

# An Organic White Light-Emitting Fluorophore

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## Introduction

During further investigations of the series of benzofluorones, we found that the original assignment of **SNAFR-1** as a mixture of tautomers based on  $^1\text{H}$  NMR evidence was incorrect. The corrected assignment is a mixture of the regioisomers **SNAFR-1** and **SNAFR-2**, in a proportion of 1:2.5, respectively, based on NMR integral areas. The formation of **SNAFR-2** during the **SNAFR-1** synthesis is unexpected. Current investigations are ongoing. Both **SNAFR-1** and **SNAFR-2** were recently prepared by us via alternative synthetic routes (Scheme S1, page S5). Their corrected structure assignments were confirmed by extensive spectroscopic investigations including 2D COSY (Figure S1-

2, page S7). The **SNAFR-2** assignment was further confirmed by X-ray crystallography (Figure S3, page S8). The purity of all new compounds was studied via HPLC.

**SNAFR-1** is more susceptible to nucleophilic attack by MeOH or H<sub>2</sub>O as compared to **SNAFR-2**. When dissolved in MeOH-*d*<sub>4</sub>, **SNAFR-1** converts to its MeOH-*d*<sub>4</sub> adduct (compound **19**, Scheme S2, page S8), the only species observed in the <sup>1</sup>H NMR spectrum (Figure S4, page S8). The conversion can be readily monitored via HPLC (Figure S21, page S22). **SNAFR-1** MeOH adduct (compound **18**) is obtained by dissolving **SNAFR-1** in MeOH followed by evaporation under vacuum.

In our previously published work, the stock solution of **SNAFR-1** and **SNAFR-2** regioisomers was prepared in MeOH. Therefore, the spectroscopic results originally reported in the text were the result of a mixture of **SNAFR-1** MeOH adduct and **SNAFR-2**. **SNAFR-1** MeOH adduct is shown to display a predominantly violet-blue emission in DMSO and MeOH (Figure S5, page S9). If MeOH is avoided during the sample preparation, the DMSO solution of **SNAFR-1** displays a violet-blue (from the H<sub>2</sub>O adduct) as well as an orange (from the neutral form) and a near infra red (from the anionic form) emission (Figure S6, page S9). Due to the fact that the Hamamatsu R928 photomultiplier tube in our fluorimeter has a relatively low sensitivity in the NIR region, the intensity of NIR emission from **SNAFR-1** is significantly underestimated.

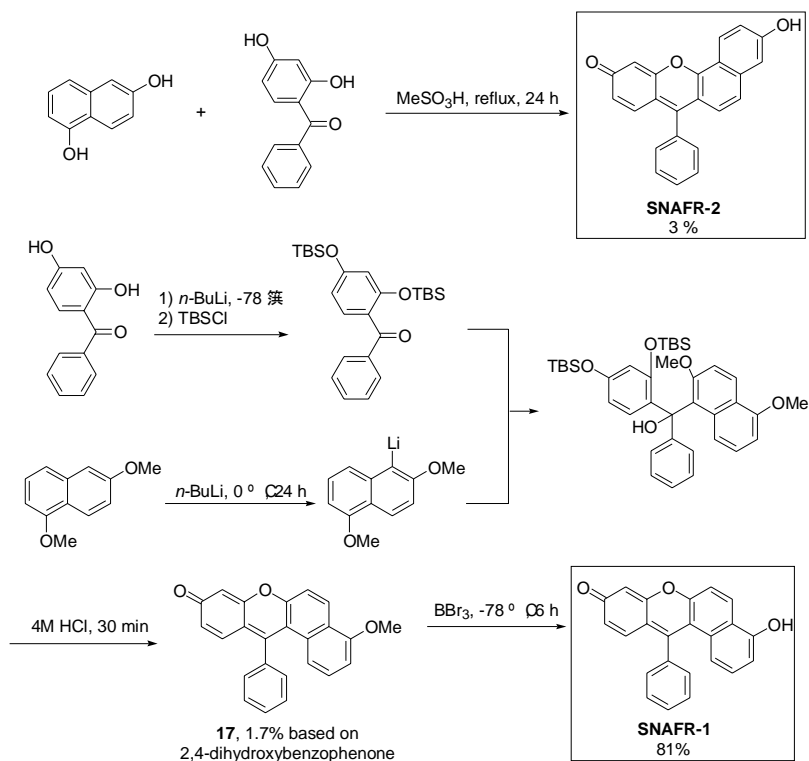
**SNAFR-2** is not as susceptible to nucleophilic attack as **SNAFR-1**. **SNAFR-2** in MeOH displays predominantly green emission from the neutral form (Figure S7A, page S9). **SNAFR-2** in DMSO displays two-band emission from the H<sub>2</sub>O adduct and neutral form of the compound (Figure S7B, page S9) although the adduct emission is relatively small. The reappearance of the adduct emission in DMSO is presumably due to the fact that DMSO, a polar aprotic solvent, facilitates nucleophilic attack from trace amounts of water present in DMSO. When 0.25% 50 mM phosphate buffer at pH 7.5 is added, both emissions from the adduct and anionic form are enhanced as a result of the increased amount of OH<sup>-</sup> in the system leading to three band emissions of approximately equal intensities when excited in the UV region (red, green and violet-blue, Figure S8, page S10). **SNAFR-2** displays the same pH-responsive behavior when 0.25% 50 mM phosphate buffer is added to its DMSO solution as compared

to the published data in the original text (Figure S9, page S10). The same isosbestic points as originally reported were observed at 311, 345, 427, and 538 nm. It is interesting to note that the adduct emission from the **SNAFR-2** H<sub>2</sub>O adduct is located at 360 nm instead of the originally reported 390 nm. It is apparent that the violet-blue emission originally reported in the text under the same conditions is largely from **18**. As a result of a 30 nm blue-shift of the violet-blue emission, the emission from **SNAFR-2** appears more yellow instead of near white (Figure S8, page S10). However, we have noted that the violet-blue emission at 390 nm from **SNAFR-2** is enhanced by activation of the central carbon via addition of dilute HCl followed by MeOH to generate the **SNAFR-2** MeOH adduct (Scheme S3, page S11). The **SNAFR-2** H<sub>2</sub>O adduct may also be enhanced as well. The ratio of green and red emissions is further fine-tuned by addition of various amounts of phosphate buffer at different pH values, leading to the regeneration of near white emission from **SNAFR-2** (Figure S10, Page S11).

Additionally, the structural correction does not affect the spectroscopic measurements for applications such as ratiometric pH studies (Figure S11, Page S11) or live cell imaging. Identical green and red peak locations at 540 and 620 nm in 50 mM phosphate buffer are observed as in the published text, which result from the neutral and anionic forms of **SNAFR-2**, respectively (rather than from **SNAFR-1** as originally reported). Moreover, the  $pK_a$  of **SNAFR-2** is essentially the same as the published data (previously assigned to **SNAFR-1**) based on absorption and fluorescence titration data.

## Experimental Section

**Scheme S1.** Alternative syntheses of **SNAFR-1** and **SNAFR-2** affording pure regioisomers for structural studies and spectroscopic investigations.



**Alternative Synthesis of SNAFR-1.** 2,4-Dihydroxybenzophenone (2.0 g, 9.3 mmol) is dissolved in THF (100 mL). The solution is cooled to  $-78^\circ\text{C}$  with a dry ice bath.  $n\text{-BuLi}$  (11.6 mL, 1.6 M in hexane) is added dropwise with constant stirring. The mixture is allowed to warm to rt overnight and cooled over an ice bath. TBDMSCl (2.9 g, 19.5 mmol) in THF (20 mL) is added dropwise. After the addition is complete, the solution is allowed to warm to rt within 4 h. The solution is re-cooled to  $-78^\circ\text{C}$  and a solution of lithiated 1,6-dimethoxynaphthalene (1.84 g, 9.8 mmol, see original supporting information for preparation of the solution) is added dropwise. After completion, the solution is allowed to warm to rt overnight. HCl (10 mL, 4 M) is added in one portion. The solution is stirred at rt for 30 min. Deionized  $\text{H}_2\text{O}$  (200 mL) is added. Much of the THF is removed under vacuum. The remaining aqueous material is extracted with  $\text{CH}_2\text{Cl}_2$  and dried over  $\text{MgSO}_4$ . Purification by flash chromatography (EtOAc) affords 56 mg (1.7 % yield based on 2,4-dihydroxybenzophenone, yield not yet optimized) of new **SNAFR-1** methyl ether (**17**). 18 mg of **17** is dissolved in anhydrous  $\text{CH}_2\text{Cl}_2$ . The

solution is cooled over a dry ice bath. The remaining methyl group is removed via addition of 0.3 mL  $\text{BBr}_3$  to obtain 14 mg (81% yield) of **SNAFR-1**.

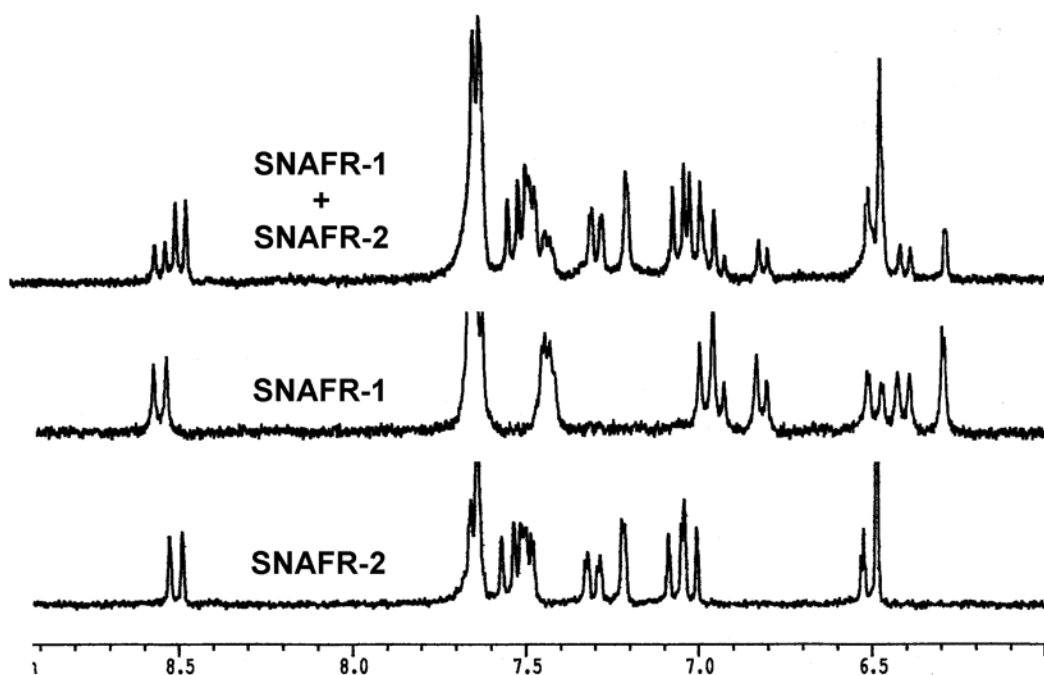
Data for compound **17**:  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz)  $\delta$  (ppm): 8.58 (d,  $J = 9.2$  Hz, 1H), 7.72 (d,  $J = 9.2$  Hz, 1H), 7.66–7.69 (m, 3H), 7.44–7.48 (m, 2H), 7.11 (d,  $J = 8.4$  Hz, 1H), 7.01 (d,  $J = 10.0$  Hz, 1H), 6.97 (d,  $J = 7.8$  Hz, 1H), 6.65 (d,  $J = 8.8$  Hz, 1H), 6.51 (dd,  $J = 10.0, 2.0$  Hz, 1H), 6.31 (d,  $J = 2.0$  Hz, 1H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75 MHz)  $\delta$  (ppm): 183.1, 157.1, 155.3, 153.2, 148.8, 136.3, 130.1, 129.7, 129.3, 129.0, 128.2, 127.8, 127.5, 125.0, 117.2, 116.0, 104.8, 103.4, 55.7. MALDI-TOF  $[\text{M}+\text{H}]^+$  calcd 353.117, found 353.330.

Data for **SNAFR-1**:  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz)  $\delta$  (ppm): 8.58 (d,  $J = 9.3$  Hz, 1H), 7.68–7.69 (m, 3H), 7.66 (d,  $J = 9.3$  Hz, 1H), 7.44–7.48 (m, 2H), 7.00 (d,  $J = 9.9$  Hz, 1H), 6.98 (dd,  $J = 8.4, 7.2$  Hz, 1H), 6.84 (d,  $J = 7.2$  Hz, 1H), 6.51 (dd,  $J = 9.9, 1.8$  Hz, 1H), 6.43 (d,  $J = 9.3$  Hz, 1H), 6.32 (d,  $J = 1.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75 MHz)  $\delta$  (ppm): 183.1, 157.2, 154.0, 149.2, 136.4, 130.8, 130.2, 130.1, 129.7, 128.9, 129.0, 128.1, 120.0, 115.9, 115.2, 108.5, 103.3. MALDI-TOF  $[\text{M}+\text{H}]^+$  calcd 339.102, found 339.319.

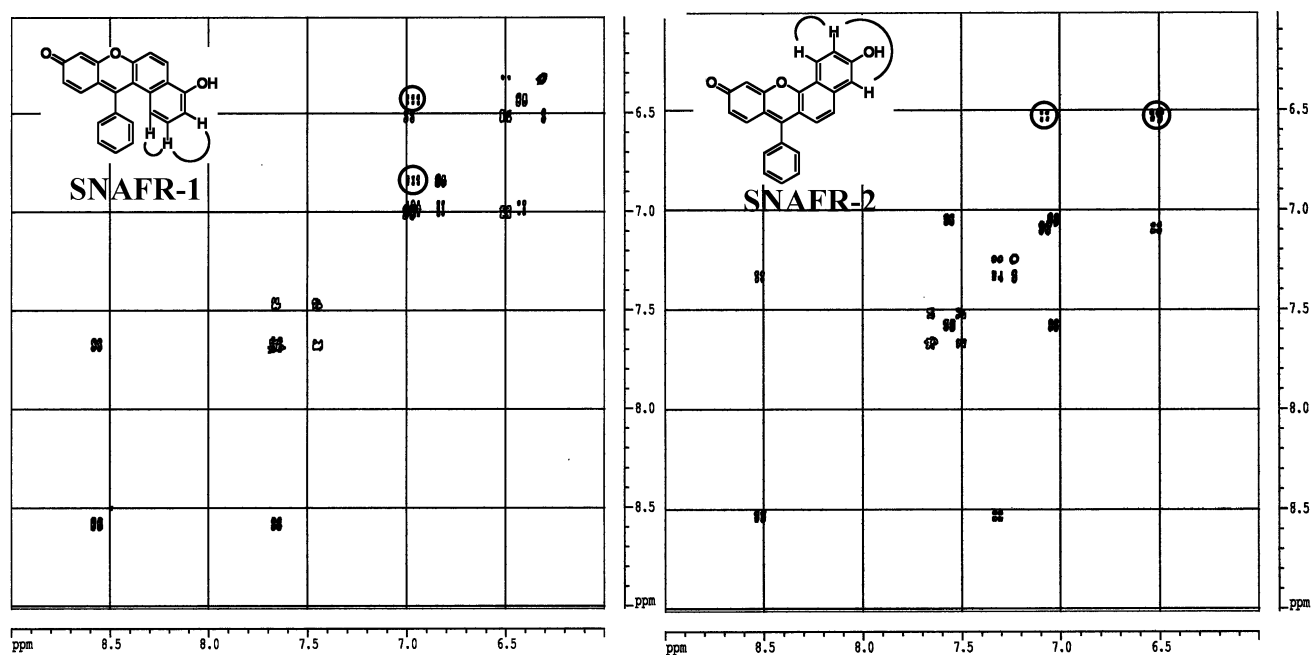
**Synthesis of SNAFR-2.** 1,6-Dihydroxynaphthalene (1.5 g, 9.3 mmol) and 2,4-dihydroxybenzophenone (2.0 g, 9.3 mmol) are added to a 100 mL round bottom flask containing 25 mL  $\text{CH}_3\text{SO}_3\text{H}$ . The mixture is heated at reflux for 24 h. The resulting dark-red liquid is poured into 200 mL distilled  $\text{H}_2\text{O}$  and neutralized by the addition of  $\text{NaHCO}_3$  until the solution turns almost colorless. The liquid is decanted and the resulting residue is dissolved in MeOH and treated with  $\text{Na}_2\text{SO}_4$ . The mixture is filtered and evaporated to dryness. The red residue is purified by flash chromatography (EtOAc:MeOH=9.5:0.5). 18.6 mg (3 % yield, not optimized) **SNAFR-2** are obtained.

