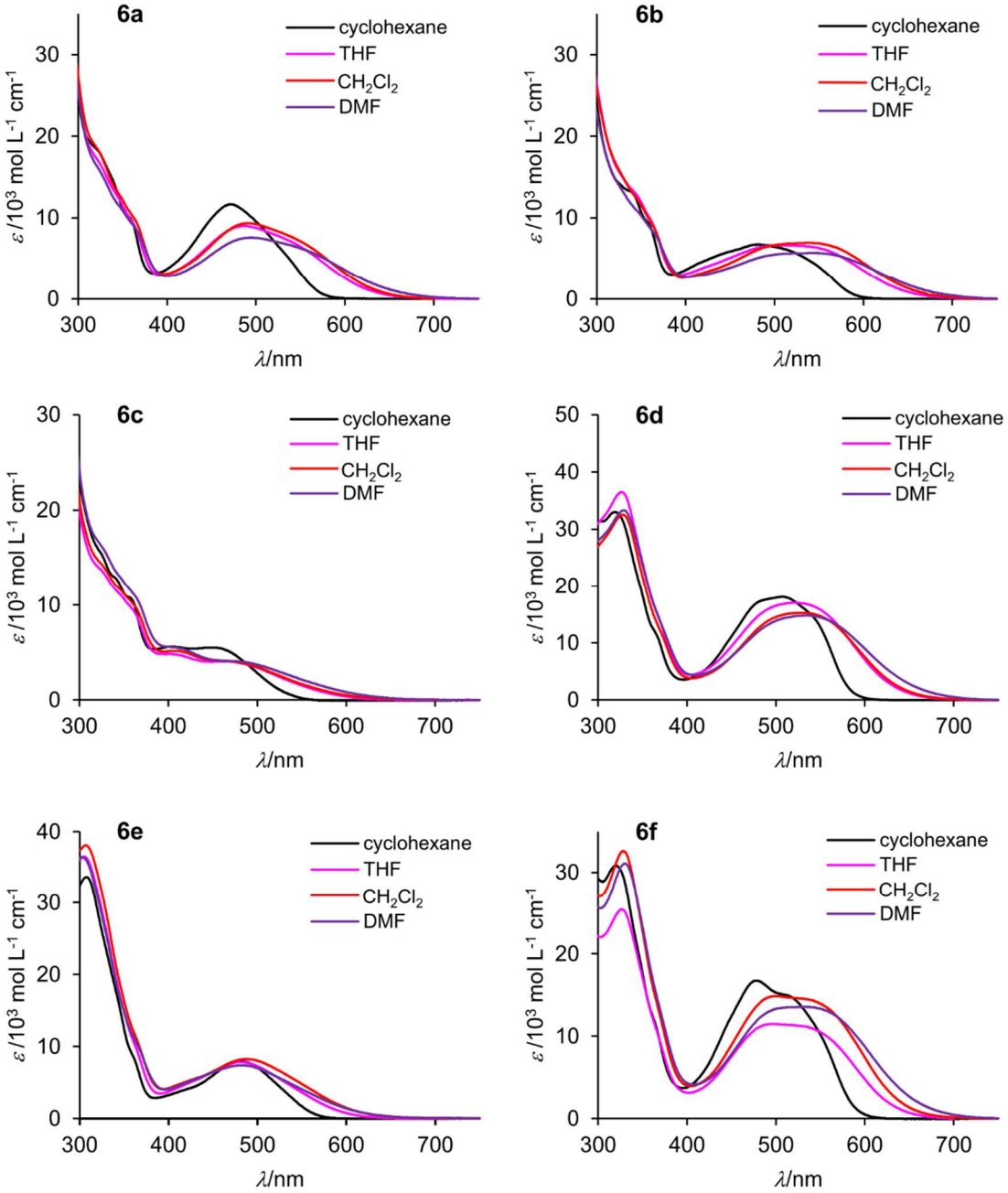


Figure S14. Electronic absorption spectra of DBDCFs **6a**–**f** in various solvents at RT.

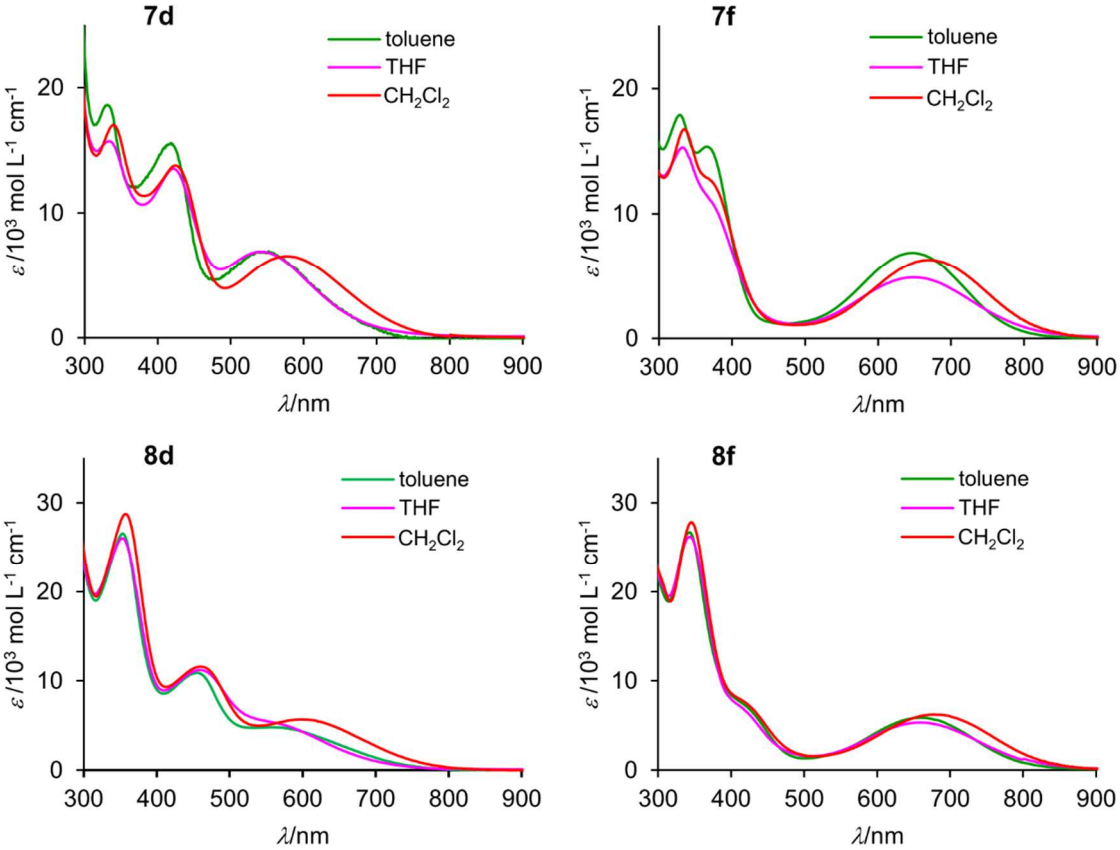


Figure S15. Electronic absorption spectra of TCBD conjugates **7d**,**f** and **8d**,**f** in various solvents at RT.

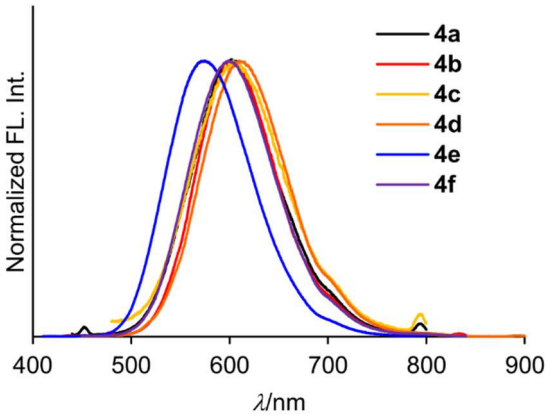


Figure S16. Fluorescence spectra of FOs **4a**–**f** in THF at RT.

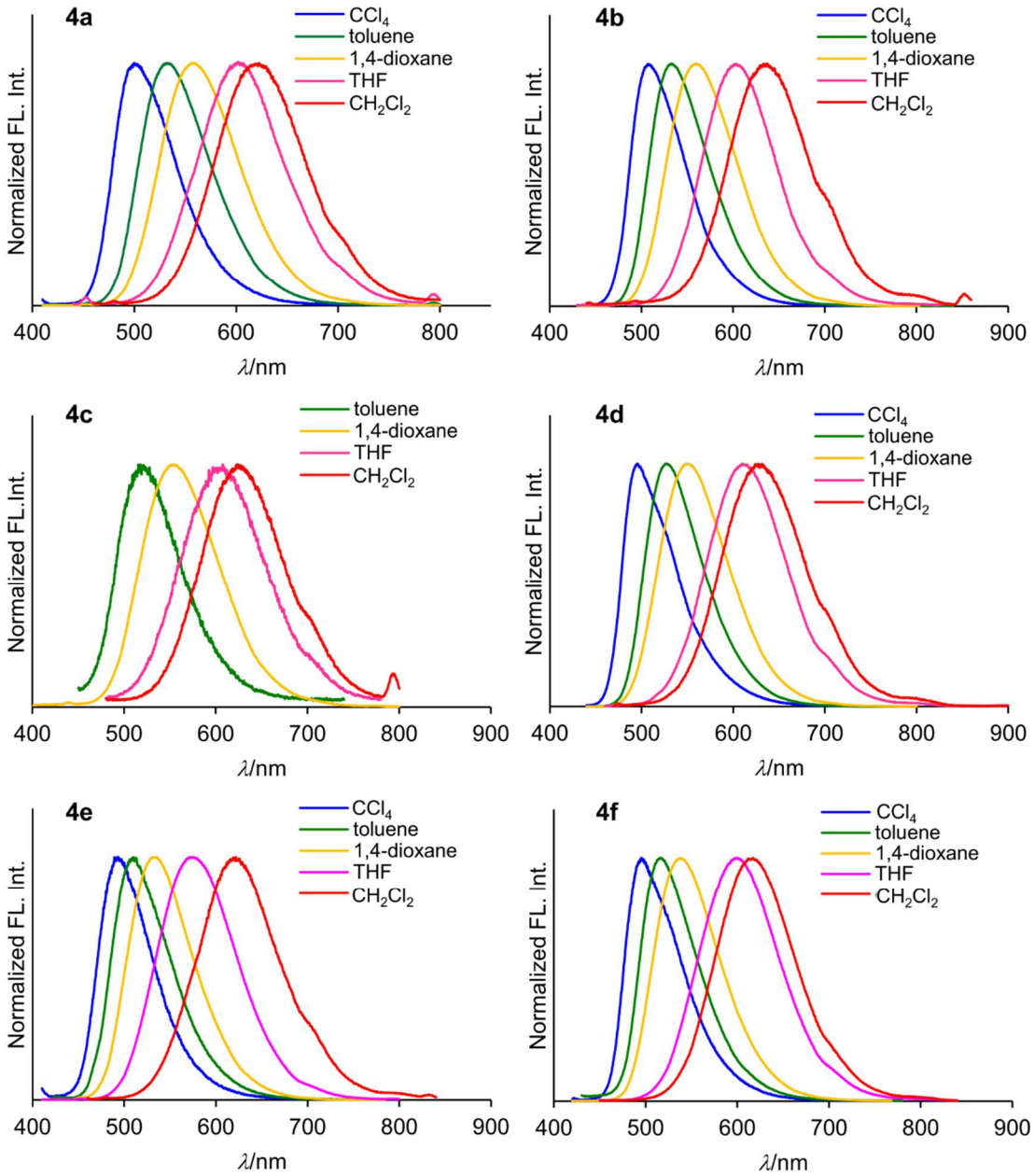


Figure S17. Fluorescence spectra of FOs **4a**–**f** in various solvents at RT.

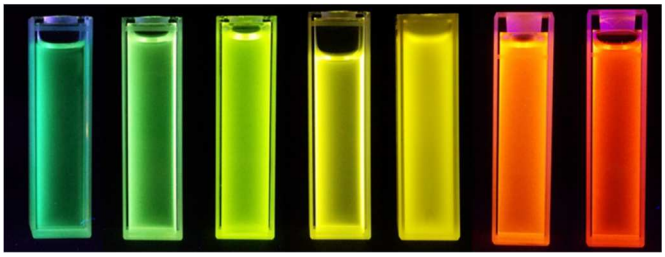


Figure S18. Photograph of FO **4a** in solution (CCl_4, $(n\text{-Bu})_2O$, toluene, Et_2O, 1,4-dioxane, THF, and CH_2Cl_2 from left to right) under UV irradiation (365 nm).

7. Electrochemical data

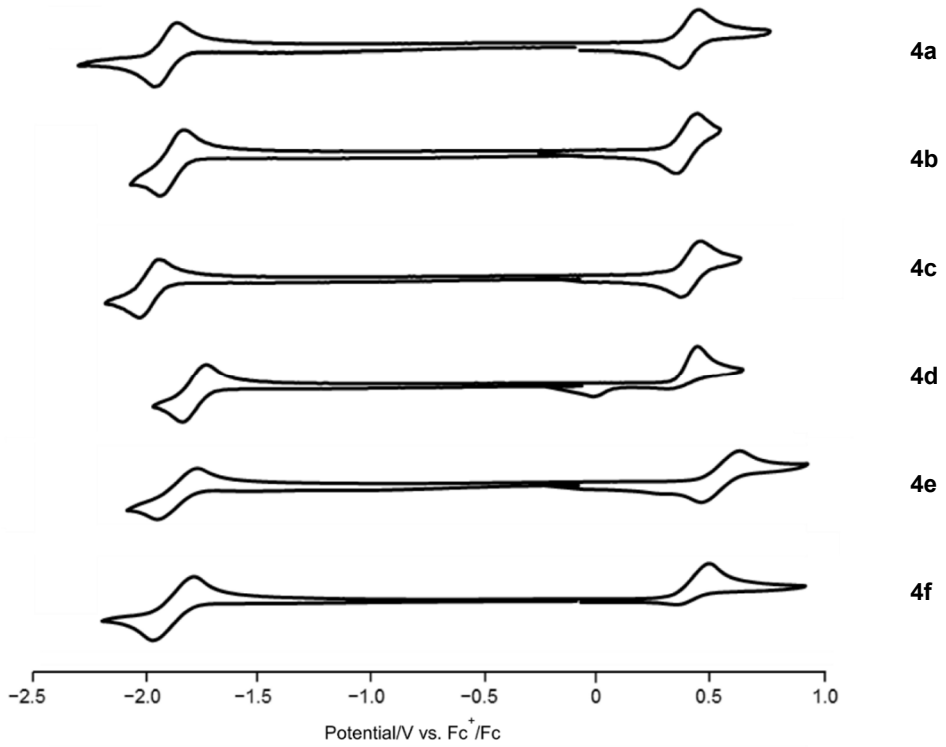


Figure S19. Cyclic voltammograms of FOs **4a**–**f** measured at scan rate 100 mV s^{-1} in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]) at room temperature.

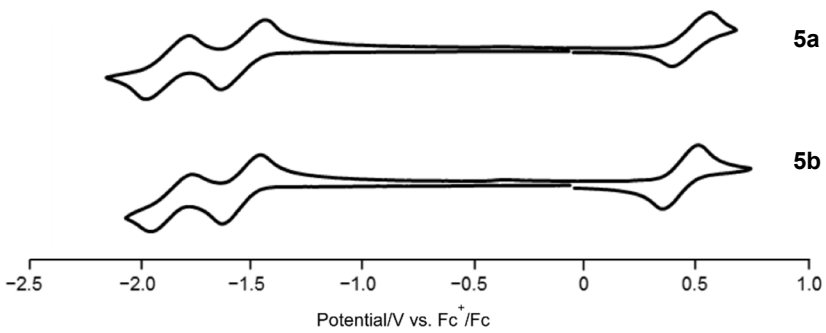


Figure S20. Cyclic voltammograms of BAQs **5a**,**b** measured at scan rate 100 mV s^{-1} in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]) at room temperature.

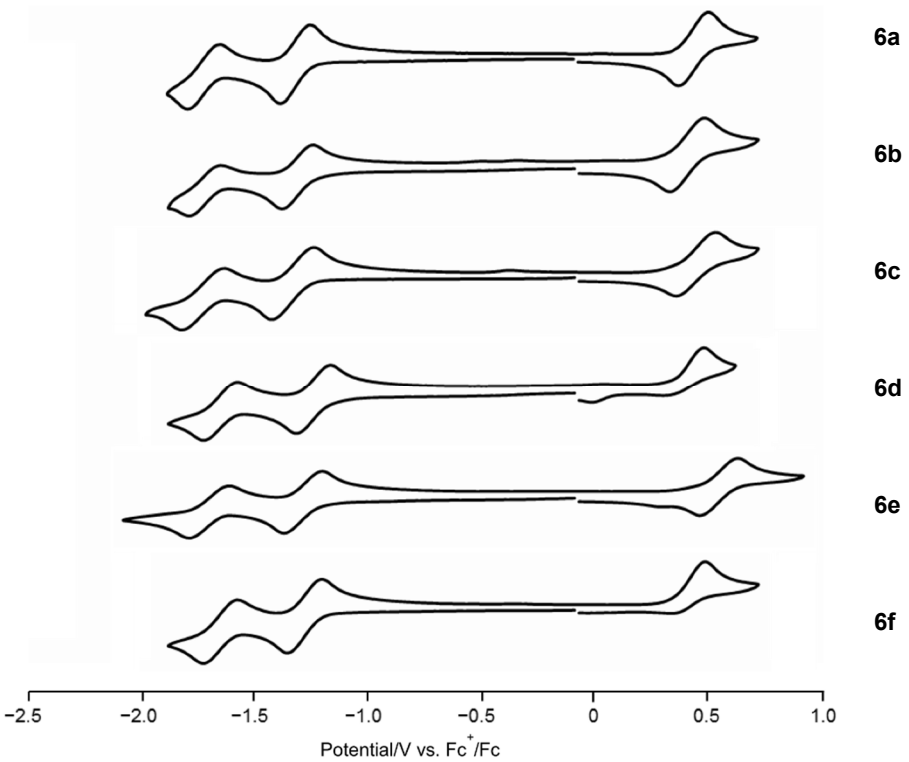


Figure S21. Cyclic voltammograms of DBDCFs **6a**–**f** measured at scan rate 100 mV s^{-1} in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]) at room temperature.

Table S2. Electrochemical (CV and DPV) Data of **4a**–**f** and **5a**,**b** in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]) at RT and Theoretically Calculated HOMO and LUMO Levels (PBE0/6-311G(d,p)//PBE0/6-31G(d))

Compd.	CV[a]		DPV[b]		HOMO	LUMO
	E_{pa} [V]	E_{pc} [V]	E_{ox} [V]	E_{red} [V]	[V]	[V]
4a	+0.43 [c]	−1.96 [c]	+0.38	−1.90	−5.48	−2.13
4b	+0.43 [c]	−1.94 [c]	+0.36	−1.90	−5.44	−2.14
4c	+0.44 [c]	−2.03 [c]	+0.40	−1.96	−5.51	−2.03
4d	+0.43 [d]	−1.84 [c]	+0.36	−1.80	−5.21	−2.03
4e	+0.62 [c]	−1.96 [c]	+0.52	−1.86	−5.43	−2.26
4f	+0.49 [d]	−1.94 [c]	+0.40	−1.86	−5.18	−2.03
5a	+0.56 [c]	−1.67 [c]	+0.46	−1.56	−5.46	−2.46
		−1.99 [c]		−1.90		
5b	+0.49 [c]	−1.64 [c]	+0.40	−1.54	−5.42	−2.50
		−1.95 [c]		−1.84		

[a] Scan rate 100 mV s^{-1}. [b] Pulse width of 0.1 s in a period of 0.2 s.
[c] Reversible wave. [d] Irreversible wave.

Table S3. Electrochemical (CV and DPV) Data of **6a–f** in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu)$_4$N][PF_6]) at RT and Theoretically Calculated HOMO and LUMO Levels (PBE0/6-311G(d,p)//PBE0/6-31G(d))

Compd.	CV[a]		DPV[b]		HOMO	LUMO
	E_{pa} [V]	E_{pc} [V]	E_{ox} [V]	E_{red} [V]	[V]	[V]
6a	+0.49 [c]	−1.39 [c]	+0.42	−1.34	−5.62	−2.91
		−1.80 [c]		−1.74		
6b	+0.48 [c]	−1.39 [c]	+0.38	−1.34	−5.57	−2.94
		−1.80 [c]		−1.74		
6c	+0.53 [c]	−1.43 [c]	+0.42	−1.36	−5.63	−2.88
		−1.83 [c]		−1.76		
6d	+0.48 [d]	−1.32 [c]	+0.38	−1.26	−5.55	−2.99
		−1.73 [c]		−1.68		
6e	+0.63 [c]	−1.38 [c]	+0.52	−1.32	−5.53	−3.05
		−1.80 [c]		−1.74		
6f	+0.48 [d]	−1.37 [c]	+0.40	−1.28	−5.53	−2.92
		−1.73 [c]		−1.66		

[a] Scan rate 100 mV s^{-1}. [b] Pulse width of 0.1 s in a period of 0.2 s.
[c] Reversible wave. [d] Irreversible wave.

Table S4. Electrochemical (CV and DPV) Data of **7d**,**f** and **8d**,**f** in *o*-DCB (0.1 mol L^{-1} [(*n*-Bu$_4$)N][PF_6]) at RT and Theoretically Calculated HOMO and LUMO Levels (PBE0/6-311G(d,p)//PBE0/6-31G(d))

Compd.	CV[a]		DPV[b]		HOMO	LUMO
	E_{pa} [V]	E_{pc} [V]	E_{ox} [V]	E_{red} [V]	[V]	[V]
7d	+1.00 [c]	−0.98 [d]	+0.88	−0.86	−6.32	−3.45
		−1.47 [d]		−1.36		
		−2.22 [d]		−2.12		
7f	+0.82 [c]	−0.82 [d]	+0.82	−0.76	−6.25	−3.69
		−1.43 [d]		−1.38		
		−2.23 [c]		−2.16		
8d	+0.89 [c]	−0.85 [d]	+0.82	−0.80	−6.35	−3.70
		−1.23 [d]		−1.18		
		−1.63 [d]		−1.58		
		−1.98 [d]		−1.92		
8f	+0.91 [c]	−0.78 [d]	+0.84	−0.70	−6.33	−3.82
		−1.34 [d]		−1.26		
		−1.60 [d]		−1.54		
		−2.05 [c]		−1.98		

[a] Scan rate 100 mV s^{-1}. [b] Pulse width of 0.1 s in a period of 0.2 s.
[c] Quasi-Reversible wave. [d] Reversible wave.

8. Theoretical data

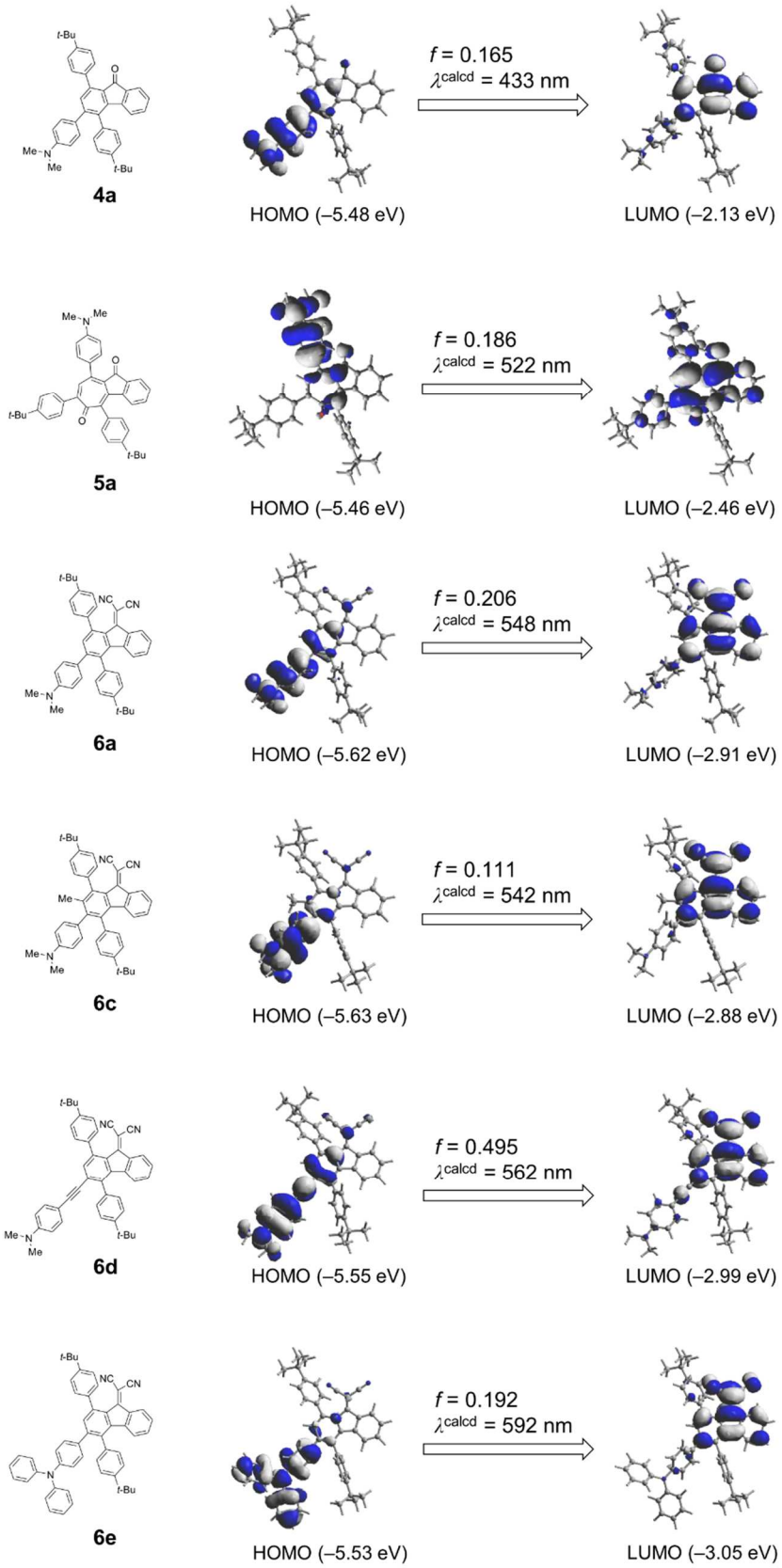


Figure S22. HOMOs and LUMOs and the calculated absorption wavelengths (λ^{calcd}) and oscillator strengths (*f*) of **4a**, **5a**, **6a**, **6c**, **6d**, and **6e** at the (TD)PBE0/6-31G(d) level of theory.

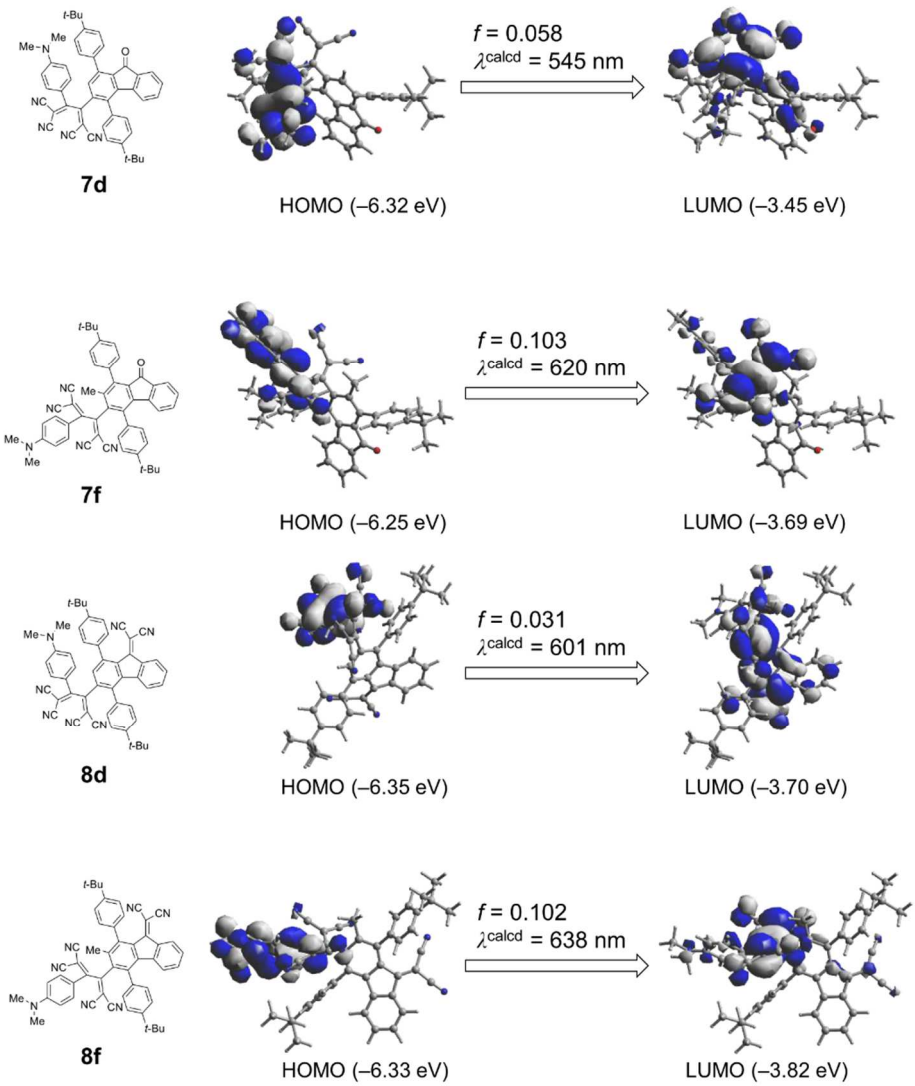
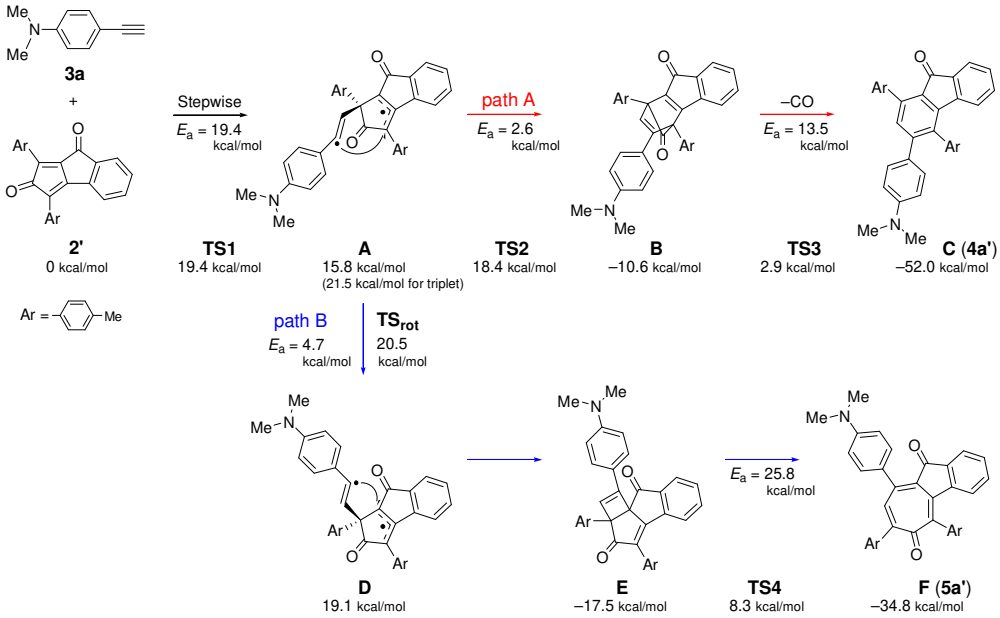


Figure S23. HOMOs and LUMOs and the calculated absorption wavelengths (λ^{calcd}) and oscillator strengths (*f*) of **7d**,**f**, and **8d**,**f** at the (TD)PBE0/6-31G(d) level of theory.

Computational method

To calculate activation energies for cycloaddition of benzopentalenequinone **2'** with alkyne **3a**, we performed DFT calculations. We optimized local minima and transition states on the potential energy surfaces using the B3LYP method[9,10] combined with the 6-31G(d,p) basis set.[11,12] To consider solvent effect corresponding to 1-butanol the PCM method was carried out. We carried out TD-DFT calculations at the PBE0/6-31G(d) level[13] of theory to look at and analyze the optical absorption. The Gaussian 09 program package[14] was used for all DFT calculations.



Scheme S4. Reaction pathways A (red) and B (blue) for the cycloaddition between benzopentalenequinone **2′** and alkyne **3a**; calculated at the B3LYP/6-31G(d) level of theory.

