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Supporting Information for

A Fluorescent Probe for Hydrazine and Its *in Vivo* Applications

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Synthesis material and instruments

All chemicals and reagents were used directly as obtained commercially unless otherwise stated. All solvents were of reagent grade and water used was ultra filter deionized. Probe 4 was synthesized according to our previous work. [S1] Absorption and emission spectra were collected by using a Shimadzu 1750 UV-visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively. NMR spectra were collected on a Bruker 500 avance III spectrometer. Chemical shifts (δ) were reported as ppm with TMS as the internal standard. Mass spectrometric (MS) data were obtained with HP1100LC/MSD MS and an LC/Q-TOF-MS instruments. The quantum yield of the sample was measured using quinine sulfate as the standard (Φ = 0.53, 0.1 M H_2SO_4).[S2]

Sample Preparation and Titration

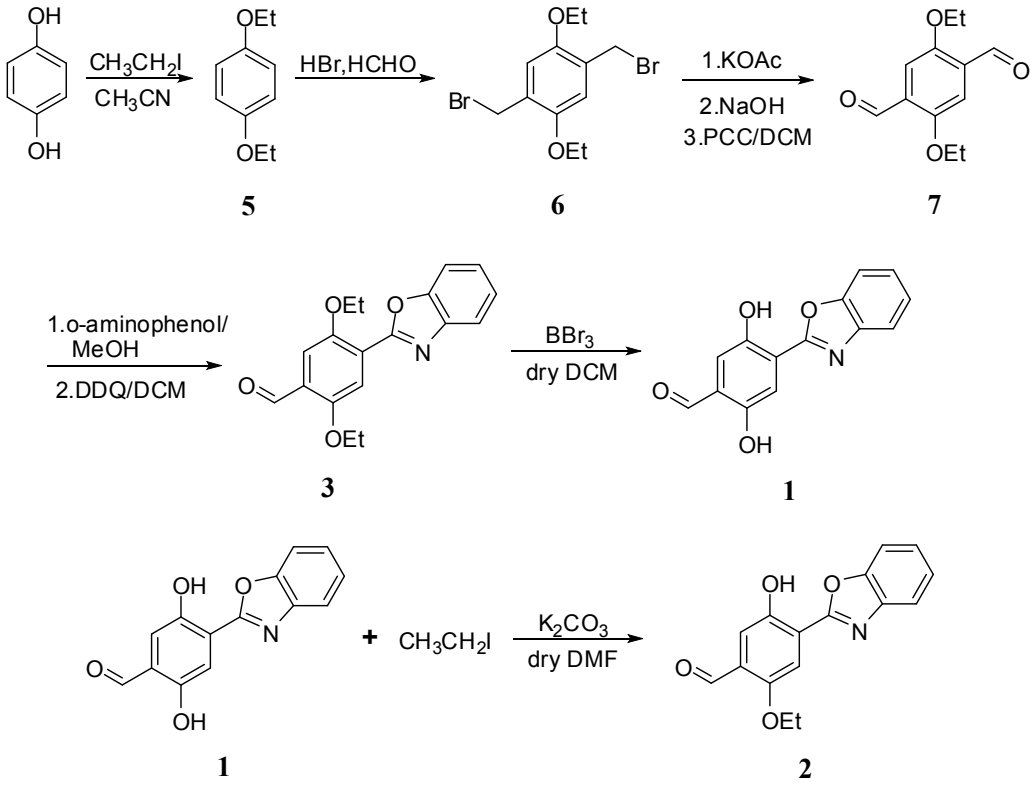
Stock solutions of metal ions, anions, amino acids and amine complexes were prepared in deionized water. The concentration are fixed to 1.0×10^{-2} M. Stock solution of fluorescent probes (5.0×10^{-4} M) were prepared in CH_3CN and then further diluted to 2.0×10^{-5} M for titration experiments. Every time an appropriate volume of each analyte was added to the test solution. Excitation was provided at 390 nm.

Cell culture and fluorescence image

Hela cells were seeded on 35 mm glass-bottomed dishes (NEST) and incubated in RPMI-1640 in an incubator (37 °C, 5% CO_2 and 20% O_2) for 24 h. The cells were rinsed slightly 3 times with fresh RPMI-1640 and incubated in RPMI-1640 medium spiked with or without sensor (5 μM) for 30 min, respectively. After washing with fresh RPMI-1640, the cells treated with sensor were further incubated in fresh RPMI-

1640 containing of 50 μM hydrazine for 0.5 h. Cells were then analyzed by Laser Scanning Confocal Microscope (A1R).

Synthesis routine



1,4-Bis(ethyoxyl)benzene (5)

A mixture of 1,4-hydroquinone (4.40 g, 40 mmol), iodoethane (10.00 mL, 120 mmol), and K_2CO_3 (22.00 g, 160 mmol) in acetonitrile (100 mL) was heated to reflux for two days. After cooling to room temperature, the precipitates were filtered, then evaporation of the solvent under reduced pressure. The solid residues were collected and purified on a silica gel column by using an eluent (petroleum ether), the product **5** was obtained as a white solid (4.90 g, 75.00% yield).

2,5-Bis(bromomethyl)-1,4-bis(ethyoxyl)benzene (6)

HBr (10 mL, 30 wt % in acetic acid) was added to a suspension of **5** (4.00 g, 23 mmol) and paraformaldehyde (1.40 g, 46 mmol) in acetic acid (80 mL). The mixture

was heated to 60 °C, and then stirred for 3 h. As the reaction proceeded, the suspension changed to clear solution first and then became a thick suspension again. After cooling to room temperature, the suspension was poured into water (400 mL). The precipitates were filtered and washed with water (3×10 mL). Then dried under vacuum and the crude product **6** was obtained as an off-white solid (6.70 g, 78.0% yield).

2,5-Bis(ethyoxyl)benzene-1,4-dialdehyde (7)

A solution of 2 (2.50 g, 7.70 mmol), potassium acetate (2.50 g, 23.10 mmol), and tetra(n-butyl)ammonium bromide (0.30 g) in a mixture of acetonitrile (50 mL) and chloroform (25 mL) was heated to reflux for 8 h. The mixture was washed with 100 mL water, and organic solution was removed on a rotary evaporator. The solid residues were dissolved in a 1:l mixture of THF and MeOH, then a solution of NaOH (1.00 g, 25 mmol) and H_2O (2 mL) was added dropwise to this solution. This mixture was heated to reflux for 8 h. After cooling to room temperature, the solvent was removed, the solid residues were washed with water to remove the salt, then dried under vacuum. The dried crude product was dissolved in 20 mL CH_2Cl_2. The solution was added dropwise to a stirred solution of freshly prepared pyridium chlorochromate (6.30 g, 29.30 mmol) in CH_2Cl_2 (200 mL) at room temperature. After addition was completed, stirring was continued for an additional 3 h. The reaction mixture was then directly transferred onto the top of a short silica gel column. The yellow and highly fluorescent compound was then washed off the column with CH_2Cl_2/petroleum ether (1:2), affording product **7** (1.10 g, 61.50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.56 (d, *J*=1.2 Hz, 2H), 7.46 (s, 2H), 4.21 (q, *J*=7.0 Hz, 4H), 1.51 (t, *J*=7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 189.49, 155.08, 129.27, 111.69, 64.85, 14.65.

