Supporting Information

Bistricyclic aromatic enes with fast conformational transition for ultrathin piezochromic film

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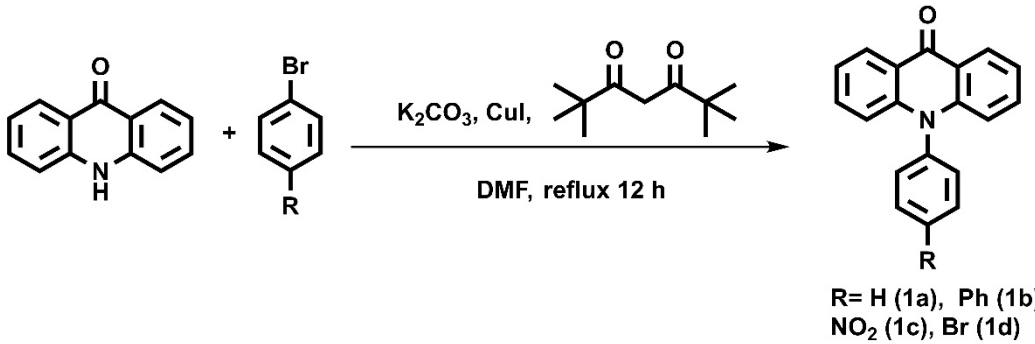
Experimental Section

General information

All commercially available reagents were used as received without further purification.

^{1}H NMR spectra were recorded at 600 MHz using a Bruker 600 MHz spectrometer. ^{13}C spectra were respectively recorded at 600 MHz on a Bruker 600 MHz system. Mass spectra were obtained using a Thermo Fisher LTQ XL and a Thermo Fisher Q Exactive. The PXRD spectra were recorded on Rigaku Miniflex600. XtaLAB Synergy Custom was used for the single crystal X-ray diffractometer. The parylene C coating is plated on the substrate using an mq-parylene MQP-3001. The thickness was measured using a JS10A step meter. Film surface folds were imaged using a 3D microscope (Olympus DSX10-SZH). The BFA_c coating was prepared using the airbrushing technique. UV absorption spectra were obtained with Shimadzu UV-3600. Fluorescence spectra were obtained with an Edinburgh FLS980. Electron microscope HITACHI SU8010 obtained the film cross sections.

General procedures for the synthesis of 10-(4-substituted-phenyl)acridin-9(10*H*)-one



Scheme S1: 1-bromo(4-substituted)benzenes (1.5 eq.), acridin-9(10*H*)-one (acridone, 1 eq.), K_2CO_3 (2 eq.), CuI (0.1 eq.), 2,2,6,6- tetramethyl-3,5-heptane-dione (0.2 eq.) were dissolved in anhydrous DMF (6 mL/mmol of acridone) into a round-bottom flask. The mixture was degassed and refluxed under a nitrogen atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was evaporated by a high-boiling-point rotary evaporator. Then, the crude product was purified by flash chromatography on silica gel. The chromatographic purification (eluent: dichloromethane/petroleum ether = 2:1) provided compound N-aryl acridone (Ca. 80% yield). TLC: R_f = 0.5 in dichloromethane: petroleum ether (2:1).

Synthesis of 1a

Acridone (1.00 g, 5.13 mmol) and bromobenzene (812 µL, 7.69 mmol) were synthesized according to the above scheme to give compound **1a** (1.15 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.74 – 7.63 (m, 3H), 7.50 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 2H), 7.37 (dd, *J* = 7.2, 1.7 Hz, 2H), 7.30 – 7.25 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H).

Synthesis of 1b

Acridone (1.00 g, 5.13 mmol) and 4-bromobiphenyl (1.79 g, 7.69 mmol) were synthesized according to the above scheme to give compound **1b** (1.56 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.0 Hz, 2H), 7.92 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.57 – 7.50 (m, 4H), 7.48 – 7.42 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H).

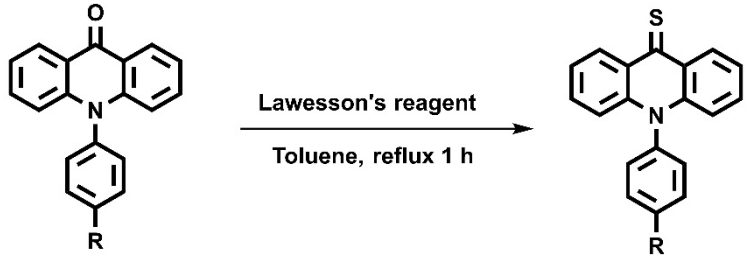
Synthesis of 1c

Acridone (1.00 g, 5.13 mmol) and p-nitro bromobenzene (1.55 g, 7.69 mmol) were synthesized according to the above scheme to give compound **1c** (1.18 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 7.9, 2.0 Hz, 4H), 7.63 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.53 (ddt, *J* = 8.7, 7.0, 1.8 Hz, 2H), 7.35 – 7.29 (m, 2H), 6.65 (dd, *J* = 8.6, 1.9 Hz, 2H).

Synthesis of 1d

Acridone (1.00 g, 5.13 mmol) and p-bromobenzene (1.81 g, 7.69 mmol) were synthesized according to the above scheme to give compound **1d** (1.36 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dq, *J* = 8.0, 2.0 Hz, 4H), 7.64 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.53 (ddt, *J* = 8.7, 7.0, 1.8 Hz, 2H), 7.37 – 7.29 (m, 2H), 6.66 (dd, *J* = 8.5, 1.9 Hz, 2H).

General procedures for the synthesis of 10-(4-substituted-phenyl)acridine-9(10*H*)-thione



Scheme S2: In a round-bottom flask, 10-arylacridin-9(10*H*)-one (1 eq.) and Lawesson's reagent (1 eq.) were stirred and heated up to reflux under a nitrogen atmosphere for 1 h in a round-bottom flask. After evaporating, a sticky brown crude product was obtained to purify silica gel column chromatography. The chromatographic purification (dichloromethane: petroleum ether = 1:1) provided the compound thioacridone (Ca. 83% yield). TLC: R_f = 0.5 in dichloromethane: petroleum ether (1:1).

Synthesis of 2a

1a (1.70 g, 6.27 mmol) and Lawesson's reagent (1.52 g, 3.76 mmol) were synthesized according to the protocol described above to give compound **2a** (0.67 g, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.76 – 7.66 (m, 3H), 7.53 (ddd, *J* = 8.6, 6.8, 1.6 Hz, 2H), 7.40 – 7.30 (m, 4H), 6.81 (dd, *J* = 8.6, 1.1 Hz, 2H).

Synthesis of 2b

1b (0.60 g, 2.88 mmol) and Lawesson's reagent (0.42 g, 1.04 mmol) were synthesized according to the protocol described above to give compound **2b** (0.35g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.97 – 7.91 (m, 2H), 7.77 – 7.71 (m, 2H), 7.56 (dddd, *J* = 9.7, 7.9, 6.6, 1.6 Hz, 4H), 7.49 – 7.42 (m, 3H), 7.36 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 2H), 6.93 (dd, *J* = 8.7, 1.1 Hz, 2H).

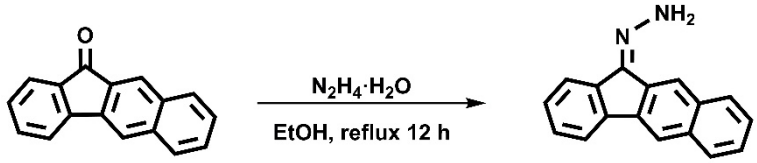
Synthesis of 2c

1c (4.14 g, 13.10 mmol) and Lawesson's reagent (0.42 g, 1.04 mmol) were synthesized according to the protocol described above to give compound **2c** (1.34 g, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 8.3, 1.6 Hz, 2H), 8.64 – 8.59 (m, 2H), 7.65 – 7.61 (m, 2H), 7.56 (ddd, *J* = 8.6, 6.9, 1.6 Hz, 2H), 7.37 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 2H), 6.71 – 6.66 (m, 2H).

Synthesis of 2d

1d (0.30 g, 1.72 mmol) and Lawesson's reagent (0.21 g, 0.52 mmol) were synthesized according to the protocol described above to give compound **2d** (0.13 g, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (t, *J* = 9.6 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.74 (dt, *J* = 12.4, 7.0 Hz, 1H), 7.57 (q, *J* = 7.4 Hz, 2H), 7.43 – 7.28 (m, 4H), 6.83 (dd, *J* = 8.8, 5.1 Hz, 2H)

Synthesis of (11*H*-benzo[*b*]fluoren-11-ylidene)hydrazine



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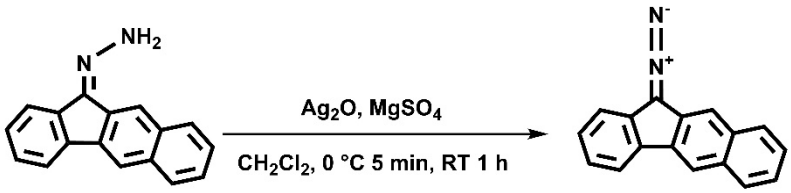
Scheme S3: 11*H*-benzo[*b*]fluoren-11-one (2.50 g, 10.87 mmol) and hydrazine monohydrate (4.21 mL, ca. 8 eq.) were dissolved in ethanol (110 mL). The reaction mixture was degassed, refluxed, and stirred for 9 h. After cooling the solution to room temperature, the solvent was evaporated to obtain light orange solids (2.30 g, ca. 87% yield) pure enough for the following reaction without further processing.

Synthesis of 11-diazo-11*H*-benzo[*b*]fluorene

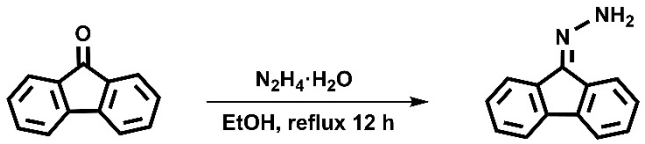


3 4

Scheme S4: (11*H*-benzo[*b*]fluoren-11-ylidene)hydrazine (2.30 g, 9.42 mmol) and an excess amount of magnesium sulfate (1.70 g, 14.13 mmol) were put in a round-bottom flask. Dichloromethane (96 mL) was added to the flask and cooled to 0 °C with an ice bath. After adding silver oxide (1.1 eq.), it was stirred for 5 min, warmed to room temperature, and stirred for 1 h. The filtrate was evaporated for the next reaction without further purification (2.26 g, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s,

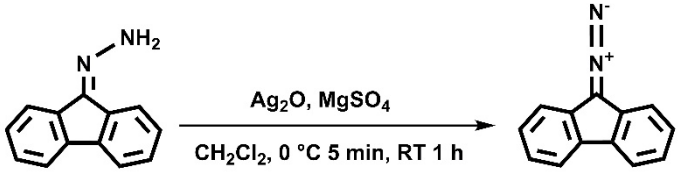
1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.47 (tdd, *J* = 11.9, 7.4, 2.9 Hz, 4H), 7.39 – 7.34 (m, 1H).

