Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information
for

Laterally π-expanded fluorone dye as an efficient near infrared fluorophore

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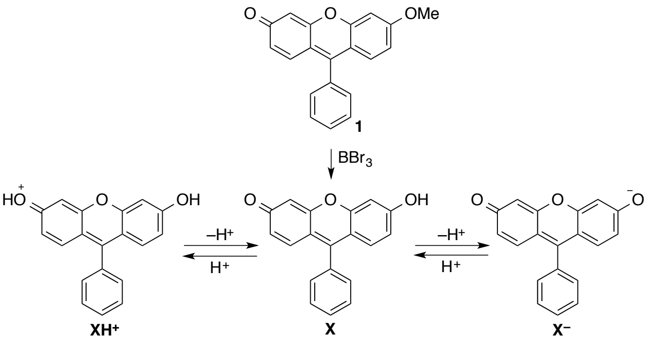
1. Instrumentation and Materials

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz and 150 MHz) spectra were recorded with JEOL JNM-ECX 400 and JEOL JNM-ECP 400 and JEOL JNM-ECA 600 spectrometers at ambient temperature by using tetramethylsilane as an internal standard. The high-resolution MS were measured by a JEOL spiralTOF JMS-S3000 spectrometer and a JEOL AccuTOF JMS-T100LC (ESI) using positive ion modes. X-ray diffraction data for **1** and **X**HBr were collected at 90 K with a Bruker APEX II X-Ray diffractometer equipped with a large area CCD detector by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). X−ray crystallographic data for **6** were recorded at 100 K on a Rigaku R-AXIS RAPID/S using Mo-Kα radiation. The structure was solved by direct method (SHELXS-97) and refined with the SHELX-97 program.

UV/Vis/NIR absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570. Fluorescence spectra for **X** were measured with a JASCO FP-6600 spectrofluorometer. Fluorescence spectra for **BX** and **FBX** were measured with a HORIBA Jobin Yvon Spectrofluorometer Fluorolog-3 (Model: FL3-11-NIR). The LN2 cooled solid detector DSS-IGA020L was used (the detection range: 800 nm-1550 nm).

TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All other solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade CH_2Cl_2, CH_3CN, THF and DMSO were purchased from Nacalai Tesque.

2. Experimental Section



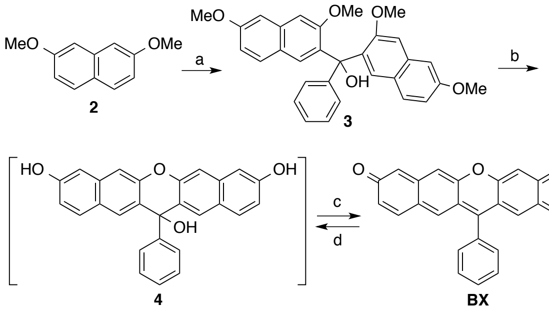
9-Phenyl-3-methoxy-3-fluorone (1): This compound was synthesized according to the literature.[S1] UV-vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 455 (4.2 × 10^4); Fl (CH_2Cl_2, λ_{ex} = 400 nm): λ_{max} = 511 nm.

9-Phenyl-3-hydroxy-3-fluorone (X): This compound was synthesized according to the literature.[S1] UV-vis (THF): λ_{max} (ε [M^{-1} cm^{-1}]) = 455 (1.9 × 10^4) nm.

9-Phenyl-3-hydroxy-3-fluorone hydrogen bromide complex (XHBr): ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.67 (m, 3H), 7.51 (m, 2H), 7.24 (d, J = 9.6 Hz, 2H) and 6.85 (m, 4H) ppm; UV-vis (THF): λ_{max} (ε [M^{-1} cm^{-1}]) = 455 (2.2 × 10^4) nm.

X-TFA complex (XH$^+$): ^{1}H NMR (400 MHz, THF-d_8): δ = 7.66-7.62 (m, 3H), 7.46 (dd, J = 7.2 and 3.6 Hz, 2H), 7.28 (d, J = 9.6 Hz, 2H), 6.89 (d, J = 2.4 Hz, 2H) and 6.80 (dd, J = 9.2 and 2.4 Hz, 2H) ppm; UV-vis-NIR (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 435 (5.1 × 10^4) nm.

9-Phenyl-3-hydroxy-3-fluorone with CsF (X$^-$Cs$^+$): ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.57 (m, 3H), 7.36 (dd, J = 7.6 and 1.6 Hz, 2H), 6.67 (d, J = 9.2 Hz, 2H), 6.07 (dd, J = 9.2 and 2.4 Hz, 2H) and 5.95 (d, J = 1.6 Hz, 2H) ppm; UV-vis (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 489 (2.6 × 10^4) and 522 (8.0 × 10^4) nm; Fl (CH_3CN, λ_{ex} = 490 nm): λ_{max} = 541 nm.



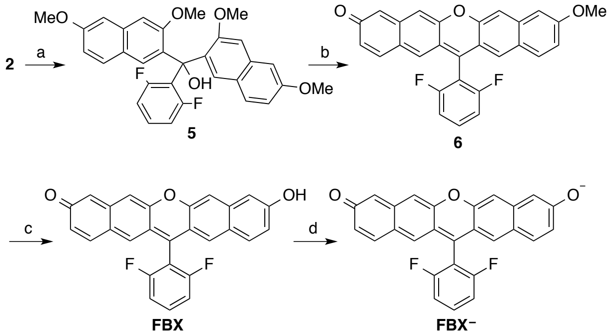
Bis(3,6-dimethoxynaphthalen-2-yl)phenylmethanol 3: A solution of **2** (4.0 g, 21 mmol) in 40 mL of dry THF was cooled to -10°C before tetramethylethylenediamine (TMEDA; 6.4 mL, 43 mmol) and *n*-butyllithium (2.5 M; 9.2 mL, 23 mmol) was added dropwise. After stirring for 1 h, the mixture was cooled to -78°C. Methyl benzoate (1.3 mL, 10 mmol) in 16 mL of dry THF was added dropwise over 10 min. The mixture was allowed to warm to room temperature over 5 h. The reaction mixture was quenched with distilled water and neutralized with 1 N HCl. After removal of THF in vacuo, the resulting mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered, and evaporated to dryness. The residue was purified by flash column chromatography (silica gel; CH_2Cl_2:hexane, 2:1) to afford 1.8 g (36%) of **3** as a white powder. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.51$ (d, $J = 9.2$ Hz, 2H), 7.43 (s, 2H), 7.29-7.23 (m, 5H), 7.15 (s, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 6.95 (dd, $J = 2.4$ and 8.6 Hz, 2H), 5.23 (s, 1H), 3.90 (s, 6H) and 3.63 (s, 6H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 158.39$, 156.90, 146.85, 135.39, 132.55, 129.66, 128.65, 127.91, 127.14, 126.52, 123.65, 116.17, 106.31, 104.58, 81.00, and 55.32 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{31}H_{28}O_5$, 503.1834 $[M + Na]^+$; found, 503.1775.

9-Hydroxy-13-phenyl-3*H*-dibenzo[*b,i*]xanthen-3-one (BX): To a solution of **3** (200 mg, 0.416 mmol) in 8 mL of dry CH_2Cl_2 at -78°C, BBr_3 in CH_2Cl_2 (1.0 M, 7.7 mL, 7.7 mmol) was added dropwise. The mixture was warmed to room temperature gradually over 8 h before quenching with 1.0 mL of distilled water. After stirring overnight with refluxing, a black precipitate was collected. The precipitate was filtered and washed with water, CH_2Cl_2 and dried in vacuo to afford a black solid of protonated-BX mixture (157 mg).

A part of the mixture (21.3 mg) was dissolved in 2.0 mL DMSO and neutralized with 2.0 mL sat. $NaHCO_3$ aq., then extracted with CH_2Cl_2. The organic layer was washed with distilled water. The extract was dried over Na_2SO_4 and filtered before evaporation to dryness to afford blue residue (**4**). The residue was heated at 150°C in vacuo for 2 h to obtain black solid of BX (18.2 mg, 83%). HR-MS (Spiral MALDI): *m/z*: calcd for $C_{27}H_{16}O_3Na$, 411.0997 $[M + Na]^+$; found, 411.0986; UV-vis-NIR (THF): λ_{max} (ε [M^{-1} cm^{-1}]) = 489 (1.9×10^4) and 608 (1.7×10^4) nm.

BX-TFA complex: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.80$ (br, 2H), 7.98 (s, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.49 (s, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.21 (t, $J = 8.0$ Hz, 2H), 7.11-7.07 (m, 3H) and 6.95 (dd, $J = 8.4$ and 1.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 156.47$, 150.31, 149.52, 135.37, 130.08, 128.76, 128.53, 127.42, 126.84, 125.66, 125.26, 118.13, 109.81, 107.86, and 70.52 ppm; UV-vis-NIR (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 578 (5.9×10^4) nm.

BX^-Cs^+: ^1H NMR (400 MHz, CD_3CN): $\delta = 7.63$-7.61 (m, 3H), 7.48 (m, 2H), 7.36-7.32 (m, 2H), 7.31 (d, $J = 9.6$ Hz, 2H) 7.23 (s, 2H), 6.83 (s, 2H), 6.50 (dd, $J = 9.6$, 1.6 Hz, 2H) and 6.36 (br, 2H) ppm; UV-vis-NIR (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 778 (9.3×10^4) nm; Fl (CH_3CN, $\lambda_{ex} = 702$ nm): $\lambda_{max} = 809$ and 916 nm.



Bis(3,6-dimethoxynaphthalen-2-yl)(2,6-difluorophenyl)methanol 5: A solution of **2** (2.0 g, 11 mmol) in 20 mL of dry THF was cooled to -10°C before tetramethylethylenediamine (TMEDA; 3.2 mL, 21 mmol) and *n*-butyllithium (2.4 M; 4.9 mL, 12 mmol) was added dropwise. After stirring for 1 h, the mixture was cooled to -78°C. Methyl 2,6-difluorobenzoate (710 μL, 5.3 mmol) in 8.0 mL of dry THF was added dropwise over 10 min. The mixture was allowed to warm to room temperature over 2 h. The reaction mixture was quenched with distilled water and neutralized with 1 N HCl. After removal of THF in vacuo, the resulting mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and filtered before evaporation to dryness. The residue was roughly separated by flash chromatography (silica gel; CH_2Cl_2:hexane, 3:1). Collected mixture was suspended in ethyl acetate and filtrated to afford 0.65 g (23%) of **5** as a white powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.64 (s, 2H), 7.57 (d, J = 9.2 Hz, 2H), 7.16-7.13 (m, 3H), 7.11 (d, J = 2.8 Hz, 2H), 6.95 (dd, J = 2.8 and 8.8 Hz, 2H), 6.71 (dd, J = 8.8 and 10.0 Hz, 2H), 5.33 (s, 1H), 3.90 (s, 6H) and 3.71 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.33, 159.82, 158.29, 156.64, 135.27, 131.00, 130.06, 127.76, 127.37, 123.90, 116.10, 111.37, 105.32, 104.68 and 55.31 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{31}H_{26}F_2O_5$, 539.1641 $[M\text{-}Na]^+$; found, 539.1646.