2,5-bis(ethyoxyl)-4-(benzoxazolyl) benzaldehyde (3)

A solution of o-aminophenol (0.24 g, 2.25 mmol) in methyl alcohol (20 mL) was added dropwise to a stirred solution of compound **7** in methyl alcohol (10 mL) at 70 °C. After addition was completed, stirring was continued for an additional 5 h. Then the solvent was removed using rotary evaporator. After that the solution of DDQ (0.50 g, 2.25 mmol) in 150 mL CH_2Cl_2 was added dropwise to the above residue. The reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was treated with 100 mL saturated Na_2CO_3, then washed with water, and dried over

Na_2SO_4. After evaporation of the solvent, the solid residues were collected and purified on a silica gel column by using an eluant (petroleum ether: CH_2Cl_2 =1:1), the product **3** was obtained as a yellow solid (0.15 g, 21.42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.56 (d, *J*=1.2 Hz, 1H), 7.93-7.79 (m, 2H), 7.73-7.60 (m, 1H), 7.55 (s, 1H), 7.49-7.38 (m, 2H), 4.35-4.19 (m, 4H), 1.55 (t, *J*=7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 189.28, 161.03, 155.16, 151.79, 150.86, 141.67, 127.08, 125.62, 124.70, 122.97, 120.37, 115.65, 112.54, 110.78, 65.69, 65.07, 14.77, 14.75.

Synthesis of probe 1

A solution of compound **3** (0.20 g, 1.60 mmol) in 10 mL of dry CH_2Cl_2 was cooled to -30°C with ice/ethyl alcohol. BBr_3 (0.30 mL) in 10 mL CH_2Cl_2 was added dropwise under a nitrogen atmosphere. The reaction mixture was stirred at -30°C for 1 h and then at room temperature for 24 h. Following the addition of 4.00 mL distilled H_2O, the reaction mixture was stirred for additional 2 h and poured into a mixture of water (20 mL) and CH_2Cl_2 (20 mL). The organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2 (30 ml). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. After removal of the solvent on a rotary evaporator, the solid residues were collected and purified on a silica gel column by using an eluent (petroleum ether/CH_2Cl_2, 1:1), the product probe **1** was obtained as a yellow solid (0.10 g, 62.5% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ = 10.59 (s, 1H), 10.47 (s, 1H), 10.31 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.63 (s, 1H), 7.46-7.53 (m, 2H), 7.26 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 190.41, 161.46, 153.35, 150.27, 149.61, 140.10, 126.91, 126.35, 125.94, 120.14, 117.42, 115.95, 115.31, 111.70. *m/z* (TOF-LD): Calcd. $[M+H]^+$ For $C_{14}H_9NO_4$: 256.0610, found: 256.0600.

Synthesis of probe 2

A solution of probe **1** (0.20 g) in anhydrous DMF (5 mL) was treated with K_2CO_3 (0.12 g) at 25 °C, and the mixture was stirred for 30 min. Ethyl iodide (0.10 g) was added, and the reaction mixture was further stirred for 20 h before being quenched by the addition of H_2O (100 mL). The aqueous layer was extracted with CH_2Cl_2 (2×100 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The product was isolated by flash chromatography on silica gel by using an eluent (petroleum ether/CH_2Cl_2, 1:1), the product probe **2** was obtained as a yellow solid (0.15 g, 65.0% yields). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 10.48 (s, 1H), 7.71

(dd, *J*=7.5, 1.5 Hz, 1H), 7.61 (t, *J*=7.3 Hz, 1H), 7.53-7.46 (m, 2H), 7.46-7.35 (m, 2H), 4.23-4.14 (m, 2H), 1.53-1.49 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 189.11, 161.58, 153.79, 152.29, 149.23, 139.90, 128.56, 126.25, 125.43, 119.73, 116.30, 115.35, 110.79, 110.35, 65.00, 14.70. m/z (TOF-LD): Calcd. [M+H]+ For $C_{16}H_{13}NO_4$: 284.0923, found: 284.0919.

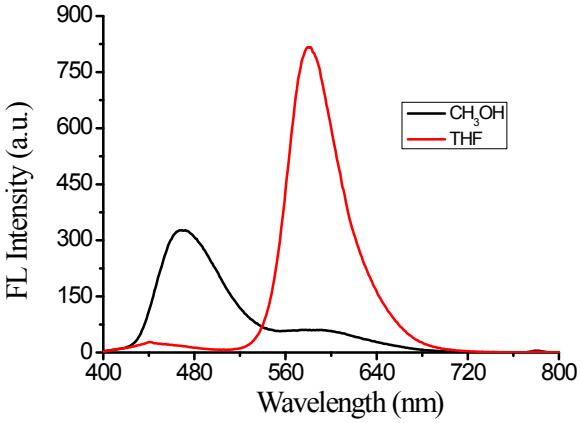


Fig. S1 The fluorescence spectra of probe **2** (20 μM) in CH_3OH and THF, λ_{ex}=390 nm. The fluorescent bands at 470 and 580 nm are attributed to *enol* and *keto* emission, which is consistent with ESIPT characteristic.

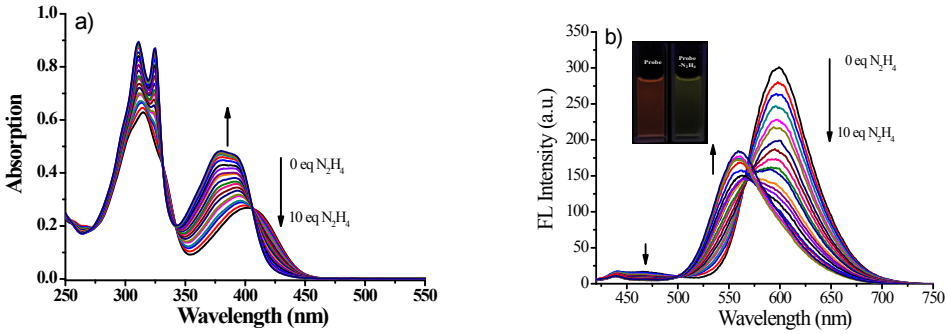


Fig. S2 UV-Vis absorption (a) and fluorescence spectra (b) of probe **1** (20 μM) upon addition of N_2H_4 in CH_3CN (λ_{ex}=390 nm). Inset: The fluorescence color change before and after addition of hydrazine excited by hand-held UV lamp. Each spectrum was recorded after 50 min of reaction.

