Electronic Supplementary Material (ESI) for Chemical Communications.

Fluorene analogues of xanthene dyes – low molecular weight near-infrared dyes

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Table of Contents

1. Experimental procedures

General

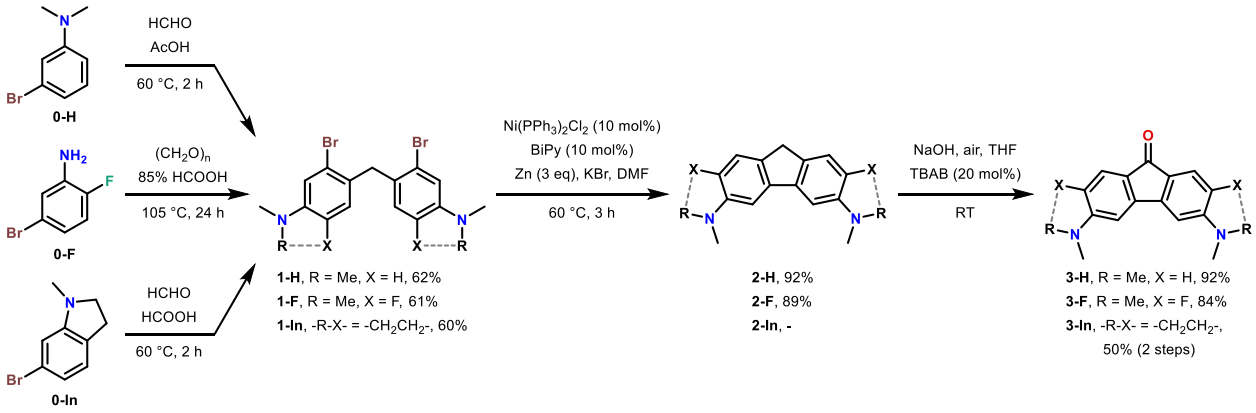
All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz, 500 MHz or 600 MHz spectrometer. Chromatography was performed on silica (pore size 60 Å, 230-400 mesh).

Diffraction experiments were performed using a Bruker APEX-II CCD apparatus and the crystal structure was solved using SHELXL-2014 software.

Absorption spectra at room temperature were recorded on a Perkin Elmer UV/VIS spectrometer, model Lambda 35 (general spectra) or Schimadzu UV-3600i Plus UV-Vis-NIR spectrophotometer (pH dependence and stability measurements). Fluorescence spectra were measured with an Edinburgh Instruments spectrophotometer, model FLS1000 with 656.7 nm diode laser as an external excitation source.

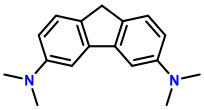
Bis(2-bromo-4-dimethylaminophenyl)methane (**1-H**),[1] bis(2-bromo-4-dimethylamino-5-fluorophenyl)methane (**1-F**),[2] and bis(6-bromo-1-methylindolin-5-yl)methane (**1-In**)[3] were prepared according to the literature procedures.

Synthesis of fluorenones 3



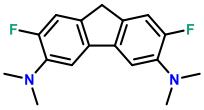
Scheme S1. Synthesis of diaminofluorenones **3-H**, **3-F**, and **3-In** by nickel-catalyzed Yamamoto-type cyclization and aerobic oxidation. Compounds **1-H**,[1] **1-F**,[2] and **1-In**[3] were prepared from **0-H**, **0-F**, and **0-In**, respectively, according to the literature procedures.

3,6-Bis(dimethylamino)fluorene (2-H)



Zinc dust was activated by suspension in 2% HCl_{aq} for 15 min. Metal was filtered off, washed with deionized water (2x), ethanol (2x) and diethyl ether (2x), and dried under vacuum. Bis(2-bromo-4-dimethylaminophenyl)methane (**1-H**) (3.01 g, 7.30 mmol), pre-activated zinc dust (1.43 g, 21.9 mmol, 3.0 equiv.), bis(triphenylphosphine)nickel(II) dichloride (478 mg, 0.73 mmol, 0.1 equiv.), 2,2'-bipyridyl (114 mg, 0.73 mmol, 0.1 equiv.), and potassium bromide (1.74 g, 14.6 mmol, 2.0 equiv.) were placed in a Schlenk flask and the vessel was evacuated and backfilled with argon (three times). Anhydrous dimethylformamide (40 mL) was added and the resulting mixture was stirred at 60 °C for 3 h. The reaction mixture was diluted with toluene and passed through celite, which was washed three times with toluene. To the combined filtrates, water was added and the layers were separated. The aqueous layer was extracted three times with toluene. The combined organic layers were washed twice with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo and the product was purified using column chromatography (silica gel, dichloromethane/ethyl acetate 95/5) to give 1.69 g (6.70 mmol, 92%) of **2-H** as an off-white solid. Mp. 148–150 °C (Lit.[4] 147–149 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 2.4 Hz, 2H), 6.73 (dd, J = 8.3, 2.5 Hz, 2H), 3.71 (s, 2H), 3.01 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 143.1, 133.3, 125.3, 112.5, 104.3, 41.6, 35.5. HRMS (ESI) m/z calcd. for $C_{17}H_{21}N_2$ ($[M+H]^+$): 253.1705; found: 253.1707.

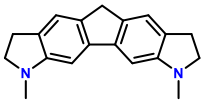
3,6-Bis(dimethylamino)-2,7-difluorofluorene (2-F)



Prepared by the same procedure as **2-H** using the following amounts of reagents: bis(2-bromo-4-dimethylamino-5-fluorophenyl)methane (**1-F**) (2.06 g, 4.60 mmol), preactivated zinc dust (903 mg, 13.8 mmol, 3.0 equiv.), bis(triphenylphosphine)nickel(II) dichloride (301 mg, 0.46 mmol, 0.1 equiv.), 2,2'-bipyridyl (72 mg, 0.46 mmol, 0.1 equiv.), potassium bromide (1.09 g, 9.24 mmol, 2.0 equiv.) and 25 mL of DMF. Column chromatography purification (silica gel, dichloromethane/ethyl acetate 95/5) provided 1.18 g (4.09 mmol, 89%) of **2-F** as an off-white solid. Mp. 105–107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J_{HF} = 8.0 Hz, 2H), 7.16 (d, J_{HF} = 12.4 Hz, 2H), 3.72 (s, 2H), 2.90 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1 (d, J_{CF} = 244.7 Hz), 140.4 (d, J_{CF} = 10.2 Hz), 137.5 (s), 136.9 (d, J_{CF} =

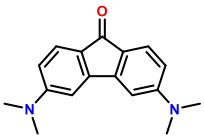
9.8 Hz), 113.0 (d, J_{CF} = 22.7 Hz), 109.1 (s), 43.5 (d, J_{CF} = 3.4 Hz), 36.1 (s). HRMS (ESI) m/z calcd. for $C_{17}H_{19}F_2N_2$ ($[M+H]^+$): 289.1516; found: 289.1518.

1,9-Dimethyl-2,3,5,7,8,9-hexahydro-1*H*-cyclopenta[1,2-*f*:4,3-*f*']diindole (2-In)



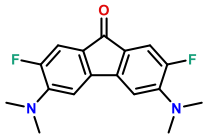
Prepared by the same procedure as **2-H** using the following amounts of reagents: bis(6-bromo-1-methylindolin-5-yl)methane (**1-In**) (3.43 g, 7.86 mmol), preactivated zinc dust (1.54 g, 23.6 mmol, 3.0 equiv.), bis(triphenylphosphine)nickel(II) dichloride (514 mg, 0.79 mmol, 0.1 equiv.), 2,2'-bipyridyl (123 mg, 0.79 mmol, 0.1 equiv.), potassium bromide (1.87 g, 15.7 mmol, 2.0 equiv.) and 40 mL of DMF. Because the product **2-In** was found to be unstable and decomposed in contact with silica gel, the crude material obtained after extraction and evaporation of the solvents was used directly in the oxidation step.

3,6-Bis(dimethylamino)-9*H*-fluoren-9-one (3-H)



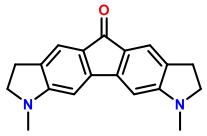
3,6-Bis(dimethylamino)fluorene (**2-H**) (883 mg, 3.50 mmol) was dissolved in 120 mL of dry THF. Powdered sodium hydroxide (2.80 g, 70 mmol, 20 equiv.) and tetrabutylammonium bromide (TBAB) (226 mg, 0.70 mmol, 0.20 equiv.) were added and the mixture was vigorously stirred under a slow flow of dry air for 3.5 h at rt. The mixture was diluted with water and NaOH was neutralized by slow addition of 2M hydrochloric acid (40 mL). The mixture was extracted with chloroform (4 times). The combined organic layers were washed with brine (2 times) and dried over anhydrous $MgSO_4$. After evaporation of the solvents, the product was purified by column chromatography (silica gel, dichloromethane/ethyl acetate 92/8 to 90/10) to give 856 mg (3.21 mmol, 92%) of ketone **3-H** as a bright orange powder. Mp. 253–255 °C (Lit.[4] 250–252 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 2.3 Hz, 2H), 6.45 (dd, J = 8.4, 2.3 Hz, 2H), 3.11 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 154.6, 146.1, 125.3, 124.5, 110.4, 103.1, 40.67. HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2O$ ($[M+H]^+$): 267.1497; found: 267.1496.

3,6-Bis(dimethylamino)-2,7-difluoro-9*H*-fluoren-9-one (3-F)



Prepared by the same procedure as **3-H** using the following amounts of reagents: 3,6-bis(dimethylamino)-2,7-difluorofluorene (**2-F**) (721 mg, 2.50 mmol), powdered sodium hydroxide (2.00 g, 50 mmol, 20 equiv.), tetrabutylammonium bromide (TBAB) (161 mg, 0.50 mmol, 0.20 equiv.), and 100 mL of dry THF. Reaction time: 2 h. After neutralization, extraction with chloroform, washing with brine, drying with $MgSO_4$, and evaporation of the solvents, the product was purified by recrystallization from ethanol/methanol ~1/1 mixture to give 636 mg (2.10 mmol, 84%) of ketone **3-F** as a red crystalline powder. Mp. 185–188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J_{HF} = 12.5 Hz, 2H), 6.80 (d, J_{HF} = 7.5 Hz, 2H), 3.04 (d, J_{HF} = 1.5 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3 (s), 153.4 (d, J_{CF} = 245.3 Hz), 145.1 (d, J_{CF} = 9.0 Hz), 140.9 (s), 126.5 (d, J_{CF} = 6.8 Hz), 112.7 (d, J_{CF} = 23.4 Hz), 108.1 (d, J_{CF} = 4.7 Hz), 42.6 (d, J_{CF} = 6.0 Hz). HRMS (ESI) m/z calcd. for $C_{17}H_{17}F_2N_2O$ ($[M+H]^+$): 303.1309; found: 303.1310.

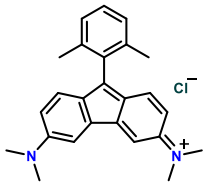
1,9-Dimethyl-1,2,3,7,8,9-hexahydro-5*H*-cyclopenta[1,2-*f*:4,3-*f*']diindol-5-one (3-In)



Prepared by the same procedure as **3-H** using the following amounts of reagents: Crude **2-In** (whole sample obtained in the previous step, assumed amount: 7.86 mmol), powdered sodium hydroxide (6.29 g, 157.2 mmol, 20 equiv.), tetrabutylammonium bromide (TBAB) (506 mg, 1.57 mmol, 0.20 equiv.), and 200 mL of dry THF. Reaction time: 4.5 h. The reaction mixture was diluted with 50 mL of deionized water and stirred, upon which a deep red precipitate formed. The solid was collected by filtration and washed with water to give 1.23 g of crude material, which was recrystallized by dissolution in a dichloromethane/methanol mixture and precipitated by slow addition of diethyl ether. After filtration, 1.14 g (3.93 mmol, 50% yield from **1-In**) of **3-In** was obtained as a dark brown powder. Mp. 320–330 °C (with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 6.45 (s, 2H), 3.48 (t, J = 8.5 Hz, 4H), 2.97 – 2.90 (m, 4H), 2.89 (s, 6H). ^{13}C NMR (101 MHz, 4/1 (*v*/*v*) CD_2Cl_2 / CD_3OD) δ 192.7, 158.9, 147.2, 129.4, 125.2, 120.2, 98.3, 55.8, 34.6, 28.0. HRMS (ESI) m/z calcd. for $C_{19}H_{18}N_2ONa$ ($[M+Na]^+$): 313.1317; found: 313.1316.

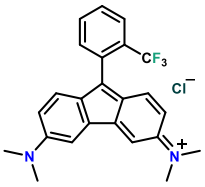
Preparation of a solution of 2,6-dimethylphenylmagnesium bromide · LiCl for the synthesis of 4-H-a and 6-F. Lithium chloride (424 mg, 10.0 mmol) and magnesium turnings (255 mg, 10.5 mmol) were placed in a Schlenk flask and dried under vacuum while the flask was heated with a heat gun and left connected to vacuum for several minutes to cool to rt. The flask was evacuated and refilled with argon (three times) and anhydrous THF (20.0 mL) was added. The obtained suspension was cooled to 0 °C and 2-bromo-1,3-dimethylbenzene (1.33 mL, 10.0 mmol) was added, followed by 1,2-dibromoethane (46 µL, 0.50 mmol) to initiate the reaction. The resulting mixture was stirred for 1 h at 0 °C and for 1 h at rt, after which the magnesium metal dissolved almost completely. The stirring was stopped and solid residues were allowed to sediment. The resulting grey-colored supernatant solution of the Grignard reagent (concentration ca. 0.50 M) was used directly in the syntheses of **4-H-a** and **6-F**, where it was transferred *via* syringes.

3,6-Bis(dimethylamino)-9-(2,6-dimethylphenyl)fluorenylium chloride (4-H)



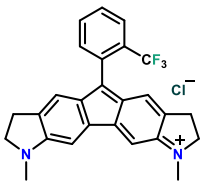
The solution of 2,6-dimethylphenylmagnesium bromide · LiCl (~0.5M in THF, 6.0 mL, ~3.0 mmol, prepared as above) was added *via* a syringe to a stirred solution of 3,6-bis(dimethylamino)-9*H*-fluoren-9-one (**3-H**) (107 mg, 0.40 mmol) in 5.0 mL of anhydrous THF in argon atmosphere. The resulting mixture was stirred overnight at 50 °C and at 60 °C for 2 h. The reaction was quenched by adding 15 mL of 0.2M HCl_{aq} and the stirring was continued for 1 h. The mixture was diluted with water and hexanes, the layers were separated, and the organic layer was washed with diluted hydrochloric acid (four times). The combined aqueous layers, which contained the product, were washed twice with hexanes in order to remove the excess *meta*-xylene and unreacted **3-H**. The product was then extracted from the aqueous phase with dichloromethane (five times). The combined yellow-green DCM extracts were washed twice with diluted brine (brine/water 1/1) and dried over anhydrous Na_2SO_4. After evaporation of the solvents under reduced pressure, the product was recrystallized by portionwise addition of diethyl ether to the dye solution in 3 mL of DCM/MeOH 2/1 and frequent sonication. After filtration and drying under vacuum, 122 mg (0.312 mmol, 78%) of **4-H** was obtained as a dark green solid. Mp. >400 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.39 (d, J = 2.2 Hz, 2H), 7.29 – 7.21 (m, 1H), 7.15 (d, J = 7.5 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 6.12 (dd, J = 8.9, 2.3 Hz, 2H), 3.45 (s, 12H), 2.22 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 173.3, 159.0, 148.3, 135.9, 133.2, 131.5, 130.0, 129.4, 128.0, 115.3, 111.4, 42.6, 20.2. HRMS (ESI) m/z calcd. for $C_{25}H_{27}N_2$ (M^+): 355.2174; found: 355.2180.

3,6-Bis(dimethylamino)-9-(2-(trifluoromethyl)phenyl)fluorenylium chloride (4-H-CF_3)



To the stirred solution of 2-bromobenzotrifluoride (272 μL, 2.00 mmol) in 5.0 mL of anhydrous THF at −78 °C under argon atmosphere *sec*-butyllithium (1.4M in cyclohexane, 1.43 mL, 2.0 mmol) was added dropwise through a syringe and the mixture was stirred for 2 h at the same temperature. The suspension of 3,6-bis(dimethylamino)-9*H*-fluoren-9-one (**3-H**) (107 mg, 0.40 mmol) in 10.0 mL of THF was slowly added, the cooling bath was removed and the stirring was continued for 1 h while the temperature reached rt. 20 mL of 0.4M HCl_{aq} and the mixture was stirred for 1 h. The mixture was diluted with water and hexanes, the layers were separated and the aqueous layer, which contained the product, was washed twice with hexanes in order to remove the excess arene and unreacted **3-H**. Then, the product was extracted from the aqueous phase with dichloromethane (five times). The combined yellow-green DCM extracts were washed twice with diluted brine (brine/water 1/1) and dried over anhydrous Na_2SO_4. After evaporation of the solvents under reduced pressure, the product was recrystallized by portion-wise addition of diethyl ether to the dye solution in 2 mL of MeOH and frequent sonication. After filtration and drying under vacuum, 94 mg (0.218 mmol, 55%) of **4-H-CF_3** were obtained as a brown solid. Mp. >400 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.46 (d, J = 2.0 Hz, 2H), 7.84 (d, J = 7.9 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 6.13 (dd, J = 9.0, 1.7 Hz, 2H), 3.45 (s, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 167.7 (s), 158.8 (s), 147.9 (s), 133.3 (s), 132.6 (s), 131.0 (s), 130.3 (s), 129.9 (s), 127.3 (q, J_{CF} = 4.8 Hz), 124.1 (q, J_{CF} = 274.0 Hz), 115.9 (s), 111.1 (s), 42.7 (s). HRMS (ESI) m/z calcd. for $C_{24}H_{22}F_2N_2$ (M^+): 395.1735; found: 395.1739.

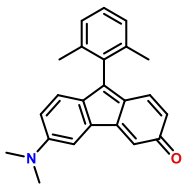
4-In



To the stirred solution of 2-bromobenzotrifluoride (150 μL, 1.10 mmol) in 5.0 mL of anhydrous THF at −78 °C in argon atmosphere *tert*-butyllithium (1.7M in *n*-pentane, 1.3 mL, 2.2 mmol) was added dropwise *via* a syringe and the mixture was stirred for 30 min at the same temperature and warmed to 0 °C. The resulting solution was transferred *via* a syringe to a stirred suspension of **3-In**

(100 mg, 0.344 mmol) in 5.0 mL of THF at 0 °C under argon atmosphere. The resulting mixture was stirred for 1 h at 0 °C and 10 mL of 2M HCl_{aq} was added and the stirring was continued for 30 min. The mixture was diluted with water, methanol and hexanes, the layers were separated and the aqueous/MeOH layer, which contained the product, was washed twice with hexanes in order to remove excess arene and unreacted **3-In**. Then, the product was extracted from the aqueous phase with dichloromethane (three times). The combined DCM extracts were washed once with diluted HCl, once with brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvents under reduced pressure, the product was precipitated by portionwise addition of diethyl ether to dye solution in 5 mL of DCM/MeOH 3/2 and frequent sonication. After filtration and drying under vacuum, 145 mg of crude product was obtained, which was slightly impure according to the ^{1}H NMR spectrum. The product was purified by column chromatography (silica gel, dichloromethane/methanol 95/5 to 93/7) and the fractions containing the product were concentrated in vacuo and subjected to recrystallization by dissolution in DCM/MeOH mixture and precipitation by slow addition of Et_2O. The first fraction of the precipitate was an impurity and was discarded. The addition of more Et_2O and sonication resulted in the precipitation of the pure product. Filtration and drying under vacuum provided 45 mg (0.099 mmol, 29%) of **4-In** as a violet-black solid. Mp. 255–259 °C (with decomposition). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.82 (d, J = 7.9 Hz, 1H), 7.71 (s, 2H), 7.70 – 7.65 (m, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 6.18 (s, 2H), 3.88 – 3.76 (m, 4H), 3.36 (s, 6H), 2.81 (t, J = 7.6 Hz, 4H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 164.5 (s), 161.3 (s), 149.4 (s), 132.7 (s), 132.1 (s), 130.7 (s), 130.1 (s), 129.7 (s), 127.3 (q, J_{CF} = 3.7 Hz), 125.6 (s), 124.2 (q, J_{CF} = 273.9 Hz), 109.2 (s), 56.2 (s), 35.4 (s), 26.2 (s). HRMS (ESI) m/z calcd. for $C_{26}H_{22}F_3N_2$ (M^+): 419.1735; found: 419.1737.

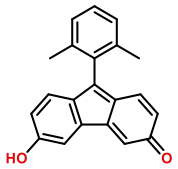
6-(Dimethylamino)-9-(2,6-dimethylphenyl)-3*H*-fluoren-3-one (5-H)



The compound **4-H** (313 mg, 0.800 mmol) was dissolved in a mixture of methanol (100 mL) and water (300 mL). A solution of sodium hydroxide (1M in water, 8.0 mL, 8.0 mmol) was added and the mixture was stirred at rt for 3 h. The reaction mixture was then acidified with 10 mL of 2M hydrochloric acid, diluted with brine, and extracted with dichloromethane (four times). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the product was purified by column chromatography (silica gel, dichloromethane/acetone 95/5) to give 99 mg (0.302 mmol, 38%) of **5-H** as a black solid. Mp. 124–127 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.27 – 7.20 (m, 1H), 7.14 (d, J = 7.6 Hz, 2H), 6.96 (d, J =

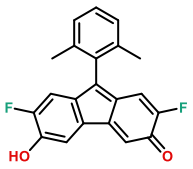
2.2 Hz, 1H), 6.68 (d, *J* = 9.5 Hz, 1H), 6.64 – 6.48 (m, 2H), 6.26 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.90 (dd, *J* = 9.5, 1.3 Hz, 1H), 3.06 (s, 6H), 2.19 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) *δ* 188.8, 157.4, 152.7, 151.2, 141.1, 136.5, 133.7, 132.2, 131.5, 129.4, 128.8, 127.8, 125.7, 125.6, 121.3, 111.1, 108.5, 40.8, 20.2. HRMS (ESI) m/z calcd. for $C_{23}H_{22}NO$ ($[M+H]^+$): 328.1701; found: 328.1704.

9-(2,6-Dimethylphenyl)-6-hydroxy-3*H*-fluoren-3-one (6-H)



To a solution of compound **4-H** (175 mg, 0.448 mmol) in 100 mL of methanol was added a solution of sodium hydroxide (1.60 g, 40 mmol) in 100 mL of water and the reaction mixture was stirred at rt for 3 days. Then solid sodium hydroxide (6.40 g, 160 mmol) was added, the reaction temperature was increased to 60 °C and stirring was continued for 2 days at 60 °C. The obtained green reaction mixture was washed with toluene and hexanes and then acidified with 20 mL of conc. hydrochloric acid (36%) and extracted with chloroform (four times). The combined chloroform extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the product was purified by column chromatography (silica gel, dichloromethane/methanol 95/5) to give the crude product (88 mg), which was dissolved in a hot mixture of toluene (6 mL) and ethanol (2 mL) and precipitated by slow addition of excess hexanes and sonication, then cooled in a refrigerator. After filtration and drying under vacuum, 67 mg (0.223 mmol, 50%) of **6-H** was obtained as a black crystalline powder. Mp. 279–282 °C. Neutral **6-H**: ^{1}H NMR (500 MHz, DMSO-d_6, 90 °C) *δ* 7.29 – 7.23 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 6.88 (s, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 6.20 (d, *J* = 8.5 Hz, 2H), 2.13 (s, 6H). Sodium salt of **6-H**: ^{1}H NMR (500 MHz, 50/10/1 (*v*/*v*/*v*) DMSO-d_6 / D_2O / 30% NaOD in D_2O) δ 7.23 – 7.16 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 1.8 Hz, 2H), 6.28 (d, *J* = 8.8 Hz, 2H), 5.69 (dd, *J* = 8.8, 1.8 Hz, 2H), 2.12 (s, 6H). ^{13}C NMR (126 MHz, 50/10/1 (*v*/*v*/*v*) DMSO-d_6 / D_2O / 30% NaOD in D_2O) *δ* 183.9, 163.8, 148.3, 135.6, 132.7, 131.9, 129.1, 128.1, 125.0, 120.2, 119.7, 20.3. HRMS (ESI) m/z calcd. for $C_{21}H_{16}O_2Na$ ($[M+Na]^+$): 323.1048; found: 323.1050.

9-(2,6-Dimethylphenyl)-2,7-difluoro-6-hydroxy-3*H*-fluoren-3-one (6-F)



Step 1. The solution of 2,6-dimethylphenylmagnesium bromide · LiCl (~0.5M in THF, 6.0 mL, ~3.0 mmol, prepared as above) was added by syringe to a stirred solution of 3,6-bis(dimethylamino)-2,7-difluoro-9H-fluoren-9-one (**3-F**) (121 mg, 0.40 mmol) in 5.0 mL of anhydrous THF at rt under argon atmosphere. The resulting mixture was stirred at 50 °C for 3 h and quenched with water and a saturated ammonium chloride solution. The mixture was extracted with chloroform (four times) and the combined organic layers (pale yellow in appearance) were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the residue (216 mg) was dissolved in a two-phase mixture of dichloromethane (10 mL), water (10 mL) and trifluoroacetic acid (1.0 mL) and stirred at rt for 3 h, during which the color of the mixture changed from pale yellow to bloody red, indicating the formation of salt **4-F**. The layers were separated, and the aqueous layer was extracted with chloroform (four times). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the solvents were removed under reduced pressure to give crude **4-F**, which was used directly in the next step.

Step 2. The crude **4-F** was dissolved in 100 mL of methanol and a solution of sodium hydroxide (0.80 g, 20 mmol) in 100 mL of water was added and the reaction mixture was stirred for 24 h. Then solid sodium hydroxide (3.20 g, 80 mmol) was added, the reaction temperature was increased to 60 °C and stirring was continued for 24 h at 60 °C. The obtained mixture was washed with toluene and hexanes and then acidified with 10 mL of conc. hydrochloric acid (36%) and extracted with chloroform (four times). The combined chloroform extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the product was purified by column chromatography (silica gel, dichloromethane/methanol 95/5) to give the crude product (84 mg), which was dissolved in a hot mixture of toluene (6 mL) and ethanol (2 mL) and precipitated by slow addition of excess hexanes and sonication, then cooled in a refrigerator. After filtration and drying under vacuum, 61 mg (0.181 mmol, 45% from **3-F**) of **6-F** was obtained as a black crystalline powder. Mp. > 280 °C (decomposition). Neutral **6-F**: ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ 7.32 – 7.26 (m, 1H), 7.20 (d, J = 7.5 Hz, 2H), 7.00 (d, J_{HF} = 5.1 Hz, 2H), 6.36 (d, J_{HF} = 10.2 Hz, 2H), 2.17 (s, 6H). Sodium salt of **6-F**: ^{1}H NMR (600 MHz, 50/1 (*v*/*v*) D_2O / 30% NaOD in D_2O) δ 6.96 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H), 6.39 (d, J_{HF} = 7.5 Hz, 2H), 5.87 (d, J_{HF} = 10.7 Hz, 2H), 1.98 (s, 6H). ^{1}H NMR (600 MHz, 50/1 (*v*/*v*) CD_3OD / 30% NaOD in D_2O) δ 7.27 – 7.22 (m, 1H), 7.16 (d, J = 7.6 Hz, 2H), 6.49 (d, J_{HF} = 7.4 Hz, 2H), 6.06 (d, J_{HF} = 10.7 Hz, 2H), 2.27 (s, 6H). ^{13}C NMR (126 MHz, 50/1 (*v*/*v*) CD_3OD / 30% NaOD in D_2O) δ 171.4 (d, J_{CF} = 16.3 Hz), 167.2 (s), 154.5 (d, J_{CF} = 244.3 Hz), 144.9 (s), 135.4 (s), 130.8 (s), 128.6 (s), 127.3 (s), 127.1 (d, J_{CF} = 7.1 Hz), 119.6 (s), 114.8 (d, J_{CF} = 20.5 Hz). HRMS (ESI) m/z calcd. for $C_{21}H_{14}F_2O_2Na$ ($[M+Na]^+$): 359.0860; found: 359.0868.

2. X-ray structure of compound 6-H

Single crystals of compound **6-H** were obtained by slow diffusion of *n*-pentane vapour into the solution of **6-H** in a chloroform/methanol mixture. The crystal selected for the X-ray experiment was a small cube with dimensions 0.171 mm x 0.170 mm x 0.131 mm.

