

Supplementary Materials: Synthesis of Catechol Derived Rosamine Dyes and Their Reactivity toward Biogenic Amines

Filipe Monteiro-Silva ^{1,†}, Carla Queirós ^{2,†}, Andreia Leite ², María Teresa Rodríguez ³, María José Rojo ³, Tomás Torroba ³, Rui C. Martins ¹, Ana M. G. Silva ^{2,*} and Maria Rangel ⁴

¹ Centre for Applied Photonics, INESC TEC, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal; filipe.m.silva@inesctec.pt (F.M.-S.);

rui.c.martins@inesctec.pt (R.C.M.)

² LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal; carla.queiros@fc.up.pt (C.Q.);

acleite@fc.up.pt (A.L.)

³ Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, España; mtrod@ubu.es (M.T.R.); mjrocam@ubu.es (M.J.R.); ttorroba@ubu.es (T.T.)

⁴ LAQV/REQUIMTE, Instituto de Ciências Biomédicas de Abel Salazar, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal; mrangel@icbas.up.pt

* Correspondence: ana.silva@fc.up.pt

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed: Tel: (+351)220402585 Fax: (+351)220402659; email: ana.silva@fc.up.pt

Contents

NMR spectrum of 2,3-dibenzyloxybenzaldehyde and 3,4-dibenzyloxybenzaldehyde	2
NMR spectra of rosamine 1	3
NMR spectra of rosamine 2	6
NMR spectra of rosamine 3	8
NMR spectra of rosamine 4	11
MS spectra of 1, 2, 3 and 4	13
The influence of pH variation in the fluorescence intensity of rosamine 4.	15
Detection study of rosamine 4 with different biogenic amines in solution (preliminary study)	16
Detection study of rosamine 4 with different amines in solution (CH ₃ CN)	18
Detection study of rosamine 4 with different biogenic amines in gas phase	19
NMR spectra of aminopyronin 5	20
¹ H NMR spectrum comparison between rosamine 4 and aminopyronin 5	21
NMR spectrum of aminopyronin 6a	22
NMR spectrum of aminopyronin 7a	22
NMR spectrum of aminopyronin 7b	23
MS spectra of 5, 6a, 7a and 7b	23

NMR spectrum of 2,3-dibenzoyloxybenzaldehyde and 3,4-dibenzoyloxybenzaldehyde

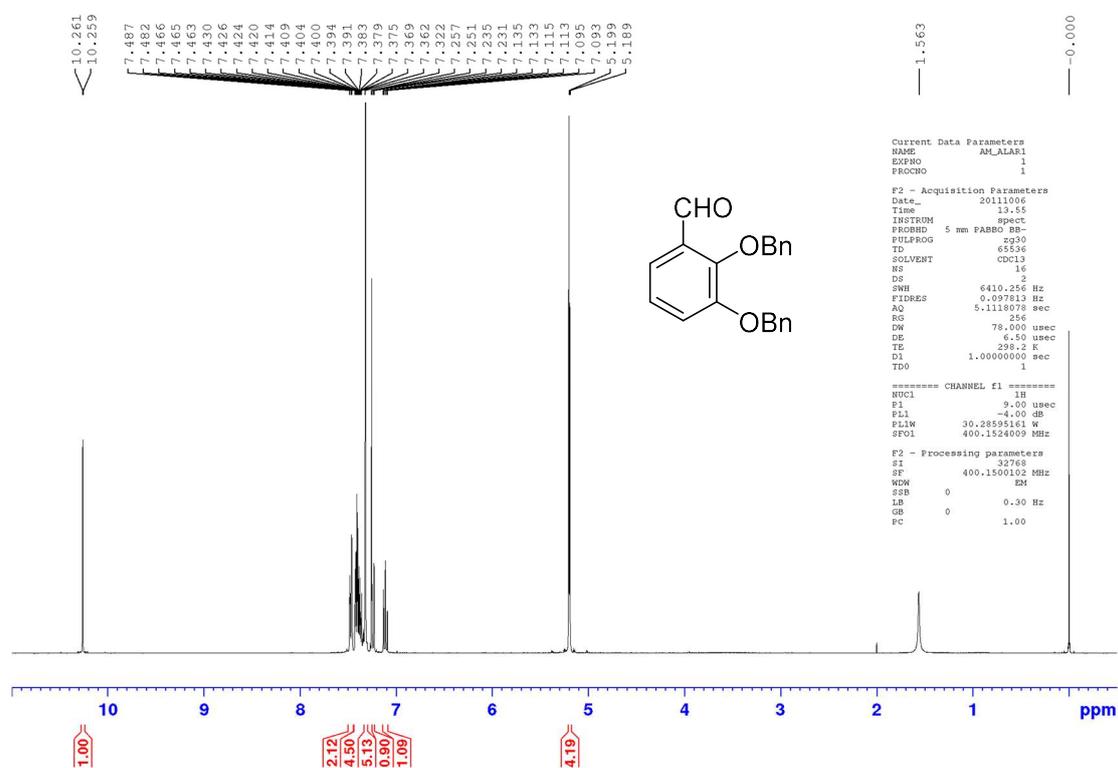


Figure S1. ¹H NMR spectrum (400.15 MHz, CDCl₃) of 2,3-dibenzoyloxybenzaldehyde.

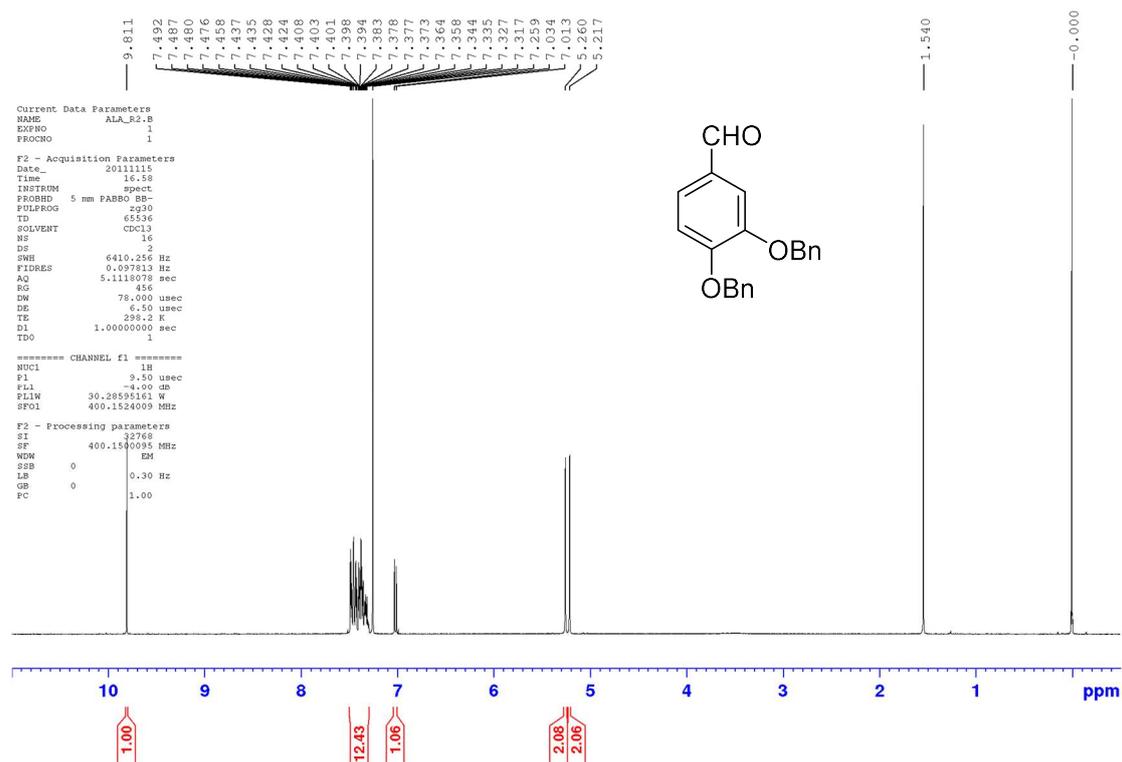


Figure S2. ¹H NMR spectrum (400.15 MHz, CDCl₃) of 3,4-dibenzyloxybenzaldehyde.

NMR spectra of rosamine 1

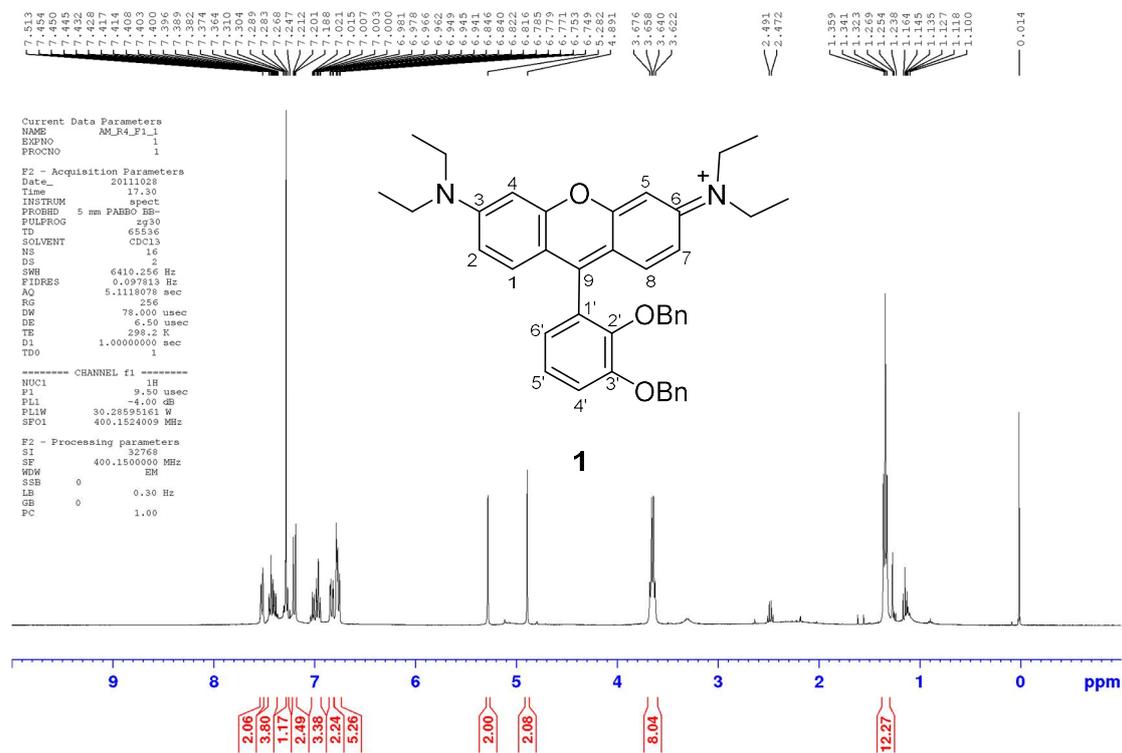


Figure S3. ¹H NMR spectrum (400.15 MHz, CDCl₃) of 1.

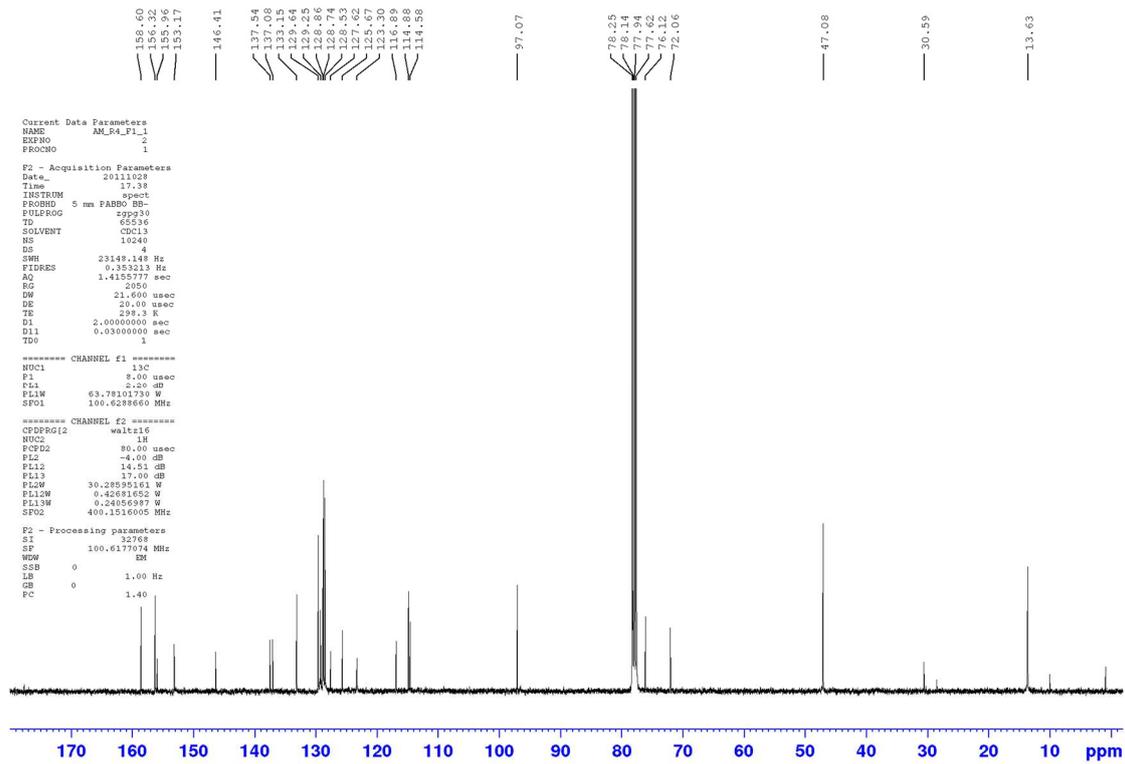


Figure S4. ^{13}C NMR spectrum (100.63 MHz, CDCl_3) of 1.