Data for **SNAFR-2**:  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz)  $\delta$  (ppm): 8.52 (d,  $J = 9.3$  Hz, 1H), 7.65–7.70 (d, 3H), 7.56 (d,  $J = 9.0$ , 1H), 7.49–7.53 (m, 2H), 7.32 (dd,  $J = 9.3, 2.7$  Hz, 1H), 7.23 (d,  $J = 2.7$  Hz, 1H), 7.09 (d,  $J = 9.3$  Hz, 1H), 7.04 (d,  $J = 9.0$ , 1H), 6.52 (dd,  $J = 9.3, 1.5$  Hz, 1H), 6.50 (d,  $J = 1.5$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75 MHz)  $\delta$  (ppm): 183.5, 159.6, 158.3, 150.0, 137.7, 132.7, 130.3, 130.0, 129.4,

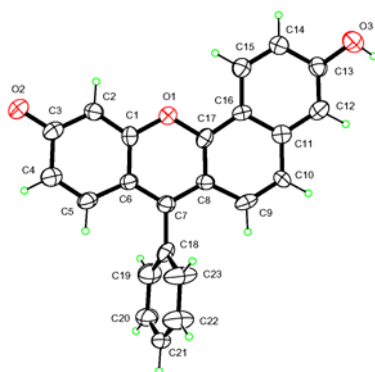
128.8, 124.6, 123.5, 123.2, 119.9, 116.0, 113.5, 110.0, 104.7. MALDI-TOF  $[M+H]^+$  calcd 339.102, found 339.431.



**Figure S1.** Top:  $^1\text{H}$  NMR spectrum of the mixture of **SNAFR-1** and **SNAFR-2** which was believed to contain a tautomeric mixture of **SNAFR-1**. Center: Pure **SNAFR-1** derived from the alternative synthetic route described above. Bottom: Pure **SNAFR-2** from the synthetic route described above. Further characterization data and evidence of purity is shown on the following pages.

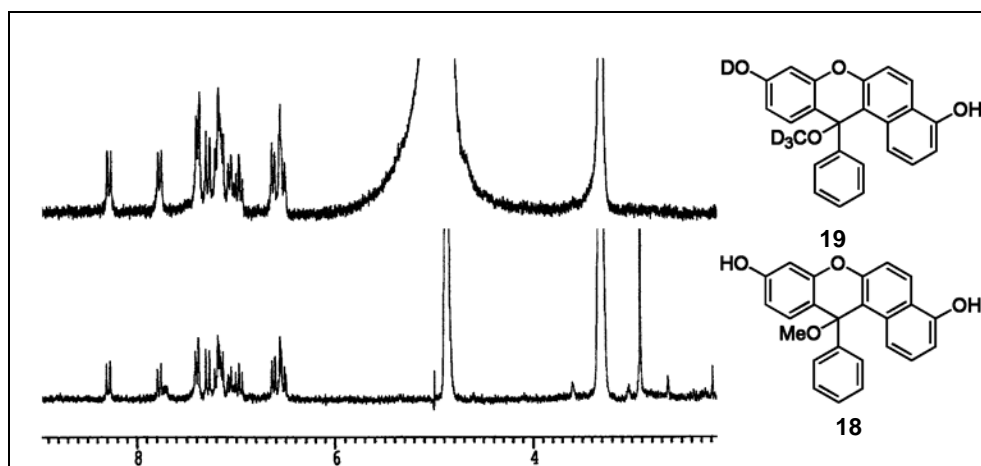
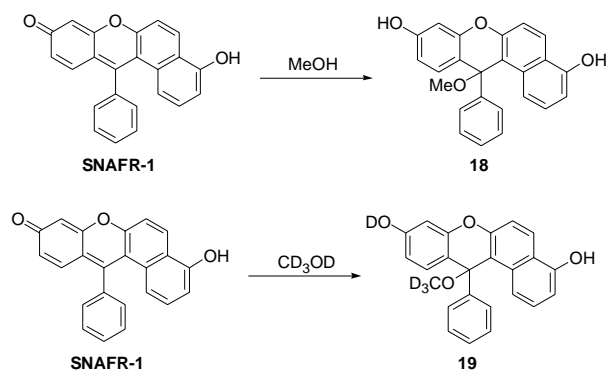


**Figure S2.** 2D COSY of **SNAFR-1** (left) and **SNAFR-2** (right) in  $\text{DMSO-}d_6$  (expansion from 6.0 to 9.0 ppm). Characteristic cross-couplings are circled for clarity. Please find detailed assignment including chemical shift, coupling constant and splitting pattern in Table S2 and Table S3. The scales are shown without the proton NMRs which correspond to those shown in Figure S1, above.



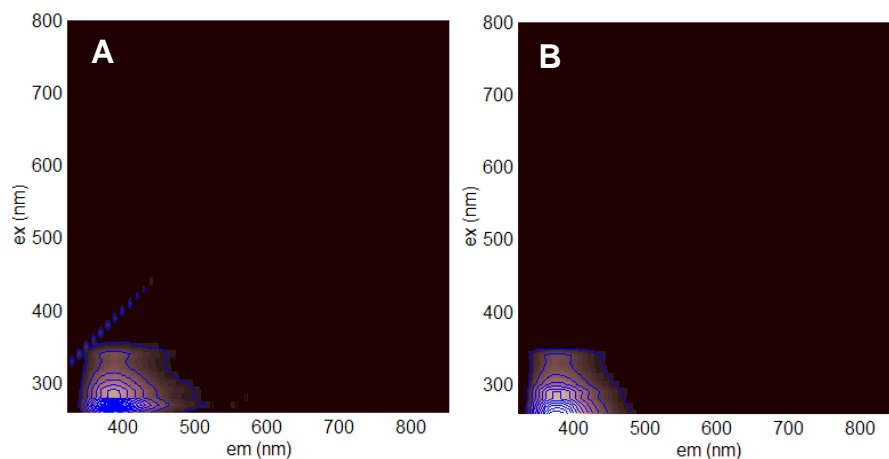
**Figure S3.** Ortep drawing of the single crystal X-ray structure of **SNAFR-2**.

**Scheme S2.** Quantitative conversion of **SNAFR-1** to its MeOH or MeOH- $d_4$  adducts.

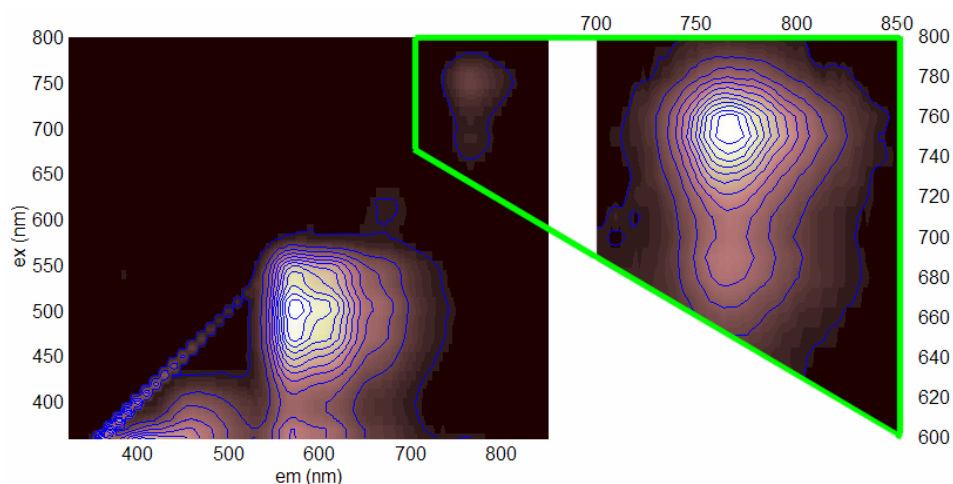


**Figure S4.** Overlay of the  $^1\text{H}$  NMR spectra in MeOH- $d_4$  of new compounds **18** and **19**. The methyl peak at 2.92 ppm observed in the NMR of compound **18** is not found in the NMR of compound **19** as expected. See also HPLC data (Figure S20, Page S22) which allows one to follow the facile conversion of **SNAFR-1** to its MeOH adduct.

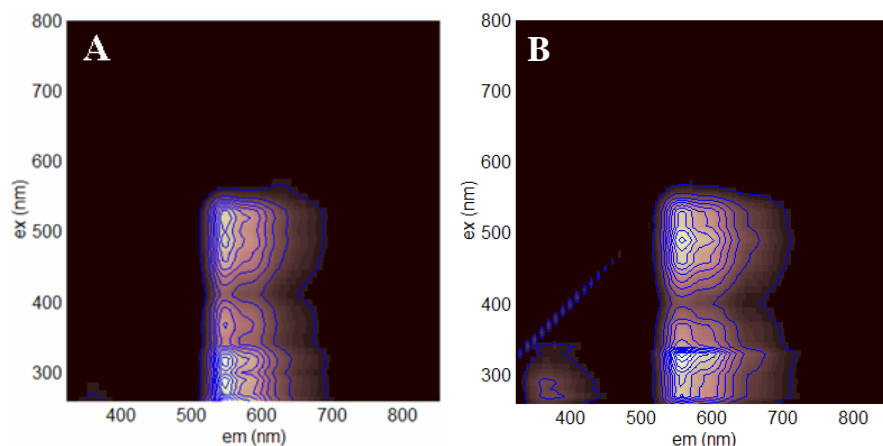




**Figure S5.** Excitation emission matrices (EEMs) of **18** in various solvents. (A) in MeOH and (B) in DMSO. Solutions of **SNAFR-1** were prepared from a MeOH stock solution and dried before reconstitution in the desired solvent. Data are normalized to the maximum emission in each EEM respectively. Only significant violet-blue emission is observed in each solvent.

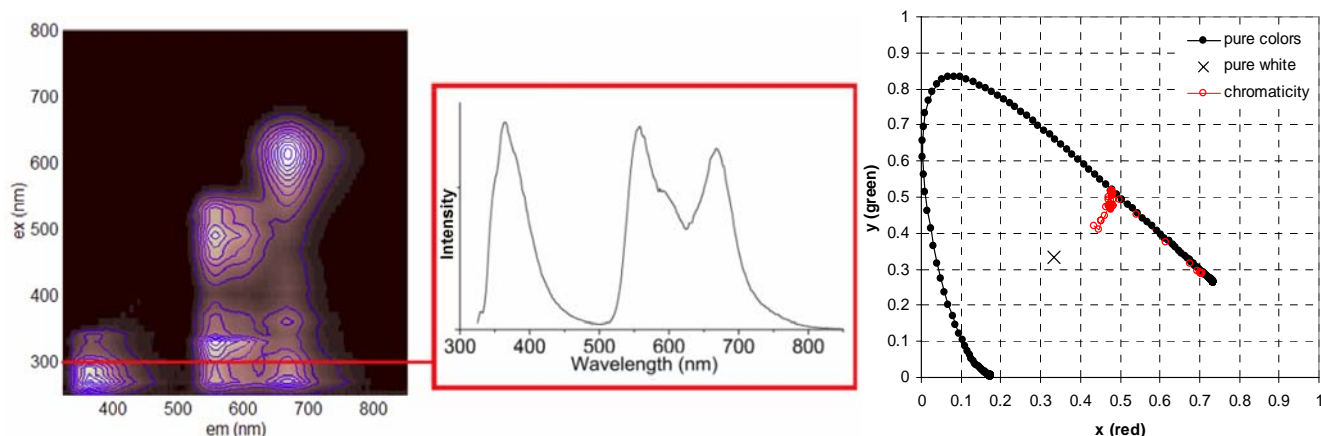


**Figure S6.** EEM of **SNAFR-1** in DMSO prepared from a DMSO stock solution. Blue, orange and NIR emissions are observed when excited at various wavelengths. MeOH was avoided in stock solution preparation to minimize adduct formation. The intensity of the NIR band shown above is underestimated due to the relatively low sensitivity of the photomultiplier tube used in this study.

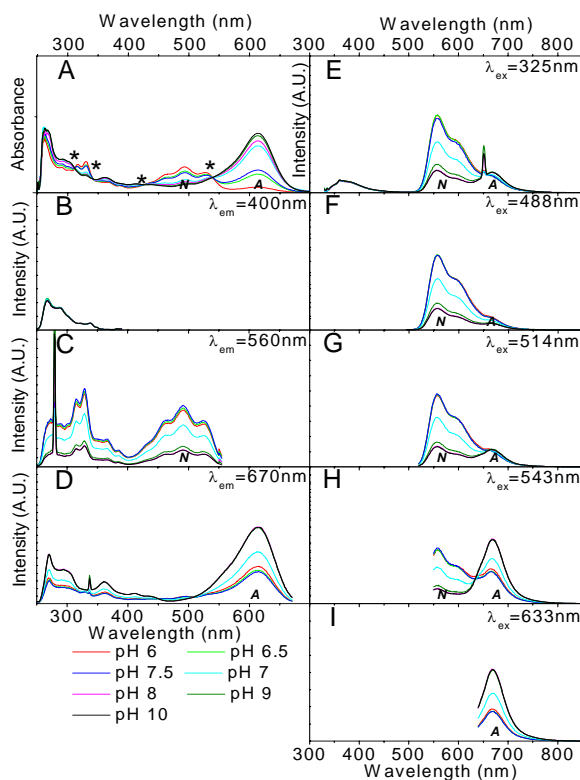


**Figure S7:** EEMs of the **SNAFR-2** and its adducts in various solvents. (A) in MeOH, (B) in DMSO,. Solutions of **SNAFR-2** were prepared from a MeOH stock solution and dried before reconstitution in

the desired solvent. Data are normalized to the maximum emission in each EEM respectively. Green emission is observed in MeOH solution. Violet-blue and green emissions are observed in DMSO solution.

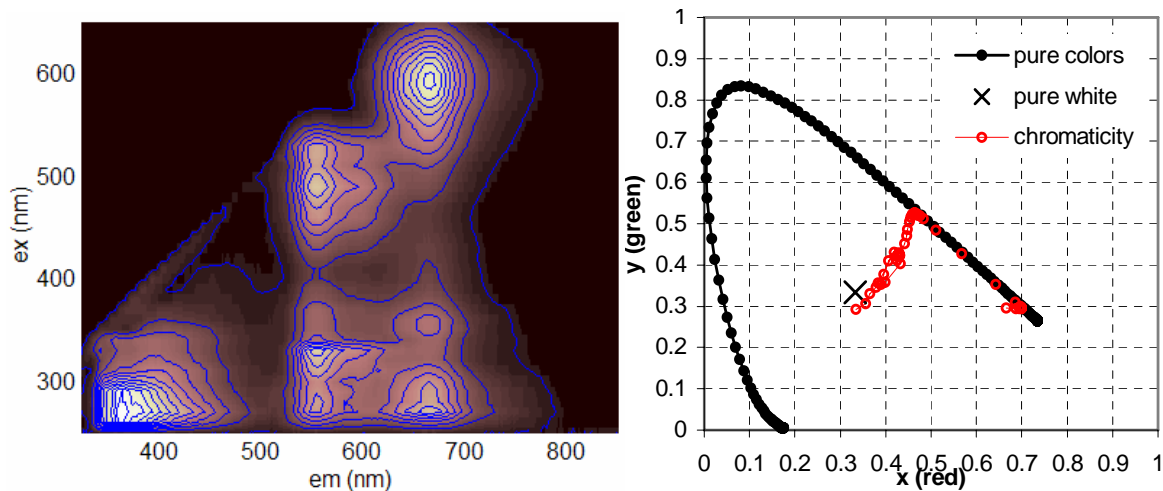
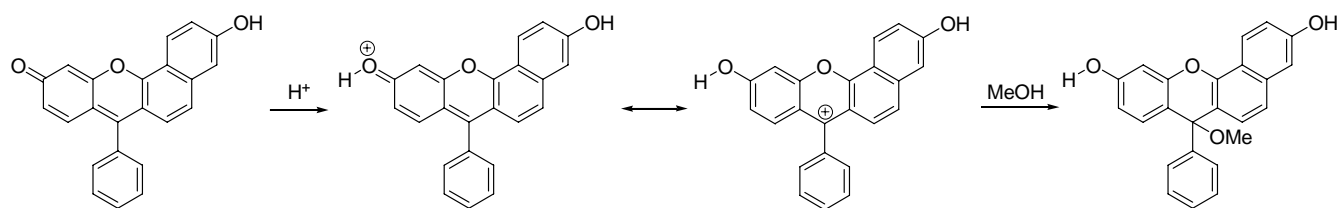


**Figure S8.** Left: EEM of the **SNAFR-2** in DMSO with 0.25% 50 mM phosphate buffer at pH 7.5. Middle: Emission spectrum of **SNAFR-2** (30  $\mu$ M, 0.25 % 50 mM phosphate buffer, pH 7.5, in DMSO) when excited at 300 nm, displays violet-blue, green and red emissions of approximately equal intensities. Right: Chromaticity coordinates for emission spectra collected with excitation wavelength between 270 nm and 650 nm for the corresponding solution.