Crystal data for compound **6-H**: $C_{21}H_{16}O_2$; M_r = 300.34, orthorhombic, a = 20.1860(15) Å, b = 7.3066(6) Å, c = 20.4874(17) Å, $\alpha = \beta = \gamma = 90°$, V = 3021.7(4) Å^3, T = 296(2) K, λ = 1.54178 Å (CuK\α), space group *Pbcn* (no. 60), Z = 8, μ = 0.664 mm^{-1}, d = 1.320 g cm^{-3}, F(000) = 1264, 43029 reflections collected, 2097 independent (R_{int} = 0.2010) which were used in all calculations, 2θ range 8.634–101.8°, Goodnes of Fit = 0.993. The final R_1 and $wR_2(F^2)$ were 0.1656 and 0.1707 (all data), 0.0684 and 0.1489 ($I > 2\sigma(I)$). Largest diff. peak and hole: 0.265 and −0.241 eÅ^{-3}. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2090872. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

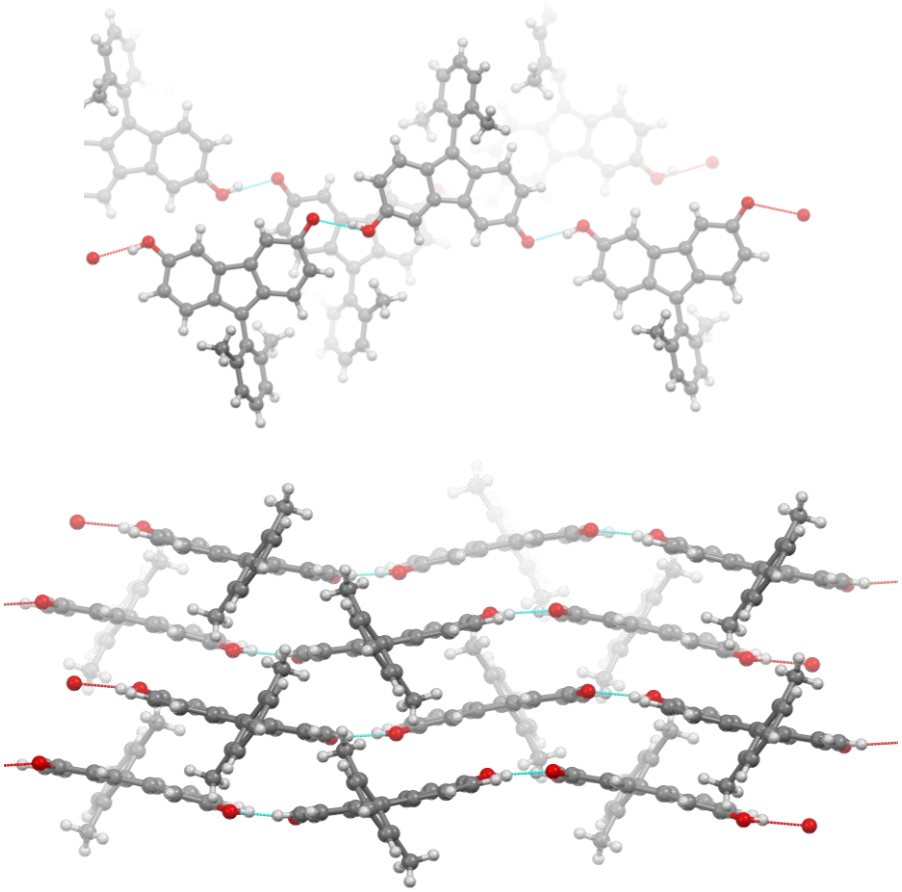


Figure S1. Hydrogen bonding in the crystal structure of compound **6-H**. Top: view perpendicular to the π-system. Bottom: view parallel to the π-system. The O···O distances are 2.67 Å.

3. pK_a of 6-H and 6-F

Solutions of dyes **6-H** and **6-F** (c_{dye} = 1.45 × 10^{-5} M and 1.25 × 10^{-5} M, respectively) in a series of aqueous pH buffers (pH = 4–10) containing 4% vol. DMSO were prepared. The following aqueous buffer systems were used: pH = 4.0–7.5: citric acid/Na_2HPO_4; pH = 8.0–9.0: HCl/Tris; pH = 10: $NaHCO_3$/Na_2CO_3. The absorption spectra of these solutions were recorded using a Schimadzu UV-3600i Plus UV-Vis-NIR spectrophotometer. The absorbance at 800 nm for **6-H** and at 850 nm for **6-F** was plotted against the pH values and analyzed by non-linear least square curve fitting using the following equation:

$$A = \frac{A_0 \cdot 10^{-\mathrm{pH}} + A_\infty \cdot 10^{-\mathrm{p}K_\mathrm{a}}}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K_\mathrm{a}}}$$

where A_0 and A_∞ represent the initial and final absorbance values, respectively.

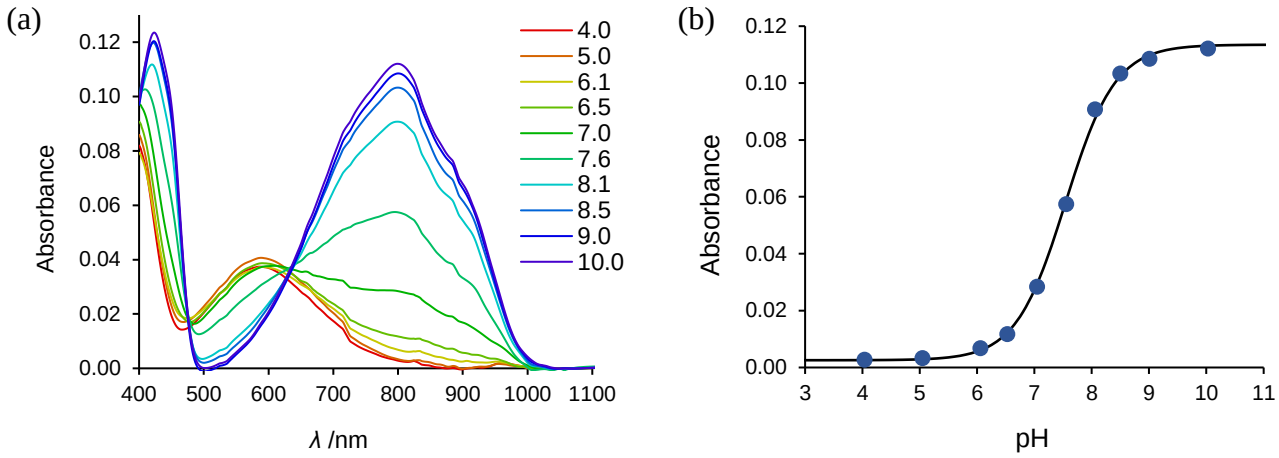


Figure S2. (a) Absorption spectra of compound **6-H** at various pH values. (b) The plots of absorbance of compound **6-H** at 800 nm as a function of the pH value and their fitting curve (pK_a = 7.54, r = 0.9995).

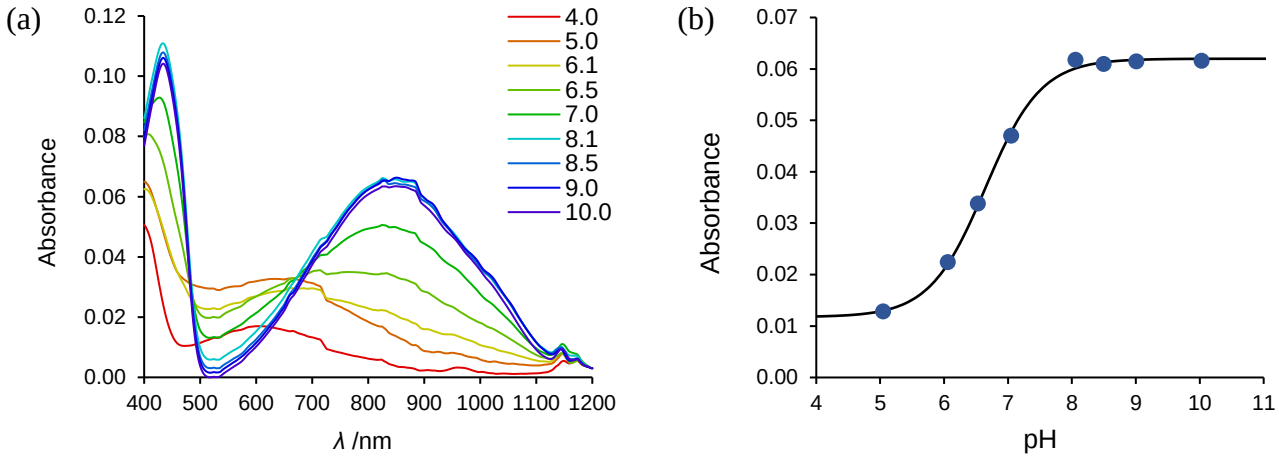


Figure S3. (a) Absorption spectra of compound **6-F** at various pH values. (b) The plots of absorbance of compound **6-F** at 850 nm as a function of the pH value and their fitting curve (pK_a = 6.65, r = 0.9993). At pH = 4.0 the dye precipitated, and therefore this point was excluded from the calculations.

4. Photophysical properties

Table S1. Wavenumber of band maximum ν_{max}, molar absorption coefficient ε_{max} and oscillator strength **f** [a] for S_1, S_2, and S_2 states of **4-H**, **4-H-CF$_3$**, **4-In, 5-H, 6-H**, and **6-F** in water containing 1-5% (*v*/*v*) DMSO as a cosolvent.

Dye	Parameter	S_1	S_2	S_3
4-H [b]	ν_{abs} / cm^{-1}	10604.0	21052.6	26595
	ε_{max} / M^{-1} cm^{-1}	14693	11845.7	40532
	f	0.15	0.16	0.43
4-H-CF$_3$ [b]	ν_{abs} / cm^{-1}	10504.2	20876.8	26660.5
	ε_{max} / M^{-1} cm^{-1}	14611	12129	44303.6
	f	0.16	0.17	0.53
4-In [b]	ν_{abs} / cm^{-1}	9496.9	21692.0	25974.0
	ε_{max} / M^{-1} cm^{-1}	5085	6909	34448
	f	0.064	0.15	0.60
5-H [b]	ν_{abs} / cm^{-1}	12330.5	23255.8	27624.3
	ε_{max} / M^{-1} cm^{-1}	4721	5465	19022
	f	0.080	0.090	0.35
6-H [c]	ν_{abs} / cm^{-1}	12484.4	23696.7	28653.3
	ε_{max} / M^{-1} cm^{-1}	7704	8916.4	35637.4
	f	0.11	0.14	0.58
6-F [c]	ν_{abs} / cm^{-1}	11876.5	23094.7	29940.1
	ε_{max} / M^{-1} cm^{-1}	4512.2	8002.4	29212.7
	f	0.079	0.14	0.54

[a] Oscillator strengths were calculated by integration of absorption bands using the formula: $f = \frac{4.49\ 10^{-9}}{n} \int \varepsilon(\vartheta) d\vartheta$, where n is solvent refraction index and $\varepsilon(\nu)$ is molar absorption coefficient.; [b] With 5% (*v*/*v*) DMSO as co-solvent; [c] In 0.1 M carbonate buffer (pH = 10.0) with 1% (*v*/*v*) DMSO as a cosolvent.

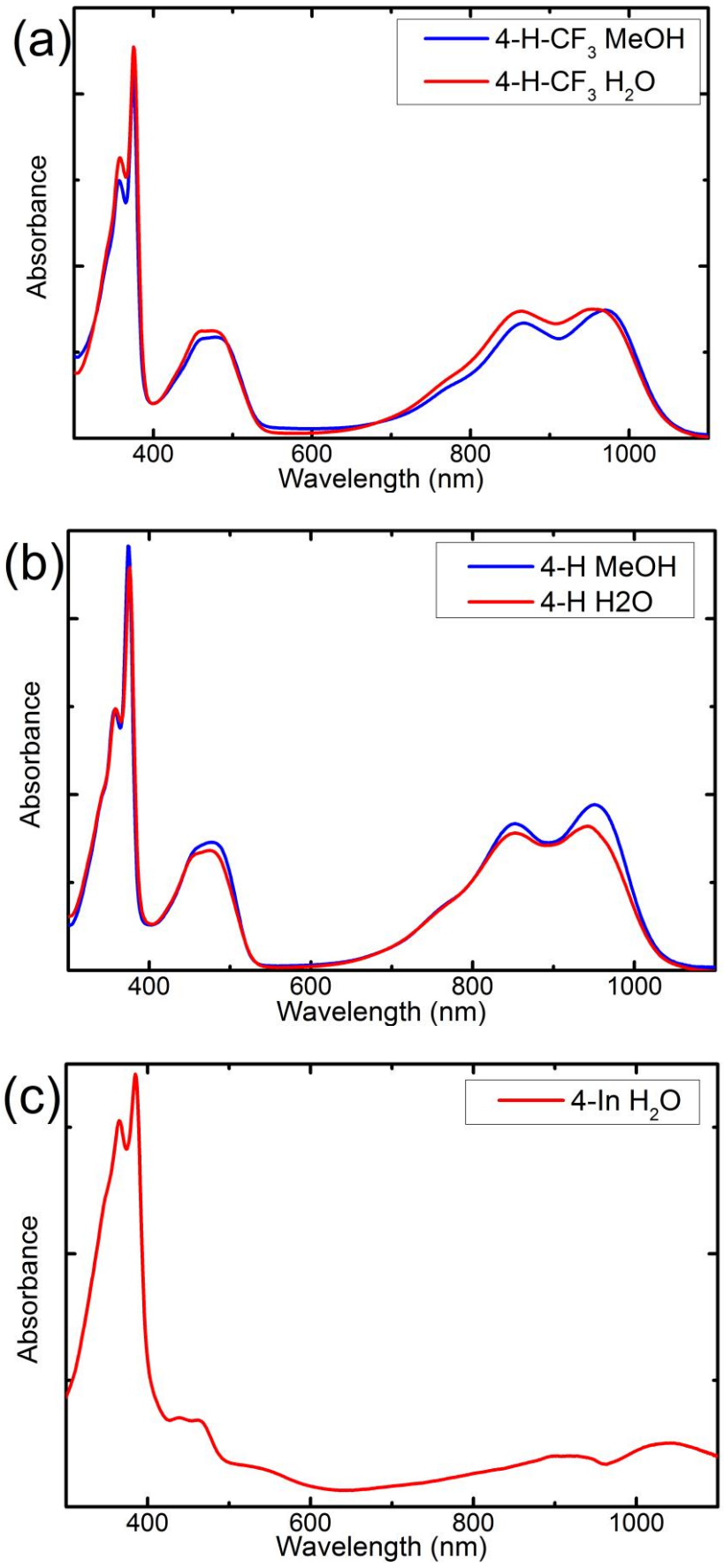


Figure S4. Absorption spectra of **4-H-CF$_3$** (a) and **4-H** (b) in methanol and water containing 5% (*v*/*v*) DMSO. Absorption spectrum of **4-In** in water containing 5% (*v*/*v*) DMSO (c).

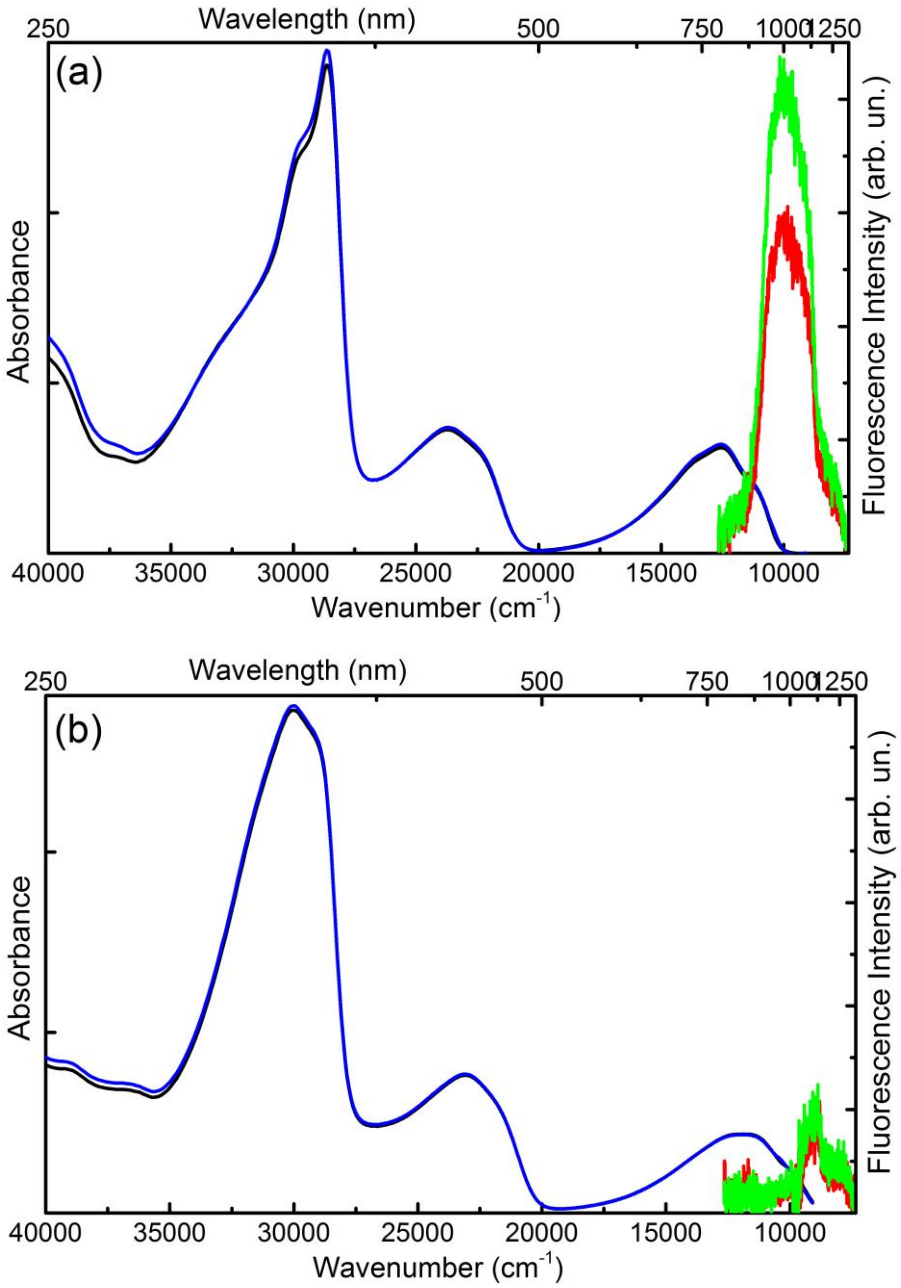


Figure S5. Absorption and fluorescence spectra of **6-H** (a) and **6-F** (b) in water at pH = 9.0 (Tris/HCl buffer): blue line for absorption and red for emission, and at pH = 10.0 ($NaHCO_3/Na_2CO_3$ buffer) – black line for absorption and green for emission. The solutions were prepared using 1% DMSO (*v*/*v*) as cosolvent.

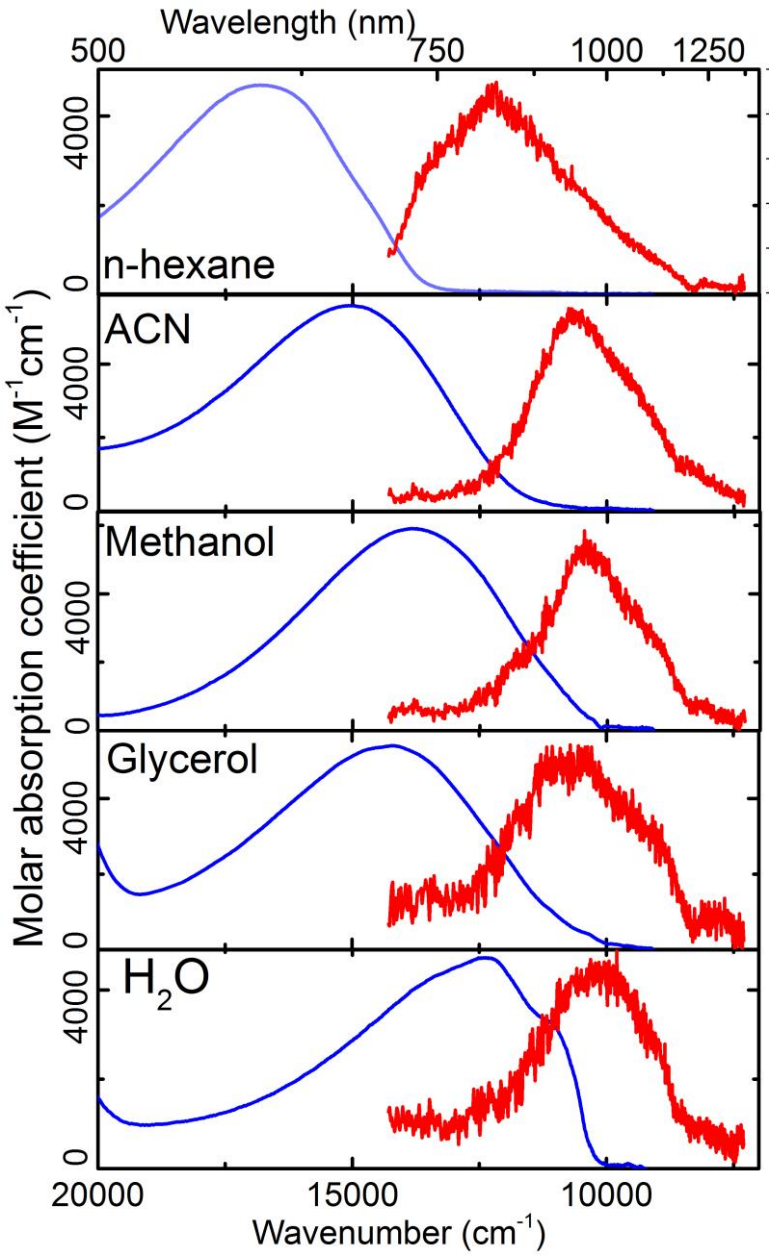


Figure S6. Absorption (blue) and normalized fluorescence spectra (red) of **5-H** in various solvents. Excitation at 656.7 nm.

Table S2. Positions of absorption (ν_{abs}) and fluorescence maxima (ν_{em}), molar absorption coefficients (ε_{max}), and fluorescence quantum yields (Φ_F) of **5-H** in various solvents. α – hydrogen-bond donor acidity.

Solvent	ν_{abs} / cm^{-1}	ε_{max} / M^{-1} cm^{-1}	ν_{em} / cm^{-1}	Φ_F	α
water[a]	12285	4714	10142	1.67×10^{-4}	1.17
methanol	13850	5907	10405	1.72×10^{-4}	0.93
glycerol	14204	5400	10707	1.8×10^{-4}	0.82
acetonitrile	15037	5586	10672	3.11×10^{-4}	0.19
n-hexane	16807	4689	12210	5.33×10^{-4}	0.0

[a] Water containing 5% vol. DMSO as a cosolvent.

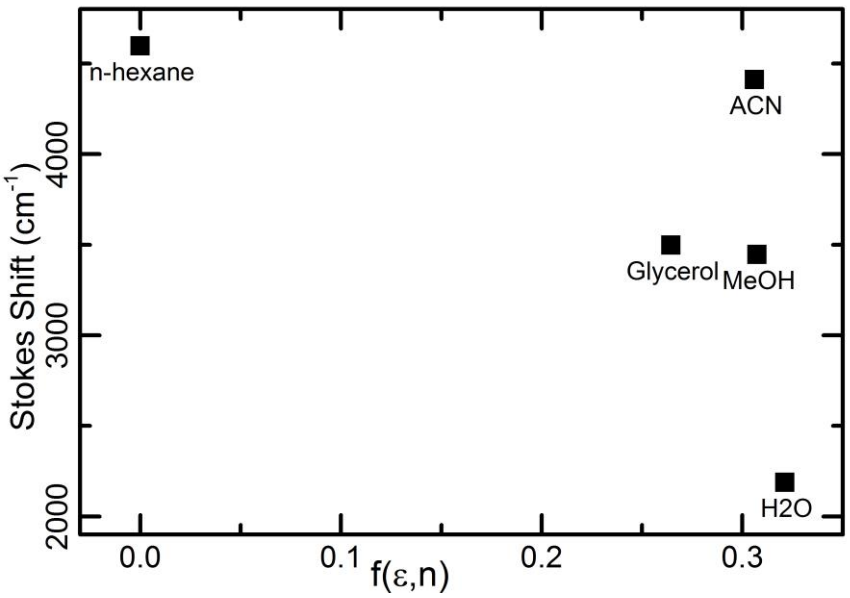


Figure S7. Stokes shifts of **5-H** in various solvents versus Lippert-Mataga solvent parameter, defined as $f(\varepsilon, n) = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}$, where ε and n are dielectric constant and refractive index of the medium, respectively.

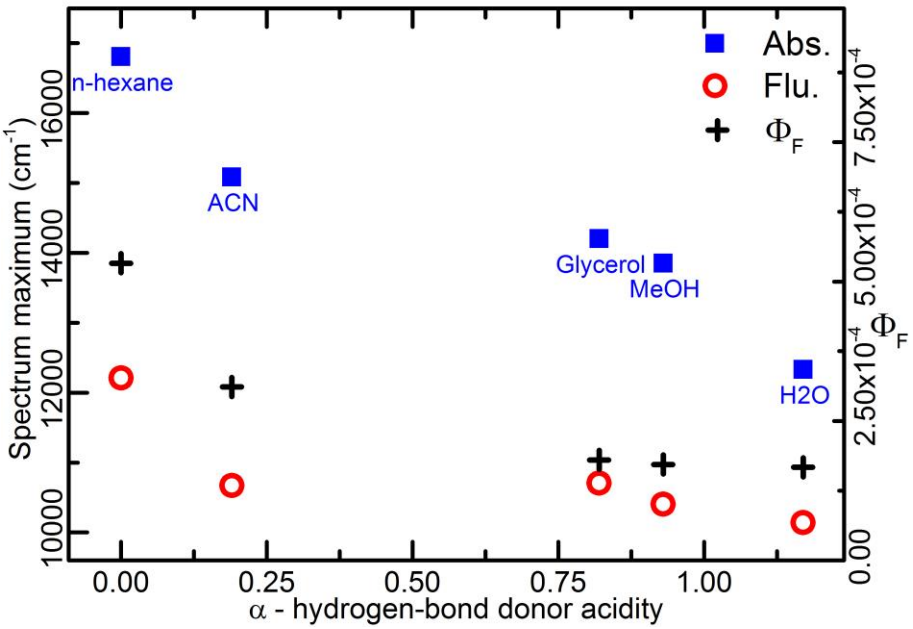


Figure S8. Solvatochromism of absorption (blue squares), fluorescence (red circles), and fluorescence quantum yield, Φ_F, of **5-H** versus α - solvent hydrogen-bond donor acidity.

5. Stability of 4-H and 4-H-CF_3 against nucleophiles

The solutions of dyes **4-H** and **4-H-CF_3** ($c_{dye} \sim 4 \times 10^{-5}$ M) were prepared in three pH buffers (pH = 7.5, citric acid/Na_2HPO_4; pH = 9.1, HCl/Tris; and pH = 10.0, $NaHCO_3/Na_2CO_3$) as well as in a buffer (pH = 7.5, citric acid/Na_2HPO_4) containing DL-homocysteine (HCys, for **4-H**: c_{HCys} = 10.0 mM, for **4-H-CF_3**: c_{HCys} = 0.25 mM, 1.00 mM, and 10.0 mM). The absorption spectra of these solutions were recorded immediately after preparation (0 h) and after 2 h and 20 h (except for **4-H-CF_3** with HCys, which were only recorded immediately, as the equilibration is very rapid).

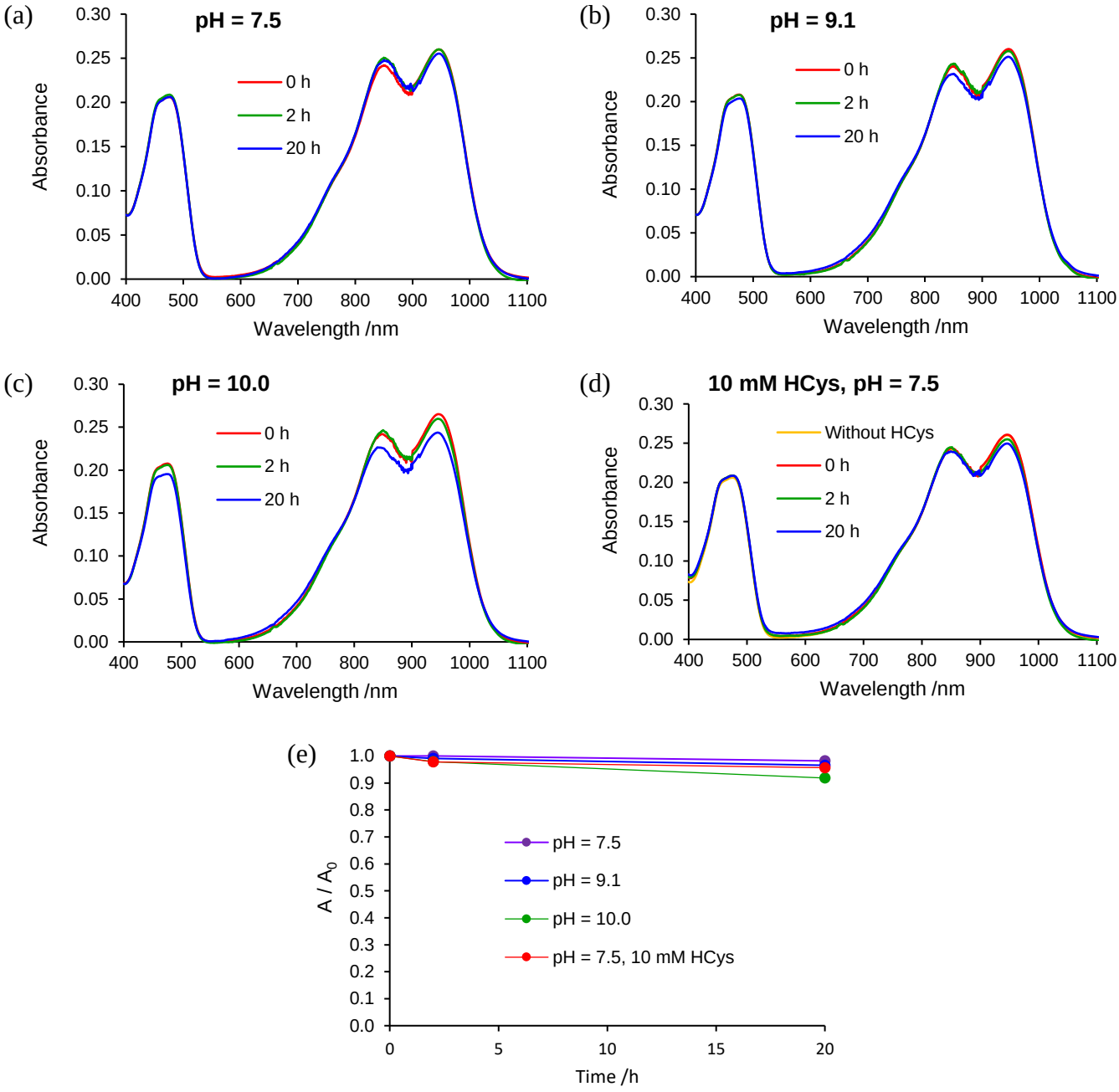


Figure S9. Changes of absorption spectra of **4-H** over time (a) at pH = 7.5, (b) at pH = 9.1, (c) at pH = 10.0, (d) at pH = 7.5 in the presence of 10 mM DL-homocysteine (HCys). (e) Normalized absorbance near the absorption maxima (λ = 950 nm) plotted against time.