9-Methoxy-13-(2,6-difluorophenyl)-3*H*-dibenzo[*b,i*]xanthen-3-one 6:

To a solution of **5** (125 mg, 0.24 mmol) in 5.0 mL of dry CH_2Cl_2 at -78°C, BBr_3 in CH_2Cl_2 (1.0 M, 4.3 mL, 4.3 mmol) was added dropwise. The mixture was warmed to 0°C gradually over 5 h before quenching with 0.5 mL of distilled water. After stirring overnight at room temperature, a black precipitate was collected. After neutralization of the reaction mixture with saturated $NaHCO_3$ aq., the precipitate was filtered and washed with water and CH_2Cl_2, then dried in vacuo. The filtrate was extracted with CH_2Cl_2, washed with water. The organic layer was dried over Na_2SO_4 and filtered before evaporation to dryness. The evaporated residue and filtered residue were combined and purified by column chromatography (silica gel; ethyl acetate only) to afford a black solid of **6** (56.2 mg, 53%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.91-7.82 (m, 2H), 7.76 (s, 1H), 7.63-7.61 (m, 2H), 7.50 (t, J = 8.4 Hz, 2H), 7.40 (d, J = 2.0 Hz, 1H), 7.28 (s, 1H), 7.10 (dd, J = 2.4 Hz, 1H), 6.92 (s, 1H), 6.43 (s, 1H), 6.43-6.38 (m, 2H), and 3.92 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.49, 161.14, 160.45, 159.52, 150.18, 149.42, 141.89, 137.96, 136.25, 133.59, 132.16, 131.24, 130.59, 130.04, 129.489, 127.52, 125.82, 124.87, 119.91, 119.48, 119.06, 112.36, 112.23, 110.54, 105.76, 104.68 and 55.53 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{28}H_{16}F_2O_3$, 439.1140 $[M\text{-}H]^+$; found, 439.1156; UV-vis (CH_2Cl_2): $\lambda_{\max}$ (ε [M^{-1} cm^{-1}]) = 492 (2.2×10^4) and 619 (1.7×10^4) nm.

9-Hydroxy-13-(2,6-difluorophenyl)-3*H*-dibenzo[*b,i*]xanthen-3-one (FBX): To a solution of **6** (72 mg, 0.16 mmol) in 10 mL of dry CH_2Cl_2 at -78°C, BBr_3 in CH_2Cl_2 (1.0 M, 6.6 mL, 6.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 12 h before quenching with 2.0 mL of distilled water. After stirring for 30 min, a black precipitate was collected. After neutralization of the reaction mixture with saturated $NaHCO_3$ aq., the precipitate was filtered and washed with water and CH_2Cl_2, then dried in vacuo to afford black solid of FBX (59 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.49 (s, 2H), 7.87-7.82 (m, 2H), 7.66 (s, 1H), 7.61 (d, J = 10.0 Hz, 1H), 7.55 (s, 1H), 7.50 (t, J = 8.4 Hz, 1H), 7.26 (s, 1H), 7.16 (s, 1H), 7.02 (d, 9.2 Hz, 1H), 6.89 (s, 1H), and 6.41-6.37 (m, 2H) ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{27}H_{15}F_2O_3$, 425.0984 $[M\text{-}H]^+$; found, 425.0971; UV-vis (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 494 (1.9×10^4) and 607 (1.6×10^4) nm.

FBX-TFA complex: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.81 (br, 2H), 7.81 (s, 2H), 7.70 (d, J = 9.2 Hz, 2H), 7.46 (s, 2H), 7.34 (m, 1H), 7.09 (s, 2H) and 6.99-6.92 (m, 4H) ppm; UV-vis (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 459 (1.2×10^4) and 605 (5.9×10^4) nm.

FBX^-Cs^+: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.83 (m, 1H), 7.61 (d, J = 10.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.29 (s, 2H), 7.12 (br, 2H) ppm and 6.60 (m, 4H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 180.49, 160.39, 158.75, 149.46, 141.60, 135.61, 133.37, 132.55, 128.65 128.49, 124.61, 115.31, 112.47 and 103.40 ppm; UV-vis-NIR (CH_3CN): λ_{max} (ε [M^{-1} cm^{-1}]) = 802 (9.6×10^4) nm; Fl (CH_3CN, λ_{ex} = 720 nm): λ_{max} = 839 and 951 nm.

3. NMR Spectra

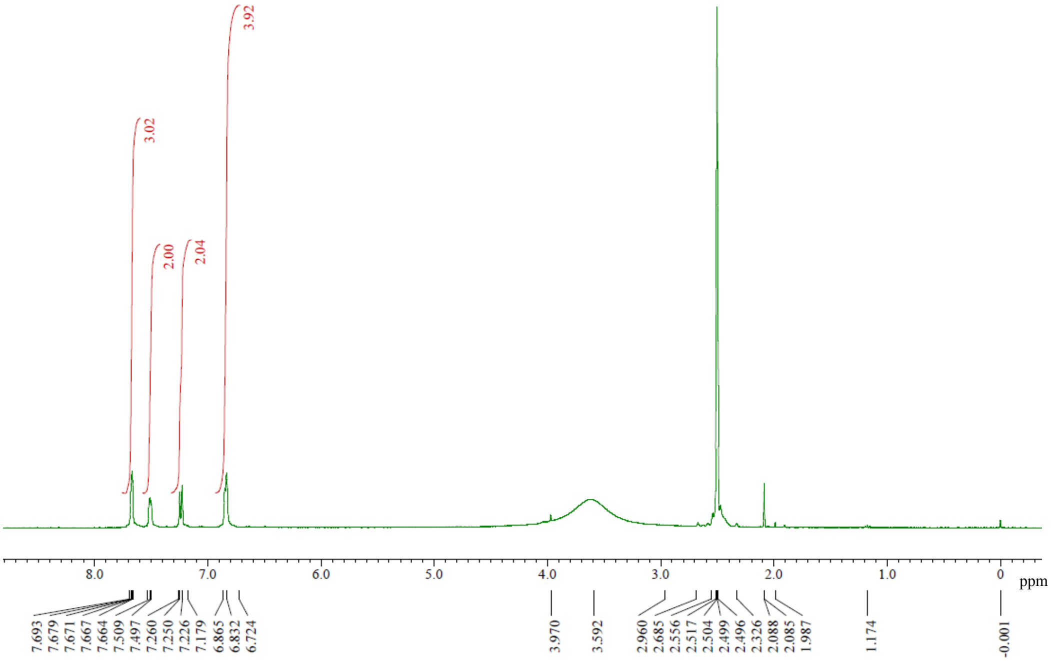


Figure S1. ^{1}H NMR spectrum of XHBr in DMSO-d_6 at room temperature.

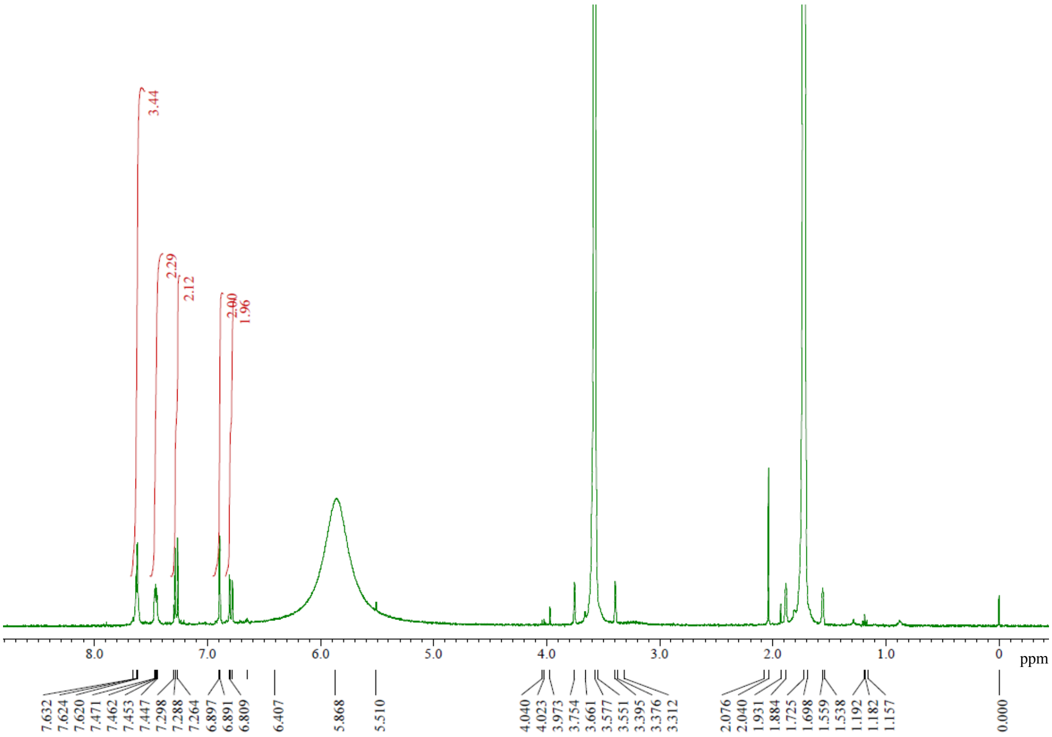


Figure S2. ^{1}H NMR spectrum of X-TFA in THF-d_8 at room temperature.

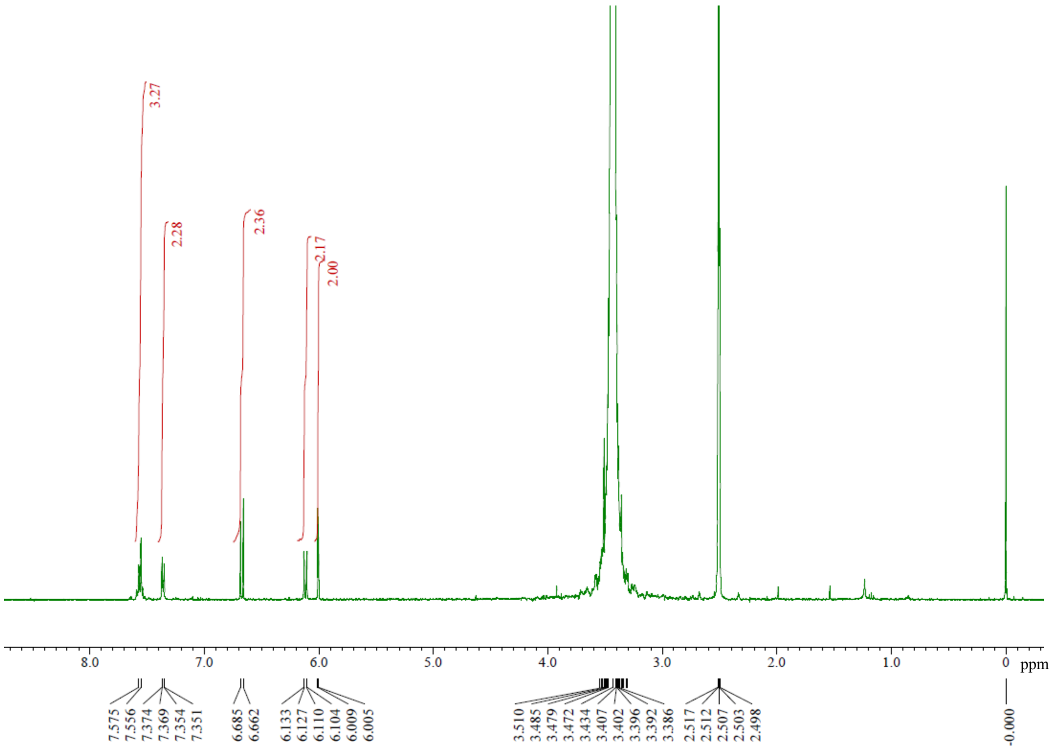


Figure S3. ^{1}H NMR spectrum of X-Cs$^+$ in DMSO-d$_6$ at room temperature.