Table S5. Cartesian Coordinates of **4a** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.229212	-0.785057	0.006973
2	6	0	1.509955	-1.557990	-0.002850
3	6	0	-0.163957	0.681902	-0.010196
4	6	0	2.134667	-2.914966	0.069806
5	6	0	1.227484	0.803508	-0.004041
6	6	0	-5.048853	-1.138021	0.042307
7	6	0	-3.008588	-0.462093	-1.107892
8	8	0	3.309990	-3.212412	0.157319
9	6	0	-0.631076	2.957686	-0.926657
10	6	0	0.104803	-1.711707	-0.023680
11	6	0	-0.962248	1.929617	-0.035366
12	6	0	-0.751851	-0.611074	-0.004975
13	6	0	-2.880386	-1.279551	1.138379
14	6	0	6.328958	0.607948	0.039349
15	6	0	0.999733	-3.874396	0.010873
16	6	0	-0.208060	-3.166667	-0.073189
17	6	0	-1.396170	-3.876496	-0.214056
18	6	0	-6.568485	-1.315338	0.020654
19	6	0	4.077712	0.935231	0.903133
20	6	0	-4.385346	-0.640300	-1.087812
21	6	0	4.447982	-0.669969	-0.833101
22	6	0	2.100927	-0.292798	0.008682
23	6	0	-2.021971	2.174344	0.846581
24	6	0	-2.393084	4.399653	-0.071617
25	7	0	-3.101177	5.583343	-0.103271
26	6	0	-4.059529	5.861956	0.938495
27	6	0	5.801690	-0.351210	-0.829954
28	6	0	3.558703	-0.032087	0.033085

29	6	0	-0.136549	-5.964524	-0.134005
30	6	0	-1.320894	4.159869	-0.954110
31	6	0	1.059295	-5.255926	-0.011878
32	6	0	-2.611612	6.677795	-0.905798
33	6	0	5.431100	1.241023	0.908149
34	6	0	-2.714389	3.374174	0.841199
35	6	0	-4.262830	-1.450458	1.154821
36	6	0	7.813445	0.975705	0.071344
37	6	0	-1.342513	-5.274481	-0.241538
38	6	0	-7.236519	0.043628	-0.244947
39	6	0	-6.950884	-2.297552	-1.098480
40	6	0	-7.108338	-1.864279	1.343801
41	6	0	8.632609	0.173251	-0.942897
42	6	0	7.975903	2.469605	-0.253158
43	6	0	8.378808	0.695645	1.473410
44	1	0	1.654041	1.802799	0.000734
45	1	0	-2.527185	-0.066659	-1.998206
46	1	0	0.182293	2.805775	-1.632399
47	1	0	-2.295839	-1.539908	2.017738
48	1	0	-2.351397	-3.373829	-0.306876
49	1	0	3.412298	1.437381	1.601219
50	1	0	-4.954239	-0.380698	-1.977297
51	1	0	4.080230	-1.422754	-1.521682
52	1	0	-2.302415	1.417551	1.572349
53	1	0	-4.854063	5.105949	0.955424
54	1	0	-4.530714	6.827111	0.742468
55	1	0	-3.603532	5.899242	1.940685
56	1	0	6.451472	-0.871959	-1.525410
57	1	0	-0.129783	-7.050783	-0.155043
58	1	0	-1.020762	4.914391	-1.672371
59	1	0	2.021383	-5.756354	0.057783
60	1	0	-1.607424	7.014094	-0.602456
61	1	0	-3.296393	7.523138	-0.814421
62	1	0	-2.570503	6.402108	-1.966826
63	1	0	5.791785	1.989280	1.609582
64	1	0	-3.511724	3.512628	1.562522
65	1	0	-4.723807	-1.837011	2.058020
66	1	0	-2.268672	-5.832942	-0.351535
67	1	0	-6.920137	0.471875	-1.201623
68	1	0	-6.985815	0.763137	0.542477
69	1	0	-8.327366	-0.067445	-0.272272
70	1	0	-6.627105	-1.940398	-2.081633
71	1	0	-8.039081	-2.430514	-1.132753
72	1	0	-6.492660	-3.278762	-0.931182
73	1	0	-8.196840	-1.972530	1.280062
74	1	0	-6.891663	-1.192770	2.182425
75	1	0	-6.690993	-2.850716	1.576064
76	1	0	8.296414	0.351764	-1.970662
77	1	0	8.580825	-0.903566	-0.746197
78	1	0	9.685625	0.470684	-0.883043
79	1	0	7.586376	2.697302	-1.251711
80	1	0	9.035548	2.752148	-0.226810
81	1	0	7.444018	3.101895	0.465647
82	1	0	8.277203	-0.364243	1.731266
83	1	0	7.863018	1.278176	2.244051
84	1	0	9.443328	0.957730	1.513172

No imaginary frequency.
Total energy: –1715.05339856 hartree.
HOMO (151): –0.20157 hartree; LUMO (152): –0.07811 hartree (PBE0/6-311G(d,p)).

Table S6. Cartesian Coordinates of **4b** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.501861	2.833922	0.117612
2	7	0	-3.922166	-4.094507	-0.162804
3	6	0	3.289408	2.838723	0.031872
4	6	0	2.346108	1.679764	-0.030044
5	6	0	2.603373	0.307507	-0.007929
6	6	0	1.484434	-0.536637	-0.018477
7	6	0	0.167365	-0.072094	-0.029475
8	6	0	-0.080387	1.326417	-0.029477
9	6	0	1.023564	2.178671	-0.054374
10	6	0	1.083461	3.665152	-0.116495
11	6	0	0.109044	4.646688	-0.266192
12	6	0	0.508647	5.986996	-0.307224
13	6	0	1.848572	6.356033	-0.204330
14	6	0	2.830723	5.373498	-0.073221
15	6	0	2.429528	4.050407	-0.037057
16	6	0	3.949998	-0.308351	0.026490
17	6	0	4.972032	0.075263	-0.843252
18	6	0	6.203603	-0.570955	-0.828008
19	6	0	6.473017	-1.617222	0.058530
20	6	0	5.443780	-1.994149	0.930635
21	6	0	4.208948	-1.361832	0.912533
22	6	0	7.819789	-2.341108	0.109366
23	6	0	8.436809	-2.169204	1.507139
24	6	0	7.607327	-3.837329	-0.172125
25	6	0	8.812678	-1.796891	-0.920956
26	6	0	-1.469078	1.858866	-0.013108
27	6	0	-2.317865	1.712065	-1.114291
28	6	0	-3.613189	2.210456	-1.084013
29	6	0	-4.124804	2.868937	0.042829
30	6	0	-3.270330	3.008778	1.140064
31	6	0	-1.967940	2.514794	1.113704
32	6	0	-5.563255	3.390020	0.035564
33	6	0	-6.528411	2.212424	-0.178709
34	6	0	-5.735560	4.403458	-1.107216
35	6	0	-5.937325	4.081436	1.348790
36	6	0	-0.915547	-1.083216	-0.058538
37	6	0	-0.853301	-2.150315	-0.960711
38	6	0	-1.820369	-3.144974	-0.994883
39	6	0	-2.924806	-3.127287	-0.118852
40	6	0	-2.978714	-2.051696	0.792343
41	6	0	-2.006158	-1.066265	0.819914
42	6	0	-4.036501	-4.949609	-1.345010
43	6	0	-3.284426	-6.276529	-1.206616
44	6	0	-5.493358	-5.174542	-1.751832
45	6	0	-4.617280	-4.556209	1.046879
46	6	0	-3.689384	-4.774241	2.242956
47	6	0	-5.856130	-3.731180	1.411444
48	1	0	1.648363	-1.610685	-0.009178

49	1	0	-0.941315	4.396273	-0.355749
50	1	0	-0.249409	6.757325	-0.424258
51	1	0	2.125565	7.406156	-0.235968
52	1	0	3.887052	5.619899	-0.007200
53	1	0	4.804887	0.886036	-1.543849
54	1	0	6.964451	-0.240661	-1.527351
55	1	0	5.606137	-2.797831	1.644760
56	1	0	3.436953	-1.672320	1.612495
57	1	0	7.790442	-2.579424	2.290122
58	1	0	8.604302	-1.110279	1.732678
59	1	0	9.401429	-2.688392	1.563087
60	1	0	8.564163	-4.371908	-0.127786
61	1	0	7.176058	-3.991079	-1.167658
62	1	0	6.933960	-4.297330	0.558728
63	1	0	9.029887	-0.735665	-0.755335
64	1	0	8.443165	-1.916794	-1.945811
65	1	0	9.758885	-2.344431	-0.844220
66	1	0	-1.956603	1.197498	-2.000527
67	1	0	-4.239828	2.076967	-1.962489
68	1	0	-3.614036	3.508828	2.039997
69	1	0	-1.326137	2.643923	1.982083
70	1	0	-7.565969	2.568092	-0.191874
71	1	0	-6.430566	1.475094	0.625941
72	1	0	-6.339374	1.698456	-1.126831
73	1	0	-5.519734	3.957181	-2.083522
74	1	0	-5.065364	5.260218	-0.974904
75	1	0	-6.766392	4.777173	-1.131489
76	1	0	-6.972928	4.435494	1.296068
77	1	0	-5.300383	4.950956	1.547272
78	1	0	-5.864546	3.399152	2.203326
79	1	0	-0.024533	-2.204120	-1.662927
80	1	0	-1.691320	-3.955695	-1.703321
81	1	0	-3.813596	-1.966394	1.476252
82	1	0	-2.102989	-0.261183	1.541701
83	1	0	-3.583993	-4.383172	-2.164589
84	1	0	-3.724866	-6.903177	-0.421840
85	1	0	-2.232440	-6.111410	-0.952168
86	1	0	-3.326938	-6.845564	-2.142292
87	1	0	-6.011586	-4.219161	-1.879932
88	1	0	-6.047973	-5.773080	-1.020595
89	1	0	-5.528569	-5.714727	-2.704356
90	1	0	-4.991132	-5.552072	0.783795
91	1	0	-4.251029	-5.236170	3.062418
92	1	0	-3.256755	-3.842590	2.616880
93	1	0	-2.864302	-5.441353	1.972942
94	1	0	-6.495256	-3.585614	0.535750
95	1	0	-5.605424	-2.744090	1.810335
96	1	0	-6.438674	-4.255274	2.178309

No imaginary frequency.
Total energy: –1872.11087073 hartree.
HOMO (167): –0.19979 hartree; LUMO (168): –0.07853 hartree (PBE0/6-311G(d,p)).

Table S7. Cartesian Coordinates of **4c** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	3.524230	-2.856932	-0.112642
2	7	0	-3.902754	5.117132	-0.106838
3	6	0	2.325586	-2.663313	-0.101881
4	6	0	1.586242	-1.363440	-0.011516
5	6	0	2.089438	-0.067114	0.027677
6	6	0	1.167605	1.005574	0.051749
7	6	0	-0.217232	0.743336	0.028027
8	6	0	-0.714186	-0.584416	0.015022
9	6	0	0.204024	-1.630444	-0.026371
10	6	0	0.004818	-3.098571	-0.154898
11	6	0	-1.131022	-3.892681	-0.274682
12	6	0	-0.969542	-5.275851	-0.410710
13	6	0	0.291609	-5.868798	-0.430944
14	6	0	1.433907	-5.074177	-0.324134
15	6	0	1.268758	-3.707474	-0.191933
16	6	0	1.671495	2.421351	0.172456
17	6	0	-1.176704	1.880936	0.010924
18	6	0	-2.057045	2.131249	1.067517
19	6	0	-2.940858	3.199902	1.044752
20	6	0	-3.002062	4.070750	-0.061635
21	6	0	-2.109221	3.824088	-1.123739
22	6	0	-1.224942	2.756665	-1.077844
23	6	0	-4.646659	5.458796	1.081045
24	6	0	-3.783675	6.102934	-1.153107
25	6	0	3.554938	0.191293	0.041165
26	6	0	4.179714	0.812637	-1.039593
27	6	0	5.547861	1.072116	-1.026810
28	6	0	6.342674	0.731199	0.069561
29	6	0	5.704440	0.110346	1.151946
30	6	0	4.344102	-0.160336	1.139947
31	6	0	7.847470	1.001812	0.123220
32	6	0	8.359375	1.690672	-1.144630
33	6	0	8.160945	1.910769	1.322773
34	6	0	8.598902	-0.329684	0.282740
35	6	0	-2.178418	-0.850726	0.043936
36	6	0	-2.776101	-1.392565	1.182575
37	6	0	-4.142400	-1.662601	1.218757
38	6	0	-4.964569	-1.404197	0.119133
39	6	0	-4.354901	-0.857910	-1.018804
40	6	0	-2.995014	-0.582770	-1.058842
41	6	0	-6.468137	-1.687542	0.118580
42	6	0	-6.946044	-2.290971	1.442021
43	6	0	-7.232930	-0.374747	-0.115883
44	6	0	-6.800597	-2.679093	-1.008145
45	1	0	-2.126557	-3.464429	-0.267511
46	1	0	-1.854054	-5.900885	-0.504645
47	1	0	0.382215	-6.946311	-0.536980
48	1	0	2.434421	-5.497634	-0.349502
49	1	0	0.948993	3.049357	0.699146
50	1	0	1.845387	2.885205	-0.806477
51	1	0	2.623261	2.448336	0.709013
52	1	0	-2.047031	1.478460	1.936154
53	1	0	-3.589571	3.353101	1.899705
54	1	0	-2.100296	4.468086	-1.995937
55	1	0	-0.553244	2.596311	-1.918188
56	1	0	-3.999194	5.749850	1.923830

57	1	0	-5.272405	4.619702	1.408693
58	1	0	-5.312632	6.294728	0.857761
59	1	0	-3.905145	5.644416	-2.142135
60	1	0	-2.815651	6.629169	-1.138587
61	1	0	-4.576664	6.844530	-1.038044
62	1	0	3.590853	1.088276	-1.911254
63	1	0	5.990244	1.549135	-1.895334
64	1	0	6.282752	-0.178630	2.026033
65	1	0	3.883932	-0.654587	1.991118
66	1	0	7.877262	2.662098	-1.304283
67	1	0	8.196217	1.074616	-2.036235
68	1	0	9.437534	1.866979	-1.057985
69	1	0	7.855971	1.453725	2.270018
70	1	0	7.641658	2.871510	1.232223
71	1	0	9.238416	2.108573	1.379153
72	1	0	8.307088	-0.854277	1.198568
73	1	0	9.680687	-0.153096	0.327333
74	1	0	8.394566	-0.996619	-0.561965
75	1	0	-2.161374	-1.613262	2.052174
76	1	0	-4.561377	-2.083817	2.126935
77	1	0	-4.954772	-0.638048	-1.898576
78	1	0	-2.556903	-0.153456	-1.955667
79	1	0	-6.767715	-1.615232	2.286297
80	1	0	-6.453147	-3.246262	1.656047
81	1	0	-8.024345	-2.479680	1.392484
82	1	0	-7.016296	0.350182	0.676609
83	1	0	-8.313905	-0.560414	-0.124827
84	1	0	-6.964400	0.086620	-1.072018
85	1	0	-7.877123	-2.888345	-1.025969
86	1	0	-6.271321	-3.627590	-0.863291
87	1	0	-6.520757	-2.286897	-1.991406

No imaginary frequency.
Total energy: –1754.31522155 hartree.
HOMO (155): –0.20237 hartree; LUMO (156): –0.07463 hartree (PBE0/6-311G(d,p)).

Table S8. Cartesian Coordinates of **4d** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.693962	-2.426110	0.076045
2	6	0	3.481429	-2.488471	0.015578
3	6	0	2.678423	-3.741938	-0.006005
4	6	0	3.135614	-5.047376	0.000700
5	6	0	2.192866	-6.074658	-0.062102
6	6	0	0.834626	-5.769657	-0.136352
7	6	0	0.377789	-4.447273	-0.140912
8	6	0	1.315109	-3.422985	-0.068295
9	6	0	1.186978	-1.943121	-0.059131
10	6	0	0.045666	-1.151706	-0.045486
11	6	0	0.230187	0.258439	-0.041614
12	6	0	1.519775	0.804301	-0.031371
13	6	0	2.673095	0.010002	-0.030400
14	6	0	2.483493	-1.375936	-0.049634
15	6	0	-0.894897	1.121088	-0.043354
16	6	0	-1.867504	1.853097	-0.048800

17	6	0	-3.025138	2.668218	-0.059928
18	6	0	-2.940946	4.069104	-0.002281
19	6	0	-4.074366	4.860483	-0.011863
20	6	0	-5.363032	4.286621	-0.085301
21	6	0	-5.446039	2.877282	-0.138255
22	6	0	-4.306813	2.094483	-0.127177
23	7	0	-6.491323	5.069580	-0.106389
24	6	0	-6.375743	6.499580	0.045159
25	6	0	-7.795079	4.452175	-0.094163
26	6	0	3.991122	0.685931	-0.010969
27	6	0	5.019796	0.347144	-0.891069
28	6	0	6.223327	1.044182	-0.884803
29	6	0	6.456932	2.098512	0.002337
30	6	0	5.420179	2.431417	0.883432
31	6	0	4.212767	1.748042	0.874611
32	6	0	7.774899	2.873815	0.045553
33	6	0	8.779350	2.372752	-0.995554
34	6	0	7.503232	4.362180	-0.226988
35	6	0	8.409290	2.719376	1.437598
36	6	0	-1.330559	-1.710883	-0.002042
37	6	0	-1.856280	-2.214020	1.187878
38	6	0	-3.151973	-2.722601	1.240013
39	6	0	-3.971616	-2.746816	0.108469
40	6	0	-3.433677	-2.236338	-1.081490
41	6	0	-2.143673	-1.725007	-1.139288
42	6	0	-5.400434	-3.293953	0.127189
43	6	0	-6.378456	-2.177615	-0.274195
44	6	0	-5.806394	-3.811233	1.509510
45	6	0	-5.516220	-4.455733	-0.873008
46	1	0	4.202559	-5.247160	0.050773
47	1	0	2.514641	-7.112426	-0.058104
48	1	0	0.109149	-6.577208	-0.192887
49	1	0	-0.684756	-4.241305	-0.202137
50	1	0	1.621956	1.885032	-0.044233
51	1	0	-1.962688	4.537684	0.053810
52	1	0	-3.956479	5.936915	0.038575
53	1	0	-6.412073	2.387588	-0.187095
54	1	0	-4.396365	1.012424	-0.170014
55	1	0	-7.369924	6.947272	0.000724
56	1	0	-5.917956	6.781359	1.005079
57	1	0	-5.774899	6.941963	-0.760528
58	1	0	-8.560717	5.229176	-0.124214
59	1	0	-7.941983	3.806398	-0.970029
60	1	0	-7.961247	3.844882	0.808169
61	1	0	4.880199	-0.468526	-1.591963
62	1	0	6.991201	0.747117	-1.591260
63	1	0	5.554706	3.239900	1.597884
64	1	0	3.434473	2.024456	1.581895
65	1	0	8.396174	2.481610	-2.016627
66	1	0	9.703872	2.956915	-0.924933
67	1	0	9.039753	1.320326	-0.836102
68	1	0	6.818710	4.792887	0.511325
69	1	0	8.439464	4.932303	-0.187212
70	1	0	7.058736	4.504042	-1.218441
71	1	0	7.754517	3.102240	2.227449
72	1	0	8.617786	1.666517	1.657295
73	1	0	9.354369	3.273907	1.488012

74	1	0	-1.243718	-2.207699	2.085793
75	1	0	-3.518364	-3.101607	2.188554
76	1	0	-4.033141	-2.235689	-1.988631
77	1	0	-1.758166	-1.331754	-2.076182
78	1	0	-6.164697	-1.790128	-1.276072
79	1	0	-7.408270	-2.555247	-0.274582
80	1	0	-6.323150	-1.339105	0.429720
81	1	0	-5.775647	-3.019104	2.266216
82	1	0	-6.832867	-4.192999	1.472594
83	1	0	-5.160732	-4.631456	1.843445
84	1	0	-5.279410	-4.140092	-1.894432
85	1	0	-4.832498	-5.269692	-0.607193
86	1	0	-6.537584	-4.855323	-0.875272

No imaginary frequency.
Total energy: –1791.12164636 hartree.
HOMO (157): –0.19168 hartree; LUMO (158): –0.07465 hartree (PBE0/6-311G(d,p)).

Table S9. Cartesian Coordinates of **4e** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.557501	2.243109	0.130788
2	6	0	-4.368685	2.478246	0.043942
3	6	0	-3.755348	3.829688	-0.051106
4	6	0	-4.400722	5.051474	-0.113710
5	6	0	-3.622331	6.199970	-0.262890
6	6	0	-2.236064	6.090914	-0.355800
7	6	0	-1.588909	4.852239	-0.287668
8	6	0	-2.360289	3.706700	-0.121431
9	6	0	-2.018258	2.261409	-0.026972
10	6	0	-0.772379	1.636806	0.017867
11	6	0	-0.750994	0.218476	0.063922
12	6	0	-1.951273	-0.492903	0.079403
13	6	0	-3.211576	0.122788	0.060116
14	6	0	-3.219991	1.518085	0.008876
15	6	0	0.514015	-0.555276	0.075036
16	6	0	0.701323	-1.604279	-0.833944
17	6	0	1.873414	-2.347262	-0.853263
18	6	0	2.896560	-2.079639	0.064411
19	6	0	2.703502	-1.054792	1.000334
20	6	0	1.540668	-0.300900	0.993470
21	7	0	4.097599	-2.816351	0.046451
22	6	0	4.076136	-4.200868	-0.238090
23	6	0	3.089629	-5.023830	0.318851
24	6	0	3.067124	-6.383335	0.030893
25	6	0	4.033453	-6.948659	-0.797848
26	6	0	5.021113	-6.133324	-1.345139
27	6	0	5.041122	-4.769415	-1.078291
28	6	0	5.330414	-2.163427	0.274124
29	6	0	6.331954	-2.783936	1.031025
30	6	0	7.548154	-2.145031	1.242289
31	6	0	7.782012	-0.874654	0.721522
32	6	0	6.783557	-0.251632	-0.023542
33	6	0	5.570562	-0.889340	-0.255926
34	6	0	-4.417796	-0.735725	0.086271

35	6	0	-5.476239	-0.559553	-0.806242
36	6	0	-6.566015	-1.423281	-0.802658
37	6	0	-6.653053	-2.491798	0.094200
38	6	0	-5.588038	-2.660521	0.988479
39	6	0	-4.492432	-1.809153	0.982790
40	6	0	-7.841339	-3.454121	0.131541
41	6	0	-8.499613	-3.396866	1.519684
42	6	0	-8.902789	-3.107003	-0.915511
43	6	0	-7.347669	-4.884437	-0.139991
44	6	0	0.493102	2.419209	-0.007084
45	6	0	0.898017	3.167502	1.099176
46	6	0	2.089849	3.888687	1.081288
47	6	0	2.920585	3.895391	-0.042779
48	6	0	2.500376	3.147110	-1.151117
49	6	0	1.317791	2.420082	-1.136186
50	6	0	4.239041	4.669047	-0.100000
51	6	0	4.537026	5.406076	1.208072
52	6	0	5.392729	3.689500	-0.373289
53	6	0	4.173183	5.706002	-1.232941
54	1	0	-5.484874	5.094285	-0.053501
55	1	0	-4.093646	7.177425	-0.315905
56	1	0	-1.637956	6.989205	-0.486085
57	1	0	-0.509504	4.804265	-0.369130
58	1	0	-1.905717	-1.578207	0.111789
59	1	0	-0.072761	-1.816292	-1.567413
60	1	0	2.006078	-3.134093	-1.589587
61	1	0	3.477495	-0.849685	1.733609
62	1	0	1.419541	0.486860	1.729950
63	1	0	2.343048	-4.589118	0.976878
64	1	0	2.294243	-7.007387	0.471888
65	1	0	4.016997	-8.012887	-1.014465
66	1	0	5.777931	-6.558053	-1.999452
67	1	0	5.805272	-4.135084	-1.517523
68	1	0	6.149437	-3.769226	1.449496
69	1	0	8.313801	-2.642013	1.832276
70	1	0	8.731301	-0.375873	0.894453
71	1	0	6.952457	0.736734	-0.443495
72	1	0	4.799951	-0.402051	-0.845810
73	1	0	-5.449008	0.259182	-1.516976
74	1	0	-7.361003	-1.246538	-1.519719
75	1	0	-5.610799	-3.472155	1.711548
76	1	0	-3.690142	-1.962622	1.700589
77	1	0	-7.799820	-3.678016	2.313647
78	1	0	-9.351723	-4.086169	1.565437
79	1	0	-8.864467	-2.387083	1.737715
80	1	0	-9.315069	-2.103764	-0.759267
81	1	0	-9.732132	-3.820101	-0.848390
82	1	0	-8.502517	-3.159886	-1.934434
83	1	0	-6.876993	-4.954558	-1.127023
84	1	0	-8.187714	-5.589189	-0.111271
85	1	0	-6.613551	-5.209659	0.604656
86	1	0	0.271207	3.186788	1.987747
87	1	0	2.365889	4.449855	1.968217
88	1	0	3.110739	3.125594	-2.050667
89	1	0	1.026746	1.842127	-2.009328
90	1	0	5.487839	5.943241	1.119102
91	1	0	4.625633	4.714901	2.053951

92	1	0	3.762395	6.144179	1.445401
93	1	0	5.265844	3.170395	-1.329464
94	1	0	5.457928	2.930594	0.414646
95	1	0	6.347224	4.228572	-0.410597
96	1	0	3.996302	5.235553	-2.205841
97	1	0	5.117171	6.260729	-1.296473
98	1	0	3.366091	6.426164	-1.057630

No imaginary frequency.
Total energy: –2098.09181093 hartree.
HOMO (183): –0.19958 hartree; LUMO (184): –0.08319 hartree (PBE0/6-311G(d,p)).

Table S10. Cartesian Coordinates of **4f** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.679399	2.242054	0.033743
2	6	0	-3.470297	2.347386	-0.014349
3	6	0	-2.704733	3.625506	-0.028180
4	6	0	-3.199412	4.917039	-0.021730
5	6	0	-2.286454	5.971998	-0.068251
6	6	0	-0.919043	5.707112	-0.125432
7	6	0	-0.423459	4.398638	-0.129976
8	6	0	-1.331031	3.346986	-0.074795
9	6	0	-1.160878	1.872468	-0.074139
10	6	0	-0.010712	1.096906	-0.069656
11	6	0	-0.169271	-0.314704	-0.097194
12	6	0	-2.600329	-0.118209	-0.076660
13	6	0	-2.434596	1.267275	-0.070720
14	6	0	0.992810	-1.128851	-0.098720
15	6	0	2.000500	-1.812844	-0.092540
16	6	0	3.200250	-2.565067	-0.087358
17	6	0	3.190876	-3.968559	-0.030242
18	6	0	4.365216	-4.697996	-0.020859
19	6	0	5.622057	-4.055811	-0.074320
20	6	0	5.629831	-2.644023	-0.125329
21	6	0	4.450215	-1.923388	-0.133587
22	7	0	6.791646	-4.777086	-0.078782
23	6	0	6.751708	-6.208636	0.097728
24	6	0	8.058527	-4.088794	-0.024837
25	6	0	-3.954955	-0.733529	-0.043894
26	6	0	-4.842613	-0.598641	-1.109937
27	6	0	-6.097925	-1.198286	-1.075758
28	6	0	-6.520356	-1.947486	0.025372
29	6	0	-5.622981	-2.073740	1.093718
30	6	0	-4.366335	-1.485105	1.061196
31	6	0	-7.895564	-2.613578	0.101421
32	6	0	-8.735778	-2.356592	-1.152137
33	6	0	-7.719255	-4.132516	0.258627
34	6	0	-8.662434	-2.061026	1.313747
35	6	0	1.353862	1.683733	-0.011670
36	6	0	1.860163	2.187590	1.186202
37	6	0	3.141678	2.729828	1.250905
38	6	0	3.965684	2.788967	0.123861
39	6	0	3.446865	2.278673	-1.074794
40	6	0	2.171234	1.734054	-1.144847

41	6	0	5.379587	3.373217	0.156466
42	6	0	6.389152	2.285885	-0.246591
43	6	0	5.762496	3.889884	1.545538
44	6	0	5.472295	4.545367	-0.833954
45	1	0	-4.272313	5.085509	0.015731
46	1	0	-2.638479	6.999900	-0.064333
47	1	0	-0.216893	6.535913	-0.168360
48	1	0	0.645452	4.223356	-0.177205
49	1	0	2.238537	-4.489327	0.011572
50	1	0	4.305046	-5.779160	0.029636
51	1	0	6.568764	-2.102841	-0.156667
52	1	0	4.482366	-0.838052	-0.174137
53	1	0	7.768777	-6.602802	0.065300
54	1	0	6.303128	-6.499454	1.059574
55	1	0	6.181219	-6.695304	-0.704115
56	1	0	8.866472	-4.821841	-0.052605
57	1	0	8.186939	-3.420600	-0.886213
58	1	0	8.172190	-3.489415	0.891140
59	1	0	-4.550668	-0.013160	-1.977313
60	1	0	-6.754645	-1.065550	-1.929309
61	1	0	-5.907469	-2.642810	1.975669
62	1	0	-3.694738	-1.600254	1.908640
63	1	0	-8.254683	-2.753161	-2.053551
64	1	0	-9.708151	-2.852015	-1.051247
65	1	0	-8.922717	-1.287493	-1.303810
66	1	0	-7.157915	-4.384906	1.164428
67	1	0	-8.697300	-4.625109	0.323005
68	1	0	-7.180542	-4.554327	-0.597356
69	1	0	-8.134093	-2.256666	2.252695
70	1	0	-8.799979	-0.977608	1.227564
71	1	0	-9.652500	-2.528303	1.383074
72	1	0	1.243425	2.155132	2.080691
73	1	0	3.493220	3.107856	2.205460
74	1	0	4.050122	2.305180	-1.979080
75	1	0	1.800444	1.342293	-2.088267
76	1	0	6.191412	1.899890	-1.252322
77	1	0	7.408615	2.690593	-0.238356
78	1	0	6.352113	1.441382	0.451449
79	1	0	5.747377	3.091132	2.295723
80	1	0	6.778759	4.298817	1.518816
81	1	0	5.092838	4.689844	1.881299
82	1	0	5.251708	4.231635	-1.859578
83	1	0	4.765388	5.339007	-0.567413
84	1	0	6.482755	4.971722	-0.825246
85	6	0	-1.522924	-2.424490	-0.172382
86	1	0	-0.793756	-2.815476	-0.889347
87	1	0	-2.519616	-2.763592	-0.459551
88	1	0	-1.279893	-2.875851	0.798248
89	6	0	-1.444842	-0.925123	-0.110413

No imaginary frequency.
Total energy: –1830.38756820 hartree.
HOMO (161): –0.19021 hartree; LUMO (162): –0.07463 hartree (PBE0/6-311G(d,p)).

Table S11. Cartesian Coordinates of **5a** at the PBE0/6-31G(d) Level

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.417665	1.156077	-0.367313
2	6	0	0.704020	0.432212	-1.011331
3	6	0	1.137821	-0.880063	-0.472113
4	6	0	0.288665	-1.912997	-0.174237
5	6	0	-1.168986	-1.894464	-0.103919
6	6	0	-2.012583	-0.804748	-0.028228
7	6	0	-1.576659	0.564496	0.031474
8	6	0	0.719781	-3.326514	0.048701
9	6	0	-0.410776	-4.120512	0.262731
10	6	0	-1.630767	-3.297942	0.167038
11	6	0	1.969665	-3.950178	0.007954
12	6	0	2.041708	-5.327091	0.216559
13	6	0	0.901741	-6.098179	0.457694
14	6	0	-0.348019	-5.490378	0.472834
15	8	0	1.350061	0.973954	-1.897521
16	8	0	-2.763868	-3.716917	0.312292
17	6	0	2.611375	-0.984210	-0.322739
18	6	0	-3.486557	-0.947216	0.029459
19	6	0	-0.266680	2.624347	-0.261406
20	6	0	-4.243549	-0.303459	1.015462
21	6	0	-5.627209	-0.371200	1.037239
22	6	0	-6.332465	-1.064598	0.032633
23	6	0	-5.569532	-1.705696	-0.967404
24	6	0	-4.188822	-1.650808	-0.956536
25	6	0	-1.354457	3.488909	-0.414354
26	6	0	-1.212079	4.864243	-0.256174
27	6	0	0.020208	5.438699	0.061888
28	6	0	1.110302	4.567007	0.200565
29	6	0	0.978880	3.198394	0.034711
30	6	0	3.493113	-0.907713	-1.407460
31	6	0	4.864775	-0.985526	-1.204400
32	6	0	5.420449	-1.118327	0.075752
33	6	0	4.531247	-1.170987	1.153206
34	6	0	3.154826	-1.104501	0.959437
35	7	0	-7.708168	-1.107640	0.021069
36	6	0	-8.385160	-1.974573	-0.913625
37	6	0	-8.446049	-0.571026	1.138617
38	1	0	-2.347989	1.245101	0.385702
39	1	0	2.878878	-3.396196	-0.184070
40	1	0	3.015150	-5.809843	0.186886
41	1	0	0.995506	-7.168465	0.619642
42	1	0	-1.265270	-6.050192	0.632530
43	1	0	-3.739187	0.233409	1.815975
44	1	0	-6.158743	0.116670	1.846054
45	1	0	-6.059580	-2.260015	-1.759457
46	1	0	-3.635971	-2.157589	-1.741436
47	1	0	-2.325187	3.090065	-0.696836
48	1	0	-2.086454	5.491041	-0.398162
49	1	0	2.092892	4.965233	0.440793
50	1	0	1.853303	2.563628	0.140261
51	1	0	3.096592	-0.789182	-2.409072
52	1	0	5.517576	-0.934131	-2.072356
53	1	0	4.905430	-1.262657	2.167665
54	1	0	2.487109	-1.153359	1.816063
55	1	0	-9.463648	-1.873377	-0.778956

56	1	0	-8.119030	-3.033841	-0.776822
57	1	0	-8.154991	-1.697168	-1.949859
58	1	0	-9.515313	-0.668261	0.941861
59	1	0	-8.232008	0.496055	1.277300
60	1	0	-8.222005	-1.089543	2.083941
61	6	0	6.939057	-1.188913	0.246996
62	6	0	7.485298	-2.398077	-0.529471
63	1	0	7.259357	-2.331635	-1.598809
64	1	0	8.575139	-2.458035	-0.421481
65	1	0	7.053957	-3.332559	-0.153092
66	6	0	7.573129	0.098764	-0.303826
67	1	0	7.207920	0.977442	0.239334
68	1	0	8.664148	0.060610	-0.198274
69	1	0	7.344717	0.243446	-1.364864
70	6	0	7.351798	-1.336434	1.713687
71	1	0	7.018980	-0.484817	2.317925
72	1	0	6.950229	-2.253448	2.160013
73	1	0	8.444116	-1.385059	1.785242
74	6	0	0.216083	6.943609	0.247067
75	6	0	-1.083939	7.727355	0.050018
76	1	0	-1.487534	7.600203	-0.961010
77	1	0	-1.854093	7.425571	0.769120
78	1	0	-0.894882	8.796538	0.197402
79	6	0	0.730629	7.216968	1.669905
80	1	0	1.684957	6.715322	1.861551
81	1	0	0.883128	8.292968	1.818339
82	1	0	0.012162	6.867591	2.419849
83	6	0	1.245582	7.454562	-0.773999
84	1	0	0.901905	7.276063	-1.798828
85	1	0	1.401474	8.532933	-0.648039
86	1	0	2.215688	6.960804	-0.656220

No imaginary frequency.
Total energy: –1828.21536281 hartree.
HOMO (158): –0.20079 hartree; LUMO (159): –0.09055 hartree (PBE0/6-311G(d,p)).