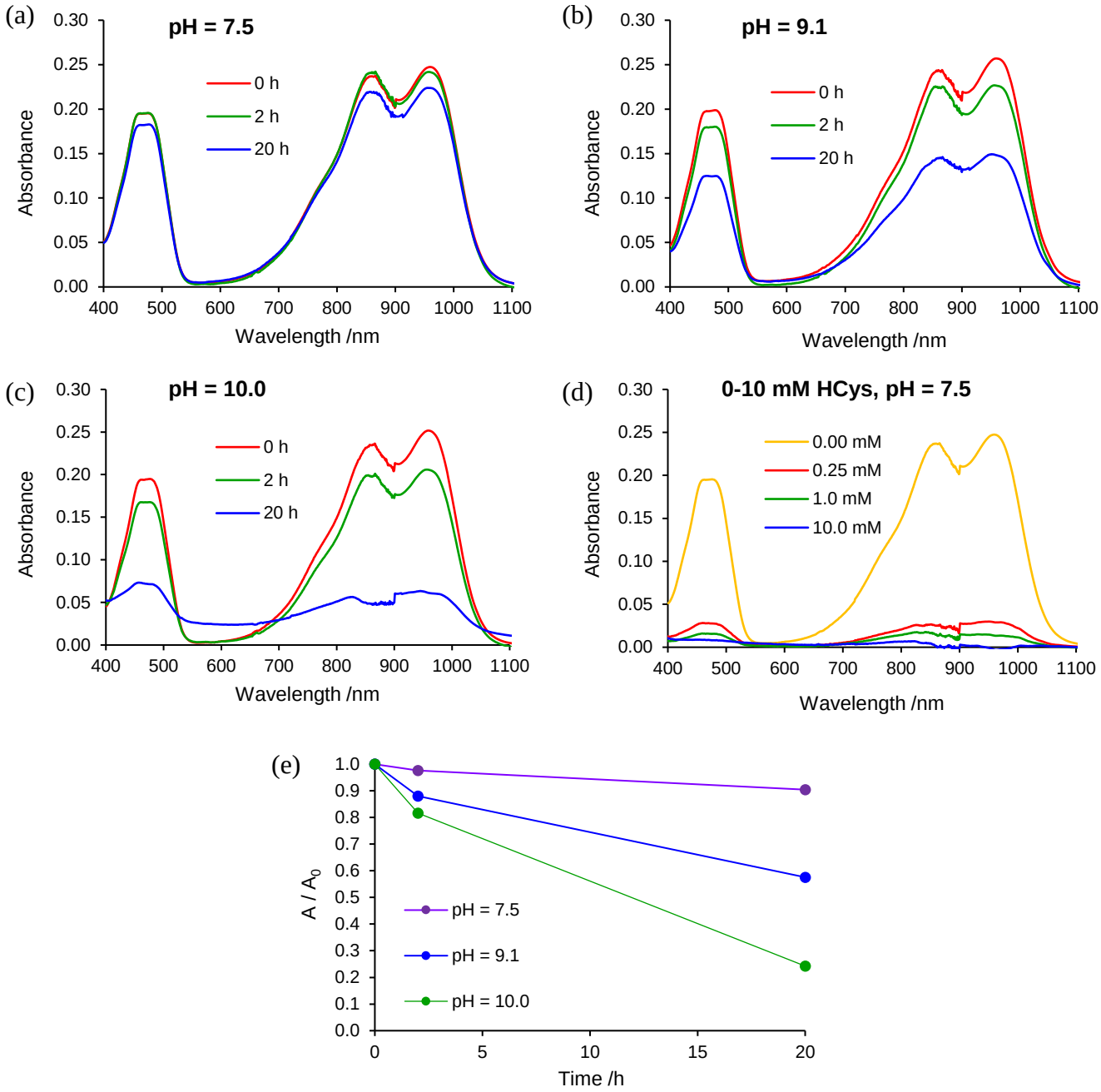


Figure S10. Changes of absorption spectra of **4-H-CF$_3$** over time (a) at pH = 7.5, (b) at pH = 9.1, (c) at pH = 10.0. (d) Spectra of **4-H-CF$_3$** at pH = 7.5 in the presence of various concentrations of DL-homocysteine (HCys). (e) Normalized absorbance near the absorption maxima (λ = 950 nm) at pH values of 7.5, 9.1, and 10.0 plotted against time.

6. DFT calculations

Geometry optimizations were performed using the M06-2X functional[5] with the 6-31+G(d) basis set,[6–8] using the SMD solvation model,[9] implemented in the Gaussian 09 program.[10] Stationary points in the lowest singlet state (S_0) were optimized and characterized by frequency analysis at the same level of theory (the number of imaginary frequencies: 0). TD-DFT calculations were performed on optimized geometries at the same level of theory. The transition energies are overestimated by 0.2-0.5 eV, the common error of the TD-DFT approach for polymethine and xanthene-type dyes.[11,12] The optimized structures and cartesian coordinates of the compounds are given below. Orbitals were visualized with Jmol,[13] and the 3D models with Mercury software.[14] Nuclear-independent nuclear shifts ($NICS(1)_{zz}$)[15] were calculated on the optimized geometries at the same level of theory. For the visualization of magnetically induced current densities and electrostatic potential maps a set of simplified molecules of xanthene dyes and fluorene analogues, where the aromatic substituents at C9 positions were replaced with hydrogen atoms, were optimized in Gaussian 09 program (M06-2X/6-31+G(d), SMD in water). Formatted checkpoint files from the gauge-independent atomic orbital (GIAO)[16] calculation were used in AIMAll[17] software to prepare vector maps of magnetically induced current density and to calculate the ring currents. Chemcraft[18] software was used to visualize molecular electrostatic potential maps.

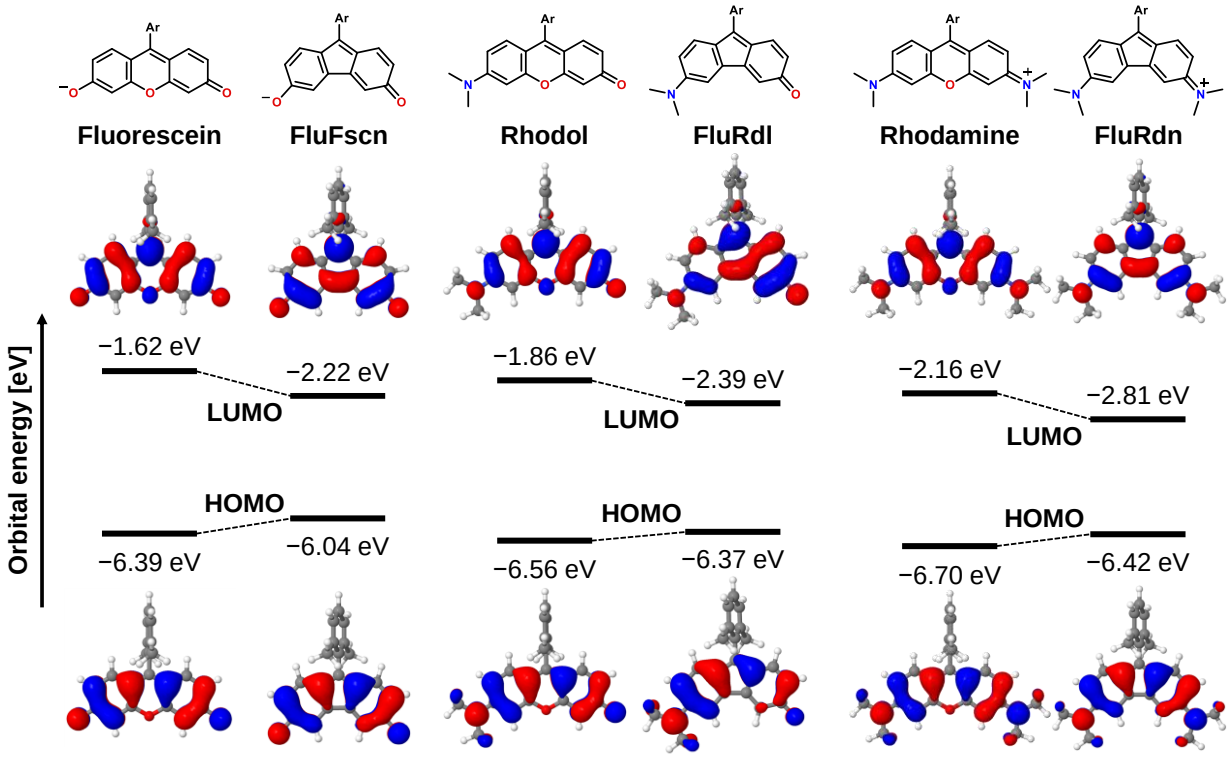


Figure S11. The structural formulas, the calculated energies of HOMO and LUMO orbitals together with their visualizations (HOMO at the bottom, LUMO at the top), calculated at the M06-2X/6-31+G(d) level of theory in water (SMD solvation). Ar = 2,6-dimethylphenyl.

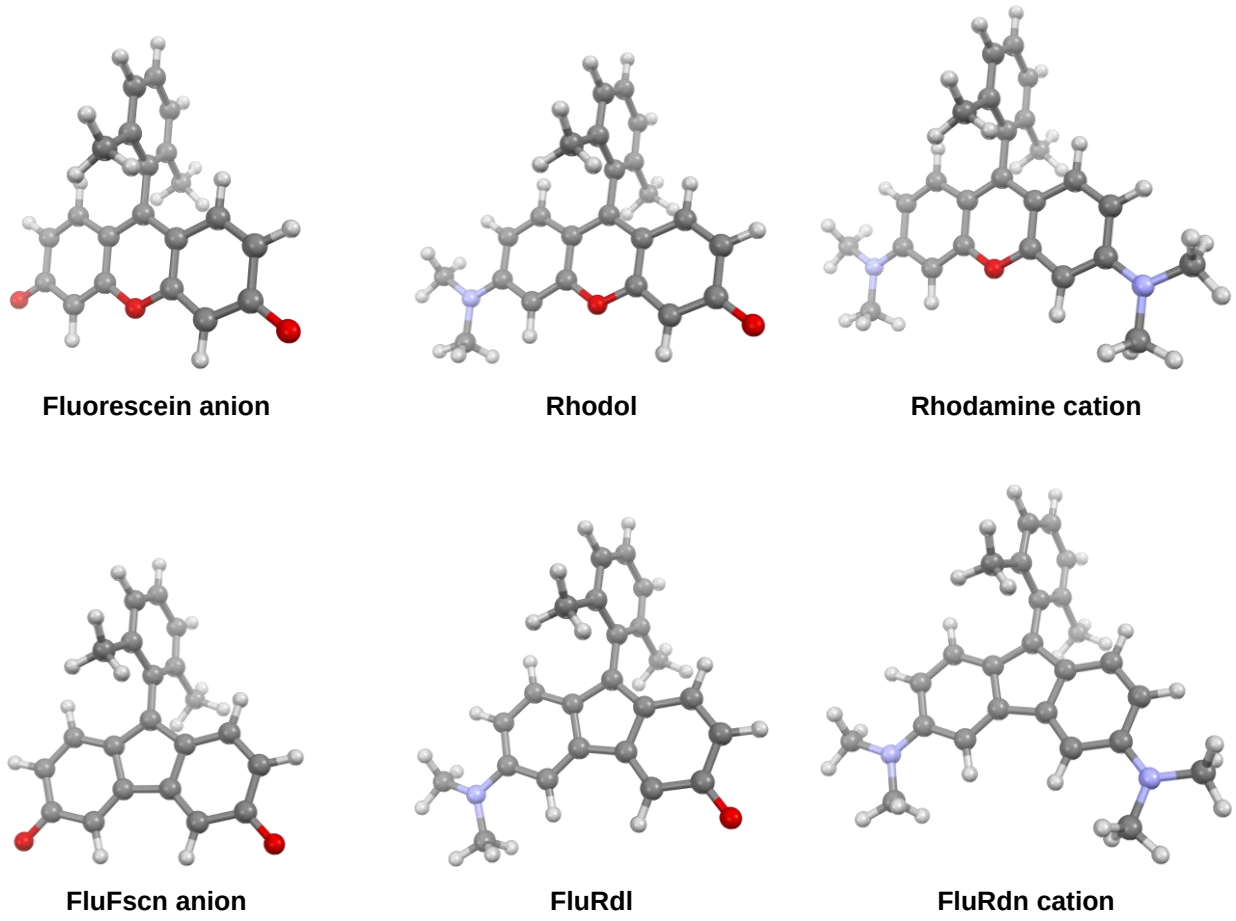


Figure S12. DFT-optimized ground-state molecular structures of xanthene dyes (top) and their fluorene-based analogues (bottom) in water.

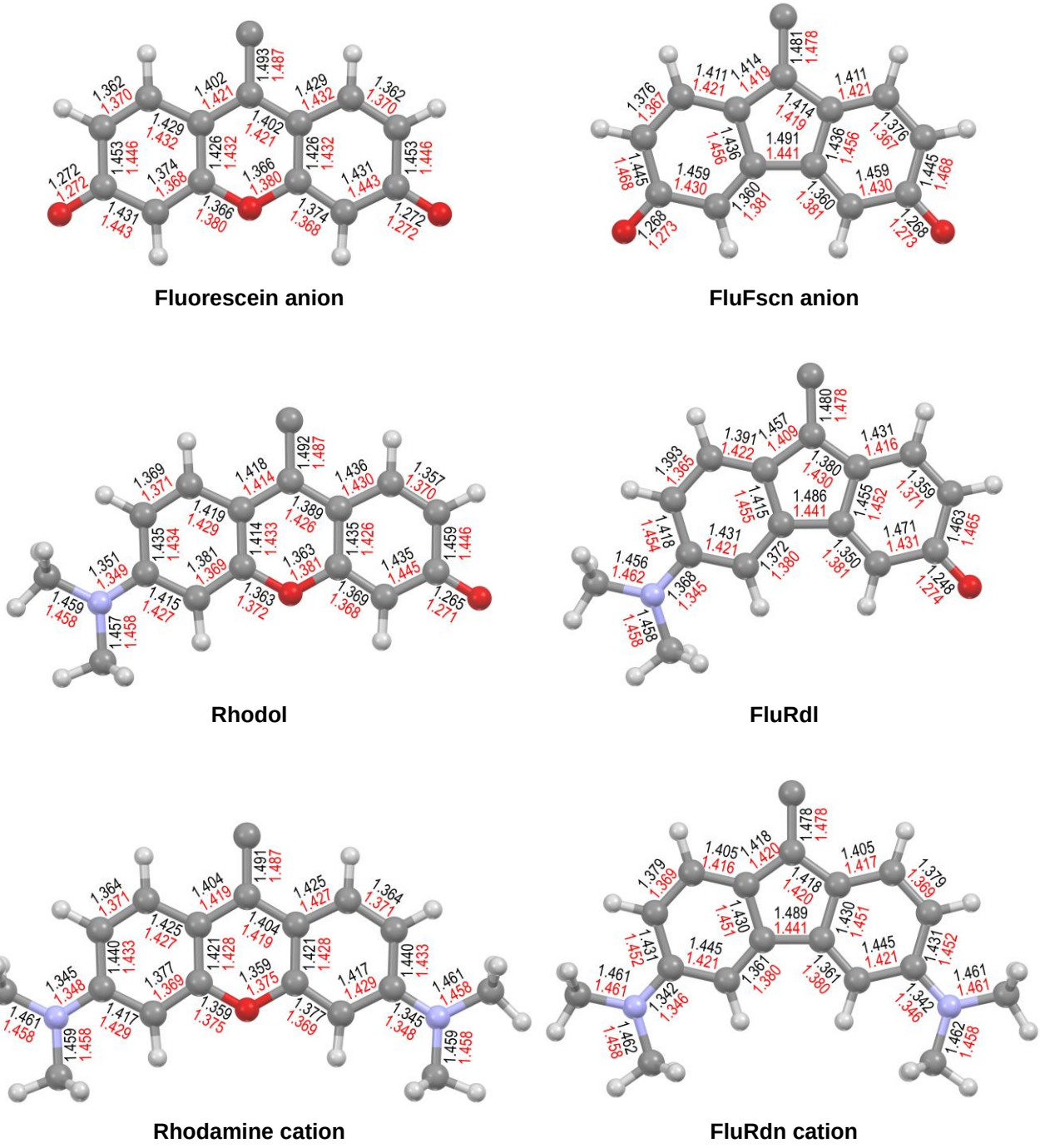


Figure S13. Calculated bond lengths (in Å) in the chromophores of xanthene dyes and their fluorene analogues in water in the ground state S_0 (black) and the first excited S_1 state (red).

Table S3. TD-DFT calculated the S_0 -> S_1 excitation energies, oscillator strengths, and wavelengths in H_2O.

Dye	Excitation energy [eV]	Wavelength [nm]	Oscillator strength *f*	Orbitals contributions
FluFscn	1.8227	680.23	0.1610	77 -> 80 -0.13840 79 -> 80 0.68102
FluRdl	1.9613	632.15	0.1580	84 -> 88 0.14234 87 -> 88 0.67719
FluRdn	1.7195	721.04	0.2223	92 -> 96 -0.17475 95 -> 96 0.67677
Fluorescein	3.0720	403.60	0.7441	83 -> 84 0.69732
Rhodol	3.0136	411.41	0.8263	91 -> 92 0.69637
Rhodamine	2.8863	429.56	0.9381	99 ->100 0.69807

Table S4. TD-DFT calculated S_1 -> S_0 emission energies, oscillator strengths, and wavelengths in H_2O.

Dye	Emission energy [eV]	Wavelength [nm]	Oscillator strength *f*	Orbitals contributions
FluFscn	1.3635	909.28	0.0785	77 -> 80 0.14319 79 -> 80 -0.68652
FluRdl	1.3595	911.96	0.0983	85 -> 88 -0.11910 87 -> 88 0.68210
FluRdn	1.3421	923.81	0.1222	92 -> 96 0.15673 95 -> 96 0.67804
Fluorescein	2.9576	419.21	0.7266	83 -> 84 -0.69831
Rhodol	2.8695	432.07	0.8183	91 -> 92 0.69741
Rhodamine	2.7790	446.15	0.9329	99 ->100 0.69885

Table S5. Mean absolute deviations (MAD)[a] of the bond lengths (in picometers, pm) on the outer rim of the xanthene and fluorene scaffold calculated for optimized geometries of the ground state and S_1 excited state.

	FluFscn	**Fluorescein**	**FluRdl**	**Rhodol**	**FluRdn**	**Rhodamine**
MAD S_0	3.29 pm	3.02 pm	3.82 pm	3.04 pm	2.88 pm	2.69 pm
MAD S_1	2.61 pm	3.08 pm	2.55 pm	2.92 pm	2.32 pm	2.71 pm

[a] Mean absolute deviations were calculated from the formula: $\mathrm{MAD} = \frac{1}{n}\sum_{i=1}^{n} |x_i - \bar{x}|$, where x_i are bond lengths and $\bar{x}$ is the average bond length.

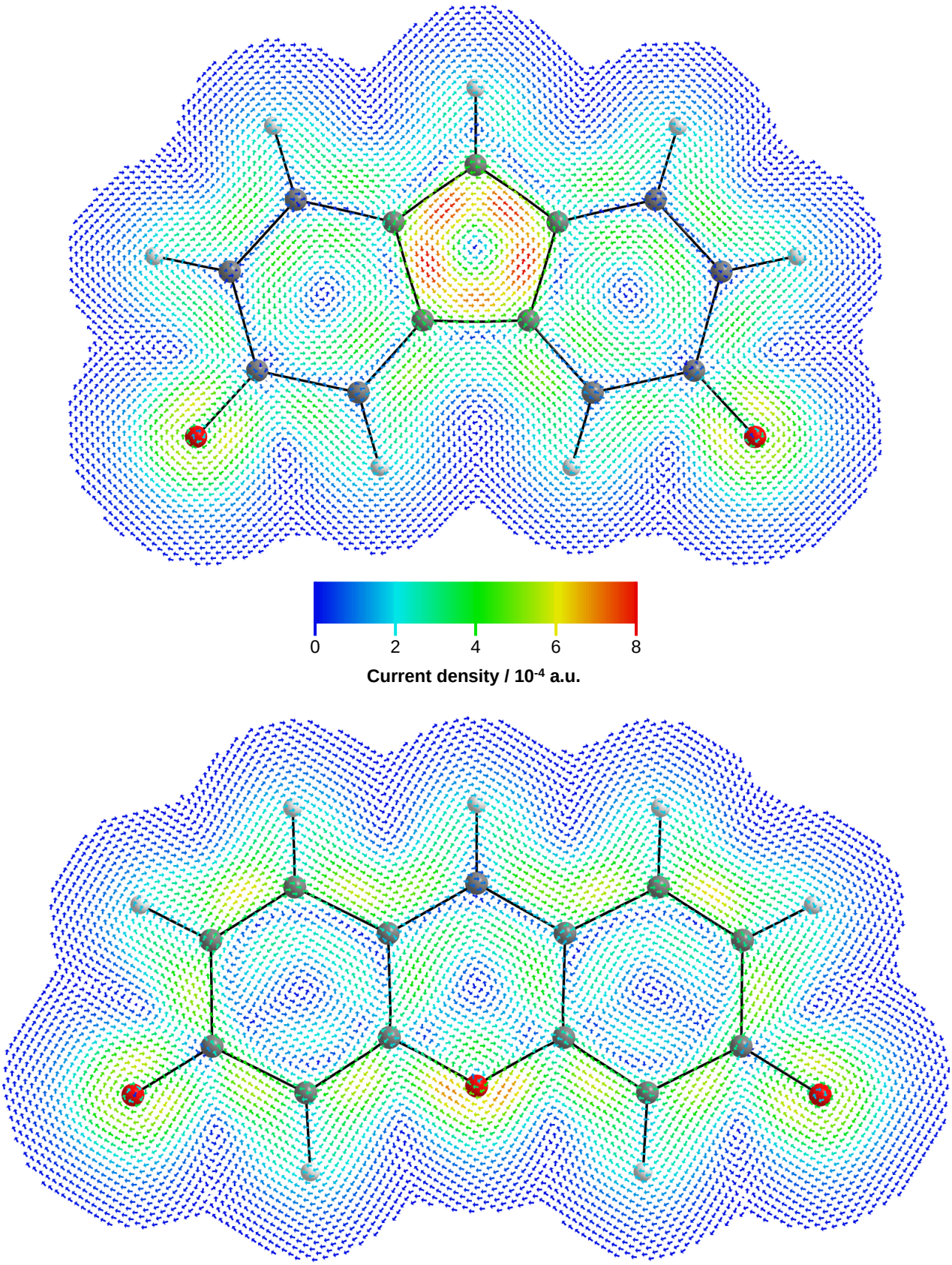


Figure S14. Magnetically induced current density profiles plotted one bohr (0.5292 Å) above the chromophore plane of the simplified molecules (Ar = H) of fluorescein anion (bottom) and its fluorene analogue (top). The colors of the arrows correspond to weak (0.0000 a.u., blue) to strong (0.0008 a.u., red) current density. The magnetic field vector is perpendicular to the chromophore plane and directed towards the reader.

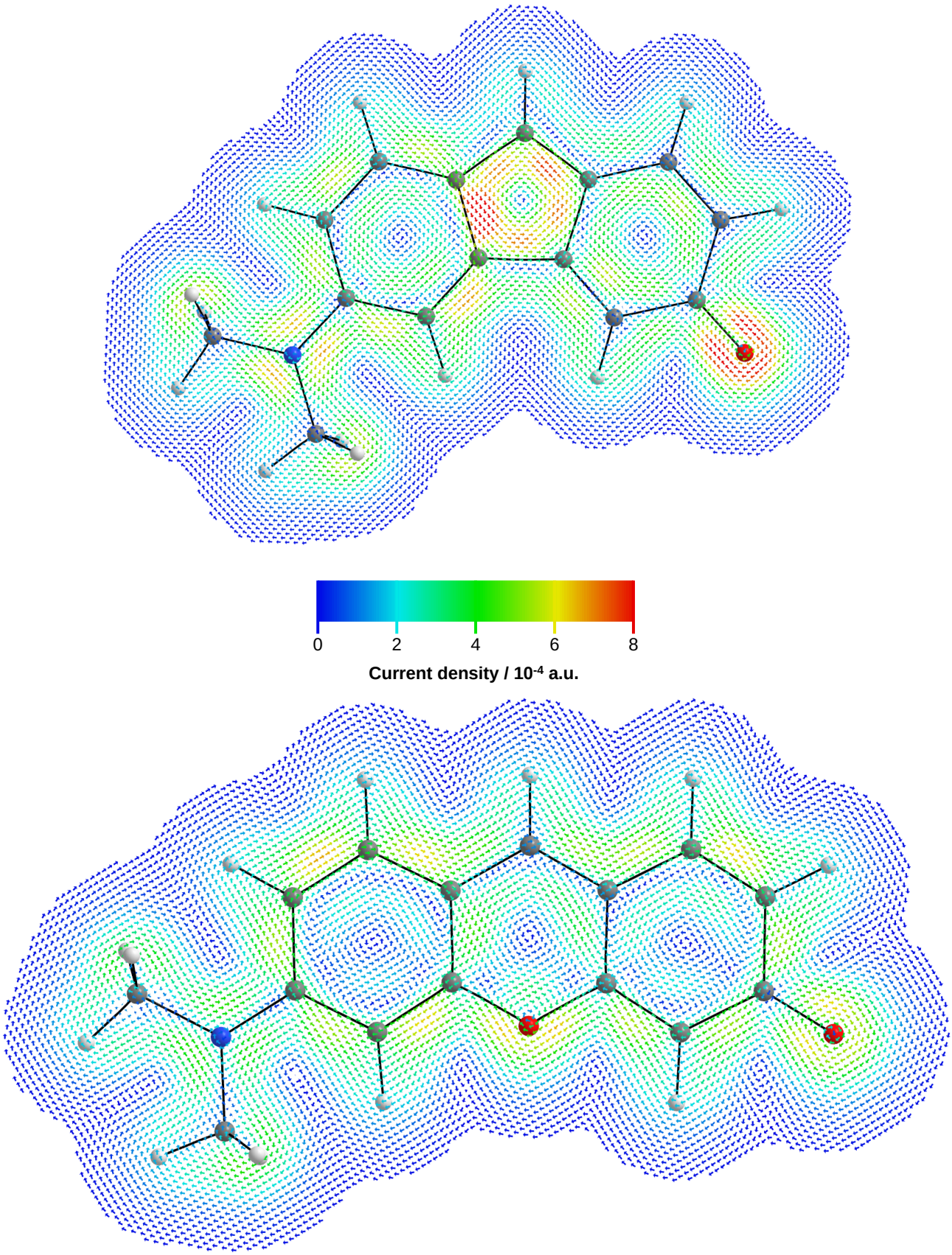


Figure S15. Magnetically induced current density profiles plotted one bohr (0.5292 Å) above the chromophore plane of the simplified molecules (Ar = H) of rhodol (bottom) and its fluorene analogue (top). The colors of the arrows correspond to weak (0.0000 a.u., blue) to strong (0.0008 a.u., red) current density. The magnetic field vector is perpendicular to the chromophore plane and directed towards the reader.