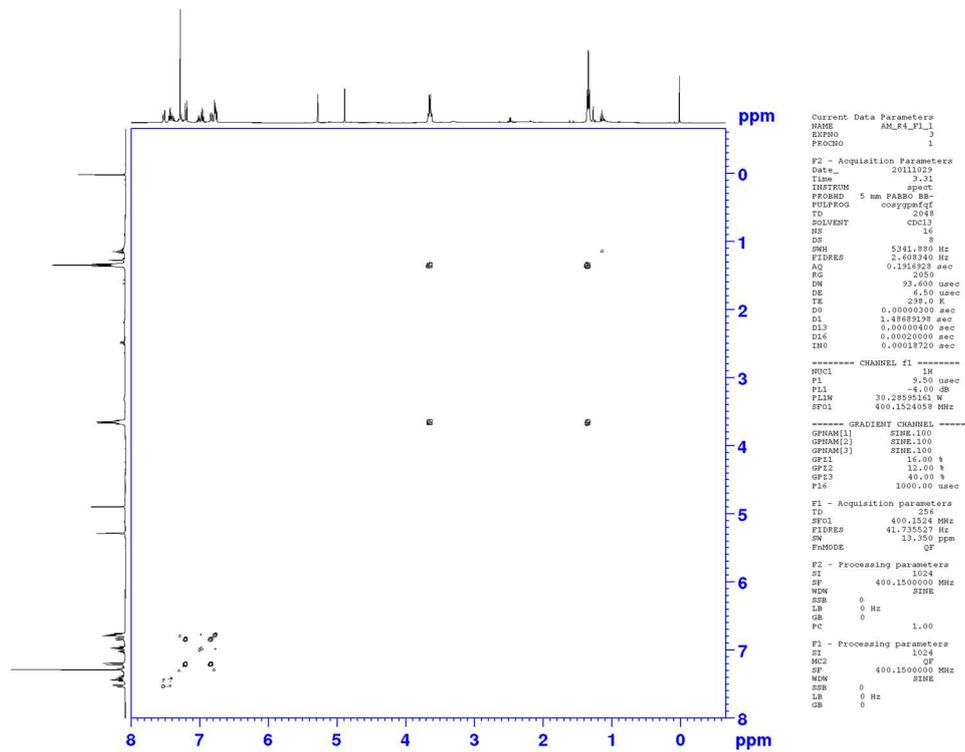
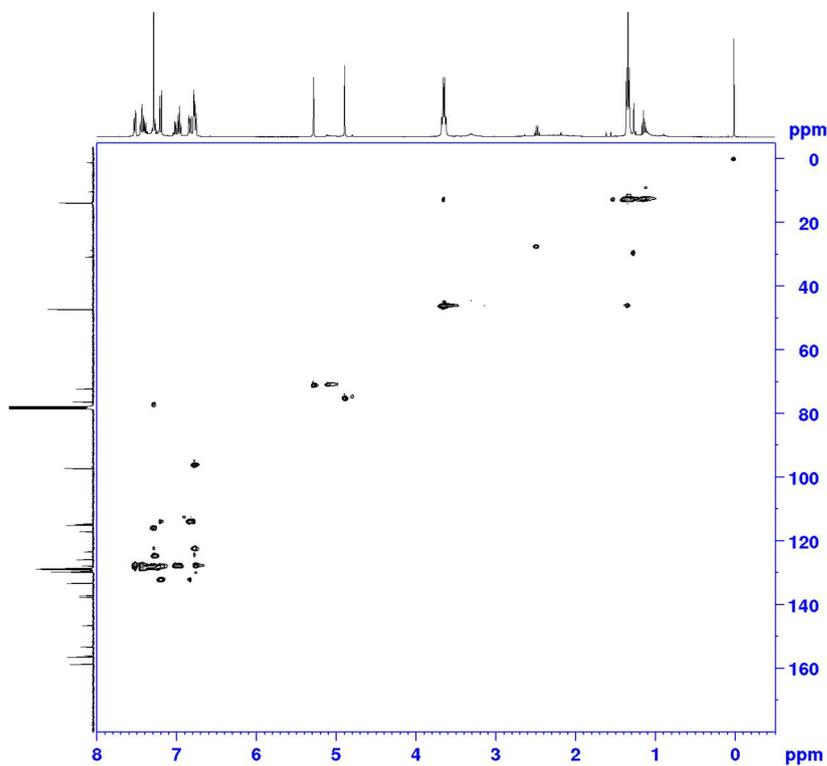


Figure S5. COSY spectrum of 1.



```

Current Data Parameters
NAME      AM_R4_FL_1
EXPNO    4
PROCNO    1

F2 - Acquisition Parameters
Date_    2011029
Time     5.28
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  hmcqzgpg2
ID       3048
SOLVENT  CDCl3
NS       24
DS       4
SWH      5351.450 Hz
FIDRES   2.402778 Hz
AQ       0.1521264 sec
RG       2550
RW       0.1833900 usec
DE       6.50 usec
TE       298.2 K
CHST2    145.0000000
D0       0.0000000 sec
D1       1.5000000 sec
D2       0.00072414 sec
D3       0.0000000 sec
D4       0.0000000 sec
D5       0.0000000 sec
D6       0.00084207 sec
IN0      0.00002485 sec
SFOFFS   0.0000000

***** CHANNEL f1 *****
NUC1     13C
P1       9.50 usec
PC       12.00 usec
PR       2.50 usec
PL1     -4.00 dB
PL1W    30.28595141 W
SFO1    400.1524000 MHz

***** CHANNEL f2 *****
CPDPRG2  913C
NUC2     13C
P2       8.00 usec
PC       16.00 usec
PR       80.00 usec
PL2     -2.20 dB
PL2W    63.78101730 W
SFO2    100.6273567 MHz

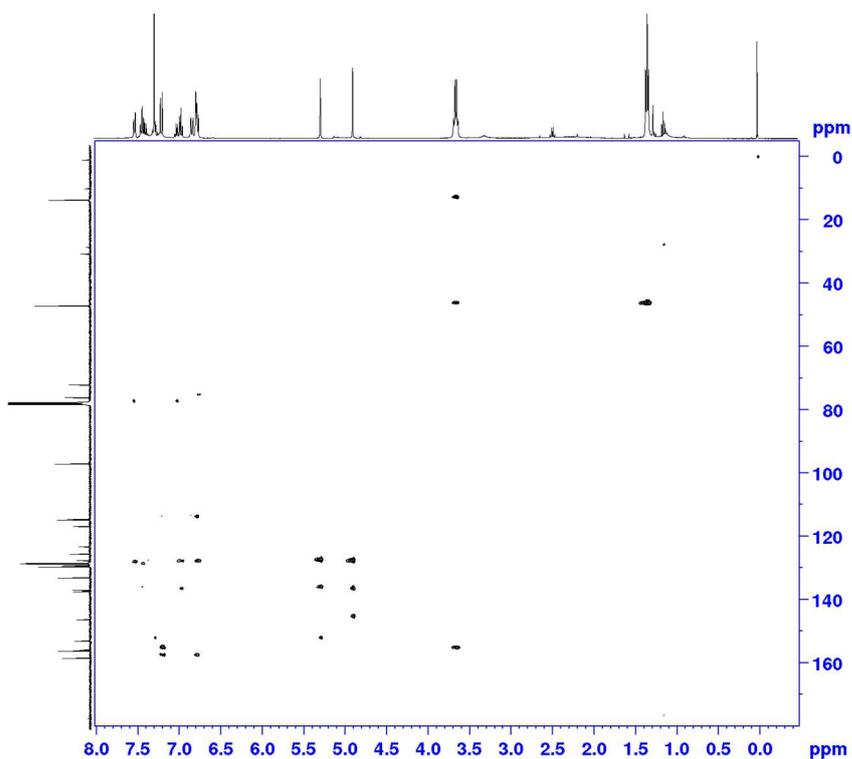
***** GRADIENT CHANNEL *****
GPM1[1]  SINE.100
GPM1[2]  SINE.100
GPM1[3]  SINE.100
GPM1[4]  SINE.100
GPE1     80.00 %
GPE2     20.00 %
GPE3     11.00 %
GPE4     -5.00 %
P16      1000.00 usec
P17      600.00 usec

F1 - Acquisition parameters
ID       256
SFO1    100.6274 MHz
FIDRES   187.230400 Hz
SW       200.000 ppm
F2 - Processing parameters
SI       1024
SF       400.1500000 MHz
WDW      QSI
SSB      2
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       1024
MC2      sub-sampling
SF       100.617780 MHz
WDW      QSI
SSB      2
LB       0 Hz
GB       0

```

Figure S6. HSQC spectrum of 1.



```

Current Data Parameters
NAME      AM_R4_FL_1
EXPNO    4
PROCNO    1

F2 - Acquisition Parameters
Date_    2011029
Time     11.35
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  hmcqzgpg2
ID       3074
SOLVENT  CDCl3
NS       32
DS       4
SWH      5197.505 Hz
FIDRES   1.268292 Hz
AQ       0.1941932 sec
RG       2050
RW       0.2000000 usec
DE       6.50 usec
TE       298.2 K
CHST2    145.0000000
D0       0.0000000 sec
D1       1.5000000 sec
D2       0.00084828 sec
D3       0.0000000 sec
D4       0.00944485 sec
D5       0.0000000 sec
D6       0.00002160 sec
IN0      0.00002160 sec

***** CHANNEL f1 *****
NUC1     13C
P1       9.50 usec
PC       12.00 usec
PR       2.50 usec
PL1     -4.00 dB
PL1W    30.28595141 W
SFO1    400.1524000 MHz

***** CHANNEL f2 *****
NUC2     13C
P2       8.00 usec
PC       16.00 usec
PR       80.00 usec
PL2     -2.20 dB
PL2W    63.78101730 W
SFO2    100.6273567 MHz

***** GRADIENT CHANNEL *****
GPM1[1]  SINE.100
GPM1[2]  SINE.100
GPM1[3]  SINE.100
GPE1     50.00 %
GPE2     30.00 %
GPE3     40.00 %
GPE4     1000.00 usec

F1 - Acquisition parameters
ID       320
SFO1    100.62800 MHz
FIDRES   144.653992 Hz
SW       200.000 ppm
F2 - Processing parameters
SI       1024
SF       400.1500000 MHz
WDW      SINE
SSB      0
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       1024
MC2      QF
SF       100.617780 MHz
WDW      SINE
SSB      0
LB       0 Hz
GB       0

```

Figure S7. HMBC spectrum of 1.

NMR spectra of rosamine 2

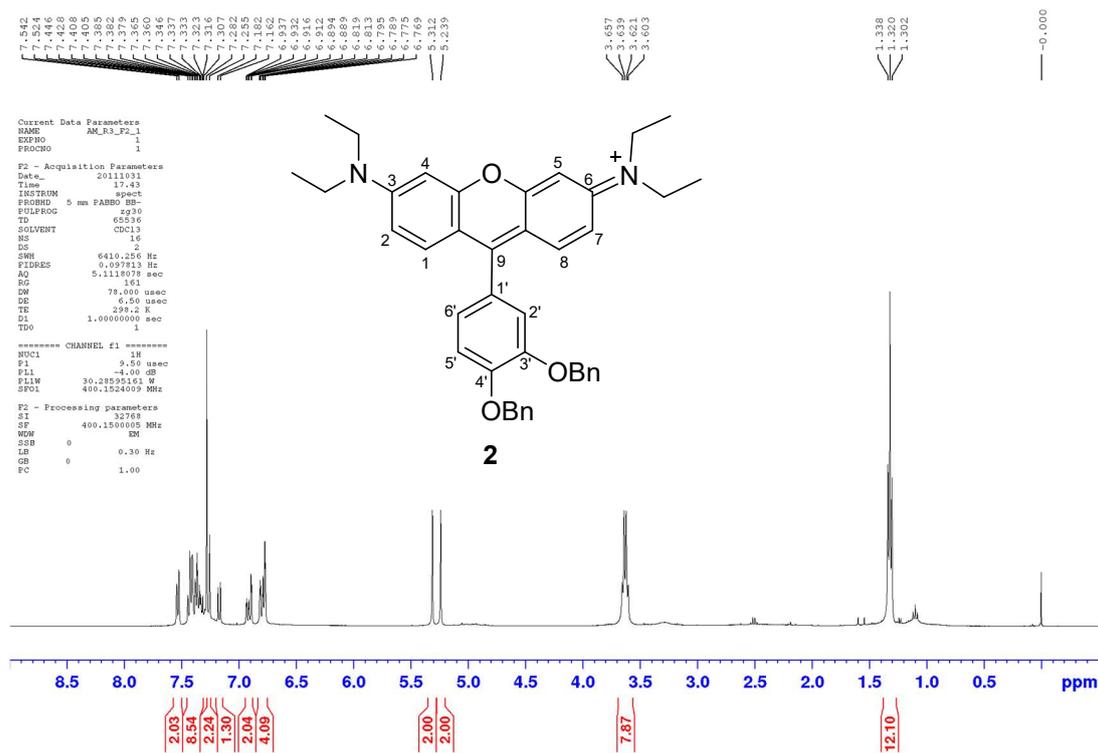


Figure S8. ¹H NMR spectrum (400.15 MHz, CDCl₃) of **2**.

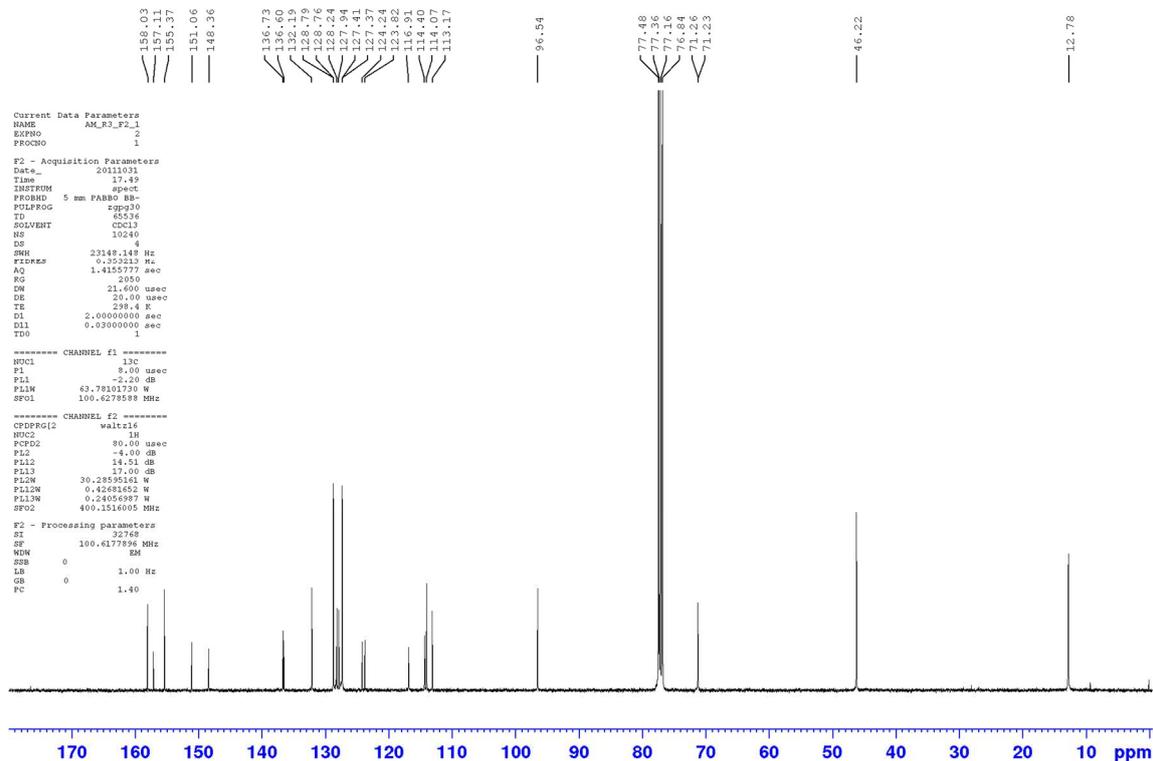


Figure S9. ¹³C NMR spectrum (100.63 MHz, CDCl₃) of **2**.