Table S12. Cartesian Coordinates of **5b** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.455681	1.245399	-0.358351
2	6	0	1.522725	0.429011	-0.984906
3	6	0	1.853381	-0.905109	-0.426377
4	6	0	0.932083	-1.862449	-0.094250
5	6	0	-0.520954	-1.734928	-0.031930
6	6	0	-1.282631	-0.584939	0.001492
7	6	0	-0.748059	0.749309	0.037439
8	6	0	1.257389	-3.295864	0.176483
9	6	0	0.069956	-3.998355	0.403758
10	6	0	-1.086140	-3.092414	0.276308
11	6	0	2.458602	-4.010246	0.174824
12	6	0	2.426878	-5.381459	0.427437
13	6	0	1.231155	-6.059702	0.676270
14	6	0	0.029641	-5.361557	0.657794
15	8	0	2.213147	0.908594	-1.873460
16	8	0	-2.247171	-3.422687	0.429365

17	6	0	3.317765	-1.125897	-0.309090
18	6	0	-2.763505	-0.621364	0.036057
19	6	0	0.715791	2.699078	-0.266358
20	6	0	-3.492842	0.109610	0.981621
21	6	0	-4.879044	0.121637	0.979785
22	6	0	-5.617309	-0.557725	-0.008654
23	6	0	-4.873659	-1.260618	-0.979984
24	6	0	-3.492906	-1.308274	-0.941843
25	6	0	-0.303776	3.640481	-0.434586
26	6	0	-0.063588	5.001957	-0.276565
27	6	0	1.203398	5.485736	0.056251
28	6	0	2.225881	4.537487	0.205817
29	6	0	1.997161	3.181569	0.040158
30	6	0	4.157725	-1.208296	-1.425375
31	6	0	5.523210	-1.401201	-1.264071
32	6	0	6.115473	-1.493141	0.003398
33	6	0	5.270160	-1.382623	1.111100
34	6	0	3.897921	-1.202828	0.959431
35	7	0	-7.004409	-0.537977	-0.033182
36	6	0	-7.805403	-1.711487	-0.400009
37	6	0	-7.791262	0.640244	0.340984
38	1	0	-1.470037	1.491464	0.371980
39	1	0	3.409271	-3.532345	-0.019572
40	1	0	3.362931	-5.934026	0.427114
41	1	0	1.244358	-7.128311	0.872209
42	1	0	-0.927891	-5.846687	0.825278
43	1	0	-2.969322	0.633359	1.778569
44	1	0	-5.396634	0.637430	1.779943
45	1	0	-5.389487	-1.755731	-1.794196
46	1	0	-2.960209	-1.860208	-1.710353
47	1	0	-1.297790	3.312367	-0.726948
48	1	0	-0.888436	5.690404	-0.429228
49	1	0	3.232123	4.863852	0.456214
50	1	0	2.821665	2.484875	0.156497
51	1	0	3.733038	-1.125638	-2.419298
52	1	0	6.142052	-1.476235	-2.154829
53	1	0	5.675440	-1.436590	2.116325
54	1	0	3.263246	-1.130527	1.839243
55	1	0	-8.747183	-1.578641	0.151369
56	1	0	-8.725773	0.532434	-0.227900
57	6	0	7.625512	-1.705109	0.126920
58	6	0	8.006353	-3.035863	-0.542025
59	1	0	7.733145	-3.049751	-1.602336
60	1	0	9.088408	-3.201448	-0.472762
61	1	0	7.500905	-3.877192	-0.054536
62	6	0	8.363688	-0.553181	-0.574292
63	1	0	8.113872	0.409305	-0.114306
64	1	0	9.448405	-0.696700	-0.499158
65	1	0	8.108387	-0.491689	-1.637206
66	6	0	8.088545	-1.751437	1.585273
67	1	0	7.865200	-0.817174	2.112965
68	1	0	7.623664	-2.577474	2.135643
69	1	0	9.173523	-1.900289	1.622133
70	6	0	1.504304	6.972592	0.246364
71	6	0	0.263210	7.845955	0.045774
72	1	0	-0.143101	7.750074	-0.967572
73	1	0	-0.529619	7.596428	0.760201

74	1	0	0.526068	8.898810	0.197443
75	6	0	2.030328	7.206263	1.672108
76	1	0	2.947261	6.640048	1.866766
77	1	0	2.255437	8.268949	1.823696
78	1	0	1.286465	6.905169	2.418222
79	6	0	2.571606	7.412039	-0.769071
80	1	0	2.219845	7.262434	-1.795797
81	1	0	2.804323	8.475933	-0.638469
82	1	0	3.503191	6.849265	-0.649779
83	6	0	-7.180233	1.957424	-0.128890
84	1	0	-6.261877	2.214182	0.405472
85	1	0	-6.945879	1.912261	-1.197164
86	1	0	-7.899133	2.767735	0.033288
87	6	0	-8.187106	0.674652	1.821534
88	1	0	-8.933765	1.457658	1.998489
89	1	0	-8.621936	-0.282035	2.131092
90	1	0	-7.331384	0.877939	2.472846
91	6	0	-8.177387	-1.759725	-1.885925
92	1	0	-7.314915	-1.988829	-2.519530
93	1	0	-8.935021	-2.531816	-2.063971
94	1	0	-8.589628	-0.799849	-2.216309
95	6	0	-7.223328	-3.030911	0.099544
96	1	0	-7.951432	-3.832076	-0.067274
97	1	0	-6.297138	-3.309199	-0.409341
98	1	0	-7.009932	-2.975760	1.171621

No imaginary frequency.
Total energy: –1985.26968731 hartree.
HOMO (174): –0.19931 hartree; LUMO (175): –0.09181 hartree (PBE0/6-311G(d,p)).

Table S13. Cartesian Coordinates of **6a** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.465972	-0.766312	-0.039370
2	6	0	1.331093	-1.148532	0.169769
3	6	0	-0.574422	0.914467	0.107457
4	6	0	2.040273	-2.426784	0.312869
5	6	0	0.797132	1.175440	0.110992
6	6	0	-5.224927	-1.432587	-0.167305
7	6	0	-3.240568	-0.410944	-1.148166
8	6	0	-1.258783	3.181212	-0.690865
9	6	0	-0.051294	-1.435516	0.014375
10	6	0	-1.498997	2.068617	0.125865
11	6	0	-1.019119	-0.433232	0.034374
12	6	0	-3.091462	-1.451330	1.003855
13	6	0	5.865077	1.454701	-0.445799
14	6	0	1.096342	-3.474218	-0.117013
15	6	0	-0.183252	-2.885315	-0.233680
16	6	0	-1.271846	-3.661620	-0.611938
17	6	0	-6.711795	-1.775315	-0.276256
18	6	0	3.719591	1.664262	0.686186
19	6	0	-4.586886	-0.743672	-1.208478
20	6	0	4.009861	-0.021296	-0.991553
21	6	0	1.780991	0.179455	0.124134
22	6	0	-2.602447	2.141271	0.986062

23	6	0	-3.185704	4.370318	0.196390
24	7	0	-4.012717	5.471900	0.216241
25	6	0	-5.030180	5.577429	1.234032
26	6	0	5.320732	0.402309	-1.186087
27	6	0	3.189577	0.593693	-0.042973
28	6	0	0.183934	-5.597610	-0.757513
29	6	0	-2.073089	4.301776	-0.666767
30	6	0	1.282992	-4.829378	-0.373811
31	6	0	-3.634556	6.655108	-0.518040
32	6	0	5.027611	2.077521	0.489486
33	6	0	-3.418556	3.258863	1.033397
34	6	0	-4.444851	-1.774913	0.940591
35	6	0	7.309760	1.928430	-0.608753
36	6	0	-1.075999	-5.019345	-0.873651
37	6	0	-7.524655	-0.479708	-0.430608
38	6	0	-6.939324	-2.668929	-1.506419
39	6	0	-7.228588	-2.519087	0.958017
40	6	0	8.065955	1.132607	-1.675661
41	6	0	7.321039	3.410606	-1.016022
42	6	0	8.046957	1.759954	0.730226
43	1	0	1.123139	2.211562	0.095018
44	1	0	-2.779731	0.130991	-1.969534
45	1	0	-0.419893	3.162336	-1.382591
46	1	0	-2.509466	-1.739811	1.875973
47	1	0	-2.259392	-3.228639	-0.714825
48	1	0	3.110658	2.148953	1.444800
49	1	0	-5.152549	-0.455283	-2.090965
50	1	0	3.614974	-0.833573	-1.596408
51	1	0	-2.818038	1.312427	1.653053
52	1	0	-5.739908	4.743360	1.170892
53	1	0	-5.594067	6.499688	1.082431
54	1	0	-4.612709	5.593307	2.253025
55	1	0	5.920220	-0.104252	-1.935187
56	1	0	0.320577	-6.653150	-0.973718
57	1	0	-1.839111	5.127387	-1.329224
58	1	0	2.260489	-5.290501	-0.300859
59	1	0	-2.679477	7.082120	-0.174061
60	1	0	-4.409983	7.414022	-0.398776
61	1	0	-3.544625	6.442535	-1.590546
62	1	0	5.408766	2.897236	1.092683
63	1	0	-4.243515	3.265860	1.736684
64	1	0	-4.887511	-2.305339	1.777416
65	1	0	-1.922750	-5.628504	-1.178411
66	1	0	-7.232910	0.081827	-1.324336
67	1	0	-7.384194	0.175329	0.436437
68	1	0	-8.593441	-0.710656	-0.515013
69	1	0	-6.627652	-2.174502	-2.432446
70	1	0	-8.002692	-2.919396	-1.603047
71	1	0	-6.375775	-3.604749	-1.420013
72	1	0	-8.293695	-2.743211	0.832353
73	1	0	-7.122857	-1.919321	1.869252
74	1	0	-6.707068	-3.471017	1.109998
75	1	0	7.603973	1.233204	-2.664689
76	1	0	8.119863	0.066853	-1.426319
77	1	0	9.093329	1.505768	-1.751980
78	1	0	6.808064	3.558441	-1.973037
79	1	0	8.352879	3.766664	-1.123243

80	1	0	6.827250	4.041913	-0.269792
81	1	0	8.039092	0.713047	1.052030
82	1	0	7.586071	2.354362	1.525885
83	1	0	9.090530	2.083085	0.632121
84	6	0	3.234663	-2.660842	0.950847
85	6	0	3.969933	-1.687235	1.690301
86	6	0	3.800020	-3.967194	1.060096
87	7	0	4.587744	-0.987010	2.382983
88	7	0	4.301484	-5.012475	1.152693

No imaginary frequency.
Total energy: –1863.41998456 hartree.
HOMO (163): –0.20643 hartree; LUMO (164): –0.10712 hartree (PBE0/6-311G(d,p)).

Table S14. Cartesian Coordinates of **6b** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-5.278771	0.003853	-2.359912
2	7	0	-6.062027	4.039216	-1.468455
3	7	0	4.691048	-3.858040	-0.150372
4	6	0	-3.189060	2.225637	-0.471865
5	6	0	-2.177509	1.191120	-0.226555
6	6	0	-2.273247	-0.205466	-0.110234
7	6	0	-1.068250	-0.915639	-0.075324
8	6	0	0.190385	-0.308594	-0.054138
9	6	0	0.270093	1.108394	0.007638
10	6	0	-0.917484	1.832026	-0.086639
11	6	0	-1.151264	3.289946	-0.063339
12	6	0	-0.282046	4.367113	0.062290
13	6	0	-0.806864	5.660323	0.110679
14	6	0	-2.177710	5.880761	0.030207
15	6	0	-3.056623	4.811310	-0.137721
16	6	0	-2.539951	3.519948	-0.196098
17	6	0	-4.406228	2.082838	-1.096141
18	6	0	-4.863512	0.892761	-1.735834
19	6	0	-5.297731	3.178583	-1.300979
20	6	0	1.377767	-1.189385	-0.066401
21	6	0	1.448339	-2.243132	-0.985515
22	6	0	2.532460	-3.106372	-1.036922
23	6	0	3.611401	-2.986739	-0.135834
24	6	0	3.520867	-1.940068	0.806236
25	6	0	2.448940	-1.065527	0.828572
26	6	0	6.051538	-3.423502	0.198646
27	6	0	6.433150	-2.064430	-0.390787
28	6	0	6.378894	-3.526903	1.692259
29	6	0	4.579169	-5.123381	-0.879014
30	6	0	5.218448	-6.284056	-0.116082
31	6	0	5.104270	-5.037675	-2.314674
32	6	0	-3.524782	-0.951263	0.134740
33	6	0	-4.456063	-0.492495	1.069126
34	6	0	-5.607260	-1.220924	1.350460
35	6	0	-5.875944	-2.435431	0.714217
36	6	0	-4.926950	-2.895629	-0.208920
37	6	0	-3.775742	-2.177728	-0.491038
38	6	0	-7.141044	-3.252180	0.978219

39	6	0	-8.060160	-2.582753	2.003271
40	6	0	-7.922299	-3.411393	-0.336620
41	6	0	-6.752189	-4.640032	1.512510
42	6	0	1.587077	1.790179	0.135216
43	6	0	2.459643	1.876079	-0.952933
44	6	0	3.693246	2.500650	-0.825527
45	6	0	4.115050	3.060380	0.388112
46	6	0	3.235023	2.970781	1.470421
47	6	0	1.994248	2.348970	1.347852
48	6	0	5.489579	3.725302	0.486259
49	6	0	6.577991	2.692413	0.150860
50	6	0	5.567268	4.889903	-0.514277
51	6	0	5.768880	4.277306	1.886385
52	1	0	-1.114648	-1.995547	0.030617
53	1	0	0.788427	4.218069	0.125160
54	1	0	-0.129994	6.503718	0.217709
55	1	0	-2.571842	6.891106	0.088629
56	1	0	-4.120496	4.999751	-0.212045
57	1	0	0.649506	-2.364567	-1.713672
58	1	0	2.545686	-3.859605	-1.816622
59	1	0	4.290165	-1.826096	1.559256
60	1	0	2.432041	-0.290110	1.587023
61	1	0	6.704907	-4.149191	-0.298244
62	1	0	7.494954	-1.870384	-0.202676
63	1	0	5.859958	-1.238871	0.039710
64	1	0	6.269201	-2.055846	-1.473288
65	1	0	5.874922	-2.763174	2.291637
66	1	0	7.457466	-3.402635	1.844525
67	1	0	6.088736	-4.505748	2.085048
68	1	0	3.509228	-5.349098	-0.917476
69	1	0	4.812216	-6.351972	0.897778
70	1	0	6.308105	-6.194649	-0.046663
71	1	0	5.003964	-7.224693	-0.634956
72	1	0	6.184630	-4.850462	-2.333137
73	1	0	4.614749	-4.228711	-2.866668
74	1	0	4.925346	-5.977004	-2.850153
75	1	0	-4.271603	0.440073	1.596235
76	1	0	-6.299863	-0.824791	2.085917
77	1	0	-5.095203	-3.832060	-0.734375
78	1	0	-3.079151	-2.550949	-1.237180
79	1	0	-8.393723	-1.594978	1.665713
80	1	0	-7.570845	-2.467924	2.977419
81	1	0	-8.953326	-3.199457	2.153235
82	1	0	-7.335692	-3.935842	-1.097932
83	1	0	-8.201092	-2.435100	-0.747331
84	1	0	-8.839165	-3.988180	-0.164356
85	1	0	-6.202912	-4.557131	2.457076
86	1	0	-6.120221	-5.185918	0.804033
87	1	0	-7.650799	-5.242988	1.691144
88	1	0	2.167540	1.444114	-1.906288
89	1	0	4.342076	2.548004	-1.696601
90	1	0	3.510565	3.387667	2.433792
91	1	0	1.330491	2.297922	2.207989
92	1	0	6.550847	1.852755	0.854675
93	1	0	7.570907	3.154536	0.208732
94	1	0	6.456861	2.286269	-0.858724
95	1	0	6.551486	5.370762	-0.461654

96	1	0	4.806415	5.647081	-0.294154
97	1	0	5.415618	4.553056	-1.545058
98	1	0	5.039604	5.042558	2.175798
99	1	0	6.760897	4.741903	1.907327
100	1	0	5.758424	3.486975	2.645668

No imaginary frequency.
Total energy: –2020.47628487 hartree.
HOMO (179): –0.20456 hartree; LUMO (180): –0.10808 hartree (PBE0/6-311G(d,p)).

Table S15. Cartesian Coordinates of **6c** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.150859	-2.242294	-0.465824
2	7	0	-4.559762	-0.598567	-2.552800
3	6	0	-1.262653	-3.368446	-0.123385
4	6	0	-1.509949	-4.732789	0.000114
5	6	0	-0.435479	-5.592786	0.226165
6	6	0	0.861970	-5.096846	0.301279
7	6	0	1.117370	-3.728593	0.186759
8	6	0	0.049979	-2.858816	-0.000918
9	6	0	-0.016799	-1.389009	-0.088029
10	6	0	0.986694	-0.429093	-0.017511
11	6	0	0.613847	0.933862	-0.083820
12	6	0	-0.744052	1.314933	-0.068233
13	6	0	-1.763195	0.333176	-0.129815
14	6	0	-1.371867	-1.011538	-0.244820
15	6	0	-3.346666	-2.379952	-1.128103
16	6	0	-4.006440	-1.344920	-1.853855
17	6	0	-3.987981	-3.644252	-1.299189
18	7	0	-4.555581	-4.649341	-1.441274
19	6	0	-1.086001	2.772406	0.115887
20	6	0	1.665308	1.983680	-0.144691
21	6	0	1.783448	2.786317	-1.284174
22	6	0	2.747912	3.776548	-1.387981
23	6	0	3.652460	4.019548	-0.334156
24	6	0	3.519382	3.226244	0.823386
25	6	0	2.556750	2.231059	0.903507
26	7	0	4.627266	4.990443	-0.434149
27	6	0	5.405742	5.334594	0.730617
28	6	0	4.598165	5.908046	-1.546975
29	6	0	-3.181355	0.703933	0.103401
30	6	0	-3.845936	1.688002	-0.638300
31	6	0	-5.161552	2.023162	-0.360190
32	6	0	-5.880510	1.401081	0.669765
33	6	0	-5.211301	0.424487	1.410512
34	6	0	-3.890604	0.082454	1.134558
35	6	0	-7.334599	1.794851	0.931218
36	6	0	-7.408828	3.296732	1.250739
37	6	0	-8.170307	1.497145	-0.324673
38	6	0	-7.942266	1.024635	2.106099
39	6	0	2.418122	-0.819698	0.113920
40	6	0	2.953075	-1.161134	1.356343
41	6	0	4.285558	-1.547768	1.482818
42	6	0	5.133558	-1.610576	0.373853

43	6	0	4.585568	-1.263504	-0.868666
44	6	0	3.259351	-0.873894	-1.000323
45	6	0	6.600478	-2.034199	0.470539
46	6	0	6.827571	-3.285825	-0.392548
47	6	0	7.017371	-2.361435	1.906805
48	6	0	7.495252	-0.893417	-0.040777
49	1	0	-2.513222	-5.135520	-0.064816
50	1	0	-0.618974	-6.657536	0.336617
51	1	0	1.692292	-5.780442	0.457025
52	1	0	2.134271	-3.361097	0.249028
53	1	0	-0.285051	3.290101	0.648483
54	1	0	-2.016090	2.890547	0.676579
55	1	0	-1.217493	3.292982	-0.840674
56	1	0	1.103797	2.626054	-2.118099
57	1	0	2.793138	4.363907	-2.298166
58	1	0	4.172768	3.383717	1.673995
59	1	0	2.490431	1.641144	1.813142
60	1	0	4.788828	5.715924	1.559904
61	1	0	6.129576	6.106410	0.461971
62	1	0	5.970071	4.468655	1.098217
63	1	0	4.703725	5.376413	-2.500785
64	1	0	5.439045	6.599141	-1.463477
65	1	0	3.669930	6.499703	-1.587858
66	1	0	-3.337545	2.168191	-1.468993
67	1	0	-5.643594	2.777983	-0.975911
68	1	0	-5.714971	-0.084905	2.225620
69	1	0	-3.396841	-0.671975	1.742100
70	1	0	-7.026575	3.908194	0.426665
71	1	0	-6.824145	3.536963	2.145963
72	1	0	-8.448625	3.594658	1.432206
73	1	0	-9.217775	1.776834	-0.158388
74	1	0	-8.135097	0.431127	-0.574098
75	1	0	-7.808382	2.053100	-1.195593
76	1	0	-7.400110	1.211651	3.040245
77	1	0	-7.952409	-0.055748	1.922886
78	1	0	-8.979861	1.343066	2.256403
79	1	0	2.315427	-1.134278	2.237071
80	1	0	4.656384	-1.804631	2.469837
81	1	0	5.206523	-1.296518	-1.760462
82	1	0	2.867641	-0.608832	-1.978662
83	1	0	6.585276	-3.104117	-1.444844
84	1	0	6.206604	-4.119090	-0.044868
85	1	0	7.877614	-3.598344	-0.340477
86	1	0	8.071432	-2.660058	1.924150
87	1	0	6.433083	-3.190281	2.322642
88	1	0	6.907826	-1.496092	2.570486
89	1	0	8.551607	-1.181287	0.023853
90	1	0	7.350893	0.014150	0.555824
91	1	0	7.280732	-0.644256	-1.085149

No imaginary frequency.
Total energy: –1902.67858214 hartree.
HOMO (167): –0.20699 hartree; LUMO (168): –0.10597 hartree (PBE0/6-311G(d,p)).

Table S16. Cartesian Coordinates of **6d** at the PBE0/6-31G(d) Level

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	7	0	-6.105834	-3.856787	-1.209545
2	7	0	-5.240858	0.087865	-2.420768
3	7	0	7.319791	4.675978	-0.158970
4	6	0	-3.204828	-2.021857	-0.356349
5	6	0	-2.595522	-3.299522	0.059217
6	6	0	-3.151961	-4.555135	0.285897
7	6	0	-2.310125	-5.607066	0.647350
8	6	0	-0.938662	-5.407398	0.770057
9	6	0	-0.372633	-4.151251	0.542412
10	6	0	-1.203916	-3.095335	0.191424
11	6	0	-0.924210	-1.664268	-0.022172
12	6	0	0.282552	-0.977906	-0.010505
13	6	0	0.228400	0.441709	-0.100450
14	6	0	-1.010176	1.094582	-0.132959
15	6	0	-2.227461	0.408216	-0.157170
16	6	0	-2.167452	-0.996474	-0.197482
17	6	0	-4.417174	-1.904802	-0.995195
18	6	0	-5.328757	-2.996902	-1.111374
19	6	0	-4.846881	-0.760522	-1.730108
20	6	0	1.420046	1.204783	-0.111599
21	6	0	2.447952	1.858111	-0.124549
22	6	0	3.667391	2.574539	-0.133595
23	6	0	4.896908	1.897696	-0.043555
24	6	0	6.096721	2.582449	-0.052678
25	6	0	6.131079	3.992065	-0.152110
26	6	0	4.894451	4.669880	-0.243834
27	6	0	3.699596	3.975952	-0.233606
28	6	0	8.567663	3.953344	-0.105664
29	6	0	7.325586	6.111515	-0.307627
30	6	0	-3.466232	1.195654	0.016442
31	6	0	-4.417116	0.825530	0.975333
32	6	0	-5.551659	1.595101	1.182217
33	6	0	-5.793492	2.763626	0.446917
34	6	0	-4.831562	3.132066	-0.496784
35	6	0	-3.687522	2.369697	-0.705082
36	6	0	-7.069245	3.570471	0.691570
37	6	0	-8.291454	2.678023	0.420049
38	6	0	-7.099086	4.049644	2.151968
39	6	0	-7.162911	4.797787	-0.218149
40	6	0	1.598337	-1.660126	0.072372
41	6	0	2.078163	-2.418803	-1.000544
42	6	0	3.315924	-3.043551	-0.929618
43	6	0	4.127278	-2.943645	0.209415
44	6	0	3.639402	-2.180638	1.274257
45	6	0	2.401513	-1.545218	1.206919
46	6	0	5.482926	-3.652383	0.246421
47	6	0	5.274484	-5.163119	0.053262
48	6	0	6.370568	-3.111604	-0.886245
49	6	0	6.215012	-3.437432	1.573431
50	1	0	-4.218425	-4.726296	0.204770
51	1	0	-2.735855	-6.587819	0.838438
52	1	0	-0.296143	-6.236884	1.052819
53	1	0	0.696356	-4.008987	0.648210
54	1	0	-1.022250	2.179003	-0.090148
55	1	0	4.895134	0.813950	0.034155

56	1	0	7.019182	2.017254	0.016257
57	1	0	4.868322	5.750432	-0.325309
58	1	0	2.763628	4.522102	-0.306212
59	1	0	9.395098	4.664373	-0.117116
60	1	0	8.651598	3.356431	0.812763
61	1	0	8.690041	3.277040	-0.963953
62	1	0	8.355906	6.470000	-0.291442
63	1	0	6.870961	6.429310	-1.256926
64	1	0	6.785513	6.606492	0.511031
65	1	0	-4.255322	-0.066167	1.575544
66	1	0	-6.263482	1.276268	1.939500
67	1	0	-4.972554	4.023409	-1.098642
68	1	0	-2.975888	2.670081	-1.469748
69	1	0	-8.315287	1.805670	1.081617
70	1	0	-9.217045	3.244035	0.581248
71	1	0	-8.286789	2.313381	-0.612856
72	1	0	-7.072681	3.211848	2.856719
73	1	0	-6.242358	4.697502	2.369294
74	1	0	-8.015917	4.619721	2.345317
75	1	0	-8.091605	5.340136	-0.008250
76	1	0	-6.330997	5.492278	-0.053557
77	1	0	-7.175328	4.517832	-1.277465
78	1	0	1.473016	-2.515977	-1.898254
79	1	0	3.655522	-3.620942	-1.786034
80	1	0	4.225247	-2.071759	2.181214
81	1	0	2.053499	-0.954947	2.050321
82	1	0	6.238806	-5.685117	0.072656
83	1	0	4.647654	-5.576319	0.851402
84	1	0	4.792146	-5.389663	-0.903289
85	1	0	7.345502	-3.613958	-0.878554
86	1	0	5.919288	-3.273670	-1.870563
87	1	0	6.540596	-2.035092	-0.770270
88	1	0	7.175483	-3.964346	1.552670
89	1	0	6.423737	-2.377285	1.757407
90	1	0	5.642503	-3.827588	2.422631

No imaginary frequency.
Total energy: –1939.48770435 hartree.
HOMO (169): –0.20392 hartree; LUMO (170): –0.1099 hartree (PBE0/6-311G(d,p)).

Table S17. Cartesian Coordinates of **6e** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	7.274467	3.200176	-1.523275
2	7	0	5.783082	-0.649267	-2.329092
3	7	0	-4.740302	-2.525688	-0.104832
4	6	0	4.126849	1.951170	-0.494512
5	6	0	2.945442	1.118742	-0.229899
6	6	0	2.791580	-0.268958	-0.080884
7	6	0	1.478225	-0.751670	-0.031551
8	6	0	0.352009	0.072851	-0.027460
9	6	0	0.523292	1.481800	-0.004881
10	6	0	1.821369	1.978810	-0.110195
11	6	0	2.312631	3.370854	-0.115358
12	6	0	1.649151	4.587412	-0.010349

13	6	0	2.396249	5.766887	0.014614
14	6	0	3.784413	5.737365	-0.068269
15	6	0	4.458649	4.525513	-0.213459
16	6	0	3.719948	3.345955	-0.248215
17	6	0	5.296940	1.578771	-1.112443
18	6	0	6.369362	2.493401	-1.339255
19	6	0	5.533698	0.312474	-1.725158
20	6	0	-0.978571	-0.577958	-0.019282
21	6	0	-1.253877	-1.586277	-0.953124
22	6	0	-2.484413	-2.225106	-0.992470
23	6	0	-3.484621	-1.892757	-0.069474
24	6	0	-3.205848	-0.910656	0.891225
25	6	0	-1.982680	-0.260010	0.904976
26	6	0	-4.836561	-3.893335	-0.455205
27	6	0	-3.934736	-4.824652	0.072853
28	6	0	-4.028599	-6.166109	-0.278698
29	6	0	-5.029594	-6.602942	-1.143142
30	6	0	-5.934073	-5.678939	-1.661182
31	6	0	-5.837061	-4.332467	-1.329804
32	6	0	-5.915635	-1.796666	0.189534
33	6	0	-6.938722	-2.381599	0.945422
34	6	0	-8.100565	-1.670190	1.220982
35	6	0	-8.256465	-0.363283	0.765679
36	6	0	-7.236179	0.223447	0.020504
37	6	0	-6.077922	-0.485568	-0.275771
38	6	0	3.889599	-1.222487	0.178234
39	6	0	4.890617	-0.922677	1.105024
40	6	0	5.892174	-1.841898	1.399173
41	6	0	5.936471	-3.095665	0.784247
42	6	0	4.918877	-3.392644	-0.132862
43	6	0	3.914592	-2.484242	-0.427039
44	6	0	7.035779	-4.120485	1.065729
45	6	0	8.043551	-3.620177	2.103497
46	6	0	7.793757	-4.415489	-0.239266
47	6	0	6.404192	-5.418107	1.595179
48	6	0	-0.657685	2.382956	0.091909
49	6	0	-1.499778	2.579858	-1.005855
50	6	0	-2.621458	3.391804	-0.903218
51	6	0	-2.959377	4.035187	0.295051
52	6	0	-2.105645	3.839987	1.384541
53	6	0	-0.975206	3.031599	1.286319
54	6	0	-4.221441	4.896202	0.370215
55	6	0	-5.446056	4.029212	0.031596
56	6	0	-4.116713	6.047901	-0.642408
57	6	0	-4.431766	5.498950	1.761684
58	1	0	1.330244	-1.820420	0.093700
59	1	0	0.569276	4.631691	0.055313
60	1	0	1.881230	6.719421	0.105530
61	1	0	4.352506	6.662126	-0.028327
62	1	0	5.539088	4.520273	-0.288052
63	1	0	-0.498788	-1.845409	-1.691303
64	1	0	-2.681307	-2.979205	-1.748134
65	1	0	-3.959785	-0.659792	1.630897
66	1	0	-1.797460	0.490968	1.665352
67	1	0	-3.162511	-4.488117	0.758318
68	1	0	-3.320959	-6.876939	0.139784
69	1	0	-5.104485	-7.653149	-1.410042

70	1	0	-6.716301	-6.004487	-2.341829
71	1	0	-6.535620	-3.611465	-1.743973
72	1	0	-6.815907	-3.396334	1.312064
73	1	0	-8.884565	-2.139963	1.809066
74	1	0	-9.163201	0.191715	0.988408
75	1	0	-7.345984	1.239609	-0.349688
76	1	0	-5.290744	-0.026813	-0.866749
77	1	0	4.878356	0.036573	1.616215
78	1	0	6.646032	-1.565536	2.128795
79	1	0	4.915153	-4.352213	-0.643248
80	1	0	3.161176	-2.738446	-1.168006
81	1	0	8.807777	-4.387014	2.272075
82	1	0	7.566715	-3.411261	3.068132
83	1	0	8.556278	-2.711789	1.767665
84	1	0	8.595061	-5.141841	-0.056159
85	1	0	8.242721	-3.502928	-0.645885
86	1	0	7.133980	-4.831453	-1.007740
87	1	0	5.856780	-5.236615	2.527008
88	1	0	7.182788	-6.163734	1.796930
89	1	0	5.704595	-5.854602	0.874727
90	1	0	-1.274830	2.084532	-1.946644
91	1	0	-3.250530	3.519218	-1.780704
92	1	0	-2.317988	4.316822	2.335944
93	1	0	-0.331725	2.899079	2.153165
94	1	0	-5.539799	3.191126	0.731542
95	1	0	-5.382226	3.615372	-0.980641
96	1	0	-6.362547	4.628908	0.089661
97	1	0	-4.001242	5.680468	-1.667473
98	1	0	-3.257185	6.689228	-0.417520
99	1	0	-5.021451	6.666815	-0.609516
100	1	0	-3.603927	6.156727	2.050231
101	1	0	-4.541236	4.724860	2.529737
102	1	0	-5.347213	6.100877	1.766748

No imaginary frequency.
Total energy: –2246.45627992 hartree.
HOMO (195): –0.20356 hartree; LUMO (196): –0.1121 hartree (PBE0/6-311G(d,p)).