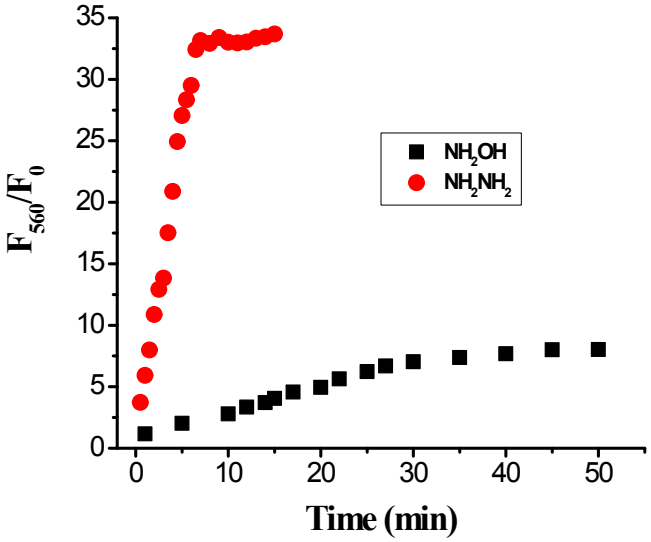


Fig. S3 Time-dependent fluorescence intensity of probe **1** (20.0 μM) upon addition of NH_2NH_2 (0.2 mM) and NH_2OH (0.2 mM) in CH_3CN/HEPES Buffer (1:2, v/v, pH 7.4), λ_{ex}=390 nm.

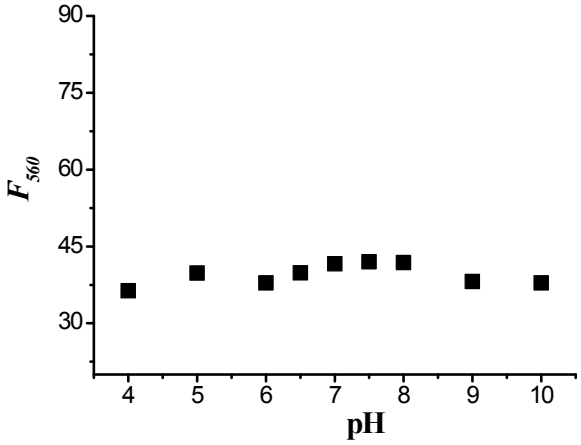


Fig. S4 The fluorescence intensity change of probe **1** (20 μM) at 560 nm response to the different value of pH.

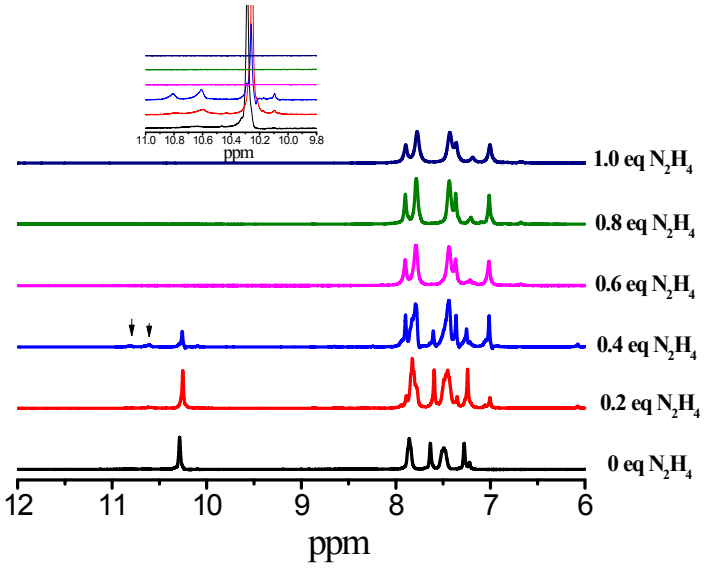


Fig. S5 The ^{1}H NMR spectra titration of probe **1** in DMSO-d_6/D_2O (10:1) upon addition of N_2H_4. Inset: the enlarged spectra in the region of 11-10.

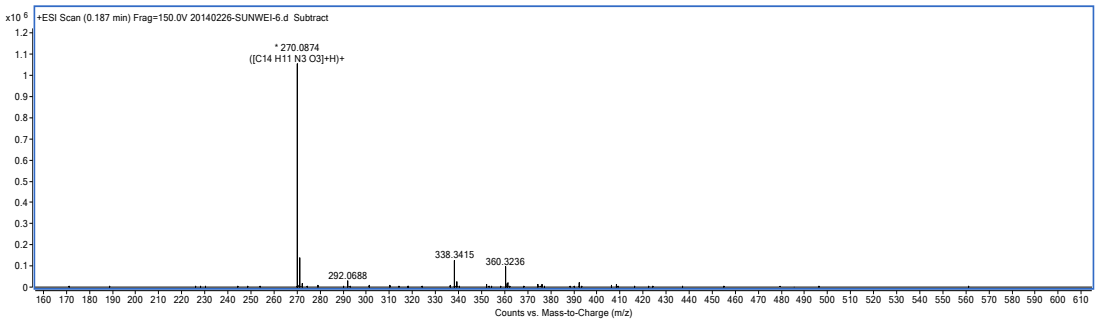


Fig. S6 HRMS spectrum of the reaction product of probe **1** with hydrazine.

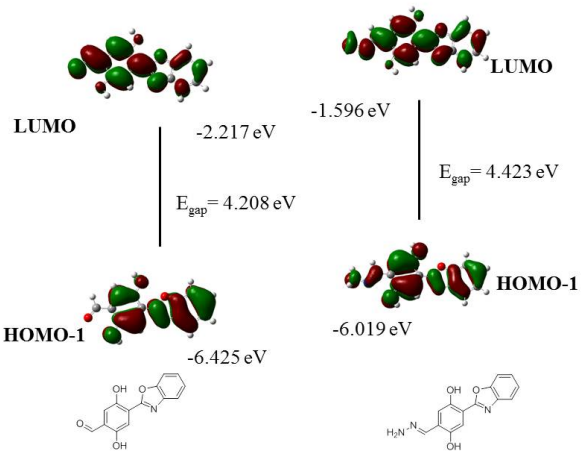


Fig. S7 HOMO–LUMO energy levels and interfacial plots of the orbitals for probe **1** and the corresponding product.

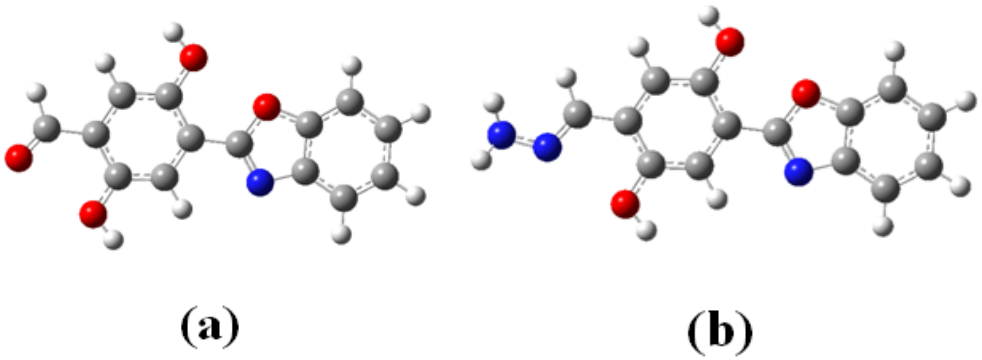


Fig. S8 The optimizational molecular structures for probe **1** (a) and the corresponding product (b).