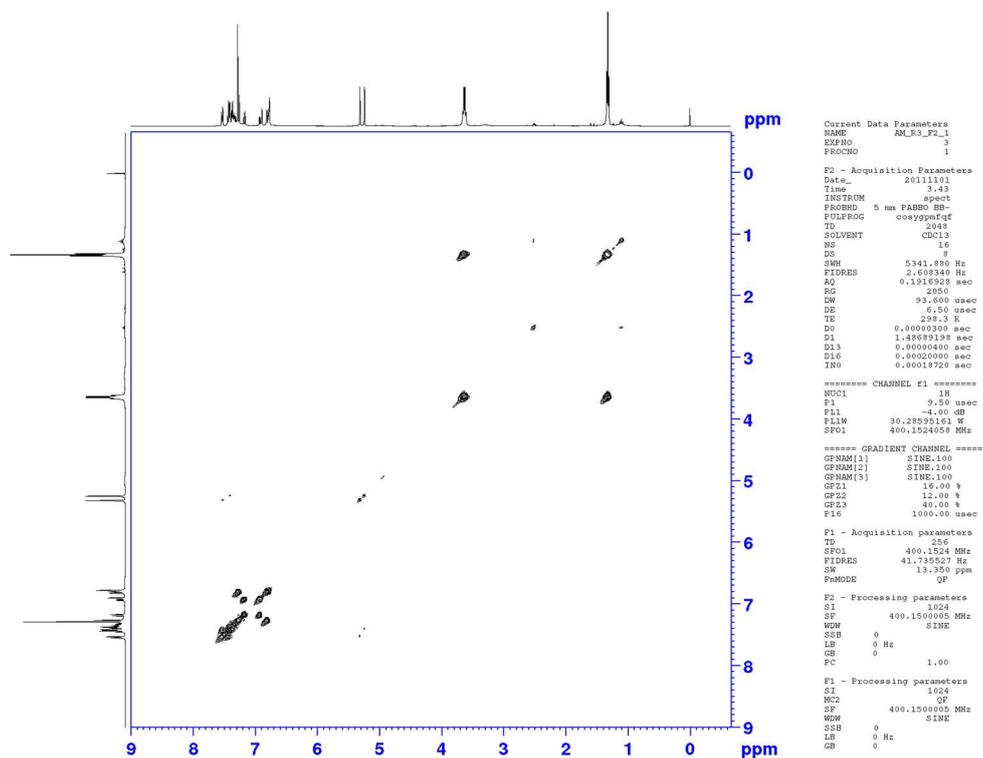


Figure S10. COSY spectrum of 2.

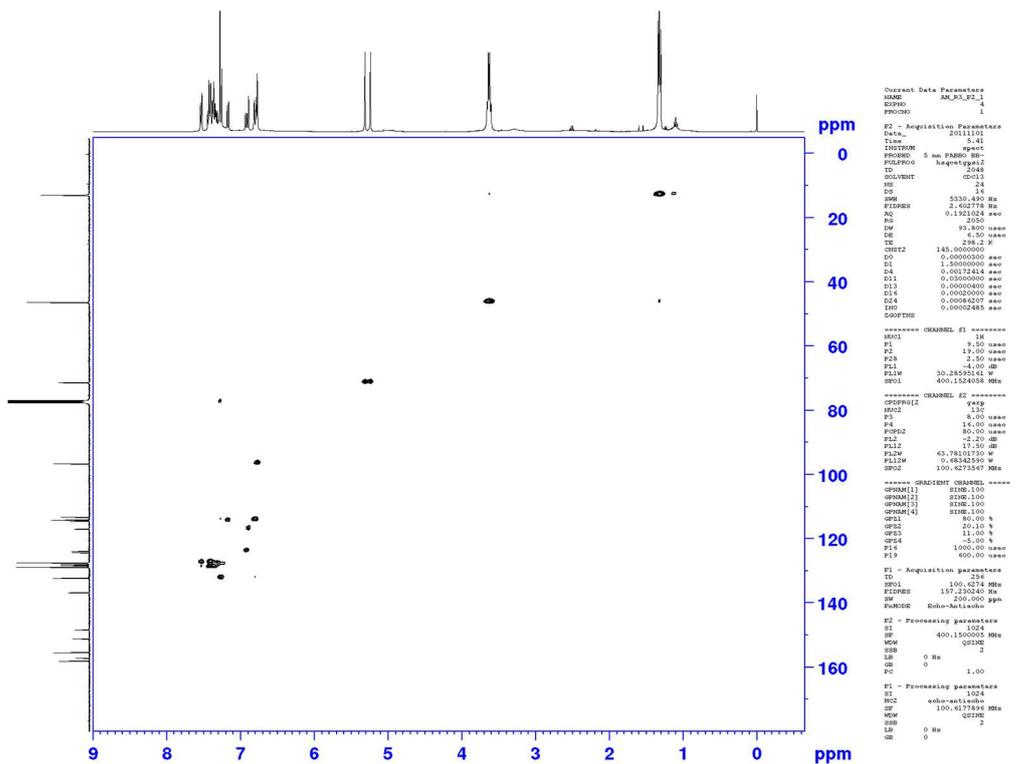


Figure S11. HSQC spectrum of 2.

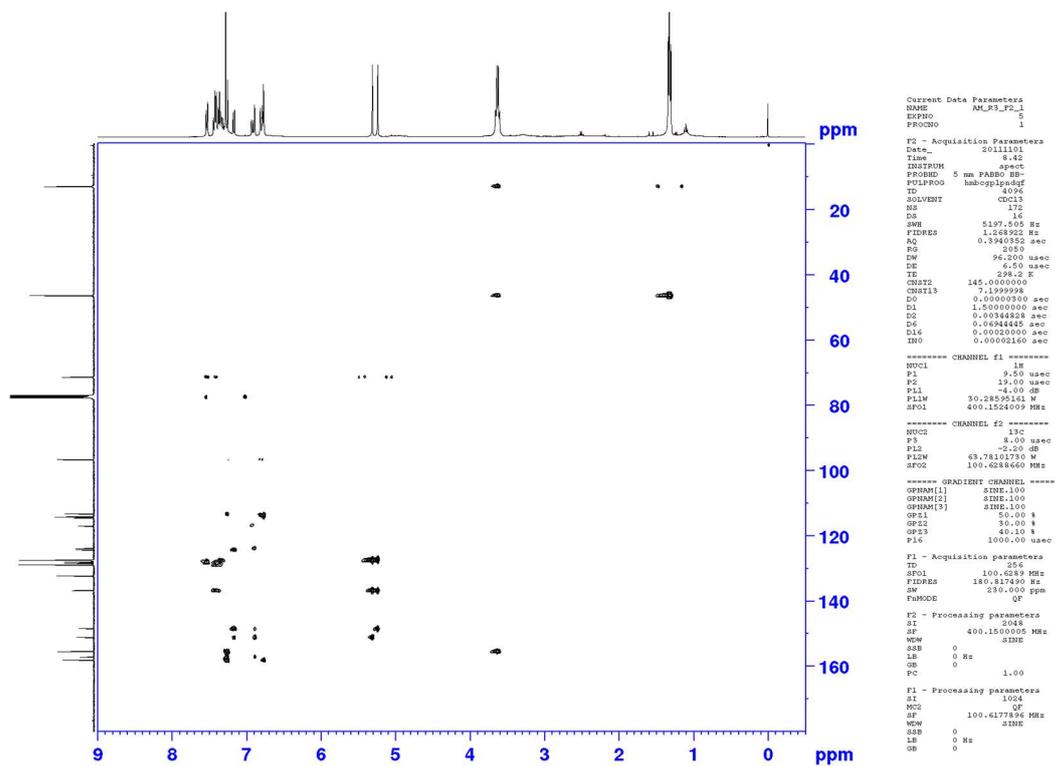


Figure S12. HMBC spectrum of 2.

NMR spectra of rosamine 3

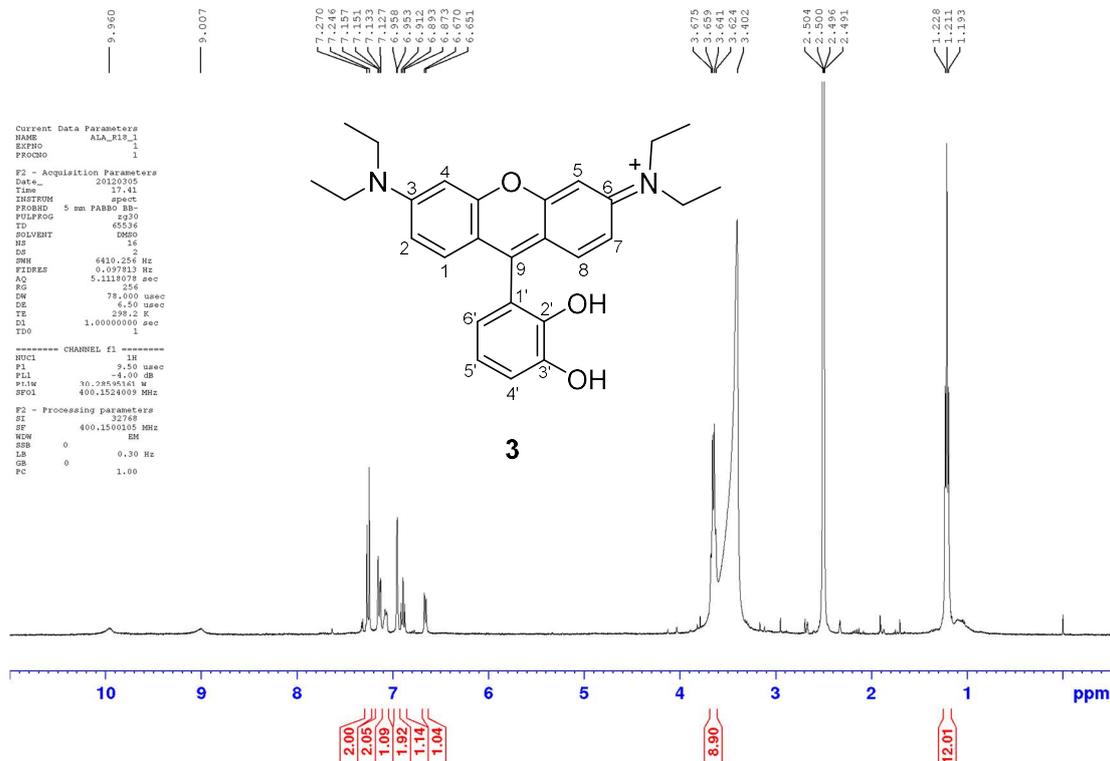


Figure S13. ¹H NMR spectrum (400.15 MHz, DMSO-d₆) of 3.

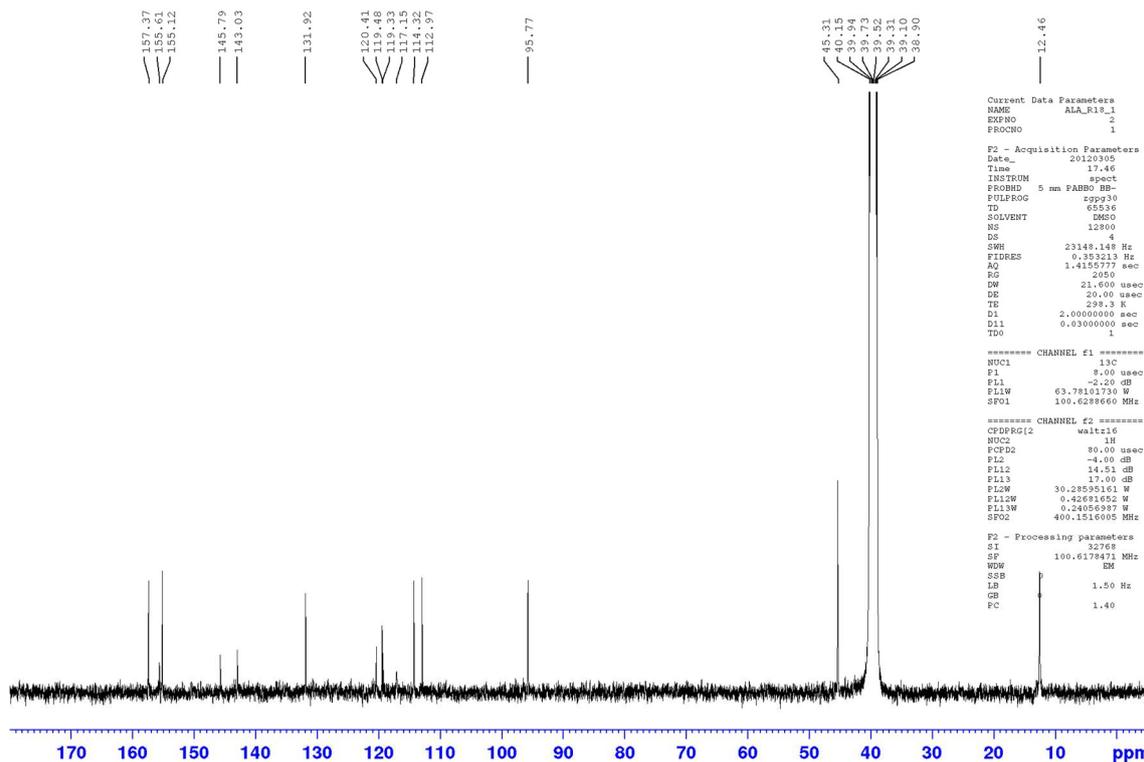


Figure S14. ^{13}C NMR spectrum (100.63 MHz, DMSO- d_6) of **3**.