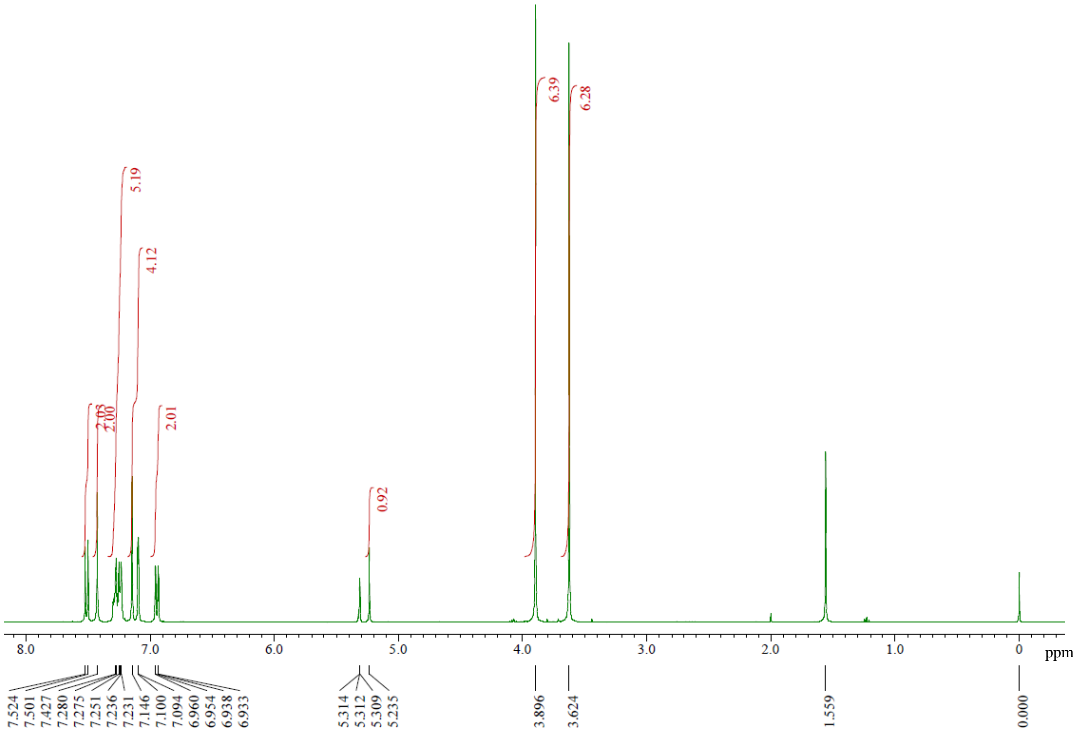


Figure S4. ^{1}H NMR spectrum of **3** in CD_2Cl_2 at room temperature.

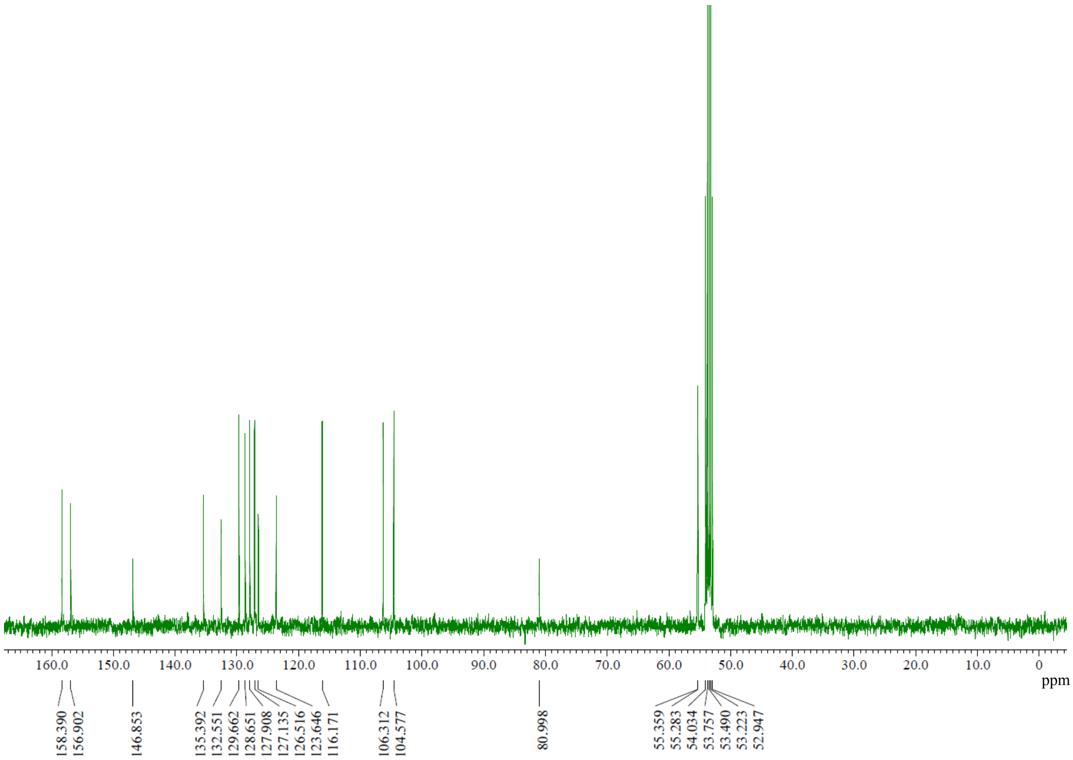


Figure S5. ^{13}C NMR spectrum of **3** in CD_2Cl_2 at room temperature.

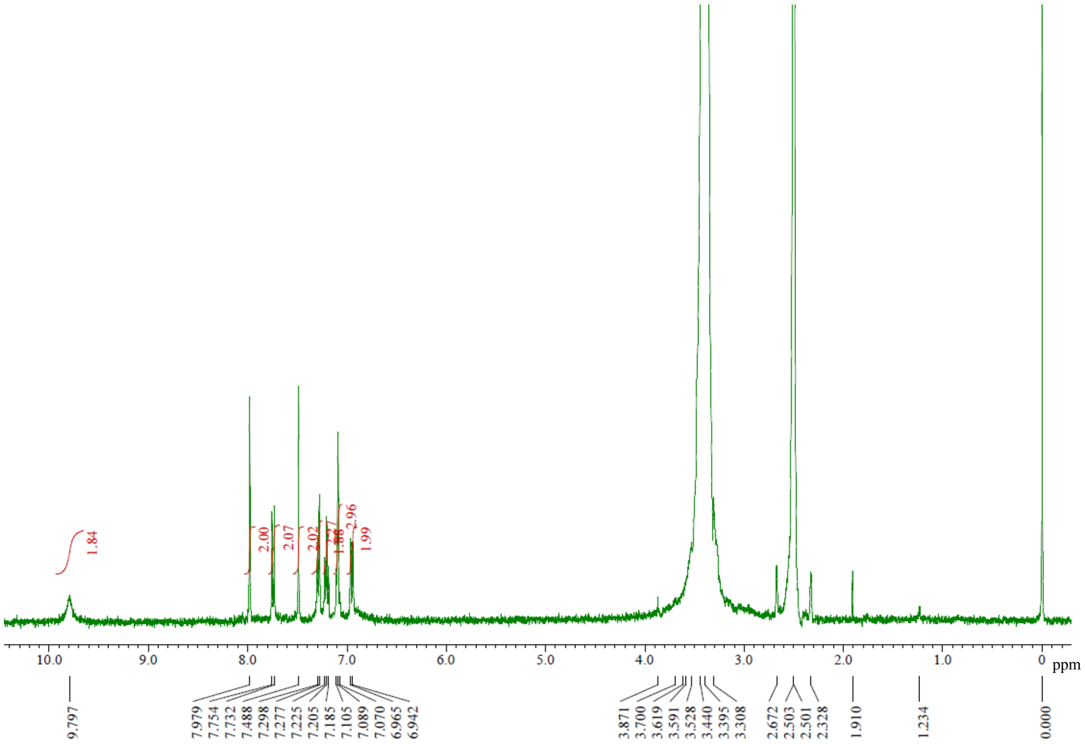


Figure S6. ^{1}H NMR spectrum of BX-TFA in DMSO-d_6 at room temperature.

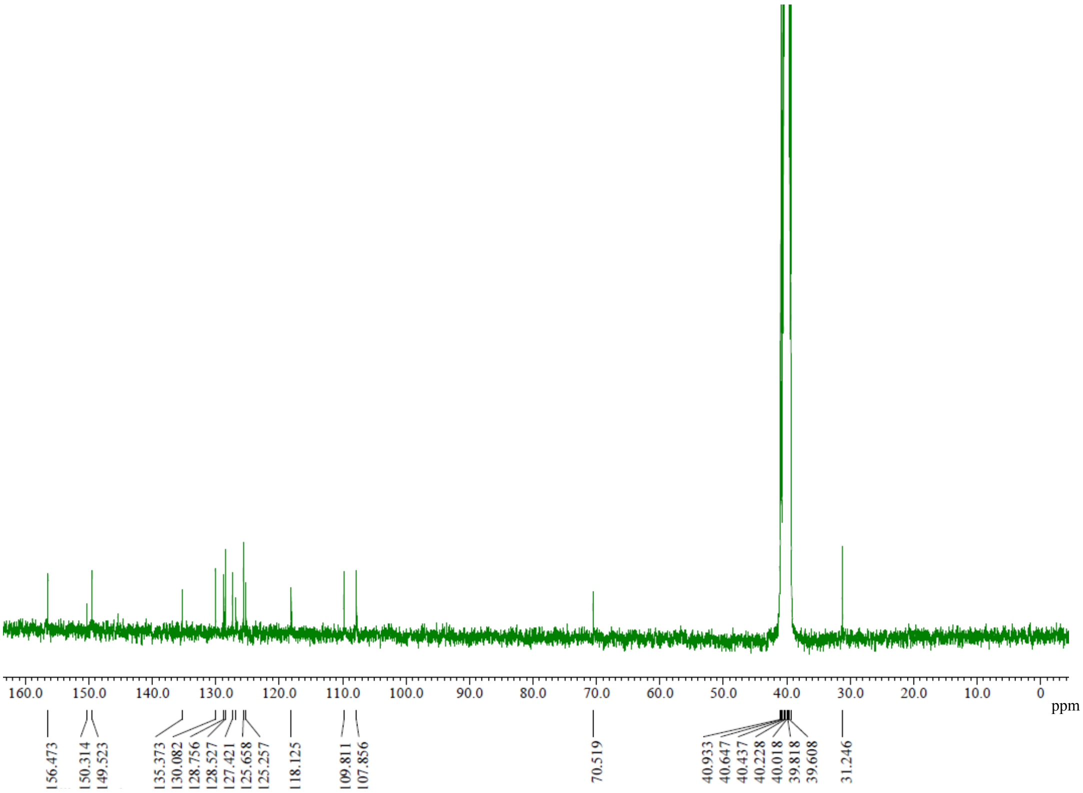


Figure S7. ^{13}C NMR spectrum of BX-TFA in DMSO-d_6 at room temperature.