Table S1 The calculated data for probe **1**

Compoud	Electronic Transition	TDDFT //B3LYP/6-31G*	
		Excitation Energy	f
Probe 1	$S_0 \rightarrow S_1$	3.3433 eV 370.84 nm	0.0000
	$S_0 \rightarrow S_2$	3.3862 eV 366.15 nm	0.3446
	$S_0 \rightarrow S_3$	3.8191 eV 324.64 nm	0.3958
	$S_0 \rightarrow S_4$	4.0772 eV 304.09 nm	0.0311
	$S_0 \rightarrow S_5$	4.8505 eV 255.61 nm	0.0858
	$S_0 \rightarrow S_6$	4.9063 eV 252.71 nm	0.0010

Table S2 The calculated data for the corresponding product

Compoud	Electronic Transition	TDDFT //B3LYP/6-31G*	
		Excitation Energy	**f**
product	$S_0 \rightarrow S_1$	3.4341 eV 361.04 nm	0.7085
	$S_0 \rightarrow S_2$	3.9832 eV 311.27 nm	0.5142
	$S_0 \rightarrow S_3$	4.3298 eV 286.35 nm	0.0185
	$S_0 \rightarrow S_4$	4.4015 eV 281.69 nm	0.0044
	$S_0 \rightarrow S_5$	4.8002 eV 258.29 nm	0.0027
	$S_0 \rightarrow S_6$	4.8426 eV 256.03 nm	0.0184

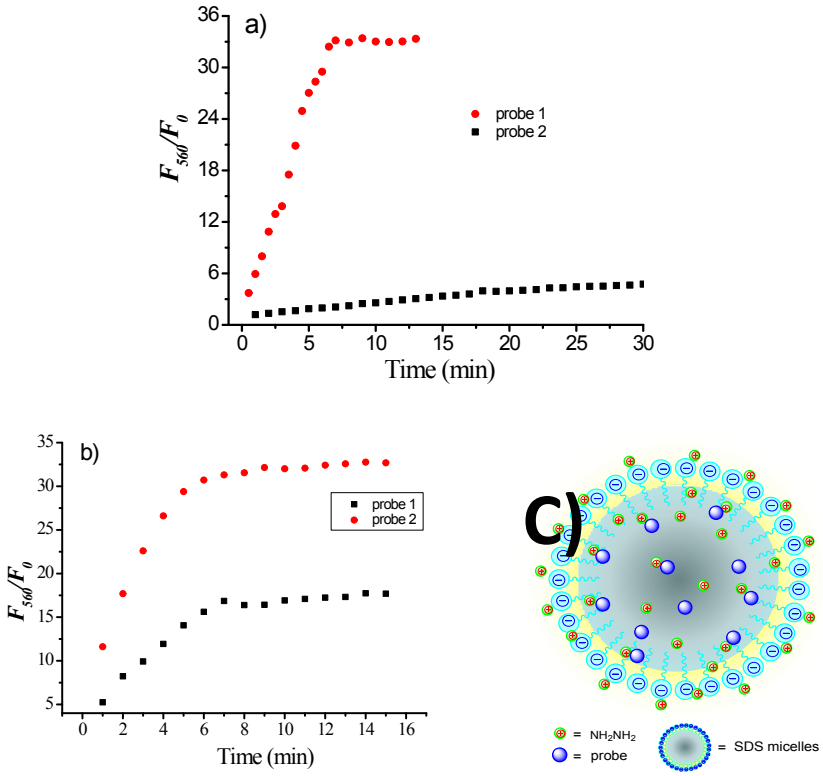


Fig. S9 Time-dependent fluorescence intensity of probe (20.0 μM) was treated with hydrazine (0.2 mM) (a) in CH_3CN/HEPES Buffer (1:2, v/v, pH 7.4) and (b) in SDS solution (10 mM), λ_{ex}=390 nm. c) Schematic diagram of micelle-induced enrichment of hydrazine on micelle surface, conductive to reaction with probe.

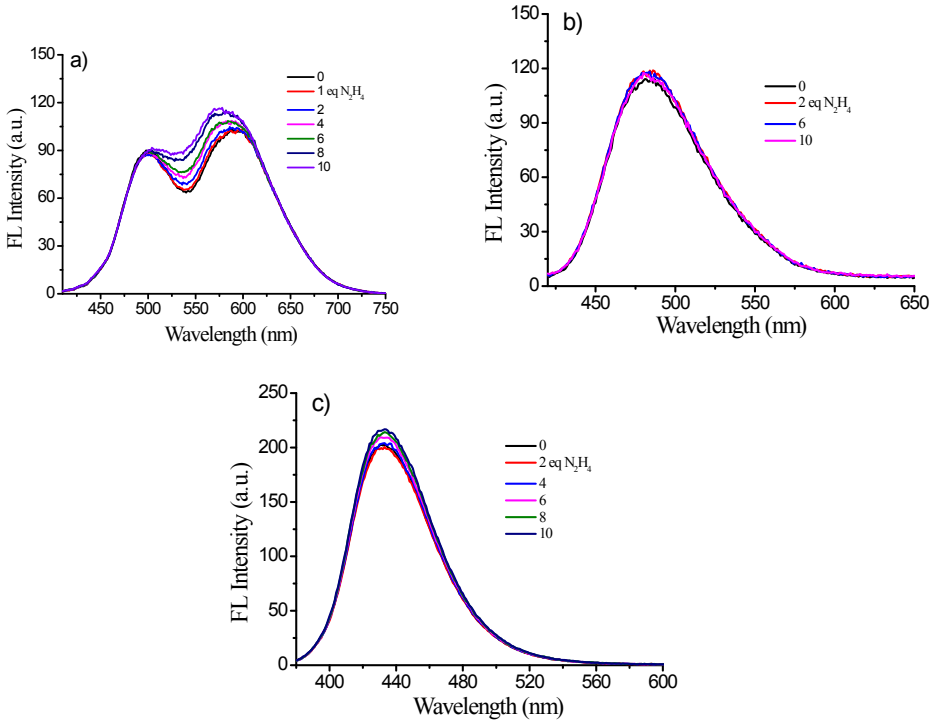


Fig. S10 Fluorescence emission spectra of (a) probe **2** (20 μM), (b) probe **3** (20 μM) and (c) probe **4** (20 μM) upon addition of N_2H_4 in CH_3CN/HEPES Buffer (1:2, v/v, pH 7.4), λ_{ex}=390 nm. Each spectrum was recorded after 15 min of reaction.