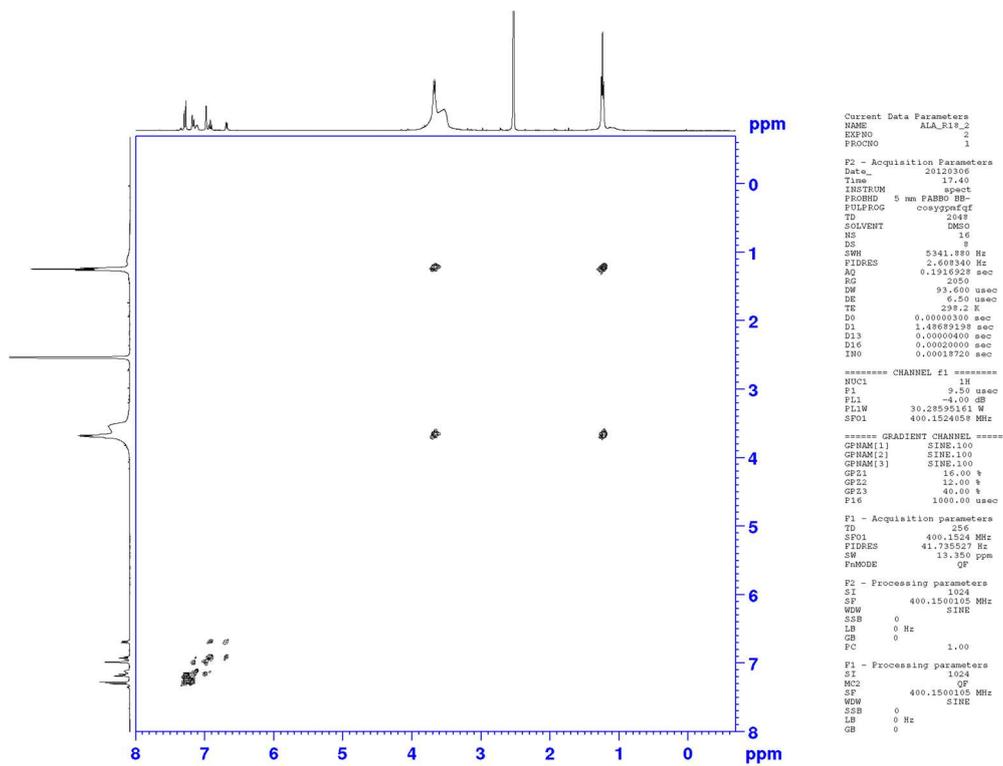


Figure S15. COSY spectrum of **3**.

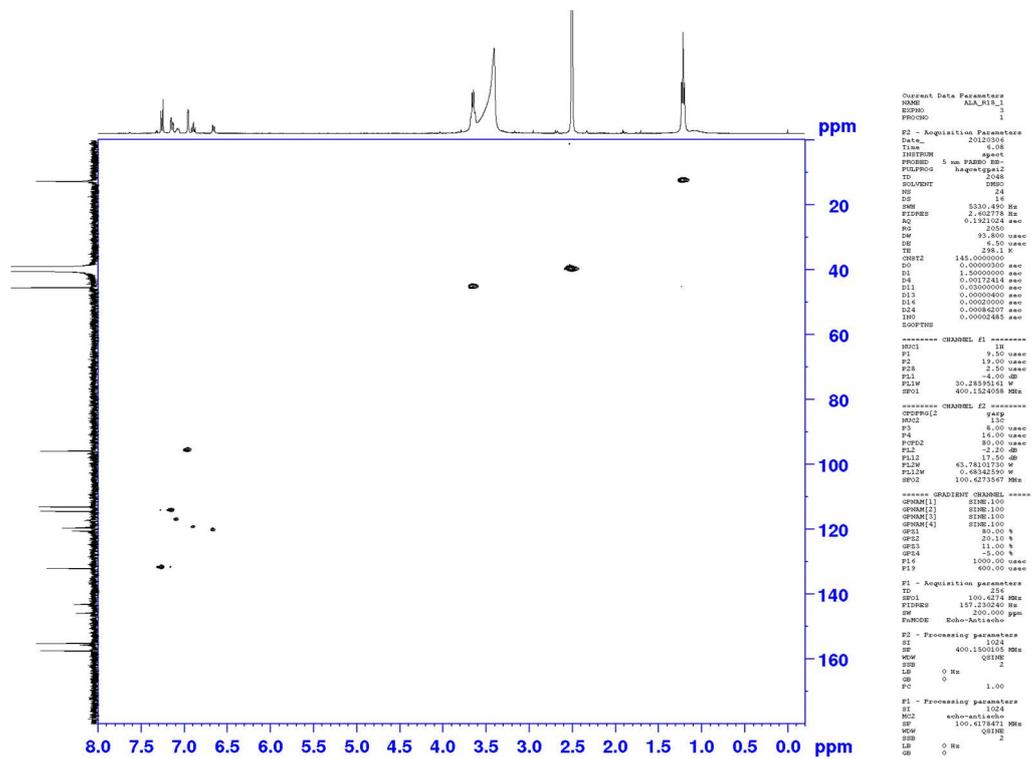


Figure S16. HSQC spectrum of 3.

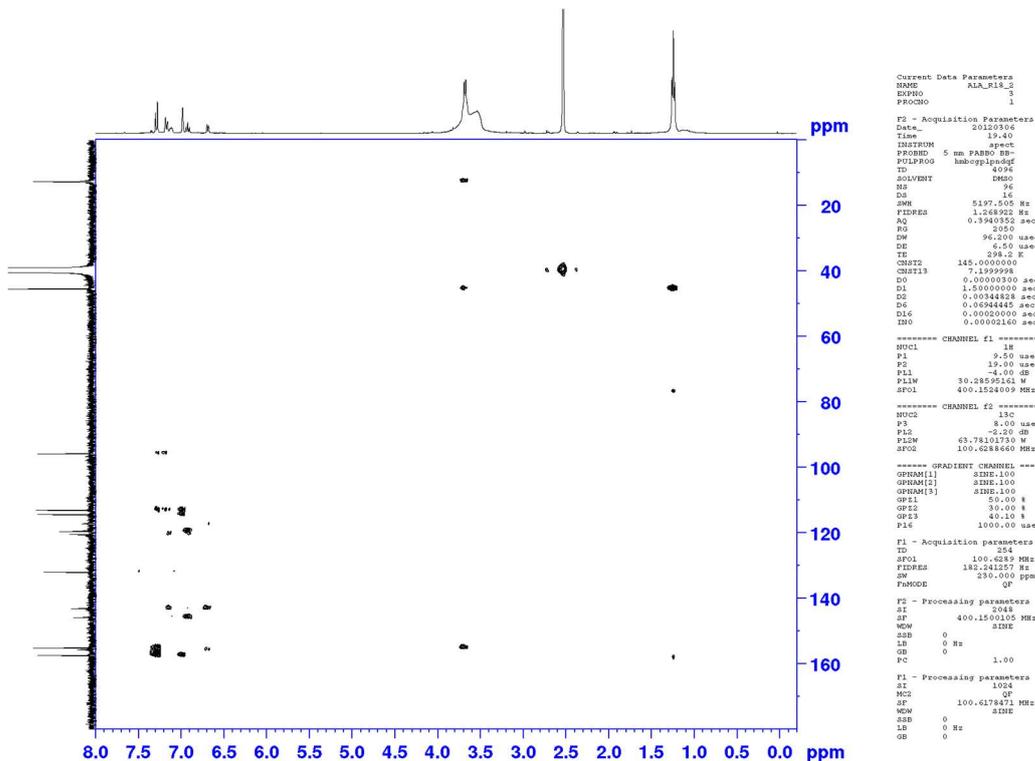


Figure S17. HMBC spectrum of 3.

NMR spectra of rosamine 4

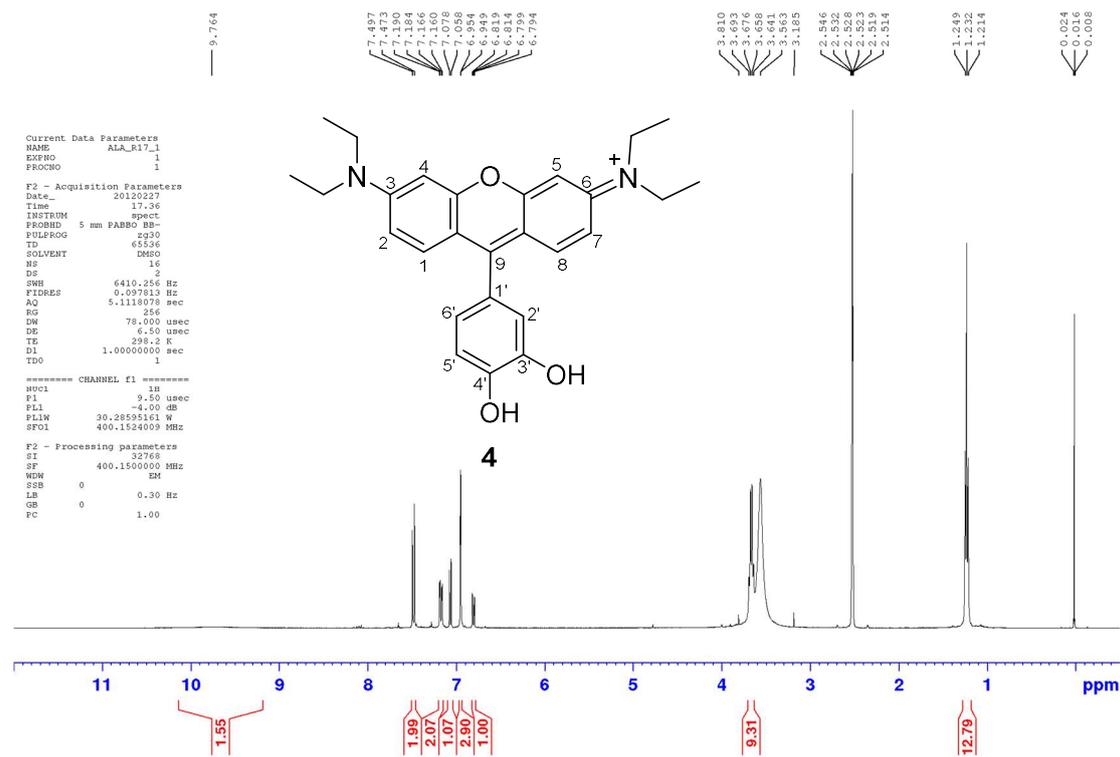


Figure S18. ¹H NMR spectrum (400.15 MHz, DMSO-d₆) of 4.

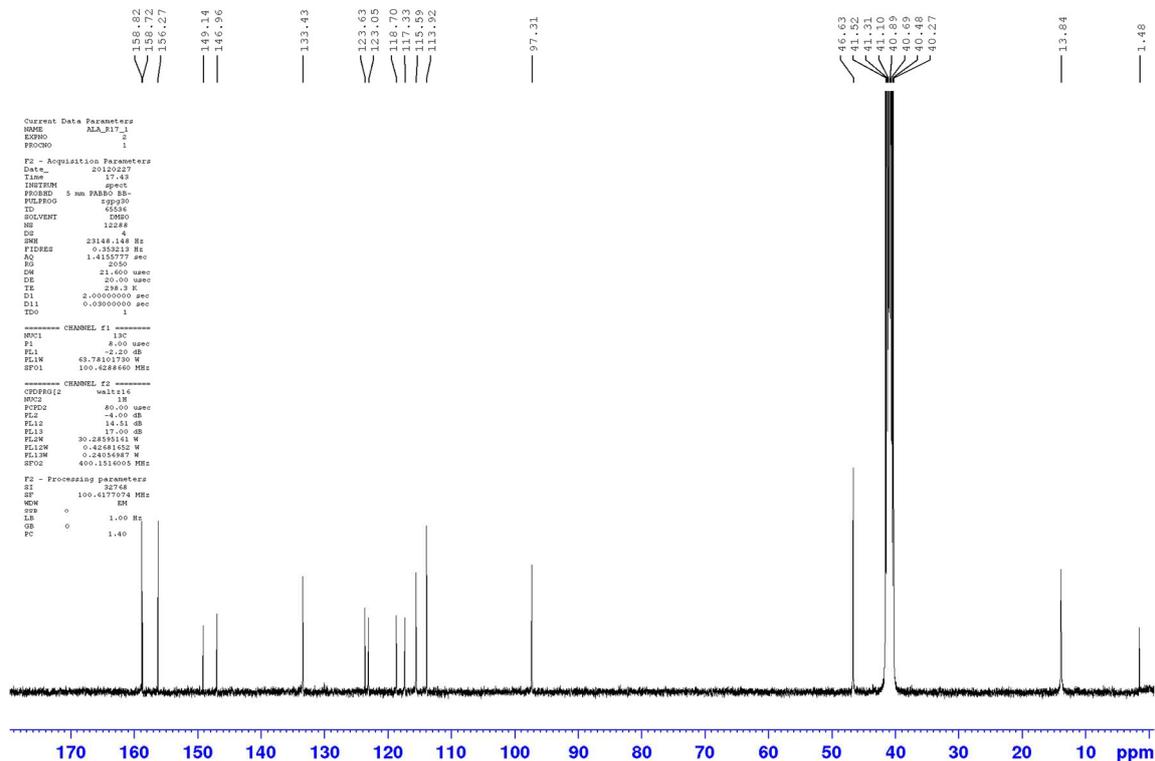


Figure S19. ¹³C NMR spectrum (100.63 MHz, DMSO-d₆) of 4.