Table S18. Cartesian Coordinates of **6f** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-5.158408	-0.068299	2.536467
2	7	0	-6.032522	3.831863	1.247048
3	7	0	7.535811	-4.390953	0.164750
4	6	0	-3.156474	1.970529	0.363764
5	6	0	-2.551411	3.248034	-0.061398
6	6	0	-3.107877	4.502845	-0.292142
7	6	0	-2.265083	5.555478	-0.649886
8	6	0	-0.892544	5.357709	-0.763203
9	6	0	-0.326638	4.101854	-0.533604
10	6	0	-1.159676	3.045019	-0.189566
11	6	0	-0.884495	1.613485	0.014764
12	6	0	0.312673	0.917083	-0.012591
13	6	0	0.249265	-0.501339	0.037025
14	6	0	-0.986852	-1.188870	0.034004

15	6	0	-2.195266	-0.463434	0.112850
16	6	0	-2.120575	0.940406	0.189482
17	6	0	-4.355447	1.869963	1.028918
18	6	0	-4.775047	0.749092	1.803755
19	6	0	-5.258974	2.969112	1.146415
20	6	0	1.462407	-1.233179	0.045233
21	6	0	2.520805	-1.836641	0.070975
22	6	0	3.776110	-2.488338	0.095008
23	6	0	3.882648	-3.885245	0.204572
24	6	0	5.112898	-4.514083	0.229922
25	6	0	6.312284	-3.771506	0.144684
26	6	0	6.203277	-2.366432	0.037031
27	6	0	4.968552	-1.747027	0.012331
28	6	0	7.616735	-5.823457	0.319445
29	6	0	8.743844	-3.603138	0.119517
30	6	0	-3.494316	-1.161017	-0.056838
31	6	0	-3.883857	-2.239664	0.745714
32	6	0	-5.092545	-2.883962	0.534282
33	6	0	-5.971211	-2.490325	-0.484185
34	6	0	-5.573693	-1.418214	-1.286202
35	6	0	-4.360943	-0.767064	-1.078983
36	6	0	-7.301455	-3.220856	-0.668541
37	6	0	-7.031805	-4.706079	-0.959178
38	6	0	-8.130058	-3.094125	0.620500
39	6	0	-8.123023	-2.646722	-1.825683
40	6	0	1.630544	1.598215	-0.080678
41	6	0	2.119549	2.314583	1.016457
42	6	0	3.355007	2.945466	0.957905
43	6	0	4.153703	2.895442	-0.193159
44	6	0	3.655229	2.176456	-1.283787
45	6	0	2.420274	1.534340	-1.228624
46	6	0	5.507660	3.608102	-0.215829
47	6	0	6.408782	3.022552	0.883476
48	6	0	5.299467	5.109134	0.042052
49	6	0	6.225327	3.449269	-1.558564
50	6	0	-0.957768	-2.686360	-0.100032
51	1	0	-4.174853	4.673370	-0.217761
52	1	0	-2.691025	6.535414	-0.844690
53	1	0	-0.249229	6.188288	-1.041058
54	1	0	0.743114	3.960088	-0.633311
55	1	0	2.976841	-4.480751	0.273099
56	1	0	5.143652	-5.593995	0.318440
57	1	0	7.094675	-1.752702	-0.026319
58	1	0	4.909305	-0.665299	-0.071694
59	1	0	7.106530	-6.348977	-0.499287
60	1	0	7.176078	-6.161829	1.268295
61	1	0	8.664584	-6.127214	0.307863
62	1	0	8.823928	-2.920021	0.977472
63	1	0	8.802467	-3.003761	-0.799268
64	1	0	9.607879	-4.269101	0.137988
65	1	0	-3.249103	-2.551631	1.569991
66	1	0	-5.362947	-3.703529	1.194770
67	1	0	-6.209851	-1.074541	-2.095419
68	1	0	-4.077874	0.054884	-1.731999
69	1	0	-6.446120	-4.825831	-1.877639
70	1	0	-7.978024	-5.246162	-1.084795
71	1	0	-6.479789	-5.186121	-0.144291

72	1	0	-9.090678	-3.611163	0.505925
73	1	0	-8.330901	-2.043265	0.855043
74	1	0	-7.614241	-3.532485	1.480980
75	1	0	-9.063770	-3.200809	-1.918182
76	1	0	-7.594879	-2.730234	-2.782590
77	1	0	-8.375419	-1.593013	-1.661579
78	1	0	1.523538	2.373574	1.923511
79	1	0	3.701945	3.488642	1.833520
80	1	0	4.230751	2.107708	-2.201253
81	1	0	2.064052	0.978345	-2.091665
82	1	0	7.383552	3.525357	0.884676
83	1	0	6.577740	1.951636	0.721964
84	1	0	5.969178	3.144159	1.878834
85	1	0	6.262714	5.633410	0.032109
86	1	0	4.828570	5.294920	1.012983
87	1	0	4.662066	5.553634	-0.730479
88	1	0	6.432571	2.397829	-1.788521
89	1	0	7.185677	3.975923	-1.526520
90	1	0	5.643442	3.873728	-2.384587
91	1	0	-0.102114	-2.995786	-0.706569
92	1	0	-1.872372	-3.068656	-0.556891
93	1	0	-0.845857	-3.174851	0.876597

No imaginary frequency.
Total energy: –1979.17430321 hartree.
HOMO (173): –0.20305 hartree; LUMO (174): –0.10749 hartree (PBE0/6-311G(d,p)).

Table S19. Cartesian Coordinates of **7d** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.415808	3.104521	1.526310
2	7	0	-1.322768	-0.123563	-4.449583
3	7	0	1.259657	-3.536184	-4.145076
4	7	0	3.732640	-0.694841	-3.751311
5	7	0	5.021415	-3.186990	-0.540088
6	7	0	0.324532	-4.169879	3.949989
7	6	0	-2.254805	2.931192	1.219524
8	6	0	-1.101163	3.767911	1.635627
9	6	0	-1.121967	4.928506	2.389073
10	6	0	0.086860	5.587447	2.613323
11	6	0	1.283399	3.900584	1.318488
12	6	0	0.081916	3.233804	1.104725
13	6	0	-0.264623	2.000161	0.350366
14	6	0	0.566051	1.083144	-0.291326
15	6	0	-0.063168	0.016629	-0.980655
16	6	0	-1.454112	-0.107981	-0.973233
17	6	0	-2.295499	0.786170	-0.294819
18	6	0	-1.668005	1.844340	0.361865
19	6	0	-3.755340	0.545872	-0.331649
20	6	0	-4.667227	1.551867	-0.669156
21	6	0	-6.021516	1.273802	-0.761607
22	6	0	-6.534480	-0.007710	-0.514538
23	6	0	-5.618251	-1.004454	-0.172132
24	6	0	-4.255196	-0.735586	-0.089603
25	6	0	-8.037889	-0.262512	-0.630156

26	6	0	-8.495619	0.050603	-2.064150
27	6	0	-8.787076	0.648753	0.355532
28	6	0	-8.407171	-1.714402	-0.316463
29	6	0	2.043980	1.220555	-0.265246
30	6	0	2.759506	0.945865	0.902774
31	6	0	4.146867	1.051093	0.928435
32	6	0	4.871140	1.442970	-0.203607
33	6	0	4.138211	1.742439	-1.358995
34	6	0	2.753660	1.632853	-1.396322
35	6	0	6.397751	1.529789	-0.225607
36	6	0	6.940087	0.524587	-1.256067
37	6	0	7.016912	1.202693	1.135810
38	6	0	6.826249	2.952004	-0.620903
39	6	0	0.712348	-1.030948	-1.693331
40	6	0	0.367902	-1.408968	-2.961666
41	6	0	-0.578654	-0.684582	-3.756418
42	6	0	0.895239	-2.576393	-3.602447
43	6	0	1.791923	-1.753813	-0.965109
44	6	0	3.041987	-1.845868	-1.535811
45	6	0	3.397029	-1.197665	-2.758356
46	6	0	4.113263	-2.596293	-0.962482
47	6	0	1.436070	-2.340072	0.320285
48	6	0	2.337795	-2.444856	1.395278
49	6	0	1.975105	-3.031922	2.589228
50	6	0	0.680613	-3.572491	2.777227
51	6	0	-0.230752	-3.461203	1.700390
52	6	0	0.140588	-2.852839	0.520325
53	6	0	1.286253	-4.291862	5.022973
54	6	0	-1.010430	-4.699175	4.118614
55	6	0	1.267356	5.076878	2.075518
56	1	0	-2.063627	5.304311	2.779691
57	1	0	0.110351	6.502289	3.198562
58	1	0	2.218088	3.534814	0.910373
59	1	0	-1.915110	-0.934071	-1.506297
60	1	0	-4.310968	2.556053	-0.871234
61	1	0	-6.695902	2.080925	-1.035621
62	1	0	-5.959811	-2.013111	0.036058
63	1	0	-3.570388	-1.532700	0.191844
64	1	0	-9.574114	-0.121528	-2.164421
65	1	0	-7.978895	-0.588790	-2.788430
66	1	0	-8.297354	1.092337	-2.336768
67	1	0	-8.485111	0.441625	1.388189
68	1	0	-9.868593	0.484797	0.275810
69	1	0	-8.594524	1.708197	0.157649
70	1	0	-9.490859	-1.845338	-0.410069
71	1	0	-8.128024	-1.994464	0.705869
72	1	0	-7.929021	-2.415707	-1.009868
73	1	0	2.223925	0.634241	1.795752
74	1	0	4.666148	0.816356	1.852036
75	1	0	4.654735	2.043309	-2.265771
76	1	0	2.220824	1.861362	-2.315590
77	1	0	6.554336	0.720866	-2.261861
78	1	0	6.665284	-0.501549	-0.987235
79	1	0	8.034318	0.582910	-1.298695
80	1	0	6.783983	0.180289	1.454393
81	1	0	6.680473	1.895576	1.916166
82	1	0	8.107441	1.283913	1.070144

83	1	0	6.454388	3.690143	0.098935
84	1	0	6.454356	3.231018	-1.612147
85	1	0	7.920107	3.021732	-0.645536
86	1	0	3.333529	-2.025377	1.307655
87	1	0	2.704519	-3.067713	3.389776
88	1	0	-1.234177	-3.860899	1.787608
89	1	0	-0.584191	-2.808033	-0.287495
90	1	0	1.616927	-3.309718	5.386880
91	1	0	2.172006	-4.859262	4.708830
92	1	0	0.826218	-4.821481	5.857954
93	1	0	-1.226751	-5.495309	3.393576
94	1	0	-1.772691	-3.916441	4.009859
95	1	0	-1.104589	-5.121789	5.119518
96	1	0	2.202177	5.604758	2.244755

No imaginary frequency.
Total energy: –2238.19691405 hartree.
HOMO (189): –0.23235 hartree; LUMO (190): –0.1267 hartree (PBE0/6-311G(d,p)).

Table S20. Cartesian Coordinates of **7f** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.681869	2.608232	0.150038
2	7	0	-0.550588	-1.388714	-3.650905
3	7	0	2.366380	-4.027633	-2.048637
4	7	0	-1.448283	-1.432216	2.849983
5	7	0	2.547317	-1.587983	4.189667
6	7	0	6.908195	-3.031431	-0.228585
7	6	0	-3.470530	2.604928	0.119509
8	6	0	-2.572692	3.788432	0.200482
9	6	0	-2.926678	5.120589	0.319373
10	6	0	-1.906595	6.071375	0.365415
11	6	0	-0.574401	5.667341	0.290939
12	6	0	-0.220281	4.319408	0.171571
13	6	0	-1.234672	3.369148	0.127740
14	6	0	-1.220886	1.890118	0.005153
15	6	0	-0.168660	0.990410	-0.102685
16	6	0	0.639103	-1.354437	-0.351342
17	6	0	-1.814309	-0.848932	-0.277323
18	6	0	-2.869494	0.084752	-0.152575
19	6	0	-2.548911	1.425033	-0.013143
20	6	0	-2.163763	-2.307295	-0.386651
21	6	0	-0.486677	-0.383697	-0.242227
22	6	0	0.826086	-2.006793	-1.541738
23	6	0	0.044369	-1.657889	-2.689888
24	6	0	1.717929	-3.104346	-1.770060
25	6	0	1.519114	-1.622034	0.803664
26	6	0	1.023549	-1.565580	2.094239
27	6	0	-0.354411	-1.474313	2.457016
28	6	0	1.889374	-1.600605	3.230711
29	6	0	2.916343	-1.964430	0.559982
30	6	0	3.677405	-1.282411	-0.407893
31	6	0	4.989508	-1.617626	-0.661013
32	6	0	5.617866	-2.680045	0.032106
33	6	0	4.850696	-3.367805	1.003393

34	6	0	3.547285	-3.006965	1.263259
35	6	0	7.646334	-2.355038	-1.271673
36	6	0	7.517287	-4.136509	0.478631
37	6	0	-4.284931	-0.377429	-0.158664
38	6	0	-4.915927	-0.742731	1.033739
39	6	0	-6.229150	-1.191835	1.022137
40	6	0	-6.963414	-1.295544	-0.167275
41	6	0	-6.316701	-0.931921	-1.350492
42	6	0	-4.998686	-0.481966	-1.349888
43	6	0	-8.410816	-1.790652	-0.129551
44	6	0	-9.246416	-0.853258	0.757230
45	6	0	-9.048734	-1.826495	-1.520759
46	6	0	-8.448838	-3.212451	0.453518
47	6	0	1.239933	1.470488	-0.155571
48	6	0	1.973451	1.722642	1.008773
49	6	0	3.259972	2.240155	0.936037
50	6	0	3.868545	2.535710	-0.292412
51	6	0	3.128034	2.277147	-1.449972
52	6	0	1.838003	1.751654	-1.385895
53	6	0	5.279473	3.126583	-0.322742
54	6	0	5.270363	4.488154	0.391761
55	6	0	5.789674	3.336929	-1.750432
56	6	0	6.249695	2.179783	0.402018
57	1	0	-3.975505	5.399566	0.372087
58	1	0	-2.147162	7.126663	0.458100
59	1	0	0.212324	6.416502	0.326314
60	1	0	0.825343	4.038597	0.115788
61	1	0	-2.910392	-2.569953	0.367772
62	1	0	-1.301948	-2.961967	-0.248115
63	1	0	-2.605203	-2.527863	-1.365681
64	1	0	3.233779	-0.455487	-0.954085
65	1	0	5.532981	-1.054498	-1.410672
66	1	0	5.273860	-4.206417	1.543166
67	1	0	2.985215	-3.582474	1.992068
68	1	0	7.160138	-2.465081	-2.250192
69	1	0	8.645979	-2.785437	-1.340538
70	1	0	7.755259	-1.283240	-1.058207
71	1	0	6.997979	-5.083869	0.280165
72	1	0	7.521820	-3.964582	1.562303
73	1	0	8.552374	-4.243166	0.152267
74	1	0	-4.368775	-0.677831	1.971137
75	1	0	-6.691124	-1.464860	1.967696
76	1	0	-6.838956	-0.992355	-2.299599
77	1	0	-4.524499	-0.202511	-2.287563
78	1	0	-10.288545	-1.193722	0.793716
79	1	0	-9.233462	0.169669	0.365311
80	1	0	-8.869377	-0.821761	1.784753
81	1	0	-9.077670	-0.832130	-1.980535
82	1	0	-10.081260	-2.185271	-1.442556
83	1	0	-8.514310	-2.503541	-2.197074
84	1	0	-7.864776	-3.904285	-0.163753
85	1	0	-9.481691	-3.579654	0.494085
86	1	0	-8.042405	-3.245880	1.469755
87	1	0	1.526213	1.523267	1.978897
88	1	0	3.796517	2.421580	1.863577
89	1	0	3.549139	2.490460	-2.427149
90	1	0	1.281135	1.574780	-2.303173

91	1	0	4.594563	5.189664	-0.110146
92	1	0	6.276562	4.924194	0.390326
93	1	0	4.946948	4.397454	1.433965
94	1	0	5.162438	4.039879	-2.310162
95	1	0	5.834885	2.395518	-2.310395
96	1	0	6.802579	3.753204	-1.719968
97	1	0	7.266294	2.590182	0.377430
98	1	0	6.264672	1.192377	-0.073050
99	1	0	5.974930	2.035792	1.451787

No imaginary frequency.
Total energy: –2277.46081177 hartree.
HOMO (193): –0.22967 hartree; LUMO (194): –0.13566 hartree (PBE0/6-311G(d,p)).

Table S21. Cartesian Coordinates of **8d** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.828760	-1.716089	-4.287892
2	7	0	1.996121	-4.674129	-2.982300
3	7	0	4.218513	-1.692667	-3.380812
4	7	0	5.566704	-2.967238	0.453442
5	7	0	0.802552	-2.765316	5.000067
6	6	0	-2.191791	2.515700	0.684176
7	6	0	-1.253443	3.643446	0.577679
8	6	0	-1.410657	4.998336	0.856435
9	6	0	-0.317596	5.847119	0.686885
10	6	0	1.074933	3.987516	-0.018281
11	6	0	-0.010026	3.134196	0.138338
12	6	0	-0.174937	1.697970	-0.155130
13	6	0	0.752772	0.752956	-0.585995
14	6	0	0.252349	-0.518329	-0.962760
15	6	0	-1.120869	-0.763437	-0.946624
16	6	0	-2.060134	0.168287	-0.483358
17	6	0	-1.546907	1.375223	0.009806
18	6	0	-3.492515	-0.134099	-0.675086
19	6	0	-4.349989	0.813355	-1.247991
20	6	0	-5.681541	0.509821	-1.485274
21	6	0	-6.221034	-0.744108	-1.166053
22	6	0	-5.354527	-1.685571	-0.604994
23	6	0	-4.016607	-1.391166	-0.368752
24	6	0	-7.699248	-1.028958	-1.431917
25	6	0	-7.993217	-0.849199	-2.930413
26	6	0	-8.555177	-0.043009	-0.619708
27	6	0	-8.096814	-2.452238	-1.032784
28	6	0	2.201123	1.059210	-0.664049
29	6	0	2.942125	1.281398	0.499820
30	6	0	4.308867	1.532683	0.434375
31	6	0	4.986013	1.581622	-0.789841
32	6	0	4.225053	1.386532	-1.949712
33	6	0	2.861665	1.126039	-1.894340
34	6	0	6.494684	1.806510	-0.896035
35	6	0	7.138835	0.557448	-1.521966
36	6	0	7.142862	2.050668	0.469189
37	6	0	6.772630	3.028619	-1.785954
38	6	0	1.148265	-1.636901	-1.352013

39	6	0	0.892819	-2.385911	-2.467922
40	6	0	-0.072196	-1.999037	-3.453224
41	6	0	1.537015	-3.635189	-2.740838
42	6	0	2.254932	-2.007895	-0.427640
43	6	0	3.528302	-2.167868	-0.929887
44	6	0	3.881183	-1.897177	-2.287148
45	6	0	4.631608	-2.613226	-0.140184
46	6	0	1.905541	-2.177308	0.975993
47	6	0	2.776844	-1.847678	2.031188
48	6	0	2.417671	-2.029696	3.349966
49	6	0	1.158250	-2.574330	3.698896
50	6	0	0.278979	-2.904270	2.639679
51	6	0	0.645425	-2.698386	1.327571
52	6	0	1.730629	-2.442528	6.061242
53	6	0	-0.513532	-3.269975	5.326698
54	6	0	-3.299893	2.480619	1.492204
55	6	0	-3.972909	1.287207	1.890420
56	6	0	-3.799588	3.644945	2.150794
57	7	0	-4.511495	0.357951	2.334955
58	7	0	-4.241953	4.576302	2.687921
59	6	0	0.907920	5.346302	0.257297
60	1	0	-2.362118	5.403988	1.178960
61	1	0	-0.430947	6.908599	0.885919
62	1	0	2.034867	3.617177	-0.357250
63	1	0	-1.494818	-1.714584	-1.312510
64	1	0	-3.962522	1.788137	-1.532490
65	1	0	-6.312191	1.269017	-1.940175
66	1	0	-5.720898	-2.669823	-0.333997
67	1	0	-3.381410	-2.139944	0.097918
68	1	0	-9.052905	-1.044800	-3.133156
69	1	0	-7.396782	-1.542419	-3.533783
70	1	0	-7.772260	0.167411	-3.271966
71	1	0	-8.361924	-0.148465	0.453421
72	1	0	-9.620619	-0.232522	-0.797218
73	1	0	-8.351135	0.996896	-0.895704
74	1	0	-9.160580	-2.607287	-1.243390
75	1	0	-7.942890	-2.633573	0.037009
76	1	0	-7.535550	-3.206145	-1.596664
77	1	0	2.445286	1.239097	1.465661
78	1	0	4.851100	1.685029	1.361787
79	1	0	4.705615	1.405598	-2.923481
80	1	0	2.307385	0.966479	-2.815640
81	1	0	6.729088	0.339334	-2.513643
82	1	0	6.977441	-0.325501	-0.893223
83	1	0	8.220121	0.705136	-1.628850
84	1	0	7.022009	1.190998	1.138047
85	1	0	6.731373	2.937805	0.965014
86	1	0	8.218136	2.214184	0.338965
87	1	0	6.321681	3.934168	-1.364187
88	1	0	6.379370	2.896597	-2.799012
89	1	0	7.853215	3.193945	-1.869593
90	1	0	3.741354	-1.401356	1.816891
91	1	0	3.118879	-1.735499	4.122015
92	1	0	-0.696018	-3.328272	2.848312
93	1	0	-0.053773	-2.983064	0.546634
94	1	0	1.964531	-1.369416	6.088341
95	1	0	2.670758	-2.998307	5.954300

96	1	0	1.287373	-2.714763	7.019683
97	1	0	-0.672421	-4.279589	4.924970
98	1	0	-1.304973	-2.614964	4.940012
99	1	0	-0.618812	-3.319575	6.410920
100	1	0	1.749303	6.021151	0.126801

No imaginary frequency.
Total energy: –2386.56218036 hartree.
HOMO (201): –0.23327 hartree; LUMO (202): –0.13615 hartree (PBE0/6-311G(d,p)).

Table S22. Cartesian Coordinates of **8f** at the PBE0/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.153182	-1.578578	-3.683290
2	7	0	2.961686	-3.975723	-2.109756
3	7	0	-0.959106	-1.498398	2.844886
4	7	0	3.062403	-1.529701	4.114880
5	7	0	7.417734	-2.748754	-0.367618
6	6	0	-3.282542	2.267982	-0.238153
7	6	0	-2.526736	3.443211	0.231151
8	6	0	-2.938300	4.729418	0.572276
9	6	0	-1.971680	5.682099	0.890920
10	6	0	-0.618808	5.359572	0.850054
11	6	0	-0.197883	4.070461	0.519538
12	6	0	-1.155237	3.105397	0.230893
13	6	0	-1.038240	1.666893	-0.055387
14	6	0	0.084723	0.852348	-0.123463
15	6	0	1.072234	-1.421950	-0.395626
16	6	0	-1.408588	-1.101100	-0.327709
17	6	0	-2.545851	-0.256457	-0.279415
18	6	0	-2.337323	1.128941	-0.220581
19	6	0	-1.582700	-2.597615	-0.306846
20	6	0	-0.121662	-0.534496	-0.291418
21	6	0	1.292003	-2.065399	-1.585688
22	6	0	0.472473	-1.786237	-2.726526
23	6	0	2.256771	-3.097884	-1.821312
24	6	0	1.978787	-1.629371	0.750149
25	6	0	1.501521	-1.590029	2.047798
26	6	0	0.128751	-1.531463	2.434423
27	6	0	2.388352	-1.579281	3.168414
28	6	0	3.389279	-1.894977	0.487776
29	6	0	4.100299	-1.164480	-0.482755
30	6	0	5.424834	-1.427823	-0.755985
31	6	0	6.116605	-2.463732	-0.082653
32	6	0	5.400631	-3.196450	0.894902
33	6	0	4.084158	-2.906202	1.175915
34	6	0	8.103709	-2.029880	-1.418004
35	6	0	8.091335	-3.830512	0.317194
36	6	0	-3.894811	-0.854170	-0.126736
37	6	0	-4.663725	-0.536807	0.999644
38	6	0	-5.916102	-1.104603	1.185869
39	6	0	-6.457272	-2.011295	0.264851
40	6	0	-5.677518	-2.328008	-0.850687
41	6	0	-4.421784	-1.764563	-1.043968
42	6	0	-7.851177	-2.595673	0.495646

43	6	0	-8.875578	-1.449476	0.523043
44	6	0	-8.257832	-3.576891	-0.606944
45	6	0	-7.880376	-3.341415	1.839411
46	6	0	1.456675	1.433037	-0.102464
47	6	0	2.156560	1.642156	1.091098
48	6	0	3.412707	2.233525	1.079941
49	6	0	4.024412	2.645918	-0.112935
50	6	0	3.315505	2.434768	-1.299125
51	6	0	2.055106	1.838341	-1.297147
52	6	0	5.403291	3.307062	-0.074245
53	6	0	5.310931	4.616806	0.725947
54	6	0	5.928091	3.634244	-1.474610
55	6	0	6.406578	2.363516	0.608699
56	6	0	-4.521579	2.338967	-0.821965
57	6	0	-5.120030	1.346406	-1.653966
58	6	0	-5.311812	3.529744	-0.787918
59	7	0	-5.661190	0.668795	-2.427902
60	7	0	-5.999303	4.467053	-0.767472
61	1	0	-3.986086	4.999786	0.608868
62	1	0	-2.283837	6.683981	1.170365
63	1	0	0.123599	6.116800	1.086766
64	1	0	0.859451	3.836172	0.499168
65	1	0	-2.412427	-2.872630	0.348111
66	1	0	-0.688821	-3.105608	0.060171
67	1	0	-1.803605	-2.998023	-1.302797
68	1	0	3.605899	-0.356961	-1.014677
69	1	0	5.927996	-0.830187	-1.507162
70	1	0	5.874638	-4.015188	1.422847
71	1	0	3.563733	-3.515292	1.908469
72	1	0	7.606107	-2.156790	-2.388665
73	1	0	9.121599	-2.410708	-1.507459
74	1	0	8.164372	-0.955736	-1.197823
75	1	0	7.612207	-4.798965	0.119825
76	1	0	8.109840	-3.667752	1.402117
77	1	0	9.123414	-3.886577	-0.030485
78	1	0	-4.263870	0.144479	1.746315
79	1	0	-6.479024	-0.835181	2.075841
80	1	0	-6.052796	-3.013412	-1.602784
81	1	0	-3.864945	-2.003775	-1.945423
82	1	0	-9.885267	-1.846768	0.682814
83	1	0	-8.869300	-0.897656	-0.423259
84	1	0	-8.665615	-0.736866	1.327629
85	1	0	-8.293994	-3.093075	-1.589443
86	1	0	-9.258173	-3.971061	-0.396044
87	1	0	-7.572237	-4.430068	-0.667003
88	1	0	-7.160581	-4.167569	1.846082
89	1	0	-8.879059	-3.757340	2.018910
90	1	0	-7.639706	-2.680713	2.678769
91	1	0	1.706109	1.353535	2.036798
92	1	0	3.923447	2.376833	2.028355
93	1	0	3.738557	2.740786	-2.250377
94	1	0	1.522982	1.699623	-2.235308
95	1	0	4.609065	5.314963	0.256183
96	1	0	6.293075	5.101863	0.773875
97	1	0	4.974719	4.441725	1.753350
98	1	0	5.277380	4.341508	-2.001191
99	1	0	6.029603	2.734623	-2.093061

100	1	0	6.918894	4.095067	-1.397164
101	1	0	7.401402	2.824121	0.631525
102	1	0	6.479456	1.411106	0.071616
103	1	0	6.121430	2.138620	1.641324

No imaginary frequency.
Total energy: –2425.82164769 hartree.
HOMO (205): –0.23262 hartree; LUMO (206): –0.14052 hartree (PBE0/6-311G(d,p)).

Table S23. Cartesian Coordinates of **3a+2′** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.427935	1.303252	-0.034946
2	6	0	-3.560564	2.273499	0.976237
3	6	0	-4.824696	2.423344	1.575161
4	6	0	-5.908077	1.648981	1.184697
5	6	0	-5.783644	0.681803	0.159093
6	6	0	-4.506874	0.523630	-0.430517
7	6	0	-2.449865	3.070771	1.387088
8	6	0	-1.511602	3.750316	1.741980
9	7	0	-6.871124	-0.073368	-0.256173
10	6	0	-8.107575	-0.027104	0.504976
11	6	0	-6.667696	-1.172345	-1.183031
12	8	0	-0.061527	0.734295	-0.847549
13	6	0	0.990870	0.216189	-0.527427
14	6	0	2.350335	0.938606	-0.350708
15	6	0	3.228652	-0.069289	-0.080597
16	6	0	2.527363	-1.389090	-0.016126
17	6	0	1.203030	-1.257542	-0.282728
18	6	0	3.500944	-2.394634	0.381837
19	6	0	4.755861	-1.754094	0.528087
20	6	0	4.658305	-0.292947	0.231197
21	6	0	5.891817	-2.455417	0.923476
22	6	0	5.769724	-3.818776	1.185971
23	6	0	4.525583	-4.460935	1.058282
24	6	0	3.387034	-3.764603	0.656816
25	6	0	2.534164	2.376294	-0.472351
26	6	0	1.430764	3.255150	-0.556026
27	6	0	1.625271	4.628282	-0.660372
28	6	0	2.910148	5.185847	-0.692525
29	6	0	4.006149	4.312341	-0.601245
30	6	0	3.832177	2.940244	-0.491938
31	6	0	3.115760	6.673277	-0.837601
32	6	0	0.126344	-2.245724	-0.392294
33	6	0	0.341434	-3.493906	-1.005054
34	6	0	-0.684627	-4.429060	-1.108020
35	6	0	-1.966673	-4.156712	-0.610774
36	6	0	-2.185214	-2.905689	-0.018866
37	6	0	-1.165734	-1.963506	0.087290
38	8	0	5.598370	0.495570	0.254272
39	6	0	-3.070284	-5.184120	-0.696652
40	1	0	2.433369	-4.273179	0.567197
41	1	0	4.450337	-5.522639	1.277153
42	1	0	6.638478	-4.393028	1.495689
43	1	0	6.839038	-1.933735	1.023985

44	1	0	1.314284	-3.715169	-1.434774
45	1	0	-0.490929	-5.381616	-1.596720
46	1	0	-3.172272	-2.658579	0.365850
47	1	0	-1.371410	-1.004766	0.549151
48	1	0	4.697257	2.291230	-0.406915
49	1	0	5.015415	4.718261	-0.613363
50	1	0	0.756510	5.280153	-0.717795
51	1	0	0.424170	2.860362	-0.529859
52	1	0	-2.960756	-5.818710	-1.582787
53	1	0	-3.066811	-5.847021	0.179351
54	1	0	-4.056781	-4.709915	-0.738967
55	1	0	3.401155	6.933020	-1.866016
56	1	0	2.203971	7.230178	-0.599727
57	1	0	3.917555	7.032982	-0.182616
58	1	0	-0.673791	4.333152	2.049374
59	1	0	-2.462593	1.156807	-0.509290
60	1	0	-4.347652	-0.213338	-1.208523
61	1	0	-6.858085	1.801243	1.682779
62	1	0	-4.952983	3.159007	2.363858
63	1	0	-7.633021	-1.624300	-1.419366
64	1	0	-6.009457	-1.958467	-0.777648
65	1	0	-6.228607	-0.818573	-2.123461
66	1	0	-8.846973	-0.671198	0.025150
67	1	0	-8.519808	0.989127	0.527358
68	1	0	-7.980509	-0.364643	1.546030

No imaginary frequency.
Total energy: –1594.42448354 hartree.