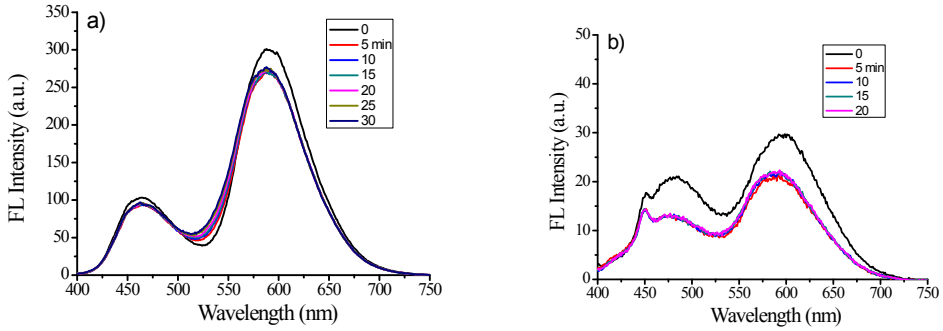


Fig. S11 The fluorescence spectra response of probe **1** (20μM) (a) and probe **2** (20μM) (b) with time duration in the presence of 100 μM hydrazine in cationic CTAB (5 mM) micelles solution, λ_{ex}=390 nm.

Probe **1** and **2** showed no obvious fluorescence spectra change with increasing time upon to 10 equivalents of hydrazine in cationic cetyltrimethyl ammonium bromide (CTAB) micelles (5 mM) solution. These phenomena are unlike that in anionic SDS micelles solution (Fig. S8b). It is presumed that cationic CTAB micelles-encapsulated probe cannot access to positively charged hydrazine (pK_a=14.9) because of electrostatic repulsion.

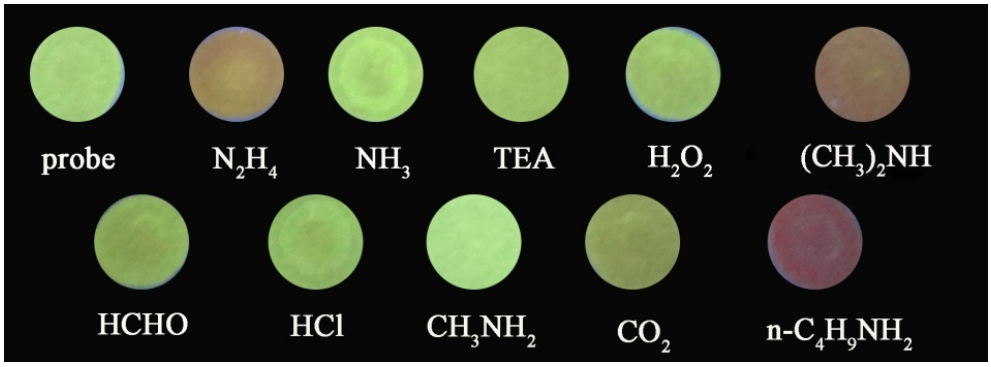
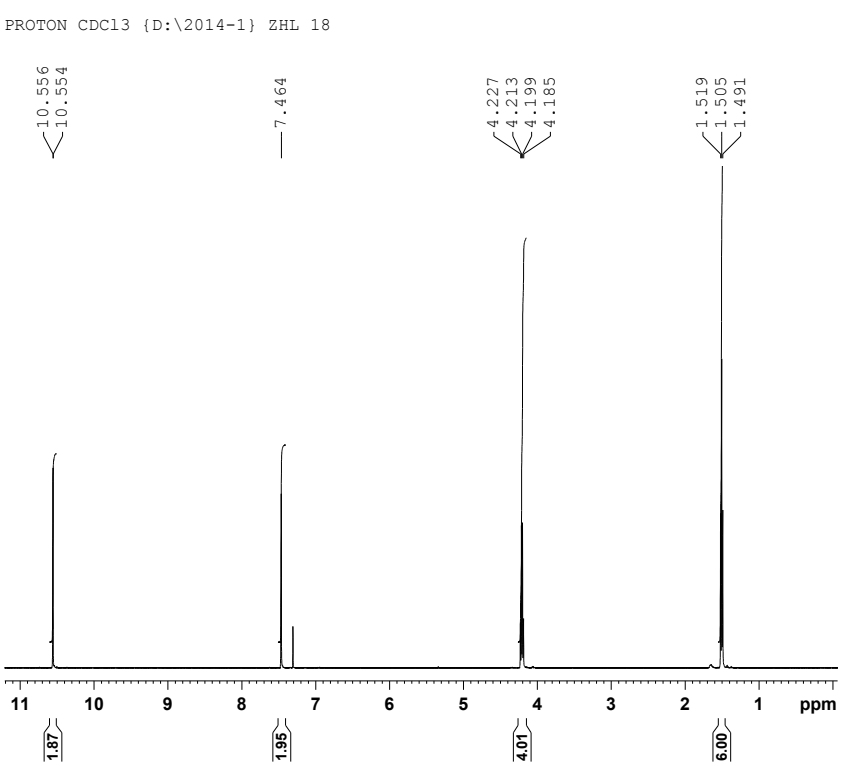


Fig. S12 Fluorescent color changes of probe **1** (20 μM)-coated filter paper after exposure to an excess quantity of various vapors, including hydrazine, ammonia, methylamine, n-butylamine, formaldehyde, dimethylamine, H_2O_2, HCl, and CO_2 for 10 min, respectively. The fluorescent color changes were observed using a hand-held UV lamp with an excitation at 365 nm.

The ^{1}H NMR spectrum of compound **7**



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TD0                   1

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F2 - Processing parameters
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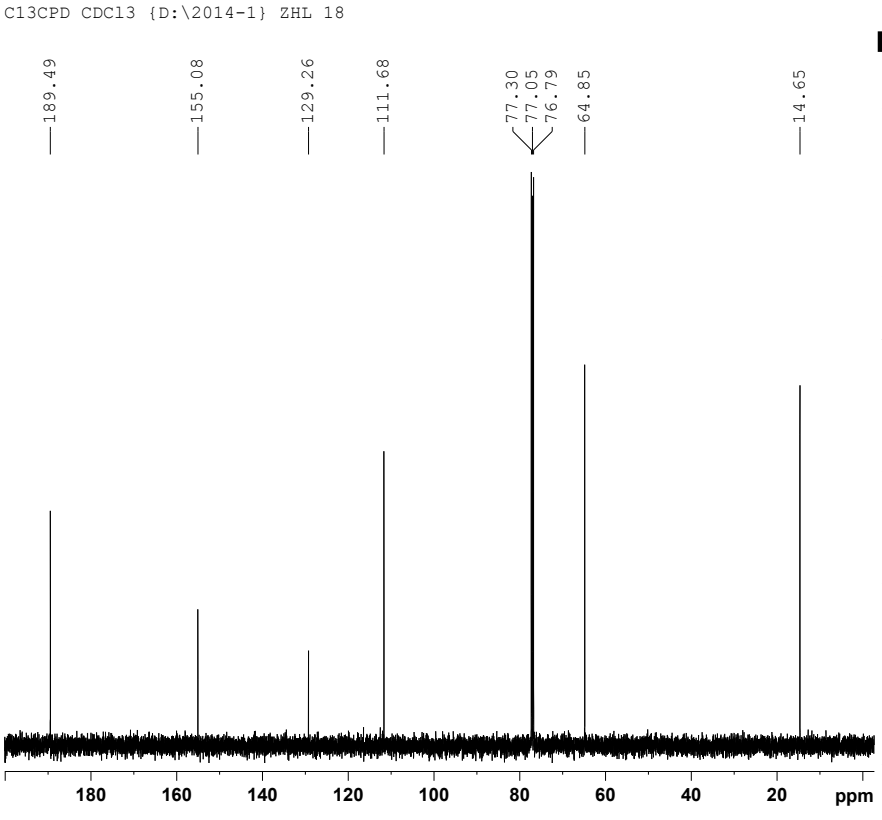
The ^{13}C NMR spectrum of compound **7**