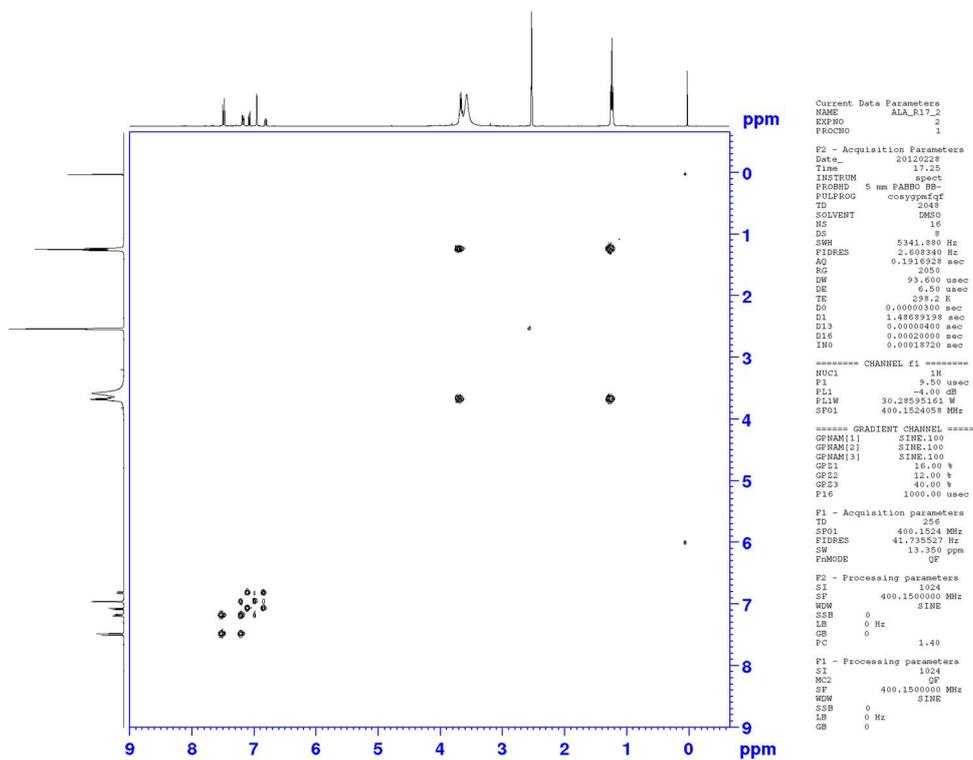


Figure S20. COSY spectrum of 4.

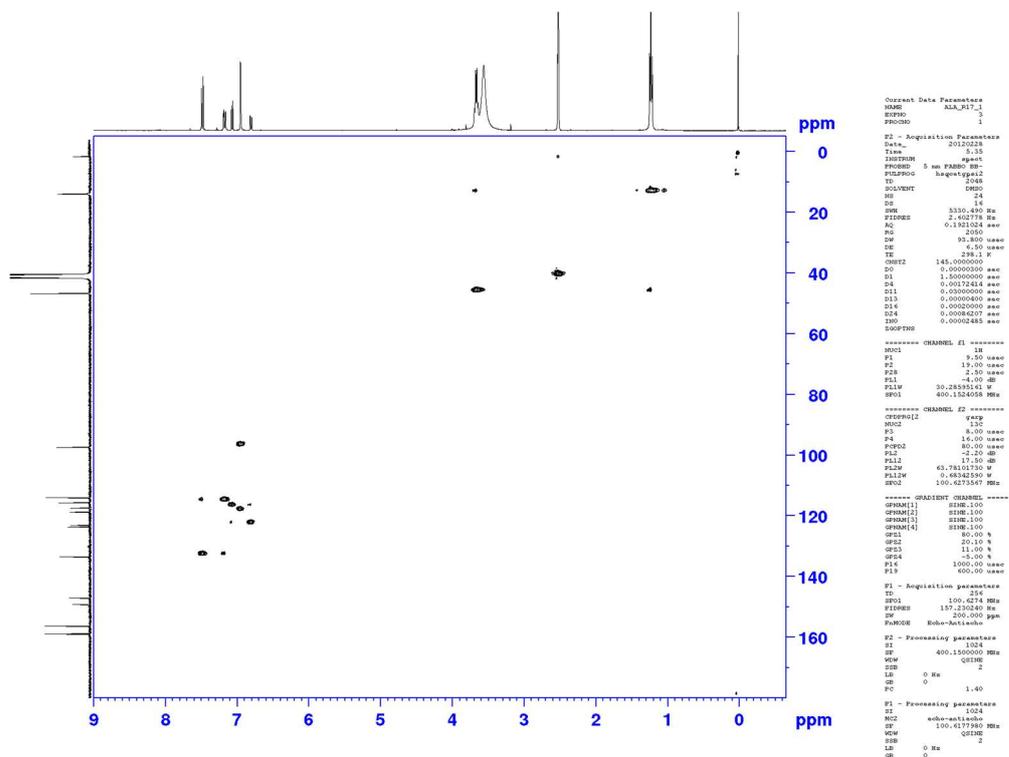


Figure S21. HSQC spectrum of 4.

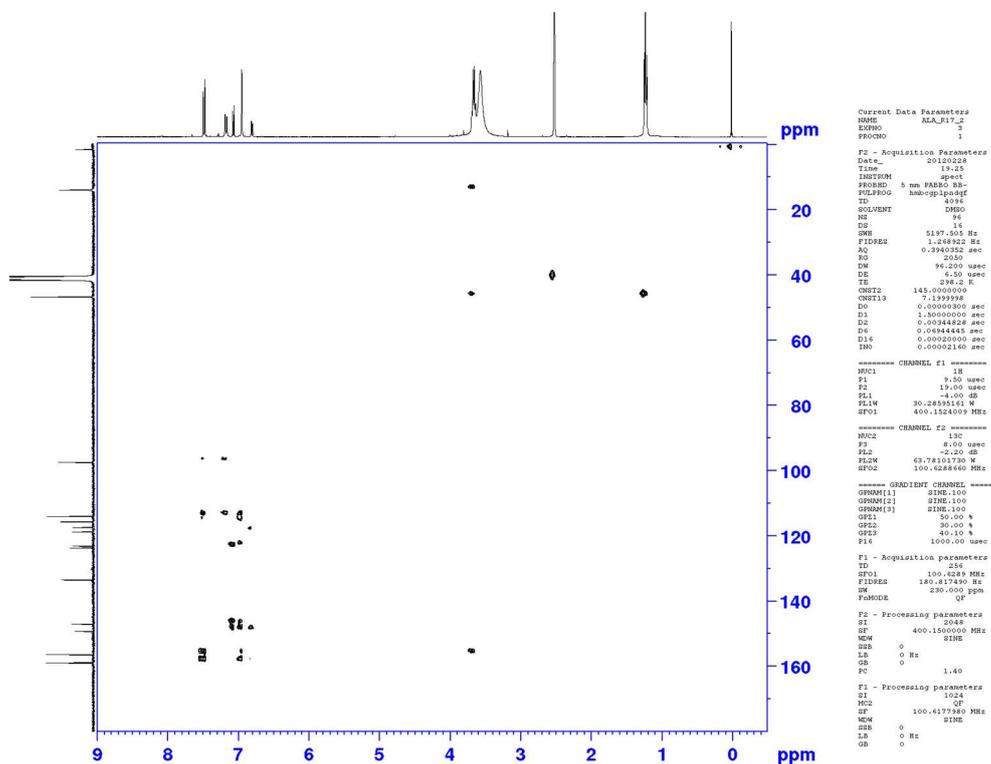


Figure S22. HMBC spectrum of 4.

MS spectra of 1, 2, 3 and 4

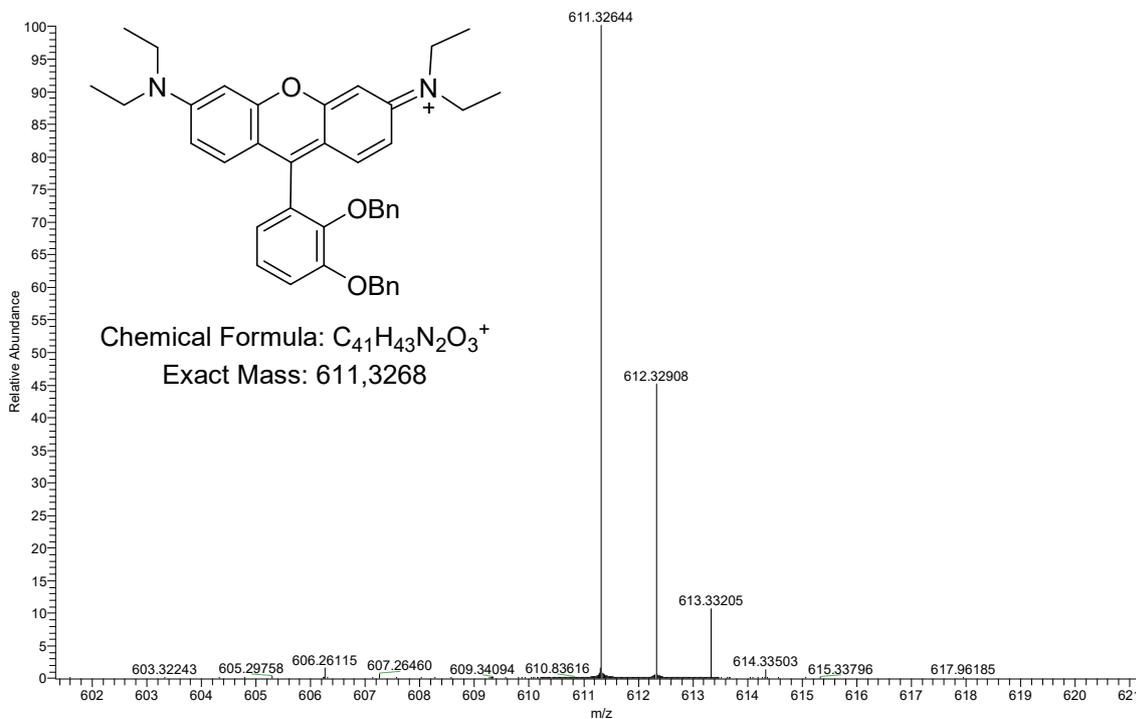


Figure S23. MS spectrum of 1

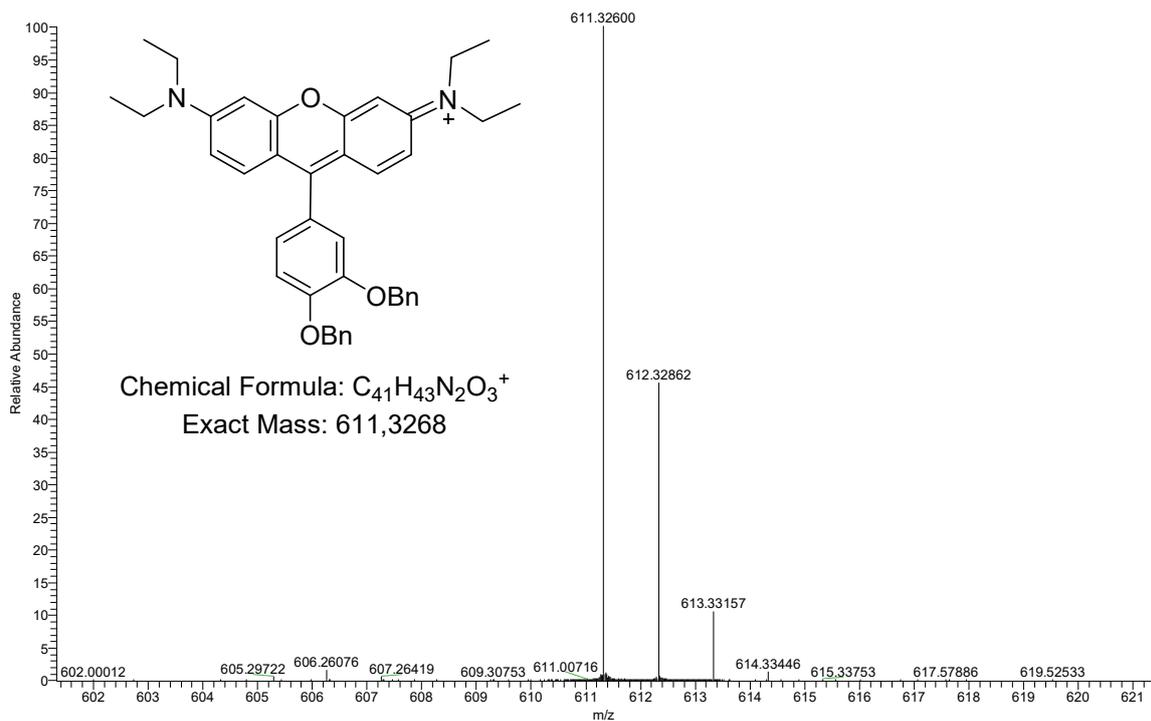


Figure S24. MS spectrum of 2

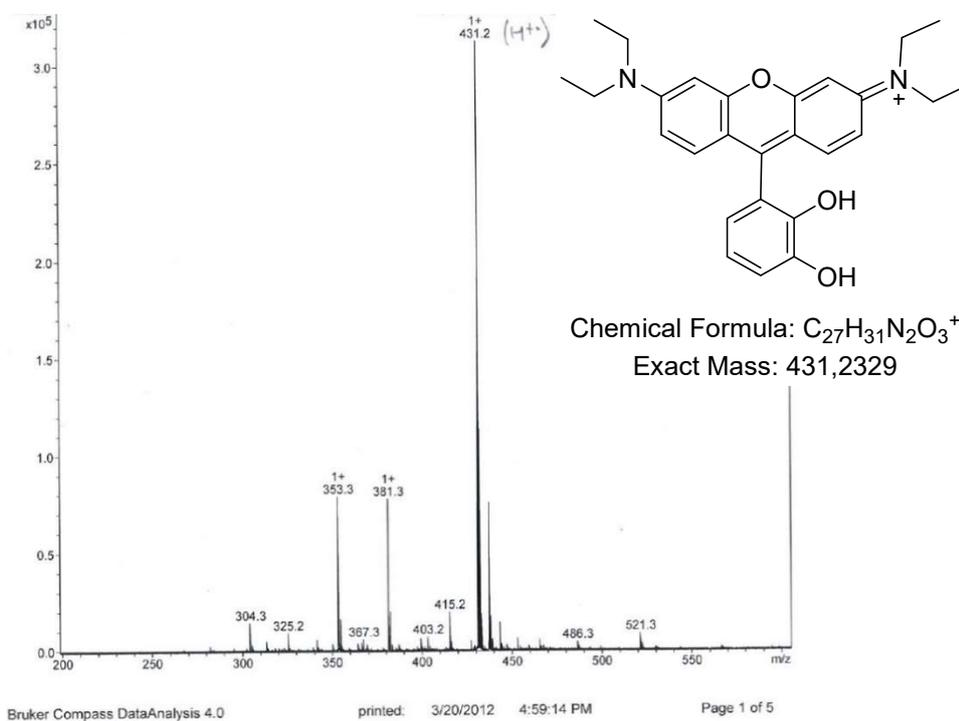
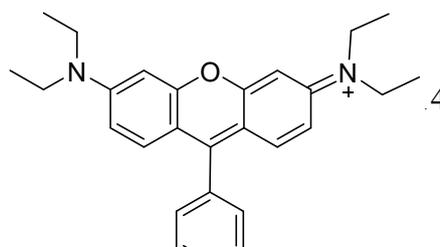


Figure S25. MS spectrum of 3



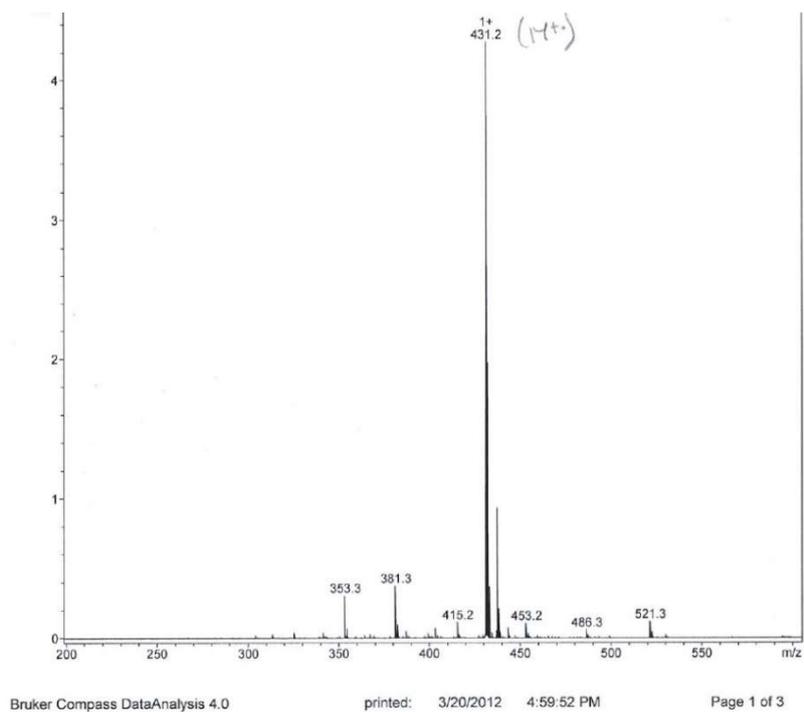


Figure S26. MS spectrum of 4

The influence of pH variation in the fluorescence intensity of rosamine 4.