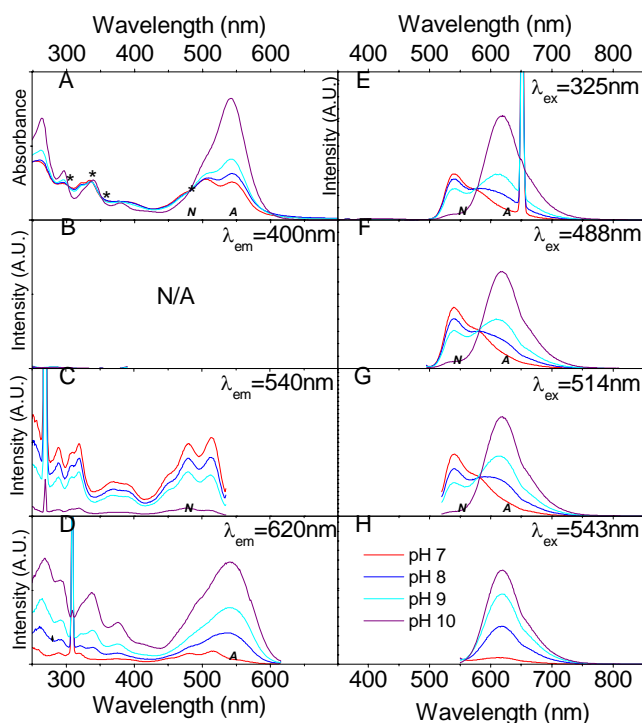


**Figure S9:** Titration of **SNAFR-2** in 99.75% DMSO with 0.25% 50 mM phosphate buffer at various pH. **A** = Anionic form. **N** = Neutral form. (A) Absorption spectra. The \* in Figure A indicates the positions of isosbestic points in absorbance spectra. (B-D) Excitation spectra with emission monitored at 400 nm, 560 nm and 670 nm respectively. (E-I) Emission spectra excited at 325 nm, 488 nm, 514 nm, 543 nm and 633 nm respectively corresponding to common laser lines. The pH-responsive ratiometric green and red emissions are the result of **SNAFR-2**.

**Scheme S3:** Protonation of **SNAFR-2** by dilute acid facilitates the nucleophilic addition of MeOH.

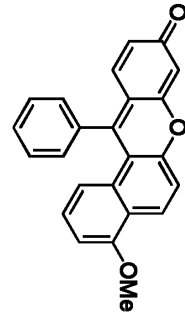


**Figure S10:** Left: EEM of a solution of **SNAFR-2** (1 ml, 30  $\mu$ M in DMSO) after addition of HCl (7  $\mu$ l, 0.1 M), MeOH (0.05 mL) and then pH 7.5 phosphate buffer (60  $\mu$ L, 50 mM). Right: Chromaticity coordinates for emission spectra collected with excitation wavelength between 270 nm and 650 nm for the corresponding solution.



**Figure S11:** Titration of **SNAFR-2** in 99.75% 50 mM phosphate buffer with 0.25% DMSO. A = anionic form. N = neutral form. (A) Absorption spectra. The \* indicates the position of isosbestic points.

(B-D) Excitation spectra with emission monitored at 400 nm, 540 nm and 620 nm respectively. (E-H) Emission spectra excited at 325 nm, 488 nm, 514 nm, and 543 nm respectively, corresponding to common laser lines. Legends for Figures A-H are shown in Figure H.



# Compound 17 in DMSO-d<sub>6</sub>

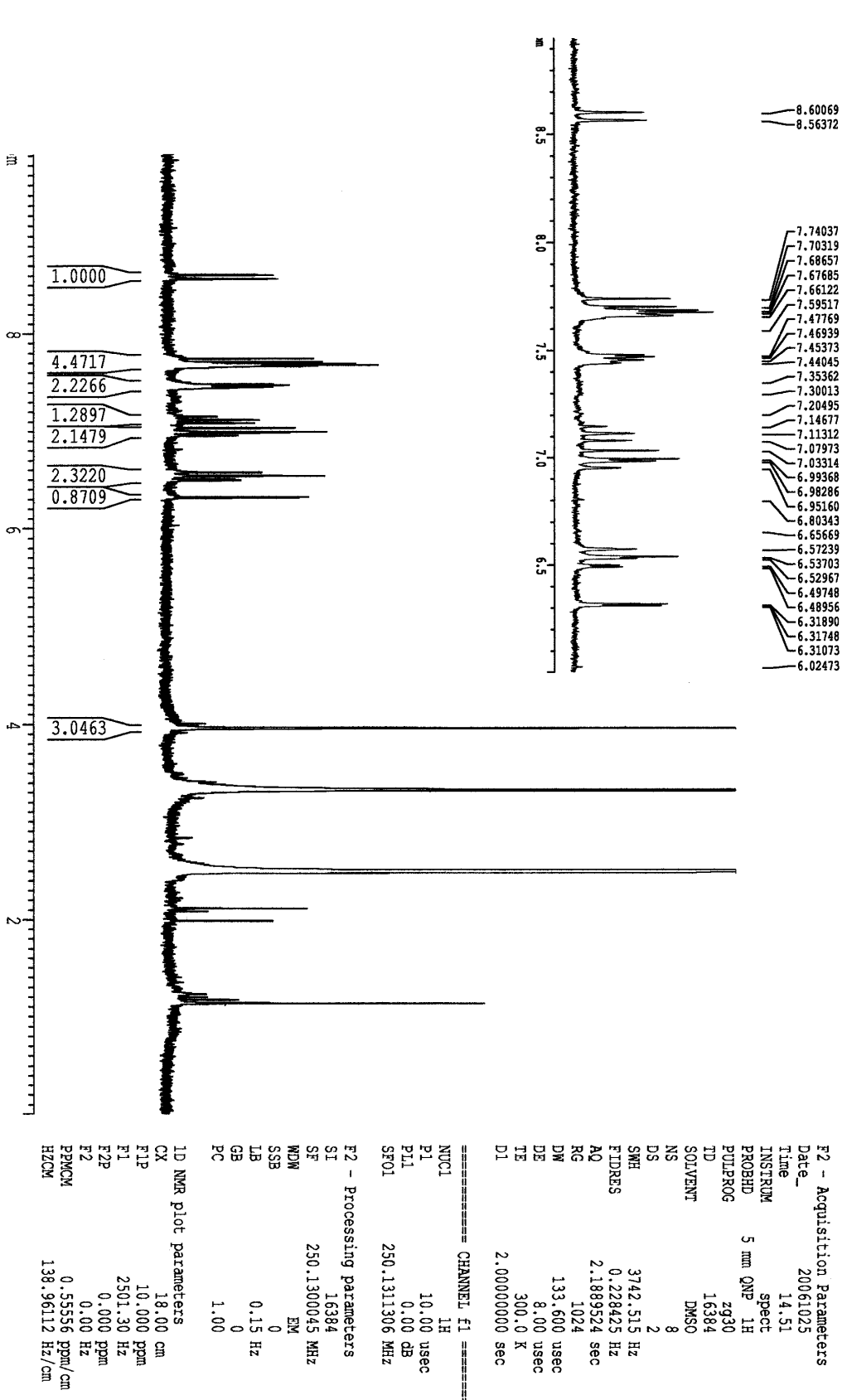


Figure S12: <sup>1</sup>H NMR of compound 17 in DMSO-d<sub>6</sub>.

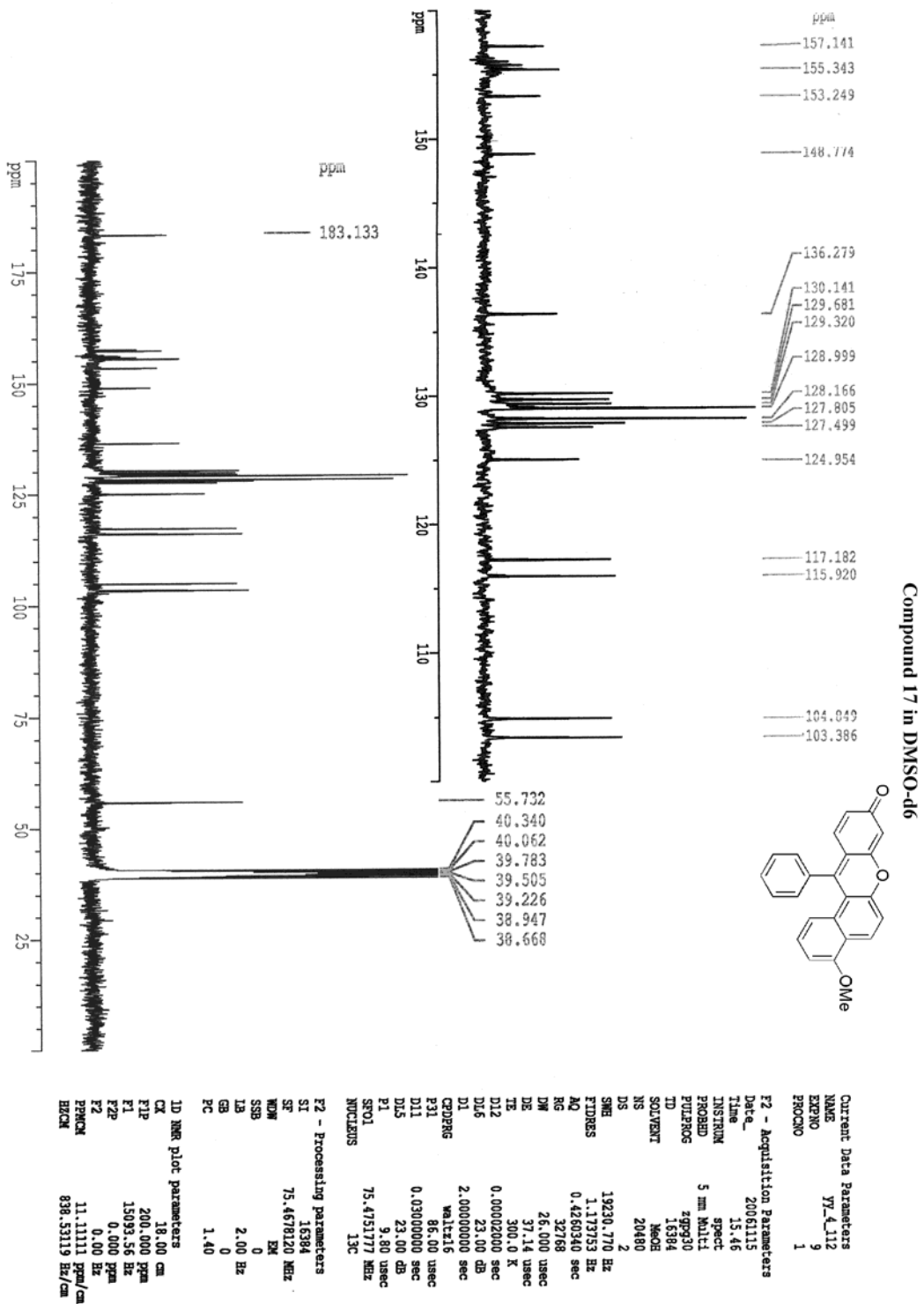
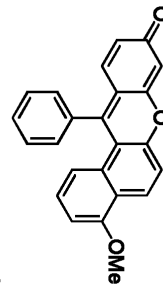
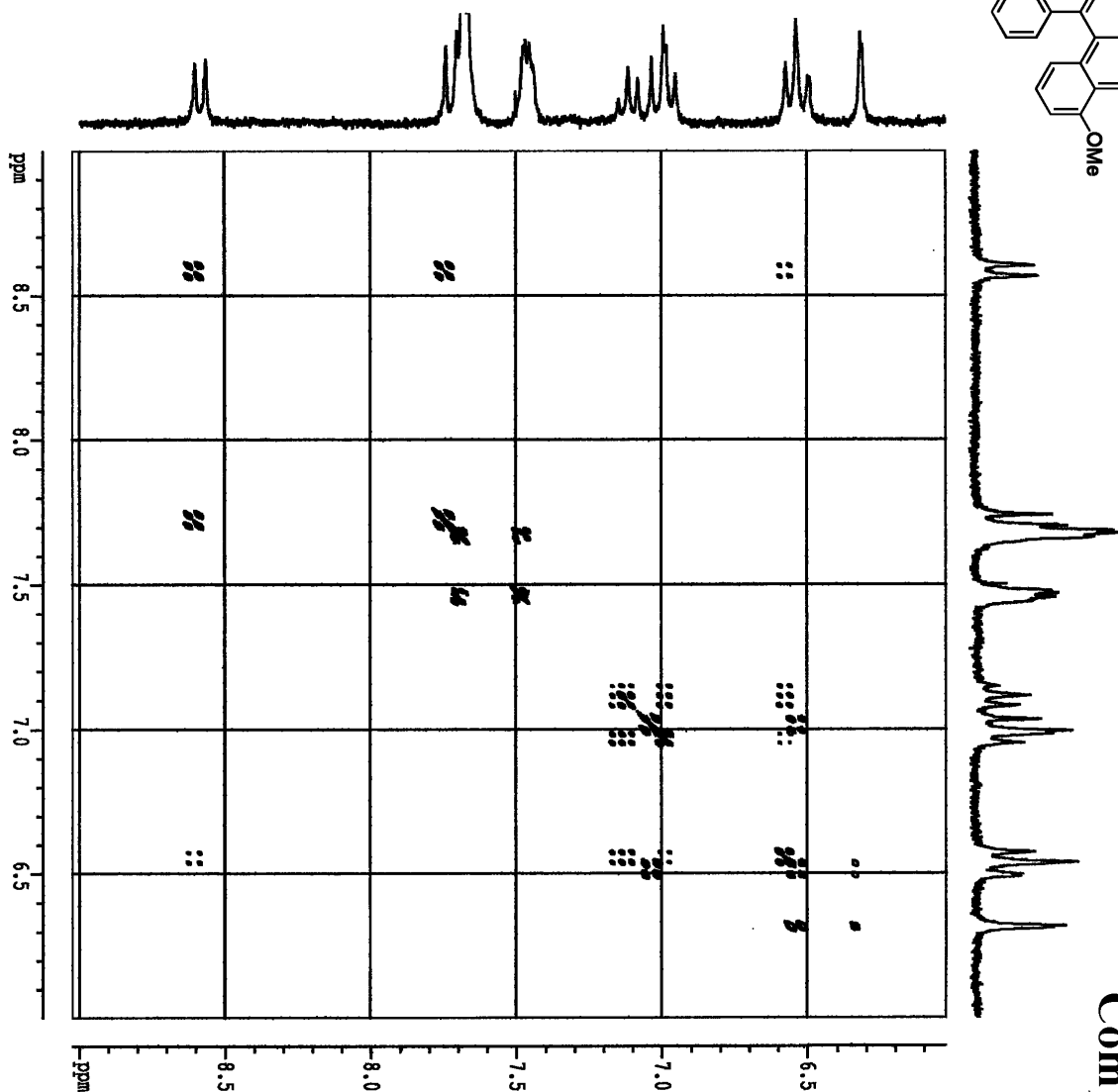


Figure S13: <sup>13</sup>C NMR of compound 17 in DMSO-d<sub>6</sub>.