Table S24. Cartesian Coordinates of **TS1** (Singlet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.859760	2.832889	-0.954707
2	6	0	1.358755	1.609567	-1.473880
3	6	0	2.306061	0.621788	-1.852136
4	6	0	3.660846	0.843485	-1.730871
5	6	0	4.160940	2.067600	-1.206650
6	6	0	3.214047	3.055236	-0.820812
7	6	0	-0.011977	1.402316	-1.599050
8	6	0	-1.253105	1.231816	-1.557557
9	7	0	5.509129	2.285605	-1.076078
10	6	0	5.997944	3.531929	-0.503362
11	6	0	6.459263	1.239464	-1.426911
12	6	0	-2.022011	0.539578	0.076186
13	6	0	-2.316238	-0.811142	-0.257426
14	6	0	-1.218357	-1.672978	0.126189
15	6	0	-0.211110	-0.988722	0.768410
16	6	0	-0.695305	0.406886	0.919970
17	6	0	-3.291488	-1.579783	-1.015164
18	6	0	-2.780488	-2.994518	-0.966564
19	6	0	-1.547624	-3.049745	-0.278161
20	6	0	-3.382851	-4.136108	-1.474759
21	6	0	-2.747461	-5.367111	-1.275831
22	6	0	-1.539037	-5.435606	-0.572541
23	6	0	-0.927159	-4.281897	-0.067330

24	6	0	1.108852	-1.436963	1.221716
25	6	0	1.849171	-2.380181	0.483513
26	6	0	3.104524	-2.808140	0.909122
27	6	0	3.682762	-2.306190	2.081975
28	6	0	2.959670	-1.345528	2.802697
29	6	0	1.703521	-0.913607	2.387007
30	6	0	-3.029153	1.597525	0.386340
31	6	0	-4.362848	1.461435	-0.041462
32	6	0	-5.301440	2.451837	0.236027
33	6	0	-4.956868	3.610393	0.944138
34	6	0	-3.624351	3.748966	1.353644
35	6	0	-2.672921	2.771292	1.077472
36	8	0	-0.174415	1.296141	1.573491
37	8	0	-4.315792	-1.228222	-1.608850
38	6	0	5.027676	-2.795909	2.565052
39	6	0	-5.988909	4.662496	1.272713
40	1	0	0.005770	-4.354224	0.481249
41	1	0	-1.065567	-6.401070	-0.414547
42	1	0	-3.196890	-6.278603	-1.661113
43	1	0	-4.328242	-4.058218	-2.004186
44	1	0	1.440355	-2.765575	-0.445959
45	1	0	3.648917	-3.538841	0.313791
46	1	0	3.388048	-0.928250	3.712071
47	1	0	1.174066	-0.161592	2.959245
48	1	0	-4.659571	0.582838	-0.606512
49	1	0	-6.325584	2.319172	-0.106758
50	1	0	-3.322670	4.642238	1.897186
51	1	0	-1.650938	2.902485	1.407665
52	1	0	4.918302	-3.588548	3.317886
53	1	0	5.623292	-3.210286	1.744243
54	1	0	5.606435	-1.990134	3.030896
55	1	0	-6.788453	4.688082	0.524485
56	1	0	-6.461108	4.465429	2.244970
57	1	0	-5.541728	5.661117	1.327735
58	1	0	-2.115916	1.362279	-2.188434
59	1	0	1.949541	-0.326398	-2.240975
60	1	0	4.344329	0.057960	-2.027748
61	1	0	3.547985	3.998400	-0.406514
62	1	0	1.153991	3.597125	-0.646563
63	1	0	7.472204	1.602824	-1.249748
64	1	0	6.379807	0.962596	-2.486196
65	1	0	6.309911	0.334432	-0.822709
66	1	0	7.088404	3.517454	-0.493580
67	1	0	5.648169	3.671777	0.528573
68	1	0	5.676352	4.398710	-1.095010

One imaginary frequency.
Total energy: –1594.39346096 hartree.

Table S25. Cartesian Coordinates of **TS1** (Triplet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.137922	2.168372	-0.829745
2	6	0	2.302958	1.192166	-1.430992
3	6	0	2.920646	-0.000795	-1.883632

4	6	0	4.278945	-0.209248	-1.741285
5	6	0	5.113219	0.770158	-1.141387
6	6	0	4.496467	1.966387	-0.688001
7	6	0	0.930825	1.412015	-1.593061
8	6	0	-0.305062	1.563177	-1.578174
9	7	0	6.469770	0.569110	-1.006098
10	6	0	7.291623	1.562426	-0.333614
11	6	0	7.065713	-0.691537	-1.417579
12	6	0	-1.395507	1.141817	0.203987
13	6	0	-2.391336	0.238736	-0.382457
14	6	0	-2.110565	-1.109412	-0.062041
15	6	0	-0.947645	-1.191979	0.714728
16	6	0	-0.479948	0.213753	0.942209
17	6	0	-3.521605	0.280294	-1.325829
18	6	0	-3.990111	-1.142497	-1.428595
19	6	0	-3.152361	-1.977379	-0.653357
20	6	0	-5.084762	-1.634746	-2.117478
21	6	0	-5.371932	-3.005017	-2.019846
22	6	0	-4.570501	-3.833191	-1.233298
23	6	0	-3.454572	-3.331769	-0.541900
24	6	0	-0.219270	-2.360253	1.183088
25	6	0	-0.218442	-3.566649	0.450480
26	6	0	0.489400	-4.677196	0.894910
27	6	0	1.221678	-4.640178	2.090774
28	6	0	1.238819	-3.436215	2.810195
29	6	0	0.546161	-2.314615	2.369443
30	6	0	-1.662713	2.517281	0.662441
31	6	0	-2.782080	3.238877	0.198226
32	6	0	-3.026804	4.537699	0.634585
33	6	0	-2.177762	5.177386	1.546587
34	6	0	-1.056607	4.464767	1.996109
35	6	0	-0.794896	3.168854	1.566989
36	8	0	0.526423	0.526147	1.584552
37	8	0	-3.989540	1.234599	-1.944515
38	6	0	1.954170	-5.859357	2.595537
39	6	0	-2.469233	6.572894	2.043715
40	1	0	-2.857673	-3.995480	0.073662
41	1	0	-4.811527	-4.889685	-1.149708
42	1	0	-6.225190	-3.420763	-2.548366
43	1	0	-5.702310	-0.963153	-2.707289
44	1	0	-0.744177	-3.614087	-0.497331
45	1	0	0.482448	-5.587938	0.299937
46	1	0	1.810245	-3.376358	3.734005
47	1	0	0.591280	-1.390590	2.931137
48	1	0	-3.452325	2.786872	-0.524572
49	1	0	-3.898967	5.066375	0.254991
50	1	0	-0.371228	4.937392	2.697360
51	1	0	0.080150	2.642432	1.926306
52	1	0	1.335061	-6.429582	3.301653
53	1	0	2.219855	-6.536651	1.776990
54	1	0	2.874122	-5.585001	3.123206
55	1	0	-3.056745	6.552047	2.972191
56	1	0	-1.546869	7.123820	2.259382
57	1	0	-3.044535	7.148409	1.310366
58	1	0	-1.147676	1.917076	-2.144133
59	1	0	2.306570	-0.767357	-2.346103
60	1	0	4.700507	-1.141906	-2.096152

61	1	0	5.088797	2.739450	-0.213566
62	1	0	2.689437	3.087450	-0.466238
63	1	0	8.141057	-0.655038	-1.237424
64	1	0	6.910151	-0.879445	-2.488166
65	1	0	6.654287	-1.544319	-0.858650
66	1	0	8.331330	1.232001	-0.341560
67	1	0	6.987929	1.710190	0.712694
68	1	0	7.243552	2.533946	-0.842611

One imaginary frequency.
Total energy: –1594.36716459 hartree.

Table S26. Cartesian Coordinates of **Intermediate A** (Singlet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.128430	2.867130	-0.814967
2	6	0	1.533906	1.689847	-1.369976
3	6	0	2.423223	0.691234	-1.879615
4	6	0	3.786167	0.862990	-1.851239
5	6	0	4.371777	2.035687	-1.289723
6	6	0	3.492886	3.028916	-0.769017
7	6	0	0.173393	1.531996	-1.397707
8	6	0	-1.109165	1.407066	-1.350240
9	7	0	5.730637	2.199803	-1.250780
10	6	0	6.310937	3.391012	-0.643964
11	6	0	6.613351	1.161069	-1.766305
12	6	0	-1.857353	0.726755	-0.128951
13	6	0	-2.176274	-0.645936	-0.564122
14	6	0	-1.243544	-1.573446	-0.036351
15	6	0	-0.325905	-0.975386	0.824409
16	6	0	-0.732127	0.441719	0.957000
17	6	0	-3.015847	-1.283783	-1.558520
18	6	0	-2.619134	-2.739878	-1.505178
19	6	0	-1.563949	-2.915677	-0.580889
20	6	0	-3.171701	-3.808756	-2.190302
21	6	0	-2.670193	-5.093908	-1.936904
22	6	0	-1.646752	-5.280904	-1.005324
23	6	0	-1.082998	-4.194777	-0.316794
24	6	0	0.858488	-1.532723	1.477355
25	6	0	1.638034	-2.526856	0.853264
26	6	0	2.769156	-3.052544	1.471969
27	6	0	3.180275	-2.605456	2.734391
28	6	0	2.422773	-1.595098	3.344291
29	6	0	1.291209	-1.062550	2.735127
30	6	0	-2.970290	1.655580	0.332057
31	6	0	-4.320096	1.311218	0.196364
32	6	0	-5.322353	2.183787	0.622489
33	6	0	-5.016025	3.424658	1.190590
34	6	0	-3.662750	3.766410	1.317838
35	6	0	-2.655716	2.904859	0.891116
36	8	0	-0.292153	1.277583	1.731228
37	8	0	-3.869668	-0.797223	-2.304876
38	6	0	4.386108	-3.199319	3.422958
39	6	0	-6.103923	4.378112	1.627029
40	1	0	-0.296014	-4.361729	0.410818

41	1	0	-1.278271	-6.283929	-0.806583
42	1	0	-3.085750	-5.951383	-2.459750
43	1	0	-3.979310	-3.640066	-2.897312
44	1	0	1.365320	-2.870930	-0.139694
45	1	0	3.349520	-3.817880	0.960107
46	1	0	2.725129	-1.217931	4.319420
47	1	0	0.733457	-0.272341	3.222409
48	1	0	-4.595170	0.369342	-0.262714
49	1	0	-6.363519	1.890008	0.506746
50	1	0	-3.391802	4.723492	1.759623
51	1	0	-1.616690	3.185466	1.016562
52	1	0	5.053398	-3.693810	2.708886
53	1	0	4.964462	-2.434146	3.953488
54	1	0	4.091437	-3.951580	4.167443
55	1	0	-7.051974	3.855420	1.791530
56	1	0	-5.836868	4.894404	2.556272
57	1	0	-6.285284	5.152385	0.869098
58	1	0	-1.788075	1.730437	-2.138993
59	1	0	2.001377	-0.217565	-2.296424
60	1	0	4.417053	0.078724	-2.250943
61	1	0	3.894141	3.931543	-0.325049
62	1	0	1.477677	3.634872	-0.409955
63	1	0	7.648740	1.483743	-1.653230
64	1	0	6.431477	0.972310	-2.832009
65	1	0	6.488485	0.215754	-1.221981
66	1	0	7.397621	3.333406	-0.712379
67	1	0	6.039362	3.478647	0.416236
68	1	0	5.986089	4.303550	-1.159926

No imaginary frequency.
Total energy: –1594.39931728 hartree.

Table S27. Cartesian Coordinates of **Intermediate A** (Triplet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.712303	1.896028	-0.153243
2	6	0	2.776837	1.121371	-0.912491
3	6	0	3.317573	0.007838	-1.633076
4	6	0	4.661907	-0.299399	-1.591834
5	6	0	5.578825	0.468300	-0.826734
6	6	0	5.054820	1.582402	-0.118991
7	6	0	1.440082	1.427051	-0.947932
8	6	0	0.187369	1.769453	-1.054628
9	7	0	6.925707	0.137402	-0.763462
10	6	0	7.861471	1.059521	-0.142535
11	6	0	7.454373	-0.885003	-1.649965
12	6	0	-0.982611	1.314175	-0.146913
13	6	0	-1.898828	0.454625	-0.960306
14	6	0	-1.941041	-0.880154	-0.503257
15	6	0	-1.115954	-1.064713	0.607299
16	6	0	-0.503173	0.268438	0.915090
17	6	0	-2.710728	0.601150	-2.171259
18	6	0	-3.330886	-0.756248	-2.370712
19	6	0	-2.887594	-1.639714	-1.358972
20	6	0	-4.242148	-1.150329	-3.336714

21	6	0	-4.740076	-2.459737	-3.287176
22	6	0	-4.329213	-3.331168	-2.276068
23	6	0	-3.400512	-2.932295	-1.301894
24	6	0	-0.783491	-2.276631	1.343767
25	6	0	-0.712192	-3.529462	0.699446
26	6	0	-0.379348	-4.680238	1.403906
27	6	0	-0.108636	-4.636266	2.779928
28	6	0	-0.158781	-3.388403	3.417040
29	6	0	-0.478062	-2.228011	2.720442
30	6	0	-1.627031	2.522675	0.538850
31	6	0	-2.995517	2.794227	0.454584
32	6	0	-3.546436	3.895830	1.112293
33	6	0	-2.752608	4.758169	1.873923
34	6	0	-1.381233	4.477061	1.959563
35	6	0	-0.824792	3.383774	1.302762
36	8	0	0.262626	0.515679	1.827100
37	8	0	-2.870798	1.592852	-2.876347
38	6	0	0.212113	-5.893641	3.550336
39	6	0	-3.342739	5.965551	2.564437
40	1	0	-3.106855	-3.622489	-0.518953
41	1	0	-4.735100	-4.338480	-2.238801
42	1	0	-5.456204	-2.796783	-4.031471
43	1	0	-4.560336	-0.447351	-4.101407
44	1	0	-0.876045	-3.588307	-0.371710
45	1	0	-0.316433	-5.629298	0.876078
46	1	0	0.062016	-3.323949	4.480080
47	1	0	-0.490816	-1.274690	3.233564
48	1	0	-3.645336	2.151270	-0.129839
49	1	0	-4.614192	4.085470	1.026422
50	1	0	-0.738060	5.126380	2.550281
51	1	0	0.237437	3.182842	1.388970
52	1	0	0.717219	-6.633312	2.919992
53	1	0	0.855234	-5.683533	4.411342
54	1	0	-0.702044	-6.365869	3.935453
55	1	0	-4.432621	5.891344	2.638623
56	1	0	-2.942516	6.084137	3.578099
57	1	0	-3.113409	6.890171	2.017950
58	1	0	-0.157115	2.436984	-1.852057
59	1	0	2.646785	-0.602198	-2.230469
60	1	0	5.010754	-1.149773	-2.166077
61	1	0	5.712615	2.212098	0.468700
62	1	0	3.347381	2.752443	0.405111
63	1	0	8.514868	-1.030328	-1.435187
64	1	0	7.350750	-0.622745	-2.715192
65	1	0	6.949966	-1.844799	-1.486829
66	1	0	8.861014	0.620848	-0.161783
67	1	0	7.599493	1.237682	0.907045
68	1	0	7.902734	2.034817	-0.653515

No imaginary frequency.
Total energy: –1594.39002934 hartree.

Table S28. Cartesian Coordinates of **TS2** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.939326	-2.652809	-0.872866
2	6	0	-1.406977	-1.373560	-1.202077
3	6	0	-2.320502	-0.397166	-1.690988
4	6	0	-3.653862	-0.687391	-1.875726
5	6	0	-4.179782	-1.970484	-1.553015
6	6	0	-3.276806	-2.942193	-1.038302
7	6	0	-0.057248	-1.094736	-1.036608
8	6	0	0.244059	0.686403	0.953797
9	6	0	0.957628	1.560359	0.109739
10	6	0	2.132569	0.973177	-0.385645
11	6	0	2.158935	-0.461739	-0.027899
12	6	0	1.233525	-1.148543	-1.129772
13	6	0	1.127625	-0.488285	1.171209
14	6	0	0.763365	2.883003	-0.544356
15	6	0	1.860369	3.069033	-1.414143
16	6	0	2.749402	1.849225	-1.379381
17	6	0	1.991023	4.200981	-2.197618
18	6	0	0.987599	5.180841	-2.127006
19	6	0	-0.114232	4.995610	-1.293172
20	6	0	-0.240042	3.845108	-0.494073
21	6	0	3.442225	-1.228881	0.171665
22	6	0	3.392963	-2.567313	0.592829
23	6	0	4.563953	-3.294615	0.791361
24	6	0	5.822303	-2.717824	0.575576
25	6	0	5.863861	-1.387787	0.142325
26	6	0	4.696597	-0.650566	-0.057252
27	6	0	7.091326	-3.499921	0.822654
28	6	0	-0.938166	0.925386	1.786061
29	6	0	-1.239241	2.200615	2.301153
30	6	0	-2.349402	2.406408	3.115477
31	6	0	-3.205024	1.351128	3.458394
32	6	0	-2.889590	0.075322	2.972489
33	6	0	-1.780746	-0.139462	2.159623
34	8	0	1.067213	-1.327092	2.047520
35	8	0	3.750293	1.685339	-2.074261
36	6	0	-4.426934	1.581520	4.315647
37	7	0	-5.508363	-2.257343	-1.728093
38	6	0	-6.417743	-1.244430	-2.247455
39	6	0	-6.030548	-3.568861	-1.368345
40	1	0	-1.113614	3.720447	0.135673
41	1	0	-0.894285	5.751757	-1.257423
42	1	0	1.062916	6.080487	-2.731976
43	1	0	2.846974	4.306563	-2.858515
44	1	0	-0.567755	3.028708	2.100289
45	1	0	-2.544322	3.402513	3.507573
46	1	0	-3.521144	-0.769001	3.241745
47	1	0	-1.553658	-1.141288	1.815777
48	1	0	4.762225	0.366296	-0.426463
49	1	0	6.825982	-0.917437	-0.049901
50	1	0	4.499092	-4.329342	1.122008
51	1	0	2.432768	-3.033755	0.783713
52	1	0	-4.296819	2.445801	4.975763
53	1	0	-5.317347	1.774400	3.701097
54	1	0	-4.649101	0.709404	4.940463
55	1	0	7.909932	-3.148218	0.185351
56	1	0	7.425115	-3.399662	1.864512
57	1	0	6.948298	-4.569217	0.631237

58	1	0	1.775529	-1.593867	-1.963086
59	1	0	-1.266916	-3.413366	-0.488224
60	1	0	-3.631641	-3.931180	-0.775680
61	1	0	-4.306463	0.086657	-2.259967
62	1	0	-1.947283	0.595424	-1.922605
63	1	0	-7.099958	-3.598150	-1.579348
64	1	0	-5.887793	-3.783079	-0.300881
65	1	0	-5.548432	-4.367693	-1.946779
66	1	0	-7.418218	-1.670493	-2.328761
67	1	0	-6.112307	-0.902980	-3.244916
68	1	0	-6.472229	-0.369628	-1.585889

One imaginary frequency.
Total energy: –1594.39504339 hartree.

Table S29. Cartesian Coordinates of **Intermediate B** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.420263	-2.322132	1.128112
2	6	0	3.388151	-1.241669	0.231216
3	6	0	4.572064	-0.892097	-0.426076
4	6	0	5.749059	-1.605276	-0.188837
5	6	0	5.788830	-2.677831	0.707397
6	6	0	4.597955	-3.025616	1.360239
7	6	0	2.079052	-0.528970	0.019687
8	6	0	1.939643	0.782042	-0.746553
9	6	0	0.749598	1.370277	-0.426394
10	6	0	0.014221	0.538563	0.598842
11	6	0	1.342305	-0.005402	1.323891
12	6	0	0.502550	2.570859	-1.258944
13	6	0	1.625020	2.705204	-2.103700
14	6	0	2.596576	1.582684	-1.821410
15	6	0	-0.553899	3.463911	-1.366411
16	6	0	-0.462009	4.498327	-2.319388
17	6	0	0.655967	4.631884	-3.137726
18	6	0	1.723163	3.718571	-3.034142
19	6	0	-0.963517	1.167763	1.558575
20	6	0	-0.878464	2.531654	1.869636
21	6	0	-1.711881	3.107139	2.828410
22	6	0	-2.646726	2.339639	3.531053
23	6	0	-2.709884	0.970580	3.241210
24	6	0	-1.881922	0.392434	2.282243
25	8	0	1.633222	-0.034205	2.477481
26	8	0	3.661823	1.419778	-2.392689
27	6	0	-3.530147	2.953846	4.591503
28	6	0	7.072658	-3.425426	0.982853
29	6	0	0.891470	-1.407056	-0.397470
30	6	0	-0.290952	-0.826456	-0.094314
31	6	0	-1.625482	-1.345305	-0.419598
32	6	0	-2.678221	-0.502222	-0.814290
33	6	0	-3.916191	-1.003872	-1.192576
34	6	0	-4.172808	-2.395283	-1.195466
35	6	0	-3.121637	-3.244115	-0.774487
36	6	0	-1.888439	-2.726326	-0.402923
37	7	0	-5.398255	-2.903734	-1.594525

38	6	0	-5.678517	-4.319368	-1.427359
39	6	0	-6.505654	-1.996560	-1.842378
40	1	0	-1.430814	3.381491	-0.732668
41	1	0	-1.282870	5.204344	-2.412387
42	1	0	0.702666	5.438808	-3.863446
43	1	0	2.600085	3.793917	-3.671101
44	1	0	-0.145517	3.156098	1.368544
45	1	0	-1.623417	4.170555	3.039762
46	1	0	-3.416832	0.341762	3.778323
47	1	0	-1.955378	-0.672870	2.095302
48	1	0	4.575796	-0.077236	-1.141858
49	1	0	6.654851	-1.318354	-0.718930
50	1	0	4.593430	-3.856796	2.062465
51	1	0	2.514662	-2.609944	1.655367
52	1	0	-3.607515	4.039227	4.469748
53	1	0	-4.543161	2.536838	4.561872
54	1	0	-3.133105	2.764926	5.597814
55	1	0	7.531644	-3.095929	1.924689
56	1	0	6.899434	-4.504255	1.070178
57	1	0	7.807818	-3.264534	0.187519
58	1	0	1.033550	-2.351310	-0.909989
59	1	0	-1.111038	-3.409784	-0.071767
60	1	0	-3.268157	-4.316485	-0.726498
61	1	0	-4.687825	-0.304198	-1.490362
62	1	0	-2.523608	0.572333	-0.837308
63	1	0	-6.671103	-4.536454	-1.826354
64	1	0	-5.654523	-4.637242	-0.372893
65	1	0	-4.957792	-4.932346	-1.982240
66	1	0	-7.376334	-2.573577	-2.159285
67	1	0	-6.265520	-1.290499	-2.646912
68	1	0	-6.785190	-1.413317	-0.950803

No imaginary frequency.
Total energy: –1594.44129594 hartree.

Table S30. Cartesian Coordinates of **TS3** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.083429	-2.564485	0.177180
2	6	0	-1.749376	-1.298670	-0.327276
3	6	0	-2.692805	-0.677376	-1.162709
4	6	0	-3.905351	-1.278505	-1.474028
5	6	0	-4.248347	-2.548435	-0.951967
6	6	0	-3.293950	-3.180038	-0.122540
7	6	0	-0.422535	-0.688780	-0.074414
8	6	0	-0.184704	0.717026	0.367725
9	6	0	0.819800	1.334048	-0.491831
10	6	0	1.979940	0.609189	-0.706729
11	6	0	2.009953	-0.704195	-0.046235
12	6	0	0.728773	-1.396755	-0.267281
13	6	0	1.272815	0.049533	1.624464
14	6	0	0.868958	2.621981	-1.235228
15	6	0	2.111642	2.670475	-1.892061
16	6	0	2.888657	1.425285	-1.569854
17	6	0	2.471898	3.720735	-2.714343

18	6	0	1.549952	4.765476	-2.898046
19	6	0	0.307809	4.718129	-2.267420
20	6	0	-0.050172	3.645501	-1.429740
21	6	0	3.206512	-1.551578	0.226438
22	6	0	3.036277	-2.700407	1.022921
23	6	0	4.106586	-3.533545	1.328712
24	6	0	5.397095	-3.253977	0.858919
25	6	0	5.565920	-2.109871	0.071213
26	6	0	4.499720	-1.265760	-0.237469
27	6	0	6.566557	-4.139696	1.217654
28	6	0	-1.135398	1.545313	1.170000
29	6	0	-0.694338	2.797052	1.646506
30	6	0	-1.490970	3.590493	2.463726
31	6	0	-2.764418	3.167145	2.868723
32	6	0	-3.188718	1.907486	2.434933
33	6	0	-2.395598	1.108049	1.612100
34	8	0	1.440955	-0.016849	2.768651
35	8	0	4.014640	1.191081	-1.982649
36	6	0	-3.638180	4.039817	3.737290
37	7	0	-5.472386	-3.141442	-1.231761
38	6	0	-6.329360	-2.561251	-2.251923
39	6	0	-5.692948	-4.527731	-0.856359
40	1	0	-1.021676	3.631720	-0.947824
41	1	0	-0.403795	5.524707	-2.423788
42	1	0	1.801908	5.606730	-3.537521
43	1	0	3.441521	3.722074	-3.204457
44	1	0	0.300579	3.146095	1.388811
45	1	0	-1.108078	4.549004	2.807652
46	1	0	-4.160610	1.533407	2.749531
47	1	0	-2.769325	0.135954	1.322455
48	1	0	4.667200	-0.399695	-0.866208
49	1	0	6.554155	-1.870023	-0.315639
50	1	0	3.938997	-4.411881	1.948548
51	1	0	2.053211	-2.934536	1.422405
52	1	0	-4.133495	4.821971	3.146135
53	1	0	-4.422643	3.456663	4.230386
54	1	0	-3.053534	4.546164	4.513733
55	1	0	7.004426	-3.848726	2.182177
56	1	0	6.264688	-5.189410	1.303875
57	1	0	7.361938	-4.075703	0.467673
58	1	0	0.720607	-2.443222	-0.551568
59	1	0	-1.382778	-3.076345	0.831593
60	1	0	-3.494431	-4.157532	0.299301
61	1	0	-4.585164	-0.756687	-2.136801
62	1	0	-2.465327	0.295335	-1.590941
63	1	0	-6.709003	-4.815490	-1.133541
64	1	0	-5.597481	-4.660786	0.227854
65	1	0	-4.991555	-5.221568	-1.347217
66	1	0	-7.250775	-3.143338	-2.317018
67	1	0	-5.859953	-2.546011	-3.248792
68	1	0	-6.607259	-1.532700	-1.992805

One imaginary frequency.
Total energy: –1594.41976196 hartree.

Table S31. Cartesian Coordinates of **C** (**4a′**) at the B3LYP/6-31G(d) Level

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.678873	-1.060313	0.931196
2	6	0	-1.636036	-1.315735	0.026752
3	6	0	-1.833944	-2.365573	-0.884800
4	6	0	-3.002757	-3.117346	-0.905294
5	6	0	-4.044047	-2.868949	0.017232
6	6	0	-3.848837	-1.809539	0.933115
7	6	0	-0.345893	-0.573192	0.041099
8	6	0	-0.264513	0.850053	0.024778
9	6	0	1.009960	1.426973	-0.000875
10	6	0	2.185923	0.633149	0.024525
11	6	0	2.120452	-0.765292	0.049063
12	6	0	0.832878	-1.329647	0.050851
13	6	0	1.415899	2.865436	-0.061371
14	6	0	2.819937	2.927141	0.011748
15	6	0	3.376411	1.544984	0.078666
16	6	0	3.518775	4.124223	-0.020157
17	6	0	2.790715	5.313217	-0.139430
18	6	0	1.397707	5.267197	-0.232980
19	6	0	0.696002	4.052358	-0.196243
20	6	0	3.295872	-1.677449	0.070974
21	6	0	3.326338	-2.757271	0.966746
22	6	0	4.388016	-3.660811	0.967352
23	6	0	5.451163	-3.526242	0.067829
24	6	0	5.412905	-2.453379	-0.834042
25	6	0	4.362143	-1.541765	-0.831440
26	6	0	6.616577	-4.487279	0.082005
27	6	0	-1.498601	1.695267	0.008466
28	6	0	-1.894347	2.413817	1.145790
29	6	0	-3.038116	3.211897	1.126563
30	6	0	-3.825210	3.321685	-0.026972
31	6	0	-3.424602	2.605579	-1.162817
32	6	0	-2.285310	1.802522	-1.146572
33	8	0	4.559908	1.257392	0.159354
34	6	0	-5.079938	4.163604	-0.039478
35	7	0	-5.201593	-3.636535	0.031009
36	6	0	-5.446248	-4.575473	-1.049981
37	6	0	-6.331179	-3.208062	0.837946
38	1	0	-0.383301	4.056988	-0.276664
39	1	0	0.838246	6.193310	-0.338199
40	1	0	3.305358	6.269695	-0.167478
41	1	0	4.603518	4.118719	0.040977
42	1	0	-1.294212	2.352698	2.050193
43	1	0	-3.321770	3.760426	2.022303
44	1	0	-4.013067	2.677643	-2.075103
45	1	0	-1.997998	1.255066	-2.039945
46	1	0	4.363875	-0.721841	-1.540522
47	1	0	6.221994	-2.328885	-1.550579
48	1	0	4.389317	-4.482508	1.680291
49	1	0	2.517680	-2.880368	1.682376
50	1	0	-5.031526	4.966967	0.703161
51	1	0	-5.247775	4.619541	-1.021344
52	1	0	-5.967282	3.559080	0.192142
53	1	0	7.467957	-4.071744	0.637781
54	1	0	6.348848	-5.436698	0.557645

55	1	0	6.970300	-4.704324	-0.932293
56	1	0	0.745407	-2.411541	0.065104
57	1	0	-2.573580	-0.265434	1.661823
58	1	0	-4.614193	-1.565663	1.660230
59	1	0	-3.100688	-3.898640	-1.649525
60	1	0	-1.060220	-2.586198	-1.615800
61	1	0	-7.138284	-3.936499	0.737436
62	1	0	-6.718967	-2.219896	0.541952
63	1	0	-6.061001	-3.160700	1.899675
64	1	0	-6.379203	-5.108509	-0.855987
65	1	0	-4.646028	-5.322696	-1.108706
66	1	0	-5.526851	-4.086079	-2.034299

No imaginary frequency.
Total energy: –1481.19782593 hartree.

Table S32. Cartesian Coordinates of **TS_{rot}** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.295744	0.107639	-1.301650
2	6	0	-3.362836	-0.756908	-0.718317
3	6	0	-3.827126	-1.962589	-0.167203
4	6	0	-5.182700	-2.279103	-0.190152
5	6	0	-6.125352	-1.412059	-0.760311
6	6	0	-5.654062	-0.219552	-1.315641
7	6	0	-1.855405	-0.461904	-0.692349
8	6	0	-1.256561	-0.520979	0.668499
9	6	0	-0.555762	0.668264	0.982399
10	6	0	-0.597683	1.595522	-0.056490
11	6	0	-1.456193	1.007384	-1.115959
12	6	0	-0.015893	0.548496	2.358447
13	6	0	-0.319260	-0.758835	2.799934
14	6	0	-1.074608	-1.500947	1.725798
15	6	0	0.622583	1.438172	3.216904
16	6	0	0.973462	0.996581	4.502769
17	6	0	0.692149	-0.305714	4.921473
18	6	0	0.032739	-1.199191	4.064866
19	6	0	-1.147132	-1.420398	-1.733234
20	6	0	0.127783	-1.634584	-1.818454
21	6	0	1.466066	-1.825037	-1.598965
22	6	0	2.476575	-1.107229	-2.315887
23	6	0	3.813787	-1.331841	-2.087424
24	6	0	4.251781	-2.294604	-1.131478
25	6	0	3.253104	-3.012301	-0.414168
26	6	0	1.913392	-2.789288	-0.636322
27	7	0	5.588312	-2.519263	-0.909972
28	6	0	6.012792	-3.502601	0.076144
29	6	0	0.085314	2.878299	-0.203317
30	6	0	1.366178	3.092020	0.345860
31	6	0	2.019057	4.311410	0.197288
32	6	0	1.429104	5.370625	-0.506714
33	6	0	0.166287	5.151587	-1.074829
34	6	0	-0.493899	3.935036	-0.936381
35	8	0	-1.780117	1.531276	-2.169982
36	8	0	-1.402306	-2.690318	1.779209

37	6	0	2.122612	6.705514	-0.635800
38	6	0	-7.597977	-1.750608	-0.755162
39	6	0	6.592946	-1.768844	-1.649267
40	1	0	0.840405	2.456432	2.913427
41	1	0	1.470992	1.683558	5.182210
42	1	0	0.977683	-0.623538	5.920827
43	1	0	-0.212285	-2.211319	4.374745
44	1	0	1.865342	2.278816	0.863378
45	1	0	3.011210	4.440629	0.625124
46	1	0	-0.309704	5.950693	-1.639270
47	1	0	-1.461604	3.789176	-1.399899
48	1	0	-3.121685	-2.644461	0.299005
49	1	0	-5.514327	-3.218617	0.247846
50	1	0	-6.357994	0.471420	-1.775234
51	1	0	-3.967730	1.030573	-1.763263
52	1	0	3.211700	6.599165	-0.586032
53	1	0	1.872422	7.198050	-1.581716
54	1	0	1.826128	7.388374	0.172305
55	1	0	-8.045113	-1.575686	0.232681
56	1	0	-8.151556	-1.141120	-1.477114
57	1	0	-7.768900	-2.804937	-1.002005
58	1	0	-1.849481	-1.887236	-2.423786
59	1	0	1.167632	-3.337216	-0.068709
60	1	0	3.539075	-3.746009	0.329901
61	1	0	4.539248	-0.758778	-2.652233
62	1	0	2.170102	-0.368911	-3.050184
63	1	0	7.102546	-3.537504	0.100730
64	1	0	5.645860	-4.507414	-0.171544
65	1	0	5.657282	-3.246521	1.083151
66	1	0	7.585375	-2.091801	-1.332765
67	1	0	6.511533	-0.689388	-1.463892
68	1	0	6.509938	-1.937864	-2.731124

One imaginary frequency.
Total energy: –1594.39174983 hartree.