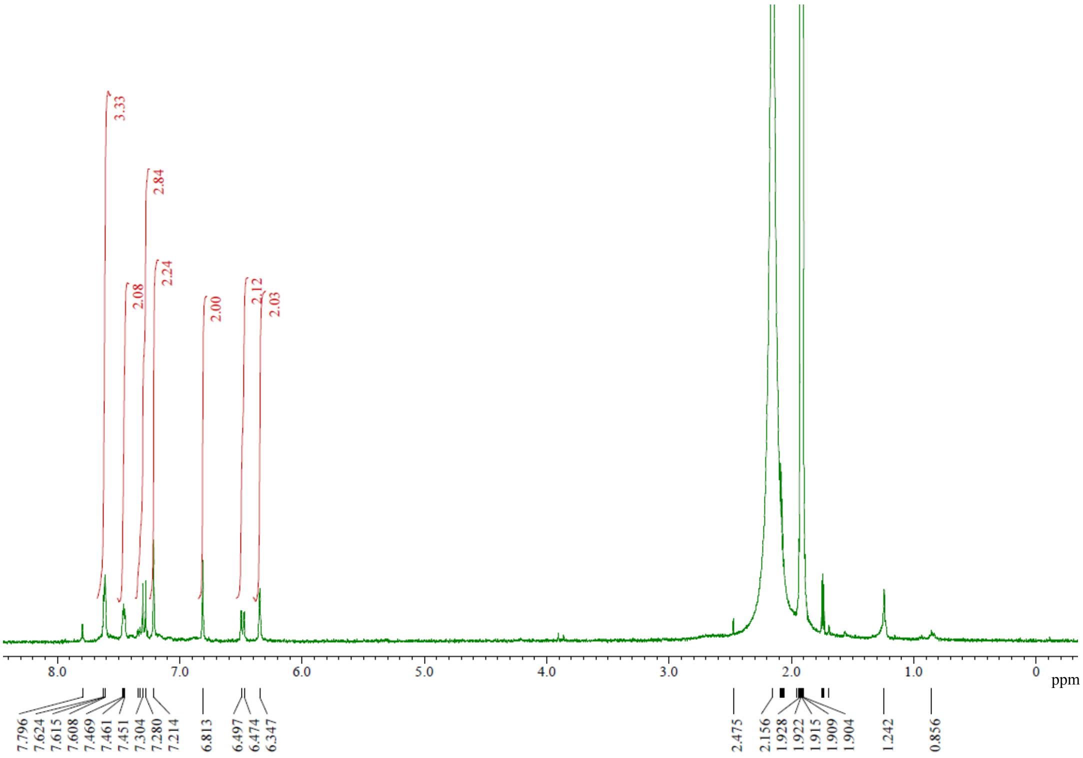


Figure S8. ^{1}H NMR spectrum of BX-Cs$^+$ in CD$_3$CN at room temperature.

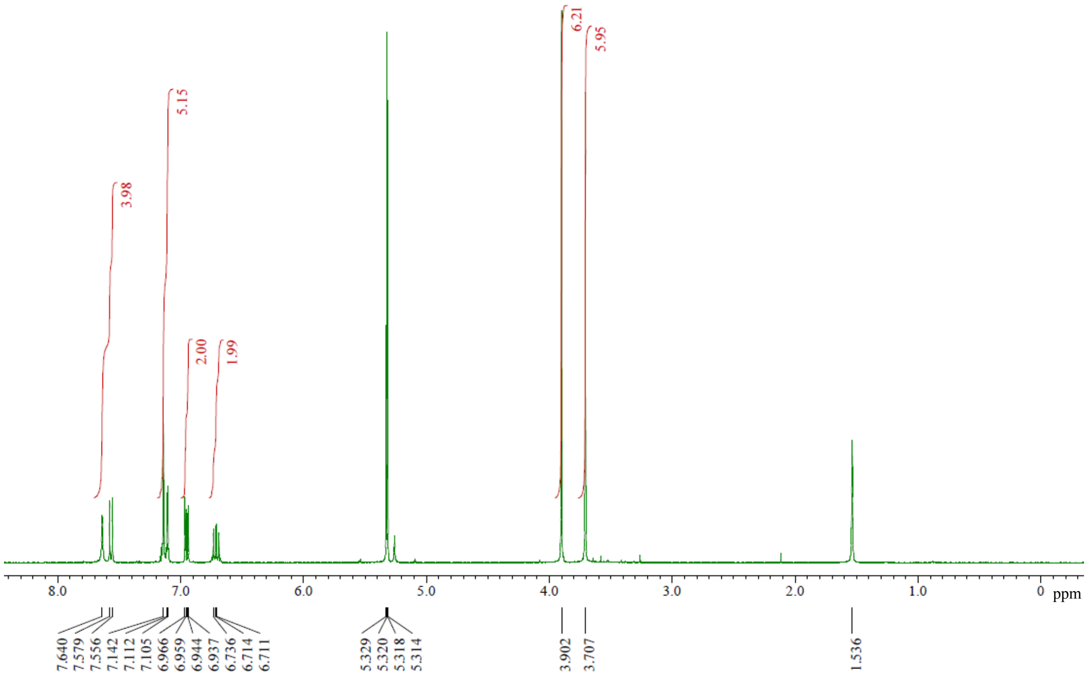


Figure S9. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at room temperature.

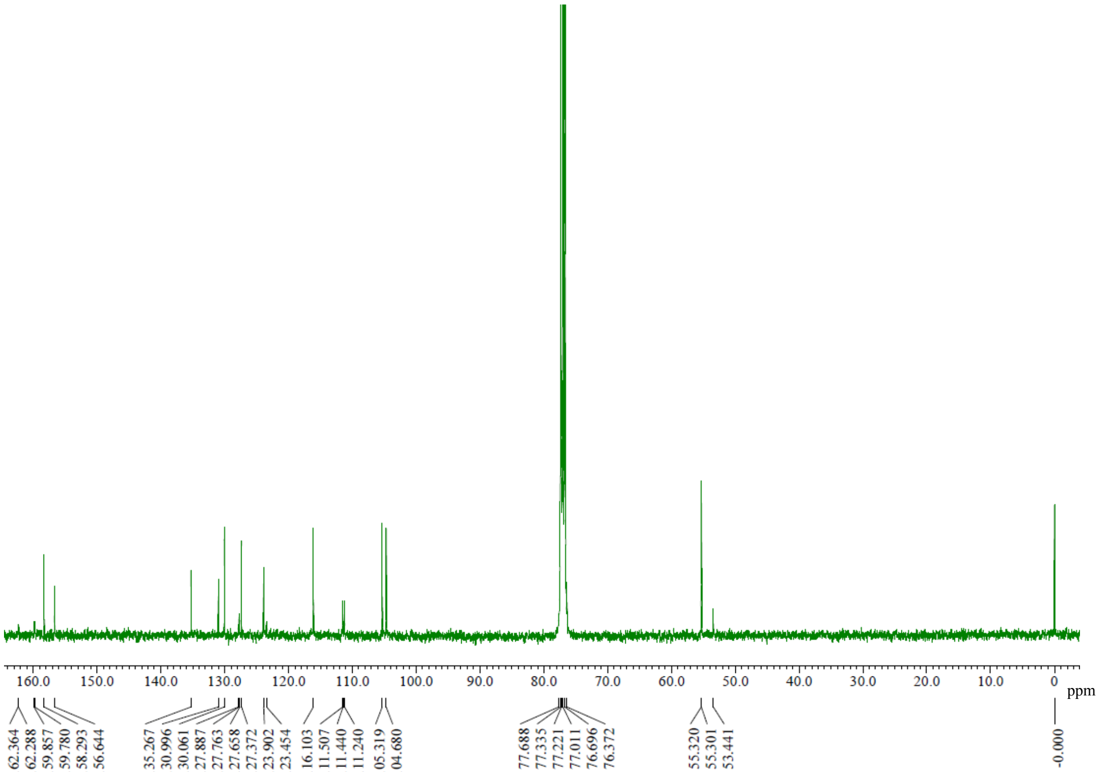


Figure S10. ^{13}C NMR spectrum of **5** in $CDCl_3$ at room temperature.

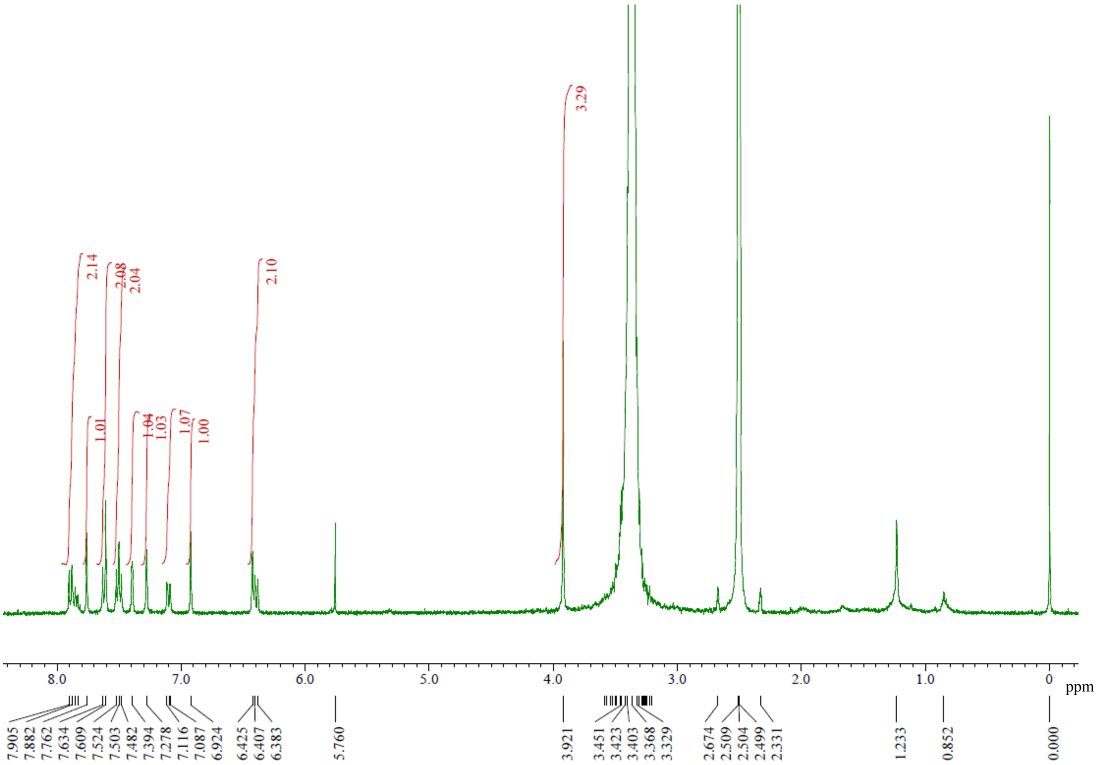


Figure S11. ^{1}H NMR spectrum of **6** in DMSO-d_6 at room temperature.

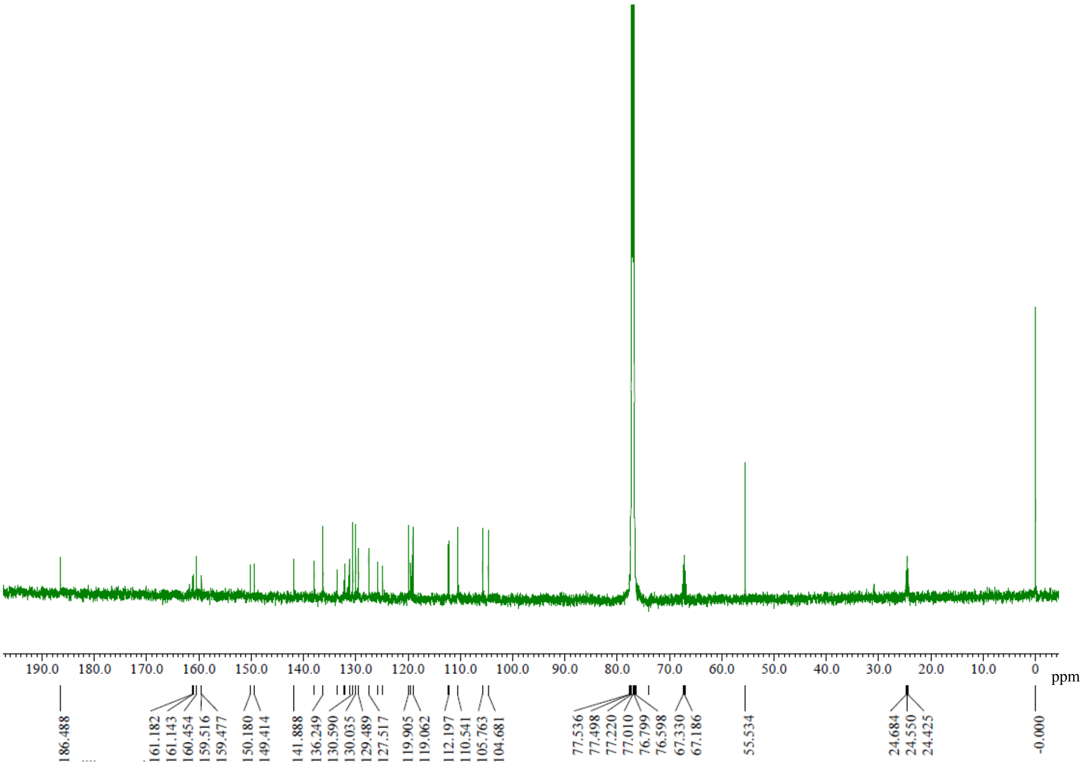


Figure S12. ^{13}C NMR spectrum of **6** in $CDCl_3$ at room temperature.