# Compound 17 in DMSO-d6



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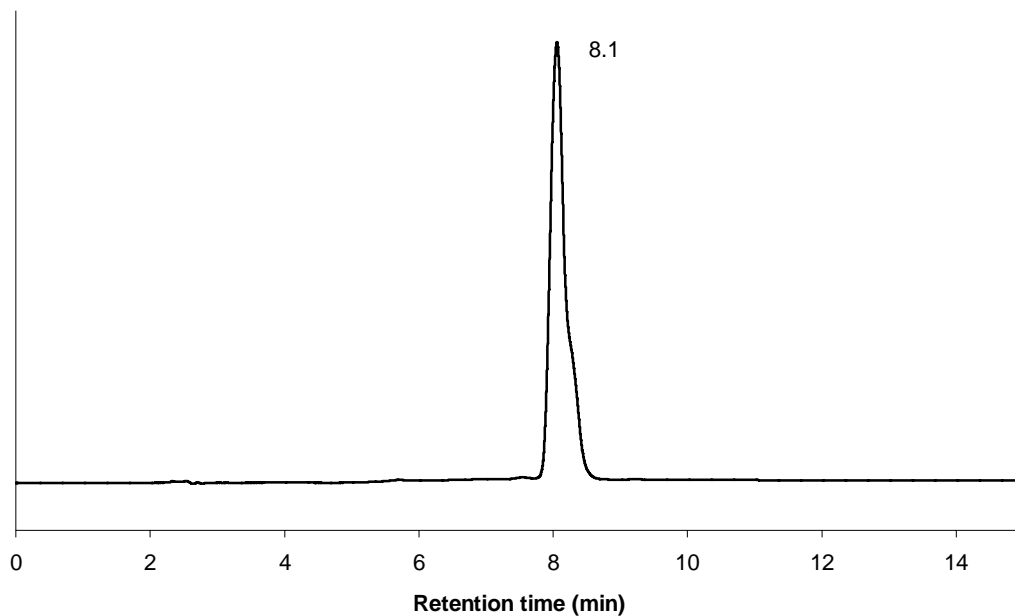
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F2 - Processing parameters
SI           512
SF           250.1300000 MHz
WDW           EM
SSB           0
GB           0
PC           1.00
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PC           1.00
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SI           512
SF           250.1300000 MHz
WDW           EM
SSB           0
GB           0
PC           1.00
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SSB           0
GB           0
PC           1.00
----- Acquisition Parameters -----
Date_         20180125
Time         15.01
INSTRUM      spect
PROBHD       5 mm QNP1
PULPROG      zgpg30
TD           1024
SOLVENT      Me2SO
AQ           0.141850 sec
RG           384
DS           4
SWH           7141.404 Hz
F2 - Processing parameters
SI           512
SF           250.1300000 MHz
WDW           EM
SSB           0
GB           0
PC           1.00
----- Processing parameters -----
SI           1024
SF           250.1300000 MHz
WDW           EM
SSB           0
GB           0
PC           1.00

```

Figure S14: 2D-COSY of compound 17 (expansion from 6.0-9.0 ppm) in DMSO-d6.







**Figure S16:** Chromatogram of a solution of **compound 17** in MeOH. HPLC purity screening is performed on a CM4000 multiple solvent delivery system connected to a SpectroMonitor 3100 UV-Vis detector (LDC/Milton Roy) using a LiChrospher 100 RP-18 (5  $\mu$ m) endcapped column (250  $\times$  4.6 mm). The flow rate is 1.0 mL/min and the detector wavelength is set to 490 nm. Mobile phase (gradient): 70/30 MeOH/H<sub>2</sub>O to 100/0 % MeOH/H<sub>2</sub>O in 5 min.

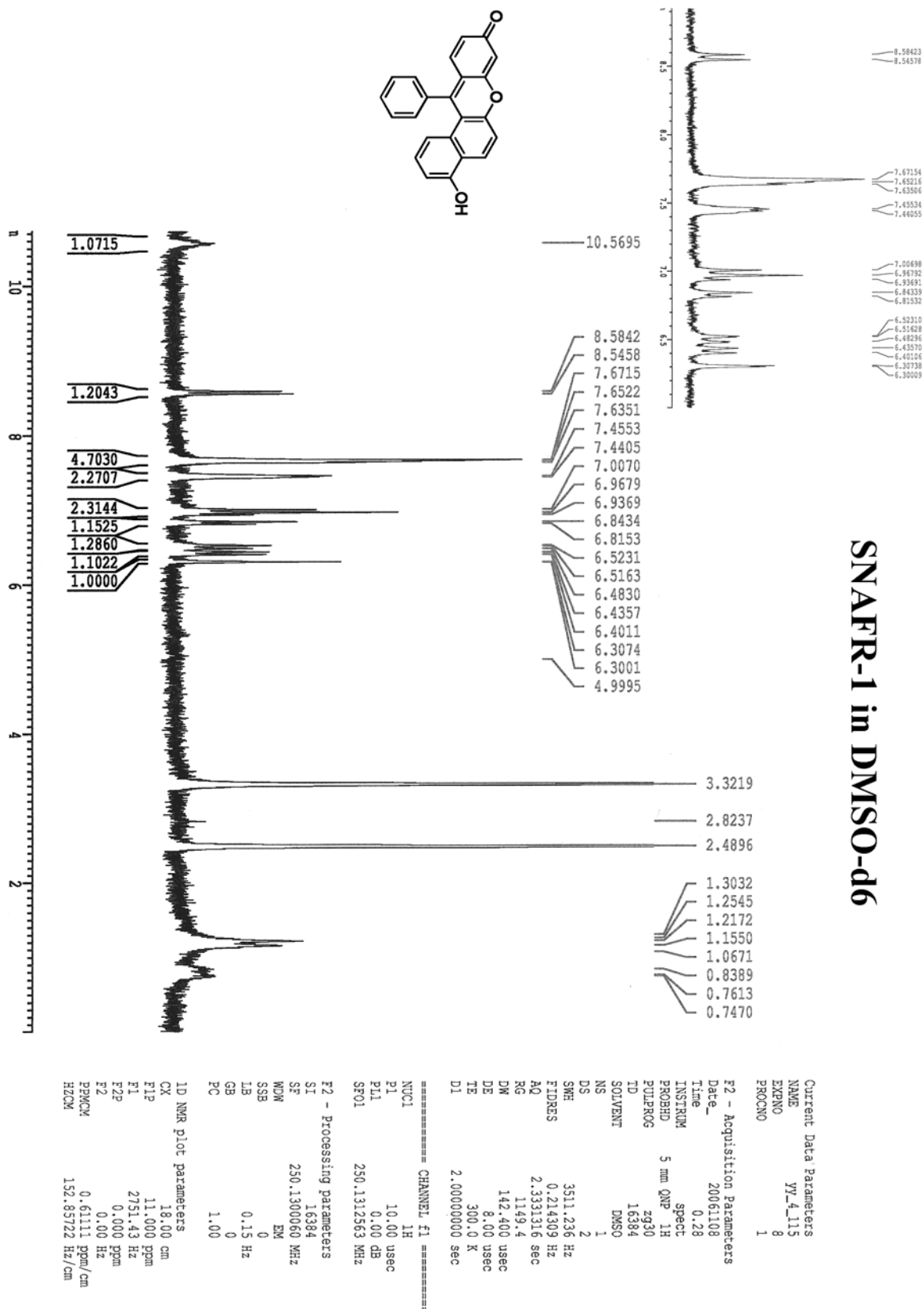
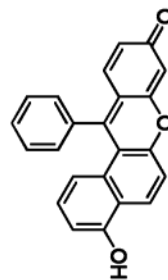
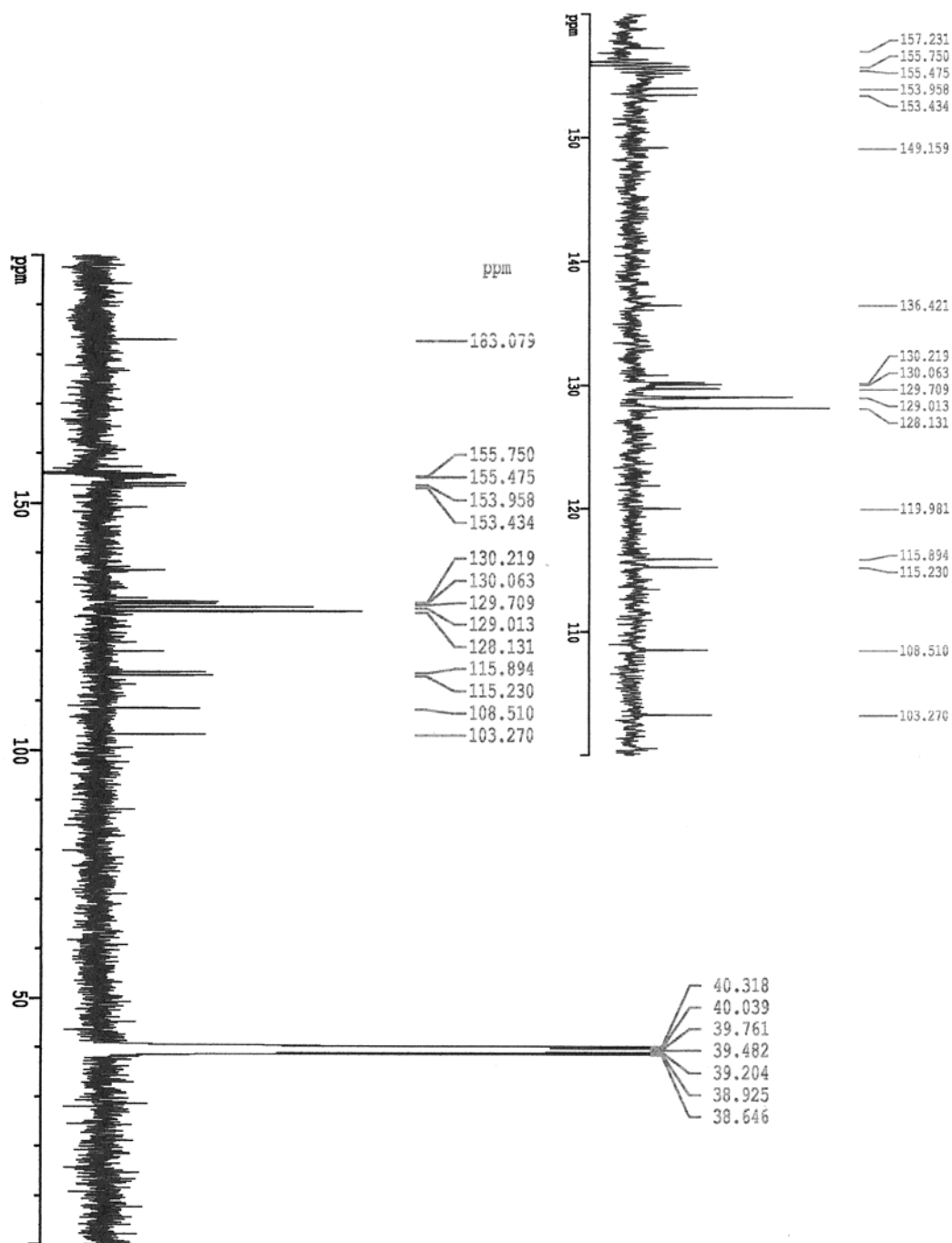


Figure S17: <sup>1</sup>H NMR of SNAFR-1 in DMSO-d<sub>6</sub>.



# SNAFR-1 in DMSO-d6



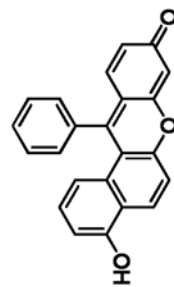
Current Data Parameters  
 NAME JACS\_2  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20061108  
 Time 18.19  
 INSTRUM spect  
 PROBD 5 mm Multi  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT MeOH  
 NS 24826  
 DS 2  
 SWH 19230.770 Hz  
 FIDRES 1.173753 Hz  
 AQ 0.4260340 sec  
 RG 32768  
 DM 26.000 usec  
 DE 37.14 usec  
 TE 300.0 K  
 D12 0.00002000 sec  
 D16 23.00 dB  
 D1 2.00000000 sec  
 CPDPRG waltz16  
 P31 86.00 usec  
 D11 0.03000000 sec  
 D15 23.00 dB  
 P1 9.80 usec  
 SFO1 75.4751777 MHz  
 NUCLEUS 13C

F2 - Processing parameters  
 SI 16384  
 SF 75.4678097 MHz  
 WDW EM  
 SSB 0  
 LB 2.00 Hz  
 GB 0  
 PC 1.40

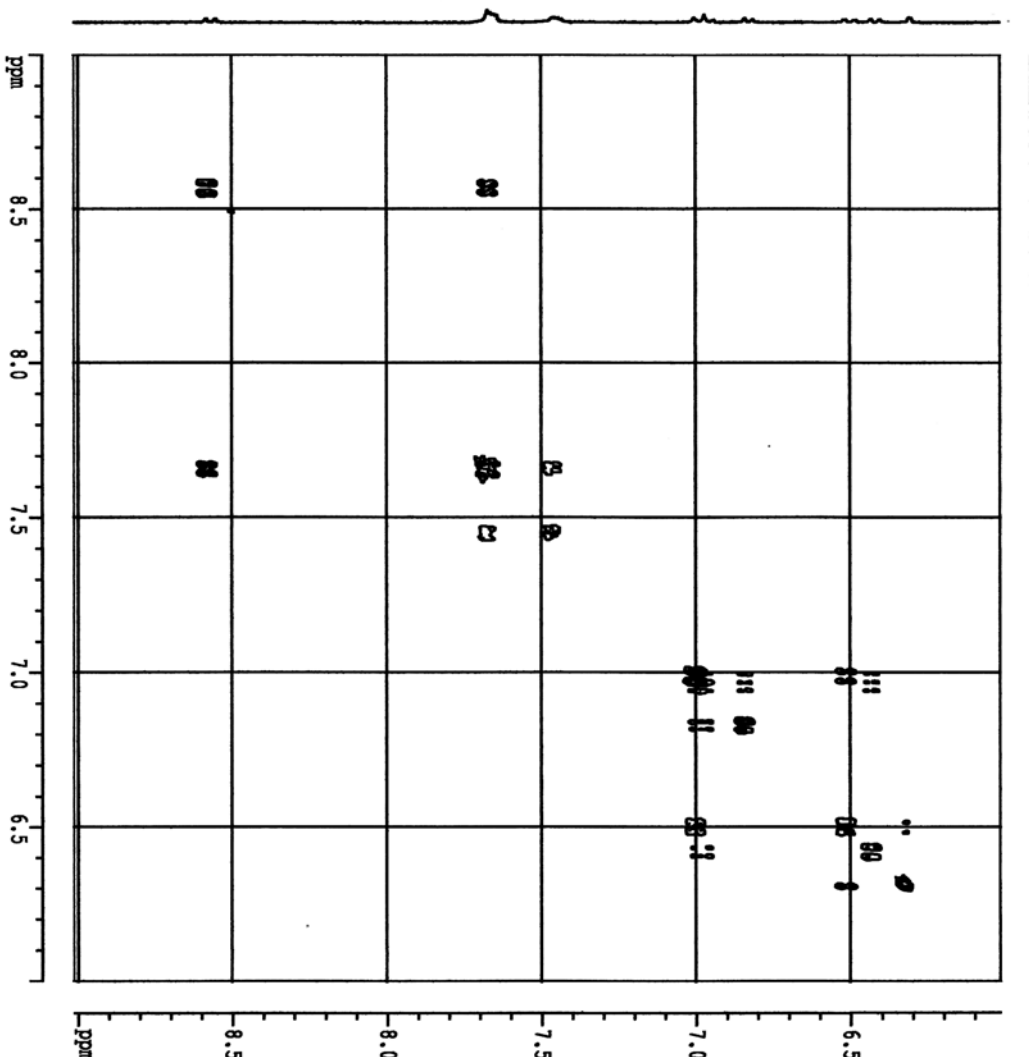
1D NMR plot parameters  
 CX 18.00 cm  
 F1P 200.000 ppm  
 F1 15093.56 Hz  
 F2P 0.000 ppm  
 F2 0.00 Hz  
 PPRCM 11.11111 ppm/cm  
 HZCM 838.53119 Hz/cm

Figure S18: <sup>13</sup>C NMR of SNAFR-1 in DMSO-d<sub>6</sub>.



# SNAFR-1 in DMSO-d6

Half down in DMSO-d6.



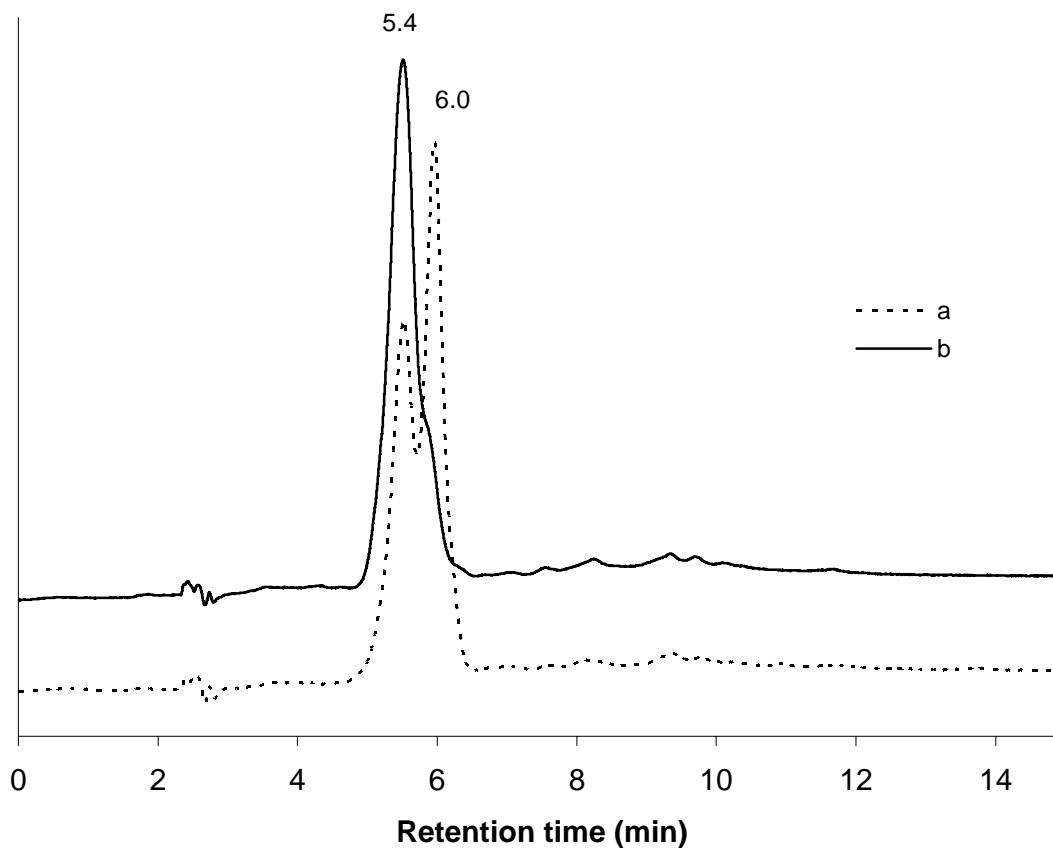
```