Synthesis of (9*H*-fluorene-9-ylidene)hydrazine



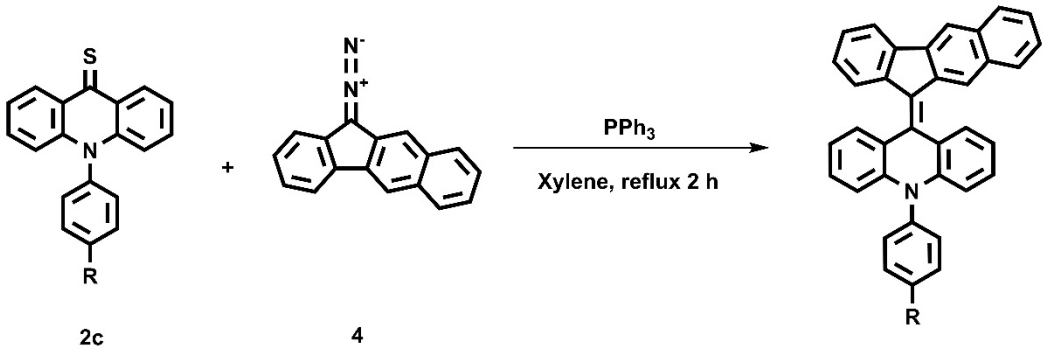
Scheme S5: 9*H*-fluoren-9-one (1.00 g, 5.56 mmol) and hydrazine monohydrate (2.15 mL, ca. 8 eq.) were dissolved in ethanol (55 mL). The reaction mixture was degassed, refluxed, and stirred for 12 h. After cooling the solution to room temperature, the solvent was evaporated to obtain pale yellow solids (ca. 99% yield) pure enough to be used for the next reaction without further processing.

Synthesis of (9*H*-fluorene-9-ylidene)hydrazine



Scheme S6: (9*H*-fluoren-9-ylidene)hydrazine (1.00 g, 5.15 mmol) and an excess amount of magnesium sulfate (0.93 g, 7.73 mmol) were put in a round-bottom flask. Dichloromethane (44 mL) was added to the flask and cooled to 0 °C with an ice bath. After silver oxide (1.1 eq.) was added and stirred for 5 min, it was warmed to room temperature and stirred for 1 h. The filtrate was evaporated for the following reaction without further purification (ca. 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H).

General procedures for the synthesis of 9-(11*H*-benzo[*b*]fluoren-11-ylidene)-10-(4-substituted-phenyl)-9,10-dihydroacridine



Scheme S7: Into a round-bottom flask, 10-(4-arylphenyl)acridine-9(10*H*)-thione (1 eq.), triphenylphosphine (PPh_3, 2 eq.) and 11-diazo-11*H*-benzo[*b*]fluorine(2 eq.) were added to the mixed xylene solution(1 mL anhydrous xylene/0.25 mmol of thiones). We filled the whole unit with N_2 at room

temperature. The mixture was degassed and refluxed for 4 h. After removing the solvent by reduced pressure distillation, the target product was separated by a chromatographic column (Petroleum ether/ethyl acetate: 30/1).

Synthesis of BFA_a

Thione derivatives **2a** (0.05 g, 0.17 mmol), PPh_3 (0.09 g, 0.34 mmol), and **4** (0.08 g, 0.34 mmol) were added to a round-bottom flask and dissolved with 2 mL xylene. The crude product was separated and purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to obtain BFA_a (0.01g, 12% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.24 (s, 1H), 8.18 (s, 1H), 7.99 (d, J = 3.4 Hz, 1H), 7.94 (dd, J = 7.8, 4.3 Hz, 2H), 7.89 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 6.6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.55 (s, 1H), 7.49 (dd, J = 10.6, 7.3 Hz, 3H), 7.40 (d, J = 7.4 Hz, 3H), 7.32 (t, J = 7.3 Hz, 2H), 7.20 (q, J = 7.5 Hz, 5H). HR ESI MS of BFA_a. m/z = 469.18271.

Synthesis of BFA_b

Thione derivatives **2b** (0.05 g, 0.14 mmol), PPh_3 (0.09 g, 0.28 mmol), and **4** (0.08 g, 0.28 mmol) were added to a round-bottom flask and dissolved with 2 mL xylene. The crude product was separated and purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to obtain BFA_b (0.01g, 13% yield). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.10 (d, J = 7.9 Hz, 3H), 7.89 – 7.86 (m, 3H), 7.67 – 7.63 (m, 4H), 7.57 (t, J = 7.7 Hz, 4H), 7.47 (dd, J = 8.5, 6.6 Hz, 3H), 7.36 (t, J = 7.9 Hz, 4H), 7.10 (s, 3H), 6.83 (d, J = 8.5 Hz, 3H). HR ESI MS of BFA_b. m/z = 545.2138.

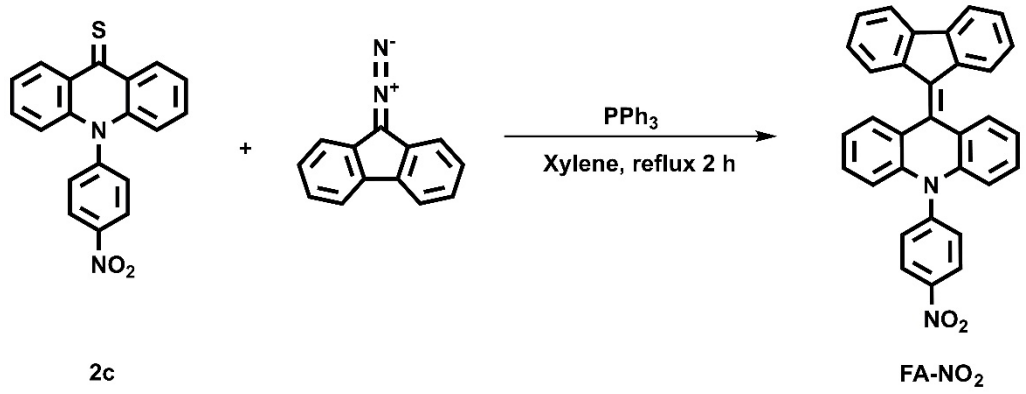
Synthesis of BFA_c

Thione derivatives **2c** (0.05 g, 0.15 mmol), PPh_3 (0.08 g, 0.30 mmol), and **4** (0.07 g, 0.30 mmol) were added to a round-bottom flask and dissolved with 2 mL xylene. The crude product was separated and purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to obtain BFA_c (0.01g, 13% yield). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.45 – 8.42 (m, 2H), 8.33 (s, 1H), 8.29 (s, 1H), 8.26 (d, J = 7.9 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.82 – 7.78 (m, 3H), 7.60 (d, J = 8.1 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.37 (m, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.20 (d, J = 8.3 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H). HR ESI MS of BFA_c. m/z = 514.1676.

Synthesis of BFA_d

Thione derivatives **2d** (0.05 g, 0.14 mmol), PPh_3 (0.07 g, 0.28 mmol), and **4** (0.07 g, 0.28 mmol) were added to a round-bottom flask and dissolved with 2 mL xylene. The crude product was separated and purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to obtain **BFA_d** (0.01g, 13% yield). ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.38 (s, 2H), 8.24 – 8.20 (m, 2H), 8.05 – 8.01 (m, 4H), 7.62 – 7.57 (m, 4H), 7.46 – 7.43 (m, 2H), 7.40 (s, 3H), 7.17 (s, 4H), 6.82 (s, 2H). HR ESI MS of **BFA_d**. m/z = 548.0961.

Synthesis of 9-(9*H*-fluoren-9-ylidene)-10-(4-nitrophenyl)-9,10-dihydroacridine



Scheme S8: Into a round-bottom flask, 10-(4-nitrophenyl)acridine-9(10*H*)-thione (1 eq.), triphenylphosphine (2 eq.) and 11-diazo-11*H*-benzo[*b*]fluorene (2 eq.) were added to the mixed xylene solution (1 mL anhydrous xylene/0.25 mmol of thiones). We filled the whole unit with N_2 at room temperature. The mixture was degassed and refluxed for 4 h. After removing the solvent by reduced pressure distillation, the target product was separated by a chromatographic column (Petroleum ether/ethyl acetate: 30/1).

Figures for the Supporting Information

^{1}H NMR charts

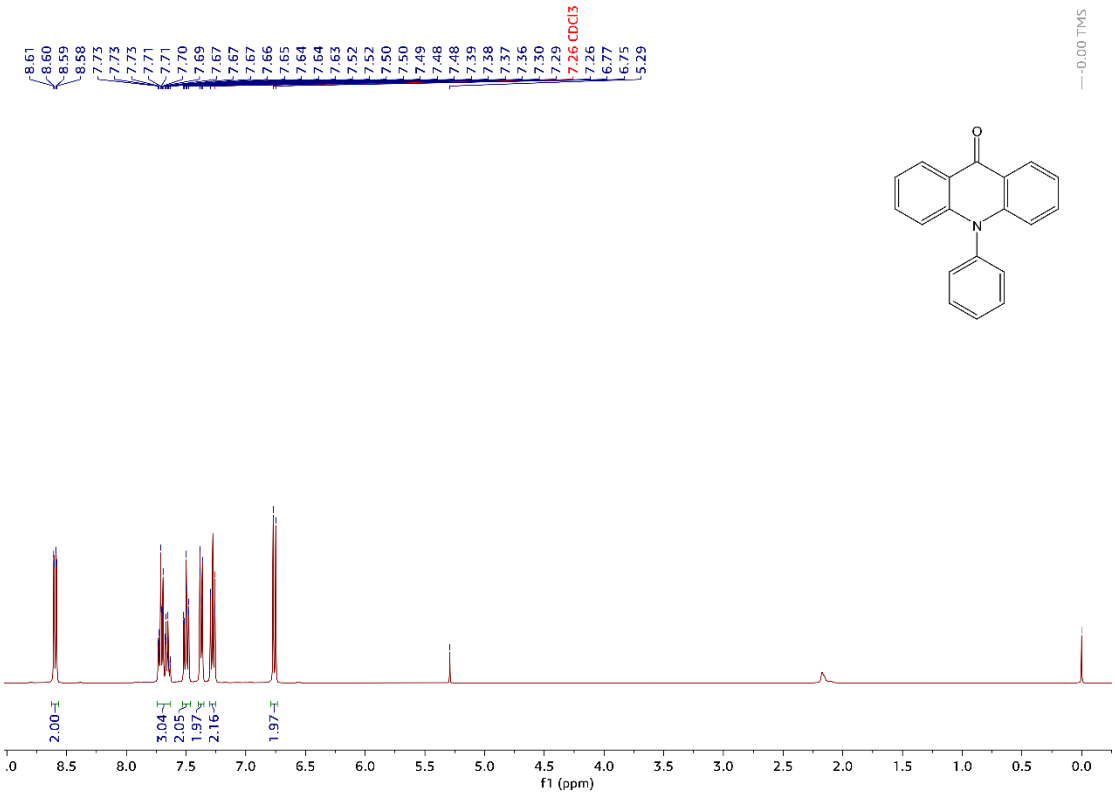


Fig. S1 ^{1}H NMR (400 MHz) of **1a** in $CDCl_3$.

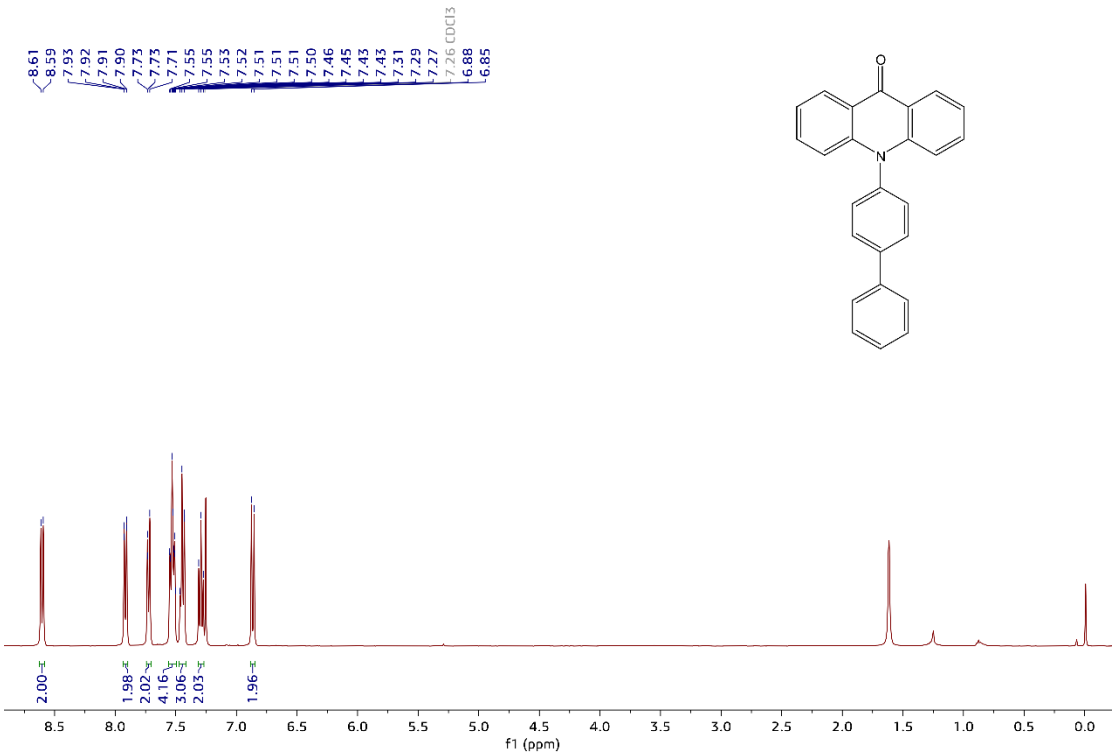


Fig. S2 ^{1}H NMR (400 MHz) of **1b** in $CDCl_3$.