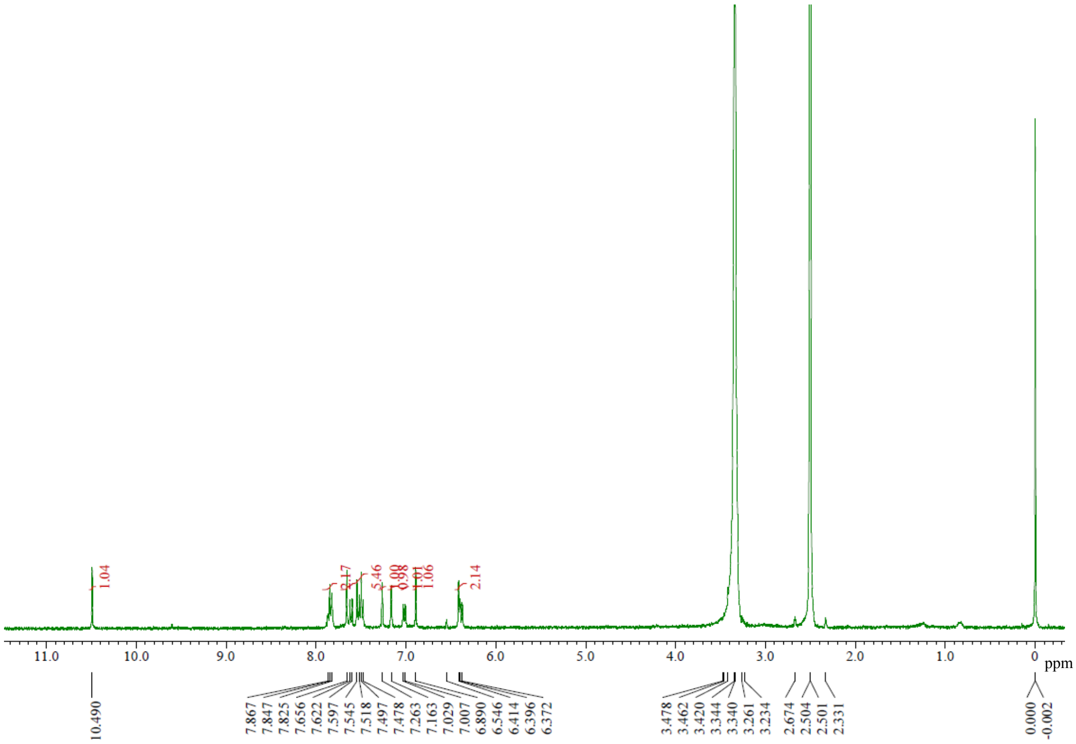


Figure S13. ^{1}H NMR spectrum of FBX in DMSO-d_6 at room temperature.

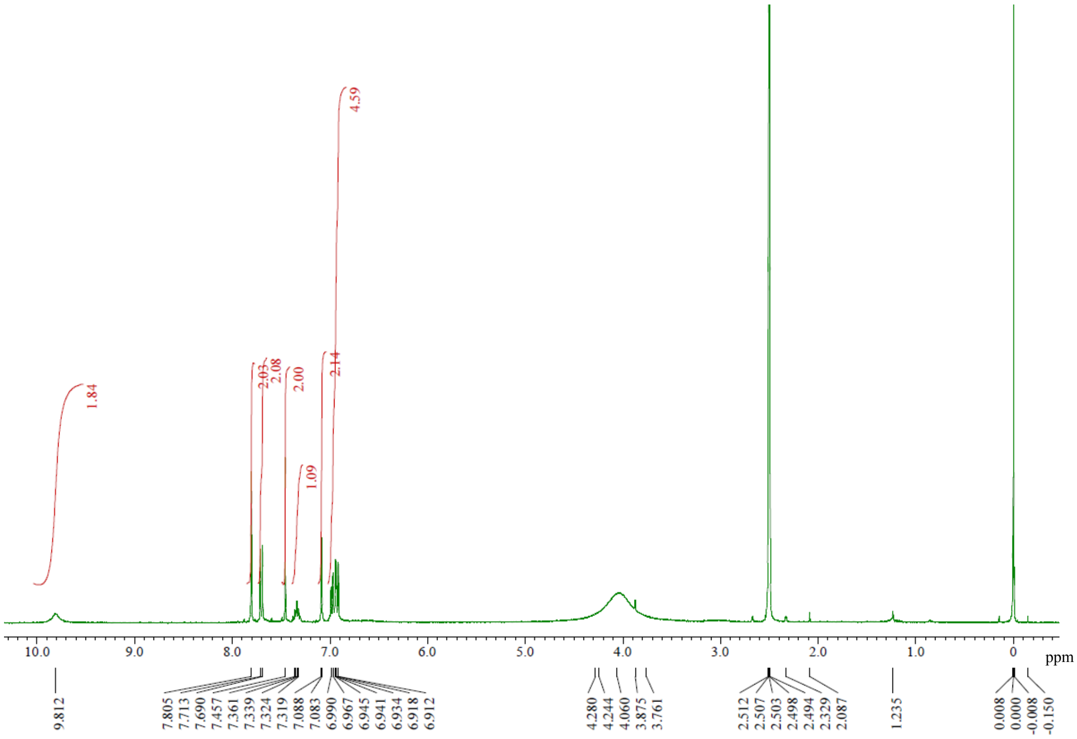


Figure S14. ^{1}H NMR spectrum of FBX-TFA in DMSO-d_6 at room temperature.

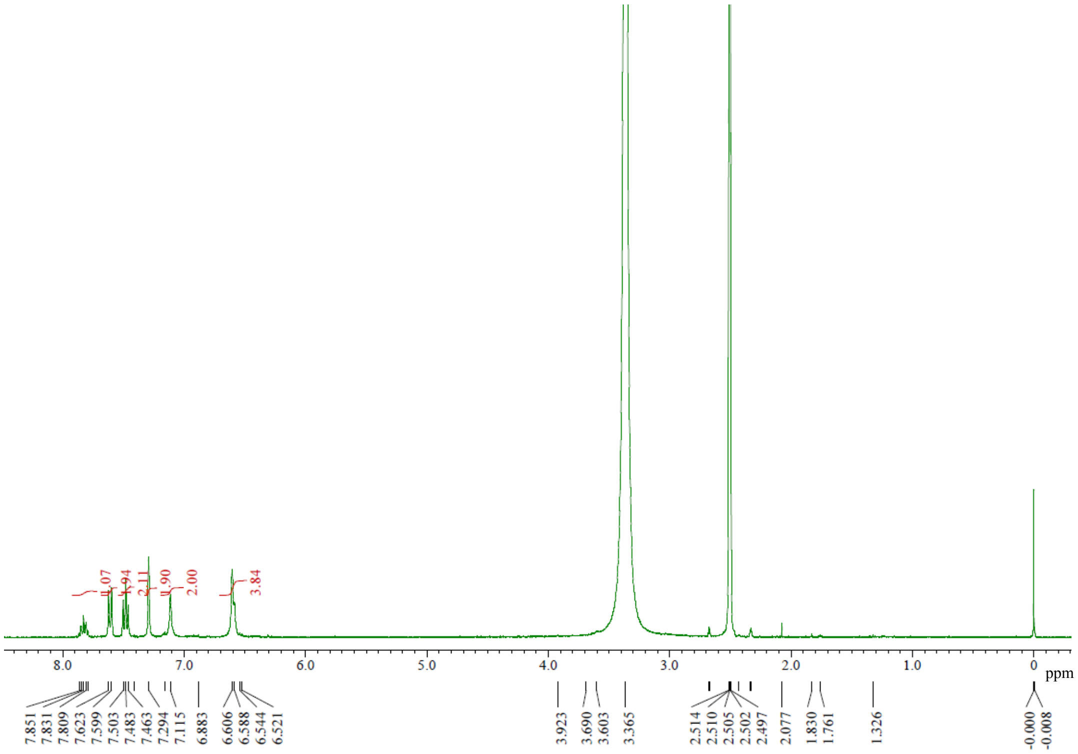


Figure S15. ^{1}H NMR spectrum of FBX-Cs$^+$ in DMSO-d$_6$ at room temperature.

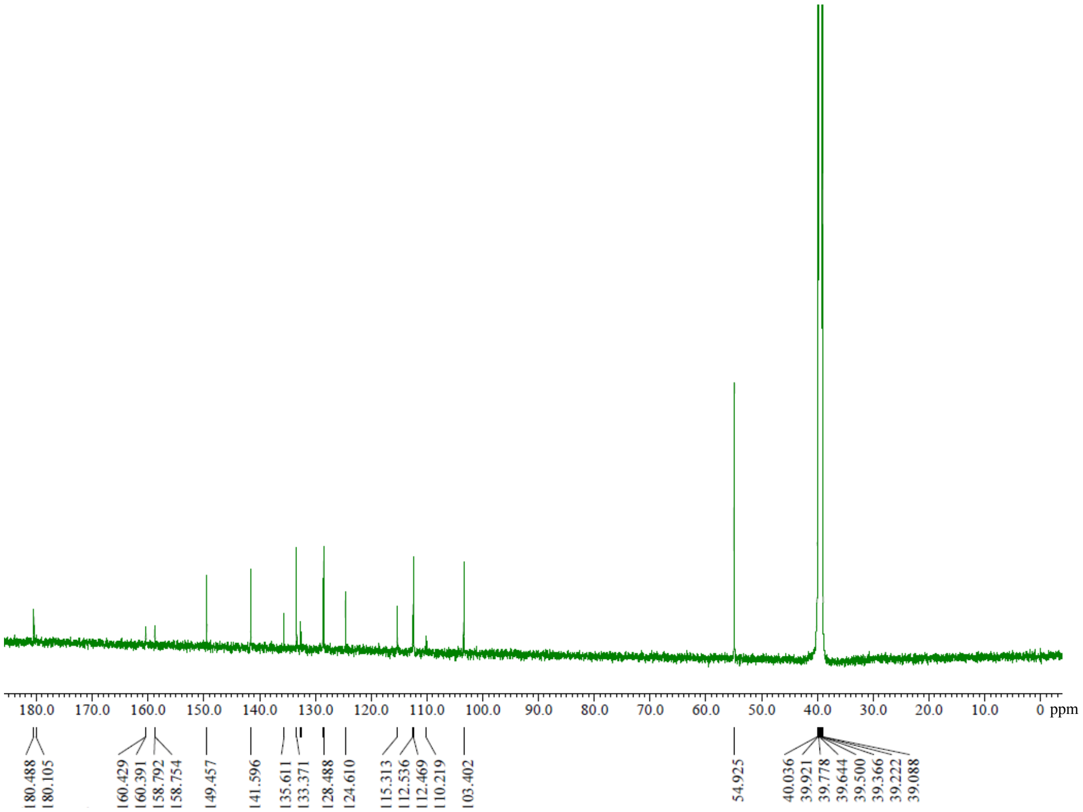
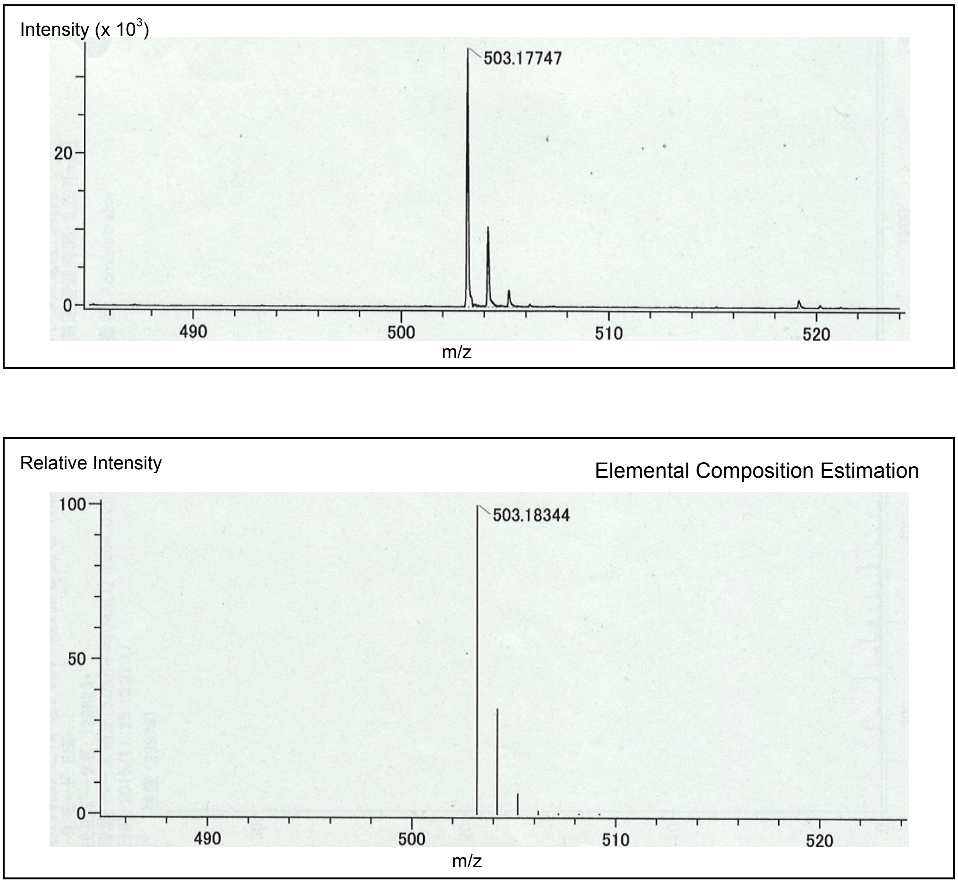