Current Data Parameters
NAME          SNAFR1
EXPNO        12
PROCNO       1
-----
F2 - Acquisition Parameters
Date_        20061114
Time         10.42
INSTRUM      spect
PROBHD       5 mm MSL1
PULPROG      coay
TD           1024
SOLVENT      DMSO
NS           8
DS           2
SWH          900.501 Hz
FIDRES      0.817185 Hz
AQ          0.3583700 sec
RG          5700
WDW          EM
SSB          0
GB          0
PC           1.00
DE          0.30 Hz
TE          300.15 K
NUC1         13
NUC2         13
AQ          2.0000000 sec
SFO1         300.1322552 MHz
SFO2         300.1322552 MHz
NUC1N1      13
NUC1N2      13
INSTRUM      spect
PROCNO       1
-----
F1 - Acquisition Parameters
NO     1
TD     219
SFO1   300.1323 MHz
SFO2   4.111401 Hz
WDW    EM
SSB    0
PC     1.00
-----
F2 - Processing parameters
SI     32768
SF     300.1300000 MHz
WDW    EM
SSB    0
GB     0
PC     1.00
-----
F1 - Processing parameters
SI     256
SF     300.1300000 MHz
WDW    EM
SSB    0
GB     0
PC     1.00
-----
2D NMR plot parameters
SI     32768
SF     300.1300000 MHz
WDW    EM
SSB    0
GB     0
PC     1.00
-----
2D NMR plot parameters
SI     32768
SF     300.1300000 MHz
WDW    EM
SSB    0
GB     0
PC     1.00
-----

```

Figure S19: 2D-COSY of SNAFR-1 (expansion from 6.0-9.0 ppm) in DMSO-d6.





**Figure S21.** a) HPLC trace of freshly dissolved **SNAFR-1** in MeOH showing two peaks (retention times = 5.4 and 6.0 min, **SNAFR-1 MeOH adduct** and **SNAFR-1**, respectively). b) HPLC trace of **SNAFR-1**. **SNAFR-1** dissolved in MeOH after sitting in the dark for 30 min. Only the peak corresponding to the **SNAFR-1 MeOH adduct** is observed showing that the MeOH present promotes the conversion of **SNAFR-1** to its MeOH adduct. HPLC analysis is performed on a CM4000 multiple solvent delivery system connected to a SpectroMonitor 3100 UV-Vis detector (LDC/Milton Roy) using a LiChrospher 100 RP-18 (5  $\mu$ m) endcapped column (250  $\times$  4.6 mm). The flow rate is 1.0 mL/min and the detector wavelength is set to 490 nm. Mobile phase (gradient): 70/30 MeOH/H<sub>2</sub>O to 100/0 % MeOH/H<sub>2</sub>O in 5 min.

# SNAFR-2 in DMSO-d<sub>6</sub>

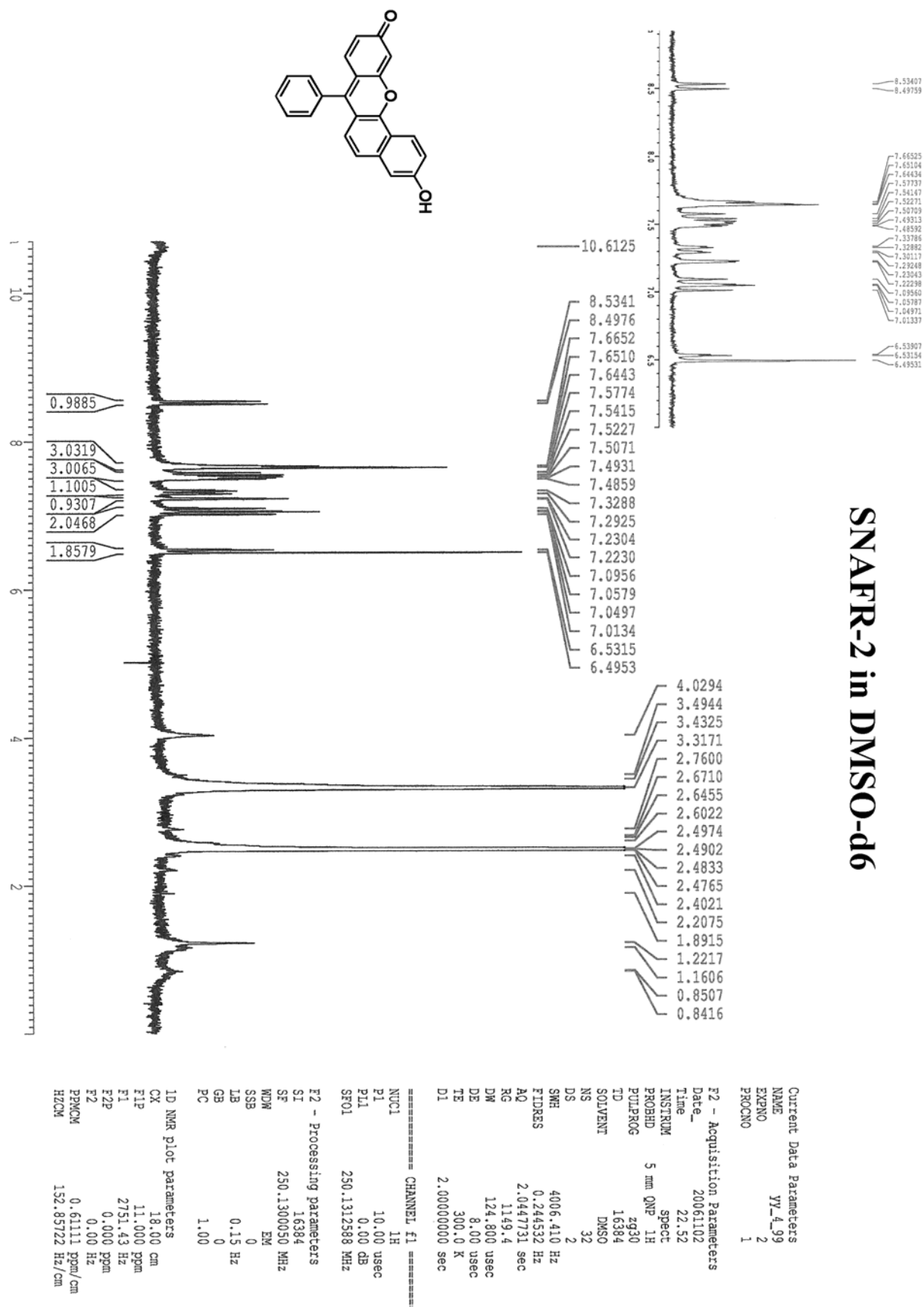
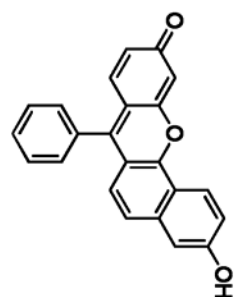
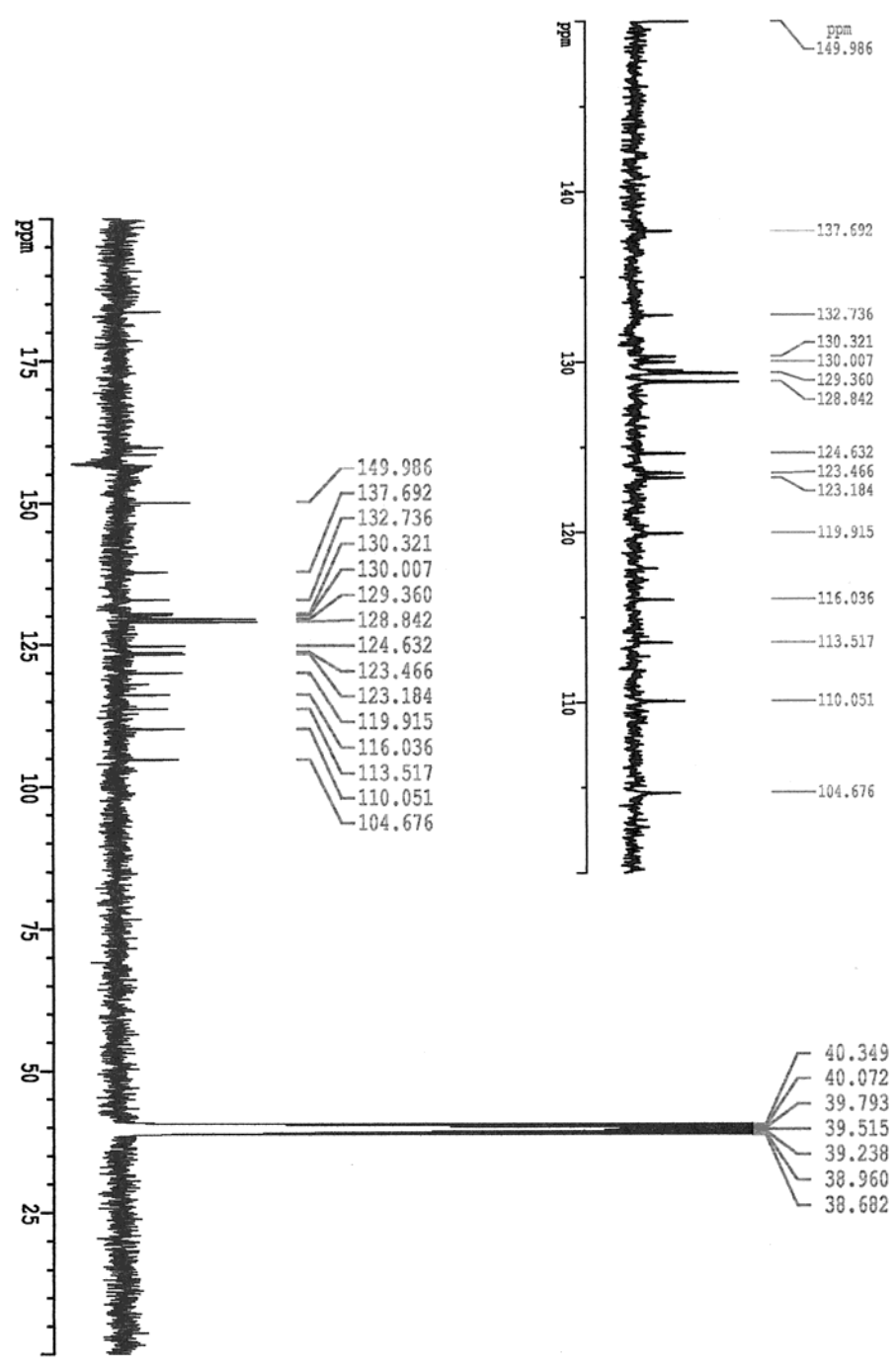


Figure S22: <sup>1</sup>H NMR of SNAFR-2 in DMSO-d<sub>6</sub>.



# SNAFR-2 in DMSO-d6



Current Data Parameters

NAME	JACS_2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20061105
Time	0.29
INSTRUM	spect
PROBHD	5 mm Malti
PULPROG	zgpg30
TD	16384
SOLVENT	DMSO
NS	10240
DS	2
SWH	19230.770 Hz
FIDRES	1.173753 Hz
AQ	0.4260340 sec
RG	32768
DW	26.000 usec
DE	37.14 usec
TE	300.0 K
D12	0.00002000 sec
DL6	23.00 dB
D1	2.00000000 sec
CPDPRG	waltz16
P31	86.00 usec
D11	0.03000000 sec
DL5	23.00 dB
P1	9.80 usec
SFO1	75.475177 MHz
NUCLEUS	<sup>13</sup> C

F2 - Processing parameters

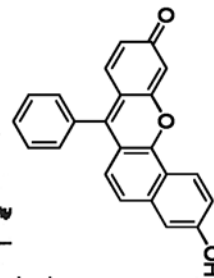
SI	16384
SF	75.4677839 MHz
NDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

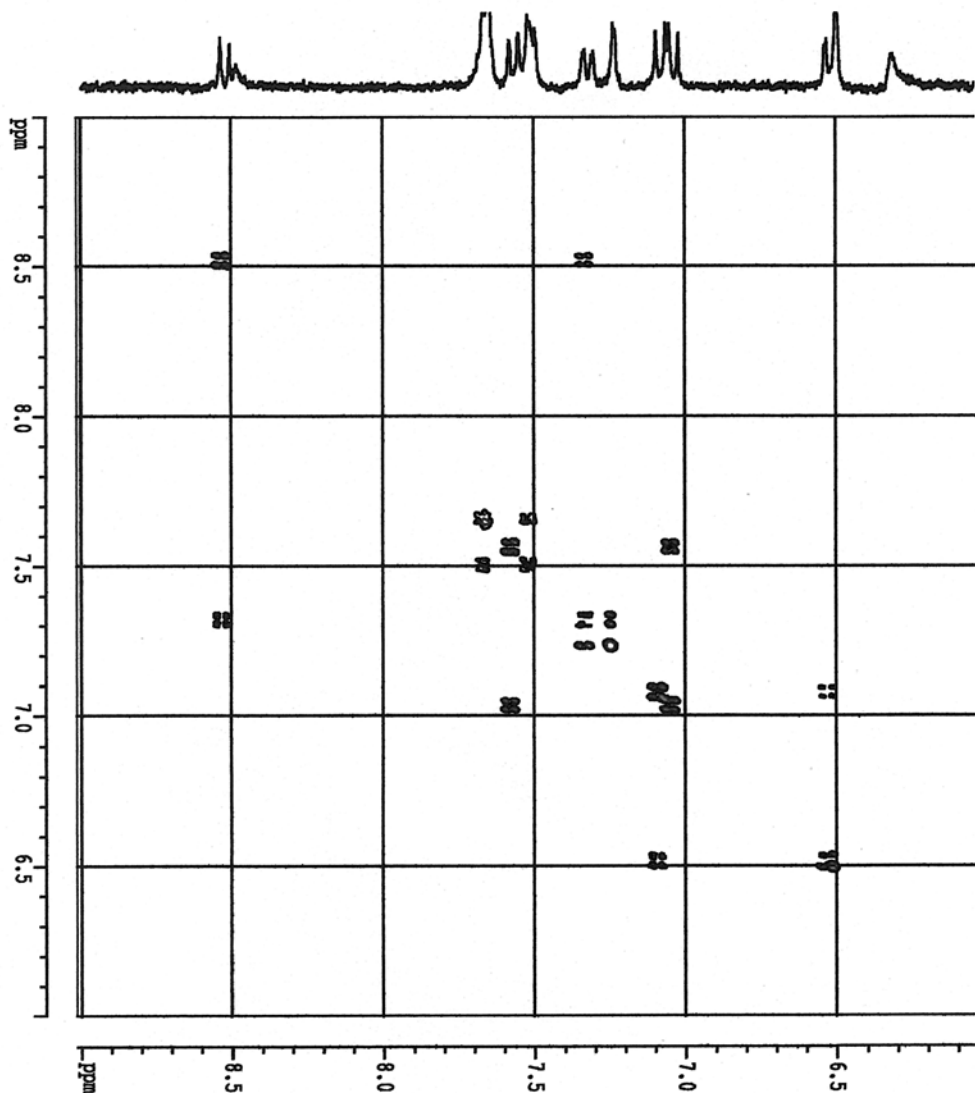
CX	18.00 cm
FTP	200.000 ppm
F1	15093.55 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	11.11111 ppm/cm
HZCM	838.53082 Hz/cm

Figure S23: <sup>13</sup>C NMR of SNAFR-2 in DMSO-d<sub>6</sub>.





# SNAFR-2