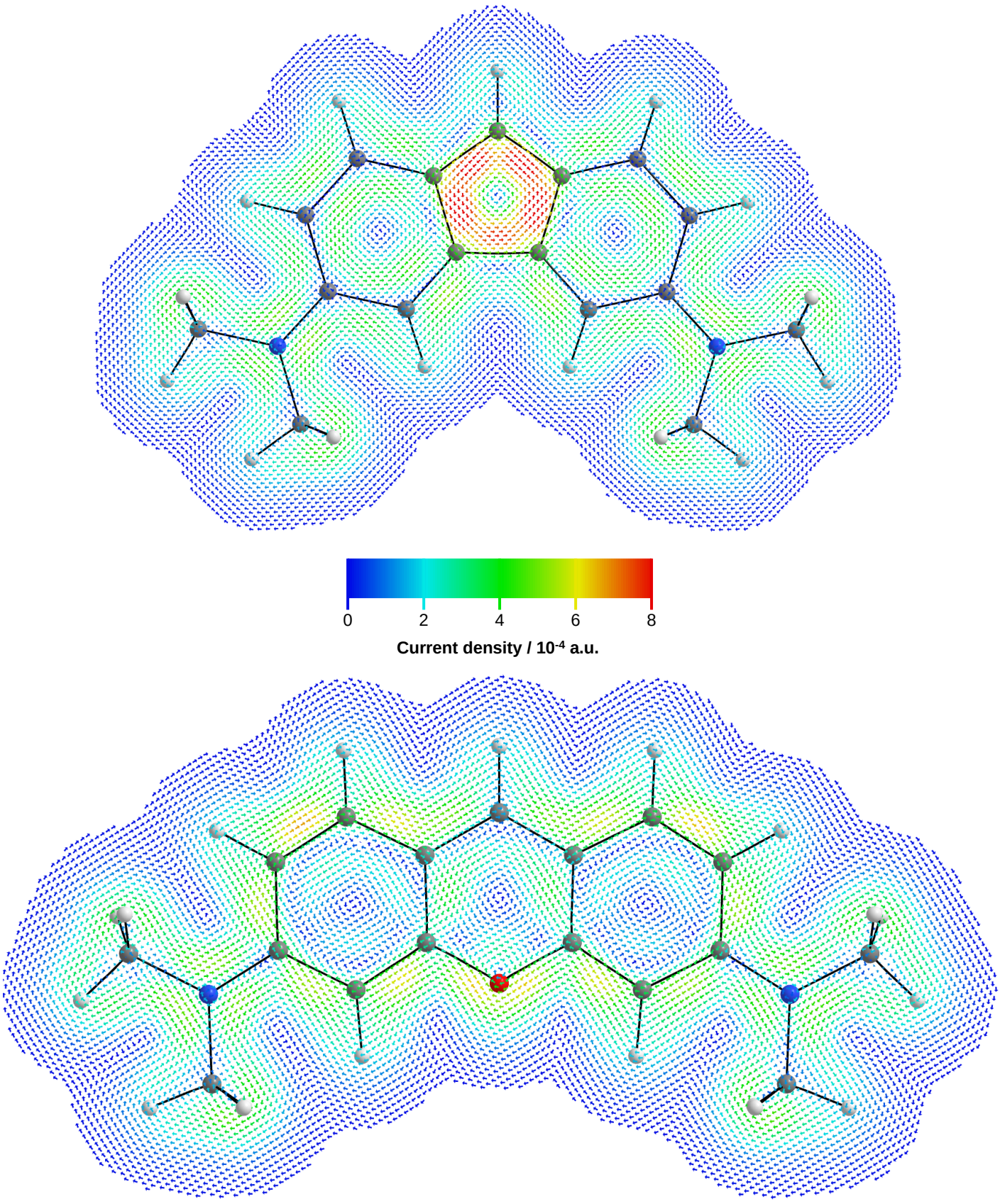


Figure S16. Magnetically induced current density profiles plotted one bohr (0.5292 Å) above the chromophore plane of the simplified molecules (Ar = H) of rhodamine cation (bottom) and its fluorene analogue (top). The colors of the arrows correspond to weak (0.0000 a.u., blue) to strong (0.0008 a.u., red) current density. The magnetic field vector is perpendicular to the chromophore plane and directed towards the reader.

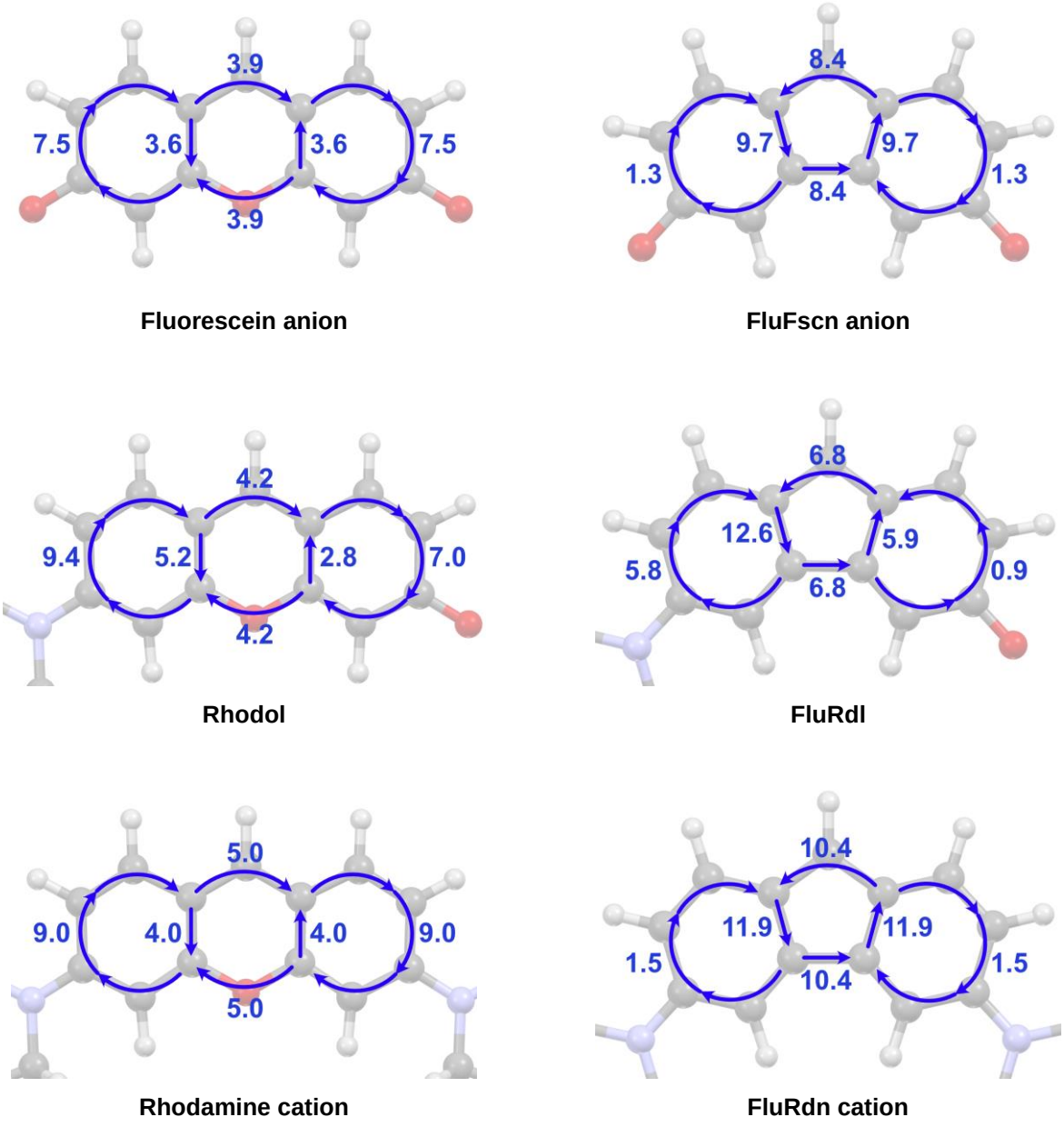


Figure S17. Magnetically induced currents (in nA/T) calculated by the AIMAll software[17] in the simplified molecules (Ar = H) of xanthene dyes (left) and their fluorene analogues (right). Circuit values were averaged from the integration values for each interatomic contact. The magnetic field vector is perpendicular to the chromophore plane and directed towards the reader.

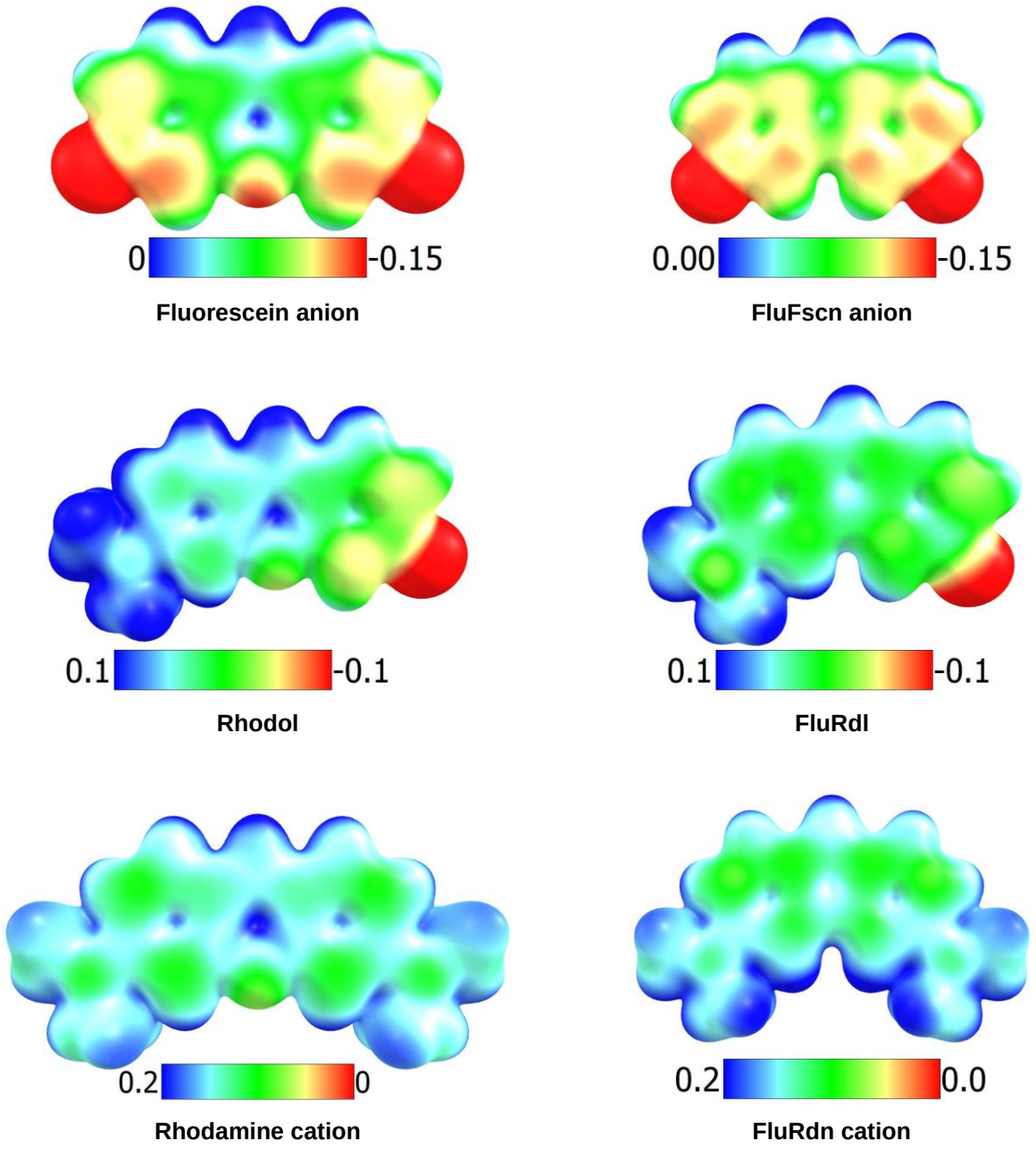


Figure S18. Comparison of the electrostatic potential maps of the simplified molecules (Ar = H) of xanthene dyes (left) and their fluorene analogues (right) mapped onto the electron density isosurfaces (contour value = 0.01). Potential ranges are given in atomic units.

Table S6. Cartesian coordinates (in Å) of the **FluFscn** anion in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	0.85116196	-1.15322624	0.02913580	20	C	-3.53810576	0.34430233	-1.15526323
2	C	2.22771904	-0.74479220	0.01778967	21	C	-2.14036060	0.35799509	-1.17299883
3	C	2.22750352	0.74546064	-0.01835218	22	C	-1.40546329	0.73588961	-2.43521059
4	C	0.85082450	1.15350969	-0.02933108	23	C	-1.40465077	-0.73628851	2.43558257
5	C	0.03272961	0.00002958	0.00000978	24	H	-0.51132142	-2.84251485	0.05690168
6	C	0.53091362	-2.52713335	0.05239774	25	H	1.32148461	-4.52329308	0.09131046
7	C	1.54192929	-3.45968384	0.07168483	26	H	4.29029381	-1.35245442	0.02266536
8	C	2.93496839	-3.07441873	0.06388935	27	H	4.28990219	1.35370765	-0.02378303
9	C	3.24374403	-1.64868367	0.03368581	28	H	1.32018183	4.52371307	-0.09164520
10	C	3.24326495	1.64963844	-0.03452308	29	H	-0.51214119	2.84241573	-0.05674573
11	C	2.93408124	3.07529004	-0.06463820	30	H	-4.07908414	-0.60866747	2.06161358
12	C	1.54092960	3.46016583	-0.07207494	31	H	-5.32124423	-0.00085776	0.00064057
13	C	0.53018488	2.52733079	-0.05251573	32	H	-4.07976870	0.60737772	-2.06061822
14	O	3.86547338	-3.93583635	0.07981168	33	H	-2.08521778	0.71464996	-3.29110304
15	O	3.86434555	3.93695565	-0.08078818	34	H	-0.98661360	1.74618600	-2.36451254
16	C	-1.44799716	-0.00019679	0.00019336	35	H	-0.57406928	0.05231031	-2.63760506
17	C	-2.13996631	-0.35862508	1.17354521	36	H	-0.57336725	-0.05250486	2.63773612
18	C	-3.53772109	-0.34540938	1.15613230	37	H	-2.08418997	-0.71517927	3.29164971
19	C	-4.23477179	-0.00067279	0.00051562	38	H	-0.98558168	-1.74648948	2.36481465

Table S7. Cartesian coordinates (in Å) of the **FluFscn** anion in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	0.85799750	-1.13707247	0.05050646	20	C	-3.56618796	0.38783380	-1.14097563
2	C	2.25298219	-0.71972806	0.03073197	21	C	-2.16816217	0.39516140	-1.15876575
3	C	2.25276186	0.72038772	-0.03130482	22	C	-1.43335886	0.79944772	-2.41229238
4	C	0.85764984	1.13732159	-0.05069981	23	C	-1.43255199	-0.79986421	2.41267395
5	C	0.01039992	0.00000049	0.00001693	24	H	-0.49613772	-2.84548084	0.09543183
6	C	0.54264709	-2.52238629	0.09153934	25	H	1.35722583	-4.49832651	0.15528911
7	C	1.56316450	-3.43133754	0.12353689	26	H	4.32350288	-1.33755142	0.04443225
8	C	2.97767497	-3.04007135	0.11327620	27	H	4.32309417	1.33882480	-0.04557364
9	C	3.27984490	-1.64285919	0.06187531	28	H	1.35585665	4.49872447	-0.15563535
10	C	3.27934085	1.64382318	-0.06273373	29	H	-0.49700105	2.84532978	-0.09526857
11	C	2.97674661	3.04094713	-0.11404639	30	H	-4.10745089	-0.68490780	2.03717722
12	C	1.56211970	3.43179675	-0.12393447	31	H	-5.35050429	-0.00078787	0.00065037
13	C	0.54188043	2.52254264	-0.09165580	32	H	-4.10813109	0.68369712	-2.03616742
14	O	3.87703183	-3.94025270	0.14415518	33	H	-2.12199026	0.84894079	-3.26004789
15	O	3.87583864	3.94138652	-0.14514531	34	H	-0.96441664	1.78442721	-2.30449509
16	C	-1.46787337	-0.00021612	0.00019494	35	H	-0.63641619	0.08785350	-2.65356674
17	C	-2.16777311	-0.39579973	1.15932067	36	H	-0.63580661	-0.08799505	2.65379049
18	C	-3.56580522	-0.38888580	1.14185798	37	H	-2.12097862	-0.84962082	3.26058044
19	C	-4.26392962	-0.00062848	0.00052322	38	H	-0.96328473	-1.78467438	2.30474502

Table S8. Cartesian coordinates (in Å) of **FluRdl** in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	-2.22324905	0.78191623	-0.02532020	24	C	-5.35311314	3.55458711	-0.25077454
2	C	-2.21058856	-0.70342420	-0.05662199	25	C	-3.68046511	5.39941666	-0.17849625
3	C	-0.81196715	-1.10464488	-0.04896354	26	H	-4.26059828	-1.33937978	-0.09045842
4	C	-0.01506461	0.02112103	-0.01526465	27	H	-1.24267232	-4.49057602	-0.10674939
5	C	-0.87142692	1.20021821	0.00068485	28	H	0.57516852	-2.79035167	-0.04983967
6	C	-3.20820384	-1.61233981	-0.08549213	29	H	0.45477148	2.90569155	0.00546726
7	C	-2.87297744	-3.04469557	-0.10757430	30	H	-1.36857197	4.54059388	-0.00557035
8	C	-1.46103629	-3.42696931	-0.09462499	31	H	-4.28847862	1.31882783	-0.06480135
9	C	-0.47213198	-2.49465895	-0.06365032	32	H	4.06434566	0.78963413	2.05164540
10	C	-0.57655755	2.55913932	0.00280573	33	H	5.33461891	0.18035898	0.00806671
11	C	-1.61600738	3.48649967	-0.00253186	34	H	4.12352061	-0.50568483	-2.04590766
12	C	-2.97385463	3.07659424	-0.00461666	35	H	0.57124259	0.13718905	2.61837601
13	C	-3.26496864	1.67539153	-0.03393465	36	H	2.05712040	0.85465201	3.27103260
14	C	1.46396360	0.05810119	-0.00892096	37	H	0.93701079	1.83741100	2.31787094
15	C	2.13871013	0.46284492	1.15972778	38	H	2.14563379	-0.70750737	-3.28173286

16	C	3.53589554	0.49290937	1.14892986	39	H	1.05374032	-1.73497505	-2.34377600
17	C	4.24870056	0.14691983	0.00321810	40	H	0.61679889	-0.05493168	-2.66021784
18	C	3.56902942	-0.24194832	-1.14861920	41	H	-5.44163394	3.10059230	-1.24688391
19	C	2.17236462	-0.29889092	-1.17301898	42	H	-5.69379056	2.83144646	0.49514131
20	C	1.38400784	0.84097693	2.40977254	43	H	-6.01304987	4.41990309	-0.20211552
21	C	1.45691981	-0.71977378	-2.43295321	44	H	-3.00508387	5.76776385	0.59869623
22	N	-3.99072808	3.99155919	0.02873147	45	H	-3.21502696	5.57586035	-1.15806074
23	O	-3.77647960	-3.90543151	-0.13278409	46	H	-4.60413712	5.97396376	-0.12029056

Table S9. Cartesian coordinates (in Å) of **FluRdl** in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	-2.24311742	0.74700628	-0.10479742	24	C	-5.36699311	3.53473975	-0.14735849
2	C	-2.22770861	-0.69390113	-0.12466644	25	C	-3.67506527	5.39389131	-0.08596770
3	C	-0.83156566	-1.09037114	-0.09872557	26	H	-4.29107835	-1.33449080	-0.16904703
4	C	0.00436011	0.06950223	-0.06272528	27	H	-1.28428259	-4.45595646	-0.10694705
5	C	-0.85586565	1.18548683	-0.06433965	28	H	0.54527398	-2.77595581	-0.05562401
6	C	-3.24431016	-1.62860547	-0.15206427	29	H	0.45590018	2.92887866	-0.03939017
7	C	-2.92447988	-3.02290751	-0.15161507	30	H	-1.38179605	4.53255419	-0.06761070
8	C	-1.50756587	-3.39200881	-0.11470870	31	H	-4.30991241	1.29835540	-0.15442955
9	C	-0.49694803	-2.46584884	-0.08716159	32	H	4.05937748	0.85999229	2.05778812
10	C	-0.57304301	2.57879515	-0.05581448	33	H	5.36077227	0.12109324	0.07813696
11	C	-1.60483516	3.47271007	-0.07217552	34	H	4.17897180	-0.63890602	-1.96756481
12	C	-2.99346826	3.04171503	-0.10109118	35	H	0.57667300	0.25596438	2.60324254
13	C	-3.28553239	1.65103310	-0.12288579	36	H	2.04043966	1.04751762	3.22276916
14	C	1.48155737	0.08652958	-0.02419716	37	H	0.90265636	1.94321375	2.20781489
15	C	2.14584696	0.52636039	1.13973867	38	H	2.22592878	-0.85871463	-3.23778236
16	C	3.54384749	0.53046468	1.15886518	39	H	1.05535691	-1.77815767	-2.28307149
17	C	4.27465537	0.11155344	0.04943560	40	H	0.71744570	-0.09676945	-2.69265812
18	C	3.61098157	-0.31955522	-1.09703457	41	H	-5.56790521	2.94420102	-1.04788942
19	C	2.21428113	-0.34057929	-1.15123951	42	H	-5.60850519	2.92675713	0.73143121
20	C	1.37468894	0.96544649	2.35945266	43	H	-6.00737811	4.41406507	-0.15372475
21	C	1.51559514	-0.79135155	-2.40946178	44	H	-3.11348547	5.66127165	0.81456144
22	N	-3.97339818	3.96276281	-0.11110132	45	H	-3.09689829	5.68955449	-0.96716989
23	O	-3.81377351	-3.93485149	-0.17622042	46	H	-4.61399837	5.94341530	-0.08537518

Table S10. Cartesian coordinates (in Å) of the **FluRdn** cation in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	1.52138168	-3.45436714	0.12243355	28	H	1.26938675	-4.50648737	0.15231678
2	C	2.89527272	-3.05261108	0.11110804	29	H	4.24573627	-1.31111799	0.04735482
3	C	3.21419212	-1.64386097	0.06367561	30	H	-0.53041818	-2.84723573	0.09316048
4	C	2.19221837	-0.74552334	0.03561913	31	H	4.24884344	1.30313951	-0.01882921
5	C	0.82146751	-1.15191251	0.05064497	32	H	1.28020507	4.50471331	-0.15014306
6	C	0.50728829	-2.52113197	0.08901864	33	H	-0.52350602	2.84927889	-0.10723564
7	C	2.19408515	0.74184104	-0.02515417	34	H	5.50220030	-2.98464253	-0.80566420
8	C	0.82438973	1.15111793	-0.05273798	35	H	5.52683823	-2.92734993	0.97506116
9	C	-0.00214648	0.00049607	-0.00502666	36	H	5.90961483	-4.43609399	0.12642430
10	C	3.21816784	1.63801205	-0.04443010	37	H	2.97864978	-5.62623325	1.07846029
11	C	2.90263341	3.04741227	-0.09533656	38	H	3.00557602	-5.69322629	-0.70076806
12	C	1.52973457	3.45207767	-0.11807933	39	H	4.49867219	-5.95061529	0.22418652
13	C	0.51343260	2.52098432	-0.09378006	40	H	3.01044915	5.68789749	0.71460733
14	N	3.88147770	-3.96219699	0.13963381	41	H	4.51279109	5.94210197	-0.19590430
15	N	3.89091351	3.95491779	-0.11670023	42	H	3.00033747	5.62045166	-1.06475175
16	C	5.28264672	-3.54724145	0.10698459	43	H	5.53840459	2.91575461	-0.94233690
17	C	3.56824868	-5.38802014	0.18760090	44	H	5.91993239	4.42454383	-0.09321376
18	C	3.58097928	5.38133519	-0.16822183	45	H	5.50456021	2.97484785	0.83817809
19	C	5.29099798	3.53702091	-0.07614665	46	H	-4.12031433	-0.61212517	2.03233782
20	C	-1.47986844	0.00197282	-0.01264049	47	H	-5.34987714	0.00449554	-0.03309903
21	C	-2.17653004	-0.36303549	1.15637067	48	H	-4.09775032	0.61976863	-2.08532382
22	C	-3.57369754	-0.34677360	1.13076356	49	H	-2.09838016	0.71858935	-3.30652241
23	C	-4.26348682	0.00383437	-0.02735028	50	H	-1.01387649	1.76207866	-2.37843950
24	C	-3.56102172	0.35366005	-1.17805285	51	H	-0.58583375	0.07009977	-2.64435655
25	C	-2.16363396	0.36813744	-1.18892250	52	H	-0.61304769	-0.06746826	2.62759272

26	C	-1.42317780	0.74788957	-2.44742249	53	H	-2.13375667	-0.71192436	3.27478897
27	C	-1.44988030	-0.74351277	2.42266803	54	H	-1.04221382	-1.75869395	2.35871660

Table S11. Cartesian coordinates (in Å) of the **FluRdn** cation in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	1.53596498	-3.43048986	0.13038524	28	H	1.29451363	-4.48596886	0.16102813
2	C	2.92955714	-3.02390104	0.12235198	29	H	4.27237034	-1.30004661	0.05688250
3	C	3.24282137	-1.63850178	0.07175116	30	H	-0.51869810	-2.85376033	0.09452237
4	C	2.21199275	-0.72180240	0.03692483	31	H	4.27558421	1.29198051	-0.02855755
5	C	0.82112951	-1.13656502	0.05174218	32	H	1.30550214	4.48422100	-0.15784679
6	C	0.51536080	-2.51903094	0.09377790	33	H	-0.51168450	2.85587178	-0.10820955
7	C	2.21383462	0.71809538	-0.02674264	34	H	5.51517246	-2.99112944	-0.79099663
8	C	0.82405616	1.13582902	-0.05423060	35	H	5.53919850	-2.92615291	0.98756740
9	C	-0.02693952	0.00054522	-0.00530302	36	H	5.92286508	-4.44297929	0.14686412
10	C	3.24690862	1.63258610	-0.05254282	37	H	2.97974003	-5.62062563	1.09498794
11	C	2.93703541	3.01863158	-0.10626167	38	H	3.02000321	-5.69370335	-0.68503790
12	C	1.54444603	3.42822668	-0.12562549	39	H	4.50395252	-5.94801295	0.25300838
13	C	0.52161673	2.51894322	-0.09842308	40	H	3.02524664	5.68816730	0.69949753
14	N	3.89632838	-3.95980634	0.15689017	41	H	4.51833657	5.93951760	-0.22447223
15	N	3.90598940	3.95249425	-0.13385530	42	H	3.00136889	5.61499510	-1.08079005
16	C	5.29620740	-3.55409017	0.12324769	43	H	5.55094866	2.91457208	-0.95479655
17	C	3.57447239	-5.38444997	0.20716818	44	H	5.93343731	4.43136966	-0.11348358
18	C	3.58740180	5.37774679	-0.18743433	45	H	5.51774626	2.98121801	0.82356173
19	C	5.30478380	3.54381858	-0.09231726	46	H	-4.15299600	-0.67068010	2.01343648
20	C	-1.50453999	0.00200101	-0.01284702	47	H	-5.38368675	0.00441440	-0.03325033
21	C	-2.20852990	-0.38858212	1.14495913	48	H	-4.13070484	0.67828683	-2.06677437
22	C	-3.60620594	-0.37954989	1.11975312	49	H	-2.13700064	0.84125063	-3.27971124
23	C	-4.29717175	0.00378974	-0.02753201	50	H	-0.98327614	1.77744761	-2.32089405
24	C	-3.59369400	0.38639653	-1.16742760	51	H	-0.65651212	0.07870818	-2.66405185
25	C	-2.19581312	0.39372097	-1.17794951	52	H	-0.68389107	-0.07571369	2.64649659
26	C	-1.45292025	0.79276922	-2.42835910	53	H	-2.17222704	-0.83468501	3.24749605
27	C	-1.47934241	-0.78827345	2.40318690	54	H	-1.01075168	-1.77404480	2.30135341

Table S12. Cartesian coordinates (in Å) of the **Fluorescein** anion in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	0.28856791	2.49811983	0.07418824	21	C	-3.37276647	0.08227394	1.20402786
2	C	0.91066076	1.21165627	0.03826346	22	C	-1.97478407	0.08683147	1.22274946
3	C	0.20536209	0.00000988	-0.00000112	23	C	-1.22437171	0.18767242	2.52609337
4	C	0.91074145	-1.21158832	-0.03833887	24	C	-1.22457981	-0.18776254	-2.52596290
5	C	0.28873666	-2.49809551	-0.07420059	25	H	-0.79778936	2.54500164	0.07284010
6	C	1.02470699	3.64395905	0.11038410	26	H	-0.79761700	-2.54505566	-0.07273421
7	C	2.47744223	3.61876130	0.11468669	27	H	0.54145859	4.61669165	0.13783691
8	C	3.10171056	2.33198057	0.07553985	28	H	4.18518463	2.26061477	0.07412504
9	C	2.33662832	1.19111683	0.03906492	29	H	4.18533576	-2.26031309	-0.07455943
10	O	3.00346056	0.00010796	-0.00014923	30	H	0.54177108	-4.61664953	-0.13787771
11	C	2.33670676	-1.19094805	-0.03929269	31	H	-3.91401923	-0.14601404	-2.14454910
12	C	3.10186673	-2.33175712	-0.07585535	32	H	-5.15564894	-0.00018884	0.00023754
13	C	2.47768609	-3.61858167	-0.11494146	33	H	-3.91384401	0.14572903	2.14491324
14	C	1.02495366	-3.64388276	-0.11047677	34	H	-1.91461867	0.13932726	3.37205187
15	O	3.14991218	-4.69834183	-0.15156394	35	H	-0.49452776	-0.62324386	2.62967047
16	O	3.14959442	4.69856950	0.15122189	36	H	-0.67170234	1.13254875	2.59148059
17	C	-1.28772785	-0.00004338	0.00006726	37	H	-0.67187442	-1.13261411	-2.59140677
18	C	-1.97488352	-0.08697026	-1.22255272	38	H	-1.91490171	-0.13944037	-3.37186148
19	C	-3.37286653	-0.08251830	-1.20370958	39	H	-0.49478049	0.62318657	-2.62959568
20	C	-4.06918252	-0.00014844	0.00018875					

Table S13. Cartesian coordinates (in Å) of the **Fluorescein** anion in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	0.30959977	2.50696466	0.14124240	21	C	-3.39579074	0.17590005	1.19363008
2	C	0.92195469	1.21410607	0.07546432	22	C	-1.99750936	0.17746688	1.21002130
3	C	0.18733010	0.00000304	0.00001479	23	C	-1.24871194	0.36007467	2.50524514

4	C	0.92203363	-1.21404670	-0.07551672
5	C	0.30976689	-2.50695051	-0.14123480
6	C	1.04614605	3.65979553	0.21412744
7	C	2.49224844	3.62960886	0.22658044
8	C	3.11245803	2.32850368	0.14858777
9	C	2.35342877	1.19292815	0.07660991
10	O	3.04258868	0.00010714	-0.00013860
11	C	2.35350606	-1.19276251	-0.07682880
12	C	3.11261032	-2.32828035	-0.14892057
13	C	2.49248801	-3.62942996	-0.22687006
14	C	1.04638945	-3.65972603	-0.21422924
15	O	3.18508658	-4.69416604	-0.30118961
16	O	3.18477443	4.69440127	0.30077726
17	C	-1.29936703	-0.00004830	0.00007649
18	C	-1.99759117	-0.17760879	-1.20981483
19	C	-3.39587127	-0.17613753	-1.19331531
20	C	-4.09329440	-0.00014289	0.00018455
24	C	-1.24888257	-0.36016157	-2.50509794
25	H	-0.77650263	2.55628687	0.13239544
26	H	-0.77633069	-2.55635343	-0.13225412
27	H	0.55964636	4.63024056	0.26459605
28	H	4.19664710	2.25953844	0.14685475
29	H	4.19679443	-2.25923499	-0.14731969
30	H	0.55995582	-4.63020651	-0.26465242
31	H	-3.93732818	-0.30990662	-2.12691218
32	H	-5.17992657	-0.00017939	0.00022647
33	H	-3.93718437	0.30963406	2.12726865
34	H	-1.93895040	0.36924912	3.35299832
35	H	-0.52128486	-0.44511692	2.65839380
36	H	-0.69005532	1.30427017	2.51315698
37	H	-0.69016707	-1.30432178	-2.51305956
38	H	-1.93918604	-0.36937405	-3.35279770
39	H	-0.52151798	0.44507665	-2.65829819

Table S14. Cartesian coordinates (in Å) of **Rhodol** in the ground state optimized in water.