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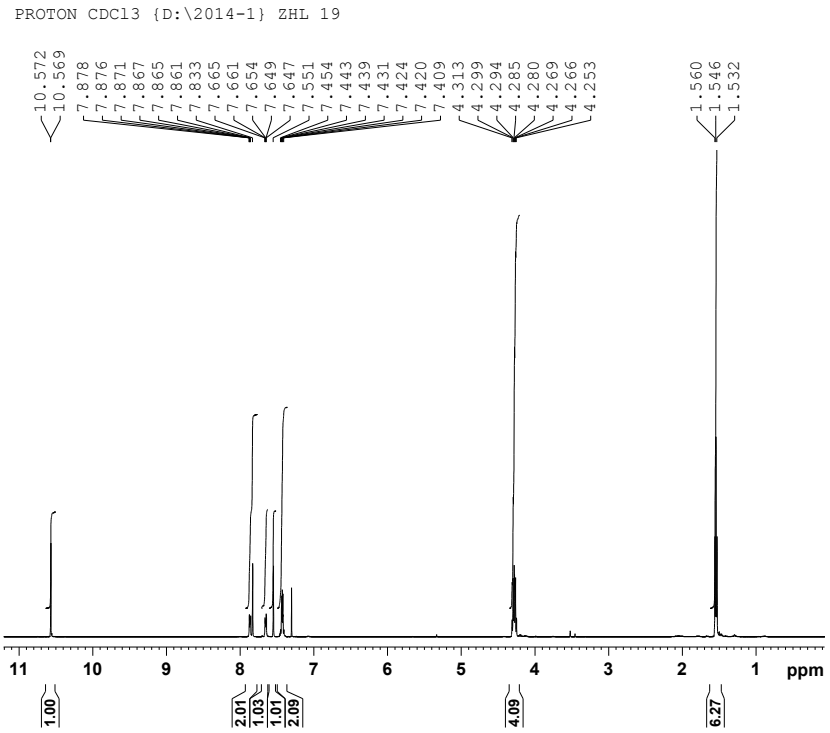
The ^{1}H NMR spectrum of probe **3**



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TD                 65536
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NS                     8
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                   128
DW                48.400 usec
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TE                298.6 K
D1           1.00000000 sec
TD0                    1

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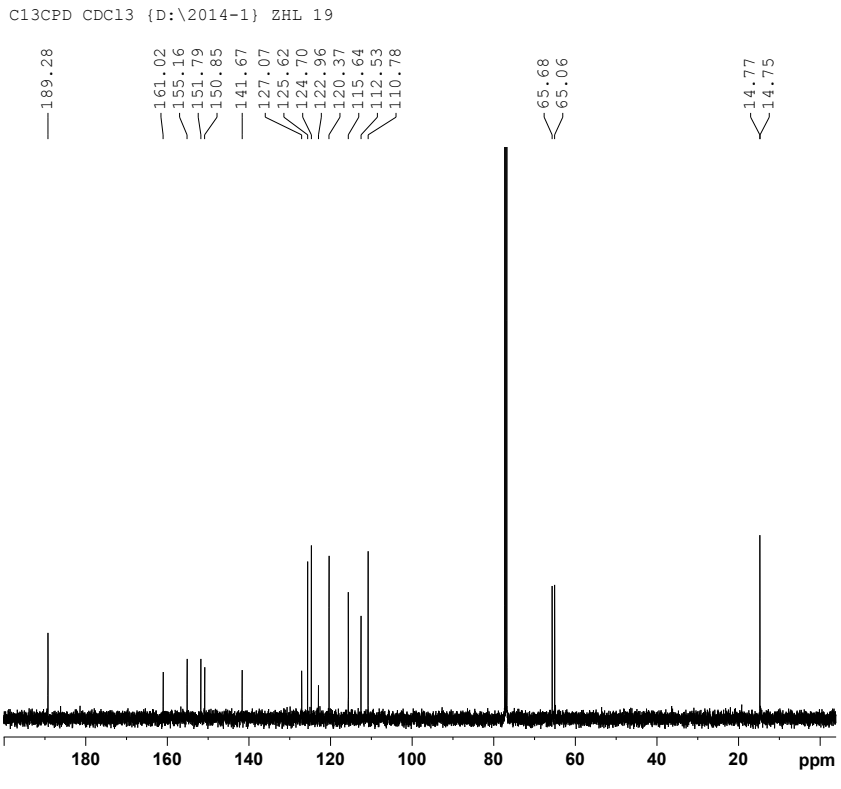
The ^{13}C NMR spectrum of probe **3**



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F2 - Processing parameters
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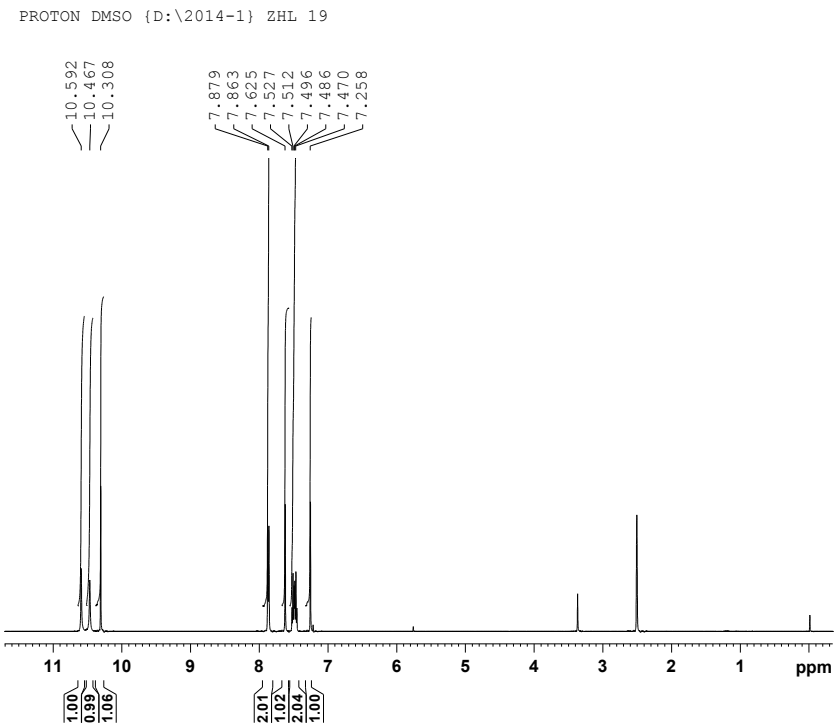
The ^{1}H NMR spectrum of probe **1**