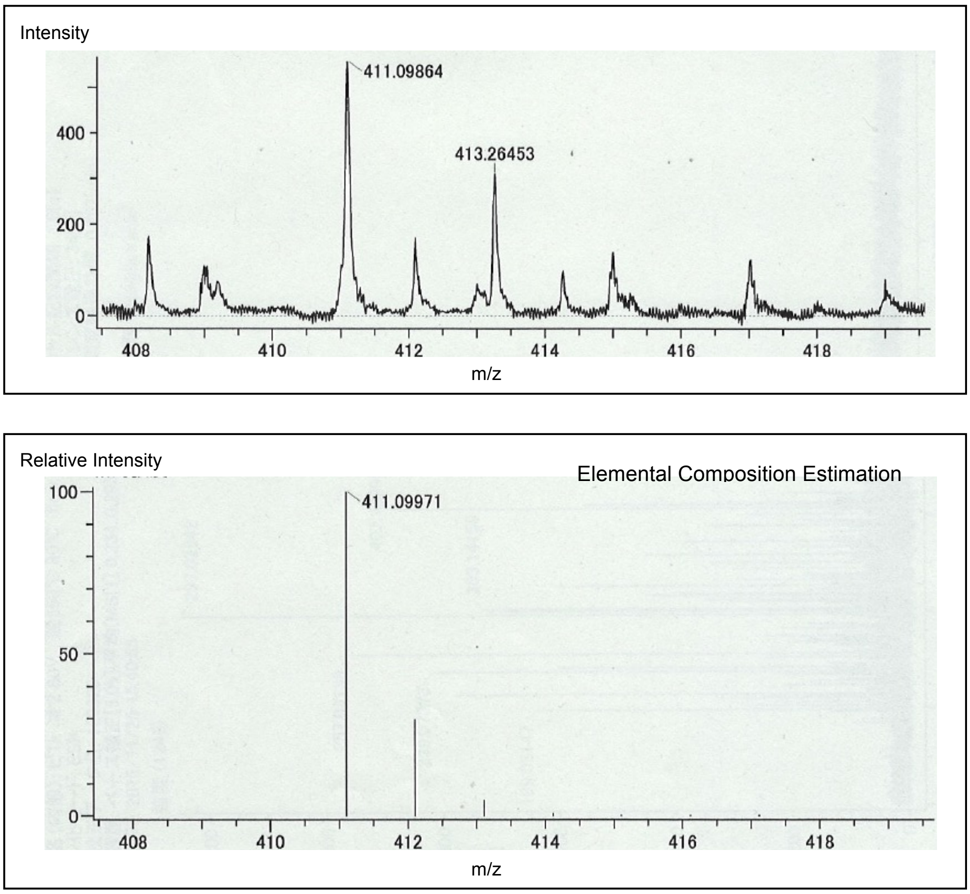
Figure S16. ^{13}C NMR spectrum of FBX-Cs$^+$ in DMSO-d$_6$ at room temperature.

4. HR-MS



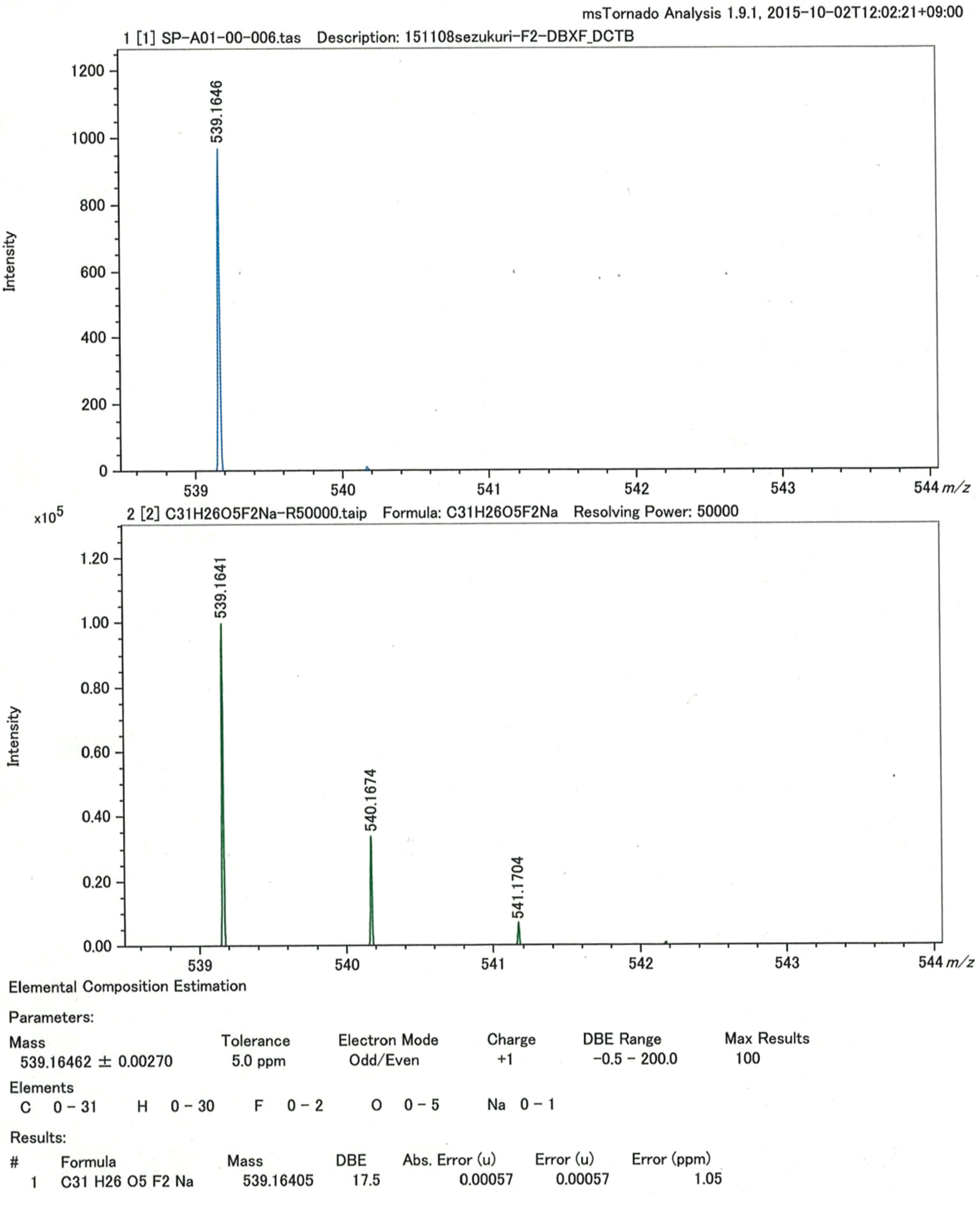
Adduct ion: Na^+, Formula: C31H38O5, Monoisotopic mass: 503.1834427, Average mass: 503.5407900.

Figure S17. HR-ESI mass spectrum of **3**.



Adduct ion: Na^+, Formula: $C_{27}H_{16}O_3$, Monoisotopic mass: 411.0997135, Average mass: 411.4039100.

Figure S18. HR-ESI mass spectrum of **BX**.


msTornado Analysis 1.9.1, 2015-10-02T12:02:21+09:00

1 [1] SP-A01-00-006.tas Description: 151108sezukuri-F2-DBXF_DCTB

2 [2] C31H26O5F2Na-R50000.taip Formula: C31H26O5F2Na Resolving Power: 50000

Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
539.16462 ± 0.00270	5.0 ppm	Odd/Even	+1	−0.5 − 200.0	100