```

Current Data Parameters
NAME          SNAFR-2
EXPNO         5
PROCNO        1

F2 - Acquisition Parameters
Date_         20081103
Time          16:44
INSTRUM       spect
PROBHD        5 mm BBO1
PULPROG       zgpg30
TD            1024
SOLVENT       DMSO
NS            8
DS            2
SWH           300.301 Hz
FIDRES        0.879786 Hz
AQ            0.5683700 sec
RG            553.9700
SR            533.9700 usec
DE            300.172 usec
TE            300.2 K
D1            5.00
D11           0.10
D12           0.10
D13           0.10
D14           0.10
D15           0.10
D16           0.10
D17           0.10
D18           0.10
D19           0.10
D20           0.10
PC            1.00
SFO1          300.1322551 MHz
NUC1          13C
NUC2          13C
NUC3          13C
NUC4          13C
NUC5          13C
NUC6          13C
NUC7          13C
NUC8          13C
NUC9          13C
NUC10         13C
NUC11         13C
NUC12         13C
NUC13         13C
NUC14         13C
NUC15         13C
NUC16         13C
NUC17         13C
NUC18         13C
NUC19         13C
NUC20         13C

F1 - Acquisition parameters
NOI           1
TD            256
SFO1          300.1322 MHz
SFO2          300.1322 MHz
SFO3          300.1322 MHz
SFO4          300.1322 MHz
SFO5          300.1322 MHz
SFO6          300.1322 MHz
SFO7          300.1322 MHz
SFO8          300.1322 MHz
SFO9          300.1322 MHz
SFO10         300.1322 MHz
SFO11         300.1322 MHz
SFO12         300.1322 MHz
SFO13         300.1322 MHz
SFO14         300.1322 MHz
SFO15         300.1322 MHz
SFO16         300.1322 MHz
SFO17         300.1322 MHz
SFO18         300.1322 MHz
SFO19         300.1322 MHz
SFO20         300.1322 MHz
SFO21         300.1322 MHz
SFO22         300.1322 MHz
SFO23         300.1322 MHz
SFO24         300.1322 MHz
SFO25         300.1322 MHz
SFO26         300.1322 MHz
SFO27         300.1322 MHz
SFO28         300.1322 MHz
SFO29         300.1322 MHz
SFO30         300.1322 MHz
SFO31         300.1322 MHz
SFO32         300.1322 MHz
SFO33         300.1322 MHz
SFO34         300.1322 MHz
SFO35         300.1322 MHz
SFO36         300.1322 MHz
SFO37         300.1322 MHz
SFO38         300.1322 MHz
SFO39         300.1322 MHz
SFO40         300.1322 MHz
SFO41         300.1322 MHz
SFO42         300.1322 MHz
SFO43         300.1322 MHz
SFO44         300.1322 MHz
SFO45         300.1322 MHz
SFO46         300.1322 MHz
SFO47         300.1322 MHz
SFO48         300.1322 MHz
SFO49         300.1322 MHz
SFO50         300.1322 MHz
SFO51         300.1322 MHz
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SFO67         300.1322 MHz
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SFO69         300.1322 MHz
SFO70         300.1322 MHz
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SFO73         300.1322 MHz
SFO74         300.1322 MHz
SFO75         300.1322 MHz
SFO76         300.1322 MHz
SFO77         300.1322 MHz
SFO78         300.1322 MHz
SFO79         300.1322 MHz
SFO80         300.1322 MHz
SFO81         300.1322 MHz
SFO82         300.1322 MHz
SFO83         300.1322 MHz
SFO84         300.1322 MHz
SFO85         300.1322 MHz
SFO86         300.1322 MHz
SFO87         300.1322 MHz
SFO88         300.1322 MHz
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SFO90         300.1322 MHz
SFO91         300.1322 MHz
SFO92         300.1322 MHz
SFO93         300.1322 MHz
SFO94         300.1322 MHz
SFO95         300.1322 MHz
SFO96         300.1322 MHz
SFO97         300.1322 MHz
SFO98         300.1322 MHz
SFO99         300.1322 MHz
SFO100        300.1322 MHz

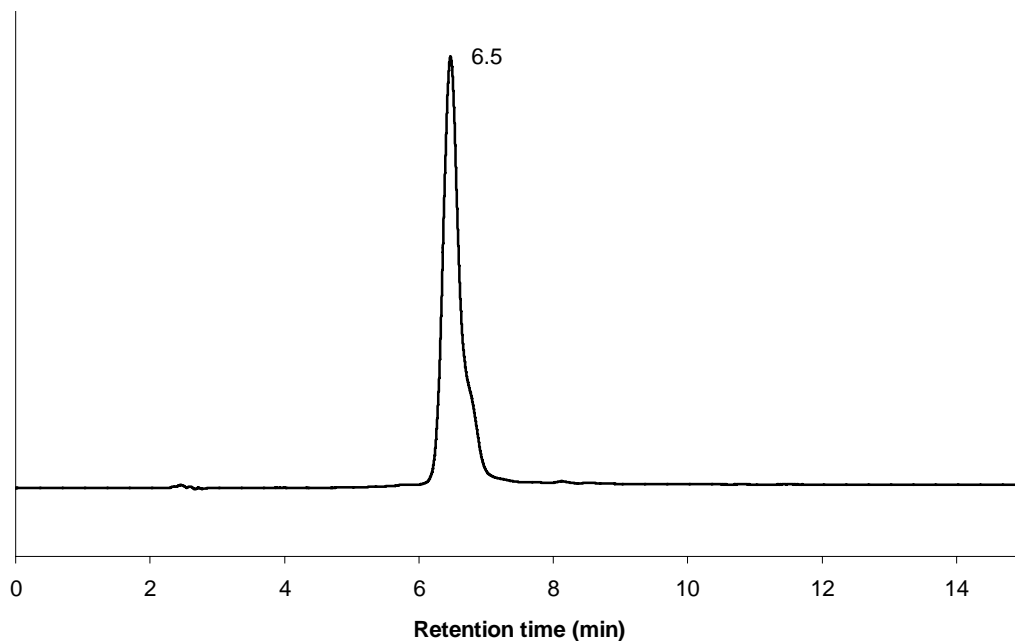
F2 - Processing parameters
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SF            300.1300042 MHz
WDW           EM
SSB           0
GB            0
PC            0.30 Hz
SC            0
SB            0
SF            1.00

F1 - Processing parameters
SI            256
SF            300.1300000 MHz
WDW           EM
SSB           0
GB            0
PC            0.00 Hz
SC            0
SB            0
SF            0.00 Hz