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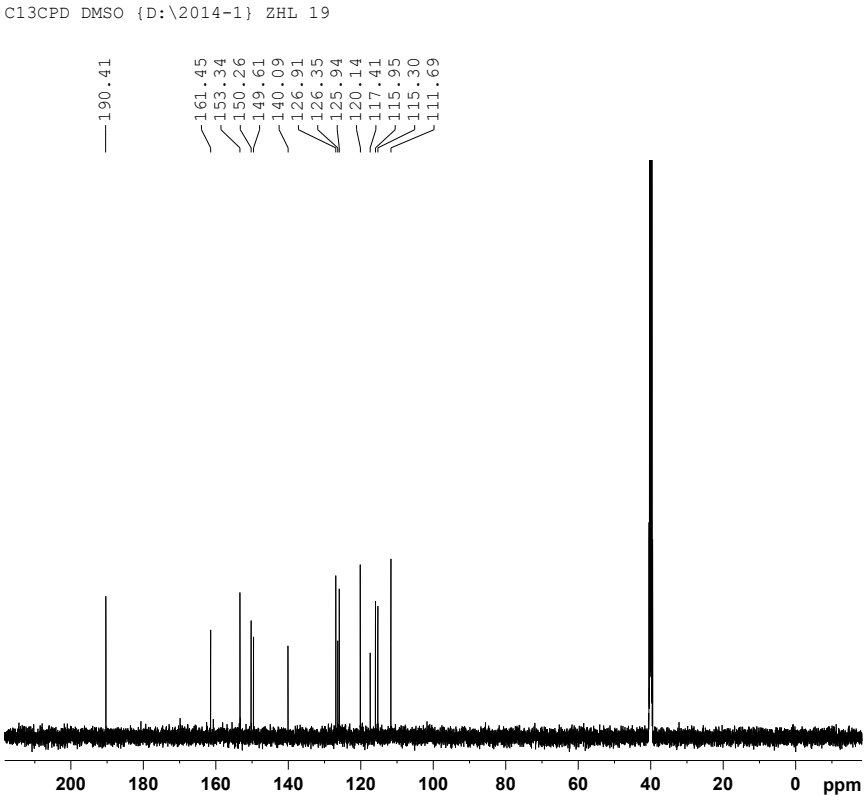
P1               9.00 usec
PL1       0 dB
PL1W       -1.#IND0000 W
SFO1       500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

The ^{13}C NMR spectrum of probe **1**




```
Current Data Parameters
NAME      SSG-0117-XL-NH
EXPNO                 11
PROCNO                 1

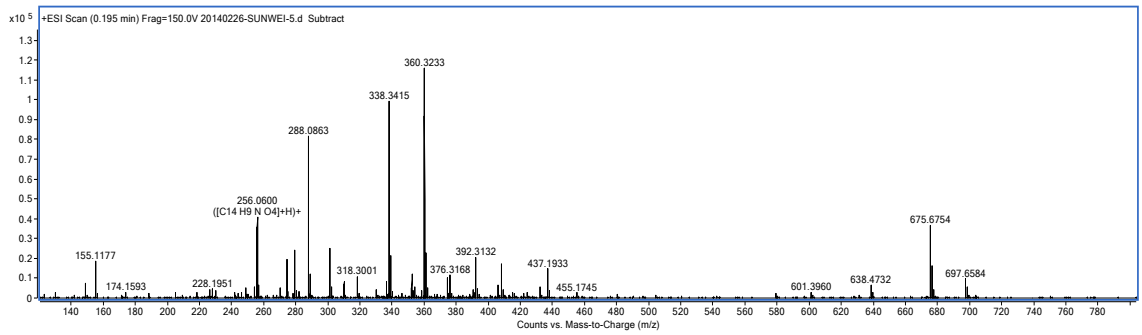
F2 - Acquisition Parameters
Date_           20140117
Time              10.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                  64
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010548 sec
RG                 203
DW              16.800 usec
DE               6.50 usec
TE              295.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               9.50 usec
PL1             -1.00 dB
PL1W       -1.#IND0000 W
SFO1       125.7703643 MHz

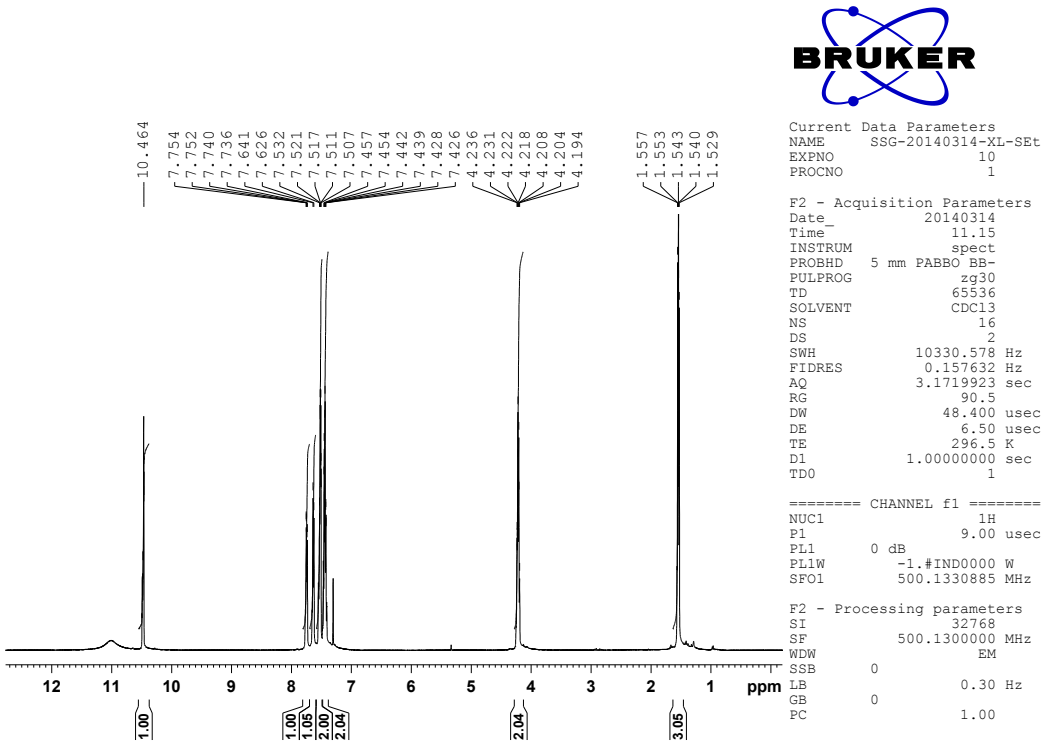
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2       0 dB
PL12            16.05 dB
PL13            17.00 dB
PL2W       -1.#IND0000 W
PL12W      -1.#IND0000 W
PL13W      -1.#IND0000 W
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

The HRMS spectrum of probe **1**



The ^{1}H NMR spectrum of probe **2**



BRUKER

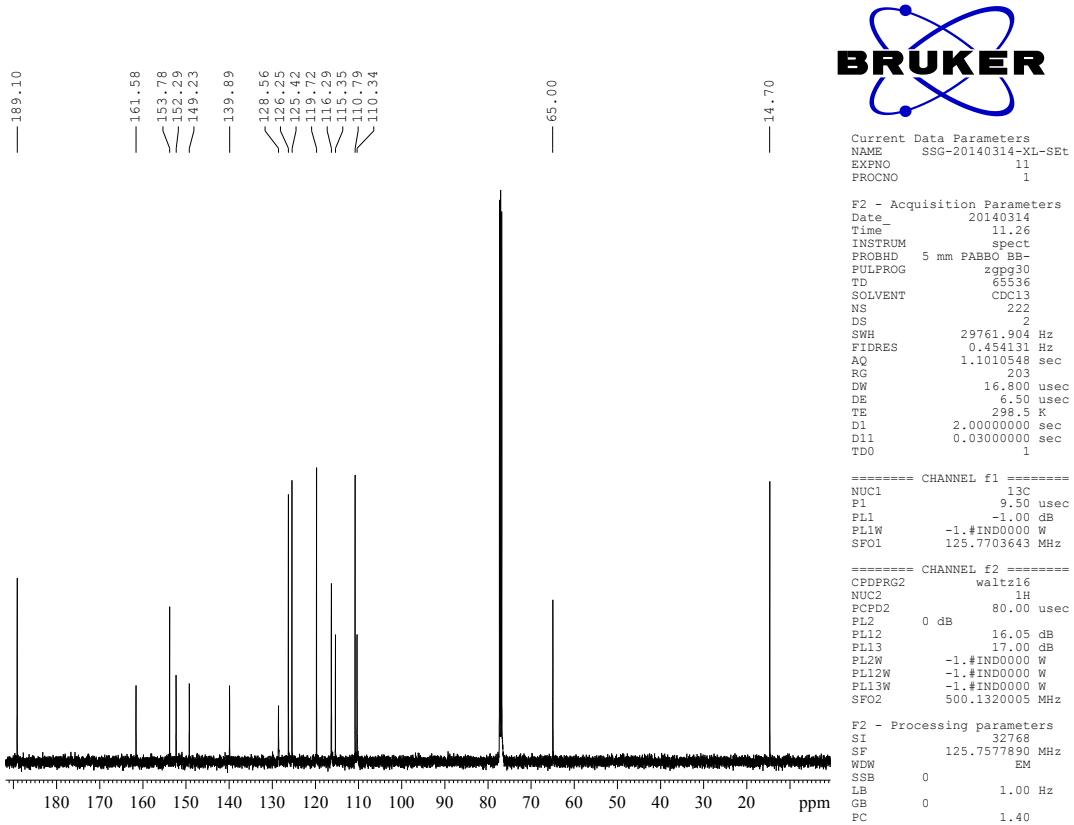
```
Current Data Parameters
NAME      SSG-20140314-XL-SEt
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140314
Time              11.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                 90.5
DW                48.400 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.00 usec
PL1       0 dB
PL1W        -1.#IND0000 W
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