	Atom	*x*	*y*	*z*
1	C	-0.43107823	2.70779167	0.07708673
2	C	-1.86505337	2.65246730	0.07619216
3	C	-2.48557145	1.38169049	0.03721924
4	C	-1.70347165	0.24394426	0.00541018
5	C	-0.28981309	0.27682313	0.00870079
6	C	0.31462991	1.56025258	0.04429473
7	C	0.43159786	-0.94333534	-0.02729269
8	C	-0.26500107	-2.14472021	-0.06589195
9	C	-1.69957582	-2.13218835	-0.06854434
10	C	-2.45500285	-3.27370354	-0.10406744
11	C	-1.81906997	-4.55922916	-0.14125534
12	C	-0.36043360	-4.57830021	-0.13669593
13	C	0.36770978	-3.43321240	-0.10088893
14	N	-2.59922330	3.78619459	0.11011727
15	O	-2.47943152	-5.63710301	-0.17625892
16	C	-1.94770562	5.08951537	0.17647097
17	C	-4.05380433	3.70983738	0.09238458
18	O	-2.36862388	-0.94496123	-0.03230072
19	C	1.92374551	-0.92398441	-0.02595015
20	C	2.61111088	-0.97982419	-1.25006641
21	C	4.00874394	-0.95208842	-1.23054841
22	C	4.70315454	-0.87606024	-0.02517188
23	C	4.00581226	-0.82440859	1.17988832
24	C	2.60811478	-0.84472419	1.19868321
25	C	1.85429136	-0.78320430	2.50237190
26	C	1.86128330	-1.07550239	-2.55402024
27	H	0.07404002	3.66519261	0.10068330
28	H	-3.56235140	1.26644396	0.03398516
29	H	1.39938564	1.62607267	0.04497390
30	H	-3.53884229	-3.21251334	-0.10386632
31	H	0.12395564	-5.55028384	-0.16300974
32	H	1.45416701	-3.47066744	-0.09828741
33	H	-1.31483560	5.17050823	1.06649561
34	H	-1.33199635	5.27278044	-0.71067772
35	H	-2.71497256	5.86008394	0.22926264
36	H	-4.40988954	3.20143597	-0.81056312
37	H	-4.43256521	3.17129872	0.96866408
38	H	-4.45941974	4.72000714	0.10318989
39	H	4.55099449	-0.99232009	-2.17197399
40	H	5.78943131	-0.85733253	-0.02486077
41	H	4.54583864	-0.76633592	2.12166744
42	H	2.54662598	-0.78975921	3.34789127
43	H	1.24723088	0.12777398	2.56565150
44	H	1.17353332	-1.63561372	2.60826556
45	H	1.11795648	-0.27545364	-2.64669160
46	H	2.54990870	-1.00466684	-3.39963971
47	H	1.32446719	-2.02861772	-2.63102471

Table S15. Cartesian coordinates (in Å) of **Rhodol** in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*
1	C	-0.44095964	2.72586973	0.11381060
2	C	-1.87339436	2.66581354	0.11172425
3	C	-2.49068876	1.38088557	0.03679908
4	C	-1.72004424	0.25050114	-0.01522895
5	C	-0.28773710	0.28015561	-0.00071941
6	C	0.30694163	1.57859193	0.05854634
7	C	0.45235085	-0.92311507	-0.05274277
8	C	-0.27681938	-2.14738717	-0.11539905
9	C	-1.70305540	-2.13180995	-0.13363293
10	C	-2.45915172	-3.27084810	-0.19311367
11	C	-1.83047841	-4.57139107	-0.24115106
12	C	-0.38489899	-4.59425828	-0.21298846
13	C	0.34387947	-3.43555014	-0.15250784
14	N	-2.61831436	3.78811306	0.17631945
15	O	-2.51896396	-5.63767650	-0.30300956
25	C	1.86195676	-0.53636799	2.46442667
26	C	1.91141823	-1.29896841	-2.53996519
27	H	0.06292626	3.68392356	0.15408949
28	H	-3.56831659	1.26924904	0.02517887
29	H	1.39118482	1.64769692	0.05846330
30	H	-3.54345119	-3.20665636	-0.20462966
31	H	0.10707150	-5.56264983	-0.24160341
32	H	1.43011187	-3.47774824	-0.13168894
33	H	-1.34488514	5.13821038	1.18302357
34	H	-1.36213223	5.30562199	-0.58964741
35	H	-2.75077399	5.85589684	0.37083993
36	H	-4.41927379	3.22090090	-0.76756677
37	H	-4.44957526	3.14577240	1.01128802
38	H	-4.48024915	4.71829300	0.18446414
39	H	4.59656324	-1.23854116	-2.13668968

16	C	-1.97861941	5.09365199	0.29087077	40	H	5.81749547	-0.90916465	-0.00007119
17	C	-4.07371004	3.70969663	0.14986248	41	H	4.55401290	-0.58515204	2.11229660
18	O	-2.39939567	-0.93955417	-0.08754721	42	H	2.54420946	-0.52301306	3.31850492
19	C	1.93905326	-0.91614752	-0.03779508	43	H	1.30471867	0.40865078	2.46188096
20	C	2.64794836	-1.10263621	-1.23982345	44	H	1.13250725	-1.34009730	2.61569223
21	C	4.04581757	-1.09771648	-1.20965508	45	H	1.18891118	-0.49294857	-2.71111305
22	C	4.73094591	-0.91082940	-0.01070520	46	H	2.61008181	-1.32171028	-3.38043242
23	C	4.02190610	-0.72687032	1.17458124	47	H	1.34934893	-2.24113666	-2.54107808
24	C	2.62352429	-0.72755011	1.17784461					

Table S16. Cartesian coordinates (in Å) of the **Rhodamine** cation in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	3.64217307	-0.85593430	0.02609897	29	H	4.59887997	-0.34939646	0.03809038
2	C	3.59228014	-2.29538267	0.02109152	30	H	2.21444676	-4.00209429	-0.00995561
3	C	2.32319222	-2.92488241	-0.00595003	31	H	2.55465669	0.96863199	0.01268632
4	C	1.18415504	-2.15039744	-0.01808458	32	H	-2.21742219	-4.00006106	-0.03768756
5	C	1.20996438	-0.72931083	-0.01012467	33	H	-4.59932085	-0.34541290	-0.04108605
6	C	2.49632683	-0.11631835	0.01008778	34	H	-2.55364333	0.97092971	-0.04117350
7	C	0.00015898	-0.01719431	-0.02208239	35	H	0.09228708	4.08787461	2.14451432
8	C	-1.21029794	-0.72818715	-0.03651460	36	H	0.00351402	5.33810426	0.00197451
9	C	-1.18557633	-2.14928467	-0.04002035	37	H	-0.08729399	4.10700190	-2.15153631
10	C	-2.32535567	-2.92277350	-0.04082362	38	H	-0.09494703	2.11103149	-3.38731696
11	C	-3.59414831	-2.29218221	-0.03273915	39	H	0.72933287	0.72480538	-2.64826251
12	C	-3.64292483	-0.85269813	-0.03699280	40	H	-1.03350472	0.82058476	-2.61492618
13	C	-2.49628982	-0.11407924	-0.03854515	41	H	1.03232127	0.79508834	2.57929648
14	O	-0.00094912	-2.81614062	-0.03688485	42	H	0.09708883	2.08140712	3.36262005
15	C	0.00083802	1.47412196	-0.01511578	43	H	-0.73079603	0.70378868	2.61153220
16	C	0.05473396	2.15298280	1.21371419	44	H	6.21081534	-1.75244903	-0.78363204
17	C	0.05283045	3.55079187	1.20017369	45	H	6.10392474	-1.72707099	0.99445779
18	C	0.00270321	4.25170562	-0.00282969	46	H	6.80020696	-3.12882079	0.16581374
19	C	-0.04853098	3.56153360	-1.21197318	47	H	4.13948024	-4.86534352	0.89071620
20	C	-0.05239216	2.16390726	-1.23782223	48	H	4.13962877	-4.82262397	-0.88945689
21	C	-0.11527236	1.41572951	-2.54454369	49	H	5.67387232	-4.87252599	-0.00159260
22	C	0.11570527	1.39331018	2.51391285	50	H	-4.13331226	-4.83069182	-0.92061801
23	N	-4.72820823	-3.01475253	-0.01980956	51	H	-4.15230288	-4.85033286	0.85987979
24	N	4.72562301	-3.01887064	0.04128165	52	H	-5.67701459	-4.86822325	-0.04911215
25	C	6.02933381	-2.36281521	0.10685987	53	H	-6.11234117	-1.72030895	0.92169898
26	C	4.66050278	-4.47582620	0.00922718	54	H	-6.20624655	-1.74828196	-0.85703722
27	C	-4.66355339	-4.47201188	-0.03223001	55	H	-6.80384044	-3.12273272	0.08963322
28	C	-6.03183288	-2.35749822	0.03553422					

Table S17. Cartesian coordinates (in Å) of the **Rhodamine** cation in the S_1 excited state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	3.66127289	-0.86716902	0.05976377	29	H	4.61684353	-0.35813403	0.08916619
2	C	3.60829304	-2.29909271	0.04596301	30	H	2.21713564	-4.00168933	-0.02587398
3	C	2.32473358	-2.92368701	-0.01141173	31	H	2.56976197	0.95887797	0.03748504
4	C	1.19133872	-2.15596847	-0.03799943	32	H	-2.21783098	-3.99832491	-0.08888861
5	C	1.21525236	-0.72856971	-0.01584971	33	H	-4.61421765	-0.35091463	-0.03563893
6	C	2.50817452	-0.12576341	0.02819017	34	H	-2.56425205	0.96276382	-0.03352176
7	C	0.00227068	0.00707709	-0.03958537	35	H	0.22670443	4.11611107	2.12421152
8	C	-1.21178769	-0.72684242	-0.05874578	36	H	0.00007120	5.36994770	-0.00644097
9	C	-1.18943438	-2.15420015	-0.07887900	37	H	-0.22805135	4.14075439	-2.15137970
10	C	-2.32435207	-2.92015273	-0.08103302	38	H	-0.29595582	2.14331141	-3.38684353
11	C	-3.60804834	-2.29359838	-0.05658760	39	H	0.56369552	0.75366586	-2.69194296
12	C	-3.65910184	-0.86153212	-0.04341898	40	H	-1.19271400	0.85551607	-2.56156804
13	C	-2.50435913	-0.12193854	-0.04489853	41	H	1.19062215	0.82933278	2.50372030
14	O	0.00098707	-2.84218780	-0.09251213	42	H	0.28525494	2.10538612	3.33735124
15	C	0.00199085	1.49434718	-0.02894157	43	H	-0.56635509	0.72130138	2.62175309
16	C	0.13149539	2.18162648	1.19182165	44	H	6.24408093	-1.77500811	-0.67848263
17	C	0.12889428	3.57987932	1.18330245	45	H	6.07954931	-1.76536856	1.09466168
18	C	0.00036191	4.28337095	-0.01275715	46	H	6.80221543	-3.16550109	0.27611334
19	C	-0.12857076	3.59376801	-1.21684600	47	H	4.12653543	-4.89041234	0.90609914

20	C	-0.13021121	2.19576314	-1.24135078
21	C	-0.27034231	1.44909652	-2.54283592
22	C	0.26672984	1.42057263	2.48550849
23	N	-4.73506205	-3.03304633	-0.04077338
24	N	4.73369541	-3.03998989	0.08644972
25	C	6.03713433	-2.39588718	0.20028207
26	C	4.66374195	-4.49554565	0.03605719
27	C	-4.66552353	-4.48874085	-0.08672996
28	C	-6.04016789	-2.38779157	0.04617931
48	H	4.15160623	-4.82656422	-0.87373162
49	H	5.67551741	-4.89542825	0.03478693
50	H	-4.13264627	-4.82196139	-0.98366232
51	H	-4.14955209	-4.88280730	0.79644174
52	H	-5.67751060	-4.88734573	-0.11112498
53	H	-6.09989370	-1.75634912	0.93891686
54	H	-6.22917404	-1.76777313	-0.83719491
55	H	-6.80718707	-3.15676381	0.10764208

Table S18. Cartesian coordinates (in Å) of a simplified (Ar = H) **FluFscn** anion in the ground state optimized in water.

	Atom	*x*	*y*	*z*
1	C	-0.95218464	1.15451465	0.00002835
2	C	0.42781768	0.74575122	0.00000113
3	C	0.42760388	-0.74587173	-0.00001156
4	C	-0.95251573	-1.15424199	-0.00000786
5	C	-1.75796029	0.00025095	0.00000945
6	C	-1.26845535	2.53103954	0.00003167
7	C	-0.25628233	3.46216215	0.00000122
8	C	1.13606467	3.07568051	-0.00004701
9	C	1.44397482	1.64845746	-0.00003363
10	C	1.44349905	-1.64887063	-0.00000595
11	C	1.13518286	-3.07600721	-0.00002333
12	C	-0.25727421	-3.46209161	-0.00000107
13	C	-1.26917925	-2.53067747	0.00000137
14	O	2.06787926	3.93516769	-0.00002226
15	O	2.06676096	-3.93574852	0.00002393
16	H	-2.84499112	0.00040700	0.00001478
17	H	-2.30880023	2.84907522	0.00005726
18	H	-0.47549964	4.52620733	0.00001198
19	H	2.49058073	1.35210605	-0.00005473
20	H	2.49019064	-1.35282106	0.00000362
21	H	-0.47679807	-4.52607348	0.00001196
22	H	-2.30961566	-2.84841406	0.00000970

Table S19. Cartesian coordinates (in Å) of simplified (Ar = H) **FluRdl** in the ground state optimized in water.

	Atom	*x*	*y*	*z*
1	C	0.31811494	-0.46662314	0.06521572
2	C	0.29513107	-1.95272305	0.06077979
3	C	1.68823067	-2.38622980	0.01983444
4	C	2.49760972	-1.27774246	-0.00166906
5	C	1.68154816	-0.07925816	0.02578140
6	C	-0.72213349	-2.83794176	0.08743640
7	C	-0.41897241	-4.27924621	0.07453742
8	C	0.98383636	-4.69465339	0.03585380
9	C	1.99372955	-3.78676565	0.00906424
10	C	2.00210683	1.27428181	0.00935358
11	C	0.98185398	2.22342153	0.03887782
12	C	-0.38226218	1.84392824	0.09654596
13	C	-0.70332417	0.44916796	0.09502011
14	H	3.58324562	-1.28703765	-0.03384171
15	N	-1.37945298	2.78170089	0.16349981
16	O	-1.34119388	-5.11801503	0.09599469
17	C	-2.75561829	2.37189819	-0.09055761
18	C	-1.04667438	4.17736767	-0.08788103
19	H	-1.76804324	-2.54261245	0.11804362
20	H	1.17599811	-5.76332244	0.02876151
21	H	3.03243051	-4.10676294	-0.02034584
22	H	3.03768456	1.60152644	-0.03267312
23	H	1.25161500	3.27177812	0.01648725
24	H	-1.73426823	0.11411349	0.11857440
25	H	-2.87341446	1.92556459	-1.08735188
26	H	-3.09507173	1.65155841	0.65812818
27	H	-3.39767699	3.24931854	-0.02299378
28	H	-0.32528784	4.54391140	0.64732388
29	H	-0.62706831	4.32410455	-1.09299727
30	H	-1.95267652	4.77529429	0.00519728

Table S20. Cartesian coordinates (in Å) of a simplified (Ar = H) **FluRdn** cation in the ground state optimized in water.

	Atom	*x*	*y*	*z*
1	C	-1.41729857	-3.45490312	-0.00014059
2	C	-0.04395757	-3.05190641	-0.00038786
3	C	0.27438323	-1.64105393	-0.00177677
4	C	-0.74742132	-0.74382405	-0.00221104
5	C	-2.12190430	-1.15042900	-0.00223753
6	C	-2.43257798	-2.52257093	-0.00132754
7	C	-0.74565855	0.74561762	-0.00212490
8	C	-2.11917695	1.15545123	-0.00240510
9	C	-2.93155455	0.00346279	-0.00250775
10	C	0.27828036	1.64042367	-0.00134751
11	C	-0.03673489	3.05203223	-0.00042043
12	C	-1.40912378	3.45824165	-0.00079766
13	C	-2.42660825	2.52831120	-0.00185204
14	N	0.94347125	-3.95961908	0.00096779
15	N	0.95283712	3.95742010	0.00098720
16	C	2.34433966	-3.54159910	-0.00660870
17	C	0.63269207	-5.38695064	0.00941594
20	H	-4.01795120	0.00474365	-0.00249655
21	H	-1.66798421	-4.50774601	-0.00008214
22	H	1.30600162	-1.30813664	-0.00107237
23	H	-3.46839145	-2.85102966	-0.00173305
24	H	1.30910061	1.30505285	-0.00073385
25	H	-1.65736198	4.51166014	-0.00059179
26	H	-3.46164301	2.85921697	-0.00229123
27	H	2.56909158	-2.94658461	-0.89691665
28	H	2.58120177	-2.95305253	0.88502037
29	H	2.97262079	-4.42960973	-0.01459059
30	H	0.05068593	-5.65192893	0.89783275
31	H	0.06285158	-5.66586789	-0.88279804
32	H	1.56397532	-5.94923773	0.02079653
33	H	0.06705665	5.65558678	0.89414824
34	H	1.57809446	5.94567348	0.01039500
35	H	0.07325714	5.66205729	-0.88654775
36	H	2.58005308	2.94274129	-0.89243453

18	C	0.64545770	5.38553234	0.00485003	37	H	2.98320516	4.42240501	-0.00398922
19	C	2.35268578	3.53595234	-0.00154141	38	H	2.58400070	2.94446933	0.88954773

Table S21. Cartesian coordinates (in Å) of a simplified (Ar = H) **Fluorescein** anion in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	-1.31291160	2.49118922	0.00003255	13	C	0.86940963	-3.62349708	-0.00002141
2	C	-0.67832589	1.21194189	-0.00000088	14	C	-0.58398222	-3.64228517	0.00000689
3	C	-1.36483531	-0.00004603	0.00000416	15	O	1.53535723	-4.70772309	-0.00001948
4	C	-0.67824425	-1.21198736	-0.00001107	16	O	1.53504020	4.70782638	0.00003207
5	C	-1.31274362	-2.49127718	0.00001238	17	H	-2.45379670	-0.00008389	0.00002102
6	C	-0.58422744	3.64224626	0.00004120	18	H	-2.40013201	2.51990751	0.00005106
7	C	0.86916543	3.62355552	0.00001895	19	H	-2.39996204	-2.52006815	0.00003362
8	C	1.50563316	2.34024111	-0.00001732	20	H	-1.07097478	4.61355919	0.00006728
9	C	0.74829301	1.19470752	-0.00002555	21	H	2.58976423	2.28005953	-0.00003631
10	O	1.41405415	0.00004755	-0.00006536	22	H	2.58991774	-2.27988475	-0.00006621
11	C	0.74837337	-1.19465727	-0.00003931	23	H	-1.07066408	-4.61363093	0.00002569
12	C	1.50579079	-2.34013981	-0.00004597					

Table S22. Cartesian coordinates (in Å) of simplified (Ar = H) **Rhodol** in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	1.10408996	-2.22556207	0.02516742	17	C	-2.50543429	-3.27430253	0.00157666
2	C	-0.33087081	-2.18697934	0.03178295	18	O	-0.87952132	1.41057082	0.03013727
3	C	-0.97194090	-0.92432350	0.03562632	19	H	2.98983618	1.42963770	0.00472501
4	C	-0.20590898	0.22374478	0.03181737	20	H	1.62020491	-3.17729266	0.02207616
5	C	1.20872560	0.20469361	0.02467977	21	H	-2.05034284	-0.82655471	0.03541368
6	C	1.83428272	-1.06762118	0.02279602	22	H	2.92031973	-1.10878179	0.01711568
7	C	1.90125333	1.42994811	0.01180538	23	H	-2.06253541	3.68734136	0.01754618
8	C	1.21367070	2.62696087	0.00563750	24	H	1.59809529	6.03207953	-0.03021892
9	C	-0.22143426	2.60656480	0.01504221	25	H	2.93508326	3.94190267	-0.01852560
10	C	-0.97863097	3.74634864	0.00989428	26	H	0.20803438	-4.70978242	-0.96988836
11	C	-0.34102583	5.03344320	-0.00697317	27	H	0.27919386	-4.78588740	0.80709226
12	C	1.11814545	5.05769543	-0.01733656	28	H	-1.13840273	-5.40834118	-0.05177796
13	C	1.84818119	3.91348027	-0.01094948	29	H	-2.89555968	-2.73543111	0.87155309
14	N	-1.05012047	-3.33136982	0.03342653	30	H	-2.86425660	-2.77722900	-0.90750350
15	O	-1.00390086	6.11014271	-0.01302534	31	H	-2.89724579	-4.28976259	0.02174254
16	C	-0.38198384	-4.62533020	-0.05045539					

Table S23. Cartesian coordinates (in Å) of a simplified (Ar = H) **Rhodamine** cation in the ground state optimized in water.

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
1	C	1.42090213	-3.63995850	-0.02828851	21	C	-0.07355551	6.03289635	0.09069473
2	C	-0.01925667	-3.59572801	-0.02422772	22	H	1.93093020	-4.59483304	-0.02655872
3	C	-0.65957157	-2.33019419	-0.03935561	23	H	-1.73759369	-2.23066661	-0.03603129
4	C	0.10788896	-1.18747939	-0.04517649	24	H	3.23964808	-2.53271263	-0.04018120
5	C	1.52992763	-1.20991642	-0.04299127	25	H	-1.73772286	2.23074432	-0.02367028
6	C	2.15393724	-2.48991339	-0.03755399	26	H	1.93077583	4.59472842	0.01060852
7	C	2.22249416	0.00009881	-0.03739011	27	H	3.23954392	2.53280596	-0.01438745
8	C	1.52986008	1.21005883	-0.03090390	28	H	0.53592996	-6.21095885	-0.83406611
9	C	0.10781528	1.18762322	-0.03533880	29	H	0.56529530	-6.10467513	0.94397540
10	C	-0.65969117	2.33025945	-0.02372764	30	H	-0.83477907	-6.80836783	0.11837516
11	C	-0.01942390	3.59568889	0.00006861	31	H	-2.57840455	-4.16473583	0.86658741
12	C	1.42074544	3.63990968	0.00115437	32	H	-2.55315749	-4.15200572	-0.91399015
13	C	2.15383173	2.48997713	-0.01433732	33	H	-2.58436431	-5.69261573	-0.03704004
14	O	-0.55708359	0.00008466	-0.04824443	34	H	-2.54721596	4.15592013	-0.90162067
15	H	3.31091202	0.00011946	-0.03387895	35	H	-2.58457491	4.16132638	0.87876976
16	N	-0.73672991	4.73299447	0.02163628	36	H	-2.58428067	5.69291344	-0.01840741
17	N	-0.73652151	-4.73311771	-0.00542225	37	H	0.56353347	6.10111265	0.97788768
18	C	-0.07318070	-6.03324708	0.05797623	38	H	0.53689265	6.21393093	-0.79981840
19	C	-2.19418904	-4.67678047	-0.02251747	39	H	-0.83530196	6.80772233	0.15293592
20	C	-2.19426503	4.67698702	-0.00554492					

7. Literature

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8. NMR spectra

NMR spectra of the obtained compounds are shown in the following pages.

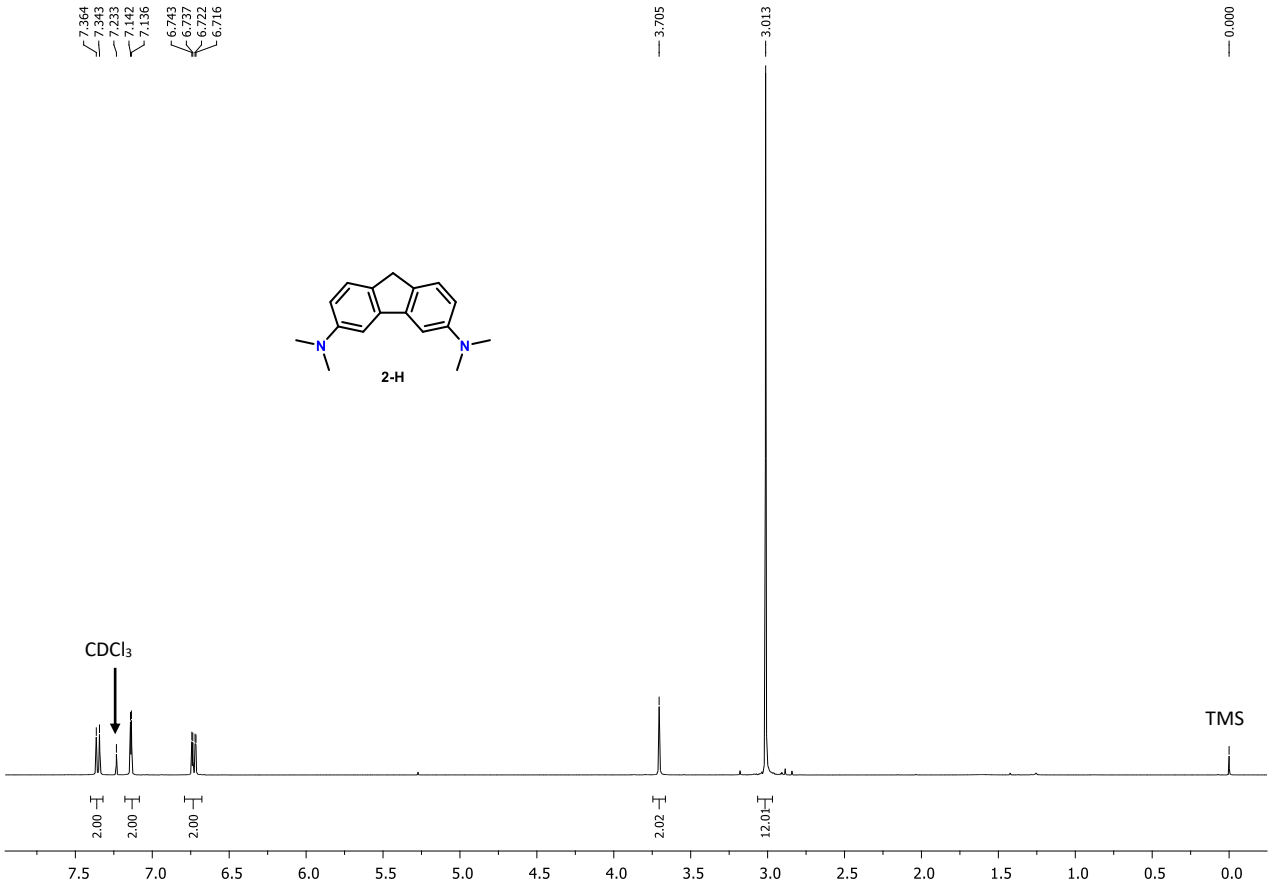

Figure S19. ^{1}H NMR spectrum of compound **2-H** (400 MHz, $CDCl_3$).