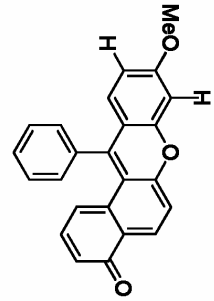
2D NMR plot parameters
CX2           15.00 cm
CY2           15.00 cm
FZ10          9.001 ppm
FZ11          9.001 ppm
FZ12          9.001 ppm
FZ13          9.001 ppm
FZ14          9.001 ppm
FZ15          9.001 ppm
FZ16          9.001 ppm
FZ17          9.001 ppm
FZ18          9.001 ppm
FZ19          9.001 ppm
FZ20          9.001 ppm
FZ21          9.001 ppm
FZ22          9.001 ppm
FZ23          9.001 ppm
FZ24          9.001 ppm
FZ25          9.001 ppm
FZ26          9.001 ppm
FZ27          9.001 ppm
FZ28          9.001 ppm
FZ29          9.001 ppm
FZ30          9.001 ppm
FZ31          9.001 ppm
FZ32          9.001 ppm
FZ33          9.001 ppm
FZ34          9.001 ppm
FZ35          9.001 ppm
FZ36          9.001 ppm
FZ37          9.001 ppm
FZ38          9.001 ppm
FZ39          9.001 ppm
FZ40          9.001 ppm
FZ41          9.001 ppm
FZ42          9.001 ppm
FZ43          9.001 ppm
FZ44          9.001 ppm
FZ45          9.001 ppm
FZ46          9.001 ppm
FZ47          9.001 ppm
FZ48          9.001 ppm
FZ49          9.001 ppm
FZ50          9.001 ppm
FZ51          9.001 ppm
FZ52          9.001 ppm
FZ53          9.001 ppm
FZ54          9.001 ppm
FZ55          9.001 ppm
FZ56          9.001 ppm
FZ57          9.001 ppm
FZ58          9.001 ppm
FZ59          9.001 ppm
FZ60          9.001 ppm
FZ61          9.001 ppm
FZ62          9.001 ppm
FZ63          9.001 ppm
FZ64          9.001 ppm
FZ65          9.001 ppm
FZ66          9.001 ppm
FZ67          9.001 ppm
FZ68          9.001 ppm
FZ69          9.001 ppm
FZ70          9.001 ppm
FZ71          9.001 ppm
FZ72          9.001 ppm
FZ73          9.001 ppm
FZ74          9.001 ppm
FZ75          9.001 ppm
FZ76          9.001 ppm
FZ77          9.001 ppm
FZ78          9.001 ppm
FZ79          9.001 ppm
FZ80          9.001 ppm
FZ81          9.001 ppm
FZ82          9.001 ppm
FZ83          9.001 ppm
FZ84          9.001 ppm
FZ85          9.001 ppm
FZ86          9.001 ppm
FZ87          9.001 ppm
FZ88          9.001 ppm
FZ89          9.001 ppm
FZ90          9.001 ppm
FZ91          9.001 ppm
FZ92          9.001 ppm
FZ93          9.001 ppm
FZ94          9.001 ppm
FZ95          9.001 ppm
FZ96          9.001 ppm
FZ97          9.001 ppm
FZ98          9.001 ppm
FZ99          9.001 ppm
FZ100         9.001 ppm
  
```

Figure S24: 2D-COSY of SNAFR-2 (expansion from 6.0-9.0 ppm) in DMSO- $d_6$





**Figure S26:** Chromatogram of a solution of **SNAFR-2** in MeOH. HPLC purity screening is performed on a CM4000 multiple solvent delivery system connected to a SpectroMonitor 3100 UV-Vis detector (LDC/Milton Roy) using a LiChrospher 100 RP-18 (5  $\mu$ m) endcapped column (250  $\times$  4.6 mm). The flow rate is 1.0 mL/min and the detector wavelength is set to 490 nm. Mobile phase (gradient): 70/30 MeOH/H<sub>2</sub>O to 100/0 % MeOH/H<sub>2</sub>O in 5 min.



## Compound 12 in DMSO-*d*<sub>6</sub>

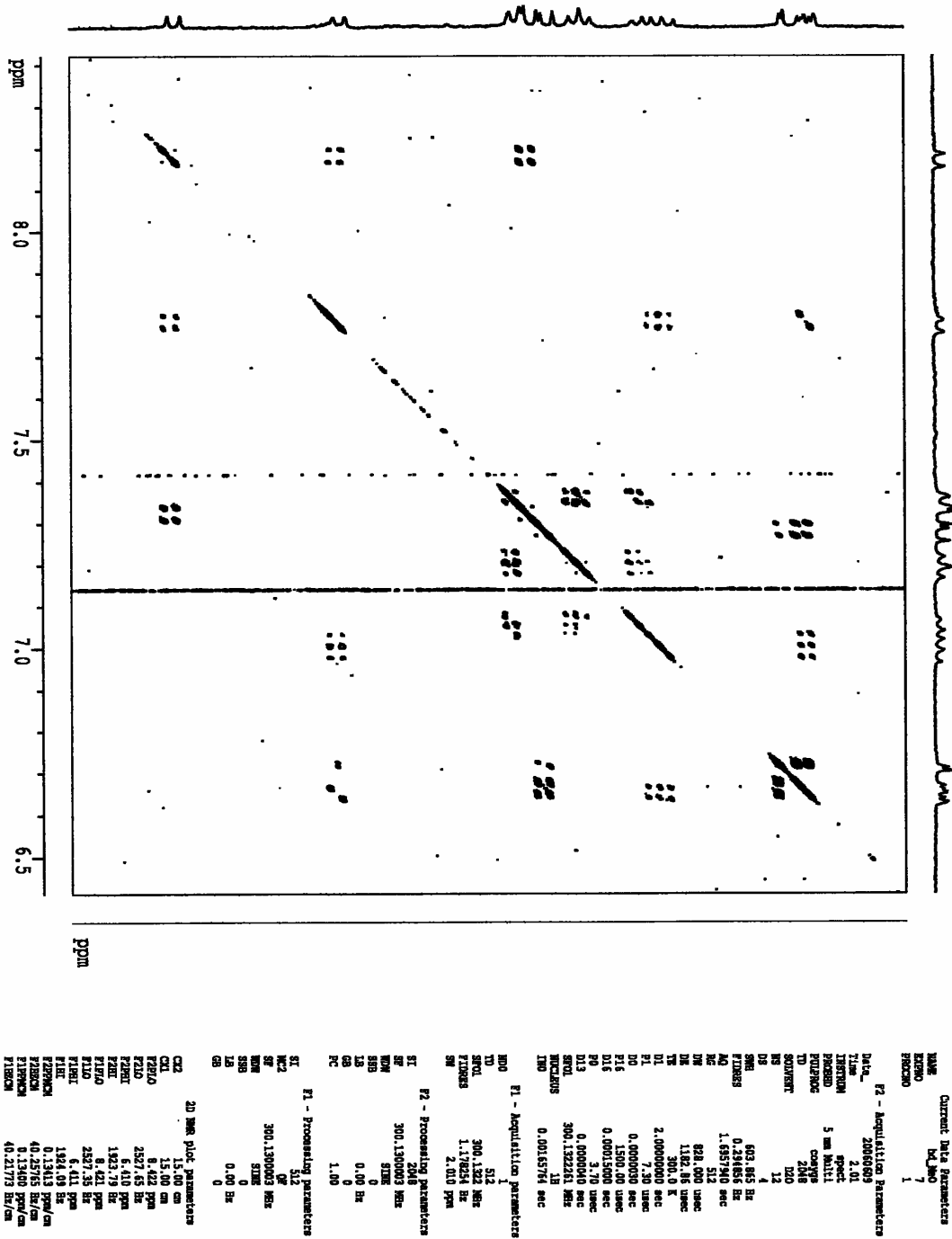
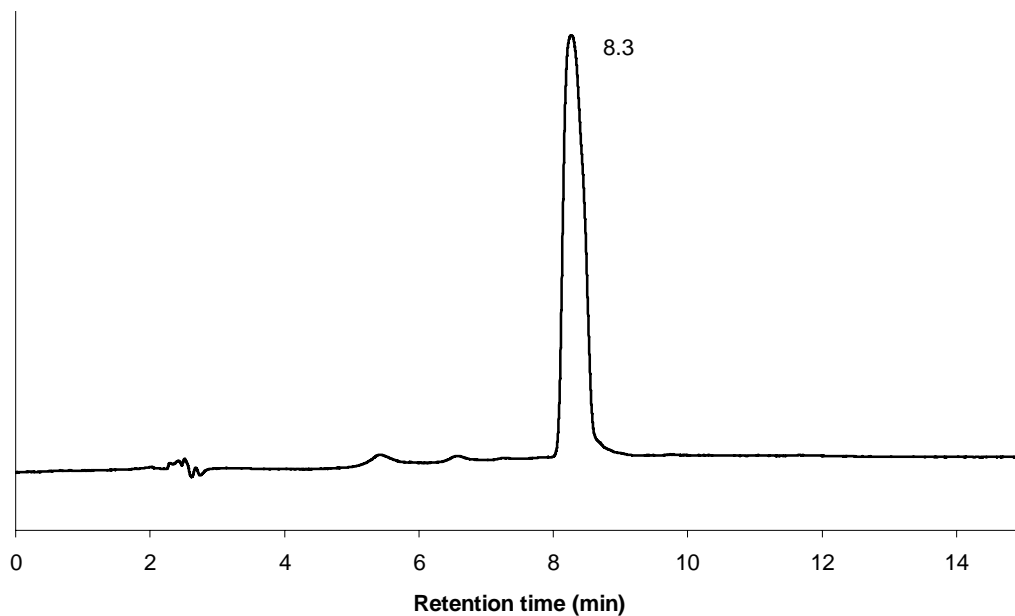
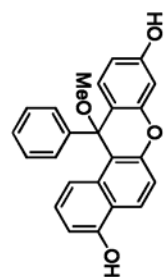


Figure S27: 2D-COSY of compound 12 (expansion from 6.0-9.0 ppm) in DMSO-*d*<sub>6</sub>





**Figure S29**, Chromatogram of a solution of compound **12** in MeOH. HPLC purity screening is performed on a CM4000 multiple solvent delivery system connected to a SpectroMonitor 3100 UV-Vis detector (LDC/Milton Roy) using a LiChrospher 100 RP-18 (5  $\mu$ m) endcapped column (250  $\times$  4.6 mm). The flow rate is 1.0 mL/min and the detector wavelength is set to 490 nm. Mobile phase (gradient): 70/30 MeOH/H<sub>2</sub>O to 100/0 % MeOH/H<sub>2</sub>O in 5 min.



### Compound 18 in MeOH-d<sub>4</sub>

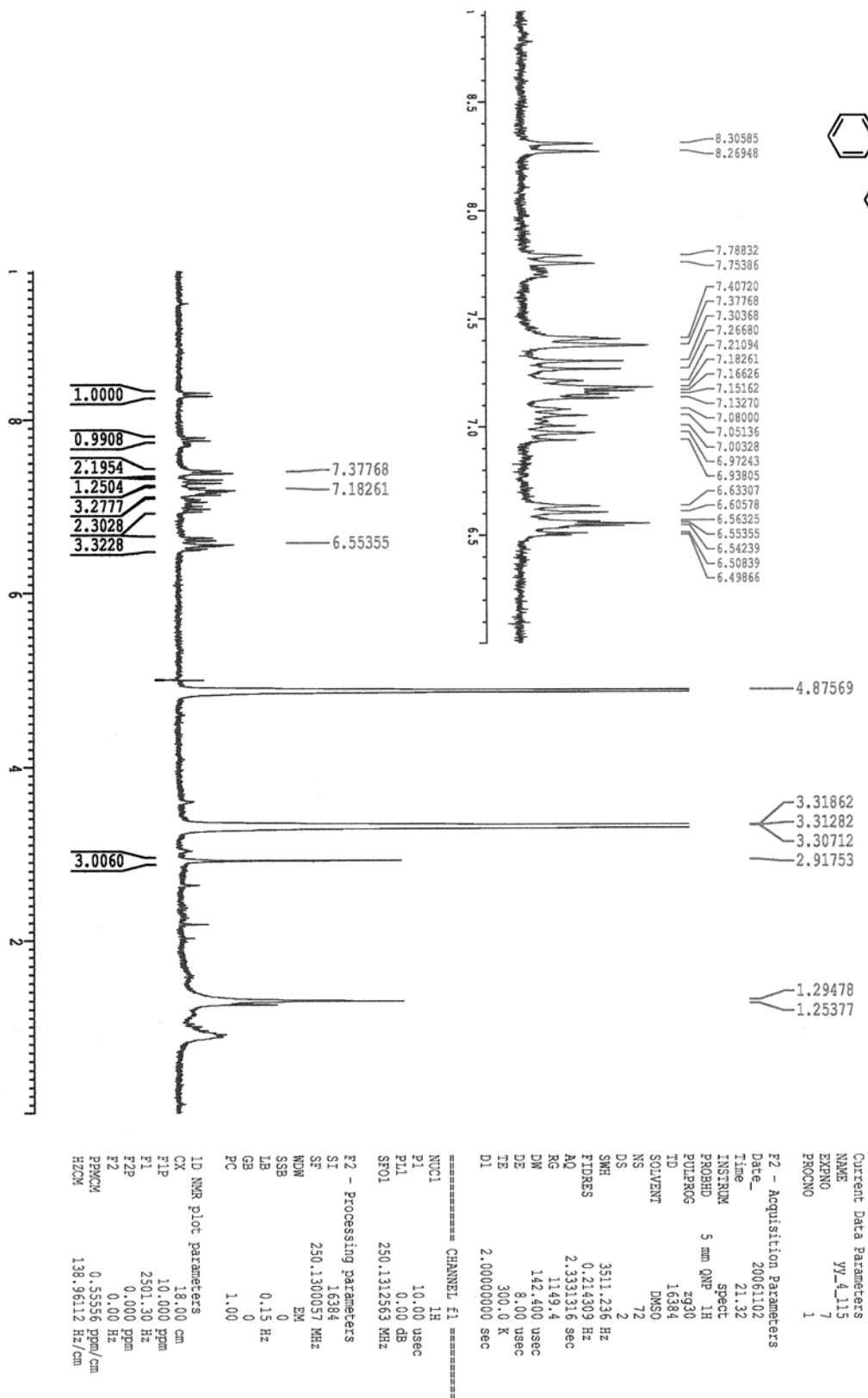
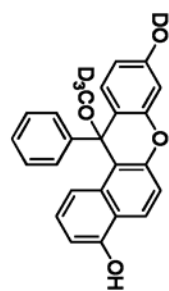


Figure S30: <sup>1</sup>H NMR of compound 18 MeOH-d<sub>4</sub>



## Compound 19 in MeOH-d<sub>4</sub>

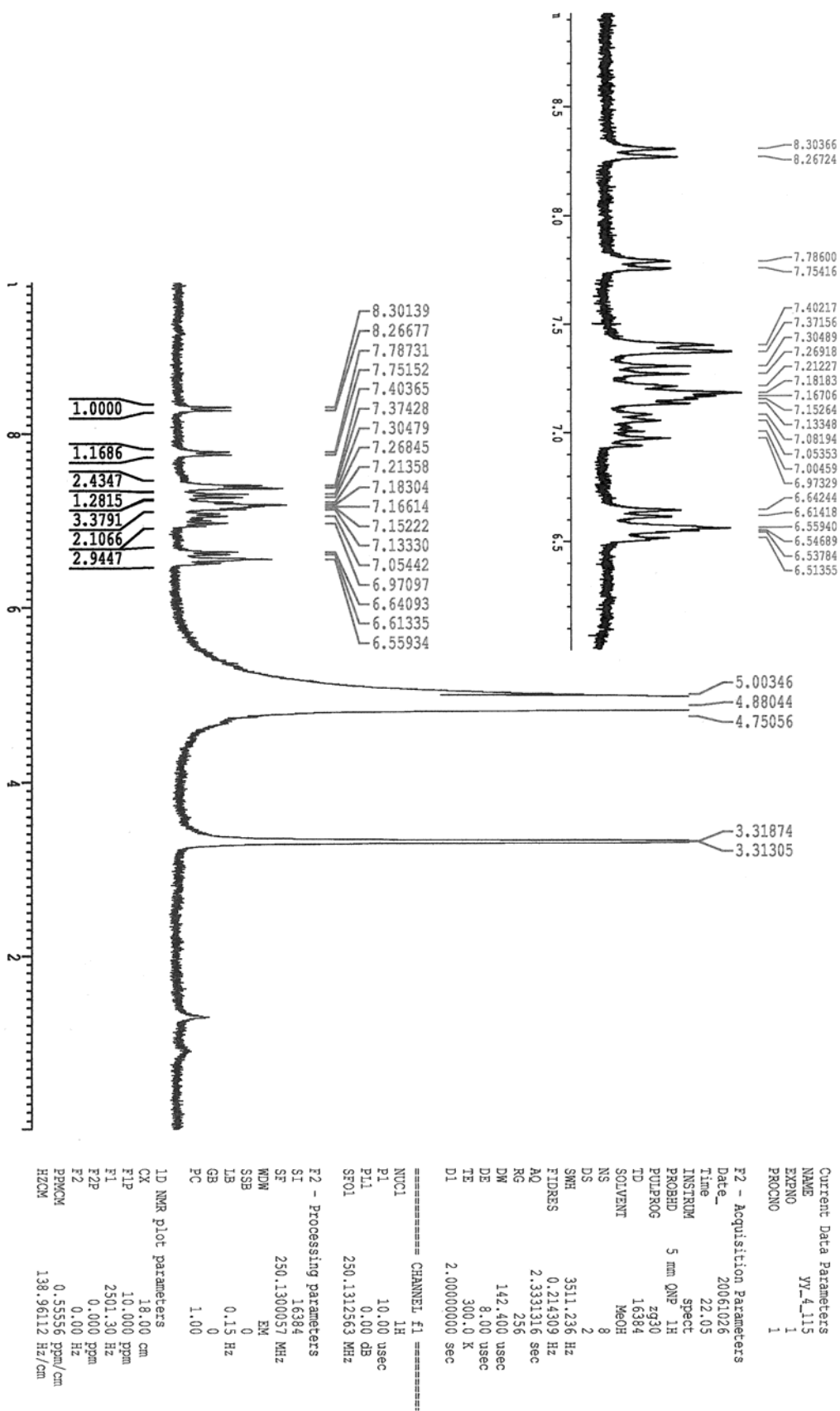
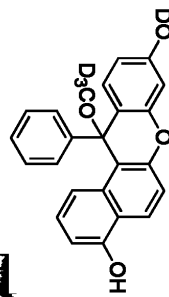
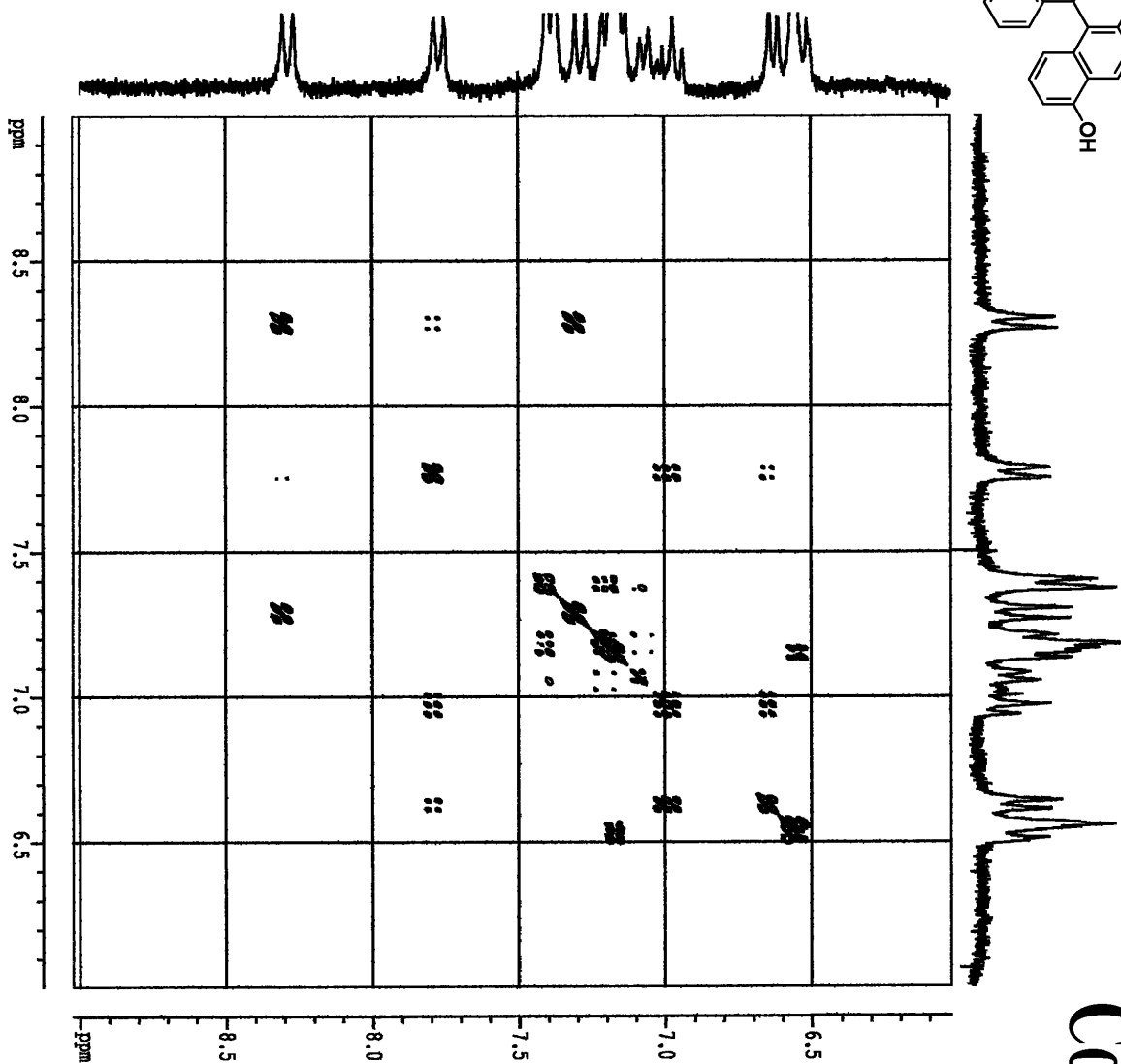


Figure S31: <sup>1</sup>H NMR of compound 19 MeOH-d<sub>4</sub>





# Compound 19



```

Current Data Parameters
NAME          YL_A115
EXPNO        3
PROCNO       1

F2 - Acquisition Parameters
Date_         20061026
Time          22.13
INSTRUM      spect
PROBHD       5 mm QNP 1H
PULPROG      zgpg30
AQ           0.683278 sec
RG           3284
AQ           1.024
TD           657200
SFO          500.136
FIDRES       0.67200
AQ           6.67200
RG           3284
AQ           1.024
WDW          EM
SSB          0
GB           0
PC           0.10000000 sec
DI           2.00000000 sec
DQ           0.00133028 sec
LIM          1

===== CHANNEL f1 =====
NUC1         13
P1           18.00
NUC2         13
P2           18.00
SFO1         250.130000 MHz
SFO2         250.130000 MHz
WDW          EM
SSB          0
GB           0
PC           0.15
RG           1.00

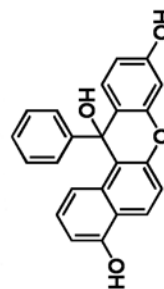
F1 - Acquisition Parameters
NUC1         1
TD           1
SFO1         250.13119 MHz
SFO2         2.137898 Hz
WDW          EM
SSB          0
GB           0
PC           3.000

F2 - Processing parameters
SI           3284
SF           250.130000 MHz
WDW          EM
SSB          0
GB           0
PC           0.00
RG           0