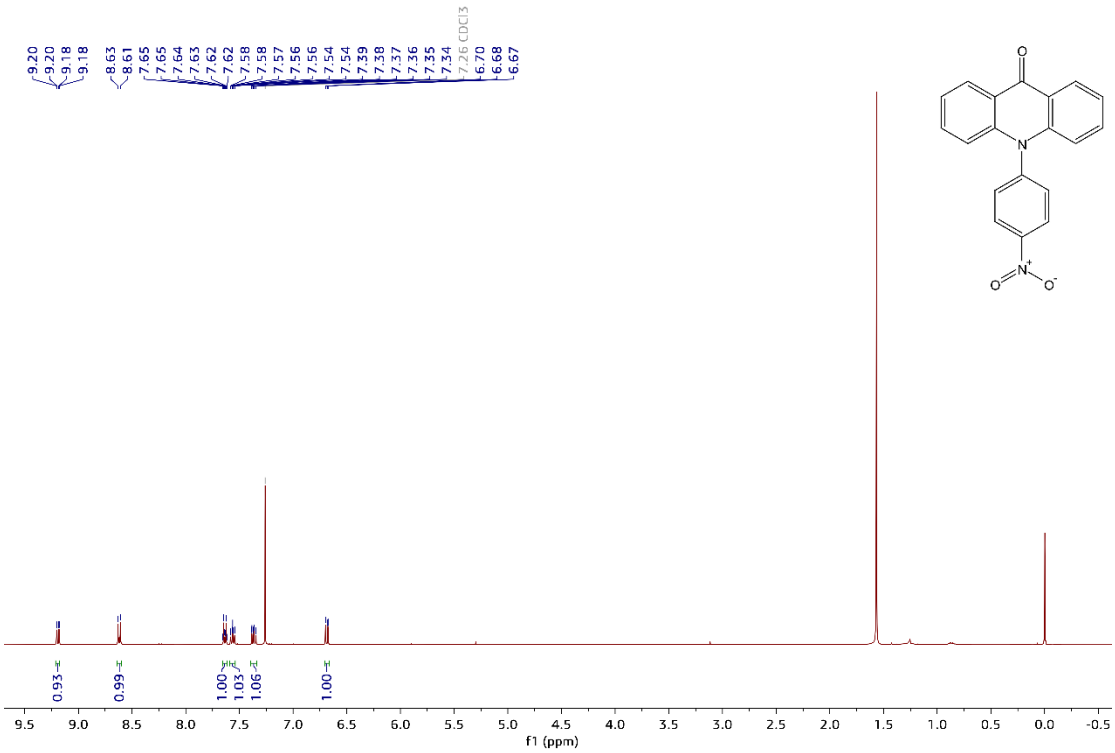


Fig. S3 ^{1}H NMR (400 MHz) of **1c** in $CDCl_3$.

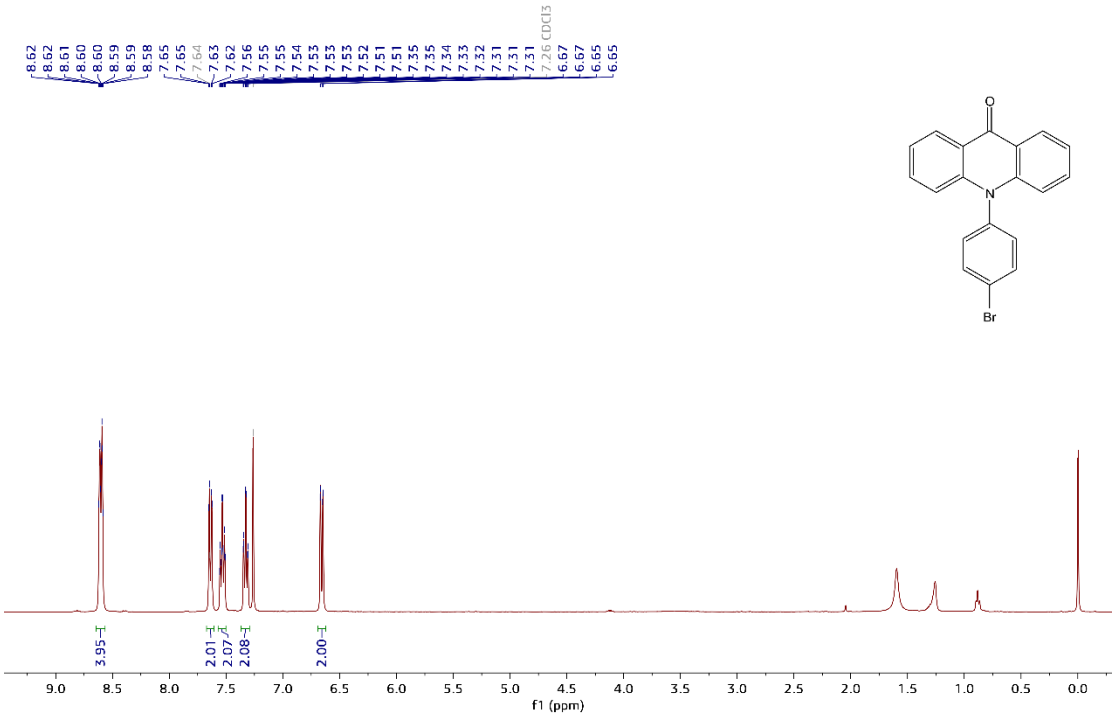


Fig. S4 ^{1}H NMR (400 MHz) of **1d** in $CDCl_3$.

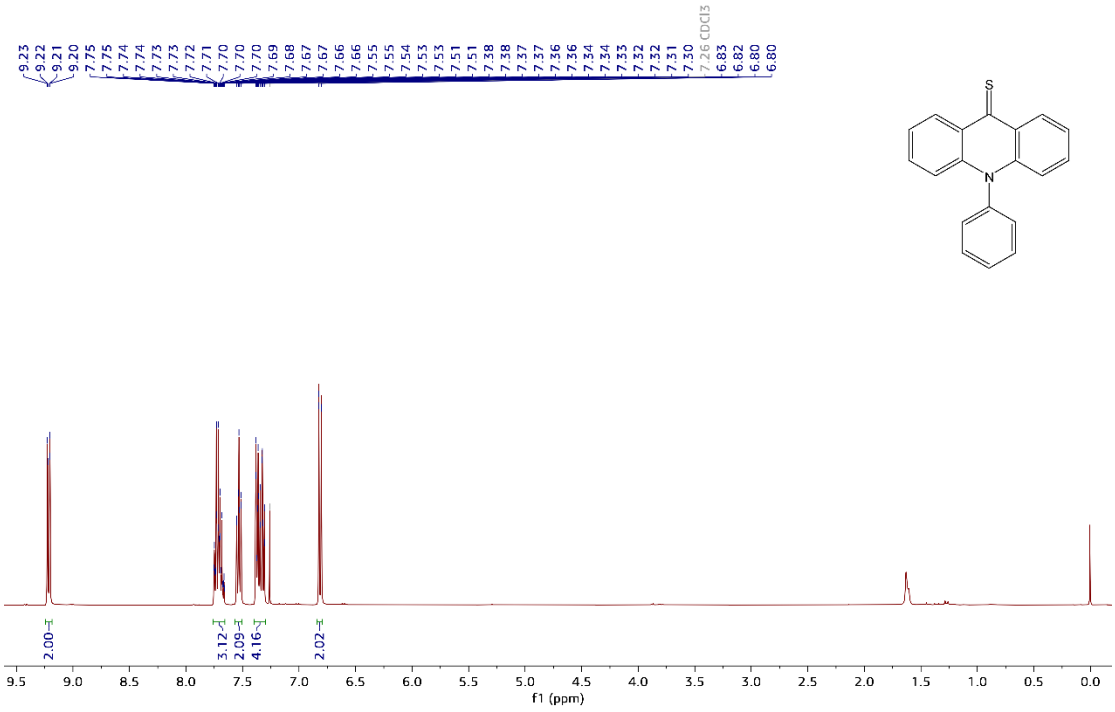


Fig. S5 ^{1}H NMR (400 MHz) of **2a** in $CDCl_3$.

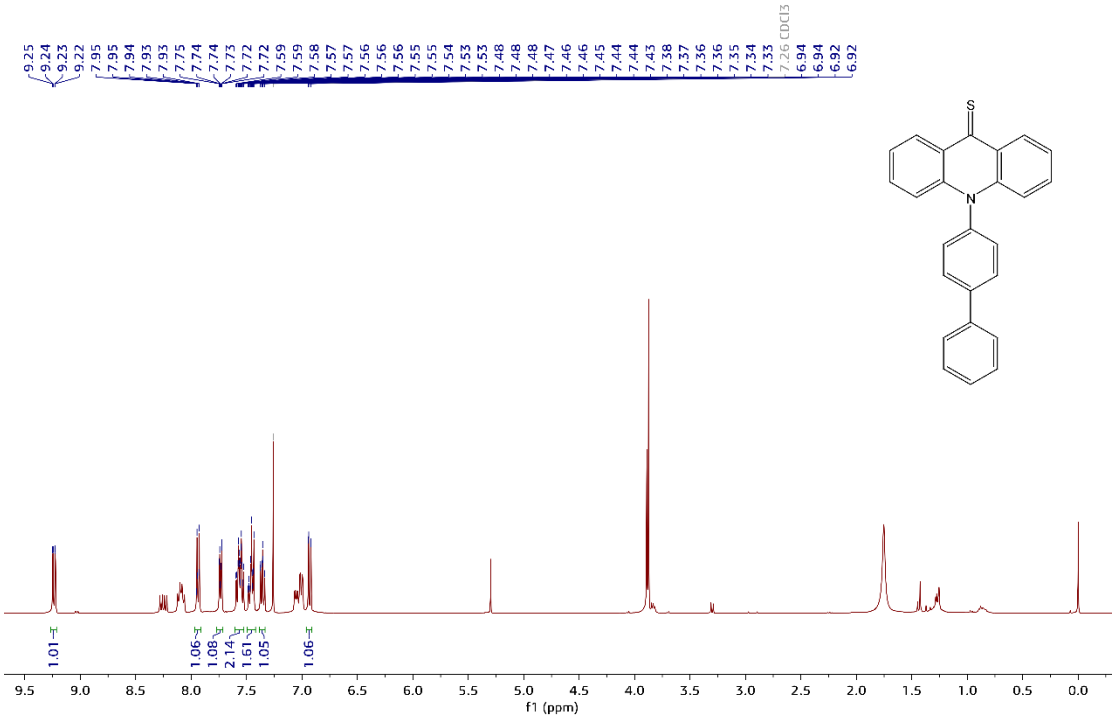


Fig. S6 ^{1}H NMR (400 MHz) of **2b** in $CDCl_3$.