Table S33. Cartesian Coordinates of **Intermediate D** (Singlet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.834555	-0.246212	-1.382239
2	6	0	-3.883883	0.618267	-0.802573
3	6	0	-4.227284	1.979787	-0.691914
4	6	0	-5.471771	2.445870	-1.106300
5	6	0	-6.425931	1.579527	-1.656308
6	6	0	-6.076061	0.228594	-1.792117
7	6	0	-2.578107	0.117450	-0.371714
8	6	0	-1.738266	0.542133	0.653594
9	6	0	-0.488606	-0.130717	0.648851
10	6	0	-0.422069	-1.140184	-0.434588
11	6	0	-1.832981	-0.913768	-1.119351
12	6	0	-1.743414	1.498453	1.786144
13	6	0	-0.456751	1.441900	2.370915
14	6	0	0.386775	0.418865	1.650730
15	6	0	-0.125063	2.214477	3.471058
16	6	0	-1.106084	3.056936	4.014769

17	6	0	-2.387212	3.099347	3.460654
18	6	0	-2.719924	2.320171	2.340941
19	6	0	-0.206715	-2.590850	0.049489
20	6	0	-0.937526	-3.670205	-0.458829
21	6	0	-0.694685	-4.969275	-0.003702
22	6	0	0.281484	-5.235552	0.959068
23	6	0	1.022195	-4.149639	1.449700
24	6	0	0.788393	-2.851676	1.006462
25	6	0	0.525581	-6.636888	1.468516
26	6	0	0.639227	-0.897206	-1.561844
27	6	0	1.813394	-0.374142	-1.452150
28	6	0	3.046841	0.194037	-1.316214
29	6	0	3.257234	1.592994	-1.545280
30	6	0	4.500587	2.162442	-1.413115
31	6	0	5.634421	1.382952	-1.039819
32	6	0	5.433968	-0.011061	-0.813985
33	6	0	4.192965	-0.583474	-0.946875
34	8	0	-2.174092	-1.481764	-2.148778
35	8	0	1.575228	0.165589	1.894565
36	7	0	6.873067	1.952325	-0.903001
37	6	0	7.052531	3.382679	-1.113878
38	6	0	-7.787424	2.079322	-2.076861
39	6	0	8.013741	1.144376	-0.490989
40	1	0	-3.723317	2.358339	1.930907
41	1	0	-3.142553	3.744246	3.901956
42	1	0	-0.873001	3.673491	4.879104
43	1	0	0.872244	2.150467	3.897487
44	1	0	-3.495191	2.683361	-0.308215
45	1	0	-5.701111	3.505686	-1.014924
46	1	0	-6.790522	-0.465442	-2.230185
47	1	0	-4.587708	-1.293044	-1.514287
48	1	0	1.379307	-2.030680	1.403046
49	1	0	1.795570	-4.322889	2.195975
50	1	0	-1.280731	-5.789802	-0.412930
51	1	0	-1.692055	-3.505314	-1.218497
52	1	0	-7.763585	3.144906	-2.329346
53	1	0	-8.163842	1.532886	-2.948700
54	1	0	-8.525722	1.952250	-1.273055
55	1	0	0.121176	-6.770974	2.480807
56	1	0	0.051960	-7.385276	0.824658
57	1	0	1.596806	-6.865695	1.519711
58	1	0	0.288504	-1.300771	-2.515083
59	1	0	4.060619	-1.643711	-0.758070
60	1	0	6.267477	-0.638897	-0.524035
61	1	0	4.607335	3.225213	-1.592564
62	1	0	2.407252	2.207271	-1.824395
63	1	0	8.900403	1.777180	-0.441425
64	1	0	8.212895	0.336023	-1.206173
65	1	0	7.856807	0.697430	0.499540
66	1	0	8.102330	3.637263	-0.964981
67	1	0	6.454047	3.974922	-0.409031
68	1	0	6.773889	3.676299	-2.134057

No imaginary frequency.
Total energy: –1594.39403889 hartree.

Table S34. Cartesian Coordinates of **Intermediate D** (Triplet) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.617414	1.291840	-0.847992
2	6	0	-2.592242	0.520493	-1.483928
3	6	0	-2.953562	-0.805099	-1.885868
4	6	0	-4.223059	-1.305203	-1.678943
5	6	0	-5.237857	-0.526629	-1.063271
6	6	0	-4.883540	0.783804	-0.645765
7	6	0	-1.336414	1.029613	-1.712005
8	6	0	-0.116011	1.475551	-1.790575
9	6	0	0.964029	1.372892	-0.678153
10	6	0	0.471701	0.705586	0.571418
11	6	0	1.092698	-0.545766	0.789591
12	6	0	1.984768	-0.861596	-0.233562
13	6	0	1.998441	0.308955	-1.165820
14	6	0	-0.518293	0.956377	1.627794
15	6	0	-0.377436	-0.214041	2.561508
16	6	0	0.599439	-1.108131	2.070072
17	6	0	-1.032747	-0.435397	3.761991
18	6	0	-0.694423	-1.575646	4.502973
19	6	0	0.288291	-2.452736	4.037387
20	6	0	0.945612	-2.230139	2.817638
21	6	0	2.740314	-2.083330	-0.480284
22	6	0	3.993593	-2.047135	-1.127512
23	6	0	4.703825	-3.218982	-1.363282
24	6	0	4.197649	-4.471773	-0.988345
25	6	0	2.937329	-4.511204	-0.373750
26	6	0	2.223307	-3.345435	-0.121674
27	6	0	4.988916	-5.734586	-1.226499
28	6	0	1.571063	2.767205	-0.429021
29	6	0	2.858485	3.122511	-0.847289
30	6	0	3.351397	4.409014	-0.616555
31	6	0	2.583948	5.380401	0.031900
32	6	0	1.290341	5.021469	0.435593
33	6	0	0.788647	3.743028	0.209285
34	8	0	2.667828	0.408215	-2.181094
35	8	0	-1.306167	1.889148	1.760024
36	6	0	3.129940	6.762401	0.304854
37	7	0	-6.521851	-1.021955	-0.883208
38	6	0	-7.473381	-0.272104	-0.080729
39	6	0	-6.789788	-2.427118	-1.136539
40	1	0	1.713032	-2.918767	2.481895
41	1	0	0.552259	-3.324925	4.629367
42	1	0	-1.190691	-1.775502	5.448620
43	1	0	-1.780800	0.271074	4.110190
44	1	0	1.233671	-3.410284	0.319021
45	1	0	2.505157	-5.471215	-0.100309
46	1	0	5.672358	-3.161284	-1.854876
47	1	0	4.400415	-1.095371	-1.445054
48	1	0	-0.214982	3.493719	0.538508
49	1	0	0.661792	5.755977	0.935330
50	1	0	4.355011	4.657872	-0.955479
51	1	0	3.478207	2.407258	-1.373919
52	1	0	4.333795	-6.606287	-1.326694
53	1	0	5.598778	-5.660542	-2.133188

54	1	0	5.673655	-5.936089	-0.391371
55	1	0	3.459691	6.862940	1.347758
56	1	0	3.991306	6.986151	-0.333119
57	1	0	2.371840	7.534990	0.132247
58	1	0	0.267547	1.966748	-2.689193
59	1	0	-3.374917	2.289392	-0.497242
60	1	0	-5.611976	1.410875	-0.145096
61	1	0	-4.433708	-2.318723	-1.999985
62	1	0	-2.203817	-1.427531	-2.365154
63	1	0	-8.429427	-0.799111	-0.075275
64	1	0	-7.647359	0.723448	-0.505916
65	1	0	-7.143859	-0.143465	0.962626
66	1	0	-7.849214	-2.626102	-0.963739
67	1	0	-6.202820	-3.097035	-0.487874
68	1	0	-6.570678	-2.687987	-2.178924

No imaginary frequency.
Total energy: –1594.39183016 hartree.

Table S35. Cartesian Coordinates of **Intermediate E** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.404568	3.762934	-0.500481
2	6	0	1.982509	2.495455	-0.672256
3	6	0	3.373112	2.386171	-0.553956
4	6	0	4.156608	3.507093	-0.273699
5	6	0	3.584125	4.771136	-0.104249
6	6	0	2.190735	4.875813	-0.220155
7	6	0	1.096249	1.300576	-0.950439
8	6	0	0.137014	0.730946	0.179317
9	6	0	0.623746	-0.672255	0.448677
10	6	0	1.458685	-1.135869	-0.524786
11	6	0	1.818055	0.011415	-1.423431
12	6	0	0.335013	-1.018921	1.842833
13	6	0	-0.048906	0.165689	2.516447
14	6	0	-0.110465	1.320347	1.570925
15	6	0	0.476684	-2.206149	2.573040
16	6	0	0.221433	-2.184432	3.945116
17	6	0	-0.163815	-1.005380	4.601698
18	6	0	-0.297155	0.184332	3.886484
19	6	0	-0.169185	1.479580	-1.777228
20	6	0	-0.999013	0.945328	-0.858953
21	6	0	-2.419930	0.642817	-0.803528
22	6	0	-3.271532	1.004735	-1.865609
23	6	0	-4.628086	0.727265	-1.844527
24	6	0	-5.220546	0.057001	-0.744937
25	6	0	-4.369593	-0.297329	0.326964
26	6	0	-3.010907	-0.011778	0.289800
27	7	0	-6.572521	-0.240900	-0.725593
28	6	0	-7.171742	-0.776520	0.484855
29	6	0	2.030122	-2.479395	-0.686549
30	6	0	1.240583	-3.620842	-0.456318
31	6	0	1.763863	-4.901578	-0.613058
32	6	0	3.093431	-5.095277	-1.011076
33	6	0	3.872263	-3.957901	-1.263948

34	6	0	3.356237	-2.673729	-1.113884
35	8	0	2.587619	-0.036760	-2.366849
36	8	0	-0.374641	2.471469	1.858326
37	6	0	3.671401	-6.483283	-1.152716
38	6	0	4.434000	5.989019	0.173805
39	6	0	-7.442938	0.293811	-1.759263
40	1	0	0.779952	-3.126381	2.086979
41	1	0	0.324824	-3.102548	4.517476
42	1	0	-0.353874	-1.023298	5.671240
43	1	0	-0.580646	1.115360	4.368966
44	1	0	0.194695	-3.496027	-0.188663
45	1	0	1.125162	-5.764848	-0.438555
46	1	0	4.902778	-4.080123	-1.590230
47	1	0	3.977507	-1.814306	-1.335461
48	1	0	3.859877	1.428203	-0.700299
49	1	0	5.235398	3.392748	-0.190728
50	1	0	1.712729	5.843967	-0.084988
51	1	0	0.326580	3.869806	-0.565073
52	1	0	2.901128	-7.213503	-1.423011
53	1	0	4.453181	-6.515444	-1.919036
54	1	0	4.125445	-6.823175	-0.211844
55	1	0	5.444509	5.708649	0.488688
56	1	0	4.531625	6.621148	-0.718987
57	1	0	3.995632	6.612548	0.961767
58	1	0	-0.291621	1.834700	-2.795585
59	1	0	-2.400337	-0.304829	1.137857
60	1	0	-4.768729	-0.796797	1.201476
61	1	0	-5.233751	1.037393	-2.687621
62	1	0	-2.858407	1.523689	-2.726661
63	1	0	-8.231539	-0.966366	0.305526
64	1	0	-7.084637	-0.089531	1.341234
65	1	0	-6.707186	-1.729488	0.766808
66	1	0	-8.461682	-0.057196	-1.585077
67	1	0	-7.137894	-0.055521	-2.753376
68	1	0	-7.456632	1.394857	-1.774983

No imaginary frequency.
Total energy: –1594.45231053 hartree.

Table S36. Cartesian Coordinates of **TS4** at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.988406	-1.548260	-1.470995
2	6	0	2.734114	-1.708462	-0.851989
3	6	0	2.390970	-2.999673	-0.404203
4	6	0	3.269826	-4.068969	-0.540355
5	6	0	4.522477	-3.904764	-1.149489
6	6	0	4.860136	-2.625838	-1.609905
7	6	0	1.777371	-0.595577	-0.718319
8	6	0	0.953835	-0.374165	0.395711
9	6	0	-0.317611	0.323808	0.400706
10	6	0	0.593420	1.414954	-1.488099
11	6	0	1.646598	0.378207	-1.791942
12	6	0	1.322659	-0.629213	1.820522
13	6	0	0.373572	-0.009995	2.655440

14	6	0	-0.684266	0.613006	1.813829
15	6	0	0.495012	0.001803	4.038939
16	6	0	1.599890	-0.633049	4.611764
17	6	0	2.560069	-1.240568	3.792729
18	6	0	2.440854	-1.237025	2.398445
19	6	0	0.916284	2.726300	-1.016401
20	6	0	2.264452	3.075482	-0.760196
21	6	0	2.592210	4.352660	-0.325586
22	6	0	1.604563	5.330059	-0.136269
23	6	0	0.263065	4.987769	-0.404703
24	6	0	-0.078751	3.722961	-0.842804
25	6	0	1.959731	6.722354	0.317657
26	6	0	-0.744141	0.915467	-1.825538
27	6	0	-1.302906	0.413758	-0.694769
28	6	0	-2.675519	-0.104263	-0.583275
29	6	0	-3.009275	-1.146981	0.295469
30	6	0	-4.293932	-1.666675	0.360174
31	6	0	-5.326906	-1.168489	-0.468598
32	6	0	-4.995825	-0.107922	-1.344765
33	6	0	-3.705522	0.401098	-1.393152
34	8	0	2.241023	0.419700	-2.873429
35	8	0	-1.657638	1.239735	2.214905
36	7	0	-6.607307	-1.700704	-0.425839
37	6	0	-6.962446	-2.622033	0.640712
38	6	0	5.458377	-5.075632	-1.333786
39	6	0	-7.678199	-1.046168	-1.157284
40	1	0	3.202628	-1.708597	1.789379
41	1	0	3.420388	-1.725089	4.247356
42	1	0	1.721481	-0.651220	5.691456
43	1	0	-0.256859	0.502347	4.642682
44	1	0	1.416759	-3.158681	0.049967
45	1	0	2.974029	-5.052340	-0.180405
46	1	0	5.826061	-2.468655	-2.085418
47	1	0	4.278701	-0.573599	-1.844903
48	1	0	-1.114317	3.470985	-1.045585
49	1	0	-0.513978	5.735950	-0.267639
50	1	0	3.632588	4.602479	-0.133967
51	1	0	3.045862	2.340280	-0.918824
52	1	0	5.393056	-5.779474	-0.496431
53	1	0	5.218423	-5.637531	-2.246799
54	1	0	6.499574	-4.747117	-1.419834
55	1	0	3.008981	6.792735	0.618893
56	1	0	1.792152	7.452797	-0.484867
57	1	0	1.338747	7.033215	1.166311
58	1	0	-1.077207	0.757983	-2.848480
59	1	0	-3.494889	1.234207	-2.059098
60	1	0	-5.752831	0.335757	-1.980294
61	1	0	-4.492250	-2.470237	1.059010
62	1	0	-2.241625	-1.573036	0.935034
63	1	0	-8.597773	-1.622060	-1.035784
64	1	0	-7.453175	-1.006396	-2.229716
65	1	0	-7.867250	-0.017318	-0.810839
66	1	0	-8.000085	-2.935495	0.510590
67	1	0	-6.859803	-2.174628	1.641979
68	1	0	-6.338864	-3.523596	0.607255

One imaginary frequency.

Total energy: –1594.41120952 hartree.

Table S37. Cartesian Coordinates of **F** (**5a′**) at the B3LYP/6-31G(d) Level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.734925	-1.090719	1.171601
2	6	0	3.364646	-1.065254	0.964076
3	6	0	2.781306	-0.264578	-0.029530
4	6	0	3.647367	0.521457	-0.804152
5	6	0	5.025542	0.491214	-0.627444
6	6	0	5.610655	-0.312287	0.377254
7	6	0	1.303888	-0.157231	-0.201410
8	6	0	0.822620	1.198920	-0.103621
9	6	0	-0.396041	1.755169	-0.378655
10	6	0	-0.575889	3.223898	-0.228237
11	6	0	0.468938	4.119669	-0.506733
12	6	0	0.314180	5.490936	-0.311639
13	6	0	-0.886012	6.024028	0.169817
14	6	0	-1.932870	5.130499	0.442325
15	6	0	-1.789440	3.763559	0.238714
16	6	0	-1.064820	7.510630	0.364654
17	7	0	6.981551	-0.327101	0.587361
18	6	0	7.855738	0.340920	-0.361632
19	6	0	0.498218	-1.271787	-0.346598
20	6	0	-0.959374	-1.367817	-0.257940
21	6	0	-1.295990	-2.832114	-0.206866
22	6	0	-0.123583	-3.576778	-0.409599
23	6	0	1.034082	-2.667705	-0.546448
24	6	0	-0.109864	-4.965095	-0.489834
25	6	0	-1.318450	-5.645389	-0.352020
26	6	0	-2.500578	-4.921116	-0.155077
27	6	0	-2.507815	-3.524004	-0.086089
28	6	0	-1.886026	-0.354748	-0.342705
29	6	0	-1.577255	1.002214	-0.875448
30	8	0	-2.370212	1.547765	-1.639836
31	8	0	2.173593	-3.013779	-0.816186
32	6	0	-3.326363	-0.546781	-0.007030
33	6	0	-3.680360	-0.781217	1.332027
34	6	0	-5.014780	-0.927148	1.705501
35	6	0	-6.043183	-0.842555	0.757478
36	6	0	-5.686287	-0.603864	-0.576497
37	6	0	-4.354709	-0.445758	-0.957428
38	6	0	-7.492298	-0.973367	1.163873
39	6	0	7.557872	-1.326451	1.471788
40	1	0	-2.897832	-0.854728	2.082682
41	1	0	-5.260809	-1.108417	2.749572
42	1	0	-4.105133	-0.249288	-1.992605
43	1	0	-6.465235	-0.537050	-1.333078
44	1	0	-8.089027	-1.444926	0.375516
45	1	0	-7.601879	-1.570102	2.075621
46	1	0	-7.939014	0.010180	1.362604
47	1	0	1.584191	1.895792	0.233495
48	1	0	-3.447067	-3.009799	0.057513
49	1	0	0.830071	-5.482699	-0.658370
50	1	0	-1.348282	-6.730330	-0.401593

51	1	0	-3.442774	-5.453952	-0.055712
52	1	0	1.406487	3.745800	-0.907544
53	1	0	-2.625100	3.105060	0.450128
54	1	0	1.140105	6.158116	-0.547782
55	1	0	-2.879066	5.514096	0.817928
56	1	0	-1.526942	7.735229	1.333161
57	1	0	-0.107384	8.039194	0.317013
58	1	0	-1.716803	7.938017	-0.408594
59	1	0	3.237428	1.149797	-1.591314
60	1	0	2.729670	-1.675768	1.598778
61	1	0	5.644684	1.095680	-1.279144
62	1	0	5.126398	-1.725044	1.957572
63	1	0	8.639474	-1.184260	1.513840
64	1	0	7.171760	-1.219996	2.492766
65	1	0	7.357206	-2.356443	1.137585
66	1	0	8.889296	0.246891	-0.022811
67	1	0	7.785628	-0.080398	-1.377220
68	1	0	7.624099	1.411062	-0.422202

No imaginary frequency.
Total energy: –1594.47995909 hartree.

9. ^{1}H and ^{13}C NMR spectral data

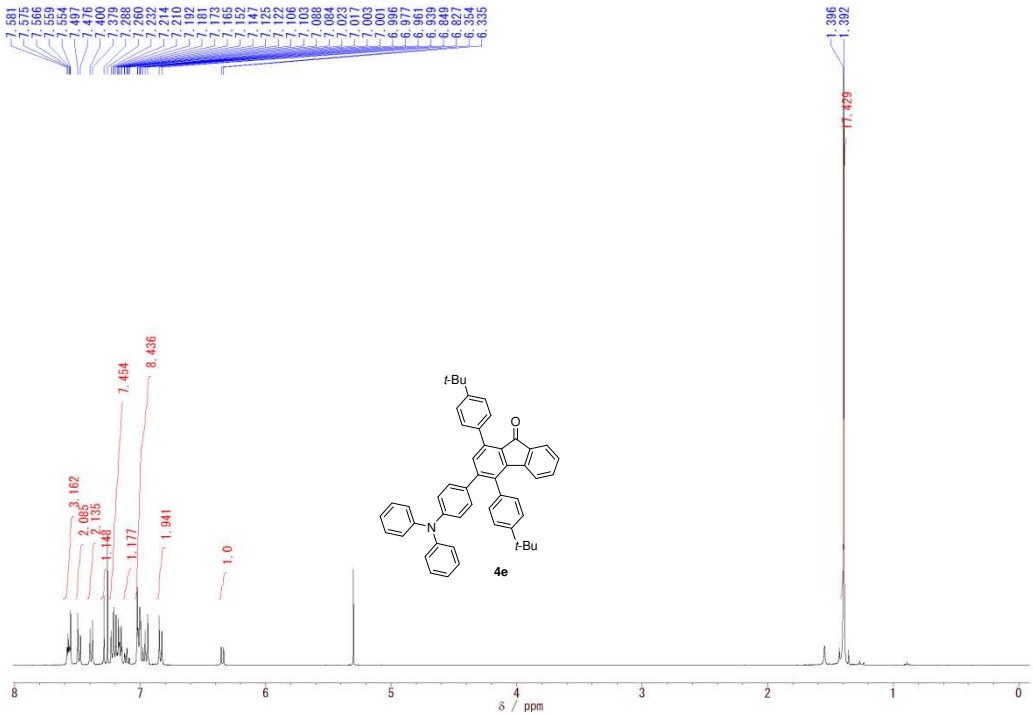

Figure S24. ^{1}H NMR spectrum of **4e** in $CDCl_3$ solution (400 MHz).

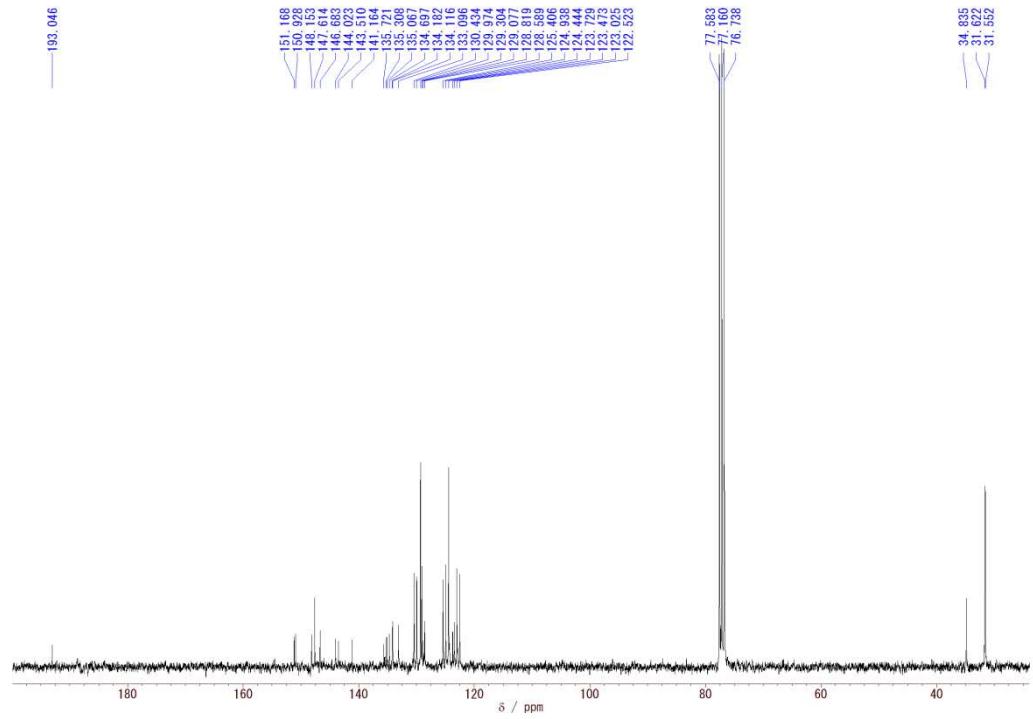

Figure S25. ^{13}C NMR spectrum of **4e** in $CDCl_3$ solution (75 MHz).

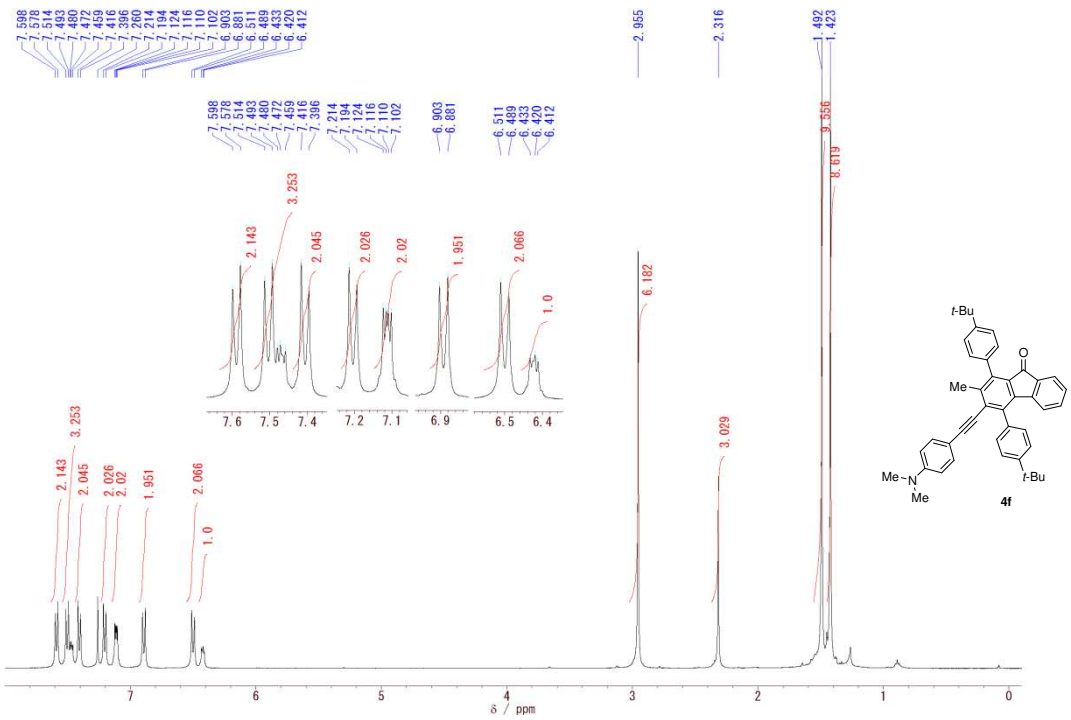

Figure S26. ^{1}H NMR spectrum of **4f** in $CDCl_3$ solution (400 MHz).

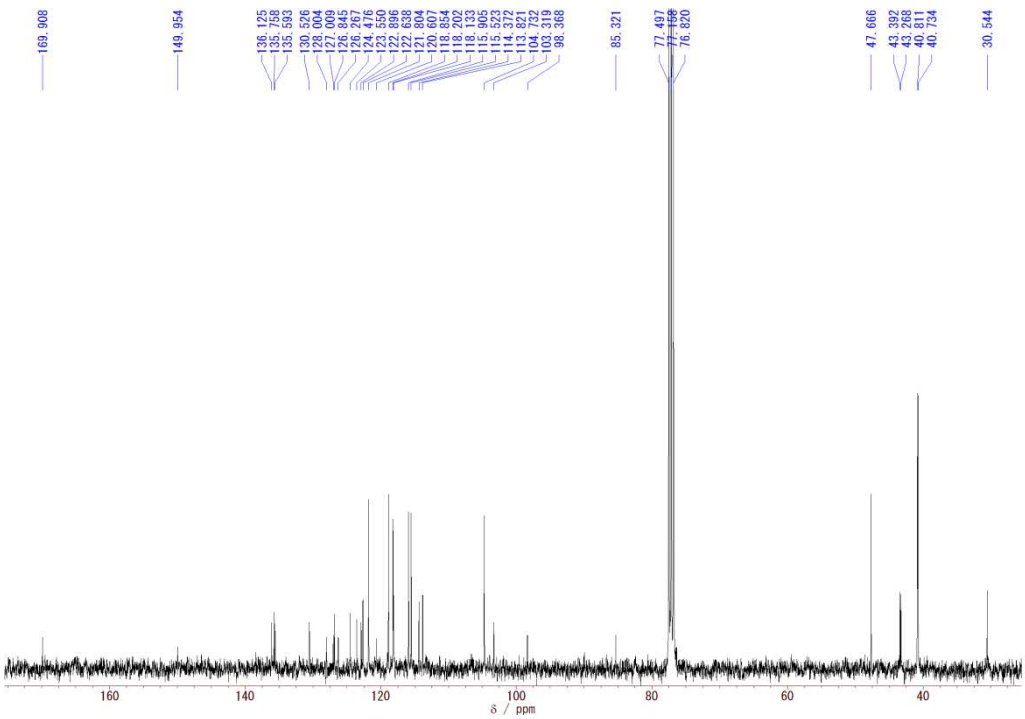

Figure S27. ^{13}C NMR spectrum of **4f** in $CDCl_3$ solution (75 MHz).

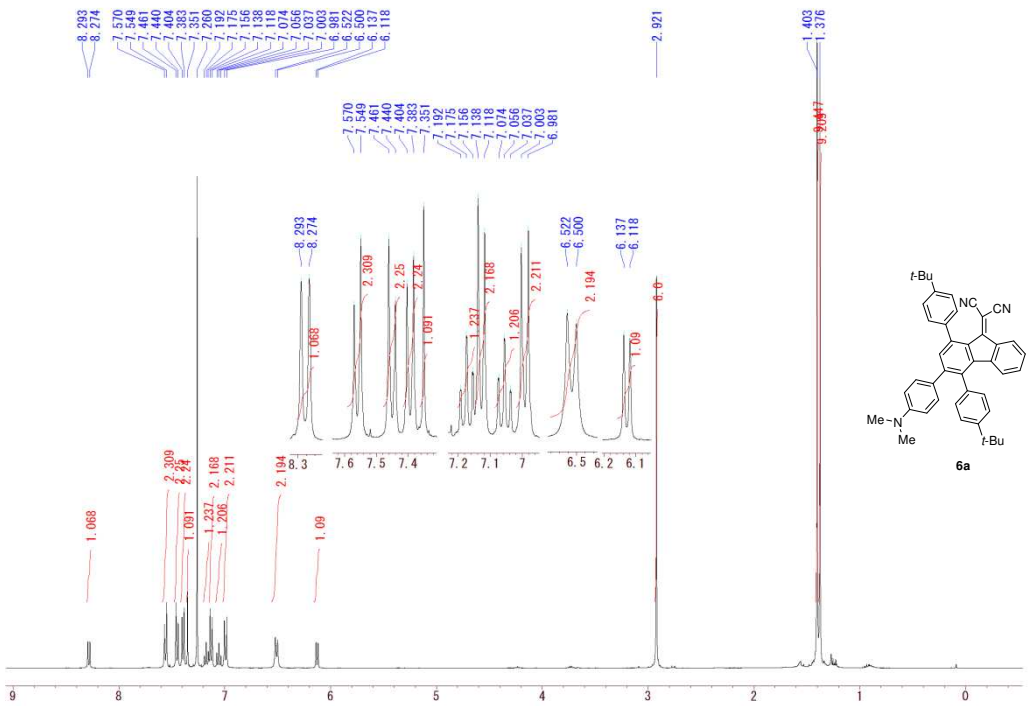

Figure S28. ^{1}H NMR spectrum of **6a** in $CDCl_3$ solution (400 MHz).