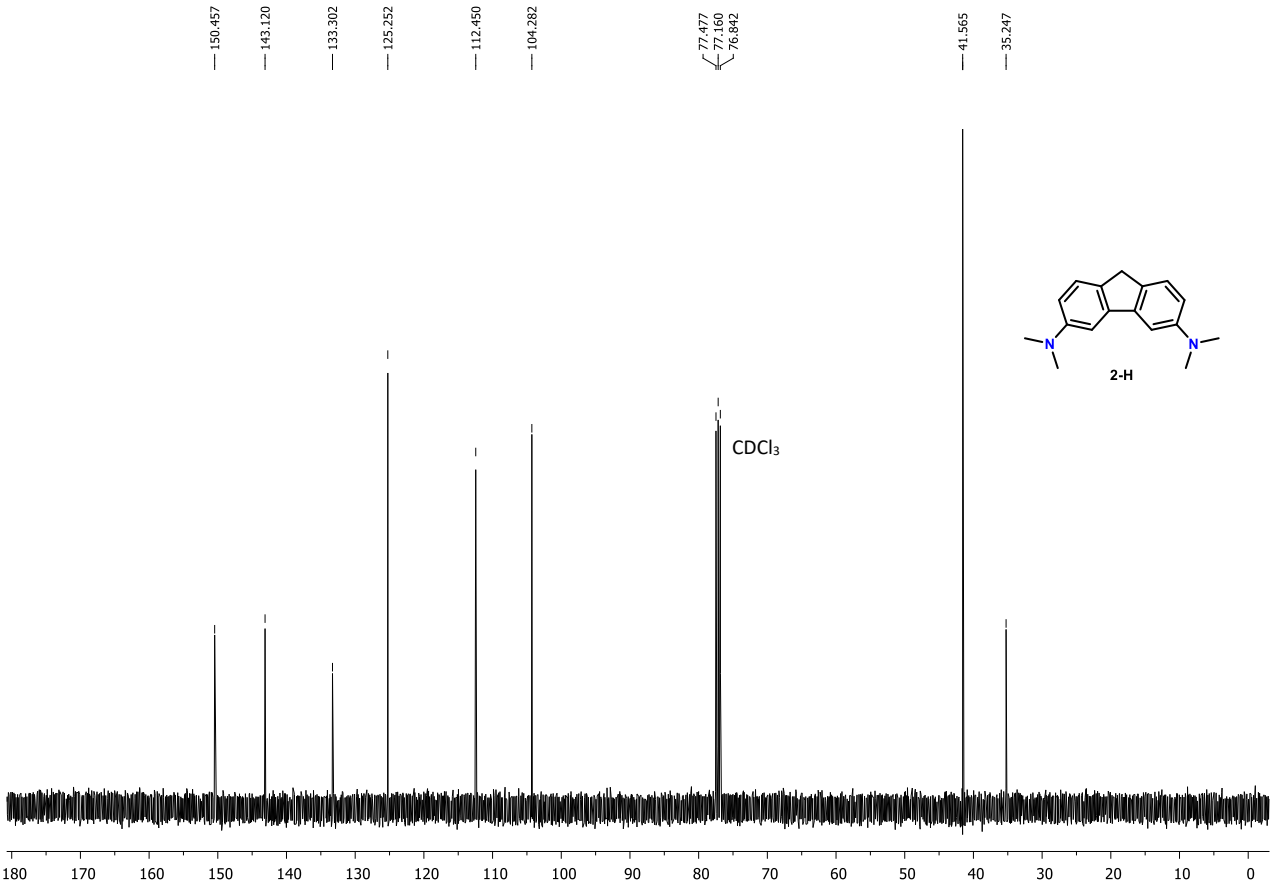

Figure S20. ^{13}C{1H} NMR spectrum of **2-H** (101 MHz, $CDCl_3$).

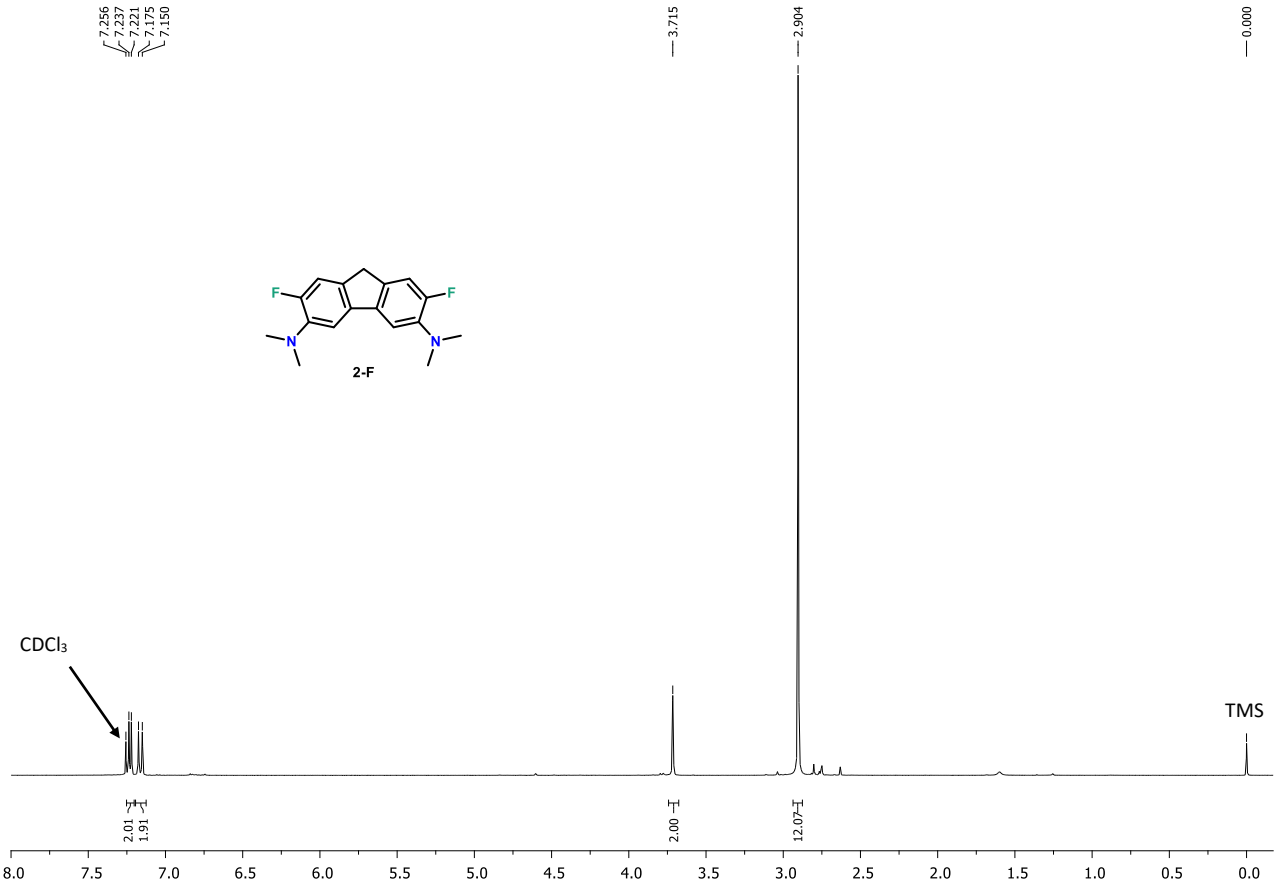

Figure S21. ^{1}H NMR spectrum of compound **2-F** (500 MHz, $CDCl_3$).

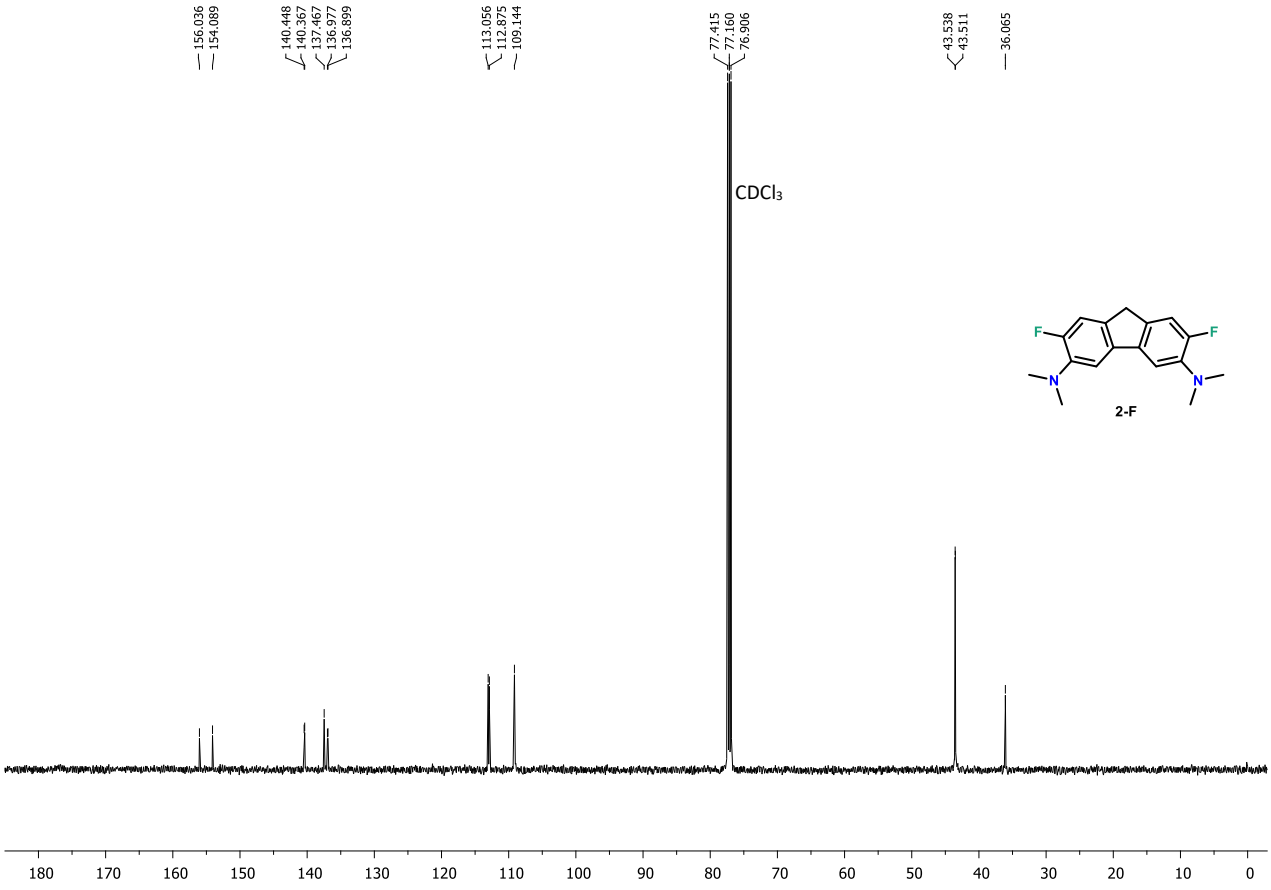

Figure S22. ^{13}C{1H} NMR spectrum of **2-F** (126 MHz, $CDCl_3$).

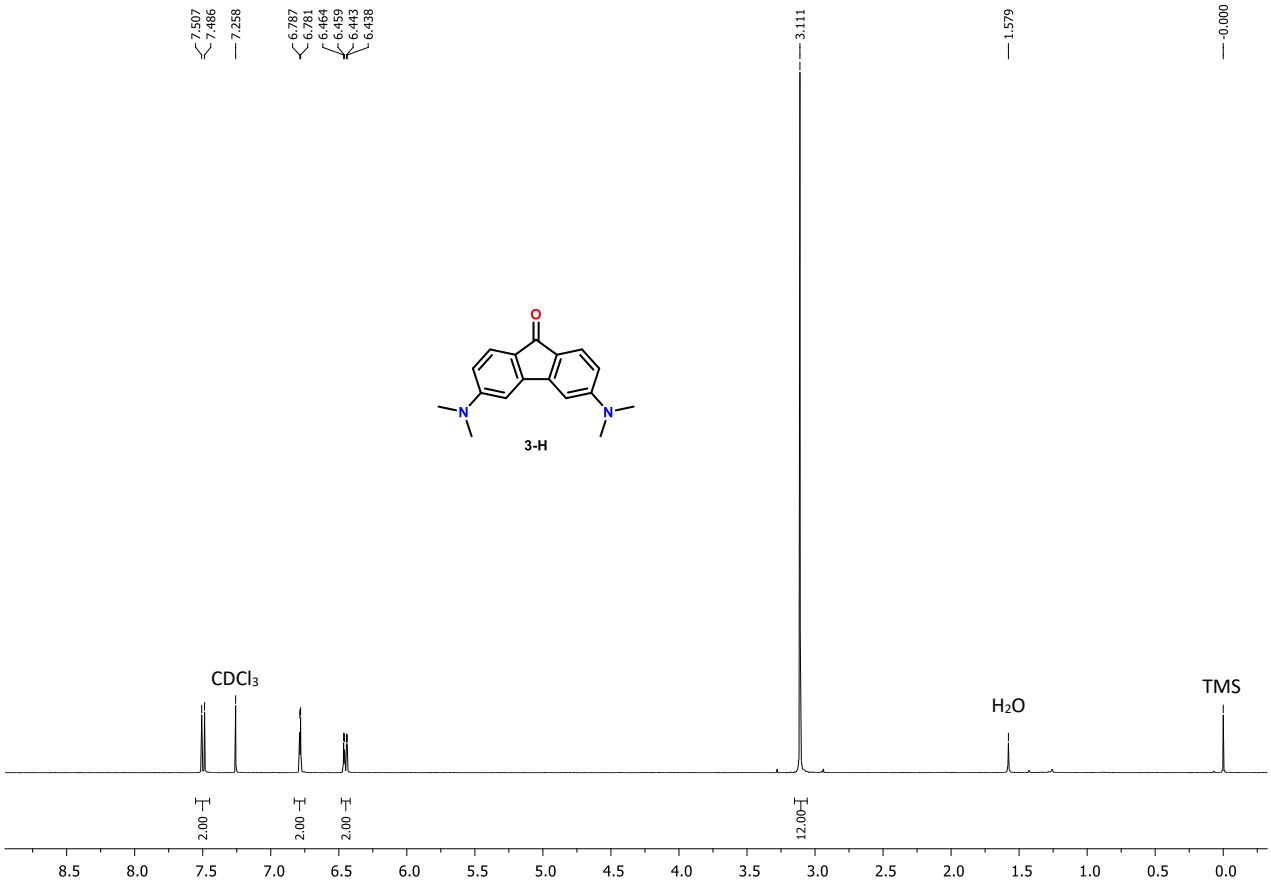

Figure S23. ^{1}H NMR spectrum of compound **3-H** (400 MHz, $CDCl_3$).

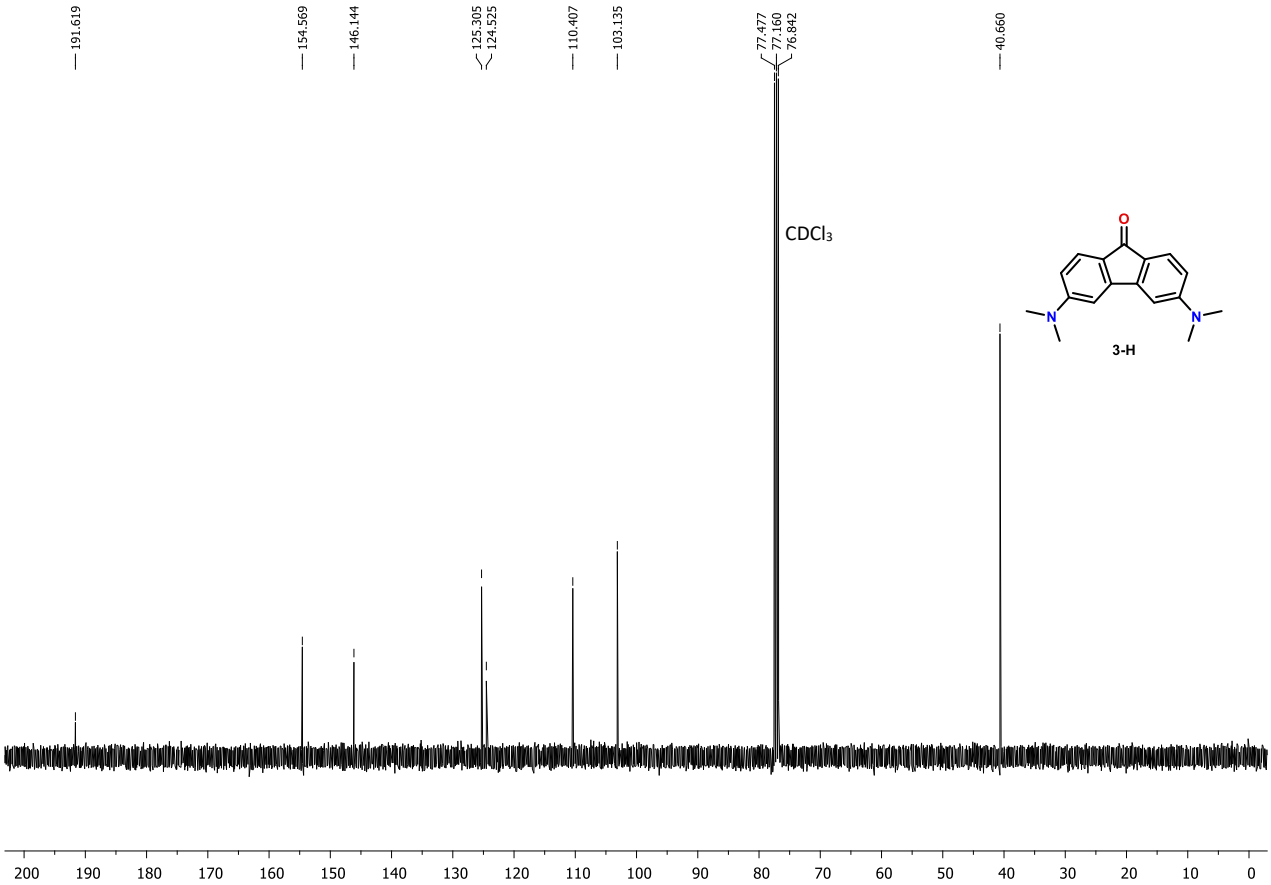

Figure S24. ^{13}C{1H} NMR spectrum of **3-H** (101 MHz, $CDCl_3$).

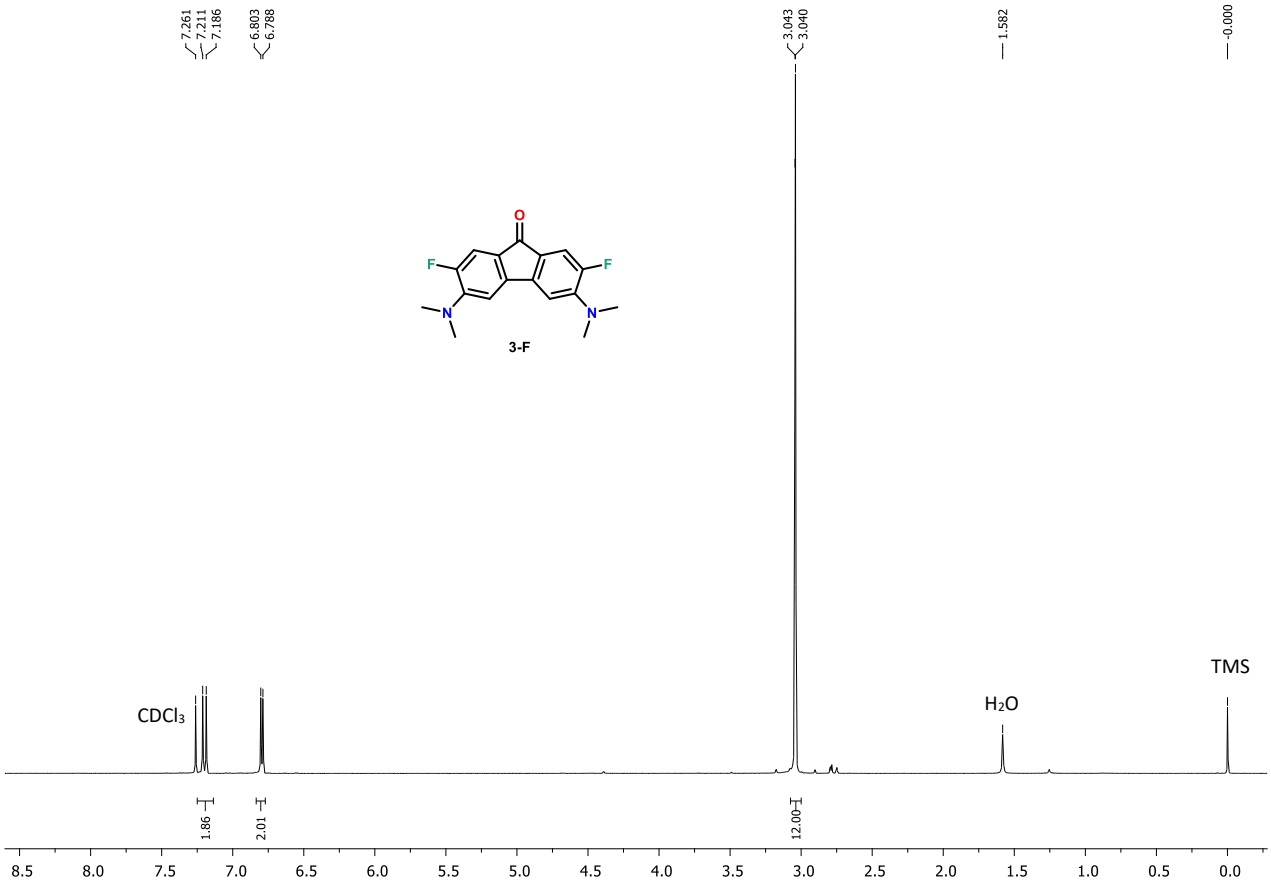

Figure S25. ^{1}H NMR spectrum of compound **3-F** (500 MHz, $CDCl_3$).

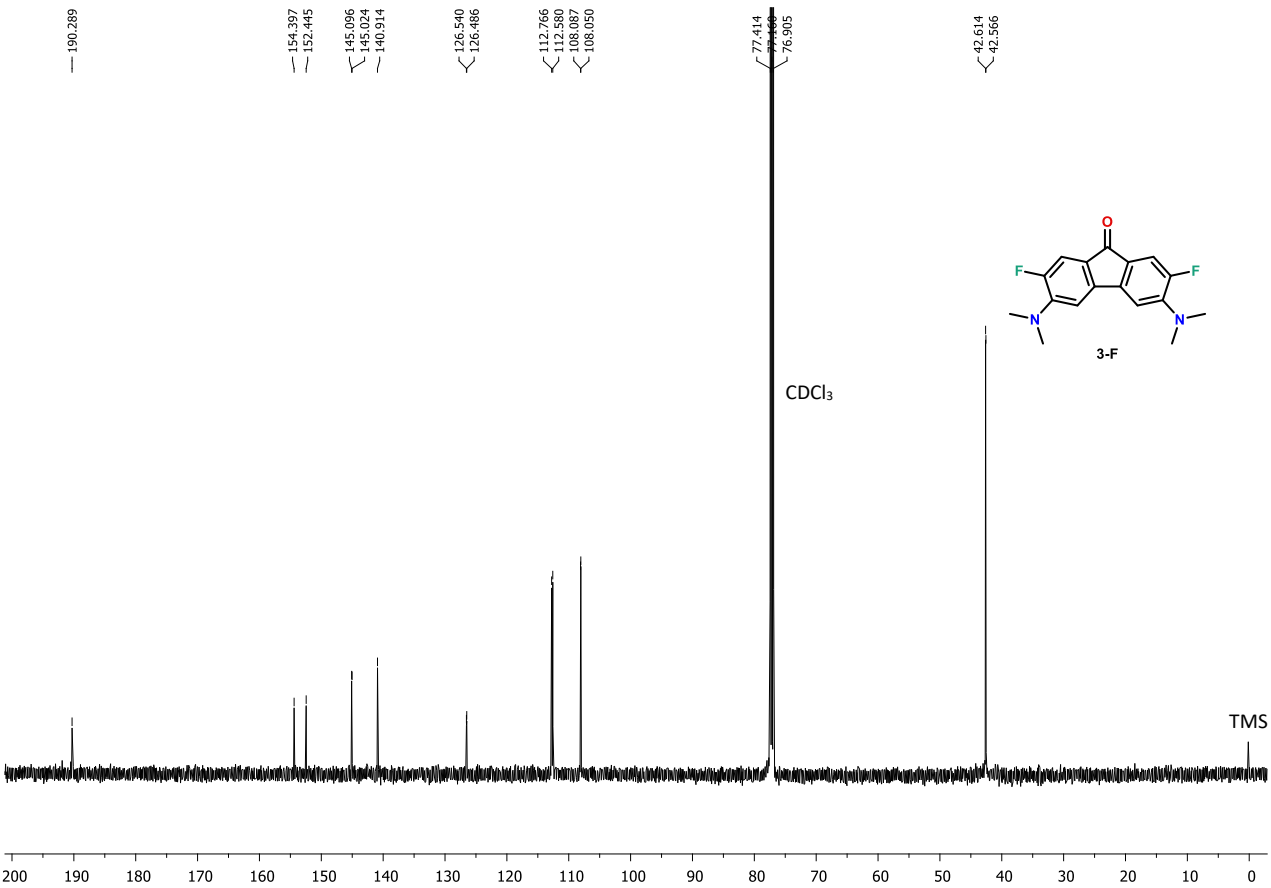

Figure S26. ^{13}C{1H} NMR spectrum of **3-F** (126 MHz, $CDCl_3$).

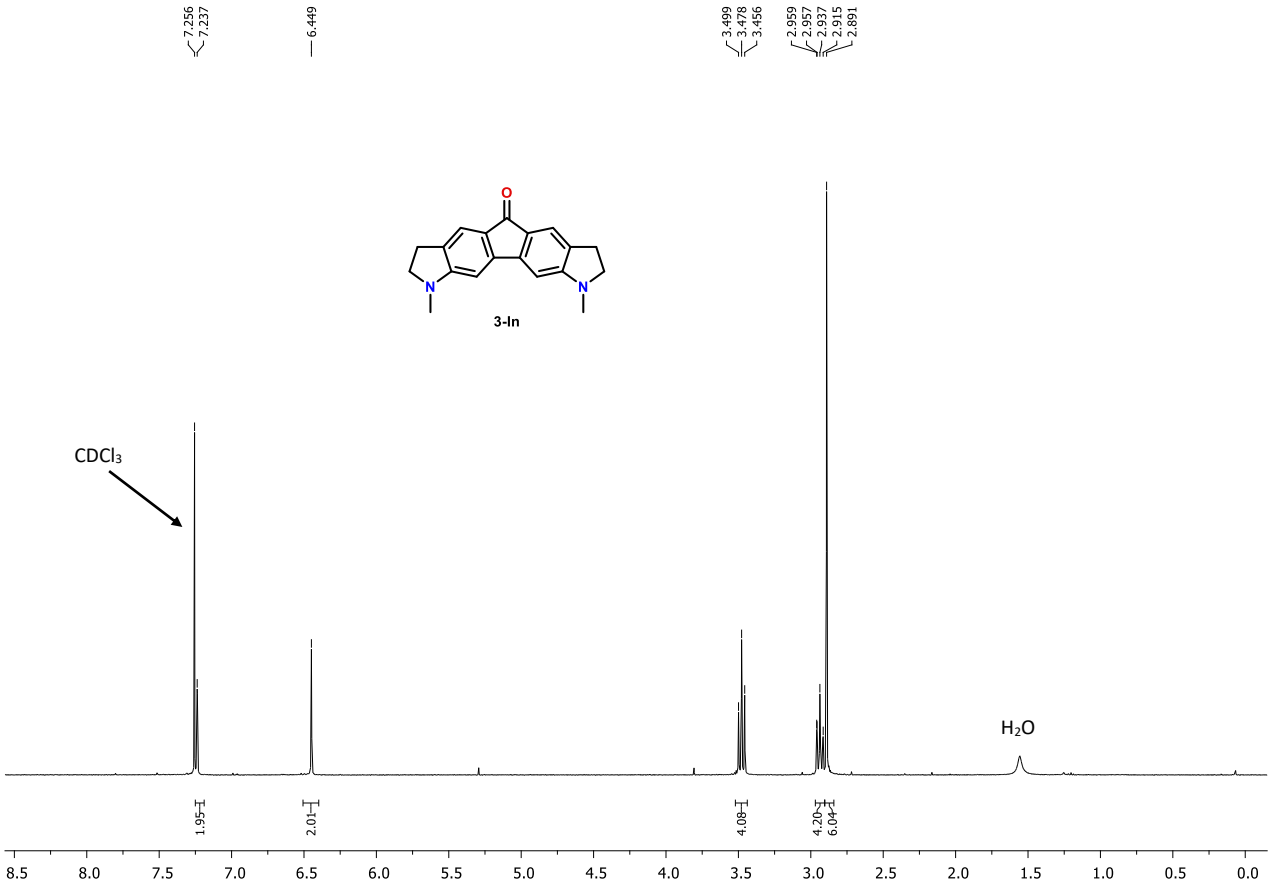

Figure S27. ^{1}H NMR spectrum of compound **3-In** (400 MHz, $CDCl_3$).