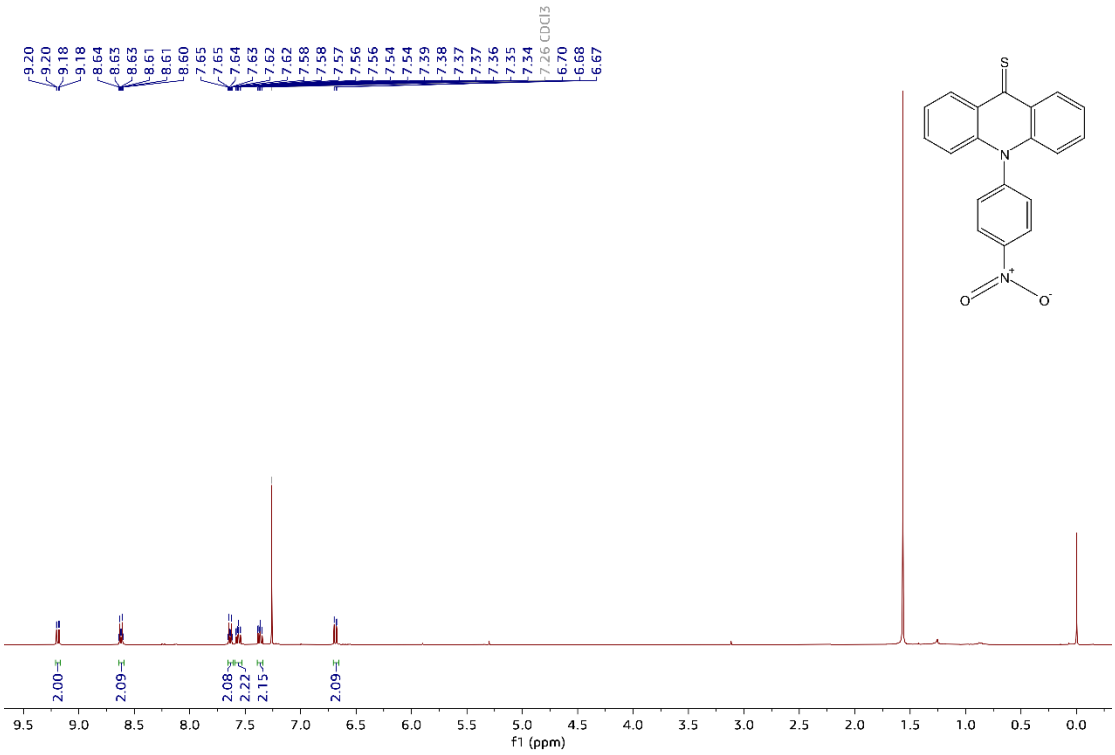


Fig. S7 ^{1}H NMR (400 MHz) of **2c** in $CDCl_3$.

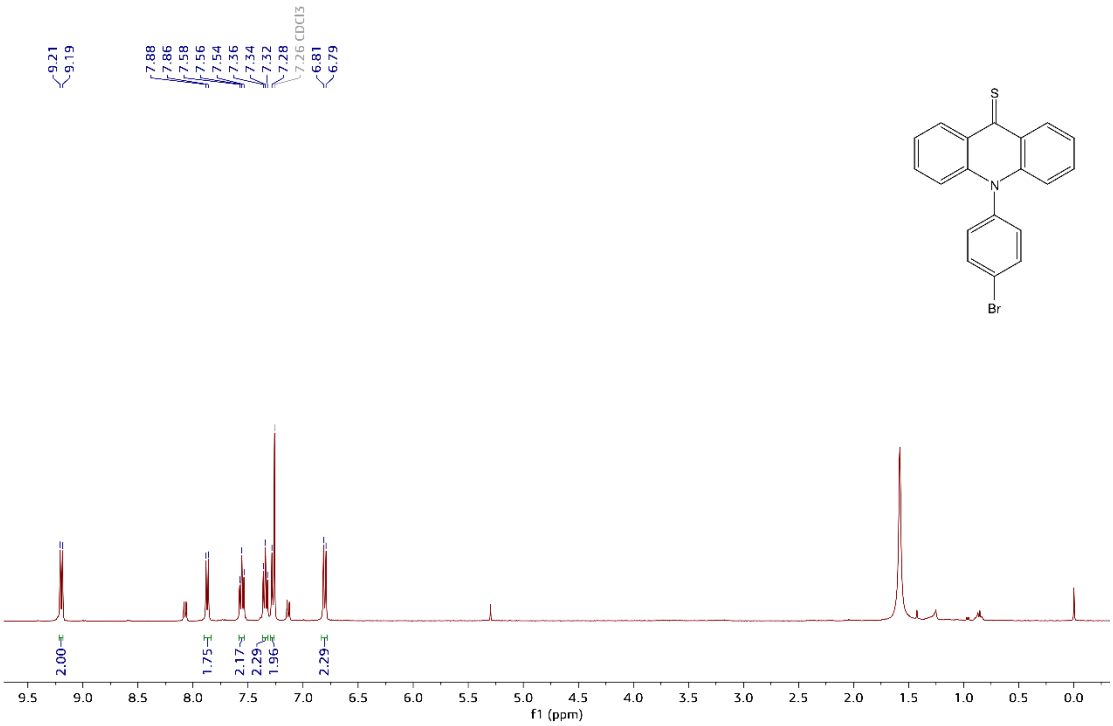


Fig. S8 ^{1}H NMR (400 MHz) of **2d** in $CDCl_3$.

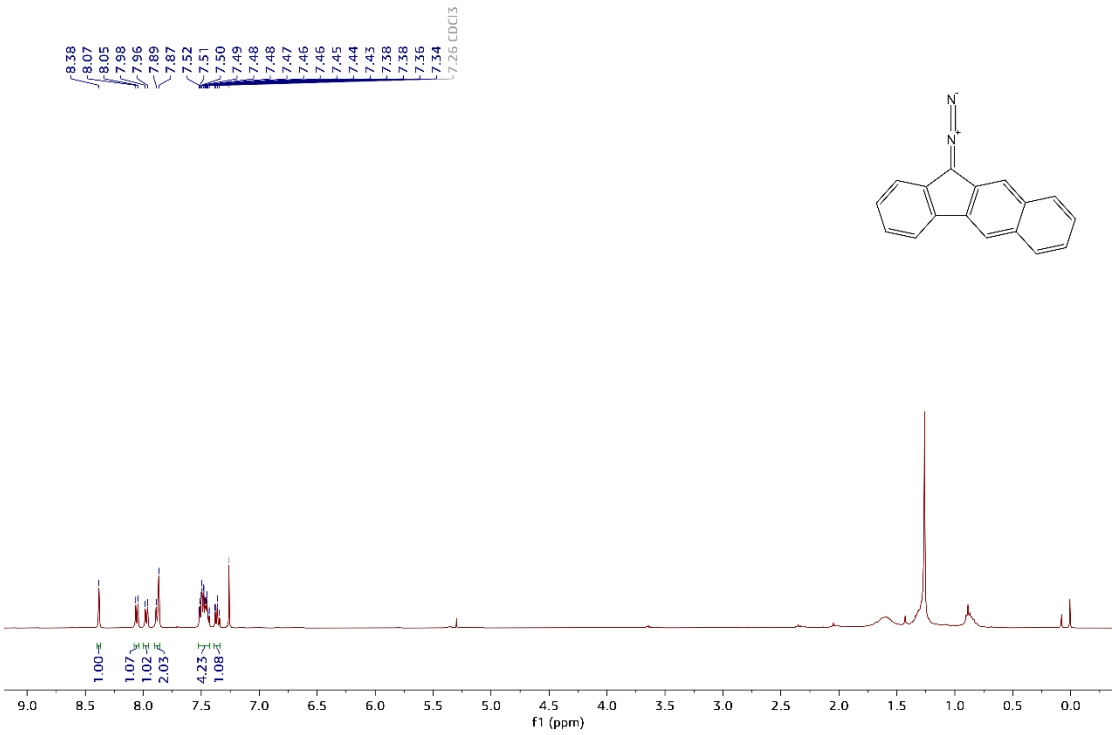


Fig. S9 ^{1}H NMR (400 MHz) of 11-diazo-11*H*-benzo[*b*]fluorine in $CDCl_3$.

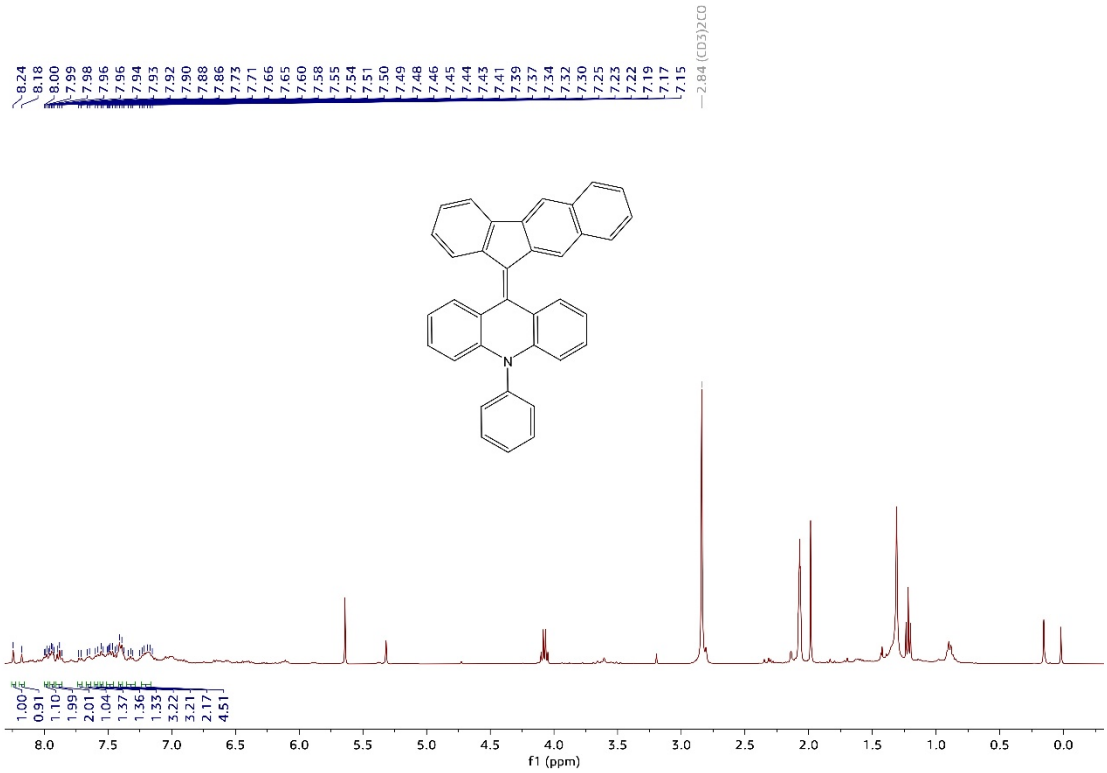


Fig. S10 ^{1}H NMR (400 MHz) of BFA_a in CD_3COCD_3.