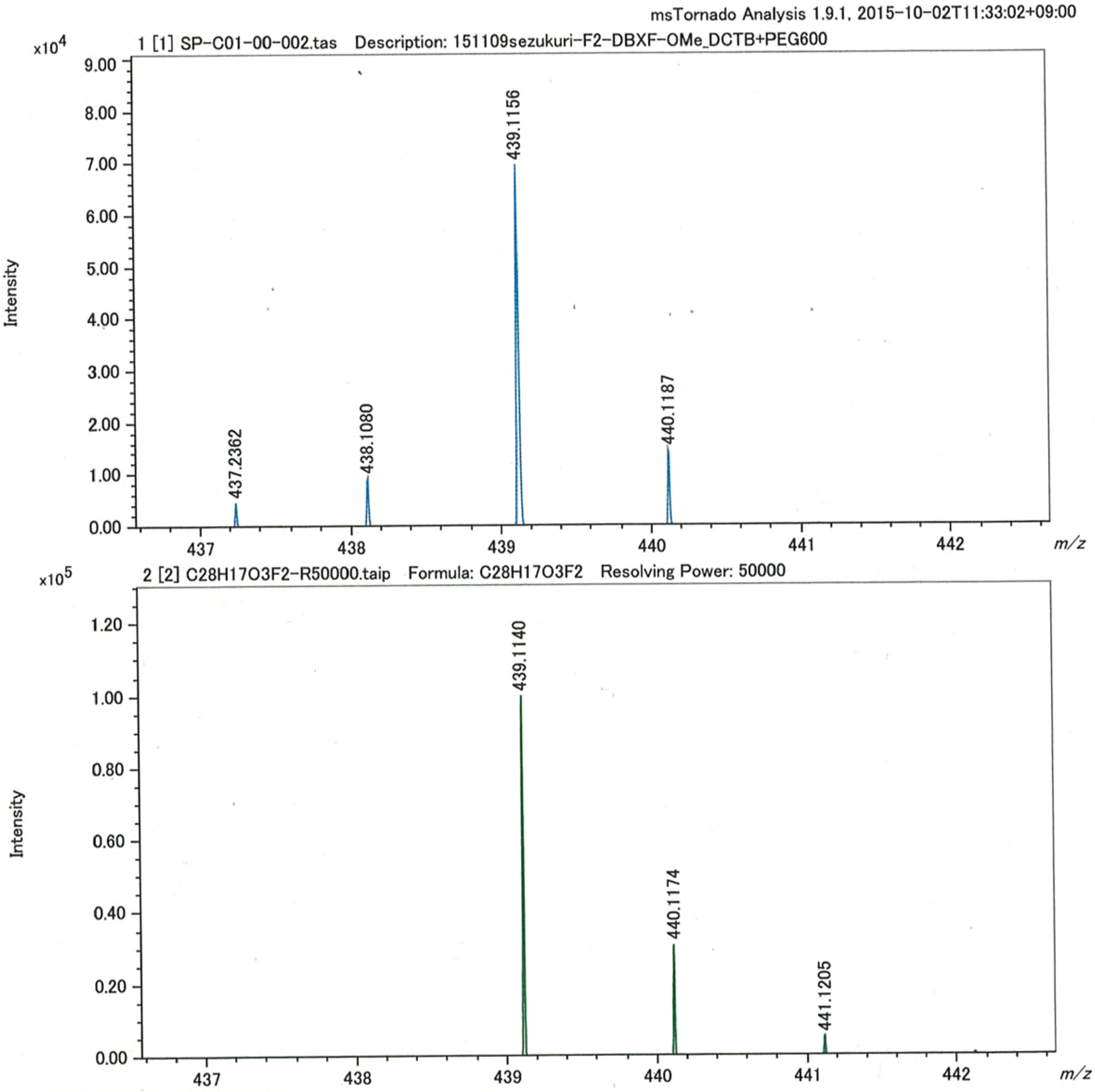
Elements

C	0 − 31	H	0 − 30	F	0 − 2	O	0 − 5	Na	0 − 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C31 H26 O5 F2 Na	539.16405	17.5	0.00057	0.00057	1.05

Figure S19. HR-Spiral-MALDI-TOF mass spectrum of **5**.



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
439.11558 ± 0.00220	5.0 ppm	Odd/Even	+1	−0.5 − 200.0	100

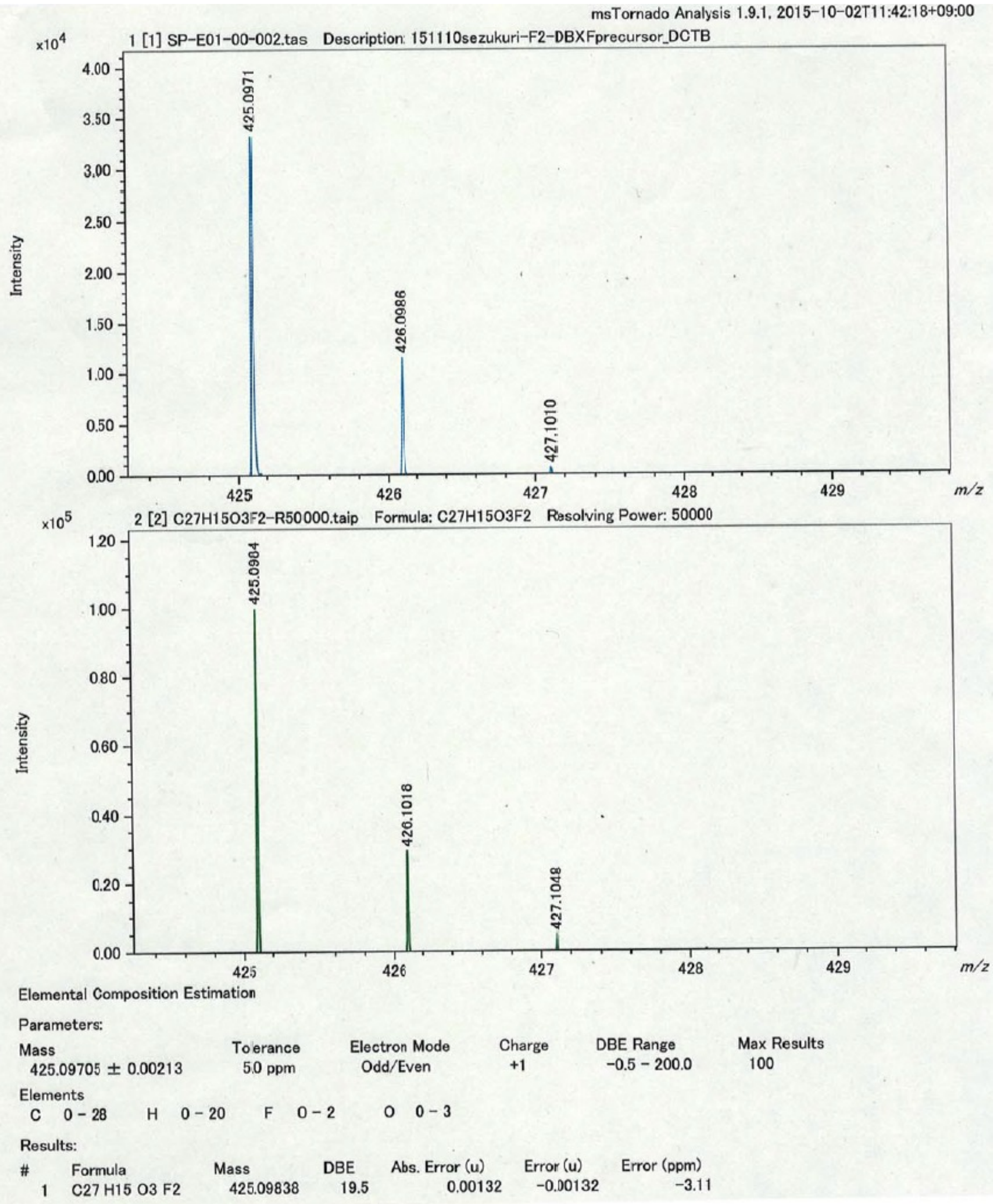
Elements

C 0 − 28 H 0 − 20 F 0 − 2 O 0 − 3

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C28 H17 O3 F2	439.11403	19.5	0.00155	0.00155	3.53

Figure S20. HR-Spiral-MALDI-TOF mass spectrum of **6**.


msTornado Analysis 1.9.1, 2015-10-02T11:42:18+09:00

1 [1] SP-E01-00-002.tas Description: 151110sezukuri-F2-DBXFprecursor_DCTB

2 [2] C27H15O3F2-R50000.taip Formula: C27H15O3F2 Resolving Power: 50000

Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
425.09705 ± 0.00213	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 28 H 0 - 20 F 0 - 2 O 0 - 3

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C27 H15 O3 F2	425.09838	19.5	0.00132	-0.00132	-3.11

Figure S21. HR-Spiral-MALDI-TOF mass spectrum of **FBX**.

5. DFT Calculations

	X	Y	Z
C 1	6.12258	−1.81361	0.00040
C 2	6.12293	−0.34069	−0.00694
C 3	4.97130	0.38148	−0.01017
C 4	3.67967	−0.25914	−0.00649
C 5	3.63871	−1.71687	−0.00018
C 6	4.82219	−2.44072	0.00344
C 7	2.50121	0.46683	−0.00759
C 8	1.22209	−0.14772	−0.00306
C 9	1.19954	−1.59044	0.00029
C 10	2.34262	−2.33740	0.00202
C 11	0.00003	0.55264	0.00047
C 12	−1.22195	−0.14776	0.00426
C 13	−1.19942	−1.59049	0.00188
C 14	−2.50115	0.46672	0.00763
C 15	−3.67956	−0.25925	0.00608
C 16	−3.63865	−1.71704	0.00040
C 17	−2.34242	−2.33752	−0.00044
C 18	−4.97120	0.38138	0.00860
C 19	−6.12298	−0.34051	0.00480
C 20	−6.12256	−1.81378	−0.00197
C 21	−4.82190	−2.44100	−0.00384
C 22	−0.00001	2.04718	0.00025
C 23	0.00713	2.79834	1.18060
C 24	0.00769	4.18884	1.21187
C 25	−0.00020	4.88225	−0.00011
C 26	−0.00804	4.18855	−1.21191
C 27	−0.00734	2.79805	−1.18030
O 1	0.00010	−2.26220	0.00232
O 2	7.20069	−2.45648	0.00388
O 3	−7.20066	−2.45679	−0.00627
F 1	0.01397	2.13636	2.36192
F 2	−0.01427	2.13579	−2.36147
H 1	7.09721	0.14266	−0.00951
H 2	4.99971	1.47119	−0.01530
H 3	4.79908	−3.52831	0.00844
H 4	2.55592	1.55309	−0.01171
H 5	2.26588	−3.42117	0.00468
H 6	−2.55591	1.55299	0.01111
H 7	−2.26561	−3.42129	−0.00227
H 8	−4.99958	1.47111	0.01332
H 9	−7.09723	0.14287	0.00650
H 10	−4.79902	−3.52858	−0.00844
H 11	0.01338	4.70087	2.16841
H 12	−0.00024	5.96859	−0.00023
H 13	−0.01383	4.70033	−2.16857

	Bond Length
C(1)–C(2)	1.47294
C(1)–C(6)	1.44371
C(1)–O(2)	1.25523
C(2)–C(3)	1.35934
C(3)–C(4)	1.44177
C(4)–C(5)	1.45832
C(4)–C(7)	1.38413
C(5)–C(6)	1.38729
C(5)–C(10)	1.43698
C(7)–C(8)	1.41909
C(8)–C(9)	1.44290
C(8)–C(11)	1.40853
C(9)–C(10)	1.36550
C(9)–O(1)	1.37475
C(11)–C(12)	1.40847
C(11)–C(22)	1.49454
C(12)–C(13)	1.44292
C(12)–C(14)	1.41914
C(13)–O(1)	1.37479
C(13)–C(17)	1.36546
C(14)–C(15)	1.38409
C(15)–C(16)	1.45837
C(15)–C(18)	1.44178
C(16)–C(17)	1.43709
C(16)–C(21)	1.38716
C(18)–C(19)	1.35931
C(19)–C(20)	1.47328
C(20)–C(21)	1.44400
C(20)–O(3)	1.25530
C(22)–C(23)	1.39912
C(22)–C(27)	1.39913
C(23)–C(24)	1.39085
C(23)–F(1)	1.35418
C(24)–C(25)	1.39634
C(25)–C(26)	1.39634
C(26)–C(27)	1.39086
C(26)–F(2)	1.35418