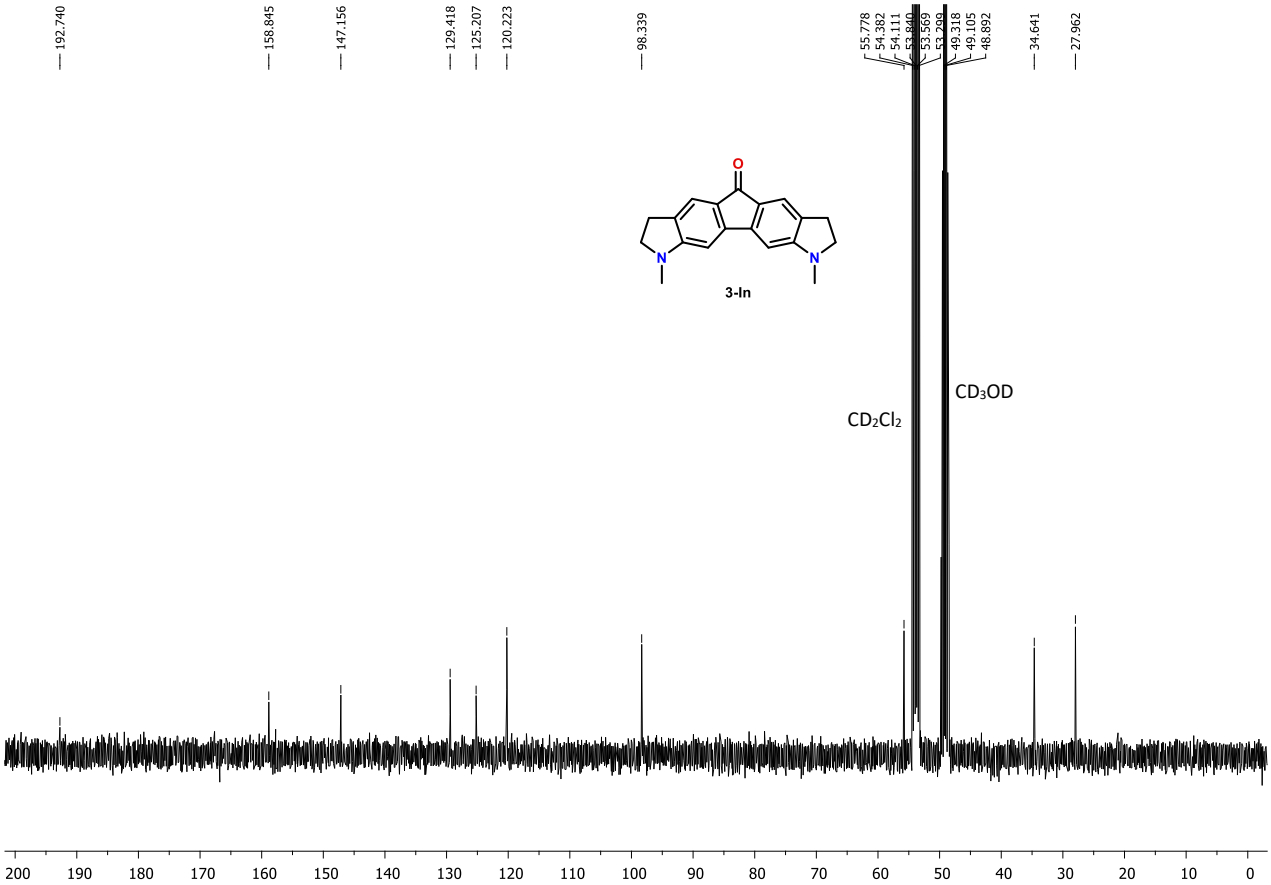

Figure S28. ^{13}C{1H} NMR spectrum of **3-In** (101 MHz, 4/1 (*v*/*v*) CD_2Cl_2 / CD_3OD).

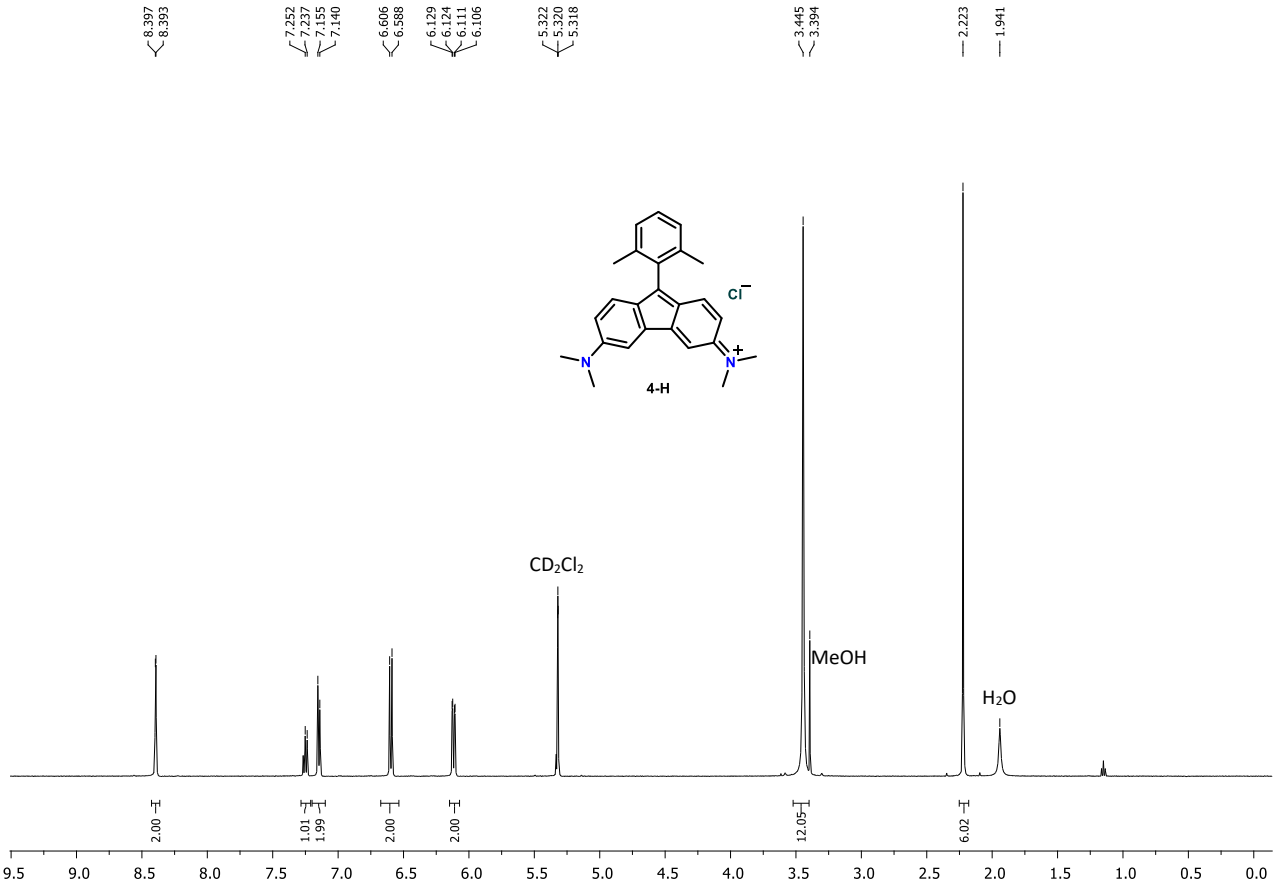

Figure S29. ^{1}H NMR spectrum of compound **4-H** (500 MHz, CD_2Cl_2).

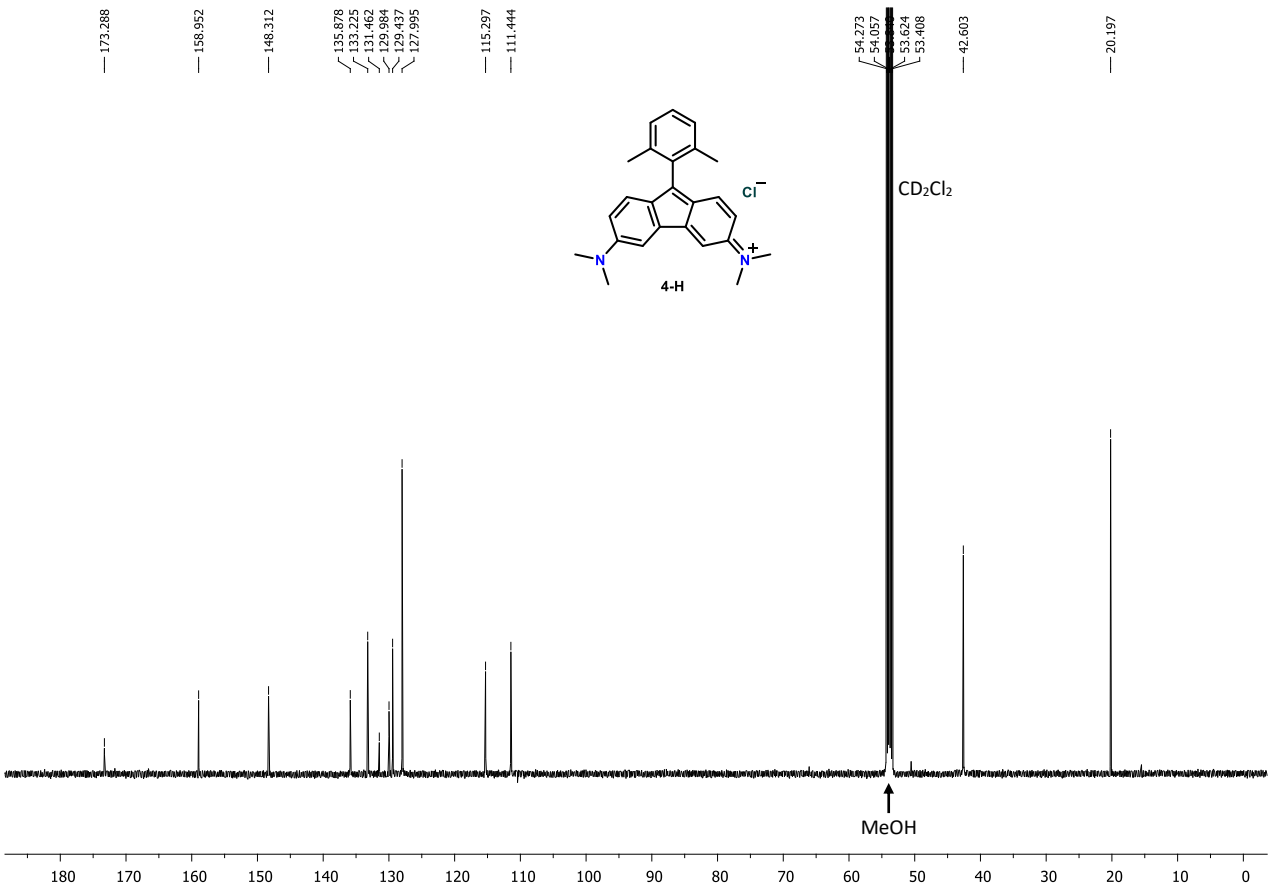

Figure S30. ^{13}C{1H} NMR spectrum of **4-H** (126 MHz, CD_2Cl_2).

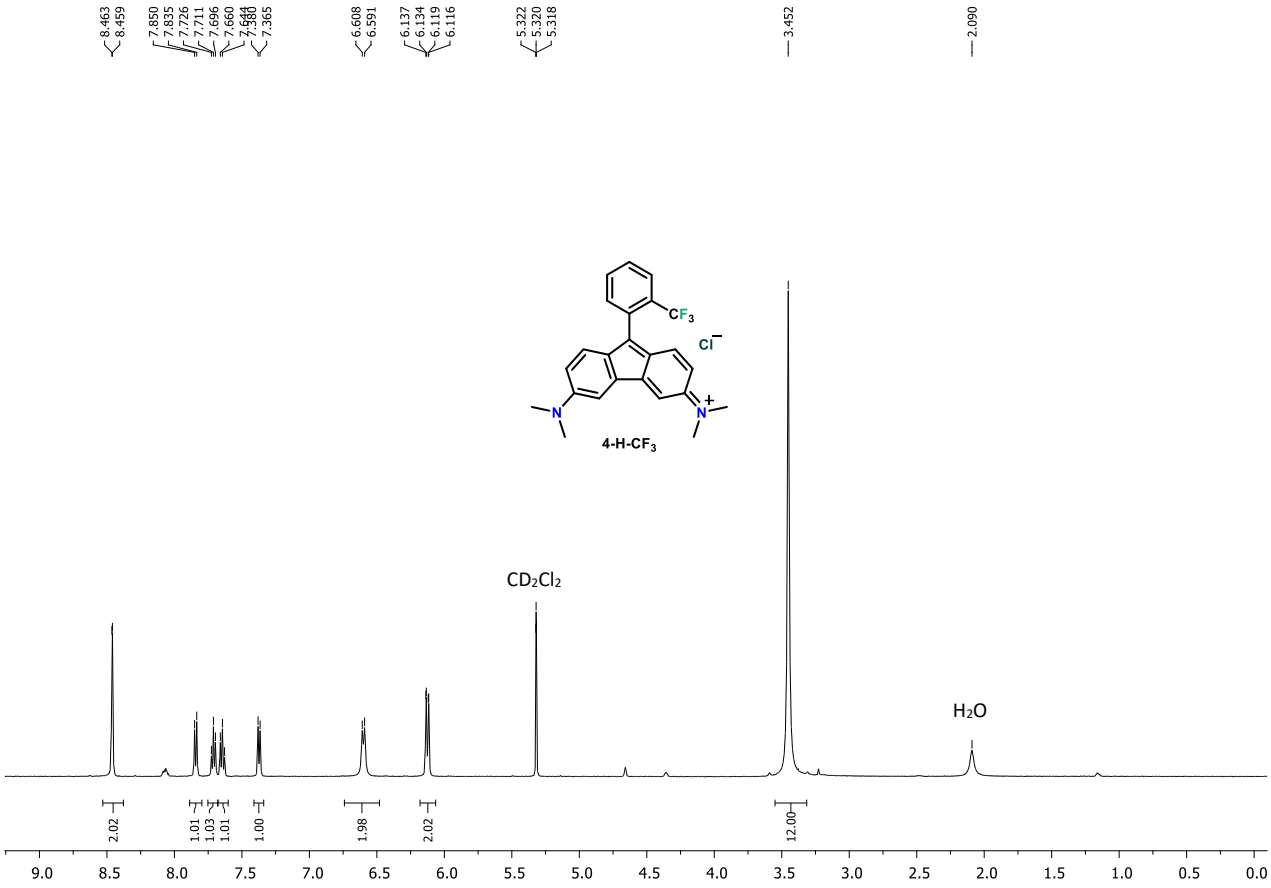

Figure S31. ^{1}H NMR spectrum of compound **4-H-CF$_3$** (500 MHz, CD_2Cl_2).

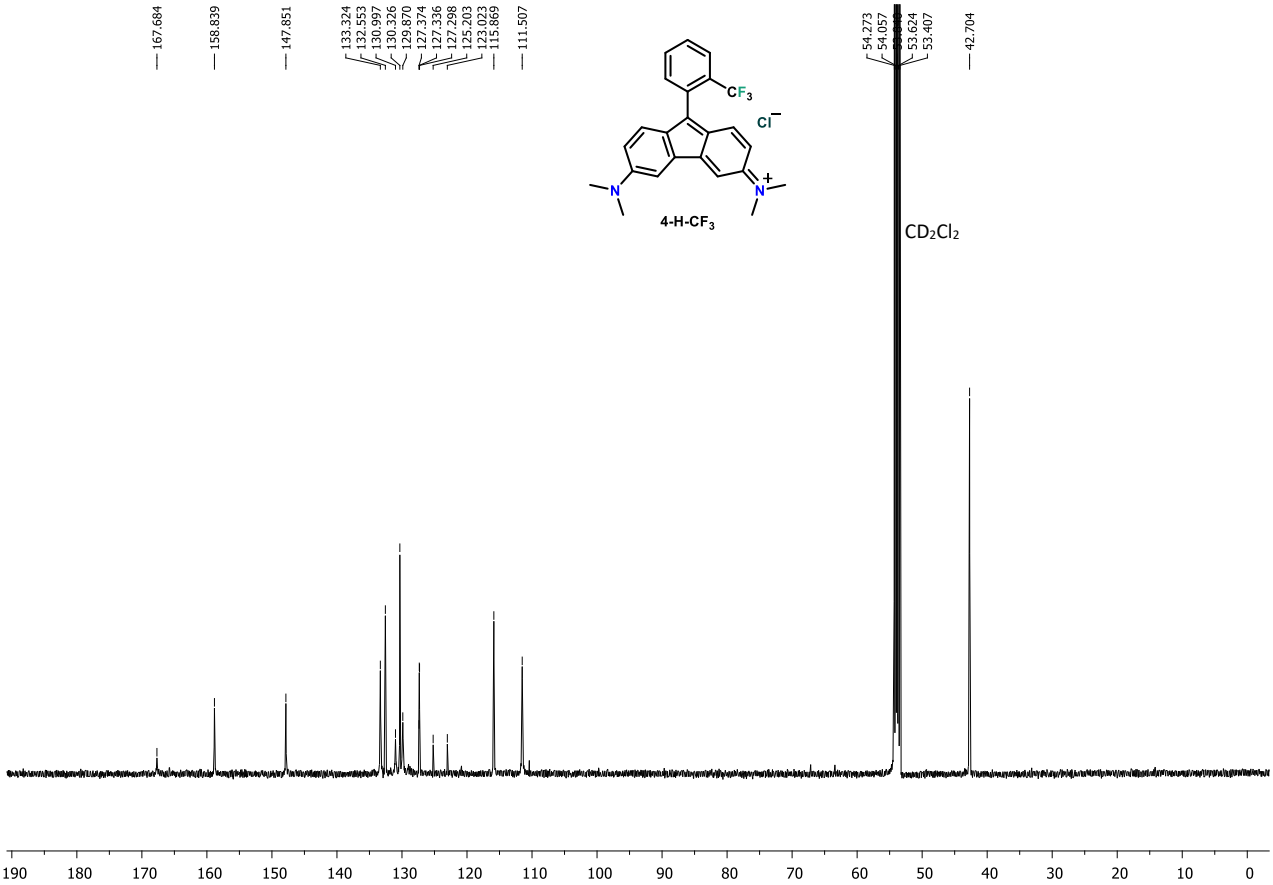

Figure S32. ^{13}C{1H} NMR spectrum of **4-H-CF$_3$** (126 MHz, CD_2Cl_2).

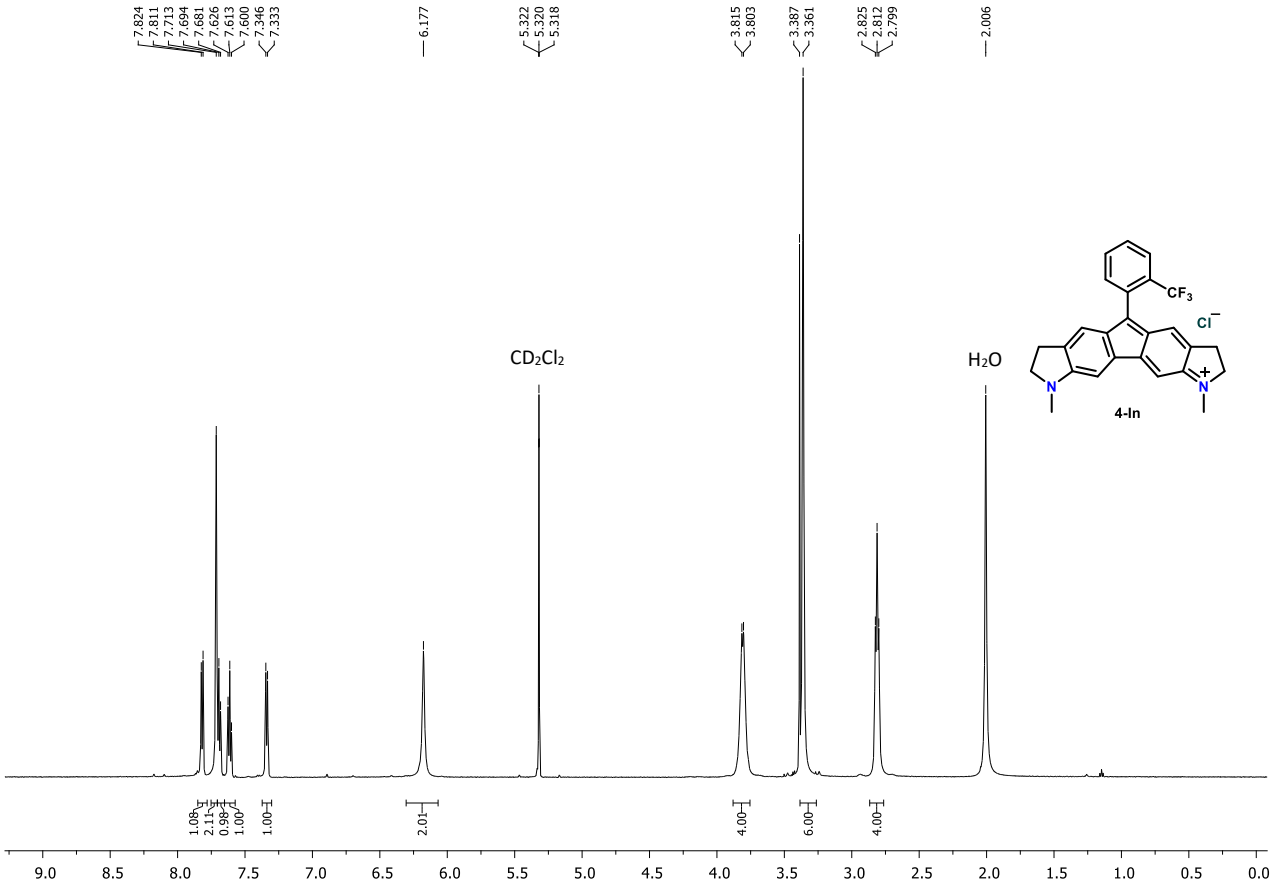

Figure S33. ^{1}H NMR spectrum of compound **4-In** (600 MHz, CD_2Cl_2).

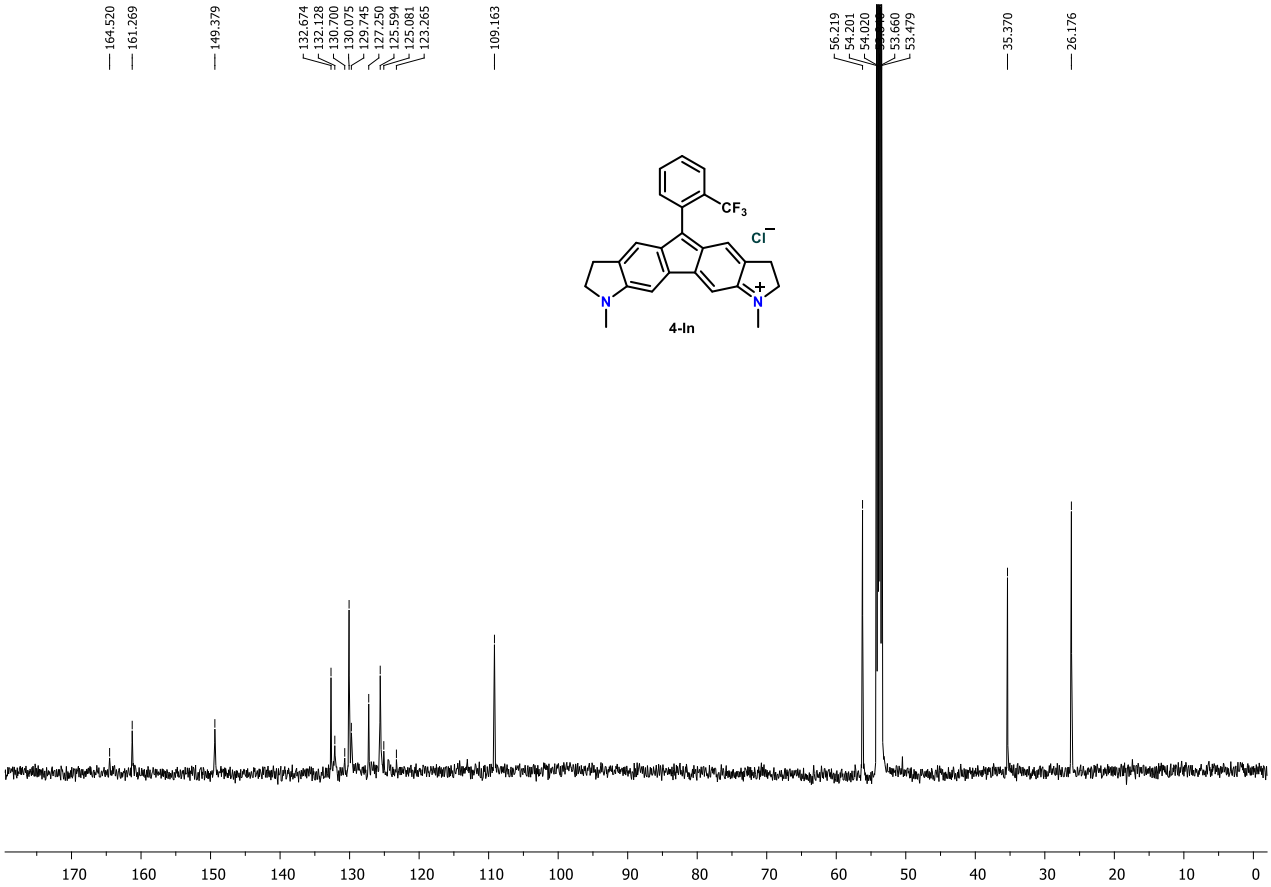

Figure S34. $^{13}C\{1H\}$ NMR spectrum of **4-In** (151 MHz, CD_2Cl_2).

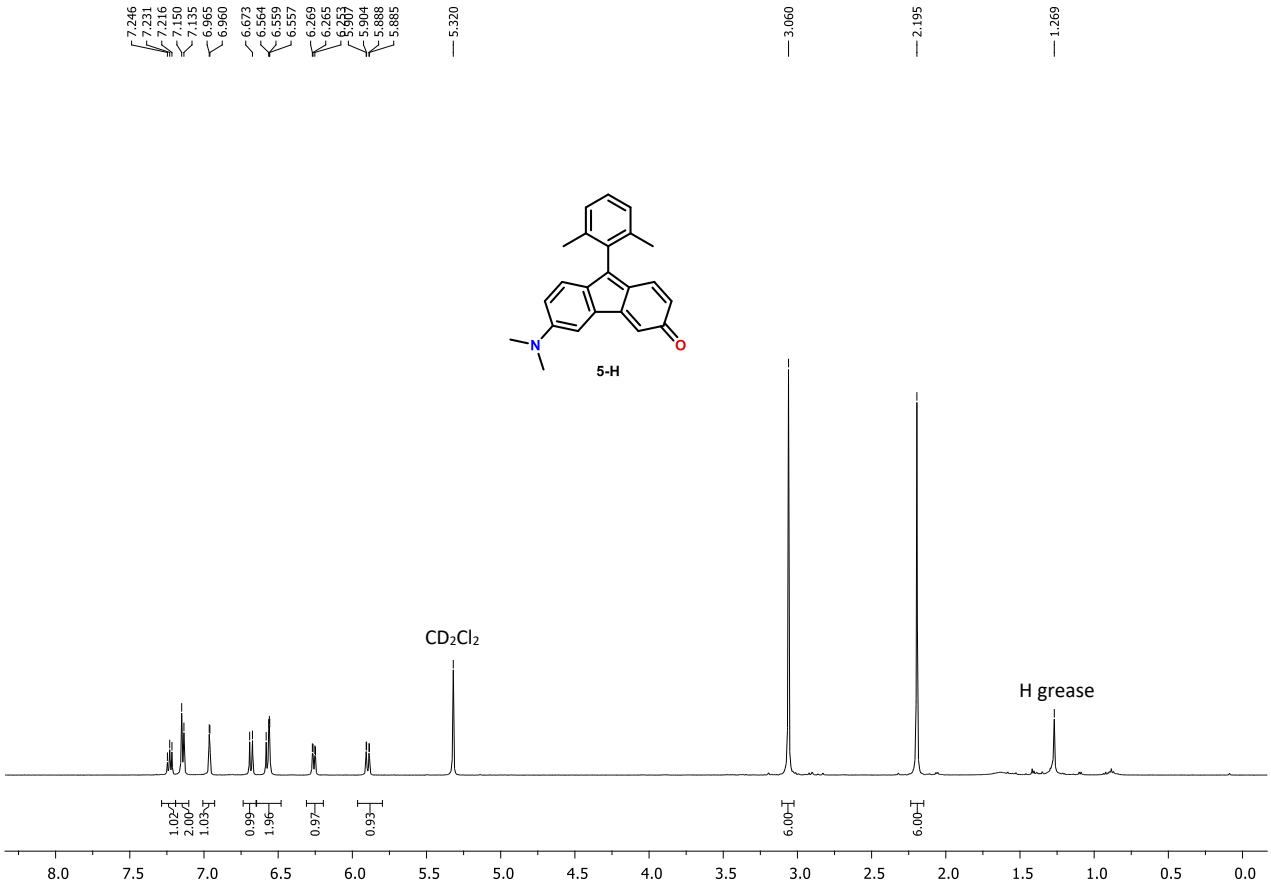

Figure S35. ^{1}H NMR spectrum of compound **5-H** (500 MHz, CD_2Cl_2).