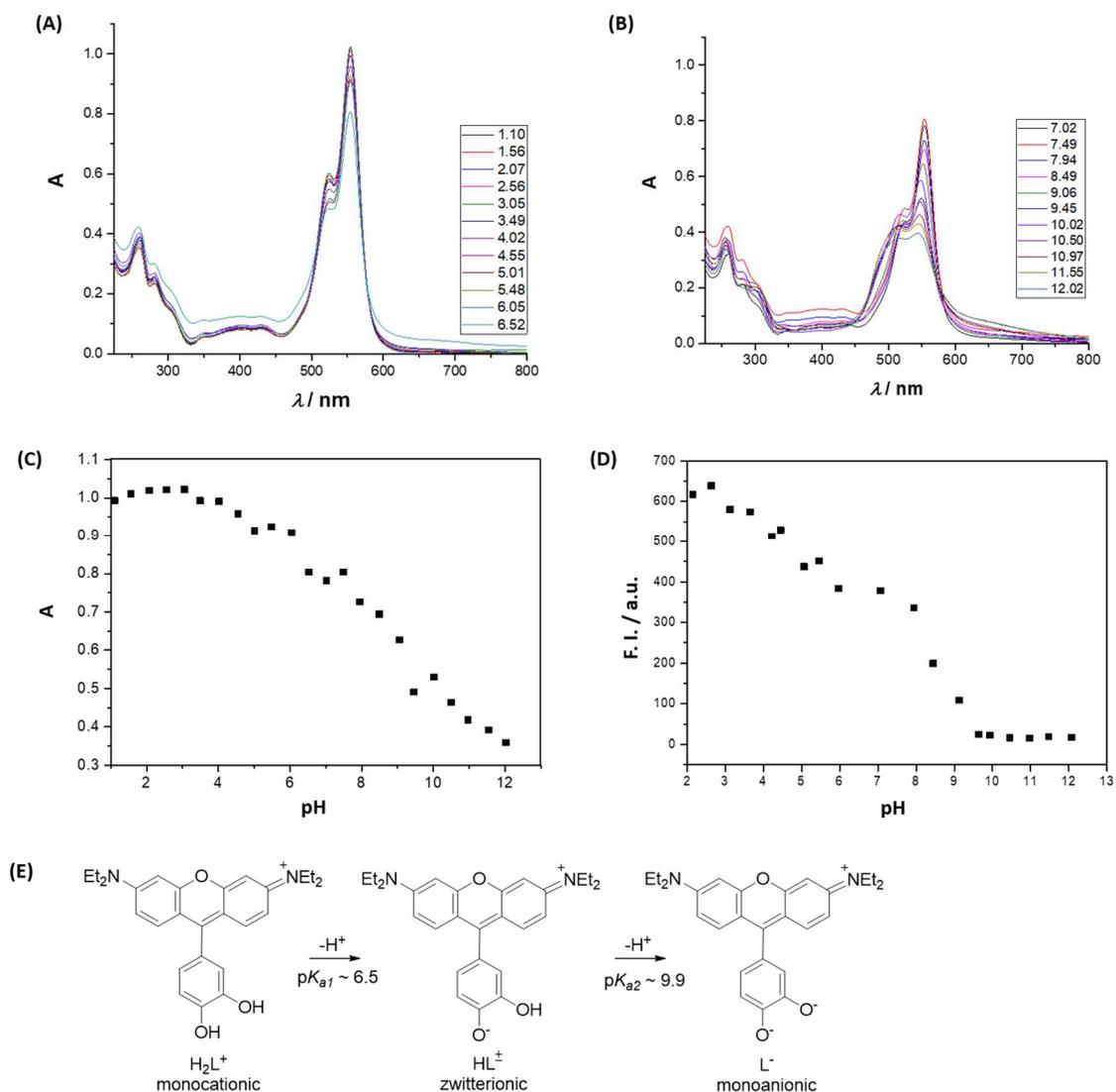


Figure S27. The influence of pH variation in the fluorescence intensity of rosamine 4. A – Absorption spectra for pH < 7; B – Absorption spectra for pH ≥ 7); C – Graphical representation of the pH in function of the maximum in absorbance; D – Graphical representation of the pH as a function of the maximum in fluorescence intensity; E – Structures and pK_a 's of rosamine 4 deprotonation.

Detection study of rosamine 4 with different biogenic amines in solution (preliminary study)

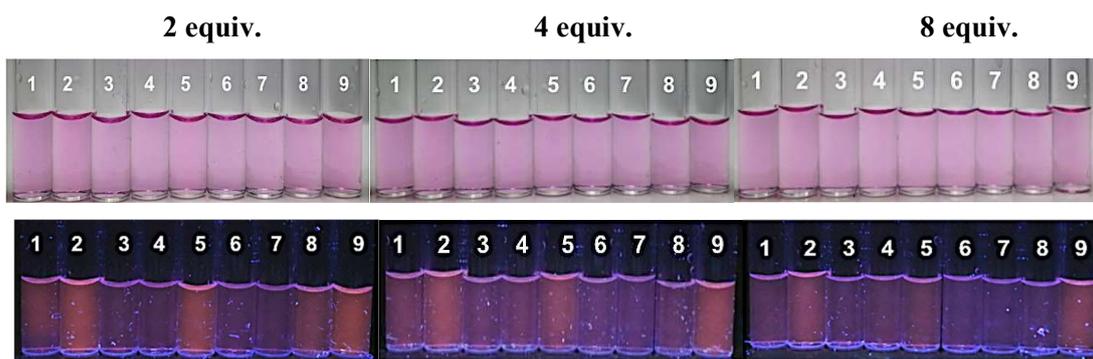


Figure S28. Samples with 2, 4 and 8 equiv. of 1-histamine, 2-tyramine, 3-cadaverine, 4-putrescine, 5-phenylethylamine, 6-spermidine, 7-spermine, 8-butylamine, 9- rosamine 4, observed under visible (top) and UV light (bottom).

Detection study of rosamine 4 with different amines in solution (CH₃CN)

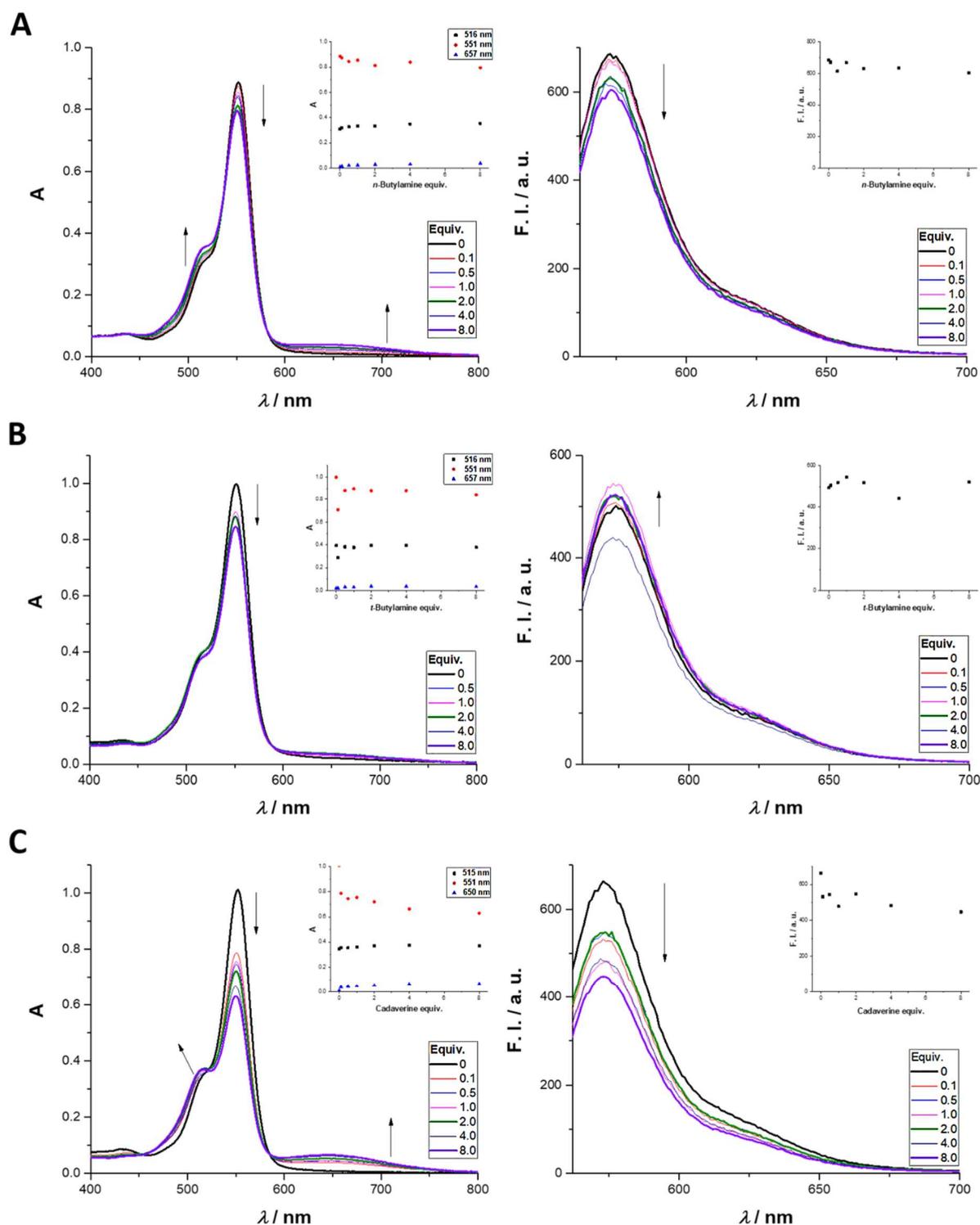


Figure S29. Absorption (left) and emission (right) spectra of **4** upon addition (0 – 8 equiv.) of *n*-butylamine (A), *t*-butylamine (B) and cadaverine (C) in CH₃CN (the inset graphs represent the variation in absorbance (right) and fluorescence intensity (left) for the wavelengths that present more variation in intensity. $|\mathbf{4}| = 35 \mu\text{M}$ and $\lambda_{\text{exc}} = 551 \text{ nm}$).

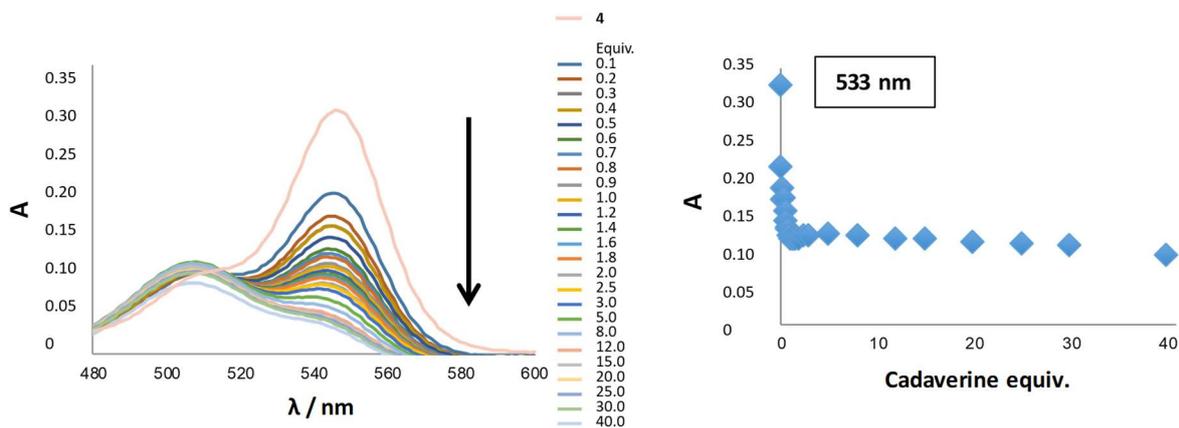


Figure S30. Absorption (left) spectrum of **4** upon addition (0.1–40 equiv.) of cadaverine in CH₃CN and graph representing the variation in absorbance (right) intensity at 533 nm [**4**] = 5 μM.