	Angle
C(1)-C(2)-C(3)	122.078
C(2)-C(3)-C(4)	121.527
C(3)-C(4)-C(5)	117.990
C(4)-C(5)-C(6)	119.842
C(5)-C(6)-C(1)	122.803
C(6)-C(1)-C(2)	115.759
C(3)-C(4)-C(7)	121.985
C(6)-C(5)-C(10)	122.965
C(4)-C(7)-C(8)	122.704
C(7)-C(8)-C(9)	116.557
C(8)-C(9)-C(10)	122.268
C(9)-C(10)-C(5)	121.253
C(10)-C(5)-C(4)	117.193
C(5)-C(4)-C(7)	120.025
C(7)-C(8)-C(11)	124.522
C(10)-C(9)-O(1)	117.585
C(9)-C(8)-C(11)	118.921
C(8)-C(11)-C(12)	120.364
C(11)-C(12)-C(13)	118.925
C(12)-C(13)-O(1)	120.143
C(13)-O(1)-C(9)	121.500
O(1)-C(9)-O(8)	120.147
C(11)-C(12)-C(14)	124.523
O(1)-C(13)-C(17)	117.585
C(12)-C(14)-C(15)	122.706
C(14)-C(15)-C(16)	120.028
C(15)-C(16)-C(17)	117.187
C(16)-C(17)-C(13)	121.253
C(17)-C(13)-C(12)	122.273
C(13)-C(12)-C(14)	116.553
C(14)-C(15)-C(18)	121.984
C(17)-C(16)-C(21)	122.960
C(15)-C(18)-C(19)	121.541
C(18)-C(19)-C(20)	122.062
C(19)-C(20)-C(21)	115.761
C(20)-C(21)-C(16)	122.795
C(21)-C(16)-C(15)	119.853
C(16)-C(15)-C(18)	117.988
C(8)-C(11)-C(22)	119.818
C(12)-C(11)-C(22)	119.818
C(11)-C(22)-C(23)	122.463
C(11)-C(22)-C(27)	179.987
C(22)-C(23)-C(24)	123.760
C(23)-C(24)-C(25)	118.486
C(24)-C(25)-C(26)	120.436
C(25)-C(26)-C(27)	118.486
C(26)-C(27)-C(22)	123.760
C(27)-C(22)-C(23)	115.071
C(6)-C(1)-O(2)	123.447
C(2)-C(1)-O(2)	120.794
C(19)-C(20)-O(3)	120.797
C(21)-C(20)-O(3)	123.442
C(22)-C(23)-F(1)	118.264
C(24)-C(23)-F(1)	117.976
C(26)-C(27)-F(2)	117.976
C(22)-C(27)-F(2)	118.265

6. Time Profiles of UV-vis Absorption Spectra

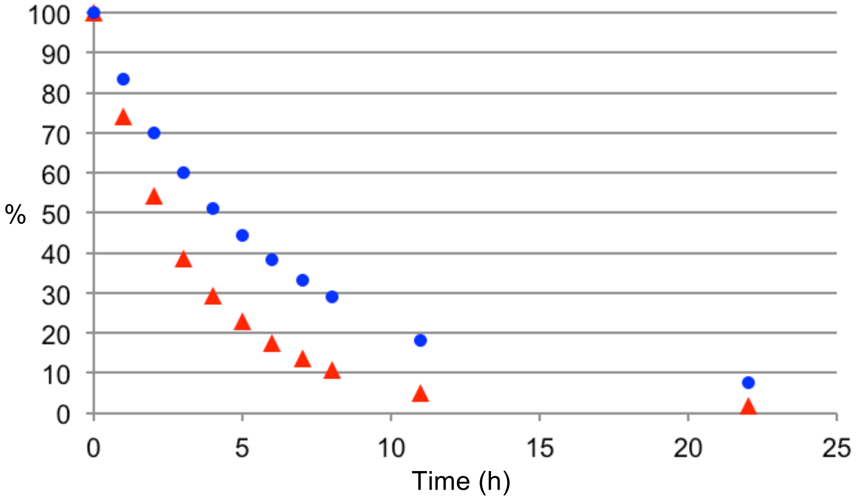
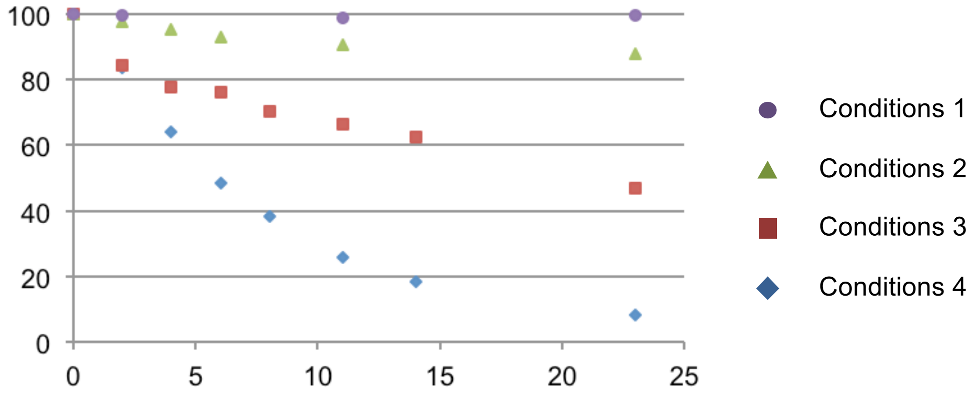


Figure S22. Time profiles of absorption maximum of **BX** (red) and **FBX** (blue) in DMSO with 1.2 eq. DBU.



	1	2	3	4
Exposure to O_2	–	+	–	+
Light irradiation	–	–	+	+

Figure S23. Time profiles of absorption maximum of **FBX** in DMSO with 1.2 eq. DBU in various conditions.

7. Calculated UV-vis-NIR Absorption Spectrum of FBX

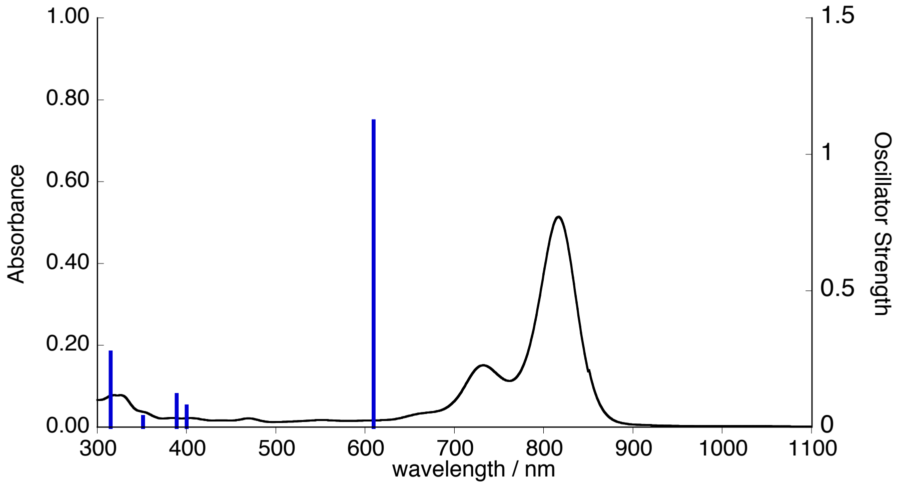


Figure S24. UV-vis-NIR absorption spectrum of **FBX** (black) along with the calculated oscillator strength (blue) by the B3LYP/6-31G(d) level.

f = Oscillator Strength

Excited State 1: Singlet-A	2.0341 eV, 609.54 nm, *f* = 1.1216
HOMO-2 → LUMO+3	2%
HOMO → LUMO	95%
Excited State 7: Singlet-A	3.0977 eV, 400.24 nm, *f* = 0.0763
HOMO-4 → LUMO	78%
HOMO-1 → LUMO	5%
HOMO → LUMO+3	8%
HOMO → LUMO+7	7%
Excited State 8: Singlet-A	3.1876 eV, 388.95 nm, *f* = 0.1177
HOMO-5 → LUMO	97%
Excited State 13: Singlet-A	3.5306 eV, 351.17 nm, *f* = 0.0378
HOMO-1 → LUMO+2	99%
Excited State 15: Singlet-A	3.9357 eV, 315.02 nm, *f* = 0.2741
HOMO-1 → LUMO+3	94%
HOMO → LUMO	2%

8. Fluorescence Lifetime Measurement

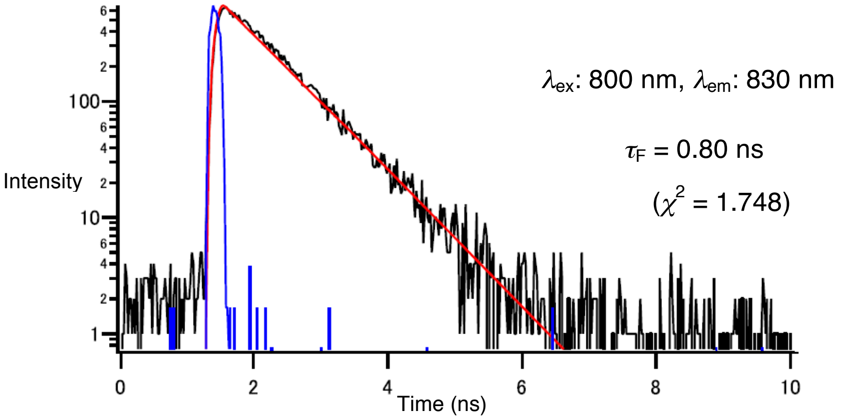
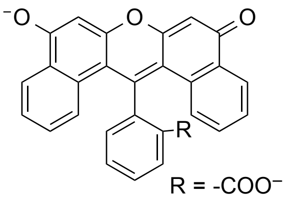


Figure S25. Fluorescence lifetime profile (black line), fitted line (red line), and excitation light (blue line) for **FBX**$^-$ in DMSO (1.2 eq. of DBU) with Ar bubbling.

Fluorescence lifetime was measured by using femtosecond pulse laser, cavity-dumped Ti:sapphire laser, Mira 900-F & Pulse Switch (COHERENT), excited by a Nd:YVO4 laser, Verdi 5W, to produce 800 nm light for excitation of the sample. A Streak Scope C4780 (Hamamatsu Photonics) was used for analysis. The excitation laser power, the pulse width and the repetition frequency were originally 20 nJ, 150 fs, and 100 Hz, respectively. To avoid detector saturation due to high laser power, the excitation laser was reduced by ND filter.

9. Several naphthofluoresceins' photophysical data

Ref. 9f

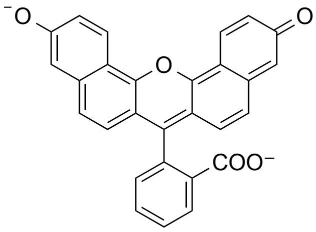


λ_{abs} = 534 nm

λ_{em} = 565 nm in H_2O/DMSO

Φ_F = 24%

Ref. 9f

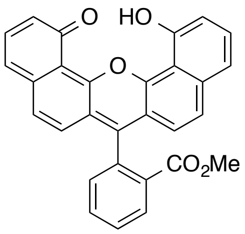


λ_{abs} = 595 nm

λ_{em} = 660 nm in H_2O/DMSO

Φ_F = 14%

Ref. 6

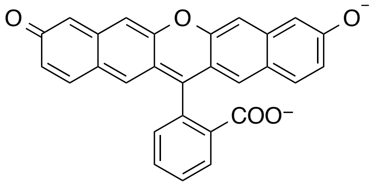


λ_{abs} = 701 nm

λ_{em} = 816 nm in MeOH

Φ_F = ~0.1%

Ref. 7

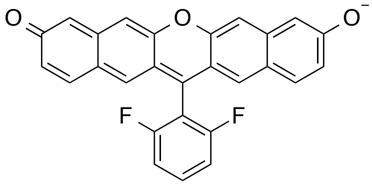


λ_{abs} = 708 nm

λ_{em} = 790 nm at pH11.0

Φ_F = 0.17%

This work



λ_{abs} = 817 nm

λ_{em} = 853 nm in DMSO with DBU

Φ_F = 6.4%

Figure S26. UV-vis absorption and fluorescence data for several naphthofluoresceins.

10. Reference

[S1] Y. Yang, J. O. Escobedo, A. Wong, C. M. Schowalter, M. C. Touchy, L. Jiao, W. E. Crowe, F. R. Fronczek and R. M. Strongin, *J. Org. Chem*., 2005, **70**, 6907−6912.