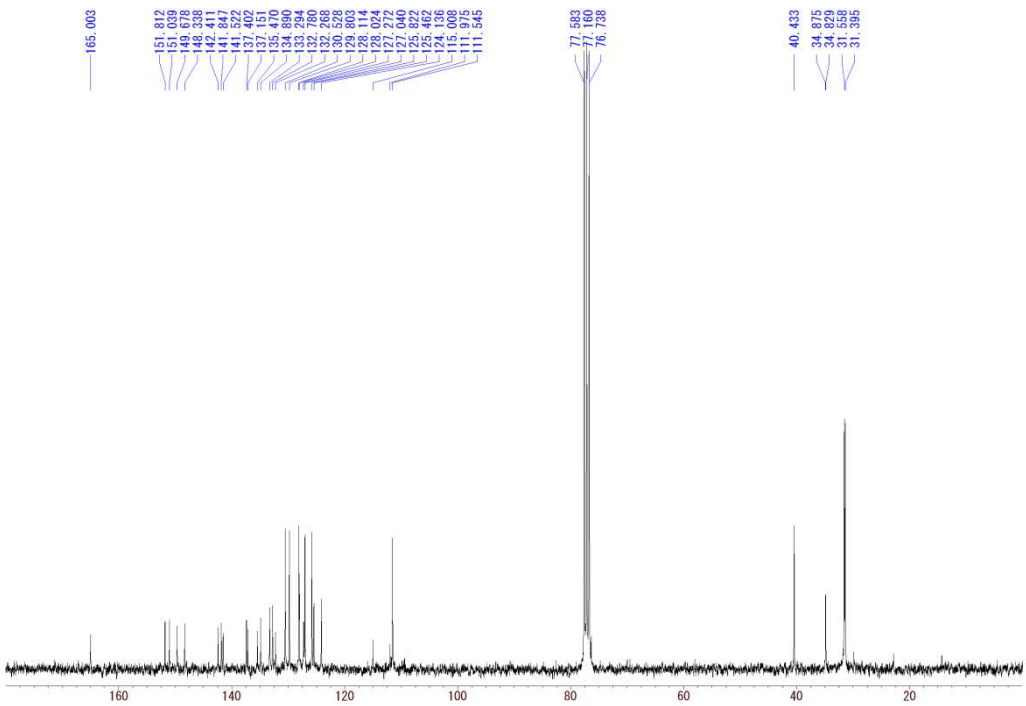

Figure S29. ^{13}C NMR spectrum of **6a** in $CDCl_3$ solution (75 MHz).

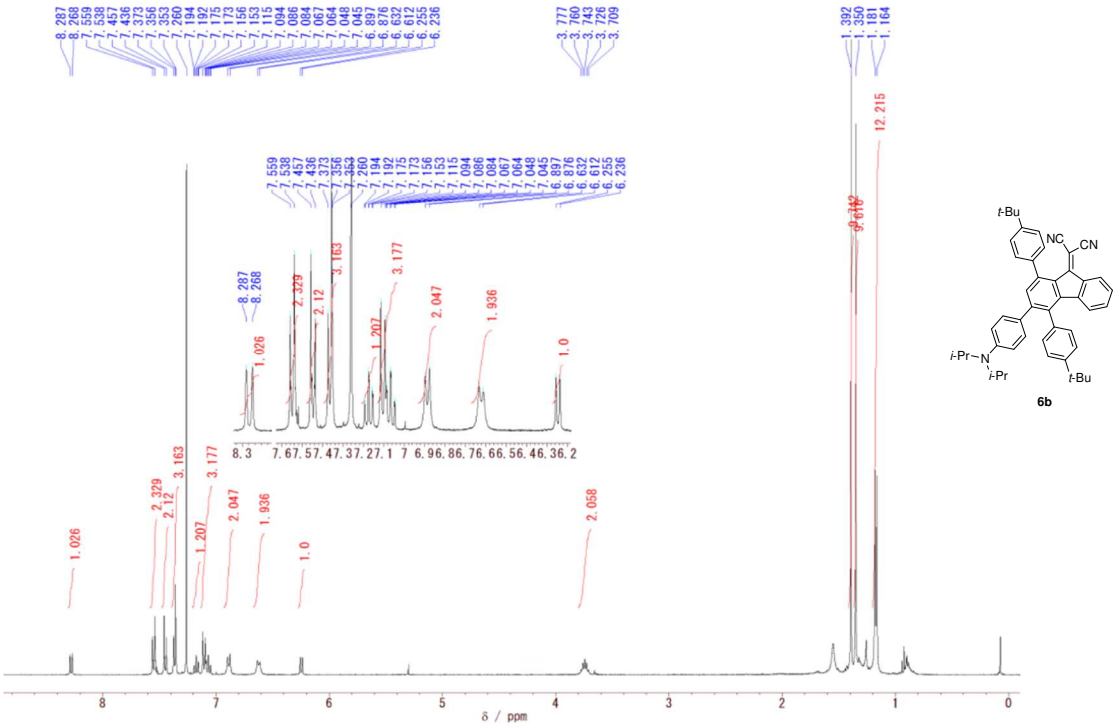

Figure S30. ^{1}H NMR spectrum of **6b** in $CDCl_3$ solution (600 MHz).

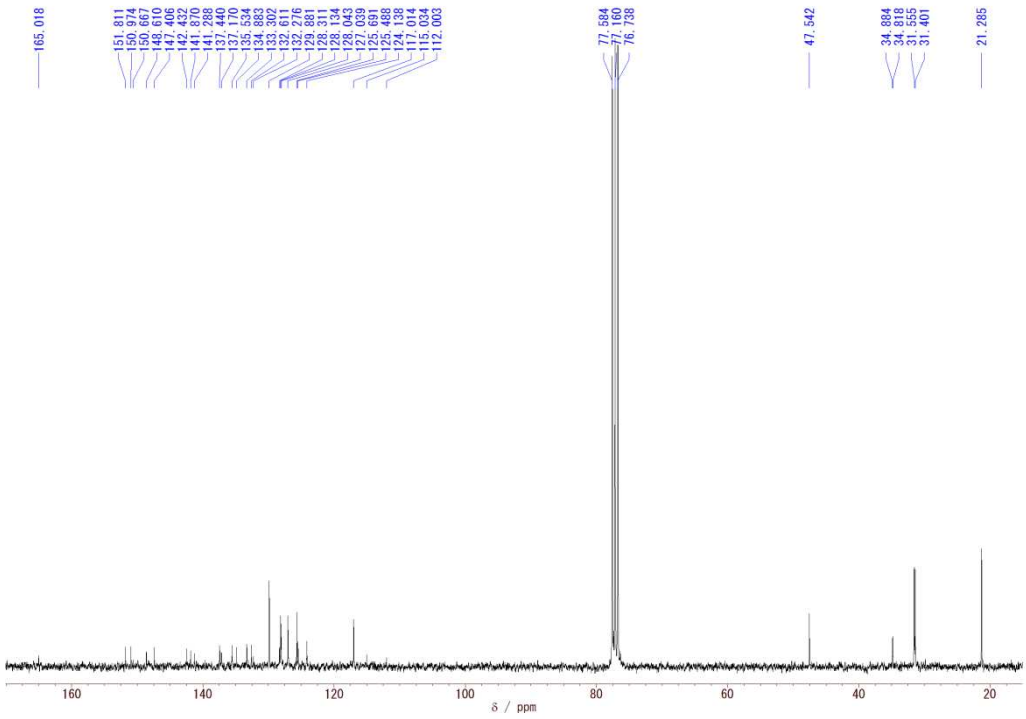

Figure S31. ^{13}C NMR spectrum of **6b** in $CDCl_3$ solution (75 MHz).

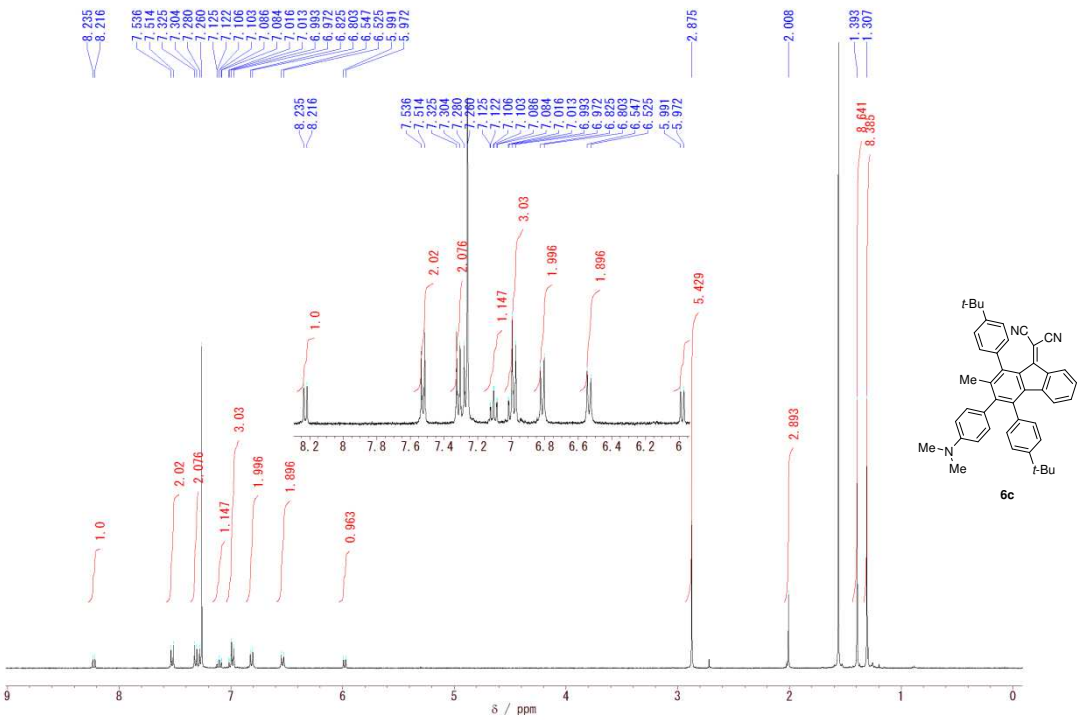

Figure S32. ^{1}H NMR spectrum of **6c** in $CDCl_3$ solution (400 MHz).

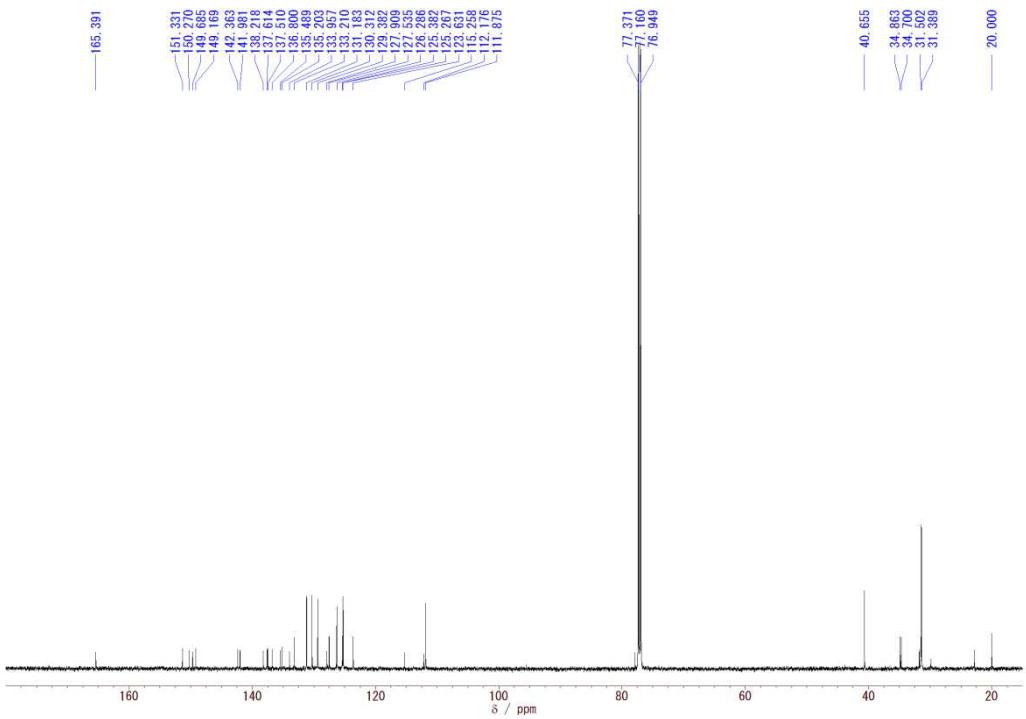

Figure S33. ^{13}C NMR spectrum of **6c** in $CDCl_3$ solution (75 MHz).

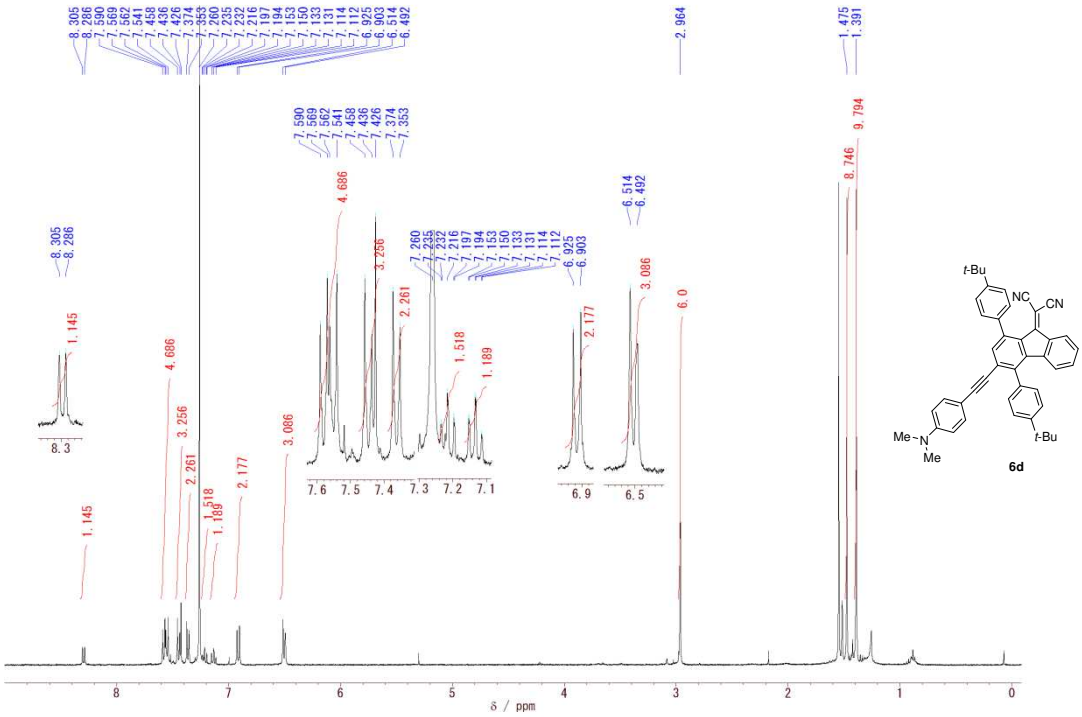

Figure S34. ^{1}H NMR spectrum of **6d** in $CDCl_3$ solution (400 MHz).

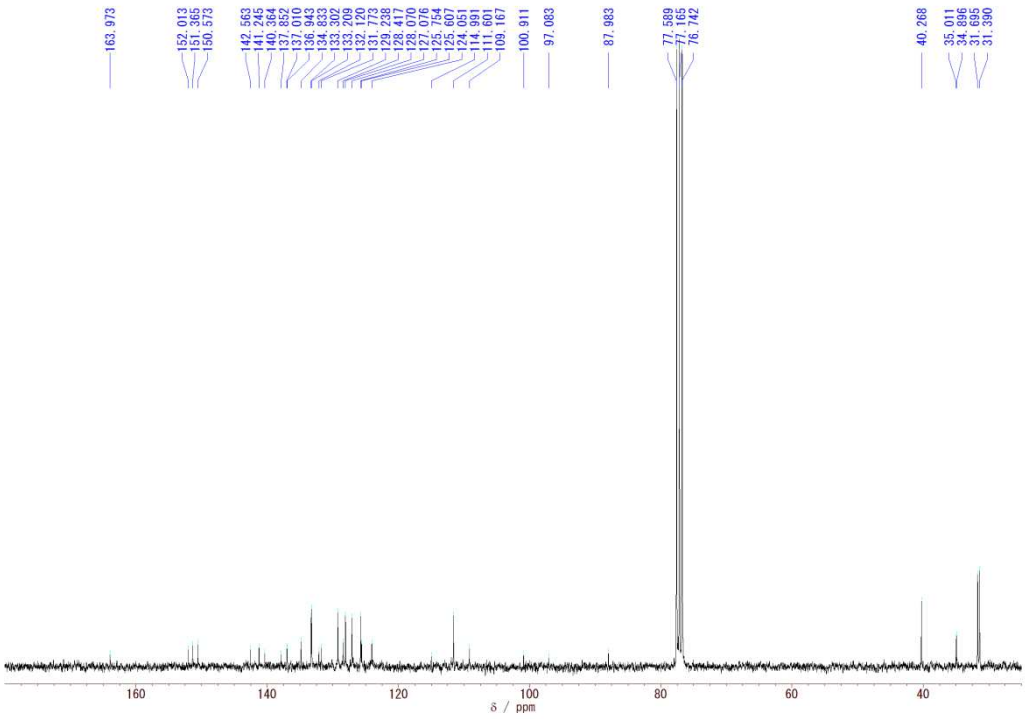

Figure S35. ^{13}C NMR spectrum of **6d** in $CDCl_3$ solution (75 MHz).

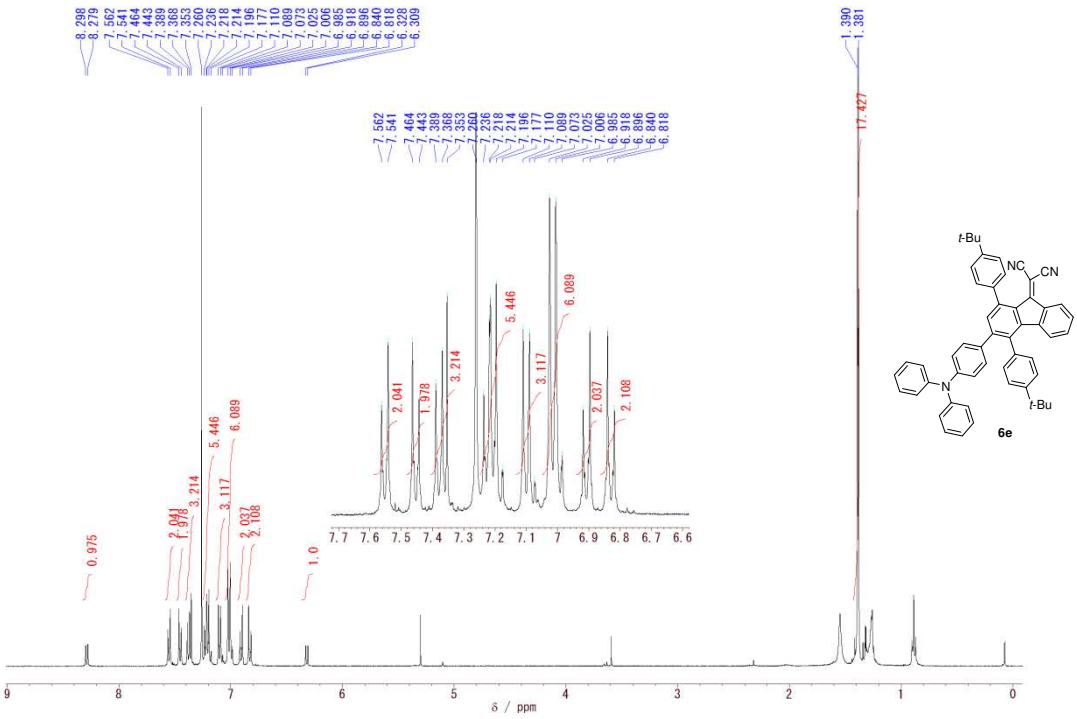

Figure S36. ^{1}H NMR spectrum of **6e** in $CDCl_3$ solution (400 MHz).

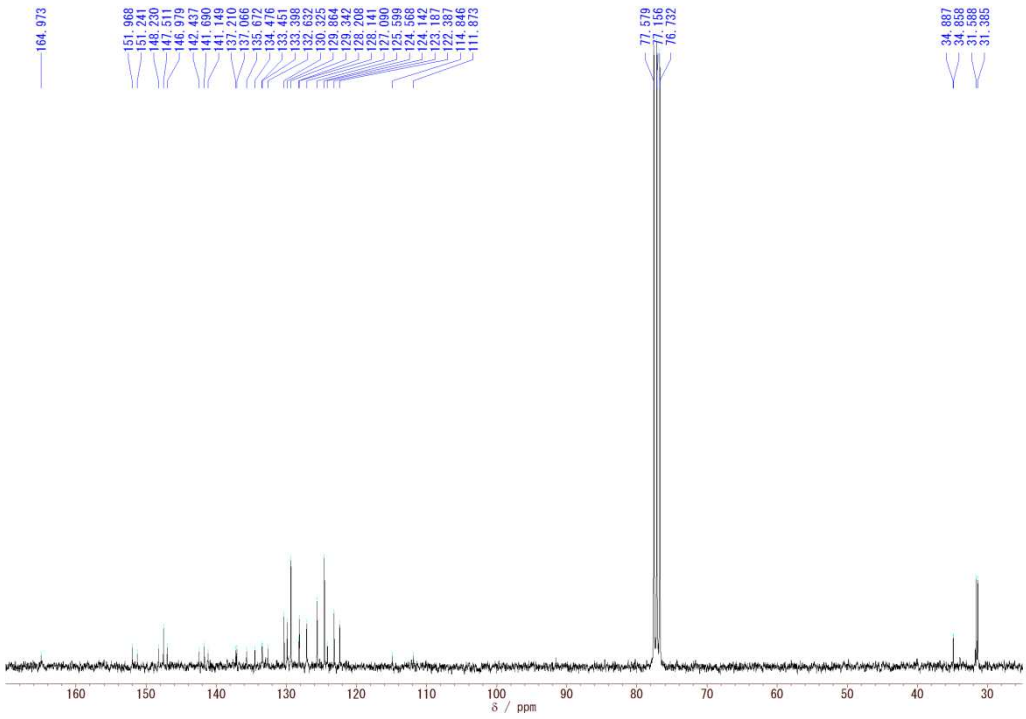

Figure S37. ^{13}C NMR spectrum of **6e** in $CDCl_3$ solution (75 MHz).

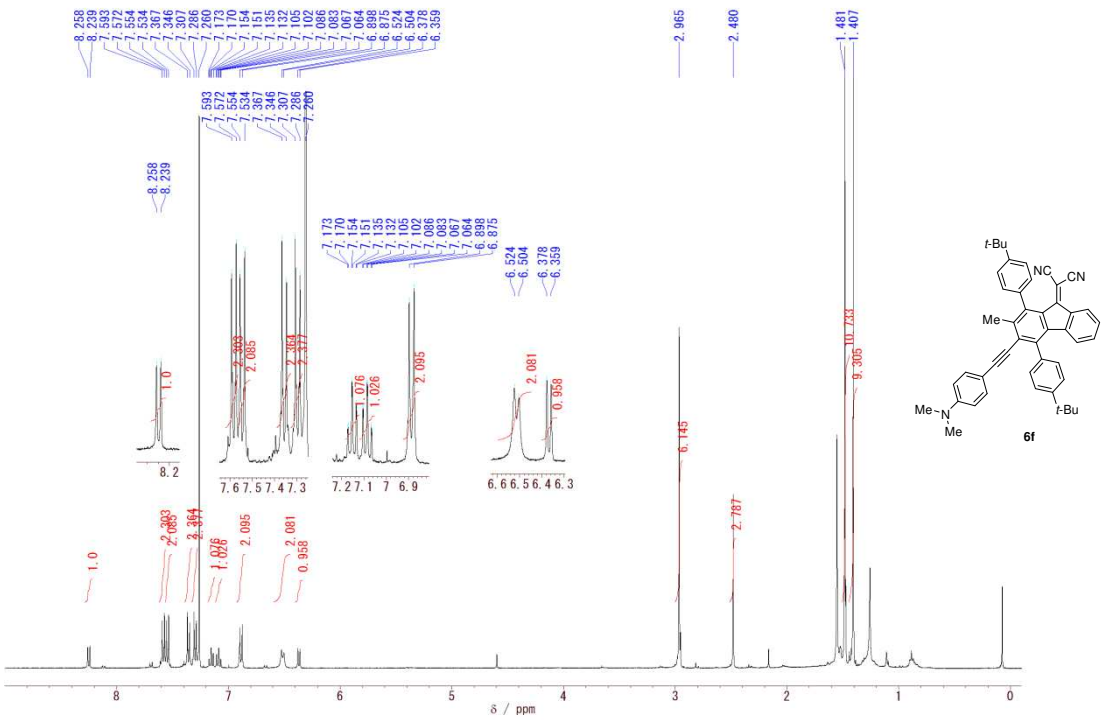

Figure S38. ^{1}H NMR spectrum of **6f** in $CDCl_3$ solution (400 MHz).

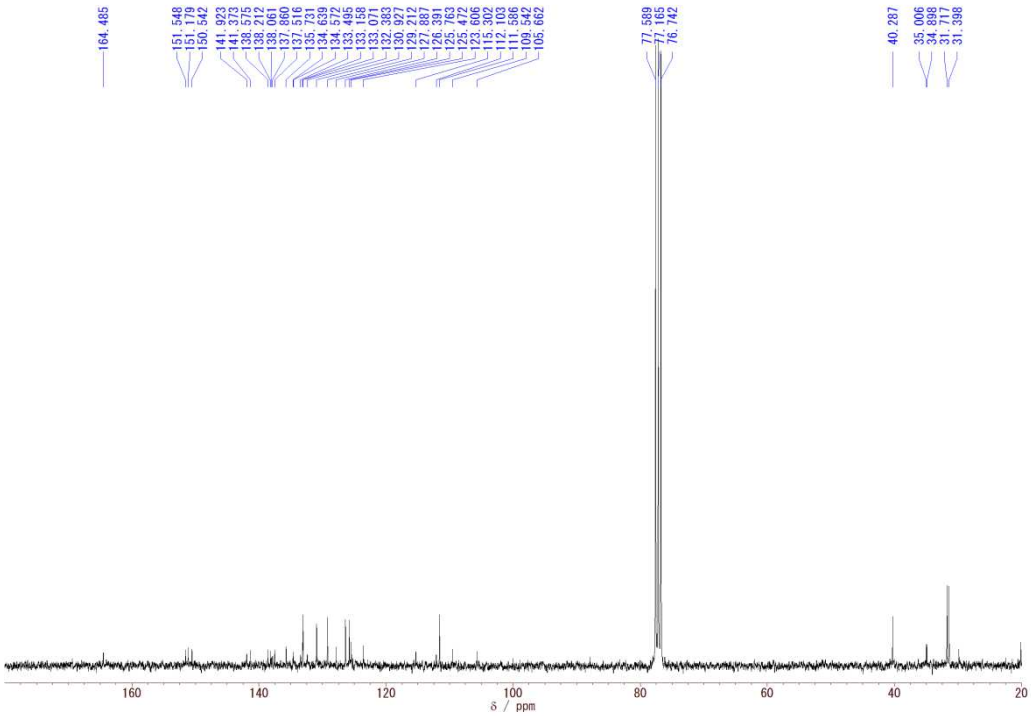

Figure S39. ^{13}C NMR spectrum of **6f** in $CDCl_3$ solution (75 MHz).

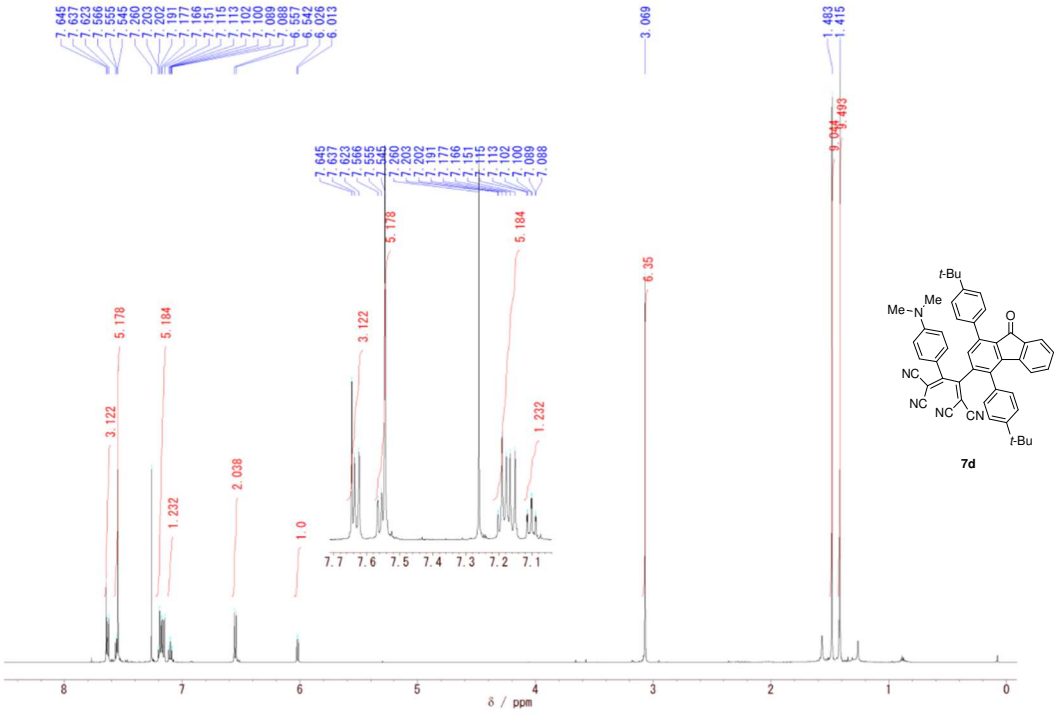

Figure S40. ^{1}H NMR spectrum of **7d** in $CDCl_3$ solution (600 MHz).

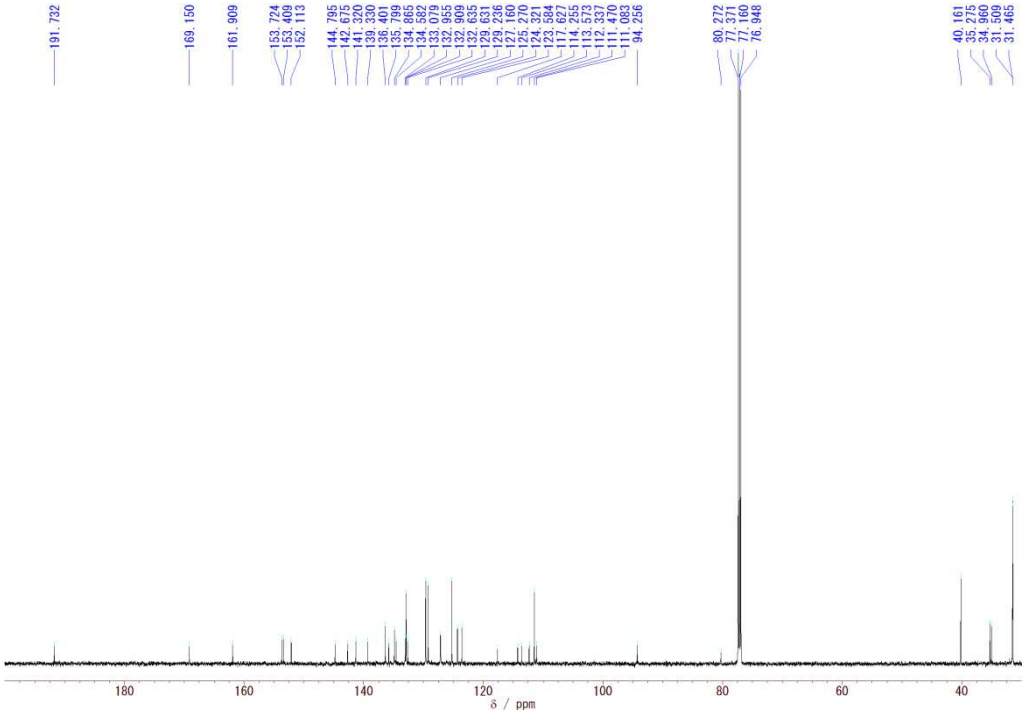

Figure S41. ^{13}C NMR spectrum of **7d** in $CDCl_3$ solution (150 MHz).