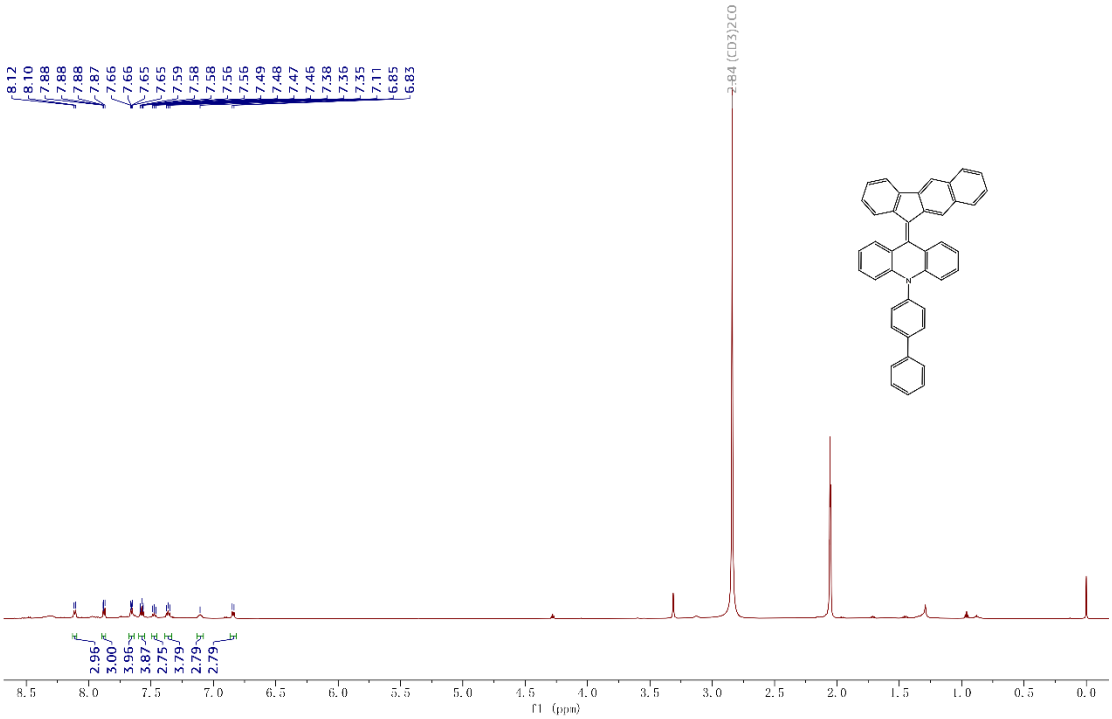


Fig. S11 ^{1}H NMR (600 MHz) of BFA_b in CD_3COCD_3.

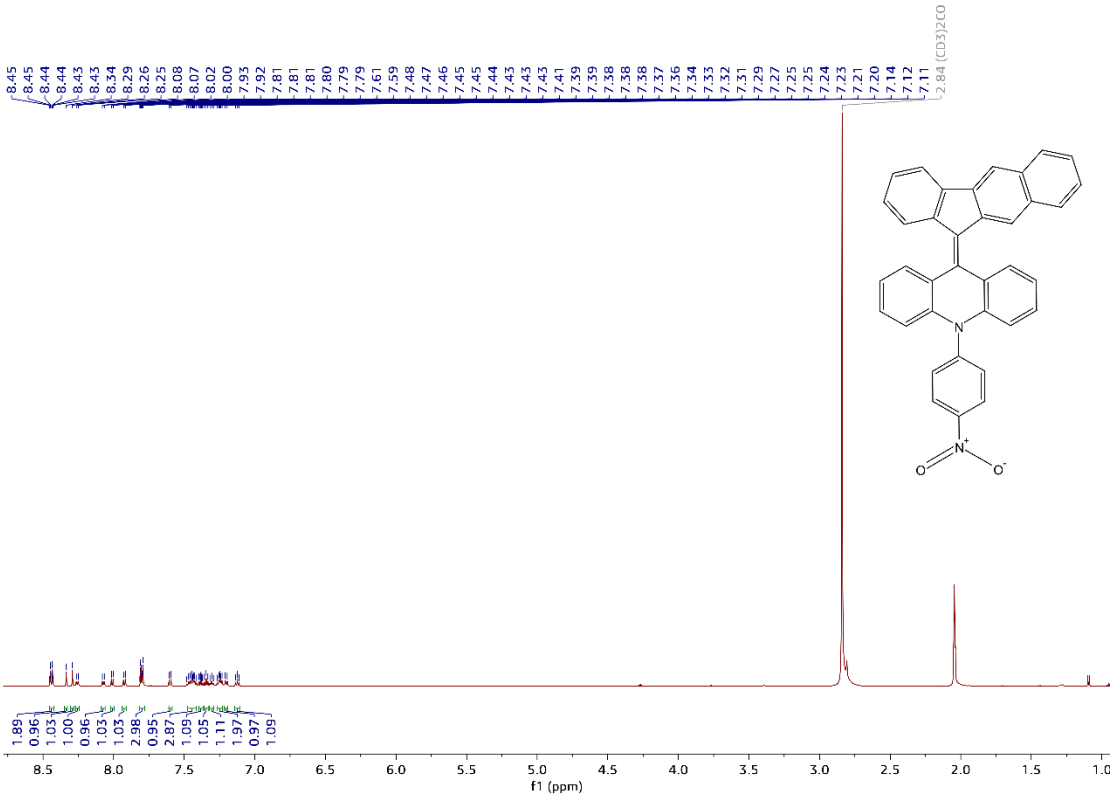


Fig. S12 ^{1}H NMR (600 MHz) of BFA_c in CD_3COCD_3.

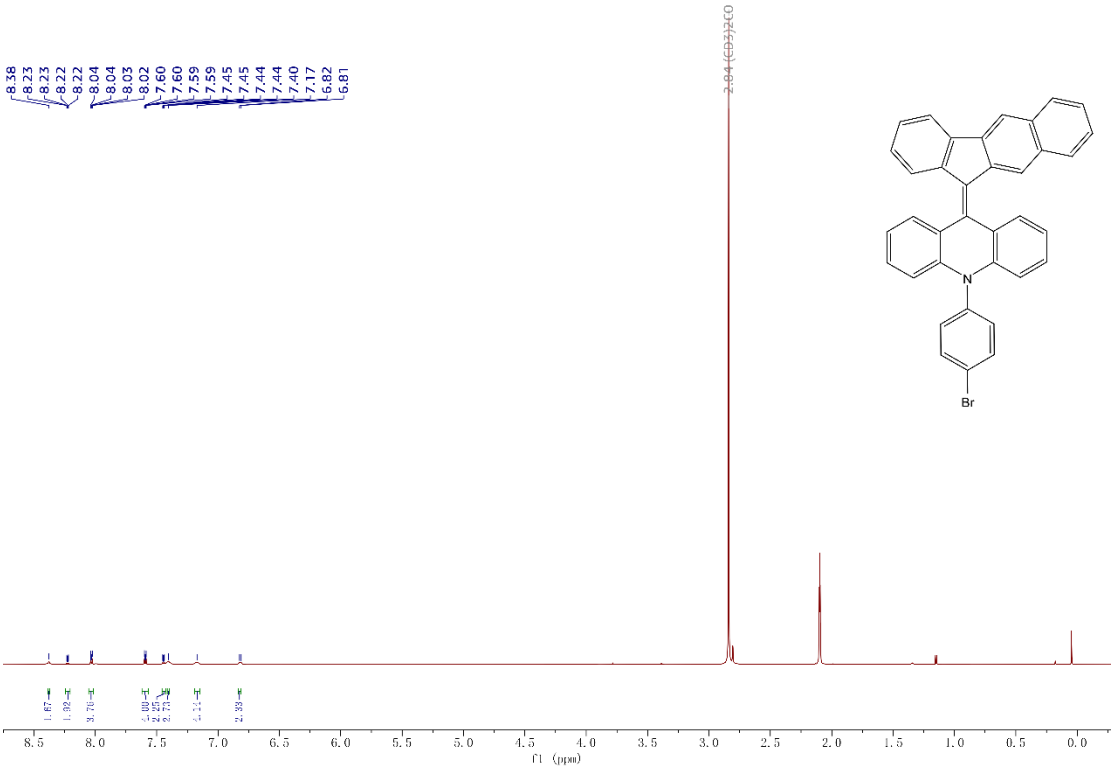


Fig. S13 ^{1}H NMR (600 MHz) of BFA_d in CD_3COCD_3.

HRMS charts

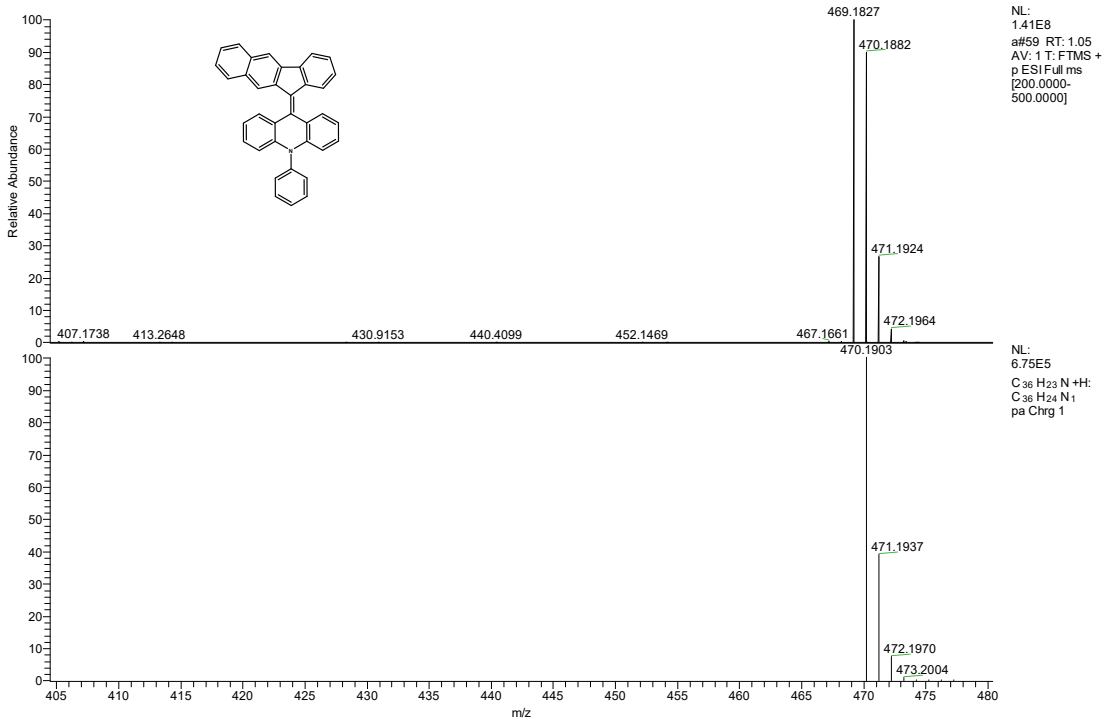


Fig. S14 HR ESI MS of BFA_a. m/z = 469.18271.

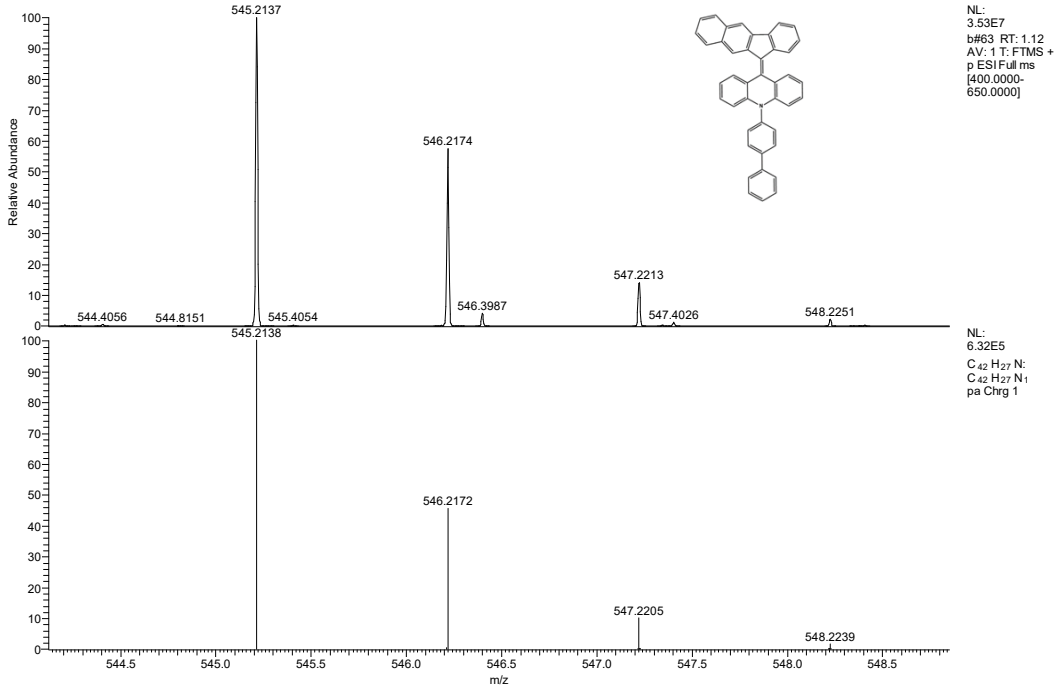


Fig. S15 HR ESI MS of BFA_b. m/z = 545.2138.