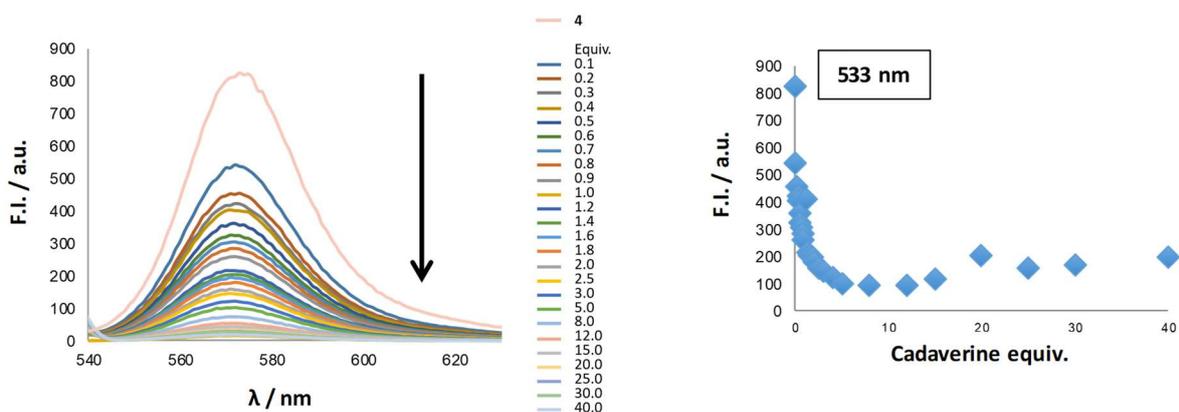


Figure S31. Emission (left) spectrum of **4** upon addition (0.1–40 equiv.) of cadaverine in CH₃CN and graph representing the variation in emission (right) intensity [**4**] = 5 μM and λ_{exc} = 533 nm.

Detection study of rosamine 4 with different biogenic amines in gas phase



Figure S32. Commercial biogenic amine samples subjected to heat

NMR spectra of aminopyronin 5

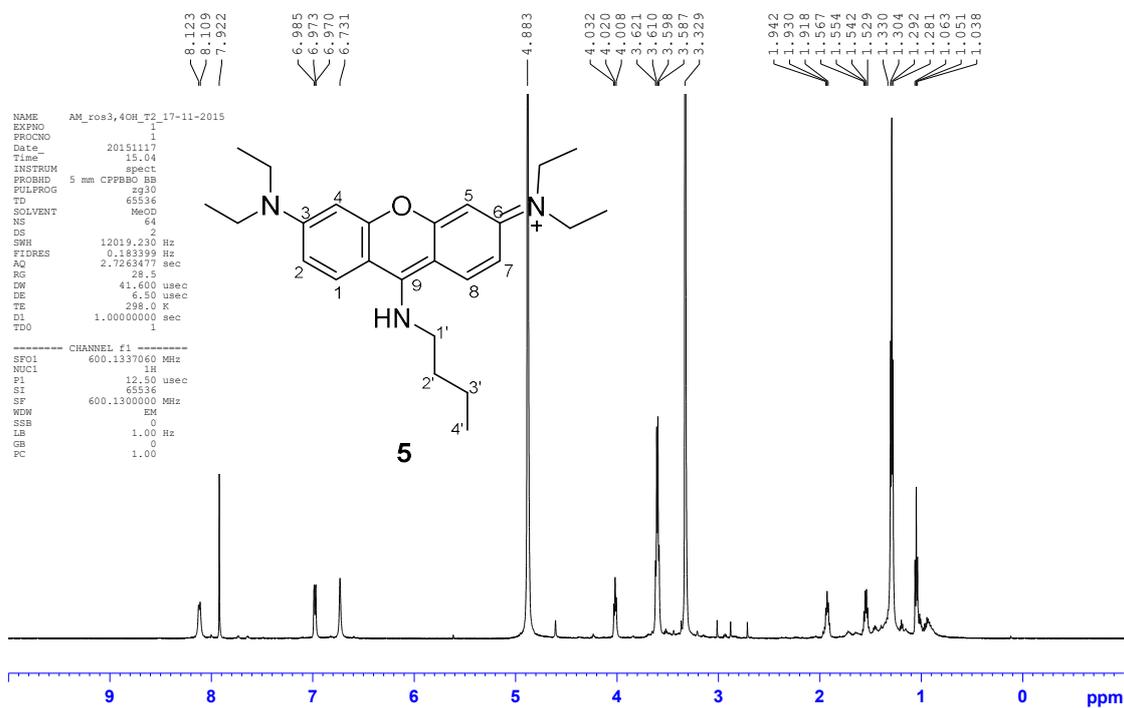


Figure S33. ¹H NMR spectrum (600.13 MHz, MeOD-d₄) of 5.

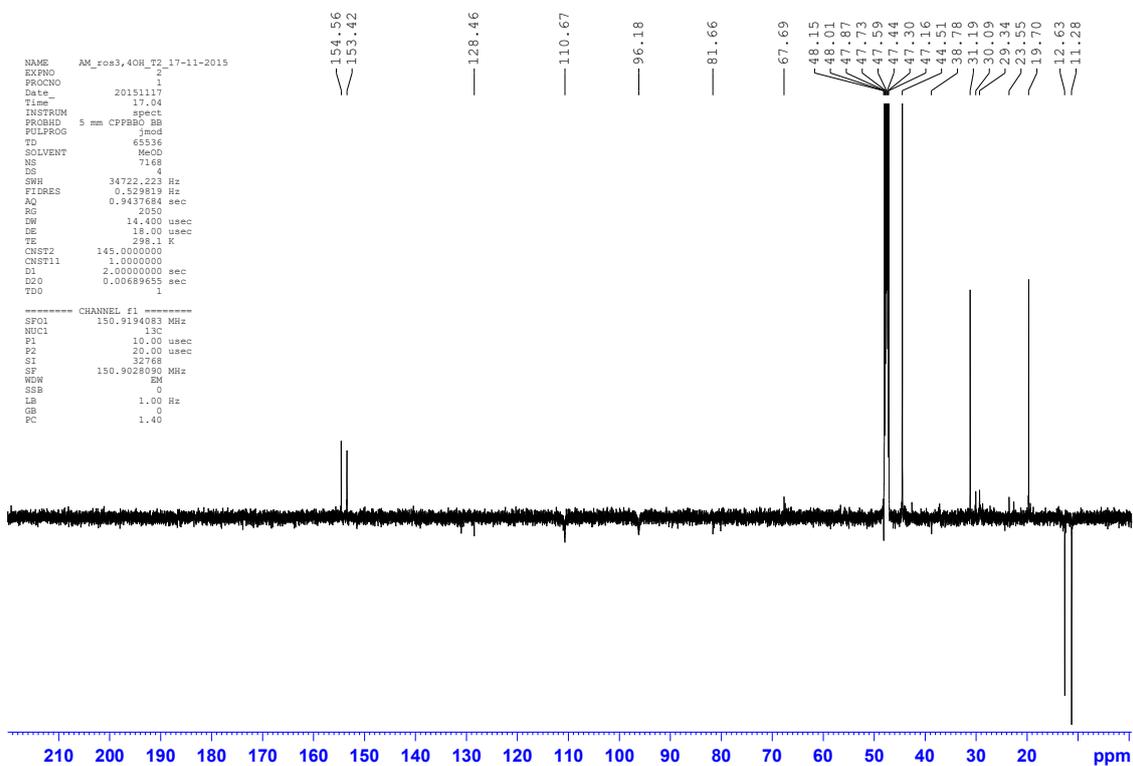


Figure S34. APT spectrum (150.90 MHz, MeOD-d₄) of 5.

¹H NMR spectrum comparison between rosamine 4 and aminopyronin 5

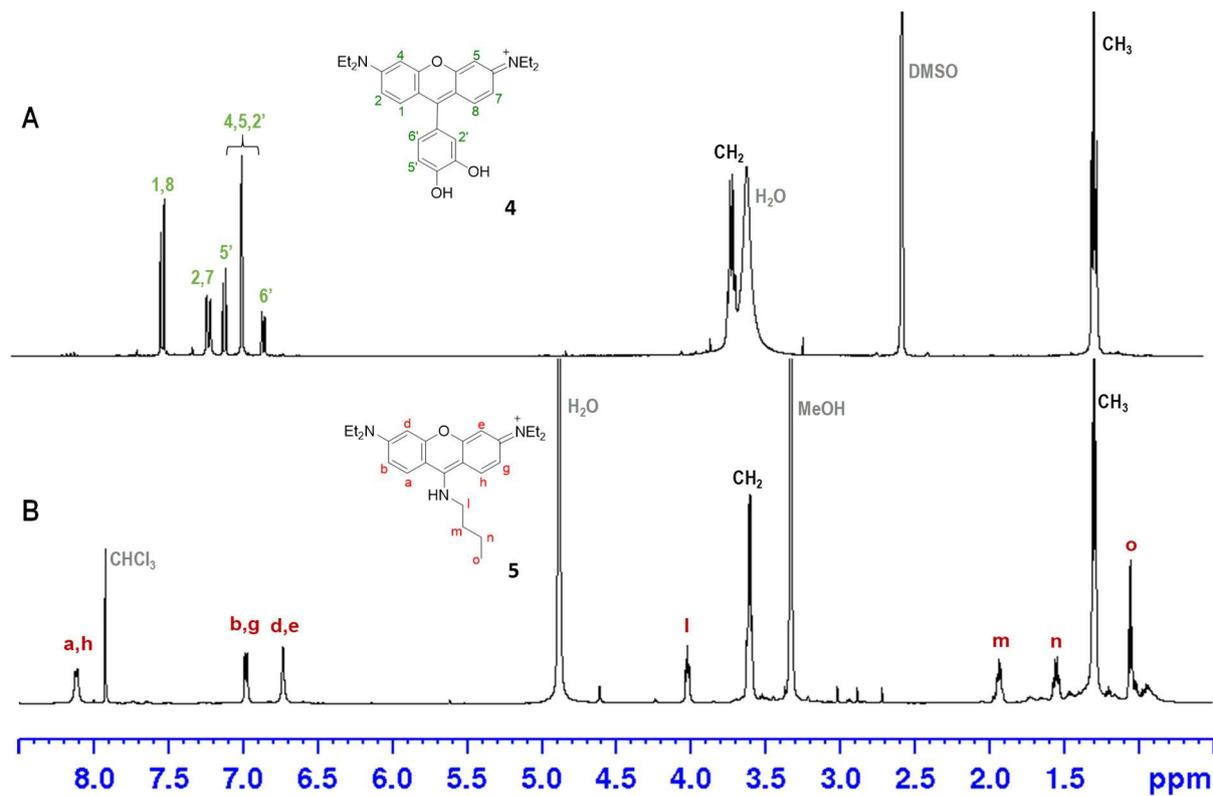


Figure S35. ¹H NMR spectra of 4 (A) and 5 (B).

NMR spectrum of aminopyronin 6a

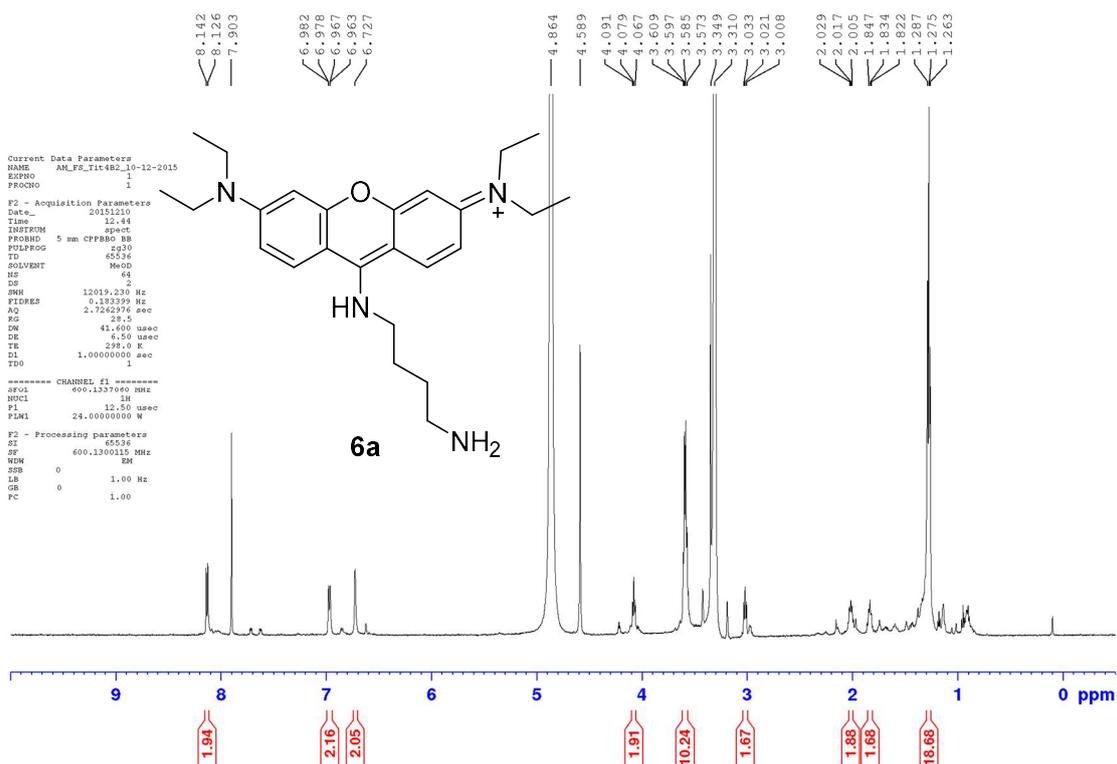


Figure S36. ¹H NMR spectrum (600.13 MHz, MeOD-d₄) of 6a.