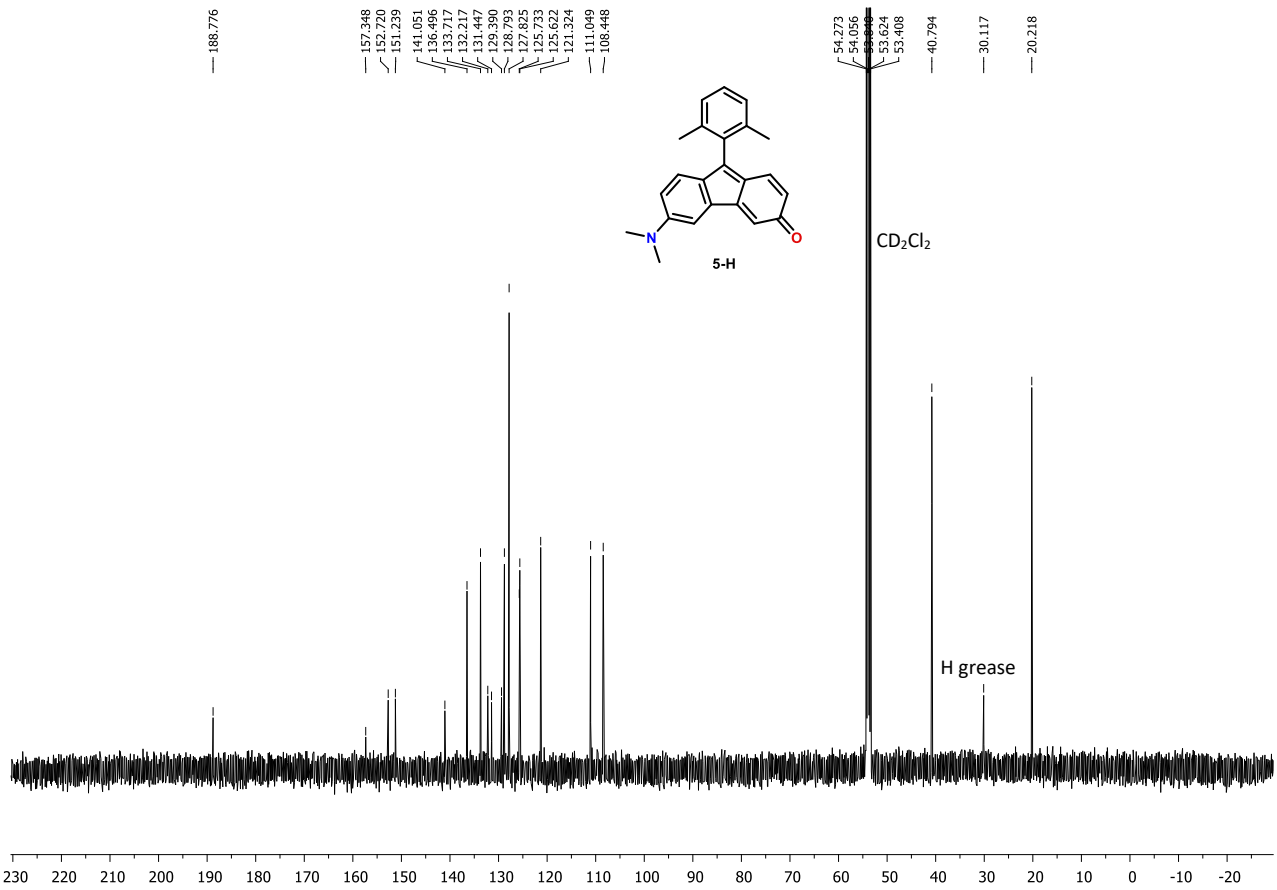

Figure S36. ^{13}C{1H} NMR spectrum of **5-H** (126 MHz, CD_2Cl_2).

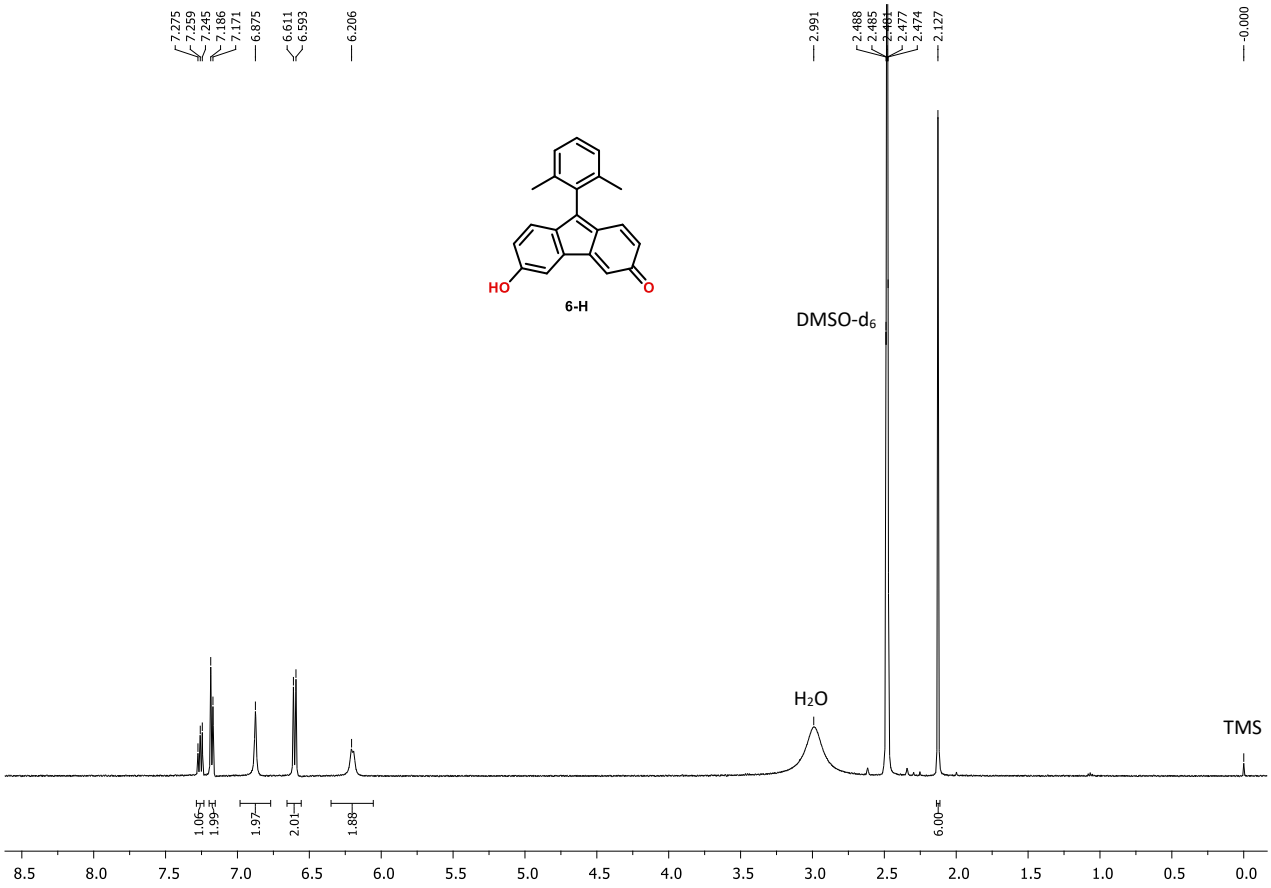

Figure S37. ^{1}H NMR spectrum of compound **6-H** (500 MHz, DMSO-d_6, 90 °C).

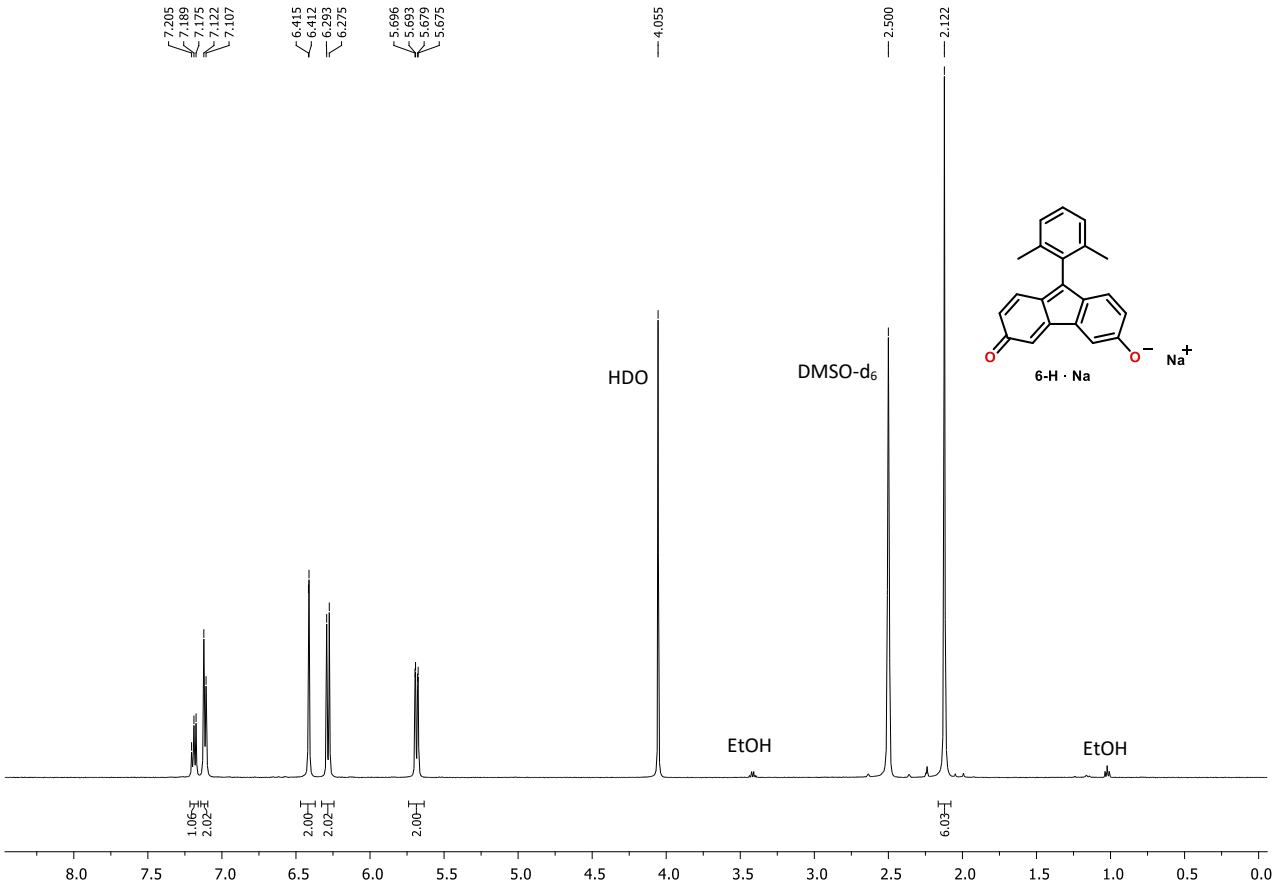

Figure S38. ^{1}H NMR spectrum of compound **6-H** (500 MHz, 50/10/1 (*v*/*v*/*v*) DMSO-d_6 / D_2O / 30% NaOD in D_2O).

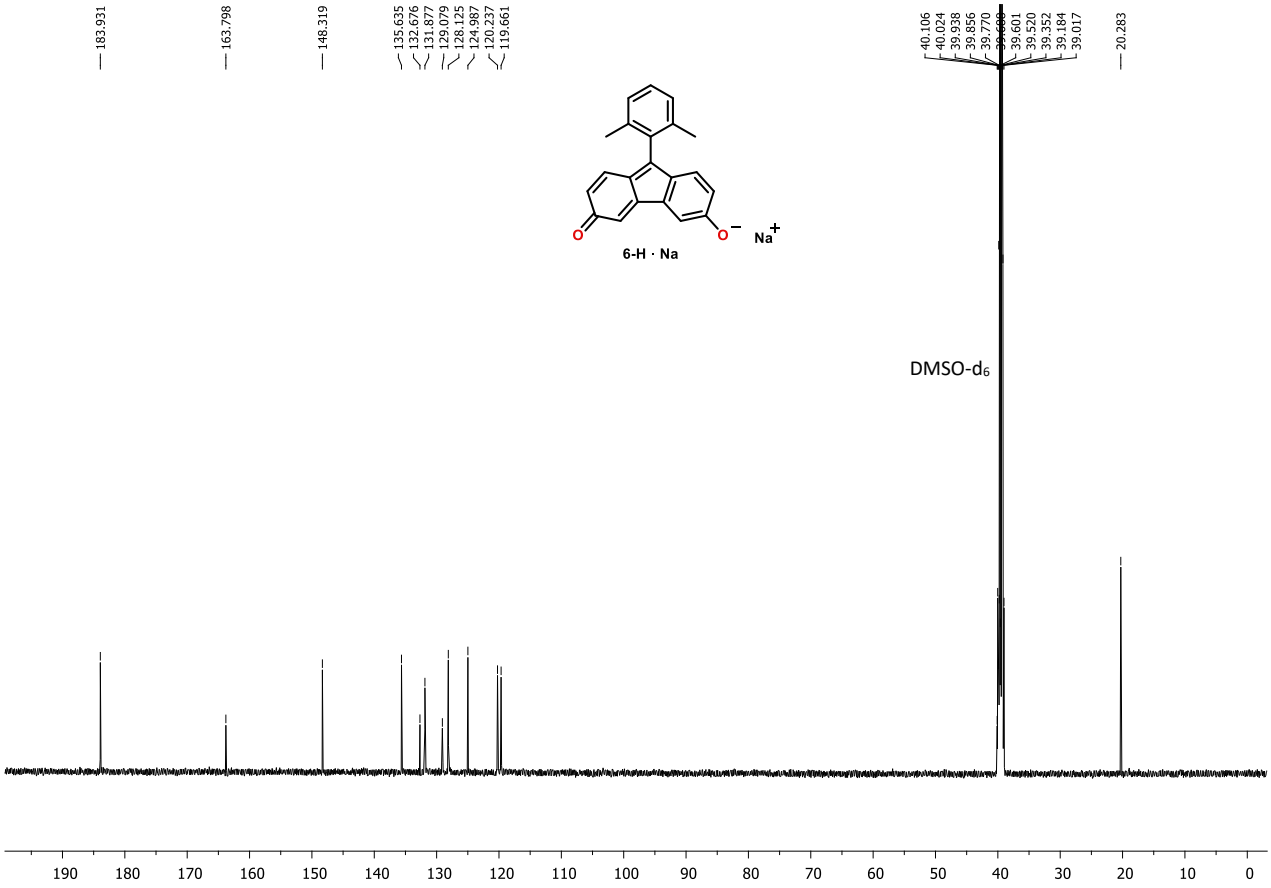

Figure S39. ^{13}C NMR spectrum of compound **6-H** (500 MHz, 50/10/1 (*v*/*v*/*v*) DMSO-d_6 / D_2O / 30% NaOD in D_2O).

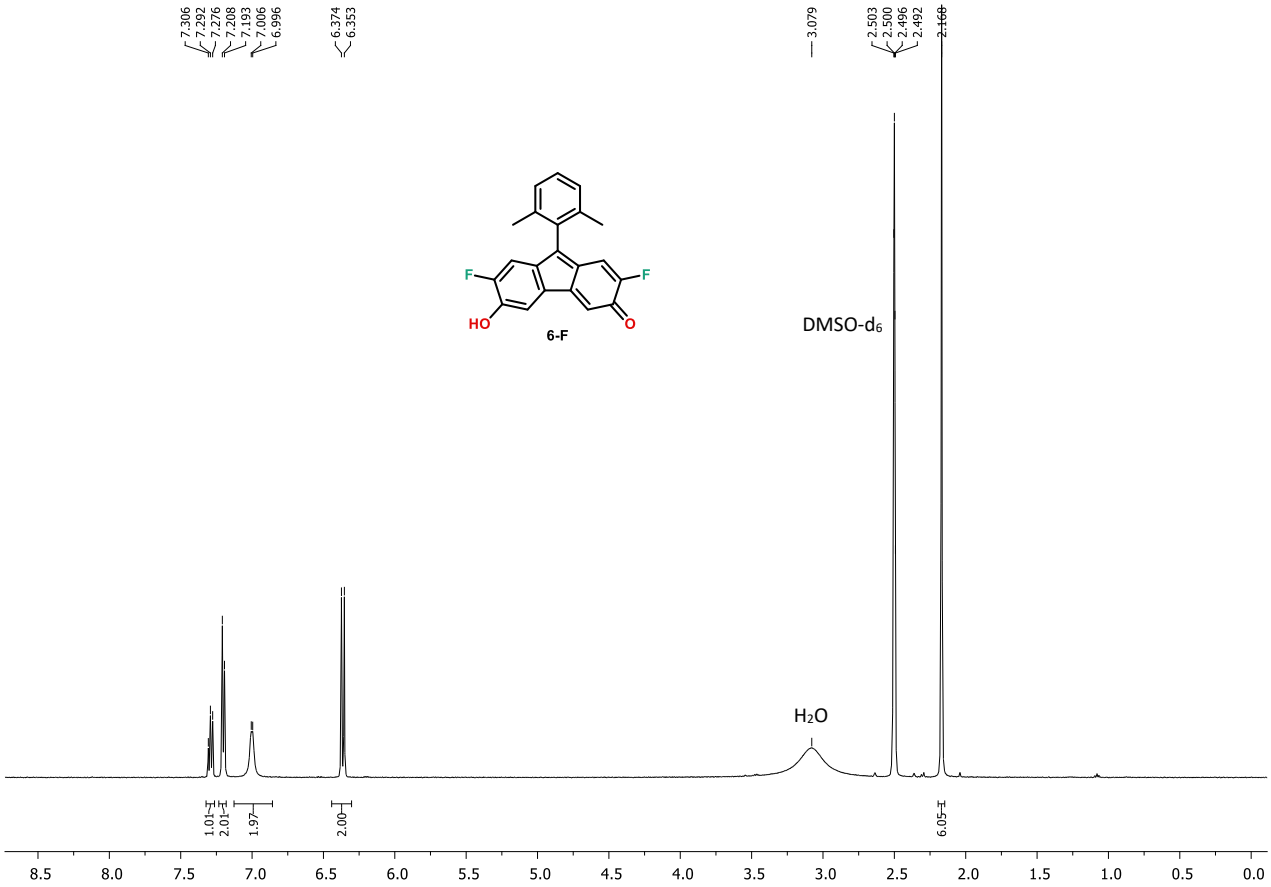

Figure S40. ^{1}H NMR spectrum of compound **6-F** (500 MHz, DMSO-d_6, 80 °C).

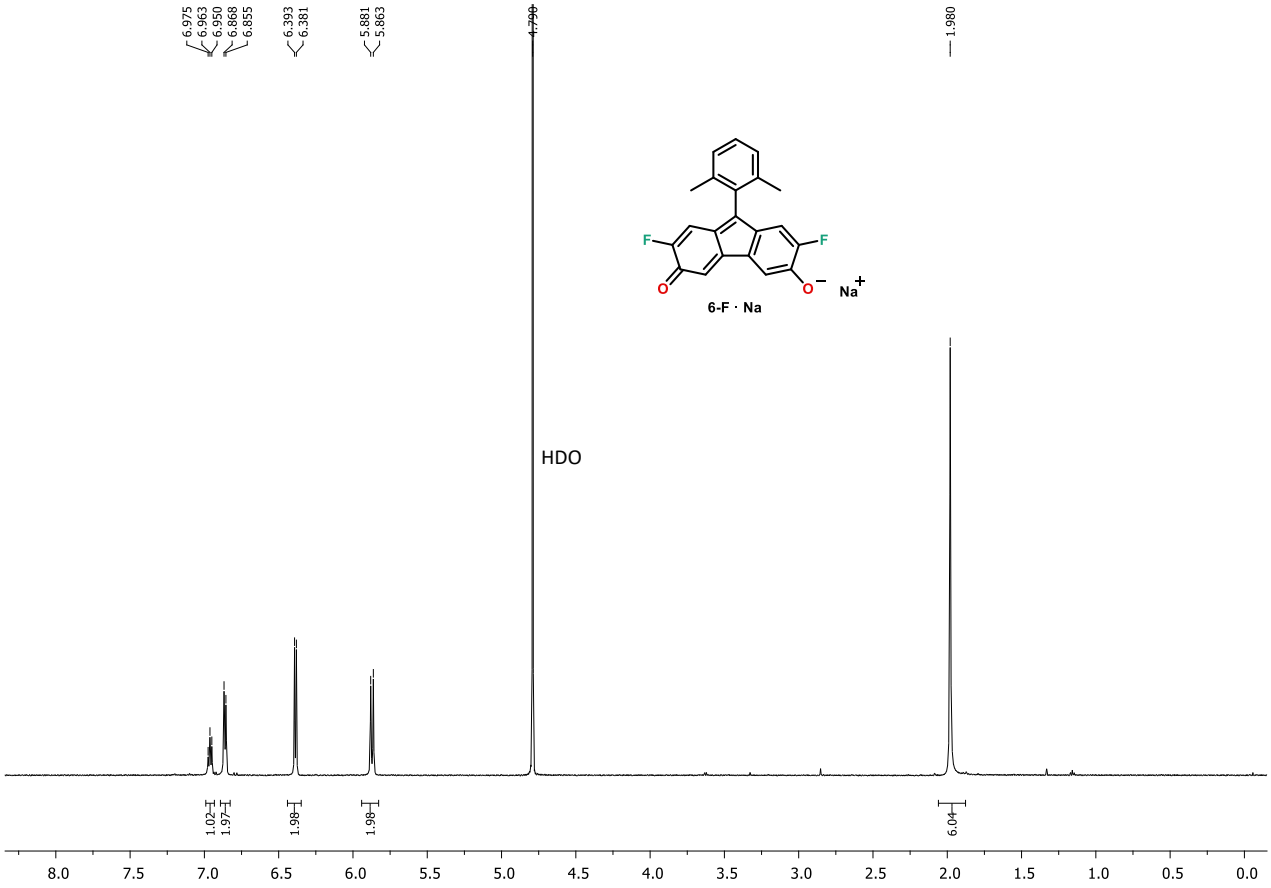

Figure S41. ^{1}H NMR spectrum of compound **6-F** (600 MHz, 50/1 (*v*/*v*) D_2O / 30% NaOD in D_2O).

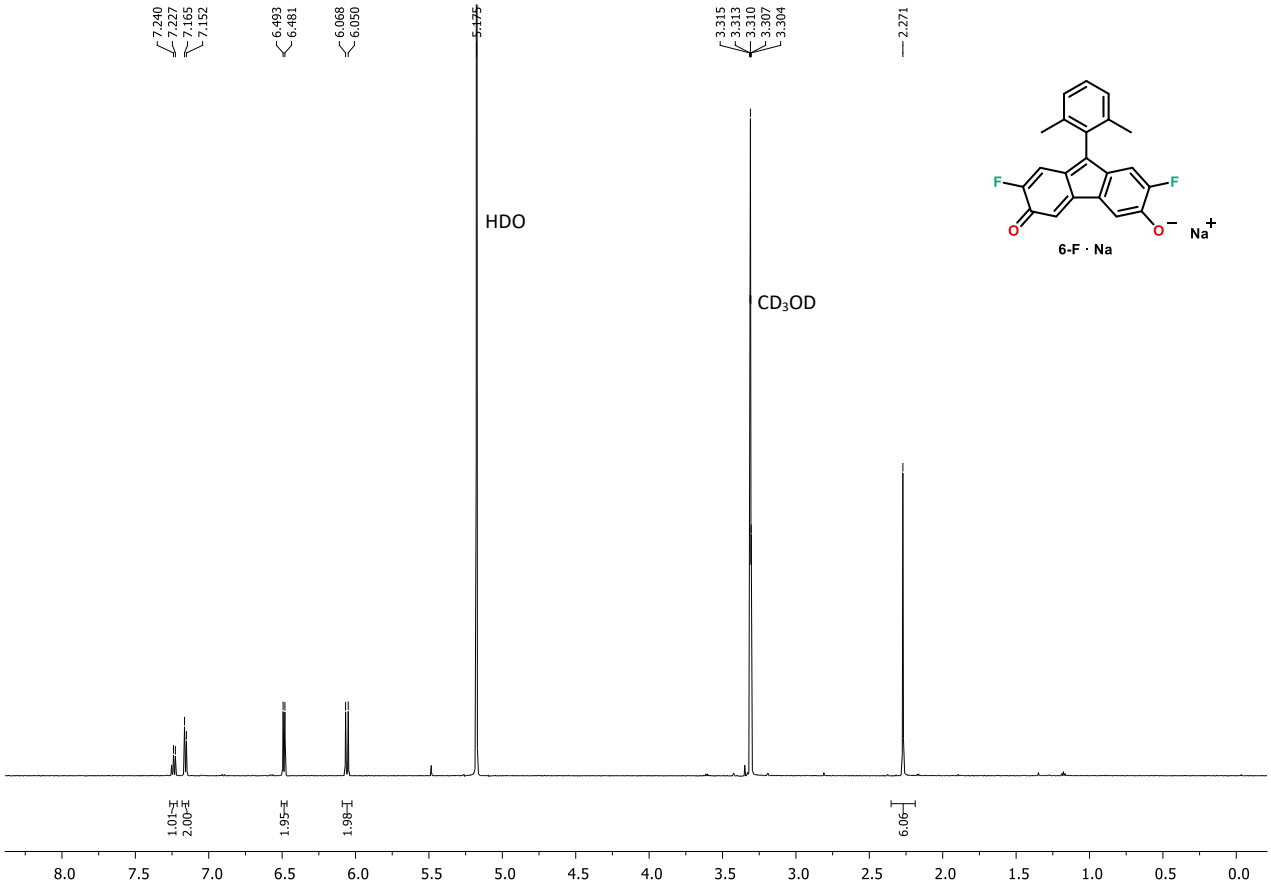

Figure S42. ^{1}H NMR spectrum of compound **6-F** (600 MHz, 50/1 (*v*/*v*) CD_3OD / 30% NaOD in D_2O).

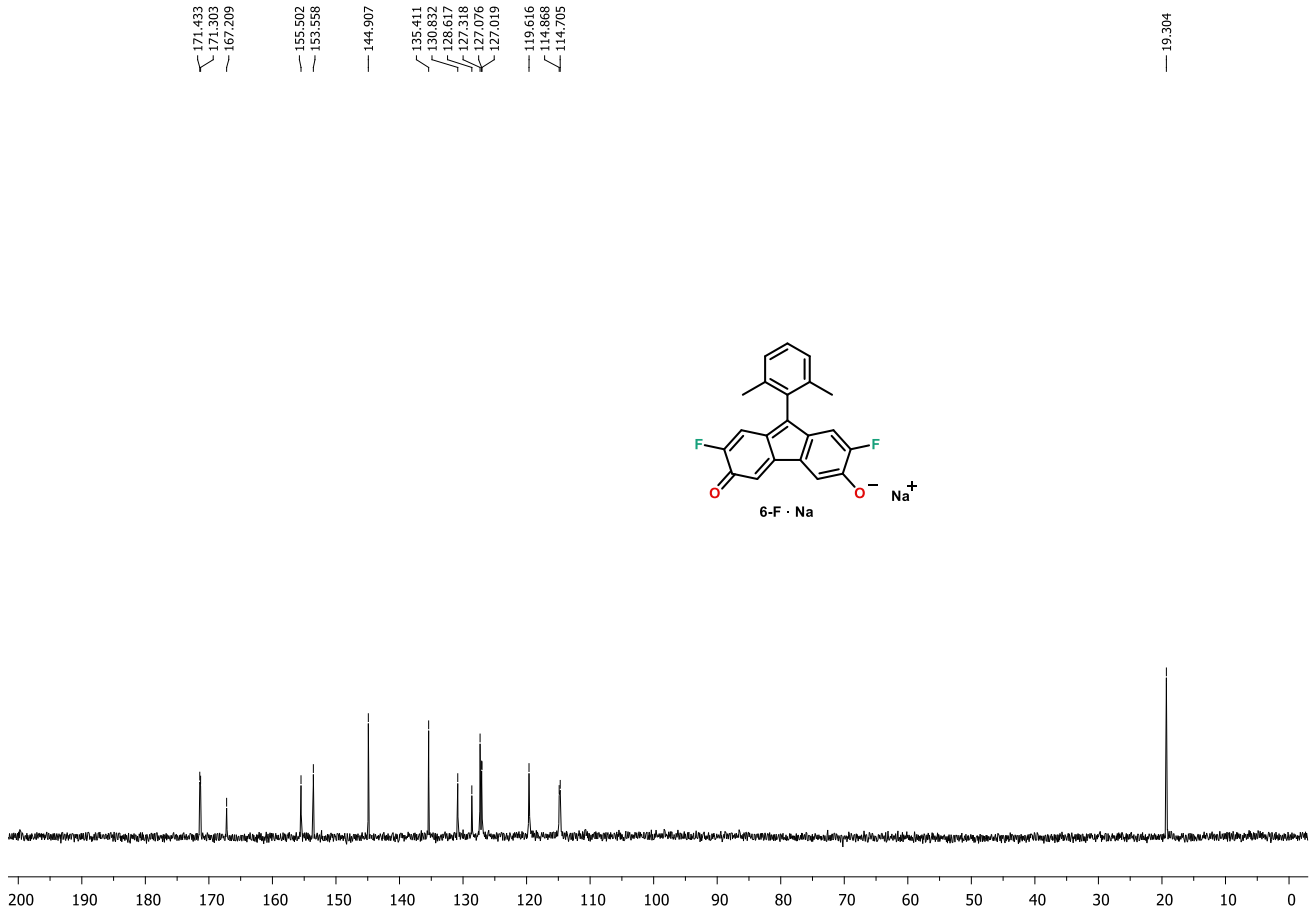

Figure S43. ^{13}C NMR spectrum of compound **6-F** (126 MHz, 50/1 (*v*/*v*) D_2O / 30% NaOD in D_2O).