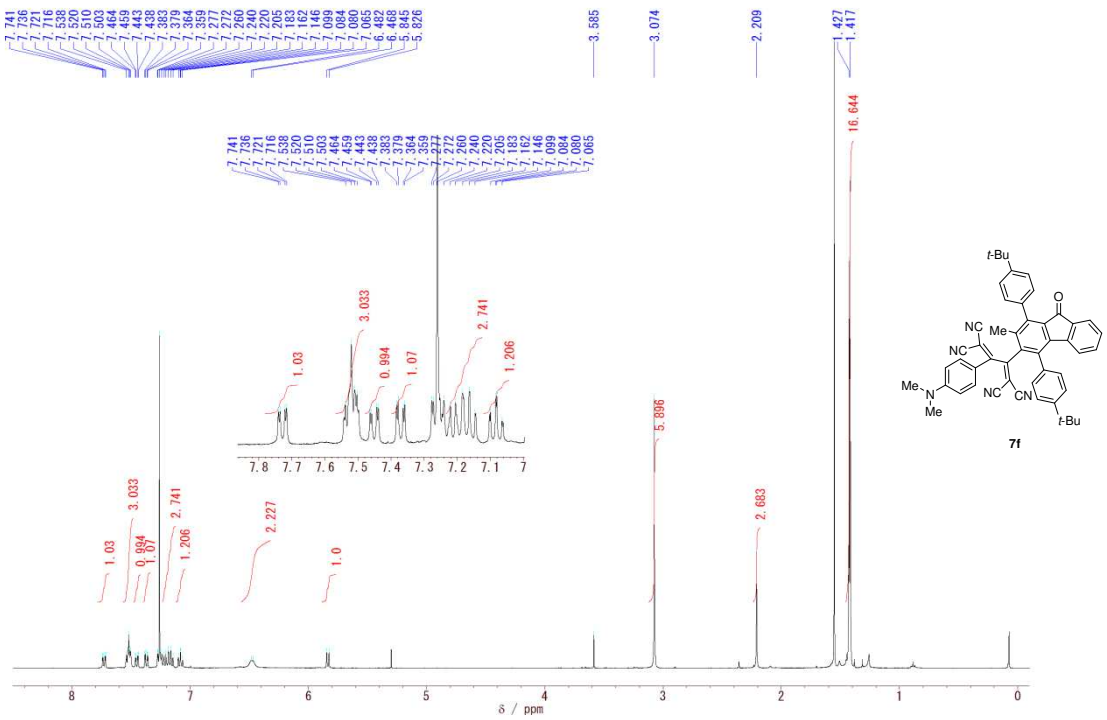

Figure S42. ^{1}H NMR spectrum of **7f** in $CDCl_3$ solution (400 MHz).

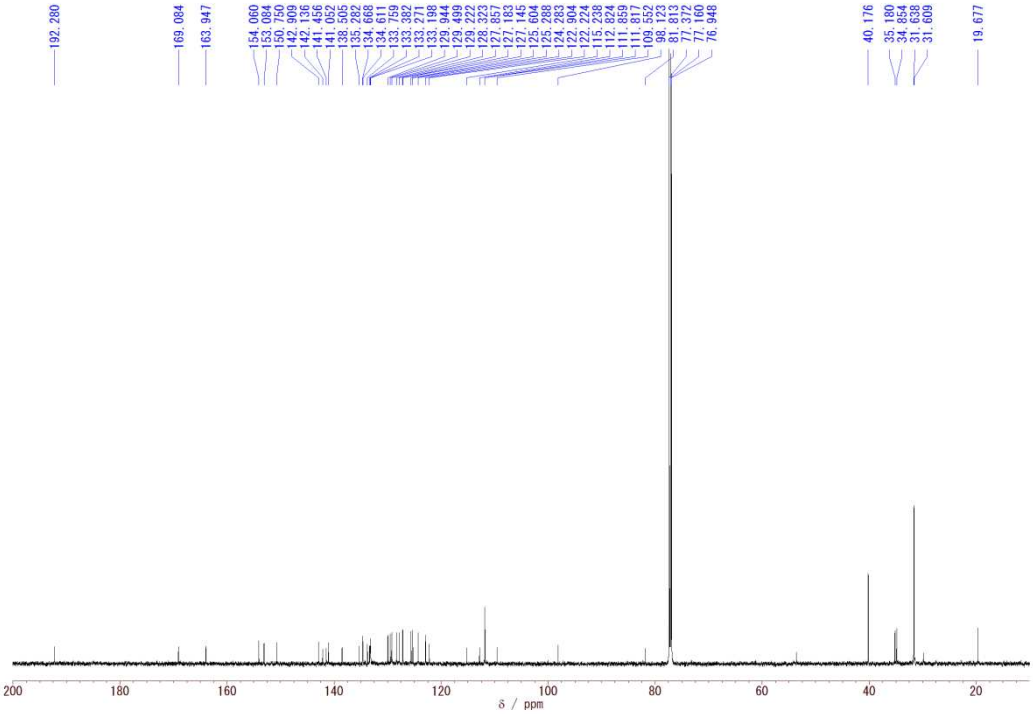

Figure S43. ^{13}C NMR spectrum of **7f** in $CDCl_3$ solution (75 MHz).

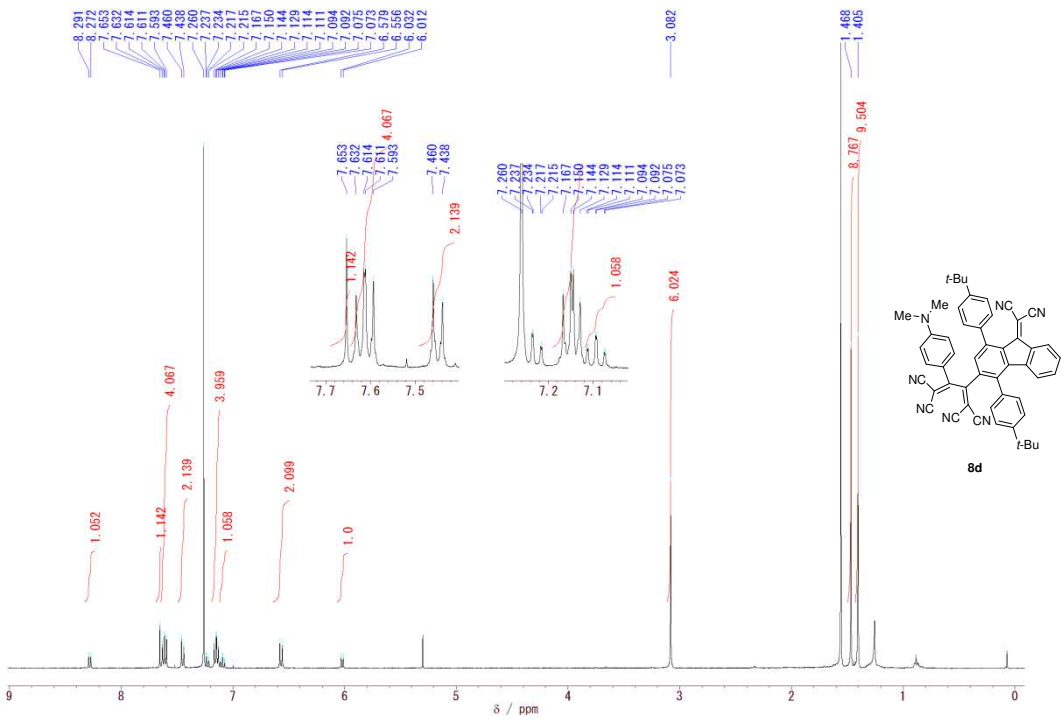

Figure S44. ^{1}H NMR spectrum of **8d** in $CDCl_3$ solution (400 MHz).

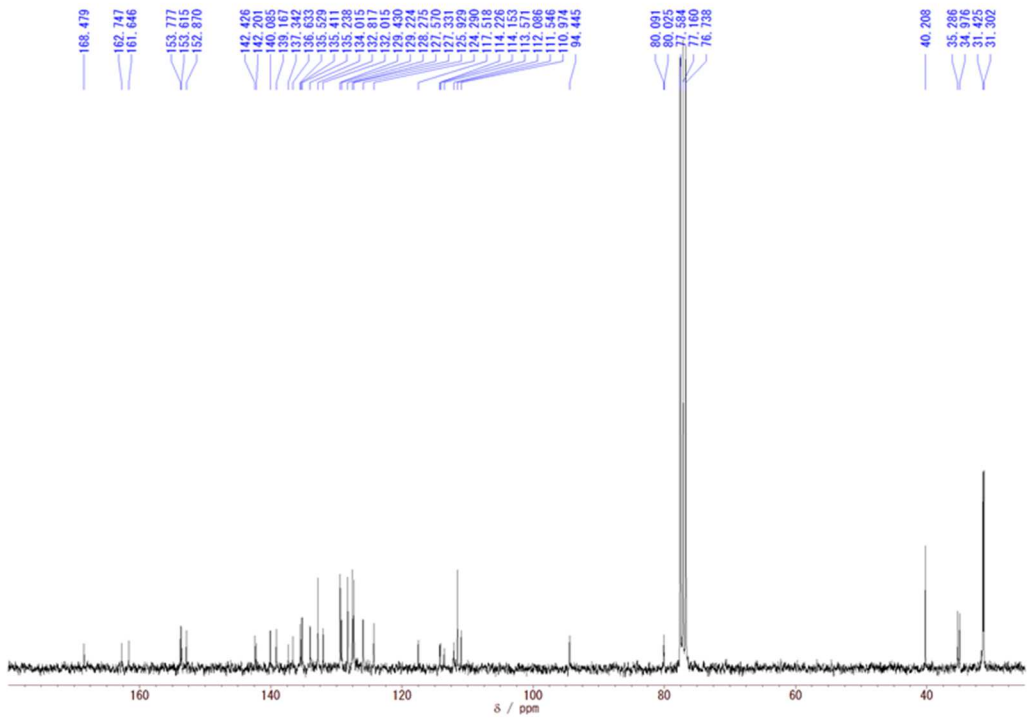

Figure S45. ^{13}C NMR spectrum of **8d** in $CDCl_3$ solution (75 MHz).

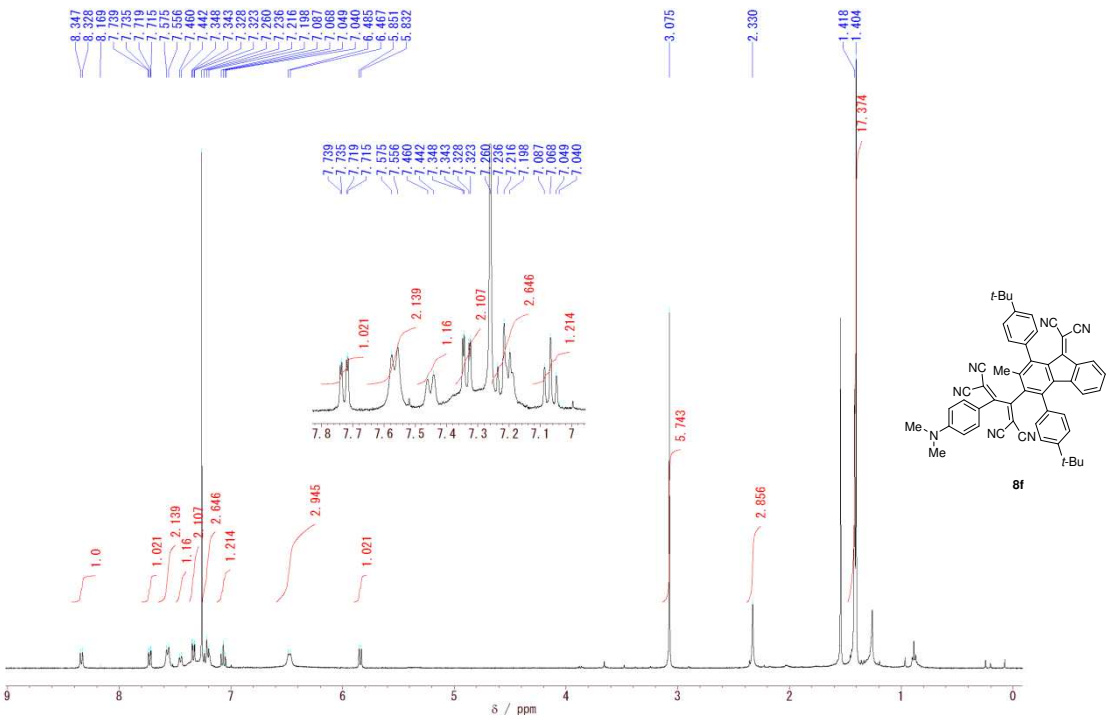

Figure S46. ^{1}H NMR spectrum of **8f** in $CDCl_3$ solution (400 MHz).

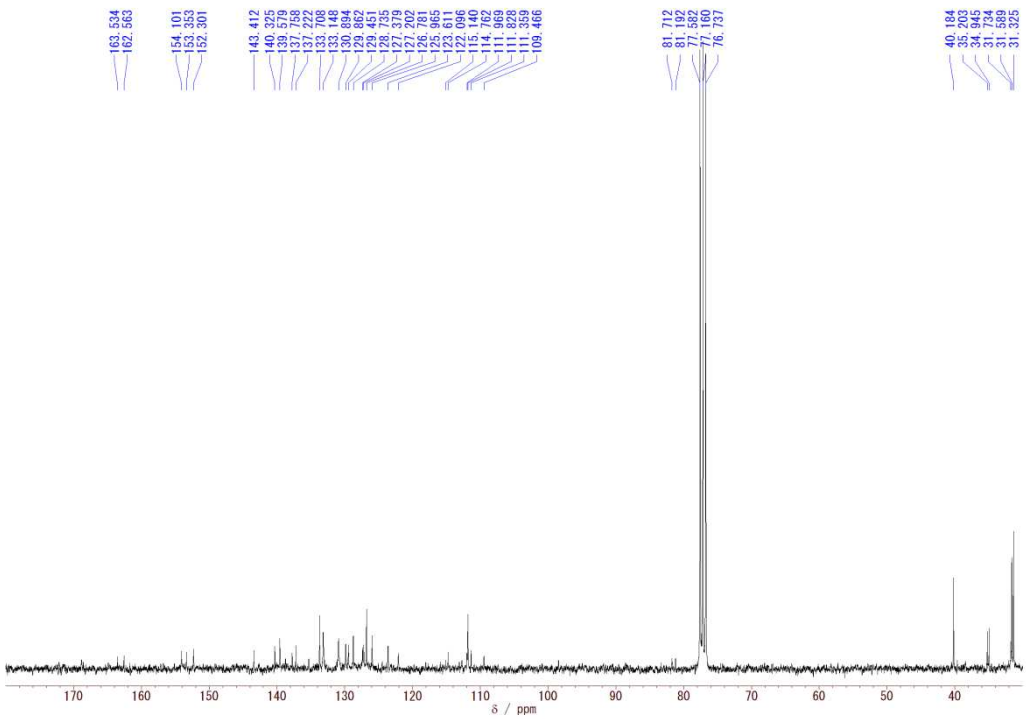

Figure S47. ^{13}C NMR spectrum of **8f** in $CDCl_3$ solution (75 MHz).

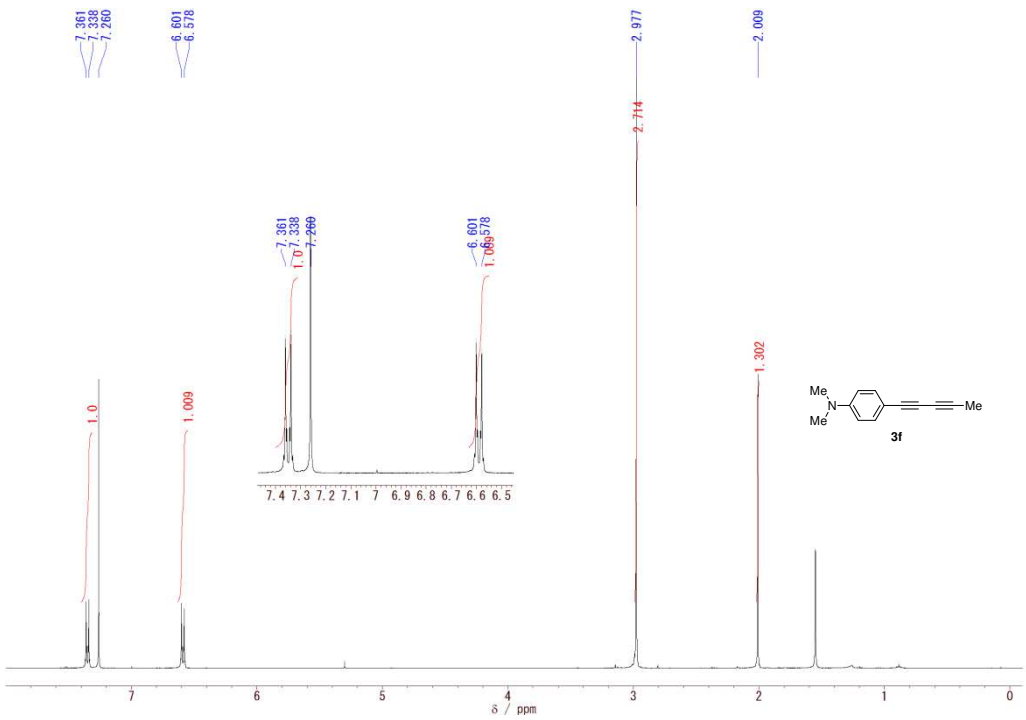

Figure S48. ^{1}H NMR spectrum of **3f** in $CDCl_3$ solution (400 MHz).

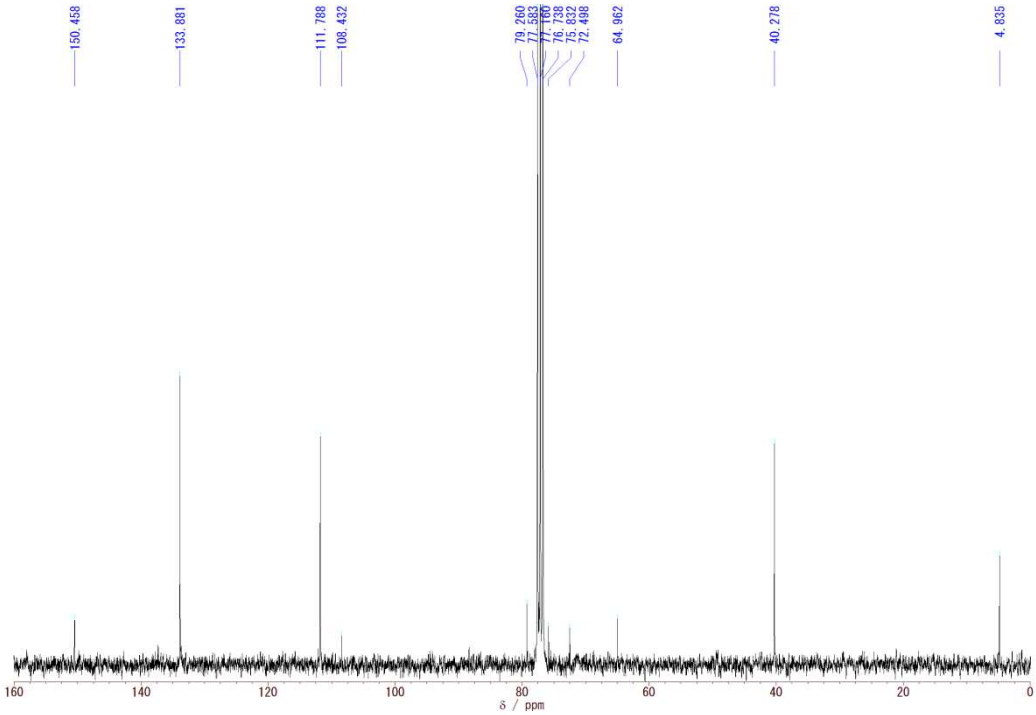

Figure S49. ^{13}C NMR spectrum of **3f** in $CDCl_3$ solution (75 MHz).

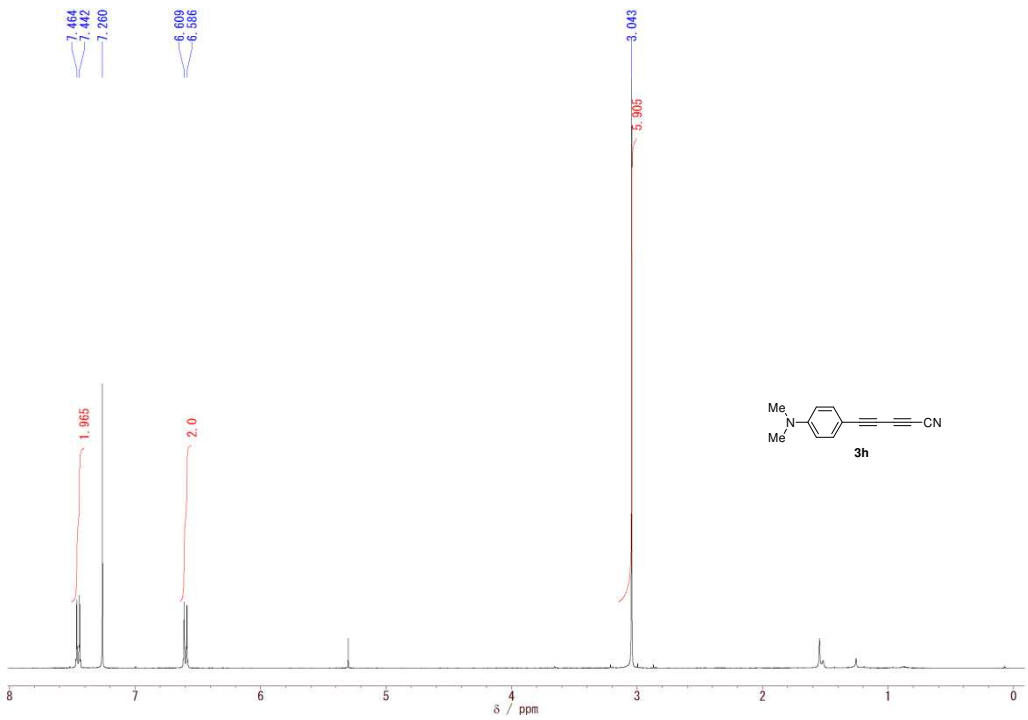

Figure S50. ^{1}H NMR spectrum of **3h** in $CDCl_3$ solution (400 MHz).

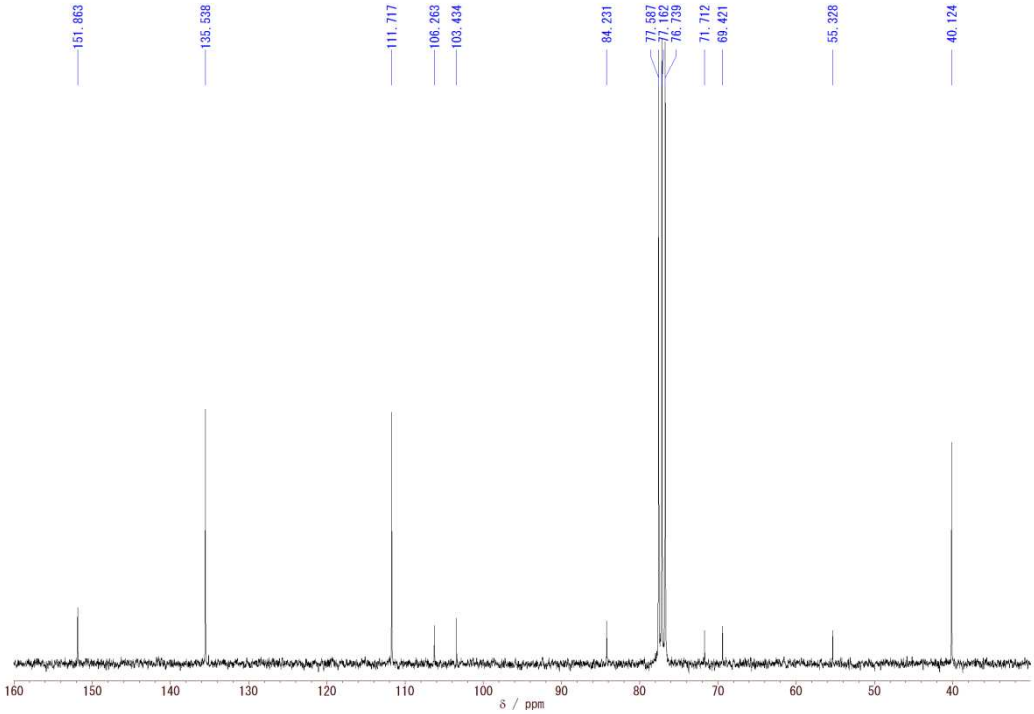

Figure S51. ^{13}C NMR spectrum of **3h** in $CDCl_3$ solution (75 MHz).

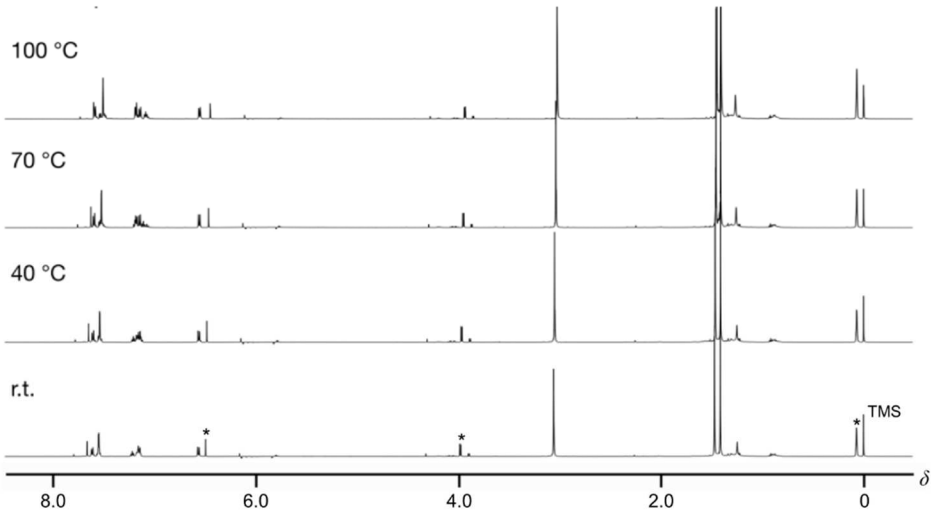

Figure S52. Variable-temperature No-D NMR spectra of **7d**. Conditions: 600 MHz, 1,1,2,2-tetrachloroethane. Asterisk: Impurity included in solvent.

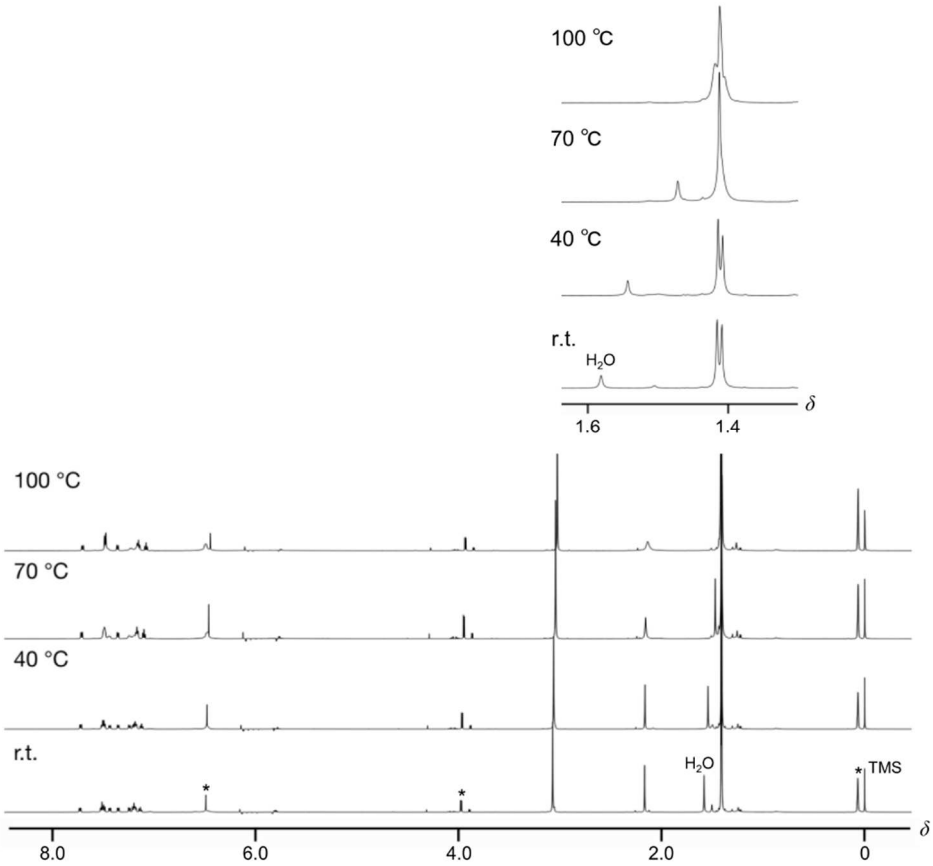

Figure S53. Variable-temperature No-D NMR spectra of **7f**. Conditions: 600 MHz, 1,1,2,2-tetrachloroethane. Asterisk: Impurity included in solvent.

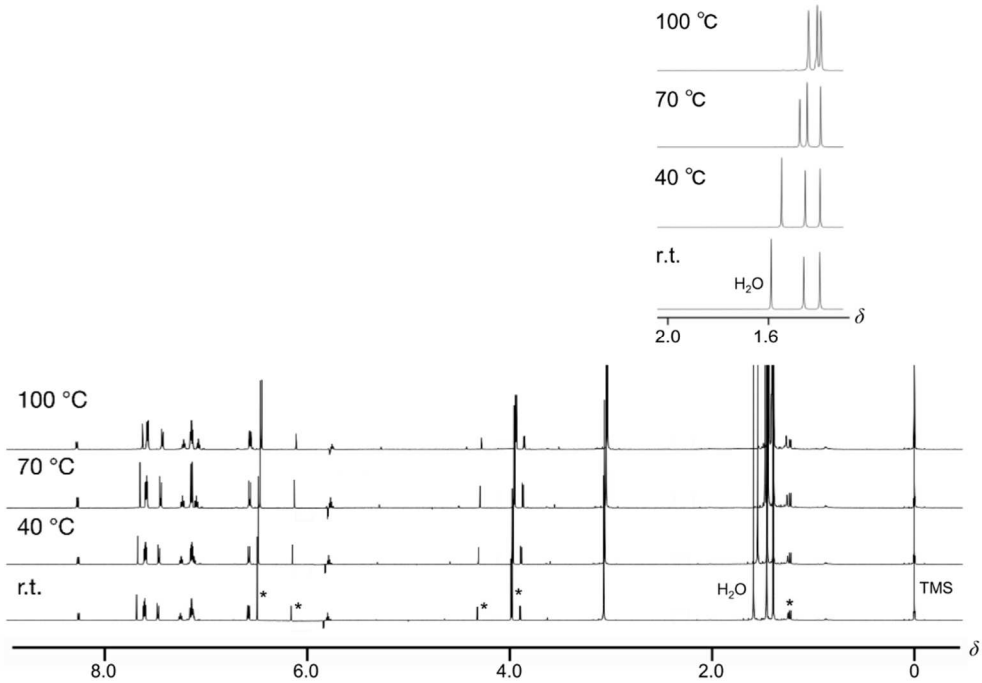

Figure S54. Variable-temperature No-D NMR spectra of **8d**. Conditions: 600 MHz, 1,1,2,2-tetrachloroethane. Asterisk: Impurity included in solvent.

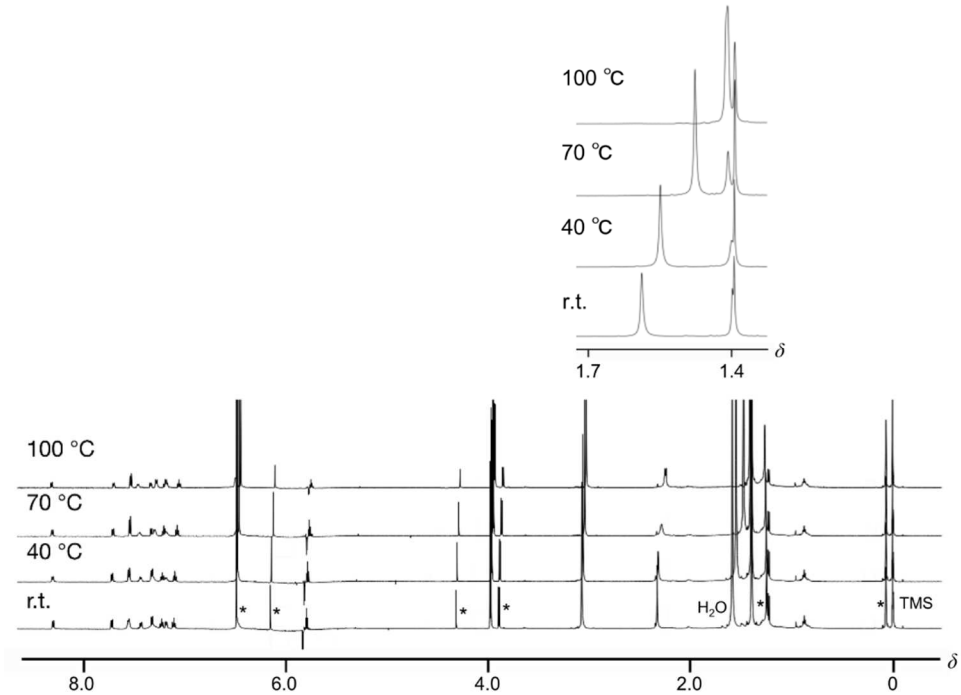

Figure S55. Variable-temperature No-D NMR spectra of **8f**. Conditions: 600 MHz, 1,1,2,2-tetrachloroethane. Asterisk: Impurity included in solvent.

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