NMR spectrum of aminopyronin 7a

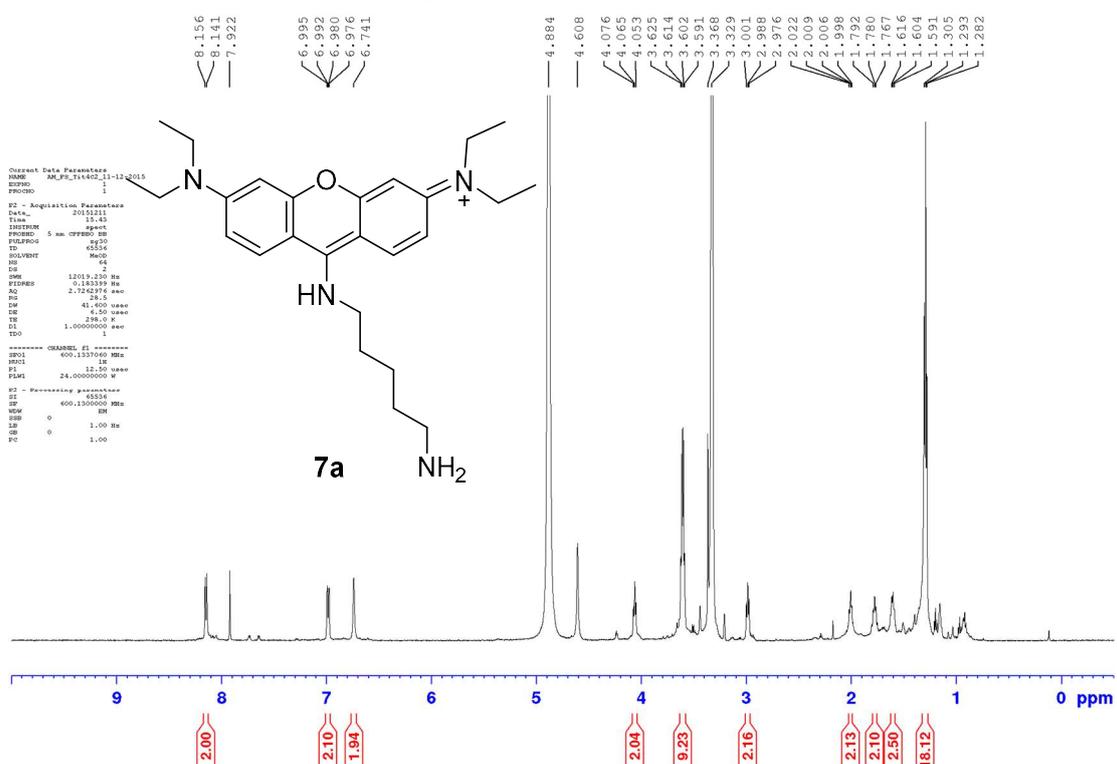


Figure S37. ¹H NMR spectrum (600.13 MHz, MeOD-d₄) of 7a.

NMR spectrum of aminopyronin 7b

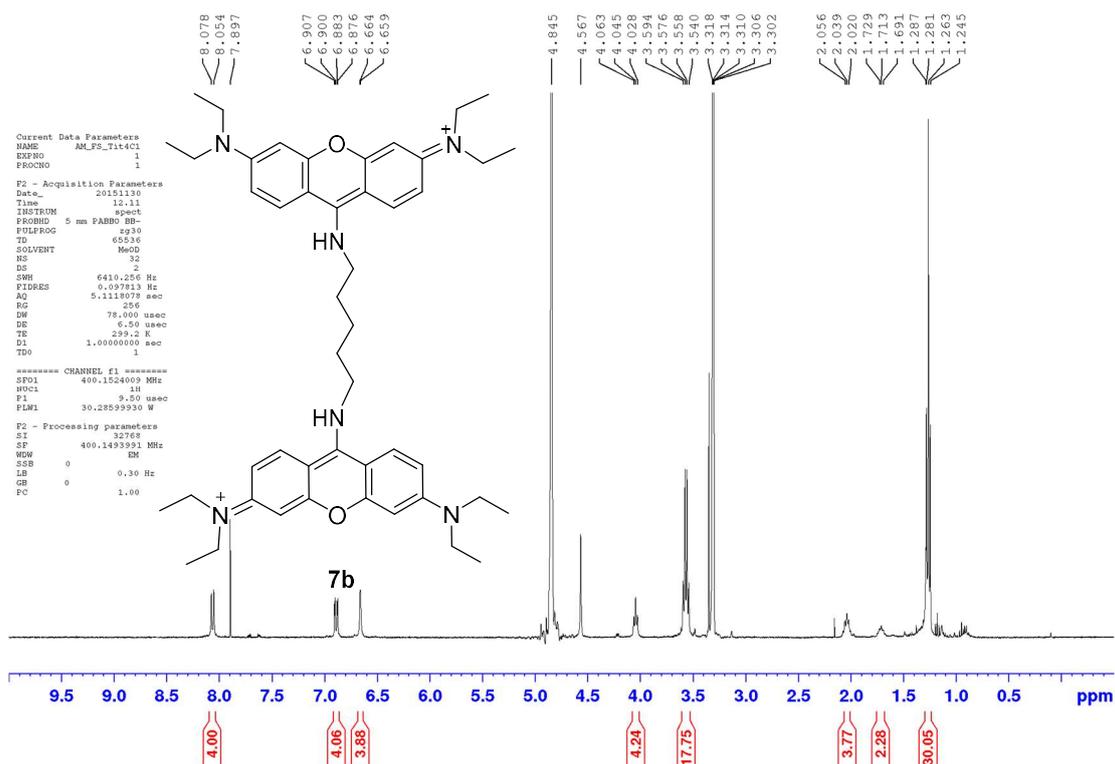


Figure S38. ¹H NMR spectrum (400.15 MHz, MeOD-d₄) of 7b.

MS spectra of 5, 6a, 7a and 7b

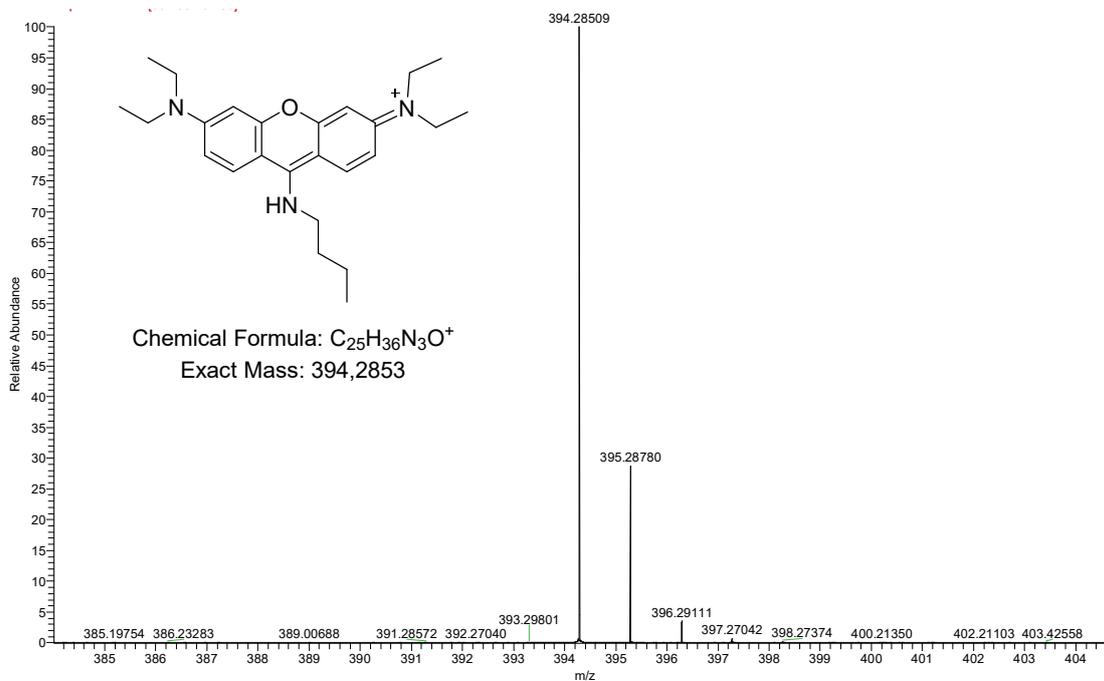


Figure S39. MS spectrum of 5.

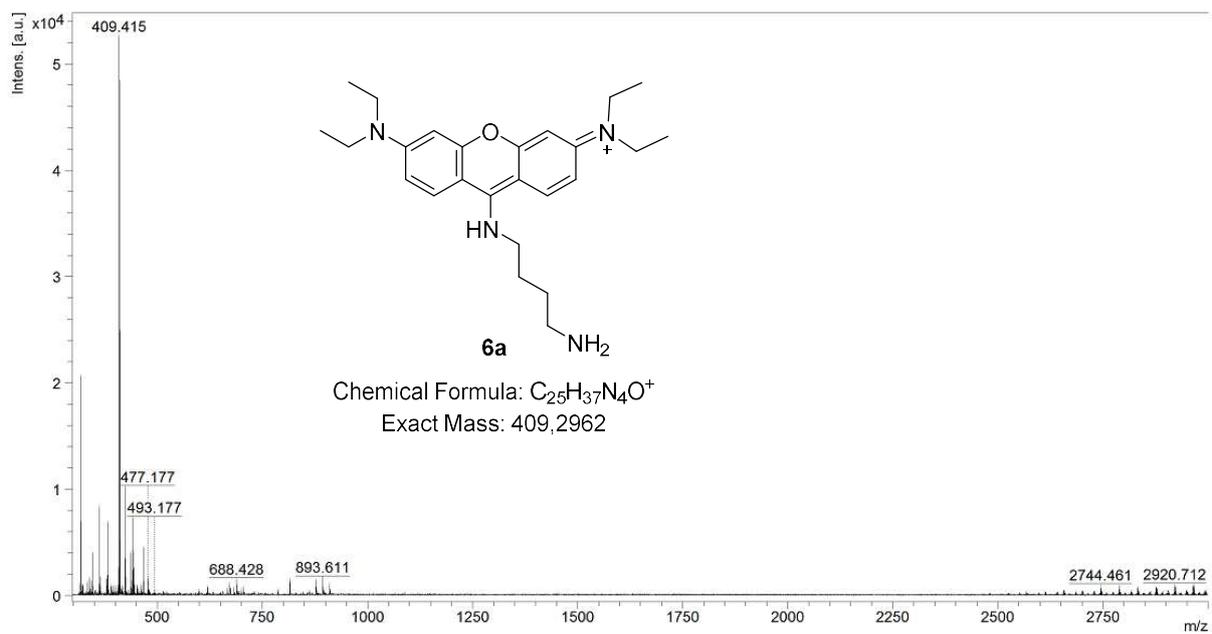


Figure S40. MS spectrum of **6a**.

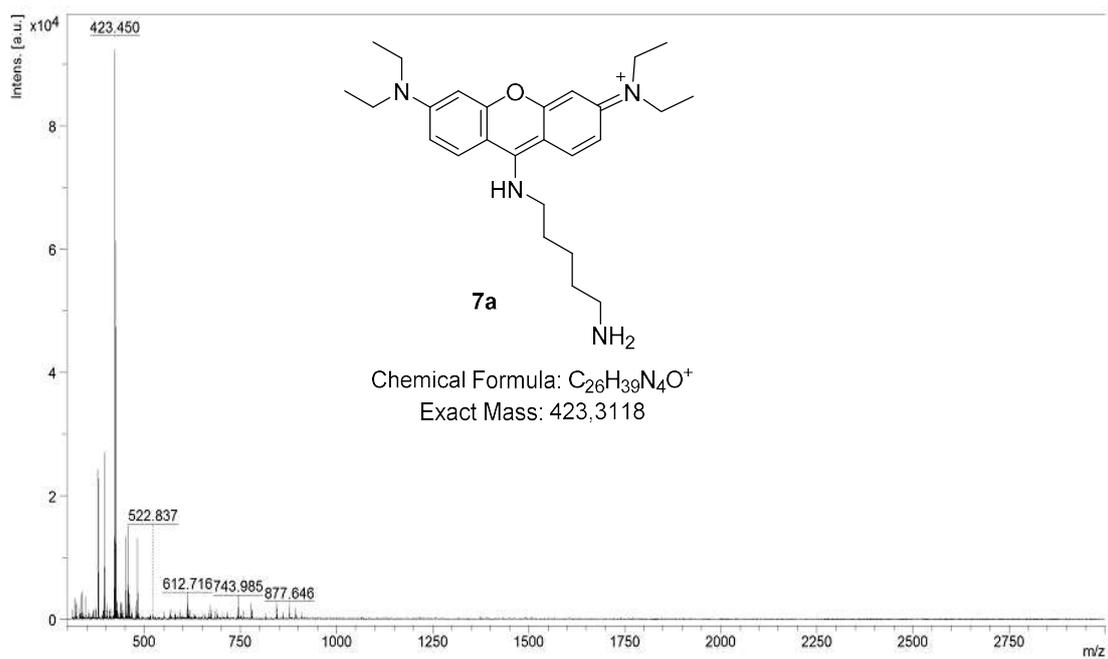


Figure S41. MS spectrum of **7a**.

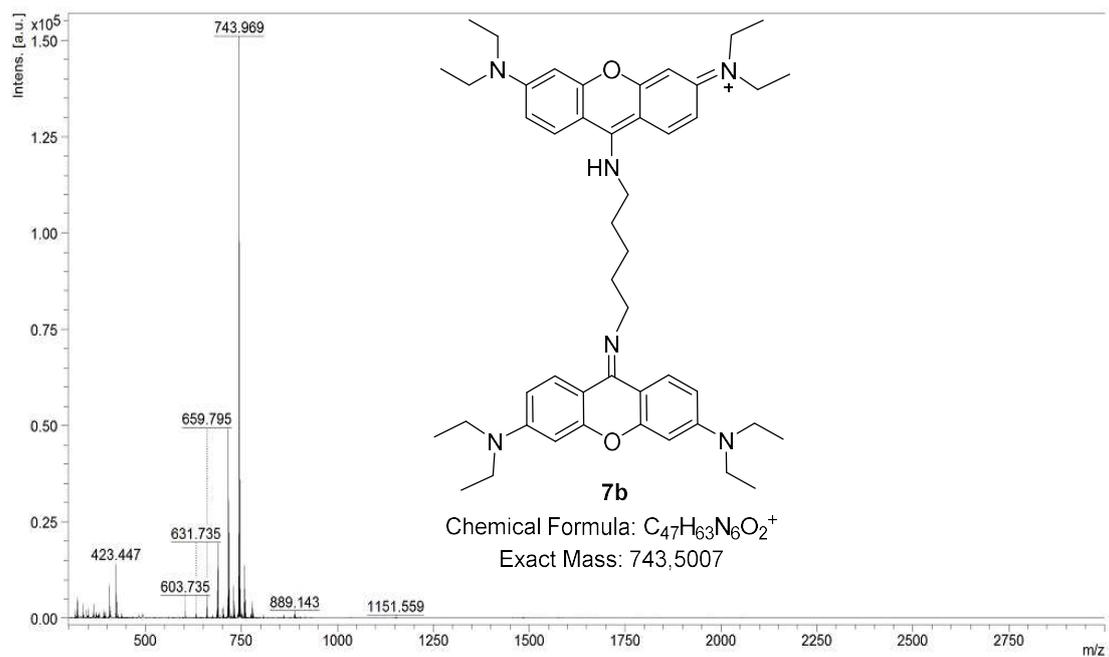


Figure S42. MS spectrum of **7b**.