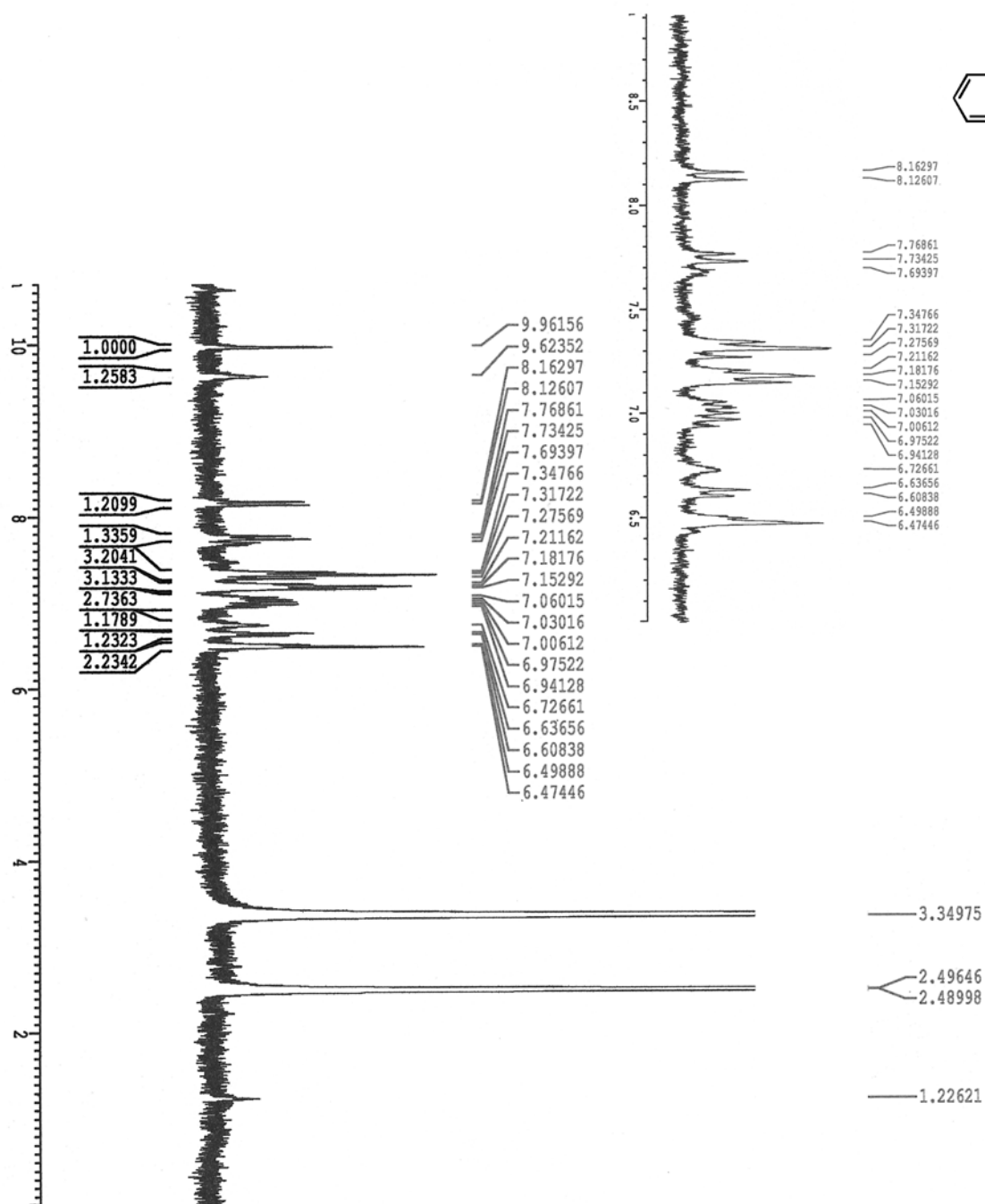
F1 - Processing parameters
SI           512
SF           250.130000 MHz
WDW          EM
SSB          0
GB           0
PC           0.00
RG           0

2D NMR plot parameters
CZ2          15.00 cm
CZ1          15.00 cm
FZ1D0       8.598 ppm
FZ1D1       22850.67 Hz
FZ1D2       5.0002 ppm
FZ1D3       1504.27 Hz
F1D0        9.2023 ppm
F1D1        26400 Hz
F1D2        4.0000 Hz
F1D3        1506.46 Hz
F1D4        0.13914 ppm/cm
F2RESOLV    49.94004 Hz/cm
F1RESOLV    0.20000 ppm/cm
F1SFO1      50.02657 Hz/cm
  
```

Figure S32: 2D-COSY of compound 19 (expansion from 6.0-9.0 ppm) in DMSO-*d*<sub>6</sub>. Compound 18 has the same 2D-COSY spectrum shown above (expansion from 6.0 ppm to 9.0 ppm).



### SNAFR-1 H<sub>2</sub>O adduct in DMSO-d<sub>6</sub>



```

Current Data Parameters
NAME          YY_4_115
EXPNO         4
PROCNO        1

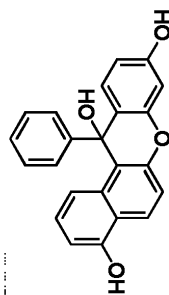
F2 - Acquisition Parameters
Date_         20061027
Time          0.51
INSTRUM      spect
PROBHD       5 mm QNP 1H
PULPROG      zg30
TD            16384
SOLVENT      MeOH
NS            8
DS            2
SWH           3511.236 Hz
FIDRES       0.214309 Hz
AQ            2.3331316 sec
RG            1448.2
DW            142.400 usec
DE            8.00 usec
TE            300.0 K
D1            2.00000000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            10.00 usec
PL1           0.00 dB
SFO1         250.1312563 MHz

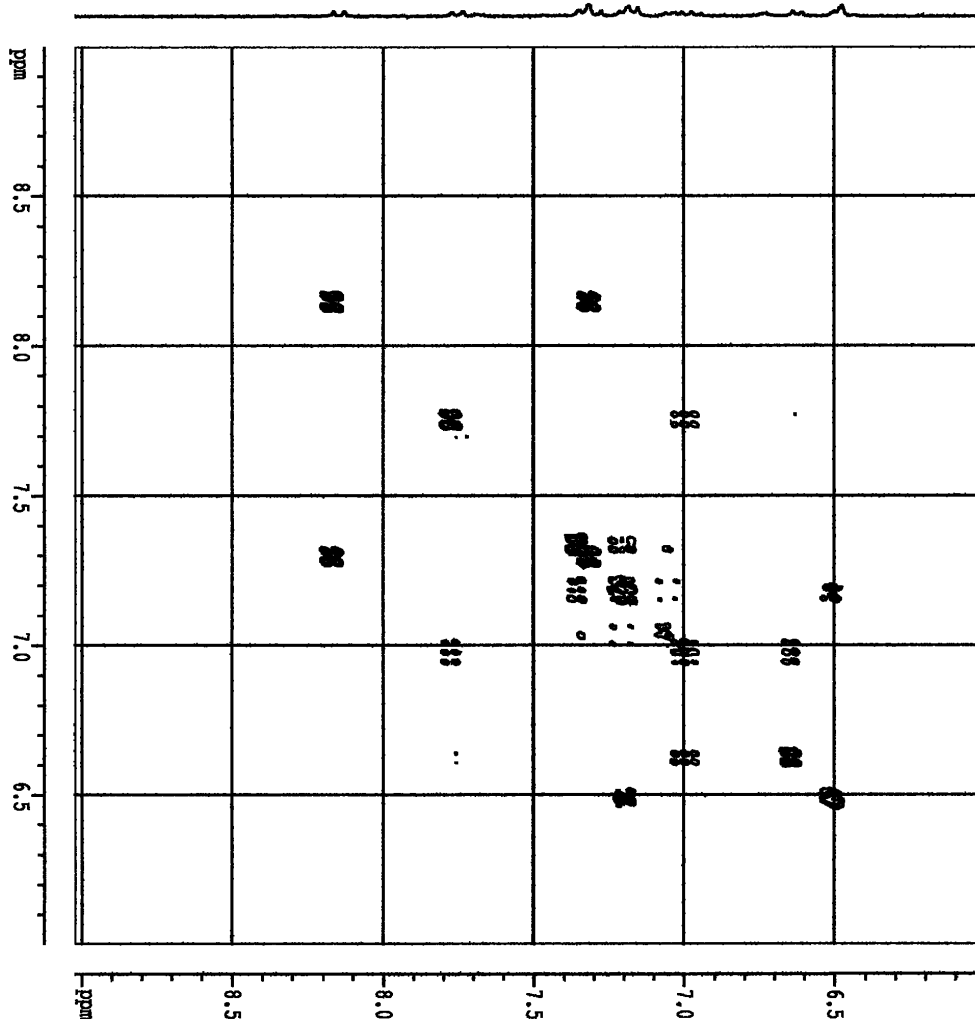
F2 - Processing parameters
SI            16384
SF            250.1300060 MHz
WDW           EM
SSB           0
LB            0.15 Hz
GB            0
PC            1.00

1D NMR plot parameters
CX            18.00 cm
F1P           11.000 ppm
F1            2751.43 Hz
F2P           0.000 ppm
F2            0.00 Hz
PWCNM         0.61111 ppm/cm
HZCM          152.85722 Hz/cm
  
```

Figure S33: <sup>1</sup>H NMR of SNAFR-1 H<sub>2</sub>O adduct (tentatively) in DMSO-d<sub>6</sub>.



# SNAFR-1 H<sub>2</sub>O adduct



Current Data Parameters

NAME	Y7.A.113
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20100327
Time	0.59
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgpg30
TD	1024
WDW	EM
SF	500.136303
WDW	EM
SSB	0
LB	3.00
GB	0
PC	1.00
DT	0.00002000
AS	0.00000000
SD	0.00000000
WDW	EM
SSB	0
LB	3.00
GB	0
PC	1.00
DT	0.00002000
AS	0.00000000
SD	0.00000000
WDW	EM
SSB	0
LB	3.00
GB	0
PC	1.00
DT	0.00002000
AS	0.00000000
SD	0.00000000

F1 - Processing parameters

SI	32768
SF	500.136303
WDW	EM
SSB	0
LB	3.00
GB	0
PC	1.00
DT	0.00002000
AS	0.00000000
SD	0.00000000
WDW	EM
SSB	0
LB	3.00
GB	0
PC	1.00
DT	0.00002000
AS	0.00000000
SD	0.00000000

F2 - Acquisition parameters

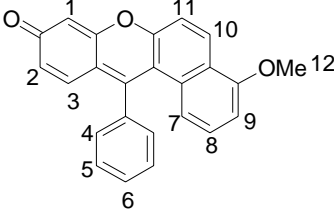
NUC1	13
PD	10.00
PL	10.00
FL	0.00
STOL	250.131817
NUC2	1
PD	235
PL	235
FL	0.00
STOL	250.131319
NUC3	13
PD	2.531245
PL	3.000
FL	0.00
STOL	250.130657
NUC4	1
PD	0
PL	0
FL	0.00
STOL	250.130657
NUC5	13
PD	0.15
PL	0
FL	0.00
STOL	250.130657
NUC6	1
PD	1.00
PL	1.00
FL	0.00
STOL	250.130657

2D NMR pick parameters

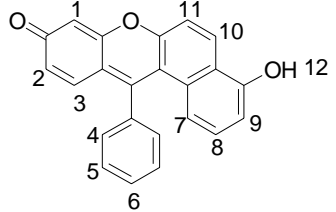
CC2	15.00
CEL	15.00
FZ10	8.398
FZ10	2250.67
FZ91	6.002
FZ91	1501.27
FZ10	8.023
FZ10	2250.67
FZ10	1506.46
FZ10	1506.46
FZ91	0.1874
FZ91	43.5604
FZ91	0.2000
FZ91	50.02657

Figure S34: 2D-COSY of SNAFR-1 H<sub>2</sub>O adduct (tentatively) (expansion from 6.0-9.0 ppm) in DMSO-d<sub>6</sub>.

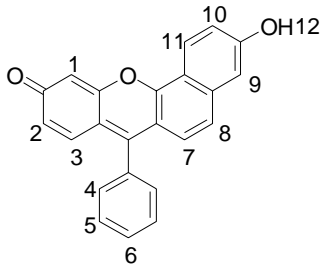
**Table S1:** Assignment of protons of compound **17** based 2D COSY (Figure S14, page S15).

Compound <b>17</b> , Page S13	# of H	ppm	J (Hz)	Splitting
	1	6.32	2.3	d
	2	6.52	9.8, 2.3	dd
	3	7.01	9.8	d
	4, 6	7.65-7.70		m
	5	7.43-7.49		m
	7	6.55	8.8	d
	8	7.11	8.8, 7.8	dd
	9	6.96	7.8	d
	10	8.58	9.5	d
	11	7.72	9.5	d
	12	3.96		s

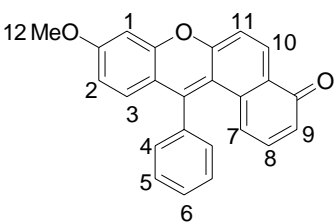
**Table S2:** Assignment of protons of **SNAFR-1** based 2D COSY (Figure S19, page S20).

<b>SNAFR-1</b> , Page S20	# of H	ppm	J (Hz)	Splitting
	1	6.32	1.8	d
	2	6.51	9.9, 1.8	dd
	3	7.00	9.9	d
	4&6	7.64-7.69		m
	5	7.44-7.48		m
	7	6.43	8.4	d
	8	6.98	8.4, 7.2	dd
	9	6.84	7.2	d
	10	8.58	9.3	d
	11	7.66	9.3	d
	12	10.57		s

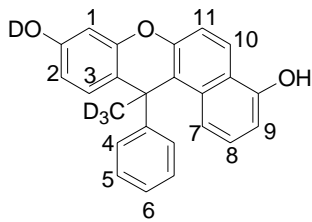
**Table S3:** Assignment of protons of **SNAFR-2** based 2D COSY (Figure S24, page S25).

SNAFR-2, Page S23	# of H	ppm	J (Hz)	Splitting
	1	7.23	2.7	d
	2	7.32	9.3, 2.7	dd
	3	8.52	9.3	d
	4&6	7.65-7.70		m
	5	7.49-7.53		m
	7	7.56	9	d
	8	7.04	9	d
	9	6.50	1.5	d
	10	6.52	9.3, 1.5	dd
	11	7.09	9.3	d
	12	10.61		s

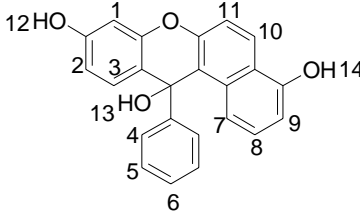
**Table S4:** Assignment of protons of compound **12** based 2D COSY (Figure S27, page S28).

Compound 12, Page S28	# of H	ppm	J (Hz)	Splitting
	1	6.72	2.7	d
	2	6.66	9.0, 2.7	dd
	3	7.28	9	d
	4	7.36	7.2	d
	5	7.21	7.2	t
	6	7.05	7.2	t
	7	7.79	8.7	d
	8	7.01	8.7, 7.5	dd
	9	6.65	7.5	d
	10	8.18	9.0	d
	11	7.32	9	d
	12	3.75		s

**Table S5:** Assignment of protons of compound **19** based 2D COSY (Figure S32, page S33).

Compound <b>19</b> , Page S32	# of H	ppm	J (Hz)	Splitting
	1	6.56	3.5	d
	2	6.52	3.5, 8.3	dd
	3	7.15	8.3	d
	4	7.39	7.3	d
	5	7.18	7.0	t
	6	7.05	6.5	t
	7	7.77	8.8	d
	8	6.97	8.8, 8.3	dd
	9	6.63	8.3	d
	10	8.29	9.0	d
	11	7.29	9.0	d

**Table S6:** Assignment of protons of **SNAFR-1** H<sub>2</sub>O adduct based 2D COSY (Figure S34, page S35).

<b>SNAFR-1</b> H <sub>2</sub> O adduct, Page S34	# of H	ppm	J (Hz)	Splitting
	1	6.51		s
	2	6.48	9.3	d
	3	7.17	9.3	d
	4	7.34	8.5	d
	5	7.19	8.0	t
	6	7.03	6.8	t
	7	7.76	8.3	d
	8	6.98	8.3, 7.0	dd
	9	6.62	7	d
	10	8.15	9.0	d
	11	7.29	9	d
	12	9.62		s
	13	6.74		s
	14	9.96		s