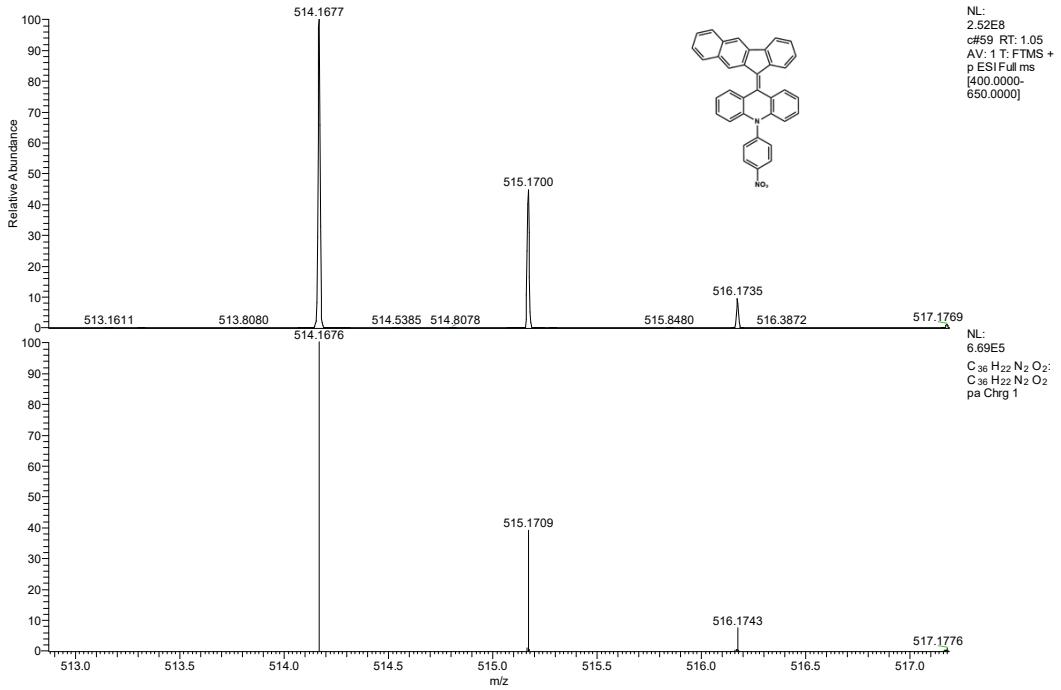


Fig. S16 HR ESI MS of BFA_c. m/z = 514.1676.

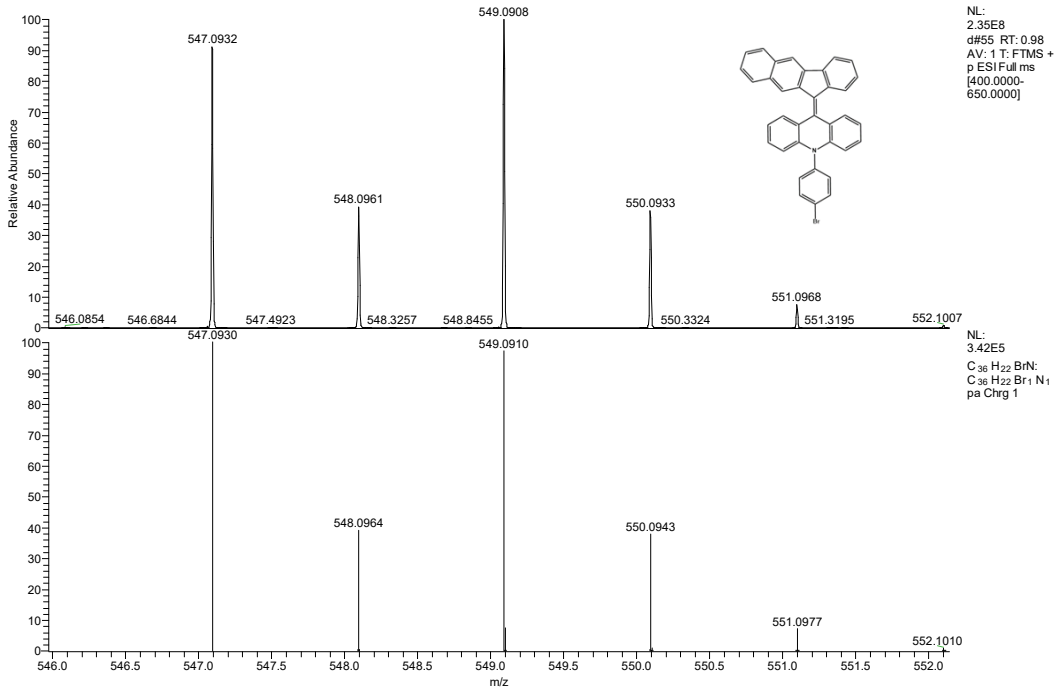


Fig. S17 HR ESI MS of BFA_d. m/z = 548.0961.

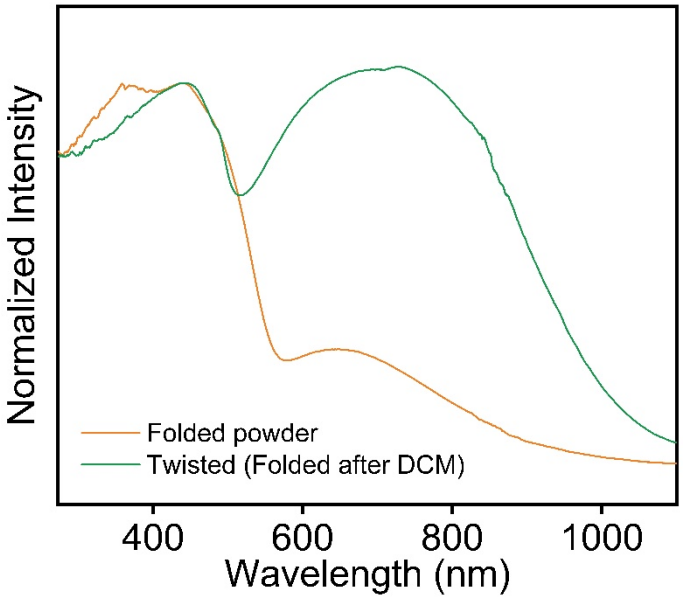


Fig. S18 Solid-state UV-vis diffuse reflectance spectra comparison.

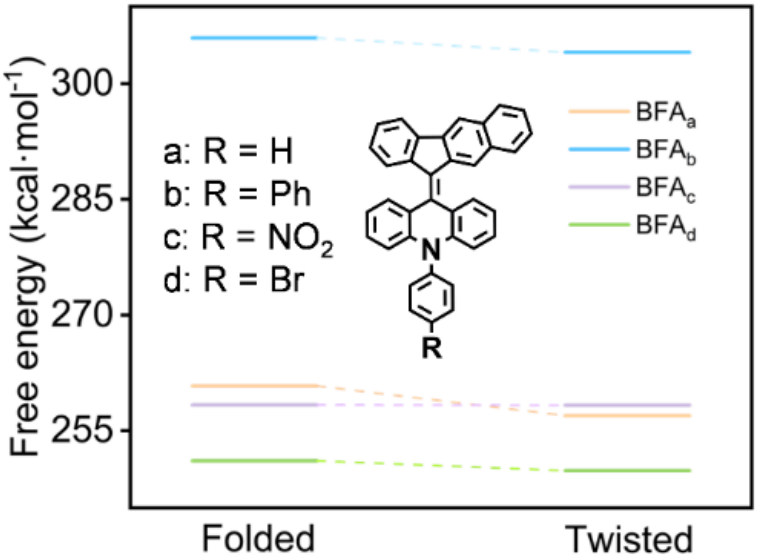


Fig. S19 Gibbs free energy of single molecules in two configurations for four BFAs.

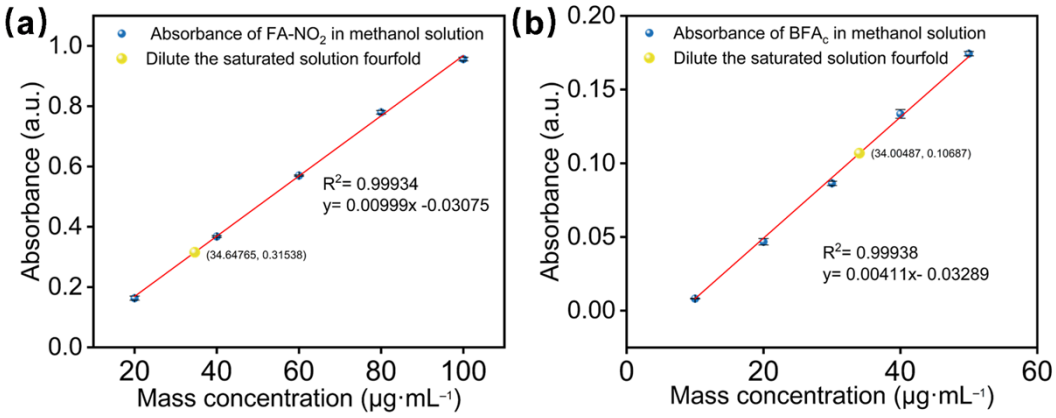


Fig. S20 Standard curve depicting the relationship between absorbance and concentration of (a) BFA_c; (b) $FA\text{-}NO_2$ dissolved in methanol. (a) A mean absorbance value of 0.31538 (The yellow dot in Fig. S20a) was obtained for the four-fold diluted saturated solution of $FA\text{-}NO_2$. Based on the fitted line, the saturated mass concentration of $FA\text{-}NO_2$ in methanol was calculated to be 138.60 $\mu g \cdot mL^{-1}$. (b) A mean absorbance value of 0.10687 (The yellow dot in Fig. S20a) was obtained for the four-fold diluted saturated solution of BFA_c. Based on the fitted line, the saturated mass concentration of BFA_c in methanol was calculated to be 136.70$\mu g \cdot mL^{-1}$.

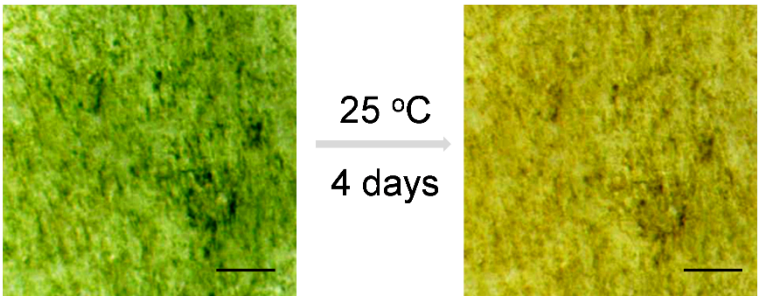


Fig. S21 Recovery of mechanochromic BFA_c. Scale bar, 1 cm.