The ^{13}C NMR spectrum of probe **2**




```
Current Data Parameters
NAME      SSG-20140314-XL-SEt
EXPNO                  11
PROCNO                  1

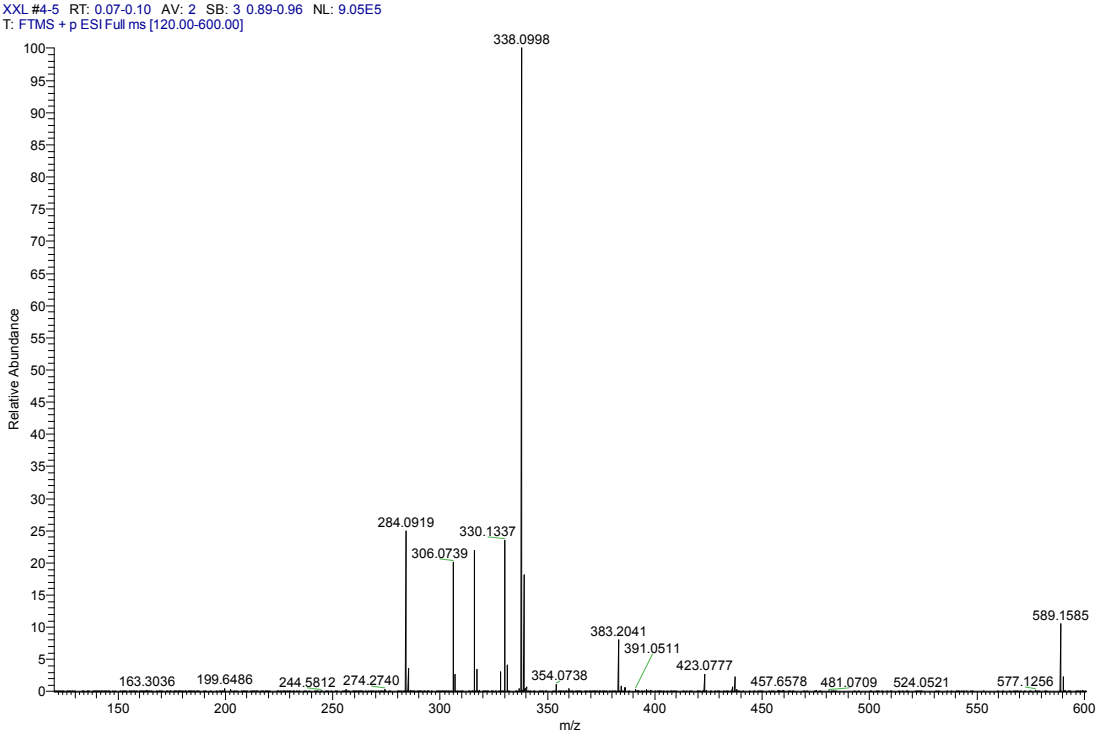
F2 - Acquisition Parameters
Date_            20140314
Time                11.26
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   222
DS                     2
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010548 sec
RG                   203
DW                16.800 usec
DE                 6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -1.00 dB
PL1W        -1.#IND0000 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2       0 dB
PL12                16.05 dB
PL13                17.00 dB
PL2W        -1.#IND0000 W
PL12W       -1.#IND0000 W
PL13W       -1.#IND0000 W
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF           125.7577890 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

The HRMS spectrum of probe **2**



S1 Y. Xu, L. Xiao, Y. Zhang, S. Sun and Y. Pang, *RSC Adv.*, 2014, **4**, 4827.

S2 J. N. Demasa and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

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