Proton-induced discoloration

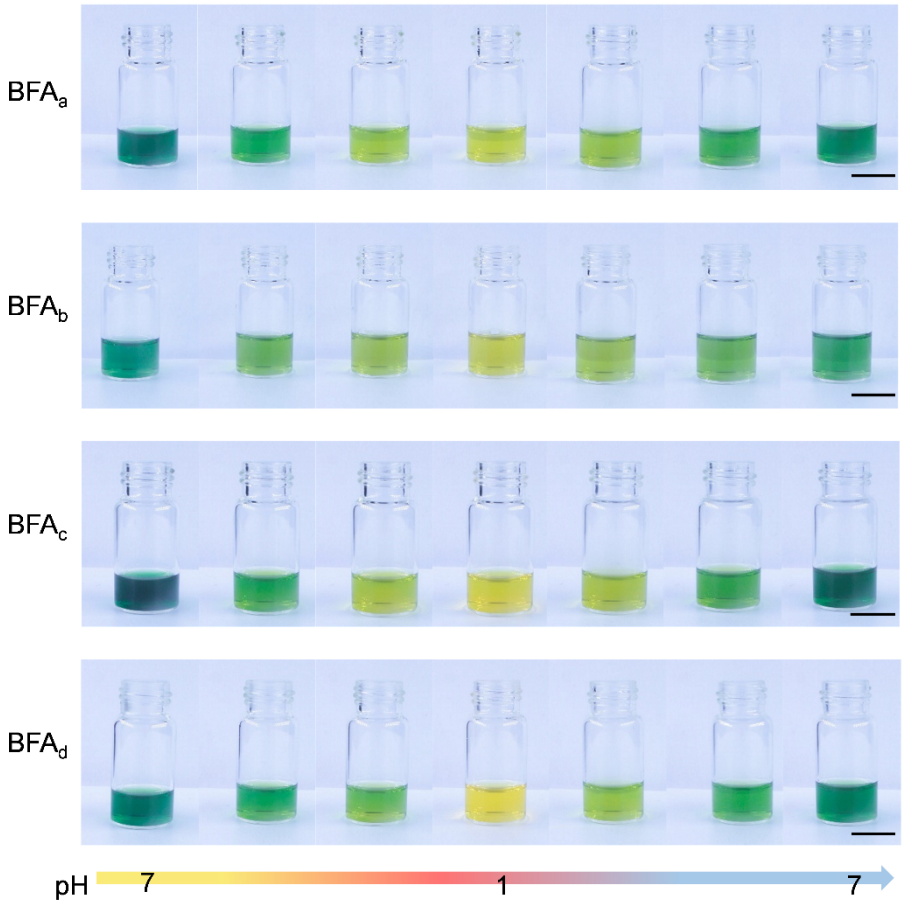


Fig. S22 The BFAs solution was gradually acidified and reneutralized. Acetic acid was added gradually to a 1.0×10^{-3} mol·L^{-1} ethyl acetate solution of BFAs. Upon the subsequent addition of triethylamine, the solution returned to its original green color as the protons were neutralized, indicating that a proton-induced color change is reversible. Scale bar, 1 cm.

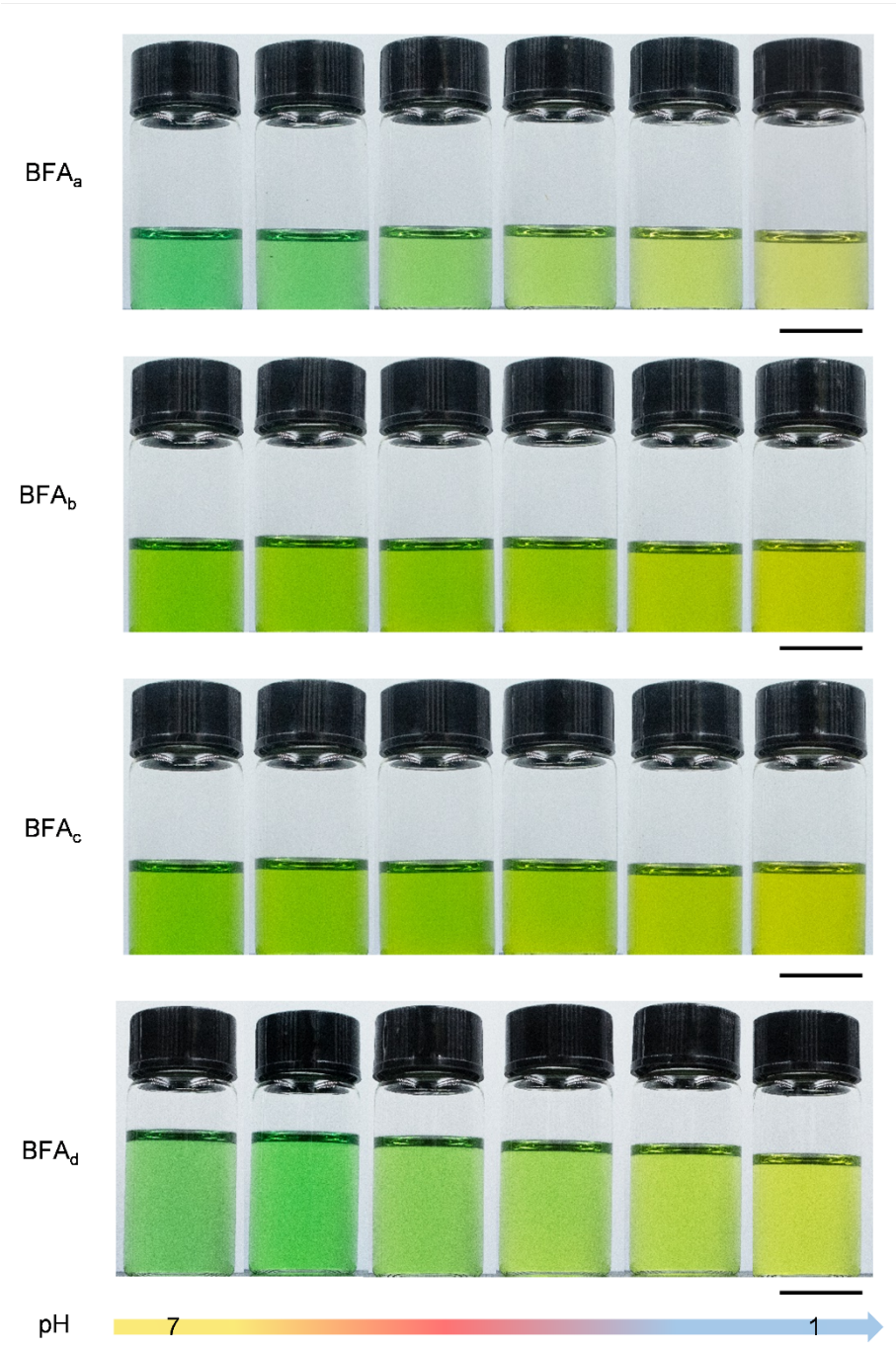


Fig. S23 The BFAs' solution was gradually acidified, and the standard curve of color difference UV-vis was created. The area intercepted by the color difference was 1 cm × 1 cm. Scale bar, 1 cm.

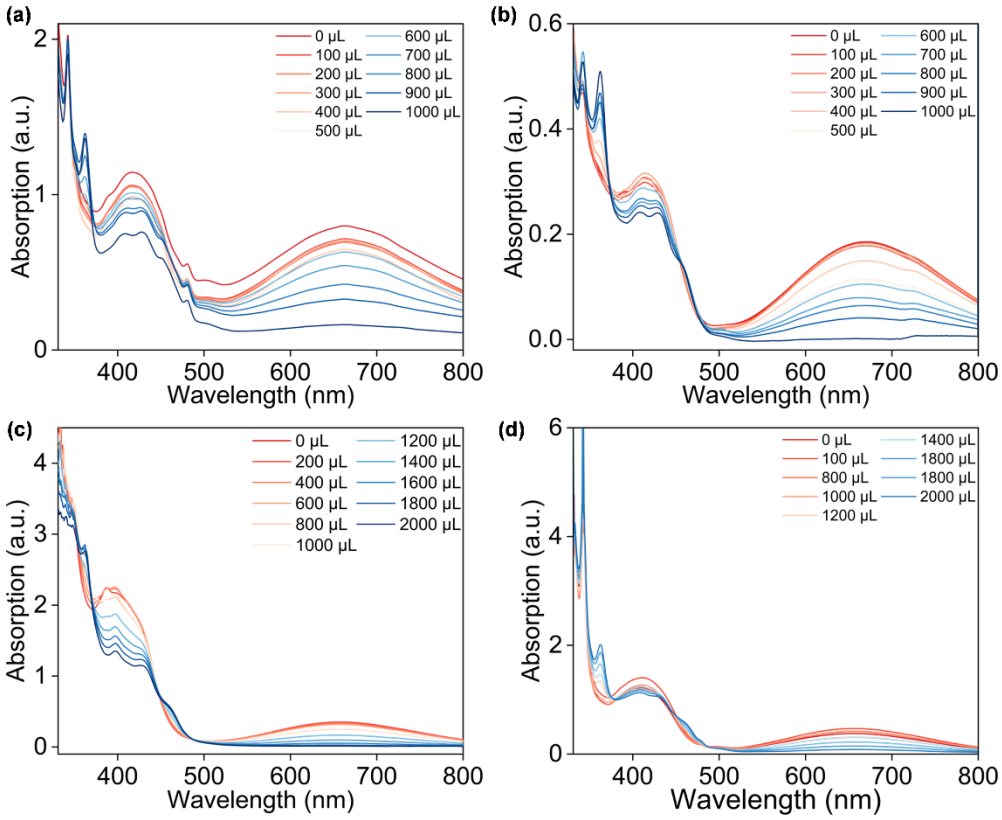


Fig. S24 The proton-induced color difference is not indicative of a transition between the two configurations. Upon the addition of acetic acid, the primary UV-vis peak at approximately 655 nm, corresponding to the twisted configuration, disappeared. Simultaneously, the prominent absorption peak near 420 nm, associated with the folded conformation, also diminished, suggesting a distinct interaction mechanism rather than a simple conformational shift. Normalized UV-vis absorption spectra of (a) BFA_a-H^+. (b) BFA_b-H^+. (c) BFA_c-H^+. (d) BFA_d-H^+. Adding an excess amount of acetic acid to the solution led to the disappearance of the primary ultraviolet (UV) absorption peak at approximately 655 nm. This observation indicated that the prominent absorption peak of the twisted conformation occurs around 655 nm, while the prominent absorption peak at around 420 nm is associated with the folded conformation. Concurrently, a new absorption peak at 350 nm emerged and intensified, suggesting the transformation of BFA_c into a different species. Nuclear Magnetic Resonance (NMR) analysis confirmed this transformation (Fig. S22).

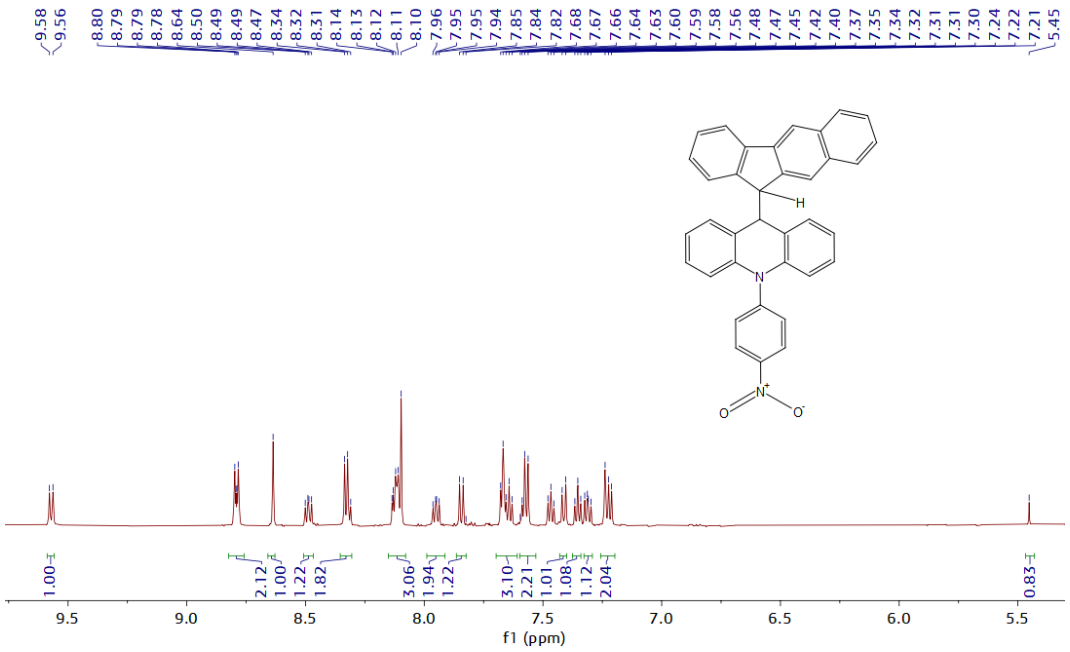


Fig. S25 ^{1}H NMR (600 MHz) of BFA_c-H^+. Nuclear magnetic resonance (NMR) analysis confirmed the appearance of a new hydrogen atom signal at δ*H* 5.45 ppm accompanied by shifts in existing proton peaks compared to S8.

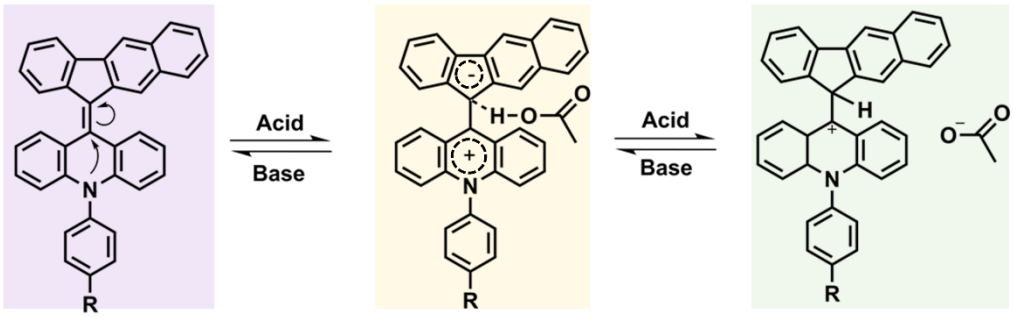


Fig. S26 Schematic of BFAs protonation.

Photochromic

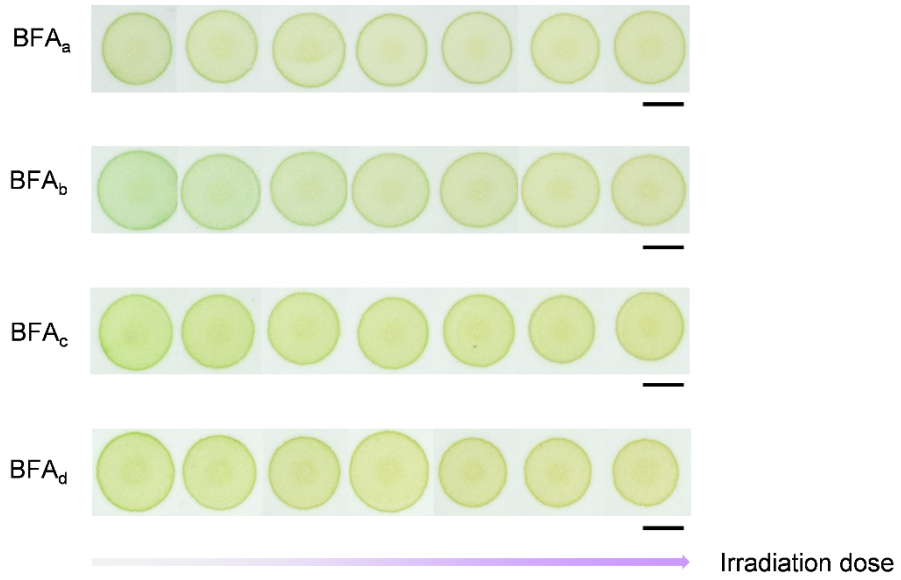


Fig. S27 Photochromic of (a) BFA$_a$. (b) BFA$_b$. (c) BFA$_c$. (d) BFA$_d$. The dosage of UV irradiation was systematically adjusted for each sample by gradually increasing the exposure time until complete color change was achieved, creating a gradient of color change. This approach enabled a semi-quantitative assessment of UV irradiation dosage. Scale bar, 2 mm.

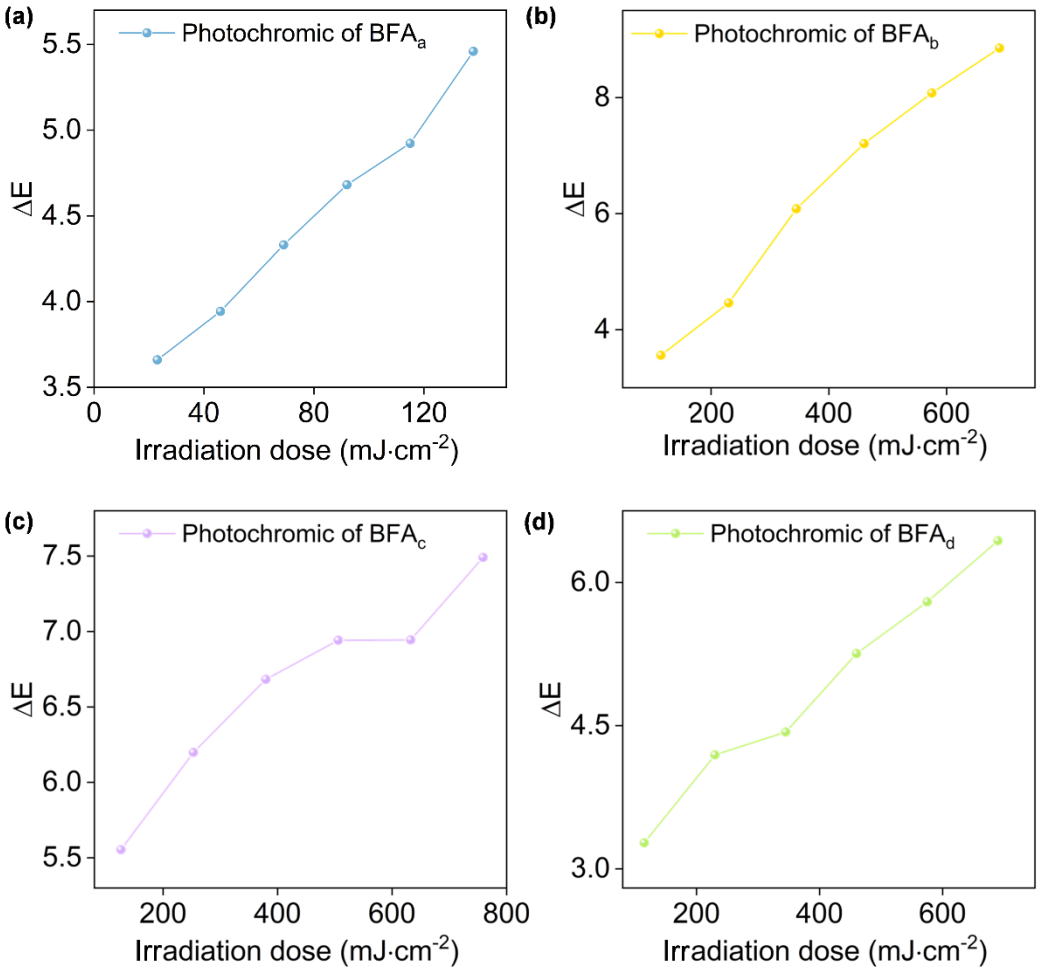


Fig. S28 Photochromic standard curve of CIELAB color difference-irradiation dose. (a) BFA_a. (b) BFA_b. (c) BFA_c. (d) BFA_d. The color difference is the difference of color before and after irradiation, using the CIELAB color difference formula mentioned in the main text.

Calculated energy

All calculations were performed on Materials Studio 2020.

1 Hartree =2625.5 kJ·mol^{-1} =27.21 eV=627.51 kcal·mol^{-1}.

Geometric optimization Settings for single molecules: Task: Geometry Optimization; Quality: Medium; Functional: GGA-PBE; Max. iterations: 1000; Integration accuracy: Medium; SCF tolerance: Medium; Core treatment: All Electron; Basisi set: DND; Basis file: 4.4; Max. SCF cycles:1000; Multipolar expansion: Hexadecapole; Use DIIS: 6; Use smearing: 0.01 Ha; Properties: Frequency. The other parameters were used by default, and the Gibbs free energy was selected for the corresponding value at 298.15 K.

The two configurations transition state finding Settings: Task: TS Search; Quality: Fine; Functional: GGA-PBE; Search protocol: Complete LST/QST; Max. number QST steps: 20; Integration accuracy: Fine; SCF tolerance: Fine; Core treatment: All Electron; Basisi set: DND; Basis file: 4.4; Max. SCF cycles:1000; Multipolar expansion: Hexadecapole; Use DIIS: 6; Use smearing: 0.01 Ha; Properties: Frequency. The other parameters were used by default.

Table S1 Energy in Hartree.

	Gibbs free energy (kcal·mol^{-1})	HOMO-1 (a.u.)	HOMO (a.u.)	LUMO (a.u.)	LUMO+1 (a.u.)	LUMO-HOMO (a.u)	LUMO-HOMO (kcal·mol^{-1})
FA-NO_2_Folded	/	-0.193208	-0.181373	-0.13323	-0.101208	0.048143	30.21021
FA-NO_2_Twisted	/	-0.189991	-0.162126	-0.133104	-0.119009	0.029022	18.2116
BFA_a_Folded	260.792	-0.182713	-0.165291	-0.092096	-0.069595	0.073195	45.93059
BFA_a_Twisted	256.964	-0.179447	-0.146461	-0.105626	-0.066097	0.040835	25.62437
BFA_b_Folded	305.930	-0.182285	-0.165088	-0.091107	-0.078178	0.073981	46.42382
BFA_b_Twisted	304.071	-0.178621	-0.145483	-0.105485	-0.087862	0.039998	25.09914
BFA_c_Folded	258.335	-0.19556	-0.178637	-0.123737	-0.105103	0.054900	34.4503
BFA_c_Twisted	258.229	-0.195955	-0.160537	-0.125593	-0.121381	0.034944	21.92771
BFA_d_Folded	251.085	-0.188337	-0.171323	-0.096878	-0.074912	0.074445	46.71498
BFA_d_Twisted	249.813	-0.184175	-0.151372	-0.111339	-0.079016	0.040033	25.12111

Table S2 The energy barrier of the two configurations transforms.

	FA-NO_2 (kcal·mol^{-1})	BFA_a (kcal·mol^{-1})	BFA_b (kcal·mol^{-1})	BFA_c (kcal·mol^{-1})	BFA_d (kcal·mol^{-1})
T to F	11.055	11.621	0.345	7.101	5.976
F to T	4.180	0.870	1.069	2.064	2.250

Table S3 The energy barrier of the two configurations transforms.

	BFA_a (kcal·mol^{-1})	BFA_b (kcal·mol^{-1})	BFA_c (kcal·mol^{-1})	BFA_d (kcal·mol^{-1})
T to F	11.621	0.345	7.101	5.976
T to T-H^+	27.614	40.831	46.517	48.937